Supporting Information

for

Copper–Catalyzed Thiocarbonylation and Thiolation of Alkyl Iodides

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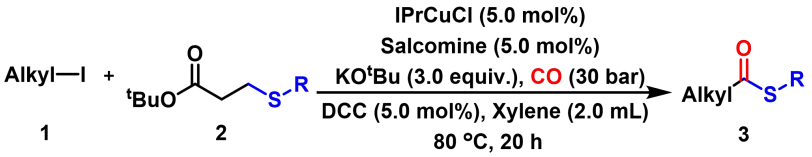
Content

1. General Information

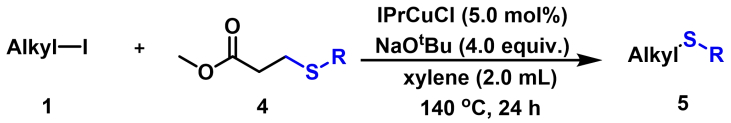
Most of the chemicals were purchased from Aladdin, TCI, Alfa Aesar, Energy–Chemical and used as such unless stated otherwise. Solvents (anhydrous and under inert atmosphere) were collected from the solvent purification system by MBRAUN and used under standard Schlenk technique. NMR spectra were recorded on Bruker Avance 600 and Bruker ARX 400 spectrometers. Chemical shifts (ppm) are given relative to solvent: references for $CDCl_3$ were 7.26 ppm (^1H NMR) and 77.00 ppm (^{13}C NMR). Multiplets were assigned as s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), dd (doublet of doublet), m (multiplet), and br. s (broad singlet). GC–yields were calculated using dodecane as internal standard. All measurements were carried out at room temperature unless otherwise stated. GC–MS analysis was performed on a Shimadzu 2010 instrument and Rtx–5 capillary column. High resolution mass spectra (HRMS) were recorded on Agilent 6210. The data are given as mass units per charge (m/z). Gas chromatography analysis was performed on a Shimadzu 2010 instrument with an FID detector and Rtx–5 capillary column. The products were isolated from the reaction mixture by column chromatography on silica gel 60, 0.063–0.2 mm, 70–230 mesh (Merck). The alkyl iodidesand3–methylthio–tert–butyl propionate derivatives were all synthesized as described previously.

2. General Procedure of Carbonylative Thiomethylation (3a - 3p)



A 4 mL screw–cap vial was charged with IPrCuCl (4.8 mg, 5.0 mol%), Salcomine (3.25 mg, 5 mol%), DCC (2.0 mg, 5.0 mol%), **1** (0.2 mmol, 1.0 equiv.), **2** (0.6 mmol, 3.0 equiv.), Xylene (2.0 mL), KO^{t}Bu (67.2 mg, 3.0 equiv.) and an oven–dried stirring bar. The vial was closed by a Teflon septum and a phenolic cap and connected to the atmosphere through a needle. Then the vial was fixed in an alloy plate and put into Kemi series autoclave (300 mL). At room temperature, the autoclave was flushed with 30 bar carbon monoxide. The autoclave was placed on a heating plate equipped with magnetic stirring and an aluminum block. The reaction was heated at 80 °C for 20 h. Afterward, the autoclave was cooled to room temperature and the pressure was carefully released. After removal of solvent under reduced pressure, pure product was obtained by column chromatography on silica gel (eluent: PE/EA = 500–30:1).

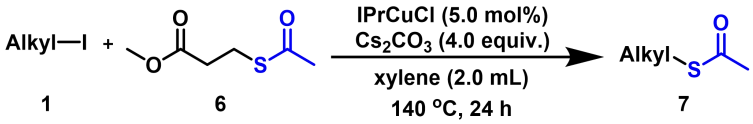
3. General Procedure of Thiomethylation (5a - 5t)



A 25 mL tube was charged with IPrCuCl (4.87 mg, 5.0 mol%), NaO^{t}Bu (76.8 mg, 4.0 equiv.) and an

oven–dried stirring bar. Under N_2 was added **1** (0.2 mmol, 1.0 equiv.), **4** (0.6 mmol, 3.0 equiv.) and xylene (2.0 mL). The reaction is allowed to be heated under 140 °C for 24 h. Afterward, the reaction is cooled to room temperature. After removal of solvent under reduced pressure, pure product was obtained by column chromatography on silica gel (eluent: PE/EA = 500–30:1).

4. General Procedure of Thioacetylation (7a - 7d)



A 25 mL tube was charged with IPrCuCl (4.87 mg, 5.0 mol%), Cs_2CO_3 (260.8 mg, 4.0 equiv.) and an oven–dried stirring bar. Under N_2 was added **1** (0.2 mmol, 1.0 equiv.), **6** (0.6 mmol, 3.0 equiv.) and xylene (2.0 mL). The reaction is allowed to be heated under 140 °C for 24 h. Afterward, the reaction is cooled to room temperature. After removal of solvent under reduced pressure, pure product was obtained by column chromatography on silica gel (eluent: PE/EA = 500–30:1).

5. Characterization Data for Products

S–Methyl 1,4–dioxaspiro[4.5]decane–8–carbothioate (**3b**). Purified by column chromatography (PE). Yield = 29.81 mg (69%). Colorless liquid, ^{1}H NMR (600 MHz, Chloroform-*d*) δ 3.91 (d, *J* = 1.9 Hz, 4H), 2.49 (t, *J* = 10.5 Hz, 1H), 2.24 (d, *J* = 2.0 Hz, 3H), 1.91 (d, *J* = 12.6 Hz, 2H), 1.84 – 1.75 (m, 4H), 1.53 (dt, *J* = 15.5, 8.1 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 202.34, 107.80, 64.25, 50.71, 33.77, 26.86, 11.18. GC–MS (EI, 70ev) m/z(%) = 216 (M^+, 3), 169 (3), 141 (15), 99 (100), 86 (35), 55 (25). HRMS (ESI) calcd for $C_{10}H_{16}O_3SNa$ $[M+Na]^+$: 239.0712, found 239.0713.

S–Methyl 4–(tert–butyl)cyclohexane–1–carbothioate (**3c**). Purified by column chromatography (PE). Yield = 19.0 mg (57%). Colorless liquid, ^{1}H NMR (600 MHz, Chloroform–*d*) δ 2.43-2.37 (m, 1H), 2.25 (s, 3H), 1.99 (d, *J* = 3.33 Hz 2H), 1.88 – 1.80 (m, 2H), 1.43 (m, 2H), 1.05 – 0.96 (m, 3H), 0.83 (s, 9H). ^{13}C NMR (151 MHz, Chloroform–*d*) δ 203.60, 52.81, 47.23, 32.36, 30.02, 27.42, 26.54, 11.17. GC–MS (EI, 70ev) m/z(%) = 167 (M^+, 30), 139 (15), 123 (8), 83 (50), 57 (100). HRMS (ESI) calcd for $C_{12}H_{22}OSNa$ $[M+Na]^+$: 237.1284, found 237.1278.

S–Methyl4–(4–(2,2–difluoroethoxy)phenyl)–2–methylbutane-thioate (**3d**). Purified by column chromatography (PE). Yield = 26.5 mg (46%). Colorless liquid, ^{1}H NMR (600 MHz, Chloroform–*d*) δ 7.11 (t, *J* = 7.7 Hz, 2H), 6.92 – 6.66 (m, 2H), 6.06 (t, *J* = 60.00 Hz, 1H), 4.18 - 4.12 (m, 2H), 2.66 (h, *J* = 7.0 Hz, 1H), 2.56 (q, *J* = 7.6 Hz, 2H), 2.36 – 2.18 (m, 3H), 2.07-1.99 (m, 1H), 1.71-1.64 (m, 1H), 1.20 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform–*d*) δ 203.84, 156.05, 135.05, 129.46, 114.63, 113.73(*J* = 241.6 Hz), 67.49, 47.81, 35.82, 32.38, 17.82, 11.31. ^{19}F NMR (564 MHz, Chloroform–*d*) δ = -125.25, -125.35. GC–MS (EI, 70ev) m/z (%) = 288 (M^+, 10), 241 (126), 184 (24), 171 (100), 104 (45), 77 (12). HRMS (ESI) calcd for $C_{14}H_{18}O_2F_2SNa$ $[M+Na]^+$: 311.0889, found 311.0880.

S–Methyl 4–(4–ethoxyphenyl)–2–methylbutanethioate (**3e**). Purified by column chromatography (PE). Yield = 28.2 mg (56%). Colorless liquid, ^{1}H NMR (600 MHz, Chloroform–*d*) δ 7.07 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.6 Hz, 2H), 4.00 (q, *J* = 6.9 Hz, 2H), 2.67 (q, *J* = 7.0 Hz, 1H), 2.57 – 2.52 (m, 2H), 2.29 (d, 3H), 2.06 – 2.00

(m,1H), 1.71 – 1.63 (m, 1H), 1.39 (t, *J* = 7.0 Hz, 3H), 1.19 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform–*d*) δ 203.99, 157.19, 133.44, 129.23, 114.39, 63.38, 47.83, 35.93, 32.39, 17.81, 14.86, 11.34. GC–MS (EI, 70ev) m/z(%) = 252 (M^+, 30), 205 (30), 148 (96), 120 (22), 107 (100), 77 (20).

S–Methyl 4–(3–chlorophenyl)–2–methylbutanethioate (**3f**). Purified by column chromatography (PE). Yield = 34.4 mg (71%). Colorless liquid, ^{1}H NMR (600 MHz, Chloroform–*d*) δ 7.19 (t, J = 7.5 Hz, 1H), 7.17 – 7.14 (m, 2H), 7.05 (d, *J* = 7.2 Hz, 1H), 2.71 – 2.61 (m, 1H),2.63 – 2.56 (m, 2H), 2.30 (s, 3H), 2.10 – 1.99 (m, 1H), 1.74 – 1.64 (m, 1H), 1.21 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform–*d*) δ 203.66, 143.54, 134.12, 129.58, 128.50, 126.55, 126.14, 47.80, 35.39, 32.99, 17.88, 11.35. GC–MS (EI, 70ev) m/z(%) = 242 (M^+, 4), 195 (14), 125 (100), 104 (30).

S-methyl 4-(3,4-dichlorophenoxy)-2-methylbutanethioate (**3g**). Purified by column chromatography (PE). Yield = 33.8 mg (55%). Colorless liquid, ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 8.8 Hz, 1H), 6.96 (s, 1H), 6.72 (d, *J* = 8.8 Hz, 1H), 3.95 – 3.86 (m, 2H), 2.71 (q, *J* = 7.0 Hz, 1H), 2.28 (d, *J* = 1.8 Hz, 3H), 1.85 (dt, *J* = 15.5, 7.4 Hz, 1H), 1.81 – 1.74 (m, 2H), 1.60 (dt, *J* = 13.9, 7.5 Hz, 1H), 1.21 (dd, *J* = 6.6, 1.9 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 203.70, 157.99, 132.78, 130.58, 123.85, 116.34, 114.53, 68.19, 48.05, 30.43, 26.67, 17.83, 11.29. GC–MS (EI, 70ev) m/z(%) = 306 (M^+, 2), 175 (10), 145 (55), 69 (100). HRMS (ESI) calcd for $C_{13}H_{16}O_2Cl_2SNa$ $[M+Na]^+$: 329.0140, found 329.0140.

S–Methyl 4–(4–isopropoxyphenyl)–2–methylbutanethioate (**3h**). Purified by column chromatography (PE). Yield = 29.8 mg (56%). Colorless liquid, ^{1}H NMR (600 MHz, Chloroform–*d*) δ 7.06 (dt, *J* = 7.9, 3.8 Hz, 2H), 6.80 (m, 2H), 4.74 – 4.33 (m, 1H), 2.69 – 2.66 (m, 1H), 2.56 – 2.53 (m, 2H), 2.29 (d, *J* = 3.4 Hz, 3H), 2.06 – 2.00 (m, 1H), 1.71 1.64 (m, 1H), 1.32 – 1.30 (m, 6H), 1.20 – 1.18 (m, 3H). ^{13}C NMR (151 MHz, Chloroform–*d*) δ 203.95, 156.13, 133.45, 129.24, 115.91, 69.92, 47.86, 35.90, 32.39, 22.08, 17.79, 11.31. GC–MS (EI, 70ev) m/z(%) = 266 (M^+, 16), 177 (18), 162 (20), 120 (32), 107 (100), 77 (13). HRMS (ESI) calcd for $C_{15}H_{22}O_2SNa$ $[M+Na]^+$: 289.1233, found 289.1231.

S–Methyl 4–(4–butoxyphenyl)–2–methylbutanethioate (**3i**). Purified by column chromatography (PE). Yield = 29.7 mg (53%). Colorless liquid, ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.07 (d, *J* = 8.1 Hz, 2H), 6.81 (d, *J* = 8.1 Hz, 2H), 3.93 (t, *J* = 6.5 Hz, 2H), 2.67 (q, *J* = 7.0 Hz, 1H), 2.55 (t, *J* = 7.7 Hz, 2H), 2.29 (s, 3H), 2.04 (dq, *J* = 14.9, 7.5 Hz, 1H), 1.75 (dt, *J* = 14.1, 6.5 Hz, 2H), 1.68 (dt, *J* = 13.7, 6.5 Hz, 1H), 1.52 – 1.45 (m, 2H), 1.20 (d, *J* = 6.4 Hz, 3H), 0.97 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 203.86, 157.45, 133.37, 129.19, 114.46, 67.71, 47.84, 35.92, 32.39, 31.38, 19.23, 17.76, 13.78, 11.28. GC–MS (EI, 70ev) m/z(%) = 280 (M^+, 18), 233 (18), 176 (55), 120 (35), 107 (100), 77 (12). HRMS (ESI) calcd for $C_{16}H_{24}O_2SNa$ $[M+Na]^+$: 303.1389, found 303.1381.

S–Methyl cyclododecanecarbothioate (**3j**). Purified by column chromatography (PE). Yield = 24.7 mg (51%). Colorless liquid, ^{1}H NMR (600 MHz, Chloroform-*d*) δ 2.72 – 2.66 (m, 1H), 2.24 (s, 3H), 1.65 – 1.55 (m, 4H), 1.33 (dd, *J* = 24.4, 10.1 Hz, 18H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 203.72, 49.44, 27.49, 23.73, 23.62, 23.52, 23.30, 22.55, 11.30. GC–MS (EI, 70ev) m/z(%) = 242 (M^+, 1), 195 (45), 167 (8), 111 (60), 97 (100), 83 (65), 55 (75). HRMS (ESI) calcd for $C_{14}H_{26}OSNa$ $[M+Na]^+$:265.1597, found 265.1596.

S–Methyl 2–methyldodecanethioate (**3k**). Purified by column chromatography (PE). Yield = 24.8 mg (63%). Colorless liquid, ^{1}H NMR (600 MHz, Chloroform–*d*) δ 2.66 – 2.59 (m, 1H), 2.27 (s, 3H), 1.72 – 1.66 (m, 1H), 1.39 (m, 1H), 1.24 (d, *J* = 6.8 Hz, 16H), 1.15 (d, *J* = 6.9 Hz, 3H), 0.86 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform–*d*) δ 204.21, 48.51, 34.14, 31.86, 29.54, 29.50, 29.40, 29.27, 27.11, 22.63, 17.63, 14.03, 11.24. GC–MS (EI, 70ev) m/z(%) = 197 (M^+, 30), 169 (7), 113 (14), 99 (18), 71 (70), 57 (100). HRMS (ESI) calcd for $C_{14}H_{28}OSNa$ $[M+Na]^+$: 267.1753, found 267.1758.

S–Methyl 2–methyldecanethioate (**3l**). Purified by column chromatography (PE). Yield = 20.9 mg (52%).

Colorless liquid, ^{1}H NMR (600 MHz, Chloroform-d) δ 2.64 (q, J = 6.9 Hz, 1H), 2.28 (s, 3H), 1.73 – 1.67 (m, 1H), 1.42 – 1.38 (m, 1H), 1.26 (d, J = 5.9 Hz, 12H), 1.16 (d, J = 6.9 Hz, 3H), 0.88 (t, J = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 204.15, 48.50, 34.12, 31.79, 29.49, 29.34, 29.17, 27.09, 22.58, 17.60, 13.99, 11.21. GC–MS (EI, 70ev) m/z (%) = 201 (M^+, 4), 169 (35), 99 (16), 85 (70), 57 (100). HRMS (ESI) calcd for $C_{12}H_{24}OSNa$ $[M+Na]^+$: 239.1440, found 239.1488.

S-Phenethyl cyclohexanecarbothioate (**3m**). Purified by column chromatography (PE). Yield = 34.2 mg (69%). Colorless liquid, ^{1}H NMR (600 MHz, Chloroform–*d*) δ = 7.29 (s, 2H), 7.22 (s, 3H), 3.10 (d, *J* = 7.3, 2H), 2.85 (s, 2H), 2.47 (t, *J* = 11.2, 1H), 1.91 (d, *J* = 11.7, 2H), 1.78 (d, *J* = 9.6, 2H), 1.67 (s, 2H), 1.46 (d, *J* = 11.9, 2H), 1.27 (d, *J*=11.7, 2H). ^{13}C NMR (151 MHz, Chloroform–*d*) δ = 202.78, 140.10, 128.56, 128.39, 126.39, 52.71, 35.96, 29.79, 29.51, 25.62, 25.48. GC–MS (EI, 70ev) m/z(%) = 248 (M^+, 10), 135 (4), 111 (25), 104 (80), 83 (100), 55 (40) HRMS (ESI) calcd for $C_{15}H_{21}OSH$ $[M+H]^+$: 249.1308, found 249.1304.

Methyl(4–(p–tolyl)butan–2–yl)sulfane (**5a**)[1]. Purified by column chromatography (PE). Yield = 31 mg (80%). Colorless liquid, ^{1}H NMR (600 MHz, Chloroform–*d*) δ 7.10 (d, *J* = 4.9 Hz, 4H), 2.75 – 2.69 (m, 2H), 2.66 (p, *J* = 6.8 Hz, 1H), 2.33 (d, *J* = 4.8 Hz, 3H), 2.07 (d, *J* = 4.9 Hz, 3H), 1.87 (m, *J* = 13.6, 8.9, 6.7 Hz, 1H), 1.77 (m, 1H), 1.31 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform–*d*) δ 138.81, 135.19, 128.99, 128.22, 40.52, 38.09, 32.73, 20.91, 20.77, 12.79. GC–MS (EI, 70ev) m/z(%) = 194 (M^+, 21), 146 (38), 131 (100), 105 (60), 75 (20).

Methyl(5–phenoxypentan–2–yl)sulfane (**5b**)[1]. Purified by column chromatography (PE). Yield = 35 mg (83%). Colorless liquid, ^{1}H NMR (600 MHz, Chloroform–*d*) δ 7.29 -7.26 (m, 2H), 6.93 (t, J = 7.3 Hz, 1H), 6.89 (d, J = 7.8 Hz, 2H), 3.99 – 3.96 (m, 2H), 2.73 (h, *J* = 6.8 Hz, 1H), 2.08 (s, 3H), 1.96 – 1.84 (m, 2H), 1.78 – 1.62 (m, 2H), 1.31 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform–*d*) δ 158.98, 129.37, 120.55, 114.49, 67.56, 40.93, 32.75, 26.80, 20.82, 12.93. GC–MS (EI, 70ev) m/z (%) = 210 (M^+, 5), 117 (100), 94 (12), 69 (65), 61 (41).

(4–(4–Ethoxyphenyl)butan–2–yl)(methyl)sulfane (**5c**)[1]. Purified by column chromatography (PE). Yield = 33mg (74%). Colorless liquid, ^{1}H NMR (600 MHz, Chloroform–*d*) δ 7.15 – 7.05 (m, 2H), 6.85 – 6.76 (m, 2H), 4.01 (q, *J* = 7.0 Hz, 2H), 2.77 – 2.55 (m, 3H), 2.06 (s, 3H), 1.88 – 1.82 (m, 1H), 1.77 – 1.71 (m, 1H), 1.39 (t, *J* = 7.0 Hz, 3H), 1.30 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform–*d*) δ 157.13, 133.85, 129.21, 114.43, 63.40, 40.47, 38.22, 32.29, 20.80, 14.86, 12.81. GC–MS (EI, 70ev) m/z(%) = 224 (M^+, 44), 176 (71), 161 (40), 133 (78), 107 (100), 89 (38), 77 (34), 61 (12).

Methyl(4–(4–(trifluoromethoxy)phenyl)butan–2–yl)sulfane(**5d**). Purified by column chromatography (PE). Yield = 34.8 mg (66%). Colorless liquid, ^{1}H NMR (600 MHz, Chloroform–*d*) δ 7.23 – 7.17 (m, 2H), 7.12 (d, *J* = 8.1 Hz, 2H), 2.75 (t, *J* = 7.9 Hz, 2H), 2.64 (h, *J* = 6.8 Hz, 1H), 2.06 (s, 3H), 1.89 – 1.82 (m, 1H), 1.80 -1.74 (m, 1H), 1.31 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform–*d*) δ 147.41, 140.65, 129.56, 120.87, 120.49 (d, *J* = 128.3 Hz), 40.43, 37.85, 32.49, 20.82, 12.74. GC–MS (EI, 70ev) m/z(%) = 264 (M^+, 40), 216 (80), 201 (100), 175 (70), 135 (12), 131 (45), 109 (30), 75 (60), 61 (14). ^{19}F NMR (564 MHz, Chloroform–*d*) δ = -57.98. HRMS (ESI) calcd for $C_{12}H_{15}OF_3SNa$ $[M+Na]^+$: 287.0688, found 287.0687.

(4–(4–Fluorophenyl)butan–2–yl)(methyl)sulfane (**5e**). Purified by column chromatography (PE). Yield = 34 mg (86%). Colorless liquid, ^{1}H NMR (600 MHz, Chloroform–*d*) δ 7.15 - 7.13 (m, 2H), 6.95 (t, *J* = 8.7 Hz, 2H), 2.71 (t, *J* = 7.9 Hz, 2H), 2.63 (h, *J* = 6.8 Hz, 1H), 2.06 (s, 3H), 1.87 – 1.81 (m, 1H), 1.78 – 1.69 (m, 1H), 1.30 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform–*d*) δ 161.24 (d, *J* = 244.6 Hz), 137.48 (d, *J* = 3.0 Hz), 129.66 (d, *J* = 7.5 Hz), 115.04 (d, *J* =19.6 Hz), 40.42, 38.08, 32.36, 20.82, 12.79. GC–MS (EI, 70ev) m/z (%) = 198 (M^+, 30), 150 (58),135 (100), 109 (92), 75 (27). ^{19}F NMR (564 MHz, Chloroform–*d*) δ = -117.79. HRMS (ESI) calcd for $C_{11}H_{16}FS$ $[M+H]^+$: 199.0951, found 199.0943.

(4–(3–Chlorophenyl)butan–2–yl)(methyl)sulfane (**5f**)[1]. Purified by column chromatography (PE). Yield = 36 mg (84%). Colorless liquid, ^{1}H NMR (600 MHz, Chloroform–*d*) δ 7.19 (d, J = 7.9 Hz, 2H), 7.17 – 7.13 (m, 1H), 7.07 (d, *J* = 7.4 Hz, 1H), 2.72 (t, *J* = 8.0 Hz, 2H), 2.64 (h, *J* = 6.8 Hz, 1H), 2.06 (s, 3H), 1.90 – 1.80 (m, 1H), 1.80 -1.74 (m,1H), 1.34 – 1.27 (m, 3H). ^{13}C NMR (151 MHz, Chloroform–*d*) δ 143.98, 134.11, 129.55, 128.50, 126.57, 126.00, 40.44, 37.68, 32.87, 20.83, 12.77. GC–MS (EI, 70ev) m/z(%) = 214 (M^+, 25), 166 (32), 151 (15), 131 (100), 89 (32), 75 (46).

Methyl(4–(3–(methylthio)butyl)phenyl)sulfane (**5g**)[1]. Purified by column chromatography (PE). Yield = 28 mg (62%). Colorless liquid, ^{1}H NMR (600 MHz, Chloroform–*d*) δ 7.23 – 7.16 (m, 2H), 7.15 – 7.07 (m, 2H), 2.72 – 2.69 (m, 2H), 2.64 (h, *J* = 6.8 Hz, 1H), 2.46 (s, 3H), 2.06 (s, 3H), 1.88 – 1.82 (m, 1H), 1.79 – 1.68 (m, 1H), 1.30 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform–*d*) δ 139.08, 135.32, 128.92, 127.24, 40.45, 37.92, 32.64, 20.81, 16.35, 12.80. GC–MS (EI, 70ev) m/z(%) = 226 (M^+, 87), 178 (96), 137 (88), 131 (100), 89 (38), 75 (28), 61 (12).

Methyl(4–(naphthalen–2–yl)butan–2–yl)sulfane (**5h**). Purified by column chromatography (PE). Yield = 41 mg (90%). Colorless liquid, ^{1}H NMR (600 MHz, Chloroform–*d*) δ 7.88 – 7.75 (m, 3H), 7.65 (s, 1H), 7.48 – 7.42(m, 2H), 7.36 (m, 1H), 2.93 (m, 2H), 2.71 (h, *J* = 6.8 Hz, 1H), 2.09 (s, 3H), 2.03 – 1.91 (m, 1H), 1.92 – 1.86 (m, 1H), 1.36 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform–*d*) δ 139.42, 133.62, 131.99, 127.89, 127.56, 127.36, 127.24, 126.39, 125.88, 125.11, 40.55, 37.84, 33.34, 20.86, 12.85. GC–MS (EI, 70ev) m/z(%) = 230 (M^+, 70), 182 (60), 167 (100), 142 (90), 115 (60), 89 (30), 75 (40), 61 (11). HRMS (ESI) calcd for $C_{15}H_{18}SNa$ $[M+Na]^+$: 253.1021, found 253.1016.

Methyl(4–phenylbutan–2–yl)sulfane (**5i**)[1]. Purified by column chromatography (PE). Yield = 27 mg (75%). Colorless liquid, ^{1}H NMR (600 MHz, Chloroform–*d*) δ 7.28 (t, *J* = 7.5 Hz, 2H), 7.21 – 7.17 (m, 3H), 2.75 (t, *J* = 7.6 Hz, 2H), 2.67 (h, *J* = 6.8 Hz, 1H), 2.07 (s, 3H), 1.93 – 1.83 (m, 1H), 1.82 – 1.74 (m, 1H), 1.32 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform–*d*) δ 141.93, 128.37, 128.32, 125.77, 40.55, 37.99, 33.21, 20.80, 12.81. GC–MS (EI, 70ev) m/z(%) = 180 (M^+, 30), 132 (50), 117 (100), 91 (75), 75 (25).

Dodecan–2–yl(methyl)sulfane (**5j**)[1]. Purified by column chromatography (PE). Yield = 35.4 mg (82%). Colorless liquid, ^{1}H NMR (600 MHz, Chloroform–*d*) δ 2.63 (h, *J* = 6.7 Hz, 1H), 2.05 (s, 3H), 1.54 (q, *J* = 6.7 Hz, 1H), 1.45 – 1.41 (m, 1H), 1.37 (t, *J* = 7.0 Hz, 2H), 1.26 (q, *J* = 5.9 Hz, 17H), 0.87 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform–*d*) δ 41.24, 36.45, 31.85, 29.56, 29.51, 29.26, 27.03, 22.61, 20.68, 14.01, 13.02. GC–MS (EI, 70ev) m/z(%) = 216 (M^+, 17), 210 (7), 168 (4), 111 (10), 97 (18), 75 (100), 57 (40).

Methyl(tridecan–2–yl)sulfane (**5k**)[1]. Purified by column chromatography (PE). Yield = 34 mg (75%). Colorless liquid, ^{1}H NMR (600 MHz, Chloroform–*d*) δ 2.62 (q, *J* = 6.7 Hz, 1H), 2.04 (s, 3H), 1.57 – 1.52 (m, 1H), 1.43 (m, 1H), 1.37 (d, *J* = 6.1 Hz, 2H), 1.28 – 1.22 (m, 19H), 0.86 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform–*d*) δ 41.24, 36.46, 31.87, 29.61, 29.57, 29.52, 29.29, 27.04, 22.62, 20.70, 14.02, 13.02. GC–MS (EI, 70ev) m/z(%) = 230 (M^+, 20), 215 (10), 182 (5), 111 (10), 97 (20), 95 (100), 55 (40).

Methyl(3–phenylpropyl)sulfane (**5l**)[1]. Purified by column chromatography (PE). Yield = 25 mg (75%). Colorless liquid, ^{1}H NMR (600 MHz, Chloroform–*d*) δ 7.32 – 7.26 (m, 2H), 7.23 – 7.13 (m, 3H), 2.73 (t, *J* = 7.6 Hz, 2H), 2.51 (t, *J* = 7.3 Hz, 2H), 2.10 (s, 3H), 1.93 (p, *J* = 7.3 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform–*d*) δ 141.57, 128.43, 128.33, 125.85, 34.73, 33.62, 30.64, 15.41. GC–MS (EI, 70ev) m/z(%) = 166 (M^+, 42), 117 (100), 91 (45), 75 (24), 61 (15).

(2,6–Dichlorophenethyl)(methyl)sulfane (**5m**)[1]. Purified by column chromatography (PE). Yield = 30 mg (68%). Colorless liquid, ^{1}H NMR (600 MHz, Chloroform–*d*) δ 7.27 – 7.26 (m, 2H), 7.15 – 7.02 (m, 1H), 3.26 – 3.16 (m, 2H), 2.75 – 2.65 (m, 2H), 2.21 (d, *J* = 0.9 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform–*d*) δ 136.24, 135.40, 128.20, 128.03, 31.86, 31.49, 15.50. GC–MS (EI, 70ev) m/z (%) = 220 (M^+, 5), 185 (75), 170 (8), 101

(8), 75 (6), 61 (100).

Dodecyl(methyl)sulfane (**5n**)[2]. Purified by column chromatography (PE). Yield = 41.2 mg (95%). Colorless liquid, ^{1}H NMR (600 MHz, Chloroform–*d*) δ 2.46 (t, *J* = 7.5 Hz, 2H), 2.07 (s, 3H), 1.56 (p, *J* = 7.5 Hz, 2H), 1.34 (q, *J* = 7.2 Hz, 2H), 1.24 (s, 16H), 0.86 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform–*d*) δ 34.31, 31.86, 29.60, 29.58, 29.55, 29.49, 29.29, 29.21, 29.18, 28.80, 22.62, 15.47, 14.02. GC–MS (EI, 70ev) m/z (%) = 216 (M^+,50), 201 (100), 111 (15), 97 (40), 69 (70), 55 (90).

Methyl(octadecyl)sulfane (**5o**)[3]. Purified by column chromatography (PE). Yield = 58 mg (97%). Colorless liquid, ^{1}H NMR (600 MHz, Chloroform–*d*) δ 2.51 – 2.42 (m, 2H), 2.07 (s, 3H), 1.57 (t, *J* = 7.6 Hz, 2H), 1.38 – 1.33 (m, 2H), 1.28 - 1.24 (m, 28H), 0.86 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform–*d*) δ 34.31, 31.89, 29.65, 29.63, 29.61, 29.57, 29.50, 29.31, 29.23, 29.19, 28.81, 22.64, 15.47, 14.03. GC–MS (EI, 70ev) m/z (%)= 300 (M^+, 32), 285 (100), 111 (17), 97 (35), 69 (45), 55 (60).

1,8–Bis(methylthio)octane (**5p**)[4]. Purified by column chromatography (PE). Yield = 38.4 mg (93%). Colorless liquid, ^{1}H NMR (600 MHz, Chloroform–*d*) δ 2.45 (t, *J* = 7.4 Hz, 4H), 2.06 (d, *J* = 1.2 Hz, 6H), 1.56 (p, *J* = 7.4 Hz, 4H), 1.37 – 1.32 (m, 4H), 1.30 – 1.26 (m, 4H). ^{13}C NMR (151 MHz, Chloroform–*d*) δ 34.26, 29.11, 29.07, 28.69, 15.49. GC–MS (EI, 70ev) m/z(%) = 206 (M^+, 40), 159 (30), 143 (35), 110 (20), 87 (14), 69 (50), 61 (100).

Benzyl(cyclohexyl)sulfane (**5q**)[5]. Purified by column chromatography (PE). Yield = 22 mg (54%). Colorless liquid, ^{1}H NMR (600 MHz, Chloroform–*d*) δ 7.33 – 7.27 (m, 4H), 7.24 – 7.19 (m, 1H), 3.74 (s, 2H), 2.56 (tt, *J* = 10.6, 3.7 Hz, 1H), 1.96 – 1.92 (m, 2H), 1.75 -1.73 (m, 2H), 1.40 – 1.30 (m, 2H), 1.30 – 1.14 (m, 4H). ^{13}C NMR (151 MHz,Chloroform–*d*) δ 138.94, 128.70, 128.38, 126.71, 42.96, 34.60, 33.37, 25.95, 25.85. GC–MS (EI, 70ev) m/z (%) = 206 (M^+, 25), 115 (20), 91 (100), 81 (16), 55 (22).

Cyclohexyl(phenethyl)sulfane (**5r**)[6]. Purified by column chromatography (PE). Yield = 32mg (73%). Colorless liquid, ^{1}H NMR (600 MHz, Chloroform–*d*) δ 7.29 (t, *J* = 7.6 Hz, 2H), 7.24 – 7.17 (m, 3H), 2.89 – 2.86 (m, 2H), 2.80 – 2.72 (m, 2H), 2.67 – 2.63 (m, 1H), 2.04 – 1.90 (m, 2H), 1.78 - 1.76 (m, 2H), 1.62 -1.60 (m, 1H), 1.38 – 1.20 (m, 5H). ^{13}C NMR (151 MHz, Chloroform–*d*) δ 140.84, 128.40, 126.22, 43.69, 36.73, 33.70, 31.64, 26.11, 25.84. GC–MS (EI, 70ev) m/z(%) = 220 (M^+, 45), 129 (90), 104 (90), 81 (100), 55 (70).

Cyclohexyl(p–tolyl)sulfane (**5s**)[7]. Purified by column chromatography (PE). Yield = 30 mg (73%). Colorless liquid,^{1}H NMR (600 MHz, Chloroform–*d*) δ 7.36 – 7.28 (m, 2H), 7.09 (d, *J* = 7.8 Hz, 2H), 3.01 (tt, *J* = 10.5, 3.7 Hz, 1H), 2.32 (s, 3H), 1.96 (m, 2H), 1.75 (m, 2H), 1.39 – 1.19 (m, 6H). ^{13}C NMR (151 MHz, Chloroform–*d*) δ 136.80, 132.75, 131.22, 129.45, 47.09, 33.37, 26.05, 25.76, 21.01. GC–MS (EI, 70ev) m/z(%)= 206 (M^+, 25), 124 (100), 91 (35), 55 (22).

Cyclohexyl(4–methoxyphenyl)sulfane (**5t**)[8]. Purified by column chromatography (PE). Yield = 29 mg (65%). Colorless liquid, ^{1}H NMR (600 MHz, Chloroform–*d*) δ 7.44 – 7.32 (m, 2H), 6.88 – 6.77 (m, 2H), 3.79 (s, 3H), 2.97 – 2.81 (m, 1H), 1.93 - 1.91 (m, 2H), 1.78 – 1.69 (m, 2H), 1.42 – 1.07 (m, 6H). ^{13}C NMR (151 MHz, Chloroform–*d*) δ 159.29, 135.51, 114.26, 55.25, 47.89, 33.36, 26.08, 25.76. GC–MS (EI, 70ev) m/z (%) = 222 (M^+, 30), 140 (100), 125 (25), 55 (22).

S–(4–Phenylbutan–2–yl) ethanethioate (**7a**)[9]. Purified by column chromatography (PE). Yield = 16.6 mg (40%). Colorless liquid, ^{1}H NMR (400 MHz, Chloroform–*d*) δ 7.30 – 7.25 (m, 2H), 7.22 – 7.15 (m, 3H), 3.59 (h, J = 7.0 Hz, 1H), 2.76 – 2.62 (m, 2H), 2.33 (s, 3H), 1.92 – 1.81 (m, 2H), 1.34 (d, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform–d) δ 195.90, 141.52, 128.42, 128.37, 125.96, 39.28, 38.26, 33.37, 30.84, 21.45. GC–MS (EI, 70ev) m/z (%) = 208 (M^+, 5), 134 (70), 117 (85), 91 (100), 65 (25), 61 (35).

S-(3-(4-Bromophenyl)propyl) ethanethioate (**7b**)[10]. Purified by column chromatography (PE). Yield = 28 mg (51%). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 8.5 Hz, 2H), 7.03 (d, *J* = 7.7 Hz, 2H), 2.85 (t, *J* = 7.3

Hz, 2H), 2.62 (t, *J* = 7.7 Hz, 2H), 2.32 (s, 3H), 1.90 – 1.82 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 195.53, 140.04, 131.43, 130.13, 119.74, 34.18, 30.90, 30.56, 28.39. GC–MS (EI, 70ev) m/z (%) = 274 (M^+, 35), 196 (80), 117 (100), 90 (75).

S-Phenethyl ethanethioate (**7c**)[11]. Purified by column chromatography (PE). Yield = 25 mg (69%). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.30 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 6.7 Hz, 3H), 3.15 – 3.09 (m, 2H), 2.87 (t, *J* = 7.7 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 195.52, 139.93, 128.41, 126.43, 35.74, 30.56, 30.45. GC–MS (EI, 70ev) m/z (%)= 180 (M^+, 3), 104 (100).

S-(4-Phenylbutyl) ethanethioate (**7d**)[12]. Purified by column chromatography (PE). Yield = 29 mg (70%). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.27 (t, *J* = 7.5 Hz, 2H), 7.17 (t, *J* = 8.7 Hz, 3H), 2.89 (t, *J* = 7.2 Hz, 2H), 2.62 (t, *J* = 7.6 Hz, 2H), 2.32 (s, 3H), 1.70 (p, *J* = 8.2, 7.6 Hz, 2H), 1.61 (p, *J* = 7.2 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 195.74, 142.01, 128.33, 128.28, 125.75, 35.34, 30.55, 30.43, 29.09, 28.91. GC–MS (EI, 70ev) m/z (%) = 208 (M^+, 25), 165 (25), 131 (55), 91 (100).

6. Reference

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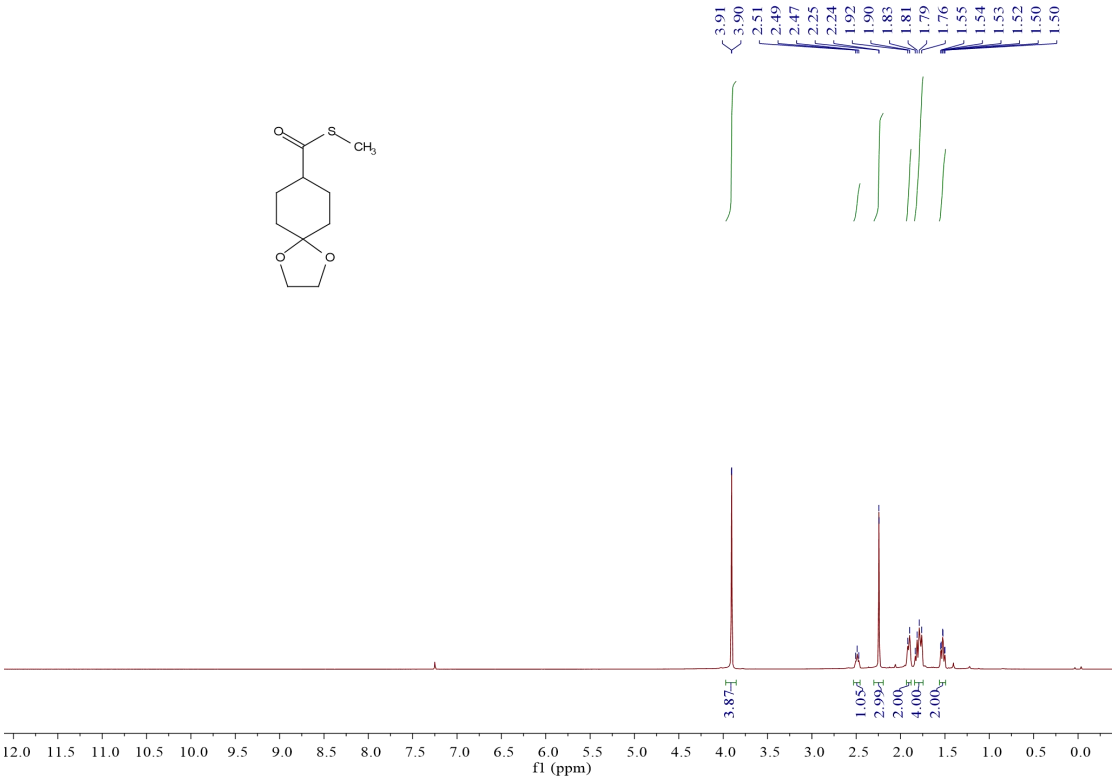
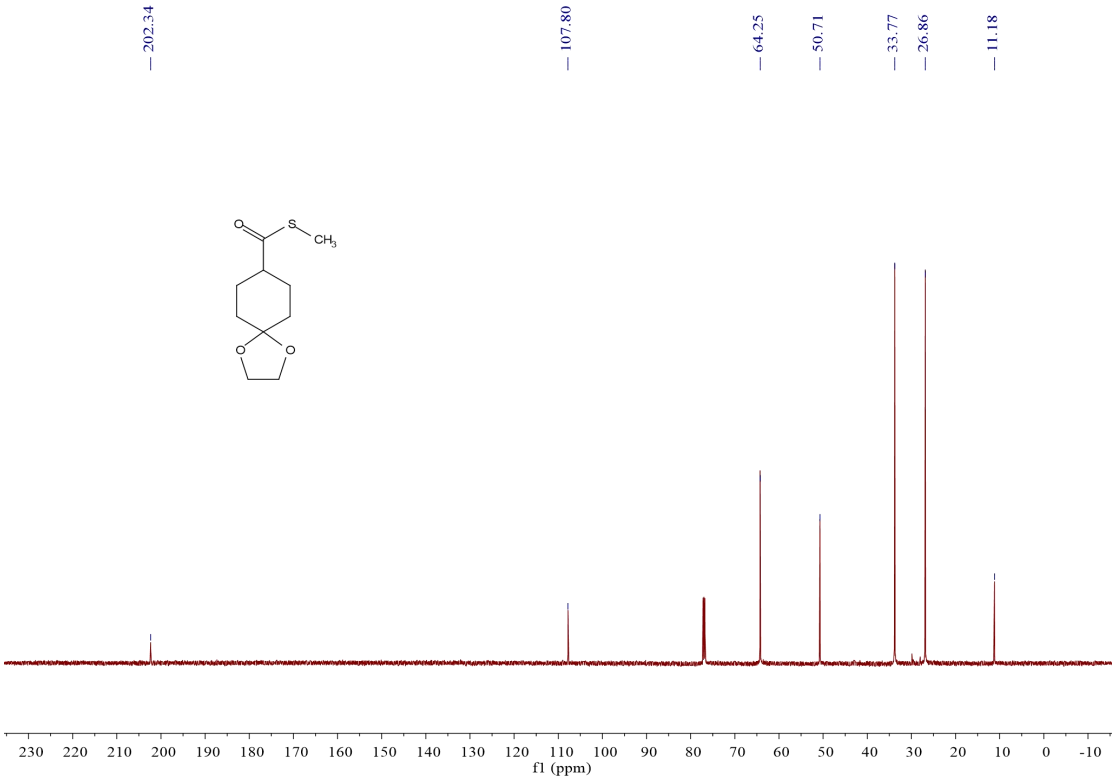
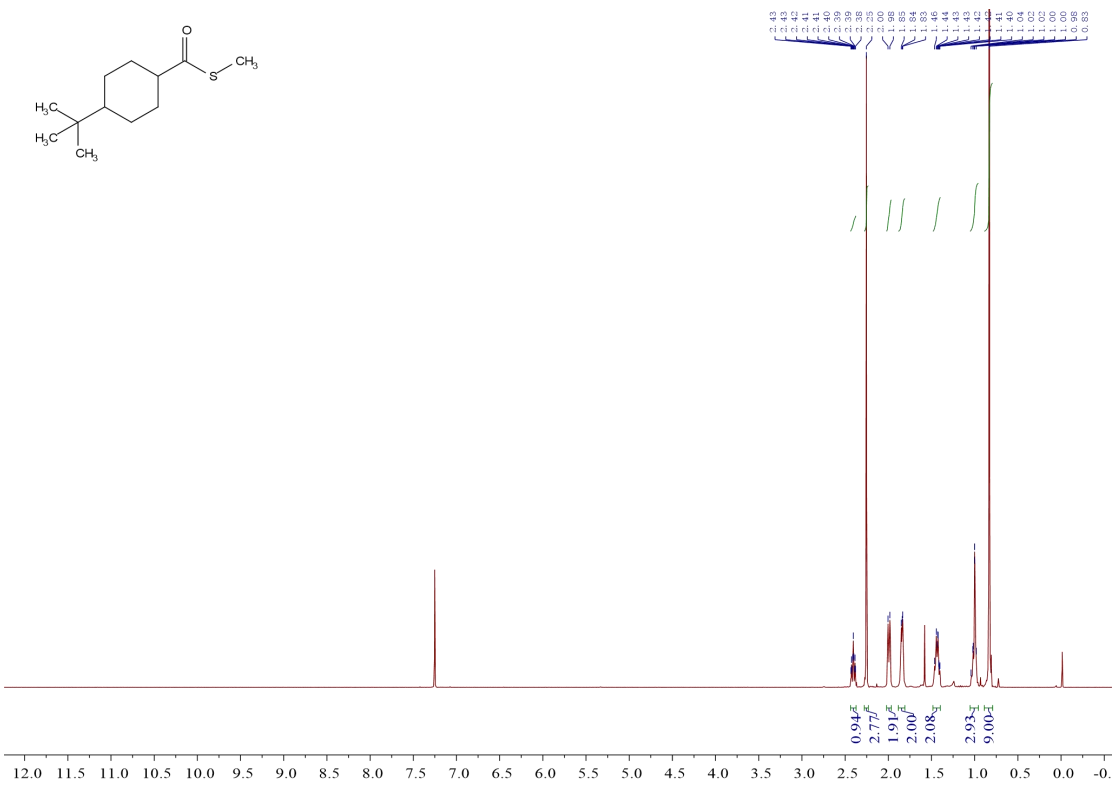
7. NMR Spectra



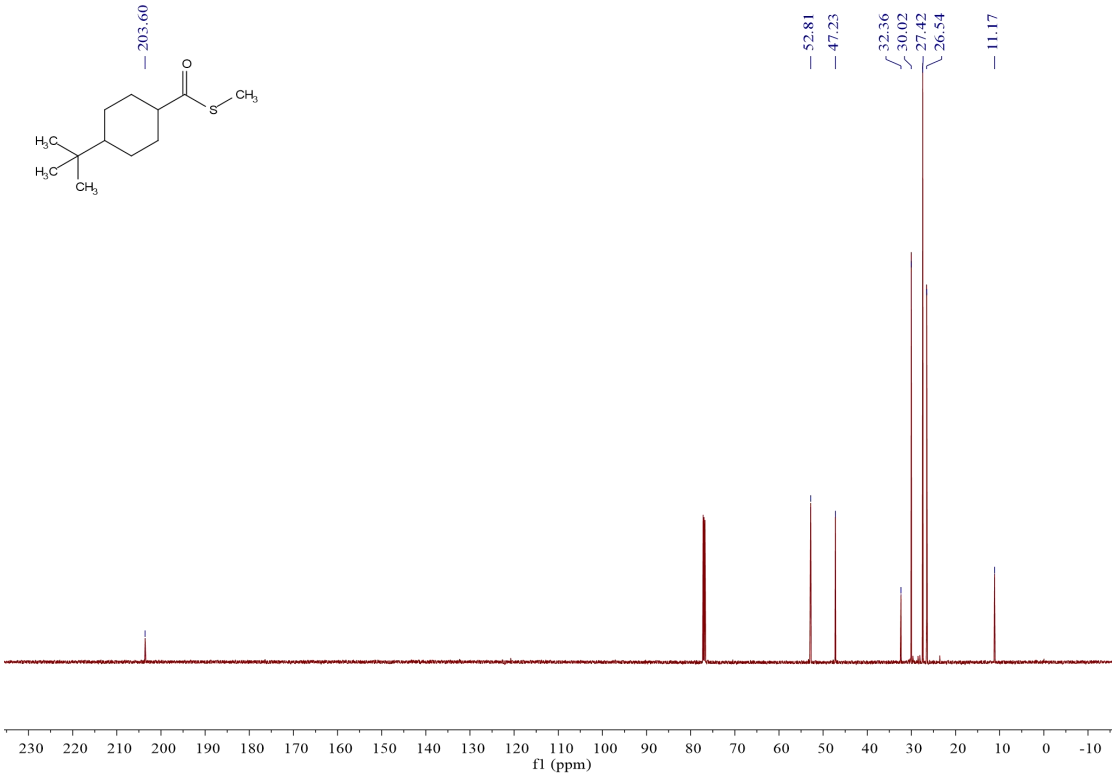
^{1}H NMR of compound 3b (600 MHz, $CDCl_3$)



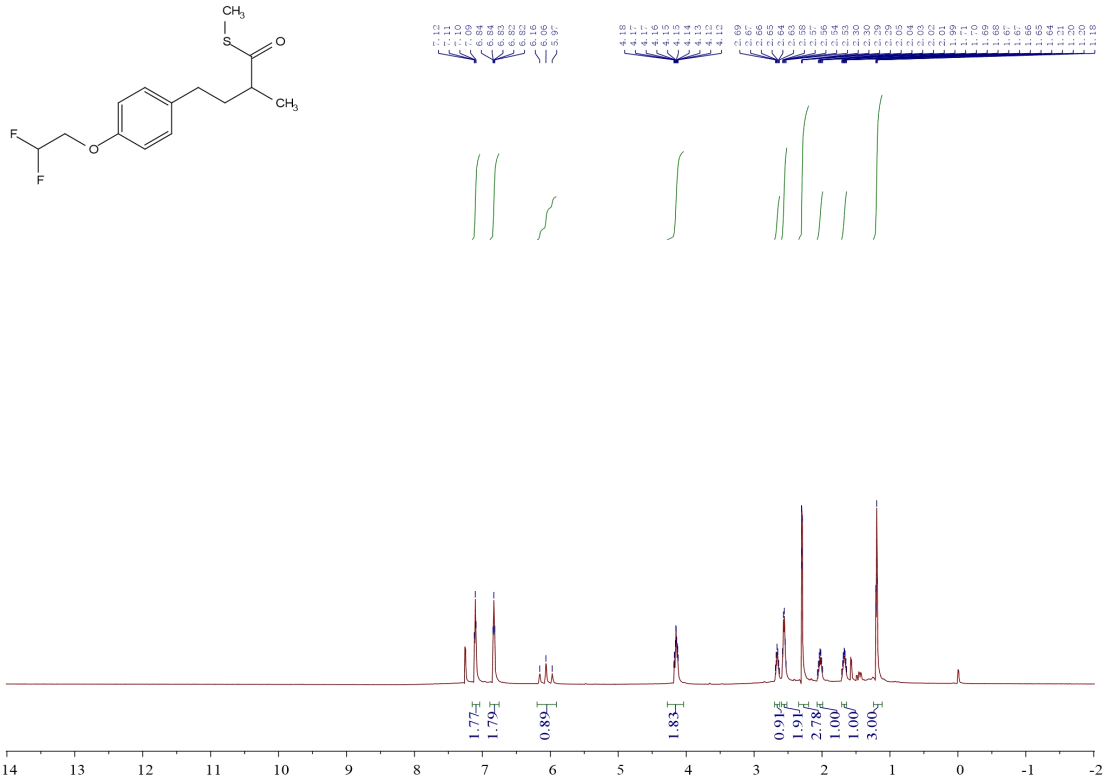
^{13}C {^{1}H} NMR of compound 3b (151 MHz, $CDCl_3$)



^{1}H NMR of compound 3c(600 MHz, $CDCl_3$)



^{13}C {^{1}H} NMR of compound 3c (151 MHz, $CDCl_3$)



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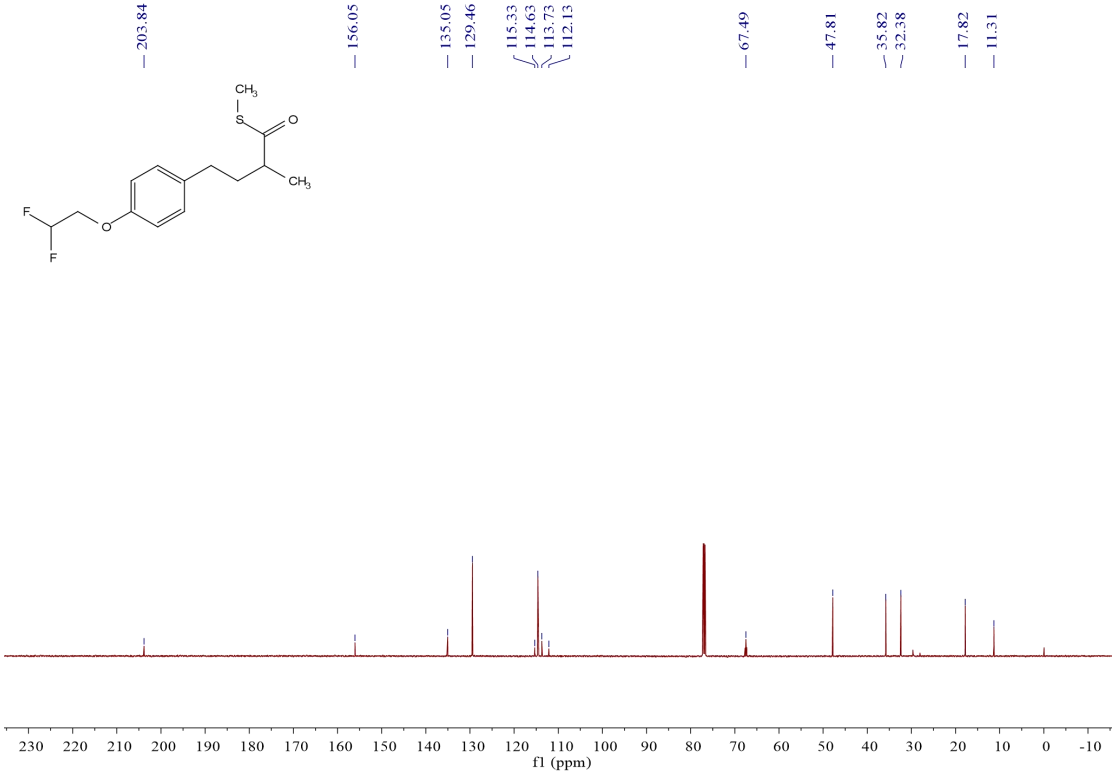
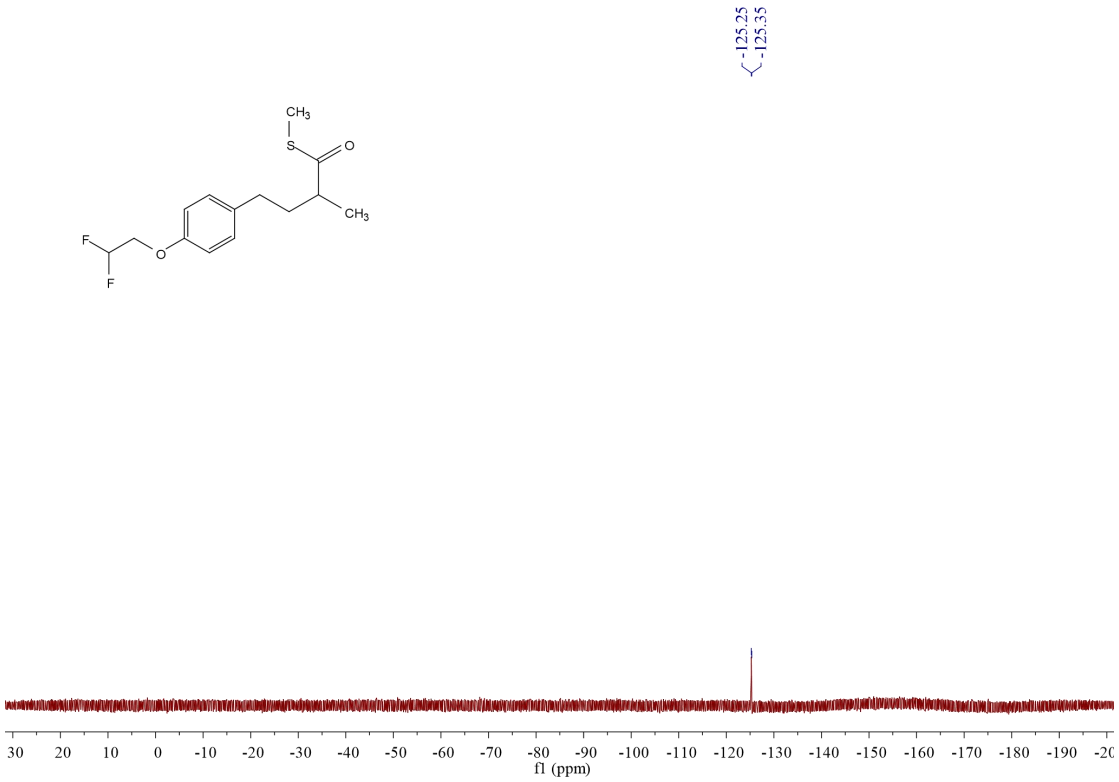
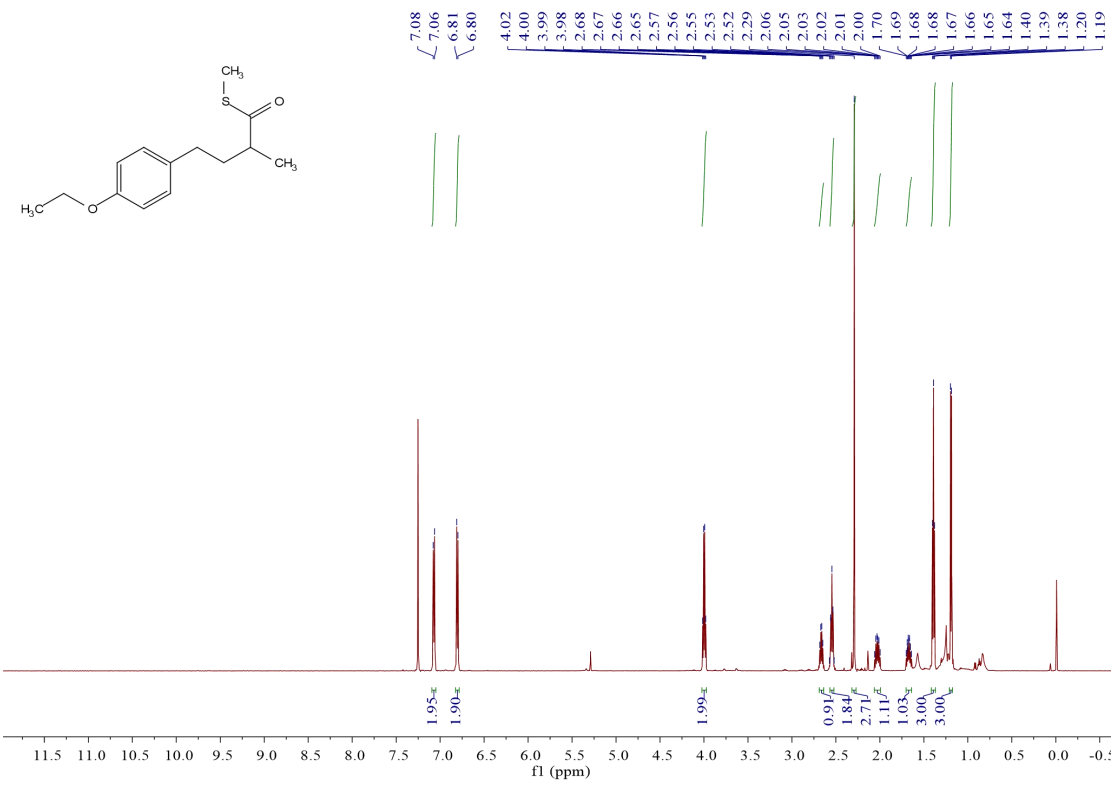


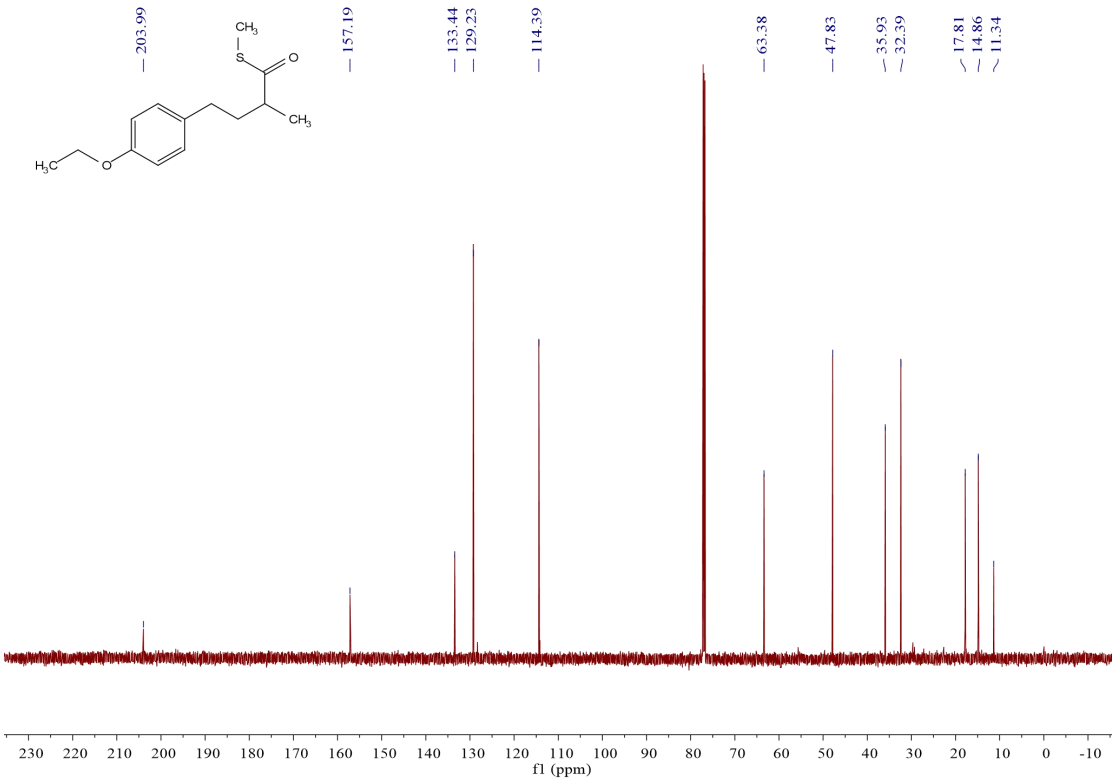
^{13}C {^{1}H} NMR of compound 3d (151 MHz, $CDCl_3$)



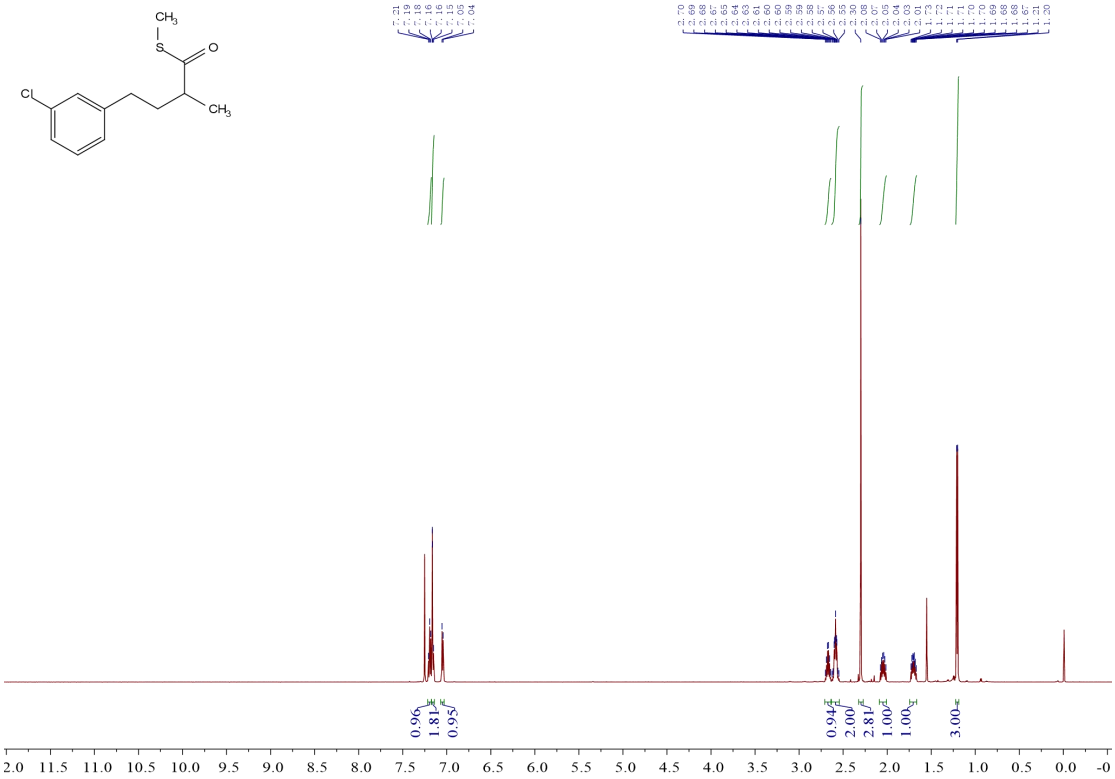
^{19}F NMR of compound 3d (654 MHz, $CDCl_3$)



^{1}H NMR of compound 3e (600 MHz, $CDCl_3$)



^{13}C {^{1}H} NMR of compound 3e (151 MHz, $CDCl_3$)



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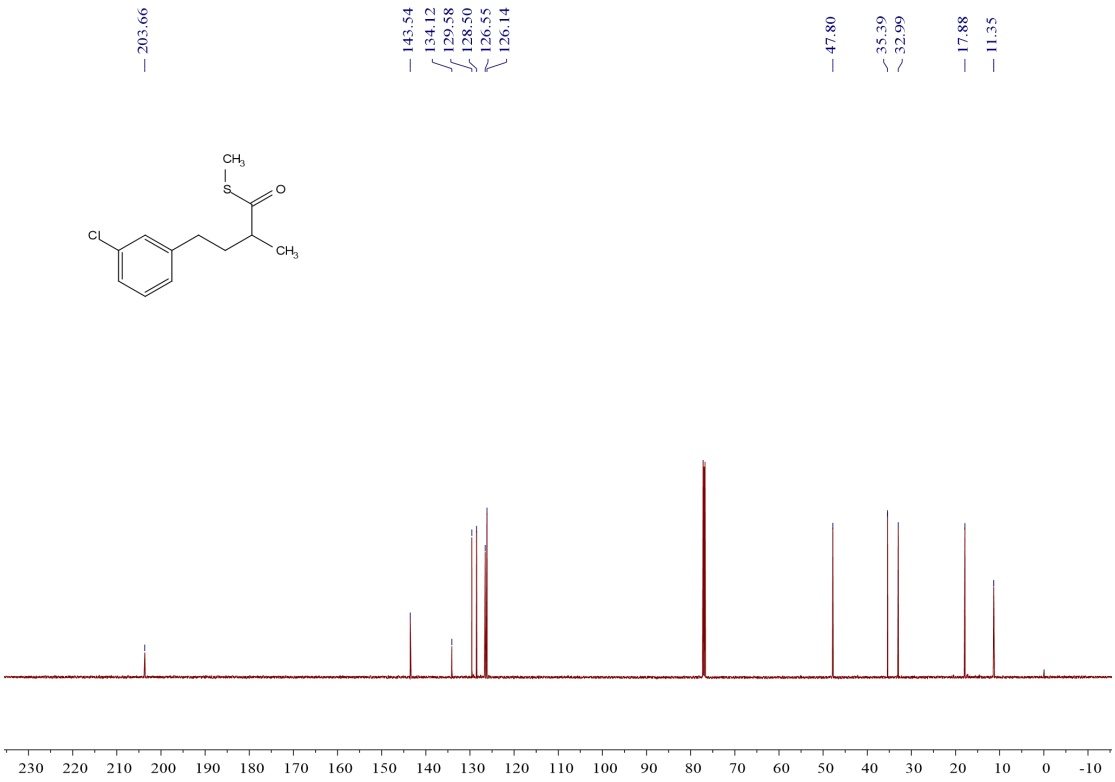

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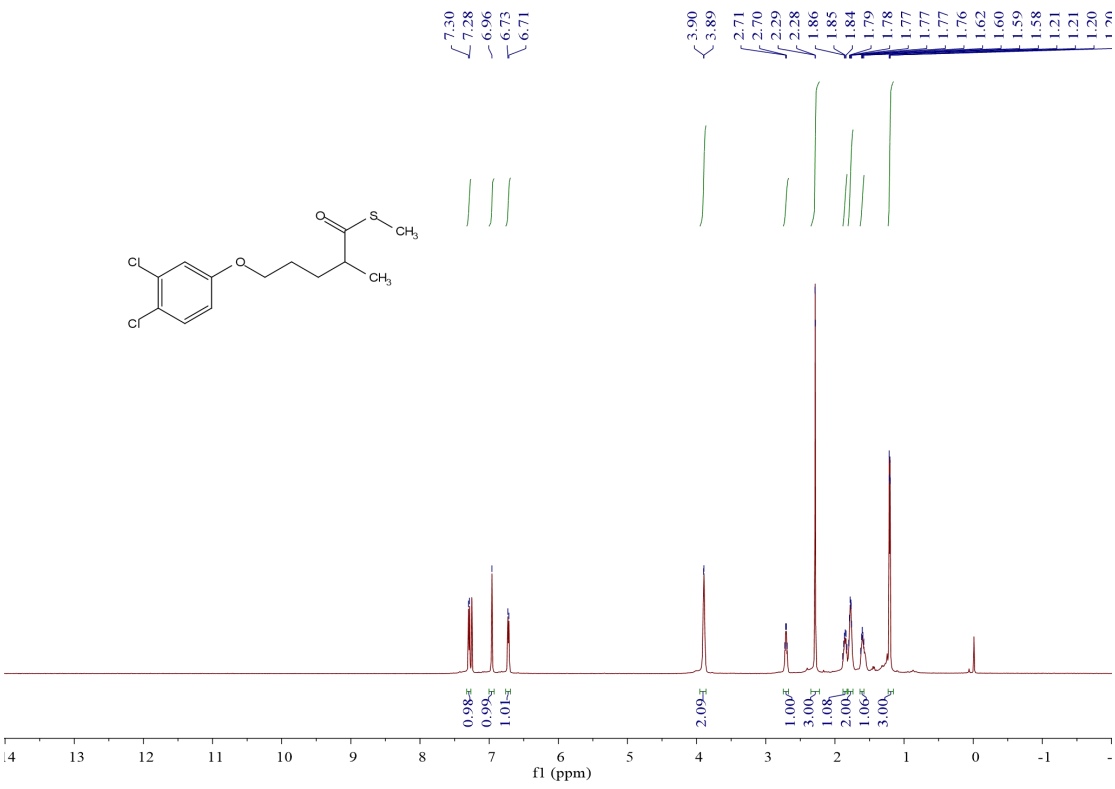
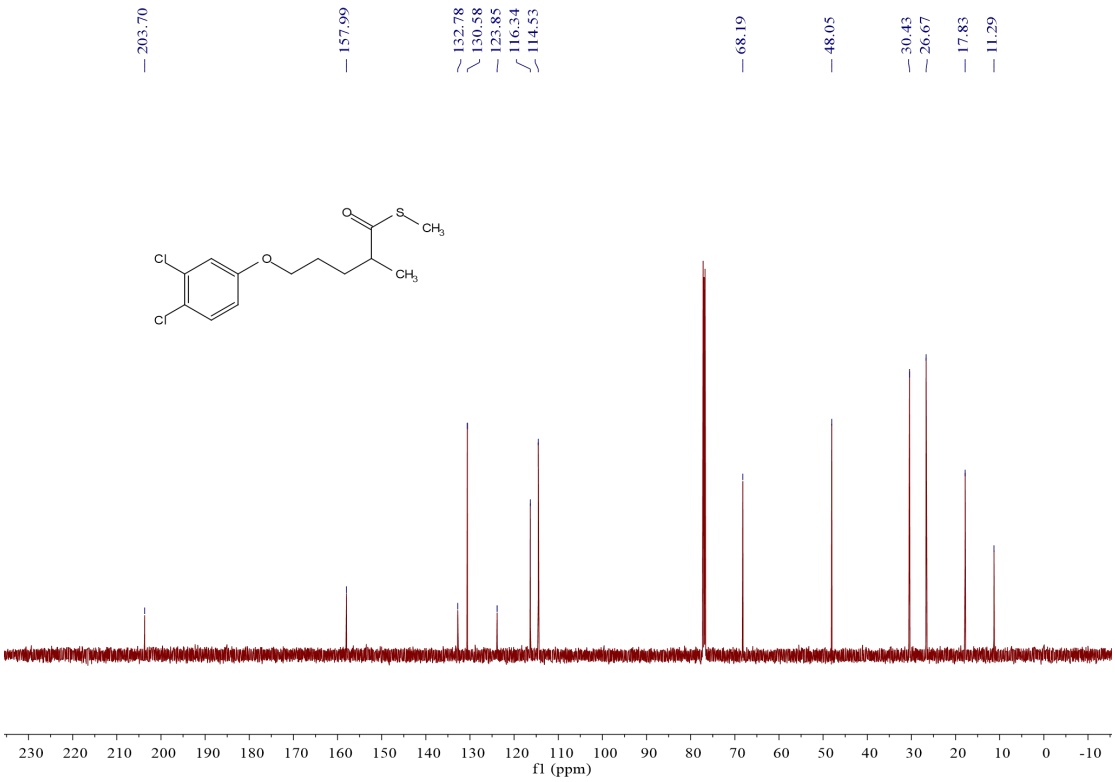
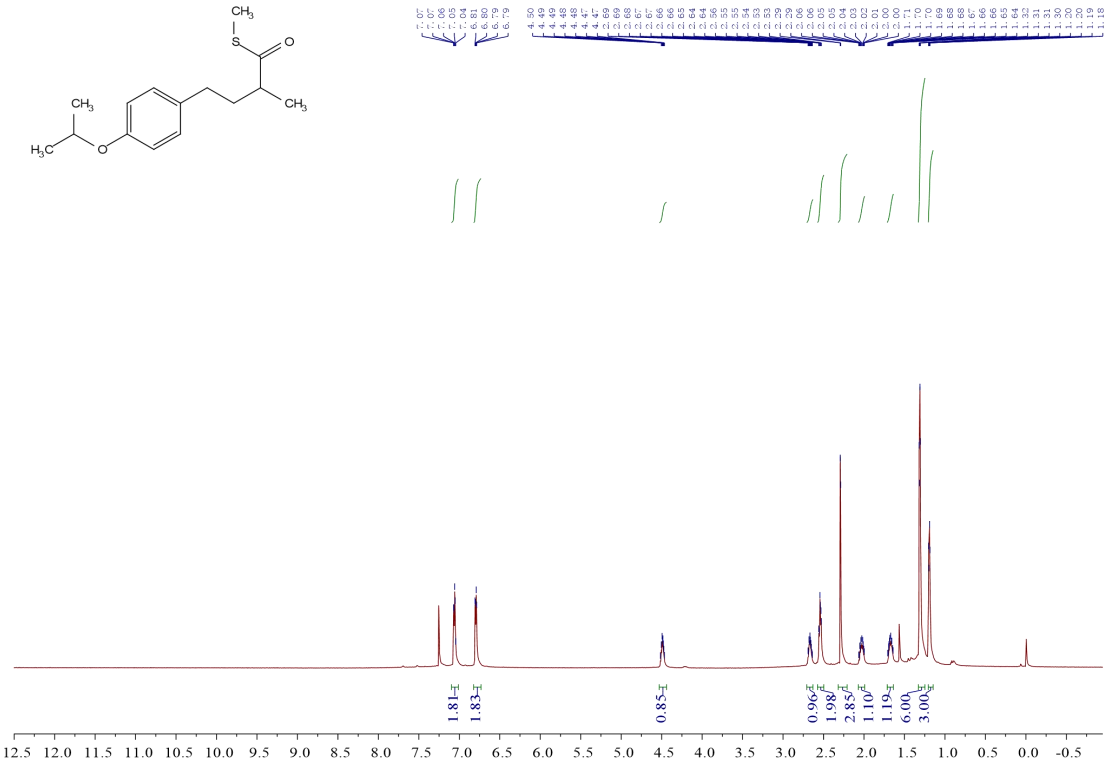


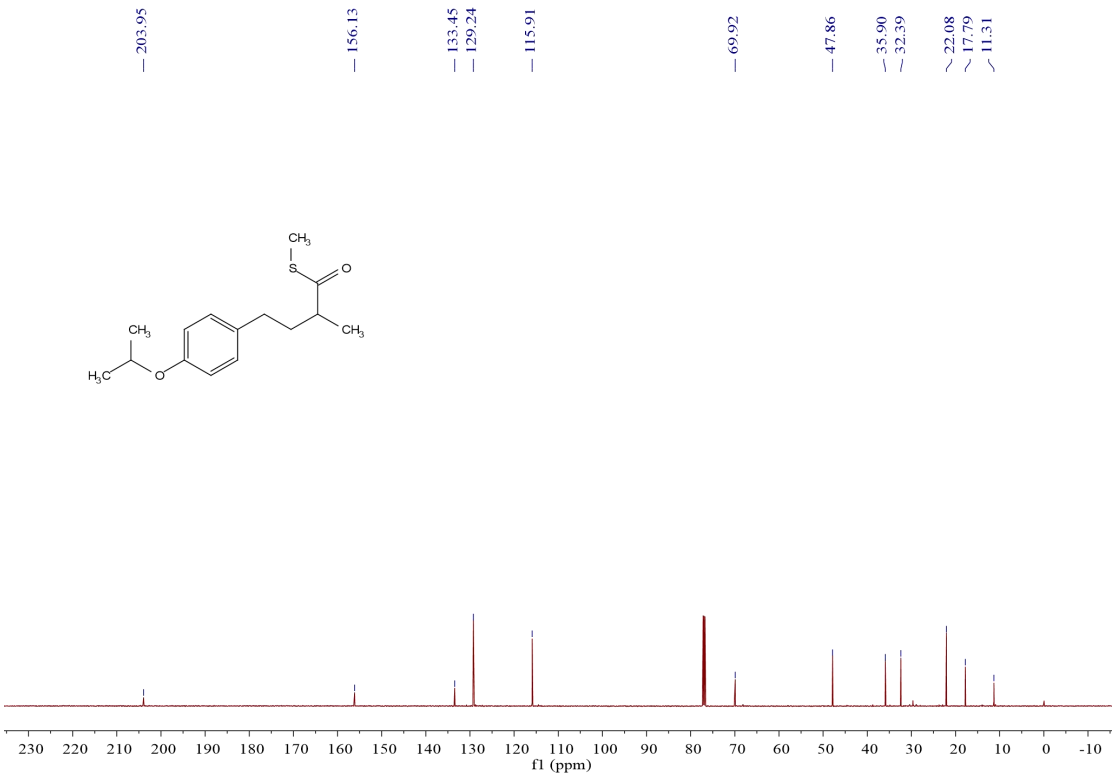
^{1}H NMR of compound 3g (600 MHz, $CDCl_3$)



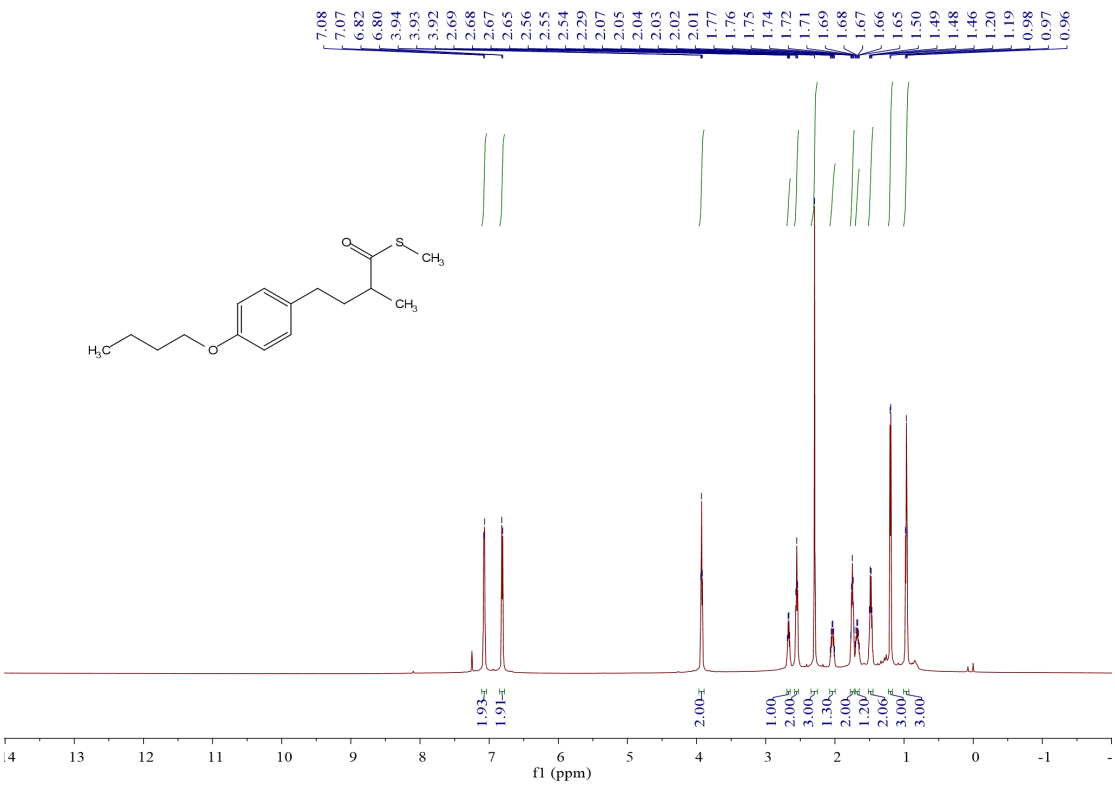
^{13}C {^{1}H} NMR of compound 3g (151 MHz, $CDCl_3$)



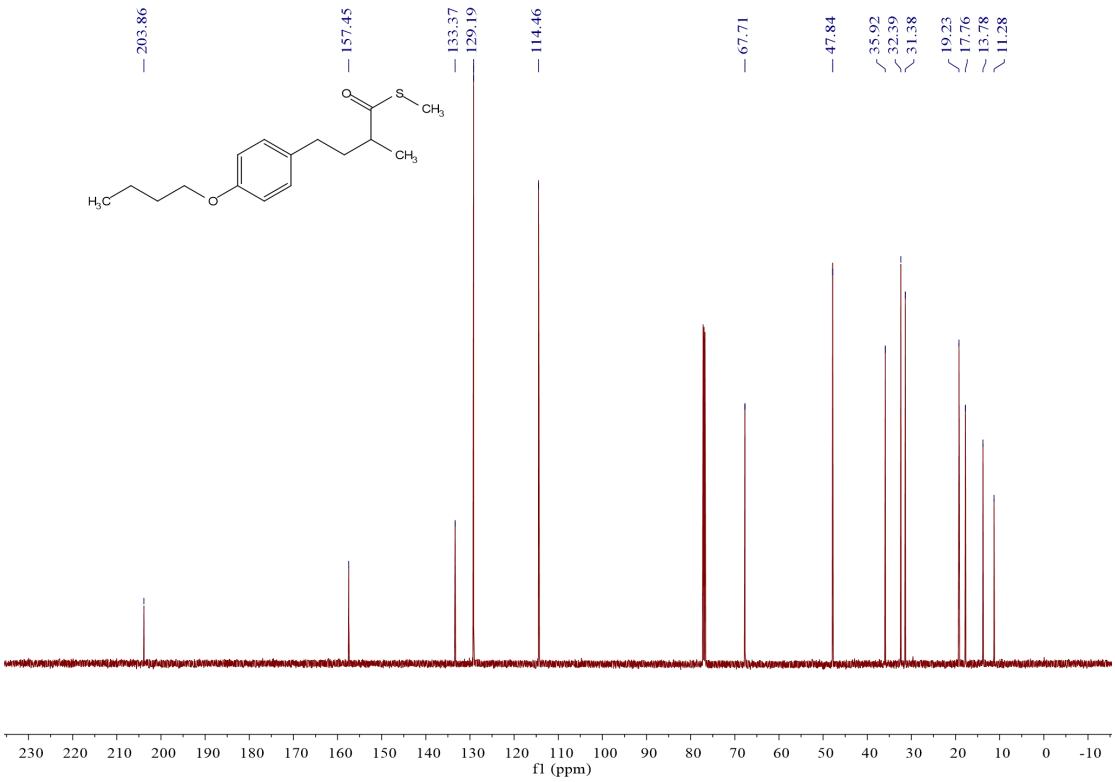
^{1}H NMR of compound 3h (600 MHz, $CDCl_3$)



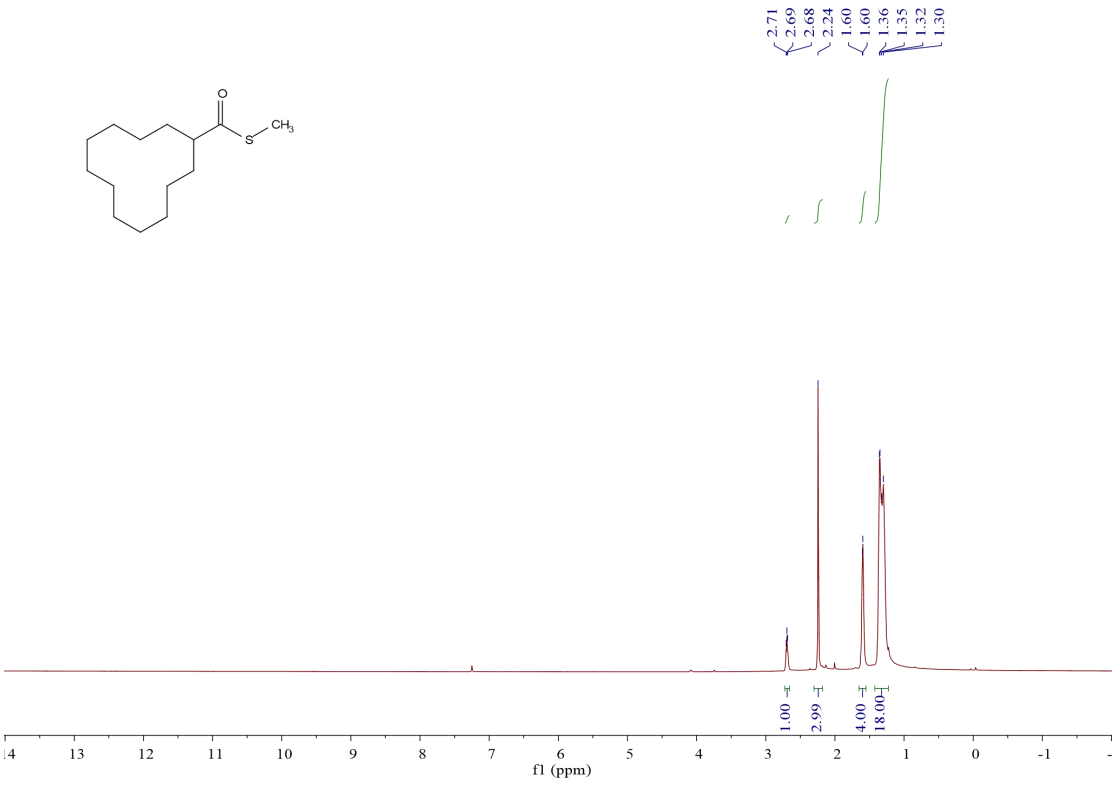
^{13}C {^{1}H} NMR of compound 3h (151 MHz, $CDCl_3$)



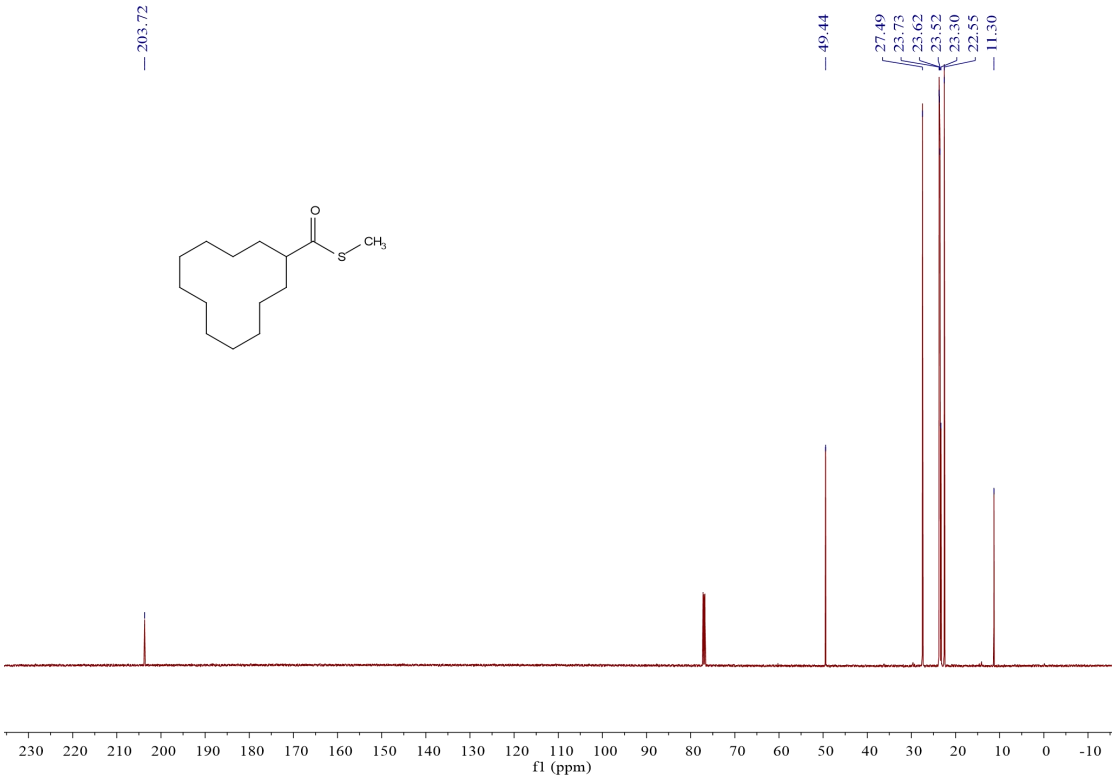
^{1}H NMR of compound 3i (600 MHz, $CDCl_3$)



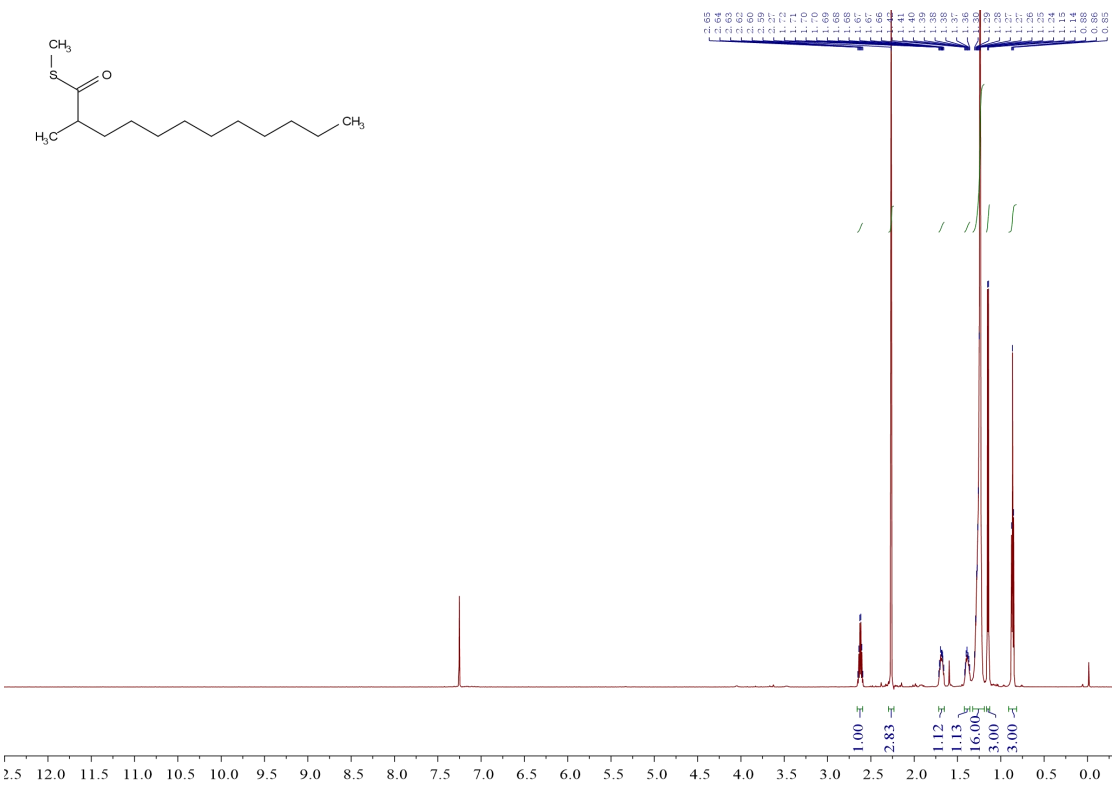
^{13}C {^{1}H} NMR of compound 3i (151 MHz, $CDCl_3$)



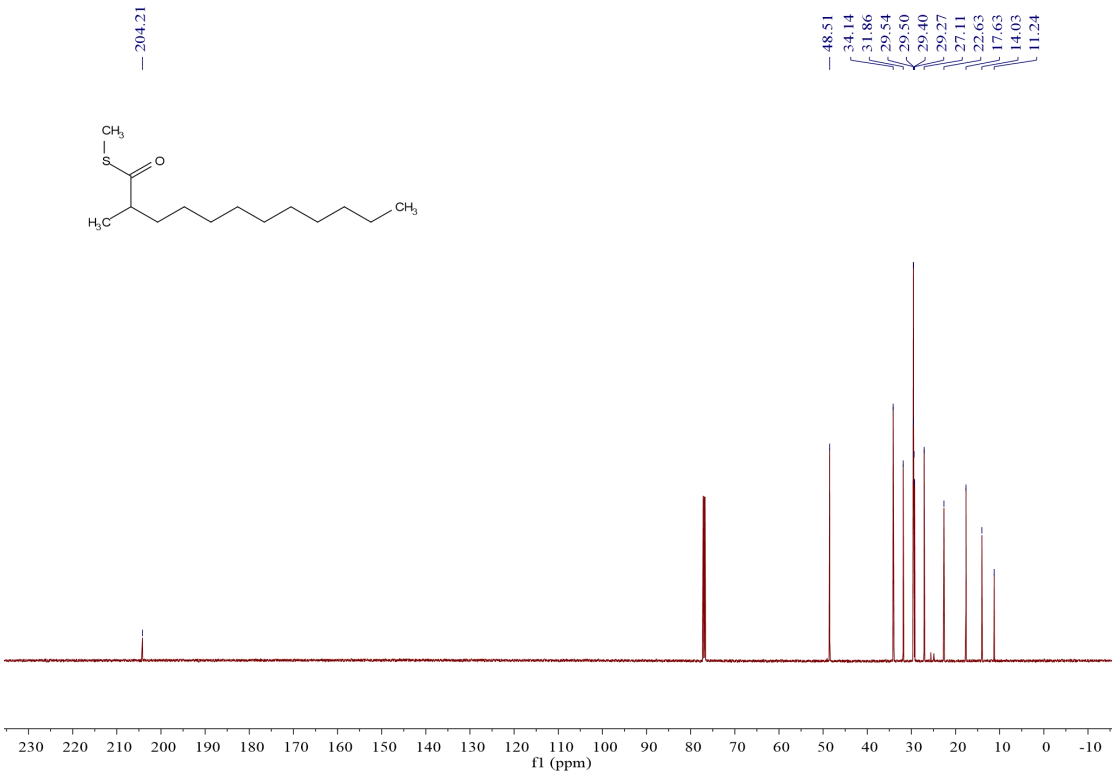
^{1}H NMR of compound 3j (600 MHz, $CDCl_3$)



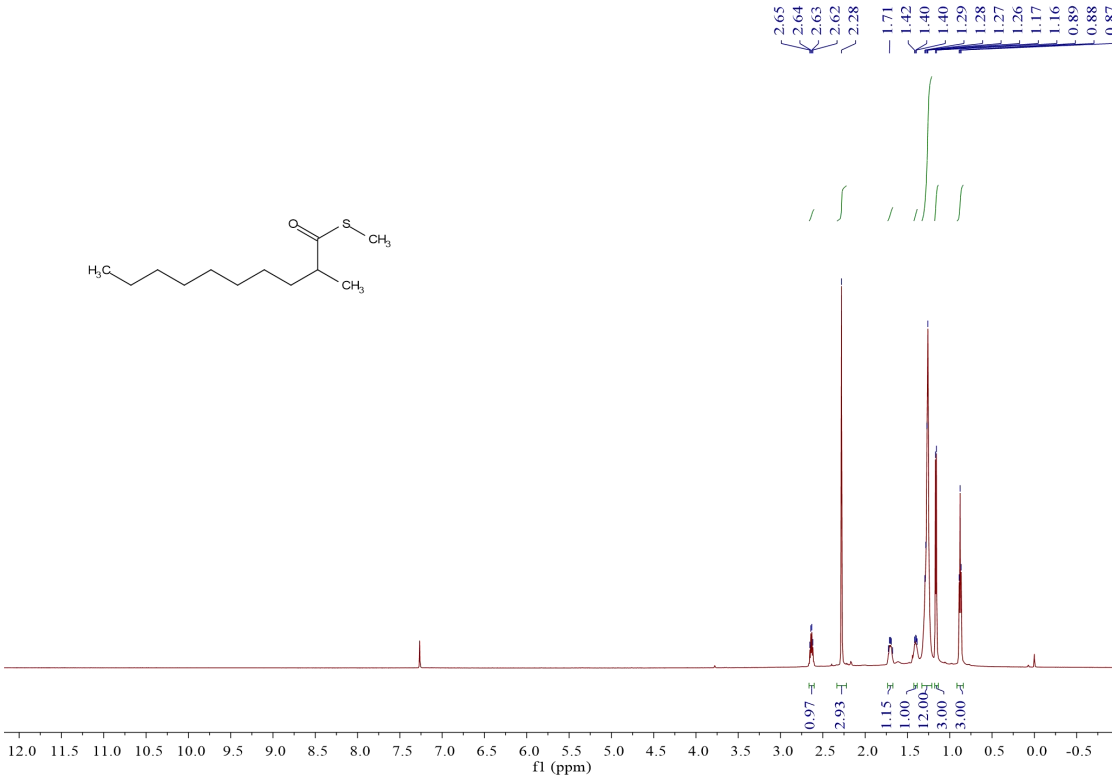
^{13}C {^{1}H} NMR of compound 3j (151 MHz, $CDCl_3$)



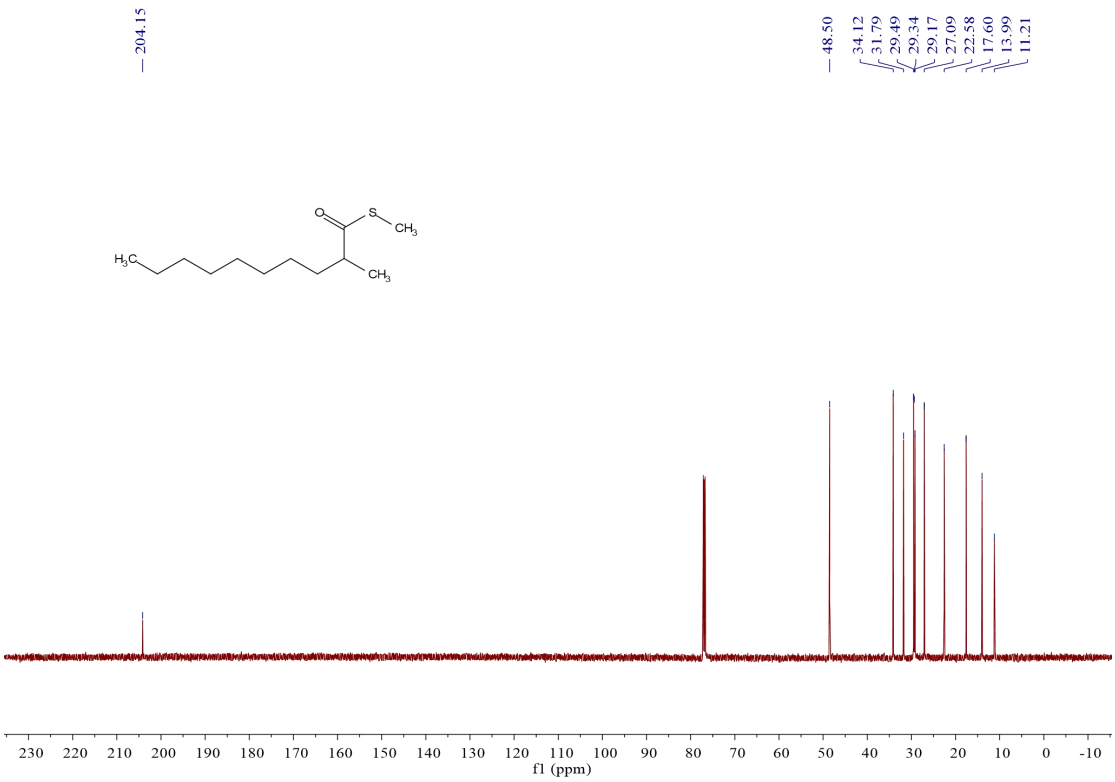
^{1}H NMR of compound 3k (600 MHz, $CDCl_3$)



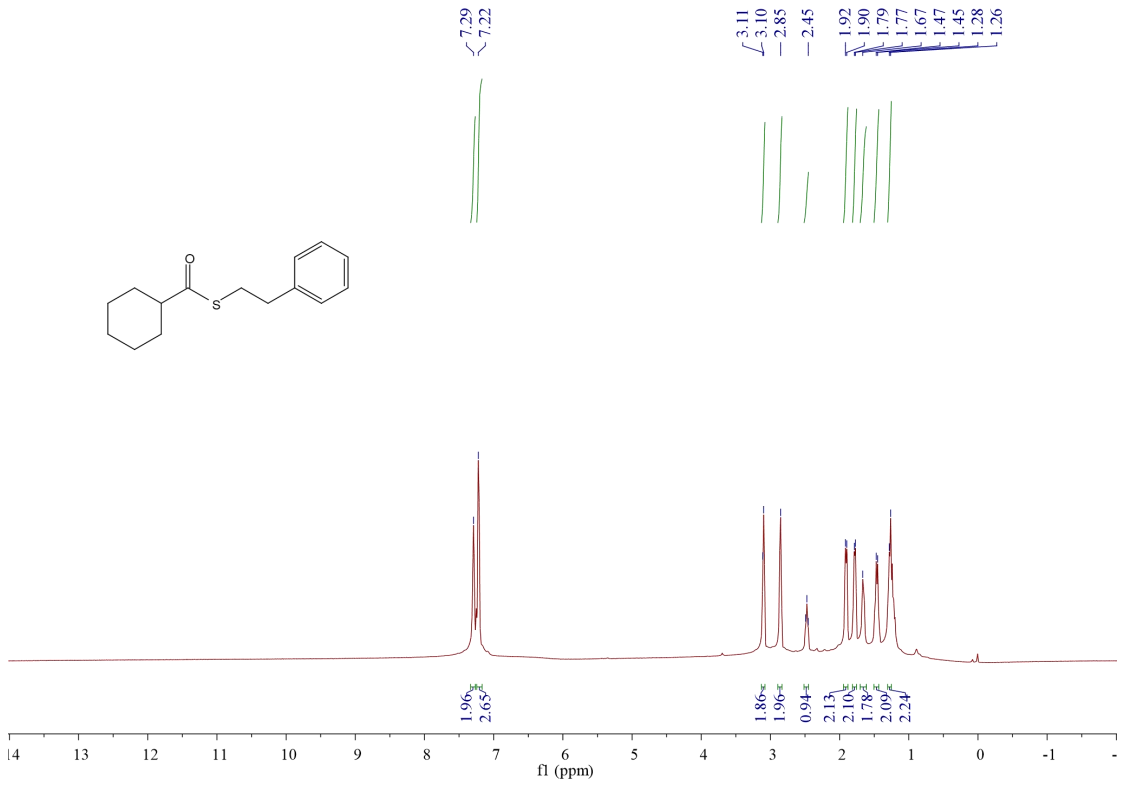
^{13}C {^{1}H} NMR of compound 3k (151 MHz, $CDCl_3$)



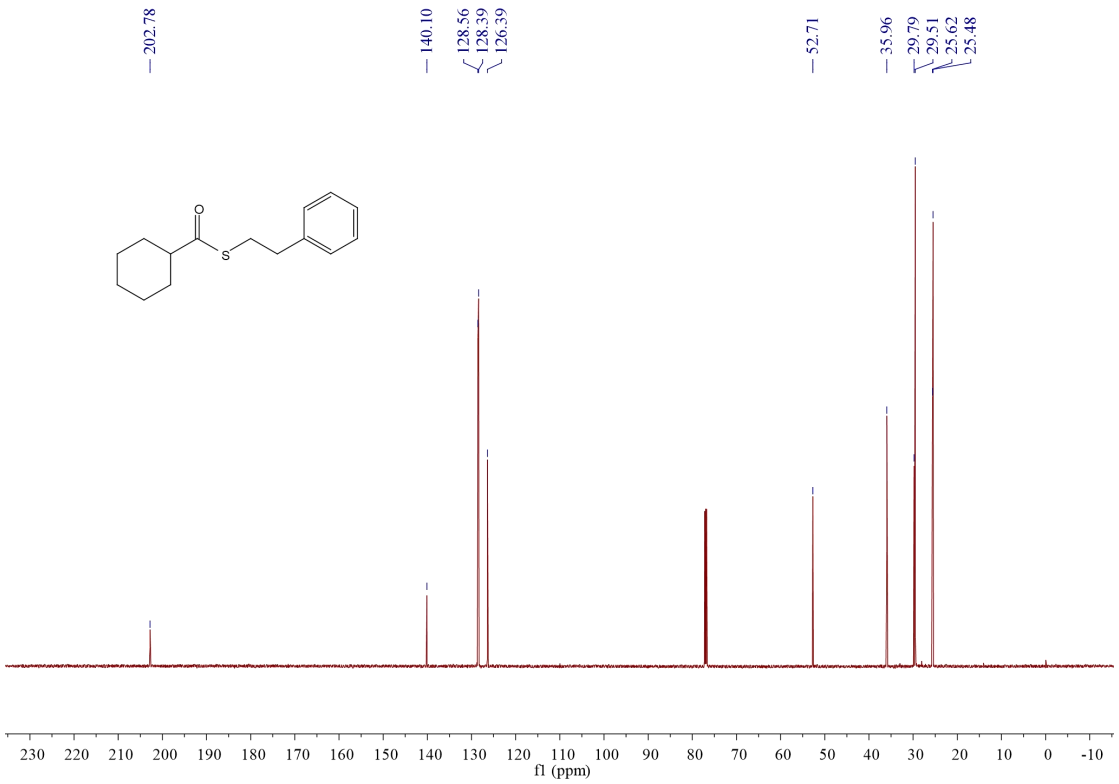
^{1}H NMR of compound 3l (600 MHz, $CDCl_3$)



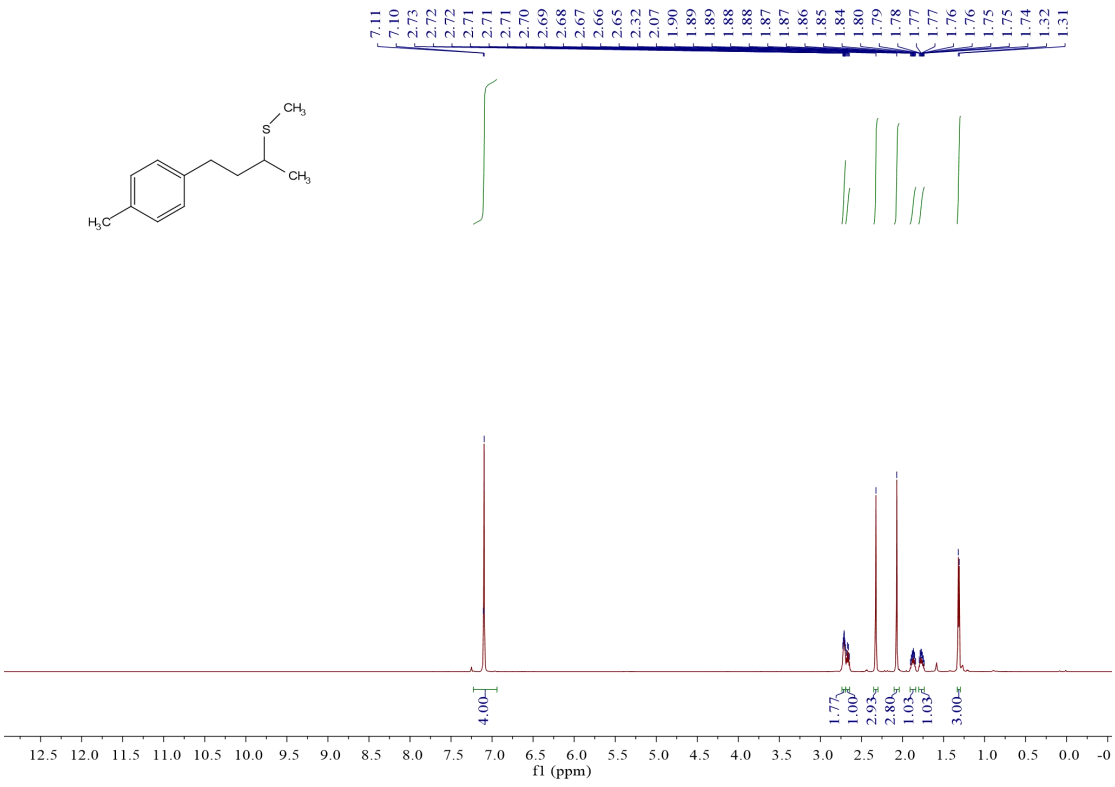
^{13}C {^{1}H} NMR of compound 3l (151 MHz, $CDCl_3$)



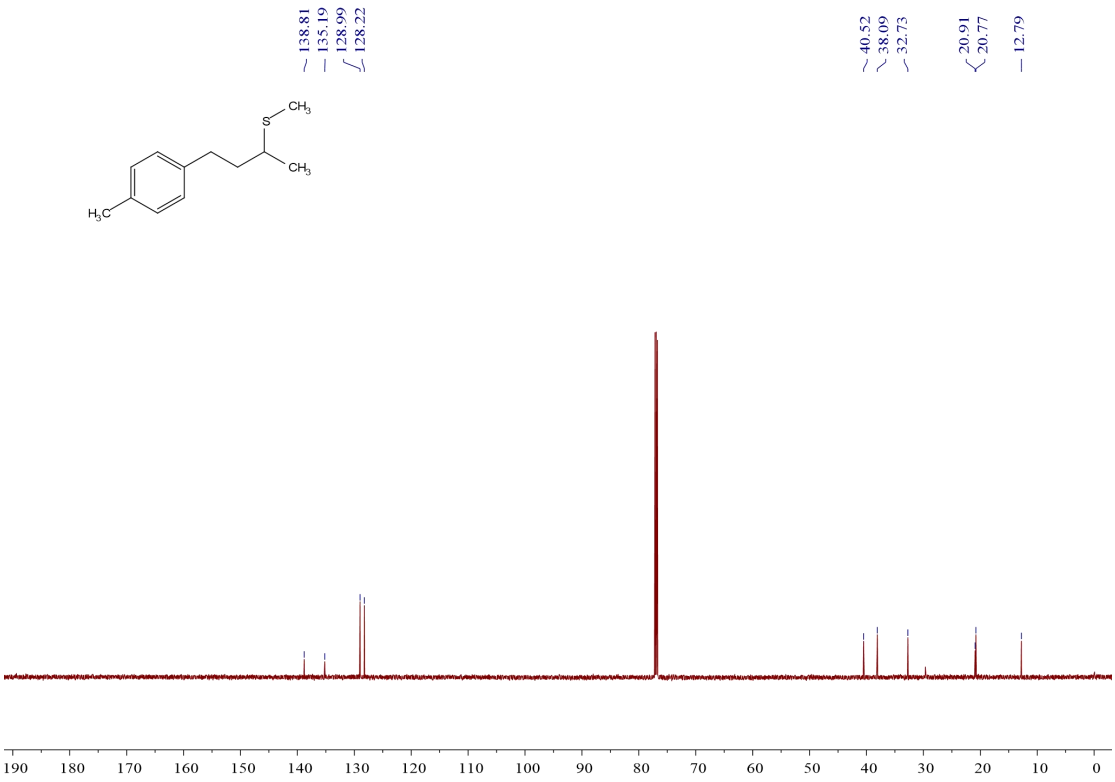
^{1}H NMR of compound 3m (151 MHz, $CDCl_3$)



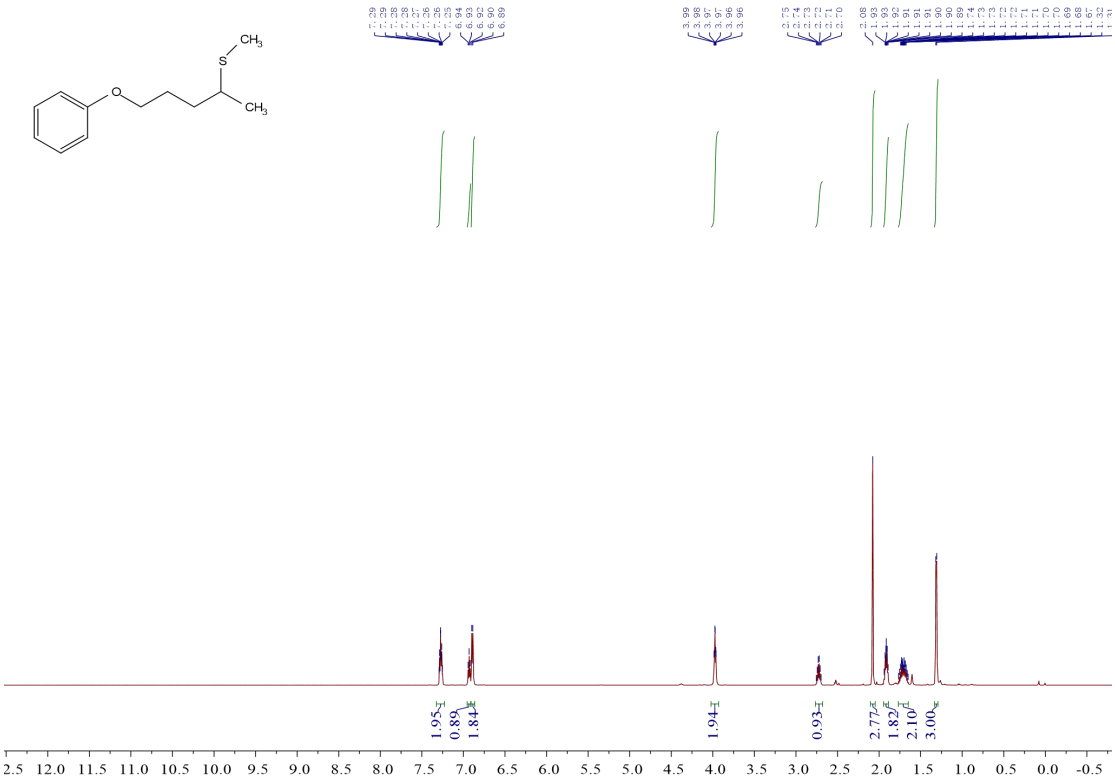
^{13}C {^{1}H} NMR of compound 3m (151 MHz, $CDCl_3$)



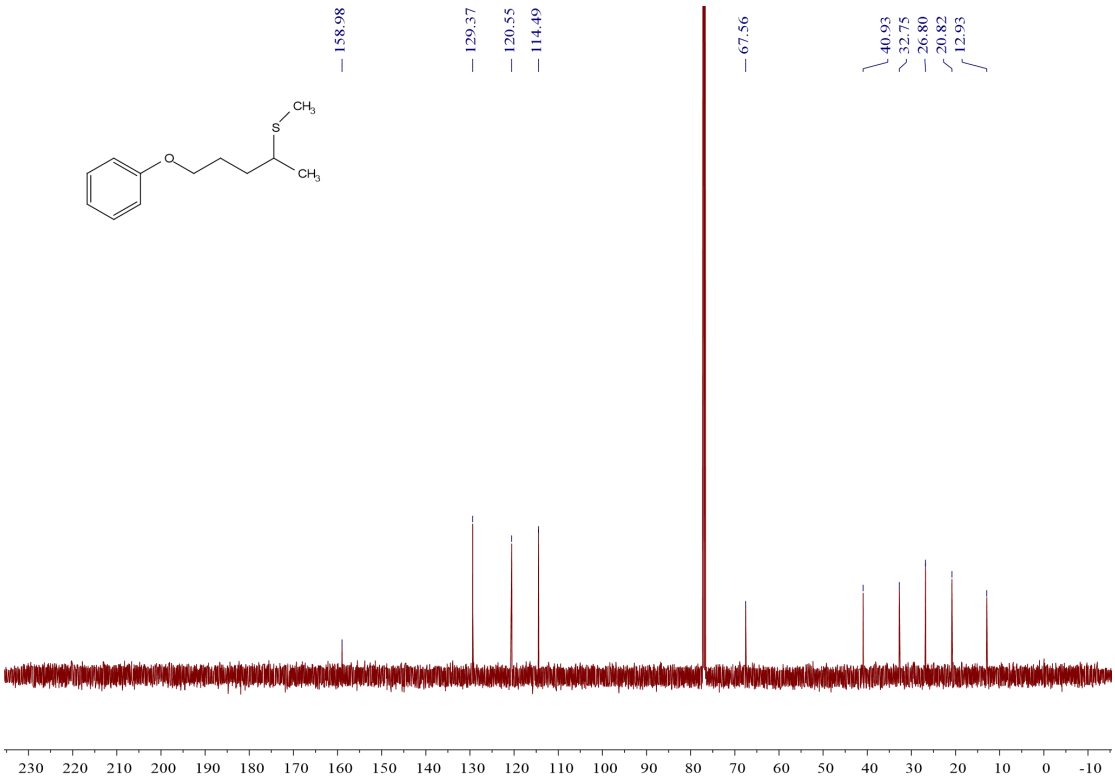
^{1}H NMR of compound 5a (600 MHz, $CDCl_3$)



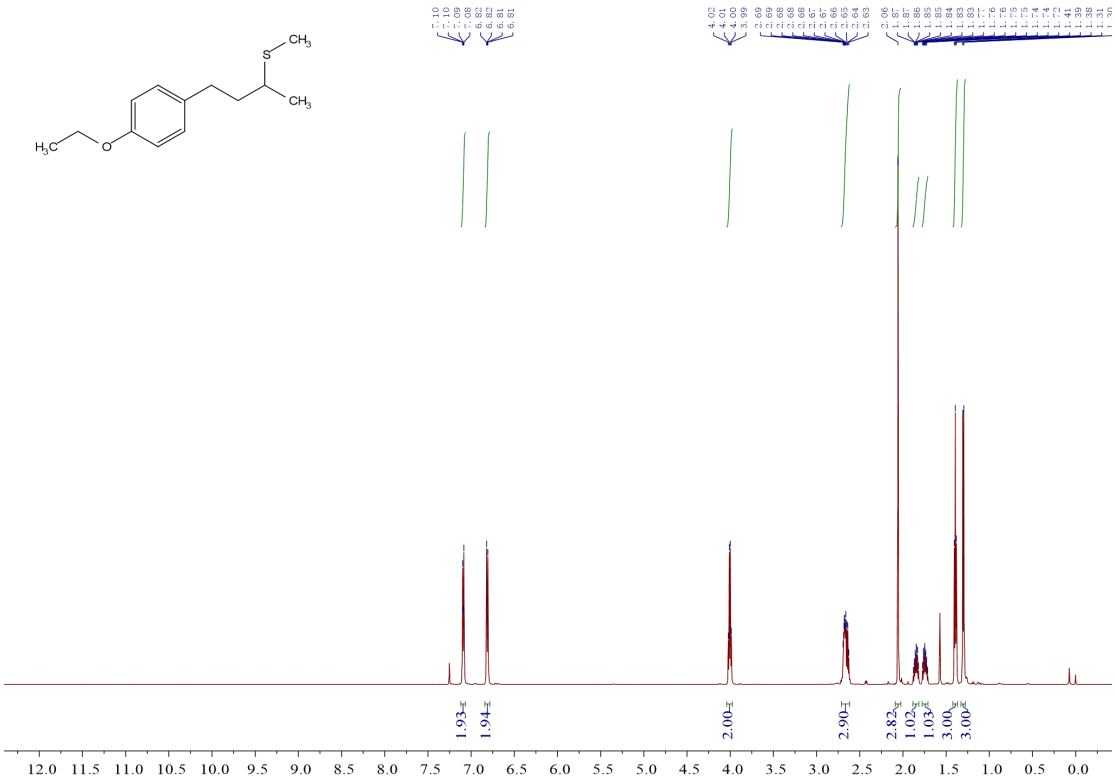
^{13}C {^{1}H} NMR of compound 5a (151 MHz, $CDCl_3$)



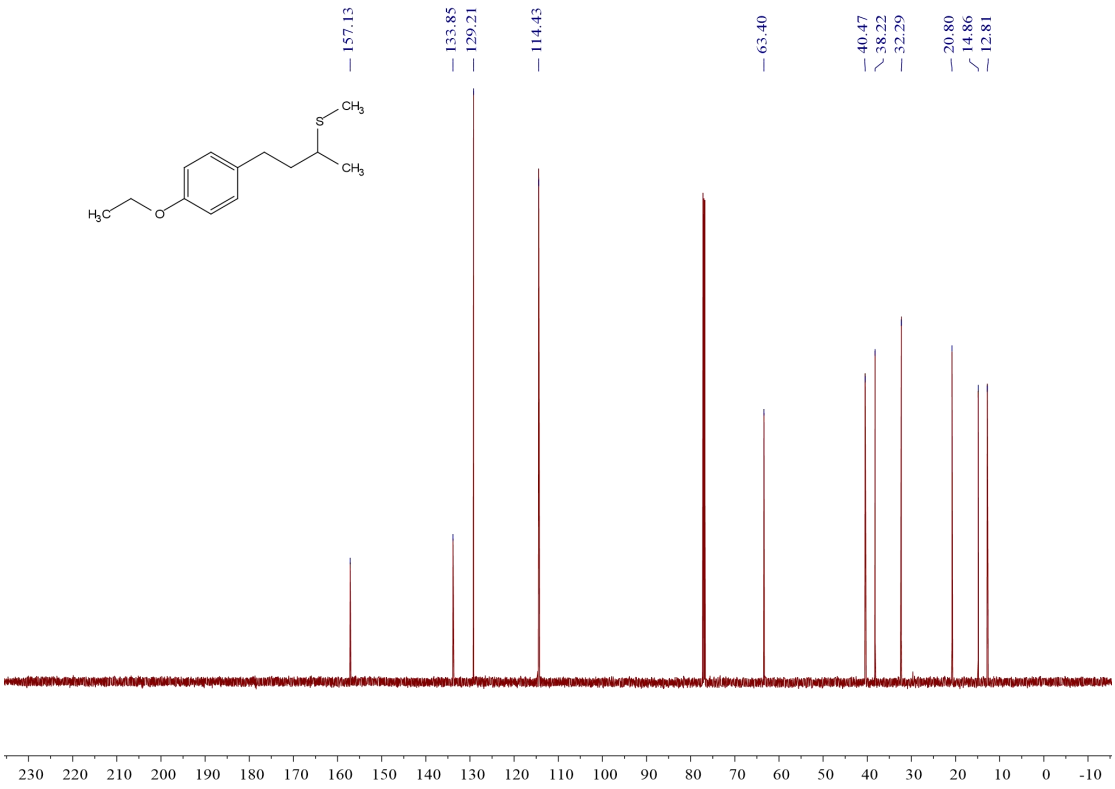
^{1}H NMR of compound 5b (600 MHz, $CDCl_3$)



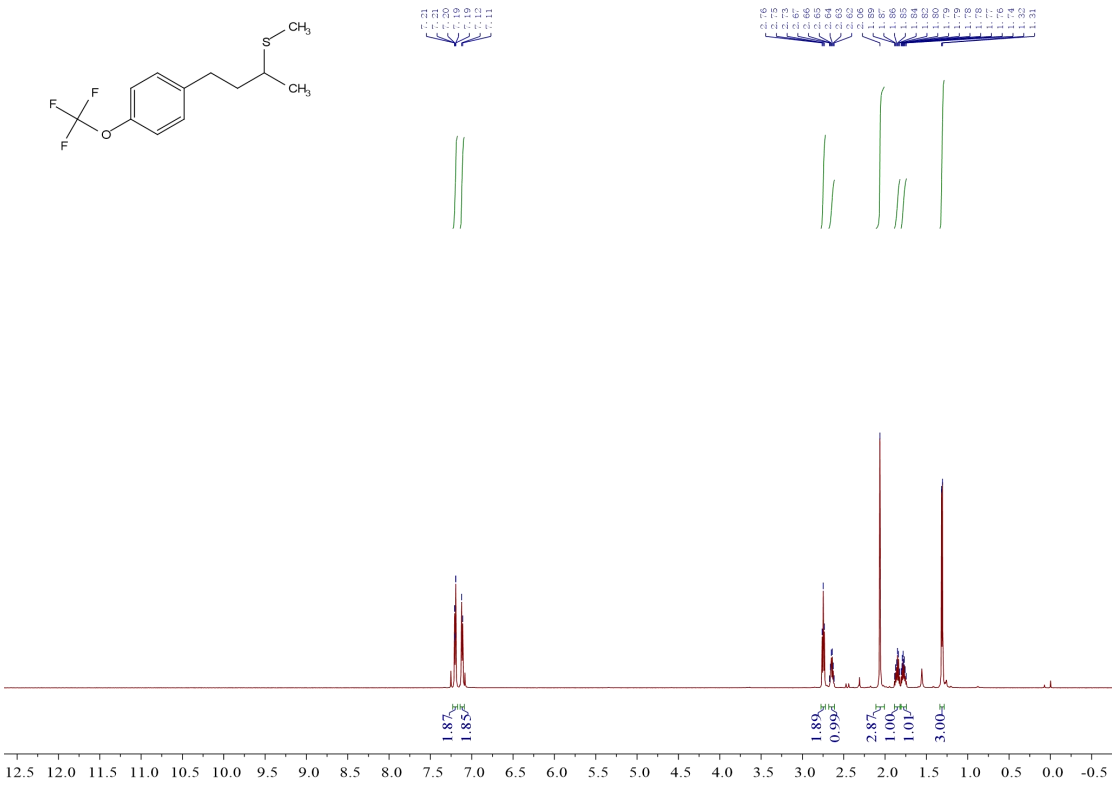
^{13}C {^{1}H} NMR of compound 5b (151 MHz, $CDCl_3$)



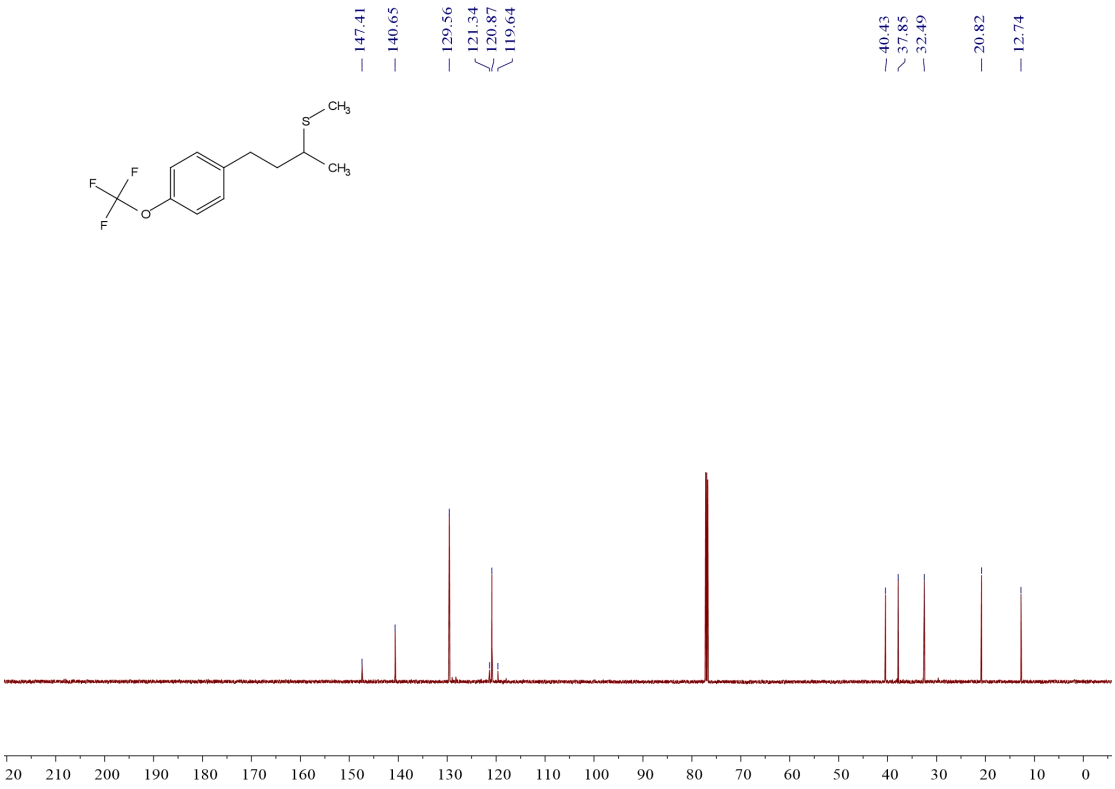
^{1}H NMR of compound 5c (600 MHz, $CDCl_3$)



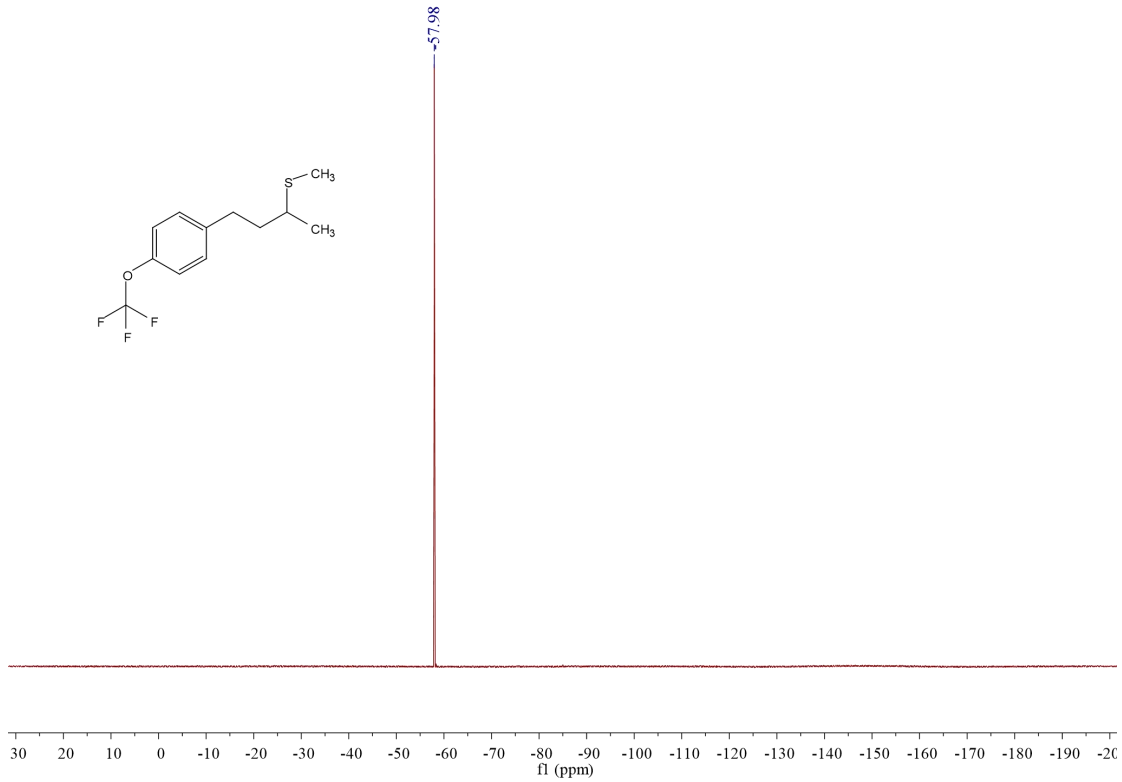
^{13}C {^{1}H} NMR of compound 5c (151 MHz, $CDCl_3$)



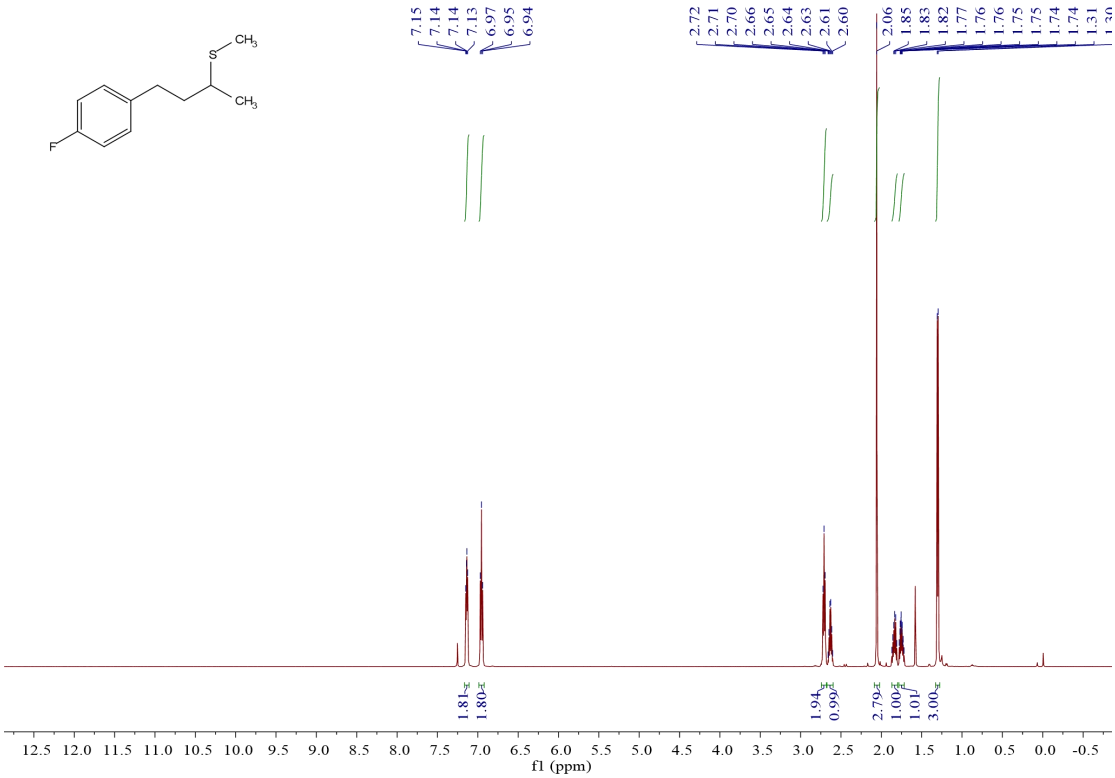
^{1}H NMR of compound 5d (600 MHz, $CDCl_3$)



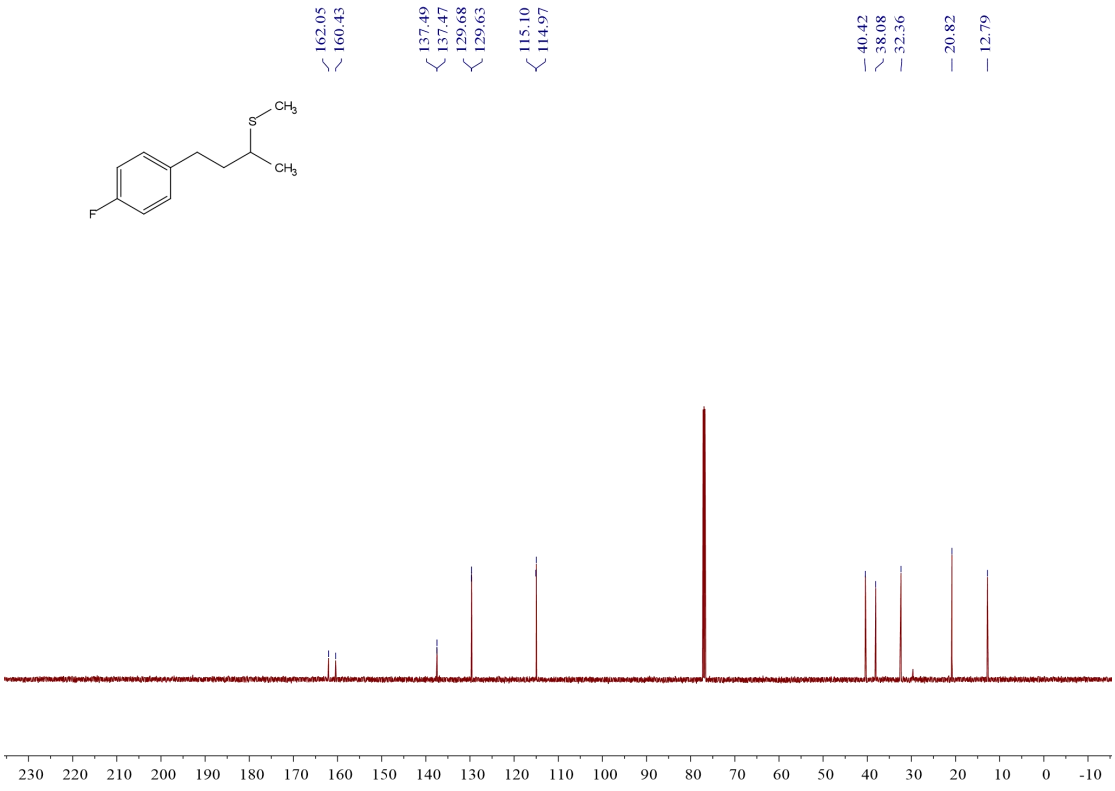
^{13}C {^{1}H} NMR of compound 5d (151 MHz, $CDCl_3$)



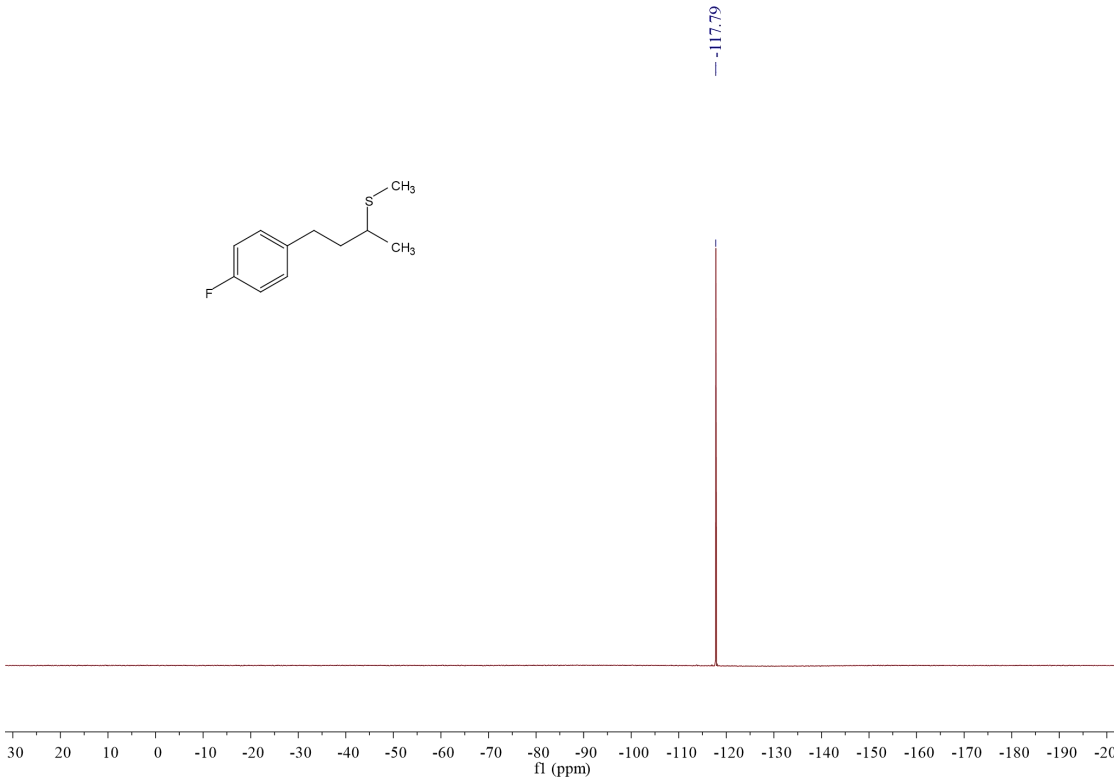
^{19}F NMR of compound 5d (564 MHz, $CDCl_3$)



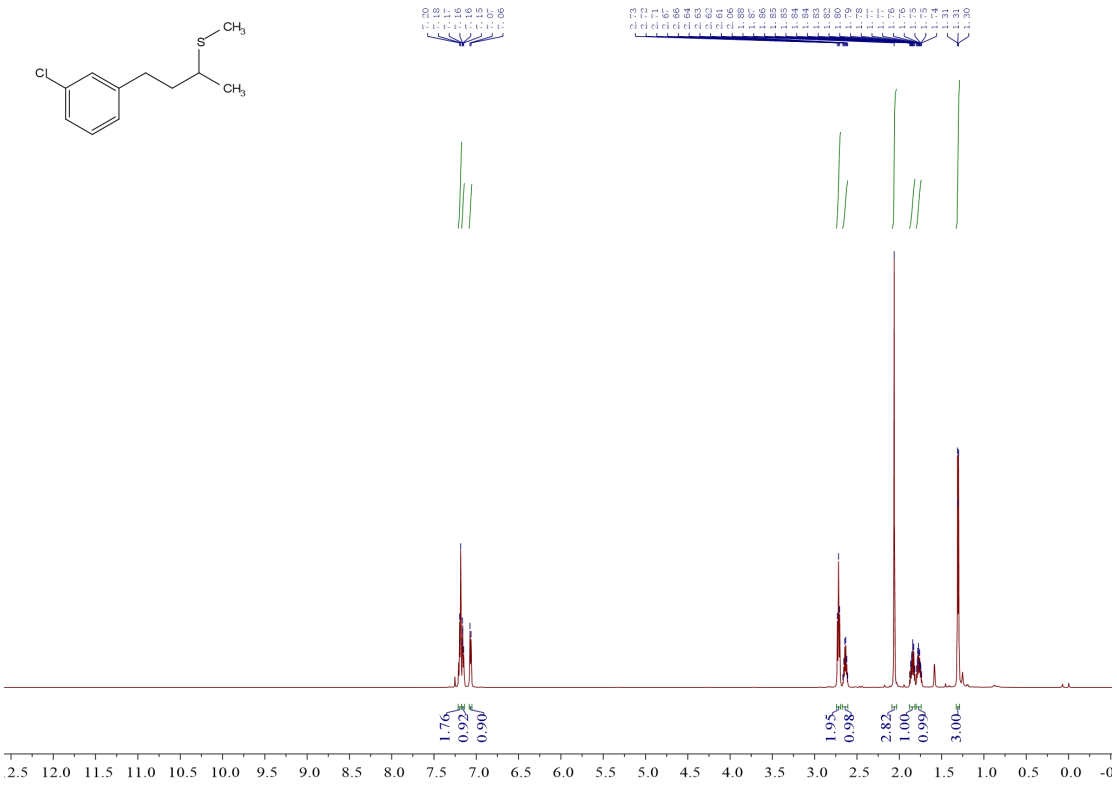
^{1}H NMR of compound 5e (600 MHz, $CDCl_3$)



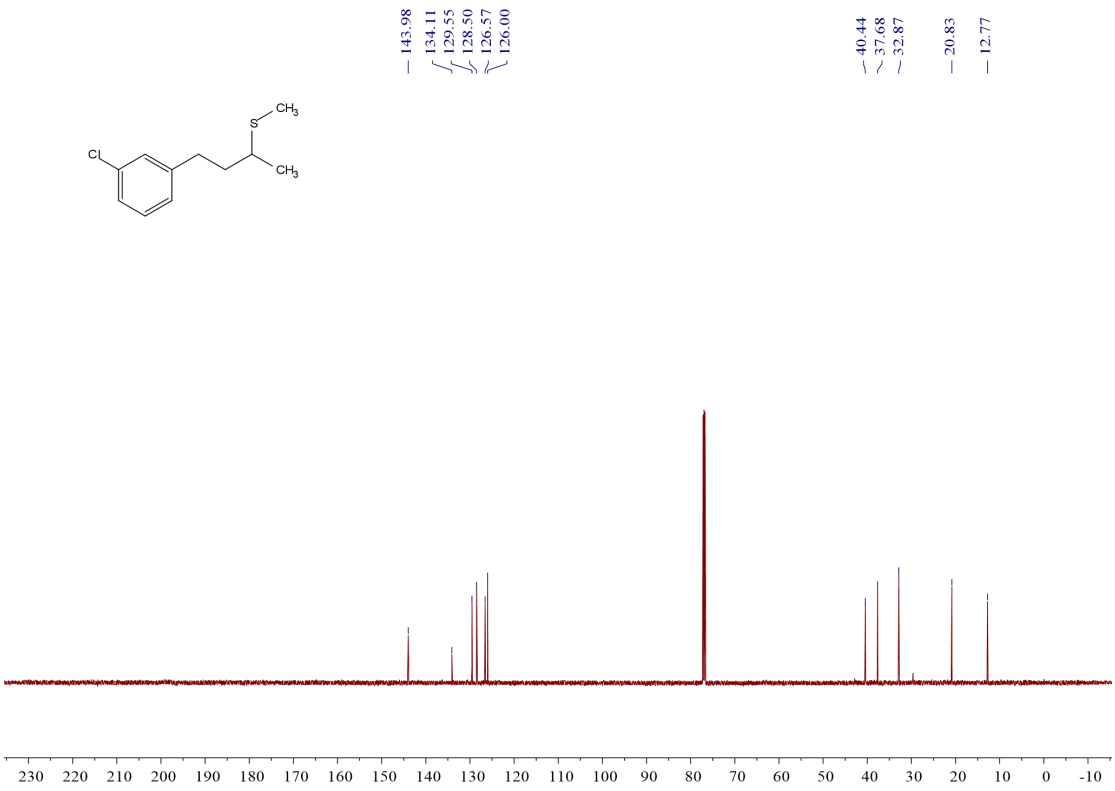
^{13}C {^{1}H} NMR of compound 5e (151 MHz, $CDCl_3$)



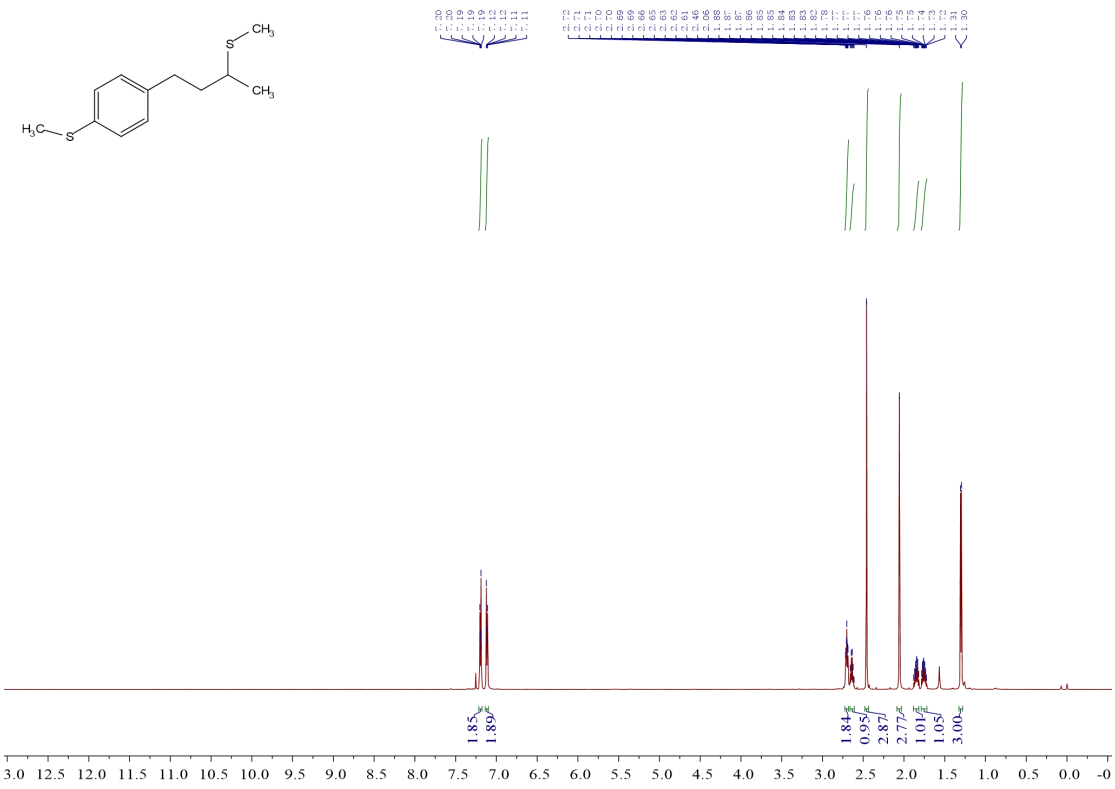
^{19}F NMR of compound 5e (564 MHz, $CDCl_3$)



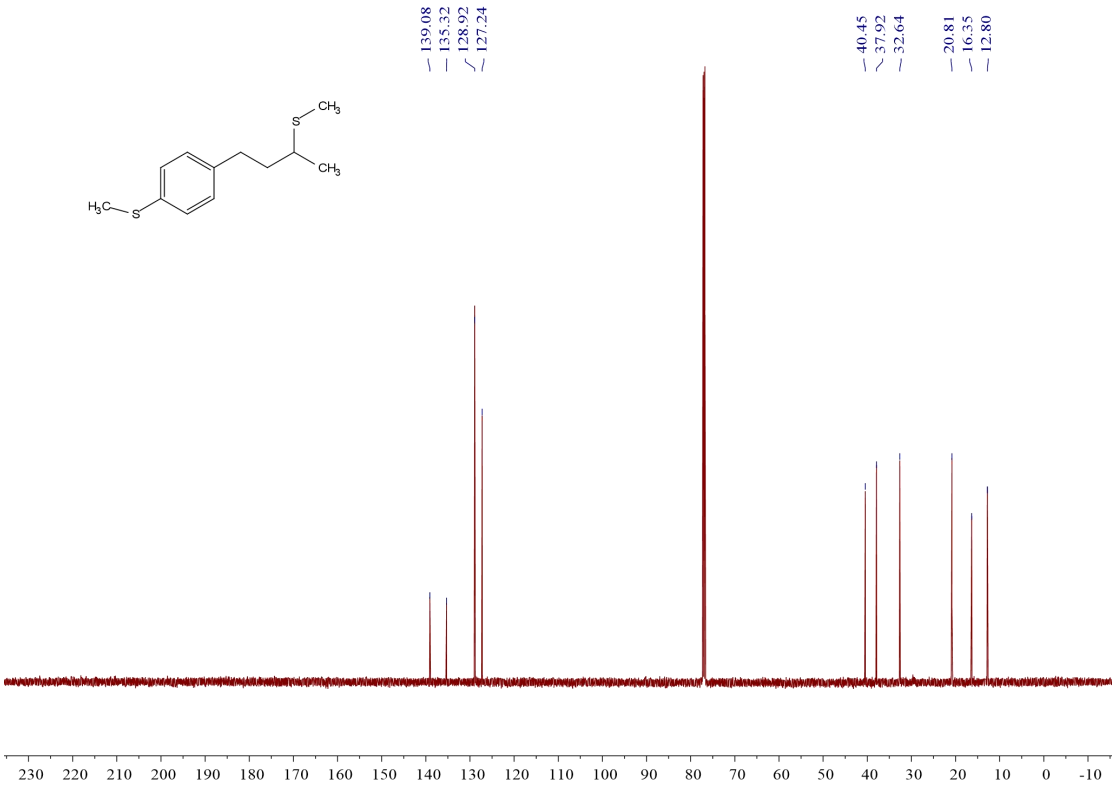
^{1}H NMR of compound 5f (600 MHz, $CDCl_3$)



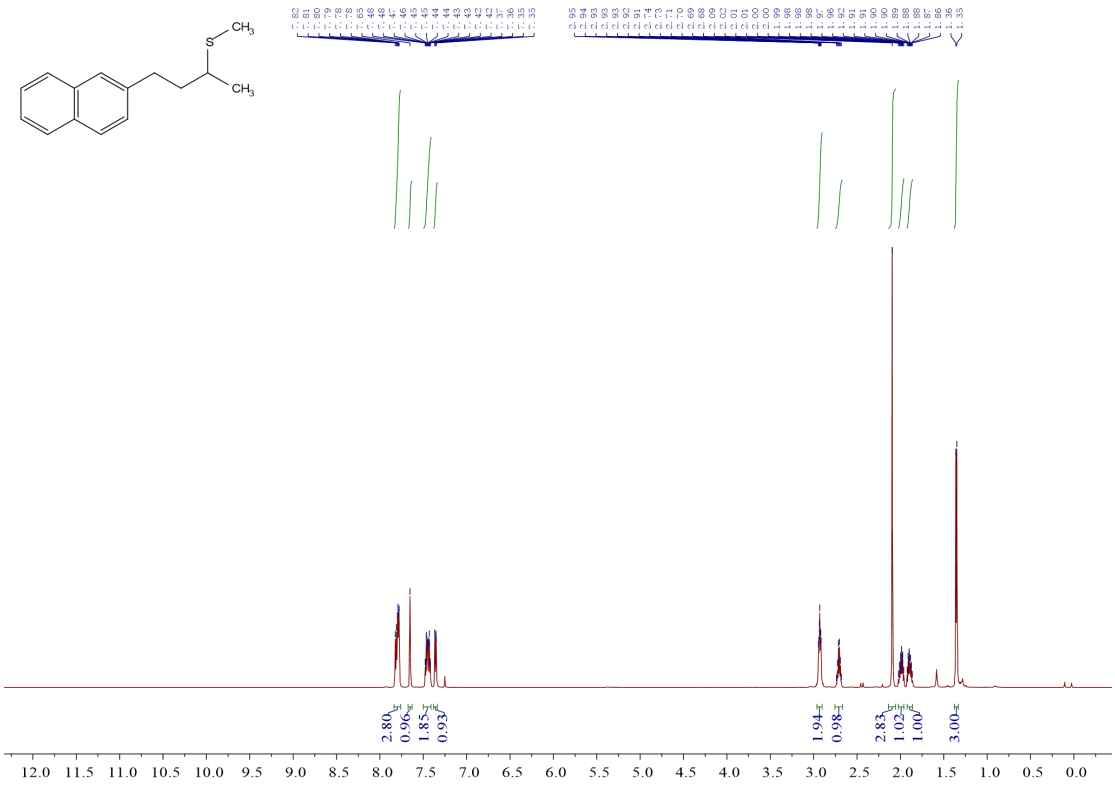
^{13}C {^{1}H} NMR of compound 5f (151 MHz, $CDCl_3$)



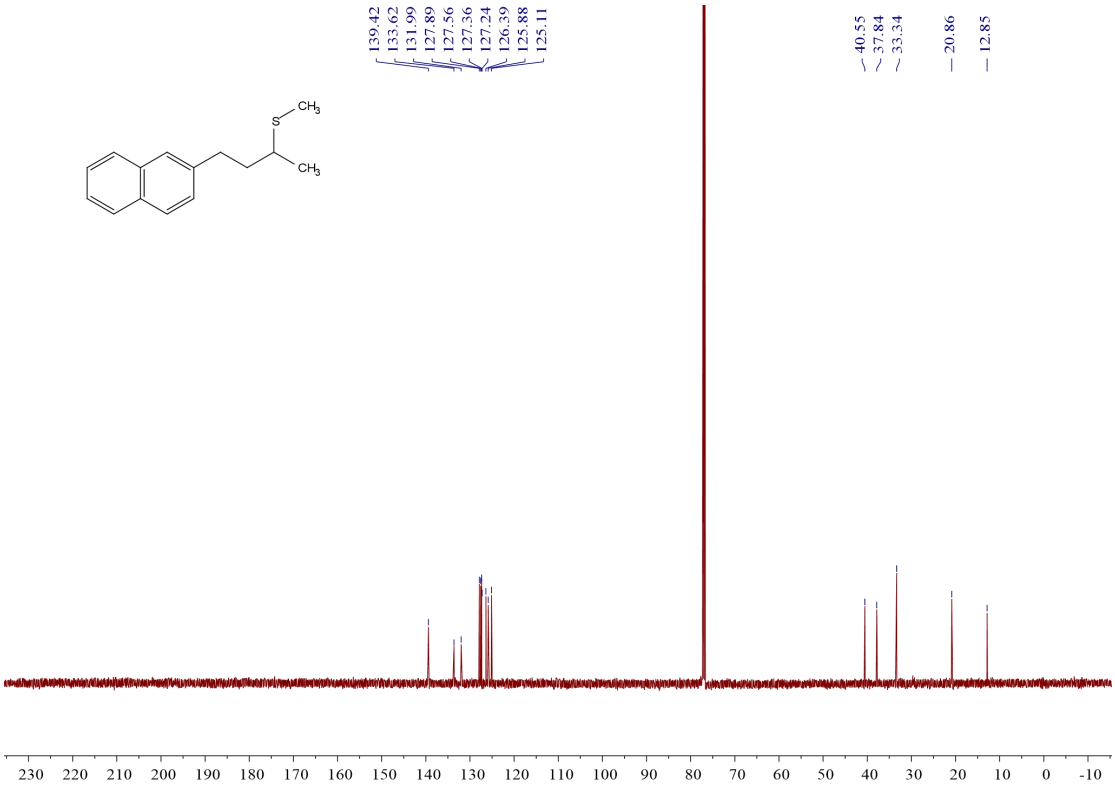
^{1}H NMR of compound 5g (600 MHz, $CDCl_3$)



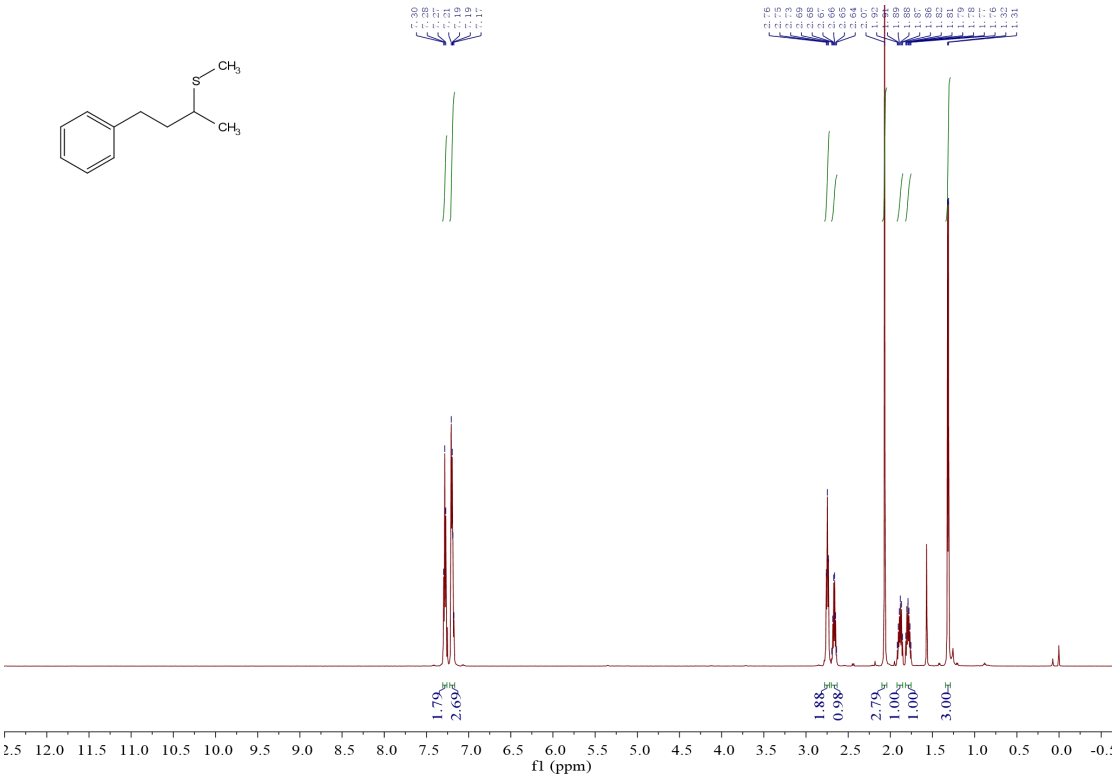
^{13}C {^{1}H} NMR of compound 5g (151 MHz, $CDCl_3$)



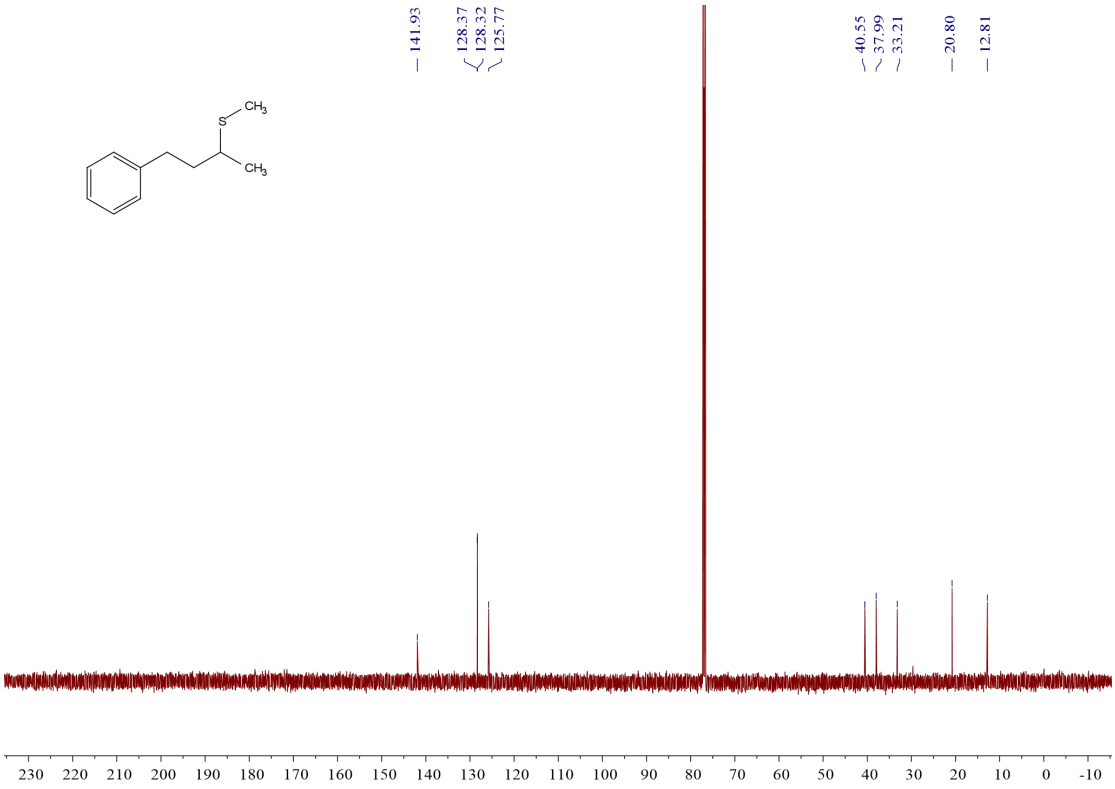
^{1}H NMR of compound 5h (600 MHz, $CDCl_3$)



^{13}C {^{1}H} NMR of compound 5h (151 MHz, $CDCl_3$)

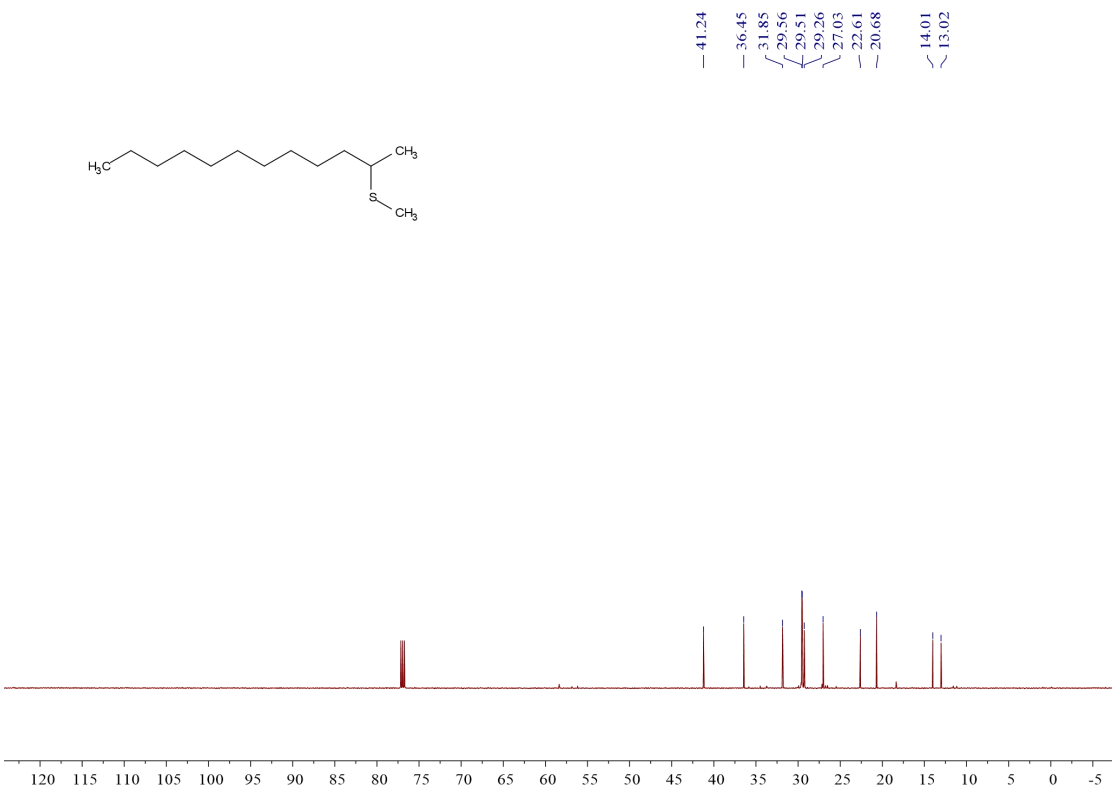


^{1}H NMR of compound 5i (600 MHz, $CDCl_3$)

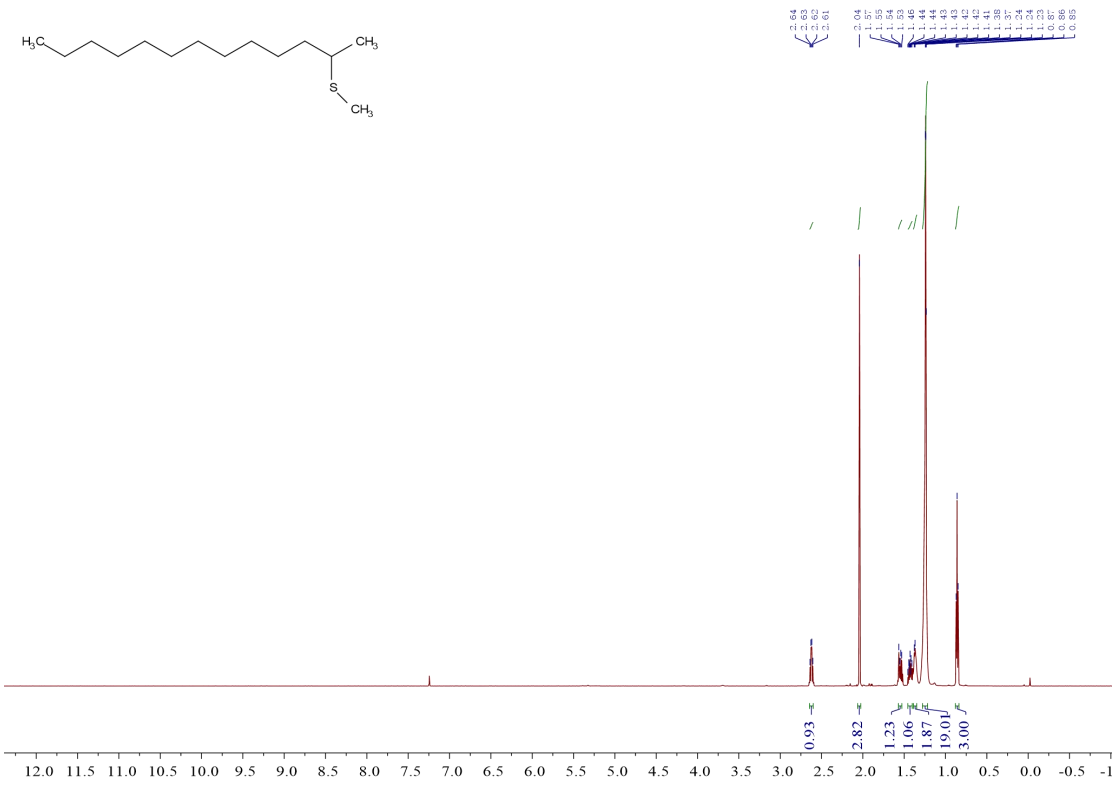


^{13}C {^{1}H} NMR of compound 5i (151 MHz, $CDCl_3$)

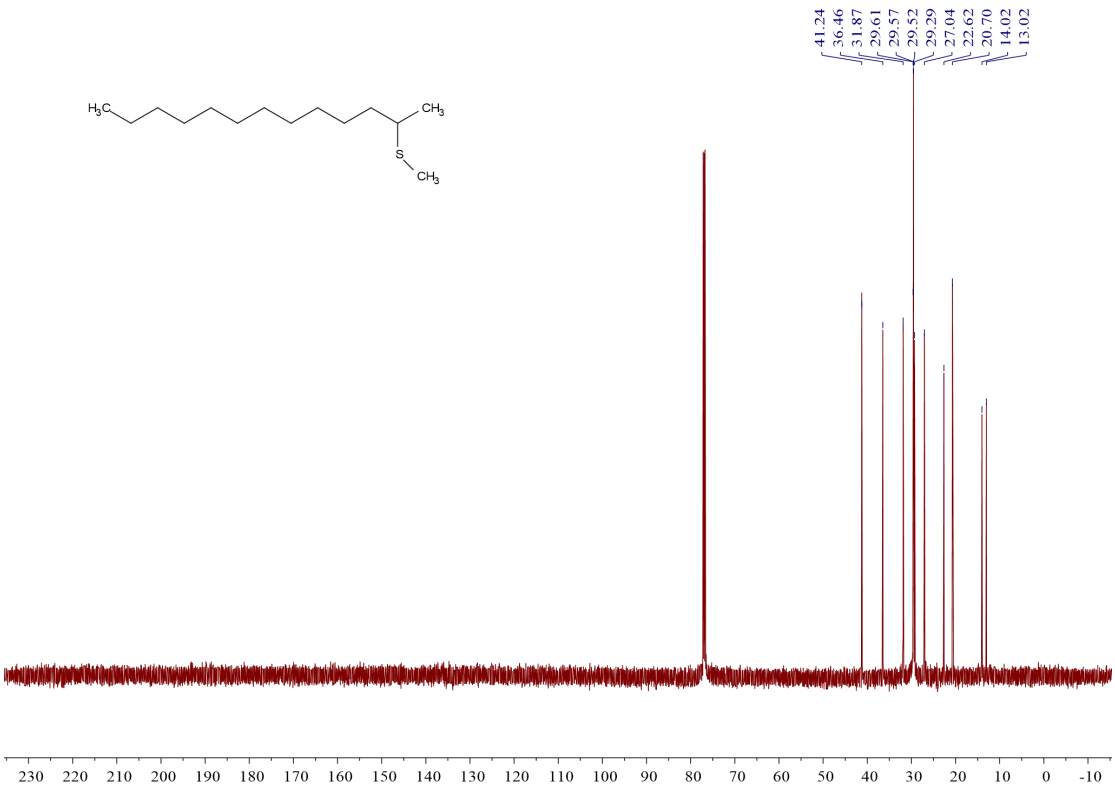
^{1}H NMR of compound 5j (600 MHz, $CDCl_3$)



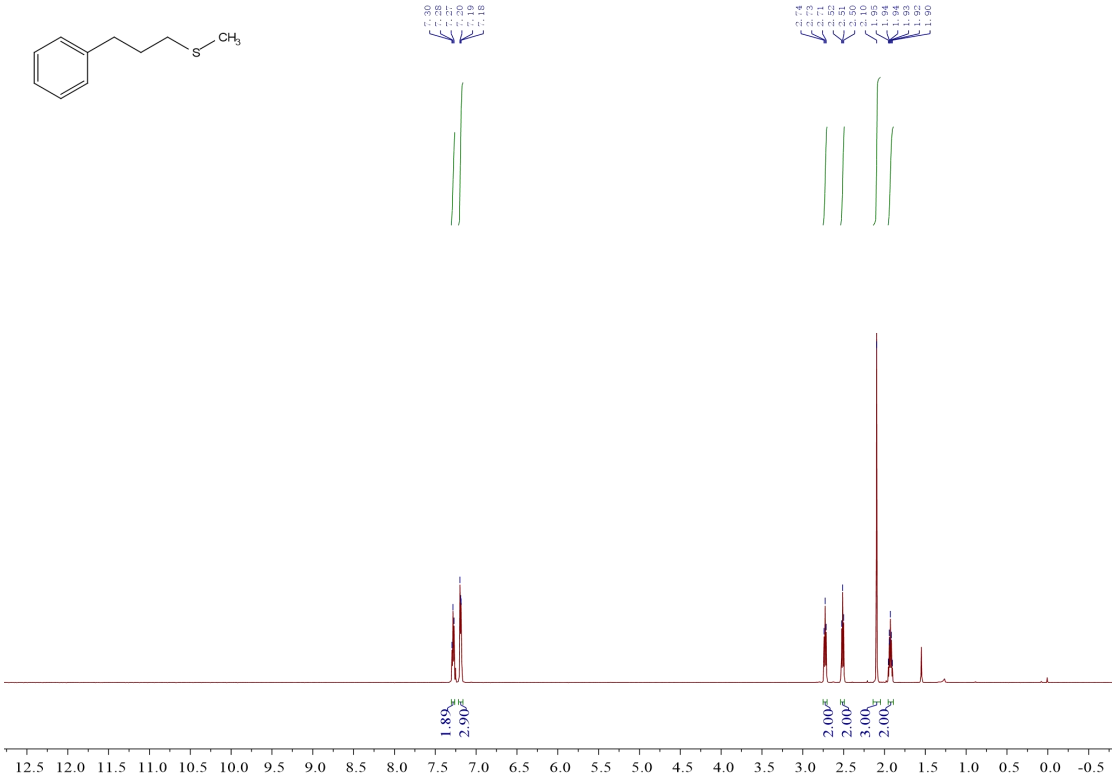
^{13}C {^{1}H} NMR of compound 5j (151 MHz, $CDCl_3$)



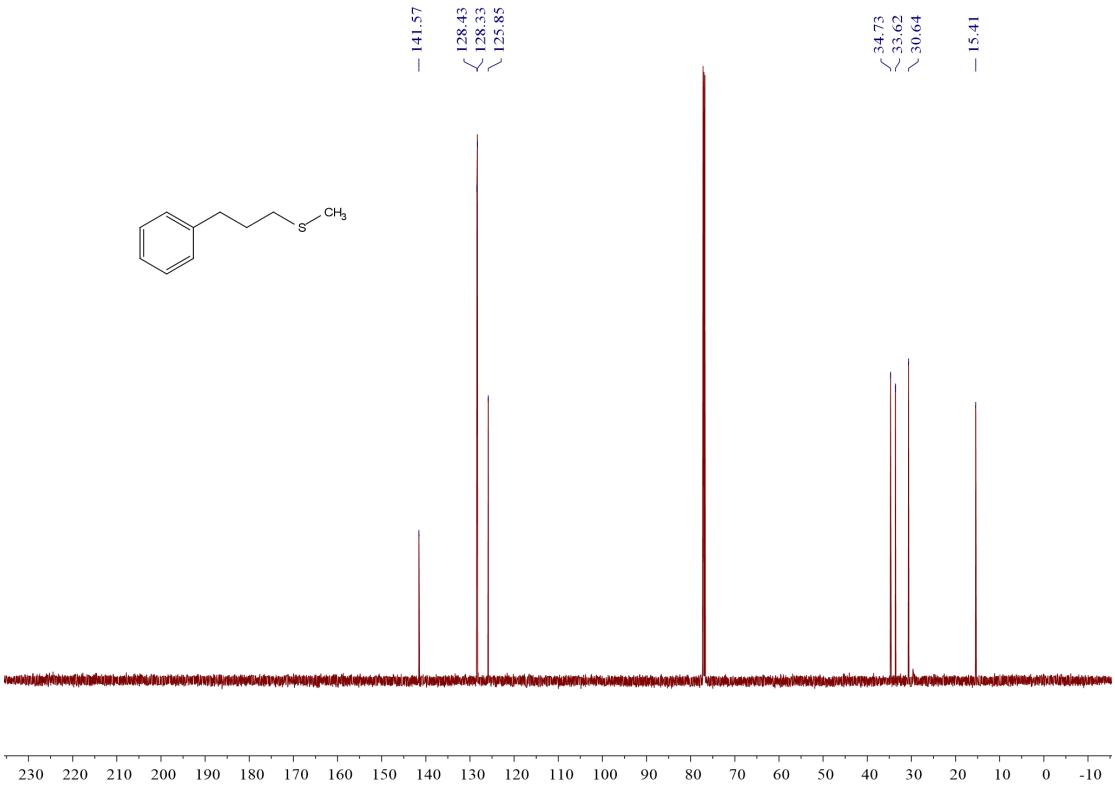
^{1}H NMR of compound 5k (600 MHz, $CDCl_3$)



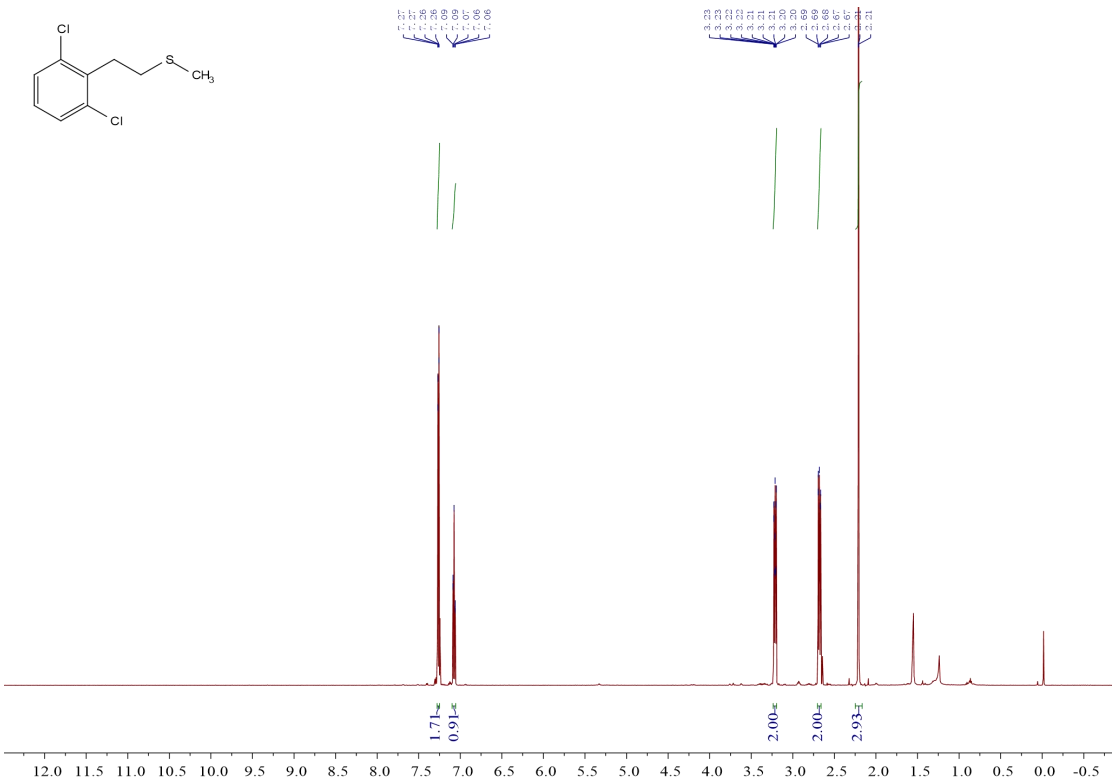
^{13}C {^{1}H} NMR of compound 5k (151 MHz, $CDCl_3$)



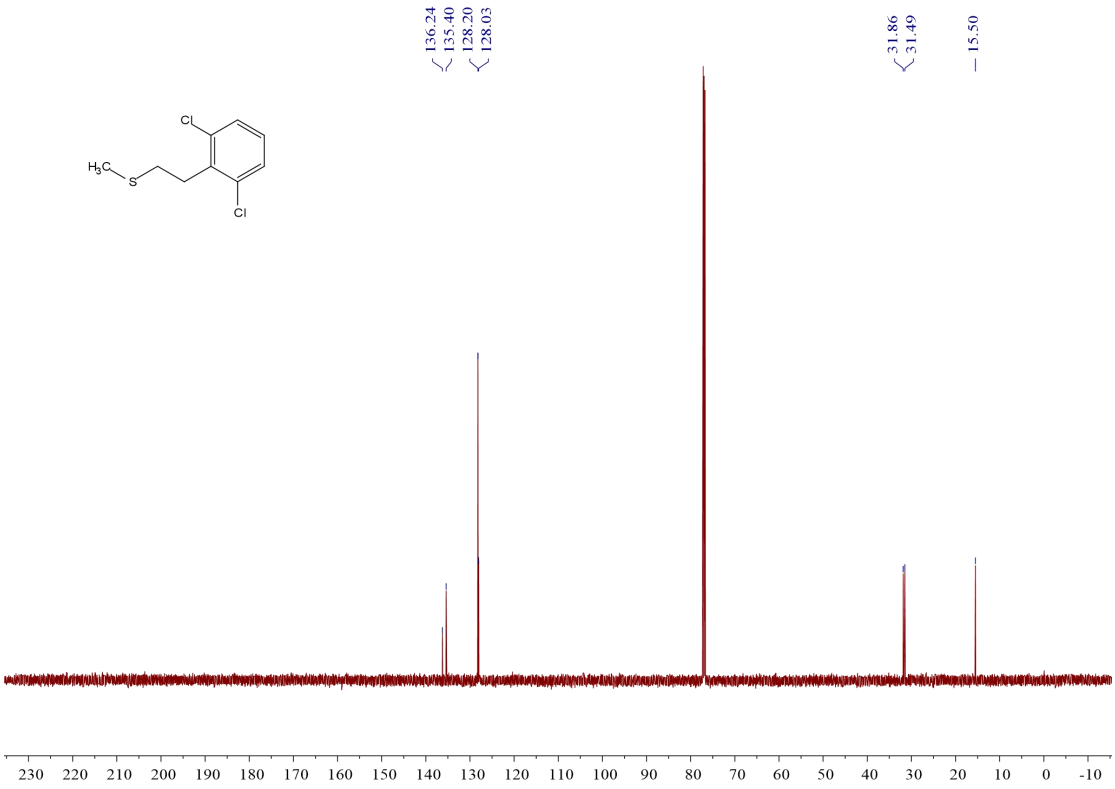
^{1}H NMR of compound 5l (600 MHz, $CDCl_3$)



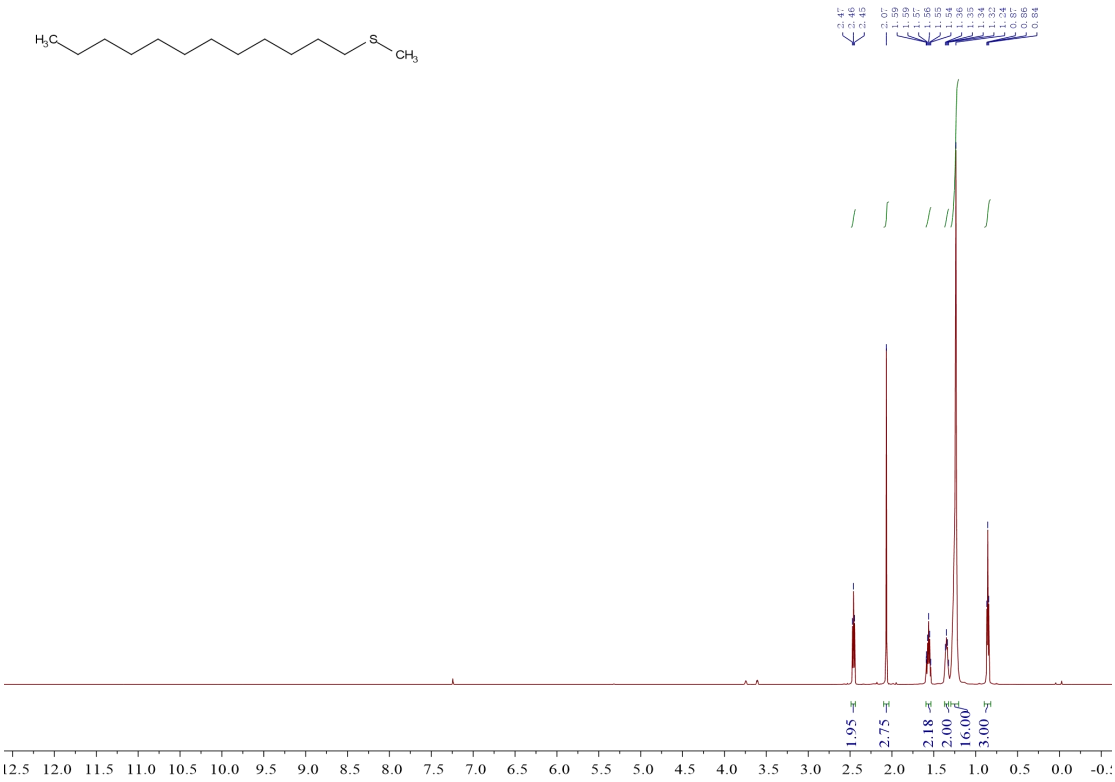
^{13}C {^{1}H} NMR of compound 5l (151 MHz, $CDCl_3$)



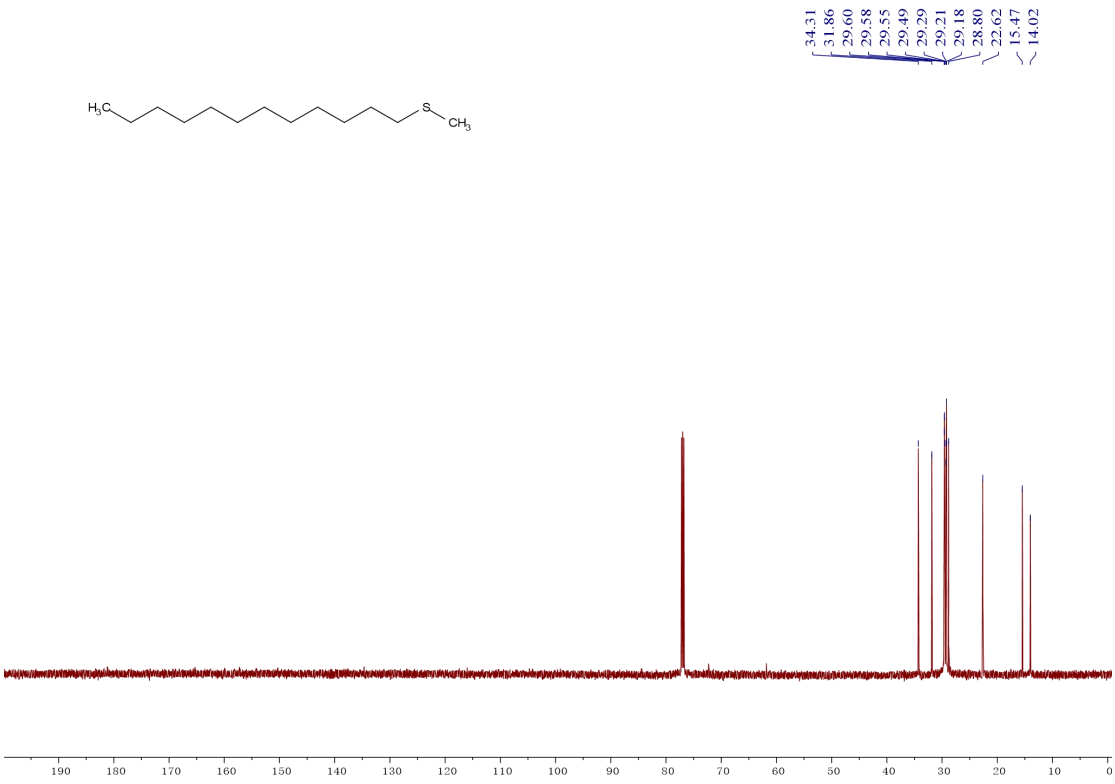
^{1}H NMR of compound 5m (600 MHz, $CDCl_3$)



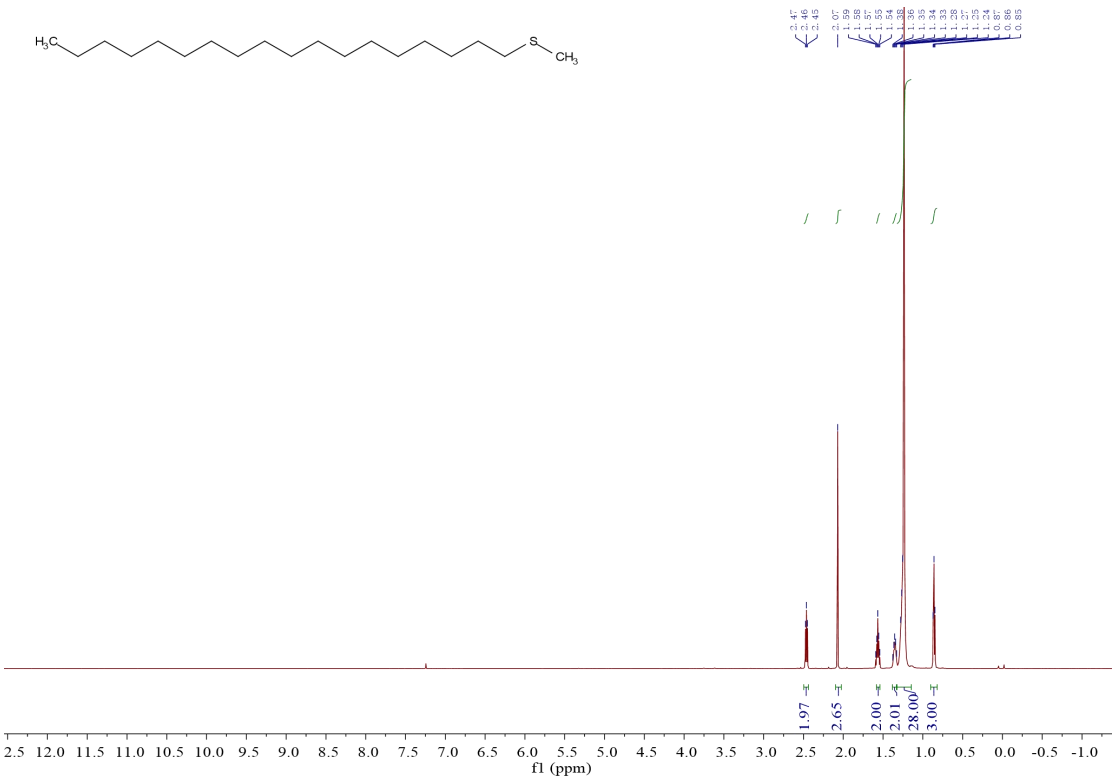
^{13}C {^{1}H} NMR of compound 5m (151 MHz, $CDCl_3$)



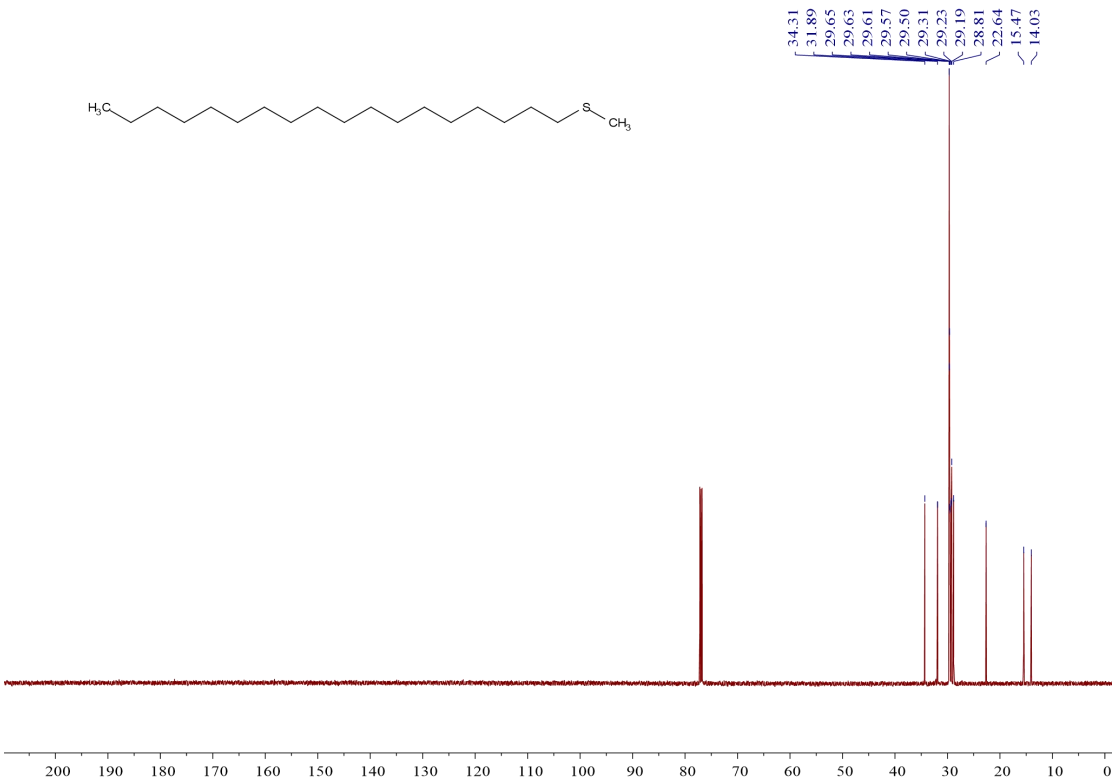
^{1}H NMR of compound 5n (600 MHz, $CDCl_3$)



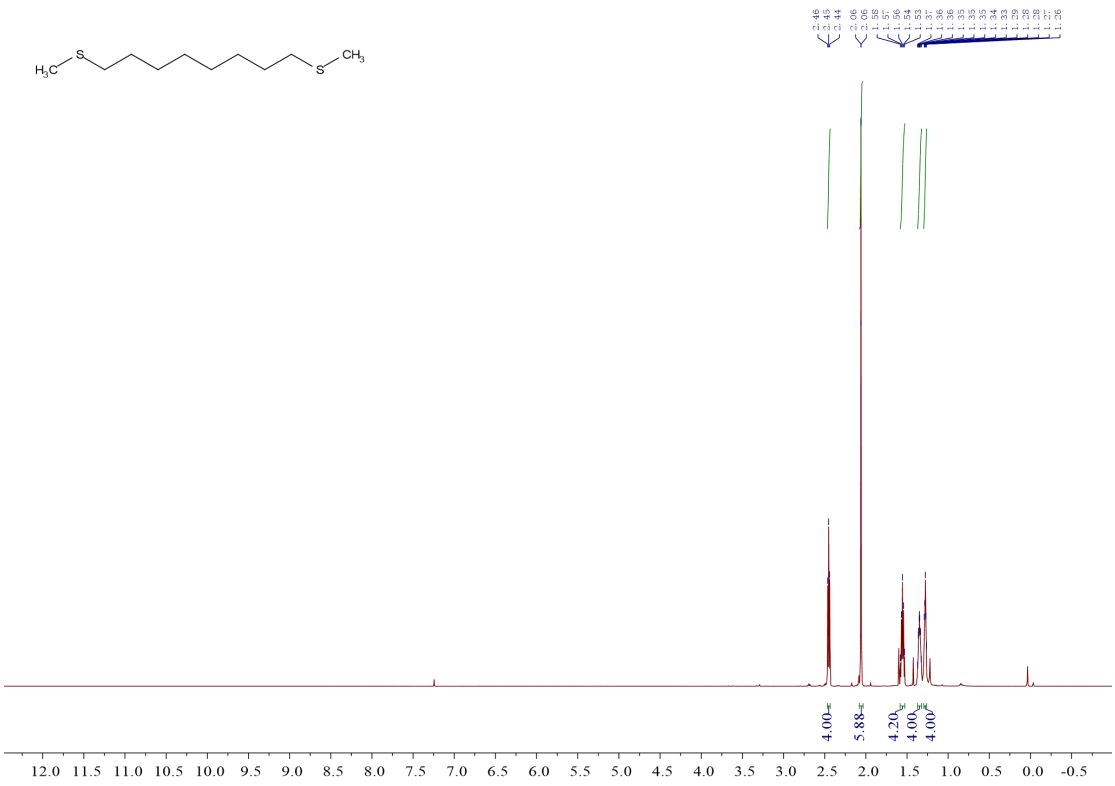
^{13}C {^{1}H} NMR of compound 5n (151 MHz, $CDCl_3$)



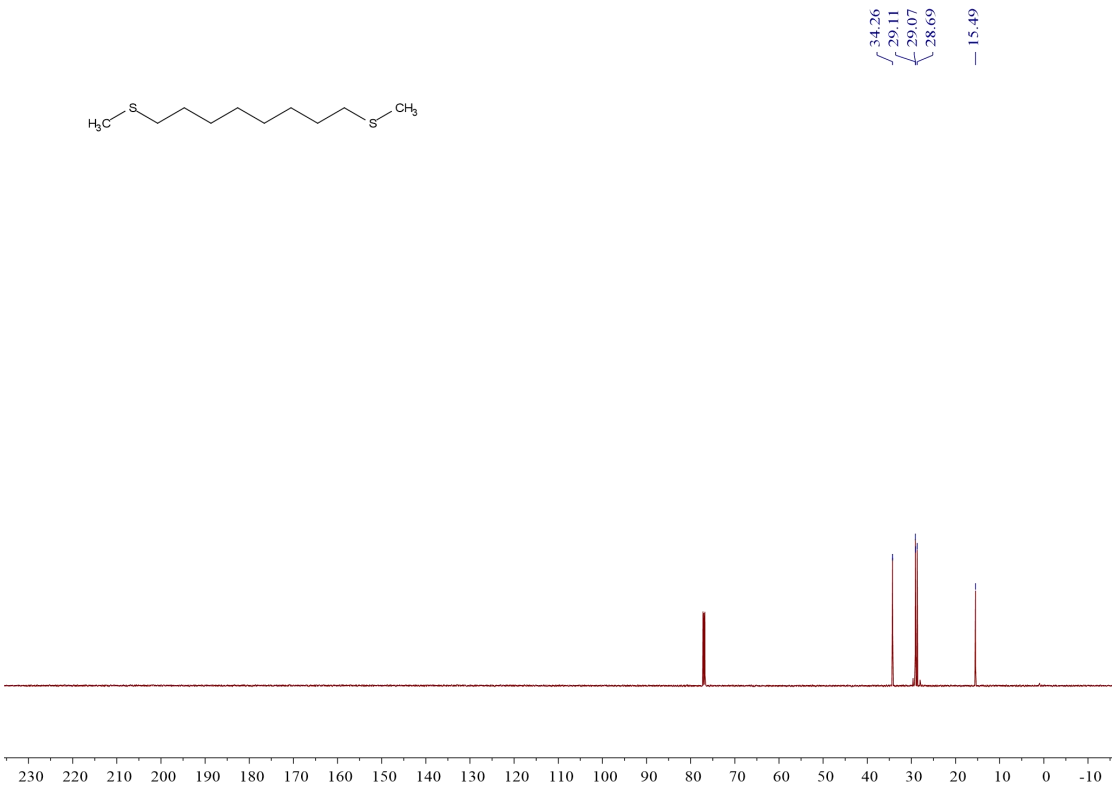
^{1}H NMR of compound 5o (600 MHz, $CDCl_3$)



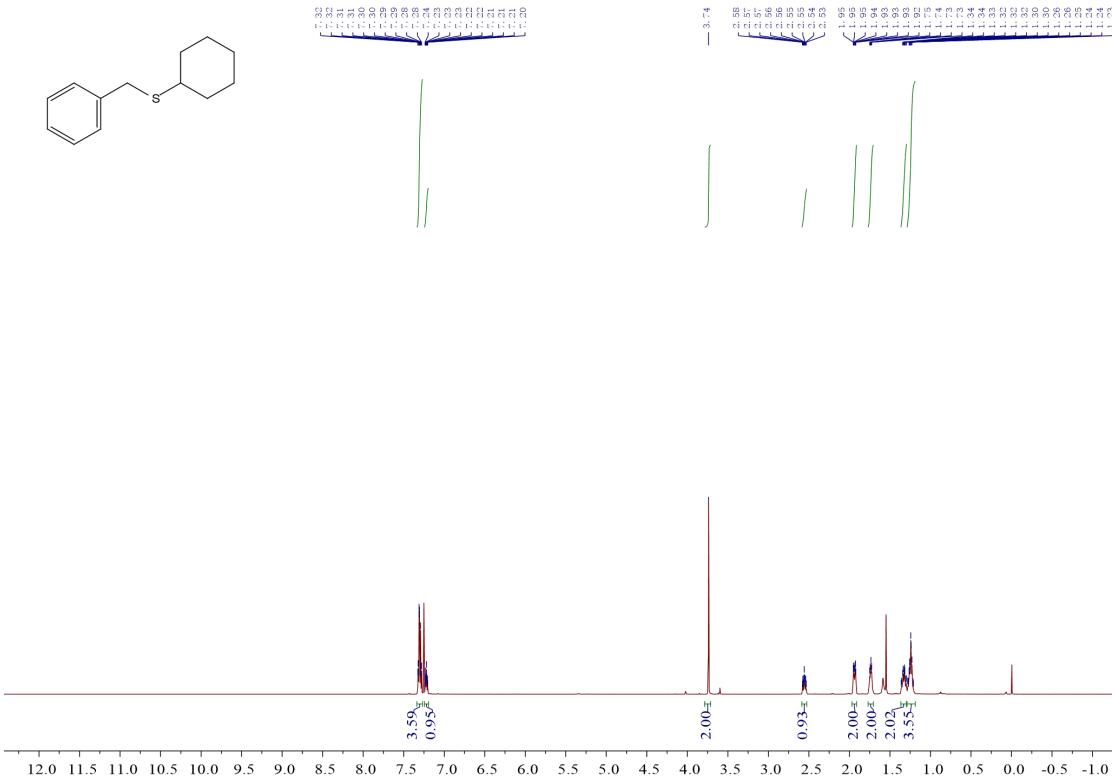
^{13}C {^{1}H} NMR of compound 5o (151 MHz, $CDCl_3$)



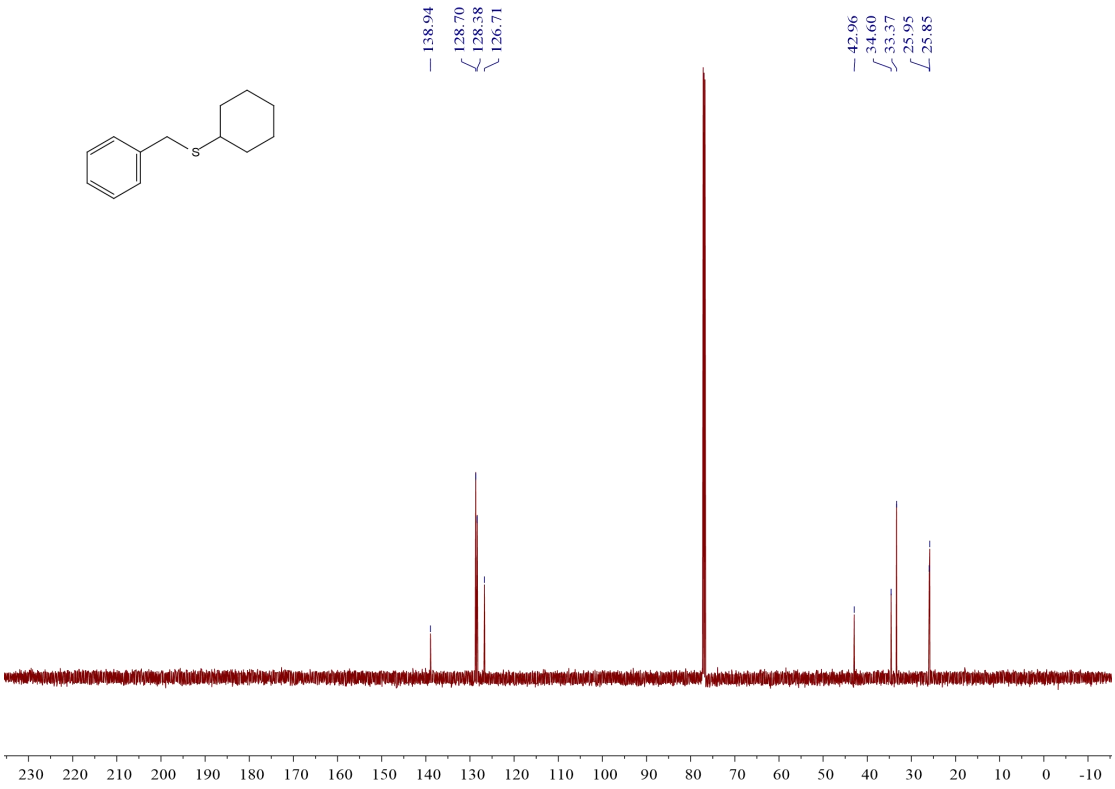
^{1}H NMR of compound 5p (600 MHz, $CDCl_3$)



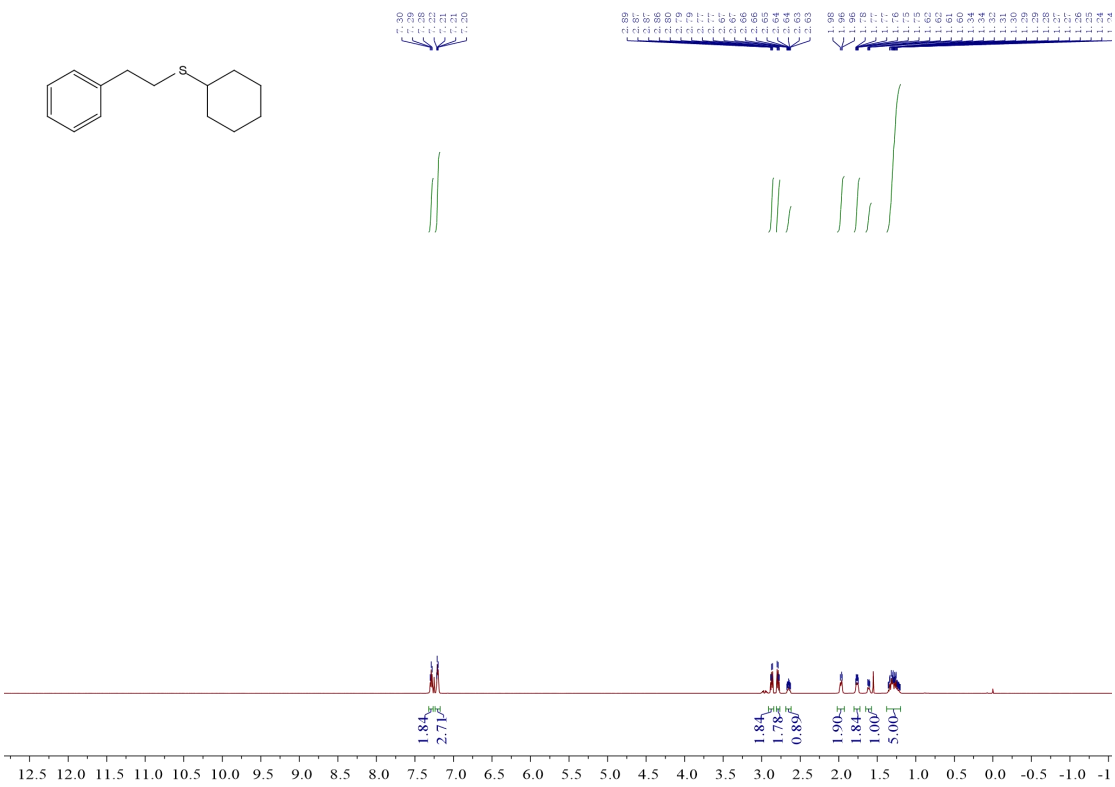
^{13}C {^{1}H} NMR of compound 5p (151 MHz, $CDCl_3$)



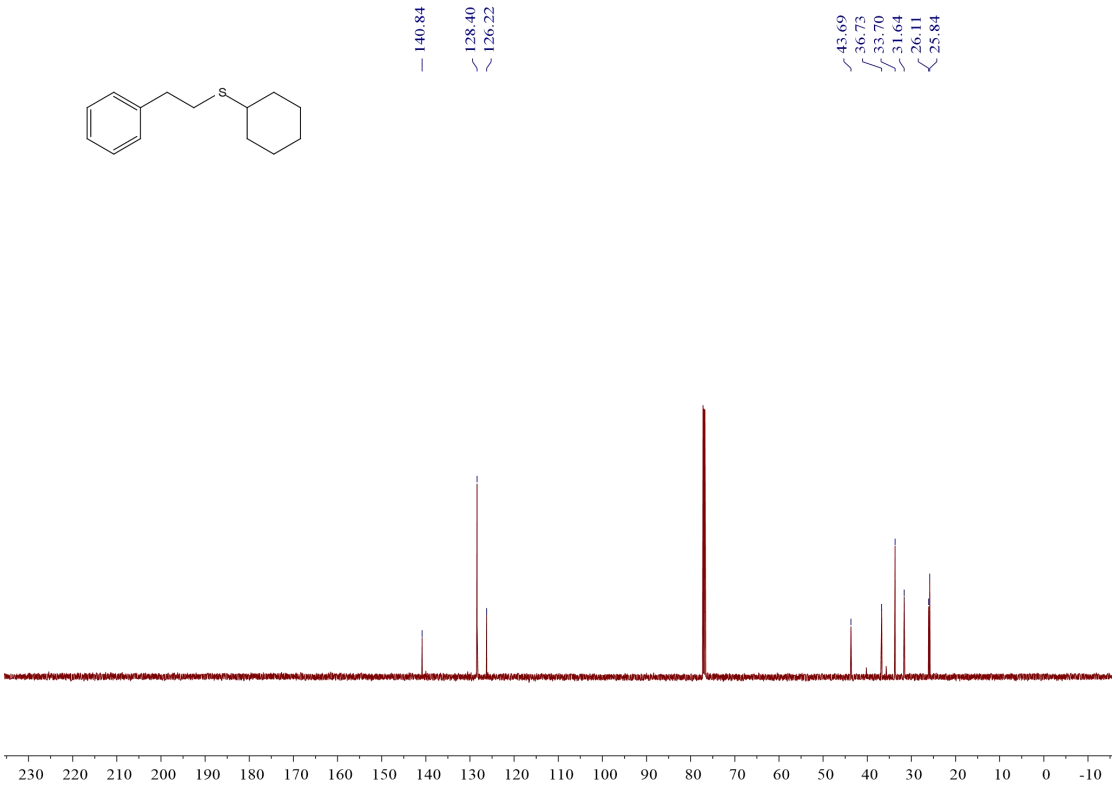
^{1}H NMR of compound 5q (600 MHz, $CDCl_3$)



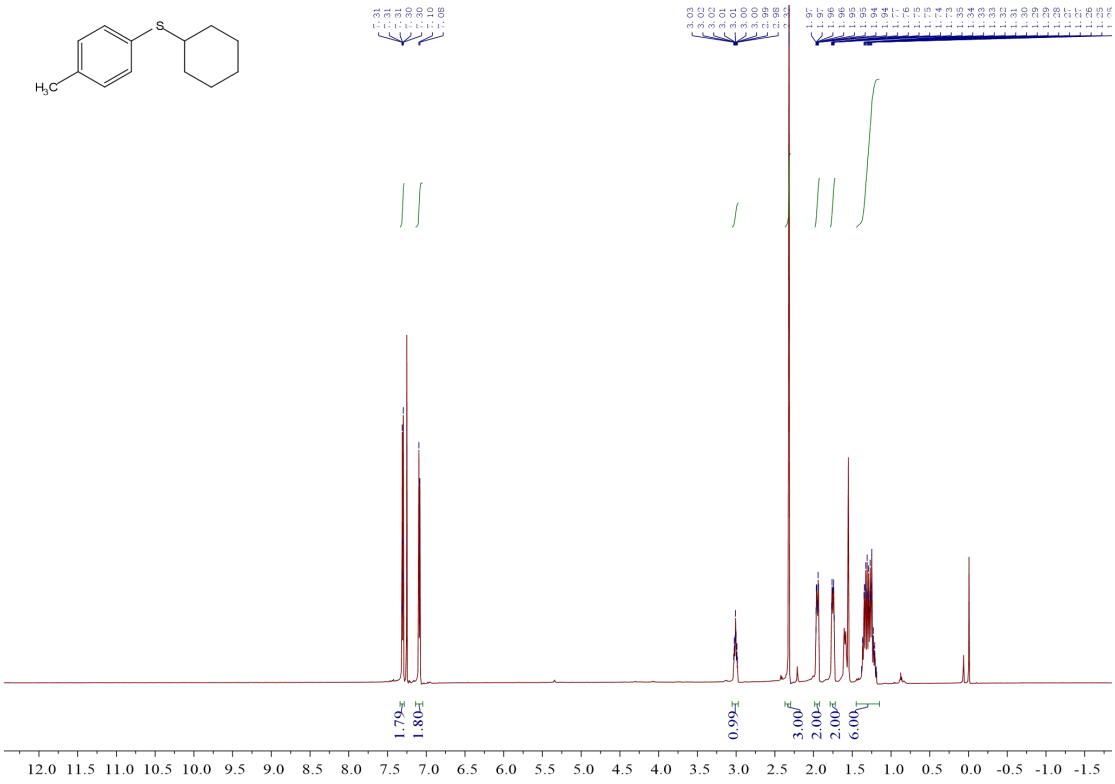
^{13}C {^{1}H} NMR of compound 5q (151 MHz, $CDCl_3$)



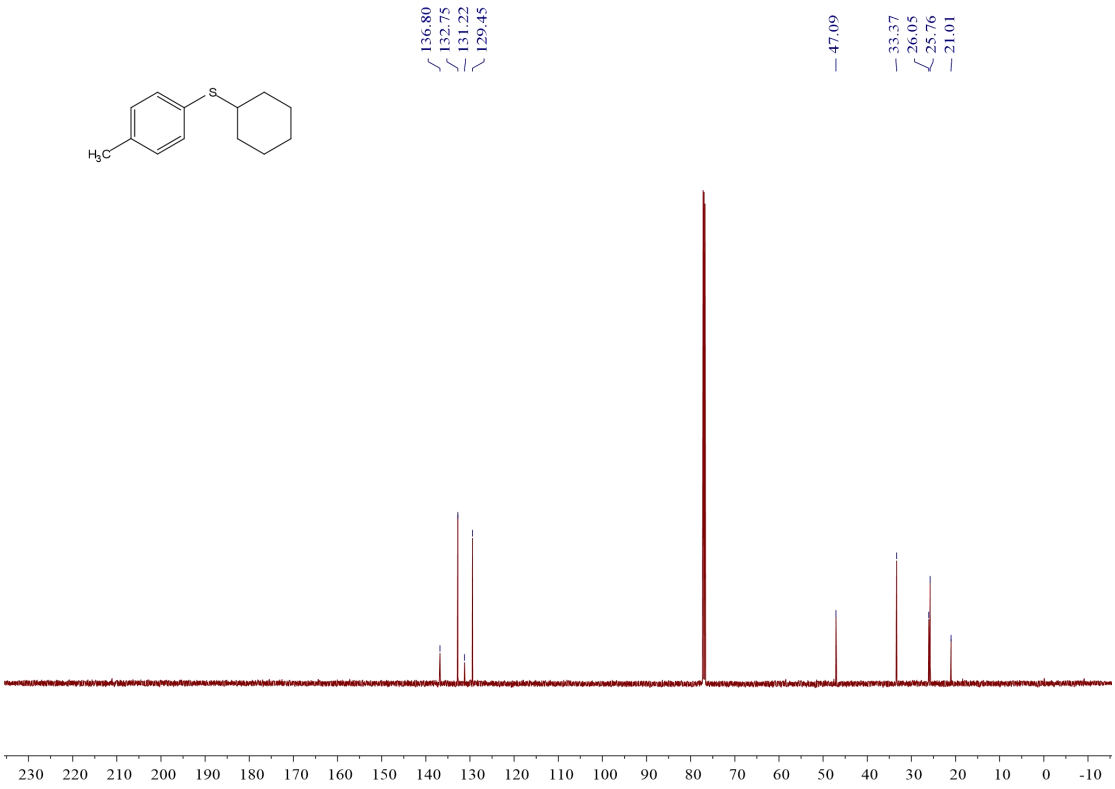
^{1}H NMR of compound 5r (600 MHz, $CDCl_3$)



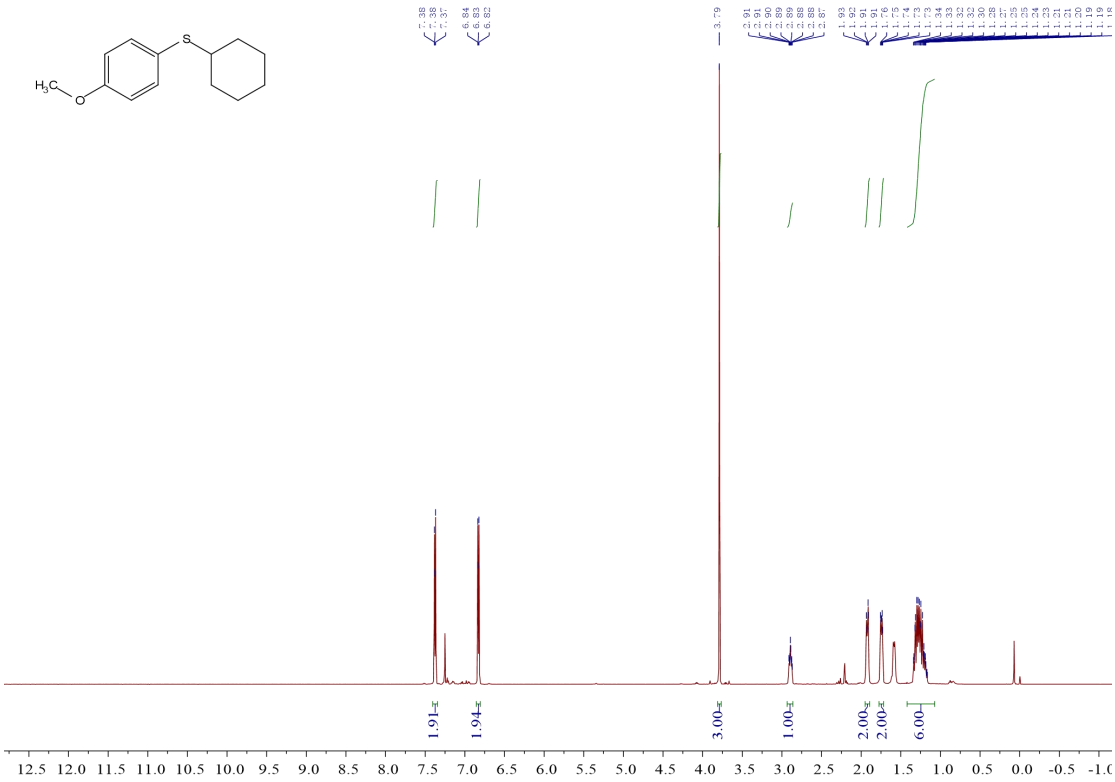
^{13}C {^{1}H} NMR of compound 5r (151 MHz, $CDCl_3$)



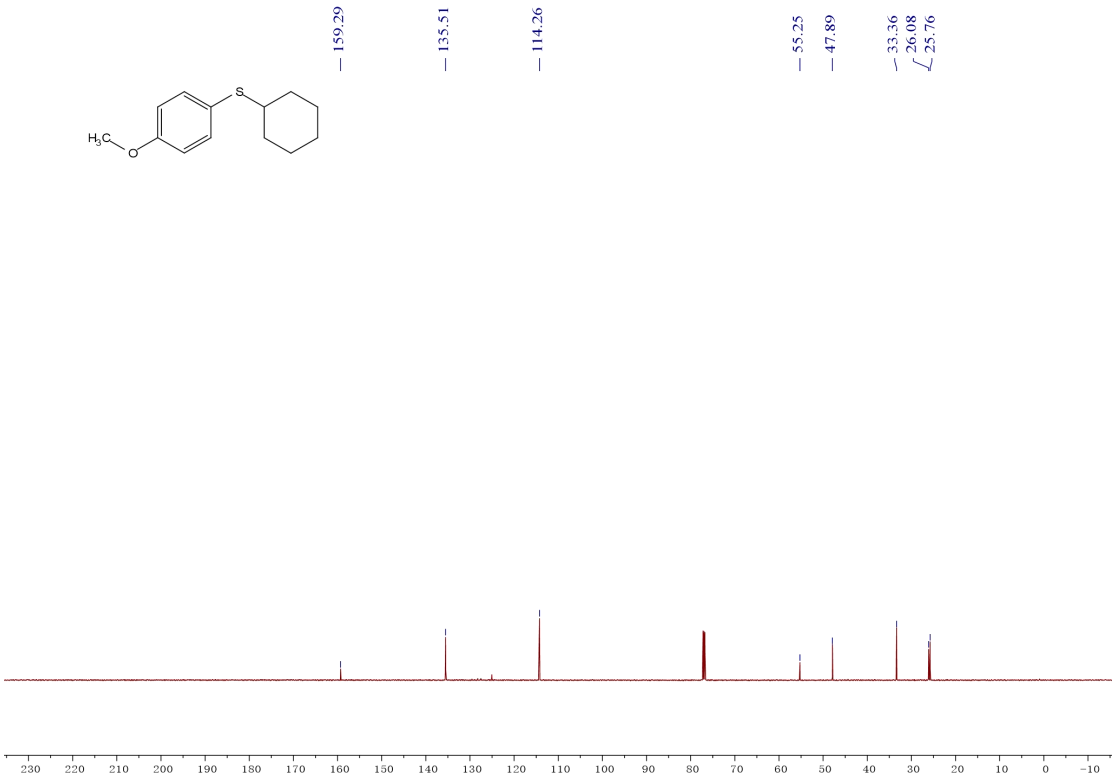
^{1}H NMR of compound 5s (600 MHz, $CDCl_3$)



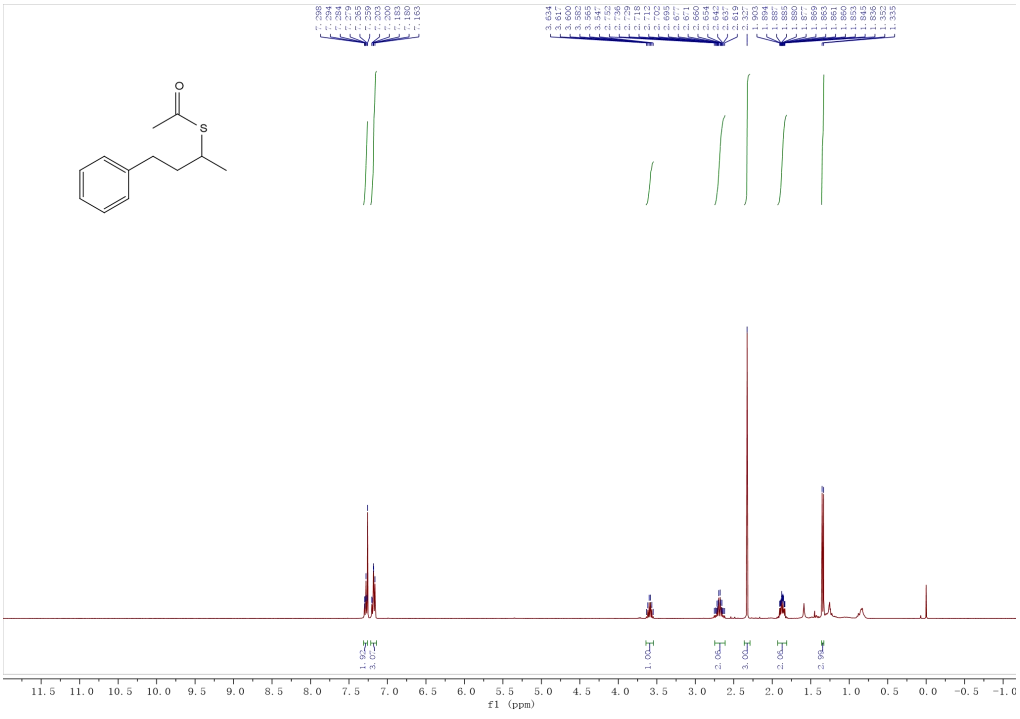
^{13}C {^{1}H} NMR of compound 5s (151 MHz, $CDCl_3$)



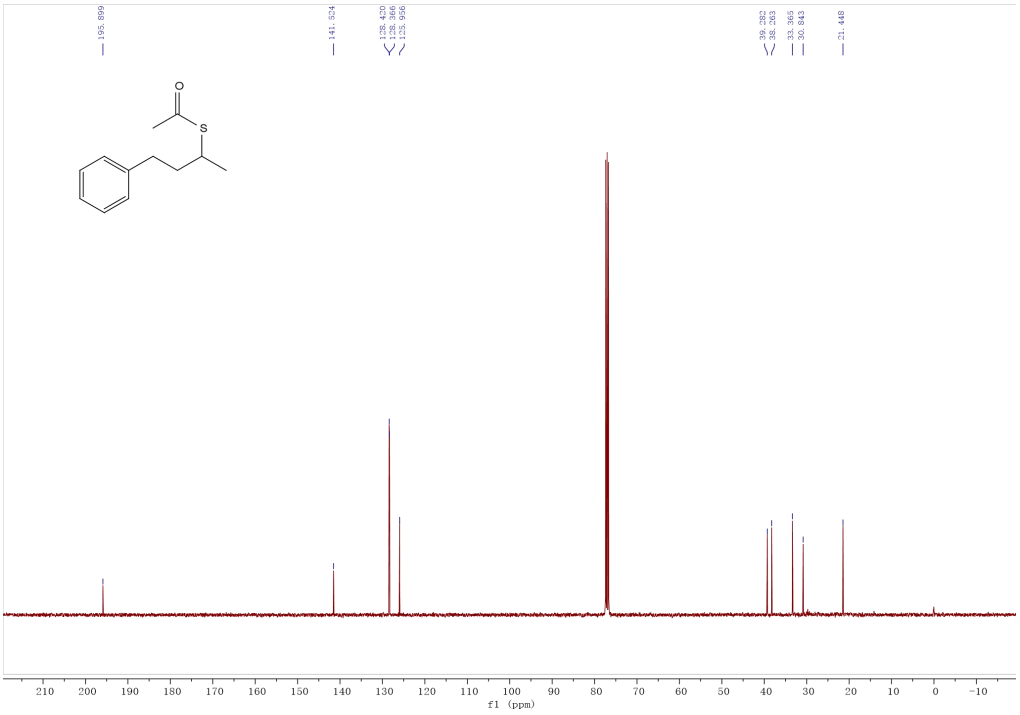
^{1}H NMR of compound 5t (600 MHz, $CDCl_3$)



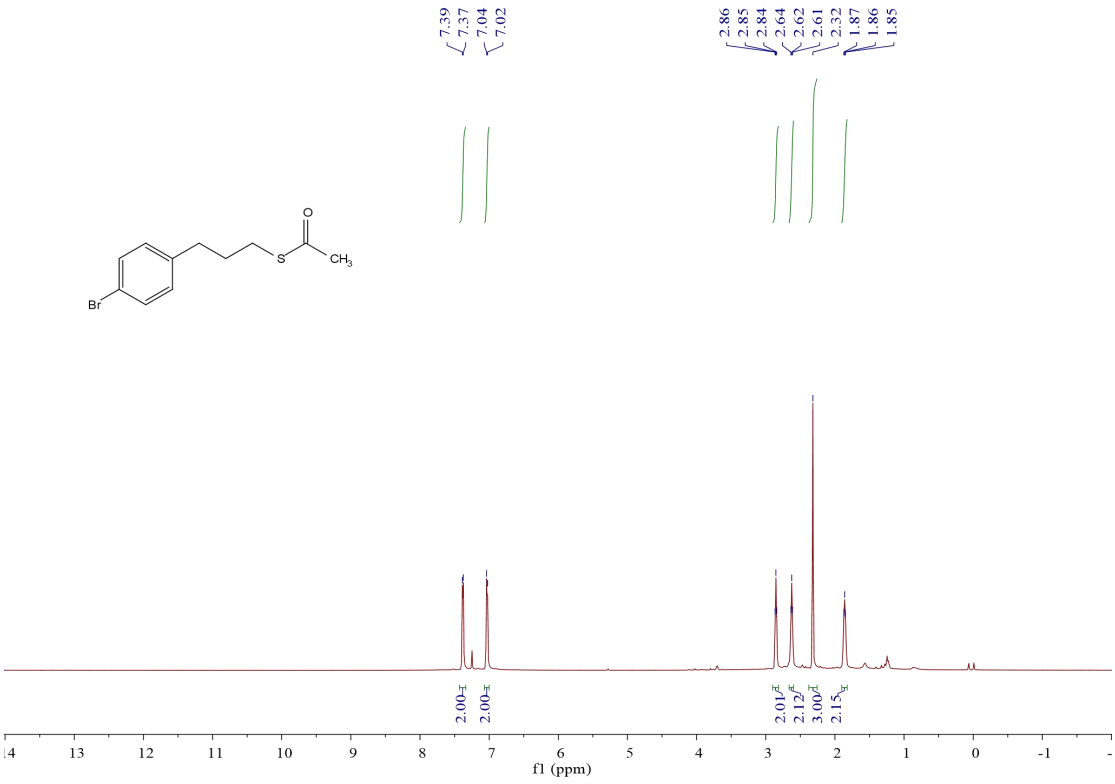
^{13}C {^{1}H} NMR of compound 5t (151 MHz, $CDCl_3$)



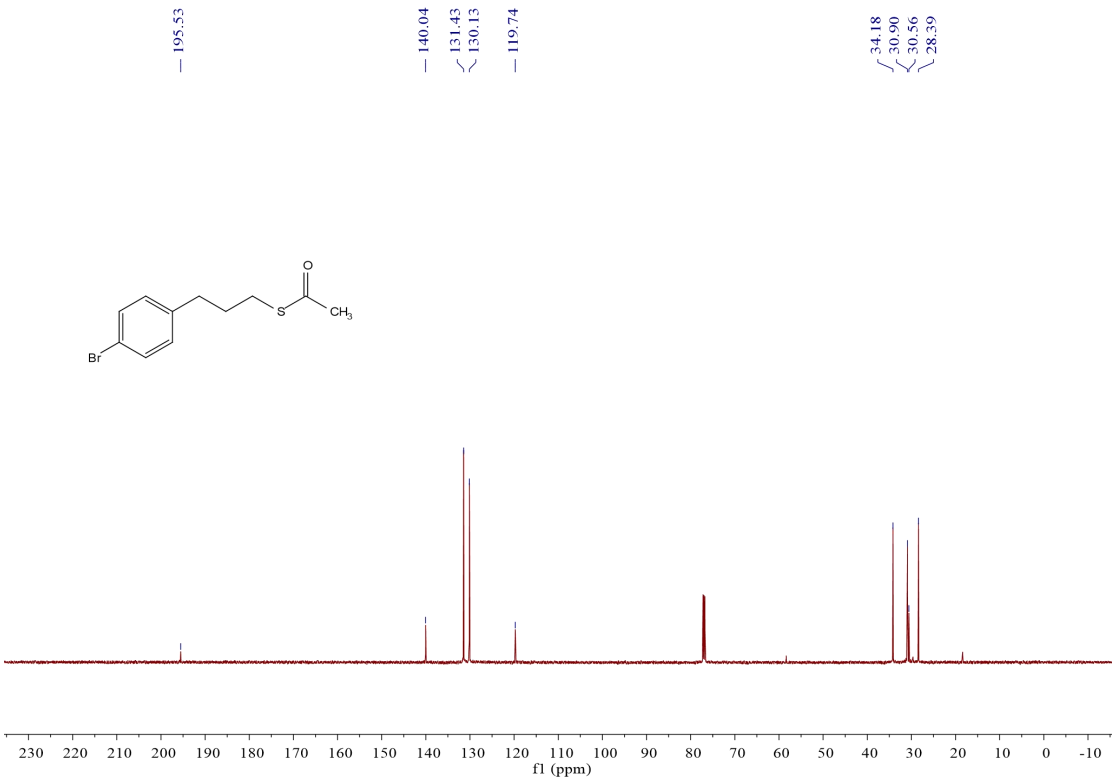
^{1}H NMR of compound 7a (600 MHz, $CDCl_3$)



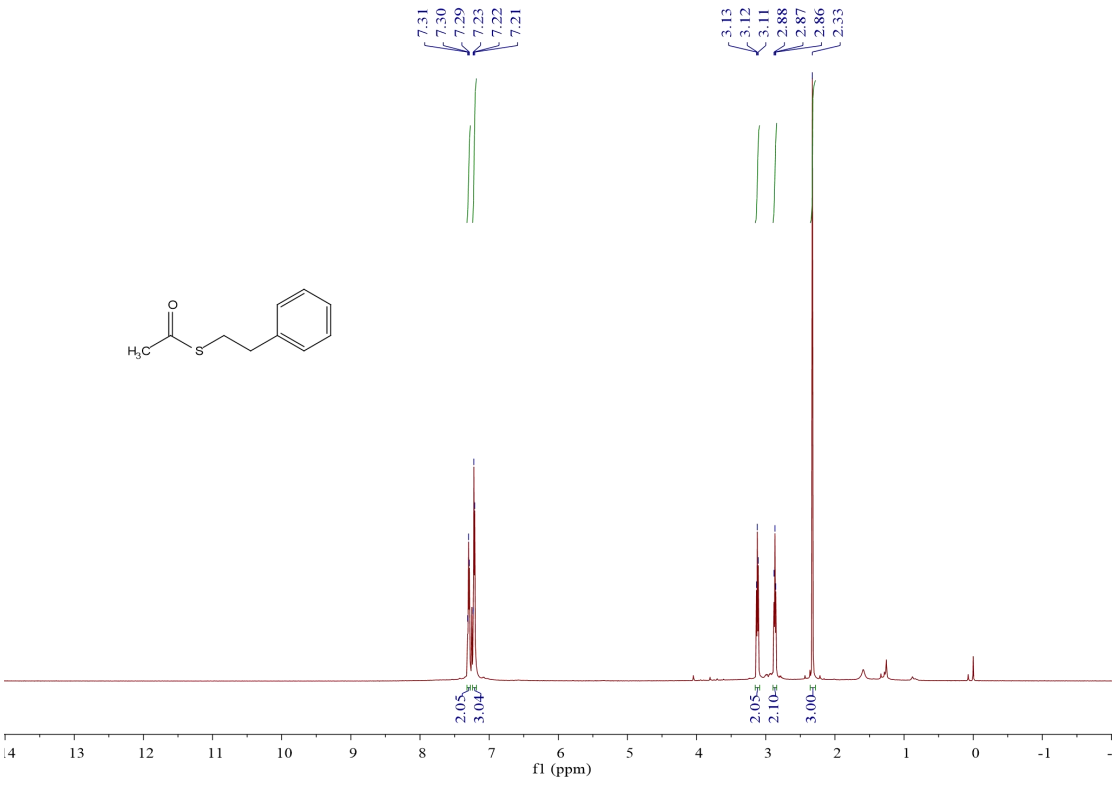
^{13}C {^{1}H} NMR of compound 7a (151 MHz, $CDCl_3$)



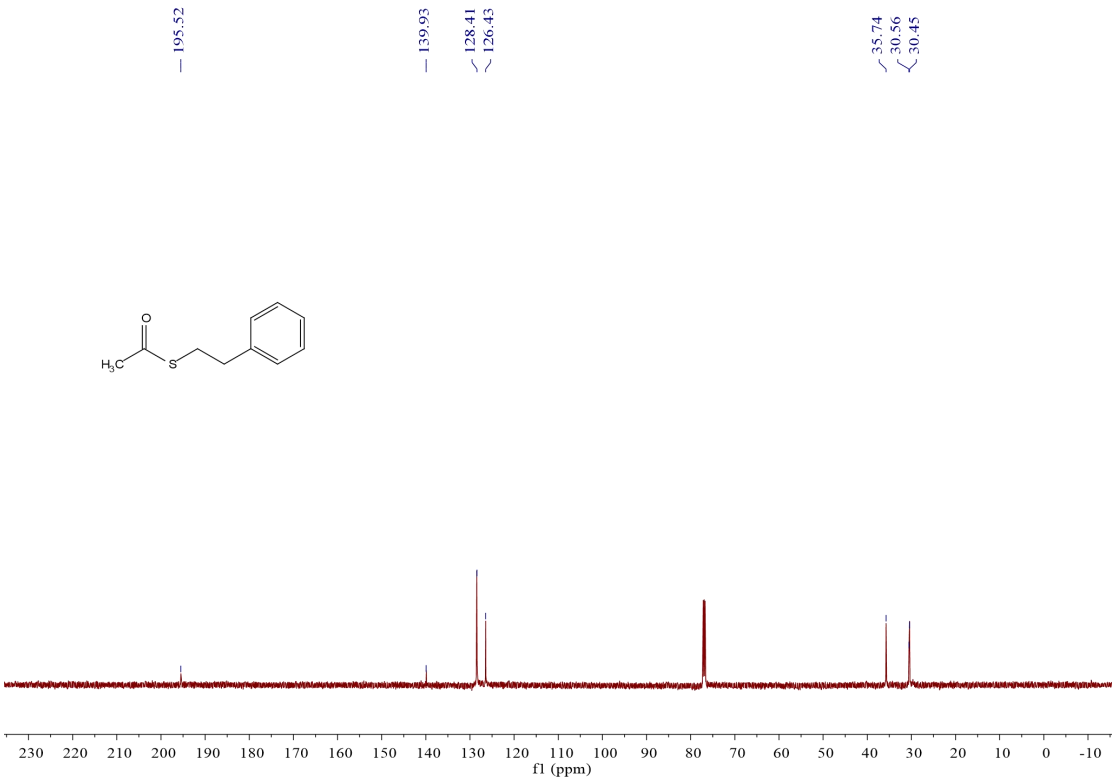
^{1}H NMR of compound 7b (600 MHz, $CDCl_3$)



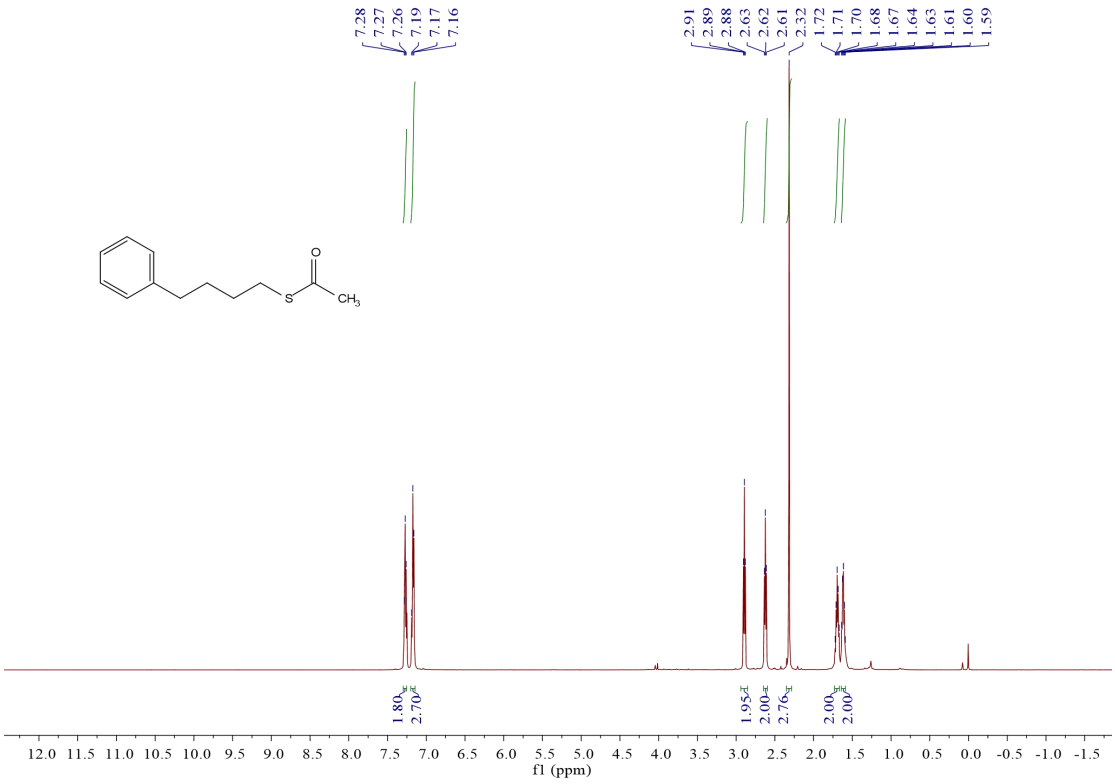
^{13}C {^{1}H} NMR of compound 7b (151 MHz, $CDCl_3$)



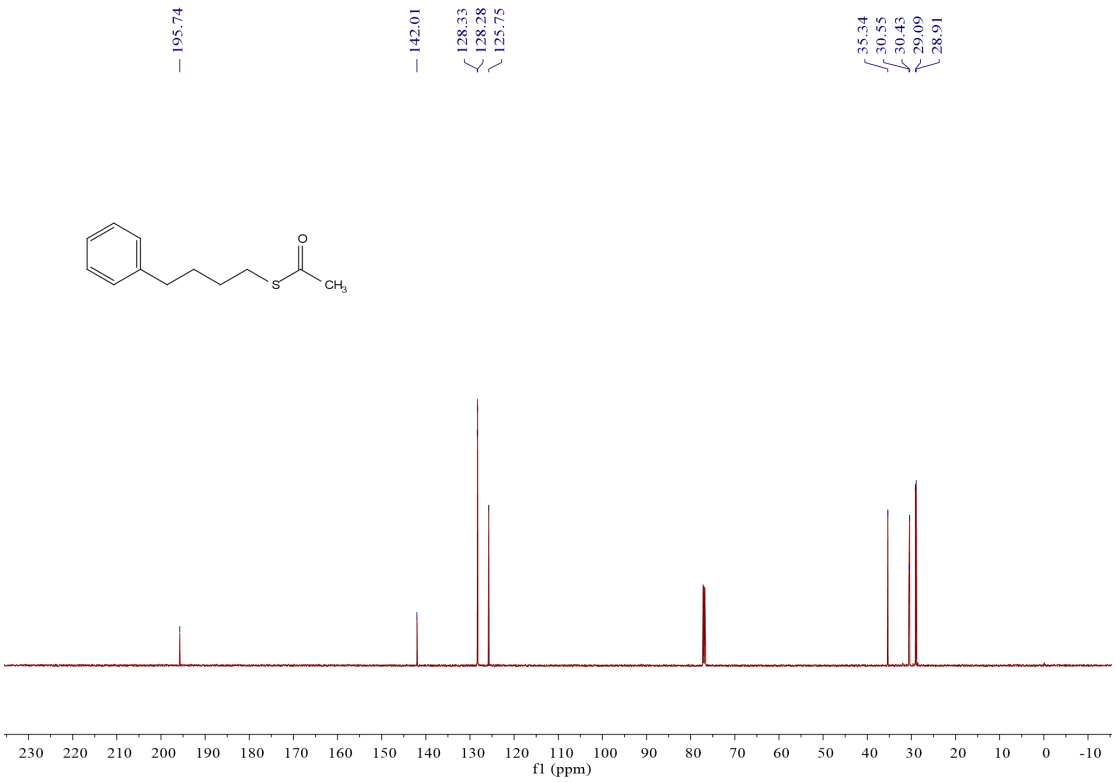
^{1}H NMR of compound 7c (600 MHz, $CDCl_3$)



^{13}C {^{1}H} NMR of compound 7c (151 MHz, $CDCl_3$)



^{1}H NMR of compound 7d (600 MHz, $CDCl_3$)



^{13}C {^{1}H} NMR of compound 7d (151 MHz, $CDCl_3$)