APPENDICES

APPENDIX A

CHAPTER TWO SUPPORING INFORMATION

Experimental Details

General Information

All reactions were carried out under an atmosphere of nitrogen in oven-dried glassware with a magnetic stirring bar. All reactions were monitored by thin layer chromatography (TLC) using Merck TLC silica gel 60 sheets, which were visualized with ultraviolet light and then developed with basic potassium permanganate solution. Flash chromatography was performed on Silacycle silica gel 60 as the stationary phase and the solvents employed were of analytical grade.

^{1}H NMR spectra were recorded at at 400 MHz or 500 MHz at ambient temperature. Data are reported as follows: chemical shift in parts per million (ppm) from deuterated chloroform ($CDCl_3$) taken as 7.27 ppm, integration, multiplicity (s = singlet, d = doublet; t = triplet; dd = double doublets, dt = double triplets, dq = double quartets, qt = quartet triplets, ddd = double double doublets, ddt = double double triplets, dddd = double double double doublets, tq = triplet quartets, dtq = double triplet quartets, dqt = double quartet triplets, m = multiplet, br = broad), and coupling constant (Hz). ^{13}C NMR spectra were recorded at 100 MHz or 125 MHz. Chemical shifts are reported in ppm from $CDCl_3$ taken as 77.0 ppm. Infrared spectra were recorded on a Perkin Elmer RX I FT-IR spectrometer as liquid films or as dilute solutions between two KBr discs. Mass spectra were recorded on either a Micromass GCT Premier or a Waters Micromass LCT Premier spectrometer using electron ionisation (EI) at 70 eV or electrospray (ES) techniques, respectively.

Unless stated otherwise, all commercially available reagents were used as received. When necessary, commonly used organic solvents were dried prior to use according to standard laboratory practices.[1]

General Procedures

General Procedure A for the Synthesis of N-Alloc-N-Allyl Ynamides[2]

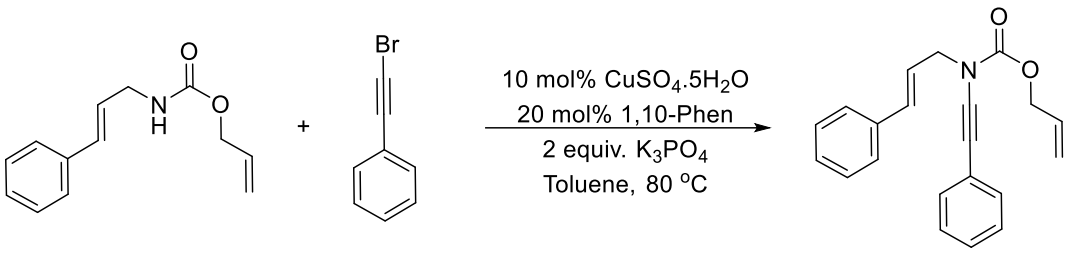
To an oven dried round bottom flask equipped with reflux condenser and magnetic stirrer bar and purged with nitrogen was added alkynyl bromide (1.20 equiv.) in anhydrous toluene (0.5 M). Carbamate (1.00 equiv.), $CuSO_4.5H_2O$ (0.10 equiv.), 1,10-phenanthroline (0.20 equiv.) and K_3PO_4 (2.00 equiv.) were added in sequentially and the mixture stirred at 80 °C on a heating mantle for 3 days. The mixture filtered through a plug of Celite™, washed with CH_2Cl_2 and concentrated *in vacuo*. The crude product was purified by flash column chromatography.

General Procedure B for the Regio and Stereoselective Synthesis of Complex Nitriles

To an oven dried 5 mL reaction vial, equipped with a magnetic stirrer bar, was added Pd2dba3 (2.5 mol%) and (R)-DTBM-MeOBIPHEP (6.0 mol%) under a nitrogen atmosphere. A solution of ynecarbamate (1.00 equiv.), BEt3 (0.25 equiv.) and N,O-BSA (1.00 equiv.) in triflurotoluene (0.044 M) was subsequently added to the mixture and was stirred at 25 °C for 15 minutes to allow for catalyst complex formation in-situ. The reaction was then heated to 60 °C using a heating mantle and stirred for 18 hours. The crude reaction mixture was concentrated in vacuo and then purified by flash column chromatography.

Synthesis of Substituted *N*-Allyl-*N*-Alloc Ynamdides

Allyl cinnamyl(phenylethynyl)carbamate (1a)

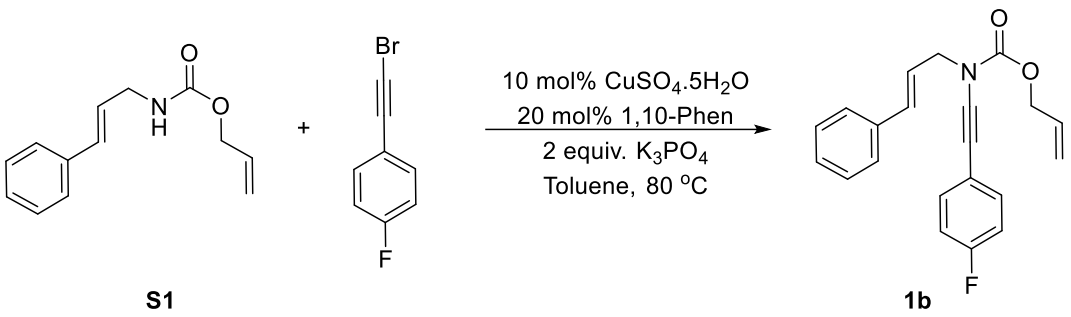


S1 **1a**

The title compound was prepared by General Procedure A from allyl cinnamyl carbamate[3] (700 mg, 3.23 mmol) and (bromoethynyl)benzene (701 mg, 3.87 mmol). The crude product was purified by flash column chromatography (Hexanes/EtOAc 20:1) to afford **1a** (541 mg, 53%) as an orange oil.

R_f (Hexanes/EtOAc 5:1) = 0.59. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.44-7.40 (4H, m), 7.38-7.33 (3H, m), 7.31-7.27 (3H, m), 6.69 (1H, d, *J* = 15.8 Hz), 6.36 (1H, dt, *J* = 15.8, 6.7 Hz), 6.00 (1H, ddt, *J* = 17.1, 10.6, 5.1 Hz), 5.45 (1H, d, *J* = 17.5, 1.8 Hz), 5.30 (1H, ddt, *J* = 10.5, 1.3, 1.3 Hz), 4.76 (2H, ddd, *J* = 5.4, 1.3, 1.3 Hz), 4.35 (2H, d, *J* = 6.7 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 154.6, 136.3, 134.2, 131.7, 131.0, 128.5, 128.1, 127.9, 127.4, 126.5, 123.1, 122.6, 118.1, 82.7, 71.0, 67.5, 52.3. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $C_{21}H_{20}NO_2$ 318.1489 found 318.1474.

Allyl cinnamyl(4-fluorophenyl)ethynyl)carbamate (1b)

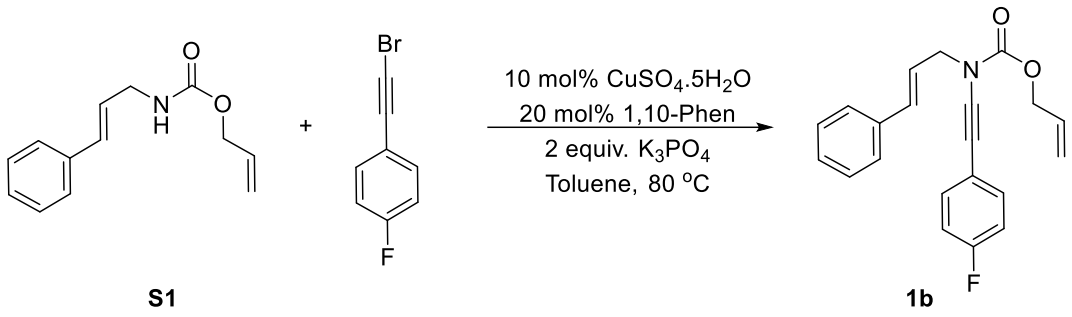


S1 **1b**

The title compound was prepared by General Procedure A from allyl cinnamyl carbamate (500 mg, 2.30 mmol) and 4-(bromoethynyl)-1-fluorobenzene (546 mg, 2.76 mmol). The crude product was purified by flash column chromatography (Hexanes/EtOAc 20:1) to afford **1b** (509 mg, 66%) as an orange oil.

R_f (Hexanes/EtOAc 5:1) = 0.54. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.42-7.40 (2H, m), 7.37-7.31 (4H, m), 7.28-7.25 (1H, m), 7.00-6.96 (2H, m), 6.68 (1H, d, *J* = 16.0, 1.3 Hz), 6.31 (1H, dt, *J* = 16.0, 6.9 Hz), 5.99 (1H, ddt, *J* = 17.2, 10.7, 5.3 Hz), 5.42 (1H, ddt, *J* = 17.2, 1.3, 1.3 Hz), 5.29 (1H, ddt, *J* = 10.7, 1.3, 1.3 Hz), 4.75 (2H, ddd, *J* = 5.3, 1.3, 1.3 Hz), 4.33 (2H, dd, *J* = 6.9, 1.3 Hz), ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.1 (d, $^1J_{CF}$ = 248.5 Hz),, 154.7, 136.4, 134.4, 133 (d, $^3J_{CF}$ = 8.2 Hz), 131.9, 128.7, 128.0, 126.7, 122.7, 119.3 (d, $^4J_{CF}$ = 3.7 Hz), 118.3, 115.6 (d, $^2J_{CF}$ = 22.0 Hz), 82.4, 70.1, 67.7, 52.4. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $C_{21}H_{19}FNO_2$ 336.1394 found 336.1379.

Allyl cinnamyl(4-(trifluoromethyl)phenyl)ethynyl)carbamate (1c)

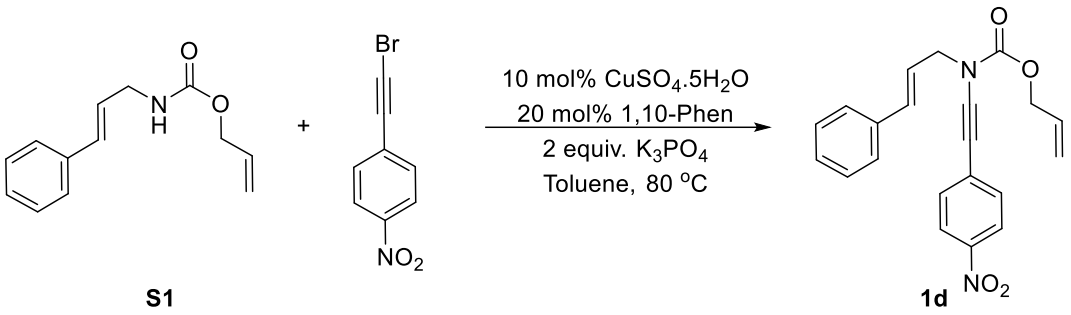


S1 **1b**

The title compound was prepared by General Procedure A from allyl cinnamyl carbamate (137 mg, 0.63 mmol) and 4-(bromoethynyl)-1-trifluoromethylbenzene (188 mg, 0.76 mmol) The crude product was purified by flash column chromatography (Hexanes/EtOAc 20:1) to afford **1c** (78 mg, 32%) as a yellow oil.

R_f (Hexanes/CH_2Cl_2 1:1) = 0.35. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.55-7.53 (2H, m), 7.48-7.45 (4H, m), 7.39-7.34 (2H, m), 7.32-7.27 (1H, m), 6.71 (1H, d, *J* = 15.8 Hz), 6.33 (1H, ddd, *J* = 15.8, 6.7, 6.7 Hz), 6.03 (1H, ddt, *J* = 17.0, 10.1, 6.0 Hz), 5.46 (1H, ddt *J* = 17.1, 1.3, 1.3 Hz), 5.33 (1H, ddt, *J* = 10.6, 1.3, 1.3 Hz), 4.79 (2H, ddt, *J* = 14.4, 13.1, 11.8 Hz), 4.38 (2H, ddd, *J* = 6.7, 1.2,.1.2 Hz), ^{13}C-NMR (100 MHz, $CDCl_3$) δ 154.5, 136.2, 134.7, 131.7, 130.9, 129.0 (q, $^2J_{CF}$ = 32.5 Hz), 128.1, 127.2, 127.2 125.2 (q, $^3J_{CF}$ = 3.9 Hz), 124.1 (q, $^1J_{CF}$ = 272.2 Hz), 122.4, 118.4, 85.4, 70.5, 67.8, 52.4, HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd. for $C_{22}H_{18}F_3NO_2Na$ 386.1362 found 386.1364.

Allyl cinnamyl((4-nitrophenyl)ethynyl)carbamate (1d)

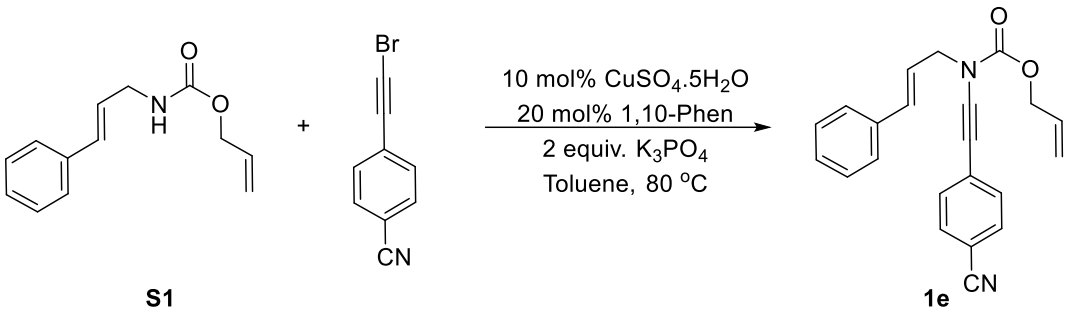


S1 1d

The title compound was prepared by General Procedure A from allyl cinnamyl carbamate (795 mg, 3.66 mmol) and 4-(bromoethynyl)-1-nitrobenzene (985 mg, 4.40 mmol). The crude product was purified by flash column chromatography (Hexanes/EtOAc 3:1) to afford **1d** (924 mg, 70%) as an orange oil.

R_f (Hexanes/EtOAc 3:1) = 0.47. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.16 (2H, dd, *J* = 8.7, 1.8 Hz), 7.49-7.41 (4H, m), 7.34-7.27 (2H, m), 7.28-7.23 (1H, m), 6.68 (1H, d, *J* = 15.8 Hz), 6.26 (1H, dt, *J* = 16.0, 6.9 Hz), 6.98 (1H, ddt, *J* = 17.2, 10.7, 5.3 Hz), 5.42 (1H, ddt, *J* = 18.3, 1.1, 1.1 Hz), 5.29 (1H, ddt, *J* = 10.5, 1.1, 1.1 Hz), 4.74 (2H, ddd, *J* = 6.8, 1.3, 1.3 Hz), 4.35 (2H, dd, *J* = 6.6, 1.1 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 154.2, 146.1, 136.1, 134.9, 131.6, 130.9, 130.7, 128.5, 128.2, 126.6, 123.6, 122.1, 118.6, 88.8, 71.0, 67.9, 52.4. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd. for $C_{21}H_{18}N_2O_4Na$ 385.1159 found 385.1153.

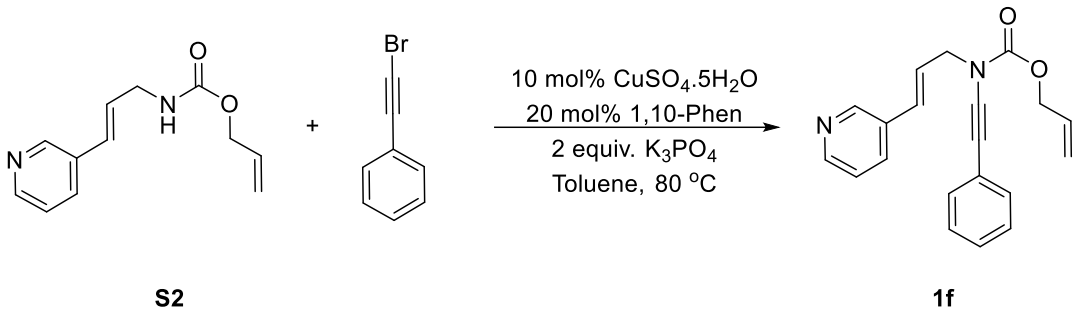
Allyl cinnamyl(4-cyanophenyl)ethynyl)carbamate (1e)



The title compound was prepared by General Procedure A from allyl cinnamyl carbamate (1.05 g, 5.07 mmol) and 4-(bromoethynyl)benzonitrile (1.32 g, 6.08 mmol). The crude product was purified by flash column chromatography (Hexanes/EtOAc 20:1) to afford **1e** (347 mg, 33%) as a yellow oil.

R_f (Hexanes/EtOAc 5:1) = 0.38. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.60-7.53 (2H, m), 7.45-7.38 (3H, m), 7.36-7.32 (2H, m), 7.30-7.26 (2H, m), 6.68 (1H, d, *J* = 15.5 Hz), 6.29 (1H, dt, *J* = 15.5, 6.8 Hz), 5.99 (1H, ddt, *J* = 17.0, 10.7, 5.3 Hz), 5.43 (1H, ddt, *J* = 17.2, 1.0 Hz), 5.31 (1H, ddt, *J* = 10.4, 1.6, 1.6 Hz), 4.76 (2H, ddd, *J* = 5.5, 1.1, 1.1 Hz), 4.36 (2H, ddd, *J* = 6.6, 1.1, 1.1 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 154.2, 136.0, 134.7, 131.9, 131.5, 130.0, 128.6, 128.4, 128.1, 126.5, 122.1, 118.7, 118.6, 110.2, 87.7, 70.6, 67.9, 52.2. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $C_{23}H_{18}N_2O_2$ 343.1441 found 343.1447.

Allyl (E)-(phenylethynyl)(3-(pyridin-3-yl)allyl)carbamate (1f)

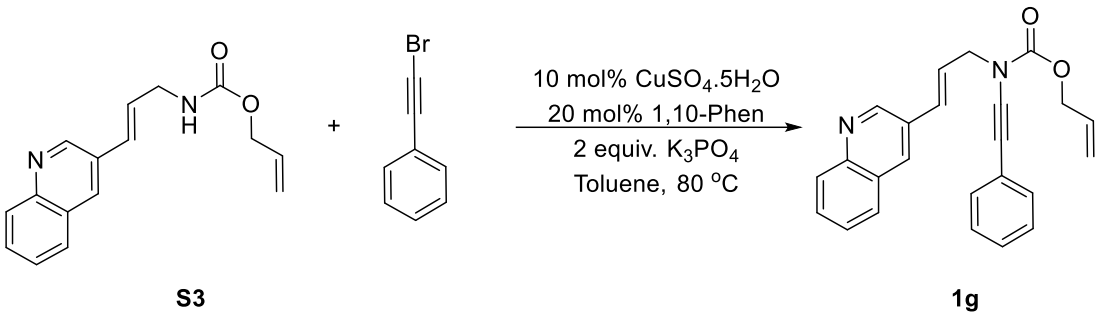


S2 **1f**

The title compound was prepared by General Procedure A from pyridyl carbamate **S2** (860 mg, 3.94 mmol) and (bromoethynyl)benzene (856 mg, 4.73 mmol). The crude product was purified by flash column chromatography (Hexanes/EtOAc 1:1) to afford **1f** (601 mg, 48%) as a yellow oil.

R_f (Hexanes/EtOAc 2:1) = 0.59. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.64 (1H, d, *J* = 1.9 Hz), 8.51-8.48 (1H, m), 7.73 (1H, dd, *J* = 7.9, 1.7 Hz), 7.40-7.36 (2H, m), 7.31-7.22 (4H, m), 6.66 (1H, dd, *J* = 15.9, 2.8 Hz), 6.39 (1H, dt, *J* = 15.8, 6.7 Hz), 5.98 (1H, ddt, *J* = 17.1, 10.6, 5.1 Hz), 5.43 (1H, ddt, *J* = 17.2, 1.2, 1.2 Hz), 5.28 (1H, ddt, *J* = 10.4, 1.4, 1.4 Hz), 4.74 (2H, ddd, *J* = 5.5, 1.5, 1.5 Hz), 4.36 (2H, dd, *J* = 6.3, 1.2 Hz). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 154.7, 149.0, 148.4, 133.1, 132.0, 131.7, 131.3, 131.1, 130.5, 127.7, 125.3, 123.5, 123.0, 118.3, 82.6, 71.1, 67.7, 52.2. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd. for $C_{20}H_{18}N_2O_2Na$ 341.1260 found 341.1259.

Allyl (*E*)-(phenylethynyl)(3-(quinolin-3-yl)allyl)carbamate (1g)

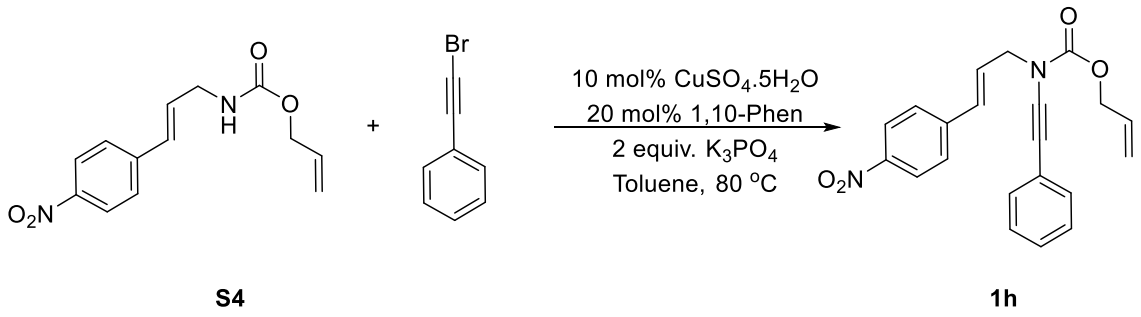


S3 **1g**

The title compound was prepared by General Procedure A from quinolyl carbamate **S3** (940 mg, 3.5 mmol) and (bromoethynyl)benzene (760 mg, 4.2 mmol). The crude product was purified by flash column chromatography (Hexanes/EtOAc 10:1) to afford **1g** (581 mg, 45%) as a yellow oil.

R_f (Hexanes/EtOAc 2:1) = 0.41. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.03 (1H, d, *J* = 2.5 Hz), 8.12-8.10 (2H, m), 7.81 (1H, ddd, *J* = 9.5, 8.1, 1.3 Hz), 7.73-7.68 (1H, m), 7.58-7.55 (1H, m), 7.42-7.38 (2H, m), 7.33-7.26 (3H, m), 6.84, (1H, dd *J* = 15.8, 1.5 Hz) 6.56, (1H, dt, *J* = 15.6, 6.2 Hz), 6.02 (1H, ddt, *J* = 17.2, 10.5, 5.1 Hz), 5.45 (1H, ddt, *J* = 17.2, 1.2, 1.2 Hz), 5.31 (1H, ddt, *J* = 10.5, 1.2, 1.2 Hz), 4.78 (2H, ddd, *J* = 5.6, 1.2, 1.2 Hz), 4.43 (2H, dd, *J* = 6.4, 1.2 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 154.8, 149.0, 147.3, 133.2, 131.7, 131.2, 130.7, 129.6, 129.3, 129.2, 128.9, 128.3, 127.9, 127.7, 127.2, 125.5, 123.0, 118.4, 67.7, 59.5, 55.9, 52.3. HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd. for $C_{24}H_{21}N_2O_2$ 369.1598 found 369.1603.

Allyl (*E*)-(3-(4-nitrophenyl)allyl)(phenylethynyl)carbamate (1h)

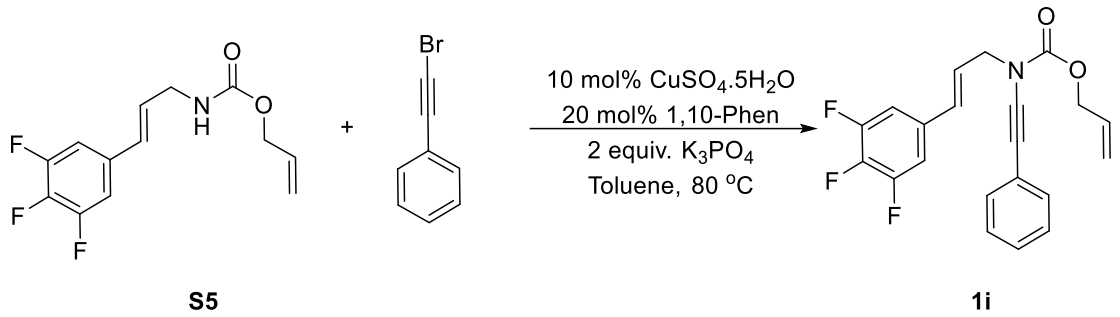


S4 **1h**

The title compound was prepared by General Procedure A from 4-nitrophenyl carbamate **S4** (1.93 g, 7.4 mmol and 1-(2-bromoethynyl)benzene (1.47 g, 8.2 mmol). The crude product was purified by flash column chromatography (Hexanes/EtOAc 5:1) to afford **1h** (904 mg 34%) as a yellow oil.

R_f (Hexanes/EtOAc 5:1) = 0.47. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.14 (2H, dd *J* = 8.9, 1.9 Hz), 7.49, (2H, dd *J* = 8.8 1.9 Hz, 7.37-7.20 (5H, m), 6.84 (1H, dd, *J* = 15.9, 1.6 Hz), 6.46 (1H, dt, *J* = 15.9, 6.5 Hz), 5.95 (1H, ddt, *J* = 17.1, 10.6, 5.2 Hz), 5.39 (1H, dd, *J* = 16.8, 1.3 Hz), 5.26 (1H, dd, *J* = 10.7, 1.3 Hz), 4.71 (2H, ddd, *J* = 5.4, 1.4, 1.4 Hz), 4.36 (2H, dd, *J* =6.4, 1.2 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 155.0, 154.7, 147.2, 142.7, 131.7, 131.1, 128.9, 128.3, 127.8, 124.0, 122.9, 119.3, 118.4, 82.5 67.8, 52.1, 48.0. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd. for $C_{21}H_{18}N_2O_4Na$ 385.1159 found 385.1153.

Allyl (*E*)-(phenylethynyl)(3-(3,4,5-trifluorophenyl)allyl)carbamate (1i)

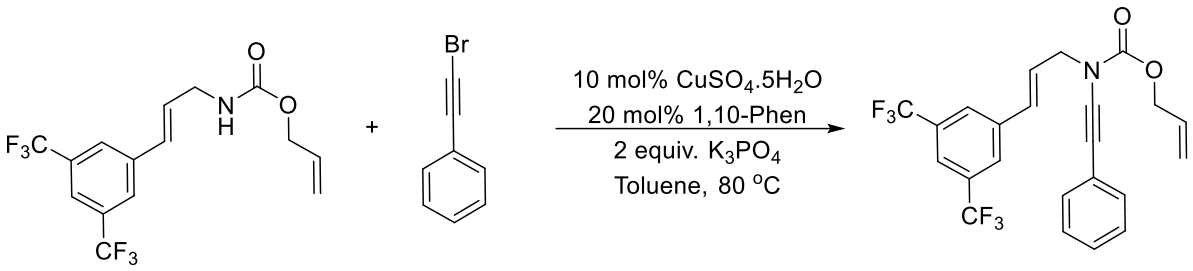


S5 **1i**

The title compound was prepared by General Procedure A from 3,4,5-trifluorophenyl carbamate **S5** (900 mg, 3.32 mmol) and (bromoethynyl)benzene (722 mg, 3.99 mmol). The crude product was purified by flash column chromatography (Hexanes/EtOAc 10:1) to afford **1i**, (457 mg 37%) as a yellow oil.

R_f (Hexanes/EtOAc 2:1) = 0.78. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.40-7.35 (2H, m), 7.32-7.24 (3H, m), 6.98 (2H, dd, J_{HF} = 14.7, 7.3 Hz) 6.51 (1H, d, J = 15.8 Hz), 6.24 (1H, dt, J = 15.6, 6.2 Hz), 5.98 (1H, ddt, J = 16.2, 10.5, 5.1 Hz), 5.43 (1H, ddt, J = 17.1, 1.3, 1.3 Hz), 5.29 (1H, ddt, J = 10.8, 1.3, 1.3 Hz), 4.74 (2H, ddd, J = 5.4, 1.3, 1.3 Hz), 4.31 (2H, dd, J = 6.3, 1.3 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 154.7, 151.4 (ddd, $^1J_{CF}$ = 249.5 Hz, $^3J_{CF}$ = 10.2 Hz, $^4J_{CF}$ = 4.0 Hz), 139.3 (dt, $^1J_{CF}$ = 252.3 Hz, $^2J_{CF}$ = 17.5 Hz), 132.5 (td, $^3J_{CF}$ = 7.8 Hz, $^4J_{CF}$ = 4.7 Hz), 131.7, 131.1, 128.4, 128.3, 127.7, 125.5, 125.5, 123.0, 110.4 (m, second order C-F coupling), 82.5, 71.1, 67.7, 51.9. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd. for $C_{21}H_{16}F_3NO_2Na$ 394.1025 found 394.1022.

Allyl (*E*)-(3-(3,5-bis(trifluoromethyl)phenyl)allyl)(phenylethynyl)carbamate (1j)

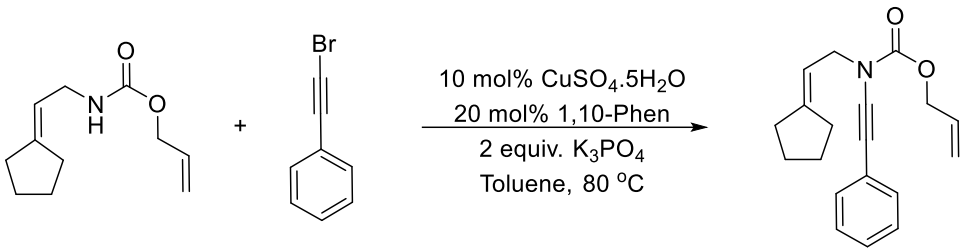


S6 **1j**

The title compound was prepared by General Procedure A from 3,5-bis(trifluoromethyl)phenyl carbamate **S6** (675 mg, 1.91 mmol) and 1-(2-bromoethynyl)-benzene (380 mg, 2.10) . The crude product was purified by silica chromatography (Hexanes/EtOAc 10:1) to afford **1j** (160 mg, 18%), as a yellow oil.

R_f (Hexanes/EtOAc 2:1) = 0.78. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.84-7.82 (2H, m), 7.78-7.76 (1H, m), 7.41-7.37 (2H, m), 7.33-7.27 (3H, m), 6.75 (1H, d, J = 15.8, 2 Hz), 6.66 (1H, dt, J = 15.9, 6.2 Hz), 6.02 (1H, ddt, J = 16.2, 10.5, 5.1 Hz), 5.46 (1H, ddt, J = 17.2, 1.3 Hz), 5.31 (1H, ddt, J = 10.5, 1.2, 1.2 Hz), 4.77 (2H, ddd, J = 5.3, 1.4, 1.4 Hz), 4.40 (2H, dd, J = 6.2, 1.3 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 154.7, 138.4, 132.0 (q, $^2J_{CF}$ = 33.4 Hz), 131.7, 131.2, 128.3, 127.8, 127.2, 126.4 (q, $^3J_{CF}$ = 3.4 Hz), 124.6, 123.3 (q, $^1J_{CF}$ = 272.2 Hz), 121.3 (sept., $^3J_{CF}$ = 3.7 Hz), 118.4, 82.5, 71.1, 67.8, 52.0. HRMS (ESI-TOF) *m/z:* $[M + Na]^+$ Calcd. for $C_{23}H_{17}F_6NO_2Na$ 454.1236 found 454.1239.

Allyl (2-cyclopentylideneethyl)(phenylethynyl)carbamate (1k)

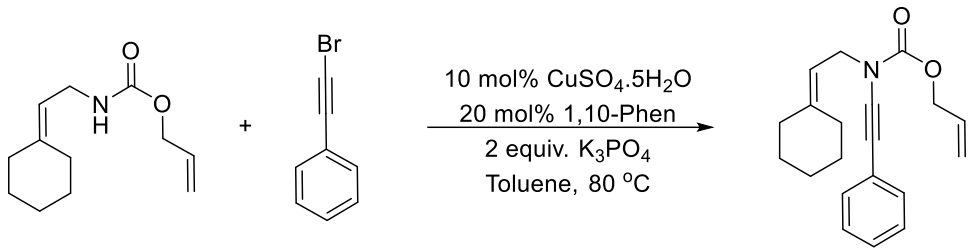


S7 **1k**

The title compound was prepared by general procedure A from cyclopentyl carbamate **S7** (291 mg, 1.49 mmol) and (bromoethynyl)benzene (322 mg, 1.79 mmol). The crude product was purified by flash column chromatography (Hexanes/Et_2O 30:1) to afford **1k** (211 mg, 48%) as a yellow oil.

R_f (Hexanes/Et_2O 20:1) = 0.35. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.40-7.23 (5H, m), 6.04 (1H, ddt, *J* = 17.2, 10.6, 5.4 Hz), 5.50 (1H, tdd, *J* = 7.3, 2.5, 2.5 Hz), 5.41 (1H, ddt, *J* = 17.2, 1.1, 1.1 Hz), 5.24 (1H, ddt, *J* = 10.5, 1.1, 1.1 Hz), 4.71 (2H, ddd, *J* = 5.4, 1.2, 1.2 Hz), 4.16 (2H, d, *J* = 7.3 Hz), 2.41-2.29 (4H, m), 1.74-1.59 (4H, m). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 154.8, 149.9, 131.9, 130.9, 128.2, 127.3, 123.8, 123.5, 118.0, 113.6, 83.4, 67.4, 49.4, 33.8, 28.9, 26.3, 26.1. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $C_{20}H_{21}NO_2$ 296.1645 found 296.1647.

Allyl (2-cyclohexylideneethyl)(phenylethynyl)carbamate (1l)

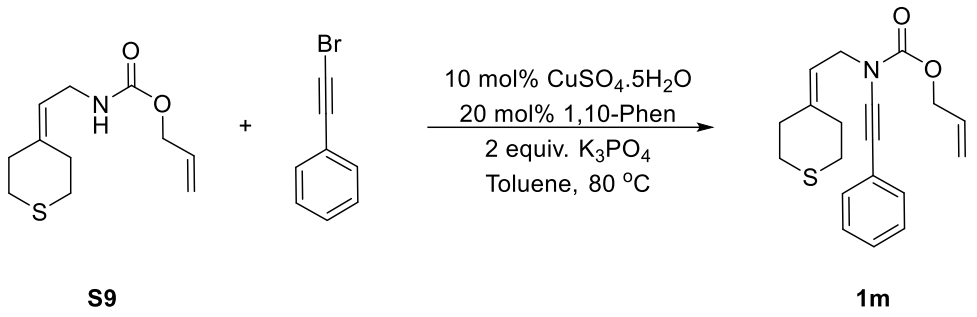


S8 **1l**

The title compound was prepared by General Procedure A from cyclohexyl carbamate **S8** (692 mg, 3.31) and (bromoethynyl)benzene (715 mg, 3.97 mmol). The crude product was purified by flash column chromatography (Hexanes/Et_2O 30:1) to afford **1l** (237 mg, 23%) as a colorless oil.

R_f (Hexanes/EtOAc 10:1) = 0.54. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.40-7.35 (2H, m), 7.32-7.24 (3H, m), 5.97 (1H, ddt, *J* = 17.6, 10.6, 5.5 Hz), 5.43 (1H, ddd, *J* = 17.6, 2.3, 2.3 Hz), 5.33 (1H, ddt, *J* = 10.6, 1.4, 1.4 Hz), 5.27 (1H, ddt, *J* = 10.4, 1.1, 1.1 Hz), 4.71 (2H, ddd, *J* = 5.3, 1.2, 1.2 Hz), 4.18 (2H, d, *J* = 7.5 Hz), 2.26-2.24 (2H, m), 2.19-2.12 (2H, m), 1.59-1.52 (6H, m). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 154.9, 146.4, 132.0, 131.0, 128.2, 127.3, 123.5, 118.0, 114.6, 83.2, 70.8, 67.4, 46.9 37.1, 29.1, 28.4, 28.0, 26.7, HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd. for $C_{20}H_{23}NO_2Na$ 332.1621 found 332.1618.

Allyl (phenylethynyl)(2-(tetrahydro-4H-thiopyran-4-ylidene)ethyl)carbamate (1m)

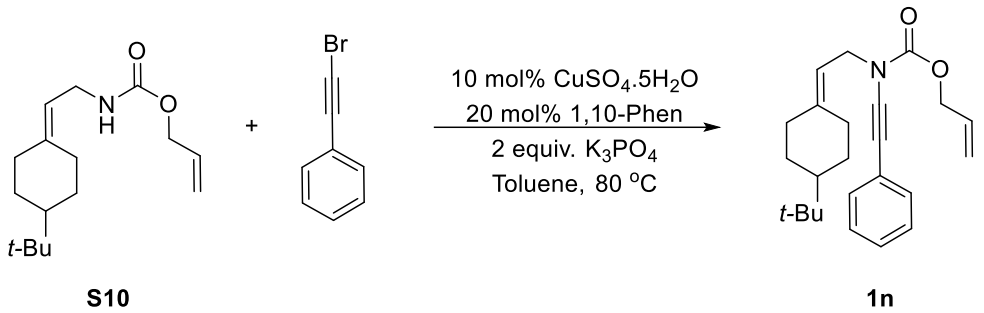


S9 **1m**

The title compound was prepared by General Procedure A from thiopyranyl carbamate **S9** (342 mg, 1.51 mmol) and 1-(2-bromoethynyl)-4-benzene (327 mg, 1.81 mmol). The crude product was purified by silica chromatography (Hexanes/Et_2O 10:1) to afford **1m** (167 mg 34%) as a colorless oil.

R_f (Hexanes/EtOAc 10:1) = 0.42. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.42-7.36 (2H, m), 7.34-7.25 (3H, m), 5.99 (1H, ddt, *J* = 16.3, 10.4, 5.4 Hz), 5.45 (1H, d, *J* = 7.5 Hz), 5.42 (1H, ddt, *J* = 16.3, 1.2, 1.2 Hz) 5.29 (1H, ddt, *J* = 10.6, 1.2, 1.2 Hz), 4.72 (2H, ddd, *J* = 5.4, 1.2, 1.2 Hz), 4.19 (2H, d, *J* = 7.6 Hz), 2.72-2.62 (6H, m) 2.53-2.48 (2H, m). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 154.7, 143.0, 131.9, 131.0, 128.3, 127.5 123.2, 118.1, 117.9, 82.9, 70.8, 67.5, 46.5, 38.8, 31.0, 31.0, 30.4. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $C_{19}H_{22}NO_2S$ 328.1366 found 328.1369.

Allyl (2-(4-(tert-butyl)cyclohexylidene)ethyl)(phenylethynyl)carbamate (1n)

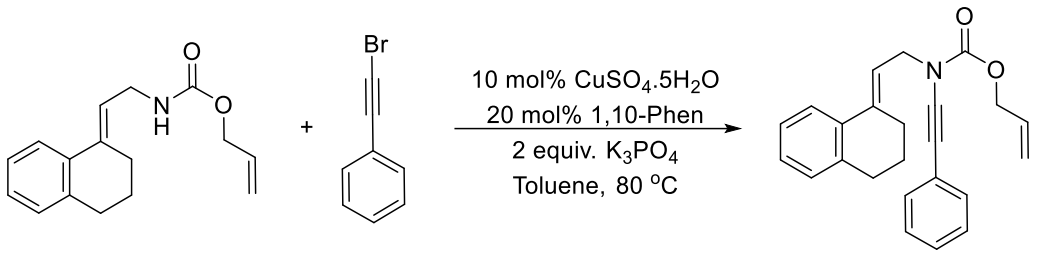


S10 **1n**

The title compound was prepared by General Procedure A from 4-*tert*-butylcyclohexyl carbamate **S10** (1.03 g, 3.89 mmol and 1-(2-bromoethynyl)-4-benzene (845 mg, 4.67 mmol) The crude product was purified by flash column chromatography (Hexanes/EtOAc 20:1) to afford **1n** (511 mg, 36%) as an amber oil.

R_f (Hexanes/EtOAc 19:1) = 0.35. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.43-7.38 (2H, m), 7.33-7.26 (3H, m), 5.99 (1H, ddt, *J* = 17.2, 10.6, 5.6 Hz), 5.43 (1H, ddt, *J* = 17.2, 1.4, 1.4 Hz), 5.34 (1H, tdd, *J* = 7.5, 1.3, 1.3 Hz), 5.29 (1H, ddt, *J* = 10.6, 1.4, 1.4 Hz), 4.73 (2H, ddd, *J* = 5.5, 1.4, 1.4 Hz), 4.41 (2H, ddd, *J* = 8.0, 2.2, 2.2 Hz), 2.83 (1H, dddd, *J* = 13.6, 2.0, 2.0, 2.0 Hz), 2.33 (1H, dddd, *J* = 13.5, 3.0, 3.0, 3.0 Hz), 2.08 (1H, ddd, *J* = 12.9, 12.9, 3.0 Hz), 1.93-1.84 (2H, m), 1.81 (1H, ddd, *J* = 13.1, 13.1, 3.5 Hz), 1.21 (1H, dddd, *J* = 11.9, 11.9, 2.8 2.8 Hz), 1.09 (1H, ddd, *J* = 12.5, 3.7 Hz), 1.04 (1H, dddd, *J* = 13.0, 13.0, 13.0, 3.3 Hz) 0.83 (9H, s). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 154.9, 146.4, 132.0, 131.1, 128.2, 127.4, 127.3, 123.5, 118.0, 114.3, 77.2 67.4, 48.3, 47.0, 37.0, 32.4, 29.1, 28.8, 28.7, 27.6. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $C_{24}H_{32}NO_2$ 366.2428 found 366.2448.

Allyl (E)-(2-(3,4-dihydronaphthalen-1(2H)-ylidene)ethyl)(phenylethynyl)carbamate (1o)

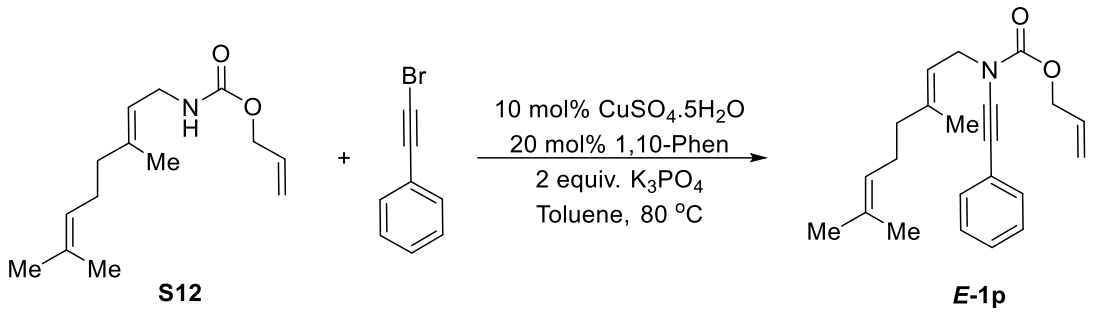


S11 **1o**

The title compound was prepared by General Procedure A from tetralone derived carbamate **S11** (216 mg, 0.84 mmol) and (bromoethynyl)benzene (227 mg, 1.26 mmol). The crude product was purified by silica chromatography (Hexanes/Et_2O 10:1) to afford **1o** (169 mg, 56%) as a colorless oil.

R_f (Hexanes/EtOAc 10:1) = 0.57. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.63-7.60 (1H, m), 7.40-7.35 (2H, m), 7.31-7.24 (3H, m), 7.19-7.14 (2H, m), 7.12-7.08 (1H, m), 6.17 (1H, dt, *J* = 7.3, 1.2, 1.2 Hz), 5.99 (1H, ddt, *J* = 17.2, 10.5, 5.2 Hz), 5.45 (1H, ddt, *J* = 17.2, 1.2, 1.2 Hz), 5.28 (1H, ddt, *J* = 10.5, 1.2, 1.2 Hz), 4.74 (2H, ddd, *J* = 8.5, 6.8, 5 Hz), 4.42 (2H, dd, *J* = 7.18, 1.2 Hz), 2.80 (2H, t, *J* = 6.2 Hz) 2.65 (2H, dd, *J* = 5.9, 1.2 Hz), 1.87 (2H, tt, *J* = 6.2, 5.9 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 154.9, 139.3, 137.9, 135.2, 131.9, 131.1, 129.0, 128.3, 127.6, 127.5, 126.2, 124.2, 123.4, 118.2, 116.9, 83.2, 70.9, 67.6, 48.0, 30.3, 26.7, 23.3, HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd. for $C_{24}H_{23}NO_2Na$ 380.1621 found 380.1622.

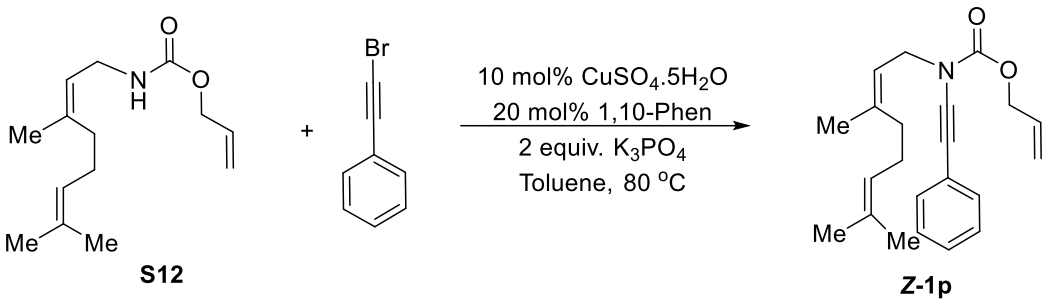
Allyl (*E*)-(3,7-dimethylocta-2,6-dien-1-yl)(phenylethynyl)carbamate (*E*-1p)



The title compound was prepared by General Procedure A from geranyl carbamate **S12** (280 mg, 1.94 mmol) and (bromoethynyl)benzene (428 mg, 2.38 mmol) The crude product was purified by flash column chromatography (Hexanes/EtOAc 30:1) to afford **1p** (280 mg, 43%) as a yellow oil.

R_f (Hexanes/Et_2O 20:1) = 0.36. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.42-7.36 (2H, m), 7.34-7.25 (3H, m), 5.99 (1H, ddt, *J* = 17.1, 10.6, 5.4 Hz), 5.42 (1H, ddt, *J* = 17.1, 1.4, 1.4 Hz), 5.41 (1H, tq, *J* = 7.8, 1.2 Hz), 5.29 (1H, ddt, *J* = 10.6, 1.2, 1.2 Hz), 5.12 (1H, tt, *J* = 6.8, 1.3 Hz), 4.74 (2H, ddd, *J* = 5.4, 1.4, 1.4 Hz), 4.22 (2H, d, *J* = 7.3 Hz), 2.18-2.07 (4H, m), 1.79 (3H, s), 1.69 (3H, s), 1.62 (3H, s). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 154.9, 141.7, 132.0, 131.8, 130.9, 128.2, 127.3, 123.8, 123.5, 118.0, 117.9, 83.2, 70.8, 67.4, 47.7, 39.6, 26.4, 25.7, 17.7, 16.5. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $C_{22}H_{28}NO_2$ 338.2115 found 338.2106.

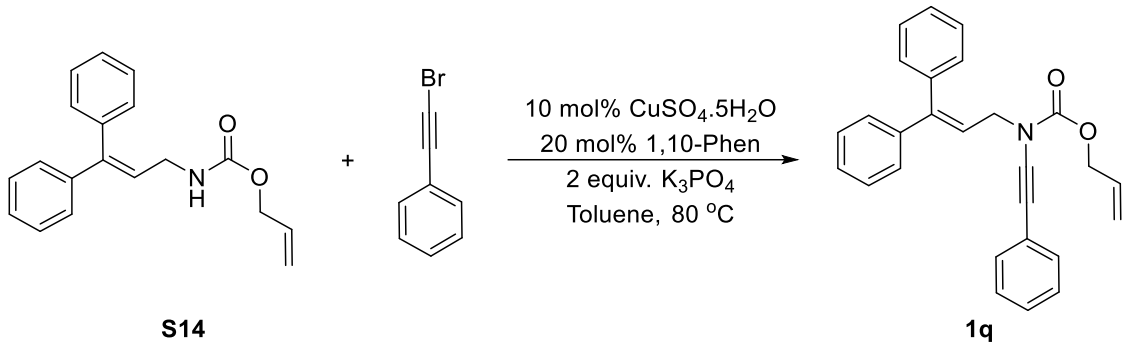
Allyl (Z)-(3,7-dimethylocta-2,6-dien-1-yl)(phenylethynyl)carbamate (*Z*-1p)



The title compound was prepared by General Procedure A from neryl carbamate **S13** (540 mg, 2.28 mmol) and (bromoethynyl)benzene (492 mg, 2.74 mmol). The crude product was purified by flash column chromatography (Hexanes/EtOAc 20:1) to afford **1p'** (499 mg, 65%) as a yellow oil.

R_f (Hexanes/Et_2O 30:1) = 0.36. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.38-736 (2H, m), 7.31-7.26 (3H, m), 5.98 (1H, ddt, *J* = 17.0, 10.5, 5.3 Hz), 5.42 (1H, ddt, *J* = 17.0, 1.2, 1.2 Hz), 5.38 (1H, t, *J* = 7.0 Hz), 5.27 (1H, ddd, *J* = 10.5, 1.2, 1.2 Hz), 5.12 (1H, tt, *J* = 7.0, 1.2, 1.2 Hz), 4.72 (2H, ddd, *J* = 5.3, 1.2, 1.2 Hz), 4.17 (2H, d, *J* = 7.3 Hz), 2.20-2.10 (4H, m), 1.79 (3H, s), 1.69 (3H, s), 1.62 (3H, s). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 154.9, 141.6, 132.1, 131.9, 130.9, 128.2 127.3, 123.7, 123.5, 118, 67.4, 47.6, 32.2, 29.7 26.7, 25.7, 23.5 17.7. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $C_{22}H_{28}NO_2$ 338.2115 found 338.2106.

Allyl (3,3-diphenylallyl)(phenylethynyl)carbamate (1q)



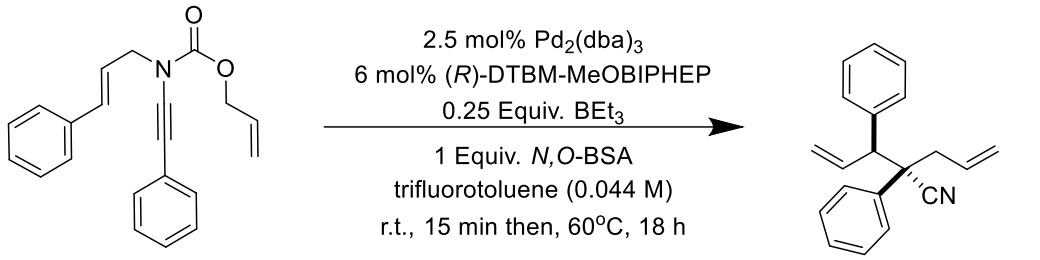
S14 **1q**

The title compound was prepared by General Procedure A from diphenyl carbamate **S14** (468 mg, 1.61 mmol) and 1-(2-bromoethynyl)-4-benzene (349 mg, 1.93 mmol). The crude product was purified by flash column chromatography (Hexanes/EtOAc 20:1) to afford **1q** (95 mg, 15%) as an amber oil.

R_f (Hexanes/EtOAc 19:1) = 0.25. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.39-7.32 (5H, m), 7.32-7.22 (10H, m), 6.23 (1H, t, *J* = 7.1 Hz), 5.97 (1H, ddt, *J* = 16.5, 10.7, 5.7 Hz), 5.40 (1H, ddt, *J* = 17.1, 1.2, 1.2, Hz), 5.27 (1H, ddt, *J* = 10.5, 1.4, 1.4 Hz), 4.71 (2H, ddd, *J* = 5.1, 1.2, 1.2 Hz), 4.26 (2H, d, *J* = 7.1 Hz). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 154.8, 146.1, 141.5, 138.7, 131.8, 131.0, 129.8, 128.4, 128.3, 128.2, 127.8, 127.6, 127.5, 127.4, 123.3, 122.2, 118.2, 82.9, 71.2, 67.6, 49.2, HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $C_{27}H_{24}NO_2H$ 394.1802 found 394.1821.

Formation of Nitriles (2) *via* Auto-Tandem Catalysis

(2*S,3*S**)-2-allyl-2,3-diphenylpent-4-enenitrile (2a)**



1a **2a**

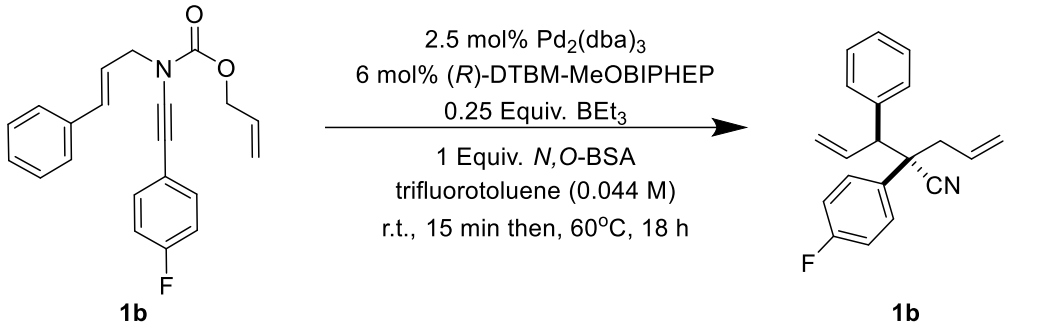
63%, >30:1 *b/l*; 13:1 d.r.

The title compound was prepared by general procedure B from carbamate **1a** (58 mg, 0.18 mmol), $Pd_2(dba)_3$ (4.1 mg, 4.5 μmol), (*R*)-DTBM-MeOBIPHEP (12.4 mg, 10.8 μmol), BEt_3 (1 M in THF, 45 μl, 45 μmol) and *N,O*-BSA (44 μl, 18 μmol) in trifluorotoluene (4.0 mL). The crude product was purified by flash column chromatography (Hexanes/CH_2Cl_2 4:1) to afford the requisite nitrile product **2a** (32 mg, 65%, 13:1 d.r) as a colorless oil.

R_f (Hexanes/CH_2Cl_2 1:1) = 0.40. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.30-7.01 (8H, m), 6.98-6.96 (2H, m), 6.34 (0.93H, ddd, *J* = 16.8, 10.0, 10.0 Hz, major), 5.99 (0.07H, ddt, *J* = 17.1, 10.2, 9.1 Hz, minor) 5.46 (0.93H, ddt, *J* = 16.9, 10.1, 6.7 Hz, major), 5.41-5.32 (0.07H, m, minor), 5.27 (0.93H, dd, *J* = 9.9, 1.1 Hz, major), 5.24 (0.93H, d, *J* = 16.3 Hz, major), 5.10 (0.93H, ddt, *J* = 17.0, 1.4, 1.4 Hz), 4.99 (0.93H, ddt, *J* = 10.2, 1.3, 1.3 Hz, major), 4.97-4.89 (0.28H, m, minor), 4.76 (0.07H, ddt, *J* = 17.1, 1.3, 1.3 Hz, minor), 3.62 (0.07H, d, *J* = 8.5 Hz, minor), 3.54 (0.93H, d, *J* = 9.8 Hz, major), 2.91 (0.93H, dd, *J* = 14.3, 7.6 Hz, major), 2.71 (0.93H, dd, *J* = 14.3, 6.5 Hz, major), 2.62 (0.07H, dd, *J* = 14.2, 6.4 Hz, minor), 2.38 (0.07H, dd, *J* = 14.0, 7.8 Hz, minor). ^{13}C-NMR (major isomer only) (100 MHz, $CDCl_3$) δ 138.6, 136.4, 135.8 131.8, 128.7, 128.3, 128.0,

127.6, 127.2, 127.1, 119.9, 119.3, 60.0, 52.6, 42.8, HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. For $C_{20}H_{20}N$ 274.1590 found 274.1579.

(2*S,3*S**)-2-Allyl-2-(4-fluorophenyl)-3-phenylpent-4-enenitrile (1b)**

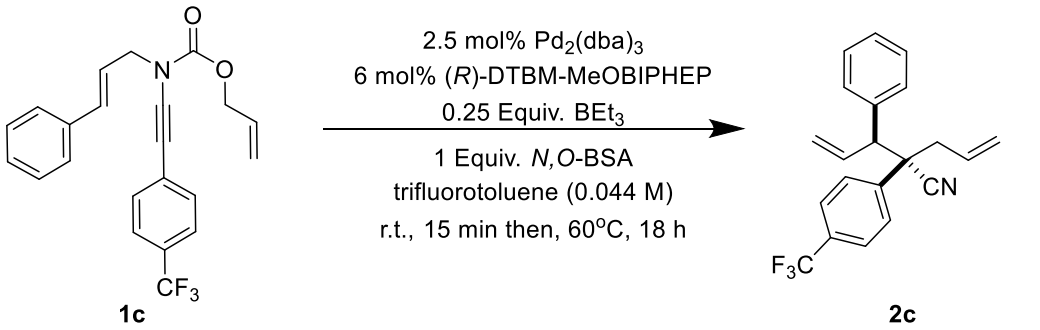


The title compound was prepared by general procedure B from carbamate **1b** (67 mg, 0.2 mmol), $Pd_2(dba)_3$ (4.6 mg, 5.0 μmol) and (*R*)-DTBM-MeOBIPHEP (13.8 mg, 12.0 μmol), BEt_3 (1 M in THF, 50 μl, 50 μmol) and *N,O*-BSA (49 μl, 20 μmol) in trifluorotoluene (4.5 mL). The crude product was purified by flash column chromatography (Hexanes/EtOAc 10:1) to afford the requisite nitrile product **2b** (21 mg, 39%, 5.3:1 d.r.) as a colorless oil.

R_f (Hexanes/EtOAc 10:1) = 0.55. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.30-7.19 (2H, m), 7.08-6.98 (2H, m), 6.89-6.80 (4H, m), 6.32 (0.84H, ddd, *J* = 16.7, 10.0, 10.0 Hz, major), 5.97 (0.16H, ddd, *J* = 16.9, 10.1, 9.0 Hz, minor), 5.46 (0.84H, ddt, *J* = 17.1, 10.1, 7.1 Hz, major), 5.41-5.34 (0.16H, m, minor), 5.27 (0.84H, dd, *J* = 10.3, 1.1 Hz, major), 5.23 (0.84H, dd, *J* = 17.3, 1.1 Hz, major), 5.07 (0.84H, dd, *J* = 17.1, 1.3 Hz, major), 5.01 (0.84H, dd, *J* = 10.1, 1.2Hz, major), 4.99 (0.16H, d, *J* = 9.9 Hz, minor), 4.94 (0.16H, ddd, *J* = 10.5, 1.2, 1.2 Hz, minor), 4.93 (0.16H, ddt, *J* = 17.1, 1.3, 1.3 Hz minor), 4.78 (0.16H, ddt, *J* = 17.1, 1.2, 1.2 Hz, minor), 3.57 (0.16H, d, *J* = 8.9 Hz, minor), 3.48 (0.84H, d, *J* = 9.8 Hz, major), 2.91 (0.84H, dd, *J* = 14.4, 7.4 Hz, major), 2.65 (0.84H, dd, *J* = 14.4, 6.7 Hz, major), 2.57 (0.16H, dddd, *J* = 14.2, 6.8, 1.2, 1.2 Hz, minor), 2.40 (0.16H, dddd, *J* = 14.4, 7.4, 1.2, 1.2 Hz, minor). ^{13}CNMR [Major isomer only] (100 MHz, $CDCl_3$)

δ 161.6 (d, $^{1}J_{CF}$ = 253.3 Hz), 137.3, 135.1, 134.0, 130.5 127.6 (d, $^{3}J_{CF}$ = 8.2 Hz), 127.6 (d, $^{4}J_{CF}$ = 3.3 Hz), 127.6, 127.1 126.2, 119.1, 118.4, 114.2 (d, $^{2}J_{CF}$ = 21.6 Hz), 59.1, 51.0, 41.8. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $C_{21}H_{19}FNO_2$ 292.1496 found 292.1509

(2*S,3*S**)-2-Allyl-3-phenyl-2-(4-(trifluoromethyl)phenyl)pent-4-enenitrile (2c)**

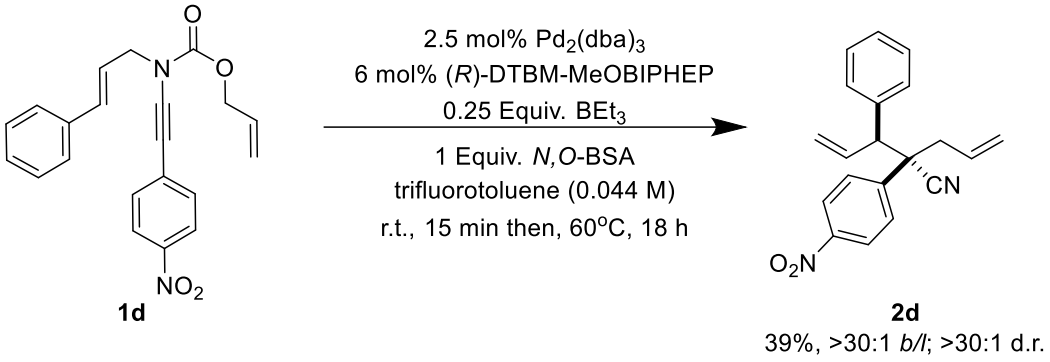


The title compound was prepared by general procedure B from carbamate **1c** (53 mg, 0.14 mmol), $Pd_2(dba)_3$ (3.2 mg, 3.5 μmol), (R)-DTBM-MeOBIPHEP (9.7 mg, 4.0 μmol), BEt_3 (1 M in THF, 35 μl, 35 μmol) and *N,O*-BSA (34 μl, 14 μmol) in trifluorotoluene (3.2 mL). The crude product was purified by flash column chromatography (Hexanes:EtOAc 10:1) to afford the respective nitrile **2c** (25 mg, 57%, 26:1 d.r.) as a colorless oil.

R_f (Hexanes/Ethyl Acetate 10:1) = 0.55. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.58-7.51 (1H, m), 7.24-7.14 (6H, m), 7.07-7.01 (2H, m), 6.37 (1H, ddd, *J* = 16.8, 9.9, 9.9 Hz), 5.48 (1H, ddt, *J* = 16.9, 7.4, 6.6, Hz), 5.41 (1H, d, *J* = 10.2 Hz), 5.32 (1H, d, *J* = 16.4 Hz), 5.11 (1H, ddt, *J* = 17.0, 1.3, 1.3 Hz), 5.03 (1H, ddt, *J* = 10.1, 1.3, 1.3, Hz), 3.67 (1H, d, *J* = 9.8 Hz), 2.91, (1H, dddd, *J* = 14.4, 7.6, 1.3, 1.3 Hz), 2.75, (1H, dddd, *J* = 14.4, 6.6, 1.3, 1.3 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 141.1, 134.9, 134.3, 131.2, 131.1 (q, $^{2}J_{CF}$ = 23.4 Hz), 128.9, 128.8 (q, $^{4}J_{CF}$ = 3.7 Hz), 128.3,

126.8, 122.9 (q, $^{1}J_{CF}$ = 272.7 Hz), 121.3, 121.1 (q, $^{3}J_{CF}$ = 7.5 Hz), 121.0, 120.5, 59.5, 52.7, 42.2. HRMS (ESI-TOF) *m/z*: $[M + Cl]^-$ Calcd. for $C_{21}H_{18}F_3NCl$ 376.1085 found 376.1099.

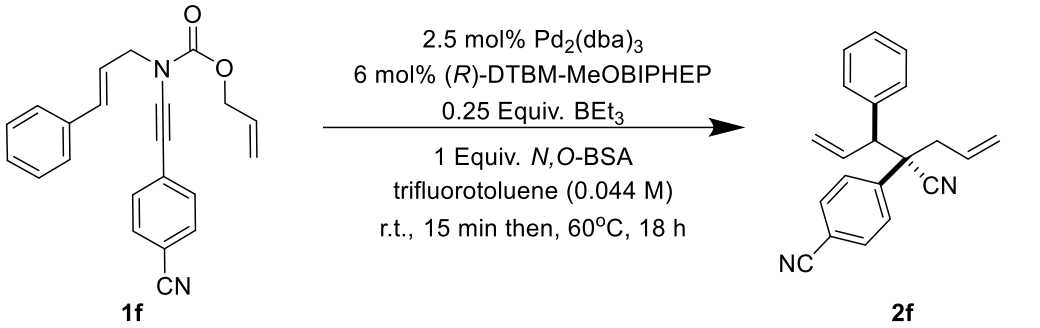
(2*S,3*S**)-2-Allyl-2-(4-nitrophenyl)-3-phenylpent-4-enenitrile (2d)**



The title compound was prepared by general procedure B from carbamate **1d** (72.4 mg, 0.2 mmol), $Pd_2(dba)_3$ (4.6 mg, 5.0 μmol), (*R*)-DTBM-MeOBIPHEP (13.8 mg, 12.0 μmol), BEt_3 (1 M in THF 50 μl, 50 μmol) and *N,O*-BSA (49 μl, 20 μmol) in trifluorotoluene (4.5 mL). The crude product was purified by flash column chromatography (Hexanes/EtOAc 10:1) to afford the requisite nitrile product **2d** (24.8 mg, 39%, >30:1 d.r.) as a colorless oil.

R_f (Hexanes/EtOAc 5:1) = 0.17. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.99 (2H, d, *J* = 8.8 Hz), 7.26 (2H, d, *J* = 8.8 Hz), 7.06-7.01 (3H, m), 6.90-6.86 (2H, m), 6.33 (1H, ddd, *J* = 16.8, 9.9 Hz), 5.47 (1H, ddt, *J* = 17.1, 10.1, 7.1 Hz), 5.31 (1H, d, *J* = 10.1 Hz), 5.27 (1H, d, *J* = 16.9 Hz), 5.05 (1H, ddt, *J* = 18.1, 17.1, 1.2, 1.2 Hz) 5.00, (1H, ddt, *J* = 10.0, 1.2, 1.2 Hz) 3.53 (1H, d, *J* = 9.8 Hz), 3.00 (1H, dddd, *J* = 14.5, 7.2, 1.2, 1.2 Hz), 2.70 (1H, dddd, *J* = 14.4, 7.1, 1.2, 1.2 Hz), ^{13}C-NMR (100 MHz, $CDCl_3$) δ 147.2, 143.5, 137.8, 135.5, 130.7, 128.5, 128.4, 128.3, 127.8, 127.7, 123.5, 120.9, 120.1, 59.9, 52.8, 42.9. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. For $C_{20}H_{19}N_2O_2$ 319.1441 Found 319.1440 .

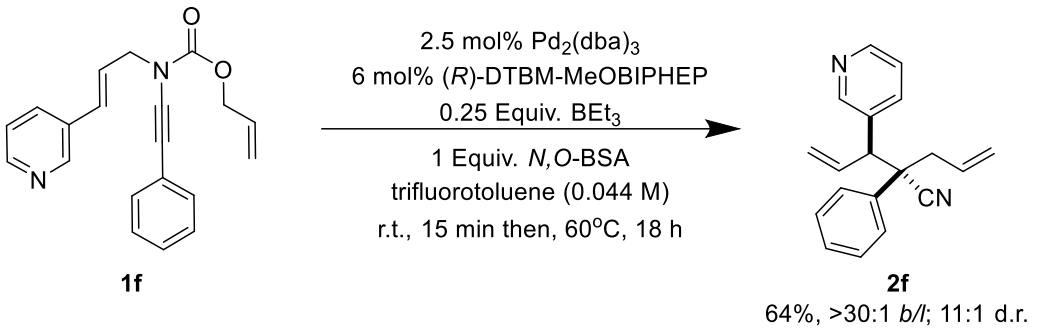
(2*S,3*S**)-2-Allyl-2-(4-cyanophenyl)-3-phenylpent-4-enenitrile (2d)**



The title compound was prepared by general procedure B from carbamate **1e** (57 mg, 0.17 mmol), $Pd_2(dba)_3$ (3.9 mg, 4.3 μmol), (*R*)-DTBM-MeOBIPHEP (11.7 mg, 10.0 μmol), BEt_3 (1 M in THF, 43 μl, 43 μmol) and *N,O*-BSA (42 μl, 0.17 μmol) in trifluorotoluene (3.9 mL). The crude product was purified by flash column chromatography (Hexanes/EtOAc 10:1) to afford the requisite nitrile product **2e** (43 mg, 85%, >30:1 d.r.) as a colorless oil

R_f (Hexanes/CH_2Cl_2 1:1) = 0.63. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.52 (2H, d, *J* = 8.6 Hz), 7.28 (2H, d, *J* = 8.6 Hz), 7.15-7.08 (3H, m), 6.98-6.92 (2H, m), 6.32 (1H, ddd, *J* = 16.8, 9.9, 9.9 Hz), 5.41 (1H, ddt, *J* = 17.1, 10.1, 7.1 Hz), 5.31 (1H, dd, 10.1, 1.0 Hz) 5.26 (1H, d, *J* = 16.8 Hz), 5.14 (1H, ddt, *J* = 17.0, 1.4, 1.4 Hz), 5.09 (1H, ddt, *J* = 10.2, 1.3, 1.3 Hz), 3.50 (1H, d, *J* =9.8 Hz), 2.98 (1H, dddd, *J* = 14.4, 7.2, 1.4, 1.4 Hz), 2.67 (1H, dddd, *J* = 14.4, 7.0, 1.3, 1.3 Hz). ^{13}CNMR (100 MHz, $CDCl_3$) δ 141.5, 137.8, 135.5, 132.1, 130.9, 128.4, 128.4, 128.0, 127.6, 120.8, 120.1, 120.1, 118.2, 111.8, 59.9, 52.9, 42.7. HRMS (ESI-TOF) *m/z*: $[M + Cl]^-$ Calcd. for $C_{21}H_{18}N_2Cl$ 337.1164 found 333.1178.

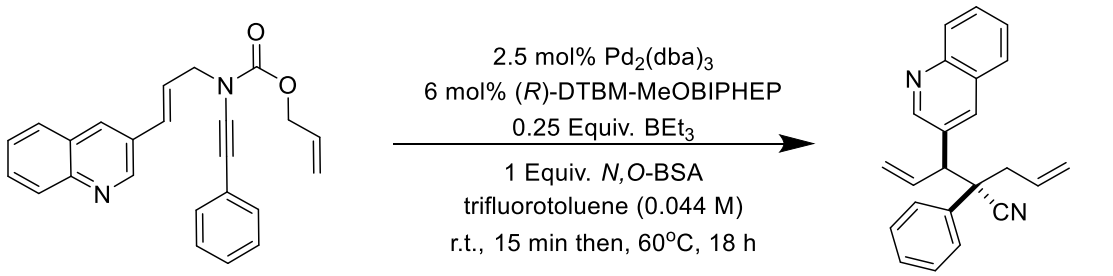
(2*S,3*S**)-2-Allyl-2-phenyl-3-(pyridin-3-yl)pent-4-enenitrile (2f)**



The title compound was prepared by general procedure B from carbamate **1f** (63.6 mg, 0.20 mmol), $Pd_2(dba)_3$ (4.6 mg, 5.0 μmol), (*R*)-DTBM-MeOBIPHEP (13.8 mg, 12.0 μmol), BEt_3 (1M in THF, 50 μl, 50 μmol) and *N,O*-BSA (49 μl, 0.2 mmol) in trifluorotoluene (4.5 mL). The crude product was purified by flash column chromatography (Hexanes/Ethyl Acetate 19:1) to afford the requisite nitrile product **2f** (35 mg, 64%, 11:1 d.r.) as a colorless oil.

R_f (Hexanes/Ethyl Acetate 2:1) = 0.27. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.38 (1H, d, *J* = 2.8 Hz), 7. 98 (1H, s), 7.69 (1H, d, *J* = 8.0 Hz), 7.21-7.13 (5H, m), 7.16 (2H, dd, *J* = 8.6, 1.3 Hz), 6.42 (1H, ddt, *J* = 26.8, 20, 16.7), 5.51 (1H, ddt, *J* = 17.0, 10.1, 6.9 Hz), 5.46 (1H, d, *J* = 10.2 Hz), 5.39 (1H, d, *J* = 16.8 Hz), 5.16 (1H, ddt, *J* = 17.0, 1.3, 1.3 Hz), 5.09 (1H, ddt, *J* = 10.1, 1.3, 1.3 Hz), 3.72 (1H, d, *J* = 9.7 Hz), 3.00 (1H, dddd, *J* = 14.2, 7.6, 1.3, 1.3 Hz), 2.81 (1H, dddd, *J* = 14.3, 6.5, 1.3, 1.3 Hz), ^{13}C-NMR (100 MHz, $CDCl_3$) δ 147.9, 146.3, 137.4, 135.0, 134.6, 131.2, 129.0, 128.4, 128.1, 126.8, 123.8, 121.1, 120.5, 120.3, 57.2, 52.6, 42.7, HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $C_{19}H_{19}N_2$ 275.1543 found 275.1548.

(2*S,3*S**)-2-Allyl-2-phenyl-3-(quinolin-3-yl)pent-4-enenitrile (2g)**

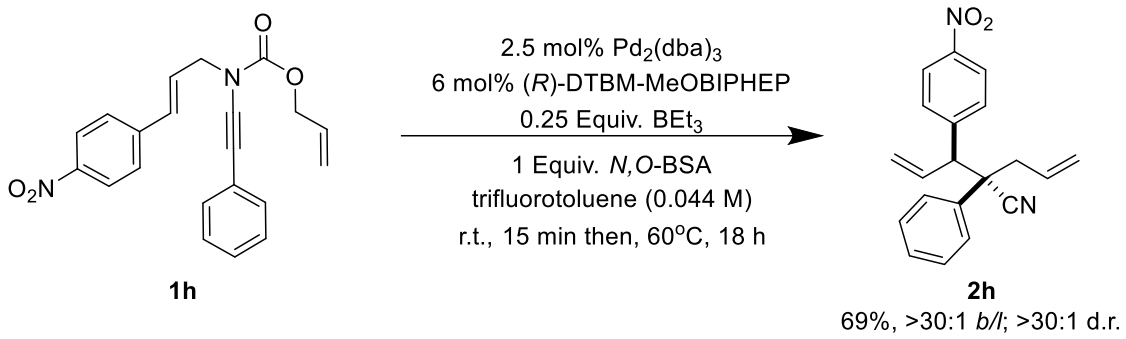


1g **2g**
70%, >30:1 *b/l*; >30:1 d.r.

The title compound was prepared by general procedure B from carbamate **1g** (43 mg, 0.12 mmol), $Pd_2(dba)_3$ (2.8 mg, 3.0 μmol), (*R*)-DTBM-MeOBIPHEP (8.3 mg, 7.2 μmol), BEt_3 (1M in THF, 30 μl, 30 μmol) and N,O-BSA (29 μl, 12 μmol) in trifluorotoluene (2.7 mL). The crude product was purified by flash column chromatography (Hexanes/Ethyl Acetate 19:1) to afford the requisite nitrile product **2g** (28 mg, 70%, >30:1 d.r.) as a colorless solid.

R_f (Hexanes/Ethyl Acetate 2:1) = 0.28. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.17 (1H, d, *J* = 1.8 Hz), 8.05 (1H, d, *J* = 1.8 Hz), 8.01 (1H, d, *J* = 8.5 Hz), 7.75 (1H, dd, *J* = 8.1, 1.2 Hz), 7.68 (1H, ddd, *J* = 8.2, 7.8, 1.2 Hz), 7.53 (1H, dd, *J* = 8.1, 7.8 Hz), 7.23-7.16 (5H, m), 6.53 (1H, ddd, *J* = 16.8, 10.0, 10.0 Hz), 5.56 (1H, ddt, *J* = 17.0, 10.1, 7.4 Hz), 5.46 (1H, d, *J* = 10.3 Hz), 5.42 (1H, d, *J* = 17.1 Hz), 5.19 (1H, ddt, *J* = 17.0, 1.3, 1.3 Hz), 5.11 (1H, dd, *J* = 10.1, 1.3, 1.3 Hz), 3.88 (1H, d, *J* = 9.8 Hz), 3.05 (1H, dddd, *J* = 14.3, 7.6, 1.3, 1.3 Hz), 2.85 (1H, dddd, *J* = 14.3, 6.5, 1.3, 1.3 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 150.6, 150.6, 135.6, 135.2, 135.1, 131.9, 131.4, 129.8, 128.8,128.5, 128.4, 128.0, 127.5, 126.9, 120.5, 120.5, 120.4, 57.1, 52.8, 42.8. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $C_{23}H_{21}N_2$ 325.1699 found 325.1710.

(2*S,3*S**)-2-Allyl-3-(4-nitrophenyl)-2-phenylpent-4-enenitrile (2h)**



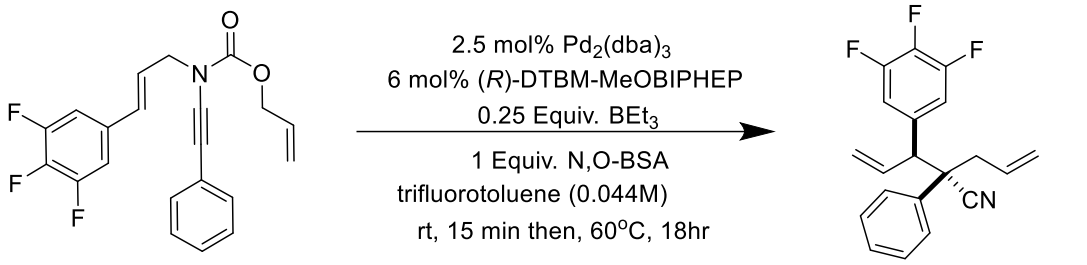
1h **2h**

69%, >30:1 *b/l*; >30:1 d.r.

The title compound was prepared by general procedure B from carbamate **1h** (54.3 mg, 0.15 mmol), $Pd_2(dba)_3$ (3.43 mg,7.5 µmol), (*R*)-DTBM-MeOBIPHEP (10.4 mg, 12.0 µmol), BEt_3 (1M in THF, 38 µl, 38 µmol) and *N,O*-BSA (37 µl, 15 µmol) in trifluorotoluene (3.4 mL). The crude product was purified by flash column chromatography (Hexanes/Ethyl Acetate 19:1) to afford requisite nitrile product **2h** (33 mg 69%, >30:1 d.r.) as a colorless oil

R_f (Hexanes/Ether 10:1) = 0.32. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.95 (2H, d, *J* = 8.8 Hz), 7.27-7.21 (3H, m), 7.16 (2H, dd, *J* = 8.1, 1.8 Hz), 7.13 (2H, d, *J* = 8.8 Hz), 6.44 (1H, ddd, *J* = 16.8, 10.0, 10.0 Hz), 5.32 (1H, ddt, *J* = 17.0, 10.1, 7.2 Hz), 5.44 (1H, d, *J* = 10.3 Hz), 5.37 (1H, d, *J* = 16.8 Hz), 5.16 (1H, ddt, *J* = 17.0, 1.2, 1.2 Hz), 5.09 (1H, ddt, *J* = 10.7, 1.2, 1.2 Hz), 3.73 (1H, d, *J* = 9.8 Hz), 3.01 (1H, dddd , *J* = 14.2, 7.6, 1.2, 1.2 Hz), 2.80 (1H, dddd, *J* = 14.2, 6.7, 1.2, 1.2 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 146.2, 135.2, 134.9, 133.4, 131.2, 129.4, 128.8, 128.2, 126.8, 123.2, 120.8, 120.4, 120.3, 59.7, 53.4, 42.9, HRMS (ESI-TOF) m/z: [M + H]+ Calcd. For $C_{20}H_{19}N_2O_2$ 319.1441 Found 319.1440.

(2*S,3*S**)-2-Allyl-2-phenyl-3-(3,4,5-trifluorophenyl)pent-4-enenitrile (2i)**



1i **2i**

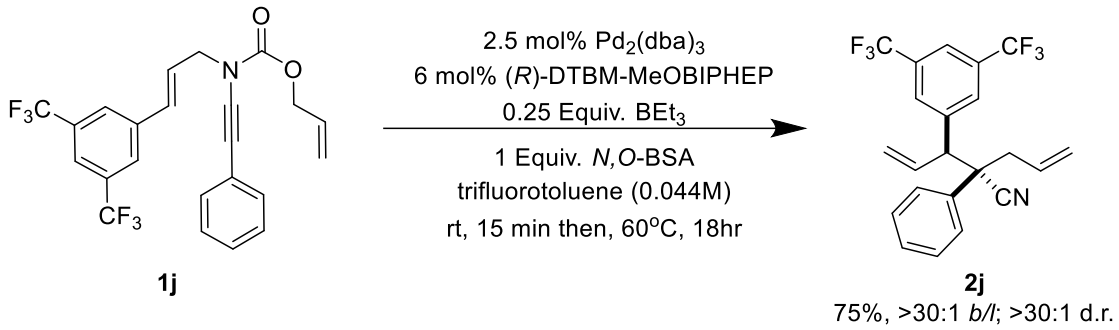
84%, >30:1 *b/l*; >30:1 d.r.

The title compound was prepared by general procedure B from carbamate **1i** (74.2 mg, 0.2 mmol), $Pd_2(dba)_3$ (4.6 mg, 10.0 μmol), (*R*)-DTBM-MeOBIPHEP (13.8 mg, 12.0 μmol), BEt_3 (1 M in THF, 50 μl, 50 μmol), *N,O*-BSA (49 μl, 0.2 μmol) in trifluorotoluene (4.5 mL). The crude product was purified by flash column chromatography (Hexanes/Ethyl Acetate 19:1) to afford the requisite nitrile product **2i** (55 mg, 84%, >30:1 d.r.) as a yellow oil.

R_f (Hexanes/Ethyl Acetate 10:1) = 0.29. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.33-7.24 (3H, m), 7.18 (2H, dd, *J* = 6.8, 1.6 Hz), 6.63-6.53 (2H, m), 6.31 (1H, ddd, *J* = 16.8, 9.9, 9.9 Hz), 5.50 (1H, ddt, *J* = 17.0, 10.2, 6.8 Hz), 5.42 (1H, d, *J* = 10.1 Hz), 5.34 (1H, d, *J* = 16.8 Hz), 5.07 (1H, ddt, *J* = 17.0, 1.3, 1.3 Hz), 5.08 (1H, ddt, *J* = 10.2, 1.3, 1.3 Hz), 3.52 (1H, d, *J* = 9.7 Hz), 2.97 (1H, dddd , *J* = 14.2, 7.5, 1.3, 1.3 Hz), 2.76 (1H, dddd, *J* = 14.2, 6.5 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 152.6-149.6 (m, second order (J_{CF}) coupling), 135.2 and 134.9 (rotamers), 134.9 and 134.8 (rotamers), 132.5 and 132.4 (rotamers), 129.1, 128.8, 126.8, 126.6, 125.1 and 125.1 (rotamers), 120.8 and 120.3 (rotamers), 120.4 and 120.0 (rotamers), 112.9-112.4 (m, second order (J_{CF}) coupling), 112.8-112.4 (m, second order (J_{CF}) coupling) and 110.3-109.9 (m, second order (J_{CF}) coupling) (rotamers), 59.1 and 59.0 (rotamers), 52.7 and 51.5 (rotamers), 42.7 and 41.9

(rotamers). HRMS (ESI-TOF) *m/z*: $[M + CH_3CN + H_2O]^+$ Calcd. for $C_{22}H_{21}F_3N_2O$ 386.1600 found 386.1584.

(2*S,3*S**)-2-Allyl-3-(3,5-bis(trifluoromethyl)phenyl)-2-phenylpent-4-enenitrile (2j)**

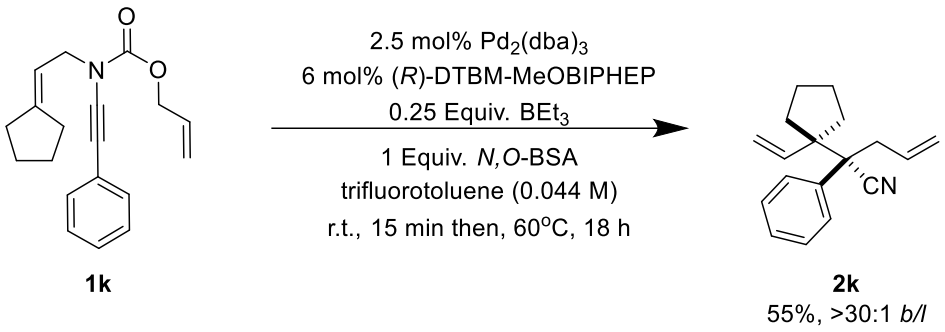


The title compound was prepared by general procedure B from carbamate **1j** (90.6 mg, 0.2 mmol), $Pd_2(dba)_3$ (4.6 mg, 10.0 μmol), (*R*)-DTBM-MeOBIPHEP (13.8 mg, 12.0 μmol), BEt_3 (1M in THF, 50 μL, 50 μmol) and *N,O*-BSA (49 μL, 0.2 μmol) in trifluorotoluene (4.5 mL). The crude product was purified by flash column chromatography (Hexanes/Ethyl Acetate 19:1) to afford the requisite nitrile product **2j** (62 mg, 75%, >30:1 d.r.) as a colorless oil.

R_f (Hexanes/Ethyl Acetate 10:1) = 0.63. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.63 (1H, br s), 7.30 (1H, br s), 7.29-7.23 (3H, m), 7.14-7.10 (2H, m), 6.46 (1H, ddd, *J* = 16.8, 10.0, 10.0 Hz), 5.57 (1H, dddd, *J* = 16.9, 10.1, 7.5, 6.6 Hz), 5.48 (1H, dd, *J* = 10.2, 0.7 Hz), 5.41 (1H, d, *J* = 16.8, 0.7 Hz), 5.18 (1H, ddt, *J* = 17.0, 1.4, 1.4 Hz), 5.11 (1H, ddt, *J* = 10.2, 1.4, 1.4 Hz), 3.74 (1H, d, *J* = 9.8 Hz), 2.99 (1H, dddd, *J* = 14.3, 7.6, 1.4, 1.4 Hz), 2.82 (1H, dddd, *J* = 14.4, 6.5, 1.4, 1.4 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 141.1, 134.9, 134.3, 131.2, 131.1 (q, $^2J_{CF}$ = 33.5 Hz), 128.9, 128.8 1 (q, $^3J_{CF}$ = 3.8 Hz), 126.8, 122.9 1 (q, $^1J_{CF}$ = 272.7 Hz), 121.3, 121.1 (sept., $^3J_{CF}$ = 3.8 Hz), 120.5,

119.9, 59.5, 52.7, 42.2. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $C_{22}H_{17}F_6N$ 410.1338 Found 410.1331.

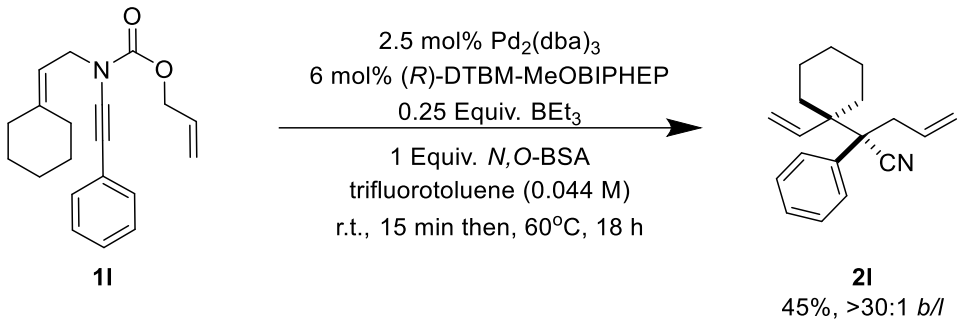
2-Phenyl-2-(1-vinylcyclopentyl)pent-4-enenitrile (2k)



The title compound was prepared by general procedure B using carbamate **1k** (48 mg, 0.16 mmol), $Pd_2(dba)_3$ (3.7 mg, 3.9 μmol), (*R*)-DTBM-MeOBIPHEP (11 mg, 9.1 μmol), BEt_3 (1M in THF, 40 μl, 40 μmol), *N,O*-BSA (39 μl, 16 μmol) in trifluorotoluene (3.6 mL). The crude product was purified by flash column chromatography (Hexanes/Et_2O 30:1) to afford requisite nitrile product **2k** (22 mg, 55%) as a yellow oil.

R_f (Hexanes/Ether 30:1) = 0.30. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.44-7.38 (2H, m), 7.37-7.27 (3H, m), 5.59 (1H, ddt, *J* = 17.0, 10.2, 6.9 Hz), 5.50 (1H, dd, *J* = 17.7, 10.9 Hz), 5.27 (1H, dd, *J* = 10.8, 0.6 Hz), 5.17 (1H, ddt, *J* = 17.0, 1.4, 1.4 Hz), 5.06 (1H, dd, *J* = 17.1, 0.6 Hz), 5.06 (1H, ddt, *J* = 10.1, 1.4, 1.4 Hz), 2.99 (1H, dddd, *J* = 14.6, 6.5, 1.4, 1.4 Hz), 2.69 (1H, dddd, *J* = 14.5, 7.4, 1.4, 1.4 Hz), 2.01-1.82 (3H, m), 1.76-1.53 (3H, m), 1.49-1.36 (1H, m), 1.34-1.25 (1H, m). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 139.3, 134.8, 132.6, 128.6, 127.8, 127.7, 122.3, 119.5, 117.1, 55.6, 55.3, 38.3, 34.4, 32.6, 23.1, 22.6, HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $C_{18}H_{22}N$ 252.1747 found 252.1758.

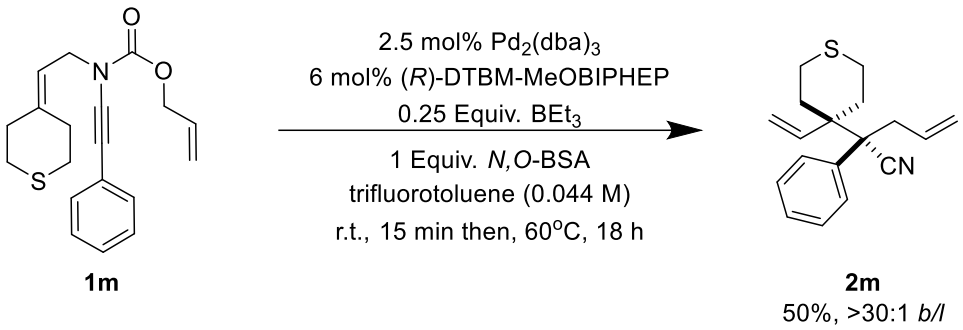
2-Phenyl-2-(1-vinylcyclohexyl)pent-4-enenitrile (2l)



The title compound was prepared by general procedure B using carbamate **1l** (58.5 mg, 0.19 mmol), $Pd_2(dba)_3$ (4.6 mg, 4.8 μmol), (*R*)-DTBM-MeOBIPHEP (13.1 mg, 11.4 μmol), BEt_3 (1M in THF, 48 μl, 48 μmol) and *N,O*-BSA (46 μl, 19 μmol) in trifluorotoluene (4.3 mL). The crude product was purified by flash column chromatography (Hexanes/Et_2O 30:1) to afford the requisite nitrile product **2l** (21.5 mg, 45%) as a yellow oil.

R_f (Hexanes/EtOAc 20:1) = 0.64.^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.41-7.27 (5H, m), 5.51(1H, ddt, *J* = 17.0, 10.1, 6.9 Hz), 5.51 (1H, dd, *J* = 11.0, 0.8 Hz), 5.33 (1H, dd, *J* = 17.8, 10.9 Hz), 5.14 (1H, ddt, *J* = 17.0, 1.3, 1.3 Hz), 5.08 (1H, dd, *J* = 17.9, 0.8 Hz), 5.02 (1H, ddt, *J* = 10.2, 1.3, 1.3 Hz), 2.92 (1H, dddd, *J* = 14.4, 6.5, 1.3, 1.3 Hz), 2.78 (1H, dddd, *J* = 14.4, 7.3, 1.3, 1.3 Hz), 2.08 (1H, d, *J* = 12.8 Hz), 1.72-1.34 (8H, m), 1.23 (1H, dtt, *J* = 12.4, 12.4, 2.5 Hz), 1.10 (1H, dtt, *J* = 12.4, 12.4, 2.6 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 138.9, 133.8, 132.8, 128.4, 127.7, 127.6, 122.2, 119.9, 119.4, 57.3, 46.4, 36.3, 32.3, 31.1, 25.7, 22.3, 22.2, HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $C_{19}H_{24}N$ 266.1903 found 266.1913.

2-Phenyl-2-(4-vinyltetrahydro-2H-thiopyran-4-yl)pent-4-enenitrile (2m)

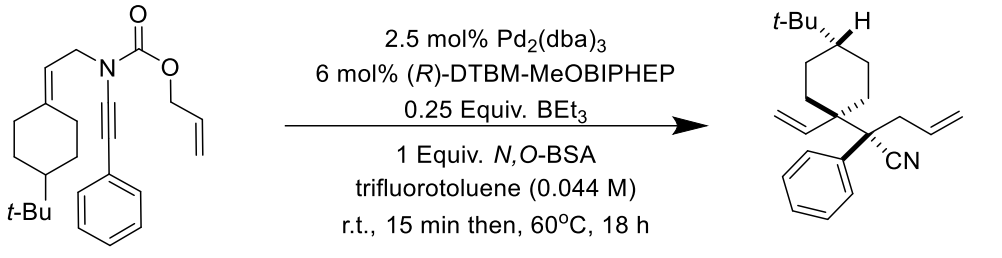


1m **2m**
50%, >30:1 *b/l*

The title compound was prepared by general procedure B using carbamate **1m** (65.4 mg, 0.2 mmol), $Pd_2(dba)_3$ (4.6 mg, 5.0 μmol), (*R*)-DTBM-MeOBIPHEP (13.9 mg, 12.0 μmol), BEt_3 (1M in THF, 50 μl, 50 μmol) and *N,O*-BSA (49 μl, 20 μmol) in trifluorotoluene (4.5 mL). The crude product was purified by flash column chromatography (Hexanes/Et_2O 30:1) to afford the requisite nitrile product **2m** (28.2 mg, 50%) as a yellow oil.

R_f (Hexanes/EtOAc 20:1) = 0.17. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.44-7.27 (5H, m), 5.63 (1H, d, *J* = 11.1 Hz), 5.49 (1H, ddt, *J* = 16.9, 10.1, 6.8 Hz), 5.35 (1H, dd, *J* = 18.1, 10.1 Hz), 5.15 (1H, dd, *J* = 16.8, 1.2 Hz), 5.10 (1H, d, *J* = 17.9 Hz), 5.03 (1H, dd, *J* = 10.1, 1.2 Hz), 2.94 (1H, dd, *J* = 14.3, 6.4 Hz), 2.90 (1H, dd, *J* = 14.7, 3.4 Hz), 2.78 (1H, ddd, *J* = 14.5, 14.5, 2.4 Hz), 2.77 (1H, dd, *J* = 14.3, 6.9 Hz), 2.44-2.28 (3H, m), 2.01 (2H, dddd, *J* = 13.9, 13.9, 13.9, 3.4 Hz), 1.85 (1H, d, *J* = 13.6 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 138.1, 133.0, 132.3,129.4, 128.0, 127.9, 121.4, 121.4, 119.8, 57.3, 45.8, 36.0, 33.1, 32.5, 24.3, 24.3. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. For $C_{18}H_{21}NS$ 284.1467 found 284.1463.

***anti*-4-(*tert*-Butyl)-1-vinylcyclohexyl)-2-phenylpent-4-enenitrile (2n)**



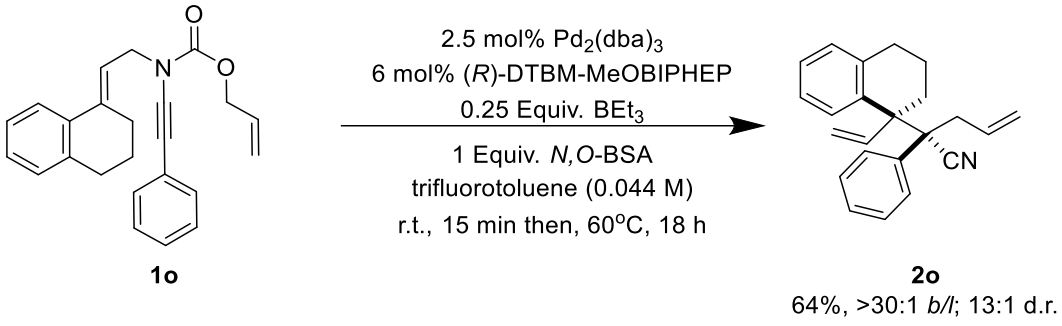
1n **2n**

45%, >30:1 *b/l*; 15:1 d.r.

The title compound was prepared by general procedure B using carbamate **1n** (26 mg, 0.071 mmol), $Pd_2(dba)_3$ (1.7 mg, 3.6 μmol), (*R*)-DTBM-MeOBIPHEP (5.0 mg, 4.3 μmol), BEt_3 (1M in THF, 18 μl, 18 μmol) and *N,O*-BSA (17 μl, 71 μmol) in trifluorotoluene (1.6 mL). The crude product was purified by flash column chromatography (Hexanes/Et_2O 30:1) to afford the requisite nitrile product **2n** (10.2 mg, 45%, 15:1 d.r.) as a colorless oil.

R_f (Hexanes/EtOAc 20:1) = 0.53. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.45-7.28 (5H, m), 5.52 (1H, ddt, *J* = 17.0, 10.1, 7.1 Hz), 5.49 (1H, dd, *J* = 18.0, 1.2 Hz), 5.32 (1H, dd, *J* = 17.7, 11.1 Hz), 5.14 (1H, ddt, *J* = 17.0, 1.3, 1.3 Hz), 5.08 (1H, dd, *J* = 18.1, 1.2 Hz), 5.02 (1H, ddt, *J* = 10.3, 1.3, 1.3 Hz), 2.93 (1H, dddd, *J* = 14.4, 6.5, 1.3, 1.3 Hz), 2.78 (1H, dddd, *J* = 14.4, 7.3, 1.2, 1.2 Hz), 2.14 (1H, dddd, *J* = 13.0, 3.2, 3.2, 3.2, Hz), 1.75-1.43 (6H, m), 1.15 (1H, dddd, *J* = 12.0, 12.0, 12.0, 3.8 Hz), 0.98 (1H, dddd, *J* = 12.3, 12.3, 12.3, 3.2 Hz), 0.78 (9H, s). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 138.0, 132.8, 131.8, 128.2, 126.6, 126.5, 121.2, 118.8, 118.4, 56.0, 46.5, 45.1, 35.5, 31.6, 31.2, 30.5, 26.4, 22.1, 22.0. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $C_{23}H_{32}N$ 322.2529 found 322.2544.

(*R)-2-Phenyl-2-((*S**)-1-vinyl-1,2,3,4-tetrahydronaphthalen-1-yl)pent-4-enenitrile (2o)**

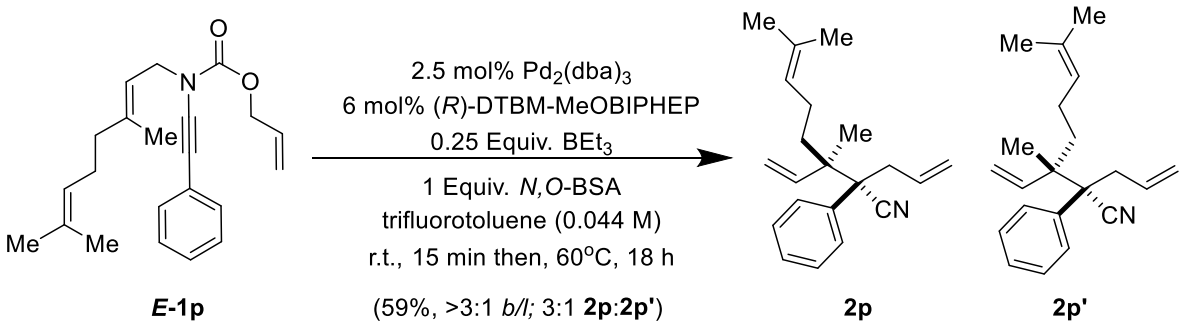


The title compound was prepared by general procedure B using carbamate **1o** (35.7 mg, 0.10 mmol), $Pd_2(dba)_3$ (4.6 mg, 2.5 μmol), (*R*)-DTBM-MeOBIPHEP (6.9 mg, 6.0 μmol), BEt_3 (1M in THF, 25 μl, 25 μmol) and *N,O*-BSA (24 μl, 10 μmol) in trifluorotoluene (4.5 mL). The crude product was purified by flash column chromatography (Hexanes/Et_2O 30:1) to afford the requsite nitrile product **2o** (19.7 mg, 63%, 13:1 d.r.) as a yellow oil.

R_f (Hexanes/EtOAc 20:1) = 0.45. ^{1}H-NMR (400 MHz, $CDCl_3$) 7.58-7.50 (1H, m), 7.27-7.03 (9H, m), 6.42 (1H, dd, *J* = 17.1, 10.7 Hz), 5.49 (1H, ddt, *J* = 17.0, 10.2, 7.0 Hz), 5.32 (1H, dd, *J* = 10.7, 1.0 Hz), 5.08 (1H, ddt, *J* = 17.0, 1.5 Hz), 5.01 (1H, ddt, *J* = 10.1, 1.5, 1.5 Hz), 4.82 (1H, dd, *J* = 17.1, 1.0 Hz), 2.99 (1H, dddd, *J* = 14.1, 6.4, 1.5, 1.5 Hz), 2.78 (1H, dddd, *J* = 14.1, 7.4, 1.5, 1.5 Hz), 2.52 (1H, dddd, *J* = 15.9, 2.1, 2.1, 2.1 Hz), 2.30-2.12 (1H, m), 1.95 (1H, ddd, *J* = 13.1, 13.1, 2.9 Hz), 1.82-1.49 (4H, m), 1.37 (1H, ddd, *J* = 12.7, 3.0, 3.0 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 142.7, 142.7, 135.3, 134.7, 132.6, 130.8, 129.5, 129.4, 129.3, 127.9, 127.6, 126.8, 125.1 119.6, 117.5, 52.1, 38.9, 34.1, 31.3, 29.7, 19.6. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. For $C_{23}H_{24}N$ 314.1903 found 314.1918.

(2*S,3*S**)-2-Allyl-3,7-dimethyl-2-phenyl-3-vinyloct-6-enenitrile (2p) and**

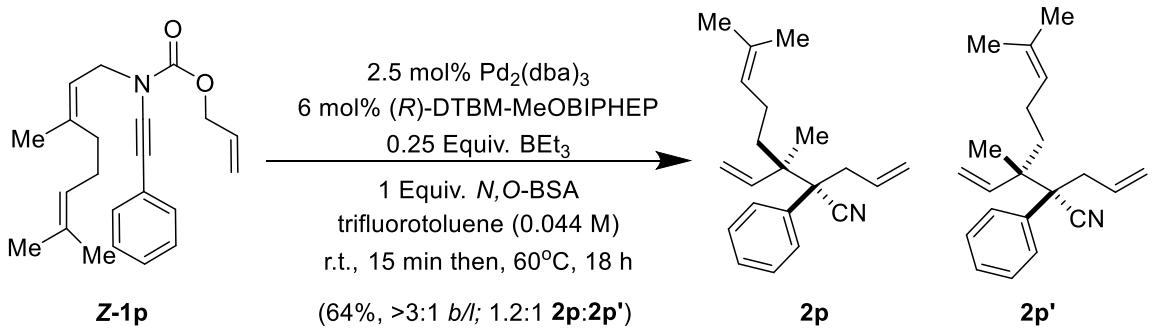
(2*S,3*R**)-2-Allyl-3,7-dimethyl-2-phenyl-3-vinyloct-6-enenitrile (2p')**



The title compound was prepared by general procedure B from carbamate **2p** (67.4 mg, 0.20 mmol), $Pd_2(dba)_3$ (4.6 mg, 5.0 μmol), (R)-DTBM-MeOBIPHEP (13.8 mg, 12.0 μmol), BEt_3 (1M in THF, 50 μl, 50 μmol) and *N,O*-BSA (49 μl, 0.2 μmol) in trifluorotoluene (4.5 mL). The crude product was purified by flash column chromatography (Hexanes/Ethyl Acetate 19:1) to afford the requisite nitrile products **2p**/**2p'** (35 mg, 59%, 3:1 d.r. [**2p**:**2p'**]) as a colorless oil.

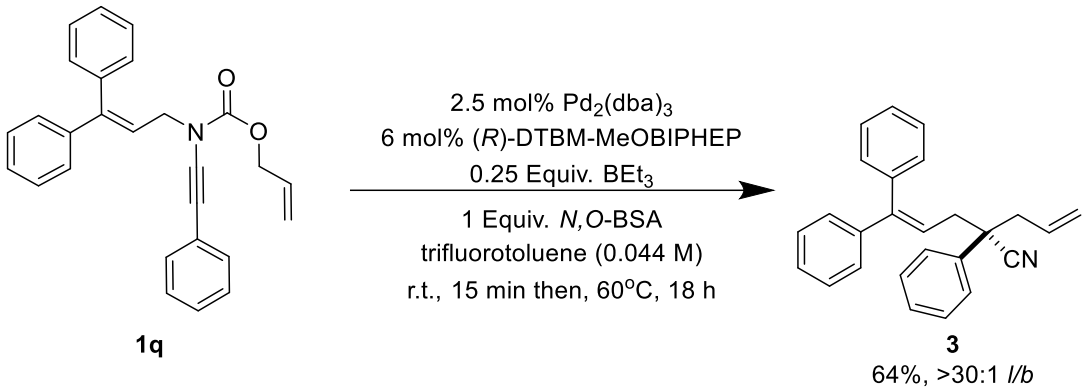
R_f (Hexanes/Ethyl acetate 10:1) = 0.33, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.42-7.29 (5H, m, **2p** and **2p'**), 5.86 (0.25H, dd, *J* = 17.5, 10.9 Hz, **2p'**), 5.64 (0.75H, dd, *J* = 17.6, 10.8 Hz, **2p**), 5.51 (0.25H, ddt, *J* = 16.6, 10.2, 7.0 Hz, **2p'**), 5.50 (0.75H, ddt, *J* = 17.0, 10.2, 7.1 Hz, **2p**), 5.35 (0.25H, d, *J* = 10.3 Hz, **2p'**), 5.32 (0.75H, dd, *J* = 10.9, 0.6 Hz, **2p'**), 5.15 (0.75H, ddt, *J* = 17.0, 1.4, 1.4 Hz, **2p**), 5.13 (0.25H, dd, *J* = 17.0, 1.4 Hz, **2p'**), 5.08 (0.75H, dd, *J* = 17.5, 0.6 Hz, **2p**), 5.05 (0.25H, d, *J* = 17.1 Hz, **2p'**), 5.03 (0.75H, ddt, *J* = 10.1, 1.4, 1.4 Hz, **2p**), 4.97 (1H, tt, *J* = 7.1, 1.3 Hz, **2p** and **2p'**), 2.94 (1H, dddd, *J* = 14.4, 6.5 Hz, **2p** and **2p'**), 2.77 (1H, dddd, *J* = 14.4, 7.2 Hz, **2p** and **2p'**), 1.90-1.49 (9H, m, **2p** and **2p'**), 1.67 (0.75H, s, **2p'**), 1.64 (2.25H, s, **2p**), 1.54 (0.75H, s, **2p'**), 1.52 (2.25H, s, **2p**), 1.38 (0.5H, td, *J* = 11.0, 4.9 Hz, **2p'**), 1.27 (2.25H, s, **2p**),

1.26 (1.5H, td, *J* = 12.9, 4.3 Hz **2p**), 1.03 (0.75H, s, **2p'**). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 141.1 (**2p'**), 140.2 (**2p**), 134.0 (**2p'**), 134.0 (**2p**), 132.7 (**2p** and **2p'**), 131.7 (**2p'**), 131.7 (**2p**), 129.3 (**2p** and **2p'**), 127.8 (**2p**), 127.7 (**2p'**), 124.1 (**2p** and **2p'**), 122.1 (**2p**), 122.0 (**2p'**), 119.5 (**2p'**), 119.4 (**2p**), 117.4 (**2p**), 117.3 (**2p'**), 56.5 (**2p'**), 56.4 (**2p**), 46.5 (**2p'**), 46.2 (**2p**), 37.0 (**2p**), 37.0 (**2p'**), 36.5 (**2p**), 36.4 (**2p'**), 25.6 (**2p** and **2p'**), 23.1 (**2p'**), 23.1 (**2p**), 18.4 (**2p**), 17.6 (**2p** and **2p'**), 17.1 (**2p'**). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $C_{21}H_{28}N$ 294.2216 found 294.2227.



Carbamate **1p'** (49 mg, 0.14 mmol), $Pd_2(dba)_3$ (3.2 mg, 3.5 μmol), (R)-DTBM-MeOBIPHEP (9.7 mg, 8.4 μmol), BEt_3 (1 M in THF, 35 μl, 35 μmol) and *N,O*-BSA (34 μl, 0.14 μmol) in trifluorotoluene (3.2 mL). The crude product was purified by flash column chromatography (Hexanes/Ethyl Acetate 19:1) to afford the requisite nitrile products **2p**/**2p'** (26.2 mg, 64%, 1.2:1 d.r [**2p**:**2p'**]) as a colorless oil.

2-Allyl-2,5,5-triphenylpent-4-enenitrile (3)



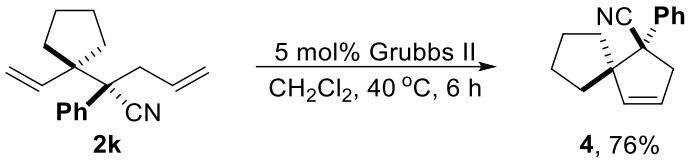
1q **3**

64%, >30:1 *l/b*

The title compound was prepared by general procedure B using carbamate **1q** (22 mg, 0.056 mmol), $Pd_2(dba)_3$ (1.3 mg, 2.8 μmol), (*R*)-DTBM-MeOBIPHEP (3.9 mg, 3.4 μmol) BEt_3 (1 M in THF, 14 μl, 14 μmol) and *N,O*-BSA (14 μl, 5.6 μmol) in trifluorotoluene (1.3 mL). The crude product was purified by flash column chromatography (Hexanes/Et_2O 30:1) to afford the linear nitrile product **3** (8.2 mg, 42%) as a colorless solid.

R_f (Hexanes/EtOAc 20:1) = 0.44. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.40-7.29 (8H, m), 7.24-7.19 (3H, m), 7.11-7.07 (2H, m), 7.03-6.99 (2H, m), 6.00 (1H, t, *J* = 7.3 Hz), 5.60 (1H, ddt, *J* = 17.2, 9.7, 7.1 Hz), 5.11 (1H, d, *J* = 9.9 Hz), 5.09 (1H, d, *J* = 16.8 Hz), 2.85 (1H, dd, *J* = 14.7, 7.1 Hz), 2.73 (1H, dd, *J* = 14.7, 7.4 Hz), 2.68 (1H, dd, *J* = 14.2, 7.6 Hz), 2.62 (1H, dd, *J* = 14.1, 6.7 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 145.7, 141.9, 137.6, 131.6, 129.8, 128.8, 128.3, 128.1, 127.9, 127.4, 127.3, 127.3, 126.3, 122.3, 120.1, 115.8, 114.6, 48.0, 44.3, 40.0. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd. for $C_{26}H_{24}N$ 350.1903 found 350.1914.

1-Cyano-1-Phenyl Spiro[3,3]non-3-ene (4a)



The title compound (**4a**) was prepared by general procedure C using nitrile **2k** (15.0 mg, 0.060 mmol), Grubb's 2nd generation catalyst (2.6 mg, 3.1 μmol) in dichloromethane (4.5 mL). The crude product was purified by flash column chromatography (Hexanes/Et_2O 30:1) to afford spirocycle **4a** (10.2 mg, 76%) as a colorless oil.

R_f (Hexanes/EtOAc 19:1) = 0.54. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.53 (2H, dd, *J* = 8.0, 1.2 Hz), 7.39-7.30 (3H, m), 5.84 (1H, ddd, *J* = 5.9, 2.0, 2.0 Hz), 5.78 (1H, ddd, *J* = 5.9, 2.0, 2.0 Hz), 3.20 (2H, dd, *J* = 2.0, 2.0 Hz), 2.14 (1H, ddd, *J* = 13.1, 8.5, 8.5 Hz), 1.86 (1H, ddd, *J* = 12.8, 8.2, 4.5 Hz), 1.80-1.63 (2H, m), 1.55-1.35 (2H, m), 1.14 (1H, ddd, *J* = 13.4, 7.8, 6.2 Hz), 1.10 (1H, ddd, *J* = 13.0, 8.0, 8.0 Hz). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 139.1, 137.7, 128.4, 127.9, 127.0, 125.7, 124.0, 63.9, 54.1, 45.0, 36.8, 34.7, 29.7, 24.0, 23.7. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd. for $C_{16}H_{18}N$ 246.1263 found 246.125

Computational Methods

General Comments

To explore the possible mechanistic pathways, we applied the two-layered QM/SE ONIOM method to palladium complexes.[4,5,6] In this model, the substrate as well as palladium and phosphorous atoms of the catalyst were included in the high layer, whereas the rest was placed in the low layer. The high level was treated with DFT using local meta-generalized gradient approximation functional M06L recommended for transition-metal chemistry calculations.[7] The 6-31G+(d) basis set was used for C, H, P, and O atoms in conjunction with the LANL2DZ relativistic pseudopotential for Pd (BSI). The low level was handled with semi-empirical method PM6. Given the bulky nature of the ligand, this two-layered ONIOM model allowed us to perform geometry optimization of palladium complexes within the reasonable timescale. The nature of stationary points in each case was confirmed by harmonic frequency calculations. The nature of located TSs was confirmed by unique imaginary vibrational mode and IRC calculations.

To get refined energies, we further performed single point (SP) energy calculations using the ONIOM geometries. The palladium complexes were fully treated by DFT. The larger basis set 6-311++G(2d,2p) for C, H, P and O atoms and LANL2DZ ECP for Pd (BSII) and M06L functional were employed. The single point solvation by trifluorotoluene was accounted by using conductor-like polarizable continuum model (C-PCM)[8,9] specifying the following parameters: static dielectric constant $\varepsilon = 9.4$, dynamic dielectric constant $n^2 = 1.414$. The calculations were performed with the Gaussian 16.0 software.[10] The corrected single point energy was calculated as follows:

$$G_{SP\ Corrected}=E_{elec}[(CPCM)|M06L|BSI]+G_{Corr\ ONIOM}[ONIOM(M06L|BSI:PM6)]$$

where $G_{corr\ ONIOM}$ is the thermal correction to Gibbs free energy obtained in the gas phase at ONIOM(M06L|BSI:PM6) or M06L|BSI.

The obtained Gibbs Free energies were temperature-corrected and reported at 333.15 K. At the same temperature all energies were corrected to 1 mol/L standard state. The Grimme's quasi-rigid-rotor harmonic oscillator (quasi-RRHO) approximation was used to account for entropic contributions of low frequency modes below 100 cm^{-1}.[11,12] All corrections were obtained using the GoodVibes 3.0.1 program by Prof. Robert Paton.[13] Trifluorotoluene parameters (molecular weight and density) were manually added to media.py.

The optimized structures were visualized using CYLview 1.0b.[14] The potential energy surfaces were generated using GoodVibes 3.0.1.[13]

Conformational studies were done in CREST.[15] Each experiment was repeated twice to ensure reproducibility; the typical run was as follows. The conformational search for **6** was performed using default iMTD-GC algorithm at the GFN2-xTB level,[16] which resulted in 781 conformers within an energy window of 4.2 kcal/mol. The generated conformational ensemble was reduced to 25 lowest energy structures that were optimized using DFT at M06L/BSI level. The redundant conformers were eliminated. The structures in reactive conformation were considered for further analysis. The conformational search for **6** bound to **Pd-L1h** was performed using special NCI mode for non-covalently bound complexes at GFN-FF level.[17] The allyl group and allene system atoms were constrained in reactive conformation during meta-dynamic simulations. The search resulted in 1784 conformers within an energy window of 5.8 kcal/mol. From generated conformational ensemble 3 conformers reflecting *exo*- and 3 conformers reflecting *endo*- binding mode of **6** to **Pd-L1h** were selected and reoptimized using

ONIOM(M06L|BSI:PM6). The conformational changes occurring between C-N bond cleavage and C-C bond formation were found during potential energy surface scans.

To evaluate noncovalent interactions between phenyl groups in transition states **TS-8** and **TS 14**, we utilized independent gradient model approach (IGM-δg).[18] Three-dimensional (3D) IGM isosurfaces representing non-covalent interactions were visualized in VMD.[19] These isosurfaces were color-coded with green and blue demonstrating van der Waals and strong attraction, respectively and yellow and red – weak and strong repulsion, respectively.

Table A. S1. Energies and Lowest Frequencies of Minimum Energy Structures

Structure	E[a], Ha	E_SPC[b], Ha	G(T)_SPC[c]	qh-G(T)_SPC[d]	Lowest freq.[e]
Pd-L1h	-813.501332	-4143.787235	-4142.463347	-4142.439363	7.63
2a	-828.153777	-828.374439	-828.095958	-828.092312	29.89
2a'	-828.154072	-828.374968	-828.097850	-828.093492	33.42
6	-828.133083	-828.352815	-828.080602	-828.073598	3.01
7	-1641.674213	-4972.203260	-4970.576857	-4970.544879	7.31
9	-1641.660257	-4972.184384	-4970.563143	-4970.531380	5.93
10	-1641.663736	-4972.201144	-4970.576452	-4970.546098	10.87
12	-1641.686505	-4972.222121	-4970.591749	-4970.562400	10.42
13	-1641.674562	-4972.196636	-4970.572826	-4970.540080	6.18
15	-1641.659140	-4972.181976	-4970.563541	-4970.530636	8.04
18	-1641.680854	-4972.212984	-4970.585144	-4970.554390	3.23
$PhCF_3$	-569.237725	-569.391876	-569.319973	-569.318936	30.35
TS-8	-1641.650520	-4972.178215	-4970.553822	-4970.523034	-311.03
TS-11	-1641.661300	-4972.201236	-4970.573806	-4970.544546	-296.81
TS-14	-1641.652256	-4972.174166	-4970.552030	-4970.520387	-311.12
TS-16	-1641.661361	-4972.184066	-4970.557784	-4970.528542	-11.10
TS-17	-1641.658554	-4972.191876	-4970.563820	-4970.534853	-321.39

a Electronic energies calculated at ONIOM(M06L/BSI:PM6), where BSI = 6-31+G(d) (C, H, P, O)/LANL2DZ (ECP Pd).

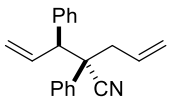
b Single point energies calculated at at CPCM(Trifluorotoluene)-M06L/BSII//[ONIOM(M06L/BSI:PM6)], where BSI = 6-31+G(d) (C, H, P, O)/LANL2DZ (ECP Pd) and BSII = 6-311++G(2d,2p) (C, H, P, O) /LANL2DZ (ECP Pd).

c Harmonic solvent and temperature (333.15 K) corrected Gibbs free energies.

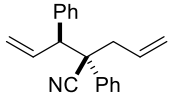
d Quasi-harmonic solvent and temperature (333.15 K) corrected Gibbs free energies at 1 mol/L standard state.

e Unscaled; calculated at ONIOM(M06L/BSI:PM6), where BSI = 6-31+G(d) (C, H, P, O)/LANL2DZ (ECP Pd).

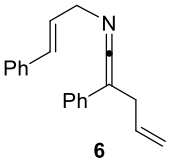
Ground States



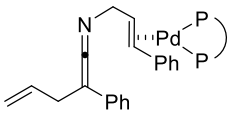
2a



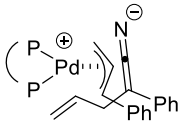
2a'



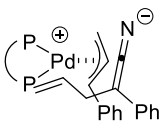
6



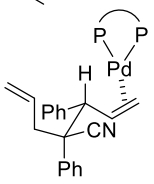
7



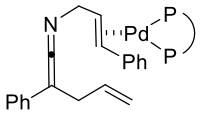
9



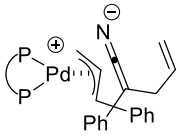
10



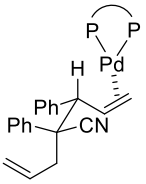
12



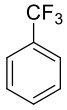
13



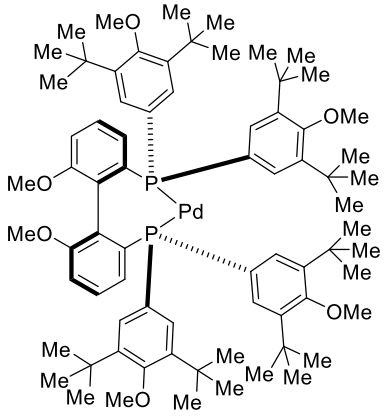
15



18

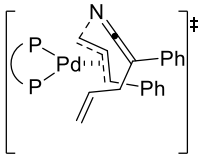


$PhCF_3$

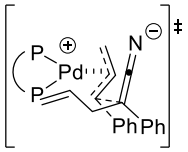


Pd-L1h

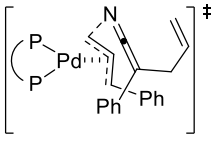
Transition States



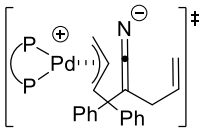
TS-8



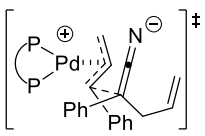
TS-11



TS-14

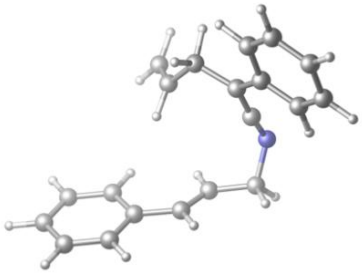


TS-16

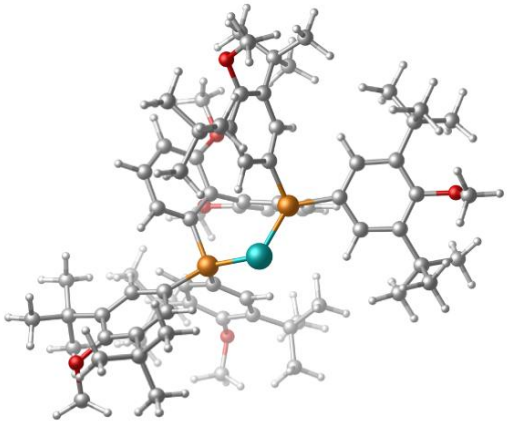


TS-17

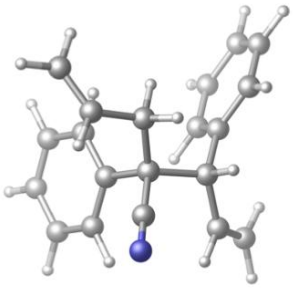
CYLview Structures



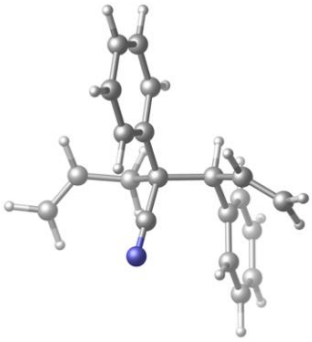
6



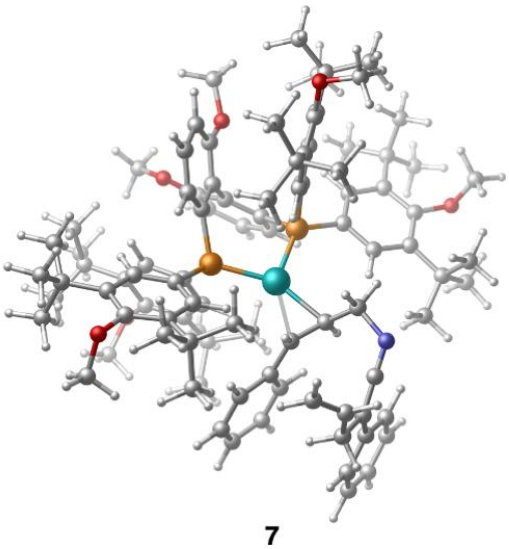
Pd-L1h



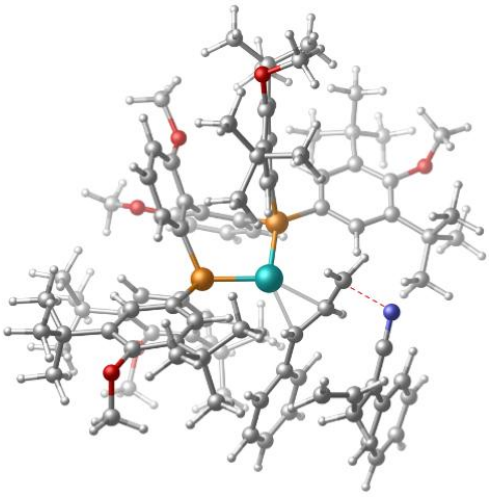
2a



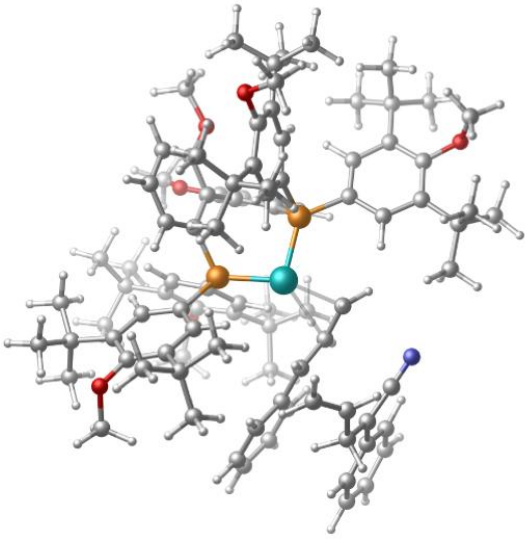
2a'



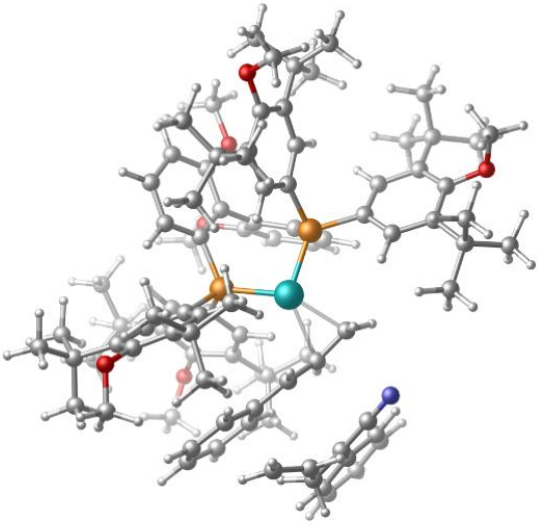
7



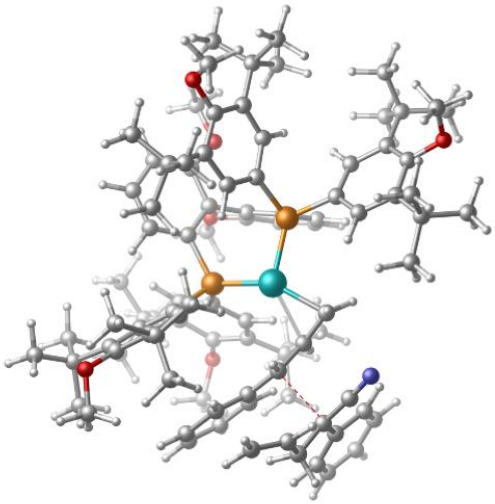
TS-8



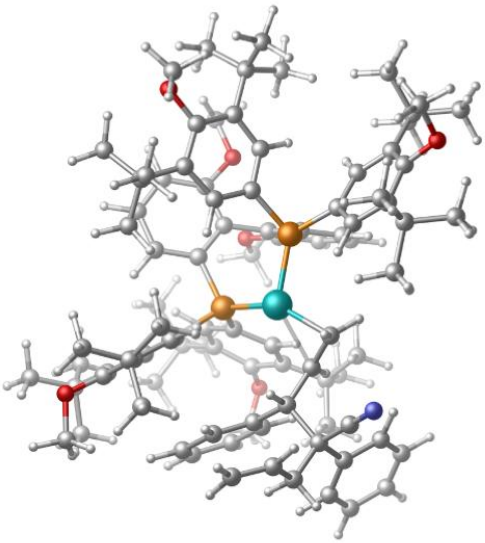
9



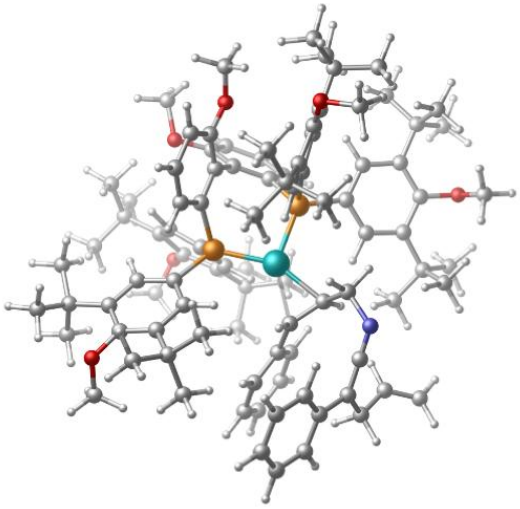
10



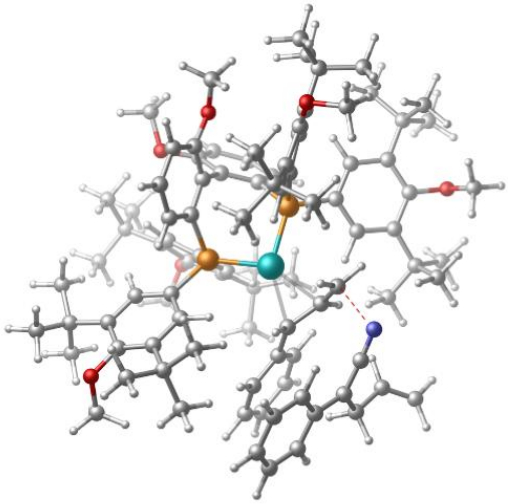
TS-11



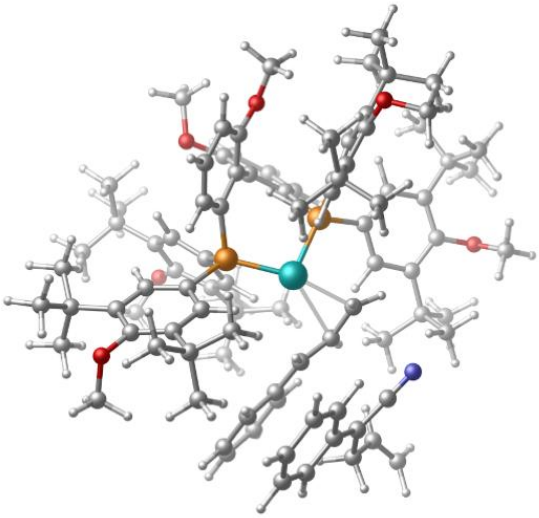
12



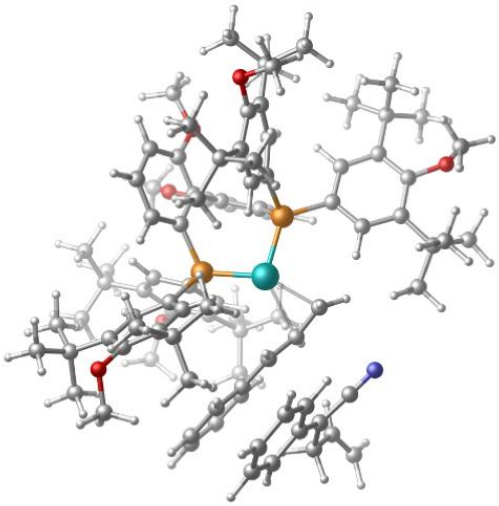
13



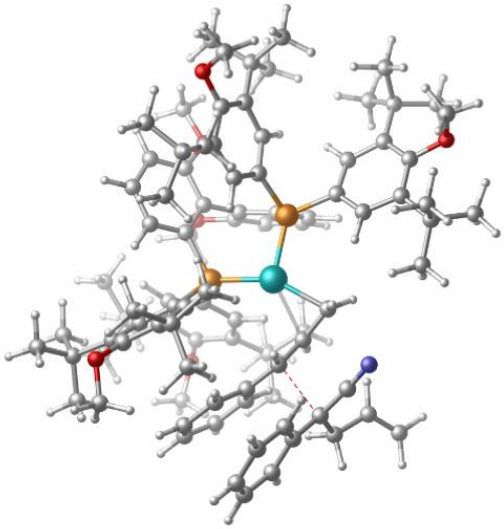
TS-14



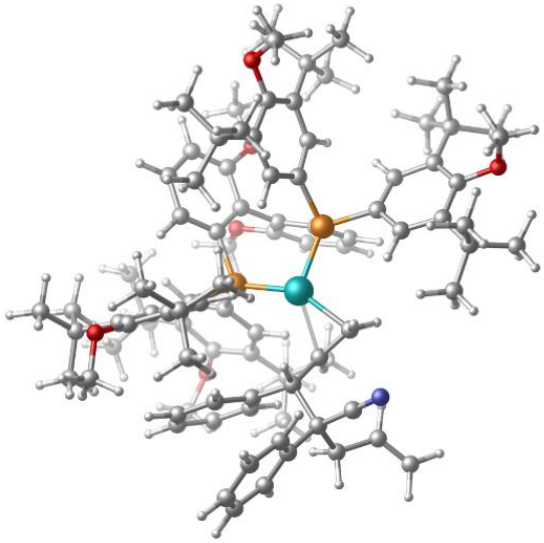
15



TS-16



TS-17



18

Cartesian Coordinates of Minimum Energy Structures

Table A.1. Cartesian Coordinates of Minimum Energy Structures

Pd-L1h

Pd	0.09654800	0.20627200	-1.69014300
P	-1.73781300	-0.17348400	-0.56038700
P	1.91417900	0.18682900	-0.46855900
C	-0.21997500	-1.01454800	1.69276700
C	-1.18624700	-1.36709300	0.74608100
C	-1.66401200	-2.68694600	0.66619300
C	-1.19476000	-3.66703600	1.53746100
C	-0.23686900	-3.35471200	2.50657400
C	0.23279700	-2.04088700	2.57822400
C	0.34558900	0.34163600	1.90149800
C	1.38071000	0.91923900	1.15709700
C	1.94498500	2.14345400	1.55281700
C	1.46723800	2.82010600	2.67343300
C	0.39583400	2.30653000	3.40919100
C	-0.15530800	1.08502500	3.01278300
C	-2.40568500	1.24591800	0.42400500
C	-1.88771400	2.50045200	0.11554700
C	-2.39199500	3.66299300	0.72650700
C	-3.49997300	3.50622600	1.58702100
C	-3.99393500	2.24131700	1.98316200
C	-3.39919500	1.11692800	1.39172000
C	-3.36364200	-0.93170300	-1.12341200
C	-4.42601000	-1.25618200	-0.28531800
C	-5.65800400	-1.68784100	-0.79774000
C	-5.76663400	-1.78553300	-2.20442600
C	-4.66903600	-1.59777500	-3.07101100

C	-3.47500600	-1.12392200	-2.49626700
C	2.54260300	-1.46180000	0.06599900
C	2.09936600	-2.55926800	-0.66448000
C	2.53241000	-3.86099700	-0.35075500
C	3.50042700	-3.98430900	0.66882200
C	3.91965600	-2.89458600	1.46998600
C	3.39379200	-1.63329700	1.15589500
C	3.49589000	1.12984400	-0.80691900
C	4.78123700	0.74183500	-0.45169400
C	5.90631300	1.48735900	-0.84954700
C	5.67742900	2.60605300	-1.67746000
C	4.38054100	3.07703600	-1.98580400
C	3.30050700	2.28826300	-1.56277700
H	-2.40633400	-2.97957300	-0.07904100
H	-1.57104700	-4.68672600	1.46645100
H	0.13471200	-4.12833400	3.16835800
H	2.77580600	2.59261800	1.00511600
H	1.92491100	3.76009700	2.97895700
H	0.01414400	2.85262100	4.26369700
H	-1.06565900	2.58982000	-0.61598100
H	-3.73662600	0.11700900	1.69302400
H	-4.30634900	-1.15930000	0.80162000
H	-2.62466000	-0.90186100	-3.15617700
H	1.38459900	-2.41430200	-1.49252800
H	3.65460000	-0.77067500	1.77809000
H	4.94863900	-0.16483100	0.13554800
H	2.28317600	2.59046400	-1.85061000
O	1.17210400	-1.61462700	3.49760900

O	-1.22358500	0.48246300	3.64663400
C	1.54074000	-2.53618100	4.55169200
H	2.17296500	-3.33984400	4.13627200
H	2.12036500	-1.88912400	5.22221900
H	0.65644200	-2.92816300	5.05968900
C	-1.87393000	1.22009600	4.70806200
H	-2.15112600	2.22681200	4.37246800
H	-2.78272200	0.61393800	4.87110200
H	-1.23470400	1.23832300	5.59314400
O	-7.00600600	-2.15935300	-2.75376600
O	-4.09517000	4.65344000	2.14234000
O	6.78399400	3.32378900	-2.16571800
O	4.00438900	-5.25900100	0.98287000
C	-7.84086400	-1.03431000	-3.12332000
H	-8.73092800	-1.52346900	-3.53152100
H	-8.08482000	-0.44113400	-2.22854100
H	-7.33429800	-0.42273700	-3.88596600
C	5.13062600	-5.67710100	0.17525400
H	5.99109500	-5.01976600	0.37286900
H	5.31631000	-6.69373100	0.53648700
H	4.86163700	-5.67435600	-0.89229900
C	7.26121000	2.84555300	-3.44789100
H	8.10692600	3.51037800	-3.64955000
H	7.58688200	1.79760400	-3.36051600
H	6.47192400	2.96038400	-4.20687100
C	-5.14133100	5.22763200	1.32124300
H	-5.95667000	4.49936500	1.19123100
H	-5.46523400	6.08751900	1.91582800

H	-4.72860000	5.54445400	0.35066400
C	-4.70606000	-1.86454200	-4.58114900
C	-5.21110200	-0.59086200	-5.28899300
H	-5.26116900	-0.73147500	-6.37248400
H	-6.21858500	-0.31577800	-4.94279500
H	-4.55196000	0.26055800	-5.09181600
C	-5.60307400	-3.06698200	-4.92332400
H	-6.65717300	-2.87565400	-4.68470600
H	-5.54614800	-3.32248900	-5.98437100
H	-5.31240400	-3.95095100	-4.34545900
C	-3.29238000	-2.19739400	-5.11515200
H	-2.58706200	-1.37187500	-4.96328000
H	-2.87953700	-3.08047800	-4.61581300
H	-3.31771400	-2.40756100	-6.18859100
C	-6.80190200	-1.99634800	0.17650700
C	-7.62582900	-3.20796400	-0.29254100
H	-8.39589500	-3.47893100	0.43378800
H	-8.12774900	-3.01538300	-1.25065900
H	-6.98474200	-4.08183600	-0.44961800
C	-7.69080700	-0.74092700	0.29004000
H	-8.53629000	-0.91252100	0.96183800
H	-7.12158300	0.11955500	0.67982900
H	-8.09822600	-0.44981600	-0.68913400
C	-6.26700000	-2.33796500	1.58772900
H	-5.54594800	-3.16120600	1.55209800
H	-5.77655900	-1.47532500	2.06751400
H	-7.08222300	-2.64710100	2.24946400
C	1.91822900	-5.03751400	-1.12129300

C	1.73608600	-6.26986700	-0.21770100
H	1.16335700	-6.01057100	0.68009700
H	1.20757200	-7.07354700	-0.73639700
H	2.69349200	-6.67354600	0.13190900
C	0.51442100	-4.66972100	-1.65752100
H	-0.15634800	-4.37958400	-0.83873600
H	0.54476900	-3.82863900	-2.36083300
H	0.05614400	-5.51435600	-2.17876900
C	2.82396700	-5.36850700	-2.32507500
H	2.92466600	-4.50674800	-2.99256600
H	3.83488800	-5.65550000	-2.00096800
H	2.41755500	-6.19846500	-2.91028000
C	4.91050000	-3.02251500	2.63409000
C	4.56619800	-4.24616100	3.50178800
H	4.64187500	-5.18196100	2.92898500
H	5.23001800	-4.33241900	4.36459500
H	3.52980400	-4.18198200	3.86647700
C	6.33640000	-3.13280600	2.05648100
H	7.08356900	-3.19877700	2.85219000
H	6.45051900	-4.02416200	1.42404000
H	6.57922000	-2.25429500	1.43846400
C	4.88312800	-1.78242900	3.55919800
H	5.27112900	-0.88783600	3.06051300
H	3.86605500	-1.55132600	3.89681400
H	5.49847800	-1.94431400	4.44908000
C	-5.15259800	2.03935900	2.96826500
C	-5.14175400	0.62503000	3.59632500
H	-5.32443200	-0.16628100	2.85079400

H	-4.18021400	0.40686500	4.08435900
H	-5.92506400	0.52952600	4.35444600
C	-5.08207200	3.04543400	4.13130300
H	-5.21491000	4.07902000	3.78198600
H	-5.85254300	2.85166600	4.88153800
H	-4.10665400	3.01174000	4.62592600
C	-6.47788100	2.19749900	2.19351500
H	-7.33989400	2.13290000	2.86312300
H	-6.52908400	3.16762800	1.67828600
H	-6.58911500	1.41095700	1.42825500
C	-1.71741000	5.00506100	0.41409100
C	-2.46040600	5.66756700	-0.76426200
H	-3.51584800	5.85456400	-0.51756000
H	-2.00829000	6.62767600	-1.02876500
H	-2.43816500	5.03053500	-1.65414000
C	-0.24096500	4.79369900	0.00382600
H	0.31790400	4.27956500	0.79652000
H	-0.14552200	4.18516800	-0.90371900
H	0.25614900	5.74830200	-0.18821900
C	-1.70913100	5.93246100	1.64212000
H	-1.15245900	6.85236600	1.44685200
H	-2.72281700	6.21661000	1.95118200
H	-1.24964100	5.43446700	2.50291800
C	7.29457300	1.04096900	-0.37253400
C	7.20297100	0.25595500	0.95793100
H	6.68254800	0.83991900	1.72438700
H	6.67538100	-0.70486600	0.84870800
H	8.20135900	0.02680700	1.34406400

C	7.90330900	0.11873600	-1.44809800
H	8.89875000	-0.22850300	-1.15769200
H	7.27546500	-0.76157100	-1.61795800
H	8.00203800	0.64342600	-2.41045900
C	8.21540400	2.24533500	-0.10653900
H	9.16961800	1.93592200	0.32683400
H	8.43620600	2.80555900	-1.02453500
H	7.74400400	2.95553900	0.58125400
C	4.09966600	4.37290800	-2.75730100
C	2.69296600	4.92286800	-2.42062800
H	1.89804800	4.22227300	-2.70216700
H	2.59316300	5.12574200	-1.34891600
H	2.50111700	5.85964900	-2.95244800
C	4.15566200	4.06224800	-4.26671100
H	3.96909100	4.95866300	-4.86471400
H	5.14160500	3.66902900	-4.55612900
H	3.40841500	3.31190500	-4.54490000
C	5.10788100	5.47644000	-2.39228700
H	6.12931000	5.21631600	-2.70102900
H	4.85253800	6.42780400	-2.86535300
H	5.14370300	5.63435700	-1.30924300

2a

C	1.29197600	1.81846900	-2.14650800
C	1.98204900	2.81421600	-1.45931000
C	2.32020300	2.61608200	-0.12241600
C	1.96525900	1.43309000	0.51981500

C	1.26078200	0.43129700	-0.15693800
C	0.93476000	0.63754900	-1.50102100
C	0.78953000	-0.81303400	0.59111500
C	1.80587100	-1.20698000	1.57668500
C	-0.55549300	-0.53664100	1.40294900
C	-0.34959300	0.45725100	2.51457300
C	-1.19454000	1.41143000	2.90552800
C	0.56780700	-2.04237600	-0.32902400
C	1.78723400	-2.49287800	-1.06566100
C	1.83959500	-2.70694500	-2.38014000
N	2.59132100	-1.55468500	2.36623200
H	1.02701800	1.95800800	-3.19333800
H	2.26222400	3.73657600	-1.96526200
H	2.86758100	3.38176100	0.42448800
H	2.24592100	1.28367800	1.56218800
H	0.38394800	-0.11932600	-2.05498100
H	-0.76193900	-1.50695000	1.88842700
H	0.57107900	0.31393900	3.08649500
H	-0.96454900	2.03910800	3.76362900
H	-2.14070000	1.60133600	2.40118800
H	0.20220200	-2.85797600	0.31527700
H	-0.24849000	-1.82326200	-1.02883300
H	2.67911500	-2.66798100	-0.45759900
H	2.74627500	-3.05669900	-2.86848000
H	0.97287800	-2.54213700	-3.02208600
C	-1.71702100	-0.24202000	0.48585600
C	-2.65826300	-1.24176900	0.21819000
C	-1.87830300	1.00520700	-0.13238000

C	-3.72590100	-1.01457000	-0.64731800
H	-2.54836800	-2.21585500	0.69813600
C	-2.94259700	1.23571400	-1.00034200
H	-1.16470700	1.80257600	0.07219900
C	-3.86859800	0.22715300	-1.26275700
H	-4.44703100	-1.80763700	-0.83841100
H	-3.04877100	2.21129500	-1.47254000
H	-4.70148700	0.41086100	-1.93950100

2a'

C	0.43926400	0.25095100	0.17515100
C	-0.51545100	-0.92753800	-0.28005400
C	-0.22580300	-2.17863100	0.50564800
C	-1.11992400	-3.05296200	0.96645700
C	0.07550300	1.55451300	-0.59625700
C	1.01392200	2.68643000	-0.33267000
C	0.67868400	3.79226600	0.33209000
H	-0.19857800	-1.11633900	-1.31994600
H	0.83689900	-2.37552400	0.67122800
H	-0.80302700	-3.94442400	1.50295400
H	-2.19210800	-2.91844500	0.83051900
H	0.06506100	1.29826100	-1.66752400
H	-0.95042400	1.84180400	-0.33466600
H	2.03731400	2.56617100	-0.69731800
H	1.39486500	4.58995600	0.51672600
H	-0.32762500	3.93720800	0.72617600
C	-1.97103800	-0.52944200	-0.33392900

C	-2.59253000	-0.35456300	-1.57397600
C	-2.72027800	-0.29707100	0.82693100
C	-3.92303800	0.04934200	-1.66273500
H	-2.01986800	-0.53648400	-2.48545100
C	-4.04837900	0.11255000	0.74169600
H	-2.26005100	-0.43762200	1.80376100
C	-4.65446000	0.28834700	-0.50185300
H	-4.38668100	0.17806000	-2.63954600
H	-4.61367100	0.29331400	1.65458400
H	-5.69374200	0.60661200	-0.56464600
C	1.89574000	-0.13608000	-0.09282700
C	2.30596700	-0.35726000	-1.41317600
C	2.83859500	-0.26667900	0.92905300
C	3.62166700	-0.70282800	-1.70403700
H	1.59171000	-0.25398100	-2.23105200
C	4.15777600	-0.61382300	0.63916200
H	2.54145000	-0.09280300	1.96259400
C	4.55485100	-0.83366200	-0.67632400
H	3.91868800	-0.86890500	-2.73825800
H	4.87621900	-0.71049000	1.45135300
H	5.58469200	-1.10400200	-0.90238600
C	0.23312400	0.50982200	1.60434300
N	0.04767500	0.72650800	2.73496500

6

N	0.79588300	-0.75610300	-2.33018000
C	1.82698100	0.61608600	-0.44494200

C	3.06863400	0.17765000	0.20495000
C	1.18831800	1.94195900	-0.07590700
C	-0.27330800	-1.77693100	-2.16593200
C	-1.50708500	-1.15907000	-1.60989600
C	-2.00370600	-1.44065300	-0.39483400
C	3.75882300	1.02655800	1.08575200
C	4.94181300	0.61667700	1.69723200
C	5.46758100	-0.64729600	1.44702600
C	4.79461100	-1.50087400	0.56999200
C	3.61585000	-1.09619400	-0.03936700
C	-0.23740200	2.07261000	-0.50648800
C	-0.69969700	2.99055700	-1.35518500
C	1.25145200	-0.13311700	-1.38003600
H	1.23470700	2.03860500	1.02081400
H	1.78417400	2.77605600	-0.48029800
H	-0.44420000	-2.20293400	-3.16077400
H	0.09179100	-2.58077600	-1.51187400
H	-1.96805600	-0.38970100	-2.23349300
H	-1.50434400	-2.21509800	0.19595000
H	3.37746200	2.02544400	1.28976800
H	5.45621900	1.29788500	2.37375500
H	6.39115300	-0.96612600	1.92656900
H	5.19242200	-2.49310800	0.36137400
H	3.10154900	-1.77503700	-0.72113100
H	-0.92878800	1.34194800	-0.07564900
H	-1.75380200	3.04497700	-1.62139700
H	-0.04217200	3.72893200	-1.81497500
C	-3.15681400	-0.81554000	0.24817100

C	-3.61219900	-1.31839500	1.47717500
C	-3.82979400	0.28995700	-0.30133800
C	-4.70175900	-0.74976800	2.12998000
H	-3.09732000	-2.17128700	1.92078300
C	-4.91629000	0.85918400	0.34941000
H	-3.49245300	0.71273400	-1.24720400
C	-5.35967000	0.34190300	1.56823500
H	-5.03626300	-1.15969700	3.08154700
H	-5.42050100	1.71685800	-0.09320900
H	-6.21079100	0.79122100	2.07672500

7

Pd	-0.04930400	0.90533500	-0.33444800
P	1.82413900	-0.19772200	0.23539600
P	-1.45793700	-0.86195200	-0.18122600
C	0.76455400	-2.57478700	1.40341600
C	1.48491700	-1.39611900	1.60479400
C	1.83795500	-0.98518000	2.90207300
C	1.49595300	-1.76052300	4.00768700
C	0.79066600	-2.95714700	3.84580000
C	0.43140600	-3.35117800	2.55448600
C	0.33315700	-3.06761100	0.07697200
C	-0.69779400	-2.49003500	-0.67098600
C	-1.08752400	-3.05481800	-1.89559500
C	-0.44905500	-4.19109100	-2.39088000
C	0.59806500	-4.78457800	-1.68107200
C	0.98036700	-4.21809300	-0.46183700

C	2.48220900	-1.20731700	-1.16297700
C	1.91203600	-0.98278000	-2.41179100
C	2.37104100	-1.66278600	-3.55560100
C	3.49790700	-2.49756900	-3.39511900
C	4.08552900	-2.76353200	-2.13266600
C	3.53088500	-2.11439000	-1.02137900
C	3.44858600	0.52223000	0.79128400
C	4.44150700	-0.27191900	1.36337600
C	5.70145900	0.25286600	1.68286000
C	5.93467200	1.60616300	1.34916000
C	4.91550400	2.46503900	0.88429900
C	3.67092200	1.88052800	0.58710100
C	-2.06252700	-1.17714200	1.52861700
C	-1.82308100	-0.18033300	2.46884300
C	-2.25629300	-0.32295600	3.80140700
C	-3.03311400	-1.46050400	4.10668100
C	-3.26910400	-2.50468600	3.17765100
C	-2.74040200	-2.34010800	1.89135400
C	-3.05561400	-0.94231500	-1.12591800
C	-4.00133400	-1.95138100	-0.95166100
C	-5.21658100	-1.94098500	-1.64987700
C	-5.44395800	-0.85293200	-2.52444700
C	-4.45580600	0.10978800	-2.81881100
C	-3.27279900	0.06716300	-2.05879200
H	2.38152300	-0.05388900	3.07725100
H	1.77158100	-1.43379100	5.01006700
H	0.51424100	-3.54171300	4.71640500
H	-1.89713600	-2.62695100	-2.49155700

H	-0.76118600	-4.61977300	-3.34276300
H	1.10422000	-5.65197200	-2.08958300
H	1.07953300	-0.26469000	-2.52151500
H	3.92813100	-2.32637100	-0.02300700
H	4.25268300	-1.33533400	1.56318500
H	2.87399000	2.51570600	0.17931100
H	-1.28584200	0.74110000	2.17708600
H	-2.86884700	-3.13838200	1.15007400
H	-3.80386000	-2.77280100	-0.25098000
H	-2.51917900	0.85592200	-2.20544300
O	-0.28412500	-4.49867800	2.27418900
O	2.02328300	-4.69419000	0.31043700
C	-0.48058300	-5.44133300	3.35623600
H	-1.20431000	-5.02660600	4.08071100
H	-0.90510100	-6.30442400	2.82895000
H	0.47011300	-5.70154100	3.82738600
C	2.57952100	-5.98241200	-0.04793900
H	3.13420500	-5.89554000	-0.99912800
H	3.26100900	-6.17557400	0.78926400
H	1.79738000	-6.74395700	-0.09728100
O	7.22217700	2.13251200	1.54758500
O	4.00284800	-3.19831100	-4.50263800
O	-6.68440500	-0.77192700	-3.17939400
O	-3.50981900	-1.63796000	5.41653700
C	8.08304000	1.98470700	0.38992400
H	9.02561500	2.41852300	0.73890000
H	8.19922400	0.91917800	0.13995800
H	7.66875000	2.55691000	-0.45500300

C	-4.76442300	-0.97631700	5.70674400
H	-5.56930500	-1.43644700	5.11391100
H	-4.89408200	-1.17448100	6.77551400
H	-4.68941200	0.10382000	5.50537200
C	-7.65387600	0.04596400	-2.47672100
H	-8.52543500	0.00002000	-3.13741000
H	-7.87198700	-0.39880800	-1.49358200
H	-7.27803300	1.07643500	-2.37976600
C	4.91983200	-2.45548800	-5.34107100
H	5.85836700	-2.28445700	-4.79295000
H	5.07225300	-3.13665500	-6.18488700
H	4.47180900	-1.50525100	-5.66904600
C	5.10492700	3.97370800	0.67464000
C	5.69982800	4.19584700	-0.73009900
H	5.87267900	5.25953200	-0.92253700
H	6.66207000	3.67666400	-0.84588100
H	5.02638100	3.82749500	-1.51116000
C	6.02051500	4.57803000	1.75392300
H	7.04483300	4.18714800	1.68998400
H	6.07929700	5.66625200	1.66629100
H	5.65720900	4.33933700	2.75879600
C	3.75526600	4.72169100	0.76161100
H	3.06796900	4.43359400	-0.04318300
H	3.25525100	4.53641200	1.71753400
H	3.90353600	5.80364800	0.67288200
C	6.73685000	-0.66900400	2.33979700
C	7.65646200	0.09842300	3.30436200
H	8.30578400	-0.57767600	3.86656900

H	8.30139200	0.81403700	2.77879900
H	7.07249600	0.68324100	4.02368200
C	7.55856500	-1.33758800	1.21938900
H	8.35883700	-1.95984300	1.62952600
H	6.92411700	-1.98197100	0.58790600
H	8.02343600	-0.58561000	0.56474400
C	6.03947300	-1.77157200	3.17173400
H	5.41235600	-1.33535700	3.95699800
H	5.39963600	-2.41657300	2.55937000
H	6.77538400	-2.41762000	3.66039500
C	-1.84797200	0.75815900	4.81276400
C	-1.54372800	0.15057800	6.19393900
H	-0.79621600	-0.64595800	6.11222400
H	-1.16253400	0.90503900	6.88688600
H	-2.42995800	-0.30195700	6.65316200
C	-0.55880700	1.48076800	4.35321800
H	0.26888400	0.77428000	4.22793400
H	-0.69865200	1.99812900	3.39314500
H	-0.24815900	2.23420600	5.08211200
C	-2.97678300	1.80251500	4.90287300
H	-3.18862300	2.23923900	3.91727800
H	-3.91301600	1.36100600	5.27174600
H	-2.71019000	2.62136100	5.57668800
C	-4.06612700	-3.77519200	3.50225100
C	-3.60365200	-4.36800800	4.84544500
H	-3.74483700	-3.65320100	5.67014100
H	-4.15381700	-5.27660500	5.09911700
H	-2.53017800	-4.60930600	4.81551500

C	-5.56891200	-3.42977000	3.54100700
H	-6.17707400	-4.32203200	3.71556300
H	-5.79992200	-2.71558900	4.34423500
H	-5.89559800	-2.97931200	2.59771200
C	-3.87953300	-4.87070000	2.42486700
H	-4.37190700	-4.60179200	1.47591800
H	-2.82005600	-5.05167300	2.20856800
H	-4.31768500	-5.81841100	2.75063000
C	5.27313600	-3.71507200	-1.93128000
C	5.54100400	-4.01092400	-0.43590000
H	5.96215200	-3.13325300	0.08382600
H	4.62774700	-4.30650800	0.09287300
H	6.26479100	-4.82321300	-0.32199700
C	4.98971100	-5.05859300	-2.62752500
H	4.79630700	-4.91945200	-3.70218700
H	5.82947100	-5.75029300	-2.53162900
H	4.09579800	-5.53814900	-2.20027400
C	6.55321400	-3.06228500	-2.49167300
H	7.43626000	-3.67114900	-2.27616400
H	6.50319200	-2.94212800	-3.58275800
H	6.71323300	-2.07041200	-2.05717500
C	1.60824500	-1.45212700	-4.87175200
C	2.29034700	-0.32023900	-5.66611700
H	3.33532800	-0.56497500	-5.90572400
H	1.77340700	-0.13164500	-6.61191900
H	2.29589400	0.61565200	-5.09787300
C	0.14337600	-1.02947400	-4.60198500
H	-0.39145500	-1.80257400	-4.03784600

H	0.07676100	-0.09967900	-4.02273800
H	-0.39882900	-0.86917200	-5.53831800
C	1.54331300	-2.74761400	-5.69924600
H	0.90343800	-2.63109600	-6.57795500
H	2.52954900	-3.07020500	-6.04995500
H	1.14648500	-3.57304800	-5.09687400
C	-6.22080800	-3.07721600	-1.41622100
C	-5.51596700	-4.35761300	-0.90874800
H	-4.72733600	-4.67658700	-1.59814100
H	-5.06266300	-4.22413900	0.08737000
H	-6.22799800	-5.18475000	-0.82250300
C	-7.22733000	-2.61562400	-0.34309000
H	-7.97263200	-3.38911700	-0.13740200
H	-6.72213100	-2.37550400	0.59852100
H	-7.76716300	-1.71258000	-0.66576000
C	-6.94859700	-3.45821100	-2.71722200
H	-7.60591400	-4.31957700	-2.57449900
H	-7.56564100	-2.63270600	-3.09817900
H	-6.23535400	-3.70359100	-3.51090800
C	-4.60006800	1.19011500	-3.89845200
C	-3.21131100	1.61136500	-4.43405300
H	-2.59083400	2.07979600	-3.65957000
H	-2.66066500	0.75176000	-4.82965200
H	-3.30932300	2.34027800	-5.24519600
C	-5.28374800	2.41577500	-3.26358200
H	-5.40318500	3.22789400	-3.98604000
H	-6.28289600	2.16255800	-2.87971000
H	-4.69454600	2.80117100	-2.41298900

C	-5.40578500	0.68366100	-5.10744800
H	-6.44901500	0.46492900	-4.84559200
H	-5.41841100	1.41818800	-5.91703000
H	-4.98411900	-0.24725900	-5.50074500
N	1.17858400	4.79877100	-2.23106200
C	-0.73319000	6.26310000	-1.38375200
C	-0.68115000	6.81250800	-0.02426700
C	-1.96884600	6.45199100	-2.23632500
C	1.18996400	3.33408300	-1.92472600
C	0.35070100	3.01144800	-0.72952500
C	-1.04344200	2.85779400	-0.86676000
C	-1.81355900	7.41559900	0.54640900
C	-1.78876100	7.88983500	1.85569100
C	-0.63638400	7.77770300	2.62862200
C	0.49930200	7.18446100	2.07210100
C	0.47791200	6.71117100	0.76762500
C	-1.81329100	5.96091600	-3.63850400
C	-2.59017300	5.04327900	-4.21453600
C	0.25430200	5.49801000	-1.83502200
H	-2.21574100	7.52760600	-2.25323000
H	-2.82618100	5.95143400	-1.75638900
H	2.24515000	3.06085700	-1.80130700
H	0.83014500	2.82740300	-2.83049400
H	0.71878700	3.47109300	0.19325800
H	-1.43052800	2.75493700	-1.88599800
H	-2.73523900	7.49518600	-0.02761800
H	-2.68557000	8.34494500	2.27497000
H	-0.61882400	8.14987600	3.65177000

H	1.41226600	7.09476900	2.66031400
H	1.37452600	6.25671300	0.34320400
H	-0.99030600	6.39993300	-4.20955400
H	-2.43999300	4.72976600	-5.24571300
H	-3.41716500	4.57774400	-3.67527300
C	-2.03670800	3.28950500	0.12163200
C	-3.40024700	3.30356000	-0.22046400
C	-1.68469400	3.75819300	1.40051000
C	-4.36652300	3.76663400	0.66711300
H	-3.70513300	2.94011800	-1.21096800
C	-2.64776000	4.22786200	2.28479200
H	-0.63698400	3.78837300	1.69766700
C	-3.99640200	4.23494100	1.92750200
H	-5.41518800	3.76539200	0.37084800
H	-2.33765900	4.61098900	3.25700300
H	-4.74874000	4.60877500	2.62027100

9

Pd	-0.05987900	0.92299100	-0.29402300
P	2.03275200	0.32447600	0.20054600
P	-1.04300900	-1.09736800	-0.08012200
C	1.45572300	-2.06601700	1.63727300
C	1.87964300	-0.73801300	1.69685700
C	2.09012900	-0.10571800	2.93253800
C	1.90350300	-0.80692800	4.12410700
C	1.48961800	-2.14100800	4.10632800

C	1.26579700	-2.75857000	2.87186500
C	1.18738800	-2.79327800	0.37813100
C	0.07468800	-2.54102300	-0.43176700
C	-0.15334700	-3.30605000	-1.58221700
C	0.72998100	-4.32648800	-1.94322100
C	1.85782600	-4.59720900	-1.16798900
C	2.07898100	-3.83022800	-0.01817400
C	2.87146700	-0.67167100	-1.07810600
C	2.30555300	-0.71133700	-2.34952100
C	2.93094200	-1.40545100	-3.40119100
C	4.20284800	-1.96112800	-3.13788600
C	4.78967000	-1.96046600	-1.84676200
C	4.07864100	-1.32278100	-0.82273400
C	3.42425900	1.42664000	0.67108100
C	4.53665000	0.89259600	1.32812000
C	5.66002900	1.67703800	1.61213700
C	5.64170200	3.01829200	1.15892800
C	4.48997700	3.62064900	0.61029400
C	3.39370000	2.77996400	0.34835600
C	-1.64854600	-1.42081500	1.61609500
C	-1.67162100	-0.33706200	2.49091500
C	-2.13175000	-0.48000200	3.81268400
C	-2.66454400	-1.73680900	4.17476300
C	-2.62132100	-2.86580200	3.31844200
C	-2.08008000	-2.67669100	2.04070800
C	-2.48888200	-1.52936100	-1.13289800
C	-3.27703200	-2.65232000	-0.88744400
C	-4.35585200	-2.98498400	-1.71847700

C	-4.63082100	-2.10932200	-2.79335100
C	-3.78503000	-1.02869700	-3.13551900
C	-2.73992300	-0.72604400	-2.24638700
H	2.40196400	0.94082000	2.99800800
H	2.07365300	-0.31059300	5.08070400
H	1.32854400	-2.66876500	5.04189800
H	-1.02036500	-3.13665600	-2.22686800
H	0.54143100	-4.91459000	-2.84211200
H	2.54878400	-5.37770600	-1.47090600
H	1.35220900	-0.19782200	-2.55264400
H	4.48096600	-1.33950300	0.19747400
H	4.55346100	-0.16512600	1.62522600
H	2.50162900	3.23010200	-0.12366400
H	-1.32669900	0.65704300	2.15894000
H	-2.00517700	-3.53088500	1.35663400
H	-3.06435000	-3.30428200	-0.03074600
H	-2.12607100	0.16503300	-2.44016300
O	0.83536800	-4.05823300	2.72406900
O	3.17709800	-3.98122600	0.80427300
C	0.74590900	-4.87773900	3.91613800
H	-0.11497400	-4.55007400	4.52648800
H	0.56459200	-5.87250800	3.48918000
H	1.68219600	-4.86081400	4.47863500
C	3.97772000	-5.17708900	0.62806900
H	4.53446100	-5.11264500	-0.32360200
H	4.65770200	-5.12219300	1.48729400
H	3.35521700	-6.07373800	0.68138900
O	6.80114100	3.78738200	1.32918200

O	4.87938800	-2.65429900	-4.14990300
O	-5.73920600	-2.37574800	-3.60927900
O	-3.15819700	-1.92734500	5.47283000
C	7.68056100	3.76209900	0.17552800
H	8.50113500	4.41486700	0.49252800
H	8.03021500	2.73464600	-0.00346200
H	7.15913600	4.17719000	-0.70212300
C	-4.54033100	-1.53806600	5.66956400
H	-5.19613900	-2.19809600	5.08193100
H	-4.67672300	-1.69475800	6.74491500
H	-4.68918200	-0.48122200	5.39705100
C	-6.96253100	-1.73597600	-3.16258900
H	-7.69221400	-2.08546200	-3.90062200
H	-7.21996000	-2.07628800	-2.14814200
H	-6.84516200	-0.64142600	-3.20479900
C	5.64010200	-1.83197600	-5.06931200
H	6.50914000	-1.40889600	-4.54364000
H	5.95121800	-2.55759300	-5.82909500
H	5.01168000	-1.04030200	-5.50487400
C	4.37605300	5.11814000	0.27544500
C	4.91537200	5.32670300	-1.15348000
H	4.86369400	6.38472500	-1.43644300
H	5.96177100	5.00688000	-1.24664400
H	4.32176500	4.77249400	-1.88810500
C	5.16393700	5.97411400	1.28335700
H	6.24508200	5.80526300	1.22309700
H	4.98991800	7.04174700	1.11319900
H	4.86258900	5.75090000	2.31198700

C	2.91257700	5.59130300	0.33201700
H	2.26967900	5.15622400	-0.44949100
H	2.44594100	5.39111600	1.30001400
H	2.83234800	6.67406400	0.16327100
C	6.83813000	1.04442700	2.36552000
C	7.52854600	2.05901400	3.29134600
H	8.28529100	1.58317400	3.92072600
H	8.02724500	2.85923100	2.72729100
H	6.80486600	2.55338000	3.94881500
C	7.83072200	0.49549500	1.32176400
H	8.73216800	0.10059800	1.79967000
H	7.38167200	-0.31859100	0.72989900
H	8.14685300	1.28281500	0.62101900
C	6.35836400	-0.12302700	3.26032600
H	5.62737400	0.22188000	3.99986400
H	5.89543800	-0.93161500	2.68548400
H	7.19738000	-0.55994500	3.81212300
C	-2.02010800	0.72935500	4.75492600
C	-1.66045100	0.29275600	6.18572200
H	-0.74882200	-0.31309700	6.19537700
H	-1.49963700	1.15751100	6.83655400
H	-2.44669600	-0.31785300	6.64515400
C	-0.89865800	1.68943200	4.29003000
H	0.07173500	1.18533800	4.25377200
H	-1.09712000	2.11045400	3.29620900
H	-0.80463700	2.53950500	4.97516000
C	-3.35083200	1.50153900	4.72778500
H	-3.61097800	1.81538600	3.70877700

H	-4.18681900	0.89654300	5.10630100
H	-3.30052700	2.40709200	5.34217900
C	-3.14434500	-4.25463600	3.71217500
C	-2.64963400	-4.63352200	5.11906200
H	-3.02580100	-3.93409300	5.88105900
H	-2.97551400	-5.63589100	5.40727800
H	-1.55149600	-4.59803800	5.17216600
C	-4.68458200	-4.24244300	3.65465800
H	-5.09863900	-5.22920100	3.88412600
H	-5.11349300	-3.53530400	4.37979900
H	-5.04512000	-3.95089400	2.66276400
C	-2.65776000	-5.35361500	2.73753800
H	-3.12065100	-5.25347200	1.74323500
H	-1.57051800	-5.33118600	2.60625300
H	-2.92369800	-6.34862600	3.10843400
C	6.14245200	-2.61627600	-1.53069000
C	6.42291800	-2.67653400	-0.01067600
H	6.65653500	-1.67906600	0.40061700
H	5.57411700	-3.08253700	0.55041500
H	7.28904300	-3.31171600	0.20074800
C	6.15955000	-4.05897200	-2.06649800
H	5.96562200	-4.08837900	-3.14976300
H	7.12567200	-4.54123500	-1.89692400
H	5.38167100	-4.66787600	-1.58206300
C	7.27329500	-1.77966700	-2.16084000
H	8.25771600	-2.15823400	-1.86741800
H	7.23631600	-1.80460000	-3.25889600
H	7.21232100	-0.73110800	-1.85199300

C	2.18563800	-1.51331100	-4.74068900
C	2.63382000	-0.35576500	-5.65259300
H	3.71362200	-0.39007800	-5.85811700
H	2.11858000	-0.38855500	-6.61849800
H	2.41869500	0.61819500	-5.19952900
C	0.65716600	-1.39313100	-4.53090900
H	0.28246400	-2.18262800	-3.87049100
H	0.37050000	-0.42779200	-4.09617900
H	0.12533400	-1.48560800	-5.48449900
C	2.42777700	-2.87592600	-5.41185500
H	1.80150300	-3.00108200	-6.30030500
H	3.46806100	-3.01123800	-5.72698600
H	2.20449000	-3.69774900	-4.72244000
C	-5.16053100	-4.25569400	-1.40970900
C	-4.29980200	-5.29091700	-0.64533800
H	-3.40074700	-5.55354000	-1.21231300
H	-3.98443500	-4.93523800	0.34754700
H	-4.86355900	-6.21605200	-0.48273900
C	-6.35893100	-3.86080100	-0.52568700
H	-6.97147000	-4.73082600	-0.27119300
H	-6.03140100	-3.39477900	0.40923300
H	-7.01187300	-3.13742400	-1.03879900
C	-5.63714700	-4.94954200	-2.69709900
H	-6.12512400	-5.90440900	-2.48331000
H	-6.35492700	-4.33523000	-3.25681700
H	-4.80083300	-5.14160900	-3.37737100
C	-3.94715000	-0.21066900	-4.42665300
C	-2.62884400	0.50324500	-4.80062200

H	-2.31394000	1.22628000	-4.03728900
H	-1.81512200	-0.20893100	-4.96011400
H	-2.74784800	1.07594400	-5.72868400
C	-5.03468600	0.85575000	-4.22069000
H	-5.19111700	1.44761900	-5.12875600
H	-6.00161000	0.41013300	-3.94925800
H	-4.76069100	1.55999100	-3.41490300
C	-4.31062200	-1.13276600	-5.60555500
H	-5.29743900	-1.59768400	-5.46948600
H	-4.34077600	-0.57960900	-6.54880300
H	-3.58846800	-1.94677900	-5.71492900
N	-0.16204100	5.94694900	-1.30605700
C	-2.72325200	5.68286000	-1.34559400
C	-3.48318400	5.96218200	-0.16091100
C	-3.41361900	5.44205900	-2.66318900
C	0.16549100	3.09795800	-0.63627900
C	-1.12464200	3.05961300	-0.07797600
C	-2.30282200	2.86541700	-0.79747700
C	-4.89888900	5.97138400	-0.17989100
C	-5.63151900	6.22717100	0.97147000
C	-4.99194500	6.48458400	2.18438800
C	-3.59424100	6.46962600	2.22760800
C	-2.85290400	6.21192100	1.08508500
C	-2.49933800	5.06698600	-3.78473400
C	-2.68454100	4.02876200	-4.60212900
C	-1.33887100	5.83265500	-1.32741100
H	-3.97787900	6.35126000	-2.94821300
H	-4.18357300	4.65986900	-2.53699200

H	0.96652600	3.57644400	-0.07593200
H	0.26149500	3.17871800	-1.71945400
H	-1.20761700	3.24400900	0.99539800
H	-2.22067900	2.75782300	-1.88030400
H	-5.42803800	5.76738300	-1.10900900
H	-6.72025400	6.22180300	0.92122700
H	-5.57104200	6.69037900	3.08265900
H	-3.07715300	6.66662800	3.16642000
H	-1.76316800	6.20844700	1.13067100
H	-1.62465400	5.70663600	-3.92792200
H	-1.99814200	3.80875400	-5.41675300
H	-3.54312800	3.36312100	-4.49252900
C	-3.62332300	2.77863000	-0.23743000
C	-4.72360400	2.52033600	-1.08106600
C	-3.89102900	2.95626400	1.13908300
C	-6.01836400	2.43301500	-0.58326700
H	-4.53725000	2.35921400	-2.14907400
C	-5.18428600	2.87395400	1.63187200
H	-3.07741500	3.18605300	1.82363700
C	-6.25697300	2.60371600	0.77934500
H	-6.84394700	2.22540500	-1.26148700
H	-5.36381400	3.03694800	2.69333800
H	-7.26894300	2.54131200	1.17335100

10

Pd	-0.06184000	0.96117600	0.20228100
P	-2.13245800	0.32313100	-0.28163700

P	1.01932200	-0.98798600	-0.11923100
C	-1.26959200	-1.57909100	-2.18309600
C	-1.86027600	-0.33088800	-1.97665100
C	-2.07092900	0.55089800	-3.04782400
C	-1.70648600	0.18427700	-4.34445100
C	-1.08284800	-1.04150800	-4.58777500
C	-0.85141000	-1.90174900	-3.50903500
C	-1.04281900	-2.59611800	-1.13139100
C	0.00537800	-2.53555200	-0.20777000
C	0.24186100	-3.59137400	0.67883400
C	-0.59207700	-4.71285900	0.67639000
C	-1.67313400	-4.79391300	-0.20259500
C	-1.88962900	-3.74077600	-1.09935300
C	-2.99161100	-1.00313600	0.64124700
C	-2.51784100	-1.41425100	1.88417600
C	-3.21651400	-2.37187700	2.64355900
C	-4.46305000	-2.80752500	2.14056200
C	-4.94357500	-2.44552500	0.85730200
C	-4.16435800	-1.54930100	0.11645300
C	-3.53634400	1.48315000	-0.45528600
C	-4.59751400	1.21405000	-1.32048400
C	-5.72133300	2.04834600	-1.36996400
C	-5.75315600	3.14111600	-0.47162900
C	-4.64725500	3.50600000	0.32688500
C	-3.54949900	2.62816300	0.33840500
C	1.98462000	-1.09220700	-1.66558600
C	2.07252100	0.06993700	-2.43166100
C	2.84633600	0.10586900	-3.60369700

C	3.59842200	-1.05020000	-3.90752000
C	3.43693400	-2.27375800	-3.21746900
C	2.60632700	-2.26611500	-2.08710200
C	2.21159700	-1.36384400	1.22069900
C	3.32519500	-2.18441600	1.07778200
C	4.16391500	-2.47076100	2.16755000
C	3.86758300	-1.83583800	3.39572400
C	2.72739100	-1.01512100	3.58084200
C	1.92765200	-0.77176300	2.45445400
H	-2.50816600	1.54207000	-2.89988100
H	-1.89563300	0.86564500	-5.17526100
H	-0.78252500	-1.30865500	-5.59672300
H	1.07408200	-3.57134600	1.38725000
H	-0.40251300	-5.53187500	1.37101100
H	-2.32861200	-5.65877000	-0.17630500
H	-1.58875100	-0.99741200	2.29060300
H	-4.48818700	-1.27535200	-0.89441200
H	-4.57604100	0.33003700	-1.97155700
H	-2.70225900	2.86714500	0.99736200
H	1.53728400	0.98440100	-2.12743700
H	2.46069300	-3.19995000	-1.53154600
H	3.57502500	-2.61489600	0.10289400
H	1.07636400	-0.08064200	2.54957400
O	-0.21189500	-3.11543600	-3.60967800
O	-2.92822500	-3.69613000	-2.00482000
C	0.53931900	-3.38132200	-4.82095400
H	1.18943100	-2.53606500	-5.07446700
H	1.15264100	-4.24779900	-4.50842000

H	-0.14580300	-3.63973100	-5.63066200
C	-3.72242000	-4.89674500	-2.17273000
H	-4.34853500	-5.05419300	-1.27689800
H	-4.33810600	-4.63825100	-3.04373200
H	-3.08746500	-5.75926200	-2.39050200
O	-6.91271800	3.92745000	-0.42390900
O	-5.22421500	-3.72889000	2.87249000
O	4.66542800	-2.11640800	4.51237500
O	4.50445600	-1.01026300	-4.97739200
C	-7.87109500	3.47617000	0.56730500
H	-8.69108800	4.19189500	0.44262800
H	-8.19460900	2.45020900	0.33730400
H	-7.42847200	3.55098700	1.57336300
C	5.82330000	-0.54548700	-4.58411300
H	6.25525500	-1.23879500	-3.84719600
H	6.37402900	-0.56927500	-5.52997700
H	5.75566600	0.48098000	-4.18756500
C	5.82165000	-1.25767100	4.67724700
H	6.31451500	-1.69687400	5.55130500
H	6.46602400	-1.30327400	3.78620600
H	5.49162400	-0.22718300	4.88289500
C	-6.05819000	-3.15530900	3.90999700
H	-6.86935800	-2.57585800	3.44478500
H	-6.44729600	-4.04606200	4.41580700
H	-5.46269400	-2.53364700	4.59569100
C	-4.58518400	4.78390900	1.18014400
C	-5.23793000	4.47859600	2.54352200
H	-5.22482100	5.36543900	3.18732800

H	-6.28557100	4.16687800	2.43103100
H	-4.70324700	3.68491500	3.07382200
C	-5.30429700	5.95165900	0.48353300
H	-6.38236300	5.77864100	0.38178900
H	-5.17242900	6.88577700	1.03921000
H	-4.91095500	6.11225200	-0.52616000
C	-3.12731000	5.22434200	1.41212800
H	-2.53487200	4.50148800	1.98551200
H	-2.59431000	5.41042900	0.47267400
H	-3.07441300	6.16109600	1.98266800
C	-6.84412300	1.71212700	-2.36104500
C	-7.54007200	2.97720500	-2.88732100
H	-8.24404200	2.74690500	-3.69172100
H	-8.10051200	3.50024100	-2.10153900
H	-6.81131800	3.69893300	-3.27386600
C	-7.85054700	0.79383900	-1.63922400
H	-8.71262000	0.57198200	-2.27546200
H	-7.38815500	-0.16579600	-1.35692200
H	-8.23066900	1.26558600	-0.72078100
C	-6.28256200	0.96584500	-3.59452600
H	-5.53703000	1.57473000	-4.11775500
H	-5.81167800	0.01283300	-3.33237200
H	-7.08032900	0.74330200	-4.31124000
C	2.83589100	1.38326800	-4.45764100
C	2.98886100	1.05750500	-5.95422600
H	2.23460000	0.33847300	-6.28527400
H	2.88870500	1.95869600	-6.56703800
H	3.96915700	0.61907500	-6.18133000

C	1.49132500	2.12952100	-4.29457000
H	0.64192900	1.49263200	-4.55779400
H	1.34037100	2.49426900	-3.27052500
H	1.45986000	3.01570100	-4.93915700
C	3.97119800	2.30347200	-3.98221800
H	3.81935200	2.63633200	-2.94028500
H	4.95108900	1.81123900	-4.03826400
H	4.02477400	3.22016800	-4.58165700
C	4.15769500	-3.57403200	-3.59587800
C	4.34587300	-3.71118800	-5.11627700
H	5.03646300	-2.95359200	-5.51281400
H	4.75226500	-4.69036600	-5.38476500
H	3.40290500	-3.57528000	-5.65276600
C	5.52406100	-3.57043400	-2.88164100
H	6.11385300	-4.45429700	-3.14112200
H	6.11452900	-2.68412900	-3.16053800
H	5.40700400	-3.55675500	-1.78605200
C	3.35191600	-4.81009000	-3.13160500
H	3.23003200	-4.84479900	-2.04367700
H	2.34552600	-4.81823600	-3.57862800
H	3.85258900	-5.73766600	-3.42698600
C	-6.25137400	-2.98499600	0.25887100
C	-6.39421500	-2.63875100	-1.24198900
H	-6.59909500	-1.56552600	-1.39591700
H	-5.49606400	-2.89903400	-1.81263400
H	-7.23258400	-3.18332100	-1.68873300
C	-6.28747100	-4.51797800	0.39035500
H	-6.21711800	-4.83342200	1.44266500

H	-7.21288400	-4.93697500	-0.01296300
H	-5.44124200	-4.97839900	-0.14164200
C	-7.44803800	-2.33972000	0.98481800
H	-8.39656000	-2.63435800	0.52431700
H	-7.49689000	-2.64348300	2.03972100
H	-7.38783400	-1.24695700	0.95799900
C	-2.58173300	-2.88330600	3.94655600
C	-3.08708700	-2.01828100	5.11694400
H	-4.17901400	-2.08391300	5.23126500
H	-2.64158400	-2.33689400	6.06544400
H	-2.83618600	-0.96218700	4.97374400
C	-1.04147500	-2.77330500	3.89465000
H	-0.63464300	-3.25790600	3.00142300
H	-0.68642800	-1.72980800	3.90705800
H	-0.58420900	-3.26222200	4.76272900
C	-2.89846600	-4.37111200	4.18089300
H	-2.34651900	-4.76738700	5.03852600
H	-3.96182700	-4.55265300	4.37039200
H	-2.63318800	-4.97036000	3.30270800
C	5.33739500	-3.43677000	1.94274600
C	5.07828600	-4.36821300	0.73194200
H	4.13532800	-4.91210300	0.83959900
H	5.05579000	-3.81982100	-0.22425100
H	5.87444200	-5.11571400	0.64385600
C	6.59810800	-2.60366600	1.64443200
H	7.45414500	-3.24204900	1.40797600
H	6.43769900	-1.92519000	0.79831600
H	6.88264300	-1.97919300	2.50521200

C	5.55240700	-4.35456100	3.15791700
H	6.34952800	-5.08092900	2.97662500
H	5.82329600	-3.79356400	4.06130400
H	4.63947900	-4.90752600	3.40240100
C	2.32919700	-0.39932900	4.93295400
C	0.87379600	0.12575600	4.91535900
H	0.74653100	0.95807600	4.21263200
H	0.15426600	-0.66415400	4.65399600
H	0.58993000	0.50706100	5.90289500
C	3.24325000	0.79735000	5.24180100
H	2.89538700	1.35839100	6.11561400
H	4.27648400	0.48872100	5.45051000
H	3.27902100	1.51153500	4.39848700
C	2.41852200	-1.46190300	6.04304700
H	3.44300500	-1.84716300	6.15261100
H	2.12134000	-1.05165200	7.01229900
H	1.77712900	-2.32084500	5.82699900
N	0.62470400	5.60263300	2.42008200
C	2.99156300	5.22407600	1.46431900
C	3.20288800	5.41500000	0.05987600
C	4.15476800	5.05620100	2.40559400
C	-0.16275300	3.15593000	0.44091100
C	1.19147000	2.88506000	0.15247900
C	2.15179700	2.55815700	1.12187100
C	4.49083000	5.27549400	-0.51807800
C	4.68675300	5.42701700	-1.88474000
C	3.61653000	5.71277400	-2.73290300
C	2.33690700	5.85626200	-2.18382400

C	2.13016300	5.71661800	-0.82142100
C	3.78852000	4.87873300	3.84516000
C	4.39386600	4.03343400	4.68220400
C	1.71136200	5.43248100	1.99154500
H	4.81119600	5.94267700	2.31105700
H	4.78352700	4.20629800	2.08555800
H	-0.76625600	3.65511200	-0.31422500
H	-0.44552600	3.36571700	1.47077800
H	1.52156400	2.98017100	-0.88331700
H	1.83020600	2.56502900	2.16448800
H	5.34189500	5.03369800	0.11636600
H	5.69054400	5.31352500	-2.29369000
H	3.77543500	5.83621400	-3.80222300
H	1.49201900	6.09150200	-2.83058500
H	1.13079400	5.84130600	-0.40397000
H	2.98031900	5.51144500	4.22119000
H	4.11504600	3.96852900	5.73159400
H	5.20603500	3.38592900	4.34774800
C	3.49909100	2.13167400	0.87129600
C	4.29722000	1.69873600	1.95358400
C	4.08727900	2.11966400	-0.41373000
C	5.60229700	1.26711600	1.76731000
H	3.85736200	1.70664300	2.95636300
C	5.39451600	1.68550900	-0.59525600
H	3.52023800	2.46093300	-1.28330300
C	6.16097100	1.25242400	0.48728000
H	6.18825800	0.93736000	2.62285800
H	5.82239800	1.69009900	-1.59630900

H	7.18339400	0.91454900	0.33653200

12

Pd	0.06245800	1.07478500	-0.40175500
P	2.13219100	0.41528900	0.17976000
P	-1.11024000	-0.75861900	0.19659800
C	1.11857900	-1.02180400	2.40666000
C	1.78210900	0.12928100	1.97615400
C	1.98777600	1.20300900	2.86225000
C	1.54577400	1.12801700	4.18110900
C	0.85336200	0.00182300	4.64037400
C	0.63497900	-1.05060500	3.74818300
C	0.88095300	-2.21765400	1.56804100
C	-0.12680100	-2.30051300	0.60430700
C	-0.34567700	-3.49907400	-0.08974700
C	0.45070500	-4.61770500	0.15615800
C	1.48406800	-4.56529100	1.09545600
C	1.68918000	-3.37080300	1.79167700
C	3.02981100	-1.11731100	-0.37500700
C	2.59273100	-1.75877800	-1.52880400
C	3.28382000	-2.87161000	-2.04818700
C	4.48340000	-3.24045700	-1.40205200
C	4.92536400	-2.64056200	-0.19751100
C	4.15502800	-1.58328300	0.30399300
C	3.63279700	1.52186900	0.22664400
C	4.63621500	1.40167500	1.18539400
C	5.79775800	2.18580100	1.12708300

C	5.92655700	3.05927200	0.02406500
C	4.88102700	3.28770700	-0.89630800
C	3.73823400	2.47600800	-0.78127800
C	-2.16115300	-0.66958700	1.71338400
C	-2.25263000	0.58614900	2.31019800
C	-3.08229300	0.79851900	3.42464500
C	-3.85420000	-0.29765200	3.86441800
C	-3.67516100	-1.60818000	3.37081100
C	-2.81075500	-1.76503200	2.27506100
C	-2.24826200	-1.44460000	-1.10147100
C	-3.33970100	-2.27598100	-0.87676600
C	-4.06248600	-2.83597100	-1.94390000
C	-3.68291600	-2.45265400	-3.25058300
C	-2.57519600	-1.61380500	-3.51388600
C	-1.88423900	-1.10100500	-2.40348400
H	2.48099500	2.12054200	2.53563400
H	1.72883000	1.95680600	4.86400100
H	0.49884500	-0.04036300	5.66339300
H	-1.13572700	-3.59323100	-0.83697900
H	0.27287800	-5.54284700	-0.39102800
H	2.11162600	-5.43396600	1.25872800
H	1.69407900	-1.40619600	-2.04779400
H	4.44489500	-1.11625400	1.25092100
H	4.53701800	0.67355700	2.00075700
H	2.92653800	2.60315000	-1.50920600
H	-1.66956900	1.43147500	1.90500200
H	-2.65603200	-2.76911600	1.86240600
H	-3.65369200	-2.50665000	0.14540700

H	-1.05059000	-0.39632300	-2.56636100
O	-0.05316100	-2.20359500	4.06391700
O	2.68239300	-3.18742100	2.73379600
C	-0.86919700	-2.19377100	5.25959900
H	-1.51668300	-1.30981800	5.28388400
H	-1.47743800	-3.10537800	5.11337000
H	-0.23316000	-2.26800500	6.14357000
C	3.42475800	-4.35682500	3.15527500
H	4.08104100	-4.69603300	2.33455300
H	4.01305800	-3.96031600	3.99192400
H	2.74997400	-5.14617300	3.49548100
O	7.12646100	3.77593600	-0.12832000
O	5.23038400	-4.32485500	-1.89455800
O	-4.36452400	-3.01415600	-4.34364200
O	-4.80868600	-0.08866200	4.87641100
C	8.11631400	3.06744600	-0.91590700
H	8.97030000	3.75181400	-0.89536300
H	8.36038000	2.10574100	-0.43942400
H	7.74123600	2.92741300	-1.94172200
C	-6.11744200	0.24592800	4.34770000
H	-6.48188000	-0.57026300	3.70596200
H	-6.72361500	0.34258400	5.25394600
H	-6.06202300	1.20063900	3.80161800
C	-5.52778400	-2.27718300	-4.78761400
H	-5.90283200	-2.90173200	-5.60567000
H	-6.26585300	-2.20093900	-3.97463000
H	-5.22500900	-1.28433200	-5.15415300
C	6.15037700	-4.00055000	-2.96410600

H	6.95890300	-3.36622600	-2.57152000
H	6.52688200	-4.98569200	-3.25845300
H	5.62544100	-3.50730100	-3.79612700
C	4.93541400	4.34574900	-2.00653600
C	5.65514600	3.73020300	-3.22437400
H	5.72737300	4.44967900	-4.04535500
H	6.67726400	3.41618800	-2.96688800
H	5.12231000	2.85011200	-3.59711200
C	5.66223400	5.61694700	-1.53382200
H	6.72001400	5.42619800	-1.30922100
H	5.62169700	6.40637500	-2.28896100
H	5.21311000	6.00782600	-0.61460900
C	3.51472400	4.77343600	-2.43722300
H	2.93500200	3.94369900	-2.85572300
H	2.94382300	5.18069900	-1.59443100
H	3.55153000	5.55487600	-3.20360400
C	6.84729800	2.02389400	2.23381500
C	7.58920400	3.34048200	2.51934100
H	8.23953300	3.25582400	3.39365200
H	8.21242400	3.65541500	1.67311000
H	6.88275400	4.15839800	2.69973200
C	7.83597800	0.92496000	1.79448600
H	8.64379400	0.80176200	2.52086900
H	7.32887400	-0.04885300	1.68888500
H	8.29326000	1.16776100	0.82397100
C	6.18104100	1.59188900	3.56204600
H	5.44072100	2.32997700	3.88919200
H	5.66920000	0.62665500	3.47838900

H	6.92387000	1.49511500	4.35970900
C	-3.11318600	2.18901400	4.07065500
C	-3.33113100	2.10292800	5.59190800
H	-2.58408700	1.45450900	6.06023600
H	-3.26540100	3.08764000	6.06188200
H	-4.31404900	1.68225000	5.84191600
C	-1.76975500	2.92100500	3.84928400
H	-0.93054400	2.33716400	4.24739700
H	-1.56340600	3.09986600	2.78650600
H	-1.76408800	3.89486000	4.34658500
C	-4.24080600	3.00440100	3.40804300
H	-4.06105900	3.12940300	2.32905100
H	-5.21552000	2.51151600	3.53025400
H	-4.31697700	4.00602800	3.84106900
C	-4.38845500	-2.84598600	3.92640600
C	-4.67134100	-2.73066000	5.43472400
H	-5.42072500	-1.95952800	5.65424100
H	-5.04175800	-3.67271300	5.84774000
H	-3.77131300	-2.44636500	5.98831400
C	-5.70824800	-3.01505300	3.14578600
H	-6.28916600	-3.86142500	3.52243300
H	-6.33358400	-2.11420100	3.23136600
H	-5.52077700	-3.18922100	2.07404300
C	-3.51673200	-4.10849900	3.73231000
H	-3.32625200	-4.32619900	2.67549300
H	-2.53664700	-3.98634200	4.22149000
H	-3.99682200	-4.99198500	4.16242300
C	6.17581800	-3.09255900	0.56897100

C	6.25886000	-2.46153300	1.97971800
H	6.49775800	-1.38542500	1.93058100
H	5.31920600	-2.57114800	2.53286400
H	7.04677100	-2.93385300	2.57359700
C	6.15339100	-4.62207100	0.74531000
H	6.12225500	-5.13628500	-0.22730300
H	7.03449600	-4.98226500	1.28045000
H	5.25732400	-4.93595100	1.30234400
C	7.43739400	-2.64350300	-0.19622200
H	8.34609200	-2.87222300	0.36818400
H	7.52363800	-3.14976800	-1.16744700
H	7.41986200	-1.56551700	-0.38632500
C	2.68872800	-3.60597400	-3.25824100
C	3.30268300	-3.02104200	-4.54660800
H	4.39296700	-3.16187300	-4.57478700
H	2.88652400	-3.50180000	-5.43689500
H	3.10972000	-1.94651300	-4.62506600
C	1.15615700	-3.41784000	-3.33065500
H	0.67721400	-3.69623500	-2.38504700
H	0.86472500	-2.37939300	-3.55705200
H	0.71835300	-4.04509500	-4.11371900
C	2.93127600	-5.12404000	-3.17174000
H	2.41317900	-5.66002200	-3.97116200
H	3.99345200	-5.38367600	-3.23711100
H	2.57613800	-5.51774300	-2.21237000
C	-5.19355900	-3.82166000	-1.61796300
C	-5.00631500	-4.45505600	-0.21678300
H	-4.02796200	-4.93818500	-0.12653000

H	-5.09814100	-3.71656400	0.59651100
H	-5.76496900	-5.22277400	-0.03308500
C	-6.53096500	-3.05414800	-1.61996800
H	-7.36275800	-3.70268300	-1.33068800
H	-6.50231500	-2.20801300	-0.92315600
H	-6.75988800	-2.65078400	-2.61749000
C	-5.22811000	-4.98828300	-2.62066300
H	-5.98911300	-5.72625200	-2.35447700
H	-5.43967500	-4.65094200	-3.64313100
H	-4.25996000	-5.49913600	-2.66140900
C	-2.09595800	-1.23668900	-4.92320200
C	-0.64926900	-0.68864200	-4.90397700
H	-0.56289200	0.22901600	-4.30970000
H	0.05501700	-1.42522000	-4.48249800
H	-0.30540300	-0.45371100	-5.91553900
C	-3.00918900	-0.12441700	-5.47602200
H	-2.64107100	0.25650600	-6.43268900
H	-4.03422000	-0.48536600	-5.63944200
H	-3.06492000	0.72461700	-4.77499500
C	-2.09991600	-2.46341400	-5.85174400
H	-3.10886200	-2.88159100	-5.97235700
H	-1.72424700	-2.21526400	-6.84751800
H	-1.47706000	-3.26677300	-5.44472900
N	-0.64914500	5.90857000	-2.69147600
C	-2.73723000	4.48548400	-1.94697300
C	-3.36166900	5.09665600	-0.69496000
C	-3.70992300	4.52645500	-3.15714800
C	0.18392900	3.20721800	-0.90868300

C	-1.15782200	2.95186600	-0.62505200
C	-2.24234900	2.98195200	-1.67277800
C	-4.73976500	5.02897400	-0.46412100
C	-5.29063600	5.52555900	0.71517400
C	-4.47302200	6.09693400	1.68693200
C	-3.09937500	6.17582400	1.46579700
C	-2.55094600	5.68347200	0.28461900
C	-3.10439000	4.14639600	-4.47043000
C	-3.67464500	3.32540900	-5.35392500
C	-1.56306200	5.27928100	-2.33062200
H	-4.10268500	5.55337900	-3.22100900
H	-4.56708800	3.87456400	-2.94831800
H	0.83622800	3.65435300	-0.15808400
H	0.51521500	3.33481300	-1.94008000
H	-1.50063000	3.15472600	0.39269700
H	-1.81879700	2.65648000	-2.63613900
H	-5.39791000	4.56662900	-1.19729000
H	-6.36611100	5.46029500	0.87302500
H	-4.90443400	6.48637200	2.60777400
H	-2.44914400	6.62933200	2.21242800
H	-1.47708800	5.76044600	0.11452100
H	-2.15075200	4.61949500	-4.72049600
H	-3.21810200	3.11683000	-6.31931500
H	-4.63198700	2.84266600	-5.15079700
C	-3.41945800	2.08918400	-1.35477500
C	-4.00425500	1.32249300	-2.36767100
C	-3.96599100	2.00601200	-0.06810900
C	-5.10190400	0.50325600	-2.11252300

H	-3.57092500	1.35170000	-3.37344900
C	-5.05652900	1.18006800	0.19498300
H	-3.54410100	2.59212500	0.75297700
C	-5.63300700	0.42808100	-0.82677700
H	-5.52376100	-0.09985400	-2.91505000
H	-5.44592800	1.11599800	1.21067000
H	-6.47456700	-0.23211900	-0.61846800

13

Pd	0.08400000	0.76380300	-0.06106400
P	-1.87229200	-0.32353400	-0.20925000
P	1.38025100	-1.05007200	0.30988000
C	-1.13519200	-3.05592000	-0.14351300
C	-1.78405300	-2.04719300	-0.86984500
C	-2.25488500	-2.29578300	-2.16538400
C	-2.10358700	-3.55545900	-2.75264900
C	-1.47224800	-4.58479800	-2.05315500
C	-0.99279100	-4.32008700	-0.76687600
C	-0.59260000	-2.89583500	1.22526900
C	0.58226200	-2.19849700	1.52652600
C	1.08911100	-2.19282400	2.83682600
C	0.41830100	-2.85745600	3.86184200
C	-0.78245500	-3.52689000	3.60820500
C	-1.27011700	-3.54372900	2.29929400
C	-2.71185500	-0.54186200	1.41786100
C	-2.13233500	0.09410500	2.51099500
C	-2.74156800	0.05415600	3.77890600

C	-4.00635700	-0.56653100	3.86355100
C	-4.59069700	-1.27267000	2.78375400
C	-3.89481800	-1.26268600	1.56801600
C	-3.27579200	0.39762600	-1.18125400
C	-4.55174300	-0.15967200	-1.23849300
C	-5.61192400	0.51158000	-1.86254300
C	-5.32754700	1.77661800	-2.43096800
C	-4.01999200	2.30115700	-2.51014200
C	-3.00858200	1.59487200	-1.83630200
C	1.65552700	-2.02560800	-1.21882400
C	1.48507200	-1.31303900	-2.40370400
C	1.76823800	-1.90152800	-3.64878000
C	2.33557300	-3.19283300	-3.63082300
C	2.43945900	-3.97047700	-2.45302800
C	2.06072900	-3.35963600	-1.24799300
C	3.09827700	-0.94457900	0.99155800
C	4.06217500	-1.93799200	0.84610200
C	5.35873900	-1.77334900	1.35944100
C	5.64505400	-0.54988300	2.00639600
C	4.66017900	0.42965600	2.26286400
C	3.39421400	0.22574500	1.68978700
H	-2.74697100	-1.51644100	-2.75348100
H	-2.46998600	-3.73269900	-3.76279200
H	-1.32537500	-5.56356600	-2.50172300
H	2.02135300	-1.68015400	3.08673100
H	0.82616600	-2.85425300	4.87246400
H	-1.31040300	-4.01520700	4.41965200
H	-1.17937200	0.63973500	2.39380300

H	-4.29927900	-1.82068100	0.71427400
H	-4.74248300	-1.13526600	-0.77306900
H	-1.98865100	2.01751200	-1.82369300
H	1.12920400	-0.26622900	-2.38243500
H	2.08596000	-3.94428900	-0.32063400
H	3.82765200	-2.86386700	0.31306900
H	2.63680900	1.01709100	1.78895500
O	-0.25222400	-5.29326000	-0.09223900
O	-2.43368900	-4.19290600	1.92405400
C	-1.01797000	-6.46598800	0.28567500
H	-1.36043600	-7.00093600	-0.60264700
H	-0.28199500	-7.05232300	0.84690500
H	-1.85539700	-6.16247900	0.92583700
C	-3.24874300	-4.76867900	2.97348800
H	-3.66544900	-3.96925000	3.60787000
H	-4.04562500	-5.25577500	2.39656800
H	-2.68021200	-5.49819300	3.55511700
O	-6.38454500	2.50353400	-3.00142800
O	-4.68448400	-0.57193400	5.09365000
O	6.95032400	-0.33568800	2.47939000
O	2.75133000	-3.76658300	-4.84475100
C	-6.99923800	3.44683000	-2.08771400
H	-7.77192200	3.90925400	-2.71040200
H	-7.43984400	2.90713900	-1.23562200
H	-6.25589500	4.18911000	-1.75578900
C	4.10960800	-3.42275100	-5.21547800
H	4.80983200	-3.81847800	-4.46370500
H	4.22867300	-3.93146100	-6.17726900

H	4.20920400	-2.33129400	-5.32394200
C	7.79674700	0.38330700	1.54742900
H	8.73565400	0.47402600	2.10260900
H	7.92823400	-0.21193200	0.63077600
H	7.36339100	1.37174400	1.32711800
C	-5.50324900	0.59944900	5.33098900
H	-6.31066900	0.64509100	4.58411600
H	-5.89881600	0.41168800	6.33447100
H	-4.88476400	1.51036000	5.30820000
C	-3.63888200	3.58852200	-3.25470100
C	-3.83884100	4.78050400	-2.29963800
H	-3.59243300	5.72890100	-2.78802600
H	-4.87916000	4.84925800	-1.95040200
H	-3.19790800	4.69916400	-1.41325300
C	-4.47445400	3.76665000	-4.53359800
H	-5.54094200	3.90351600	-4.31281300
H	-4.14456200	4.63517400	-5.11008800
H	-4.40168300	2.88531800	-5.17943100
C	-2.15368800	3.55040400	-3.68703400
H	-1.47187100	3.48758200	-2.82281200
H	-1.94872400	2.69560000	-4.33908100
H	-1.88360400	4.45665200	-4.23934900
C	-7.00244800	-0.13735900	-1.86039200
C	-7.75165200	0.13733700	-3.17510100
H	-8.70671800	-0.39256800	-3.21523400
H	-7.96276100	1.20690100	-3.31155700
H	-7.15604300	-0.17221400	-4.04054400
C	-7.78918300	0.41731200	-0.65526800

H	-8.81215500	0.03046600	-0.63793000
H	-7.31171700	0.14245000	0.29960100
H	-7.85096200	1.51525000	-0.69000900
C	-6.90810400	-1.67481600	-1.71191600
H	-6.27132100	-2.11159300	-2.48799300
H	-6.50915100	-1.97752700	-0.73007400
H	-7.89711100	-2.13534300	-1.80582600
C	1.45492400	-1.10255100	-4.92043100
C	1.02445100	-2.02103700	-6.07733600
H	0.19723400	-2.67184200	-5.77471600
H	0.70220300	-1.44484200	-6.94832800
H	1.83650000	-2.68408200	-6.40099500
C	0.28361600	-0.12270500	-4.66664600
H	-0.61522500	-0.65754200	-4.34156300
H	0.52702900	0.61597900	-3.88973500
H	0.03170000	0.43235400	-5.57456000
C	2.70546300	-0.28885200	-5.30551200
H	2.99687600	0.39572800	-4.49861500
H	3.56520600	-0.94541800	-5.50398000
H	2.53184600	0.31004500	-6.20358900
C	2.97740200	-5.40764600	-2.42847400
C	2.48516800	-6.21108200	-3.64508000
H	2.87241400	-5.80377600	-4.58884600
H	2.79237700	-7.25802400	-3.58766500
H	1.39302300	-6.17966600	-3.71676700
C	4.51899000	-5.33755900	-2.40410600
H	4.96081900	-6.33767900	-2.40630100
H	4.91167600	-4.79950600	-3.27870400

H	4.87827100	-4.81402100	-1.50326600
C	2.51021300	-6.16778700	-1.16815100
H	2.90741200	-5.73341200	-0.24557400
H	1.41217700	-6.15234900	-1.08482800
H	2.82631800	-7.21358800	-1.19730600
C	-5.93606800	-2.00580500	2.86583500
C	-6.11693400	-3.02295900	1.71337400
H	-6.23009200	-2.52667500	0.73502600
H	-5.26875800	-3.71150700	1.64034200
H	-7.01882500	-3.62467400	1.86415400
C	-6.04196600	-2.79047300	4.18565100
H	-6.05172900	-2.11788000	5.05583400
H	-6.95084700	-3.39500100	4.22878900
H	-5.17740700	-3.45460700	4.31483500
C	-7.06962800	-0.96738700	2.74496600
H	-8.05198000	-1.44032500	2.83326500
H	-7.00213800	-0.19996200	3.52944200
H	-7.03461000	-0.44821600	1.77250200
C	-1.99485600	0.68503800	4.96257300
C	-2.46031700	2.14636500	5.11688800
H	-3.54001400	2.20707100	5.31825000
H	-1.94458900	2.64260300	5.94475100
H	-2.26345900	2.72649500	4.20914200
C	-0.46814800	0.68429700	4.70947800
H	-0.09464600	-0.33478300	4.55144900
H	-0.19242500	1.27265400	3.82558100
H	0.07206500	1.10709800	5.56154500
C	-2.22803900	-0.10397700	6.26258000

H	-1.62518700	0.29108800	7.08467700
H	-3.27710700	-0.07830500	6.58117300
H	-1.96952500	-1.16022200	6.13038200
C	6.38038800	-2.90480600	1.18085700
C	5.68390400	-4.26700600	0.95107500
H	4.96568800	-4.48835000	1.74688600
H	5.15073600	-4.30752200	-0.01376600
H	6.41599900	-5.08107700	0.93960500
C	7.24254000	-2.58866500	-0.05784400
H	7.98423500	-3.37224200	-0.23663600
H	6.62590800	-2.49615200	-0.95773100
H	7.78687800	-1.64036200	0.06551800
C	7.26083100	-3.06135700	2.43314500
H	7.94445600	-3.90909800	2.34212600
H	7.86995000	-2.16584600	2.61967600
H	6.64919000	-3.21338000	3.32838300
C	4.89137500	1.68619700	3.11331300
C	3.56069300	2.17909100	3.73275000
H	2.84206600	2.49381200	2.96648300
H	3.09070800	1.39981700	4.34003400
H	3.73186000	3.04529600	4.38012600
C	5.45040100	2.79576100	2.20602400
H	5.63975400	3.71672900	2.76649700
H	6.39334200	2.49353100	1.72926900
H	4.74060300	3.05019800	1.39853800
C	5.84773500	1.40519200	4.28590900
H	6.85912400	1.15488100	3.94054000
H	5.93316300	2.26975100	4.94926900

H	5.50396500	0.55296000	4.88095200
N	-0.82900100	5.06143600	0.77218000
C	1.34653600	6.07431000	-0.09784800
C	2.49993600	6.15862800	0.80455100
C	1.48622100	6.49126800	-1.54614900
C	-1.06225100	3.58422800	0.72280900
C	-0.23449600	2.90205400	-0.31860000
C	1.15407000	2.72707100	-0.11649000
C	3.73696600	6.64300700	0.34669000
C	4.84337400	6.69693000	1.19105900
C	4.74755000	6.27327500	2.51391700
C	3.52285700	5.79389600	2.98509900
C	2.41914400	5.73642000	2.14568900
C	0.29713600	6.17548300	-2.39152000
C	-0.42071200	7.06921300	-3.07133100
C	0.20671300	5.54637500	0.33712000
H	2.36184100	5.95696600	-1.95678800
H	1.72169200	7.56578900	-1.61229900
H	-2.13878000	3.44702500	0.56429200
H	-0.83973300	3.21948500	1.73516800
H	-0.57274400	3.11017800	-1.34445300
H	1.53248100	2.92589500	0.89181700
H	3.84139700	6.97756400	-0.68389000
H	5.78898800	7.07870000	0.80731000
H	5.61175500	6.32335100	3.17421900
H	3.42758900	5.46450600	4.01933500
H	1.46767400	5.36684800	2.53124200
H	0.02409600	5.11614300	-2.44010000

H	-1.27357000	6.77756200	-3.68111600
H	-0.18087000	8.13264100	-3.04383800
C	2.16177400	2.86082200	-1.17254300
C	3.48098900	3.20617500	-0.83353700
C	1.85440200	2.72725800	-2.53921200
C	4.44497400	3.42738700	-1.81237700
H	3.74858800	3.31956200	0.22467600
C	2.81634400	2.95038600	-3.51764800
H	0.84397000	2.44621400	-2.83996400
C	4.11902900	3.30507200	-3.16253900
H	5.45517200	3.70839500	-1.51547100
H	2.54595900	2.84920800	-4.56881700
H	4.87022300	3.48279600	-3.93040400

15

Pd	-0.01463800	0.65813000	0.06263600
P	-2.00617500	-0.30133100	-0.15948000
P	1.24930200	-1.17853200	0.31516700
C	-1.35341600	-3.03262100	-0.16039900
C	-1.94566500	-1.98498400	-0.87719100
C	-2.42460000	-2.19094000	-2.17541400
C	-2.33295500	-3.45181200	-2.77609600
C	-1.75620000	-4.51794600	-2.08660600
C	-1.27035300	-4.29642400	-0.79306800
C	-0.81970900	-2.90360100	1.21389600
C	0.39551900	-2.28394000	1.52794400
C	0.89734800	-2.33395200	2.83462300

C	0.18006800	-2.97664900	3.84795700
C	-1.06516700	-3.54823000	3.58434200
C	-1.55446100	-3.50148700	2.27431500
C	-2.93181800	-0.47311300	1.39601500
C	-2.37153900	0.10984100	2.53146400
C	-3.06299000	0.12057600	3.75487100
C	-4.38652100	-0.37366500	3.74881400
C	-4.95482000	-1.03178200	2.63054300
C	-4.17903500	-1.09224300	1.46508100
C	-3.18234800	0.55701600	-1.25614800
C	-4.54023800	0.24371800	-1.30497600
C	-5.44014500	1.03120700	-2.03336500
C	-4.92135400	2.18437000	-2.67202900
C	-3.53545100	2.44460000	-2.76317300
C	-2.68274300	1.60094600	-2.03426100
C	1.48565500	-2.12739300	-1.21913100
C	1.36924500	-1.38816400	-2.39570000
C	1.64666600	-1.96788600	-3.64439400
C	2.15054200	-3.28711800	-3.63893500
C	2.19397900	-4.08728900	-2.47173600
C	1.82987700	-3.47823200	-1.26168400
C	2.93060800	-1.08629700	1.02674600
C	3.89335600	-2.07360100	0.83792000
C	5.15497800	-1.97937900	1.44628400
C	5.41645400	-0.82490000	2.21940100
C	4.43038100	0.15186000	2.49810500
C	3.20132500	0.02174000	1.83498200
H	-2.87803800	-1.38256300	-2.75842900

H	-2.70481600	-3.59861700	-3.79043400
H	-1.65779600	-5.50042400	-2.54515600
H	1.86029700	-1.88709300	3.10126700
H	0.59282400	-3.02548500	4.85690100
H	-1.62802800	-4.02332900	4.38225800
H	-1.37537900	0.58372300	2.48744000
H	-4.57735000	-1.61286000	0.58432800
H	-4.93070700	-0.62657100	-0.76253800
H	-1.60034800	1.79886000	-2.07392700
H	1.06672300	-0.32849900	-2.36852800
H	1.81934700	-4.07766000	-0.34289200
H	3.69046400	-2.93818200	0.19903500
H	2.45417700	0.81886100	1.95807100
O	-0.58523800	-5.31322900	-0.13036600
O	-2.76865300	-4.03503200	1.88681500
C	-1.43113700	-6.41094500	0.30472300
H	-1.85424200	-6.93012600	-0.55782300
H	-0.72136800	-7.04717300	0.84600900
H	-2.21238700	-6.02789500	0.97370000
C	-3.74270900	-4.30013100	2.92711700
H	-3.81234200	-3.45915300	3.62760600
H	-4.67673300	-4.37872600	2.34180000
H	-3.49587100	-5.23759200	3.42986100
O	-5.82069500	3.05865500	-3.29177900
O	-5.15106200	-0.29071700	4.91896600
O	6.68070500	-0.69432400	2.80772600
O	2.55517800	-3.86259200	-4.85159700
C	-6.25860900	4.14221800	-2.42827500

H	-6.91737600	4.71568600	-3.08885900
H	-6.80600800	3.73207300	-1.56707500
H	-5.38999200	4.74483700	-2.11108700
C	3.93049400	-3.57082000	-5.20978100
H	4.60752800	-4.02266100	-4.46855400
H	4.02706900	-4.05810100	-6.18587700
H	4.08338800	-2.48293600	-5.28796700
C	7.63025300	0.06229700	2.01341100
H	8.52315400	0.05371300	2.64741700
H	7.80920200	-0.44962900	1.05622300
H	7.25971600	1.08973300	1.86181300
C	-5.86023900	0.96558300	5.07957400
H	-6.60047300	1.07782500	4.27276500
H	-6.34559800	0.83726400	6.05315200
H	-5.14915600	1.80726000	5.09520900
C	-2.91626500	3.61157100	-3.55173300
C	-2.90734000	4.85138000	-2.64479300
H	-2.48816300	5.72519100	-3.15853700
H	-3.91336500	5.12714500	-2.30130900
H	-2.28574900	4.71513200	-1.74398800
C	-3.69626700	3.88019500	-4.84972500
H	-4.72108600	4.21975400	-4.65172100
H	-3.21105500	4.65781600	-5.44845300
H	-3.77361900	2.97965000	-5.46571500
C	-1.45873300	3.29008200	-3.95823200
H	-0.80066300	3.16571800	-3.08152400
H	-1.39661900	2.39162700	-4.57652300
H	-1.03164800	4.11999500	-4.53630000

C	-6.92042000	0.62557100	-2.05953000
C	-7.57481600	0.97419300	-3.40595900
H	-8.59937000	0.59748600	-3.46831100
H	-7.61603600	2.05997700	-3.57376000
H	-7.00926400	0.55485200	-4.24476000
C	-7.63369800	1.35000300	-0.90151700
H	-8.71406300	1.17839900	-0.93019900
H	-7.26672600	1.00512200	0.07807200
H	-7.47263900	2.43818000	-0.95273800
C	-7.08320900	-0.90154400	-1.86386300
H	-6.53044800	-1.45941100	-2.62642100
H	-6.74407600	-1.24323600	-0.87438100
H	-8.13672200	-1.19010000	-1.95160800
C	1.40249700	-1.12923700	-4.90707100
C	0.96458300	-2.00262300	-6.09442200
H	0.10595100	-2.62880300	-5.83095500
H	0.68563200	-1.39258500	-6.95861300
H	1.75768800	-2.68652400	-6.42140100
C	0.26678300	-0.10544800	-4.66296900
H	-0.66432100	-0.60433900	-4.37667300
H	0.52153400	0.61560000	-3.87662500
H	0.06488500	0.47340700	-5.57121400
C	2.69596300	-0.36222600	-5.23715000
H	2.99042900	0.30429000	-4.41635700
H	3.53674700	-1.04803100	-5.41903700
H	2.57689900	0.25507300	-6.13327000
C	2.65945600	-5.55086800	-2.46427300
C	2.12977000	-6.31014500	-3.69255200

H	2.53187800	-5.90442000	-4.63142600
H	2.39655500	-7.36980700	-3.65556600
H	1.03983800	-6.23740400	-3.76059400
C	4.20145000	-5.55551700	-2.43700300
H	4.59393000	-6.57669400	-2.42131500
H	4.62385900	-5.05544600	-3.32053300
H	4.58792000	-5.03588300	-1.54539800
C	2.15172900	-6.30130400	-1.21414500
H	2.57515100	-5.90433600	-0.28628800
H	1.05635400	-6.23576300	-1.12843600
H	2.41458600	-7.36225300	-1.25893200
C	-6.37849400	-1.60696900	2.60691300
C	-6.55576000	-2.64944700	1.47734200
H	-6.48777100	-2.19461900	0.47683300
H	-5.80693000	-3.45148400	1.54489400
H	-7.54318300	-3.12091600	1.53629000
C	-6.72759600	-2.31141300	3.92871400
H	-6.71543800	-1.61359000	4.77909800
H	-7.72625900	-2.75704700	3.89467600
H	-6.01300800	-3.10258500	4.16814600
C	-7.35389500	-0.44320500	2.34021700
H	-8.38975600	-0.79396300	2.29737900
H	-7.29960400	0.31773900	3.13357500
H	-7.13621400	0.06479100	1.38609200
C	-2.34359500	0.68231700	4.99136100
C	-2.66239100	2.18363300	5.10238700
H	-3.74020500	2.36627700	5.22265100
H	-2.15800300	2.63635600	5.96330600

H	-2.33545800	2.73521900	4.21247600
C	-0.81221900	0.51355500	4.84959400
H	-0.53554000	-0.53612700	4.70579900
H	-0.40608900	1.08866500	4.00817600
H	-0.29656300	0.87069500	5.74829500
C	-2.75693600	-0.06374000	6.27107500
H	-2.18180300	0.28218000	7.13580500
H	-3.81788900	0.07751400	6.51134300
H	-2.59788400	-1.14189200	6.17157300
C	6.16634400	-3.11566200	1.23417400
C	5.45812300	-4.43965900	0.85904700
H	4.70732000	-4.71595300	1.60595100
H	4.96406700	-4.39266500	-0.12509700
H	6.18018900	-5.26208100	0.80776800
C	7.10233000	-2.71789200	0.07670000
H	7.84505600	-3.49650400	-0.12083200
H	6.54401800	-2.54249700	-0.84817300
H	7.65163400	-1.79164000	0.30714000
C	6.96948800	-3.39495100	2.51604500
H	7.63159900	-4.25681800	2.39761100
H	7.59666000	-2.53959300	2.80390100
H	6.30653000	-3.59121600	3.36495600
C	4.62887600	1.31573200	3.48449700
C	3.26839100	1.84706100	3.99376900
H	2.67174300	2.29467500	3.18850400
H	2.67946700	1.06911300	4.48287400
H	3.42378900	2.65500700	4.72162000
C	5.35467500	2.46374600	2.77173400

H	5.49787800	3.32597700	3.43924500
H	6.34178100	2.17070000	2.39475900
H	4.76998400	2.85552000	1.91843800
C	5.42043400	0.84850900	4.71970900
H	6.44306100	0.54408500	4.45972000
H	5.50188900	1.64983400	5.46092300
H	4.94416600	-0.00977400	5.20108900
N	-0.62874200	5.79284700	0.28057200
C	1.91964800	5.90326400	-0.08586500
C	2.81381600	5.85782400	1.03191800
C	2.43177300	6.16437500	-1.47858900
C	-0.70956800	2.82705700	0.18736200
C	0.38853400	2.89928000	-0.67750400
C	1.72143100	2.92748600	-0.27452500
C	4.20905300	6.05891900	0.87053900
C	5.07319000	6.01500900	1.95725300
C	4.59380200	5.76627500	3.24372100
C	3.21991000	5.55902900	3.42444600
C	2.34929200	5.60395200	2.35032000
C	1.41642700	5.95472000	-2.55321900
C	1.13775600	6.81527500	-3.53258000
C	0.54167400	5.85138400	0.12070000
H	3.28221700	5.48063000	-1.66406300
H	2.85543500	7.18127600	-1.55833200
H	-1.70443700	3.07233800	-0.16970000
H	-0.55367000	3.00670300	1.25085600
H	0.17144800	2.93315600	-1.75318600
H	1.91527600	3.01835300	0.79402200

H	4.61218000	6.25756400	-0.12101900
H	6.13784100	6.18480400	1.79759300
H	5.27226000	5.74949300	4.09420900
H	2.82731600	5.36809800	4.42272600
H	1.28068500	5.44921800	2.50569800
H	0.87255600	5.00579600	-2.50533200
H	0.39475000	6.59623700	-4.29581900
H	1.64334900	7.77841600	-3.60453200
C	2.87478500	2.91261200	-1.13016700
C	4.15689100	3.05543100	-0.55626800
C	2.80347100	2.78309600	-2.53598000
C	5.30160100	3.08710800	-1.34088600
H	4.23575400	3.15192800	0.53177300
C	3.95057800	2.81370500	-3.31593200
H	1.83693300	2.66520600	-3.02239700
C	5.20863100	2.96511300	-2.72790000
H	6.27354700	3.21011200	-0.86640500
H	3.86445300	2.72219500	-4.39742900
H	6.10365900	2.99083800	-3.34475100

18

Pd	-0.06140800	1.11689400	-0.34887100
P	-2.17452000	0.33447200	-0.35315800
P	1.04784300	-0.82172400	-0.04521100
C	-1.38513300	-2.08695300	-1.60932300
C	-2.03002600	-0.85613700	-1.76613900
C	-2.38052000	-0.39367900	-3.04685100

C	-2.07777000	-1.14773000	-4.17894000
C	-1.39036300	-2.36122300	-4.06615800
C	-1.04397700	-2.81140200	-2.78945800
C	-1.04537900	-2.70147700	-0.30532800
C	0.03064900	-2.29823200	0.48961500
C	0.30670800	-2.95123900	1.69961600
C	-0.48825100	-4.01206500	2.13207700
C	-1.56858800	-4.44927000	1.36194300
C	-1.83320600	-3.79855500	0.15325400
C	-2.99667600	-0.68712400	0.96406900
C	-2.50601400	-0.64271300	2.26341700
C	-3.14853600	-1.34399100	3.30338700
C	-4.35598500	-2.00234400	2.98549100
C	-4.84614800	-2.11616000	1.66159700
C	-4.11983900	-1.45711300	0.66294800
C	-3.67595300	1.34896900	-0.80421100
C	-4.85525600	0.78954900	-1.29460200
C	-6.00849800	1.56358400	-1.48158300
C	-5.91636800	2.94011800	-1.16502300
C	-4.70397900	3.56013000	-0.79763100
C	-3.59702900	2.71875400	-0.57731600
C	1.94594400	-1.58036600	-1.47037900
C	1.97405700	-0.82420000	-2.64074400
C	2.67516900	-1.27179300	-3.77333500
C	3.39820000	-2.47703200	-3.64292700
C	3.27706800	-3.32539900	-2.52188900
C	2.53463900	-2.84079900	-1.43224100
C	2.30351800	-0.79778400	1.32272700

C	3.36600100	-1.68184100	1.47463100
C	4.17803500	-1.65527800	2.62110800
C	3.92616900	-0.63393400	3.56560100
C	2.84919600	0.27446000	3.44581300
C	2.05861000	0.17830100	2.28873200
H	-2.88522800	0.56465200	-3.18347100
H	-2.36775900	-0.78815300	-5.16552000
H	-1.14024900	-2.93026600	-4.95372700
H	1.14124500	-2.65272400	2.33687700
H	-0.27037800	-4.50626100	3.07813600
H	-2.18989700	-5.26411400	1.71642600
H	-1.60468900	-0.06362800	2.49281000
H	-4.44589500	-1.54830800	-0.38062300
H	-4.89287800	-0.28390300	-1.51893800
H	-2.66207300	3.16833500	-0.21631300
H	1.44013700	0.13998300	-2.68474900
H	2.42686200	-3.47398300	-0.54326200
H	3.58494600	-2.41825200	0.69590200
H	1.23992500	0.90283400	2.13389500
O	-0.35291200	-3.97856000	-2.54010600
O	-2.87771300	-4.14517500	-0.68359100
C	0.31810800	-4.61705600	-3.65229100
H	0.94344900	-3.89874700	-4.19452200
H	0.95329400	-5.35260400	-3.12521900
H	-0.41360300	-5.10364400	-4.29981000
C	-3.53373000	-5.41180600	-0.42584700
H	-4.14618500	-5.32998300	0.48845000
H	-4.16481400	-5.52479100	-1.31595100

H	-2.80472500	-6.22345600	-0.36269100
O	-7.07080500	3.72951800	-1.30377800
O	-5.06455200	-2.66945200	4.00046700
O	4.71217600	-0.58122500	4.72914900
O	4.23462000	-2.87798600	-4.70050200
C	-7.81593300	3.90161200	-0.07323600
H	-8.63336500	4.56091900	-0.38235600
H	-8.19556500	2.92694900	0.26946600
H	-7.18369900	4.37910500	0.69150800
C	5.59860100	-2.41089300	-4.53994000
H	6.01765700	-2.78852300	-3.59527800
H	6.10491500	-2.84943100	-5.40571900
H	5.61688100	-1.31092900	-4.58317100
C	5.91145900	0.22147500	4.61964800
H	6.36182400	0.10651900	5.61144400
H	6.56948500	-0.18128400	3.83468300
H	5.64405900	1.27116100	4.42427700
C	-5.97769400	-1.83185000	4.74912200
H	-6.77842500	-1.47266700	4.08476200
H	-6.36786400	-2.52279300	5.50334000
H	-5.43841600	-0.99244000	5.21429300
C	-4.52379600	5.07432900	-0.61899400
C	-4.88853500	5.44049000	0.83399500
H	-4.77130500	6.51404000	1.01158800
H	-5.93068900	5.17663000	1.06522000
H	-4.24712200	4.91493400	1.54854300
C	-5.38894600	5.86899000	-1.61324000
H	-6.46167900	5.73842500	-1.42769500

H	-5.17380800	6.93989000	-1.56304100
H	-5.20965900	5.53704000	-2.64158100
C	-3.05763400	5.48842100	-0.87726500
H	-2.35941800	5.03765000	-0.16159200
H	-2.73108800	5.20319900	-1.88253600
H	-2.93028600	6.57312700	-0.79018600
C	-7.29182600	0.88725900	-1.98154300
C	-8.03375000	1.78225700	-2.98938600
H	-8.91511400	1.28399600	-3.40026900
H	-8.36969300	2.72270600	-2.53009000
H	-7.38110600	2.06025300	-3.82347500
C	-8.18515300	0.57837700	-0.76257600
H	-9.11492900	0.08962600	-1.06666300
H	-7.67512600	-0.08664800	-0.04604000
H	-8.45588400	1.49688700	-0.22188500
C	-6.98849800	-0.44706400	-2.70297000
H	-6.26873200	-0.30860400	-3.51612100
H	-6.58570800	-1.20730800	-2.01374700
H	-7.89805200	-0.86840800	-3.14266400
C	2.62382600	-0.43897900	-5.05966300
C	2.63767500	-1.33571700	-6.31072700
H	1.82922500	-2.07248900	-6.27615800
H	2.51971000	-0.74894100	-7.22550400
H	3.57618700	-1.89999200	-6.39859400
C	1.32442500	0.39597200	-5.11729600
H	0.43735600	-0.24776600	-5.05800000
H	1.25435000	1.11641800	-4.29345000
H	1.26018800	0.96344800	-6.05008900

C	3.83288700	0.51819000	-5.07065400
H	3.80160900	1.20680100	-4.21805600
H	4.78020900	-0.03804300	-5.01954200
H	3.85311000	1.12121800	-5.98336500
C	3.92523200	-4.70978900	-2.40768400
C	4.07104100	-5.40583300	-3.77255400
H	4.82224400	-4.91803400	-4.40557200
H	4.36899500	-6.45189200	-3.66084700
H	3.13381000	-5.37663300	-4.33691900
C	5.30917900	-4.52483100	-1.75188100
H	5.84695700	-5.47427600	-1.68017400
H	5.93029900	-3.83001900	-2.33593900
H	5.21950600	-4.11475500	-0.73311700
C	3.05984600	-5.63903500	-1.52509500
H	2.96357400	-5.26939800	-0.49803700
H	2.04093100	-5.72880000	-1.93542000
H	3.48746300	-6.64389600	-1.46756900
C	-6.10369400	-2.90539900	1.27279000
C	-6.19333400	-3.15011600	-0.25283100
H	-6.42051400	-2.22725100	-0.81163500
H	-5.25438400	-3.54909400	-0.65549600
H	-6.98722700	-3.86441600	-0.48797200
C	-6.09246000	-4.28572500	1.95502500
H	-6.04147700	-4.19275000	3.05021200
H	-6.98735300	-4.86409300	1.71546400
H	-5.21197700	-4.86583000	1.64028900
C	-7.35274600	-2.09511600	1.67332200
H	-8.27077700	-2.64379900	1.44457700

H	-7.36484600	-1.86795300	2.74786400
H	-7.39169000	-1.13638900	1.12970900
C	-2.49620400	-1.35392300	4.69295100
C	-3.08229600	-0.19450700	5.52381100
H	-4.16800400	-0.30669900	5.66032300
H	-2.62857200	-0.15068400	6.51827500
H	-2.91176000	0.76985500	5.03503500
C	-0.96618300	-1.15396400	4.59310800
H	-0.51689500	-1.87725400	3.90245300
H	-0.68846100	-0.14637500	4.24436100
H	-0.48691200	-1.29247200	5.56747300
C	-2.70968800	-2.70186600	5.40590600
H	-2.15403500	-2.75230800	6.34572300
H	-3.76458100	-2.88927100	5.63700100
H	-2.38086100	-3.53218800	4.77063000
C	5.25692400	-2.73673400	2.77481000
C	4.92441700	-3.99005000	1.92722600
H	3.93391300	-4.38563900	2.17457500
H	4.94936300	-3.78649700	0.84422400
H	5.64886800	-4.78913900	2.11508000
C	6.60215300	-2.16911100	2.28007800
H	7.39370100	-2.92251900	2.32816500
H	6.52693200	-1.82343200	1.24357700
H	6.92548500	-1.31372900	2.89155100
C	5.36682300	-3.21342300	4.23376300
H	6.08377300	-4.03176600	4.33774400
H	5.68464400	-2.40890200	4.90934500
H	4.39790900	-3.56217700	4.60705100

C	2.50360400	1.34351500	4.49255000
C	1.06109100	1.87144800	4.30848100
H	0.91747700	2.35278400	3.33357200
H	0.32047000	1.05844600	4.38967000
H	0.81359100	2.61182800	5.07507400
C	3.46780000	2.53459800	4.32115300
H	3.16887100	3.38458200	4.94061700
H	4.49513800	2.26680300	4.60677200
H	3.49847800	2.87544800	3.27324500
C	2.59266400	0.76723700	5.91638700
H	3.60705500	0.41664300	6.15261300
H	2.31678900	1.51048800	6.66861500
H	1.92979400	-0.09632100	6.03372900
N	0.93886300	6.31580100	0.12558500
C	2.91097300	4.69192700	-0.51453600
C	4.08906600	4.99082300	0.41382900
C	3.29500300	4.90190300	-2.00793700
C	-0.08469600	3.25322900	-0.84671500
C	1.22037500	2.81030200	-1.06907000
C	2.39463100	3.19296600	-0.20558800
C	5.40655500	4.77484000	-0.00355500
C	6.47077800	4.95600200	0.87577400
C	6.23676800	5.35090300	2.19095500
C	4.92808200	5.56590600	2.61818500
C	3.86489600	5.38633900	1.73687300
C	2.17867300	5.26581100	-2.93685200
C	2.21884600	6.31729200	-3.75553300
C	1.81275500	5.60329300	-0.17423700

H	3.79277100	3.98135700	-2.35054800
H	4.05481400	5.69281700	-2.05825900
H	-0.77350500	3.37513800	-1.68321000
H	-0.32687600	3.83558900	0.04234800
H	1.47870300	2.53285000	-2.09445900
H	2.06617200	3.24357500	0.84416600
H	5.61014100	4.43026200	-1.01675100
H	7.48797700	4.77764300	0.53009400
H	7.06962500	5.49561100	2.87709000
H	4.73035100	5.88240800	3.64118800
H	2.84592100	5.56830200	2.07910000
H	1.29142600	4.63170300	-2.93223000
H	1.39610200	6.55018700	-4.42809400
H	3.07571700	6.99164500	-3.78079700
C	3.54400300	2.21171600	-0.27777400
C	4.28878200	1.93618900	0.87423600
C	3.92469600	1.58067800	-1.46803200
C	5.38064300	1.07464100	0.84359900
H	4.00196000	2.41312200	1.81870100
C	5.01672500	0.71448000	-1.50539400
H	3.35848800	1.74250800	-2.38640800
C	5.75400700	0.46244800	-0.35121700
H	5.93323500	0.87290400	1.75976500
H	5.27799300	0.22154500	-2.44111400
H	6.60199800	-0.21957200	-0.37953700

$PhCF_3$

C	-2.11953100	1.18619600	0.23657100
C	-0.72965500	1.17154300	0.22824700
C	-0.05059100	-0.02493100	-0.01386200
C	-0.75807900	-1.20268000	-0.24579000
C	-2.15131300	-1.18159500	-0.23622600
C	-2.83181800	0.00926500	0.00422600
H	-2.64929700	2.11808300	0.42401500
H	-0.16604100	2.08555500	0.40747200
H	-0.22149100	-2.12907500	-0.43415300
H	-2.70480500	-2.10065100	-0.41845800
H	-3.92022200	0.02253000	0.01041600
C	1.44664500	-0.01132100	-0.00654600
F	1.98127100	-1.20614100	-0.33220600
F	1.94080500	0.32437100	1.21117200
F	1.94616700	0.89885300	-0.87795900

TS-8

Pd	-0.05755000	0.90910100	-0.21436100
P	1.85493000	-0.17861100	0.25605600
P	-1.41526800	-0.88098600	-0.18619600
C	0.87573700	-2.67655800	1.18338700
C	1.56372000	-1.50485300	1.50551400
C	1.91945800	-1.22426500	2.83412800
C	1.61113700	-2.12592200	3.85268600
C	0.93905700	-3.31732000	3.56822300
C	0.57736100	-3.58306900	2.24385100
C	0.45097100	-3.03136700	-0.18816800

C	-0.59761200	-2.40136300	-0.86521100
C	-0.98038500	-2.83432100	-2.14292000
C	-0.31521800	-3.89332200	-2.76261500
C	0.75207300	-4.53164000	-2.12769000
C	1.12899600	-4.09486900	-0.85367400
C	2.55432900	-1.00916000	-1.22765000
C	1.98541300	-0.68855900	-2.45655600
C	2.49146900	-1.22282500	-3.65591900
C	3.65935500	-2.01143000	-3.56363300
C	4.24730800	-2.37325000	-2.32481000
C	3.64921300	-1.86986500	-1.16221000
C	3.41112300	0.59780600	0.87642600
C	4.46142400	-0.17697800	1.36714200
C	5.68564900	0.40298600	1.72586800
C	5.82450100	1.79379700	1.51270600
C	4.74399400	2.62069900	1.13339900
C	3.53767700	1.98233300	0.79606900
C	-1.98162500	-1.39232300	1.47627300
C	-1.75787700	-0.51106500	2.53005000
C	-2.17031300	-0.82858200	3.83809500
C	-2.91186000	-2.01789000	4.00884100
C	-3.13529100	-2.94406500	2.95887800
C	-2.62924400	-2.60746900	1.69761600
C	-2.98908300	-0.87685200	-1.13912100
C	-3.91869300	-1.91531200	-1.08863700
C	-5.11306000	-1.85693600	-1.81820700
C	-5.34129800	-0.69223300	-2.59076300
C	-4.37012100	0.31811100	-2.75164600

C	-3.20848800	0.22067700	-1.96587600
H	2.43949800	-0.30215000	3.10606800
H	1.88947400	-1.90031800	4.88256400
H	0.68934300	-4.00161800	4.37276200
H	-1.80296800	-2.36403400	-2.68840200
H	-0.62321000	-4.22219500	-3.75547800
H	1.27861700	-5.33550000	-2.63187700
H	1.12003800	-0.00633400	-2.51058200
H	4.05125800	-2.15770200	-0.18475000
H	4.34942500	-1.26463300	1.46955700
H	2.69603100	2.59925500	0.45610100
H	-1.25381500	0.45497300	2.35113400
H	-2.75279500	-3.31050300	0.86410000
H	-3.72450000	-2.79778500	-0.46567900
H	-2.47368000	1.04193400	-2.00765100
O	-0.10695300	-4.71229000	1.84510100
O	2.18748600	-4.61983800	-0.14126900
C	-0.26025200	-5.77753700	2.81553400
H	-0.99489700	-5.47416900	3.58302400
H	-0.65571100	-6.59148000	2.19508400
H	0.70250200	-6.05344700	3.25207600
C	2.81933400	-5.81353100	-0.66543400
H	3.37583800	-5.56592400	-1.58718000
H	3.50568300	-6.07975600	0.14801500
H	2.08388000	-6.60500300	-0.82873600
O	7.07527100	2.38344400	1.75019100
O	4.20971600	-2.57225000	-4.72533000
O	-6.55564400	-0.58626600	-3.28423500

O	-3.35509100	-2.37319600	5.29165600
C	7.93307200	2.39587100	0.58014900
H	8.84844800	2.85802200	0.96447400
H	8.11544600	1.36744300	0.23454200
H	7.47503300	3.01563600	-0.20731400
C	-4.62888000	-1.80748200	5.68525500
H	-5.42750000	-2.21234300	5.04548900
H	-4.73069700	-2.15618200	6.71837000
H	-4.59663300	-0.70772400	5.63538700
C	-7.57448700	0.15760400	-2.56804200
H	-8.41723300	0.13288400	-3.26701700
H	-7.81846000	-0.35892400	-1.62749400
H	-7.23427200	1.18951100	-2.38952800
C	5.09350800	-1.70624900	-5.47840400
H	6.02004200	-1.54574700	-4.90715700
H	5.28227200	-2.29348200	-6.38357300
H	4.60163300	-0.75061100	-5.71613900
C	4.82865400	4.15283900	1.05280600
C	5.40296900	4.53203900	-0.32585800
H	5.49982400	5.61909900	-0.42536100
H	6.39774400	4.09466000	-0.48749600
H	4.75021300	4.19468900	-1.13866500
C	5.70550800	4.71864100	2.18344700
H	6.75212700	4.39963100	2.09368200
H	5.69688000	5.81281800	2.18394600
H	5.35438800	4.38144500	3.16392300
C	3.43332300	4.79738000	1.19653700
H	2.76886600	4.55785800	0.35639500

H	2.93651900	4.49637400	2.12368600
H	3.50765900	5.89218300	1.21373400
C	6.78795400	-0.50287100	2.29068900
C	7.67618600	0.23738600	3.30371400
H	8.36933700	-0.44257100	3.80618700
H	8.27505500	1.02631300	2.83113900
H	7.07154700	0.73237200	4.07201900
C	7.62696700	-1.02318100	1.10638100
H	8.47751000	-1.61775700	1.45222800
H	7.02536700	-1.65912400	0.43645900
H	8.02584000	-0.19107100	0.50701300
C	6.17358900	-1.71146300	3.03671900
H	5.53832000	-1.38089300	3.86567200
H	5.56345600	-2.34292800	2.38216100
H	6.95737000	-2.34839000	3.45938100
C	-1.78221600	0.13026700	4.97452100
C	-1.41972100	-0.64083400	6.25610500
H	-0.63549700	-1.37949800	6.06001000
H	-1.06239500	0.03380000	7.03914900
H	-2.27380100	-1.19366900	6.66465800
C	-0.53655900	0.96424700	4.59111500
H	0.31793100	0.32190200	4.35543100
H	-0.72398800	1.60733200	3.71996200
H	-0.23861000	1.62404500	5.41210600
C	-2.94998500	1.10235800	5.22241800
H	-3.22091200	1.63906900	4.30301300
H	-3.85141000	0.58164000	5.57402600
H	-2.69144600	1.85273600	5.97580800

C	-3.89968300	-4.26467400	3.12904100
C	-3.41973800	-5.00537600	4.38955600
H	-3.58325100	-4.40596500	5.29769100
H	-3.94274100	-5.95491500	4.52542500
H	-2.33969000	-5.20997300	4.33608200
C	-5.40926100	-3.96113900	3.21010700
H	-5.99661300	-4.88221700	3.27376200
H	-5.65592800	-3.35767400	4.09566500
H	-5.75106700	-3.40598200	2.33045800
C	-3.68937100	-5.21561100	1.92622900
H	-4.19201000	-4.84681400	1.01746300
H	-2.62674700	-5.34625400	1.69105500
H	-4.10502700	-6.20622200	2.13453400
C	5.48563500	-3.27312900	-2.20343000
C	5.75685800	-3.70356700	-0.74176400
H	6.11773700	-2.85944300	-0.12951700
H	4.86212700	-4.11226800	-0.26029600
H	6.53213400	-4.47507700	-0.70072700
C	5.28429100	-4.55153300	-3.03662000
H	5.10952500	-4.31497200	-4.09755100
H	6.15562900	-5.20883200	-2.98762100
H	4.40664000	-5.11445300	-2.68478500
C	6.73015700	-2.49569600	-2.67630700
H	7.64562500	-3.07148400	-2.50878700
H	6.68558500	-2.27044800	-3.75114500
H	6.82934200	-1.54408300	-2.14422400
C	1.73665600	-0.91105200	-4.95761000
C	2.37363400	0.32745600	-5.61611100

H	3.43237600	0.16210900	-5.86257900
H	1.86056700	0.59172400	-6.54664600
H	2.32528500	1.20126700	-4.95670300
C	0.24960100	-0.58608000	-4.67305700
H	-0.25694300	-1.43273700	-4.19761700
H	0.13078300	0.28475600	-4.01645600
H	-0.28561400	-0.36110200	-5.60145800
C	1.74412000	-2.11568100	-5.91431100
H	1.11612200	-1.93407700	-6.79126600
H	2.74921300	-2.35702000	-6.27696100
H	1.37310500	-3.01591900	-5.41195000
C	-6.10134600	-3.02793400	-1.72807100
C	-5.39312400	-4.33522600	-1.29972500
H	-4.58246400	-4.59201400	-1.98946100
H	-4.97118700	-4.27742200	-0.28357500
H	-6.09742000	-5.17409200	-1.30023200
C	-7.16404300	-2.67675300	-0.66813500
H	-7.90222100	-3.47740800	-0.56403300
H	-6.70915300	-2.50861900	0.31317500
H	-7.70914700	-1.75956200	-0.93874500
C	-6.76063100	-3.30724200	-3.08957300
H	-7.40310400	-4.19090600	-3.05337300
H	-7.38173200	-2.46454400	-3.42485000
H	-6.00866500	-3.46701900	-3.86912000
C	-4.50117100	1.51138200	-3.70954700
C	-3.10314500	2.02629100	-4.12296300
H	-2.55426900	2.47194600	-3.28016100
H	-2.48896100	1.23043700	-4.55302300

H	-3.18390700	2.81791700	-4.87862500
C	-5.24875000	2.63461200	-2.96958800
H	-5.20892000	3.58062400	-3.53305800
H	-6.30423900	2.38344100	-2.80272800
H	-4.79170800	2.83722100	-1.98412800
C	-5.23446800	1.12303800	-5.00422200
H	-6.26678400	0.80135000	-4.81783900
H	-5.27642500	1.96412900	-5.70295600
H	-4.73409800	0.29044000	-5.50887700
N	0.83293000	5.25127600	-2.25828400
C	-1.27572900	6.11999100	-1.09973600
C	-1.18723000	6.46694800	0.30500200
C	-2.58688000	6.24103300	-1.83316200
C	0.95335300	3.21877100	-1.67645100
C	0.16101000	3.11980600	-0.52242900
C	-1.23440000	2.84857800	-0.57624000
C	-2.34117500	6.80928400	1.04085100
C	-2.26598900	7.11811700	2.39449200
C	-1.04431000	7.09789400	3.06392200
C	0.10985000	6.75548200	2.35292900
C	0.04211600	6.44542100	1.00338500
C	-2.48154300	6.11095300	-3.31805000
C	-3.30571600	5.40517900	-4.09311600
C	-0.16559700	5.69021100	-1.75770500
H	-3.01625200	7.23216800	-1.60083700
H	-3.31740500	5.51226600	-1.43703900
H	2.03157200	3.30830600	-1.60418900
H	0.57647300	2.84731100	-2.62581700

H	0.57422100	3.53114800	0.40029800
H	-1.68186700	2.77290400	-1.57380300
H	-3.31458400	6.80822800	0.55354300
H	-3.17927100	7.36711000	2.93453900
H	-0.98908100	7.34305500	4.12304800
H	1.07545500	6.73761800	2.85794700
H	0.95220800	6.19375600	0.45780400
H	-1.66641900	6.67146400	-3.78424400
H	-3.19337500	5.38354400	-5.17482900
H	-4.13485600	4.82410800	-3.67493800
C	-2.16031300	3.13837000	0.50704800
C	-3.54636400	3.14991500	0.25924100
C	-1.73368200	3.42865400	1.81925700
C	-4.46108800	3.43342200	1.26761400
H	-3.90461000	2.92428900	-0.75391700
C	-2.64723400	3.72222900	2.82134900
H	-0.66979200	3.45228900	2.05048200
C	-4.01823700	3.71962100	2.55823800
H	-5.52701600	3.43286100	1.04343600
H	-2.28338200	3.97107600	3.81780800
H	-4.73112800	3.95290000	3.34673400

TS-11

Pd	-0.07805700	1.02888000	0.25168500
P	-2.14911500	0.36371300	-0.25130200
P	1.05347600	-0.89120900	-0.15264800
C	-1.22528400	-1.40842900	-2.25570000

C	-1.84879300	-0.18912500	-1.98413400
C	-2.06232300	0.74925200	-3.00782400
C	-1.66822500	0.46957300	-4.31591200
C	-1.01588400	-0.72810100	-4.62266500
C	-0.78556500	-1.64491600	-3.59280900
C	-0.98509200	-2.47862900	-1.26138500
C	0.05571700	-2.45240500	-0.32866700
C	0.29466300	-3.55167000	0.50531800
C	-0.52370300	-4.68104100	0.43705000
C	-1.59491500	-4.73170000	-0.45749400
C	-1.81562000	-3.63593300	-1.29877000
C	-3.02130100	-1.03773700	0.56594100
C	-2.55494500	-1.51816600	1.78587400
C	-3.24740400	-2.53040100	2.47830100
C	-4.47897900	-2.95530600	1.93296500
C	-4.95042400	-2.52374700	0.66849000
C	-4.17795700	-1.56972300	-0.00518800
C	-3.59433600	1.49871100	-0.39714700
C	-4.63527100	1.26027200	-1.29354000
C	-5.77307300	2.07813500	-1.31973800
C	-5.83974900	3.11778600	-0.36370200
C	-4.75515100	3.45564100	0.47472800
C	-3.64038500	2.59916800	0.45518700
C	2.04818800	-0.95072100	-1.69363000
C	2.14130400	0.23900900	-2.41377500
C	2.93225900	0.32224900	-3.57226800
C	3.68371000	-0.82205600	-3.91637600
C	3.51245100	-2.07207900	-3.27969400

C	2.67217000	-2.10722100	-2.15622200
C	2.23936200	-1.36006700	1.17975500
C	3.34780200	-2.18229400	1.01186800
C	4.14587800	-2.56247900	2.10400700
C	3.82052900	-2.01056300	3.36390000
C	2.68988300	-1.18384800	3.57165300
C	1.92651600	-0.85104500	2.44206000
H	-2.52420600	1.71903400	-2.80751800
H	-1.85710700	1.19499900	-5.10759700
H	-0.69567100	-0.92843800	-5.63980500
H	1.11786000	-3.55873600	1.22338200
H	-0.33133200	-5.53183000	1.09078700
H	-2.23873000	-5.60449100	-0.48213600
H	-1.63468500	-1.11498500	2.22443500
H	-4.49337100	-1.23840300	-1.00091900
H	-4.58588900	0.41255600	-1.98968100
H	-2.80507900	2.81496000	1.13538500
H	1.59254900	1.13581400	-2.08027600
H	2.51818500	-3.06213900	-1.64009100
H	3.62209700	-2.54466400	0.01638700
H	1.07761000	-0.15897300	2.55713400
O	-0.12612100	-2.84282200	-3.75584300
O	-2.84438500	-3.55919400	-2.21487600
C	0.64009200	-3.02833500	-4.97153400
H	1.29119000	-2.16699800	-5.15995100
H	1.25025400	-3.91294500	-4.70893200
H	-0.03330900	-3.23310000	-5.80594700
C	-3.61913500	-4.76002700	-2.45216500

H	-4.25258400	-4.97183100	-1.57287000
H	-4.22905100	-4.46670200	-3.31587300
H	-2.96943100	-5.60158700	-2.70519700
O	-7.01362100	3.88375300	-0.29168300
O	-5.23260400	-3.93327500	2.59998400
O	4.57869400	-2.38372500	4.48358800
O	4.60225100	-0.73732600	-4.97524900
C	-7.98782100	3.35055800	0.64111900
H	-8.82078800	4.05420200	0.53923100
H	-8.28132100	2.33387600	0.33962100
H	-7.57312400	3.36994500	1.66133500
C	5.92199300	-0.31424000	-4.54334000
H	6.33235100	-1.04639000	-3.83187900
H	6.48713300	-0.30576200	-5.48084000
H	5.86478400	0.69434600	-4.10307700
C	5.74596300	-1.56450100	4.73735900
H	6.20417000	-2.07000300	5.59431600
H	6.41632700	-1.56753600	3.86445800
H	5.43124900	-0.54281800	5.00097800
C	-6.09609000	-3.43380300	3.65053700
H	-6.90716100	-2.83978800	3.20384000
H	-6.48076400	-4.35728200	4.09680500
H	-5.52374900	-2.84365300	4.38221400
C	-4.73574900	4.68123800	1.40121500
C	-5.41973900	4.28982200	2.72719400
H	-5.43773100	5.13616300	3.42197200
H	-6.45943400	3.97166100	2.56571300
H	-4.89056900	3.46974100	3.22160400

C	-5.45258100	5.87897300	0.75447200
H	-6.52392600	5.69273900	0.60828400
H	-5.35527800	6.77960300	1.36819400
H	-5.03306100	6.10375600	-0.23207400
C	-3.29054800	5.12769400	1.70092900
H	-2.70721600	4.37220200	2.23877700
H	-2.73755900	5.37641100	0.78738900
H	-3.26989300	6.02835500	2.32674500
C	-6.86878800	1.77858800	-2.35137600
C	-7.58223400	3.05796800	-2.81758600
H	-8.26558500	2.86008200	-3.64769700
H	-8.16738500	3.52267300	-2.01380900
H	-6.86107900	3.81476600	-3.14670100
C	-7.86974200	0.79835400	-1.70734200
H	-8.71195900	0.59427800	-2.37478800
H	-7.39024200	-0.16544700	-1.46980900
H	-8.27926800	1.20697400	-0.77158300
C	-6.26688700	1.11859300	-3.61482300
H	-5.52199300	1.77125300	-4.08317700
H	-5.78057900	0.16155100	-3.39789300
H	-7.04403400	0.92271700	-4.36074200
C	2.94166100	1.63596100	-4.36656600
C	3.11581200	1.38221700	-5.87467400
H	2.36142900	0.68411600	-6.24903900
H	3.02986300	2.31092100	-6.44621400
H	4.09539100	0.94515200	-6.10744800
C	1.60029900	2.38441000	-4.18876000
H	0.75157100	1.76261700	-4.49290800

H	1.43166700	2.69396300	-3.14947300
H	1.57991200	3.29770800	-4.79254700
C	4.07942800	2.52153100	-3.82973700
H	3.92115300	2.78991500	-2.77235100
H	5.05492300	2.02240500	-3.90685400
H	4.14611800	3.46677900	-4.37960400
C	4.22510800	-3.36049900	-3.70886800
C	4.43578900	-3.42876400	-5.23130700
H	5.14427700	-2.66551600	-5.58113400
H	4.82833500	-4.40152700	-5.53999600
H	3.50307800	-3.25023000	-5.77376900
C	5.58111600	-3.40787800	-2.97579700
H	6.16303300	-4.28662100	-3.26775000
H	6.18546500	-2.51705900	-3.20464000
H	5.44644600	-3.44418600	-1.88274200
C	3.39713800	-4.60648700	-3.31626900
H	3.25701100	-4.69054200	-2.23307200
H	2.39661100	-4.57667700	-3.77638200
H	3.88807700	-5.52611600	-3.64888400
C	-6.23888100	-3.04878500	0.01888800
C	-6.36302600	-2.62211100	-1.46310300
H	-6.58126100	-1.54493100	-1.56056100
H	-5.44991100	-2.83493600	-2.02993700
H	-7.18381400	-3.15402400	-1.95444500
C	-6.25305100	-4.58741600	0.06345100
H	-6.19790500	-4.95967300	1.09784800
H	-7.16190700	-4.99747900	-0.38325300
H	-5.38698500	-5.00252900	-0.47414300

C	-7.45863700	-2.46354500	0.75810300
H	-8.39408900	-2.74834600	0.26660500
H	-7.51735800	-2.82402500	1.79440800
H	-7.41531300	-1.37013700	0.79074900
C	-2.62153000	-3.10697500	3.75738000
C	-3.16192800	-2.32470800	4.97054800
H	-4.25382500	-2.41997300	5.06172000
H	-2.72345000	-2.69078700	5.90446800
H	-2.93220900	-1.25725400	4.89228200
C	-1.08300700	-2.96388700	3.73843800
H	-0.65420500	-3.38673200	2.82361300
H	-0.75058500	-1.91569500	3.81247700
H	-0.62870500	-3.49335500	4.58313900
C	-2.91101900	-4.61237900	3.89741000
H	-2.36715800	-5.04846900	4.74015900
H	-3.97433600	-4.82474100	4.05236400
H	-2.61700300	-5.15113300	2.98946100
C	5.30113800	-3.54229500	1.84988300
C	5.05472800	-4.38608000	0.57416800
H	4.09528800	-4.91020000	0.62141000
H	5.06909500	-3.77624400	-0.34430600
H	5.83399900	-5.14679100	0.45718300
C	6.59244700	-2.72730000	1.64316700
H	7.43993400	-3.37514300	1.40176200
H	6.47760200	-2.00202000	0.82966300
H	6.85912700	-2.15974300	2.54753600
C	5.45729200	-4.54306000	3.00757200
H	6.23410200	-5.28320500	2.79733400

H	5.72223100	-4.05075700	3.95146200
H	4.52048500	-5.07888700	3.19415200
C	2.26198600	-0.65285300	4.94901400
C	0.81129800	-0.11526100	4.92918200
H	0.70169400	0.74882700	4.26345700
H	0.09431800	-0.88726400	4.60880800
H	0.50608200	0.21378100	5.92819700
C	3.18012700	0.51494000	5.35019900
H	2.82993300	1.00782100	6.26255500
H	4.21032400	0.18280700	5.53779000
H	3.22064700	1.28402300	4.55901900
C	2.31556200	-1.77955400	5.99607700
H	3.33433800	-2.17738100	6.11158800
H	1.98883900	-1.42882200	6.97866400
H	1.67897200	-2.62118600	5.70725300
N	0.53527400	5.76972300	2.30078100
C	2.89941300	4.97193100	1.61491000
C	3.34262700	5.27529200	0.26344200
C	3.92580200	4.89262000	2.72506500
C	-0.17970000	3.18183800	0.58168300
C	1.17945300	2.91163100	0.31235500
C	2.18128900	2.76012300	1.31175300
C	4.69661200	5.14573900	-0.11136800
C	5.10494600	5.37993100	-1.42001000
C	4.17963000	5.73746500	-2.39884200
C	2.83338700	5.86680100	-2.04767700
C	2.42015900	5.64391600	-0.74179000
C	3.37504700	4.63509300	4.09206100

C	3.95091100	3.84719900	5.00236500
C	1.61766000	5.43372100	1.98760700
H	4.48487100	5.84716800	2.74104700
H	4.67564800	4.12387100	2.48427500
H	-0.78608900	3.66839400	-0.18124500
H	-0.48880400	3.38068600	1.60710700
H	1.52177000	3.02262300	-0.71864800
H	1.83580300	2.71197300	2.34709600
H	5.43848500	4.85127200	0.62905600
H	6.15862800	5.27648100	-1.67649800
H	4.50275300	5.92596200	-3.42087500
H	2.09987100	6.15577100	-2.79941700
H	1.37002900	5.76253700	-0.47411700
H	2.45475600	5.16463500	4.35288200
H	3.53533900	3.72722000	6.00048600
H	4.87479700	3.30735500	4.78789500
C	3.47783100	2.15879000	1.05896600
C	4.22544700	1.65054500	2.13798000
C	4.04380300	2.06994900	-0.22804600
C	5.47526700	1.07463800	1.94652900
H	3.79131200	1.70083800	3.14269500
C	5.29270400	1.48851300	-0.41902100
H	3.50919900	2.46512400	-1.09553100
C	6.01658900	0.98883500	0.66305700
H	6.02470800	0.68101700	2.79953200
H	5.70461600	1.42840500	-1.42529900
H	6.99286100	0.53423100	0.50746900

TS-14

Pd	0.07211900	0.75276100	-0.02663400
P	-1.89155400	-0.33937600	-0.11494600
P	1.38875100	-1.01913700	0.36955200
C	-1.15336200	-3.04118700	0.13192900
C	-1.80951300	-2.09420800	-0.66606600
C	-2.30406600	-2.44668400	-1.92689800
C	-2.17509900	-3.75565700	-2.40374200
C	-1.54650400	-4.72782200	-1.62554700
C	-1.04070300	-4.35824900	-0.37497600
C	-0.57725700	-2.76142400	1.46712700
C	0.61341600	-2.05971100	1.68307600
C	1.16055500	-1.96861700	2.97189900
C	0.51399500	-2.55355300	4.06188200
C	-0.70944700	-3.20621500	3.89448700
C	-1.24392400	-3.29661600	2.60604700
C	-2.77515700	-0.42448900	1.49531200
C	-2.20299000	0.26642500	2.56060600
C	-2.85887900	0.35657600	3.80106400
C	-4.15792800	-0.19172200	3.88246600
C	-4.73140800	-0.96464300	2.84451000
C	-3.99327900	-1.08187900	1.65818100
C	-3.21636200	0.35992900	-1.18624300
C	-4.50854800	-0.15981200	-1.24772200
C	-5.51752700	0.48499000	-1.97410600
C	-5.17110500	1.69190500	-2.63025900
C	-3.84491200	2.17198200	-2.69325800

C	-2.88425500	1.49047800	-1.92668300
C	1.55062300	-2.05927700	-1.12035400
C	1.33497600	-1.40419400	-2.33147200
C	1.52658600	-2.06640200	-3.55615900
C	2.06003000	-3.37181000	-3.50094700
C	2.21548600	-4.08742300	-2.28907100
C	1.92130300	-3.40429100	-1.10006300
C	3.12197700	-0.90941100	0.96729700
C	4.04120400	-1.94633500	0.82794500
C	5.35701900	-1.81873800	1.29862500
C	5.71323000	-0.58628200	1.89321000
C	4.77702900	0.44409800	2.13856500
C	3.48726700	0.27363900	1.61090800
H	-2.79692000	-1.71597100	-2.57466600
H	-2.55903500	-4.01532100	-3.38994400
H	-1.42234300	-5.74635200	-1.98594400
H	2.10610600	-1.45187200	3.16030800
H	0.96076000	-2.49483400	5.05497200
H	-1.21983600	-3.63491200	4.75115600
H	-1.22364300	0.76032000	2.44462900
H	-4.39909800	-1.68545200	0.83598300
H	-4.75369000	-1.08347500	-0.70759800
H	-1.85299900	1.88201400	-1.91432700
H	1.01671700	-0.34608700	-2.35222600
H	1.98717400	-3.94163200	-0.14552500
H	3.75705000	-2.88062900	0.33501900
H	2.76900000	1.10046100	1.70620900
O	-0.30209200	-5.27983600	0.36846700

O	-2.44355800	-3.91963700	2.31605200
C	-1.09154900	-6.36829100	0.91578900
H	-1.50783200	-6.97883900	0.11181500
H	-0.34681000	-6.92414700	1.49641500
H	-1.87689100	-5.95870500	1.56419700
C	-3.36343300	-4.13296900	3.41509100
H	-3.45527300	-3.23159200	4.03351300
H	-4.31156800	-4.31633900	2.87770500
H	-3.04788300	-5.00230700	3.99532300
O	-6.18089000	2.38924700	-3.30730800
O	-4.88832000	-0.03738600	5.06993800
O	7.03431300	-0.42149900	2.33301100
O	2.37839900	-4.02490100	-4.70152000
C	-6.79732700	3.43976300	-2.51907900
H	-7.51344400	3.87310200	-3.22528600
H	-7.30701800	2.99938100	-1.64898200
H	-6.03989000	4.18006900	-2.21382100
C	3.71512200	-3.74332100	-5.18752300
H	4.45774100	-4.11535200	-4.46490100
H	3.75000100	-4.31197800	-6.12262300
H	3.83482900	-2.66384300	-5.37019700
C	7.90101200	0.22986800	1.36976200
H	8.84884600	0.29493700	1.91418600
H	7.99525700	-0.39857500	0.47134900
H	7.51157400	1.23134000	1.12464300
C	-5.66398800	1.18701000	5.13110500
H	-6.42184400	1.18717000	4.33282900
H	-6.12629800	1.12351900	6.12171600

H	-4.99925700	2.06240800	5.05536900
C	-3.39281900	3.39060400	-3.51352300
C	-3.59180500	4.65342600	-2.65704000
H	-3.29182800	5.55648100	-3.20118600
H	-4.64039700	4.78507700	-2.35560800
H	-2.98644200	4.62770900	-1.74092000
C	-4.16927300	3.49439400	-4.83681400
H	-5.23833100	3.68169400	-4.67601800
H	-3.78704400	4.30882300	-5.45969000
H	-4.09737900	2.56700300	-5.41399500
C	-1.89362500	3.27962700	-3.87829900
H	-1.24738200	3.28337200	-2.98420600
H	-1.68250800	2.37292700	-4.45218100
H	-1.57746600	4.13530100	-4.48735300
C	-6.92582700	-0.12570400	-1.98947500
C	-7.58551800	0.03362600	-3.36907400
H	-8.55735100	-0.46497400	-3.41337000
H	-7.74755100	1.09036900	-3.62595600
H	-6.95507400	-0.38377000	-4.16115400
C	-7.76265200	0.56907900	-0.89740100
H	-8.79523500	0.20757800	-0.89809600
H	-7.34470300	0.38720800	0.10635300
H	-7.79575100	1.65848200	-1.04943900
C	-6.88945100	-1.64197900	-1.68006000
H	-6.23882400	-2.17596000	-2.37996900
H	-6.54420800	-1.85568200	-0.65646800
H	-7.89009600	-2.07839900	-1.77190300
C	1.15685000	-1.32728600	-4.84980000

C	0.62376300	-2.29338100	-5.92140900
H	-0.20581500	-2.89390800	-5.53398100
H	0.26848100	-1.75511900	-6.80448400
H	1.39037300	-3.00345200	-6.25630200
C	0.03551700	-0.29461600	-4.57979500
H	-0.85792800	-0.77597700	-4.16892600
H	0.35301000	0.48253000	-3.87125000
H	-0.25803900	0.21402900	-5.50356800
C	2.40367400	-0.57949700	-5.35750500
H	2.77418900	0.13244800	-4.60880400
H	3.22611700	-1.27383600	-5.58386200
H	2.18793600	-0.01675400	-6.27055800
C	2.72451600	-5.53452900	-2.21803000
C	2.13123900	-6.39076600	-3.35011700
H	2.46254800	-6.04926000	-4.34029100
H	2.41874300	-7.44089000	-3.25335900
H	1.03780900	-6.33662100	-3.35036500
C	4.26464100	-5.49913500	-2.30307600
H	4.68518500	-6.50870100	-2.28170800
H	4.60873200	-5.01864900	-3.23007900
H	4.69703000	-4.93936000	-1.45787300
C	2.33394800	-6.21290300	-0.88752600
H	2.79265000	-5.73081400	-0.01872600
H	1.24396800	-6.18727500	-0.73355500
H	2.64286800	-7.26185900	-0.87478100
C	-6.12000300	-1.61455000	2.92326900
C	-6.27004300	-2.77048800	1.90534500
H	-6.24340100	-2.41504000	0.86281800

H	-5.47816800	-3.52331900	2.03004000
H	-7.23028400	-3.28082000	2.03565800
C	-6.39207700	-2.20523600	4.31763000
H	-6.41175200	-1.42570500	5.09315400
H	-7.35547900	-2.72157700	4.35490100
H	-5.61582700	-2.91472800	4.61477800
C	-7.17017800	-0.53873000	2.58046700
H	-8.18635500	-0.93838800	2.64971300
H	-7.10658900	0.31891400	3.26692200
H	-7.03485800	-0.15022100	1.55698700
C	-2.13260700	1.05425300	4.96072800
C	-2.52413000	2.54346800	4.95850200
H	-3.60712000	2.67985300	5.09407800
H	-2.02352300	3.08877800	5.76562500
H	-2.24870000	3.03334500	4.01739900
C	-0.59908200	0.94915200	4.78419300
H	-0.27534500	-0.09596300	4.72606100
H	-0.24898200	1.45783000	3.87778900
H	-0.07634100	1.41120500	5.62835300
C	-2.46985600	0.40166300	6.31228400
H	-1.88669200	0.84433600	7.12523400
H	-3.52965700	0.51311900	6.57351800
H	-2.26271300	-0.67294600	6.29516200
C	6.32575100	-2.99903800	1.13588700
C	5.56766000	-4.33636700	0.96126300
H	4.85854300	-4.50494100	1.77772400
H	5.01605600	-4.38478300	0.00769200
H	6.26597700	-5.18031300	0.96175700

C	7.17534400	-2.75798900	-0.12750300
H	7.87854700	-3.57885200	-0.29624400
H	6.54731500	-2.66367100	-1.01897700
H	7.76540700	-1.83268100	-0.04274900
C	7.22193000	-3.15519800	2.37647200
H	7.86684900	-4.03447600	2.30029800
H	7.87433500	-2.28276500	2.52382400
H	6.62302700	-3.25247500	3.28777300
C	5.08831300	1.71996600	2.93642200
C	3.79845500	2.31239100	3.55116200
H	3.08962100	2.64958300	2.78456100
H	3.29375300	1.59728800	4.20461600
H	4.03259100	3.20255400	4.14906400
C	5.69337900	2.75958400	1.98078600
H	5.94547400	3.68861800	2.50812300
H	6.60617600	2.39521100	1.49262800
H	4.97855600	3.04499300	1.18797000
C	6.04398300	1.42545700	4.10631800
H	7.03567100	1.10878900	3.75944600
H	6.18751800	2.31093200	4.73286200
H	5.66072500	0.62086900	4.74102800
N	-0.75113900	5.49711200	0.63191400
C	1.60902300	5.93896700	-0.25740600
C	2.72997200	5.97578100	0.65546700
C	1.82760500	6.14237200	-1.73725100
C	-0.99274300	3.40094700	0.58140400
C	-0.14738800	2.94466800	-0.44072600
C	1.24105600	2.69785000	-0.23618400

C	4.04499800	6.19388200	0.18743900
C	5.12279100	6.23989500	1.06472200
C	4.93429800	6.06850800	2.43527200
C	3.64098000	5.83944700	2.91635600
C	2.56222800	5.79062700	2.04819700
C	0.61182000	5.93817600	-2.57804100
C	0.12736300	6.81311800	-3.45943300
C	0.34839000	5.73934100	0.21782000
H	2.60119800	5.42066900	-2.06218100
H	2.25293400	7.14124400	-1.93168500
H	-2.06103200	3.49093900	0.41409700
H	-0.68539900	3.30682400	1.61953400
H	-0.51872500	3.05241300	-1.46811100
H	1.62403900	2.92688700	0.76097200
H	4.22238800	6.33274900	-0.87744500
H	6.12277300	6.42003900	0.67106100
H	5.77735600	6.12340000	3.12129700
H	3.47390000	5.70804600	3.98494500
H	1.55719000	5.62776500	2.43937100
H	0.10181100	4.97943100	-2.44066900
H	-0.75781400	6.59931200	-4.05431300
H	0.59889200	7.78359500	-3.61606600
C	2.23938300	2.71768300	-1.29476800
C	3.59311000	2.92566600	-0.96692500
C	1.91599600	2.57983200	-2.65987600
C	4.57115100	3.00678600	-1.95149300
H	3.87374800	3.04769900	0.08624400
C	2.89393400	2.66756200	-3.64254200

H	0.88082100	2.41231100	-2.95731100
C	4.22999600	2.87972000	-3.29801100
H	5.60683000	3.18282700	-1.66327800
H	2.60968000	2.57416100	-4.69014700
H	4.99328800	2.95052100	-4.07009300

TS-16

Pd	0.00325700	0.93484600	-0.28287200
P	-2.12896800	0.28546900	-0.30086300
P	0.94967200	-1.03760400	0.21348800
C	-1.69349000	-2.49264900	-0.73895700
C	-2.13446200	-1.27909900	-1.27315200
C	-2.49124600	-1.17143100	-2.62548600
C	-2.42258600	-2.28513000	-3.46339600
C	-1.98447300	-3.51590800	-2.97116600
C	-1.62418500	-3.61334600	-1.62258800
C	-1.29126000	-2.69403800	0.67233700
C	-0.10460200	-2.18556300	1.21502600
C	0.26462700	-2.46946900	2.53393900
C	-0.55908600	-3.25675900	3.34299700
C	-1.75815500	-3.76755900	2.84715400
C	-2.11263200	-3.49027000	1.52038100
C	-2.93315600	-0.15682500	1.27771400
C	-2.35708500	0.23997000	2.48150800
C	-3.00439200	-0.01074100	3.70590400
C	-4.29971200	-0.57041600	3.64788100

C	-4.87414900	-1.05457400	2.44664600
C	-4.14513200	-0.85012400	1.27050600
C	-3.47373800	1.25462800	-1.08966800
C	-4.74409000	0.70657400	-1.29141900
C	-5.80685400	1.48709100	-1.75948700
C	-5.54032200	2.85438200	-2.02091500
C	-4.23837200	3.39466200	-1.98457100
C	-3.22417400	2.57070200	-1.46628900
C	1.44698900	-2.10261800	-1.18279600
C	1.44868400	-1.53678900	-2.45506800
C	1.83892300	-2.28740600	-3.57815700
C	2.32708100	-3.59124000	-3.33986900
C	2.27722300	-4.21067500	-2.06718000
C	1.80673500	-3.43730600	-0.99790700
C	2.45943700	-0.89880200	1.23967900
C	3.48678500	-1.83605600	1.23902000
C	4.59619100	-1.70156100	2.09041400
C	4.66054700	-0.53762400	2.88882500
C	3.61042400	0.41342300	2.94559900
C	2.52857100	0.22128400	2.07529300
H	-2.82803300	-0.22528700	-3.05875900
H	-2.70666900	-2.19591200	-4.51287700
H	-1.91449800	-4.37035000	-3.63832800
H	1.19850600	-2.09644500	2.96468100
H	-0.26551400	-3.47278200	4.37102400
H	-2.40070400	-4.35921800	3.49218300
H	-1.38664700	0.75415100	2.49345600
H	-4.54408800	-1.23897300	0.32355800

H	-4.92748400	-0.35275100	-1.06791400
H	-2.21309000	3.00730900	-1.36566600
H	1.14120000	-0.48965700	-2.59867700
H	1.72630000	-3.89195900	-0.00399700
H	3.46113300	-2.69523700	0.56213400
H	1.73441800	0.98077700	2.04346800
O	-1.16808800	-4.76847900	-1.02975200
O	-3.27804700	-3.93971200	0.93468000
C	-1.14221100	-5.97641000	-1.83150300
H	-0.30365400	-5.92393500	-2.54702500
H	-0.95446700	-6.74416000	-1.06904500
H	-2.10087300	-6.14804800	-2.32602600
C	-4.03032500	-4.95452900	1.64859200
H	-4.54038300	-4.49184200	2.51134000
H	-4.75447700	-5.27480600	0.88864500
H	-3.38704800	-5.78682100	1.94445200
O	-6.61413000	3.67045400	-2.39986000
O	-5.02677000	-0.75243600	4.83223800
O	5.75634400	-0.36467600	3.74277700
O	2.79399500	-4.35273700	-4.42081400
C	-7.18731400	4.42250700	-1.29915200
H	-7.95071000	5.02674400	-1.80140100
H	-7.63776700	3.72657100	-0.57611400
H	-6.41962100	5.05988000	-0.83127200
C	4.19331700	-4.14565700	-4.73963000
H	4.81825500	-4.47880000	-3.89687200
H	4.33147100	-4.78683000	-5.61671300
H	4.37810900	-3.08770300	-4.98408200

C	6.89105300	0.31501700	3.14583500
H	7.63762600	0.26695200	3.94551000
H	7.22820900	-0.21618800	2.24354600
H	6.61700200	1.35906300	2.92101600
C	-5.75990400	0.41901500	5.27211200
H	-6.55425600	0.64660100	4.54504300
H	-6.17971100	0.08697200	6.22802200
H	-5.07970700	1.27409000	5.40839100
C	-3.86910100	4.81220000	-2.45522400
C	-4.01640400	5.76712400	-1.25574700
H	-3.77966800	6.79809400	-1.54639600
H	-5.03619000	5.76065100	-0.84852300
H	-3.32395900	5.50522900	-0.44767700
C	-4.76099800	5.26536100	-3.62470900
H	-5.80534600	5.40784200	-3.32676800
H	-4.40975800	6.21519200	-4.04184700
H	-4.75999300	4.52742700	-4.43345100
C	-2.41357400	4.86262900	-2.95945100
H	-1.66590000	4.65166800	-2.17332500
H	-2.24030200	4.17321900	-3.78873100
H	-2.15040600	5.86920600	-3.31347200
C	-7.19274800	0.85131200	-1.93659300
C	-7.90206600	1.40263100	-3.18485000
H	-8.85014100	0.89108200	-3.37099000
H	-8.12399900	2.47572100	-3.09080000
H	-7.27796600	1.29269000	-4.07787000
C	-8.01767300	1.14157500	-0.66681000
H	-9.03231500	0.74138800	-0.75430300

H	-7.55805200	0.69499600	0.22949200
H	-8.10585400	2.22388400	-0.48836900
C	-7.09277500	-0.68069300	-2.11882500
H	-6.42900300	-0.94273500	-2.94888200
H	-6.72802400	-1.18624100	-1.21047300
H	-8.07550200	-1.10934400	-2.34421500
C	1.70576900	-1.64723800	-4.96812800
C	1.29842500	-2.68606500	-6.02729400
H	0.38699900	-3.21522600	-5.73172500
H	1.11649500	-2.21572100	-6.99816700
H	2.07065100	-3.45116500	-6.17614200
C	0.60529600	-0.55917300	-4.96536600
H	-0.36056900	-0.96864200	-4.65123600
H	0.84839100	0.27724200	-4.29954600
H	0.47409700	-0.13491000	-5.96693700
C	3.04471600	-0.98339700	-5.33705400
H	3.32637700	-0.21393200	-4.60834600
H	3.86507500	-1.71494400	-5.37572400
H	2.99297900	-0.49938500	-6.31817300
C	2.73332000	-5.65150700	-1.79837800
C	2.25140700	-6.59166700	-2.91658500
H	2.70810200	-6.33979100	-3.88488800
H	2.49692100	-7.63502200	-2.70298600
H	1.16354200	-6.51296900	-3.05204900
C	4.27043300	-5.65729900	-1.68764400
H	4.65187700	-6.66344600	-1.48942300
H	4.74690400	-5.30355800	-2.61363000
H	4.61308000	-5.00279400	-0.87042900

C	2.16444200	-6.19543600	-0.46643100
H	2.58612500	-5.68067400	0.40377000
H	1.07520600	-6.08889500	-0.41580600
H	2.39892000	-7.25828500	-0.34785500
C	-6.23417800	-1.76444200	2.37889500
C	-6.44035300	-2.50165300	1.03544900
H	-6.60492600	-1.80430400	0.19696800
H	-5.58033900	-3.12949400	0.77662500
H	-7.32222000	-3.14879600	1.07799800
C	-6.33685100	-2.81674700	3.49736800
H	-6.23752500	-2.36024600	4.49393200
H	-7.29732000	-3.33812500	3.47534700
H	-5.53714000	-3.56631400	3.40475400
C	-7.35143200	-0.71042200	2.50031200
H	-8.34016400	-1.17993500	2.49990100
H	-7.26750000	-0.12975700	3.42944400
H	-7.32224300	0.00180300	1.65874800
C	-2.26817100	0.32934100	5.01042400
C	-2.61695700	1.77513600	5.40954200
H	-3.69682300	1.89955400	5.57876300
H	-2.10621400	2.06574700	6.33394800
H	-2.32164400	2.49005900	4.63429700
C	-0.73875100	0.22348200	4.81468600
H	-0.45440100	-0.76069600	4.42648400
H	-0.34312900	0.98362700	4.12875700
H	-0.21451700	0.36081300	5.76799000
C	-2.62968400	-0.65282300	6.13873400
H	-2.00453600	-0.49358100	7.02266400

H	-3.67281500	-0.55812100	6.46073300
H	-2.49738200	-1.69072900	5.81453300
C	5.65272900	-2.81682500	2.08767900
C	5.04609600	-4.16432600	1.62136200
H	4.17679600	-4.43916500	2.22633000
H	4.74053700	-4.14761000	0.56359400
H	5.77984300	-4.97157700	1.72261200
C	6.77006000	-2.42237700	1.10393500
H	7.54028400	-3.19615500	1.04051000
H	6.37547900	-2.25368400	0.09601100
H	7.26622900	-1.48892600	1.41338300
C	6.21865100	-3.06145000	3.49681300
H	6.91054200	-3.90793800	3.51158400
H	6.76333900	-2.19017200	3.88296400
H	5.41782600	-3.26492600	4.21533900
C	3.60351900	1.60745400	3.91595500
C	2.19980400	2.25031400	4.01700300
H	1.89593500	2.71282900	3.06989800
H	1.43499900	1.53043200	4.32156000
H	2.20393600	3.05721100	4.76014200
C	4.56944600	2.68865900	3.41788000
H	4.48801400	3.61495800	4.00249700
H	5.62010700	2.37750500	3.47145200
H	4.36704900	2.98565600	2.37138900
C	3.99301800	1.12969700	5.32769700
H	5.01034100	0.71148700	5.34395800
H	3.97477700	1.95687600	6.04346600
H	3.31764900	0.35112300	5.69031100

N	0.99333800	5.88171900	-1.41324300
C	3.47172000	5.24289800	-1.09765100
C	4.10188900	5.43072300	0.17419000
C	4.28585800	4.89055800	-2.31521200
C	0.03257500	3.10691900	-0.81100600
C	1.25951600	2.62601900	-1.30079900
C	2.43614000	2.56237600	-0.55058300
C	5.49878500	5.24452800	0.34067700
C	6.10822100	5.43665600	1.57414300
C	5.36176800	5.81646500	2.68940300
C	3.97960600	6.00027700	2.54819600
C	3.36153500	5.81111700	1.32560900
C	3.47444000	4.55546100	-3.52320200
C	3.66764300	5.05605600	-4.74349800
C	2.13034000	5.59649000	-1.26686200
H	4.91780700	4.01752000	-2.06439400
H	4.99693600	5.70067500	-2.55585100
H	-0.72468000	3.45006300	-1.51809200
H	0.02908200	3.63732700	0.14083800
H	1.29974300	2.32377100	-2.34994400
H	2.39872700	2.96791200	0.46113800
H	6.10816800	4.95520600	-0.51344300
H	7.18512400	5.29609600	1.66331200
H	5.84612700	5.98044800	3.64961500
H	3.38211900	6.30182800	3.40779400
H	2.28636300	5.96524500	1.22677900
H	2.66411000	3.83784500	-3.36145100
H	3.05014400	4.76218100	-5.58908500

H	4.45024400	5.78881700	-4.94073900
C	3.68889100	1.99044000	-0.95389300
C	4.78952200	2.05833300	-0.07131100
C	3.89567300	1.37094600	-2.20749800
C	6.03200100	1.55111300	-0.42555100
H	4.64519300	2.52991100	0.90608300
C	5.13881000	0.86022800	-2.55431900
H	3.07092400	1.29119800	-2.91440300
C	6.21623700	0.94501900	-1.66926800
H	6.86280200	1.63041800	0.27239700
H	5.27217700	0.38941100	-3.52669800
H	7.18783500	0.54512600	-1.94856800

TS-17

Pd	-0.06852200	1.00415600	-0.41727800
P	-2.18886700	0.29107800	-0.38979200
P	0.98954000	-0.94347200	0.02287300
C	-1.47455700	-2.23790700	-1.44905900
C	-2.07821300	-1.00252100	-1.70181900
C	-2.42290900	-0.62621200	-3.00990600
C	-2.15624500	-1.47730300	-4.08240000
C	-1.50785200	-2.69862500	-3.87801000
C	-1.16254300	-3.06097700	-2.57235300
C	-1.14678200	-2.76845300	-0.10490500
C	-0.04710400	-2.35209300	0.65141400
C	0.23796900	-2.94039300	1.89005300
C	-0.58225300	-3.94862300	2.39866000

C	-1.69232100	-4.39084900	1.67674900
C	-1.96068400	-3.80767700	0.43344500
C	-3.00148800	-0.58888500	1.00963700
C	-2.49704800	-0.47556600	2.30041400
C	-3.15768300	-1.08002500	3.38782300
C	-4.39496100	-1.70715600	3.12287500
C	-4.89842100	-1.89395500	1.81194300
C	-4.15624300	-1.33402800	0.76647000
C	-3.62693600	1.33588900	-0.89068900
C	-4.82412700	0.78464000	-1.34958700
C	-5.95168900	1.58234800	-1.57974600
C	-5.81698600	2.97289900	-1.34406700
C	-4.58531300	3.57534300	-1.01202300
C	-3.50657600	2.71387000	-0.73851600
C	1.85006300	-1.75807500	-1.37959600
C	1.88822800	-1.04067100	-2.57415500
C	2.56865800	-1.54252100	-3.69619200
C	3.27514100	-2.75283200	-3.52705100
C	3.15013100	-3.55801100	-2.37335800
C	2.41820300	-3.02709100	-1.29935400
C	2.26747000	-0.81503300	1.34536200
C	3.35113600	-1.67200500	1.50183400
C	4.22151100	-1.55260400	2.59827100
C	3.99758600	-0.47609800	3.48698300
C	2.89451100	0.40301000	3.36511700
C	2.05225700	0.22018300	2.25762600
H	-2.89485600	0.33630800	-3.22041000
H	-2.44335900	-1.18532000	-5.09268200

H	-1.28292300	-3.34353200	-4.72090500
H	1.09921400	-2.63309700	2.48799100
H	-0.35890700	-4.39583600	3.36724300
H	-2.33280200	-5.16286200	2.09047100
H	-1.57377500	0.08388000	2.48775800
H	-4.49690900	-1.48475000	-0.26606700
H	-4.89709900	-0.29800800	-1.51330700
H	-2.56255000	3.15994700	-0.39572100
H	1.38193600	-0.06409000	-2.65231100
H	2.30476900	-3.62721100	-0.38869300
H	3.54790900	-2.45549700	0.76402000
H	1.21867000	0.92324300	2.10063800
O	-0.50016900	-4.22146700	-2.23948400
O	-3.03028200	-4.16849400	-0.36208200
C	0.14216500	-4.96239000	-3.30566600
H	0.77064000	-4.30388200	-3.91582200
H	0.77499000	-5.66251500	-2.72835300
H	-0.60886300	-5.48882400	-3.89766000
C	-3.73038000	-5.38948300	-0.01218700
H	-4.33011200	-5.22089600	0.89871600
H	-4.37454600	-5.53901000	-0.88780500
H	-3.03205700	-6.22257800	0.10048900
O	-6.94708000	3.78198600	-1.53484100
O	-5.12423100	-2.26817400	4.18314900
O	4.83586200	-0.33504300	4.60217600
O	4.09683200	-3.20683000	-4.57190200
C	-7.67620600	4.07720900	-0.31747600
H	-8.46513300	4.74818800	-0.67381600

H	-8.09701000	3.14769700	0.09457900
H	-7.02065600	4.58249200	0.40923600
C	5.45877400	-2.71530200	-4.46678300
H	5.90875400	-3.06185500	-3.52422400
H	5.94431800	-3.17313000	-5.33462000
H	5.46329700	-1.61644600	-4.54028600
C	6.01723200	0.47534200	4.38510600
H	6.51855300	0.42132400	5.35744900
H	6.63905300	0.03925600	3.58887200
H	5.72310900	1.51001100	4.14750800
C	-5.99180400	-1.33896800	4.87790400
H	-6.78272200	-0.99263700	4.19521800
H	-6.40421400	-1.95857900	5.68130500
H	-5.41102800	-0.49469900	5.28030900
C	-4.35199500	5.09247300	-0.92767500
C	-4.69662500	5.55788800	0.50102300
H	-4.53767800	6.63651500	0.60960100
H	-5.74533100	5.34945700	0.75480900
H	-4.06576100	5.06097700	1.24497900
C	-5.19746900	5.84986900	-1.96667100
H	-6.27254700	5.77308800	-1.77023700
H	-4.94282600	6.91411700	-1.98500000
H	-5.03332100	5.45104900	-2.97355400
C	-2.87675000	5.43963100	-1.21673700
H	-2.18244700	5.04472800	-0.46366000
H	-2.55320100	5.07052500	-2.19463400
H	-2.71369000	6.52496000	-1.21699300
C	-7.25924300	0.92128300	-2.03736200

C	-7.96185900	1.77188700	-3.10888600
H	-8.86131300	1.28131800	-3.48950400
H	-8.26395800	2.75436700	-2.71805300
H	-7.29774900	1.96667000	-3.95745900
C	-8.16526800	0.73493500	-0.80337600
H	-9.11258200	0.26078400	-1.07624300
H	-7.68348900	0.10552500	-0.03743400
H	-8.40473900	1.69987100	-0.33288900
C	-7.00697800	-0.47162200	-2.66076700
H	-6.28699200	-0.41915800	-3.48364800
H	-6.63334900	-1.19619900	-1.91933200
H	-7.93381400	-0.88784600	-3.06960700
C	2.51593300	-0.74941200	-5.00851800
C	2.54812200	-1.67881700	-6.23436100
H	1.75439300	-2.43015300	-6.18281400
H	2.42096500	-1.11740300	-7.16437400
H	3.49676600	-2.22679300	-6.30970900
C	1.20459300	0.06511600	-5.09543900
H	0.32602200	-0.58627900	-5.02005200
H	1.12565000	0.81529400	-4.29917900
H	1.13864100	0.60281400	-6.04666800
C	3.71069700	0.22258400	-5.03495600
H	3.66395900	0.93561300	-4.19948200
H	4.66659000	-0.31618100	-4.96166500
H	3.73078400	0.80553300	-5.96118700
C	3.79948200	-4.93773500	-2.21070000
C	3.89276800	-5.70010600	-3.54384400
H	4.60025100	-5.22792600	-4.23820400

H	4.22460800	-6.73142100	-3.39476200
H	2.92898800	-5.72394700	-4.06054900
C	5.20595800	-4.72194800	-1.61661000
H	5.74286300	-5.66839300	-1.50609900
H	5.81127200	-4.06837700	-2.26262000
H	5.15572400	-4.24898200	-0.62253600
C	2.97131700	-5.82116300	-1.24879400
H	2.91513500	-5.40023700	-0.23887300
H	1.93872000	-5.93925500	-1.61418900
H	3.40785300	-6.82022100	-1.15604400
C	-6.18986700	-2.65822000	1.48692800
C	-6.29796900	-3.01041400	-0.01589200
H	-6.49090200	-2.12335900	-0.64169700
H	-5.38122200	-3.48071200	-0.39086900
H	-7.12437100	-3.70484000	-0.19470900
C	-6.22971000	-3.98325500	2.26940600
H	-6.17525600	-3.81304300	3.35521700
H	-7.14751200	-4.54250800	2.07262000
H	-5.37428700	-4.62060400	1.99994000
C	-7.40045000	-1.76925600	1.83252300
H	-8.34231000	-2.29781500	1.65712400
H	-7.39219400	-1.45725500	2.88581000
H	-7.41127900	-0.85594800	1.21444000
C	-2.49471900	-1.02681400	4.77227600
C	-3.01759100	0.21349900	5.52285000
H	-4.10644900	0.16631900	5.67196200
H	-2.55567900	0.30208500	6.51133600
H	-2.80174700	1.13470300	4.97226300

C	-0.95852300	-0.91054700	4.64838000
H	-0.54981500	-1.69813900	4.00567300
H	-0.63373600	0.05948000	4.23823000
H	-0.47740200	-1.00887200	5.62768400
C	-2.76732000	-2.31069000	5.57671900
H	-2.20162200	-2.32537900	6.51251000
H	-3.82623100	-2.42692000	5.83455900
H	-2.48979900	-3.19924500	4.99873700
C	5.34163200	-2.59214700	2.75220400
C	4.99510500	-3.90859900	2.01245300
H	4.03589600	-4.31401500	2.34887800
H	4.94916000	-3.77925500	0.91876000
H	5.75565500	-4.67244600	2.20660800
C	6.62867300	-2.01648900	2.13076500
H	7.44467500	-2.74432700	2.15461600
H	6.46795800	-1.72091800	1.08789400
H	6.97088700	-1.12194200	2.67318000
C	5.56131700	-2.96825900	4.22753800
H	6.31285700	-3.75497000	4.33470200
H	5.89524300	-2.11313200	4.82915000
H	4.63232100	-3.32184800	4.68711100
C	2.57814700	1.52485200	4.36717600
C	1.12943400	2.04322900	4.20266000
H	0.96645900	2.50499200	3.22158500
H	0.38975700	1.23769400	4.32996400
H	0.90504700	2.80933000	4.95273700
C	3.52729800	2.70865600	4.11395300
H	3.23508800	3.59234400	4.68989500

H	4.56462900	2.47380100	4.39095700
H	3.53664200	3.00501700	3.04991100
C	2.71315400	1.00939600	5.81101800
H	3.73601800	0.66825300	6.02647800
H	2.46991500	1.78929400	6.53772200
H	2.05136500	0.15743300	5.99271000
N	0.80701700	6.05791200	-0.20434100
C	3.10845800	4.99255000	-0.72336300
C	4.13750200	5.11664300	0.29962900
C	3.53776900	4.94552000	-2.17745500
C	-0.07846100	3.09092900	-1.04777500
C	1.24716800	2.65466800	-1.25869600
C	2.32267400	2.84861300	-0.34187400
C	5.48831500	4.83352400	0.01029500
C	6.46586800	4.91372600	0.99569400
C	6.12991200	5.26550300	2.30150600
C	4.79494700	5.54156900	2.60876300
C	3.81518600	5.46718100	1.62895600
C	2.43602900	5.14995800	-3.16961900
C	2.52882800	5.93446000	-4.24367000
C	1.86537900	5.60894800	-0.44894100
H	4.02492800	3.96944100	-2.36060000
H	4.32764900	5.69411500	-2.35427000
H	-0.72398200	3.24862000	-1.91105600
H	-0.29966000	3.71896800	-0.18601700
H	1.50909500	2.31114000	-2.26195400
H	2.04655100	3.16719600	0.66543900
H	5.77332100	4.52967500	-0.99617100

H	7.50073400	4.68927900	0.73976500
H	6.89793600	5.33458000	3.06922300
H	4.51747900	5.82779300	3.62237000
H	2.78004100	5.70225700	1.87745600
H	1.50214000	4.61575600	-2.97940800
H	1.70471400	6.04530300	-4.94470400
H	3.43326300	6.50453300	-4.45876600
C	3.57710900	2.11956800	-0.43561400
C	4.39623200	2.00491400	0.70236100
C	4.03261600	1.52571300	-1.63017300
C	5.60404100	1.31963800	0.65943300
H	4.06159000	2.46512500	1.63892500
C	5.24445900	0.84436500	-1.67319700
H	3.42818100	1.57733600	-2.53893600
C	6.03635800	0.73536800	-0.52966200
H	6.21184400	1.24623300	1.55897000
H	5.56812000	0.38515000	-2.60573300
H	6.98118500	0.19685100	-0.56667100

References

1. Armarego, W. L. F.; Chai, C., Purification of Laboratory Chemicals (Seventh Edition), Armarego, W. L. F.; Chai, C., Eds. Butterworth-Heinemann: Boston, 2013.

2. 2(a) De Korver, K. A.; Hsung, R. P.; Lohse, A. G.; Zhang, Y., Org. Lett. 2010, 12, 1840−1843; (b) DeKorver, K. A.; Wang, X.-N.; Walton, M. C.; Hsung, R. P., Org. Lett. 2012, 14, 1768−1771; (c) Alexander, J. A., Shchetepkina, V. I.; Stankevich, K. S.; Benedict, R. J.; Bernhard, S. P.; Dreiling, R. J.; Cook, M. J., Org. Lett. 2021, 23 (2), 559-564.

3. Martínez, R.; Ramón, D. J,; Yus, M. Adv. Synth. Catal. 2008, 350, 1235-1240.

4. Ananikov, V. P.; Musaev, D. G.; Morokuma, K., Real size of ligands, reactants and catalysts: Studies of structure, reactivity and selectivity by ONIOM and other hybrid computational approaches. Journal of Molecular Catalysis A: Chemical 2010, 324, 104-119.

5. Li, Z.; Liu, L.; Fu, Y.; Guo, Q.-X., Assessing performance of diverse ONIOM methods in calculation of structures of organonickel and organopalladium compounds. Journal of Molecular Structure: THEOCHEM 2005, 757, 69-76.

6. Karami, K.; Abedanzadeh, S.; Farrokhpour, H.; Lipkowski, J., Synthesis and characterization of the P,C palladacycles with bridging and chelating dinitrogen ligands and ONIOM calculations on the pyrazine-bridged organometallic polymers (n = 1 to n = 10). Journal of Organometallic Chemistry 2016, 805, 68-76.

7. Zhao, Y.; Truhlar, D. G., The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. Theoretical Chemistry Accounts 2008, 120, 215-241.

8. Barone, V.; Cossi, M., Quantum Calculation of Molecular Energies and Energy Gradients in Solution by a Conductor Solvent Model. The Journal of Physical Chemistry A 1998, 102, 1995-2001.

9. Klamt, A.; Schüürmann, G., COSMO: a new approach to dielectric screening in solvents with explicit expressions for the screening energy and its gradient. Journal of the Chemical Society, Perkin Transactions 2 1993, 5, 799-805.

10. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.;

Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian 16 Rev. A.03, Wallingford, CT, 2016.

11. Grimme, S., Supramolecular Binding Thermodynamics by Dispersion-Corrected Density Functional Theory. Chemistry – A European Journal 2012, 18, 9955-9964.

12. Li, Y.-P.; Gomes, J.; Mallikarjun Sharada, S.; Bell, A. T.; Head-Gordon, M., Improved Force-Field Parameters for QM/MM Simulations of the Energies of Adsorption for Molecules in Zeolites and a Free Rotor Correction to the Rigid Rotor Harmonic Oscillator Model for Adsorption Enthalpies. The Journal of Physical Chemistry C 2015, 119, 1840-1850.

13. Luchini, G.; Alegre-Requena, J.; IFunes; Rodríguez-Guerra, J.; Chen, J.; Paton, R. bobbypaton/GoodVibes: GoodVibes v3.0.0. https://doi.org/10.5281/zenodo.3346166.

14. Legault, C. Y. CYLview 1.0b. Université de Sherbrooke (2009) (http://www.cylview.org) Dennington, R., Keith, T.A. & Millam J.M. GaussView 6.0.16. Semichem Inc., Shawnee Mission, KS (2016).

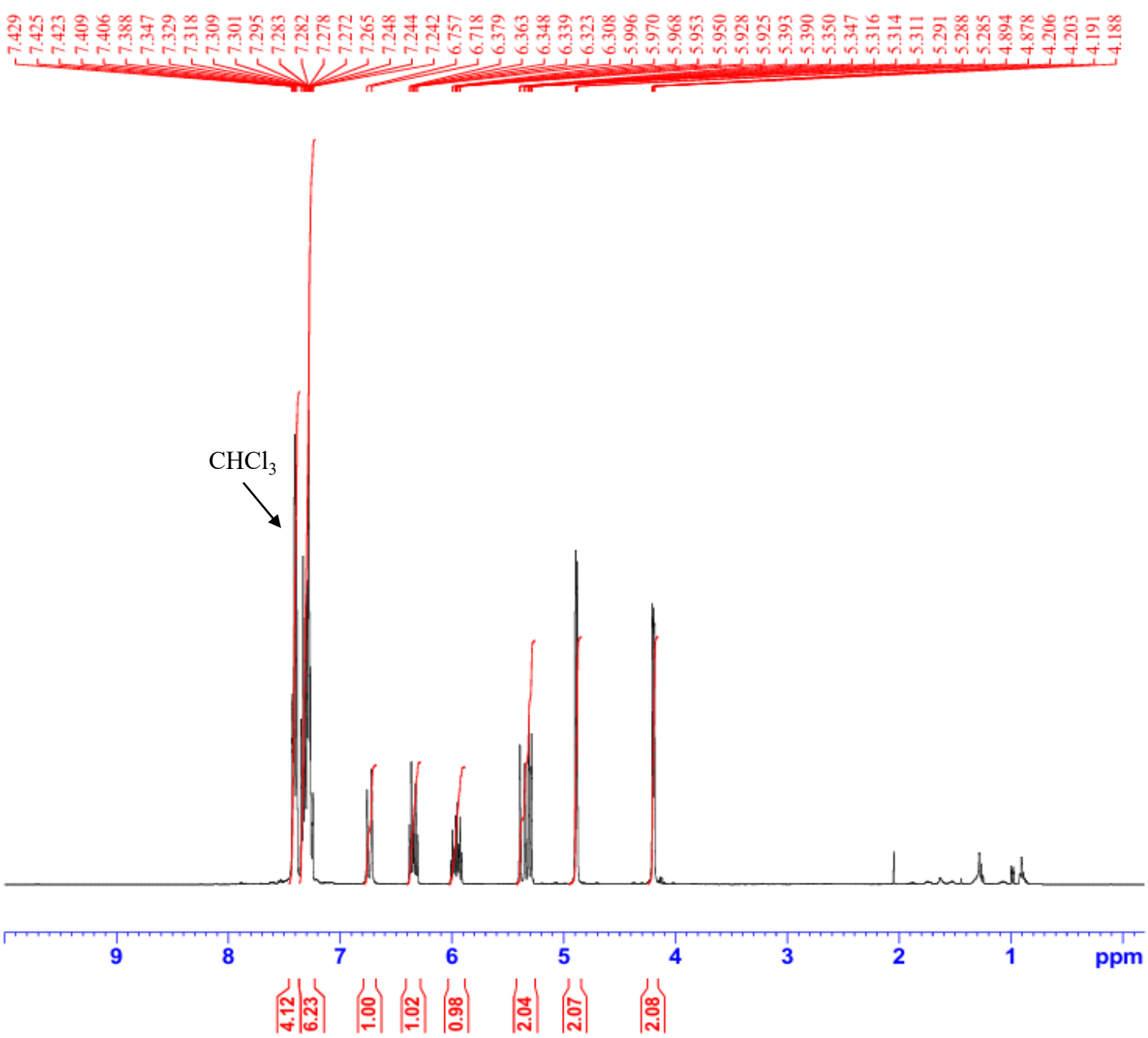
15. Pracht, P.; Bohle, F.; Grimme, S., Automated exploration of the low-energy chemical space with fast quantum chemical methods. Physical Chemistry Chemical Physics 2020, 22, 7169-7192.

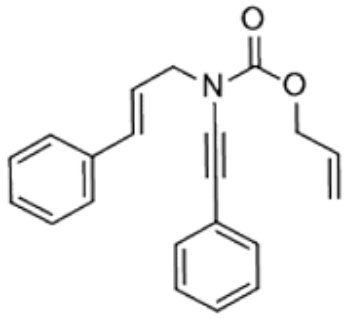
16. Bannwarth, C.; Ehlert, S.; Grimme, S., GFN2-xTB—An Accurate and Broadly Parametrized Self-Consistent Tight-Binding Quantum Chemical Method with Multipole Electrostatics and Density-Dependent Dispersion Contributions. Journal of Chemical Theory and Computation 2019, 15, 1652-1671.

17. Spicher, S.; Grimme, S., Robust Atomistic Modeling of Materials, Organometallic, and Biochemical Systems. Angewandte Chemie International Edition 2020, 59, 15665-15673.

18. Calculated using IGMPlot. http://igmplot.univ-reims.fr. See: C. Levfebvre, H. Khartabil, J.-C. Boisson, J. Contreras-Garcia, J.-P. Piquemal, E. Hénon, ChemPhysChem 2018, 19, 724.

19. Humphrey, W.; Dalke, A.; Schulten, K. J. Mol. Graph. 1996, 14, 33-38.





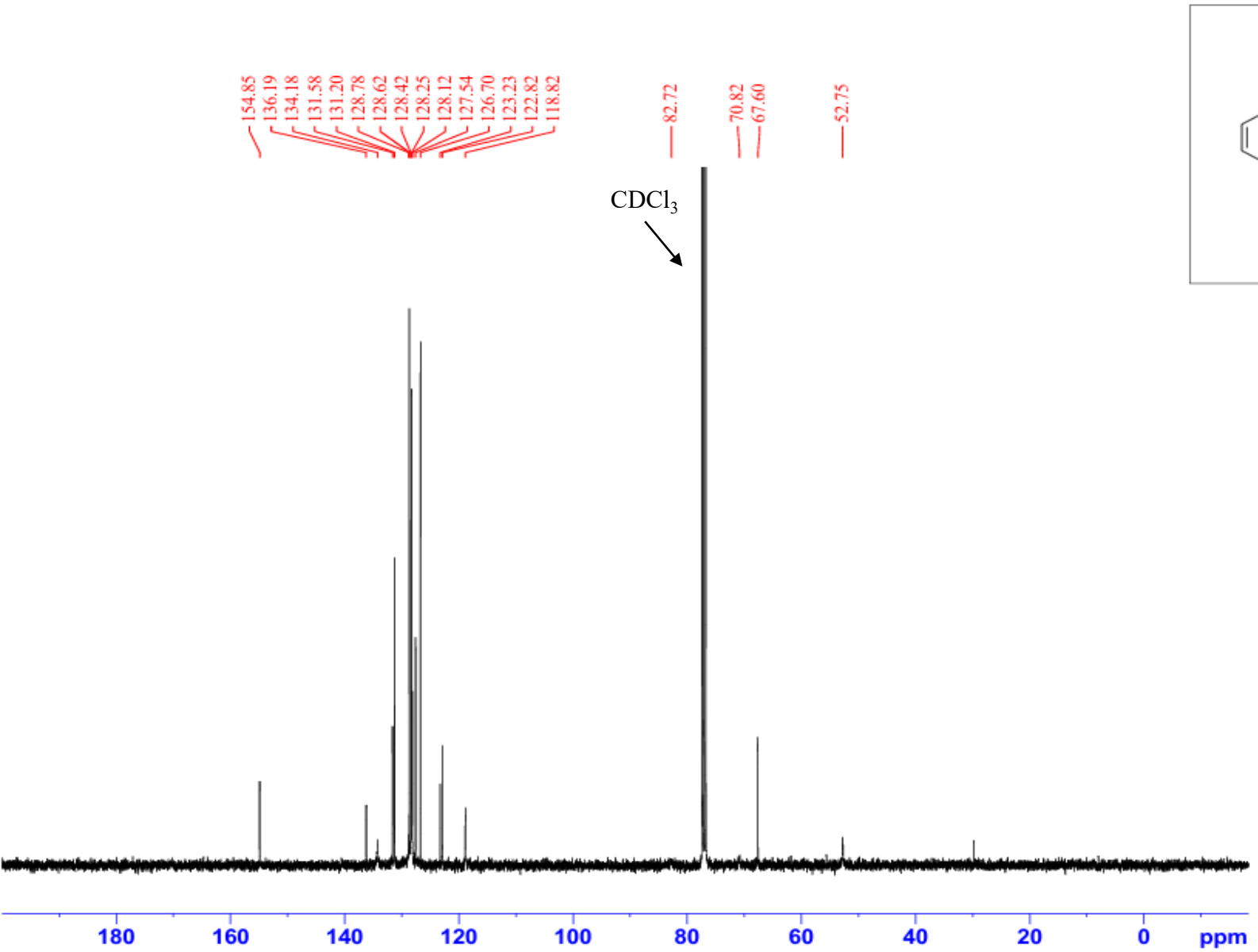
1a

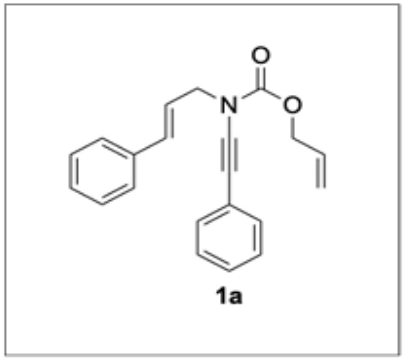
```
Current Data Parameters
NAME                  CS-1-19pure
EXPNO                          10
PROCNO                          1

F2 - Acquisition Parameters
Date_                    20211005
Time                        14.43 h
INSTRUM                Avance Neo
PROBHD    Z152088_0031 (
PULPROG                      zg30
TD                          65536
SOLVENT                     CDCl3
NS                             16
DS                              2
SWH                      8196.722 Hz
FIDRES                   0.250144 Hz
AQ                       3.9976959 sec
RG                             52
DW                          61.000 usec
DE                          13.89 usec
TE                          298.0 K
D1                       1.00000000 sec
TD0                             1
SFO1                400.1324708 MHz
NUC1                         1H
P0                          2.67 usec
P1                          8.00 usec
PLW1                24.03499985 W

F2 - Processing parameters
SI                          65536
SF                  400.1300164 MHz
WDW                           EM
SSB                            0
LB                          0.30 Hz
GB                             0
PC                          1.00
```

[1]H NMR spectrum of **1a**



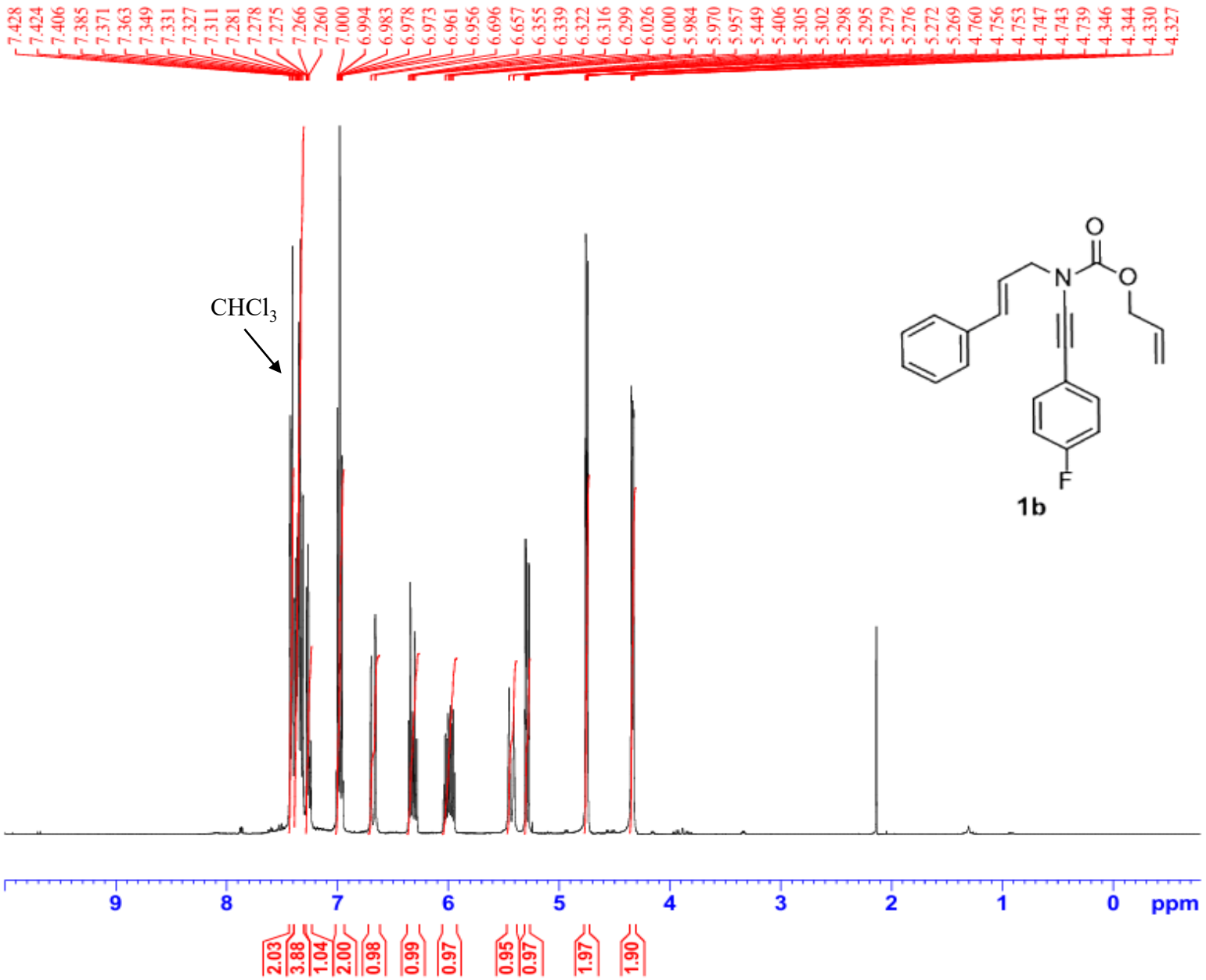



```
Current Data Parameters
NAME          OJ-1-184-C
EXPNO                 19
PROCNO                 1

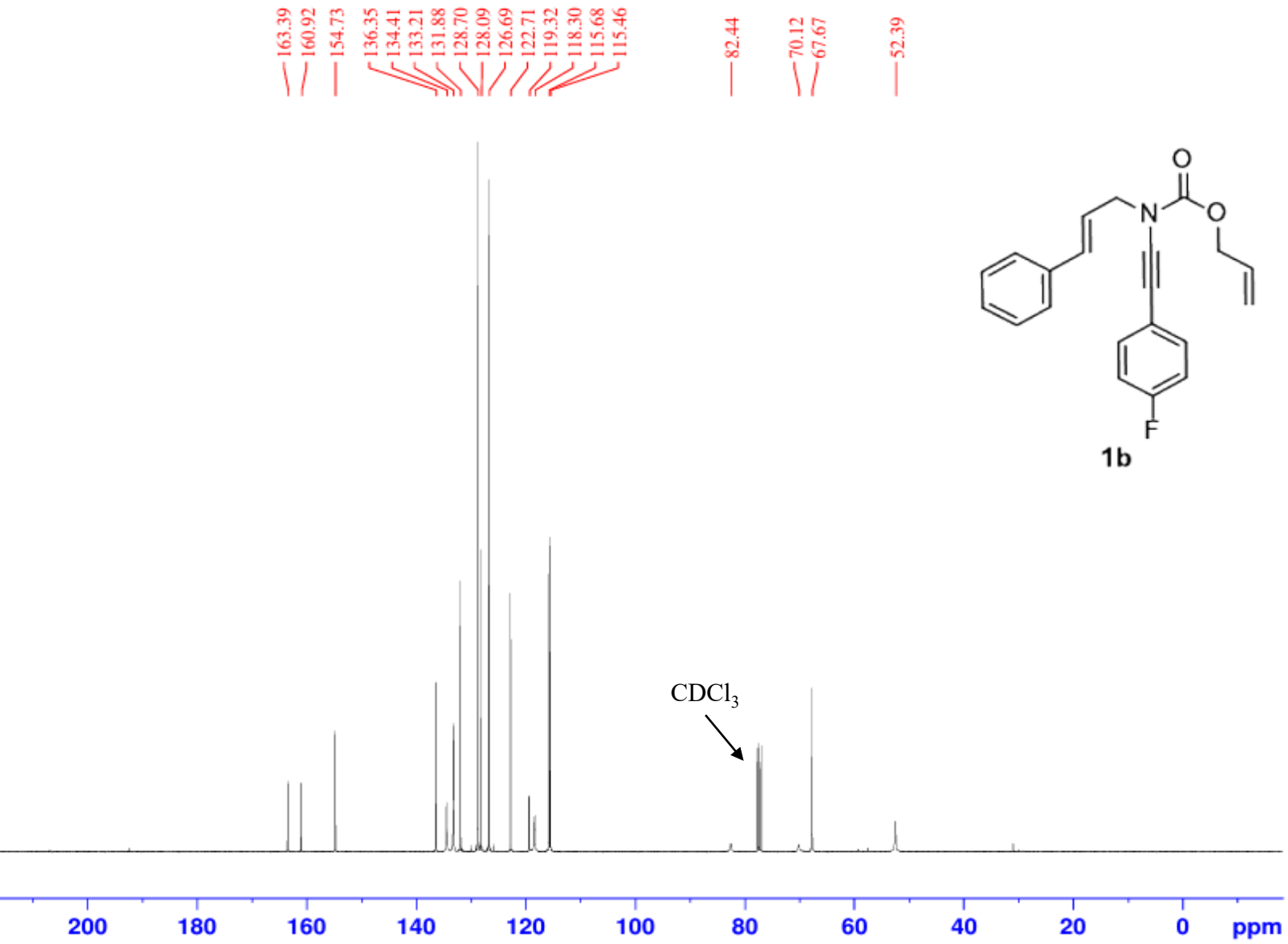
F2 - Acquisition Parameters
Date_           20220904
Time                0.59 h
INSTRUM       Avance Neo
PROBHD    Z152088_0031 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           23809.523 Hz
FIDRES        0.726609 Hz
AQ            1.3762560 sec
RG                8.125
DW               21.000 usec
DE                6.50 usec
TE                298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1        100.6228298 MHz
NUC1               13C
P0                2.67 usec
P1                8.00 usec
PLW1        86.55400085 W
SFO2        400.1316005 MHz
NUC2               1H
CPDPRG[2        waltz65
PCPD2            90.00 usec
PLW2        24.03499985 W
PLW12        0.18990999 W
PLW13        0.09552100 W

F2 - Processing parameters
SI                32768
SF          100.6127685 MHz
WDW                EM
SSB                   0
LB                1.00 Hz
GB                    0
PC                1.40
```


^{13}C NMR spectrum of **1a**



^{1}H NMR spectrum of **1b**

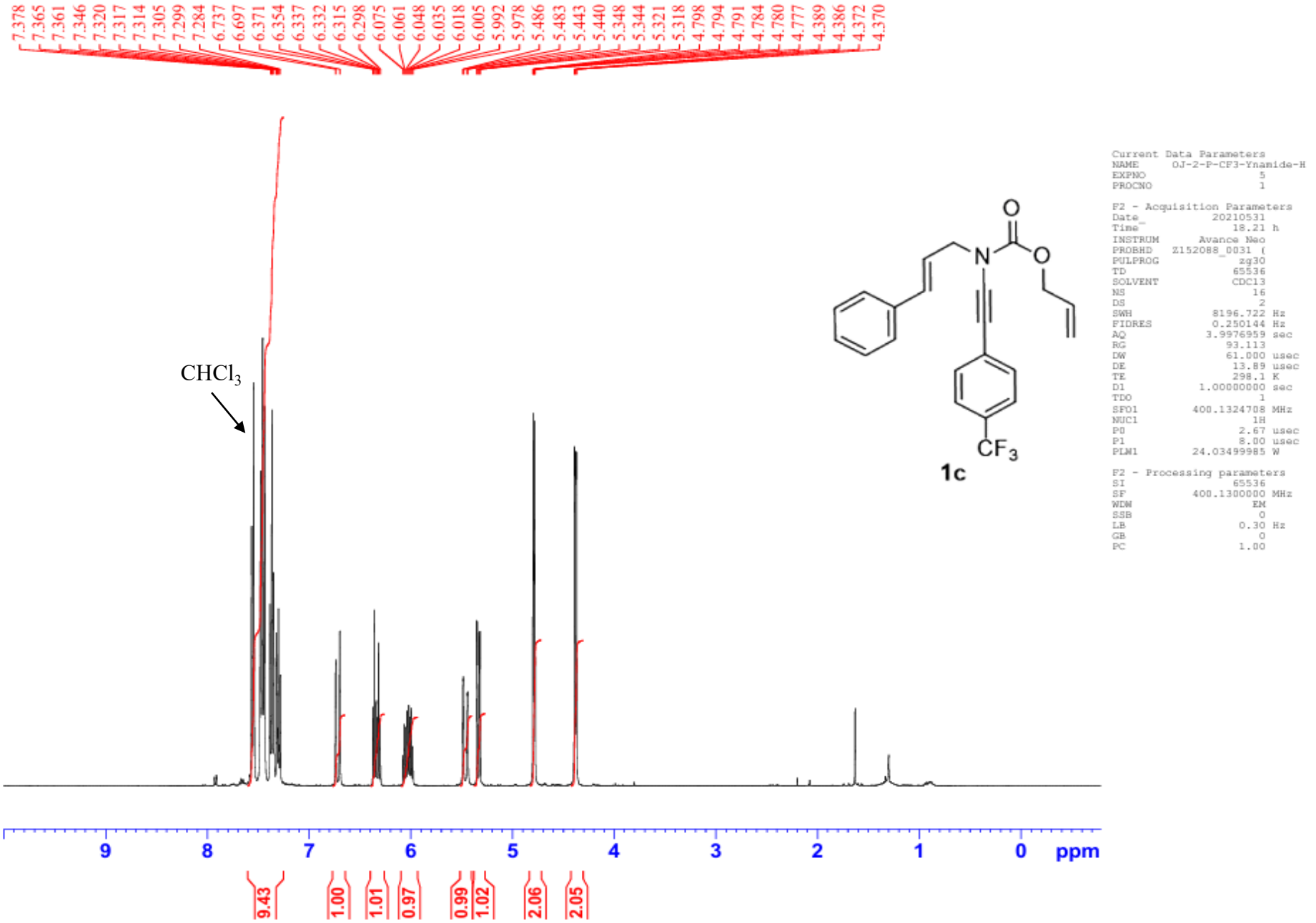



```
Current Data Parameters
NAME      Ph-F-Yneamide-C
EXPNO                 14
PROCNO                 1

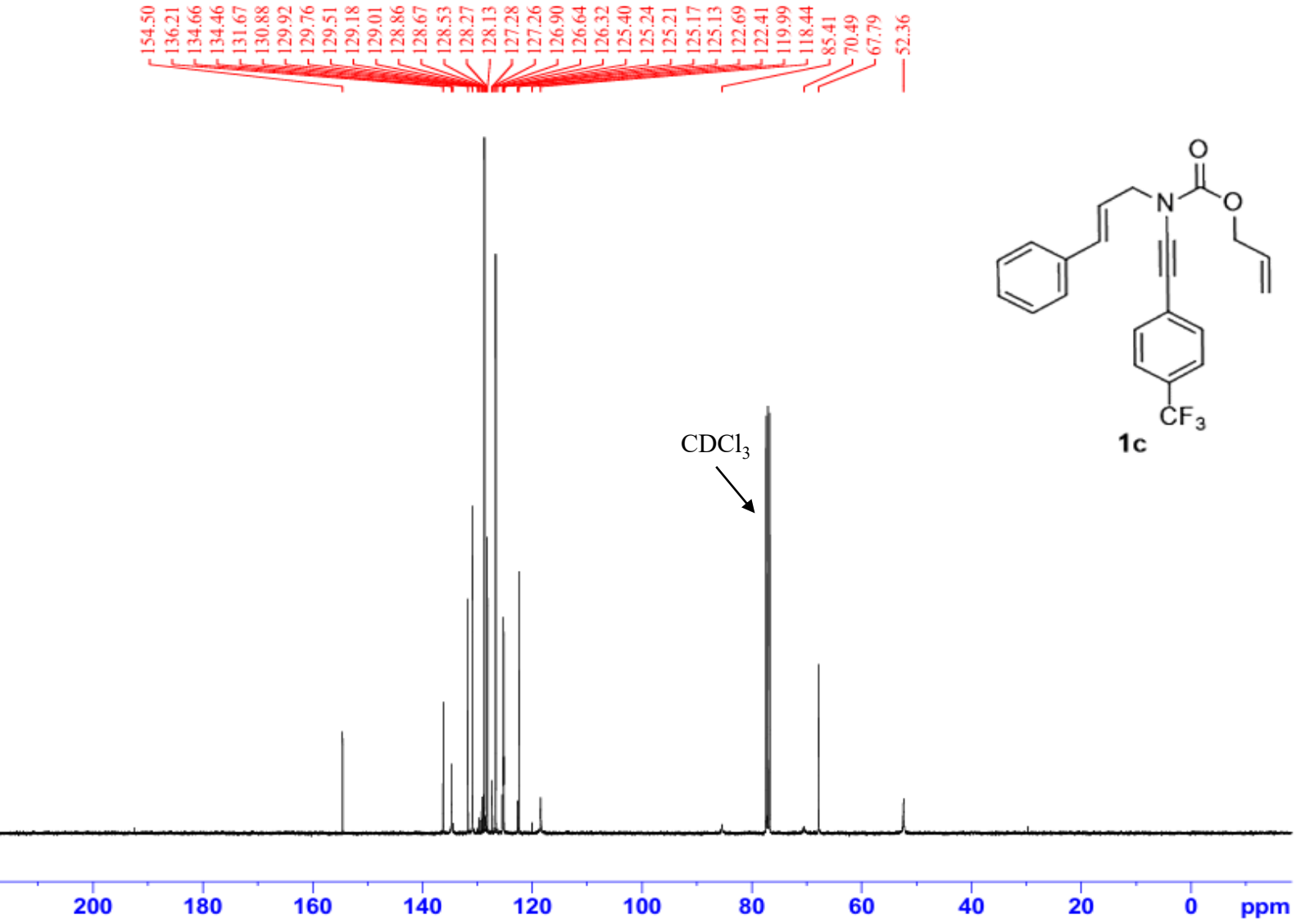
F2 - Acquisition Parameters
Date_           20210327
Time              17.03 h
INSTRUM       Avance Neo
PROBHD    Z152088_0031 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           23809.523 Hz
FIDRES        0.726609 Hz
AQ            1.3762560 sec
RG               11.0026
DW               21.000 usec
DE                6.50 usec
TE               293.1 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1        100.6228298 MHz
NUC1               13C
P0                2.67 usec
P1                8.00 usec
PLW1         86.55400085 W
SFO2        400.1316005 MHz
NUC2               1H
CPDPRG[2        waltz65
PCPD2            90.00 usec
PLW2         24.03499985 W
PLW12         0.18990999 W
PLW13         0.09552100 W

F2 - Processing parameters
SI                32768
SF          100.6127685 MHz
WDW                EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

^{13}C NMR spectrum of **1b**



^{1}H NMR spectrum of **1c**

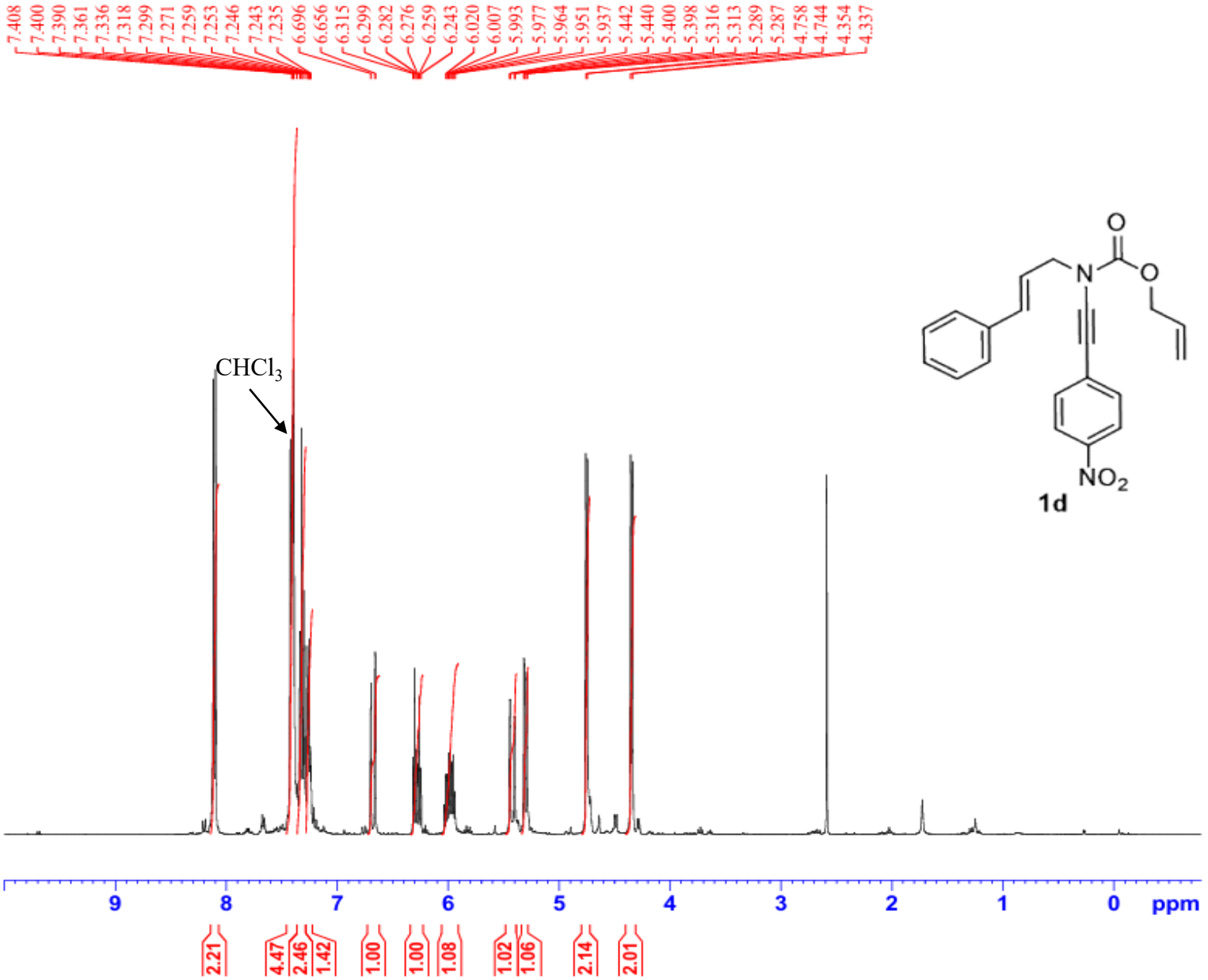



```
Current Data Parameters
NAME      OJ-2-P-CF3-Ynamide-C
EXPNO                        7
PROCNO                       1

F2 - Acquisition Parameters
Date_              20210531
Time                 19.23 h
INSTRUM       Avance Neo
PROBHD    Z152088_0031 (
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    1024
DS                       4
SWH              23809.523 Hz
FIDRES           0.726609 Hz
AQ               1.3762560 sec
RG                   8.125
DW                  21.000 usec
DE                   6.50 usec
TE                  298.1 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                      1
SFO1           100.6228298 MHz
NUC1                   13C
P0                   2.67 usec
P1                   8.00 usec
PLW1           86.55400085 W
SFO2           400.1316005 MHz
NUC2                   1H
CPDPRG[2          waltz65
PCPD2               90.00 usec
PLW2           24.03499985 W
PLW12           0.18990999 W
PLW13           0.09552100 W

F2 - Processing parameters
SI                   32768
SF             100.6127685 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

[1]H NMR spectrum of **6a or 6b**

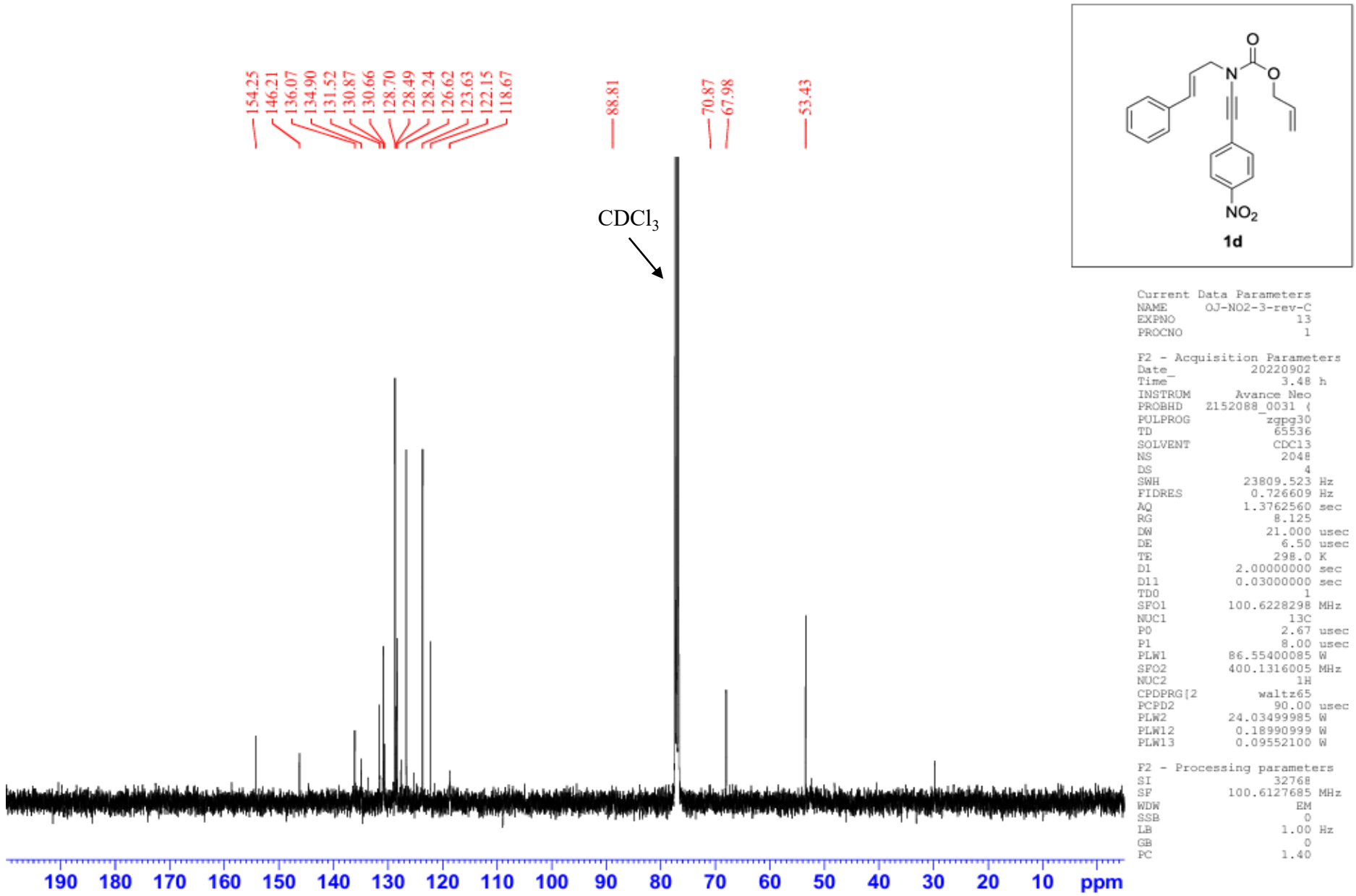



```
Current Data Parameters
NAME                  OJ-2-257-H
EXPNO                         19
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20210802
Time                       22.01 h
INSTRUM              Avance Neo
PROBHD          Z152088_0031 (
PULPROG                    zg30
TD                        65536
SOLVENT                   CDCl3
NS                           16
DS                            2
SWH                    8196.722 Hz
FIDRES                 0.250144 Hz
AQ                     3.9976959 sec
RG                        50.7317
DW                        61.000 usec
DE                        13.89 usec
TE                        298.1 K
D1                     1.00000000 sec
TD0                           1
SFO1                400.1324708 MHz
NUC1                         1H
P0                        2.67 usec
P1                        8.00 usec
PLW1                24.03499985 W

F2 - Processing parameters
SI                        65536
SF                  400.1300163 MHz
WDW                          EM
SSB                           0
LB                         0.30 Hz
GB                            0
PC                         1.00
```

[1]H NMR spectrum of **1d**

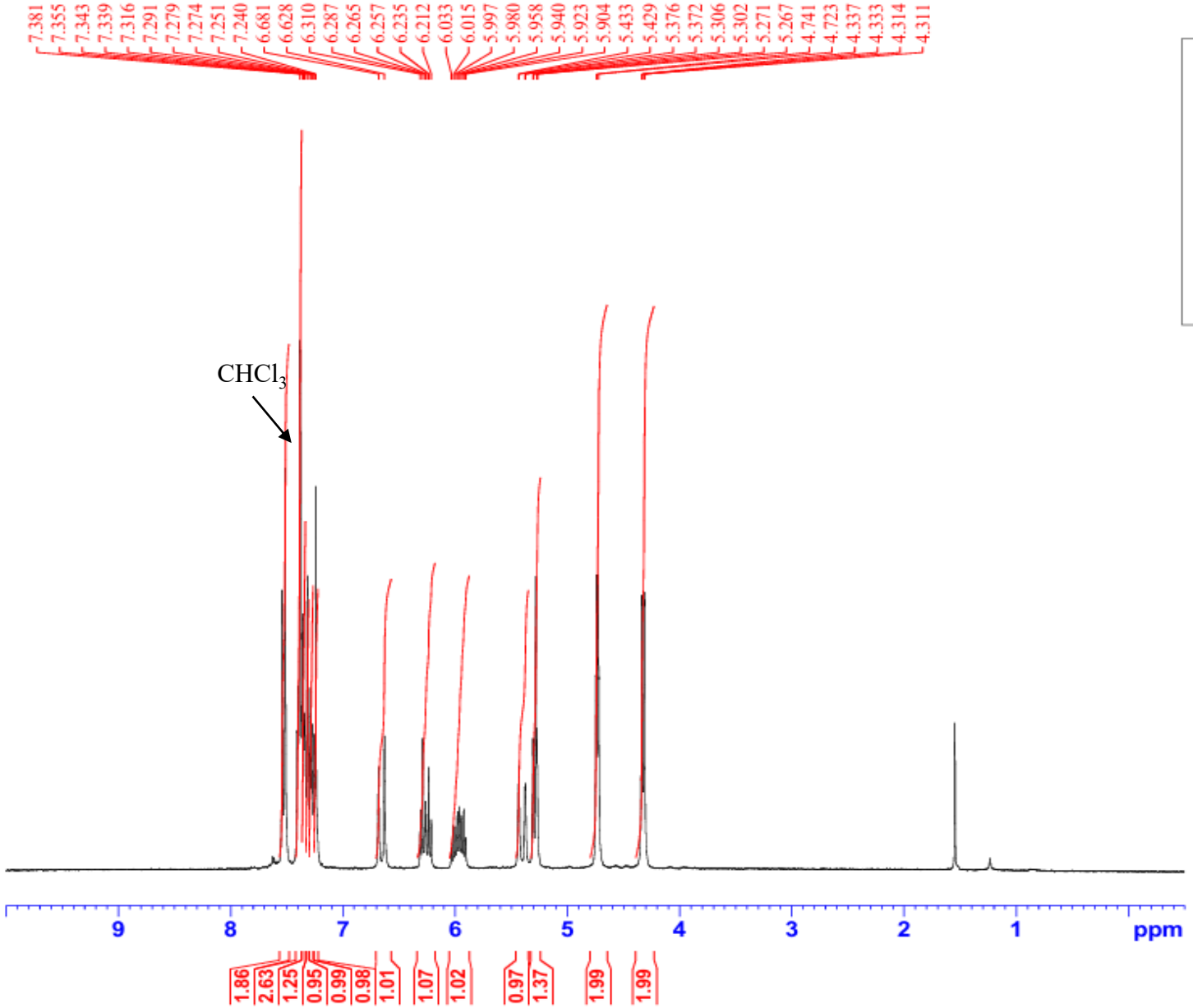


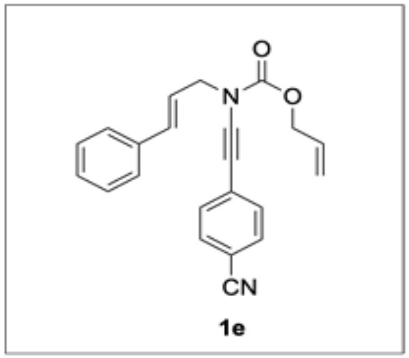

```
Current Data Parameters
NAME      OJ-NO2-3-rev-C
EXPNO                 13
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220902
Time                3.48 h
INSTRUM       Avance Neo
PROBHD    2152088_0031 (
PULPROG           zgpg30
TD                65536
SOLVENT            CDCl3
NS                 2048
DS                    4
SWH           23809.523 Hz
FIDRES         0.726609 Hz
AQ             1.3762560 sec
RG                 8.125
DW                21.000 usec
DE                 6.50 usec
TE                298.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                   1
SFO1         100.6228298 MHz
NUC1                13C
P0                 2.67 usec
P1                 8.00 usec
PLW1          86.55400085 W
SFO2         400.1316005 MHz
NUC2                1H
CPDPRG[2         waltz65
PCPD2             90.00 usec
PLW2          24.03499985 W
PLW12          0.18990999 W
PLW13          0.09552100 W

F2 - Processing parameters
SI                 32768
SF           100.6127685 MHz
WDW                   EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

^{13}C NMR spectrum of **1d**





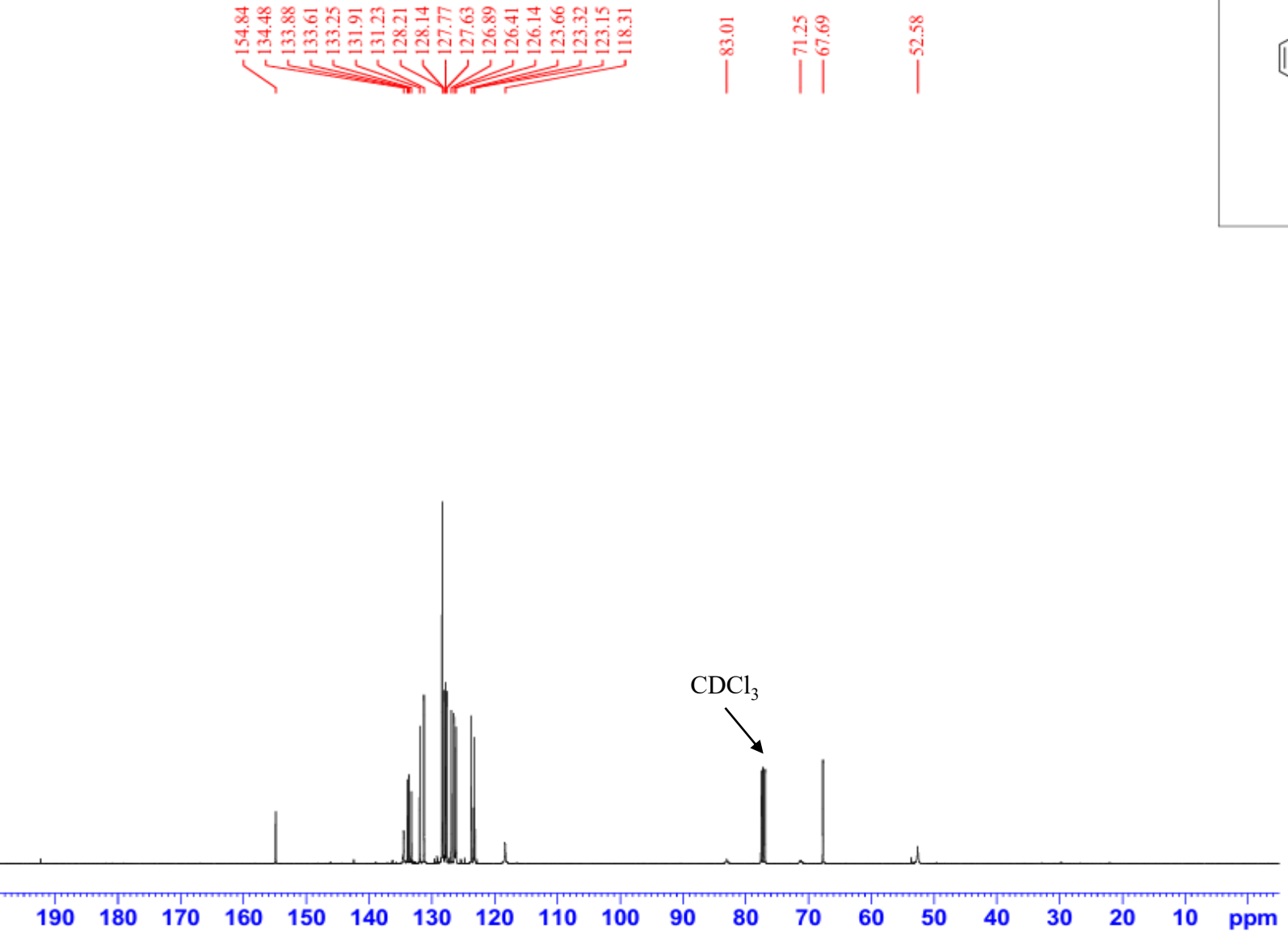

```
Current Data Parameters
NAME                  OJ-1e-H
EXPNO                       1
PROCNO                      1

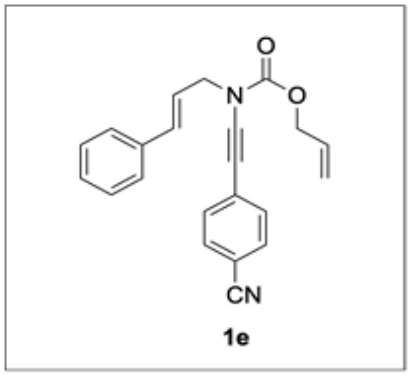
F2 - Acquisition Parameters
Date_              20180205
Time               10.02
INSTRUM            spect
PROBHD    5 mm QNP 1H/13
PULPROG            zg
TD                 32768
SOLVENT            CDCl3
NS                 8
DS                 0
SWH                3591.954 Hz
FIDRES             0.109618 Hz
AQ                 4.5613055 sec
RG                 322.5
DW                 139.200 usec
DE                 6.00 usec
TE                 683.2 K
D1                 1.00000000 sec
TD0                1

======== CHANNEL f1 ========
NUC1               1H
P1                 10.00 usec
PL1                0 dB
SFO1               300.1715008 MHz

F2 - Processing parameters
SI                 32768
SF                 300.1700170 MHz
WDW                EM
SSB                0
LB                 0.50 Hz
GB                 0
PC                 1.00
```

[1]H NMR spectrum of **1e**



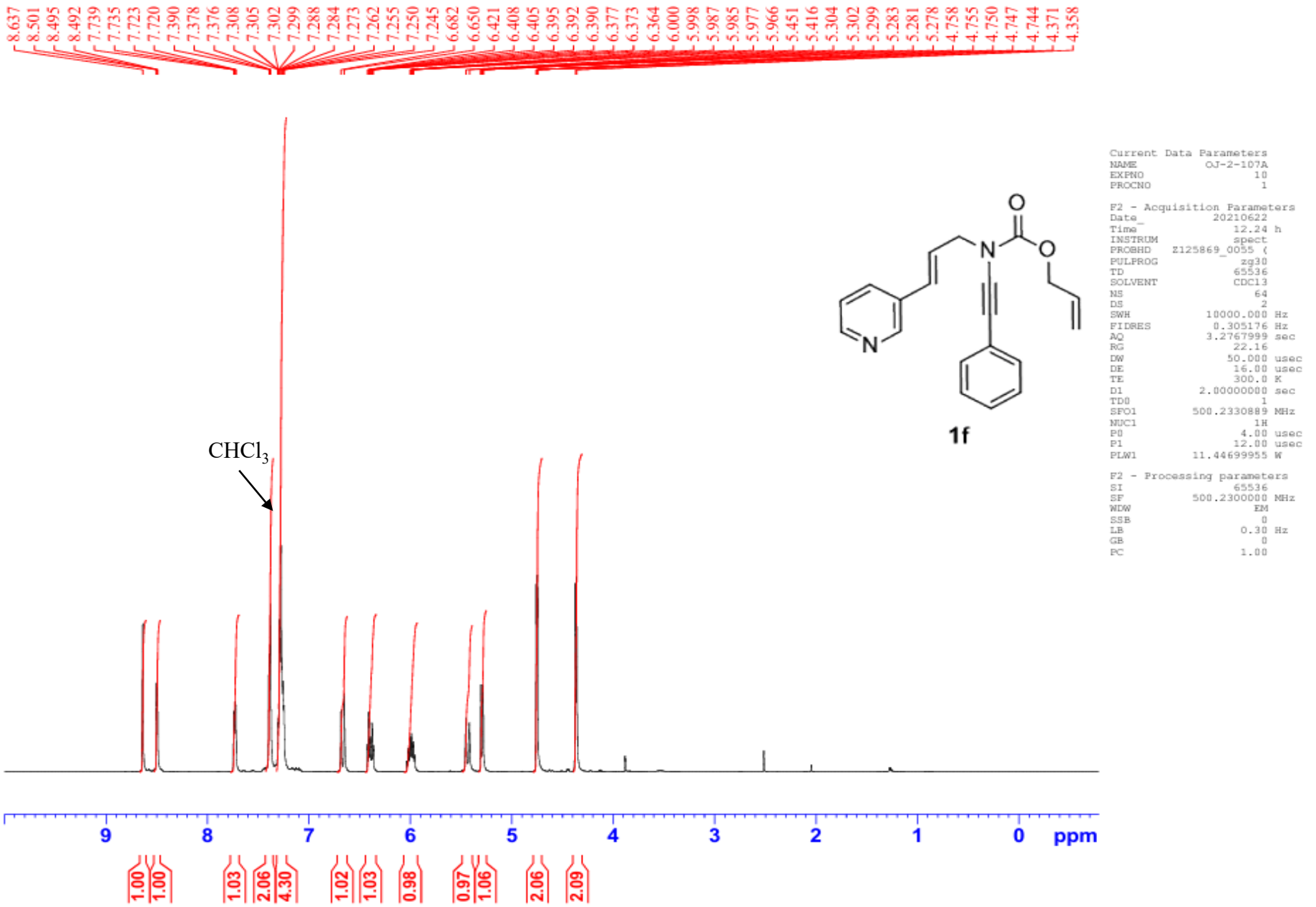



```
Current Data Parameters
NAME                  OJ-1-E-C
EXPNO                       12
PROCNO                       1

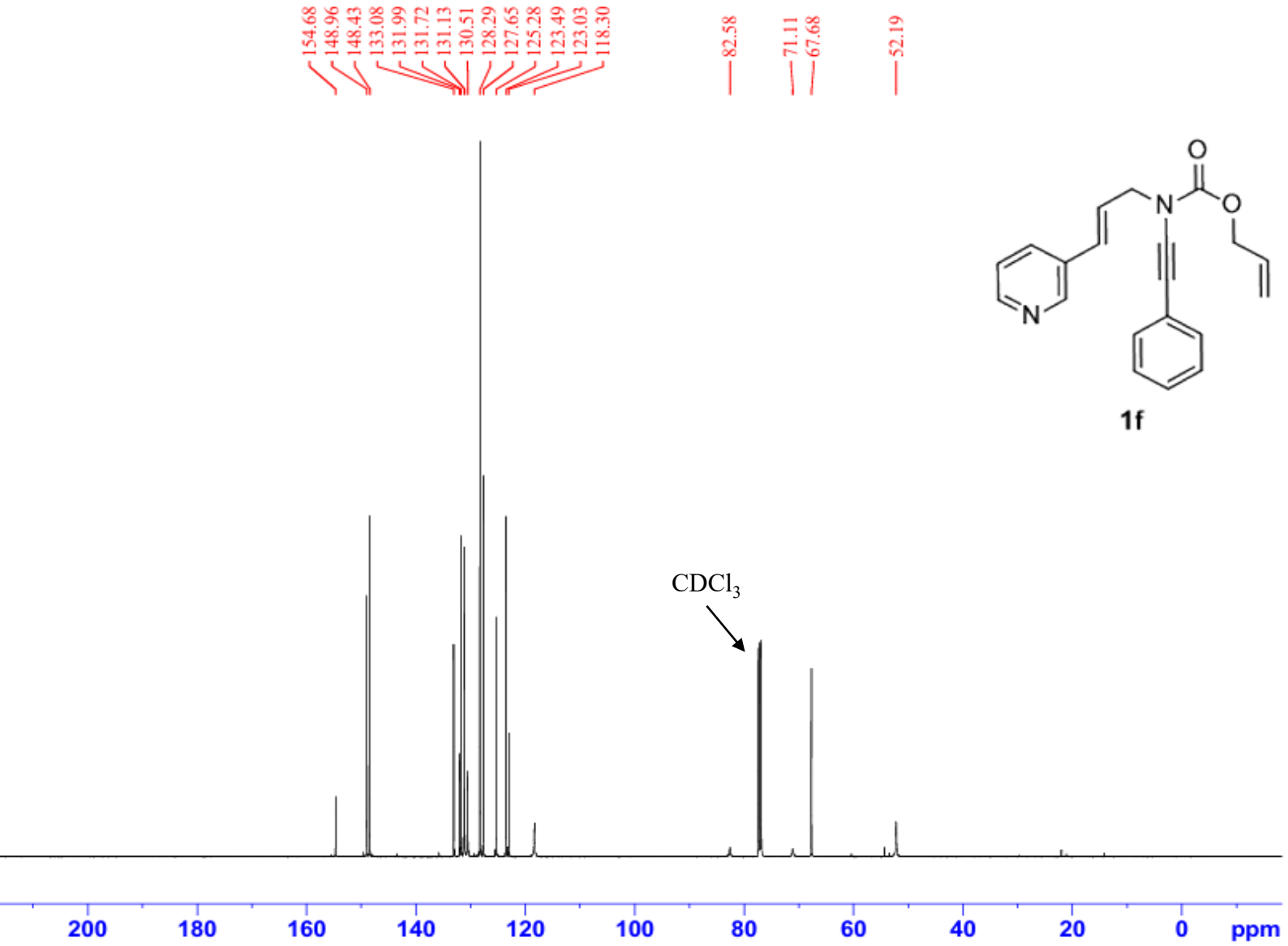
F2 - Acquisition Parameters
Date_                 20210615
Time                      0.13 h
INSTRUM              Avance Neo
PROBHD    2152088_0031 (
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                        1024
DS                           4
SWH                  23809.523 Hz
FIDRES                0.726609 Hz
AQ                    1.3762560 sec
RG                        8.125
DW                       21.000 usec
DE                        6.50 usec
TE                       298.1 K
D1                    2.00000000 sec
D11                   0.03000000 sec
TD0                          1
SFO1                100.6228298 MHz
NUC1                        13C
P0                        2.67 usec
P1                        8.00 usec
PLW1                86.55400085 W
SFO2                400.1316005 MHz
NUC2                        1H
CPDPRG[2                waltz65
PCPD2                    90.00 usec
PLW2                24.03499985 W
PLW12                0.18990999 W
PLW13                0.09552100 W

F2 - Processing parameters
SI                       32768
SF                  100.6127685 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40
```


^{13}C NMR spectrum of **1e**



^{1}H NMR spectrum of **1f**



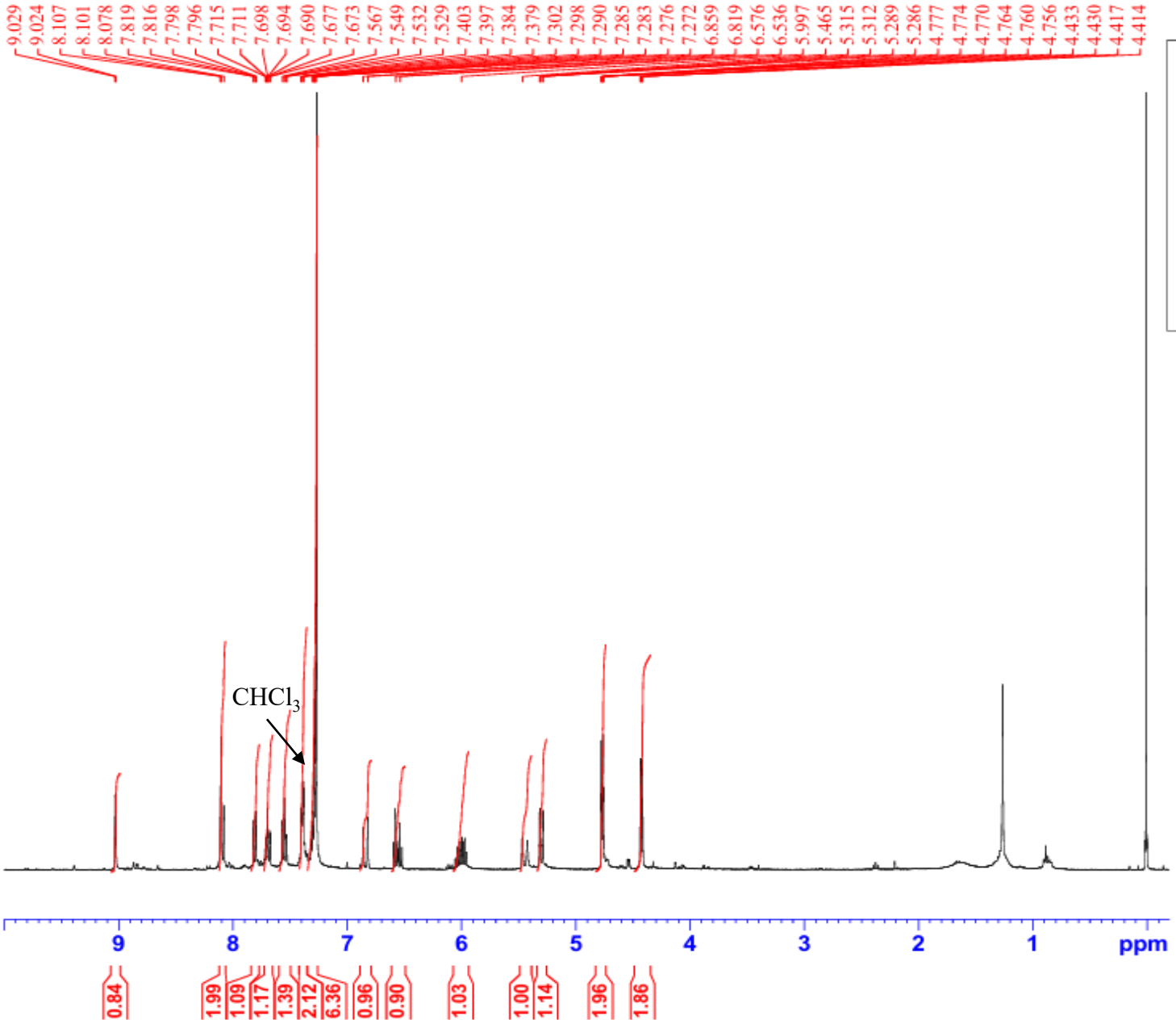
1f

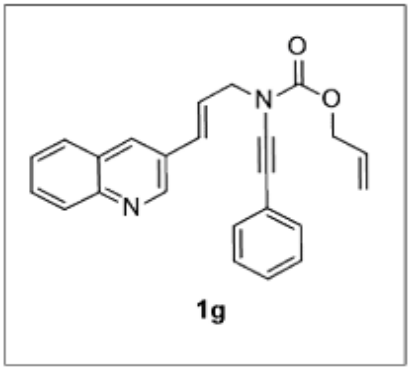
```
Current Data Parameters
NAME                  OJ-2-107-C
EXPNO                         10
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20210622
Time                       13.20 h
INSTRUM                    spect
PROBHD    Z125869_0055 (
PULPROG                 zgpg30
TD                         65536
SOLVENT                    CDCl3
NS                          1024
DS                             4
SWH                    29761.904 Hz
FIDRES                 0.908261 Hz
AQ                     1.1010048 sec
RG                        190.44
DW                        16.800 usec
DE                        18.00 usec
TE                        300.0 K
D1                     2.00000000 sec
D11                    0.03000000 sec
TD0                            1
SFO1                 125.7955118 MHz
NUC1                        13C
P0                         3.33 usec
P1                        10.00 usec
PLW1                56.90299988 W
SFO2                 500.2320009 MHz
NUC2                        1H
CPDPRG[2                waltz16
PCPD2                     80.00 usec
PLW2                11.44699955 W
PLW12                0.25756001 W
PLW13                0.12955000 W

F2 - Processing parameters
SI                         32768
SF                   125.7829335 MHz
WDW                           EM
SSB                            0
LB                         1.00 Hz
GB                             0
PC                          1.40
```

^{13}C NMR spectrum of **1f**



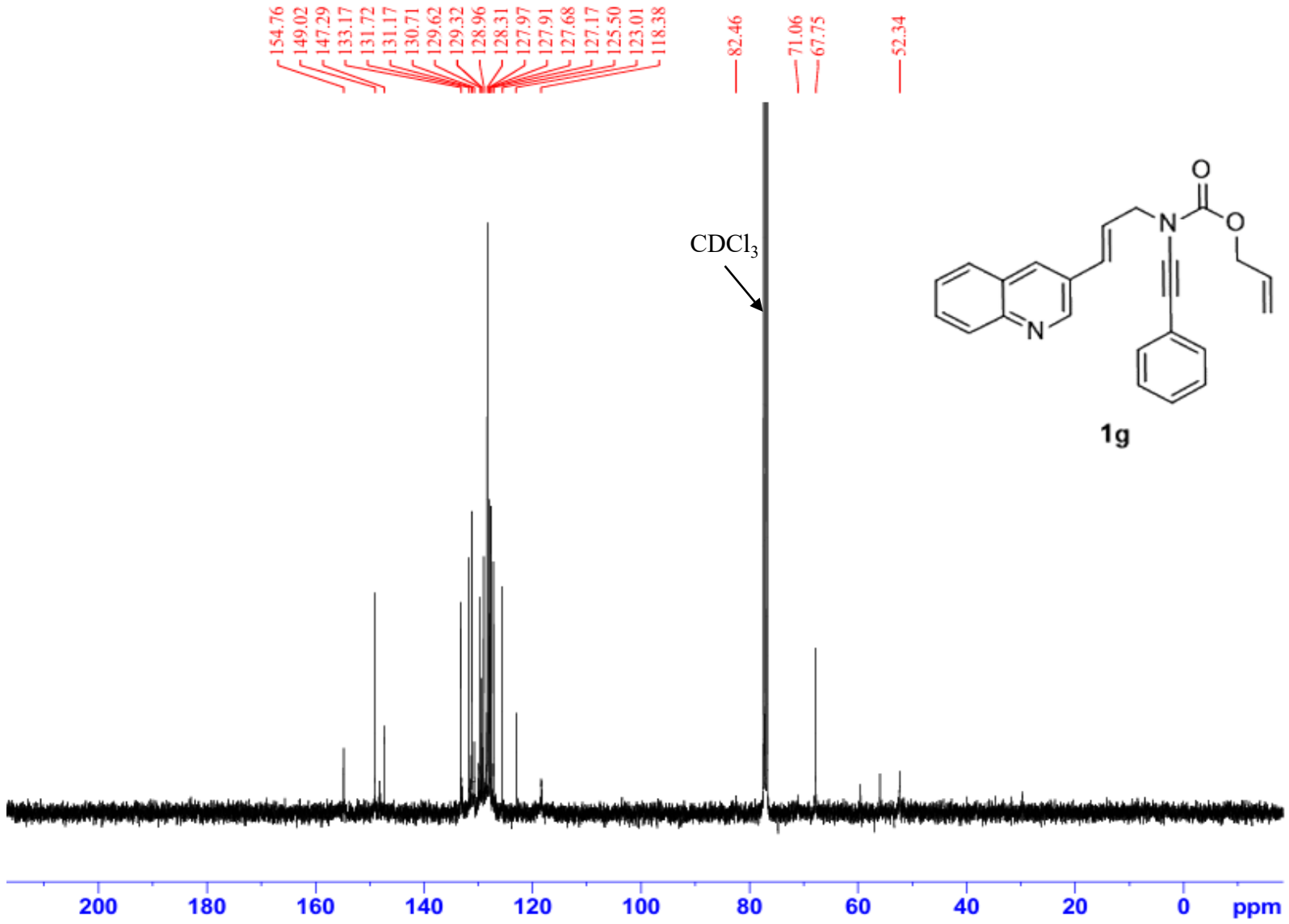



```
Current Data Parameters
NAME          OJ-1g-vac-H
EXPNO                  16
PROCNO                  1

F2 - Acquisition Parameters
Date_            20220312
Time               17.48 h
INSTRUM       Avance Neo
PROBHD    Z152088_0031 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8196.722 Hz
FIDRES          0.250144 Hz
AQ              3.9976959 sec
RG                   101
DW                61.000 usec
DE                13.89 usec
TE                298.0 K
D1             1.00000000 sec
TD0                    1
SFO1          400.1324708 MHz
NUC1                  1H
P0                 2.67 usec
P1                 8.00 usec
PLW1          24.03499985 W

F2 - Processing parameters
SI                 65536
SF            400.1300067 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

[1]H NMR spectrum of **1g**

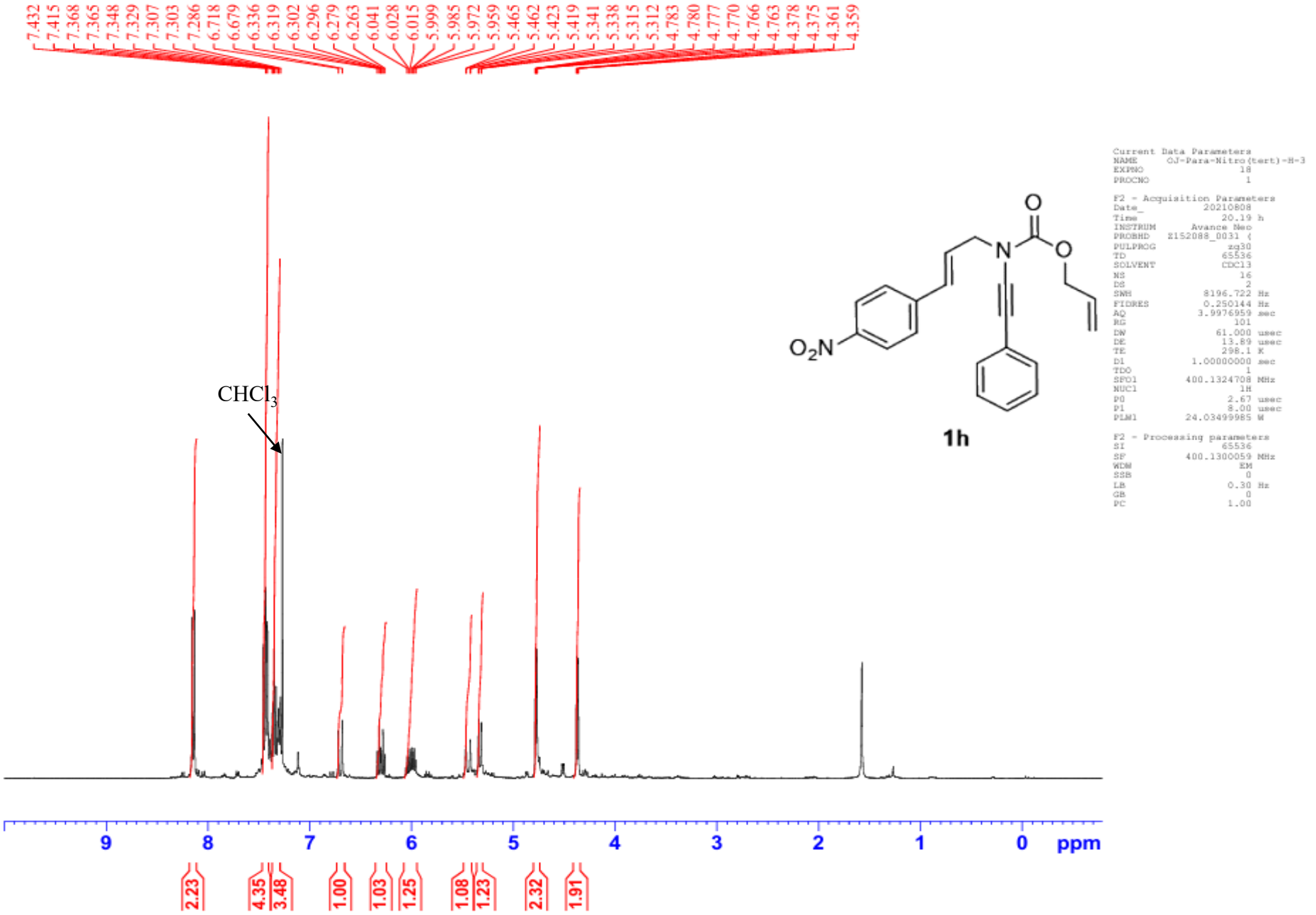


Current Data Parameters
NAME OJ-2-Quinoline ynamide-C
EXPNO 12
PROCNO 1

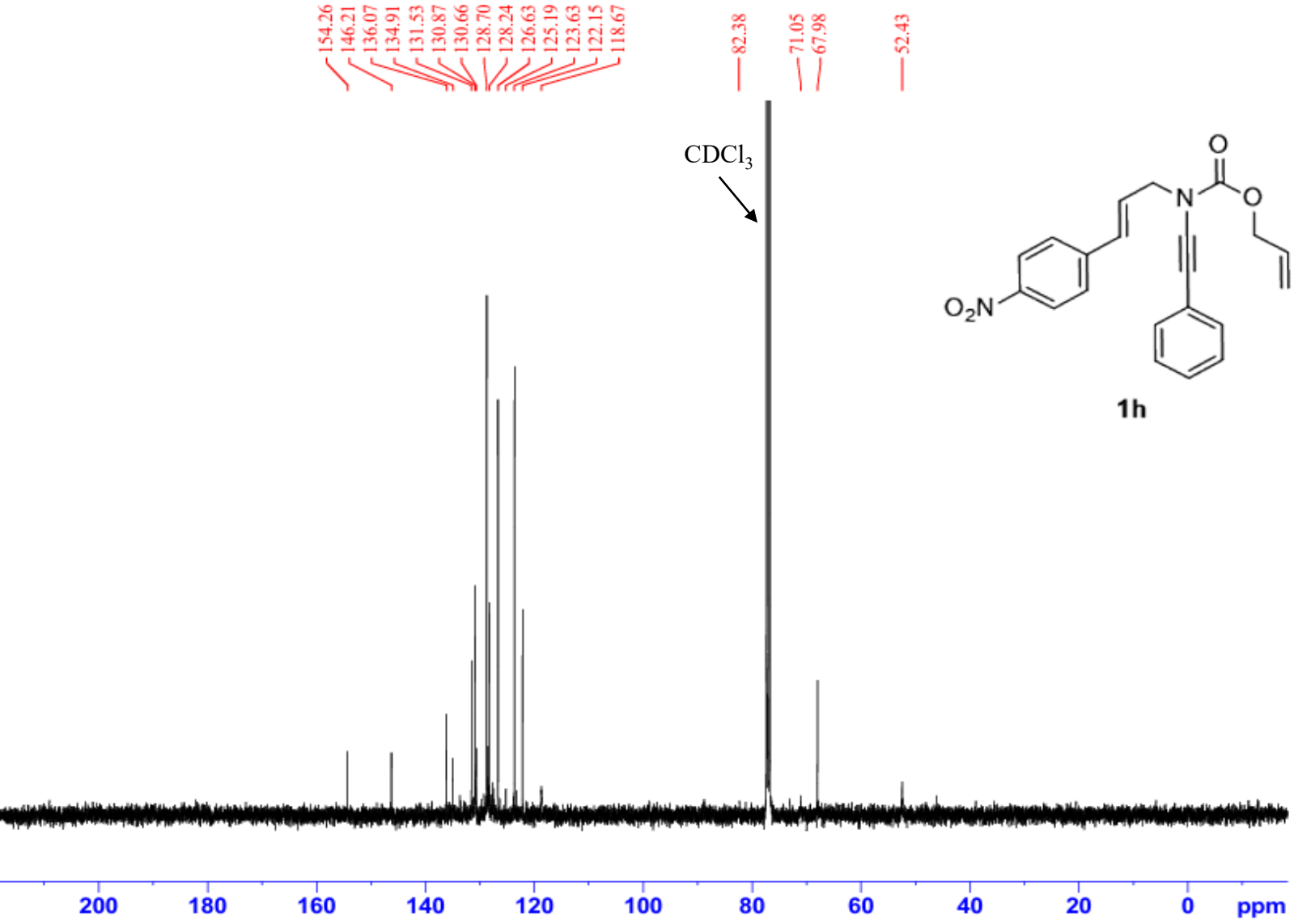
F2 - Acquisition Parameters
Date_ 20210911
Time 2.42 h
INSTRUM Avance Neo
PROBHD 2152088_0031 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 23809.523 Hz
FIDRES 0.726609 Hz
AQ 1.3762560 sec
RG 8.125
DW 21.000 usec
DE 6.50 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 100.6228298 MHz
NUC1 13C
P0 2.67 usec
P1 8.00 usec
PLW1 86.55400085 W
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz65
PCPD2 90.00 usec
PLW2 24.03499985 W
PLW12 0.18990999 W
PLW13 0.09552100 W

F2 - Processing parameters
SI 32768
SF 100.6127685 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

^{13}C NMR spectrum of **1g**



[1]H NMR spectrum of **1h**

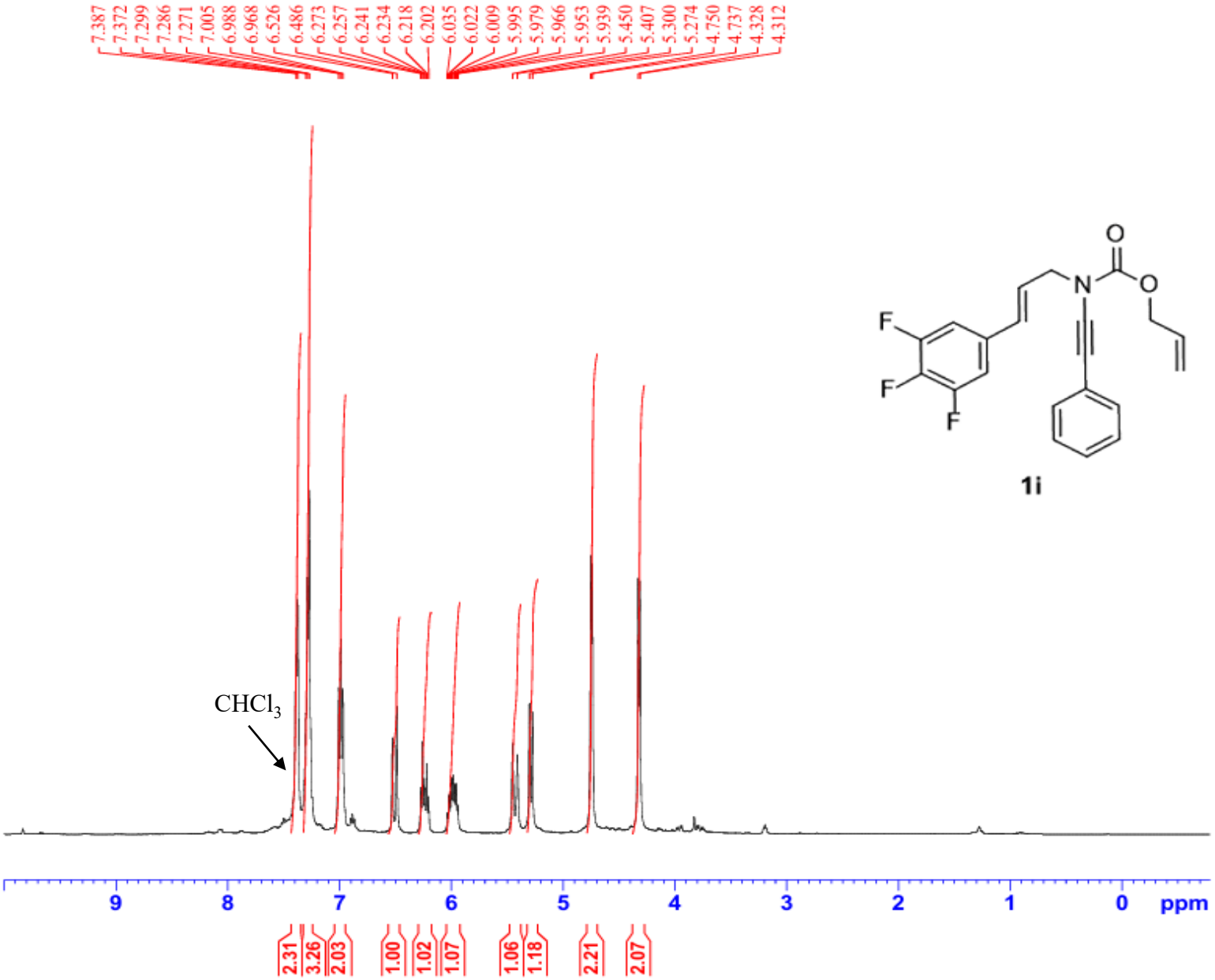



```
Current Data Parameters
NAME      OJ-Para-Nitro(tert)-C-3
EXPNO                          20
PROCNO                          1

F2 - Acquisition Parameters
Date_                    20210808
Time                        21.20 h
INSTRUM                Avance Neo
PROBHD    2152088_0031 (
PULPROG                  zgpg30
TD                            65536
SOLVENT                     CDCl3
NS                             1024
DS                                4
SWH                     23809.523 Hz
FIDRES                  0.726609 Hz
AQ                      1.3762560 sec
RG                            8.125
DW                           21.000 usec
DE                            6.50 usec
TE                          298.1 K
D1                      2.00000000 sec
D11                     0.03000000 sec
TD0                               1
SFO1                  100.6228298 MHz
NUC1                          13C
P0                            2.67 usec
P1                            8.00 usec
PLW1                  86.55400085 W
SFO2                  400.1316005 MHz
NUC2                          1H
CPDPRG[2                  waltz65
PCPD2                        90.00 usec
PLW2                  24.03499985 W
PLW12                 0.18990999 W
PLW13                 0.09552100 W

F2 - Processing parameters
SI                            32768
SF                    100.6127685 MHz
WDW                             EM
SSB                              0
LB                            1.00 Hz
GB                               0
PC                            1.40
```


^{13}C NMR spectrum of **1h**



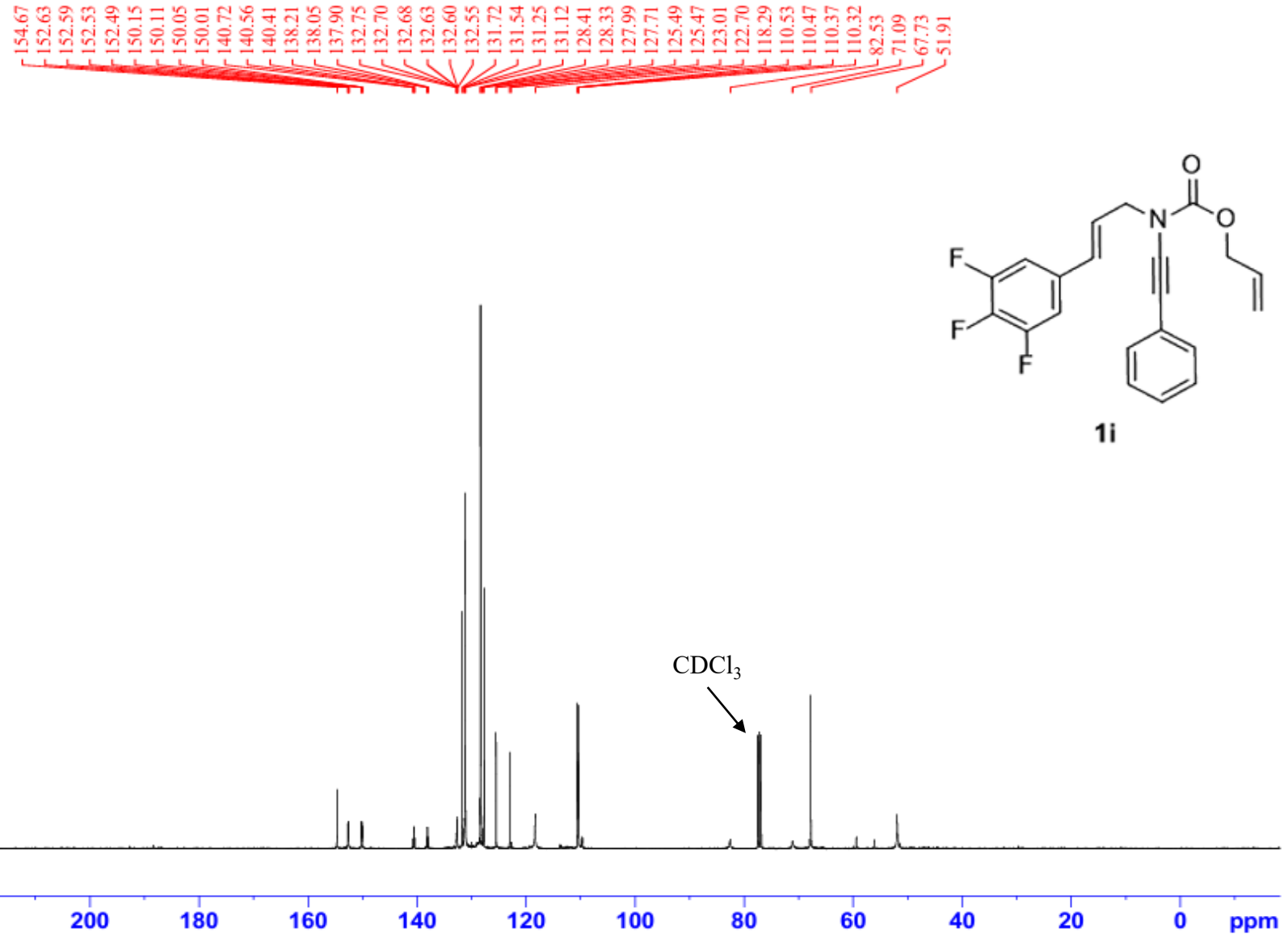
1i

```
Current Data Parameters
NAME                  OJ-2-116-H
EXPNO                          7
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20210705
Time                       15.28 h
INSTRUM                Avance Neo
PROBHD    Z152088_0031 (
PULPROG                     zg30
TD                         65536
SOLVENT                    CDCl3
NS                            16
DS                             2
SWH                     8196.722 Hz
FIDRES                  0.250144 Hz
AQ                      3.9976959 sec
RG                            32
DW                         61.000 usec
DE                         13.89 usec
TE                         298.0 K
D1                     1.00000000 sec
TD0                            1
SFO1                400.1324708 MHz
NUC1                          1H
P0                         2.67 usec
P1                         8.00 usec
PLW1                24.03499985 W

F2 - Processing parameters
SI                         65536
SF                  400.1300115 MHz
WDW                           EM
SSB                            0
LB                          0.30 Hz
GB                             0
PC                          1.00
```

[1]H NMR spectrum of **1i**

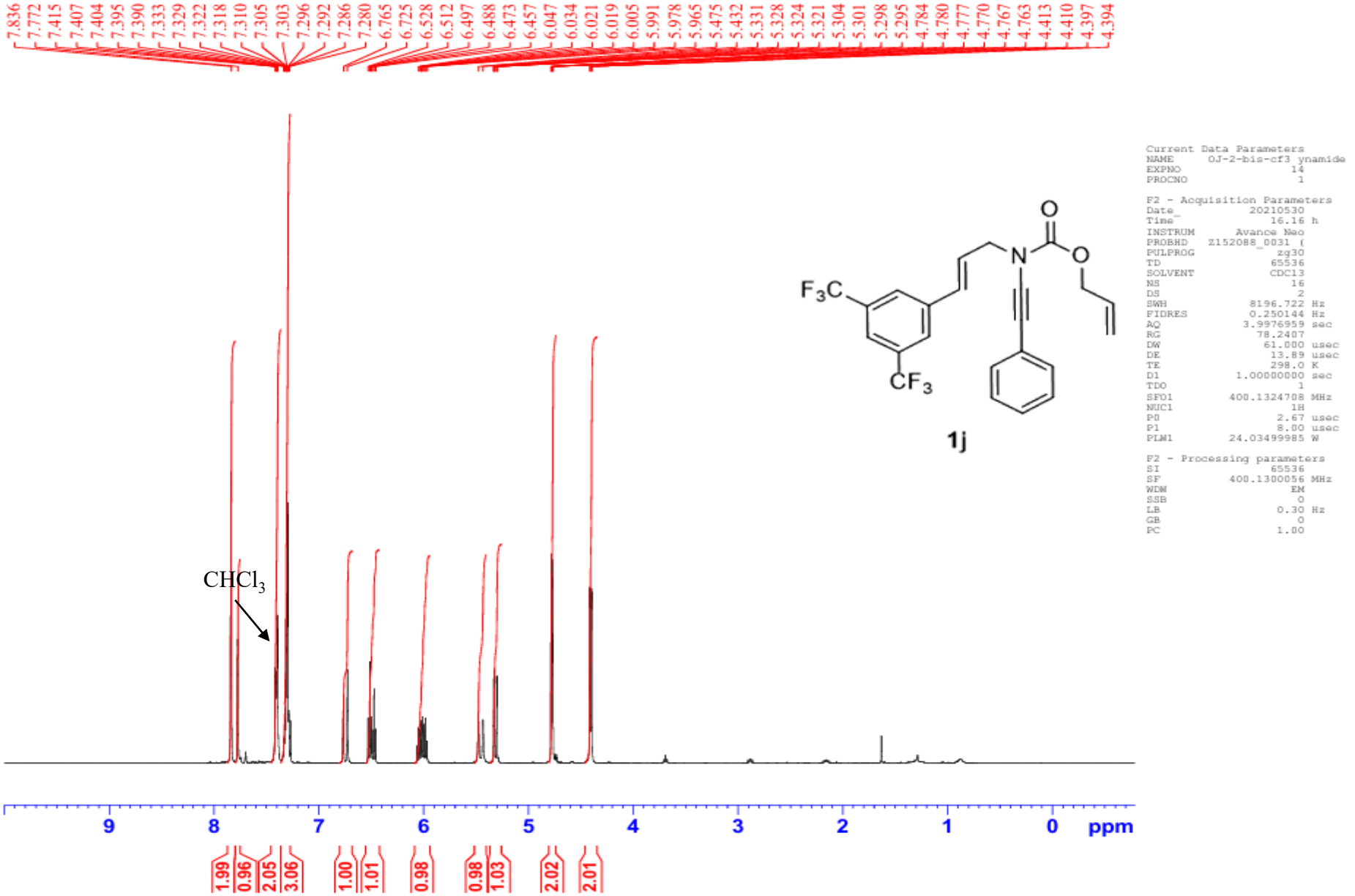



```
Current Data Parameters
NAME          OJ-2-116-C
EXPNO                  9
PROCNO                 1

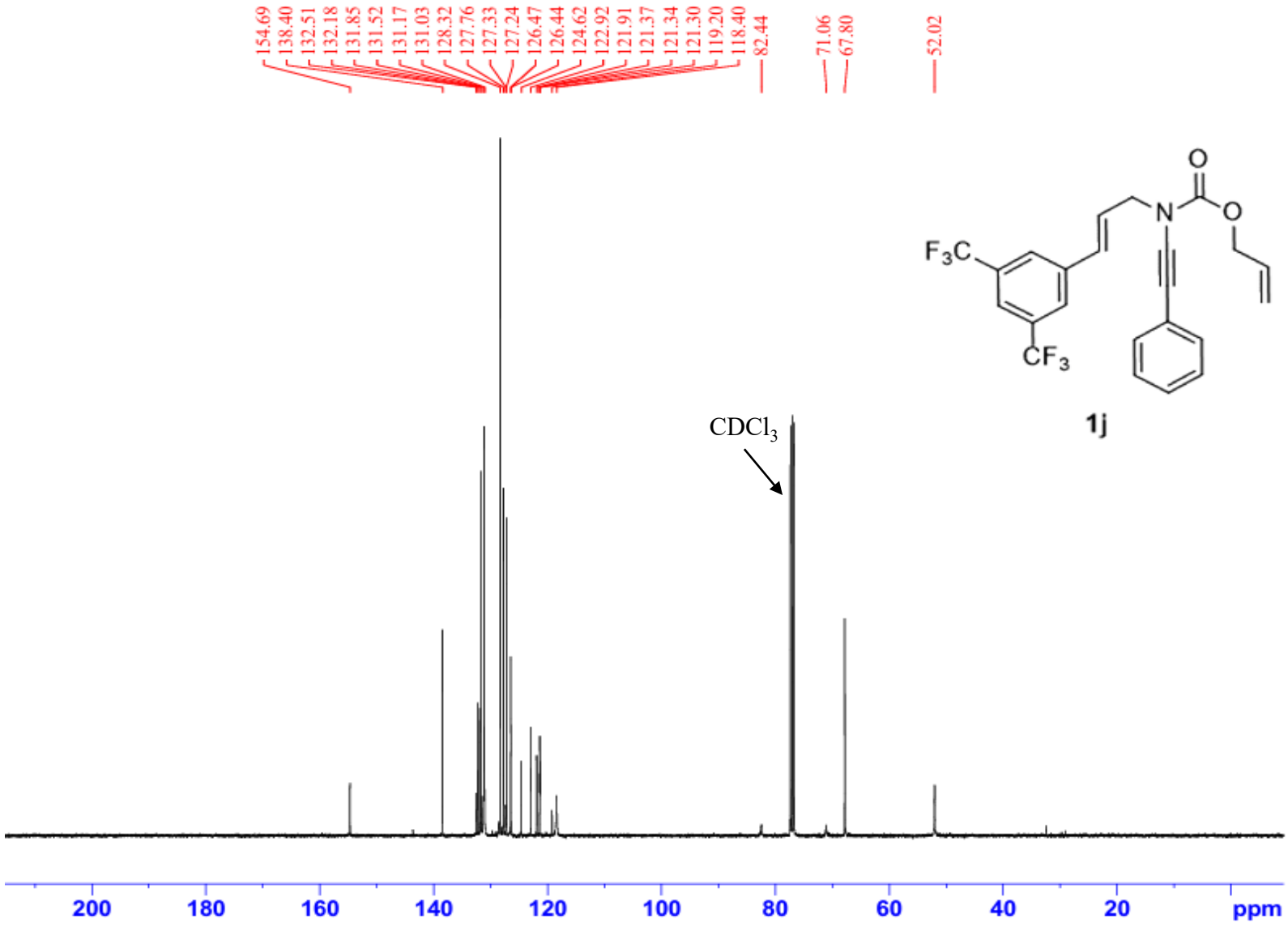
F2 - Acquisition Parameters
Date_          20210705
Time_             16.30 h
INSTRUM       Avance Neo
PROBHD    Z152088_0031 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           23809.523 Hz
FIDRES        0.726609 Hz
AQ            1.3762560 sec
RG               12.5744
DW               21.000 usec
DE                6.50 usec
TE                298.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1
SFO1         100.6228298 MHz
NUC1                13C
P0                2.67 usec
P1                8.00 usec
PLW1         86.55400085 W
SFO2         400.1316005 MHz
NUC2                1H
CPDPRG[2         waltz65
PCPD2            90.00 usec
PLW2         24.03499985 W
PLW12         0.18990999 W
PLW13         0.09552100 W

F2 - Processing parameters
SI                 32768
SF           100.6127685 MHz
WDW                   EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

^{13}C NMR spectrum of **1i**



[1]H NMR spectrum of **1j**

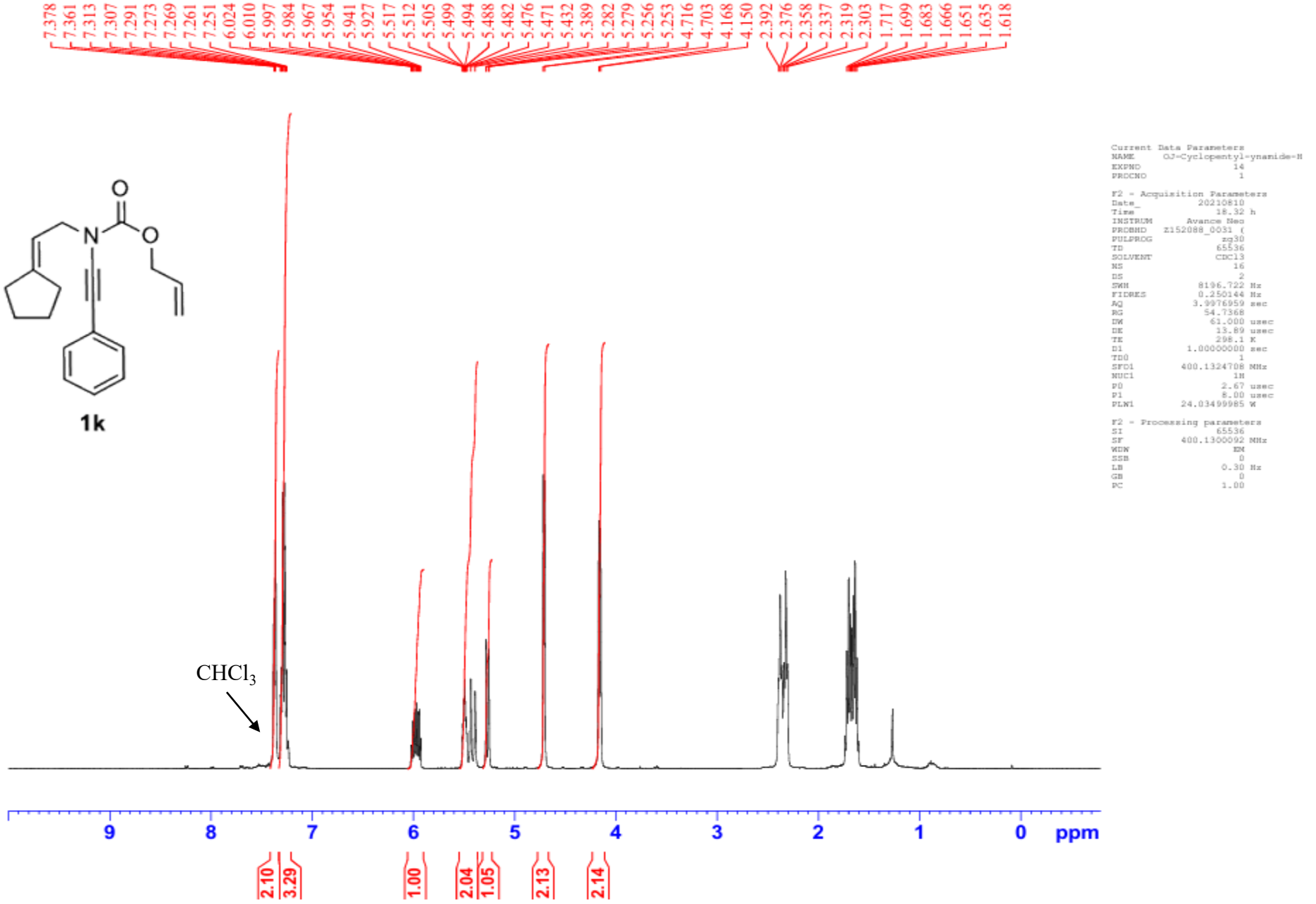



```
Current Data Parameters
NAME      OJ-2-bis-cf3 ynamide-C
EXPNO                 16
PROCNO                 1

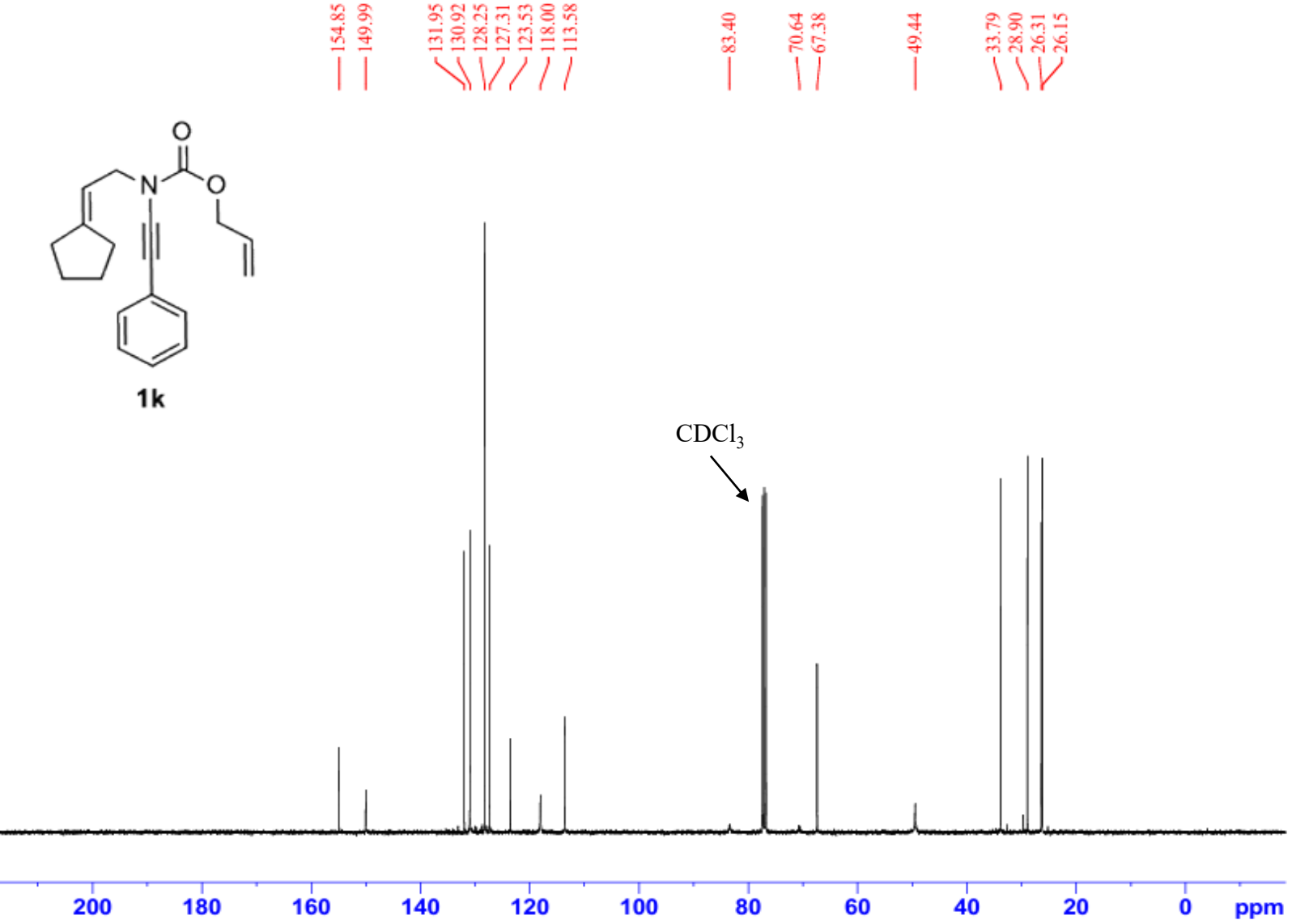
F2 - Acquisition Parameters
Date_           20210530
Time              17.29 h
INSTRUM       Avance Neo
PROBHD    Z152088_0031 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           23809.523 Hz
FIDRES        0.726609 Hz
AQ            1.3762560 sec
RG                8.125
DW               21.000 usec
DE                6.50 usec
TE                298.1 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1        100.6228298 MHz
NUC1                13C
P0                 2.67 usec
P1                 8.00 usec
PLW1        86.55400085 W
SFO2        400.1316005 MHz
NUC2                1H
CPDPRG[2         waltz65
PCPD2             90.00 usec
PLW2        24.03499985 W
PLW12        0.18990999 W
PLW13        0.09552100 W

F2 - Processing parameters
SI                32768
SF          100.6127685 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

^{13}C NMR spectrum of **1j**



^{1}H NMR spectrum of **1k**

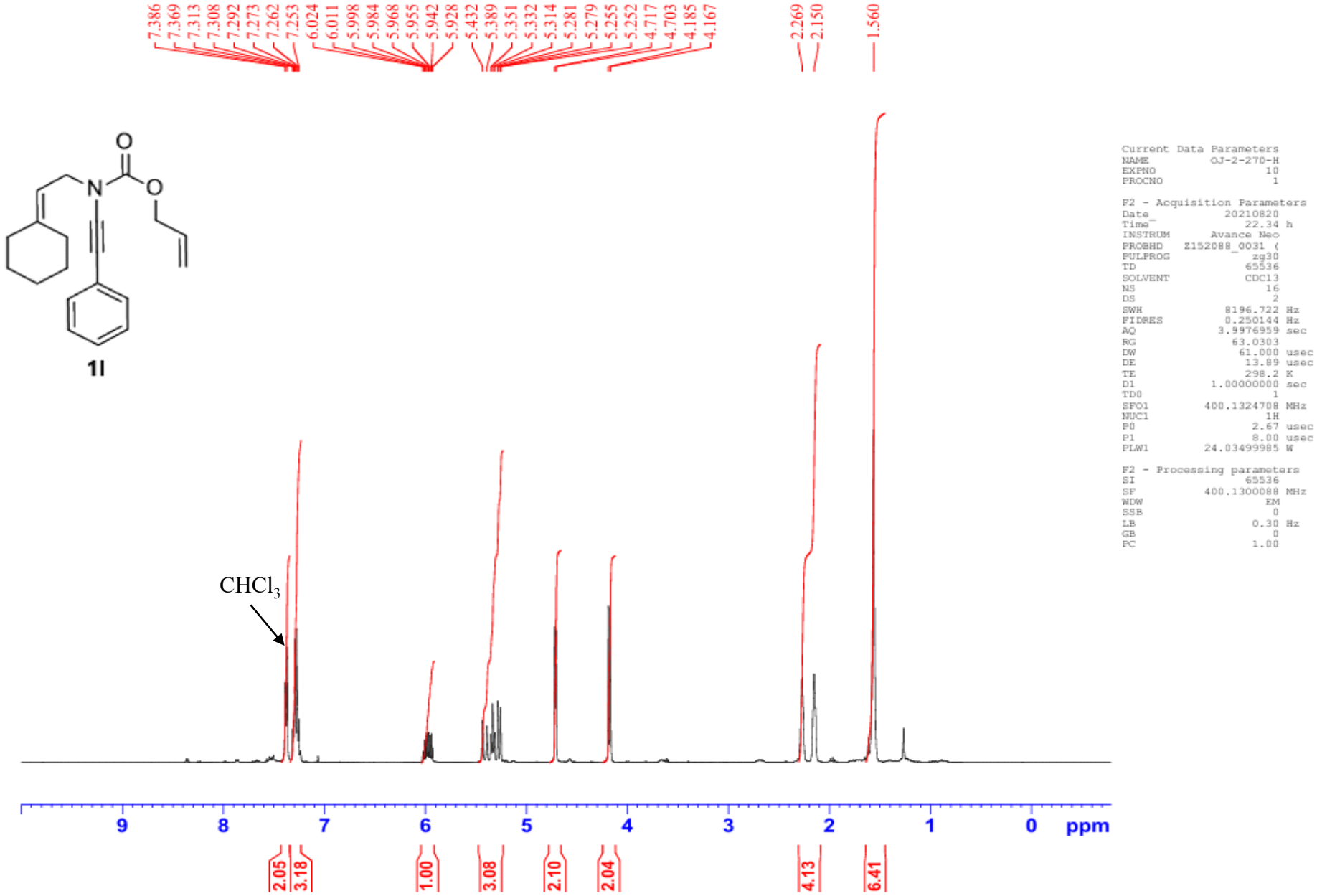



```
Current Data Parameters
NAME      OJ-Cyclopentyl-ynamide-C
EXPNO                 16
PROCNO                 1

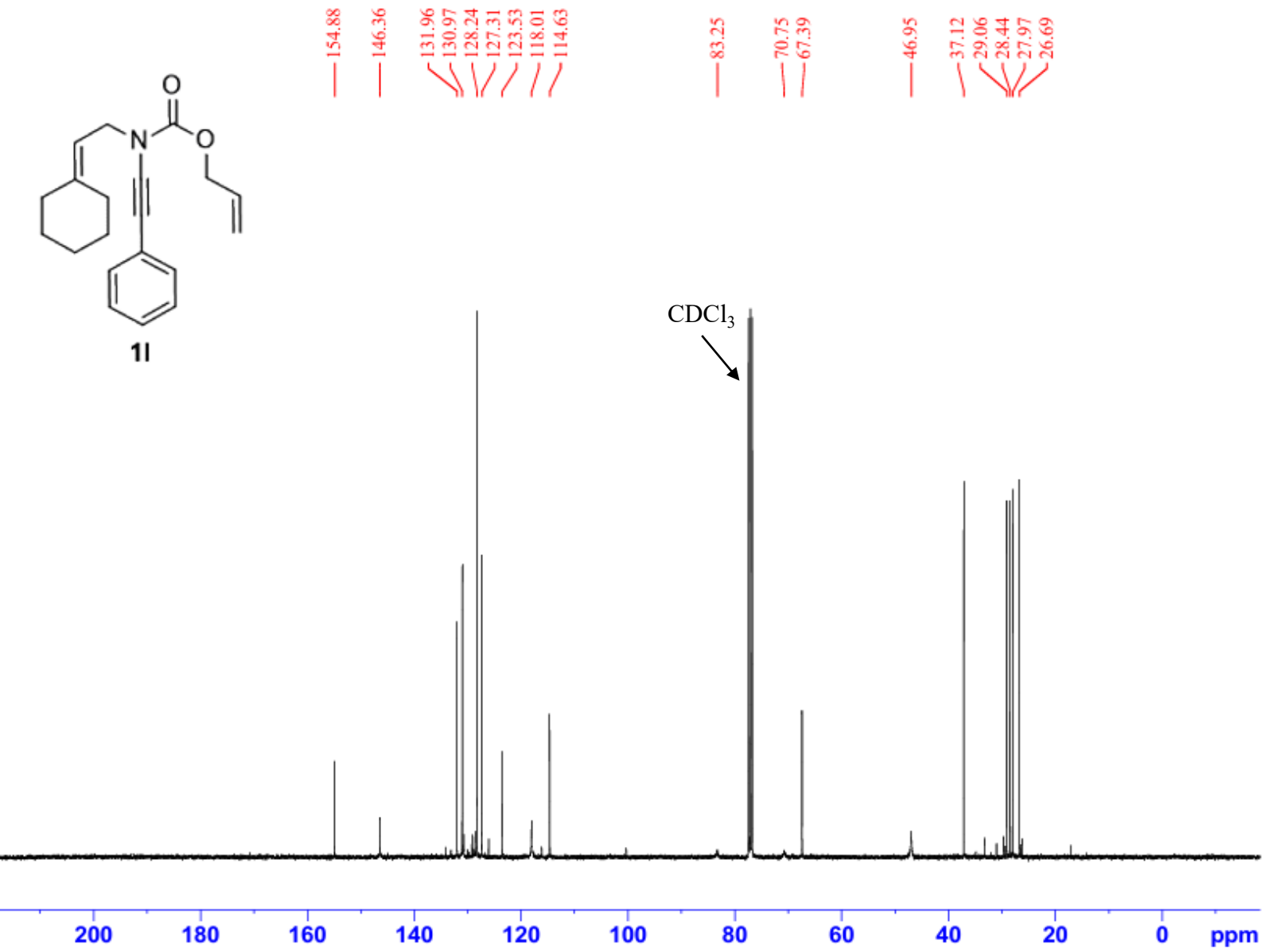
F2 - Acquisition Parameters
Date_           20210810
Time              19.15 h
INSTRUM       Avance Neo
PROBHD   2152088_0031 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  538
DS                    4
SWH           23809.523 Hz
FIDRES        0.726609 Hz
AQ            1.3762560 sec
RG                8.125
DW               21.000 usec
DE                6.50 usec
TE              298.1 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1        100.6228298 MHz
NUC1               13C
P0                2.67 usec
P1                8.00 usec
PLW1        86.55400085 W
SFO2        400.1316005 MHz
NUC2               1H
CPDPRG[2         waltz65
PCPD2             90.00 usec
PLW2        24.03499985 W
PLW12        0.18990999 W
PLW13        0.09552100 W

F2 - Processing parameters
SI                32768
SF          100.6127685 MHz
WDW                EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

^{13}C NMR spectrum of **1k**



^{1}H NMR spectrum of **1l**

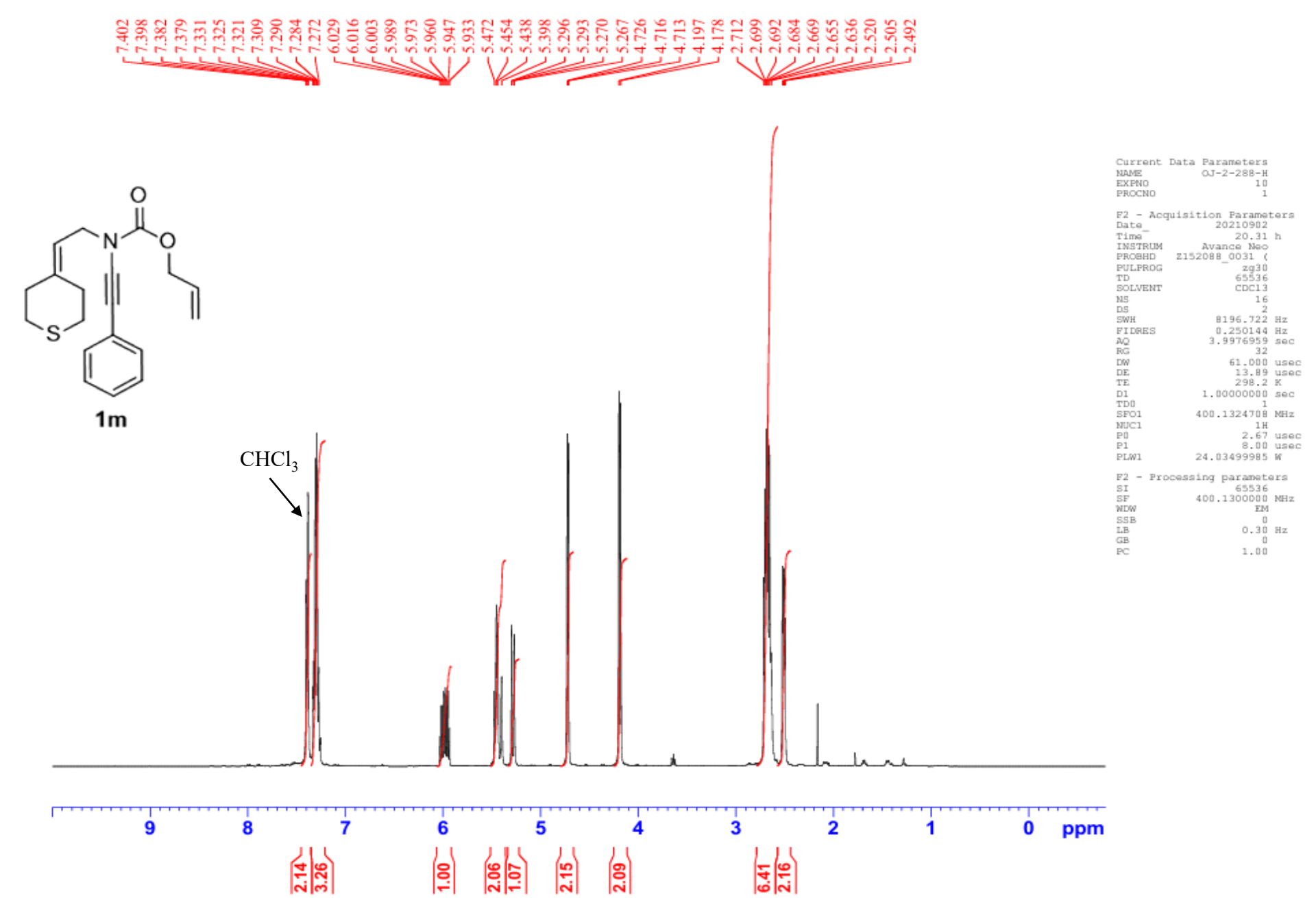



```
Current Data Parameters
NAME                  OJ-2-270-C
EXPNO                         12
PROCNO                         1

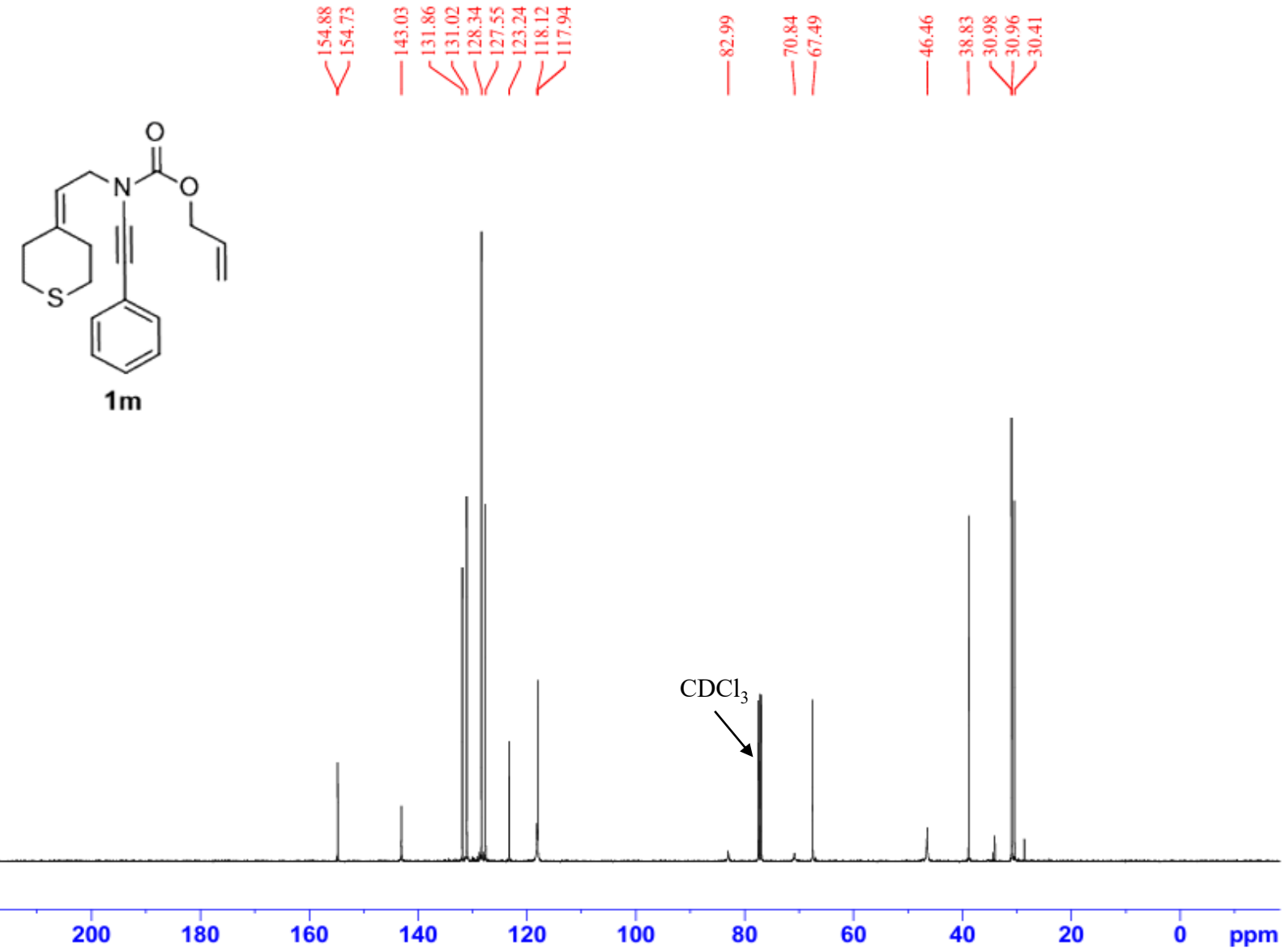
F2 - Acquisition Parameters
Date_                   20210821
Time_                       1.47 h
INSTRUM               Avance Neo
PROBHD           Z152088_0031 (
PULPROG                  zgpg30
TD                            65536
SOLVENT                     CDCl3
NS                             1024
DS                                4
SWH                   23809.523 Hz
FIDRES                 0.726609 Hz
AQ                     1.3762560 sec
RG                             8.125
DW                            21.000 usec
DE                             6.50 usec
TE                           298.1 K
D1                     2.00000000 sec
D11                    0.03000000 sec
TD0                               1
SFO1                 100.6228298 MHz
NUC1                         13C
P0                             2.67 usec
P1                             8.00 usec
PLW1                86.55400085 W
SFO2                 400.1316005 MHz
NUC2                         1H
CPDPRG[2                 waltz65
PCPD2                         90.00 usec
PLW2                24.03499985 W
PLW12                0.18990999 W
PLW13                0.09552100 W

F2 - Processing parameters
SI                            32768
SF                   100.6127685 MHz
WDW                           EM
SSB                               0
LB                             1.00 Hz
GB                                0
PC                             1.40
```

^{13}C NMR spectrum of **1l**



^{1}H NMR spectrum of **1m**

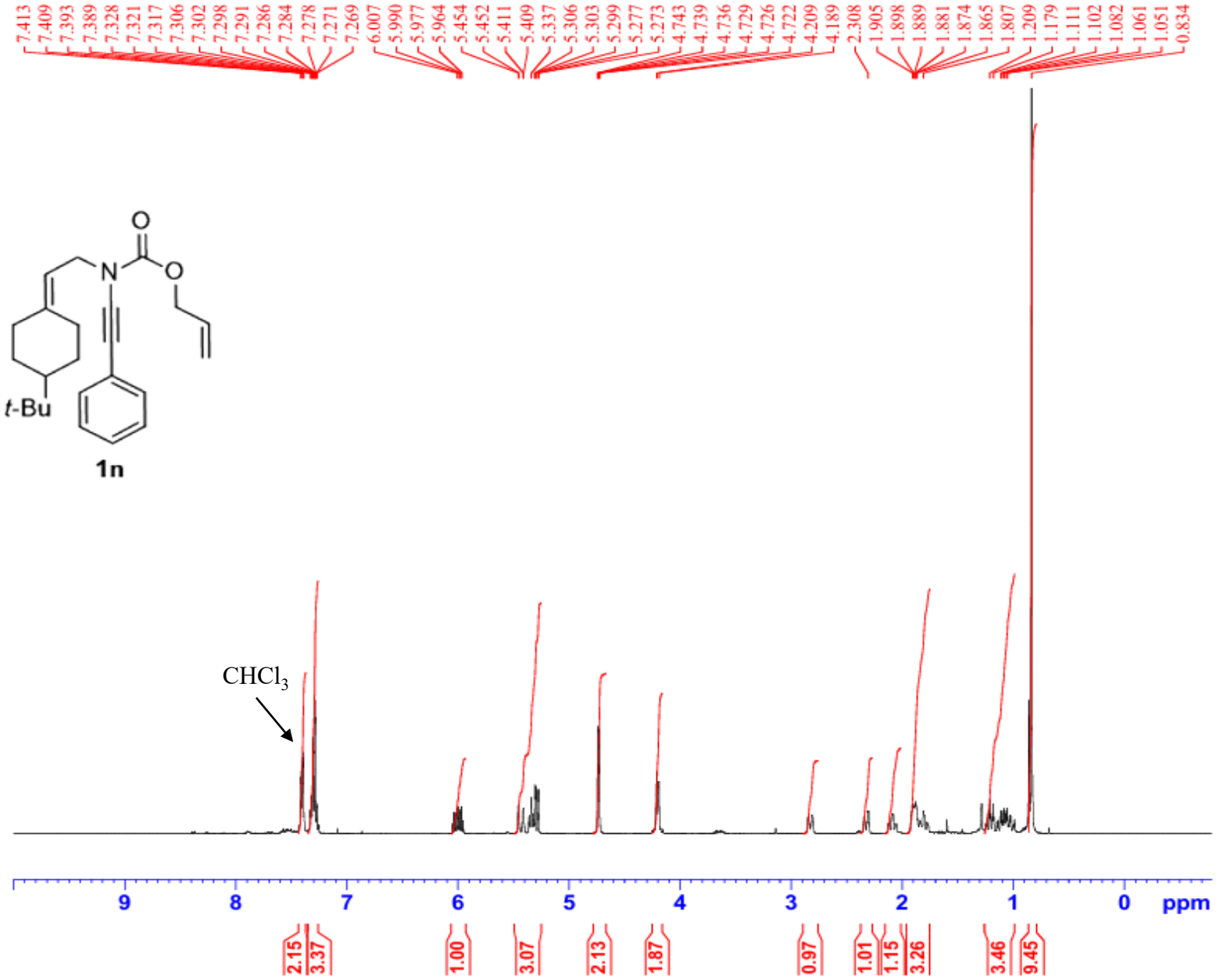



```
Current Data Parameters
NAME                  OJ-2-288-C
EXPNO                         12
PROCNO                         1

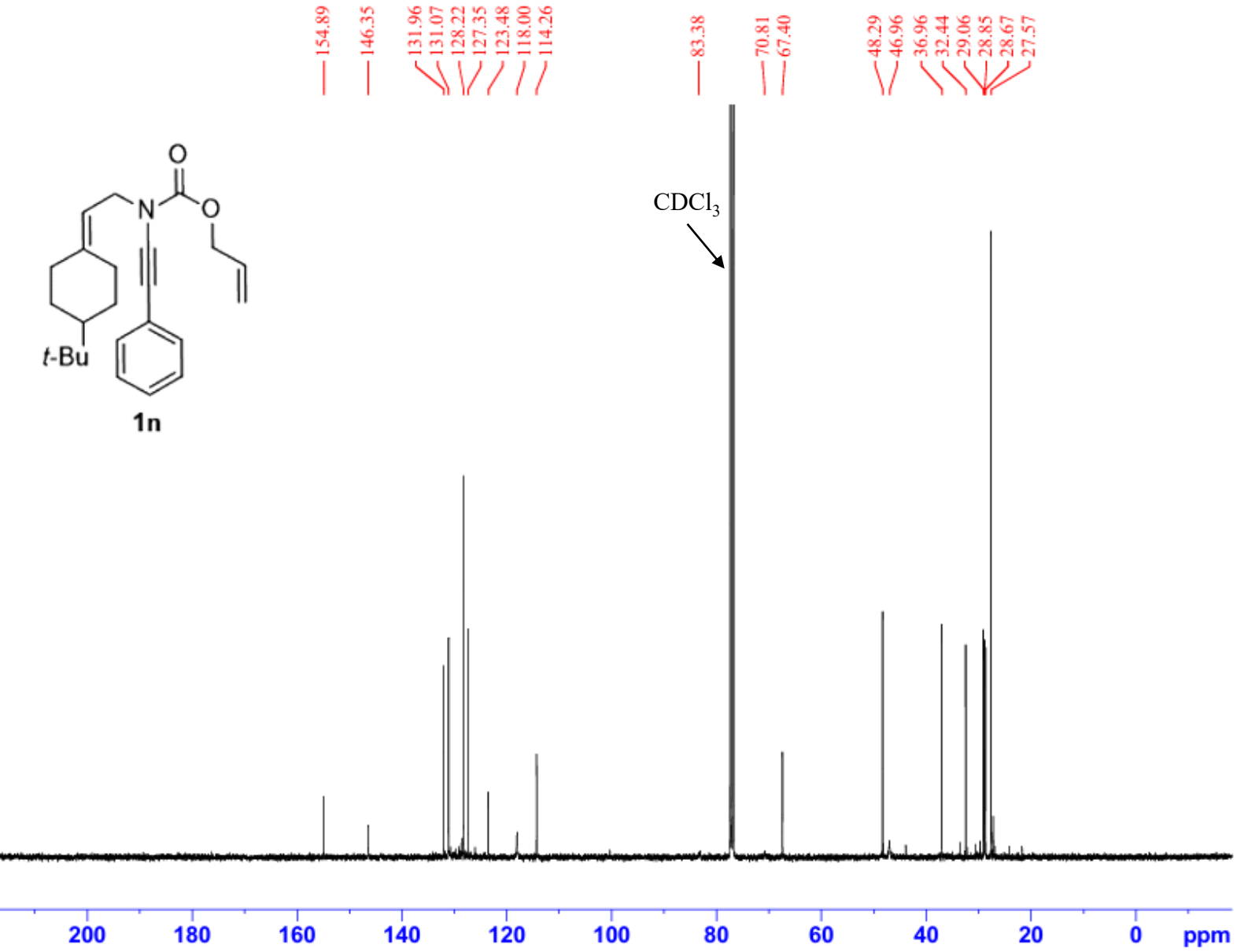
F2 - Acquisition Parameters
Date_                   20210902
Time                       21.31 h
INSTRUM                Avance Neo
PROBHD          Z152088_0031 (
PULPROG                  zgpg30
TD                        65536
SOLVENT                   CDCl3
NS                         1024
DS                            4
SWH                    23809.523 Hz
FIDRES                 0.726609 Hz
AQ                     1.3762560 sec
RG                         8.125
DW                        21.000 usec
DE                         6.50 usec
TE                        298.2 K
D1                     2.00000000 sec
D11                    0.03000000 sec
TD0                           1
SFO1                 100.6228298 MHz
NUC1                         13C
P0                         2.67 usec
P1                         8.00 usec
PLW1                86.55400085 W
SFO2                400.1316005 MHz
NUC2                         1H
CPDPRG[2                waltz65
PCPD2                     90.00 usec
PLW2                24.03499985 W
PLW12                0.18990999 W
PLW13                0.09552100 W

F2 - Processing parameters
SI                        32768
SF                  100.6127685 MHz
WDW                          EM
SSB                           0
LB                         1.00 Hz
GB                            0
PC                         1.40
```

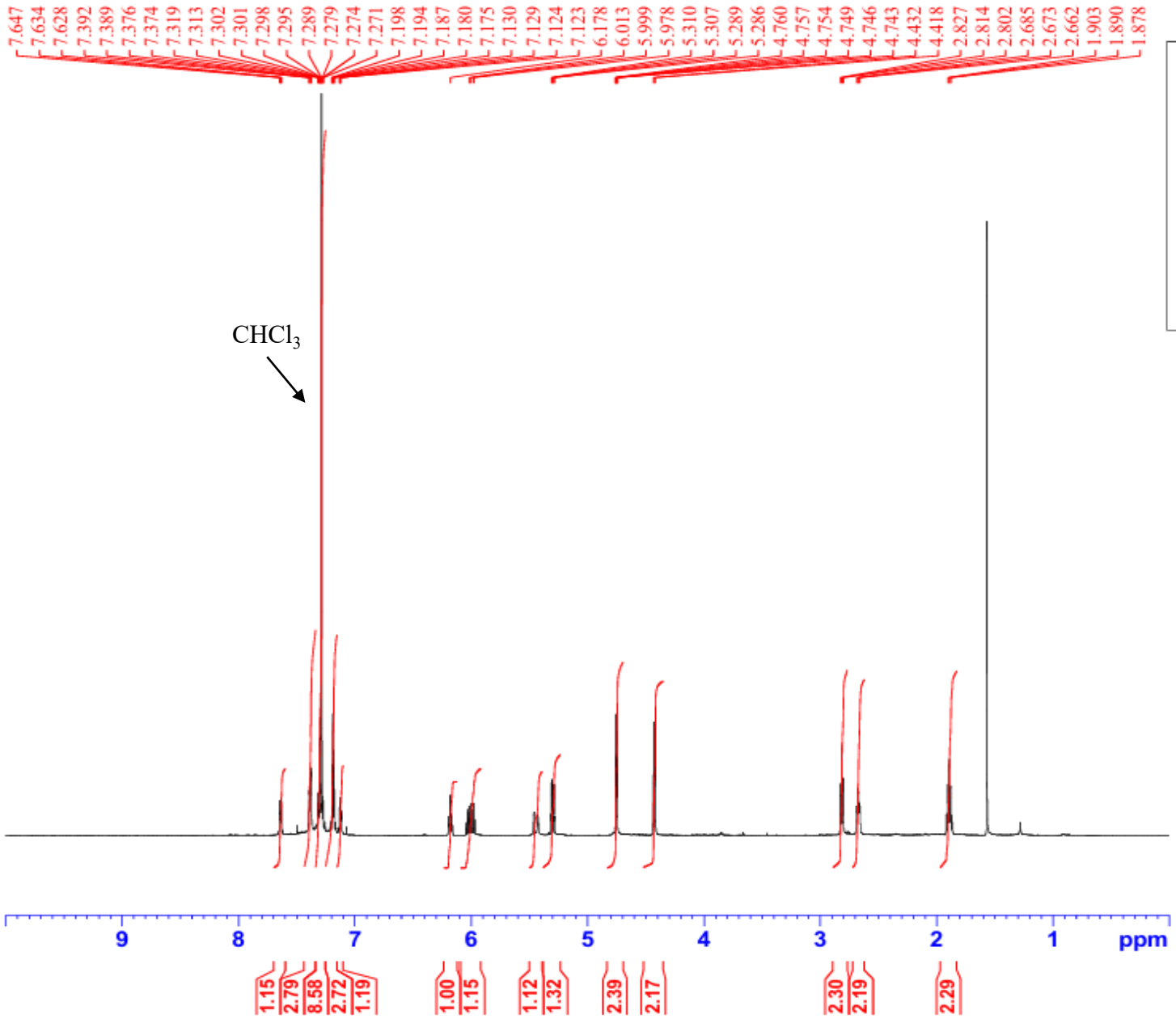
^{13}C NMR spectrum of **1m**

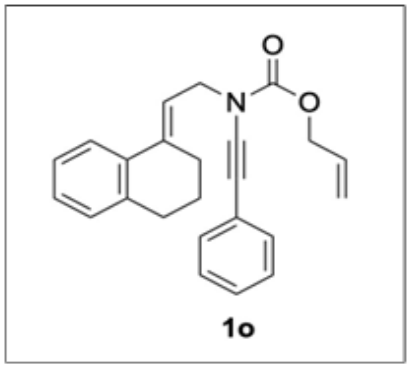


^{1}H NMR spectrum of **1n**



^{13}C NMR spectrum of **1n**



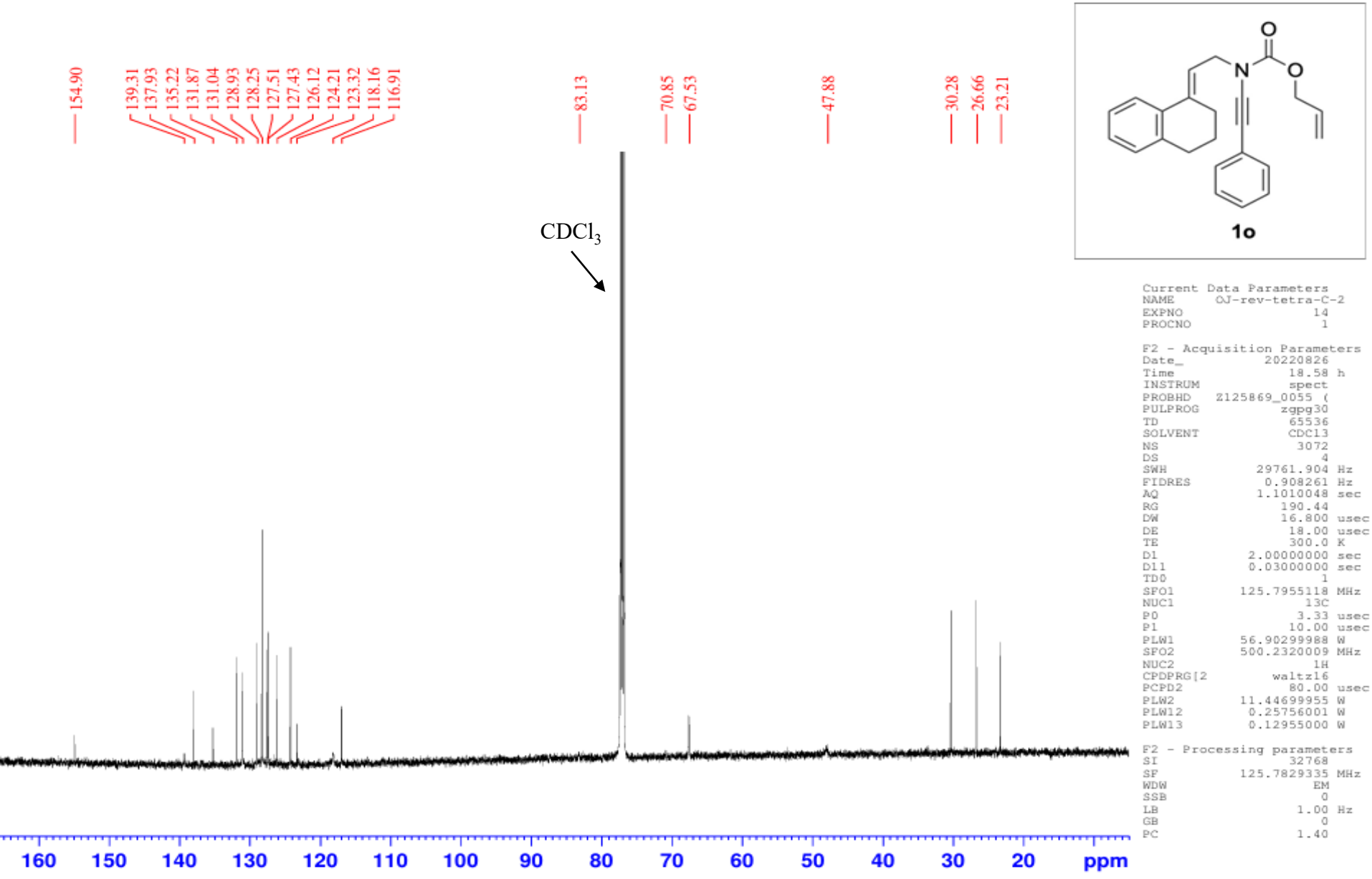



```
Current Data Parameters
NAME          OJ-rev-tetra
EXPNO                   10
PROCNO                   1

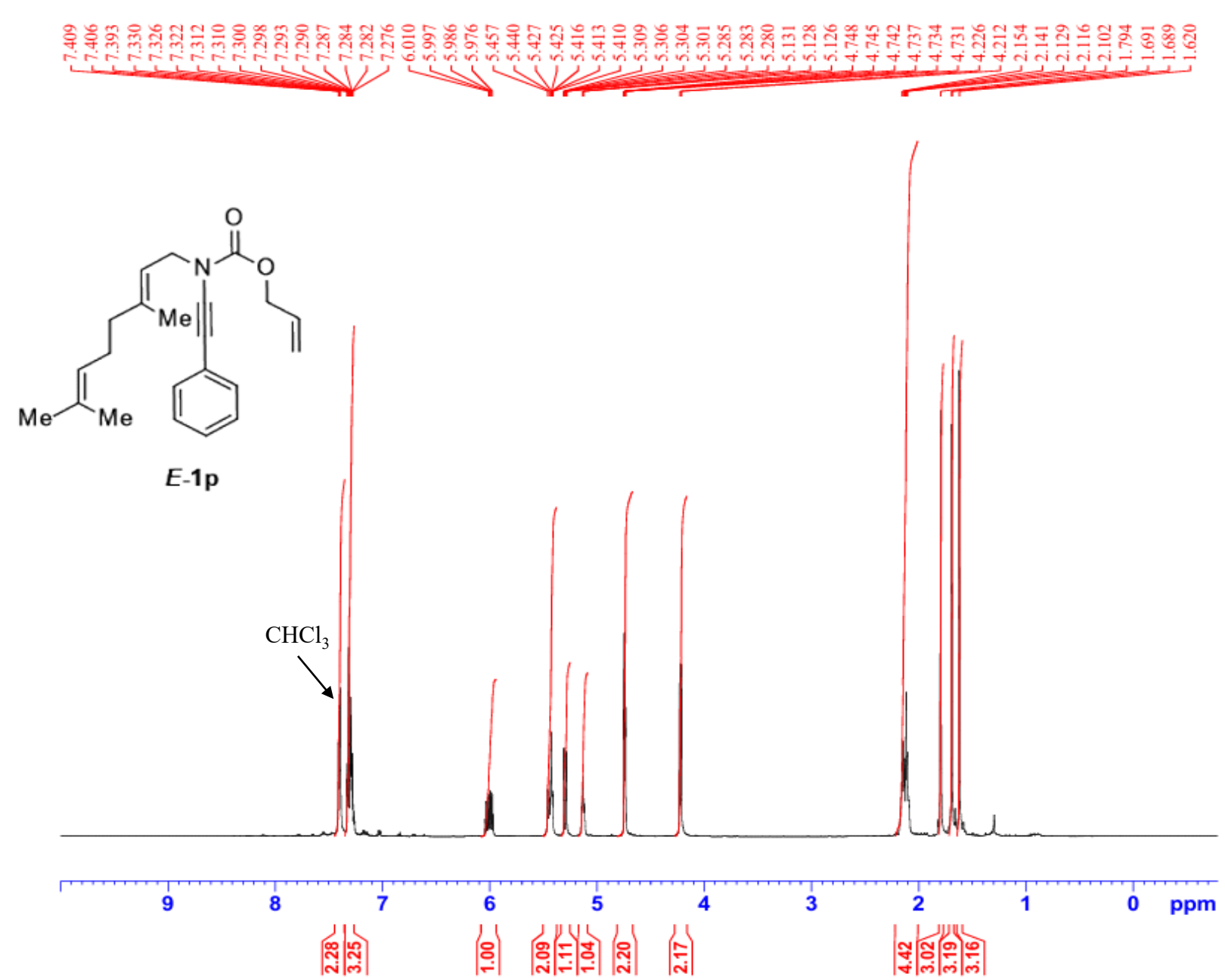
F2 - Acquisition Parameters
Date_              20220825
Time                 23.21 h
INSTRUM                spect
PROBHD    Z125869_0055 (
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       64
DS                        2
SWH               10000.000 Hz
FIDRES                0.305176 Hz
AQ                3.2767999 sec
RG                     151.18
DW                     50.000 usec
DE                     16.00 usec
TE                     300.0 K
D1                2.00000000 sec
TD0                       1
SFO1           500.2330889 MHz
NUC1                      1H
P0                     4.00 usec
P1                    12.00 usec
PLW1          11.44699955 W

F2 - Processing parameters
SI                    65536
SF             500.2300000 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```

[1]H NMR spectrum of **1o**



^{13}C NMR spectrum of **1o**

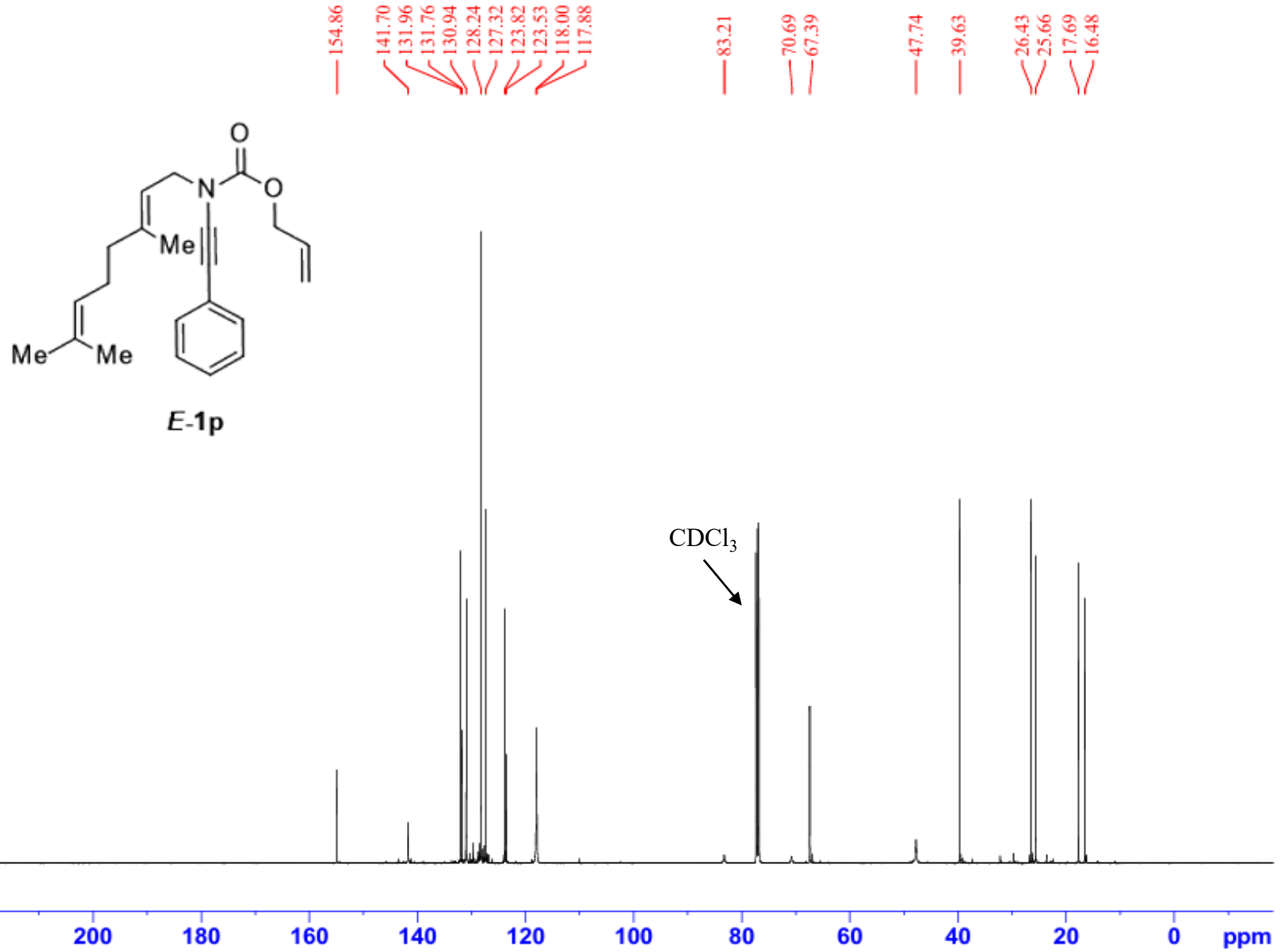



```
Current Data Parameters
NAME                  OJ-2-109
EXPNO                       10
PROCNO                       1

F2 - Acquisition Parameters
Date_               20210622
Time                   13.39 h
INSTRUM                spect
PROBHD    Z125869_0055 (
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                        64
DS                         2
SWH                10000.000 Hz
FIDRES             0.305176 Hz
AQ                 3.2767999 sec
RG                     19.46
DW                    50.000 usec
DE                    16.00 usec
TE                    300.0 K
D1                2.00000000 sec
TD0                        1
SFO1            500.2330889 MHz
NUC1                      1H
P0                     4.00 usec
P1                    12.00 usec
PLW1             11.44699955 W

F2 - Processing parameters
SI                     65536
SF              500.2300000 MHz
WDW                       EM
SSB                        0
LB                    0.30 Hz
GB                         0
PC                     1.00
```

[1]H NMR spectrum of ***E*-1p**

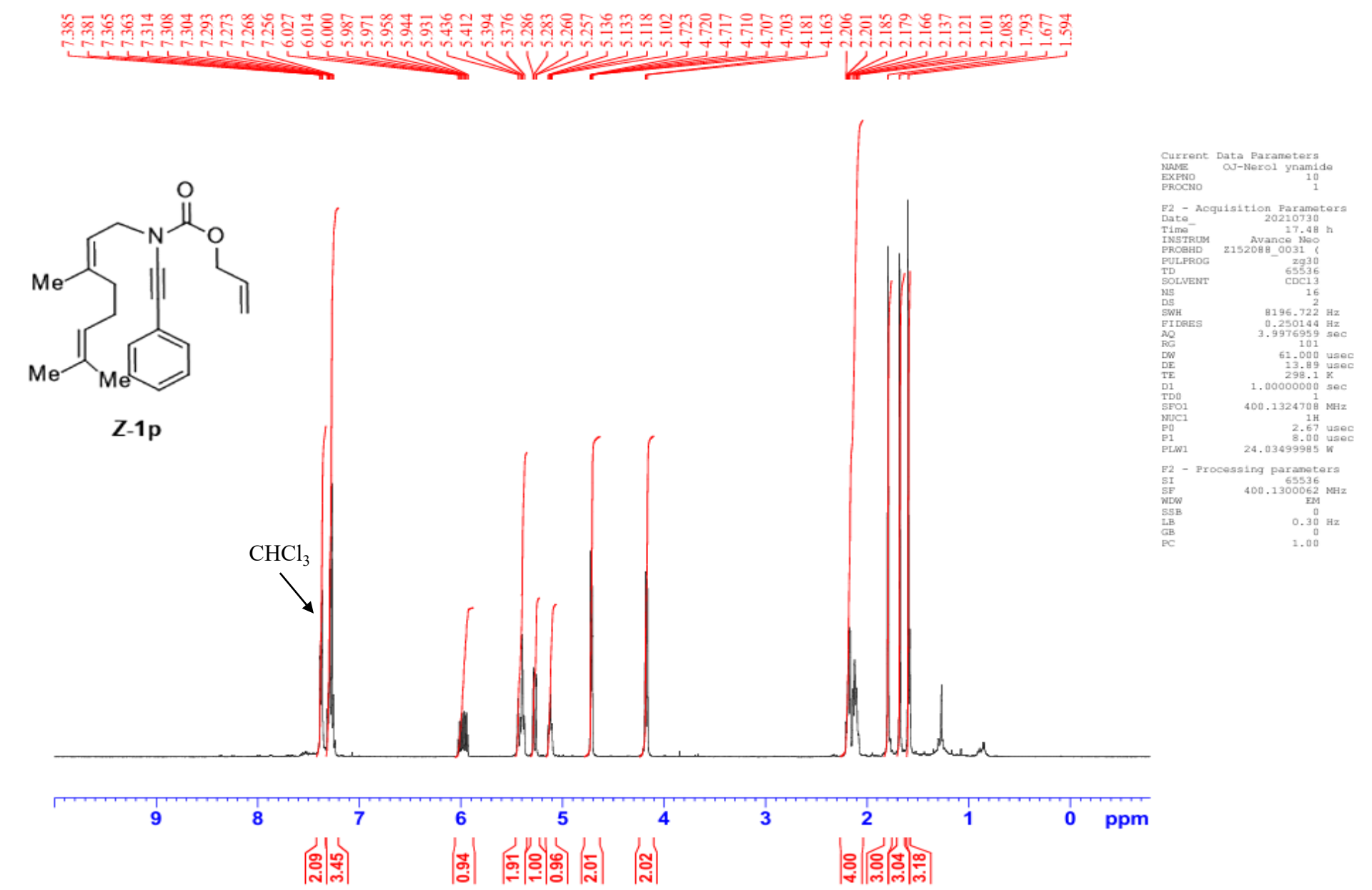



```
Current Data Parameters
NAME                  OJ-2-109-C
EXPNO                         10
PROCNO                         1

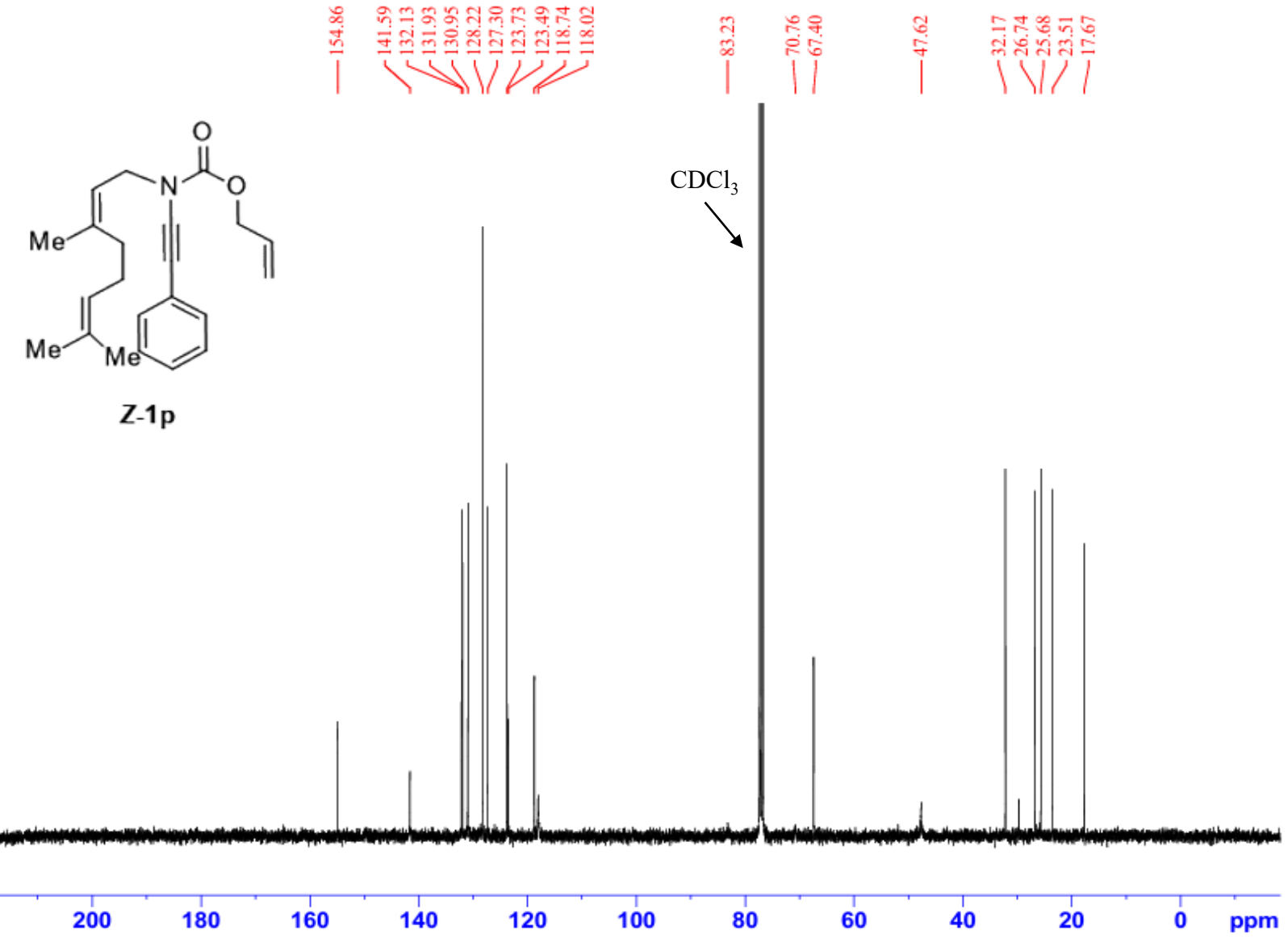
F2 - Acquisition Parameters
Date_                   20210622
Time                       14.35 h
INSTRUM                    spect
PROBHD     Z125869_0055 (
PULPROG                 zgpg30
TD                         65536
SOLVENT                    CDCl3
NS                          1024
DS                             4
SWH                    29761.904 Hz
FIDRES                 0.908261 Hz
AQ                     1.1010048 sec
RG                         190.44
DW                         16.800 usec
DE                         18.00 usec
TE                         300.0 K
D1                     2.00000000 sec
D11                    0.03000000 sec
TD0                            1
SFO1                 125.7955118 MHz
NUC1                        13C
P0                          3.33 usec
P1                         10.00 usec
PLW1                56.90299988 W
SFO2                 500.2320009 MHz
NUC2                        1H
CPDPRG[2                waltz16
PCPD2                      80.00 usec
PLW2                11.44699955 W
PLW12                0.25756001 W
PLW13                0.12955000 W

F2 - Processing parameters
SI                         32768
SF                   125.7829335 MHz
WDW                           EM
SSB                            0
LB                          1.00 Hz
GB                             0
PC                          1.40
```

^{13}C NMR spectrum of ***E*-1p**



^{1}H NMR spectrum of ***Z*-1p**

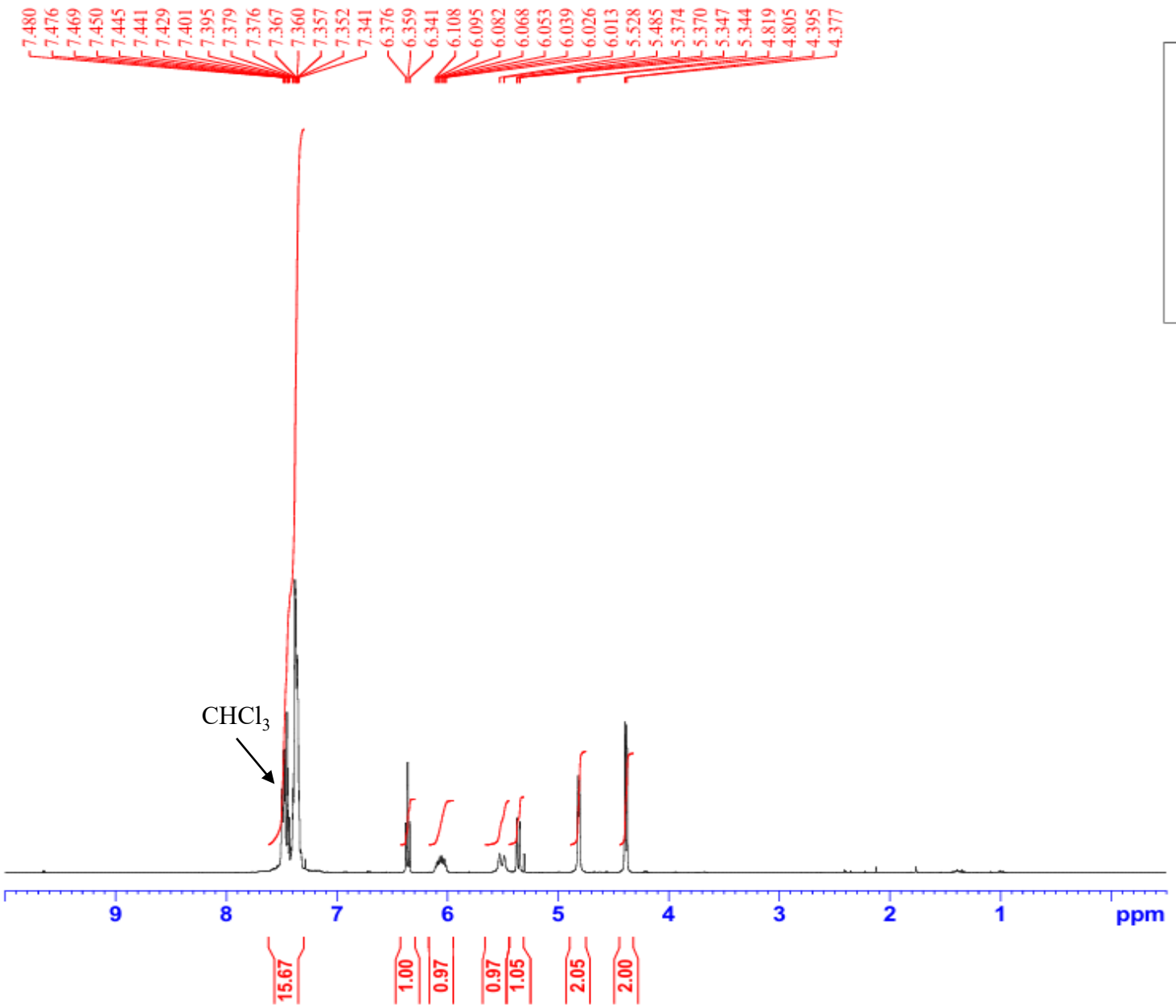


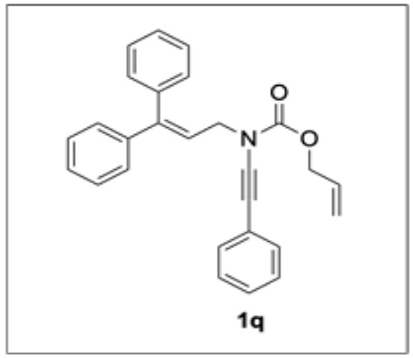

```
Current Data Parameters
NAME      OJ-Nerol ynamide-C
EXPNO                 12
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210730
Time                18.54 h
INSTRUM       Avance Neo
PROBHD   Z152088_0031 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           23809.523 Hz
FIDRES         0.726609 Hz
AQ             1.3762560 sec
RG                 8.125
DW                21.000 usec
DE                 6.50 usec
TE                298.1 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1
SFO1         100.6228298 MHz
NUC1                13C
P0                 2.67 usec
P1                 8.00 usec
PLW1         86.55400085 W
SFO2         400.1316005 MHz
NUC2                1H
CPDPRG[2         waltz65
PCPD2             90.00 usec
PLW2         24.03499985 W
PLW12         0.18990999 W
PLW13         0.09552100 W

F2 - Processing parameters
SI                32768
SF           100.6127685 MHz
WDW                 EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

^{13}C NMR spectrum of ***Z*-1p**



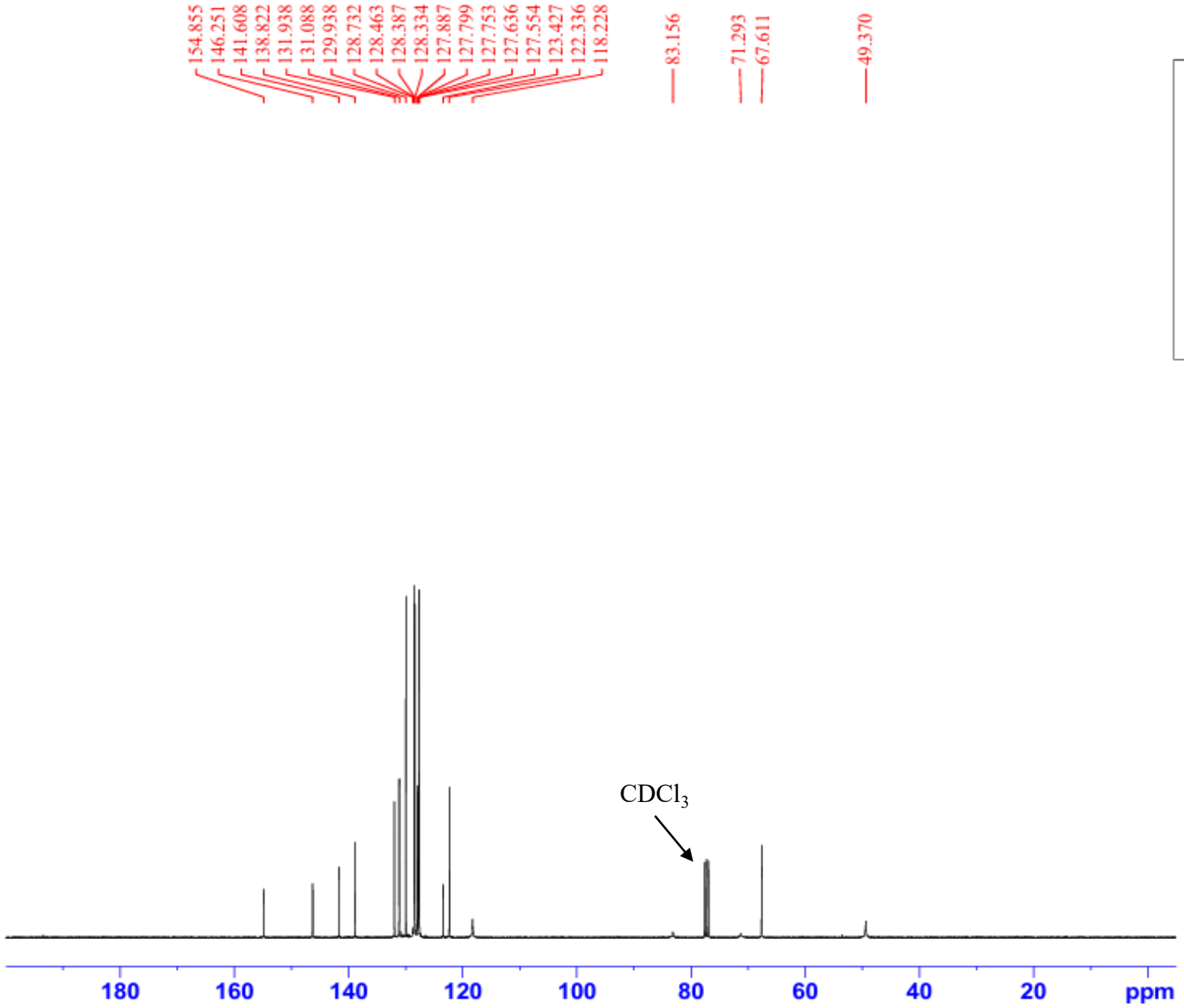


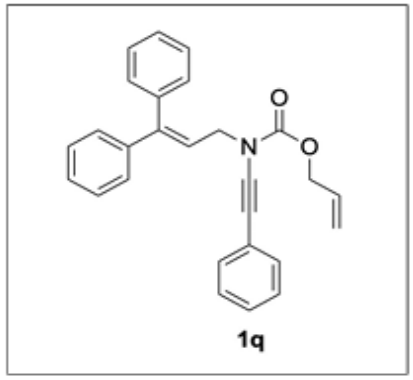

```
Current Data Parameters
NAME          OJ-1-183-H
EXPNO                 17
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220903
Time_            21.41 h
INSTRUM       Avance Neo
PROBHD    Z152088_0031 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8196.722 Hz
FIDRES          0.250144 Hz
AQ              3.9976959 sec
RG                    32
DW                61.000 usec
DE                13.89 usec
TE                298.0 K
D1             1.00000000 sec
TD0                    1
SFO1          400.1324708 MHz
NUC1                  1H
P0                 2.67 usec
P1                 8.00 usec
PLW1          24.03499985 W

F2 - Processing parameters
SI                 65536
SF          400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

[1]H NMR spectrum of **1q**



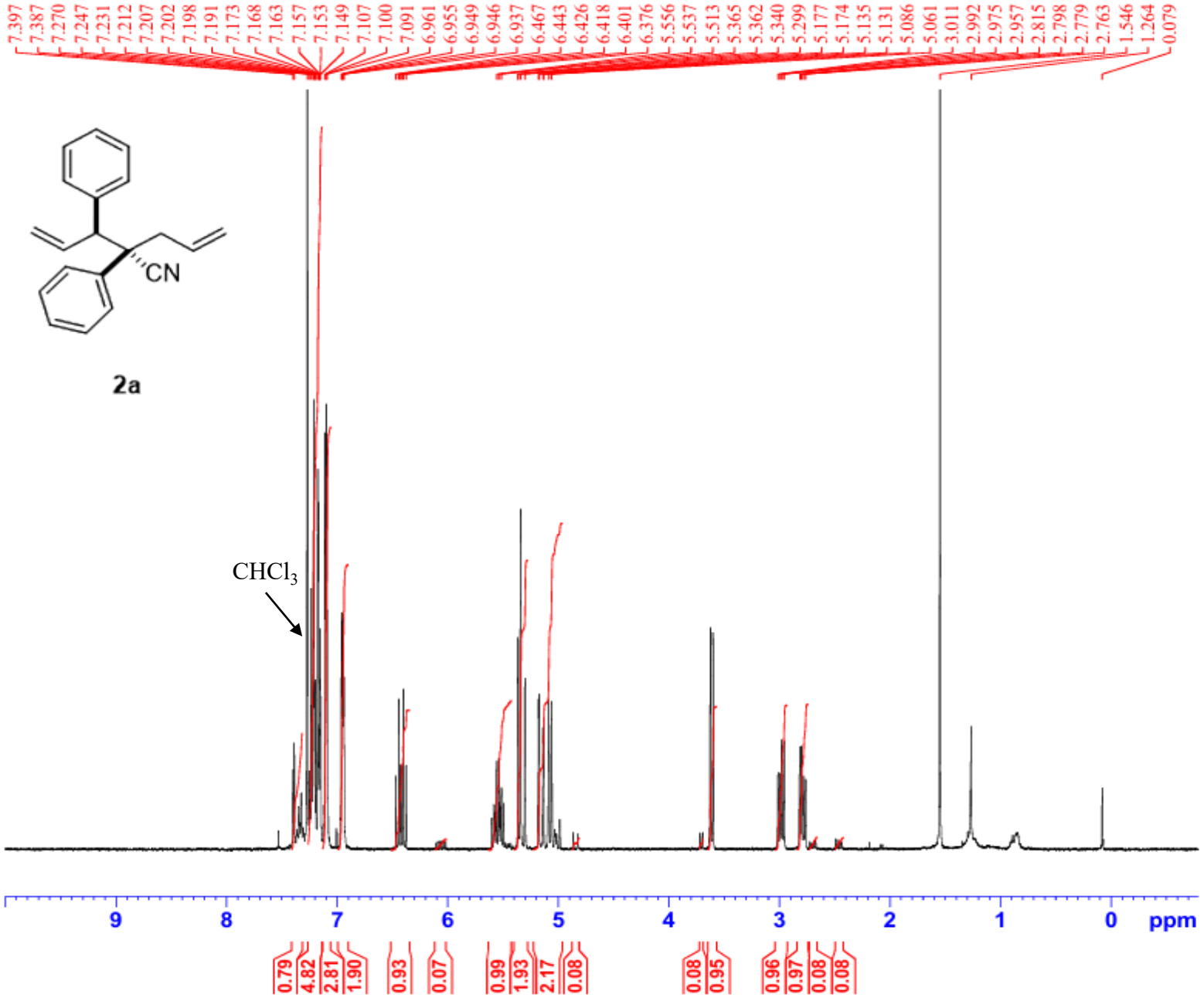



```
Current Data Parameters
NAME                  OJ-1-183-C
EXPNO                         19
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20220903
Time                       22.41 h
INSTRUM                Avance Neo
PROBHD    Z152088_0031 (
PULPROG                 zgpg30
TD                           65536
SOLVENT                    CDCl3
NS                            1024
DS                               4
SWH                    23809.523 Hz
FIDRES                  0.726609 Hz
AQ                      1.3762560 sec
RG                        10.7781
DW                        21.000 usec
DE                         6.50 usec
TE                          298.0 K
D1                    2.00000000 sec
D11                   0.03000000 sec
TD0                            1
SFO1                100.6228298 MHz
NUC1                         13C
P0                         2.67 usec
P1                         8.00 usec
PLW1                86.55400085 W
SFO2                400.1316005 MHz
NUC2                         1H
CPDPRG[2                waltz65
PCPD2                     90.00 usec
PLW2                24.03499985 W
PLW12                0.18990999 W
PLW13                0.09552100 W

F2 - Processing parameters
SI                           32768
SF                  100.6127685 MHz
WDW                             EM
SSB                              0
LB                            1.00 Hz
GB                               0
PC                            1.40
```


^{13}C NMR spectrum of **1q**

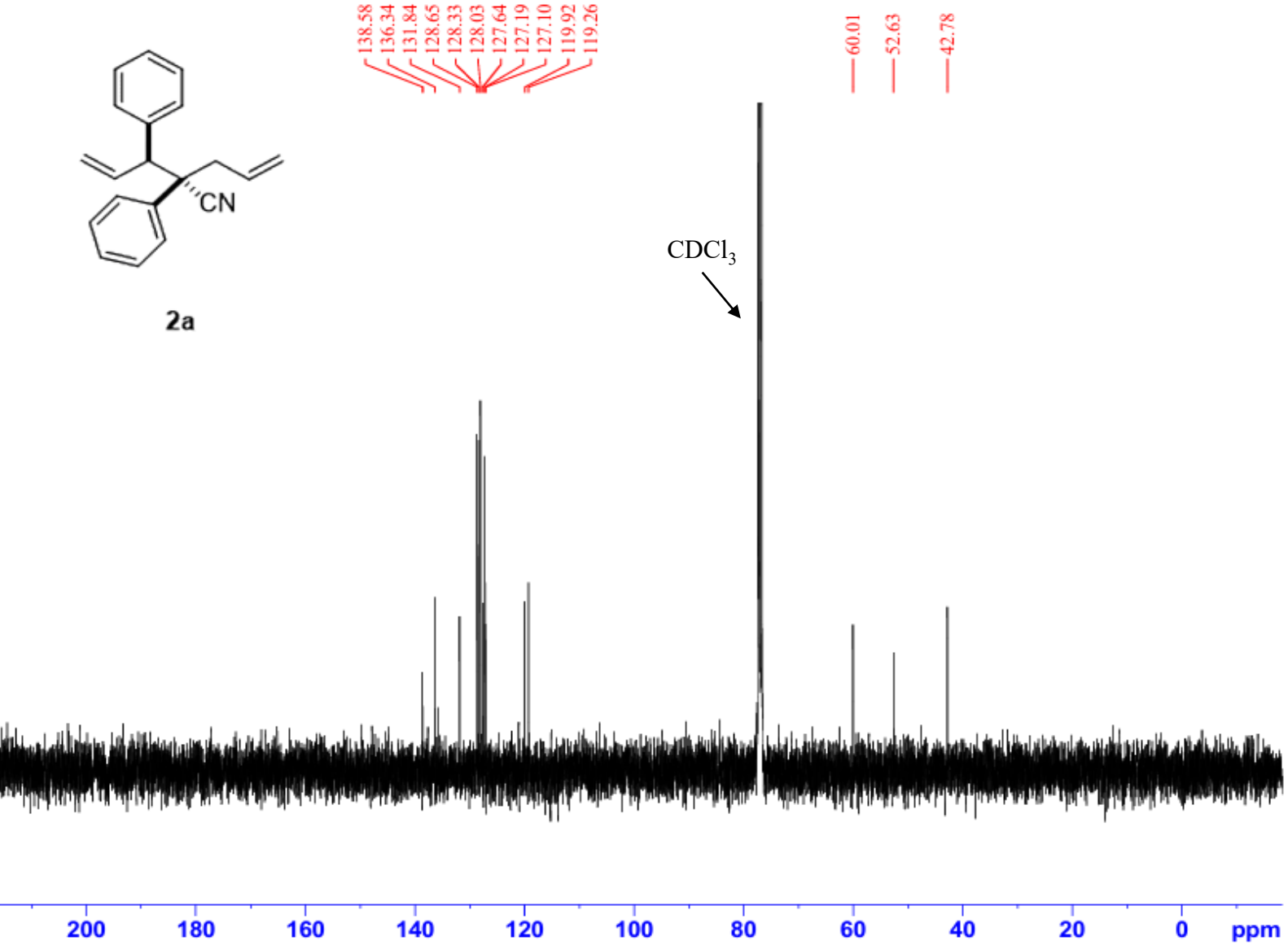



```
Current Data Parameters
NAME        OJ-2-48-pure
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210516
Time_            23.32 h
INSTRUM      Avance Neo
PROBHD   Z152088_0031 (
PULPROG          zg30
TD              65536
SOLVENT         CDCl3
NS                 16
DS                  2
SWH          8196.722 Hz
FIDRES       0.250144 Hz
AQ           3.9976959 sec
RG                101
DW             61.000 usec
DE             13.89 usec
TE             298.0 K
D1          1.00000000 sec
TD0                1
SFO1       400.1324708 MHz
NUC1               1H
P0              2.67 usec
P1              8.00 usec
PLW1       24.03499985 W

F2 - Processing parameters
SI              65536
SF       400.1300057 MHz
WDW               EM
SSB                0
LB              0.30 Hz
GB                 0
PC              1.00
```

[1]H NMR spectrum of **2a**

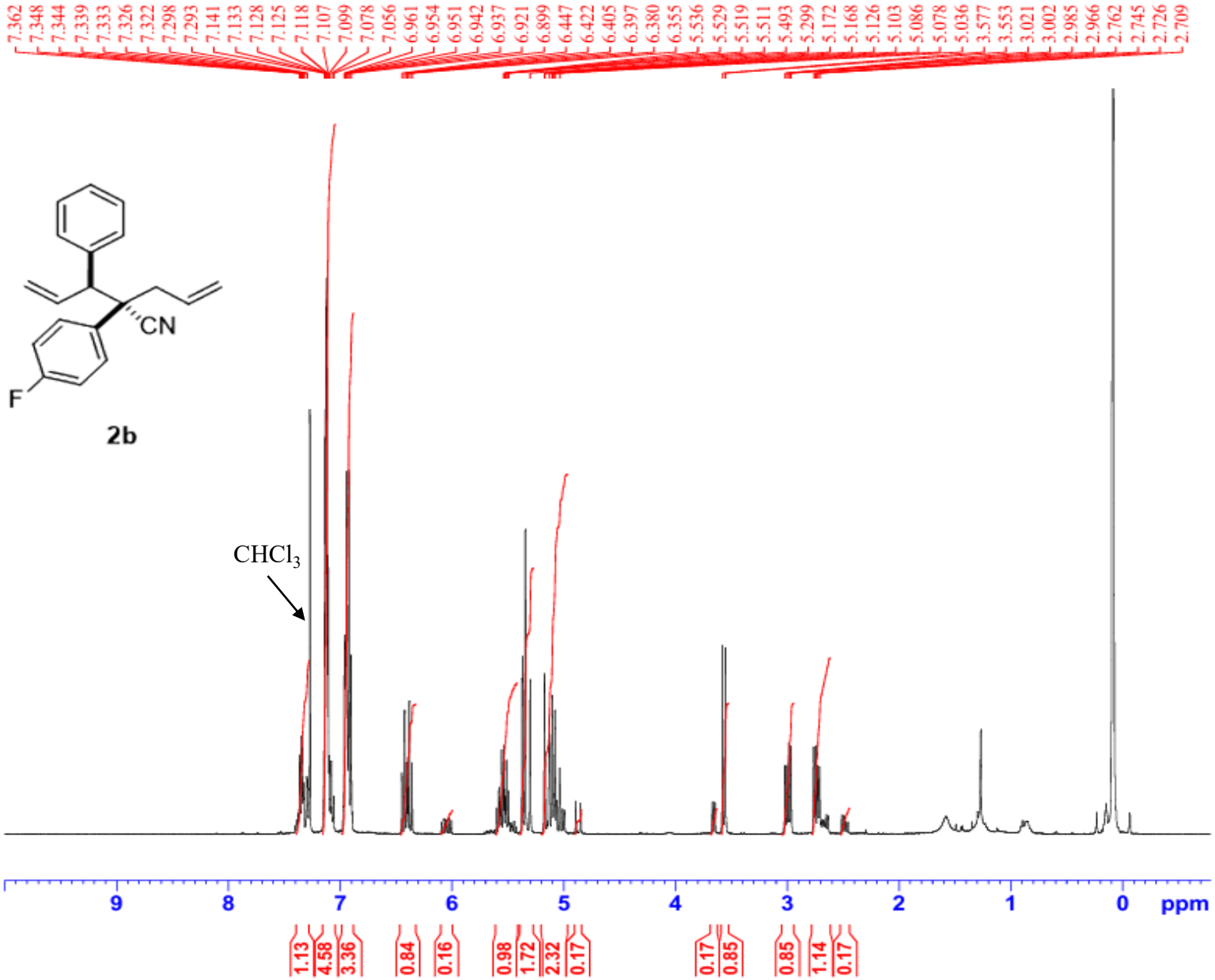



```
Current Data Parameters
NAME        OJ-2-48-pure
EXPNO                 11
PROCNO                 1

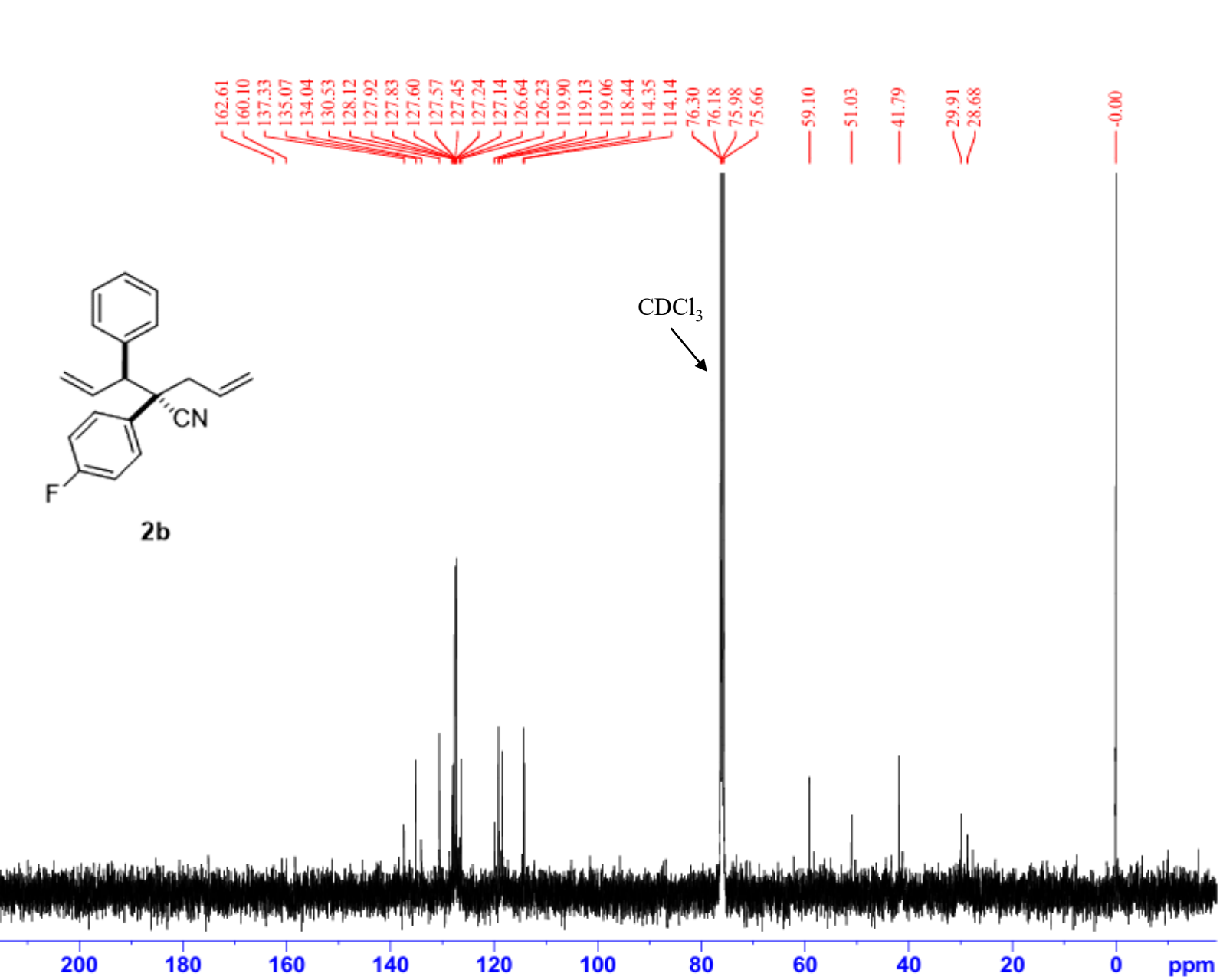
F2 - Acquisition Parameters
Date_           20210517
Time                1.55 h
INSTRUM       Avance Neo
PROBHD   Z152088_0031 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           23809.523 Hz
FIDRES         0.726609 Hz
AQ             1.3762560 sec
RG                 8.125
DW                21.000 usec
DE                 6.50 usec
TE                298.1 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                   1
SFO1         100.6228298 MHz
NUC1                 13C
P0                 2.67 usec
P1                 8.00 usec
PLW1          86.55400085 W
SFO2         400.1316005 MHz
NUC2                 1H
CPDPRG[2          waltz65
PCPD2             90.00 usec
PLW2          24.03499985 W
PLW12          0.18990999 W
PLW13          0.09552100 W

F2 - Processing parameters
SI                32768
SF           100.6127685 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

^{13}C NMR spectrum of **2a**



^{1}H NMR spectrum of **2b**

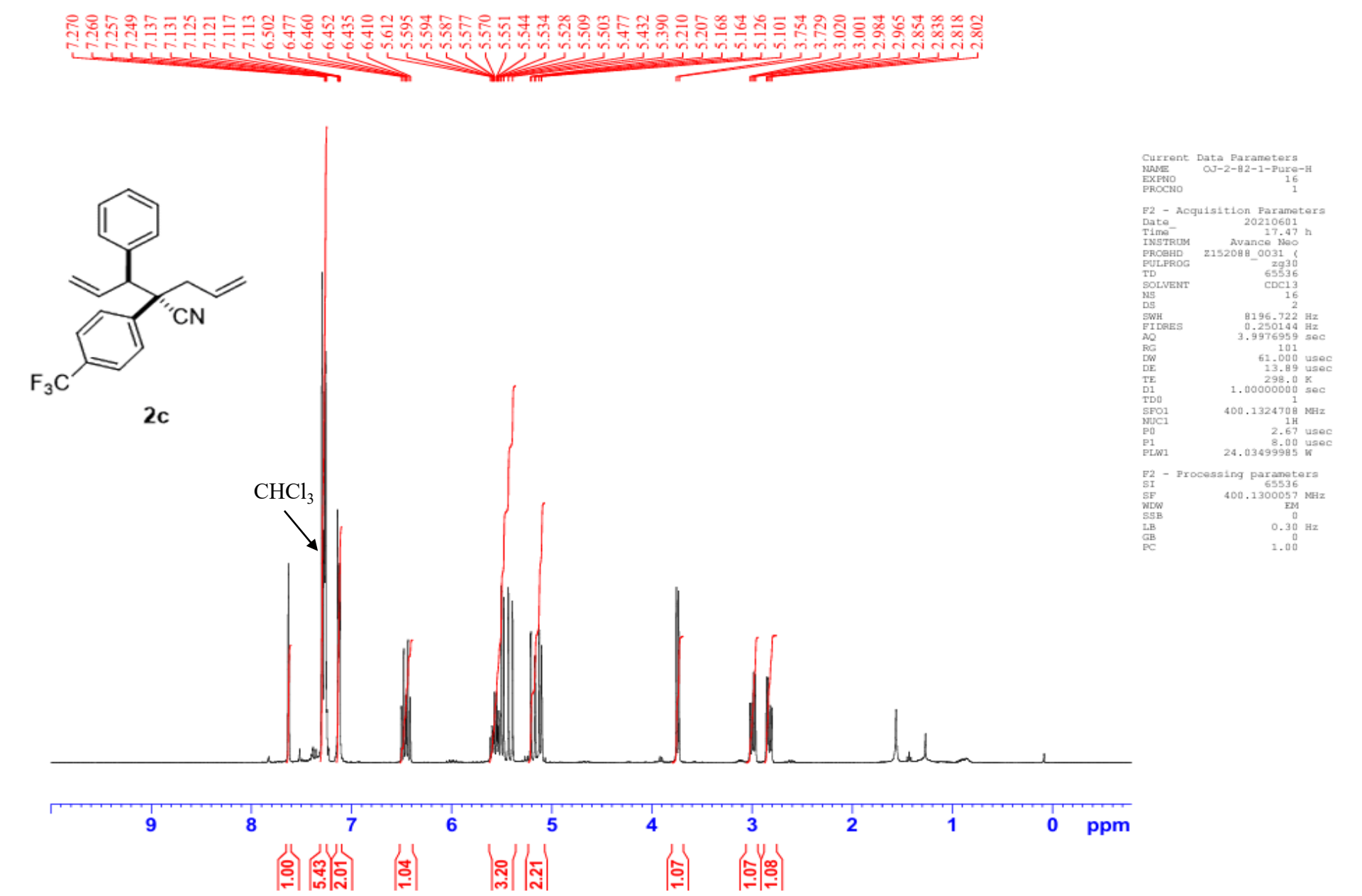



```
Current Data Parameters
NAME      DJ-2-Para-fluoro-nitrile-C
EXPNO                 13
PROCNO                 1

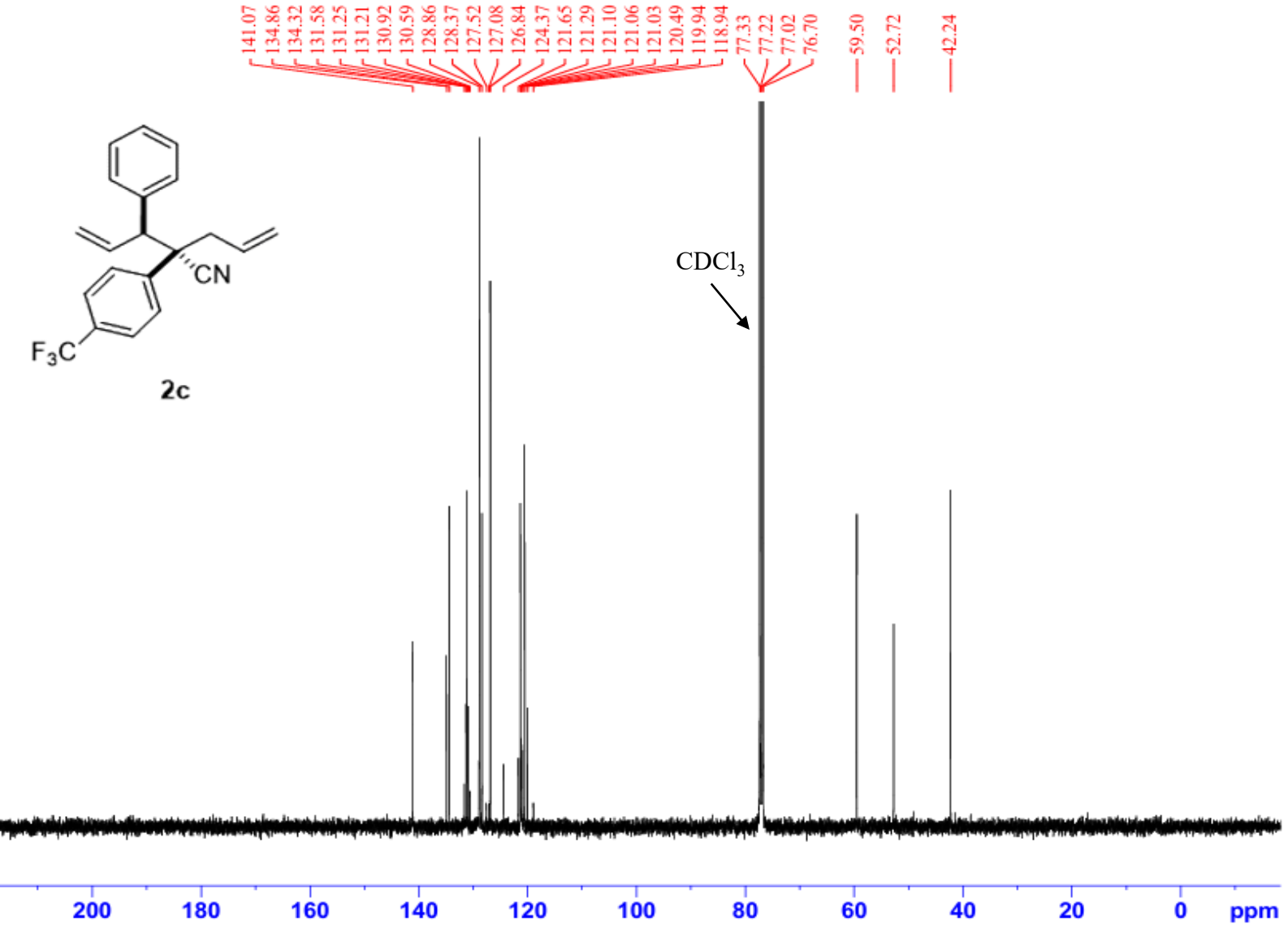
F2 - Acquisition Parameters
Date_           20210910
Time                23.27 h
INSTRUM       Avance Neo
PROBHD    z152088_0031 (
PULPROG           zgpg30
TD                65536
SOLVENT           CDCl3
NS                 2048
DS                    4
SWH           23809.523 Hz
FIDRES        0.726609 Hz
AQ            1.3762560 sec
RG                 8.125
DW                21.000 usec
DE                 6.50 usec
TE                298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1        100.6228298 MHz
NUC1               13C
P0                 2.67 usec
P1                 8.00 usec
PLW1        86.55400085 W
SFO2        400.1316005 MHz
NUC2               1H
CPDPRG[2        waltz65
PCPD2             90.00 usec
PLW2        24.03499985 W
PLW12        0.18990999 W
PLW13        0.09552100 W

F2 - Processing parameters
SI                32768
SF          100.6128727 MHz
WDW                EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

^{13}C NMR spectrum of **2b**



^{1}H NMR spectrum of **2c**

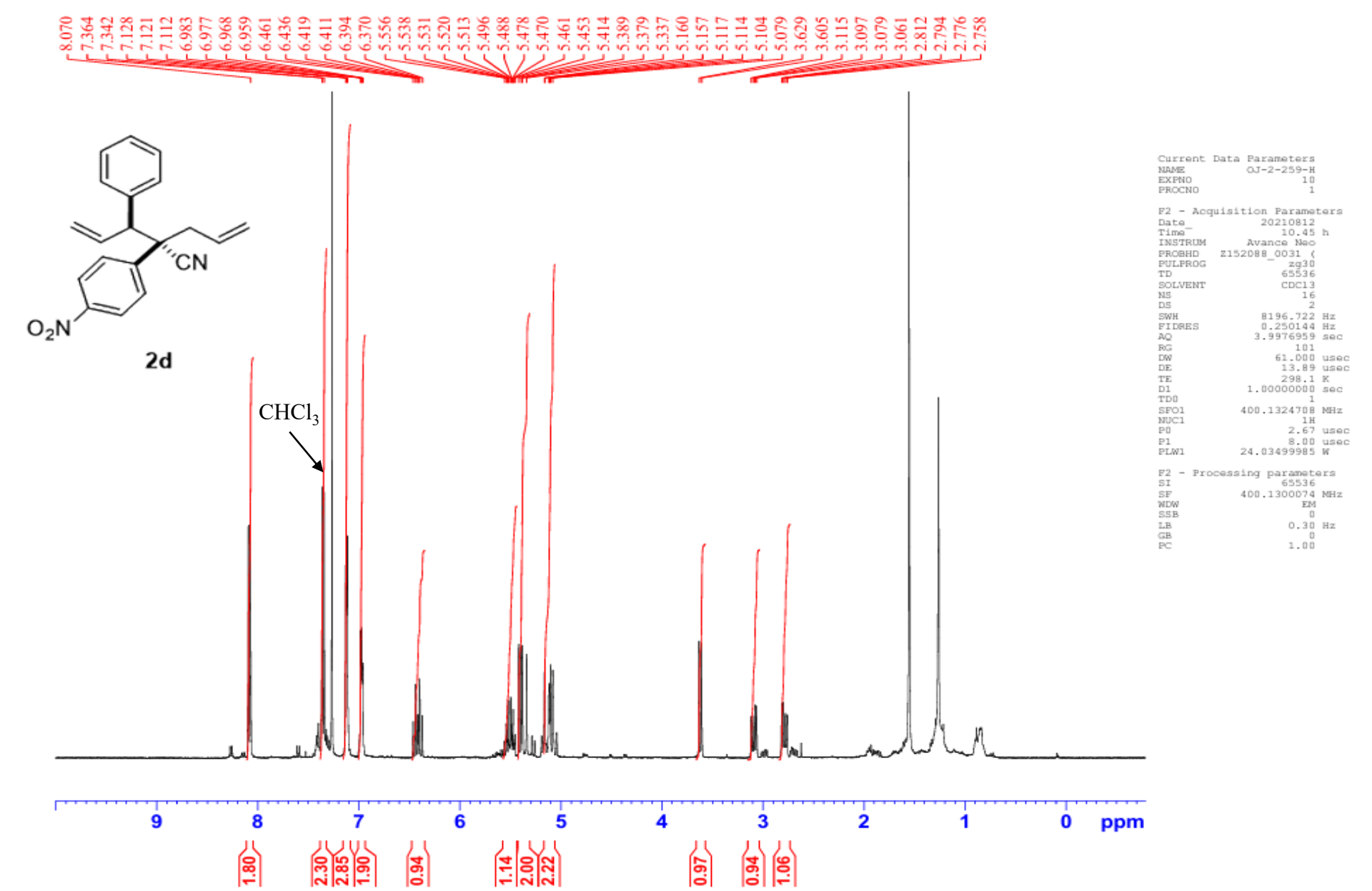



```
Current Data Parameters
NAME      OJ-2-82-1-Pure-C
EXPNO                   17
PROCNO                   1

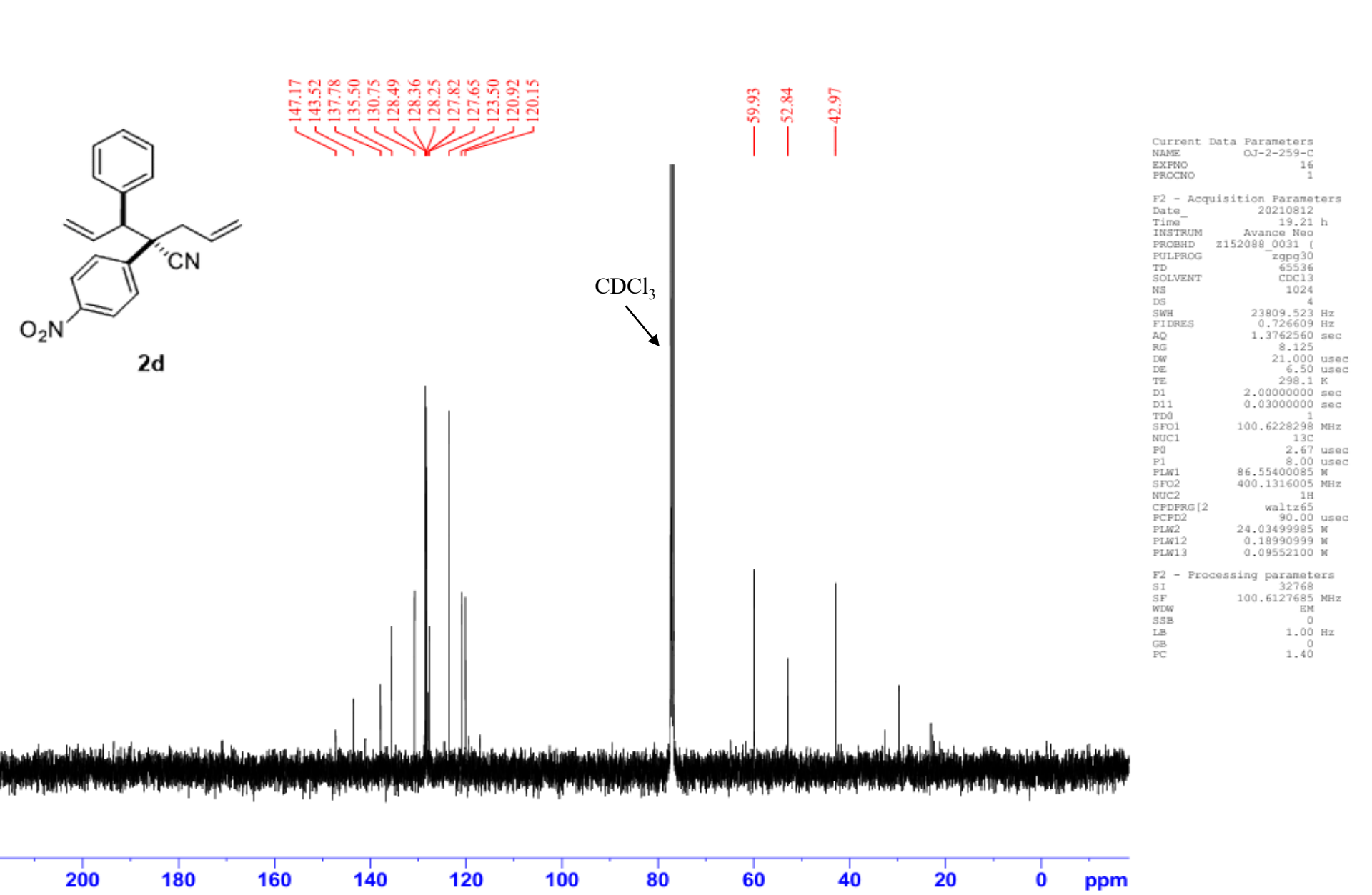
F2 - Acquisition Parameters
Date_           20210601
Time               18.49 h
INSTRUM       Avance Neo
PROBHD   Z152088_0031 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           23809.523 Hz
FIDRES        0.726609 Hz
AQ            1.3762560 sec
RG                8.125
DW               21.000 usec
DE                6.50 usec
TE               298.1 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1
SFO1         100.6228298 MHz
NUC1                 13C
P0                2.67 usec
P1                8.00 usec
PLW1         86.55400085 W
SFO2         400.1316005 MHz
NUC2                 1H
CPDPRG[2          waltz65
PCPD2            90.00 usec
PLW2         24.03499985 W
PLW12         0.18990999 W
PLW13         0.09552100 W

F2 - Processing parameters
SI                32768
SF           100.6127685 MHz
WDW                  EM
SSB                   0
LB                1.00 Hz
GB                    0
PC                1.40
```

^{13}C NMR spectrum of **2c**



[1]H NMR spectrum of **2d**

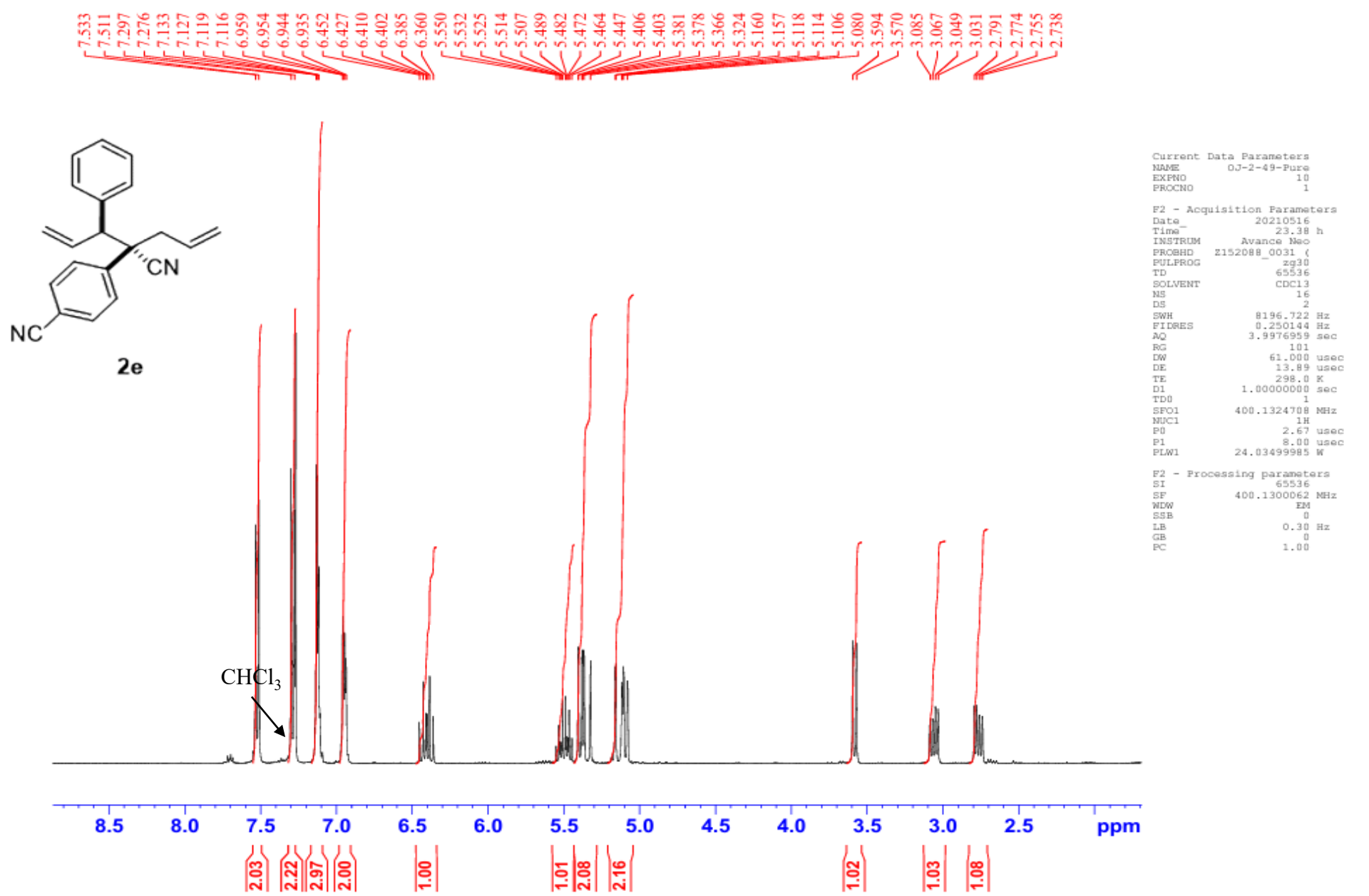



```
Current Data Parameters
NAME                  OJ-2-259-C
EXPNO                         16
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20210812
Time                       19.21 h
INSTRUM                Avance Neo
PROBHD    Z152088_0031 (
PULPROG                  zgpg30
TD                        65536
SOLVENT                   CDCl3
NS                         1024
DS                            4
SWH                   23809.523 Hz
FIDRES                0.726609 Hz
AQ                    1.3762560 sec
RG                        8.125
DW                       21.000 usec
DE                        6.50 usec
TE                       298.1 K
D1                    2.00000000 sec
D11                   0.03000000 sec
TD0                           1
SFO1                100.6228298 MHz
NUC1                        13C
P0                        2.67 usec
P1                        8.00 usec
PLW1                86.55400085 W
SFO2                400.1316005 MHz
NUC2                        1H
CPDPRG[2                waltz65
PCPD2                    90.00 usec
PLW2                24.03499985 W
PLW12                0.18990999 W
PLW13                0.09552100 W

F2 - Processing parameters
SI                        32768
SF                  100.6127685 MHz
WDW                          EM
SSB                           0
LB                        1.00 Hz
GB                            0
PC                        1.40
```

^{13}C NMR spectrum of **2d**

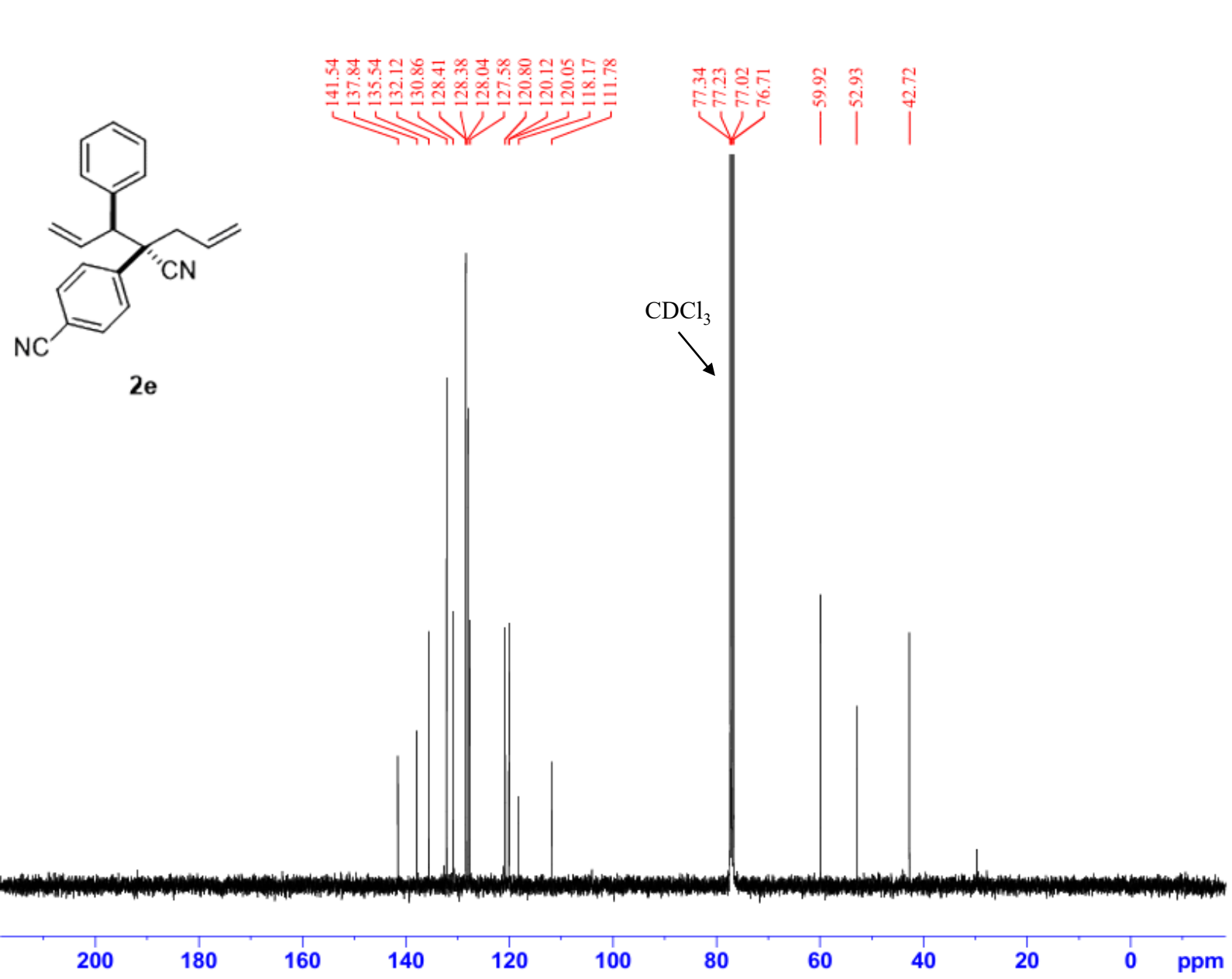



```
Current Data Parameters
NAME          OJ-2-49-Pure
EXPNO                   10
PROCNO                   1

F2 - Acquisition Parameters
Date_              20210516
Time                 23.38 h
INSTRUM         Avance Neo
PROBHD    Z152088_0031 (
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8196.722 Hz
FIDRES             0.250144 Hz
AQ                 3.9976959 sec
RG                      101
DW                   61.000 usec
DE                   13.89 usec
TE                   298.0 K
D1                1.00000000 sec
TD0                       1
SFO1              400.1324708 MHz
NUC1                     1H
P0                    2.67 usec
P1                    8.00 usec
PLW1             24.03499985 W

F2 - Processing parameters
SI                    65536
SF              400.1300062 MHz
WDW                      EM
SSB                       0
LB                    0.30 Hz
GB                        0
PC                    1.00
```

[1]H NMR spectrum of **2e**

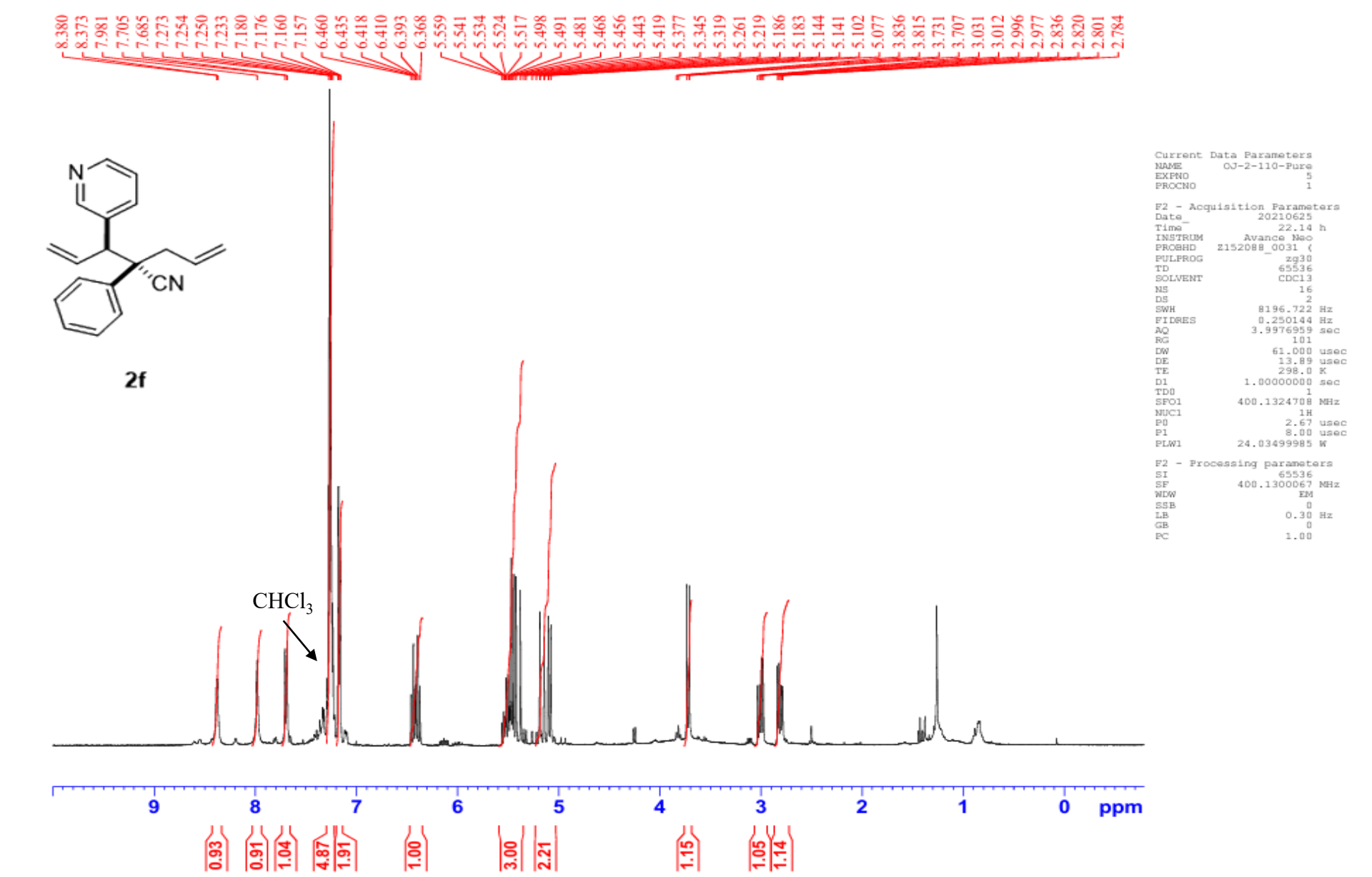



```
Current Data Parameters
NAME          OJ-2-49-Pure
EXPNO                   11
PROCNO                   1

F2 - Acquisition Parameters
Date_              20210517
Time_                  0.48 h
INSTRUM          Avance Neo
PROBHD     Z152088_0031 (
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     1024
DS                        4
SWH               23809.523 Hz
FIDRES             0.726609 Hz
AQ                 1.3762560 sec
RG                     8.125
DW                    21.000 usec
DE                     6.50 usec
TE                    298.0 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                       1
SFO1             100.6228298 MHz
NUC1                    13C
P0                     2.67 usec
P1                     8.00 usec
PLW1              86.55400085 W
SFO2             400.1316005 MHz
NUC2                    1H
CPDPRG[2             waltz65
PCPD2                 90.00 usec
PLW2              24.03499985 W
PLW12              0.18990999 W
PLW13              0.09552100 W

F2 - Processing parameters
SI                    32768
SF               100.6127685 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```

^{13}C NMR spectrum of **2e**

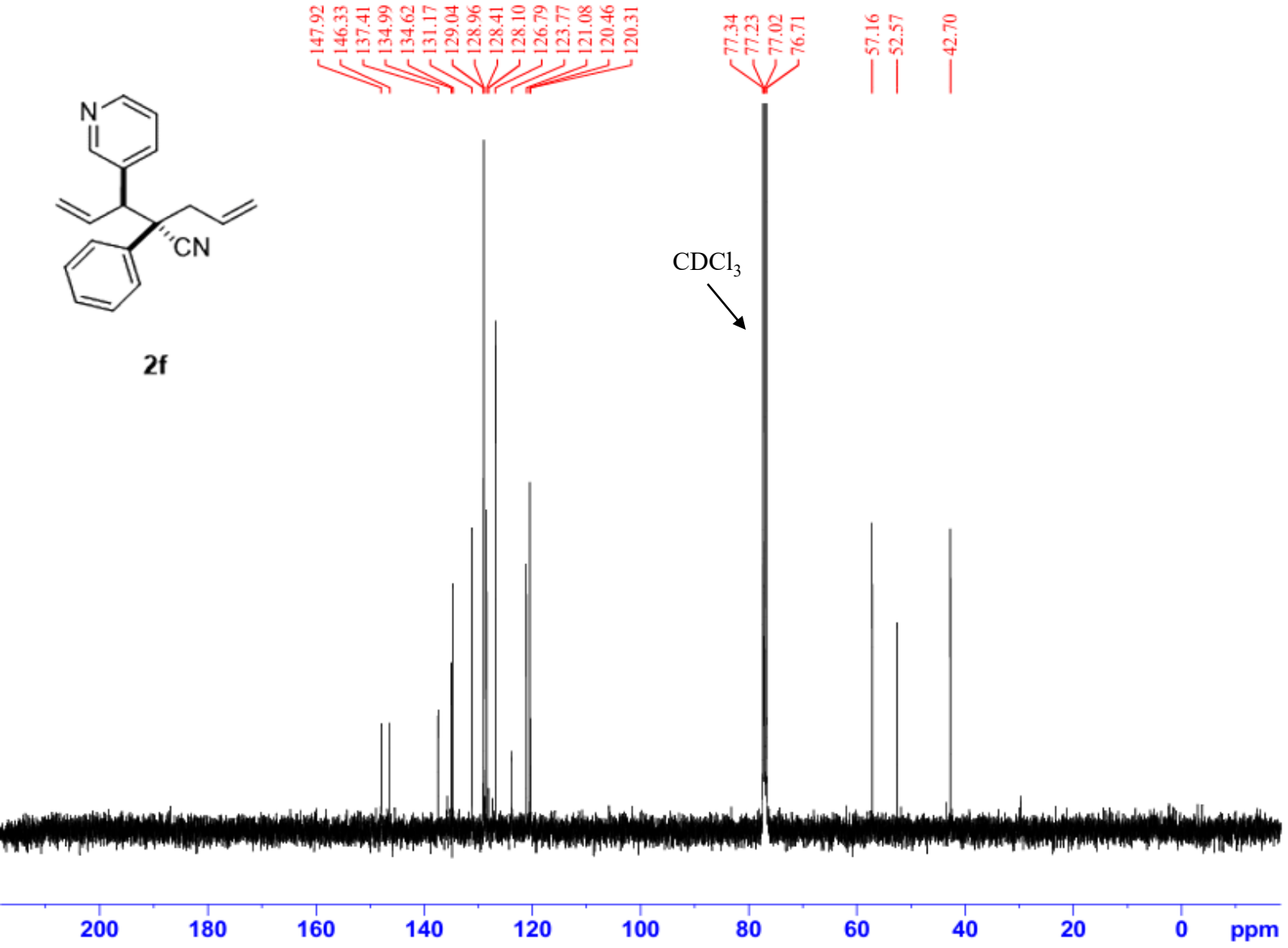



```
Current Data Parameters
NAME        OJ-2-110-Pure
EXPNO                   5
PROCNO                  1

F2 - Acquisition Parameters
Date_            20210625
Time                22.14 h
INSTRUM       Avance Neo
PROBHD    Z152088_0031 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8196.722 Hz
FIDRES          0.250144 Hz
AQ              3.9976959 sec
RG                   101
DW                61.000 usec
DE                13.89 usec
TE                298.0 K
D1             1.00000000 sec
TD0                    1
SFO1         400.1324708 MHz
NUC1                  1H
P0                  2.67 usec
P1                  8.00 usec
PLW1         24.03499985 W

F2 - Processing parameters
SI                 65536
SF          400.1300067 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

[1]H NMR spectrum of **2f**

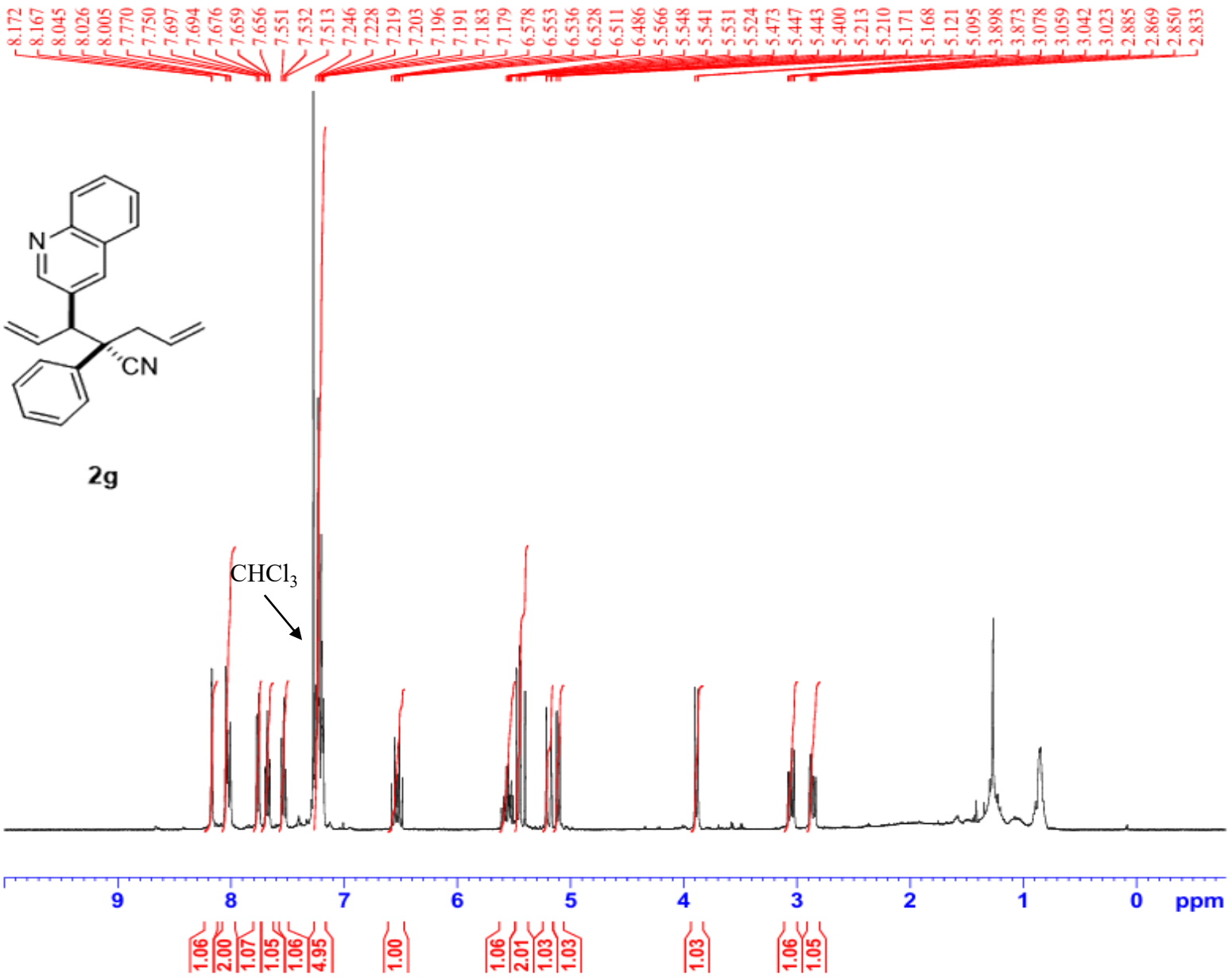



```
Current Data Parameters
NAME      OJ-2-110-Pure-C
EXPNO                   8
PROCNO                  1

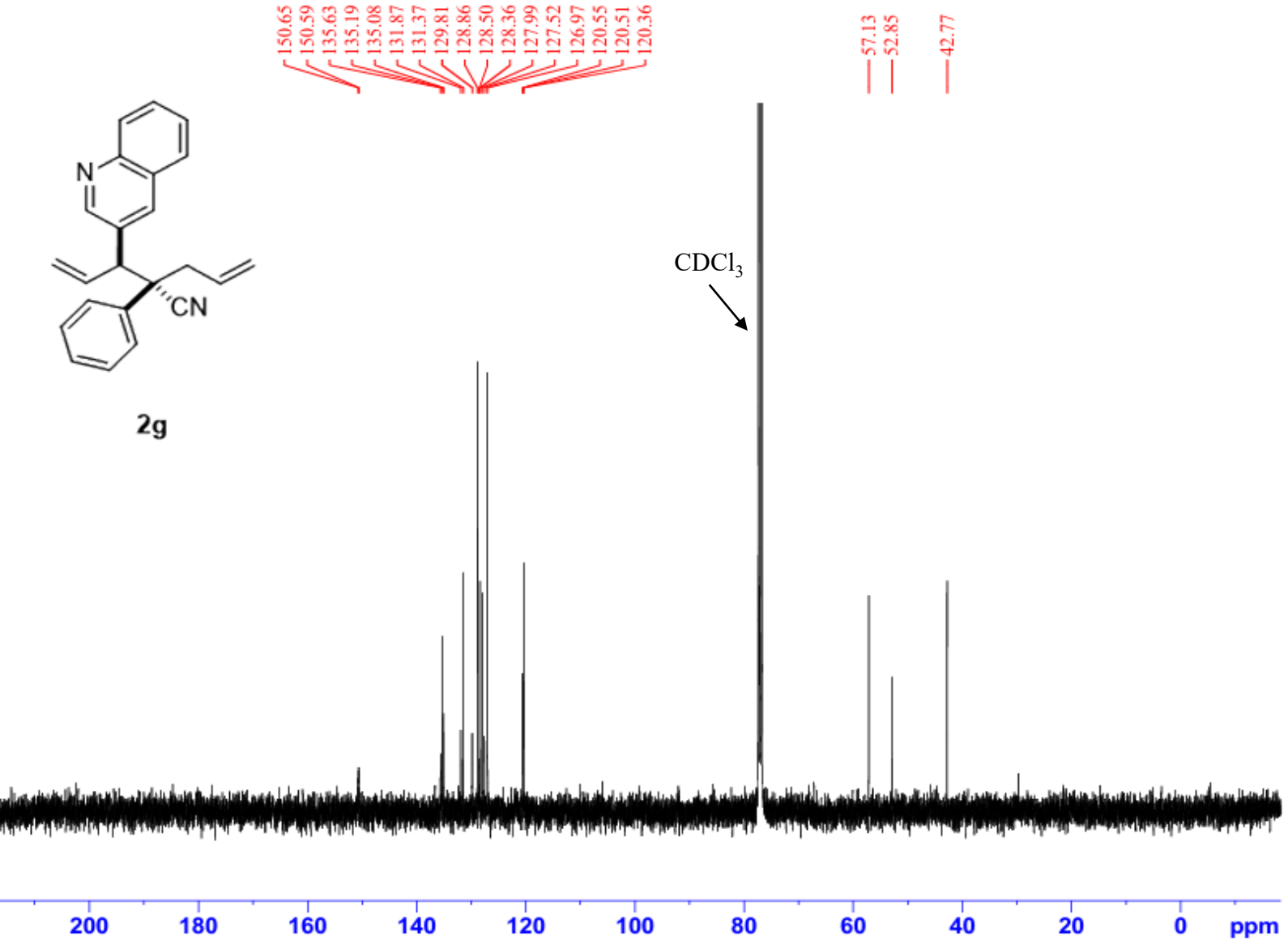
F2 - Acquisition Parameters
Date_           20210625
Time_              23.16 h
INSTRUM       Avance Neo
PROBHD   Z152088_0031 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           23809.523 Hz
FIDRES        0.726609 Hz
AQ            1.3762560 sec
RG                8.125
DW               21.000 usec
DE                6.50 usec
TE                298.1 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1
SFO1         100.6228298 MHz
NUC1                13C
P0                 2.67 usec
P1                 8.00 usec
PLW1         86.55400085 W
SFO2         400.1316005 MHz
NUC2                1H
CPDPRG[2         waltz65
PCPD2             90.00 usec
PLW2         24.03499985 W
PLW12         0.18990999 W
PLW13         0.09552100 W

F2 - Processing parameters
SI                32768
SF           100.6127685 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

^{13}C NMR spectrum of 2**f**



^{1}H NMR spectrum of **2g**

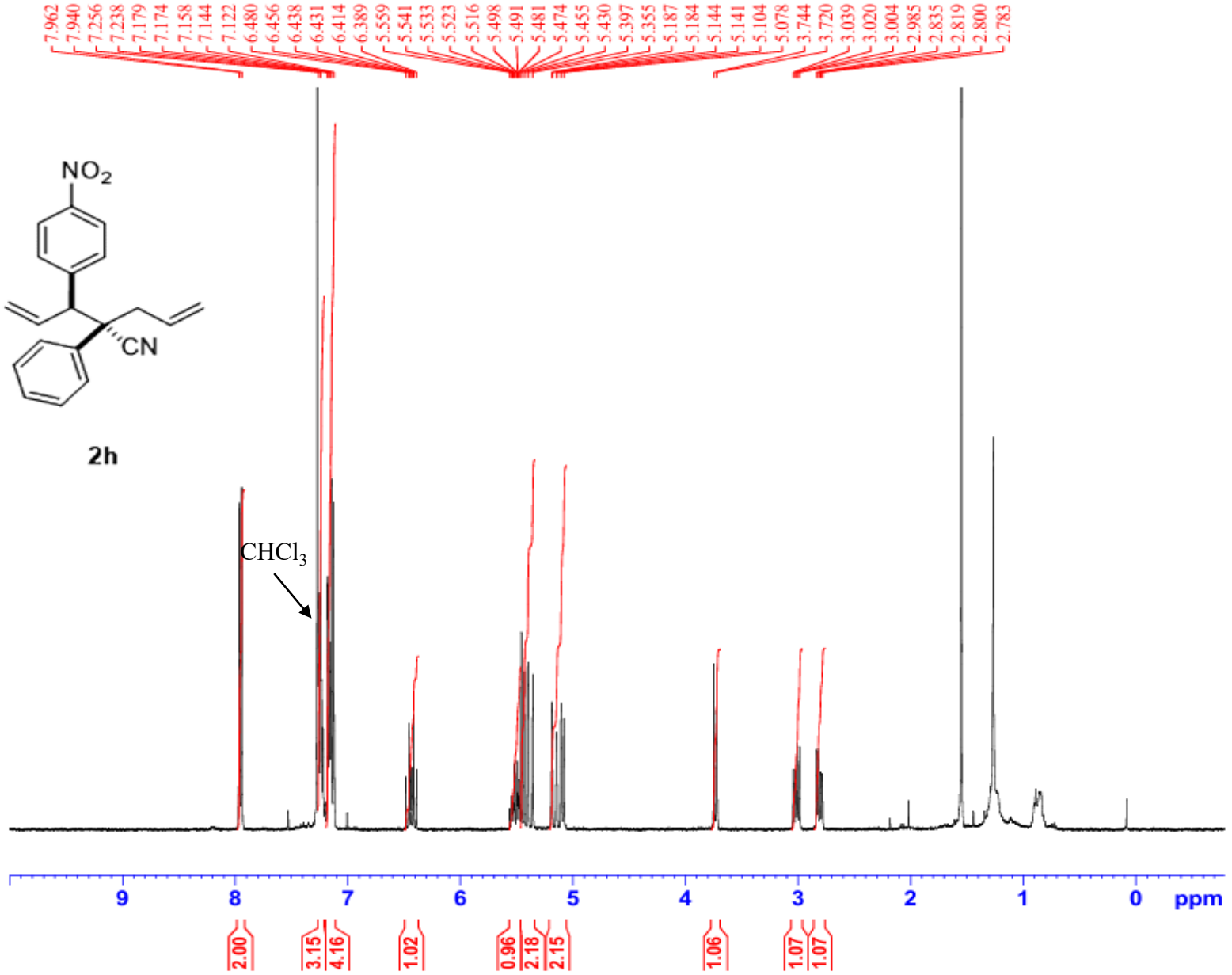



```
Current Data Parameters
NAME      OJ-Quinoline Nitrile-C
EXPNO                 13
PROCNO                 1

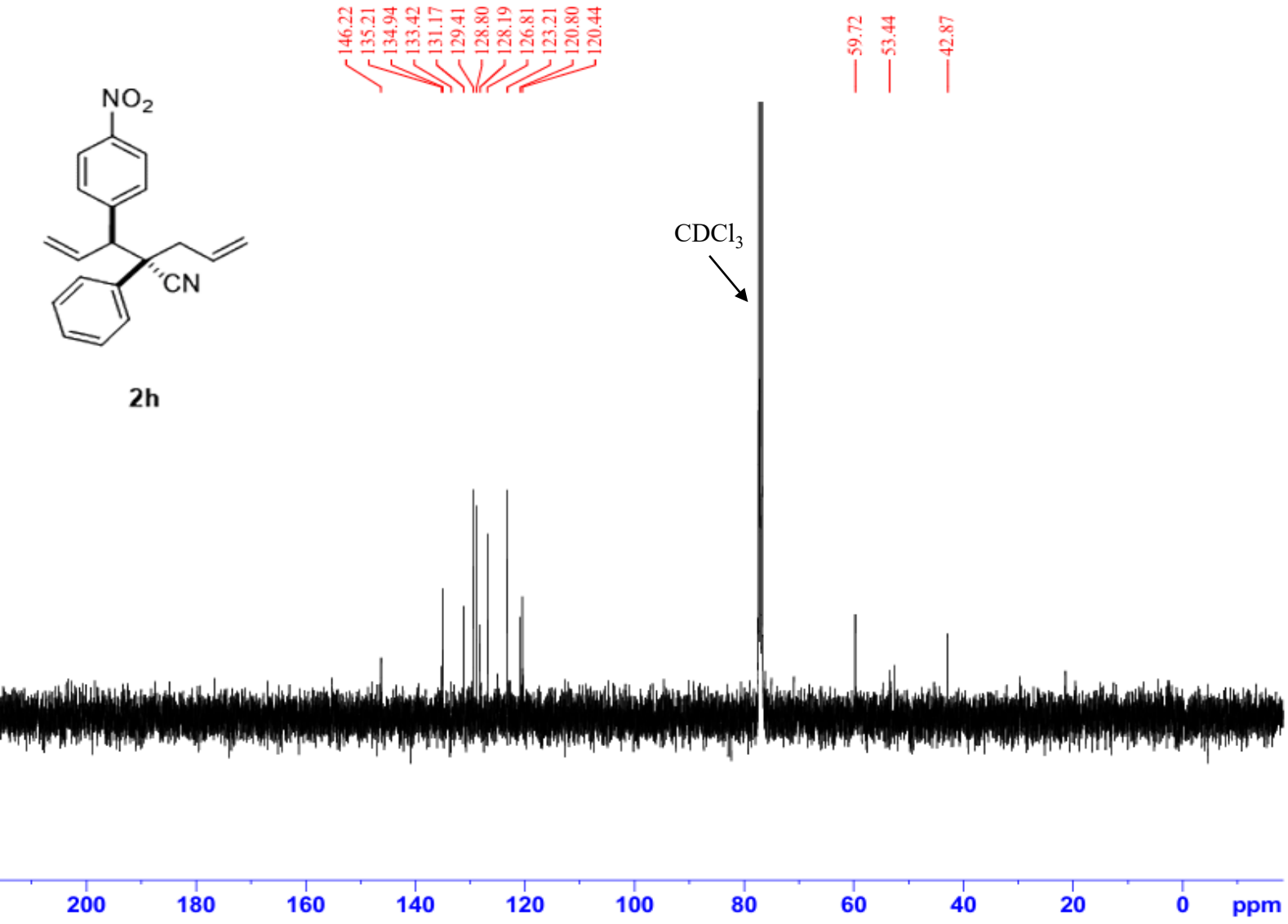
F2 - Acquisition Parameters
Date_           20210705
Time               1.42 h
INSTRUM       Avance Neo
PROBHD   Z152088_0031 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           23809.523 Hz
FIDRES        0.726609 Hz
AQ            1.3762560 sec
RG                 8.125
DW                21.000 usec
DE                 6.50 usec
TE                298.1 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1
SFO1         100.6228298 MHz
NUC1                13C
P0                 2.67 usec
P1                 8.00 usec
PLW1         86.55400085 W
SFO2         400.1316005 MHz
NUC2                1H
CPDPRG[2         waltz65
PCPD2             90.00 usec
PLW2         24.03499985 W
PLW12         0.18990999 W
PLW13         0.09552100 W

F2 - Processing parameters
SI                32768
SF           100.6127685 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

^{13}C NMR spectrum of 2**g**



^{1}H NMR spectrum of **2h**

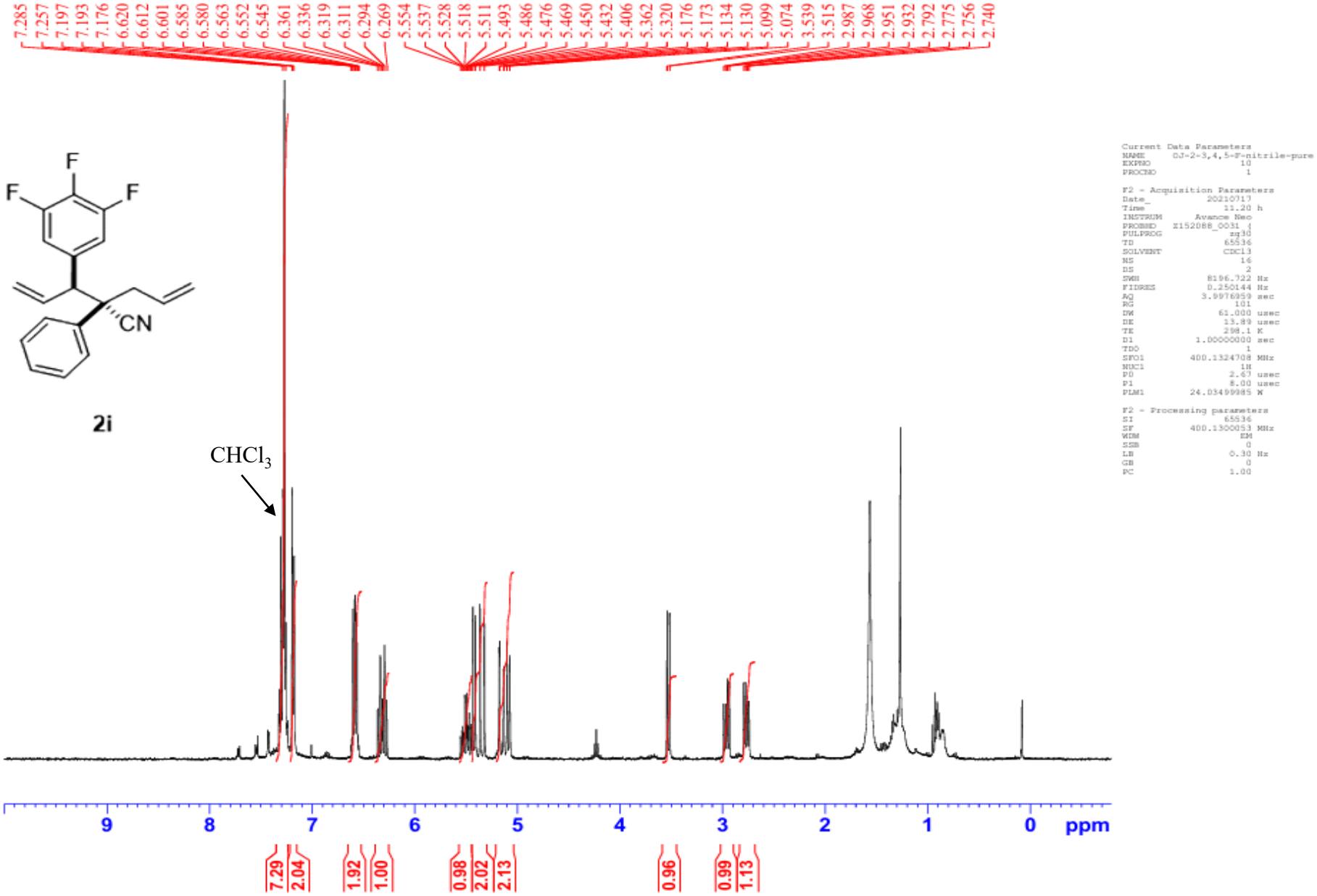



```
Current Data Parameters
NAME      OJ-2-105-Pure-C
EXPNO                  15
PROCNO                  1

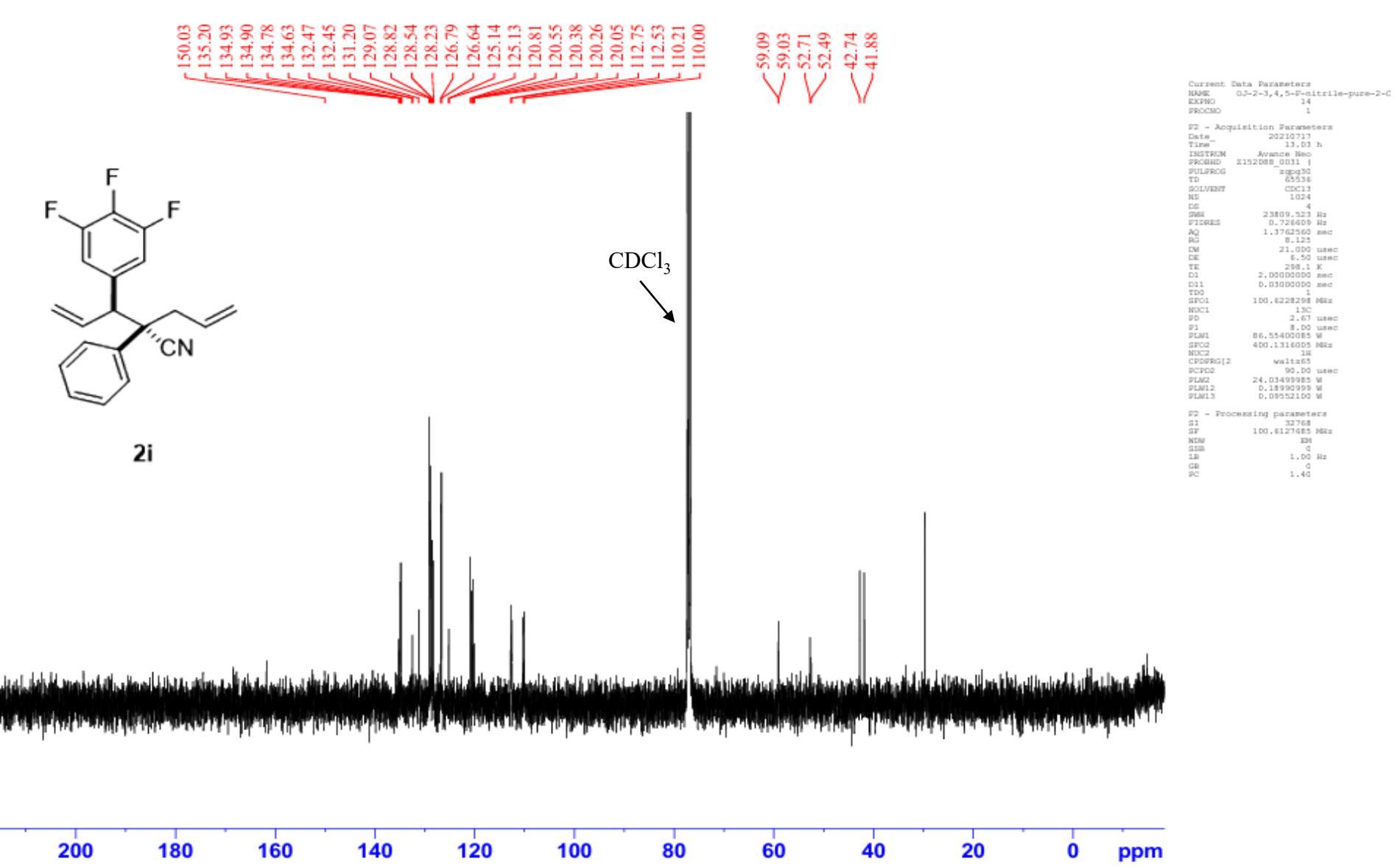
F2 - Acquisition Parameters
Date_            20210626
Time                0.22 h
INSTRUM       Avance Neo
PROBHD   Z152088_0031 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           23809.523 Hz
FIDRES         0.726609 Hz
AQ             1.3762560 sec
RG                 8.125
DW                21.000 usec
DE                 6.50 usec
TE                298.1 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                   1
SFO1         100.6228298 MHz
NUC1                13C
P0                 2.67 usec
P1                 8.00 usec
PLW1          86.55400085 W
SFO2         400.1316005 MHz
NUC2                1H
CPDPRG[2        waltz65
PCPD2             90.00 usec
PLW2          24.03499985 W
PLW12          0.18990999 W
PLW13          0.09552100 W

F2 - Processing parameters
SI                32768
SF           100.6127685 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

^{13}C NMR spectrum of 2**h**



^{1}H NMR spectrum of **2i**

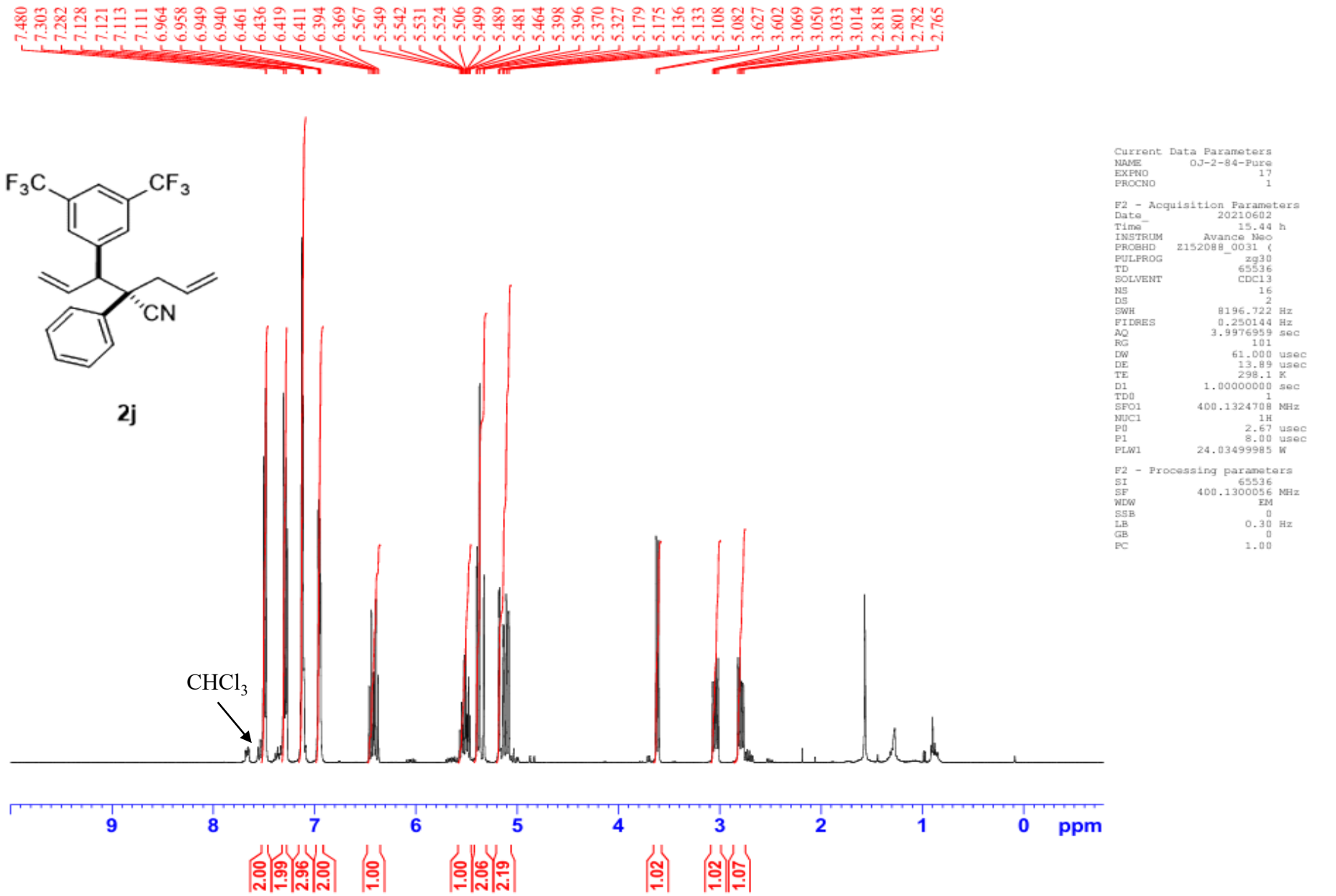


Current Data Parameters
NAME GJ-2-3,4,5-F-nitrile-pure-2-C
EXPNO 14
PROCNO 1

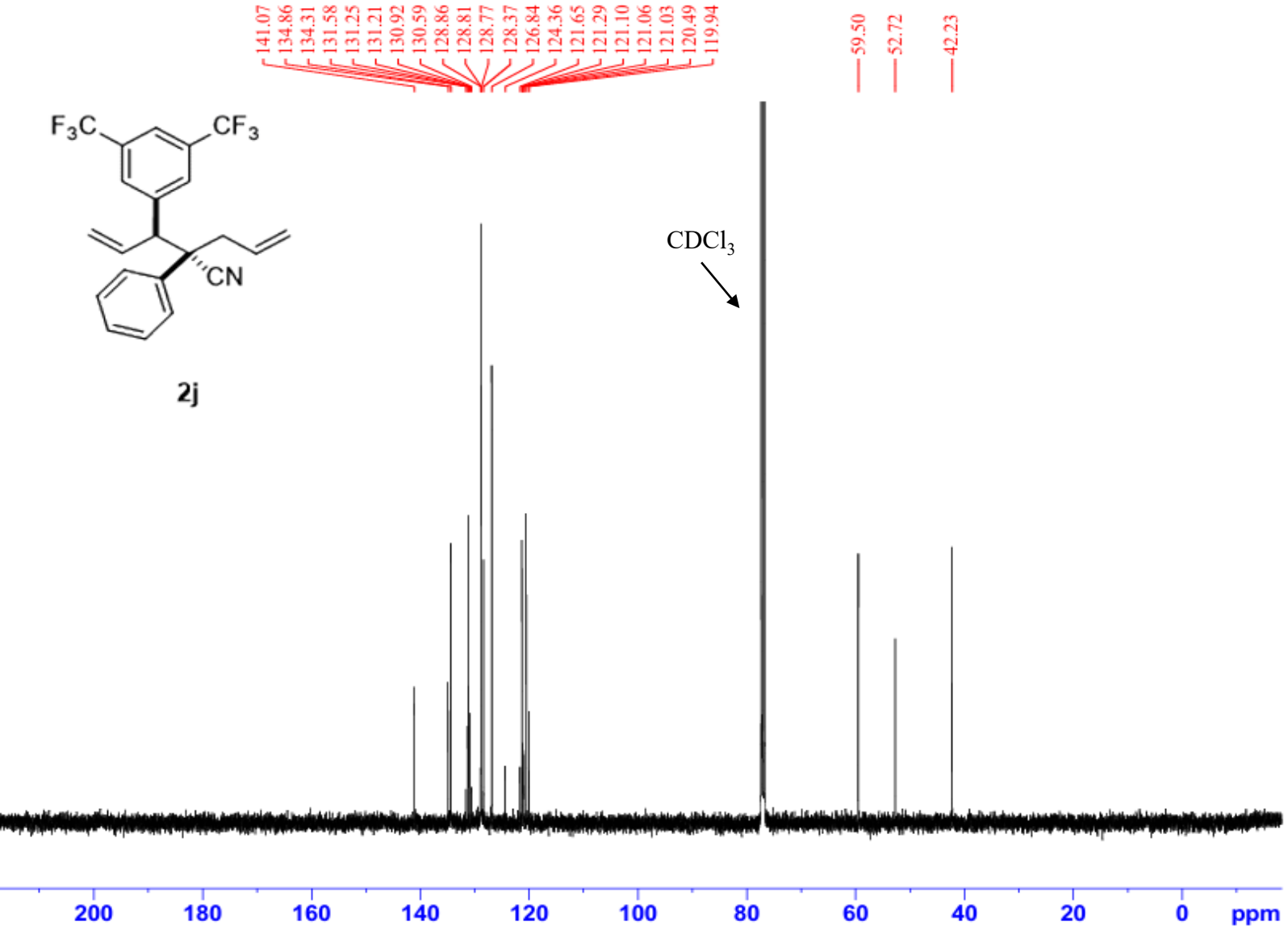
F2 - Acquisition Parameters
Date_ 20210717
Time 13.03 h
INSTRUM Avance Neo
PROBHD Z152088_0031 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 23809.523 Hz
FIDRES 0.726609 Hz
AQ 1.3762560 sec
RG 8.125
DW 21.000 usec
DE 6.50 usec
TE 298.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 100.6228298 MHz
NUC1 13C
P0 2.67 usec
P1 8.00 usec
PLW1 86.55400085 W
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz65
PCPD2 90.00 usec
PLW2 24.03499985 W
PLW12 0.18990999 W
PLW13 0.09552100 W

F2 - Processing parameters
SI 32768
SF 100.6127685 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

^{13}C NMR spectrum of 2**i**



[1]H NMR spectrum of **2i**

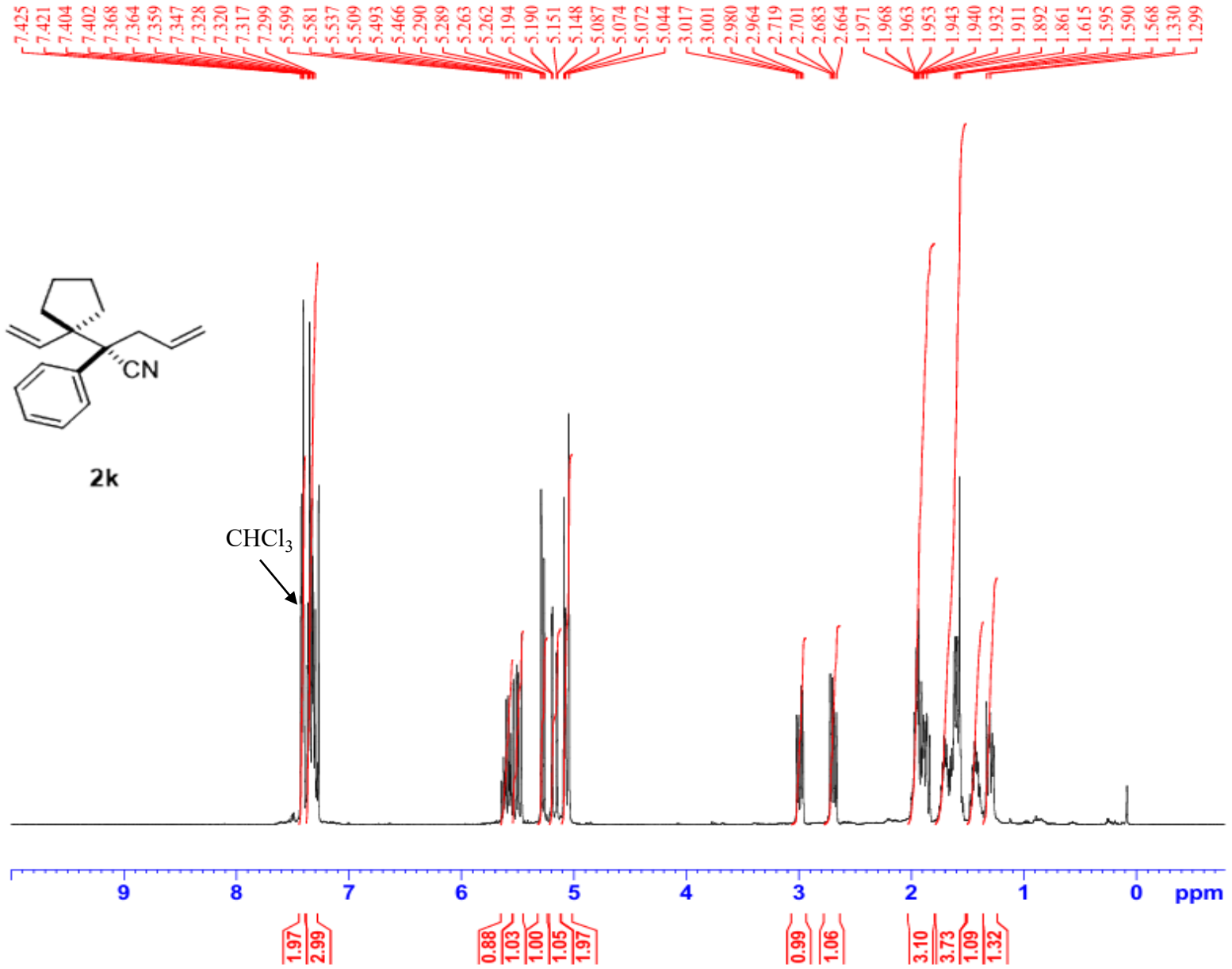



```
Current Data Parameters
NAME      OJ-Bis-CF3-Nitrile-C-2
EXPNO                          6
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20210704
Time                       23.35 h
INSTRUM                Avance Neo
PROBHD    2152088_0031 (
PULPROG                   zgpg30
TD                         65536
SOLVENT                    CDCl3
NS                          1024
DS                             4
SWH                    23809.523 Hz
FIDRES                 0.726609 Hz
AQ                     1.3762560 sec
RG                         8.125
DW                        21.000 usec
DE                         6.50 usec
TE                        298.0 K
D1                    2.00000000 sec
D11                   0.03000000 sec
TD0                            1
SFO1                100.6228298 MHz
NUC1                        13C
P0                         2.67 usec
P1                         8.00 usec
PLW1                86.55400085 W
SFO2                400.1316005 MHz
NUC2                        1H
CPDPRG[2                waltz65
PCPD2                     90.00 usec
PLW2                24.03499985 W
PLW12                0.18990999 W
PLW13                0.09552100 W

F2 - Processing parameters
SI                         32768
SF                  100.6127685 MHz
WDW                           EM
SSB                            0
LB                          1.00 Hz
GB                             0
PC                          1.40
```

^{13}C NMR spectrum of 2**j**

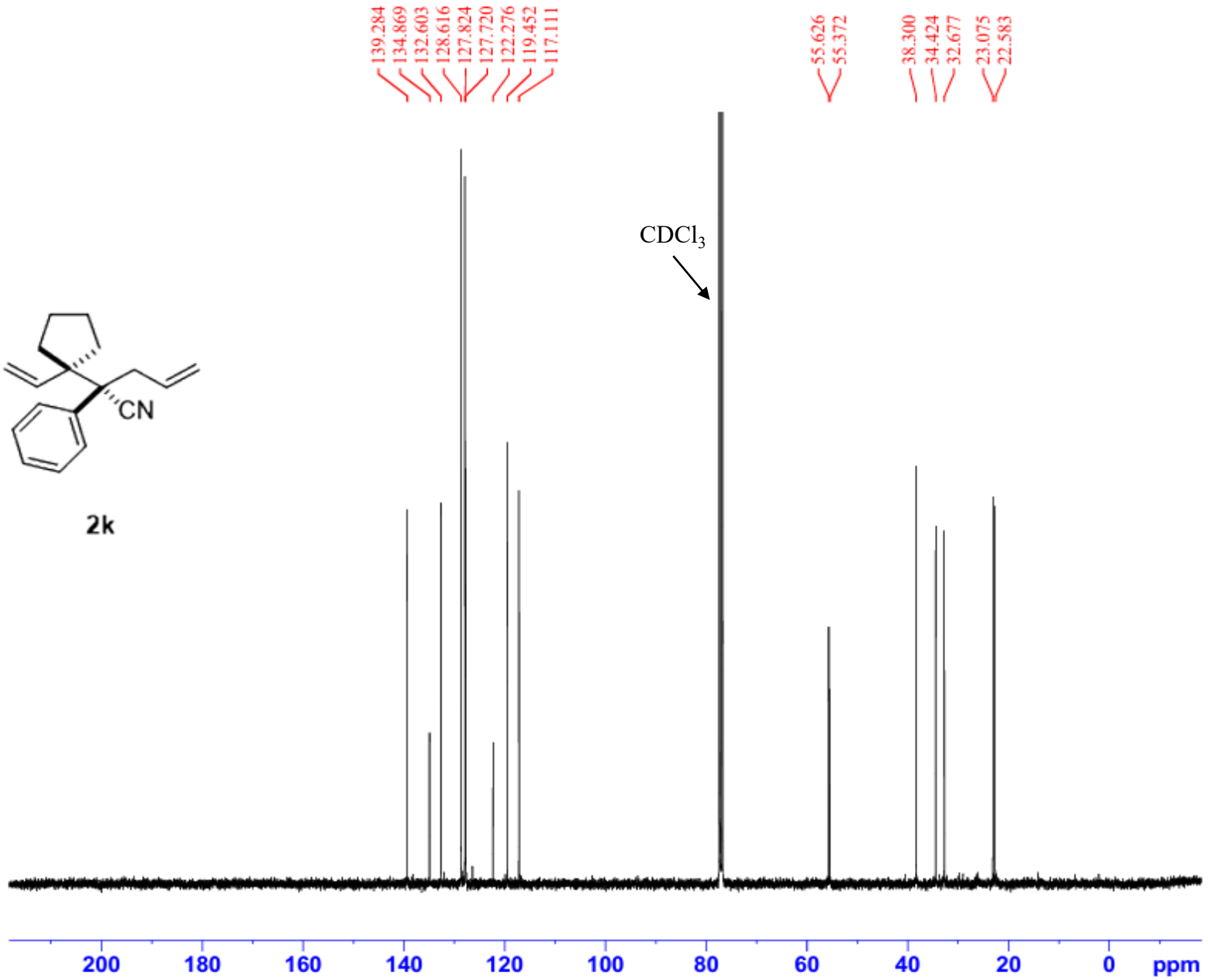



```
Current Data Parameters
NAME                  OJ-2-264-H
EXPNO                         10
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20210812
Time                       10.52 h
INSTRUM                Avance Neo
PROBHD     Z152088_0031 (
PULPROG                    zg30
TD                        65536
SOLVENT                   CDCl3
NS                           16
DS                            2
SWH                     8196.722 Hz
FIDRES                  0.250144 Hz
AQ                      3.9976959 sec
RG                          101
DW                       61.000 usec
DE                       13.89 usec
TE                        298.1 K
D1                    1.00000000 sec
TD0                           1
SFO1                400.1324708 MHz
NUC1                         1H
P0                        2.67 usec
P1                        8.00 usec
PLW1                24.03499985 W

F2 - Processing parameters
SI                        65536
SF                  400.1300060 MHz
WDW                          EM
SSB                           0
LB                         0.30 Hz
GB                            0
PC                         1.00
```

[1]H NMR spectrum of **2k**

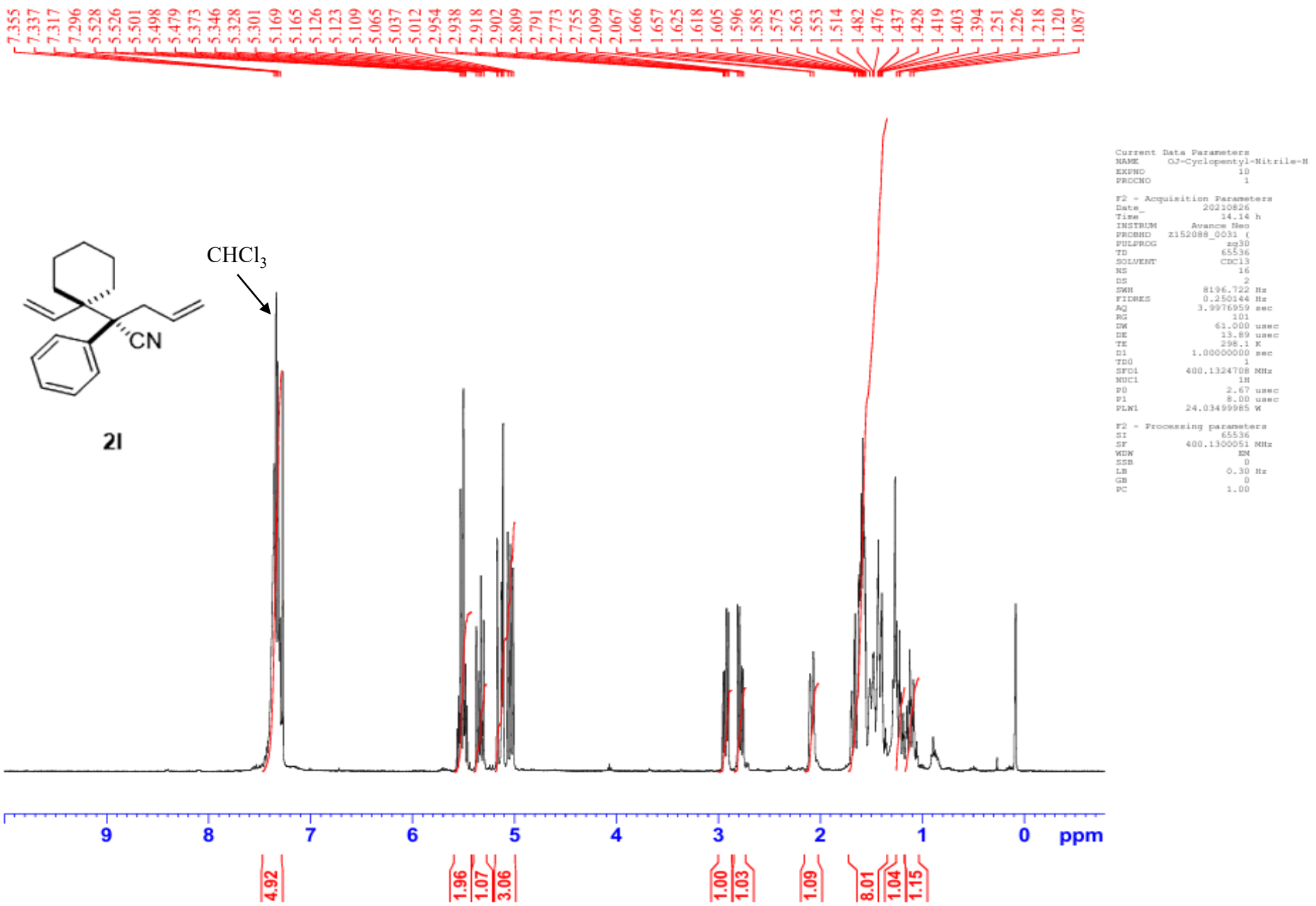



```
Current Data Parameters
NAME        OJ-2-264-H-C
EXPNO               12
PROCNO               1

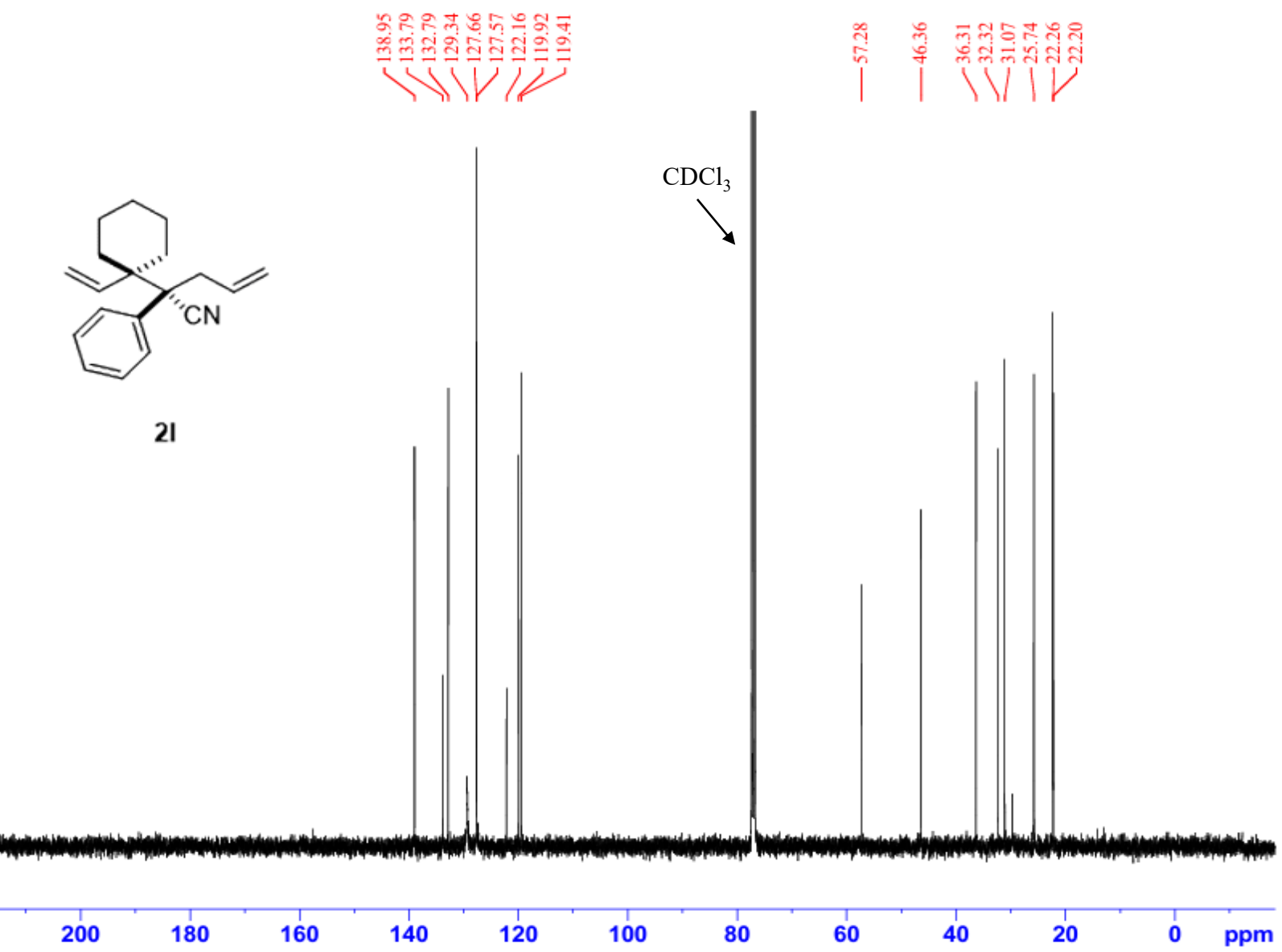
F2 - Acquisition Parameters
Date_          20210812
Time              12.05 h
INSTRUM      Avance Neo
PROBHD   Z152088_0031 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           23809.523 Hz
FIDRES        0.726609 Hz
AQ            1.3762560 sec
RG                8.125
DW               21.000 usec
DE                6.50 usec
TE               298.1 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1
SFO1        100.6228298 MHz
NUC1               13C
P0                2.67 usec
P1                8.00 usec
PLW1         86.55400085 W
SFO2        400.1316005 MHz
NUC2               1H
CPDPRG[2        waltz65
PCPD2            90.00 usec
PLW2         24.03499985 W
PLW12         0.18990999 W
PLW13         0.09552100 W

F2 - Processing parameters
SI                32768
SF          100.6127685 MHz
WDW                EM
SSB                   0
LB                1.00 Hz
GB                    0
PC                1.40
```

^{13}C NMR spectrum of 2**k**



^{1}H NMR spectrum of **2l**

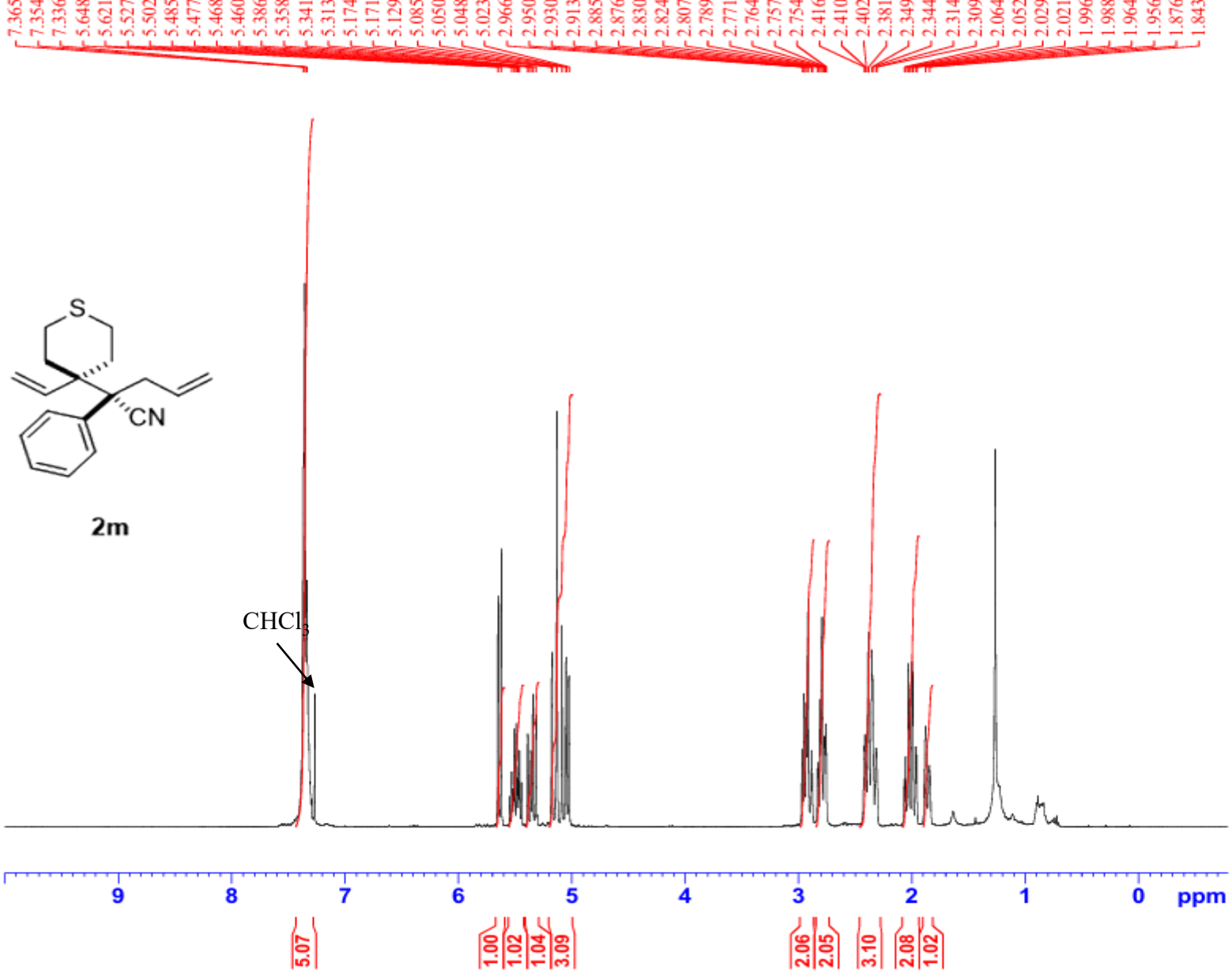


Current Data Parameters
NAME OJ-Cyclohexyl-Nitrile-C
EXPNO 13
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210826
Time 15.19 h
INSTRUM Avance Neo
PROBHD 2152088_0031 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 23809.523 Hz
FIDRES 0.726609 Hz
AQ 1.3762560 sec
RG 8.125
DW 21.000 usec
DE 6.50 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 100.6228298 MHz
NUC1 13C
P0 2.67 usec
P1 8.00 usec
PLW1 86.55400085 W
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz65
PCPD2 90.00 usec
PLW2 24.03499985 W
PLW12 0.18990999 W
PLW13 0.09552100 W

F2 - Processing parameters
SI 32768
SF 100.6127685 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

^{13}C NMR spectrum of **2l**

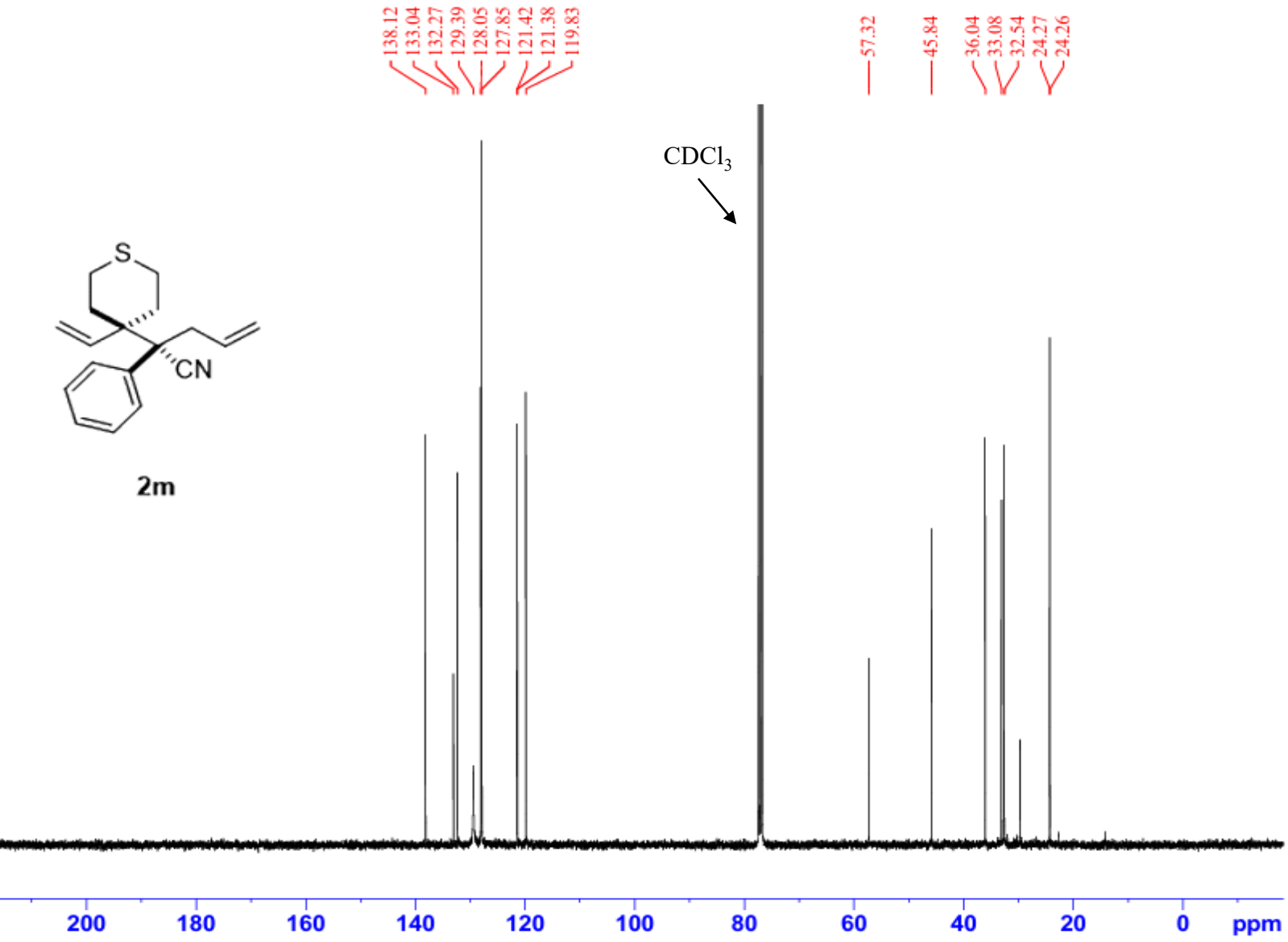



```
Current Data Parameters
NAME          OJ-2-290-H
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210905
Time              18.28 h
INSTRUM       Avance Neo
PROBHD    Z152088_0031 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8196.722 Hz
FIDRES          0.250144 Hz
AQ              3.9976959 sec
RG                   101
DW                61.000 usec
DE                13.89 usec
TE                298.1 K
D1            1.00000000 sec
TD0                    1
SFO1          400.1324708 MHz
NUC1                  1H
P0                 2.67 usec
P1                 8.00 usec
PLW1         24.03499985 W

F2 - Processing parameters
SI                 65536
SF          400.1300070 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

[1]H NMR spectrum of **2m**

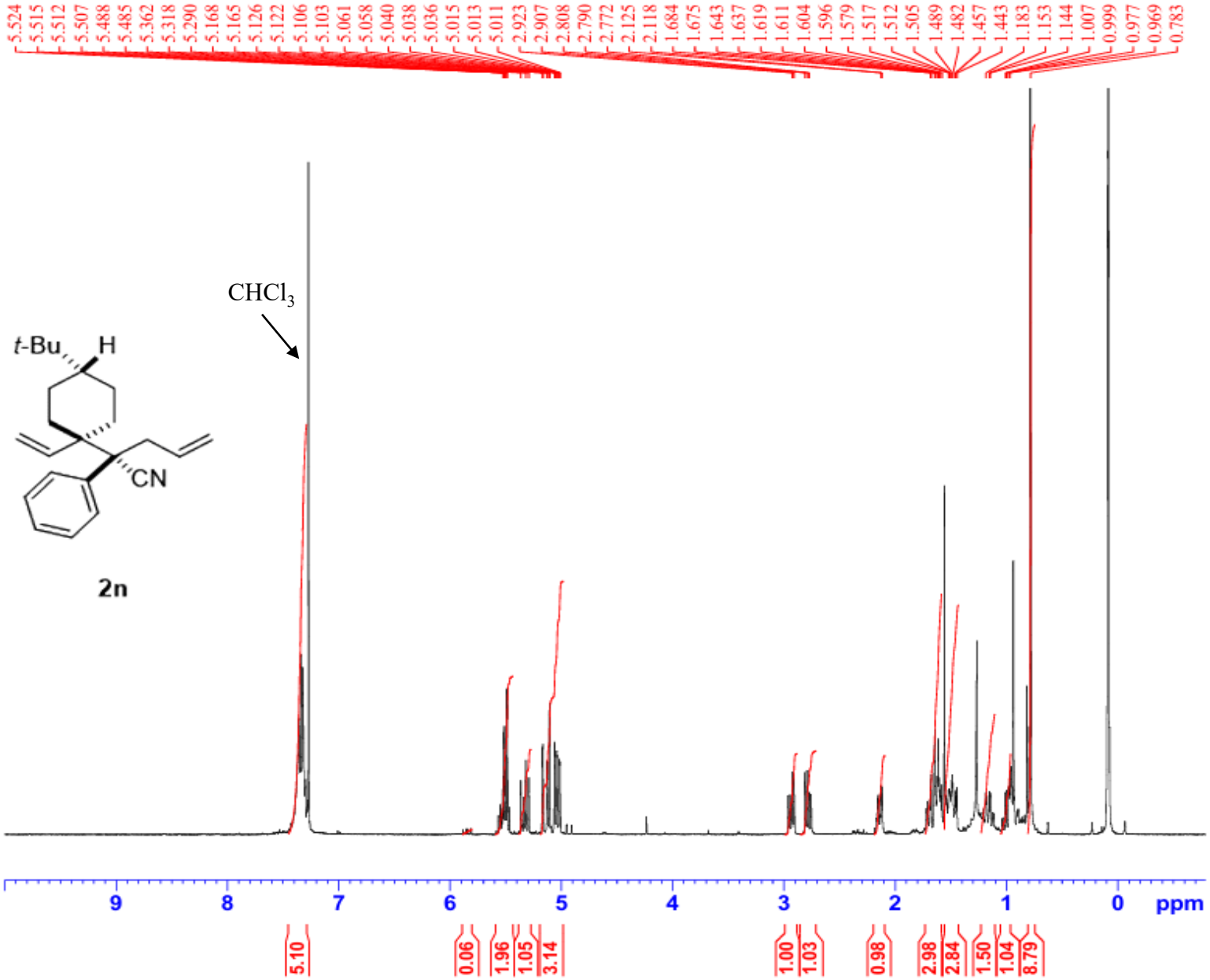



```
Current Data Parameters
NAME                  OJ-2-290-C
EXPNO                          7
PROCNO                         1

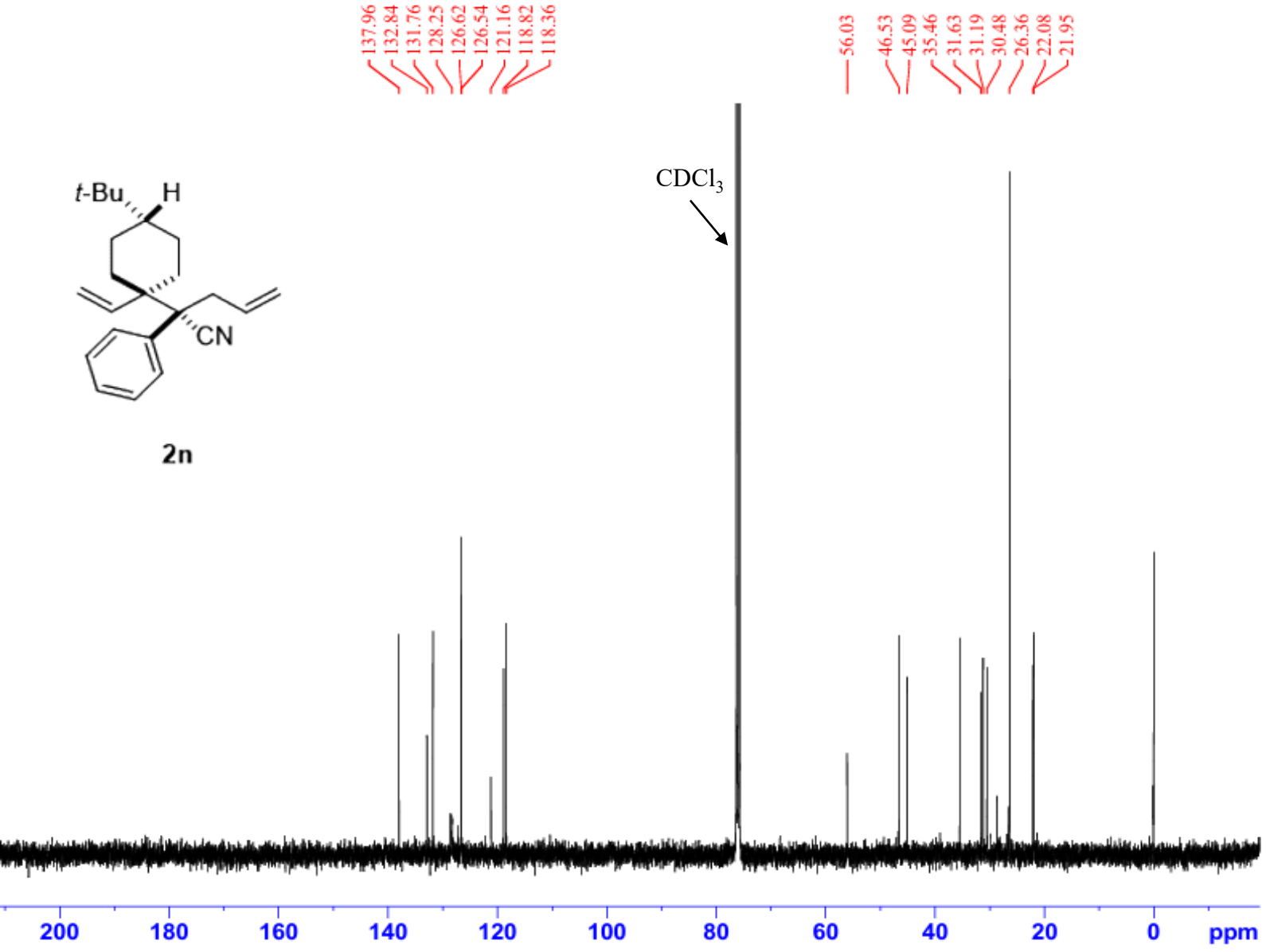
F2 - Acquisition Parameters
Date_                   20210905
Time                       19.29 h
INSTRUM                Avance Neo
PROBHD    Z152088_0031 (
PULPROG                  zgpg30
TD                          65536
SOLVENT                   CDCl3
NS                           1024
DS                              4
SWH                     23809.523 Hz
FIDRES                  0.726609 Hz
AQ                      1.3762560 sec
RG                          8.125
DW                         21.000 usec
DE                          6.50 usec
TE                         298.1 K
D1                    2.00000000 sec
D11                   0.03000000 sec
TD0                             1
SFO1                100.6228298 MHz
NUC1                         13C
P0                          2.67 usec
P1                          8.00 usec
PLW1                86.55400085 W
SFO2                400.1316005 MHz
NUC2                         1H
CPDPRG[2                waltz65
PCPD2                      90.00 usec
PLW2                24.03499985 W
PLW12                0.18990999 W
PLW13                0.09552100 W

F2 - Processing parameters
SI                          32768
SF                  100.6127685 MHz
WDW                            EM
SSB                             0
LB                           1.00 Hz
GB                              0
PC                           1.40
```

^{13}C NMR spectrum of **2m**



^{1}H NMR spectrum of **2n**

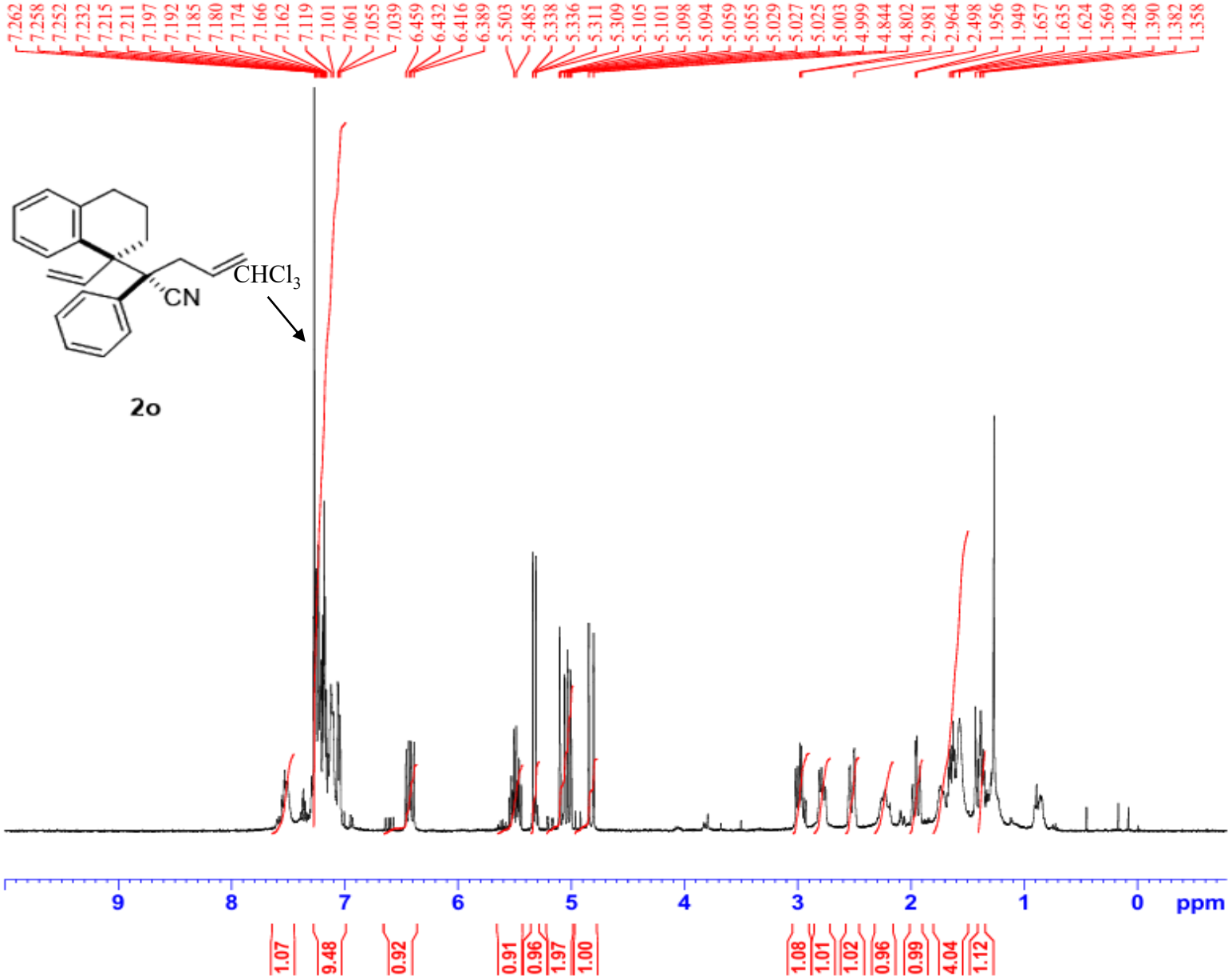



```
Current Data Parameters
NAME      OJ-2-334-Product-A-C
EXPNO                       12
PROCNO                       1

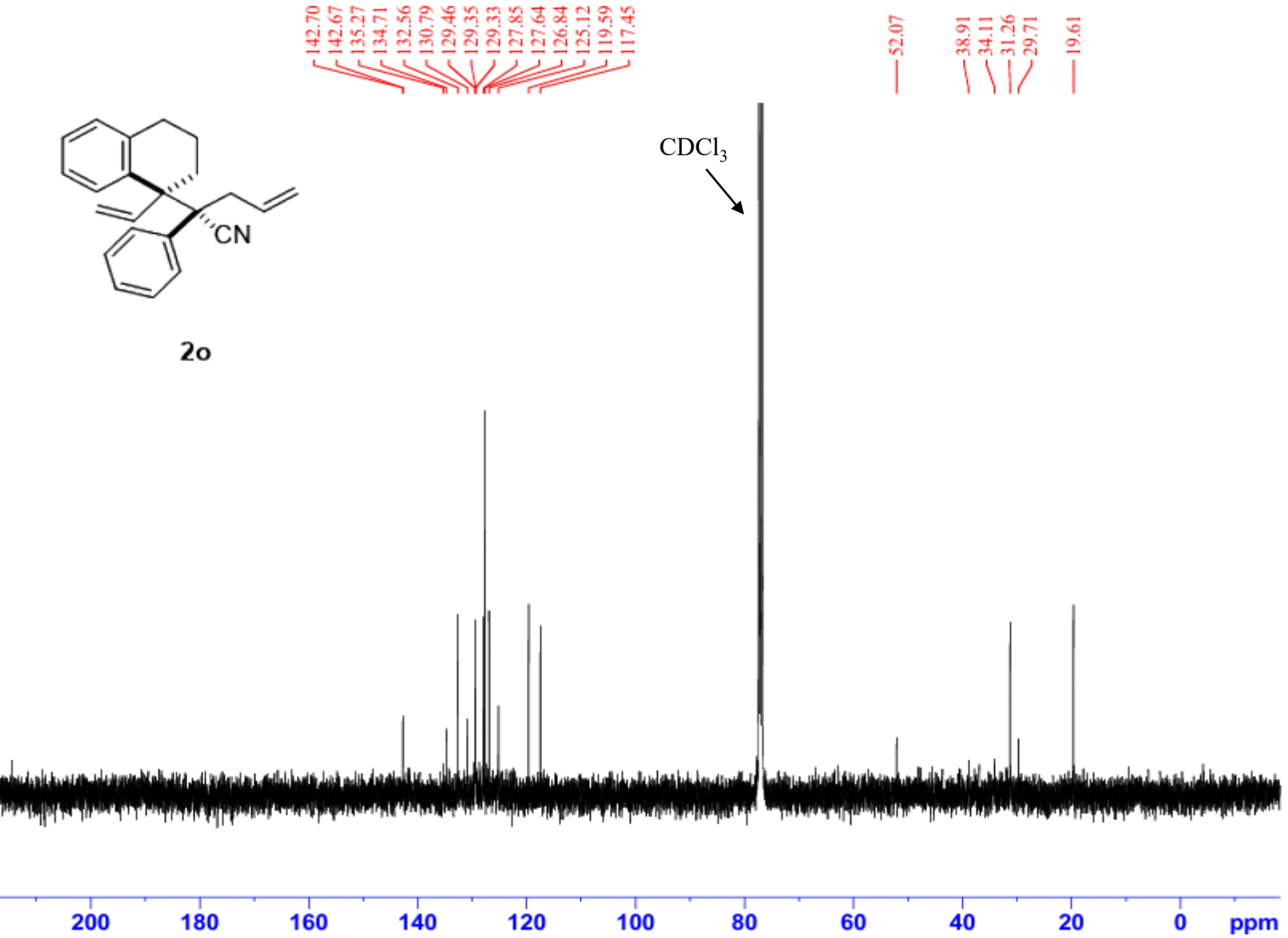
F2 - Acquisition Parameters
Date_              20211121
Time                 22.13 h
INSTRUM       Avance Neo
PROBHD    Z152088_0031 (
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    1024
DS                       4
SWH              23809.523 Hz
FIDRES           0.726609 Hz
AQ               1.3762560 sec
RG                   8.125
DW                  21.000 usec
DE                   6.50 usec
TE                  298.0 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1
SFO1          100.6228298 MHz
NUC1                   13C
P0                   2.67 usec
P1                   8.00 usec
PLW1          86.55400085 W
SFO2          400.1316005 MHz
NUC2                   1H
CPDPRG[2          waltz65
PCPD2               90.00 usec
PLW2          24.03499985 W
PLW12          0.18990999 W
PLW13          0.09552100 W

F2 - Processing parameters
SI                   32768
SF            100.6128730 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

^{13}C NMR spectrum of **2n**



^{1}H NMR spectrum of **2o**

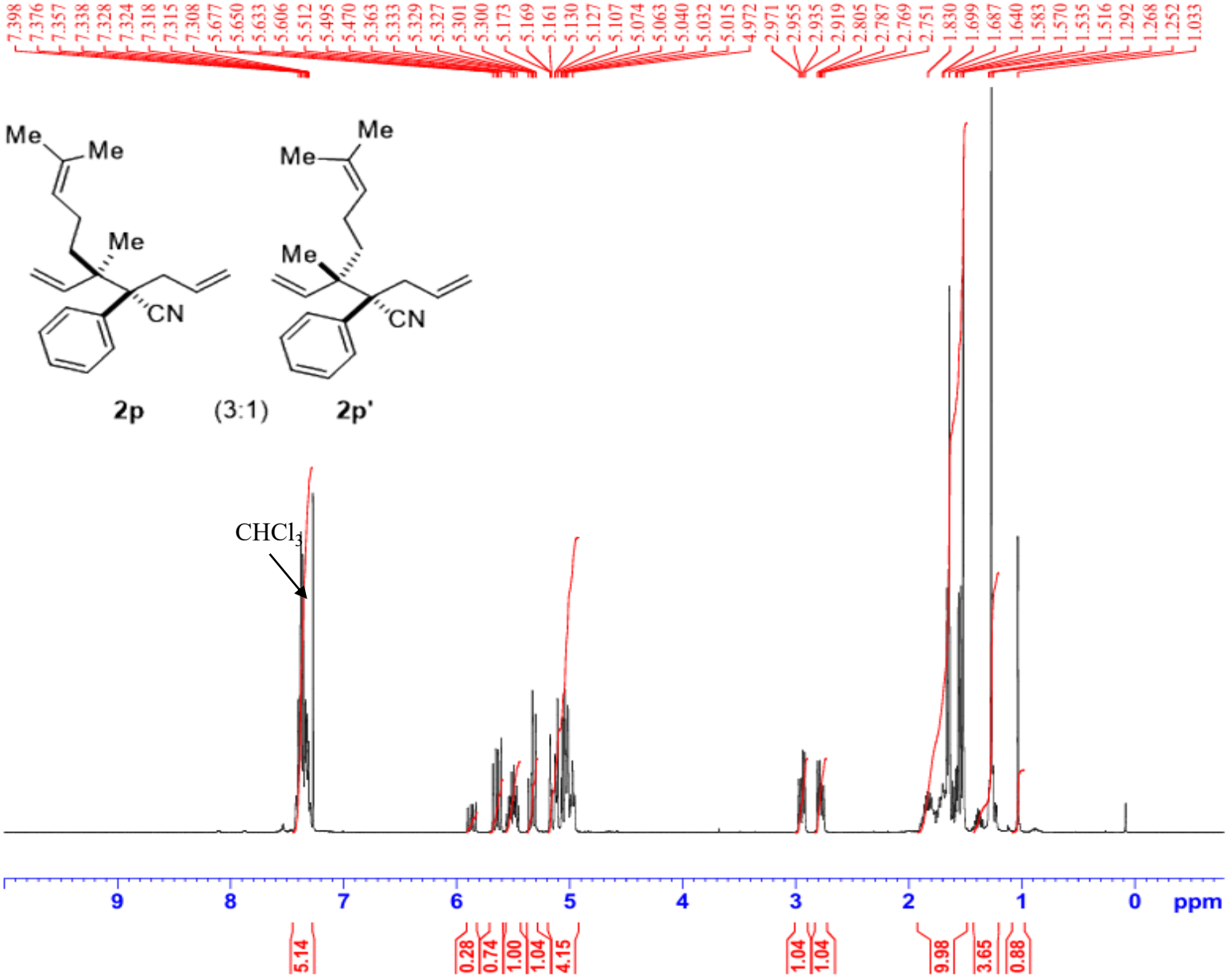



```
Current Data Parameters
NAME      OJ-2-Tetralone-nitrile-C
EXPNO                 12
PROCNO                 1

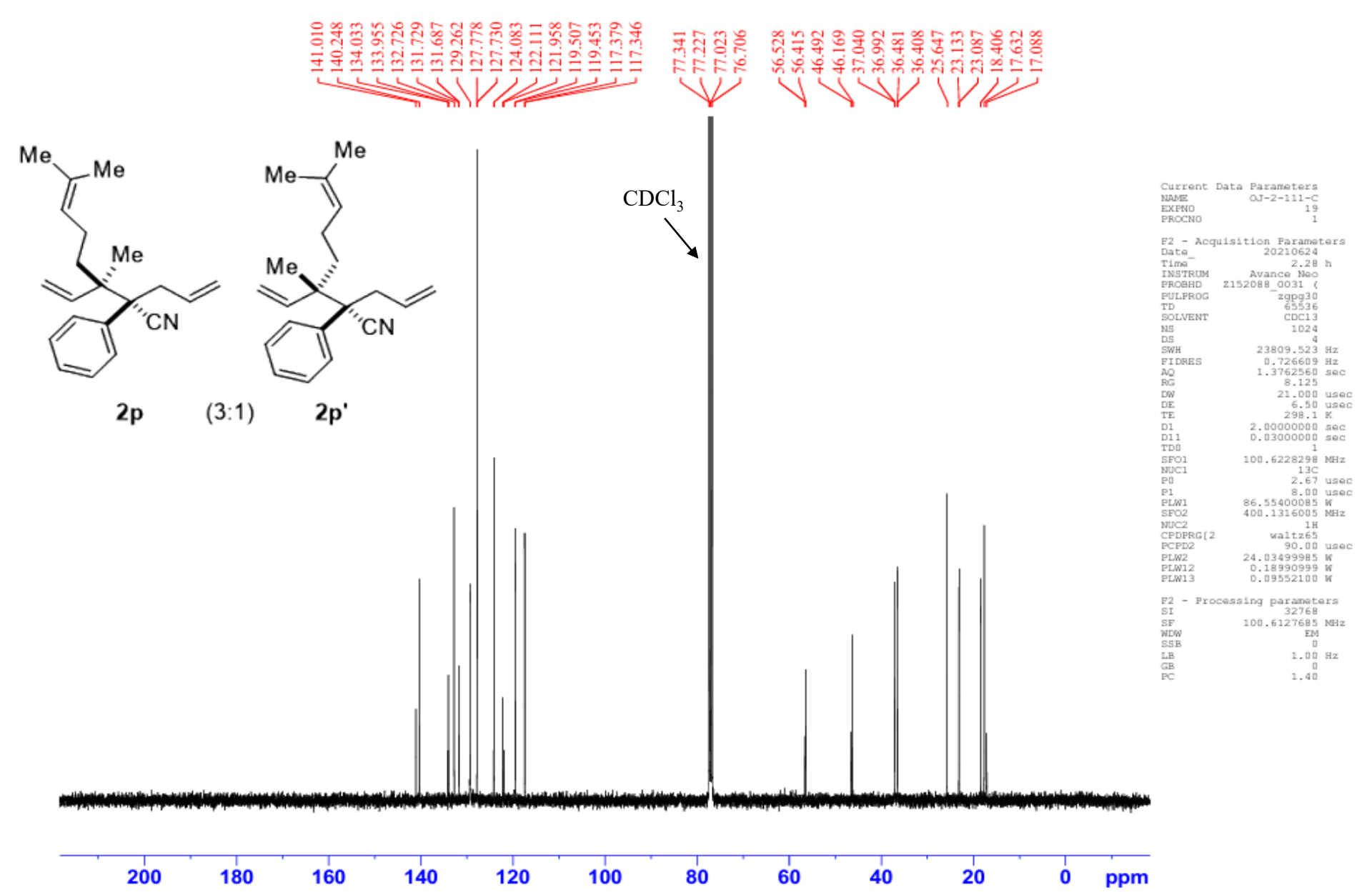
F2 - Acquisition Parameters
Date_           20210911
Time                1.36 h
INSTRUM         Avance Neo
PROBHD    2152088_0031 (
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  2048
DS                     4
SWH            23809.523 Hz
FIDRES          0.726609 Hz
AQ              1.3762560 sec
RG                 8.125
DW                21.000 usec
DE                 6.50 usec
TE                298.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1
SFO1          100.6228298 MHz
NUC1                 13C
P0                  2.67 usec
P1                  8.00 usec
PLW1          86.55400085 W
SFO2          400.1316005 MHz
NUC2                 1H
CPDPRG[2          waltz65
PCPD2              90.00 usec
PLW2          24.03499985 W
PLW12          0.18990999 W
PLW13          0.09552100 W

F2 - Processing parameters
SI                 32768
SF            100.6127685 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

^{13}C NMR spectrum of **2o**



^{1}H NMR spectrum of **2p and 2p'**

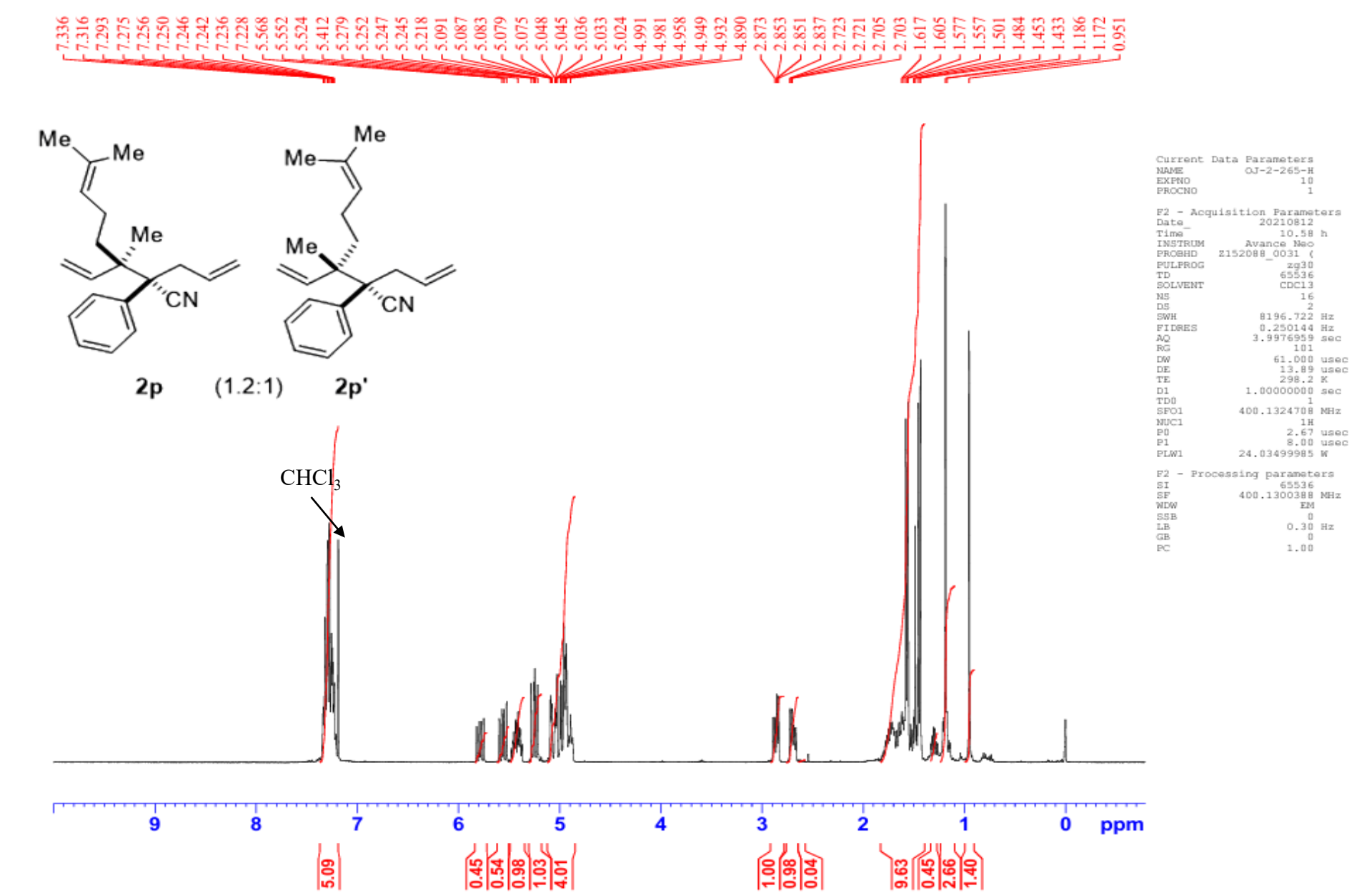



```
Current Data Parameters
NAME                  OJ-2-111-C
EXPNO                         19
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20210624
Time                        2.28 h
INSTRUM                Avance Neo
PROBHD          Z152088_0031 (
PULPROG                  zgpg30
TD                        65536
SOLVENT                   CDCl3
NS                         1024
DS                            4
SWH                   23809.523 Hz
FIDRES                 0.726609 Hz
AQ                     1.3762560 sec
RG                         8.125
DW                        21.000 usec
DE                         6.50 usec
TE                        298.1 K
D1                    2.00000000 sec
D11                   0.03000000 sec
TD0                           1
SFO1                100.6228298 MHz
NUC1                        13C
P0                         2.67 usec
P1                         8.00 usec
PLW1                86.55400085 W
SFO2                400.1316005 MHz
NUC2                        1H
CPDPRG[2                waltz65
PCPD2                     90.00 usec
PLW2                24.03499985 W
PLW12                0.18990999 W
PLW13                0.09552100 W

F2 - Processing parameters
SI                        32768
SF                  100.6127685 MHz
WDW                          EM
SSB                           0
LB                         1.00 Hz
GB                            0
PC                         1.40
```

^{13}C NMR spectrum of **2p and 2p'**

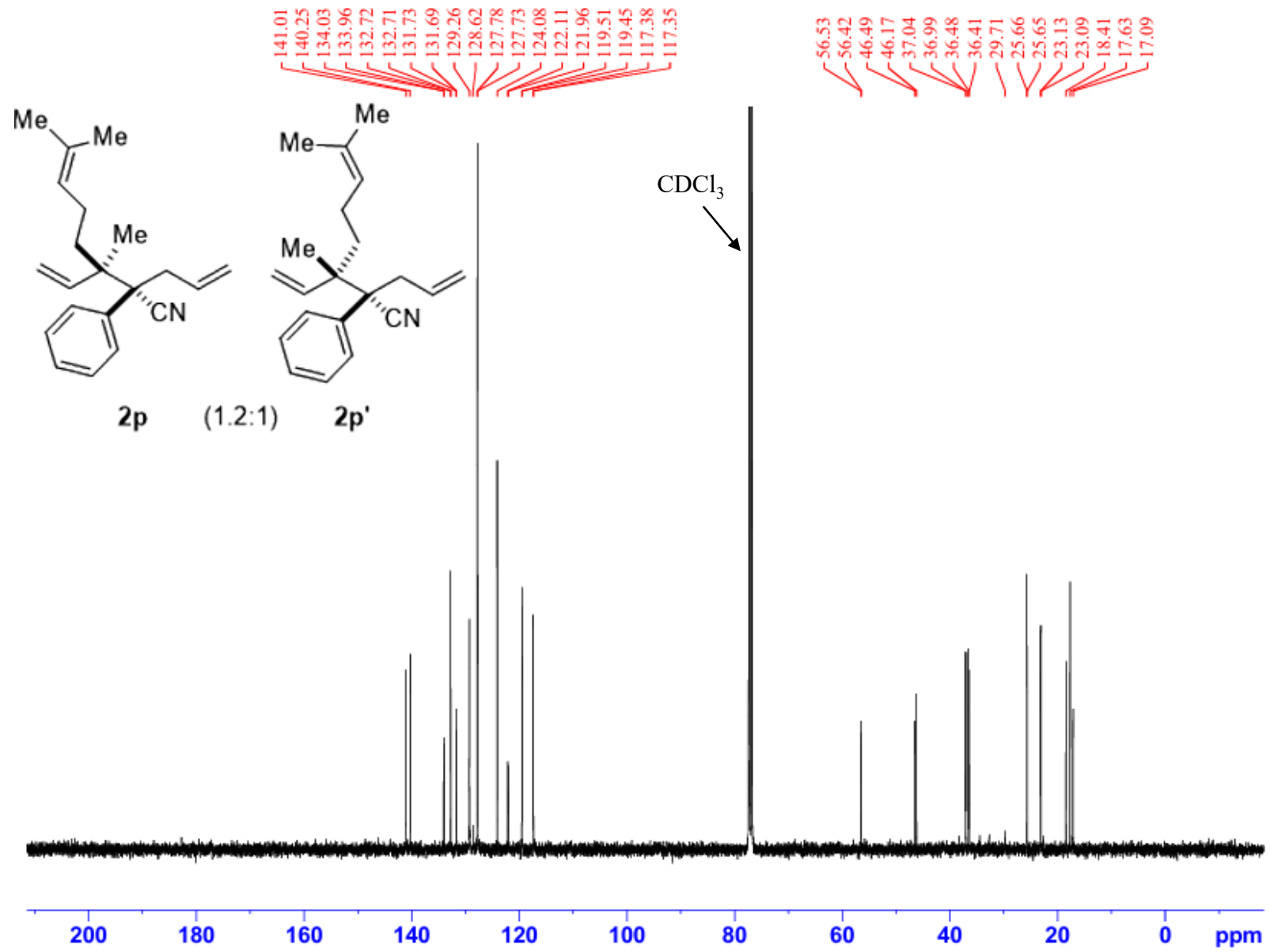



```
Current Data Parameters
NAME                  OJ-2-265-H
EXPNO                         10
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20210812
Time                       10.58 h
INSTRUM             Avance Neo
PROBHD          Z152088_0031 (
PULPROG                    zg30
TD                        65536
SOLVENT                   CDCl3
NS                           16
DS                            2
SWH                    8196.722 Hz
FIDRES                 0.250144 Hz
AQ                     3.9976959 sec
RG                          101
DW                       61.000 usec
DE                       13.89 usec
TE                       298.2 K
D1                  1.00000000 sec
TD0                           1
SFO1                400.1324708 MHz
NUC1                        1H
P0                        2.67 usec
P1                        8.00 usec
PLW1                24.03499985 W

F2 - Processing parameters
SI                        65536
SF                  400.1300388 MHz
WDW                          EM
SSB                           0
LB                         0.30 Hz
GB                            0
PC                         1.00
```

[1]H NMR spectrum of **2p and 2p'**

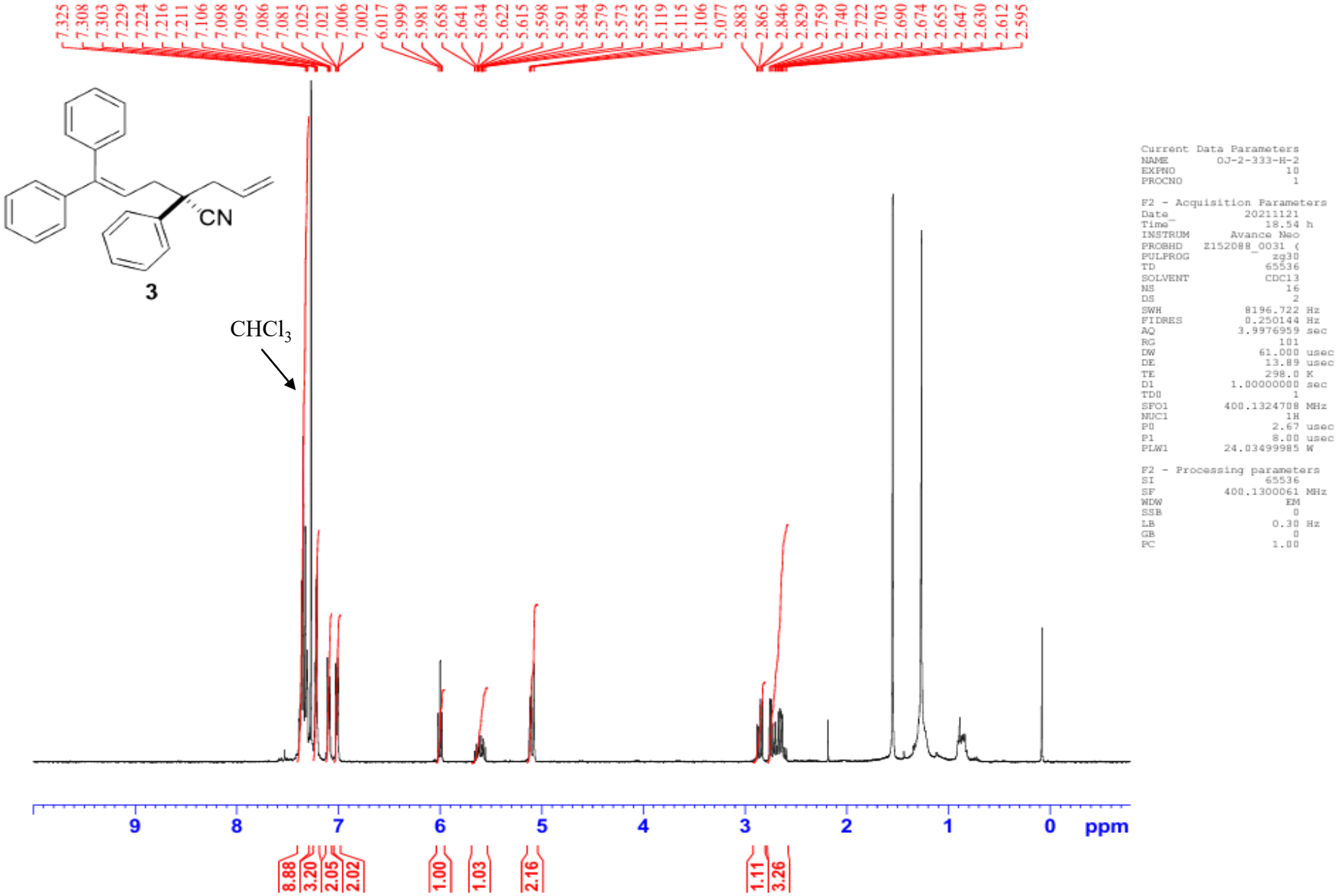



```
Current Data Parameters
NAME                  OJ-2-265-C
EXPNO                         12
PROCNO                         1

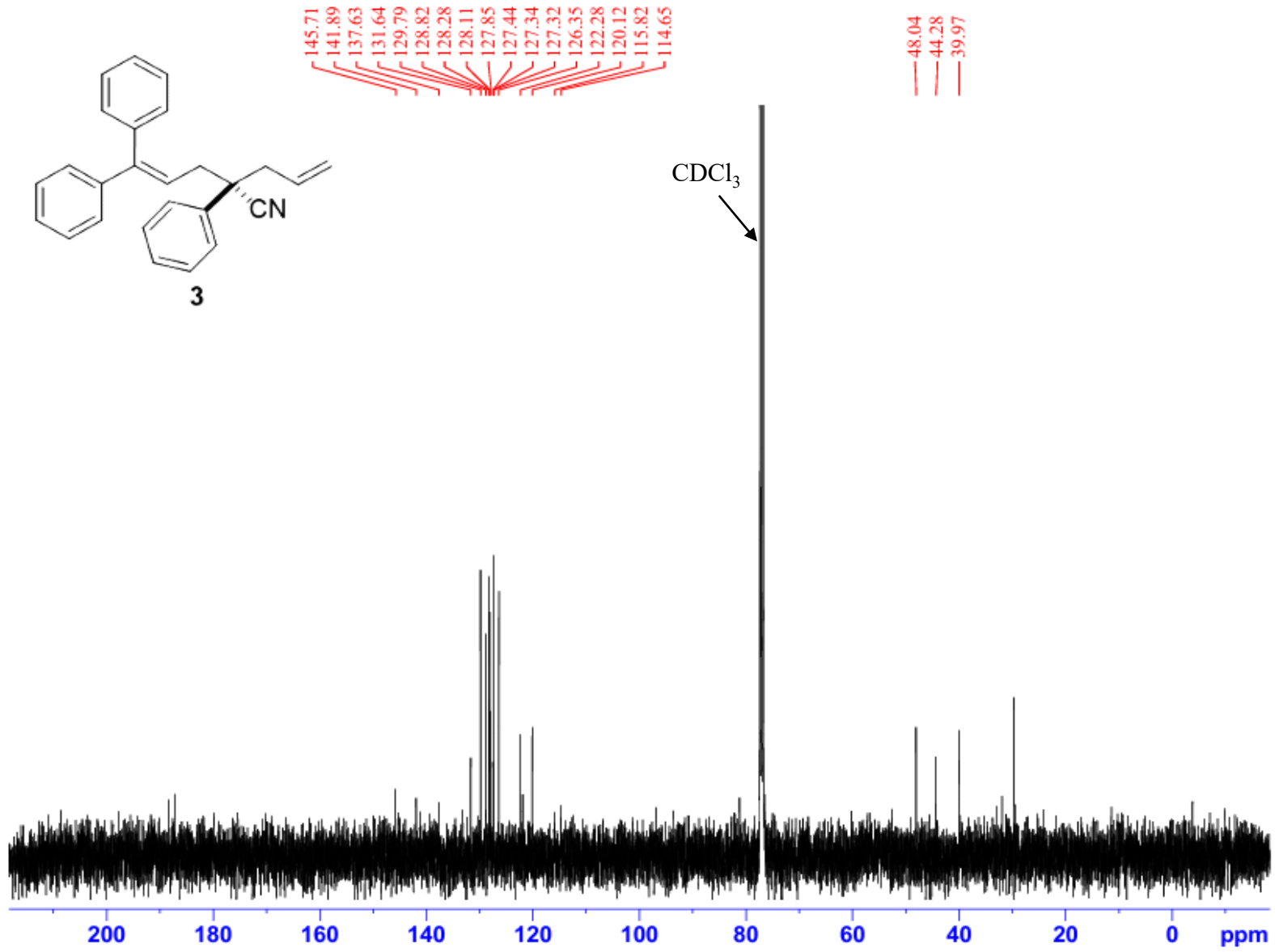
F2 - Acquisition Parameters
Date_                   20210812
Time                       14.35 h
INSTRUM                Avance Neo
PROBHD    Z152088_0031 (
PULPROG                  zgpg30
TD                          65536
SOLVENT                   CDCl3
NS                           1024
DS                              4
SWH                    23809.523 Hz
FIDRES                 0.726609 Hz
AQ                     1.3762560 sec
RG                         8.125
DW                        21.000 usec
DE                         6.50 usec
TE                        298.2 K
D1                     2.00000000 sec
D11                    0.03000000 sec
TD0                             1
SFO1                 100.6228298 MHz
NUC1                         13C
P0                         2.67 usec
P1                         8.00 usec
PLW1                86.55400085 W
SFO2                 400.1316005 MHz
NUC2                         1H
CPDPRG[2                waltz65
PCPD2                     90.00 usec
PLW2                24.03499985 W
PLW12                0.18990999 W
PLW13                0.09552100 W

F2 - Processing parameters
SI                          32768
SF                   100.6127685 MHz
WDW                            EM
SSB                             0
LB                         1.00 Hz
GB                              0
PC                         1.40
```

^{13}C NMR spectrum of **2p and 2p'**



^{1}H NMR spectrum of **3**

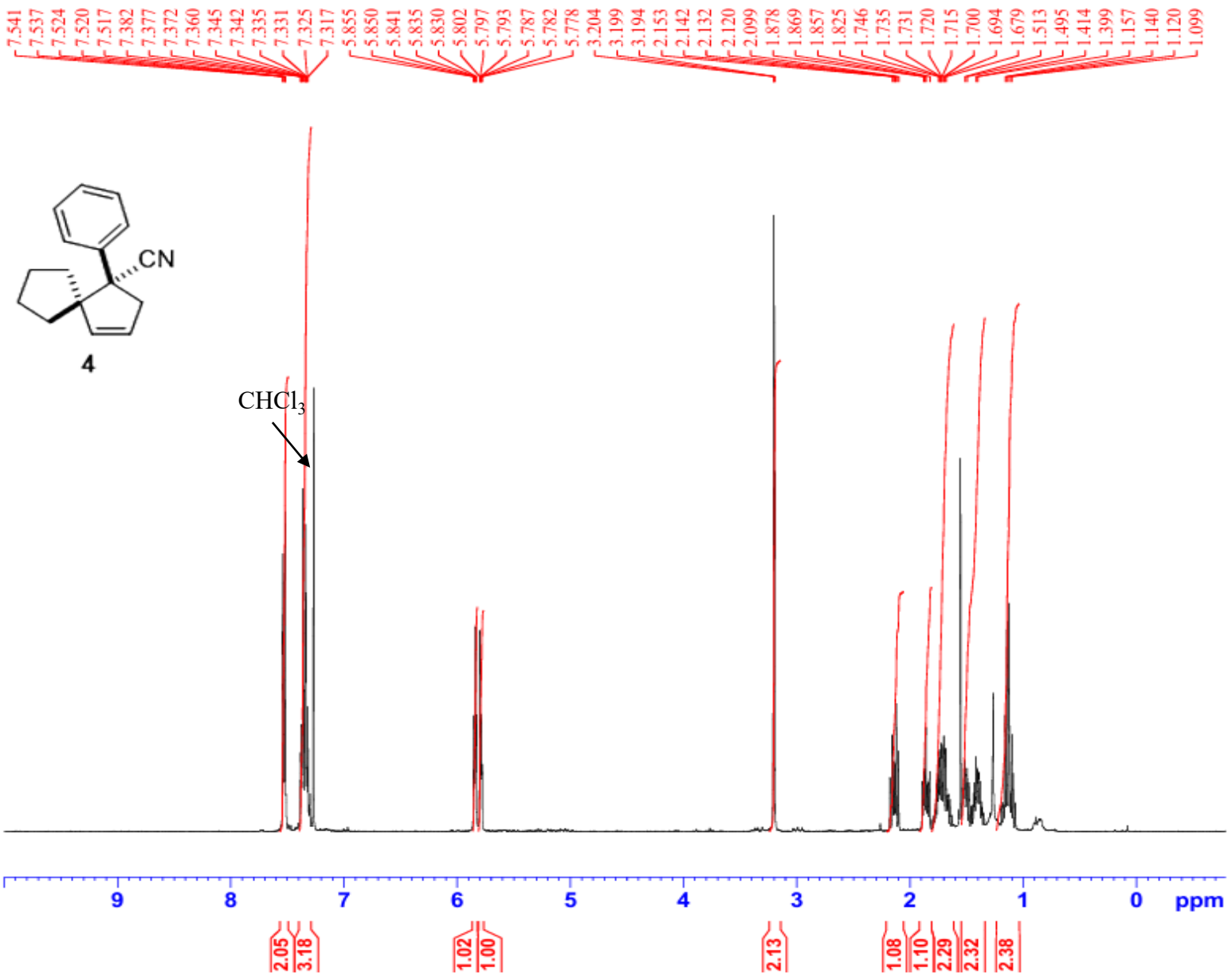



```
Current Data Parameters
NAME                 OJ-2-333-C
EXPNO                        10
PROCNO                        1

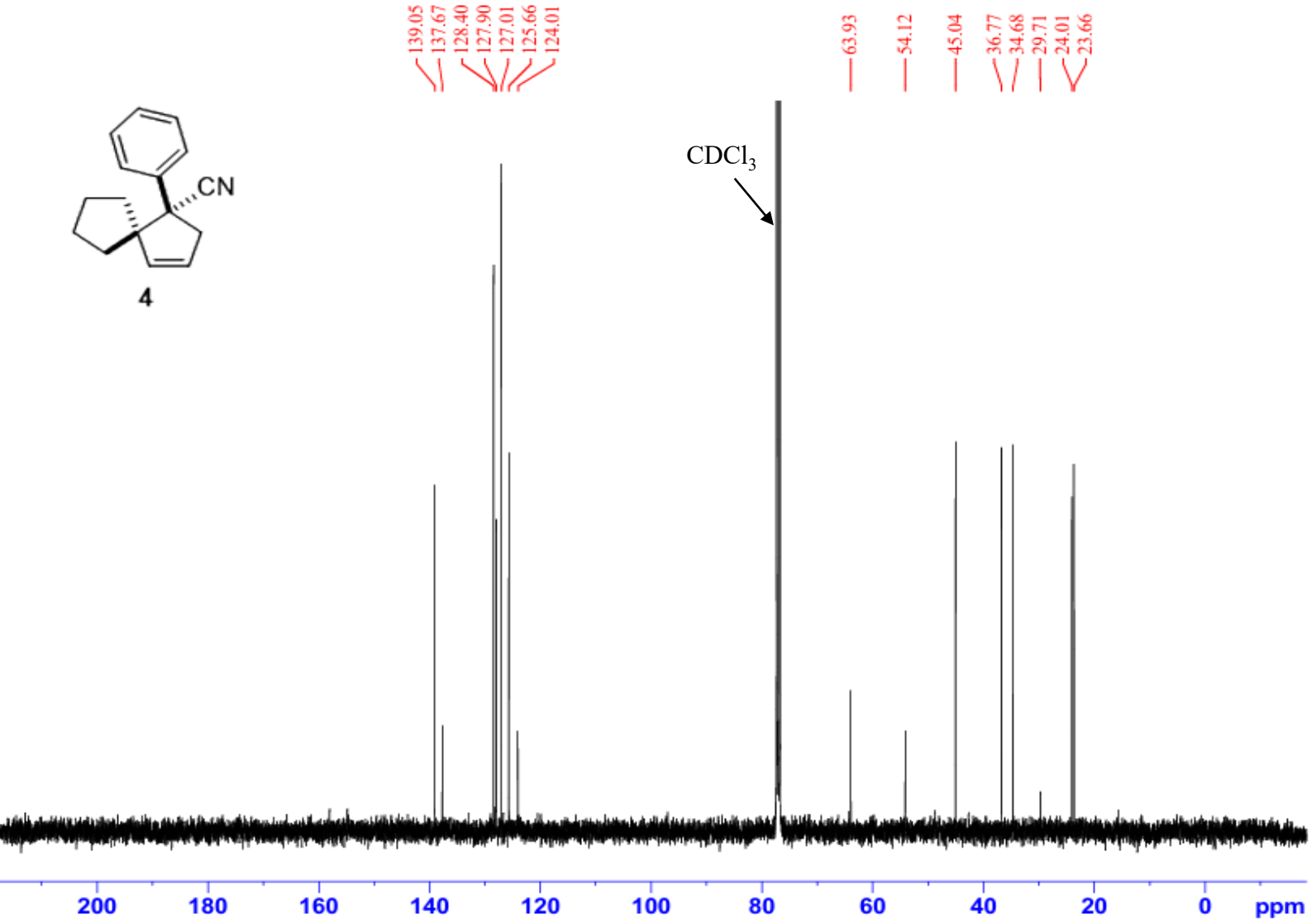
F2 - Acquisition Parameters
Date_               20211121
Time                    20.11 h
INSTRUM              Avance Neo
PROBHD    Z152088_0031 (
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                        1024
DS                           4
SWH                  23809.523 Hz
FIDRES                0.726609 Hz
AQ                    1.3762560 sec
RG                        8.125
DW                       21.000 usec
DE                        6.50 usec
TE                       298.0 K
D1                    2.00000000 sec
D11                   0.03000000 sec
TD0                          1
SFO1                100.6228298 MHz
NUC1                        13C
P0                        2.67 usec
P1                        8.00 usec
PLW1                86.55400085 W
SFO2                400.1316005 MHz
NUC2                        1H
CPDPRG[2                waltz65
PCPD2                    90.00 usec
PLW2                24.03499985 W
PLW12                0.18990999 W
PLW13                0.09552100 W

F2 - Processing parameters
SI                       32768
SF                  100.6127685 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40
```

^{13}C NMR spectrum of **3**



^{1}H NMR spectrum of **4**




```
Current Data Parameters
NAME                  OJ-2-274-C
EXPNO                          7
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20210822
Time                       21.15 h
INSTRUM                Avance Neo
PROBHD          Z152088_0031 (
PULPROG                   zgpg30
TD                         65536
SOLVENT                    CDCl3
NS                          1024
DS                             4
SWH                    23809.523 Hz
FIDRES                 0.726609 Hz
AQ                     1.3762560 sec
RG                         8.125
DW                        21.000 usec
DE                         6.50 usec
TE                        298.2 K
D1                     2.00000000 sec
D11                    0.03000000 sec
TD0                            1
SFO1                 100.6228298 MHz
NUC1                        13C
P0                         2.67 usec
P1                         8.00 usec
PLW1                86.55400085 W
SFO2                 400.1316005 MHz
NUC2                        1H
CPDPRG[2                waltz65
PCPD2                     90.00 usec
PLW2                24.03499985 W
PLW12                0.18990999 W
PLW13                0.09552100 W

F2 - Processing parameters
SI                         32768
SF                   100.6127685 MHz
WDW                           EM
SSB                            0
LB                         1.00 Hz
GB                             0
PC                          1.40
```

^{13}C NMR spectrum of **4**

APPENDIX B

CHAPTER THREE SUPPORING INFORMATION

Experimental Details

General Materials and Methods

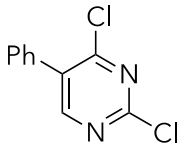
NMR spectra were recorded at 298 K on a Bruker DRX 500 MHz (500.233 MHz for ^{1}H, 125.795 MHz for ^{13}C, 470.639 MHz for ^{19}F) or a Bruker Ascend 400 MHz (400.130 MHz for ^{1}H NMR, 100.613 for ^{13}C). ^{1}H and ^{13}C NMR chemical shifts are reported in parts per million (ppm) relative to TMS, with the residual solvent peak used as an internal reference [^{1}H NMR: $CHCl_3$ (7.26 ppm), C_6D_5H (7.16 ppm), $(CHD_2)OD$ (3.31 ppm), $(CD_3)CO(CD_2H)$ (2.05 ppm); ^{13}C NMR: $CDCl_3$ (77.16 ppm), C_6D_6 (128.06 ppm), $(CD_3)OD$ (49.00 ppm), $(CD_3)_2CO$ (29.84 ppm)]. ^{19}F NMR chemical shifts are reported in parts per million (ppm) relative to trifluorotoluene (-63.72 ppm) as an internal reference. Multiplicities are reported as follows: singlet (s), broad singlet (br s), doublet (d), doublet of doublets (dd), doublet of doublets of doublets (ddd), triplet (t), quartet (q), triplet of triplets (tt), quintet (quint), and multiplet (m). GC data were collected using a Shimadzu GC-2010 Plus with a flame ionization detector equipped with a SH-Rxi-5ms capillary column (15 m x 0.25 mm ID x 0.25 μm df). GCMS data were collected with a Shimadzu GC-2030 paired with a Shimadzu GCMS-QP2020 NX and equipped with a SH-Rxi-5ms capillary column (30 m x 0.25 mm ID x 0.25 μm df). LC-MS analyses were performed on an Agilent 6538 Q-TOF MS coupled to an Agilent 1290 Infinity UHPLC system or a Bruker Autoflex III MALDI TOF MS. A 50 mm long Eclipse Plus C18 column (Agilent Technologies, Santa Barbara, CA; i.d. 2.1 mm, 1.8 μm particle size) was used for liquid chromatography separation at a column temperature of 50 ºC. Electrospray ionization was operated in positive-ion mode with an m/z range of 50-1700 at 2 Hz. For analysis with the MALDI TOF MS, a matrix of saturated 2,5-dihydroxybenzoic acid in 50/50 MeOH:H2O was used. The MALDI TOF MS was operated in positive-ion mode with an m/z range of 100-3500, with 1000 laser shots at 100 Hz. All reactions that require heating were conducted in aluminum single-size vial reaction blocks (Chemglass) fitted to an IKA stirring hot plate equipped with a temperature probe.

Unless otherwise noted below, all commercially-obtained chemicals were used as received. Pd-PEPPSI-IPr, Pd-PEPPSI-IPent, benzyl mercaptan, 6-mercapto-1-hexanol, *N*-(*tert*-butoxycarbonyl)-*L*-cysteine, [1,3-bis(diphenylphosphino)propane]palladium(II) chloride

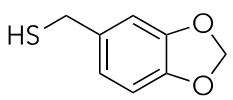
dichlorobis(tri-*o*-tolylphosphine)palladium(II), (η^3-1-allyl)Pd(IPr)(Cl) and (η^3-1-cinnamyl)Pd(IPr)(Cl) were obtained from Sigma-Aldrich. (η^3-1-^{t}Bu-indenyl)$_2$(μ-Cl)$_2$Pd$_2$, (η^3-1-^{t}Bu-indenyl)Pd(IPr)(Cl), and (η^3-1-^{t}Bu-indenyl)Pd(IPent)(Cl) were obtained from Umicore. Other (η^3-1-^{t}Bu-indenyl)Pd(NHC)(Cl) precatalysts were prepared according to a literature procedure.[1] IPent•HCl, 1-pentanethiol and cyclopentanethiol were obtained from TCI America. 2-Aminoethanethiol, 2-methyl-3-tetrahydrofuranthiol, 2-phenylethanethiol, 4-(trifluoromethyl)phenyl-methanethiol, 4-methoxy-α-toluenethiol, [4-(*tert*-butyl)phenyl]methanethiol, 4-fluorobenzylmercaptan, methyl-3-mercaptopropionate, ethyl thioglycolate, 4-bromothiophenol, 4-nitrothiophenol, 4-methoxythiophenol, 2-methoxythiophenol, 2,4-dichloropyrimidine, 2,4-dibromopyrimidine, 2,4-diiodopyrimidine, 2,4,6-trichloropyrimidine, 2,4-dichloro-5-methoxypyrimidine, 2,4-dichloro-5-iodopyrimidine, 2,4-dichloro-6-methoxypyrimidine, 2,4-dichloro-5-(trifluoromethyl)pyrimidine, 5-bromo-2,4-dichloropyrimidine, 2,4-dichloropyrido[2,3-d]pyrimidine, 2,4-dichloro-6-methoxypyrimidine, 5-amino-2,4-dichloropyrimidine and 2,4-dichloro-5-methoxypyrimidine were obtained from Ambeed Chemical. Potassium phosphate, potassium fluoride, 1,4-dioxane, benzyl bromide, iodine, potassium *tert*-butoxide, palladium (II) chloride, and ethanethiol were obtained from Acros Organics. 1-Nonanethiol was obtained from Lancaster Synthesis. Potassium carbonate, triphenylphosphine, tri-*tert*-butylphosphine, and thiophenol were obtained from Alfa Aesar. Sodium carbonate, THF, DMF, diethyl ether toluene, acetonitrile, benzonitrile and methanol were obtained from Fisher Scientific. Tetrabutylammonium bromide, tetrabutylammonium chloride, sodium methoxide, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), tris(dibenzylideneacetone)-dipalladium(0), diphenylphosphinoferrocene, tri-*o*-tolylphosphine, tricyclohexylphosphine, cyclohexanethiol, 2-methyl-2-propanethiol, furfuryl mercaptan, 6-amino-2,4-dichloropyrimidine, 2,4-dichloro-6-methylpyrimidine, 2,4-dichloro-6-(trifluoromethyl)pyrimidine, 2-methylthiophenol, 4-chlorothiophenol, and 4-methylthiophenol were obtained from Oakwood Chemical. Methanesulfonato(tri-t-butylphosphino)(2'-methylamino-1,1'-biphenyl-2-yl)palladium(II) (P^tBu_3-Pd-G4) was obtained from Strem Chemical. 2-(Boc-amino)ethanethiol[2] and 2,4-dichloro-5-(trimethylsilyl)pyrimidine[3] was prepared according to a literature procedure. Benzene was obtained from Beantown Chemical. Deuterated solvents ($CDCl_3$, C_6D_6, acetone-d_6, methanol-d_4) were obtained from Cambridge Isotopes and stored over molecular sieves. Manual flash column chromatography was performed on SiliCycle silica gel 60 (40-63 μm particle size)

and thin layer chromatography was performed on SiliCycle TLC plates pre-coated with extra hard silica gel 60 F_{254}. Automated flash column chromatography was performed with a Biotage Selekt equipped with Biotage Sfär silica flash cartridges (20 μm particle size; 50 Å pore width) for normal phase separations, or Silica C18 cartridges (30 μm particle size; 100 Å pore width) for reversed phase separations.

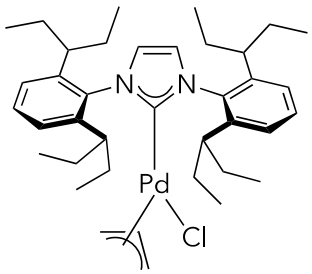
Synthesis and Characterization of Reagents



2,4-Dichloro-5-phenylpyrimidine (**S52**): To a 20 mL scintillation vial equipped with a Teflon-coated stir bar was added palladium acetate (13.5 mg, 0.06 mmol, 0.03 equiv), triphenylphosphine (31.5 mg, 0.12 mmol, 0.06 equiv), K_2CO_3 (552.8 mg, 4 mmol, 2 equiv), 5-iodo-2,4-dichloropyrimidine (824.6 mg, 3 mmol, 1.5 equiv) and phenylboronic acid (243.9 mg, 2 mmol, 1 equiv). The headspace of the vial was sparged with nitrogen followed by the addition of degassed THF (8 mL). Degassed, deionized water (0.36 mL, 20 mmol, 10 equiv) was added via 1-mL syringe and the vial was sealed with a Teflon-lined cap. The reaction mixture was left to stir for 24 h at 60 ºC. The crude reaction mixture was filtered through celite and the filtrate was concentrated under reduced pressure prior to purification by flash column chromatography on silica gel (R_f = 0.31 in 95:5 hexanes:EtOAc) to yield **S52** as a white solid (182.2 mg, 40% yield). Spectral data are consistent with those previously reported.[3]



1,3-Benzodioxole-5-methanethiol (S53). The preparation of compound **S53** was adapted from the literature.[4] Piperonyl alcohol (608.6 mg, 4 mmol, 1 equiv) and Lawesson's reagent (1.94 g, 4.8 mmol, 1.2 equiv) were combined with toluene (70 mL) in a 250 mL round bottom flask equipped with a stir bar and a reflux condenser. The reaction was stirred at reflux for 48 h under an inert atmosphere (N_2). The solvent was removed under vacuum and the residue was purified by flash column chromatography using an eluent of CH_2Cl_2:hexanes (1:1) (R_f = 0.39) to yield **S53** as a tan solid (70.2 mg, 10.4% yield). ^{1}H NMR (400 MHz, $CDCl_3$ δ): 6.85-6.81 (multiplet, 1H), 6.77-6.71 (multiple overlapping signals, 2H), 5.93 (s, 2H), 3.67 (d, *J* = 7.4 Hz, 2H), 1.76 (t, *J* = 7.4 Hz, 1H). ^{13}C{1H} NMR (101 MHz, CDCl3, δ): 147.9, 146.8, 135.1, 121.2, 108.7, 108.4, 101.2, 29.1. HRMS (MALDI TOF) m/z: $[M+H]^+$ Calcd for 169.0318; found 169.091.



(IPent)Pd(η³-allyl)Cl (6): The preparation of compound **6** was adapted from the literature.[5] In a nitrogen-atmosphere glovebox, IPent•HCl (1.0 g, 1.86 mmol, 1 equiv), KO^{t}Bu (229 mg, 2.04 mmol, 1.1 equiv), and THF (30 mL) were combined in a 250 mL round bottom flask equipped with a stir bar. The flask was sealed with a rubber septum and the reaction mixture was stirred at room temperature for 16 h inside the glovebox. The rubber septum was removed and $[Pd(allyl)(\mu\text{-}Cl)]_2$ (329 mg, 0.90 mmol, 0.5 equiv) was added. The flask was again sealed with a rubber septum and the reaction mixture was stirred for an additional 16 h at room temperature inside the glovebox. The flask was removed from the glovebox and the reaction mixture was filtered under air through a pad of silica over a layer of Celite™. The silica was washed with CH_2Cl_2 (20 mL). The combined filtrate was concentrated under reduced pressure. The solute was precipitated in pentane, and then the supernatant removed. The pale yellow crystals were then filtered and dried under vacuum to afford **6** (678.0 mg, 51.9% yield). ^{1}H NMR (400 MHz, $CDCl_3$ δ): 7.38 (t, J = 7.8 Hz, 2H), 7.16 (d, J = 7.8 Hz, 4H), 7.09 (s, 2H), 4.85-4.71 (m, 1H), 3.92-3.88 (multiplet, 1H), 2.91-2.86 (multiplet, 1H), 2.85-2.79 (multiplet, 1H), 2.63-2.38 (multiple overlapping signals, 4H), 2.08-1.86 (multiple overlapping signals, 4H), 1.82-1.51 (multiple overlapping signals, 10H), 1.49-1.36 (multiple overlapping signals, 3H), 0.97 (t, J = 7.4 Hz, 12H), 0.84-0.66 (multiple overlapping signals, 12H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 183.2, 144.2, 144.0, 137.7, 129.1, 125.2, 124.9, 124.3, 113.9, 73.7, 49.6, 42.0, 41.7, 28.1, 27.7, 27.4, 13.1, 12.7, 11.8, 11.2. HRMS (ESI Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{39}H_{65}ClN_2Pd$; 702.3866 found 702.3985.

Note on the Use of -196 ºC Bath for Set-Up of Cross-Coupling Reactions

During set up of both small- and larger-scale C—S coupling reactions, the entire reaction mixture minus the thiol was frozen in a liquid nitrogen bath (–196 ºC) immediately prior to addition of the thiol reagent (see representative procedures in the following sections). The reason for freezing the reaction mixture was to inhibit any undesired reaction (e.g., catalyst decomposition) during the brief period of time that the vial contents might be exposed to air during the subsequent addition of the thiol. Unlike all of the other reagents and solvent, the thiol should not be added in a glovebox (thiols are poisons for glovebox catalysts). Thus, after adding the reaction solvent in the glovebox (*vide infra*), the vial was removed from the glovebox and the thiol was added.

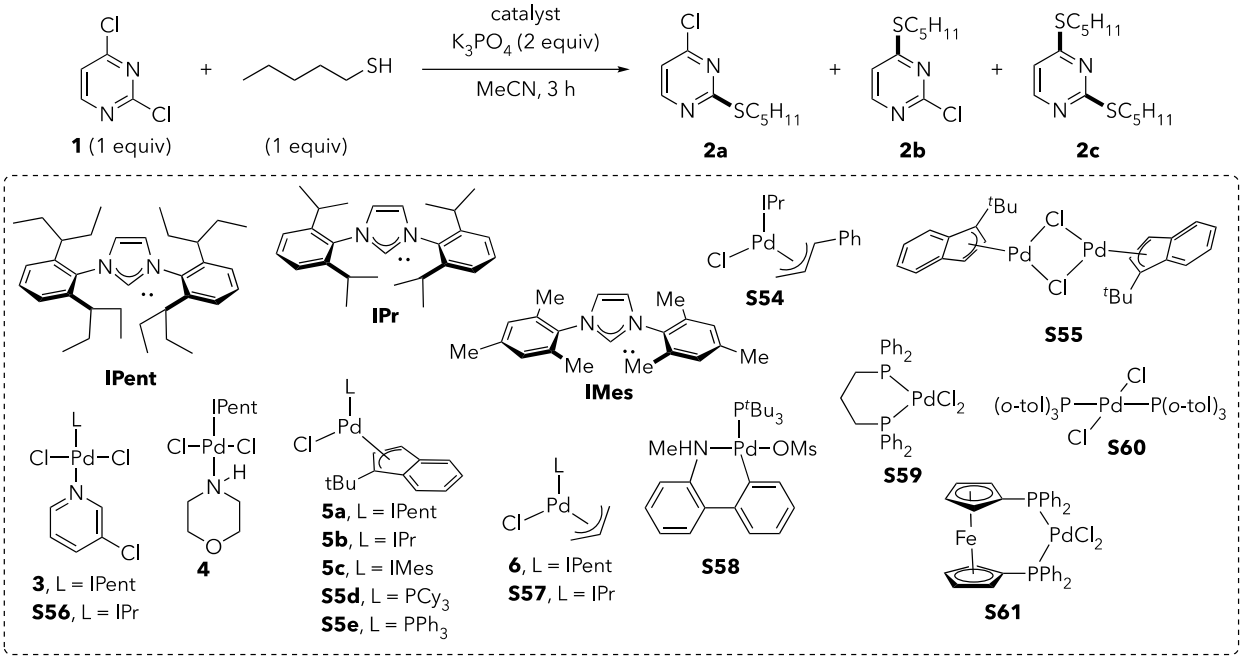
Reproducibility was sometimes poor when the thiol was added via syringe through a septum-cap (these caps may be slightly leaky toward air), and the best reproducibility for vial-scale reactions was obtained with solid Teflon-lined caps. Thus, for vial-scale reactions, the best procedure we found involved freezing the contents of the vial in liquid nitrogen, then opening up the vial completely to add the thiol reagent, then flushing the headspace with nitrogen, and finally sealing the vial again with a solid cap. Larger scale reactions using more traditional air-free methods (e.g., set up in a Schlenk flask) do not require pre-freezing to –196 ºC.

Screening of Reaction Conditions for C—S Cross-Coupling with Pentanethiol

Procedure for Small Scale Reactions using Pentanethiol Open to air unless otherwise indicated, palladium precatalyst, additional ligand (if applicable), 2,4-dichloropyrimidine (**1**, 11.9 mg, 0.080 mmol, 1.0 equiv), and base (0.16 mmol, 2.0 equiv) were combined in a 1-dram vial equipped with a Teflon-coated stir bar. The vial was taken into a nitrogen-atmosphere glovebox and solvent (0.2 mL) was added via a 1-mL syringe. The vial was sealed with a Teflon-lined cap and removed from the glovebox. The bottom portion of the vial containing the reaction mixture was submerged in a liquid nitrogen bath (-196 ºC) for 10-15 seconds to freeze the reaction mixture. The cap was then removed and the degassed pentanethiol was quickly added via syringe (9.9 µL, 0.080 mmol, 1 equiv). The vial headspace was flushed for 10-20 seconds with N_2 and the vial was then re-sealed with the Teflon-lined cap. The reaction was placed in a 0 ºC or -20 ºC bath, heated to 40 ºC, or allowed to warm to room temperature and stirred for the indicated time. The reaction mixture was then diluted with ethyl acetate and filtered through Celite™. The filtrate was concentrated under reduced pressure and mesitylene was added as an internal standard (11.1 µL, 0.080 mmol, 1 equiv). The residue was taken up in $CDCl_3$ and analyzed by ^1H NMR spectroscopy.

Results of Screening Reactions Using Pentanethiol (Includes Catalyst-Free Controls)

Table B.1. Precatalyst and Temperature Screen with Pentanethiol[a]



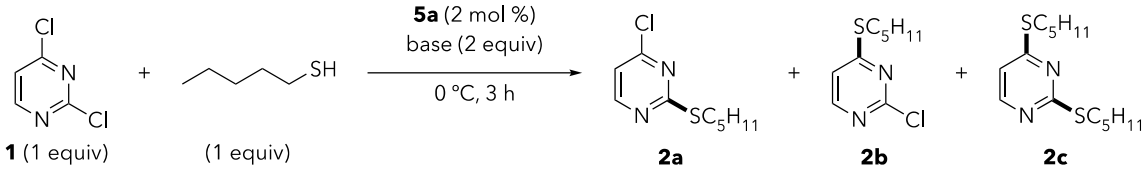
entry	trial	temp. (°C)	precatalyst (mol %)	**2a** (%)	**2b** (%)	**S2c** (%)	**2a** : **2b**
1	1	25	**3** (2)	3.0	67.0	2.0	1 : 22
2	2	25	**3** (2)	3.2	67.5	1.8	1 : 21
3	avg	25	**3** (2)	3.1	67.3	1.9	1 : 22
4	1	25	**4** (2)	23.7	47.3	1.0	1 : 2
5	2	25	**4** (2)	22.3	47.9	<1	1 : 2
6	avg	25	**4** (2)	23.0	47.6	0.5	1 : 2
7	1	25	none	11.0	78.0	<1	1 : 7
8	2	25	none	10.0	65.0	<1	1 : 7
9	avg	25	none	10.5	71.5	<1	1 : 7
10	1	25	**5a** (2)	54.8	4.2	4.3	13 : 1
11	2	25	**5a** (2)	60.2	3.8	3.9	16 : 1
12	avg	25	**5a** (2)	57.5	4.0	4.1	14 : 1
13	1	25	**6** (2)	50.0	<1	<1	>99 : 1
14	2	25	**6** (2)	51.0	<1	<1	>99 : 1
15	avg	25	**6** (2)	50.5	<1	<1	>99 : 1
16	1	25	**S57** (2)	56.3	14.5	4.3	4 : 1
17	2	25	**S57** (2)	50.1	12.6	2.8	4 : 1
18	avg	25	**S57** (2)	53.2	13.6	3.6	4 : 1
19	1	25	**S54** (2)	82.1	2.2	3.4	37 : 1
20	2	25	**S54** (2)	77.9	2.6	3.1	30 : 1
21	avg	25	**S54** (2)	80.0	2.4	3.3	34 : 1
22	1	0	**5a** (2)	90.2	<1	3.9	>99 : 1
23	2	0	**5a** (2)	90.0	<1	3.0	>99 : 1
24	avg	0	**5a** (2)	90.1	<1	3.5	>99 : 1
25	1	0	none	7.0	43	<1	1 : 6
26	2	0	none	7.2	44	<1	1 : 6
27	avg	0	none	7.1	43.5	<1	1 : 6

28	1	0	**5a** (1)	75.6	<1	3.9	>99 : 1
29	2	0	**5a** (1)	89.1	<1	4.8	>99 : 1
30	avg	0	**5a** (1)	82.4	<1	4.4	>99 : 1
31	1	0	**5a** (4)	78.1	<1	8.3	>99 : 1
32	2	0	**5a** (4)	77.8	<1	4.3	>99 : 1
33	avg	0	**5a** (4)	78.0	<1	6.3	>99 : 1
34	1	0	**5a** (8)	76.8	<1	4.1	>99 : 1
35	2	0	**5a** (8)	70.3	<1	5.8	>99 : 1
36	avg	0	**5a** (8)	73.6	<1	5.0	>99 : 1
37	1	0	**S55** (1)	5.8	41.5	<1	1 : 7
38	2	0	**S55** (1)	6.1	40.3	<1	1 : 7
39	avg	0	**S55** (1)	6.0	40.9	<1	1 : 7
40[b]	1	0	**S55** (1 mol %) + IPent•HCl (2 mol %)	6.5	43.0	1.0	1 : 7
41[b]	2	0	**S55** (1 mol %) + IPent•HCl (2 mol %)	7.9	45.0	1.4	1 : 6
42[b]	avg	0	**S55** (1 mol %) + IPent•HCl (2 mol %)	7.2	44.0	1.2	1 : 6
43	1	0	**6** (2)	74.4	1.1	5.9	67 : 1
44	2	0	**6** (2)	69.8	0.8	4.6	87 : 1
45	avg	0	**6** (2)	72.1	1.0	5.3	72 : 1
46[b]	1	0	**S58** (2)	3.4	38.9	2.4	1 : 11
47[b]	2	0	**S58** (2)	3.2	37.0	2.1	1 : 12
48[b]	avg	0	**S58** (2)	3.3	38.0	2.3	1 : 12
49	1	0	**S5d** (2)	6.6	43.9	<1	1 : 7
50	2	0	**S5d** (2)	5.4	29.1	<1	1 : 5
51	avg	0	**S5d** (2)	6.0	36.5	<1	1 : 6
52	1	0	**S5e** (2)	6.0	42.6	<1	1 : 7
53	2	0	**S5e** (2)	3.3	19.7	<1	1 : 6
54	avg	0	**S5e** (2)	4.7	31.2	<1	1 : 7
55	1	0	**S59** (2)	6.1	39.9	<1	1 : 7
56	2	0	**S59** (2)	4.2	31.4	<1	1 : 7
57	avg	0	**S59** (2)	5.2	35.7	<1	1 : 7
58	1	0	**S61** (2)	6.9	46.6	<1	1 : 7
59	2	0	**S61** (2)	6.5	41.4	<1	1 : 6
60	avg	0	**S61** (2)	6.7	44.0	<1	1 : 7
61[b]	1	0	**S60** (2)	6.9	46.1	<1	1 : 7
62[b]	2	0	**S60** (2)	5.1	36.4	<1	1 : 7
63[b]	avg	0	**S60** (2)	6.0	41.3	<1	1 : 7
64	1	0	**S56** (2)	3.5	63.0	2.0	1 : 18
65	2	0	**S56** (2)	1.5	64.9	1.8	1 : 43
66	avg	0	**S56** (2)	2.5	64.0	1.9	1 : 26
67	1	0	**3** (2)	3.2	66.8	2.0	1 : 21
68	2	0	**3** (2)	3.0	67.0	2.0	1 : 22
69	avg	0	**3** (2)	3.1	66.9	2.0	1 : 22
70	1	0	**5b** (2)	83.2	3.4	3.4	24 : 1
71	2	0	**5b** (2)	81.4	3.1	3.2	26 : 1
72	avg	0	**5b** (2)	82.3	3.3	3.3	25 : 1
73	1	0	**5c** (2)	45.6	15.4	<1	3 : 1
74	2	0	**5c** (2)	40.2	19.8	1.6	2 : 1
75	avg	0	**5c** (2)	45.6	15.4	0.8	3 : 1
76	1	-20	**5a** (2)	26.2	1.7	1.6	15 : 1
77	2	-20	**5a** (2)	26.9	1.5	<1	18 : 1
78	avg	-20	**5a** (2)	26.6	1.6	0.8	17 : 1

79	1	40	**5a** (2)	29.5	49.6	6.6	1 : 2
80	2	40	**5a** (2)	27.5	46.1	4.4	1 : 2
81	avg	40	**5a** (2)	28.5	47.9	5.5	1 : 2

[a]Crude yields determined by ^{1}H-NMR spectroscopy using mesitylene as an internal standard. Values reported as <1 indicate measured yield less than 0.5%. [b]The following ligands or catalysts were added inside the nitrogen-atmosphere glovebox: IPent•HCl, P^{t}Bu$_3$-Pd-G4 (**S58**), and $PdCl_2[P(o\text{-tol})_3]_2$ (**S60**)

Table B2. Solvent and Base Screen with Pentanethiol and Precatalyst **5a**[a]



entry	trial	solvent	base	**2a** (%)	**2b** (%)	**2c** (%)	**2a** : **2b**
1	1	MeCN	K_3PO_4	90.2	<1	3.9	>99 : 1
2	2	MeCN	K_3PO_4	90.0	<1	3.0	>99 : 1
3	avg	MeCN	K_3PO_4	90.1	<1	3.5	>99 : 1
4	1	MeCN	NaOMe	74.3	<1	7.0	>99 : 1
5	2	MeCN	NaOMe	72.2	<1	4.4	>99 : 1
6	avg	MeCN	NaOMe	73.3	<1	5.7	>99 : 1
7	1	MeCN	Na_2CO_3	76.3	<1	8.0	>99 : 1
8	2	MeCN	Na_2CO_3	74.2	3.6	8.1	21 : 1
9	avg	MeCN	Na_2CO_3	75.3	1.8	8.1	42 : 1
10	1	MeCN	NaOH	28.3	43.7	5.2	1 : 2
11	2	MeCN	NaOH	26.4	44.5	<1	1 : 2
12	avg	MeCN	NaOH	27.2	44.3	2.5	1 : 2
13	1	MeCN	K_2CO_3	70.1	<1	4.6	>99 : 1
14	2	MeCN	K_2CO_3	72.2	<1	4.4	>99 : 1
15	avg	MeCN	K_2CO_3	71.2	<1	4.5	>99 : 1
16	1	MeCN	Cs_2CO_3	35.0	39.1	3.4	1 : 1
17	2	MeCN	Cs_2CO_3	31.7	16.8	10.8	2 : 1
18	avg	MeCN	Cs_2CO_3	33.4	27.9	6.9	1 : 1
19	1	MeCN	none	2.3	0.8	<1	3 : 1
20	2	MeCN	none	2.3	0.5	<1	3 : 1
21	avg	MeCN	none	2.3	0.7	<1	3 : 1
22	1	DMF	K_3PO_4	84.9	9.0	4.2	9 : 1
23	2	DMF	K_3PO_4	85.4	9.2	3.5	9 : 1
24	avg	DMF	K_3PO_4	85.2	9.1	3.9	9 : 1
25	1	PhCN	K_3PO_4	48.6	34.8	12.3	1 : 1
26	2	PhCN	K_3PO_4	32.8	24.9	10.2	1 : 1
27	avg	PhCN	K_3PO_4	40.9	29.9	11.1	1 : 1
28	1	THF	K_3PO_4	9.7	48.2	<1	1 : 5
29	2	THF	K_3PO_4	5.7	56.6	<1	1 : 10
30	avg	THF	K_3PO_4	7.7	52.4	<1	1 : 7
31	1	Et_2O	K_3PO_4	6.6	42.1	1.0	1 : 6
32	2	Et_2O	K_3PO_4	4.6	46.5	<1	1 : 10
33	avg	Et_2O	K_3PO_4	5.6	44.3	0.5	1 : 8

34	1	MeOH	K_3PO_4	33.6	32.7	3.9	1 : 1
35	2	MeOH	K_3PO_4	54.3	16.0	3.0	3 : 1
36	avg	MeOH	K_3PO_4	44.0	24.4	3.5	2 : 1

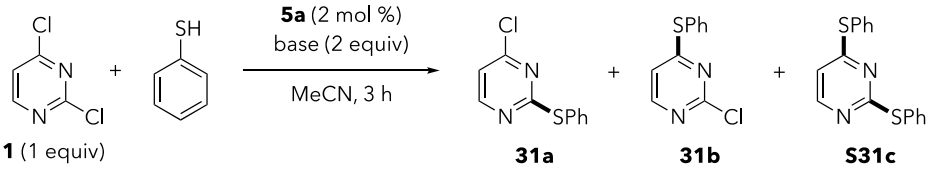
[a]Crude yields determined by ^{1}H-NMR spectroscopy using mesitylene as an internal standard. Values reported as <1 indicate measured yield less than 0.5%.

Screening of Reaction Conditions for C—S Cross-Coupling with Thiophenol

Procedure for Small Scale Reactions Using Thiophenol Open to air, (η^3-1-^{t}Bu-indenyl)Pd(IPent)Cl (**5a**, 1.3 mg, 0.0016 mmol, 2 mol %), 2,4-dichloropyrimidine (**1**, 11.9 mg, 0.080 mmol, 1.0 equiv), and base (K_3PO_4, KF, or K_2CO_3, 0.16 mmol, 2 equiv) were combined in a 1-dram vial equipped with a Teflon-coated stir bar. The vial was brought into the glovebox and acetonitrile (0.4 mL) was added via a 1-mL syringe. The vial was sealed with a Teflon-lined cap and removed from the glovebox. The bottom portion of the vial containing the reaction mixture was submerged in a liquid nitrogen bath (-196 ºC) for 10-15 seconds to freeze the reaction mixture. The cap was then removed and degassed organic base (if applicable, NEt_3 or DBU, 0.16 mmol, 2 equiv) and degassed thiophenol were quickly added via syringe. The vial headspace was then flushed for 10-20 seconds with N_2 and the vial was then re-sealed with the Teflon-lined cap. The reaction was then placed in a 0 ºC or room temperature water bath or heated to the indicated temperature and stirred for 3 h. The reaction mixture was diluted with ethyl acetate, 1,4-dimethoxybenzene was added as an internal standard (50 µL of a 0.4 *M* solution in EtOAc, 0.02 mmol, 0.25 equiv), and the crude reaction mixture was filtered through Celite™. The filtrate was concentrated under reduced pressure and the residue was taken up in $CDCl_3$ (~0.5 mL) and analyzed by ^{1}H NMR spectroscopy.

Results of Screening Reactions With Thiophenol (Includes Catalyst-Free Control)

Table S3. Base and Temperature Screen with Thiophenols



entry	trial	base	PhSH equiv	temp (ºC)	**31a** (%)	**31b** (%)	**S31c** (%)	**31a** : **S31b**

1	1	K_3PO_4	1	0	5.7	83.5	7.5	1 : 15
2	2	K_3PO_4	1	0	5.0	82.0	3.2	1 : 16
3	Average	K_3PO_4	1	0	5.3	82.7	5.3	1 : 16
4	1	KF	1	0	11.1	39.0	17.5	1 : 4
5	2	KF	1	0	10.1	40.1	16.8	1 : 4
6	Average	KF	1	0	10.6	39.6	17.2	1 : 4
7	1	K_2CO_3	1	0	1.5	92.1	5.9	1 : 61
8	2	K_2CO_3	1	0	2.4	95.3	3.9	1 : 40
9	Average	K_2CO_3	1	0	1.9	93.7	4.9	1 : 49
10	1	NEt_3	1	0	1.7	94.2	3.8	1 : 55
11	2	NEt_3	1	0	1.3	97.5	4.2	1 : 75
12	Average	NEt_3	1	0	1.5	95.8	4.0	1 : 64
13	1	DBU	1	0	11.1	54.5	5.1	1 : 5
14	2	DBU	1	0	6.6	49.1	1.8	1 : 7
15	Average	DBU	1	0	8.9	51.8	3.5	1 : 6
16	1	KF	1.1	0	31.0	21.0	5.0	1 : 1
17	2	KF	1.1	0	34.3	20.5	4.8	2 : 1
18	Average	KF	1.1	0	32.7	20.7	4.9	2 : 1
19	1	KF	2	0	32.3	14.3	17.4	2 : 1
20	2	KF	2	0	29.2	15.0	24.4	2 : 1
21	Average	KF	2	0	30.7	14.6	20.8	2 : 1
22	1	KF	1.1	rt	31.3	25.7	14.2	1 : 1
23	2	KF	1.1	rt	31.6	15.3	5.2	2 : 1
24	Average	KF	1.1	rt	31.5	20.5	9.7	2 : 1
25	1	KF	1.1	40	88.5	4.7	5.5	19 : 1
26	2	KF	1.1	40	72.4	8.4	11.8	9 : 1
27	Average	KF	1.1	40	80.4	6.5	8.7	12 : 1
28	1	KF	1.1	80	95.6	0	5.4	>99 : 1
29	2	KF	1.1	80	95.2	0	6.2	>99 : 1
30	Average	KF	1.1	80	95.4	0	5.8	>99 : 1
31[b]	1	KF	1.1	80	3.4	63.8	0	1 : 19
32[b]	2	KF	1.1	80	5.0	68.5	0	1 : 14
33[b]	Average	KF	1.1	80	4.2	66.1	0	1 : 16

[a] Yields determined by ^{1}H-NMR spectroscopy using 1,4-dimethoxybenzene as an internal standard. [b]Palladium-free control reactions.

Characterization of Regioselectivity

Overview: Regioselectivity was tentatively assigned by comparing the product obtained during the catalytic conditions to that obtained in the absence of Pd (the S_NAr product). In most cases, the products under the optimized catalytic conditions versus the S_NAr conditions are different based on ^{1}H NMR spectroscopy (exceptions for which S_NAr and catalysis favor the same product are noted in Sections I.G and I.H).

To further verify the regioselectivity, products were analyzed by NOE experiments (see Section V). In particular, C4-functionalized isomers (generally isolated from S_NAr reactions) display an NOE correlation between the pyrimidine proton at C5 and protons on the organic group attached to sulfur. Conversely, for the C2-functionalized isomers, no NOE is detected between

these protons. In most cases the NOE correlations were small, so the peaks were integrated to verify that a correlation was in the opposite phase to the pulsed proton. In some ambiguous cases, the C4-functionalized isomer was also prepared via S_NAr for comparison (see section I.I.) In several cases, crystal structures were obtained (see section III). In the case of product **7a**, its regioselectivity was confirmed by subsequent functionalization using a Liebeskind-Srogl cross-coupling with $PhB(OH)_2$ to yield the known compound 4-chloro-2-phenylpyrimidine (**S51a**, see section I.I).

Finally, we note that the C6 proton of chlorothiopyrimidines is often diagnostic of regioselectivity: in $CDCl_3$, its chemical shift tends to be around 8.35-8.39 ppm for 4-chloro-2-thiopyrimidines, but it appears further upfield at around 8.15-8.24 ppm for 2-chloro-4-thiopyrimidines (See Sections I.G, I.H, and V).

Representative 1D NOE Spectra Demonstrating Regioselectivity Assignments:

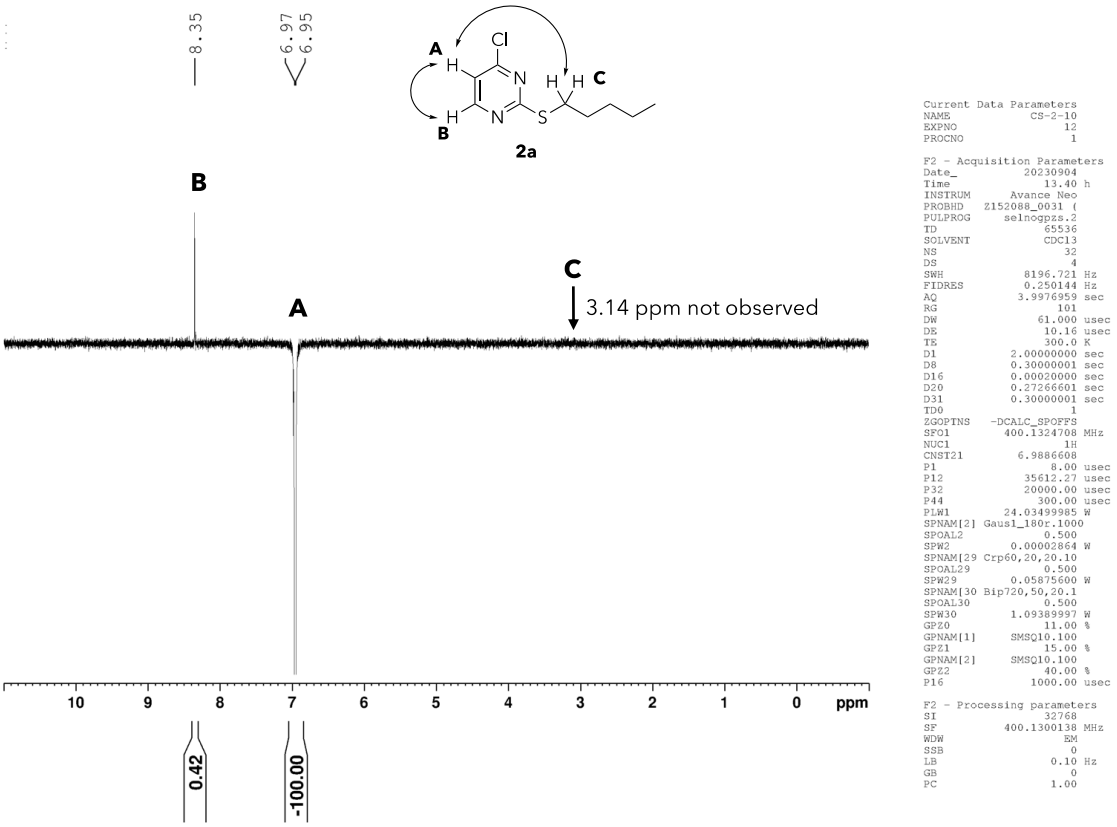


Figure B.1. 1D NOE spectrum of product **2a** with $\mathbf{H_A}$ pulsed showing no correlation to $\mathbf{H_C}$.

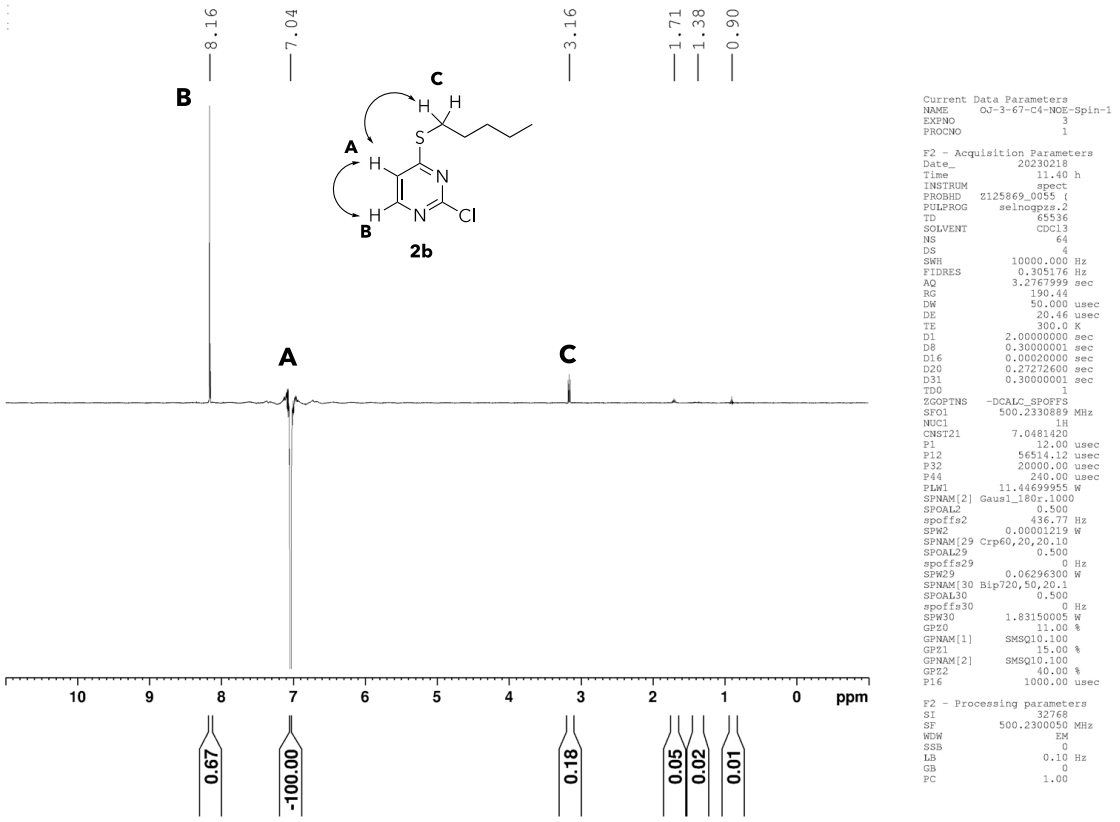


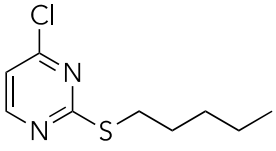
Figure B2. 1D NOE spectrum of product **2b** with $\mathbf{H_A}$ pulsed showing a correlation to $\mathbf{H_C}$

Isolation and Characterization of Cross-Coupled Products
Using Alkyl Thiols

General Procedure for Cross-Couplings. Open to air, (η^3-1-^{t}Bu-indenyl)Pd(IPent)Cl (**5a,** 0.02 equiv), 2,4-dihalopyrimidine (1.0 equiv), and K_3PO_4 (2.0 equiv) were combined in a 5- or 10-mL round bottom flask or a 1-dram vial equipped with a Teflon-coated stir bar. The reaction vessel was taken into a nitrogen-atmosphere glovebox. For reactions using liquid thiols, acetonitrile (volume calculated such that the dihalopyrimidine would have a concentration of 0.4 *M*) was then added via a 2-mL syringe. The vessel was sealed with a rubber septum and copper wire (round bottom flasks) or with a Teflon-lined cap (for 1-dram vial) and removed from the glovebox. The bottom portion of the reaction vessel containing the reaction mixture was submerged in a liquid nitrogen bath (-196 ºC) for 10-15 seconds to freeze the reaction mixture. For reactions in a round bottom flask, the degassed thiol (or solution of thiol in acetonitrile, for reactions using solid thiols) was added through the septum using a syringe. For reactions in a vial, the cap was removed, and the degassed thiol (or solution of thiol in acetonitrile) was quickly added via syringe. The vial

headspace was then flushed for 10-20 seconds with N_2 and the vial was re-sealed with the Teflon-lined cap. For both types of vessels, liquid thiols were measured by volume, while solid thiols were added as a solution in dry degassed acetonitrile (0.4 *M*). The reaction mixture was stirred vigorously at the indicated temperature for the indicated time. The reaction mixture was then diluted with ethyl acetate and filtered through Celite™. The filtrate was concentrated under vacuum, and a portion of the residue was taken up in deuterated solvent for ^{1}H NMR analysis to obtain the crude ratio of C2:C4 functionalized products. The NMR sample was recombined with the bulk filtrate, and the filtrate was again concentrated under vacuum prior to purification.

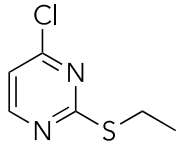
General Procedure for Catalyst-Free S_NAr Reactions. Open to air, 2,4-dihalopyrimidine (0.080 mmol, 1.0 equiv) and K_3PO_4 (33.9 mg, 0.16 mmol, 2.0 equiv) were combined in a 1-dram vial equipped with a Teflon-coated stir bar. The reaction vial was taken into a nitrogen-atmosphere glovebox. For reactions using liquid thiols, acetonitrile (0.2 mL) was added via a 1-mL syringe. The vial was sealed with a Teflon-lined cap and removed from the glovebox. The bottom portion of the vial containing the reaction mixture was submerged in a liquid nitrogen bath (-196 ºC) for 10-15 seconds to freeze the reaction mixture. The cap was then removed, and the degassed thiol (or solution of thiol in acetonitrile, for reactions using solid thiols) was quickly added via syringe (0.080 mmol, 1.0 equiv). Liquid thiols were measured by volume, while solid thiols were added as a solution in acetonitrile. The vial headspace was then flushed for 10-20 seconds with N_2 and the vial was then re-sealed with the Teflon-lined cap. The reaction mixture was stirred vigorously at the indicated temperature for the indicated time. The reaction mixture was then diluted with ethyl acetate and filtered through Celite™. The filtrate was concentrated under reduced pressure and mesitylene was added as an internal standard (11.1 μL, 0.080 mmol, 1.0 equiv). The residue was taken up in deuterated solvent and analyzed by ^{1}H NMR.



4-Chloro-2-(pentylthio)pyrimidine (2a). Compound **2a** was prepared according to the general procedure using a 5 mL round bottom flask, 2,4-dichloropyrimidine (**1**, 149.0 mg, 1.0 mmol, 1.0 equiv), and 1-pentanethiol (124.1 μL, 1.0 mmol, 1.0 equiv) with stirring for 3 h at 0 ºC. Analysis of the crude reaction mixture by ^{1}H NMR spectroscopy indicated a >99 : 1 ratio of C2:C4-functionalized products. Purification by flash column chromatography on silica gel using an eluent of hexanes:CH_2Cl_2 = 60:40 (R_f = 0.24) provided **2a** as a yellow oil (157.9 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.36 (d,

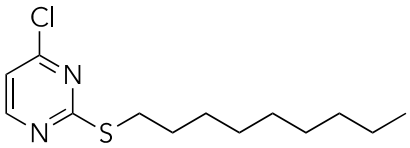
J = 5.2 Hz, 1H), 6.97 (d, *J* = 5.2 Hz, 1H), 3.14 (t, *J* = 7.4 Hz, 2H), 1.73 (tt, *J* = 7.4, 7.4 Hz, 2H), 1.48-1.31 (multiple overlapping signals, 4H), 0.91 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, δ): 174.1, 161.1, 158.1, 116.5, 31.3, 31.1, 28.7, 22.3, 14.1. HRMS (ESI Q-TOF) m/z: $[M+H]^+$ Calcd for $C_9H_{14}ClN_2S$ 217.0561; found 217.0568. Regioselectivity was confirmed by 1D NOE of **2a** (see section V) and by comparison to the separately synthesized C4-regioisomer **2b** (see section I.I and section V).

Under the corresponding catalyst-free S_NAr conditions at 0 ºC for 3 h, the C2 and C4-functionalized products were formed in a 1 : 6 ratio based on ^{1}H NMR analysis of the crude reaction mixture.



4-Chloro-2-(ethylthio)pyrimidine (7a). Compound **7a** was prepared according to the general procedure using a 5 mL round bottom flask, 2,4-dichloropyrimidine (**1**, 74.5 mg, 0.50 mmol, 1.0 equiv), and ethanethiol (36 µl, 0.50 mmol, 1.0 equiv) with stirring for 3 h at 0 ºC. Analysis of the crude reaction mixture by ^{1}H NMR spectroscopy indicated a >99 : 1 ratio of C2:C4-functionalized products. Purification by flash column chromatography on silica gel using an eluent of pentane:Et_2O = 96:4 (R_f = 0.17) provided **7a** as a colorless oil (62.6 mg, 72% yield). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.35 (d, *J* = 5.2 Hz, 1H), 6.97 (d, *J* = 5.2 Hz, 1H), 3.14 (q, *J* = 7.4 Hz, 2H), 1.38 (t, *J* = 7.4 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, δ): 173.8, 161.1, 158.1, 116.5, 25.6, 14.3. HRMS (ESI Q-TOF) m/z: $[M+H]^+$ Calcd for $C_6H_8ClN_2S$ 175.0091; found 175.0094. Regioselectivity was confirmed by subsequent transformation of **7a** into the known compound 4-chloro-2-phenylpyrimidine (**S51a**, see section I.I).

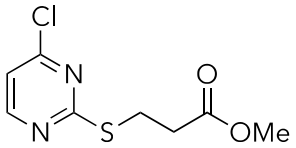
Under the corresponding catalyst-free S_NAr conditions at 0 ºC for 3 h, the C2 and C4-functionalized products were formed in a 1 : 7 ratio based on ^{1}H NMR analysis of the crude reaction mixture.



4-Chloro-2-(nonylthio)pyrimidine (8a). Compound **8a** was prepared according to the general procedure using a 5 mL round bottom flask, 2,4-dichloropyrimidine (**1**, 74.5 mg, 0.50 mmol, 1.0 equiv), and 1-nonanethiol (95 µL, 0.50 mmol, 1.0 equiv) with stirring for 3 h at 0 ºC. Analysis of the crude reaction mixture by ^{1}H NMR spectroscopy indicated a >99 : 1 ratio of C2:C4-

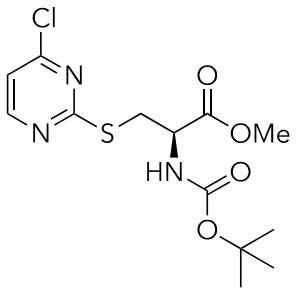
functionalized products. Purification was performed by reversed phase flash column chromatography with a 30 g C18 silica column, using an initial automated program comprising a flow rate of 25 mL/min of water:acetonitrile (98:2 to 0:100) over 20 column volumes. Fractions containing **8a** were partitioned between dichloromethane and saturated brine. The organic layers were combined and dried over magnesium sulfate and solvent was removed under reduced to afford **8a** as a yellow oil (75.6 mg, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.35 (d, J = 5.2 Hz, 1H), 6.96 (d, J = 5.2 Hz, 1H), 3.13 (t, J = 7.4 Hz, 2H), 1.72 (tt J = 7.4, 7.4 Hz, 2H), 1.49-1.38 (m, 2H), 1.37-1.20 (multiple overlapping signals, 10H), 0.87 (t, J = 6.9 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 174.1, 161.1, 158.1, 116.5, 32.0, 31.3, 29.6, 29.4, 29.3, 29.01, 28.96, 22.8, 14.2. HRMS (ESI Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{22}ClN_2S$ 273.1187; found 273.1193. Regioselectivity was confirmed by 1D NOE of **8a** (see section V).

Under the corresponding catalyst-free S_NAr conditions at 0 ºC for 3 h, the C2 and C4-functionalized products were formed in a 1 : 7 ratio based on ^{1}H NMR analysis of the crude reaction mixture.



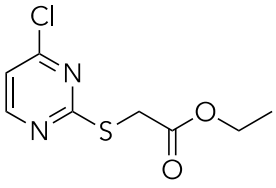
Methyl 3-[(4-chloro-2-pyrimidinyl)thio] propanoate (9a). Compound **9a** was prepared according to the general procedure using a 5 mL round bottom flask, 2,4-dichloropyrimidine (**1**, 74.5 mg, 0.50 mmol, 1.0 equiv) and methyl 3-mercaptopropionate (55 µL, 0.50 mmol, 1.0 equiv) with stirring for 3 h at 0 ºC. Analysis of the crude reaction mixture by ^{1}H NMR spectroscopy indicated a >99 : 1 ratio of C2:C4-functionalized products. Purification by flash column chromatography on silica gel using an eluent of pentane:Et_2O = 100:0 to 60:40 (R_f = 0.30 in 80:20 pentane:Et_2O) provided **9a** as a colorless oil (94.0 mg, 81% yield). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.37 (d, J = 5.2 Hz, 1H), 7.00 (d, J = 5.2 Hz, 1H), 3.71 (s, 3H), 3.38 (t, J = 7.1 Hz, 2H), 2.81 (t, J = 7.1 Hz, 2H). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$, δ): 173.0, 172.3, 161.3, 158.3, 116.9, 52.0, 34.0, 26.3. HRMS (ESI Q-TOF) m/z: $[M+H]^+$ Calcd for $C_8H_{10}ClN_2O_2S$ 233.0146; found 233.0153. Regioselectivity was confirmed by 1D NOE of **9a** (see section V).

Under the corresponding catalyst-free S_NAr conditions at 0 ºC for 3 h, the C2 and C4-functionalized products were formed in a 1 : 5 ratio based on ^{1}H NMR analysis of the crude reaction mixture.



Methyl N-[(tert-butoxycarbonyl]-S-(4-chloropyrimidin-2-yl)-L-cysteinate (10a). Compound **10a** was prepared according to the general procedure using a 5 mL round bottom flask, 2,4-dichloropyrimidine (**1**, 74.5 mg, 0.50 mmol, 1.0 equiv) and *N*-(*tert*-butoxycarbonyl)-*L*-cysteine methyl ester (117.6 mg dissolved in 1.25 mL of acetonitrile, 0.50 mmol, 1.0 equiv) with stirring for 16 h at room temperature. Analysis of the crude reaction mixture by ^{1}H NMR spectroscopy indicated a 25 : 1 ratio of C2:C4-functionalized products. Purification by flash column chromatography on silica gel using an eluent of pentane:EtOAc = 95:5 to 80:20 (R_f = 0.22 in 80:20 pentane:EtOAc) provided **10a** as a white solid (83.3 mg, 48% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.36 (d, J = 5.2 Hz, 1H), 7.01 (d, J = 5.2 Hz, 1H), 5.54 (broad doublet, J = 6.4 Hz, 1H), 4.70-4.62 (m, 1H), 3.77-3.63 (multiple overlapping signals, 4H), 3.55 (dd, J = 14.3, 6.4, 1H), 1.39 (s, 9H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 172.5, 171.3, 161.3, 158.2, 155.2, 117.2, 80.2, 53.4, 52.7, 33.3, 28.4. HRMS (ESI Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{19}ClN_3O_4S$ 348.0779; found 348.0770. Regioselectivity was confirmed by 1D NOE of **10a** (see section V).

Under the corresponding catalyst-free S_NAr conditions at room temperature for 16 h, the C2 and C4-functionalized products were formed in a 1 : 5 ratio based on ^{1}H NMR analysis of the crude reaction mixture.

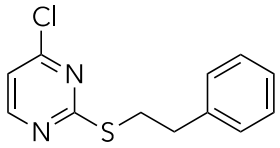


Ethyl 2-[(4-chloro-2-pyrimidinyl)thio] acetate (11a). Compound **11a** was prepared according to the general procedure using a 5 mL round bottom flask, 2,4-dichloropyrimidine (**1**, 74.5 mg, 0.50 mmol, 1.0 equiv), and ethyl thioglycolate (55 μL, 0.50 mmol, 1.0 equiv) with stirring for 16 h at room temperature. Analysis of the crude reaction mixture by ^{1}H NMR indicated a 1 : 1 ratio of C2:C4-functionalized products. Purification by flash column chromatography on silica gel using an eluent of hexanes:EtOAc = 80:20

(R_f = 0.44) provided **11a** as a colorless oil in 96% purity, contaminated with the C4-functionalized regioisomer **S11b** (isolated mass and yield adjusted for purity: 35.7 mg, 31% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.38 (d, J = 5.2 Hz, 1H), 7.02 (d, J = 5.2 Hz, 1H), 4.23 (q, J = 7.2, 2H), 3.92 (s, 3H), 1.29 (t, J = 7.2 Hz, 3H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, δ): 172.0, 168.9, 161.3, 158.2, 117.2, 62.0, 33.8, 14.3. HRMS (ESI Q-TOF) m/z: $[M+H]^+$ Calcd for $C_8H_{10}ClN_2O_2S$ 233.0146;

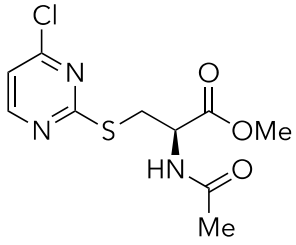
found 233.0147. Regioselectivity was confirmed by 1D NOE of **11a** (see section V) and by comparison to the separately synthesized C4-regioisomer **11b** (see section I.I and section V).

Under the corresponding catalyst-free S_NAr conditions at room temperature for 16 h, the C2 and C4-functionalized products were formed in a 1 : 8 ratio based on ^1H NMR analysis of the crude reaction mixture.



4-Chloro-2-[(2-phenylethyl)thio]pyrimidine (12a). Compound **12a** was prepared according to the general procedure using a 5 mL round bottom flask, 2,4-dichloropyrimidine (**1**, 74.5 mg, 0.50 mmol, 1.0 equiv) and phenylethanethiol (67 µL, 0.50 mmol, 1.0 equiv) with stirring for 3 h at 0 ºC. Analysis of the crude reaction mixture by ^1H NMR indicated a >99 : 1 ratio of C2:C4-functionalized products. Purification by flash column chromatography on silica gel using an eluent of pentane:Et_2O = 96:4 (R_f = 0.30) provided **12a** as a colorless oil (109.1 mg, 87% yield). ^1H NMR (400 MHz, CD_3OD, δ): 8.46 (d, J = 5.3 Hz, 1H), 7.28-7.26 (multiple overlapping signals, 4H), 7.22-7.16 (multiple overlapping signals, 2H), 3.37 (t, J = 7.5 Hz, 2H), 3.00 (t, J = 7.5 Hz, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, CD_3OD, δ): 174.5, 162.3, 159.9, 141.5, 129.7, 129.5, 127.5, 117.9, 36.6, 33.5. HRMS (ESI Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_{12}ClN_2S$ 251.0404; found 251.0412. Regioselectivity was confirmed by 1D NOE of **12a** (see section V).

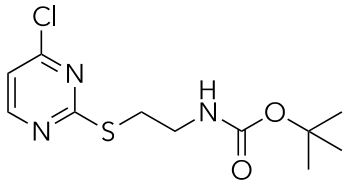
Under the corresponding catalyst-free S_NAr conditions at 0 ºC for 3 h, the C2 and C4-functionalized products were formed in a 1 : 8 ratio based on ^1H NMR analysis of the crude reaction mixture.



N-Acetyl-S-2-(4-chloropyrimidinyl)-L-cysteine methyl ester **(13a)**. Compound **13a** was prepared according to the general procedure using 2,4-dichloropyrimidine (**1**, 74.5 mg, 0.50 mmol, 1.0 equiv) and (*R*)-methyl-2-acetamido-3-mercaptopropionate (88.6 mg dissolved in 1.25 mL of acetonitrile, 0.50 mmol, 1.0 equiv) with stirring for 16 h at room temperature. Analysis of the crude reaction mixture by ^1H NMR indicated a >99 : 1 ratio of C2:C4-functionalized products. Purification by flash column chromatography on silica gel using an eluent of CH_2Cl_2:MeOH = 98:2 (R_f = 0.17) provided **13a** as a white solid (83.9 mg, 58% yield). ^1H NMR (400 MHz, $CDCl_3$, δ): 8.37 (d, J = 5.2 Hz, 1H), 7.04 (d, J = 5.2 Hz, 1H), 6.70 (broad d, J = 7.2

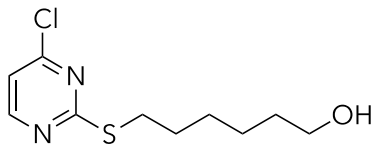
Hz, 1H), 4.93 (ddd, *J* = 7.2, 6.6, 4.6 Hz, 1H), 3.73-3.69 (multiple overlapping signals 4H), 3.56 (dd, *J* = 14.4, 6.6 Hz, 1H) 1.97 (s, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, δ): 172.5, 171.0, 170.0, 161.3, 158.2, 117.4, 52.8, 52.4, 32.8, 23.1. HRMS (ESI Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{10}H_{13}ClN_3O_3S$ 290.0361; found 290.0347. Regioselectivity was confirmed by 1D NOE of **13a** (see section V).

Under the corresponding catalyst-free S_NAr conditions at room temperature for 16 h, the C2 and C4-functionalized products were formed in a 1 : 7 ratio based on ^{1}H NMR analysis of the crude reaction mixture.



tert-Butyl [2-((4-chloro-2-pyrimidin-2-yl)thio)ethyl]carbamate (14a). Compound **14a** was prepared according to the general procedure using a 5 mL round bottom flask, 2,4-dichloropyrimidine (**1**, 74.5 mg, 0.50 mmol, 1.0 equiv), and *N*-boc-cysteamine (88.6 mg dissolved in 1.25 mL of acetonitrile, 0.50 mmol, 1.0 equiv) with stirring for 16 h at room temperature. Analysis of the crude reaction mixture by ^{1}H NMR indicated a 5 : 1 ratio of C2:C4-functionalized products. Purification by flash column chromatography on silica gel using an eluent of hexanes:EtOAc = 20:1 (R_f = 0.36 provided **14a** as a white solid (89.6 mg, 62% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.37 (d, *J* = 5.2, Hz, 1H), 7.01 (d, *J* = 5.2 Hz, 1H), 4.99 (broad singlet, 1H), 3.47 (t, *J* = 6.3 Hz, 2H), 3.28 (t, *J* = 6.3 Hz, 2H), 1.42 (s, 9H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, δ): 173.0, 161.3, 158.2, 155.9, 117.0, 79.6, 40.0, 31.5, 28.5. HRMS (ESI Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{11}H_{17}ClN_3O_2S$ 290.0725; found 290.0721. X-ray quality crystals were grown from chloroform at 0 °C and the regioselectivity was verified by X-ray diffraction (see Section III).

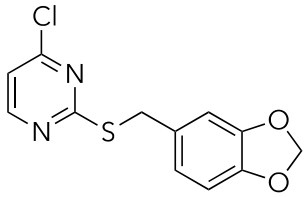
Under the corresponding catalyst-free S_NAr conditions at room temperature for 16 h, the C2 and C4-functionalized products were formed in a 1 : 5 ratio based on ^{1}H NMR analysis of the crude reaction mixture.



6-(4-Chloro-2-pyrimidinylthio)hexan-1-ol (15a). Compound **15a** was prepared according to the general procedure using a 5 mL round bottom flask, 2,4-dichloropyrimidine (**1**, 74.5 mg, 0.50 mmol, 1.0 equiv), and 6-mercaptohexanol (68 μL, 0.50 mmol, 1.0 equiv) with stirring for 16 h at room temperature. Analysis of the crude reaction mixture by ^{1}H NMR indicated a >99 : 1 ratio of

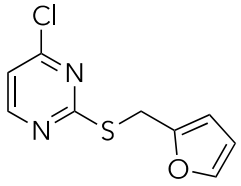
C2:C4-functionalized products. Purification by flash column chromatography on silica gel using an eluent of hexanes:EtOAc = 1:1 (R_f = 0.38 in 1:1 hexanes:EtOAc) provided **15a** as a white solid (59.0 mg, 48% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.35 (d, J = 5.2 Hz, 1H), 6.97 (d, J = 5.2 Hz, 1H), 3.64 (t, J = 6.6 Hz, 2H), 3.13 (t, J = 7.1 Hz, 2H), 1.74 (tt, J = 7.1, 7.1 Hz, 2H), 1.63-1.53 (multiple overlapping signals, 3H) 1.53-1.37 (multiple overlapping signals, 4H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 173.9, 161.3, 158.0, 116.5, 63.0, 32.7, 31.2, 29.08, 28.7, 25.4. HRMS (ESI Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{10}H_{16}ClN_2OS$ 247.0666; found 247.0677. Regioselectivity was confirmed by 1D NOE of **15a** (see section V).

Under the corresponding catalyst-free S_NAr conditions at room temperature for 16 h, the C2 and C4-functionalized products were formed in a 1 : 7 ratio based on ^{1}H NMR analysis of the crude reaction mixture.



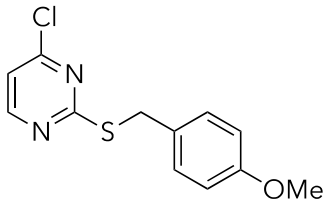
2-[(1,3-Benzodioxol-5-ylmethyl)thio]-4-chloropyrimidine **(16a).** Compound **16a** was prepared according to the general procedure using a 5 mL round bottom flask, 2,4-dichloropyrimidine (**1**, 41.7 mg, 0.28 mmol, 1.0 equiv), and 1,3-benzodioxole-5-methanethiol (**S53**, 47.1 mg dissolved in 0.7 mL of acetonitrile, 0.28 mmol, 1.0 equiv) with stirring for 16 h at room temperature. Analysis of the crude reaction mixture by ^{1}H NMR indicated a >99 : 1 ratio of C2:C4-functionalized products. Purification by flash column chromatography on silica gel using an eluent of pentane:EtOAc = 95:5 to 90:10 (R_f = 0.46 in 90:10 pentane:EtOAc) provided **16a** as colorless oil (44.7 mg, 57% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.38 (d, J = 5.2 Hz, 1H), 7.00 (d, J = 5.2 Hz, 1H), 6.94-6.86 (multiple overlapping signals, 2H), 6.74 (d, 8.0 Hz, 1H), 5.93 (s, 2H), 4.33 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 173.2, 161.2, 158.2, 147.8, 147.1, 130.7, 122.6, 116.8, 109.7, 108.3, 101.2, 35.7. HRMS (ESI Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_{10}ClN_2O_2S$ 281.0146; found 281.0137. Regioselectivity was confirmed by 1D NOE of **16a** (see section V).

Under the corresponding catalyst-free S_NAr conditions at room temperature for 16 h, the C2 and C4-functionalized products were formed in a 1 : 4 ratio based on ^{1}H NMR analysis of the crude reaction mixture.



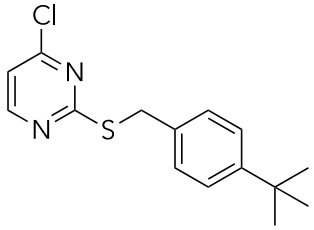
4-Chloro-2-[(2-furanylmethyl)thio]pyrimidine (17a). Compound **17a** was prepared according to the general procedure using a 1-dram vial, 2,4-dichloropyrimidine (**1**, 74.5 mg, 0.50 mmol, 1.0 equiv), and furfuryl mercaptan (50 μL, 0.50 mmol, 1.0 equiv) with stirring at room temperature for 16 h. Analysis of the crude reaction mixture by ^{1}H NMR indicated a 34 : 1 ratio of C2:C4-functionalized products. This selectivity was reproduced across two trials at this scale (0.5 mmol scale), but on a smaller (0.08 mmol) scale, the observed selectivity ranged from 34:1 to 3:1 (C2:C4) across three separate trials. Purification by flash column chromatography on silica gel using an eluent of pentane:Et_2O = 90:10 (R_f = 0.44) provided **17a** as a yellow oil: (62.2 mg, 55% yield). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.39 (d, J = 5.2 Hz, 1H), 7.35-7.34 (m, 1H), 7.01 (d, J = 5.2 Hz, 1H), 6.33-6.28 (multiple overlapping signals, 2H), 4.43 (s, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 172.6, 161.2, 158.2, 150.3, 142.4, 116.9, 110.7, 108.4, 28.1. HRMS (ESI Q-TOF) m/z: $[M+H]^+$ Calcd for $C_9H_8ClN_2OS$ 227.0040; found 227.0045. Regioselectivity was confirmed by 1D NOE of **17a** (see section V).

Under the corresponding catalyst-free S_NAr conditions at room temperature for 16 h, the C2 and C4-functionalized products were formed in a 1 : 7 ratio based on ^{1}H NMR analysis of the crude reaction mixture.



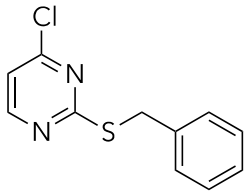
4-Chloro-2-[[(4-methoxyphenyl)methyl]thio]pyrimidine (18a). Compound **18a** was prepared according to the general procedure using a 5 mL round bottom flask, 2,4-dichloropyrimidine (**1**, 74.5 mg, 0.50 mmol, 1.0 equiv), and 4-methoxybenzylmercaptan (69.7 μL, 0.50 mmol, 1.0 equiv) with stirring at 0 ºC for 3 h. Analysis of the crude reaction mixture by ^{1}H NMR indicated a >99 : 1 ratio of C2:C4-functionalized products. Purification by flash column chromatography on silica gel using eluent of hexanes:EtOAc = 100:0 to 85:15 (R_f = 0.31 in hexanes:EtOAc = 90:10) provided **18a** as a yellow oil (116.9 mg, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.38 (d, J = 5.2 Hz, 1H), 7.36 (d, J = 8.5 Hz, 2H), 6.99 (d, J = 5.2 Hz, 1H), 6.83 (d, J = 8.5 Hz, 2H), 4.35 (s, 2H), 3.79 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 173.4, 161.2, 159.1, 158.2, 130.5, 128.9, 116.8, 114.1, 55.4, 35.3. HRMS (ESI Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_{12}ClN_2OS$ 267.0353; found 267.0386. X-ray quality crystals were grown from Et_2O/hexanes at –30 °C and the regioselectivity was verified by X-ray diffraction (see Section III).

Under the corresponding catalyst-free S_NAr conditions at 0 ºC for 3 h, the C2 and C4-functionalized products were formed in a 1 : 7 ratio based on ^1H NMR analysis of the crude reaction mixture.



4-Chloro-2-[[(4-(tert-butyl)phenyl)methyl]thio]pyrimidine (19a). Compound **19a** was prepared according to the general procedure using a 5 mL round bottom flask, 2,4-dichloropyrimidine (**1**, 74.5 mg, 0.50 mmol, 1.0 equiv), and 4-*tert*-butylbenzyl mercaptan (93 µL, 0.50 mmol, 1.0 equiv) with stirring for at 0 ºC for 3 h. Analysis of the crude reaction mixture by ^1H NMR indicated a >99 : 1 ratio of C2:C4-functionalized products. Purification by flash column chromatography on silica gel using an eluent of pentane:Et_2O = 98:2 (R_f = 0.12) provided **19a** as a colorless oil (80.3 mg, 55% yield). ^1H NMR (500 MHz, $CDCl_3$, δ): 8.38 (d, J = 5.3 Hz*,* 1H*),* 7.39-7.33 (multiple overlapping signals, 4H), 7.00 (d, J = 5.3 Hz*,* 1H), 4.39 (s, 2H), 1.32 (s, 9H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, δ): 173.4, 161.1, 158.2, 150.4, 133.8, 129.0, 125.6, 116.7, 35.3, 34.6, 31.4. HRMS (ESI Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{18}ClN_2S$ 293.0874; found 293.0885. X-ray quality crystals were grown from chloroform at 0 °C and the regioselectivity was verified by X-ray diffraction (see Section III).

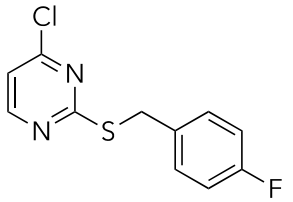
Under the corresponding catalyst-free S_NAr conditions at 0 ºC for 3 h, the C2 and C4-functionalized products were formed in a 1 : 7 ratio based on ^1H NMR analysis of the crude reaction mixture.



4-Chloro-2-[(phenylmethyl)thio]pyrimidine (20a). Compound 20**a** was prepared according to the general procedure using a 5 mL round bottom flask, 2,4-dichloropyrimidine (**1**, 74.5 mg, 0.50 mmol, 1.0 equiv), and benzyl mercaptan (59 µL, 0.50 mmol, 1.0 equiv) with stirring for 3 h at 0 ºC. Analysis of the crude reaction mixture by ^1H NMR indicated a >99 : 1 ratio of C2:C4-functionalized products. Purification by flash column chromatography on silica gel using an eluent of pentane:Et_2O = 100:0 to 98:2 (R_f = 0.13 in 98:2 pentane:Et_2O) provided **20a** as a yellow oil (80.2 mg, 68% yield). ^1H NMR (500 MHz, $(CD_3)_2CO$ δ): 8.56 (d, J = 5.2 Hz, 1H), 7.50-7.45 (m, 2H), 7.35-7.29 (m, 2H), 7.28-7.23 (multiple overlapping signals, 2H), 4.44 (s, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $(CD_3)_2CO$, δ): 173.4, 161.5, 159.9, 138.3, 129.9, 129.3, 128.1, 117.9, 35.7. HRMS (ESI

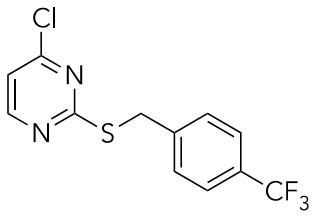
Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{11}H_{10}ClN_2S$ 237.0248; found 237.0257. Regioselectivity was confirmed by 1D NOE of **20a** (see section V) and by comparison to the separately synthesized C4-regioisomer **S20b** (see section I.I and section V).

Under the corresponding catalyst-free S_NAr conditions at 0 ºC for 3 h, the C2 and C4-functionalized products were formed in a 1 : 7 ratio based on ^1H NMR analysis of the crude reaction mixture.



4-Chloro-2-[[(4-fluorophenyl)methyl]thio]pyrimidine (21a). Compound **21a** was prepared according to the general procedure using a 5 mL round bottom flask, 2,4-dichloropyrimidine (**1**, 74.5 mg, 0.50 mmol, 1.0 equiv), and 4-fluorobenzyl mercaptan (61.4 µl, 0.50 mmol, 1.0 equiv) with stirring for 16 h at room temperature. Analysis of the crude reaction mixture by ^1H NMR indicated a >99 : 1 ratio of C2:C4-functionalized products. Purification by flash column chromatography on silica gel using an eluent of pentane:Et_2O = 98:2 (R_f = 0.19) provided **21a** as a colorless oil (91.4 mg, 72% yield). ^1H NMR (400 MHz, CD_3OD, δ): 8.44 (d, J = 5.2 Hz, 1H), 7.46-7.41 (m, 2H), 7.18 (d, J = 5.2 Hz, 1H), 7.03-6.97 (m, 2H), 4.37 (s, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, CD_3OD, δ): 173.9, 163.5 (d, $^1J_{CF}$ = 244.8 Hz), 162.3, 159.9, 134.8 (d, $^4J_{CF}$ = 2.9 Hz), 132.0 (d, $^3J_{CF}$ = 8.1 Hz), 118.1, 116.1 (d, $^2J_{CF}$ = 22.1 Hz), 35.3. ^{19}F NMR (376 MHz, CD_3OD, δ): –116.90. HRMS (ESI Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{11}H_9ClFN_2S$ 255.0154; found 255.0154. Single crystals for X-ray quality crystals were grown from chloroform at 0 °C and the regioselectivity was verified by X-ray diffraction (see Section III).

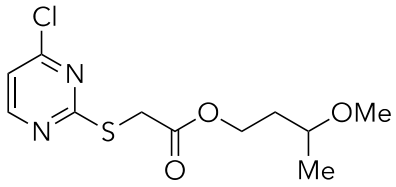
Under the corresponding catalyst-free S_NAr conditions at room temperature for 16 h, the C2 and C4-functionalized products were formed in a 1 : 6 ratio based on ^1H NMR analysis of the crude reaction mixture.



4-Chloro-2-[[(4-(trifluoromethyl)phenyl)methyl]thio]pyrimidine (22a). Compound **22a** was prepared according to the general procedure using a 5 mL round bottom flask, 2,4-dichloropyrimidine (**1**, 74.5 mg, 0.50 mmol, 1.0 equiv), and 4-trifluoromethyl benzyl mercaptan (96.1 mg, 0.50 mmol, 1.0 equiv) with stirring at room temperature for 16 h. Analysis of the crude reaction

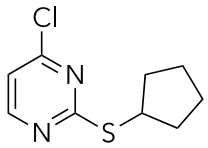
mixture by ^{1}H NMR indicated a 2.5 : 1 ratio of C2:C4-functionalized products. Purification by flash column chromatography on silica gel using an eluent of hexanes:EtOAc = 96:4 (R_f = 0.33) provided **22a** as a yellow oil: (46.7 mg, 31% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.38 (d, J = 5.2 Hz, 1H), 7.56 (apparent s, 4H), 7.01 (d, J = 5.2 Hz, 1H), 4.42 (s, 2H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, δ): 172.5, 161.3, 158.3, 141.6, 129.7 (q, $^2J_{CF}$ = 32.5 Hz), 129.6, 125.5 (q, $^3J_{CF}$ = 3.6 Hz), 124.2 (q, $^1J_{CF}$ = 272.0 Hz), 117.1, 35.0. ^{19}F NMR (376 MHz, $CDCl_3$, δ): –63.52. HRMS (ESI Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_9ClF_3N_2S$ 305.0122; found 305.0135. Regioselectivity was confirmed by 1D NOE of **22a** (see section V).

Under the corresponding catalyst-free S_NAr conditions at room temperature for 16 h, the C2 and C4-functionalized products were formed in a 1 : 6 ratio based on ^{1}H NMR analysis of the crude reaction mixture.



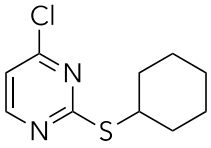
3-Methoxy-2-oxobutyl 2-[(4-chloro-2-pyrimidinyl)thio] acetate (23a). Compound **23a** was prepared according to the general procedure using a 5 mL round bottom flask, 2,4-dichloropyrimidine (**1**, 74.5 mg, 0.50 mmol, 1.0 equiv) and 3-methoxybutyl-2-mercaptoacetate (84 µL, 0.50 mmol, 1.0 equiv) with stirring for 16 h at room temperature. Analysis of the crude reaction mixture by ^{1}H NMR indicated a 2 : 1 ratio of C2:C4-functionalized products. Purification by flash column chromatography on silica gel using an eluent of hexanes:EtOAc = 80:20 to 60:40 (R_f = 0.30 in 70:30 hexanes:EtOAc) provided **23a** as a yellow oil (42.1 mg, 29% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.37 (d, J = 5.2 Hz, 1H), 7.02 (d, J = 5.2 Hz, 1H), 4.25 (t, J = 6.6 Hz, 2H), 3.92 (s, 2H), 3.38 (qt, J = 6.2, 6.2, 1H), 3.28 (s, 3H), 1.86-1.70 (m, 2H), 1.13 (d, J = 6.2 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 171.9, 168.8, 161.3, 158.2, 117.2, 73.6, 62.9, 56.2, 35.6, 33.7, 19.2. HRMS (ESI Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{11}H_{16}ClN_2O_3S$ 291.0565; found 291.0559. Regioselectivity was confirmed by 1D NOE of **23a** (see section V) and by comparison to the separately synthesized C4-regioisomer **S23b** (see section I.I and section V).

Under the corresponding catalyst-free S_NAr conditions at room temperature for 16 h, the C2 and C4-functionalized products were formed in a 1 : 8 ratio based on ^{1}H NMR analysis of the crude reaction mixture.



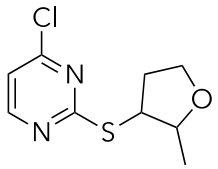
4-Chloro-2-(cyclopentylthio)pyrimidine (24a). Compound **24a** was prepared according to the general procedure using a 1-dram reaction vial, 2,4-dichloropyrimidine (**1**, 74.5 mg, 0.50 mmol, 1.0 equiv), and cyclopentanethiol (54 μL, 0.50 mmol, 1.0 equiv) with stirring at room temperature for 16 h. Analysis of the crude reaction mixture by ^{1}H NMR indicated a 3 : 1 ratio of C2:C4-functionalized products. We note that on a smaller (0.08 mmol) scale, the observed selectivity ranged from 3:1 to 1:3 (C2:C4) across three separate trials. Purification by flash column chromatography on silica gel using an eluent of pentane:Et_2O = 100:0 to 98:2 (R_f = 0.30 in 98:2 pentane:Et_2O provided **24a** as a yellow oil (35.3 mg, 33% yield). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.35 (d, J = 5.2 Hz, 1H), 6.96 (d, J = 5.2 Hz, 1H), 4.02-3.95 (m, 1H), 2.28-2.17 (m, 2H), 1.83-1.71 (m, 2H), 1.71-1.59 (multiple overlapping signals, 4H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 174.5, 160.9, 158.0, 116.3, 44.0, 33.2, 25.0. HRMS (ESI Q-TOF) m/z: $[M+H]^+$ Calcd for $C_9H_{12}ClN_2S$ 215.0404; found 215.0399. Regioselectivity was confirmed by 1D NOE of **24a** (see section V).

Under the corresponding catalyst-free S_NAr conditions at room temperature for 16 h, the C2 and C4-functionalized products were formed in a 1 : 7 ratio based on ^{1}H NMR analysis of the crude reaction mixture.



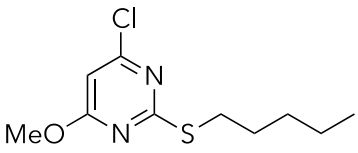
4-Chloro-2-(cyclohexylthio)pyrimidine (25a). Compound **25a** was prepared according to the general procedure using a 1-dram reaction vial, 2,4-dichloropyrimidine (**1**, 74.5 mg, 0.50 mmol, 1.0 equiv), and cyclohexanethiol (61 μL, 0.50 mmol, 1.0 equiv) with stirring at room temperature for 16 h. Analysis of the crude reaction mixture by ^{1}H NMR indicated a 3 : 1 ratio of C2:C4-functionalized products. We note that on a smaller (0.08 mmol) scale, the observed selectivity ranged from 3:1 to 1:3 (C2:C4) across three separate trials. Purification by flash column chromatography on silica gel using an eluent of pentane:Et_2O = 100:0 to 98:2 (R_f = 0.23 in 98:2 pentane:Et_2O) provided **25a** as a yellow oil (49.0 mg, 43% yield). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.34 (d, J = 5.2 Hz, 1H), 6.94 (d, J = 5.2 Hz, 1H), 3.85-3.72 (m, 1H), 2.10-2.05 (m, 2H), 1.79-1.72 (m, 2H), 1.65-1.58 (m, 1H), 1.55-1.39 (multiple overlapping signals, 4H), 1.35-1.26 (m, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 173.8, 161.0, 158.1, 116.3, 44.0, 32.8, 26.0, 25.8. HRMS (ESI Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{10}H_{14}ClN_2S$ 229.0561; found 229.0566. Regioselectivity was confirmed by 1D NOE of **25a** (see section V).

Under the corresponding catalyst-free S_NAr conditions at room temperature for 16 h, the C2 and C4-functionalized products were formed in a 1 : 6 ratio based on ^1H NMR analysis of the crude reaction mixture.



4-Chloro-2-[(2-methyloxolan-3-yl)thio]pyrimidine (26a). Compound **26a** was prepared according to the general procedure using a 5 mL round bottom flask, 2,4-dichloropyrimidine (**1**, 74.5 mg, 0.50 mmol, 1.0 equiv) and 2-methyl-3-tetrahydrofuranthiol (57 µL, 0.50 mmol, 1.0 equiv) with stirring for 16 h at room temperature. Analysis of the crude reaction mixture by ^1H NMR indicated a 1.5 : 1 ratio of C2:C4-functionalized products. Purification by flash column chromatography on silica gel using an eluent of pentane:Et_2O = 95:5 to 70:30 (R_f = 0.38 in 70:30 pentane:Et_2O) provided **26a** as a colorless oil: (50.8 mg, 44% yield). ^1H NMR (400 MHz, $CDCl_3$, δ): 8.36 (d, J = 5.2 Hz, 1H), 6.99 (d, J = 5.2 Hz, 1H), 4.37 (ddd, J = 11.9, 7.7, 7.4 Hz, 1H), 4.32 (dq J = 11.9, 6.1 Hz, 1H), 4.02 (ddd, J = 8.3, 8.3, 5.5 Hz, 1H), 3.79 (ddd, J = 8.3, 8.3, 6.9 Hz, 1H), 2.54 (dddd, J = 13.1, 8.3, 7.7, 5.5 Hz, 1H), 2.10-2.00 (m, 1H), 1.26 (d, J = 6.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, δ): 173.4, 161.1, 158.1, 116.8, 76.7, 66.0, 47.4, 33.2, 17.1. HRMS (ESI Q-TOF) m/z: $[M+H]^+$ Calcd for $C_9H_{12}ClN_2OS$ 231.0353; found 231.0348. Regioselectivity was confirmed by 1D NOE of **26a** (see section V).

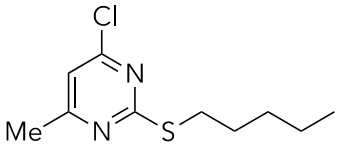
Under the corresponding catalyst-free S_NAr conditions at room temperature for 16 h, the C2 and C4-functionalized products were formed in a 1 : 6 ratio based on ^1H NMR analysis of the crude reaction mixture.



4-Chloro-6-methoxy-2-(pentylthio)pyrimidine (34a). Compound **34a** was prepared according to the general procedure using a 5 mL round bottom flask, 2,4-dichloro-5-methoxypyrimidine (89.5 mg, 0.50 mmol, 1.0 equiv), and 1-pentanethiol (62 µl, 0.50 mmol, 1.0 equiv) with stirring for 22 h at room temperature. Analysis of the crude reaction mixture by ^1H NMR indicated a 5 : 1 ratio of C2:C4-functionalized products. Purification by flash column chromatography on silica gel using an eluent of hexanes:Et_2O = 99:1 to 80:20 (R_f = 0.58 in 90:10 hexanes:Et_2O) provided **34a** as a colorless oil (53.0 mg, 43% yield). ^1H NMR (400 MHz, $CDCl_3$, δ): 6.37 (s, 1H), 3.94 (s, 3H), 3.10 (t, J = 7.4 Hz, 2H), 1.72 (tt, J = 7.4, 7.2 Hz, 2H), 1.43-1.31 (multiple overlapping signals, 4H),

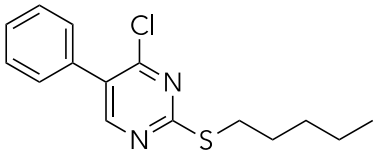
0.89 (t, J = 7.1 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, δ): 172.8, 169.9, 160.3, 102.4, 54.5, 31.17, 31.15, 28.9, 22.3, 14.0 ppm. HRMS (ESI^+) m/z: $[M+H]^+$ Calcd for $C_{10}H_{16}ClN_2OS$ 247.0666; found 247.0659. Regioselectivity was confirmed by 1D NOE of **34a** (see section V).

Under the corresponding catalyst-free S_NAr conditions at room temperature for 16 h, the C2 and C4-functionalized products were formed in a 5 : 1 ratio based on ^1H NMR analysis of the crude reaction mixture. Therefore, the uncatalyzed SNAr reaction favors the same product as the catalytic thiolation conditions.



6-Chloro-4-methyl-2-(pentylthio)pyrimidine (35a). Compound **35a** was prepared according to the general procedure using a 10 mL round bottom flask, 2,4-dichloro-6-methylpyrimidine (81.5 mg, 0.50 mmol, 1.0 equiv), and 1-pentanethiol (62 µL, 0.50 mmol, 1.0 equiv) with stirring for 19 h at 3 ºC. Analysis of the crude reaction mixture by ^1H NMR indicated an 18 : 1 ratio of C2:C4-functionalized products. Purification by flash column chromatography on silica gel using an eluent of hexanes:EtOAc = 95:5 (R_f = 0.34 in 95:5 hexanes:EtOAc) provided **35a** as a yellow oil (75.7 mg, 66% yield). ^1H NMR (400 MHz, $CDCl_3$, δ): 6.83 (s, 1H), 3.13 (t, J = 7.3 Hz, 2H), 2.42 (s, 3H), 1.73 (tt, J = 7.3, 7.3 Hz, 2H), 1.48-1.30 (multiple overlapping signals, 4H), 0.91 (t, J = 7.1 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, δ): 173.2, 169.0, 160.9, 115.7, 31.2, 31.1, 28.8, 24.0, 22.3, 14.1. HRMS (ESI Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{10}H_{16}ClN_2S$ 230.0644; found 230.0639. Regioselectivity was confirmed by 1D NOE of **35a** (see section V).

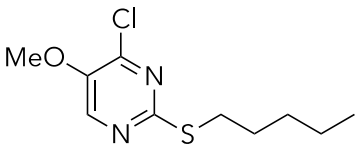
Under catalyst-free S_NAr conditions at 0 ºC for 3 h, the C2 and C4-functionalized products were formed in a 1 : 4 ratio based on ^1H NMR analysis of the crude reaction mixture.



4-Chloro-2-(pentylthio)-5-phenylpyrimidine (36a). Compound **36a** was prepared according to the general procedure using a 10 mL round bottom flask, 2,4-dichloro-5-phenylpyrimidine (**S52**, 112 mg, 0.50 mmol, 1.0 equiv), and 1-pentanethiol (62 µL, 0.5.0 mmol, 1.0 equiv) with stirring at 3 ºC for 18 h. Analysis of the crude reaction mixture by ^1H NMR indicated a 49 : 1 ratio of C2:C4-functionalized products. Purification by flash column chromatography on silica gel using an eluent of hexanes:EtOAc = 98:2 (R_f = 0.19 in 98:2 hexanes:EtOAc) provided **36a** as a yellow oil (105.5

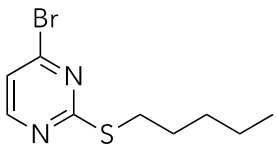
mg, 72% yield). ^{1}H NMR (400 MHz, C_6D_6, δ): 7.99 (s, 1H), 7.11-7.02 (multiple overlapping signals, 5H), 3.06 (t, J = 7.5 Hz, 2H), 1.65 (tt, J = 7.5, 7.5 Hz, 2H), 1.32-1.15 (multiple overlapping signals, 4H), 0.82 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, δ): 172.0, 159.1, 158.2, 133.9, 129.4, 129.3, 128.9, 128.8, 31.3, 31.2, 28.8, 22.4, 14.1. HRMS (ESI Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{18}ClN_2S$ 292.0801, found 292.0804. Regioselectivity was confirmed by 1D NOE of **36a** (see section V).

Under the corresponding catalyst-free S_NAr conditions at 0 ºC for 3 h, the C2 and C4-functionalized products were formed in a 1 : 10 ratio based on ^{1}H NMR analysis of the crude reaction mixture.



4-Chloro-2-(pentylthio)-5-methoxypyrimidine **(37a).** Compound **37a** was prepared according to the general procedure using a 5 mL round bottom flask, 2,4-dichloro-5-methoxypyrimidine (89.5 mg, 0.50 mmol, 1.0 equiv), and 1-pentanethiol (62 µL, 0.50 mmol, 1.0 equiv) with stirring for 16 h at room temperature. Analysis of the crude reaction mixture by ^{1}H NMR indicated a 3 : 1 ratio of C2:C4-functionalized products. Purification by flash column chromatography on silica gel using an eluent of hexanes:EtOAc = 95:5 to 90:10 (R_f = 0.78 in 90:10 hexanes:EtOAc) provided **37a** as a colorless oil (43.1 mg, 35% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.15 (s, 1H), 3.95 (s, 3H), 3.11 (t, J = 7.4 Hz, 2H), 1.72 (tt, J = 7.4, 7.4 Hz, 2H), 1.48-1.30 (multiple overlapping signals, 4H), 0.91 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 163.5, 150.7, 146.9, 141.2, 57.2, 31.6, 31.2, 28.9, 22.4, 14.1. HRMS (ESI Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{10}H_{16}ClN_2OS$ 247.0666; found 247.0659. Regioselectivity was confirmed by 1D NOE of **37a** (see section V) and by comparison to the separately synthesized C4-regioisomer **S37b** (see section I.I and section V).

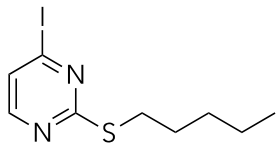
Under the corresponding catalyst-free S_NAr conditions at room temperature for 16 h, only the C4-functionalized product was detected based on ^{1}H NMR analysis of the crude reaction mixture.



6-Bromo-2-(pentylthio)pyrimidine (38a). Compound **38a** was prepared according to the general procedure using a 10 mL round bottom flask, 2,4-dibromopyrimidine (118.9 mg, 0.50 mmol, 1.0 equiv), and 1-pentanethiol (62 µL, 0.50 mmol, 1.0 equiv) with stirring for 16 h at 3 ºC. Analysis of the crude reaction mixture by ^{1}H NMR indicated a 1.5 : 1 ratio of C2:C4-functionalized products. Note: the selectivity of the

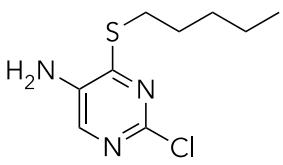
crude reaction mixture was sometimes more C2-selective when performed on a smaller scale. Purification by flash column chromatography on silica gel using an eluent of hexanes:CH_2Cl_2 = 60:40 (R_f = 0.18 in 60:40 hexanes:CH_2Cl_2) provided **38a** as a yellow oil (36.5 mg, 28% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.23 (d, *J* = 5.2 Hz, 1H), 7.13 (d, *J* = 5.2 Hz, 1H), 3.13 (t, *J* = 7.4 Hz, 2H), 1.73 (tt *J* = 7.4, 7.4 Hz, 2H), 1.49-1.30 (multiple overlapping signals, 4H), 0.91 (t, *J* = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 173.9, 157.4, 152.6, 120.4, 31.3, 31.1, 28.7, 22.5, 14.1. HRMS (ESI Q-TOF) m/z: $[M+H]^+$ Calcd for $C_9H_{14}BrN_2S$ 259.9983; found 259.9974. Regioselectivity was confirmed by 1D NOE of **38a** (see section V).

Under the corresponding catalyst-free S_NAr conditions at 0 ºC for 3 h, the C2 and C4-functionalized products were formed in a 1 : 7 ratio based on ^{1}H NMR analysis of the crude reaction mixture.



6-Iodo-2-(pentylthio)pyrimidine (39a). Compound **39a** was prepared according to the general procedure using a 10 mL round bottom flask, 2,4-diiodopyrimidine (165.9 mg, 0.50 mmol, 1.0 equiv), and 1-pentanethiol (62 μL, 0.50 mmol, 1.0 equiv.) with stirring at 3 ºC for 16 h. Analysis of the crude reaction mixture by ^{1}H NMR indicated a 41 : 1 ratio of C2:C4-functionalized products. Purification by flash column chromatography on silica gel using an eluent of hexanes:CH_2Cl_2 = 50:50 (R_f = 0.34) provided **39a** as a brown oil (86.2 mg, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.97 (d, *J* = 5.1 Hz, 1H), 7.38 (d, *J* = 5.1, 1H), 3.11 (t, *J* = 7.4, 2H) 1.72 (tt *J* = 7.4, 7.4 Hz, 2H), 1.48-1.30 (multiple overlapping signals, 4H), 0.91 (t, *J* = 7.3 Hz, 3H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, δ): 173.4, 156.0, 129.4, 127.4, 31.3, 31.1, 28.7, 22.4, 14.1. HRMS (ESI Q-TOF) m/z: $[M+H]^+$ Calcd for $C_9H_{14}IN_2S$ 307.9844; found 307.9839. Regioselectivity was confirmed by 1D NOE of **39a** (see section V).

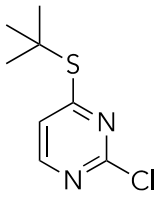
Under the corresponding catalyst-free S_NAr conditions at 0 ºC for 3 h, the C2 and C4-functionalized products were formed in a 1 : 13 ratio based on ^{1}H NMR analysis of the crude reaction mixture.



6-Chloro-2-(pentylthio)-5-pyrimidinamine (40b). Compound **40b** was prepared according to the general procedure using a 10 mL round bottom flask, 5-amino-2,4-dichloropyrimidine (82.0 mg, 0.5 mmol, 1 equiv), and

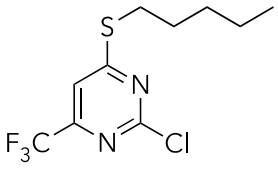
1-pentanethiol (62 µL, 0.5 mmol, 1 equiv) with stirring at 3 ºC for 20 h. Analysis of the crude reaction mixture by ^{1}H NMR indicated a <1 : 99 ratio of C2:C4-functionalized products. Purification by flash column chromatography on silica gel using an eluent of hexanes:EtOAc = 80:20 (R_f = 0.13 in 80:20 hexanes:EtOAc) provided **40b** as a brown solid (88.3 mg, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.73 (s, 1H), 3.77 (broad s, 2H), 3.24 (t, J = 7.3 Hz, 2H), 1.73 (tt, J = 7.3, 7.3 Hz, 2H), 1.49-1.31 (multiple overlapping signals, 4H), 0.91 (t, J = 7.1 Hz, 3H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, δ): 157.8, 149.8, 140.4, 136.6, 31.0, 30.0, 28.7, 22.3, 14.1. HRMS (ESI Q-TOF) m/z: $[M+H]^+$ Calcd for $C_9H_{15}ClN_3S$ 231.0597; found 231.0592. X-ray quality crystals were grown from EtOAc/hexanes at –20 °C and the regioselectivity was verified by X-ray diffraction (see Section III).

Under the corresponding catalyst-free S_NAr conditions at 3 ºC for 20 h, the C2 and C4-functionalized products were formed in a <1 : 99 ratio based on ^{1}H NMR analysis of the crude reaction mixture. Therefore, the uncatalyzed SNAr reaction favors the same product as the catalytic thiolation conditions.



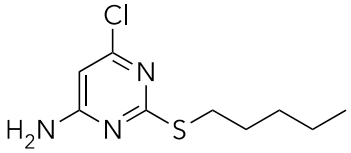
2-Chloro-4-[(1,1-dimethylethyl)thio]pyrimidine (41b). Compound **41b** was prepared according to the general procedure using a 5 mL round b0ttom flask, 2,4-dichloropyrimidine (**1**, 74.5 mg, 0.50 mmol, 1.0 equiv), and *tert*-butyl mercaptan (56 µL, 0.50 mmol, 1.0 equiv) with stirring for 16 h at room temperature. Analysis of the crude reaction mixture by ^{1}H NMR indicated a 1 : 7 ratio of C2:C4-functionalized products. Purification by flash column chromatography on silica gel using an eluent of CH_2Cl_2:MeOH = 98:2 (R_f = 0.74) provided **41b** as a yellow oil (38.4 mg, 38% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.15 (d, J = 5.5 Hz, 1H), 6.97 (d, J = 5.5 Hz, 1H), 1.63 (s, 9H), ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 174.8, 160.3, 156.0, 118.3, 49.8, 30.2. HRMS (ESI Q-TOF) m/z: $[M+H]^+$ Calcd for $C_8H_{12}ClN_2S$ 203.0404; found 203.0416. Regioselectivity was confirmed by 1D NOE of **41b** (see section V).

Under the corresponding catalyst-free S_NAr conditions at room temperature for 16 h, the C2 and C4-functionalized products were formed in a 1 : 6 ratio based on ^{1}H NMR analysis of the crude reaction mixture.



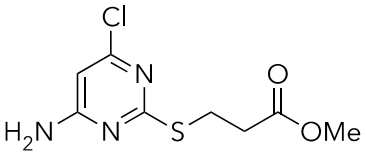
2-Chloro-6-(trifluoromethyl)-4-(pentylthio)pyrimidine (43b). Compound **43b** was prepared according to the general procedure using a 5 mL round bottom flask, 2,4-dichloro-6-(trifluoromethyl)pyrimidine (108.5 mg, 0.50 mmol, 1.0 equiv), and 1-pentanethiol (62 µL, 0.50 mmol, 1.0 equiv) with stirring for 16 h at room temperature. Analysis of the crude reaction mixture by ^{1}H NMR indicated a <1 : 99 ratio of C2:C4-functionalized products. Purification by flash column chromatography on silica gel using an eluent of CH_2Cl_2:MeOH = 98:2 (R_f = 0.82) provided **43b** as a yellow oil (133.5 mg, 94% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.34 (s, 1H), 3.24 (t, J = 7.2 Hz, 2H), 1.74 (tt, J = 7.2, 7.2 Hz, 2H), 1.46-1.32 (multiple overlapping signals, 4H), 0.92 (t, J = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 177.0, 161.6, 154.9 (q, $^{2}J_{CF}$ = 36.7 Hz), 119.9 (q, $^{1}J_{CF}$ = 275.4 Hz), 113.6 (q, $^{3}J_{CF}$ = 2.9 Hz), 31.0, 30.4, 28.2, 22.2, 14.0. ^{19}F NMR (376 MHz, $CDCl_3$, δ): –71.08. HRMS (ESI Q-TOF) m/z: $[M+H]^+$ calc for $C_{10}H_{13}ClF_3N_2S$ 285.0435 found 285.0456. Regioselectivity was confirmed by 1D NOE of **43b** (see section V).

Under the corresponding catalyst-free S_NAr conditions at room temperature for 16 h, the C2 and C4-functionalized products were formed in a <1 : 99 ratio based on ^{1}H NMR analysis of the crude reaction mixture.



6-Chloro-2-(pentylthio)pyrimidin-4-amine (44a). Compound **44a** was prepared according to the general procedure using a 5 mL round bottom flask, 6-amino-2,4-dichloropyrimidine (82.0 mg, 0.50 mmol, 1.0 equiv), and 1-pentanethiol (62 µL, 0.50 mmol, 1.0 equiv) with stirring for 3 h at 0 ºC. Analysis of the crude reaction mixture by ^{1}H NMR indicated a >99 : 1 ratio of C2:C4-functionalized products. Purification by flash column chromatography on silica gel using an eluent of hexanes:EtOAc = 80:20 (R_f = 0.33 in 80:20 hexanes:EtOAc) provided **44a** as a colorless solid (93.4 mg, 81% yield). ^{1}H NMR (400 MHz, C_6D_6, δ): 5.37 (s, 1H), 4.38 (broad s, 2H), 3.04 (t, J = 7.3 Hz, 2H), 1.61 (tt, J = 7.3, 7.3, 2H), 1.30-1.13 (multiple overlapping signals, 4H), 0.80 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, δ): 172.9, 163.7, 159.8, 99.2, 31.3, 31.0, 29.4, 22.5, 14.1. HRMS (ESI Q-TOF) m/z: $[M]^+$ Calcd for $C_9H_{15}ClN_3S$ 231.0597; found 231.0604. X-ray quality crystals were grown from EtOAc/hexanes at –20 °C and the regioselectivity was verified by X-ray diffraction (see Section III).

Under the corresponding catalyst-free S_NAr conditions at 0 ºC for 3 h, only trace conversion to products could be detected by ^1H NMR. At 40 ºC for 3 h under catalyst-free S_NAr conditions, the C2 and C4-functionalized products were formed in a 3 : 1 ratio based on ^1H NMR analysis of the crude reaction mixture. Therefore, the uncatalyzed SNAr reaction favors the same product as the catalytic thiolation conditions, although warmer temperatures are needed to observe products in the absence of catalyst.



***Methyl 3-[(6-amino-4-chloro-2-pyrimidinyl)thio] propanoate* (46a).** Compound **46a** was prepared according to the general procedure using a 1-dram reaction vial, 6-amino-2,4-dichloropyrimidine (82.0 mg, 0.50 mmol, 1.0 equiv), and methyl-3-mercaptopropionate (55 µL, 0.50 mmol, 1.0 equiv) with stirring for 16 h at room temperature. Analysis of the crude reaction mixture by ^1H NMR indicated a 16 : 1 ratio of C2:C4-functionalized products. Purification by flash column chromatography on silica gel using an eluent of pentane:Et_2O = 90:10 to 60:40 (R_f = 0.18 in 60:40 pentane:Et_2O) provided **46a** as a white solid (66.7 mg, 54% yield). ^1H NMR (500 MHz, $CDCl_3$, δ): 6.15 (s, 1H), 5.06 (broad s, 2H), 3.70 (s, 3H), 3.32 (t, J = 7.1 Hz, 2H), 2.80 (t, J = 7.1 Hz, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, δ): 172.6, 171.7, 163.4, 159.9, 99.4, 52.0, 34.3, 26.0. HRMS (ESI Q-TOF) m/z: $[M+H]^+$ Calcd for $C_8H_{11}ClN_3O_2S$ 248.0255; found 248.0256. Regioselectivity was confirmed by 1D NOE of **46a** (see section V).

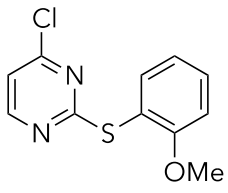
Under the corresponding catalyst-free S_NAr conditions at room temperature for 16 h, the C2 and C4-functionalized products were formed in a 5 : 1 ratio based on ^1H NMR analysis of the crude reaction mixture. Therefore, the uncatalyzed SNAr reaction favors the same product as the catalytic thiolation conditions.

H. Isolation and Characterization of Cross-Coupled Products Using Aromatic Thiols

<u>*General Procedure for Cross-Couplings*</u>. Open to air, (η^3-1-^{t}Bu-indenyl)Pd(IPent)Cl (**5a**, 8.1 mg, 0.010 mmol, 0.020 equiv), 2,4-dichloropyrimidine (0.50 mmol, 1.0 equiv), and KF (58.1 mg, 1.0 mmol, 2.0 equiv) were combined in a 1-dram vial or a 5 mL round bottom flask equipped with a Teflon-coated stir bar. The vial was taken into a nitrogen-atmosphere glovebox and acetonitrile (2.5 mL) was added via a 3-mL syringe unless otherwise indicated. The reaction vessel was sealed

with a Teflon-lined cap and removed from the glovebox. The bottom portion of the reaction vessel containing the reaction mixture was submerged in a liquid nitrogen bath (-196 ºC) for 10-15 seconds to freeze the reaction mixture. The cap was then removed and the thiol (0.55 mmol, 1.1 equiv) was quickly added via syringe (for degassed liquid thiols) or directly in one portion (for solid thiols, unless otherwise noted). The vial headspace was then flushed for 10-20 seconds with N_2 and the vial was re-sealed with the Teflon-lined cap. The reaction mixture was stirred vigorously at 80 ºC for the indicated time. The reaction mixture was then diluted with ethyl acetate, filtered through Celite™, and concentrated under vacuum. The residue was taken up in $CDCl_3$ or C_6D_6 and an aliquot was analyzed by ^1H NMR to obtain the crude ratio of C2:C4 functionalized products. The NMR sample was recombined with the bulk filtrate, and the filtrate was concentrated under vacuum prior to purification.

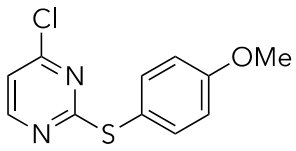
General Procedure for Catalyst-Free S_NAr Reactions. Open to air, 2,4-dichloropyrimidine (0.080 mmol, 1.0 equiv) and KF (9.3 mg, 0.16 mmol, 2.0 equiv) were combined in a 1-dram vial equipped with a Teflon-coated stir bar. The reaction vial was taken into a nitrogen-atmosphere glovebox and acetonitrile (0.4 mL) was added via a 1-mL syringe. The vial was sealed with a Teflon-lined cap and removed from the glovebox. The bottom portion of the vial containing the reaction mixture was submerged in a liquid nitrogen bath (-196 ºC) for 10-15 seconds to freeze the reaction mixture. The cap was then removed and the thiol (0.088 mmol, 1.1 equiv) was quickly added via syringe (for degassed liquid thiols) or directly in one portion (solid thiols). The vial headspace was then flushed for 10-20 seconds with N_2 and the vial was re-sealed with the Teflon-lined cap. The reaction mixture was stirred vigorously at 80 ºC for the indicated time. The reaction mixture was then diluted with ethyl acetate, filtered through Celite™, and concentrated under vacuum. The residue was taken up in $CDCl_3$ or C_6D_6 and analyzed by ^1H NMR to obtain the crude ratio of C2:C4 functionalized products.



4-Chloro-2-[(2-methyoxyphenyl)thio]pyrimidine (27a). Compound **27a** was prepared according to the general procedure using a 1-dram vial, 2,4-dichloropyrimidine (**1**, 74.5 mg, 0.50 mmol, 1.0 equiv), and 2-methoxythiophenol (67 µL, 0.55 mmol, 1.1 equiv) with a reaction time of 16 h. Analysis of the crude reaction mixture by ^1H NMR indicated a 19 : 1 ratio of C2:C4 functionalized products. Purification by flash column chromatography on silica gel using an eluent

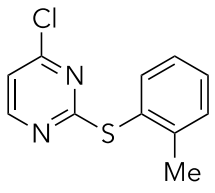
of hexanes:EtOAc = 100:0 to 85:15 (R_f = 0.17 in 90:10 hexanes:EtOAc) provided **27a** as a yellow oil (109.3 mg, 86% yield). ^{1}H NMR (400 MHz, C_6D_6, δ): 7.56 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.48 (d, *J* = 5.2 Hz, 1H), 7.08 (ddd, *J* = 8.3, 7.6, 1.7 Hz, 1H), 6.73 (ddd, *J* = 7.6, 7.6, 1.0 Hz, 1H), 6.50 (dd, *J* = 8.3, 1.0 Hz, 1H), 5.98 (d, *J* = 5.2 Hz, 1H), 3.23 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, δ): 174.0, 161.0, 160.7, 158.1, 137.7, 131.8, 121.2, 117.8, 116.6, 111.8, 55.4. HRMS (ESI Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{11}H_{10}ClN_2OS$ 253.0197; found 253.0203. X-ray quality crystals were grown from Et_2O/hexanes at –30 °C and the regioselectivity was verified by X-ray diffraction (see Section III).

Under the corresponding catalyst-free S_NAr conditions for 4 h, the C2 and C4-functionalized products were formed in a 1 : 22 ratio based on ^{1}H NMR analysis of the crude reaction mixture.



4-Chloro-2-[(4-methyoxyphenyl)thio]pyrimidine (28a). Compound **28a** was prepared according to the general procedure using a 1-dram vial, 2,4-dichloropyrimidine (**1**, 74.5 mg, 0.50 mmol, 1.0 equiv), and 4-methoxythiophenol (68 µL, 0.55 mmol, 1.1 equiv) with a reaction time of 16 h. Analysis of the crude reaction mixture by ^{1}H NMR indicated a 92 : 1 ratio of C2:C4 functionalized products. Purification by flash column chromatography on silica gel using an eluent of hexanes:Et_2O = 100:0 to 85:15 (R_f = 0.03 in 99:1 hexanes:Et_2O) provided **28a** as a yellow oil (110.7 mg, 88% yield). ^{1}H NMR (400 MHz, C_6D_6, δ): 7.52 (d, *J* = 5.2 Hz, 1H), 7.44 (d, *J* = 8.8 Hz, 2H), 6.66 (d, *J* = 8.8 Hz, 2H), 6.04 (d, *J* = 5.2 Hz, 1H), 3.17 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 174.3, 161.2, 160.9, 158.3, 137.1, 119.1, 117.0, 115.0, 55.4. HRMS (ESI Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{11}H_{10}ClN_2OS$ 253.0197; found 253.0201. Regioselectivity was confirmed by 1D NOE of **28a** (see section V).

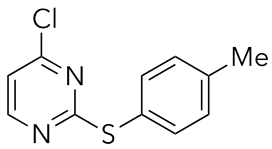
Under the corresponding catalyst-free S_NAr conditions for 4 h, the C2 and C4-functionalized products were formed in a 1 : 27 ratio based on ^{1}H NMR analysis of the crude reaction mixture.



4-Chloro-2-[(2-methylphenyl)thio]pyrimidine (29a). Compound **29a** was prepared according to the general procedure using a 1-dram vial, 2,4-dichloropyrimidine (**1**, 74.5 mg, 0.50 mmol, 1.0 equiv), and 2-methylthiophenol (65 µL, 0.55 mmol, 1.1 equiv) with a reaction time of 16 h. Analysis of the crude reaction mixture by ^{1}H NMR indicated a >99 : 1 ratio of C2:C4 functionalized products.

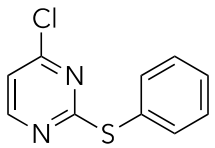
Purification by flash column chromatography on silica gel using an eluent of hexanes:CH_2Cl_2 = 100:0 to 60:40 (R_f = 0.27 in 50:50 hexanes:CH_2Cl_2) provided **29a** as a white solid (77.0 mg, 65% yield). ^{1}H NMR (500 MHz, C_6D_6, δ): 7.54 (d, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 5.1 Hz, 1H), 7.06-7.01 (multiple overlapping peaks, 2H), 6.97-6.91 (m, 1H), 6.01 (d, *J* = 5.1 Hz, 1H), 2.31 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, δ): 173.7, 161.2, 158.3, 143.4, 137.1, 131.0, 130.4, 128.7, 126.9, 116.8, 20.9. HRMS (ESI Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{11}H_{10}ClN_2S$ 237.0248; found 237.0249. X-ray quality crystals were grown from Et_2O/hexanes at –30 °C and the regioselectivity was verified by X-ray diffraction (see Section III).

Under the corresponding catalyst-free S_NAr conditions for 4 h, the C2 and C4-functionalized products were formed in a 1 : 19 ratio based on ^{1}H NMR analysis of the crude reaction mixture.



4-Chloro-2-[(4-methylphenyl)thio]pyrimidine (30a). Compound **30a** was prepared according to the general procedure using a 1-dram vial, 2,4-dichloropyrimidine (**1**, 74.5 mg, 0.50 mmol, 1.0 equiv), and 4-methylthiophenol (68.3 mg, 0.55 mmol, 1.1 equiv) with a reaction time of 16 h. Analysis of the crude reaction mixture by ^{1}H NMR indicated a 90 : 1 ratio of C2:C4 functionalized products. Purification by flash column chromatography on silica gel using an eluent of hexanes:Et_2O = 100:0 to 85:15 (R_f = 0.39 in 90:10 hexanes:Et_2O) provided **30a** as a pale yellow oil (80.0 mg, 68% yield). ^{1}H NMR (500 MHz, C_6D_6, δ): 7.49 (d, *J* = 5.2 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 2H), 6.88 (d, *J* = 8.0 Hz, 2H), 6.03 (d, *J* = 5.2 Hz, 1H), 1.97 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, δ): 174.5, 161.2, 158.2, 139.7, 135.9, 130.3, 125.9, 116.9, 21.1. HRMS (ESI Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{11}H_{10}ClN_2S$ 237.0248; found 237.0253. Regioselectivity was confirmed by 1D NOE of **30a** (see section V).

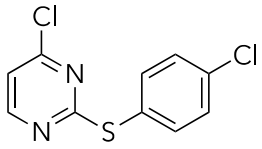
Under the corresponding catalyst-free S_NAr conditions for 3 h, the C2 and C4-functionalized products were formed in a 1 : 15 ratio based on ^{1}H NMR analysis of the crude reaction mixture.



4-Chloro-2-(phenylthio)pyrimidine (31a). Compound **31a** was prepared according to the general procedure using a 1-dram vial, 2,4-dichloropyrimidine (**1**, 74.5 mg, 0.50 mmol, 1.0 equiv), and thiophenol (56 μL, 0.55 mmol, 1.1 equiv) with a reaction time of 16 h. Analysis of the crude reaction mixture by ^{1}H NMR indicated a 92 : 1 ratio of C2:C4 functionalized products. Purification by flash column chromatography on

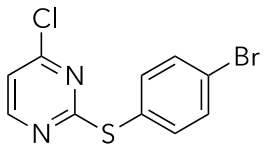
silica gel using an eluent of hexanes:Et_2O = 100:0 to 90:10 (R_f = 0.18 in 90:10 hexanes:Et_2O) provided **31a** as a yellow oil (84.7 mg, 76% yield). ^1H NMR (500 MHz, $CDCl_3$, δ): 8.32 (d, *J* = 5.2 Hz, 1H), 7.64-7.60 (m, 2H), 7.47-7.41 (multiple overlapping peaks, 3H), 6.99 (d, *J* = 5.2 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, δ): 173.8, 161.4, 158.4, 135.4, 129.7, 129.4, 128.8, 117.3. HRMS (ESI Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{10}H_8ClN_2S$ 223.0091; found 223.0092. Regioselectivity was confirmed by 1D NOE of **31a** (see section V) and by comparison to the separately synthesized C4-regioisomer **31b** (see section I.I and section V).

Under the corresponding catalyst-free S_NAr conditions for 3 h, the C2 and C4-functionalized products were formed in a 1 : 16 ratio based on ^1H NMR analysis of the crude reaction mixture.



4-Chloro-2-[(4-chlorophenyl)thio]pyrimidine (32a). Compound **32a** was prepared according to the general procedure using a 1-dram vial, 2,4-dichloropyrimidine (**1**, 74.5 mg, 0.50 mmol, 1.0 equiv), and 4-chlorothiophenol (79.5 mg, 0.55 mmol, 1.1 equiv) with a reaction time of 16 h. Analysis of the crude reaction mixture by ^1H NMR indicated a 42 : 1 ratio of C2:C4 functionalized products. Purification by flash column chromatography on silica gel using an eluent of hexanes:EtOAc = 100:0 to 85:15 (R_f = 0.27 in 90:10 hexanes:EtOAc) provided **32a** as a white solid (78.7 mg, 61% yield). ^1H NMR (500 MHz, $CDCl_3$, δ): 8.32 (d, *J* = 5.2 Hz, 1H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.01 (d, *J* = 5.2 Hz, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, δ): 173.1, 161.5, 158.4, 136.6, 136.1, 129.6, 127.1, 117.5. HRMS (ESI Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{10}H_7Cl_2N_2S$ 256.9702; found 256.9709. Regioselectivity was confirmed by 1D NOE of **32a** (see section V) and by comparison to the separately synthesized C4-regioisomer **S32b** (see section I.I and section V).

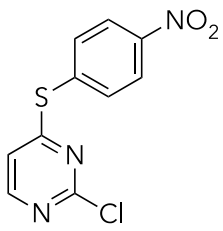
Under the corresponding catalyst-free S_NAr conditions for 3 h, the C2 and C4-functionalized products were formed in a 1 : 31 ratio based on ^1H NMR analysis of the crude reaction mixture.



4-Chloro-2-[(4-bromophenyl)thio]pyrimidine (33a). Compound **33a** was prepared according to the general procedure using a 1-dram vial, 2,4-dichloropyrimidine (**1**, 74.5 mg, 0.50 mmol, 1.0 equiv), and 4-bromothiophenol (104.0 mg, 0.55 mmol, 1.1 equiv) with a reaction time of 16 h. Analysis of the crude reaction mixture by ^1H NMR indicated a 27 : 1 ratio of C2:C4 functionalized products.

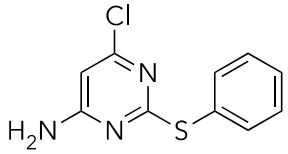
Purification by flash column chromatography on silica gel using an eluent of hexanes:EtOAc = 100:0 to 85:15 (R_f = 0.26 in 90:10 hexanes:EtOAc) provided **33a** as a white solid (115.0 mg, 76% yield). ^{1}H NMR (500 MHz, $CDCl_3$, d): 8.31 (d, J = 5.2 Hz, 1H), 7.54 (d, J = 8.5 Hz, 2H), 7.46 (d, J = 8.5 Hz, 2H), 7.01 (d, J = 5.2 Hz, 1H). ^{13}C{^{1}H} NMR(126 MHz, $CDCl_3$, d): 172.8, 161.4, 158.4, 136.8, 132.5, 127.7, 124.3, 117.5. HRMS (ESI Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{10}H_7BrClN_2S$ 300.9196; found 300.9201. Regioselectivity was confirmed by 1D NOE of **33a** (see section V).

Under the corresponding catalyst-free S_NAr conditions for 3 h, the C2 and C4-functionalized products were formed in a 1 : 28 ratio based on ^{1}H NMR analysis of the crude reaction mixture.



4-Nitrothiophenol-2-chloropyrimidine (42b). Compound **42b** was prepared according to the general procedure using a 1-dram vial, 2,4-dichloropyrimidine (**1**, 74.5 mg, 0.50 mmol, 1.0 equiv), and 4-nitrothiophenol (77.6 mg, dissolved in 2.5 mL of acetonitrile, 0.50 mmol, 1.0 equiv) with a reaction time of 16 h. Analysis of the crude reaction mixture by ^{1}H NMR indicated a 1 : 11 ratio of C2:C4 functionalized products. Purification by flash column chromatography on silica gel using an eluent of hexanes:EtOAc = 90:10 to 60:40 (R_f = 0.68 in 70:30 hexanes:EtOAc) provided **42b** as a white solid (49.4 mg, 37% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.33-8.31 (multiple overlapping signals, 3H), 7.79 (d, J = 8.9 Hz, 2H), 6.93 (d, J = 5.3 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 172.5, 161.3, 158.1, 148.9, 135.8, 135.5, 124.7, 116.4. HRMS (ESI Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{10}H_7ClN_3O_2S$ 267.9942; found 267.9942. Regioselectivity was confirmed by 1D NOE of **42b** (see section V).

Under the corresponding catalyst-free S_NAr conditions for 16 h, the C2 and C4-functionalized products were formed in a 1 : 56 ratio based on ^{1}H NMR analysis of the crude reaction mixture.

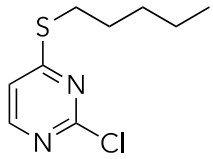


6-Chloro-2-(phenylthio)-4-pyrimidinamine (45a). Compound **45a** was prepared according to the general procedure using a 5 mL round bottom flask, 6-amino-2,4-dichloropyrimidine (82.0 mg, 0.50 mmol, 1.0 equiv), and thiophenol (51 µl, 0.55 mmol, 1.1 equiv) with a reaction time of 3 h. Analysis of the crude reaction mixture by ^{1}H NMR indicated a >99 : 1 ratio of C2:C4-functionalized products. Purification by flash column chromatography on silica gel using an eluent of hexanes:Et_2O = 95:5 to 60:40 (R_f = 0.58 in 60:40 hexanes:EtOAc) provided **45a** as a white solid (45.0 mg, 38% yield).

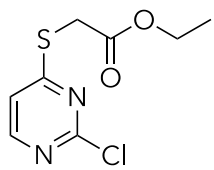
^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.61-7.58 (m, 2H), 7.43-7.37 (multiple overlapping signals, 3H), 6.14 (s, 1H), 5.06 (broad s, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, δ): 172.1, 163.3, 160.1, 135.4, 129.32, 129.26, 129.16, 99.8. HRMS (ESI Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{10}H_9ClN_3S$ 238.0200; found 238.0191. Regioselectivity was confirmed by 1D NOE of **45a** (see section V).

Under the corresponding catalyst-free S_NAr conditions for 3 h, the C2 and C4-functionalized products were formed in a 1 : 1 ratio based on ^{1}H NMR analysis of the crude reaction mixture.

Synthesis and Characterization of Products for
Confirmation of Regioselectivity

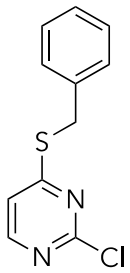


2-Chloro-4-(pentylthio)pyrimidine (2b). Open to air, 2,4-dichloropyrimidine (**1**, 74.5 mg, 0.50 mmol, 1.0 equiv) and K_3PO_4 (212 mg, 1.0 mmol, 2.0 equiv) were combined in a 5 mL round bottom flask equipped with a Teflon-coated stir bar. The flask was taken into a nitrogen-atmosphere glovebox and acetonitrile (1.25 mL) was added via a 2-mL syringe. The flask was sealed with a rubber septum and copper wire and removed from the glovebox. The bottom portion of the flask containing the reaction mixture was submerged in a liquid nitrogen bath (-196 ºC) for 10-15 seconds to freeze the reaction mixture. Degassed 1-pentanethiol (62 µl, 0.50 mmol, 1.0 equiv) was added through the septum using a syringe. The reaction mixture was stirred vigorously at 0 ºC for 3 h. The reaction mixture was diluted with ethyl acetate and filtered through Celite™. The filtrate was concentrated under vacuum and the crude residue was purified by flash column chromatography on silica gel using an eluent of pentane:Et_2O = 98:2 (R_f = 0.14) to provide **2b** as a colorless oil (63.7 mg, 59% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.16 (d, J = 5.2 Hz, 1H), 7.04 (d, J = 5.2 Hz, 1H), 3.16 (t, J = 7.3 Hz, 2H), 1.72 (tt J = 7.3, 7.3 Hz, 2H), 1.44-1.29 (multiple overlapping signals, 4H), 0.89 (t, J = 7.3 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, δ): 174.0, 161.0, 156.1, 117.5, 31.0, 29.8, 28.5, 22.2, 14.0. HRMS (ESI Q-TOF) m/z: $[M+H]^+$ Calcd for $C_9H_{14}ClN_2S$ 217.0561; found 217.0568. Regioselectivity was confirmed by 1D NOE of **2b** (see section V).

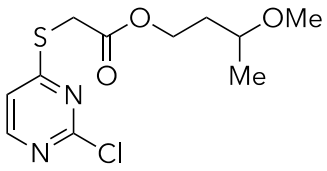


Ethyl 2-[(2-chloro-4-pyrimidinyl)thio] acetate (S11b). Open to air, 2,4-dichloropyrimidine (**1**, 74.5 mg, 0.50 mmol, 1.0 equiv) and K_3PO_4 (212 mg, 1.0 mmol, 2.0 equiv) were combined in a 5 mL round bottom flask equipped with a Teflon-coated stir bar. The flask was taken into a nitrogen-atmosphere glovebox and acetonitrile (1.25 mL) was added via a 2-mL syringe. The flask was sealed with a

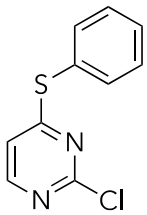
rubber septum and copper wire and removed from the glovebox. The bottom portion of the flask containing the reaction mixture was submerged in a liquid nitrogen bath (-196 ºC) for 10-15 seconds to freeze the reaction mixture. Degassed ethyl thioglycolate (55 µl, 0.50 mmol, 1.0 equiv) was added through the septum using a syringe. The reaction mixture was stirred vigorously at 25 ºC for 16 h. The reaction mixture was diluted with ethyl acetate and filtered through celite. The filtrate was concentrated under vacuum and the crude residue was purified by flash column chromatography on silica gel using an eluent of hexanes:ethyl acetate = 70:30 (R_f = 0.40) to provide **S11b** as a colorless oil (35.4 mg, 31% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.24 (d, J = 5.2 Hz, 1H), 7.15 (d, J = 5.2 Hz, 1H), 4.24 (q, J = 7.2 Hz, 2H), 3.96 (s, 2H), 1.30 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 171.4, 168.4, 161.0, 156.7, 117.4, 62.2, 32.2, 14.3. HRMS (ESI Q-TOF) m/z: $[M+H]^+$ Calcd for $C_8H_{10}ClN_2O_2S$; 233.0146 found 233.0141. Regioselectivity was confirmed by 1D NOE of **S11b** (see section V).



2-chloro-4-[(phenylmethyl)thio]pyrimidine (S20b). Open to air, 2,4-dichloropyrimidine (**1**, 297.9 mg, 2.0 mmol, 1.0 equiv) and K_3PO_4 (849.0 mg, 4 mmol, 2 equiv) were combined in a 10 mL round bottom equipped with a Teflon-coated stir bar. The round bottom was taken into a nitrogen-atmosphere glovebox and acetonitrile (5 mL) was added via a 5-mL syringe. The vial was sealed with a rubber septum and removed from the glovebox. The bottom portion of the vial containing the reaction mixture was submerged in a liquid nitrogen bath (-196 ºC) for 10-15 seconds to freeze the reaction mixture. The septum was punctured and the degassed benzylmercaptan was quickly added via syringe (235 µL, 2.0 mmol, 1.0 equiv) through a rubber septum. The reaction mixture was stirred vigorously at 25 ºC for 21 h. The reaction mixture was diluted with ethyl acetate and filtered through celite. The filtrate was concentrated under vacuum and the crude residue was purified by flash column chromatography on silica gel using an eluent of hexanes : EtOAc = 100:0 to 80:20 (R_f = 0.26 in hexanes:EtOAc = 90:10) to provide **S20b** as a yellow oil (138.7 mg, 29% yield). ^{1}H NMR (500 MHz, $(CD_3)_2CO$, δ): 8.33 (d, J = 5.4 Hz, 1H), 7.48 (d, J = 7.4 Hz, 2H), 7.37-7.31 (multiple overlapping peaks, 3H), 7.27 (tt, J = 7.3, 2.2 Hz, 1H), 4.48 (s, 2H).^{13}C{^{1}H} NMR (101 MHz, $(CD_3)_2CO$, δ): 173.8,161.2, 158.2, 137.6, 130.0, 129.4, 128.3, 118.3, 34.2. HRMS (ESI Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{11}H_{10}ClN_2S$; 237.0248 found 237.0252. Regioselectivity was confirmed by 1D NOE of **S20b** (see section V).

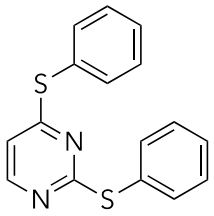


3-Methoxy-2-oxobutyl 2-[(2-chloro-4-pyrimidinyl)thio] acetate (S23b). Open to air, 2,4-dichloropyrimidine (**1**, 74.5 mg, 0.50 mmol, 1.0 equiv) and K_3PO_4 (212 mg, 1.0 mmol, 2.0 equiv) were combined in a 5 mL round bottom flask equipped with a Teflon-coated stir bar. The flask was taken into a nitrogen-atmosphere glovebox and acetonitrile (1.25 mL) was added via a 2-mL syringe. The flask was sealed with a rubber septum and copper wire and removed from the glovebox. The bottom portion of the flask containing the reaction mixture was submerged in a liquid nitrogen bath (-196 ºC) for 10-15 seconds to freeze the reaction mixture. Degassed 3-methoxybutyl-2-mercaptoacetate (84 µL, 0.50 mmol, 1.0 equiv) was added through the septum using a syringe. The reaction mixture was stirred vigorously at 25 ºC for 16 h. The reaction mixture was diluted with ethyl acetate and filtered through celite. The filtrate was concentrated under vacuum and the crude residue was purified by flash column chromatography on silica gel using an eluent of hexanes:EtOAc = 80:20 (R_f = 0.48) to provide **S23b** as a yellow oil (70.8 mg 49% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.23 (d, J = 5.2 Hz, 1H), 7.15 (d, J = 5.2 Hz, 1H), 4.27 (t, J = 6.6 Hz, 2H), 3.96 (s, 2H), 3.39 (qt, J = 6.2, 6.2 1H), 3.28 (s, 3H), 1.86-1.73 (m, 2H), 1.14 (d, J = 6.2 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 171.4, 168.3, 160.9, 156.7, 117.4, 73.6, 63.2, 56.2, 35.6, 32.1, 19.2. HRMS (ESI Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{11}H_{16}ClN_2O_3S$; 291.0565 found 291.0572. Regioselectivity was confirmed by 1D NOE of **37a** (see section V) and by comparison to the separately synthesized C4-regioisomer **S37b** (see section I.I and section V).

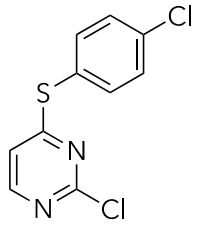


2-Chloro-4-(phenylthio)pyrimidine (31b). Open to air, 2,4-dichloropyrimidine (**1**, 744.9 mg, 5.0 mmol, 1.0 equiv) was added to a 50 mL round bottom equipped with a Teflon-coated stir bar. The flask was sealed with a rubber septum and the headspace was flushed with N_2. Dry degassed acetonitrile (12.5 mL) and N_2-sparged Et_3N (1.39 mL, 10 mmol, 2.0 equiv) were added through the septum by syringe. N_2-Sparged thiophenol (510 µL, 5.0 mmol, 1.0 equiv) was added. The reaction mixture was stirred vigorously at 80 ºC for 23.5 h. The reaction was then diluted with ethyl acetate, filtered through Celite™ and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel using an eluent of hexanes:EtOAc = 100:0 to 90:10 (R_f = 0.18 in 90:10 hexanes:EtOAc) to

provide **31b** as a white solid (0.993 g, 89% yield). Spectral data are consistent with those previously reported.[6]

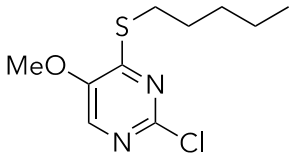


2,4-Bis(phenylthio)pyrimidine (S31c). Open to air, 2,4-dichloropyrimidine (**1**, 74.5 mg, 0.50 mmol, 1.0 equiv) and KF (72.6 mg, 1.25 mmol, 2.5 equiv) were combined to a 1.5-dram vial equipped with a Teflon-coated stir bar. The vial was taken into a nitrogen-atmosphere glovebox and acetonitrile (2.5 mL) was added via a 3-mL syringe. The vial was sealed with a rubber septum and copper wire and removed from the glovebox. The bottom portion of the vial was submerged in a liquid nitrogen bath (-196 ºC) for 10-15 seconds to freeze the reaction mixture. Thiophenol (127.5 µL, 1.25 mmol 2.5 equiv.) was added through the septum via a syringe. The reaction was stirred vigorously at 80 ºC overnight. The reaction was then diluted with ethyl acetate and filtered through Celite™. The filtrate was concentrated under vacuum. The residue was purified by flash column chromatography on silica gel using an eluent of hexanes:Et_2O = 100:0 to 85:85 (Rf = 0.17 in 90:10 hexanes:Et_2O) to provide **S31c** as a white solid (52.5 mg, 35% yield). Spectral data are consistent with those previously reported.[7]

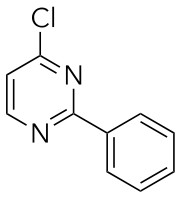


2-Chloro-4-[(4-chlorophenyl)thio]pyrimidine (S32b). Open to air, 2,4-dichloropyrimidine (**1**, 149.0 mg, 1.0 mmol, 1.0 equiv) and KF (116.2 mg, 2.0 mmol, 2.0 equiv) were combined in a 20 mL vial equipped with a Teflon-coated stir bar. The reaction vial was taken into a nitrogen-atmosphere glovebox and acetonitrile (5 mL) was added via a 5-mL syringe. The vial was sealed with a Teflon-lined cap and removed from the glovebox. The bottom portion of the vial containing the reaction mixture was submerged in a liquid nitrogen bath (-196 ºC) for 10-15 seconds to freeze the reaction mixture. The cap was then removed and the degassed 4-chlorothiophenol (121 µL, 1 mmol, 1 equiv) was quickly added in one portion. The vial headspace was then flushed for ~10 seconds with N_2 and the vial was then re-sealed with the Teflon-lined cap. The reaction mixture was stirred vigorously at 25 ºC for 23 h. The reaction mixture was then diluted with ethyl acetate and filtered through celite. Analysis of the crude reaction mixture by ^{1}H NMR spectroscopy indicated a 1 : 23 ratio of C2:C4-functionalized products. Purification by flash column chromatography on silica gel using an eluent of hexanes:EtOAc = 100:0 to 80:20 (R_f = 0.27 in

hexanes:EtOAc = 90:10) provided **S32b** as a white solid (107.1 mg, 42% yield).^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.22 (d, *J* = 5.4 Hz, 1H), 7.54 (d, *J* = 8.6 Hz, 2H), 7.48 (d, *J* = 8.6 Hz, 2H), 6.69 (d, *J* = 5.4 Hz, 1H).^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, δ): 175.6, 161.0, 157.9, 137.4, 137.1, 130.6, 125.5, 115.5. HRMS (ESI Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{10}H_7Cl_2N_2S$; 256.9702 found 256.9704. Regioselectivity was confirmed by 1D NOE of **S32b** (see section V).



2-Chloro-4-(pentylthio)-5-methoxypyrimidine (S37b). Open to air, 2,4-dichloro-5-methoxypyrimidine (179.0 mg, 1.0 mmol, 1.0 equiv) and K_3PO_4 (424.5 mg, 2.0 mmol, 2.0 equiv) were combined in a 1-dram reaction vial equipped with a Teflon-coated stir bar. Acetonitrile (2.5 mL) was added via a 3-mL syringe and the degassed 1-pentanethiol (124 µl, 1.0 mmol, 1 equiv) was quickly added in one portion. The vial headspace was then flushed for ~10 seconds with N_2 and the vial was then re-sealed with the Teflon-lined cap. The reaction mixture was stirred vigorously at 25 ºC for 19 h. The reaction mixture was then diluted with ethyl acetate and filtered through Celite. Analysis of the crude reaction mixture by ^{1}H NMR spectroscopy indicated a ratio of 1:9 C2:C4-functionalized products. Purification by flash column chromatography on silica gel using an eluent of hexanes:EtOAc = 100:0 to 60:40 (R_f = 0.56 in 80:20 hexanes:EtOAc) provided **S37b** as a white solid (185.3 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.76 (s, 1H), 7.54 (d, *J* = 8.6 Hz, 2H), 3.92 (s, 3H), 3.11 (t, *J* = 7.4 Hz, 2H), 1.70 (tt, *J* = 7.4, 7.4 Hz, 2H), 1.45-1.30 (multiple overlapping signals, 4H) 0.91 (t, *J* = 7.2 Hz, 3H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, δ): 163.8, 151.5, 149.6, 135.5, 56.6, 31.0, 29.2, 28.4, 22.3, 14.0. HRMS (ESI Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{10}H_{15}ClN_2OS$; 247.0666 found 247.0667. Regioselectivity was confirmed by 1D NOE of **S37b** (see section V).



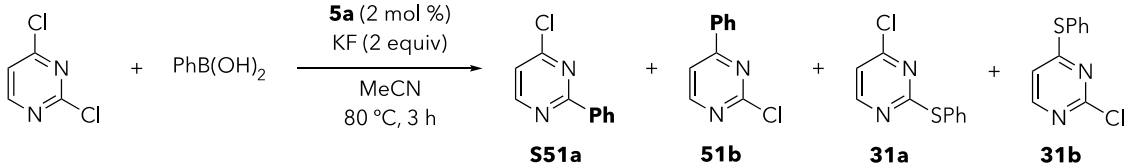
2-Phenyl-4-chloropyrimidine (S51a). The preparation of **S51a** was adapted from literature.[8] Open to air, Pd-PEPPSI-IPr (**S56**, 17 mg, 0.025 mmol, 0.05 equiv), 2-(ethylthio)-4-chloropyrimidine (**7a**, 87.3 mg, 0.50 mmol, 1.0 equiv) phenylboronic acid (122 mg, 1.0 mmol, 2.0 equiv), and copper 3-methylsalicylate (215 mg, 1.0 mmol, 2.0 equiv) were combined in a 50 mL round bottom flask equipped with a Teflon-coated stir bar. The flask was taken into a nitrogen-atmosphere glovebox and tetrahydrofuran (5 mL) was added via a 10-mL syringe. The flask was sealed with a rubber septum

and copper wire and removed from the glovebox. The reaction mixture was stirred vigorously at 50 ºC for 16 h. The reaction mixture was passed through Celite™ using vacuum filtration. The filtrate was then washed with 4.5 wt% aqueous NH_4OH (2x 50 mL). The organic layer was then washed with a saturated NaCl solution and dried over magnesium sulfate. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel using an eluent of hexanes:EtOAc = 95:5 (R_f = 0.42 in 95:5 hexanes:EtOAc) to provide **S51a** as a colorless oil (70.3 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.66 (m, 2H), 8.46-8.43 (m, 2H), 7.54-7.47 (m, 3H), 7.23 (d, J = 5.2 Hz, 1H). Spectral data are consistent with those previously reported.[8]

Experiments To Investigate Mechanism

Suzuki Cross-Coupling Reaction Under Conditions Analogous to the Thiolation

Scheme B.1. Suzuki cross-coupling of 1 without or with thiophenol as an additive.



	S51a	51b	31a	31b
as written:	*not detected*	27%	–	–
with PhSH (25 mol %):	*not detected*	17%	22%	2%

Open to air, (η^3-1-^{t}Bu-indenyl)Pd(IPent)Cl (**5a**, 1.3 mg, 0.0016 mmol, 0.02 equiv), 2,4-dichloropyrimidine (11.9 mg, 0.080 mmol, 1.0 equiv), KF (9.3 mg, 0.16 mmol, 2.0 equiv), and phenylboronic acid (9.8 mg, 0.080 mmol, 1.0 equiv) were combined in a 1-dram vial equipped with a Teflon-coated stir bar. The vial was taken into a nitrogen-atmosphere glovebox and acetonitrile (0.4 mL) was added via a 1-mL syringe. The vial was sealed with a Teflon-lined cap and removed from the glovebox. The bottom portion of the vial containing the reaction mixture was submerged in a liquid nitrogen bath (-196 ºC) for 10-15 seconds to freeze the reaction mixture. The reaction mixture was then stirred vigorously at 80 ºC for 3 h. The reaction mixture was diluted with ethyl acetate and filtered through Celite™. The filtrate was concentrated under vacuum prior to the addition of mesitylene internal standard (11.1 µl, 0.080 mmol, 1.0 equiv) and the residue

was taken up in $CDCl_3$ (0.4 mL) for ^{1}H-NMR analysis. ^{1}H-NMR of the crude reaction mixture indicated 27% yield of **51b** (**51b** was identified by comparison to previously reported spectral data).[9] Product **S51a** was not detected.

To evaluate whether the presence of a thiol could influence the regioselectivity of the Suzuki coupling, the experiment above was duplicated with the addition of thiophenol (25 mol %). Analogous to the reaction without the thiophenol additive, the only C—C coupling product was **51b** (no **S51a**), indicating that the thiol does not affect the regioselectivity of the Suzuki cross-coupling reaction.

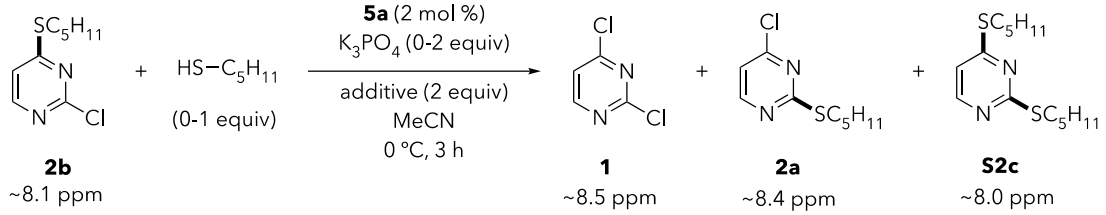
Experiments to Evaluate the Overall Reversibility of the Reaction

Discussion. We considered the hypothesis that selectivity under the optimized conditions could be under thermodynamic control, wherein an initially formed C4-functionalized compound might isomerize to the C2-functionalized product (if the latter product is more stable). To evaluate this hypothesis, a C4-thioether **2b** or **31b** was resubjected to the optimized reaction conditions for alkyl and aromatic thiols, respectively. A chloride source (KCl, NBu_4Cl, or **1**) was added to potentially enable reversion to dichloropyrimidine or isomerization of the 4-thiopyrimidine, as described below. However, neither **2b** nor **31b** displayed any reactivity consistent with a reversible reaction.

Reaction of 2b with 1-pentanethiol in the presence of chloride salts. Open to air, (η^3-1-^{t}Bu-indenyl)Pd(IPent)Cl (**5a**, 1.3 mg, 0.0016 mmol, 0.02 equiv), 2-chloro-4-(pentylthio)pyrimidine (**2b**, 17.3 mg, 0.080 mmol, 1.0 equiv), K_3PO_4 (34.0 mg, 0.16 mmol, 2.0 equiv) and potassium chloride (11.9 mg, 0.16 mmol, 2.0 equiv) or tetrabutylammonium chloride (44.5 mg, 0.16 mmol, 2.0 equiv) were combined in a 1-dram vial equipped with a Teflon-coated stir bar. The reaction vial was taken into a nitrogen-atmosphere glovebox, and acetonitrile (0.2 mL) was added via a 1-mL syringe. The reaction vial was sealed with a Teflon-lined cap and removed from the glovebox. The bottom portion of the reaction vial containing the reaction mixture was submerged in a liquid nitrogen bath (-196 °C) for 10-15 seconds to freeze the reaction mixture. When applicable, the cap was removed and the degassed 1-pentanethiol (9.9 µl, 0.080 mmol, 1.0 equiv) was quickly added via syringe. The vial headspace was then flushed for 10-20 seconds with N_2 and the vial was re-sealed with the Teflon-lined cap. The reaction mixture was stirred vigorously at 0 °C for 3 h. The reaction mixture was then diluted with ethyl acetate and filtered through Celite™. The filtrate was

dried prior to the addition of mesitylene internal standard (11.1 µl, 0.080 mmol, 1.0 equiv) and the residue was taken up in $CDCl_3$ (0.4 mL) for ^1H NMR analysis to obtain a crude ratio of the products. Additionally, an aliquot was analyzed by GCMS to identify and confirm the presence (or absence) of products that could result from a reversible reaction. The results are described in Table S4. In all cases, there was no evidence of formation of **1** or **2a**, products that would result from a reversible reaction.

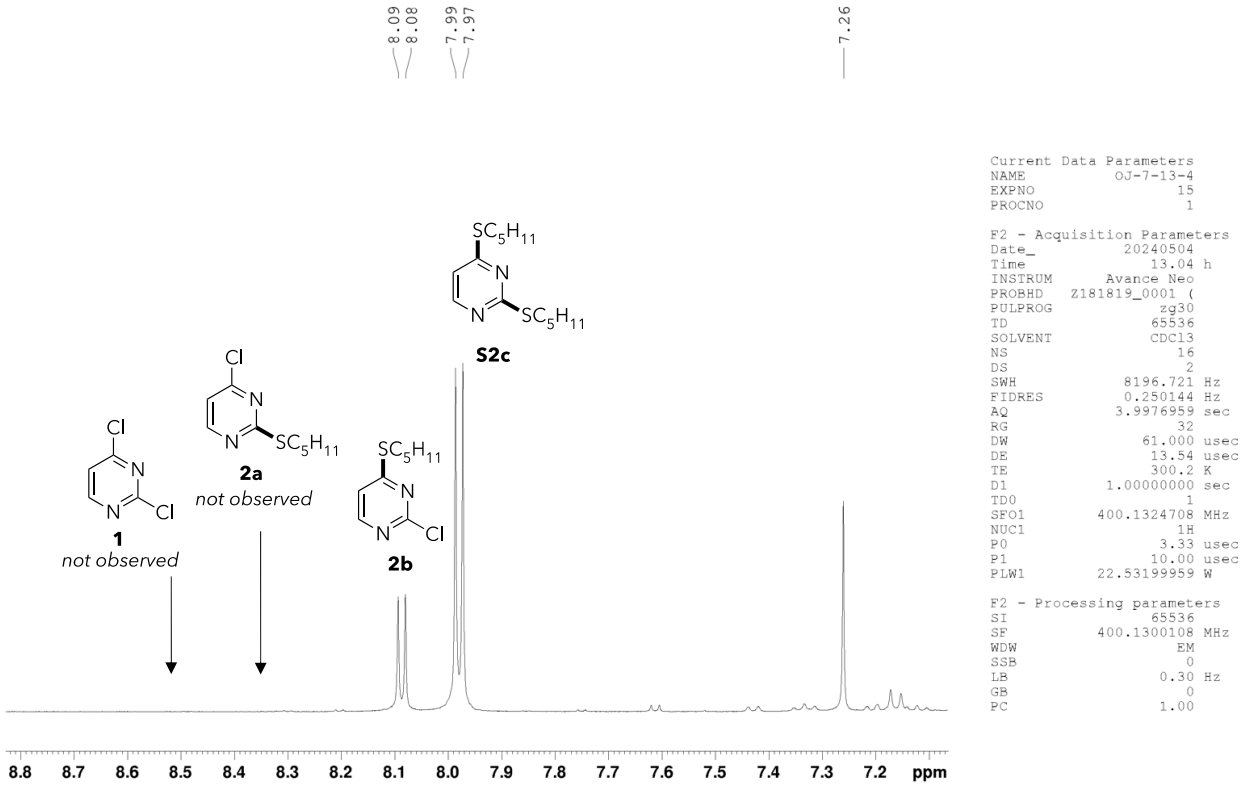
Table B.4. Evaluation of Overall Reaction Reversibility Using **2b** with 1-Pentanethiol.[a]



entry	HSC_5H_{11} (equiv)	K_3PO_4 (equiv)	additive	**2b** (%)	**1** (%)	**2a** (%)	**S2c** (%)
1	0	0	KCl (2 equiv)	95	nd	nd	nd
2	1	0	KCl (2 equiv)	94	nd	nd	<1
3	0	2	KCl (2 equiv)	93	nd	nd	nd
4	1	2	KCl (2 equiv)	41	nd	nd	59
5	0	2	NBu_4Cl (2 equiv)	95	nd	nd	nd
6	1	2	NBu_4Cl (2 equiv)	23	nd	nd	74

[a]NMR yields calibrated against mesitylene as an internal standard. nd = not detected.

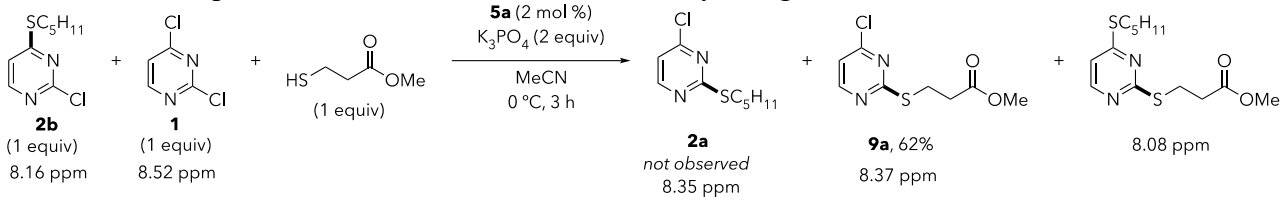
Figure B.1. ^{1}H NMR spectrum for the reaction shown in Table S4, entry 4.

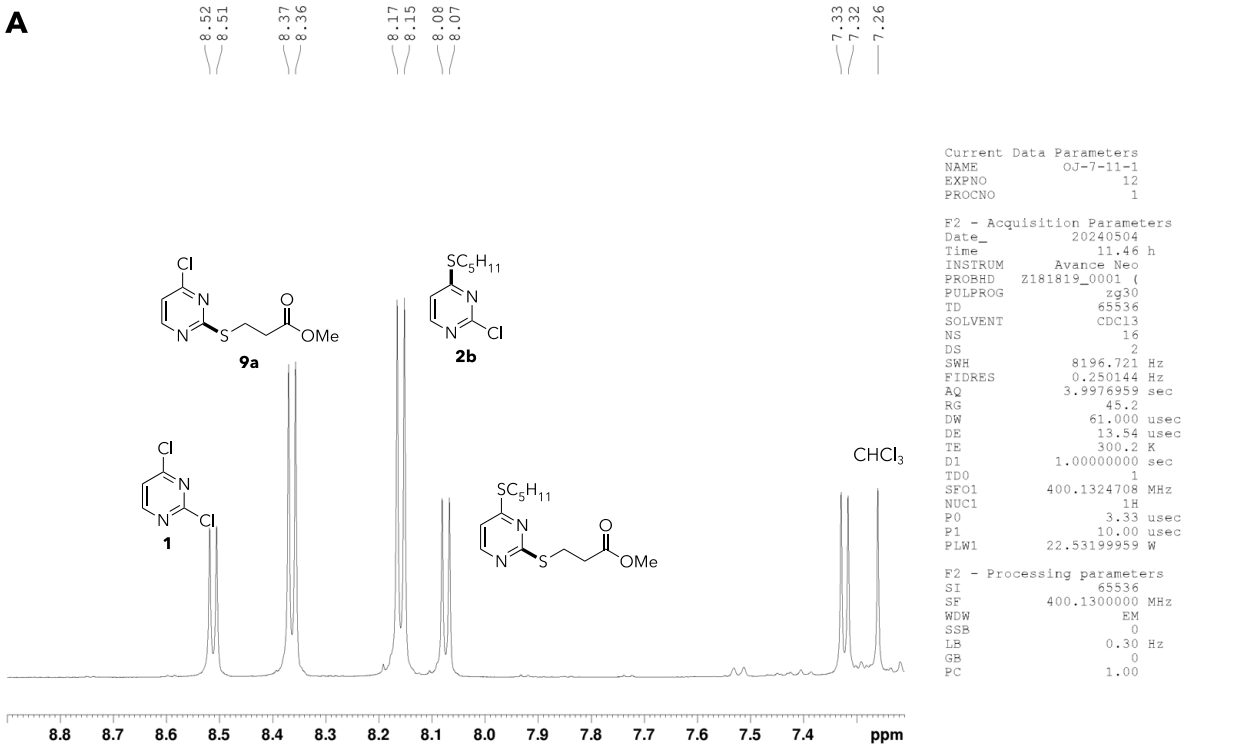


Reaction of 2b with 1-pentanethiol in the presence of 1 as a chloride source. Open to air, (η^3-1-^{t}Bu-indenyl)Pd(IPent)Cl (**5a**, 1.3 mg, 0.0016 mmol, 0.02 equiv), 2-chloro-4-(pentylthio)pyrimidine (**2b**, 17.3 mg, 0.080 mmol, 1.0 equiv), 2,4-dichloropyrimidine (**1**, 11.9 mg, 0.080 mmol, 1.0 equiv) and K_3PO_4 (33.9 mg, 0.16 mmol, 2.0 equiv) were combined in a 1-dram vial equipped with a Teflon-coated stir bar. The reaction vial was taken into a nitrogen-atmosphere glovebox and acetonitrile (0.2 mL) was added via a 1-mL syringe. The reaction vial was sealed with a Teflon-lined cap and removed from the glovebox. The bottom portion of the reaction vial containing the reaction mixture was submerged in a liquid nitrogen bath (-196 ºC) for 10-15 seconds to freeze the reaction mixture. The Teflon-lined cap was removed and degassed methyl-3-mercaptopropionate (8.8 µl, 0.080 mmol, 1.0 equiv) was quickly added via syringe. The vial headspace was then flushed with N_2 and the vial was resealed with a Teflon-lined cap. The reaction mixture was stirred vigorously at 0 ºC for 3 h. The reaction mixture was diluted with ethyl acetate and filtered through Celite™. The filtrate was dried prior to the addition of mesitylene internal standard (11.1 µl, 0.080 mmol, 1.0 equiv) and the residue was taken up in $CDCl_3$ (0.4 mL) for ^{1}H-

NMR analysis. The results are described in Scheme S2. There was no evidence of formation of **2a**, a product that could result from a reversible reaction.

Scheme B.2. Experiment to test for overall reversibility using **2b** and **1**.






```
Current Data Parameters
NAME          OJ-7-11-1
EXPNO                12
PROCNO                1

F2 - Acquisition Parameters
Date_          20240504
Time              11.46 h
INSTRUM      Avance Neo
PROBHD   Z181819_0001 (
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8196.721 Hz
FIDRES         0.250144 Hz
AQ             3.9976959 sec
RG                 45.2
DW                61.000 usec
DE                13.54 usec
TE                300.2 K
D1           1.00000000 sec
TD0                   1
SFO1        400.1324708 MHz
NUC1                1H
P0                3.33 usec
P1               10.00 usec
PLW1        22.53199959 W

F2 - Processing parameters
SI                65536
SF          400.1300000 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

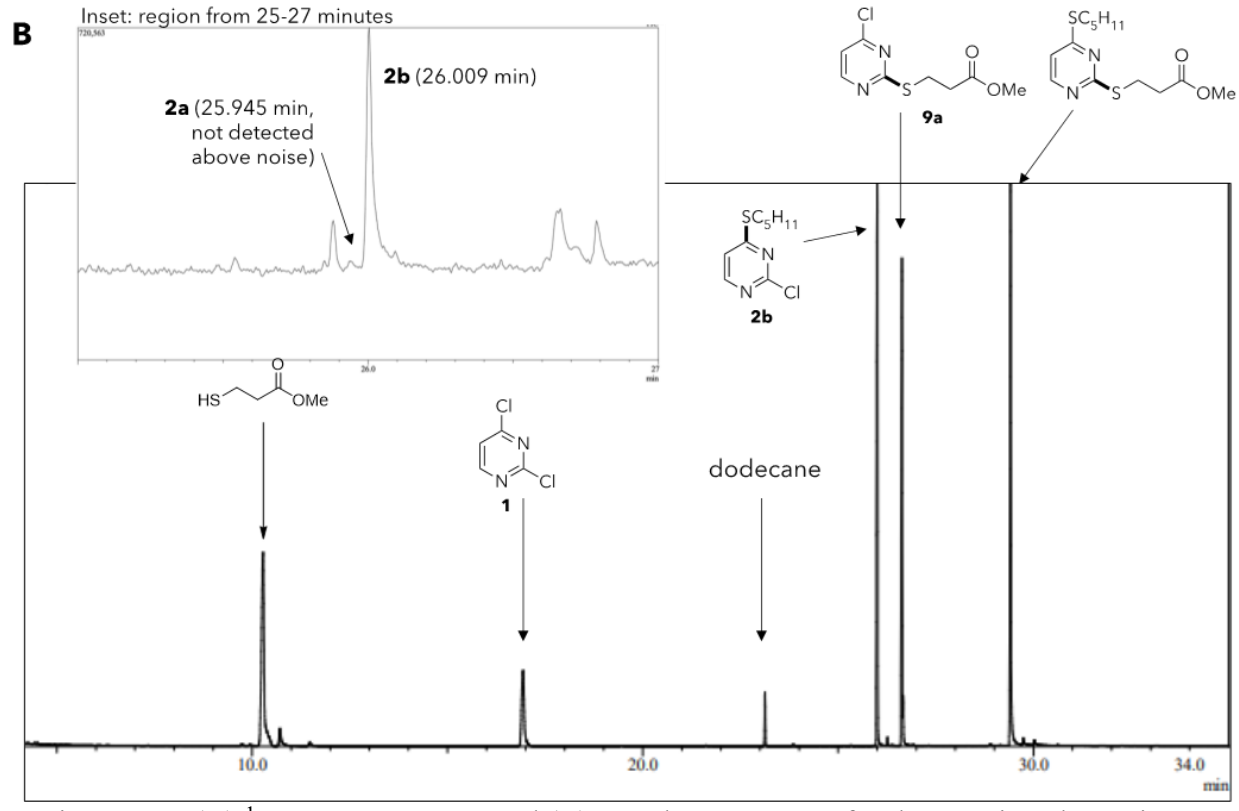
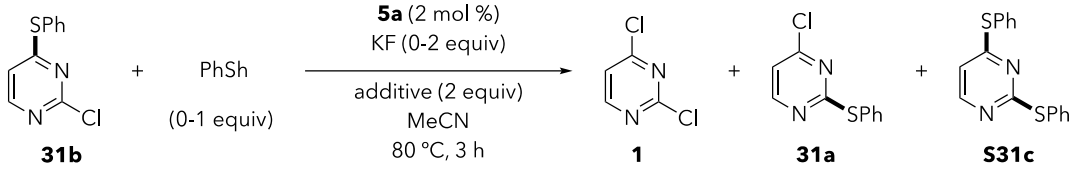


Figure B.2. (A) ^{1}H NMR spectrum and (B) gas chromatogram for the reaction shown in Scheme S1; products identified by comparison to retention times of authentic standards and by mass analysis.

Reaction of 31b with thiophenol in the presence of chloride salts. Open to air, (η^3-1-^{t}Bu-indenyl)Pd(IPent)Cl (**5a**, 1.3 mg, 0.0016 mmol, 0.02 equiv), 2-chloro-4-(phenylthiol)-pyrimidine (**31b**, 17.8 mg, 0.080 mmol, 1.0 equiv), KF (9.3 mg, 0.16 mmol, 2.0 equiv) and KCl (11.9 mg, 0.16 mmol, 2.0 equiv) or tetrabutylammonium chloride (44.5 mg, 0.16 mmol, 2.0 equiv) were combined in a 1-dram vial equipped with a Teflon-coated stir bar. The reaction vial was taken into a nitrogen-atmosphere glovebox and acetonitrile (0.4 mL) was added via a 1-mL syringe. The vessel was sealed with a Teflon-lined cap and removed from the glovebox. The bottom portion of the reaction vial containing the reaction mixture was submerged in a liquid nitrogen bath (-196 ºC) for 10-15 seconds to freeze the reaction mixture. When applicable, the cap was removed and N_2-sparged thiophenol (8.2 µL, 0.080 mmol, 1.0 equiv) was quickly added via a 25 µL syringe. The vial headspace was then flushed for 10 seconds with N_2 and the vial was re-sealed with the Teflon-lined cap. The reaction mixture was stirred vigorously at 80 ºC for 3 h. The reaction mixture was then diluted with ethyl acetate and 1,4-dimethoxybenzene (50 µL of a 0.4 *M* solution in EtOAc,

0.02 mmol, 0.25 equiv) was added as an internal standard. The crude mixture was filtered through Celite™ and the filtrate was dried under vacuum. The residue was taken up in $CDCl_3$ (~0.5 mL) for ^1H NMR analysis to obtain the crude yield of the products. The results are described in Table S5. In all cases, there was no evidence of formation of **1** or **31a**, products that would result from a reversible reaction.

Table B.5. Evaluation of Overall Reaction Reversibility Using **31b** with Thiophenol.[a]



entry	trial	PhSH (equiv)	KF (equiv)	additive	**31b** (%)	**1** (%)	**31a** (%)	**S31c** (%)
1	1	0	0	KCl	100	nd	nd	nd
2	2	0	0	KCl	100	nd	nd	nd
3	avg	0	0	KCl	100	nd	nd	nd
4	1	1	0	KCl	51	nd	nd	50
5	2	1	0	KCl	57	nd	nd	44
6	avg	1	0	KCl	54	nd	nd	47
7	1	0	2	KCl	100	nd	nd	nd
8	2	0	2	KCl	92	nd	nd	nd
9	avg	0	2	KCl	97	nd	nd	nd
10	1	1	2	KCl	1	nd	nd	103
11	2	1	2	KCl	1	nd	nd	100
12	avg	1	2	KCl	1	nd	nd	101
13	1	0	2	NBu_4Cl	52	nd	nd	nd
14	2	0	2	NBu_4Cl	54	nd	nd	nd
15	avg	0	2	NBu_4Cl	53	nd	nd	nd
16	1	1	2	NBu_4Cl	40	nd	nd	60
17	2	1	2	NBu_4Cl	33	nd	nd	68
18	avg	1	2	NBu_4Cl	37	nd	nd	64

[a]NMR yields calibrated against 1,4-dimethoxybenzene as the internal standard. Average of two trials. nd = not detected

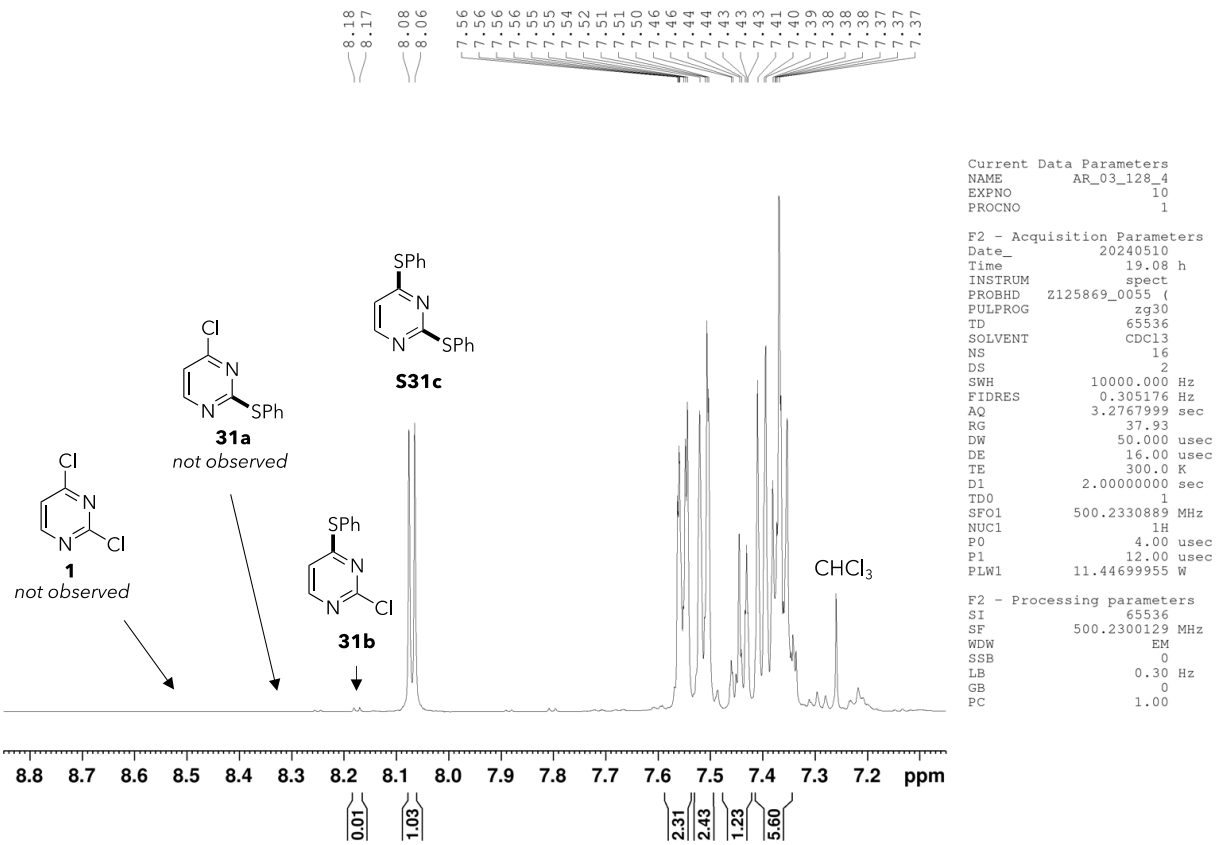


Figure B.3. ^{1}H NMR spectrum for the reaction shown in Table S5, entry 10.

Reaction of 31b with 4-methoxythiophenol in the presence of 1 as a chloride source. Open to air, (η^3-1-^{t}Bu-indenyl)Pd(IPent)Cl (**5a**, 1.3 mg, 0.0016 mmol, 0.02 equiv), 2-chloro-4-(phenylthiol)-pyrimidine (**S31b**, 17.8 mg, 0.080 mmol, 1.0 equiv), 2,4-dichloropyrimidine (**1**, 11.9 mg, 0.080 mmol, 1.0 equiv), and KF (9.3 mg, 0.16 mmol, 2.0 equiv) were combined in a 1-dram vial equipped with a Teflon-coated stir bar. The reaction vial was taken into a nitrogen-atmosphere glovebox and acetonitrile (0.4 mL) was added via a 1-mL syringe. The reaction vial was sealed with a Teflon-lined cap and removed from the glovebox. The bottom portion of the reaction vial containing the reaction mixture was submerged in a liquid nitrogen bath (-196 ºC) for 10-15 seconds to freeze the reaction mixture. The cap was removed and N_2-sparged 4-methoxythiophenol (9.8 µL, 0.080 mmol, 1.0 equiv) was quickly added via a 25 µL syringe. The vial headspace was then flushed for 10 seconds with N_2 and the vial was re-sealed with the Teflon-lined cap. The reaction mixture was stirred vigorously at 80 ºC for 3 h. The reaction mixture was diluted with

ethyl acetate and 1,4-dimethoxybenzene (50 µL of a 0.4 *M* solution in EtOAc, 0.02 mmol, 0.25 equiv) was added as an internal standard. The crude reaction mixture was filtered through Celite™ and the filtrate was dried under vacuum. The residue was taken up in $CDCl_3$ (~0.5 mL) for ^1H NMR analysis to obtain the crude yield of the functionalized products. Additionally, an aliquot was analyzed by GCMS to identify and confirm the presence (or absence) of products that could result from a reversible reaction. There was no evidence of formation of **31a**, the product that could result from a reversible reaction.

Scheme B3. Experiment to test for overall reversibility using **31b** and **1**.

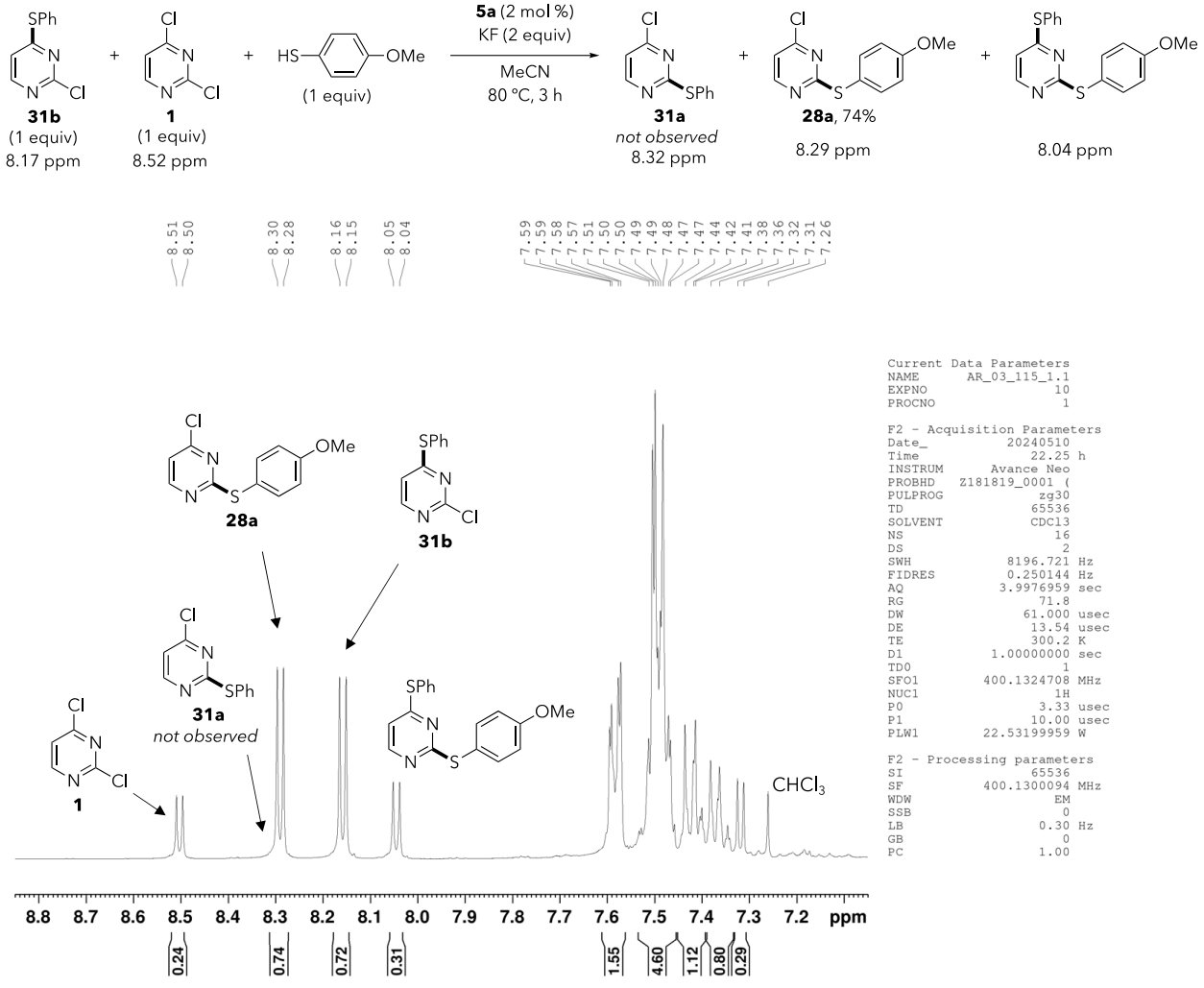


Figure B.4. ^1H NMR spectrum for the reaction shown in Scheme S3.

Computational Details

General Methods

Calculations were performed with Gaussian 16.[10] An ultrafine integration grid and the keyword 5d were used for all calculations. The orbital calculations in Figure 2A and the transition state calculations in Figure 2B were performed with Method A, the calculations in Figure 2D were performed with Method B, and the calculations in Figure S10 were performed with Method C, as described below. Frequency analyses were carried out at the same level to evaluate the zero-point vibrational energy and thermal corrections at the default temperature and pressure (298.15 K and 1 atm). The nature of the stationary points was determined in each case according to the appropriate number of negative eigenvalues of the Hessian matrix. Multiple conformations/configurations were considered when applicable, and the lowest energy conformations are reported. 3D images of molecular orbitals were generated with Avogadro.[11]

Method A. Geometry optimizations of stationary points were carried out in implicit solvent using the CPCM continuum solvation model[12] for acetonitrile with the MN15L[13] functional and t he def2SVP basis set. The final reported energies were obtained from single point energy calculations on the optimized geometries using MN15,[14] the CPCM solvation model (MeCN), and the def2-TZVPD basis set. Gibbs free energy values are reported after applying Cramer and Truhlar's anharmonic correction to frequencies that are less than 100 cm^{-1}.[15]

Method B. Geometry optimizations of stationary points were carried out in implicit solvent using the SMD continuum solvation model for acetonitrile with the B2PLYP functional and the def2-QZVP basis set. Gibbs free energy values are reported after applying Cramer and Truhlar's anharmonic correction to frequencies that are less than 100 cm^{-1}.[14]

Method C. Geometry optimizations of stationary points were carried out in implicit solvent using the SMD continuum solvation model for acetonitrile with the B3LYP functional and the def2-TZVP basis set. Gibbs free energy values are reported after applying Cramer and Truhlar's anharmonic correction to frequencies that are less than 100 cm^{-1}.[14]

Free Energy Diagrams for Oxidative Addition

Oxidative additions at both 12e^- Pd(IPr) and at 14e^- Pd(IPr)(SMe) are computed to be highly exergonic (Figures S7 and S8). Reaction at 12e^- Pd(IPr) is calculated to take place through a 3-centered concerted mechanism (**TS49a** and **TS49b**) and is exergonic by ~19 kcal/mol relative to the π-complex **S62** that precedes oxidative addition. Thus, the barrier for the reverse reaction (C—Cl reductive elimination) is calculated to be at least 30 kcal/mol, which is unreasonable for a reaction that is fast at 0 ºC. Reaction at 14e^- Pd(IPr)(SMe) is calculated to take place through a nucleophilic displacement mechanism (**TS50a** and **TS50b**) and is exergonic by ~30 kcal/mol relative to the preceding π-complex **S64**. Thus, the barrier for C—Cl reductive elimination from the tetracoordinate Pd species **S65a** and **S65b** is calculated to be >30 kcal/mol, which is also unreasonable for the experimental reaction conditions.

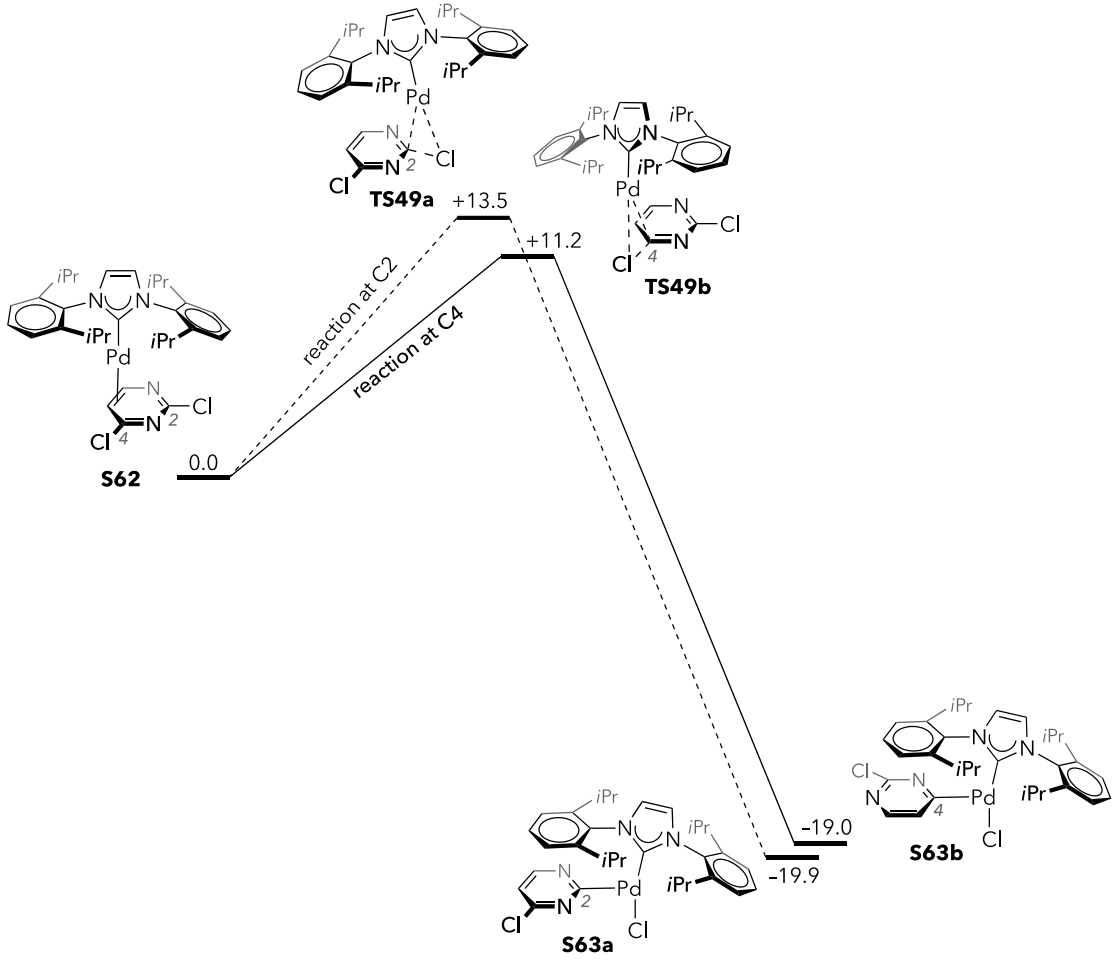


Figure B.5. Reaction free energy diagram for oxidative addition at 12e^- Pd(IPr). Free energies in kcal/mol. Calculated at the CPCM(MeCN)-MN15/def2-TZVPD// CPCM(MeCN)-MN15L/def2-SVP level of theory.

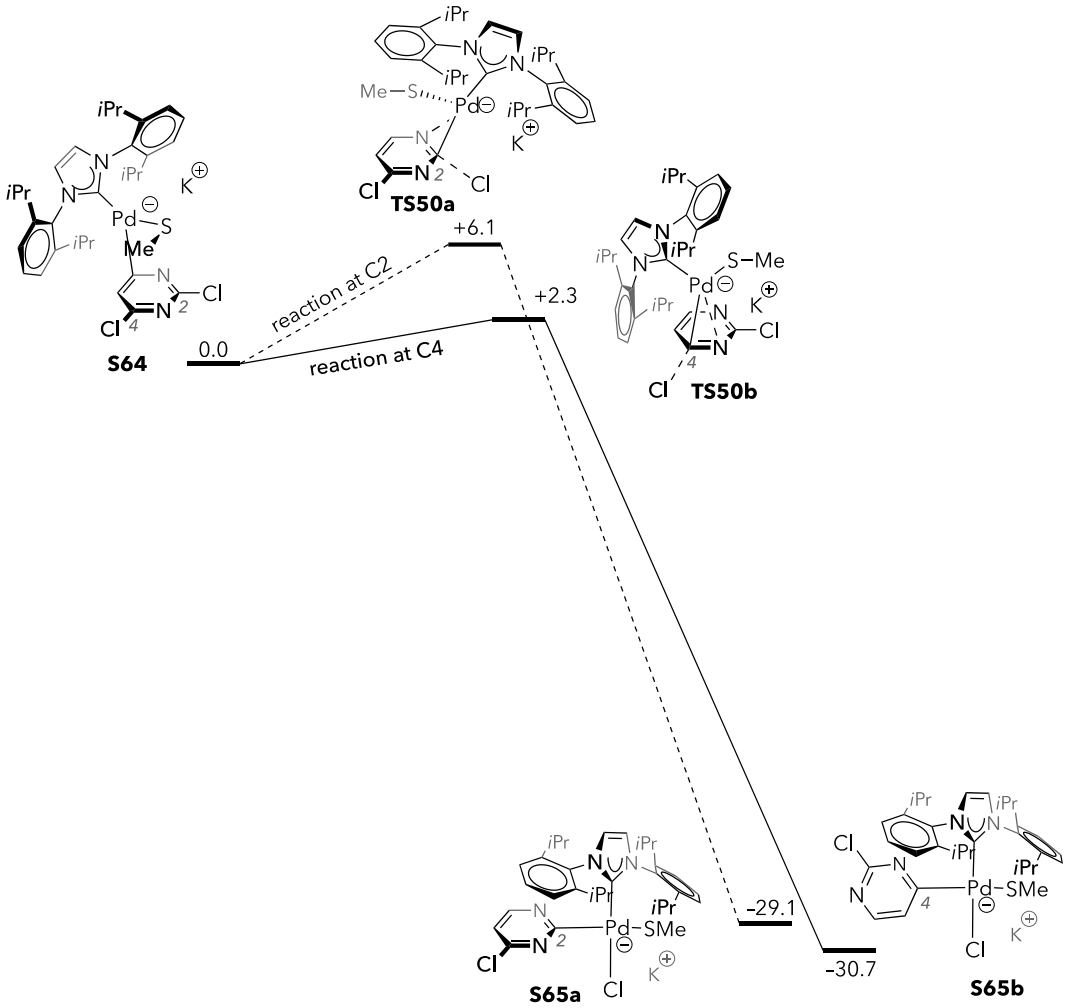
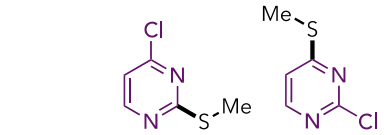


Figure B.6. Reaction free energy diagram for oxidative addition at anionic 14e^- Pd(IPr)(SMe). Free energies in kcal/mol. Calculated at the CPCM(MeCN)-MN15/def2-TZVPD// CPCM(MeCN)-MN15L/def2-SVP level of theory.

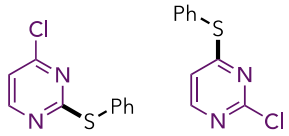
Relative Free Energies of C2-versus C4-Products

DFT calculations indicate that C2-thio products are *not* lower energy than C4-thio products, suggesting that C2-selectivity in the thiolation reaction does not result from thermodynamic control.



	S66a	S66b
Method B	+0.1	0.0
Method C	0.0	0.0

Figure B.7. Relative free energies of 4-chloro-(2-methylthio)pyrimidine and 2-chloro-(4-methylthio)pyrimidine, calculated with two high-level DFT methods.



S67a	S67b
+0.3	0.0

Figure B.8. Relative free energies of 4-chloro-(2-phenylthio)pyrimidine and 2-chloro-(4-phenylthio)pyrimidine, calculated with a relatively high-level DFT method (Method C).

Energies, Entropies and Lowest Frequencies of Minimum Energy Structures

Table B.6. Calculations with Method A[a]

Structure	E_{elec} (Hartree)	E_{elec} + ZPE (Hartree)	H (Hartree)	S (cal mol^{-1} K^{-1})	G[b] (Hartree)	$G_{corrected}$[c] (Hartree)	Lowest freq. (cm^{-1})	# of imag freq.
S62	-2469.908663	-2469.280126	-2469.239845	236.7	-2469.352329	-2469.343386	19.7	0
TS49a	-2469.887222	-2469.258998	-2469.219257	232.7	-2469.329840	-2469.321813	-78.9	1
TS49b	-2469.890940	-2469.262735	-2469.222885	233.8	-2469.333952	-2469.325575	-108.0	1
S63a	-2469.942862	-2469.312079	-2469.272277	230.2	-2469.381641	-2469.375031	20.1	0
S63b	-2469.941405	-2469.310566	-2469.270633	233.2	-2469.381444	-2469.373645	11.7	0
S64	-3507.833902	-3507.165415	-3507.118848	264.0	-3507.244285	-3507.235522	27.8	0
TS50a	-3507.825617	-3507.157039	-3507.111645	256.0	-3507.233256	-3507.225724	-183.0	1
TS50b	-3507.831512	-3507.163061	-3507.117578	256.9	-3507.239619	-3507.231861	-159.8	1
S65a	-3507.882296	-3507.212645	-3507.166598	258.6	-3507.289466	-3507.281975	22.6	0
S65b	-3507.888135	-3507.216320	-3507.171182	252.4	-3507.291109	-3507.284437	23.8	0

[a]Energy values calculated at the CPCM(MeCN)-MN15/def2-TZVPD//CPCM(MeCN)-MN15L/def2-SVP level of theory. 1 Hartree = 627.51 kcal mol^{-1}. Thermal corrections at 298.15 K and 1 atm. [b]Solvent-corrected free energy given by $G = E_{elec} + G_{corr}$, where G_{corr} is the thermal correction to Gibbs free energy. [c]Solvent-corrected free energy given by $G = E_{elec} + G_{corr*}$, where G_{corr*} is the thermal correction to Gibbs free energy obtained after applying Cramer and Truhlar's anharmonic correction.[14]

Table B7. Calculations with Method B[a]

Structure	E_{elec} (Hartree)	E_{elec} + ZPE (Hartree)	H (Hartree)	S (cal mol⁻¹ K⁻¹)	G[b] (Hartree)	$G_{corrected}$[c] (Hartree)	Lowest freq. (cm⁻¹)	# of imag freq.
S66a	-1160.613233	-1160.517151	-1161.052163	92.1	-1161.095901	-1160.551311	83.5	0
S66b	-1160.613465	-1160.517324	-1161.052493	91.9	-1161.096166	-1160.551406	79.1	0

[a]Energy values calculated at the SMD(MeCN)-B2PLYP/def2QZVP level of theory. 1 Hartree = 627.51 kcal mol^{-1}. Thermal corrections at 298.15 K. [b]Solvent-corrected free energy given by G = E_{elec} + G_{corr}, where G_{corr} is the thermal correction to Gibbs free energy. [c]Solvent-corrected free energy given by G = E_{elec} + G_{corr*}, where G_{corr*} is the thermal correction to Gibbs free energy obtained after applying Cramer and Truhlar's anharmonic correction.[14]

Table B8. Calculations with Method C[a]

Structure	E_{elec} (Hartree)	E_{elec} + ZPE (Hartree)	H (Hartree)	S (cal mol⁻¹ K⁻¹)	G[b] (Hartree)	$G_{corrected}$[c] (Hartree)	Lowest freq. (cm⁻¹)	# of imag freq.
S66a	-1161.619804	-1161.524282	-1161.514819	92.3	-1161.558696	-1161.558512	82.1	0
S66b	-1161.619925	-1161.524307	-1161.514882	92.2	-1161.558698	-1161.558445	76.1	0
S67a	-1353.425765	-1353.277329	-1353.264756	111.3	-1353.317632	-1353.314951	31.0	0
S67b	-1353.426486	-1353.277862	-1353.265351	110.6	-1353.317913	-1353.315461	30.9	0

[a]Energy values calculated at the SMD(MeCN)-B3LYP/def2TZVP level of theory. 1 Hartree = 627.51 kcal mol^{-1}. Thermal corrections at 298.15 K. [b]Solvent-corrected free energy given by G = E_{elec} + G_{corr}, where G_{corr} is the thermal correction to Gibbs free energy. [c]Solvent-corrected free energy given by G = E_{elec} + G_{corr*}, where G_{corr*} is the thermal correction to Gibbs free energy obtained after applying Cramer and Truhlar's anharmonic correction.[14]

X-Ray Crystallographic Details

X-Ray Crystallographic Details for Compound **14a** (CCDC Deposition Number: 2385752)

Data for **14a** were collected at 100 K on a Bruker D8 VENTURE Duo Fixed Chi Three-Circle Diffractometer using MoK_α radiation (λ = 0.71073 Å). All data were integrated with SAINT V8.40B and corrected for absorption using SADABS 2016/2.[16,17] The structure was solved by dual methods with SHELXT and refined by full-matrix least-squares methods against F^2 using SHELXL.[18,19] All non-hydrogen atoms were refined with anisotropic displacement parameters. The locations of hydrogen atoms in the investigated could be identified from difference Fourier maps. The hydrogen atom bound to nitrogen atom of the carbamate group was placed and refined. Hydrogen atoms bound to carbon atoms were placed in geometrically calculated positions and refined using a riding model. Isotropic thermal parameters of the placed hydrogen atoms were

fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups). Calculations and refinement of the structure was carried out using APEX4[20] and Olex2[21] software.

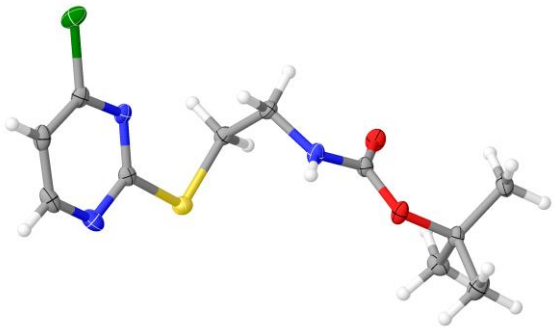


Figure B.9. X-ray crystal structure of **14a.**

Table B.9. Crystal data and structure refinement for **14a**.

CCDC number	2385752
Identification code	0J-6-42
Empirical formula	$C_{11}H_{16}ClN_3O_2S$
Formula weight	289.78
Temperature [K]	100
Crystal system	monoclinic
Space group (number)	$P2_1/c$ (14)
a [Å]	15.1462(9)
b [Å]	9.0730(5)
c [Å]	10.1184(6)
α [°]	90
β [°]	90.108(2)
γ [°]	90
Volume [Å^3]	1390.48(14)
Z	4
ρ_{calc} [gcm^{-3}]	1.384
μ [mm^{-1}]	0.423
F(000)	608
Crystal size [mm^3]	0.08×0.19×0.39
Crystal colour	colourless
Crystal shape	prism
Radiation	MoK_α (λ=0.71073 Å)
2θ range [°]	5.23 to 61.01 (0.70 Å)
Index ranges	−21 ≤ h ≤ 21
	−12 ≤ k ≤ 12
	−14 ≤ l ≤ 14
Reflections collected	51219
Independent reflections	4233

	R_{int} = 0.0393
	R_{sigma} = 0.0227
Completeness to θ = 25.242°	99.9 %
Data / Restraints / Parameters	4233 / 0 / 170
Goodness-of-fit on F^2	1.143
Final R indexes	R_1 = 0.0403
[$I \geq 2\sigma(I)$]	wR_2 = 0.0713
Final R indexes	R_1 = 0.0523
[all data]	wR_2 = 0.0765
Largest peak/hole [eÅ^{-3}]	0.38/−0.31

Table B.10. Atomic coordinates and Ueq [Å^2] for **14a**.

Atom	***x***	***y***	***z***	U_{eq}
Cl1	0.16536(3)	0.12864(4)	0.43458(4)	0.02604(9)
S1	0.11201(2)	0.69639(4)	0.51965(3)	0.01889(8)
O1	0.32778(7)	0.83706(12)	0.79230(9)	0.0217(2)
O2	0.37452(7)	0.95745(11)	0.60630(9)	0.0194(2)
N1	0.13398(8)	0.40893(13)	0.46546(11)	0.0163(2)
N2	0.06262(8)	0.56316(15)	0.30552(12)	0.0229(3)
N3	0.31715(8)	0.73470(14)	0.58770(12)	0.0186(2)
H3	0.3245(12)	0.748(2)	0.5087(19)	0.025(5)
C1	0.10292(9)	0.53808(16)	0.42137(13)	0.0168(3)
C2	0.12424(9)	0.29746(16)	0.38181(13)	0.0182(3)
C3	0.08512(9)	0.30798(18)	0.25896(14)	0.0220(3)
H3A	0.079914	0.226073	0.200977	0.026
C4	0.05417(10)	0.44611(19)	0.22666(15)	0.0242(3)
H4	0.025311	0.458708	0.143988	0.029
C5	0.17378(9)	0.62961(15)	0.66034(13)	0.0180(3)
H5A	0.168337	0.701842	0.733209	0.022
H5B	0.147109	0.535936	0.690661	0.022
C6	0.27149(9)	0.60366(15)	0.63271(14)	0.0189(3)
H6A	0.300297	0.567523	0.714422	0.023
H6B	0.277245	0.525800	0.564723	0.023
C7	0.33883(9)	0.84326(15)	0.67299(13)	0.0171(3)
C8	0.40297(9)	1.09220(15)	0.67554(13)	0.0174(3)
C9	0.32436(10)	1.16415(17)	0.74328(15)	0.0230(3)
H9A	0.275491	1.173271	0.680195	0.034
H9B	0.341244	1.262239	0.775055	0.034
H9C	0.305727	1.103280	0.818220	0.034
C10	0.47740(10)	1.05769(17)	0.77158(16)	0.0243(3)
H10A	0.454531	0.998042	0.844641	0.036
H10B	0.501812	1.149880	0.806451	0.036
H10C	0.523864	1.002886	0.725569	0.036
C11	0.43514(11)	1.18817(18)	0.56244(15)	0.0273(3)
H11A	0.484272	1.139017	0.517544	0.041
H11B	0.455111	1.283312	0.597265	0.041
H11C	0.386784	1.204100	0.499557	0.041

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table B.11. Anisotropic displacement parameters (Å2) for 14a. The anisotropic displacement factor exponent takes the form: −2π2[h2(a*)2U11 + k2(b*)2U22 + … + 2hka*b*U12]

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl1	0.0432(2)	0.01624(16)	0.01869(16)	−0.00212(12)	0.00373(14)	−0.00266(15)
S1	0.01951(16)	0.01687(16)	0.02030(16)	−0.00068(13)	0.00161(12)	0.00228(13)
O1	0.0280(5)	0.0234(5)	0.0136(5)	−0.0008(4)	0.0013(4)	−0.0059(4)
O2	0.0240(5)	0.0201(5)	0.0140(4)	−0.0029(4)	0.0032(4)	−0.0083(4)
N1	0.0167(5)	0.0172(5)	0.0150(5)	−0.0010(4)	0.0032(4)	−0.0036(4)
N2	0.0180(6)	0.0317(7)	0.0191(6)	0.0003(5)	−0.0006(5)	0.0049(5)
N3	0.0210(6)	0.0204(6)	0.0145(6)	−0.0026(4)	0.0017(4)	−0.0057(5)
C1	0.0133(6)	0.0213(7)	0.0157(6)	−0.0010(5)	0.0030(5)	−0.0006(5)
C2	0.0177(6)	0.0196(6)	0.0173(6)	−0.0010(5)	0.0050(5)	−0.0040(5)
C3	0.0197(7)	0.0291(8)	0.0170(6)	−0.0059(6)	0.0024(5)	−0.0064(6)
C4	0.0167(6)	0.0384(9)	0.0173(7)	−0.0032(6)	−0.0014(5)	0.0013(6)
C5	0.0229(7)	0.0161(6)	0.0150(6)	−0.0003(5)	0.0015(5)	−0.0023(5)
C6	0.0212(7)	0.0151(6)	0.0204(7)	−0.0004(5)	−0.0018(5)	−0.0015(5)
C7	0.0150(6)	0.0195(6)	0.0169(6)	−0.0009(5)	0.0007(5)	−0.0019(5)
C8	0.0182(6)	0.0173(6)	0.0168(6)	−0.0030(5)	0.0005(5)	−0.0032(5)
C9	0.0207(7)	0.0271(7)	0.0212(7)	−0.0027(6)	0.0011(5)	0.0038(6)
C10	0.0171(7)	0.0255(7)	0.0304(8)	−0.0049(6)	−0.0042(6)	−0.0009(6)
C11	0.0354(9)	0.0239(7)	0.0227(7)	−0.0019(6)	0.0068(6)	−0.0087(7)

X-Ray Crystallographic Details for Compound **18a** (CCDC Deposition Number: 2385751)

Data for **18a** were collected at 100 K on a Bruker D8 VENTURE Duo Fixed Chi Three-Circle Diffractometer using MoK_α radiation (λ = 0.71073 Å). All data were integrated with SAINT V8.40B and corrected for absorption using SADABS 2016/2.[16,17] The structure was solved by dual methods with SHELXT and refined by full-matrix least-squares methods against F^2 using SHELXL.[18,19] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atom locations in the investigated structure were initially identified from difference Fourier maps, but their final positions were determined geometrically and refined using a riding model. Isotropic thermal parameters of the placed hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups). Calculations and refinement of the structure was carried out using APEX4[20] and Olex[21] software.

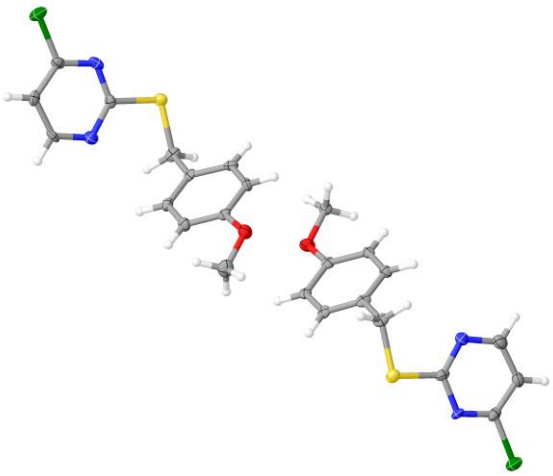


Figure B.10. X-ray crystal structure of 18a.

Table B.12. Crystal data and structure refinement for **18a**.

CCDC number	2385751
Identification code	AR-183
Empirical formula	$C_{12}H_{11}ClN_2OS$
Formula weight	266.74
Temperature [K]	100
Crystal system	orthorhombic
Space group (number)	$Pca2_1$ (29)
a [Å]	8.6332(5)
b [Å]	6.0348(3)
c [Å]	46.857(3)
α [°]	90
β [°]	90
γ [°]	90
Volume [Å^3]	2441.2(2)
Z	8
ρ_{calc} [gcm^{-3}]	1.452
μ [mm^{-1}]	0.467
F(000)	1104
Crystal size [mm^3]	0.05×0.17×0.22
Crystal colour	colourless
Crystal shape	plate
Radiation	MoK_α (λ=0.71073 Å)
2θ range [°]	5.22 to 52.74 (0.80 Å)
Index ranges	−10 ≤ h ≤ 10
	−7 ≤ k ≤ 7
	−58 ≤ l ≤ 58
Reflections collected	33831
Independent reflections	4896
	R_{int} = 0.0287
	R_{sigma} = 0.0292
Completeness to θ = 25.242°	99.8 %

Data / Restraints / Parameters	4896 / 1 / 309
Goodness-of-fit on F^2	1.138
Final R indexes	R_1 = 0.0446
[$I \geq 2\sigma(I)$]	wR_2 = 0.0822
Final R indexes	R_1 = 0.0547
[all data]	wR_2 = 0.0854
Largest peak/hole [eÅ^{-3}]	0.31/−0.42
Flack X parameter	0.01(3)

Table B.13. Atomic coordinates and Ueq [Å^2] for **18a**.

Atom	***x***	***y***	***z***	U_{eq}
Cl1A	0.50135(19)	0.5829(3)	0.26736(3)	0.0281(3)
S1A	0.14648(17)	0.5688(3)	0.35613(3)	0.0205(3)
O1A	0.4963(5)	0.2007(7)	0.47346(9)	0.0218(9)
N1A	0.3255(7)	0.5358(9)	0.31172(14)	0.0156(13)
N2A	0.2706(6)	0.1937(8)	0.33590(11)	0.0231(12)
C1A	0.2593(7)	0.4124(11)	0.33275(12)	0.0187(13)
C2A	0.4137(7)	0.4247(12)	0.29401(13)	0.0202(13)
C3A	0.4392(8)	0.2004(10)	0.29508(13)	0.0247(14)
H3A	0.504754	0.126338	0.281882	0.030
C4A	0.3632(8)	0.0907(11)	0.31661(14)	0.0282(15)
H4A	0.375997	−0.065208	0.318064	0.034
C5A	0.0820(7)	0.3588(11)	0.38186(13)	0.0215(13)
H5AB	−0.016616	0.408194	0.390546	0.026
H5AA	0.061534	0.218698	0.371539	0.026
C6A	0.1969(7)	0.3149(11)	0.40515(13)	0.0199(13)
C7A	0.2284(11)	0.4741(11)	0.4253(2)	0.0176(18)
H7A	0.180269	0.615013	0.423523	0.021
C8A	0.3279(7)	0.4368(12)	0.44806(13)	0.0182(13)
H8A	0.345837	0.548606	0.461948	0.022
C9A	0.4018(7)	0.2290(10)	0.45007(13)	0.0174(12)
C10A	0.3759(7)	0.0689(11)	0.42925(13)	0.0166(12)
H10A	0.427684	−0.069735	0.430249	0.020
C11A	0.2739(7)	0.1124(10)	0.40695(13)	0.0185(12)
H11A	0.256615	0.002747	0.392760	0.022
C12A	0.5512(11)	−0.0170(9)	0.4794(2)	0.0173(19)
H12E	0.462876	−0.116186	0.482458	0.026
H12D	0.615950	−0.014181	0.496546	0.026
H12F	0.612530	−0.070573	0.463179	0.026
Cl1B	0.74157(19)	−0.0787(3)	0.73256(3)	0.0293(4)
S1B	1.09919(17)	−0.0785(3)	0.64390(3)	0.0196(3)
O1B	0.7527(5)	0.2983(7)	0.52705(9)	0.0226(10)
N1B	0.9179(8)	−0.0393(9)	0.68753(16)	0.0201(15)
N2B	0.9816(6)	0.3016(8)	0.66450(11)	0.0237(12)
C1B	0.9869(7)	0.0833(10)	0.66771(12)	0.0172(12)
C2B	0.8339(7)	0.0753(11)	0.70610(13)	0.0196(13)
C3B	0.8146(7)	0.3015(10)	0.70537(13)	0.0238(14)
H3B	0.751347	0.378311	0.718693	0.029
C4B	0.8946(8)	0.4096(10)	0.68360(14)	0.0248(14)
H4B	0.887154	0.566293	0.682275	0.030

C5B	1.1683(7)	0.1254(11)	0.61872(13)	0.0217(13)
H5BB	1.194482	0.262962	0.629162	0.026
H5BA	1.264405	0.069584	0.609713	0.026
C6B	1.0514(6)	0.1802(10)	0.59541(12)	0.0167(12)
C7B	0.9769(7)	0.3806(10)	0.59349(12)	0.0192(13)
H7B	0.995013	0.489382	0.607766	0.023
C8B	0.8745(7)	0.4297(11)	0.57105(13)	0.0200(12)
H8B	0.824005	0.569351	0.570177	0.024
C9B	0.8484(6)	0.2713(10)	0.55024(12)	0.0161(12)
C10B	0.9205(7)	0.0669(11)	0.55207(13)	0.0180(13)
H10B	0.898555	−0.043299	0.538163	0.022
C11B	1.0233(12)	0.0206(11)	0.5737(2)	0.0192(19)
H11B	1.075477	−0.117944	0.574153	0.023
C12B	0.6998(13)	0.5225(12)	0.5216(2)	0.031(2)
H12B	0.788323	0.615631	0.516337	0.046
H12A	0.650698	0.582115	0.538807	0.046
H12C	0.624599	0.521201	0.505916	0.046

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table B.14. Anisotropic displacement parameters (Å^2) for **18a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2(a^*)^2U_{11} + k^2(b^*)^2U_{22} + \ldots + 2hka^*b^*U_{12}\,]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl1A	0.0314(9)	0.0317(9)	0.0212(8)	0.0072(8)	0.0043(7)	0.0002(8)
S1A	0.0181(7)	0.0246(8)	0.0187(8)	0.0027(8)	−0.0011(6)	0.0038(7)
O1A	0.024(2)	0.020(2)	0.021(2)	0.0043(19)	−0.0095(18)	0.0006(19)
N1A	0.015(3)	0.020(3)	0.011(3)	0.006(2)	0.002(2)	0.002(2)
N2A	0.028(3)	0.019(3)	0.022(3)	−0.001(2)	0.001(2)	−0.005(2)
C1A	0.019(3)	0.023(4)	0.014(3)	0.003(3)	−0.004(2)	−0.008(3)
C2A	0.018(3)	0.029(4)	0.014(3)	0.000(3)	−0.002(2)	−0.007(3)
C3A	0.030(4)	0.021(3)	0.022(3)	−0.005(3)	0.000(3)	0.003(3)
C4A	0.037(4)	0.021(4)	0.026(4)	−0.003(3)	−0.004(3)	−0.006(3)
C5A	0.013(3)	0.029(4)	0.022(3)	0.004(3)	0.003(2)	−0.002(3)
C6A	0.013(3)	0.025(3)	0.022(3)	0.004(3)	0.001(2)	−0.007(3)
C7A	0.012(4)	0.022(4)	0.019(5)	0.000(3)	0.005(3)	0.002(3)
C8A	0.019(3)	0.018(3)	0.017(3)	0.000(3)	0.006(2)	−0.008(3)
C9A	0.013(3)	0.021(3)	0.019(3)	0.002(2)	0.002(2)	−0.005(2)
C10A	0.015(3)	0.016(3)	0.019(3)	0.001(3)	0.004(2)	−0.002(3)
C11A	0.018(3)	0.016(3)	0.022(3)	−0.001(2)	0.001(2)	−0.001(3)
C12A	0.015(4)	0.019(4)	0.018(5)	0.002(2)	0.000(4)	0.007(2)
Cl1B	0.0299(9)	0.0349(10)	0.0231(8)	0.0111(8)	0.0064(7)	0.0057(8)
S1B	0.0205(8)	0.0182(8)	0.0202(8)	0.0017(8)	0.0000(6)	0.0026(7)
O1B	0.024(2)	0.022(2)	0.022(2)	−0.0014(19)	−0.0050(19)	−0.0007(19)
N1B	0.019(3)	0.013(2)	0.028(4)	0.000(3)	−0.010(3)	−0.001(3)
N2B	0.027(3)	0.019(3)	0.025(3)	0.000(2)	0.000(2)	−0.003(2)
C1B	0.015(3)	0.017(3)	0.019(3)	−0.004(3)	−0.003(2)	0.005(3)
C2B	0.025(3)	0.017(3)	0.017(3)	0.003(3)	−0.009(3)	0.000(3)
C3B	0.028(3)	0.028(4)	0.015(3)	−0.005(3)	0.001(2)	0.000(3)
C4B	0.035(4)	0.009(3)	0.030(4)	−0.005(3)	0.004(3)	0.000(3)
C5B	0.015(3)	0.030(4)	0.020(3)	0.003(3)	−0.001(2)	0.001(3)
C6B	0.012(3)	0.025(3)	0.014(3)	0.001(2)	0.006(2)	0.001(2)
C7B	0.020(3)	0.023(3)	0.015(3)	−0.002(2)	0.003(2)	−0.005(3)
C8B	0.020(3)	0.019(3)	0.021(3)	−0.002(3)	0.002(3)	0.005(3)
C9B	0.014(3)	0.020(3)	0.014(3)	0.001(2)	0.003(2)	0.001(2)

C10B	0.020(3)	0.015(3)	0.019(3)	−0.005(3)	0.002(3)	0.000(3)
C11B	0.018(4)	0.017(3)	0.023(5)	0.007(3)	0.003(3)	0.001(3)
C12B	0.032(6)	0.035(5)	0.027(6)	0.000(3)	−0.006(5)	0.008(3)

X-Ray Crystallographic Details for Compound **19a** (CCDC Deposition Number: 2385748)

Data for **19a** were collected at 100 K on a Bruker D8 VENTURE Duo Fixed Chi Three-Circle Diffractometer using MoK_α radiation (λ = 0.71073 Å). All data were integrated with SAINT V8.40B and corrected for absorption using SADABS 2016/2.[16,17] The structure was solved by dual methods with SHELXT and refined by full-matrix least-squares methods against F^2 using SHELXL.[18,19] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atom locations in the investigated structure were initially identified from difference Fourier maps, but their final positions were determined geometrically and refined using a riding model. Isotropic thermal parameters of the placed hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups). The tert-butyl group was modeled as disordered. This disorder is likely dynamic in nature and several disorder models were considered. The model that was eventually utilized modeled the disorder over three positions using three free variables tied to a SUMP command and restraining the occupancy to one. The model necessitated the use of bond distance similarity restraints as well as thermal ellipsoid restraints. Calculations and refinement of the structure was carried out using APEX4[20] and Olex2[21] software.

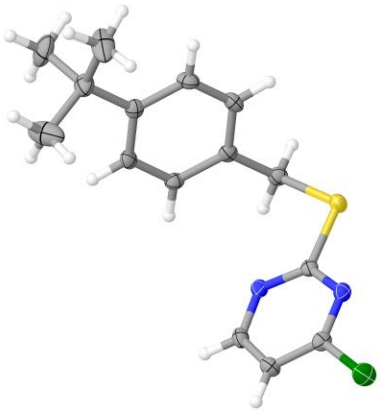


Figure B.11. X-ray crystal structure of 19a.

Table S15. Crystal data and structure refinement for **19a**.

CCDC number	2385748
Identification code	OJ-5-108
Empirical formula	$C_{15}H_{17}ClN_2S$
Formula weight	292.81
Temperature [K]	100
Crystal system	monoclinic
Space group (number)	$C2/c$ (15)
a [Å]	28.278(2)
b [Å]	6.1225(4)
c [Å]	20.5471(16)
α [°]	90
β [°]	122.030(2)
γ [°]	90
Volume [Å^3]	3015.9(4)
Z	8
ρ_{calc} [gcm^{-3}]	1.290
μ [mm^{-1}]	0.380
F(000)	1232
Crystal size [mm^3]	0.02×0.11×0.22
Crystal colour	colourless
Crystal shape	plate
Radiation	MoK_α (λ=0.71073 Å)
2θ range [°]	5.86 to 50.06 (0.84 Å)
Index ranges	−33 ≤ h ≤ 33 −7 ≤ k ≤ 7 −24 ≤ l ≤ 24
Reflections collected	26120
Independent reflections	2669 R_{int} = 0.0742 R_{sigma} = 0.0342
Completeness to θ = 25.028°	99.9 %
Data / Restraints / Parameters	2669 / 145 / 238
Goodness-of-fit on F^2	1.049
Final R indexes [I≥2σ(I)]	R_1 = 0.0369 wR_2 = 0.0818
Final R indexes [all data]	R_1 = 0.0560 wR_2 = 0.0915
Largest peak/hole [eÅ^{-3}]	0.30/−0.27

Table B.16. Atomic coordinates and Ueq [Å^2] for **19a**.

Atom	***x***	***y***	***z***	U_{eq}
Cl1	0.45098(2)	−0.07633(10)	0.35888(4)	0.03170(18)
S1	0.65986(2)	0.00193(9)	0.57354(3)	0.02287(16)
N1	0.55426(7)	−0.0008(3)	0.46685(10)	0.0202(4)
N2	0.59392(7)	0.3525(3)	0.51443(10)	0.0192(4)
C1	0.59641(9)	0.1354(3)	0.51258(12)	0.0179(5)
C2	0.50601(9)	0.0951(4)	0.41987(13)	0.0212(5)
C3	0.49735(9)	0.3185(4)	0.41689(13)	0.0235(5)

H3	0.461934	0.383042	0.383277	0.028
C4	0.54390(9)	0.4404(4)	0.46630(13)	0.0215(5)
H4	0.540197	0.594655	0.466096	0.026
C5	0.70212(9)	0.2225(4)	0.63738(13)	0.0224(5)
H5A	0.741700	0.176449	0.666151	0.027
H5B	0.698758	0.351122	0.605987	0.027
C6	0.68634(8)	0.2893(4)	0.69380(12)	0.0193(5)
C7	0.69564(9)	0.1511(4)	0.75322(13)	0.0238(5)
H7	0.712142	0.012204	0.757927	0.029
C8	0.68150(10)	0.2108(4)	0.80541(13)	0.0251(5)
H8	0.688858	0.112568	0.845527	0.030
C9	0.65662(9)	0.4121(4)	0.80088(13)	0.0207(5)
C10	0.64824(9)	0.5523(4)	0.74206(12)	0.0204(5)
H10	0.632230	0.692002	0.737788	0.024
C11	0.66271(9)	0.4925(4)	0.68962(12)	0.0200(5)
H11	0.656388	0.591906	0.650269	0.024
C12	0.64011(10)	0.4774(4)	0.85825(14)	0.0292(6)
C13	0.6320(6)	0.2870(18)	0.8975(7)	0.055(3)
H13A	0.603330	0.189505	0.858784	0.083
H13B	0.620057	0.340245	0.931556	0.083
H13C	0.667153	0.206968	0.927597	0.083
C14	0.6878(4)	0.6233(14)	0.9204(6)	0.044(2)
H14D	0.678045	0.672109	0.957270	0.067
H14E	0.692823	0.750634	0.895796	0.067
H14F	0.722499	0.538952	0.947271	0.067
C15	0.5882(5)	0.622(2)	0.8218(10)	0.052(4)
H15A	0.556382	0.541369	0.780849	0.078
H15B	0.594784	0.753190	0.800220	0.078
H15C	0.580205	0.665289	0.860929	0.078
C13B	0.6067(6)	0.287(2)	0.8636(8)	0.053(4)
H13D	0.630822	0.158510	0.885120	0.079
H13E	0.574951	0.252340	0.812167	0.079
H13F	0.593037	0.329096	0.896768	0.079
C14B	0.6926(6)	0.524(3)	0.9353(8)	0.081(5)
H14A	0.682519	0.568422	0.972176	0.121
H14B	0.713774	0.640766	0.929632	0.121
H14C	0.715575	0.391191	0.953998	0.121
C15B	0.5996(8)	0.669(3)	0.8286(13)	0.046(4)
H15D	0.568435	0.637080	0.776472	0.069
H15E	0.618972	0.800877	0.827756	0.069
H15F	0.585400	0.692643	0.862342	0.069
C13C	0.671(3)	0.329(9)	0.929(2)	0.065(11)
H13G	0.661973	0.373143	0.967026	0.097
H13H	0.711265	0.341362	0.951342	0.097
H13I	0.659352	0.177040	0.913708	0.097
C14C	0.649(2)	0.712(4)	0.884(3)	0.055(9)
H14G	0.620724	0.752386	0.896483	0.083
H14H	0.645113	0.806196	0.843579	0.083
H14I	0.686137	0.728444	0.930430	0.083
C15C	0.5783(10)	0.413(11)	0.819(3)	0.062(9)
H15G	0.569334	0.304478	0.778772	0.093
H15H	0.554953	0.542589	0.795672	0.093
H15I	0.571349	0.350500	0.856876	0.093

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table B.17. Anisotropic displacement parameters (Å^2) for **19a**.The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2(a^*)^2U_{11} + k^2(b^*)^2U_{22} + \ldots + 2hka^*b^*U_{12}\,]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl1	0.0246(3)	0.0256(3)	0.0331(3)	−0.0038(3)	0.0073(3)	−0.0067(2)
S1	0.0230(3)	0.0184(3)	0.0228(3)	−0.0005(2)	0.0091(2)	0.0033(2)
N1	0.0238(10)	0.0166(9)	0.0206(10)	−0.0009(8)	0.0120(8)	−0.0017(8)
N2	0.0243(10)	0.0153(10)	0.0183(9)	0.0003(8)	0.0116(8)	−0.0007(8)
C1	0.0217(11)	0.0182(12)	0.0167(11)	0.0013(9)	0.0121(10)	0.0008(9)
C2	0.0212(11)	0.0213(12)	0.0212(12)	−0.0012(10)	0.0114(10)	−0.0040(9)
C3	0.0217(12)	0.0219(12)	0.0261(13)	0.0028(10)	0.0122(10)	0.0027(10)
C4	0.0281(12)	0.0153(11)	0.0251(12)	0.0001(9)	0.0168(11)	0.0006(9)
C5	0.0189(11)	0.0230(12)	0.0219(12)	0.0000(10)	0.0085(10)	−0.0006(9)
C6	0.0135(11)	0.0209(12)	0.0191(12)	−0.0021(9)	0.0057(9)	−0.0031(9)
C7	0.0213(12)	0.0202(12)	0.0283(13)	0.0042(10)	0.0121(10)	0.0049(9)
C8	0.0267(12)	0.0265(13)	0.0218(12)	0.0083(10)	0.0128(11)	0.0045(10)
C9	0.0181(11)	0.0208(12)	0.0219(12)	−0.0025(9)	0.0097(10)	−0.0023(9)
C10	0.0203(11)	0.0144(12)	0.0229(12)	−0.0023(9)	0.0090(10)	−0.0023(9)
C11	0.0220(11)	0.0187(11)	0.0169(11)	0.0017(9)	0.0086(9)	−0.0031(9)
C12	0.0399(14)	0.0271(13)	0.0287(13)	0.0003(11)	0.0236(12)	0.0023(11)
C13	0.111(10)	0.032(4)	0.062(8)	0.012(5)	0.072(7)	0.010(6)
C14	0.045(4)	0.053(5)	0.043(5)	−0.021(4)	0.029(4)	−0.002(4)
C15	0.043(5)	0.080(10)	0.050(6)	0.030(6)	0.036(4)	0.025(6)
C13B	0.107(10)	0.028(4)	0.080(10)	0.005(6)	0.088(9)	0.009(6)
C14B	0.060(6)	0.139(15)	0.034(6)	−0.035(9)	0.019(5)	0.013(9)
C15B	0.080(10)	0.028(5)	0.077(8)	0.007(5)	0.073(8)	0.016(6)
C13C	0.11(2)	0.051(17)	0.034(15)	0.005(13)	0.041(16)	0.026(18)
C14C	0.069(19)	0.040(9)	0.06(2)	−0.011(11)	0.036(17)	0.002(13)
C15C	0.053(9)	0.08(2)	0.057(18)	−0.004(18)	0.034(11)	−0.014(13)

X-Ray Crystallographic Details for Compound **21a** (CCDC Deposition Number: 2385750)

Data for **21a** were collected at 100 K on a Bruker D8 VENTURE Duo Fixed Chi Three-Circle Diffractometer using MoK_α radiation ($\lambda = 0.71073$ Å). All data were integrated with SAINT V8.40B and corrected for absorption using SADABS 2016/2.[16,17] The structure was solved by dual methods with SHELXT and refined by full-matrix least-squares methods against F^2 using SHELXL.[18,19] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atom locations in the investigated structure were initially identified from difference Fourier maps, but their final positions were determined geometrically and refined using a riding model. Isotropic thermal parameters of the placed hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups). Calculations and refinement of the structure was carried out using APEX4[20] and Olex2[21] software

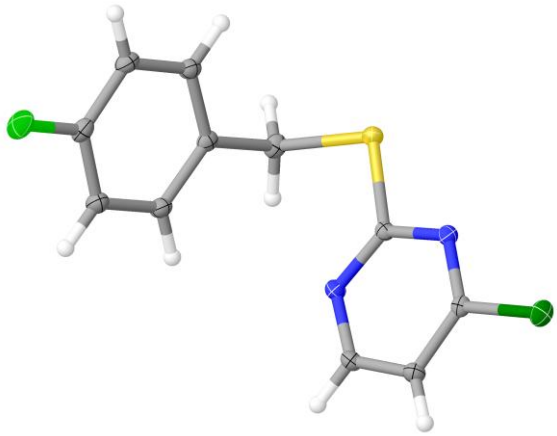


Figure B.12. X-ray crystal structure of 21a.

Table B.18. Crystal data and structure refinement for **21a**.

CCDC number	2385750
Identification code	OJ-6-49
Empirical formula	$C_{11}H_8ClFN_2S$
Formula weight	254.70
Temperature [K]	100
Crystal system	triclinic
Space group (number)	$P\overline{1}$ (2)
a [Å]	6.05180(10)
b [Å]	7.0245(2)
c [Å]	13.5533(3)
α [°]	88.6820(10)
β [°]	80.7270(10)
γ [°]	74.4330(10)
Volume [Å^3]	547.65(2)
Z	2
ρ_{calc} [gcm^{-3}]	1.545
μ [mm^{-1}]	0.523
F(000)	260
Crystal size [mm^3]	0.26×0.28×0.4
Crystal colour	colourless
Crystal shape	prism
Radiation	MoK_α (λ=0.71073 Å)
2θ range [°]	6.02 to 72.66 (0.60 Å)
Index ranges	−10 ≤ h ≤ 10 −11 ≤ k ≤ 11 −22 ≤ l ≤ 22
Reflections collected	51765
Independent reflections	5291 R_{int} = 0.0236 R_{sigma} = 0.0131
Completeness to θ = 25.242°	99.5 %
Data / Restraints / Parameters	5291 / 0 / 145
Goodness-of-fit on F^2	1.111

Final *R* indexes	R_1 = 0.0267
[$I \geq 2\sigma(I)$]	wR_2 = 0.0678
Final *R* indexes	R_1 = 0.0305
[all data]	wR_2 = 0.0704
Largest peak/hole [eÅ^{-3}]	0.57/−0.23

Table B.19. Atomic coordinates and Ueq [Å2] for 21a.

Atom	***x***	***y***	***z***	U_{eq}
Cl1	−0.16176(3)	0.70372(3)	0.65632(2)	0.01761(4)
S1	−0.02419(3)	0.84173(3)	0.27725(2)	0.01412(4)
F1	0.72920(11)	0.02972(8)	0.08146(4)	0.02506(11)
N1	−0.05266(11)	0.76745(9)	0.46700(4)	0.01259(10)
N2	0.32277(11)	0.78409(10)	0.38483(5)	0.01403(10)
C1	0.10005(12)	0.79092(10)	0.38669(5)	0.01178(10)
C2	0.03134(12)	0.73450(10)	0.55194(5)	0.01262(11)
C3	0.25959(13)	0.72434(11)	0.56087(6)	0.01553(12)
H3	0.315847	0.700766	0.622772	0.019
C4	0.39950(12)	0.75111(11)	0.47290(6)	0.01561(12)
H4	0.557145	0.745848	0.475063	0.019
C5	0.23258(14)	0.81924(11)	0.18279(5)	0.01587(12)
H5A	0.184418	0.885682	0.121497	0.019
H5B	0.336316	0.888331	0.207457	0.019
C6	0.36606(13)	0.60782(11)	0.15670(5)	0.01339(11)
C7	0.27132(13)	0.48768(12)	0.10461(5)	0.01545(12)
H7	0.122034	0.540254	0.086360	0.019
C8	0.39196(14)	0.29260(12)	0.07908(6)	0.01695(12)
H8	0.327412	0.211294	0.043632	0.020
C9	0.60870(14)	0.22053(11)	0.10684(6)	0.01679(12)
C10	0.70978(14)	0.33360(12)	0.15801(6)	0.01710(12)
H10	0.859465	0.279928	0.175670	0.021
C11	0.58556(13)	0.52913(11)	0.18303(5)	0.01539(12)
H11	0.651375	0.609541	0.218415	0.018

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table B.20. Anisotropic displacement parameters (Å^2) for **21a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2(a^*)^2U_{11} + k^2(b^*)^2U_{22} + \ldots + 2hka^*b^*U_{12}\,]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl1	0.02096(8)	0.01826(8)	0.01371(7)	0.00162(5)	0.00157(6)	−0.00808(6)
S1	0.01356(7)	0.01588(8)	0.01284(7)	0.00043(5)	−0.00349(5)	−0.00303(5)
F1	0.0314(3)	0.0170(2)	0.0238(2)	−0.00567(18)	−0.0058(2)	−0.0001(2)
N1	0.0122(2)	0.0134(2)	0.0127(2)	0.00047(18)	−0.00121(18)	−0.00471(18)
N2	0.0116(2)	0.0161(2)	0.0147(2)	−0.00017(19)	−0.00175(18)	−0.00441(19)
C1	0.0116(2)	0.0112(2)	0.0127(2)	0.00008(19)	−0.00205(19)	−0.00322(19)
C2	0.0137(3)	0.0112(2)	0.0126(2)	0.00018(19)	−0.0008(2)	−0.0034(2)
C3	0.0141(3)	0.0175(3)	0.0146(3)	0.0005(2)	−0.0042(2)	−0.0025(2)
C4	0.0114(3)	0.0188(3)	0.0166(3)	−0.0009(2)	−0.0031(2)	−0.0033(2)
C5	0.0193(3)	0.0149(3)	0.0132(3)	0.0021(2)	−0.0009(2)	−0.0055(2)
C6	0.0156(3)	0.0149(3)	0.0102(2)	0.0011(2)	−0.0008(2)	−0.0059(2)

C7	0.0160(3)	0.0191(3)	0.0128(3)	0.0004(2)	−0.0028(2)	−0.0069(2)
C8	0.0208(3)	0.0186(3)	0.0135(3)	−0.0016(2)	−0.0026(2)	−0.0088(3)
C9	0.0214(3)	0.0153(3)	0.0128(3)	−0.0012(2)	−0.0018(2)	−0.0040(2)
C10	0.0177(3)	0.0191(3)	0.0143(3)	−0.0009(2)	−0.0040(2)	−0.0037(2)
C11	0.0167(3)	0.0175(3)	0.0131(3)	−0.0009(2)	−0.0033(2)	−0.0060(2)

X-Ray Crystallographic Details for Compound **27a** (CCDC Deposition Number: 2385749)

Data for **27a** were collected at 100 K on a Bruker D8 VENTURE Duo Fixed Chi Three-Circle Diffractometer using MoK_α radiation (λ = 0.71073 Å). All data were integrated with SAINT V8.40B and corrected for absorption using SADABS 2016/2.[16,17] The structure was solved by dual methods with SHELXT and refined by full-matrix least-squares methods against F^2 using SHELXL.[18,19] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atom locations in the investigated structure were initially identified from difference Fourier maps, but their final positions were determined geometrically and refined using a riding model. Isotropic thermal parameters of the placed hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups). Calculations and refinement of the structure was carried out using APEX4[20] and Olex2[21] software.

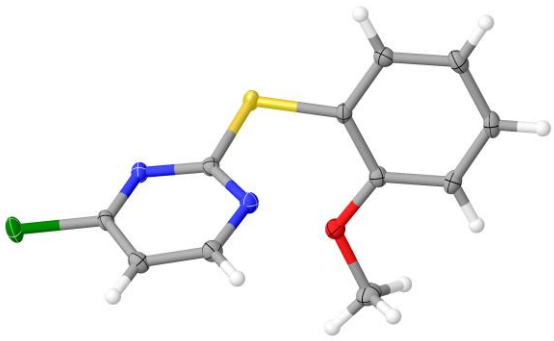


Figure B.13. X-ray crystal structure of 27a.

Table B.21. Crystal data and structure refinement for **27a**.

CCDC number	2385749
Identification code	AR_29
Empirical formula	$C_{11}H_9ClN_2OS$
Formula weight	252.71
Temperature [K]	100

Crystal system	triclinic
Space group (number)	$P\bar{1}$ (2)
a [Å]	7.4398(3)
b [Å]	8.2528(3)
c [Å]	9.8182(4)
α [°]	73.462(2)
β [°]	77.946(2)
γ [°]	82.090(2)
Volume [Å^3]	563.18(4)
Z	2
ρ_{calc} [gcm^{-3}]	1.490
μ [mm^{-1}]	0.502
F(000)	260
Crystal size [mm^3]	0.12×0.15×0.24
Crystal colour	colourless
Crystal shape	prism
Radiation	MoK_α (λ=0.71073 Å)
2θ range [°]	5.17 to 60.99 (0.70 Å)
Index ranges	−10 ≤ h ≤ 10
	−11 ≤ k ≤ 11
	−14 ≤ l ≤ 14
Reflections collected	34488
Independent reflections	3434
	R_{int} = 0.0291
	R_{sigma} = 0.0163
Completeness to θ = 25.242°	99.9 %
Data / Restraints / Parameters	3434 / 0 / 146
Goodness-of-fit on F^2	1.095
Final R indexes	R_1 = 0.0295
[I≥2σ(I)]	wR_2 = 0.0632
Final R indexes	R_1 = 0.0349
[all data]	wR_2 = 0.0661
Largest peak/hole [eÅ^{-3}]	0.41/−0.22

Table B.22. Atomic coordinates and Ueq [Å^2] for 27a.

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table B.23. Anisotropic displacement parameters (Å^2) for **27a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2(a^*)^2U_{11} + k^2(b^*)^2U_{22} + \ldots + 2hka^*b^*U_{12}\,]$

Atom	***x***	***y***	***z***	U_{eq}
Cl1	−0.10994(4)	0.21288(4)	0.39222(3)	0.02051(7)
S1	0.19516(4)	0.77814(4)	0.19432(3)	0.01530(7)
O1	0.56630(11)	0.63790(11)	0.09220(9)	0.01714(17)
N1	0.06724(13)	0.48467(12)	0.30785(10)	0.01362(18)
N2	0.33423(13)	0.52195(12)	0.39379(10)	0.01477(18)
C1	0.20460(15)	0.57294(14)	0.31213(12)	0.01280(19)

C2	0.06472(15)	0.33045(14)	0.39596(12)	0.0139(2)
C3	0.19083(17)	0.25975(15)	0.48700(13)	0.0168(2)
H3	0.185455	0.148055	0.549008	0.020
C4	0.32560(16)	0.36372(15)	0.48116(12)	0.0162(2)
H4	0.415441	0.321240	0.541436	0.019
C5	0.40602(15)	0.85388(14)	0.19290(12)	0.0137(2)
C6	0.57479(15)	0.77895(14)	0.13459(12)	0.0138(2)
C7	0.73689(16)	0.85195(15)	0.12407(12)	0.0163(2)
H7	0.852245	0.801100	0.087001	0.020
C8	0.73002(17)	0.99930(15)	0.16780(13)	0.0180(2)
H8	0.841114	1.049166	0.158747	0.022
C9	0.56397(17)	1.07444(15)	0.22429(14)	0.0191(2)
H9	0.560611	1.175381	0.253341	0.023
C10	0.40205(16)	0.99994(14)	0.23789(13)	0.0166(2)
H10	0.287690	1.049270	0.278282	0.020
C11	0.73663(18)	0.55720(17)	0.03500(15)	0.0234(3)
H11A	0.798259	0.636877	−0.050973	0.035
H11B	0.711962	0.457356	0.008842	0.035
H11C	0.816313	0.522113	0.107955	0.035

X-Ray Crystallographic Details for Compound **29a** (CCDC Deposition Number: 2385747)

Data for **29a** were collected at 100 K on a Bruker D8 VENTURE Duo Fixed Chi Three-Circle Diffractometer using MoK_α radiation (λ = 0.71073 Å). All data were integrated with SAINT V8.40B and corrected for absorption using SADABS 2016/2.[16,17] The structure was solved by dual methods with SHELXT and refined by full-matrix least-squares methods against F^2 using SHELXL.[18,19] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atom locations in the investigated structure were initially identified from difference Fourier maps, but their final positions were determined geometrically and refined using a riding model. Isotropic thermal parameters of the placed hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups). Calculations and refinement of the structure was carried out using APEX4[20] and Olex2[21] software.

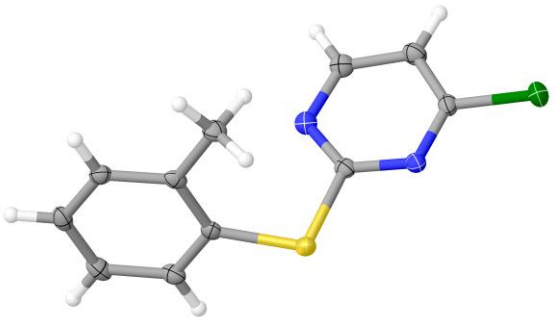


Figure B.14. X-ray crystal structure of 29a.

Table B.24. Crystal data and structure refinement for **29a**.

CCDC number	2385747
Identification code	AR_30
Empirical formula	$C_{11}H_9ClN_2S$
Formula weight	236.71
Temperature [K]	100
Crystal system	triclinic
Space group (number)	$P\bar{1}$ (2)
a [Å]	7.0444(3)
b [Å]	7.5521(3)
c [Å]	10.9795(4)
α [°]	86.717(2)
β [°]	74.314(2)
γ [°]	71.736(2)
Volume [Å^3]	533.79(4)
Z	2
ρ_{calc} [gcm^{-3}]	1.473
μ [mm^{-1}]	0.518
F(000)	244
Crystal size [mm^3]	0.04×0.04×0.21
Crystal colour	colourless
Crystal shape	Rod
Radiation	MoK_α (λ=0.71073 Å)
2θ range [°]	5.68 to 50.07 (0.84 Å)
Index ranges	−8 ≤ h ≤ 8
	−8 ≤ k ≤ 8
	−13 ≤ l ≤ 13
Reflections collected	14077
Independent reflections	1883
	R_{int} = 0.0481
	R_{sigma} = 0.0275
Completeness to θ = 25.037°	99.9 %
Data / Restraints / Parameters	1883 / 0 / 137
Goodness-of-fit on F^2	1.076
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0365
	wR_2 = 0.0781

Final *R* indexes	R_1 = 0.0470
[all data]	wR_2 = 0.0822
Largest peak/hole [eÅ^{-3}]	0.38/−0.32

Table B.25. Atomic coordinates and Ueq [Å^2] for **29a**.

Atom	*x*	*y*	*z*	U_{eq}
Cl1	0.91257(10)	−0.29469(8)	0.44121(6)	0.02618(18)
S1	0.84427(9)	0.26521(9)	0.14432(6)	0.02031(17)
N1	0.8608(3)	0.0065(3)	0.31049(19)	0.0172(4)
N2	0.6615(3)	0.3154(3)	0.39447(19)	0.0186(5)
C1	0.7783(4)	0.1924(3)	0.3019(2)	0.0165(5)
C2	0.8170(4)	−0.0548(3)	0.4266(2)	0.0180(5)
C3	0.6994(4)	0.0565(4)	0.5321(2)	0.0218(6)
H3	0.671645	0.007128	0.614255	0.026
C4	0.6240(4)	0.2451(3)	0.5112(2)	0.0207(5)
H4	0.543142	0.327703	0.581396	0.025
C5	0.6723(4)	0.4968(3)	0.1518(2)	0.0163(5)
C6	0.4600(4)	0.5297(3)	0.1650(2)	0.0164(5)
C7	0.3389(4)	0.7138(3)	0.1591(2)	0.0182(5)
H7	0.194357	0.740175	0.169251	0.022
C8	0.4227(4)	0.8594(3)	0.1388(2)	0.0207(5)
H8	0.336638	0.983105	0.133233	0.025
C9	0.6330(4)	0.8248(3)	0.1267(2)	0.0218(6)
H9	0.691158	0.924384	0.114372	0.026
C10	0.7564(4)	0.6430(3)	0.1329(2)	0.0198(5)
H10	0.900390	0.617930	0.124118	0.024
C11	0.3630(4)	0.3758(3)	0.1871(2)	0.0210(5)
H11A	0.441293	0.276180	0.122695	0.031
H11B	0.219294	0.424869	0.181698	0.031
H11C	0.365072	0.325961	0.271278	0.031

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table B.26. Anisotropic displacement parameters (Å^2) for **29a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2(a^*)^2U_{11} + k^2(b^*)^2U_{22} + \ldots + 2hka^*b^*U_{12}\,]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl1	0.0278(4)	0.0176(3)	0.0274(4)	0.0065(2)	−0.0037(3)	−0.0033(3)
S1	0.0175(3)	0.0196(3)	0.0181(3)	0.0037(2)	0.0002(2)	−0.0026(2)
N1	0.0139(10)	0.0180(11)	0.0192(11)	0.0037(8)	−0.0040(8)	−0.0051(8)
N2	0.0191(11)	0.0187(11)	0.0187(11)	0.0004(8)	−0.0060(9)	−0.0060(9)
C1	0.0142(12)	0.0192(12)	0.0174(12)	0.0027(10)	−0.0052(10)	−0.0063(10)
C2	0.0158(12)	0.0158(12)	0.0227(13)	0.0038(10)	−0.0056(10)	−0.0052(10)
C3	0.0239(13)	0.0248(14)	0.0170(13)	0.0044(10)	−0.0057(11)	−0.0082(11)
C4	0.0199(13)	0.0234(13)	0.0199(13)	0.0005(10)	−0.0062(10)	−0.0075(10)
C5	0.0178(12)	0.0181(12)	0.0115(11)	0.0023(9)	−0.0023(9)	−0.0049(10)
C6	0.0203(12)	0.0183(12)	0.0109(11)	0.0001(9)	−0.0021(9)	−0.0082(10)
C7	0.0164(12)	0.0213(13)	0.0152(12)	0.0011(10)	−0.0022(10)	−0.0051(10)

C8	0.0299(14)	0.0153(12)	0.0151(12)	0.0019(9)	−0.0057(11)	−0.0048(10)
C9	0.0317(14)	0.0202(13)	0.0169(12)	0.0023(10)	−0.0063(11)	−0.0135(11)
C10	0.0201(13)	0.0245(13)	0.0168(12)	0.0052(10)	−0.0055(10)	−0.0100(11)
C11	0.0189(13)	0.0227(13)	0.0222(13)	0.0026(10)	−0.0045(10)	−0.0090(10)

X-Ray Crystallographic Details for Compound **41b** (CCDC Deposition Number: 2385781)

A total of 2071 frames were collected. The total exposure time was 0.58 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 120001 reflections to a maximum θ angle of 33.73° (0.64 Å resolution), of which 8884 were independent (average redundancy 13.508, completeness = 99.9%, R_{int} = 7.17%, R_{sig} = 3.33%) and 8033 (90.42%) were greater than $2\sigma(F^2)$. The final cell constants of a = 19.7033(10) Å, b = 8.7698(5) Å, c = 13.7035(7) Å, β = 110.060(2)°, volume = 2224.2(2) Å^3, are based upon the refinement of the XYZ-centroids of 9639 reflections above 2 $\sigma(I)$ with 5.621° < 2θ < 65.59°. Data was corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.917. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8230 and 0.8840.

The structure was solved and refined using the Bruker SHELXTL Software Package,[18,21] using the space group $P2_1/c$, with Z = 8 for the formula unit, $C_9H_{14}ClN_3S$. The asymmetric consists of two well-ordered $C_9H_{14}ClN_3S$ compound molecules. All nonhydrogen atoms were located in successive Fourier maps and refined anisotropically. The H atoms were also located in the Fourier maps but were refined isotropically. Two crystallographically unique but chemically identical compound molecules differ from each other with respect to their packing.

The final anisotropic full-matrix least-squares refinement on F^2 with 366 variables converged at R_1 = 3.80%, for the observed data and wR_2 = 9.68% for all data. The goodness-of-fit was 1.057. The largest peak in the final difference electron density synthesis was 1.184 e$^-$/Å^3 and the largest hole was -0.466 e$^-$/Å^3 with an RMS deviation of 0.068 e$^-$/Å^3. On the basis of the final model, the calculated density was 1.384 g/cm^3 and F(000), 976 e$^-$.

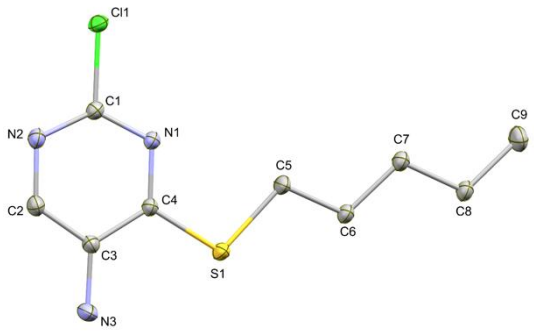


Figure B.15. X-ray crystal structure of **40b**.

Table B.27. Crystal data and structure refinement for **40b**.

CCDC	2385781
Identification code	CS238
Chemical formula	$C_9H_{14}ClN_3S$
Formula weight	231.74 g/mol
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal size	0.255 × 0.354 × 0.407 mm
Crystal habit	colorless prism
Crystal system	monoclinic
Space group	$P2_1/c$
a	19.7033(10) Å
b	8.7698(5) Å
c	13.7035(7) Å
α	90°
β	110.060(2)°
γ	90°

Volume	2224.2(2) Å^3
Z	8
Density (calculated)	1.384 g/cm^3
Absorption coefficient	0.497 mm^{-1}
F(000)	976
Theta range for data collection	2.22 to 33.73°
Index ranges	$-30 \le h \le 30$, $-13 \le k \le 13$, $-21 \le l \le 21$
Reflections collected	120001
Independent reflections	8884 [R_{int} = 0.0717]
Coverage of independent reflections	99.9%
Absorption correction	Multi-Scan
Max. and min. transmission	0.8840 and 0.8230
Structure solution technique	direct methods
Structure solution program	XT, VERSION 2018/2
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2019/1 (Sheldrick, 2019)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	8884 / 0 / 366
Goodness-of-fit on F^2	1.057
Δ/σ_{max}	0.001
Final R indices 8033 data; $I > 2\sigma(I)$	R_1 = 0.0380, wR_2 = 0.0919
Final R indexes [all data]	R_1 = 0.0439, wR_2 = 0.0968

Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0409P)^2 + 1.3573P]$ where $P = (F_o^2 + 2F_c^2)/3$
Largest diff. peak and hole	1.184 and -0.466 eÅ^{-3}
R.M.S. deviation from mean	0.068 eÅ^{-3}

Table B.28. Atomic coordinates and Ueq [Å^2] for **40b**.

	x/a	y/b	z/c	U(eq)
S2	0.10683(2)	0.79850(4)	0.50208(3)	0.01692(7)
N1	0.40632(6)	0.46594(13)	0.97422(9)	0.01313(19)
C1	0.42915(7)	0.56278(15)	0.05315(10)	0.0134(2)
Cl1	0.40563(2)	0.75229(4)	0.02270(3)	0.01615(7)
N2	0.46651(7)	0.53269(14)	0.15111(9)	0.0161(2)
C2	0.48376(8)	0.38504(16)	0.17210(11)	0.0166(2)
C3	0.46261(7)	0.26993(15)	0.09835(10)	0.0140(2)
N3	0.47721(8)	0.11962(15)	0.12305(11)	0.0217(3)
C4	0.42214(7)	0.31929(14)	0.99653(10)	0.0126(2)
S1	0.39171(2)	0.18096(4)	0.89989(3)	0.01675(7)
C5	0.34595(8)	0.29638(16)	0.78668(11)	0.0180(3)
C6	0.30771(8)	0.19168(15)	0.69617(10)	0.0149(2)
C7	0.27109(8)	0.28091(16)	0.59646(11)	0.0153(2)
C8	0.23392(8)	0.17488(16)	0.50558(11)	0.0166(2)
C9	0.18928(10)	0.2588(2)	0.40777(13)	0.0253(3)
N4	0.09345(6)	0.51605(13)	0.56776(9)	0.01356(19)
C10	0.07172(7)	0.42286(15)	0.62740(10)	0.0136(2)
Cl2	0.09521(2)	0.23243(4)	0.62393(3)	0.01704(7)
N5	0.03528(7)	0.45650(14)	0.68951(9)	0.0161(2)
C11	0.01753(8)	0.60434(16)	0.69040(11)	0.0161(2)
C12	0.03705(7)	0.71603(16)	0.63361(10)	0.0145(2)
N6	0.02190(8)	0.86684(15)	0.64066(11)	0.0213(3)
C13	0.07712(7)	0.66331(15)	0.57175(10)	0.0134(2)
C14	0.15216(8)	0.68169(16)	0.43384(12)	0.0171(2)
C15	0.19252(8)	0.78773(16)	0.38457(11)	0.0156(2)
C16	0.22720(8)	0.70367(16)	0.31616(11)	0.0152(2)
C17	0.26543(8)	0.81508(16)	0.26682(11)	0.0165(2)
C18	0.30784(10)	0.7390(2)	0.20631(14)	0.0260(3)

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table B.29. Anisotropic displacement parameters (Å^2) for **40b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2(a^*)^2U_{11} + k^2(b^*)^2U_{22} + \ldots + 2hka^*b^*U_{12}\,]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S2	0.02058(16)	0.01352(14)	0.02131(16)	0.00210(11)	0.01315(13)	0.00046(11)
N1	0.0139(5)	0.0127(5)	0.0123(5)	-0.0013(4)	0.0038(4)	-0.0001(4)
C1	0.0141(5)	0.0124(5)	0.0141(5)	-0.0014(4)	0.0053(4)	-0.0007(4)
Cl1	0.01838(14)	0.01154(12)	0.01829(14)	-0.00189(10)	0.00598(11)	0.00018(10)
N2	0.0174(5)	0.0170(5)	0.0129(5)	-0.0025(4)	0.0039(4)	-0.0006(4)
C2	0.0182(6)	0.0175(6)	0.0124(5)	0.0004(5)	0.0032(5)	0.0001(5)
C3	0.0147(5)	0.0148(5)	0.0120(5)	0.0009(4)	0.0041(4)	0.0009(4)
N3	0.0298(7)	0.0148(5)	0.0166(6)	0.0031(4)	0.0029(5)	0.0037(5)
C4	0.0132(5)	0.0125(5)	0.0114(5)	-0.0013(4)	0.0032(4)	-0.0003(4)
S1	0.02014(16)	0.01210(13)	0.01404(14)	-0.00233(11)	0.00077(12)	0.00130(11)
C5	0.0232(7)	0.0135(5)	0.0131(6)	-0.0026(4)	0.0007(5)	-0.0008(5)
C6	0.0163(6)	0.0138(5)	0.0131(5)	-0.0031(4)	0.0032(4)	-0.0007(4)
C7	0.0161(6)	0.0147(5)	0.0137(5)	-0.0028(4)	0.0035(5)	-0.0013(4)
C8	0.0181(6)	0.0167(6)	0.0135(5)	-0.0039(5)	0.0035(5)	-0.0006(5)
C9	0.0285(8)	0.0267(7)	0.0145(6)	-0.0012(6)	-0.0005(6)	-0.0012(6)
N4	0.0141(5)	0.0143(5)	0.0130(5)	0.0004(4)	0.0057(4)	-0.0005(4)
C10	0.0137(5)	0.0133(5)	0.0139(5)	0.0001(4)	0.0049(4)	-0.0006(4)
Cl2	0.01901(15)	0.01340(13)	0.01978(15)	0.00121(11)	0.00805(12)	0.00031(11)
N5	0.0178(5)	0.0169(5)	0.0156(5)	0.0007(4)	0.0083(4)	-0.0009(4)
C11	0.0184(6)	0.0172(6)	0.0152(6)	-0.0008(5)	0.0089(5)	-0.0004(5)
C12	0.0148(5)	0.0159(5)	0.0139(5)	-0.0013(4)	0.0064(4)	-0.0006(4)
N6	0.0308(7)	0.0153(5)	0.0240(6)	-0.0011(5)	0.0173(6)	0.0021(5)
C13	0.0130(5)	0.0151(5)	0.0130(5)	0.0001(4)	0.0057(4)	-0.0013(4)
C14	0.0208(6)	0.0149(6)	0.0203(6)	-0.0006(5)	0.0131(5)	-0.0010(5)
C15	0.0175(6)	0.0145(5)	0.0171(6)	0.0005(5)	0.0088(5)	-0.0014(4)
C16	0.0176(6)	0.0145(5)	0.0153(6)	-0.0010(4)	0.0080(5)	-0.0028(4)
C17	0.0181(6)	0.0160(6)	0.0177(6)	0.0018(5)	0.0092(5)	-0.0019(5)
C18	0.0283(8)	0.0298(8)	0.0279(8)	-0.0028(6)	0.0202(7)	-0.0031(6)

X-Ray Crystallographic Details for Compound **44a** (CCDC Deposition Number: 2385780)

A colorless, prism-like specimen of $C_9H_{14}ClN_3S$, approximate dimensions 0.120 mm × 0.240 mm × 0.380 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured (λ = 0.71073 Å) on a *Bruker D8 Venture Duo* X-ray diffractometer equipped with a CMOS IμS 3.0 Mo source and a PHOTON detector.

The total exposure time was 1.46 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic

unit cell yielded a total of 46380 reflections to a maximum θ angle of 31.51° (0.68 Å resolution), of which 3990 were independent (average redundancy 11.624, completeness = 99.8%, R_{int} = 5.51%, R_{sig} = 2.71%) and 2986 (74.84%) were greater than $2\sigma(F^2)$. The final cell constants of a = 13.2617(7) Å, b = 8.0429(4) Å, c = 12.0521(6) Å, β = 111.155(2)°, volume = 1198.87(11) Å^3, are based upon the refinement of the XYZ-centroids of 9909 reflections above 2 $\sigma(I)$ with 6.042° < 2θ < 61.39°. Data was corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.866. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8440 and 0.9470.

The structure was solved and refined using the Bruker SHELXTL Software Package,[18,21] using the space group $P2_1/c$, with Z = 4 for the formula unit, $C_9H_{14}ClN_3S$. The asymmetric unit consists of a reasonably well-ordered compound molecule. All non-hydrogen atoms were located in the Fourier maps and refined anisotropically. The H atoms were also located in the Fourier maps but were refined isotropically. The compound molecules exhibit intermolecular H-bonding interactions between the two amino N–H hydrogen atoms and both ring N atoms.

The final anisotropic full-matrix least-squares refinement on F^2 with 183 variables converged at R_1 = 3.76%, for the observed data and wR_2 = 10.93% for all data. The goodness-of-fit was 1.061. The largest peak in the final difference electron density synthesis was 0.415 e$^-$/Å^3 and the largest hole was -0.345 e$^-$/Å^3 with an RMS deviation of 0.050 e$^-$/Å^3. On the basis of the final model, the calculated density was 1.284 g/cm^3 and F(000), 488 e$^-$.

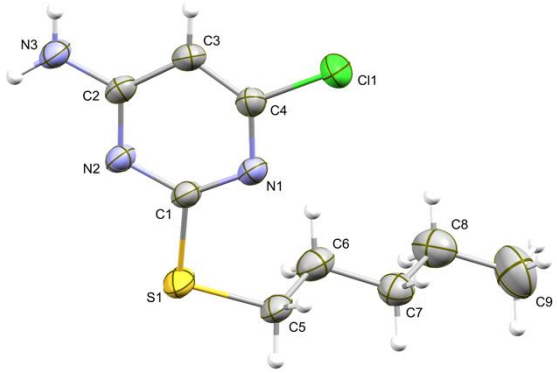


Figure B.16. X-ray Crystal structure of 44a.

Table B.30. Crystal data and structure refinement for **44a**

CCDC	2385780
Identification code	CS28
Chemical formula	$C_9H_{14}ClN_3S$
Formula weight	231.74 g/mol
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal size	0.120 × 0.240 × 0.380 mm
Crystal habit	colorless prism
Crystal system	monoclinic
Space group	$P2_1/c$
a	13.2617(7) Å
b	8.0429(4) Å
c	12.0521(6) Å
α	90°
β	111.155(2)°
γ	90°
Volume	1198.87(11) Å^3
Z	4
Density (calculated)	1.284 g/cm^3
Absorption coefficient	0.461 mm^{-1}
F(000)	488
Theta range for data collection	3.02 to 31.51°
Index ranges	$-19 \le h \le 19$, $-11 \le k \le 11$, $-17 \le l \le 17$
Reflections collected	46380
Independent reflections	3990 [R_{int} = 0.0551]
Coverage of independent reflections	99.8%
Absorption correction	Multi-Scan
Max. and min. transmission	0.9470 and 0.8440
Structure solution technique	direct methods
Structure solution program	XT, VERSION 2018/2
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2019/1 (Sheldrick, 2019)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	3990 / 0 / 183
Goodness-of-fit on F^2	1.061
Δ/σ_{max}	0.001
Final R indices 2986 data; I > 2σ(I)	R_1 = 0.0376, wR_2 = 0.0971
Final R indices [all data]	R_1 = 0.0554, wR_2 = 0.1093
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0541P)^2 + 0.2214P]$ where $P = (F_o^2 + 2F_c^2)/3$
Largest diff. peak and hole	0.415 and -0.345 eÅ^{-3}
R.M.S. deviation from mean	0.050 eÅ^{-3}

Theta range for data collection	3.02 to 31.51°

Table B.31. Atomic coordinates and Ueq [Å^2] for **44a**.

	x/a	y/b	z/c	U(eq)
N1	0.29989(9)	0.62278(13)	0.64755(9)	0.0317(2)
C1	0.37871(10)	0.53451(16)	0.72539(10)	0.0309(2)
N2	0.41092(9)	0.53812(13)	0.84374(9)	0.0308(2)
C2	0.35552(10)	0.63893(15)	0.89073(10)	0.0293(2)
C3	0.26626(10)	0.73178(16)	0.81622(11)	0.0321(3)
N3	0.38863(11)	0.64662(15)	0.00890(10)	0.0363(2)
C4	0.24594(10)	0.71962(16)	0.69750(11)	0.0314(2)
Cl1	0.14421(3)	0.83918(5)	0.59847(3)	0.04860(12)
S1	0.45508(3)	0.39646(6)	0.67477(3)	0.04825(13)
C5	0.37723(12)	0.3814(2)	0.51688(12)	0.0403(3)
C6	0.27322(14)	0.2838(2)	0.48652(14)	0.0446(3)
C7	0.21216(13)	0.2709(2)	0.35320(14)	0.0426(3)
C8	0.11053(16)	0.1671(3)	0.32048(19)	0.0581(4)
C9	0.0486(2)	0.1549(4)	0.1883(2)	0.0779(7)

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table B.32. Anisotropic displacement parameters (Å^2) for **44a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2(a^*)^2U_{11} + k^2(b^*)^2U_{22} + \ldots + 2hka^*b^*U_{12}\,]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N1	0.0341(5)	0.0380(5)	0.0265(5)	0.0023(4)	0.0153(4)	0.0031(4)
C1	0.0358(6)	0.0348(6)	0.0267(5)	0.0010(4)	0.0167(5)	0.0035(5)
N2	0.0377(5)	0.0328(5)	0.0257(5)	0.0021(4)	0.0162(4)	0.0025(4)
C2	0.0351(6)	0.0297(6)	0.0276(5)	0.0001(4)	0.0167(5)	-0.0031(4)
C3	0.0332(6)	0.0357(6)	0.0327(6)	-0.0014(5)	0.0181(5)	0.0012(5)
N3	0.0449(7)	0.0419(6)	0.0264(5)	-0.0001(4)	0.0180(5)	0.0070(5)
C4	0.0293(6)	0.0354(6)	0.0311(6)	0.0030(5)	0.0128(5)	0.0014(5)
Cl1	0.0417(2)	0.0635(3)	0.03837(19)	0.00673(15)	0.01165(14)	0.01935(16)
S1	0.0515(2)	0.0653(3)	0.02809(17)	-0.00156(15)	0.01460(15)	0.02666(18)
C5	0.0456(7)	0.0505(8)	0.0285(6)	-0.0013(6)	0.0180(5)	0.0126(6)
C6	0.0580(9)	0.0430(8)	0.0404(7)	-0.0009(6)	0.0267(7)	0.0052(7)
C7	0.0448(8)	0.0416(8)	0.0434(7)	-0.0006(6)	0.0183(6)	0.0066(6)
C8	0.0537(10)	0.0574(11)	0.0677(12)	-0.0090(9)	0.0273(9)	-0.0038(8)
C9	0.0550(12)	0.0809(16)	0.0803(16)	-0.0083(12)	0.0033(11)	-0.0068(11)

References

1. Melvin, P. R.; Nova, A.; Balcells, D.; Dai, W.; Hazari, N.; Hruszkewycz, D. P; Shah, H. P.; Tudge, M. T. Design of a versatile and improved Precatalyst Scaffold for Palladium-Catalyzed Cross-Coupling: (η3-1-tBu indenyl)$_2$(μ-Cl)$_2$Pd$_2$. *ACS Catal.* **2015**, *5*, 3680–3688

2. Kim, Y. Z.; Kim, J. P. A novel synthesis of sulfuric acid mono-[2-(2-amino-ethanesulfonyl)-ethyl]ester for use as an intermediate in the preparation of reactive dyes. *Synthetic Communications*, **2002**, *32*, 1601–1605.

3. Smith, S.; Buchwald, S. Regioselective 2-Amination of Polychloropyrimidines, *Org. Lett*. **2016**, *18*, 2180–2183.

4. Bandgar, B.P.; Sadavarte, V. S.; Uppalla L. S. Remarkably Fast Direct Synthesis of Thiols from Alcohols under Mild Conditions. *Chem. Lett*. **2000**, *11*, 1304–1308.

5. Chartoire, A.; Lesieur, M.; Falivene, L.; Slawin, A. M. Z.; Cavallo, L.; Cazin, C. S. J.; Nolan, S. P. [Pd(IPr*)(cinnamyl)Cl]: An Efficient Pre-catalyst for the preparation of Tetra-ortho-substituted Biaryls by Suzuki-Miyaura cross-coupling. *Chem. Eur. J.* **2012**, *18*, 4517–4521.

6. Bhujabul, Y. B.; Vadagaonker. K. S.; Gholap. A.; Sanghvi. Y. S.; Dandela. R.; Kapdi. A. R. HFIP Promoted Low Temperature SNAr of Chloroheteroarenes using Thiols and Amines. *J. Org. Chem*. **2019**, *84*, 15343–15354.

7. Bandaru, S. S. M.; Bhilare, S.; Cardozo, J.; Chrysochos, N.; Schulzke, C.; Sanghvi, Y. S.; Gunturu, K. C.; Kapdi, A. R. Pd/PTABS: Low-Temperature Thioetherification of Chloro(hetero)arenes. *J. Org. Chem.* **2019**, *84*, 8921 8940.

8. Koolma, V.; Staiger, R.; SchÜhle, M.; Bixenmann, A.; Bauschatz, E.; Schmid, M.; Miloserdov, F. M.; Herlé. A Platform for the Liebskind-Srogl Coupling of Heteroaromatic Thioethers for Medicinal-Chemistry-Relevant Transformations, *Org. Lett.* **2024**, *26,* 2852-2856.

9. Dolsak, A.; Mrgole, K.; Sova, M. Microwave-Assisted Regioselective Suzuki Coupling of 2,4 Dichloropyrimidines with Aryl and Heteroaryl Boronic Acids. *Catalysts* **2021**, *11*, 439.

10. Gaussian 16, Revision C.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven,

T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2016**

11. Avogadro: an open-source molecular builder and visualization tool. Version 1. http://avogadro.cc/ (b) Hanwell, M. D.; Curtis, D. E.; Lonie, D. C.; Vandermeersch, T.; Zurek, E.; Hutchison; G. R. Avogadro: An advanced semantic chemical editor, visualization, and analysis platform. *J. Cheminformatics* **2012**, *4*, 17.

12. Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. Energies, structures, and electronic properties of molecules in solution with the C-PCM solvation model. *J. Comput. Chem*. **2003**, *24*, 669–681.

13. Yu, H. S.; He, X.; Truhlar, D. G. MN15-L: A New Local Exchange-Correlation Functional for Kohn–Sham Density Functional Theory with Broad Accuracy for Atoms, Molecules, and Solids. *J. Chem. Theory Comput.* **2016**, *12*, 1280–1293.
14. Yu, H. S.; He, X.; Li, S. L.; Truhlar, D. G. MN15: A Kohn–Sham global-hybrid exchange–correlation density functional with broad accuracy for multi-reference and single-reference systems and noncovalent interactions. *Chem. Sci.* **2016**, *7*, 5032-5051.

15. Ribeiro, R. F.; Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. Use of Solution-Phase Vibrational Frequencies in Continuum Models for the Free Energy of Solvation. *J. Phys. Chem. B.* **2011**, *115*, 14556-14562.

16. Bruker, SAINT, V8.40B, Bruker AXS Inc., Madison, Wisconsin, USA.

17. Krause, L.; Herbst-Irmer, R.; Sheldrick, G. M.; Stalke, D. Comparison of silver and molybdenum microfocus X ray sources for single-crystal structure determination. *J. Appl. Cryst.* **2015**, *48*, 3–10.

18. Sheldrick, G. M. SHELXT – Integrated space-group and crystalstructure determination. *Acta Cryst.* **2015**, *A71*, 3–8.

19. Bruker (**2021**). APEX4. Bruker AXS Inc., Madison, Wisconsin, USA.

20. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339-341.

21. APEX5 Software Suite V2023.9-2, Bruker AXS Inc.: Madison, WI, **2023**.