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Supporting Information for

Ni(Ⅱ)-catalyzed Reductive Cross-coupling Reaction of Oxalates and Thiosulfonates/Selenosulfonates

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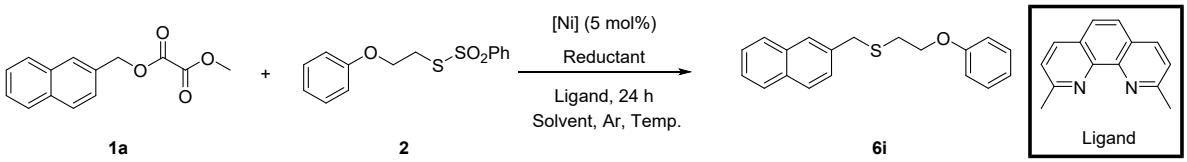
Ⅰ. General Information

Unless otherwise noted, all commercially available compounds were used as provided without further purification. Solvents for chromatography were analytical grade and used without further purification. Anhydrous DMSO, was purchased from Beijing InnoChem Science & Technology Co., Ltd. Analytical thin-layer chromatography (TLC) was performed on silica gel, visualized by irradiation with UV light. For column chromatography, 300-400 mesh silica gel was used. ^{1}H-NMR and ^{13}C-NMR were recorded on a BRUKER 400 MHz spectrometer in $CDCl_3$. Chemical shifts (δ) were reported referenced to an internal tetramethylsilane standard or the $CDCl_3$ residual peak (δ 7.26) for ^{1}H NMR. Chemical shifts of ^{13}C NMR are reported relative to $CDCl_3$ (δ 77.16). Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated s (singlet), bs (broad singlet), d (doublet), t (triplet), m (multiplet); coupling constants (J) are in Hertz (Hz). IR spectra were recorded on a BRUKER VERTEX 70 spectrophotometer and are reported in terms of frequency of absorption (cm^{-1}). HRMS spectra were obtained by using GCT Premier TOF-MS with EI source. The starting materials were isolated by SepaBean machine Flash Chromatography, which was purchased from Santai Technologies Inc.

Supplementary Table 1. Optimization of the reaction conditions



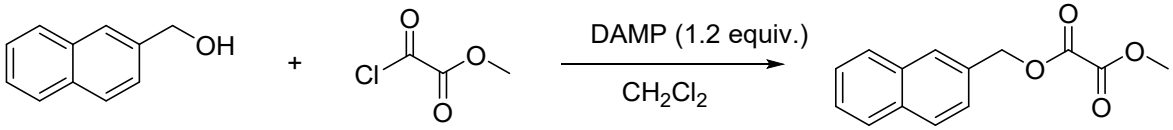
Entry	[Ni]	Reductant	Solvent	Temp(°C)	Yield[b] (%)
1	$NiBr_2$	Mn	DMSO	80	34
2	$NiBr_2$	Zn	DMSO	80	39
3	$NiBr_2$	Zn	DMF	80	32
4	$NiBr_2$	Zn	DMA	80	30
5	$NiBr_2$	Zn	MeCN	80	Trace
6	$NiBr_2$	Zn	DMSO	100	40

7[c]	$NiBr_2$	Zn	DMSO	120	44

[a] Reaction conditions: 1 (0.20 mmol), 2a (0.40 mmol), [Ni] (5.0 mol %), ligand (10.0 mol %), Mn (l 1.5 equiv), DMSO (1 mL), Ar atmosphere, 80 ^{0}C, 24 h. [b] LC-MS yield using biphenyl as an internal standard. [c] Reaction was conducted at 120 ^{0}C (oil bath) for 24 h

II. Synthesis of Substrates

General procedure for the synthesis of Methyl (naphthalen-2-ylmethyl) oxalate.[1]

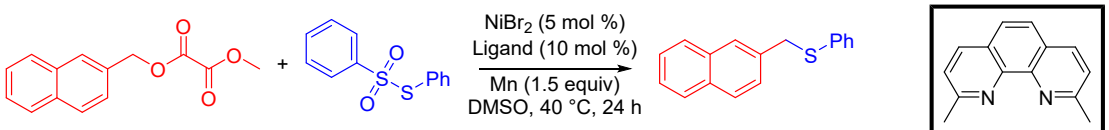


To a solution of DMAP (3.0 mmol, 1.2 equiv.) in CH_2Cl_2 (10 mL) was dropwise added methyl chlorooxoacetate (3.0 mmol, 1.2 equiv.) at 0 °C. The reaction mixture was stirred at room temperature for 5 min, and a solution of naphthalen-2-ylmethanol (2.5 mmol) in CH_2Cl_2 (5 mL) was dropwise added. After stirring for 10 min, the reaction was quenched with water (20 mL), extracted twice with CH_2Cl_2 (20 mL). The combine organic layers was washed with brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The residue was purified by flash chromatography on silica gel to afford oxalate.

III. General Procedure and Product Characterization

1. General Procedure A

A representative procedure synthesis of (naphthalen-2-ylmethyl)(phenyl) sulfane (3a) is shown below.



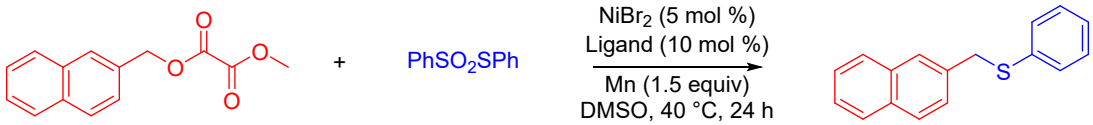
1a, 1.0 equiv **2a, 1.2 equiv** **3a**

In glovebox, an oven-dried screw-capped 8-mL vial equipped with a magnetic stir bar was charged with Methyl (naphthalen-2-ylmethyl) oxalate 1a (48.8 mg, 0.2 mmol), Thiosulfinate 2a (60.0 mg, 0.24 mmol), $NiBr_2$ (5.0 mol %), Ligand (10 mol %), Mn (1.5 equiv.), DMSO (1 mL) was added via syringe and the mixture was stirred at 40 °C for 24 h. After 24 h, the crude reaction mixture was diluted with ethyl acetate (20 mL) and washed with water (20 mL × 3). The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography

to afford pure product **3a** (69% yield).

2. General Procedure B

The procedure scale-up synthesis of 3a is shown below.



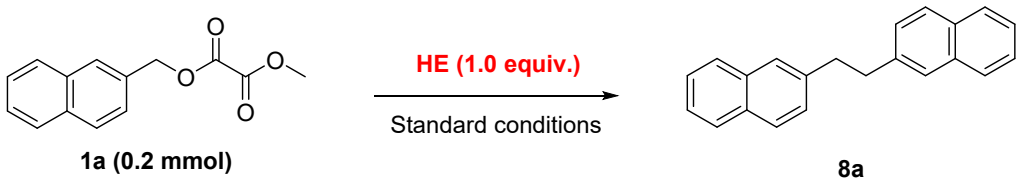
1a (3.0 mmol) **2a (3.6 mmol)** **3a, 60%(1.8 mmol, 0.451 g)**

In glovebox, An oven-dried screw-capped 100-mL vial equipped with Methyl (naphthalen-2-ylmethyl) oxalate 1a (732.2 mg, 3 mmol), Thiosulfinate 2a (900.0 mg, 3.6 mmol), $NiBr_2$ (5.0 mol %), Ligand (10 mol %), Mn (1.5 equiv.), DMSO (15.0 mL) was added via syringe. The reaction mixture was stirred for 24 h at 40 °C. After 24 h, the crude reaction mixture was diluted with ethyl acetate (20 mL) and washed with water (20 mL × 3). The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography to afford pure product **3a** (60% yield, 0.451 g).

IV. Mechanistic Investigation

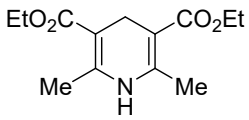
General procedure for reaction without HE. In glovebox, an oven-dried screw-capped 8-mL vial equipped with a magnetic stir bar was charged with Methyl (naphthalen-2-ylmethyl) oxalate 1a (48.8 mg, 0.2 mmol), $NiBr_2$ (5.0 mol %), Ligand (10 mol %), Mn (1.5 equiv.), DMSO (1 mL) was added via syringe and the mixture was stirred at 40 °C for 24 h. After 24 h, the crude reaction mixture was diluted with ethyl acetate (20 mL) and washed with water (20 mL × 3). The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography.

General procedure for reaction of 1a in the presence of HE: In glovebox, an oven-dried screw-capped 8-mL vial equipped with a magnetic stir bar was charged with Methyl (naphthalen-2-ylmethyl) oxalate 1a (48.8 mg, 0.2 mmol), hantzsch ester (1.0 equiv.), $NiBr_2$ (5.0 mol %), Ligand (10 mol %), Mn (1.5 equiv.), DMSO (1 mL) was added via syringe and the mixture was stirred at 40 °C for 24 h. After 24 h, the crude reaction mixture was diluted with ethyl acetate (20 mL) and washed with water (20 mL × 3). The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography.



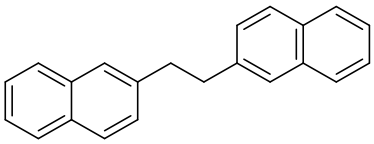
1a (0.2 mmol)

8a



Hantzsch ester (HE)

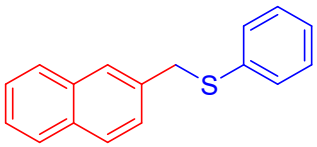
conditions	8a
a) without HE	27 %
b) with HE	14 %



1,2-di(naphthalen-2-yl)ethane (8a)

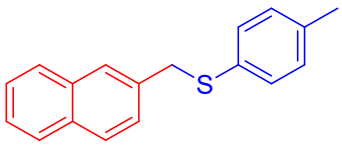
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.79 (m, 4H),7.54 – 7.44 (m, 3H), 4.88 – 4.85 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 138.3, 133.4, 133.0, 128.4, 127.9, 127.7, 126.2, 125.9, 125.5, 125.2, 65.5.

V. Product Characterization



(naphthalen-2-ylmethyl)(phenyl)sulfane (3a)

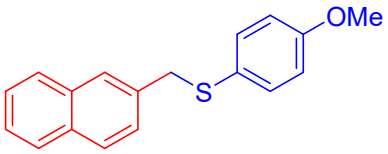
Yield: 69% (69.2 mg). White solid. **IR** (neat, ν, cm^{-1}): 2953, 2921, 2852,1730, 1477, 1438, 1270, 1089, 1022, 776, 686, 453, 470. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (dd, J = 9.1, 6.9 Hz, 2H), 7.75 – 7.70 (m, 1H), 7.68 – 7.64 (m, 1H), 7.47 – 7.43 (m, 2H), 7.43 – 7.41 (m, 1H), 7.34 – 7.31 (m, 1H), 7.30 (d, J = 1.1 Hz, 1H), 7.24 (d, J = 5.8 Hz, 1H), 7.21 (d, J = 6.0 Hz, 1H), 7.19 – 7.13 (m, 1H), 4.26 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.2, 134.9, 133.3, 132.6, 130.0, 128.9, 128.3, 127.7, 127.7, 127.4, 127.0, 126.5, 126.1, 125.8, 39.5. **HRMS** (CI) m/z (M^+) calcd for $C_{17}H_{14}S$: 250.0816, found 250.0817.



(naphthalen-2-ylmethyl)(p-tolyl)sulfane (3b)

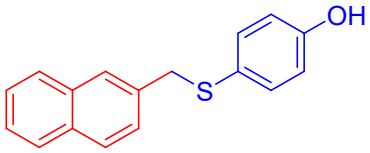
Yield: 75% (79.6 mg). White solid. **IR** (neat, ν, cm^{-1}):2967, 2908, 2362, 2337, 1491, 1400, 1084, 803, 757, 488. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 – 7.67 (m, 3H), 7.60

(d, J = 1.7 Hz, 1H), 7.45 – 7.35 (m, 3H), 7.23 – 7.16 (m, 2H), 7.00 (d, J = 8.0 Hz, 2H), 4.17 (s, 2H), 2.24 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.8, 135.4, 133.5, 132.7, 132.6, 131.0, 129.8, 128.4, 127.9, 127.8, 127.6, 127.2, 126.3, 125.9, 40.3, 21.2. **HRMS** (CI) m/z (M^+) calcd for $C_{18}H_{17}S$: 264.0973, found 264.0979.



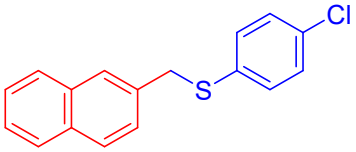
(4-methoxyphenyl)(naphthalen-2-ylmethyl)sulfane (3c)

Yield: 72% (80.9 mg). White solid. **IR** (neat, ν, cm^{-1}): 2920, 2844, 2362, 1587, 1486, 1236, 1023, 811, 750, 486. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (dd, J = 6.1, 3.4 Hz, 1H), 7.79 – 7.73 (m, 1H), 7.58 (s, 1H), 7.55 – 7.42 (m, 3H), 7.31 (d, J = 2.0 Hz, 1H), 7.30 (d, J = 2.2 Hz, 1H), 6.82 (d, J = 2.1 Hz, 1H), 6.80 (d, J = 2.2 Hz, 1H), 4.19 (s, 2H), 3.79 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.4, 135.7, 134.3, 133.4, 132.6, 128.3, 127.8, 127.7, 127.5, 127.3, 126.1, 126.0, 125.8, 114.5, 55.4, 41.7. **HRMS** (CI) m/z (M^+) calcd for $C_{18}H_{16}OS$: 280.0922, found 280.0917.



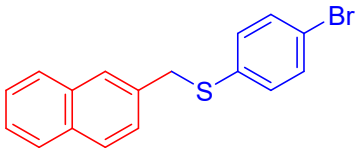
4-((naphthalen-2-ylmethyl)thio)phenol (3d)

Yield: 67% (71.3 mg). White solid. **IR** (neat, ν, cm^{-1}): 3421, 1496, 1051, 1023, 821, 758, 614. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.48 (s, 1H), 7.74 (dd, J = 11.8, 7.5 Hz, 2H), 7.71 – 7.65 (m, 1H), 7.54 (d, J = 1.7 Hz, 1H), 7.38 – 7.32 (m, 3H), 7.09 – 7.05 (m, 2H), 6.60 – 6.56 (m, 2H), 4.10 (s, 2H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.1, 141.0, 138.6, 138.0, 137.2, 133.1, 132.7, 132.7, 132.5, 132.3, 131.4, 131.0, 128.4, 121.2. **HRMS** (CI) m/z (M^+) calcd for $C_{17}H_{14}OS$: 266.0765, found 266.0772.



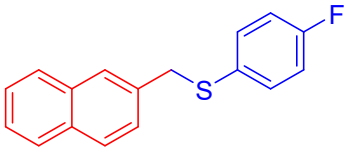
(4-chlorophenyl)(naphthalen-2-ylmethyl)sulfane (3e)

Yield: 79% (90.0 mg). White solid. **IR** (neat, ν, cm^{-1}): 2919, 2361, 1472, 1391, 1094, 812, 755, 487. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (t, J = 8.3 Hz, 2H), 7.73 – 7.69 (m, 1H), 7.61 (d, J = 1.7 Hz, 1H), 7.41 (td, J = 8.2, 7.8, 3.2 Hz, 3H), 7.19 (d, J = 8.7 Hz, 2H), 7.15 (d, J = 8.8 Hz, 2H), 4.18 (s, 2H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 134.7, 134.6, 133.3, 132. 7, 132.6, 131.6, 129.0, 128.5, 127.8, 127.7, 127.5, 126.9, 126.3, 126.0, 39.7. **HRMS** (CI) m/z (M^+) calcd for $C_{17}H_{13}ClS$: 284.0426, found 284.0430.



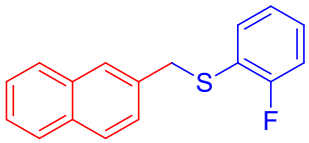
(4-bromophenyl)(naphthalen-2-ylmethyl)sulfane (3f)

Yield: 46% (60.4 mg). White solid. **IR** (neat, ν, cm^{-1}): 2919, 2365, 1465, 1085, 998, 830, 806, 755, 474. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 9.1, 7.0 Hz, 2H), 7.75 – 7.71 (m, 1H), 7.65 – 7.62 (m, 1H), 7.45 (dd, *J* = 3.1, 1.4 Hz, 1H), 7.44 – 7.41 (m, 2H), 7.34 – 7.30 (m, 2H), 7.16 – 7.12 (m, 2H), 4.21 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.4, 134.5, 133.3, 132.7, 131.9, 131.6, 128.5, 127.8, 127.7, 127.5, 126.9, 126.3, 126.0, 120.5, 39.5. **HRMS** (CI) m/z (M^+) calcd for $C_{17}H_{13}BrS$: 327.9921, found 327.9926.



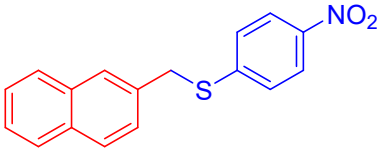
(4-fluorophenyl)(naphthalen-2-ylmethyl)sulfane (3g)

Yield: 73% (78.3 mg). White solid. **IR** (neat, ν, cm^{-1}): 3386, 1647, 1592, 1489, 1024, 994, 821, 752, 491. **^{1}H NMR** (400 MHz, DMSO) δ 7.85 (t, *J* = 6.9 Hz, 2H), 7.82 – 7.77 (m, 1H), 7.75 (s, 1H), 7.48 (td, *J* = 8.4, 3.2 Hz, 3H), 7.40 (d, *J* = 5.5 Hz, 1H), 7.38 (d, *J* = 5.4 Hz, 1H), 7.11 (t, *J* = 8.8 Hz, 2H), 4.35 (s, 2H).**^{13}C NMR** (101 MHz, DMSO) δ 161.5 (*J* = 242.4), 135.5, 133.2, 132.5, 132.3 (*J* = 8.0), 131.54 (*J* = 3.2), 128.5, 128.0, 127.9, 127.6, 127.5, 126.7, 126.3, 116.4 (*J* = 21.8), 38.6. **HRMS** (CI) m/z (M^+) calcd for $C_{17}H_{13}FS$: 268.0722, found 268.0728.



(2-fluorophenyl)(naphthalen-2-ylmethyl)sulfane (3h)

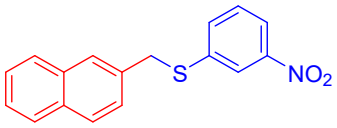
Yield: 71% (76.3 mg). White solid. **IR** (neat, ν, cm^{-1}): 2920, 1470, 1444, 1218, 1068, 820, 742, 472. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 8.8, 3.7 Hz, 2H), 7.69 (d, *J* = 6.3 Hz, 2H), 7.41 (d, *J* = 8.8 Hz, 1H), 7.39 – 7.32 (m, 3H), 7.17 – 7.04 (m, 2H), 7.04 – 6.96 (m, 1H), 4.28 (s, 2H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.3 (*J* = 241.2), 139.9, 138.0, 137.4, 136.42 (*J* = 2.0), 133.6 (*J* = 7.9), 133.29, 132.7 (*J* = 2.6), 132.5, 132.3, 131.5, 131.2, 130.2 (*J* = 3.2), 127.9, 127.7, 120.7 (*J* = 22.2), 41.76, 41.74.**HRMS** (CI) m/z (M^+) calcd for $C_{17}H_{13}FS$: 268.0722, found 268.0727.



(naphthalen-2-ylmethyl)(4-nitrophenyl)sulfane (3i)

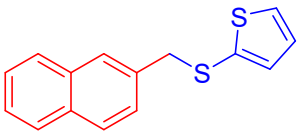
Yield: 47% (55.6 mg). White solid. **IR** (neat, ν, cm^{-1}): 2922, 2852, 1569, 1502, 1331,

1084, 830, 736, 680, 473. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.6 Hz, 2H), 7.86 (d, *J* = 8.4 Hz, 3H), 7.82 (d, *J* = 5.0 Hz, 1H), 7.52 (td, *J* = 10.0, 9.5, 3.8 Hz, 3H), 7.39 (d, *J* = 8.6 Hz, 2H), 4.43 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.1, 145.3, 133.3, 132.9, 132.8, 128.8, 127.8, 127.7, 127.6, 126.8, 126.5, 126.4, 126.3, 124.0, 37.4. **HRMS** (CI) m/z (M^+) calcd for $C_{17}H_{13}NO_2S$: 295.0667, found 295.0673.



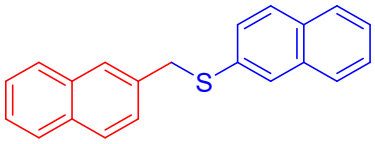
(naphthalen-2-ylmethyl)(3-nitrophenyl)sulfane (3j)

Yield: 36% (42.5 mg). Yellow solid. **IR** (neat, ν, cm^{-1}): 3392, 2921, 2851, 1517, 1346, 1024, 996, 724, 663, 447. **^{1}H NMR** (400 MHz, DMSO) δ 8.09 (t, *J* = 2.0 Hz, 1H), 7.93 (ddd, *J* = 8.2, 2.3, 1.0 Hz, 1H), 7.88 – 7.84 (m, 2H), 7.82 (d, *J* = 3.2 Hz, 1H), 7.81 – 7.77 (m, 1H), 7.76 (ddd, *J* = 7.9, 2.0, 1.0 Hz, 1H), 7.56 – 7.49 (m, 2H), 7.48 – 7.40 (m, 2H), 4.53 (s, 2H).**^{13}C NMR** (101 MHz, DMSO) δ 148.6, 139.5, 134.7, 134.6, 133.2, 132.6, 130.7, 128.7, 128.0, 128.0, 127.9, 127.5, 126.9, 126.5, 122.3, 120.9, 36.8. **HRMS** (CI) m/z (M^+) calcd for $C_{17}H_{13}NO_2S$: 295.0667, found 295.0674.



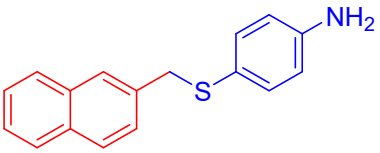
2-((naphthalen-2-ylmethyl)thio)thiophene (3k)

Yield: 83% (85.3 mg). White solid. **IR** (neat, ν, cm^{-1}): 2914, 1505, 1401, 1216, 820, 754, 693, 483. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 – 7.84 (m, 2H), 7.78 (dd, *J* = 6.1, 3.4 Hz, 1H), 7.58 – 7.55 (m, 1H), 7.52 (dt, *J* = 6.2, 3.4 Hz, 2H), 7.46 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.34 (dd, *J* = 5.2, 1.3 Hz, 1H), 6.98 (dd, *J* = 3.6, 1.3 Hz, 1H), 6.93 (dd, *J* = 5.3, 3.6 Hz, 1H), 4.17 (s, 2H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.1, 134.5, 133.5, 133.3, 132.7, 129.9, 128.3, 127.8, 127.7, 127.7, 127.5, 127.1, 126.2, 125.9, 44.2. **HRMS** (CI) m/z (M^+) calcd for $C_{15}H_{12}S_2$: 256.0380, found 256.0384.



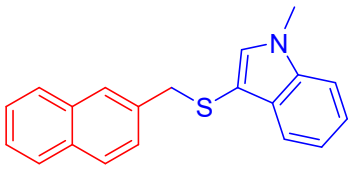
naphthalen-2-yl(naphthalen-2-ylmethyl)sulfane (3l)

Yield: 61% (73.2 mg). White solid. **IR** (neat, ν, cm^{-1}): 2920, 2848, 1505, 864, 815, 739, 478, 472. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 5.1 Hz, 1H), 7.83 – 7.78 (m, 3H), 7.77 (d, *J* = 2.7 Hz, 2H), 7.75 – 7.69 (m, 2H), 7.53 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.51 – 7.47 (m, 2H), 7.47 – 7.42 (m, 3H), 4.41 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 134.8, 133.8, 133.7, 133.3, 132.6, 131.9, 128.4, 127.8, 127.8, 127.7, 127.7, 127.6, 127.5, 127.2, 127.0, 126.5, 126.2, 125.9, 125.8, 39.3. **HRMS** (CI) m/z (M^+) calcd for $C_{21}H_{16}S$: 300.0973, found 300.0978.



4-((naphthalen-2-ylmethyl)thio)aniline (3q)

Yield: 55% (58.3 mg). Pale yellow solid. **IR** (neat, ν, cm^{-1}): 3613, 3364, 2351, 1750, 1569, 1019, 1083, 773, 659, 462, 447. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 – 7.71 (m, 3H), 7.53 (d, *J* = 1.6 Hz, 1H), 7.49 – 7.37 (m, 3H), 7.18 – 7.11 (m, 2H), 6.57 – 6.49 (m, 2H), 4.10 (s, 2H), 3.67 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.4, 136.0, 134.9, 133.4, 132.6, 128.2, 127.8, 127.7, 127.5, 127.4, 126.1, 125.7, 122.9, 115.5, 42.2. **HRMS** (CI) m/z (M^+) calcd for $C_{17}H_{15}NS$: 265.0925, found 265.0921.

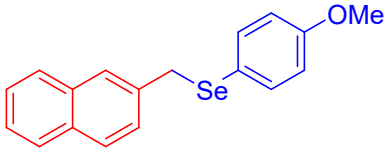


1-methyl-3-((naphthalen-2-ylmethyl)thio)-1H-indole (3r)

Yield: 59% (71.5 mg). White solid. **IR** (neat, ν, cm^{-1}): 3113, 2930, 2849, 1505, 1237, 864, 824, 740, 544, 474, 425. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 – 7.75 (m, 3H), 7.68 – 7.63 (m, 1H), 7.48 – 7.37 (m, 4H), 7.35 – 7.27 (m, 2H), 7.21 (ddd, *J* = 8.0, 6.7, 1.4 Hz, 1H), 6.82 (s, 1H), 4.02 (s, 2H), 3.64 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.3, 136.5, 134.5, 133.2, 132.4, 129.9, 128.0, 127.6, 127.4, 125.9, 125. 6, 122.2, 120.1, 119.4, 109.6, 103.1, 41.7, 32.8. **HRMS** (CI) m/z (M^+) calcd for $C_{20}H_{17}NS$: 303.1082, found 303.1086.

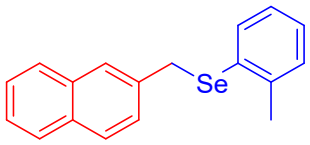
(naphthalen-2-ylmethyl)(phenyl)selane (5a)

Yield: 73% (82.7 mg). White solid. **IR** (neat, ν, cm^{-1}): 2924, 2361, 2337, 1431, 826, 727, 686, 472. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 – 7.84 (m, 1H), 7.82 (d, *J* = 8.5 Hz, 1H), 7.79 – 7.73 (m, 1H), 7.60 (d, *J* = 1.7 Hz, 1H), 7.54 (t, *J* = 1.7 Hz, 1H), 7.52 (dt, *J* = 3.7, 2.0 Hz, 2H), 7.51 – 7.49 (m, 1H), 7.47 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.35 – 7.25 (m, 3H), 4.32 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.1, 133.8, 133.3, 132.5, 130.4, 129.1, 128.3, 127.7, 127.7, 127.4, 127.3, 127.3, 126.2, 125.8, 32.8. **HRMS** (CI) m/z (M^+) calcd for $C_{17}H_{14}Se$: 298.0261, found 298.0268.



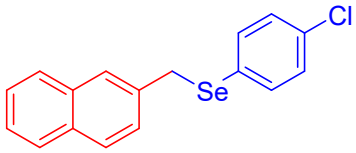
(4-methoxyphenyl)(naphthalen-2-ylmethyl)selane (5b)

Yield: 82% (107.6 mg). Pale yellow solid. **IR** (neat, ν, cm^{-1}): 2922, 2362, 2337, 1486, 1239, 1023, 810, 741, 486. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 – 7.63 (m, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.57 – 7.51 (m, 1H), 7.33 – 7.25 (m, 3H), 7.22 (d, *J* = 8.6 Hz, 3H), 6.63 – 6.56 (m, 2H), 4.00 (s, 2H), 3.59 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.7, 136.8, 136.7, 133.4, 132.4, 128.2, 127.7, 127.4, 127.2, 126.1, 125.7, 120.1, 114.7, 55.3, 33.7. **HRMS** (CI) m/z (M^+) calcd for $C_{18}H_{16}OSe$: 328.0366, found 328.0368.



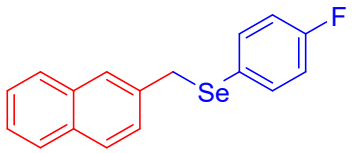
(naphthalen-2-ylmethyl)(o-tolyl)selane (5c)

Yield: 75% (93.3 mg). White solid. **IR** (neat, ν, cm^{-1}): 2920, 2850, 2361, 2336, 1456, 1029, 857, 820, 733, 474. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 – 7.85 (m, 1H), 7.83 (d, *J* = 8.5 Hz, 1H), 7.80 – 7.76 (m, 1H), 7.64 (d, *J* = 1.7 Hz, 1H), 7.56 – 7.53 (m, 1H), 7.53 – 7.51 (m, 1H), 7.51 – 7.46 (m, 2H), 7.26 – 7.22 (m, 2H), 7.15 (ddd, *J* = 8.7, 5.5, 3.5 Hz, 1H), 4.29 (s, 2H), 2.41 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.0, 135.8, 133.4, 133.1, 132.5, 131.9, 130.0, 128.3, 127.7, 127.7, 127.4, 127.3, 127.3, 126.6, 126.2, 125.8, 31.8, 22.5. **HRMS** (CI) m/z (M^+) calcd for $C_{18}H_{16}Se$: 312.0417, found 312.0419.



(4-chlorophenyl)(naphthalen-2-ylmethyl)selane (5d)

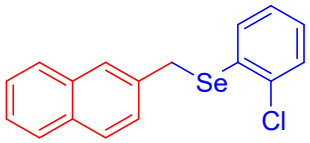
Yield: 71% (94.2 mg). Pale yellow solid. **IR** (neat, ν, cm^{-1}): 2921, 2852, 2361, 1466, 1086, 1002, 827, 807, 749, 482. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 – 7.82 (m, 1H), 7.81 (d, *J* = 8.5 Hz, 1H), 7.77 – 7.72 (m, 1H), 7.56 (d, *J* = 1.7 Hz, 1H), 7.53 – 7.46 (m, 2H), 7.42 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.40 – 7.36 (m, 2H), 7.25 – 7.19 (m, 2H), 4.26 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.7, 135.3, 133.8, 133.3, 132.5, 129.2, 128.4, 128.3, 127.7, 127.7, 127.3, 127.2, 126.3, 125.9, 33.0. **HRMS** (CI) m/z (M^+) calcd for $C_{17}H_{13}ClSe$: 331.9871, found 331.9873.



(4-fluorophenyl)(naphthalen-2-ylmethyl)selane (5e)

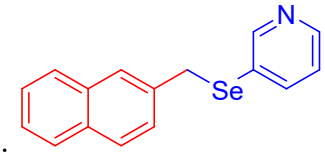
Yield: 62% (77.4 mg). White solid. **IR** (neat, ν, cm^{-1}): 2924, 2852, 1724, 1580, 1480, 1234, 820, 743, 493. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 – 7.80 (m, 1H), 7.78 (d, *J* = 8.5 Hz, 1H), 7.73 – 7.68 (m, 1H), 7.47 (td, *J* = 3.9, 2.5 Hz, 3H), 7.44 – 7.34 (m, 3H), 6.92 (t, *J* = 8.7 Hz, 2H), 4.21 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.6 (*J* =

246.0), 136.7 (J = 7.9), 136.0, 133.2, 132.4, 128.3, 127.6, 127.6, 127.2, 127.1, 126.2, 125.8, 124.3 (J = 3.4) 116.1 (J = 21.2), 33.4. **HRMS** (CI) m/z (M^+) calcd for $C_{17}H_{13}FSe$: 316.0167, found 316.0170.



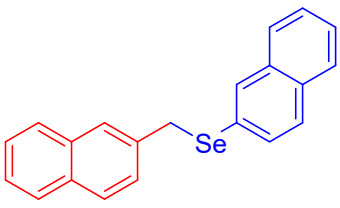
(2-chlorophenyl)(naphthalen-2-ylmethyl)selane (5f)

Yield: 54% (71.7 mg). Pale yellow solid. **IR** (neat, ν, cm^{-1}): 2920, 2851, 1444, 1427, 1021, 821, 740, 473. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (dd, J = 12.0, 7.0 Hz, 2H), 7.80 – 7.76 (m, 1H), 7.75 (d, J = 1.7 Hz, 1H), 7.51 (td, J = 7.8, 7.4, 3.3 Hz, 3H), 7.43 (ddd, J = 7.6, 5.8, 1.7 Hz, 2H), 7.17 (dtd, J = 18.5, 7.4, 1.7 Hz, 2H), 4.37 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.6, 134.7, 133.4, 132.5, 132.3, 131.8, 129.5, 128.4, 127.9, 127.7, 127.7, 127.6, 127.2, 126.2, 125.9, 31.2. **HRMS** (CI) m/z (M^+) calcd for $C_{17}H_{13}ClSe$: 331.9871, found 331.9871.



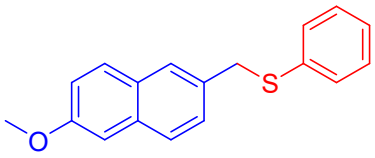
3-((naphthalen-2-ylmethyl)selanyl)pyridine (5g)

Yield: 22% (26.2 mg). Yellow solid. **IR** (neat, ν, cm^{-1}): 3041, 2921, 2849, 1567, 1550, 1446, 1409, 1104, 820, 749, 467. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.56 (dd, J = 5.0, 1.8 Hz, 1H), 7.87 – 7.74 (m, 4H), 7.54 (dd, J = 8.5, 1.7 Hz, 1H), 7.47 (tdd, J = 7.6, 5.5, 1.9 Hz, 3H), 7.33 (d, J = 7.9 Hz, 1H), 7.13 – 7.04 (m, 1H), 4.66 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.5, 150.1, 136.5, 136.0, 133.4, 132.5, 128.3, 127.6, 127.6, 127.4, 127.4, 126.1, 125.7, 125.6, 120.6, 29.7. **HRMS** (CI) m/z (M^+) calcd for $C_{16}H_{13}NSe$: 299.0213, found 299.0222.



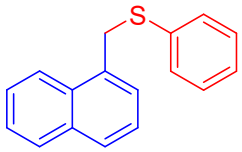
naphthalen-2-yl(naphthalen-2-ylmethyl)selane (5h)

Yield: 40% (55.5 mg). White solid. **IR** (neat, ν, cm^{-1}): 2921, 2854, 2363, 1725, 1498, 1370, 1251, 815, 785, 763, 742, 469. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.49 (dd, J = 7.7, 1.8 Hz, 1H), 7.89 (dd, J = 7.3, 2.0 Hz, 1H), 7.83 (dd, J = 10.0, 6.8 Hz, 2H), 7.77 (d, J = 8.4 Hz, 1H), 7.72 (d, J = 7.0 Hz, 1H), 7.69 – 7.64 (m, 1H), 7.56 (pd, J = 7.0, 1.6 Hz, 2H), 7.50 – 7.44 (m, 3H), 7.40 (dd, J = 8.4, 1.8 Hz, 1H), 7.32 (t, J = 7.7 Hz, 1H), 4.31 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.0, 134.5, 134.0, 133.8, 133.3, 132.4, 129.7, 128.9, 128.7, 128.2, 127.8, 127.6, 127.6, 127.3, 126.7, 126.2, 126.1, 125.7, 125.7, 32.7. **HRMS** (CI) m/z (M^+) calcd for $C_{21}H_{16}Se$: 348.0417, found 348.0426.



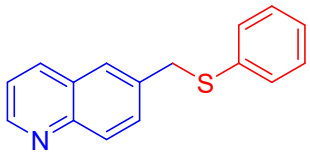
((6-methoxynaphthalen-2-yl)methyl)(phenyl)sulfane (6a)

Yield: 67% (75.1 mg). Yellow solid. **IR** (neat, ν, cm^{-1}): 2920, 2850, 2361, 1599, 1435, 1261, 1163, 1024, 856, 814, 732, 685, 480. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.5 Hz, 1H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.60 – 7.57 (m, 1H), 7.41 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.34 – 7.27 (m, 2H), 7.25 – 7.18 (m, 2H), 7.18 – 7.14 (m, 1H), 7.14 – 7.06 (m, 2H), 4.22 (s, 2H), 3.88 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.7, 136.5, 133.8, 132.5, 130.0, 129.2, 128.9, 128.8, 127.6, 127.3, 127.2, 126.4, 119.0, 105.8, 55.3, 39.4. **HRMS** (CI) m/z (M^+) calcd for $C_{18}H_{16}OS$: 280.0922, found 280.0925.



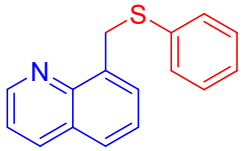
(naphthalen-1-ylmethyl)(phenyl)sulfane (6b)

Yield: 63% (63.2 mg). White solid. **IR** (neat, ν, cm^{-1}): 2922, 2852, 1721, 1478, 1437, 1265, 1121, 1071, 800, 778, 735, 686, 545, 469. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (dq, *J* = 8.7, 0.9 Hz, 1H), 7.87 – 7.81 (m, 1H), 7.73 (t, *J* = 4.8 Hz, 1H), 7.49 (dddd, *J* = 19.6, 8.1, 6.9, 1.5 Hz, 2H), 7.37 – 7.27 (m, 4H), 7.27 – 7.20 (m, 2H), 7.20 – 7.13 (m, 1H), 4.53 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.8, 134.0, 132.8, 131.6, 130.3, 129.0, 128.9, 128.3, 127.4, 126.6, 126.3, 125.9, 125.4, 124.0, 37.2. **HRMS** (CI) m/z (M^+) calcd for $C_{17}H_{14}S$: 250.0816, found 250.0814.



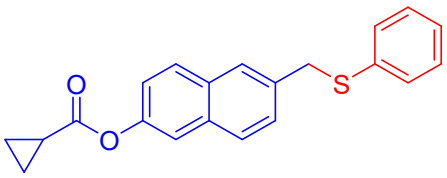
6-((phenylthio)methyl)quinoline (6d)

Yield: 36% (34.6 mg). White solid. **IR** (neat, ν, cm^{-1}): 2920, 2855, 2361, 1724, 1571, 1474, 1080, 840, 737, 689, 473. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.90 (dd, *J* = 4.3, 1.7 Hz, 1H), 8.06 (dd, *J* = 8.3, 2.1 Hz, 2H), 7.71 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.64 (d, *J* = 1.9 Hz, 1H), 7.38 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.35 – 7.30 (m, 2H), 7.30 – 7.23 (m, 2H), 7.23 – 7.18 (m, 1H), 4.29 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.3, 147.6, 136.0, 135.8, 135.6, 130.7, 130.4, 129.8, 128.9, 128.1, 127.1, 126.7, 121.3, 39.3. **HRMS** (CI) m/z (M^+) calcd for $C_{16}H_{13}NS$: 251.0769, found 251.0770.



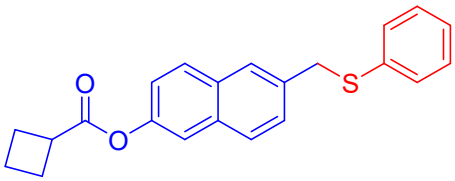
8-((phenylthio)methyl)quinoline (6e)

Yield: 63% (63.2 mg). White solid. **IR** (neat, ν, cm^{-1}): 2921, 2853, 1725, 1573, 1472, 1272, 1071, 793, 728, 688. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.00 (dd, *J* = 4.3, 1.8 Hz, 1H), 8.15 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.74 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.68 (dd, *J* = 7.1, 1.4 Hz, 1H), 7.49 – 7.44 (m, 1H), 7.44 – 7.37 (m, 3H), 7.27 (dd, *J* = 8.5, 6.8 Hz, 2H), 7.22 – 7.16 (m, 1H), 4.90 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.8, 146.4, 137.1, 136.3, 136.0, 129.7, 129.5, 128.8, 128.4, 127.4, 126.2, 126.1, 121.2, 34.3. **HRMS** (CI) m/z (M^+) calcd for $C_{16}H_{13}NS$: 251.0769, found 251.0772.



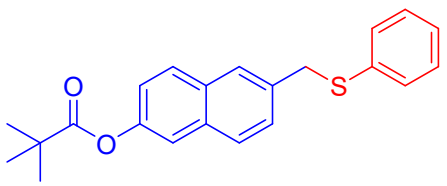
6-((phenylthio)methyl)naphthalen-2-yl cyclopropanecarboxylate (6f)

Yield: 57% (76.2 mg). White solid. **IR** (neat, ν, cm^{-1}): 2921, 1746, 1479, 1383, 1251, 1216, 1150, 1023, 896, 733, 484. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.6 Hz, 2H), 7.68 (s, 1H), 7.57 (d, *J* = 2.3 Hz, 1H), 7.50 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.35 (d, *J* = 6.9 Hz, 2H), 7.25 (dtd, *J* = 16.7, 7.1, 2.8 Hz, 4H), 4.28 (s, 2H), 1.93 (tt, *J* = 8.2, 4.6 Hz, 1H), 1.25 (dd, *J* = 4.5, 3.0 Hz, 2H), 1.08 (dd, *J* = 7.9, 3.4 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.7, 148.5, 136.0, 134.8, 132.9, 131.3, 130.2, 129.1, 128.9, 128.0, 127.7, 127.3, 126.6, 121.5, 118.4, 39.4, 13.1, 9.4. **HRMS** (CI) m/z (M^+) calcd for $C_{21}H_{18}O_2S$: 334.1028, found 334.1029.



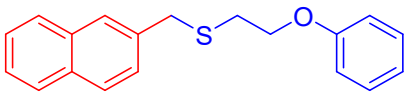
6-((phenylthio)methyl)naphthalen-2-yl cyclobutanecarboxylate (6g)

Yield: 42% (58.5 mg). White solid. **IR** (neat, ν, cm^{-1}): 2947, 1748, 1478, 1357, 1245, 1210, 1146, 899, 741, 481. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 8.7, 1.9 Hz, 2H), 7.69 (s, 1H), 7.56 (d, *J* = 2.2 Hz, 1H), 7.50 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.35 (d, *J* = 7.2 Hz, 2H), 7.31 – 7.18 (m, 4H), 4.28 (s, 2H), 3.47 (t, *J* = 8.5 Hz, 1H), 2.60 – 2.46 (m, 2H), 2.45 – 2.33 (m, 2H), 2.10 (dqd, *J* = 19.9, 10.6, 9.7, 4.1 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.1, 148.5, 136.0, 134.8, 132.9, 131.3, 130.2, 129.1, 128.9, 128.0, 127.7, 127.3, 126.6, 121.5, 118.3, 39.4, 38.2, 25.4, 18.5. **HRMS** (CI) m/z (M^+) calcd for $C_{22}H_{20}O_2S$: 348.1184, found 348.1187.



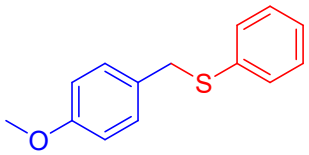
6-((phenylthio)methyl)naphthalen-2-yl pivalate (6h)

Yield: 61% (85.5 mg). White solid. **IR** (neat, ν, cm^{-1}): 2971, 1746, 1475, 1365, 1275, 1210, 1130, 908, 739, 691, 475. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 – 7.74 (m, 2H), 7.69 (d, *J* = 1.7 Hz, 1H), 7.56 – 7.48 (m, 2H), 7.40 – 7.33 (m, 2H), 7.28 (ddd, *J* = 7.7, 6.6, 1.4 Hz, 2H), 7.25 – 7.18 (m, 2H), 4.29 (s, 2H), 1.45 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.3, 148.8, 136.1, 134.8, 133.0, 131.2, 130.2, 129.1, 128.9, 128.0, 127.7, 127.3, 126.6, 121.5, 118.3, 39.4, 27.2. **HRMS** (CI) m/z (M^+) calcd for $C_{22}H_{22}O_2S$: 350.1341, found 350.1348.



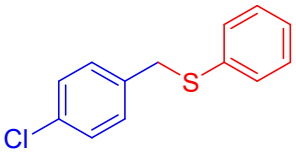
(naphthalen-2-ylmethyl)(2-phenoxyethyl)sulfane (6i)

Yield: 44% (51.3mg). White solid. **IR** (neat, ν, cm^{-1}): 3053, 2919, 1598, 1494, 1238, 1030, 817, 748, 689, 474. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 16.7, 7.2 Hz, 3H), 7.75 (d, *J* = 1.7 Hz, 1H), 7.56 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.54 – 7.46 (m, 2H), 7.32 – 7.24 (m, 2H), 6.98 (t, *J* = 7.4 Hz, 1H), 6.92 – 6.83 (m, 2H), 4.14 (t, *J* = 6.7 Hz, 2H), 4.02 (s, 2H), 2.83 (t, *J* = 6.7 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.4, 135.5, 133.2, 132.6, 129.5, 128.6, 127.7, 127.7, 127.5, 127.1, 126.3, 125.9, 121.0, 114.6, 67.7, 37.0, 29.9. **HRMS** (CI) m/z (M^+) calcd for $C_{19}H_{18}OS$: 294.1078, found 294.1072.



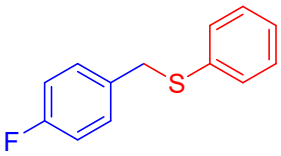
(4-methoxybenzyl)(phenyl)sulfane (7a)

Yield: 54% (64.9 mg). White solid. **IR** (neat, ν, cm^{-1}): 2920, 1577, 1504, 1232, 1029, 824, 734, 688, 472. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 2H), 7.32 – 7.26 (m, 2H), 7.27 – 7.18 (m, 3H), 6.88 – 6.83 (m, 2H), 4.11 (s, 2H), 3.81 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.8, 136.6, 130.0, 129.8, 129.4, 128.8, 126.3, 113.9, 55.3, 38.4. **HRMS** (CI) m/z (M^+) calcd for $C_{14}H_{14}OS$: 230.0765, found 230.0771.



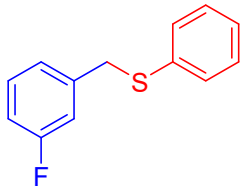
(4-chlorobenzyl)(phenyl)sulfane (7b)

Yield: 56% (52.5 mg). White solid. **IR** (neat, ν, cm^{-1}): 2920, 2851, 2361, 1576, 1472, 1082, 1008, 731, 686, 482. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.14 (m, 9H), 4.09 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.1, 135.7, 132.9, 130.3, 130.1, 128.9, 128.6, 126.7, 38.6. **HRMS** (CI) m/z (M^+) calcd for $C_{13}H_{11}ClS$: 234.0270, found 234.0273.



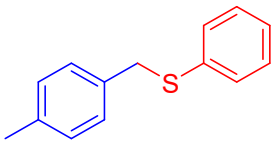
(4-fluorobenzyl)(phenyl)sulfane (7c)

Yield: 56% (57.5 mg). White solid. **IR** (neat, ν, cm^{-1}): 2922, 2852, 1503, 1473, 1224, 1083, 832, 729, 686, 485. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.14 (m, 7H), 6.95 (td, *J* = 8.5, 3.2 Hz, 2H), 4.06 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.0 (*J* = 244.1), 135.9, 133.3 (*J* = 3.2), 130.4 (*J* = 8.0), 130.2, 128.9, 126.6, 115.4 (*J* = 21.4), 38.5. **HRMS** (CI) m/z (M^+) calcd for $C_{13}H_{11}FS$: 218.0565, found 218.0564.



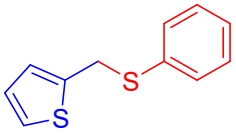
(3-fluorobenzyl)(phenyl)sulfane (7d)

Yield: 58% (59.5 mg). White solid. **IR** (neat, ν, cm^{-1}): 2925, 1615, 1586, 1480, 1439, 1255, 1134, 943, 881, 783, 736, 688, 473. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.27 – 7.20 (m, 3H), 7.19 – 7.15 (m, 1H), 7.05 – 6.96 (m, 2H), 6.91 (tdd, *J* = 8.4, 2.6, 0.9 Hz, 1H), 4.07 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.8 (*J* = 244.6), 140.2 (*J* = 7.6), 135.7, 130.2, 129.9 (*J* = 8.5), 129.0, 126.7, 124.5 (*J* = 2.3), 115.7 (*J* = 21.7), 114.1 (*J* = 21.0), 38.8. **HRMS** (CI) m/z (M^+) calcd for $C_{13}H_{11}FS$: 218.0565, found 218.0563.



(4-methylbenzyl)(phenyl)sulfane (7e)

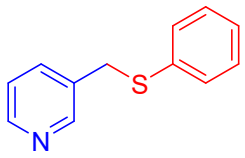
Yield: 57% (46.8 mg). White solid. **IR** (neat, ν, cm^{-1}): 2922, 2852, 2361, 1733, 1459, 1287, 1080, 818, 736, 688, 473. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 7.0 Hz, 2H), 7.23 (t, *J* = 7.7 Hz, 2H), 7.17 (dd, *J* = 7.7, 5.8 Hz, 3H), 7.07 (d, *J* = 7.8 Hz, 2H), 4.07 (s, 2H), 2.30 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.9, 136.7, 134.4, 129.7, 129.2, 128.9, 128.8, 126.2, 38.7, 21.2. **HRMS** (CI) m/z (M^+) calcd for $C_{14}H_{14}S$: 214.0816, found 214.0815.



2-((phenylthio)methyl)thiophene (7f)

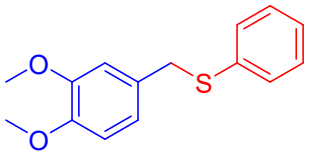
Yield: 54% (44.8 mg). White solid. **IR** (neat, ν, cm^{-1}): 2920, 1728, 1581, 1479, 1437, 1229, 850, 736, 687, 473. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.36 (m, 2H), 7.34 –

7.28 (m, 2H), 7.28 – 7.22 (m, 1H), 7.21 (dd, J = 4.3, 2.1 Hz, 1H), 6.94 – 6.88 (m, 2H), 4.35 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.9, 135.7, 130.4, 128.9, 126.8, 126.8, 126.3, 125.0 33.8. **HRMS** (CI) m/z (M^+) calcd for $C_{11}H_{10}S_2$: 206.0224, found 206.0229.



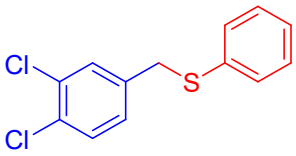
3-((phenylthio)methyl)pyridine (7g)

Yield: 80% (64.6 mg). Yellow solid. **IR** (neat, ν, cm^{-1}): 2956, 2926, 1721, 1577, 1479, 1438, 1423, 1266, 1025, 739, 710, 690, 474. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.46 (dd, J = 5.0, 1.8 Hz, 2H), 7.58 (dt, J = 8.0, 2.0 Hz, 1H), 7.32 – 7.28 (m, 2H), 7.28 – 7.23 (m, 2H), 7.20 (td, J = 7.9, 3.2 Hz, 2H), 4.06 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.9, 148.5, 136.2, 134.9, 133.5, 130.7, 129.0, 127.0, 123.4, 36.5. **HRMS** (CI) m/z (M^+) calcd for $C_{12}H_{11}NS$: 201.0612, found 201.0616.



(3,4-dimethoxybenzyl)(phenyl)sulfane (7k)

Yield: 65% (66.6 mg). White solid. **IR** (neat, ν, cm^{-1}): 2929, 1728, 1575, 1513, 1478, 1421, 1261, 1025, 738, 710, 472. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 2H), 7.31 – 7.24 (m, 2H), 7.24 – 7.17 (m, 1H), 6.87 – 6.81 (m, 2H), 6.79 (d, J = 8.1 Hz, 1H), 4.09 (s, 2H), 3.85 (d, J = 14.2 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.9, 148.2, 136.4, 130.1, 129.9, 128.9, 126.4, 121.0, 111.9, 111.0, 55.9, 55.8, 39.0. **HRMS** (CI) m/z (M^+) calcd for $C_{15}H_{16}O_2S$: 260.0871, found 260.0873.



(3,4-dichlorobenzyl)(phenyl)sulfane (7l)

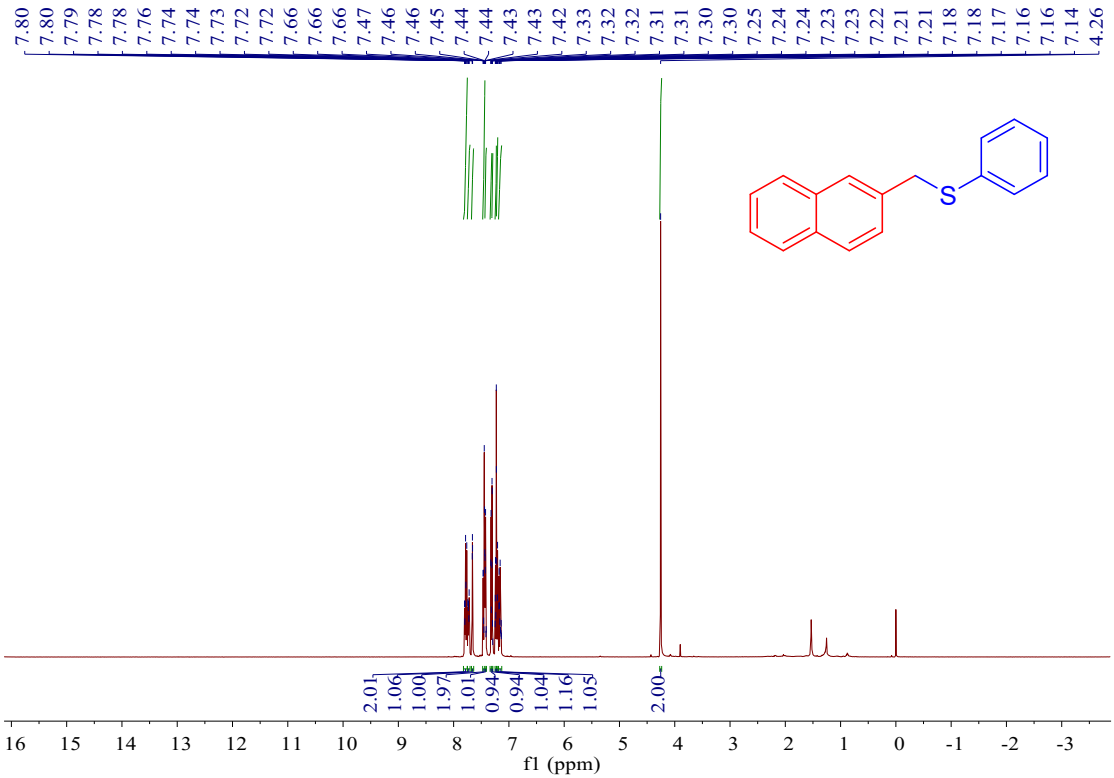
Yield: 68% (73.0 mg). White solid. **IR** (neat, ν, cm^{-1}): 2924, 1730, 1583, 1513, 1469, 1438, 1131, 1028, 889, 735, 688, 438. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.34 (m, 2H), 7.33 – 7.28 (m, 4H), 7.28 – 7.24 (m, 1H), 7.11 (dd, J = 8.2, 2.1 Hz, 1H), 4.04 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.0, 135.1, 132.4, 131.1, 130.7, 130.6, 130.4, 129.0, 128.1, 127.0, 38.3. **HRMS** (CI) m/z (M^+) calcd for $C_{13}H_{10}Cl_2S$: 267.9880, found 267.9879.

V. References

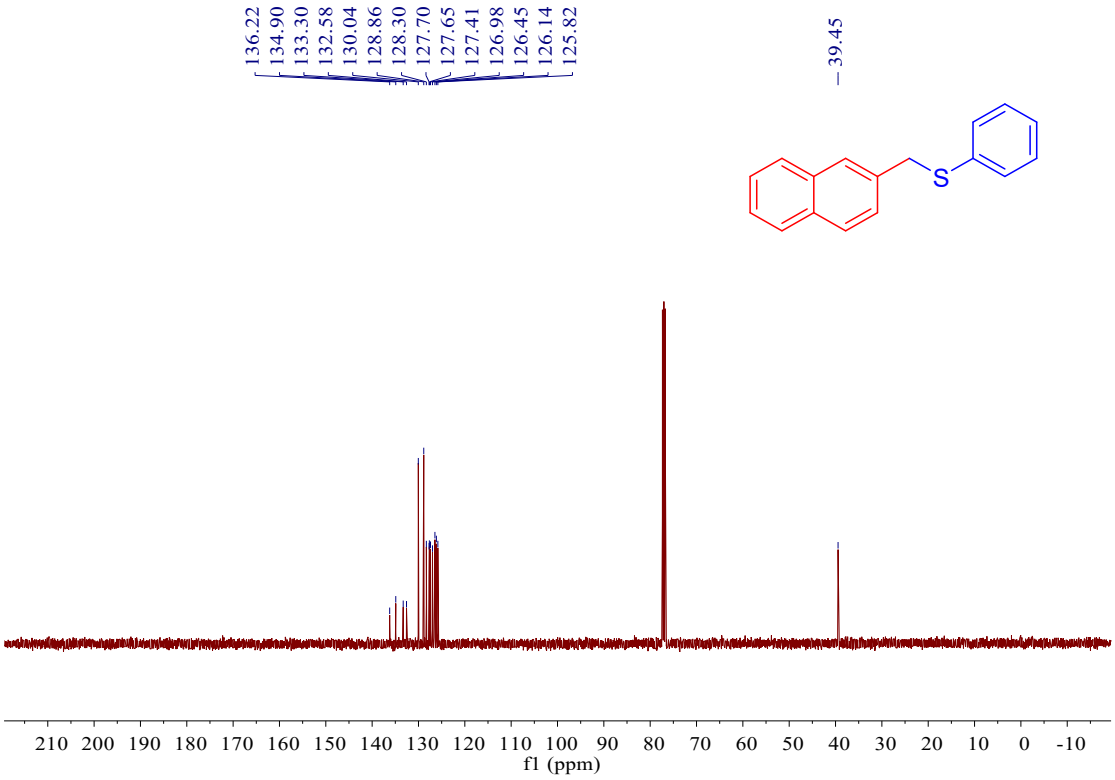
[1] He, R.-D.; Li, C.-L.; Pan, Q.-Q.; Guo, P.; Liu, X.-Y.; Shu, X.-Z. Reductive Coupling between C–N and C–O Electrophiles. *J. Am. Chem. Soc.* **2019**, *141*, 12481–12486.
[2] Fang, Y.; Rogge, T.; Ackermann, L.; Wang, S.-Y.; Ji, S.-J. *Nat. Commun*. **2018**, *9*, 2240.
[3] Liang, G.; Liu, M.; Chen, J.; Ding, J.; Gao, W.; Wu, H. NBS-Promoted Sulfenylation of Sulfinates with Disulfides Leading to Unsymmetrical or Symmetrical Thiosulfonates. *Chin. J. Chem.* **2012**, *30*, 1611–1616.
[4] Stoll, A. H., Krasovskiy, A. & Knochel, P. Functionalized Benzylic Magnesium Reagents through a Sulfur–Magnesium Exchange. *Angew. Chem. Int. Ed*. **2006**.*45*, 606-609.

VI. Copies of ^{1}H NMR and ^{13}C NMR Spectra

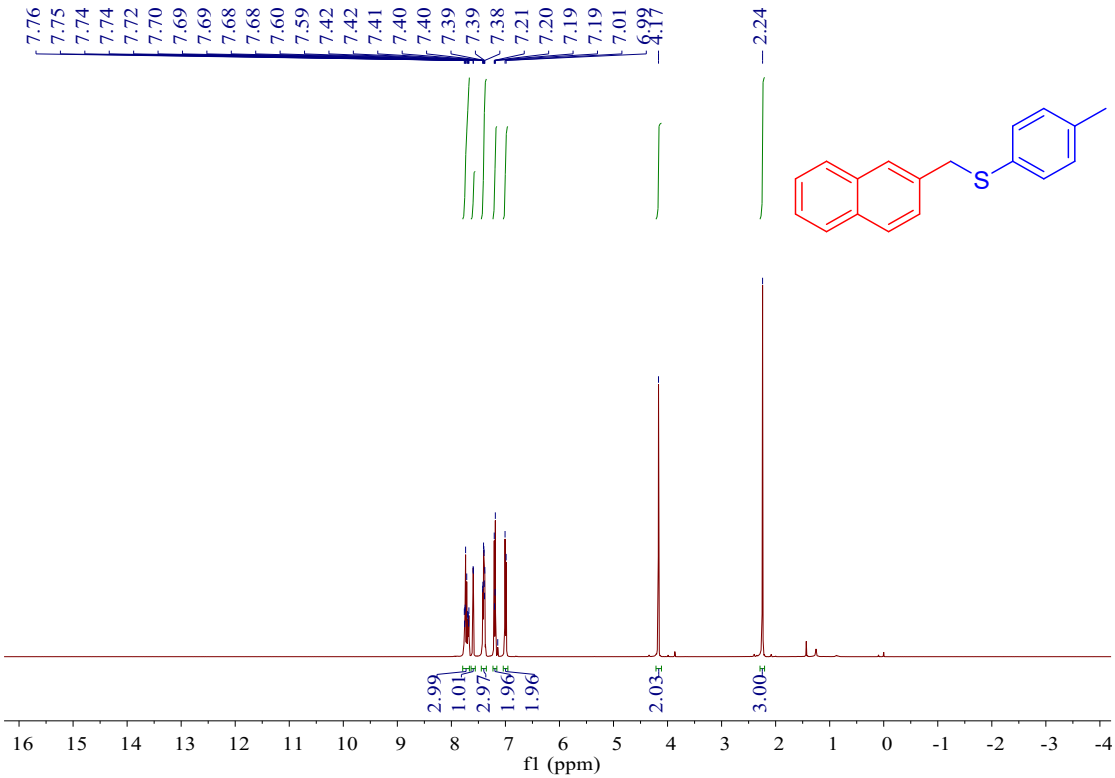
^{1}H NMR Spectra of **3a** (400 MHz, $CDCl_3$)



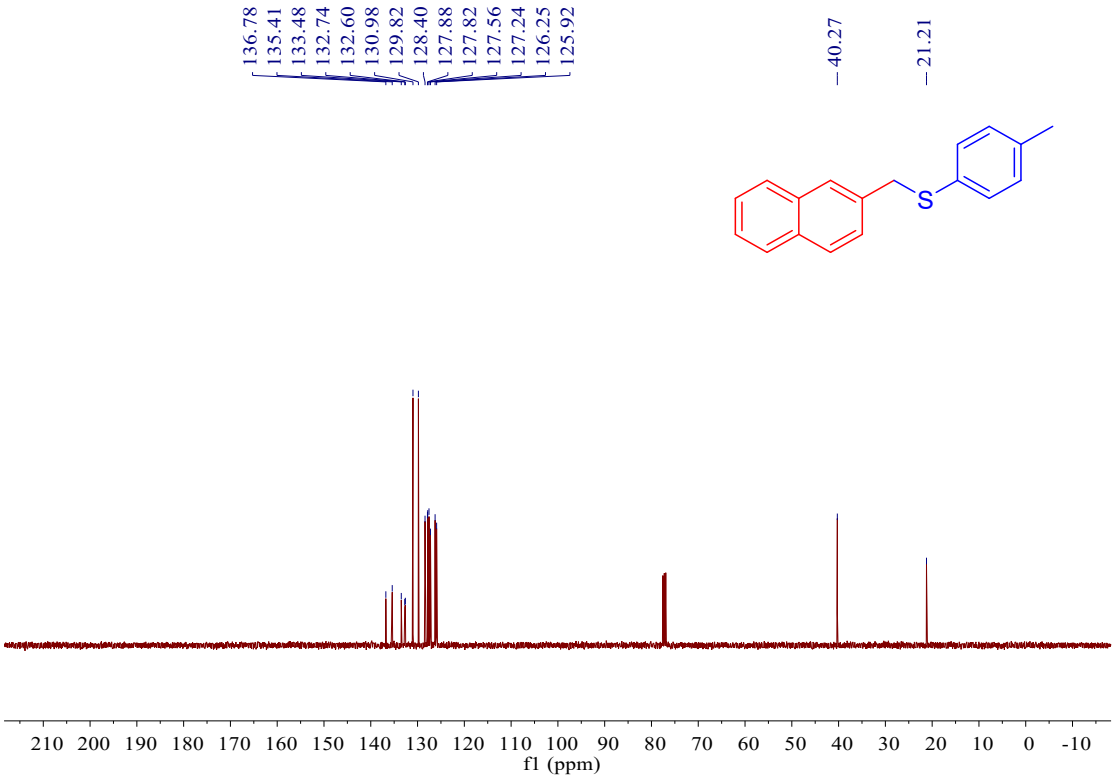
^{13}C NMR Spectra of **3a** (400 MHz, $CDCl_3$)



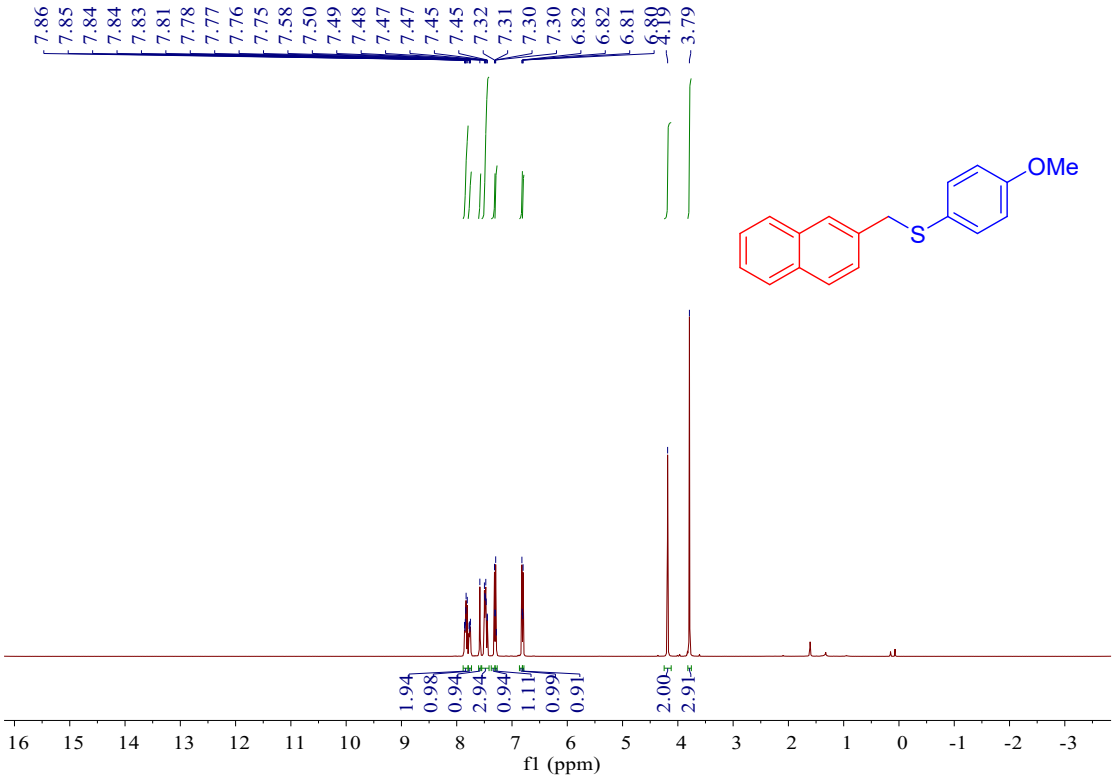
^{1}H NMR Spectra of **3b** (400 MHz, $CDCl_3$)



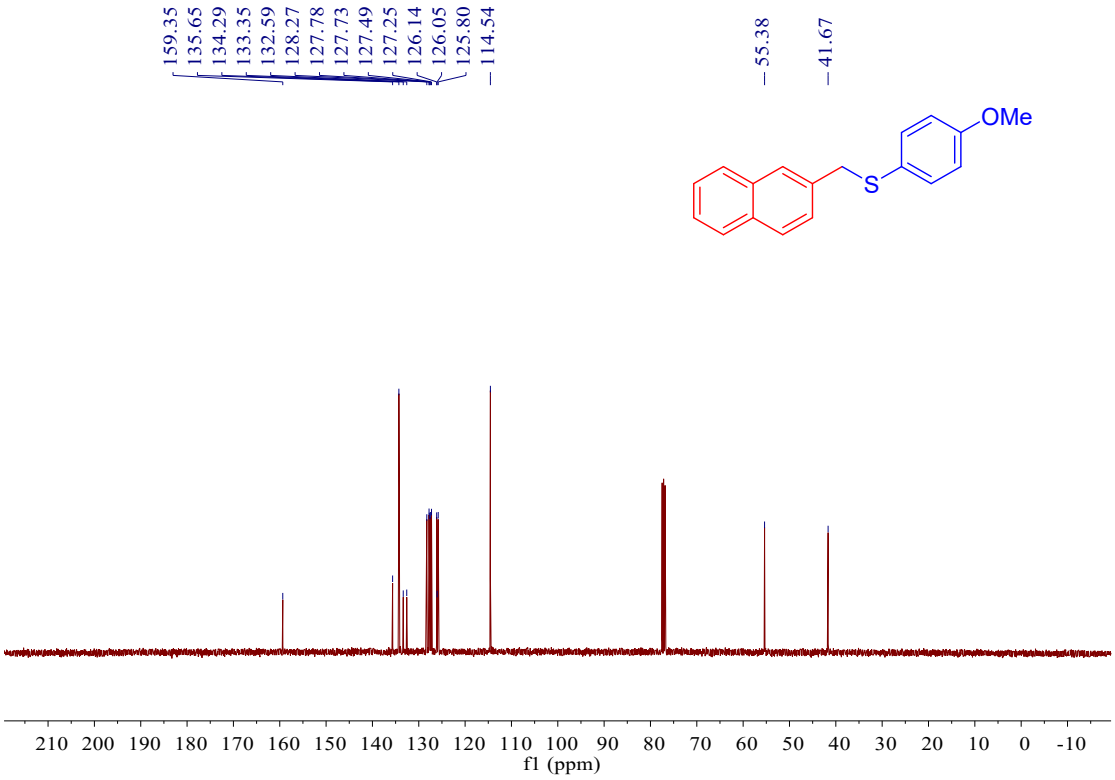
^{13}C NMR Spectra of **3b** (400 MHz, $CDCl_3$)



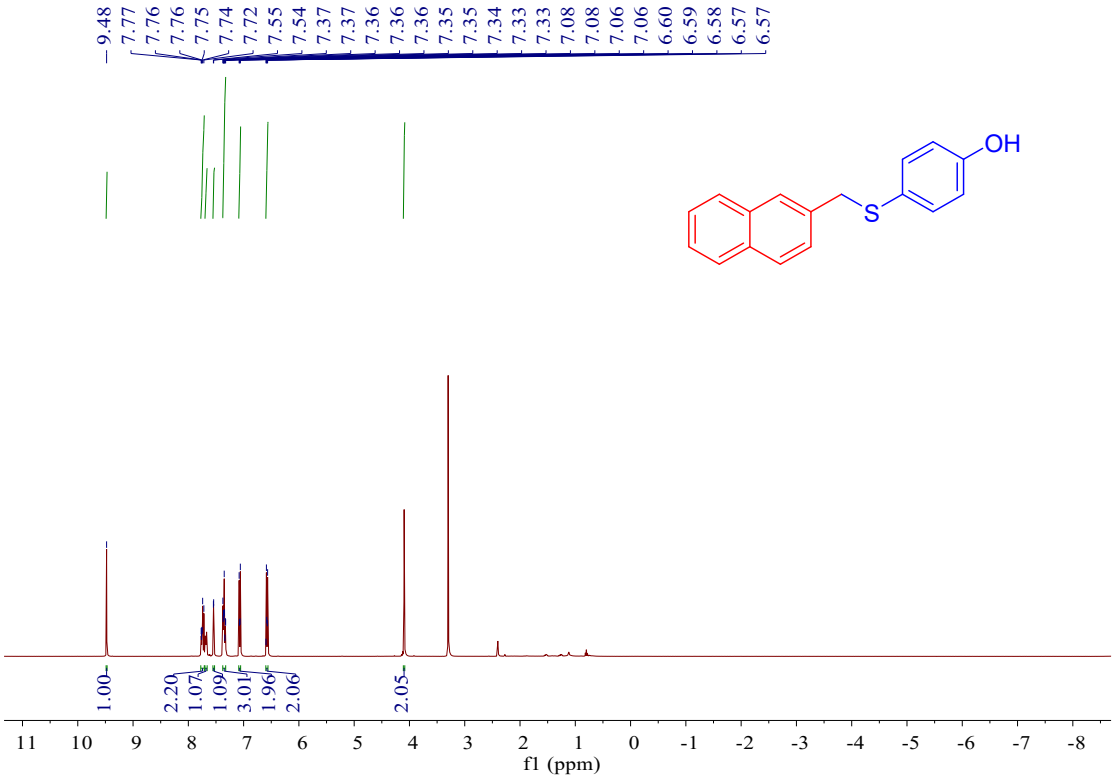
^{1}H NMR Spectra of **3c** (400 MHz, $CDCl_3$)



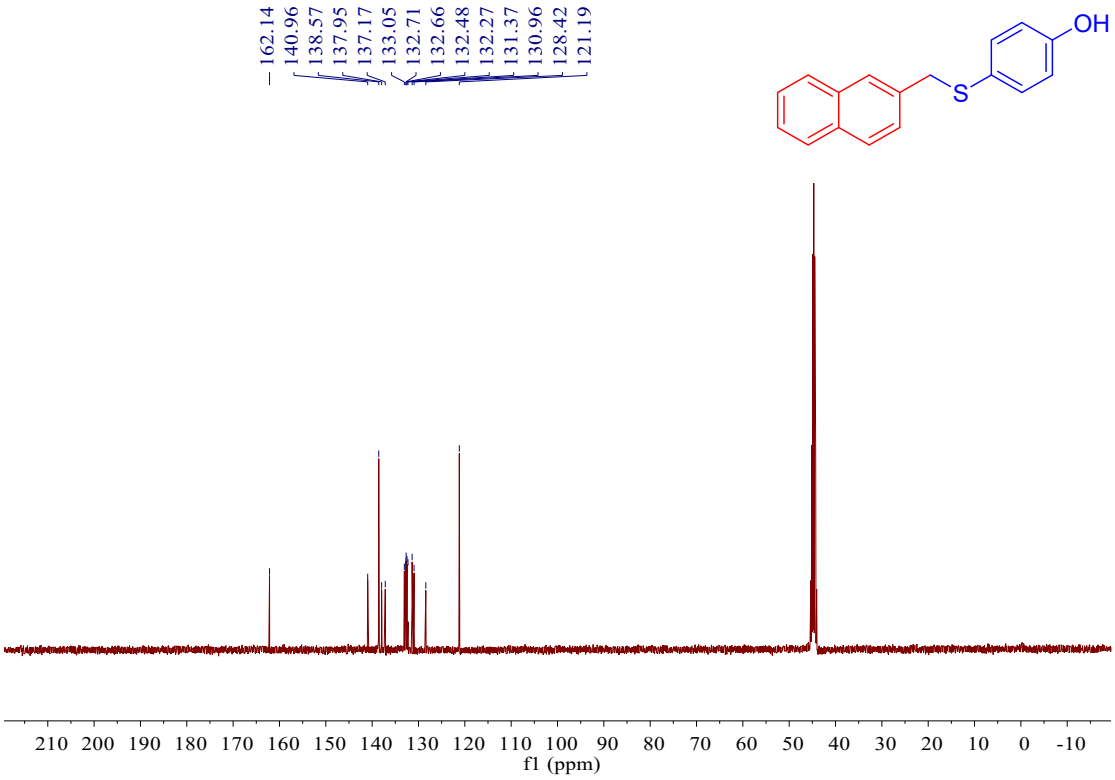
^{13}C NMR Spectra of **3c** (400 MHz, $CDCl_3$)



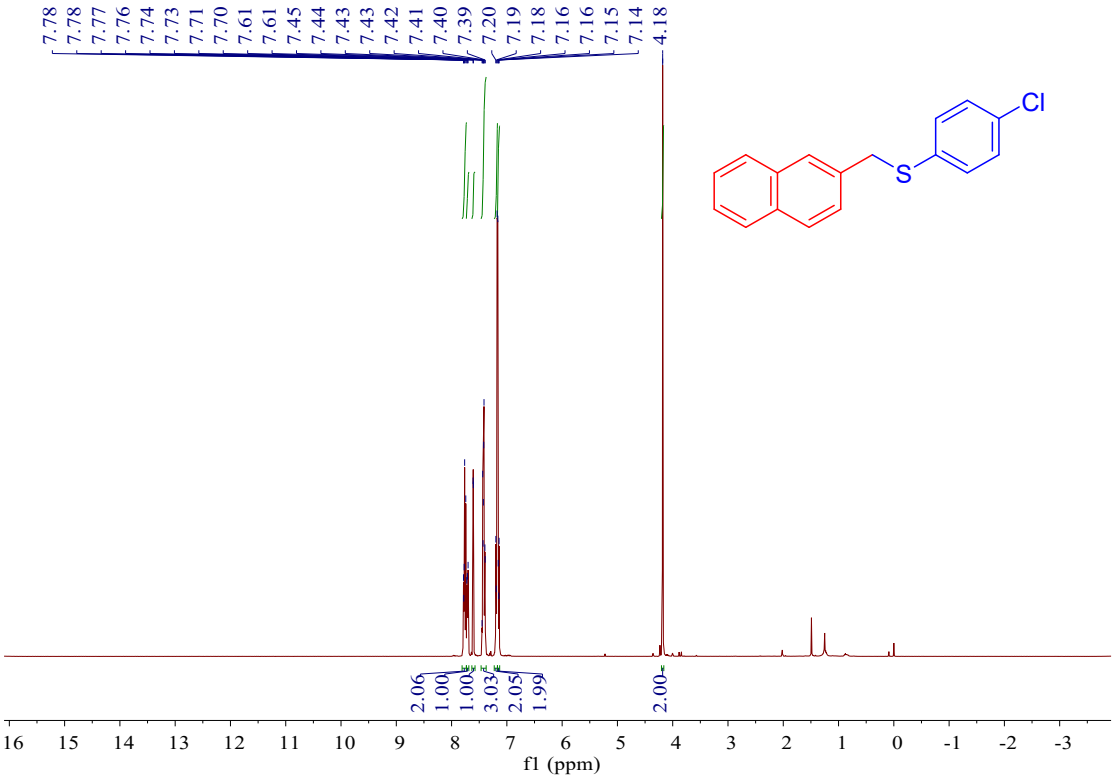
^{1}H NMR Spectra of **3d** (400 MHz, DMSO)



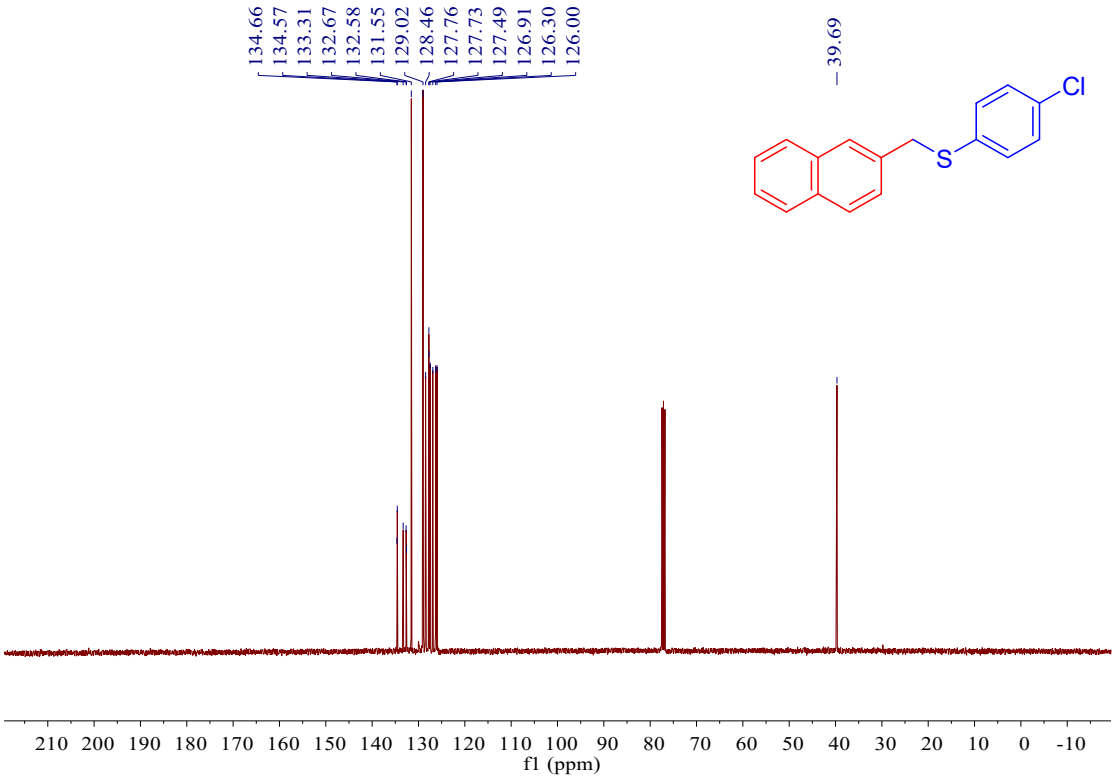
^{13}C NMR Spectra of **3d** (400 MHz, DMSO)



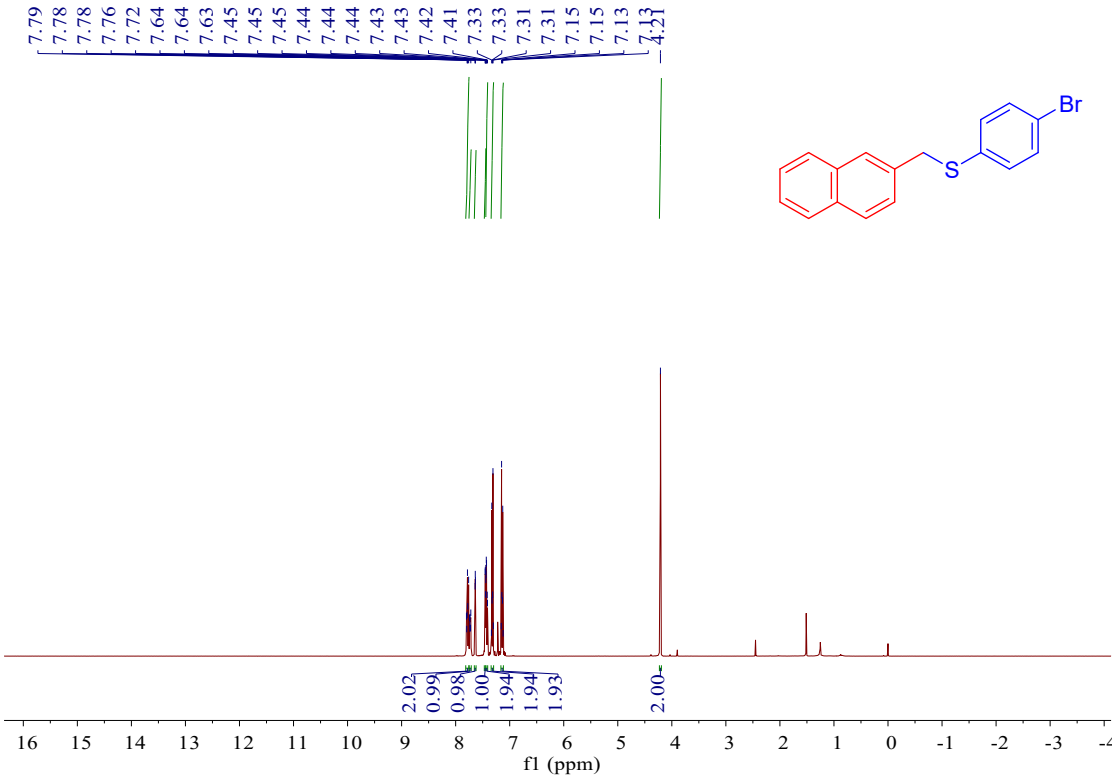
^{1}H NMR Spectra of **3e** (400 MHz, $CDCl_3$)



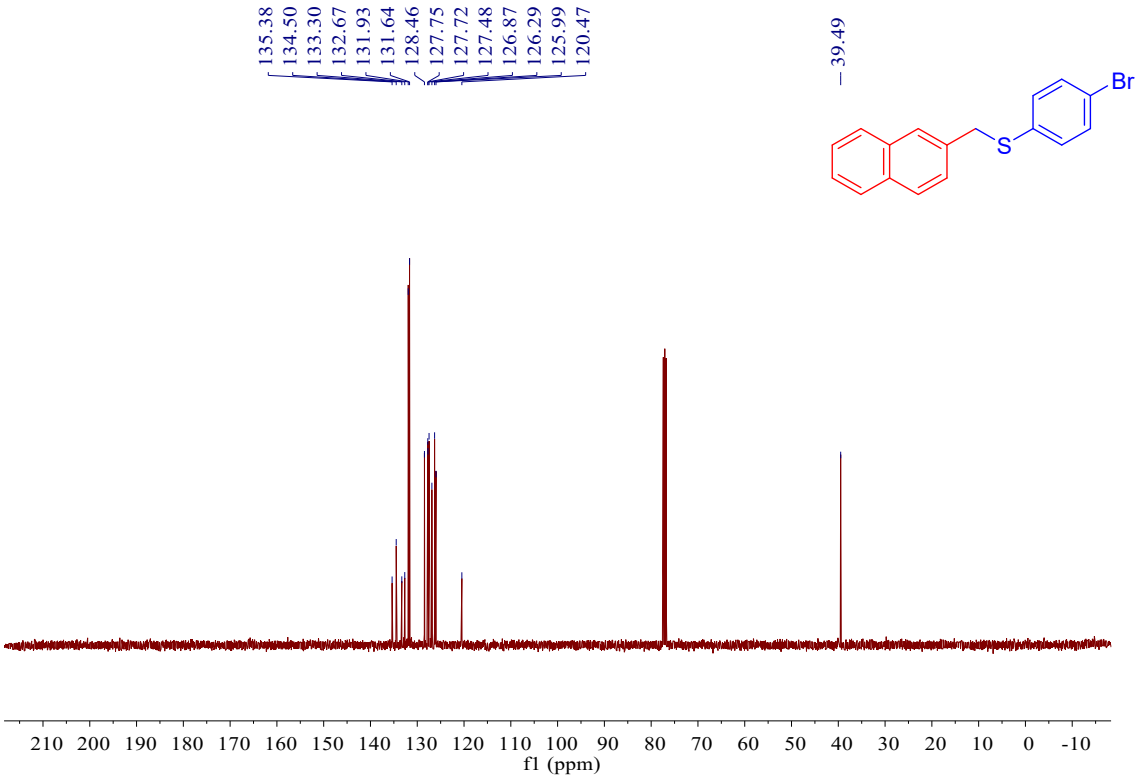
^{13}C NMR Spectra of **3e** (400 MHz, $CDCl_3$)



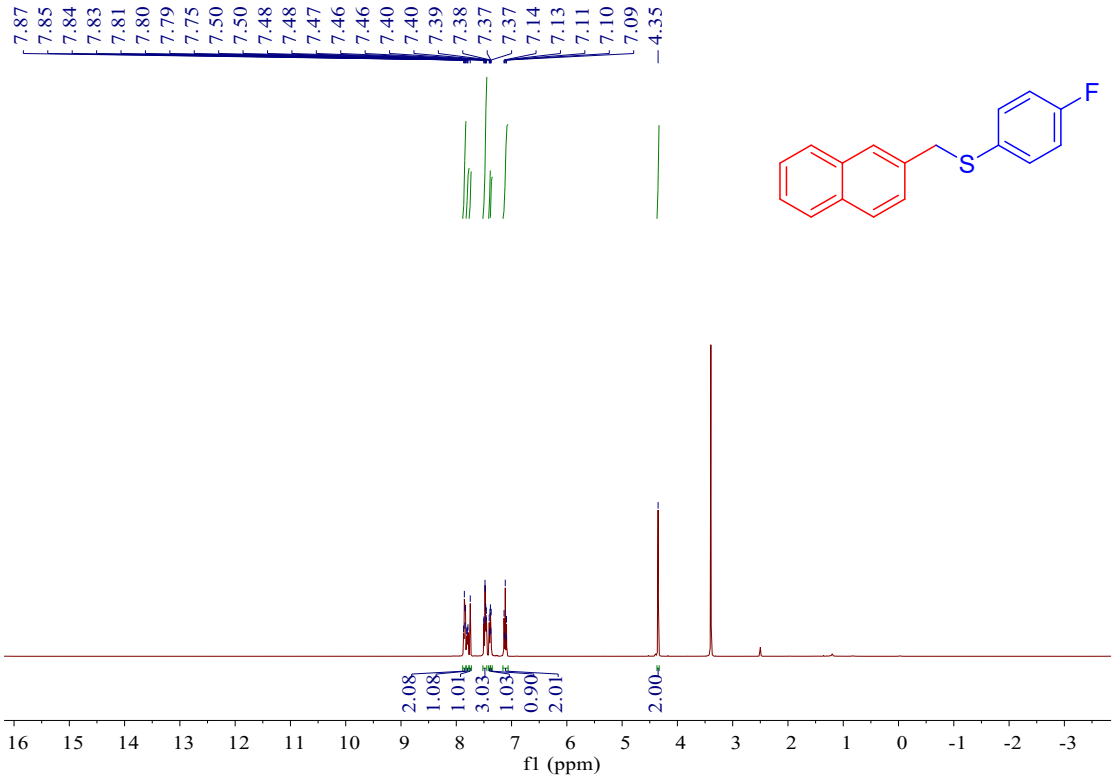
^{1}H NMR Spectra of **3f** (400 MHz, $CDCl_3$)



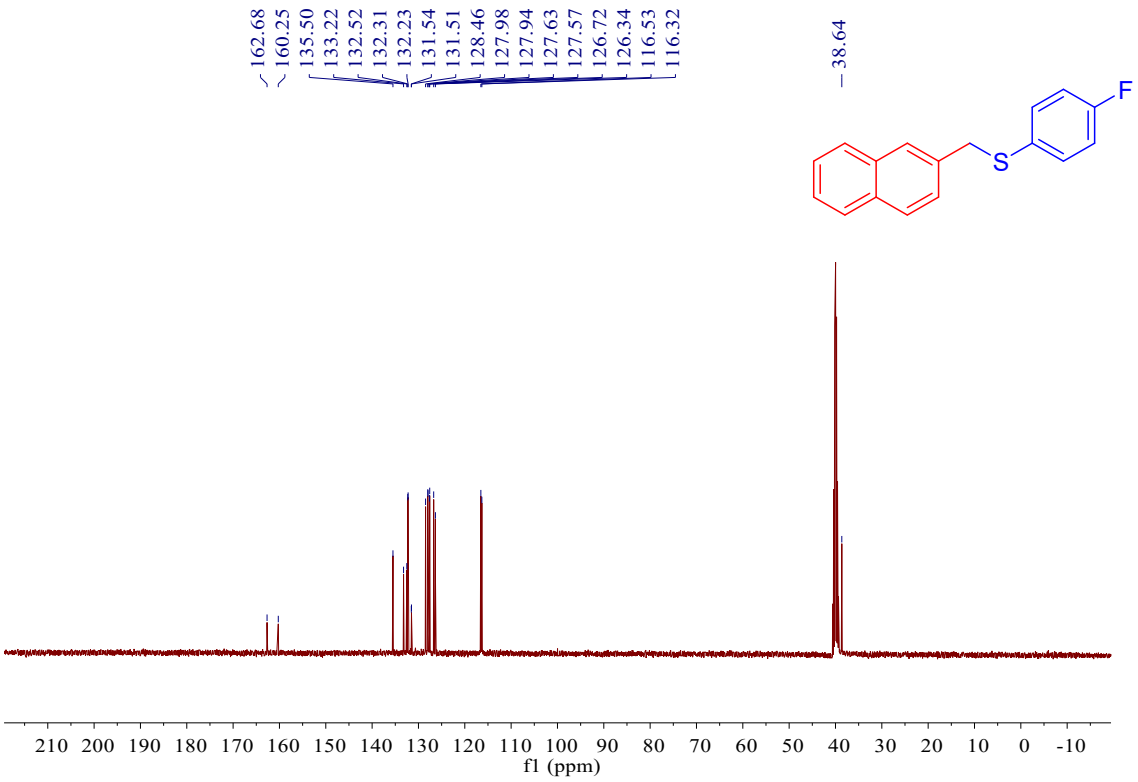
^{13}C NMR Spectra of **3f** (400 MHz, $CDCl_3$)



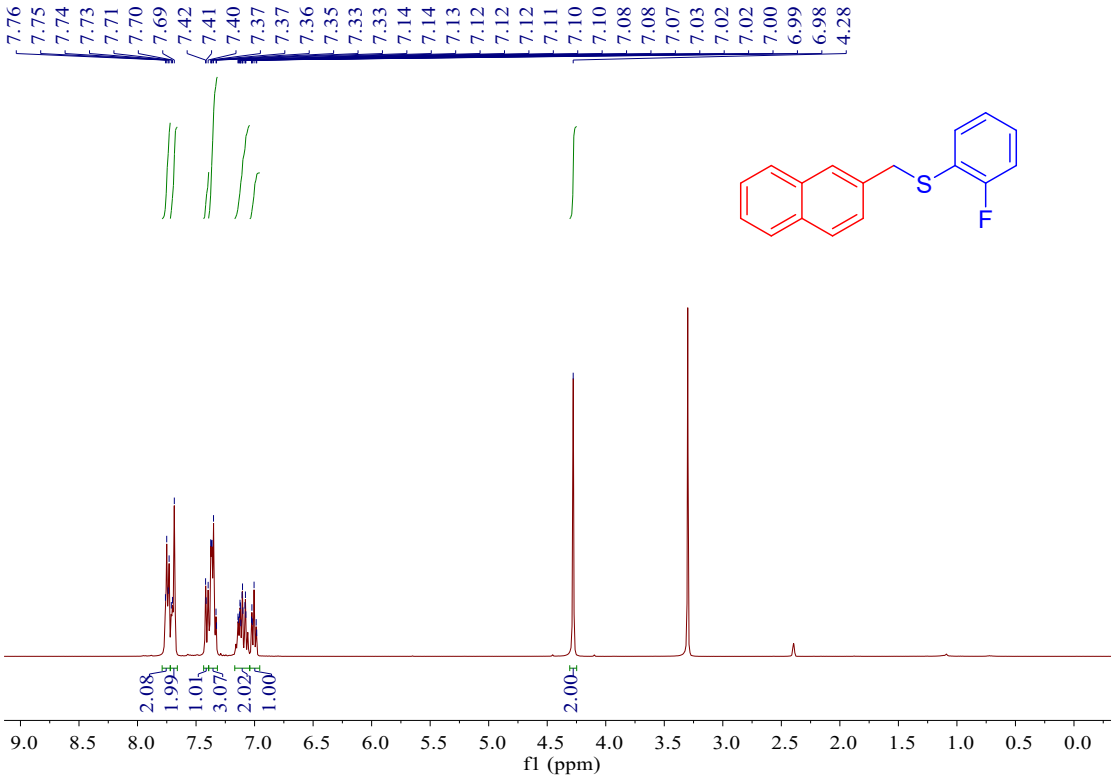
^{1}H NMR Spectra of **3g** (400 MHz, DMSO)



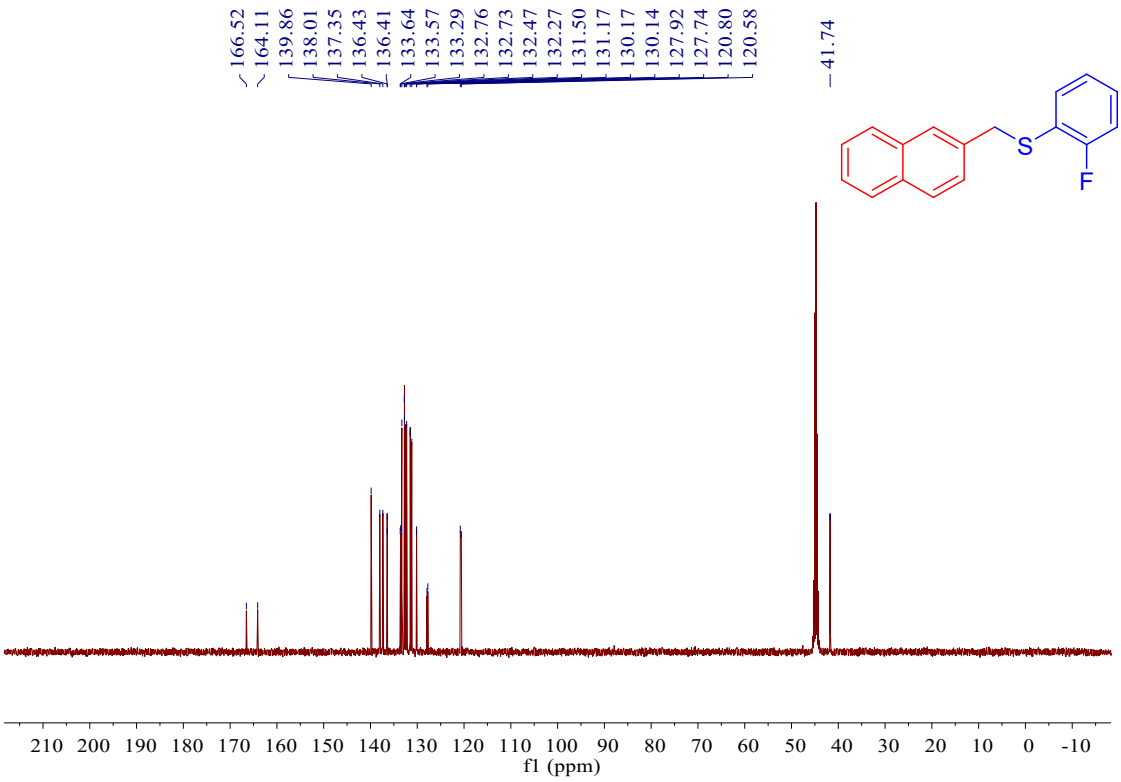
^{13}C NMR Spectra of **3g** (400 MHz, DMSO)



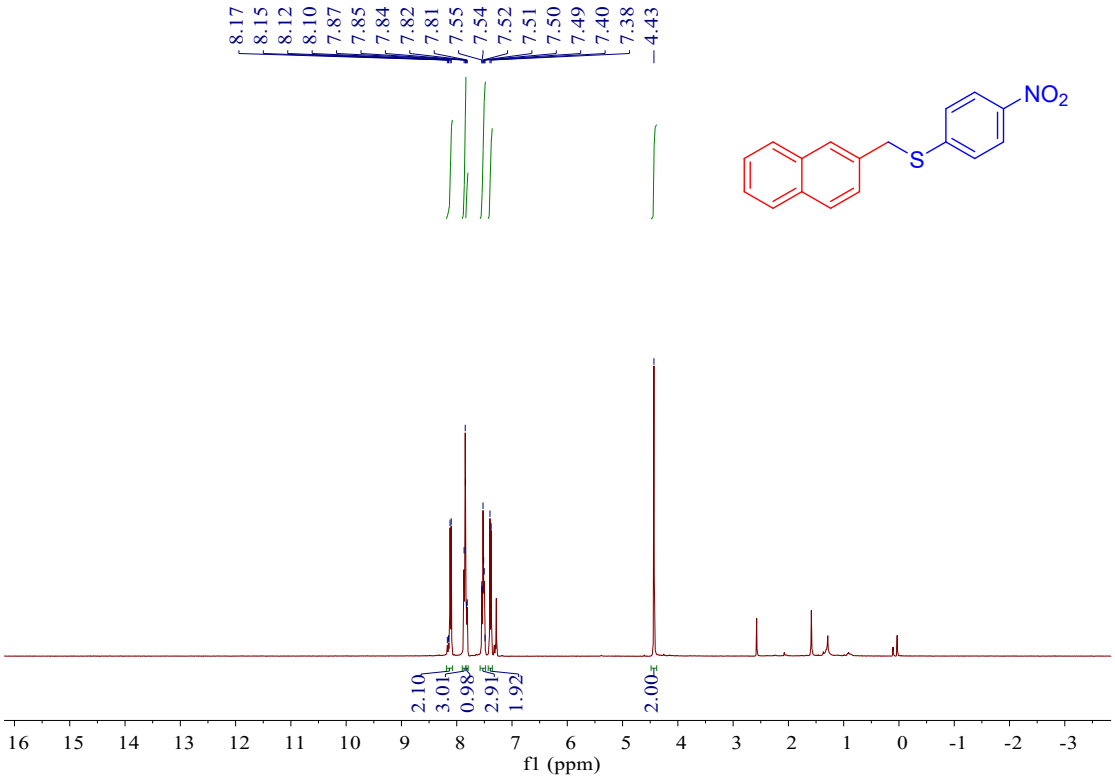
^{1}H NMR Spectra of **3h** (400 MHz, DMSO)



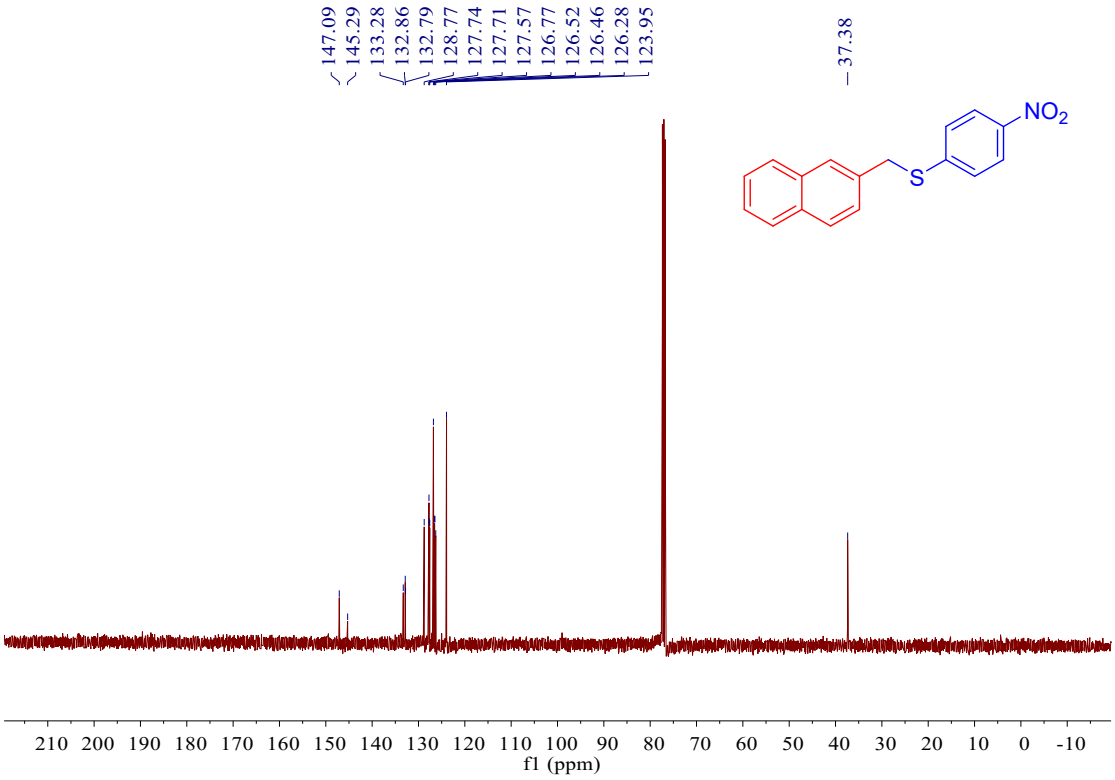
^{13}C NMR Spectra of **3h** (400 MHz, DMSO)



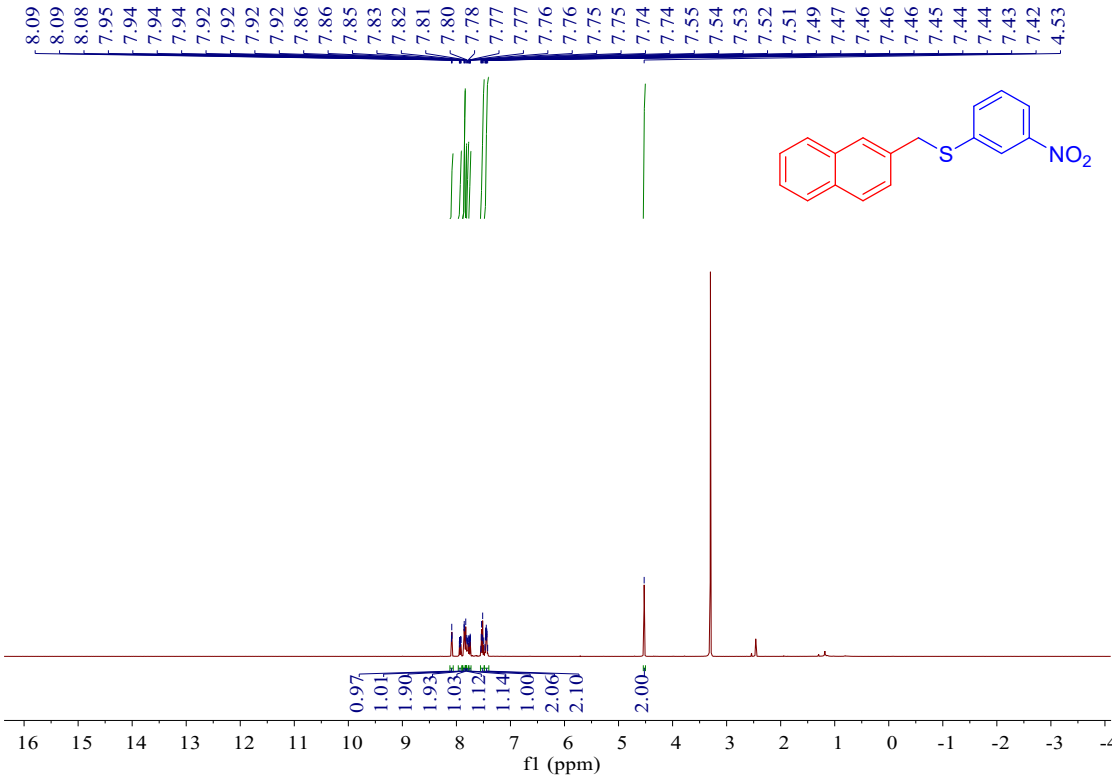
^{1}H NMR Spectra of **3i** (400 MHz, $CDCl_3$)



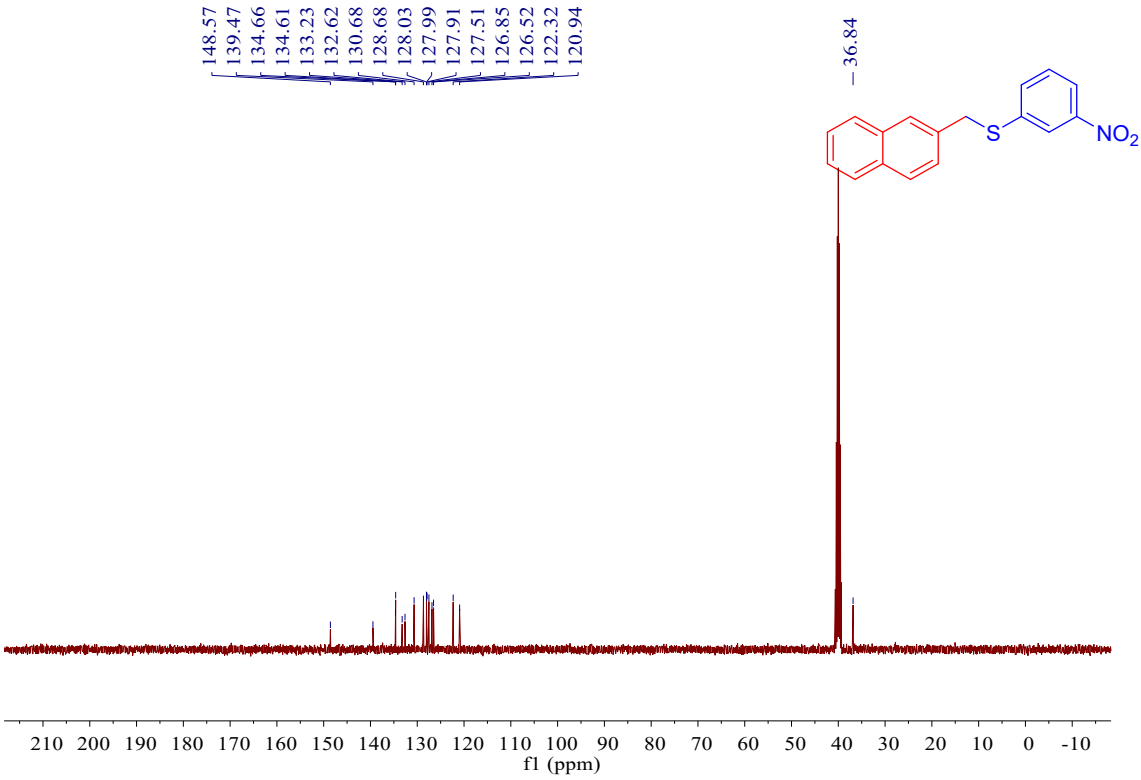
^{13}C NMR Spectra of **3i** (400 MHz, $CDCl_3$)



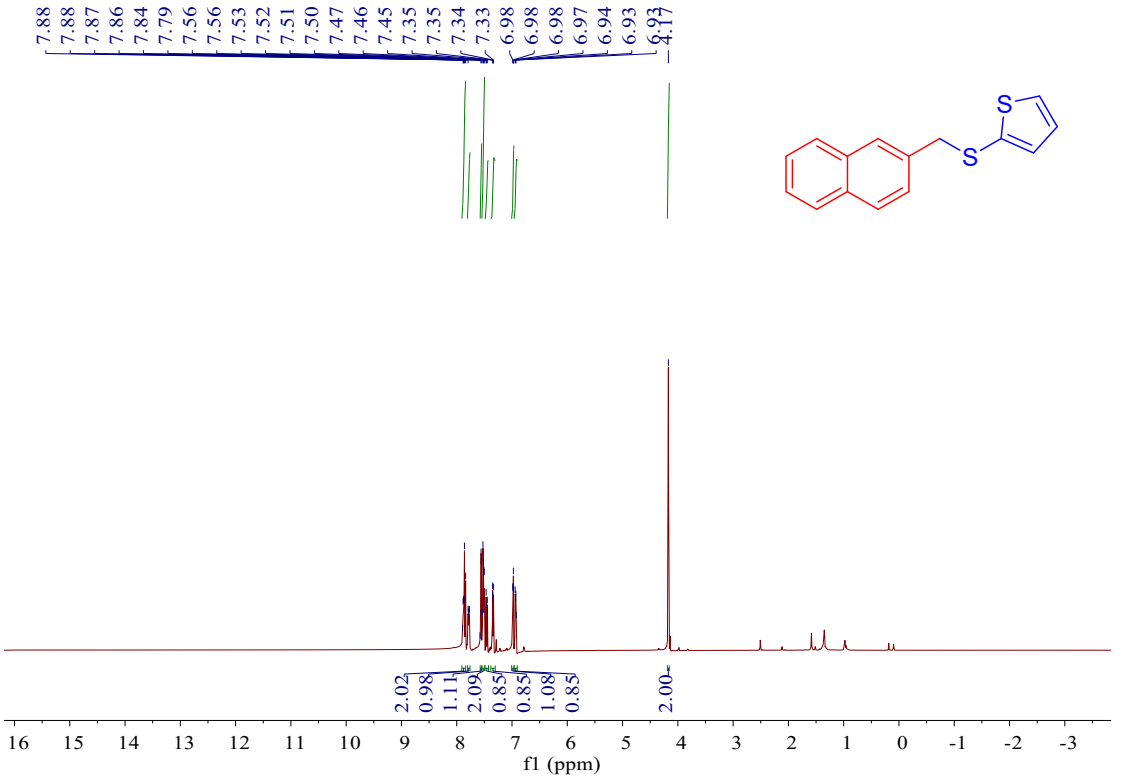
^{1}H NMR Spectra of **3j** (400 MHz, DMSO)



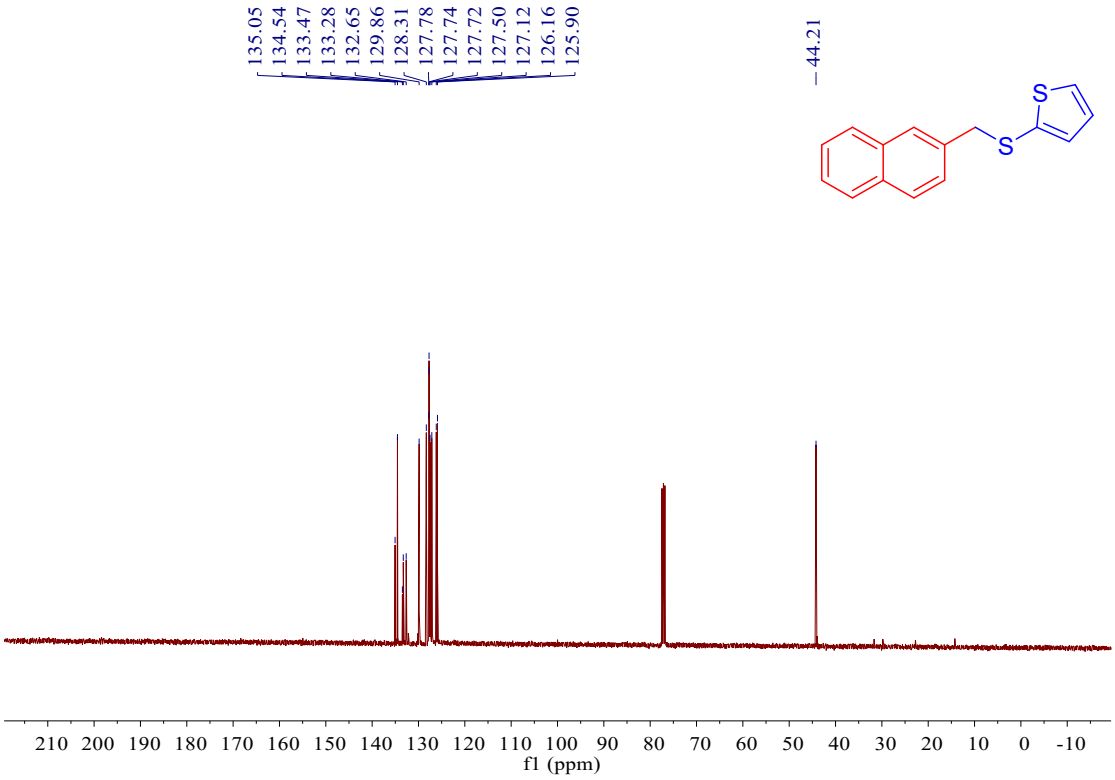
^{13}C NMR Spectra of **3j** (400 MHz, DMSO)



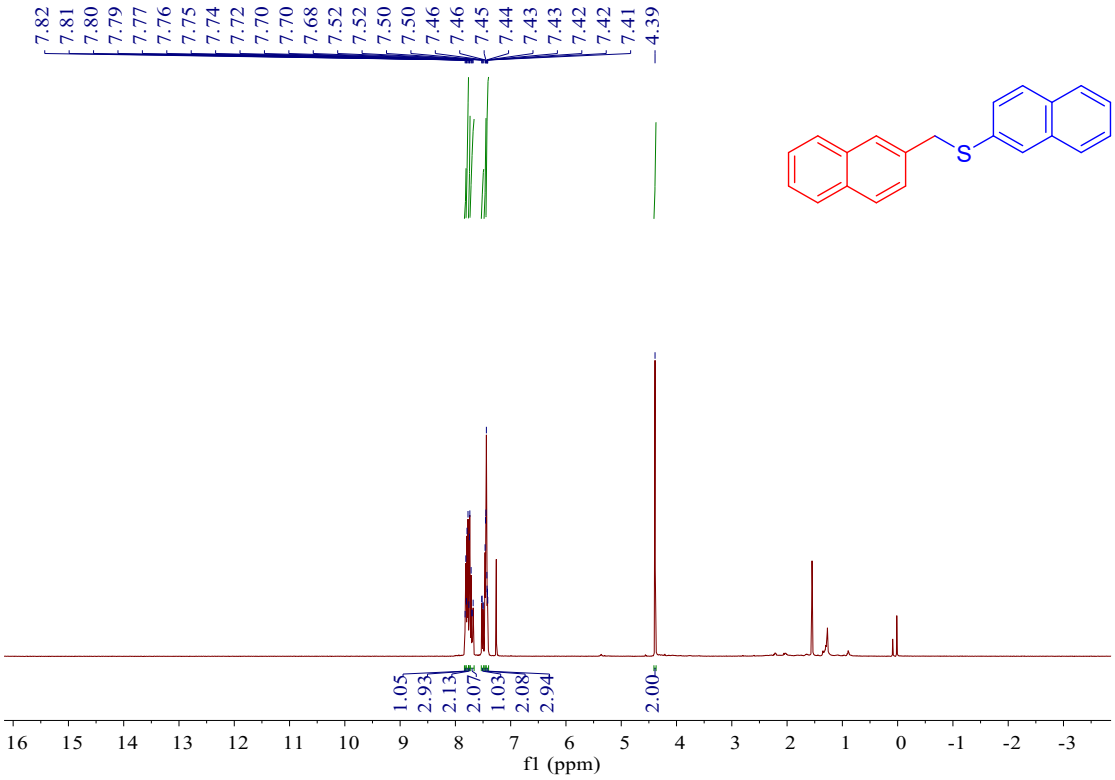
^{1}H NMR Spectra of **3k** (400 MHz, $CDCl_3$)



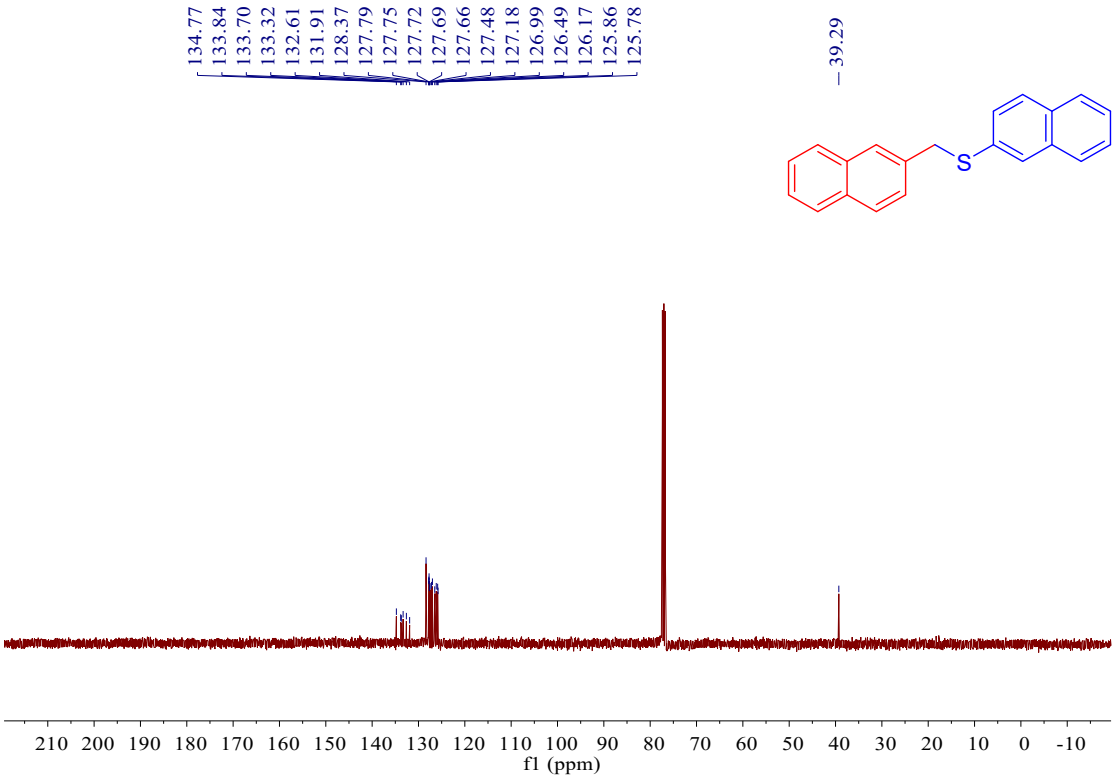
^{13}C NMR Spectra of **3k** (400 MHz, $CDCl_3$)



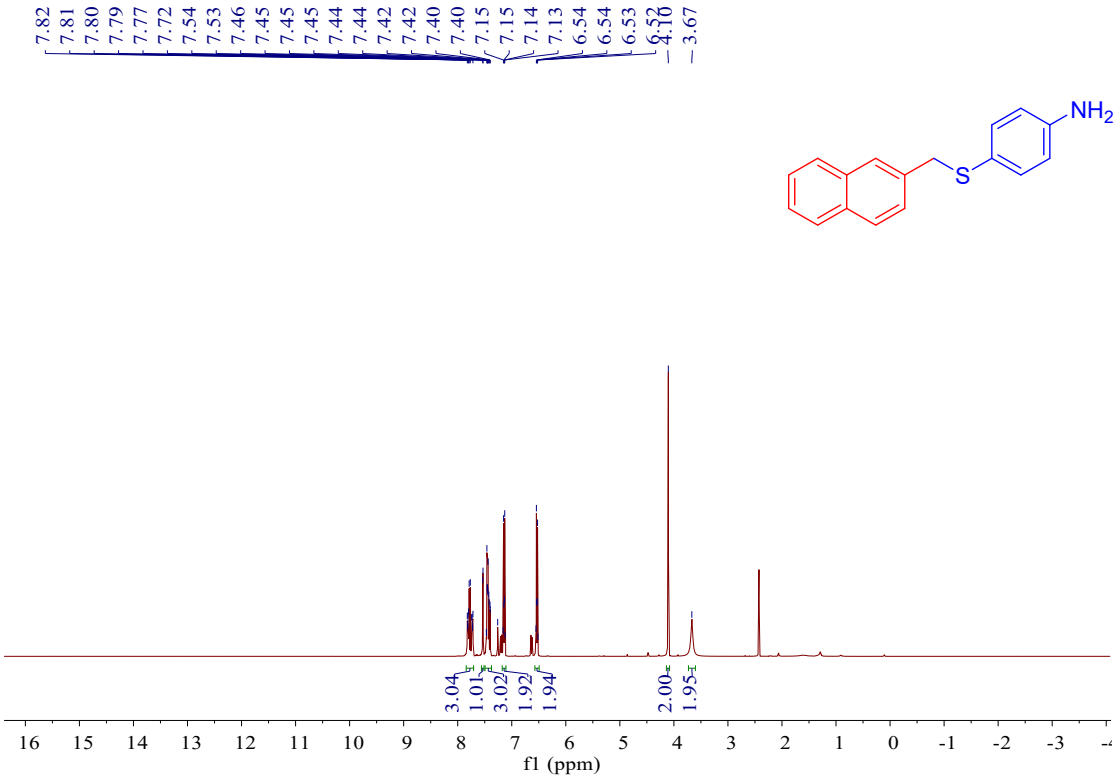
^{1}H NMR Spectra of **3l** (400 MHz, $CDCl_3$)



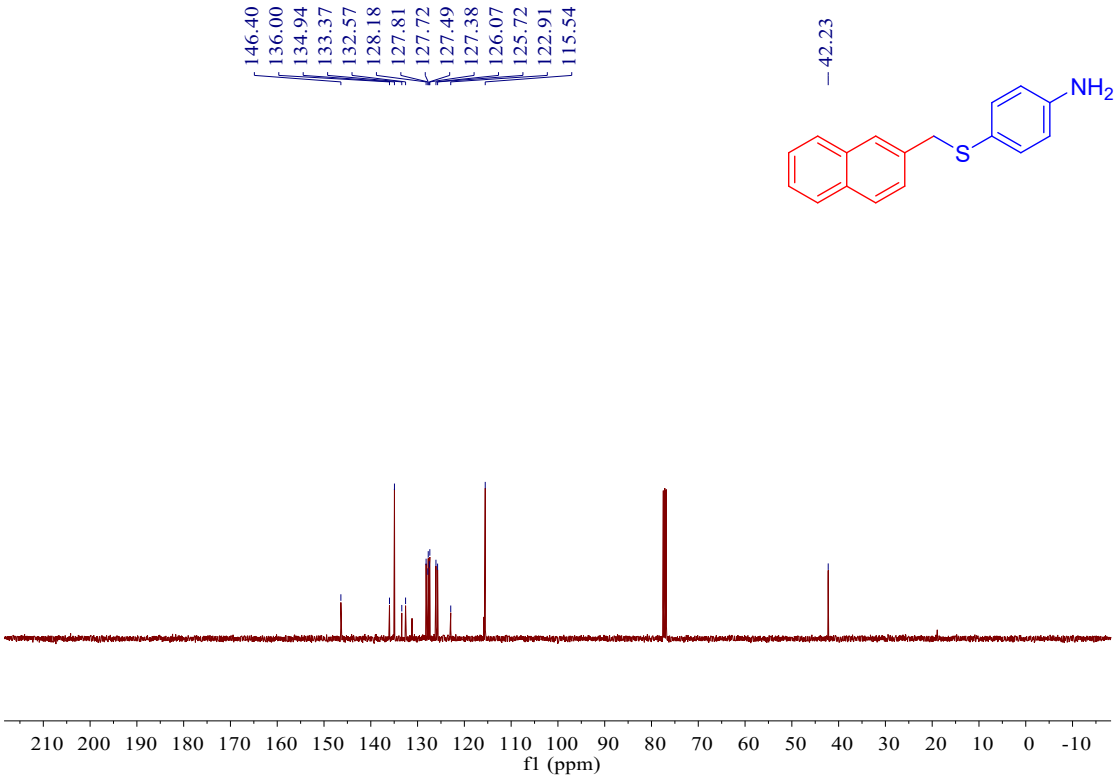
^{13}C NMR Spectra of **3l** (400 MHz, $CDCl_3$)



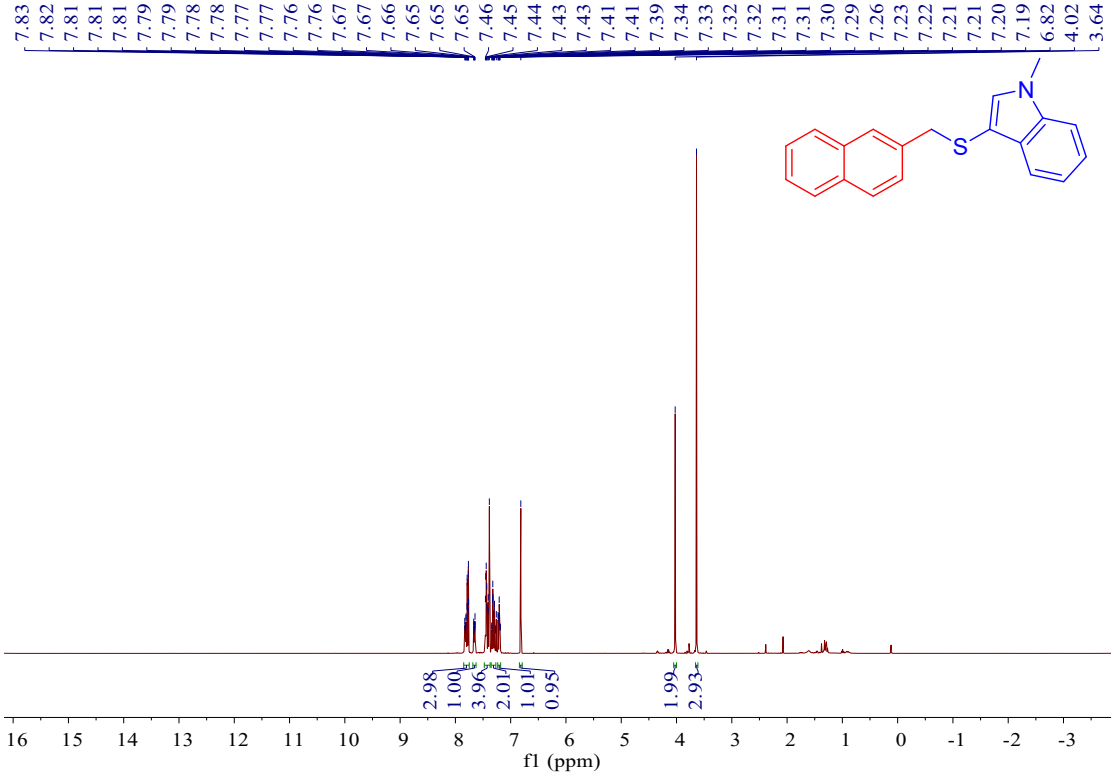
^{1}H NMR Spectra of **3q** (400 MHz, $CDCl_3$)



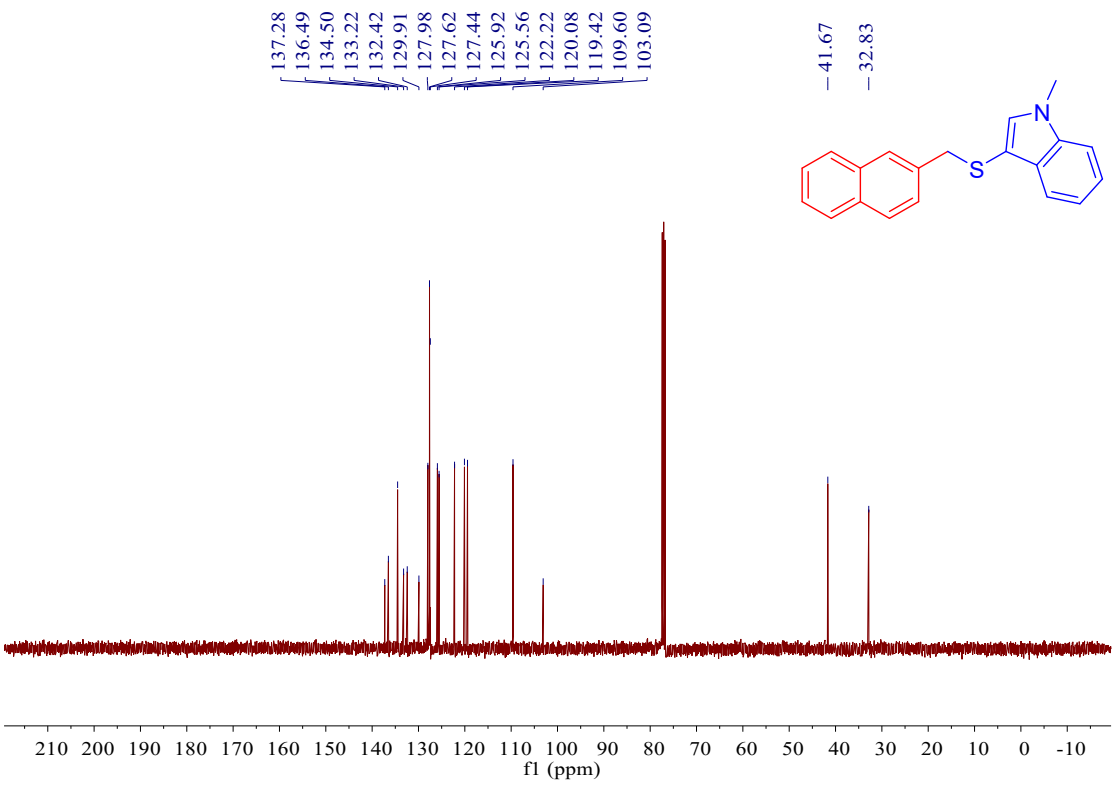
^{13}C NMR Spectra of **3q** (400 MHz, $CDCl_3$)



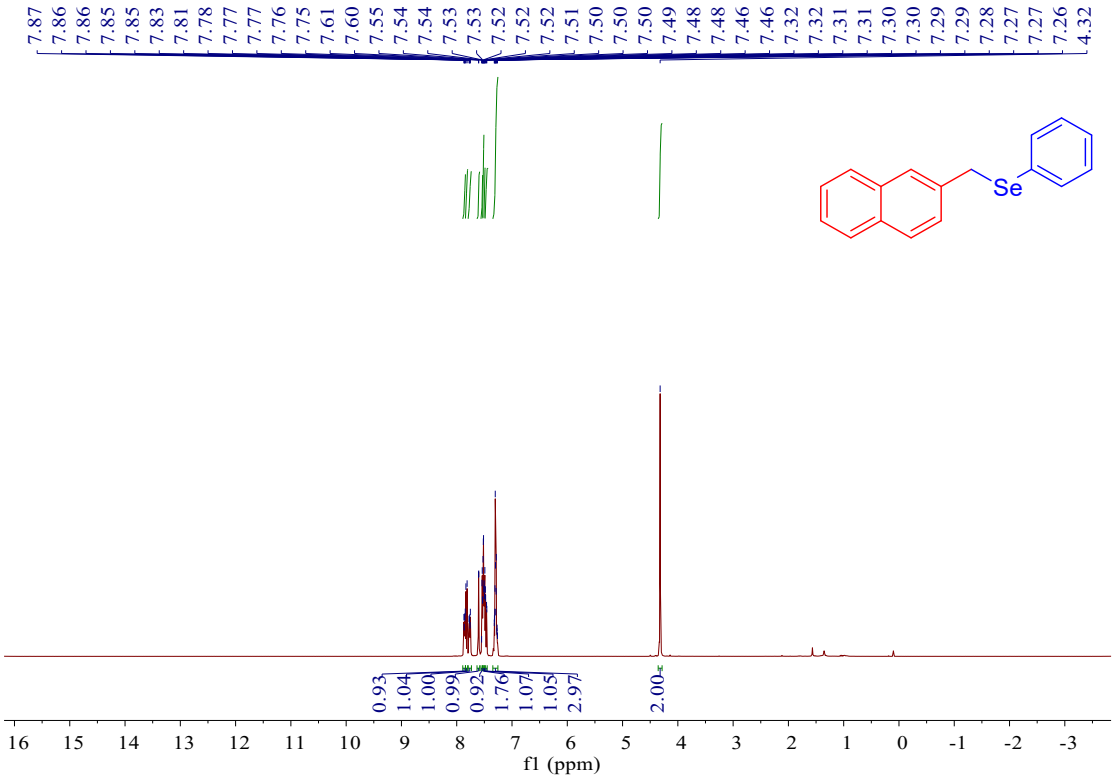
^{1}H NMR Spectra of **3r** (400 MHz, $CDCl_3$)



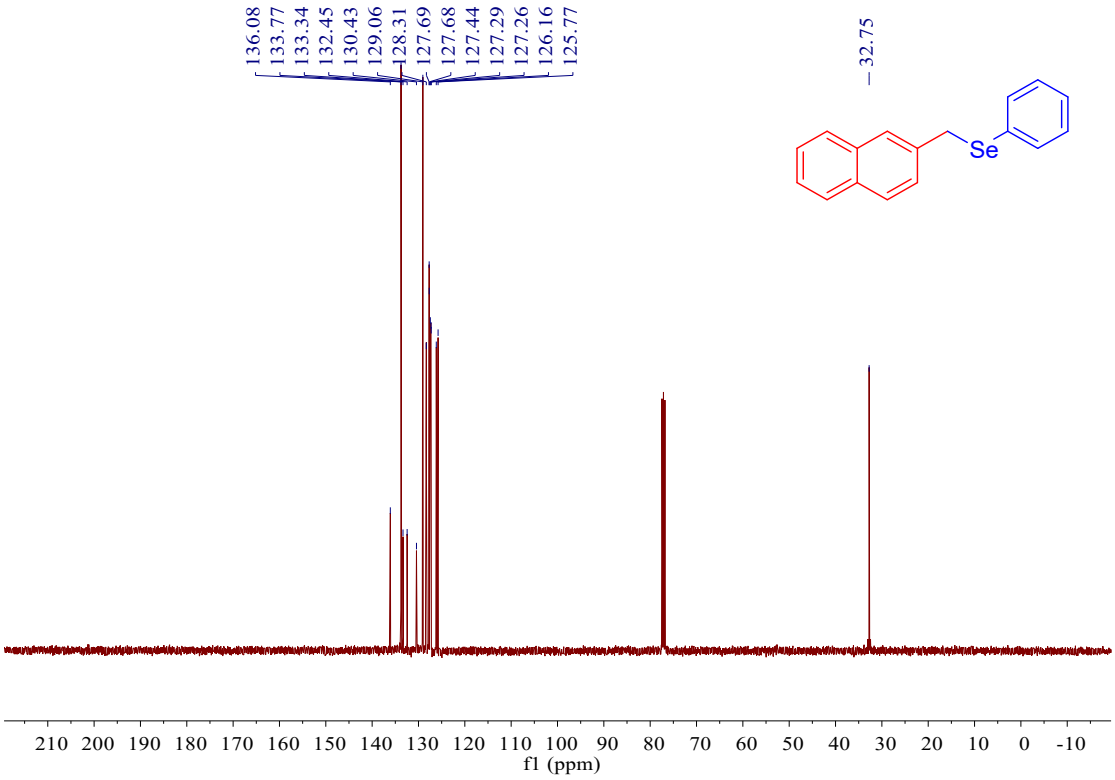
^{13}C NMR Spectra of **3r** (400 MHz, $CDCl_3$)



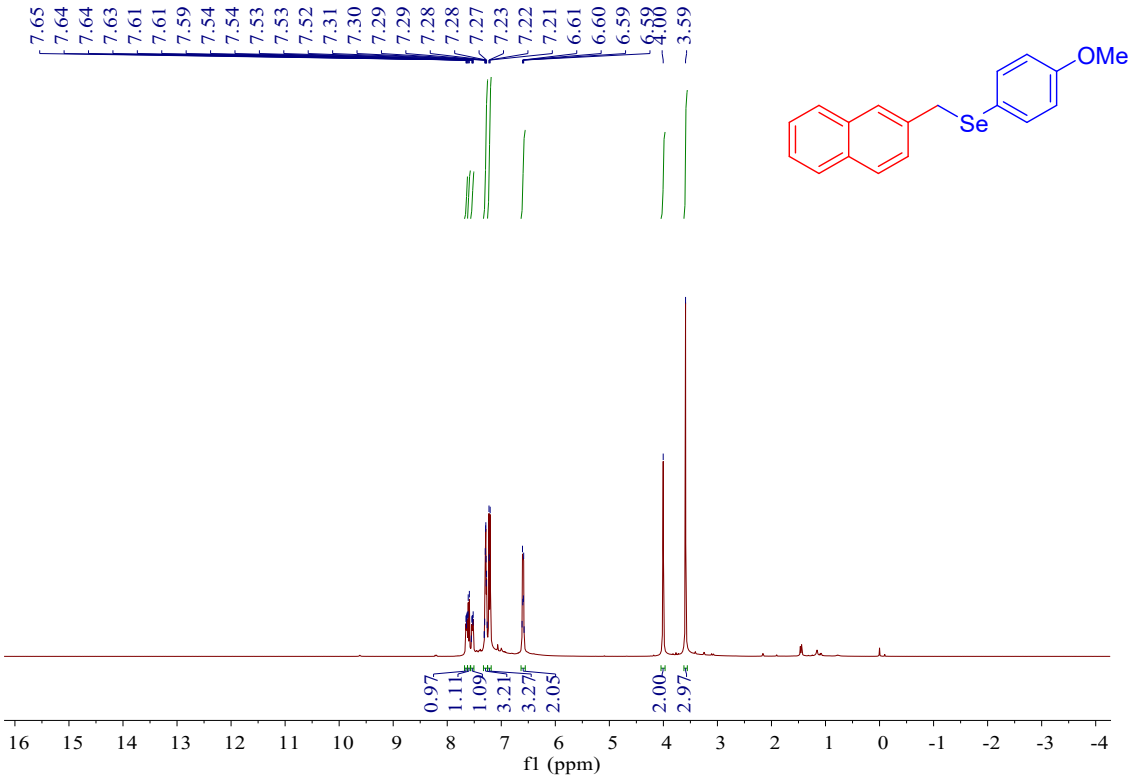
^{1}H NMR Spectra of **5a** (400 MHz, $CDCl_3$)



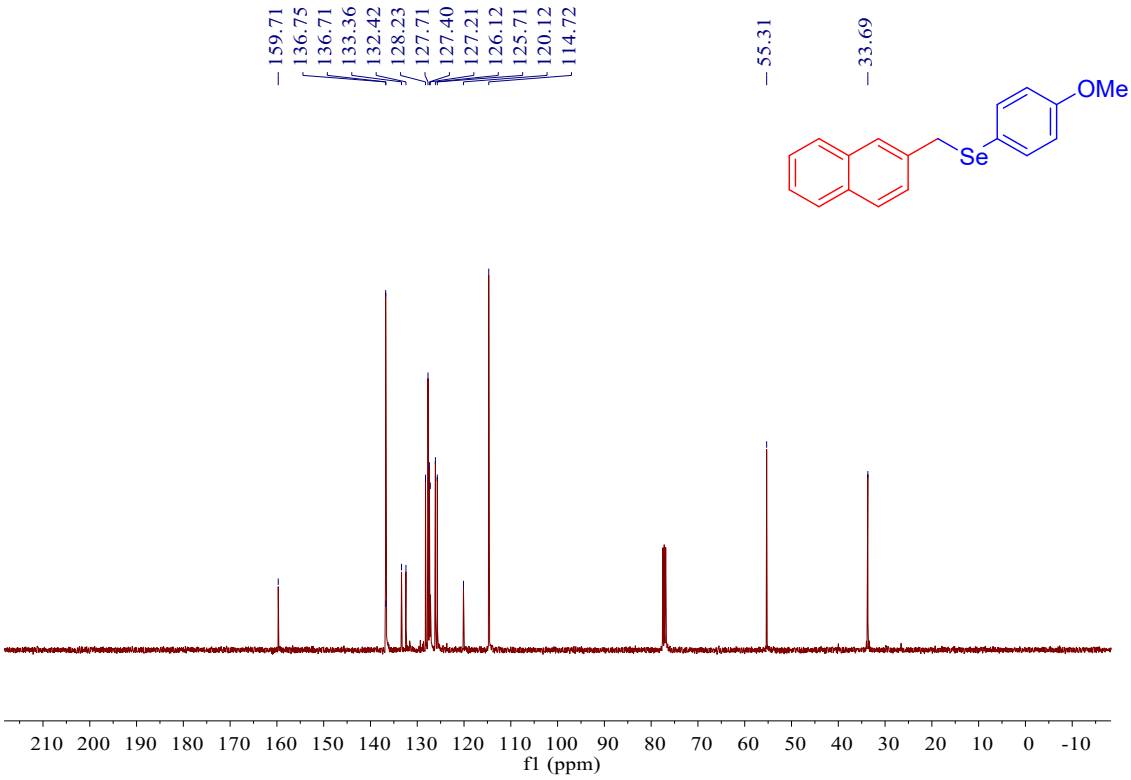
^{13}C NMR Spectra of **5a** (400 MHz, $CDCl_3$)



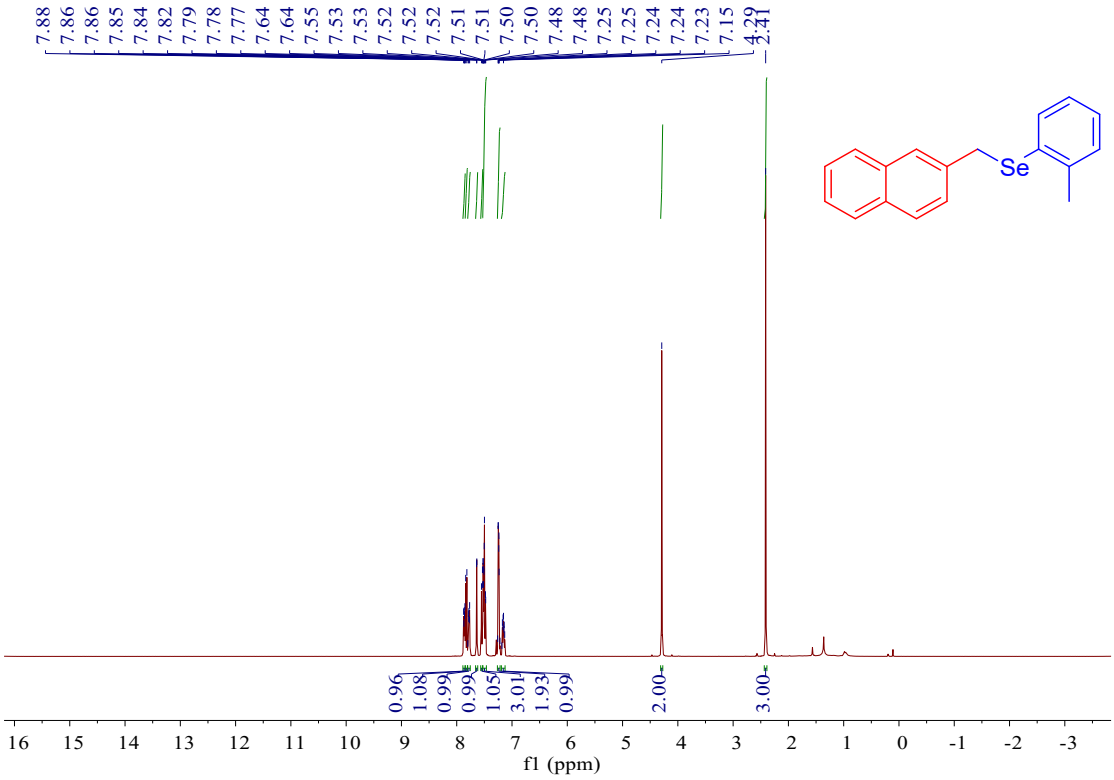
^{1}H NMR Spectra of **5b** (400 MHz, $CDCl_3$)



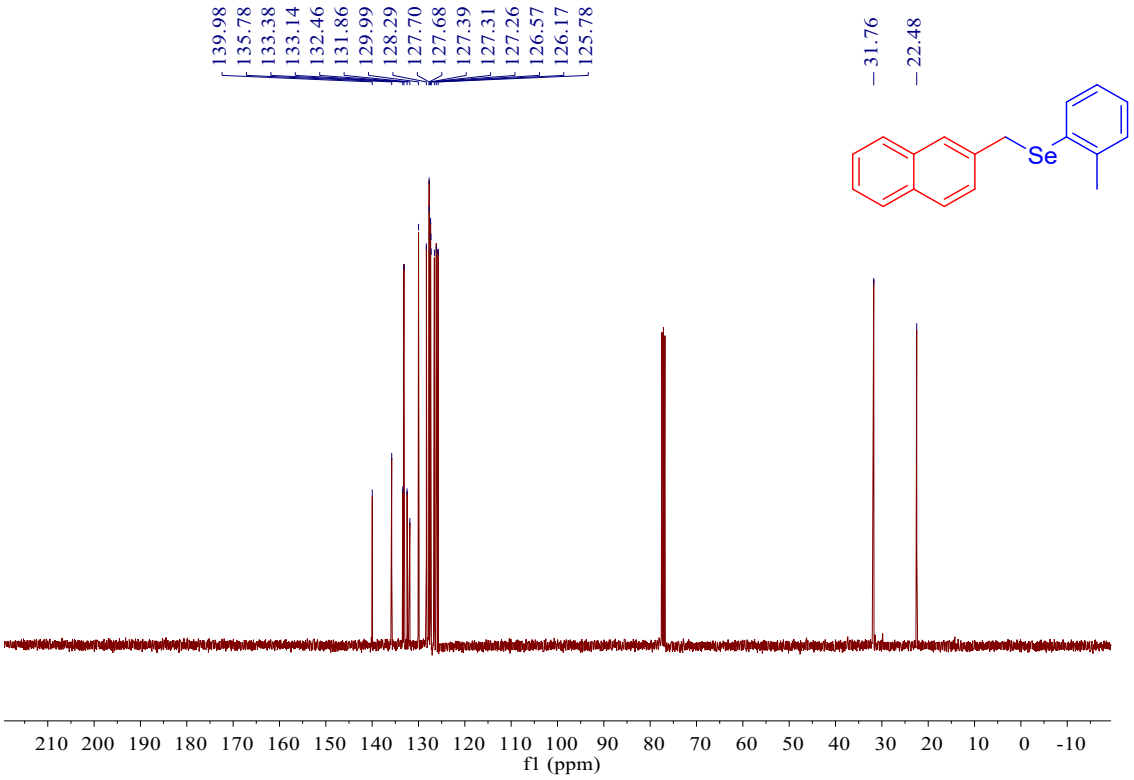
^{13}C NMR Spectra of **5b** (400 MHz, $CDCl_3$)



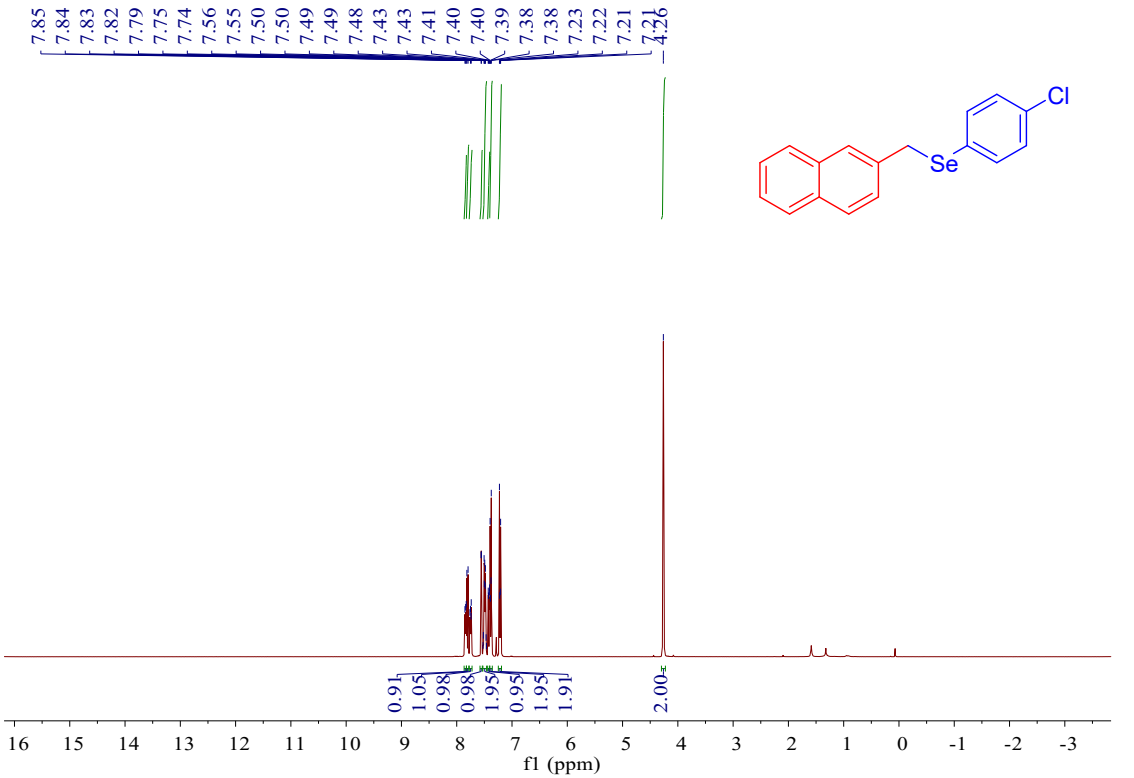
^{1}H NMR Spectra of **5c** (400 MHz, $CDCl_3$)



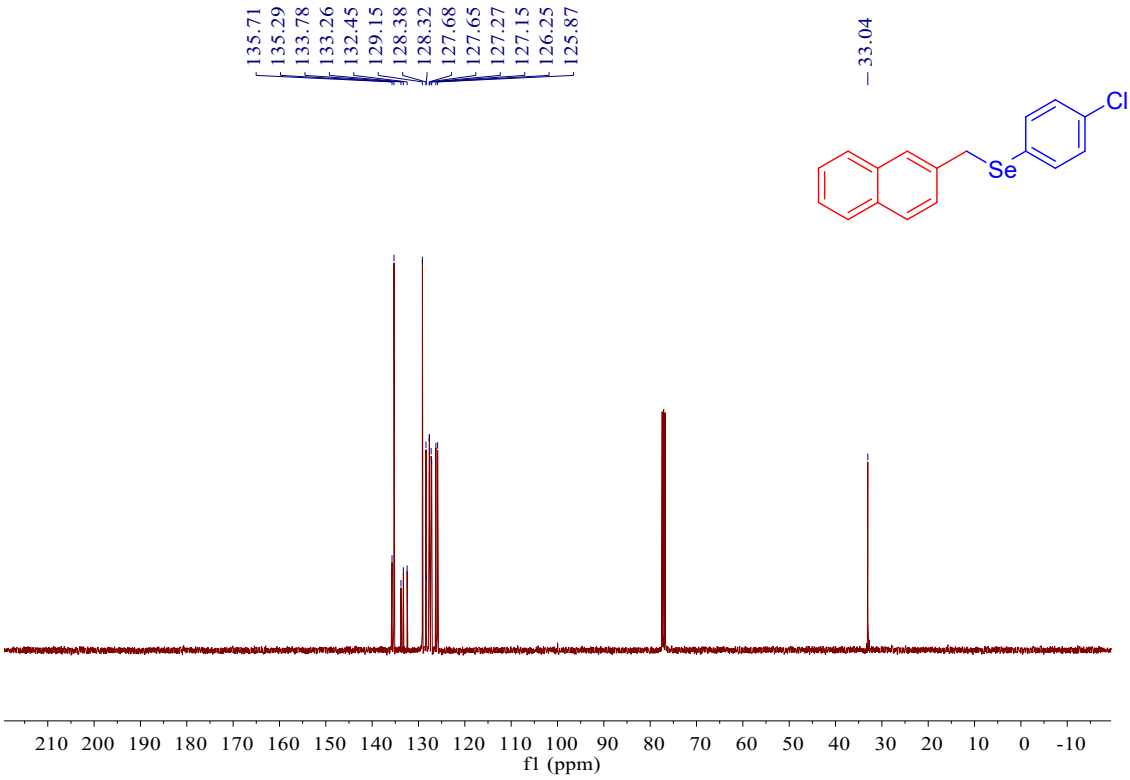
^{13}C NMR Spectra of **5c** (400 MHz, $CDCl_3$)



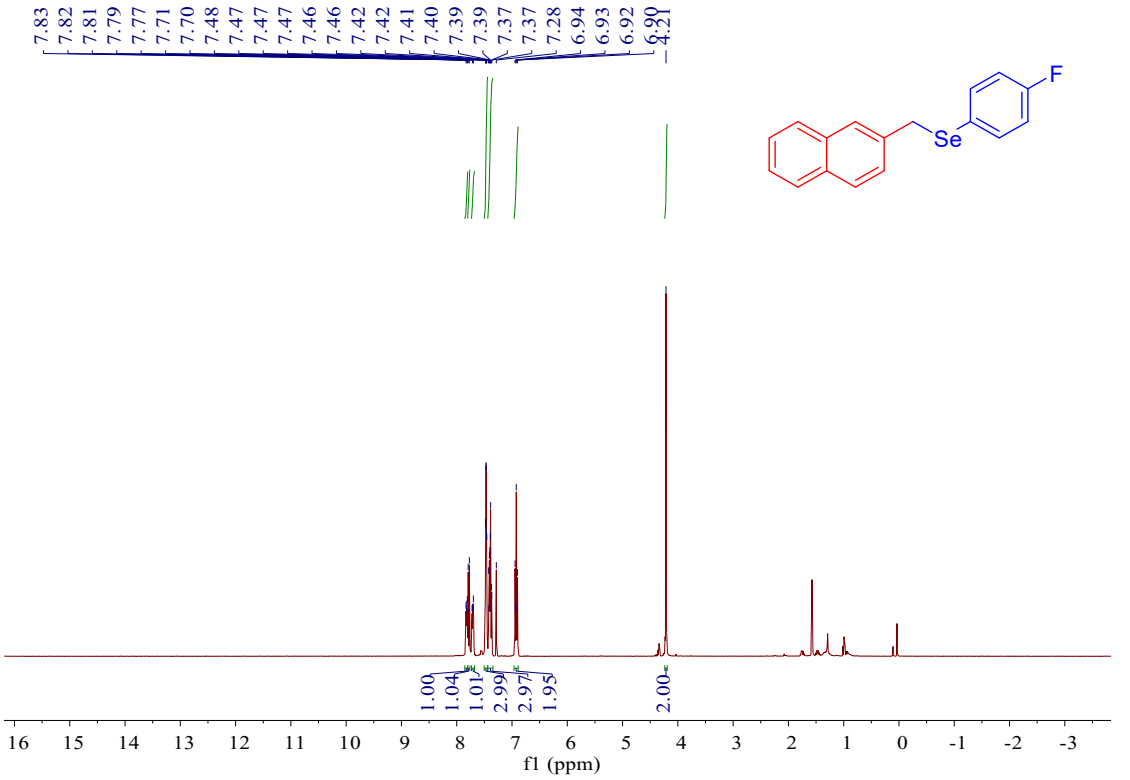
^{1}H NMR Spectra of **5d** (400 MHz, $CDCl_3$)



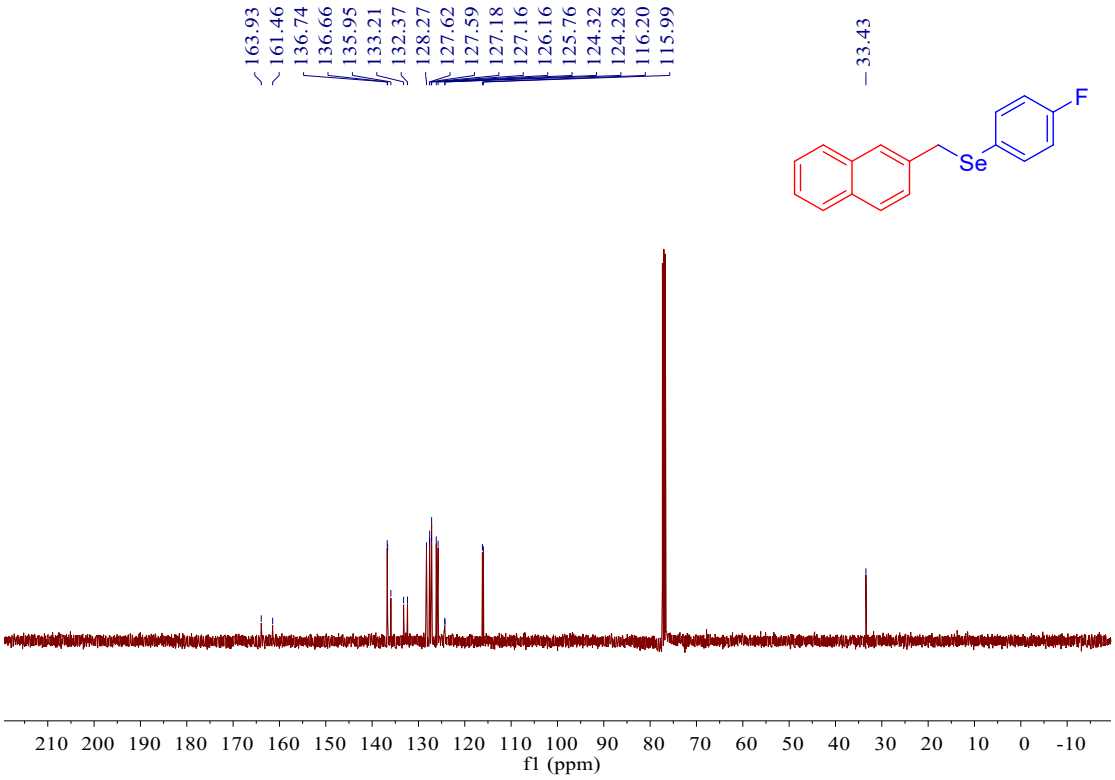
^{13}C NMR Spectra of **5d** (400 MHz, $CDCl_3$)



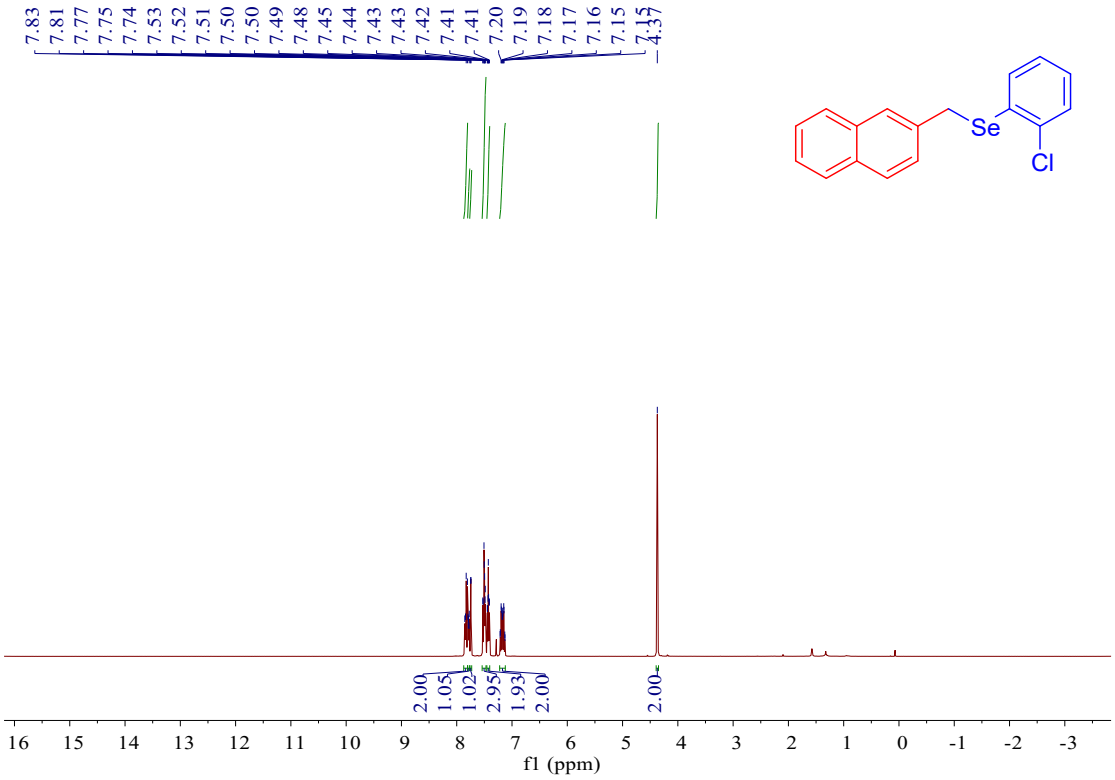
^{1}H NMR Spectra of **5e** (400 MHz, $CDCl_3$)



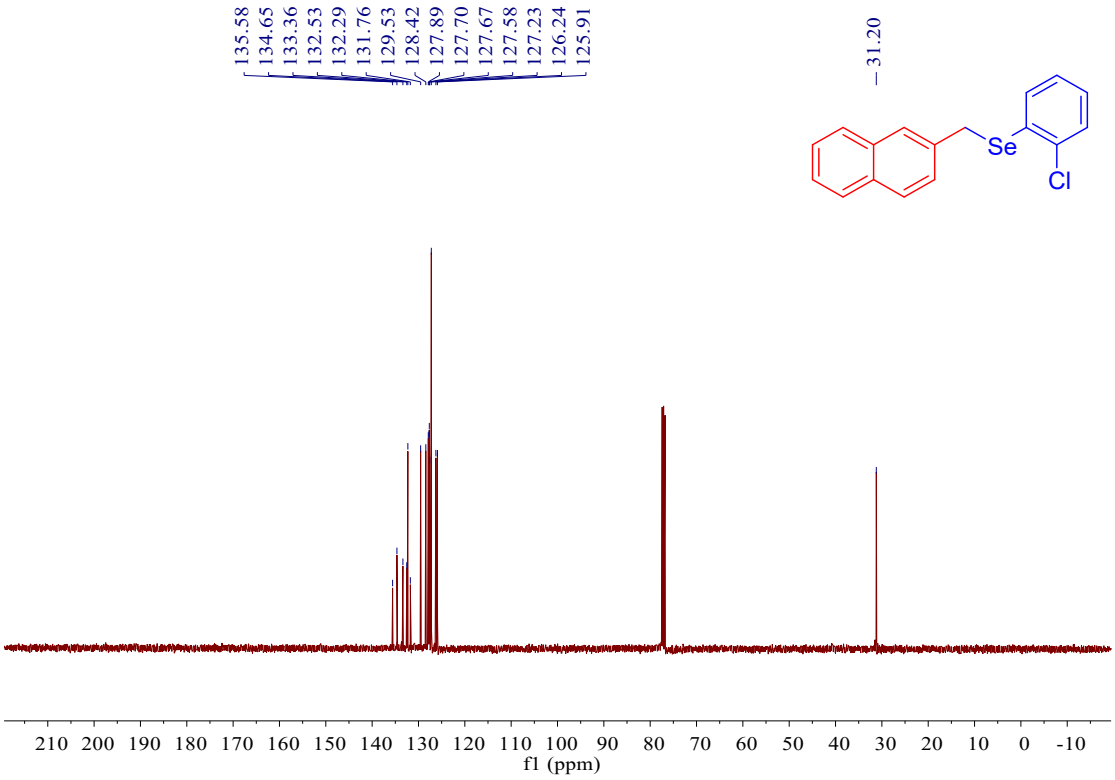
^{13}C NMR Spectra of **5e** (400 MHz, $CDCl_3$)



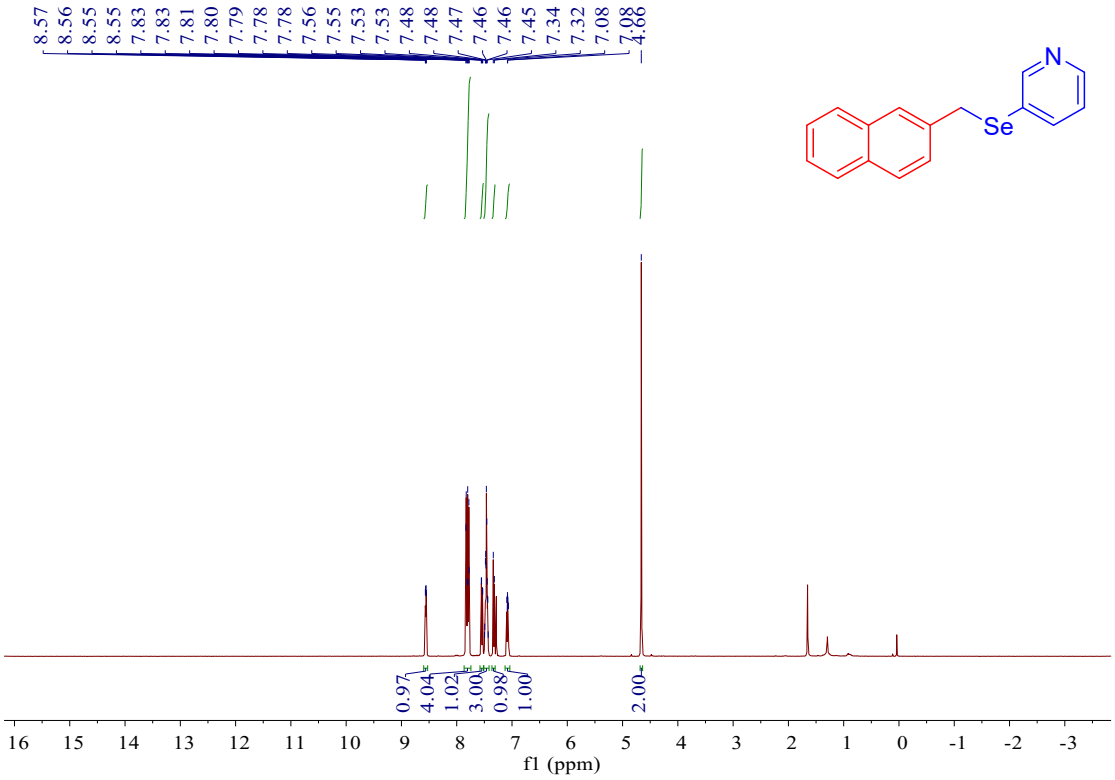
^{1}H NMR Spectra of **5f** (400 MHz, $CDCl_3$)



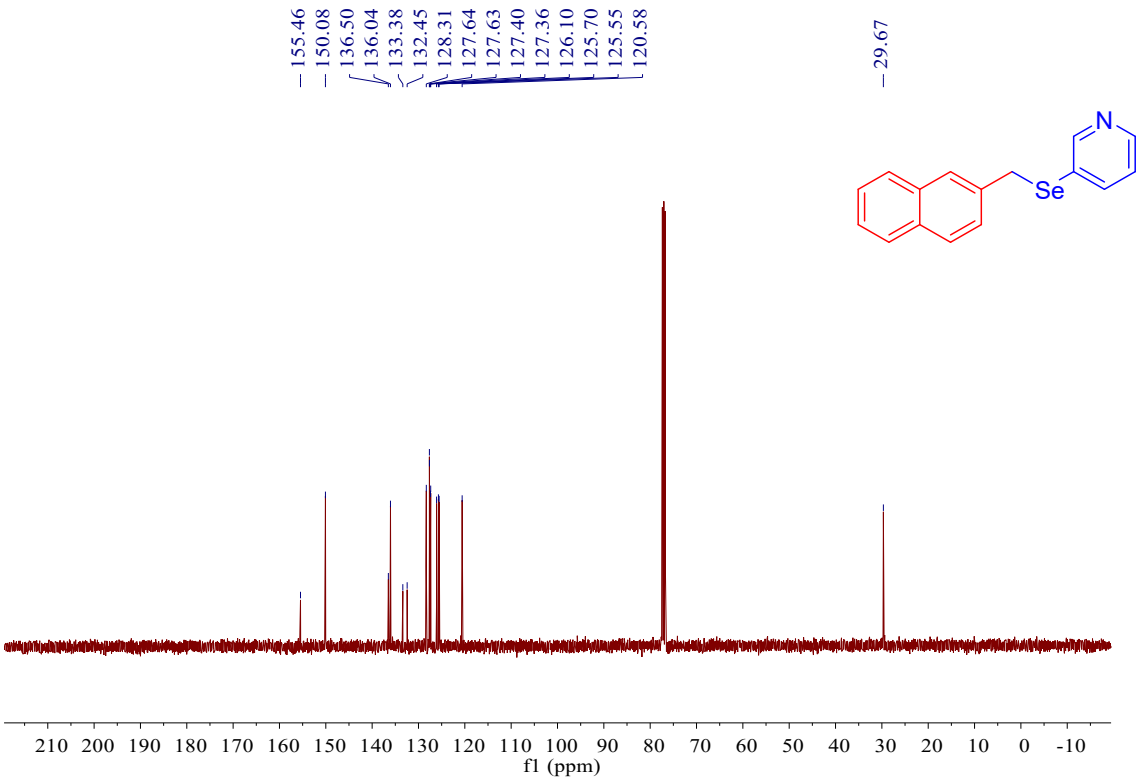
^{13}C NMR Spectra of **5f** (400 MHz, $CDCl_3$)



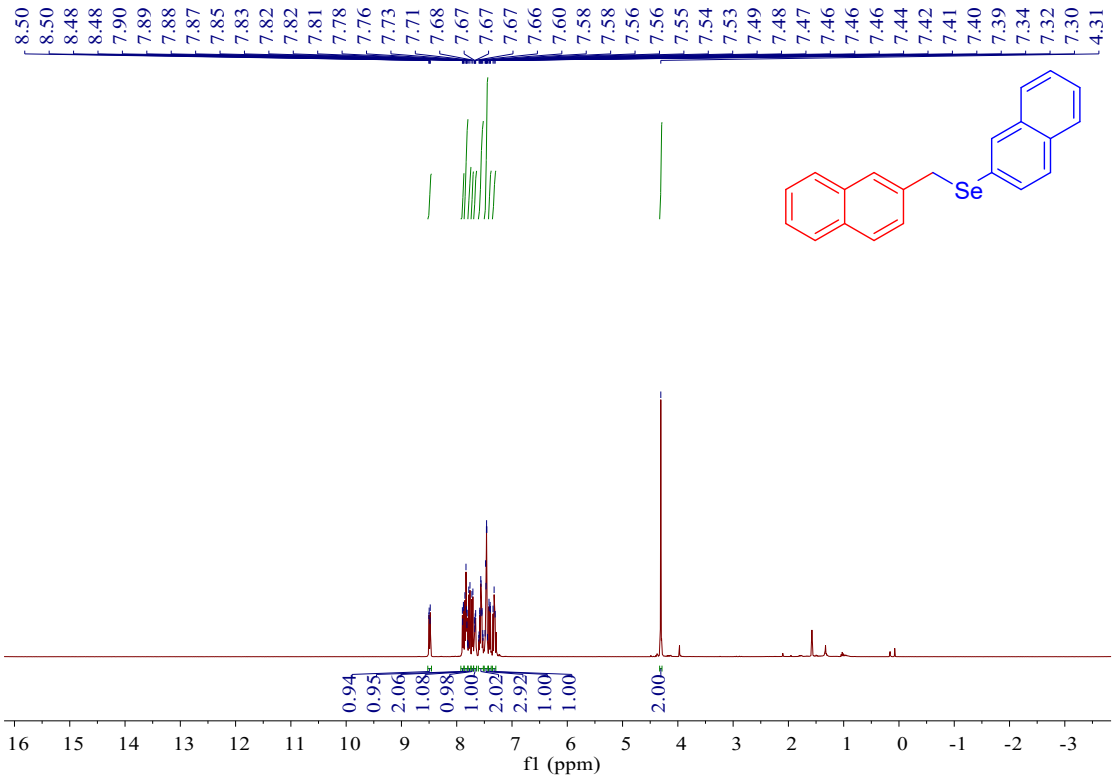
^{1}H NMR Spectra of **5g** (400 MHz, $CDCl_3$)



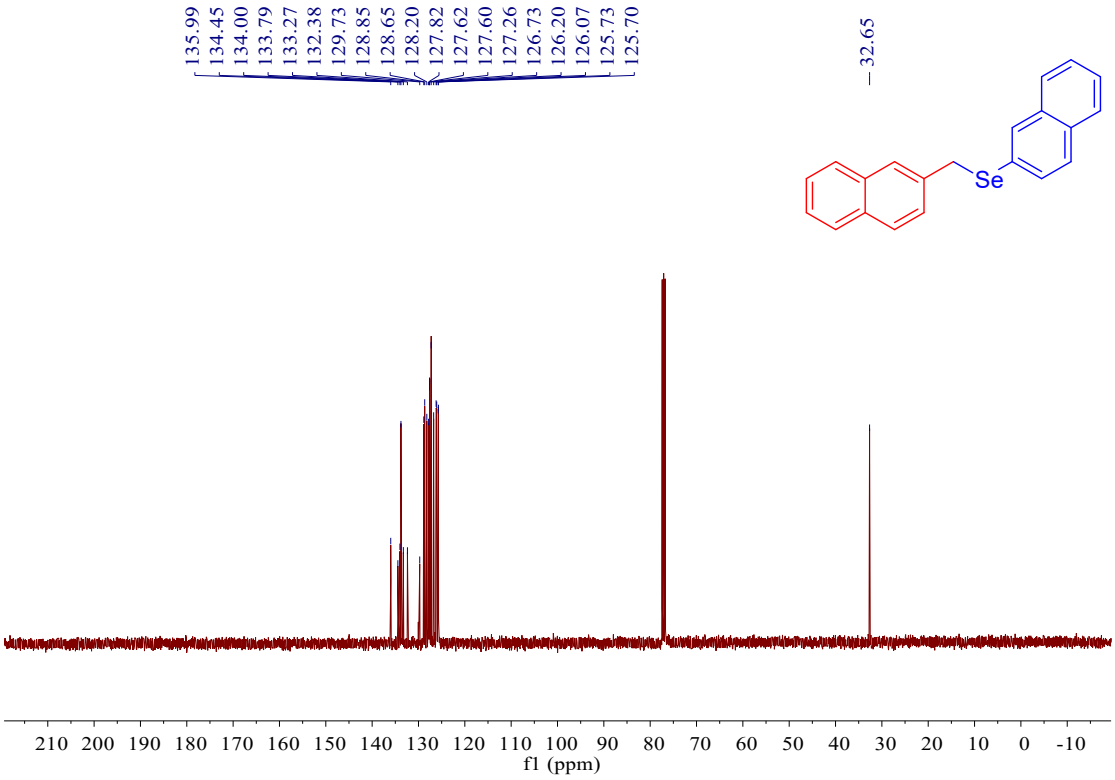
^{13}C NMR Spectra of **5g** (400 MHz, $CDCl_3$)



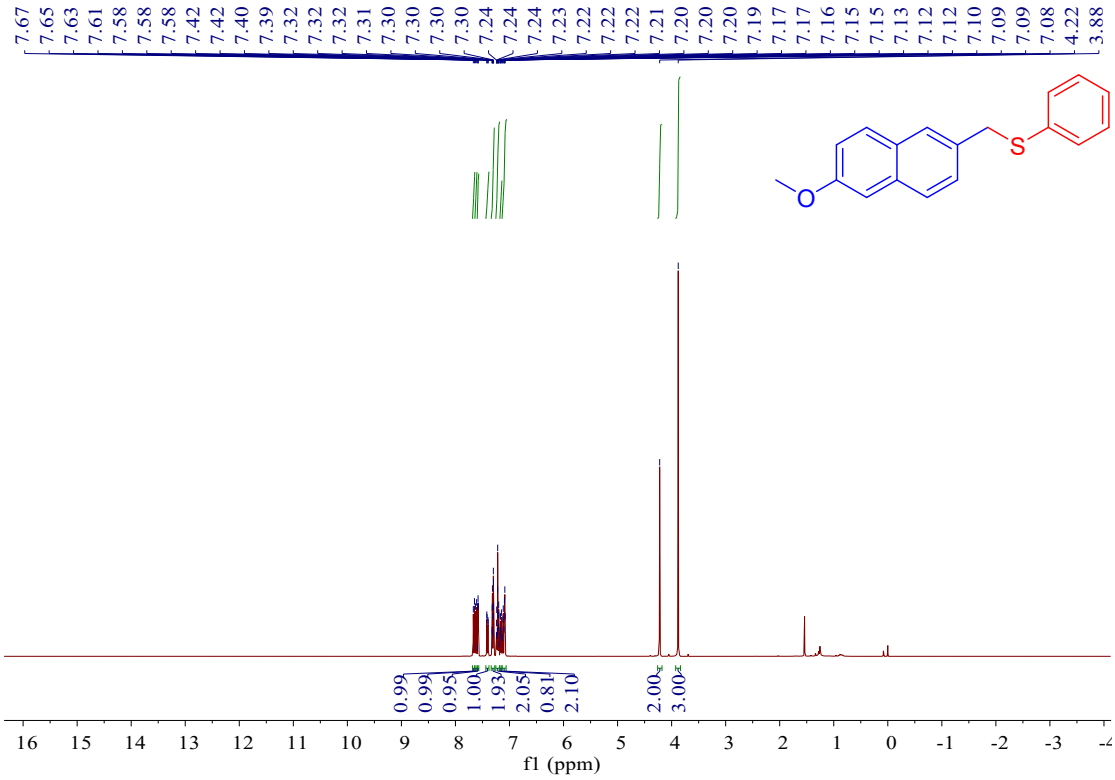
^{1}H NMR Spectra of **5h** (400 MHz, $CDCl_3$)



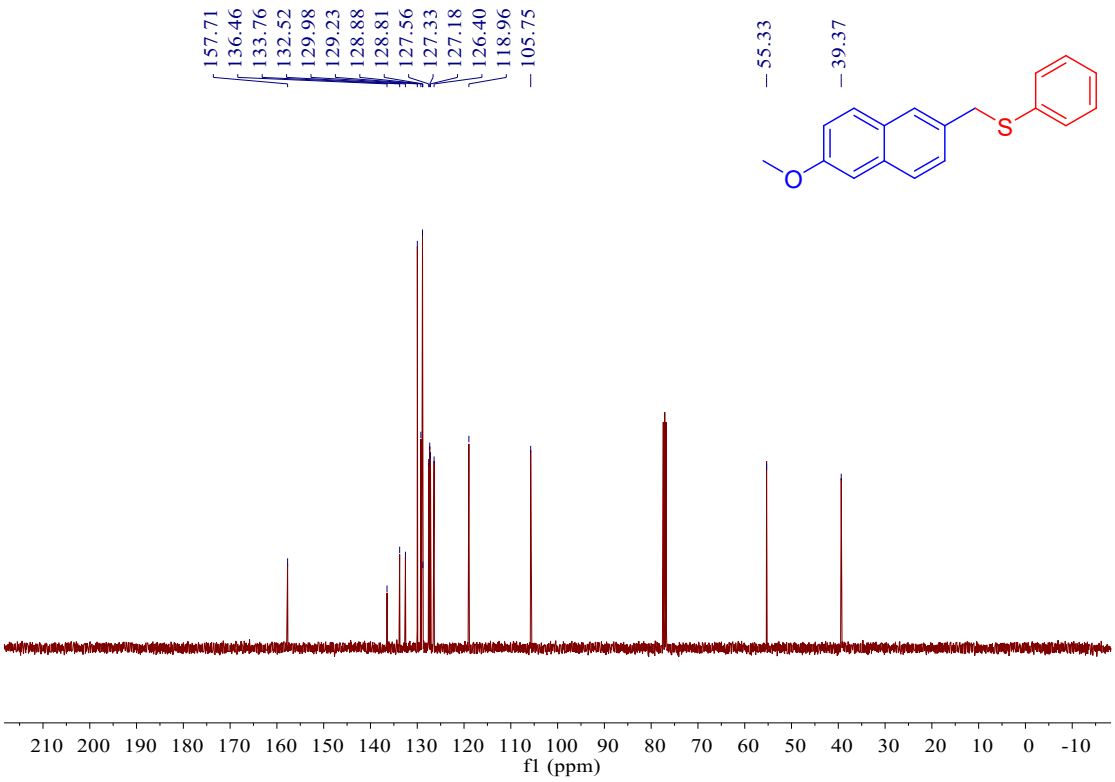
^{13}C NMR Spectra of **5h** (400 MHz, $CDCl_3$)



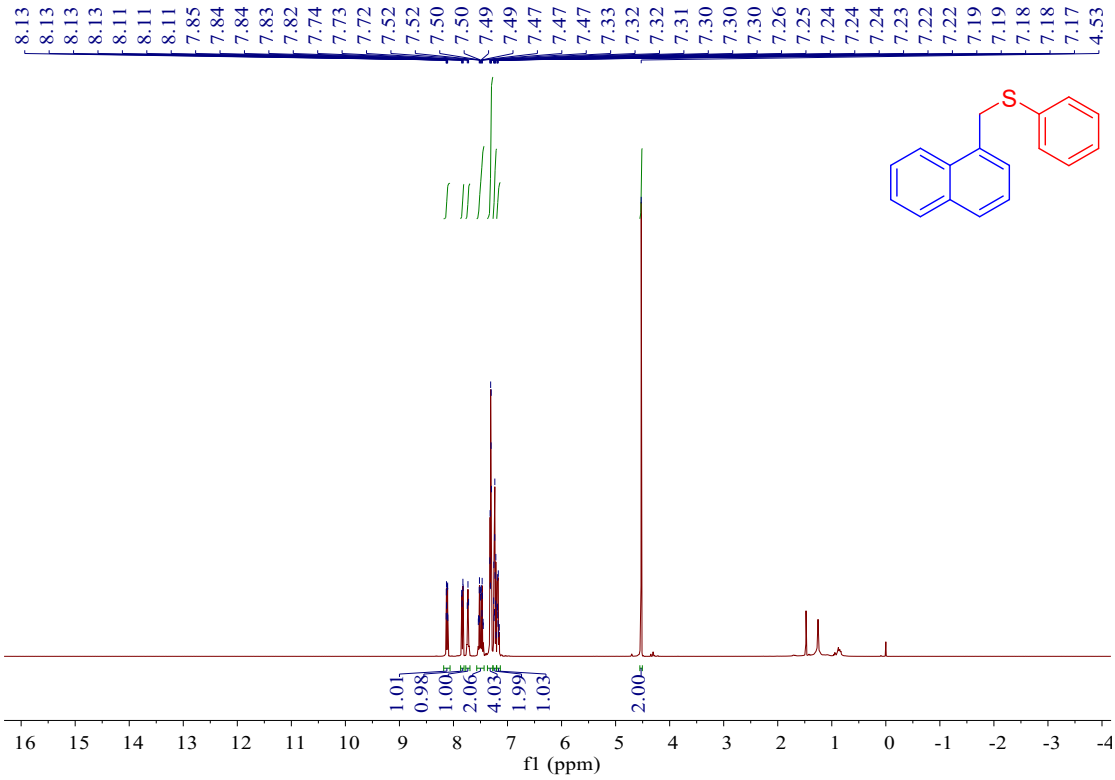
^{1}H NMR Spectra of **6a** (400 MHz, $CDCl_3$)



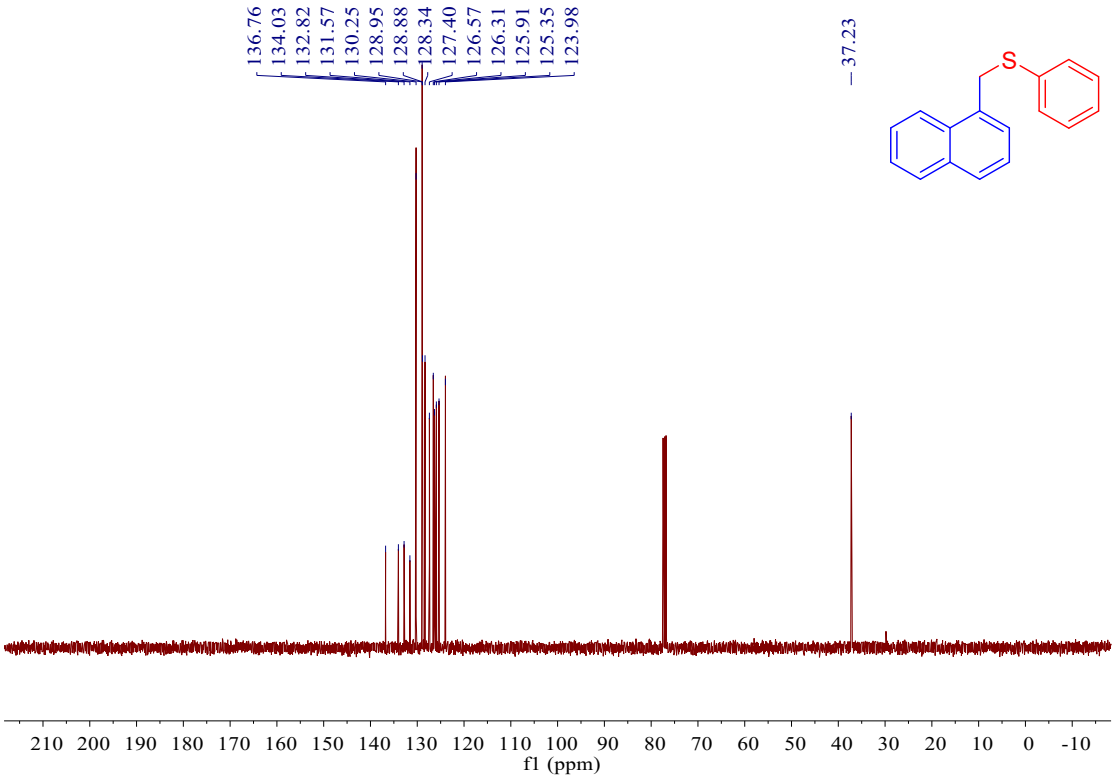
^{13}C NMR Spectra of **6a** (400 MHz, $CDCl_3$)



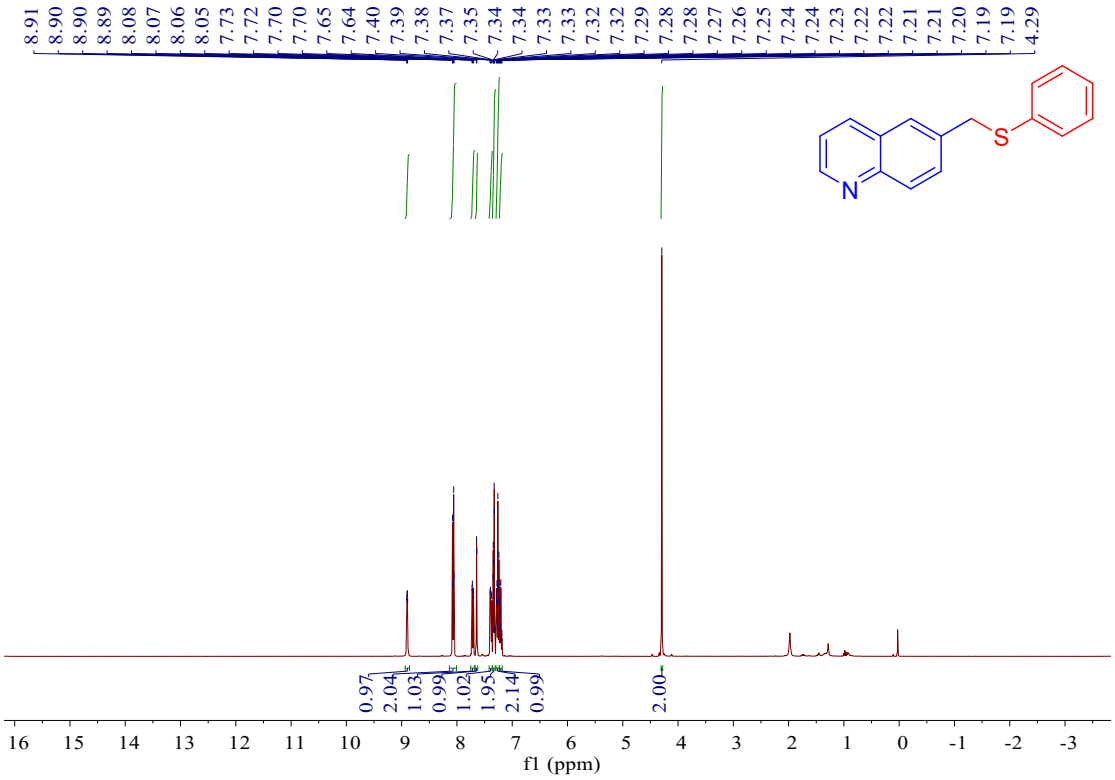
^{1}H NMR Spectra of **6b** (400 MHz, $CDCl_3$)



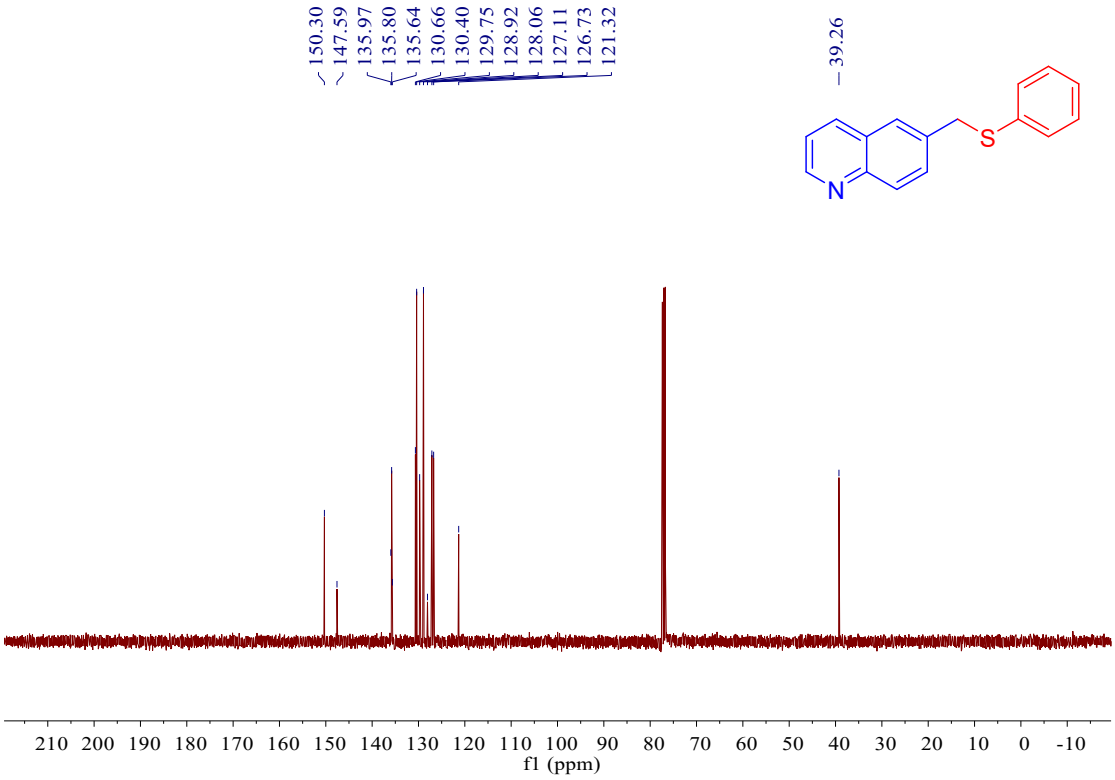
^{13}C NMR Spectra of **6b** (400 MHz, $CDCl_3$)



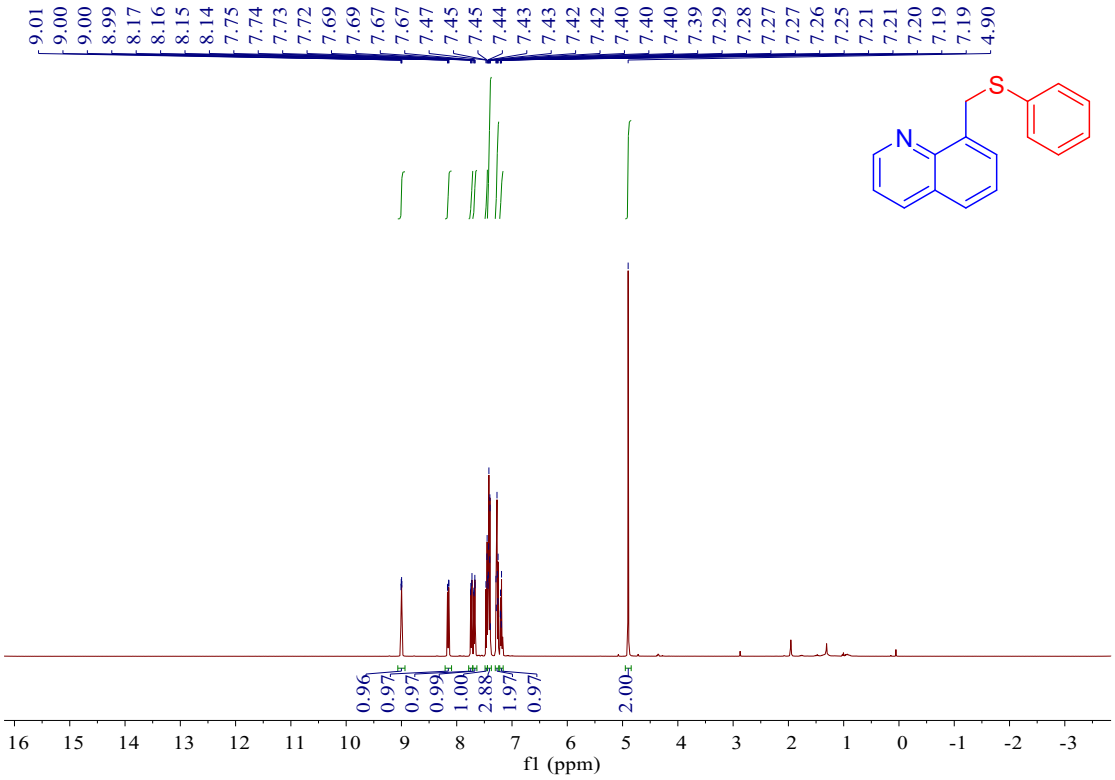
^{1}H NMR Spectra of **6d** (400 MHz, $CDCl_3$)



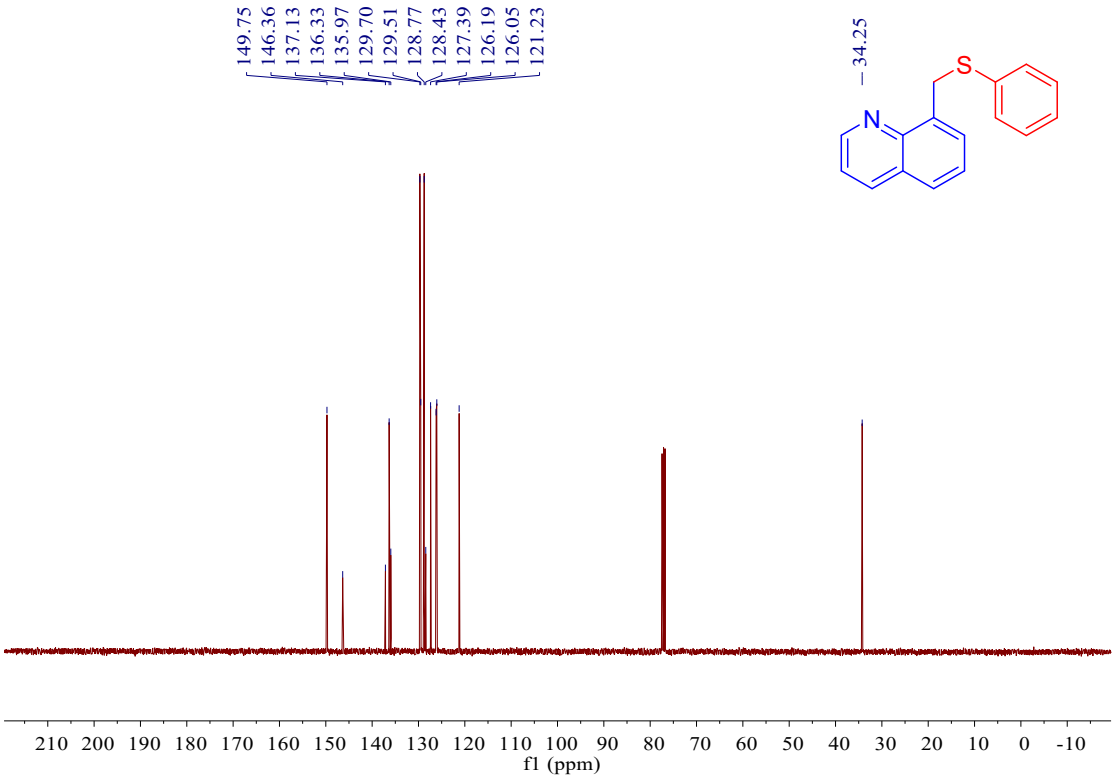
^{13}C NMR Spectra of **6d** (400 MHz, $CDCl_3$)



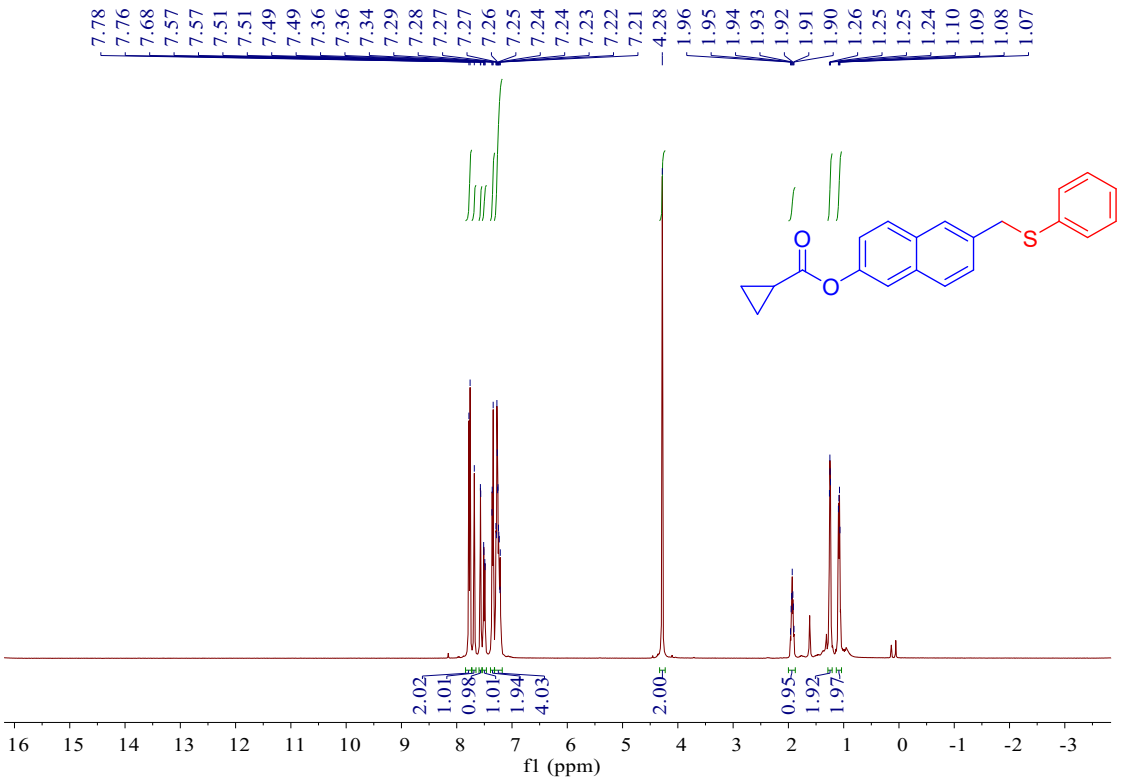
^{1}H NMR Spectra of **6e** (400 MHz, $CDCl_3$)



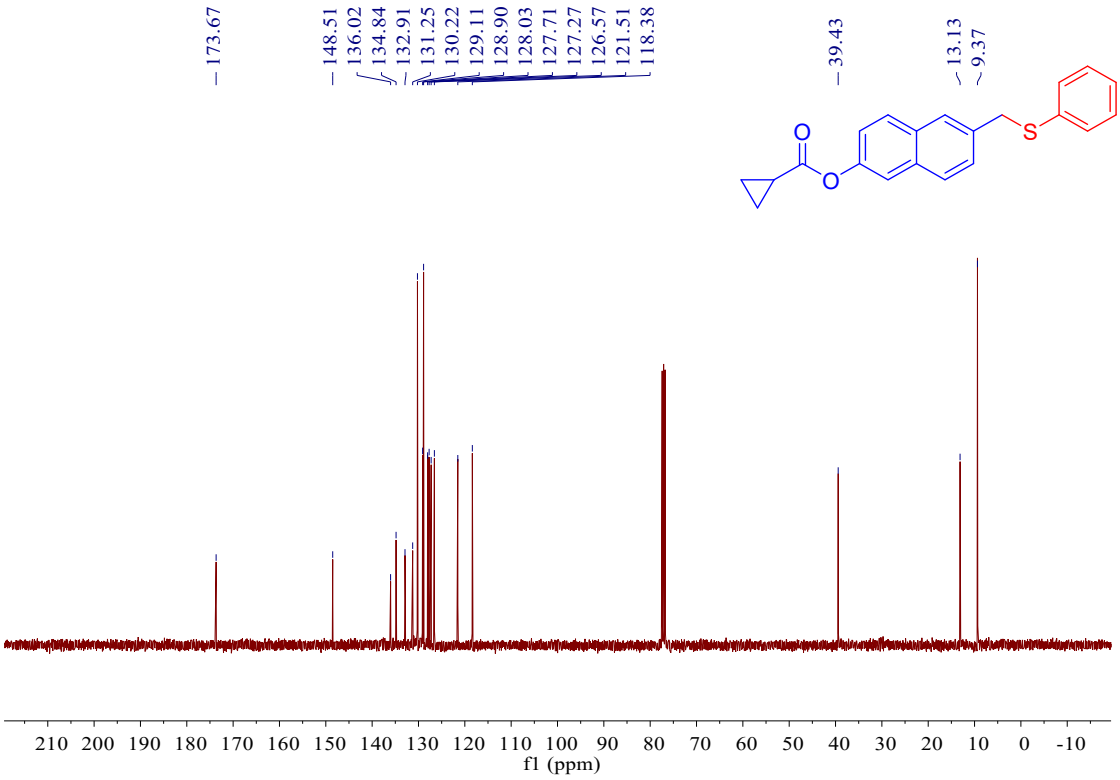
^{13}C NMR Spectra of **6e** (400 MHz, $CDCl_3$)



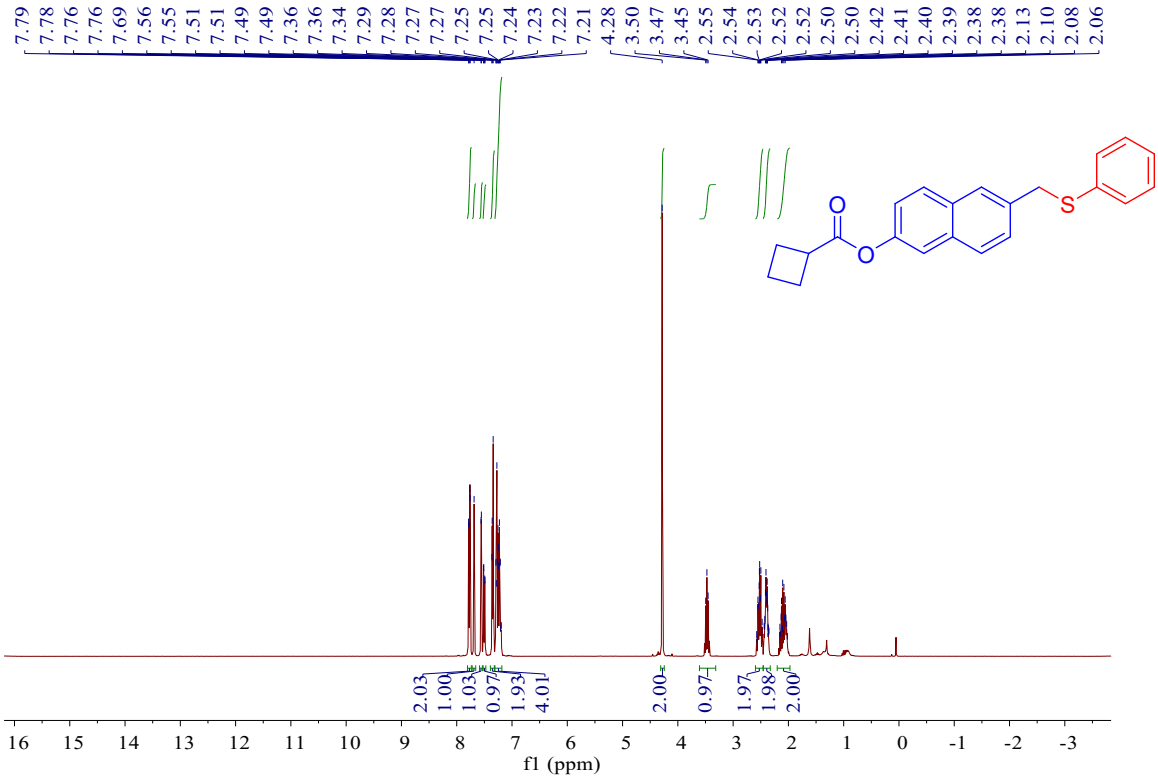
^{1}H NMR Spectra of **6f** (400 MHz, $CDCl_3$)



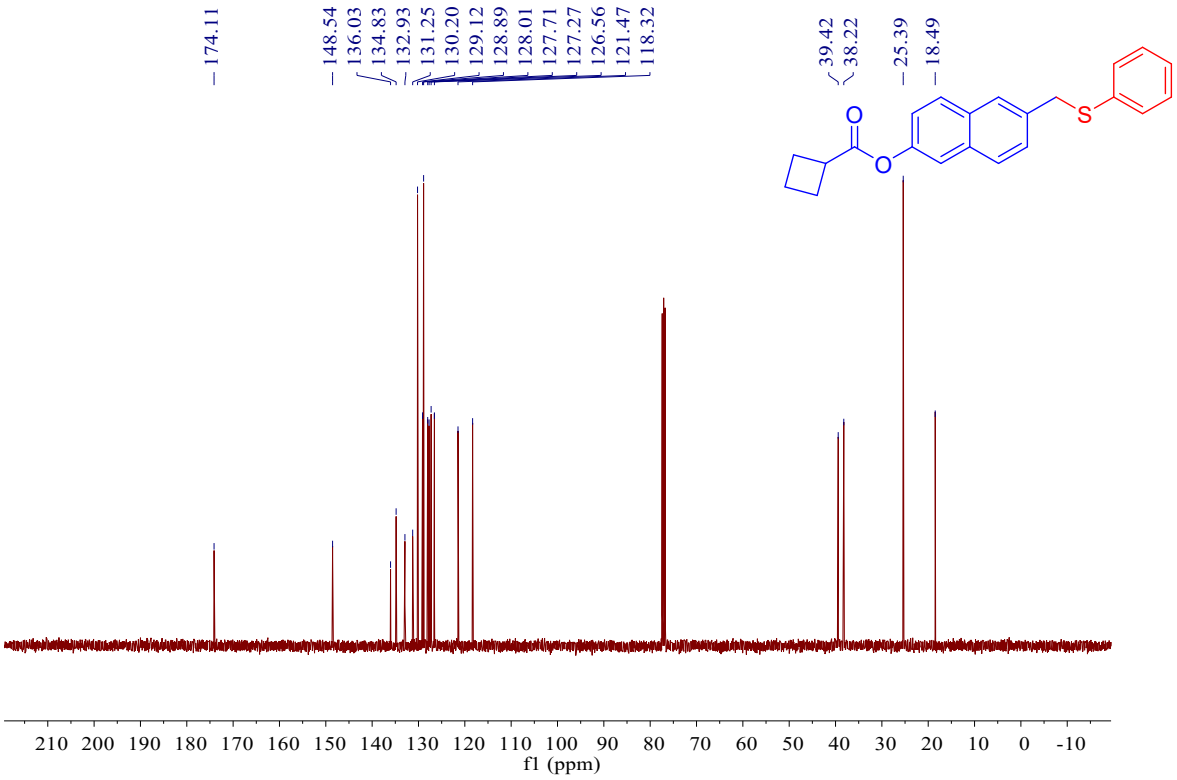
^{13}C NMR Spectra of **6f** (400 MHz, $CDCl_3$)



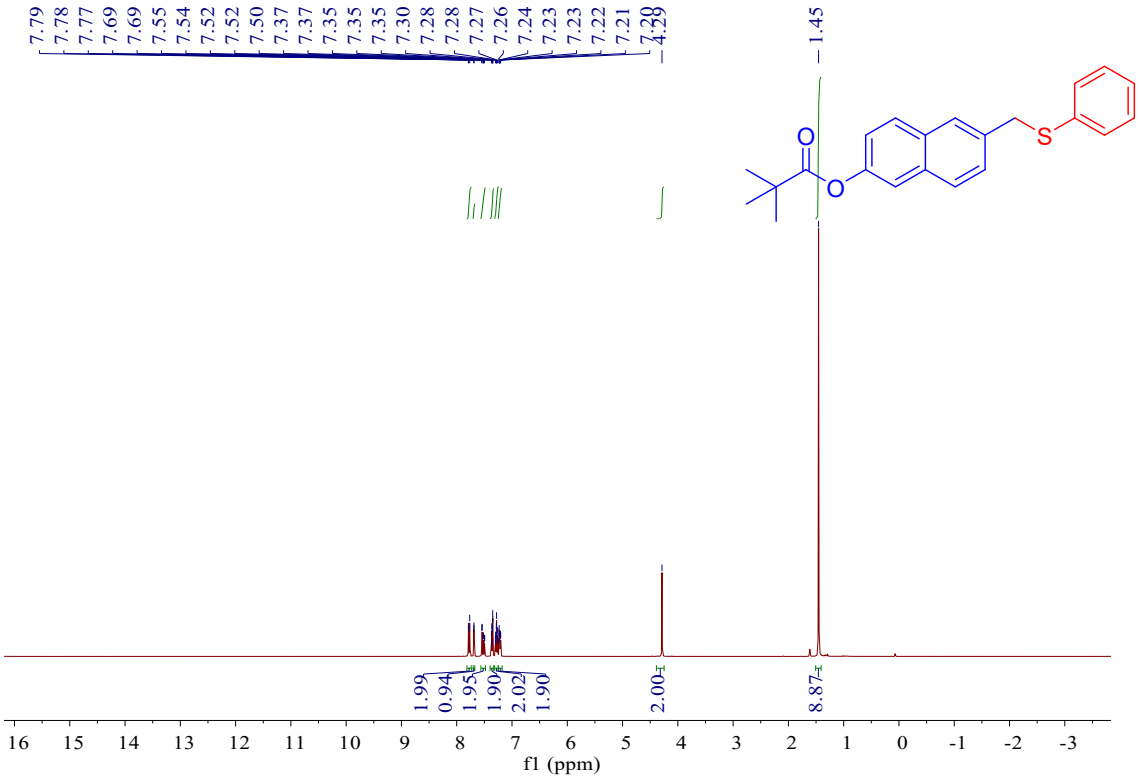
^{1}H NMR Spectra of **6g** (400 MHz, $CDCl_3$)



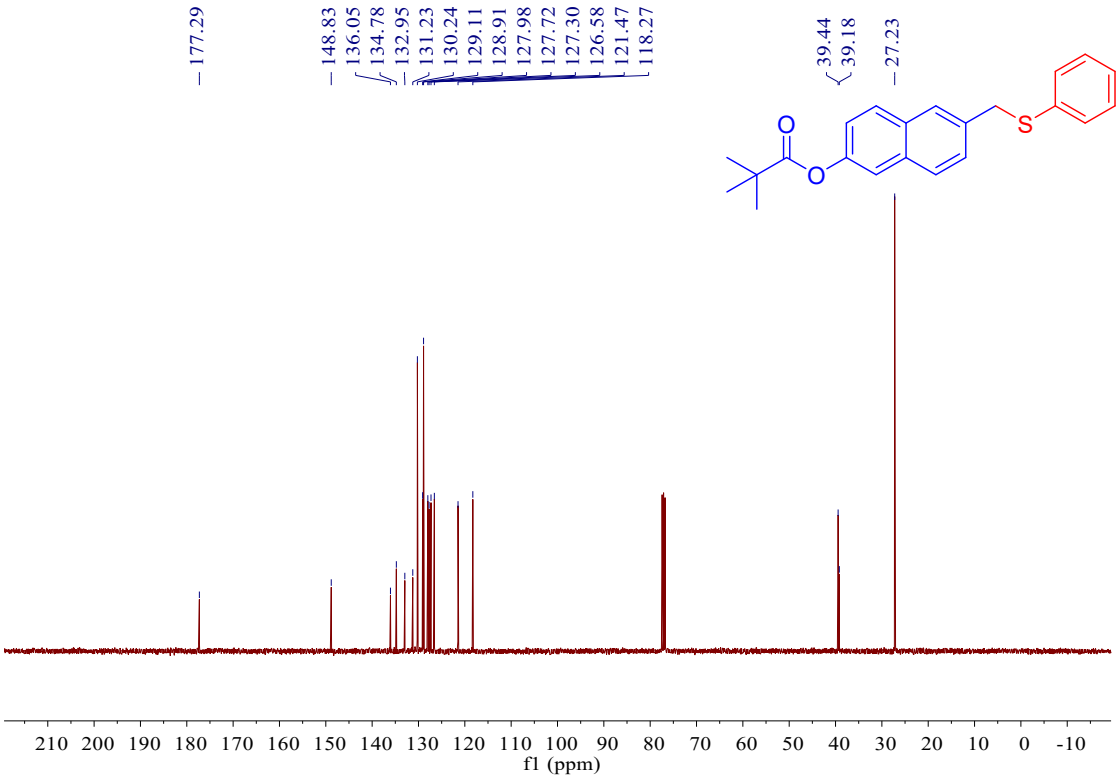
^{13}C NMR Spectra of **6g** (400 MHz, $CDCl_3$)



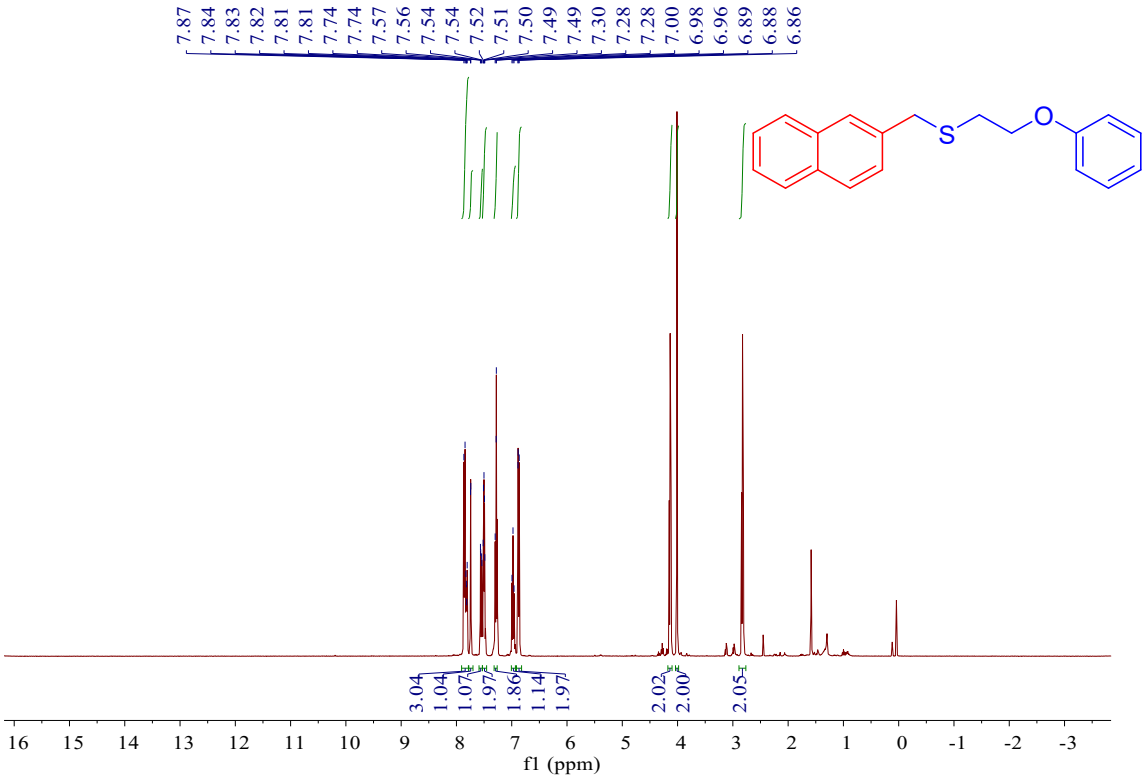
^{1}H NMR Spectra of **6h** (400 MHz, $CDCl_3$)



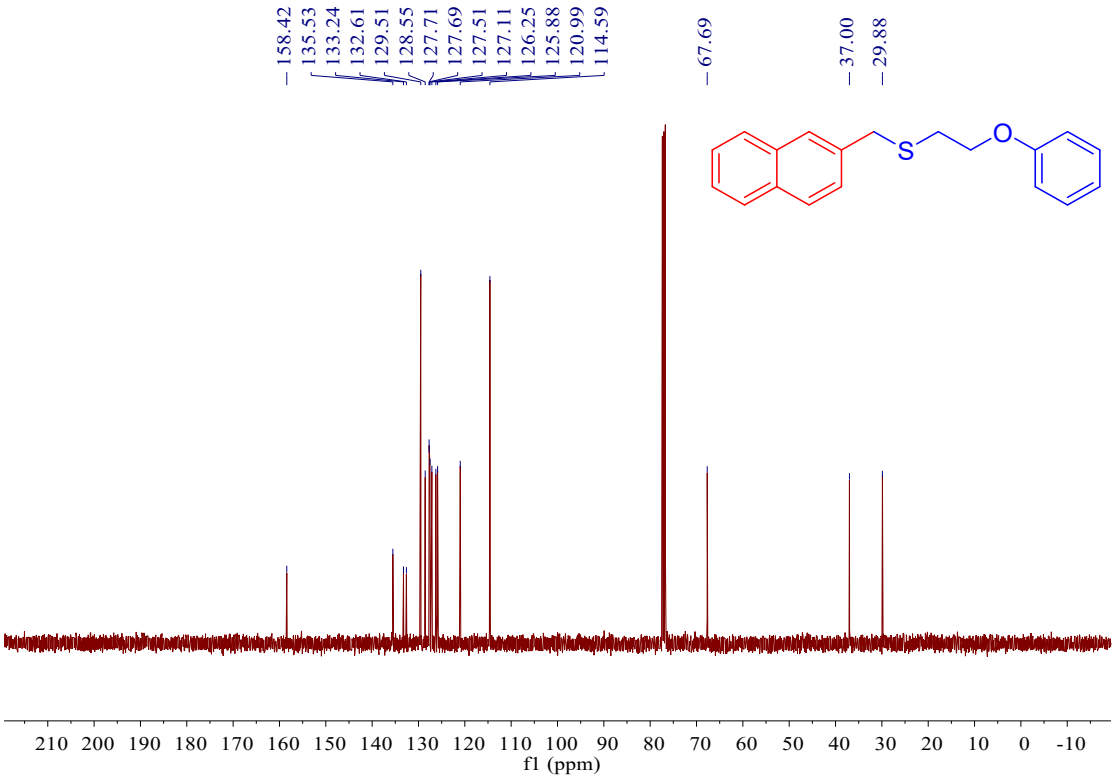
^{13}C NMR Spectra of **6h** (400 MHz, $CDCl_3$)



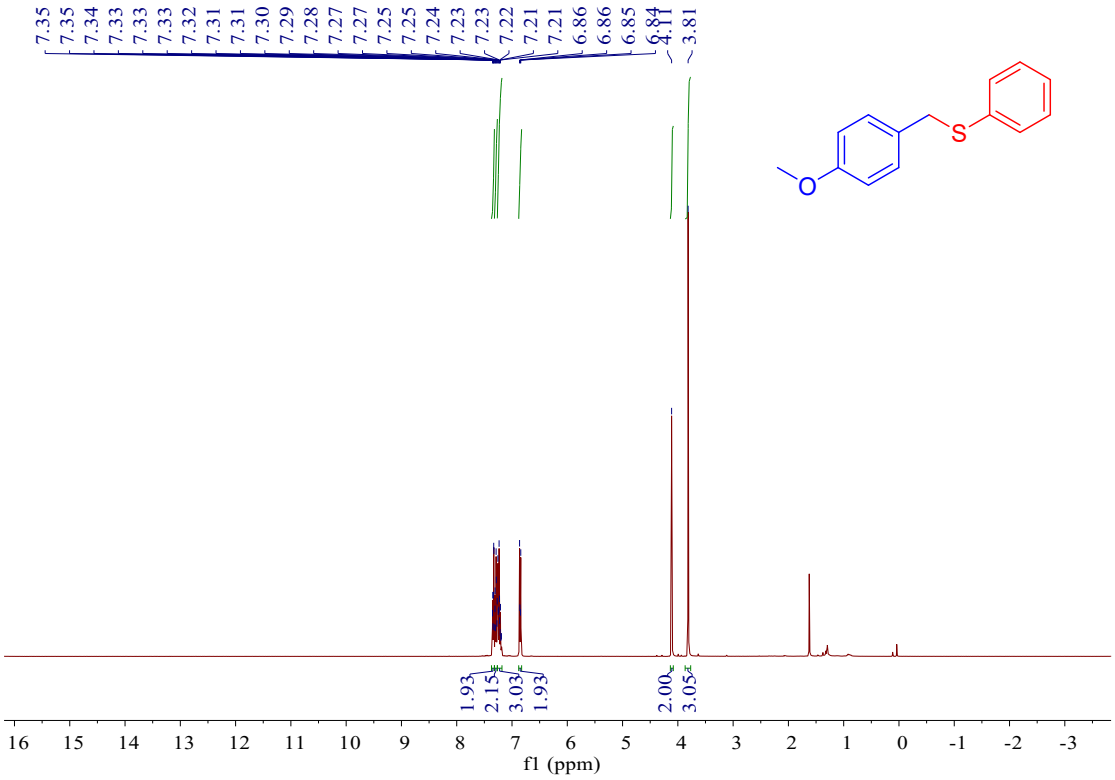
^{1}H NMR Spectra of **6i** (400 MHz, $CDCl_3$)



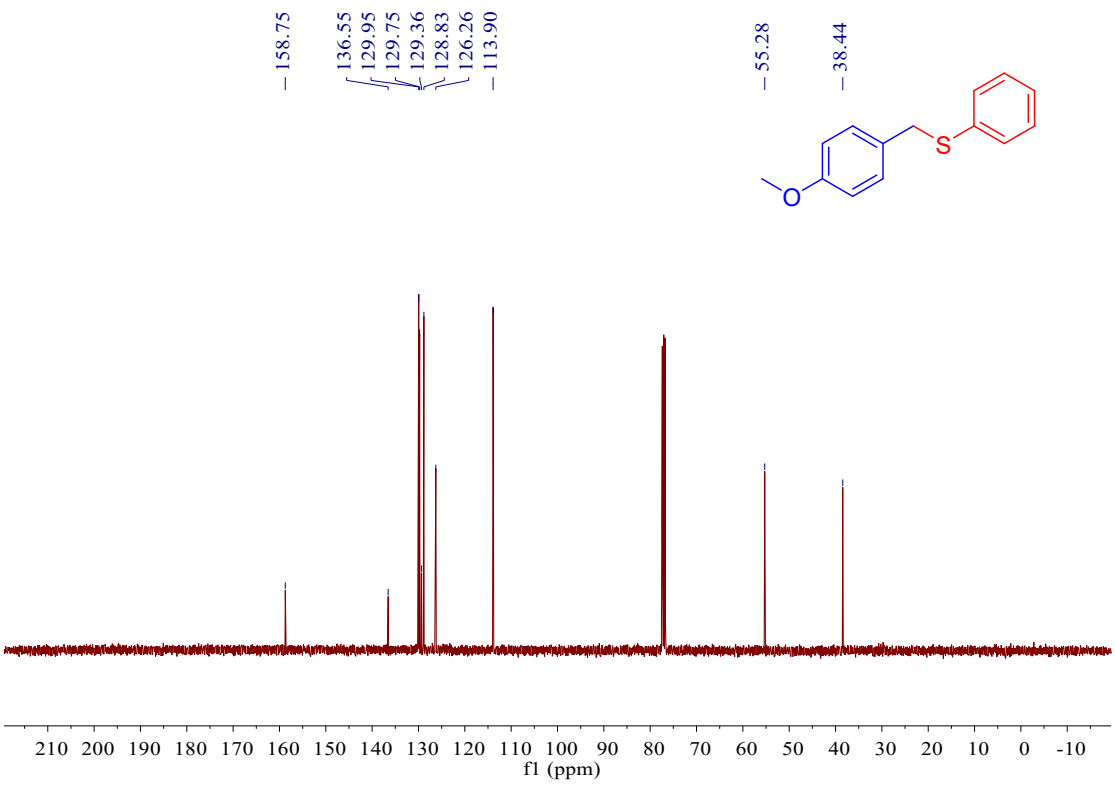
^{13}C NMR Spectra of **6i** (400 MHz, $CDCl_3$)



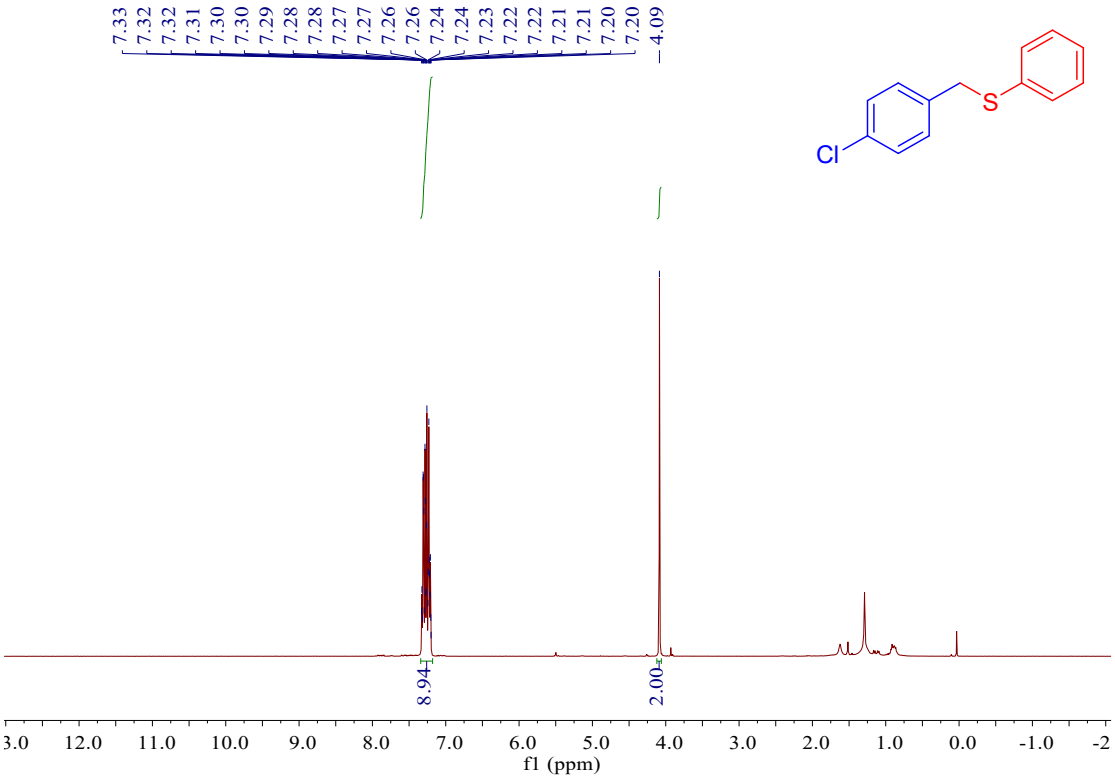
^{1}H NMR Spectra of **7a** (400 MHz, $CDCl_3$)



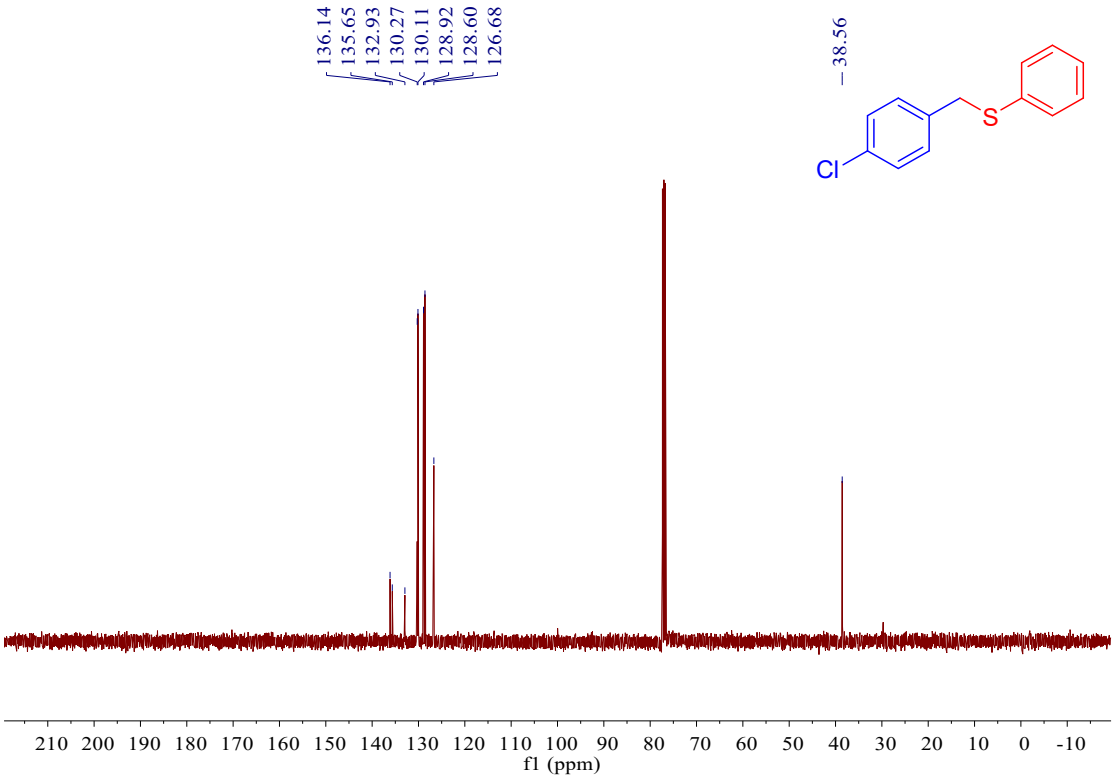
^{13}C NMR Spectra of **7a** (400 MHz, $CDCl_3$)



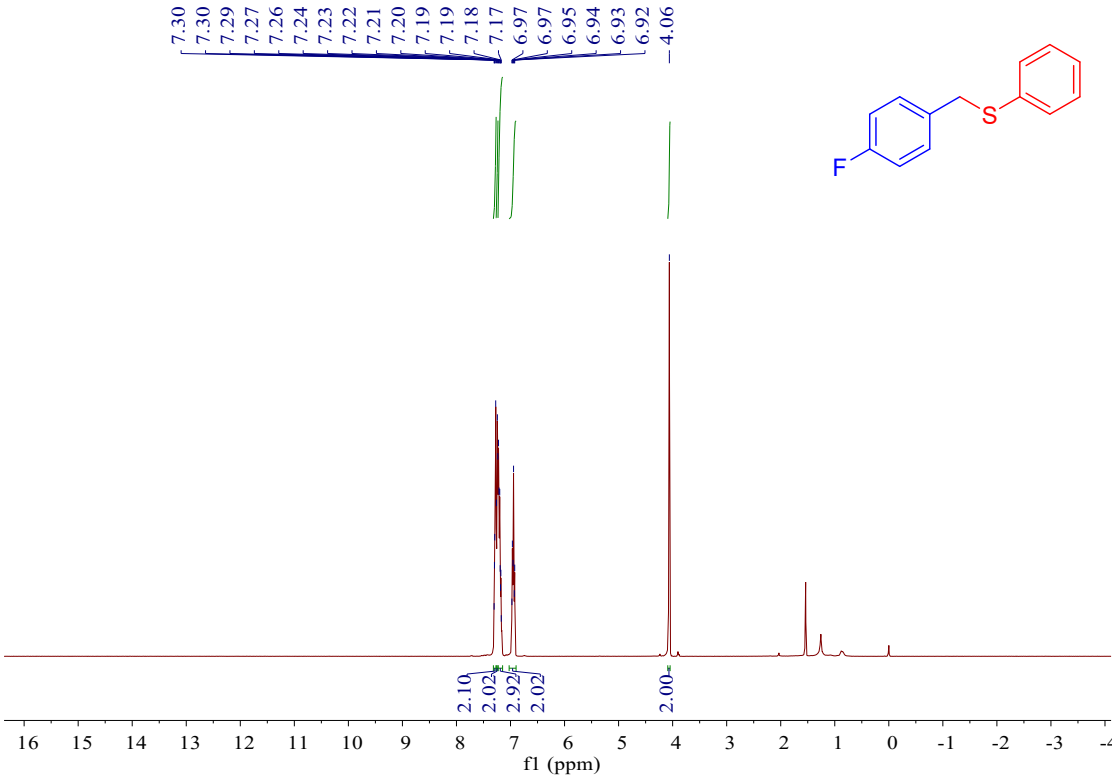
^{1}H NMR Spectra of **7b** (400 MHz, $CDCl_3$)



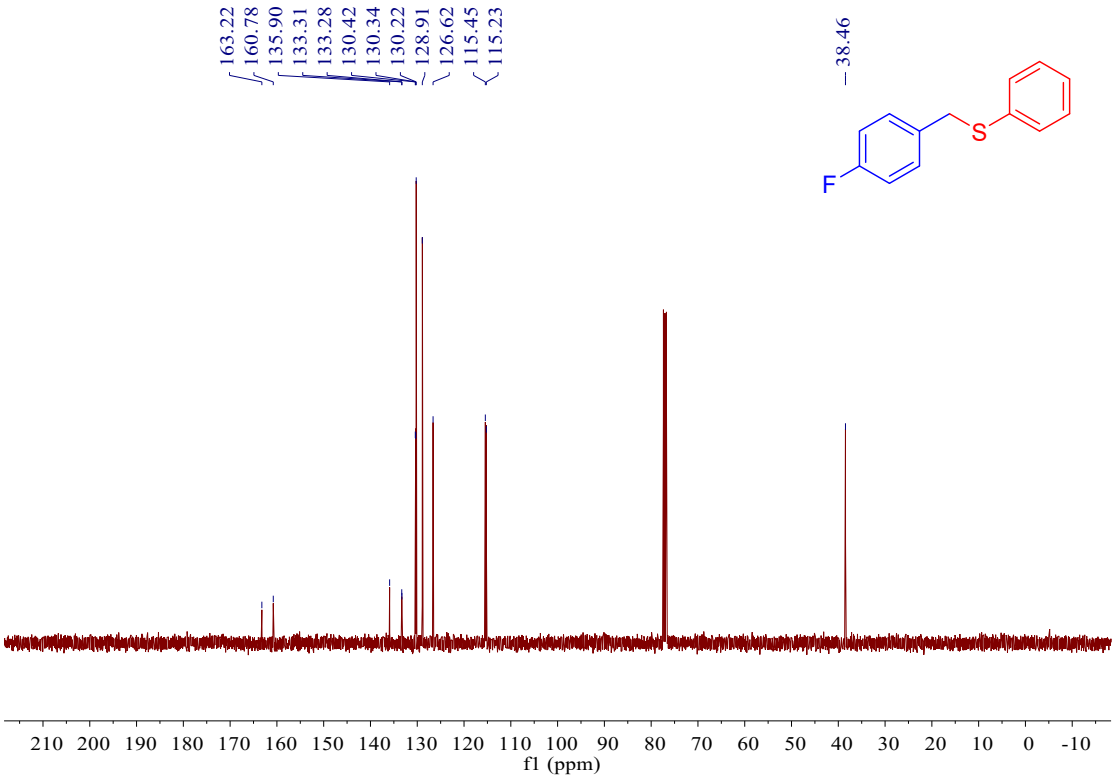
^{13}C NMR Spectra of **7b** (400 MHz, $CDCl_3$)



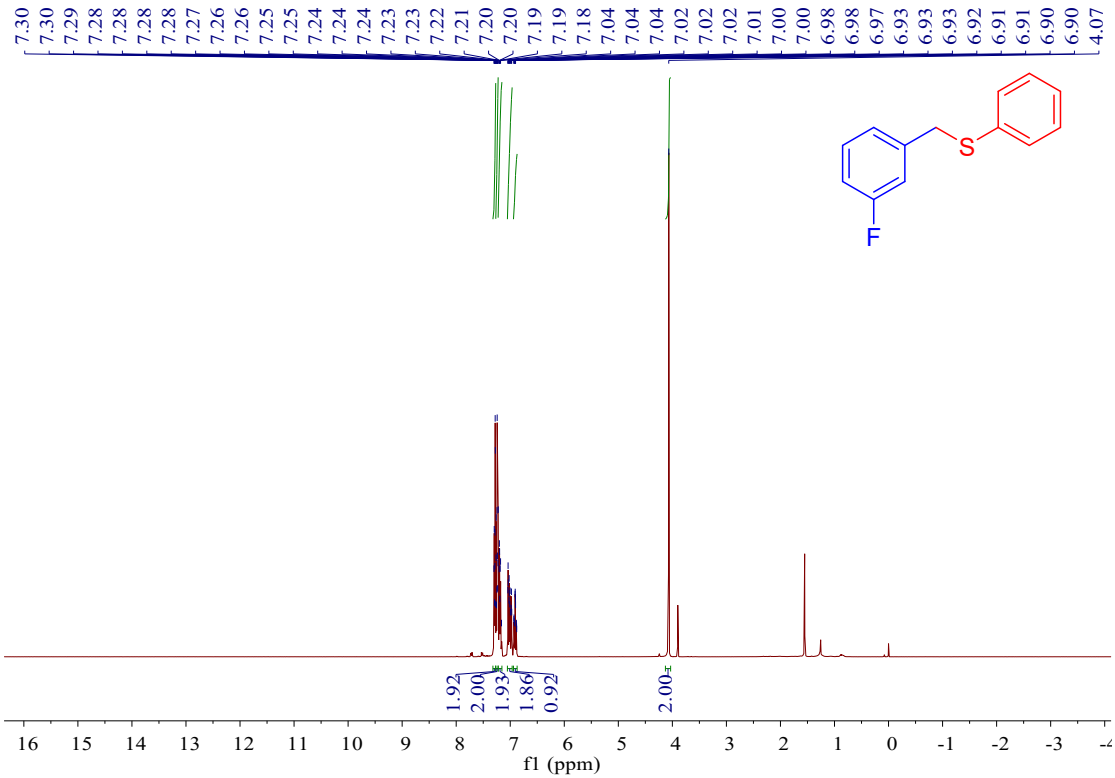
^{1}H NMR Spectra of **7c** (400 MHz, $CDCl_3$)



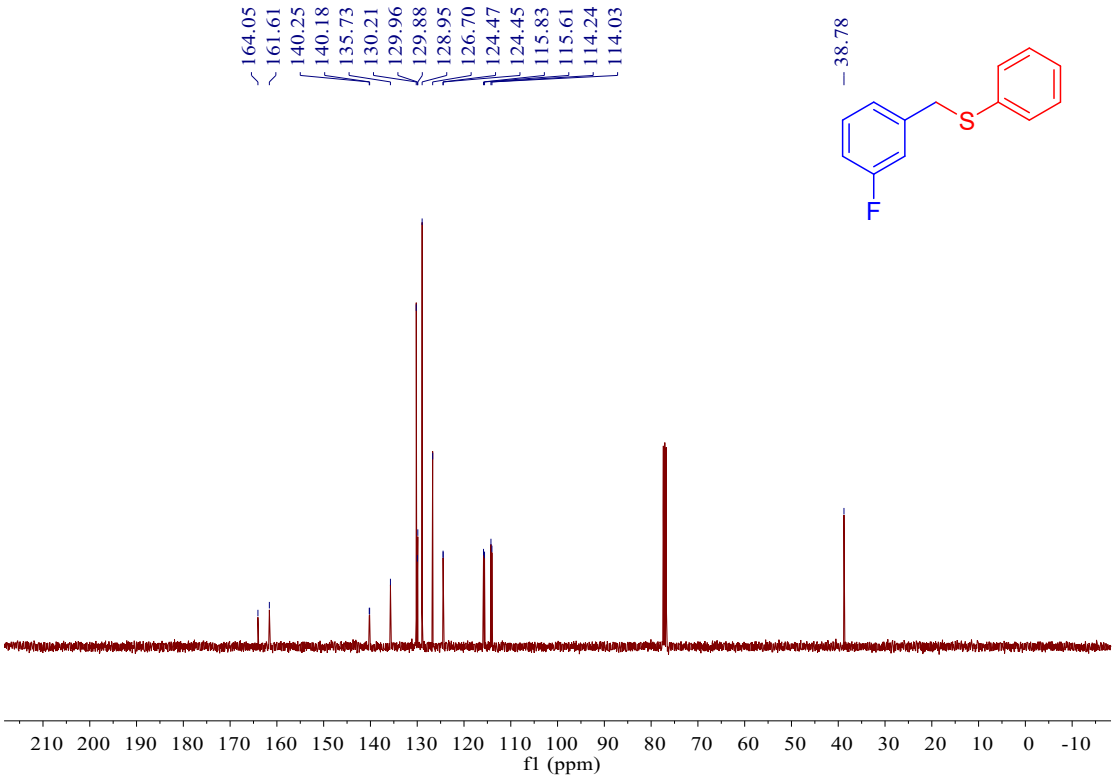
^{13}C NMR Spectra of **7c** (400 MHz, $CDCl_3$)



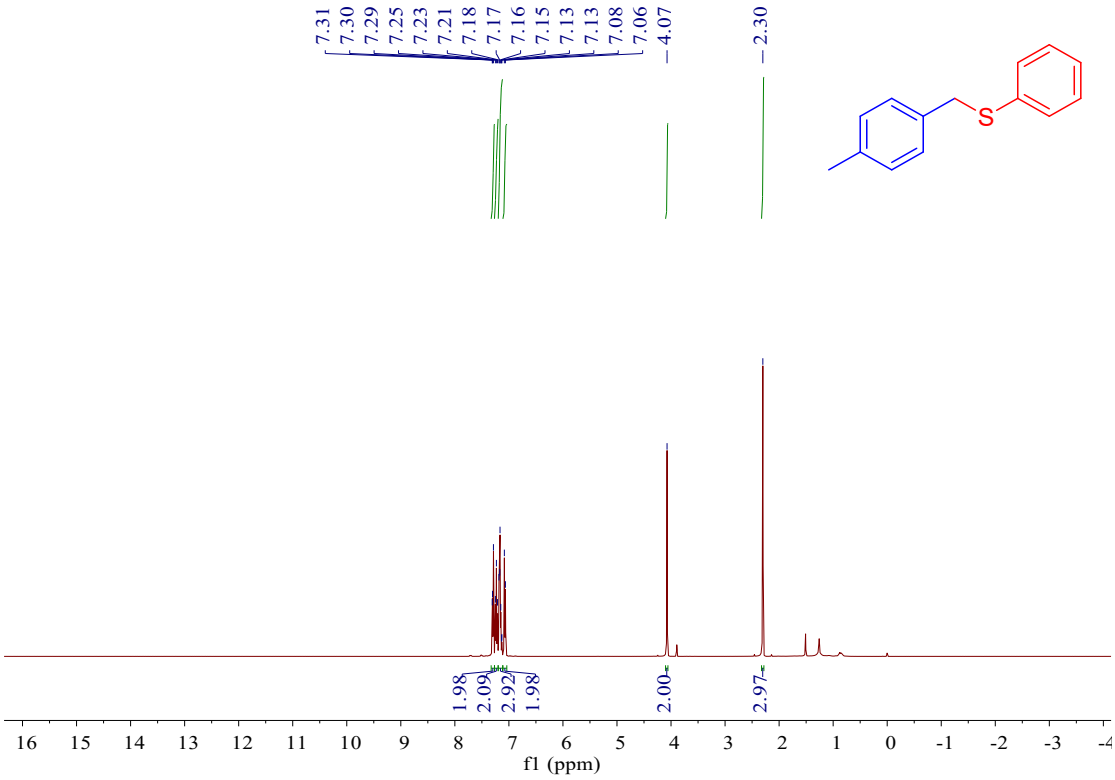
^{1}H NMR Spectra of **7d** (400 MHz, $CDCl_3$)



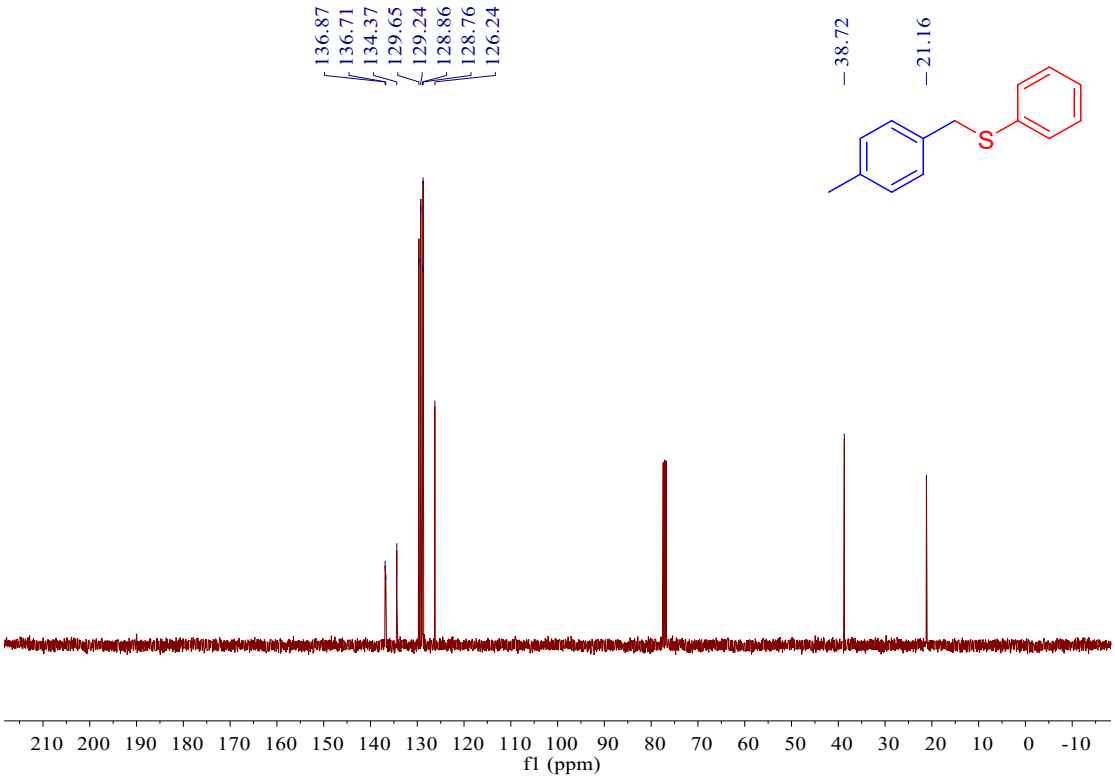
^{13}C NMR Spectra of **7d** (400 MHz, $CDCl_3$)



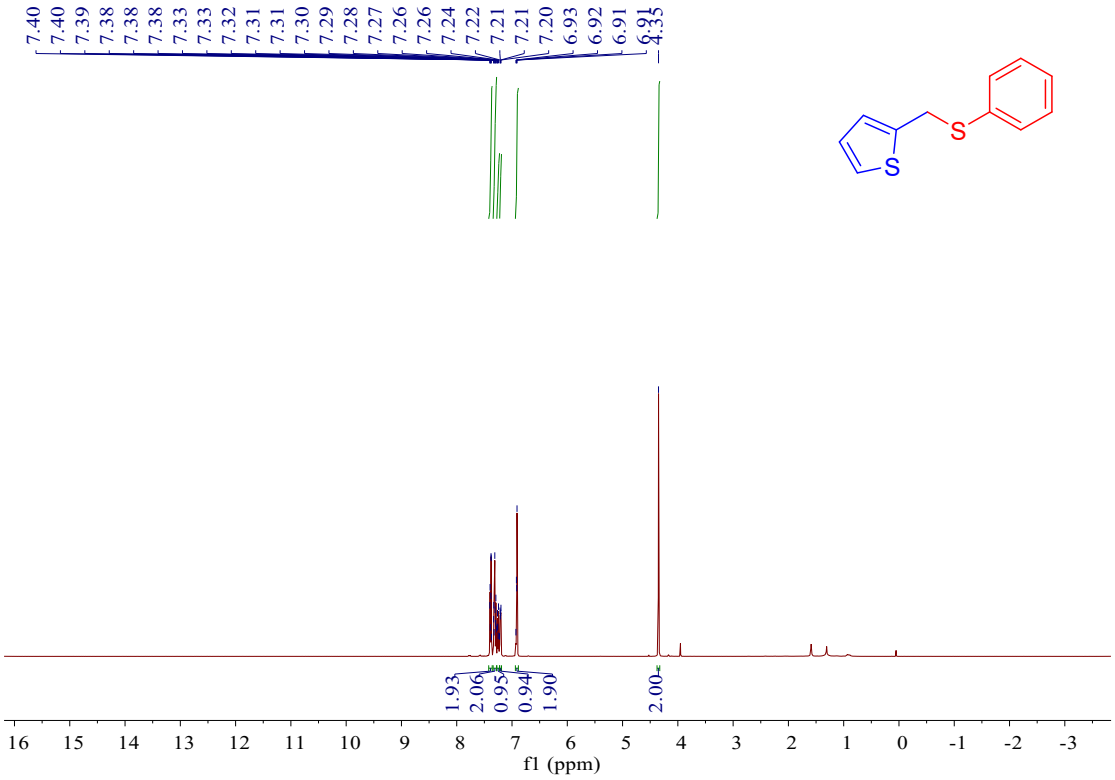
^{1}H NMR Spectra of **7e** (400 MHz, $CDCl_3$)



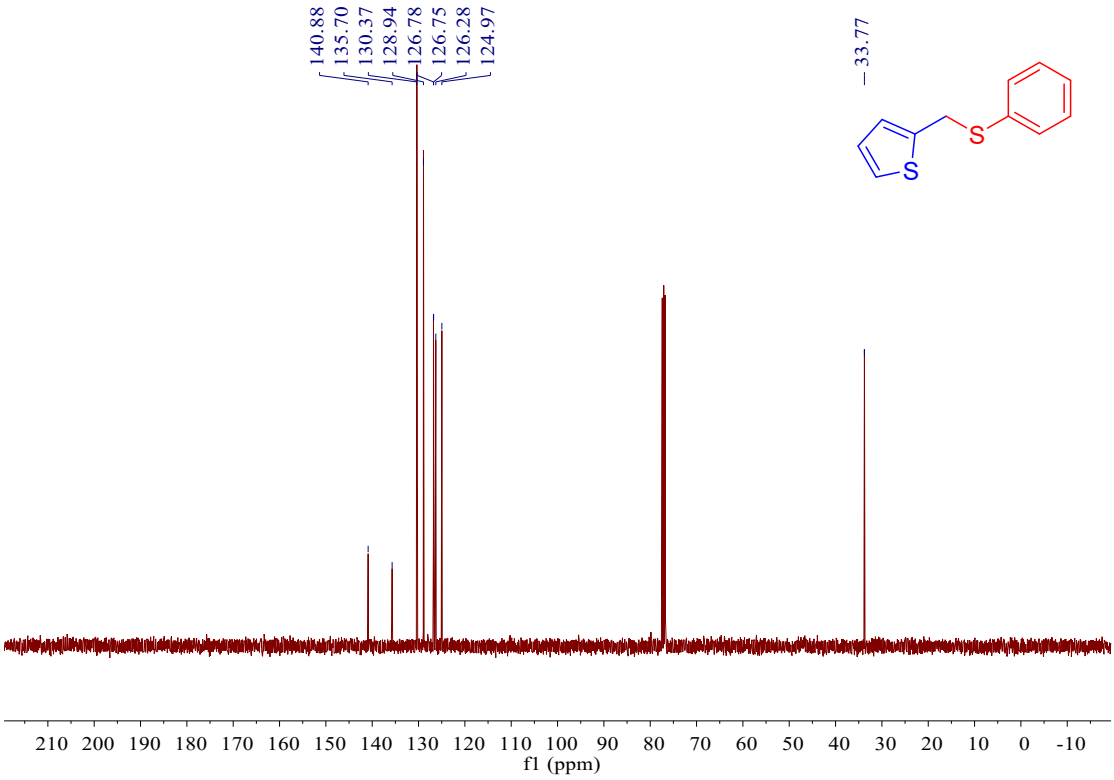
^{13}C NMR Spectra of **7e** (400 MHz, $CDCl_3$)



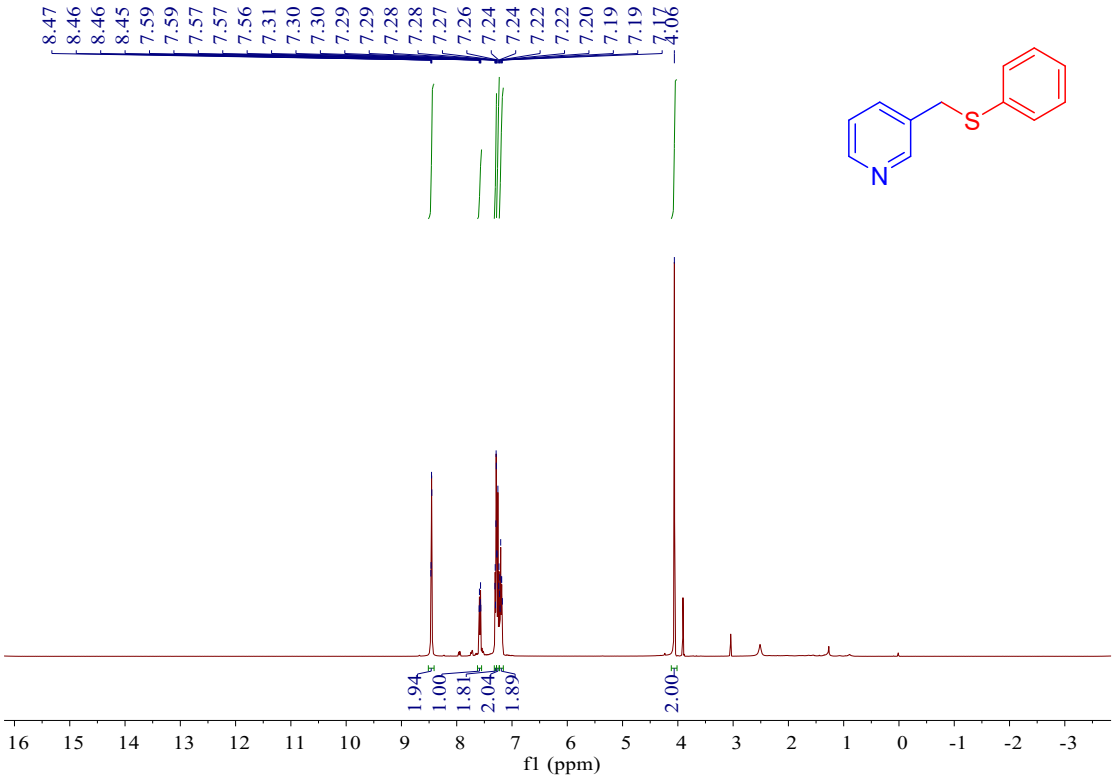
^{1}H NMR Spectra of **7f** (400 MHz, $CDCl_3$)



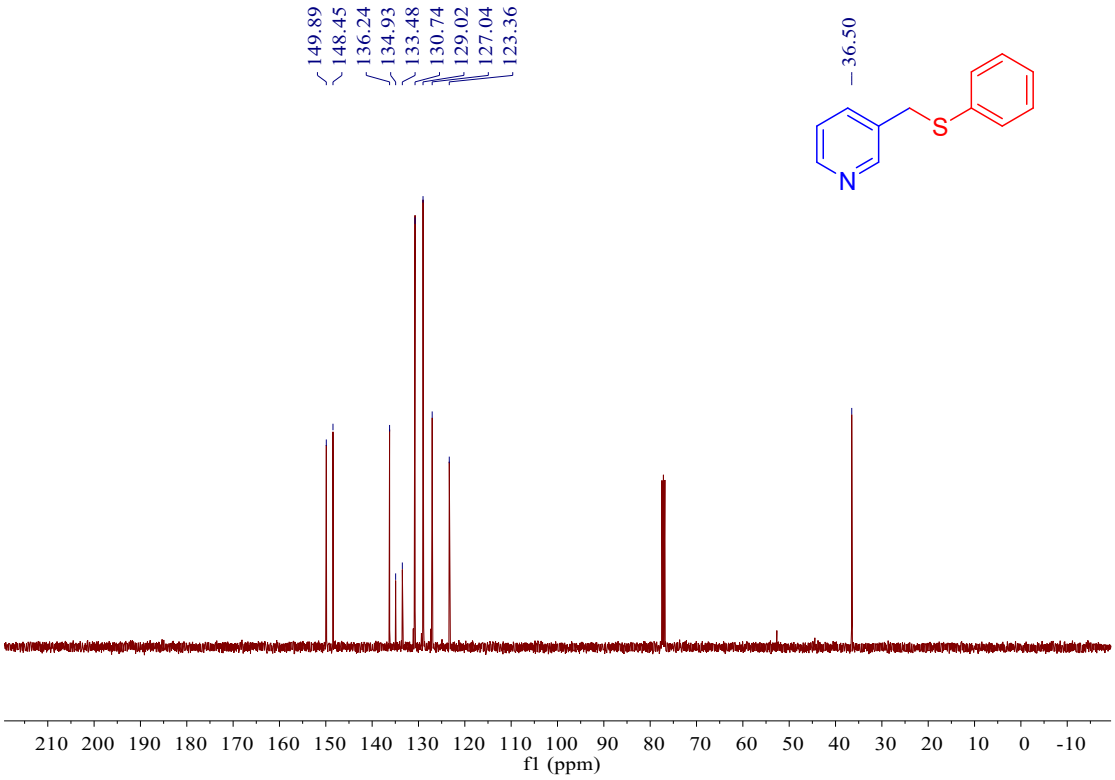
^{13}C NMR Spectra of **7f** (400 MHz, $CDCl_3$)



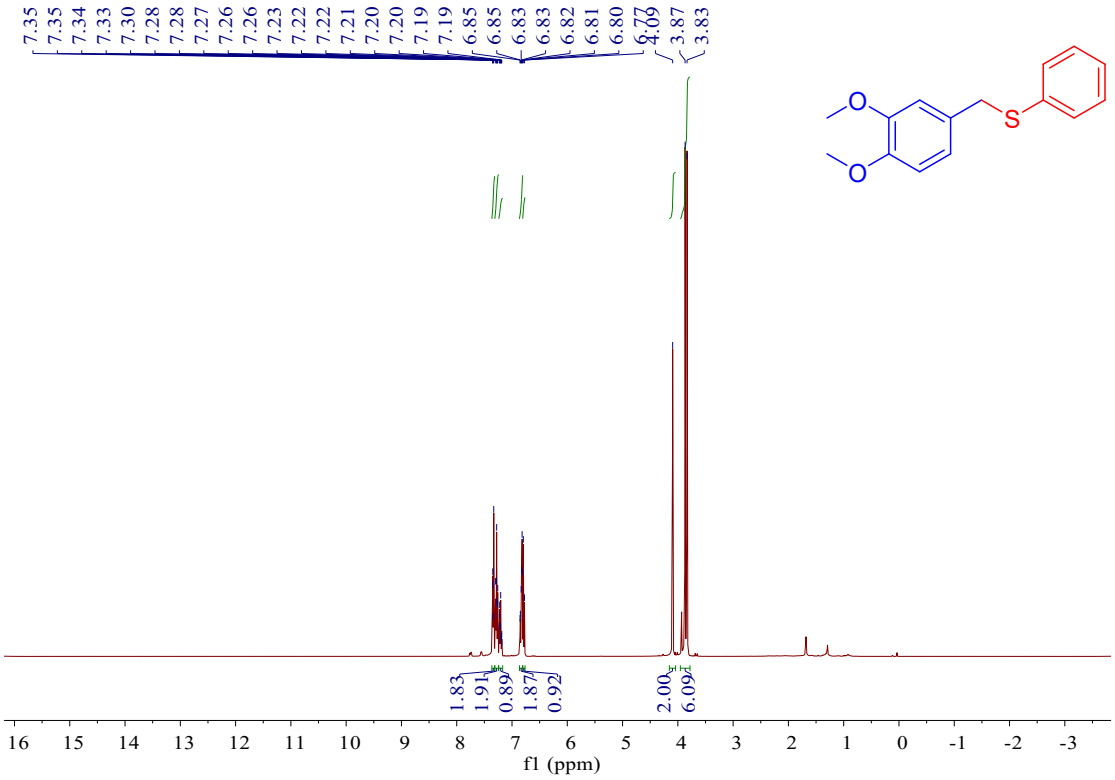
^{1}H NMR Spectra of **7g** (400 MHz, $CDCl_3$)



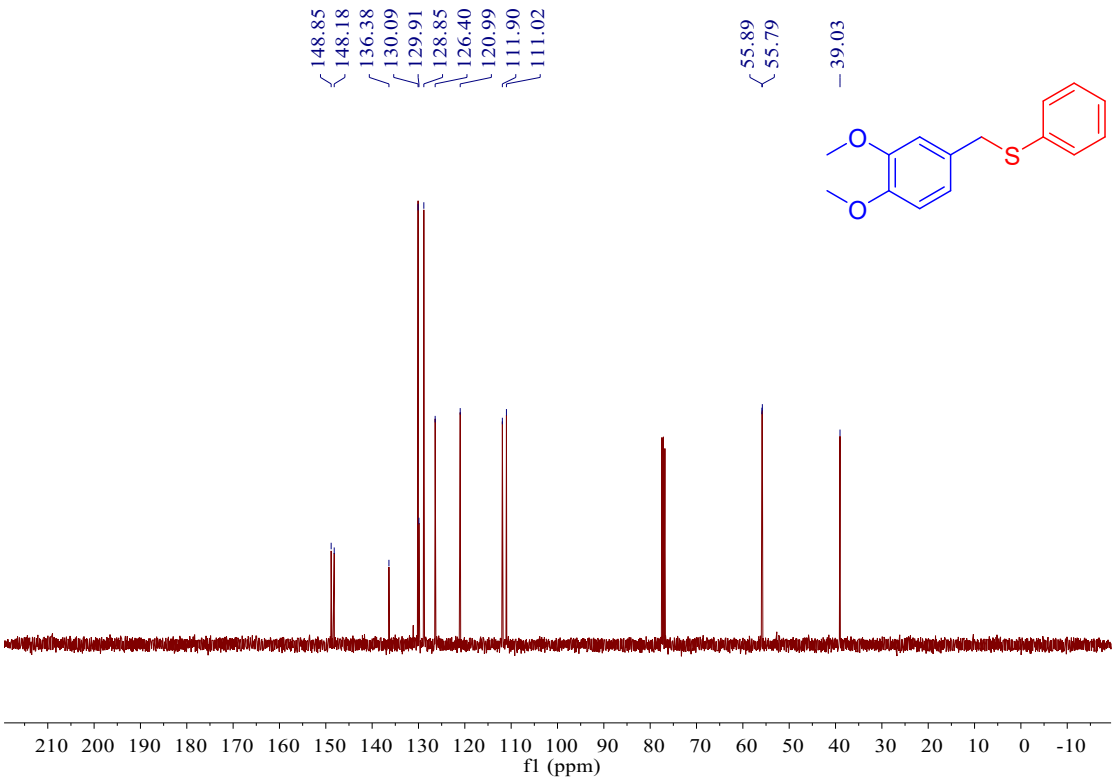
^{13}C NMR Spectra of **7g** (400 MHz, $CDCl_3$)



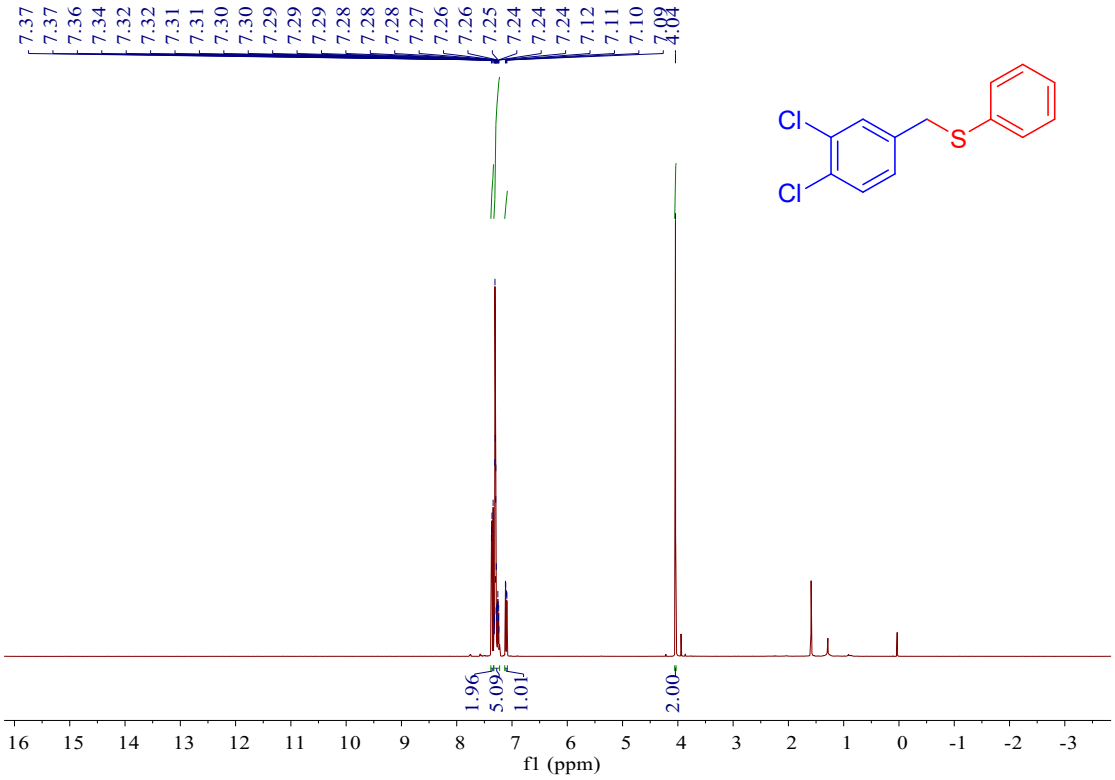
^{1}H NMR Spectra of **7k** (400 MHz, $CDCl_3$)



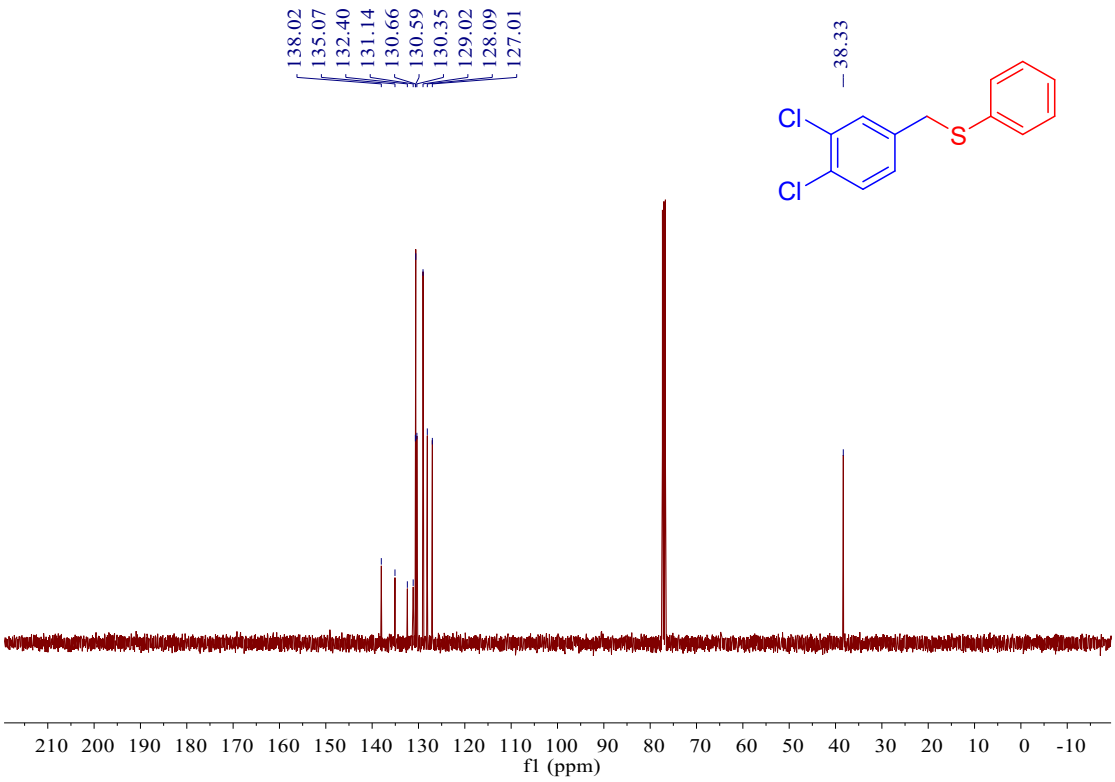
^{13}C NMR Spectra of **7k** (400 MHz, $CDCl_3$)



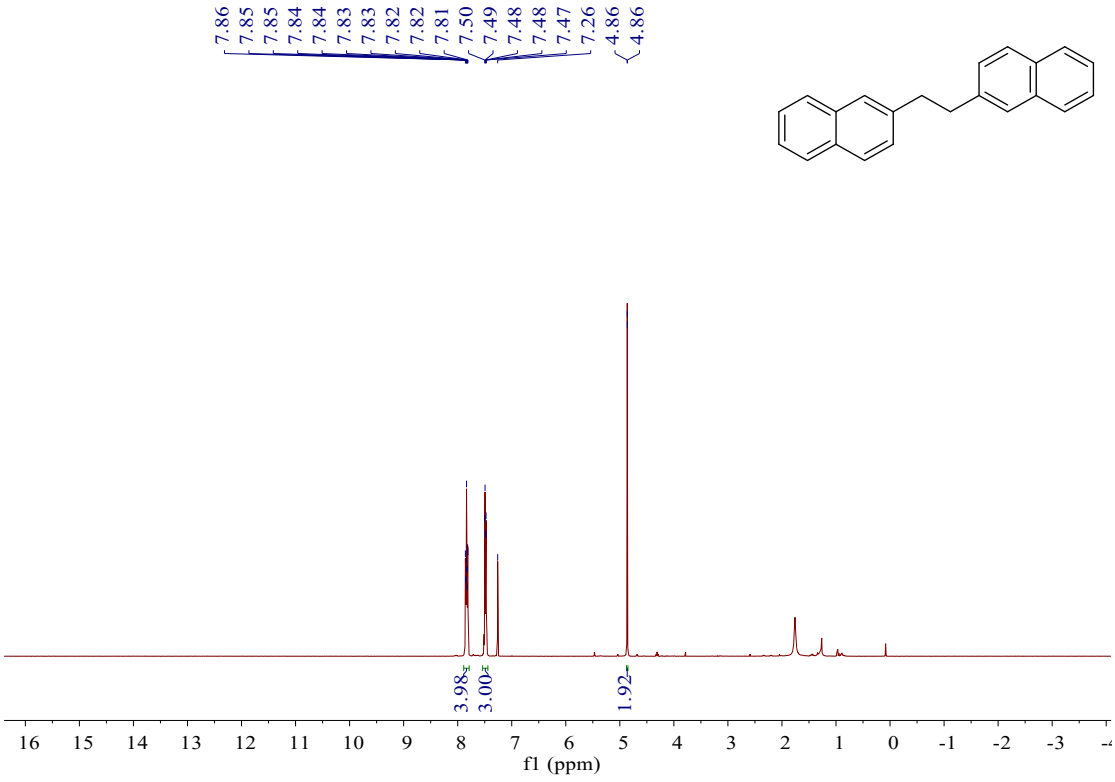
^{1}H NMR Spectra of **7l** (400 MHz, $CDCl_3$)



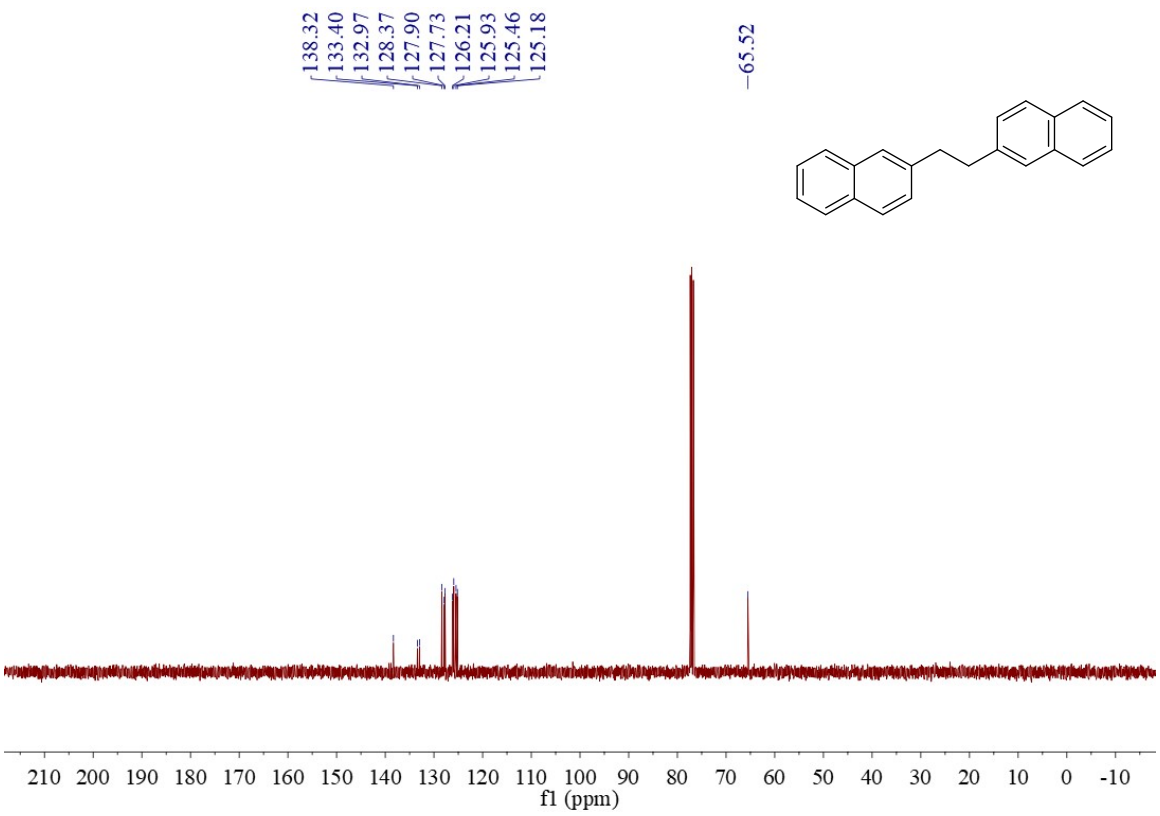
^{13}C NMR Spectra of **7l** (400 MHz, $CDCl_3$)



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



^{13}C NMR Spectra of **8a** (400 MHz, $CDCl_3$)


138.32
133.40
132.97
128.37
127.90
127.73
126.21
125.93
125.46
125.18
65.52
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)