Supporting Information

Electrochemical oxidative radical oxysulfuration of styrene derivatives with thiols and nucleophilic oxygen sources

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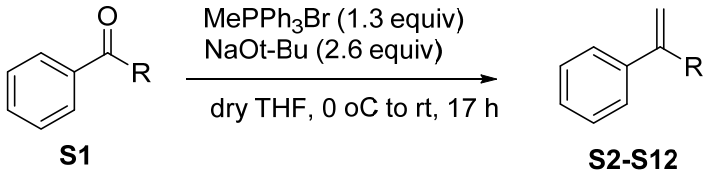
1. General information

All commercial reagents were used without additional purification unless otherwise specified. Solvents were purified and dried according to standard methods prior to use. All reactions were carried out under a nitrogen atmosphere with dry, freshly distilled solvents under anhydrous conditions, unless otherwise noted. All experiments were monitored by thin layer chromatography (TLC) using UV light as visualizing agent. TLC was performed on pre-coated silica gel plated. Column chromatography was performed using silica gel 60 (300-400 mesh).

^{1}H NMR (400 MHz), ^{13}C NMR (101 MHz) were measured on a Bruker AVANCE III-400 spectrometer. Chemical shifts are reported in ppm (δ) relative to internal tetramethylsilane (TMS, δ 0.0 ppm) or with the solvent reference relative to TMS employed as the internal standard. Data are reported as follows: chemical shift (multiplicity [singlet (s), doublet (d), triplet (t), quartet (q), broad (br) and multiplet (m)], coupling constants [Hz], integration). Melting points are uncorrected. Values of optical rotation were measured on Rudolph Automatic Polarimeter A21101 at the wavelength of the sodium D-line (589 nm). Infrared spectra were obtained on agilent Cary630. HRMS were recorded on a Bruker miccOTOF-Q111.

2. General procedure and Characterization data of styrene.

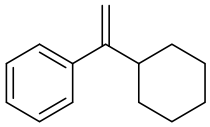
2.1. General procedures for the synthesis of styrene



An oven-dried 200 mL round-bottom-flask equipped with a magnetic stir bar was charged with $MePPh_3Br$ (1.3 equiv, 36.5 mmol). The flask was sealed with a rubber septum and connected to a Schlenk line though a needle. The flask was then evacuated and backfilled with argon (This sequence was repeated a total of three times). The dry THF (67 mL) was added via syringe. The mixture was the cooled to 0 ^{o}C, and NaO*t*-Bu (2.6 equiv, 73 mmol) was added slowly on 0 ^{o}C. After stirred for 30 min, ketone (**s1**, 1 equiv, 28 mmol) was added slowly. The resulting mixture was warmed to room temperature and stirred for 17 h under argon atmosphere. Then, the solvent was removed in vacuo, and the result solid was dissolved in water (150 mL). The resulting aqueous was extracted with DCM (50 mL × 3). The combined organic phase was dried over sodium sulfate. The solvent was removed in vacuo and the residue was purified by flash chromatography to afford the product styrene (**s2**).

2.2 Characterization data of styrene **S2- S12**

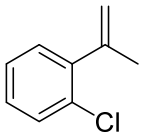
S2



(1-cyclohexylvinyl)benzene

Colorless oil, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.21 (m, 5H), 5.13 (s, 1H), 5.01 – 4.98 (m, 1H), 2.41 (m, 1H), 1.88 – 1.66 (m, 5H), 1.39 – 1.09 (m, 5H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.0, 143.0, 128.1, 127.0, 126.6, 110.3, 42.6, 32.7, 26.9, 26.5.

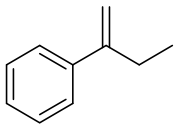
S3



1-chloro-2-(prop-1-en-2-yl)benzene

Colorless oil, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.32 (m, 1H), 7.24 – 7.14 (m, 3H), 5.25 – 5.21 (m, 1H), 4.98 – 4.95 (m, 1H), 2.11 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.4, 142.8, 131.8, 129.8, 129.6, 128.2, 126.6, 116.2, 23.4.

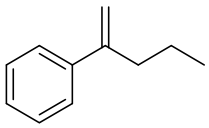
S4



but-1-en-2-ylbenzene

Colorless oil, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.17 (m, 5H), 5.31 – 5.25 (m, 1H), 5.08 – 5.03 (m, 1H), 2.56 – 2.45 (m, 2H), 1.12 – 1.08 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.1, 141.6, 128.3, 127.3, 126.1, 111.0, 28.1, 13.0.

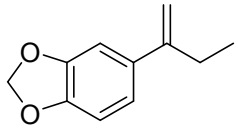
S5



pent-1-en-2-ylbenzene

Colorless oil, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.18 (m, 5H), 5.30 – 5.22 (m, 1H), 5.07 – 5.03 (m, 1H), 2.51 – 2.44 (m, 2H), 1.52 – 1.42 (m, 2H), 0.94 – 0.90 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.5, 141.5, 128.3, 127.3, 126.2, 112.2, 37.5, 21.4, 13.8.

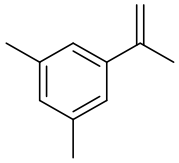
S6



5-(but-1-en-2-yl)benzo[d][1,3]dioxole

Colorless oil, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 6.70 (m, 3H), 5.93 (s, 2H), 5.17 (s, 1H), 4.99 – 4.95 (m, 1H), 2.45 (q, *J* = 7.4 Hz, 2H), 1.10 – 1.06 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.5, 147.6, 146.8, 135.8, 119.4, 110.1, 108.0, 106.7, 101.0, 28.3, 13.0.

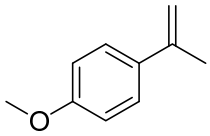
S7



1,3-dimethyl-5-(prop-1-en-2-yl)benzene

Colorless oil, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.08 (s, 2H), 6.91 (s, 1H), 5.33 (s, 1H), 5.04 (s, 1H), 2.31 (s, 6H), 2.13 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.6, 141.4, 137.7, 129.1, 123.5, 112.1, 22.0, 21.4.

S8



1-methoxy-4-(prop-1-en-2-yl)benzene

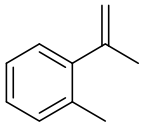
Colorless oil, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.38 (m, 2H), 6.88 – 6.83 (m, 2H), 5.29 – 5.27 (m, 1H), 5.00 – 4.97 (m, 1H), 3.80 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.1, 142.6, 133.8, 126.6, 113.6, 110.7, 55.3, 21.9.

S9

1-bromo-2-(prop-1-en-2-yl)benzene

Colorless oil, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 8.0 Hz, 1H), 7.27 – 7.16 (m, 2H), 7.12 – 7.06 (m, 1H), 5.23 – 5.21 (m, 1H), 4.94 – 4.92 (m, 1H), 2.09 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.8, 144.9, 132.8, 129.8, 128.4, 127.3, 121.6, 116.0, 23.6.

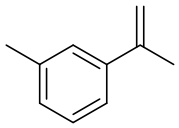
S10



1-methyl-2-(prop-1-en-2-yl)benzene

Colorless oil, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 6.98 (m, 4H), 5.18 (s, 1H), 4.83 (s, 1H), 2.31 (s, 3H), 2.03 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.9, 143.9, 134.5, 130.1, 127.9, 126.8, 125.6, 114.7, 24.4, 19.8.

S11

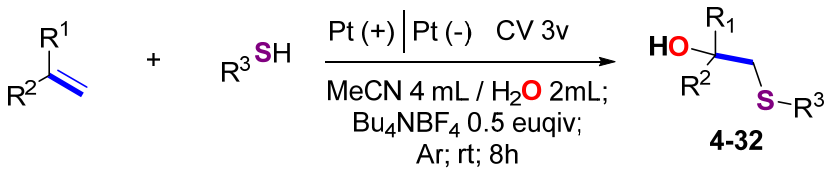


1-methyl-3-(prop-1-en-2-yl)benzene

Colorless oil, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 – 7.17 (m, 3H), 7.11 – 7.04 (m, 1H), 5.34 (dd, *J* = 1.5, 0.7 Hz, 1H), 5.08 – 5.03 (m, 1H), 2.35 (s, 3H), 2.13 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.5, 141.3, 137.8, 128.2, 128.2, 126.3, 122.7, 112.3, 22.0, 21.6.

3. General procedure and Characterization data of the hydrosulfu-ration reactions.

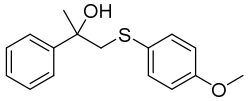
3.1 General procedures for hydrosulfuration reaction.



In an oven-dried undivided three-necked bottle (10 mL) equipped with a stir bar and Bu_4NBF_4 (0.1 mmol). The bottle was equipped with platinum electrodes (10× 10× 1 mm) as both the anode and cathode and was then charged with argon. Alkene (0.2 mmol) and a solution of thiophenol (0.8 mmol dissolved in 2 mL MeCN) was injected into the bottle by syringe. Then, 2 mL MeCN and 2 mL H_2O was added into bottle by syringe. The reaction mixture was stirred and electrolyzed at a constant voltage of 3 V (The dual display potentiostat was operating in constant voltage mode) under room temperature for 8 h. When the reaction was finished, the solution was diluted by EtOH/EA (1:1) 40 mL, and the combined organic solvent and water was removed with a rotary evaporator. The pure product was obtained by flash column chromatography on silica gel (PE: EA= 20:1).

3.2 Characterization data of product **4- 32**

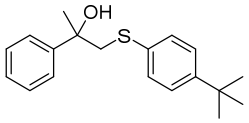
4



1-((4-methoxyphenyl)thio)-2-phenylpropan-2-ol

colorless oil, 45mg (83% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.37 (m, 2H), 7.34 – 7.15 (m, 5H), 6.80 – 6.73 (m, 2H), 3.76 (s, 3H), 3.48 – 3.23 (m, 2H), 2.98 (s, 1H), 1.58 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.0, 146.3, 133.4, 128.2, 127.0, 126.8, 124.9, 114.6, 74.0, 55.4, 51.6, 29.5. HRMS (TOF MS ESI): calcd for $C_{16}H_{18}NaO_2S^+$ $[M+Na]^+$ 297.0920, found 297.0922. IR (cm^{-1}): 3455, 2928, 1592, 1493, 1444, 1239, 1172, 1027, 824, 766, 699.

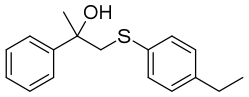
5



1-((4-(tert-butyl)phenyl)thio)-2-phenylpropan-2-ol

colorless oil, 49mg (81% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.41 (m, 2H), 7.35 – 7.28 (m, 2H), 7.27 – 7.20 (m, 3H), 7.03 (d, *J* = 7.9 Hz, 2H), 3.51 – 3.28 (m, 2H), 2.93 (s, 1H), 2.29 (s, 3H), 1.59 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.3, 136.6, 132.8, 130.7, 129.8, 128.3, 127.1, 124.9, 74.0, 50.3, 29.4, 21.0. HRMS (TOF MS ESI): calcd for $C_{19}H_{25}OSNa^+$ $[M+Na]^+$ 323.1440, found 323.1448. IR (cm^{-1}): 3453, 2974, 2865, 1493, 1446, 1374, 1064, 942, 805, 699, 580.

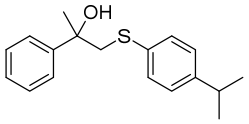
6



1-((4-ethylphenyl)thio)-2-phenylpropan-2-ol

colorless oil, 27mg (50% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.41 (m, 2H), 7.35 – 7.20 (m, 5H), 7.09 – 7.04 (m, 2H), 3.53 – 3.30 (m, 2H), 2.85 (s, 1H), 2.59 (q, *J* = 7.6 Hz, 2H), 1.60 (s, 3H), 1.20 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.3, 143.0, 133.0, 130.7, 128.6, 128.3, 127.1, 124.8, 74.0, 50.3, 29.4, 28.4, 15.5. HRMS (TOF MS ESI): calcd for $C_{17}H_{20}NaOS^+$ $[M+Na]^+$ 295.1127, found 295.1125. IR (cm^{-1}): 3442, 2965, 2928, 1493, 1446, 1374, 1060, 941, 822, 764, 697, 580.

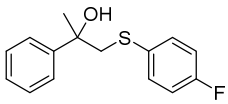
7



1-((4-isopropylphenyl)thio)-2-phenylpropan-2-ol

colorless oil, 37mg (65% yield), ^{1}H NMR (400 MHz, Chloroform-d) δ 7.45 – 7.40 (m, 2H), 7.33 – 7.19 (m, 5H), 7.11 – 7.06 (m, 2H), 3.54 – 3.29 (m, 2H), 2.95 (s, 1H), 2.90 – 2.78 (m, 1H), 1.60 (s, 3H), 1.21 (d, J = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.6, 146.3, 133.1, 130.7, 128.3, 127.2, 127.1, 124.9, 74.0, 50.2, 33.7, 29.5, 23.9. HRMS (TOF MS ESI): calcd for $C_{18}H_{22}NaOS^+$ $[M+Na]^+$ 309.1284, found 309.1285. IR (cm^{-1}): 3450, 3025, 2960, 2928, 2868, 1493, 1446, 1374, 1267, 1051, 1014, 941, 822, 764, 699, 580.

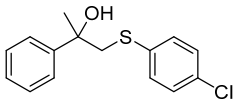
8



1-((4-fluorophenyl)thio)-2-phenylpropan-2-ol

colorless oil, 33mg (63% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.39 (m, 2H), 7.33 – 7.20 (m, 5H), 6.95 – 6.86 (m, 2H), 3.51 – 3.26 (m, 2H), 2.86 (s, 1H), 1.60 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.9 (d, *J* = 246.8 Hz), 146.0, 132.9 (d, *J* = 8.1 Hz), 131.4 (d, *J* = 3.3 Hz), 128.3, 127.1, 124.8, 116.0 (d, *J* = 21.9 Hz), 74.0 , 50.8, 29.4. HRMS (TOF MS ESI): calcd for $C_{15}H_{15}FNaOS^{+}$ $[M+Na]^{+}$ 285.0720, found 285.0718. IR (cm^{-1}): 3450, 2976, 1590, 1489, 1446, 1374, 1223, 1157, 1088, 941, 824, 764, 699, 628.

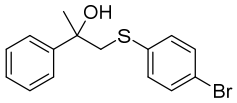
9



1-((4-chlorophenyl)thio)-2-phenylpropan-2-ol

colorless oil, 48mg (87% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.40 (m, 2H), 7.35 – 7.29 (m, 2H), 7.28 – 7.15 (m, 5H), 3.52 – 3.29 (m, 2H), 2.79 (s, 1H), 1.62 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.0, 135.1, 132.4, 131.3, 129.0, 128.3, 127.2, 124.8, 74.0, 49.8, 29.4. HRMS (TOF MS ESI): calcd for $C_{15}H_{15}ClNaOS^{+}$ $[M+Na]^{+}$ 301.0424, found 301.0423. IR (cm^{-1}): 3442, 2976, 1474, 1446, 1331, 1178, 1094, 1010, 939, 813, 764, 699.

10



1-((4-bromophenyl)thio)-2-phenylpropan-2-ol

colorless oil, 46mg (72% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.40 (m, 2H), 7.35 – 7.21 (m, 5H), 7.19 – 7.12 (m, 2H), 3.51 – 3.29 (m, 2H), 2.66 (s, 1H), 1.62 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.9, 135.8, 131.9, 131.5, 128.4, 127.2, 124.8, 120.3, 74.0, 49.6, 29.4. HRMS (TOF MS ESI): calcd for $C_{15}H_{15}BrNaOS^{+}$ $[M+Na]^{+}$ 344.9919, found 344.9914. IR (cm^{-1}): 3444, 2974, 2926, 1720, 1472, 1446, 1374, 1239, 1178, 1088, 1006, 939, 807, 764, 697, 582.

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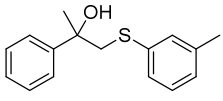
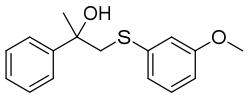


2-phenyl-1-(m-tolylthio)propan-2-ol

colorless oil, 38mg (73% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.20 (m, 5H), 7.16 – 7.08 (m, 3H), 7.00 – 6.94 (m, 1H), 3.53 – 3.32 (m, 2H), 2.91 (s, 1H), 2.27 (s, 3H), 1.61 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.3, 138.8, 136.2, 130.7, 128.8, 128.3, 127.4, 127.1, 124.9, 74.0, 49.6, 29.4, 21.3. HRMS (TOF MS ESI): calcd for $C_{16}H_{18}NaOS^{+}$ $[M+Na]^{+}$ 281.0971, found 281.0969. IR (cm^{-1}): 3450, 2974, 1592, 1474, 1446, 1374, 1333, 1066, 941, 855, 766, 699.

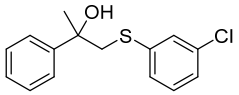
12



1-((3-methoxyphenyl)thio)-2-phenylpropan-2-ol

colorless oil, 28mg (51% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.43 (m, 2H), 7.36 – 7.29 (m, 2H), 7.28 – 7.21 (m, 1H), 7.15 (t, *J* = 8.0 Hz, 1H), 6.95 – 6.85 (m, 2H), 6.74 – 6.68 (m, 1H), 3.76 (s, 3H), 3.55 – 3.33 (m, 2H), 2.84 (s, 1H), 1.62 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.8, 146.2, 137.8, 129.8, 128.3, 127.1, 124.8, 122.0, 115.2, 112.2, 74.0, 55.3, 49.3, 29.4. HRMS (TOF MS ESI): calcd for $C_{16}H_{18}NaO_2S^+$ $[M+Na]^+$ 297.0920, found 297.0922. IR (cm^{-1}): 3488, 2932, 2835, 1588, 1478, 1274, 1282, 1228, 1180, 1038, 941, 859, 766, 699.

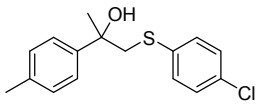
13



1-((3-chlorophenyl)thio)-2-phenylpropan-2-ol

colorless oil, 47mg (85% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.40 (m, 2H), 7.35 – 7.29 (m, 2H), 7.27 – 7.08 (m, 5H), 3.53 – 3.30 (m, 2H), 2.68 (s, 1H), 1.63 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.9, 138.6, 134.6, 129.9, 129.3, 128.3, 127.7, 127.3, 126.5, 124.8, 74.0, 49.2, 29.4. HRMS (TOF MS ESI): calcd for $C_{15}H_{15}ClNaOS^+$ $[M+Na]^+$ 301.0424, found 301.0422. IR (cm^{-1}): 3446, 3058, 2974, 2926,1577, 1461, 1400, 1374, 1329, 1068, 941, 870, 773, 697, 678, 582.

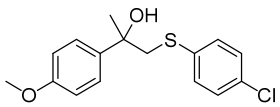
14



1-((4-chlorophenyl)thio)-2-(p-tolyl)propan-2-ol

colorless oil, 41mg (70% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.28 (m, 2H), 7.24 – 7.19 (m, 2H), 7.19 – 7.14 (m, 2H), 7.14 – 7.09 (m, 2H), 3.51 – 3.26 (m, 2H), 2.76 (s, 1H), 2.32 (s, 3H), 1.60 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.0, 136.9, 135.1, 132.3, 131.3, 129.0, 129.0, 124.7, 73.9, 49.8, 29.4, 21.0. HRMS (TOF MS ESI): calcd for $C_{16}H_{17}ClNaOS^+$ $[M+Na]^+$ 315.0581, found 315.0580. IR (cm^{-1}): 3463, 2976, 2924, 1735, 1476, 1372, 1239, 1094, 1042, 1012, 937, 814, 721, 576.

15

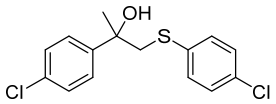


1-((4-chlorophenyl)thio)-2-(4-methoxyphenyl)propan-2-ol

colorless oil, 51mg (82% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.30 (m, 2H), 7.26 – 7.14 (m, 4H), 6.86 – 6.81 (m, 2H), 3.79 (s, 3H), 3.50 – 3.26 (m, 2H), 2.74 (s, 1H), 1.60 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.7, 138.1, 135.1, 132.3, 131.3, 129.0, 126.1, 113.6, 73.8, 55.3, 49.9, 29.4. HRMS (TOF MS ESI): calcd for $C_{16}H_{17}ClNaO_2S^+$ $[M+Na]^+$ 331.0530, found 331.0532. IR (cm^{-1}): 3461, 2930, 2835, 1608, 1510, 1474, 1398, 1299, 1247, 1177, 1094, 1031, 941, 811, 744, 576.

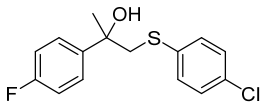
16



2-(4-chlorophenyl)-1-((4-chlorophenyl)thio)propan-2-ol

colorless oil, 46mg (74% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.32 (m, 2H), 7.28 – 7.24 (m, 2H), 7.24 – 7.16 (m, 4H), 3.47 – 3.26 (m, 2H), 2.80 (s, 1H), 1.58 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.5, 134.6, 133.1, 132.7, 131.5, 129.1, 128.4, 126.4, 73.8, 49.8, 29.4. HRMS (TOF MS ESI): calcd for $C_{15}H_{14}Cl_2NaOS^+$ $[M+Na]^+$ 335.0035, found 335.0033. IR (cm^{-1}): 3446, 2976, 2928, 1720, 1476, 1388, 1331, 1239, 1176, 1094, 1012, 937, 814, 755, 568.

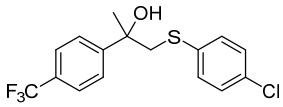
17



1-((4-chlorophenyl)thio)-2-(4-fluorophenyl)propan-2-ol

colorless oil, 49mg (83% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.35 (m, 2H), 7.26 – 7.16 (m, 4H), 7.02 – 6.94 (m, 2H), 3.47 – 3.26 (m, 2H), 2.82 (s, 1H), 1.59 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.9 (d, *J* = 245.8 Hz), 141.7 (d, *J* = 3.1 Hz), 134.8, 132.6, 131.4, 129.1, 126.7 (d, *J* = 8.1 Hz), 115.1 (d, *J* = 21.3 Hz), 73.8, 49.9, 29.5. HRMS (TOF MS ESI): calcd for $C_{15}H_{14}ClFNaOS^+$ $[M+Na]^+$ 319.0330, found 319.0328. IR (cm^{-1}): 3446, 2976, 2928, 1601, 1508, 1476, 1388, 1333, 1224, 1161, 1094, 1012, 943, 835, 813, 744, 662, 568.

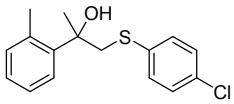
18



1-((4-chlorophenyl)thio)-2-(4-(trifluoromethyl)phenyl)propan-2-ol

colorless oil, 54mg (78% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 – 7.48 (m, 4H), 7.21 – 7.13 (m, 4H), 3.52 – 3.28 (m, 2H), 2.94 (s, 1H), 1.61 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.9 – 149.8 (m), 134.3, 132.9, 131.8,129.4 (q, *J* = 32.32 Hz), 129.1, 125.4, 125.2 (q, *J* = 4.04 Hz), 124.1 (q, *J* = 272.7 Hz), 74.0, 49.7, 29.4. HRMS (TOF MS ESI): calcd for $C_{16}H_{14}ClF_3NaOS^+$ $[M+Na]^+$ 369.0298, found 369.0299. IR (cm^{-1}): 3446, 2980, 2932, 1619, 1476, 1409, 1323, 1163, 1111, 1068, 1012, 941, 814, 721, 613.

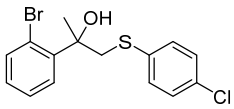
19



1-((4-chlorophenyl)thio)-2-(o-tolyl)propan-2-ol

colorless oil, 24mg (41% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.43 (m, 1H), 7.26 – 7.22 (m, 2H), 7.21 – 7.13 (m, 4H), 7.11 – 7.07 (m, 1H), 3.74 – 3.31 (m , 2H), 2.80 (s, 1H), 2.49 (s, 3H), 1.68 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.9, 135.4, 135.0, 132.8, 132.5, 131.6, 129.0, 127.6, 126.1, 125.9, 75.2, 48.4, 28.5, 22.4. HRMS (TOF MS ESI): calcd for $C_{16}H_{17}ClNaOS^{+}$ $[M+Na]^{+}$ 315.0581, found 315.0580. IR (cm^{-1}): 3440, 2973, 2928, 1474, 1374, 1288, 1094, 1010, 932, 814, 725, 593, 544.

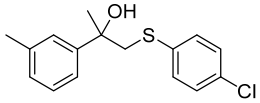
20



2-(2-bromophenyl)-1-((4-chlorophenyl)thio)propan-2-ol

colorless oil, 43mg (61% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.39 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.32 – 7.25 (m, 1H), 7.18 – 7.08 (m, 4H), 7.04 (m, 1H), 4.16 – 3.43 (m, 2H), 3.30 (s, 1H), 1.78 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.6, 134.9, 133.7, 132.6, 132.1, 129.0, 128.8, 128.4, 127.5, 120.1, 74.8, 45.9, 26.9. HRMS (TOF MS ESI): calcd for $C_{15}H_{14}BrClNaOS^{+}$ $[M+Na]^{+}$ 378.9529, found 378.9530. IR (cm^{-1}): 3453, 2973, 2928, 1560, 1474, 1422, 1374, 1333, 1236, 1269, 1176, 1094, 1012, 937, 814, 755, 587.

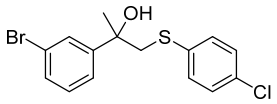
21



1-((4-chlorophenyl)thio)-2-(m-tolyl)propan-2-ol

colorless oil, 47mg (81% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.22 (s, 1H), 7.21 – 7.18 (m, 4H), 7.18 – 7.13 (m, 2H), 7.04 (m, 1H), 3.50 – 3.26 (m, 2H), 2.81 (s, 1H), 2.32 (s, 3H), 1.59 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.9, 137.9, 135.1, 132.4, 131.4, 129.0, 128.3, 127.9, 125.6, 121.9, 74.0, 49.8, 29.4, 21.6. HRMS (TOF MS ESI): calcd for $C_{16}H_{17}ClNaOS^{+}$ $[M+Na]^{+}$ 315.0581, found 315.0581. IR (cm^{-1}): 3446, 2974, 2924, 1605, 1474, 1388, 1329, 1239, 1164, 1094, 1010, 943, 813, 787, 705, 619, 542.

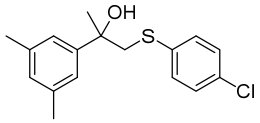
22



2-(3-bromophenyl)-1-((4-chlorophenyl)thio)propan-2-ol

colorless oil, 53mg (75% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (t, *J* = 1.8 Hz, 1H), 7.36 – 7.28 (m, 2H), 7.26 – 7.11 (m, 5H), 3.48 – 3.23 (m, 2H), 2.89 (s, 1H), 1.58 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.3, 134.4, 132.8, 131.7, 130.2, 129.9, 129.1, 128.3, 123.6, 122.6, 73.8, 49.7, 29.4. HRMS (TOF MS ESI): calcd for $C_{15}H_{14}BrClNaOS^{+}$ $[M+Na]^{+}$ 378.9529, found 378.9531. IR (cm^{-1}): 3446, 3066, 2976, 2926, 1584, 1474, 1415, 1388, 1258, 1176, 1094, 1012, 941, 882, 814, 785, 764, 695.

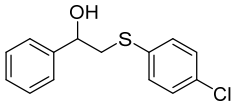
23



1-((4-chlorophenyl)thio)-2-(3,5-dimethylphenyl)propan-2-ol

colorless oil, 54mg (88% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 – 7.13 (m, 4H), 7.00 (s, 2H), 6.86 (s, 1H), 3.50 – 3.25 (m, 2H), 2.79 (s, 1H), 2.28 (s, 6H), 1.58 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.9, 137.8, 135.1, 132.4, 131.5, 128.9, 128.8, 122.7, 74.0, 49.8, 29.5, 21.5. HRMS (TOF MS ESI): calcd for $C_{16}H_{17}ClNaO_2S^+$ $[M+Na]^+$ 329.0737, found 329.0736. IR (cm^{-1}): 3453, 2973, 2917, 1603, 1474, 1374, 1331, 1092, 1010, 943, 848, 811, 705, 542.

24



2-((4-chlorophenyl)thio)-1-phenylethan-1-ol

colorless oil, 22mg (42% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.33 (m, 5H), 7.33 – 7.30 (m, 2H), 7.29 – 7.25 (m, 2H), 4.71 (dd, *J* = 9.2, 3.7 Hz, 1H), 3.29 – 3.07 (m, 1H), 3.14 – 3.06 (m, 1H), 2.75 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.0, 133.6, 132.8, 131.5, 129.3, 128.6, 128.1, 125.9, 71.8, 44.1. HRMS (TOF MS ESI): calcd for $C_{14}H_{13}ClNaOS^+$ $[M+Na]^+$ 287.0268, found 287.0272. IR (cm^{-1}): 3401, 3029, 2920, 1474. 1388, 1193, 1094, 1053, 1010, 915, 811, 744, 699, 615, 652.

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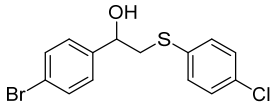
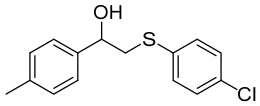


1-(4-bromophenyl)-2-((4-chlorophenyl)thio)ethan-1-ol

colorless oil, 26mg (38% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 – 7.44 (m, 2H), 7.35 – 7.25 (m, 4H), 7.23 – 7.18 (m, 2H), 4.66 (dd, *J* = 9.1, 3.7 Hz, 1H), 3.27 – 3.19 (m, 1H), 3.09 – 2.99 (m, 1H), 2.83 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.9, 133.2, 133.1, 131.8, 131.7, 129.3, 127.6, 121.9, 71.1, 44.2. HRMS (TOF MS ESI): calcd for $C_{14}H_{12}BrClNaOS^+$ $[M+Na]^+$ 364.9373, found 364.9370. IR (cm^{-1}): 3398, 2922, 1895, 1592, 1474, 1402, 1232, 1189, 1084, 1068, 1008, 811, 740.

26

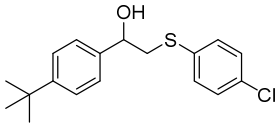


2-((4-chlorophenyl)thio)-1-(p-tolyl)ethan-1-ol

colorless oil, 24mg (44% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.29 (m, 2H), 7.28 – 7.20 (m, 4H), 7.15 (d, *J* = 8.0 Hz, 2H), 4.68 (dd, 1H), 3.30 – 3.19 (m, 1H), 3.15 – 3.05 (m, 1H), 2.67 (s, 1H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.0, 137.9, 133.7, 132.7, 131.4, 129.3, 129.2, 125.8, 71.7. 44.0, 21.2. HRMS (TOF MS ESI): calcd for $C_{15}H_{15}ClNaOS^+$ $[M+Na]^+$

301.0424, found 301.0422. IR (cm^{-1}): 3381, 2920, 1901, 1513, 1474, 1388, 1292, 1178, 1094, 1053, 1010, 811, 731, 703.

27



1-(4-(tert-butyl)phenyl)-2-((4-chlorophenyl)thio)ethan-1-ol

colorless oil, 27mg (42% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.34 (m, 2H), 7.32 – 7.22 (m, 6H), 4.71 (dd, *J* = 9.0, 3.8 Hz, 1H), 3.32 – 3.23 (m, 1H), 3.17 – 3.09 (m, 1H), 2.71 (s, 1H), 1.31 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.2, 139.0, 133.8, 132.6, 131.4, 129.2, 125.6, 125.5, 71.8, 43.8, 34.6, 31.4. HRMS (TOF MS ESI): calcd for $C_{18}H_{21}ClNaOS^+$ $[M+Na]^+$ 343.0894, found 343.0893. IR (cm^{-1}): 3371, 2961, 1476, 1388, 1362, 1269, 1202, 1094, 1055, 1010, 811, 744.

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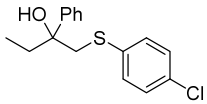

1-((4-chlorophenyl)thio)-2-phenylbutan-2-ol

colorless oil, 43mg (74% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.13 (m, 9H), 3.56 – 3.30 (m, 2H), 2.77 (s, 1H), 2.02 – 1.78 (m, 2H), 0.77 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.1, 135.1, 132.4, 131.4, 129.0, 128.2, 127.0, 125.4, 76.4, 49.0, 34.7, 8.0. HRMS (TOF MS ESI): calcd for $C_{16}H_{17}ClNaOS^+$ $[M+Na]^+$ 315.0581, found 315.0580. IR (cm^{-1}): 3478, 3058, 2969, 2928, 1476, 1388, 1323, 1094, 1012, 973, 813, 759, 699, 609.

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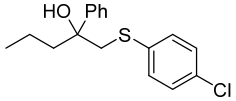
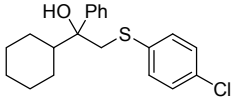


1-((4-chlorophenyl)thio)-2-phenylpentan-2-ol

colorless oil, 44mg (72% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.11 (m, 9H), 3.57 – 3.29 (m, 2H), 2.80 (s, 1H), 1.99 – 1.74 (m, 2H), 1.47 – 0.96 (m, 2H), 0.83 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.5, 135.1, 132.4, 131.4, 129.0, 128.2, 127.0, 125.3, 76.2, 49.3, 44.4, 17.0, 14.3. HRMS (TOF MS ESI): calcd for $C_{17}H_{19}ClNaOS^+$ $[M+Na]^+$ 329.0737, found 329.0739. IR (cm^{-1}): 3481, 3058, 2958, 2932, 2872, 1476, 1446, 1388, 1236, 1094, 1064,1012, 975, 814, 699, 632.

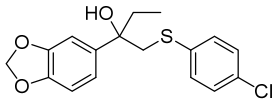
30



2-((4-chlorophenyl)thio)-1-cyclohexyl-1-phenylethan-1-ol

colorless oil, 42mg (60% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.12 (m, 9H), 3.76 – 3.37 (m, 2H), 2.81 (s, 1H), 1.95 – 1.46 (m, 6H), 1.31 – 0.86 (m, 5H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.9, 135.4, 132.4, 131.5, 129.0, 127.9, 126.9, 126.1, 78.0, 48.2, 46.8, 27.5, 27.0, 26.6, 26.5, 26.3. HRMS (TOF MS ESI): calcd for $C_{20}H_{23}ClNaOS^{+}$ $[M+Na]^{+}$ 369.1050, found 369.1049. IR (cm^{-1}): 3504, 2928, 2851, 1476, 1446, 1388, 1323, 1238, 1094, 1070, 1012, 893, 814, 759, 699, 656.

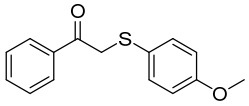
31



2-(benzo[d][1,3]dioxol-5-yl)-1-((4-chlorophenyl)thio)butan-2-ol

white solid, m.p. 63-64°C, 55mg (82% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 – 7.13 (m, 4H), 6.87 – 6.67 (m, 3H), 5.93 – 5.91 (m, 2H), 3.52 – 3.22 (m, 2H), 2.79 (s, 1H), 1.94 – 1.74 (m, 3H), 0.77 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.6, 146.4, 138.2, 134.9, 132.4, 131.6, 128.9, 118.7, 107.8, 106.4, 101.1, 76.3, 49.2, 34.8, 8.0. HRMS (TOF MS ESI): calcd for $C_{17}H_{17}ClNaO_3S^{+}$ $[M+Na]^{+}$ 359.0479, found 359.0480. IR (cm^{-1}): 3532, 2956, 2927, 1489, 1429, 1318, 1236, 1092, 1034, 978, 934, 814, 554.

32

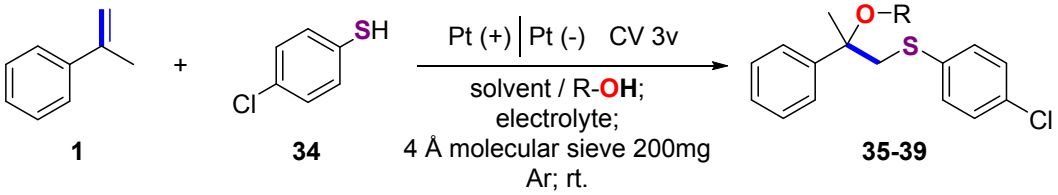


2-((4-methoxyphenyl)thio)-1-phenylethan-1-one

colorless oil, 42mg (81% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 – 7.89 (m, 2H), 7.59 – 7.54 (m, 1H), 7.47 – 7.42 (m, 2H), 7.38 – 7.33 (m, 2H), 6.83 – 6.79 (m, 2H), 4.13 (s, 2H), 3.77 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 194.3, 159.8, 135.5, 134.7, 133.4, 128.7, 128.7, 124.6, 114.7, 55.3, 42.8. HRMS (TOF MS ESI): calcd for $C_{14}H_{11}ClNaOS^{+}$ $[M+Na]^{+}$ 281.0607, found 281.0612. IR (cm^{-1}): 2837, 1675, 1590, 1493, 1275, 1243, 1172, 1027, 826, 688.

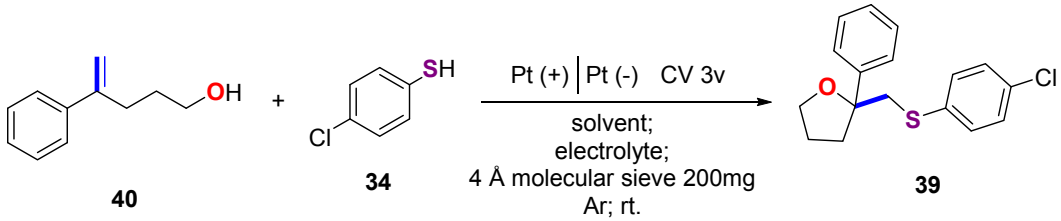
4. General procedure and Characterization data for oxysulfuration reaction of alcohols.

4.1 General procedures for oxysulfuration reaction of alcohols.



Procedure A: In an oven-dried undivided three-necked bottle (10 mL) equipped with a stir bar

and Bu_4NBF_4 (0.1 mmol) and 4 Å molecular sieve (200 mg). The bottle was equipped with platinum electrodes (10× 10× 1 mm) as both the anode and cathode and was then charged with argon. Alkene (0.2 mmol) and a solution of thiophenol (0.8 mmol dissolved in 2 mL MeCN) was injected into the bottle by syringe. Then, 2 mL MeCN and 2 mL alcohol was added into bottle by syringe. The reaction mixture was stirred and electrolyzed at a constant voltage of 3 V (The dual display potentiostat was operating in constant voltage mode) under room temperature for 8 h. When the reaction was finished, the solution was diluted by EA 40 mL, and the combined organic solvent was removed with a rotary evaporator. The pure product was obtained by flash column chromatography on silica gel (PE: EA = 50:1).

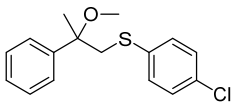


40 **34** **39**

Procedure B: In an oven-dried undivided three-necked bottle (10 mL) equipped with a stir bar and Bu_4NBF_4 (0.1 mmol) and 4 Å molecular sieve (200 mg). The bottle was equipped with platinum electrodes (10× 10× 1 mm) as both the anode and cathode and was then charged with argon. Alkene (0.2 mmol) and a solution of thiophenol (0.8 mmol dissolved in 2 mL MeCN) was injected into the bottle by syringe. Then, 4 mL MeCN was added into bottle by syringe. The reaction mixture was stirred and electrolyzed at a constant voltage of 3 V (The dual display potentiostat was operating in constant voltage mode) under room temperature for 8 h. When the reaction was finished, the solution was diluted by EA 40 mL, and the combined organic solvent was removed with a rotary evaporator. The pure product was obtained by flash column chromatography on silica gel (PE: EA = 50:1).

4.2 Characterization data of product **35- 39**

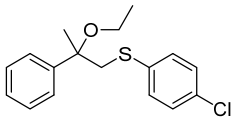
35



(4-chlorophenyl)(2-methoxy-2-phenylpropyl)sulfane

colorless oil, 47mg (80% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.38 (m, 2H), 7.37 – 7.31 (m, 2H), 7.30 – 7.24 (m, 1H), 7.16 (m, 4H), 3.37 – 3.20 (m, 2H), 3.12 (s, 3H), 1.70 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.2, 136.1, 131.7, 130.6, 128.8, 128.4, 127.6, 126.3, 79.0, 50.9, 48.1, 22.2. HRMS (TOF MS ESI): calcd for $C_{16}H_{17}ClNaOS^+$ $[M+Na]^+$ 315.0581, found 315.0584. IR (cm^{-1}): 2980, 2932, 2825, 1474, 1444, 1370, 1210, 1165, 1094, 1072, 1040, 1010, 926, 811, 764, 613, 542.

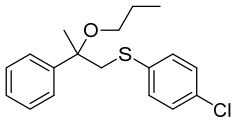
36



(4-chlorophenyl)(2-ethoxy-2-phenylpropyl)sulfane

colorless oil, 46mg (75% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.38 (m, 2H), 7.33 (m, 2H), 7.29 – 7.23 (m, 1H), 7.22 – 7.11 (m, 4H), 3.40 – 3.31 (m, 2H), 3.24 – 3.12 (m, 2H), 1.70 (s, 3H), 1.16 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.0, 136.3, 131.6, 130.6, 128.7, 128.3, 127.5, 126.2, 78.8, 58.4, 48.1, 23.0, 15.7. HRMS (TOF MS ESI): calcd for $C_{17}H_{19}ClNaOS^{+}$ $[M+Na]^{+}$ 329.0737, found 329.0734. IR (cm^{-1}): 2974, 2928, 2876, 1474, 1444, 1388, 1273, 1180, 1094, 1072, 1010, 951, 811, 764, 699, 611, 544.

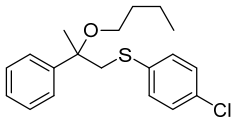
37



(4-chlorophenyl)(2-phenyl-2-propoxypropyl)sulfane

colorless oil, 45mg (70% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.38 (m, 2H), 7.36 – 7.30 (m, 2H), 7.29 – 7.23 (m, 1H), 7.22 – 7.13 (m, 4H), 3.37 – 3.33 (m, 1H), 3.26 – 3.19 (m, 2H), 3.10 – 3.04 (m, 1H), 1.70 (s, 3H), 1.61 – 1.52 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.0, 136.4, 131.5, 130.5, 128.7, 128.3, 127.4, 126.3, 78.5, 64.5, 48.2, 23.4, 22.8, 10.8. HRMS (TOF MS ESI): calcd for $C_{18}H_{21}ClNaOS^{+}$ $[M+Na]^{+}$ 343.0894, found 343.0890. IR (cm^{-1}): 2961, 2930, 2872, 1474,1446, 1388, 1370, 1277, 1094, 1072, 1010, 811, 764, 699, 611, 544.

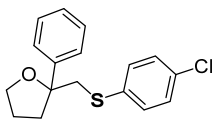
38



(2-butoxy-2-phenylpropyl)(4-chlorophenyl)sulfane

colorless oil, 46mg (69% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.23 (m, 5H), 7.20 – 7.12 (m, 4H), 3.37 – 3.33 (m, 1H), 3.29 – 3.24 (m, 1H), 3.22 – 3.18 (m, 1H), 3.13 – 3.07 (m, 1H), 1.70 (s, 3H), 1.56 – 1.47 (m, 2H), 1.38 – 1.28 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.0, 136.4, 131.5, 130.5, 128.7, 128.3, 127.4, 126.3, 78.5, 62.6, 48.2, 32.4, 22.8, 19.4, 14.0. HRMS (TOF MS ESI): calcd for $C_{19}H_{23}ClNaOS^{+}$ $[M+Na]^{+}$ 357.1050, found 357.1049. IR (cm^{-1}): 2958, 2932, 2868, 1737, 1476, 1370, 1239, 1178, 1094, 1012, 911, 811, 764, 699, 611, 542.

39

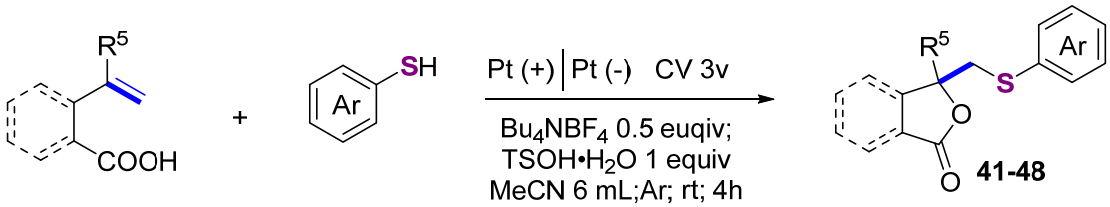


2-(((4-chlorophenyl)thio)methyl)-2-phenyltetrahydrofuran

colorless oil, 31mg (51% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.13 (m, 9H), 4.06 – 3.99 (m, 1H), 3.95 – 3.87 (m, 1H), 3.43 – 3.28 (m, 2H), 2.42 – 2.20 (m, 2H), 2.08 – 1.96 (m, 1H), 1.88 – 1.76 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.4, 136.2, 131.6, 130.5, 128.8, 128.2, 127.1, 125.3, 86.1, 68.3, 46.9, 37.1, 25.9. HRMS (TOF MS ESI): calcd for $C_{17}H_{17}ClNaOS^{+}$ $[M+Na]^{+}$ 327.0581, found 327.0585. IR (cm^{-1}): 1474, 1446, 1388, 1239, 1094, 1049, 1010, 978, 811, 727, 699, 611, 572, 541.

5. General procedure and Characterization data for oxysulfuration reaction of alcohols.

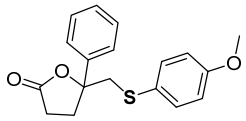
5.1 General procedures for prepare sulfuration lactones.



In an oven-dried undivided three-necked bottle (10 mL) equipped with a stir bar and Bu_4NBF_4 (0.1 mmol), $TSOH{\cdot}H_2O$ (0.2 mmol) and unsaturated carboxylic acids (0.2 mg). The bottle was equipped with platinum electrodes (10× 10× 1 mm) as both the anode and cathode and was then charged with argon. A solution of thiophenol (0.6 mmol dissolved in 2 mL MeCN) was injected into the bottle by syringe. Then, 4 mL MeCN was added into bottle by syringe. The reaction mixture was stirred and electrolyzed at a constant voltage of 3 V (The dual display potentiostat was operating in constant voltage mode) under room temperature for 8 h. When the reaction was finished, the solution was diluted by EA 40 mL, and the combined organic solvent was removed with a rotary evaporator. The pure product was obtained by flash column chromatography on silica gel (PE: EA = 10:1).

5.2 Characterization data of product **41- 48**

41

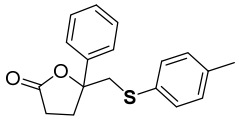


5-(((4-methoxyphenyl)thio)methyl)-5-phenyldihydrofuran-2(3H)-one

colorless oil, 55mg (87% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.33 (m, 4H), 7.33 – 7.27 (m, 3H), 6.82 – 6.77 (m, 2H), 3.77 (s, 3H), 3.41 – 3.32 (m, 2H), 2.78 – 2.67 (m, 2H), 2.55 – 2.43 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.0, 159.3, 142.5, 133.7, 128.6, 128.1, 126.4, 124.8, 114.7, 88.4, 55.4, 49.2, 32.7, 29.0. HRMS (TOF MS ESI): calcd for $C_{18}H_{18}NaO_3S^{+}$ $[M+Na]^{+}$

337.0869, found 337.0867. IR (cm^{-1}): 2939, 2835, 1772, 1590, 1493, 1448, 1284, 1243, 1163, 1105, 1027, 923, 824, 766, 699.

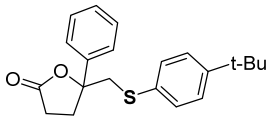
42



5-phenyl-5-((p-tolylthio)methyl)dihydrofuran-2(3H)-one

white solid, m.p. 62-63°C, 39mg (65% yield),^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.26 (m, 5H), 7.24 – 7.22 (m, 2H), 7.06 – 7.04 (m, 2H), 3.48 – 3.33 (m, 2H), 2.75 – 2.64 (m, 2H), 2.52 – 2.41 (m, 2H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.0, 142.5, 137.0, 132.4, 130.8, 129.9, 128.7, 128.2, 124.8, 88.4, 47.9, 32.6, 29.1, 21.1. HRMS (TOF MS ESI): calcd for $C_{18}H_{18}NaO_2S^+$ $[M+Na]^+$ 321.0920, found 321.0917. IR (cm^{-1}): 3021, 2920, 1763, 1491, 1448, 1409, 1299, 1251, 1172, 1046, 1008, 928, 805, 766, 725, 697, 641, 570.

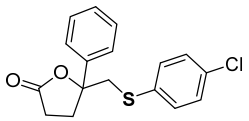
43



5-(((4-(tert-butyl)phenyl)thio)methyl)-5-phenyldihydrofuran-2(3H)-one

colorless oil, 41mg (60% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.25 (m, 8H), 3.49 – 3.38 (m, 2H), 2.80 – 2.65 (m, 2H), 2.57 – 2.43 (m, 2H), 1.29 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.0, 150.1, 142.4, 132.4, 130.4, 128.6, 128.2, 126.2, 124.8, 88.3, 47.7, 34.5, 32.6, 31.3, 29.1. HRMS (TOF MS ESI): calcd for $C_{21}H_{24}NaO_2S^+$ $[M+Na]^+$ 363.1389, found 363.1386. IR (cm^{-1}): 2958, 1774, 1489, 1448, 1396, 1362, 1267, 1159, 1120, 1012, 923, 824, 699, 550.

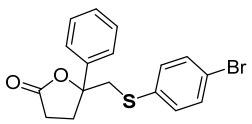
44



5-(((4-chlorophenyl)thio)methyl)-5-phenyldihydrofuran-2(3H)-one

white solid, m.p. 65-66°C, 43mg (67% yield),^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.36 (m, 4H), 7.35 – 7.30 (m, 1H), 7.27 – 7.19 (m, 4H), 3.48 – 3.38 (m, 2H), 2.77 – 2.67 (m, 2H), 2.55 – 2.48 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.7, 142.1, 134.4, 132.9, 131.7, 129.2, 128.7, 128.3, 124.8, 88.1, 47.5, 32.8, 28.9. HRMS (TOF MS ESI): calcd for $C_{17}H_{15}ClNaO_2S^+$ $[M+Na]^+$ 341.0373, found 341.0371. IR (cm^{-1}): 1763, 1474, 1387, 1299, 1251, 1172, 1094, 1012, 930, 723, 695, 572, 542.

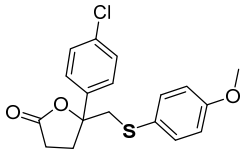
45



5-(((4-bromophenyl)thio)methyl)-5-phenyldihydrofuran-2(3H)-one

colorless oil, 51mg (70% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.29 (m, 7H), 7.20 – 7.15 (m, 2H), 3.48 – 3.38 (m, 2H), 2.79 – 2.64 (m, 2H), 2.59 – 2.47 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.7, 142.1, 135.1, 132.1, 131.8, 128.7, 128.3, 124.8, 120.8, 88.1, 47.3, 32.8, 28.9. HRMS (TOF MS ESI): calcd for $C_{17}H_{15}BrNaO_2S^+$ $[M+Na]^+$ 384.9868, found 384.9867. IR (cm^{-1}): 3340, 2928, 2851, 1771, 1638, 1472, 1327, 1195, 1094, 1049, 988, 923, 800, 755, 695, 652, 585.

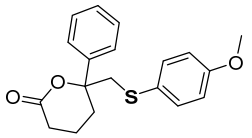
46



5-(4-chlorophenyl)-5-(((4-methoxyphenyl)thio)methyl)dihydrofuran-2(3H)-one

colorless oil, 50mg (72% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29– 7.25 (m, 6H), 6.81 – 6.76 (m, 2H), 3.77 (s, 3H), 3.37 – 3.29 (m, 2H), 2.79 – 2.63 (m, 2H), 2.54 – 2.39 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.7, 159.3, 140.8, 134.0, 133.7, 128.7, 126.4, 126.0, 114.7, 88.0, 55.4, 49.0, 32.7, 28.9. HRMS (TOF MS ESI): calcd for $C_{18}H_{17}ClNaO_3S^+$ $[M+Na]^+$ 371.0479, found 371.0484. IR (cm^{-1}): 2835, 1776, 1592, 1491, 1459, 1400, 1284, 1243, 1159, 1092, 1012, 930, 824, 723, 639.

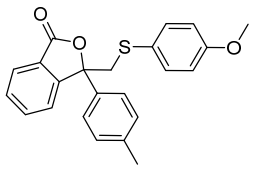
47



6-(((4-methoxyphenyl)thio)methyl)-6-phenyltetrahydro-2H-pyran-2-one

colorless oil, 38mg (58% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.35 (m, 3H), 7.33 – 7.26 (m, 3H), 6.80 – 6.75 (m, 2H), 3.77 (s, 3H), 3.39 – 3.27 (m, 2H), 2.56 – 2.28 (m, 4H), 1.86 – 1.50 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.9, 159.1, 142.0, 133.7, 128.7, 127.9, 126.9, 125.3, 114.6, 87.1, 55.3, 50.2, 30.5, 29.3, 16.3. HRMS (TOF MS ESI): calcd for $C_{19}H_{20}NaO_3S^+$ $[M+Na]^+$ 351.1025, found 351.1021. IR (cm^{-1}): 2954, 2835, 1731, 1590, 1493, 1446, 1284, 1239, 1172, 1090, 1027, 928, 826, 699.

48

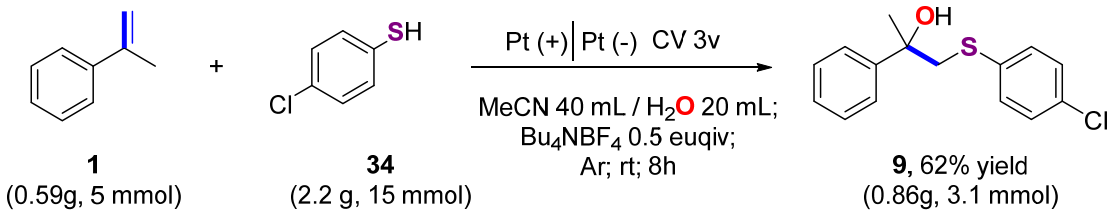


3-(((4-methoxyphenyl)thio)methyl)-3-(p-tolyl)isobenzofuran-1(3H)-one

colorless oil, 50mg (66% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 – 7.90 (m, 1H), 7.53 – 7.47 (m, 2H), 7.41 – 7.34 (m, 3H), 7.15 – 7.13 (m, 2H), 7.10 – 7.05 (m, 2H), 6.71 – 6.66 (m, 2H), 3.77 (s, 2H), 3.75 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.7, 159.3, 150.6, 138.6, 136.3, 134.2, 133.8, 129.4, 129.4, 126.9, 126.5, 125.6, 125.3, 122.8, 114.4, 88.8,

55.3, 47.8, 21.1. HRMS (TOF MS ESI): calcd for $C_{23}H_{20}NaO_3S^+$ $[M+Na]^+$ 399.1025, found 399.1021. IR (cm^{-1}): 2924, 2831, 1756, 1590, 1493, 1463, 1407, 1286, 1241, 1088, 1033, 984, 820, 736, 688, 583, 518.

6. General procedures for gram-scale reaction.

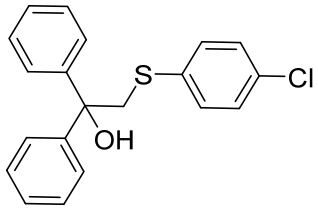


1 (0.59g, 5 mmol) + **34** (2.2 g, 15 mmol) → **9**, 62% yield (0.86g, 3.1 mmol)

In an oven-dried undivided three-necked bottle (100 mL) equipped with a stir bar and Bu_4NBF_4 (2.5 mmol). The bottle was equipped with platinum electrodes (10× 10× 1 mm) as both the anode and cathode and was then charged with argon. Alkene (5 mmol) and a solution of thiophenol (15 mmol dissolved in 20 mL MeCN) was injected into the bottle by syringe. Then, 20 mL MeCN and 20 mL H_2O was added into bottle by syringe. The reaction mixture was stirred and electrolyzed at a constant voltage of 3 V (The dual display potentiostat was operating in constant voltage mode) under room temperature for 8 h. When the reaction was finished, the solution was extracted with EtOAc (3×100 mL). The combined organic layer was dried with Na_2SO_4, filtered. The solvent was removed with a rotary evaporator. The pure product was obtained by flash column chromatography on silica gel (PE: EA= 20:1).

7. Characterization data for control experiment.

50

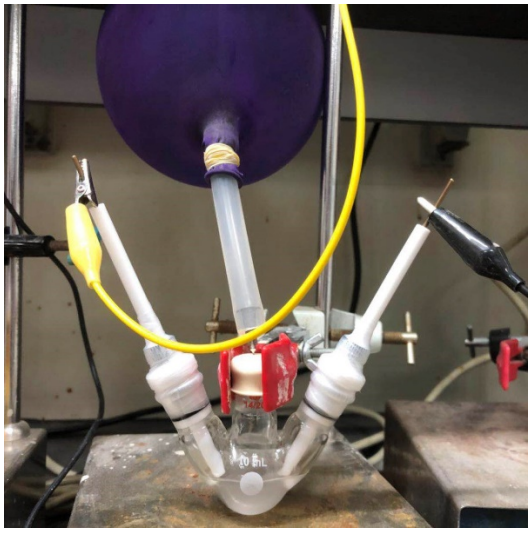


2-((4-chlorophenyl)thio)-1,1-diphenylethan-1-ol

Light yellow oil, 49mg (72%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.40 (m, 4H), 7.35 – 7.16 (m, 10H), 3.84 (s, 2H), 3.45 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.0, 135.0,

132.7, 131.7, 129.1, 128.3, 127.5, 126.1, 49.3.

8. Reaction vessel



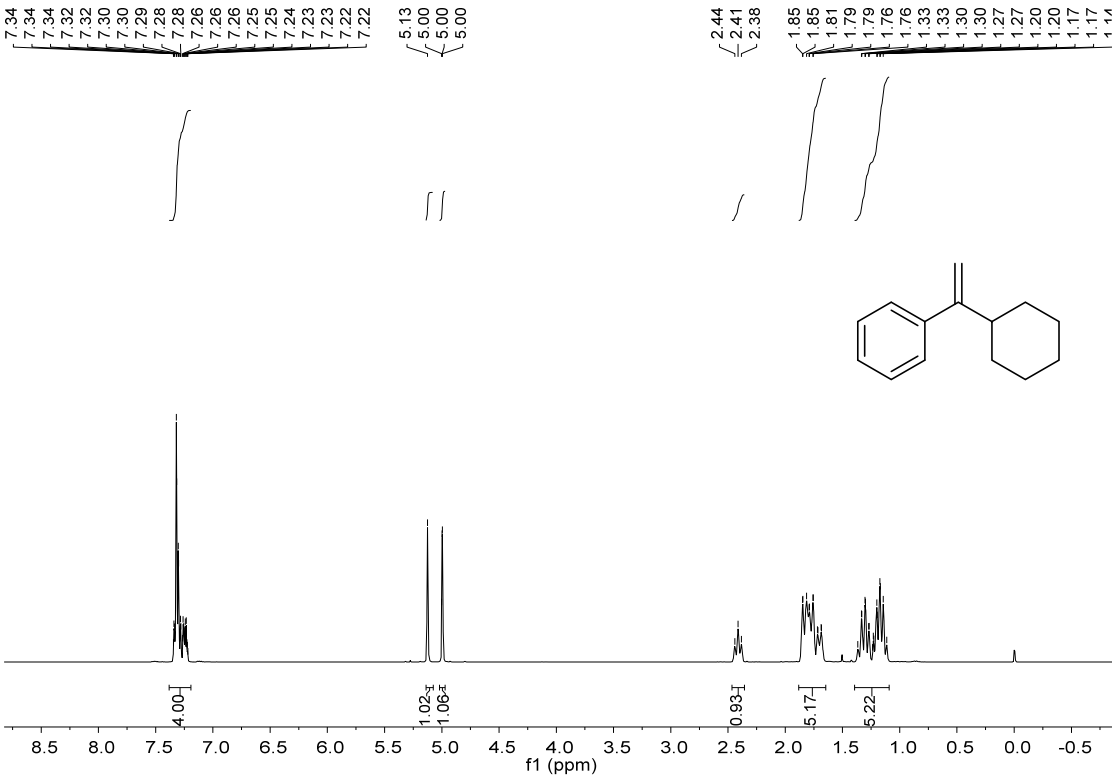
10ml for 0.2mmol scale

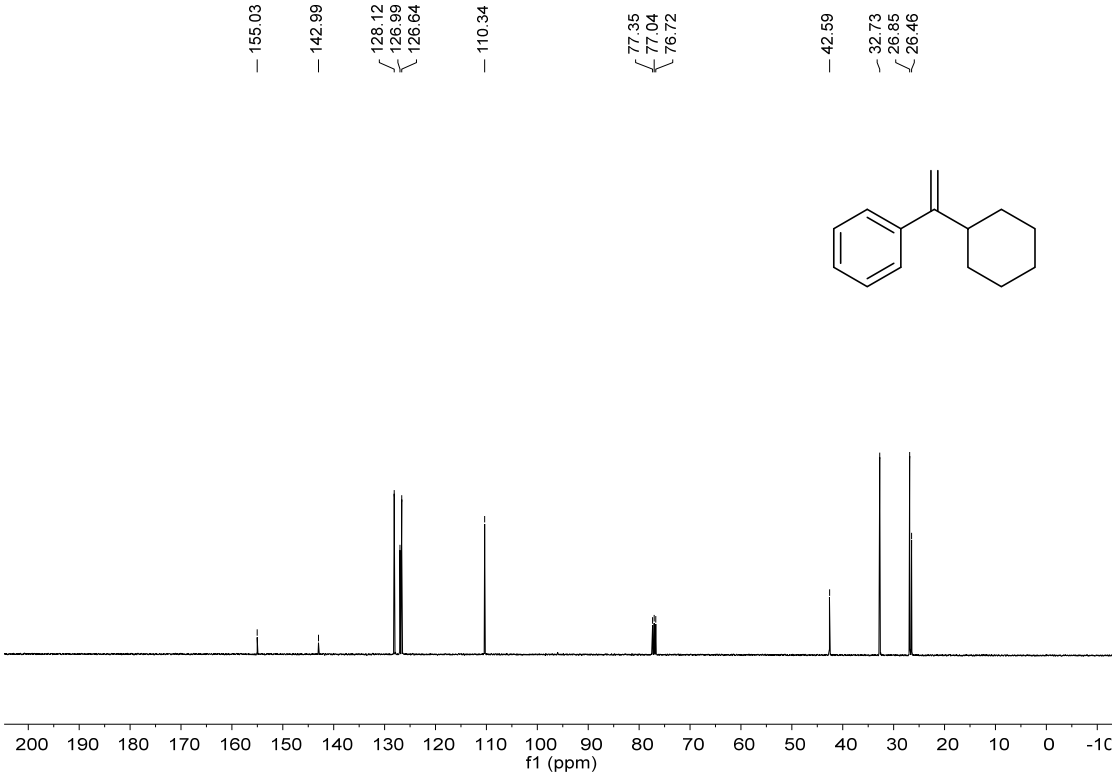
100ml for gram scale

9. NMR spectra

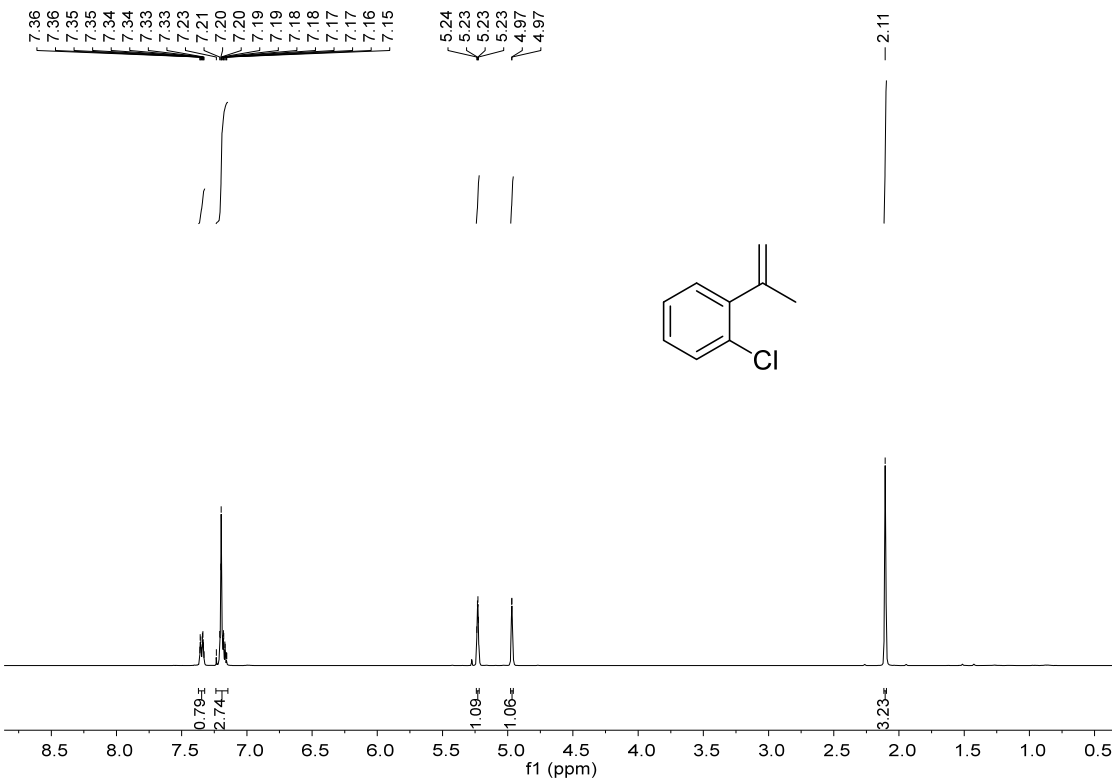
9. NMR spectra for styrenes **S2**- **S12**

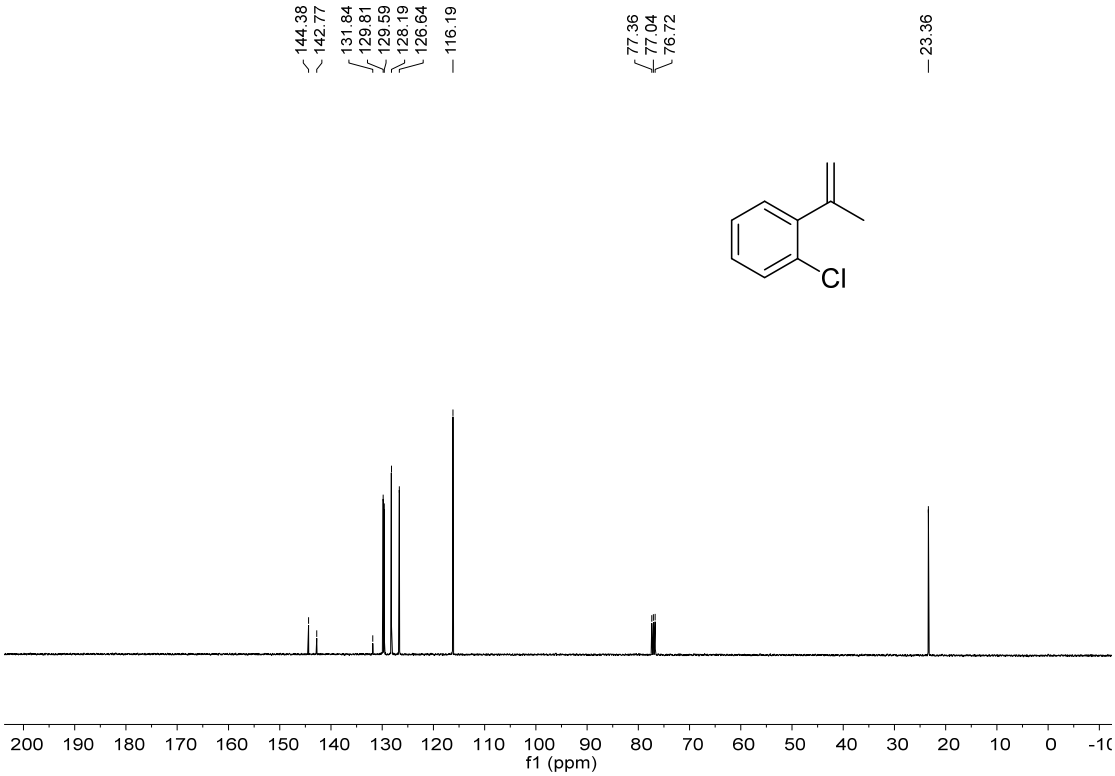
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **S2**



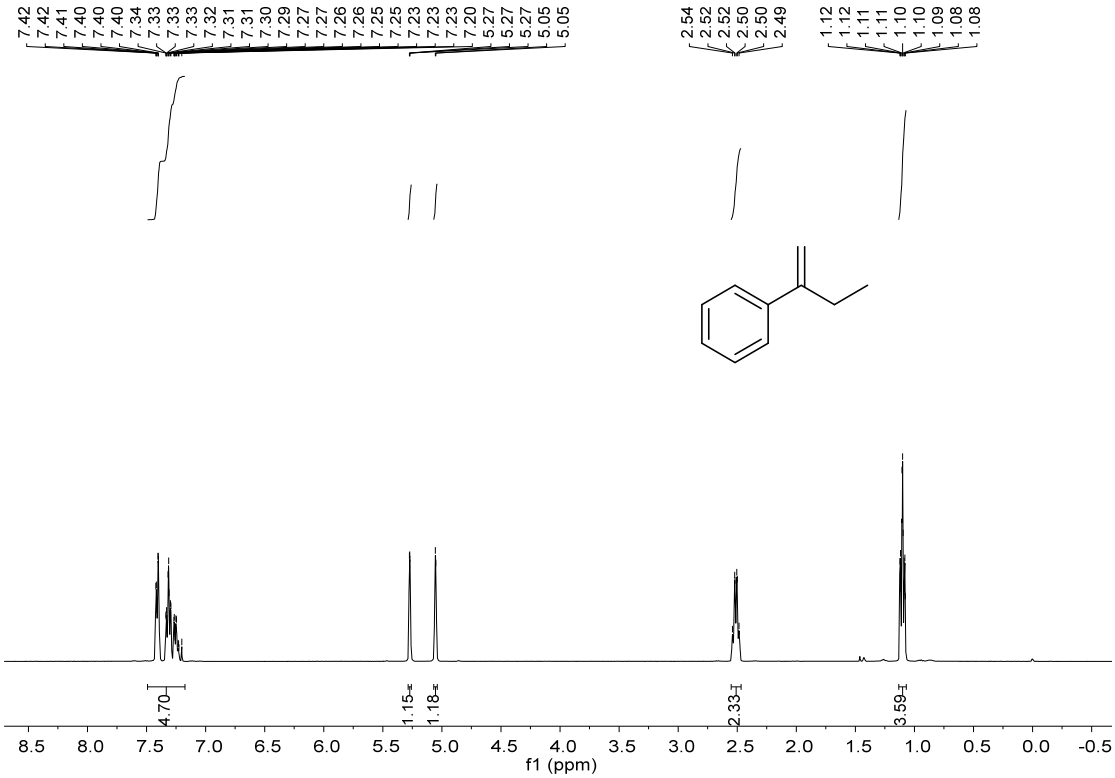


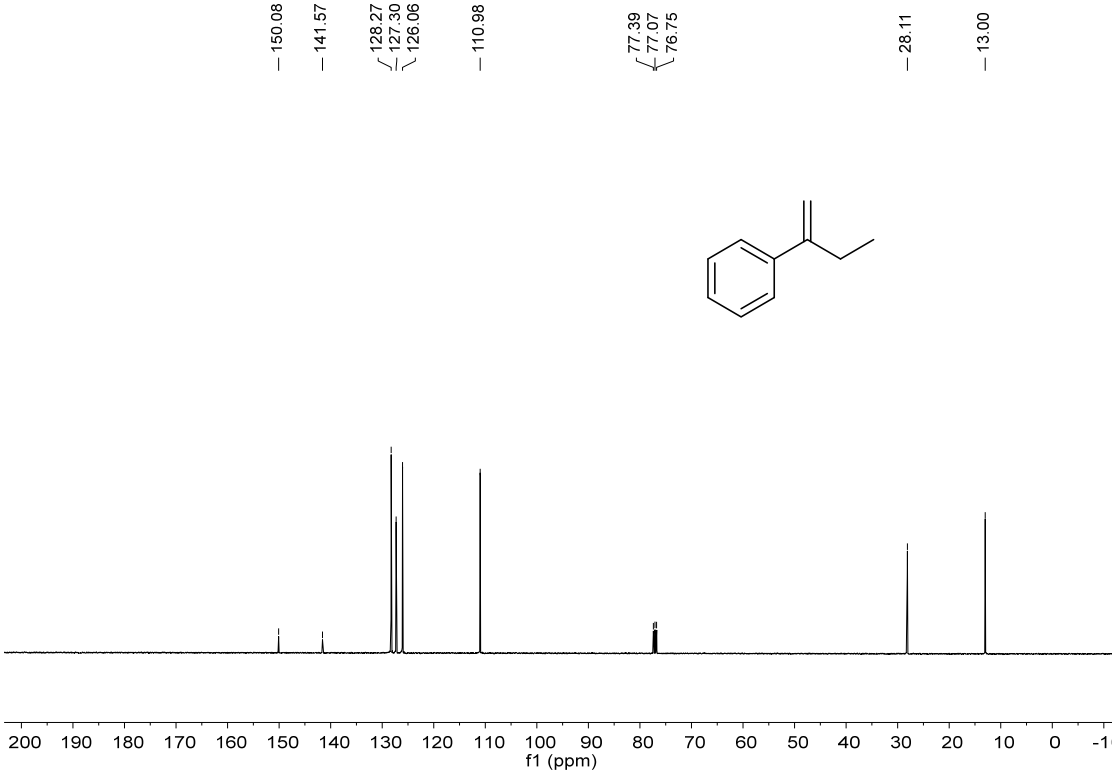
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **S3**



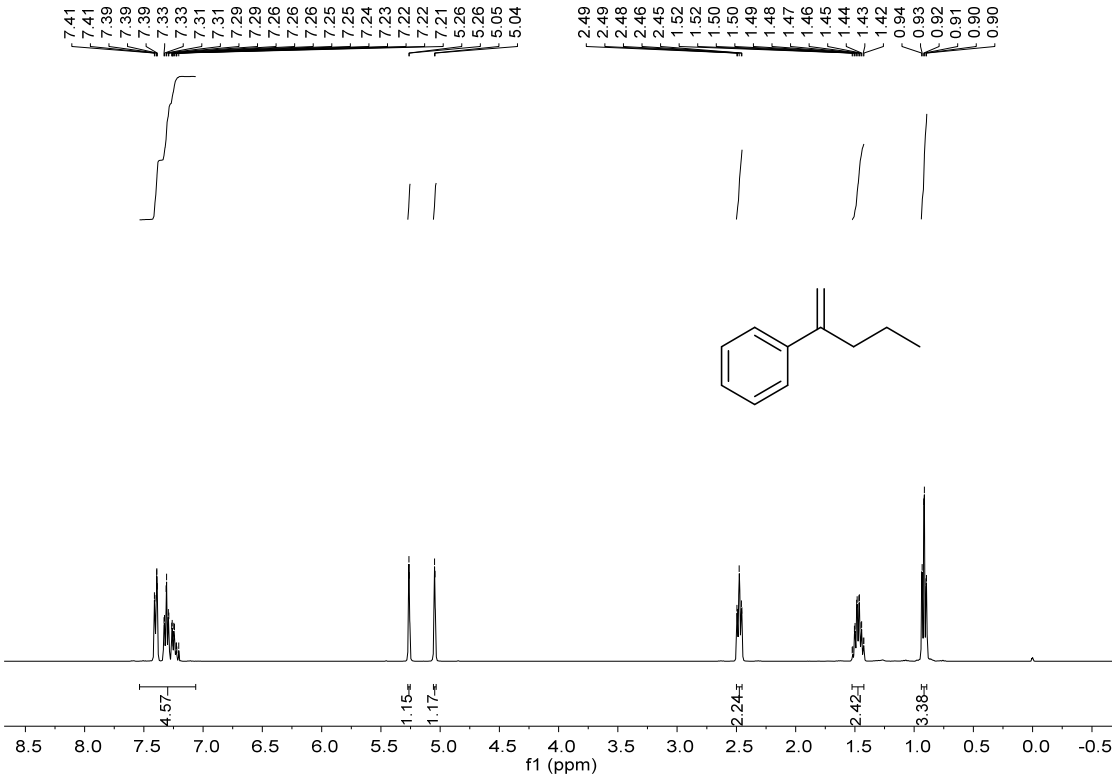


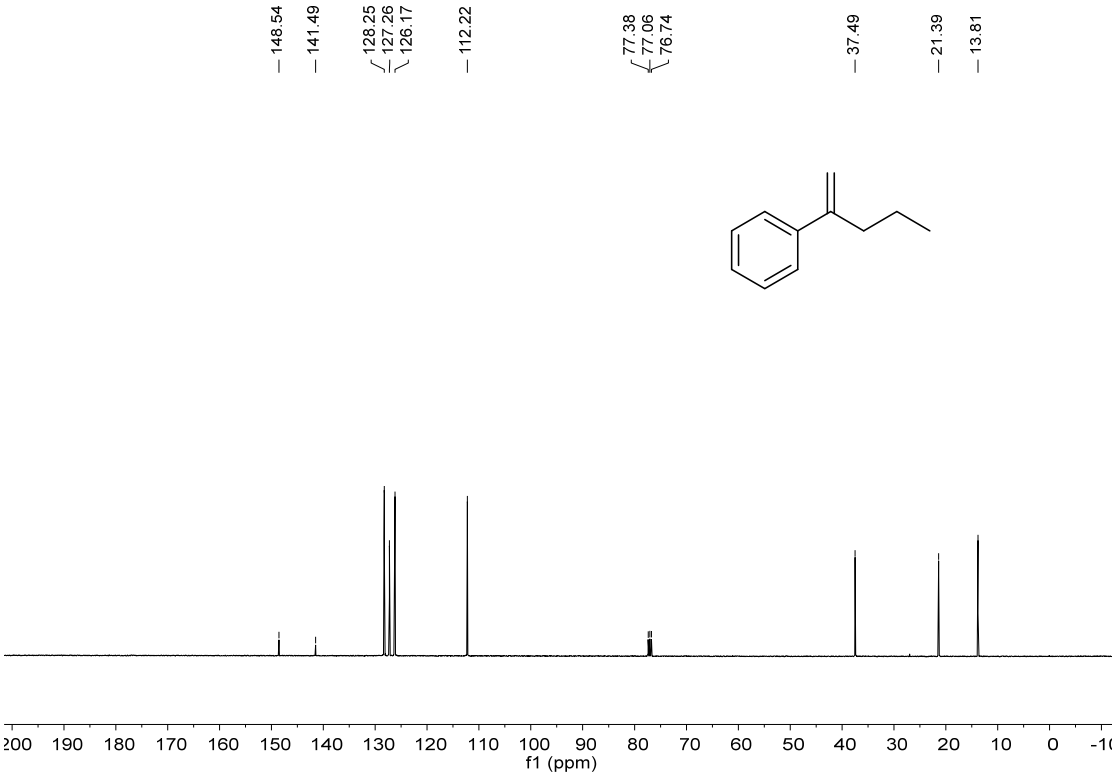
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **S4**



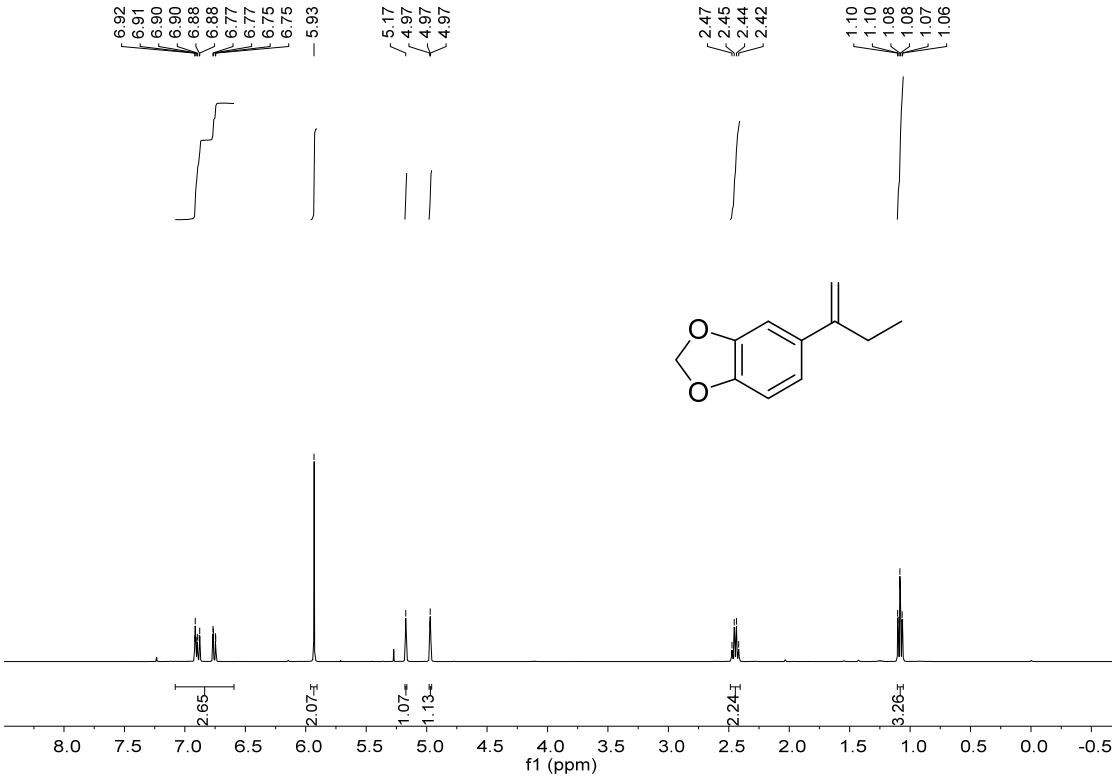


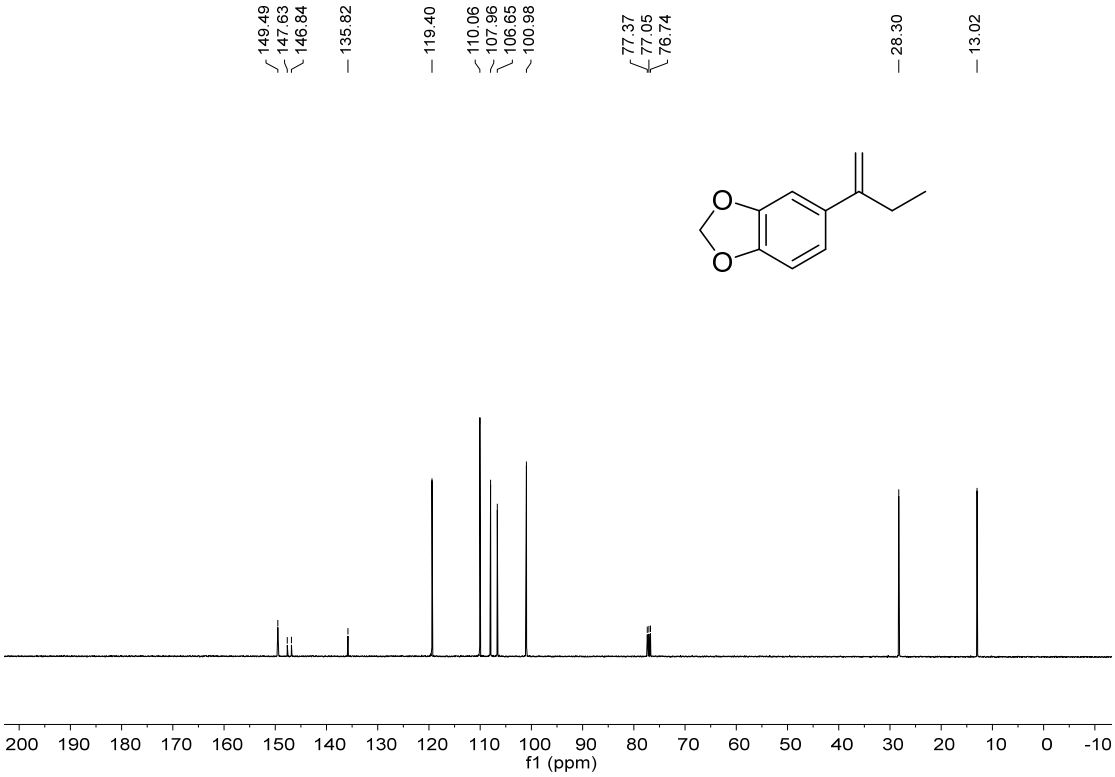
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **S5**



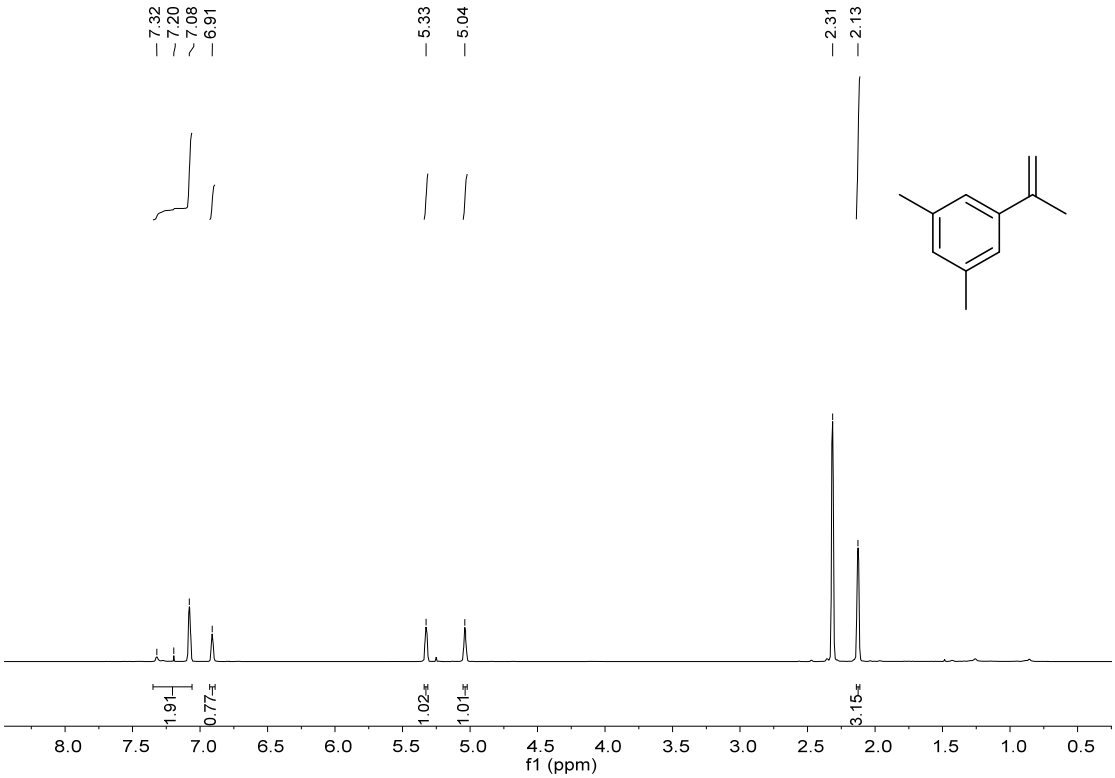


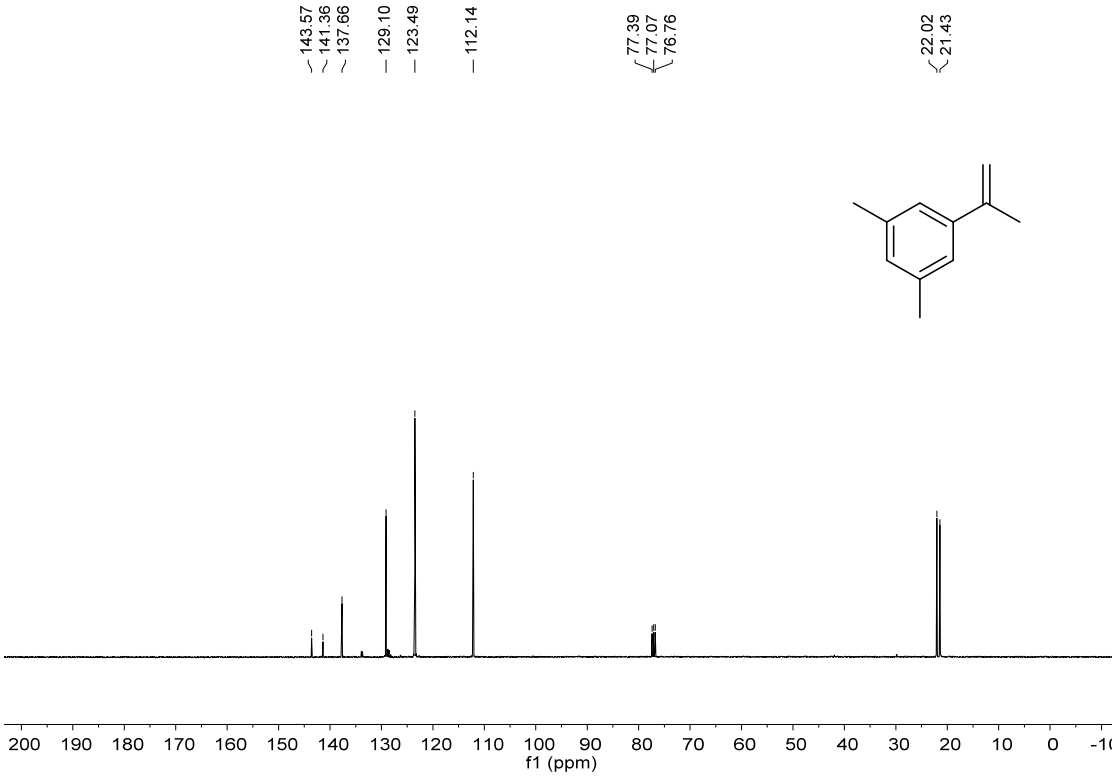
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **S6**



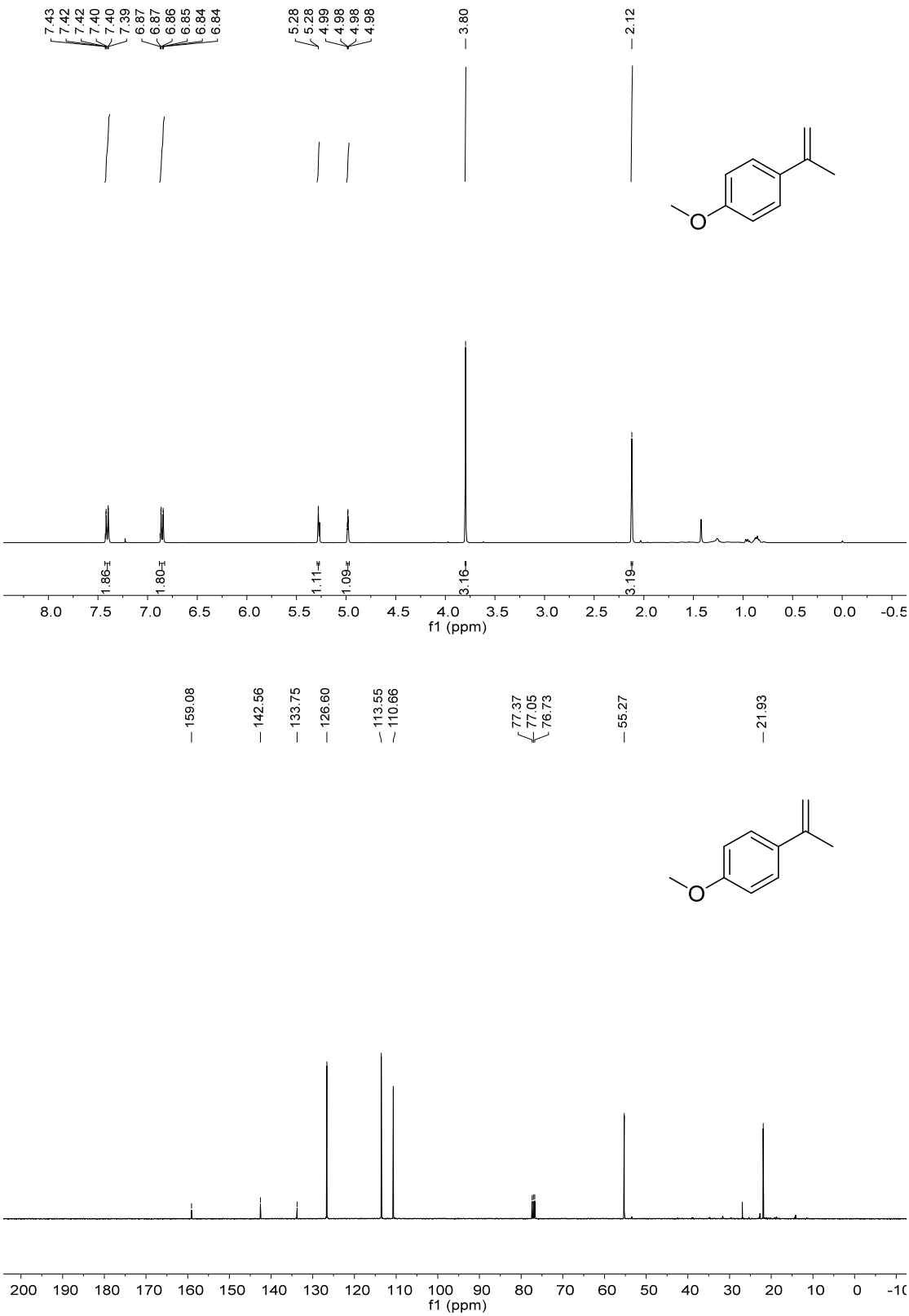


^{1}H NMR (400 MHz, $CDCl_3$) spectra of **S7**

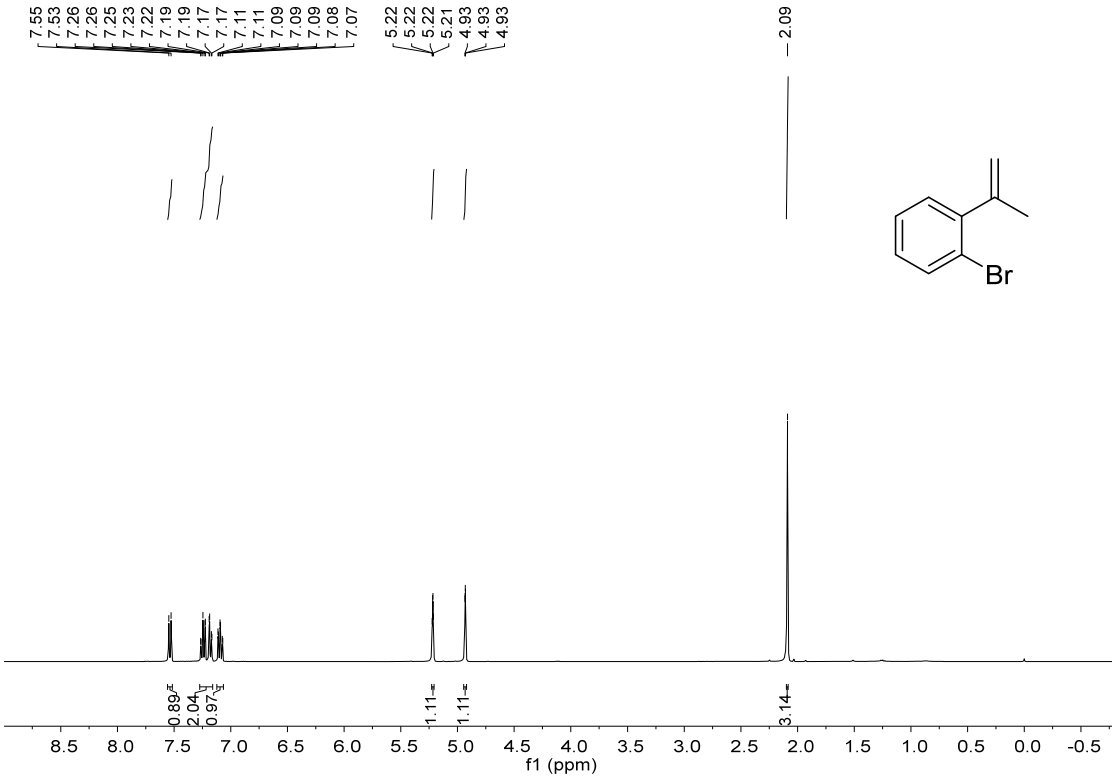


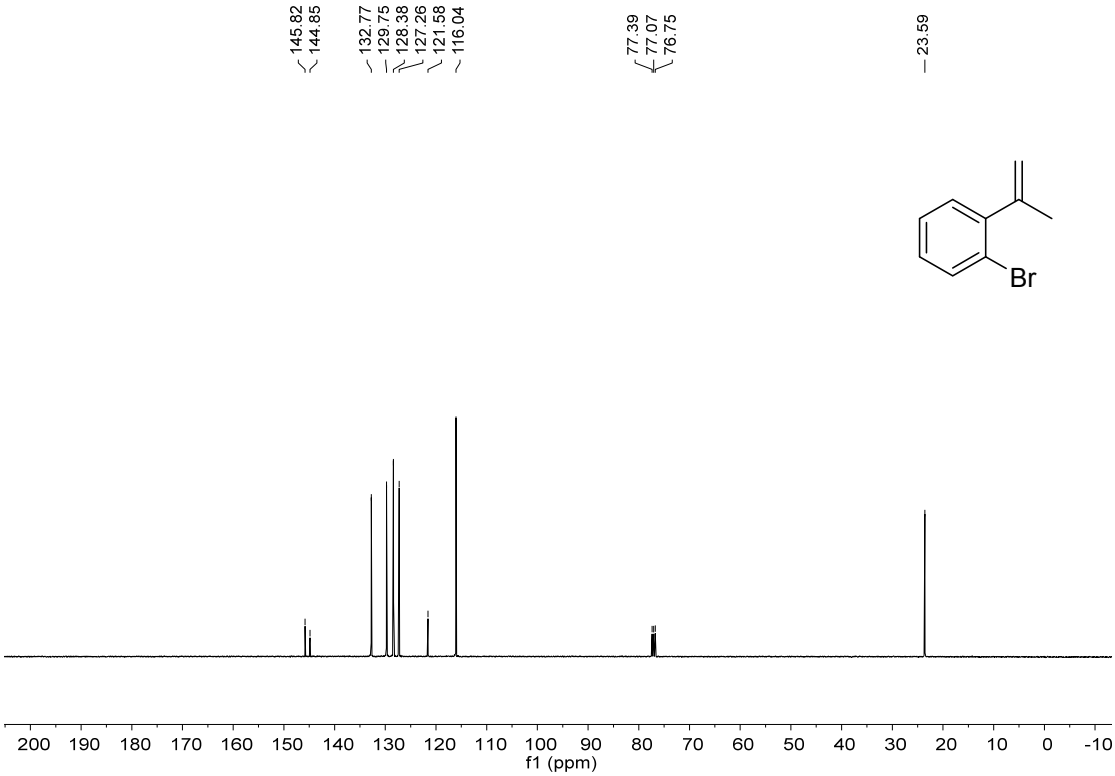


^{1}H NMR (400 MHz, $CDCl_3$) spectra of **S8**

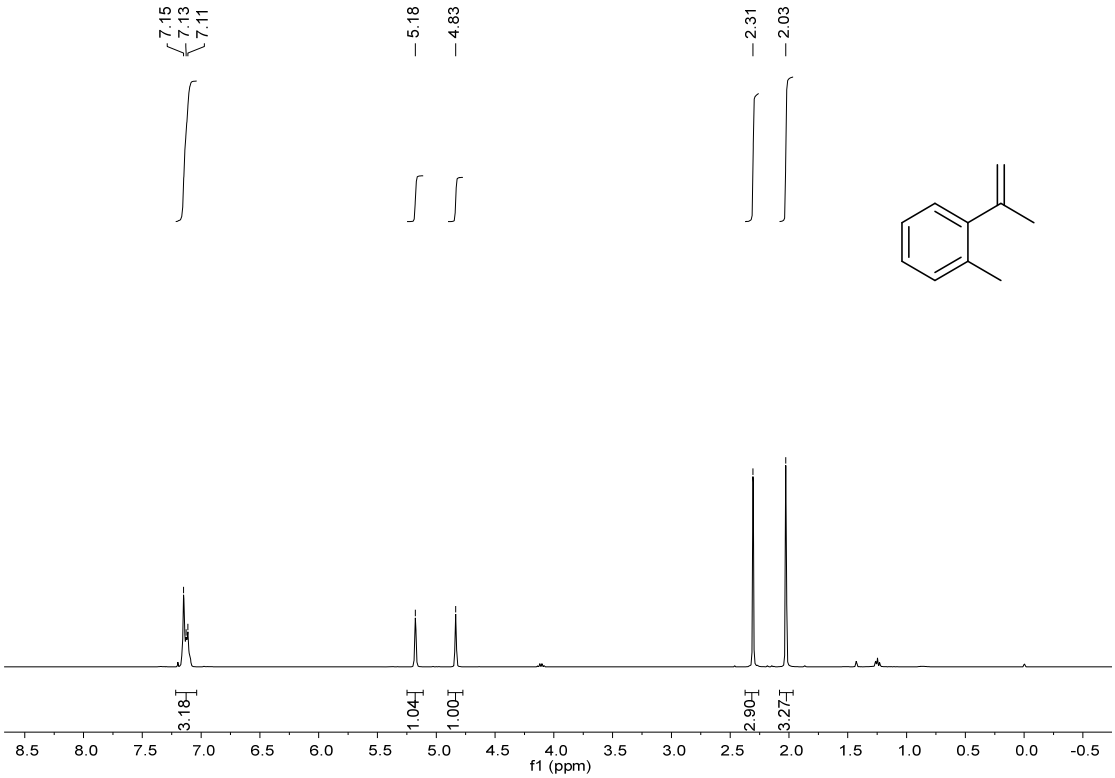


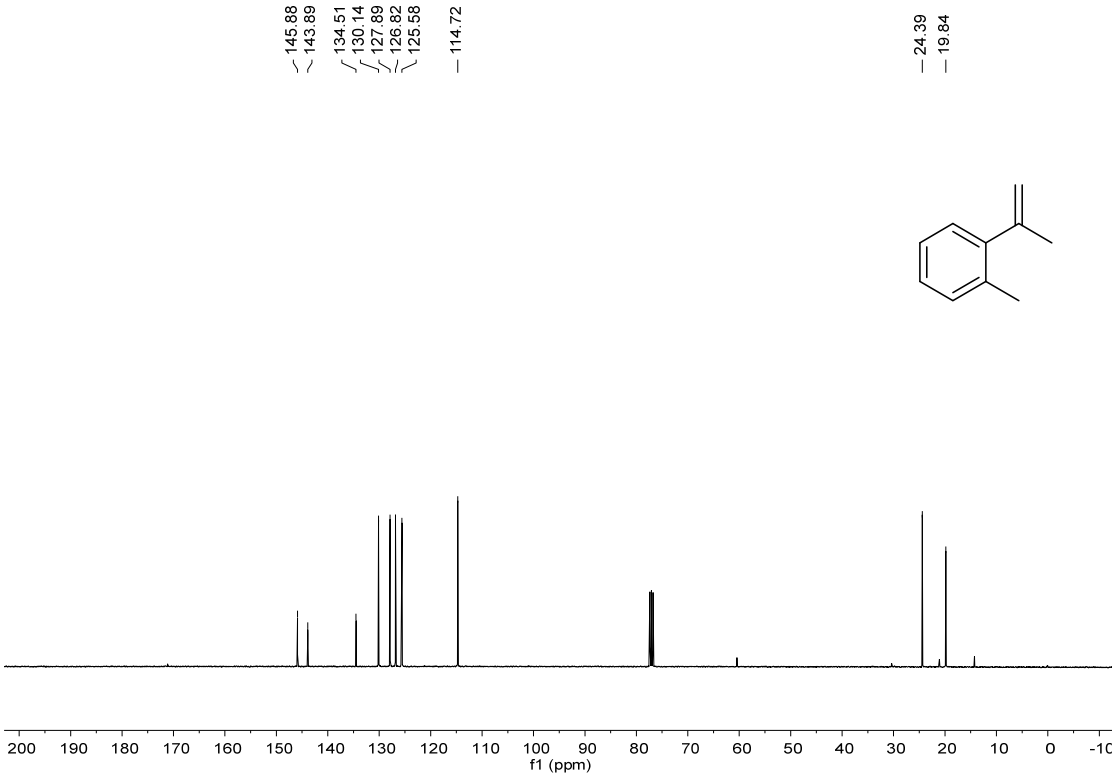
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **S9**



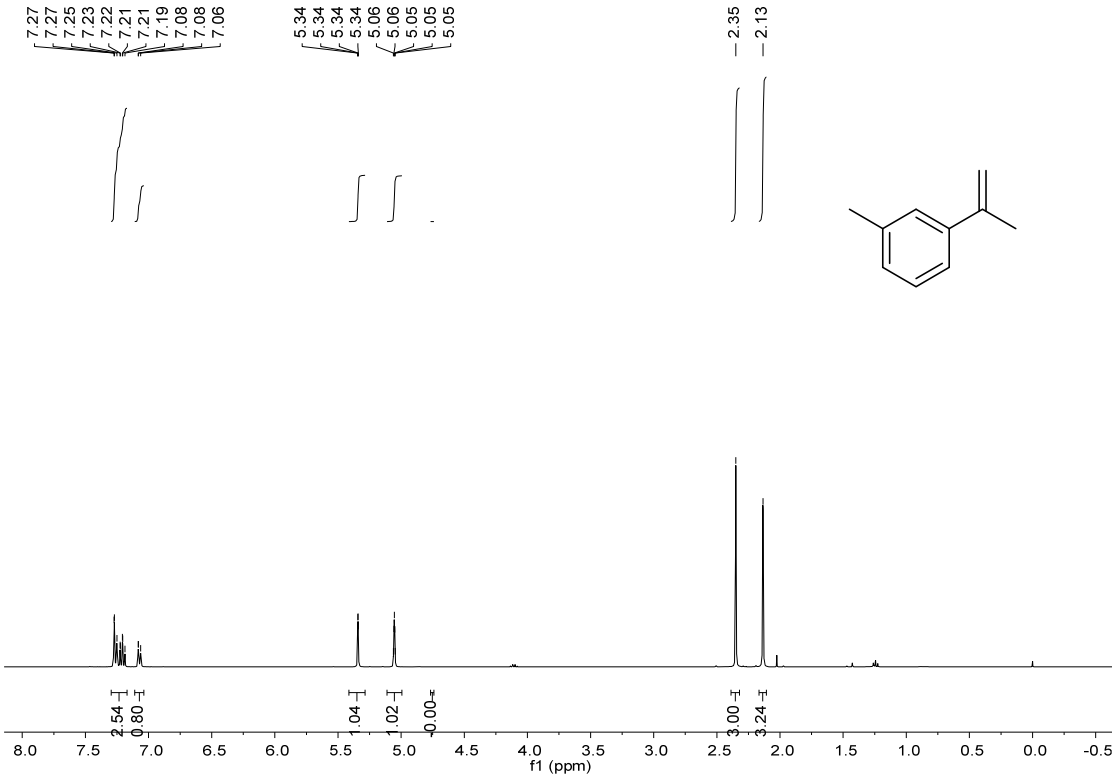


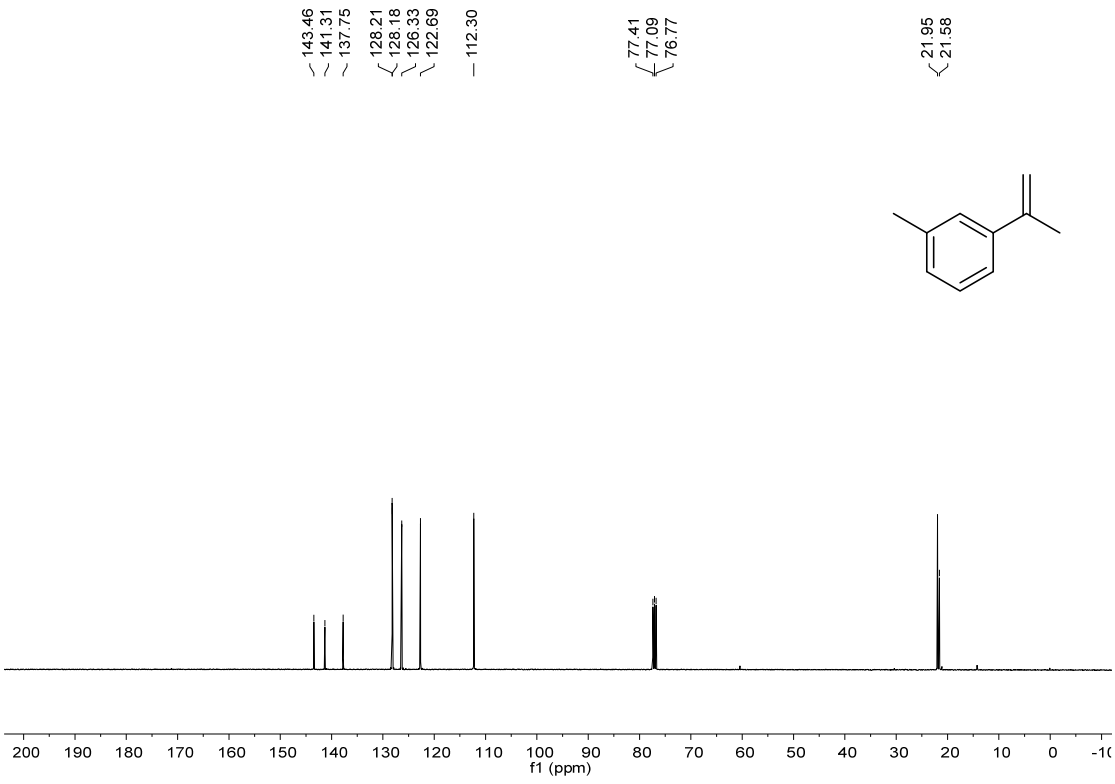
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **S10**





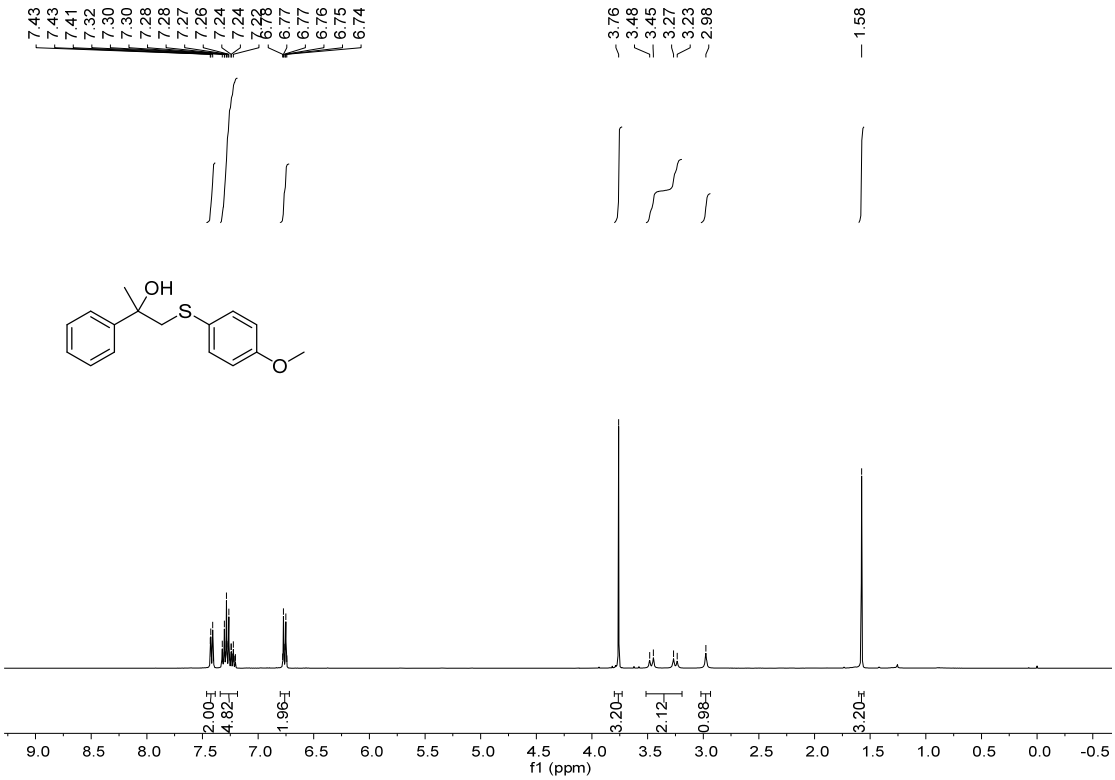
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **S11**



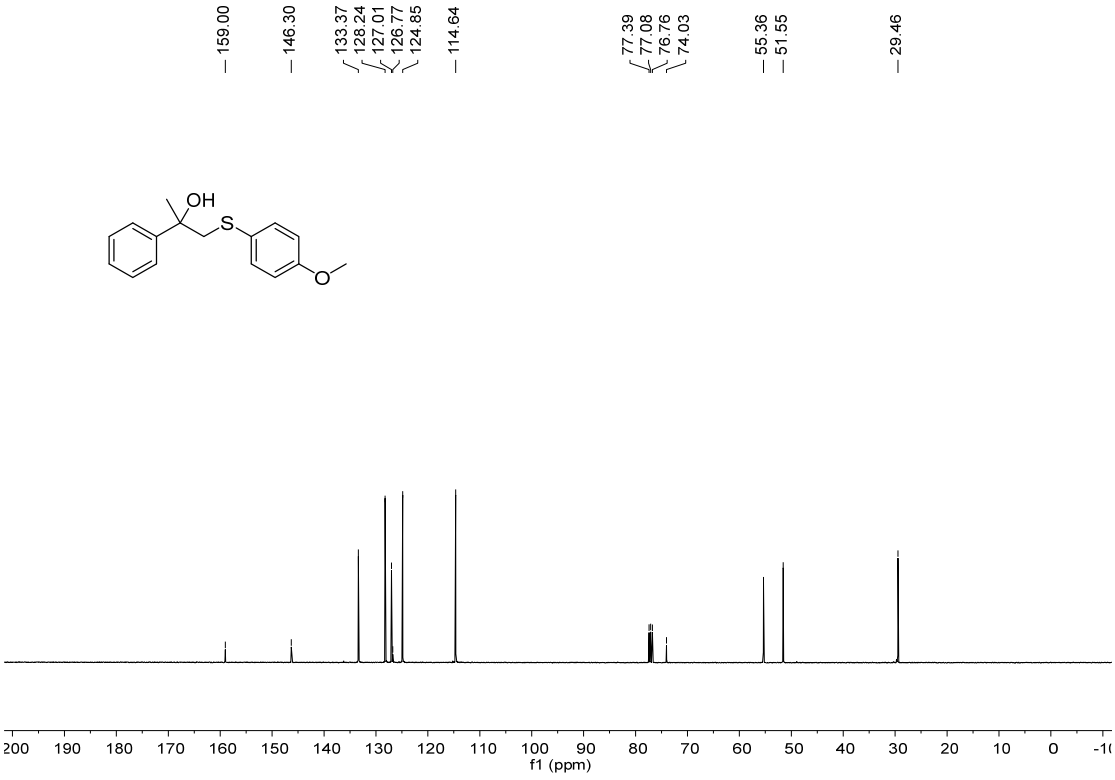


9.2 NMR spectra for hydrosulfuration products **4-32**

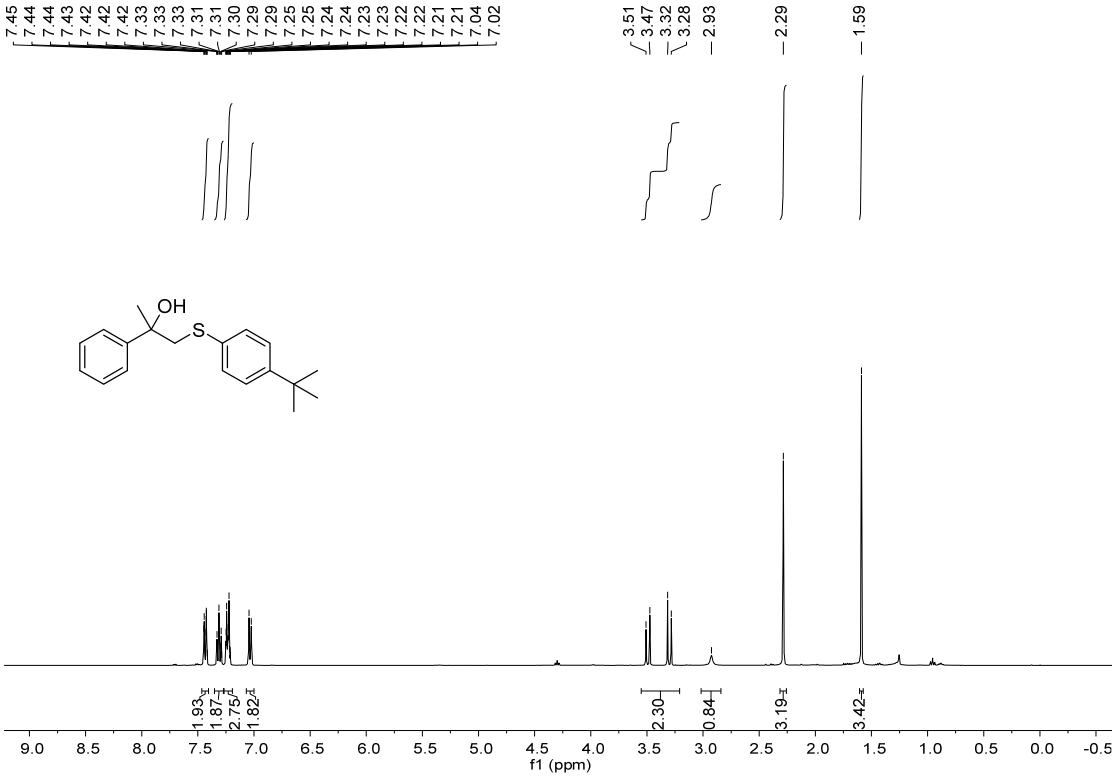
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **4**



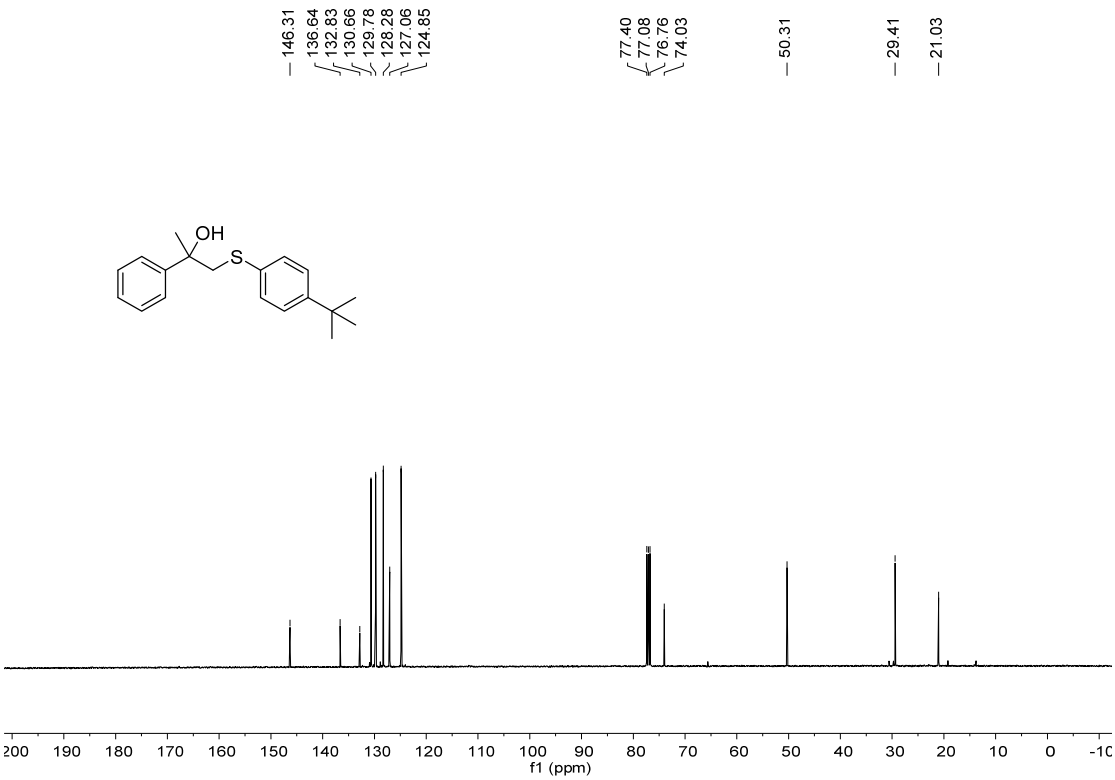
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **4**



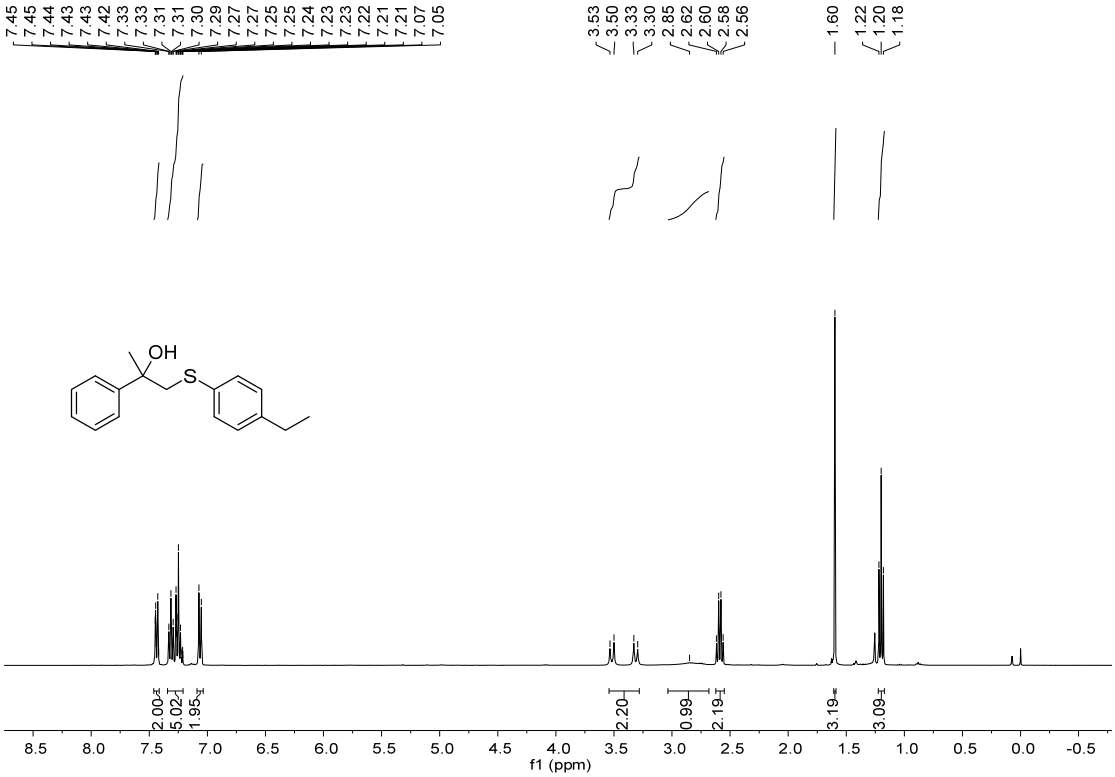
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **5**



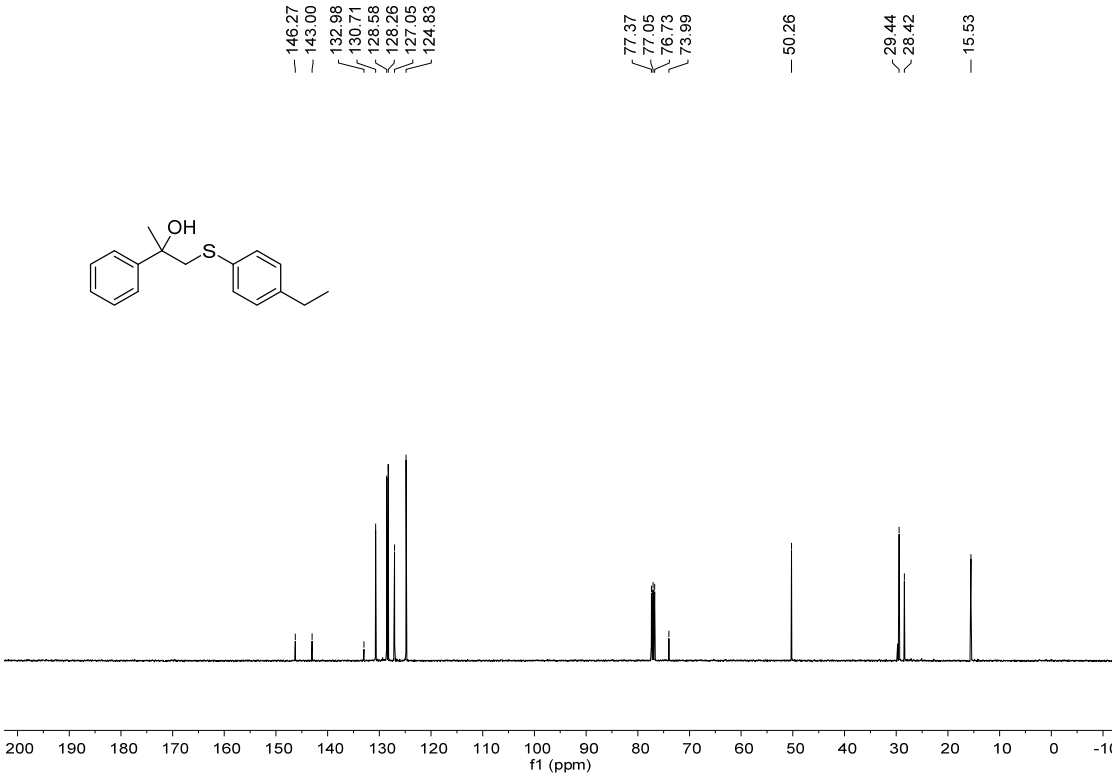
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **5**



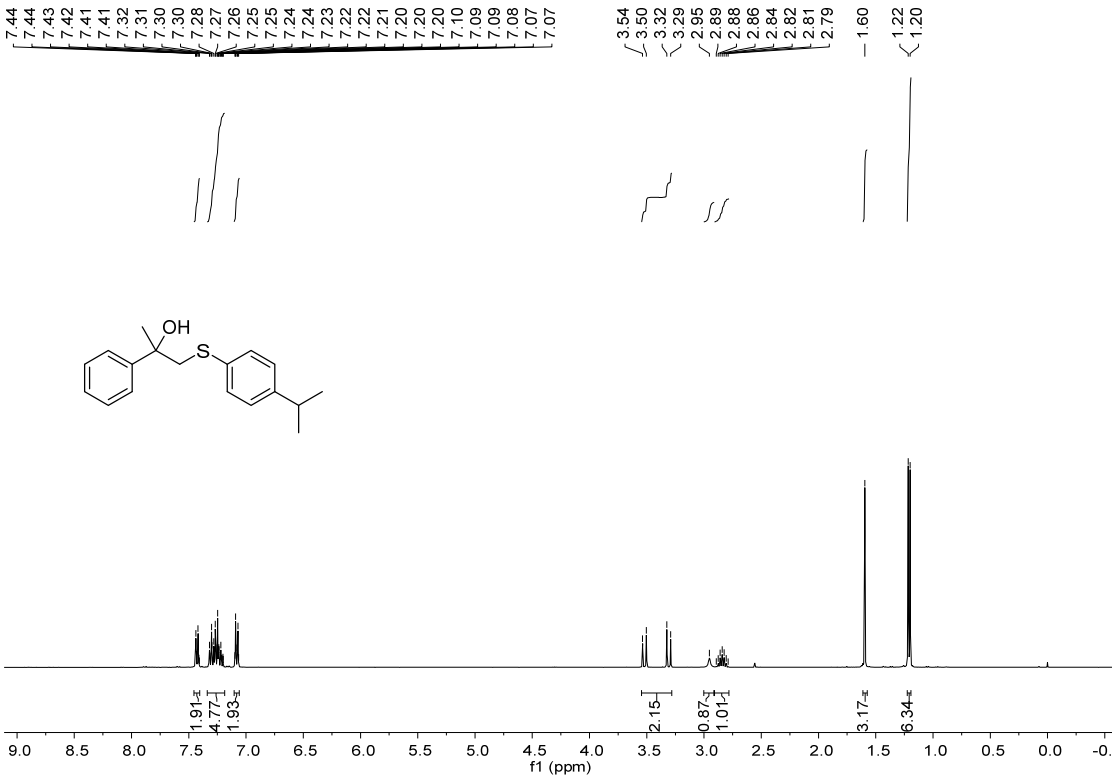
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **6**



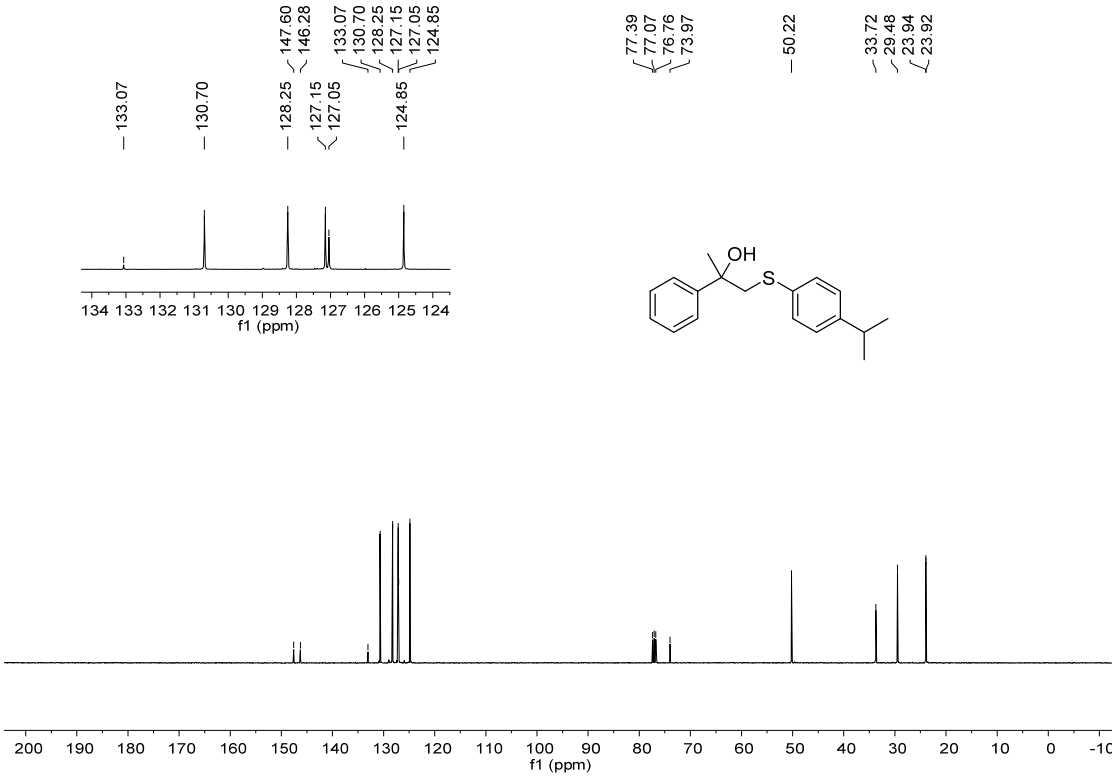
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **6**



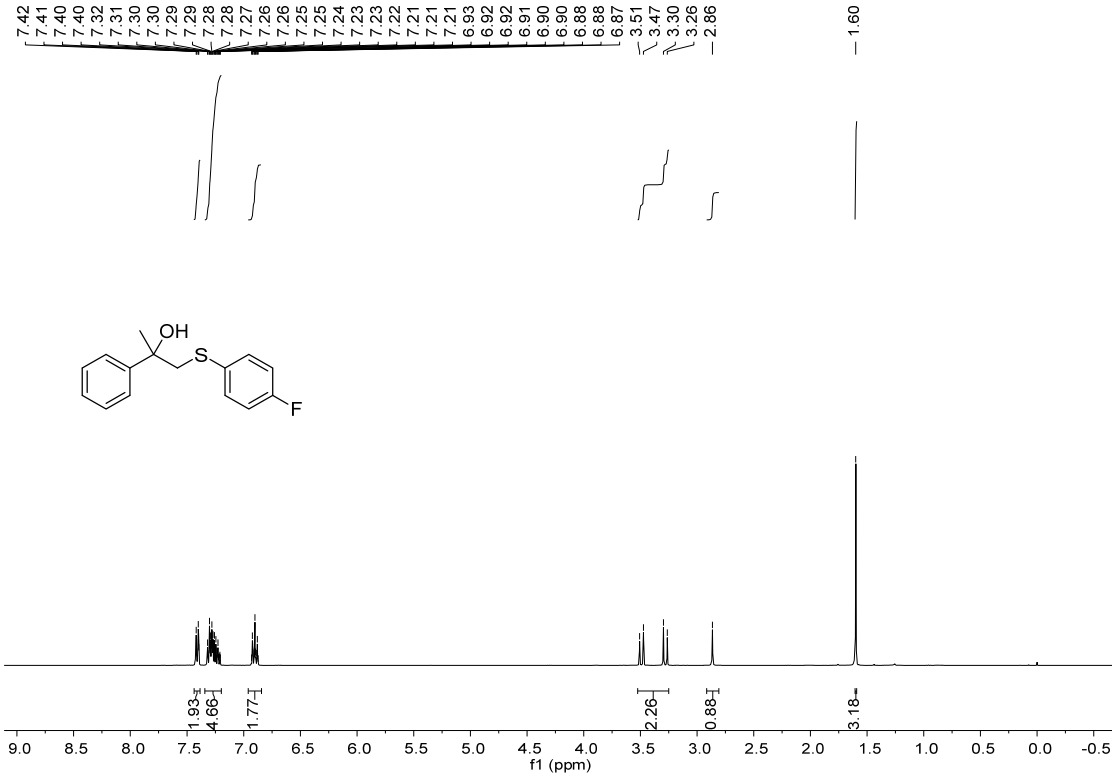
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **7**



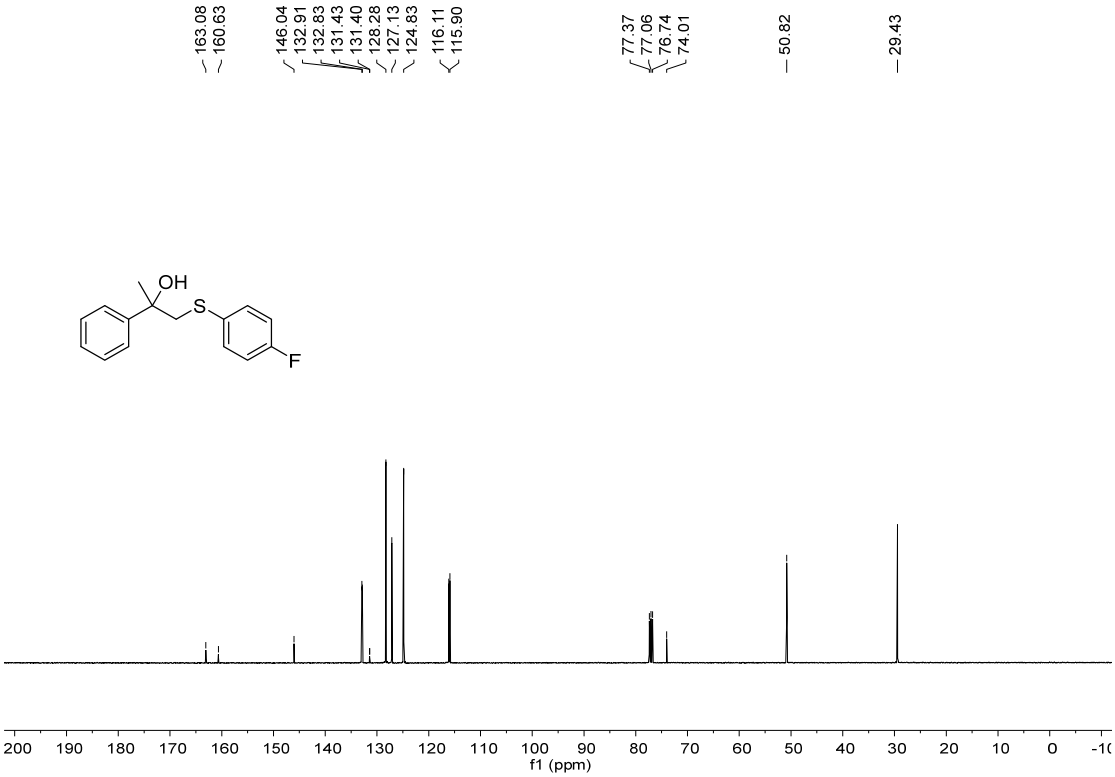
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **7**



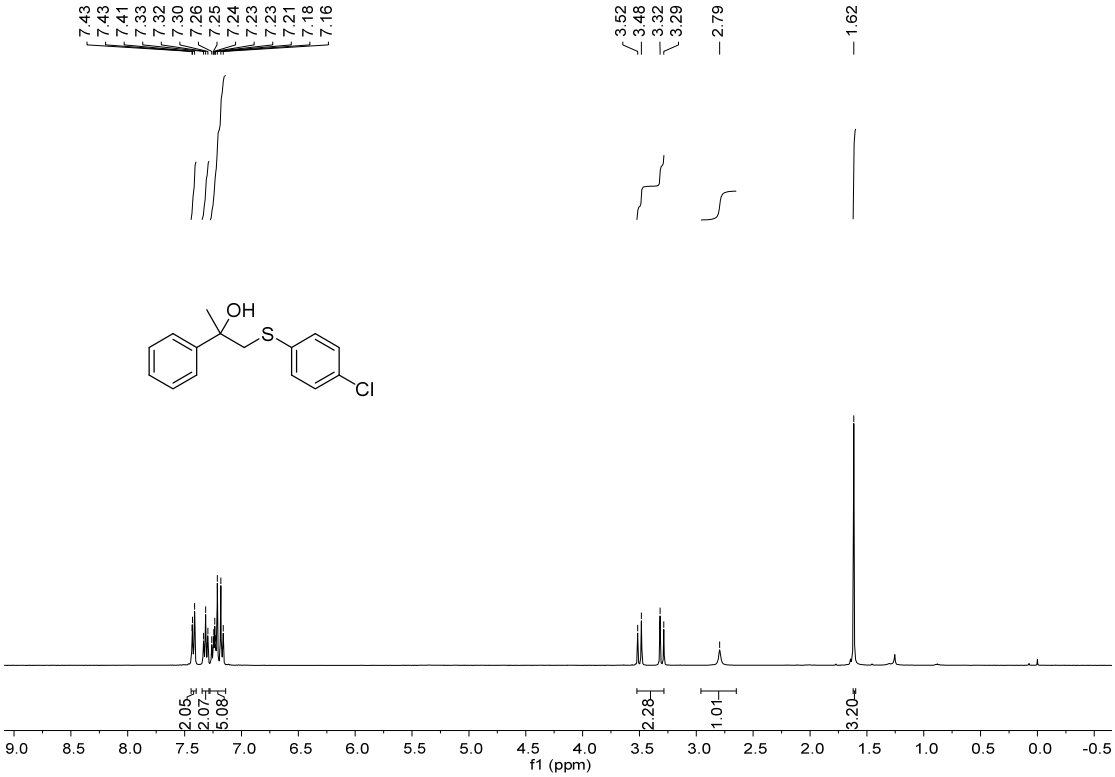
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **8**



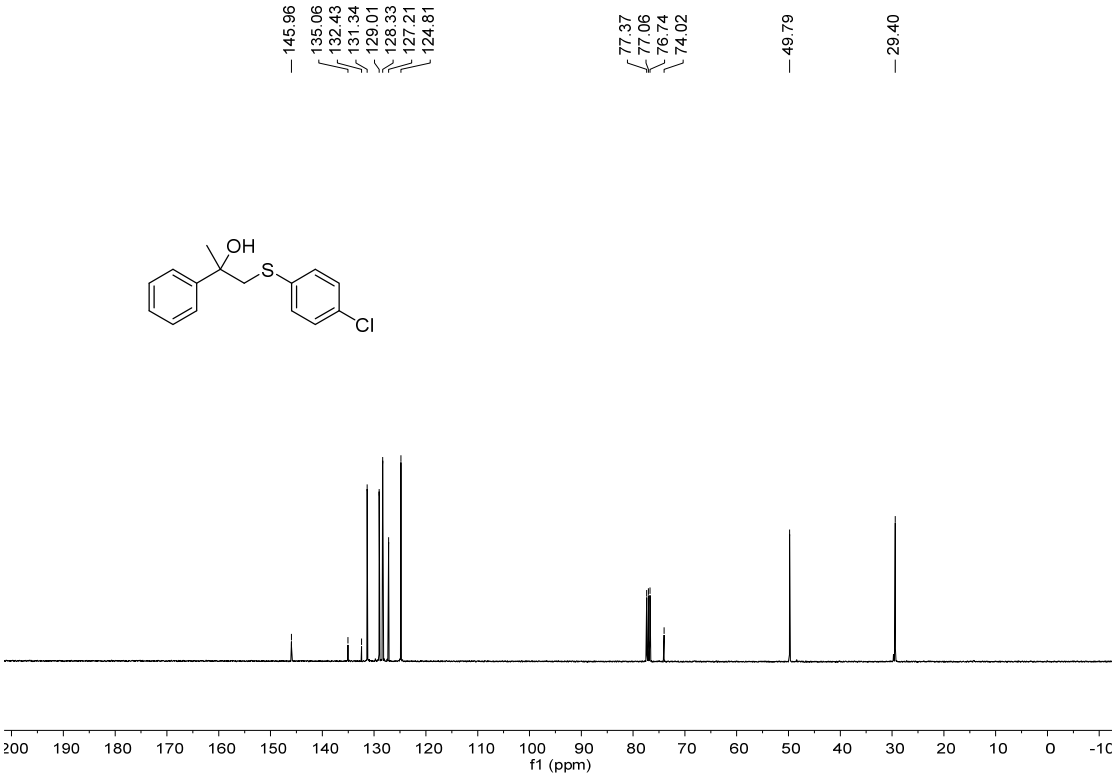
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **8**



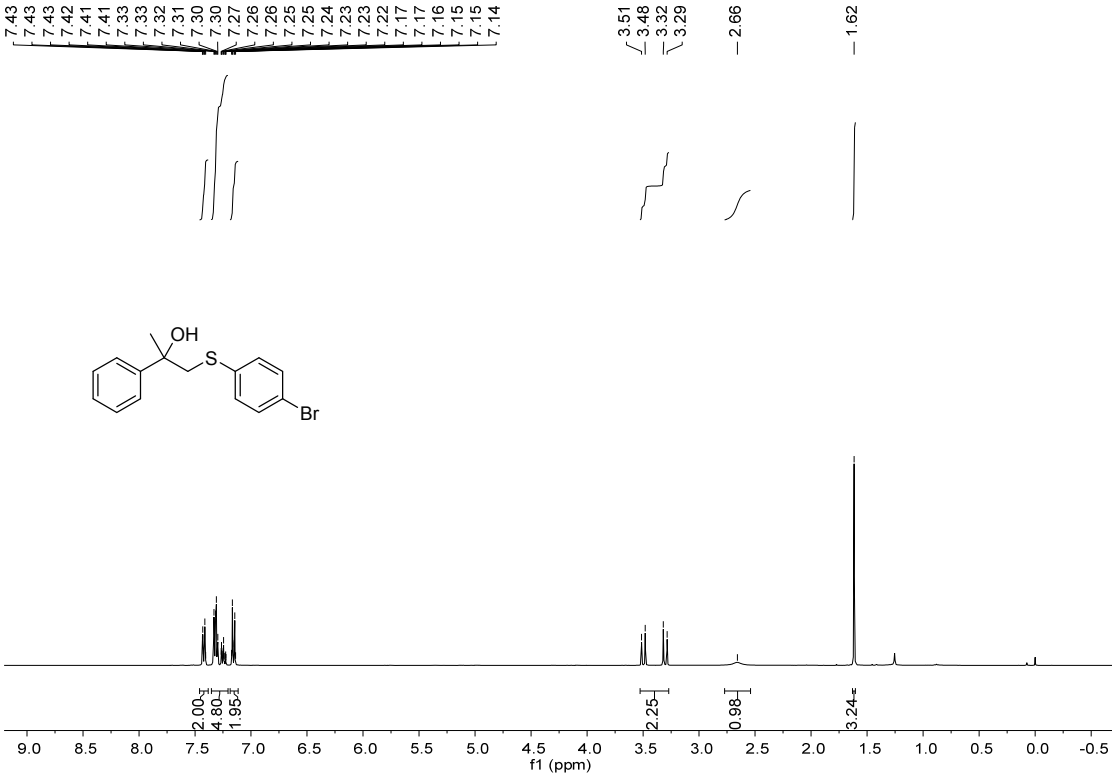
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **9**



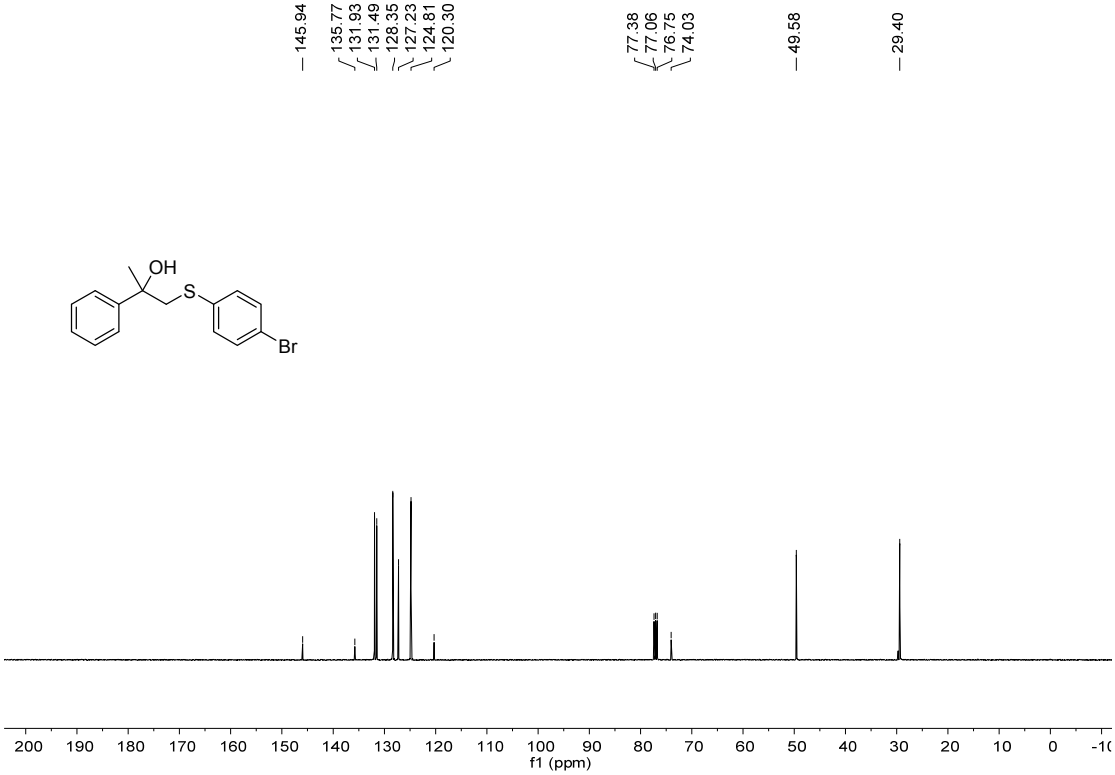
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **9**



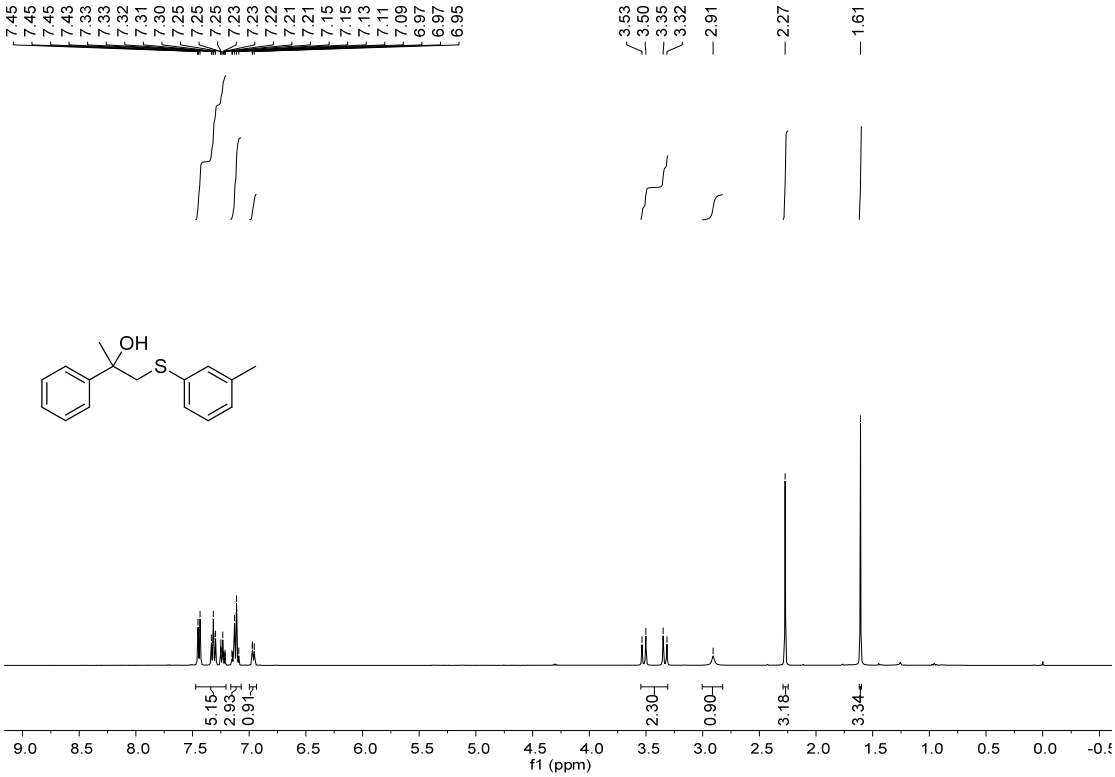
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **10**



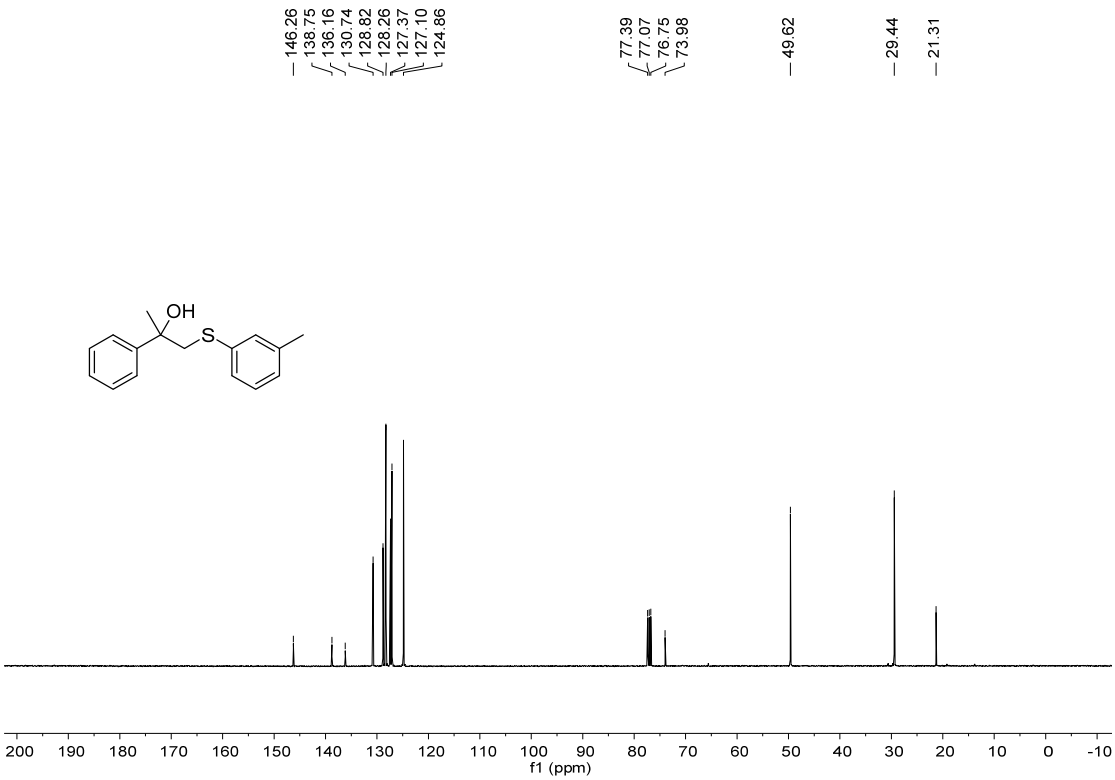
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **10**



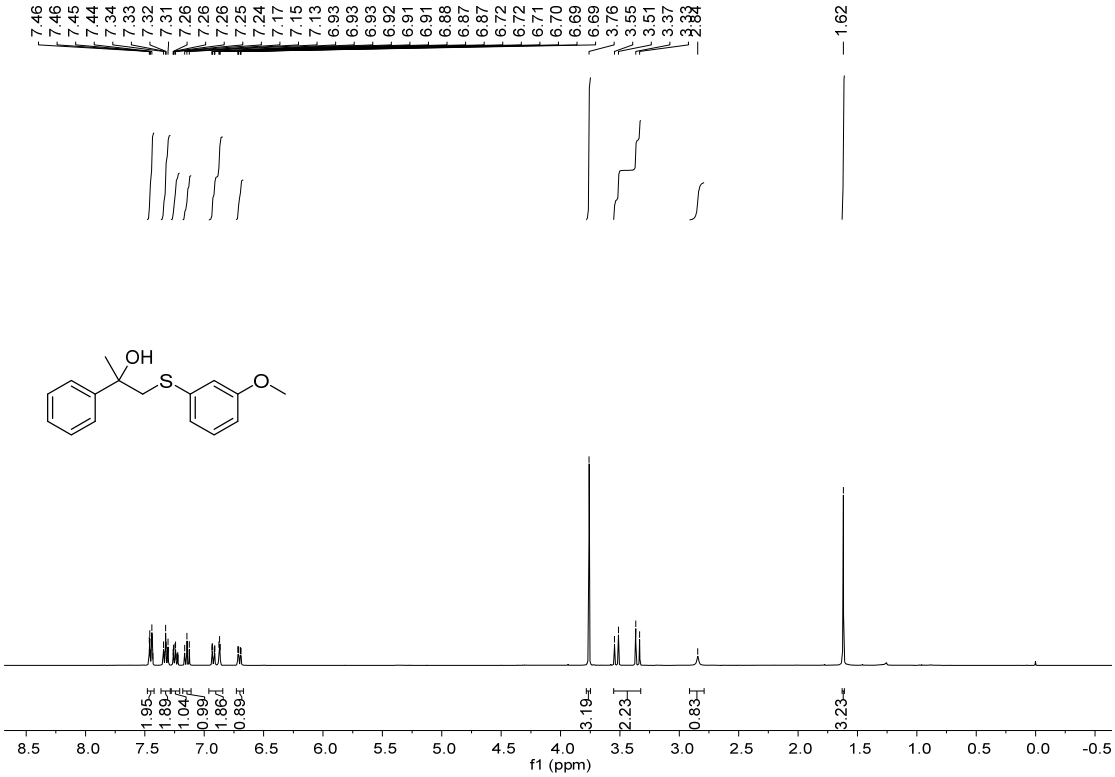
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **11**



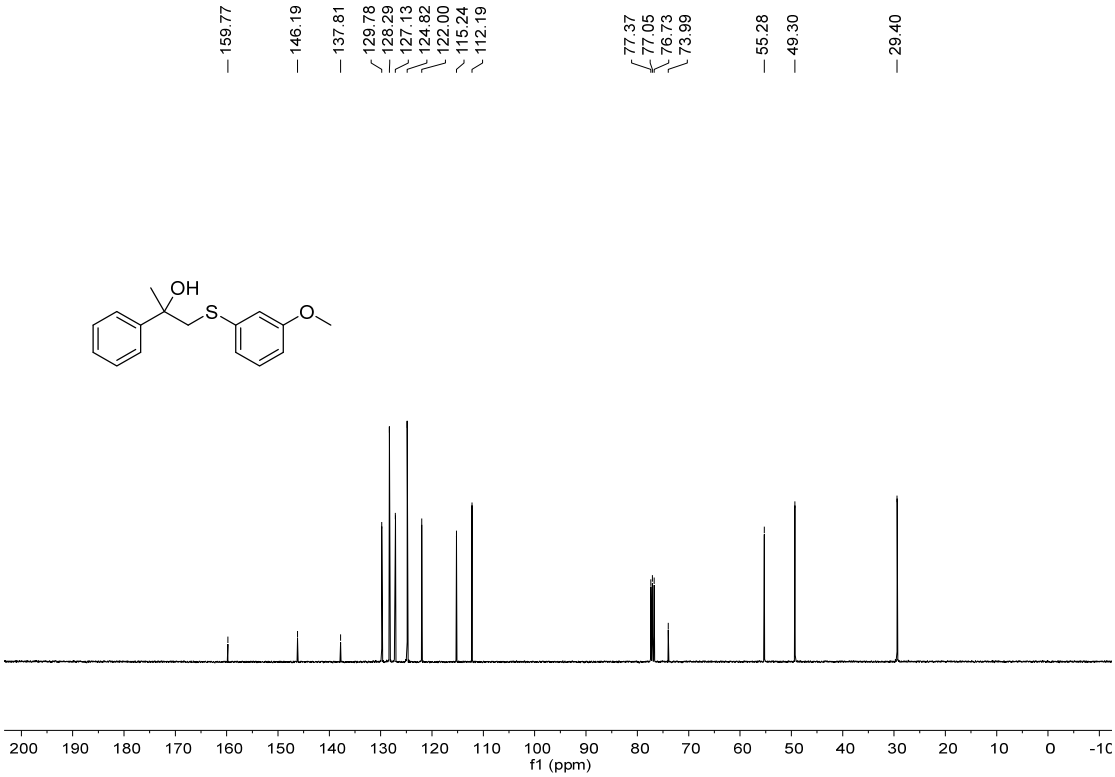
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **11**



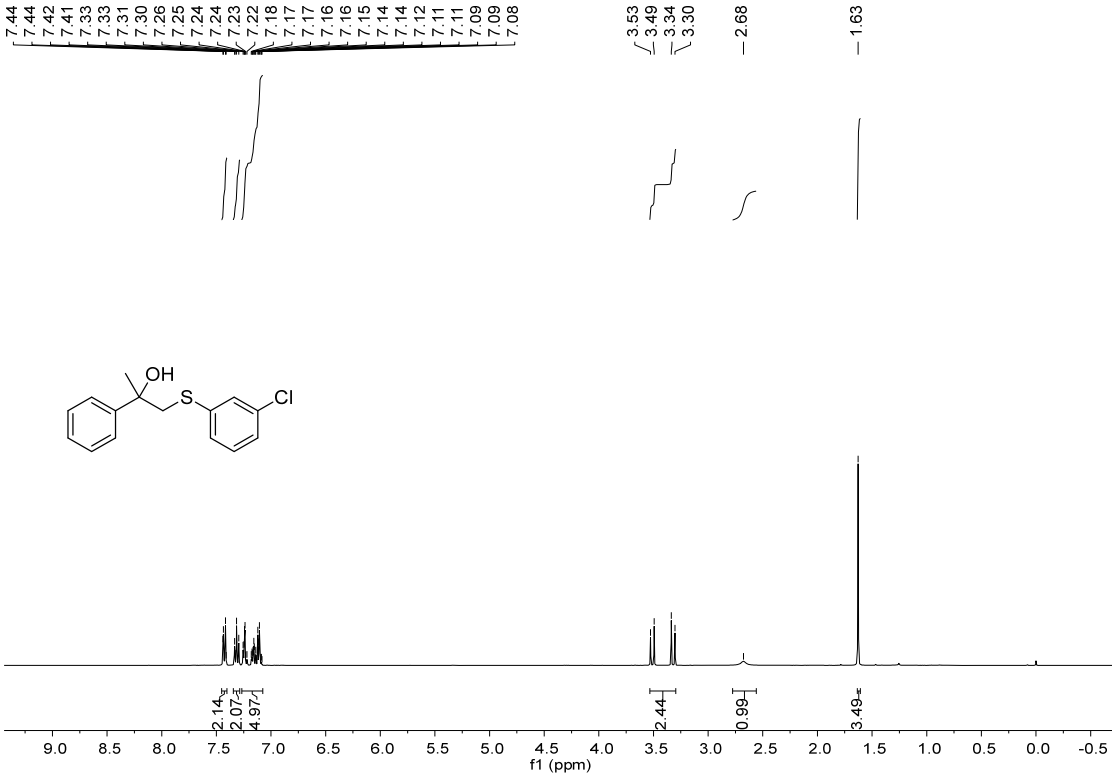
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **12**



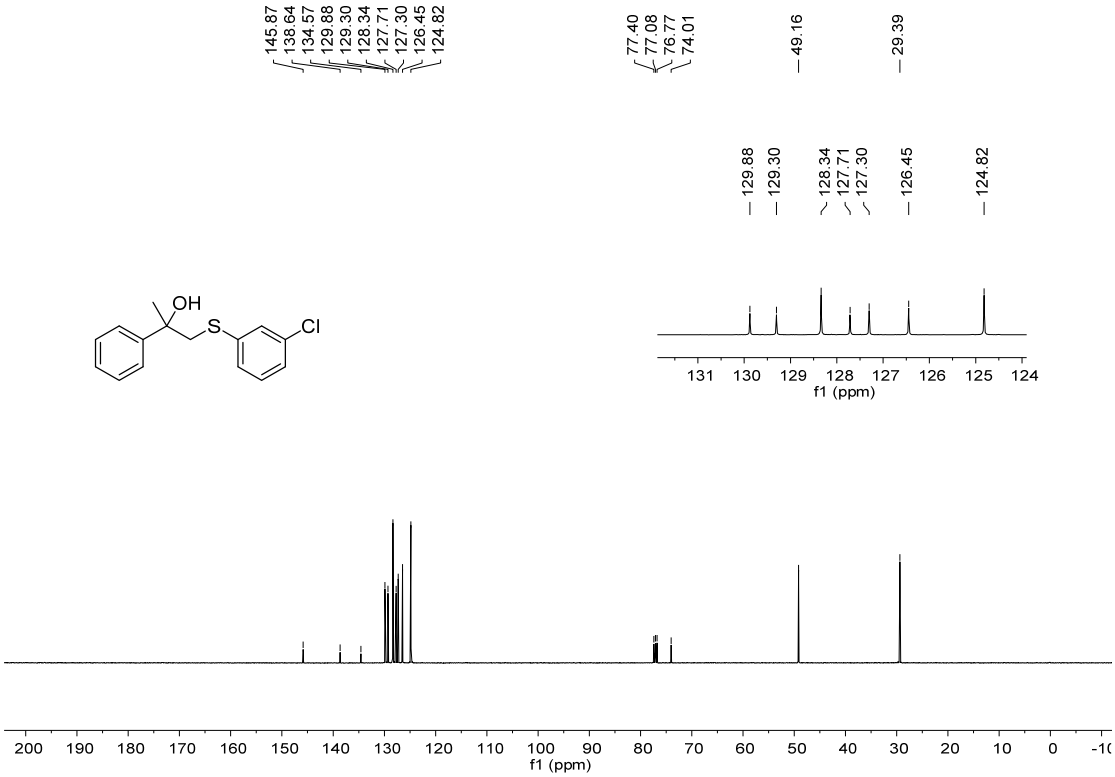
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **12**



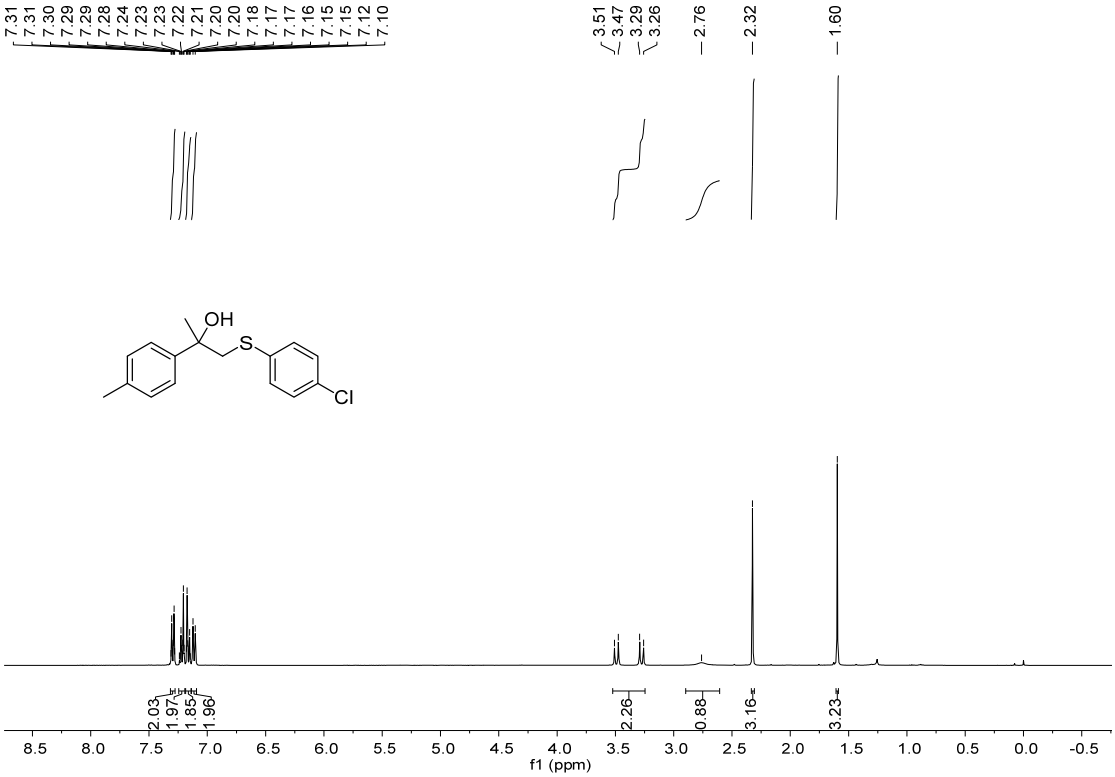
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **13**



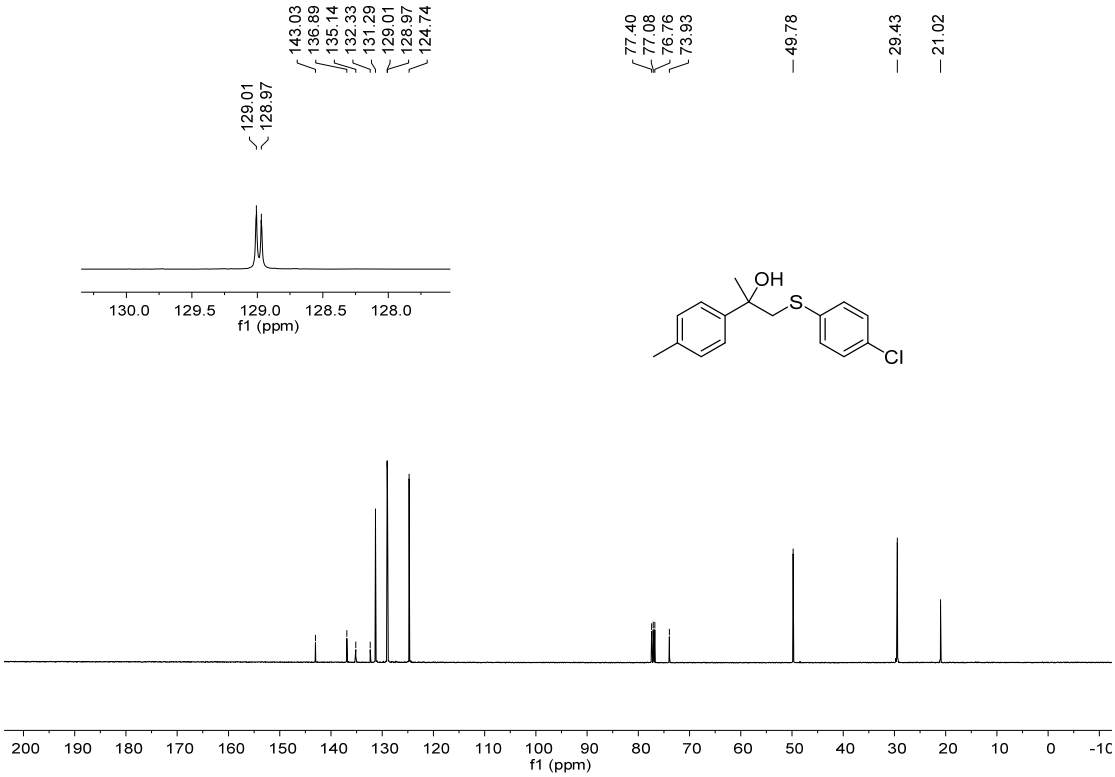
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **13**



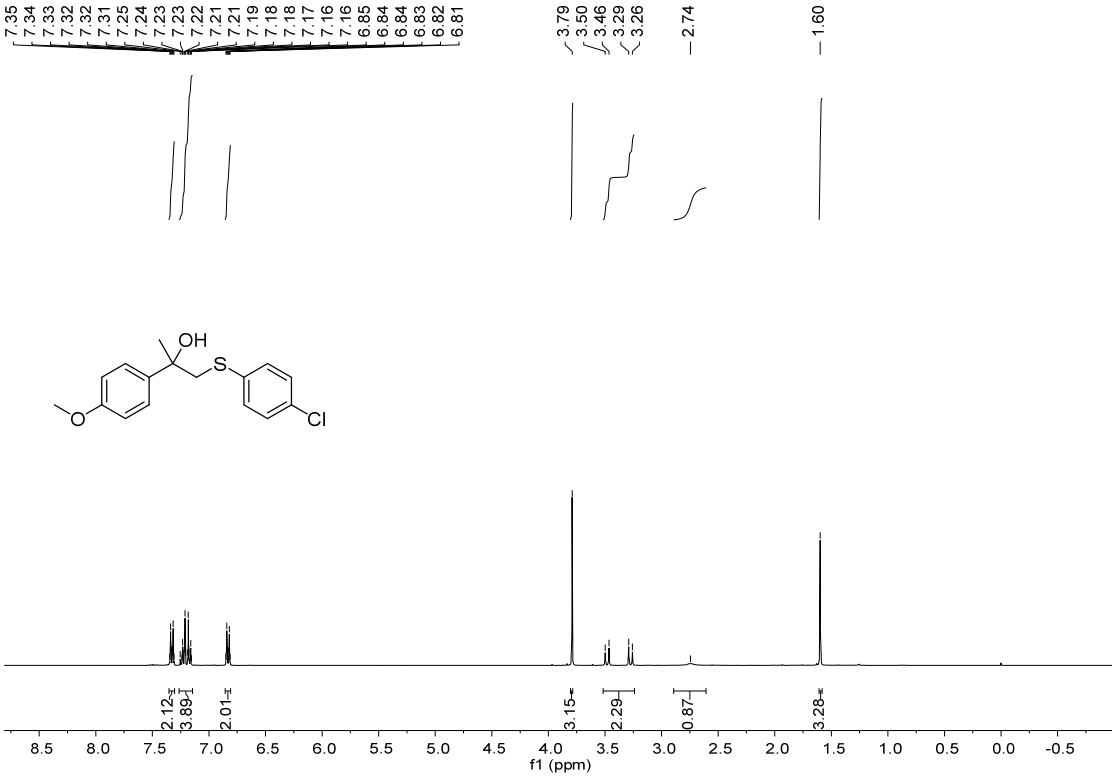
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **14**



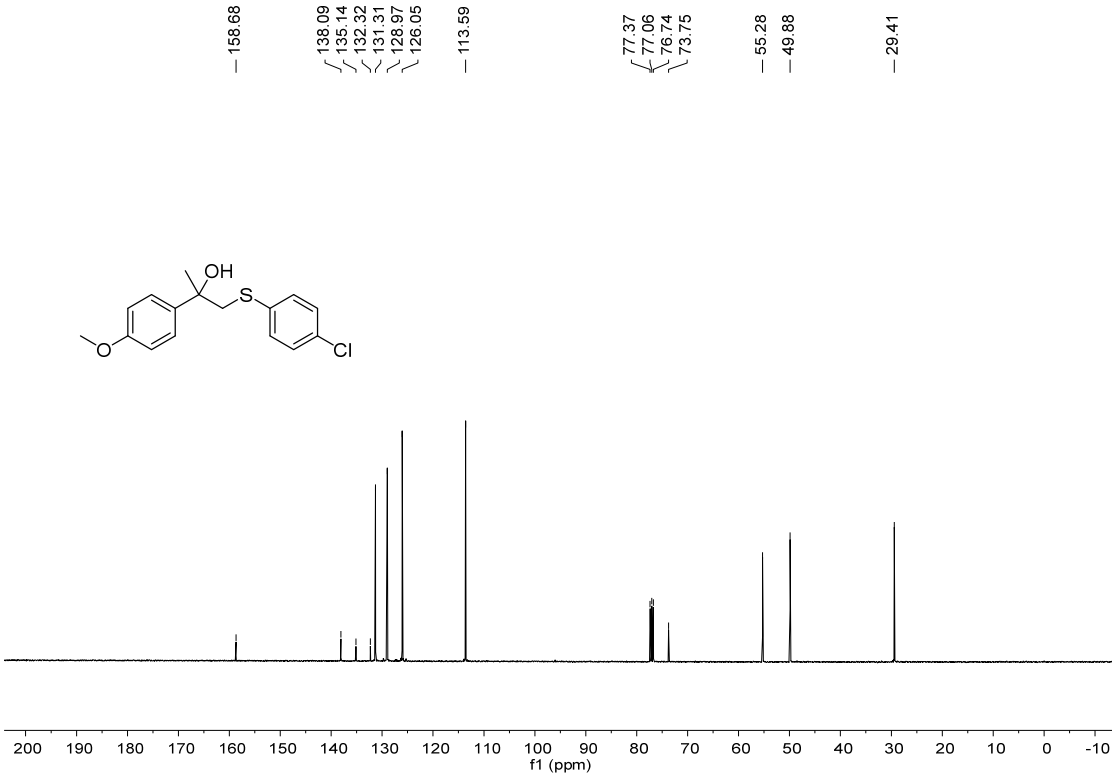
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **14**



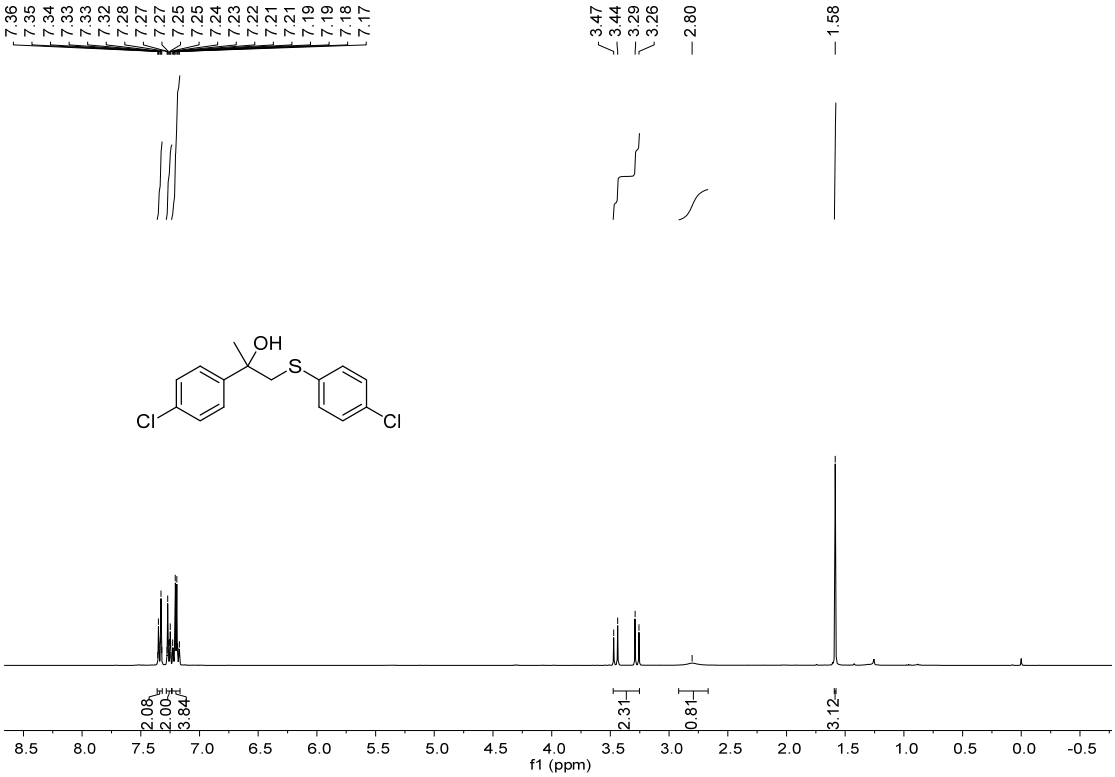
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **15**



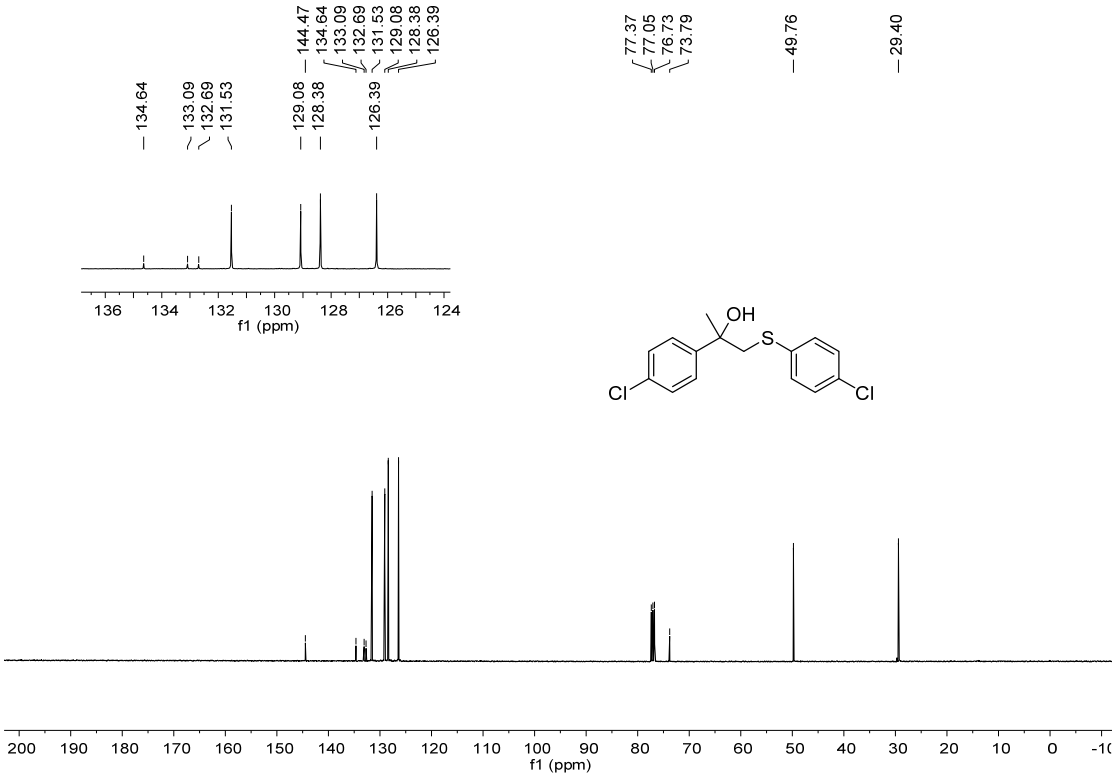
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **15**



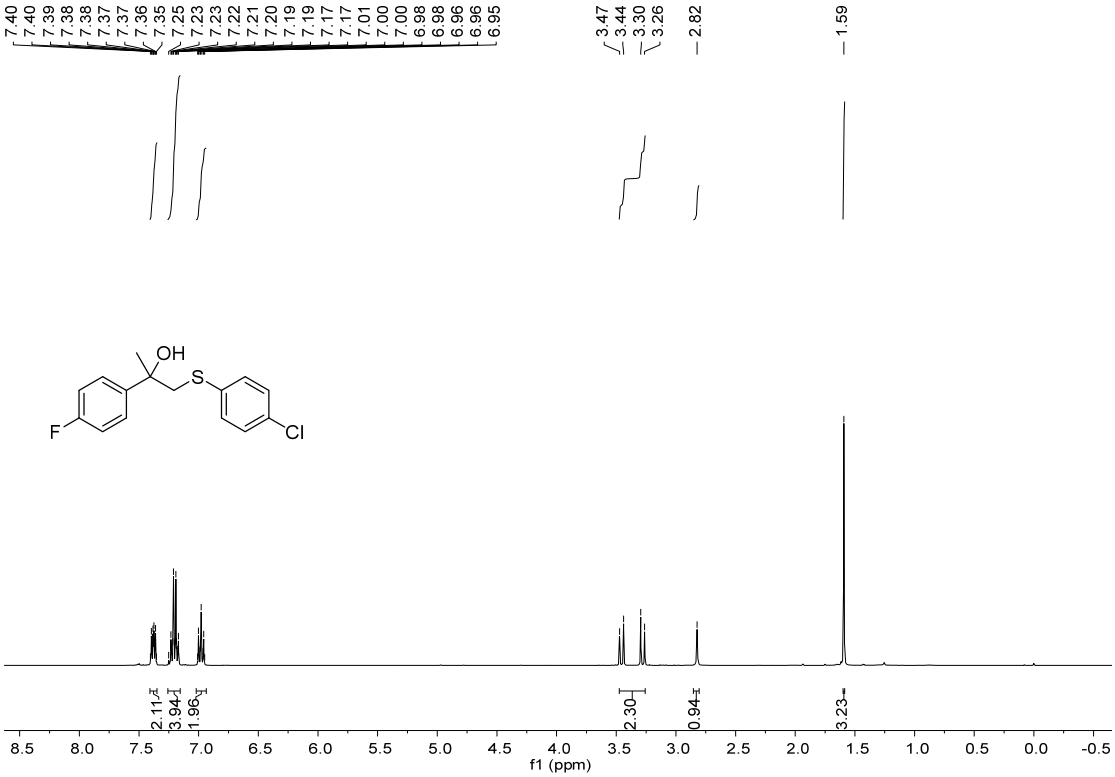
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **16**



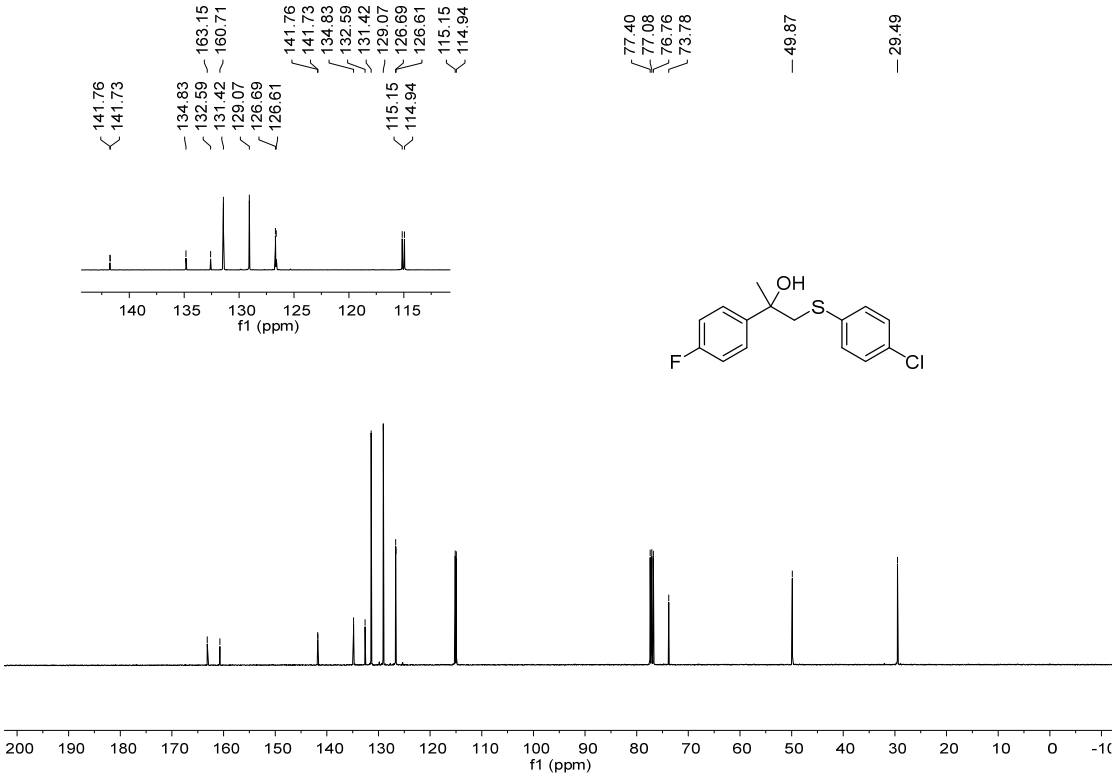
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **16**



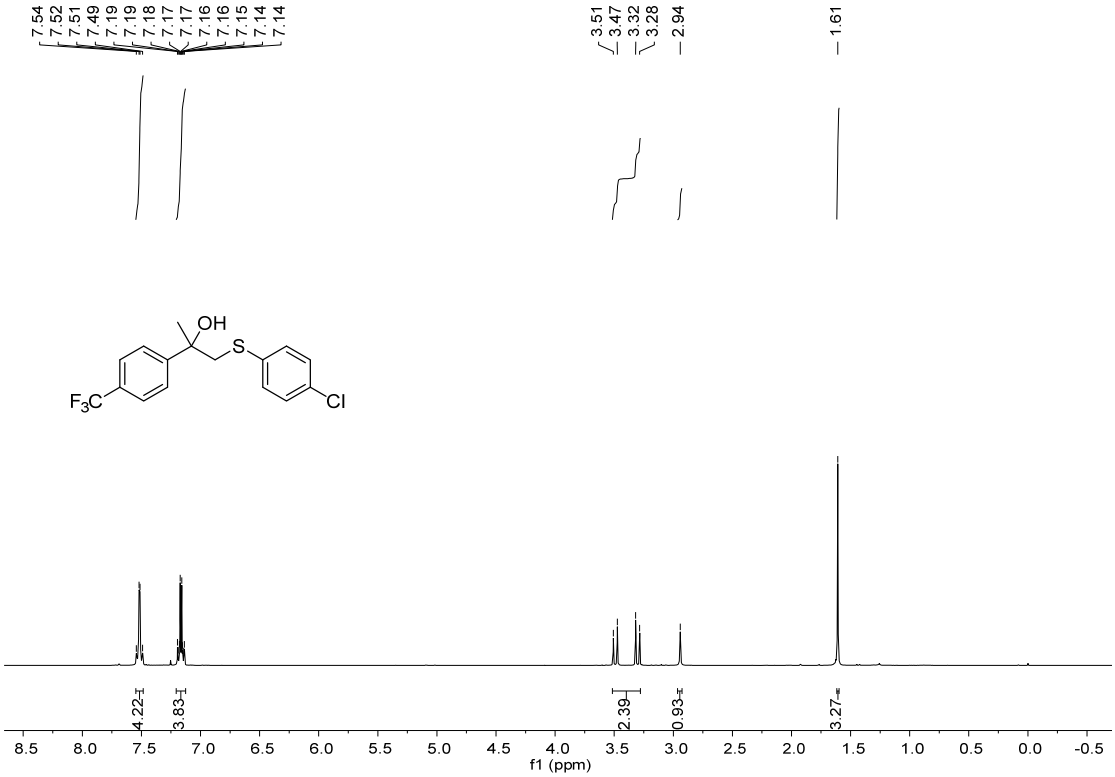
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **17**



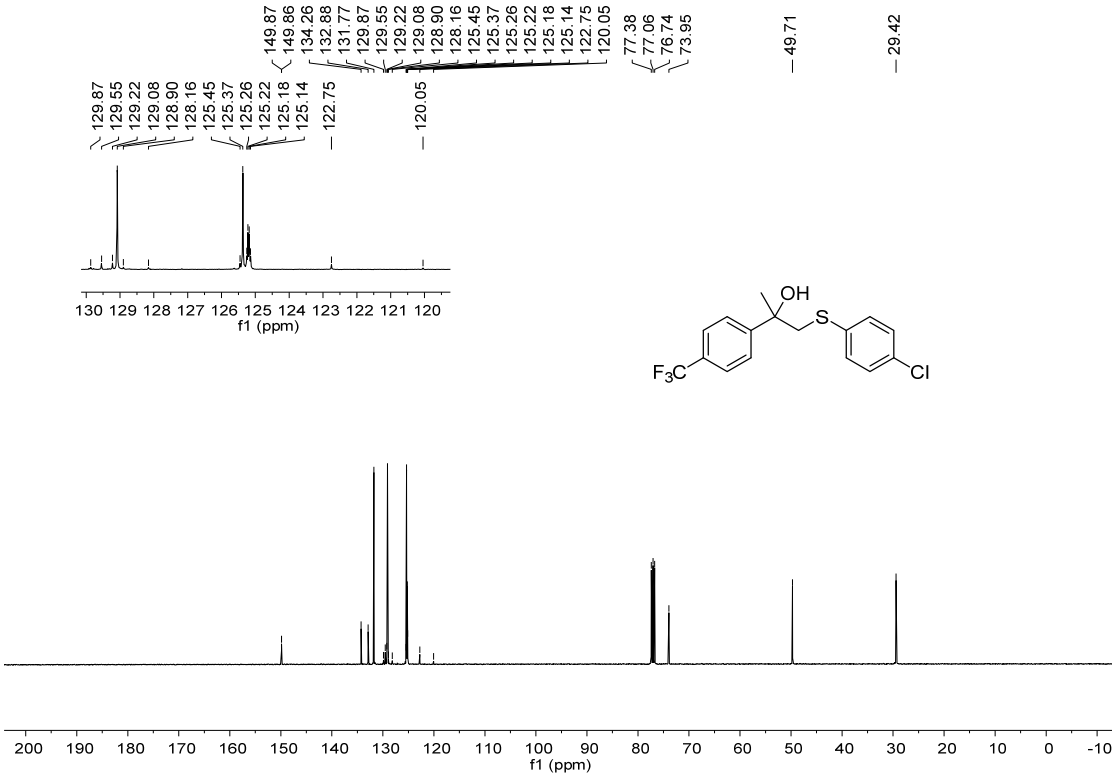
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **17**



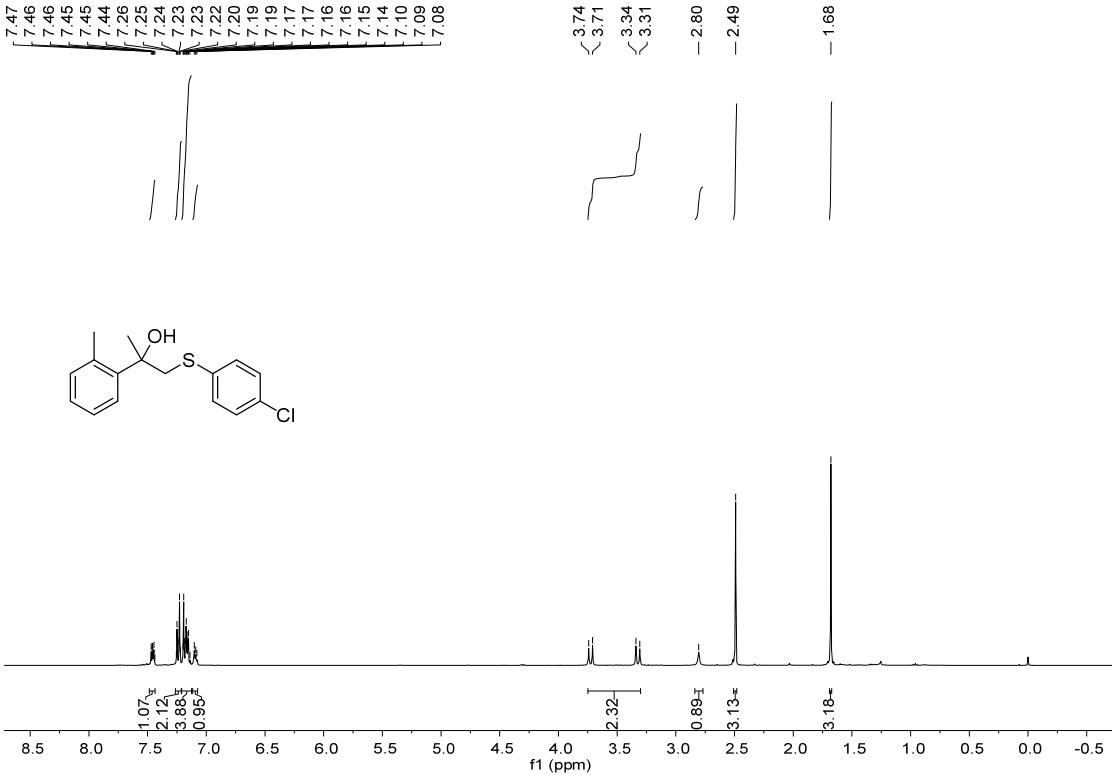
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **18**



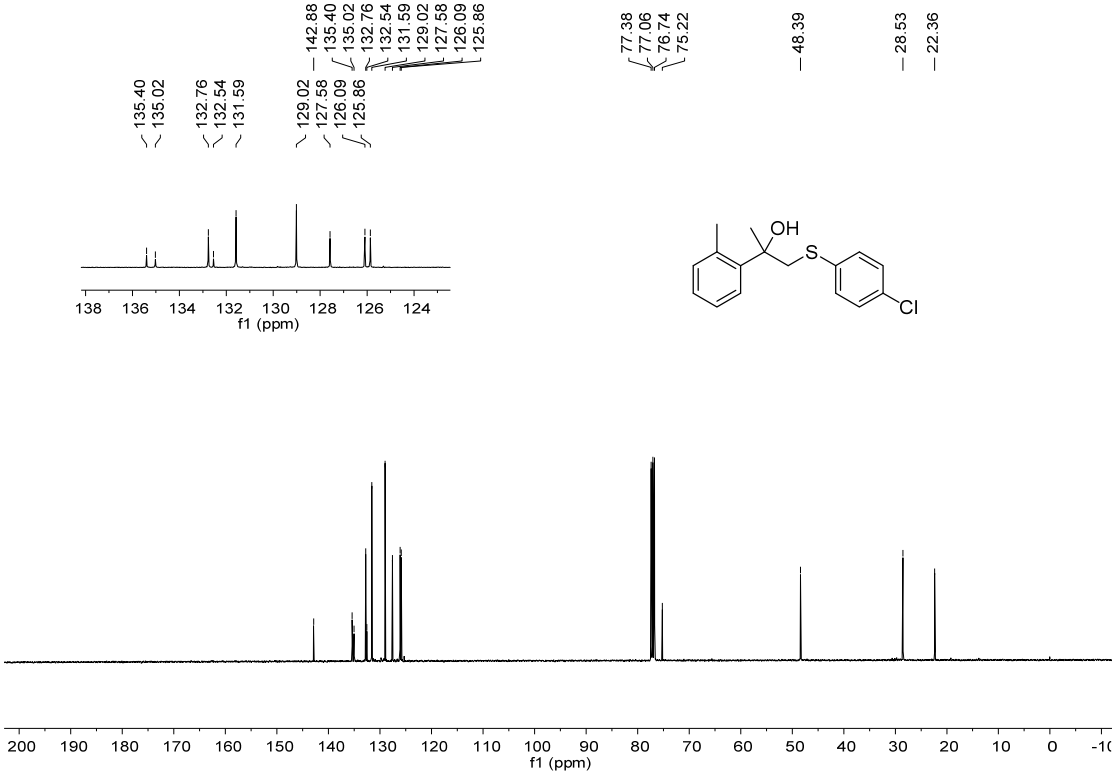
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **18**



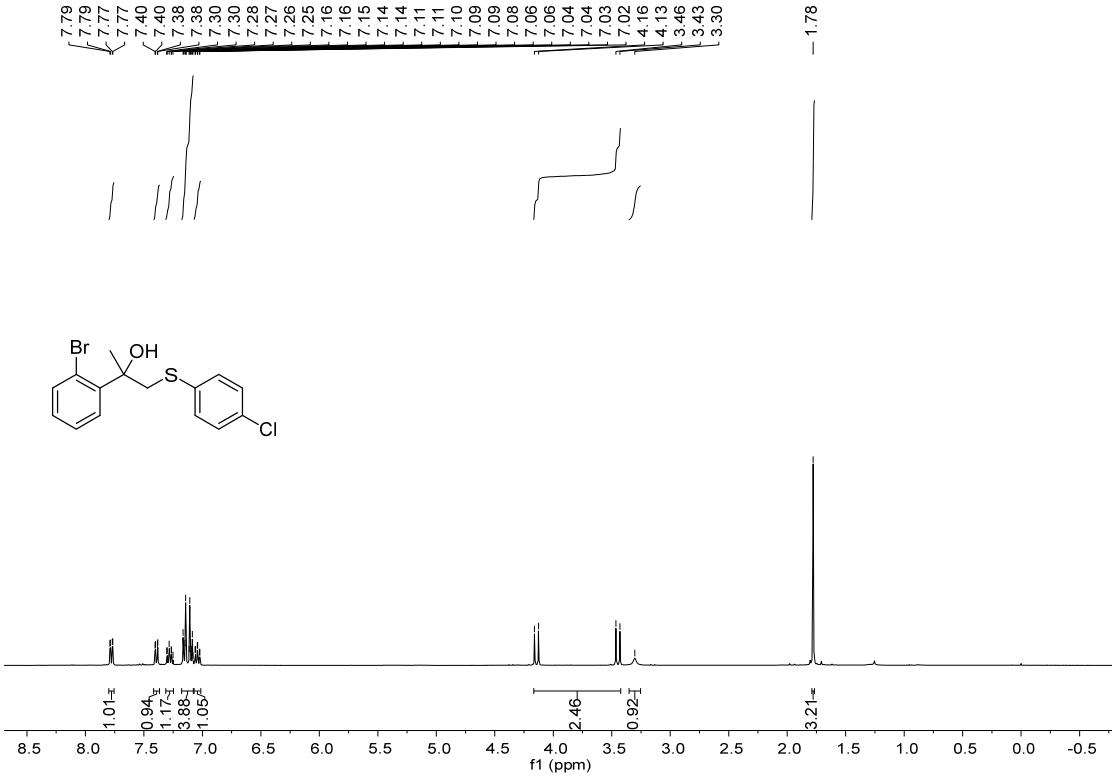
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **19**



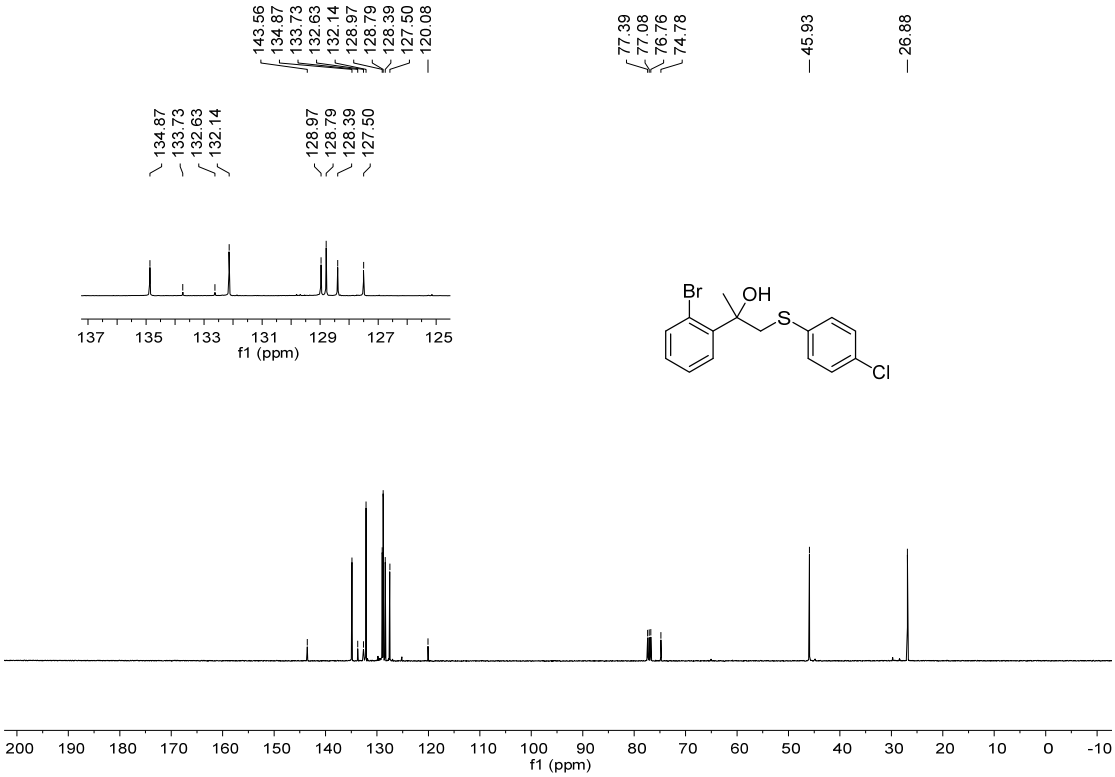
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **19**



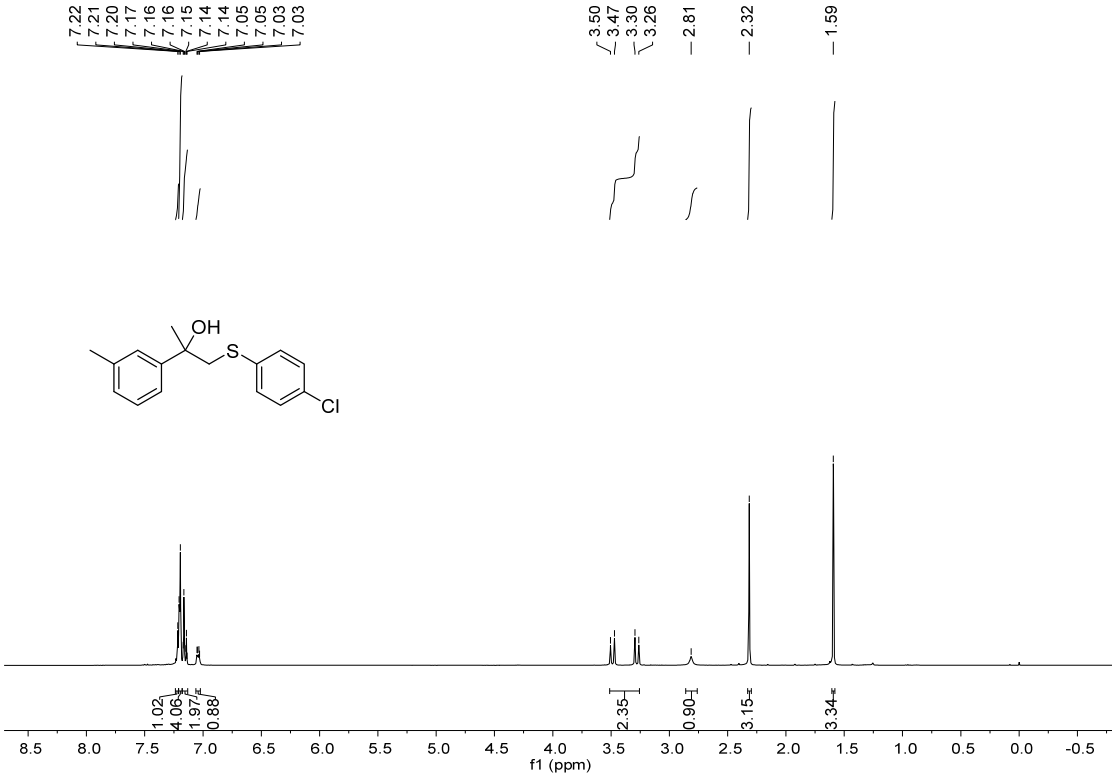
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **20**



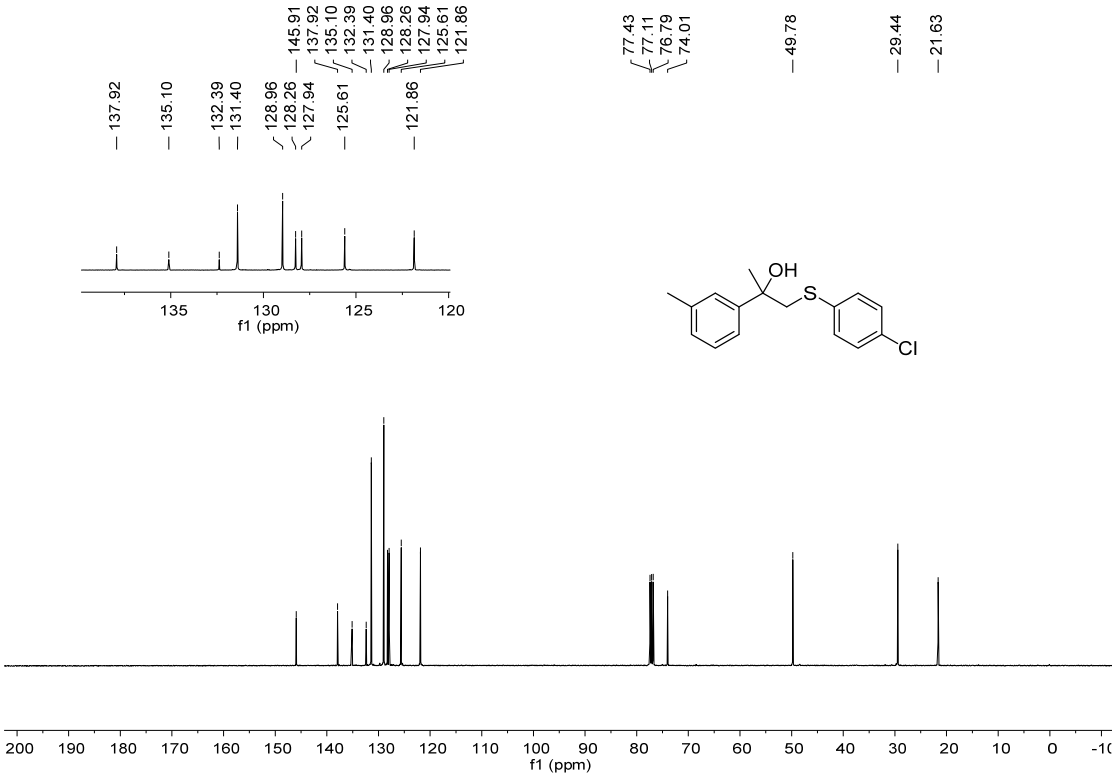
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **20**



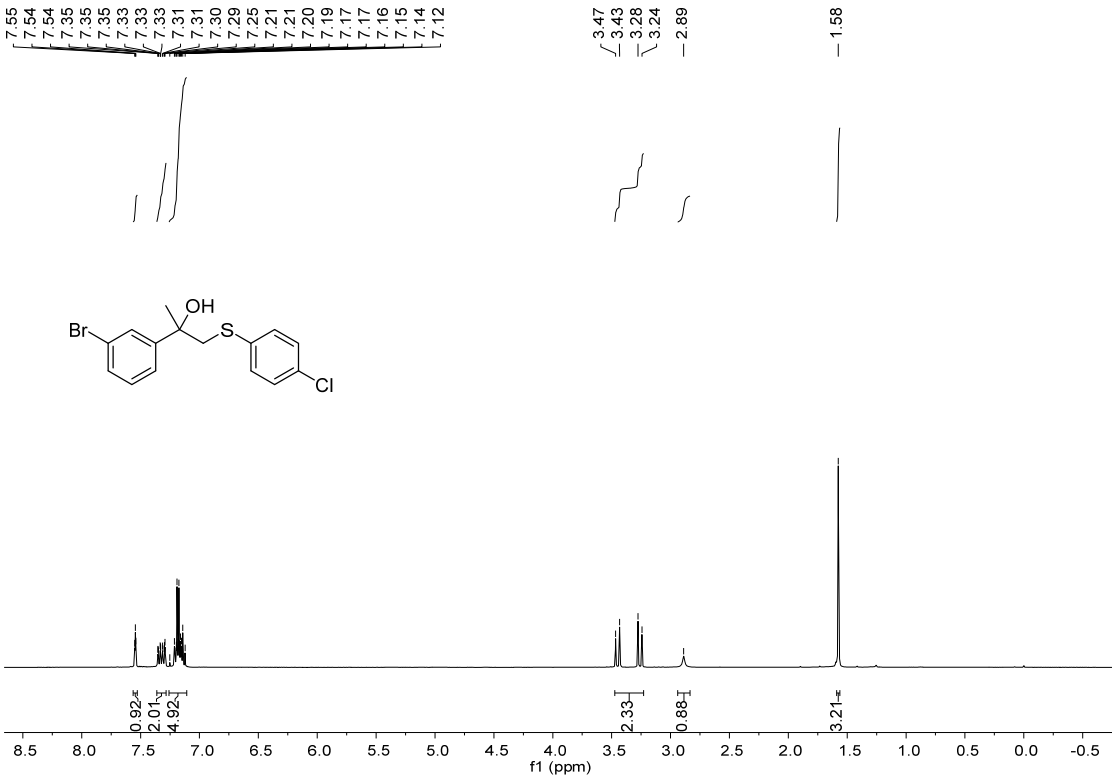
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **21**



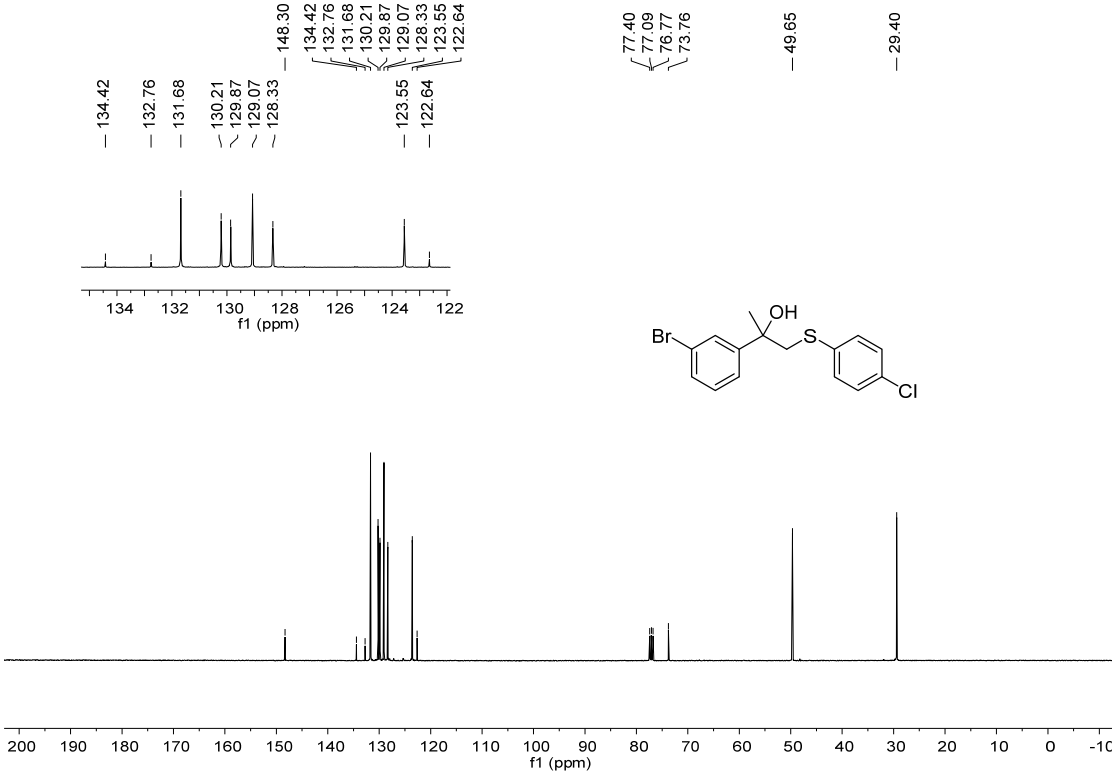
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **21**



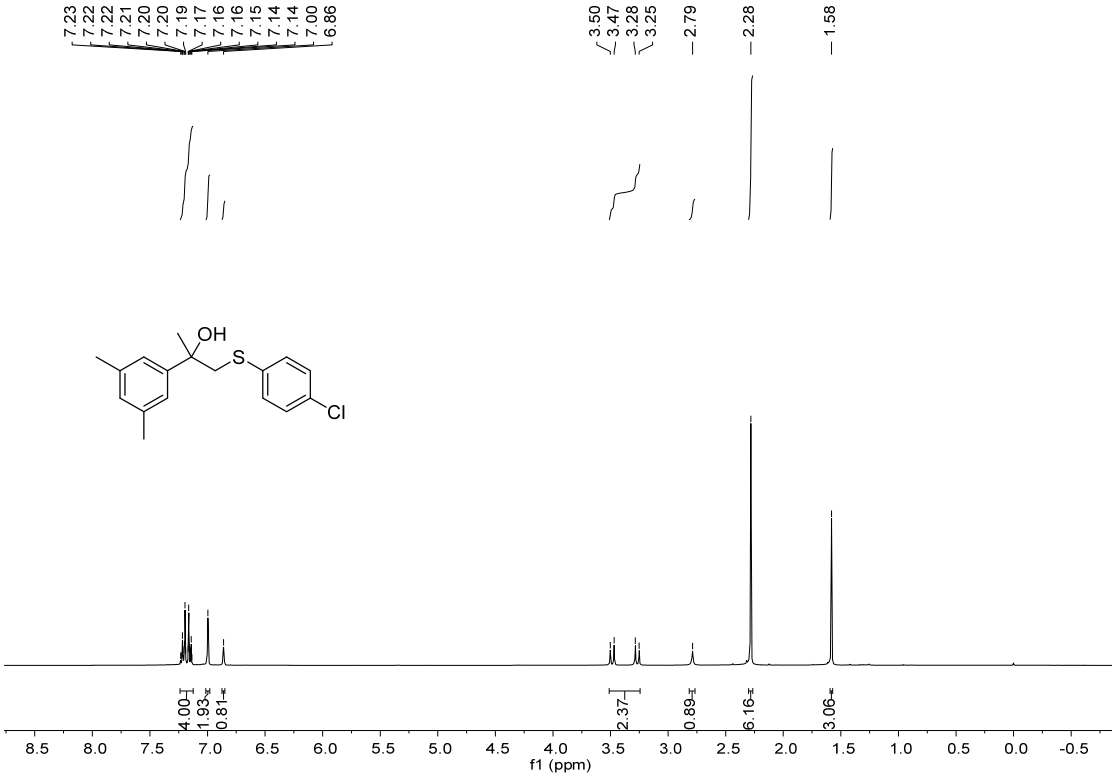
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **22**



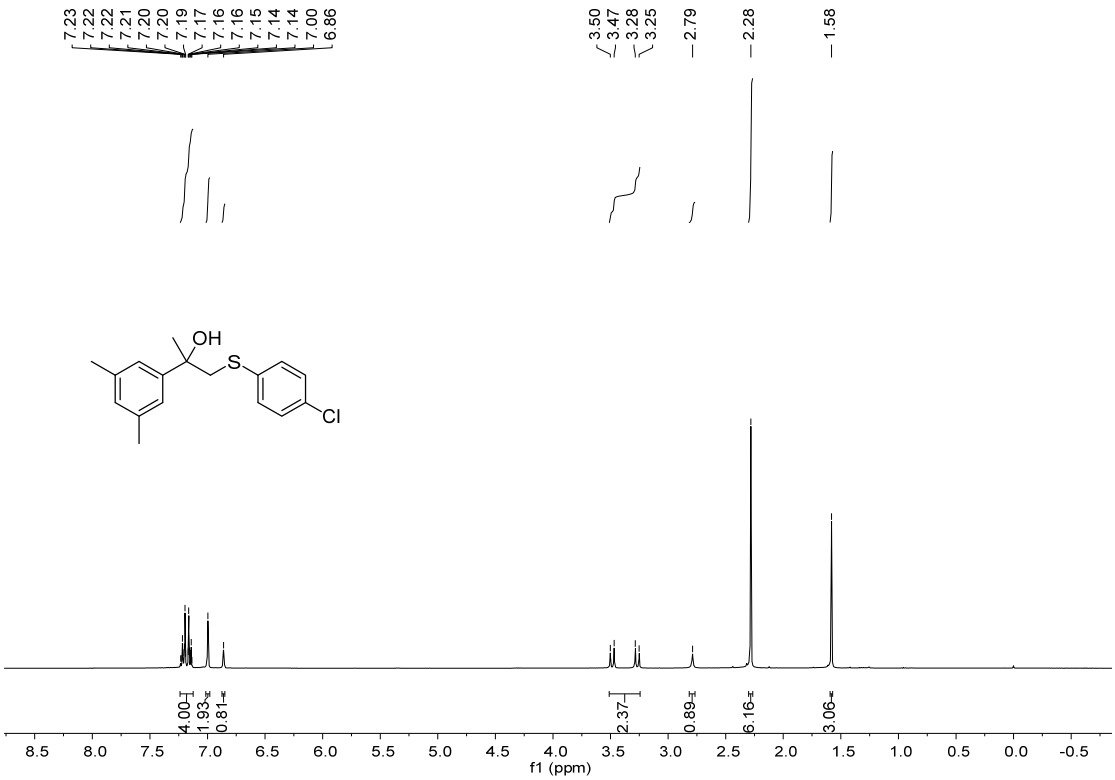
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **22**



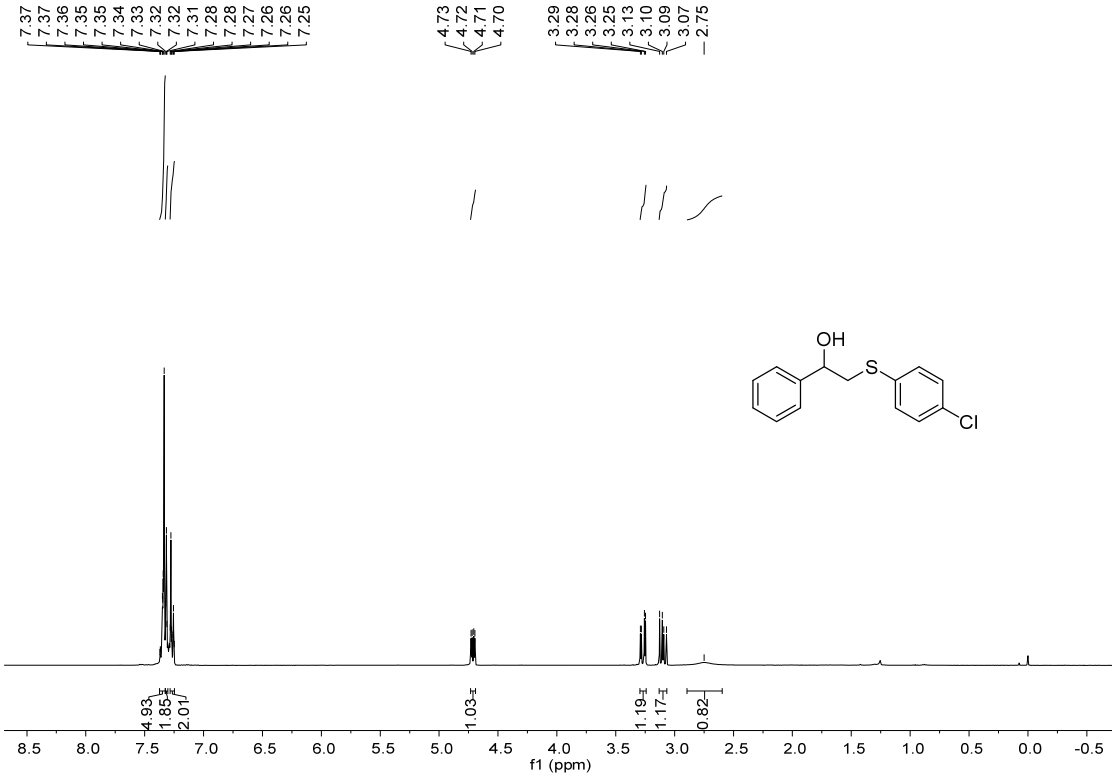
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **23**



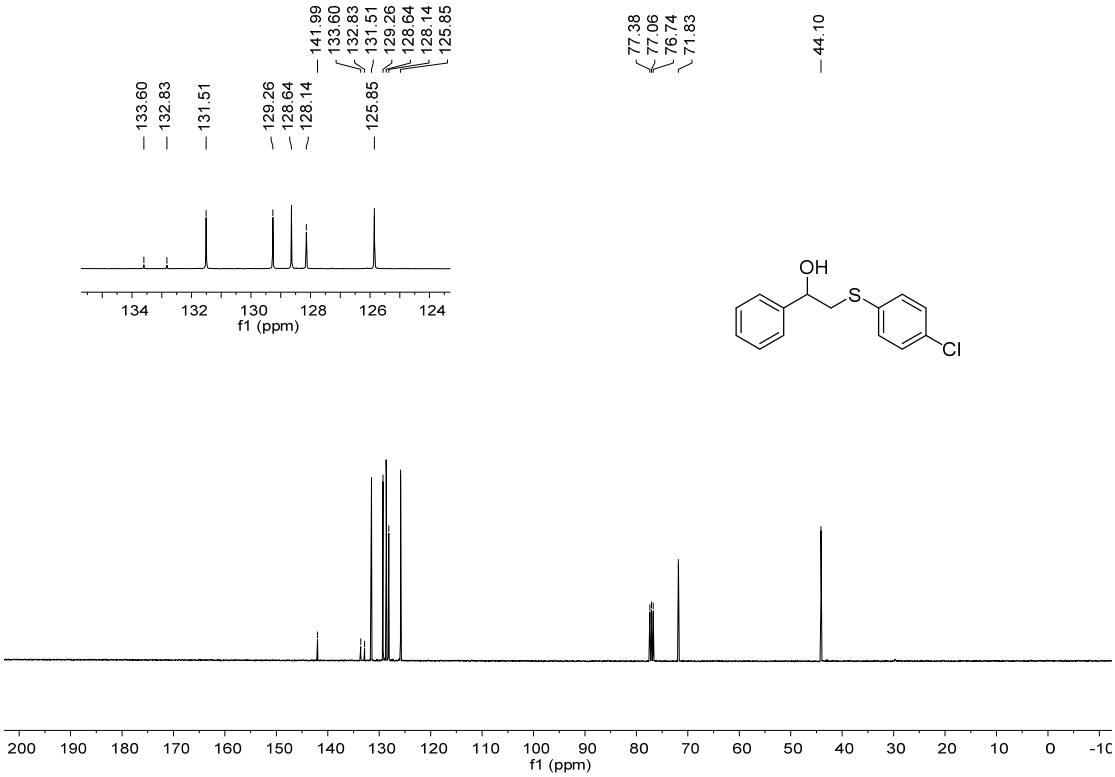
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **23**



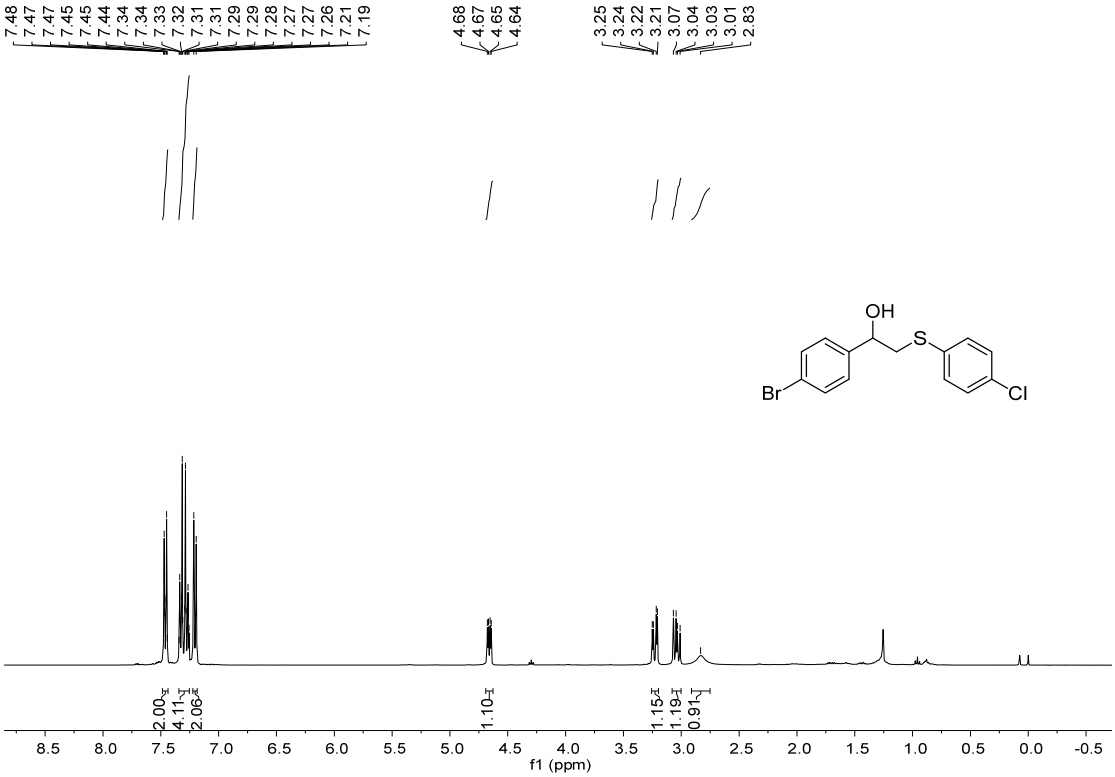
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **24**



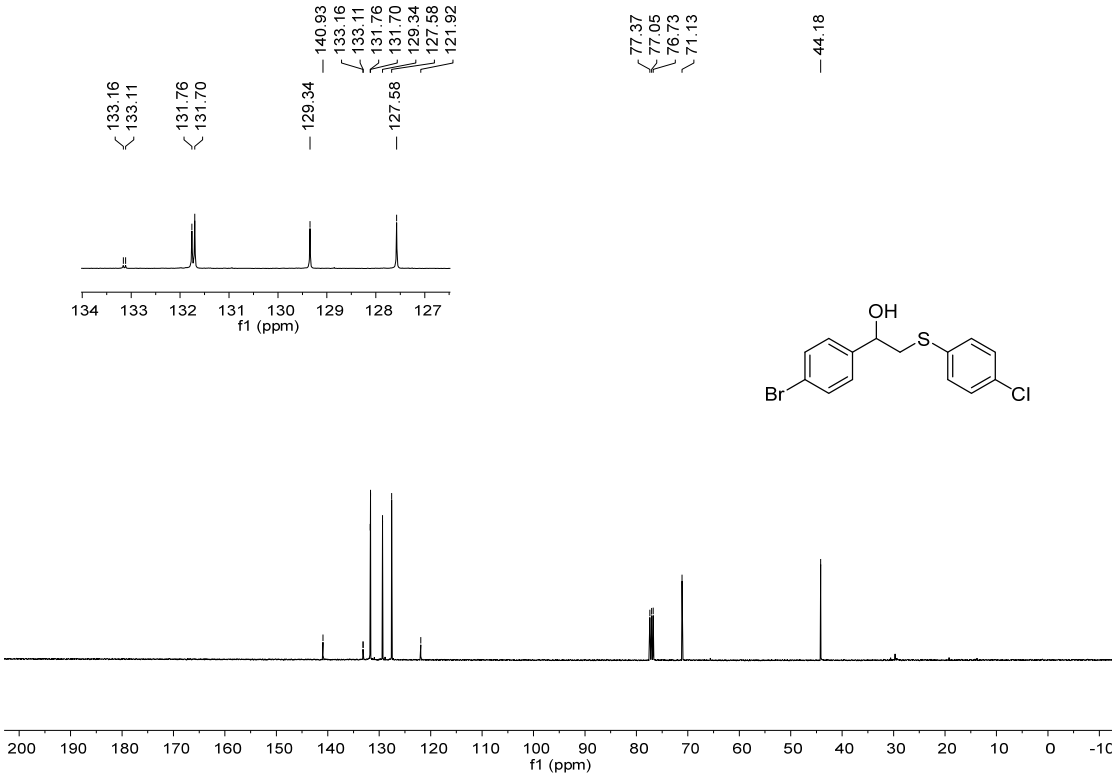
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **24**



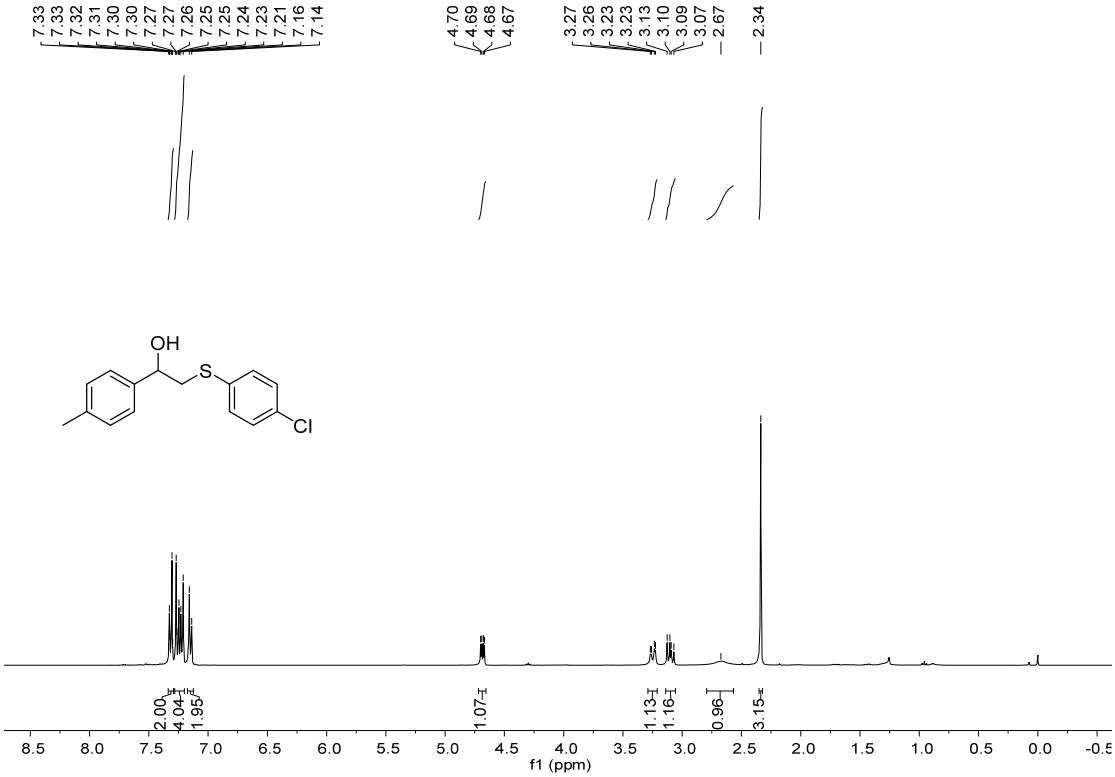
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **25**



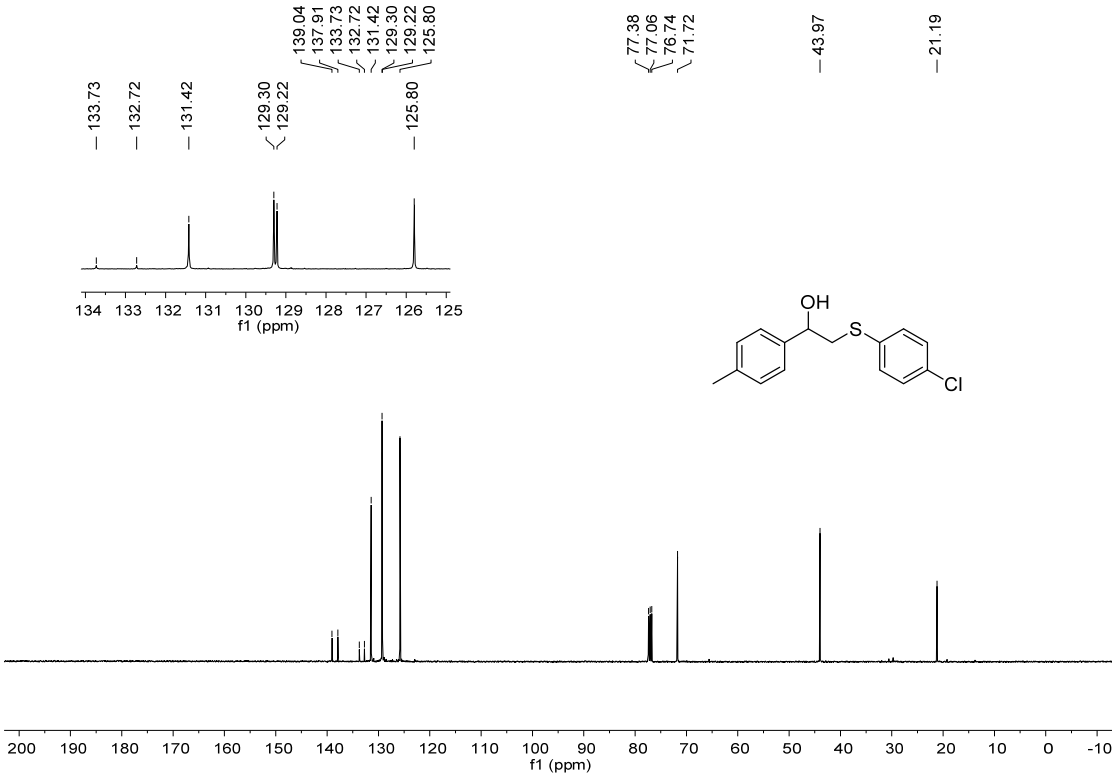
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **25**



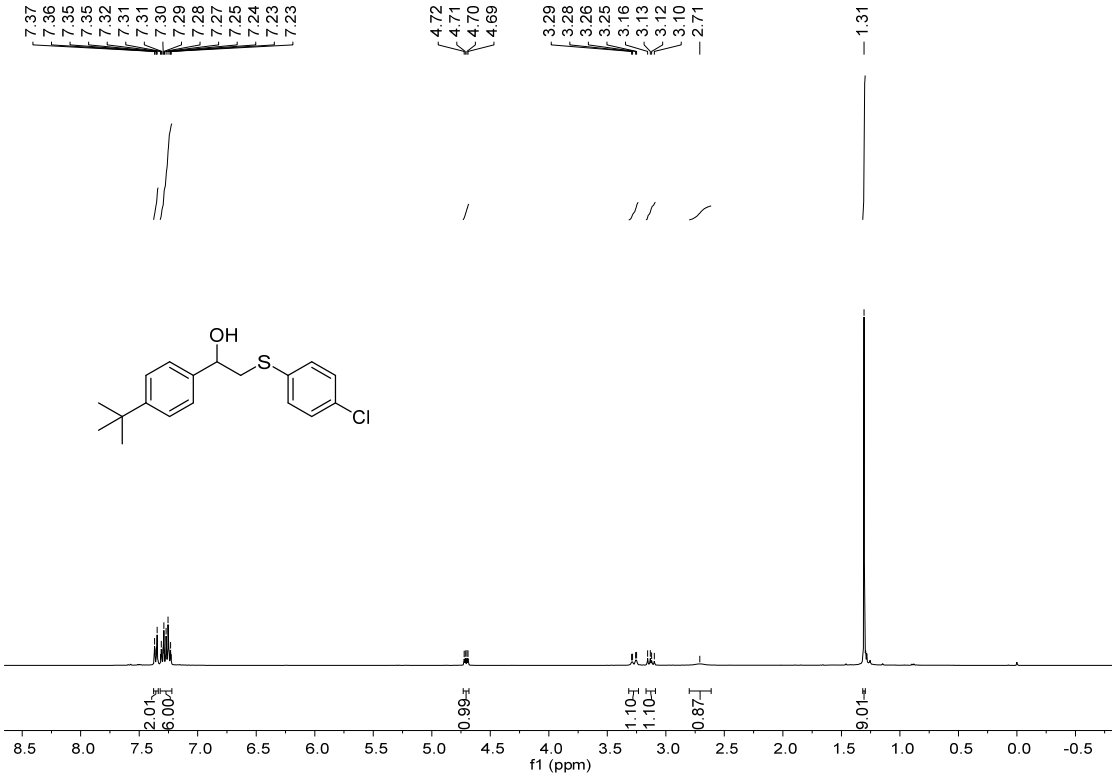
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **26**



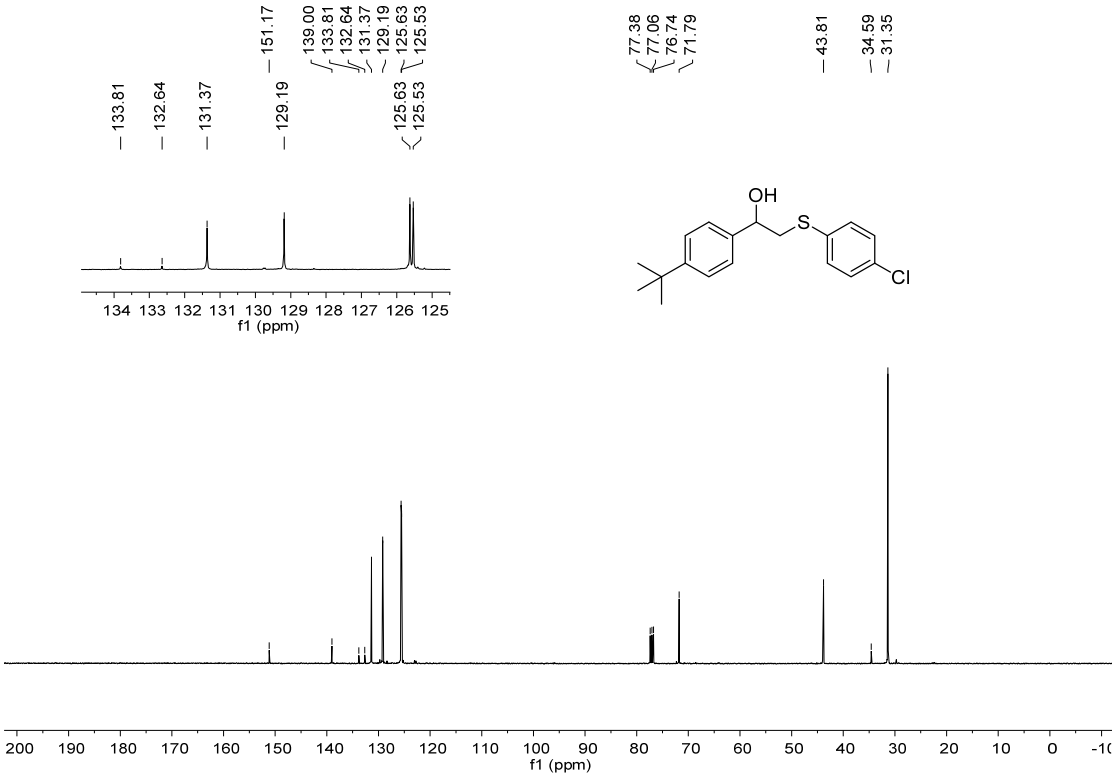
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **26**



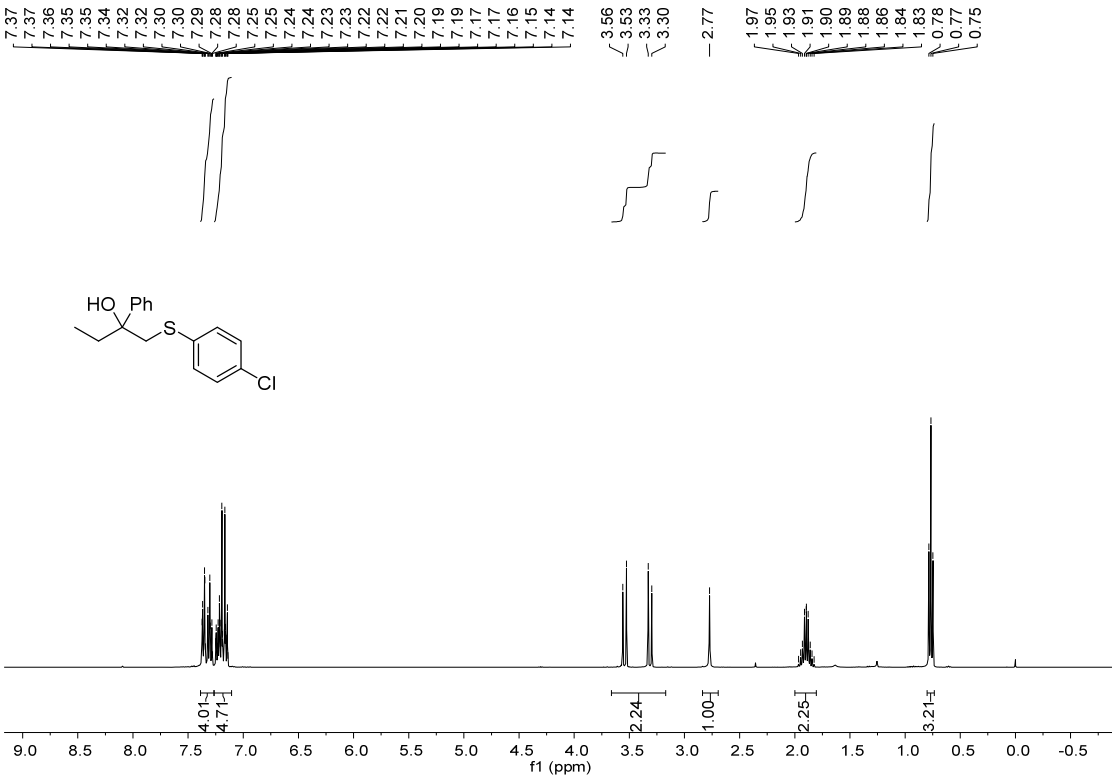
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **27**



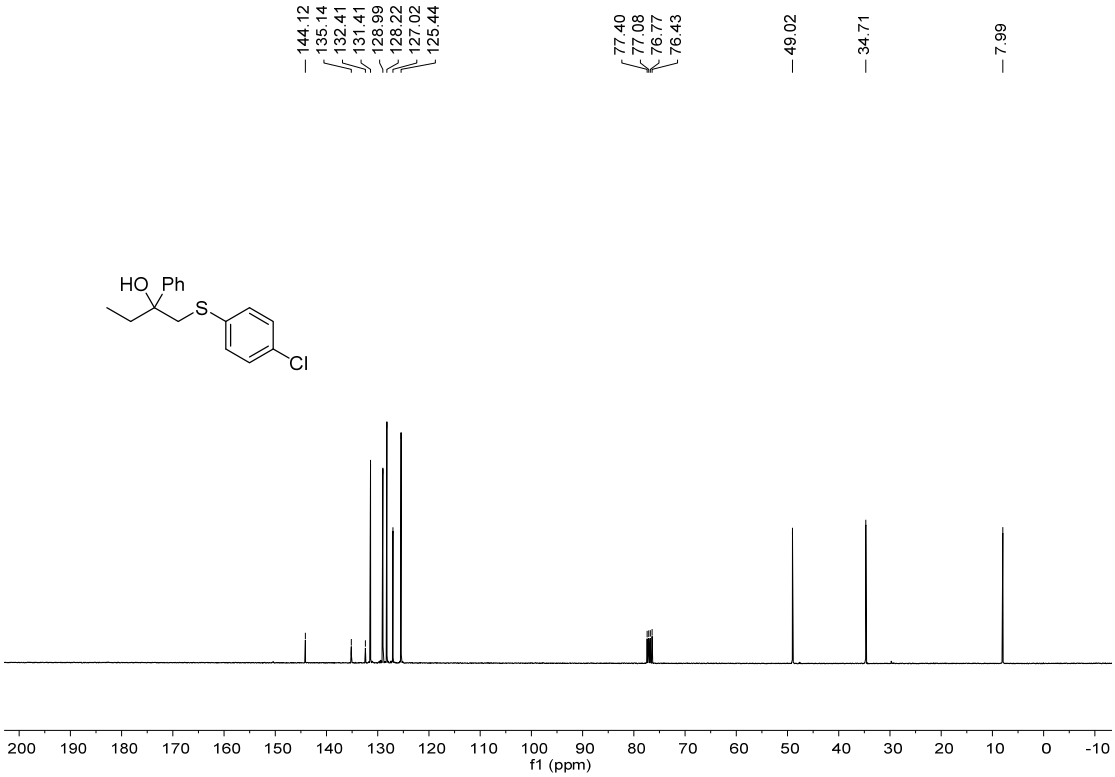
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **27**



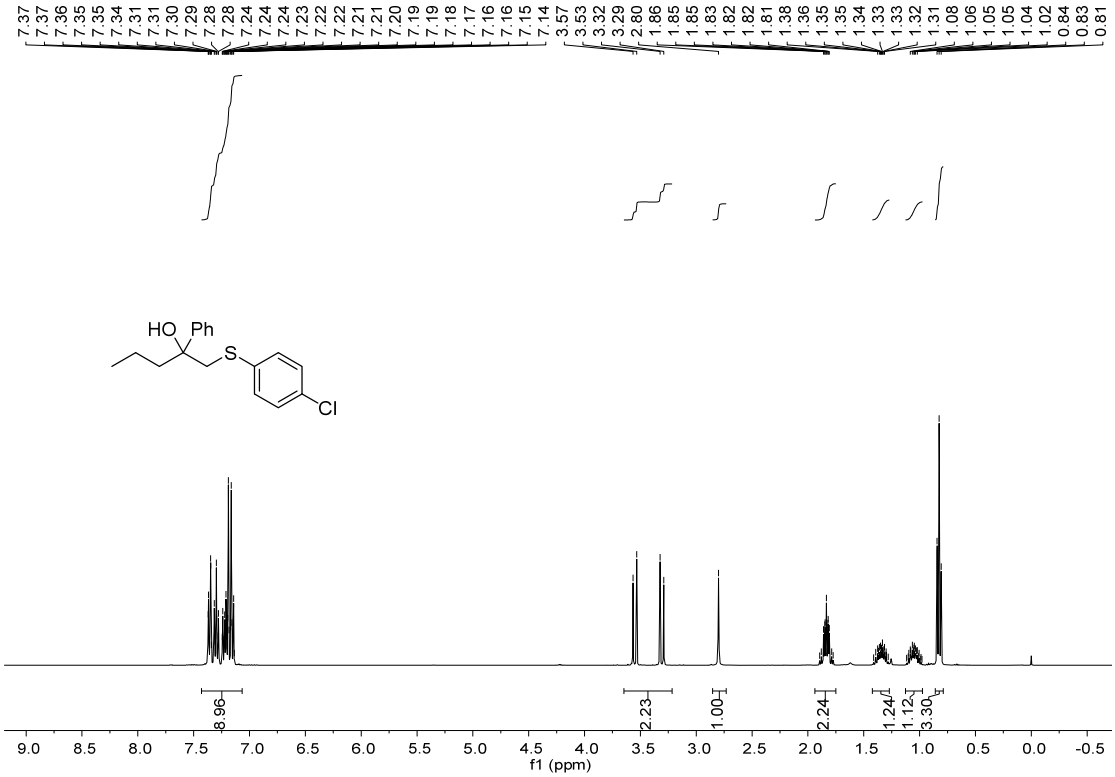
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **28**



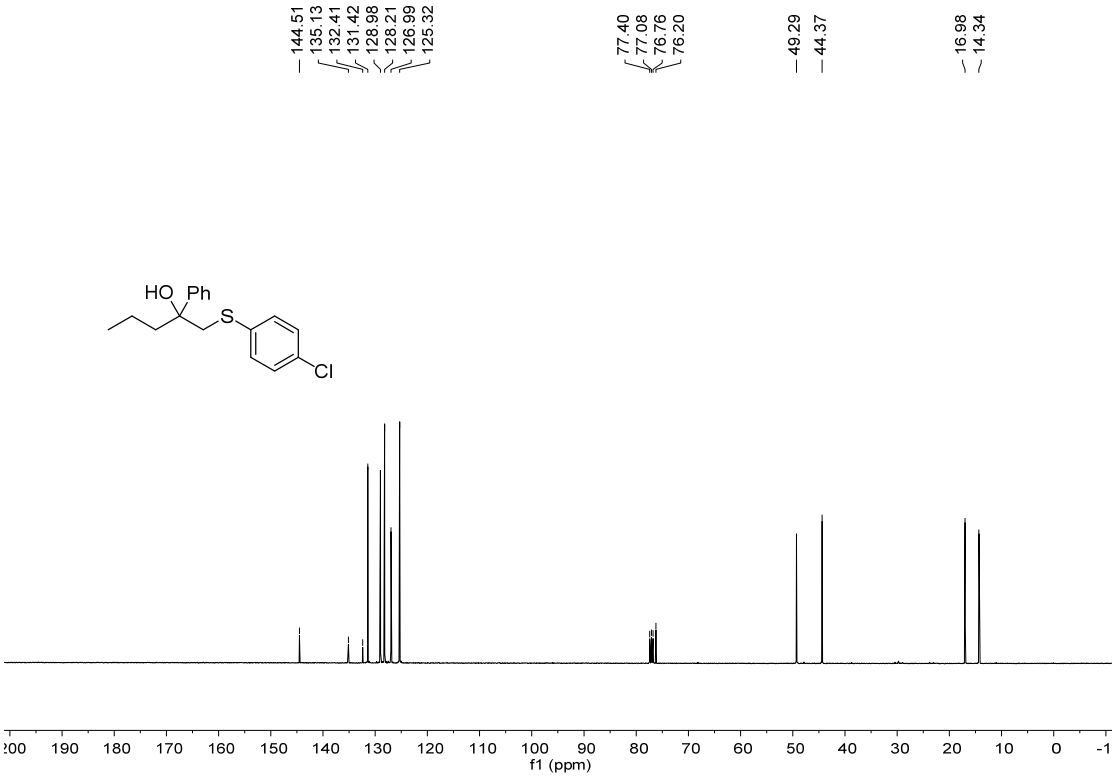
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **28**



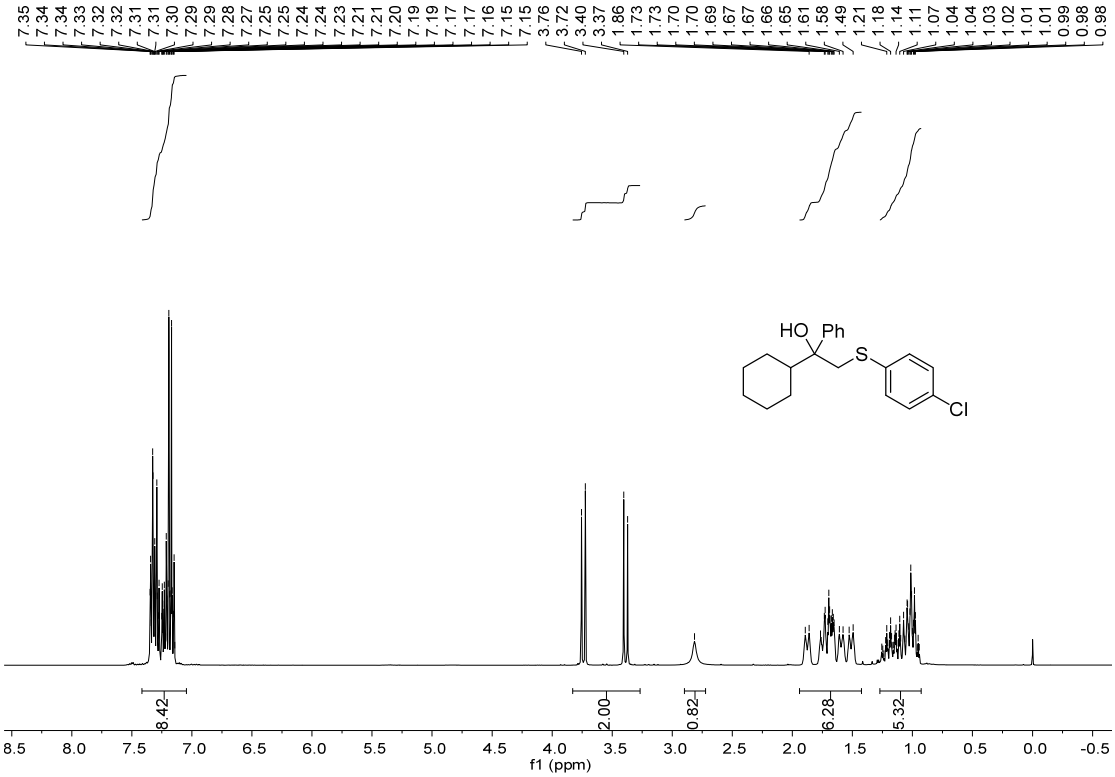
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **29**



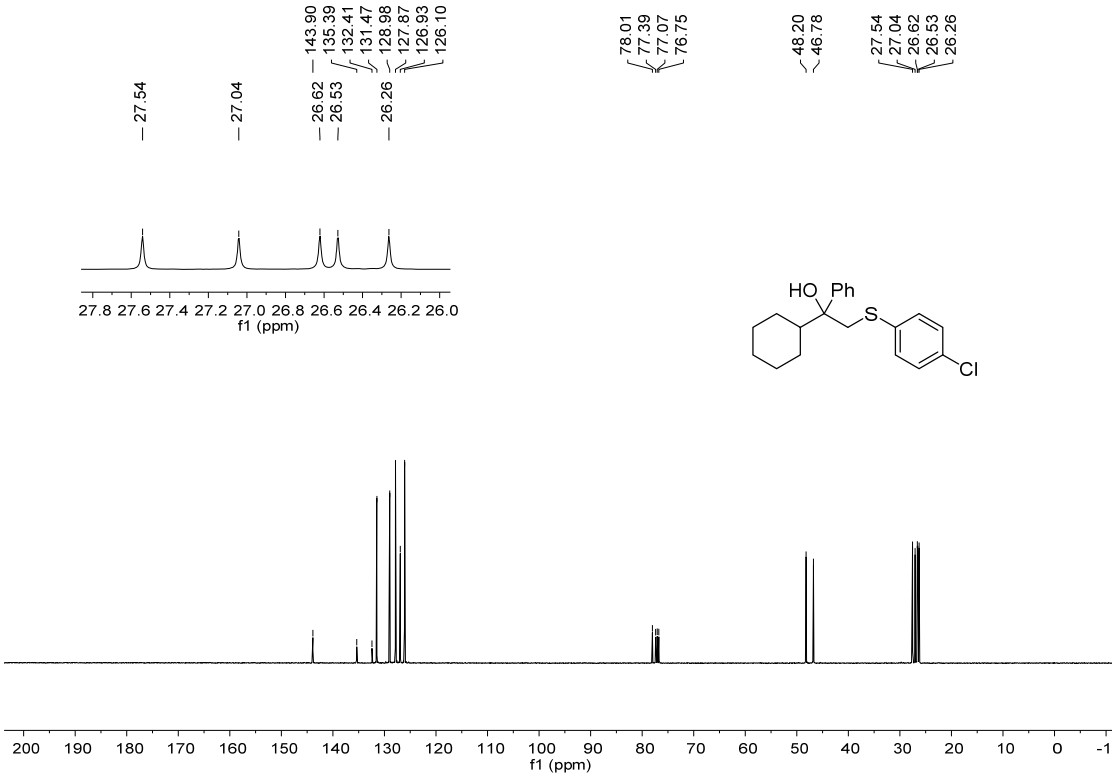
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **29**



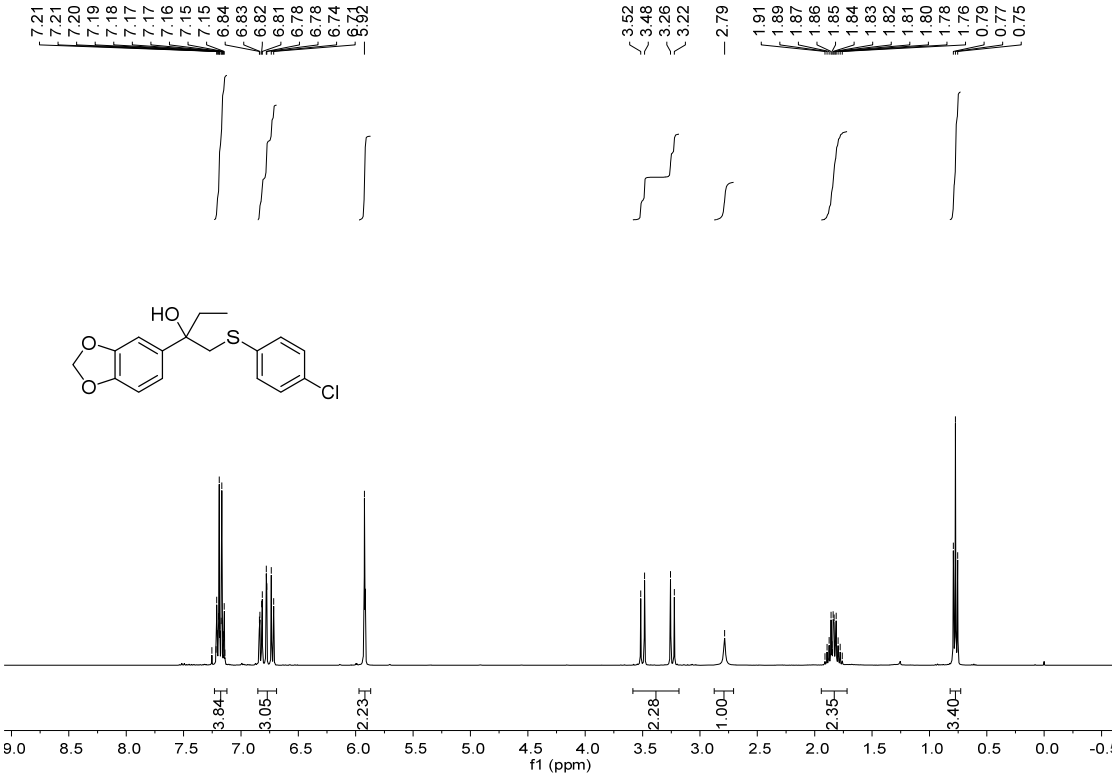
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **30**



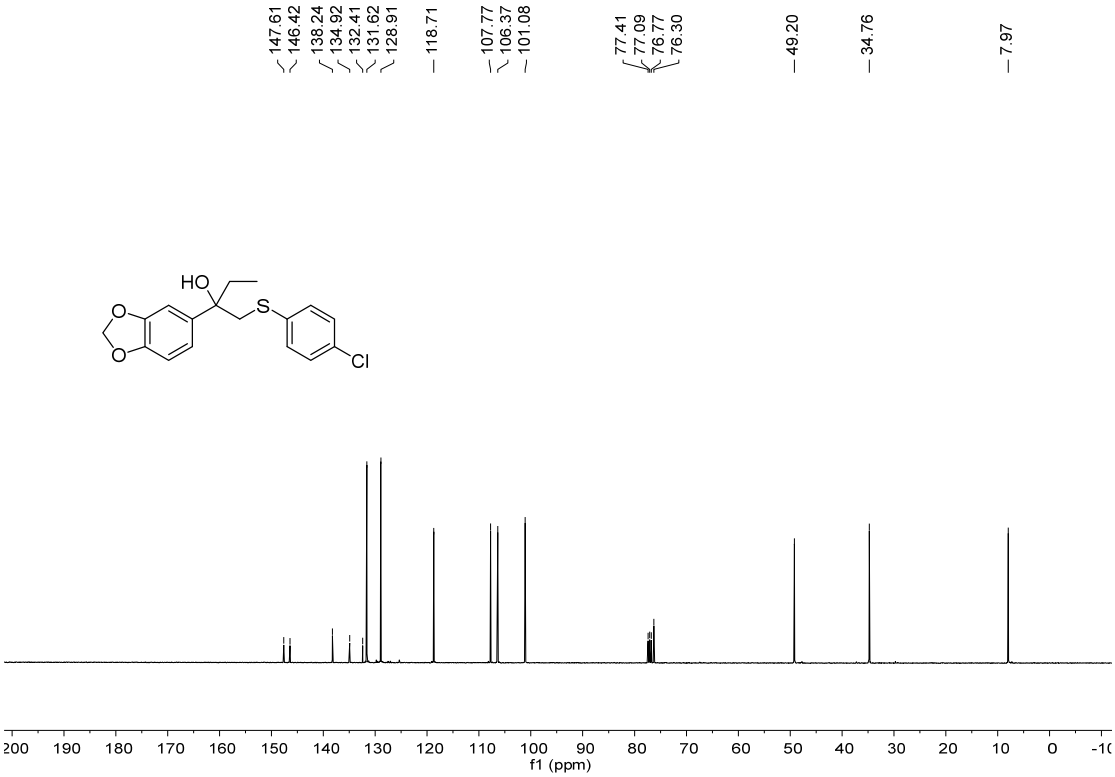
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **30**



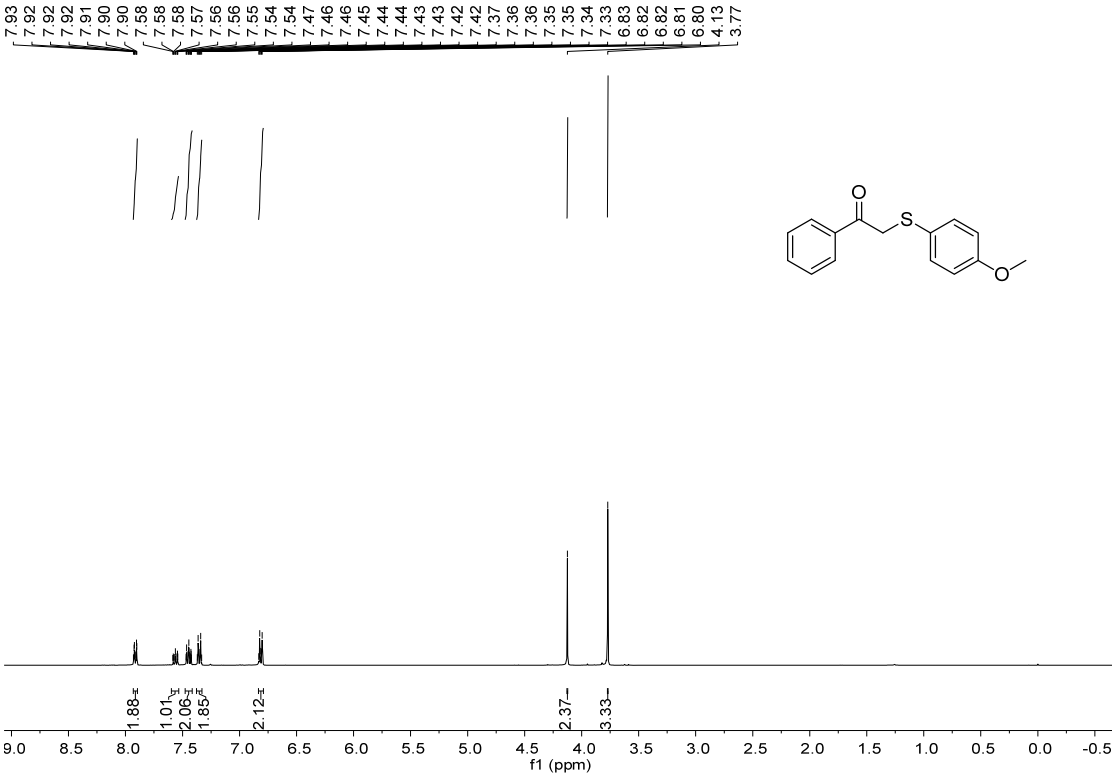
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **31**



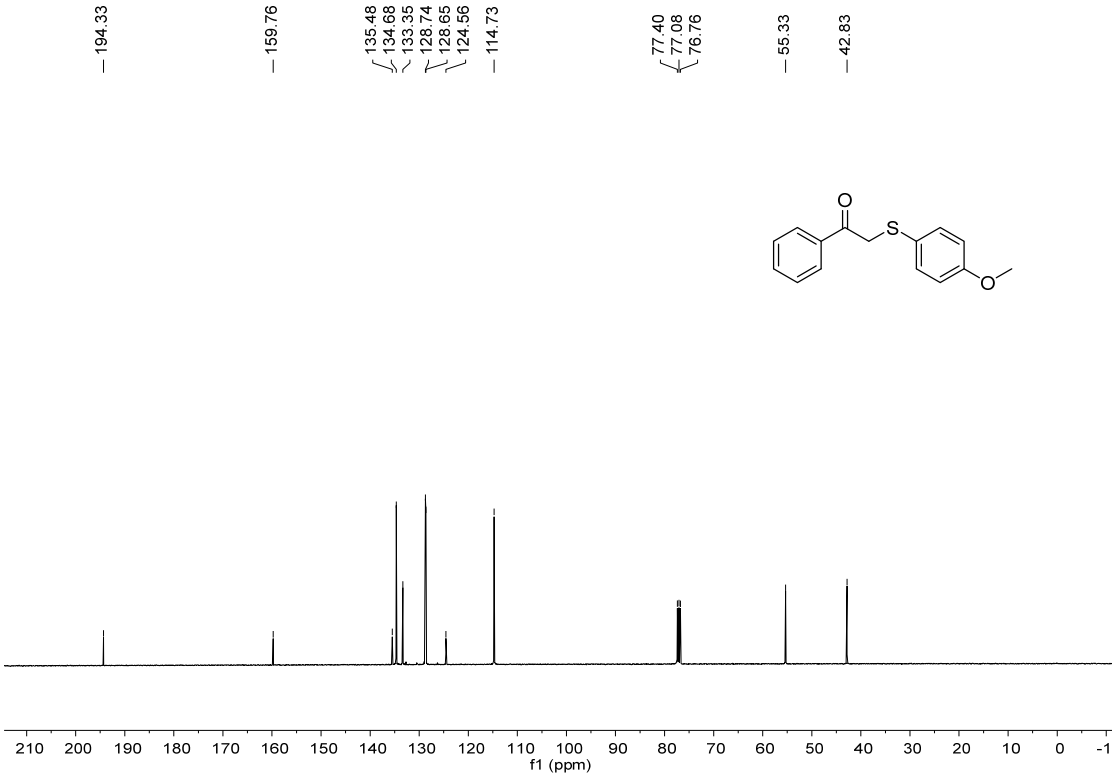
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **31**



^{1}H NMR (400 MHz, $CDCl_3$) spectra of **32**

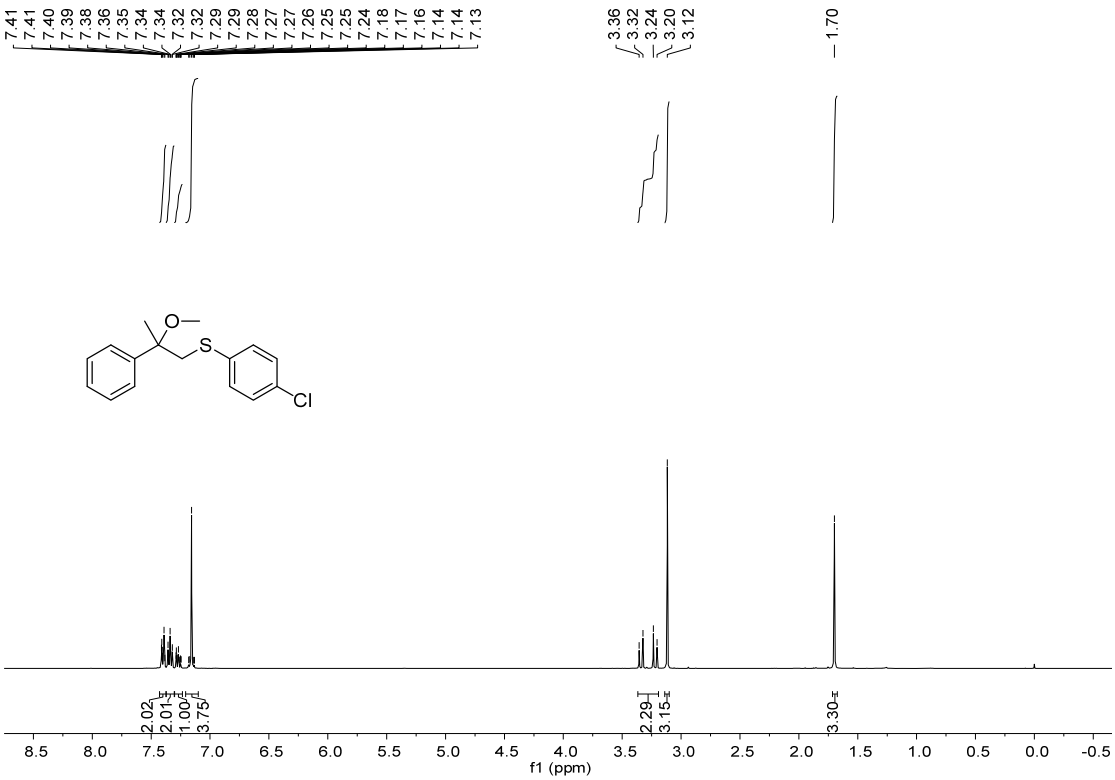


^{13}C NMR (101 MHz, $CDCl_3$) spectra of **32**

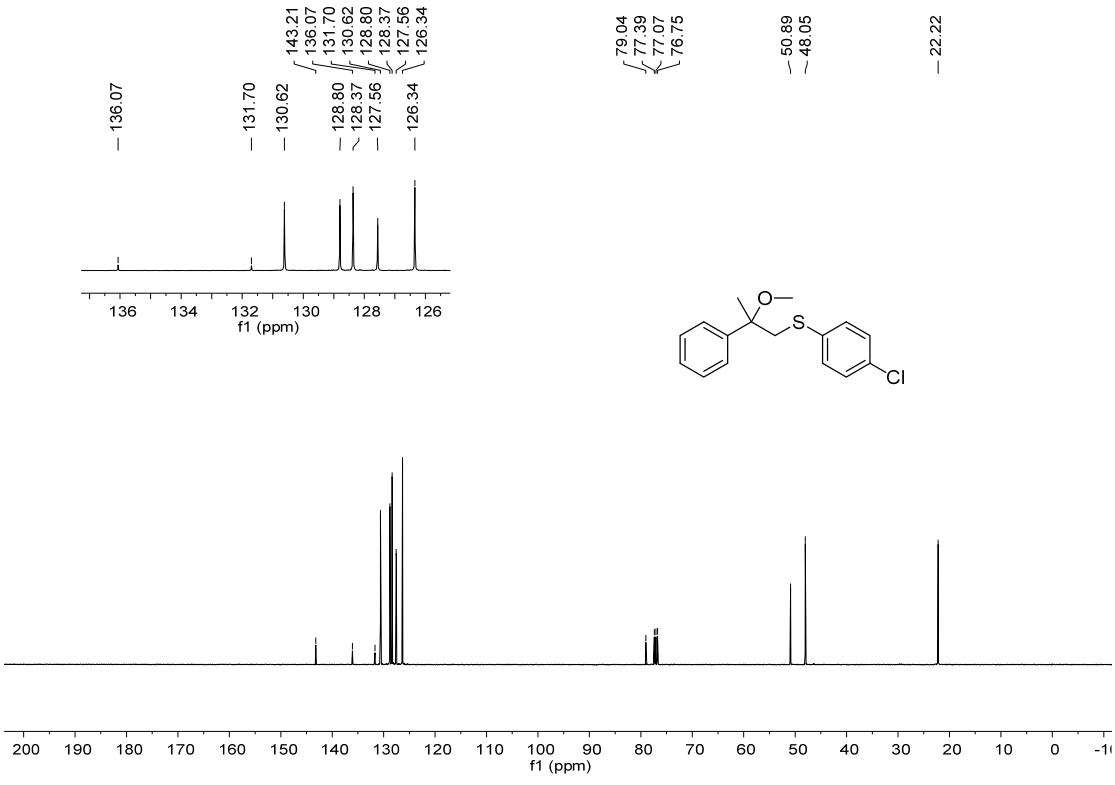


9.3. NMR spectra for ether products **35-39**

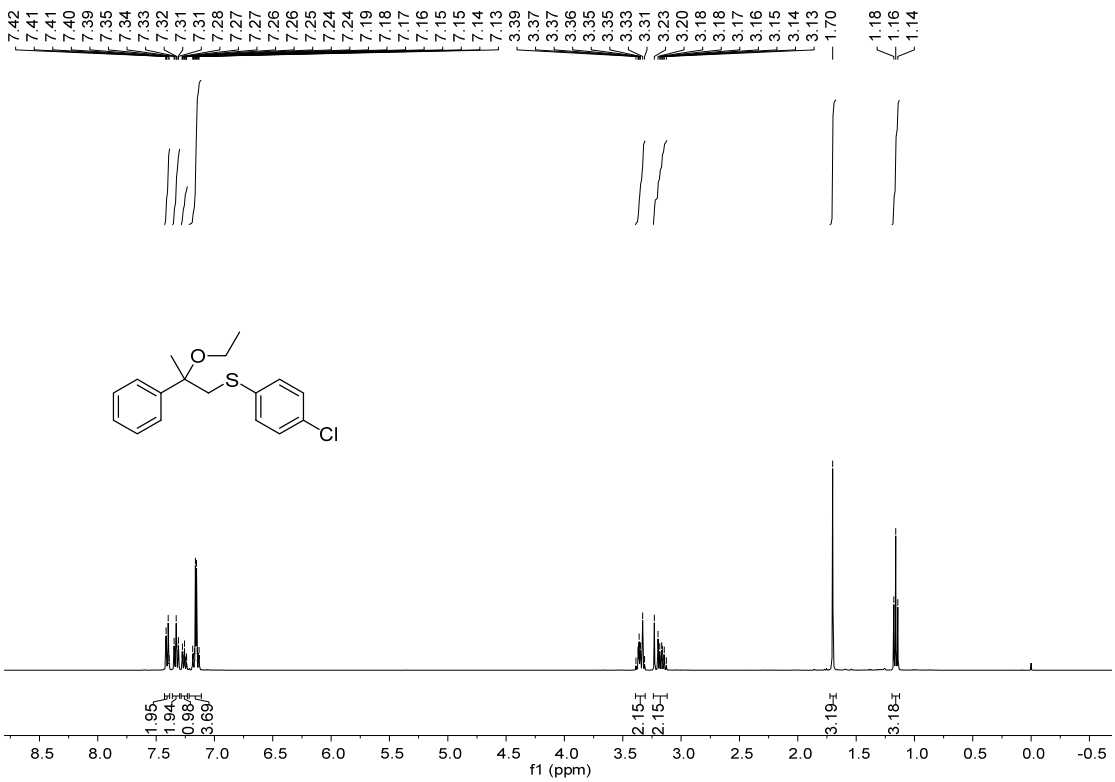
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **35**



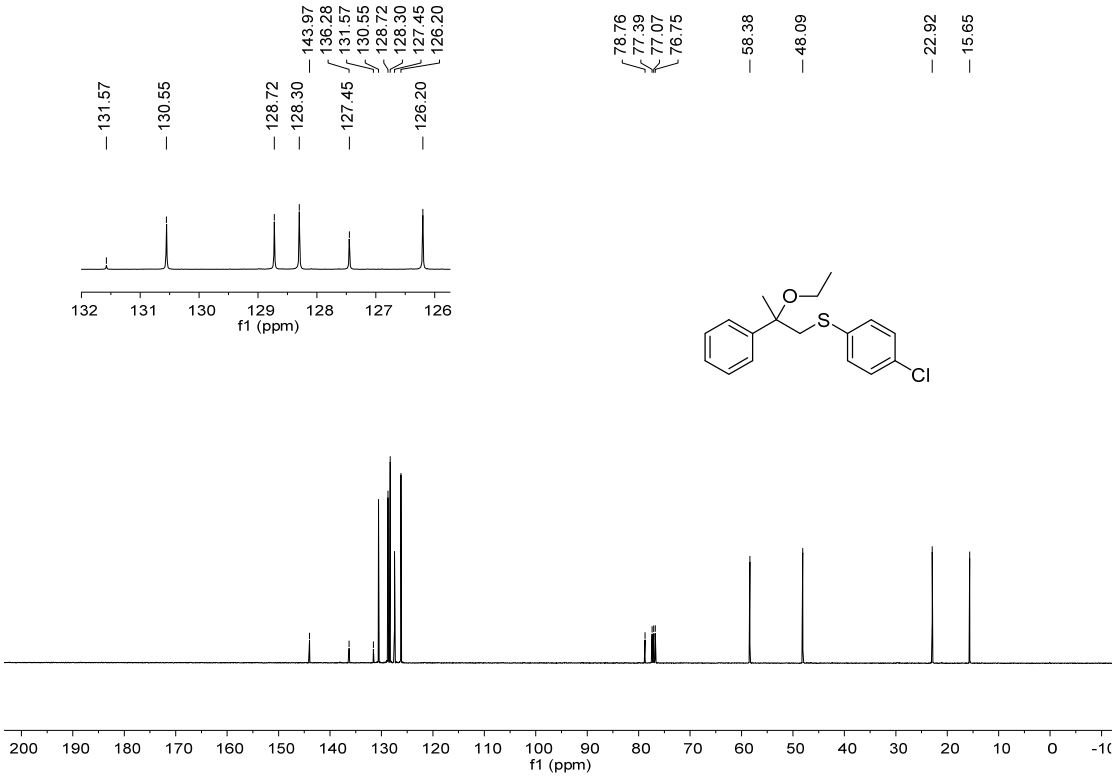
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **35**



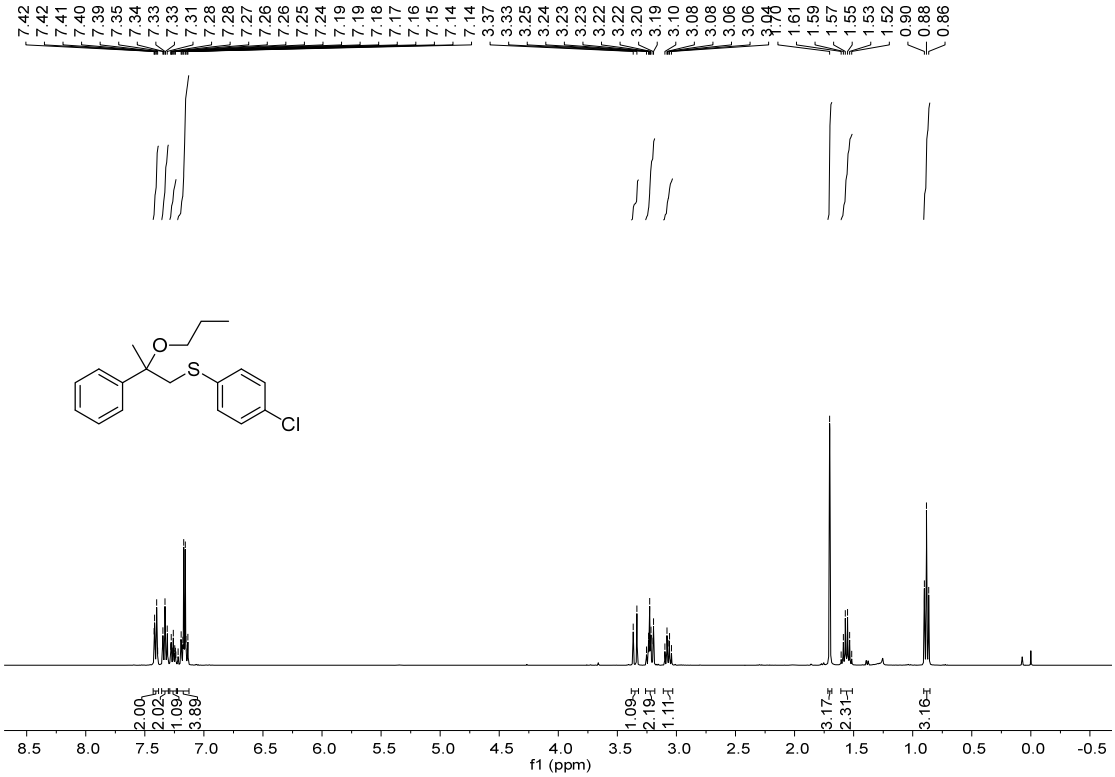
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **36**



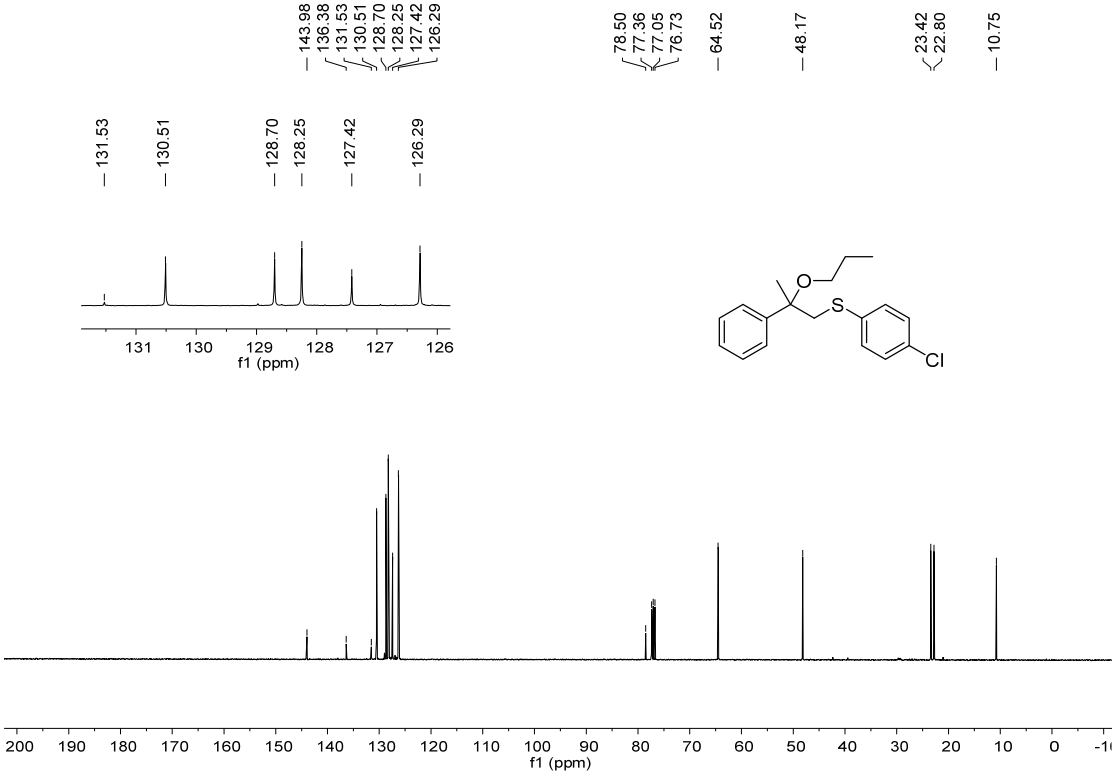
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **36**



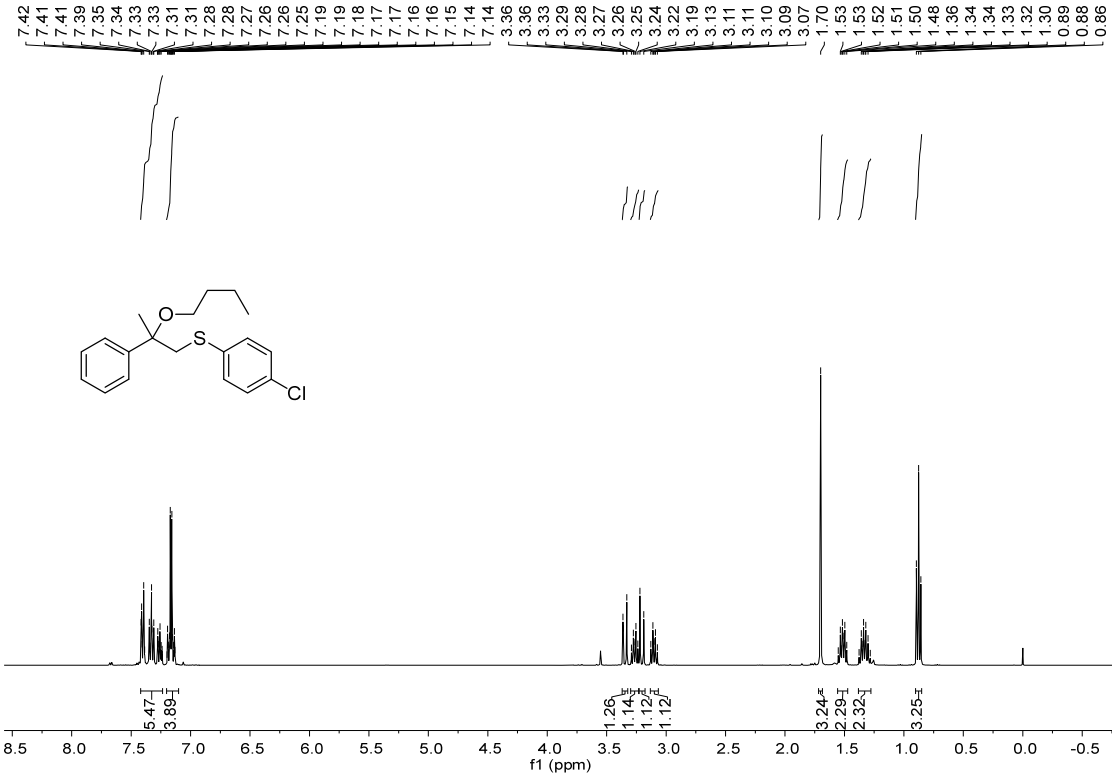
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **37**



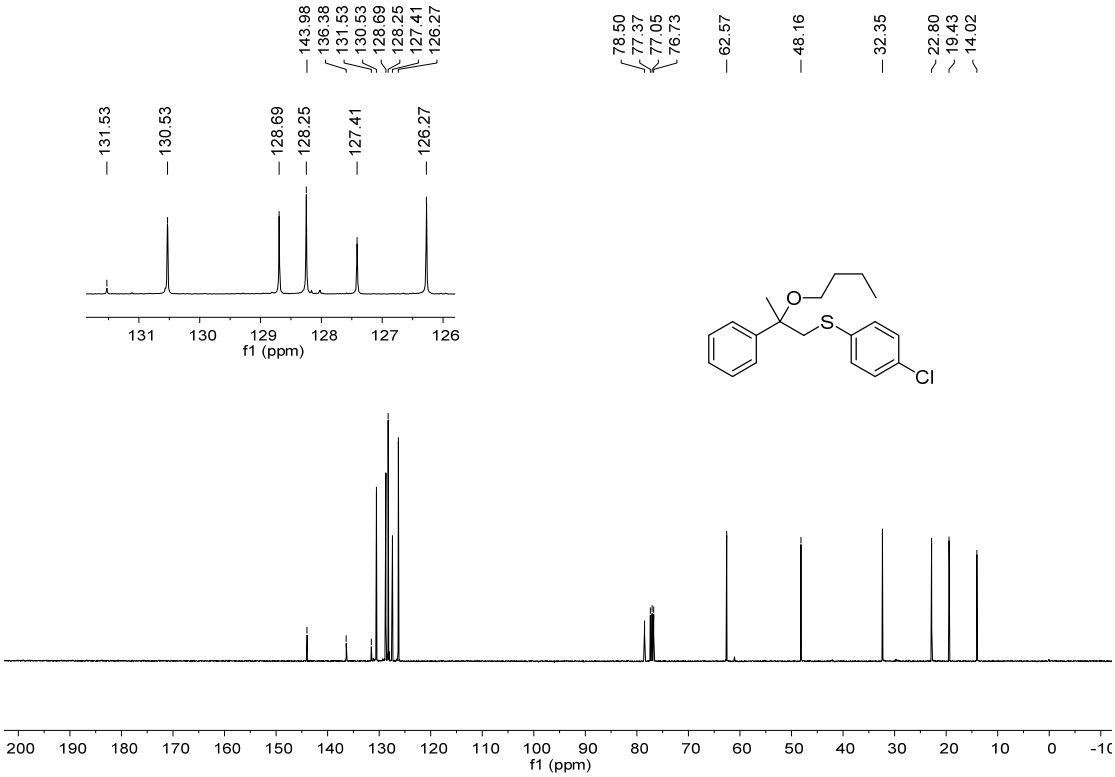
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **37**



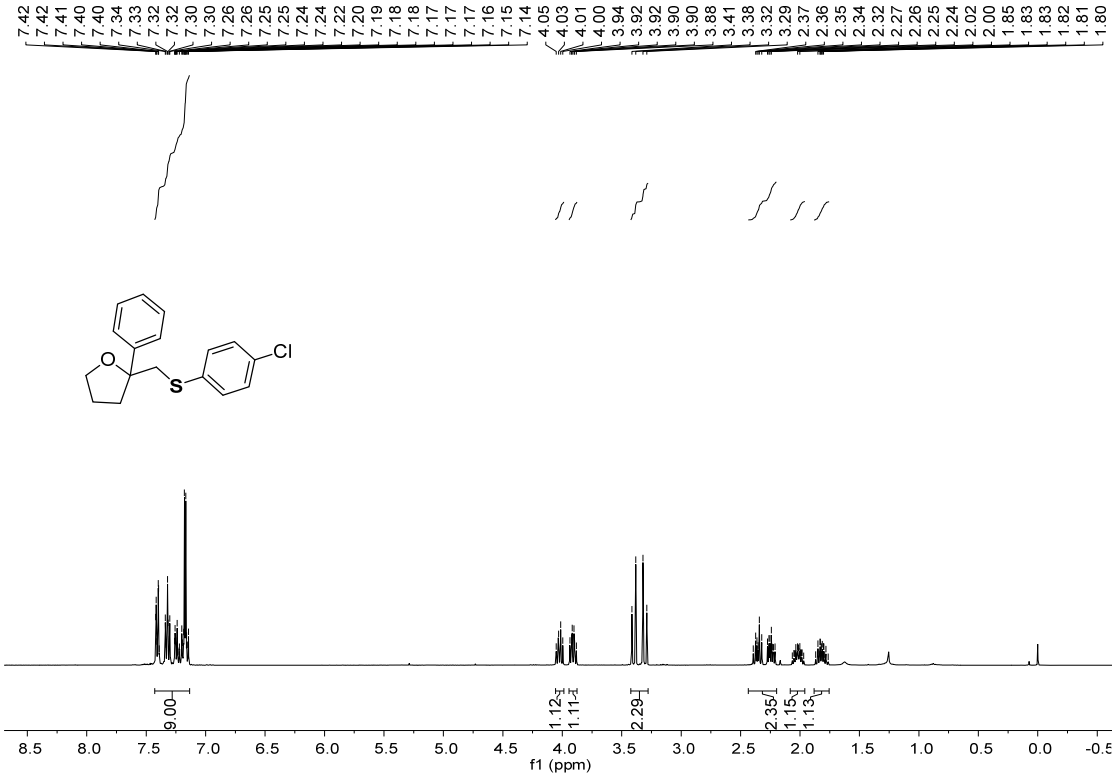
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **38**



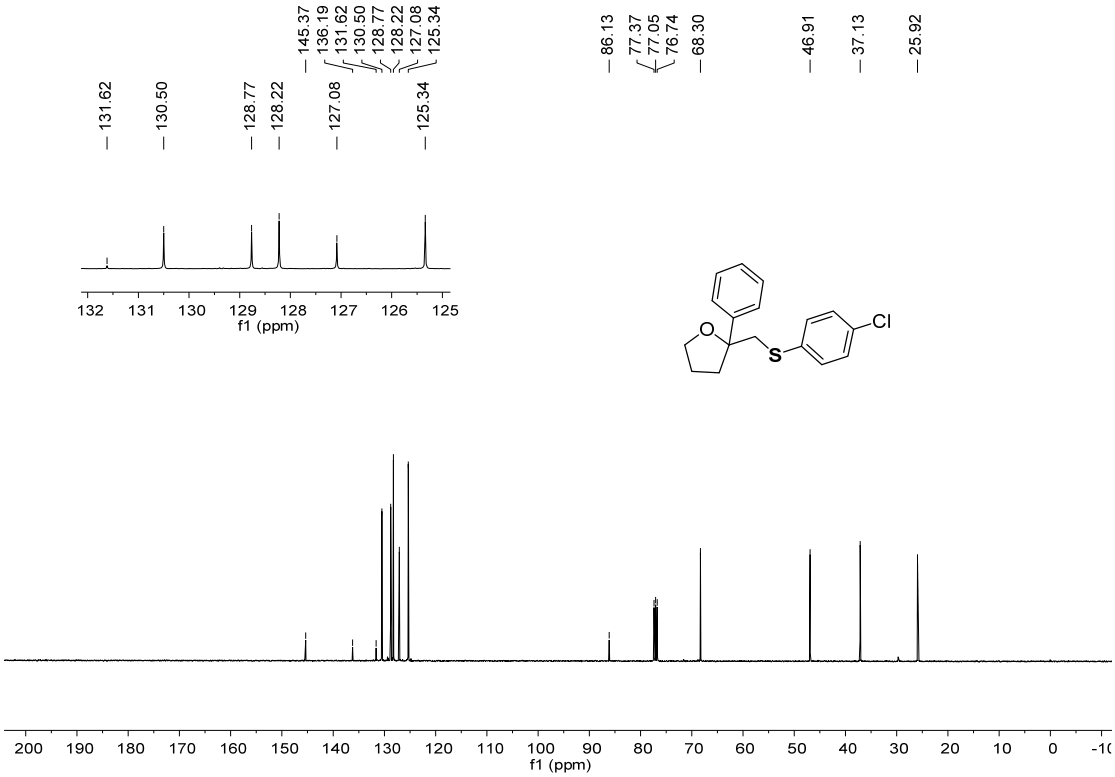
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **38**



^{1}H NMR (400 MHz, $CDCl_3$) spectra of **39**

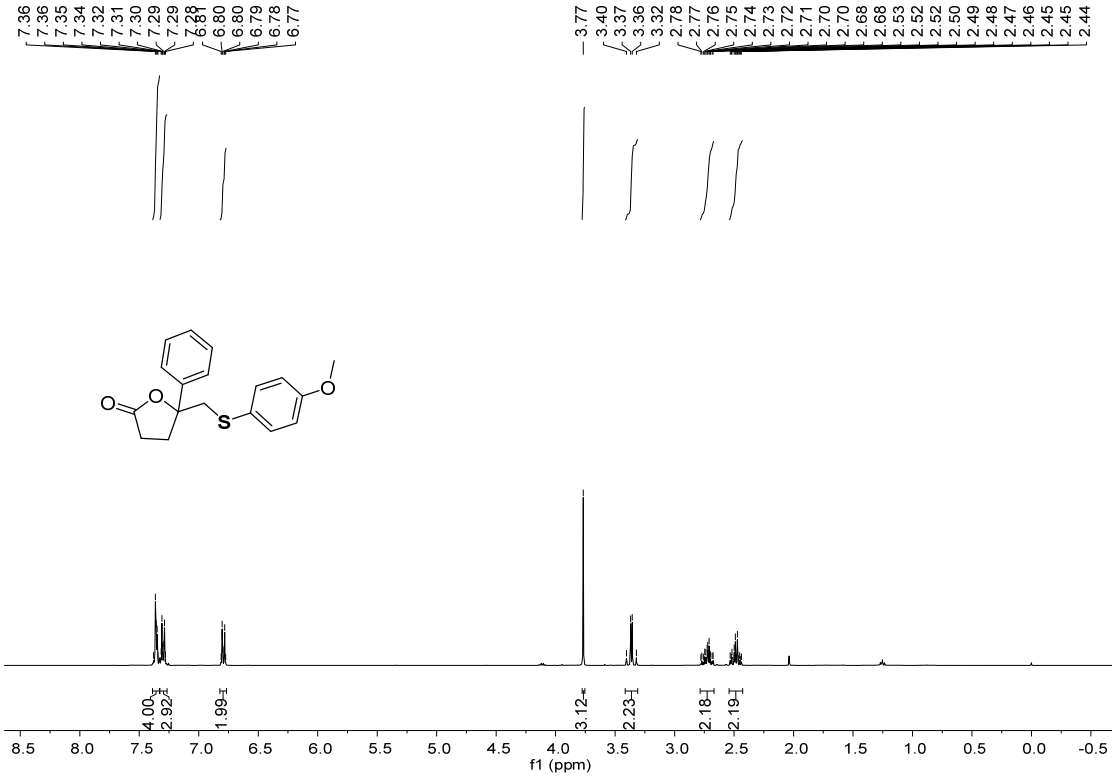


^{13}C NMR (101 MHz, $CDCl_3$) spectra of **39**

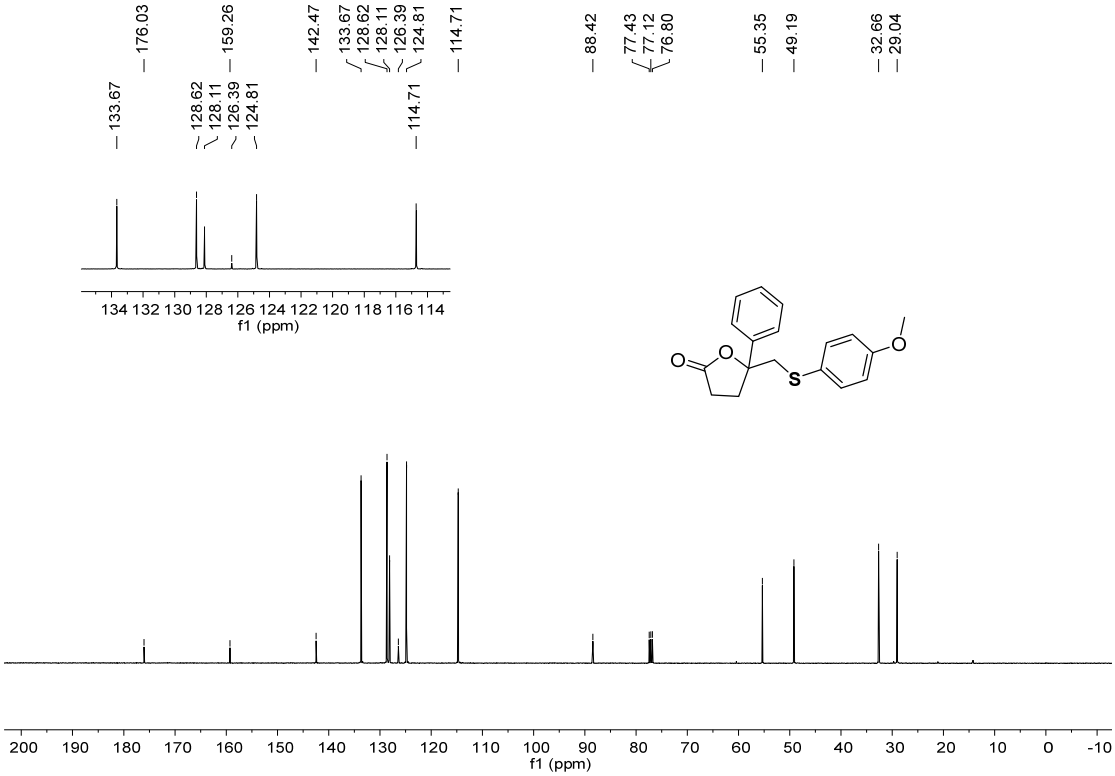


9.4. NMR spectra for lactone products **41-48**

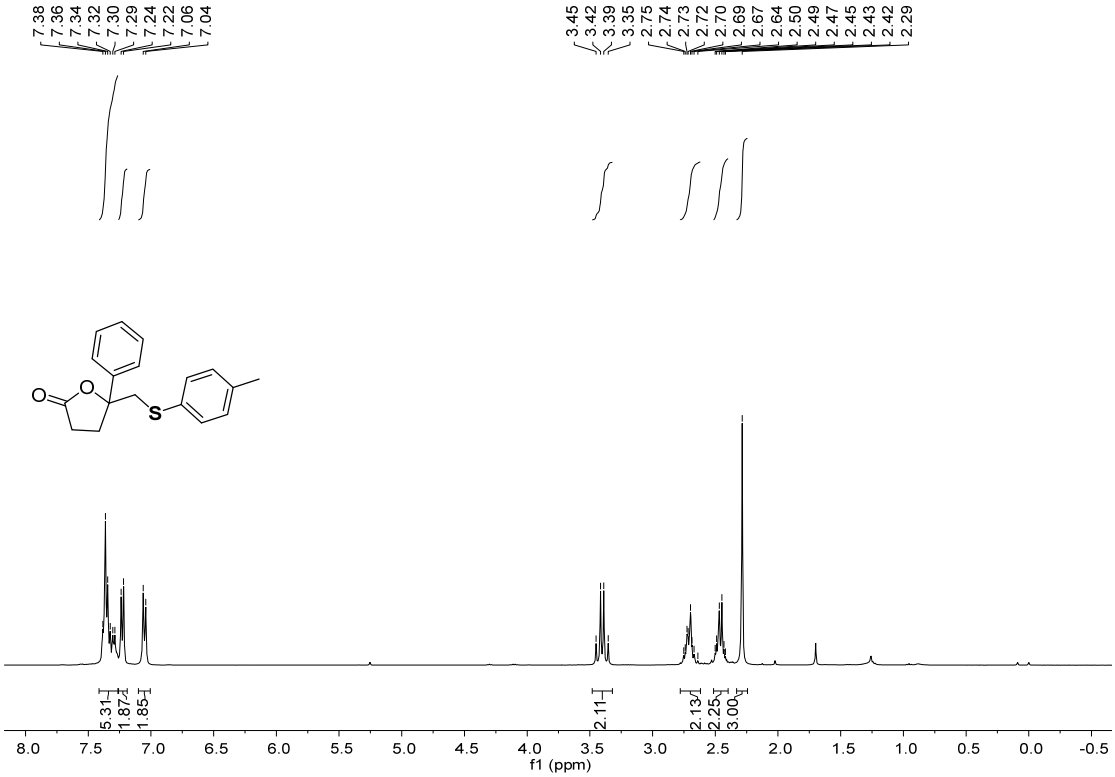
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **41**



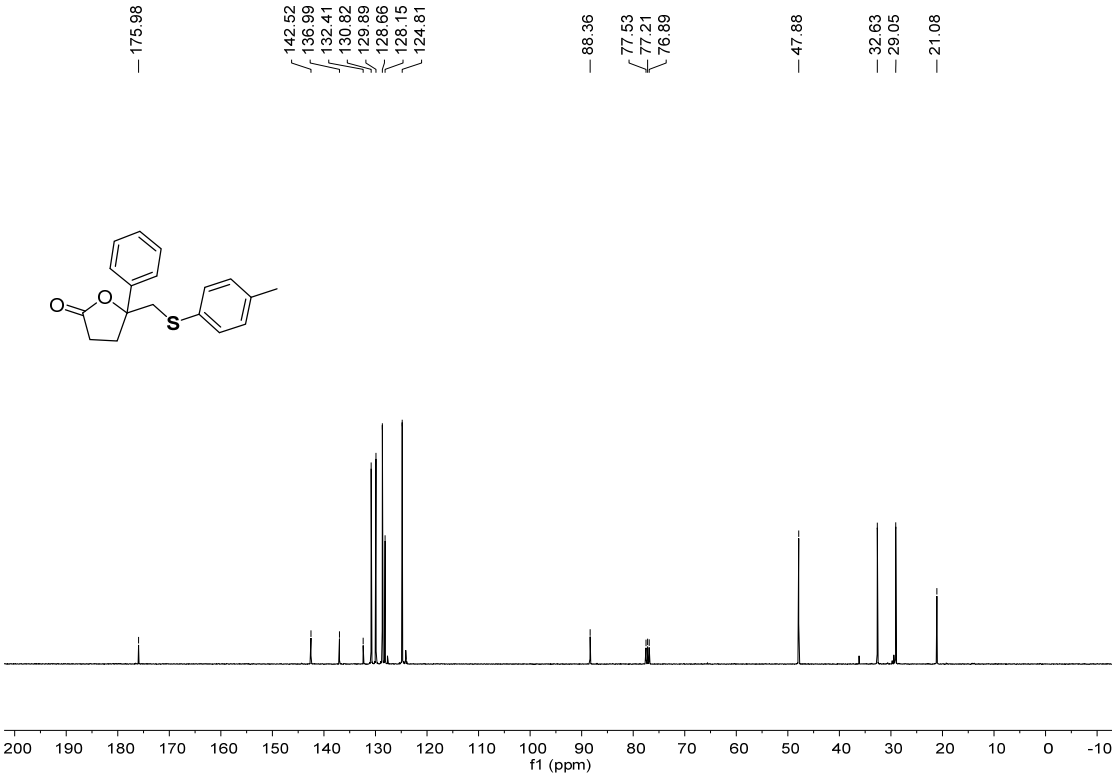
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **41**



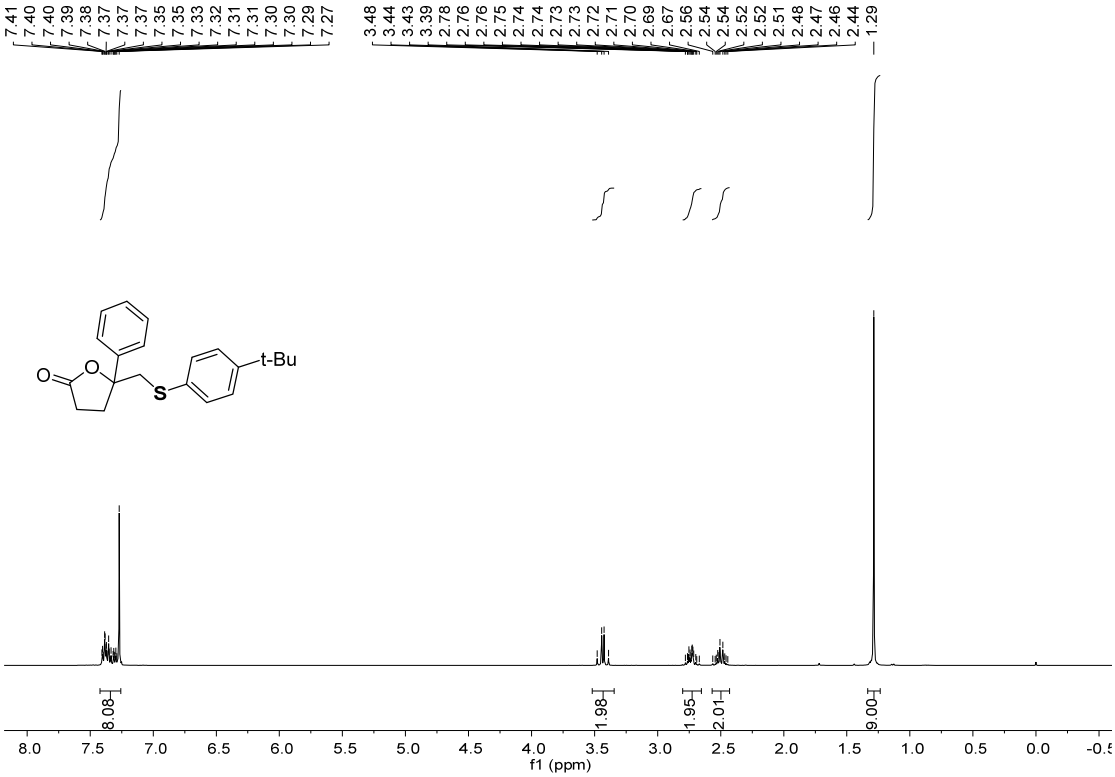
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **42**



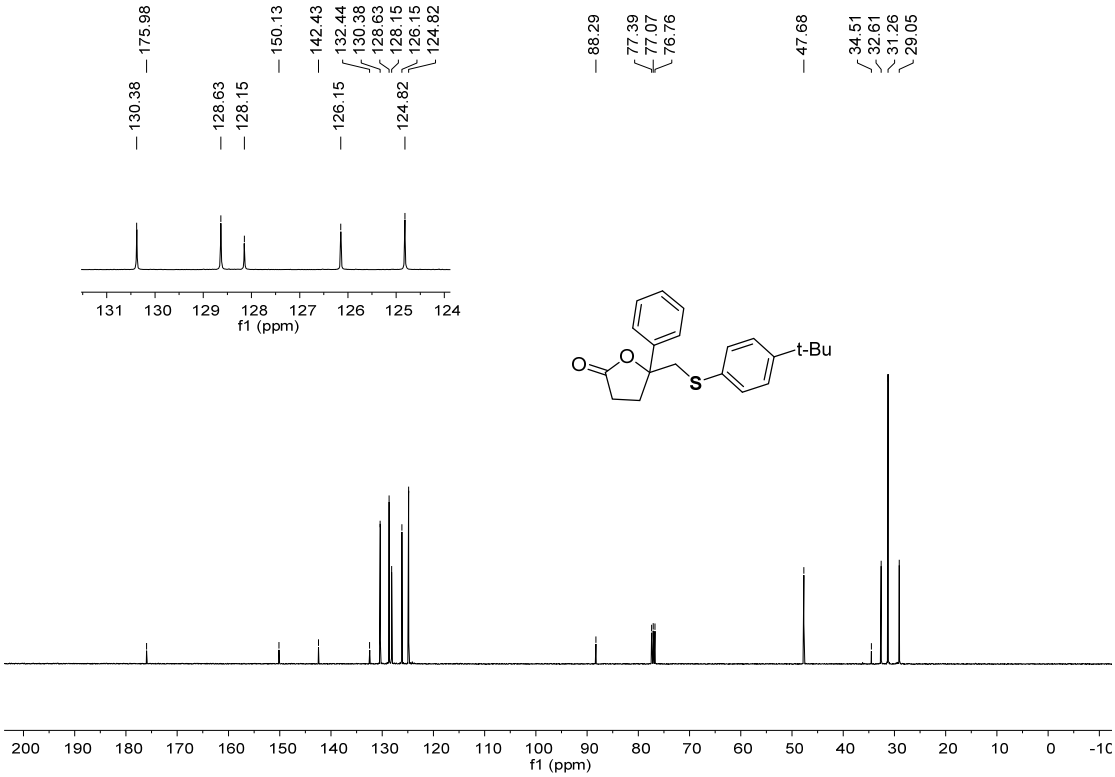
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **42**



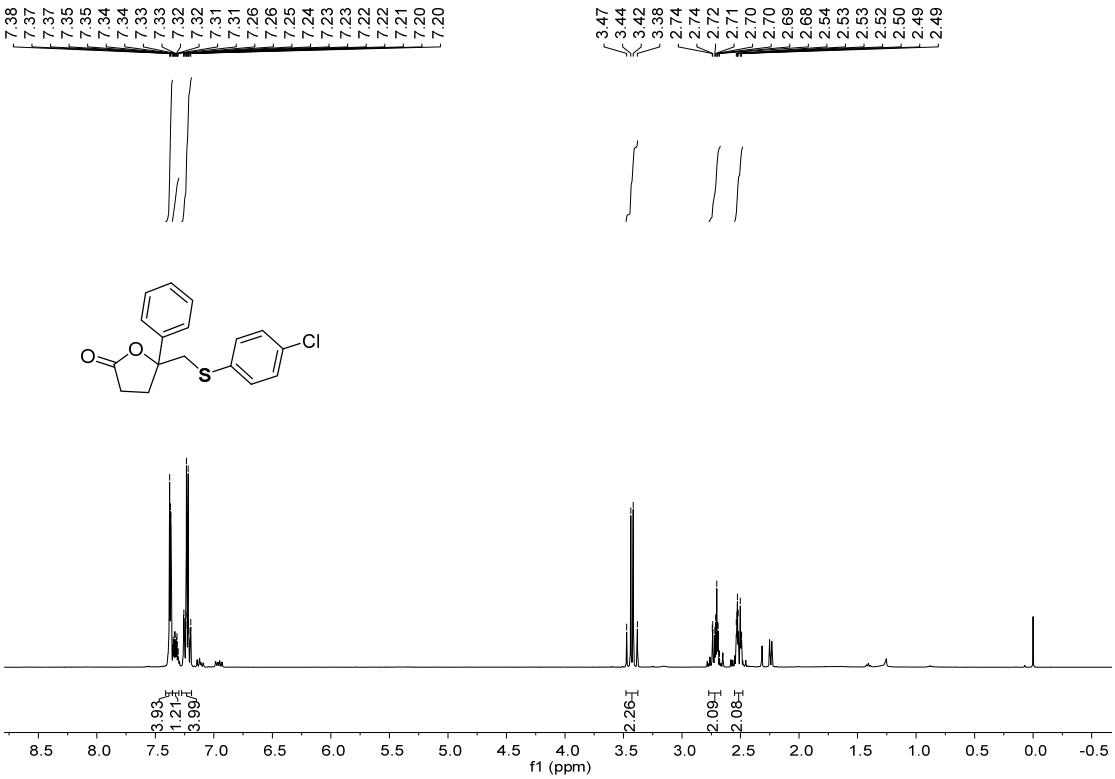
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **43**



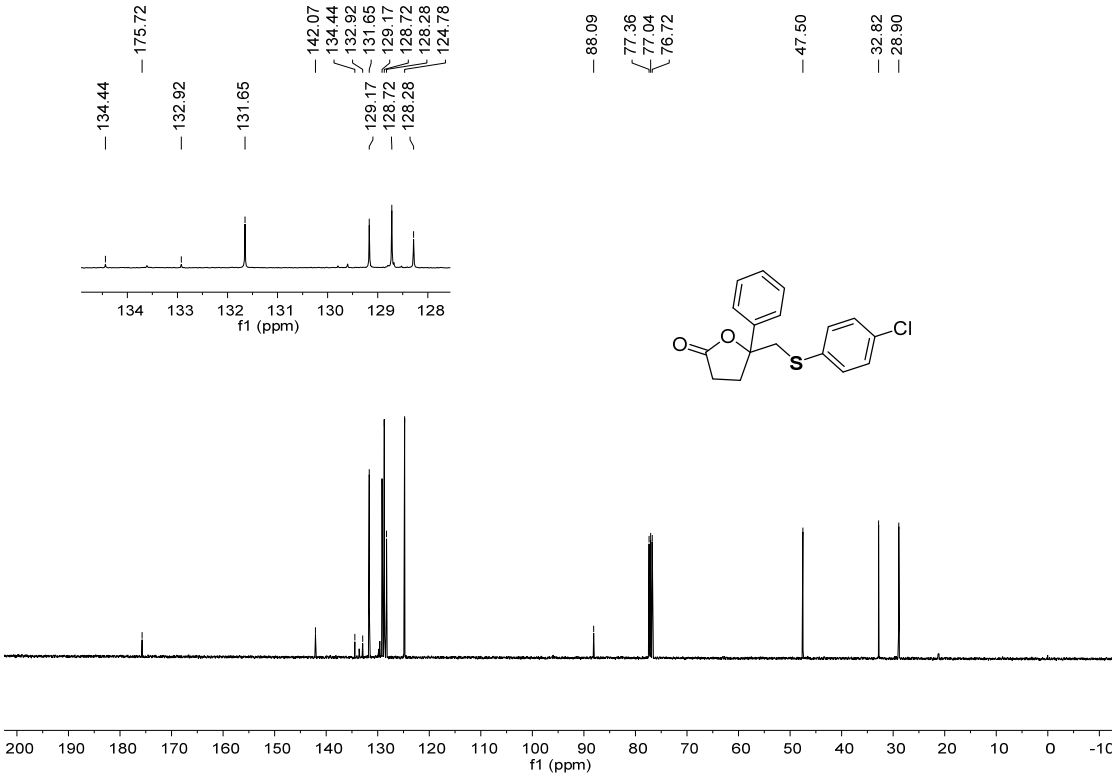
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **43**



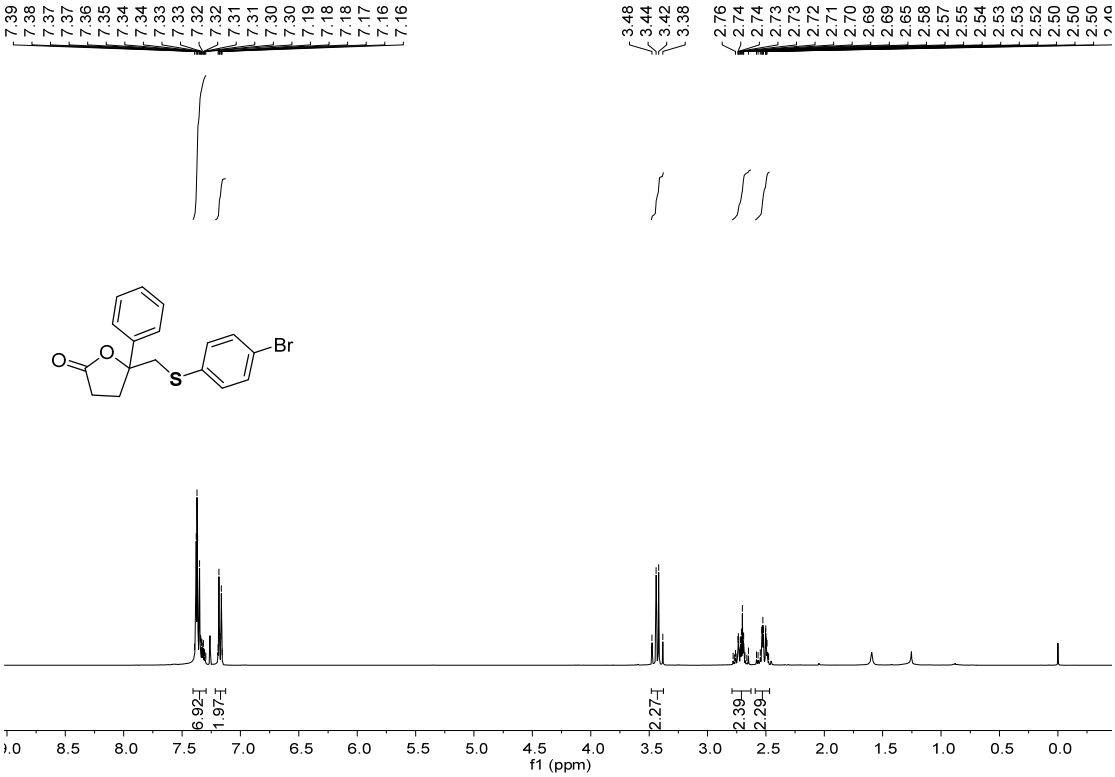
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **44**



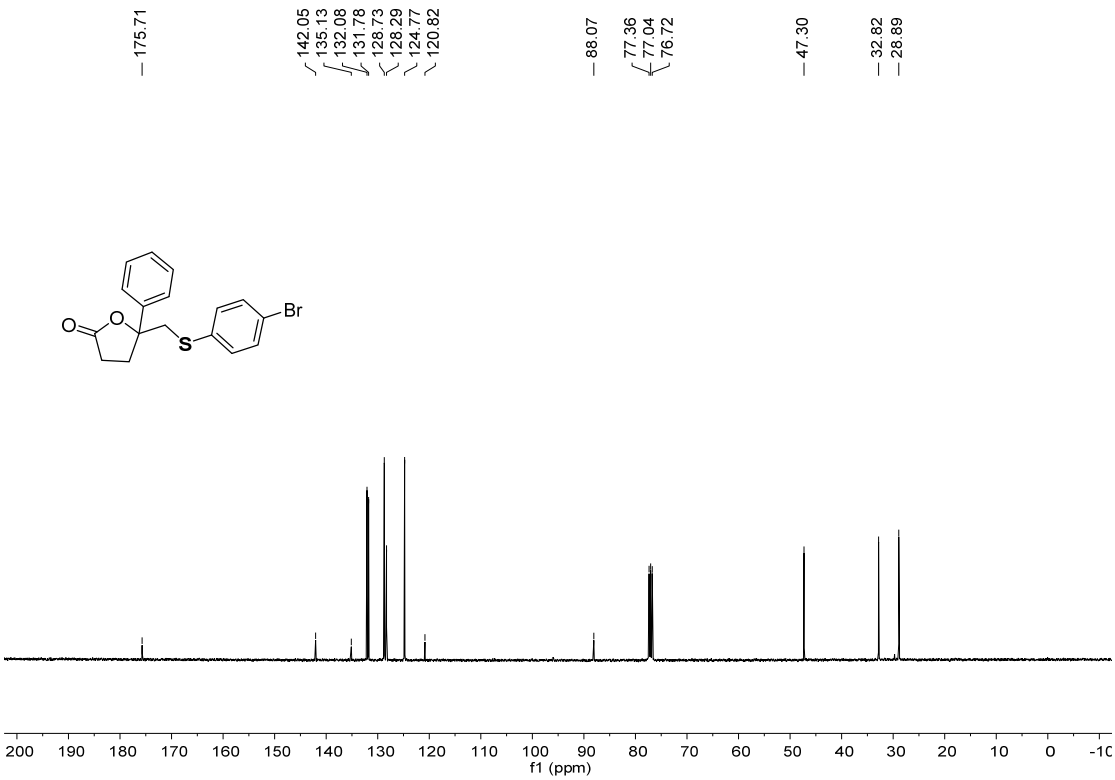
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **44**



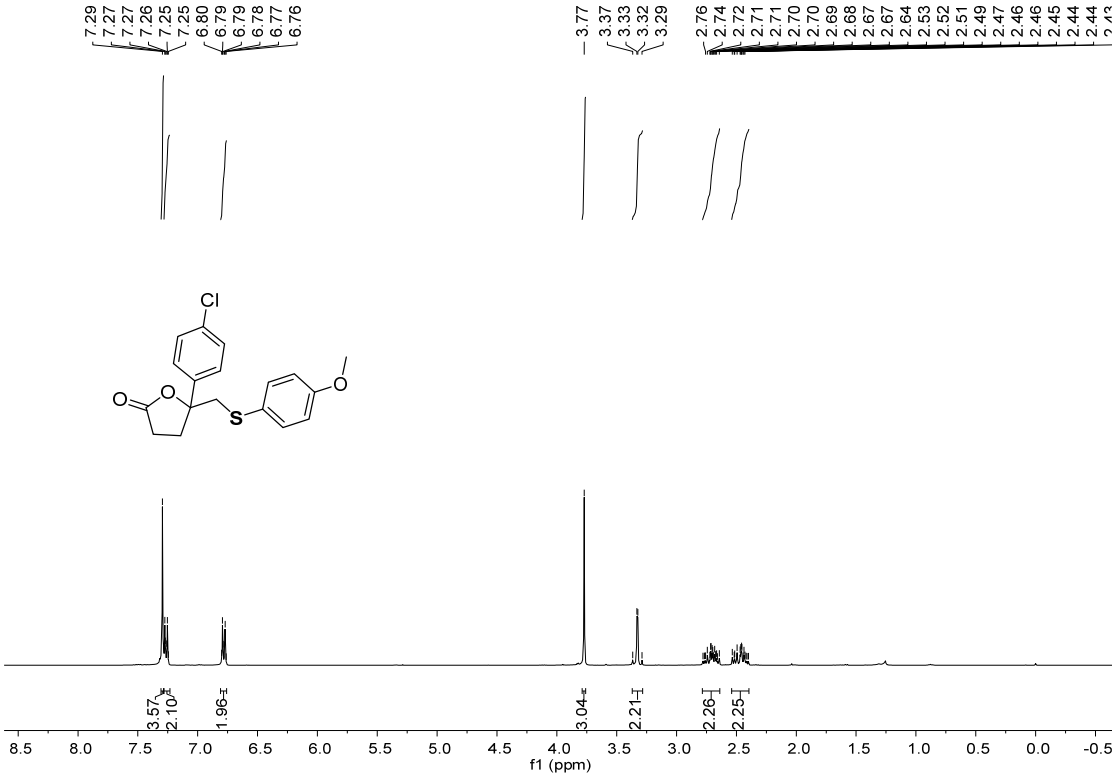
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **45**



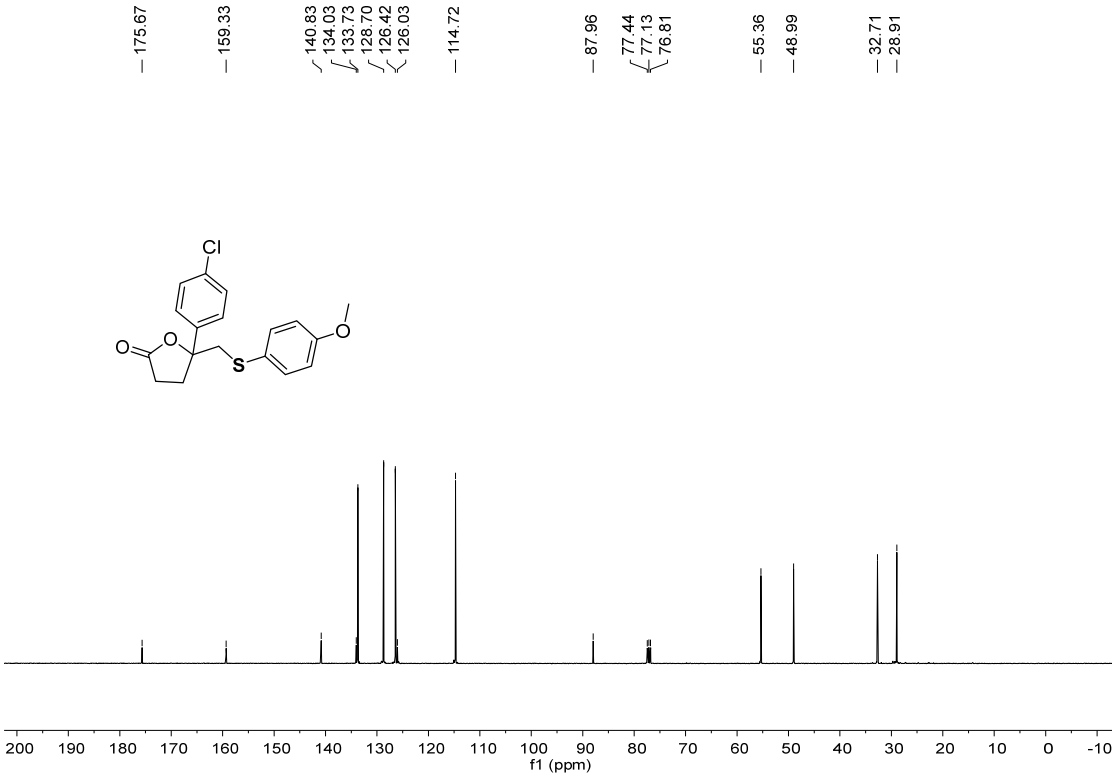
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **45**



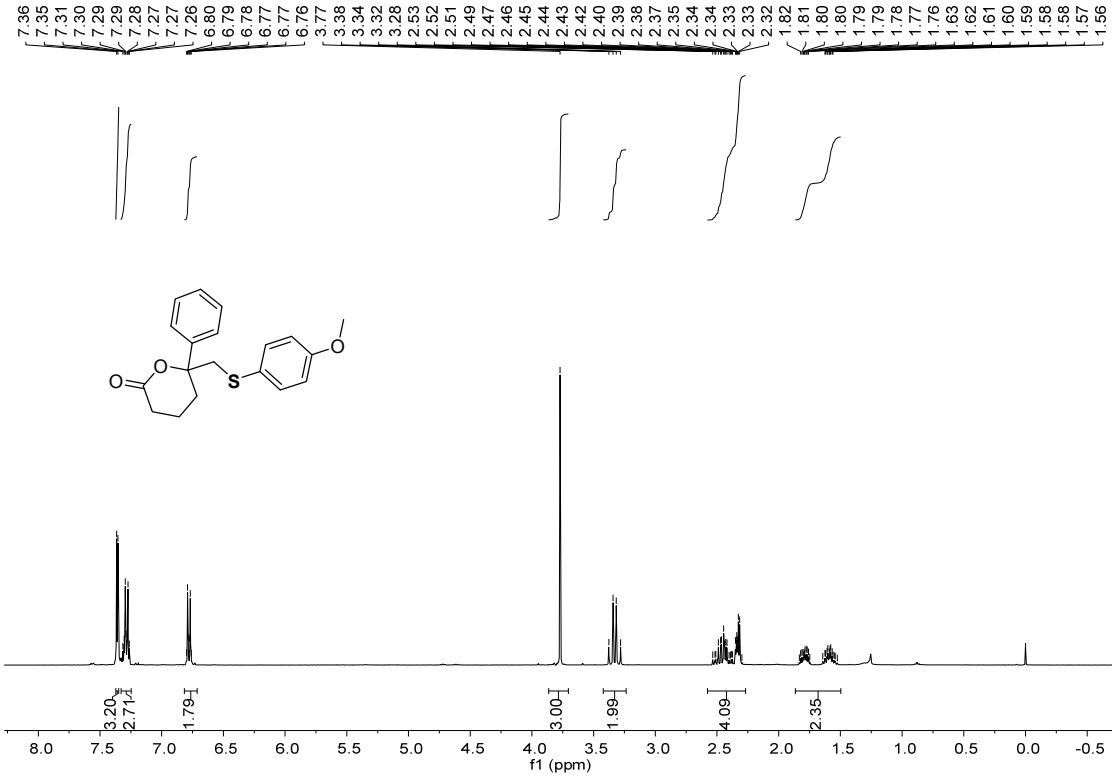
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **46**



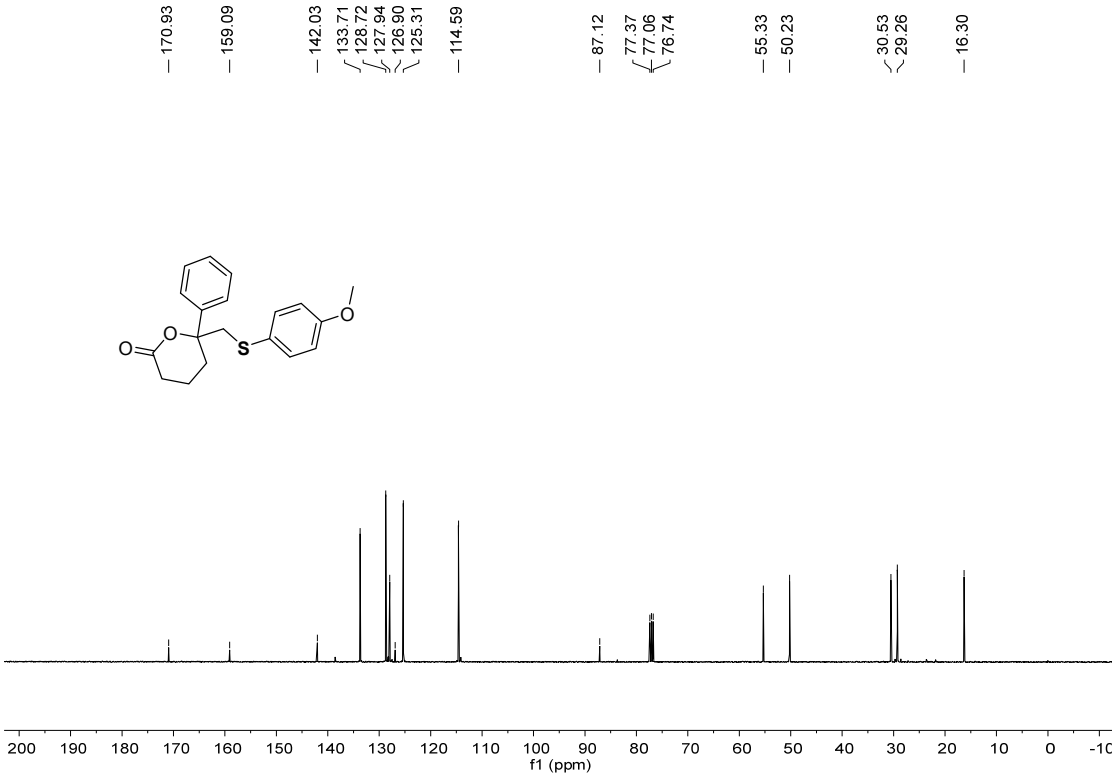
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **46**



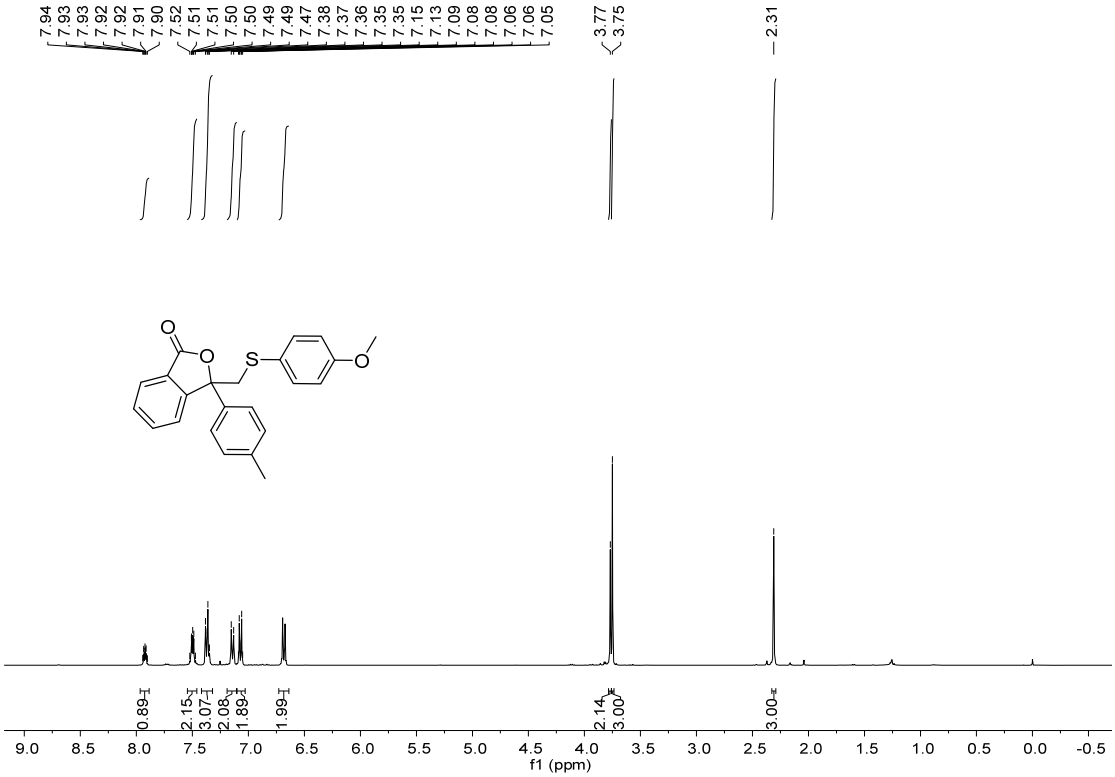
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **47**



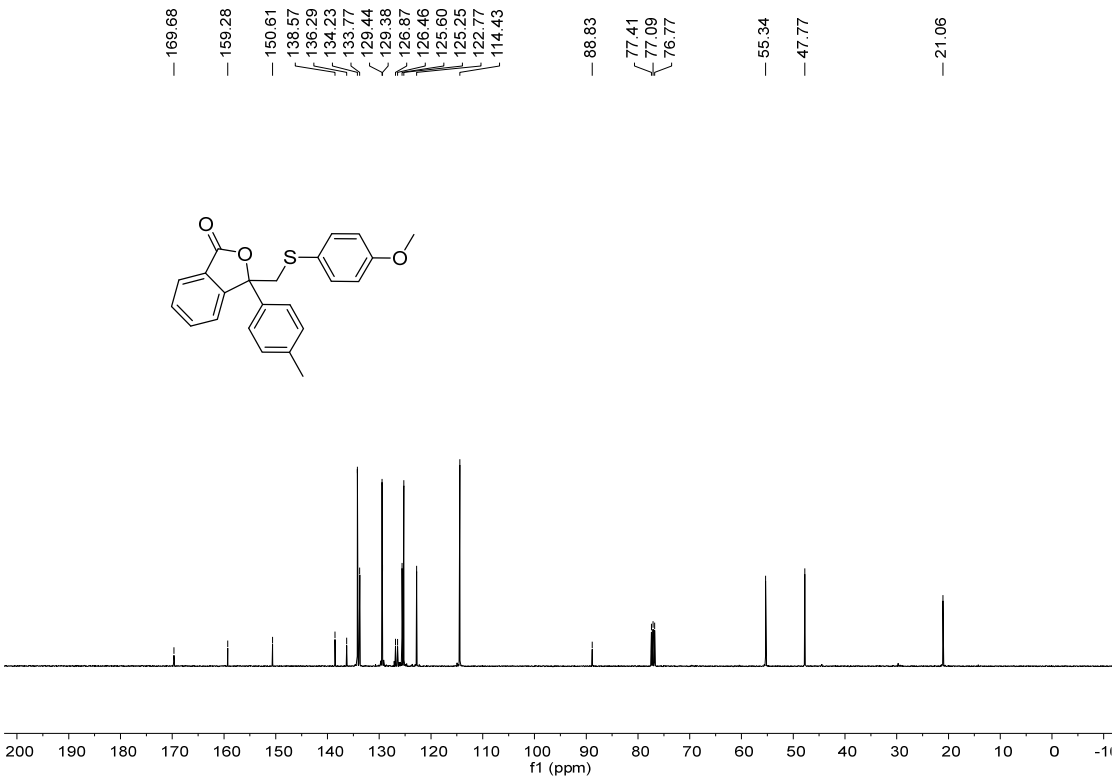
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **47**



^{1}H NMR (400 MHz, $CDCl_3$) spectra of **48**

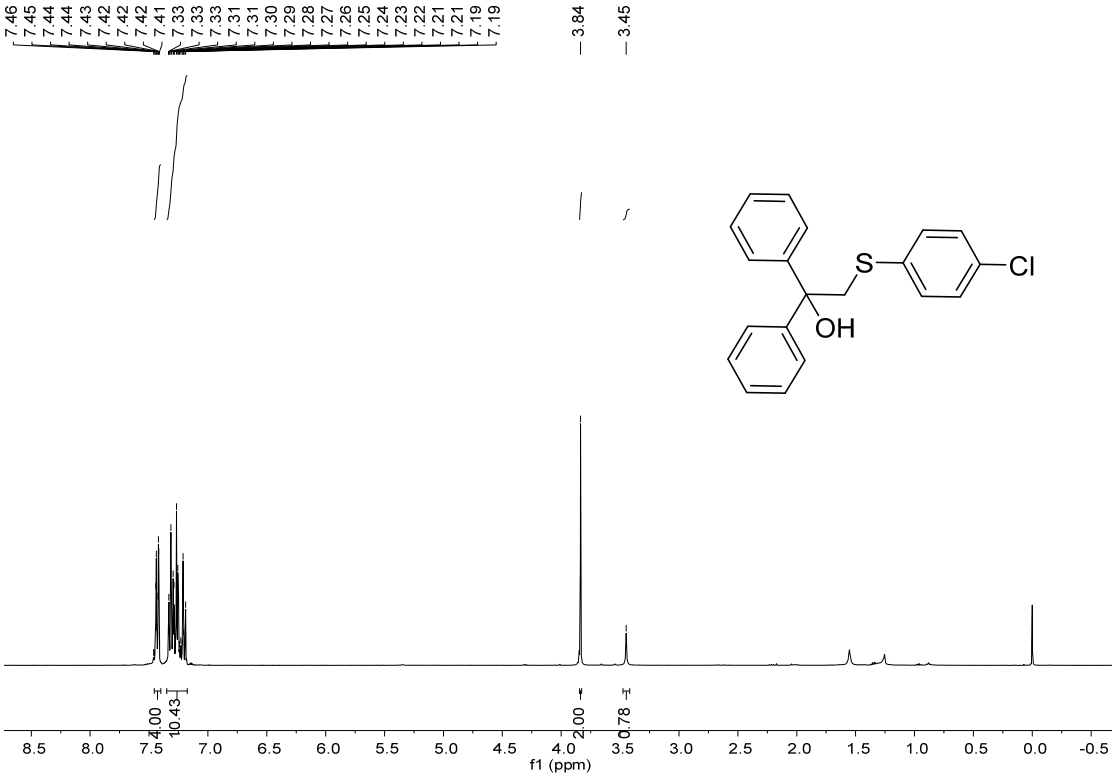


^{13}C NMR (101 MHz, $CDCl_3$) spectra of **48**



9.5. NMR spectra for control experiments products **50.**

^{1}H NMR (400 MHz, $CDCl_3$) spectra of **50**



^{13}C NMR (101 MHz, $CDCl_3$) spectra of **50**