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Electronic Supplementary Information

External Oxidant-Free and Selective Thiofunctionalization of Alkenes Enabled by Photoredox-Neutral Catalysis

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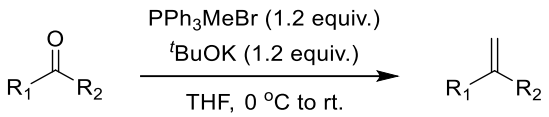
1. Experimental section

1) General information

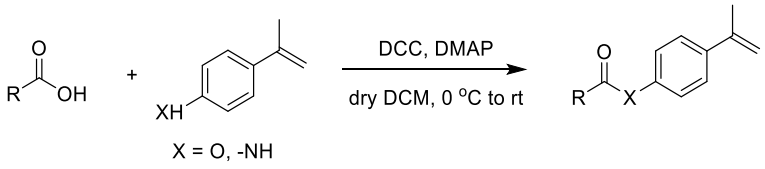
All chemicals, unless otherwise noted, were purchased from commercial sources and were used without further purification. Unless stated otherwise, all reactions were carried out under argon atmosphere. The substrates alkenes (**a**) and *N*-phenyl-sulfenyl phthalimides (**b**) were synthesized according to the literature methods with slight modification.[1-5] Irradiation with visible light was performed using blue LEDs ($\lambda = 450 \pm 10$ nm) illumination instruments (The instruments were designed by ourselves and the actual output power density of the LEDs at 0.5 cm distance is 33.70 mW/cm^2 detected by CEL-NP2000-10 (Beijing Ceau Light Co. Ltd., China) light power meter). For irradiation, the material of the reaction vessel is common glass; the distance from the light source is about 0.5 cm.

The nuclear magnetic resonance spectra were recorded on the Bruker Ascend^{TM} 400 MHz NMR spectrometer with tetramethylsilane (TMS) as an internal standard. High resolution mass spectra were recorded using a Q Exactive mass spectrometer (Thermo Fisher Scientific, USA). Cyclic voltammogram experiments were measured on the CHI-Instrument CHI660E.

2) Preparation of alkenes[1-2]



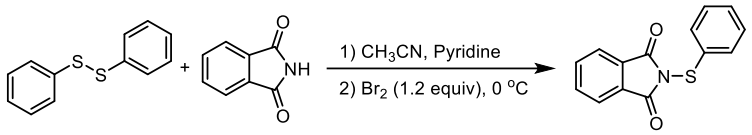
A solution of methyl triphenylphosphonium bromide (4.28 g, 12.0 mmol) in anhydrous THF (15.0 mL) was cooled to 0 ℃, followed by addition of ^{t}BuOK (1.35 g, 12.0 mmol). The reaction mixture was stirred at 0 ℃ for 1 h, and then the ketones (10.0 mmol, 1.0 equiv.) was added. The resulting mixture was warmed gradually to r.t. and kept stirring for 12 h. The resultant reaction solution was filtered over Celite, and the filtrate was concentrated under reduced pressure to yield a residue which was further purified over silica gel flash column chromatography to afford the product.



To a solution of carboxylic acid (1.0 equiv., 5.0 mmol), 4-dimethylaminopyridine (DMAP) (20%, 1.0 mmol, 122 mg) and **a'** (1.1 equiv., 5.5 mmol) in dry DCM (15 mL), followed by adding *N,N*'-dicyclohexylcarbodiimide (DCC) (1.1 equiv., 5.5 mmol, 1.14 g). The reaction mixture was stirred at room temperature for 12h. Upon completion, the resulting mixture was filtered through a pad of Celite. The filtrate was concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography to afford the desired products.

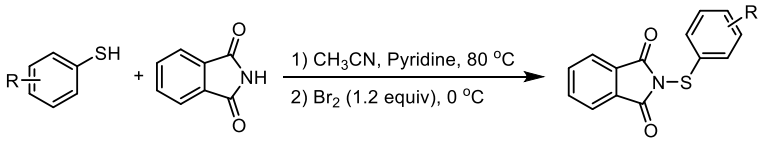
3) Preparation of *N*-phenyl-sulfenyl phthalimides[3-4]

Method A:



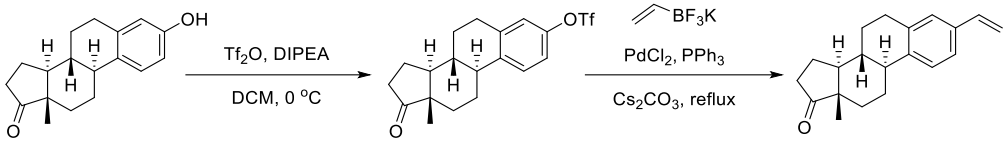
A suspension of phthalimide (1.047 g, 10.0 mmol) and diphenyl disulfide (1.30 g, 6.0 mmol) in CH_3CN (5.0 mL) and pyridine (4.0 mL) were treated with a solution of Br_2 (615 μL in 5.0 mL CH_3CN, 12.0 mmol, 1.2 equiv) dropwise over 30 mins. Upon complete addition of Br_2 solution, the mixture was stirred for 1 h at 0 ℃, and was subsequently quenched by dropwise addition of CH_3OH (15.0 mL). Filtration of the suspension and washing of the precipitate with pre-cooled CH_3OH (0 ℃, 3 × 10.0 mL). Further purification was achieved by recrystallization from a hexane/CH_2Cl_2 mixture.

Method B:



A suspension of phthalimide (1.047 g, 10.0 mmol) and thiophenols (11.0 mmol, 1.1 equiv) in CH_3CN (5.0 mL) and pyridine (4.0 mL) was heated to 80 ℃ and then cooled to room temperature. The mixture was treated with a solution of Br_2 (615 μL in 5.0 mL CH_3CN, 12.0 mmol, 1.2 equiv) dropwise over 30 mins. Upon complete addition of Br_2 solution, the mixture was stirred for 1 h at 0 ℃ and was subsequently quenched by dropwise addition of H_2O (15.0 mL). Filtration of the suspension and washing of the precipitate with pre-cooled CH_3OH (0 ℃, 3 × 10.0 mL). Further purification was achieved by recrystallization from a hexane/CH_2Cl_2 mixture.

4) Preparation of vinyl estrone[5]

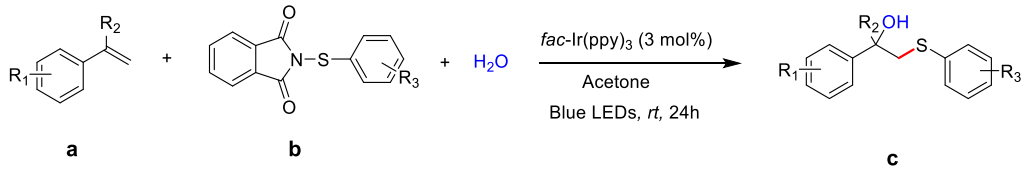


ES-0 ES-1 ES-2

Estrone (10.0 mmol, 1.0 equiv., 2.70 g), and DIPEA (12.0 mmol, 1.2 equiv.) were dissolved in DCM (30.0 mL) in a two-neck flask with a stir bar under argon atmosphere. The reaction mixture was stirred at 0 °C, and Tf_2O (12.0 mmol, 1.2 equiv., 2.0 mL) was dropwise added into reaction system over 5 min. The reaction mixture was then allowed to warm to room temperature and stirred for 30 min. Upon completion, water (50.0 mL) was added to quench the reaction. The reaction mixture was then extracted with DCM (30.0 mL x 3). The combined organic extracts were dried with anhydrous $MgSO_4$ and concentrated under vacuum. The crude product was purified by flash column chromatography on silica gel to afford the corresponding product **ES-1** as white solid in 81% yield.

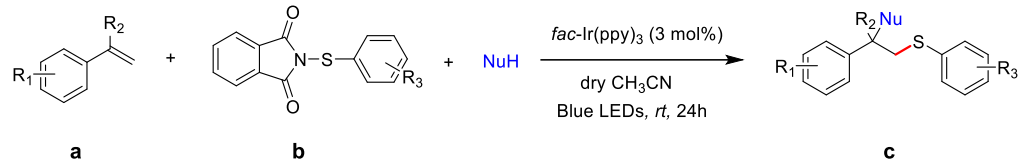
An oven dried 2-neck round bottom flask was charged with triflate (2.01 g, 5 mmol, 1 equiv.), potassium vinyltrifluoroborate (675 mg, 5 mmol, 1 equiv.), $PdCl_2$ (17.7 mg, 0.1 mmol, 0.02 equiv.), PPh_3 (78.7 mg, 0.3 mmol, 0.06 equiv.), Cs_2CO_3 (4.89 g, 15 mmol, 3 equiv.), THF (9 mL), H_2O (1 mL) and stirred under reflux until completion. Reaction mixture was then diluted with 50 mL H_2O and extracted 3 times with 25 mL DCM. Combined organic phases were dried over magnesium sulfate, filtered through short pad of Celite and concentrated under reduced pressure. Purification by column chromatography (Hexane : EtOAc = 5:1) afforded corresponding product **ES-2** as white solid in 63% yield.

5) General procedure for the photochemical reactions



a **b** **c**

a (1.0 equiv., 0.2 mmol), **b** (1.1 equiv., 0.22 mmol), *fac*-Ir(ppy)$_3$ (4.0 mg, 3.0 mol%) were dissolved in 4.0 mL co-solvent (acetone: H_2O = 20:1 (v/v)) in a 10.0 mL flask equipped with magnetic stirring bar, then the reaction tube was irradiated by blue LEDs (λ = 450 ± 10 nm) at room temperature for 24 h. After reaction, the solvent was removed by rotary evaporation and purified by column-chromatography on silica gel using hexane/ ethyl acetate as the eluent to afford the desired product **c**.



a **b** **c**

a (1.0 equiv., 0.2 mmol), **b** (1.1 equiv., 0.22 mmol), NuH (ROH: 8.0-15.0 equiv.; R_2NH: 2.0 equiv.), *fac*-Ir(ppy)$_3$ (4.0 mg, 3.0 mol%) were dissolved in 4.0 mL dry CH_3CN in a 10.0 mL flask equipped with magnetic stirring bar, then the reaction tube was irradiated by blue LEDs (λ = 450 ± 10 nm) at room temperature for 24 h. After reaction, the solvent was removed by rotary evaporation and purified by column-chromatography on silica gel using hexane/ ethyl acetate as the eluent to afford the desired product **c**.

450 nm photoreactor

6) Luminescence Quenching Experiments

General procedure: The luminescence quenching experiments were measured with excitation at 449 nm. A co-solvent (acetone: H_2O = 20:1 (v/v)) solution of 1×10^{-4} M *fac*-Ir(ppy)$_3$ and 3.0×10^{-1} M **b1** respectively were prepared. The experiments were conducted in 1.25 cm x 1.25 cm x 4.5 cm quartz cuvette at room temperature. Appropriate volume (the whole solution volume change < 5%) of the quencher **b1** was respectively injected to the co-solvent (acetone: H_2O = 20:1 (v/v)) solution (3.0 mL) of 1×10^{-4} M *fac*-Ir(ppy)$_3$ in the quartz cuvette by microsyringe.

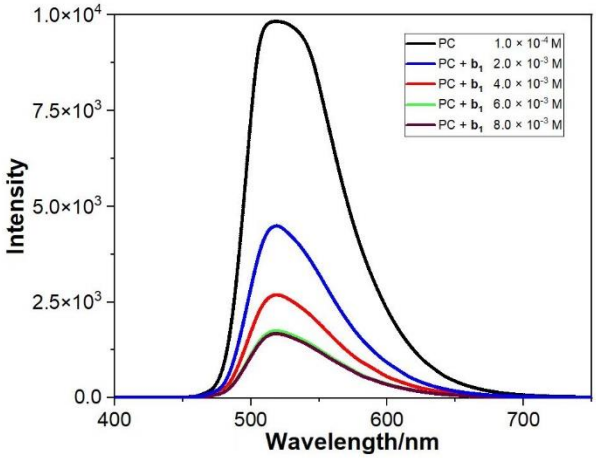


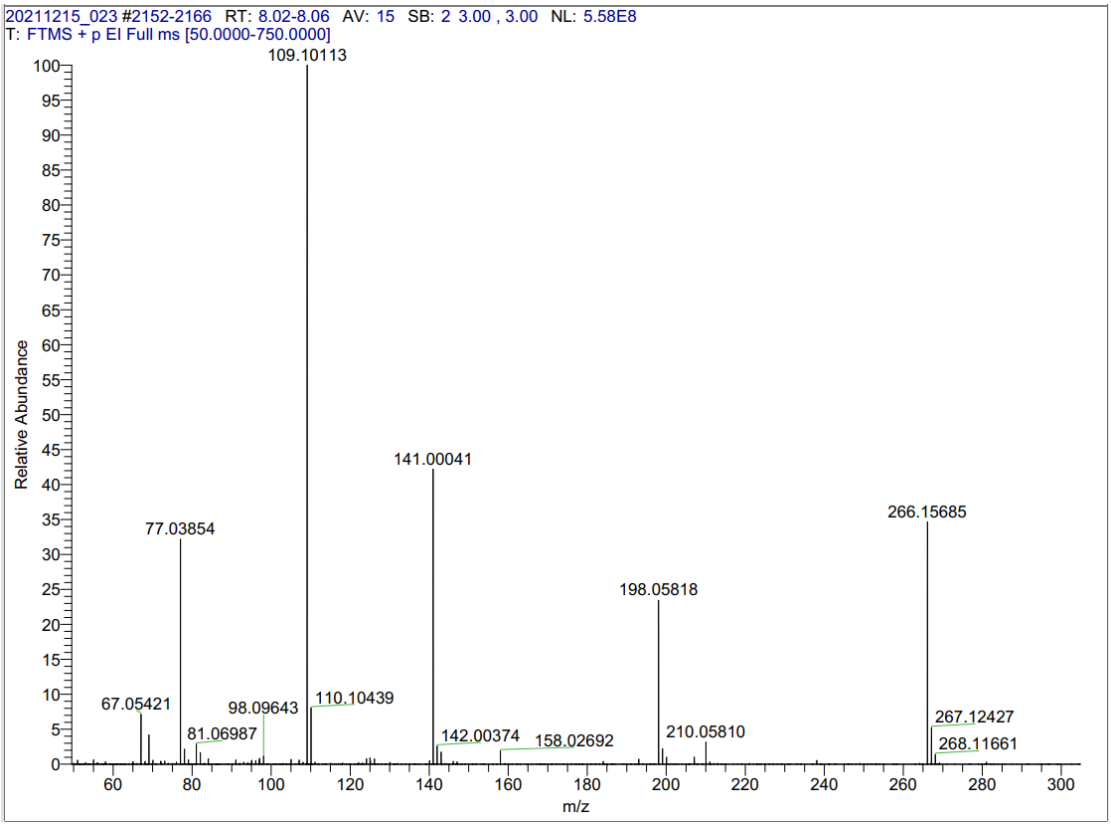
Figure S1. Luminescence quenching spectra of *fac*-Ir(ppy)$_3$ (1.0 x 10^{-4} M) by various concentration of **b1**

7) Radical inhibition experiment

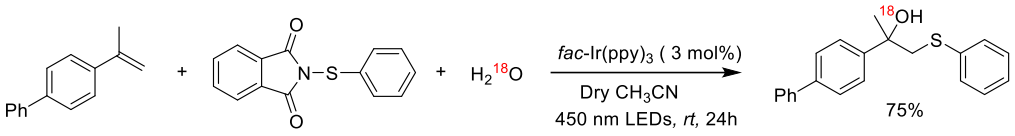
detected by HRMS

HRMS (ES^+) Calcd [$M+H]^+$: 266.1573

Found : 266.1568



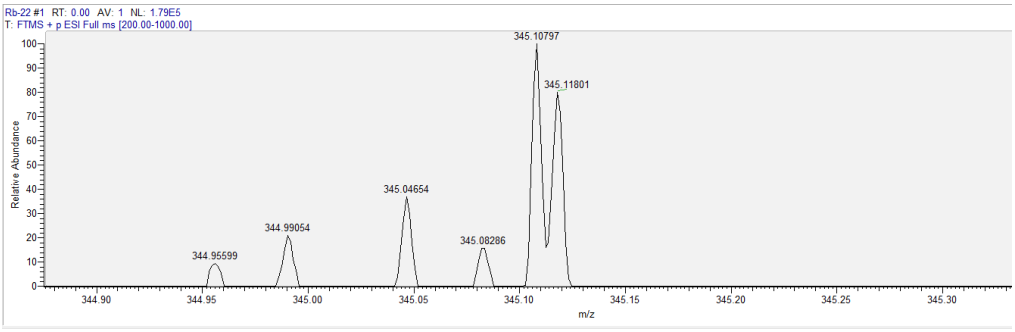
8) Isotope labelling experiment



detected by HRMS

HRMS (ES$^+$) Calcd [M+Na]$^+$: 345.1170

Found : 345.1180



9) References

[1] X.-T. Li and X.-Y. Liu, *Angew. Chem. Int. Ed.* 2018, **57**, 7668.

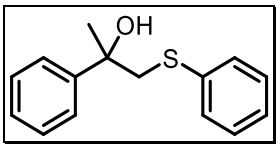
[2] X. Lu, S.-J. He and Y. Fu, *Chem. Sci.* 2019, **10**, 809.

[3] S. E. Denmark, D. J. P. Kornfilt and H. Wang, *Nat. Chem.* 2014, **6**, 1056.

[4] J. Klose, C. B. Reese and Q. Song, *Tetrahedron* 1997, **53**, 14411.

[5] C.-Y. Huang and A. G. Doyle, *J. Am. Chem. Soc.* 2012, **134**, 9541.

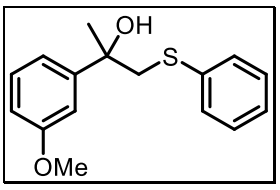
2. Characterization data of the products



c1

Purification by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v) afforded **c1** as a colorless oil (44.9 mg, 92% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 5.2, 3.4 Hz, 2H), 7.37 (dd, *J* = 11.3, 4.4 Hz, 4H), 7.32 – 7.23 (m, 3H), 7.20 (ddd, *J* = 7.3, 3.6, 1.2 Hz, 1H), 3.57 (d, *J* = 13.3 Hz, 1H), 3.39 (d, *J* = 13.3 Hz, 1H), 2.91 (s, 1H), 1.65 (s, 3H)； **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.2, 136.5, 130.0, 130.0, 128.3, 127.1, 126.4, 124.8, 74.0, 49.6, 29.4.

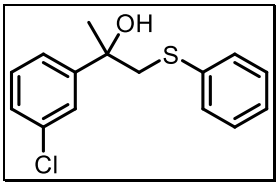
HRMS (ESI) m/z calcd. for $C_{15}H_{16}OSNa$ $[M+Na]^+$: 267.0814, found: 267.0814.



c2

Purification by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v) afforded **c2** as a colorless oil (39.4 mg, 72% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.30 (m, 2H), 7.26 – 7.19 (m, 3H), 7.18 – 7.12 (m, 1H), 7.05 – 6.96 (m, 2H), 6.77 (ddd, *J* = 8.2, 2.6, 0.8 Hz, 1H), 3.79 (s, 3H), 3.53 (d, *J* = 13.3 Hz, 1H), 3.32 (d, *J* = 13.3 Hz, 1H), 2.93 (s, 1H), 1.60 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.6, 148.0, 136.5, 130.0, 129.3, 128.9, 126.4, 117.2, 112.3, 111.0, 74.0, 55.2, 49.5, 29.4.

HRMS (ESI) m/z calcd. for $C_{16}H_{18}O_2SNa$ $[M+Na]^+$: 297.0920, found: 297.0920.

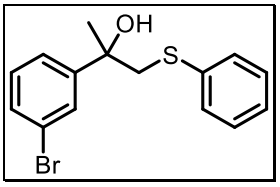


c3

Purification by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v) afforded **c3** as a pale yellow oil (41.7 mg, 75% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (t, *J* = 1.8 Hz, 1H), 7.37 – 7.33 (m, 2H), 7.32 (dt, *J* = 7.3, 1.8 Hz, 1H), 7.29 – 7.24 (m, 2H), 7.24 – 7.17 (m, 3H), 3.52 (d, *J* = 13.5 Hz, 1H), 3.34 (d, *J* = 13.5 Hz, 1H), 2.99 (d, *J* = 20.7 Hz, 1H), 1.61 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.4, 136.0, 134.3,

130.3, 129.5, 129.0, 127.2, 126.7, 125.4, 123.1, 73.8, 49.5, 29.4.

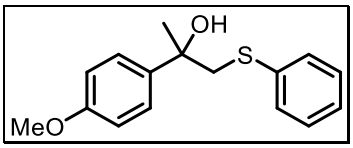
HRMS (ESI) m/z calcd. for $C_{15}H_{15}ClOSNa$ $[M+Na]^+$: 301.0424, found: 301.0423.



c4

Purification by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v) afforded **c4** as a colorless oil (52.2 mg, 81% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 (t, *J* = 1.8 Hz, 1H), 7.41 – 7.31 (m, 4H), 7.29 – 7.23 (m, 2H), 7.22 – 7.15 (m, 2H), 3.56 – 3.47 (m, 1H), 3.34 (d, *J* = 13.5 Hz, 1H), 3.00 (s, 1H), 1.61 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.6, 135.9, 130.3, 130.2, 129.8, 129.0, 128.3, 126.7, 123.6, 122.6, 73.7, 49.4, 29.4.

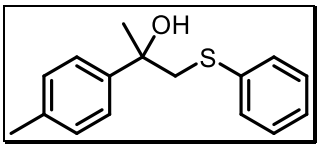
HRMS (ESI) m/z calcd. for $C_{15}H_{15}BrOSNa$ $[M+Na]^+$: 344.9919, found: 344.9916.



c5

Purification by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v) afforded **c5** as a pale yellow oil (42.3 mg, 77% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.33 (m, 4H), 7.26 (t, *J* = 7.4 Hz, 2H), 7.20 (d, *J* = 7.3 Hz, 1H), 6.92 – 6.85 (m, 2H), 3.82 (s, 3H), 3.55 (d, *J* = 13.2 Hz, 1H), 3.35 (d, *J* = 13.2 Hz, 1H), 2.90 (s, 1H), 1.63 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.6, 138.4, 136.6, 129.9, 130.0, 126.4, 126.1, 113.6, 73.7, 55.3, 49.6, 29.4.

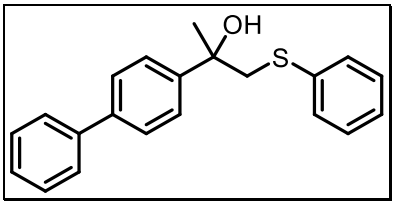
HRMS (ESI) m/z calcd. for $C_{16}H_{18}O_2SNa$ $[M+Na]^+$: 297.0920, found: 297.0917.



c6

Purification by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v) afforded **c6** as a yellow oil (42.3 mg, 82% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.34 (m, 4H), 7.30 – 7.23 (m, 2H), 7.23 – 7.15 (m, 3H), 3.58 (d, *J* = 13.2 Hz, 1H), 3.37 (d, *J* = 13.2 Hz, 1H), 2.91 (s, 1H), 2.37 (s, 3H), 1.65 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.3, 136.8, 136.7, 129.9, 129.0, 130.0, 126.3, 124.8, 73.9, 49.6, 29.4, 21.0.

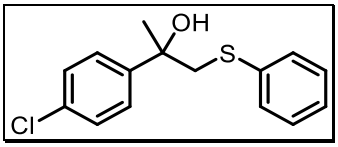
HRMS (ESI) m/z calcd. for $C_{16}H_{18}OSNa$ $[M+Na]^+$: 281.0971, found: 281.0971.



c7

Purification by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v) afforded **c7** as a white solid (58.2 mg, 91% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (dt, *J* = 3.1, 2.0 Hz, 2H), 7.54 – 7.46 (m, 4H), 7.45 – 7.38 (m, 2H), 7.36 – 7.29 (m, 3H), 7.23 – 7.17 (m, 2H), 7.16 – 7.11 (m, 1H), 3.56 (d, *J* = 13.4 Hz, 1H), 3.36 (d, *J* = 13.4 Hz, 1H), 2.96 (s, 1H), 1.64 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.3, 140.8, 140.0, 136.4, 130.2, 129.0, 128.8, 127.3, 127.1, 127.0, 126.5, 125.4, 74.0, 49.6, 29.4.

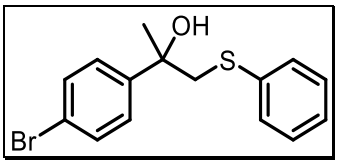
HRMS (ESI) m/z calcd. for $C_{21}H_{20}OSNa$ $[M+Na]^+$: 343.1127, found: 343.1123



c8

Purification by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v) afforded **c8** as a colorless oil (41.7 mg, 75% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 2H), 7.32 – 7.28 (m, 2H), 7.28 – 7.14 (m, 5H), 3.49 (d, *J* = 13.4 Hz, 1H), 3.31 (d, *J* = 13.4 Hz, 1H), 2.93 (s, 1H), 1.58 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.7, 136.1, 132.9, 130.2, 129.0, 128.3, 126.6, 126.4, 73.8, 49.6, 29.4.

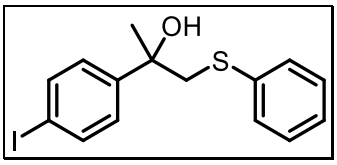
HRMS (ESI) m/z calcd. for $C_{15}H_{15}ClOSNa$ $[M+Na]^+$: 301.0424, found: 301.0420.



c9

Purification by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v) afforded **c9** as a colorless oil (48.9 mg, 76% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.41 (m, 2H), 7.36 – 7.29 (m, 4H), 7.29 – 7.18 (m, 3H), 3.51 (d, *J* = 13.4 Hz, 1H), 3.34 (d, *J* = 13.4 Hz, 1H), 2.99 (s, 1H), 1.61 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.2, 136.0, 131.3, 130.3, 129.0, 126.8, 126.6, 121.1, 73.8, 49.5, 29.4.

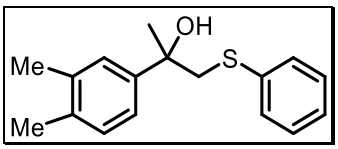
HRMS (ESI) m/z calcd. for $C_{15}H_{15}BrOSNa$ $[M+Na]^+$: 344.9919, found: 344.9914.



c10

Purification by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v) afforded **c10** as a pale yellow oil (50.3 mg, 68% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 – 7.57 (m, 2H), 7.31 – 7.26 (m, 2H), 7.24 – 7.13 (m, 5H), 3.48 (d, *J* = 13.4 Hz, 1H), 3.29 (d, *J* = 13.4 Hz, 1H), 2.95 (s, 1H), 1.56 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.9, 137.3, 136.0, 130.3, 129.0, 127.1, 126.6, 92.8, 73.8, 49.4, 29.4.

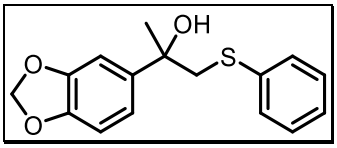
HRMS (ESI) m/z calcd. for $C_{15}H_{15}IOSNa$ $[M+Na]^+$: 392.9780, found: 392.9781.



c11

Purification by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v) afforded **c11** as a colorless oil (46.2 mg, 85% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 2H), 7.30 – 7.23 (m, 3H), 7.23 – 7.17 (m, 2H), 7.13 (d, *J* = 7.8 Hz, 1H), 3.58 (d, *J* = 13.2 Hz, 1H), 3.37 (d, *J* = 13.2 Hz, 1H), 2.89 (s, 1H), 2.28 (d, *J* = 4.8 Hz, 6H), 1.64 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.7, 136.7, 136.4, 135.4, 129.9, 129.6, 128.9, 126.3, 126.1, 122.2, 73.8, 49.6, 29.5, 20.0, 19.4.

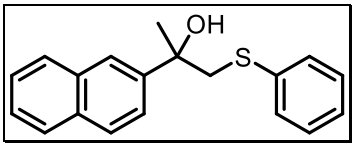
HRMS (ESI) m/z calcd. for $C_{17}H_{20}OSNa$ $[M+Na]^+$: 295.1127, found: 295.1122.



c12

Purification by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v) afforded **c12** as a brown oil (49.5 mg, 86% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 2H), 7.25 (ddd, *J* = 6.1, 5.5, 2.1 Hz, 2H), 7.22 – 7.16 (m, 1H), 6.96 (d, *J* = 1.8 Hz, 1H), 6.92 (dd, *J* = 8.1, 1.9 Hz, 1H), 6.77 (dd, *J* = 7.7, 4.0 Hz, 1H), 5.95 (dd, *J* = 3.1, 1.4 Hz, 2H), 3.52 (d, *J* = 13.3 Hz, 1H), 3.32 (d, *J* = 13.3 Hz, 1H), 2.94 (s, 1H), 1.60 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.6, 146.5, 140.4, 136.4, 130.0, 128.9, 126.4, 118.1, 107.9, 106.0, 101.0, 73.9, 49.7, 29.5.

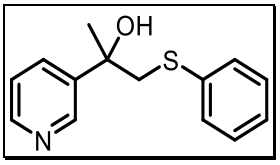
HRMS (ESI) m/z calcd. for $C_{16}H_{16}O_3SNa$ $[M+Na]^+$: 311.0812, found: 377.0709.



c13

Purification by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v) afforded **c13** as a colorless oil (38.8 mg, 66% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.85 – 7.73 (m, 3H), 7.52 – 7.41 (m, 3H), 7.34 – 7.28 (m, 2H), 7.20 – 7.07 (m, 3H), 3.63 (d, *J* = 13.3 Hz, 1H), 3.41 (d, *J* = 13.3 Hz, 1H), 3.05 (s, 1H), 1.68 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.6, 136.4, 133.2, 132.5, 130.1, 129.0, 128.3, 128.1, 127.5, 126.5, 126.2, 126.0, 123.6, 123.3, 74.2, 49.5, 29.4.

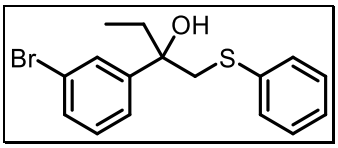
HRMS (ESI) m/z calcd. for $C_{19}H_{18}OSNa$ $[M+Na]^+$: 317.0971, found: 317.0963.



c14

Purification by column chromatography on silica gel (hexane/ethyl acetate = 5/1, v/v) afforded **c14** as a yellow oil (27.0 mg, 55% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 2.3 Hz, 1H), 8.44 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.84 – 7.72 (m, 1H), 7.37 – 7.27 (m, 2H), 7.25 – 7.13 (m, 4H), 3.71 (dt, *J* = 25.7, 12.9 Hz, 1H), 3.49 (d, *J* = 13.4 Hz, 1H), 3.37 (d, *J* = 13.4 Hz, 1H), 1.65 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.1, 146.8, 141.7, 135.9, 132.9, 130.2, 129.0, 126.7, 123.0, 72.9, 49.33, 29.2.

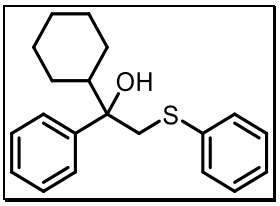
HRMS (ESI) m/z calcd. for $C_{14}H_{16}NOS$ $[M+H]^+$: 246.0947, found: 246.0947



c15

Purification by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v) afforded **c15** as a colorless oil (55.1 mg, 82% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.39 – 7.28 (m, 4H), 7.25 (dd, *J* = 13.1, 6.1 Hz, 2H), 7.21 – 7.14 (m, 2H), 3.55 (d, *J* = 13.4 Hz, 1H), 3.35 (d, *J* = 13.4 Hz, 1H), 2.96 (s, 1H), 1.89 (qq, *J* = 14.5, 7.4 Hz, 2H), 0.79 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.9, 136.0, 130.4, 130.0, 129.7, 129.0, 128.9, 126.7, 124.2, 122.6, 76.2, 48.7, 34.7, 8.0.

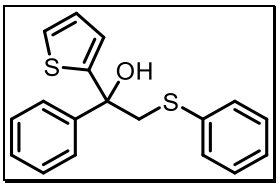
HRMS (ESI) m/z calcd. for $C_{16}H_{17}BrOSNa$ $[M+Na]^+$:359.0076, found: 359.0076.



c16

Purification by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v) afforded **c16** as a colorless oil (37.4 mg, 60% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 5.3, 3.4 Hz, 2H), 7.37 – 7.30 (m, 4H), 7.26 (ddd, *J* = 14.6, 5.2, 3.8 Hz, 3H), 7.18 (ddd, *J* = 7.4, 3.6, 1.2 Hz, 1H), 3.81 (d, *J* = 12.9 Hz, 1H), 3.46 (d, *J* = 12.9 Hz, 1H), 2.93 (s, 1H), 1.91 (d, *J* = 12.7 Hz, 1H), 1.80 – 1.66 (m, 3H), 1.57 (dd, *J* = 13.1, 10.6 Hz, 2H), 1.26 – 0.96 (m, 5H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.1, 136.8, 130.1, 128.9, 127.8, 126.9, 126.4, 126.2, 78.0, 48.2, 46.4, 27.6, 27.1, 26.6, 26.5, 26.3.

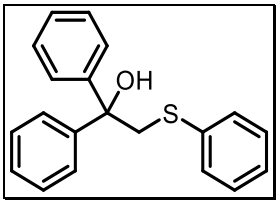
HRMS (ESI) m/z calcd. for $C_{20}H_{24}OSNa$ $[M+Na]^+$: 335.1440, found: 335.1437



c17

Purification by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v) afforded **c17** as a yellow oil (31.2 mg, 50% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 5.3, 3.5 Hz, 2H), 7.45 – 7.36 (m, 4H), 7.35 – 7.30 (m, 3H), 7.29 – 7.22 (m, 2H), 7.00 – 6.94 (m, 2H), 3.98 (d, *J* = 13.5 Hz, 1H), 3.91 – 3.84 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.5, 144.4, 136.2, 130.5, 129.1, 128.4, 127.8, 126.9, 126.7, 125.7, 125.5, 124.7, 76.6, 50.4.

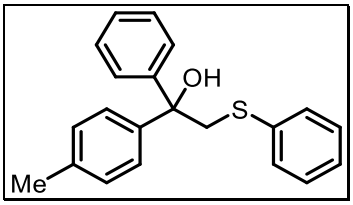
HRMS (ESI) m/z calcd. for $C_{18}H_{16}OS_2Na$ $[M+Na]^+$: 335.0535, found: 335.0534.



c18

Purification by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v) afforded **c18** as a white solid (53.2 mg, 87% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 – 7.49 (m, 4H), 7.48 – 7.42 (m, 2H), 7.42 – 7.35 (m, 4H), 7.32 (ddd, *J* = 8.7, 5.5, 1.4 Hz, 4H), 7.28 – 7.22 (m, 1H), 3.95 (s, 2H), 3.67 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.2, 136.6, 130.3, 129.1, 128.4, 127.4, 126.7, 126.2, 77.8, 49.1.

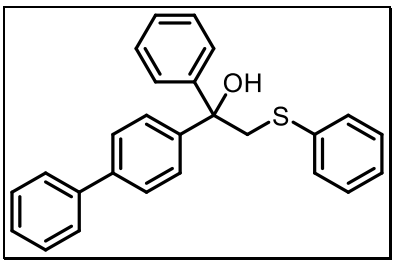
HRMS (ESI) m/z calcd. for $C_{20}H_{18}OSNa$ $[M+Na]^+$: 329.0971, found: 329.0967.



c19

Purification by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v) afforded **c19** as a colorless oil (59.5 mg, 93% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 (qd, *J* = 3.2, 1.9 Hz, 2H), 7.46 – 7.33 (m, 6H), 7.32 – 7.26 (m, 3H), 7.26 – 7.20 (m, 1H), 7.18 (d, *J* = 7.9 Hz, 2H), 3.94 (d, *J* = 13.3 Hz, 1H), 3.88 (d, *J* = 13.3 Hz, 1H), 3.58 (s, 1H), 2.37 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.4, 142.3, 137.1, 136.7, 130.2, 129.0, 129.0, 128.3, 127.3, 126.6, 126.2, 77.6, 49.1, 21.1.

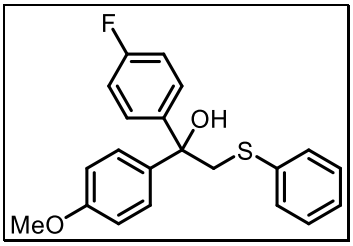
HRMS (ESI) m/z calcd. for $C_{21}H_{20}OSNa$ $[M+Na]^+$: 343.1127, found: 343.1128.



c20

Purification by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v) afforded **c20** as a white solid (68.8 mg, 90% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 – 7.58 (m, 8H), 7.55 – 7.46 (m, 4H), 7.46 – 7.39 (m, 3H), 7.39 – 7.30 (m, 3H), 7.27 (dd, *J* = 8.4, 6.1 Hz, 1H), 4.04 – 3.95 (m, 2H), 3.75 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.2, 144.3, 140.7, 140.2, 136.6, 130.4, 129.1, 128.9, 128.5, 127.5, 127.4, 127.2, 127.1, 126.8, 126.3, 77.7, 49.1.

HRMS (ESI) m/z calcd. for $C_{26}H_{22}OSNa$ $[M+Na]^+$: 405.1284, found: 405.1279

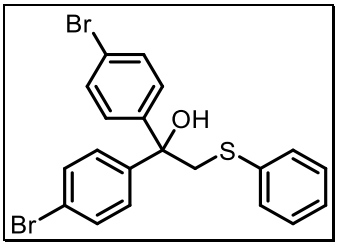


c21

Purification by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v) afforded **c21** as a colorless oil (60.9 mg, 86% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 – 7.35 (m, 6H), 7.32 – 7.26 (m, 2H), 7.26 – 7.20 (m, 1H), 7.05 – 6.98 (m, 2H),

6.91 – 6.85 (m, 2H), 3.92 – 3.86 (m, 1H), 3.84 – 3.78 (m, 4H), 3.63 (d, *J* = 4.3 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.9 (d, *J* = 247.0 Hz), 158.9, 141.3 (d, *J* = 3.2 Hz), 137.2, 136.4, 130.4, 129.1, 128.0 (d, *J* = 8.1 Hz), 127.5, 126.8, 115.0 (d, *J* = 21.4 Hz), 113.7, 77.2, 55.3, 49.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.40.

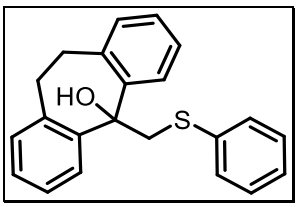
HRMS (ESI) m/z calcd. for $C_{21}H_{19}FO_2SNa$ $[M+Na]^+$: 377.0982, found: 377.0982.



c22

Purification by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v) afforded **c22** as a pale-yellow oil (61.2 mg, 66% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.42 (m, 4H), 7.38 – 7.34 (m, 2H), 7.32 – 7.23 (m, 7H), 3.80 (s, 2H), 3.66 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.7, 135.7, 131.5, 130.7, 129.2, 127.9, 127.1, 121.7, 77.2, 48.8.

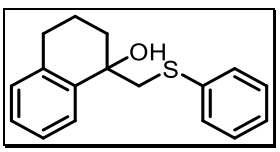
HRMS (ESI) m/z calcd. for $C_{20}H_{16}Br_2OSNa$ $[M+Na]^+$: 486.9160, found: 486.9166.



c23

Purification by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v) afforded **c23** as a pale-yellow oil (54.4 mg, 82% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 2.8 Hz, 2H), 7.26 – 7.12 (m, 7H), 7.08 (d, *J* = 7.4 Hz, 2H), 3.93 (s, 2H), 3.57 (s, 1H), 3.39 (ddd, *J* = 14.0, 8.7, 4.9 Hz, 2H), 3.04 – 2.92 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.3, 138.5, 135.7, 130.5, 130.5, 128.8, 127.9, 126.8, 126.5, 126.4, 77.2, 50.5, 34.3.

HRMS (ESI) m/z calcd. for $C_{22}H_{20}OSNa$ $[M+Na]^+$: 355.1127, found: 355.1124.

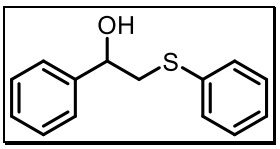


c24

Purification by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v) afforded **c24** as a colorless oil (43.2 mg, 80% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ

7.66 – 7.58 (m, 1H), 7.45 (dt, *J* = 8.5, 1.8 Hz, 2H), 7.38 – 7.28 (m, 2H), 7.27 – 7.19 (m, 3H), 7.15 – 7.08 (m, 1H), 3.51 (d, *J* = 13.4 Hz, 1H), 3.41 (dd, *J* = 13.4, 0.9 Hz, 1H), 2.89 – 2.74 (m, 2H), 2.70 (s, 1H), 2.29 (ddd, *J* = 10.5, 7.1, 2.9 Hz, 1H), 1.95 – 1.82 (m, 2H), 1.80 – 1.66 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.6, 137.0, 136.9, 129.8, 129.0, 128.9, 127.6, 126.4, 126.4, 126.3, 74.0, 53.0, 35.1, 29.2, 19.6.

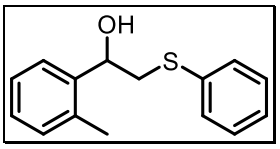
HRMS (ESI) m/z calcd. for $C_{17}H_{18}OSNa$ $[M+Na]^+$: 293.0971, found: 293.0967.



c25

Purification by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v) afforded **c25** as a colorless oil (36.8 mg, 80% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.42 (m, 2H), 7.42 – 7.31 (m, 7H), 7.30 – 7.24 (m, 1H), 4.75 (dd, *J* = 9.4, 1.3 Hz, 1H), 3.35 (dd, *J* = 13.8, 3.6 Hz, 1H), 3.13 (dd, *J* = 13.8, 9.4 Hz, 1H), 2.98 (d, *J* = 1.8 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.2, 135.0, 130.2, 129.2, 128.,6 128.0, 126.8, 125.9, 71.7, 44.0.

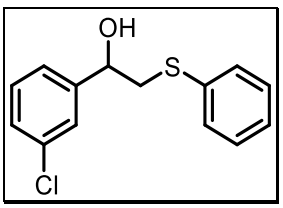
HRMS (ESI) m/z calcd. for $C_{14}H_{14}OSNa$ $[M+Na]^+$: 253.0658, found: 253.0657.



c26

Purification by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v) afforded **c26** as a colorless oil (42.9 mg, 88% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.53 – 7.48 (m, 2H), 7.40 – 7.33 (m, 2H), 7.29 (tdd, *J* = 9.8, 5.2, 4.2 Hz, 2H), 7.23 (td, *J* = 7.4, 1.4 Hz, 1H), 7.15 (d, *J* = 7.4 Hz, 1H), 4.96 (dd, *J* = 9.7, 2.5 Hz, 1H), 3.31 (dd, *J* = 13.9, 3.1 Hz, 1H), 3.06 (dd, *J* = 13.9, 9.7 Hz, 1H), 2.98 (s, 1H), 2.21 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.2, 134.9, 134.5, 130.7, 130.5, 129.2, 127.7, 127.0, 126.5, 125.4, 68.2, 43.2, 18.9.

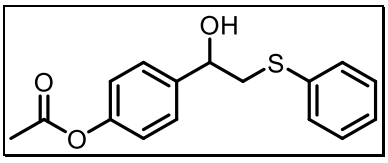
HRMS (ESI) m/z calcd. for $C_{15}H_{16}OS$ $[M]^+$: 244.0922, found: 244.0914.



c27

Purification by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v) afforded **c27** as a colorless oil (26.9 mg, 51% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.39 – 7.31 (m, 3H), 7.31 – 7.25 (m, 3H), 7.24 (dd, *J* = 2.6, 1.2 Hz, 1H), 4.69 (dt, *J* = 9.5, 2.8 Hz, 1H), 3.32 (dd, *J* = 13.9, 3.4 Hz, 1H), 3.05 (dd, *J* = 13.9, 9.5 Hz, 1H), 2.99 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.1, 136.9, 134.5, 130.5, 129.8, 129.2, 128.1, 127.1, 126.1, 124.0, 71.0, 44.2.

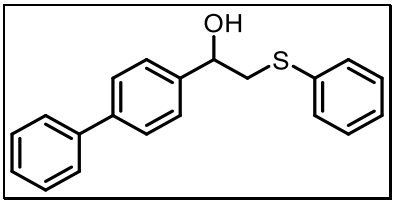
HRMS (ESI) m/z calcd. for $C_{14}H_{13}ClOSNa$ $[M+Na]^+$: 287.0268, found: 287.0266.



c28

Purification by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v) afforded **c28** as a colorless oil (50.0 mg, 85% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.40 (m, 2H), 7.40 – 7.29 (m, 4H), 7.26 (dt, *J* = 9.4, 4.4 Hz, 1H), 7.06 (t, *J* = 9.2 Hz, 2H), 4.72 (dd, *J* = 9.3, 3.2 Hz, 1H), 3.36 – 3.25 (m, 1H), 3.07 (dt, *J* = 16.2, 10.6 Hz, 2H), 2.31 (s, 3H); **^{13}C NMR** (101 MHz, DMSO) δ 169.7, 150.0, 142.2, 134.8, 129.4, 128.4, 127.7, 125.9, 121.9, 71.2, 41.9, 21.3.

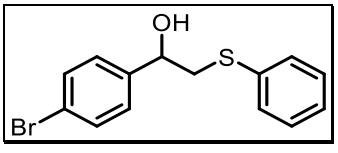
HRMS (ESI) m/z calcd. for $C_{16}H_{16}O_3SNa$ $[M+Na]^+$: 311.0712, found: 311.0713.



c29

Purification by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v) afforded **c29** as a white solid (55.1 mg, 90% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 – 7.58 (m, 4H), 7.51 – 7.43 (m, 6H), 7.42 – 7.32 (m, 3H), 7.31 – 7.25 (m, 1H), 4.80 (d, *J* = 9.2 Hz, 1H), 3.39 (dd, *J* = 13.8, 3.6 Hz, 1H), 3.17 (dd, *J* = 13.8, 9.4 Hz, 1H), 3.03 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.2, 140.9, 140.8, 134.9, 130.3, 129.2, 128.8, 127.4, 127.3, 127.1, 126.8, 126.4, 71.5, 44.0.

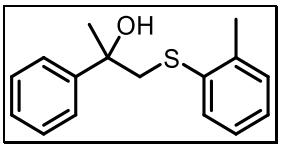
HRMS (ESI) m/z calcd. for $C_{20}H_{18}OSNa$ $[M+Na]^+$: 329.0971, found: 329.0966.



c30

Purification by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v) afforded **c30** as a colorless oil (38.7 mg, 63% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 – 7.42 (m, 2H), 7.40 (dt, *J* = 3.4, 2.0 Hz, 2H), 7.34 – 7.27 (m, 2H), 7.25 (dt, *J* = 4.8, 1.9 Hz, 1H), 7.23 – 7.17 (m, 2H), 4.65 (dd, *J* = 9.3, 3.6 Hz, 1H), 3.26 (dd, *J* = 13.9, 3.6 Hz, 1H), 3.07 – 3.01 (m, 1H), 2.99 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.1, 134.5, 131.6, 130.4, 129.2, 127.6, 127.0, 121.8, 71.0, 44.0.

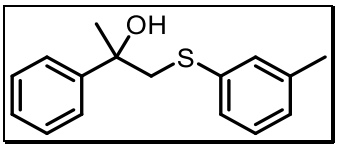
HRMS (ESI) m/z calcd. for $C_{14}H_{13}BrOSNa$ $[M+Na]^+$: 330.9763, found: 330.9753.



c34

Purification by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v) afforded **c34** as a colorless oil (37.7 mg, 73% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 2H), 7.40 – 7.31 (m, 3H), 7.28 (d, *J* = 7.9 Hz, 1H), 7.18 – 7.09 (m, 3H), 3.52 (d, *J* = 13.0 Hz, 1H), 3.33 (d, *J* = 13.0 Hz, 1H), 2.90 (s, 1H), 2.39 (s, 3H), 1.66 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.3, 138.3, 135.6, 130.2, 129.8, 128.3, 127.1, 126.6, 126.4, 124.8, 74.0, 48.9, 29.5, 20.7.

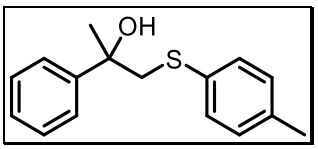
HRMS (ESI) m/z calcd. for $C_{16}H_{18}OSNa$ $[M+Na]^+$: 281.0971, found: 281.0971.



c35

Purification by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v) afforded **c35** as a colorless oil (38.7 mg, 75% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.45 (m, 2H), 7.37 (t, *J* = 4.3 Hz, 2H), 7.31 – 7.24 (m, 1H), 7.21 – 7.12 (m, 3H), 7.02 (d, *J* = 1.0 Hz, 1H), 3.56 (d, *J* = 13.3 Hz, 1H), 3.38 (d, *J* = 13.3 Hz, 1H), 2.99 (s, 1H), 2.32 (s, 3H), 1.66 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.3, 138.7, 136.2, 130.7, 128.8, 128.3, 127.4, 127.1, 124.9, 74.0, 49.6, 29.4, 21.3.

HRMS (ESI) m/z calcd. for $C_{16}H_{18}OSNa$ $[M+Na]^+$: 281.0971, found: 281.0971

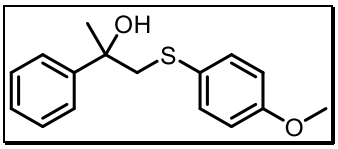


c36

Purification by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v)

afforded **c36** as a brown oil (36.6 mg, 71% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.8 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 3H), 7.09 (d, *J* = 7.9 Hz, 2H), 3.55 (d, *J* = 13.3 Hz, 1H), 3.35 (d, *J* = 13.3 Hz, 1H), 2.86 (s, 1H), 2.34 (s, 3H), 1.64 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.3, 136.6, 132.9, 130.6, 129.8, 128.3, 127.1, 124.9, 74.0, 50.3, 29.4, 21.0.

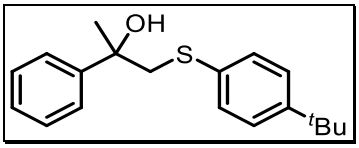
HRMS (ESI) m/z calcd. for $C_{16}H_{18}OSNa$ $[M+Na]^+$: 281.0971, found: 281.0969.



c37

Purification by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v) afforded **c37** as a yellow oil (36.2 mg, 66% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 – 7.38 (m, 2H), 7.38 – 7.21 (m, 5H), 6.79 (d, *J* = 8.8 Hz, 2H), 3.79 (s, 3H), 3.49 (d, *J* = 13.3 Hz, 1H), 3.27 (d, *J* = 13.3 Hz, 1H), 3.01 (s, 1H), 1.60 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.0, 146.3, 133.4, 128.2, 127.0, 126.8, 124.8, 114.6, 74.0, 55.4, 51.5, 29.4.

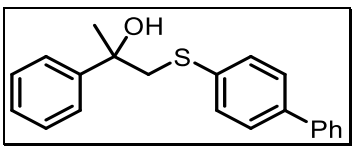
HRMS (ESI) m/z calcd. for $C_{16}H_{18}O_2SNa$ $[M+Na]^+$: 297.0920, found: 297.0918.



c38

Purification by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v) afforded **c38** as a colorless oil (39.0 mg, 65% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 2H), 7.38 – 7.33 (m, 2H), 7.32 – 7.29 (m, 4H), 7.27 (dd, *J* = 5.7, 3.5 Hz, 1H), 3.59 (d, *J* = 13.3 Hz, 1H), 3.37 (d, *J* = 13.3 Hz, 1H), 3.02 (s, 1H), 1.66 (s, 3H), 1.34 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.8, 146.3, 132.8, 130.3, 128.3, 127.1, 126.1, 124.9, 74.0, 50.1, 34.5, 31.3, 29.5.

HRMS (ESI) m/z calcd. for $C_{19}H_{24}OSNa$ $[M+Na]^+$: 323.1440, found: 323.1136.

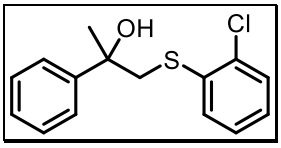


c39

Purification by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v) afforded **c39** as a yellow oil (35.2 mg, 55% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 – 7.55 (m, 2H), 7.52 – 7.46 (m, 5H), 7.43 (ddd, *J* = 8.6, 3.8, 2.1 Hz, 3H), 7.40 – 7.33

(m, 3H), 7.29 (tt, *J* = 5.3, 1.2 Hz, 1H), 3.61 (d, *J* = 13.3 Hz, 1H), 3.42 (d, *J* = 13.3 Hz, 1H), 2.95 (s, 1H), 1.68 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.2, 140.3, 139.4, 135.6, 130.4, 128.8, 128.3, 127.6, 127.4, 127.1, 126.9, 124.9, 74.0, 49.6, 29.5.

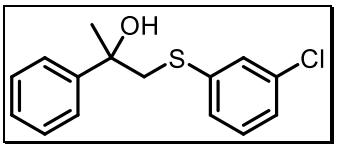
HRMS (ESI) m/z calcd. for $C_{21}H_{20}OSNa$ $[M+Na]^+$: 343.1127, found: 343.1122.



c40

Purification by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v) afforded **c40** as a colorless oil (45.0 mg, 81% yield). **^{1}H NMR** (400 MHz, CD_3CN) δ 7.40 (d, *J* = 7.7 Hz, 2H), 7.34 – 7.20 (m, 4H), 7.21 – 7.14 (m, 1H), 7.05 (pd, *J* = 7.3, 1.6 Hz, 2H), 3.49 (d, *J* = 13.1 Hz, 1H), 3.26 (d, *J* = 13.1 Hz, 1H), 2.85 (s, 1H), 1.59 (s, 3H); **^{13}C NMR** (101 MHz, CD_3CN) δ 140.7, 130.1, 129.5, 125.6, 124.5, 123.0, 122.2, 121.9, 121.9, 119.5, 68.7, 43.1, 24.2.

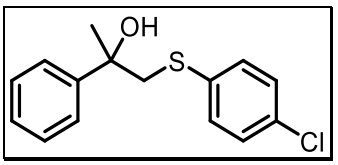
HRMS (ESI) m/z calcd. for $C_{15}H_{15}ClOSNa$ $[M+Na]^+$: 301.0424, found: 301.0419.



c41

Purification by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v) afforded **c41** as a colorless oil (50.0 mg, 90% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 8.1, 1.0 Hz, 2H), 7.34 – 7.27 (m, 2H), 7.27 – 7.20 (m, 2H), 7.18 – 7.12 (m, 1H), 7.12 – 7.07 (m, 2H), 3.50 (d, *J* = 13.3 Hz, 1H), 3.31 (d, *J* = 13.3 Hz, 1H), 2.82 (s, 1H), 1.62 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.9, 138.7, 134.6, 129.7, 129.3, 128.3, 127.7, 127.3, 126.4, 124.8, 74.0, 49.1, 29.4.

HRMS (ESI) m/z calcd. for $C_{15}H_{15}ClOSNa$ $[M+Na]^+$: 301.0424, found: 301.0422.

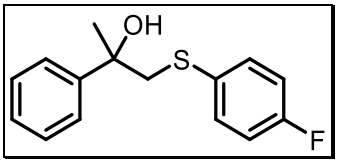


c42

Purification by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v) afforded **c42** as a yellow oil (45.6 mg, 82% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.38 (m, 2H), 7.34 – 7.27 (m, 2H), 7.27 – 7.18 (m, 3H), 7.18 – 7.13 (m, 2H), 3.48 (d, *J* = 13.3 Hz, 1H), 3.29 (d, *J* = 13.3 Hz, 1H), 2.85 (s, 1H), 1.60 (s, 3H); **^{13}C NMR** (101

MHz, $CDCl_3$) δ 146.0, 135.1, 132.4, 131.3, 129.0, 128.3, 127.2, 124.8, 74.0, 49.8, 29.4.

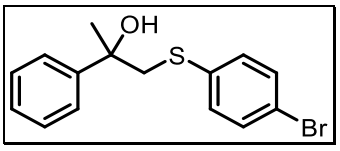
HRMS (ESI) m/z calcd. for $C_{15}H_{15}ClOSNa$ $[M+Na]^+$: 301.0424, found: 301.0420.



c43

Purification by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v) afforded **c43** as a yellow oil (45.6 mg, 87% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 8.1, 1.0 Hz, 2H), 7.37 – 7.23 (m, 5H), 6.98 – 6.88 (m, 2H), 3.52 (d, *J* = 13.3 Hz, 1H), 3.34 – 3.26 (m, 1H), 2.98 (s, 1H), 1.63 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.8 (d, *J* = 247.7 Hz), 146.06, 132.8 (d, *J* = 8.1 Hz), 131.4(d, *J* = 3.4 Hz), 128.29, 127.14, 124.86, 116.0 (d, *J* = 22.0 Hz), 74.04, 50.78, 29.41; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.05.

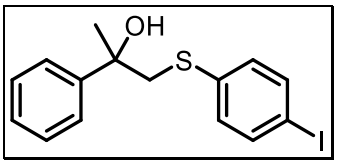
HRMS (ESI) m/z calcd. for $C_{15}H_{15}FOSNa$ $[M+Na]^+$: 285.0720, found: 285.0721.



c44

Purification by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v) afforded **c44** as a yellow oil (60.0 mg, 93% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 – 7.43 (m, 2H), 7.41 – 7.32 (m, 4H), 7.31 – 7.24 (m, 1H), 7.23 – 7.15 (m, 2H), 3.52 (d, *J* = 13.3 Hz, 1H), 3.33 (d, *J* = 13.3 Hz, 1H), 2.87 (s, 1H), 1.65 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.0, 135.8, 131.9, 131.5, 128.3, 127.2, 124.8, 120.3, 74.0, 49.6, 29.4.

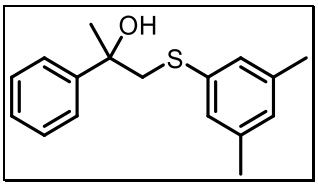
HRMS (ESI) m/z calcd. for $C_{15}H_{15}BrOSNa$ $[M+Na]^+$: 344.9919, found: 344.9918.



c45

Purification by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v) afforded **c45** as a colorless oil (37.0 mg, 50% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 – 7.51 (m, 2H), 7.45 (dt, *J* = 3.4, 2.2 Hz, 2H), 7.38 – 7.31 (m, 2H), 7.30 – 7.25 (m, 1H), 7.08 – 7.02 (m, 2H), 3.52 (d, *J* = 13.3 Hz, 1H), 3.33 (d, *J* = 13.3 Hz, 1H), 2.80 (s, 1H), 1.64 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.0, 137.8, 136.7, 131.5, 128.4, 127.2, 124.8, 91.2, 74.0, 49.3, 29.4.

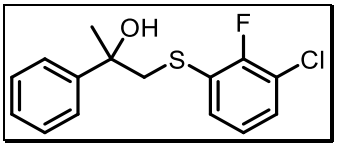
HRMS (ESI) m/z calcd. for $C_{15}H_{15}IOSNa$ $[M+Na]^+$: 392.9780, found: 392.9779.



c46

Purification by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v) afforded **c46** as a colorless oil (33.2 mg, 61% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 8.2, 1.0 Hz, 2H), 7.37 (dd, *J* = 10.3, 4.8 Hz, 2H), 7.28 (ddd, *J* = 7.2, 5.7, 1.2 Hz, 1H), 6.98 (s, 2H), 6.83 (s, 1H), 3.56 (d, *J* = 13.2 Hz, 1H), 3.37 (d, *J* = 13.2 Hz, 1H), 3.01 (s, 1H), 2.28 (s, 6H), 1.65 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.3, 138.58, 135.85, 128.42, 128.23, 127.83, 127.07, 124.88, 73.97, 49.63, 29.45, 21.20.

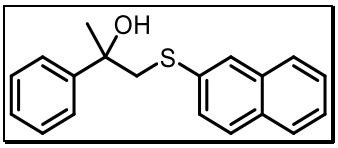
HRMS (ESI) m/z calcd. for $C_{17}H_{20}OSNa$ $[M+Na]^+$: 295.1127, found: 295.1126.



c47

Purification by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v) afforded **c47** as a pale-yellow oil (43.8 mg, 74% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (dt, *J* = 3.2, 2.0 Hz, 2H), 7.33 – 7.27 (m, 2H), 7.25 – 7.18 (m, 3H), 6.92 (td, *J* = 8.0, 1.2 Hz, 1H), 3.59 (d, *J* = 13.4 Hz, 1H), 3.29 (d, *J* = 13.4 Hz, 1H), 2.94 (s, 1H), 1.65 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.0 (d, *J* = 247.7 Hz), 145.6, 131.2, 129.5, 128.2, 127.2, 125.0 (d, *J* = 17.4 Hz), 124.8, 124.5 (d, *J* = 5.0 Hz), 121.5 (d, *J* = 19.1 Hz), 74.0, 48.7, 29.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -109.47.

HRMS (ESI) m/z calcd. for $C_{15}H_{14}ClFOSNa$ $[M+Na]^+$: 319.0330, found: 319.0329.

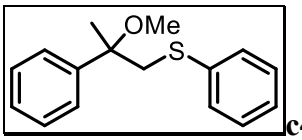


c48

Purification by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v) afforded **c48** as a yellow oil (41.2 mg, 70% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 – 7.76 (m, 2H), 7.76 – 7.68 (m, 2H), 7.54 – 7.41 (m, 5H), 7.38 – 7.31 (m, 2H), 7.26 (ddt, *J* = 6.5, 5.2, 1.3 Hz, 1H), 3.65 (d, *J* = 13.3 Hz, 1H), 3.48 (d, *J* = 13.3 Hz, 1H), 2.94 (s, 1H), 1.68 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.2, 133.9, 133.7, 131.9, 128.5,

128.3, 128.1, 127.8, 127.7, 127.2, 126.6, 125.9, 124.9, 74.1, 49.4, 29.4.

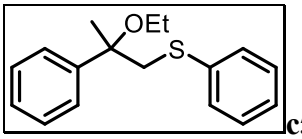
HRMS (ESI) m/z calcd. for $C_{19}H_{18}OSNa$ $[M+Na]^+$: 317.0971, found: 317.0968.



c49

Purification by column chromatography on silica gel (hexane/ethyl acetate = 20/1, v/v) afforded **c49** as a colorless oil (48.0 mg, 93% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 8.2, 1.0 Hz, 2H), 7.42 (dd, *J* = 10.4, 4.9 Hz, 2H), 7.33 (dd, *J* = 10.1, 4.2 Hz, 3H), 7.27 (dd, *J* = 10.7, 5.1 Hz, 2H), 7.18 (dd, *J* = 10.5, 4.2 Hz, 1H), 3.47 (d, *J* = 12.5 Hz, 1H), 3.35 (d, *J* = 12.5 Hz, 1H), 3.20 (s, 3H), 1.78 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.5, 137.6, 129.3, 128.8, 128.4, 127.6, 126.4, 125.8, 79.1, 50.9, 47.6, 22.5.

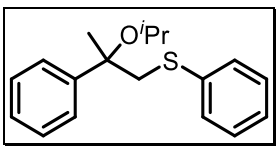
HRMS (ESI) m/z calcd. for $C_{16}H_{18}OSNa$ $[M+Na]^+$: 281.0971, found: 281.0973.



c50

Purification by column chromatography on silica gel (hexane/ethyl acetate = 20/1, v/v) afforded **c50** as a colorless oil (49.0 mg, 90% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 2H), 7.24 (dd, *J* = 10.3, 4.9 Hz, 2H), 7.20 – 7.13 (m, 3H), 7.12 – 7.06 (m, 2H), 7.03 – 6.97 (m, 1H), 3.31 (d, *J* = 12.5 Hz, 1H), 3.25 (dq, *J* = 8.6, 6.9 Hz, 1H), 3.18 (d, *J* = 12.5 Hz, 1H), 3.09 (dq, *J* = 8.6, 7.0 Hz, 1H), 1.62 (d, *J* = 6.8 Hz, 3H), 1.07 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.3, 137.8, 129.2, 128.8, 128.3, 127.4, 126.2, 125.7, 78.8, 58.4, 47.6, 23.3, 15.7.

HRMS (ESI) m/z calcd. for $C_{17}H_{20}OSNa$ $[M+Na]^+$: 295.1127, found: 295.1127.

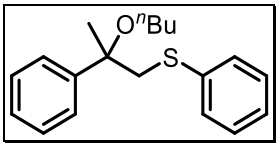


c51

Purification by column chromatography on silica gel (hexane/ethyl acetate = 30/1, v/v) afforded **c51** as a colorless oil (42.9 mg, 75% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.57 – 7.51 (m, 2H), 7.38 (td, *J* = 8.2, 6.7 Hz, 2H), 7.31 (ddd, *J* = 9.8, 7.5, 3.3 Hz, 3H), 7.27 – 7.20 (m, 2H), 7.15 (ddt, *J* = 7.7, 6.5, 3.3 Hz, 1H), 3.61 (hept, *J* = 6.1 Hz, 1H), 3.44 (d, *J* = 12.4 Hz, 1H), 3.32 (d, *J* = 12.4 Hz, 1H), 1.82 (d, *J* = 6.9 Hz, 3H), 1.19 (t, *J*

= 6.4 Hz, 3H), 1.06 (d, *J* = 6.1 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.4, 137.8, 136.5, 129.2, 128.7, 128.0, 126.9, 125.6, 79.2, 66.0, 48.2, 25.0, 24.5, 23.2.

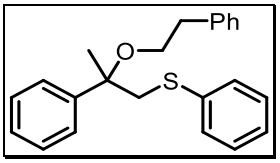
HRMS (ESI) m/z calcd. for $C_{18}H_{22}OSNa$ $[M+Na]^+$: 309.1284, found: 309.1284.



c52

Purification by column chromatography on silica gel (hexane/ethyl acetate = 40/1, v/v) afforded **c52** as a colorless oil (51.6 mg, 86% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.44 (m, 2H), 7.38 (dd, *J* = 10.2, 4.8 Hz, 2H), 7.35 – 7.28 (m, 3H), 7.25 (dd, *J* = 10.3, 4.9 Hz, 2H), 7.15 (dd, *J* = 8.3, 6.3 Hz, 1H), 3.46 (d, *J* = 12.5 Hz, 1H), 3.36 – 3.28 (m, 2H), 3.17 (dt, *J* = 8.6, 6.7 Hz, 1H), 1.76 (s, 3H), 1.58 (dt, *J* = 14.7, 6.7 Hz, 2H), 1.44 – 1.34 (m, 2H), 0.93 (dd, *J* = 9.3, 5.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.2, 137.8, 129.2, 128.7, 128.2, 127.3, 126.3, 125.6, 78.5, 62.6, 47.6, 32.4, 23.1, 19.4, 14.0.

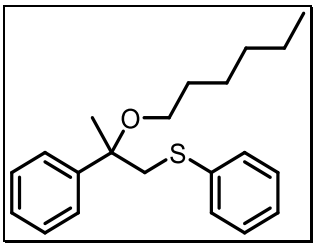
HRMS (ESI) m/z calcd. for $C_{19}H_{24}OSNa$ $[M+Na]^+$: 323.1440, found: 323.1440.



c53

Purification by column chromatography on silica gel (hexane/ethyl acetate = 30/1, v/v) afforded **c53** as a colorless oil (57.1 mg, 82% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.28 (m, 12H), 7.27 – 7.19 (m, 3H), 3.65 – 3.56 (m, 1H), 3.53 – 3.47 (m, 1H), 3.48 – 3.40 (m, 1H), 3.35 (d, *J* = 12.6 Hz, 1H), 2.96 (dd, *J* = 14.0, 6.9 Hz, 2H), 1.80 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.0, 139.2, 137.8, 129.4, 129.2, 128.8, 128.3, 127.4, 126.4, 126.3, 126.2, 125.8, 79.0, 64.2, 47.8, 36.9, 23.0.

HRMS (ESI) m/z calcd. for $C_{23}H_{24}OSNa$ $[M+Na]^+$: 371.1440, found: 371.1440.

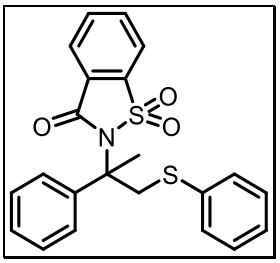


c54

Purification by column chromatography on silica gel (hexane/ethyl acetate = 40/1, v/v)

afforded **c54** as a colorless oil (54.4 mg, 83% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (dt, *J* = 3.2, 2.1 Hz, 2H), 7.43 – 7.36 (m, 2H), 7.35 – 7.28 (m, 3H), 7.28 – 7.22 (m, 2H), 7.18 – 7.13 (m, 1H), 3.47 (d, *J* = 12.5 Hz, 1H), 3.37 – 3.28 (m, 2H), 3.17 (dt, *J* = 8.5, 6.8 Hz, 1H), 1.77 (d, *J* = 4.5 Hz, 3H), 1.65 – 1.51 (m, 2H), 1.41 – 1.28 (m, 6H), 0.93 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.3, 137.9, 129.2, 128.7, 128.2, 127.3, 126.3, 125.6, 78.6, 62.9, 47.6, 31.8, 30.2, 25.9, 23.1, 22.7, 14.1.

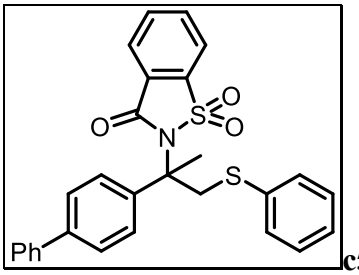
HRMS (ESI) m/z calcd. for $C_{21}H_{28}OSNa$ $[M+Na]^+$: 351.1753, found: 351.1754.



c55

Purification by column chromatography on silica gel (hexane/ethyl acetate = 5/1, v/v) afforded **c55** as a white solid (65.4 mg, 80% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 8.1, 4.3 Hz, 1H), 7.86 – 7.79 (m, 1H), 7.73 – 7.67 (m, 2H), 7.57 – 7.51 (m, 2H), 7.44 – 7.33 (m, 4H), 7.33 – 7.25 (m, 1H), 7.15 – 7.03 (m, 3H), 4.65 (d, *J* = 13.0 Hz, 1H), 3.85 (d, *J* = 13.0 Hz, 1H), 2.25 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.8, 143.8, 137.9, 135.5, 135.4, 134.7, 133.9, 131.3, 128.6, 127.6, 126.6, 126.3, 125.3, 124.9, 120.2, 67.8, 42.9, 25.1.

HRMS (ESI) m/z calcd. for $C_{22}H_{19}NO_3S_2Na$ $[M+Na]^+$: 432.0699, found: 432.0699.

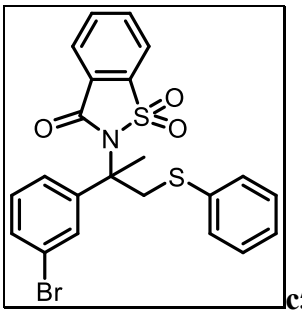


c56

Purification by column chromatography on silica gel (hexane/ethyl acetate = 5/1, v/v) afforded **c56** as a white solid (75.7 mg, 78% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 – 7.84 (m, 2H), 7.74 – 7.68 (m, 2H), 7.62 – 7.54 (m, 6H), 7.47 – 7.39 (m, 4H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.14 – 7.00 (m, 3H), 4.67 (d, *J* = 13.0 Hz, 1H), 3.89 (d, *J* = 13.0 Hz, 1H), 2.28 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.9, 142.7, 140.5, 140.3, 135.5,

134.7, 134.3, 133.9, 131.4, 128.7, 128.6, 127.4, 127.2, 127.1, 126.6, 125.8, 124.9, 123.6, 120.3, 67.8, 43.1, 25.0.

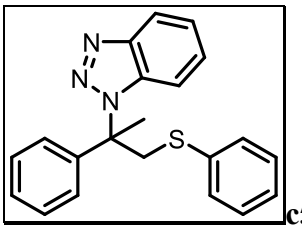
HRMS (ESI) m/z calcd. for $C_{28}H_{23}NO_3S_2Na$ $[M+Na]^+$: 508.1012, found: 508.1014.



c57

Purification by column chromatography on silica gel (hexane/ethyl acetate = 5/1, v/v) afforded **c57** as a white solid (53.6 mg, 55% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.7 Hz, 1H), 7.86 – 7.80 (m, 1H), 7.69 (ddt, *J* = 10.2, 3.6, 1.4 Hz, 3H), 7.50 – 7.44 (m, 1H), 7.42 – 7.34 (m, 3H), 7.19 (t, *J* = 8.0 Hz, 1H), 7.14 – 7.01 (m, 3H), 4.57 (d, *J* = 13.1 Hz, 1H), 3.80 (d, *J* = 13.1 Hz, 1H), 2.21 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.8, 146.1, 137.8, 135.2, 134.8, 134.0, 131.4, 130.7, 130.1, 128.6, 128.6, 126.8, 126.2, 124.9, 124.2, 122.7, 120.3, 67.3, 42.8, 24.8.

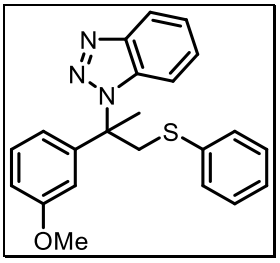
HRMS (ESI) m/z calcd. for $C_{22}H_{18}BrNO_3S_2Na$ $[M+Na]^+$: 509.9804, found: 509.9806.



c58

Purification by column chromatography on silica gel (hexane/ethyl acetate = 5/1, v/v) afforded **c58** as a white solid (42.1 mg, 61% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (dt, *J* = 8.4, 0.8 Hz, 1H), 7.36 – 7.29 (m, 3H), 7.27 – 7.03 (m, 9H), 6.64 (dd, *J* = 7.6, 0.8 Hz, 1H), 4.37 (d, *J* = 13.5 Hz, 1H), 4.15 – 4.09 (m, 1H), 2.27 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.8, 141.6, 135.9, 132.2, 130.5, 128.8, 128.7, 128.4, 126.6, 126.6, 126.1, 123.6, 120.0, 112.0, 67.8, 47.0, 26.5.

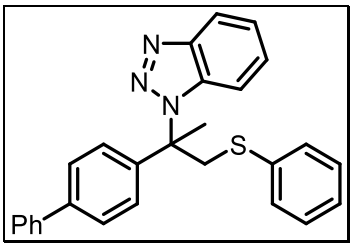
HRMS (ESI) m/z calcd. for $C_{21}H_{19}N_3SNa$ $[M+Na]^+$: 368.1192, found: 368.1192.



c59

Purification by column chromatography on silica gel (hexane/ethyl acetate = 5/1, v/v) afforded **c59** as a white solid (40.5 mg, 54% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.3 Hz, 1H), 7.26 – 7.20 (m, 2H), 7.19 – 7.03 (m, 6H), 6.84 (dd, *J* = 8.0, 2.2 Hz, 1H), 6.80 – 6.74 (m, 1H), 6.74 – 6.68 (m, 2H), 4.36 (d, *J* = 13.5 Hz, 1H), 4.10 (d, *J* = 13.5 Hz, 1H), 3.69 (s, 3H), 2.24 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.8, 146.8, 143.2, 135.9, 132.2, 130.6, 129.9, 128.7, 126.7, 126.6, 123.6, 120.0, 118.4, 113.1, 112.7, 112.0, 67.7, 55.3, 46.9, 26.4.

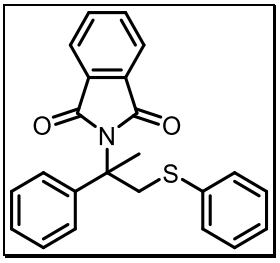
HRMS (ESI) m/z calcd. for $C_{22}H_{21}N_3OSNa$ $[M+Na]^+$: 398.1298, found: 398.1298.



c60

Purification by column chromatography on silica gel (hexane/ethyl acetate = 5/1, v/v) afforded **c60** as a white solid (43.8 mg, 52% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.3 Hz, 1H), 7.61 – 7.56 (m, 2H), 7.55 – 7.50 (m, 2H), 7.46 (dd, *J* = 8.1, 6.9 Hz, 2H), 7.38 (d, *J* = 7.3 Hz, 1H), 7.28 – 7.21 (m, 3H), 7.17 (ddd, *J* = 4.9, 3.9, 2.3 Hz, 3H), 7.14 – 7.07 (m, 3H), 6.75 (d, *J* = 8.4 Hz, 1H), 4.41 (d, *J* = 13.5 Hz, 1H), 4.19 (d, *J* = 13.5 Hz, 1H), 2.31 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.9, 141.1, 140.4, 140.0, 135.9, 132.3, 130.7, 128.9, 128.7, 127.7, 127.4, 127.0, 126.7, 126.7, 126.6, 123.6, 120.1, 112.1, 67.8, 47.2, 26.4.

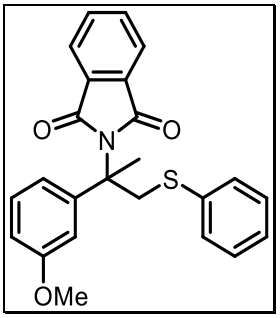
HRMS (ESI) m/z calcd. for $C_{27}H_{23}N_3SNa$ $[M+Na]^+$: 444.1505, found: 444.1505.



c61

Purification by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v) afforded **c61** as a white solid (39.5 mg, 53% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 – 7.62 (m, 4H), 7.39 – 7.30 (m, 6H), 7.30 – 7.24 (m, 1H), 7.10 – 7.04 (m, 2H), 7.03 – 6.96 (m, 1H), 4.61 (d, *J* = 13.4 Hz, 1H), 3.65 (d, *J* = 13.4 Hz, 1H), 2.19 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.2, 145.5, 135.9, 133.8, 131.7, 130.9, 128.7, 128.6, 127.2, 126.4, 124.6, 123.0, 64.9, 44.7, 27.6.

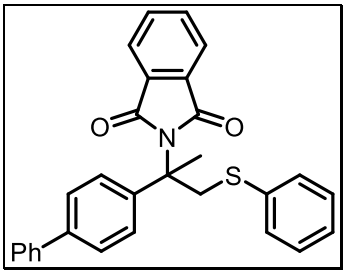
HRMS (ESI) m/z calcd. for $C_{23}H_{19}NO_2SNa$ $[M+Na]^+$: 396.1029, found: 396.1028.



c62

Purification by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v) afforded **c62** as a colorless oil (58.8 mg, 73% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 – 7.61 (m, 4H), 7.35 – 7.29 (m, 2H), 7.26 (td, *J* = 7.9, 3.4 Hz, 1H), 7.07 (dd, *J* = 10.3, 4.7 Hz, 2H), 7.01 – 6.92 (m, 2H), 6.90 (t, *J* = 2.1 Hz, 1H), 6.79 (dd, *J* = 8.2, 2.2 Hz, 1H), 4.60 (d, *J* = 13.4 Hz, 1H), 3.77 (s, 3H), 3.66 – 3.59 (m, 1H), 2.18 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.1, 159.7, 147.2, 135.9, 133.8, 131.7, 130.8, 129.6, 128.7, 126.4, 123.0, 117.0, 111.6, 111.4, 64.8, 55.2, 44.6, 27.5.

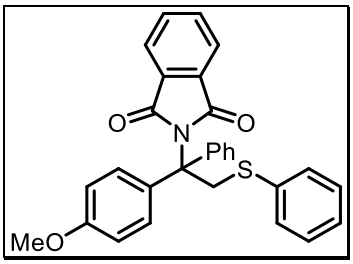
HRMS (ESI) m/z calcd. for $C_{24}H_{21}NO_3SNa$ $[M+Na]^+$: 426.1134, found: 426.1134.



c63

Purification by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v) afforded **c64** as a white solid (50.3 mg, 56% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 – 7.64 (m, 4H), 7.60 – 7.55 (m, 4H), 7.44 (ddd, *J* = 8.6, 6.9, 2.1 Hz, 4H), 7.38 – 7.32 (m, 3H), 7.12 – 7.05 (m, 2H), 7.04 – 6.97 (m, 1H), 4.64 (d, *J* = 13.4 Hz, 1H), 3.71 (d, *J* = 13.4 Hz, 1H), 2.24 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.2, 144.4, 140.5, 140.0, 135.9, 133.8, 131.7, 130.9, 128.8, 128.7, 127.3, 127.3, 127.1, 126.4, 125.1, 123.0, 64.8, 44.8, 27.5.

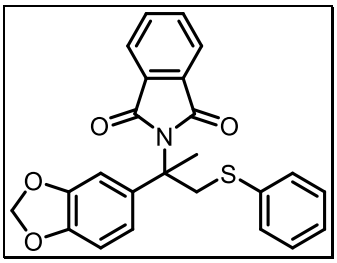
HRMS (ESI) m/z calcd. for $C_{29}H_{23}NO_2SNa$ $[M+Na]^+$: 472.1342, found: 472.1344.



c64

Purification by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v) afforded **c63** as a yellow oil (39.1 mg, 42% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 – 7.74 (m, 2H), 7.73 – 7.67 (m, 2H), 7.48 – 7.39 (m, 4H), 7.34 – 7.28 (m, 3H), 7.17 – 7.06 (m, 5H), 6.86 – 6.78 (m, 2H), 4.63 (q, *J* = 12.9 Hz, 2H), 3.80 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.8, 158.8, 141.2, 136.8, 134.1, 133.0, 131.8, 130.1, 129.4, 128.6, 127.9, 127.8, 127.5, 126.1, 123.2, 113.1, 69.4, 55.2, 46.4.

HRMS (ESI) m/z calcd. for $C_{29}H_{23}NO_3SNa$ $[M+Na]^+$: 488.1291, found: 488.1291.

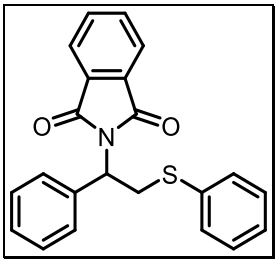


c65

Purification by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v) afforded **c65** as a white solid (37.5 mg, 45% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 – 7.62 (m, 4H), 7.31 (dt, *J* = 3.3, 1.9 Hz, 2H), 7.12 – 7.05 (m, 2H), 7.03 – 6.97 (m, 1H), 6.86 – 6.79 (m, 2H), 6.77 – 6.72 (m, 1H), 5.93 (ddd, *J* = 5.3, 3.6, 1.6 Hz, 2H), 4.58 –

4.49 (m, 1H), 3.61 (dd, *J* = 13.1, 7.4 Hz, 1H), 2.14 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.1, 147.8, 146.5, 139.4, 133.8, 131.7, 130.8, 128.7, 126.4, 122.9, 117.9, 108.0, 105.8, 101.2, 100.0, 64.8, 45.0, 27.3.

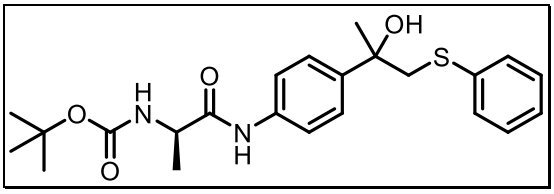
HRMS (ESI) m/z calcd. for $C_{24}H_{19}NO_4SNa$ $[M+Na]^+$: 440.0928, found: 440.0928.



c66

Purification by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v) afforded **c66** as a colorless oil (37.3 mg, 52% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 – 7.76 (m, 2H), 7.73 – 7.66 (m, 2H), 7.54 – 7.48 (m, 2H), 7.40 (dt, *J* = 8.0, 1.6 Hz, 2H), 7.35 – 7.33 (m, 1H), 7.33 – 7.28 (m, 2H), 7.27 – 7.21 (m, 2H), 7.19 – 7.14 (m, 1H), 5.49 (dd, *J* = 11.2, 4.8 Hz, 1H), 4.32 (dt, *J* = 14.0, 9.4 Hz, 1H), 3.59 (ddd, *J* = 14.2, 9.5, 4.8 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.2, 138.6, 133.9, 131.8, 131.4, 129.0, 128.7, 128.2, 128.0, 127.1, 125.9, 123.3, 54.7, 36.1.

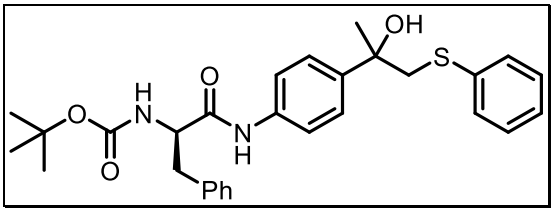
HRMS (ESI) m/z calcd. for $C_{22}H_{17}NO_2SNa$ $[M+Na]^+$: 382.0872, found: 382.0872.



c67

Purification by column chromatography on silica gel (hexane/ethyl acetate = 3/1, v/v) afforded **c67** as a white solid (61.9 mg, 72% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.88 (s, 1H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.41 – 7.31 (m, 4H), 7.25 (t, *J* = 7.5 Hz, 2H), 7.19 (d, *J* = 7.3 Hz, 1H), 5.48 (s, 1H), 4.43 (s, 1H), 3.49 (dd, *J* = 13.2, 6.0 Hz, 1H), 3.34 (t, *J* = 11.1 Hz, 1H), 3.20 (s, 1H), 1.61 (s, 3H), 1.50 – 1.45 (m, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.4, 156.2, 142.1, 136.9, 136.7, 129.9, 129.0, 126.3, 125.5, 119.7, 80.5, 73.9, 50.8, 49.4, 29.2, 28.4, 18.0.

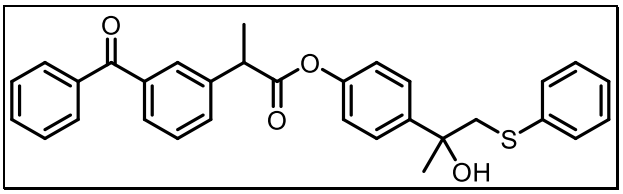
HRMS (ESI) m/z calcd. for $C_{23}H_{30}N_2O_4SNa$ $[M+Na]^+$: 453.1818, found: 453.1809.



c68

Purification by column chromatography on silica gel (hexane/ethyl acetate = 3/1, v/v) afforded **c68** as a white solid (68.8 mg, 68% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.31 (m, 7H), 7.30 – 7.23 (m, 7H), 7.21 – 7.15 (m, 1H), 5.81 (s, 1H), 4.75 (s, 1H), 3.49 (d, *J* = 13.1 Hz, 1H), 3.43 – 2.98 (m, 4H), 1.62 (s, 3H), 1.43 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.4, 156.2, 142.3, 136.7, 134.2, 129.9, 129.4, 129.0, 128.7, 126.9, 126.3, 125.5, 123.5, 120.0, 80.5, 73.9, 56.8, 49.4, 38.8, 29.2, 28.4.

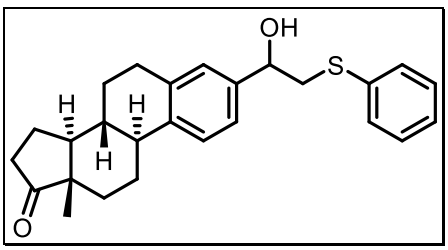
HRMS (ESI) m/z calcd. for $C_{29}H_{34}N_2O_4SNa$ $[M+Na]^+$: 529.2132, found: 529.2127.



c69

Purification by column chromatography on silica gel (hexane/ethyl acetate = 3/1, v/v) afforded **c67** as a white solid (84.3 mg, 85% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 – 7.95 (m, 3H), 7.88 (s, 1H), 7.81 (d, *J* = 7.4 Hz, 1H), 7.73 (dd, *J* = 10.5, 4.1 Hz, 1H), 7.64 (d, *J* = 7.2 Hz, 3H), 7.46 (d, *J* = 7.2 Hz, 2H), 7.42 – 7.29 (m, 6H), 7.05 (d, *J* = 6.8 Hz, 1H), 4.25 – 4.14 (m, 1H), 3.63 (d, *J* = 13.4 Hz, 1H), 3.48 (d, *J* = 13.4 Hz, 1H), 3.13 (s, 1H), 1.82 (d, *J* = 6.3 Hz, 3H), 1.74 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.6, 172.7, 150.9, 148.4, 140.5, 138.3, 137.6, 134.4, 132.7, 131.7, 130.3, 129.4, 129.1, 128.9, 128.5, 126.7, 123.7, 122.6, 120.1, 118.2, 74.0, 49.5, 45.7, 29.5, 18.7.

HRMS (ESI) m/z calcd. for $C_{31}H_{28}O_4SNa$ $[M+Na]^+$: 519.1601, found: 519.1600.



c70

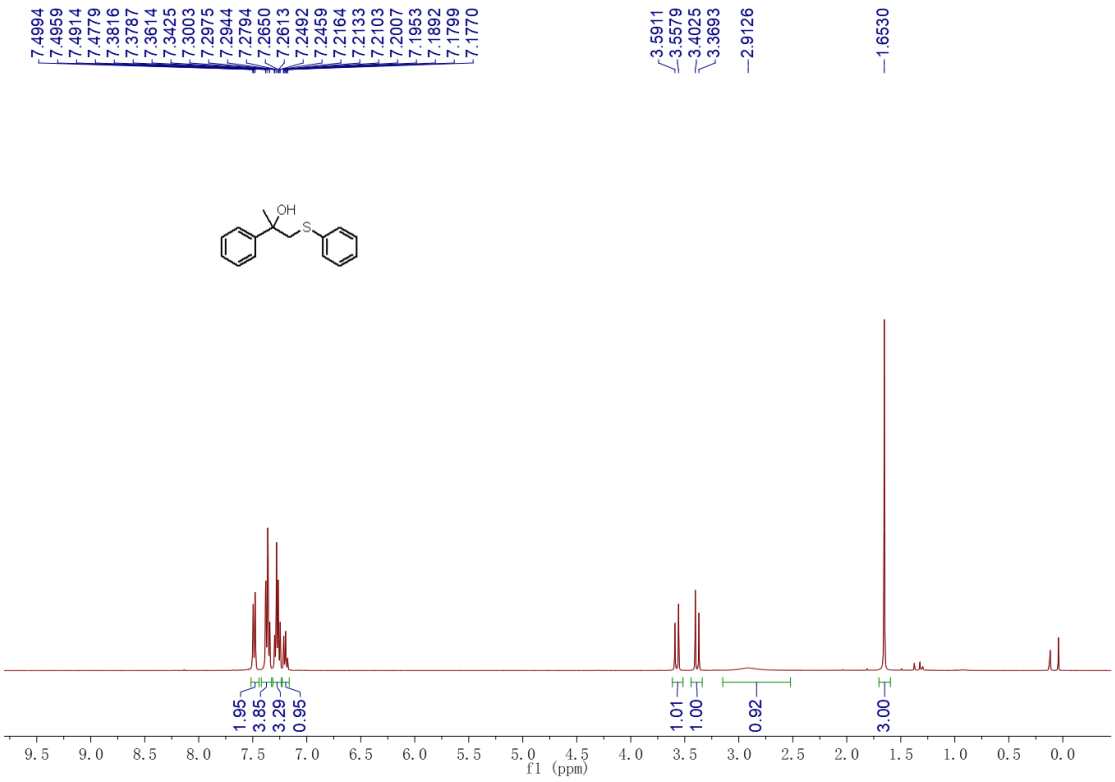
Purification by column chromatography on silica gel (hexane/ethyl acetate = 3/1, v/v) afforded **c67** as a white solid (57.6 mg, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44

(d, *J* = 7.4 Hz, 2H), 7.33 (dd, *J* = 12.5, 4.7 Hz, 3H), 7.27 (d, *J* = 7.2 Hz, 1H), 7.15 (dd, *J* = 8.1, 6.5 Hz, 2H), 4.72 (dd, *J* = 9.2, 3.4 Hz, 1H), 3.35 (dd, *J* = 13.7, 3.7 Hz, 1H), 3.15 (dd, *J* = 13.7, 9.3 Hz, 1H), 2.99 (s, 1H), 2.94 (dd, *J* = 8.9, 4.0 Hz, 2H), 2.59 – 2.42 (m, 2H), 2.32 (dd, *J* = 13.5, 7.1 Hz, 1H), 2.22 – 2.01 (m, 4H), 1.68 – 1.49 (m, 6H), 0.94 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 221.0, 139.7, 136.8, 134.3, 130.1, 129.1, 126.7, 126.5, 125.6, 123.6, 123.4, 71.5, 50.5, 48.0, 44.4, 43.7, 38.1, 35.9, 31.6, 29.5, 26.5, 25.7, 21.6, 13.9.

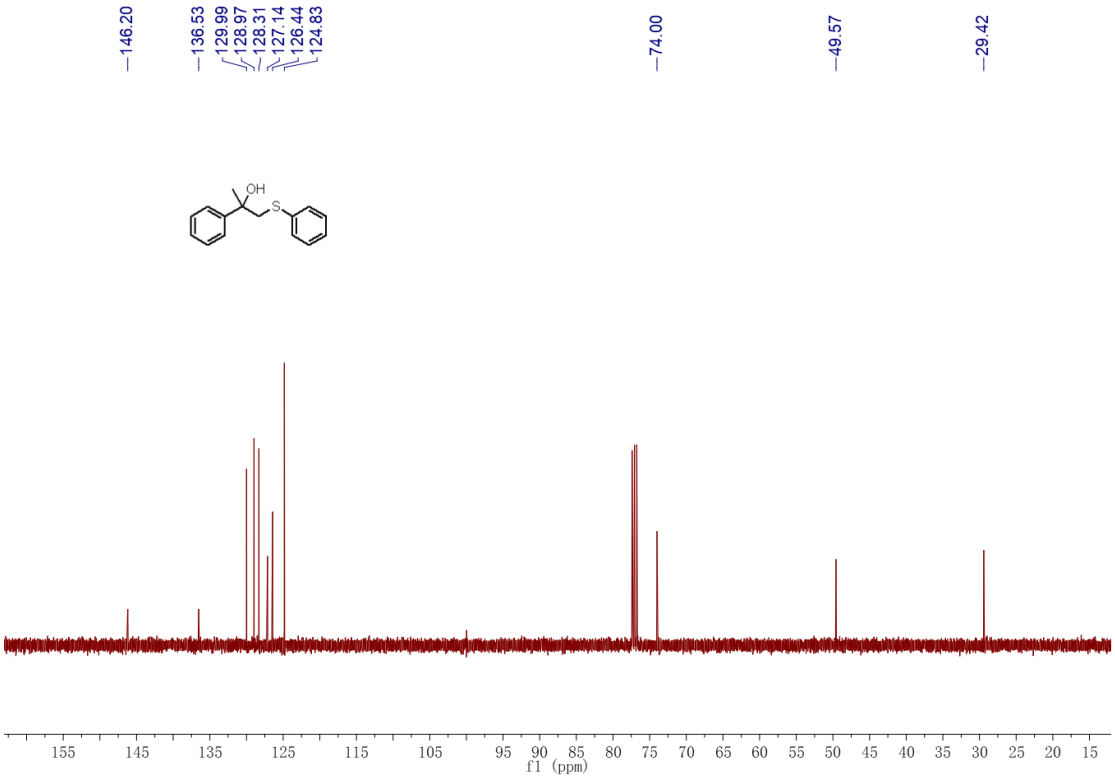
HRMS (ESI) m/z calcd. for $C_{26}H_{30}O_2SNa$ $[M+Na]^+$: 429.1859, found: 429.1858.

3. NMR spectra for the products

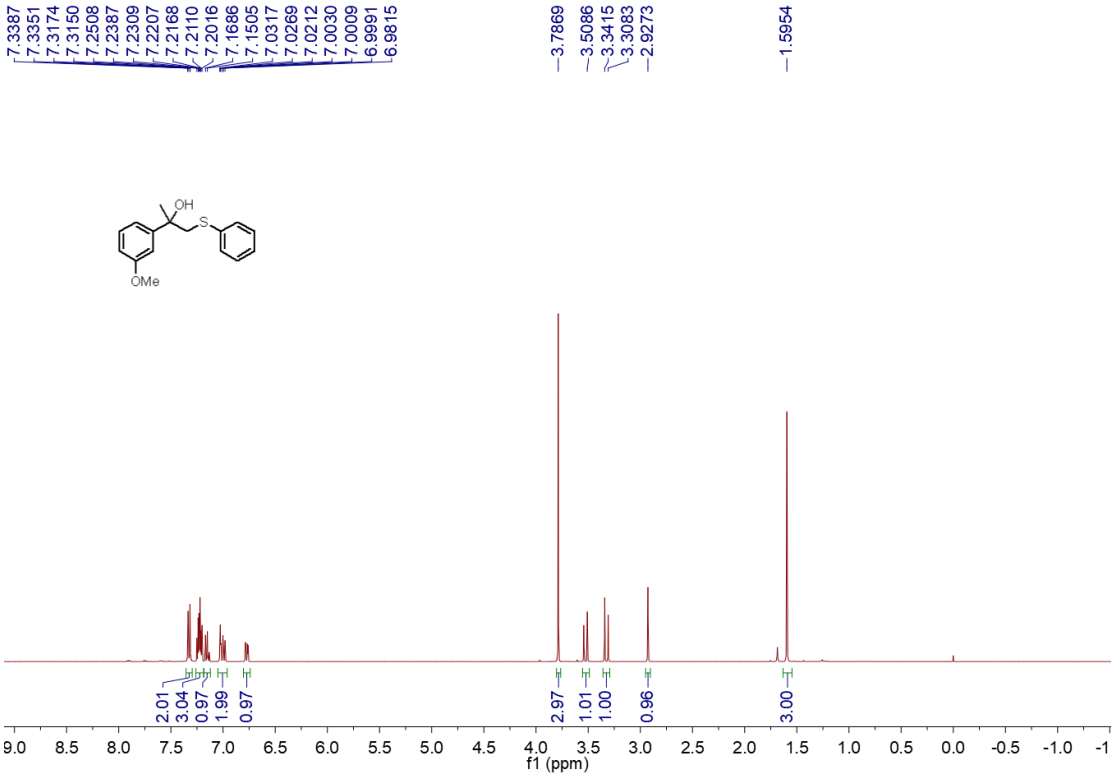
^{1}H NMR spectrum of c1



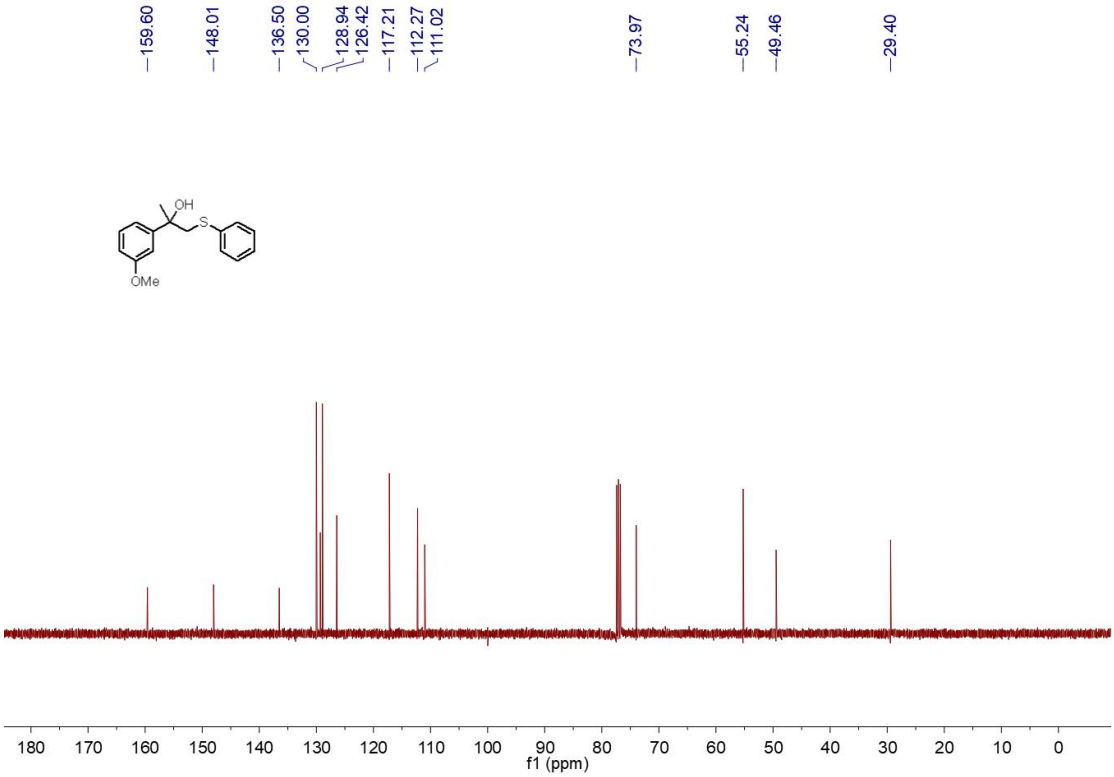
^{13}C NMR spectrum of c1



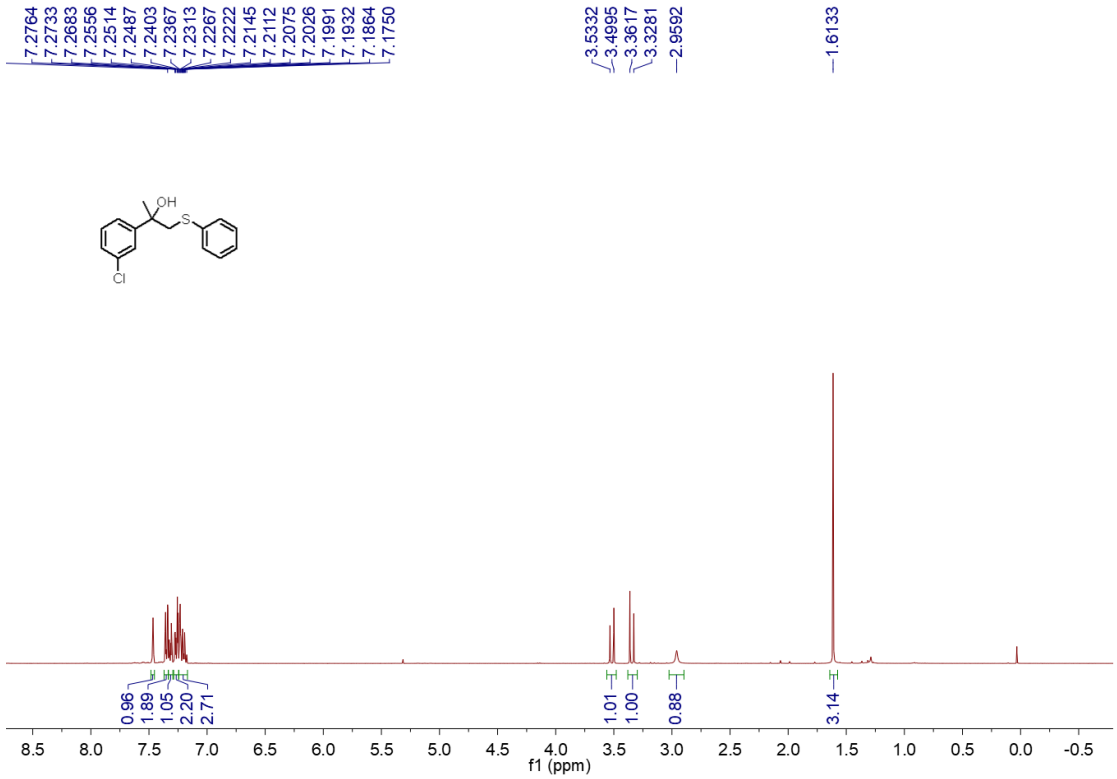
^{1}H NMR spectrum of c2



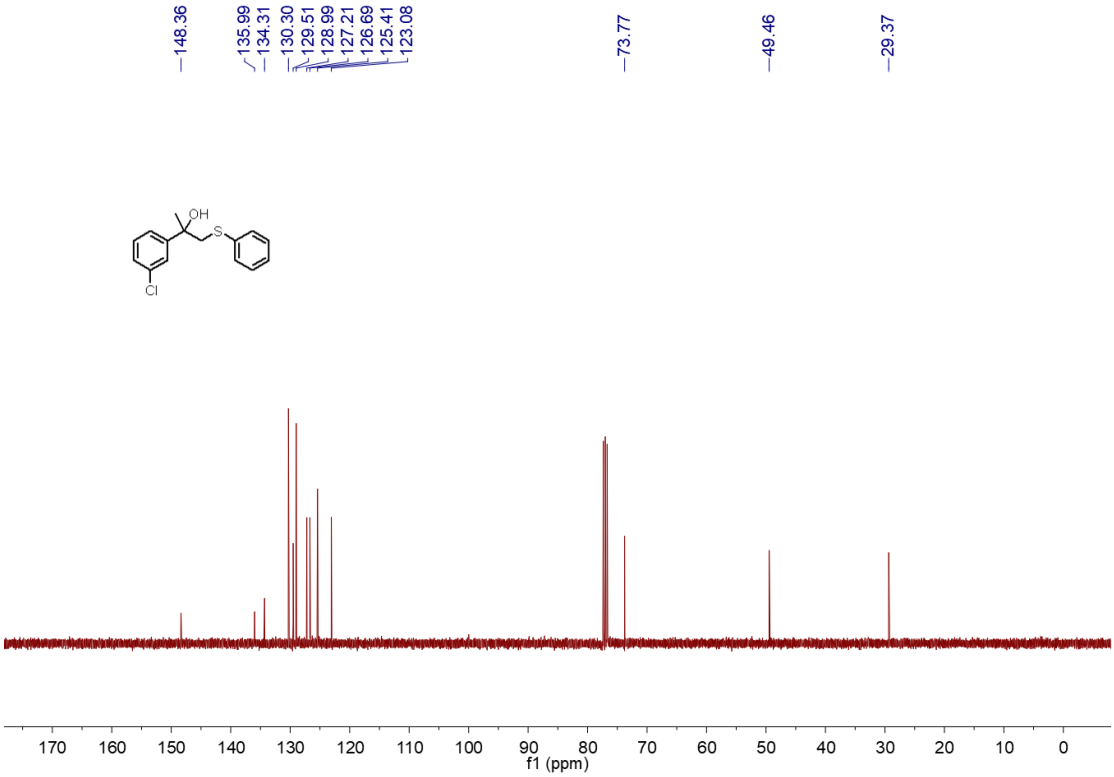
^{13}C NMR spectrum of c2



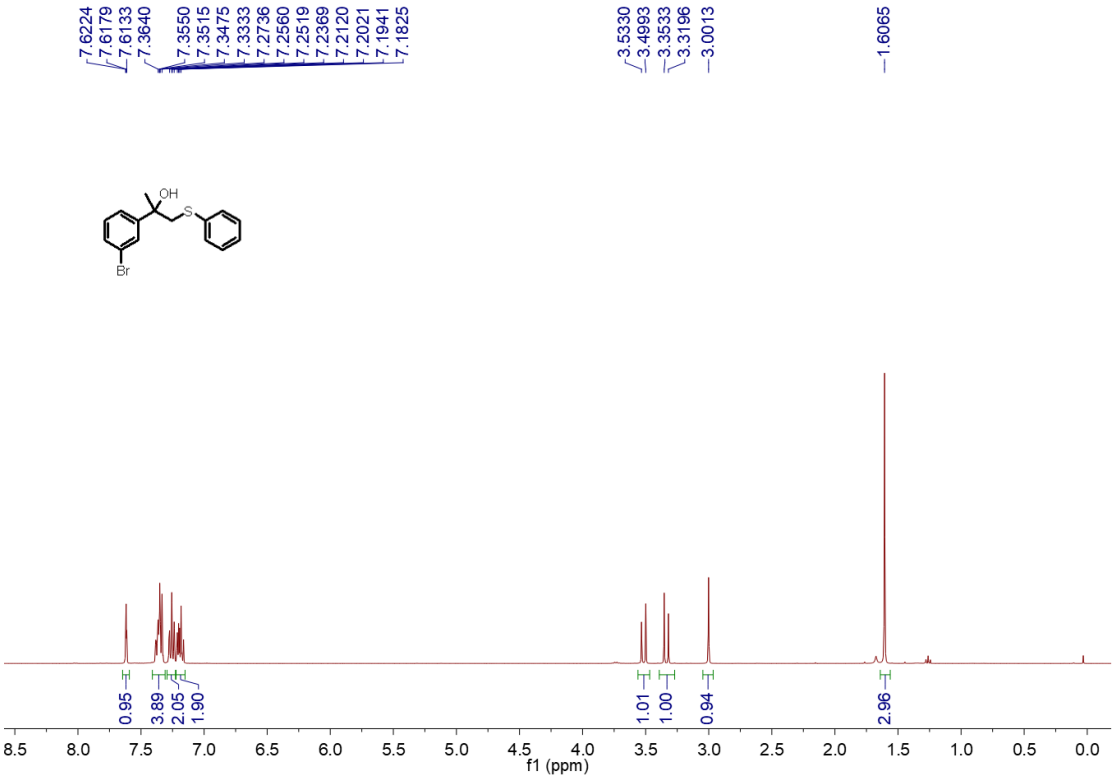
^{1}H NMR spectrum of c3



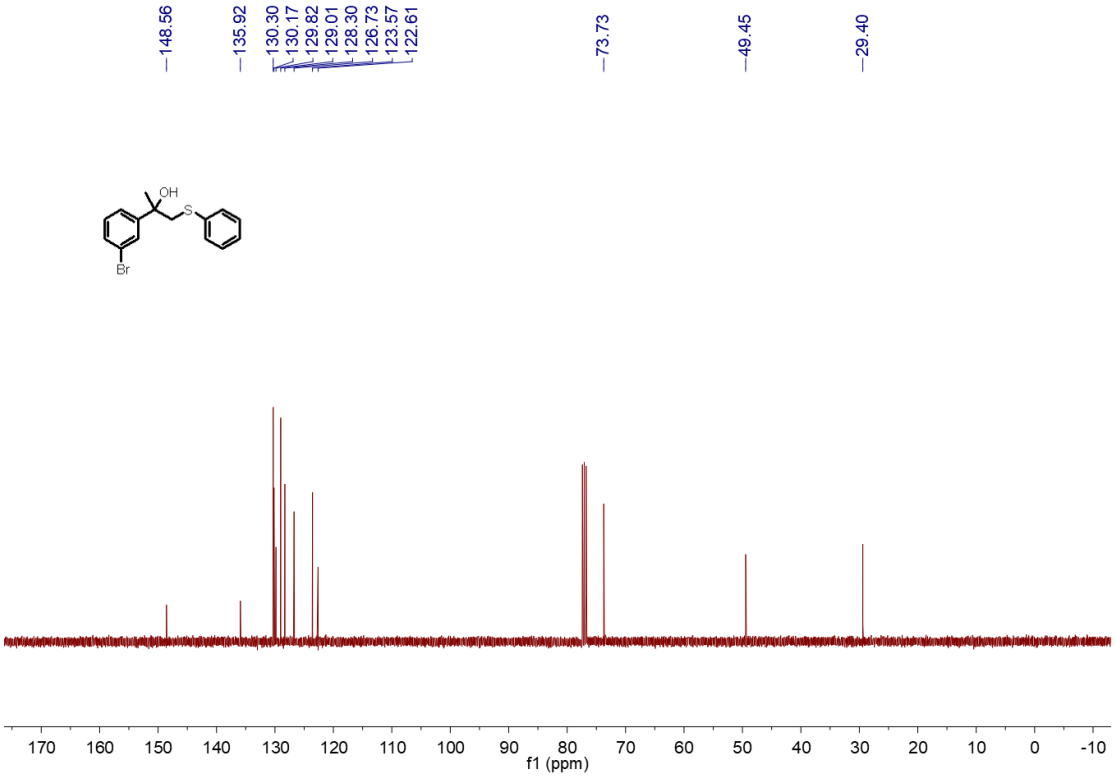
^{13}C NMR spectrum of c3



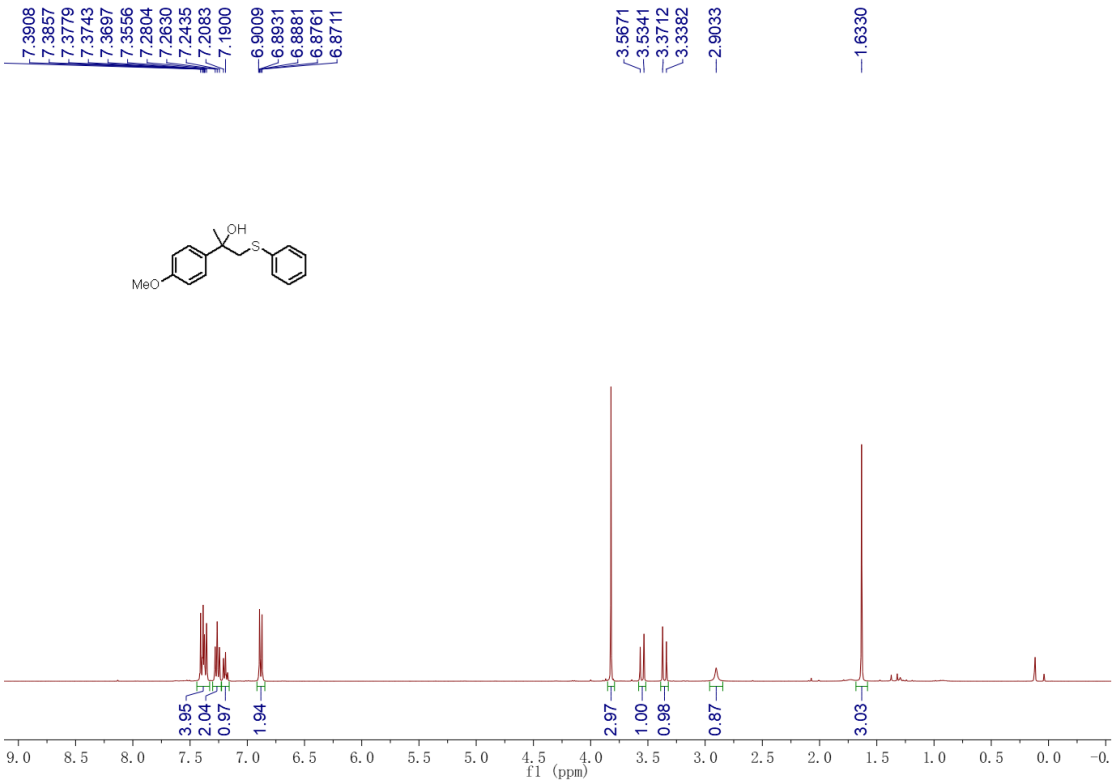
^{1}H NMR spectrum of c4



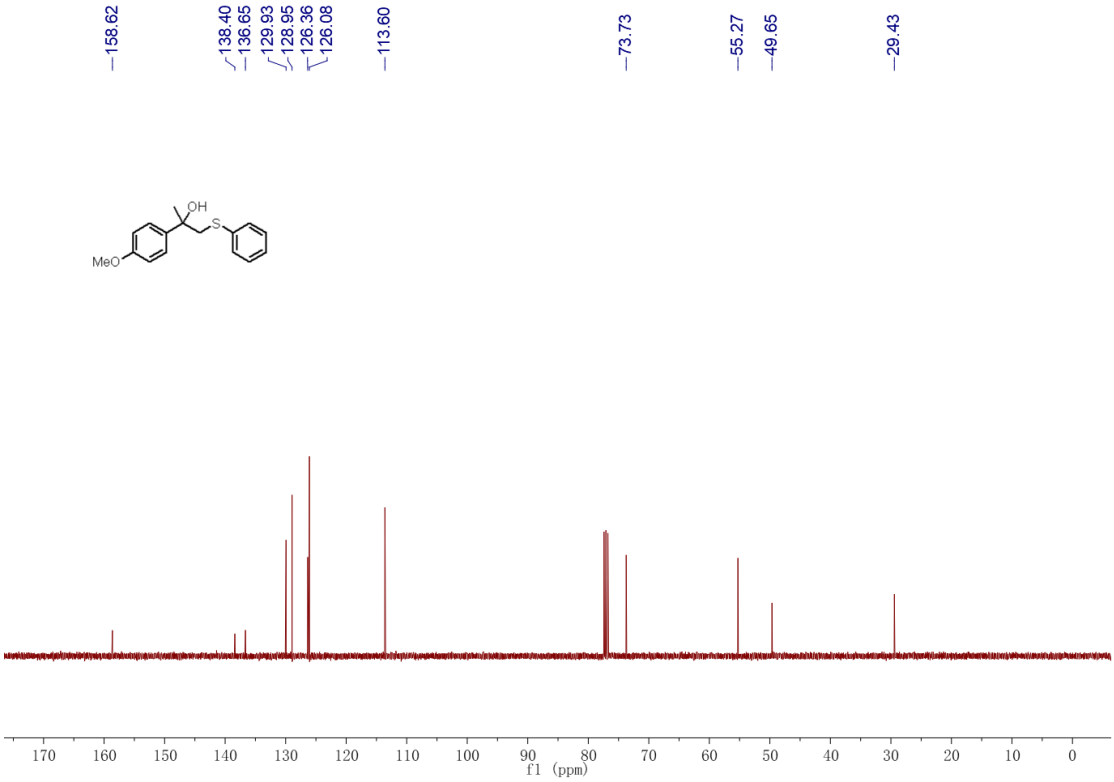
^{13}C NMR spectrum of c4



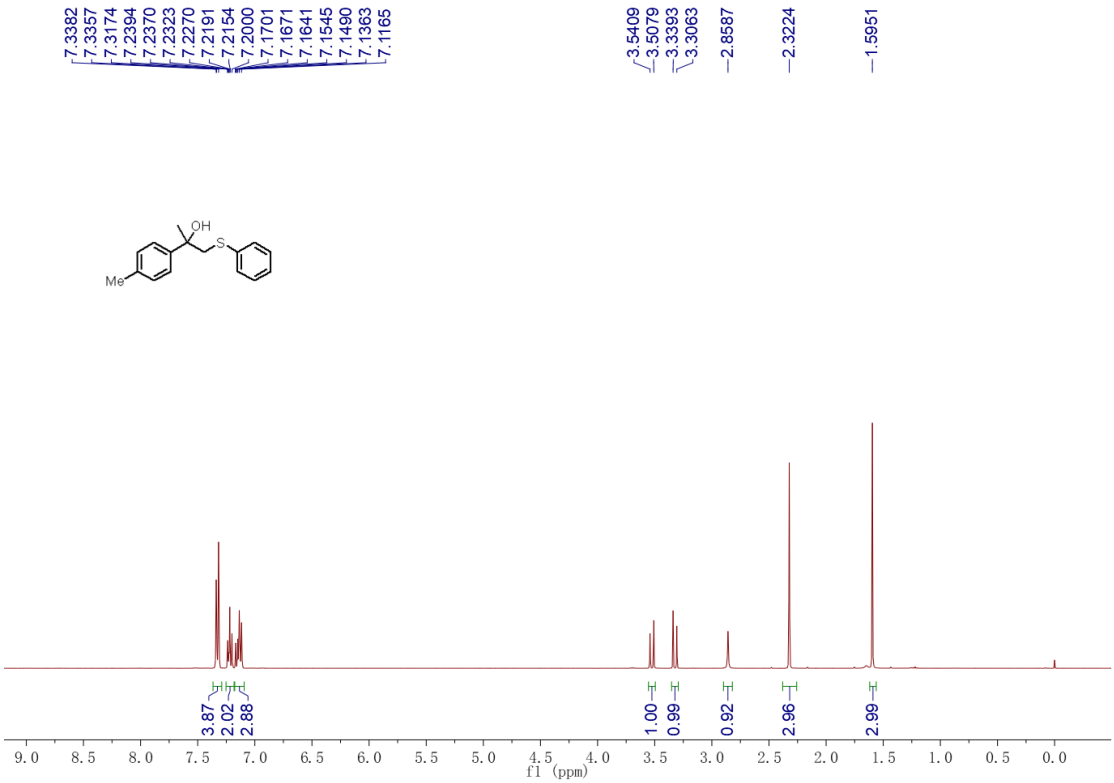
^{1}H NMR spectrum of c5



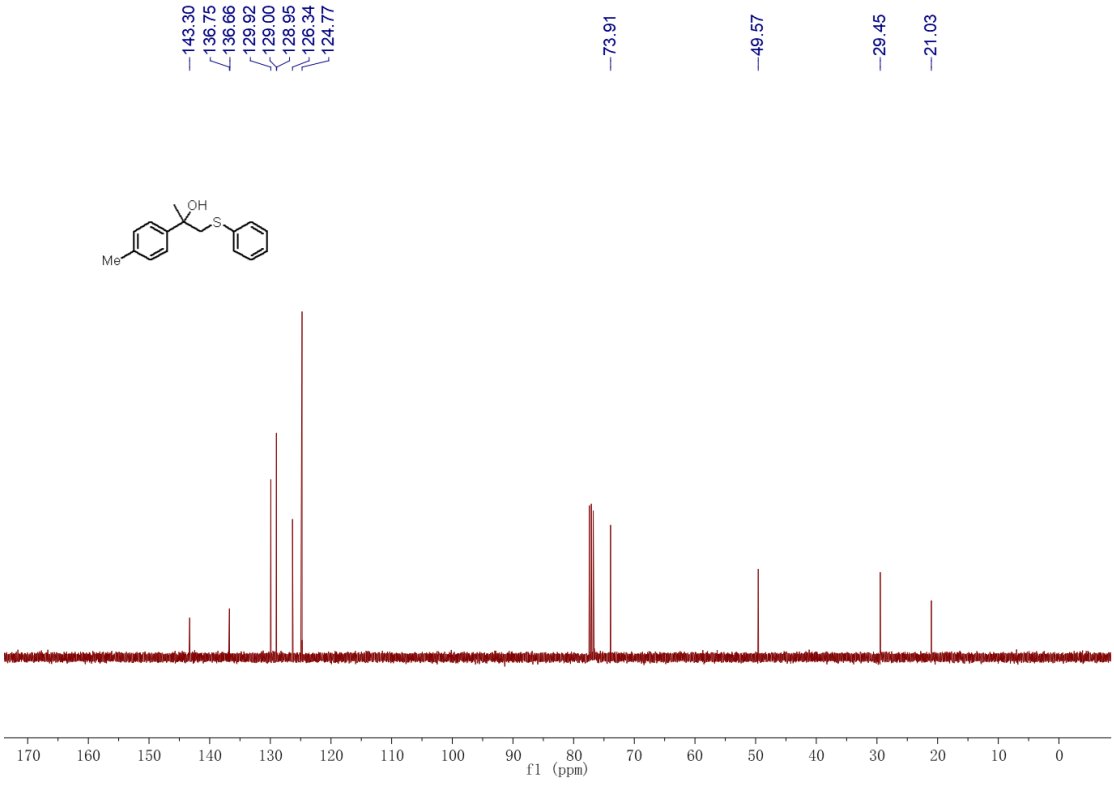
^{13}C NMR spectrum of c5



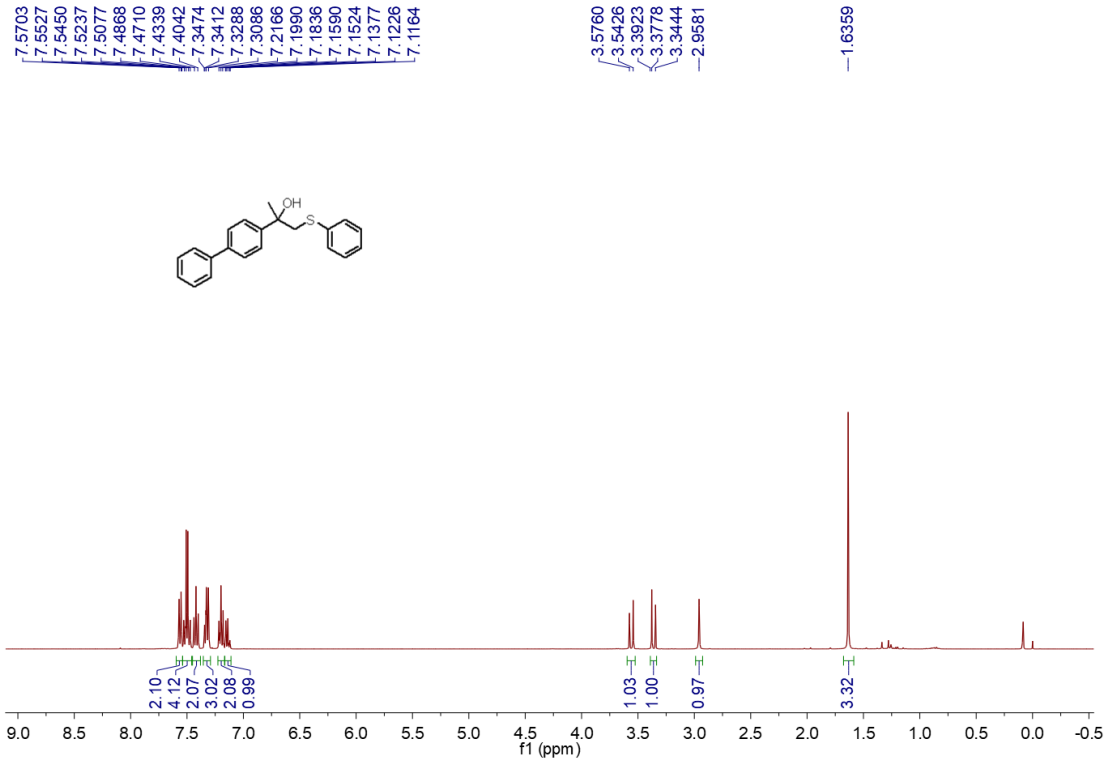
^{1}H NMR spectrum of c6



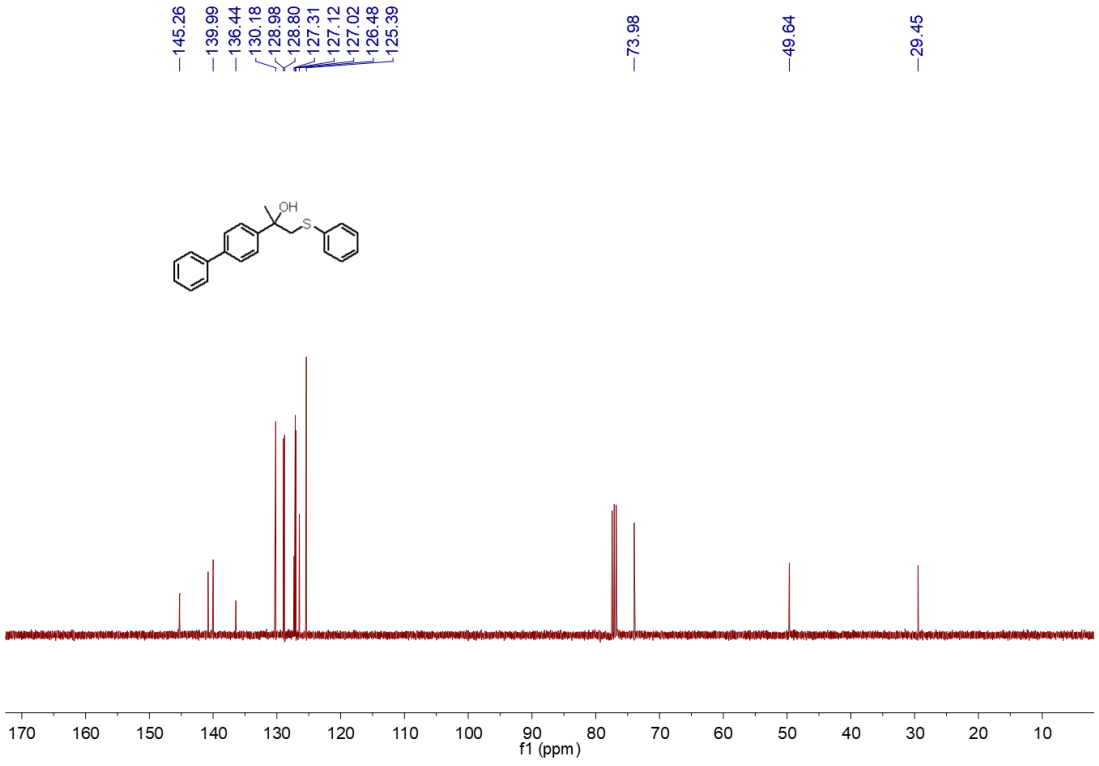
^{13}C NMR spectrum of c6



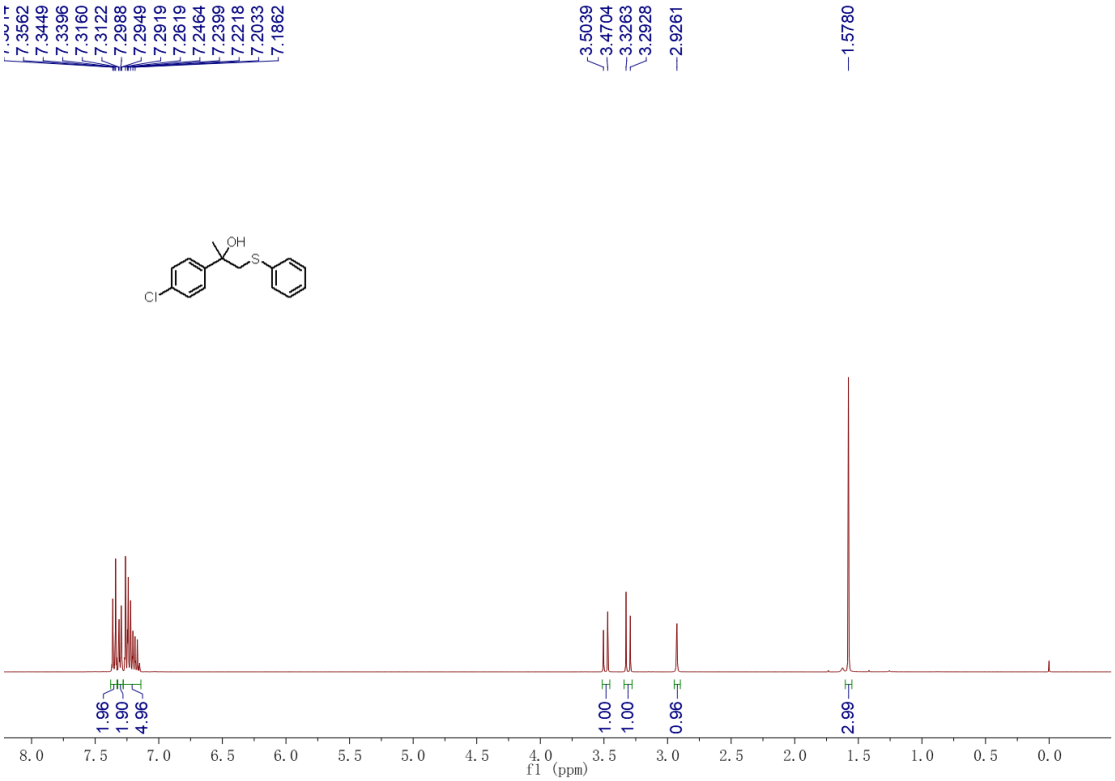
^{1}H NMR spectrum of c7



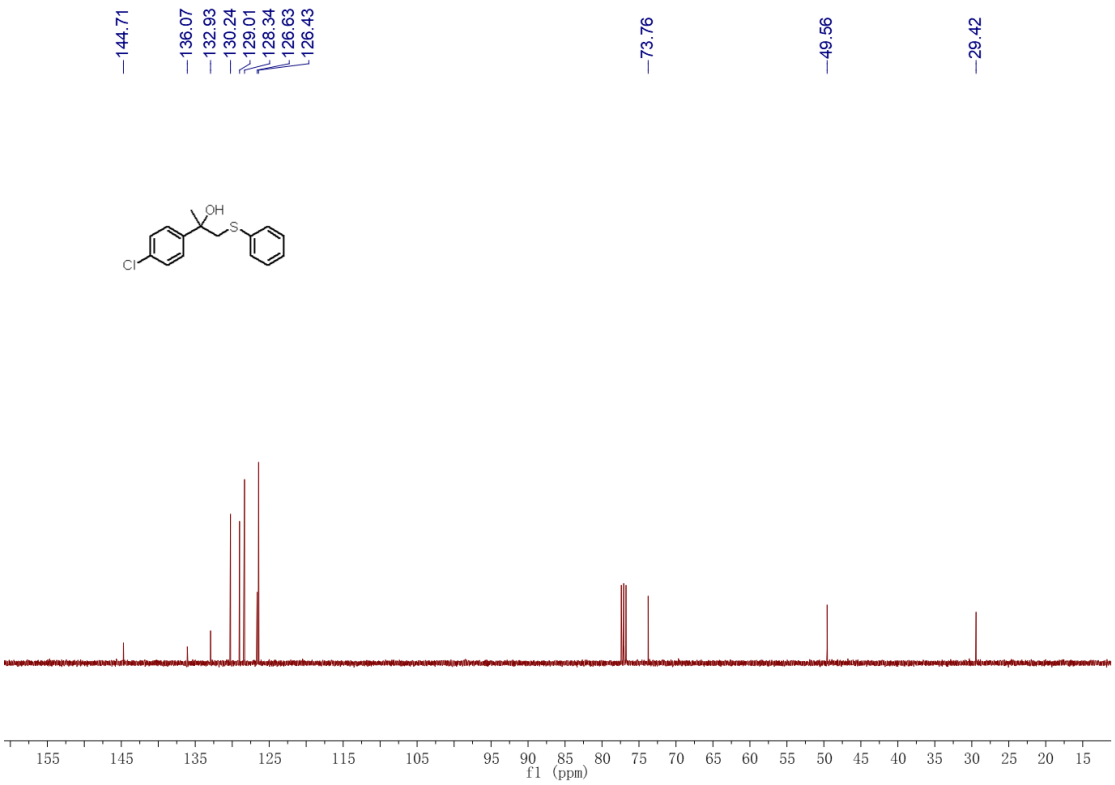
^{13}C NMR spectrum of c7



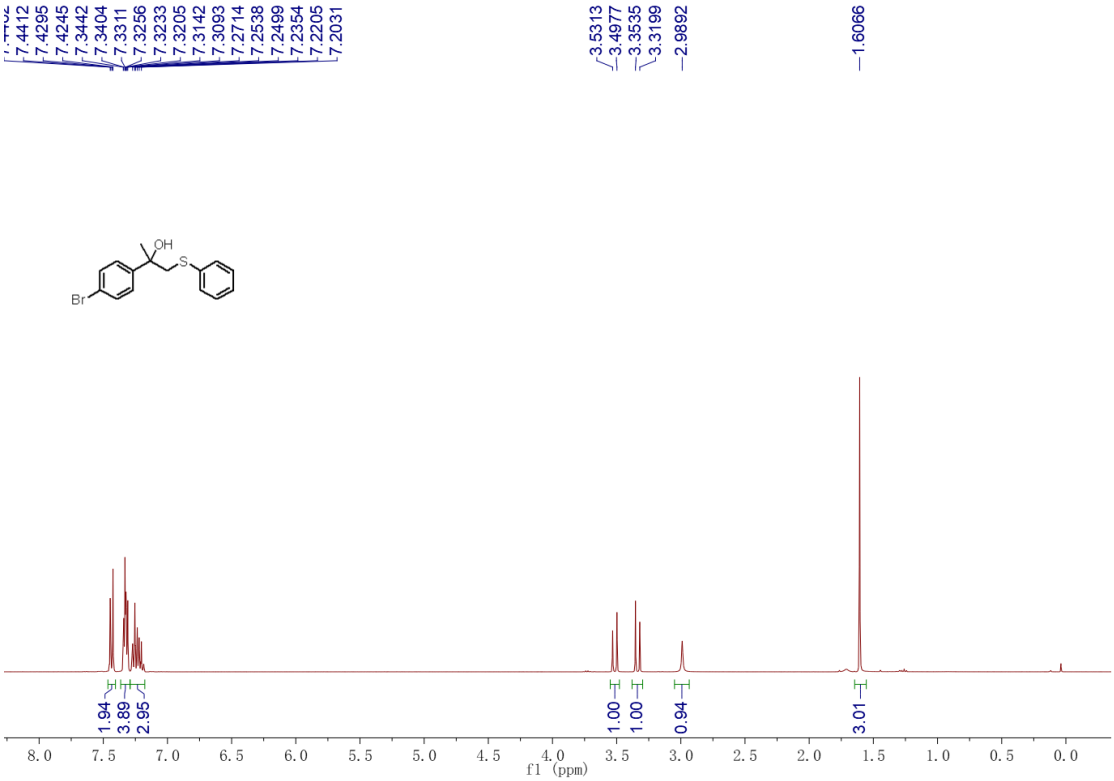
^{1}H NMR spectrum of c8



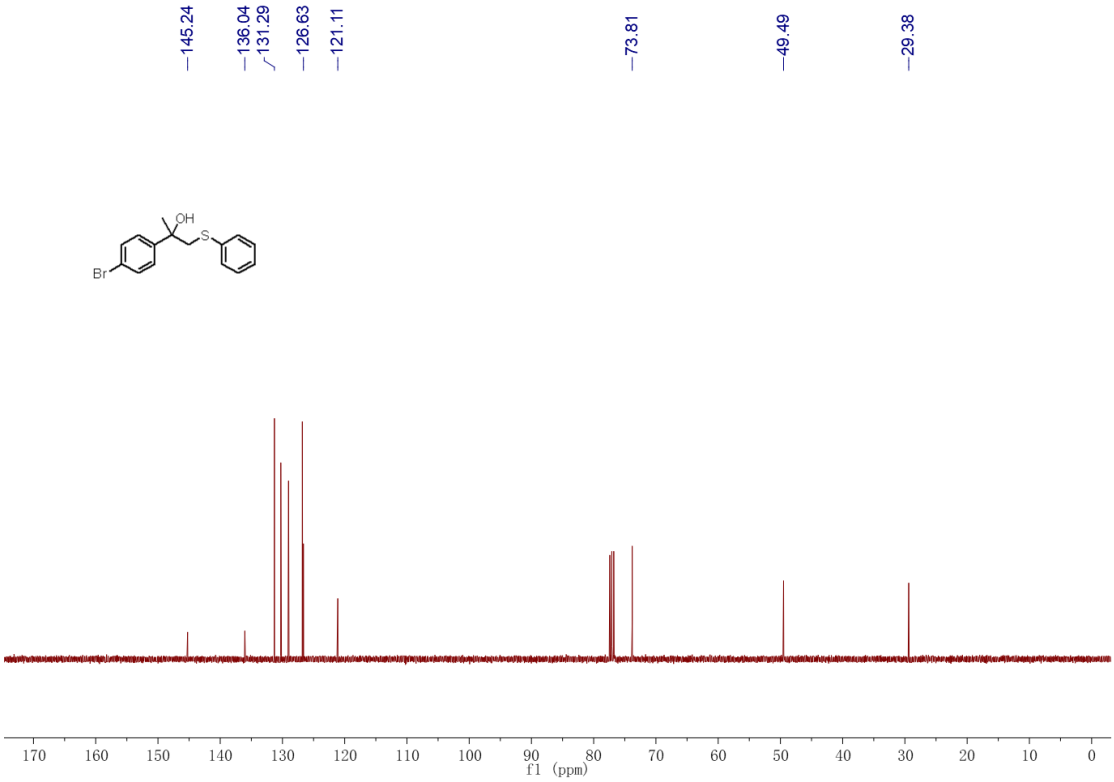
^{13}C NMR spectrum of c8



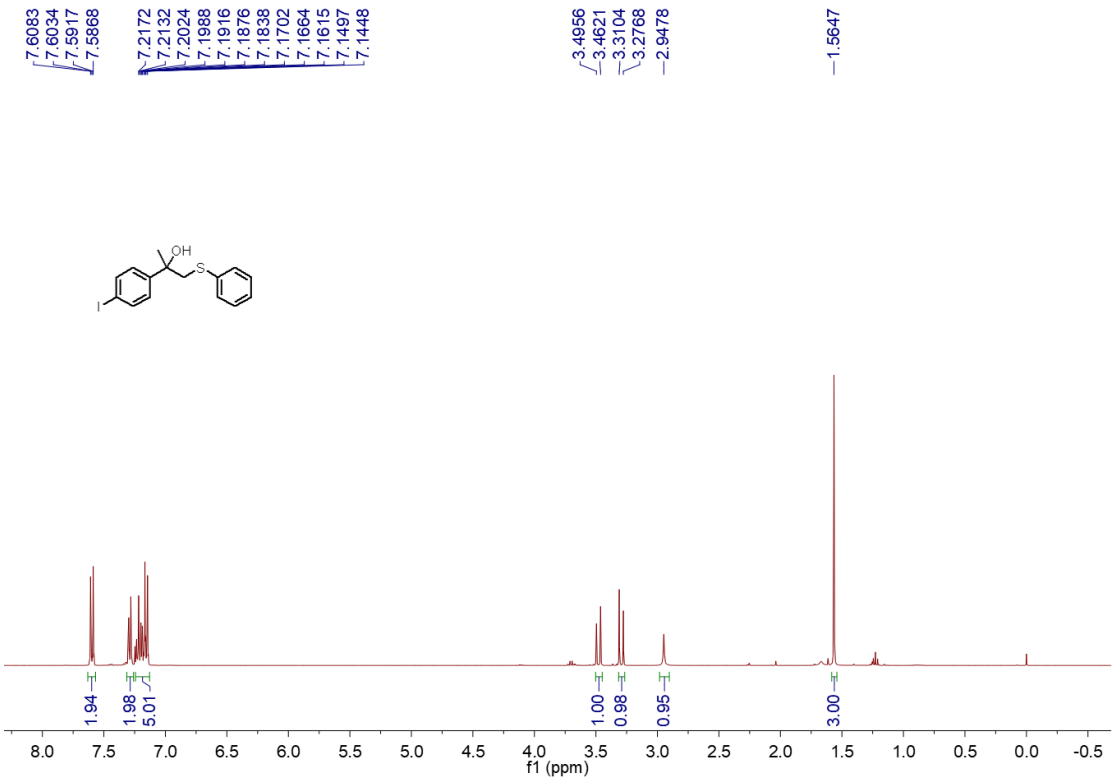
^{1}H NMR spectrum of c9



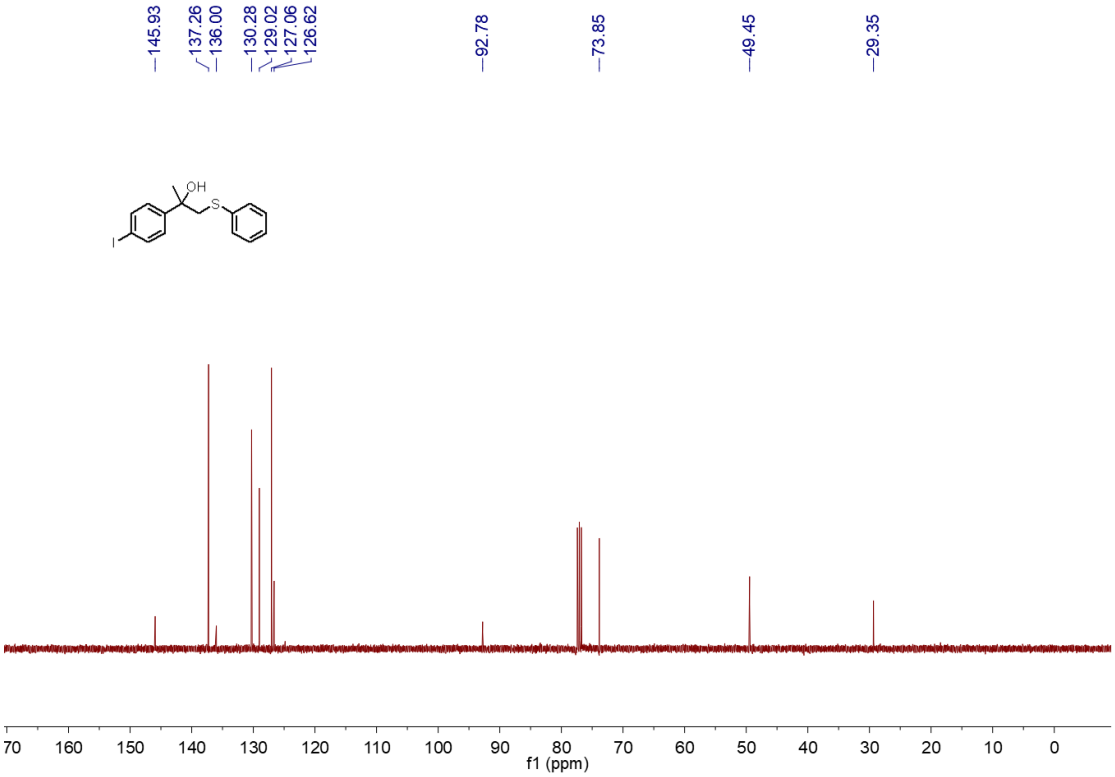
^{13}C NMR spectrum of c9



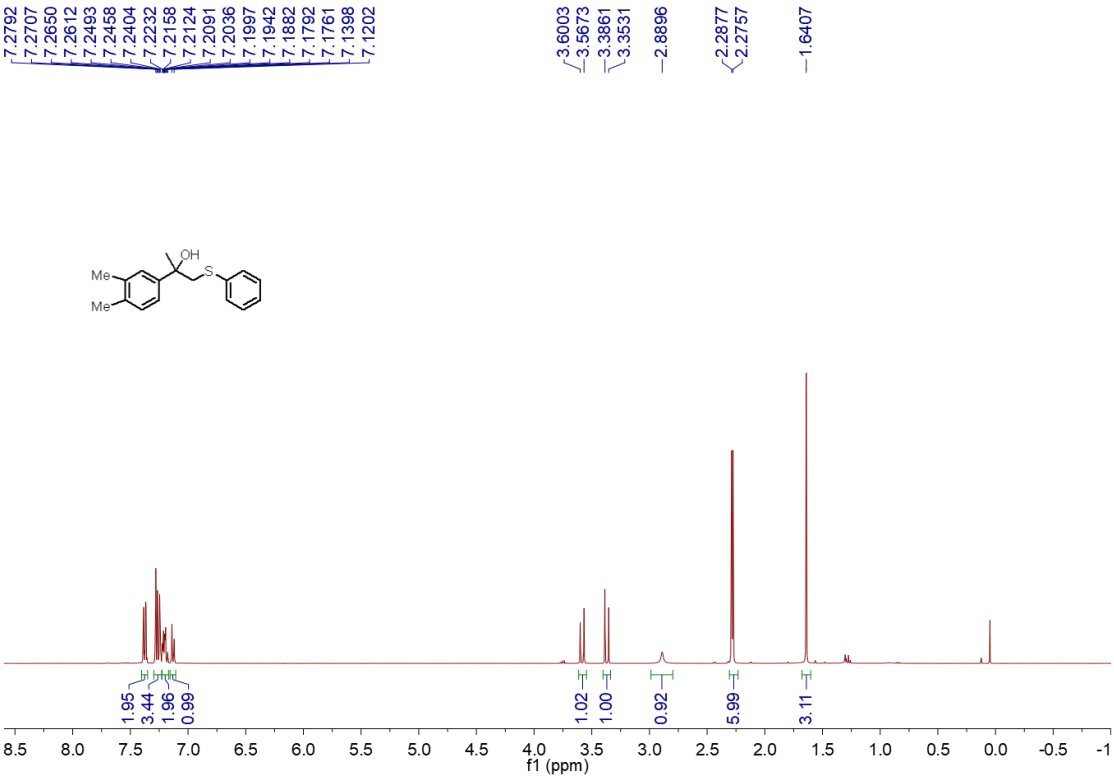
^{1}H NMR spectrum of c10



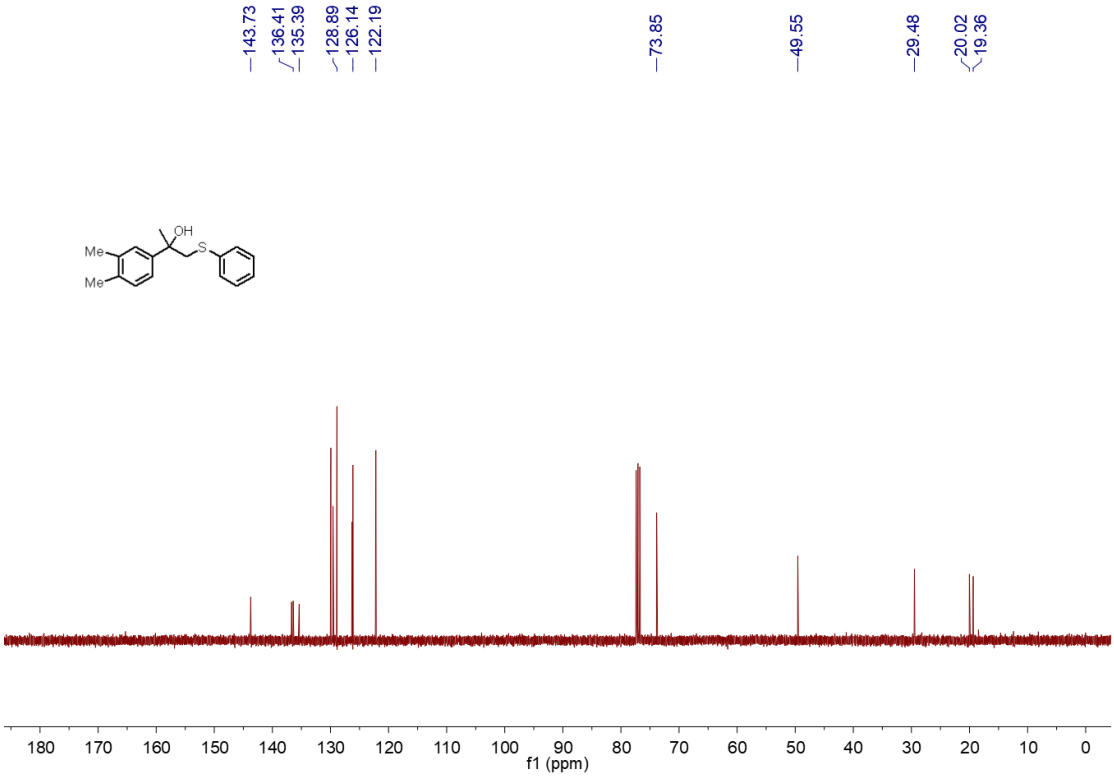
^{13}C NMR spectrum of c10



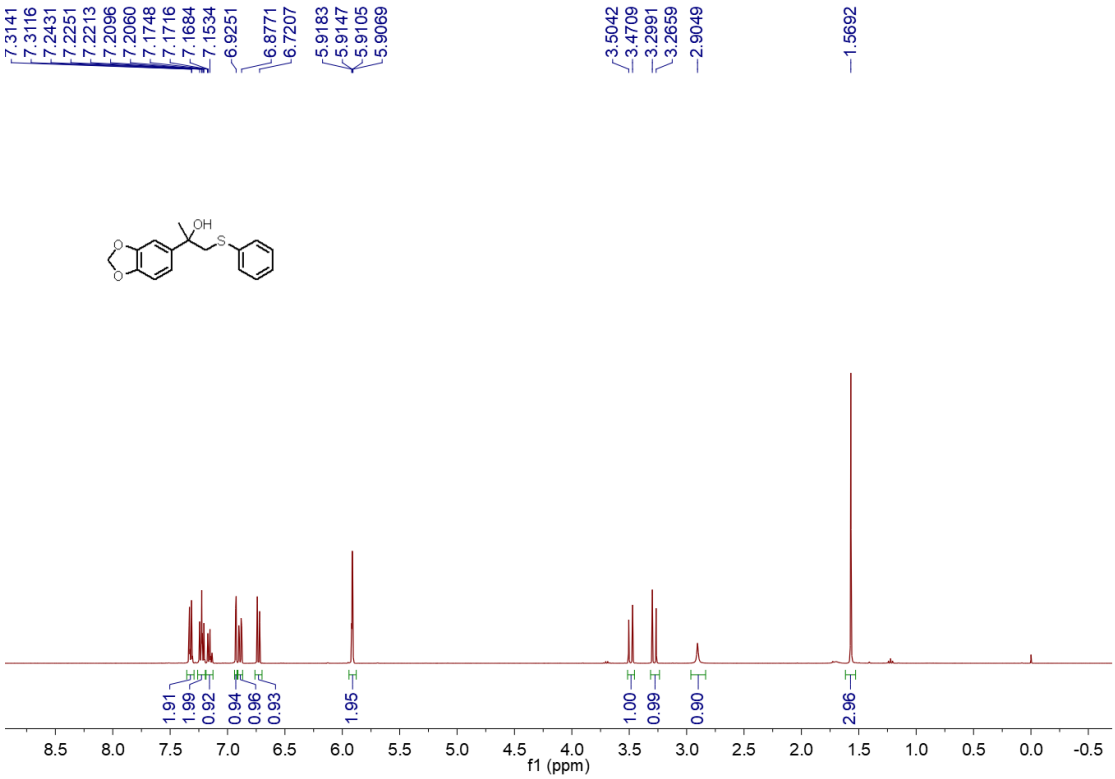
^{1}H NMR spectrum of c11



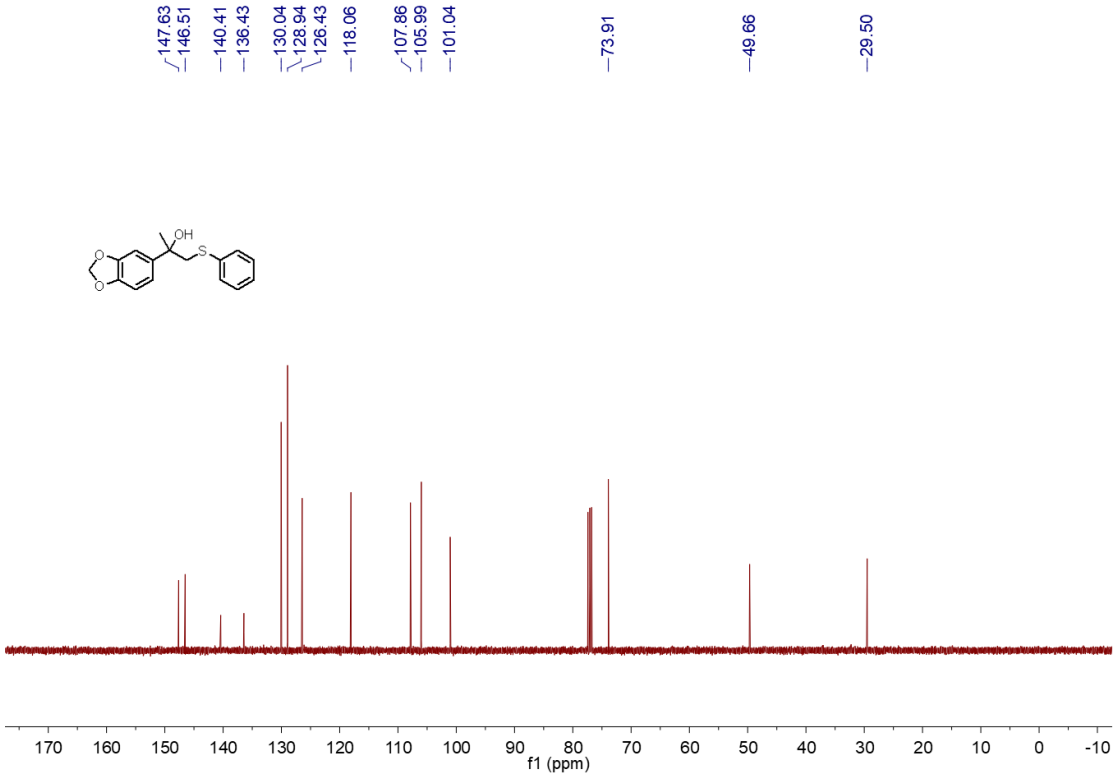
^{13}C NMR spectrum of c11



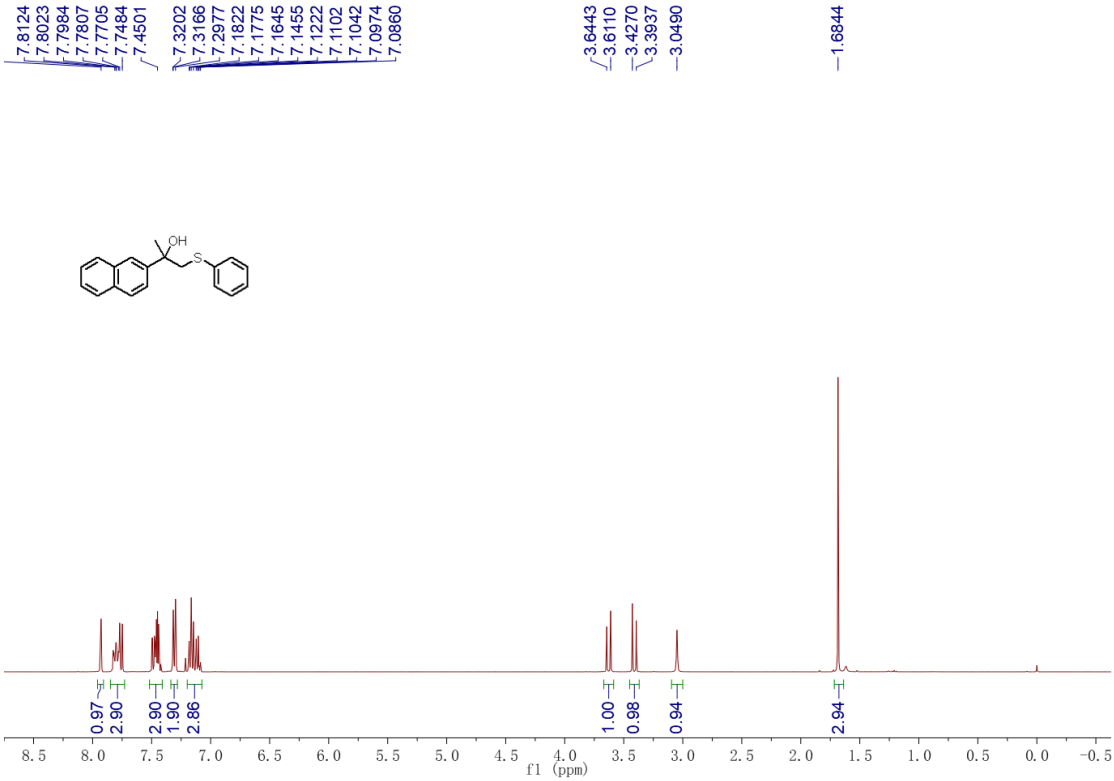
^{1}H NMR spectrum of c12



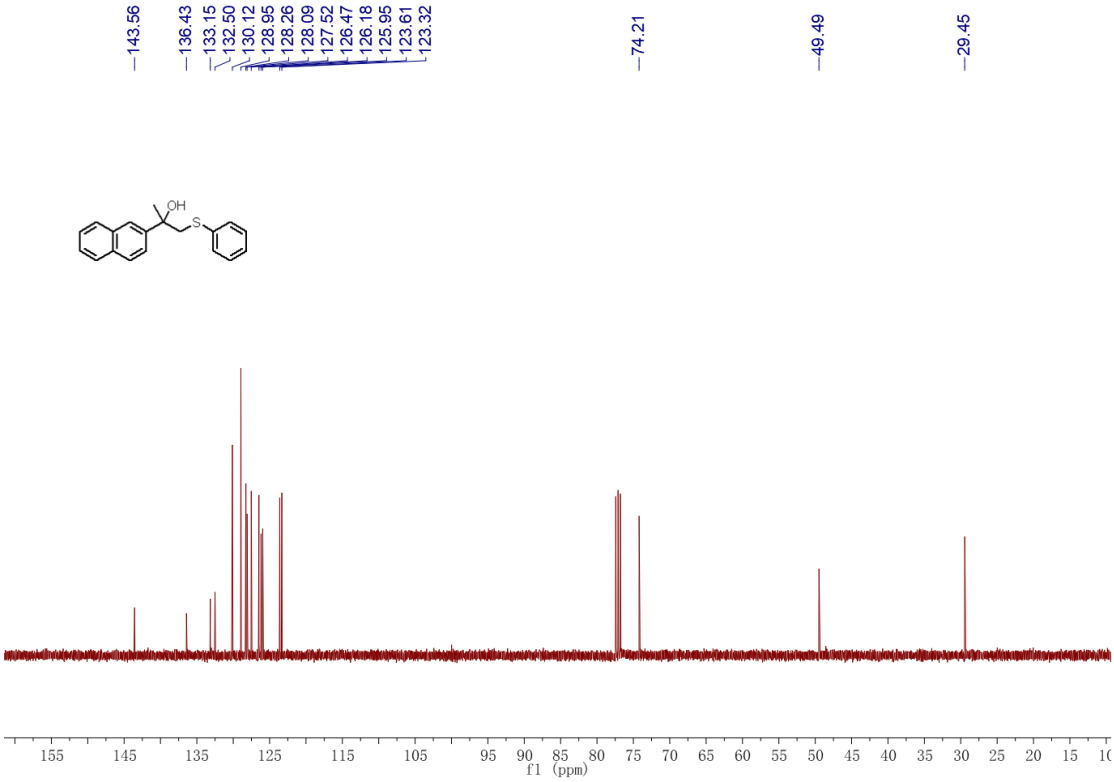
^{13}C NMR spectrum of c12



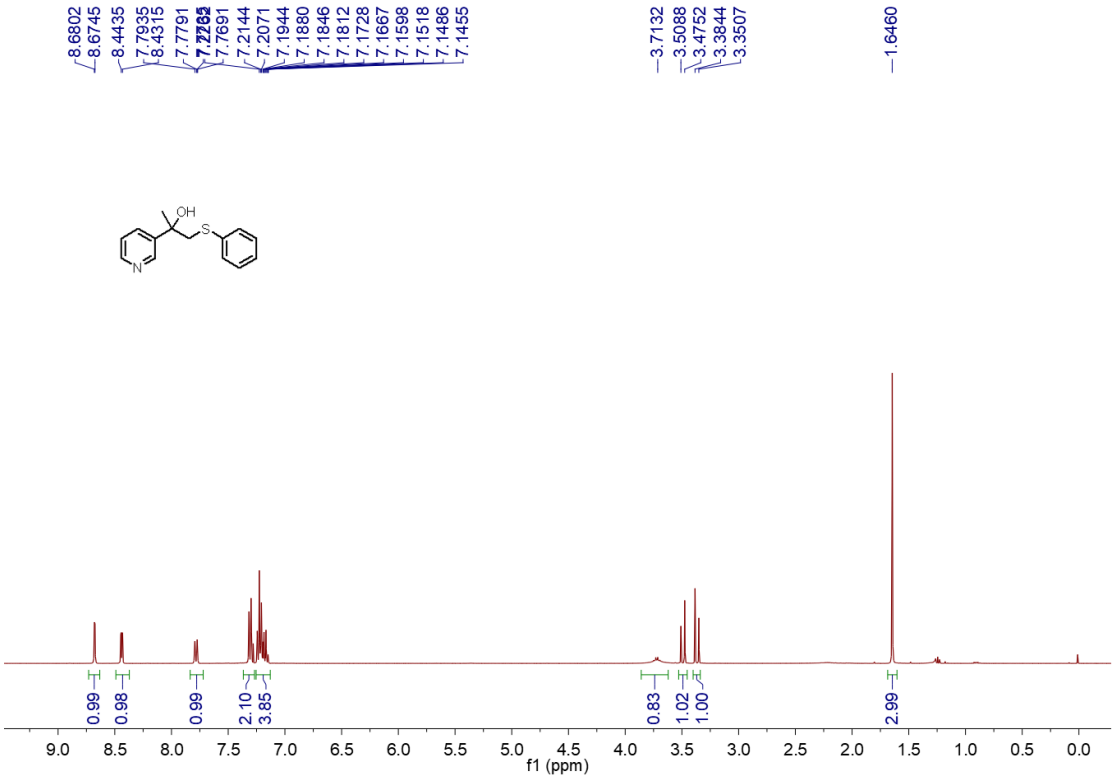
^{1}H NMR spectrum of c13



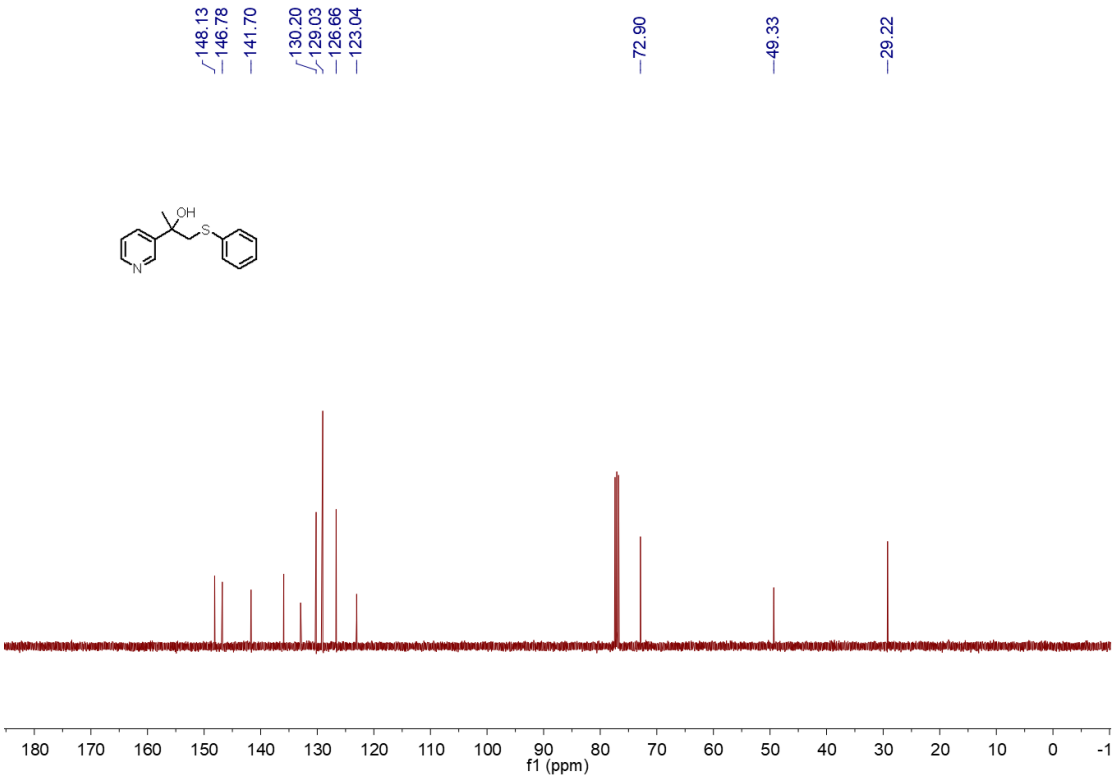
^{13}C NMR spectrum of c13



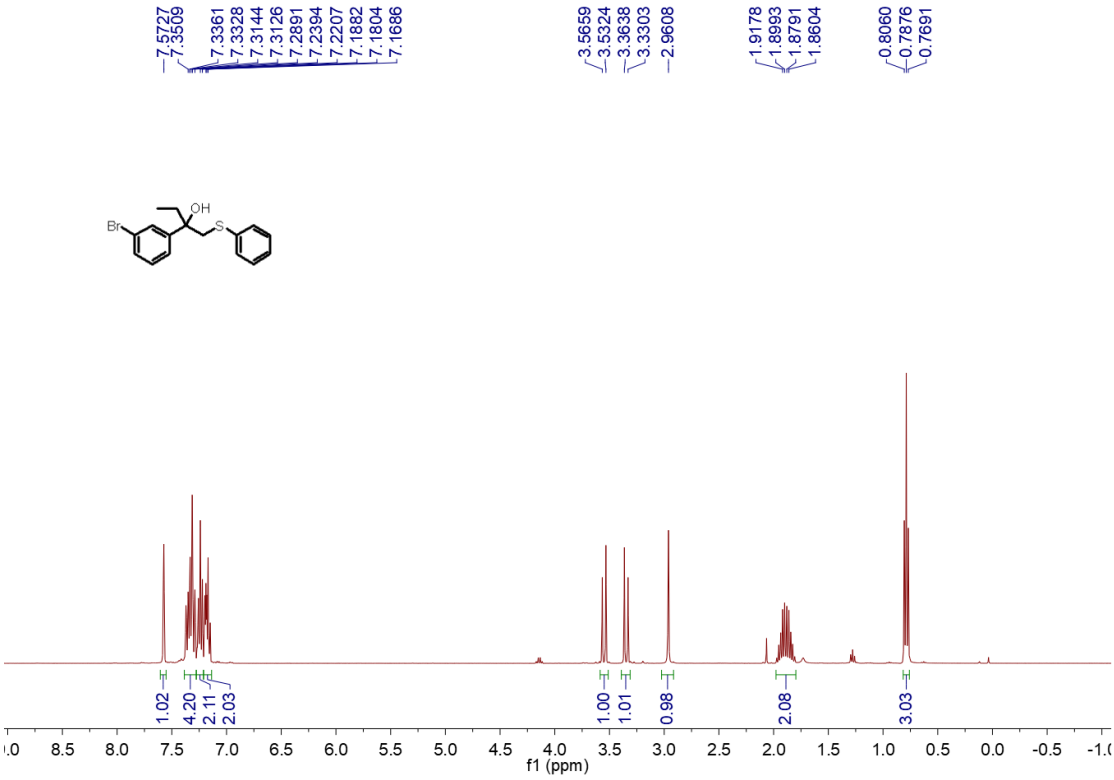
^{1}H NMR spectrum of c14



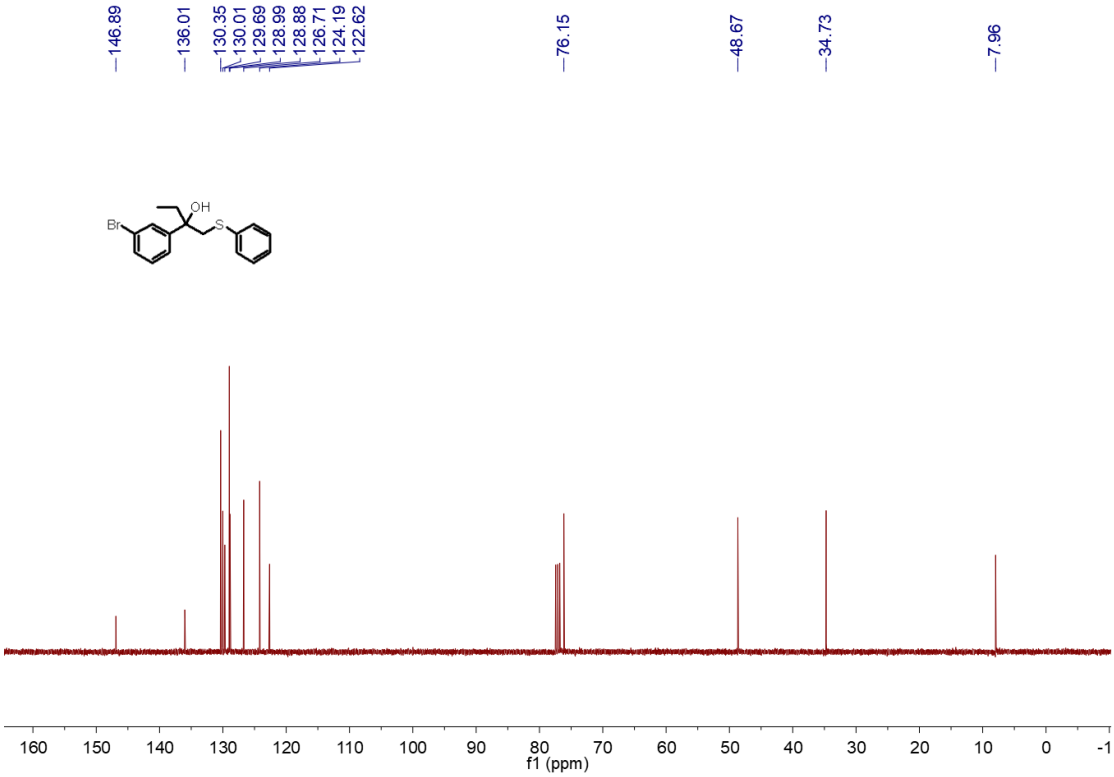
^{13}C NMR spectrum of c14



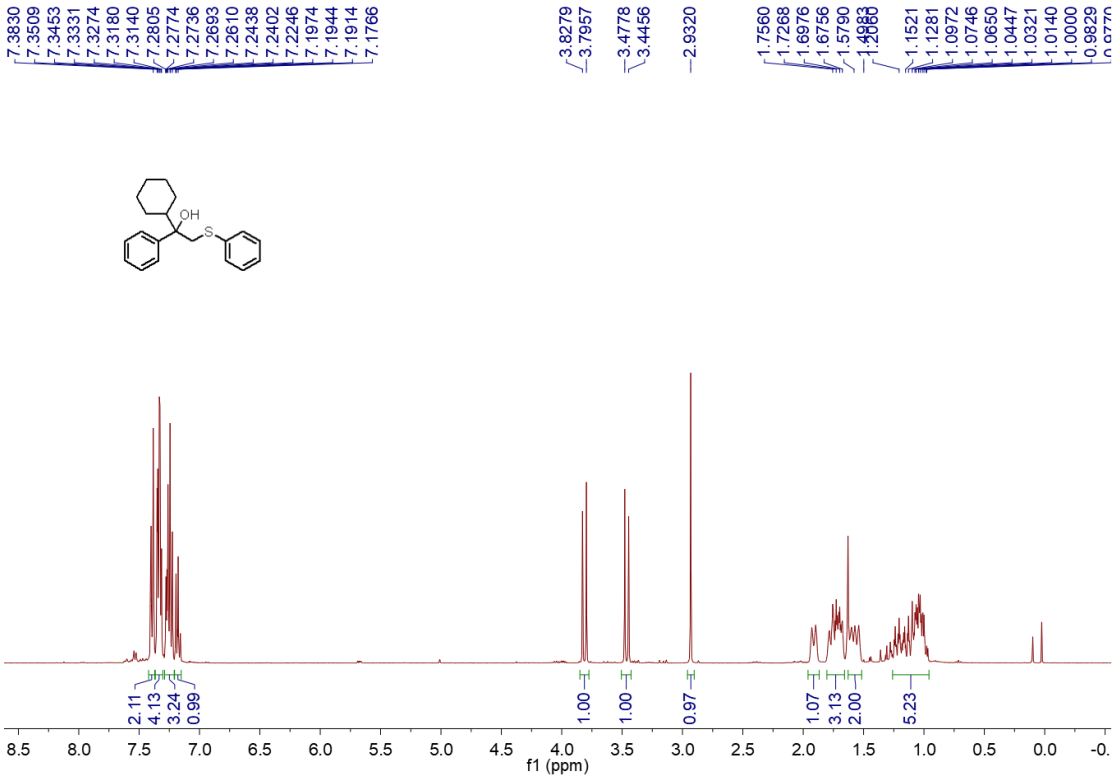
^{1}H NMR spectrum of c15



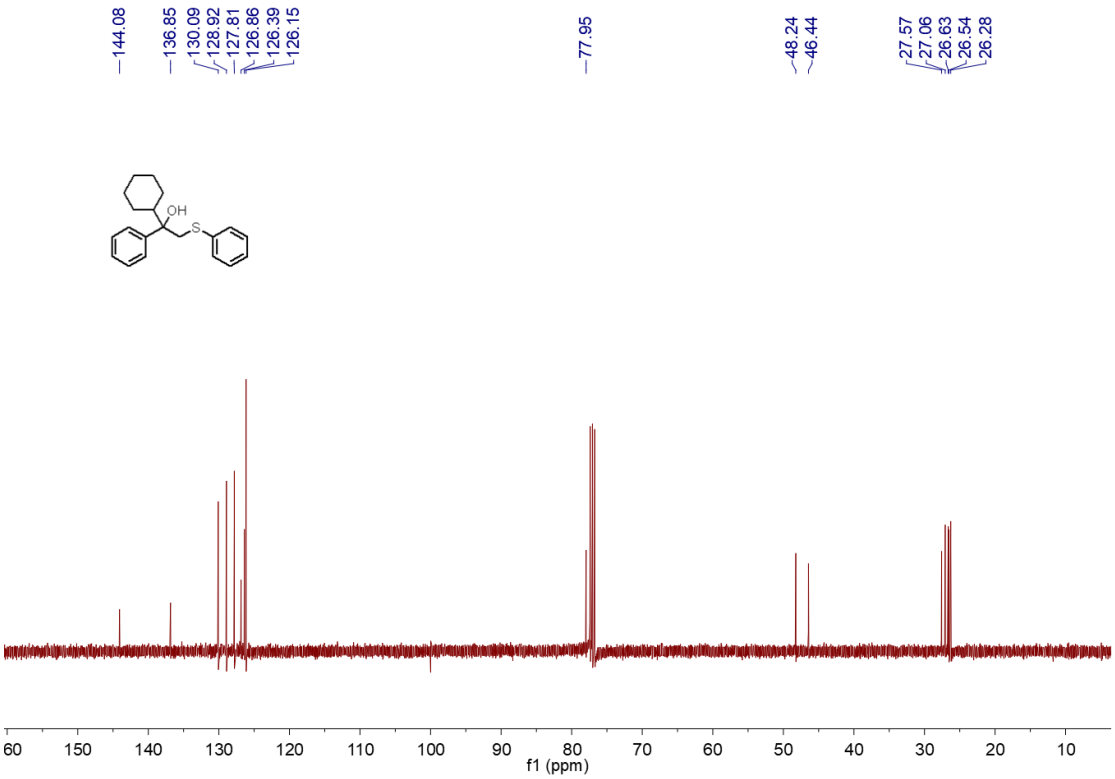
^{13}C NMR spectrum of c15



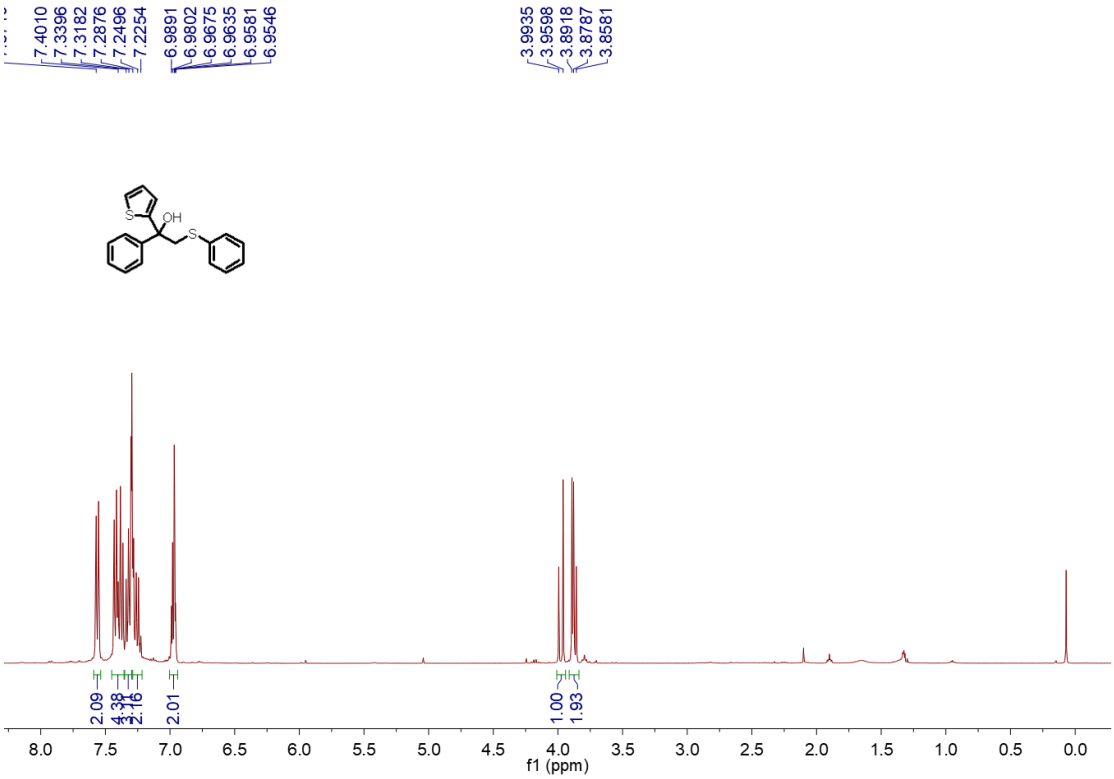
^{1}H NMR spectrum of c16



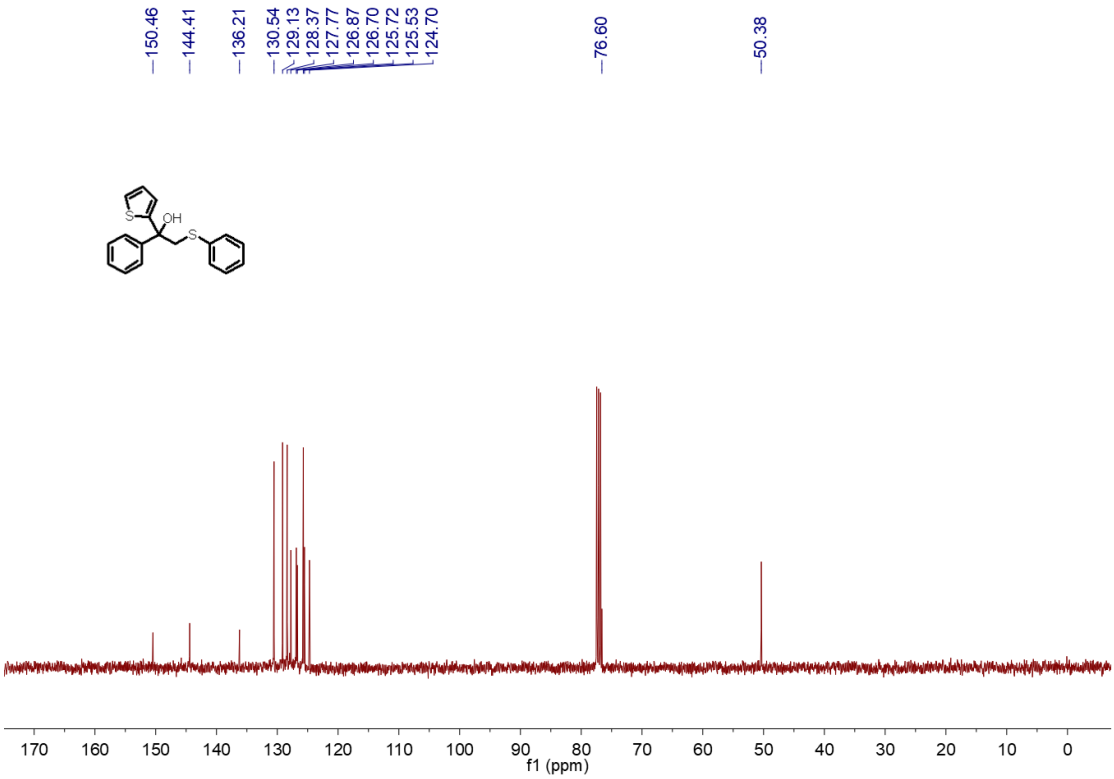
^{13}C NMR spectrum of c16



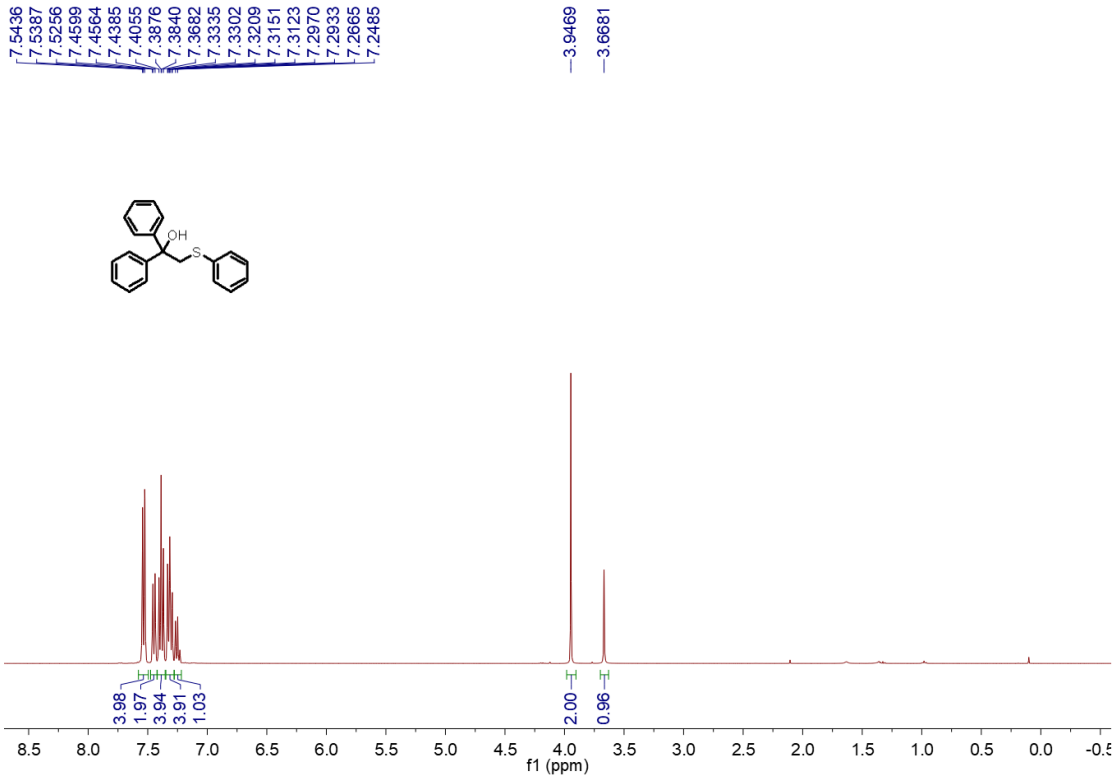
^{1}H NMR spectrum of c17



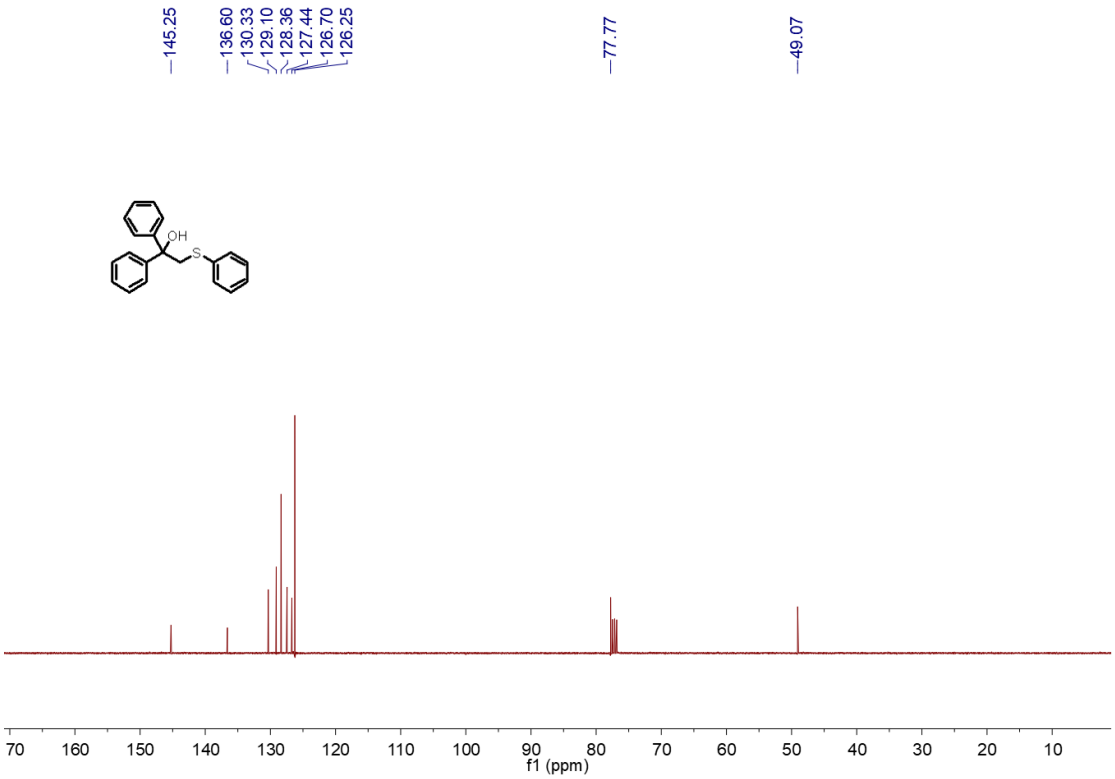
^{13}C NMR spectrum of c17



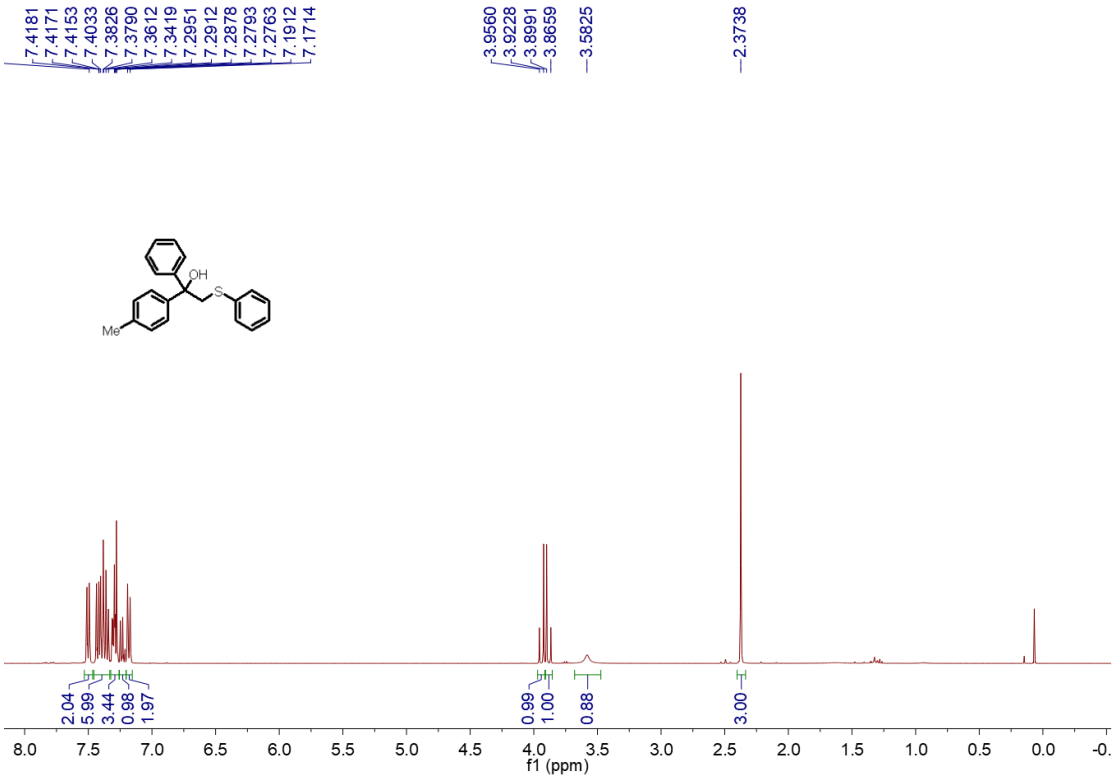
^{1}H NMR spectrum of c18



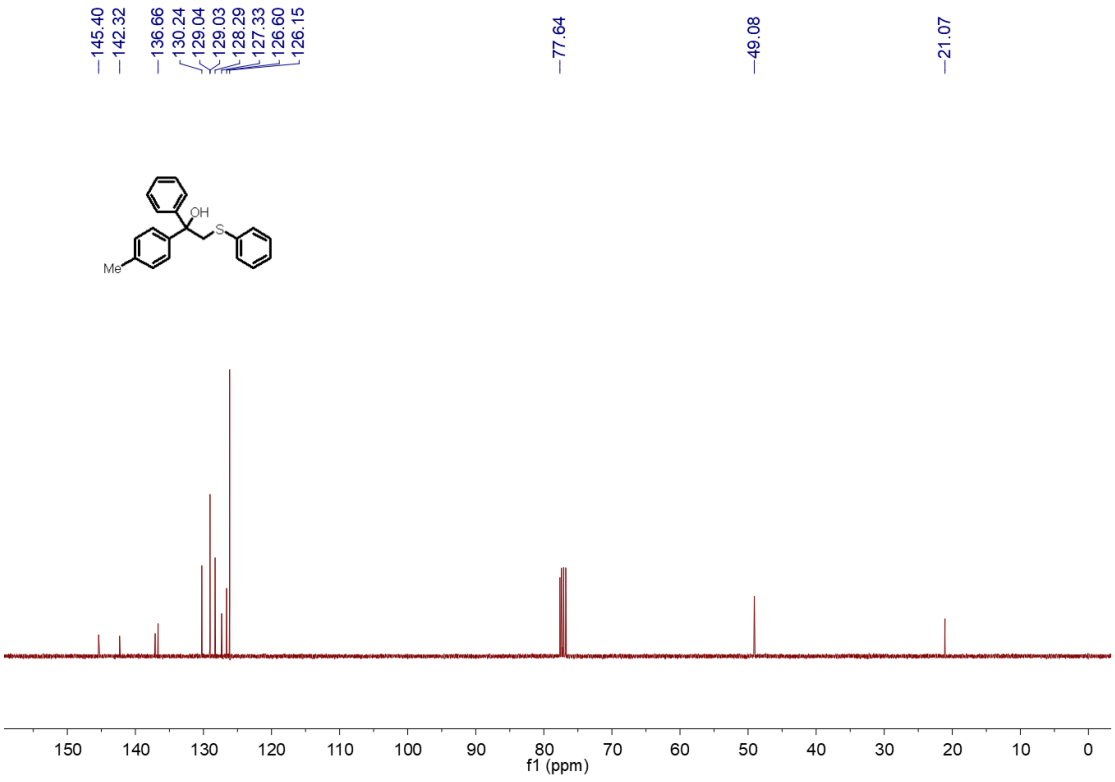
^{13}C NMR spectrum of c18



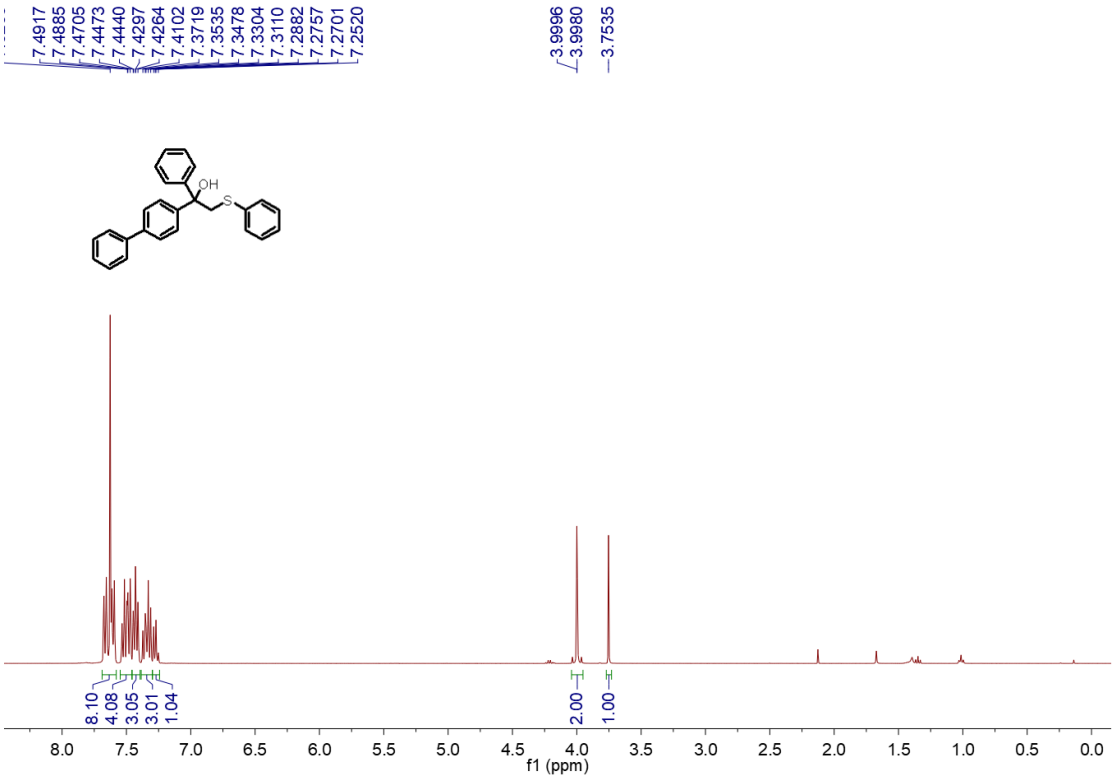
^{1}H NMR spectrum of c19



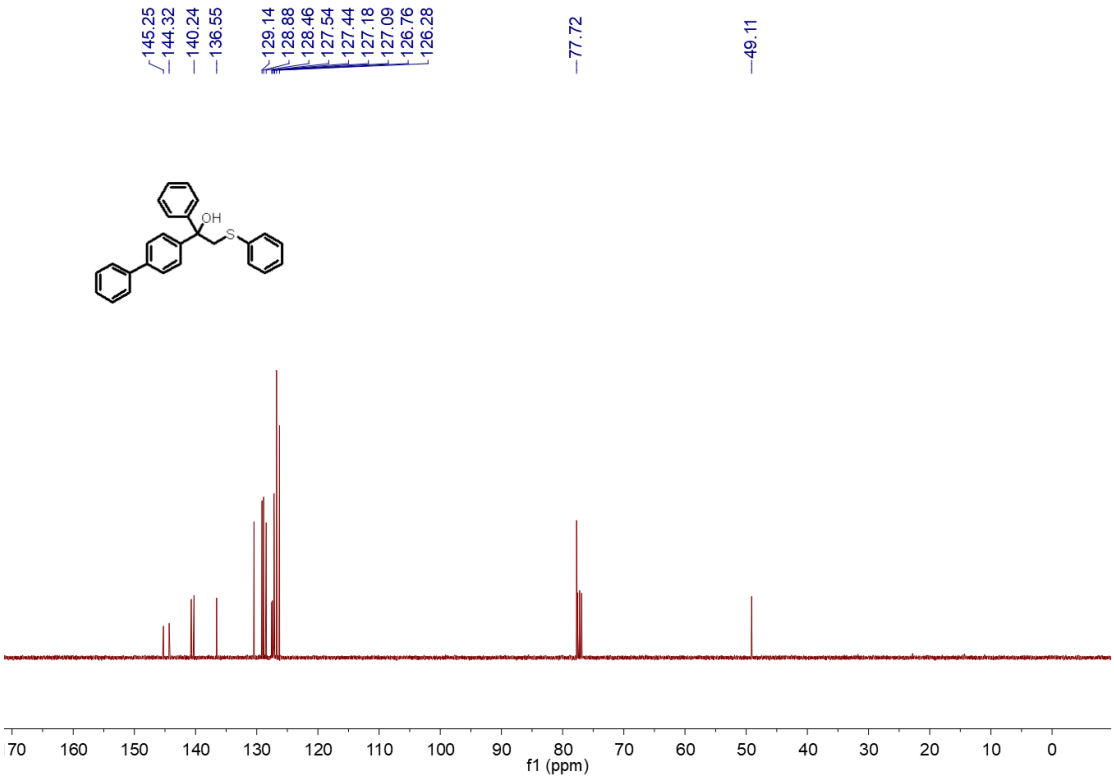
^{13}C NMR spectrum of c19



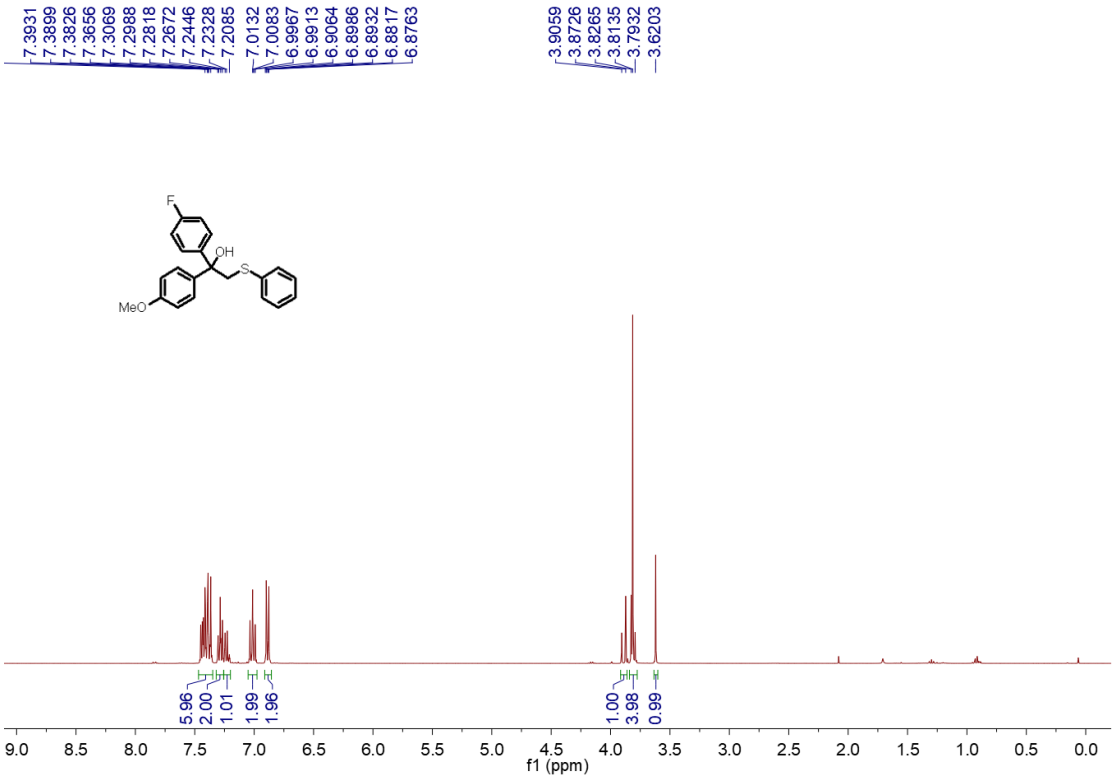
^{1}H NMR spectrum of c20



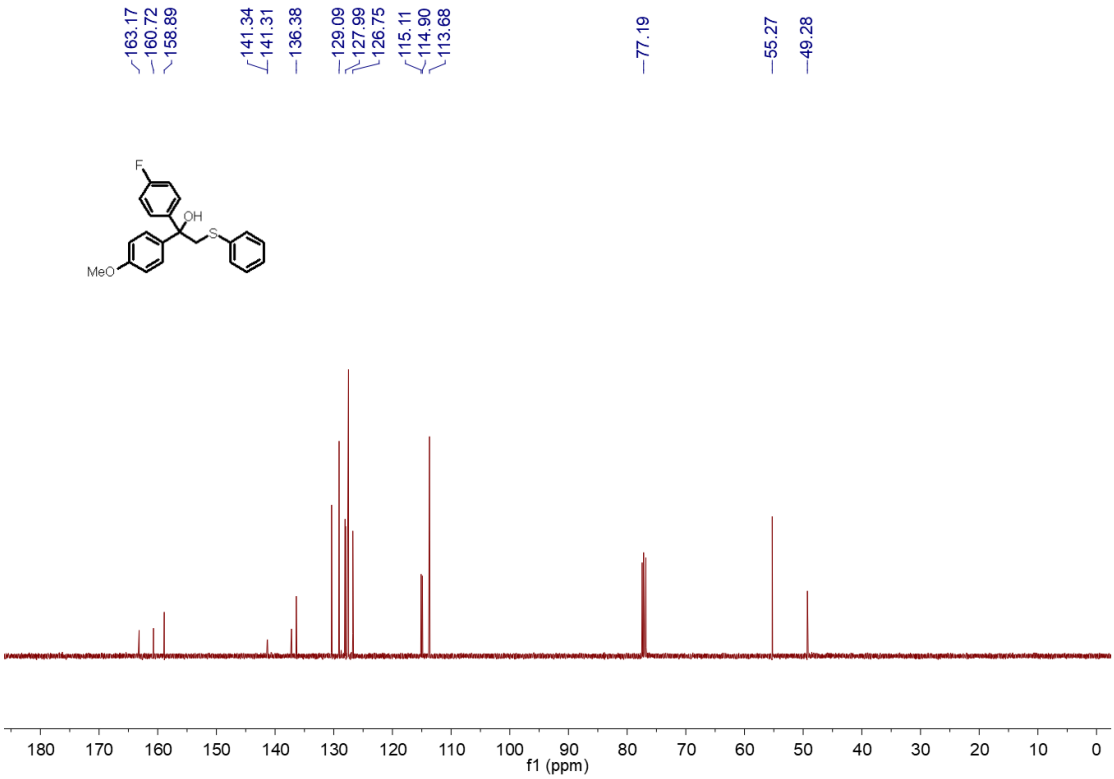
^{13}C NMR spectrum of c20



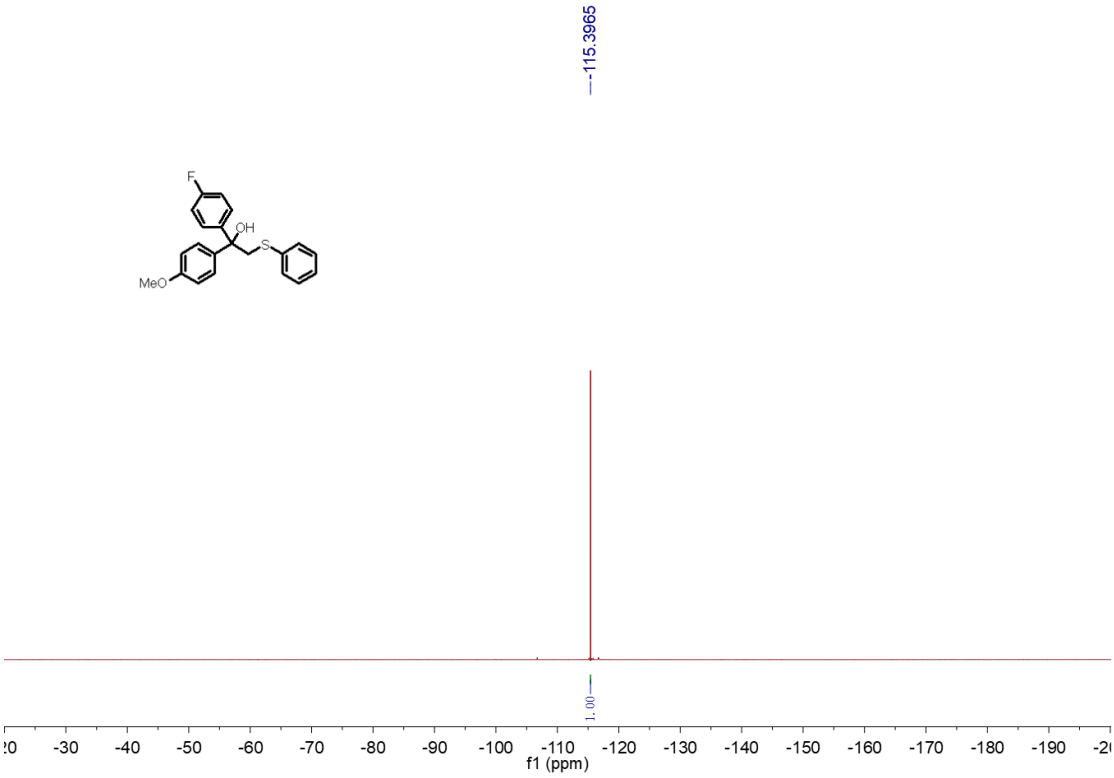
^{1}H NMR spectrum of c21



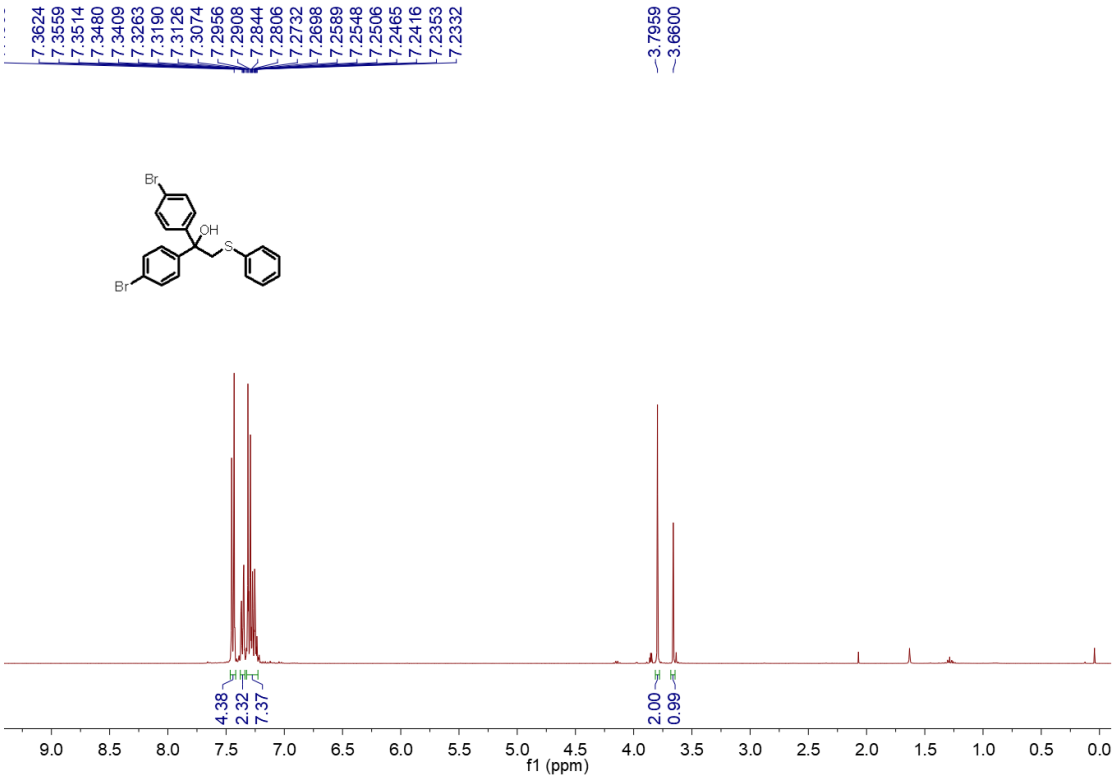
^{13}C NMR spectrum of c21



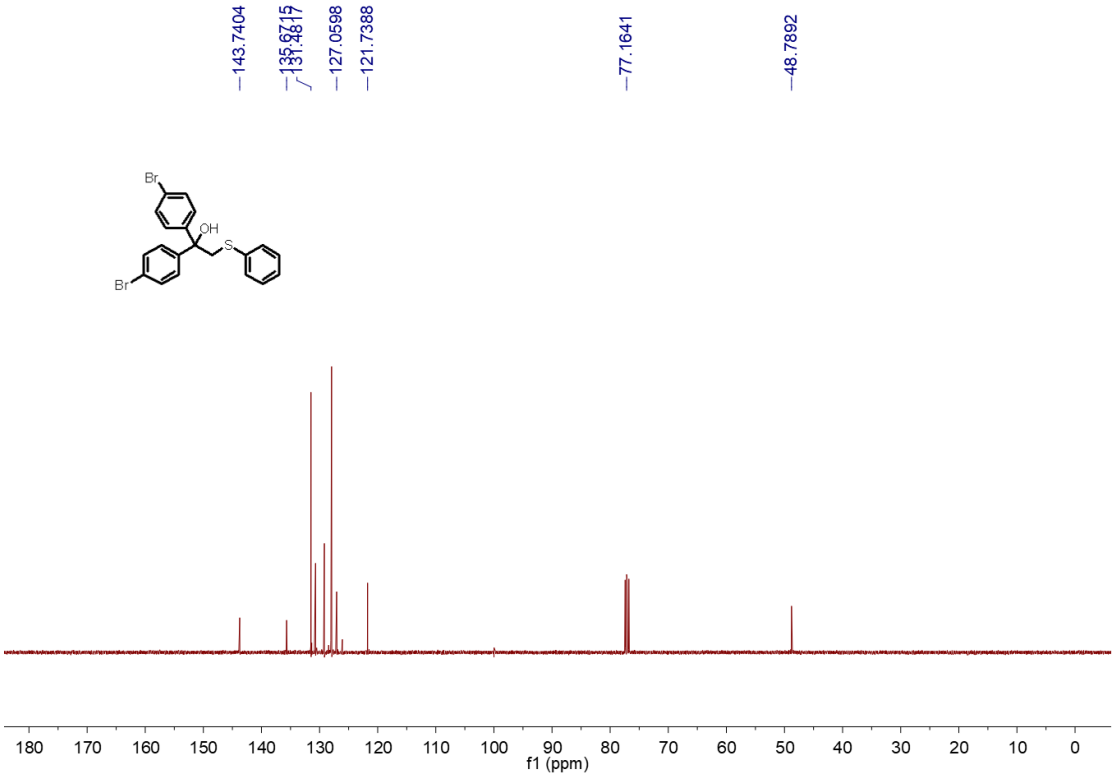
^{19}F NMR spectrum of c21



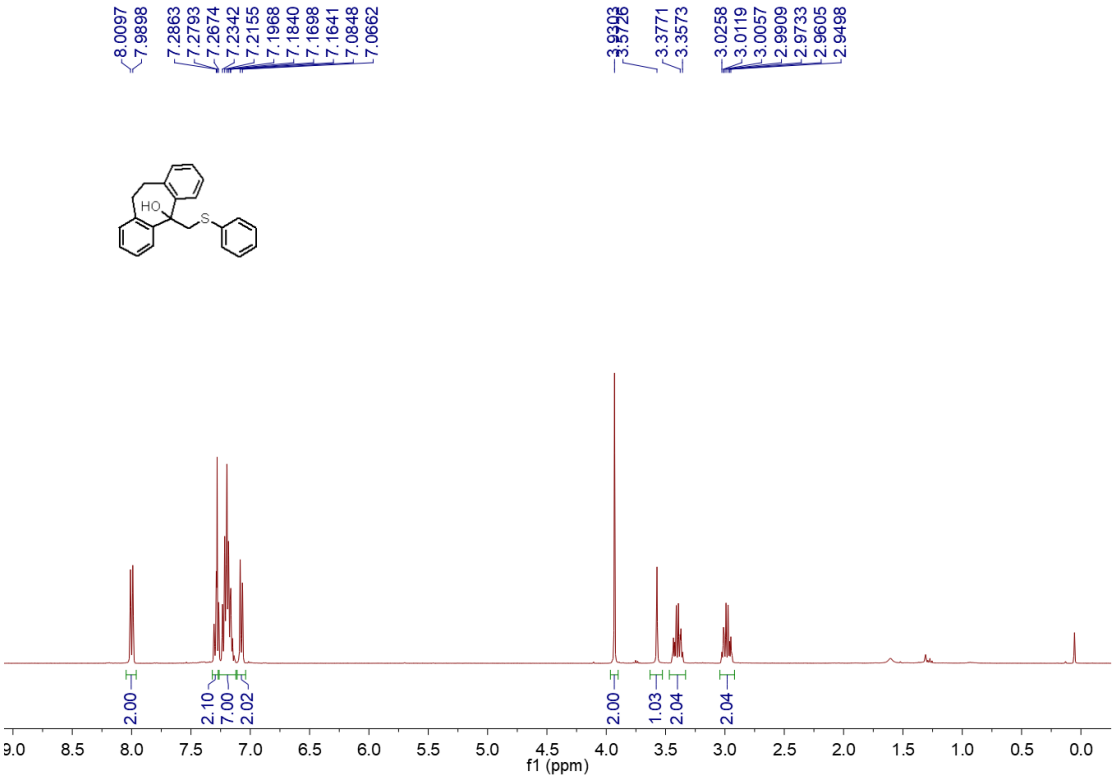
^{1}H NMR spectrum of c22



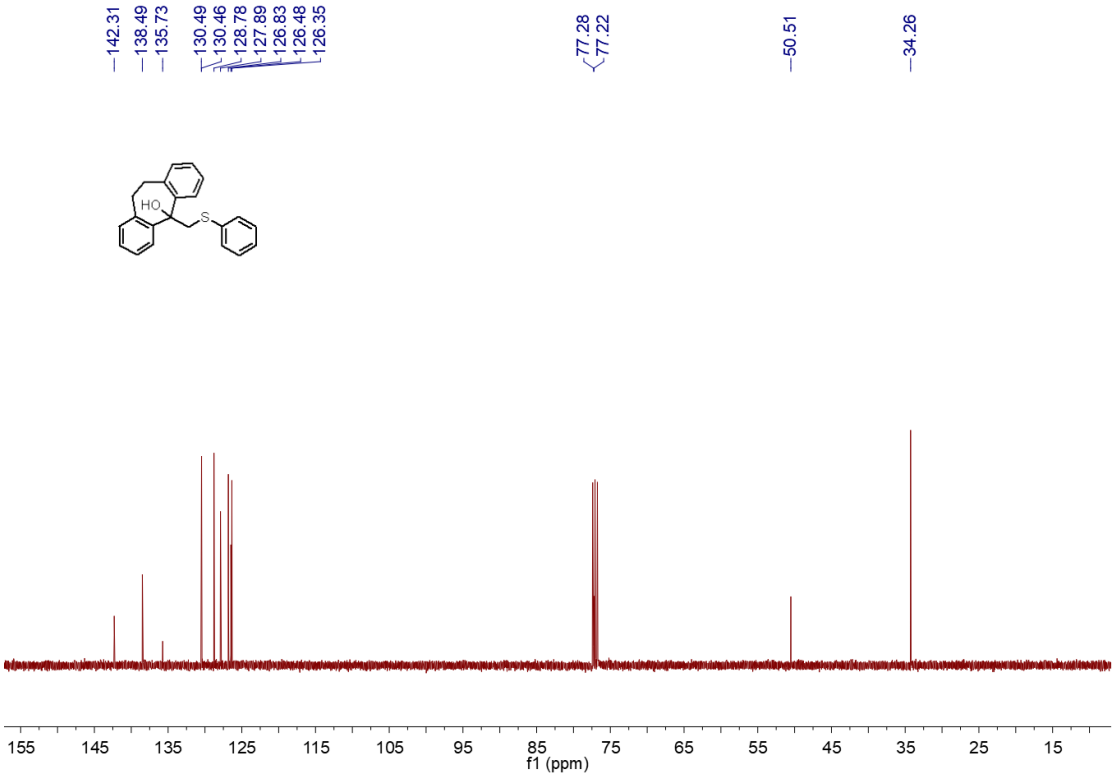
^{13}C NMR spectrum of c22



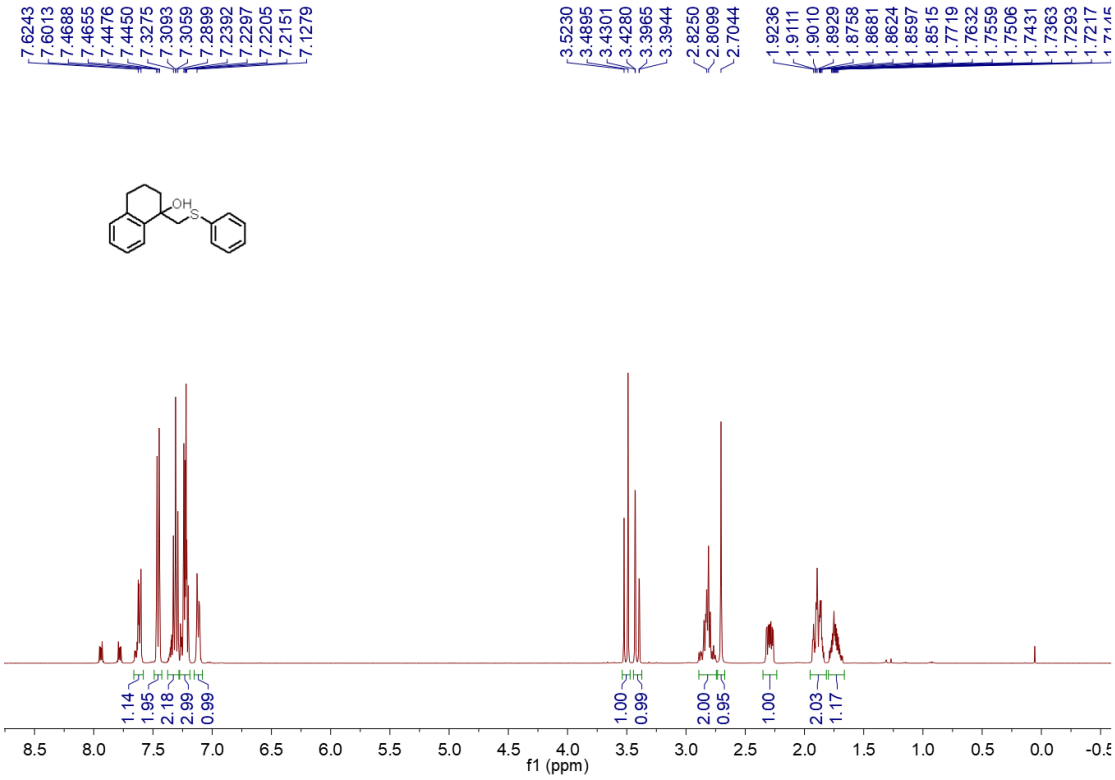
^{1}H NMR spectrum of c23



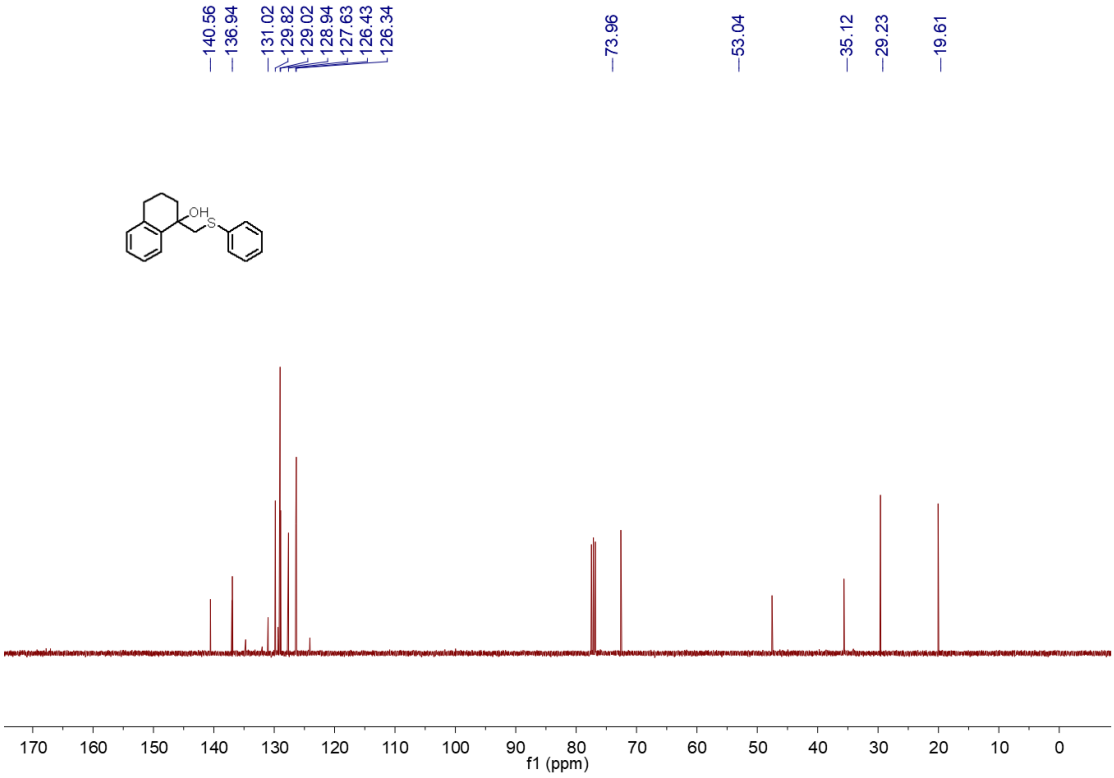
^{13}C NMR spectrum of c23



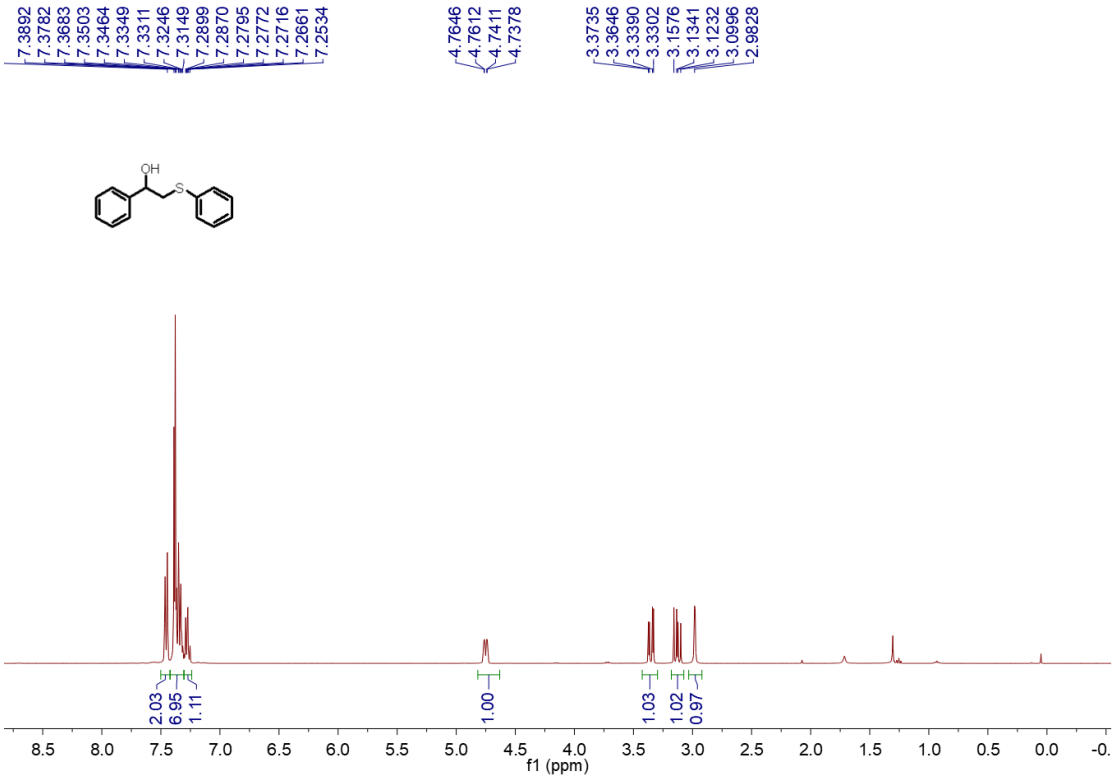
^{1}H NMR spectrum of c24



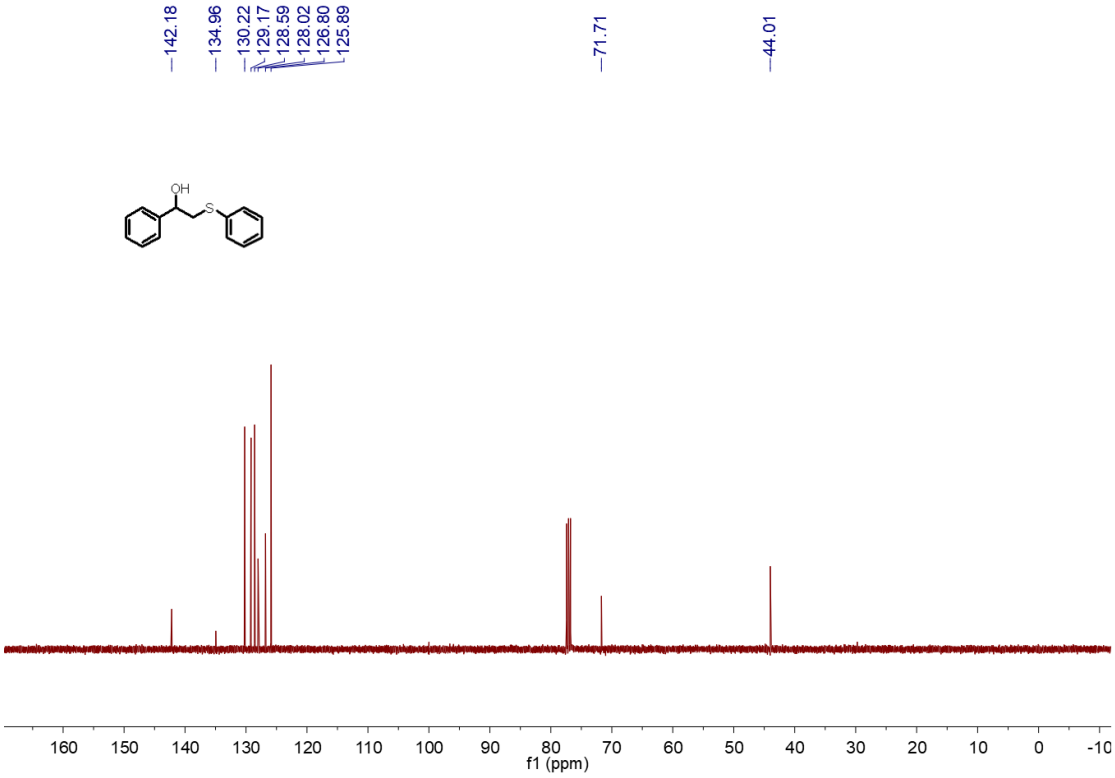
^{13}C NMR spectrum of c24



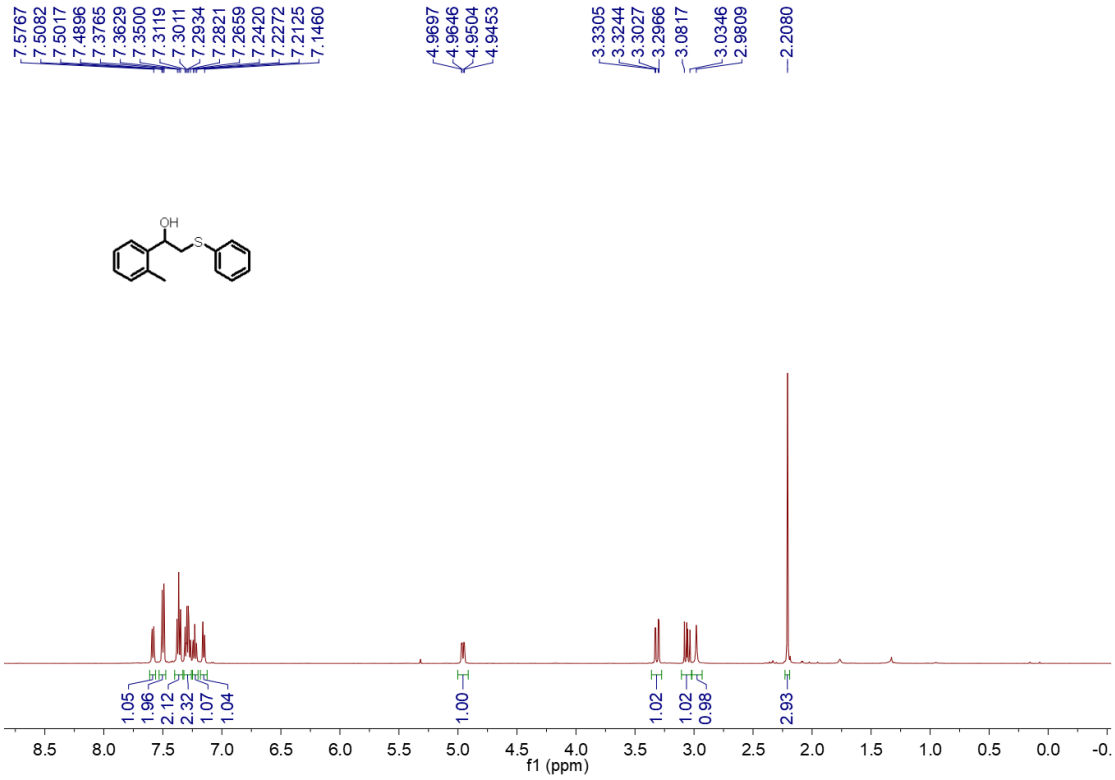
^{1}H NMR spectrum of c25



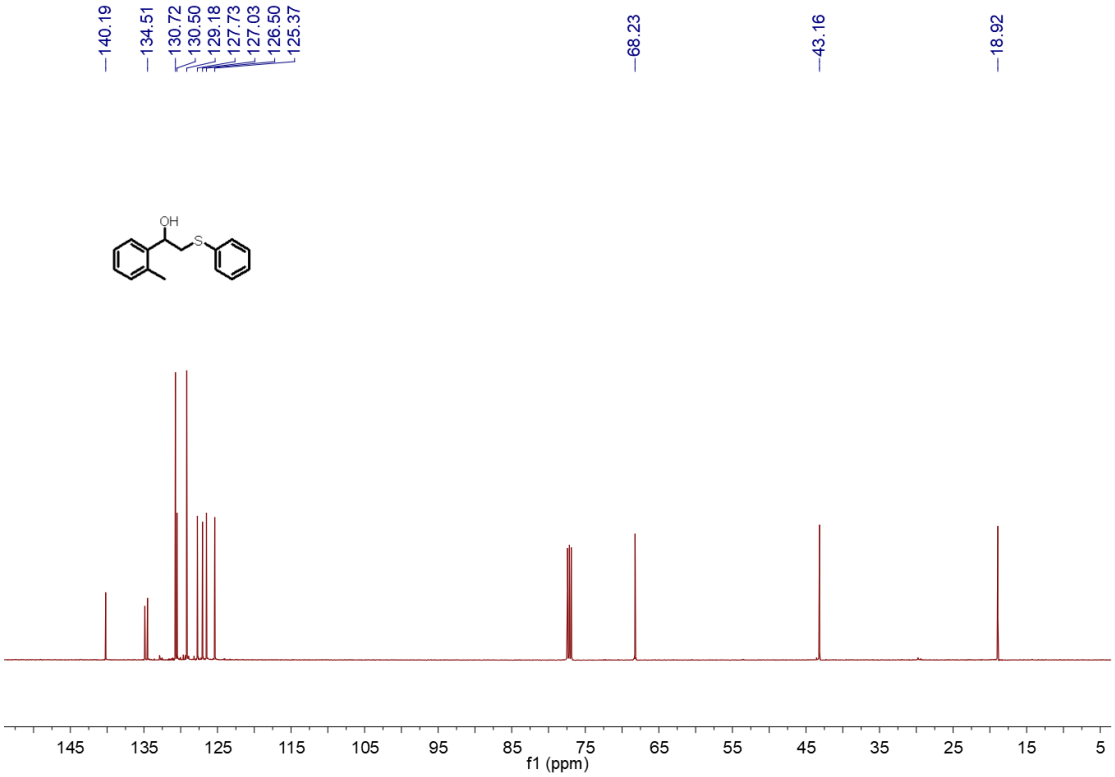
^{13}C NMR spectrum of c25



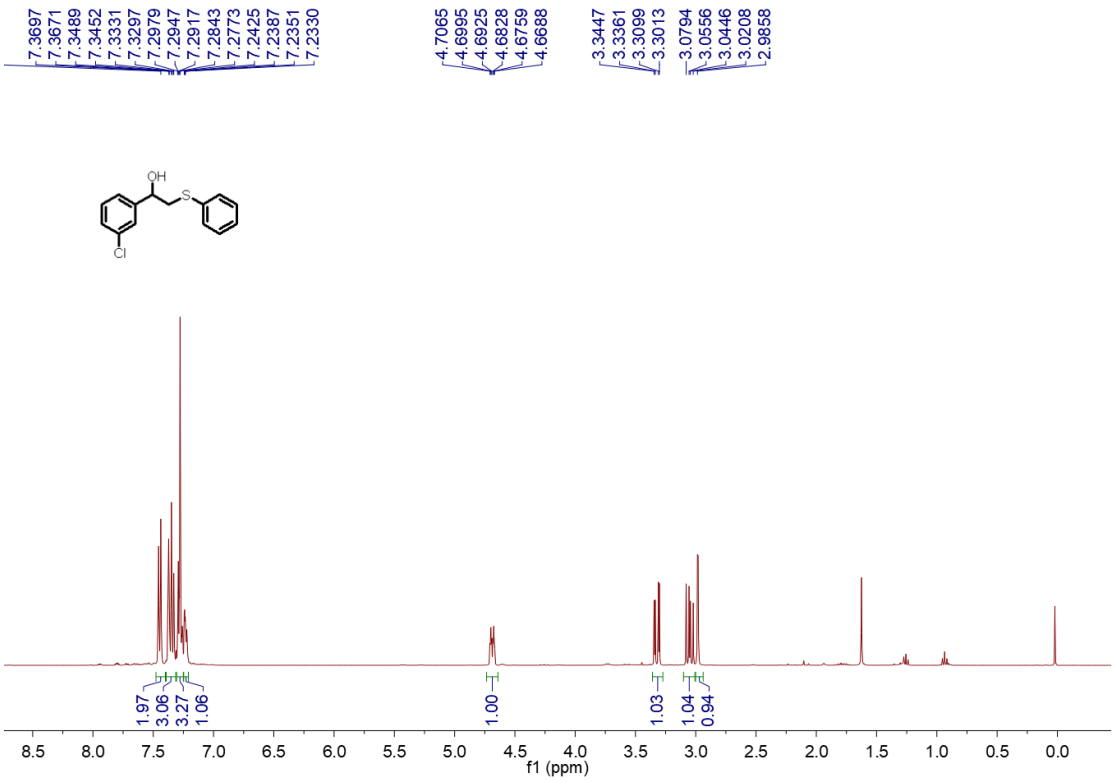
^{1}H NMR spectrum of c26



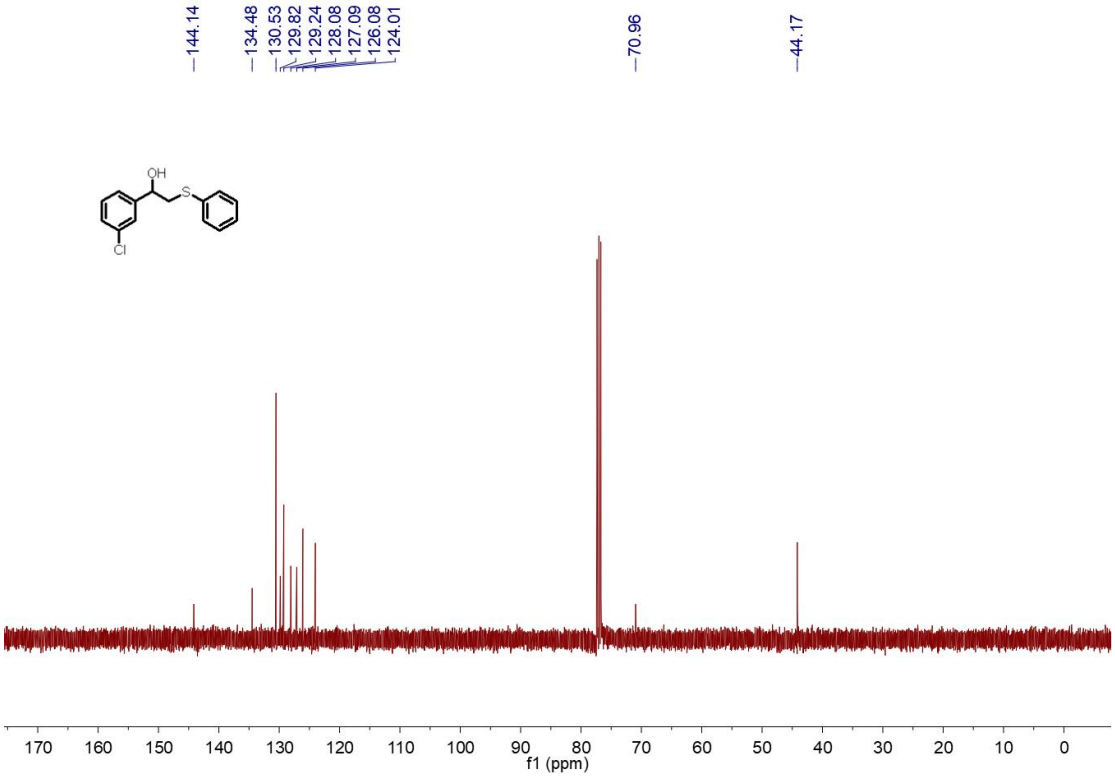
^{13}C NMR spectrum of c26



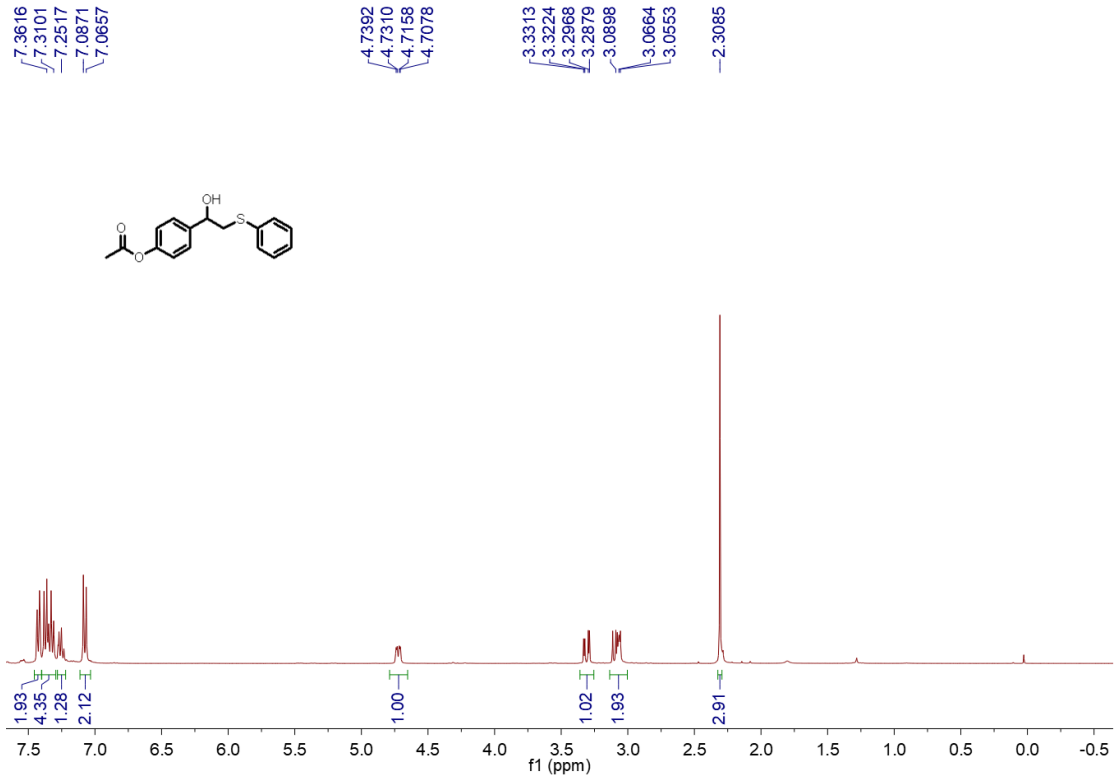
^{1}H NMR spectrum of c27



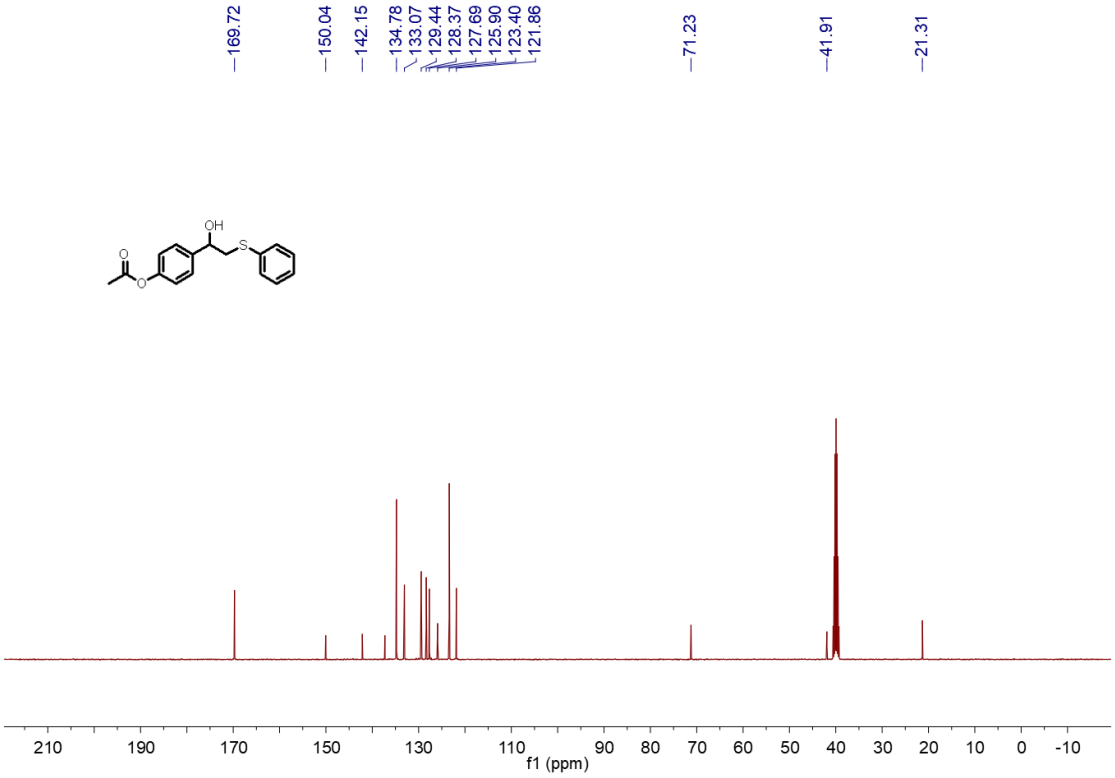
^{13}C NMR spectrum of c27



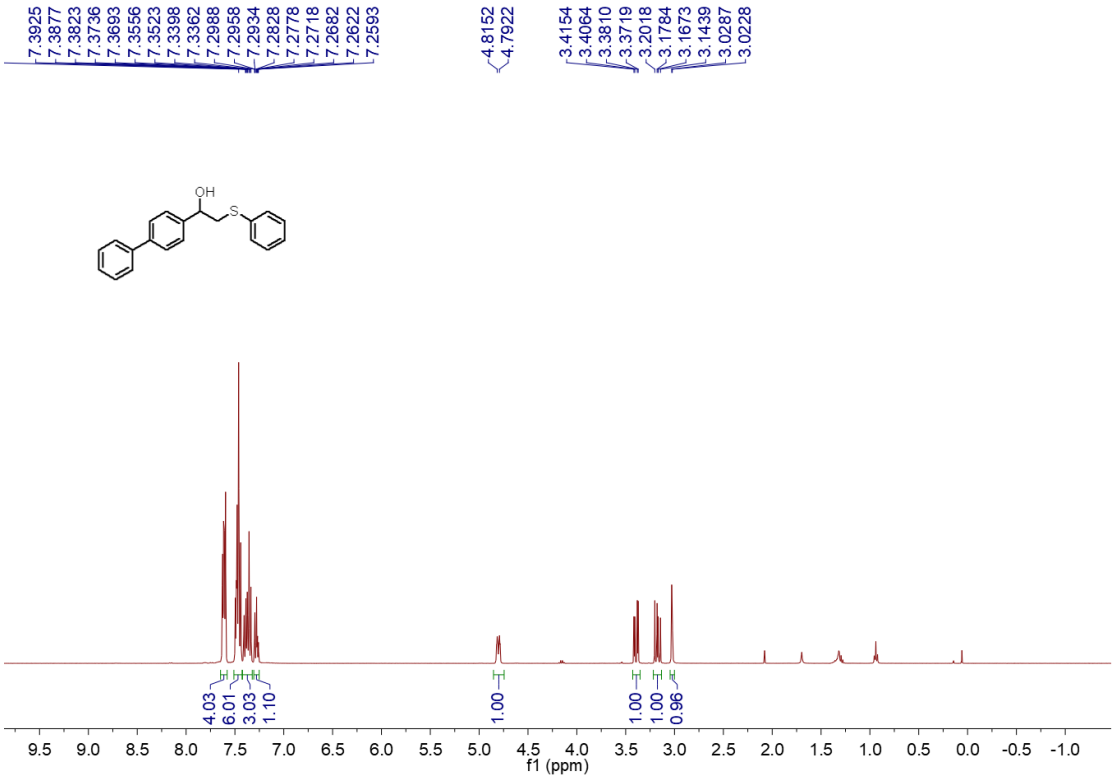
^{1}H NMR spectrum of c28



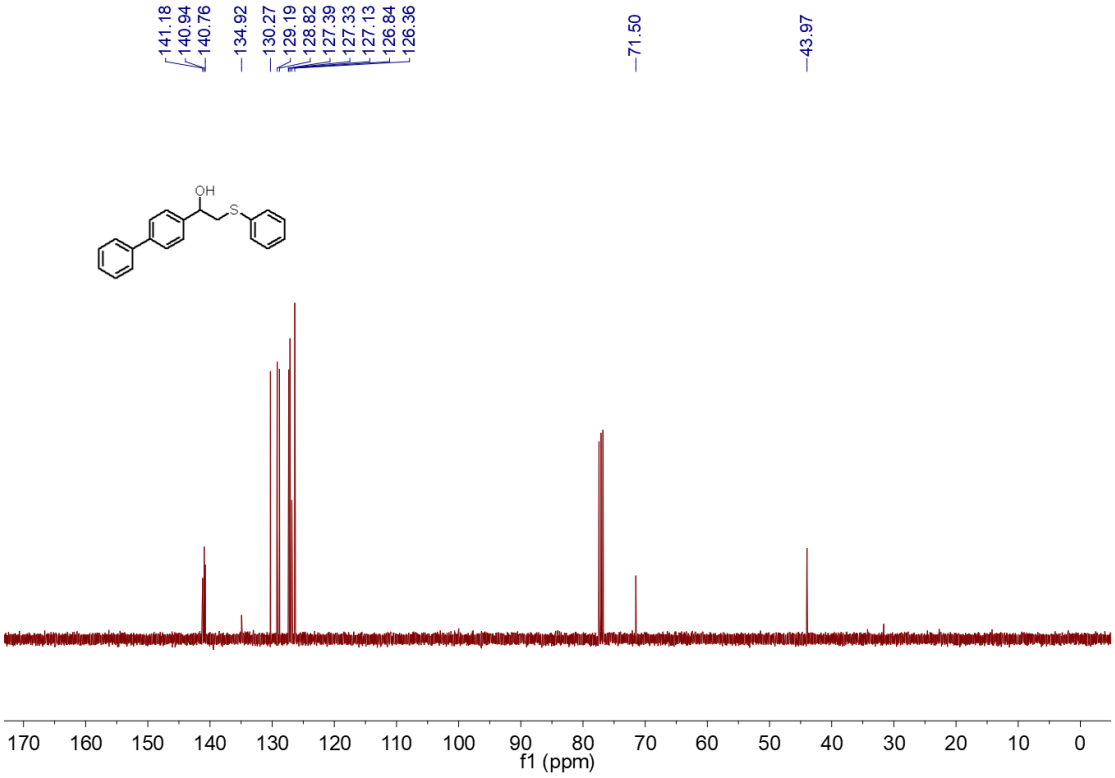
^{13}C NMR spectrum of c28



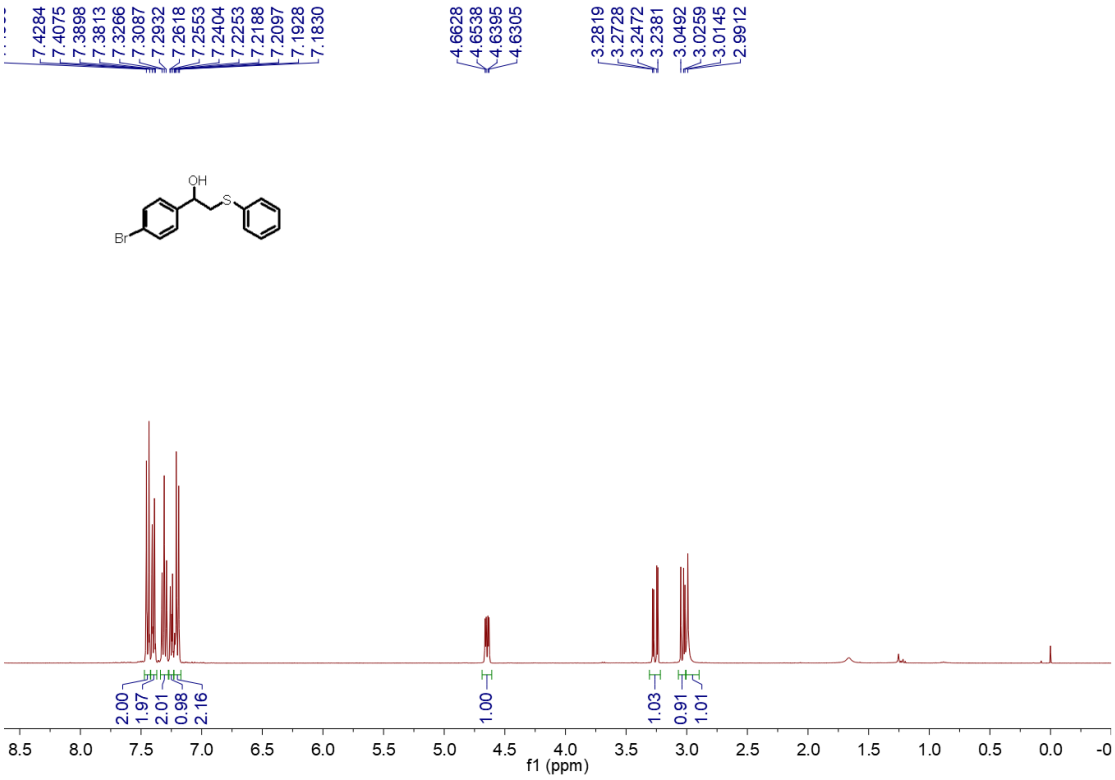
^{1}H NMR spectrum of c29



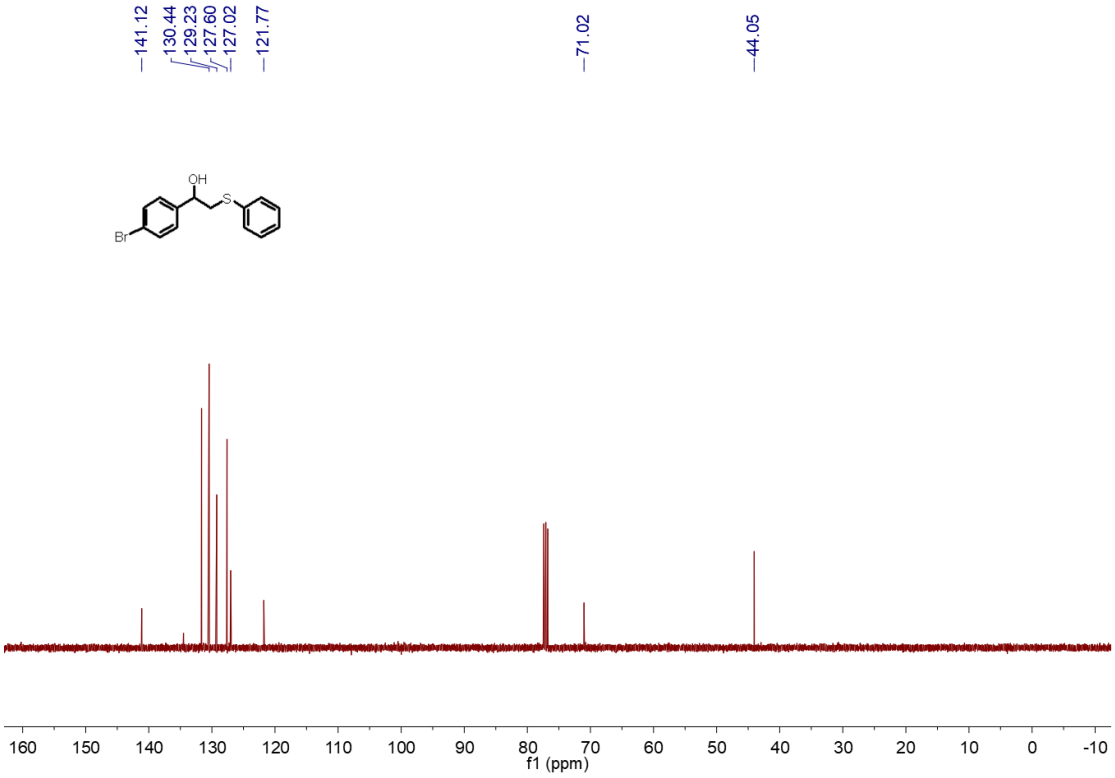
^{13}C NMR spectrum of c29



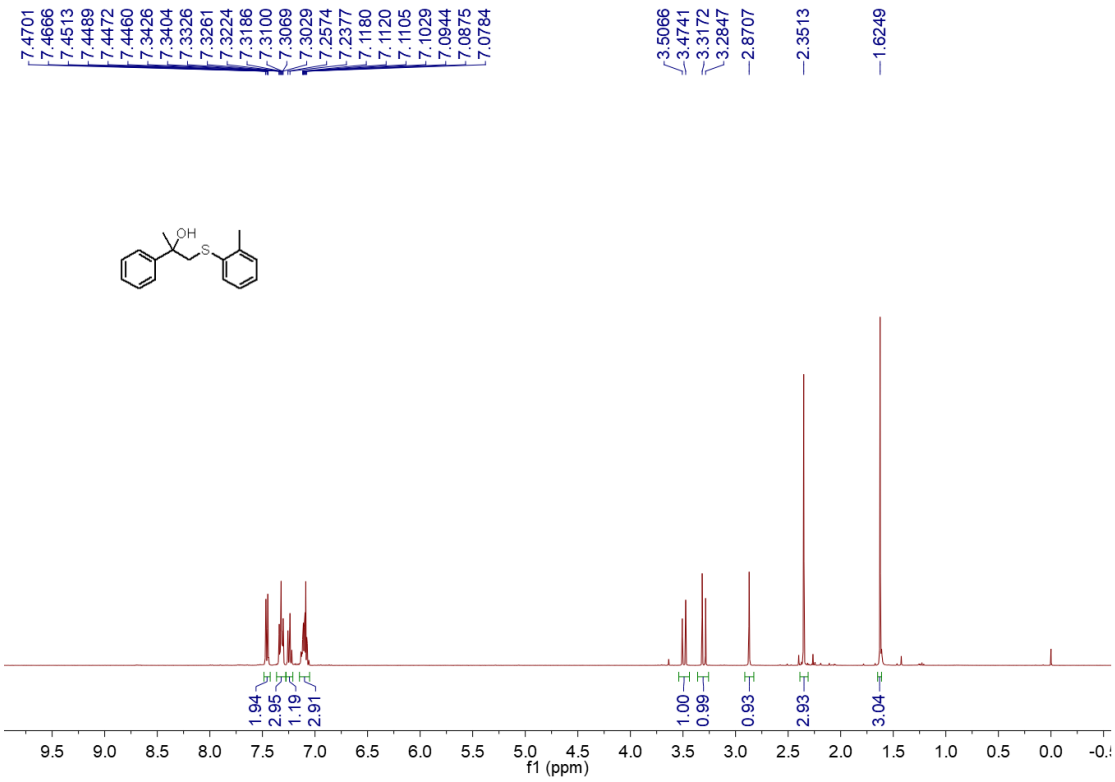
^{1}H NMR spectrum of c30



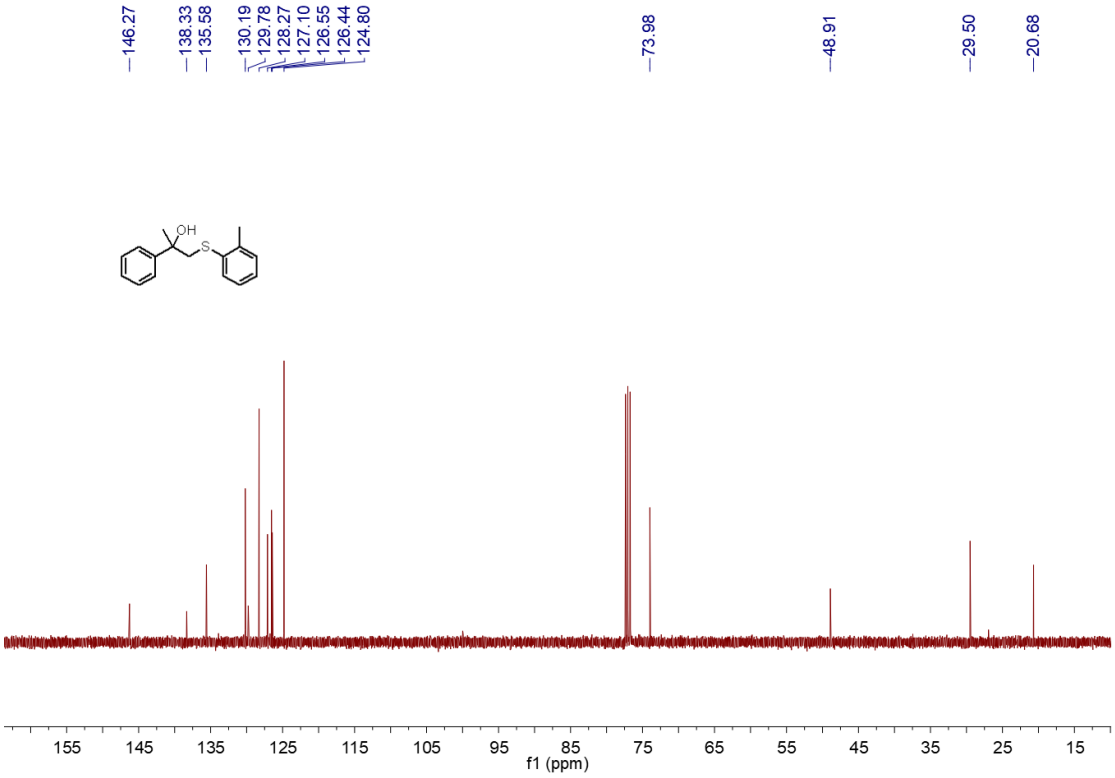
^{13}C NMR spectrum of c30



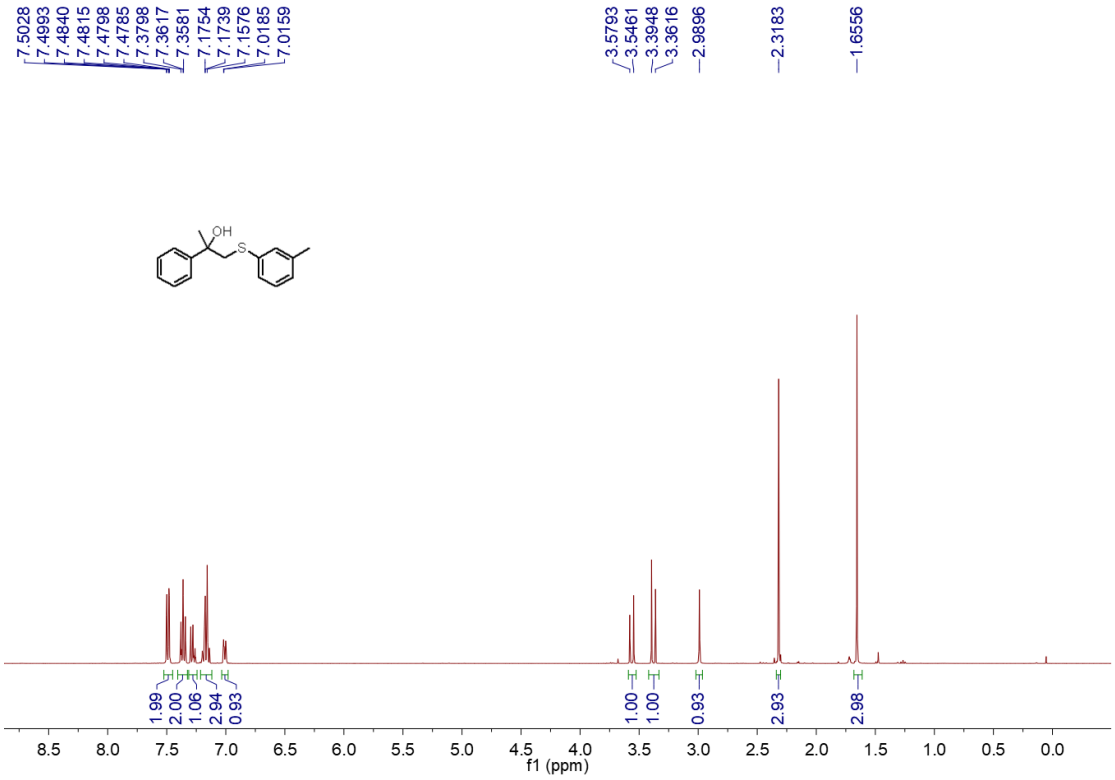
^{1}H NMR spectrum of c34



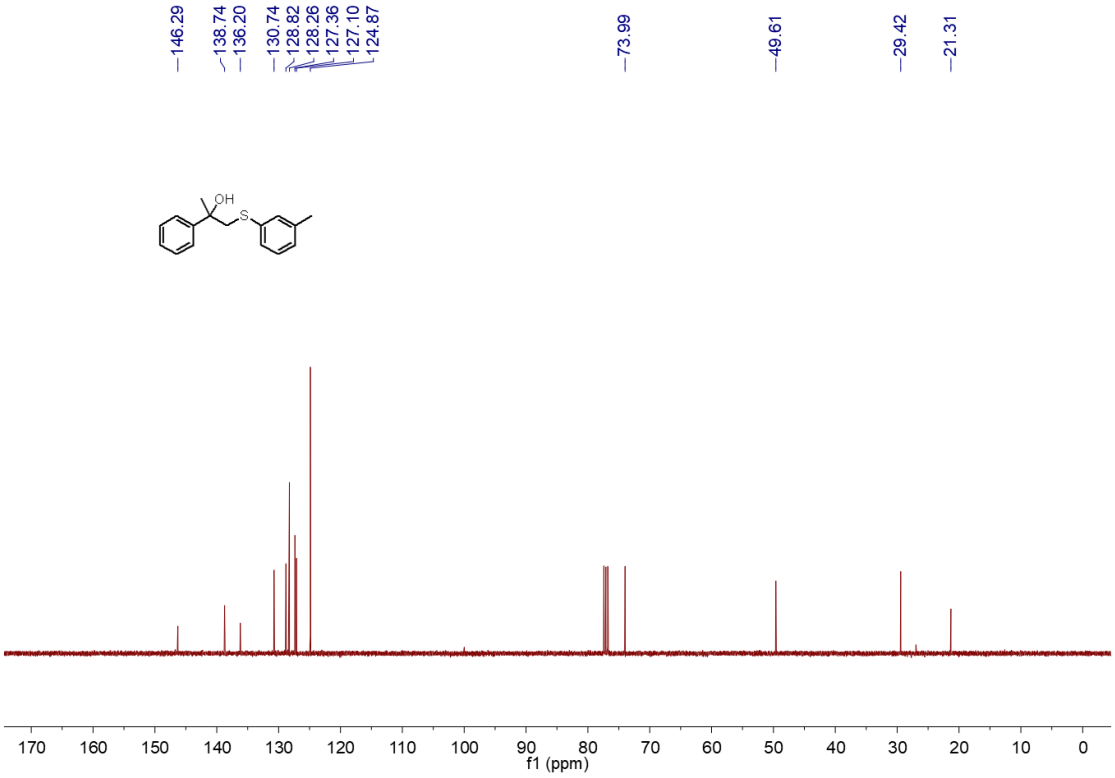
^{13}C NMR spectrum of c34



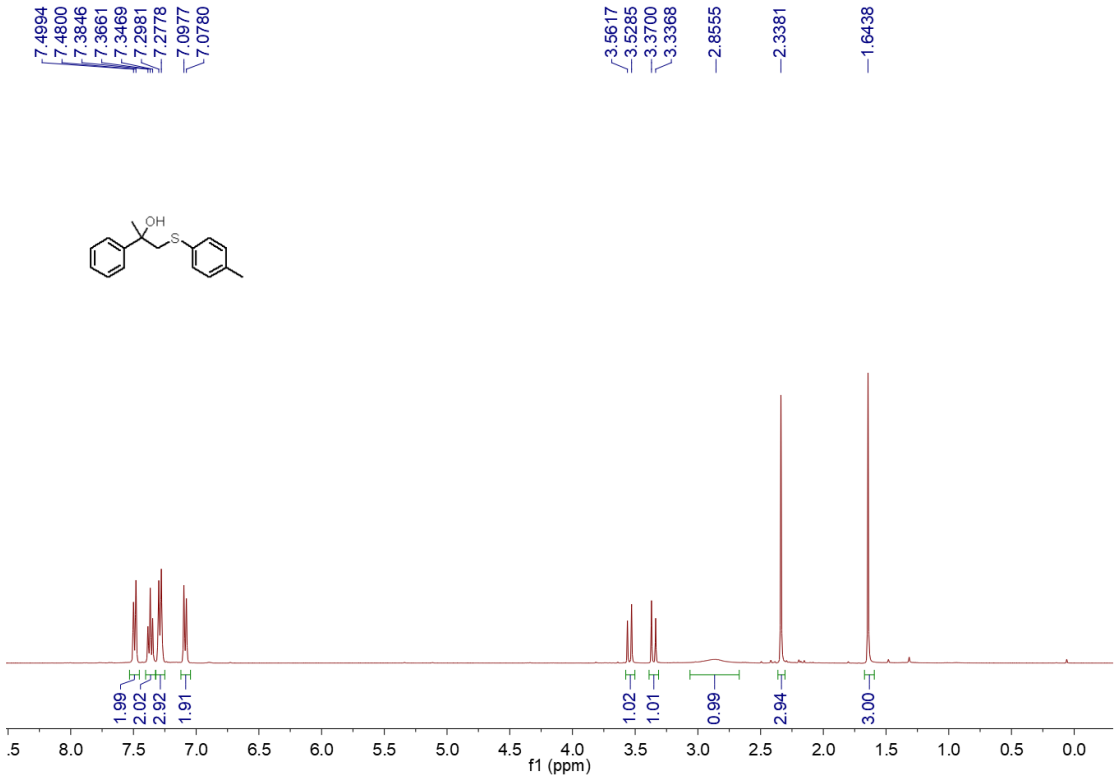
^{1}H NMR spectrum of c35



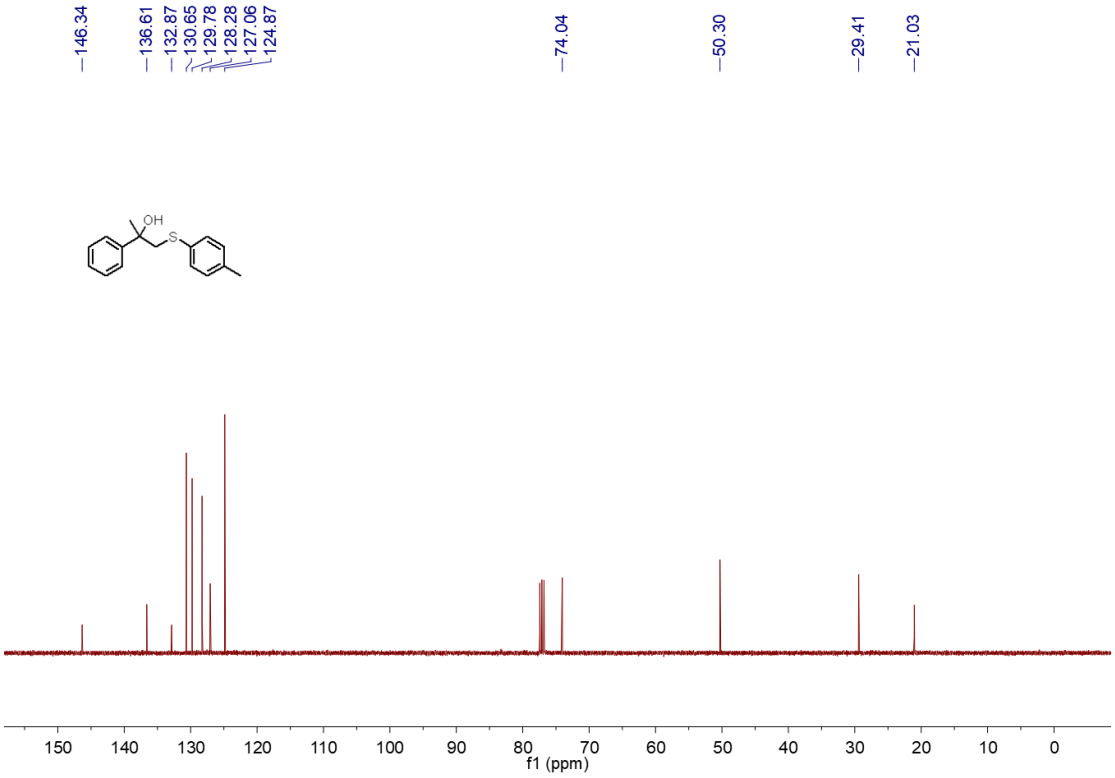
^{13}C NMR spectrum of c35



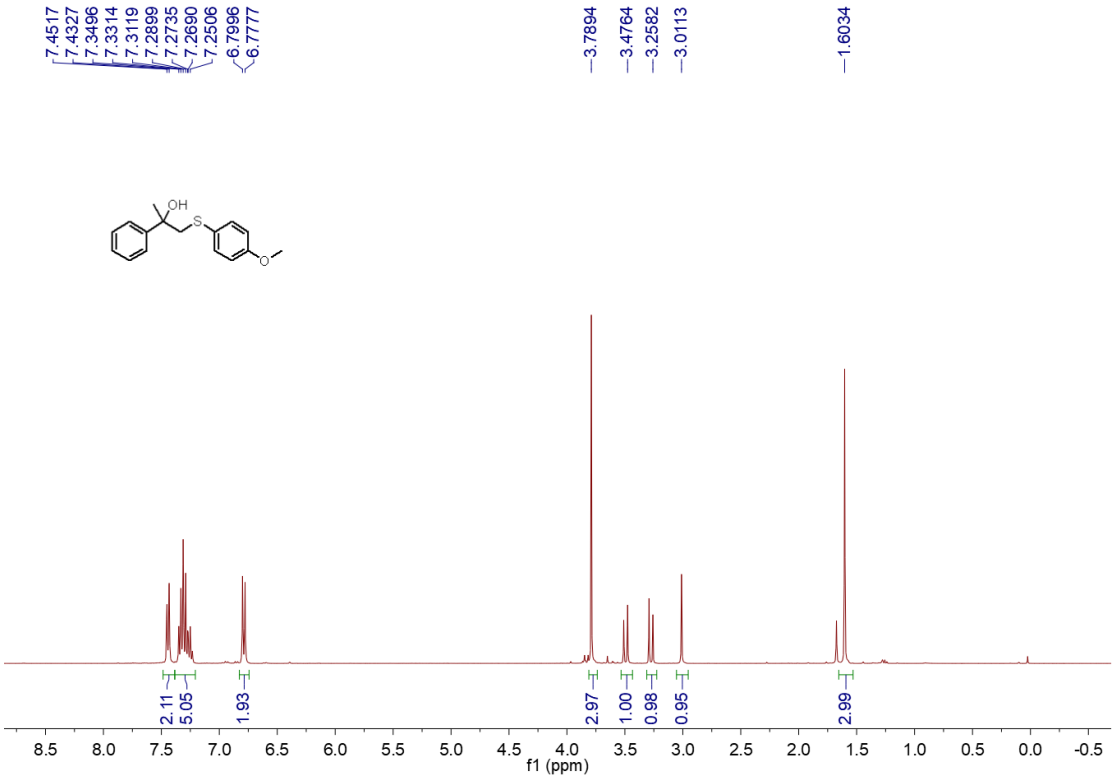
^{1}H NMR spectrum of c36



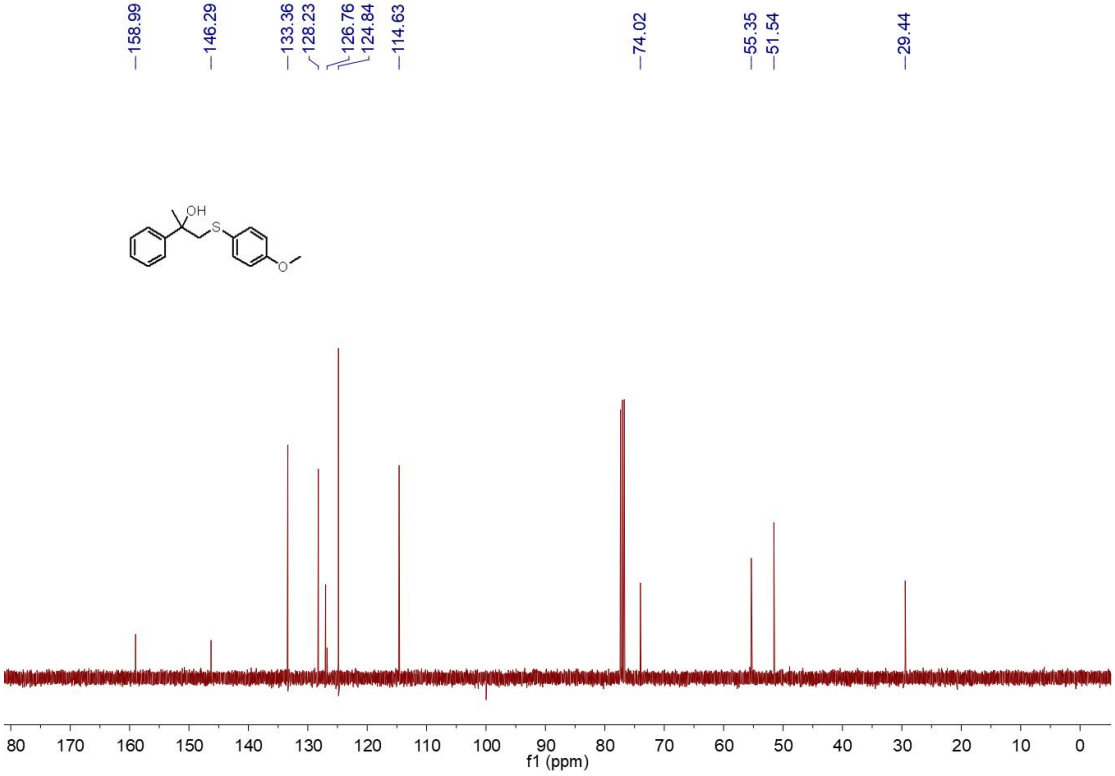
^{13}C NMR spectrum of c36



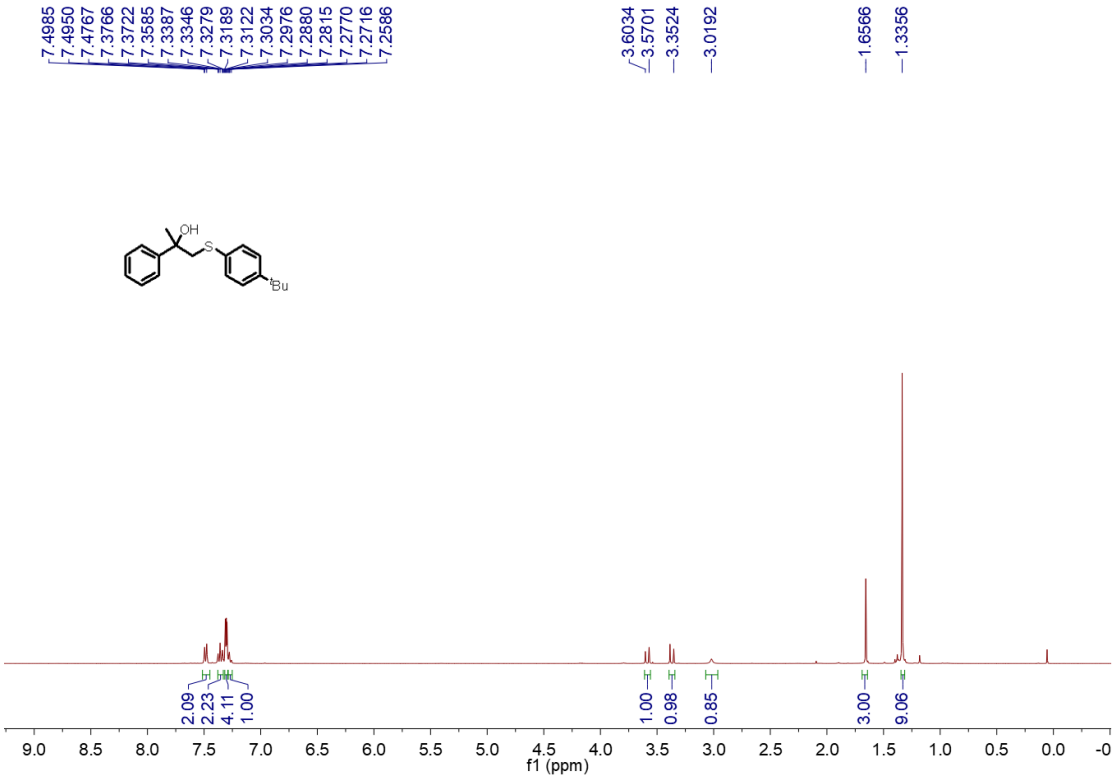
^{1}H NMR spectrum of c37



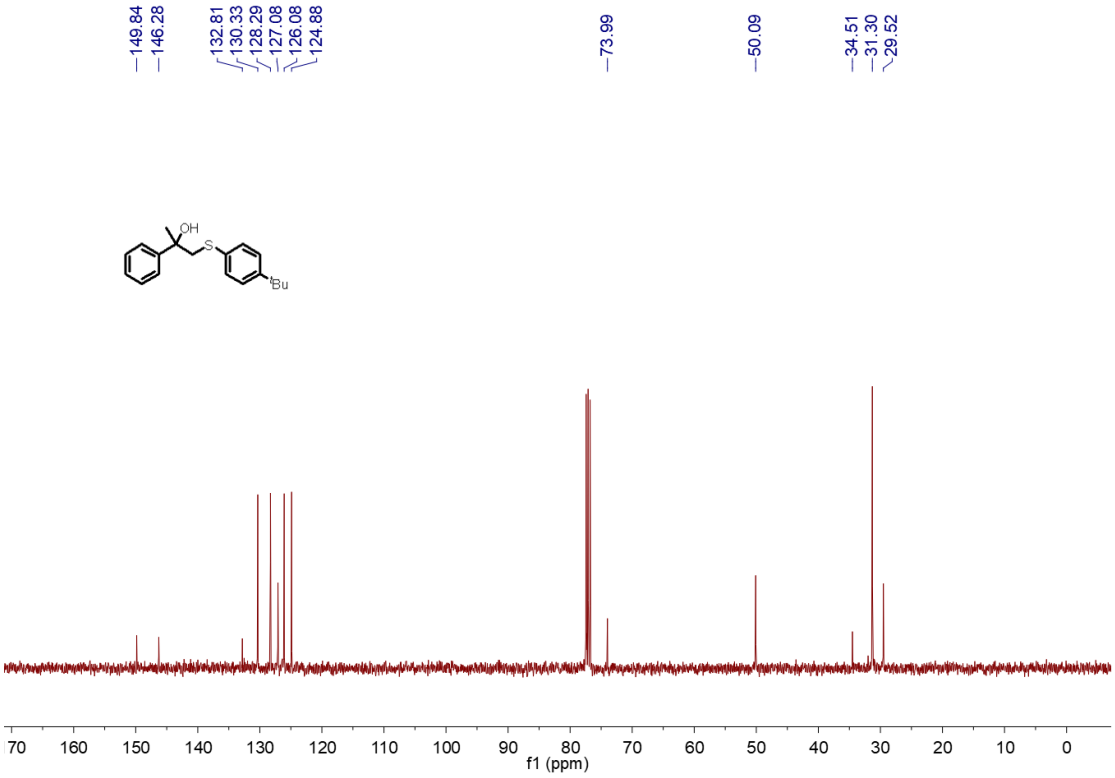
^{13}C NMR spectrum of c37



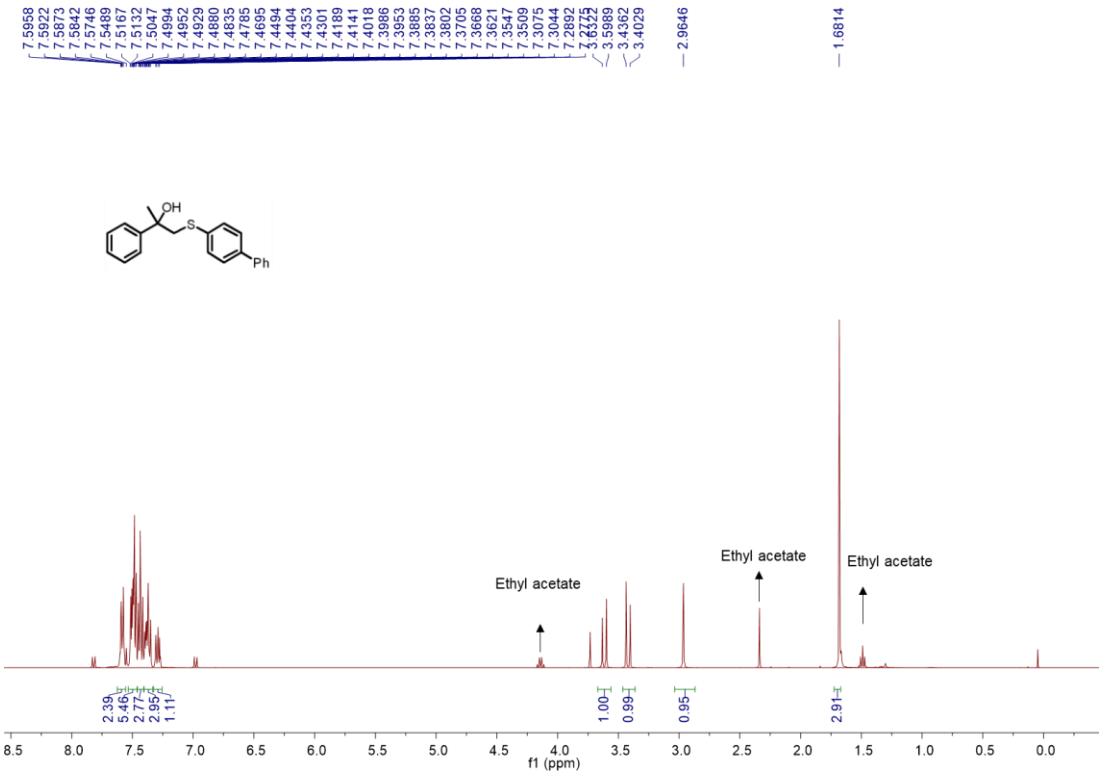
^{1}H NMR spectrum of c38



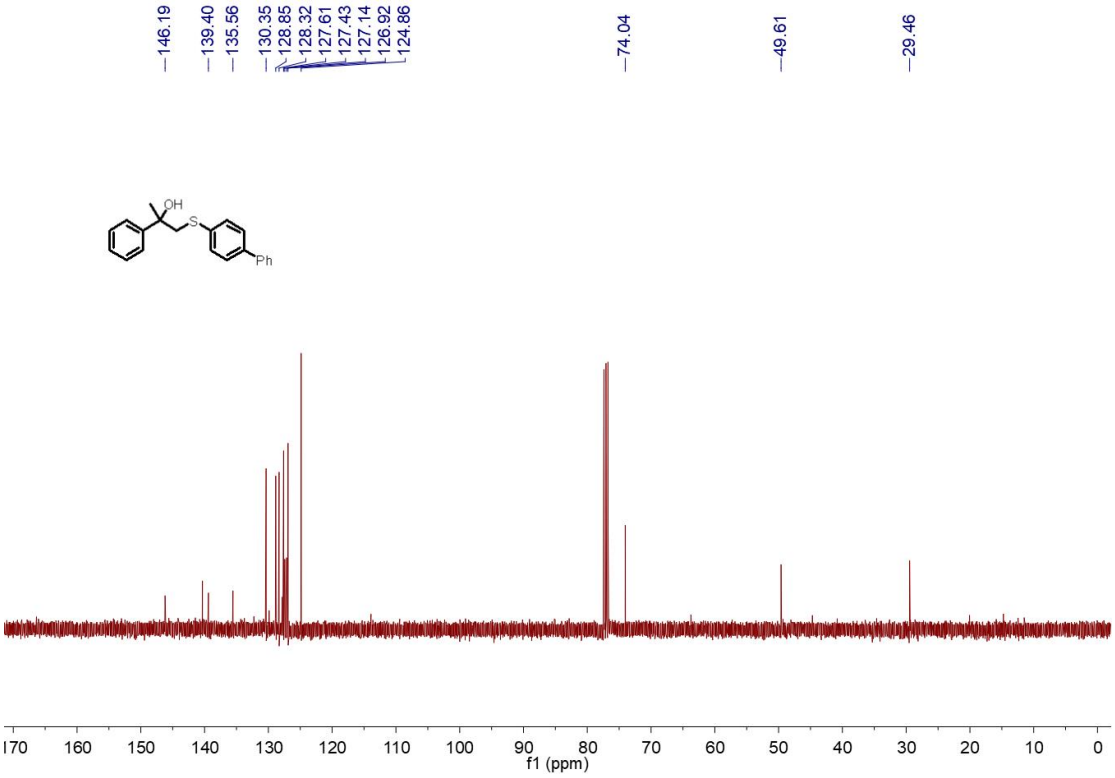
^{13}C NMR spectrum of c38



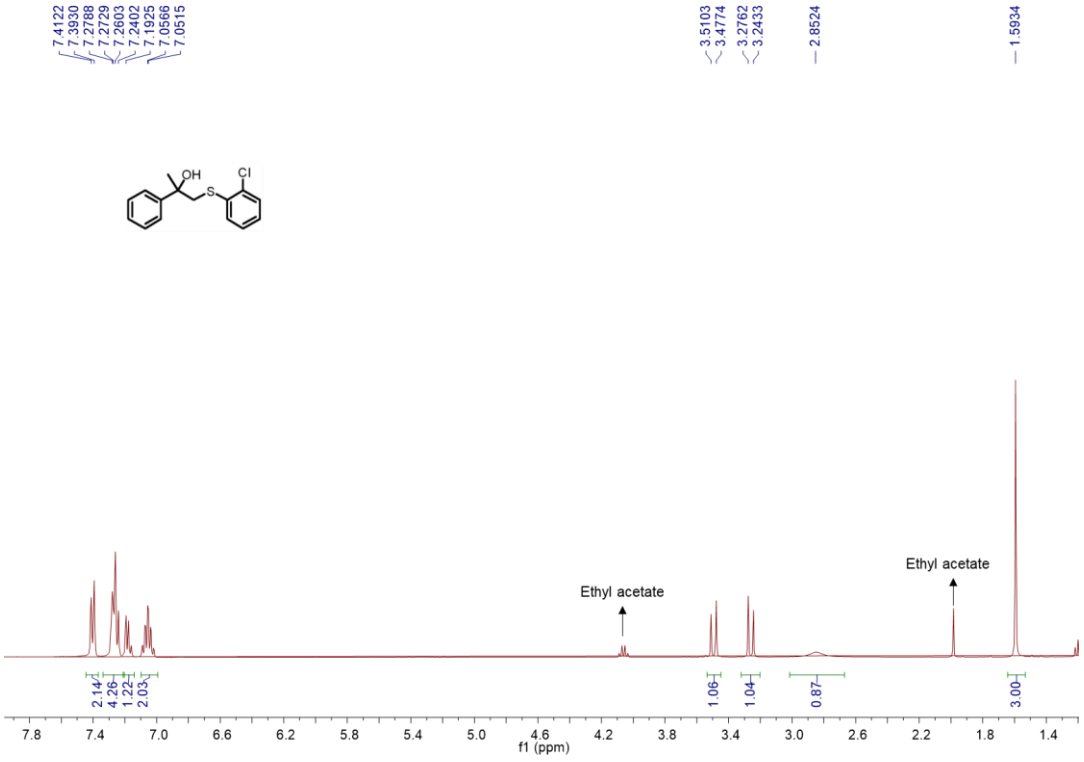
^{1}H NMR spectrum of c39



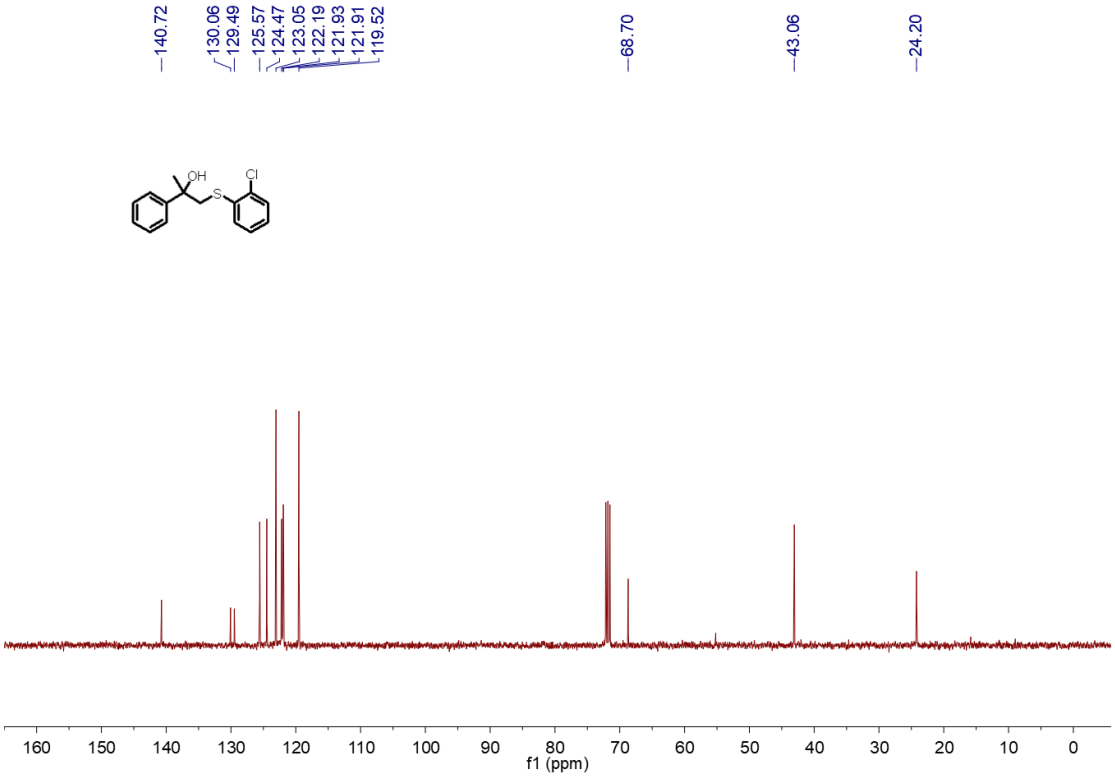
^{13}C NMR spectrum of c39



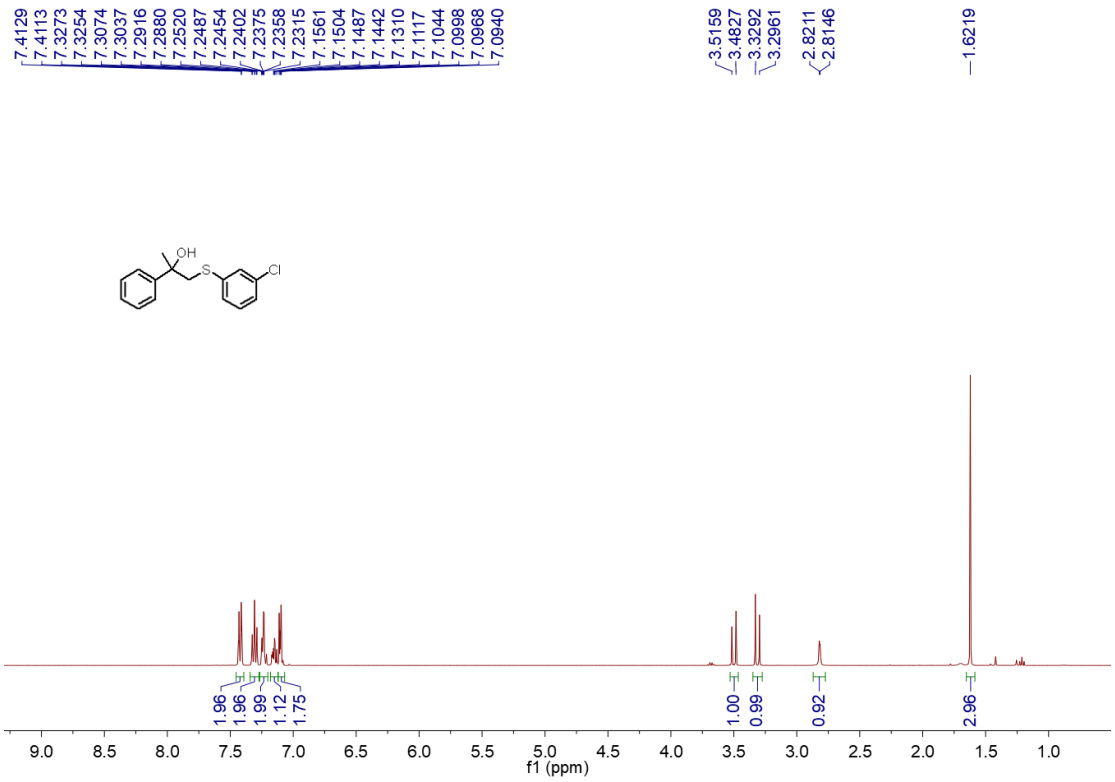
^{1}H NMR spectrum of c40



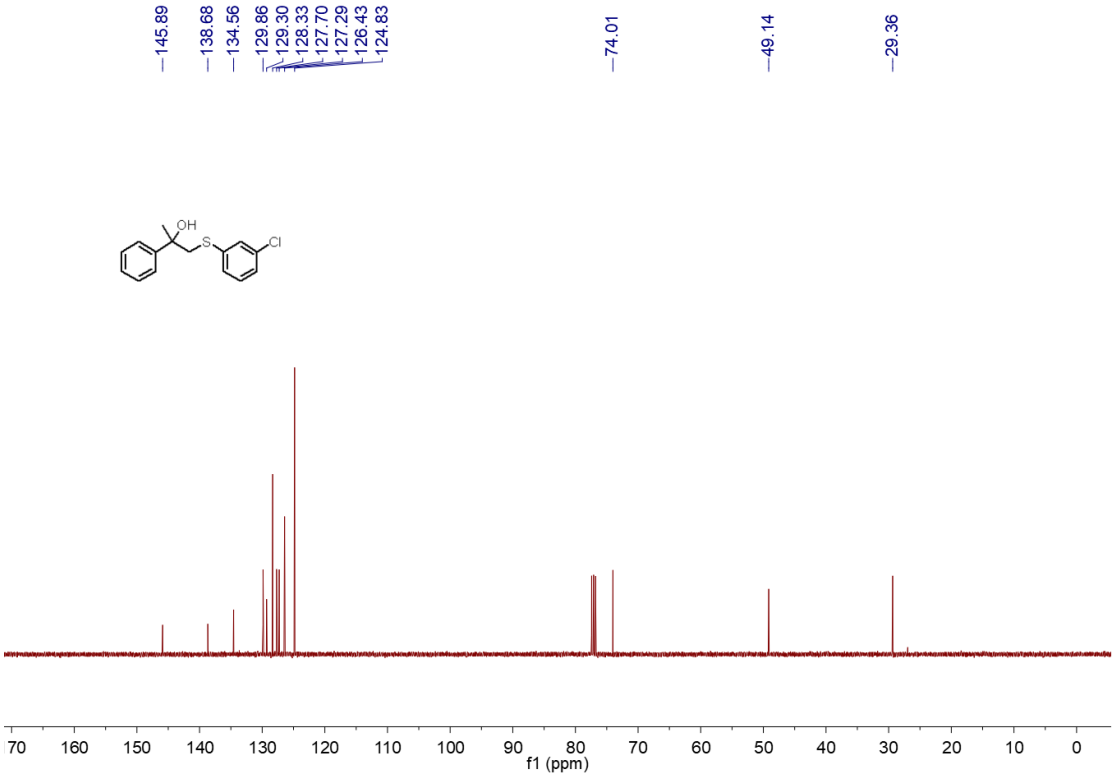
^{13}C NMR spectrum of c40



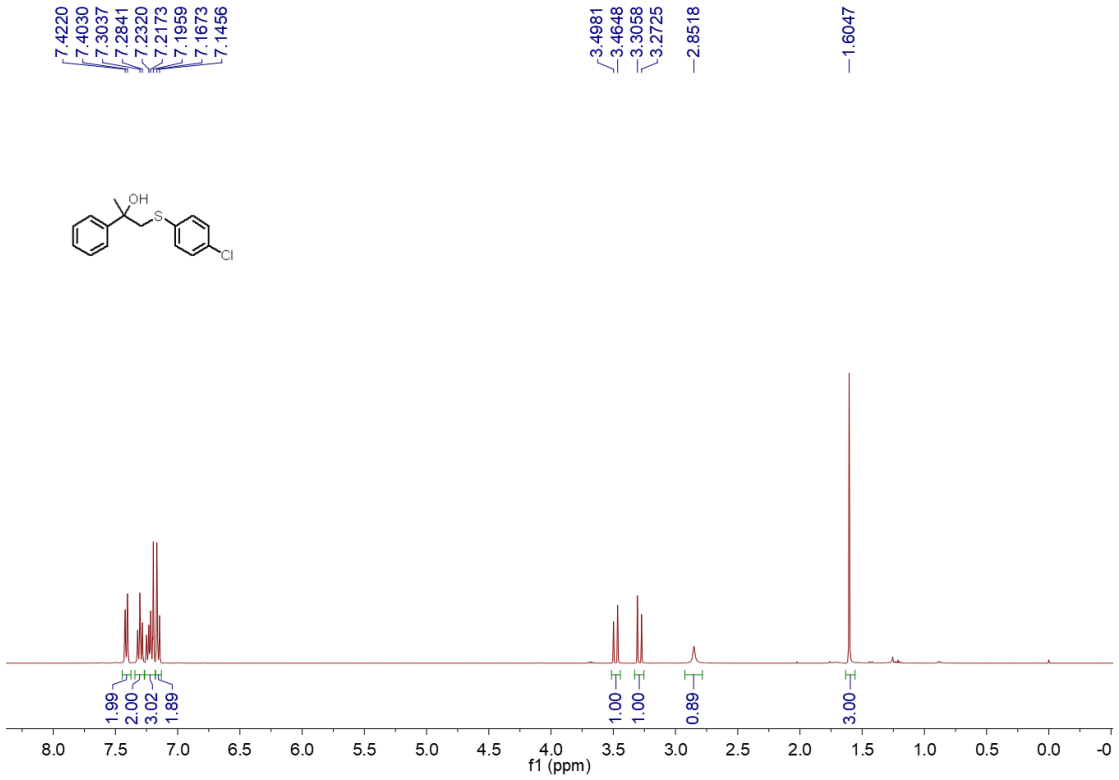
^{1}H NMR spectrum of c41



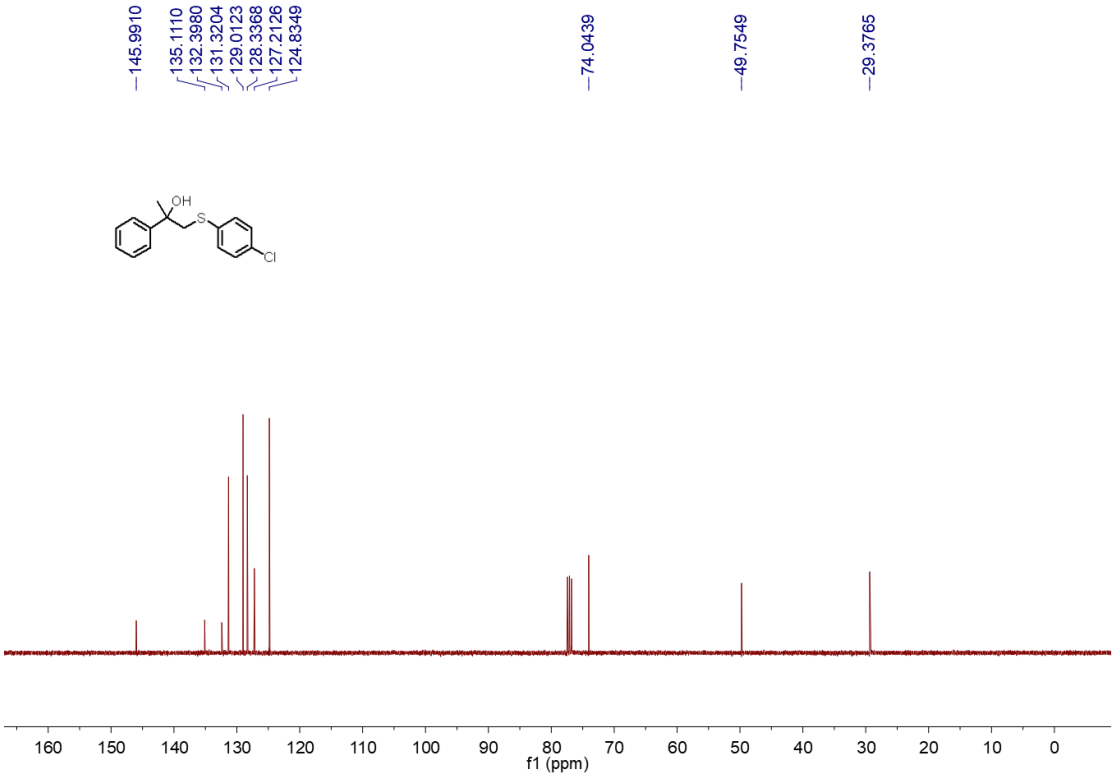
^{13}C NMR spectrum of c41



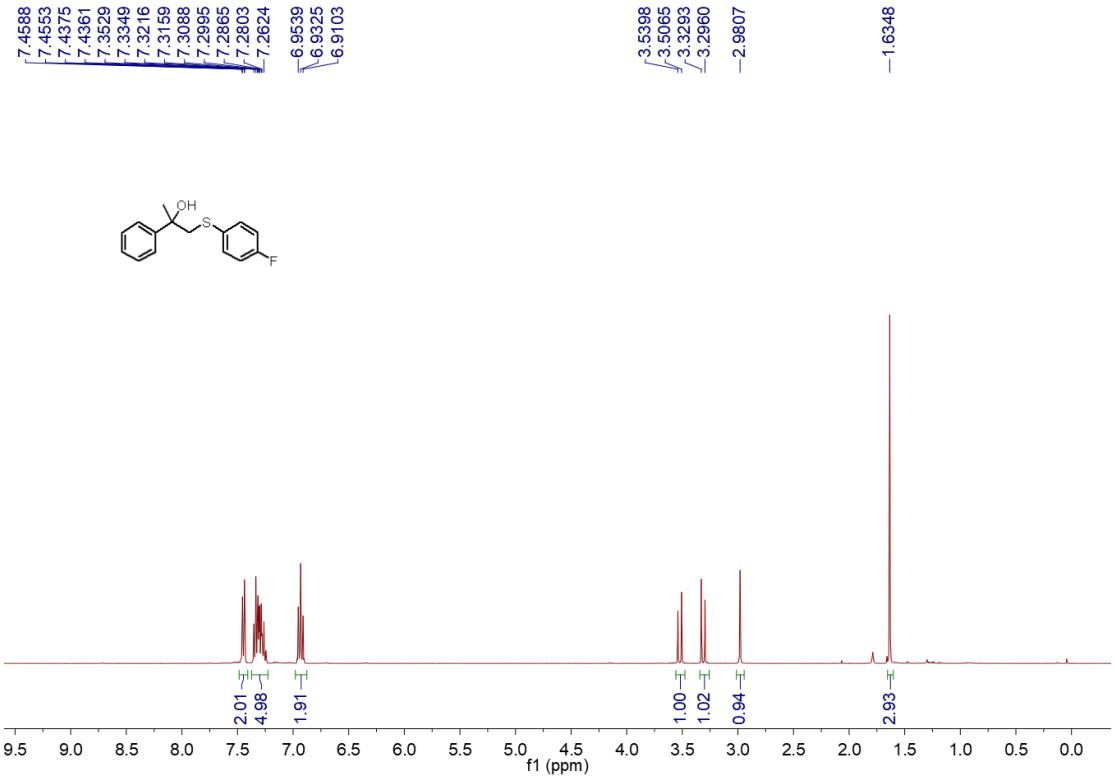
^{1}H NMR spectrum of c42



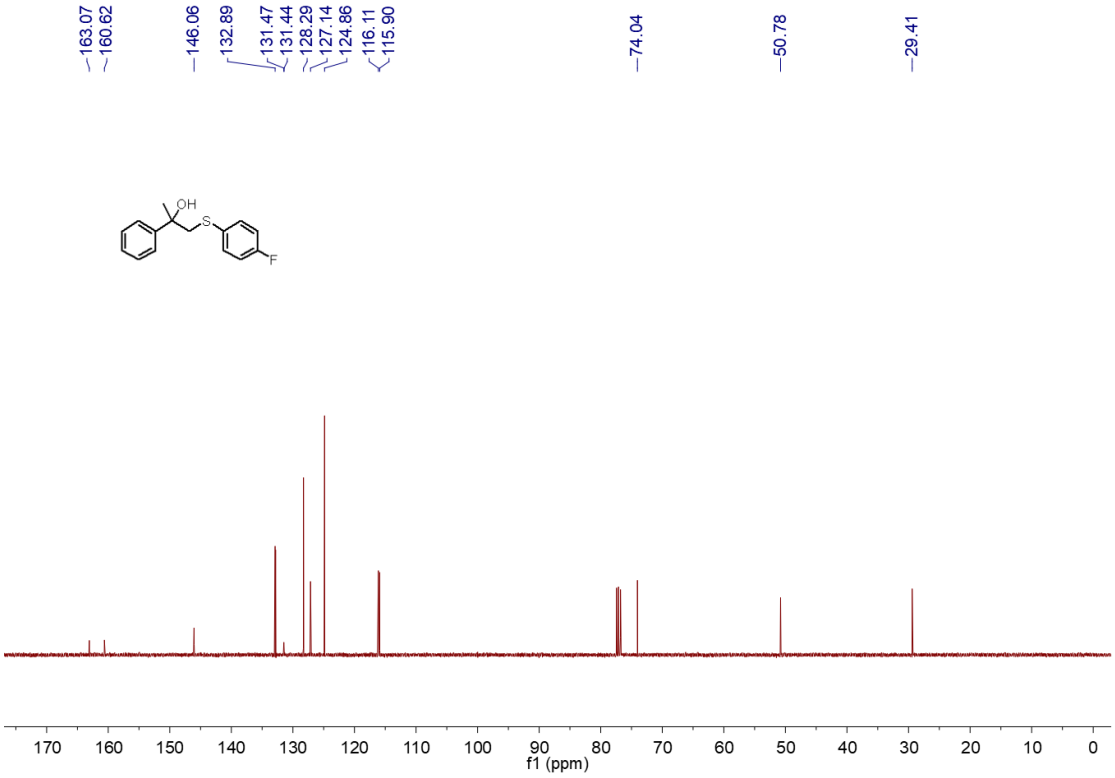
^{13}C NMR spectrum of c42



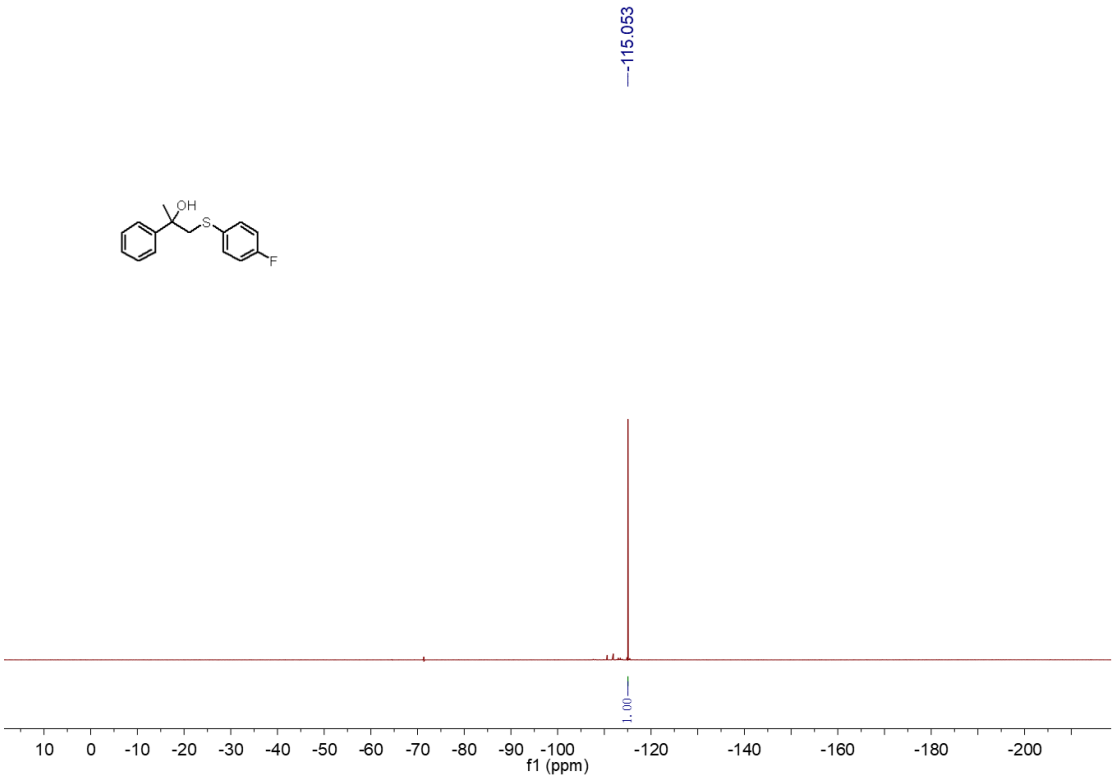
^{1}H NMR spectrum of c43



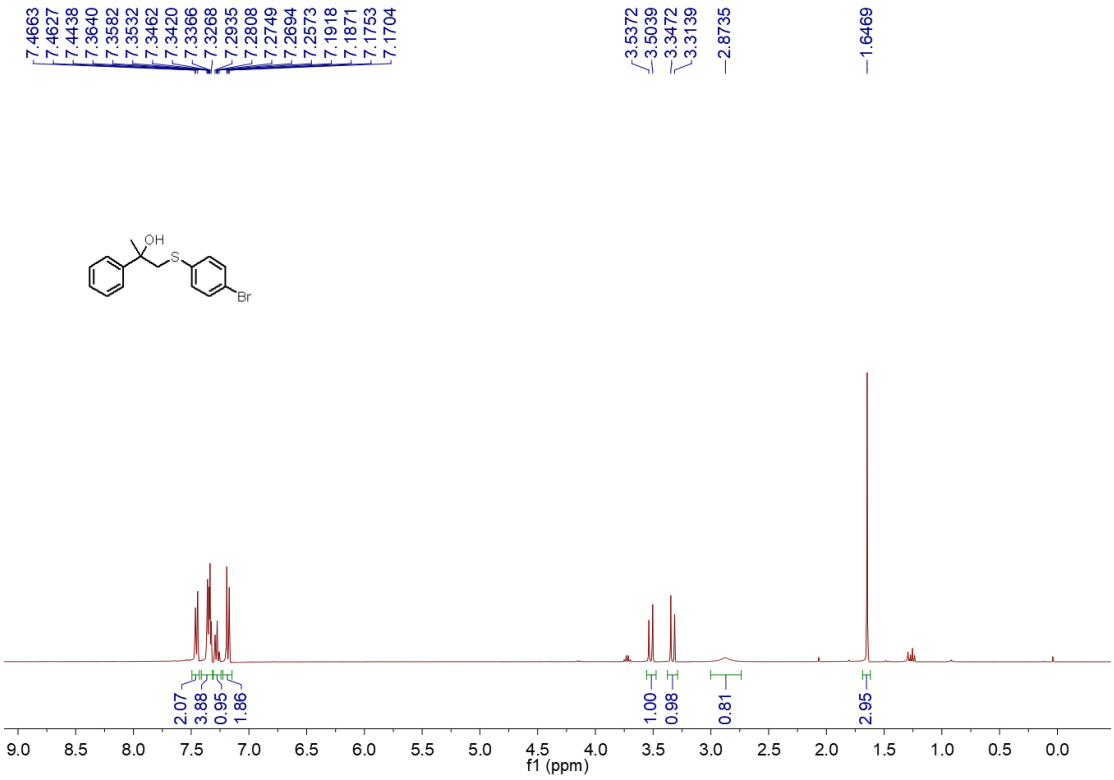
^{13}C NMR spectrum of c43



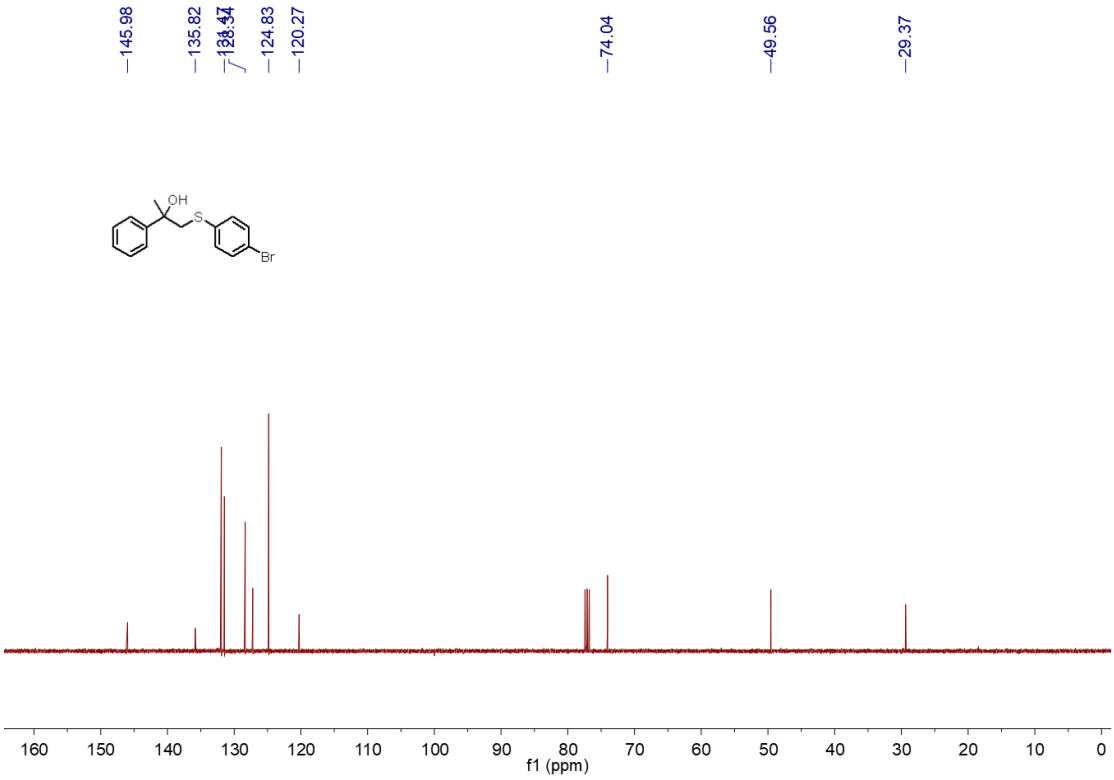
^{19}F NMR spectrum of c43



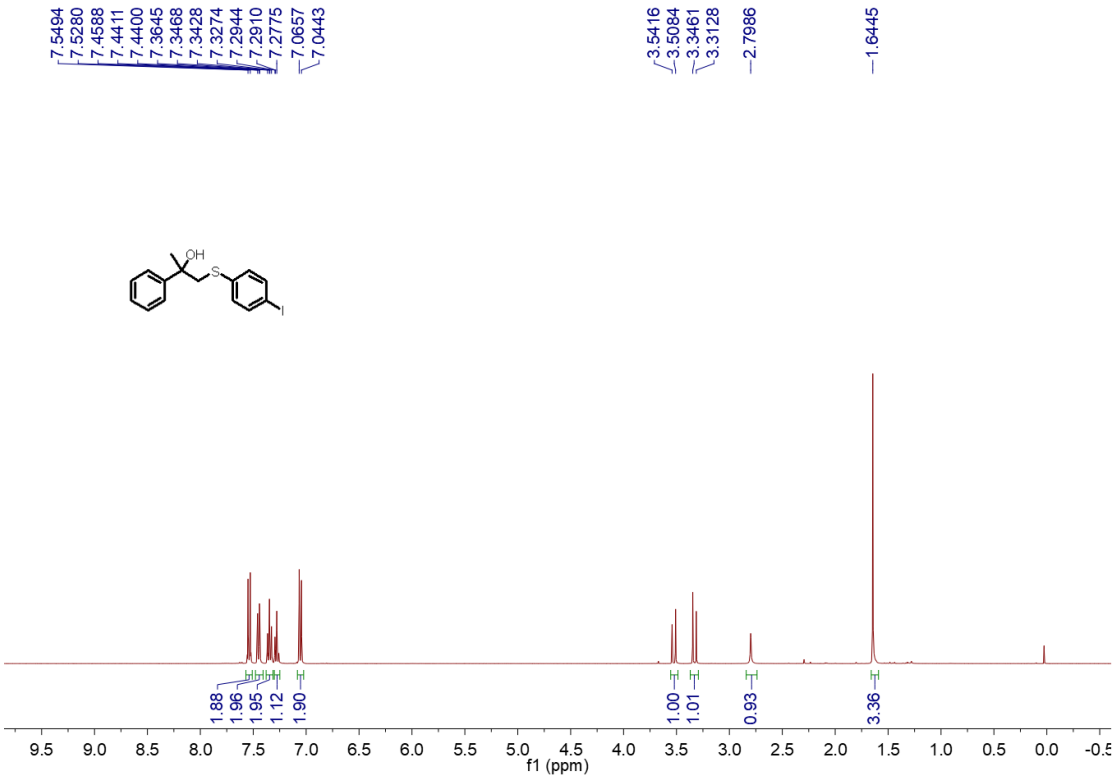
^{1}H NMR spectrum of c44



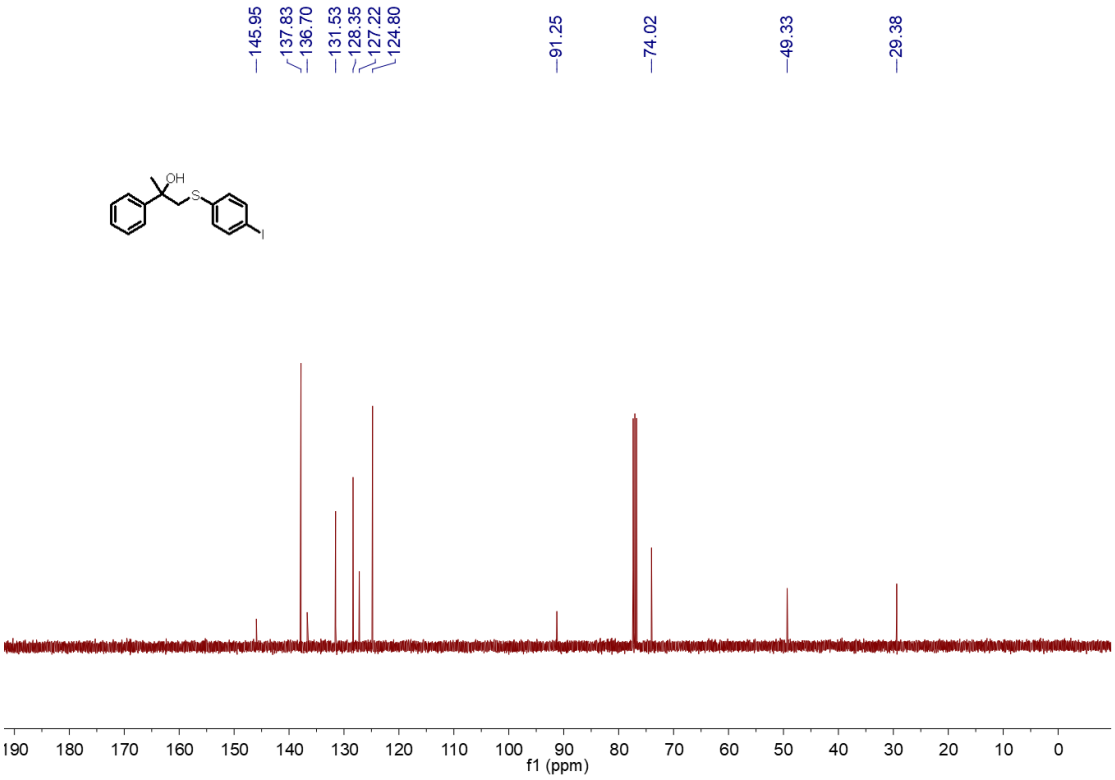
^{13}C NMR spectrum of c44



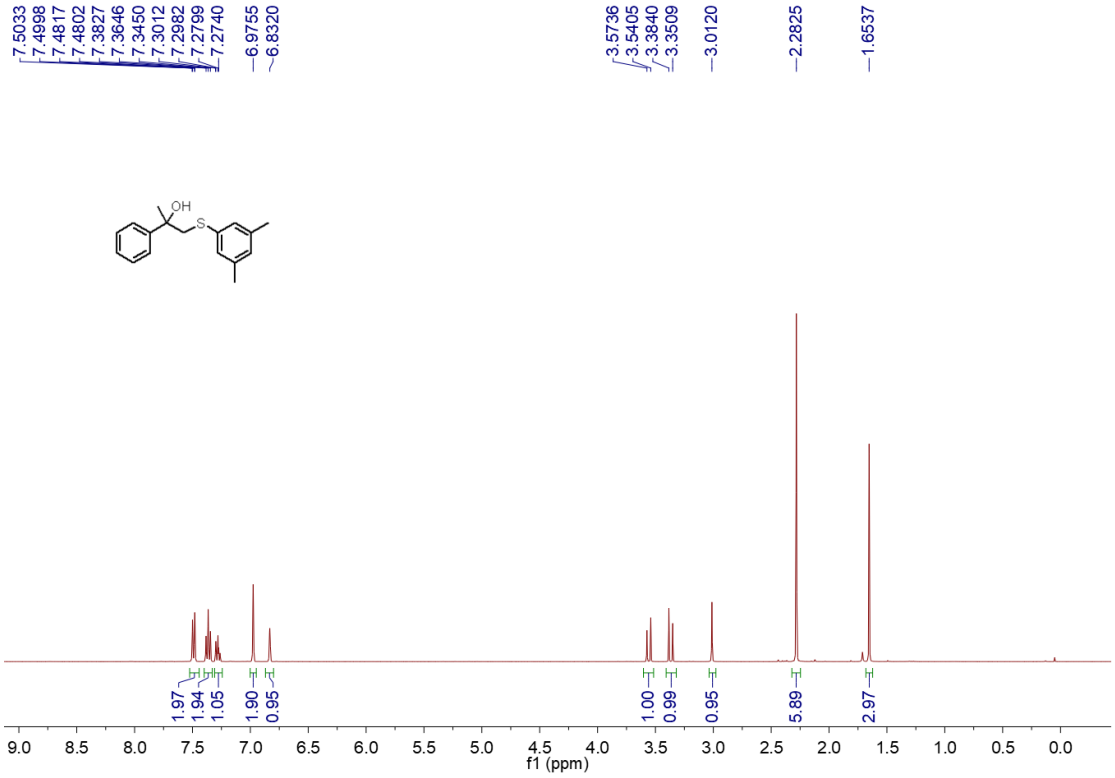
^{1}H NMR spectrum of c45



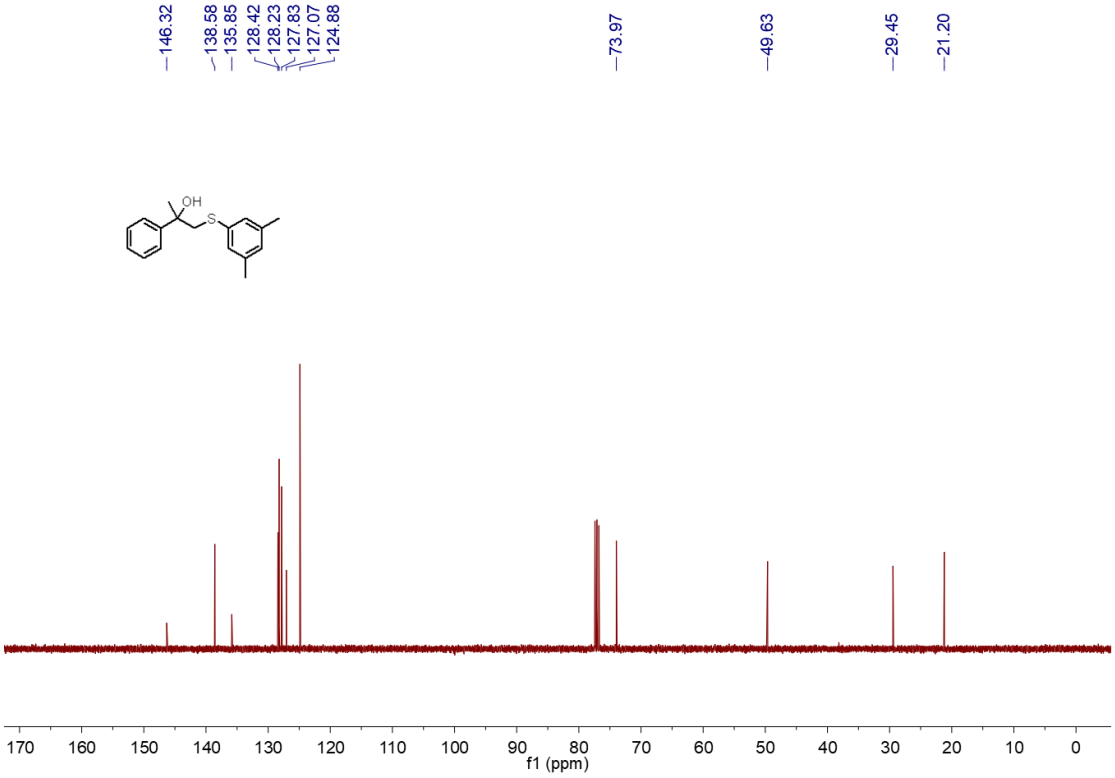
^{13}C NMR spectrum of c45



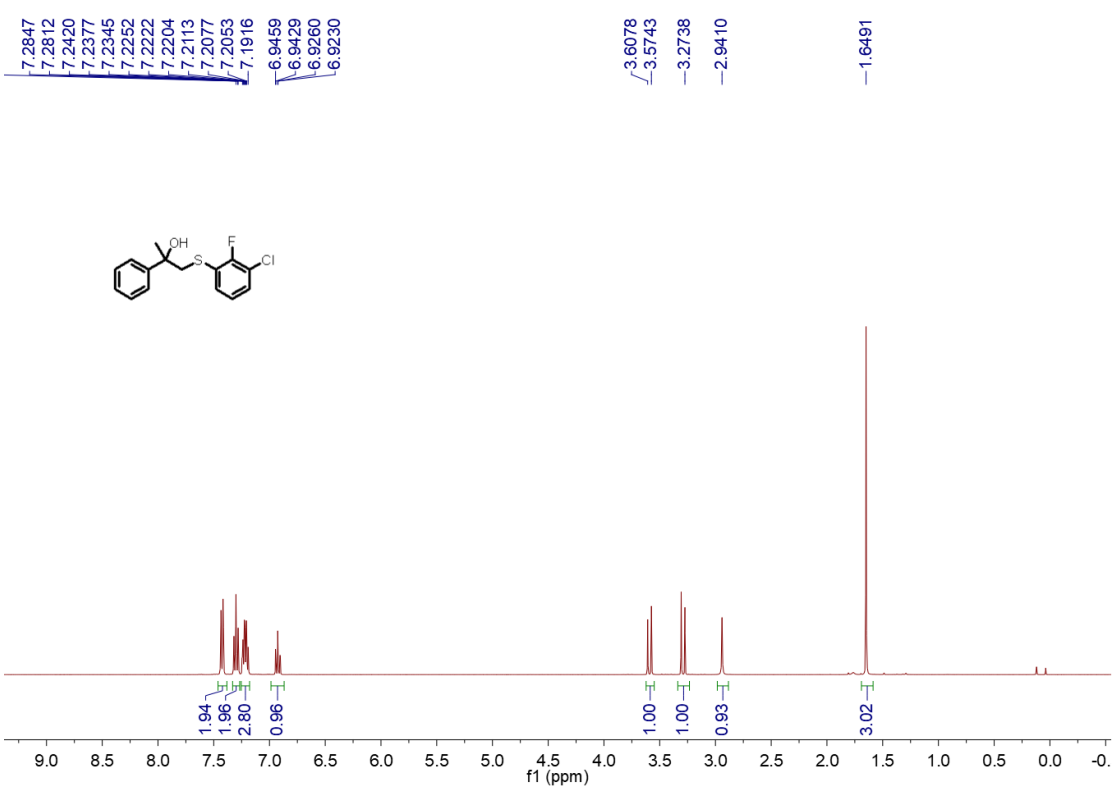
^{1}H NMR spectrum of c46



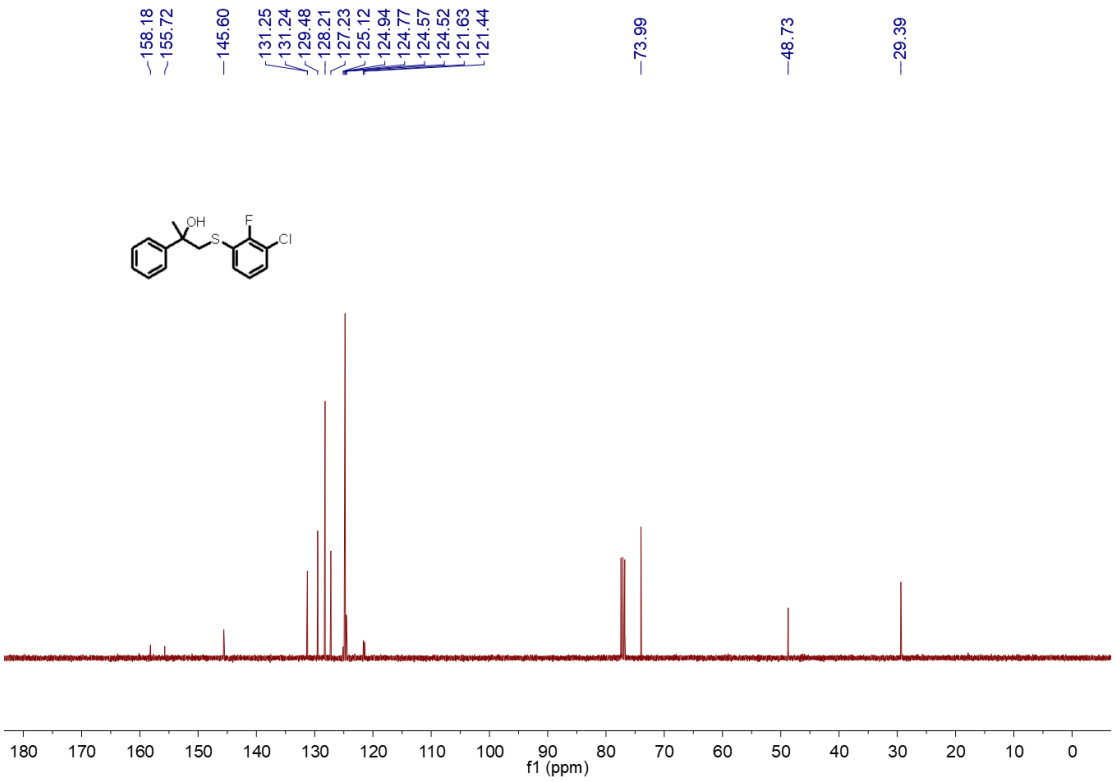
^{13}C NMR spectrum of c46



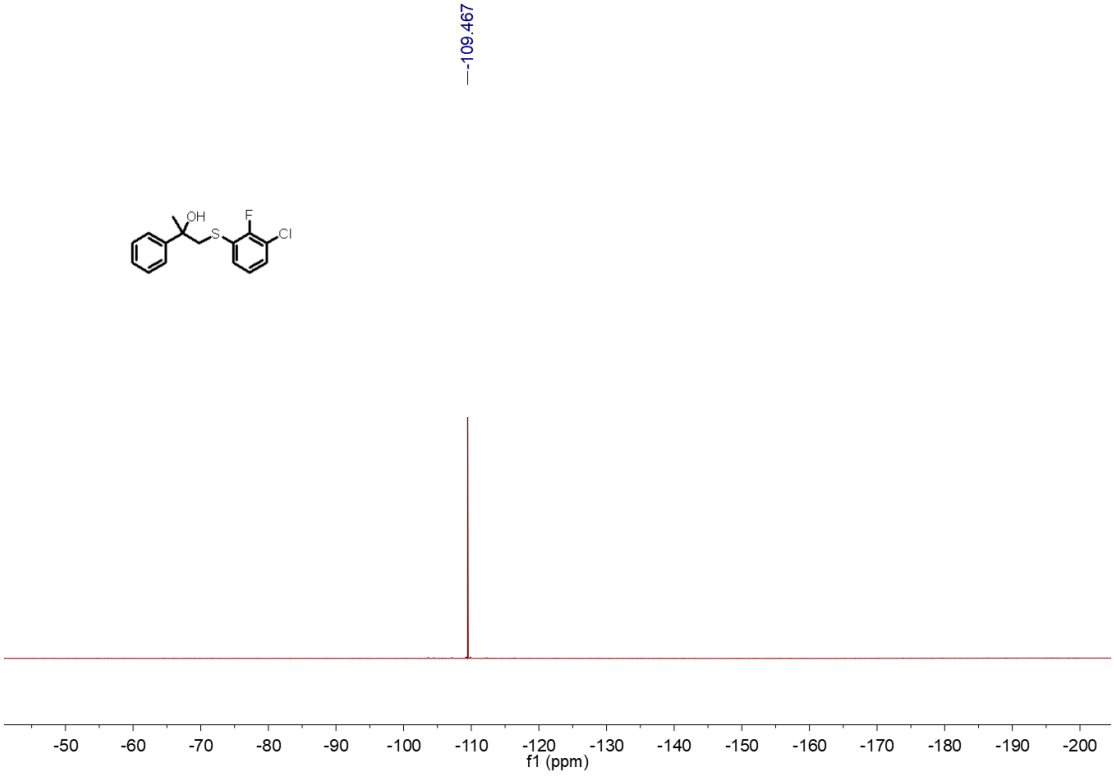
^{1}H NMR spectrum of c47



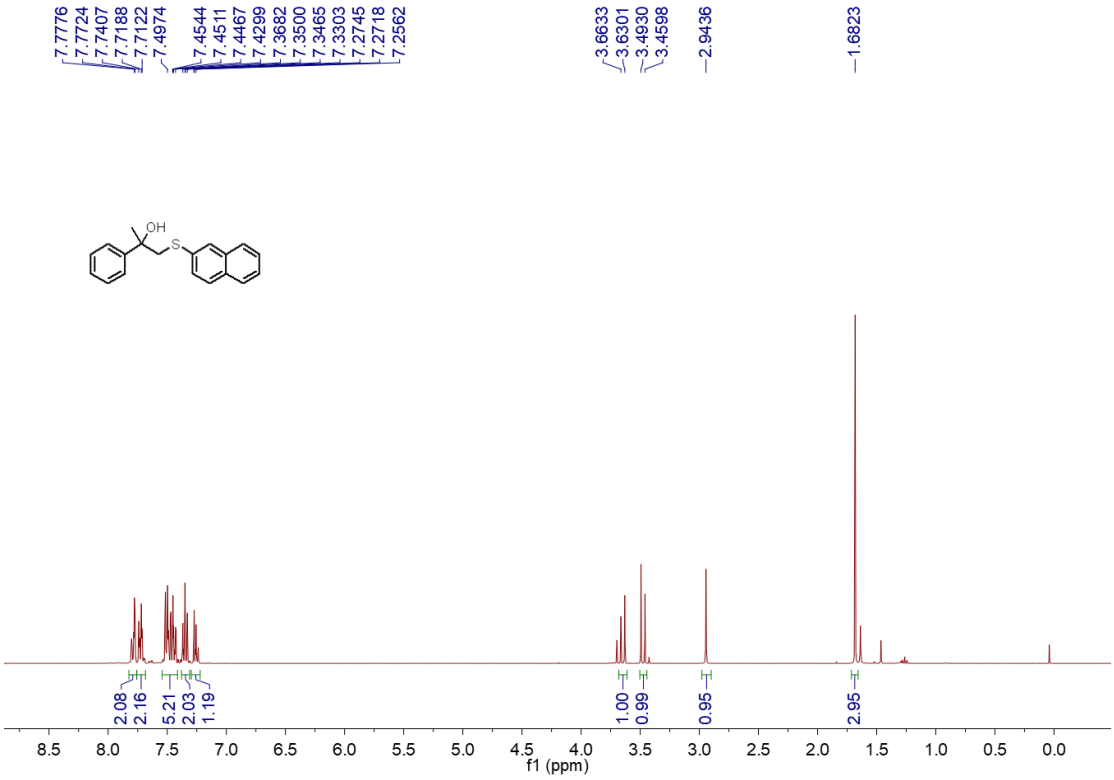
^{13}C NMR spectrum of c47



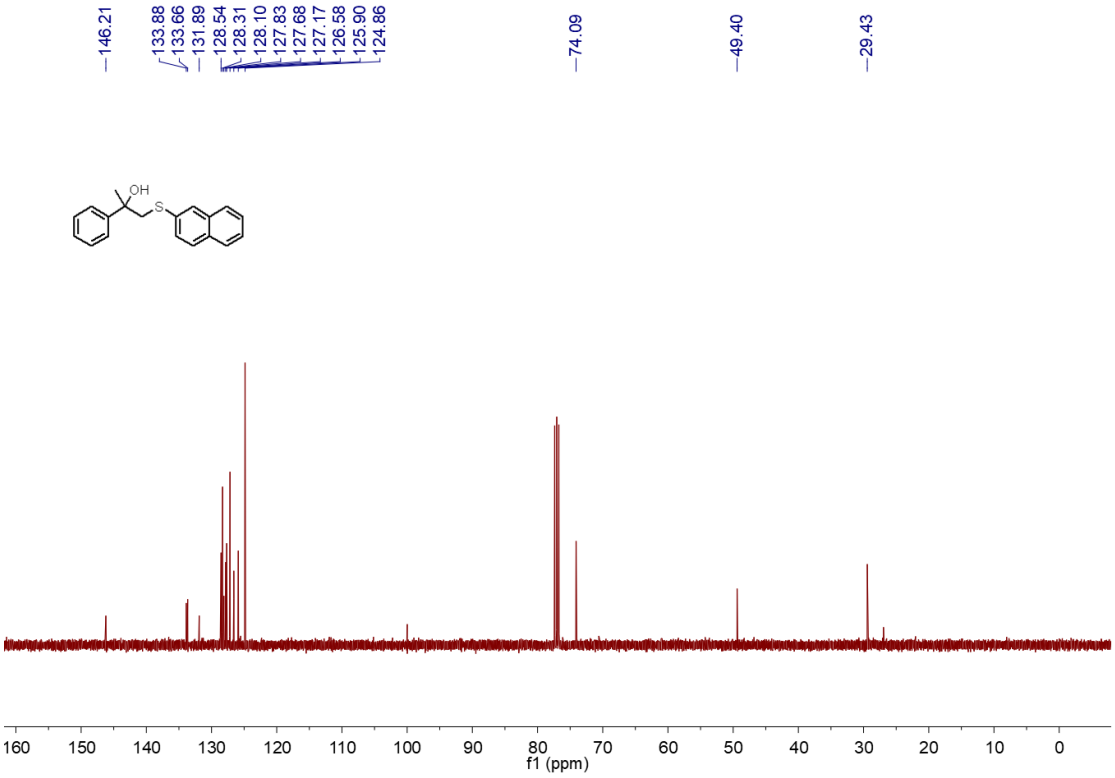
^{19}F NMR spectrum of c47



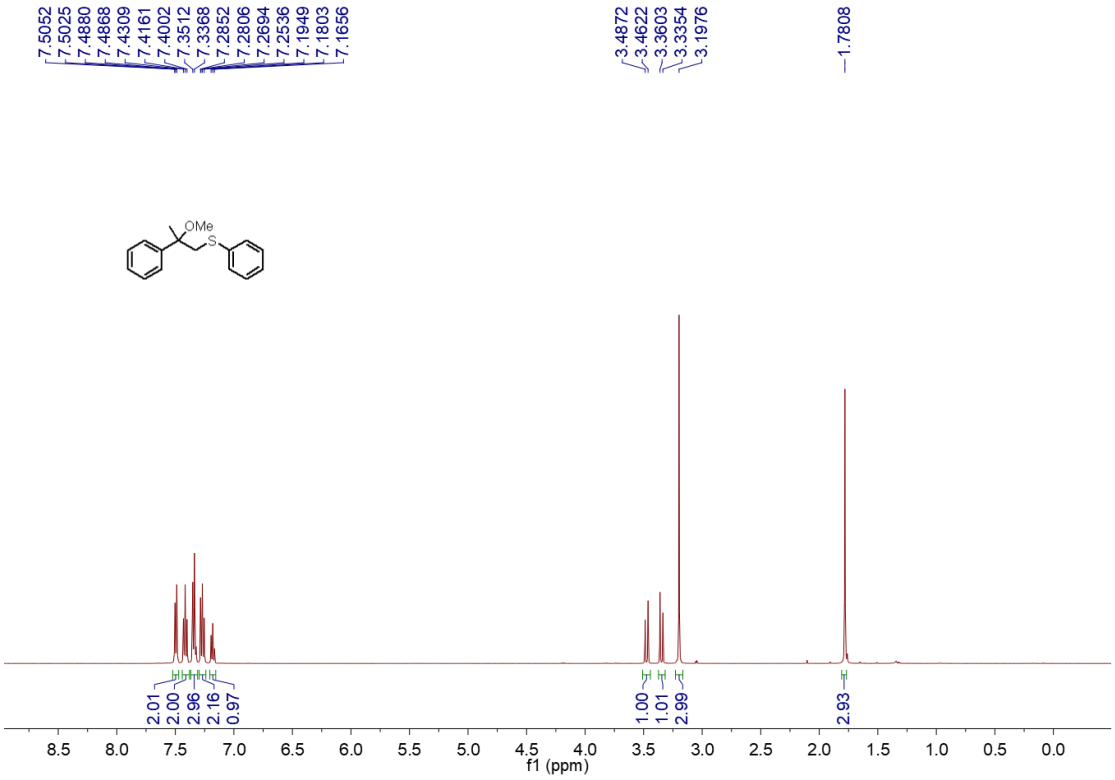
^{1}H NMR spectrum of c48



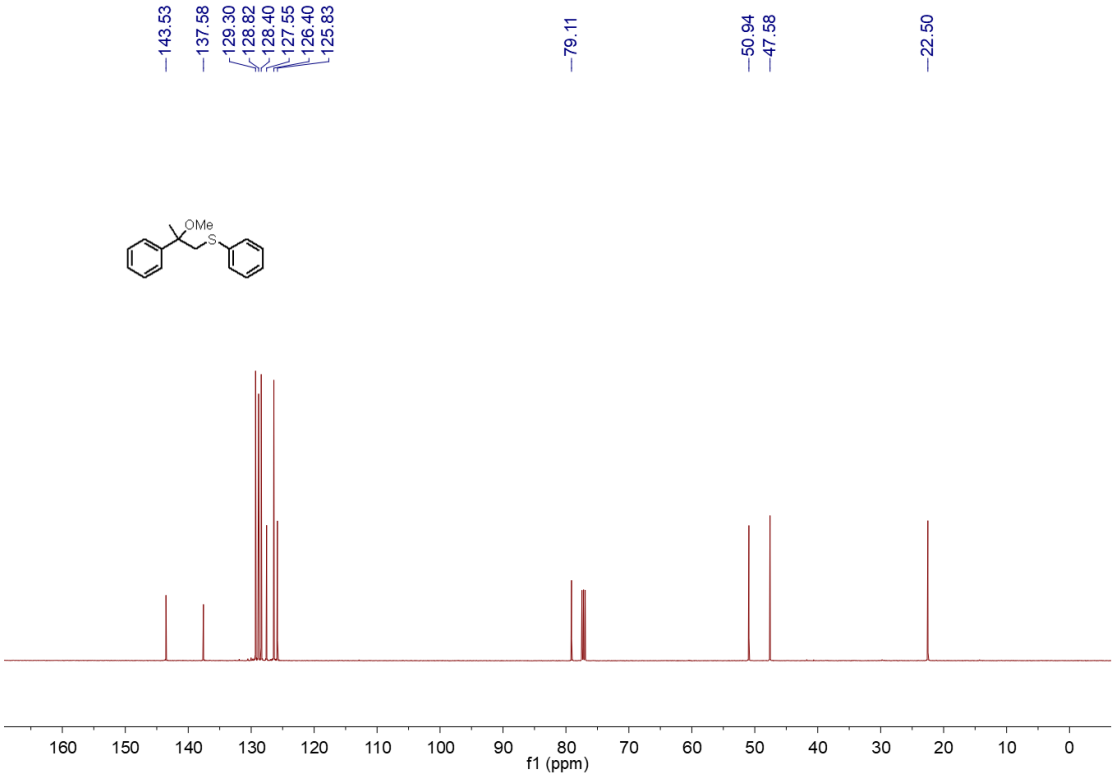
^{13}C NMR spectrum of c48



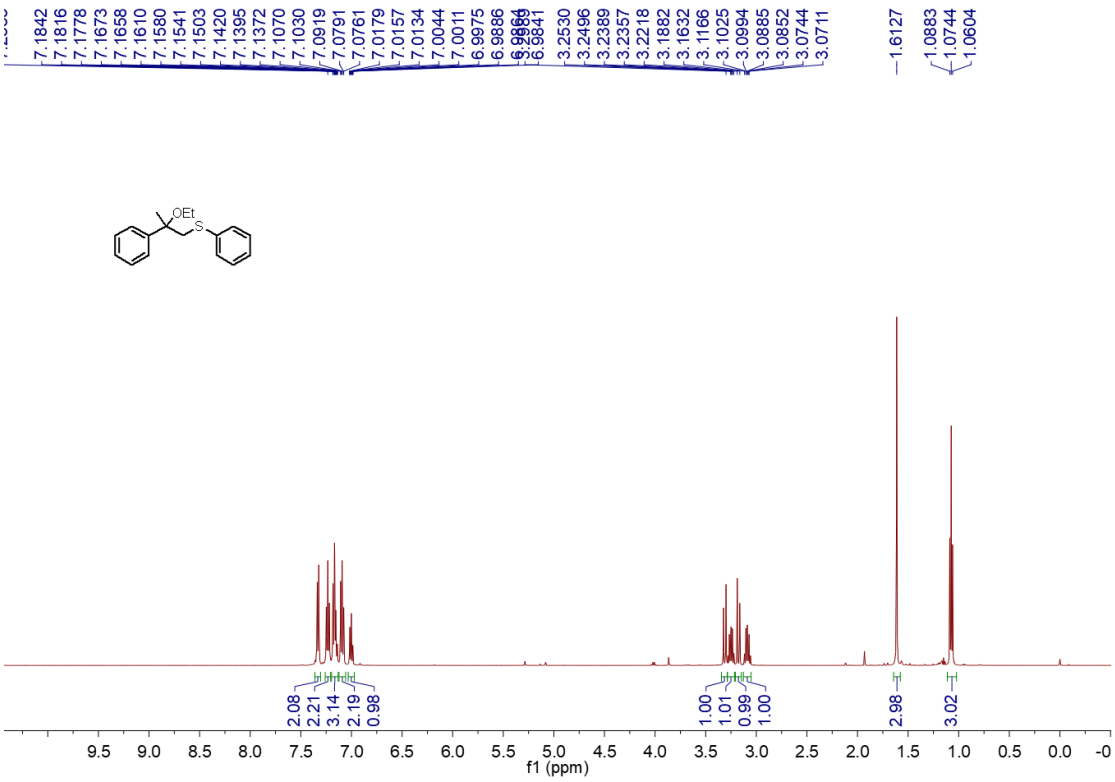
^{1}H NMR spectrum of c49



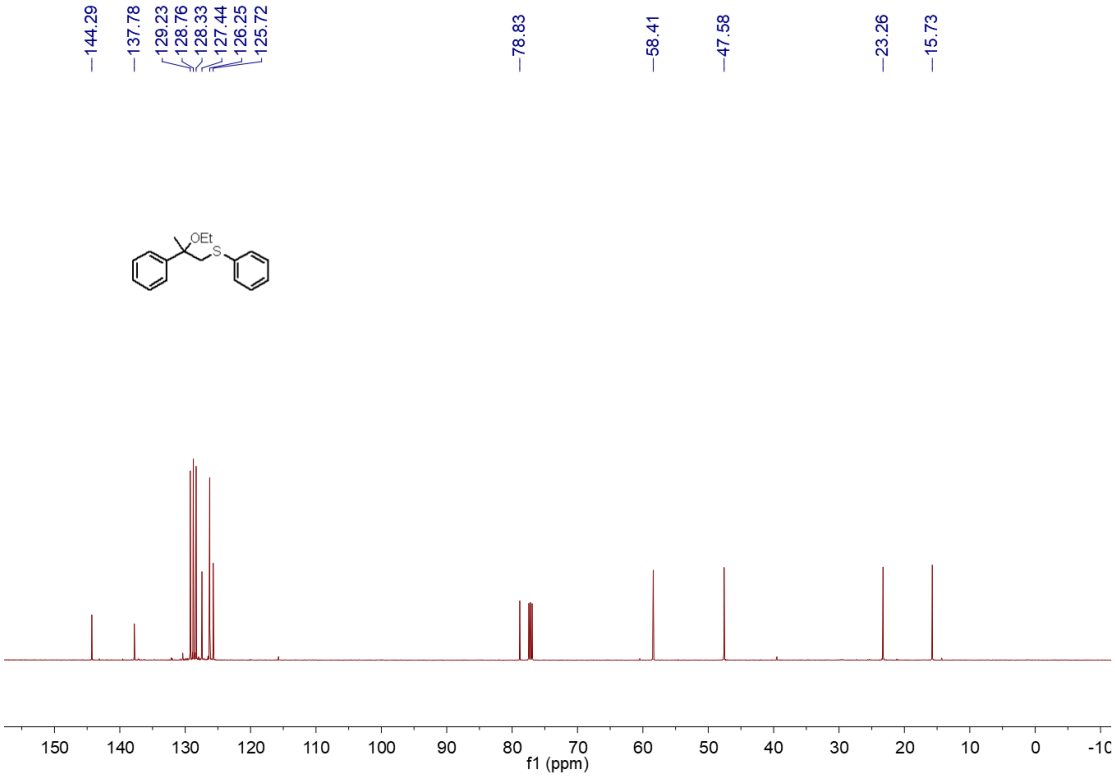
^{13}C NMR spectrum of c49



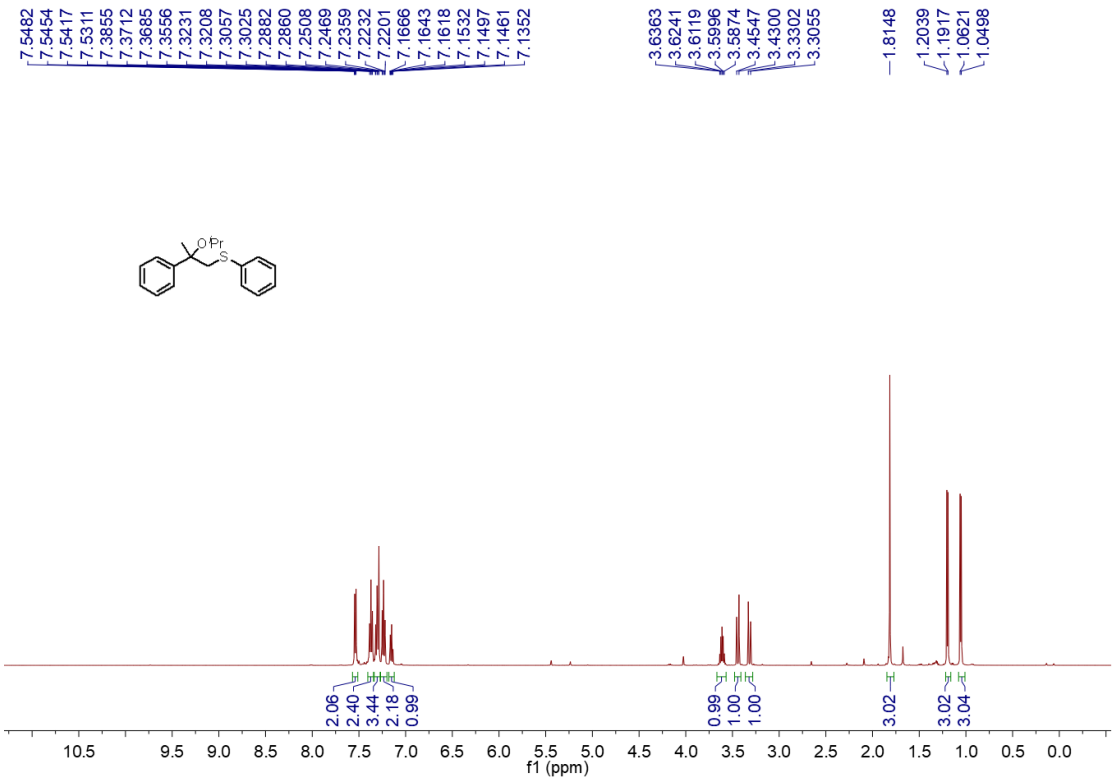
^{1}H NMR spectrum of c50



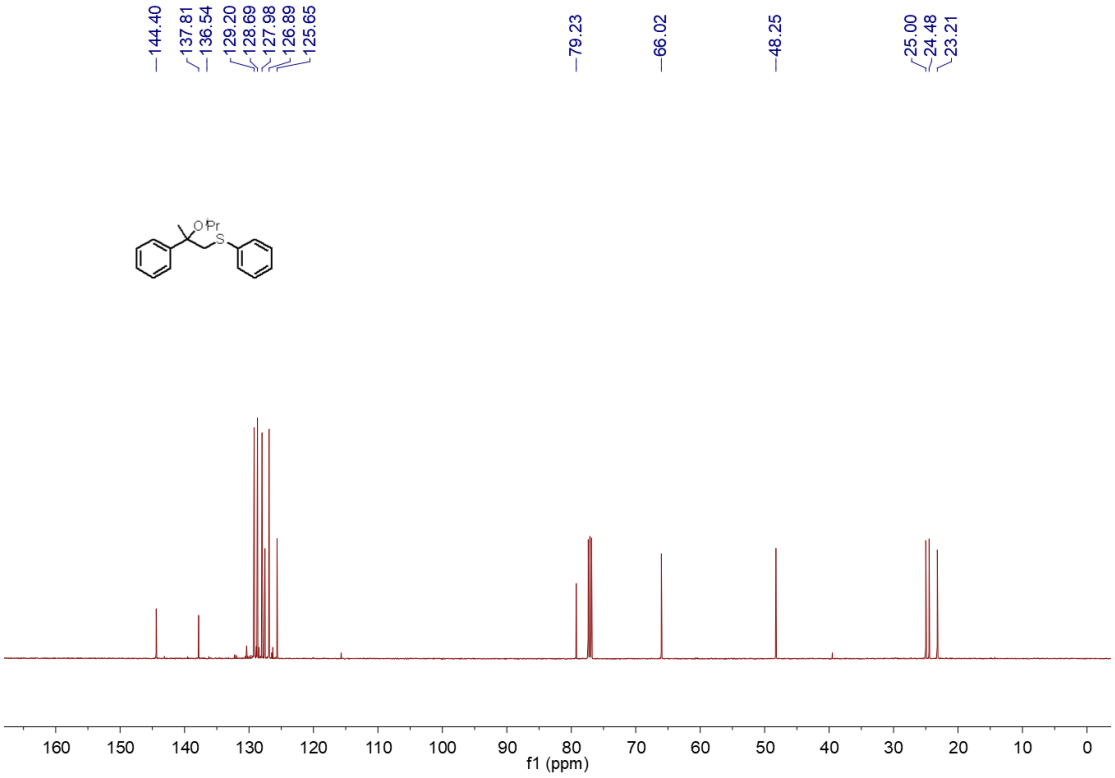
^{13}C NMR spectrum of c50



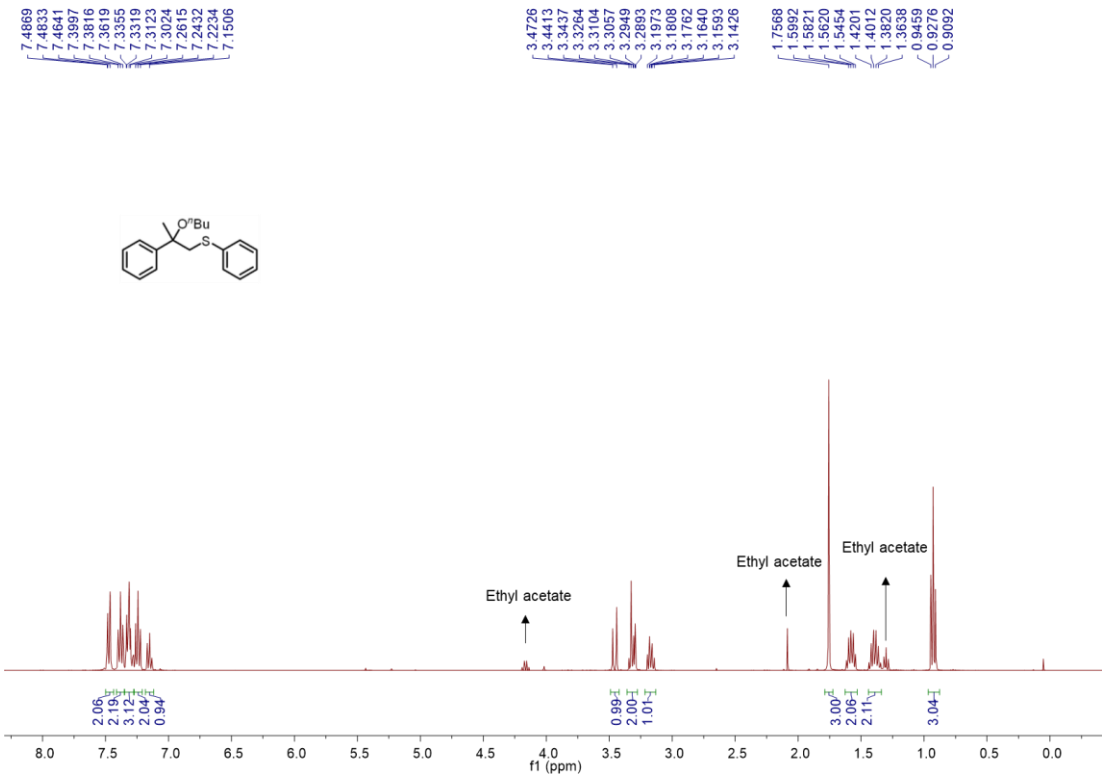
^{1}H NMR spectrum of c51



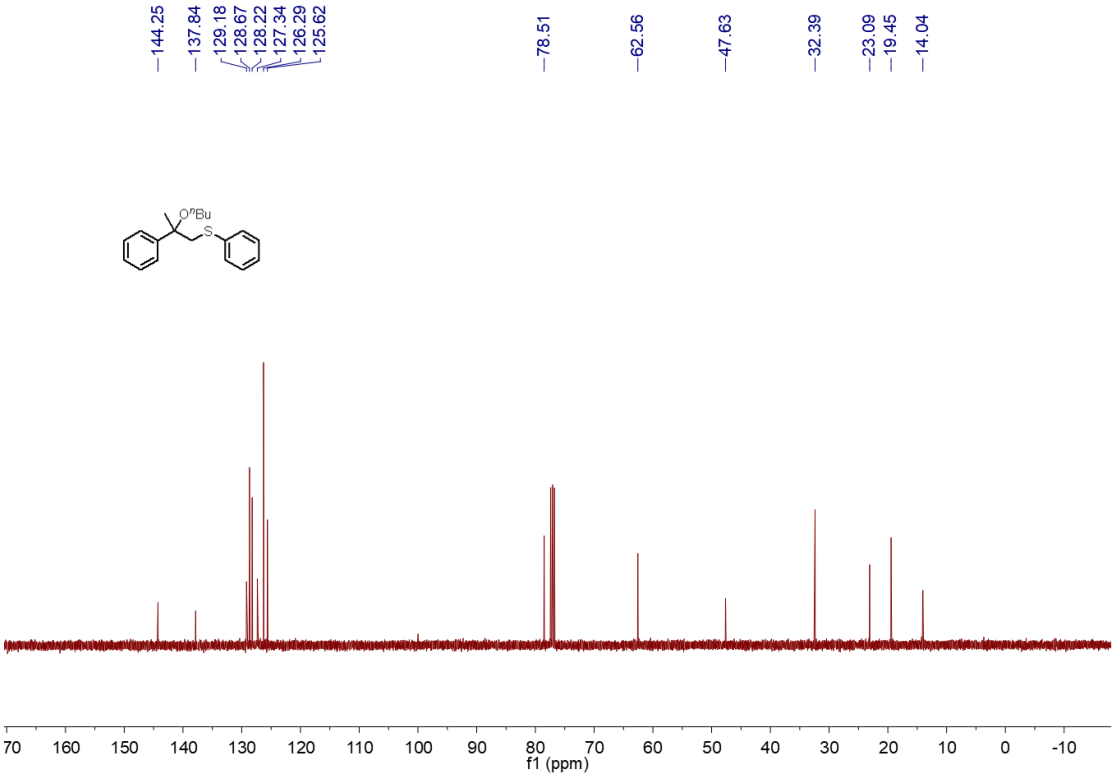
^{13}C NMR spectrum of c51



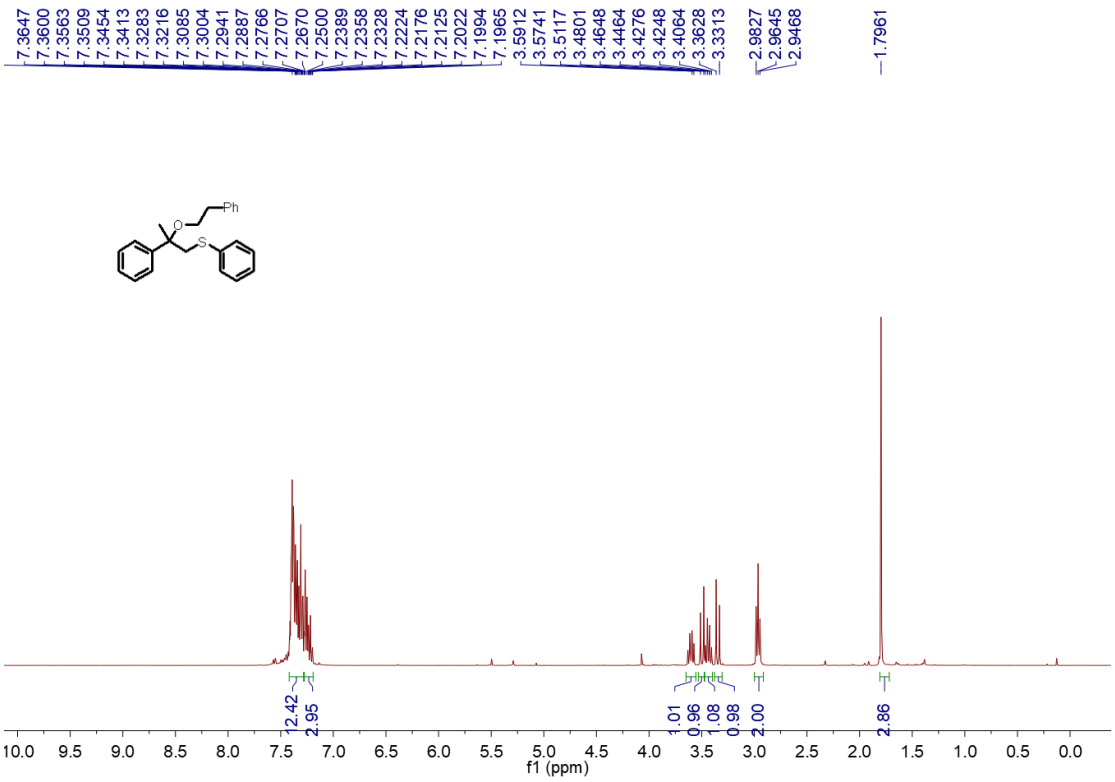
^{1}H NMR spectrum of c52



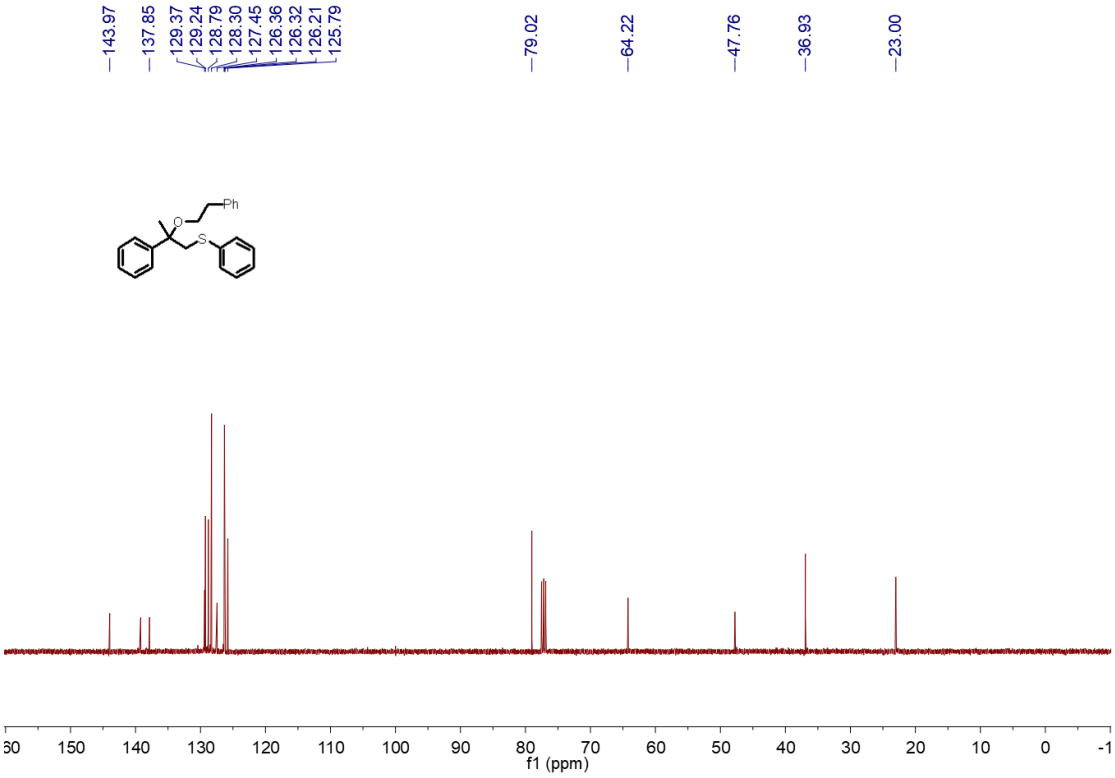
^{13}C NMR spectrum of c52



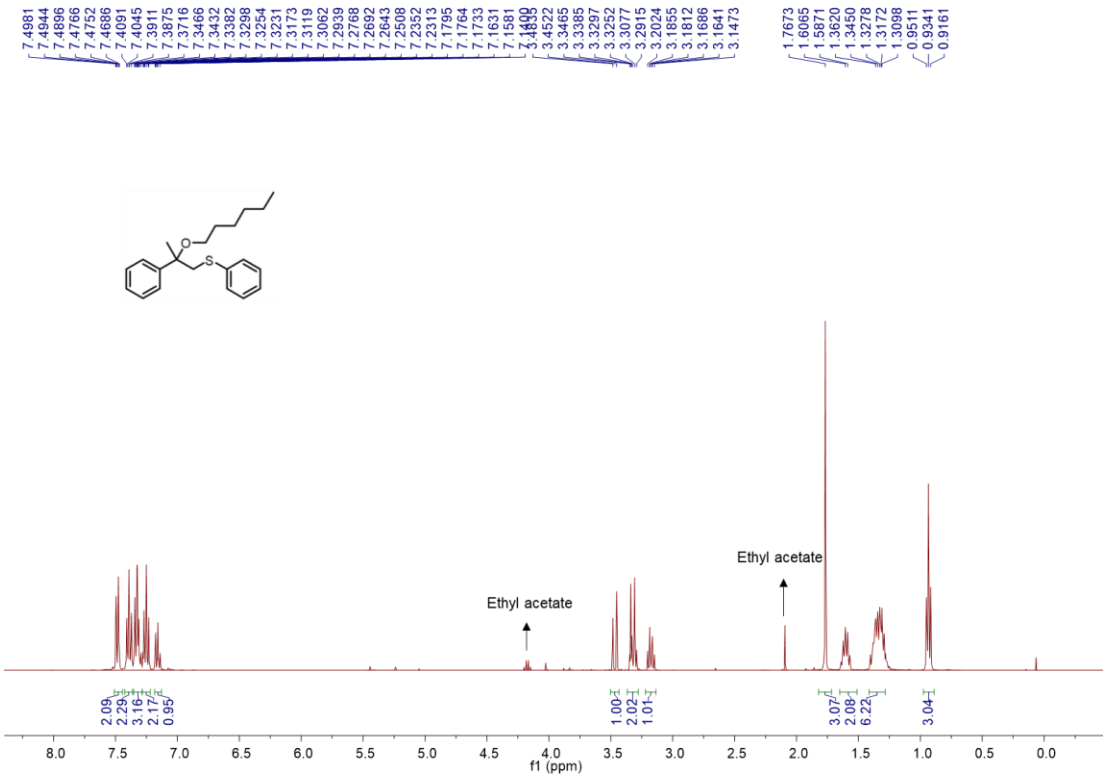
^{1}H NMR spectrum of c53



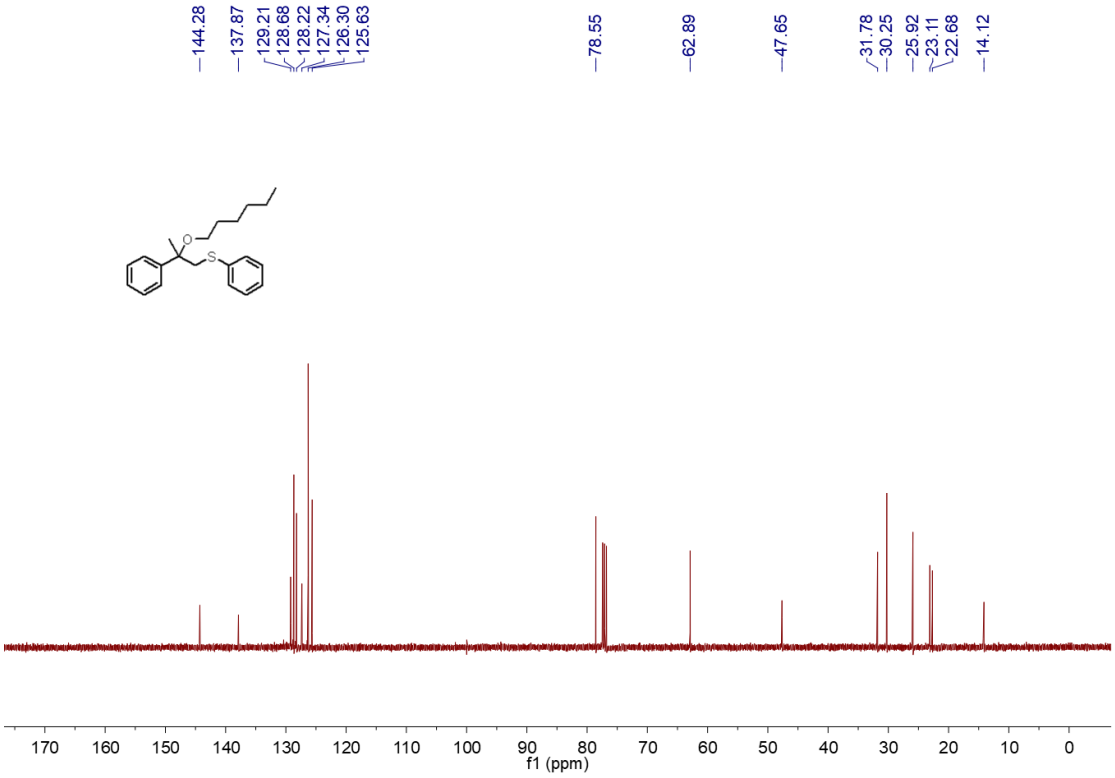
^{13}C NMR spectrum of c53



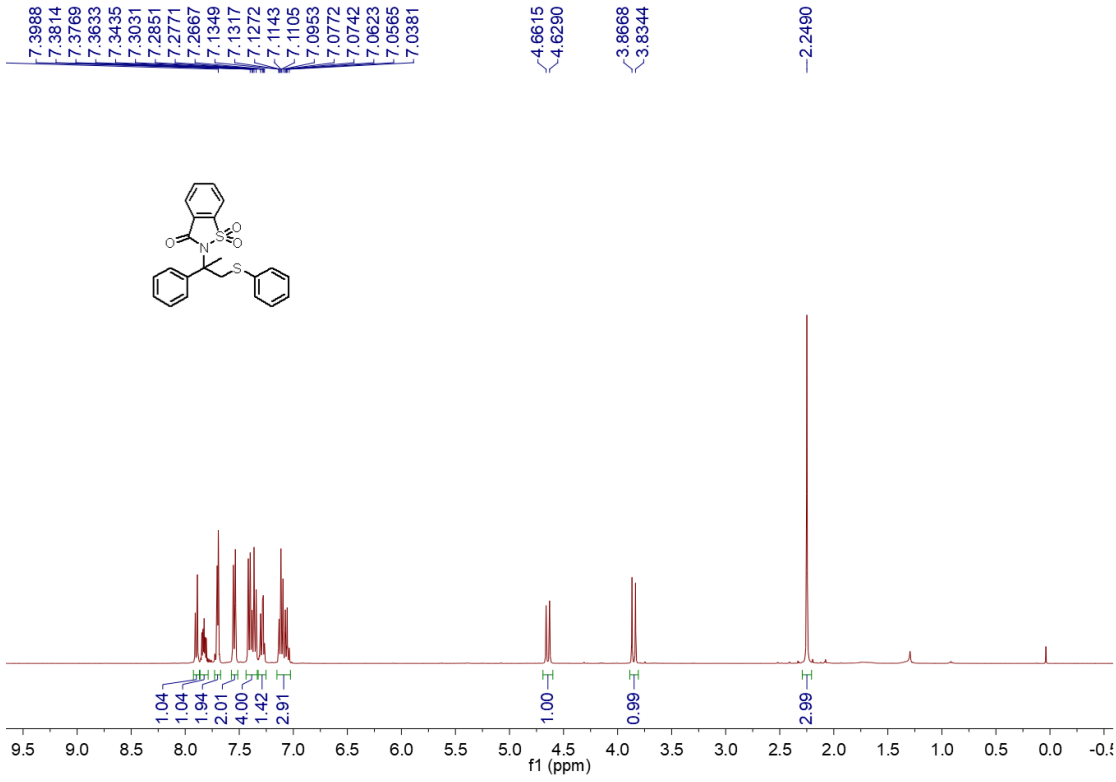
^{1}H NMR spectrum of c54



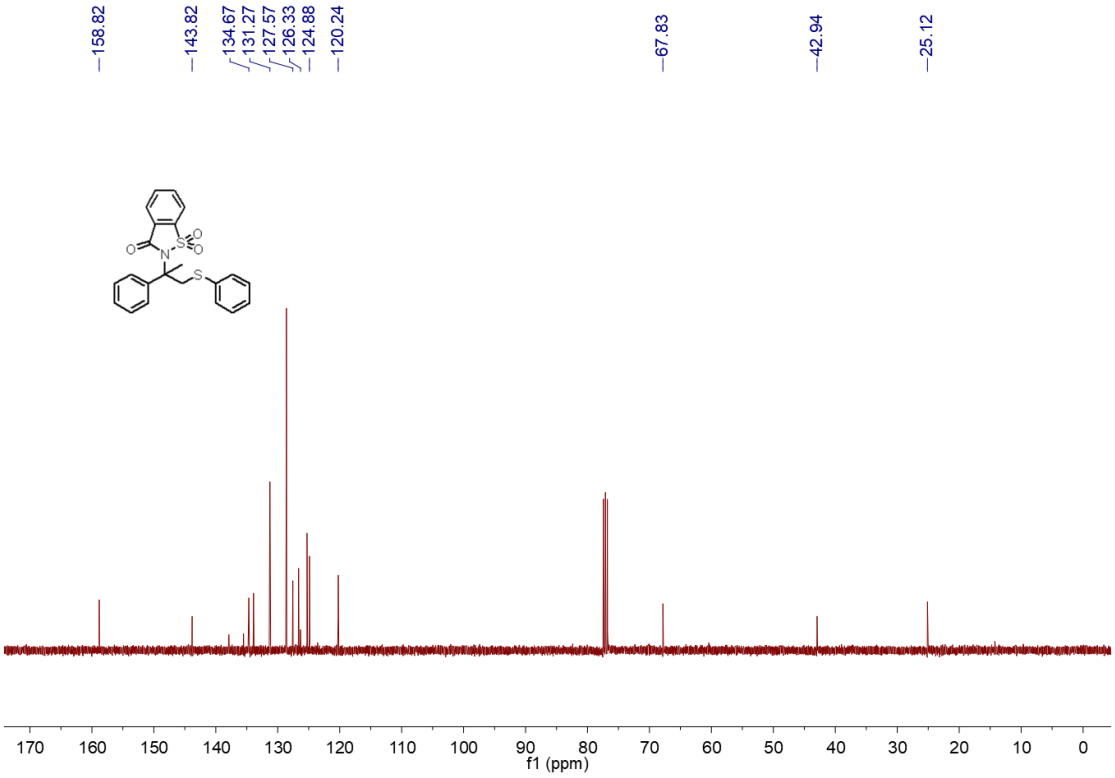
^{13}C NMR spectrum of c54



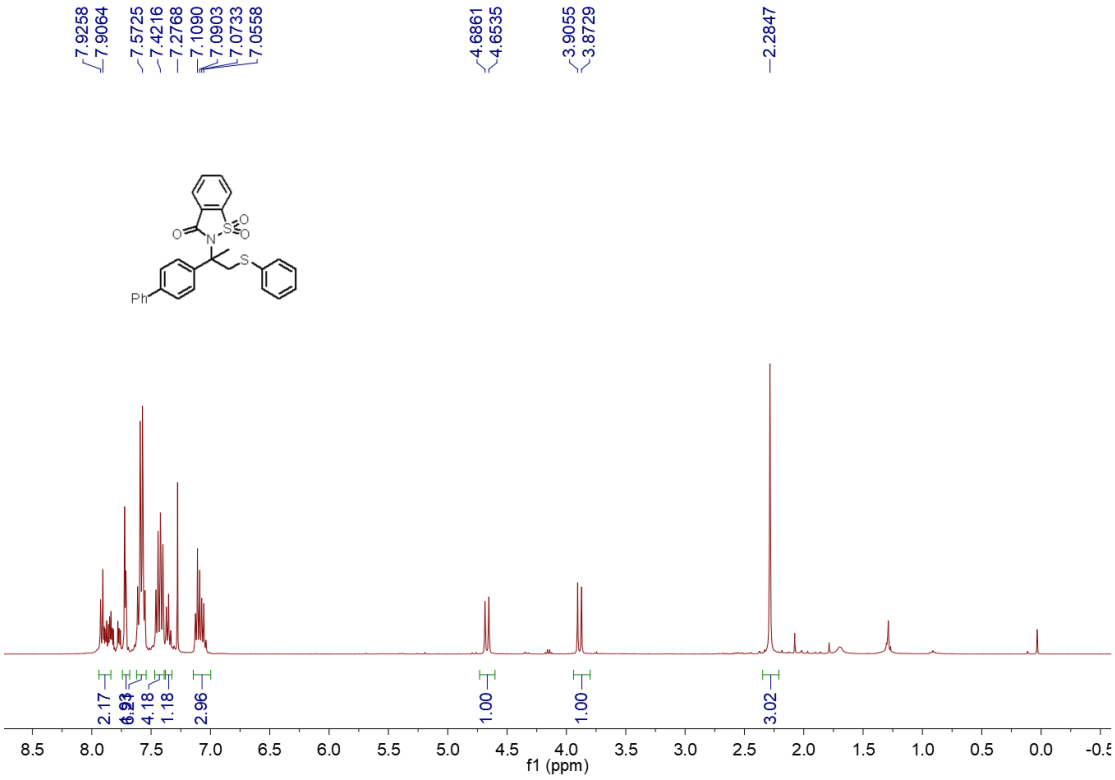
^{1}H NMR spectrum of c55



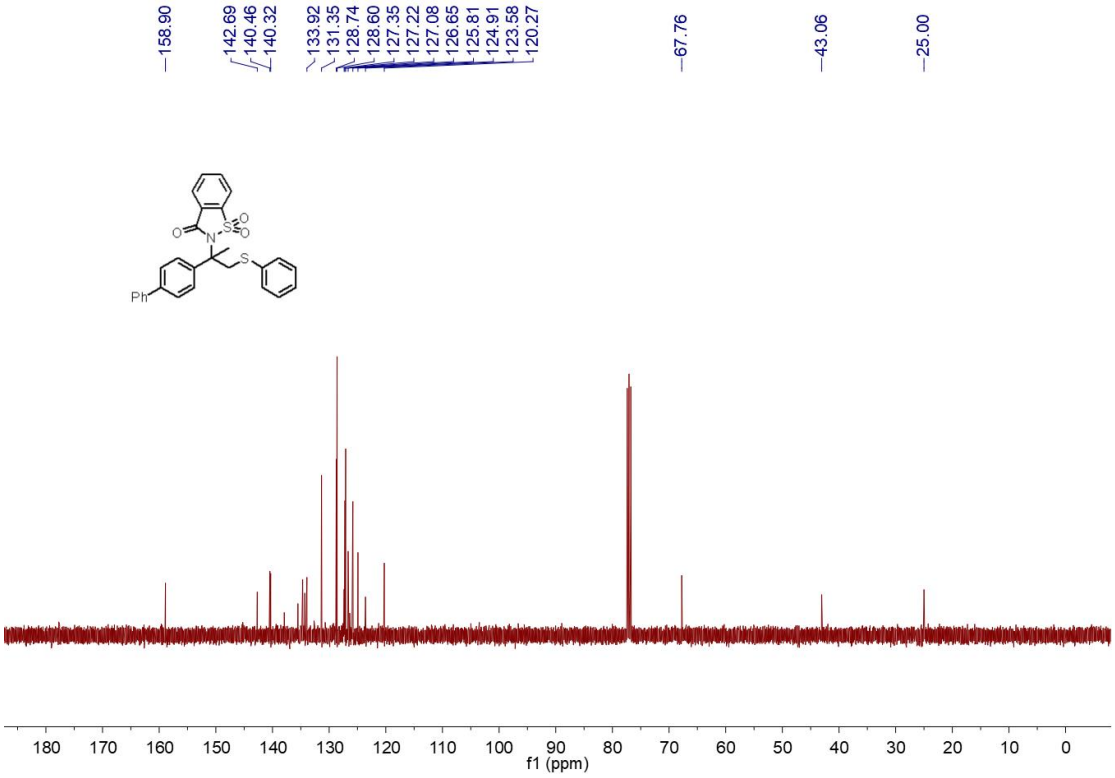
^{13}C NMR spectrum of c55



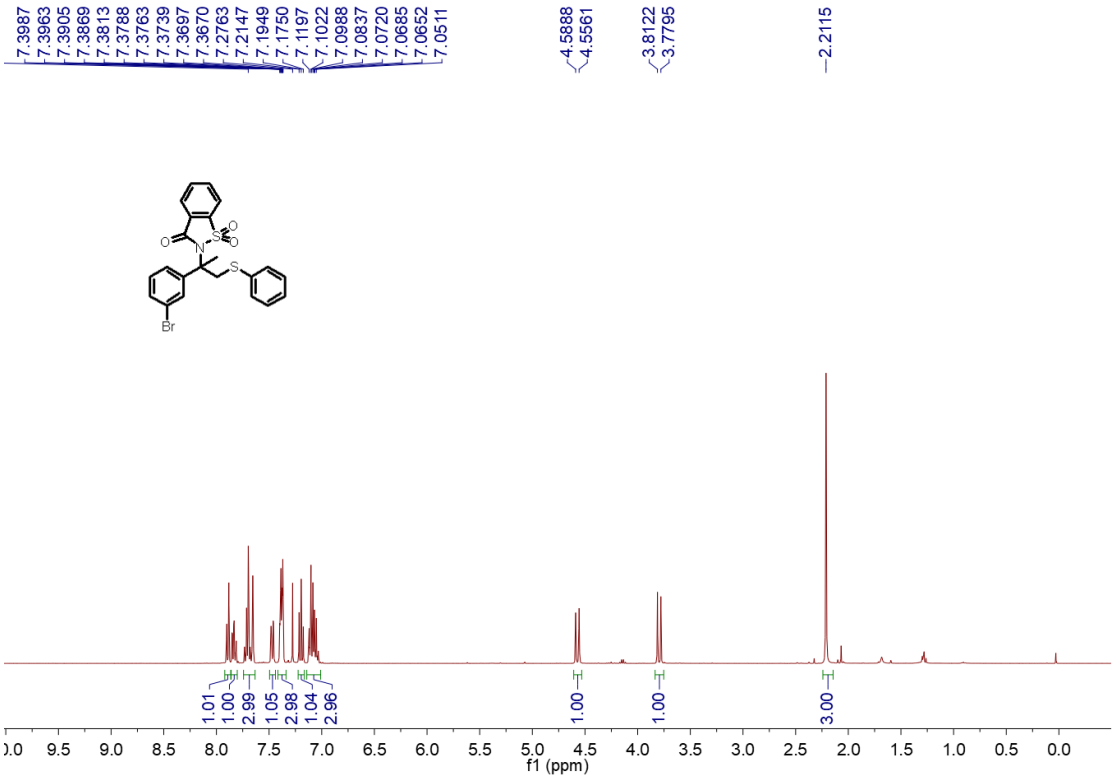
^{1}H NMR spectrum of c56



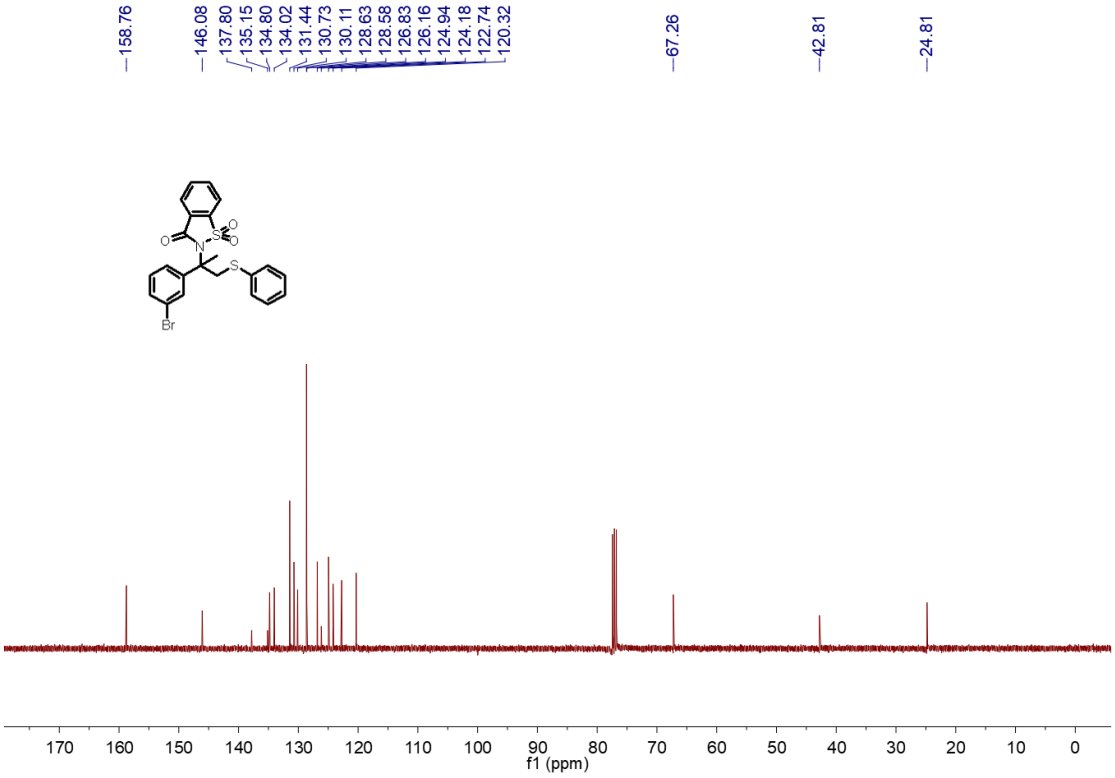
^{13}C NMR spectrum of c56



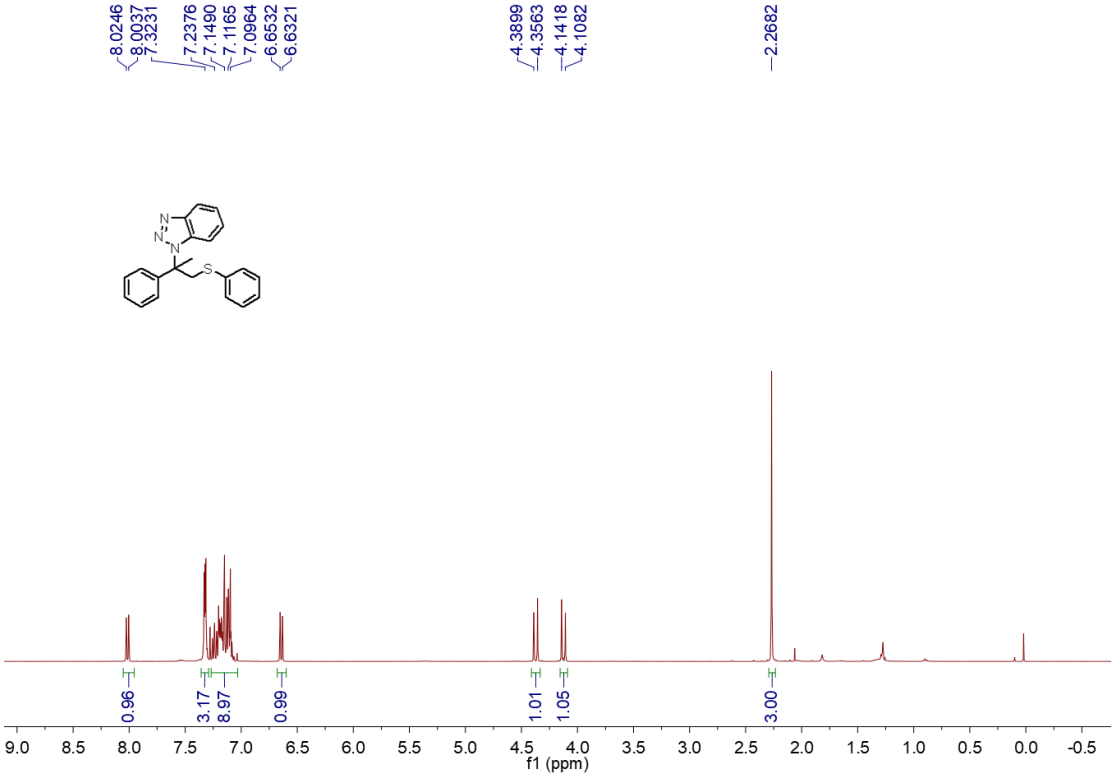
^{1}H NMR spectrum of c57



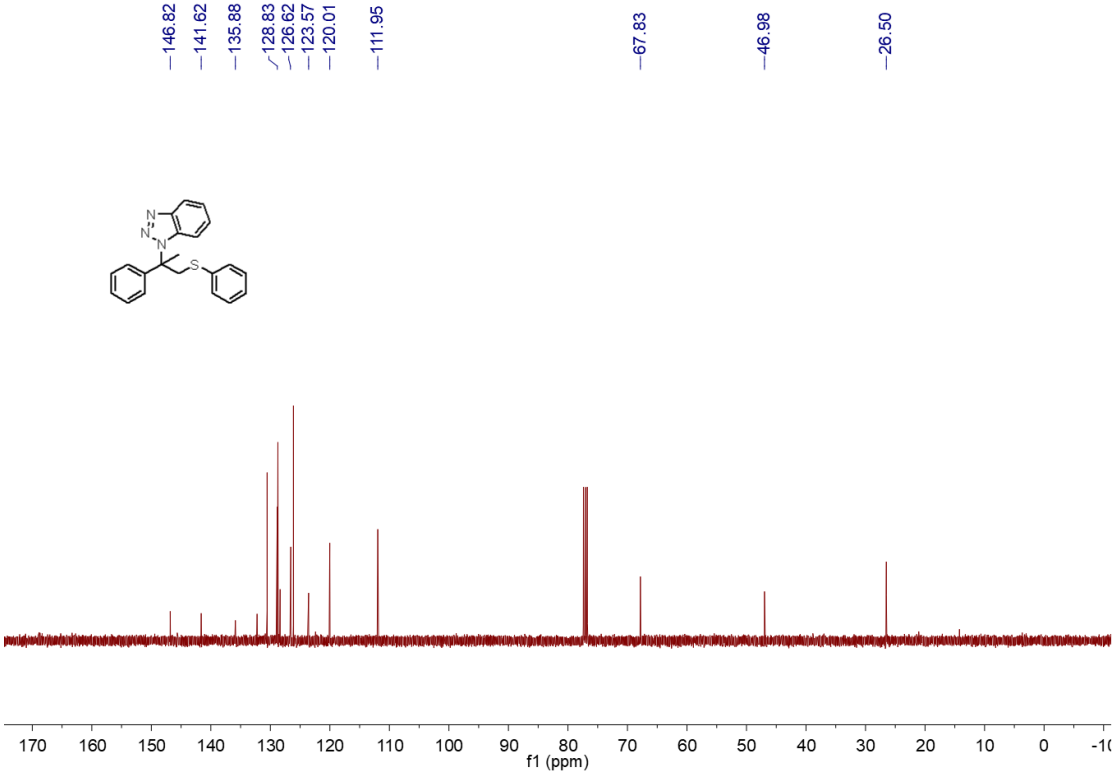
^{13}C NMR spectrum of c57



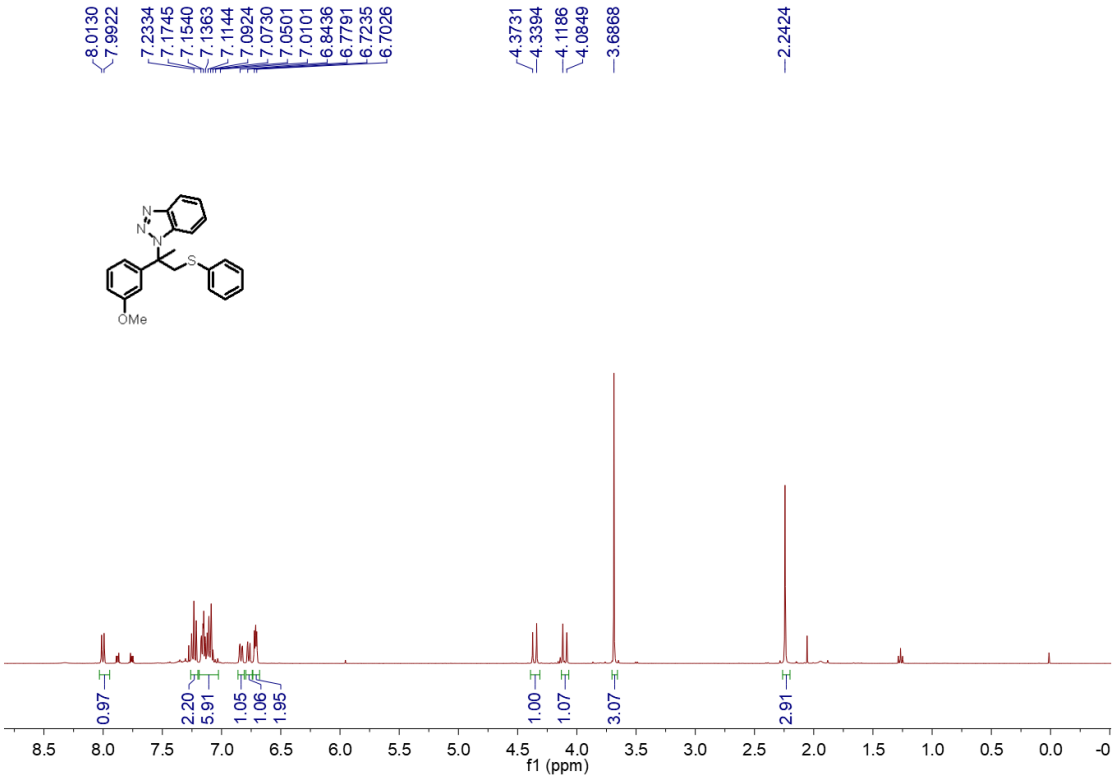
^{1}H NMR spectrum of c58



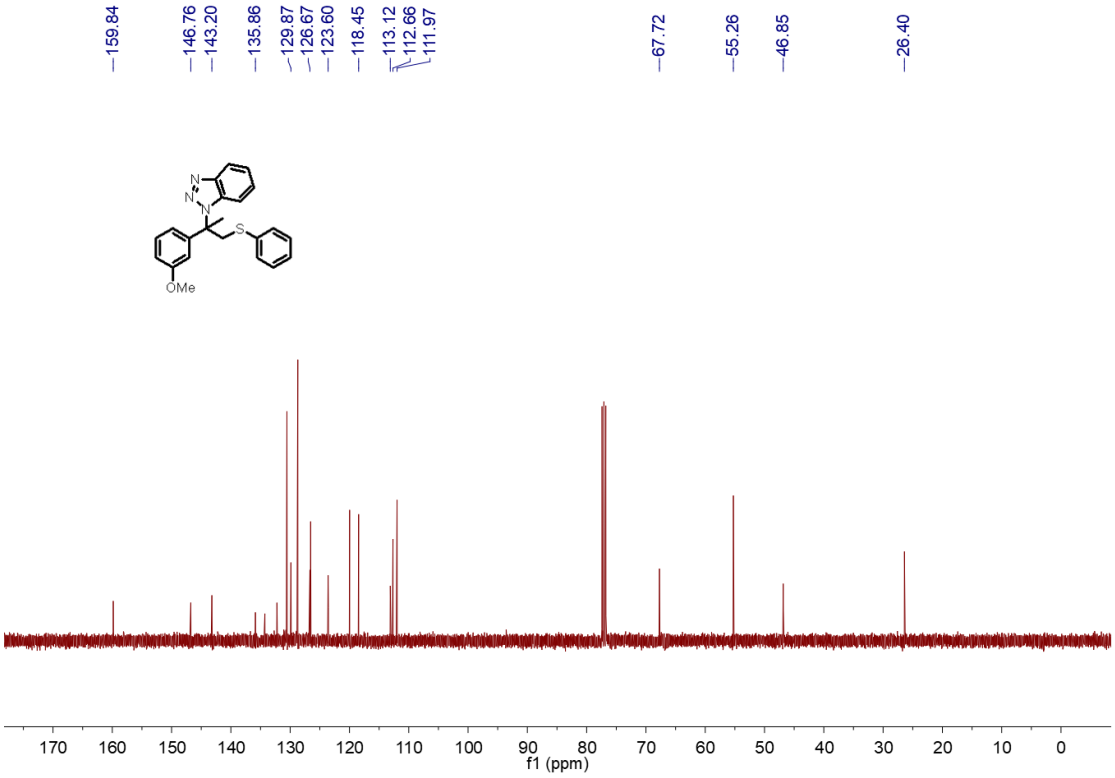
^{13}C NMR spectrum of c58



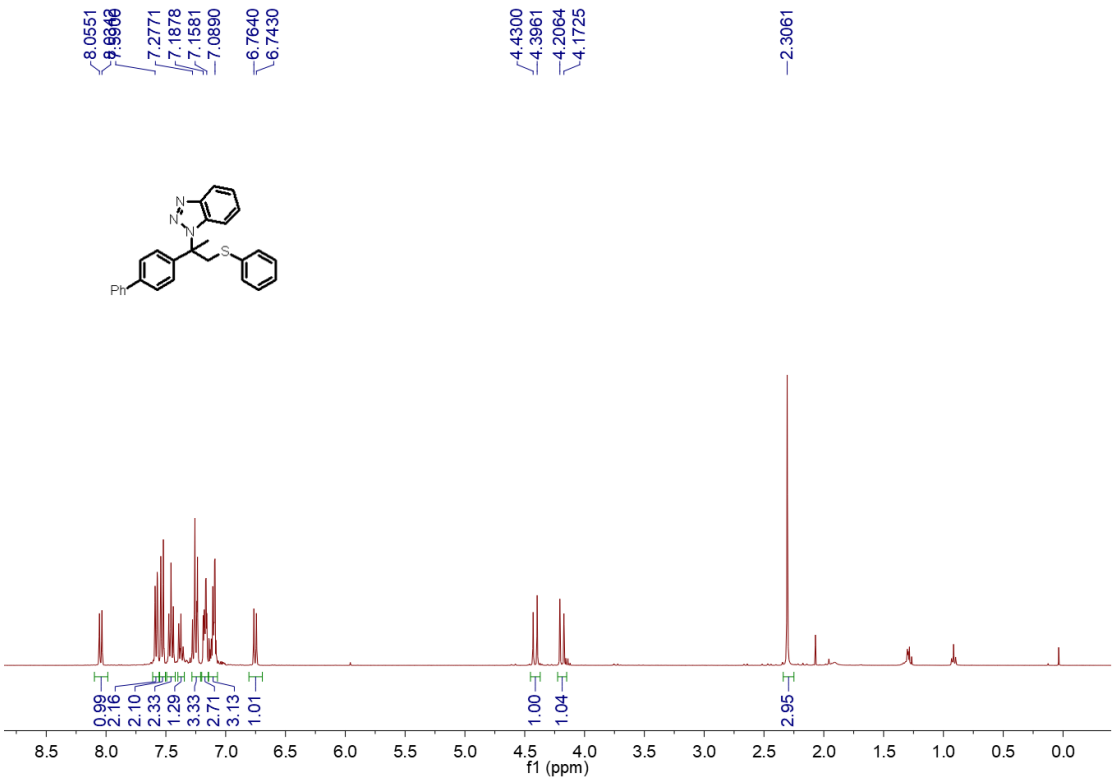
^{1}H NMR spectrum of c59



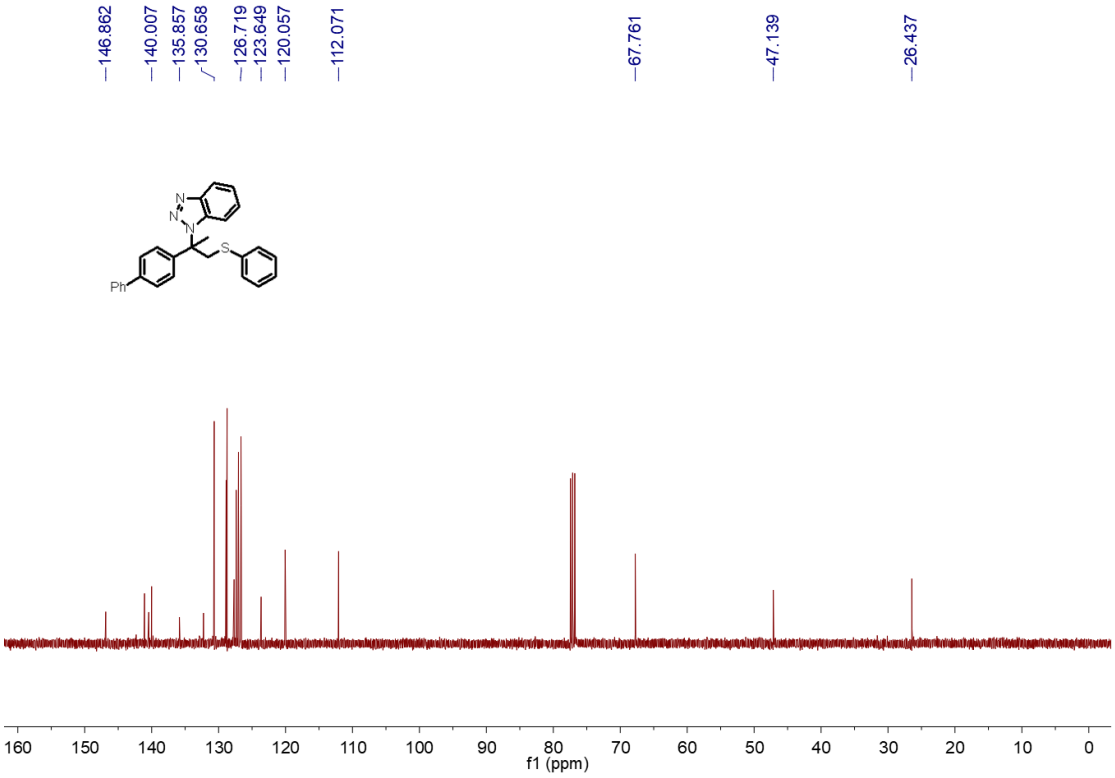
^{13}C NMR spectrum of c59



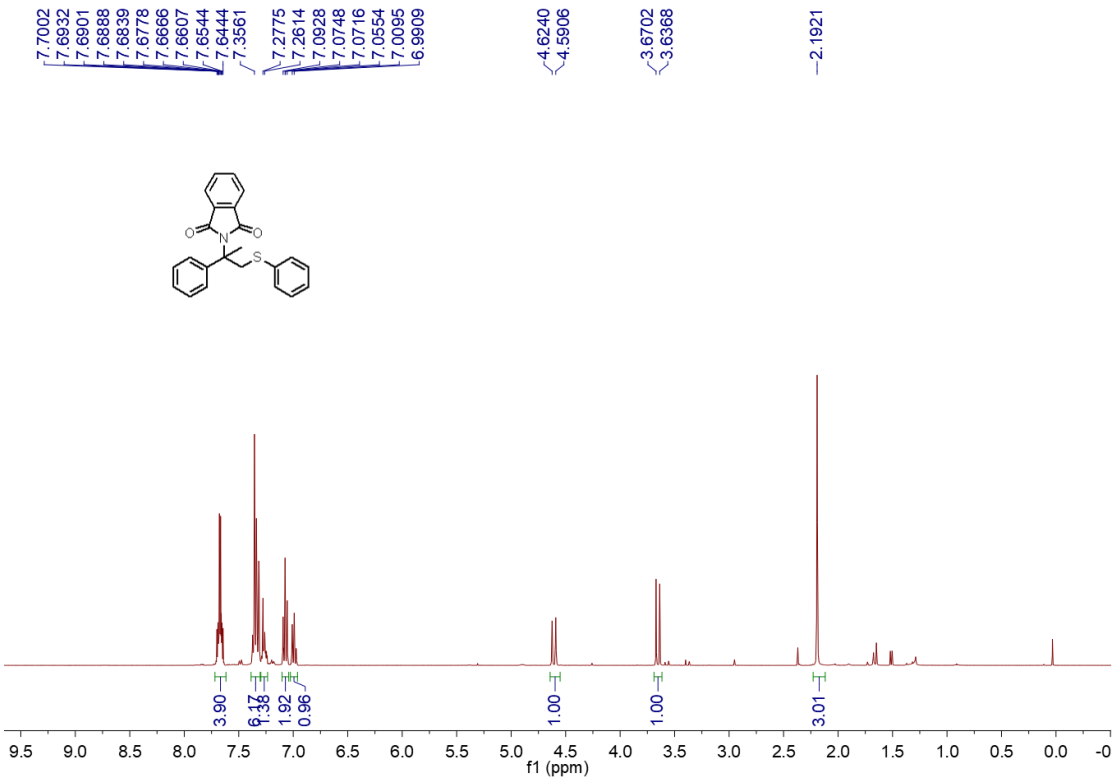
^{1}H NMR spectrum of c60



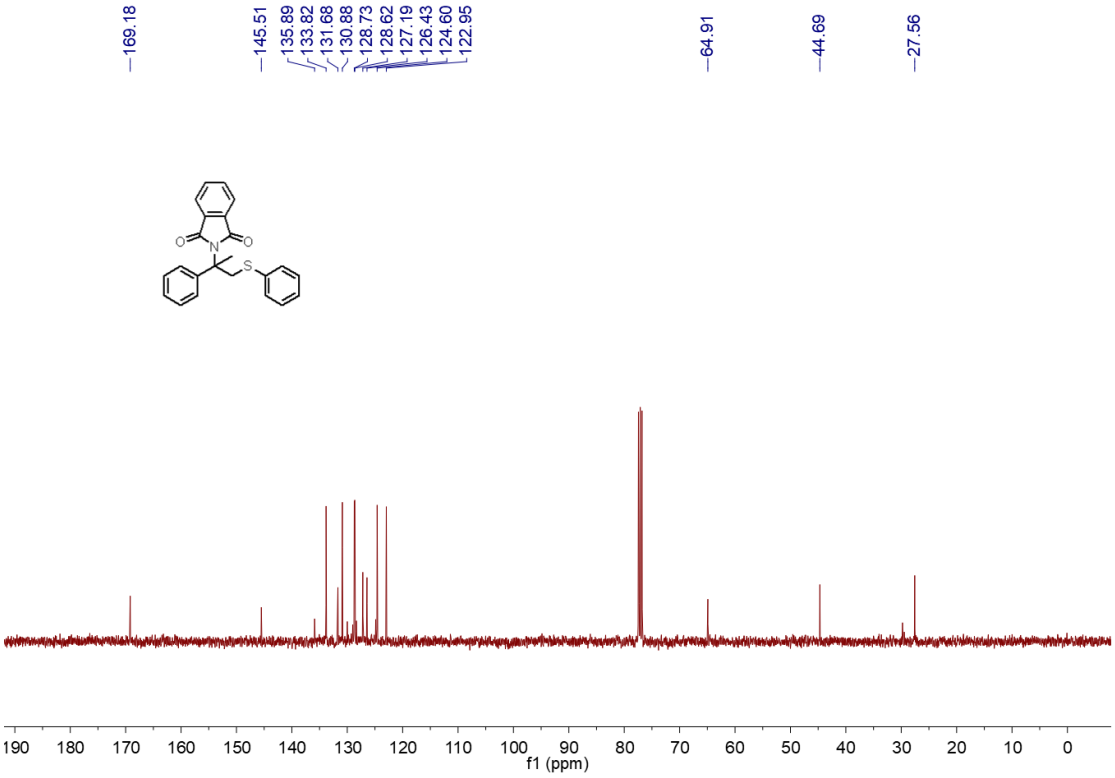
^{13}C NMR spectrum of c60



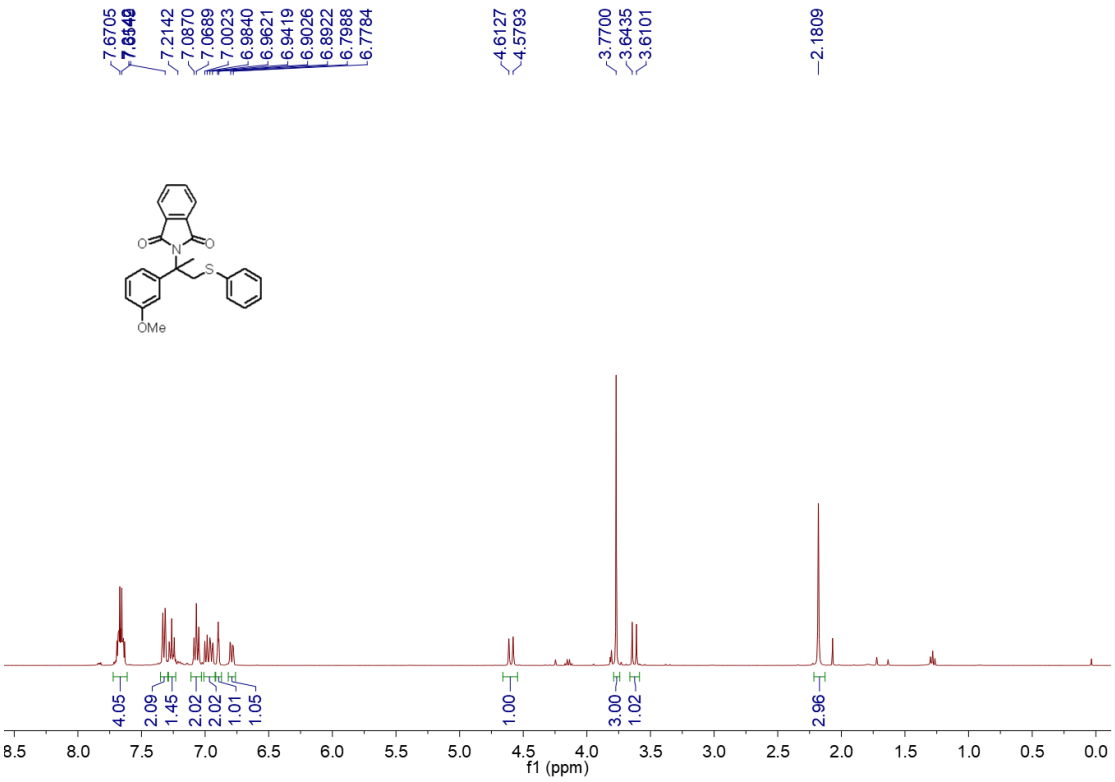
^{1}H NMR spectrum of c61



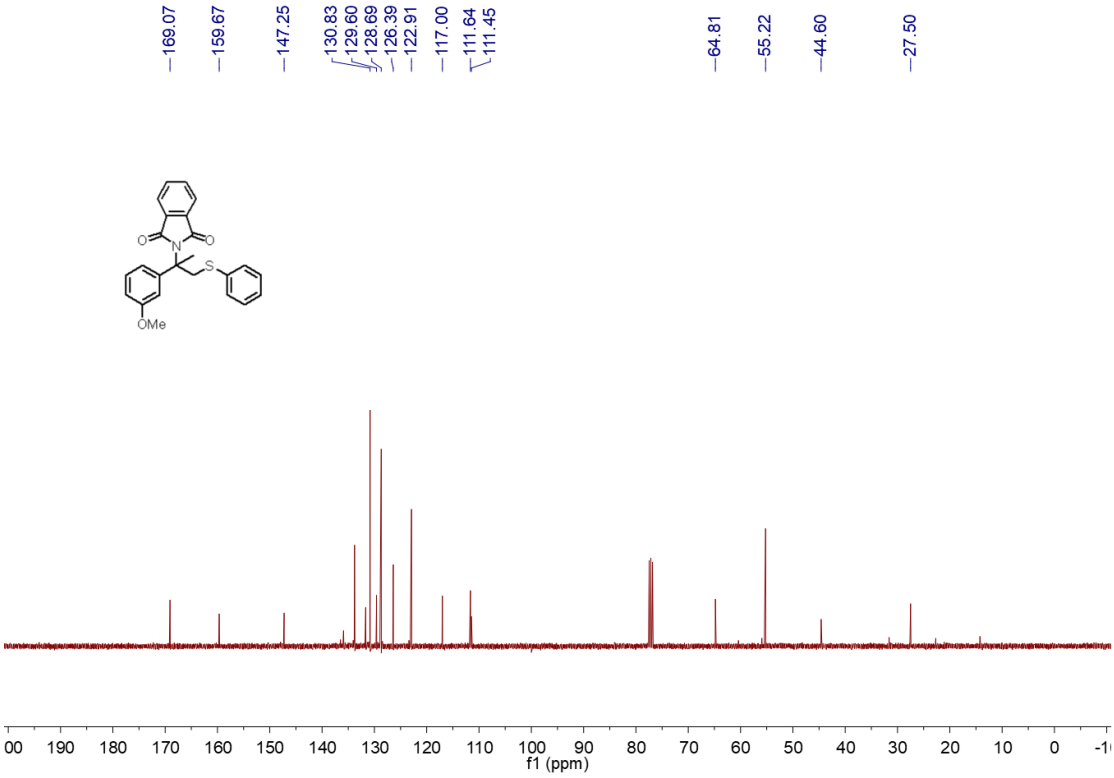
^{13}C NMR spectrum of c61



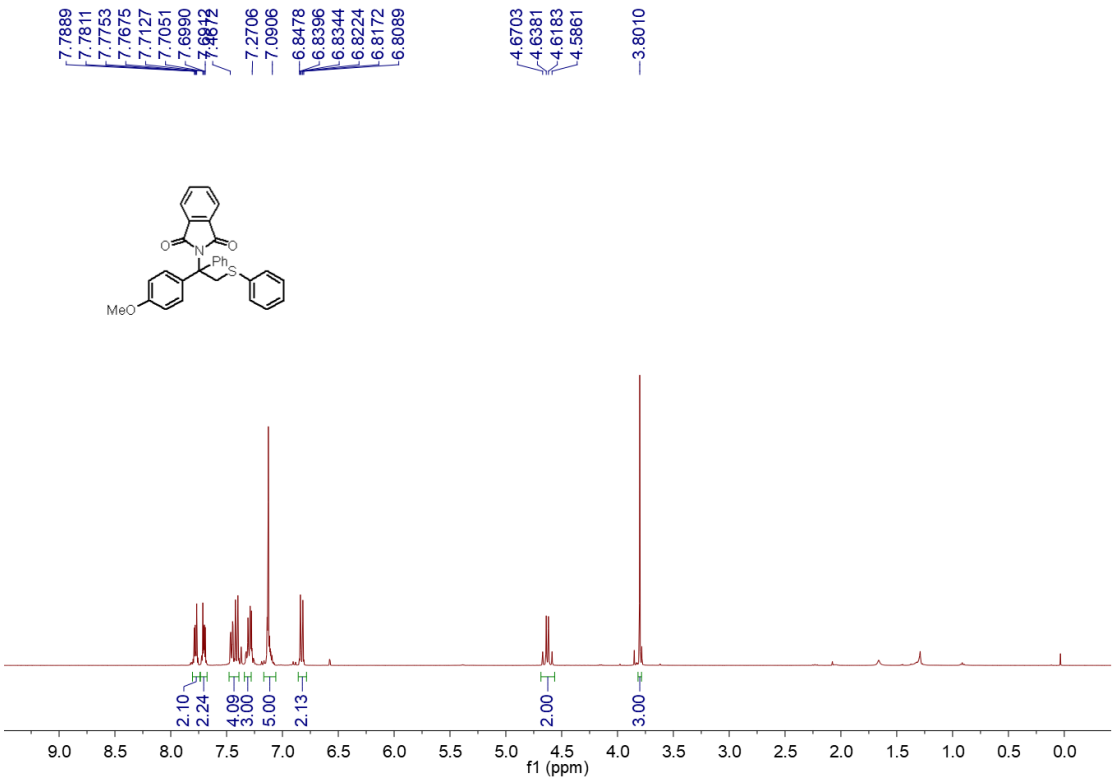
^{1}H NMR spectrum of c62



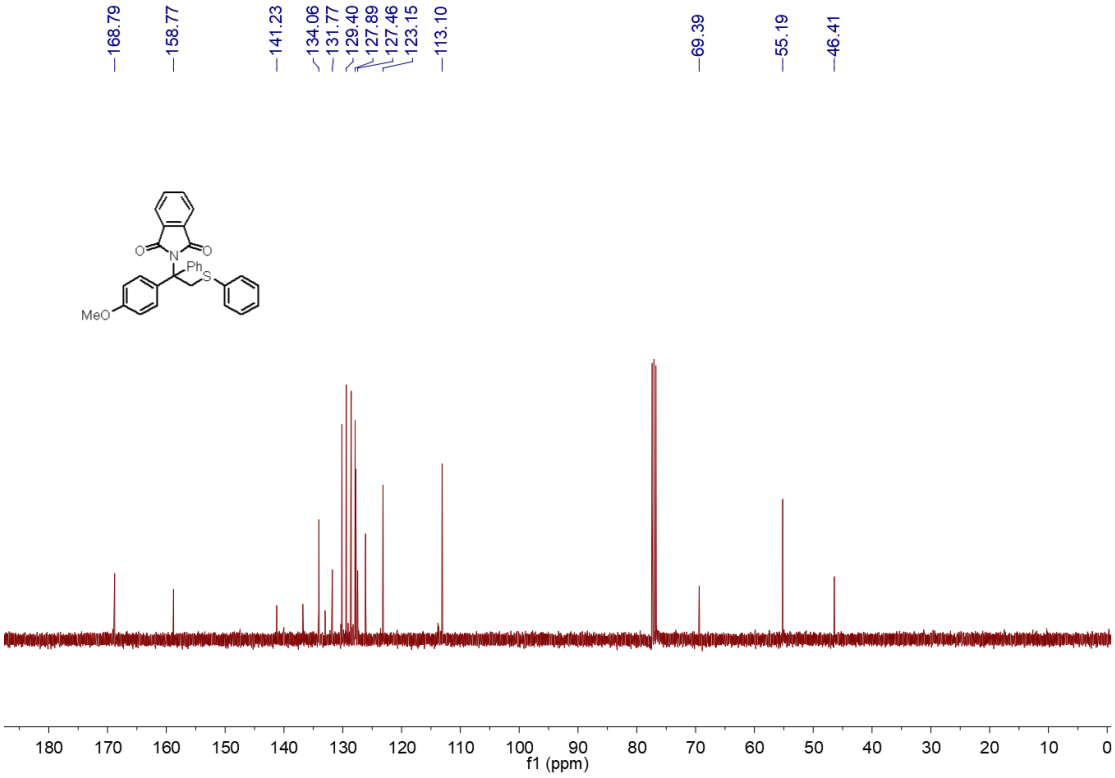
^{13}C NMR spectrum of c62



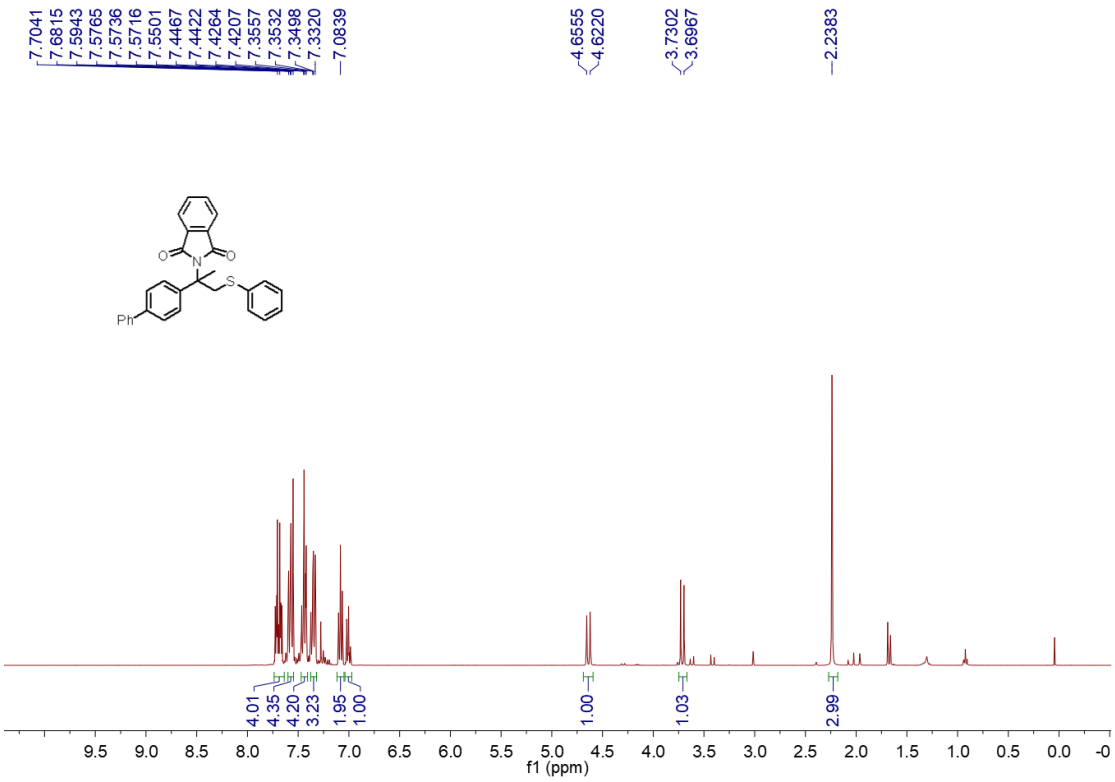
^{1}H NMR spectrum of c63



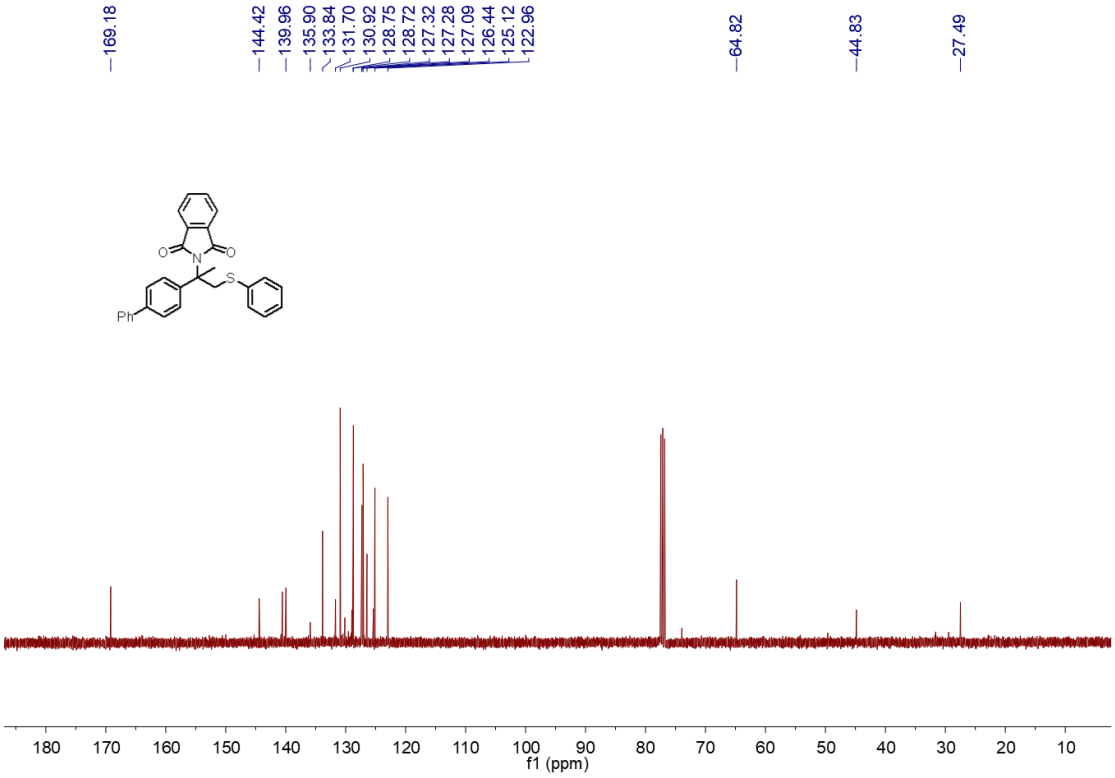
^{13}C NMR spectrum of c63



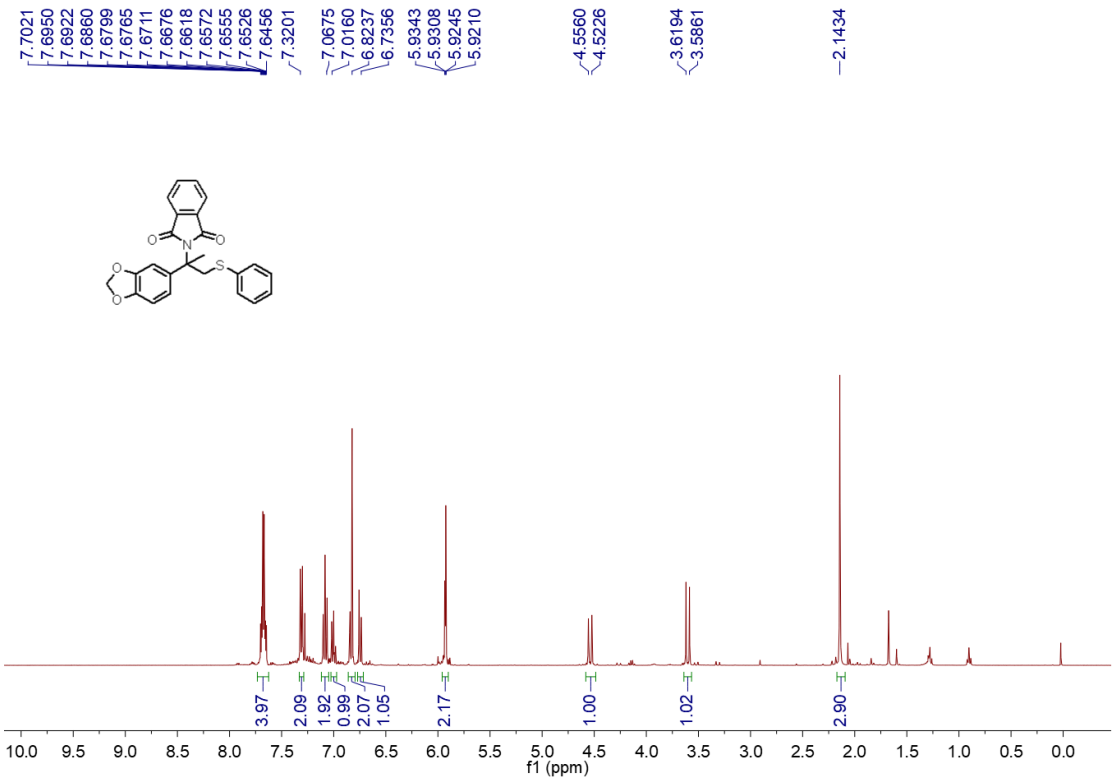
^{1}H NMR spectrum of c64



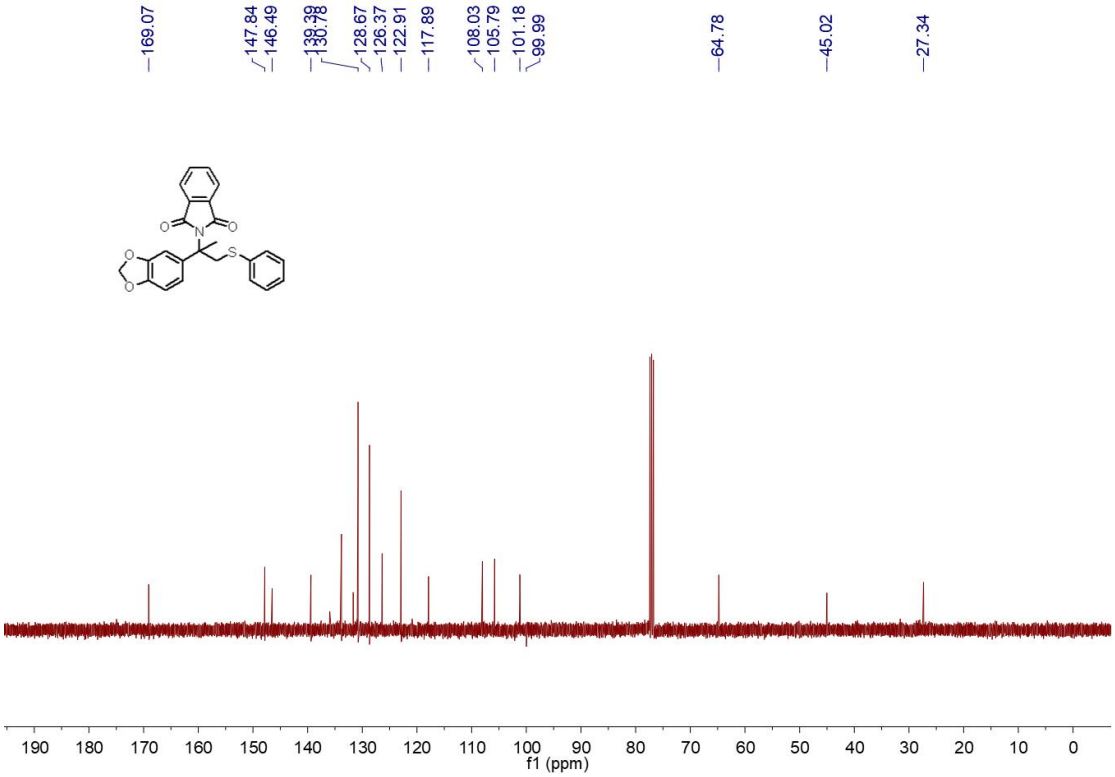
^{13}C NMR spectrum of c64



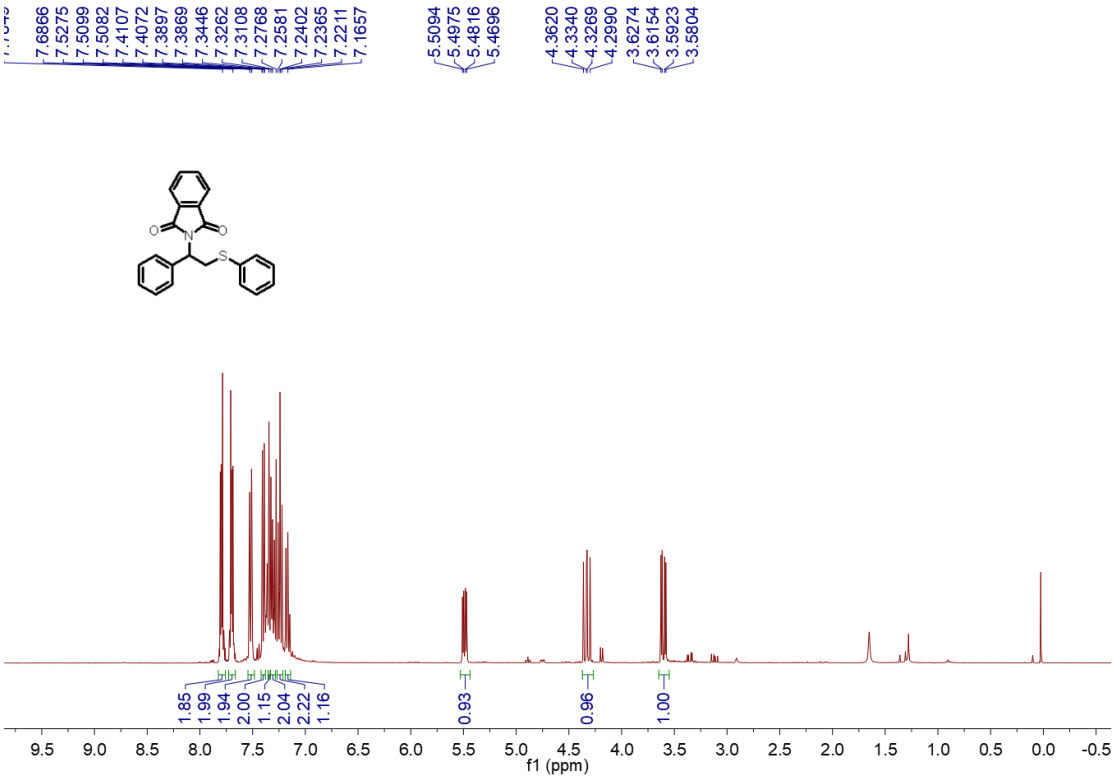
^{1}H NMR spectrum of c65



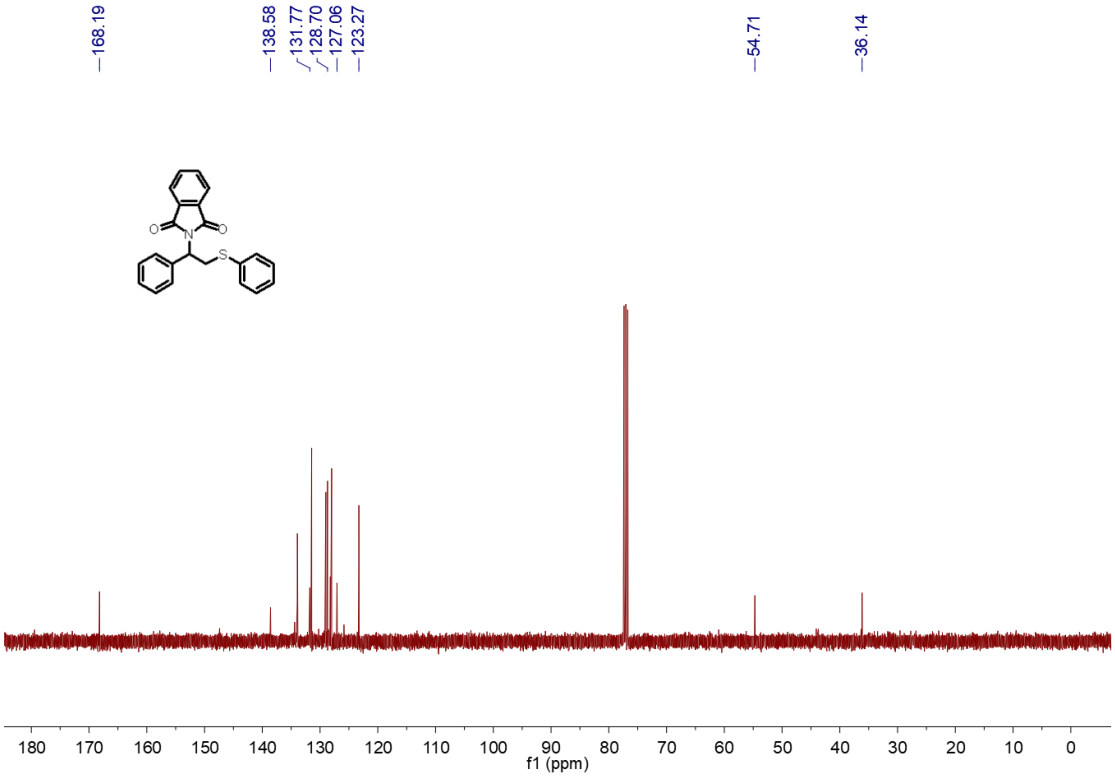
^{13}C NMR spectrum of c65



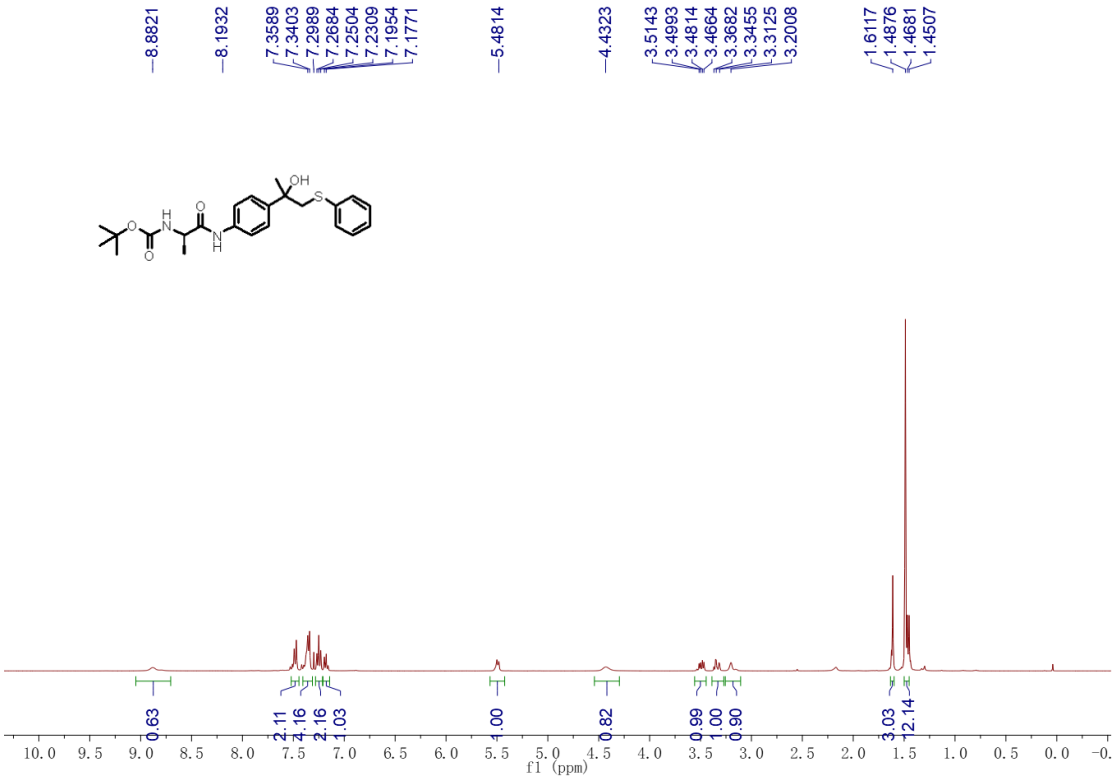
^{1}H NMR spectrum of c66



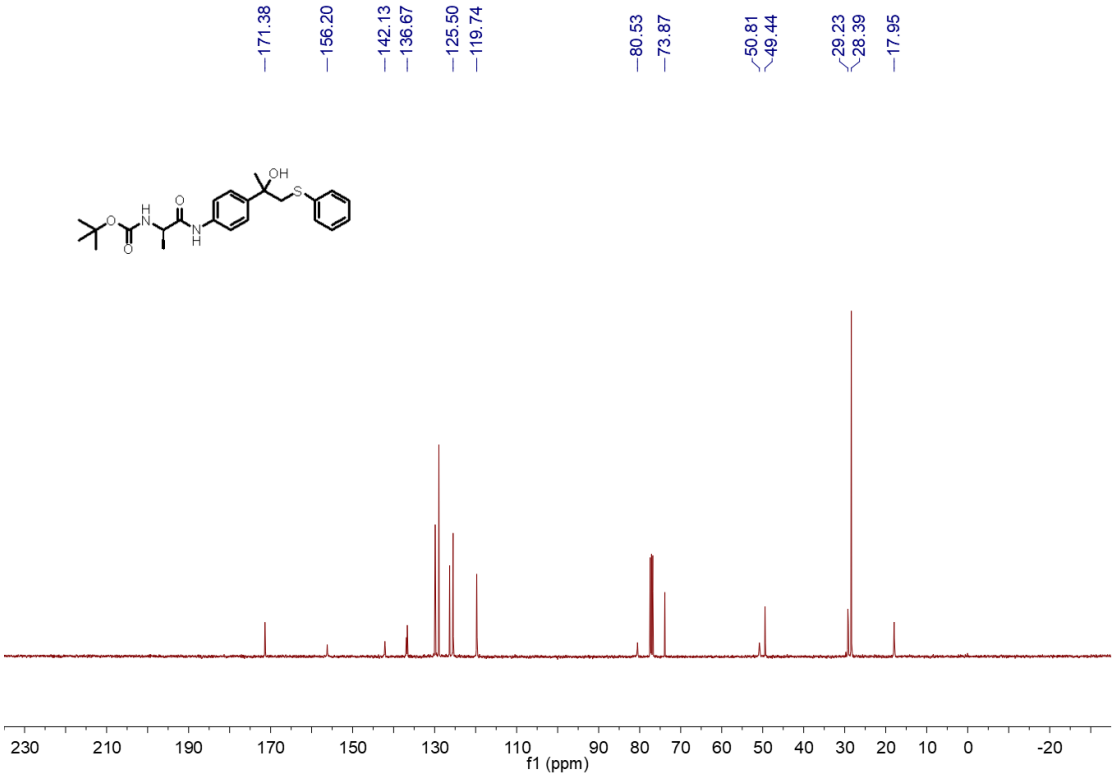
^{13}C NMR spectrum of c66



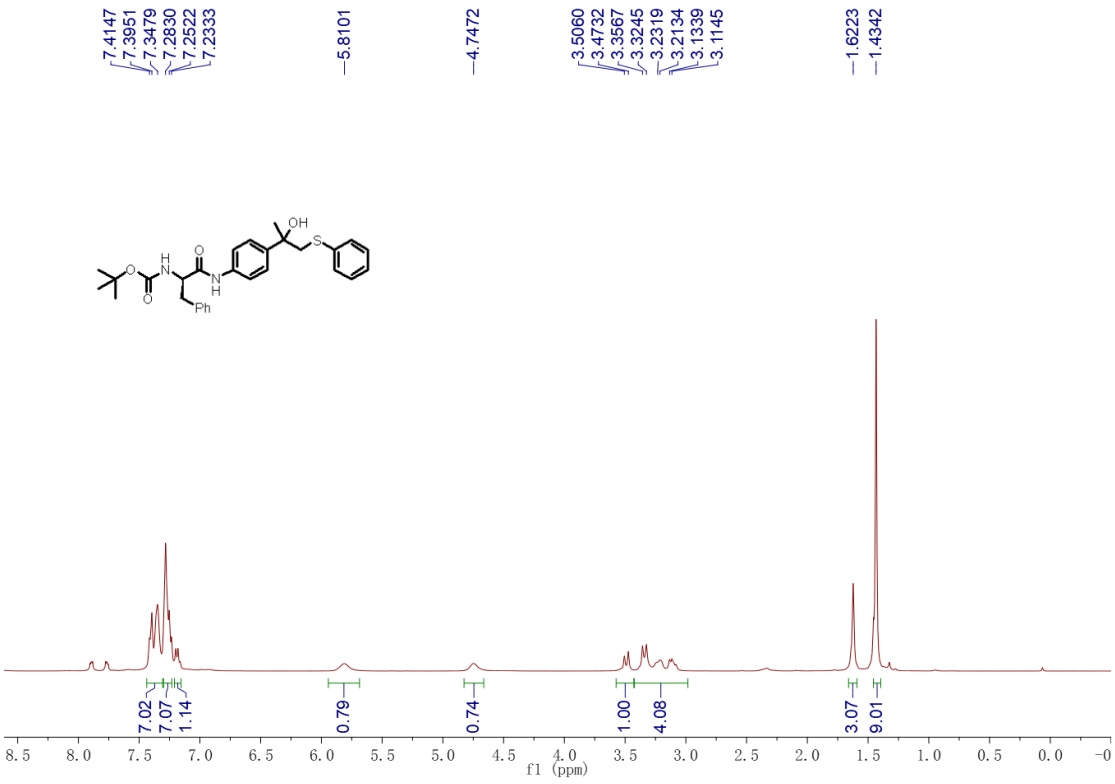
^{1}H NMR spectrum of c67



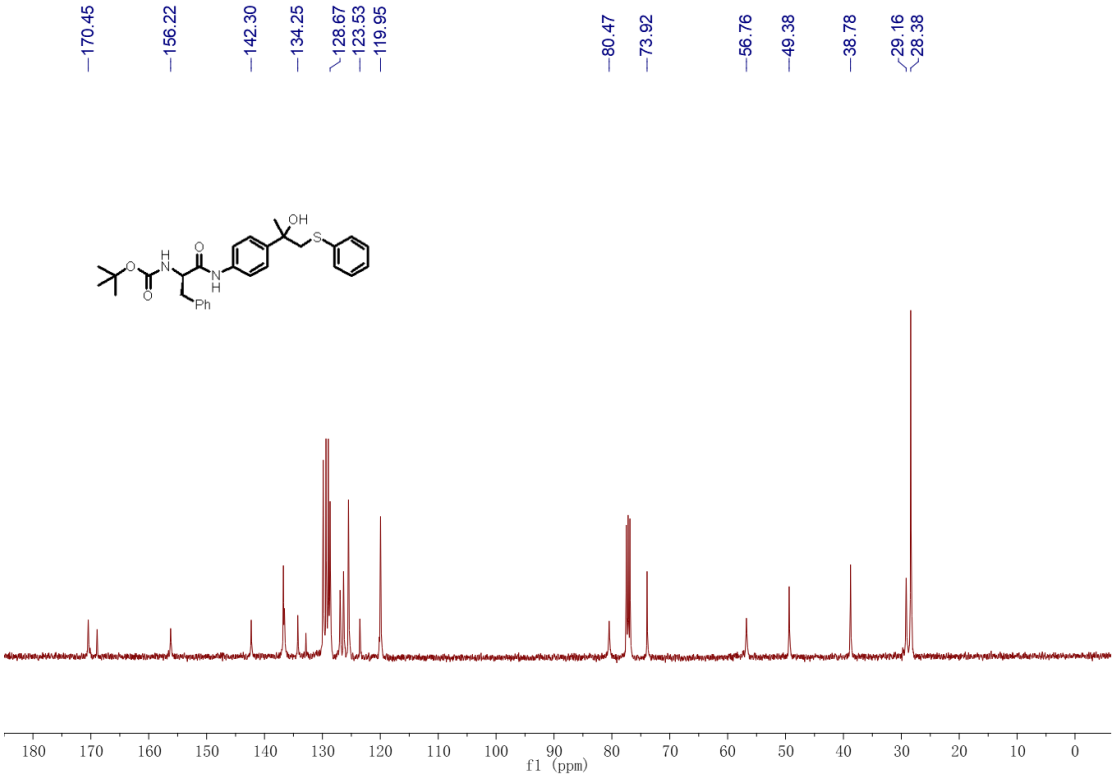
^{13}C NMR spectrum of c67



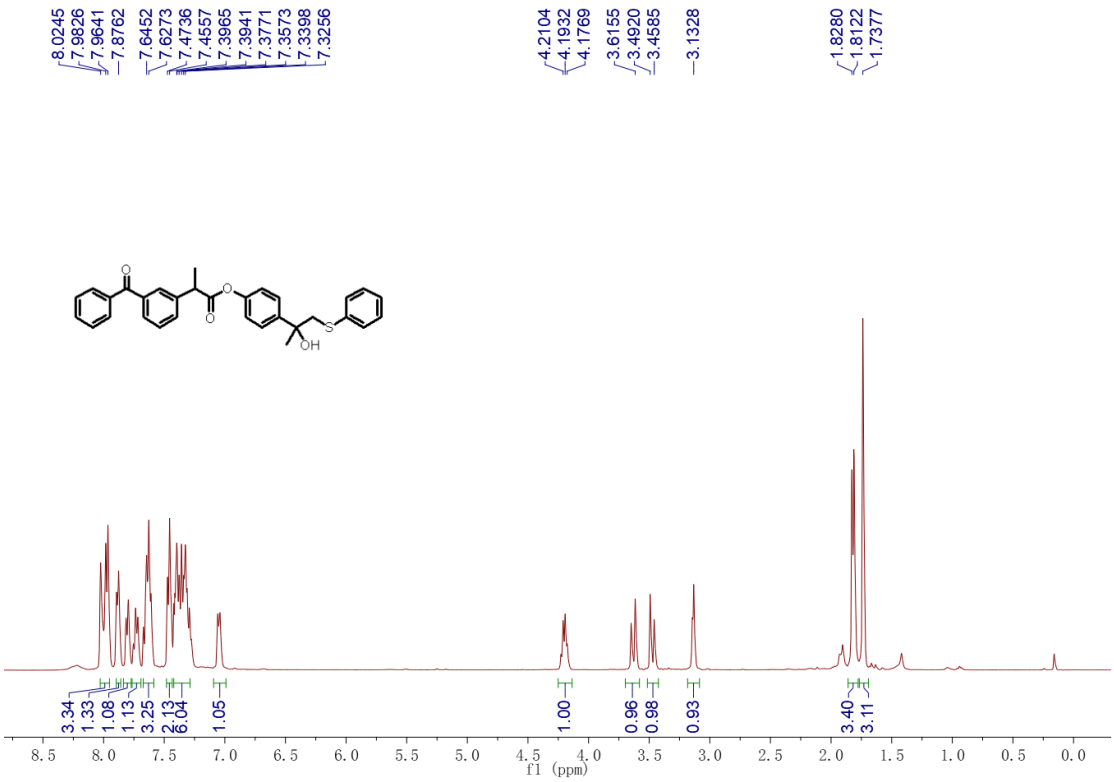
^{1}H NMR spectrum of c68



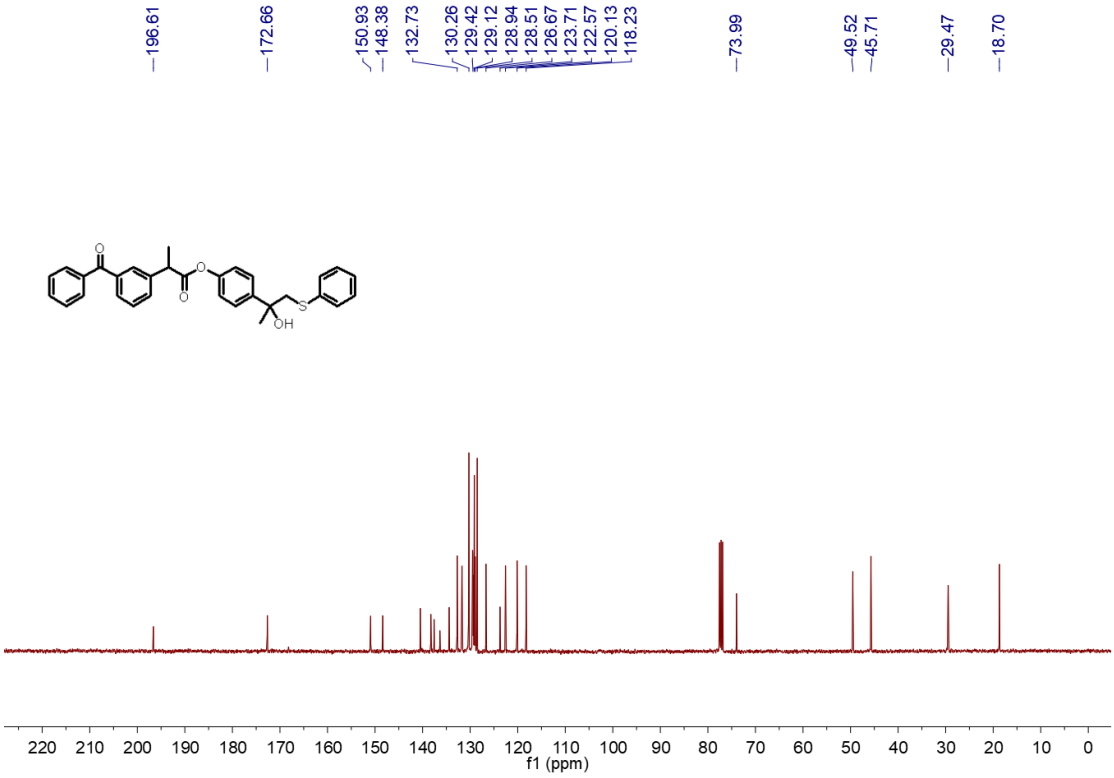
^{13}C NMR spectrum of c68



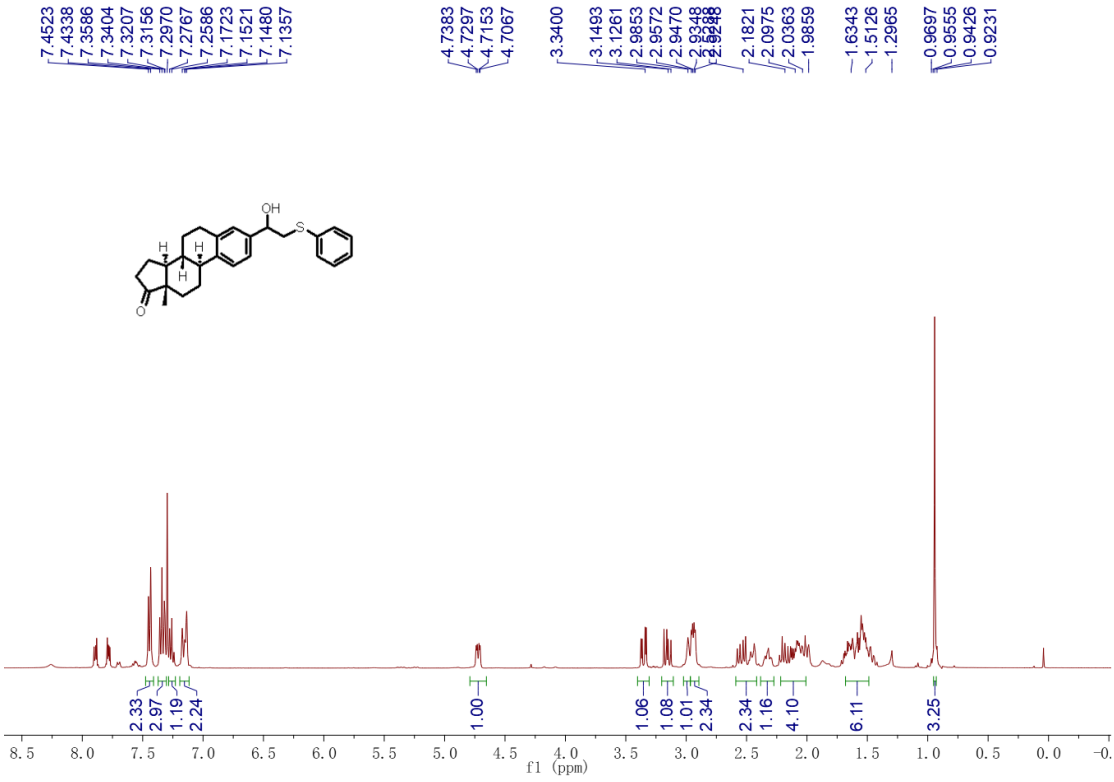
^{1}H NMR spectrum of c69



^{13}C NMR spectrum of c69



^{1}H NMR spectrum of c70



^{13}C NMR spectrum of c70