Supporting Information

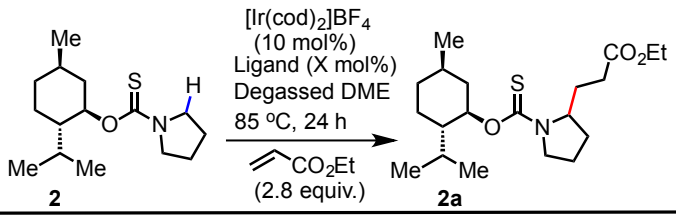
Contents

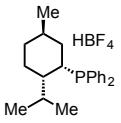
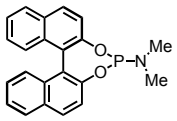
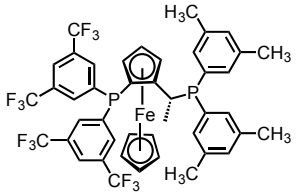
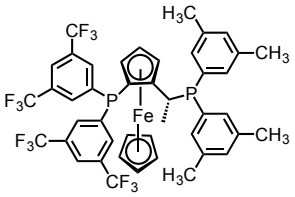
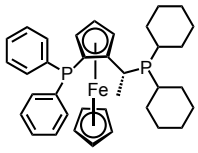
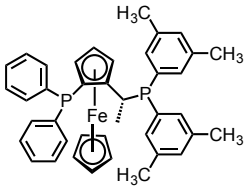
1. General Information

Unless otherwise noted, all materials were used as received from commercial sources without further purification. Amine substrates were purchased from Acros, Sigma-Aldrich, Alfa-Aesar, or Combi-blocks and used as received. Alkene coupling partners were procured from Sigma Aldrich, or Combi-Blocks and used as received. $[Ir(cod)_2]OTf$ and other Ir(I) catalysts were synthesized according to literature procedure[1]. Anhydrous 1,2-dimethoxyethane (DME) and chlorobenzene were purchased from Sigma Aldrich and Acros, respectively and used as received. All reactions were run in heating block on hot plate. Prior to beginning an experiment, the hot plate was turned on, and the heating block was allowed to equilibrate to the desired temperature for 30 minutes. Thin-layer chromatography (TLC) was performed on EMD 250 mm silica gel F-254 plates. Visualization of the developed plates was performed by fluorescence quenching or by $KMnO_4$ stain. Chromatographic purification of products was accomplished using force-flow chromatography on ICN 60 32-64 mesh silica gel 63 or Analtech Preparative TLC uniplates (20x20cm, 500mm thickness). ^1H and ^{13}C NMR spectra were recorded on Varian Inova (400 MHz and 100 MHz, respectively) or Bruker DRX equipped with a 5mm DCH cryoprobe (600 MHz and 150 MHz, respectively) and instruments internally referenced to tetramethylsilane or chloroform or acetone signals (note: $CDCl_3$ referenced at δ 7.26 ppm for ^1H and δ 77.16 ppm for ^{13}C; Acetone-d_6 referenced at δ 2.05 ppm for ^1H and δ 29.84 ppm for ^{13}C). The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and a = apparent. High-resolution mass spectra (HRMS) were recorded on an Agilent Mass spectrometer using ESI-TOF (electrospray ionization-time of flight).

2. Experimental Section

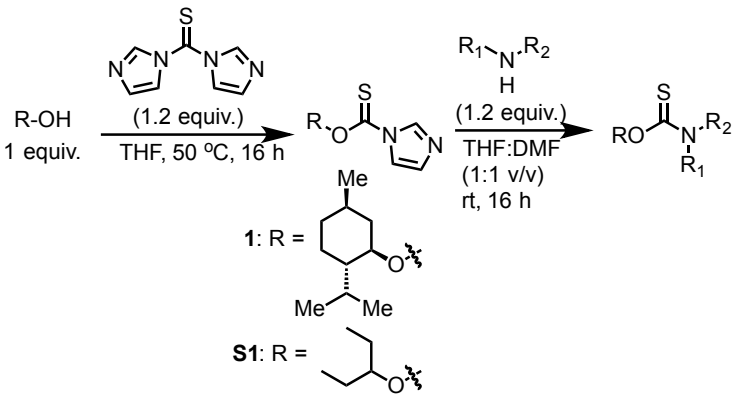
A. *Table S1.* Ligand Evaluation for α–C–H Alkylation of Pyrrolidine.[a,b]



Entry	Ligand	Loading (mol%)	Yield **2a** (%)	d.r.
1	No ligand		60%	1.5:1
2		10	26%	1.5:1
3		10	25%	1.5:1
4		5	28%	1.5:1
5		2.5	50%	1.5:1
6		2.5	38%	1.5:1
7		2.5	40%	1.5:1

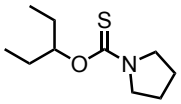
[a] Conditions: 2 (0.1 mmol), ethyl acrylate (0.28 mmol), $[Ir(cod)_2]BF_4$ (10 mol%), Ligand (2.5–10 mol%), degassed DME (0.5 mL), 85 °C, Argon (1 atm), 24 h.
[b] Crude yields were determined by ^1H NMR analysis using 1,3,5–trimethylbenzene as internal standard.

B. General Procedure for Installation of Alkoxythiocarbonyl Auxiliaries

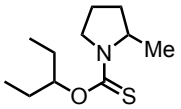


To a stirring solution of 1,1'–thiocarbonyldiimidazole (8.0 g, 45 mmol, 2 equiv.) in THF (30 mL, 0.75 M) under N_2 was added (–)–menthol or 3–pentanol (22.5 mmol, 1.0 equiv.) and the reaction was allowed to heat to 50 °C for 16 h. At this point, reaction was diluted with water (50 mL) and EtOAc (100 mL). The layers were separated and the organic layer was repeatedly washed with 0.5 M HCl (40 mL), water (3× 30 mL) and brine (30 mL). The organic layer was dried over anhydrous Na_2SO_4. Solvent was removed *in vacuo* to give a crude residue that was purified by column chromatography (Hexanes: EtOAc, 3:1 v/v) to give intermediates **1** or **S1**.

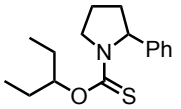
To a solution of intermediate **1** or **S1** (1.0 equiv.) in a mixture of THF and DMF (1:1 v/v, 1 M) was added an appropriate secondary amine (1.2 equiv.). The reaction was allowed to stir at room temperature until demonstrated to be completed by TLC (3–16 h). Upon completion, the reaction was diluted with water (50 mL) and EtOAc (100 mL). The layers were separated and the organic layer was repeatedly washed with 0.5 M HCl (40 mL), water (3× 30 mL) and brine (30 mL). The organic layer was dried over anhydrous Na_2SO_4. Solvent was removed *in vacuo* to give a crude residue that was purified by column chromatography (Hexanes: EtOAc eluent) to give the desired substrates.



***O*–(pentan–3–yl) pyrrolidine–1–carbothioate (3)**. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.34 (p, *J* = 6.0 Hz, 1H), 3.73 (*app.* dd, *J* = 7.2, 6.0 Hz, 2H), 3.51 (*app.* dd, *J* = 7.3, 6.1 Hz, 2H), 2.03–1.84 (m, 4H), 1.74–1.62 (m, 4H), 0.91 (t, *J* = 7.5 Hz, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 184.5, 82.2, 51.2, 47.0, 25.4, 25.0, 24.0, 8.7. **HRMS** (ESI-TOF) calculated for $C_{10}H_{20}NOS$ [M+H]: m/*z* = 202.1260, found 202.1264 (ESI+).

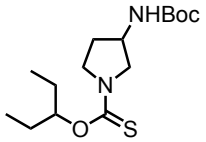


***O*–(pentan–3–yl) 2–methylpyrrolidine–1–carbothioate (5a)**. **^{1}H NMR** (600 MHz, $CDCl_3$, 2:1 mixture of rotamers, peaks corresponded to minor rotamer starred): δ 5.40–5.30 (m, 1H), 4.58–4.43 (m, 0.33H)*, 4.28–4.12 (m, 0.66H)*, 3.84–3.63 (m, 1.35 H), 3.58–3.39 (m, 0.66)*, 2.11–1.84 (m, 3H), 1.74–1.58 (m, 5H), 1.29 (d, *J* = 6.5 Hz, 1H), 1.17 (d, *J* = 6.5 Hz, 2H), 1.00–0.73 (m, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 184.7, 184.5*, 82.5, 81.9*, 57.5*, 54.5, 51.6, 47.1*, 32.5, 31.0*, 25.5, 25.5*, 25.4*, 25.4, 22.6*, 21.8, 19.2, 17.7*, 9.1, 8.9*, 8.8. **HRMS** (ESI-TOF) calculated for $C_{11}H_{22}NOS$ [M+H]: m/*z* = 216.1417, found 216.1412 (ESI+).

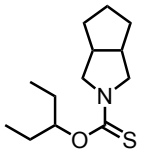


***O*–(pentan–3–yl) 2–phenylpyrrolidine–1–carbothioate (5b). ^{1}H NMR** (600 MHz, $CDCl_3$, 4:1 mixture of rotamers, peaks corresponded to minor rotamer starred): δ 7.38–7.28 (m, 2H), 7.25–7.17 (m, 1H), 7.15–7.02 (m, 2H), 5.59 (*app.* d, *J* = 8.0 Hz, 0.2 H)*, 5.38 (p, *J* = 6.0 Hz, 0.2 H)*, 5.22 (p, *J* = 5.9 Hz, 0.8 H), 5.14 (dd, *J* = 8.1, 2.9 Hz, 0.8 H), 4.10–4.02 (m, 0.8 H), 3.98 (ddd, *J* = 12.4, 8.5, 7.0 Hz, 0.8 H), 3.88–3.83 (m, 0.2 H)*, 3.71 (dt, *J* = 12.4, 8.5 Hz, 0.2 H)*, 2.45–2.29 (m, 1H), 2.05–1.89 (m, 3H), 1.76–1.68 (m, 0.8 H), 1.56 (qd, *J* = 7.5, 5.9 Hz, 1.6H), 1.21 (qd, *J* = 7.4, 5.8 Hz, 1.6 H), 0.96 (t, *J* = 7.5 Hz, 1H), 0.85 (t, *J* = 7.5 Hz, 2.5 H), 0.34 (t, *J* = 7.5 Hz, 2.5 H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 186.0*, 185.2, 142.7, 141.5*, 127.9, 127.9, 126.4, 126.2*, 125.0*, 124.8, 82.9,

82.5*, 65.1*, 62.4, 52.5, 48.2*, 35.1, 33.5*, 25.6*, 25.6*, 25.3, 24.9, 22.3*, 21.7, 9.0*, 8.9*, 8.8, 8.1. **HRMS** (ESI-TOF) calculated for $C_{16}H_{24}NOS$ [M+H]: m/*z* = 278.1573, found 278.1571 (ESI+).

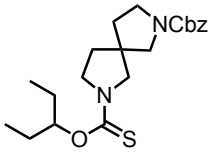


***O*–(pentan–3–yl) 3–((*tert*–butoxycarbonyl)amino)pyrrolidine–1–carbothioate (5c)**. **^{1}H NMR** (600 MHz, $CDCl_3$, 1:1 mixture of rotamers): δ 5.37–5.11 (m, 1H), 4.86–4.71 (m, 1H), 4.19 (*app.* d, *J* = 7.6 Hz, 1H), 3.98–3.65 (m, 2H), 3.60–3.49 (m, 1H), 3.39–3.29 (m, 1H), 2.13 (tdd, *J* = 9.4, 8.3, 6.8, 3.8 Hz, 1H), 1.91–1.76 (m, 1H), 1.65–1.55 (m, 4H), 1.46–1.26 (m, 9H), 0.92–0.73 (m, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 185.4*, 185.2, 154.7, 82.9*, 82.8, 79.3, 56.4, 52.7, 49.8, 49.0, 48.7*, 45.1, 31.3, 30.0*, 27.9*, 27.8, 25.4*, 25.4, 25.4*, 25.4, 8.8, 8.8*. **HRMS** (ESI-TOF) calculated for $C_{15}H_{29}N_2O_3S$ [M+H]: m/*z* = 317.1893, found 317.1890 (ESI+).



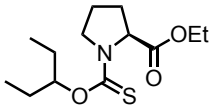
***O*–(pentan–3–yl) hexahydrocyclopenta[*c*]pyrrole–2(1*H*)–carbothioate (5d)**. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 5.33 (p, *J* = 6.0 Hz, 1H), 4.02–3.87 (m, 1H), 3.78–3.67 (m, 1H), 3.59–3.47 (m, 1H), 3.37–3.23 (m, 1H), 2.70 (dddd, *J* = 13.1, 10.3, 8.1, 4.9 Hz, 2H), 1.87–1.72 (m, 3H), 1.72–1.60 (m, 5H), 1.55–1.39 (m, 2H), 0.90 (td, *J* = 7.4, 2.2 Hz, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 184.5, 82.4, 57.2, 52.8, 42.8, 41.4, 31.3, 31.2, 25.5, 24.8, 8.9, 8.8. **HRMS** (ESI-TOF) calculated for $C_{13}H_{24}NOS$ [M+H]: m/*z* = 242.1573, found 242.1568 (ESI+).

Benzyl 7–((pentan–3–yloxy)carbonothioyl)–2,7–diazaspiro[4.4]nonane–2 carboxylate (5e)

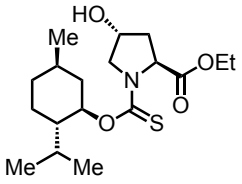


^{1}H NMR (600 MHz, $CDCl_3$, mixture of rotamers, rotameric peaks are overlapped in ^{1}H NMR): δ 7.53–7.32 (m, 5H), 5.43–5.33 (m, 1H), 5.14 (s, 2H), 3.91–3.28 (m, 8H),

2.05–1.83 (m, 4H), 1.76–1.62 (m, 4H), 1.01–0.85 (m, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$, peaks corresponded to the minor rotamer starred): δ 185.4*, 185.2, 154.3, 154.3*, 136.3, 136.1*, 128.0, 127.6, 127.5, 127.4*, 127.1*, 126.5*, 83.0, 66.5*, 66.4, 59.6, 55.7, 55.7*, 54.5, 54.3*, 50.2, 48.3*, 47.4, 47.2*, 46.3, 46.2*, 44.8, 44.5*, 34.6, 34.5*, 34.3, 34.2*, 33.8, 33.2*, 25.5, 25.5*, 8.9, 8.9*. **HRMS** (ESI-TOF) calculated for $C_{21}H_{31}N_2O_3S$ [M+H]: m/*z* = 391.2050, found 391.2054 (ESI+).



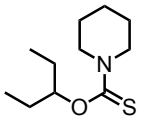
ethyl ((pentan–3–yloxy)carbonothioyl)–*L*–prolinate (5f). ^{1}H NMR (600 MHz, $CDCl_3$, 1.3:1 mixture of rotamers, peaks corresponded to minor rotamer starred): δ 5.30–5.22 (m, 1H), 4.72 (dd, *J* = 8.9, 2.6 Hz, 0.45 H)*, 4.41 (dd, *J* = 8.8, 3.5 Hz, 0.55 H), 4.18–4.00 (m, 2H), 3.85 (ddd, *J* = 12.1, 8.0, 4.3 Hz, 0.55 H), 3.74 (*app.* dt, *J* = 11.8, 7.6 Hz, 0.55 H), 3.71–3.64 (m, 0.45 H)*, 3.52 (*app.* dt, *J* = 11.8, 7.5 Hz, 0.45 H)*, 2.31–2.12 (m, 1H), 2.05–1.81 (m, 3H), 1.66–1.44 (m, 4H), 1.26–1.14 (m, 3H), 0.92–0.69 (m, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 186.3*, 185.3, 170.9*, 170.9, 83.1, 63.4, 60.7*, 60.5*, 59.6, 51.7, 47.5, 30.3, 29.0*, 25.5*, 25.5, 25.4*, 25.3, 23.5*, 22.6, 13.7, 8.8*, 8.7. **HRMS** (ESI-TOF) calculated for $C_{13}H_{24}NO_3S$ [M+H]: m/*z* = 274.1471, found 274.1475 (ESI+).



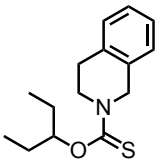
ethyl (2*S*,4*R*)–4–hydroxy–1–((((1*R*,2*S*,5*R*)–2–isopropyl–5 methylcyclohexyl)oxy)carbonothioyl)pyrrolidine–2–carboxylate (5g).

^{1}H NMR (600 MHz, $CDCl_3$, 1.5:1 mixture of rotamers, peaks corresponded to the minor rotamer starred): δ 5.19 (tdd, *J* = 10.8, 4.4, 2.4 Hz, 1H), 4.84 (dd, *J* = 8.5, 6.4 Hz, 0.4 H)*, 4.60–4.49 (m, 1.6 H), 4.27–4.07 (m, 2H), 4.03 (dt, *J* = 12.8, 2.0 Hz, 0.6 H), 3.96 (dd, *J* = 12.8, 4.5 Hz, 0.6 H), 3.79 (dd, *J* = 12.5, 5.2 Hz, 0.4 H)*, 3.69 (ddd, *J* = 12.5, 3.5, 1.4 Hz, 0.4 H)*, 2.42–2.36 (m, 0.6 H), 2.35–2.29 (m, 0.4 H)*, 2.22–2.13 (m, 2H), 1.95–1.80 (m, 2H), 1.68 (ddt, *J* = 12.7, 5.8, 3.7 Hz, 2H), 1.56–1.39 (m, 2H),

1.27 (dt, *J* = 16.0, 7.1 Hz, 3H), 1.16–1.05 (m, 1H), 0.98–0.87 (m, 7H), 0.82 (dd, *J* = 6.9, 2.4 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 186.5*, 185.4, 171.1, 170.8*, 81.3*, 81.2, 69.1*, 68.3, 61.8, 60.9*, 60.8, 59.6*, 58.7, 55.2, 47.1*, 47.0, 40.4*, 40.0, 38.5, 37.5*, 33.9, 30.8*, 30.7, 26.4*, 26.0, 23.5*, 23.1, 21.6, 20.3*, 16.8*, 16.5, 13.8, 13.6*. **HRMS** (ESI-TOF) calculated for $C_{18}H_{32}NO_4S$ [M+H]: m/*z* = 358.2047, found 358.2051 (ESI+).



***O*–(pentan–3–yl) piperidine–1–carbothioate (5h). ^{1}H NMR** (600 MHz, $CDCl_3$): δ 5.36 (p, *J* = 6.0 Hz, 1H), 3.99 (*app.* t, *J* = 5.2 Hz, 2H), 3.74–3.48 (m, 2H), 1.71–1.54 (m, 8H), 1.54–1.38 (m, 2H), 0.85 (t, *J* = 7.7 Hz, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 186.2, 83.0, 50.5, 45.7, 25.5, 24.8, 24.0, 8.9. **HRMS** (ESI-TOF) calculated for $C_{11}H_{22}NOS$ [M+H]: m/*z* = 216.1417, found 216.1413 (ESI+).

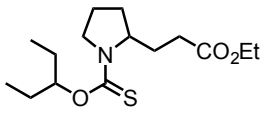


***O*–(pentan–3–yl) 3,4–dihydroisoquinoline–2(1*H*)–carbothioate (5i)**. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.37–6.84 (m, 4H), 5.51–5.44 (m, 1H), 5.12 (s, 1H), 4.80 (s, 1H), 4.21 (*app.* t, *J* = 6.0 Hz, 1H), 3.97–3.77 (m, 1H), 2.94–2.81 (m, 2H), 1.78–1.57 (m, 4H), 0.98–0.85 (m, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 187.0*, 186.8, 134.6*, 134.0, 132.8, 132.0*, 128.0*, 127.6, 126.5*, 126.3, 126.2, 126.1*, 126.1, 125.7, 83.3*, 83.2, 51.0, 47.1*, 46.6, 42.9, 28.6, 28.1*, 25.6, 9.1, 9.0*. **HRMS** (ESI-TOF) calculated for $C_{15}H_{22}NOS$ [M+H]: m/*z* = 264.1417, found 264.1419 (ESI+).

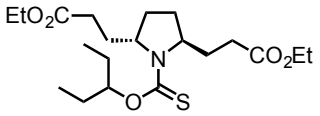
C. General procedure for product formation:

A 2-dram vial was charged with substrate (0.1 mmol) and the vial was evacuated by passing through alternative cycles of vacuum/Argon. Degassed PhCl (0.5 mL) was then added to the above vial. In a separate 2-dram vial, under an Argon atmosphere (glovebox), $[Ir(cod)_2]OTf$ (5.7 mg, 0.01 mmol) was added followed by a solution of substrate in degassed PhCl (0.5 mL). Subsequently, alkene (0.8 mmol) was added to the above reaction mixture and the reaction was allowed to stir at 85 ^{o}C, under an Argon atmosphere, for 6 or 24 h. Upon completion, the reaction was filtered over Celite®

and the filter cake was thoroughly washed with EtOAc: MeOH (9:1 v/v). Solvent was removed *in vacuo* to give a crude residue that was purified by preparative TLC. NB: addition of degassed PhCl and alkene was performed outside of glovebox.

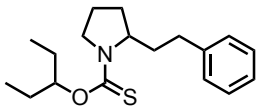


Ethyl 3–(1–((pentan–3–yloxy)carbonothioyl)pyrrolidin–2–yl)propanoate ($4a_{mono}$)
Prepared according to general procedure B using *O*–(pentan–3–yl) pyrrolidine–1–carbothioate **3** (20.2 mg, 0.1 mmol, 1 equiv.), $[Ir(cod)_2]OTf$ (5.7 mg, 0.01 mmol, 10 mol%), ethyl acrylate (80 μL, 0.8 mmol, 8 equiv.) in degassed PhCl (0.5 mL) at 80 ^oC under Ar for 6 h. The reaction was purified by preparative TLC (2:1 v/v Hexanes/EtOAc) to give **$4a_{mono}$** (7.30 mg, 24%) and **$4a_{di}$** (17.6 mg, 44%) as colourless oils. **^{1}H NMR** (600 MHz, $CDCl_3$, 1.8:1 mixture of rotamers): δ 5.46–5.41 (m, 0.65 H), 5.39–5.35 (m, 0.35 H), 4.45–4.38 (m, 0.35 H), 4.21–4.09 (m, 2.65 H), 3.88–3.69 (m, 1.3 H), 3.63–3.50 (m, 0.7 H), 2.52–2.24 (m, 2H), 2.14–1.90 (m, 4H), 1.87–1.62 (m, 6H), 1.35–1.20 (m, 4H), 1.02–0.84 (m, 7H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 185.3, 185.1*, 172.8*, 172.3, 82.9, 82.3*, 61.2*, 60.1, 60.0*, 58.1, 51.6, 47.1*, 31.3*, 30.9, 29.7, 29.2*, 28.3, 28.2*, 26.9*, 25.5, 25.4*, 25.3, 22.7*, 21.8, 13.8*, 13.7, 9.1, 8.9*, 8.9*, 8.8. **HRMS** (ESI-TOF) calculated for $C_{15}H_{28}NO_3S$ [M+H]: m/*z* = 302.1784, found 302.1781 (ESI+).

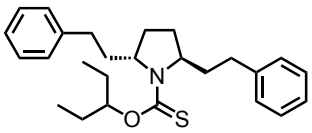


Diethyl 3,3'–((2*S*,5*S*)–1–((pentan–3–yloxy)carbonothioyl)pyrrolidine–2,5–diyl)dipropionate ($4a_{di}$, trans diastereomer, relative stereochemistry shown). **^{1}H NMR** (600 MHz, $CDCl_3$, mixture of rotamers, rotameric peaks are overlapped in ^{1}H NMR): δ 5.45–5.37 (m, 1H), 4.26–4.20 (m, 1H), 4.19–4.07 (m, 4H), 4.03–3.96 (m, 1H), 2.67–2.53 (m, 1H), 2.47–2.34 (m, 2H), 2.32–2.21 (m, 3H), 2.19–2.09 (m, 2H), 2.08–1.97 (m, 2H), 1.84–1.62 (m, 6H), 1.32–1.17 (m, 6H), 1.00–0.80 (m, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 186.4, 185.0, 172.7, 172.2, 82.8*, 82.6, 62.3*, 61.6, 60.1*, 60.0, 59.0*, 58.6, 31.7, 31.5, 31.3*, 31.2*, 30.7*, 30.0*, 29.2*, 29.1*, 28.9*, 28.1, 27.7*, 27.4, 26.4, 25.9, 25.5, 25.4*, 25.3, 13.8, 13.7, 13.6*, 9.2, 9.2*, 8.9. **HRMS**

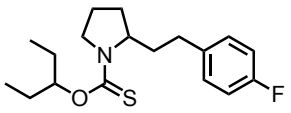
(ESI-TOF) calculated for $C_{20}H_{36}NO_5S$ [M+H]: m/*z* = 402.2309, found 402.2308 (ESI+).



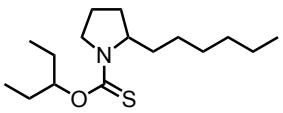
***O*–(pentan–3–yl) 2–phenethylpyrrolidine–1–carbothioate ($4c_{mono}$).** Prepared according to general procedure B using *O*–(pentan–3–yl) pyrrolidine–1–carbothioate **3** (20.2 mg, 0.1 mmol, 1 equiv.), $[Ir(cod)_2]OTf$ (5.7 mg, 0.01 mmol, 10 mol%), styrene (92 μL, 0.8 mmol, 8 equiv.) in degassed PhCl (0.5 mL) at 80 ^oC under Ar for 6 h. The reaction was purified by preparative TLC (2:1 v/v Hexanes/EtOAc) to give $\mathbf{4c_{mono}}$ (5.83 mg, 19%) and $\mathbf{4c_{di}}$ (9.42 mg, 23%) as colourless oils. **^{1}H NMR** (600 MHz, $CDCl_3$, 2.3:1 mixture of rotamers, peaks corresponding to minor rotamer starred): δ 7.54–7.01 (m, 5H), 5.41–5.32 (m, 1H), 4.42 (ddd, *J* = 10.1, 5.2, 2.5 Hz, 0.3H)*, 4.10 (tt, *J* = 7.2, 2.9 Hz, 0.7H), 3.76 (ddd, *J* = 6.4, 5.3, 2.6 Hz, 1.4H), 3.69–3.45 (m, 0.6H)*, 2.79–2.38 (m, 2H), 2.20–1.74 (m, 5H), 1.76–1.58 (m, 5H), 0.99–0.70 (m, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 184.9, 184.7*, 141.2*, 140.7, 128.0, 127.9*, 127.8, 125.6, 125.3*, 82.7, 82.1*, 61.9*, 58.3, 51.6, 47.2*, 34.3, 33.0*, 32.5*, 32.4, 29.4, 28.2*, 25.5*, 25.5*, 25.4, 25.4, 22.8*, 21.9, 9.2, 8.9*, 8.9*, 8.8. **HRMS** (ESI-TOF) calculated for $C_{18}H_{28}NOS$ [M+H]: m/*z* = 306.1886, found 306.1881 (ESI+).



***O*–(pentan–3–yl) (2*R*,5*R*)–2,5–diphenethylpyrrolidine–1–carbothioate ($4c_{di}$).** **^{1}H NMR** (600 MHz, $CDCl_3$, 1.8:1 mixture of rotamers, peaks corresponding to minor rotamer starred): δ 7.48–7.00 (m, 10H), 5.48–5.38 (m, 1H), 4.52 (td, *J* = 7.2, 3.8 Hz, 0.35H)*, 4.32 (dd, *J* = 10.1, 6.7 Hz, 0.65H), 4.20–4.10 (m, 0.35H)*, 4.03 (ddd, *J* = 9.9, 7.2, 2.2 Hz, 0.65H), 2.85–2.48 (m, 5H), 2.32–1.93 (m, 3H), 1.91–1.77 (m, 2H), 1.74–1.46 (m, 6H), 1.08–0.77 (m, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 185.5*, 184.6, 141.3, 141.2*, 140.7, 140.7*, 128.0, 128.0*, 128.0, 127.9*, 127.9, 127.8*, 127.8, 127.8*, 125.5, 125.4*, 125.3, 82.3*, 82.2, 62.7*, 62.2, 59.1*, 58.8, 37.7, 36.4*, 35.3, 34.1*, 32.9, 32.3*, 29.2, 29.0*, 27.9, 27.3*, 26.1, 25.4*, 22.2, 21.6*, 13.7, 13.7*, 9.4, 9.2*, 8.9. **HRMS** (ESI-TOF) calculated for $C_{26}H_{36}NOS$ [M+H]: m/*z* = 410.2512, found 410.2521 (ESI+).

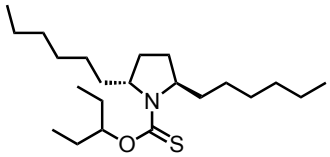


***O*–(pentan–3–yl) 2–(4–fluorophenethyl)pyrrolidine–1–carbothioate (4d$_{mono}$,** ^{1}H and ^{13}C NMR data were only obtained for **4d$_{mono}$** as **4d$_{di}$** could not be isolated with sufficient purity for NMR characterization**)**. Prepared according to general procedure B using *O*–(pentan–3–yl) pyrrolidine–1–carbothioate **3** (20.2 mg, 0.1 mmol, 1 equiv.), [Ir(cod)$_2$]OTf (5.7 mg, 0.01 mmol, 10 mol%), 4-fluorostyrene (96 μL, 0.8 mmol, 8 equiv.) in degassed PhCl (0.5 mL) at 80 ^{o}C under Ar for 6 h. The reaction was purified by preparative TLC (100:1 v/v Toluene/Acetone) to give **4d$_{mono}$** (10.0 mg, 31%) and **4d$_{di}$** (2.60 mg, 6%) as colourless oils. **^{1}H NMR** (600 MHz, $CDCl_3$, rotamers in 1.8:1 ratio, peaks corresponding to minor rotamer starred): δ 7.22–7.07 (m, 2H), 7.04–6.89 (m, 2H), 5.36 (td, *J* = 6.1, 4.6 Hz, 1H), 4.38 (ddt, *J* = 9.9, 5.7, 2.4 Hz, 0.35H)*, 4.11–4.02 (m, 0.65H), 3.75 (ddd, *J* = 8.2, 5.9, 3.3 Hz, 1.3H), 3.60–3.47 (m, 0.7H)*, 2.73–2.45 (m, 2H), 2.08–1.79 (m, 5H), 1.71–1.57 (m, 5H), 1.00–0.78 (m, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ –117.7, –118.1*. **^{13}C NMR** (151 MHz, $CDCl_3$): δ 184.9, 184.8*, 160.9 (d, $J_{F–C}$ = 243 Hz), 160.8 (d, $J_{F–C}$ = 243 Hz)*, 136.7 (d, $J_{F–C}$ = 3.0 Hz)*, 136.2 (d, $J_{F–C}$ = 3.0 Hz), 129.3 (d, $J_{F–C}$ = 7.6 Hz)*, 129.1 (d, $J_{F–C}$ = 7.6 Hz), 114.7 (d, $J_{F–C}$ = 20 Hz), 114.5 (d, $J_{F–C}$ = 20 Hz)*, 82.6, 82.1*, 61.7*, 58.1, 51.6, 47.2*, 34.4, 33.1*, 31.7*, 31.6, 29.4, 28.2*, 25.5*, 25.5*, 25.5, 25.4, 22.8*, 21.9, 9.2, 8.9*, 8.9*, 8.8. **HRMS** (ESI-TOF) calculated for $C_{18}H_{27}FNOS$ [M+H]: m/*z* = 324.1792, found 324.1798 (ESI+).

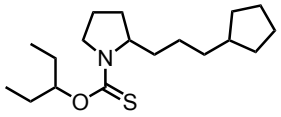


***O*–(pentan–3–yl) 2–hexylpyrrolidine–1–carbothioate (4e$_{mono}$).** Prepared according to general procedure B using *O*–(pentan–3–yl) pyrrolidine–1–carbothioate **3** (20.2 mg, 0.1 mmol, 1 equiv.), [Ir(cod)$_2$]OTf (5.7 mg, 0.01 mmol, 10 mol%), 1-hexene (100 μL, 0.8 mmol, 8 equiv.) in degassed PhCl (0.5 mL) at 80 ^{o}C under Ar for 6 h. The reaction was purified by preparative TLC (100:1 v/v Toluene/Acetone) to give **4e$_{mono}$** (8.05 mg, 28%) and **4e$_{di}$** (12.5 mg, 34%) as colourless oils. **^{1}H NMR** (600 MHz, $CDCl_3$, peaks corresponded to the minor rotamer starred): δ 5.44–5.33 (m, 1H), 4.37–4.29 (m, 0.3 H)*, 4.09–4.02 (m, 0.7 H), 3.79–3.69 (m, 1.4 H),

3.56–3.43 (m, 0.6 H)*, 2.18–1.76 (m, 4H), 1.74–1.63 (m, 3H), 1.40–1.18 (m, 10H), 1.01–0.82 (m, 10H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 184.7, 184.5*, 82.5, 81.9*, 62.1, 59.0*, 51.6, 47.2*, 32.8, 31.4, 31.2*, 31.0*, 29.6, 28.7*, 28.6, 27.9*, 26.0*, 25.9, 25.5, 25.5, 25.4*, 22.7*, 22.2, 22.1*, 22.1*, 21.9, 13.6, 13.6*, 9.1, 8.9, 8.8*. **HRMS** (ESI-TOF) calculated for $C_{16}H_{32}NOS$ [M+H]: m/*z* = 286.2199, found 286.2132 (ESI+).



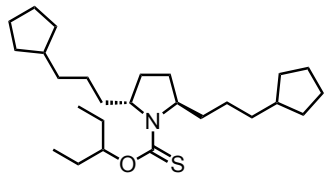
***O*–(pentan–3–yl) (2*R*,5*R*)–2,5–dihexylpyrrolidine–1–carbothioate ($4e_{di}$, trans diastereoisomer). ^{1}H NMR** (600 MHz, $CDCl_3$, 1.5:1 mixture of rotamers, peaks corresponding to minor rotamer starred): δ 5.43 (td, *J* = 6.0, 3.2 Hz, 1H), 4.38 (td, *J* = 7.1, 3.7 Hz, 0.4H)*, 4.19 (ddd, *J* = 9.9, 7.2, 2.3 Hz, 0.6H), 4.08–4.00 (m, 0.4H)*, 3.92 (dd, *J* = 9.6, 6.8 Hz, 0.6H), 2.36–2.15 (m, 1H), 2.09–1.91 (m, 2H), 1.86–1.60 (m, 7H), 1.37–1.17 (m, 20H), 1.01–0.81 (m, 10H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 185.1*, 184.3, 82.0*, 81.8, 62.9*, 62.4, 59.7*, 59.6, 34.8*, 33.2, 32.8*, 31.4, 31.4*, 31.3, 31.3*, 30.6, 29.1, 28.7*, 28.6, 27.6*, 27.4, 26.5*, 26.5, 26.0*, 25.8, 25.8*, 25.5, 25.5*, 25.4, 25.3, 22.2*, 22.1, 13.6*, 13.6, 13.6*, 13.6, 9.2*, 9.1, 9.1, 8.8*, 8.8. **HRMS** (ESI-TOF) calculated for $C_{22}H_{44}NOS$ [M+H]: m/*z* = 370.3138, found 370.3143 (ESI+).



***O*–(pentan–3–yl) 2–(3–cyclopentylpropyl)pyrrolidine–1–carbothioate ($4f_{mono}$)**. Prepared according to general procedure B using *O*–(pentan–3–yl) pyrrolidine–1–carbothioate **3** (20.2 mg, 0.1 mmol, 1 equiv.), $[Ir(cod)_2]OTf$ (5.7 mg, 0.01 mmol, 10 mol%), allylcyclopentane (112 μL, 0.8 mmol, 8 equiv.) in degassed PhCl (0.5 mL) at 80 °C under Ar for 6 h. The reaction was purified by preparative TLC (100:1 v/v Toluene/Acetone) to give **$4f_{mono}$** (6.90 mg, 22%) and **$4f_{di}$** (14.3 mg, 34%) as colourless oils.

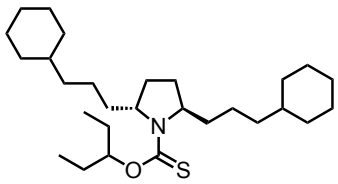
^{1}H NMR (600 MHz, $CDCl_3$, rotamers in 1.8:1 ratio, peaks corresponding to minor rotamer starred): δ 5.43–5.34 (m, 1H), 4.33 (td, *J* = 7.4, 3.0 Hz, 0.42H)*, 4.05 (ddd, *J* = 10.5, 6.4, 2.7 Hz, 0.75H), 3.77–3.70 (m, 1.33H), 3.55–3.46 (m, 0.8H)*, 2.14–2.09 (m,

0.42H)*, 1.99–1.86 (m, 3H), 1.80 (ddd, *J* = 10.1, 4.9, 2.2 Hz, 1H), 1.78–1.65 (m, 7H), 1.62–1.56 (m, 2H), 1.52–1.47 (m, 2H), 1.39–1.22 (m, 6H), 1.12–0.99 (m, 2H), 0.99–0.84 (m, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 184.7, 184.5*, 82.5, 81.9*, 62.1*, 59.0, 51.6, 47.2*, 39.6*, 39.5, 35.5, 33.0, 32.3, 32.2*, 32.2, 32.1*, 31.2*, 29.6, 27.9*, 25.5, 25.5, 25.4*, 25.2*, 25.2, 24.7, 24.7, 22.8*, 21.9, 9.1, 8.9*, 8.8*, 8.8. **HRMS** (ESI-TOF) calculated for $C_{18}H_{34}NOS$ [M+H]: m/*z* = 312.2356, found 312.2358 (ESI+).



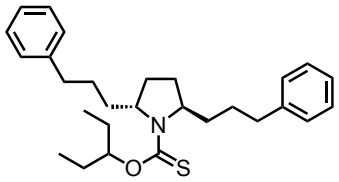
***O*–(pentan–3–yl) (2*R*,5*R*)–2,5–bis(3–cyclopentylpropyl)pyrrolidine–1–carbothioate ($4f_{di}$)**

^{1}H NMR (600 MHz, $CDCl_3$, rotamers in 1.2:1 ratio, peaks corresponding to minor rotamer starred): δ 5.47–5.39 (m, 1H), 4.42–4.34 (m, 0.45H)*, 4.19 (ddd, *J* = 9.9, 7.3, 2.3 Hz, 0.55H), 4.09–4.03 (m, 0.45H)*, 3.93 (td, *J* = 7.4, 3.6 Hz, 0.55H), 2.34–2.25 (m, 0.55H), 2.24–2.15 (m, 0.45H)*, 2.08–1.93 (m, 2H), 1.86–1.44 (m, 20H), 1.42–1.12 (m, 11H), 1.12–0.99 (m, 4H), 0.99–0.81 (m, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 185.1*, 184.3, 82.0*, 81.8, 62.9*, 62.4, 59.7*, 59.6, 39.7, 39.6*, 39.5, 39.5*, 35.5*, 35.5*, 35.5, 35.4, 35.0*, 33.3*, 33.0, 32.3, 32.2*, 32.2, 32.2*, 30.8, 30.5*, 29.2*, 29.1, 27.6*, 27.5, 25.9, 25.7, 25.7, 25.5, 25.5*, 25.4, 25.3, 25.2*, 25.0*, 24.7, 24.7, 24.7, 9.2, 9.1*, 8.8, 8.8*. **HRMS** (ESI-TOF) calculated for $C_{26}H_{48}NOS$ [M+H]: m/*z* = 422.3451, found 422.3447 (ESI+).

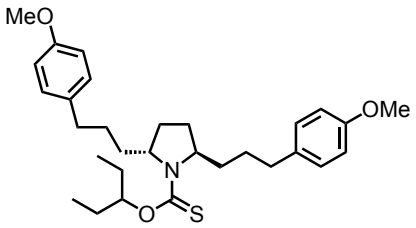


***O*–(pentan–3–yl) (2*R*,5*R*)–2,5–bis(3–cyclohexylpropyl)pyrrolidine–1–carbothioate (4g)**. Prepared according to general procedure B using *O*–(pentan–3–yl) pyrrolidine–1–carbothioate **3** (20.2 mg, 0.1 mmol, 1 equiv.), $[Ir(cod)_2]OTf$ (5.7 mg, 0.01 mmol, 10 mol%), allylcyclohexane (124 μL, 0.8 mmol, 8 equiv.) in degassed PhCl (0.5 mL) at 80 ^{o}C under Ar for 6 h. The reaction was purified by preparative TLC (100:1 v/v Toluene/Acetone) to give **4g** (23.3 mg, 52%) as colourless oil. **^{1}H NMR** (600 MHz,

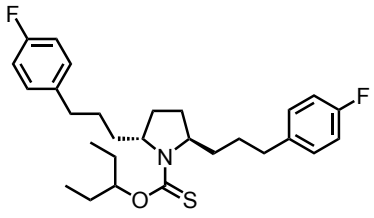
$CDCl_3$, rotamers in 1.1:1 ratio, peaks corresponding to minor rotamer starred): δ 5.43 (p, *J* = 6.0 Hz, 1H), 4.38 (td, *J* = 7.0, 3.6 Hz, 0.47H)*, 4.19 (ddd, *J* = 9.9, 7.2, 2.3 Hz, 0.53H), 4.08–4.00 (m, 0.48H)*, 3.92 (td, *J* = 7.3, 3.3 Hz, 0.52H), 2.30–2.14 (m, 1H), 2.10–1.91 (m, 2H), 1.82–1.53 (m, 16H), 1.37–1.08 (m, 19H), 1.02–0.78 (m, 10H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 185.1*, 184.3, 82.0*, 81.8, 62.9*, 62.4, 59.7*, 59.6, 37.2, 37.2*, 37.0, 36.9*, 36.8, 36.8*, 36.7*, 35.0, 33.4*, 33.1*, 33.0*, 33.0, 33.0*, 32.9, 32.9*, 32.8, 30.8, 29.1, 27.6*, 27.5, 26.3, 26.2, 26.2*, 26.0, 25.9, 25.9*, 25.9, 25.5, 25.5*, 25.4, 25.4*, 23.8, 23.7, 23.3, 23.0, 9.2, 9.1*, 8.8, 8.8. **HRMS** (ESI-TOF) calculated for $C_{28}H_{52}NOS$ [M+H]: m/*z* = 450.3764, found 450.3768 (ESI+).



***O*–(pentan–3–yl) (2*R*,5*R*)–2,5–bis(3–phenylpropyl)pyrrolidine–1–carbothioate (4h, trans diastereoisomer).** Prepared according to general procedure B using *O*–(pentan–3–yl) pyrrolidine–1–carbothioate **3** (20.2 mg, 0.1 mmol, 1 equiv.), $[Ir(cod)_2]OTf$ (5.7 mg, 0.01 mmol, 10 mol%), allylbenzene (110 μL, 0.8 mmol, 8 equiv.) in degassed PhCl (0.5 mL) at 80 °C under Ar for 6 h. The reaction was purified by preparative TLC (100:1 v/v Toluene/Acetone) to give **4h** (27.1 mg, 62%) as a colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$, 1.5:1 mixture of rotamers, peaks corresponding to minor rotamer starred): δ 7.36–6.92 (m, 10H), 5.44–5.35 (m, 1H), 4.49 (ddd, *J* = 10.5, 7.2, 3.7 Hz, 0.4H)*, 4.28 (ddd, *J* = 9.9, 7.1, 2.3 Hz, 0.6H), 4.14–4.04 (m, 0.4H)*, 3.97 (ddd, *J* = 9.8, 7.2, 2.2 Hz, 0.6H), 2.76 (tdd, *J* = 13.0, 9.8, 5.6 Hz, 1H), 2.70–2.55 (m, 3H), 2.42–2.19 (m, 1H), 2.06–1.90 (m, 2H), 1.89–1.76 (m, 1H), 1.72–1.43 (m, 10H), 1.37–1.22 (m, 2H), 0.91–0.82 (m, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 185.3*, 184.4, 142.1, 142.1*, 141.5, 141.5*, 127.9, 127.9*, 127.9, 127.9*, 127.9, 127.8*, 127.8, 125.4, 125.4*, 125.2*, 125.2, 82.2*, 81.9, 62.7*, 62.2, 59.6, 59.4, 35.4, 35.4*, 35.3*, 35.3, 34.5*, 33.1*, 32.6, 30.6, 29.2*, 28.5, 28.0*, 27.6*, 27.6*, 27.5, 25.9, 25.4, 25.4*, 25.2*, 25.2, 9.2, 9.1*, 8.8. **HRMS** (ESI-TOF) calculated for $C_{28}H_{40}NOS$ [M+H]: m/*z* = 438.2825, found 438.2823 (ESI+).

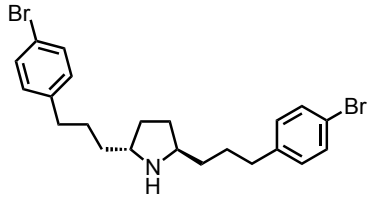


***O*–(pentan–3–yl) (2*R*,5*R*)–2,5–bis(3–(4–methoxyphenyl)propyl)pyrrolidine–1–carbothioate (4i)**. Prepared according to general procedure B using *O*–(pentan–3–yl) pyrrolidine–1–carbothioate **3** (20.2 mg, 0.1 mmol, 1 equiv.), $[Ir(cod)_2]OTf$ (5.7 mg, 0.01 mmol, 10 mol%), 4-allylanisole (123 μL, 0.8 mmol, 8 equiv.) in degassed PhCl (0.5 mL) at 80 ^oC under Ar for 6 h. The reaction was purified by preparative TLC (95:5 v/v Toluene/Acetone) to give **4i** (29.2 mg, 59%) as a colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$, rotamers in 1.5:1 ratio, peaks corresponding to minor rotamer starred): δ 7.13–7.09 (m, 2H), 7.08–7.01 (m, 2H), 6.85–6.77 (m, 4H), 5.45–5.34 (m, 1H), 4.44 (ddt, *J* = 10.5, 7.2, 3.5 Hz, 0.4H)*, 4.23 (ddd, *J* = 9.9, 7.1, 2.3 Hz, 0.6H), 4.04 (dt, *J* = 8.6, 4.4 Hz, 0.4H)*, 3.92 (ddd, *J* = 9.9, 7.3, 2.2 Hz, 0.6H), 3.79 (s, 3H), 3.78 (s, 3H), 2.73–2.63 (m, 1H), 2.61–2.47 (m, 3H), 2.39–2.19 (m, 1H), 2.04–1.92 (m, 2H), 1.88–1.75 (m, 1H), 1.73–1.45 (m, 10H), 1.37–1.21 (m, 2H), 0.91–0.83 (m, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 185.3*, 184.4, 157.4, 157.3*, 157.2*, 157.2, 134.2, 134.2*, 133.6*, 133.6, 128.8*, 128.7, 128.7, 113.3, 113.3*, 113.2, 82.1*, 81.9, 62.7*, 62.2, 59.7*, 59.5, 54.8, 34.5, 34.4*, 34.4, 34.3, 33.0*, 32.5, 30.5, 29.2*, 28.7, 28.7, 28.3*, 27.8*, 27.6*, 27.5, 25.9, 25.4, 25.4*, 25.2*, 25.2, 9.1, 9.1*, 8.8. **HRMS** (ESI-TOF) calculated for $C_{30}H_{44}NO_3S$ [M+H]: m/*z* = 498.3036, found 498.3035 (ESI+).



***O*–(pentan–3–yl) (2*R*,5*R*)–2,5–bis(3–(4–fluorophenyl)propyl)pyrrolidine–1–carbothioate (4j).** Prepared according to general procedure B using *O*–(pentan–3–yl) pyrrolidine–1–carbothioate **3** (20.2 mg, 0.1 mmol, 1 equiv.), $[Ir(cod)_2]OTf$ (5.7 mg, 0.01 mmol, 10 mol%), 1-allyl-4-fluorobenzene (108 μL, 0.8 mmol, 8 equiv.) in degassed PhCl

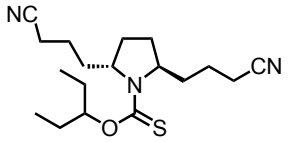
(0.5 mL) at 80 °C under Ar for 6 h. The reaction was purified by preparative TLC (100:1 v/v Toluene/Acetone) to give **4j** (45.4 mg, 96%) as a colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$, 1.5:1 mixture of rotamers, peaks corresponding to minor rotamer starred): δ 7.19–7.07 (m, 4H), 7.02–6.91 (m, 4H), 5.47–5.30 (m, 1H), 4.44 (ddt, *J* = 10.6, 7.1, 3.5 Hz, 0.4H)*, 4.23 (ddd, *J* = 9.9, 7.2, 2.3 Hz, 0.6H), 4.10–3.99 (m, 0.4H)*, 3.92 (ddd, *J* = 9.9, 7.2, 2.1 Hz, 0.6H), 2.69 (dtd, *J* = 17.0, 11.5, 10.7, 5.7 Hz, 1H), 2.64–2.40 (m, 3H), 2.40–2.16 (m, 1H), 2.08–1.93 (m, 2H), 1.85–1.73 (m, 1H), 1.72–1.55 (m, 7H), 1.53–1.42 (m, 2H), 1.38–1.24 (m, 3H), 0.95–0.81 (m, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ –118.0, –118.4*. **^{13}C NMR** (151 MHz, $CDCl_3$): δ 185.4*, 184.4, 160.8 (d, $J_{F–C}$ = 243 Hz), 160.7 (d, $J_{F–C}$ = 243 Hz), 137.6 (d, $J_{F–C}$ = 3.0 Hz), 137.0 (d, $J_{F–C}$ = 3.0 Hz), 129.2 (d, $J_{F–C}$ = 7.0 Hz), 129.1 (d, $J_{F–C}$ = 7.0 Hz), 114.7 (d, $J_{F–C}$ = 21 Hz), 114.4 (d, $J_{F–C}$ = 21 Hz), 82.2*, 81.9, 62.7*, 62.1, 59.6*, 59.4, 34.5, 34.5, 34.5*, 34.4*, 34.3*, 32.9*, 32.4, 31.5*, 30.8*, 30.4, 29.2, 29.2*, 28.9*, 28.6, 28.1*, 27.7*, 27.7*, 27.5, 25.9, 25.4, 25.4*, 25.2*, 25.2, 9.1, 9.1*, 8.7. **HRMS** (ESI-TOF) calculated for $C_{28}H_{38}F_2NOS$ [M+H]: m/*z* = 474.2637, found 474.2631 (ESI+).



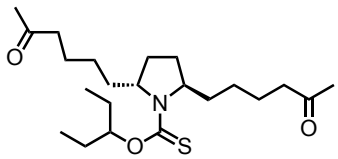
(2*R*,5*R*)–2,5–bis(3–(4–bromophenyl)propyl)pyrrolidine (4k). Prepared according to general procedure B using *O*–(pentan–3–yl) pyrrolidine–1–carbothioate **3** (20.2 mg, 0.1 mmol, 1 equiv.), $[Ir(cod)_2]OTf$ (5.7 mg, 0.01 mmol, 10 mol%), 1-allyl-4-bromobenzene (158 mg, 0.8 mmol, 8 equiv.) in degassed PhCl (0.5 mL) at 80 °C under Ar for 6 h. The reaction was purified by preparative TLC (100:1 v/v Toluene/Acetone) to give the desired di-alkylated product which co-eluted with 1-allyl-4-bromobenzene. The mixture was subjected to treatment with 75% TFA in H_2O for 2 h to give, after column chromatography (9:1 v/v CH_2Cl_2: MeOH), **4k** (28.8 mg, 62%) as a colourless oil.

^{1}H NMR (600 MHz, Acetone–d_6): δ 7.43 (d, *J* = 8.3 Hz, 4H), 7.23–7.08 (m, 4H), 3.08 (td, *J* = 6.3, 3.1 Hz, 1H), 2.98 (ddt, *J* = 6.7, 4.9, 2.1 Hz, 1H), 2.59 (td, *J* = 7.4, 1.4 Hz, 4H), 1.89 (ddd, *J* = 5.4, 3.0, 1.2 Hz, 1H), 1.78 (tt, *J* = 5.0, 2.2 Hz, 1H), 1.72–1.55

(m, 4H), 1.46–1.33 (m, 4H), 1.25–1.16 (m, 2H). **^{13}C NMR** (151 MHz, Acetone–d_6, 4 ^{13}C signals are overlapping): δ 141.7, 130.7, 130.0, 118.3, 58.1, 57.3, 36.0, 35.9, 34.6, 34.6, 32.1, 30.6, 29.2, 29.0. **HRMS** (ESI-TOF) calculated for $C_{22}H_{28}Br_2N$ [M+H]: m/*z* = 464.0583, found 464.0578 (ESI+).

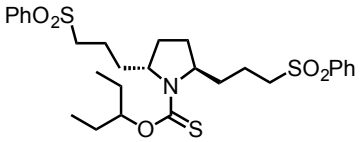


***O*–(pentan–3–yl) (2*R*,5*R*)–2,5–bis(3–cyanopropyl)pyrrolidine–1–carbothioate (4l)**. Prepared according to general procedure B using *O*–(pentan–3–yl) pyrrolidine–1–carbothioate **3** (20.2 mg, 0.1 mmol, 1 equiv.), [Ir(cod)$_2$]OTf (5.7 mg, 0.01 mmol, 10 mol%), allyl cyanide (65 μL, 0.8 mmol, 8 equiv.) in degassed PhCl (0.5 mL) at 80 ^{o}C under Ar for 6 h. The reaction was purified by preparative TLC (9:1 v/v Toluene/Acetone) to give **4l** (14.0 mg, 40%) as a colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$, rotamers in 4:1 ratio, peaks corresponding to minor rotamer starred): δ 5.42 (p, *J* = 6.1 Hz, 1H), 4.47 (td, *J* = 10.6, 9.7, 4.2 Hz, 0.2H)*, 4.22 (ddd, *J* = 9.9, 7.5, 2.0 Hz, 0.8H), 4.12 (ddd, *J* = 12.5, 8.8, 5.1 Hz, 0.2H)*, 3.99 (ddd, *J* = 9.9, 7.6, 2.2 Hz, 0.8H), 2.50 (ddd, *J* = 16.9, 7.4, 5.6 Hz, 1H), 2.44–2.33 (m, 4H), 2.29–1.89 (m, 3H), 1.83–1.61 (m, 10H), 1.53–1.34 (m, 2H), 0.92 (dt, *J* = 21.1, 7.4 Hz, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 186.3*, 184.9, 119.2*, 118.6, 83.0*, 82.8, 61.9*, 61.3, 58.7*, 58.4, 34.0*, 33.0*, 32.0, 30.2, 29.3*, 28.0*, 27.6, 26.1, 25.5, 25.5, 25.5, 25.4*, 22.7, 22.6, 22.2*, 21.9*, 16.8*, 16.8, 16.7*, 16.5, 9.3, 9.3*, 8.9. **HRMS** (ESI-TOF) calculated for $C_{18}H_{30}N_3OS$ [M+H]: m/*z* = 336.2104, found 336.2107 (ESI+).

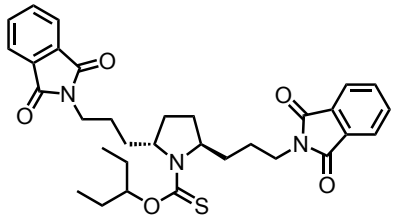


***O*–(pentan–3–yl) (2*R*,5*R*)–2,5–bis(5–oxohexyl)pyrrolidine–1–carbothioate (4m)**. Prepared according to general procedure B using *O*–(pentan–3–yl) pyrrolidine–1–carbothioate **3** (20.2 mg, 0.1 mmol, 1 equiv.), [Ir(cod)$_2$]OTf (5.7 mg, 0.01 mmol, 10 mol%), allylacetone (95 μL, 0.8 mmol, 8 equiv.) in degassed PhCl (0.5 mL) at 80 ^{o}C under Ar for 6 h. The reaction was purified by preparative TLC (2:1 v/v

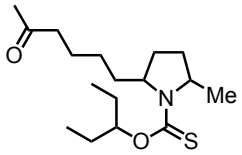
Hexanes/EtOAc) to give **4m** (29.0 mg, 73%) as a colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$, rotamers in 1.8:1 ratio, peaks corresponding to minor rotamer starred): δ 5.46–5.30 (m, 1H), 4.36 (tt, *J* = 7.1, 3.7 Hz, 0.35H)*, 4.17 (ddd, *J* = 10.2, 7.4, 2.3 Hz, 0.65H), 4.07–4.01 (m, 0.35H)*, 3.92 (ddd, *J* = 9.9, 7.3, 2.1 Hz, 0.65H), 2.54–2.38 (m, 4H), 2.34–2.18 (m, 1H), 2.13–2.11 (m, 6H), 2.06–1.93 (m, 2H), 1.82–1.51 (m, 11H), 1.39–1.08 (m, 6H), 0.91 (dt, *J* = 22.0, 7.5 Hz, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 208.8, 208.7*, 208.2*, 208.1, 185.3*, 184.4, 82.2*, 82.0, 62.6*, 62.1, 59.5*, 59.3, 43.1, 43.0, 34.6*, 32.7*, 32.6, 30.1, 29.5, 29.5*, 29.4, 29.1*, 27.6*, 27.5, 26.0, 25.9, 25.8*, 25.5, 25.5*, 25.4*, 25.4, 25.3, 23.1*, 23.1, 23.0*, 22.9, 9.2, 9.1*, 8.8, 8.8*. **HRMS** (ESI-TOF) calculated for $C_{22}H_{40}NO_3S$ [M+H]: m/*z* = 398.2723, found 398.2719 (ESI+).



***O*–(pentan–3–yl) (2*S*,5*S*)–2,5–bis(3–(phenylsulfonyl)propyl)pyrrolidine–1–carbothioate (4n)**. Prepared according to general procedure B using *O*–(pentan–3–yl) pyrrolidine–1–carbothioate **3** (20.2 mg, 0.1 mmol, 1 equiv.), $[Ir(cod)_2]OTf$ (5.7 mg, 0.01 mmol, 10 mol%), allyl phenyl sulfone (122 μL, 0.8 mmol, 8 equiv.) in degassed PhCl (0.5 mL) at 80 °C under Ar for 6 h. The reaction was purified by preparative TLC (1:1 v/v Hexanes/EtOAc) to give **4n** (31.1 mg, 55%) as a colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$, rotamers in 1.8:1 ratio, peaks corresponding to minor rotamer starred): δ 7.92–7.81 (m, 4H), 7.72–7.64 (m, 2H), 7.62–7.51 (m, 4H), 5.40–5.28 (m, 1H), 4.32 (td, *J* = 7.0, 3.8 Hz, 0.35H)*, 4.09 (ddd, *J* = 9.9, 7.4, 2.0 Hz, 0.65H), 4.01 (t, *J* = 7.6 Hz, 0.35H)*, 3.86 (ddd, *J* = 9.9, 7.8, 1.8 Hz, 0.65H), 3.33–3.18 (m, 1H), 3.16–2.95 (m, 3H), 2.36–2.13 (m, 1H), 2.11–1.89 (m, 2H), 1.88–1.66 (m, 7H), 1.65–1.51 (m, 4H), 1.45–1.28 (m, 2H), 0.83 (dt, *J* = 9.9, 7.4 Hz, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 186.0*, 184.6, 138.7, 138.7*, 138.6*, 138.5, 133.4, 133.4, 133.2*, 128.9, 128.8, 127.6*, 127.6, 127.5, 127.5*, 82.7*, 82.5, 61.9*, 61.3, 59.0*, 58.6, 55.5*, 55.4, 55.3*, 55.2, 33.5*, 31.9*, 31.6, 29.2, 29.1*, 27.7*, 27.5, 25.9, 25.4, 25.4, 25.4, 25.3*, 19.7, 19.4*, 19.1, 9.2, 9.2*, 8.8, 8.8*. **HRMS** (ESI-TOF) calculated for $C_{28}H_{40}NO_5S_3$ [M+H]: m/*z* = 566.2063, found 566.2058 (ESI+).

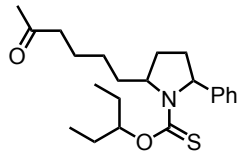


***O*–(pentan–3–yl) (2*R*,5*R*)–2,5–bis(3–(1,3–dioxoisoindolin–2–yl)propyl)pyrrolidine–1–carbothioate (4o)**. Prepared according to general procedure B using *O*–(pentan–3–yl) pyrrolidine–1–carbothioate **3** (20.2 mg, 0.1 mmol, 1 equiv.), $[Ir(cod)_2]OTf$ (5.7 mg, 0.01 mmol, 10 mol%), 2-allylisoindoline-1,3-dione (150 mg, 0.8 mmol, 8 equiv.) in degassed PhCl (0.5 mL) at 80 °C under Ar for 6 h. The reaction was purified by preparative TLC (1:1 v/v Hexanes/EtOAc) to give **4o** (40.2 mg, 70%) as a colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$, rotamers in 1.8:1 ratio, peaks corresponding to minor rotamer starred): δ 7.86–7.80 (m, 4H), 7.76–7.65 (m, 4H), 5.37–5.27 (m, 1H), 4.42 (ddt, *J* = 10.8, 7.4, 3.7 Hz, 0.35H)*, 4.20 (ddd, *J* = 9.8, 7.1, 2.3 Hz, 0.65H), 4.04 (tt, *J* = 8.1, 4.6 Hz, 0.35H)*, 3.91 (ddd, *J* = 9.8, 7.2, 2.1 Hz, 0.65H), 3.79–3.72 (m, 1H), 3.71–3.62 (m, 3H), 2.40–2.23 (m, 1H), 2.01 (tdt, *J* = 14.1, 11.9, 7.0 Hz, 2H), 1.91–1.50 (m, 10H), 1.44 (ddd, *J* = 13.9, 7.5, 6.3 Hz, 1H), 1.38–1.23 (m, 2H), 0.89–0.69 (m, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 185.7*, 184.6, 167.9, 167.9*, 167.8*, 167.8, 133.5, 133.4, 131.8*, 131.7, 131.6, 131.6*, 122.8, 122.7*, 122.7, 82.3*, 82.0, 62.3*, 61.7, 59.3*, 59.0, 37.4*, 37.3, 37.2, 32.1*, 30.4*, 30.3, 29.2*, 28.0, 27.6*, 27.6, 25.9, 25.7, 25.5, 25.3, 25.2, 25.2*, 25.1*, 25.0*, 9.1, 9.0*, 8.7. **HRMS** (ESI-TOF) calculated for $C_{32}H_{38}N_3O_5S$ [M+H]: m/*z* = 576.2527, found 576.2530 (ESI+).

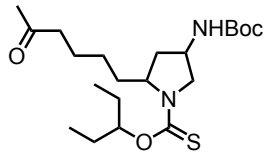


***O*–(pentan–3–yl) 2–methyl–5–(5–oxohexyl)pyrrolidine–1–carbothioate (6a)**. Prepared according to general procedure B using *O*-(pentan-3-yl) 2-methylpyrrolidine-1-carbothioate **5a** (21.5 mg, 0.1 mmol, 1 equiv.), $[Ir(cod)_2]OTf$ (5.7 mg, 0.01 mmol, 10 mol%), allylacetone (95 μL, 0.8 mmol, 8 equiv.) in degassed PhCl (0.5 mL) at 80 °C under Ar for 6 h. The reaction was purified by preparative TLC (9:1 v/v Toluene/Acetone) to give **6a** (23.8 mg, 76%) as a colourless oil. **^{1}H NMR** (600 MHz,

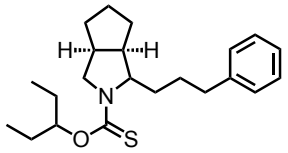
$CDCl_3$, mixture of rotamers and 1.2:1 inseparable mixture of diastereomers): δ 5.41 (td, *J* = 6.0, 4.1 Hz, 1H), 4.58–4.31 (m, 0.75H), 4.27–4.09 (m, 1H), 4.08–3.88 (m, 0.5H), 2.59–2.38 (m, 2H), 2.33–1.85 (m, 6H), 1.85–1.41 (m, 8H), 1.41–1.13 (m, 6H), 1.08–0.76 (m, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 208.8, 208.8, 208.2, 208.1, 185.2, 185.1, 184.6, 184.5, 82.2, 82.1, 82.0, 62.8, 62.3, 59.6, 59.4, 58.5, 57.6, 55.3, 54.7, 43.1, 43.0, 34.7, 32.7, 32.6, 31.4, 30.3, 30.2, 30.1, 29.5, 29.5, 29.4, 29.1, 28.8, 27.5, 27.3, 26.0, 25.8, 25.6, 25.5, 25.5, 25.4, 25.4, 25.4, 25.4, 25.3, 23.1, 23.1, 23.0, 22.9, 21.2, 19.5, 19.4, 17.5, 9.2, 9.2, 9.1, 9.1, 8.8, 8.8. **HRMS** (ESI-TOF) calculated for $C_{17}H_{32}NO_2S$ [M+H]: m/*z* = 314.2148, found 314.2143 (ESI+).



***O*–(pentan–3–yl) 2–(5–oxohexyl)–5–phenylpyrrolidine–1–carbothioate (6b)**. Prepared according to general procedure B using *O*-(pentan-3-yl) 2-phenylpyrrolidine-1-carbothioate **5b** (27.7 mg, 0.1 mmol, 1 equiv.), $[Ir(cod)_2]OTf$ (5.7 mg, 0.01 mmol, 10 mol%), allylacetone (95 μL, 0.8 mmol, 8 equiv.) in degassed PhCl (0.5 mL) at 80 ^{o}C under Ar for 6 h. The reaction was purified by preparative TLC (9:1 v/v Toluene/Acetone) to give **6b** (25.5 mg, 68%) as a colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$, mixture of rotamers and 1:1 inseparable mixture of diastereomers): δ 7.33–7.13 (m, 3H), 7.08–7.00 (m, 2H), 5.51 (d, *J* = 8.3 Hz, 0.22H), 5.40 (t, *J* = 6.0 Hz, 0.21H), 5.24–5.05 (m, 1.4H), 4.88 (t, *J* = 7.9 Hz, 0.12H), 4.52 (ddd, *J* = 9.9, 7.8, 2.4 Hz, 0.75H), 4.25 (ddd, *J* = 10.2, 7.9, 2.1 Hz, 0.17H), 2.61–2.33 (m, 4H), 2.20–1.91 (m, 4H), 1.85–1.64 (m, 4H), 1.54–1.30 (m, 5H), 1.13–0.90 (m, 3H), 0.80 (t, *J* = 7.4 Hz, 3H), 0.27 (dt, *J* = 46.4, 7.4 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 208.8, 208.1, 185.8, 185.0, 143.3, 142.1, 128.0, 127.9, 127.8, 126.3, 126.1, 125.0, 124.9, 124.5, 82.8, 82.5, 82.3, 65.5, 64.3, 63.7, 62.8, 60.2, 43.1, 43.1, 43.1, 34.5, 32.9, 32.3, 31.2, 30.6, 29.5, 29.5, 29.2, 26.5, 26.1, 25.9, 25.9, 25.6, 25.5, 25.2, 24.9, 24.6, 23.1, 22.9, 9.3, 8.9, 8.7, 8.7, 8.0. **HRMS** (ESI-TOF) calculated for $C_{22}H_{34}NO_2S$ [M+H]: m/*z* = 376.2305, found 376.2300 (ESI+).

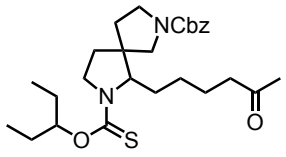


***O*–(pentan–3–yl) 4–((*tert*–butoxycarbonyl)amino)–2–(5–oxohexyl)pyrrolidine–1–carbothioate (6c)**. Prepared according to general procedure B using *O*-(pentan-3-yl) 3-((*tert*-butoxycarbonyl)amino)pyrrolidine-1-carbothioate **5c** (31.7 mg, 0.1 mmol, 1 equiv.), $[Ir(cod)_2]OTf$ (5.7 mg, 0.01 mmol, 10 mol%), allylacetone (95 μL, 0.8 mmol, 8 equiv.) in degassed PhCl (0.5 mL) at 80 °C under Ar for 6 h. The reaction was purified by preparative TLC (9:1 v/v Toluene/Acetone) to give **6c** (12.4 mg, 30%) as a colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$, mixture of rotamers and 1.3:1 inseparable mixture of diastereomers): δ 5.55–5.25 (m, 1H), 4.58–4.49 (m, 0.6H), 4.38 (td, *J* = 15.6, 12.8, 7.8 Hz, 1.4H), 4.22–4.11 (q, *J* = 9.0, 7.8 Hz, 0.8H), 4.03 (dd, *J* = 12.6, 7.5 Hz, 0.6H), 3.83 (dd, *J* = 12.5, 7.0 Hz, 0.3H), 3.60 (dd, *J* = 12.7, 7.5 Hz, 0.35H), 3.39 (dd, *J* = 12.7, 7.1 Hz, 0.45H), 2.65–2.37 (m, 2H), 2.16 (t, *J* = 2.7 Hz, 4H), 1.99–1.84 (m, 1H), 1.79–1.62 (m, 6H), 1.54–1.44 (m, 9H), 1.38–1.24 (m, 4H), 1.04–0.82 (m, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 208.5, 208.0, 185.4, 185.4, 154.8, 154.6, 83.1, 82.5, 60.2, 57.7, 56.2, 52.8, 48.3, 47.3, 42.9, 42.9, 36.5, 34.8, 33.1, 31.1, 30.5, 29.5, 29.5, 29.5, 27.9, 27.9, 25.5, 25.5, 25.5, 25.4, 25.3, 25.2, 25.0, 22.9, 22.8, 9.1, 8.9, 8.9, 8.8, 8.8. **HRMS** (ESI-TOF) calculated for $C_{21}H_{39}N_2O_4S$ [M+H]: m/*z* = 415.2625, found 415.2630 (ESI+).



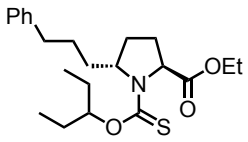
***O*–(pentan–3–yl) (3a*S*,6a*R*)–1–(3–phenylpropyl)hexahydrocyclopenta[*c*]pyrrole–2(1*H*)–carbothioate (6d)**. Prepared according to general procedure B using *O*-(pentan-3-yl) hexahydrocyclopenta[*c*]pyrrole-2(1*H*)-carbothioate **5d** (24.1 mg, 0.1 mmol, 1 equiv.), $[Ir(cod)_2]OTf$ (5.7 mg, 0.01 mmol, 10 mol%), allylbenzene (110 μL, 0.8 mmol, 8 equiv.) in degassed PhCl (0.5 mL) at 80 °C under Ar for 6 h. The reaction was purified by preparative TLC (100:1 v/v

Toluene/Acetone) to give **6d** (14.3 mg, 42%) as a colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$, rotamers in 2:1 ratio, peaks corresponding to minor rotamer starred): δ 7.31–7.23 (m, 2H), 7.23–7.10 (m, 3H), 5.42–5.33 (m, 1H), 4.34 (ddd, *J* = 10.0, 3.9, 1.7 Hz, 0.35H)*, 3.97 (ddd, *J* = 9.3, 3.4, 1.5 Hz, 0.7H), 3.78 (d, *J* = 7.2 Hz, 1.4H), 3.52 (qd, *J* = 12.8, 6.6 Hz, 0.7H)*, 2.77–2.65 (m, 1H), 2.65–2.54 (m, 2H), 2.44–2.29 (m, 1H), 2.03 (dddd, *J* = 12.8, 11.0, 5.5, 3.7 Hz, 0.39H)*, 1.92–1.76 (m, 2H), 1.73–1.37 (m, 12H), 0.96–0.80 (m, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 184.6, 142.1*, 141.5, 127.9*, 127.9, 127.9, 127.8*, 125.4, 125.2*, 82.5, 82.0*, 68.6*, 65.4, 57.5, 52.8*, 48.7, 47.0*, 41.1*, 39.8, 35.4*, 35.4, 33.6, 32.5*, 32.3, 32.1*, 31.9, 27.6*, 27.5, 25.6*, 25.6*, 25.5, 25.4, 25.3*, 25.0, 9.1, 8.9*, 8.9*, 8.8. **HRMS** (ESI-TOF) calculated for $C_{22}H_{34}NOS$ [M+H]: m/*z* = 360.2356, found 360.2362 (ESI+).

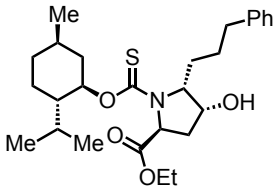


Benzyl 6–(5–oxohexyl)–7–((pentan–3–yloxy)carbonothioyl)–2,7–diazaspiro[4.4]nonane–2–carboxylate (6e). Prepared according to general procedure B using benzyl 7-((pentan-3-yloxy)carbonothioyl)-2,7-diazaspiro[4.4]nonane-2-carboxylate **5e** (39.0 mg, 0.1 mmol, 1 equiv.), $[Ir(cod)_2]OTf$ (5.7 mg, 0.01 mmol, 10 mol%), $HBF_4.Et_2O$ (1.4 µl, 0.01 mmol), allylacetone (95 µL, 0.8 mmol, 8 equiv.) in degassed PhCl (0.5 mL) at 80 ^oC under Ar for 6 h. The reaction was purified by preparative TLC (9:1 v/v Toluene/Acetone) to give **6e** (20.5 mg, 40%) as a colourless oil. **^{1}H NMR** (600 MHz, Acetone–d_6, rotamers in 2.6:1 ratio, rotameric peaks overlapping): δ 7.52–7.12 (m, 5H), 5.46–5.28 (m, 1H), 5.19–4.96 (m, 2H), 4.35–3.82 (m, 2H), 3.61–3.09 (m, 5H), 2.47 (dd, *J* = 8.4, 6.2 Hz, 2H), 2.40–2.19 (m, 1H), 2.09–2.06 (m, 3H), 2.02–1.78 (m, 3H), 1.75–1.47 (m, 8H), 1.30 (dt, *J* = 9.1, 6.2 Hz, 3H), 0.99–0.78 (m, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$, peaks corresponding to minor rotamer starred): δ 208.6*, 208.0, 185.8*, 185.7, 154.3, 136.3, 128.0*, 128.0, 127.6, 127.5*, 127.5, 83.2, 82.4*, 66.5*, 66.4, 60.9, 58.3, 56.3*, 55.5*, 54.8, 54.2*, 47.4*, 46.5, 45.6*, 45.0, 44.6*, 44.3, 42.9, 40.6*, 40.0*, 39.0, 35.8*, 34.9, 34.2*, 33.8, 29.5, 29.3*, 25.6, 25.3*, 25.0, 24.7*, 23.1*, 22.9, 9.1, 9.0, 8.9*, 8.8*. **HRMS** (ESI-TOF) calculated for $C_{27}H_{41}N_2O_4S$ [M+H]: m/*z* = 489.2782,

found 489.2781 (ESI+).



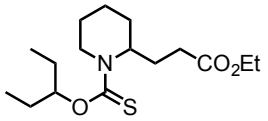
Ethyl (2*S*,5*R*)–1–((pentan–3–yloxy)carbonothioyl)–5–(3–phenylpropyl)pyrrolidine–2–carboxylate (6f). Prepared according to general procedure B using ethyl ((pentan-3-yloxy)carbonothioyl)-*L*-prolinate **5f** (27.3 mg, 0.1 mmol, 1 equiv.), $[Ir(cod)_2]OTf$ (5.7 mg, 0.01 mmol, 10 mol%), allylbenzene (110 μL, 0.8 mmol, 8 equiv.) in degassed PhCl (0.5 mL) at 80 ^oC under Ar for 6 h. The reaction was purified by preparative HPLC (20-100% MeCN over 40 min) to give **6f** (18.8 mg, 48%, major diastereomer) as a colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$, 1.5:1 mixture of rotamers, peaks corresponding to minor rotamer starred, *trans*–diastereomer): δ 7.39–7.08 (m, 5H), 5.37 (dt, *J* = 7.8, 6.0 Hz, 1H), 4.78 (*app.* d, *J* = 9.0 Hz, 0.45H), 4.50 (ddd, *J* = 10.6, 7.9, 2.6 Hz, 0.3H)*, 4.48–4.45 (m, 0.3H)*, 4.25–4.19 (m, 2H), 4.18–4.09 (m, 0.45H), 2.82–2.59 (m, 2H), 2.39–2.12 (m, 2H), 2.09–1.95 (m, 2H), 1.87–1.62 (m, 9H), 1.44–1.24 (m, 6H), 1.02–0.83 (m, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 186.5, 185.2*, 171.0*, 170.9, 141.9*, 141.4, 127.9, 127.9*, 127.9, 127.8*, 125.5, 125.3*, 83.2, 82.7*, 63.8, 62.7*, 60.7*, 60.6, 60.0*, 59.7, 35.3, 35.2*, 32.7, 30.9*, 30.5, 29.2, 28.3*, 28.2*, 28.1, 26.9, 26.3*, 25.5, 25.3*, 13.7, 13.6*, 9.1, 9.0*, 8.8, 8.8*. **HRMS** (ESI-TOF) calculated for $C_{22}H_{34}NO_3S$ [M+H]: m/*z* = 392.2254, found 392.2258 (ESI+).



Ethyl (2*S*,4*R*,5*R*)–4–hydroxy–1–((((1*R*,2*S*,5*R*)–2–isopropyl–5–methylcyclohexyl)oxy)carbonothioyl)–5–(3–phenylpropyl)pyrrolidine–2–carboxylate (6g). Prepared according to general procedure B using ethyl (2*S*,4*R*)-4-hydroxy-1-((((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)carbonothioyl) pyrrolidine-2-carboxylate **5g** (35.7 mg, 0.1 mmol, 1 equiv.), $[Ir(cod)_2]OTf$ (5.7 mg, 0.01 mmol, 10 mol%), $HBF_4.Et_2O$ (1.4 μl, 0.01 mmol), allylbenzene (110 μL, 0.8 mmol, 8

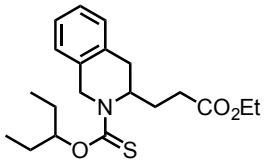
equiv.) in degassed PhCl (0.5 mL) at 80 °C under Ar for 24 h. The reaction was purified by preparative HPLC (20-100% MeCN over 40 min) to give **6g** (16.6 mg, 35%, major diastereomer) as a colourless oil.

^{1}H NMR (600 MHz, $CDCl_3$, 1.5:1 mixture of rotamers, peaks corresponding to minor rotamer starred, major, *trans*–diastereomer): δ 7.33–7.29 (m, 2H), 7.25–7.11 (m, 3H), 5.30 (td, *J* = 10.8, 4.6 Hz, 0.4H)*, 5.26–5.21 (m, 0.6H), 4.92–4.86 (m, 0.4H)*, 4.59 (dd, *J* = 10.2, 7.6 Hz, 0.6H), 4.48–4.44 (m, 0.4H)*, 4.28–4.18 (m, 2.4H), 4.16–4.08 (m, 0.4H), 2.83–2.59 (m, 2H), 2.36 (dddd, *J* = 13.9, 9.6, 7.9, 1.5 Hz, 1H), 2.30–2.14 (m, 2H), 1.99–1.68 (m, 6H), 1.49–1.37 (m, 3H), 1.33–1.26 (m, 6H), 1.18–1.08 (m, 1H), 0.98–0.88 (m, 12H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 187.0*, 185.5, 171.4, 171.0*, 141.8, 141.4*, 128.0*, 127.9, 127.9*, 127.8, 125.5*, 125.3, 80.9, 80.9*, 73.6*, 72.4, 71.9, 68.4*, 62.2, 60.8, 60.7*, 59.0, 47.2*, 47.0, 40.5*, 40.0, 36.4, 35.8*, 35.5*, 35.3, 33.9, 33.8*, 32.0*, 30.8*, 30.7, 30.2, 29.3*, 28.1, 25.9, 25.6*, 23.0, 22.5*, 21.6, 20.6*, 16.4, 16.0*, 13.7, 13.6*. **HRMS** (ESI-TOF) calculated for $C_{27}H_{42}NO_4S$ [M+H]: m/*z* = 476.2829, found 476.2821 (ESI+).



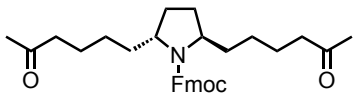
Ethyl 3–(1–((pentan–3–yloxy)carbonothioyl)piperidin–2–yl)propanoate (6h). Prepared according to general procedure B using *O*–(pentan–3–yl) piperidine–1–carbothioate **5h** (21.5 mg, 0.1 mmol, 1 equiv.), $[Ir(cod)_2]OTf$ (5.7 mg, 0.01 mmol, 10 mol%), $HBF_4.Et_2O$ (1.4 μl, 0.01 mmol), ethyl acrylate (80 μL, 0.8 mmol, 8 equiv.) in degassed PhCl (0.5 mL) at 80 °C under Ar for 24 h. The reaction was purified by preparative TLC (2:1 v/v Hexanes/EtOAc) to give **6h** (9.50 mg, 30%) as colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$, 1:1 mixture of rotamers): δ 5.56–5.39 (m, 1H), 5.16 (dd, *J* = 13.4, 3.9 Hz, 0.5H), 4.87–4.80 (m, 0.5H), 4.61–4.46 (m, 0.5H), 4.21–4.08 (m, 2H), 3.15–3.01 (m, 0.6H), 2.87 (t, *J* = 13.7 Hz, 0.6H), 2.53–2.41 (m, 0.5H), 2.24 (ddtd, *J* = 45.0, 24.4, 9.9, 5.4 Hz, 2H), 1.94–1.55 (m, 10H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.05–0.85 (m, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 187.2, 187.2, 172.9, 172.5, 83.3, 83.0, 60.1, 60.0, 55.5, 51.6, 48.4, 44.4, 39.9, 30.6, 30.5, 28.7, 27.6, 27.1, 25.6, 25.5, 25.4, 25.4, 25.3, 24.7, 24.6, 24.5, 24.1, 18.6, 18.5, 13.7, 13.7, 10.8, 9.1, 9.0,

8.9, 8.9. **HRMS** (ESI-TOF) calculated for $C_{16}H_{30}NO_3S$ [M+H]: m/*z* = 316.1941, found 316.1946 (ESI+).



Ethyl 3–(2–((pentan–3–yloxy)carbonothioyl)–1,2,3,4–tetrahydroisoquinolin–3–yl)propanoate (6i). Prepared according to general procedure B using *O*-(pentan-3-yl) 3,4-dihydroisoquinoline-2(1*H*)-carbothioate **5i** (26.3 mg, 0.1 mmol, 1 equiv.), $[Ir(cod)_2]OTf$ (5.7 mg, 0.01 mmol, 10 mol%), $HBF_4.Et_2O$ (1.4 μl, 0.01 mmol), ethyl acrylate (80 μL, 0.8 mmol, 8 equiv.) in degassed PhCl (0.5 mL) at 80 °C under Ar for 24 h. The reaction was purified by preparative TLC (2:1 v/v Hexanes/EtOAc) to give **6i** (12.7 mg, 30%) as colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$, 1.3:1 mixture of rotamers, peaks corresponding to minor rotamer starred): δ 7.24–7.08 (m, 4H), 5.70 (dtd, *J* = 8.4, 6.0, 2.0 Hz, 0.40H)*, 5.61 (d, *J* = 17.7 Hz, 0.47H), 5.55–5.48 (m, 1H), 5.17 (d, *J* = 17.7 Hz, 0.4H)*, 5.05 (ddt, *J* = 9.2, 6.0, 2.9 Hz, 0.47H), 4.58 (d, *J* = 17.7 Hz, 0.48H), 4.38 (d, *J* = 17.7 Hz, 0.42H)*, 4.15–4.00 (m, 2H), 3.18 (dd, *J* = 16.1, 5.5 Hz, 0.44H)*, 3.07 (dd, *J* = 16.0, 5.5 Hz, 0.55H), 2.74 (dt, *J* = 16.1, 1.7 Hz, 1H), 2.47–2.20 (m, 2H), 1.94–1.58 (m, 6H), 1.22 (td, *J* = 7.1, 1.6 Hz, 3H), 1.01–0.88 (m, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 187.6*, 187.2, 172.5*, 172.2, 131.9*, 131.7, 131.1, 130.9*, 128.8*, 128.4, 126.6*, 126.4, 126.2, 126.0*, 125.8, 125.5*, 83.5, 60.1, 60.0*, 53.8*, 50.5, 48.4, 43.9*, 32.8, 32.1*, 30.7*, 30.5, 26.5, 26.1*, 25.5*, 25.5, 25.4, 13.7, 13.7*, 9.2, 9.0*, 9.0*, 8.9. **HRMS** (ESI-TOF) calculated for $C_{20}H_{30}NO_3S$ [M+H]: m/*z* = 364.1941, found 364.1941 (ESI+).

D. Deprotection of Auxiliary



(9*H*-fluoren-9-yl)methyl (2*R*,5*R*)-2,5-bis(5-oxohexyl)pyrrolidine-1-carboxylate (7)

4m (120 mg, 0.3 mmol) was dissolved in 75% TFA in H_2O (vol/vol, 3 mL) and the reaction was heated to 75 °C for 2 h. At this point, solvent was removed in vacuo to give the crude amine intermediate as a trifluoroacetate salt. This amine was immediately

suspended into a 1:1 (vol/vol) mixture of dioxane and H_2O (1 mL). Saturated aqueous $NaHCO_3$ solution (0.8 mL) along with solid $NaHCO_3$ were added to the above reaction mixture until pH > 7. The reaction mixture was allowed to stir at room temperature for 16 h. At this point, water (20 mL) was added and the reaction was extracted into EtOAc (40 mL). The organic layer was washed with brine and dried over anhydrous Na_2SO_4 to give a crude intermediate that was purified by column chromatography to give **7** as a colourless oil (100 mg, 68% over two steps).

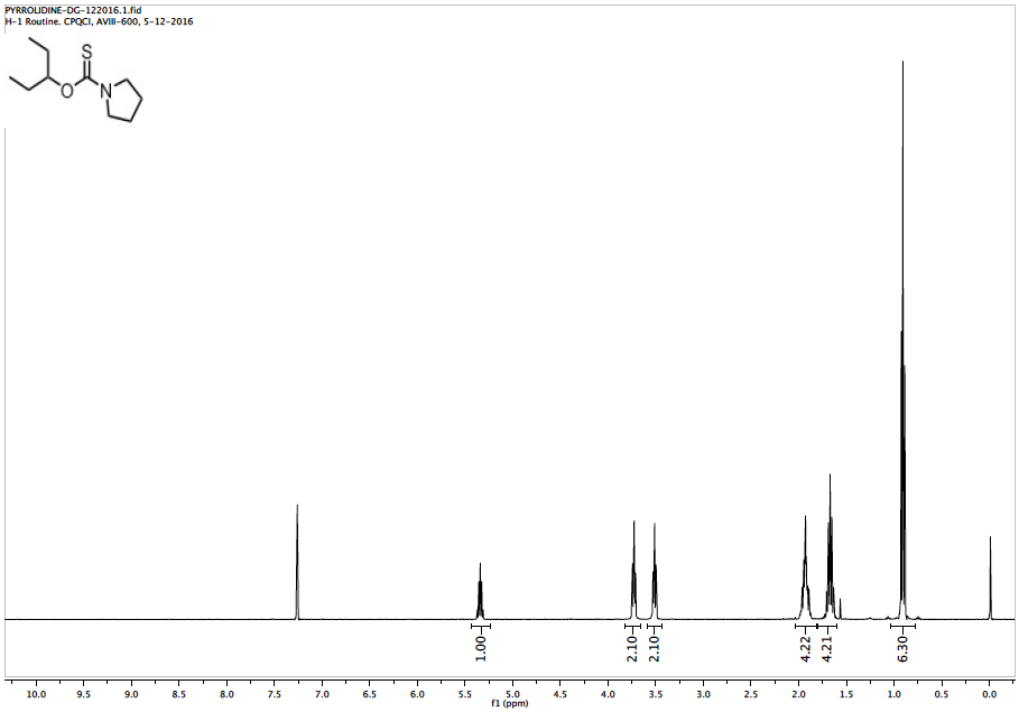
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.76 (dd, *J* = 7.4, 1.2 Hz, 2H), 7.59 (ddd, *J* = 7.6, 3.4, 1.0 Hz, 2H), 7.44–7.36 (m, 2H), 7.31 (tt, *J* = 7.4, 1.5 Hz, 2H), 4.63–4.45 (m, 2H), 4.24–4.18 (m, 1H), 3.78–3.68 (m, 1H), 3.50–3.42 (m, 1H), 2.46–2.30 (m, 4H), 2.12 (s, 3H), 2.10 (s, 3H), 1.89–1.80 (m, 2H), 1.62–1.53 (m, 4H), 1.47–1.33 (m, 3H), 1.27–0.95 (m, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 208.6, 208.3, 155.0, 153.8, 143.8, 143.7, 141.0, 140.9, 140.9, 127.1, 126.6, 126.5, 126.5, 124.3, 119.4, 119.4, 65.4, 57.4, 57.0, 47.1, 43.2, 43.2, 43.1, 32.9, 31.6, 29.4, 26.8, 26.0, 25.8, 25.6, 23.3, 23.2. **HRMS** (ESI-TOF) calculated for $C_{31}H_{40}NO_4$ [M+H]: m/*z* = 490.2952, found 490.2956 (ESI+).

3. References

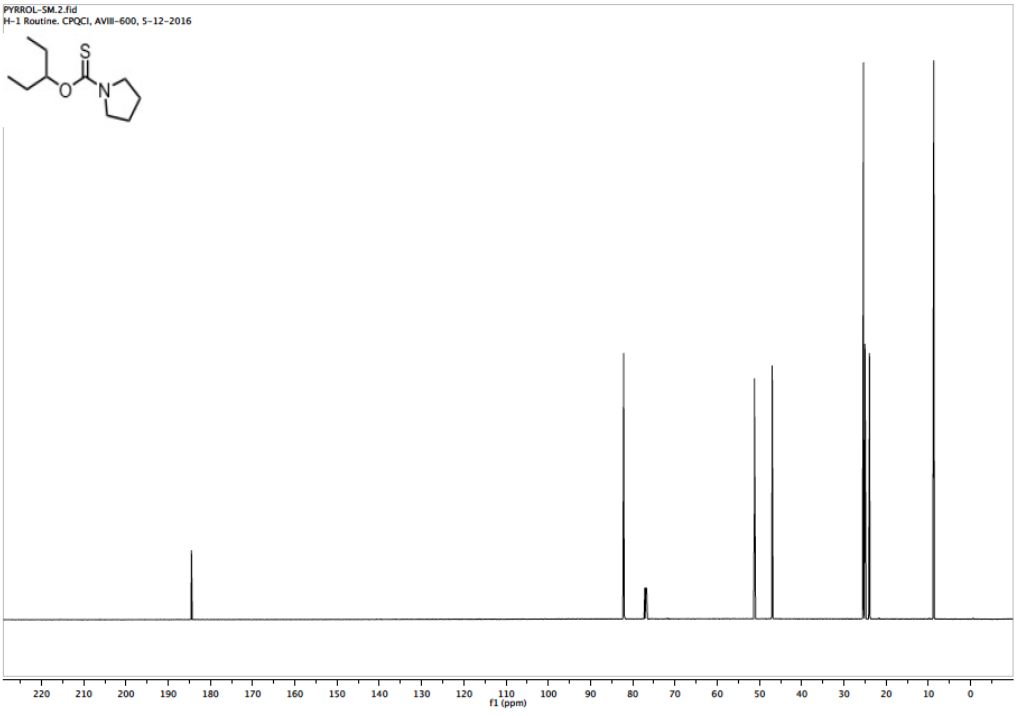
1. K. Tsuchikama, M. Kasagawa, K. Endo, T. Shibata, *Org. Lett.* **2009**, *11*, 1821.

4. NMR spectra

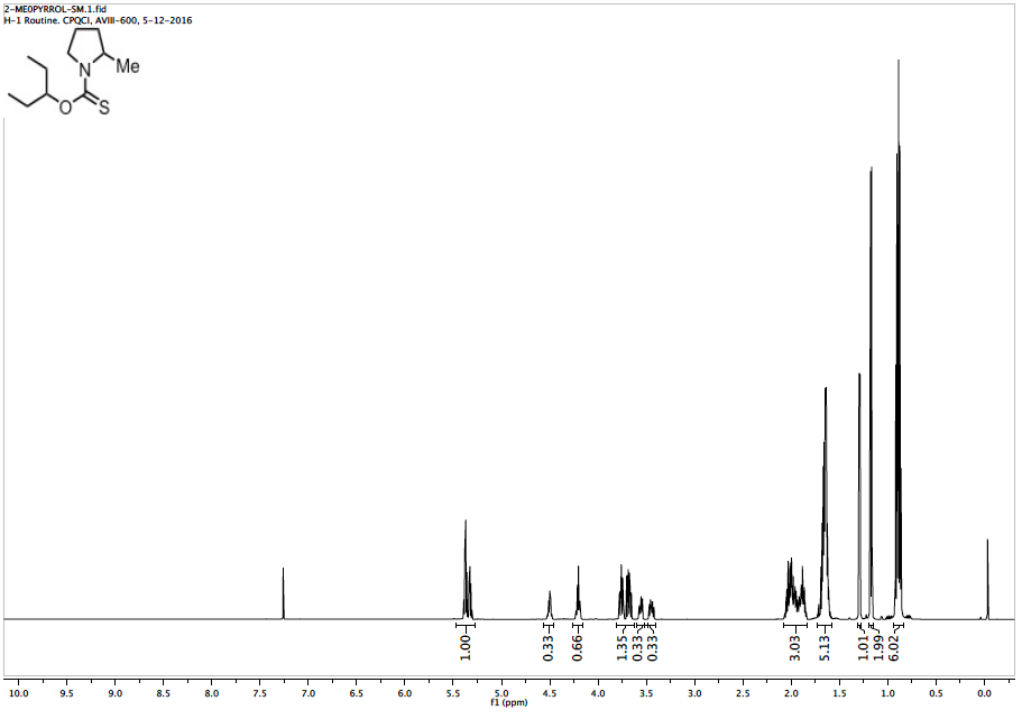
^{1}H NMR spectrum of compound **3**



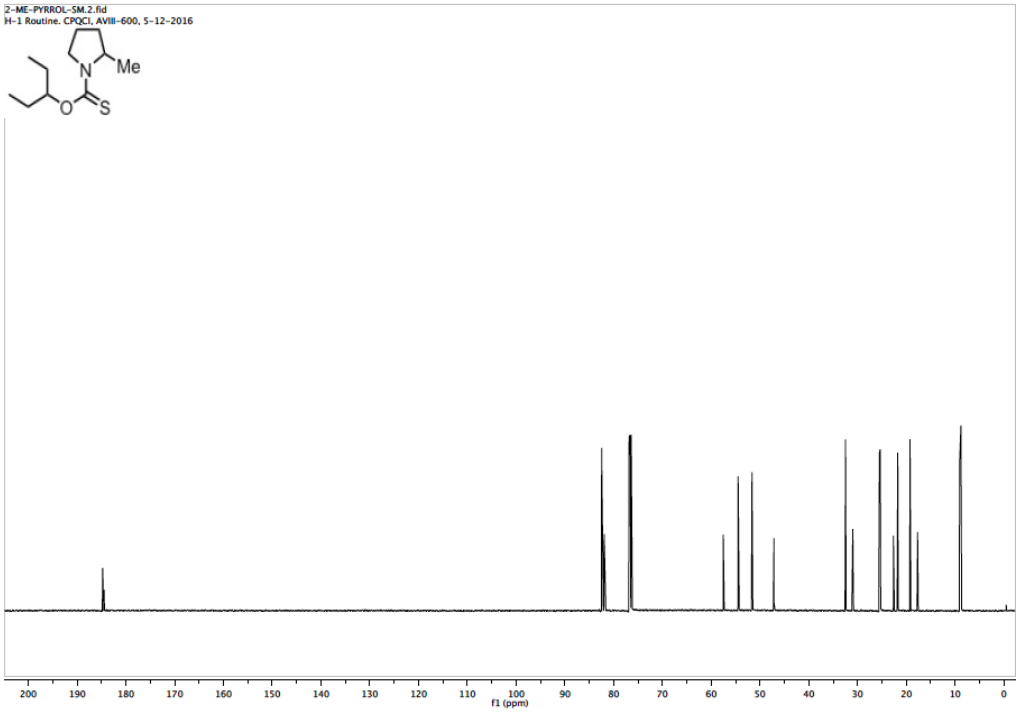
^{13}C NMR spectrum of compound **3**



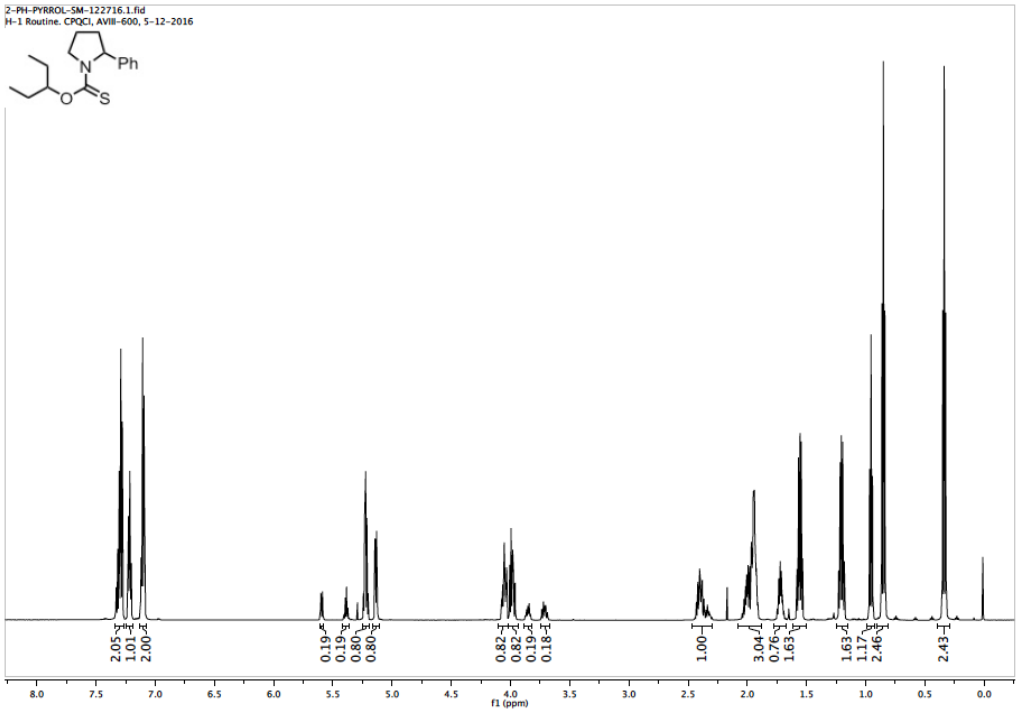
^{1}H NMR spectrum of compound **5a**



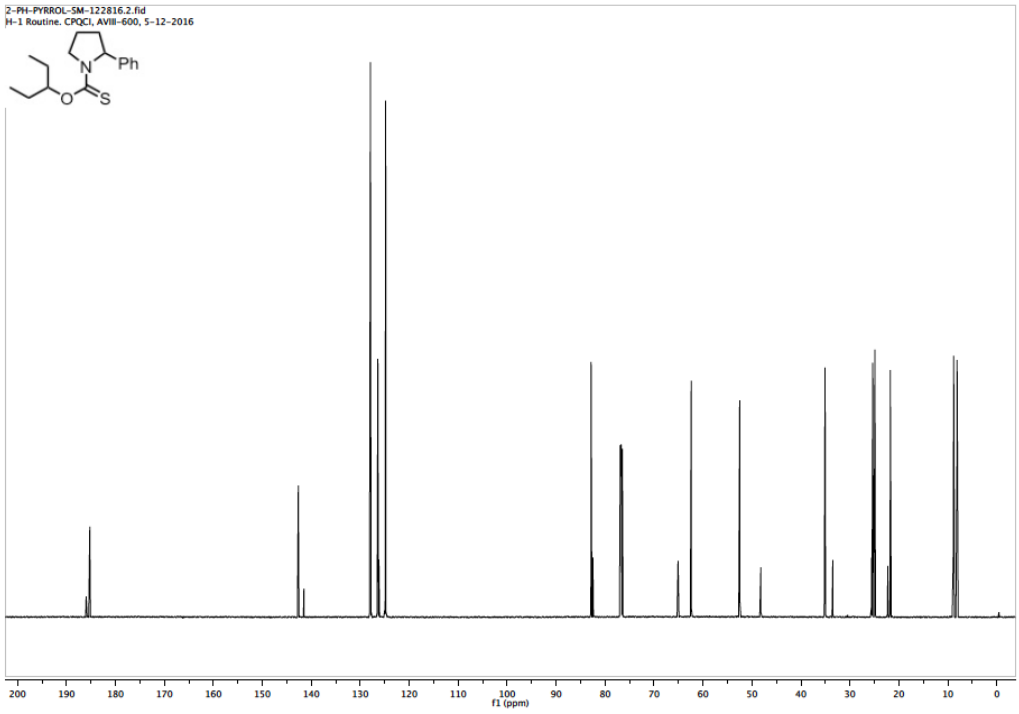
^{13}C NMR spectrum of compound **5a**



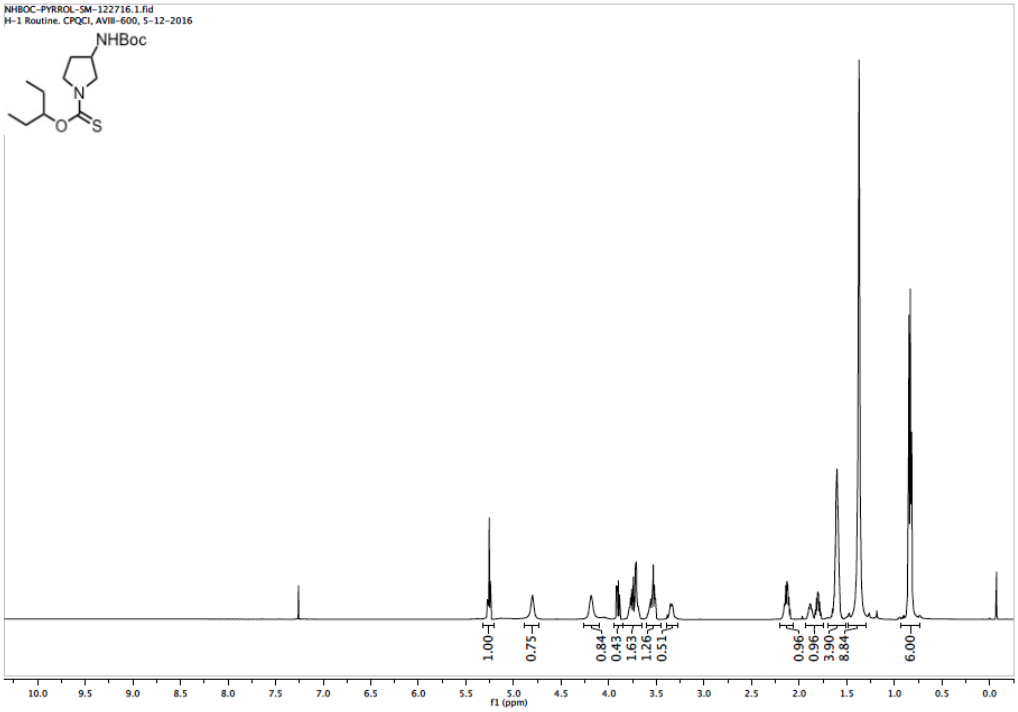
^{1}H NMR spectrum of compound **5b**



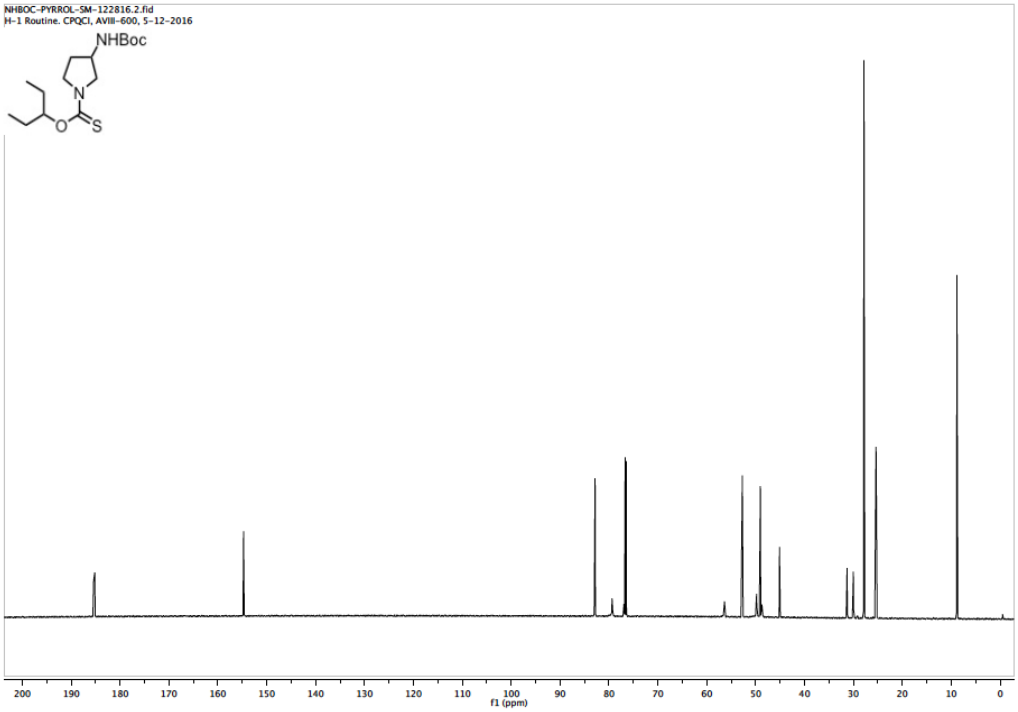
^{13}C NMR spectrum of compound **5b**



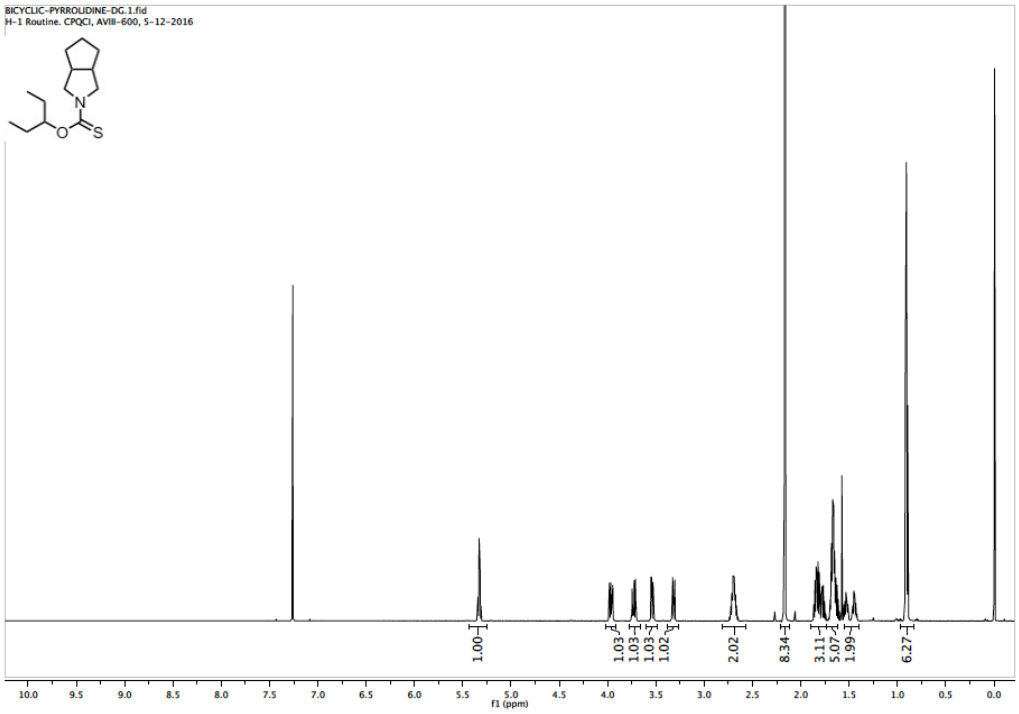
^{1}H NMR spectrum of compound **5c**



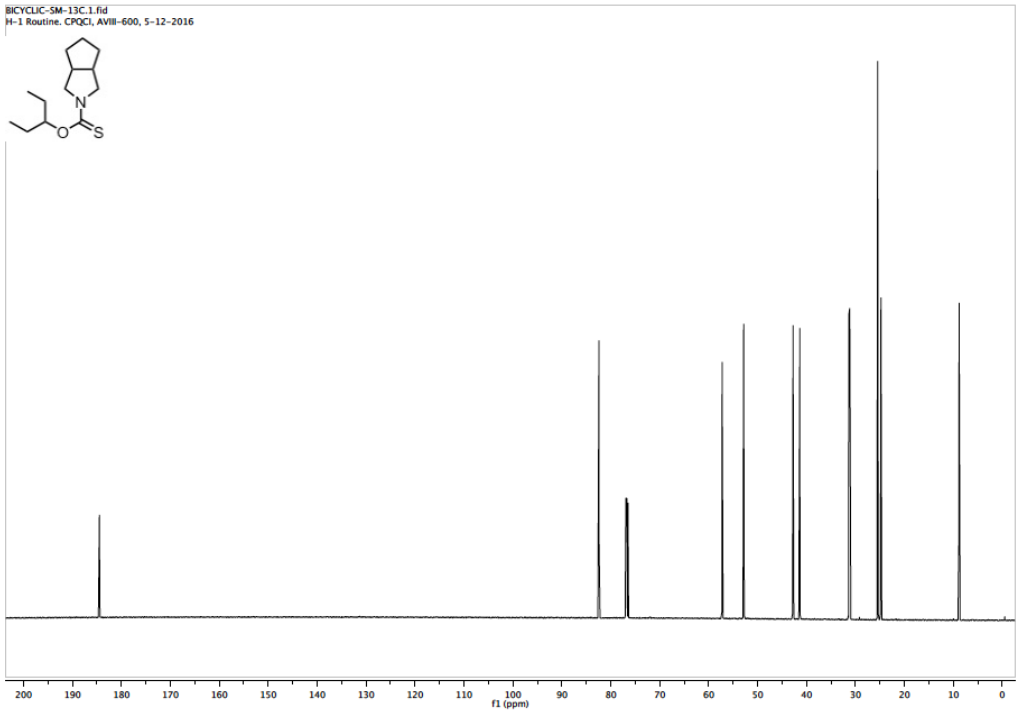
^{13}C NMR spectrum of compound **5c**



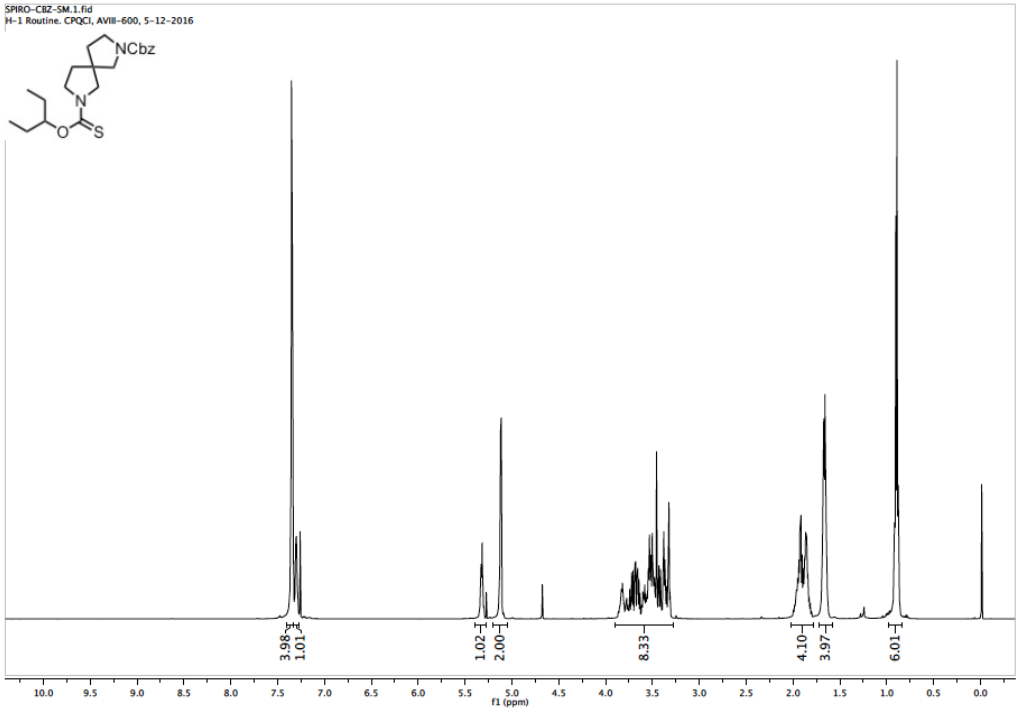
^{1}H NMR spectrum of compound **5d**



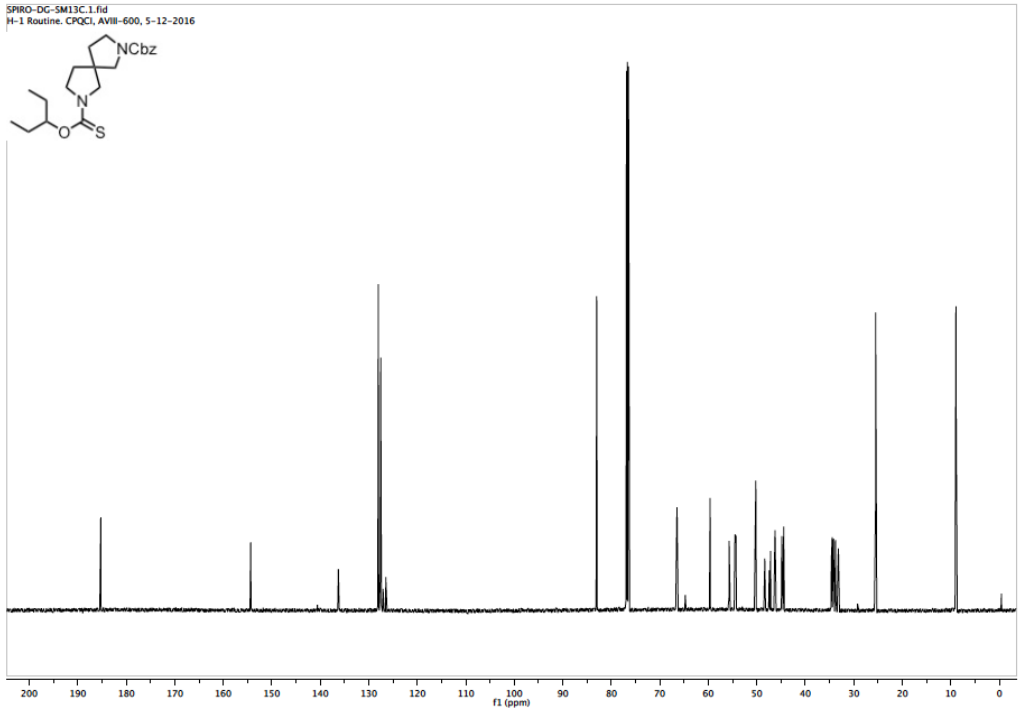
^{13}C NMR spectrum of compound **5d**



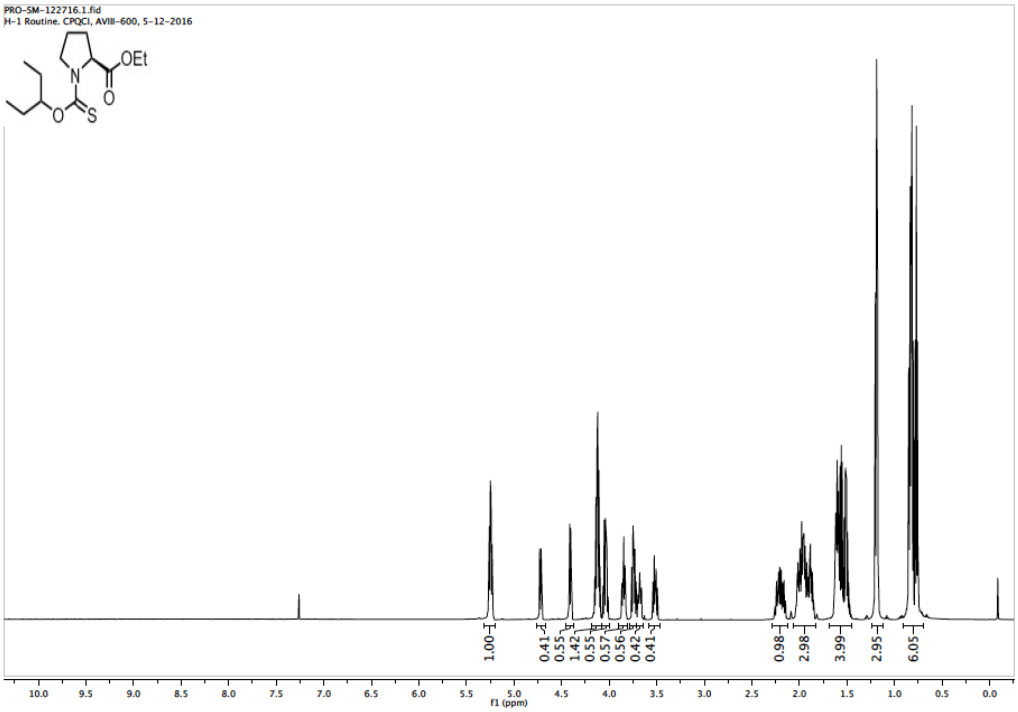
^{1}H NMR spectrum of compound **5e**



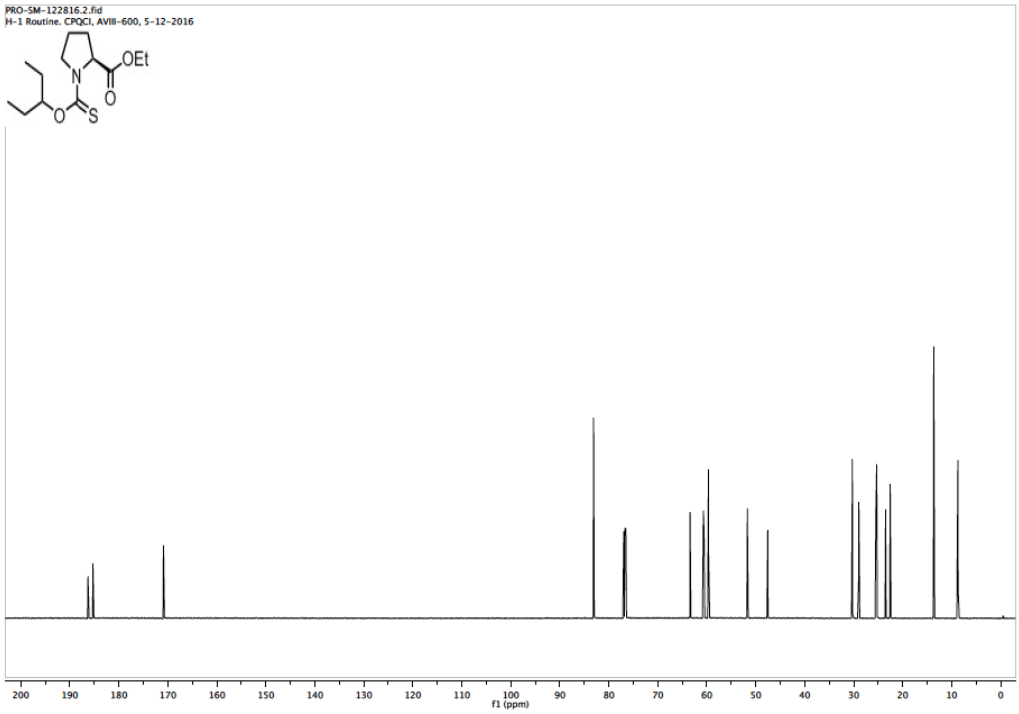
^{13}C NMR spectrum of compound **5e**



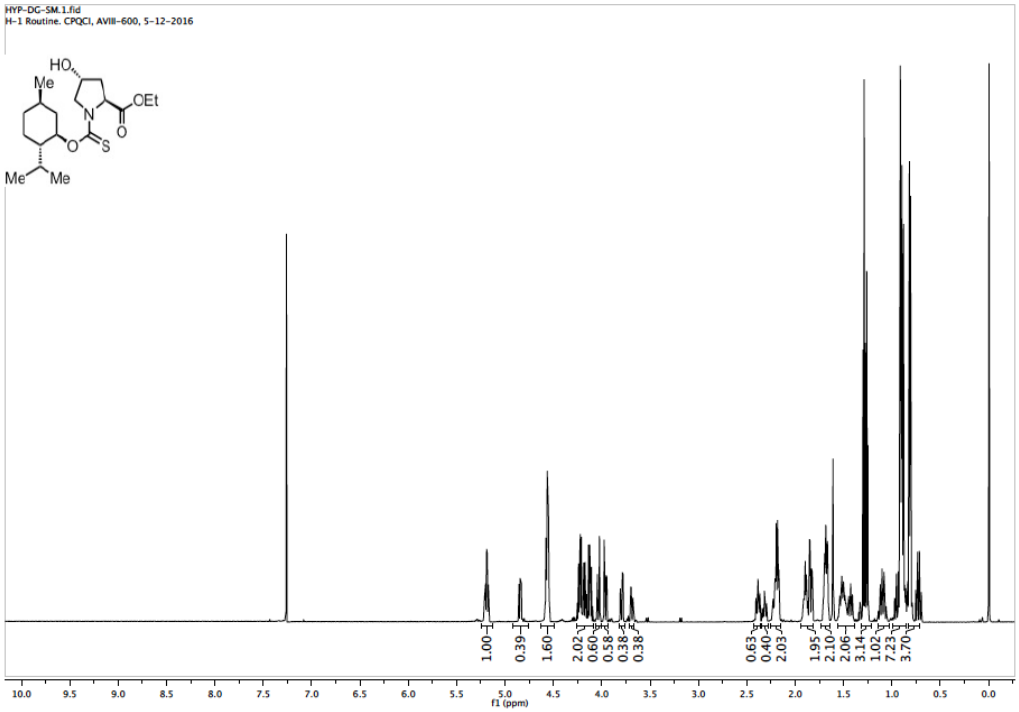
^{1}H NMR spectrum of compound **5f**



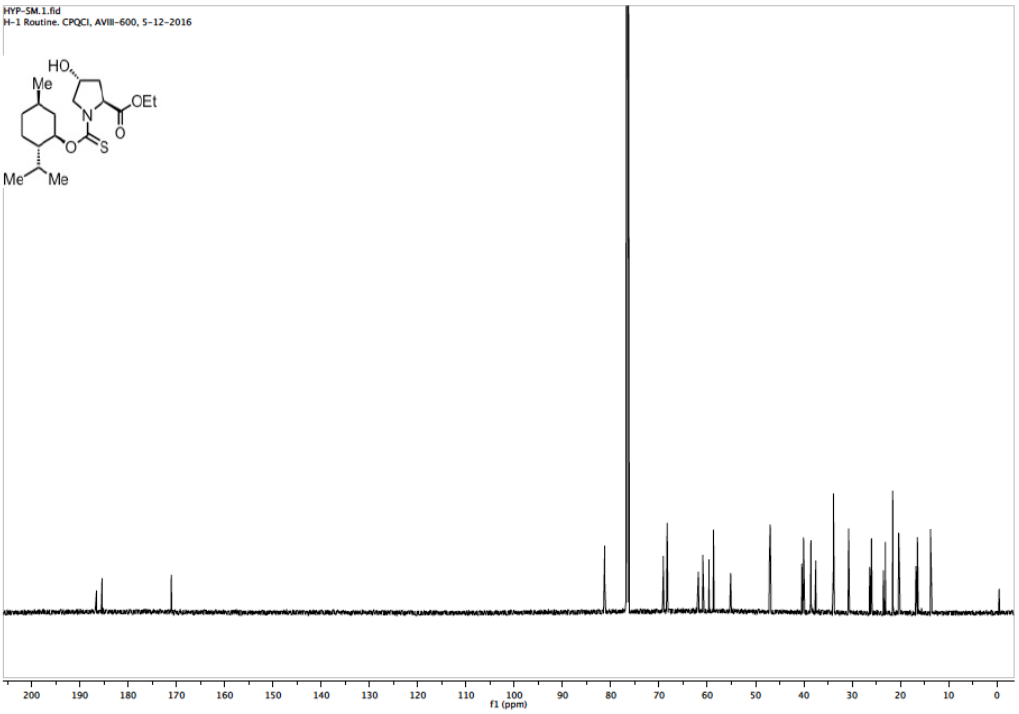
^{13}C NMR spectrum of compound **5f**



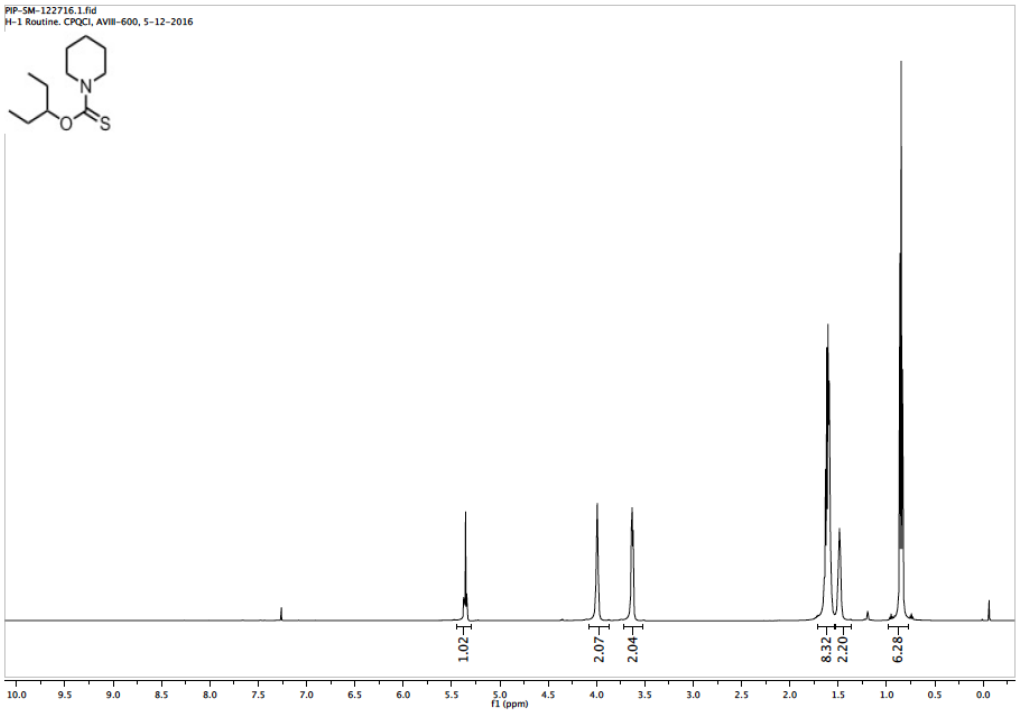
^{1}H NMR spectrum of compound **5g**



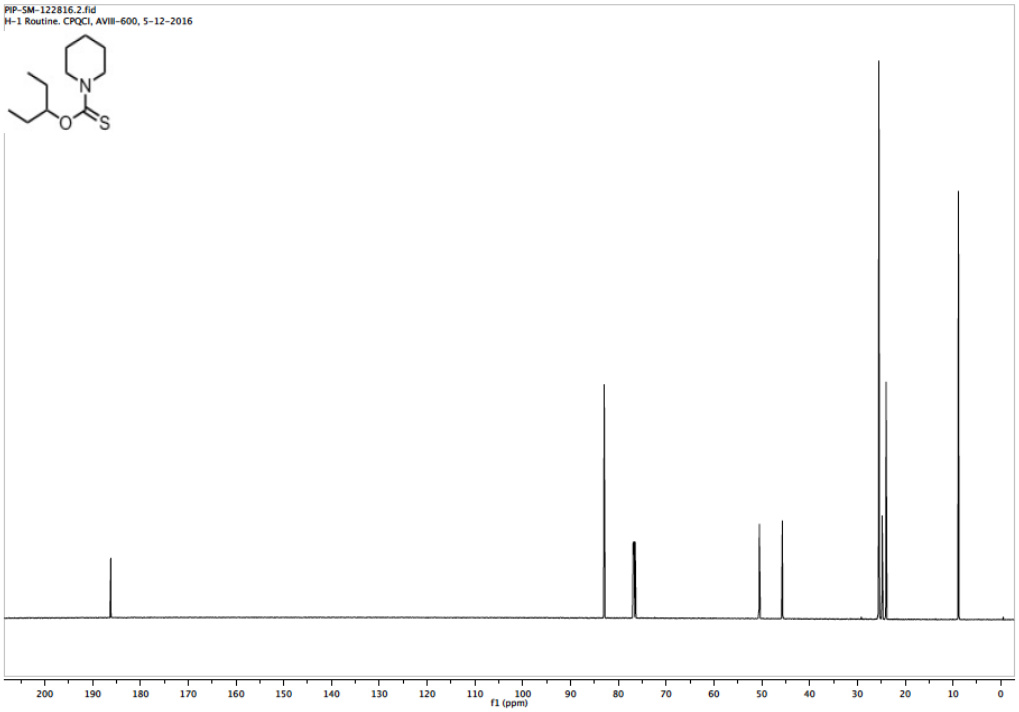
^{13}C NMR spectrum of compound **5g**



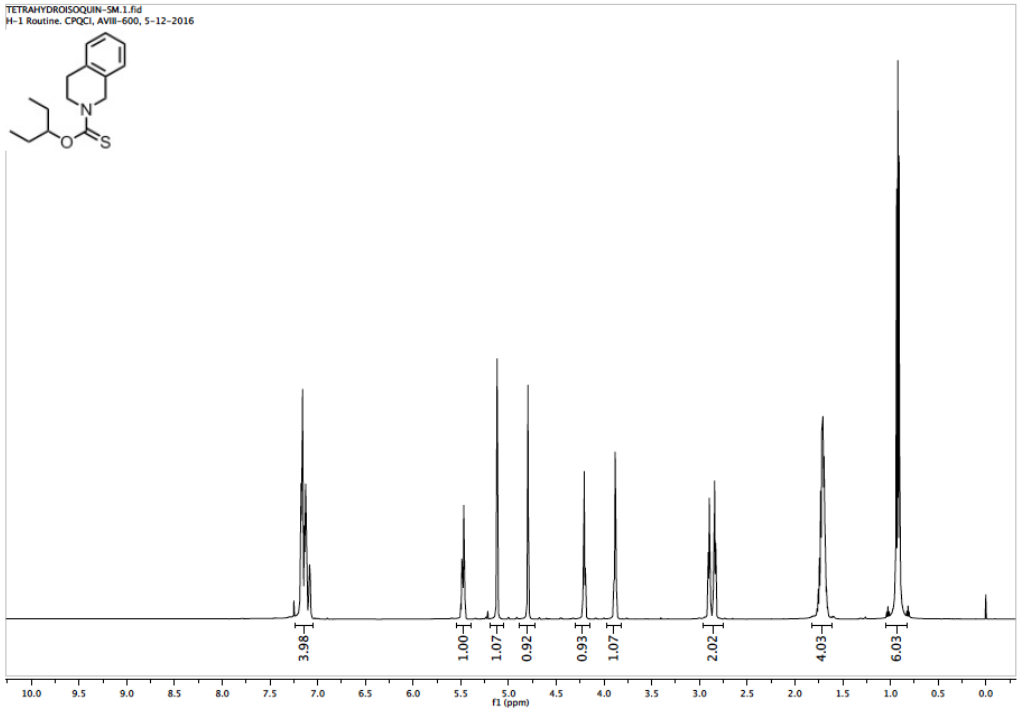
^{1}H NMR spectrum of compound **5h**



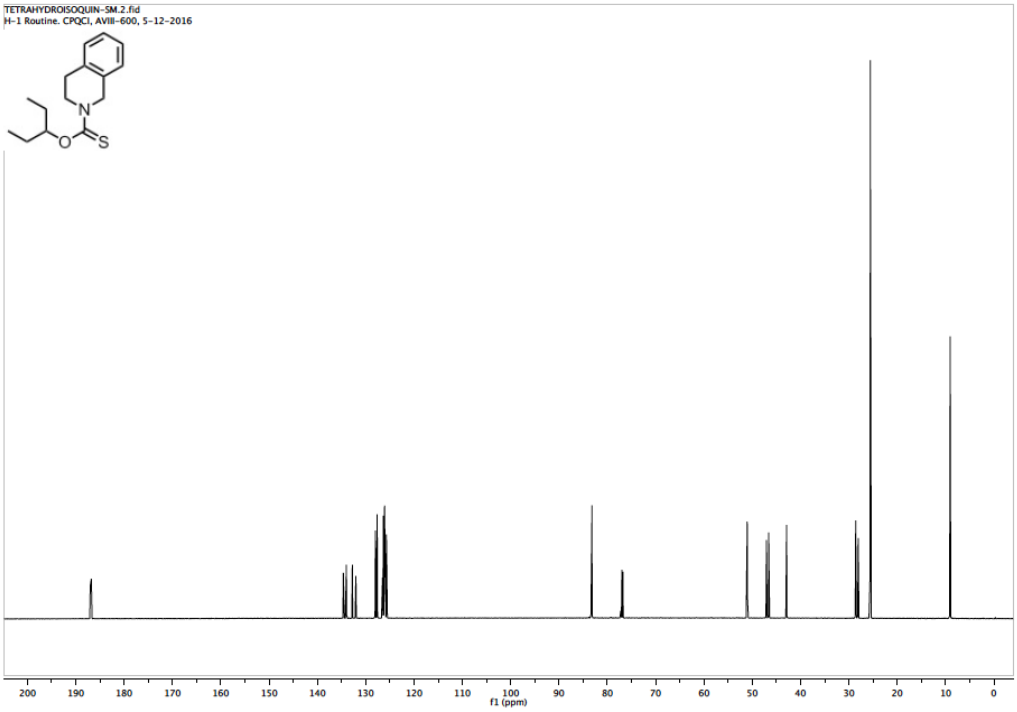
^{13}C NMR spectrum of compound **5h**



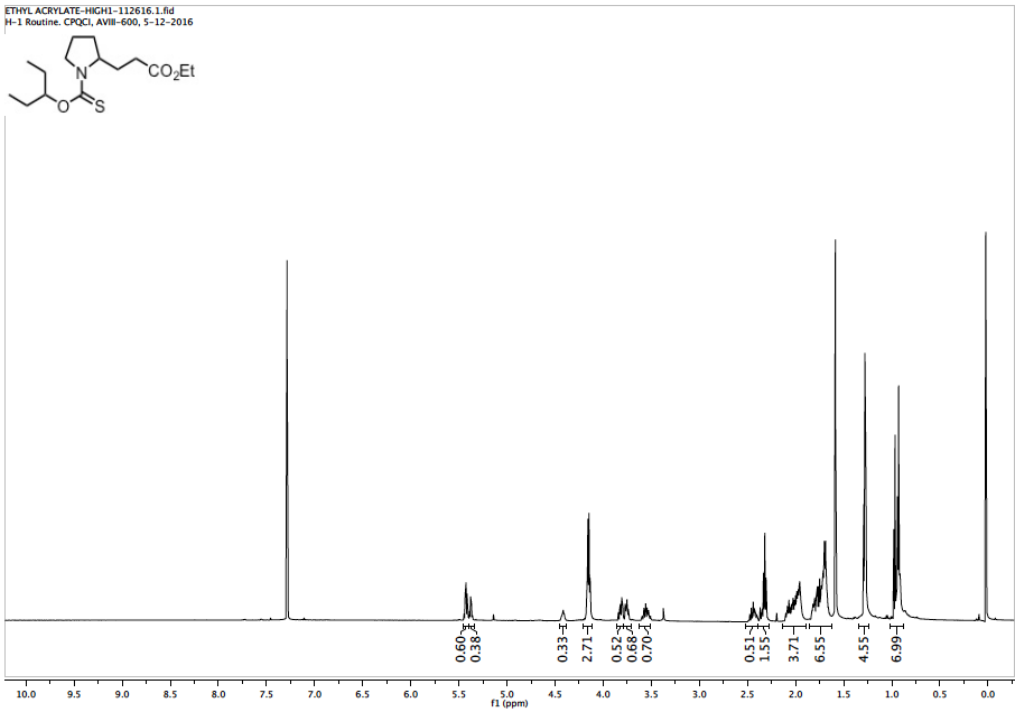
^{1}H NMR spectrum of compound **5i**



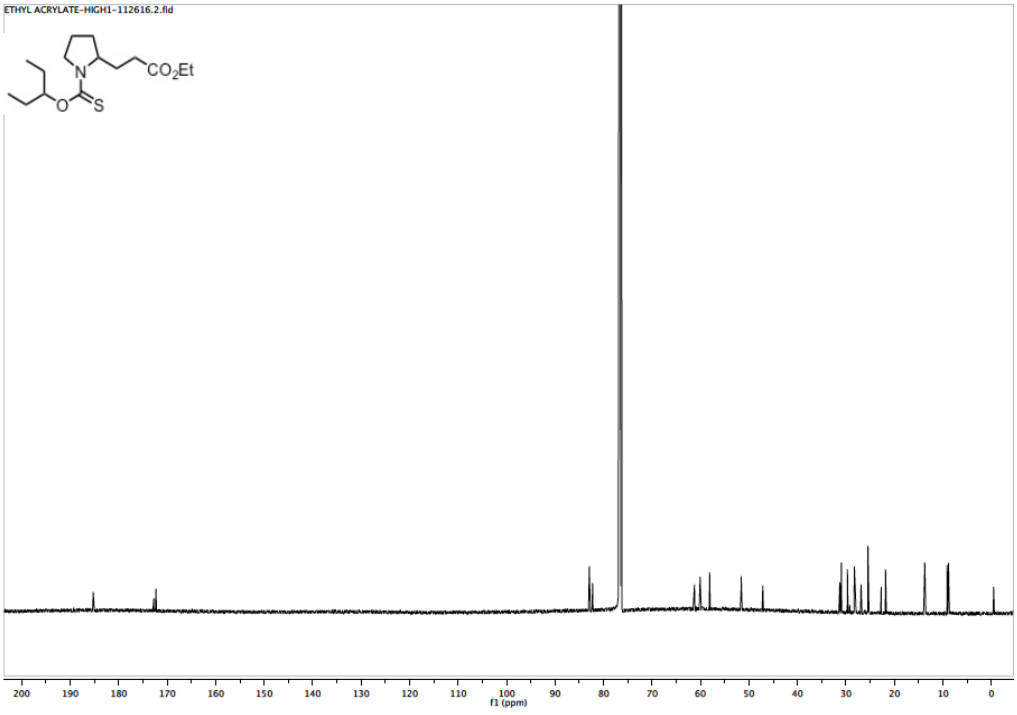
^{13}C NMR spectrum of compound **5i**



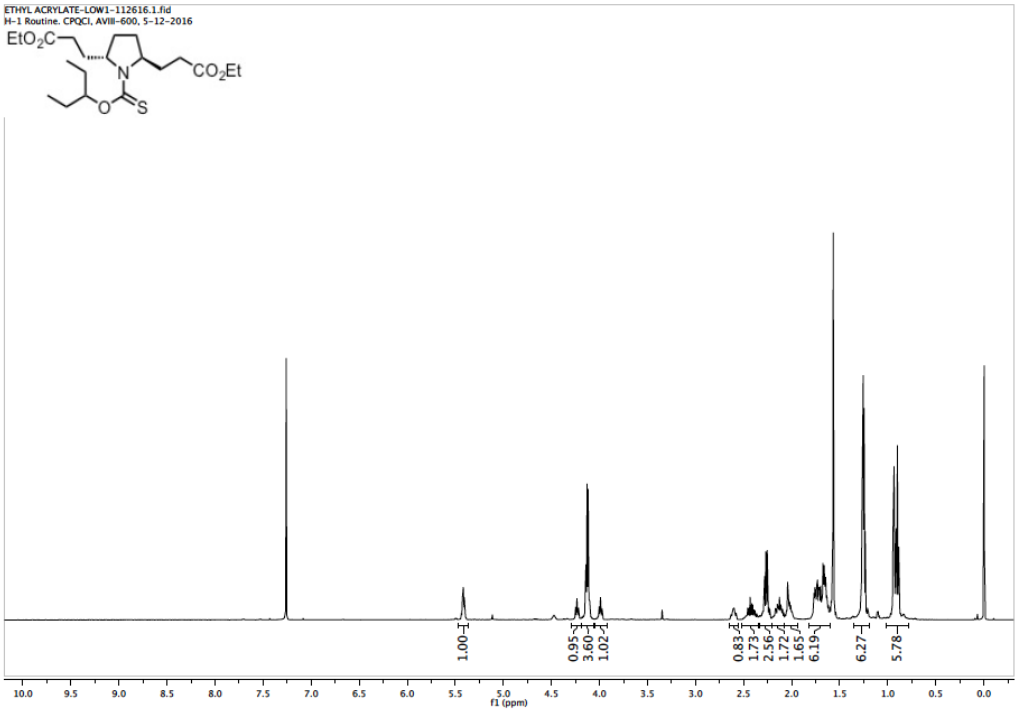
^{1}H NMR spectrum of compound **4a$_{mono}$**



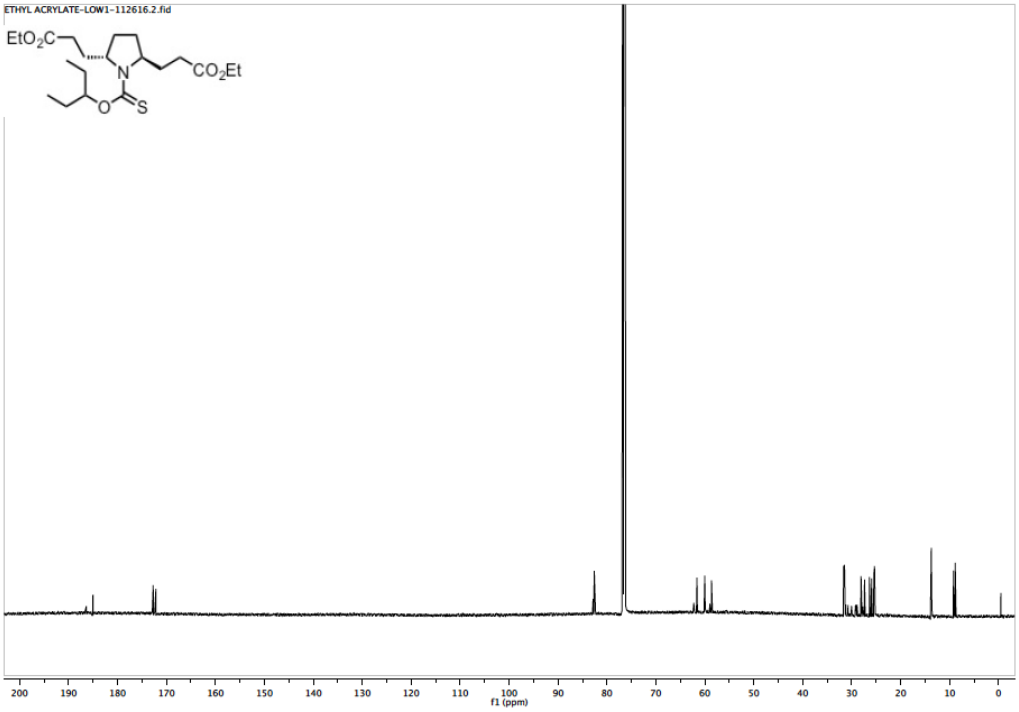
^{13}C NMR spectrum of compound **4a$_{mono}$**



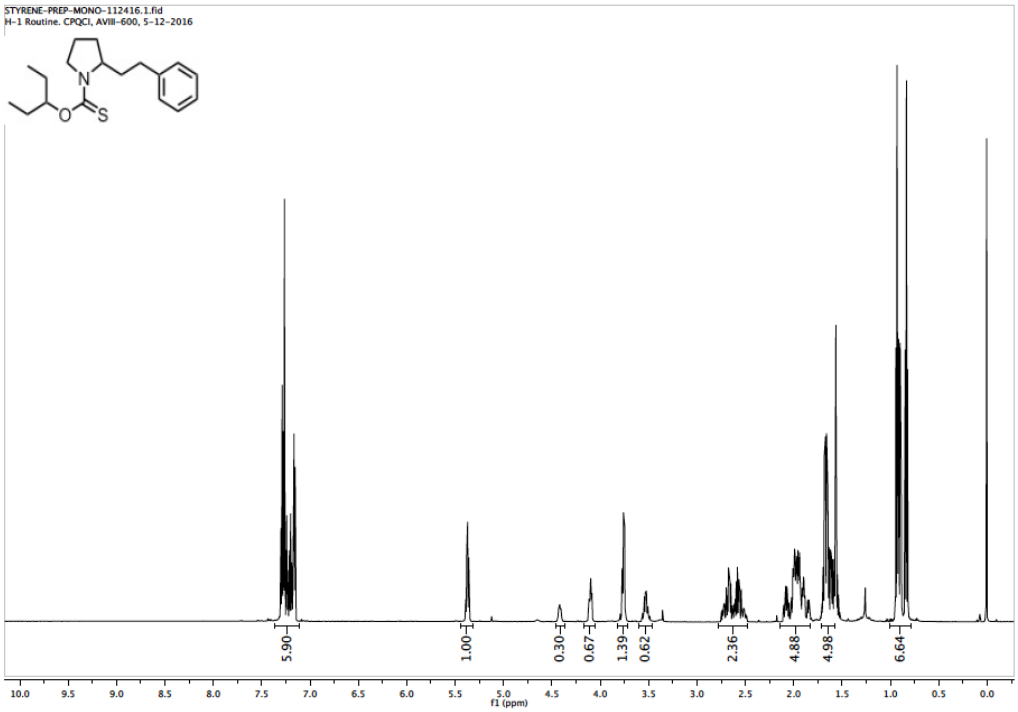
^{1}H NMR spectrum of compound **4a$_{di}$**



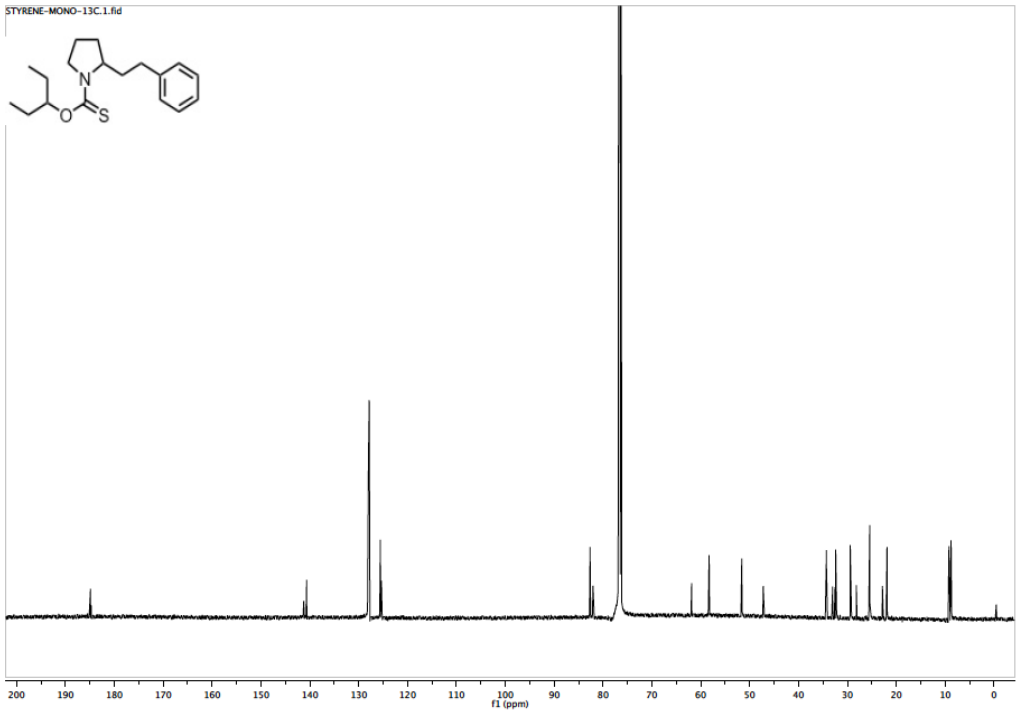
^{13}C NMR spectrum of compound **4a$_{di}$**



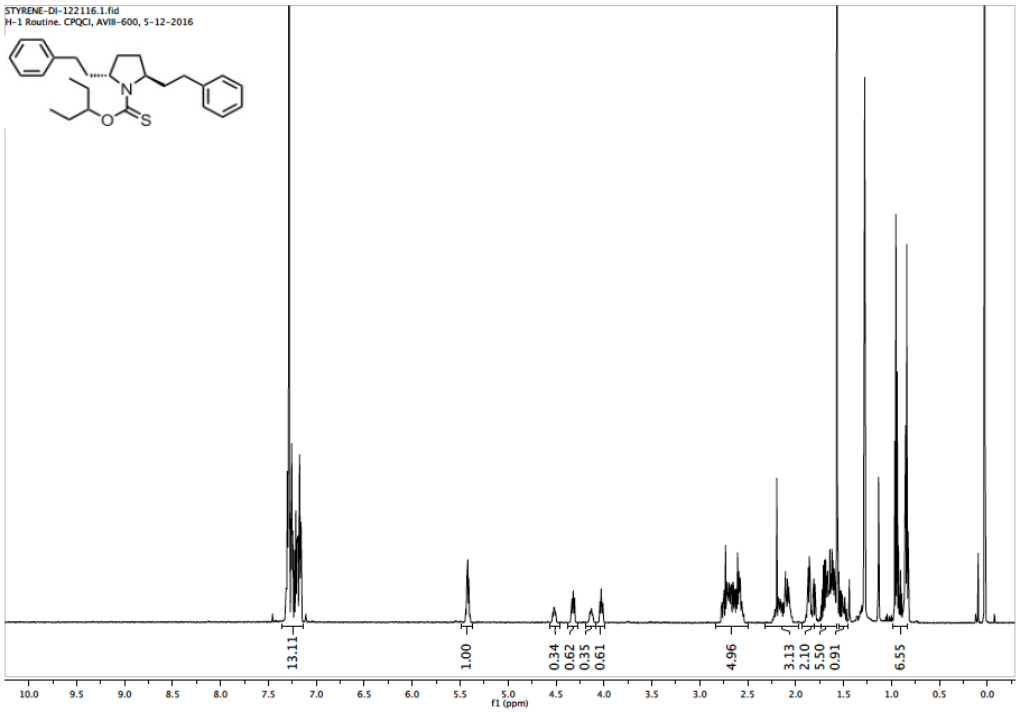
^{1}H NMR spectrum of compound **4c$_{mono}$**



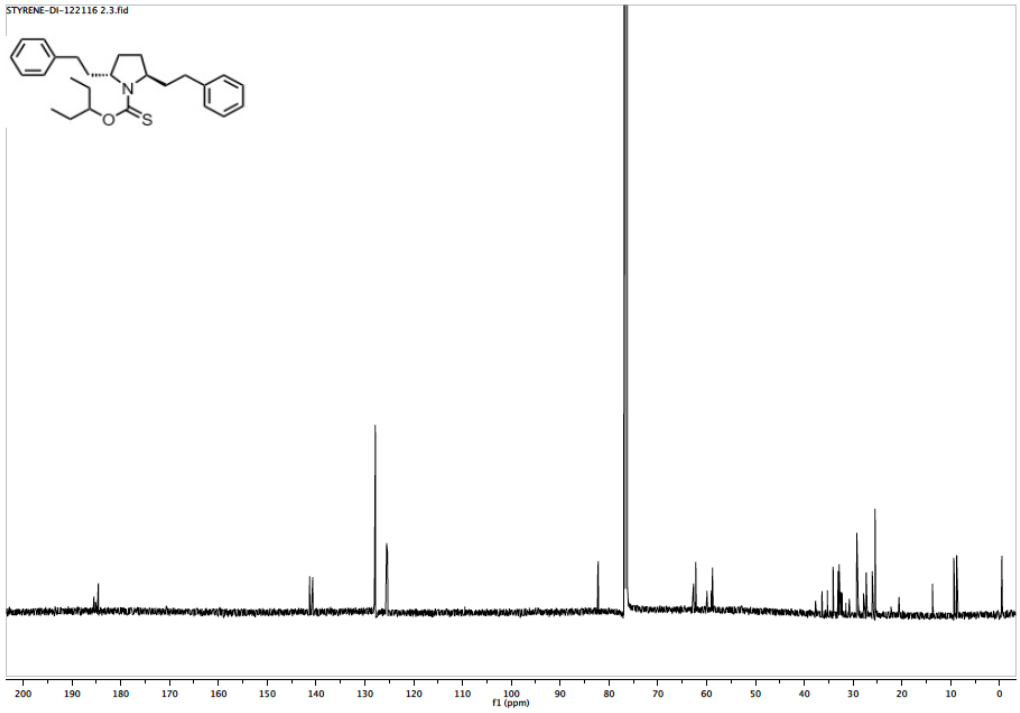
^{13}C NMR spectrum of compound **4c$_{mono}$**



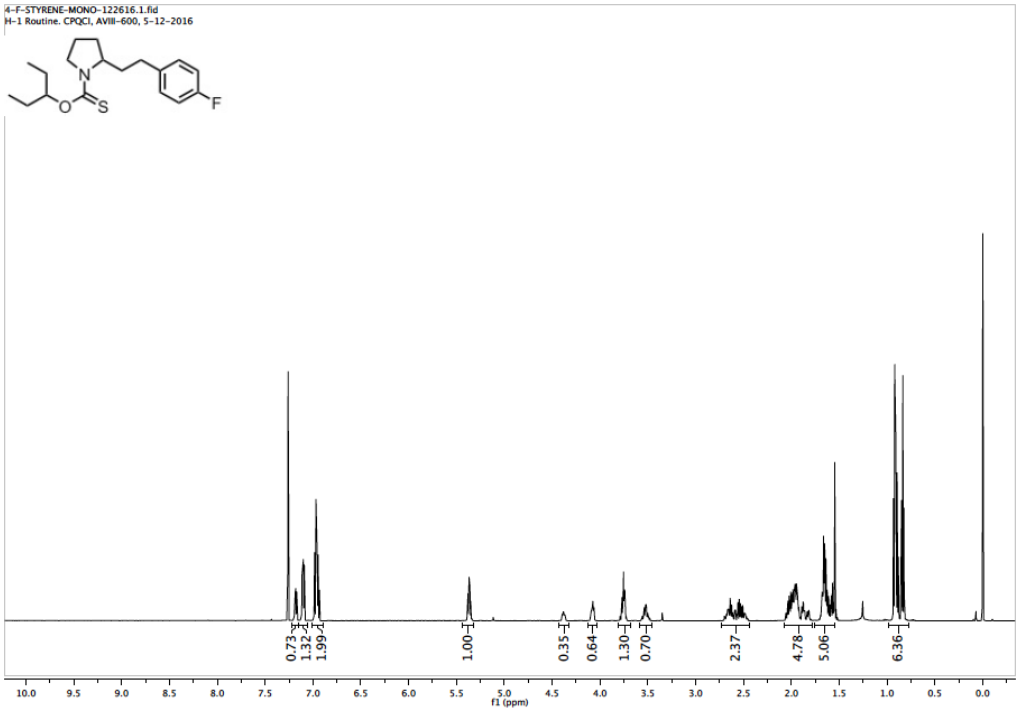
^{1}H NMR spectrum of compound **4c$_{di}$**



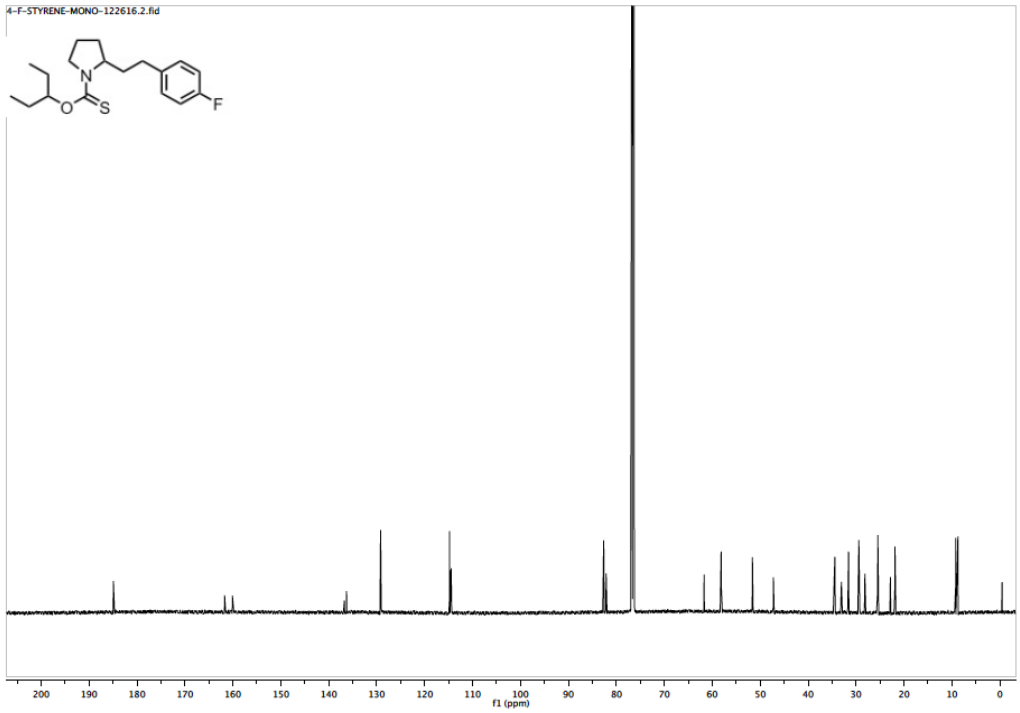
^{13}C NMR spectrum of compound **4c$_{di}$**



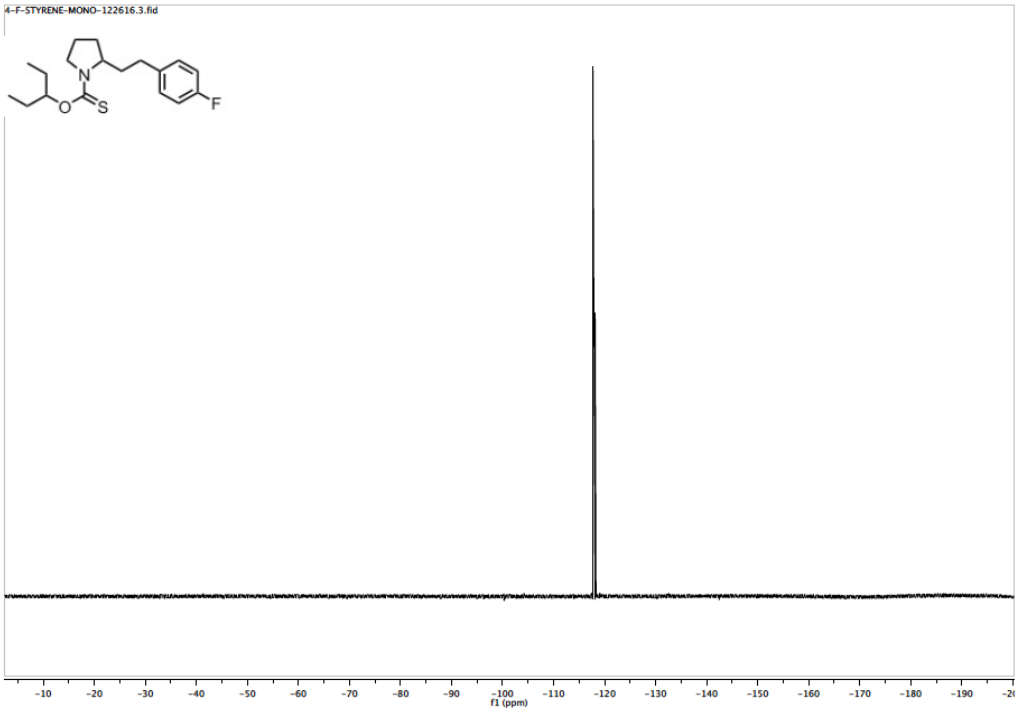
^{1}H NMR spectrum of compound **4d**



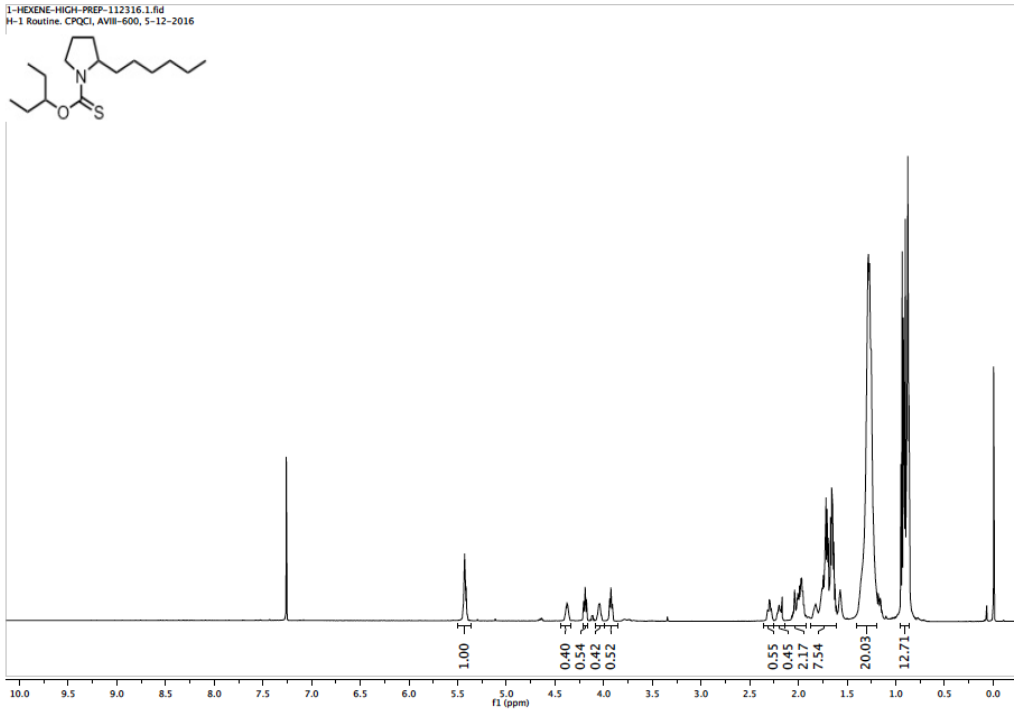
^{13}C NMR spectrum of compound **4d**



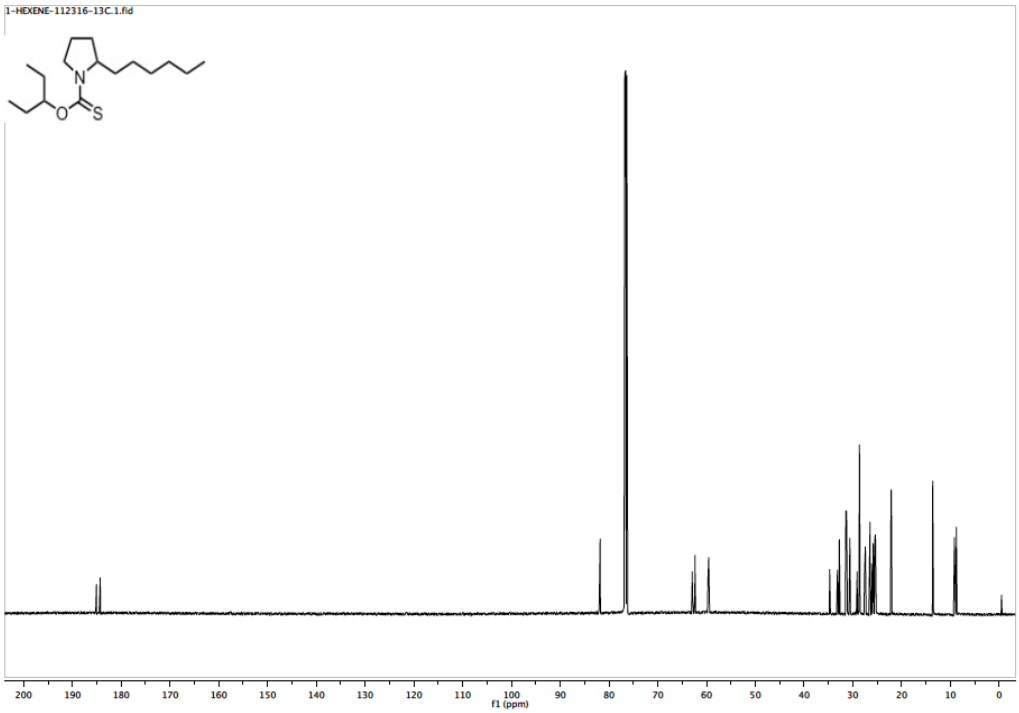
^{19}F NMR spectrum of compound **4d**



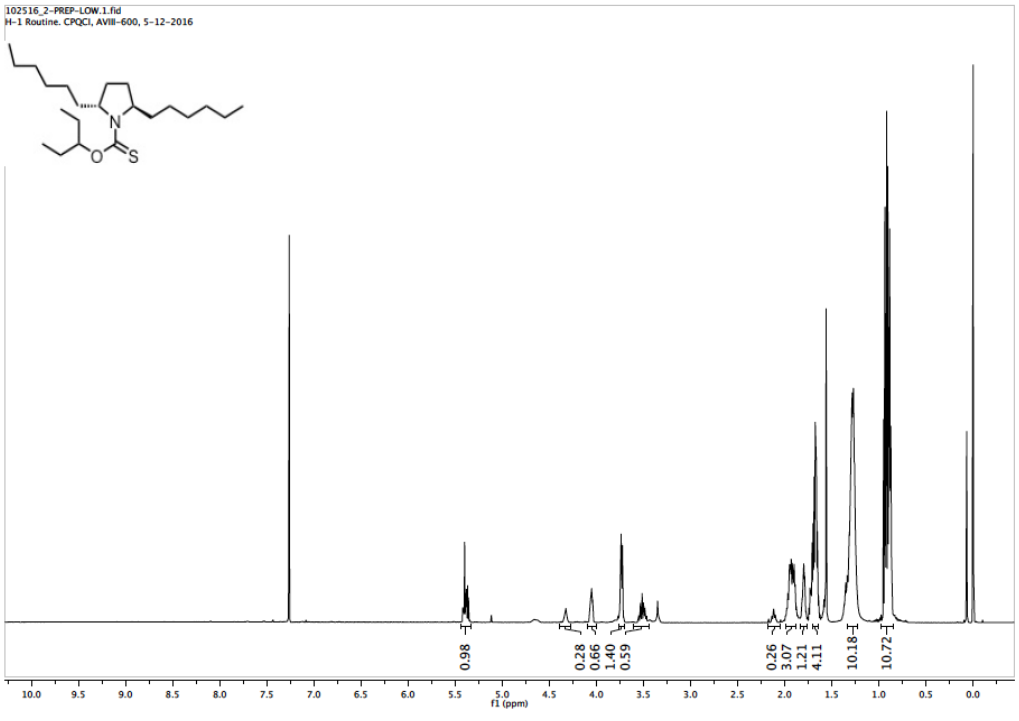
^{1}H NMR spectrum of compound **4e$_{mono}$**



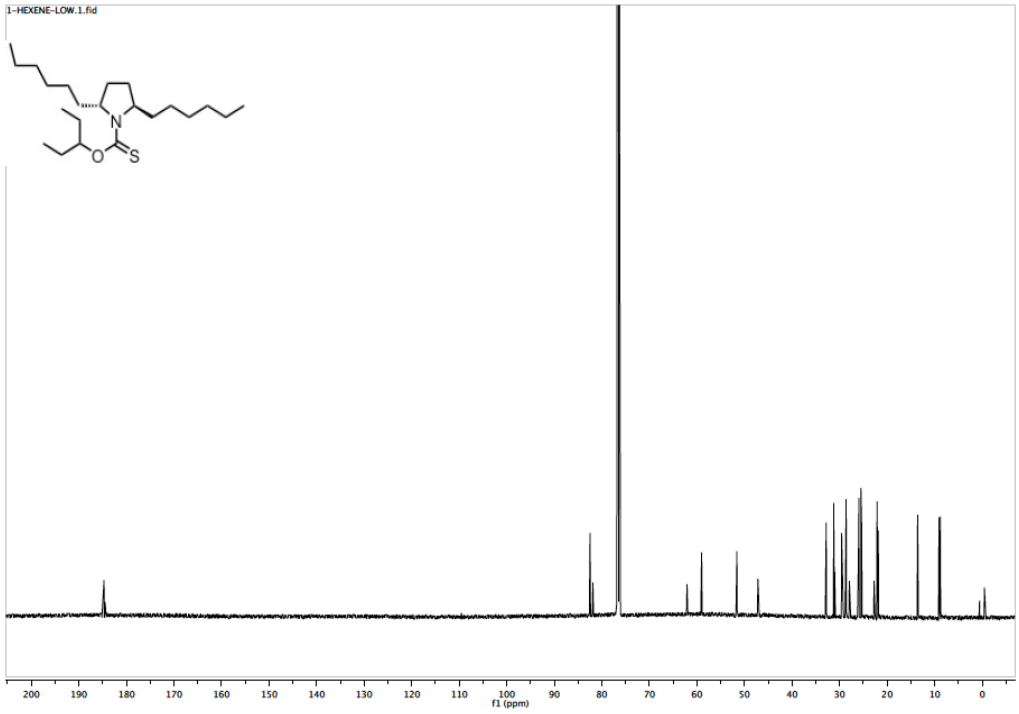
^{13}C NMR spectrum of compound **4e$_{mono}$**



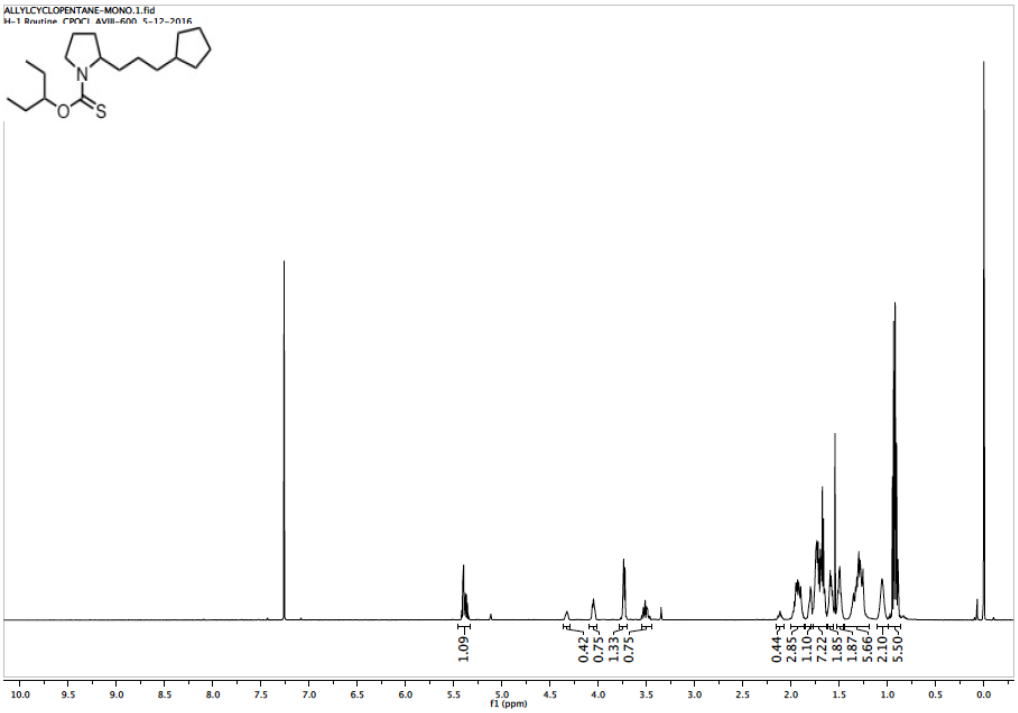
^{1}H NMR spectrum of compound **4e$_{di}$**



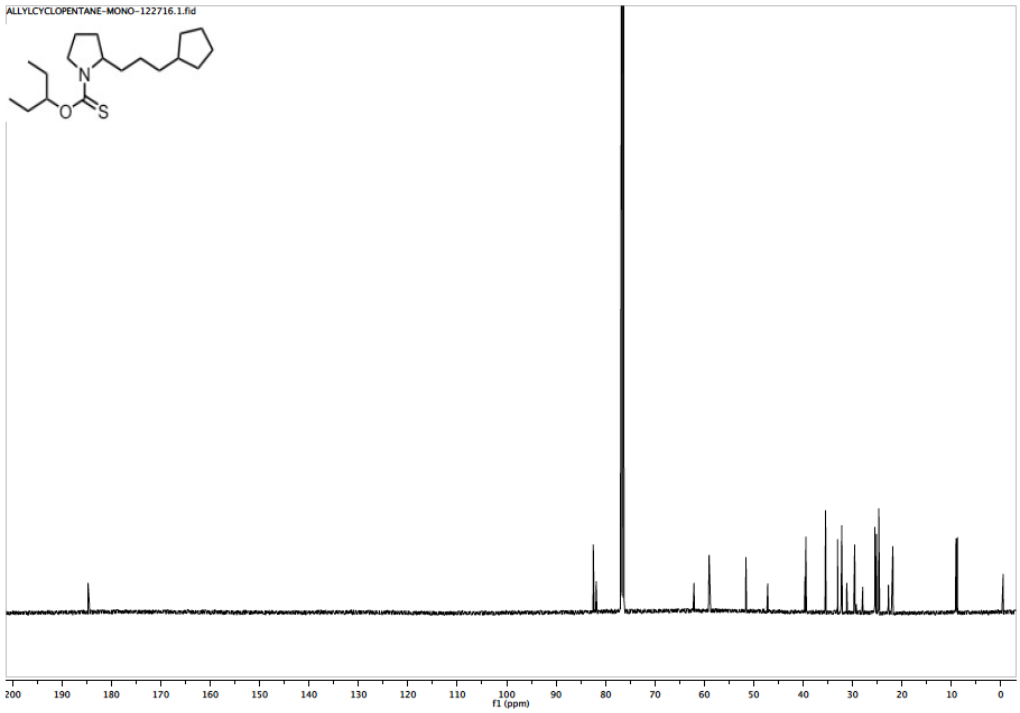
^{13}C NMR spectrum of compound **4e$_{di}$**



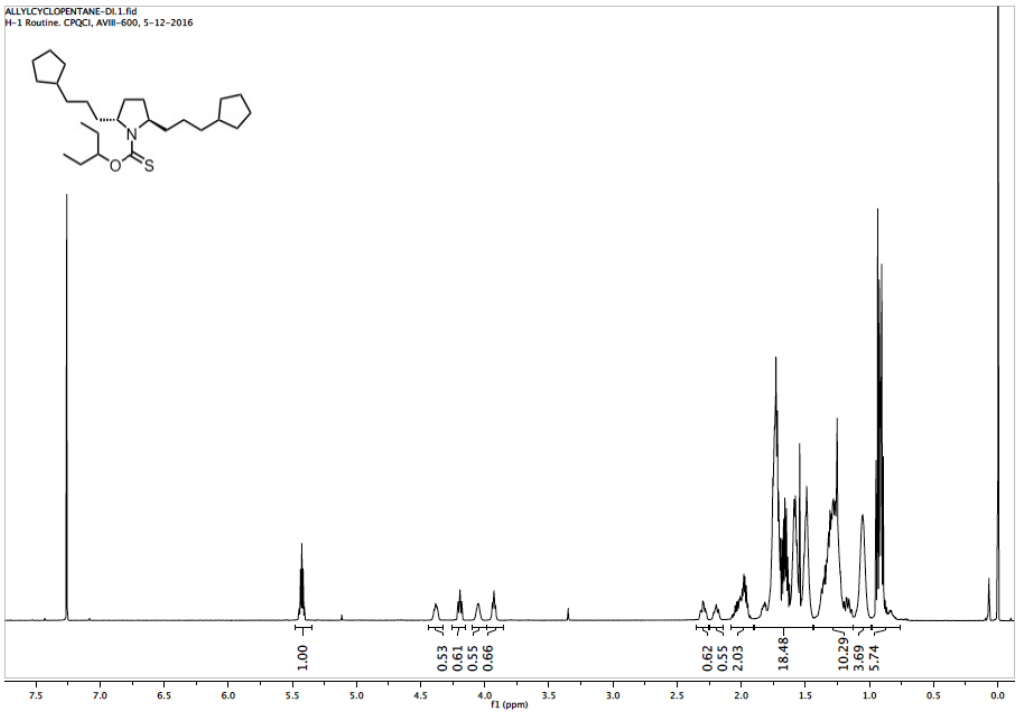
^{1}H NMR spectrum of compound **4f$_{mono}$**



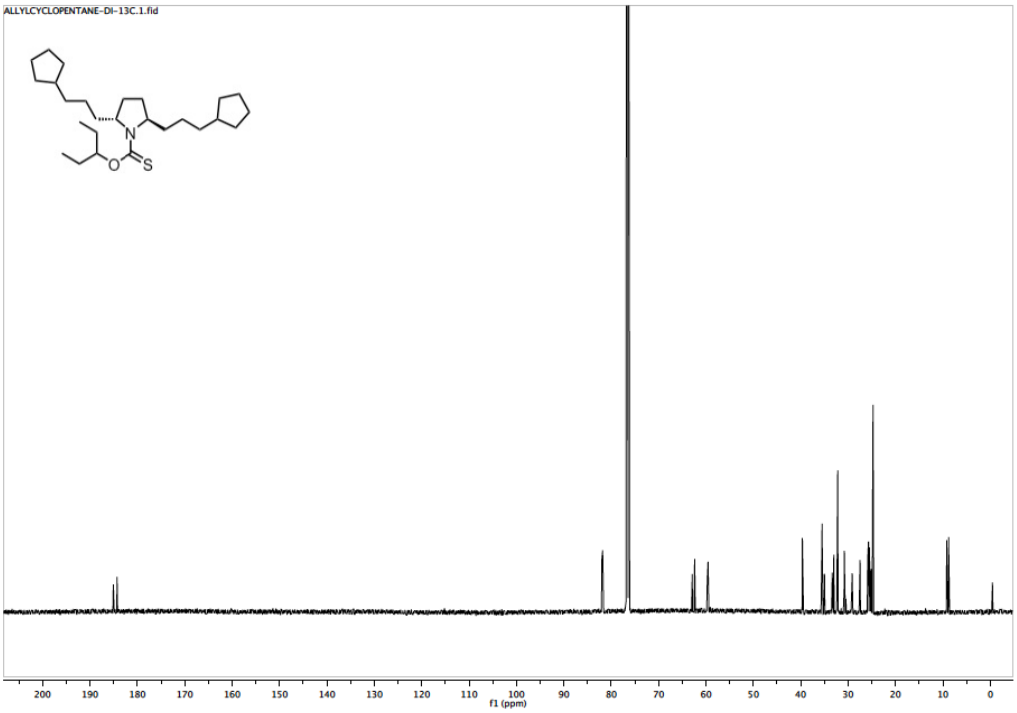
^{13}C NMR spectrum of compound **4f$_{mono}$**



^{1}H NMR spectrum of compound **4f$_{di}$**



^{13}C NMR spectrum of compound **4f$_{di}$**



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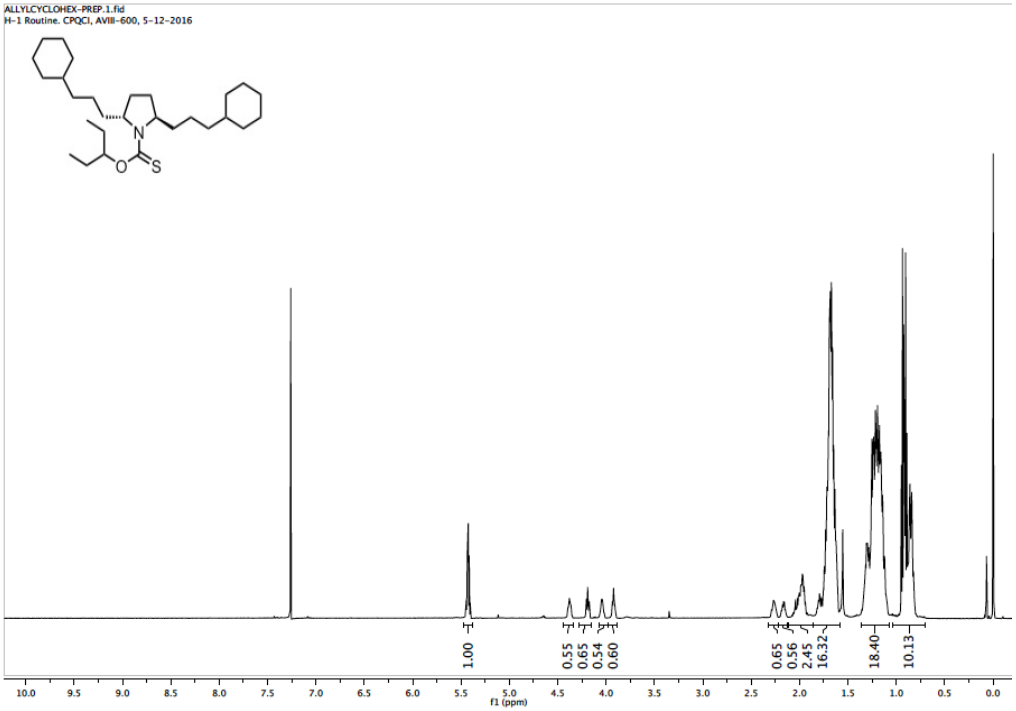
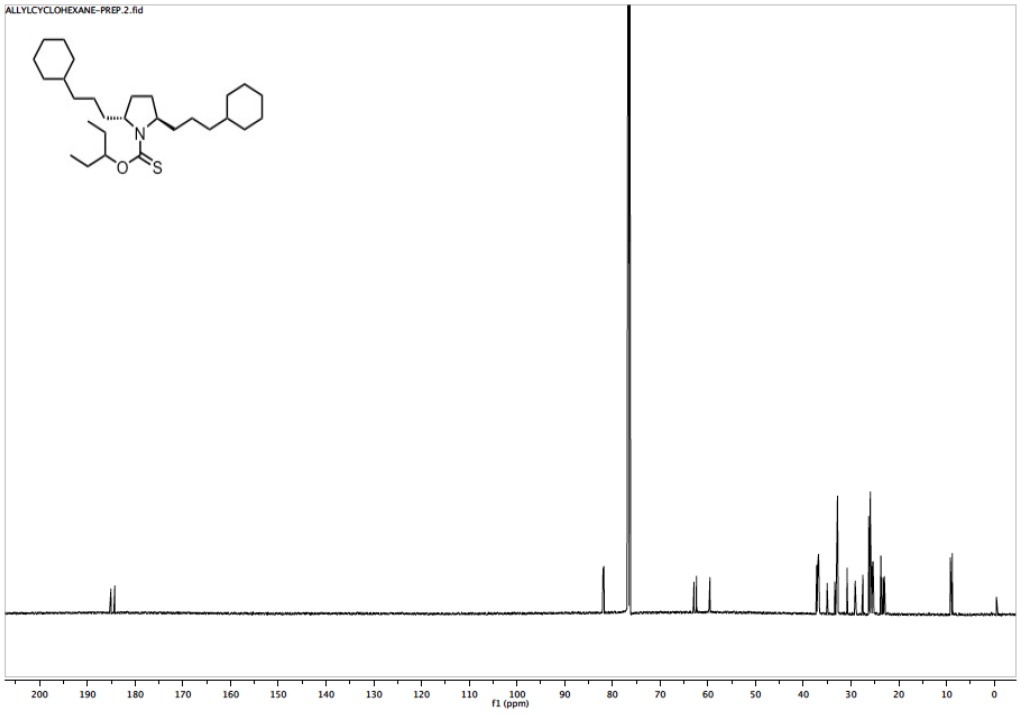
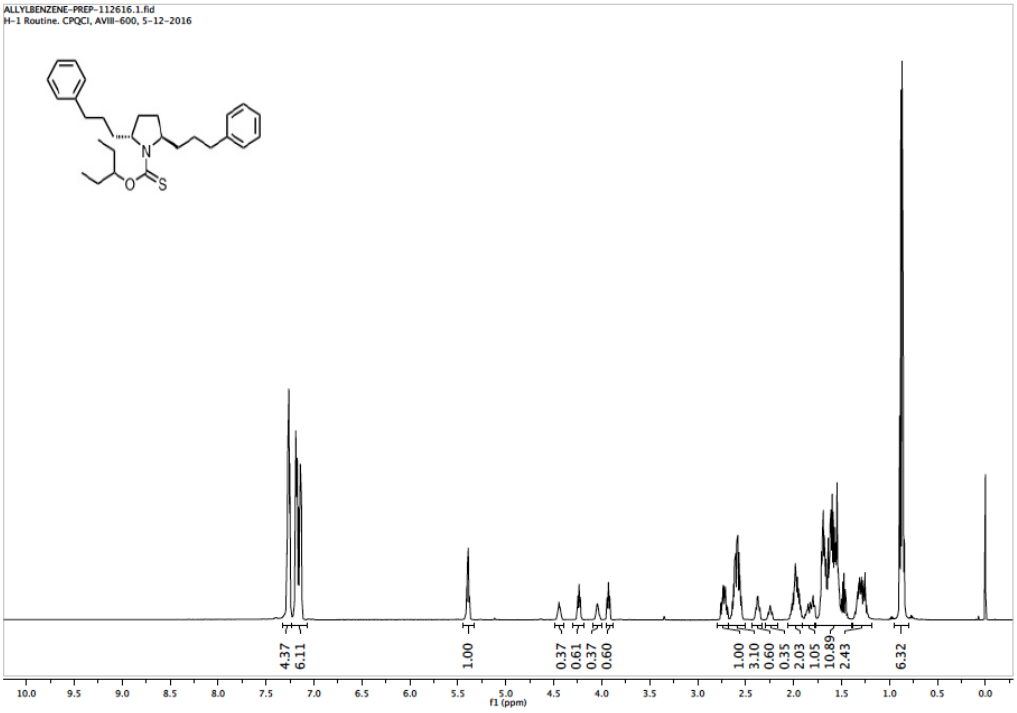


^{13}C NMR spectrum of compound **4g**



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



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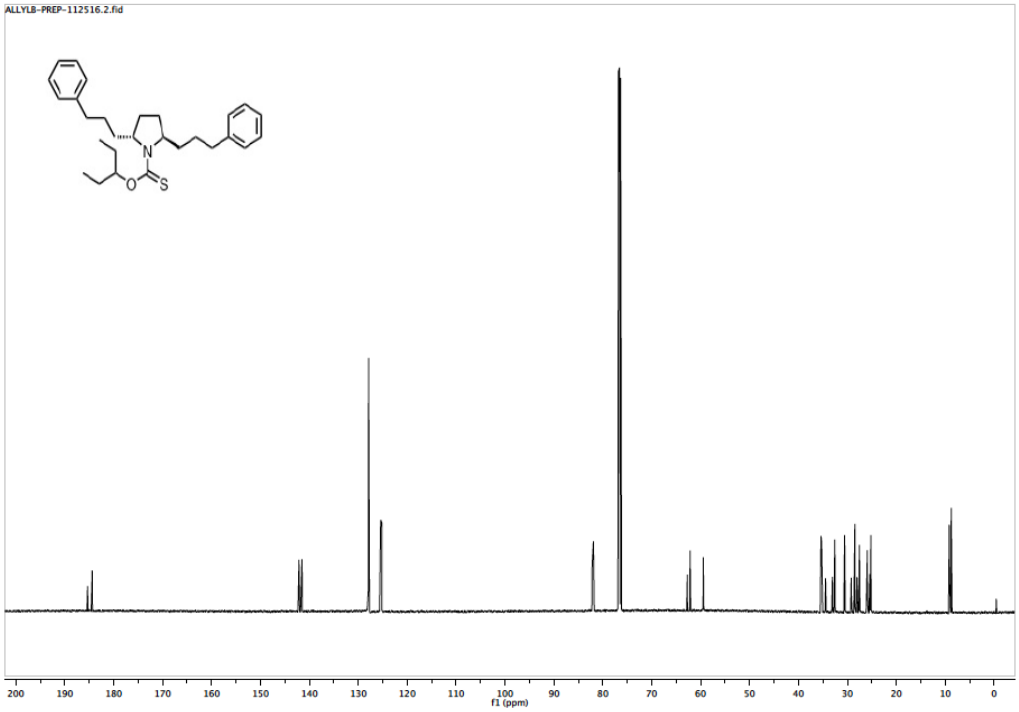
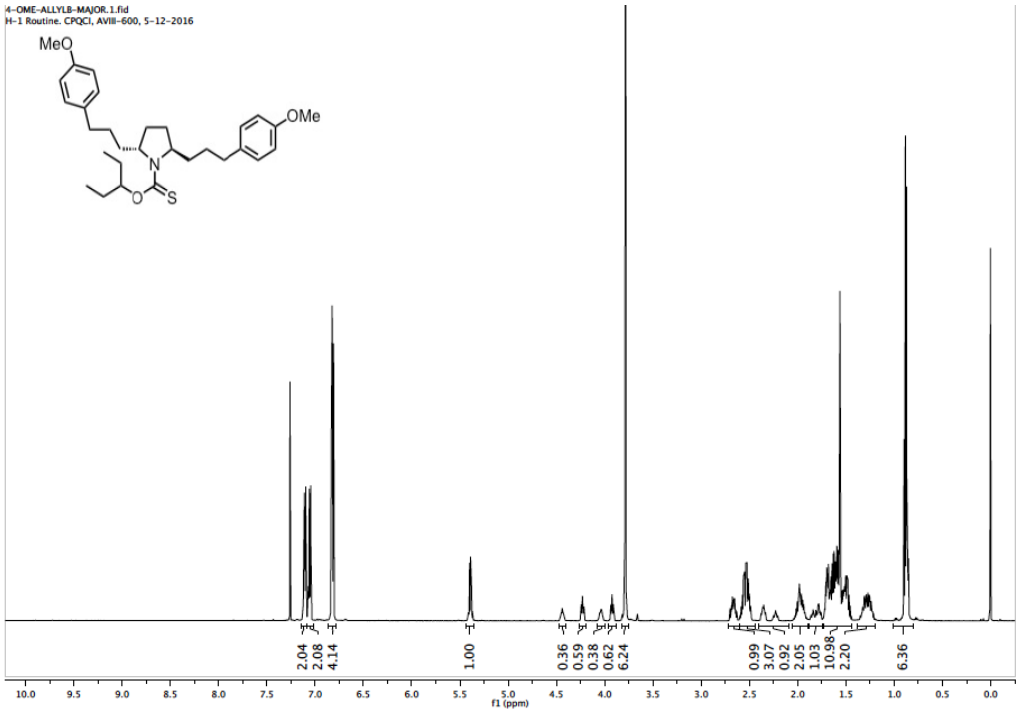


^{1}H NMR spectrum of compound **4i**



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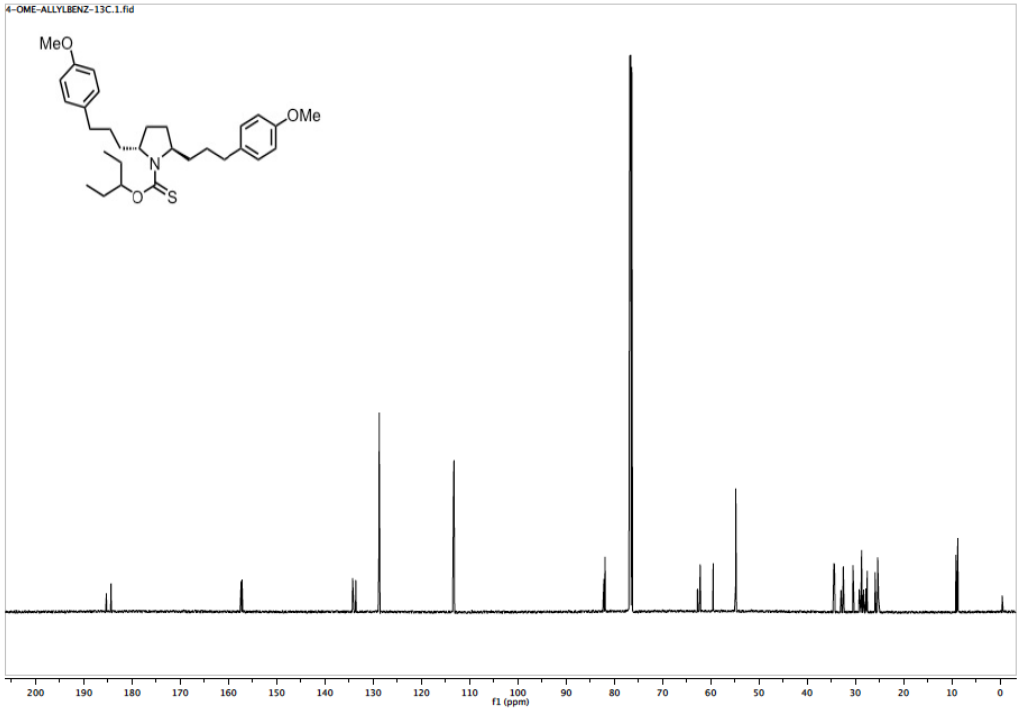

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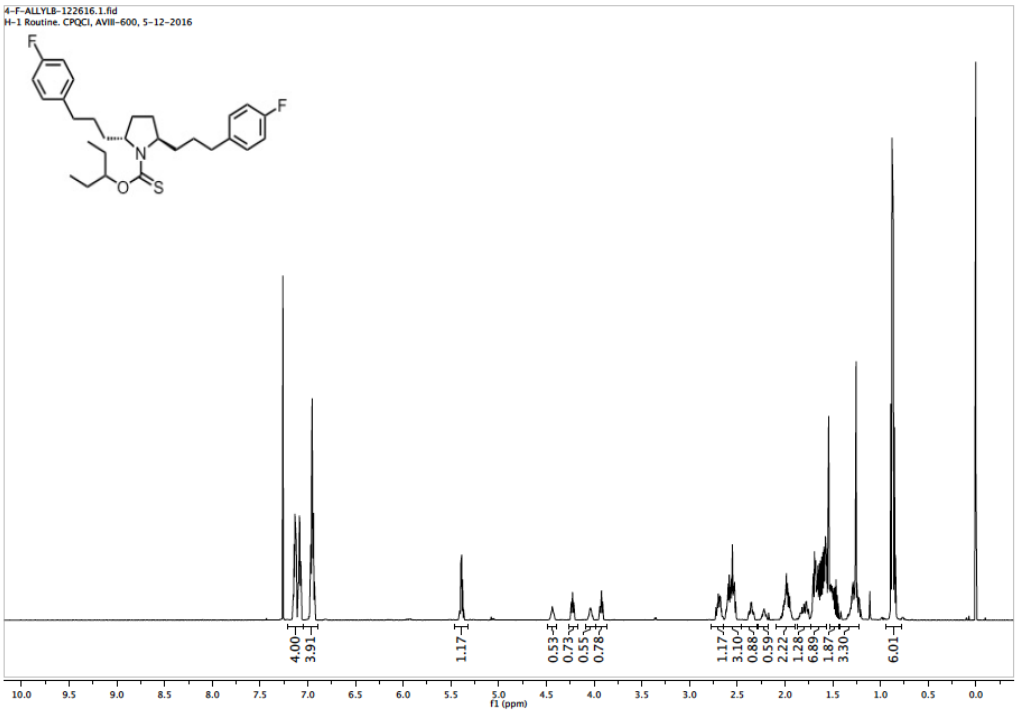

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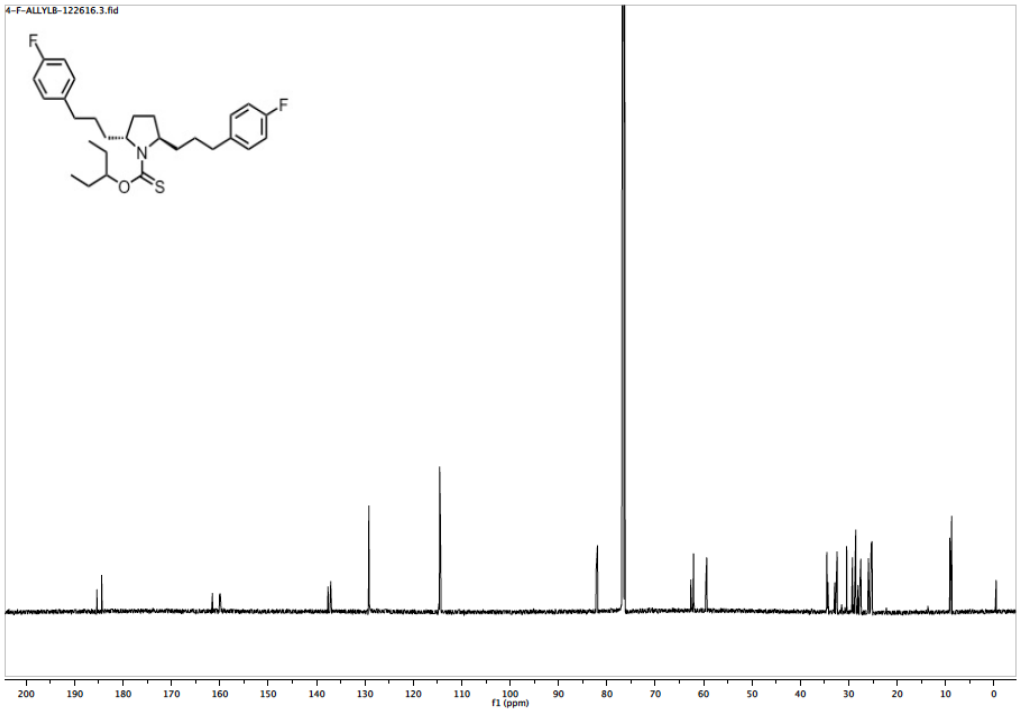
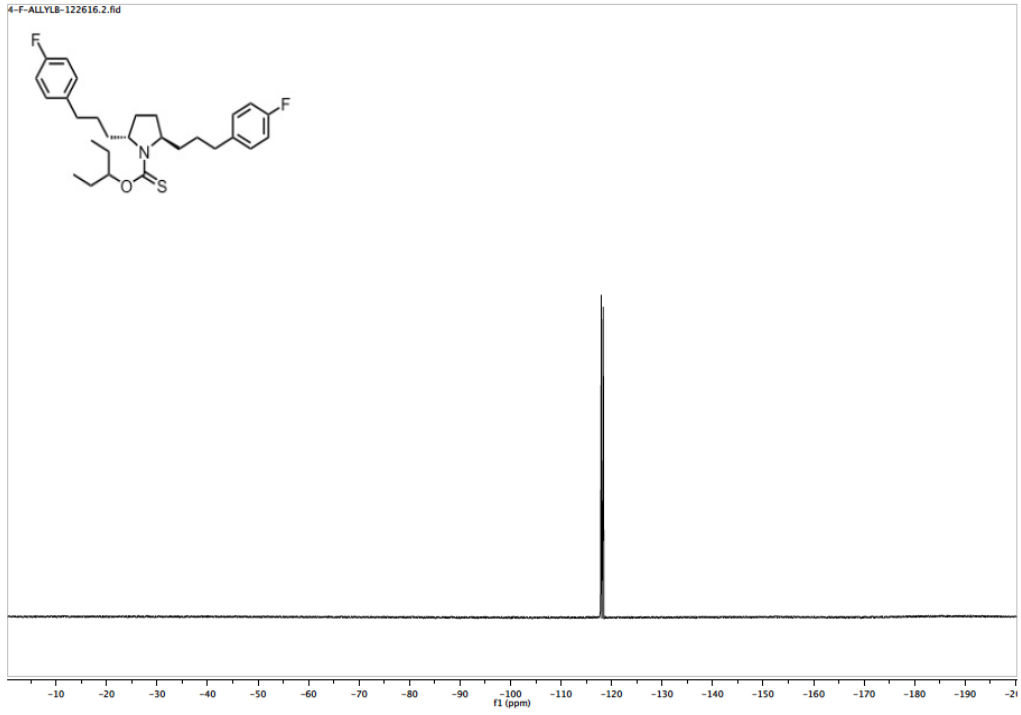
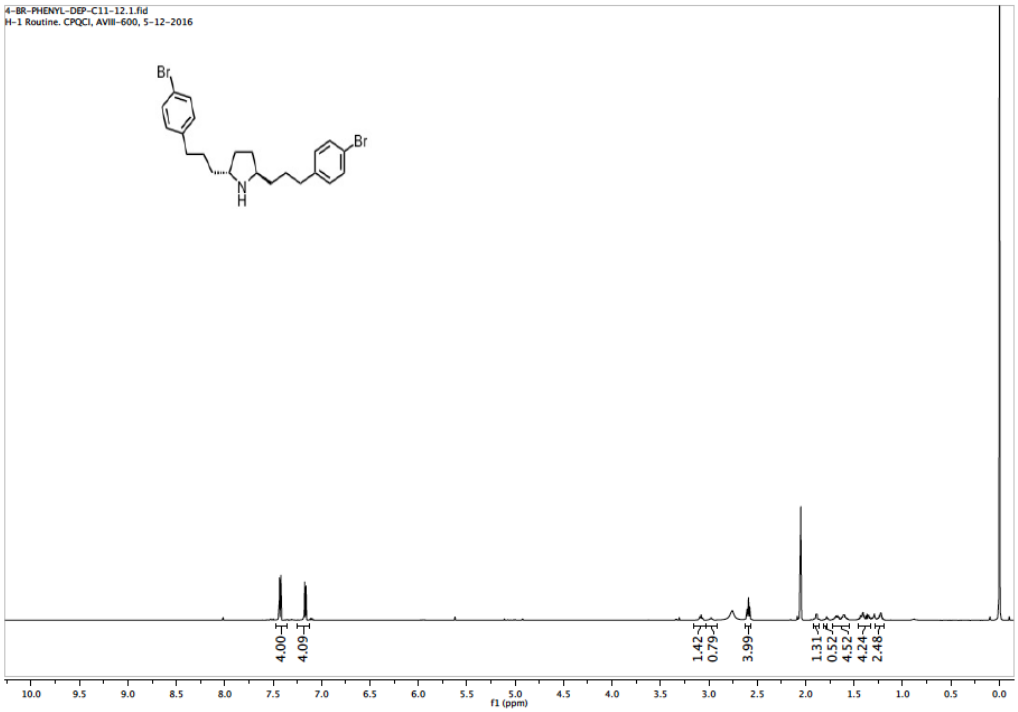


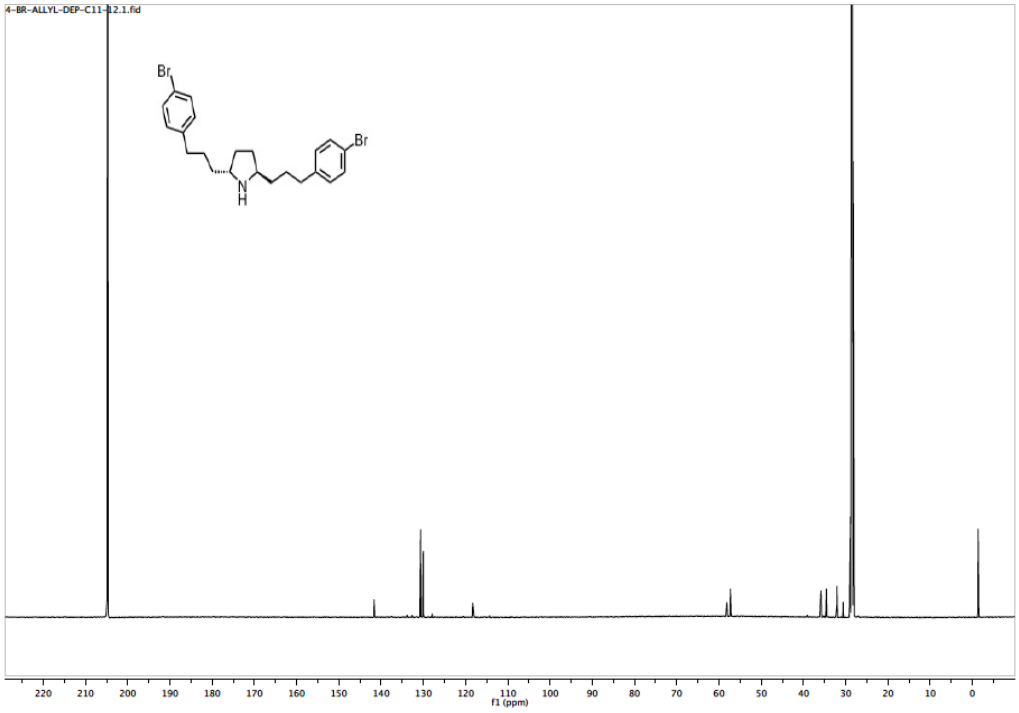
^{19}F NMR spectrum of compound **4j**



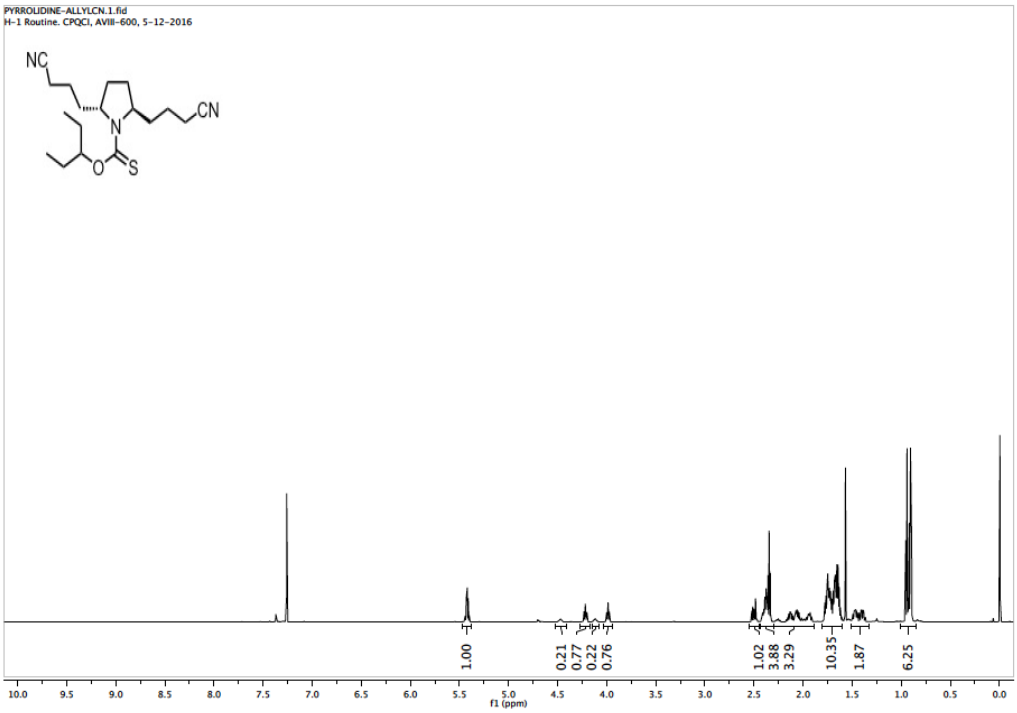
^{1}H NMR spectrum of compound **4k**



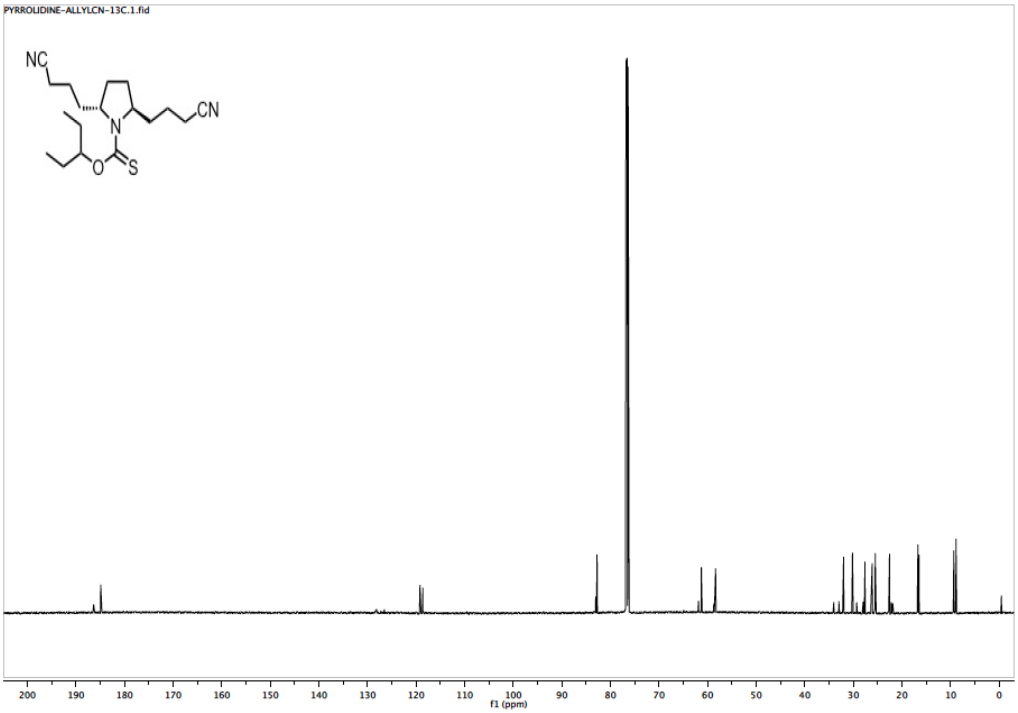
^{13}C NMR spectrum of compound **4k**



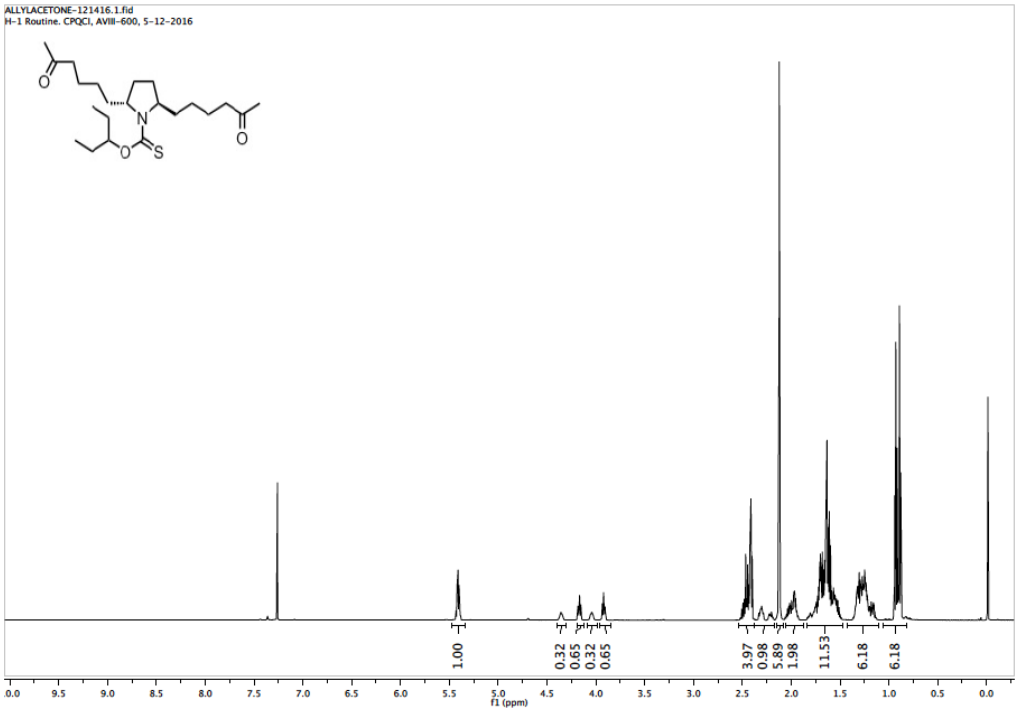
^{1}H NMR spectrum of compound **4l**



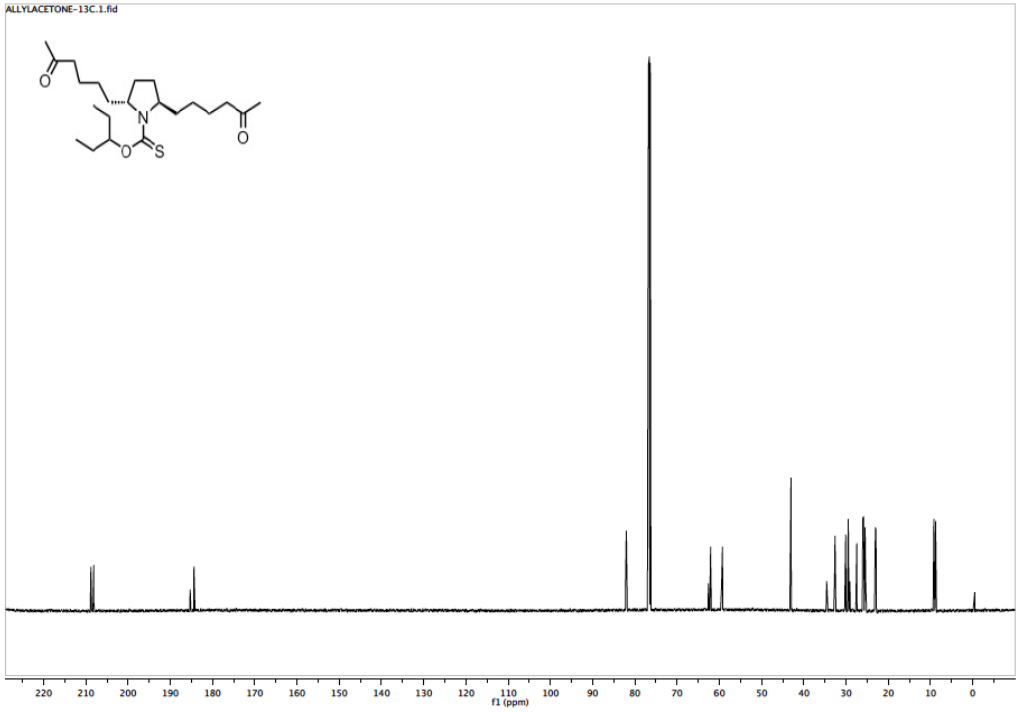
^{13}C NMR spectrum of compound **4l**



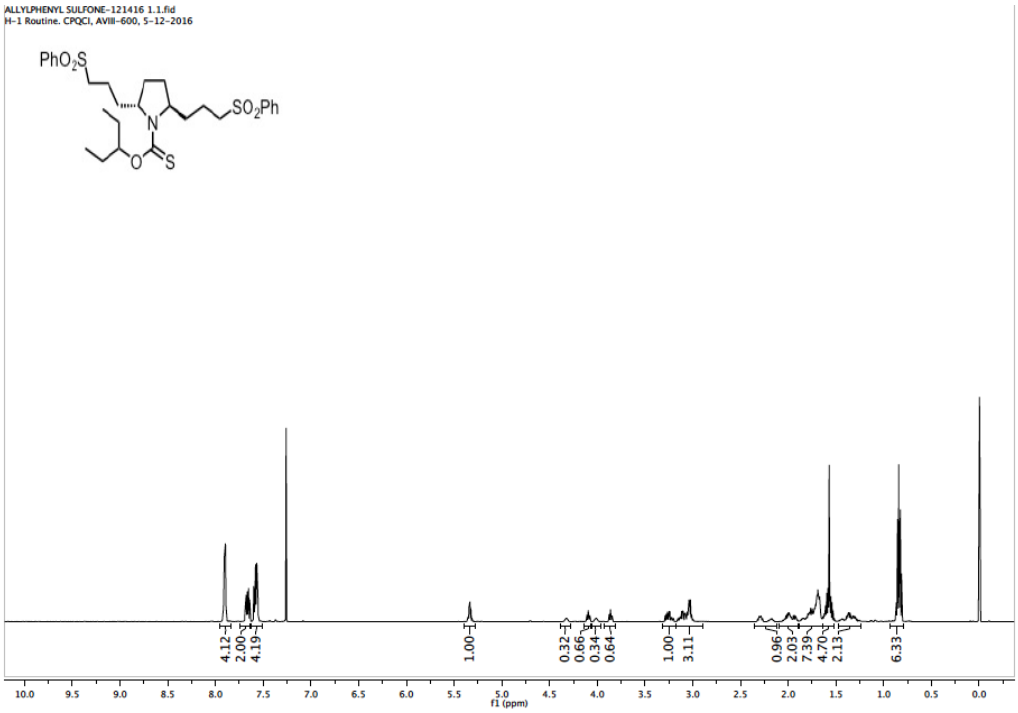
^{1}H NMR spectrum of compound **4m**



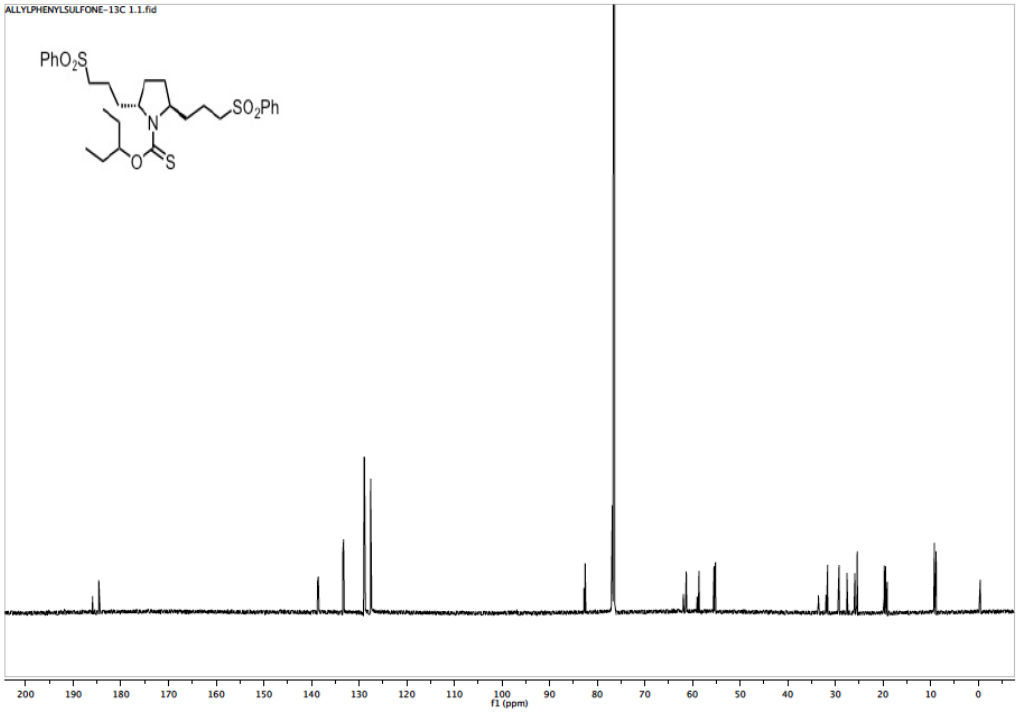
^{13}C NMR spectrum of compound **4m**



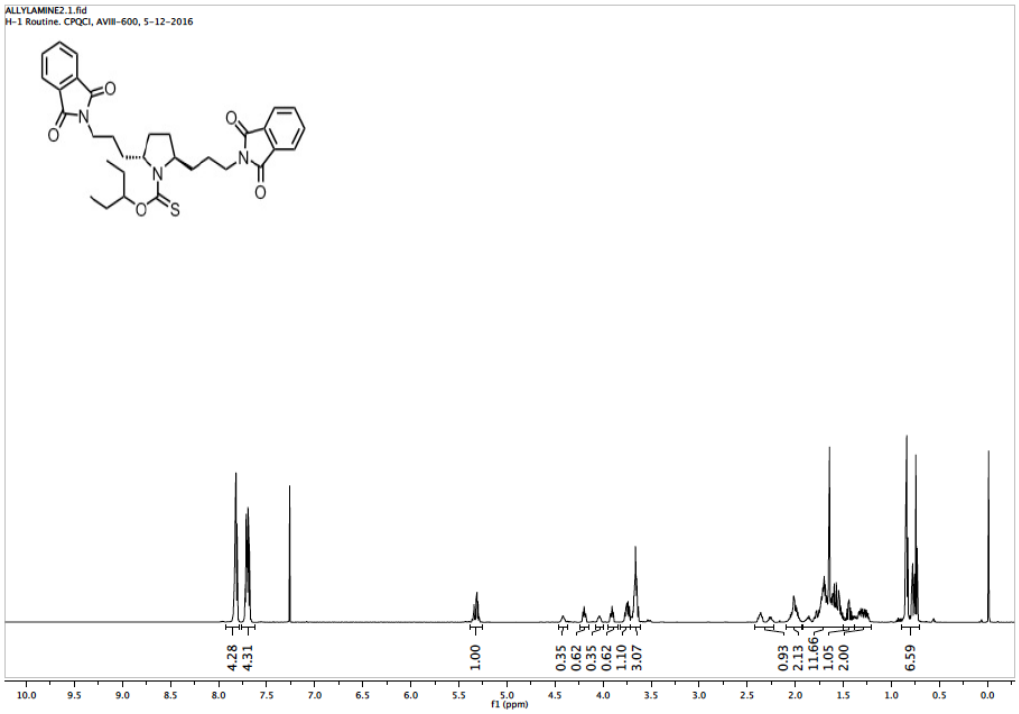
^{1}H NMR spectrum of compound **4n**



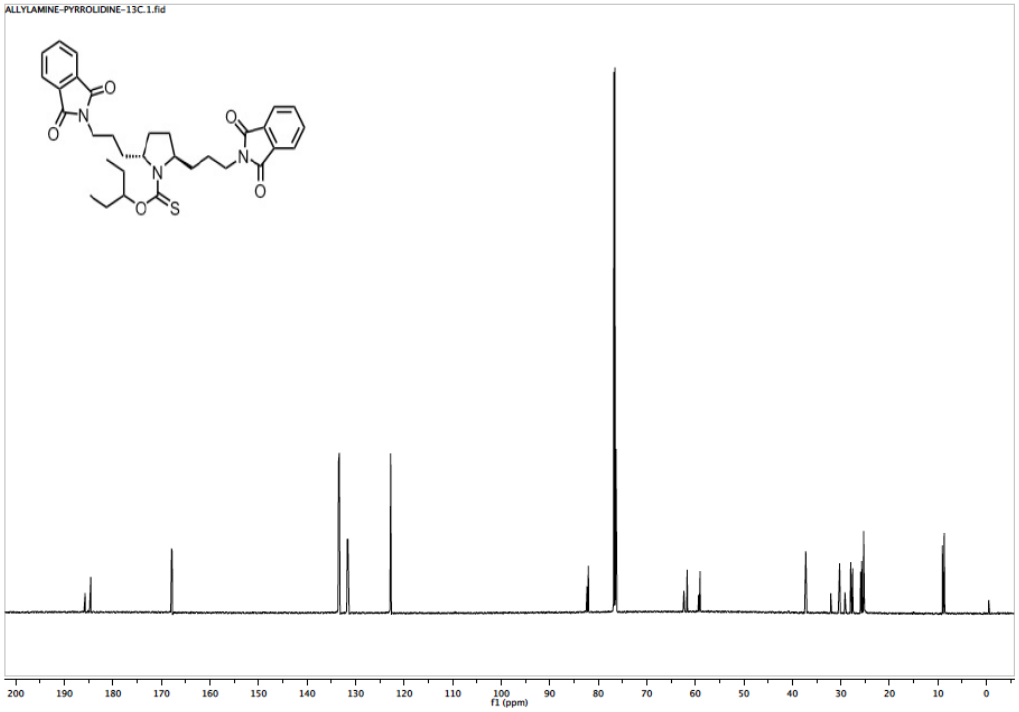
^{13}C NMR spectrum of compound **4n**



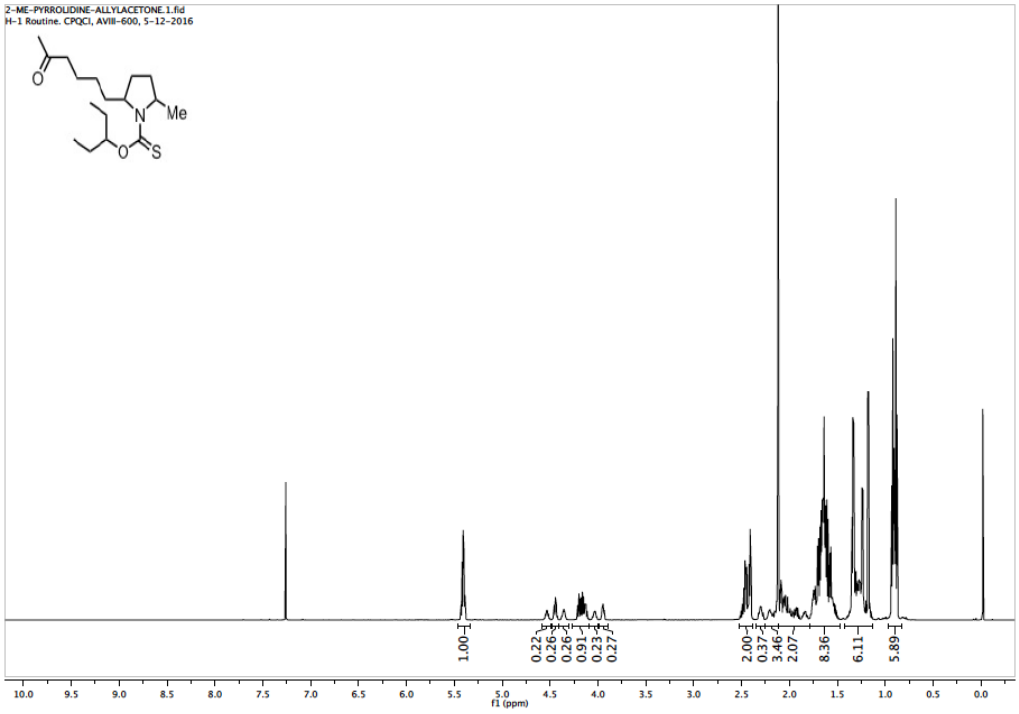
^{1}H NMR spectrum of compound **4o**



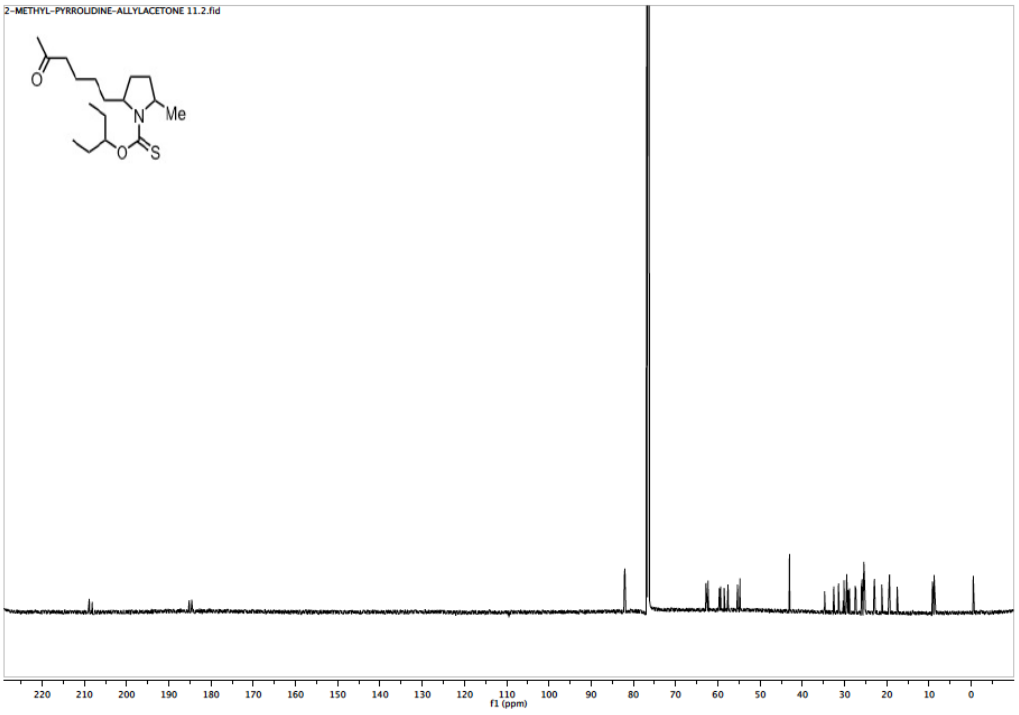
^{13}C NMR spectrum of compound **4o**



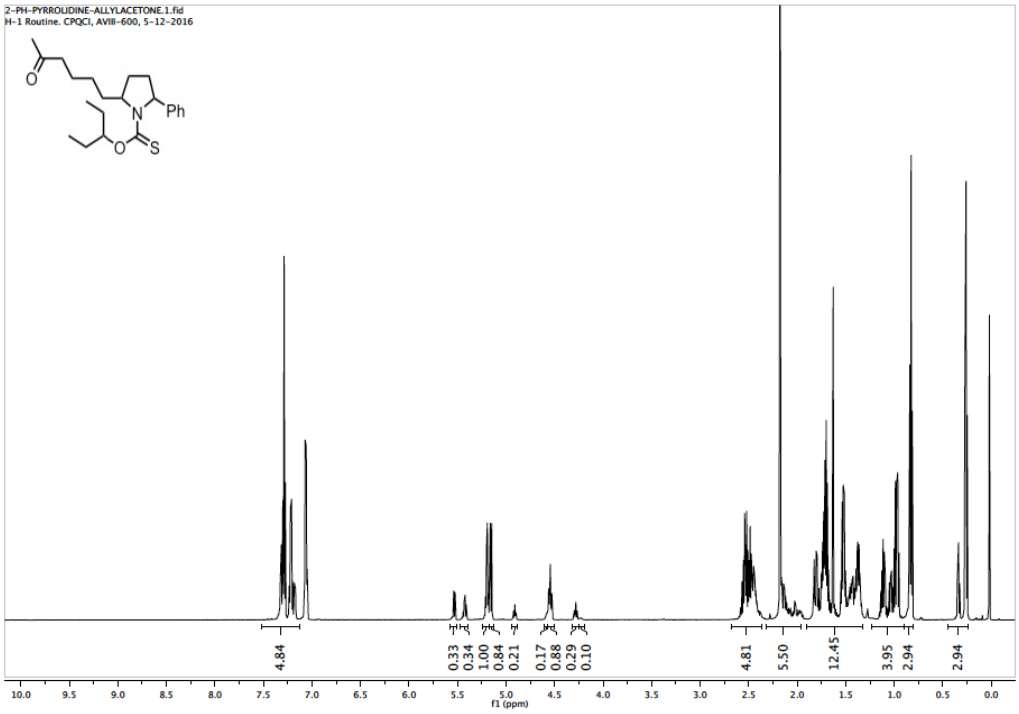
^{1}H NMR spectrum of compound **6a**



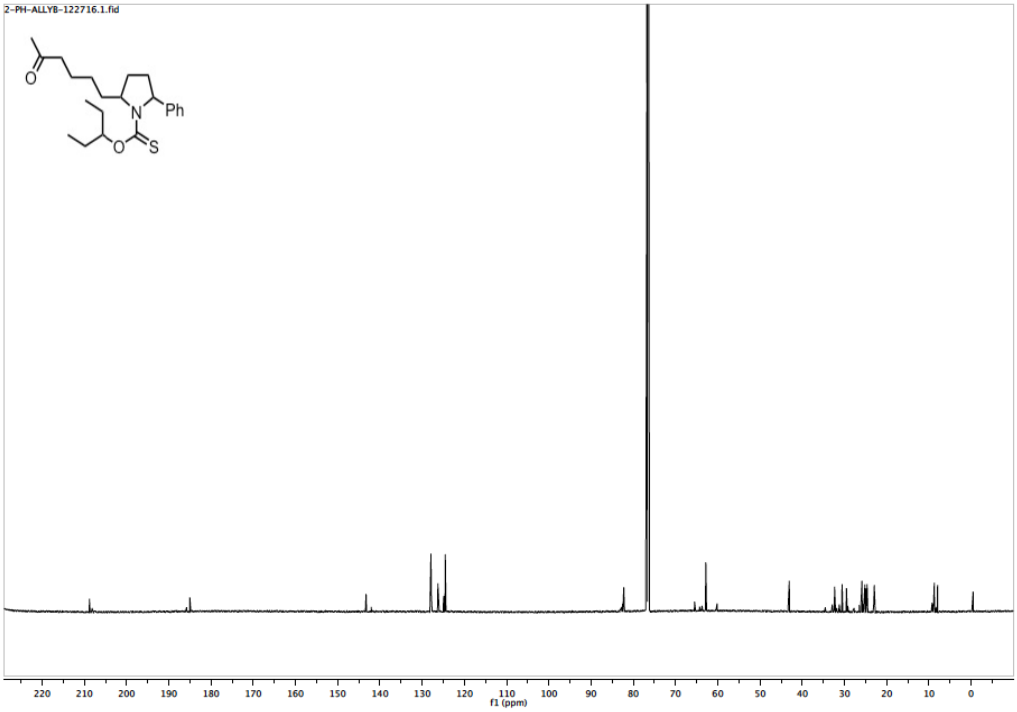
^{13}C NMR spectrum of compound **6a**



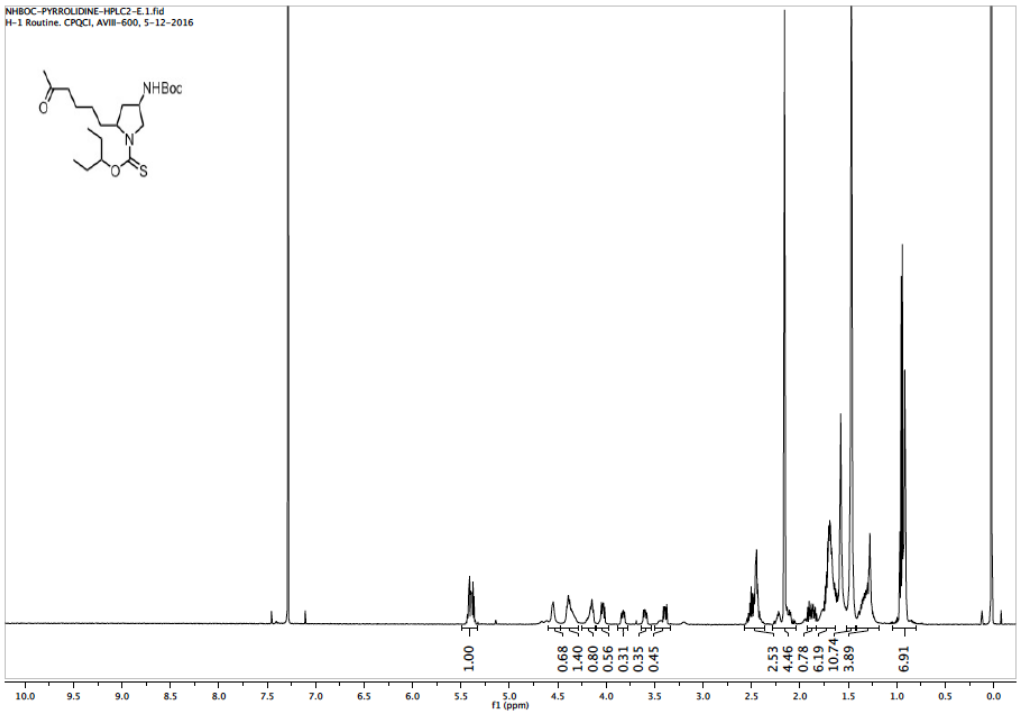
^{1}H NMR spectrum of compound **6b**



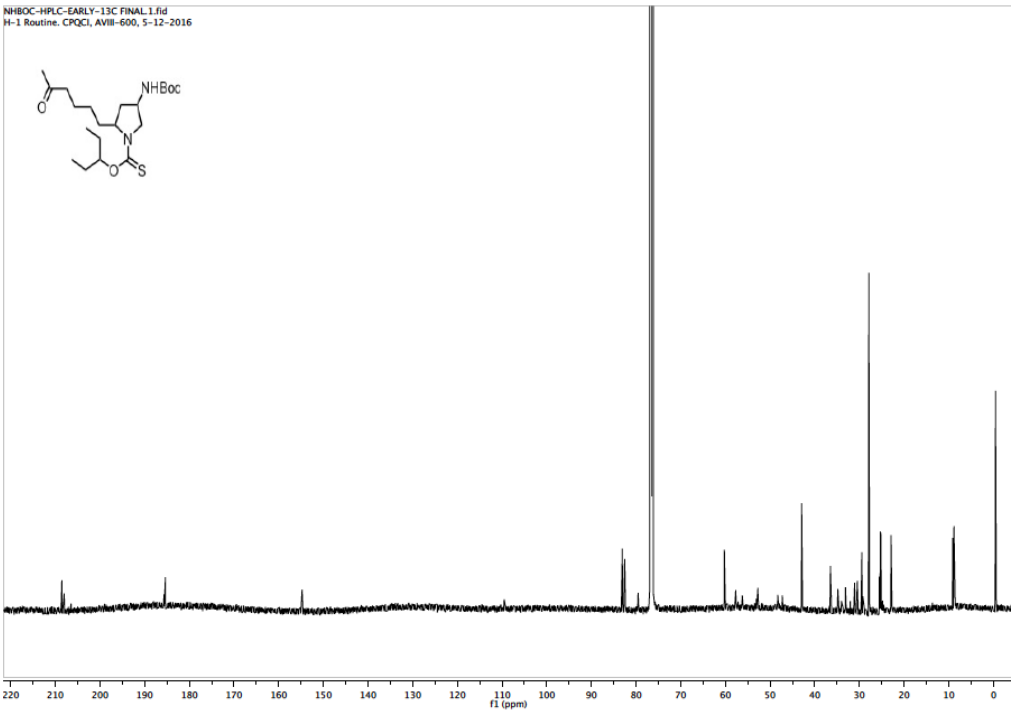
^{13}C NMR spectrum of compound **6b**



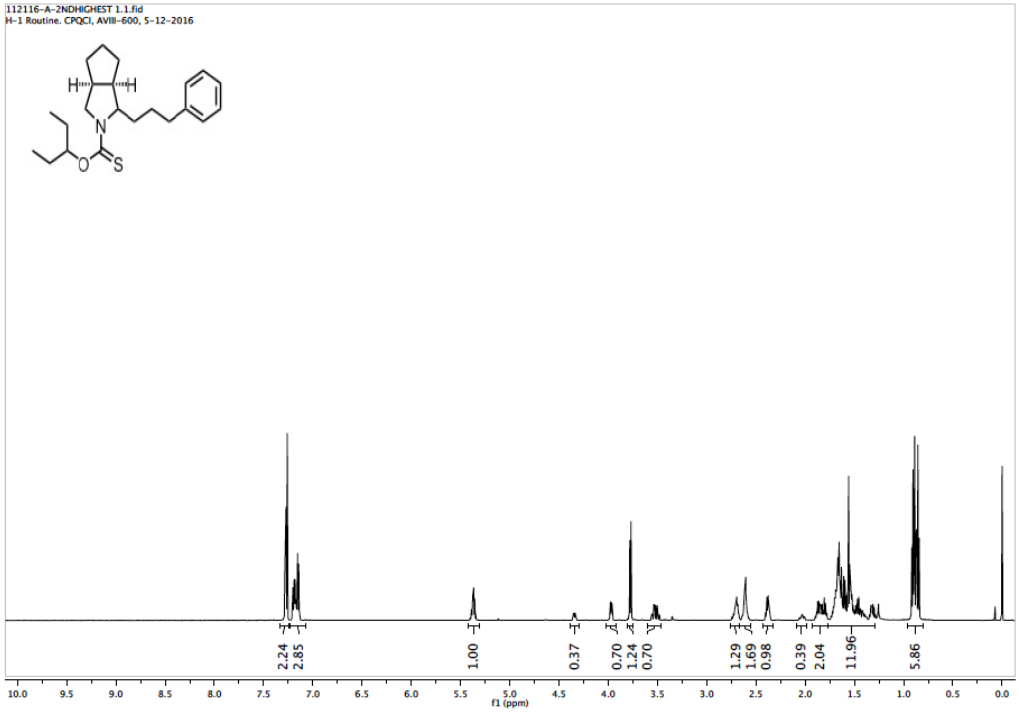
^{1}H NMR spectrum of compound **6c**



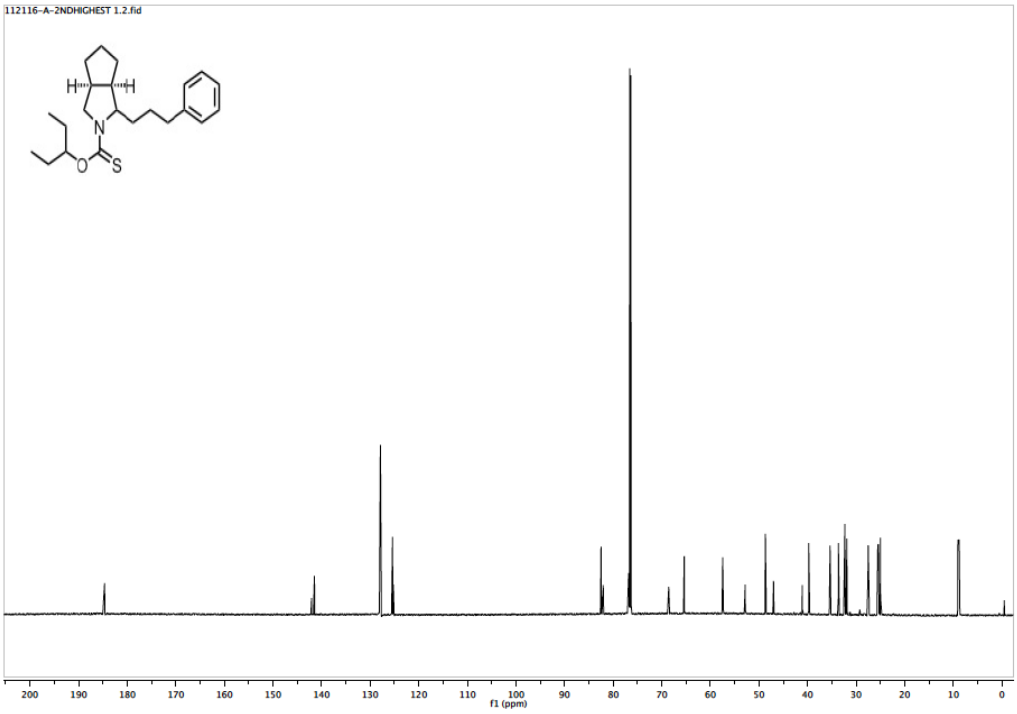
^{13}C NMR spectrum of compound **6c**



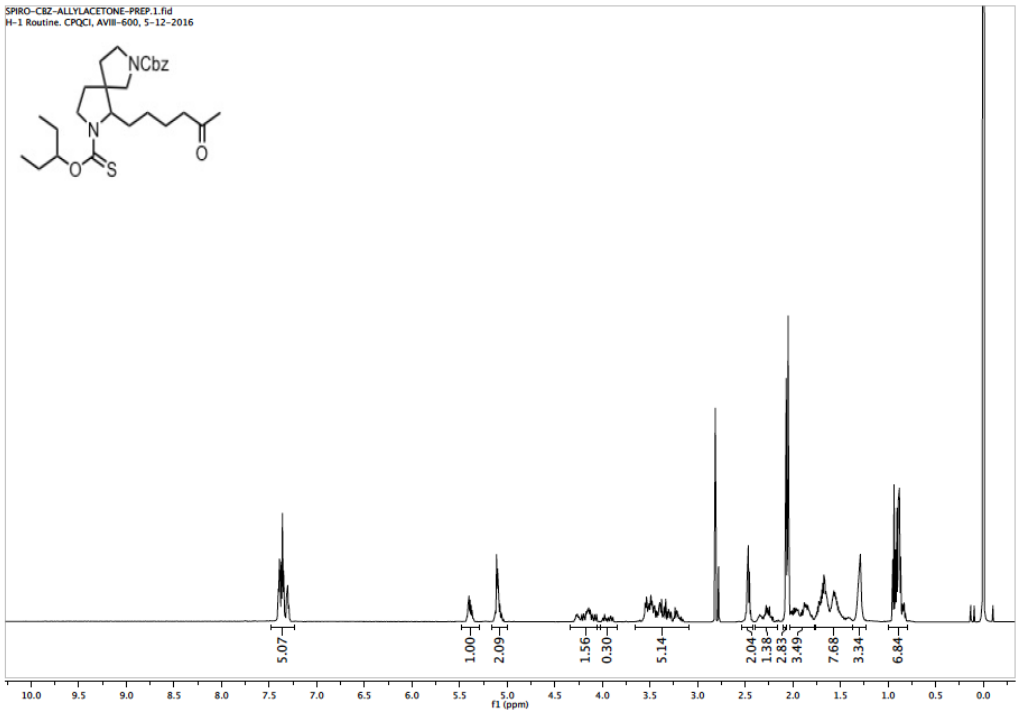
^{1}H NMR spectrum of compound **6d**



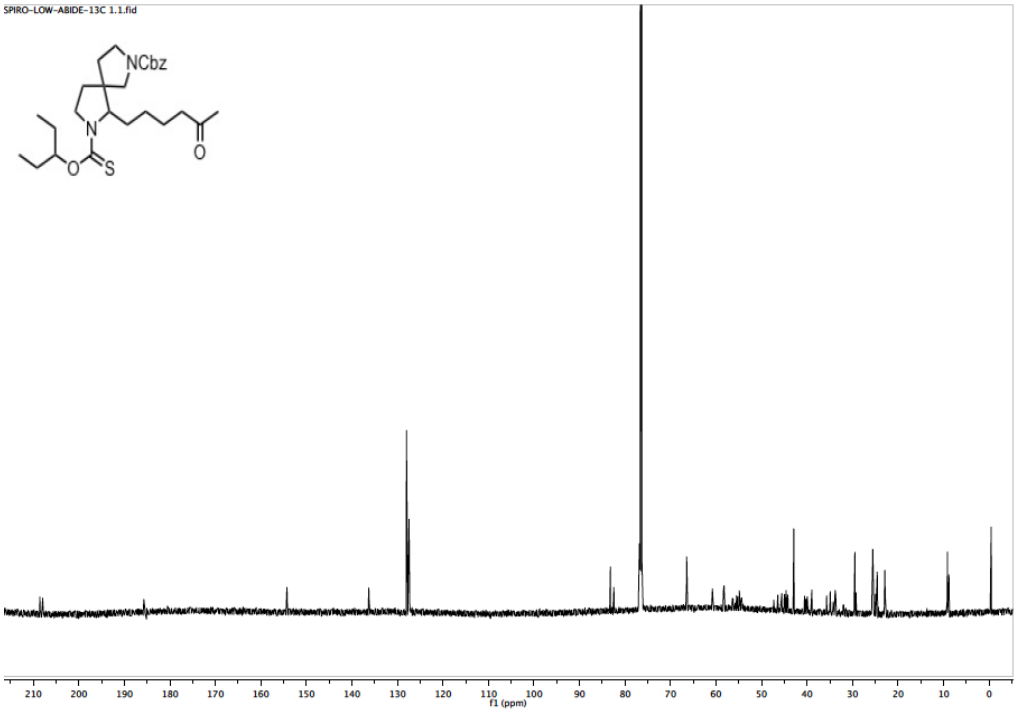
^{13}C NMR spectrum of compound **6d**



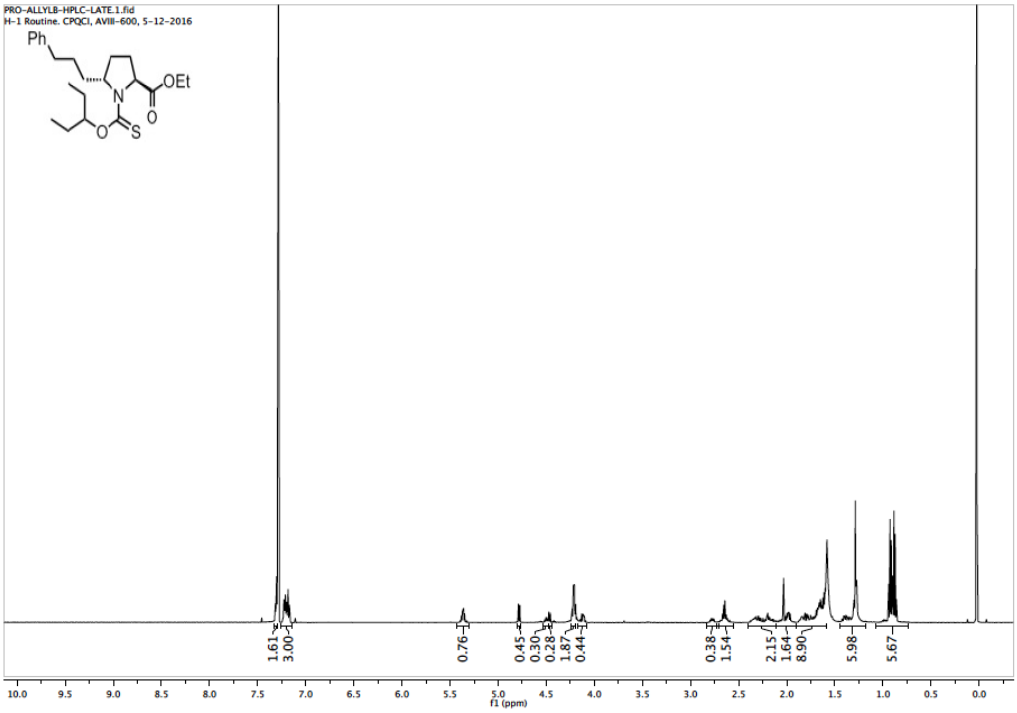
^{1}H NMR spectrum of compound **6e**



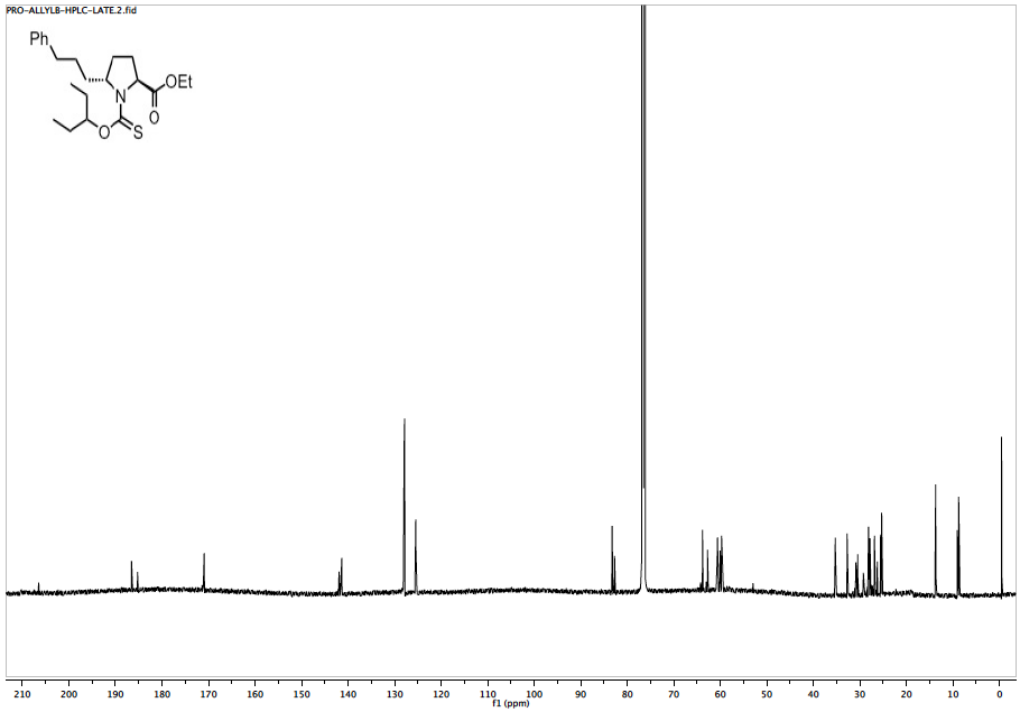
^{13}C NMR spectrum of compound **6e**



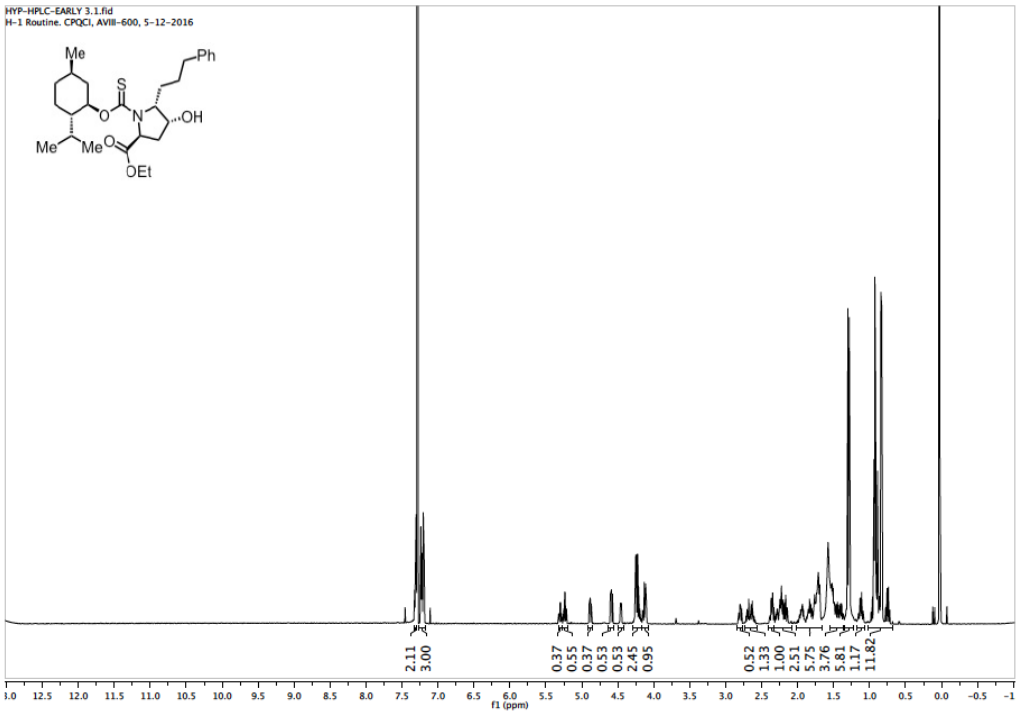
^{1}H NMR spectrum of compound **6f**



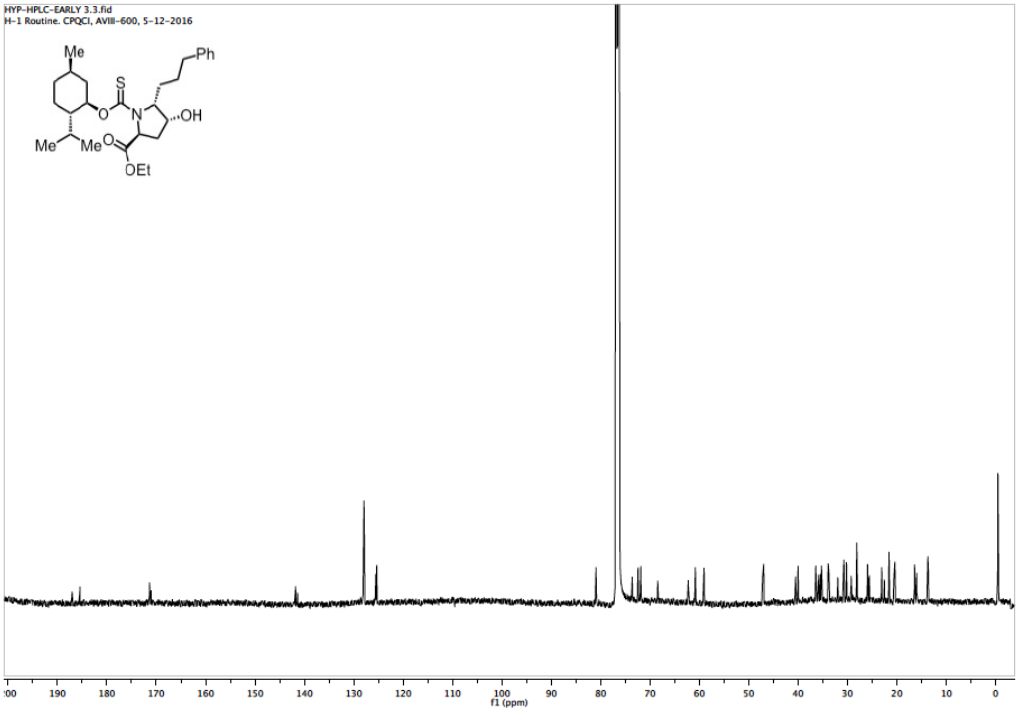
^{13}C NMR spectrum of compound **6f**



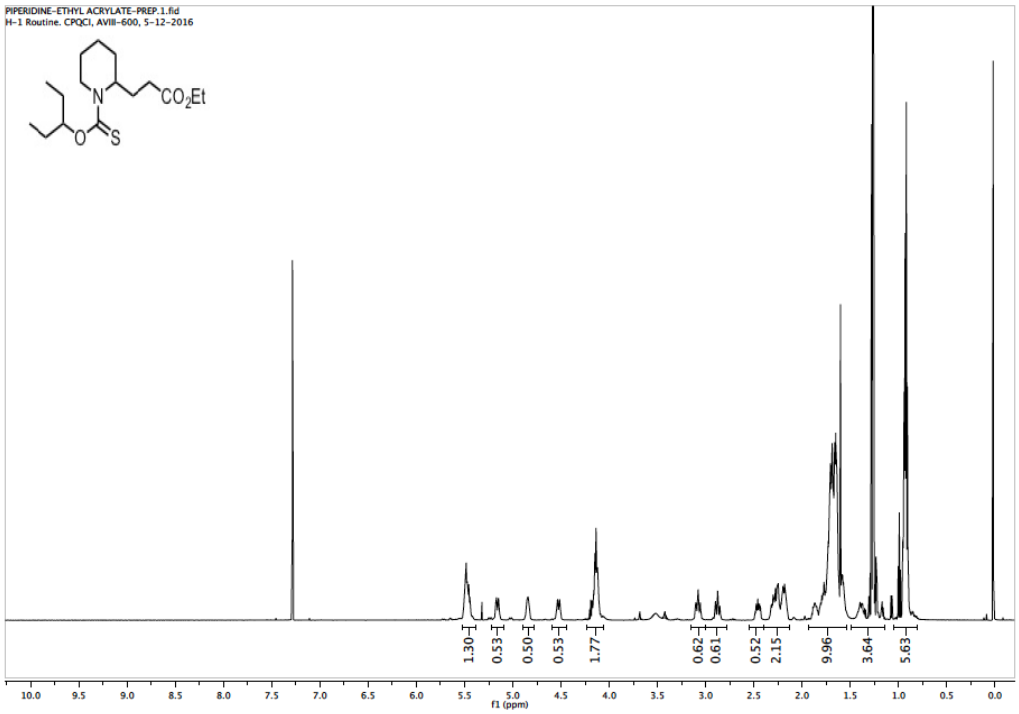
^{1}H NMR spectrum of compound **6g**



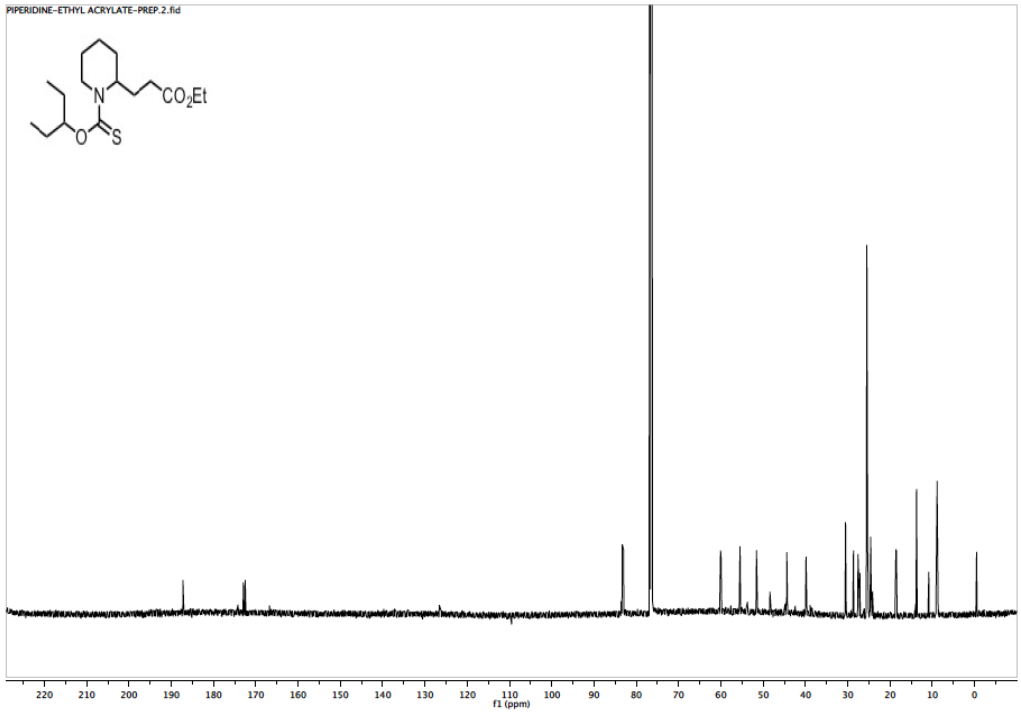
^{13}C NMR spectrum of compound **6g**



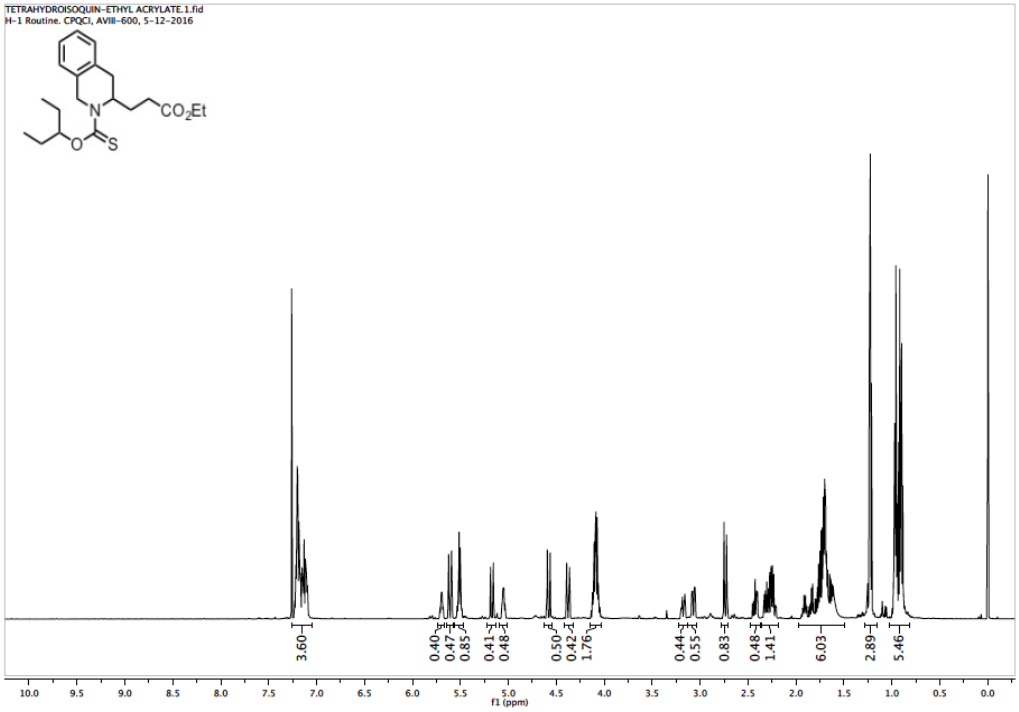
^{1}H NMR spectrum of compound **6h**



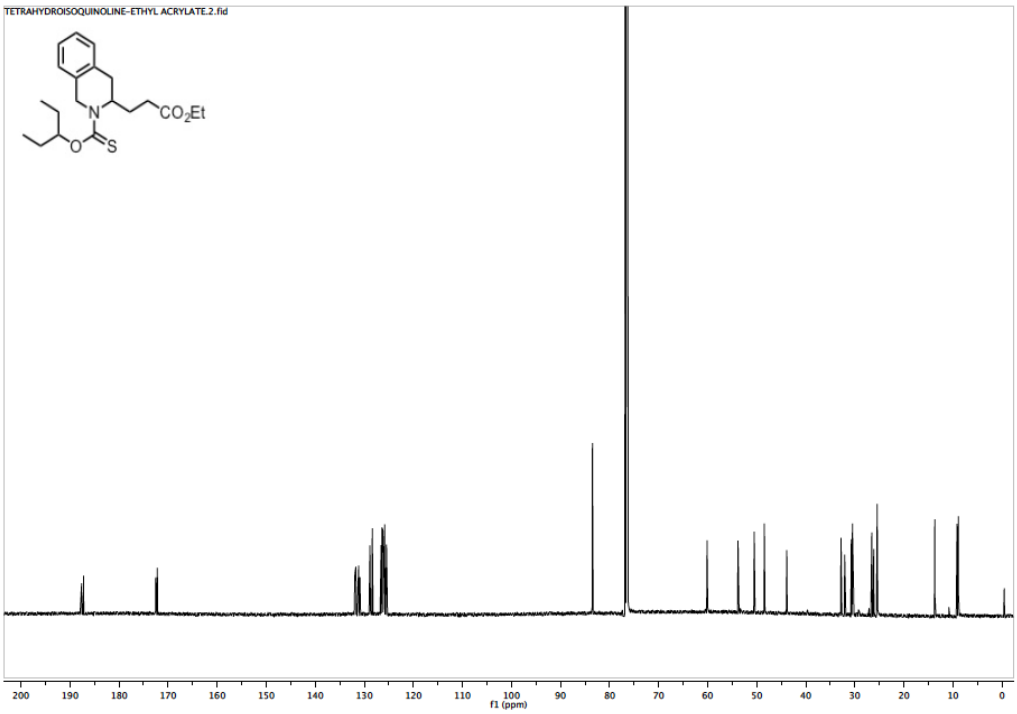
^{13}C NMR spectrum of compound **6h**



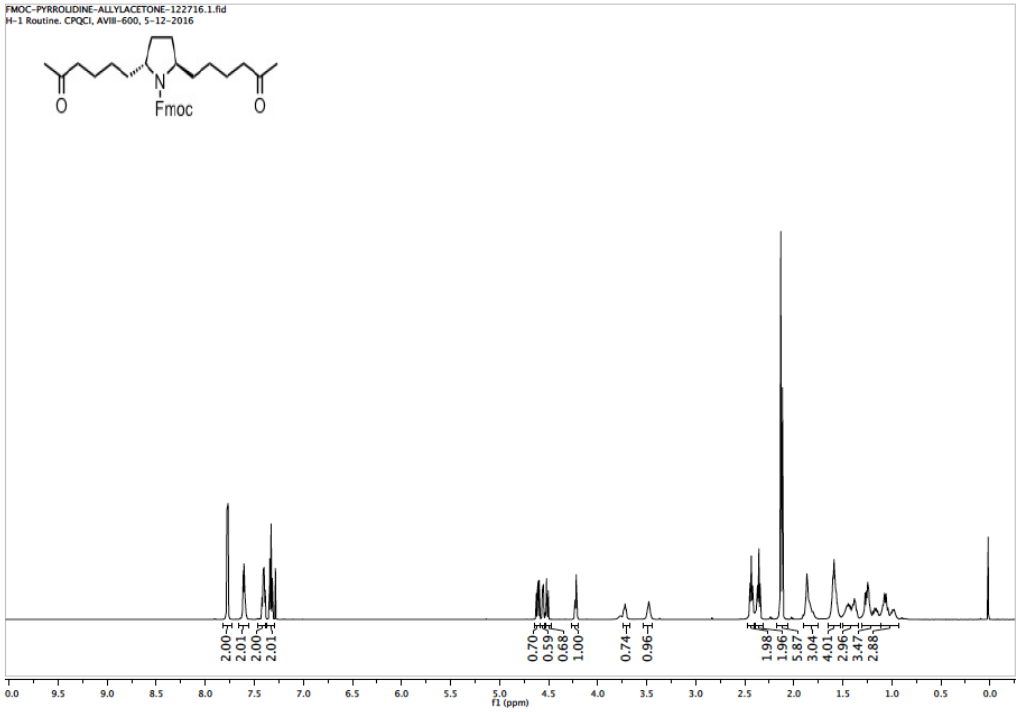
^{1}H NMR spectrum of compound **6i**



^{13}C NMR spectrum of compound **6i**



^{1}H NMR spectrum of compound **7**



^{13}C NMR spectrum of compound **7**