Supporting Information for….

Aerial dioxygen activation vs. thiol–ene click reaction within a system

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Content

EXPERIMENTAL SECTION

General information. All the chemicals were purchased from the commercially available sources and used without further purification. The reactions were done mainly under open atmosphere. Column chromatographic purification of the compounds was performed using (230-400) mess silica gel and hexane/ethyl acetate as an eluent. ^{1}H and ^{13}C spectra of the compounds were recorded on Bruker 400 and 700 MHz instrument at 25 ^{o}C. The chemical shift value (δ, ppm) were reported with respect to the residual chloroform (7.26 for ^{1}H and 77.16 ppm for ^{13}C). High resolution mass spectroscopy (HR-ESIMS) was recorded on ESI-TOF (Time-of-flight) mass spectroscopy.

SYNTHESIS AND CHARACTERIZATION

General procedure for the preparation of thioethers (3). Styrene (60 μL, 0.522 mmol) and thiophenol (80 μL, 0.784 mmol) were placed in an oven dried round bottom flask. Then the mixture was allowed to stir for 30 min at room temperature (35-40 ^{o}C). The resulting mixture was purified by silica gel column chromatography using hexane as eluent.

General procedure for the preparation of *β*-hydroxysulfides (4). An oven dried round bottom flask was charged with thiophenol (0.213 μL, 2.09 mmol) and ^{t}BuOLi (8.5 mg, 0.104 mmol) in ethanol solvent. Then styrene (60 μL, 0.522 mmol) was added and the resulting mixture was stirred for 4 h at room temperature (35-40 ^{o}C) in open atmosphere. After that the mixture was concentrated under vacuum. The mixture was diluted with dichloromethane and washed with water and dried over anhydride sodium sulphate. The resulting mixture was purified by silica gel column chromatography hexane/ethyl acetate mixture an eluent.

Preparation of phenyl(1-phenylethyl)sulfane (5aa). An oven dried round bottom flask was charged with thiophenol (1.06 μL, 1.04 mmol) and Ag(OTf) (161 mg, 0.627 mmol) in benzene. Then styrene (60 μL, 0.522 mmol) was added. Then the resulting mixture was stirred for 8 h at room temperature in open atmosphere. After that the mixture was filtered using celite and diluted with dichloromethane, washed with brine solution and then dried over anhydrous

sodium sulphate. After that the mixture was purified over silica gel column chromatography and hexane/ethyl acetate as eluent.

H_2O^{18} and $^{16}O_2$ labelling experiments. In an oven dried Schlenk tube charged with dry ethanol, thiophenol (0.213 µL, 2.09 mmol), lithium tert-butoxide (8.5 mg, 0.104 mmol) and styrene (60 µL, 0.522 mmol). Then 0.5 mL of H_2O^{18} was added to the mixture and stirred for 4 h at room temperature in open atmosphere. Then the resulting mixture was concentrated under vacuum and diluted with dichloromethane, washed with water and dried over anhydride sodium sulphate. After that the mixture was purified with silica gel column chromatography to afford the product **4aa** in 94% yield.

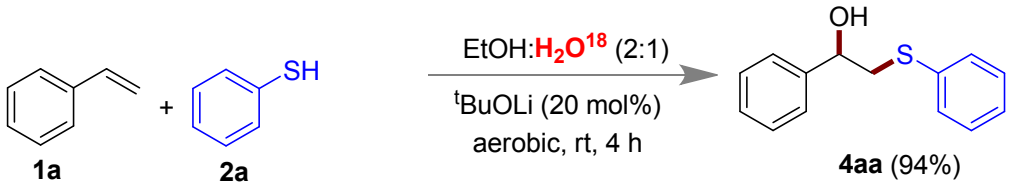


Fig. S1

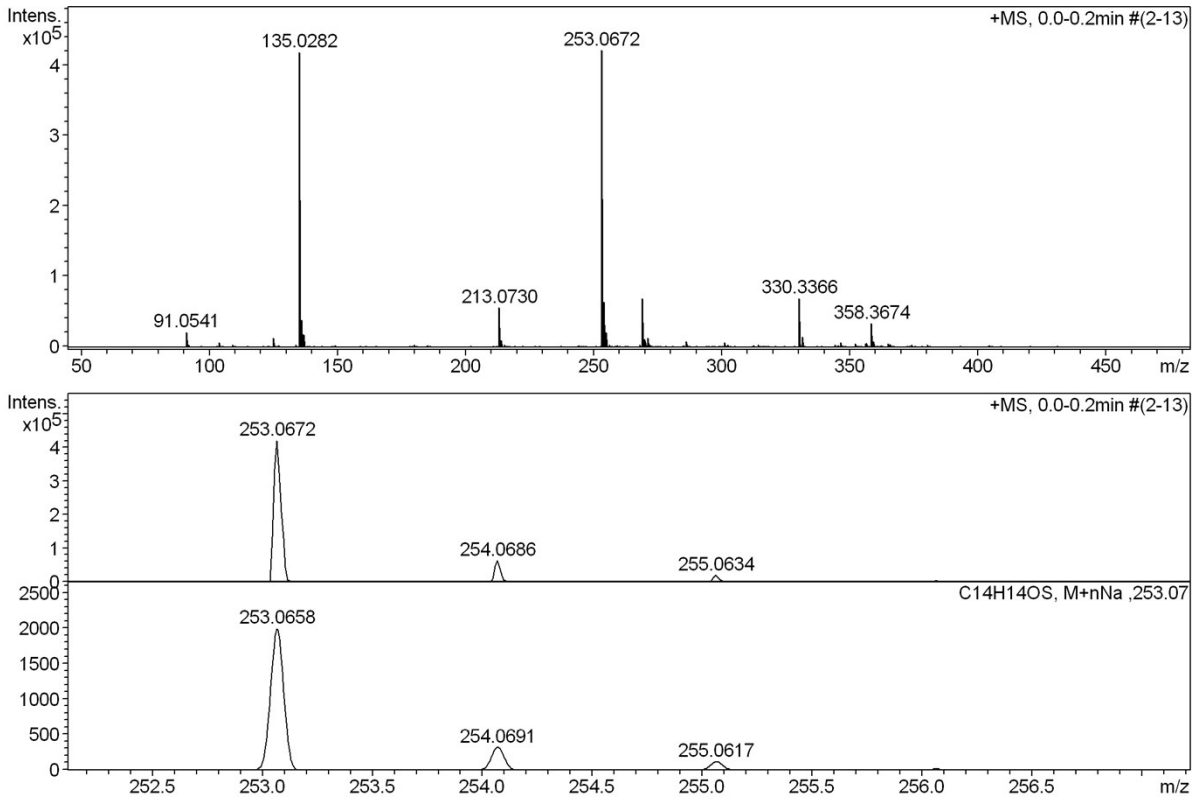


Fig. S2 The ESI-TOF Mass spectra of **4aa** in $(M + Na)^+$ mode.

O^{18} Labelling experiments. An oven dried Schlenk tube was charged with dry ethanol, thiophenol (0.213 µL, 2.09 mmol), ^{t}BuOLi (8.5 mg, 0.104 mmol) and styrene (60 µL, 0.522 mmol) in an argon atmosphere. Then the schlenk tube was purged with labelling O^{18} isotope. The mixture was stirred for 4h at room temperature. Then the resulting mixture was concentrated with vacuum and diluted with dichloromethane, washed with water and dried over sodium sulphate. Column chromatography purification using silica gel affords the product 70% yield.

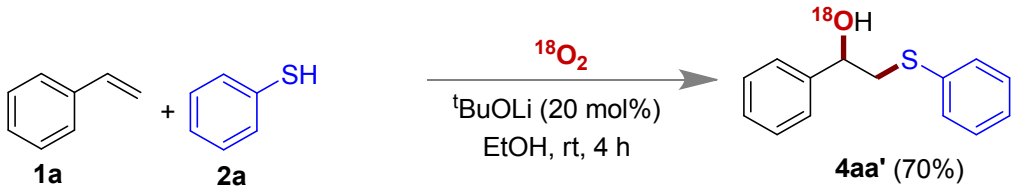


Fig. S3

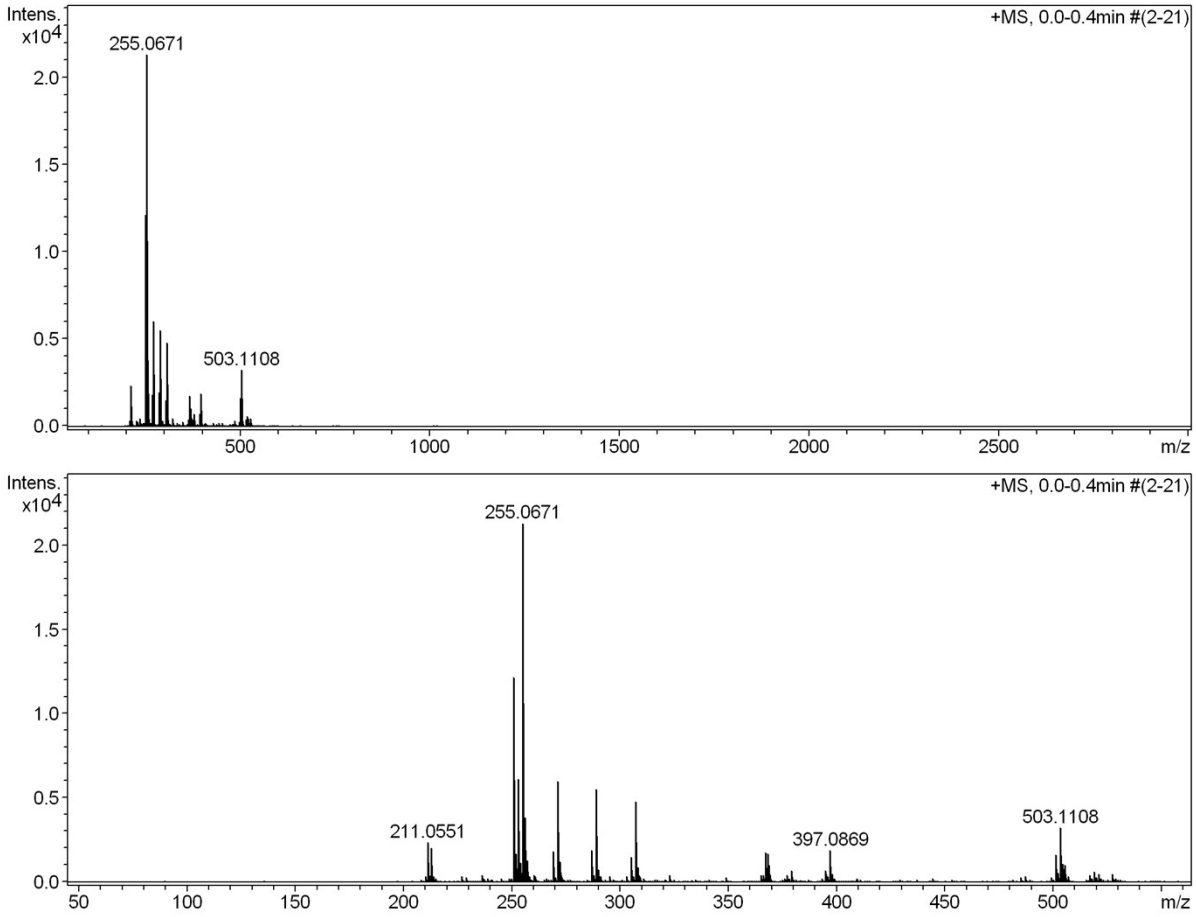
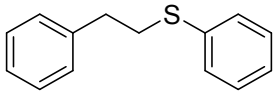


Fig. S4 The ESI-TOF Mass spectra of **4aa′** in $(M + Na)^{+}$ mode.

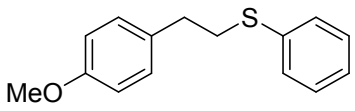
CHARACTERIZATION DATA

Phenethyl(phenyl)sulfane (3aa):[1] R_f= 0.75 (in hexane); colorless liquid; yield 98% (119 mg);

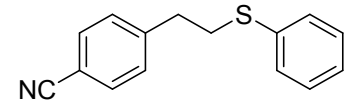


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.34 (m, 2H), 7.34 – 7.26 (m, 4H), 7.25 – 7.15 (m, 4H), 3.21 – 3.15 (m, 2H), 2.97 – 2.91 (m, 2H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 140.3, 136.5, 129.3, 129.1, 128.6 (×2), 126.6, 126.1, 35.7, 35.2.

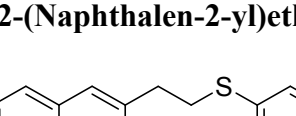
(4-Methoxyphenethyl)(phenyl)sulfane (3ba):[1] R_f = 0.75 (5% ethyl acetate in hexane); colorless liquid; yield 98% (105 mg); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 2H), 7.31 – 7.27 (m, 2H), 7.21 – 7.16 (m, 1H), 7.14 – 7.09 (m, 2H), 6.86 – 6.82 (m, 2H), 3.79 (s, 3H), 3.17 – 3.10 (m, 2H), 2.91 – 2.83 (m, 2H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 158.4, 136.6, 132.5, 129.6, 129.3, 129.1, 126.1, 114.1, 55.4, 35.5, 34.9.



4-(2-(Phenylthio)ethyl)benzonitrile (3da): R_f = 0.2 (5% ethyl acetate in hexane); colorless liquid; yield 76% (100 mg); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.32 – 7.27 (m, 4H), 7.23 – 7.20 (m, 1H), 3.17 (t, *J* = 7.7 Hz, 2H), 2.98 (t, *J* = 7.7 Hz, 2H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 145.7, 135.7, 132.4, 129.9, 129.6, 129.2, 126.6, 119.0, 110.5, 35.7, 34.8; IR (KBr) $\bar{\upsilon}$ 3056, 2923, 2227, 1920, 1606, 1582, 1480; HRMS (ESI-TOF) calcd for $C_{15}H_{13}NS$ $(M + H)^+$ 240.0841, found 240.0836.



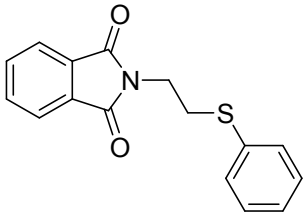
(2-(Naphthalen-2-yl)ethyl)(phenyl)sulfane (3ga):[1] R_f = 0.75 (5% ethyl acetate in hexane); colorless liquid; yield 72% (75 mg); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.84 – 7.75 (m, 3H), 7.64 (s, 1H), 7.49 – 7.41 (m, 2H), 7.41 – 7.36 (m, 2H), 7.35 – 7.27 (m, 3H), 7.23 – 7.17 (m, 1H), 3.30 – 3.23 (m, 2H), 3.14 – 3.06 (m, 2H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 137.8, 136.5, 133.7, 132.4, 129.5, 129.1, 128.3, 127.8, 127.7, 127.2, 127.0, 126.2, 126.2, 125.6, 36.0, 35.2.



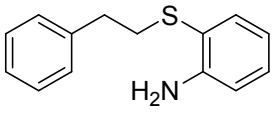
1-(2-(Phenylthio)ethyl)azepan-2-one (3ia):[2] R_f = 0.2 (20% ethyl acetate in hexane); colorless liquid; yield 84% (90 mg); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.7 Hz, 2H), 7.29 (t, *J* = 7.7 Hz, 2H), 7.17 (t, *J* = 7.0 Hz, 1H), 3.62 – 3.55 (m, 2H), 3.37 – 3.32 (m, 2H), 3.10 (t, *J* = 7.0 Hz, 2H), 2.54 –

2.48 (m, 2H), 1.74 – 1.62 (m, 6H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 176.1, 135.9, 129.1, 128.8, 126.1, 51.1, 49.1, 37.3, 31.3, 30.0, 28.9, 23.4.

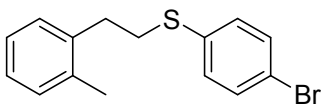
2-(2-(Phenylthio)ethyl)isoindoline-1,3-dione (3ja):[3] R_f = 0.25 (5% ethyl acetate in hexane); colorless liquid; yield 84% (82 mg); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 5.6, 2.8 Hz, 2H), 7.70 (dd, *J* = 5.6, 2.8 Hz, 2H), 7.43 – 7.39 (m, 2H), 7.25 – 7.23 (m, 2H), 7.15 – 7.11 (m, 1H), 3.95 – 3.92 (m, 2H), 3.27 – 3.20 (m, 2H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 168.2, 135.0, 134.1, 132.1, 129.9, 129.2, 126.6, 123.4, 37.7, 31.8. HRMS (ESI-TOF) calcd for $C_{16}H_{13}NO_2S$ $(M + H)^+$ 284.0740, found 284.0747.



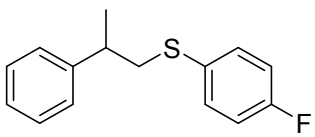
2-(Phenethylthio)aniline (3af):[4] R_f= (10% hexane/ethyl acetate); colorless liquid; yield 72% (87 mg); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.45 – 7.38 (m, 1H), 7.31 – 7.27 (m, 2H), 7.23 – 7.19 (m, 1H), 7.18 – 7.15 (m, 2H), 7.15 – 7.11 (m, 1H), 6.78 – 6.68 (m, 2H), 4.08 (br, 2H), 3.03 – 2.99 (m, 2H), 2.89 – 2.83 (m, 2H). ^{13}C NMR (175 MHz, $CDCl_3$) δ 148.0, 140.4, 135.9, 129.8, 128.7, 128.5, 126.4, 118.9, 118.1, 115.3, 36.2, 36.1; HRMS (ESI-TOF) calcd for $C_{14}H_{15}NS$ $(M + H)^+$ 230.0998, found 230.0856.



(4-Bromophenyl)(2-methylphenethyl)sulfane (3cb): R_f = 0.7 (in hexane); colorless liquid; yield 98% (140 mg); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.48 – 7.34 (m, 2H), 7.27 – 7.21 (m, 2H), 7.19 – 7.09 (m, 4H), 3.14 – 3.07 (m, 2H), 2.96 – 2.88 (m, 2H), 2.28 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 138.2, 136.1, 135.8, 132.1, 130.9, 130.5, 129.2, 126.9, 126.3, 119.9, 34.1, 33.1, 19.4; IR (KBr) ῡ 3061, 2923, 1603, 1566, 1470; HRMS (ESI-TOF) calcd for $C_{15}H_{15}BrS$ $(M + O + Na^+)$ 344.9919, found 344.9921.

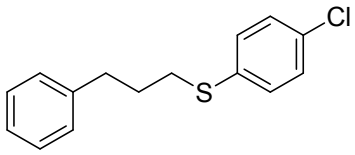


(4-Fluorophenyl)(2-phenylpropyl)sulfane (3ec): R_f = 0.6 (hexane); colorless liquid; yield 96% (108 mg); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.45 – 7.30 (m, 4H), 7.28 – 7.15 (m, 3H), 7.12 – 6.92 (m, 2H), 3.25 – 3.18 (m, 1H), 3.11 – 3.03 (m, 1H), 3.00 – 2.93 (m, 1H), 1.43 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 161.8 (d, $^1J_{CF}$ = 246.2 Hz), 145.5, 132.3 (d, $^3J_{CF}$ = 8.0 Hz), 131.7 (d, $^4J_{CF}$ = 3.2 Hz), 128.7, 127.1, 126.7, 116.1 (d, $^4J_{CF}$ = 21.9 Hz), 43.6, 39.7, 21.1, IR (KBr) ῡ 3060, 2962,

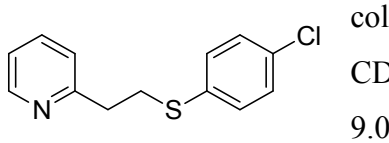


1601, 1589, 1505; HRMS (ESI-TOF) calcd for $C_{15}H_{15}FS$ (M + O + Na^+) 385.0720, found 385.0722.

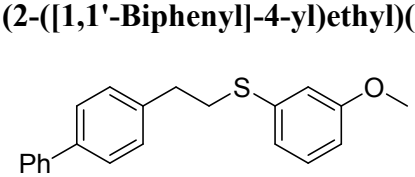
(4-Chlorophenyl)(3-phenylpropyl)sulfane (3kd):[5] R_f = 0.8 (hexane); colorless liquid; yield 85% (100 mg); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.25 – 7.19 (m, 5H), 7.18 – 7.15 (m, 2H), 2.89 (t, *J* = 7.7 Hz, 2H), 2.75 (t, *J* = 7.7 Hz, 2H), 1.99 – 1.91 (m, 2H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 141.2, 135.2, 131.9, 130.6, 129.1, 128.6, 128.6, 126.2, 34.7, 33.2, 30.6.



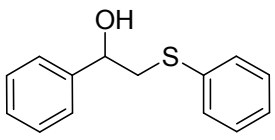
2-(2-((4-Chlorophenyl)thio)ethyl)pyridine (3hd): R_f = 0.2 (5% ethyl acetate in hexane); colorless liquid; yield 98% (138 mg); ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.58 – 8.52 (m, 1H), 7.65 – 7.58 (m, 1H), 7.29 (d, *J* = 9.0 Hz, 2H), 7.25 (d, *J* = 9.0 Hz, 2H), 7.18 – 7.12 (m, 2H), 3.34 (t, *J* = 7.7 Hz, 2H), 3.10 (t, *J* = 7.7 Hz, 2H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 159.5, 149.5, 136.4, 134.9, 132.0, 130.7, 129.1, 123.3, 121.7, 37.7, 33.4; IR (KBr) ῡ 3060, 2926, 1592, 1568, 1474; HRMS (ESI-TOF) calcd for $C_{13}H_{12}NClS$ $(M + H)^+$ 250.0452, found 250.0438.



(2-([1,1'-Biphenyl]-4-yl)ethyl)(3-methoxyphenyl)sulfane (3fe): R_f = 0.2 (hexane); colorless liquid; yield 88% (94 mg); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.7 Hz, 2H), 7.54 (d, *J* = 7.7 Hz, 2H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.30 – 7.27(m, 2H), 7.24 – 7.21 (m, 1H), 6.96 (d, *J* = 7.7 Hz, 1H), 6.92 (s, 1H), 6.78 – 6.72 (m, 1H), 3.81 (s, 3H), 3.26 – 3.19 (m, 2H), 3.04 – 2.96 (m, 2H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 160.0, 141.0, 139.6, 139.4, 137.8, 129.9, 129.1, 128.9, 127.4, 127.3, 127.2, 121.3, 114.6, 111.8, 55.4, 35.4, 35.0; IR (KBr) ῡ 3054, 2933, 1589, 1573, 1480; HRMS (ESI-TOF) calcd for $C_{21}H_{20}OS$ $(M + Na)^+$ 343.1127 found 343.1226.

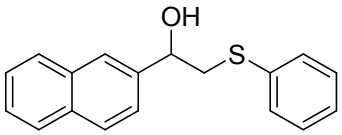


1-Phenyl-2-(phenylthio)ethanol (4aa):[6] R_f = 0.2 (5% ethyl acetate in hexane); colorless liquid; yield 98% (119 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 2H), 7.31 – 7.27 (m, 4H), 7.25 – 7.18 (m, 3H), 7.18 – 7.14 (m, 1H), 4.65 (dd, *J* = 6.8, 2.0 Hz, 1H), 3.25 (dd, *J* = 13.6, 3.6 Hz, 1H), 3.03 (dd, *J* = 13.6, 9.4 Hz, 1H), 2.86 (d, -OH, *J* = 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$)



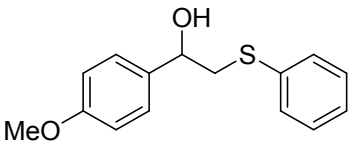
δ 142.3, 135.0, 130.3, 129.2, 128.7, 128.1, 126.9, 126.0, 71.8, 44.1; HRMS (ESI-TOF) calcd for $C_{14}H_{14}SO$ $(M + Na)^+$ 253.0658, found 253.0686.

1-(Naphthalen-2-yl)-2-(phenylthio)ethanol (4ga):[7] R_f = 0.2 (5% ethyl acetate in hexane);



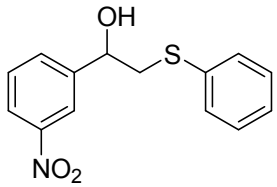
colorless liquid; yield 81% (89 mg);^{1}H NMR (700 MHz, $CDCl_3$) δ 7.87 – 7.82 (m, 4H), 7.53 – 7.45 (m, 5H), 7.38 – 7.32 (m, 2H), 7.29 – 7.27 (m, 1H), 4.91 (d, *J* = 9.0 Hz, 1H), 3.43 (dd, *J* = 14.0, 3.5 Hz, 1H), 3.19 (dd, *J* = 14.0, 9.0 Hz, 1H), 2.99 (s, -OH, 1H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 139.6, 134.9, 133.4, 133.3, 130.5, 129.3, 128.6, 128.1, 127.9, 127.0, 126.4, 126.2, 124.9, 123.9, 71.9, 44.2; HRMS (ESI-TOF) calcd for $C_{18}H_{16}OS$ $(M + Na)^+$ 303.0814, found 303.0797.

1-(4-Methoxyphenyl)-2-(phenylthio)ethanol (4ba):[8] R_f = 0.2 (10% ethyl acetate in hexane);



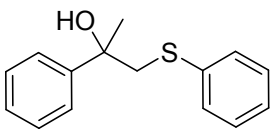
colorless liquid; yield 98% (115 mg);^{1}H NMR (700 MHz, $CDCl_3$) δ 7.47 – 7.39 (m, 2H), 7.36 – 7.31 (m, 2H), 7.30 – 7.27 (m, 2H), 7.27 – 7.23 (m, 1H), 6.93 – 6.86 (m, 2H), 4.70 (dd, *J* = 9.8, 4.2 Hz, 1H), 3.82 (s, 3H), 3.31 (dd, *J* = 14.0, 3.5 Hz, 1H), 3.12 (dd, *J* = 14.0, 8.4 Hz, 1H), 2.82 (s, -OH, 1H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 159.5, 135.1, 134.4, 130.3, 129.3, 127.3, 126.9, 114.1, 71.5, 55.4, 44.0.

1-(3-Nitrophenyl)-2-(phenylthio)ethanol (4pa): R_f = 0.4 (20% ethyl acetate in hexane); light



yellow colour liquid; yield 96% (116 mg);^{1}H NMR (700 MHz, $CDCl_3$) δ 8.21 (s, 1H), 8.16 – 8.09 (m, 1H), 7.69 (d, *J* = 7.7 Hz, 1H), 7.51 (t, *J* = 8.4 Hz, 1H), 7.46 – 7.40 (m, 2H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.28 – 7.26 (m, 1H), 4.88 – 4.70 (m, 1H), 3.34 (dd, *J* = 14.0, 3.6 Hz, 1H), 3.11 (s, -OH, 1H), 3.07 (dd, *J* = 14.0, 8.4 Hz, 1H). ^{13}C NMR (175 MHz, $CDCl_3$) δ 148.5, 144.3, 134.0, 132.1, 131.0, 129.6, 129.5, 127.5, 123.0, 121.2, 70.7, 44.4; IR (KBr) ῡ 3437 (br), 3037, 2920, 1582, 1530, 1479,; HRMS (ESI-TOF) calcd for $C_{14}H_{13}NO_3S$ $(M + Na)^+$ 298.0508, found 298.0506.

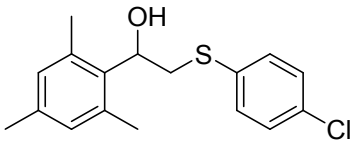
2-Phenyl-1-(phenylthio)propan-2-ol (4ea):[8] R_f = 0.3 (5% ethyl acetate in hexane); colorless



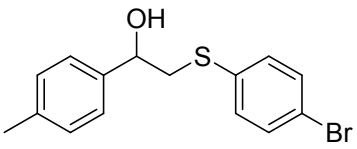
liquid; yield 77% (86 mg); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.54 – 7.42

(m, 2H), 7.41 – 7.30 (m, 4H), 7.29 – 7.24 (m, 3H), 7.21 – 7.17 (m, 1H), 3.57 (d, *J* = 14.0 Hz, 1H), 3.38 (d, *J* = 14.0 Hz, 1H), 2.92 (brs, -OH, 1H), 1.65 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 146.3, 136.6, 130.1, 129.1, 128.4, 127.2, 126.6, 124.9, 74.1, 49.7, 29.5.

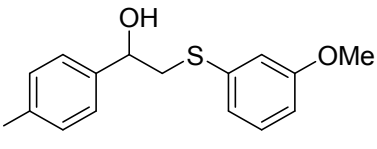
2-((4-Chlorophenyl)thio)-1-mesitylethanol (4qd): R_f = 0.25 (5% ethyl acetate in hexane); colorless liquid; yield 76% (86 mg); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 2H), 7.31 – 7.27 (m, 2H), 6.82 (s, 2H), 5.13 (dd, *J* = 9.8, 4.2 Hz, 1H), 3.40 (dd, *J* = 14.0, 9.8 Hz, 1H), 3.20 (dd, *J* = 14.0, 3.6 Hz, 1H), 2.59 (brs, -OH, 1H), 2.32 (s, 6H), 2.26 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 137.4, 136.4, 134.1, 133.78, 133.0, 131.9, 130.4, 129.3, 69.4, 40.7, 20.9, 20.8; IR (KBr) ῡ 3418 (br), 2921, 1609, 1506, 1475; HRMS (ESI-TOF) calcd for $C_{17}H_{19}ClOS$ $(M + Na)^+$ 329.0737, found 329.0728.



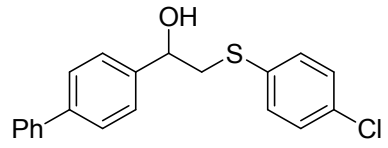
2-((4-Bromophenyl)thio)-1-(*p*-tolyl)ethanol (4rb):[9] R_f = 0.2 (5% ethyl acetate in hexane); colorless liquid; yield 79% (116 mg); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.48 – 7.40 (m, 2H), 7.29 – 7.26 (m, 2H), 7.26 – 7.22 (m, 2H), 7.20 – 7.15 (m, 2H), 4.84 – 4.64 (m, 1H), 3.27 (dd, *J* = 14.0, 3.6 Hz, 1H), 3.13 (dd, *J* = 14.0, 9.8 Hz, 1H), 2.71 (brs, -OH, 1H), 2.36 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 139.2, 138.0, 134.6, 132.2, 131.6, 129.4, 125.9, 120.7, 71.9, 43.9, 21.3.



1-(4-Chlorophenyl)-2-((3-methoxyphenyl)thio)ethanol (4se): R_f = 0.15 (5% ethyl acetate in hexane); colorless liquid; yield 79% (111 mg); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.23 (t, *J* = 7.7 Hz, 1H), 6.98 (d, *J* = 7.7 Hz, 1H), 6.94 (s, 1H), 6.82 – 6.74 (m, 1H), 4.71 (dd, *J* = 9.8, 4.2 Hz, 1H), 3.80 (s, 3H), 3.28 (dd, *J* = 14.0, 3.6 Hz, 1H), 3.05 (dd, *J* = 14.0, 9.8 Hz, 1H), 2.95 (brs, -OH, 1H). ^{13}C NMR (175 MHz, $CDCl_3$) δ 160.1, 140.7, 136.0, 133.8, 130.2, 128.8, 127.4, 122.4, 115.8, 112.6, 71.2, 55.4, 43.9; IR (KBr) ῡ 3427 (br), 3001, 2934, 1589, 1479; HRMS (ESI-TOF) calcd for $C_{15}H_{15}ClO_2S$ $(M + Na)^+$ 317.0373, found 317.0356.

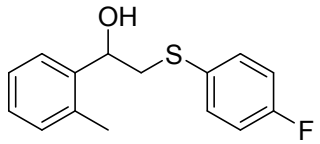


1-([1,1'-Biphenyl]-4-yl)-2-((4-chlorophenyl)thio)ethanol (4fd): R_f = 0.2 (5% ethyl acetate in hexane); colorless liquid; yield 98% (112 mg); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.62 – 7.54 (m, 4H), 7.47 – 7.43 (m, 2H), 7.43

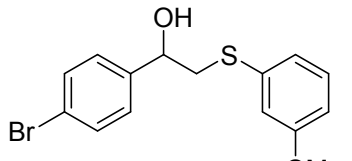


– 7.40 (m, 2H), 7.39 – 7.31(m, 3H), 7.31 – 7.27 (m, 2H), 4.81 – 4.75 (m, 1H), 3.33 (dd, J = 14.0, 3.6 Hz, 1H), 3.19 – 3.14 (m, 1H), 2.79 (brs, -OH, 1H). ^{13}C NMR (175 MHz, $CDCl_3$) δ 141.2, 141.1, 140.8, 133.7, 133.0, 131.7, 129.4, 128.9, 127.6, 127.5, 127.2, 126.4, 71.8, 44.2; IR (KBr) ῡ 3404 (br), 3054, 2920, 1622, 1485, 1475; HRMS (ESI-TOF) calcd for $C_{20}H_{17}ClOS$ $(M + Na)^+$ 363.0581 found 363.0577.

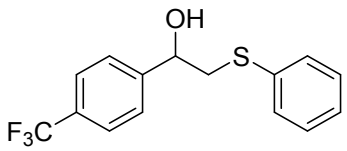
2-((4-Fluorophenyl)thio)-1-(o-tolyl)ethanol (4cc): R_f = 0.2 (5% ethyl acetate in hexane); colorless liquid; yield 96% (117 mg);^{1}H NMR (700 MHz, $CDCl_3$) δ 7.52 (d, J = 7.7 Hz, 1H), 7.49 – 7.41 (m, 2H), 7.23 (t, J = 7.7 Hz, 1H), 7.19 (t, J = 7.7 Hz, 1H), 7.11 (d, J = 7.7 Hz, 1H), 7.06 – 6.98 (m, 2H), 4.89 (d, J = 9.8 Hz, 1H), 3.20 (dd, J = 14.0, 3.6 Hz, 1H), 2.98 (dd, J = 14.0, 9.8 Hz, 1H), 2.87 (brs, 1H), 2.14 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 162.4 (d, J_{CF1} = 247.6 Hz), 140.1, 134.5, 133.7 (d, J_{CF3} = 8.2 Hz), 130.6, 129.9 (d, J_{CF4} = 3.4 Hz), 127.8, 126.6, 125.4, 116.3 (d, J_{CF2} = 21.8 Hz), 68.3, 44.3, 18.9; IR (KBr) ῡ 3408 (br), 3065, 2923, 1589, 1487; HRMS (ESI-TOF) calcd for $C_{15}H_{15}FOS$ $(M + Na)^+$ 285.0720, found 285.0701.



1-(4-Bromophenyl)-2-((3-methoxyphenyl)thio)ethanol (4te): R_f = 0.15 (5% ethyl acetate in hexane); colorless liquid; yield 96% (148 mg);^{1}H NMR (700 MHz, $CDCl_3$) δ 7.46 (d, J = 9.1 Hz, 2H), 7.25 – 7.19 (m, 3H), 6.98 (d, J = 7.7 Hz, 1H), 6.93 (s, 1H), 6.80 – 6.76 (m, 1H), 4.69 (dd, J = 9.8, 3.5 Hz, 1H), 3.80 (s, 3H), 3.27 (dd, J = 14.0, 3.5 Hz, 1H), 3.04 (dd, J = 14.0, 9.8 Hz, 1H), 2.99 (s, 1H). ^{13}C NMR (175 MHz, $CDCl_3$) δ 160.0, 141.2, 136.0, 131.7, 130.1, 127.7, 122.3, 121.9, 115.8, 112.6, 71.2, 55.4, 43.8; IR (KBr) ῡ 3429 (br), 3061, 3001, 2957, 1589, 1574, 1479; HRMS (ESI-TOF) calcd for $C_{15}H_{15}BrO_2S$ $(M + Na)^+$ 360.9868, found 360.9868.

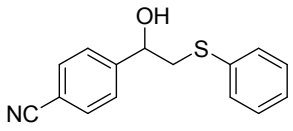


2-(Phenylthio)-1-(4-(trifluoromethyl)phenyl)ethanol (4la): R_f = 0.2 (5% ethyl acetate in hexane); colorless liquid; yield 97% (118 mg);^{1}H NMR (700 MHz, $CDCl_3$) δ 7.59 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H), 7.44 – 7.40 (m, 2H), 7.36 – 7.29 (m, 2H), 7.28 – 7.25 (m, 1H), 4.81 – 4.72 (m, 1H), 3.32 (dd, J = 14.0, 3.5 Hz, 1H), 3.05 – 3.05 (m, 1H), 3.04 (s, 1H). ^{13}C NMR (175 MHz, $CDCl_3$) δ 146.2, 134.4, 130.7, 130.2 (q, $^2J_{FC}$ = 32 Hz), 129.4, 127.3, 126.3, 124.2 (q, $^1J_{FC}$ = 270 Hz), 125.6 (q, $^3J_{FC}$ = 3.7 Hz), 71.1, 44.3; IR



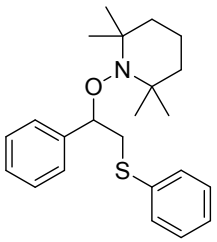
(KBr) ῡ 3408 (br), 3059, 2920, 1619, 1583, 1480; HRMS (ESI-TOF) calcd for $C_{15}H_{13}F_3OS$ (M + Na)$^+$ 321.0531 found 321.0544.

4-(1-Hydroxy-2-(phenylthio)ethyl)benzonitrile (4da):[8] R_f= 0.1 (5% ethyl acetate in hexane);

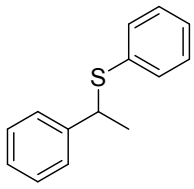


colorless liquid; yield 86% (119 mg);^{1}H NMR (700 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.28 – 7.25 (m, 1H), 4.75 (d, *J* = 7.0 Hz, 1H), 3.30 (dd, *J* = 14.0, 3.5 Hz, 1H), 3.16 (s, 1H), 3.04 (dd, *J* = 14.0, 9.8 Hz, 1H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 147.5, 134.2, 132.4, 130.8, 129.4, 127.4, 126.7, 118.8, 111.7, 71.0, 44.2; HRMS (ESI-TOF) calcd for $C_{15}H_{13}NOS$ (M + Na)$^+$ 278.610, found 278.0617.

2,2,6,6-Tetramethyl-1-(1-phenyl-2-(phenylthio)ethoxy)piperidine (6): R_f= 0.2 (In hexane);



colorless liquid; yield 50% (160 mg); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.34 – 7.30 (m, 4H), 7.28 – 7.24 (m, 3H), 7.22 (t, *J* = 7.7 Hz, 2H), 7.13 (t, *J* = 7.0 Hz, 1H), 4.82 (dd, *J* = 9.1, 3.5 Hz, 1H), 3.76 (dd, *J* = 12.6, 4.2 Hz, 1H), 3.23 (dd, *J* = 12.6, 9.8 Hz, 1H), 1.50 – 1.44 (m, 2H), 1.40 – 1.34 (m, 2H), 1.32 – 1.23 (m, 5H), 1.17 (s, 3H), 1.01 (s, 3H), 0.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 136.9, 130.9, 129.6, 128.8, 128.0, 127.8, 126.0, 85.4, 60.1, 40.6, 39.6, 34.4, 20.5, 17.3; IR (KBr) ῡ 3058, 2929, 1583, 1454; HRMS (ESI-TOF) calcd for $C_{23}H_{31}NOS$ (M + nH)$^+$ 370.2199 found 370.2196.



Phenyl(1-phenylethyl)sulfane (5aa):[10] R_f= 0.4 (In hexane); colorless liquid; yield 84% (90 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.25 (m, 6H), 7.25 – 7.16 (m, 4H), 4.34 (q, *J* = 6.8 Hz, 1H), 1.63 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl3) δ 143.4, 135.3, 132.7, 128.8, 128.6, 127.4, 127.3 (×2), 48.1, 22.5.

NATURAL BOND ORBITAL (NBO) CALCULATION

The geometry optimization of the proposed S-H...π interaction assembled molecular pair has been performed with DFT calculations at rM06-2X/6-31+G(d,p) level of theory following frequency calculation to ensure that the structure corresponded to global minimum. Natural

Bond Orbital (NBO) calculation[11] performed on the optimized structure at M06-2X/6-31++G(d,p) level reveals considerable π-π stacking interaction.

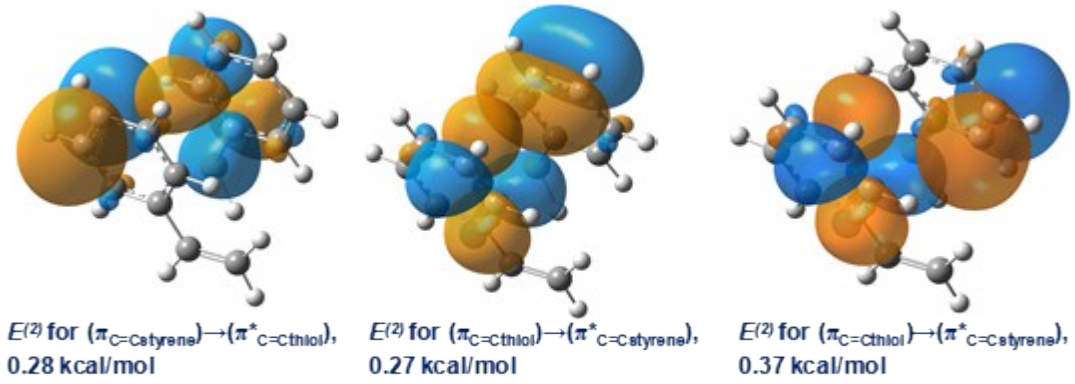


Fig. S5. Natural bond orbital analysis showing π-π stacking interaction.

TIME-DEPENDENT DENSITY FUNCTIONAL THEORY CALCULATIONS

All calculations were performed using software package Gaussian 09 ver. D01.[1213] Ground state geometry of the thiol-styrene EDA complex was optimized at the rM06/6-31+G(d,p) level of theory. Employing this geometry, single point time-dependent density functional theory (TD-DFT) calculation has been performed using the rCAM-B3LYP/6-31+G(d,p)/CPCM level of theory in EtOH solvent. The first ten excited states of the EDA complex comprised of thiol and styrene are listed below and the charge transfer peak is highlighted.

Table S1. First ten excited states calculated with RCAM-B3LYP/6-31+G(d,p)/CPCM in EtOH medium

Calculated wavelength (nm)	Oscillator Strength *f*	Orbital Contribution	Energy (eV)
291	0.005	HOMO-1→ LUMO, 19% HOMO→LUMO, 81% (This has significant charge transfer origin)	4.26

265	0.256	HOMO-2→ LUMO, 14% HOMO-1→LUMO, 46% HOMO-1→ LUMO+2, 10% HOMO-1→LUMO+3, 11% HOMO→LUMO, 12% HOMO→ LUMO+1, 9%	4.69
258	0.634	HOMO-3→ LUMO+2, 8% HOMO-2→LUMO, 41% HOMO-1→ LUMO, 16% HOMO-1→LUMO+1, 10% HOMO-1→ LUMO+3, 15% HOMO→LUMO+2, 12%	4.80
257	0.013	HOMO-3→ LUMO, 10% HOMO-3→LUMO+2, 13% HOMO-2→ LUMO, 21% HOMO→LUMO+1, 12% HOMO-1→ LUMO+3, 11% HOMO→LUMO+2, 32% HOMO→LUMO+3, 8%	4.82
244	0.068	HOMO-3→ LUMO, 35% HOMO→LUMO+1, 12% HOMO-1→ LUMO+2, 38% HOMO→LUMO+4, 15%	5.07
243	0.041	HOMO-3→ LUMO, 37% HOMO-2→LUMO, 13% HOMO-1→ LUMO+1, 16% HOMO→LUMO+2, 22% HOMO→ LUMO+4, 12%	5.11

241	0.064	HOMO-3→ LUMO, 12% HOMO-1→LUMO+1, 44% HOMO-1→ LUMO+2, 16% HOMO→LUMO+2, 10% HOMO→ LUMO+3, 18%	5.15
238	0.043	HOMO-3→ LUMO, 11% HOMO-1→LUMO+2, 22% HOMO-1→ LUMO+2, 13% HOMO-1→ LUMO+3, 30% HOMO→LUMO+1, 12% HOMO→LUMO+3, 31% HOMO→LUMO+4, 10%	5.20
236	0.070	HOMO-1→ LUMO+2, 11% HOMO→LUMO+1, 10% HOMO→LUMO+2, 14% HOMO-1→ LUMO+2, 12% HOMO→LUMO+3, 25% HOMO-1→ LUMO+5, 10% HOMO→LUMO+6, 11% HOMO→LUMO+7, 8%	5.25

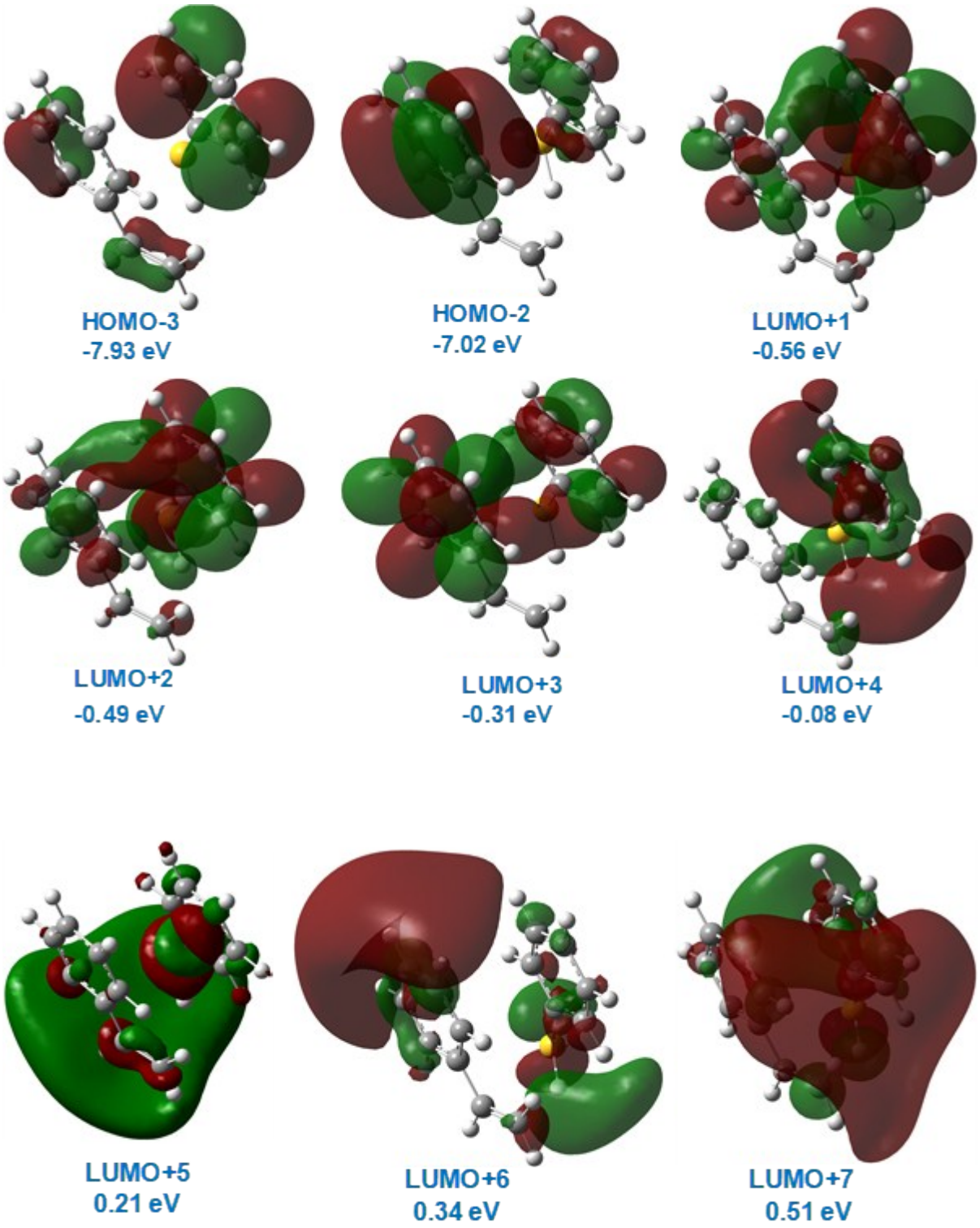


Fig. S6. Molecular orbitals which take part in electronic transition other than charge transfer transition shown with corresponding energies are MOs are delocalized over the whole system.

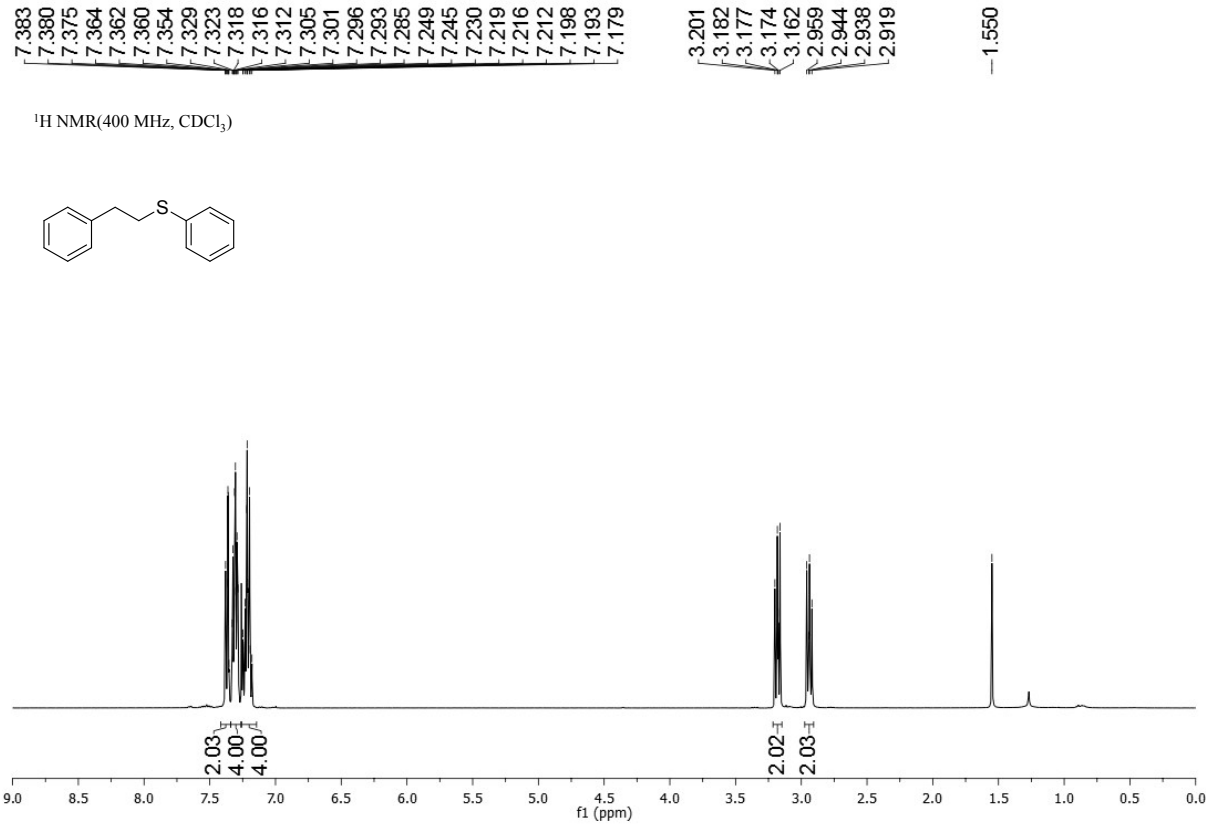
Table S2. The Coordinates of Optimized Geometry of S-H…π and π…π Interactions Assembled Molecular Pair Calculated at rM06-2x/6-31+G(d,p) Level

C	-2.63750400	1.33866500	-0.53129300
C	-2.57934100	0.17884200	-1.30136000
C	-1.97458300	-0.96660700	-0.78974500
C	-1.41121600	-0.97159100	0.49259100
C	-1.47861600	0.20073300	1.25789900
C	-2.08536800	1.34380200	0.75063300
H	-3.11221200	2.23250500	-0.92435600
H	-3.00636200	0.16410600	-2.29948200
H	-1.05850300	0.21852500	2.25908600
H	-2.12494800	2.24423600	1.35616900
H	-1.92057400	-1.86787400	-1.39489300
C	-0.76812400	-2.20355600	0.98437200
C	0.03914700	-2.30885000	2.04526100
H	-0.97649200	-3.09719800	0.39622400
H	0.45960900	-3.26703000	2.33237400
H	0.30588600	-1.45046500	2.65537500
C	1.42945200	2.42558900	0.74868700
C	0.89963400	2.31877100	-0.53551100
C	0.94640600	1.10649900	-1.21946200
C	1.54850200	-0.00628100	-0.62744600
C	2.09168900	0.10068500	0.65619700
C	2.01847100	1.31013300	1.34318900
H	1.38168900	3.36860200	1.28374400
H	0.42505600	3.17612100	-1.00311500
H	0.49683400	1.01646600	-2.20395000
H	2.43759700	1.38239600	2.34251300
S	1.64053300	-1.51401000	-1.56569000
H	1.63824900	-2.33920300	-0.50646600
H	2.57433800	-0.75803500	1.11373900

REFERENCES

1. R. Kumar, Saima, A. Shard, N. H. Andhare, Richa and A. K. Sinha, *Angew. Chem. Int. Ed.*, 2015, **54**, 828.
2. E. Fenster, B. T. Smith, V. Gracias, G. L. Milligan and J. Aubé, *J. Org. Chem.*, 2008, **73**, 201.
3. T. Bousquet, J.-F. Fleury, A. Daïch and P. Netchitaïlo, *Tetrahedron*, 2006, **62**, 706.
4. S. Du, E. A. Kimball and J. R. Ragains, *Org. Lett.*, 2017, **19**, 5553.
5. K. Saito, K. Kondo and T. Akiyama, *Org. Lett.*, 2015, **17**, 3366.
6. H. Wang, Q. Lu, C. Qian, C. Liu, W. Liu, K. Chen and A. Lei, *Angew. Chem., Int. Ed.*, 2016, **55**, 1094.
7. M.-Y. Chang, Y.-H. Huang and H.-S. Wang, *Tetrahedron*, 2016, **72**, 3022.
8. S. F. Zhou, X. Pan, Z. H. Zhou, A. Shoberu and J. P. Zou, *J. Org. Chem.*, 2015, **80**, 3682.
9. B. Movassagh and M. Navidi, *Tetrahedron Lett.*, 2008, **49**, 6712.
10. S. S. Badsara, Y.-C. Liu, P.-A. Hsieh, J.-W. Zeng, S.-Y. Lu, Y.-W. Liu and C.-F. Lee, *Chem. Commun.*, 2014, **50**, 11374.
11. NBO Version 3.1, E. D. Glendening, A. E. Reed, J. E. Carpenter and F. Weinhold.
12. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Journal*, 2009.
13. GaussView, Version 5, Roy Dennington, Todd Keith, and John Millam, Semichem Inc., Shawnee Mission, KS, 2009.

NMR SPECTRA



^{1}H NMR(400 MHz, $CDCl_3$)

Fig. S7. ^{1}H NMR spectrum of phenethyl(phenyl)sulfane **(3aa)**

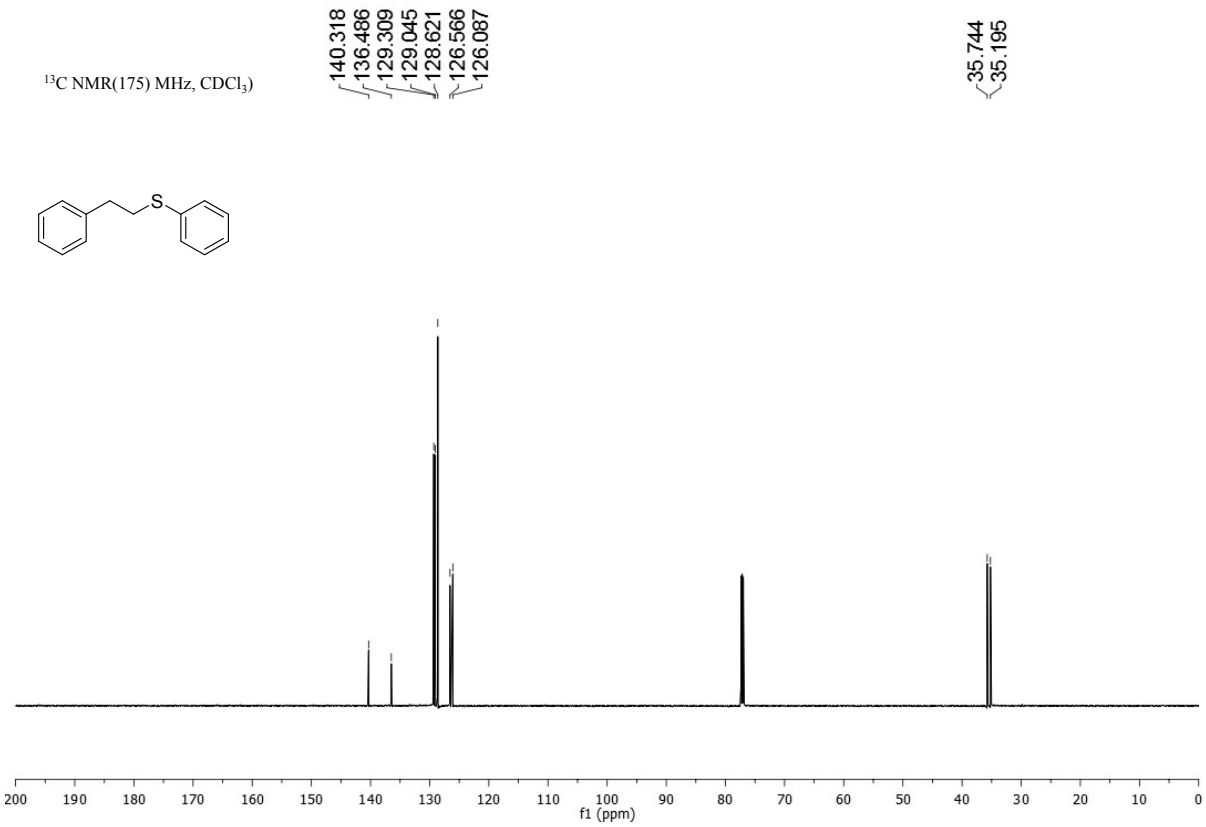


Fig. S8. ^{13}C NMR spectrum of phenethyl(phenyl)sulfane **(3aa)**

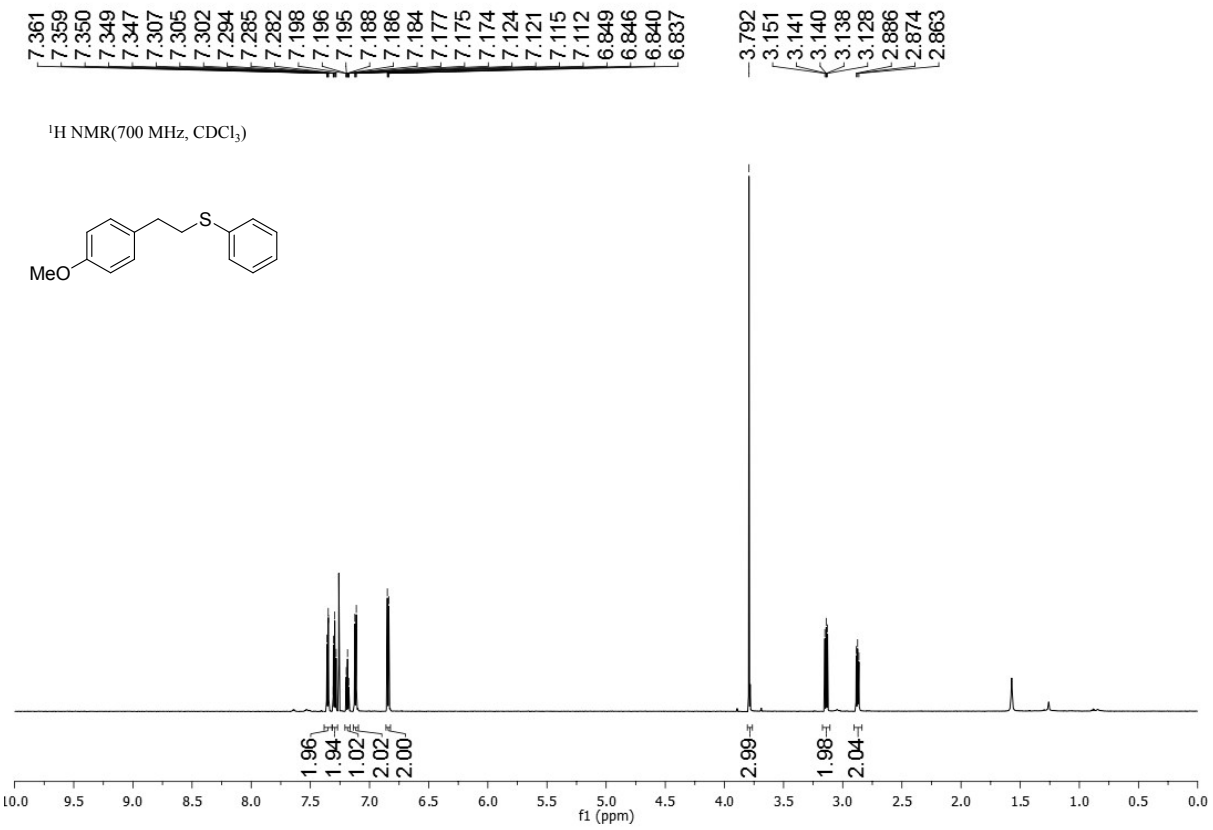


Fig. S9. ^{1}H NMR spectrum of (4-methoxyphenethyl)(phenyl)sulfane **(3ba)**

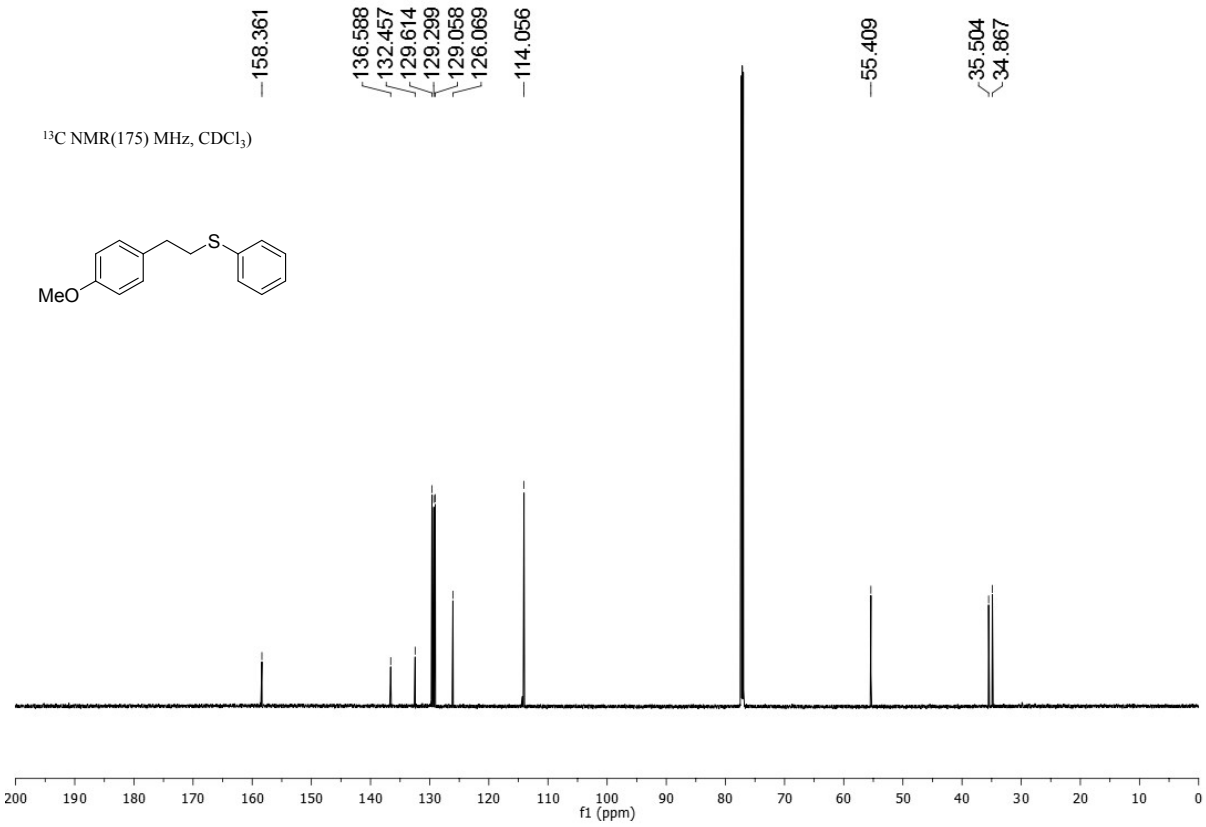


Fig. S10. ^{13}C NMR spectrum of (4-methoxyphenethyl)(phenyl)sulfane **(3ba)**

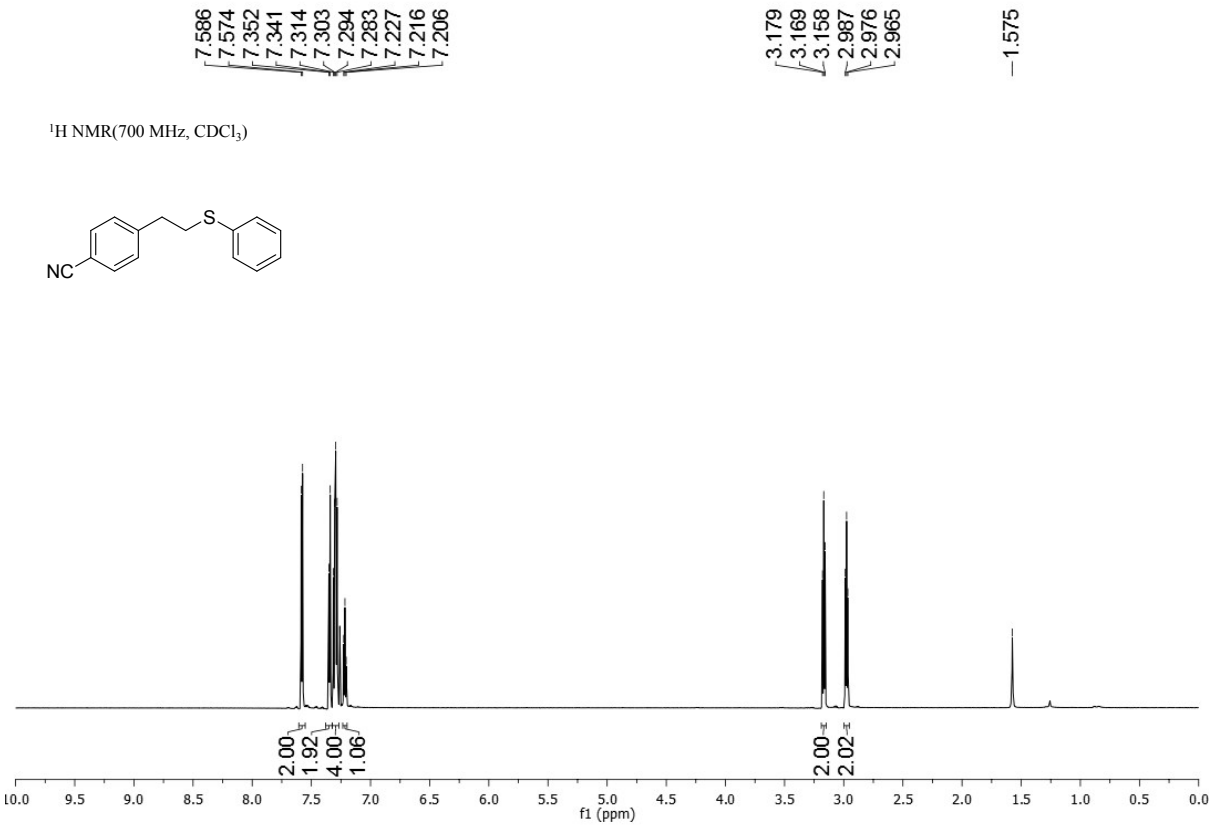


Fig. S11. ^{1}H NMR spectrum of 4-(2-(phenylthio)ethyl)benzonitrile **(3da)**

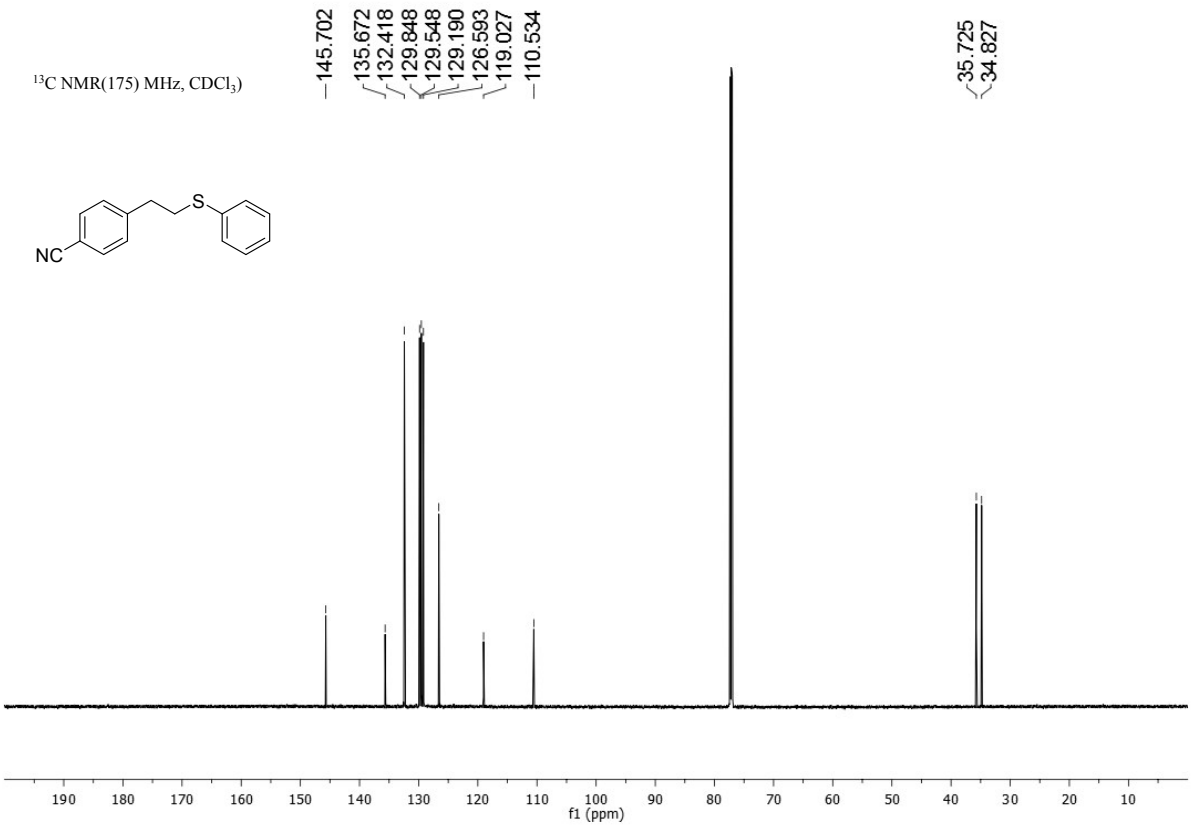


Fig. S12. ^{13}C NMR spectrum of 4-(2-(phenylthio)ethyl)benzonitrile **(3da)**

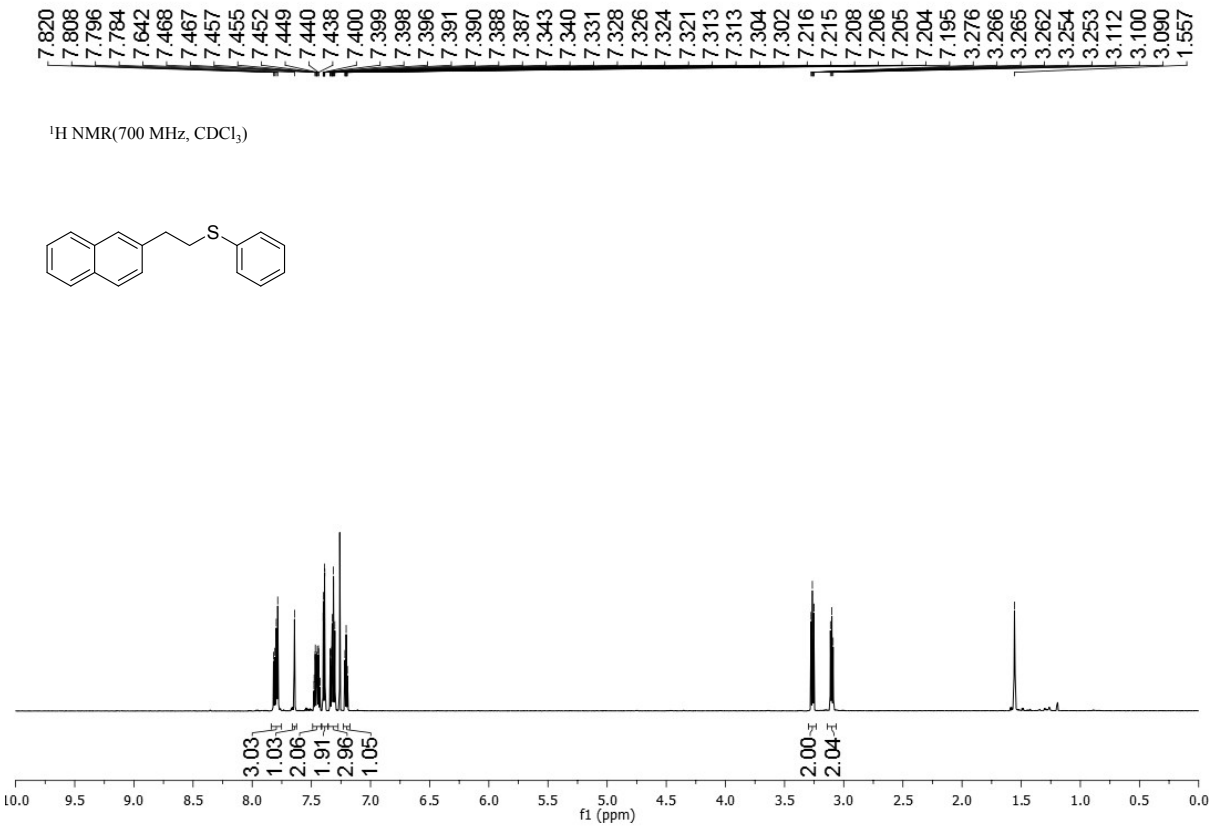


Fig. S13. ^{1}H NMR spectrum of (2-(naphthalen-2-yl)ethyl)(phenyl)sulfane **(3ga)**

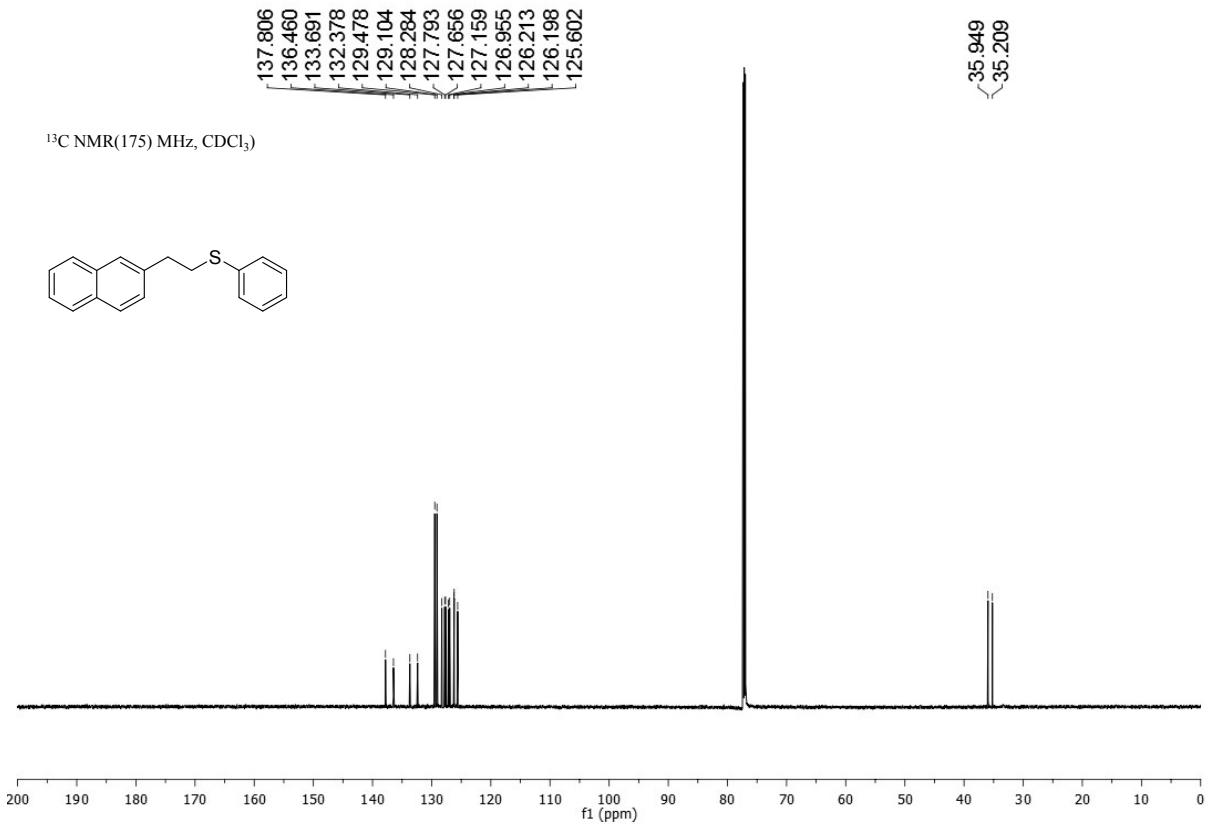


Fig. S14. ^{13}C NMR spectrum of (2-(naphthalen-2-yl)ethyl)(phenyl)sulfane **(3ga)**

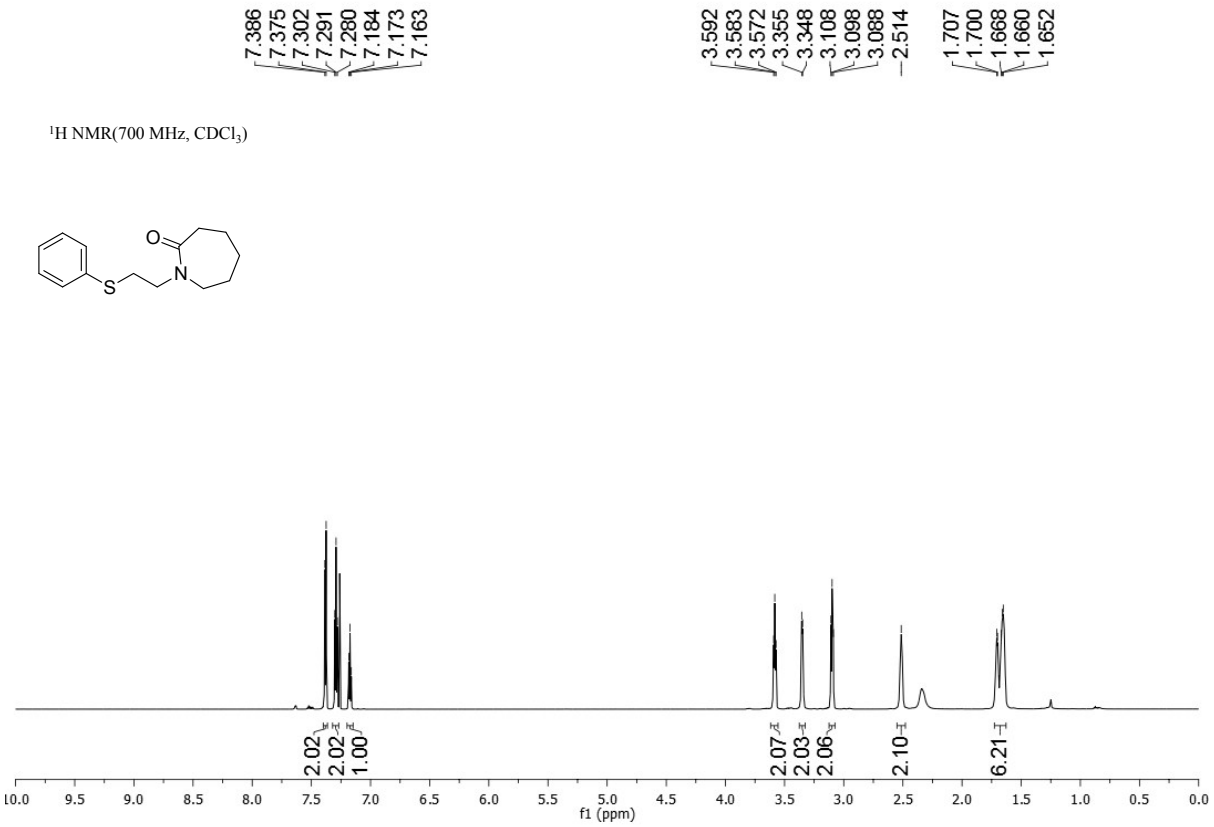


Fig. S15. ^{1}H NMR spectrum of 1-(2-(phenylthio)ethyl)azepan-2-one **(3ia)**

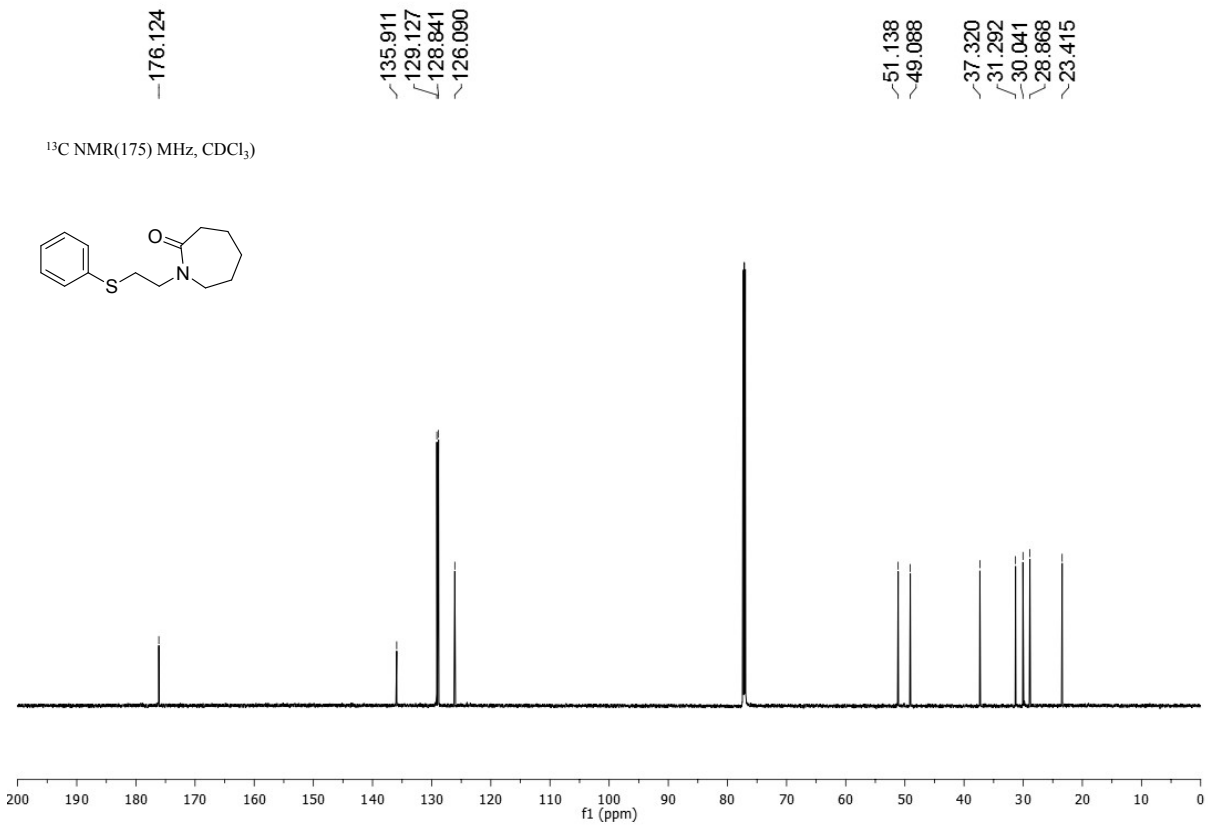


Fig. S16. ^{13}C NMR spectrum of 1-(2-(phenylthio)ethyl)azepan-2-one **(3ia)**

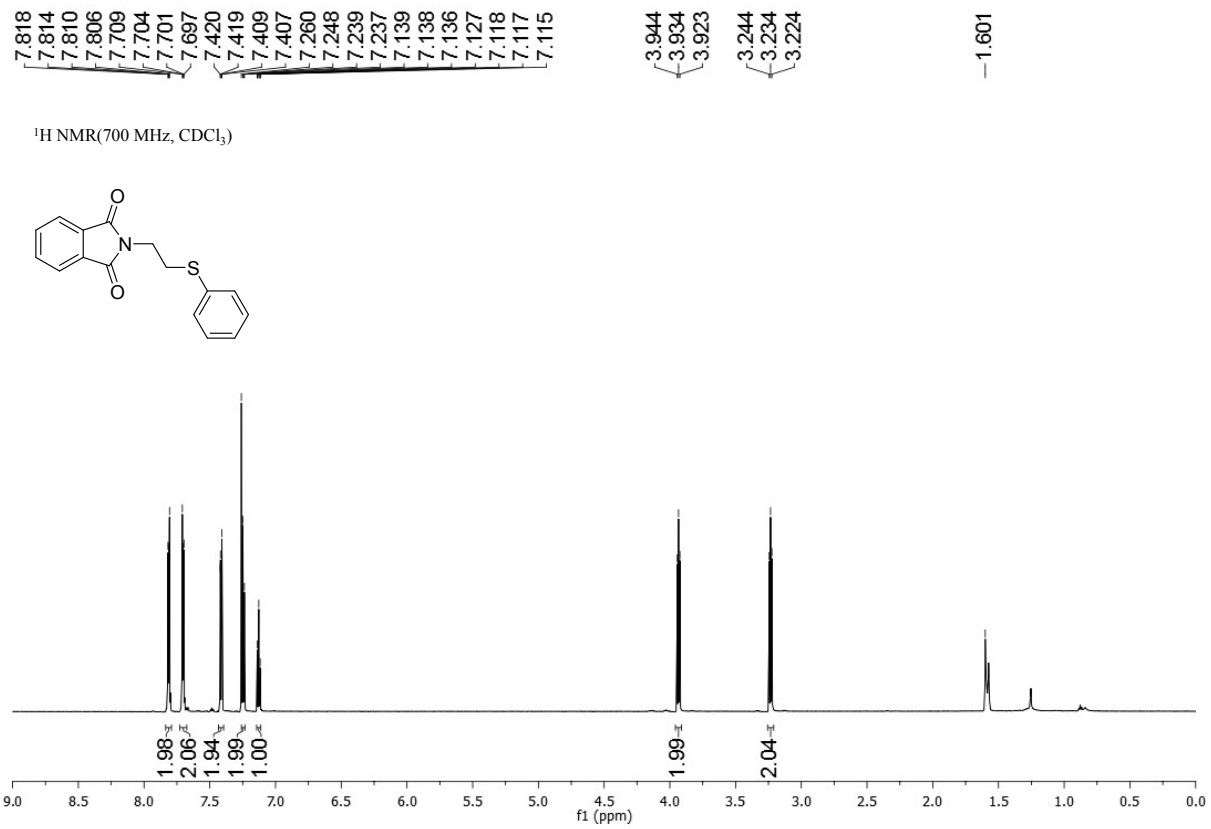


Fig. S17. ^{1}H NMR spectrum of 2-(2-(phenylthio)ethyl)isoindoline-1,3-dione **(3ja)**

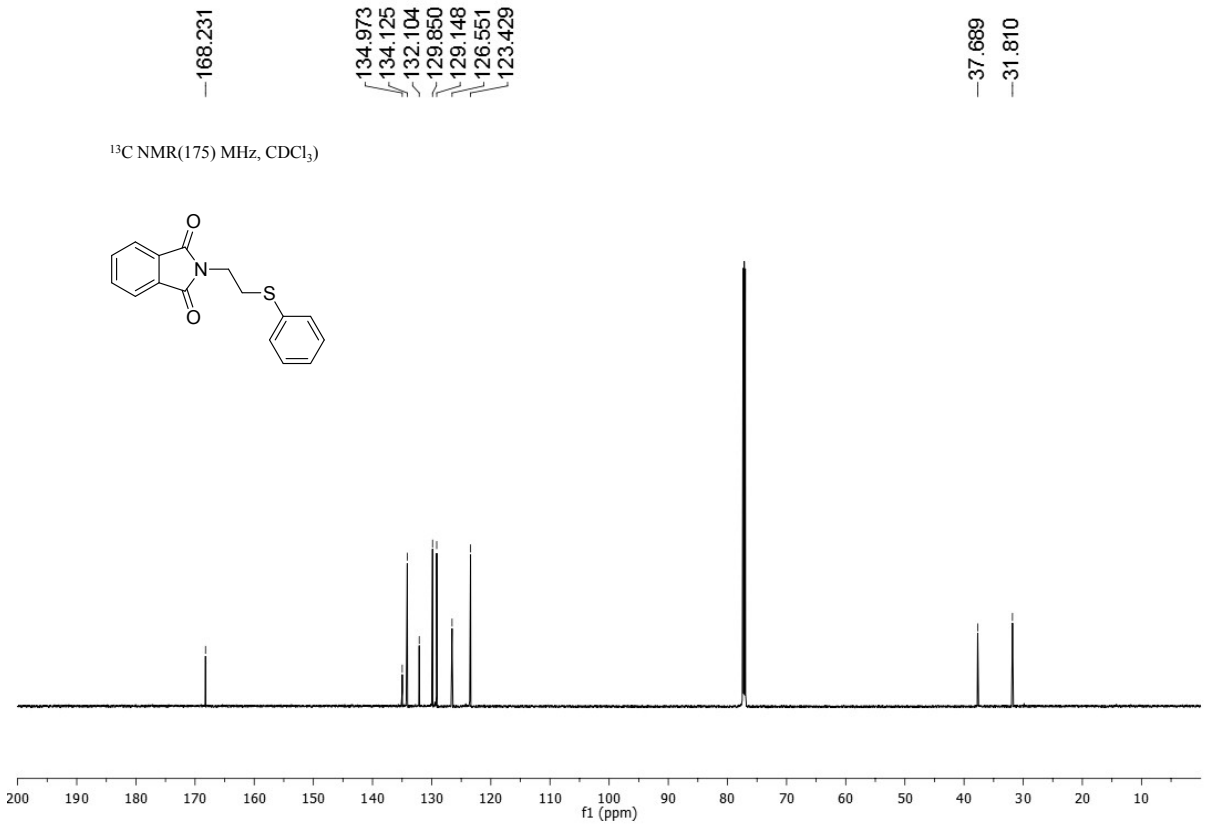


Fig. S18. ^{13}C NMR spectrum of 2-(2-(phenylthio)ethyl)isoindoline-1,3-dione **(3ja)**

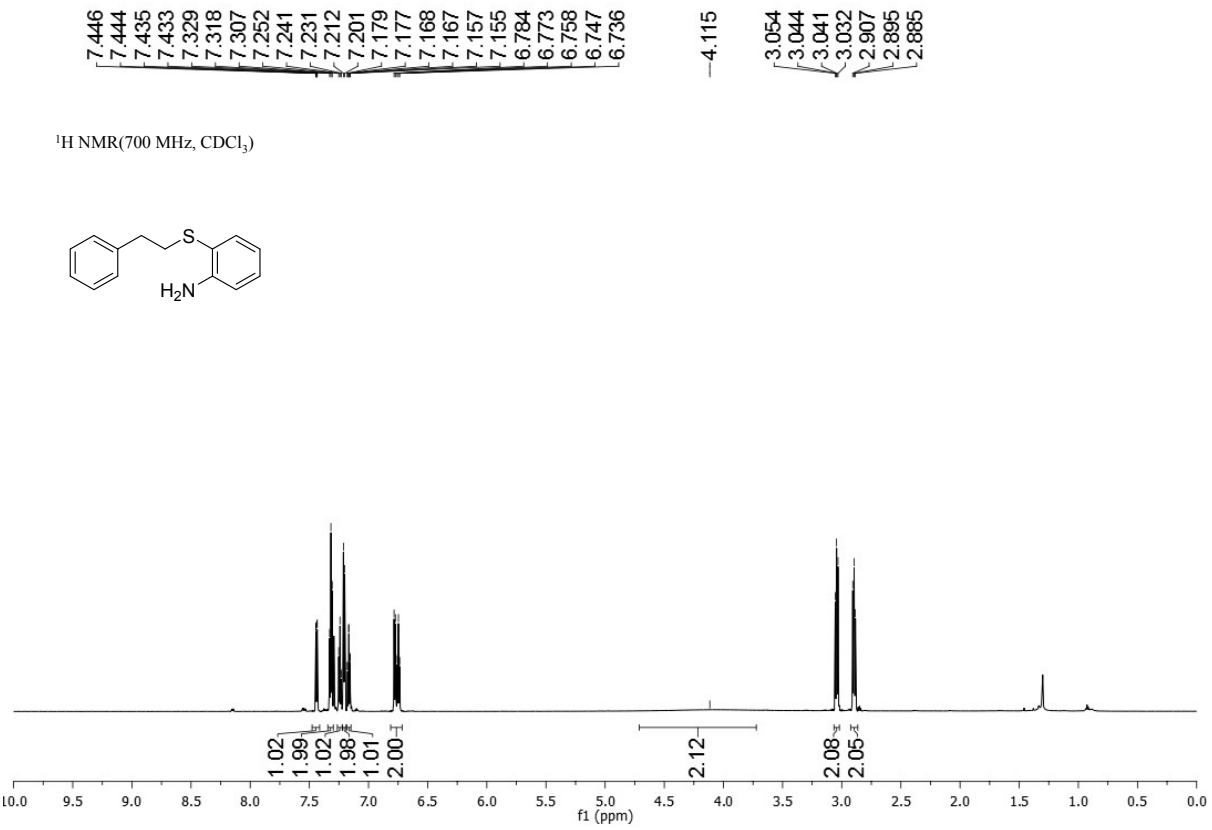


Fig. S19. ^{1}H NMR spectrum of 2-(phenethylthio)aniline **(3af)**

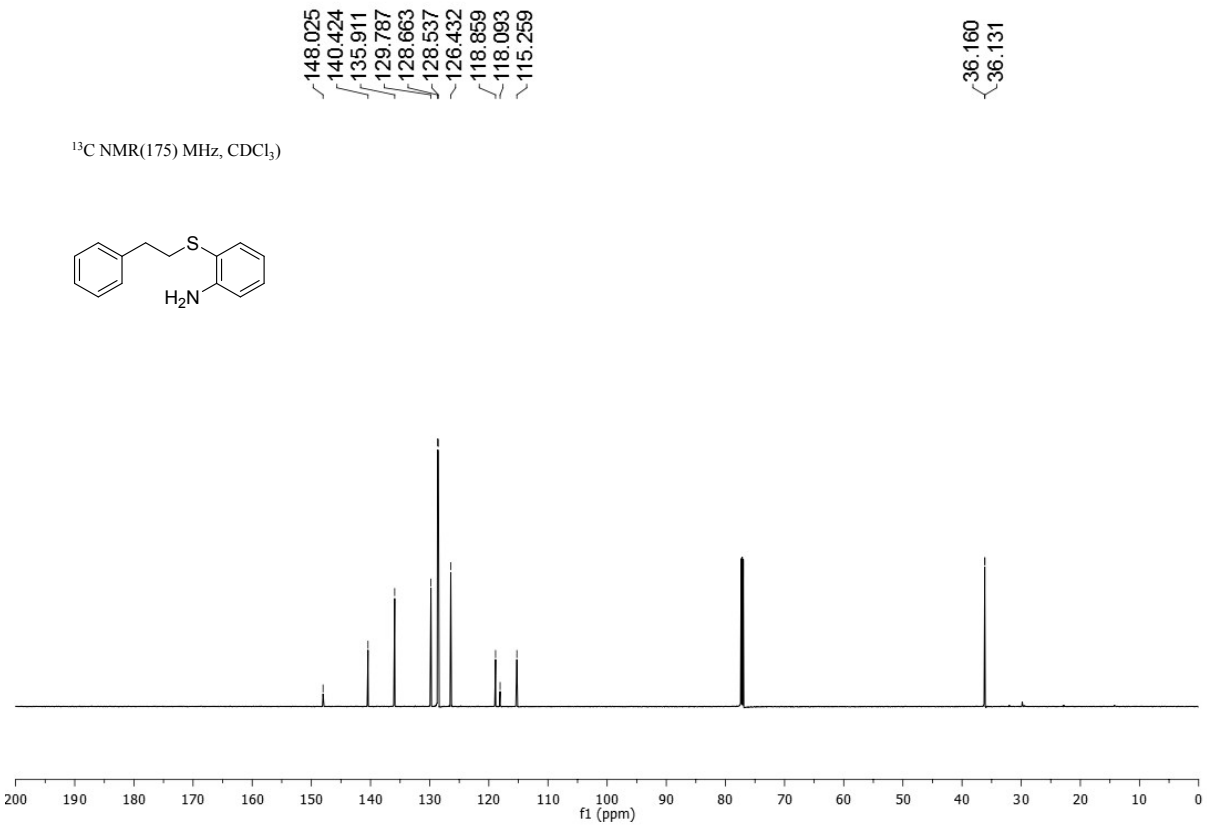


Fig. S20. ^{13}C NMR spectrum of 2-(phenethylthio)aniline **(3af)**

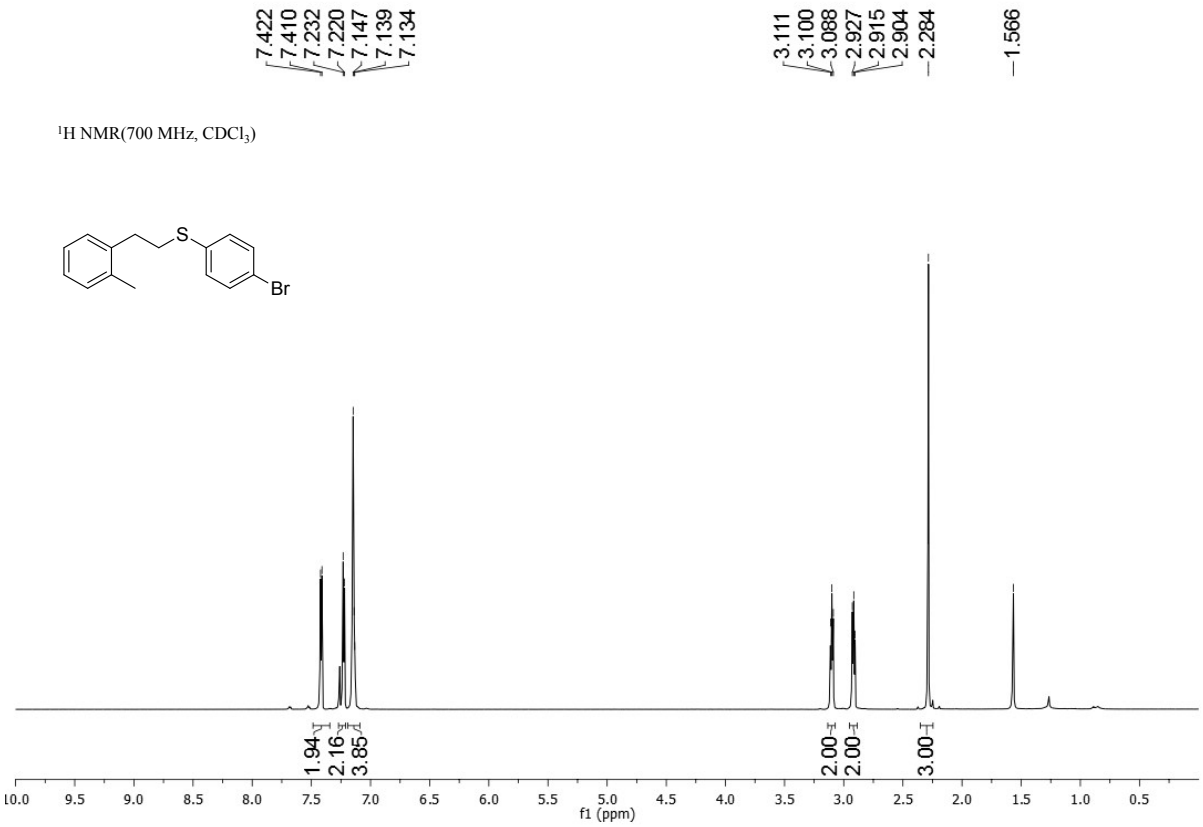


Fig. S21. ^{1}H NMR spectrum of (4-bromophenyl)(2-methylphenethyl)sulfane **(3cb)**

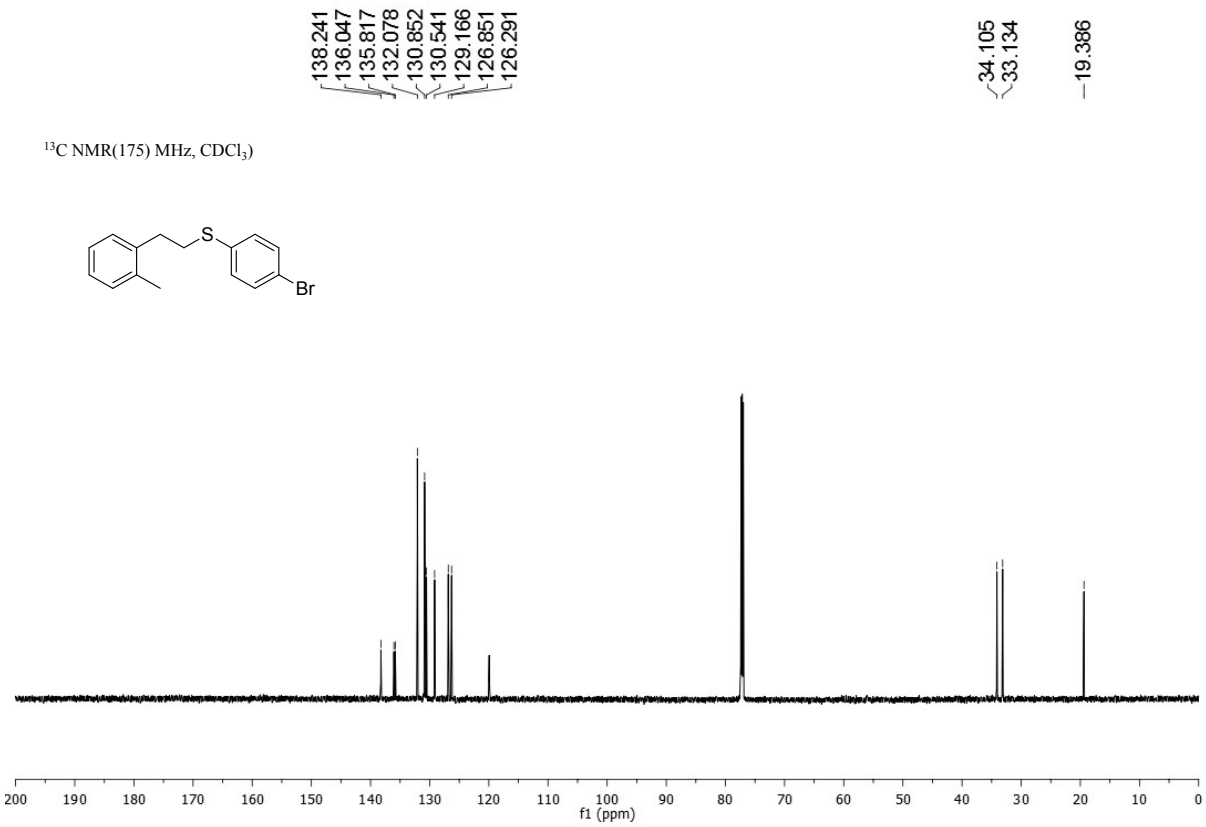


Fig. S22. ^{13}C NMR spectrum of (4-bromophenyl)(2-methylphenethyl)sulfane **(3cb)**

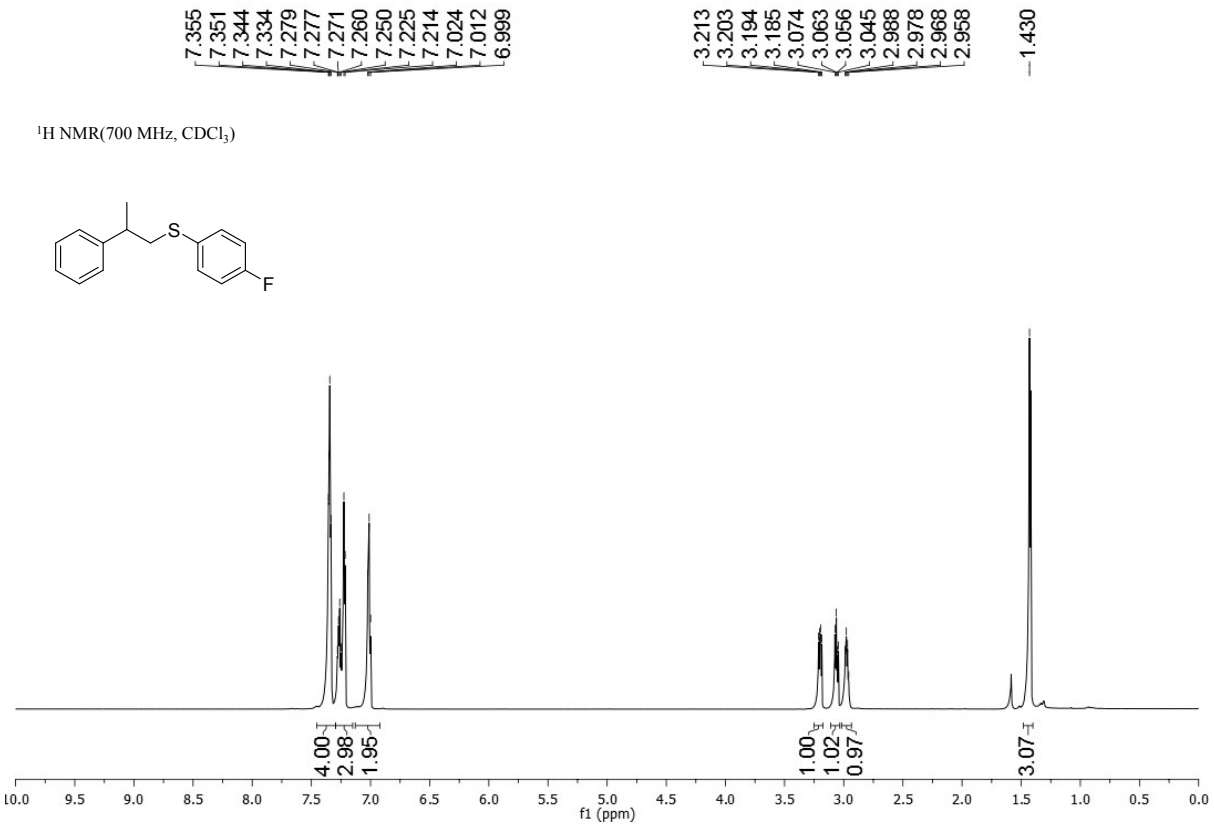


Fig. S23. ^{1}H NMR spectrum of (4-fluorophenyl)(2-phenylpropyl)sulfane **(3ec)**

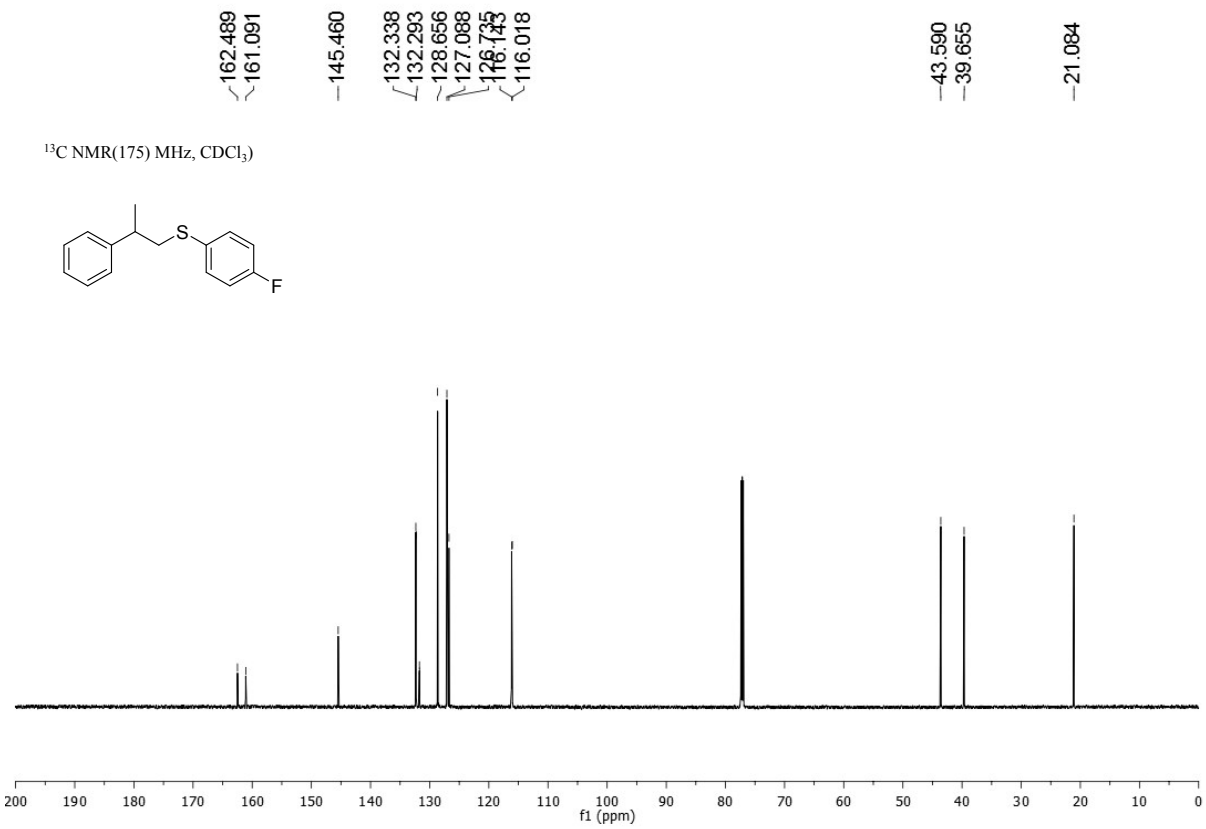


Fig. S24. ^{13}C NMR spectrum of (4-fluorophenyl)(2-phenylpropyl)sulfane **(3ec)**

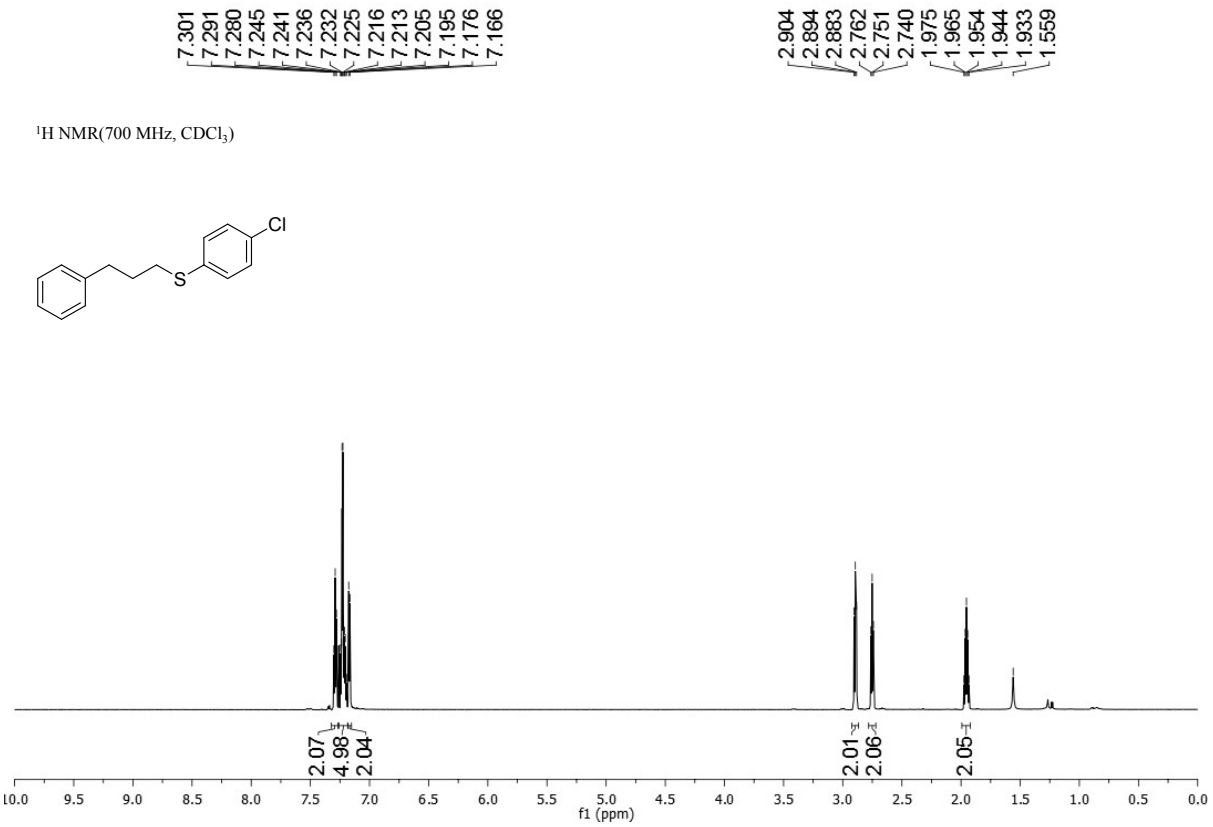


Fig. S25. ^{1}H NMR spectrum of (4-chlorophenyl)(3-phenylpropyl)sulfane **(3kd)**

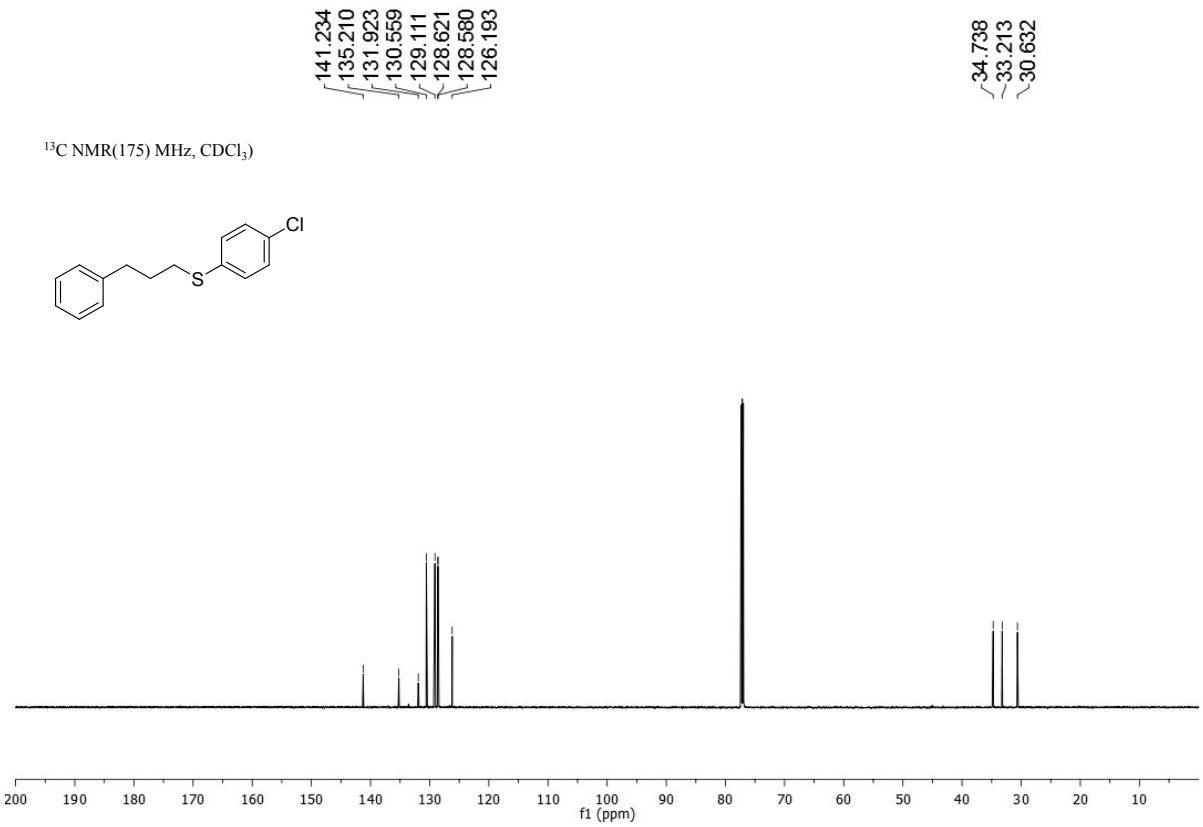


Fig. S26. ^{13}C NMR spectrum of (4-chlorophenyl)(3-phenylpropyl)sulfane **(3kd)**

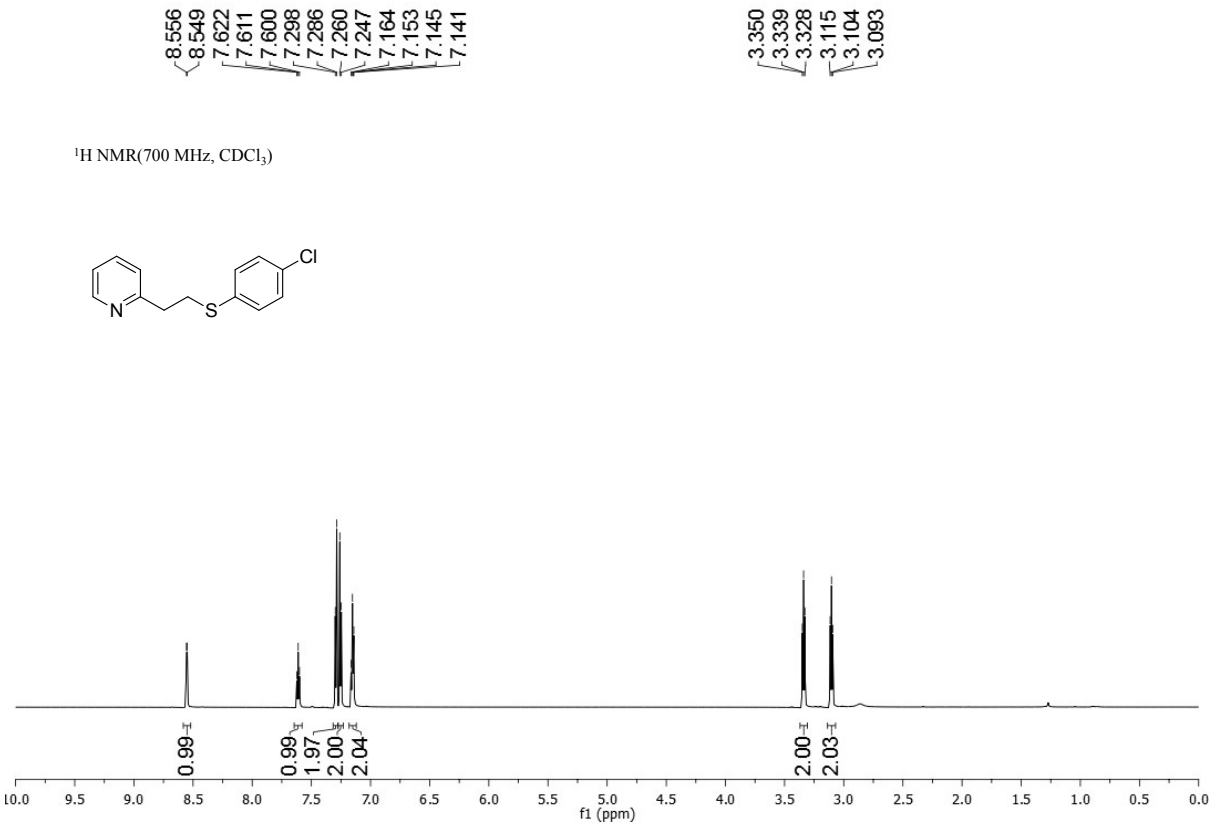


Fig. S27. ^{1}H NMR spectrum of 2-(2-((4-chlorophenyl)thio)ethyl)pyridine **(3hd)**

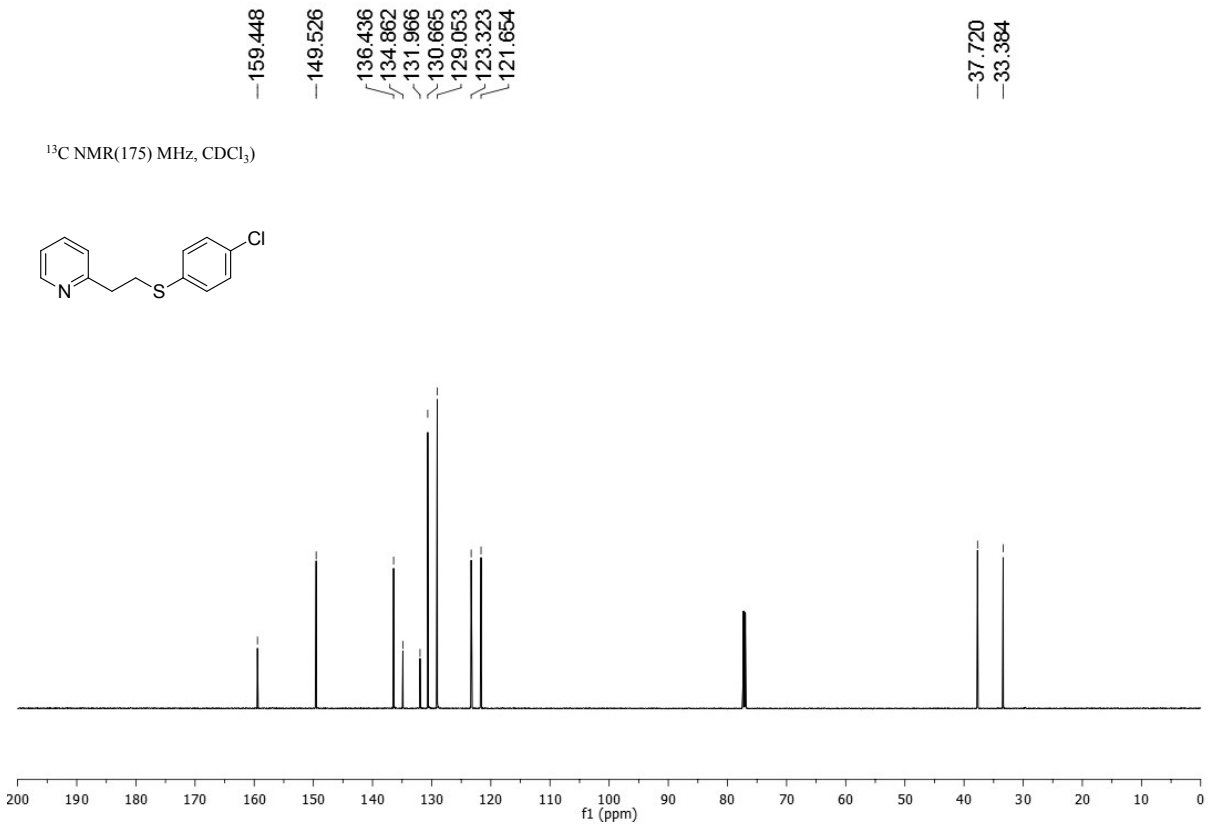


Fig. S28. ^{13}C NMR spectrum of 2-(2-((4-chlorophenyl)thio)ethyl)pyridine **(3hd)**

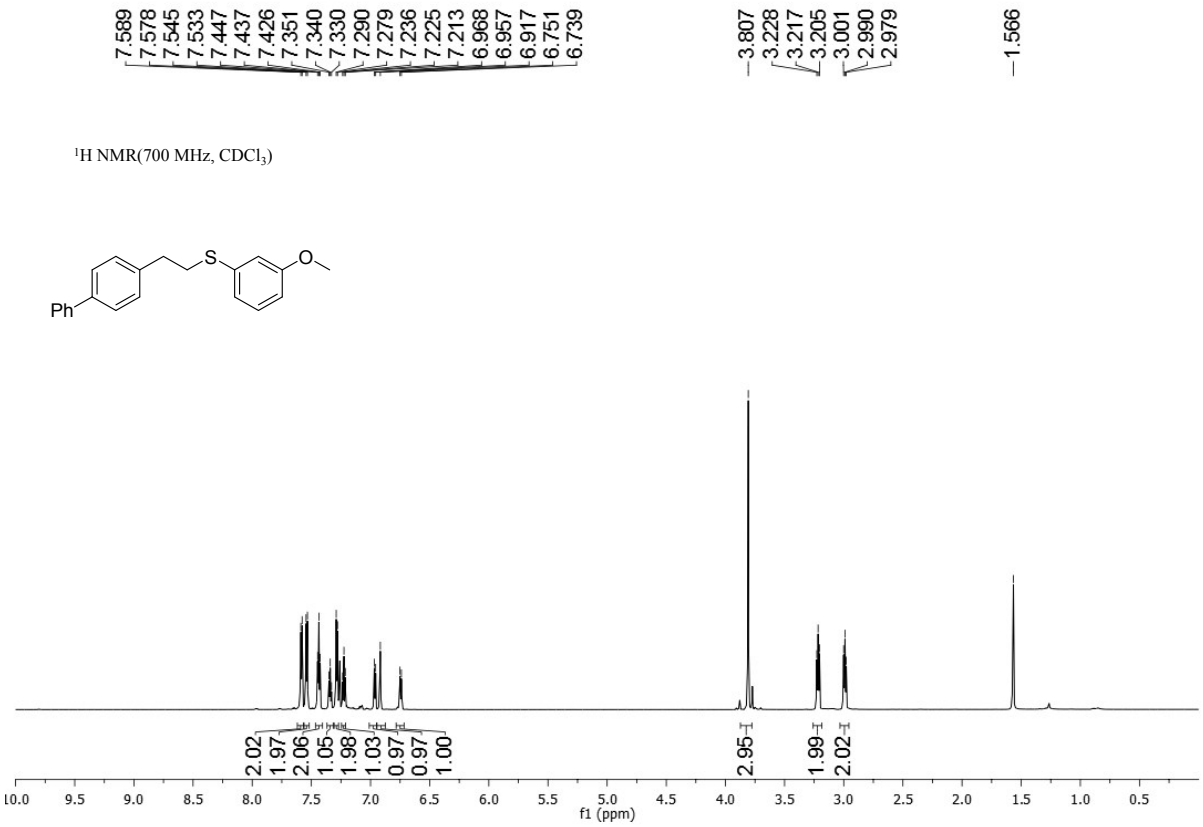


Fig. S29. ^{13}C NMR spectrum of (2-([1,1'-biphenyl]-4-yl)ethyl)(3-methoxyphenyl)sulfane **(3fe)**

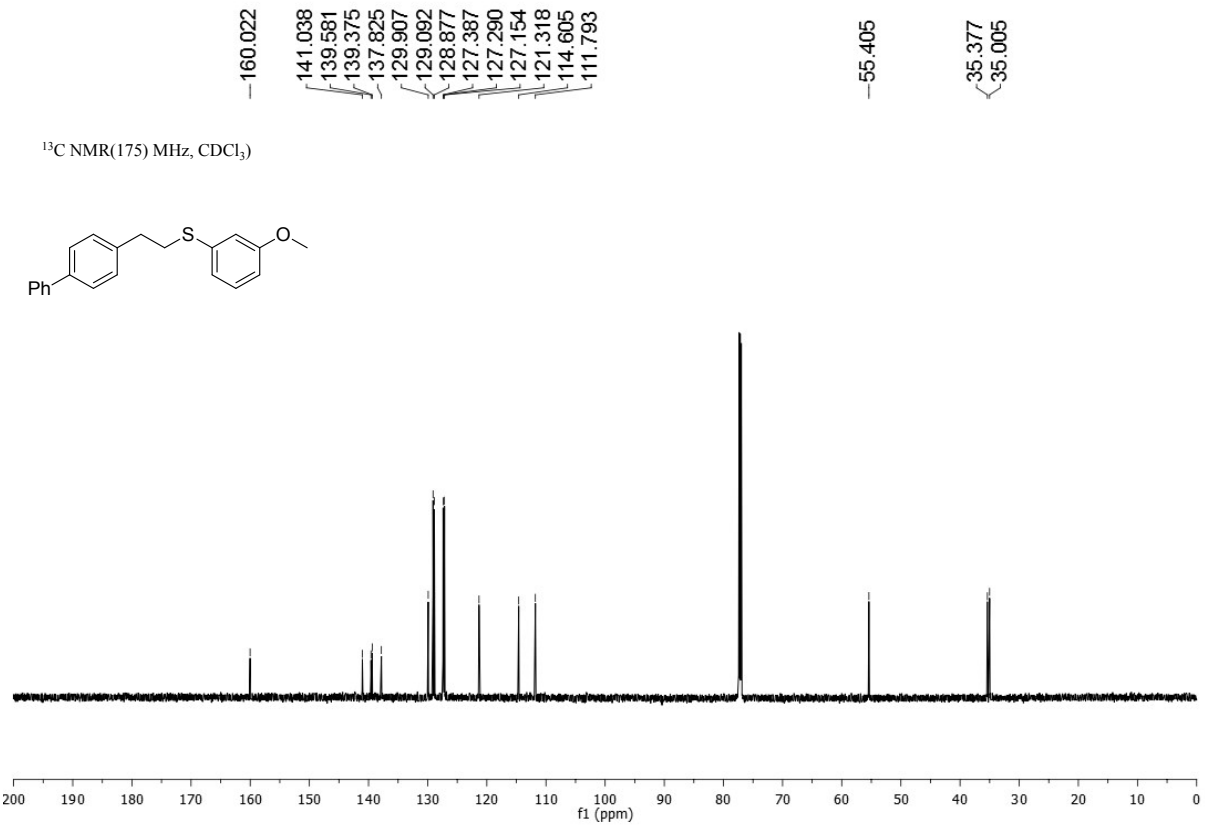


Fig. S30. ^{13}C NMR spectrum of (2-([1,1'-biphenyl]-4-yl)ethyl)(3-methoxyphenyl)sulfane **(3fe)**

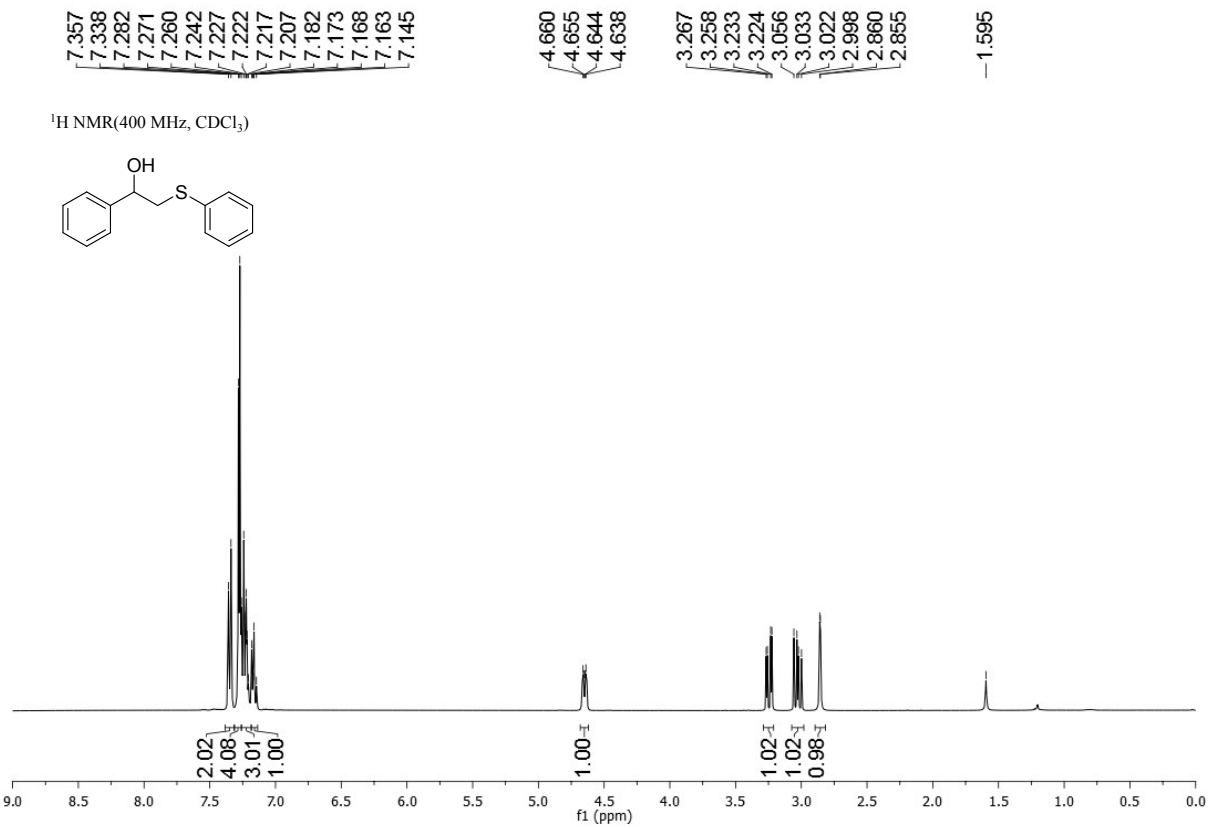


Fig. S31. [1]H NMR spectrum of 1-phenyl-2-(phenylthio)ethanol **(4aa)**

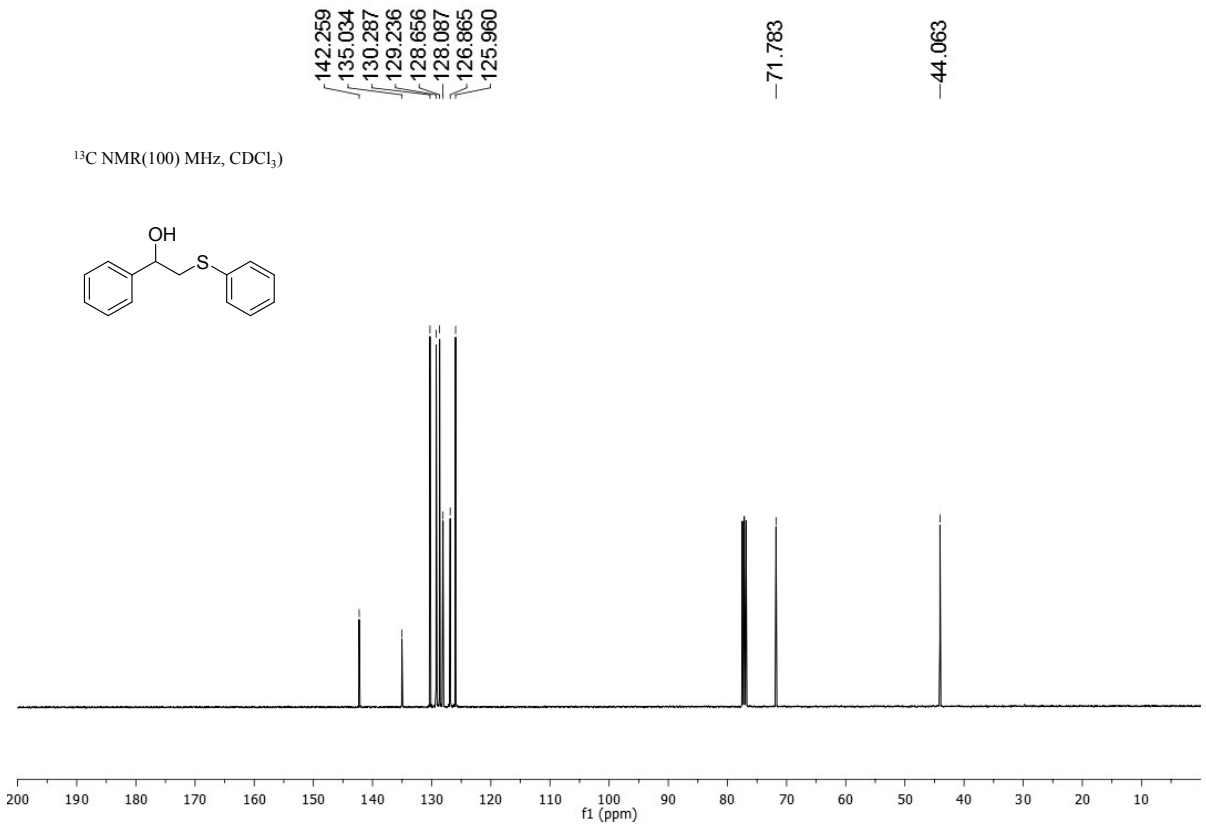


Fig. S32. ^{13}C NMR spectrum of 1-phenyl-2-(phenylthio)ethanol **(4aa)**

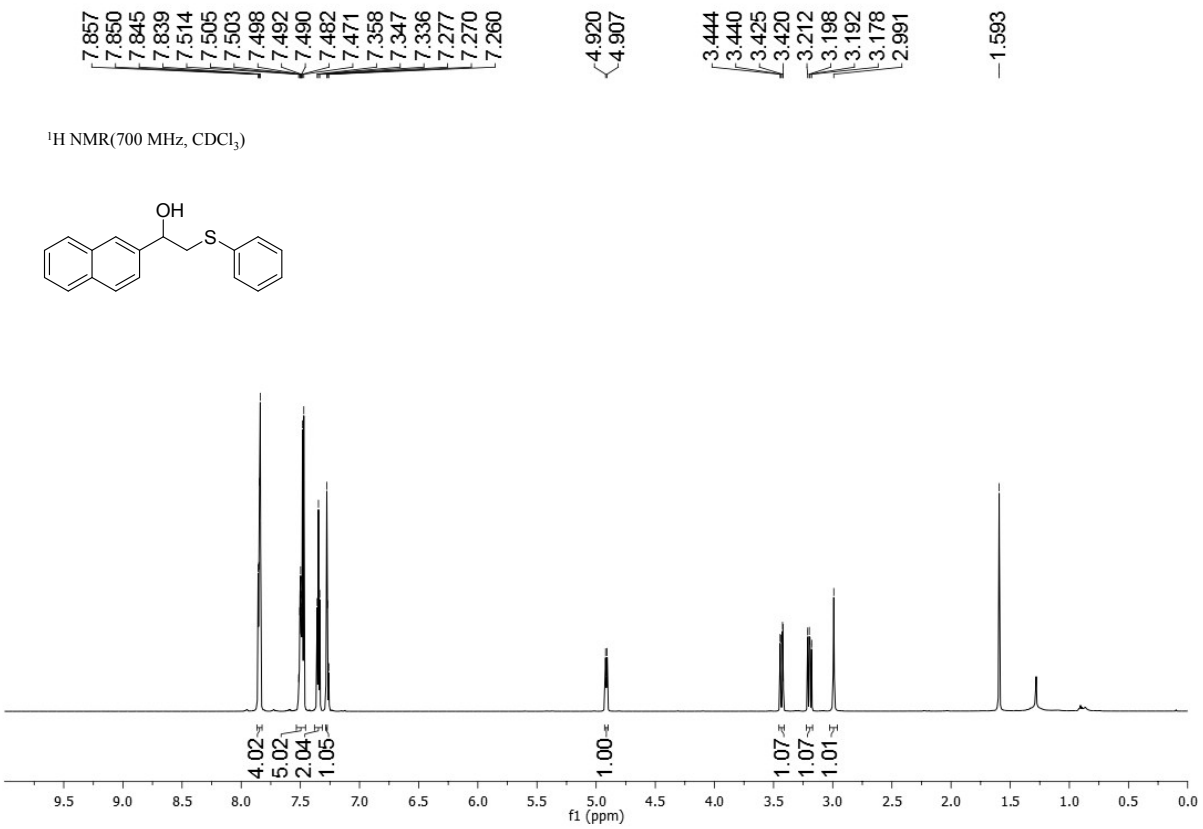


Fig. S33. ^{1}H NMR spectrum of 1-(naphthalen-2-yl)-2-(phenylthio)ethanol **(4ga)**

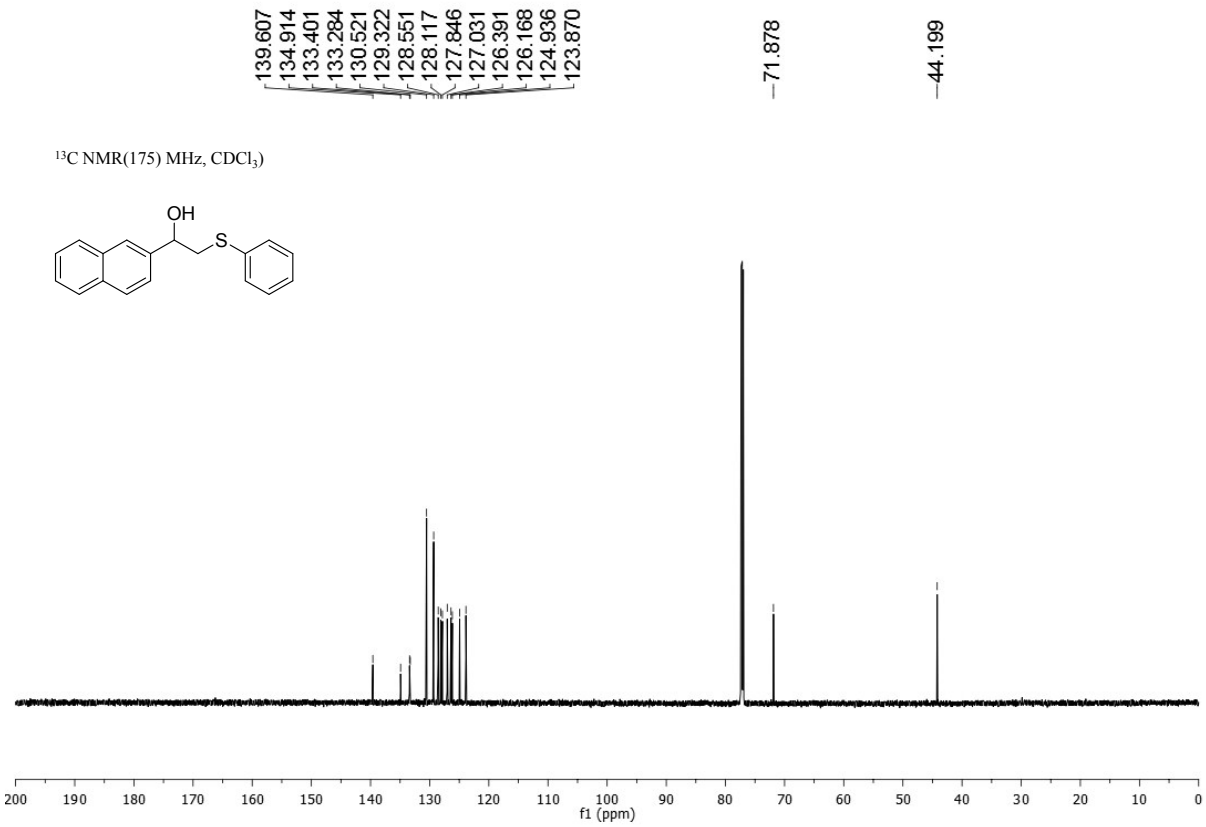


Fig. S34. ^{13}C NMR spectrum of 1-(naphthalen-2-yl)-2-(phenylthio)ethanol **(4ga)**

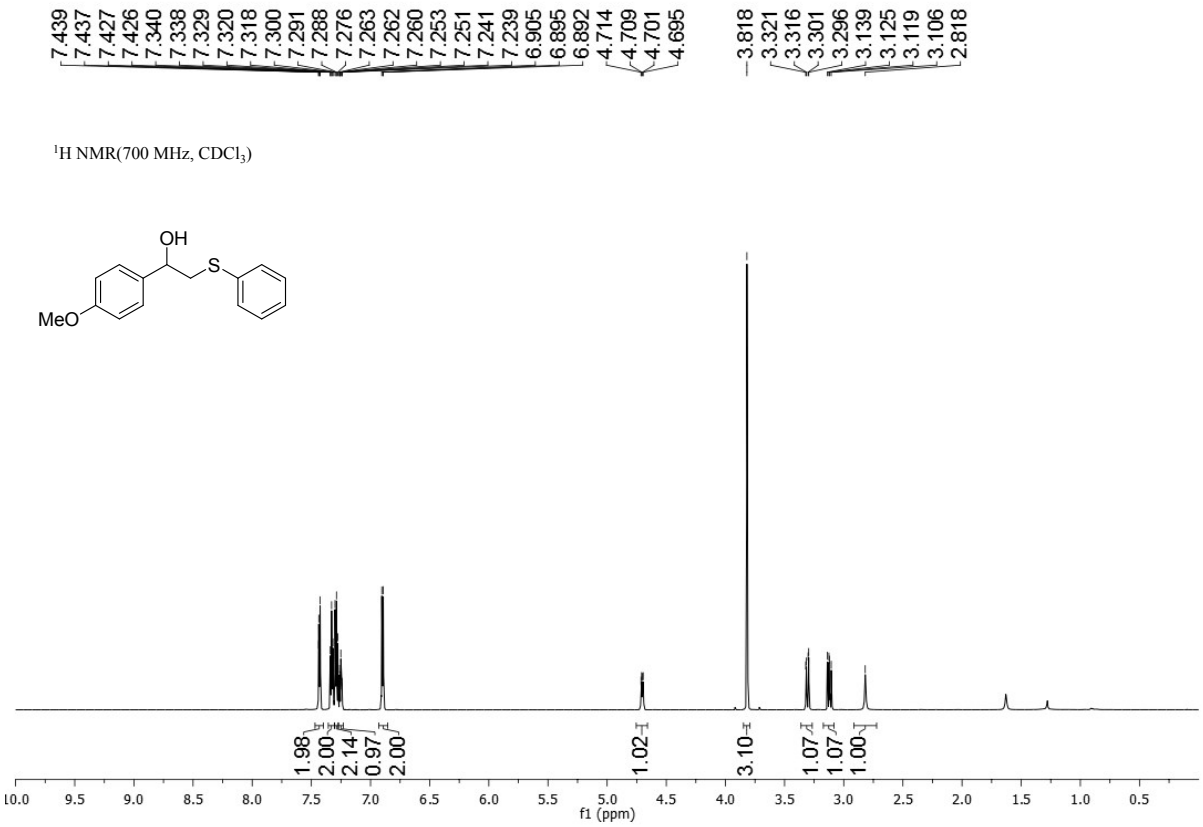


Fig. S35. ^{1}H NMR spectrum of 1-(4-methoxyphenyl)-2-(phenylthio)ethanol **(4ba)**

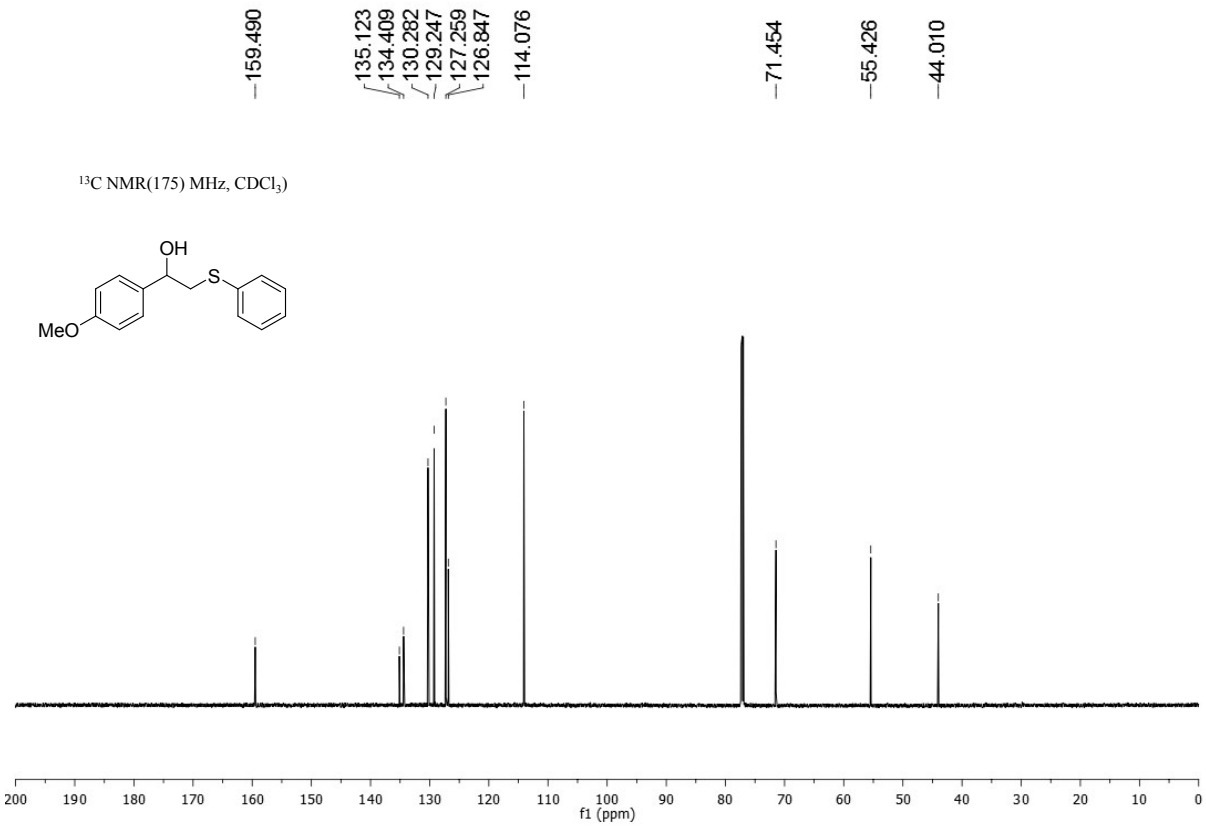


Fig. S36. ^{13}C NMR spectrum of 1-(4-methoxyphenyl)-2-(phenylthio)ethanol **(4ba)**

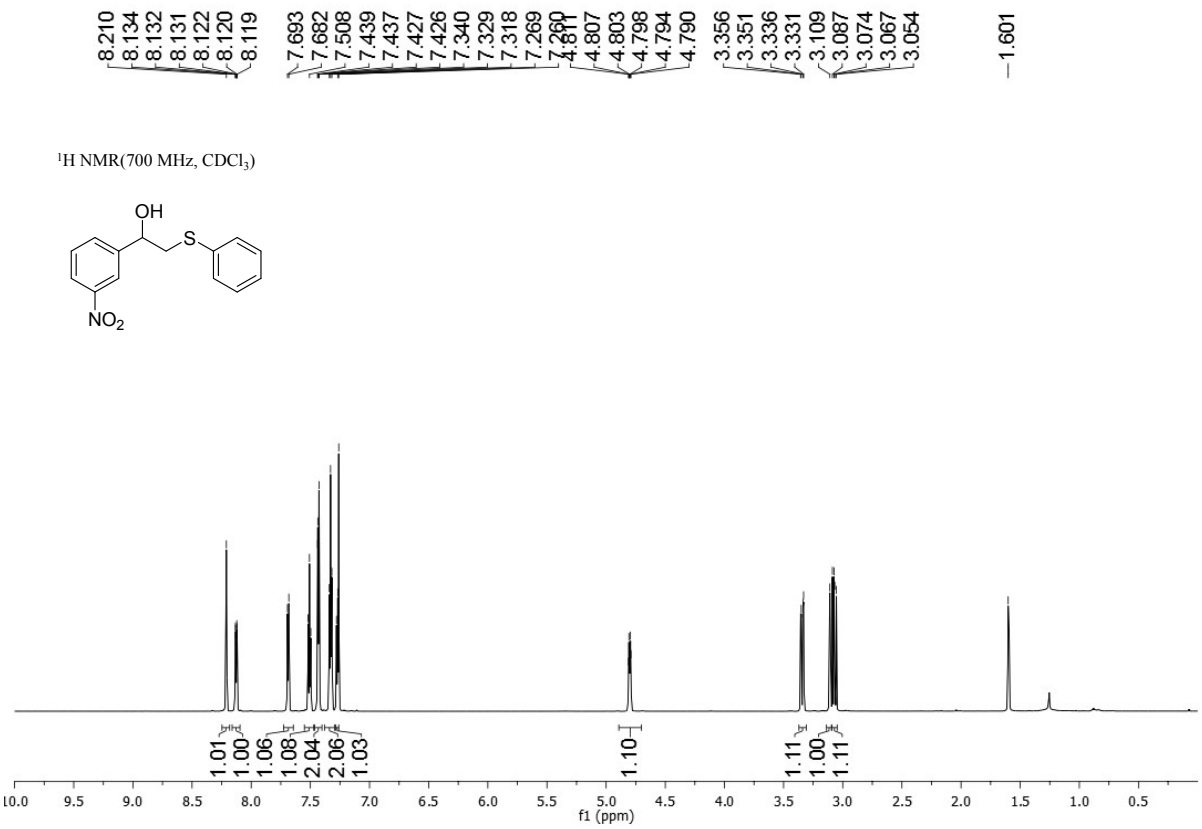


Fig. S37. ^{1}H NMR spectrum of 1-(3-nitrophenyl)-2-(phenylthio)ethanol **(4pa)**

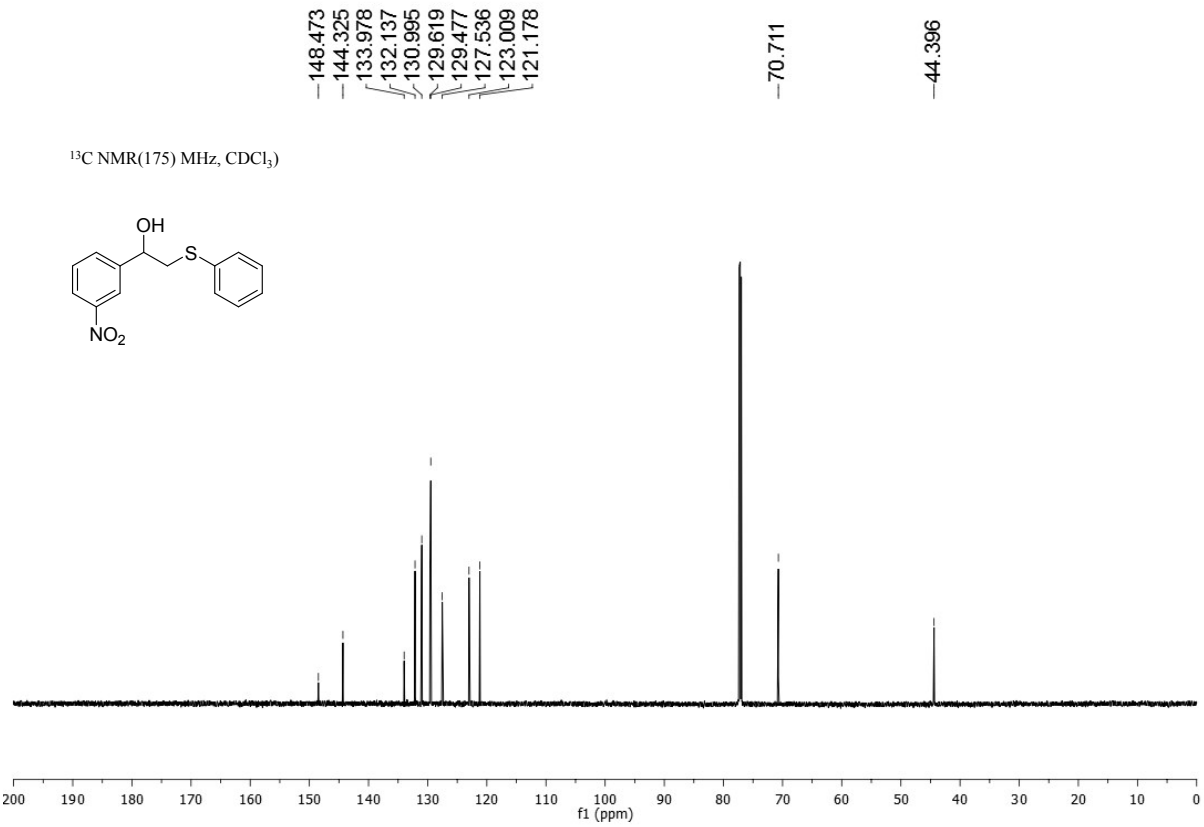


Fig. S38. ^{13}C NMR spectrum of 1-(3-nitrophenyl)-2-(phenylthio)ethanol **(4pa)**

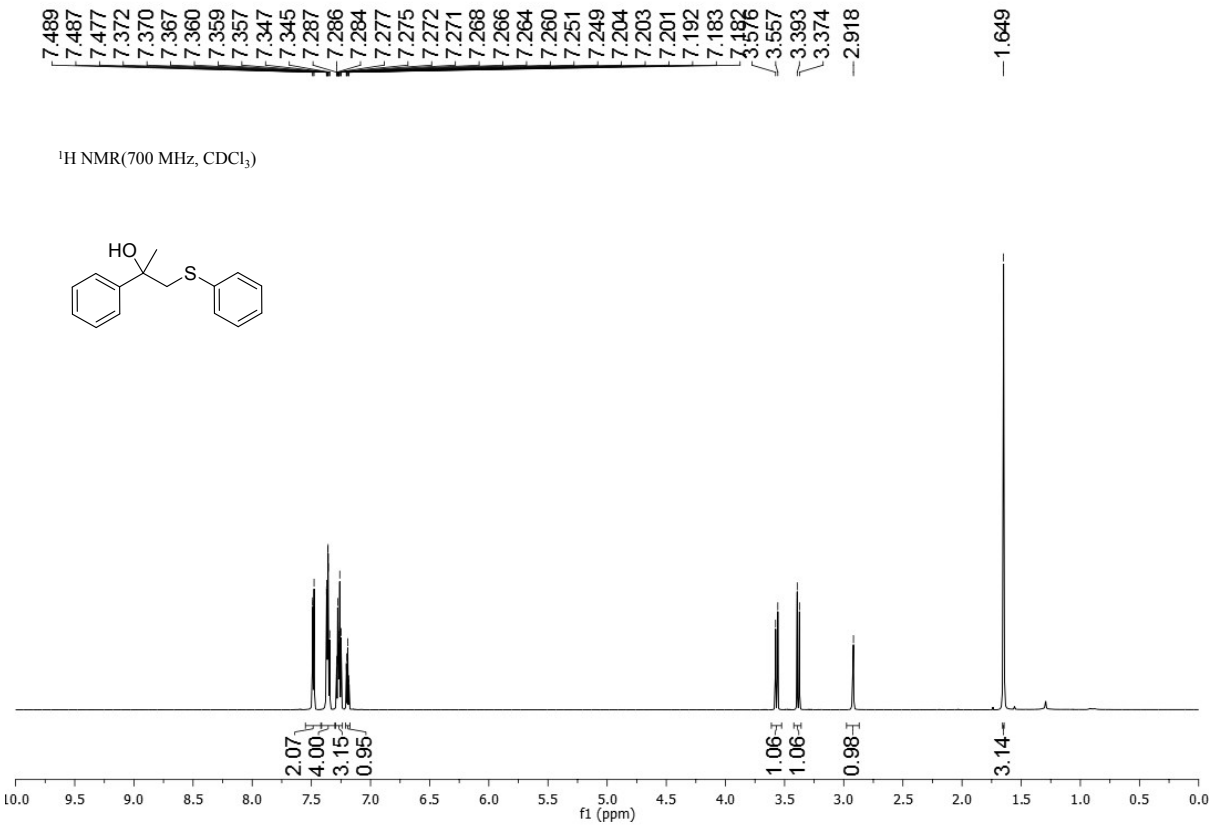


Fig. S39. ^{1}H NMR spectrum of 2-phenyl-1-(phenylthio)propan-2-ol **(4ea)**

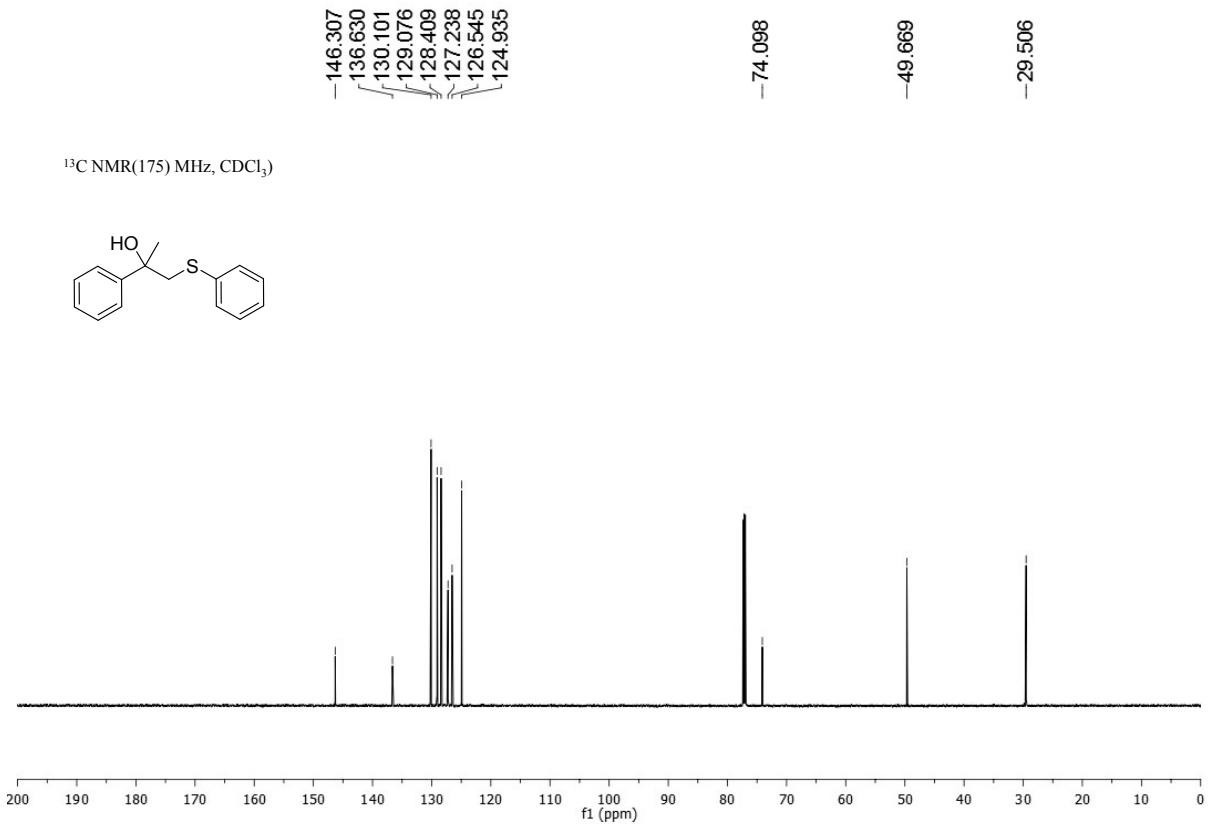


Fig. S40. ^{13}C NMR spectrum of 2-phenyl-1-(phenylthio)propan-2-ol **(4ea)**

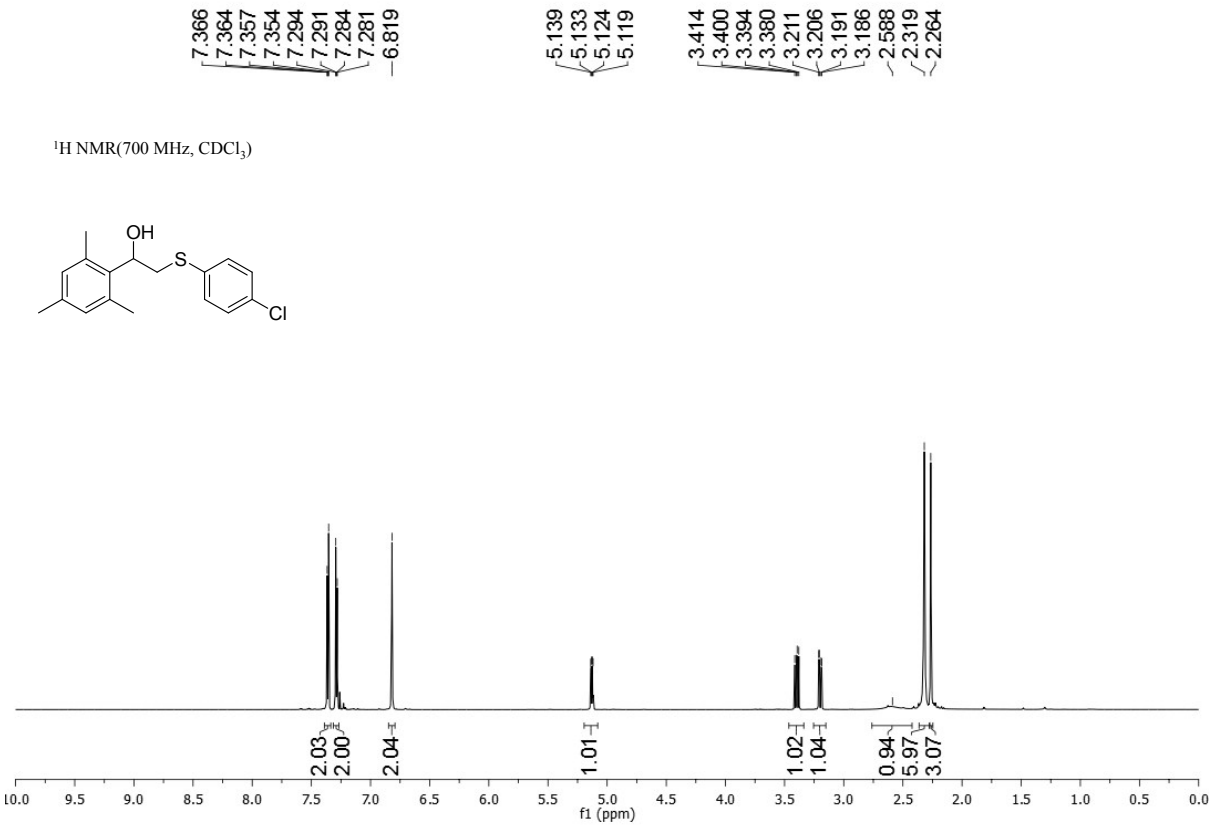


Fig. S41. ^{1}H NMR spectrum of 2-((4-chlorophenyl)thio)-1-mesitylethanol **(4qd)**

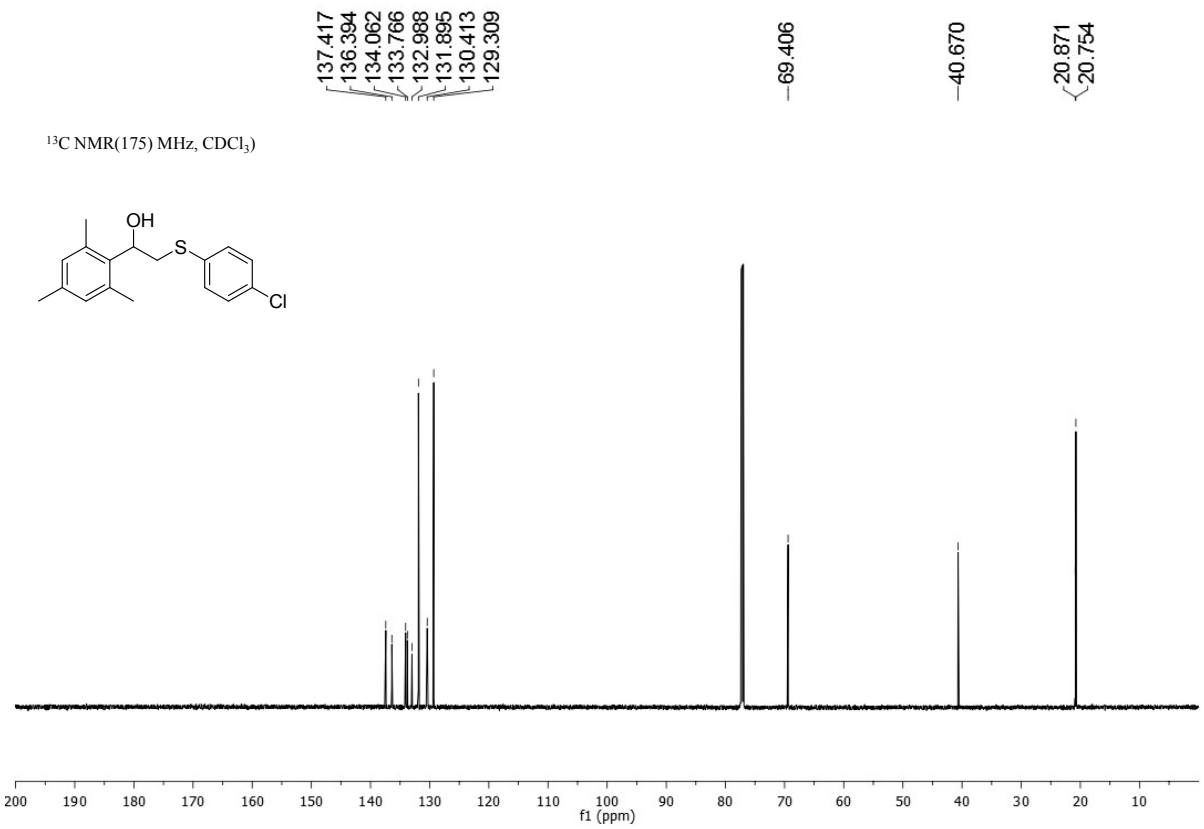


Fig. S42. ^{13}C NMR spectrum of 2-((4-chlorophenyl)thio)-1-mesitylethanol **(4qd)**

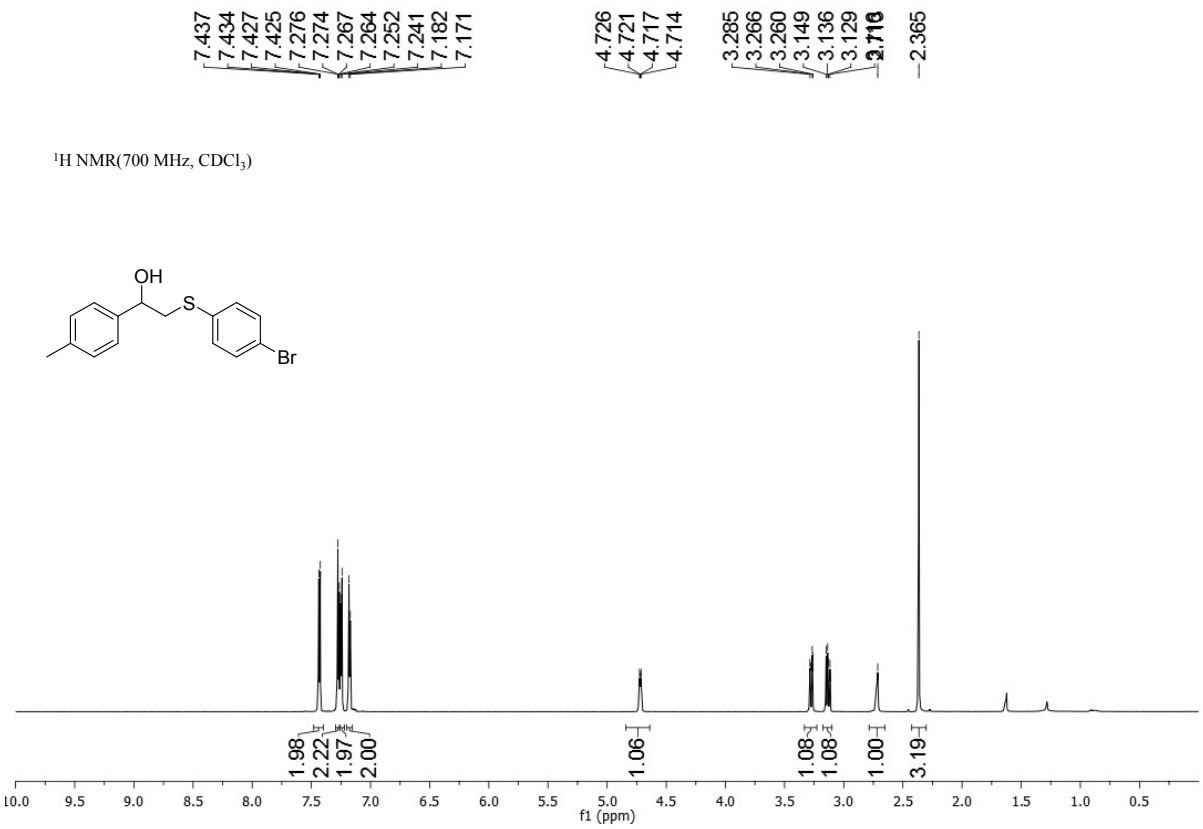


Fig. S43. ^{1}H NMR spectrum of 2-((4-bromophenyl)thio)-1-(p-tolyl)ethanol **(4rb)**

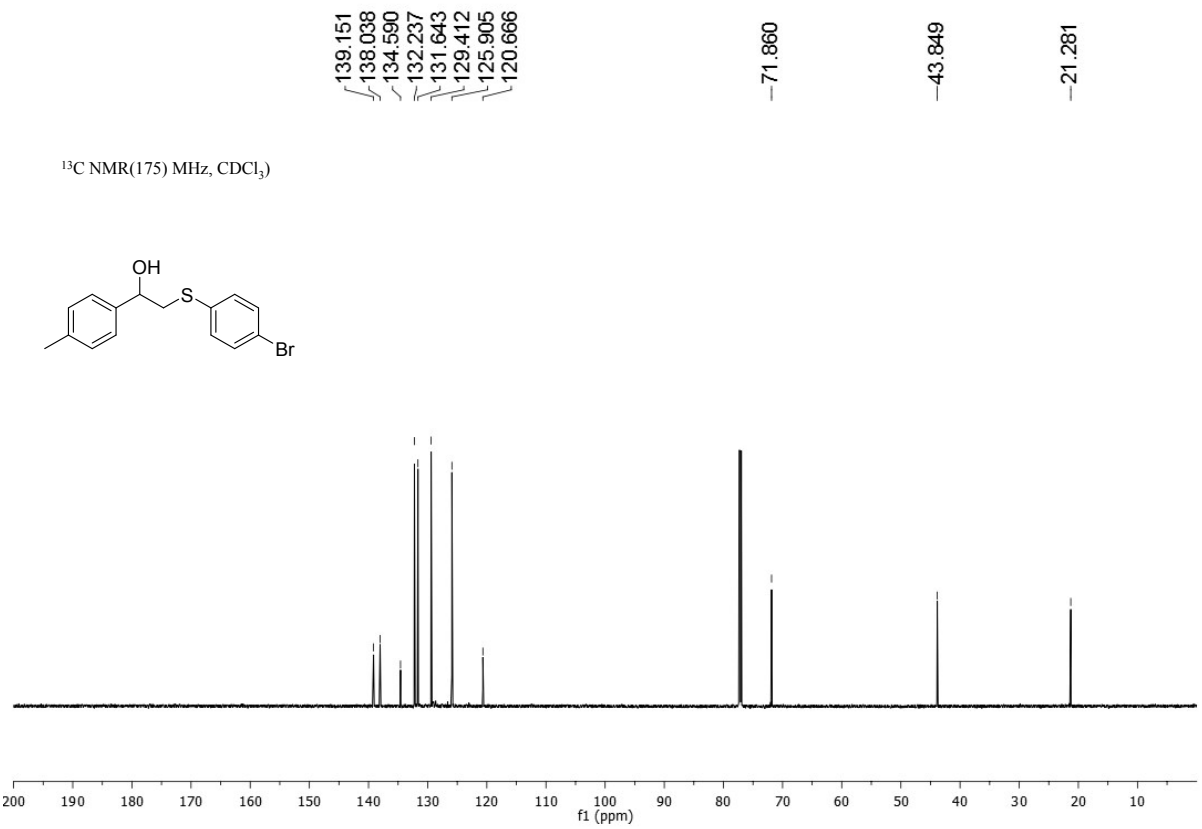


Fig. S44. ^{1}H NMR spectrum of 2-((4-bromophenyl)thio)-1-(p-tolyl)ethanol **(4rb)**

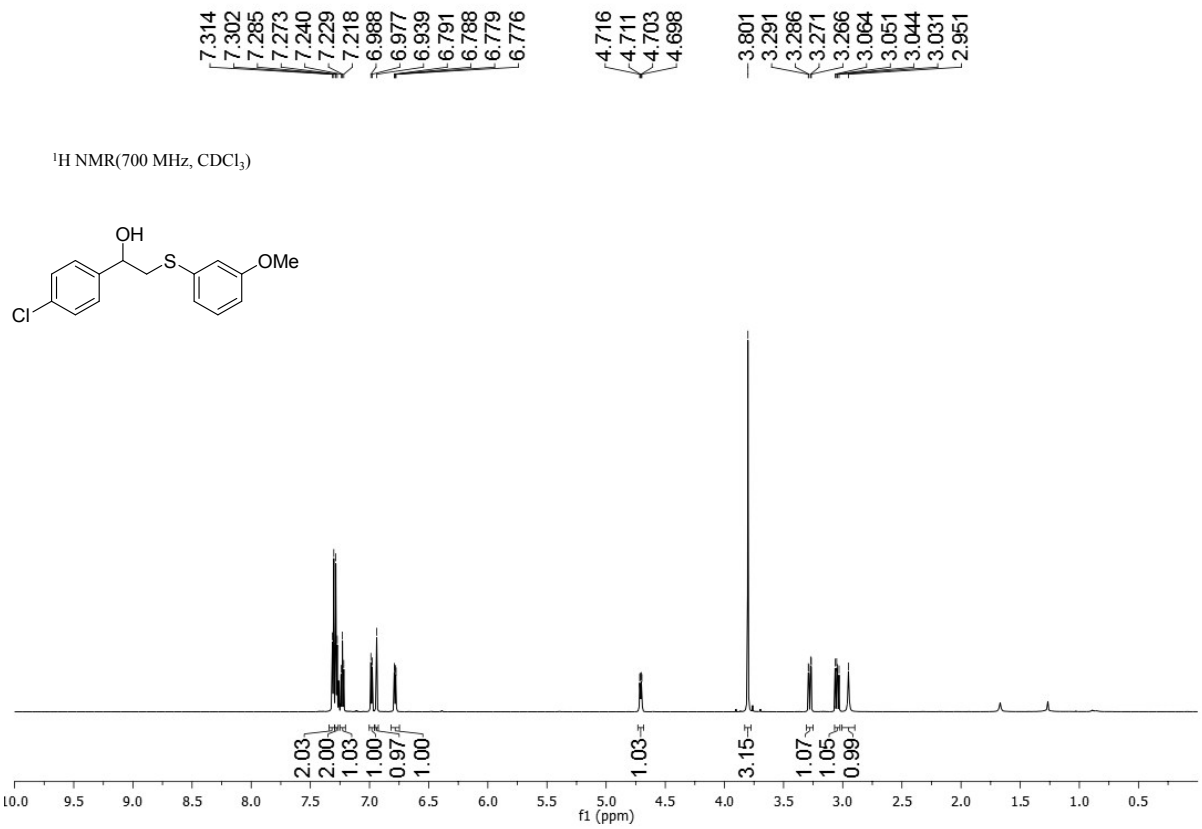


Fig. S45. ^{1}H NMR spectrum of 1-(4-chlorophenyl)-2-((3-methoxyphenyl)thio)ethanol **(4se)**

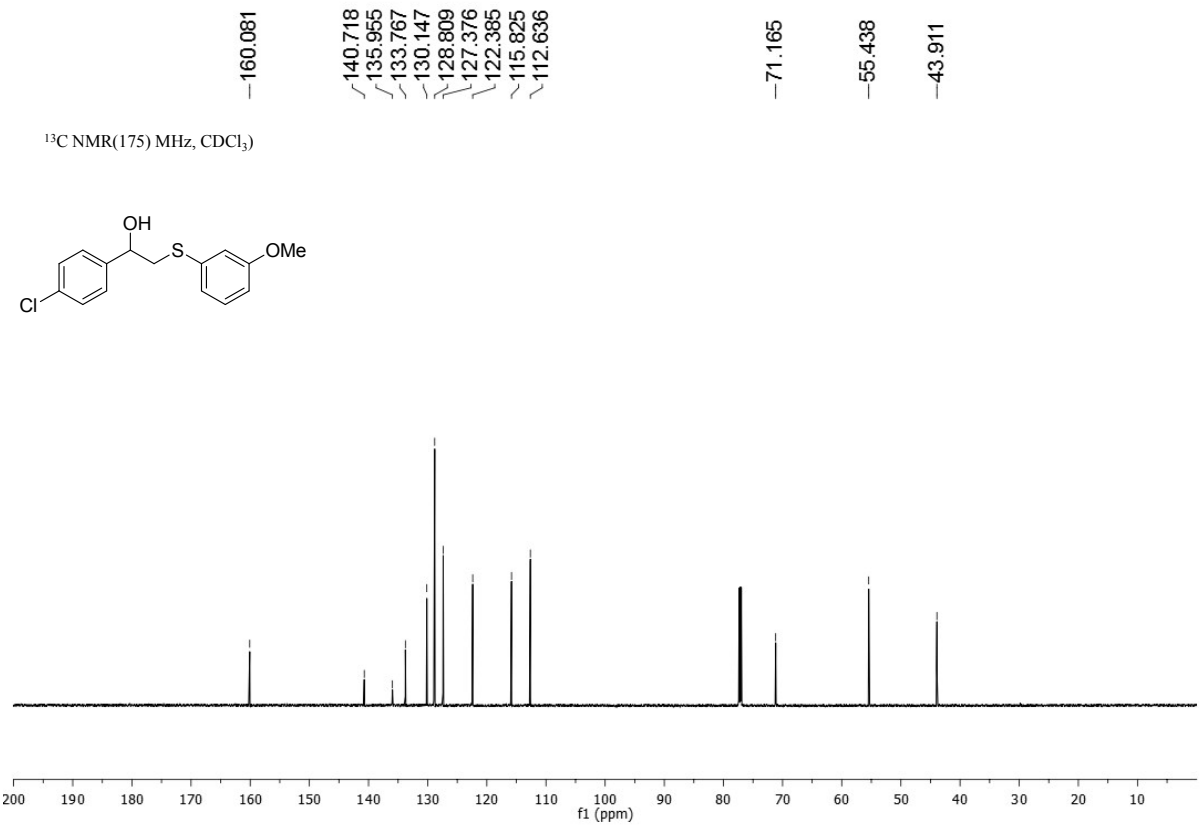


Fig. S46. ^{13}C NMR spectrum of 1-(4-chlorophenyl)-2-((3-methoxyphenyl)thio)ethanol **(4se)**

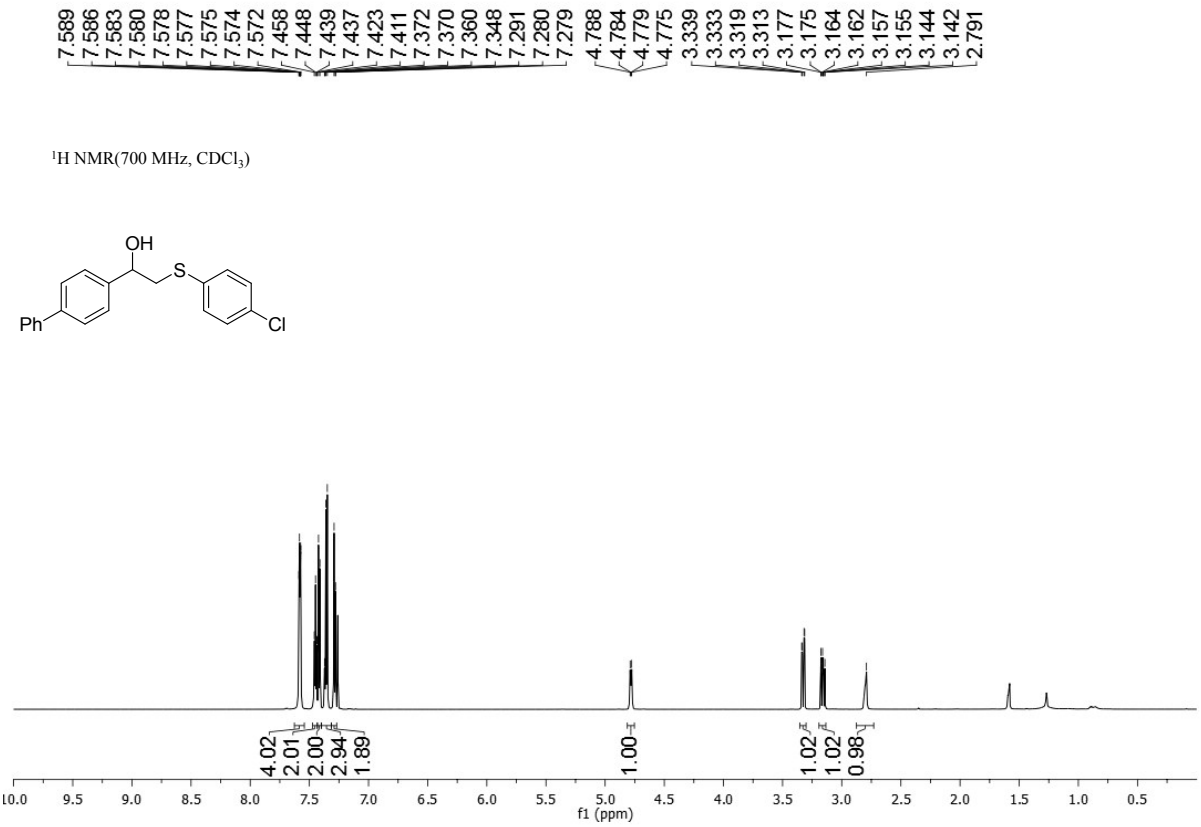


Fig. S47. ^{1}H NMR spectrum of 1-([1,1'-biphenyl]-4-yl)-2-((4-chlorophenyl)thio)ethanol **(4fd)**

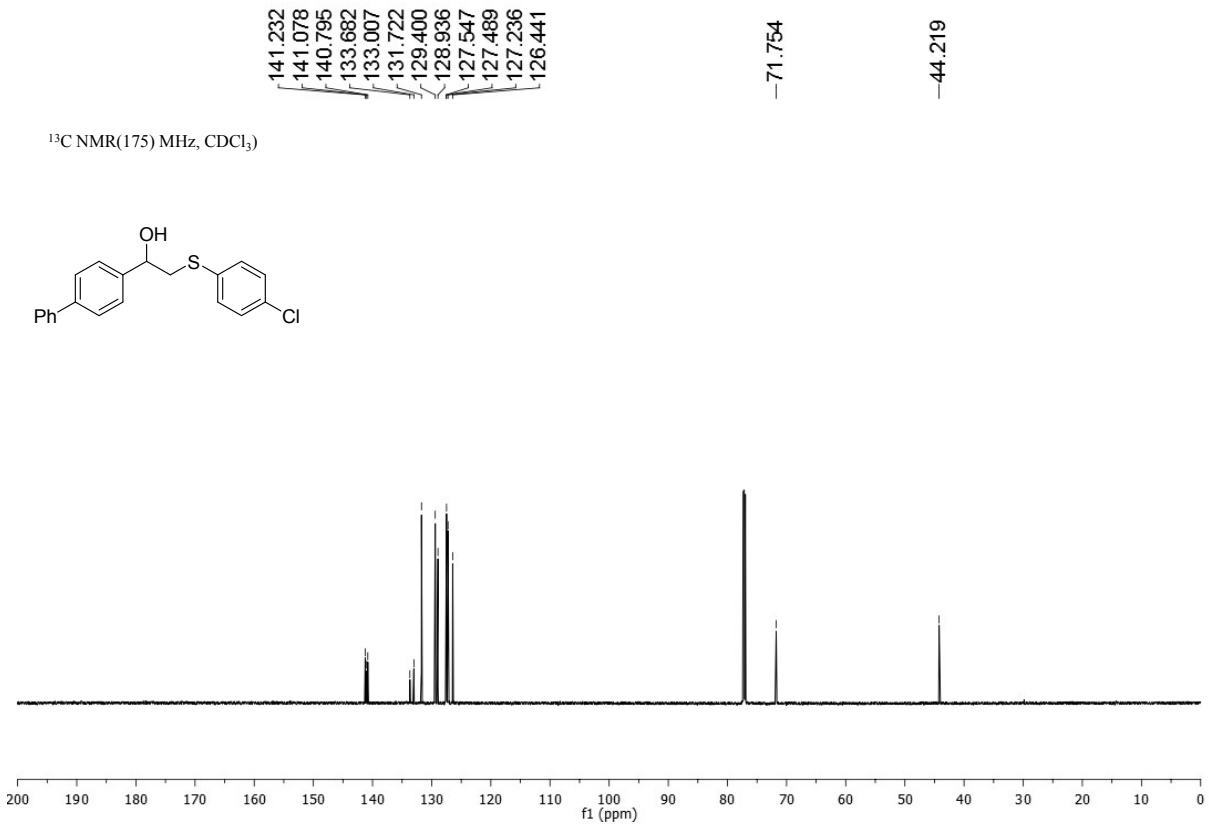


Fig. S48. ^{13}C NMR spectrum of 1-([1,1'-biphenyl]-4-yl)-2-((4-chlorophenyl)thio)ethanol **(4fd)**

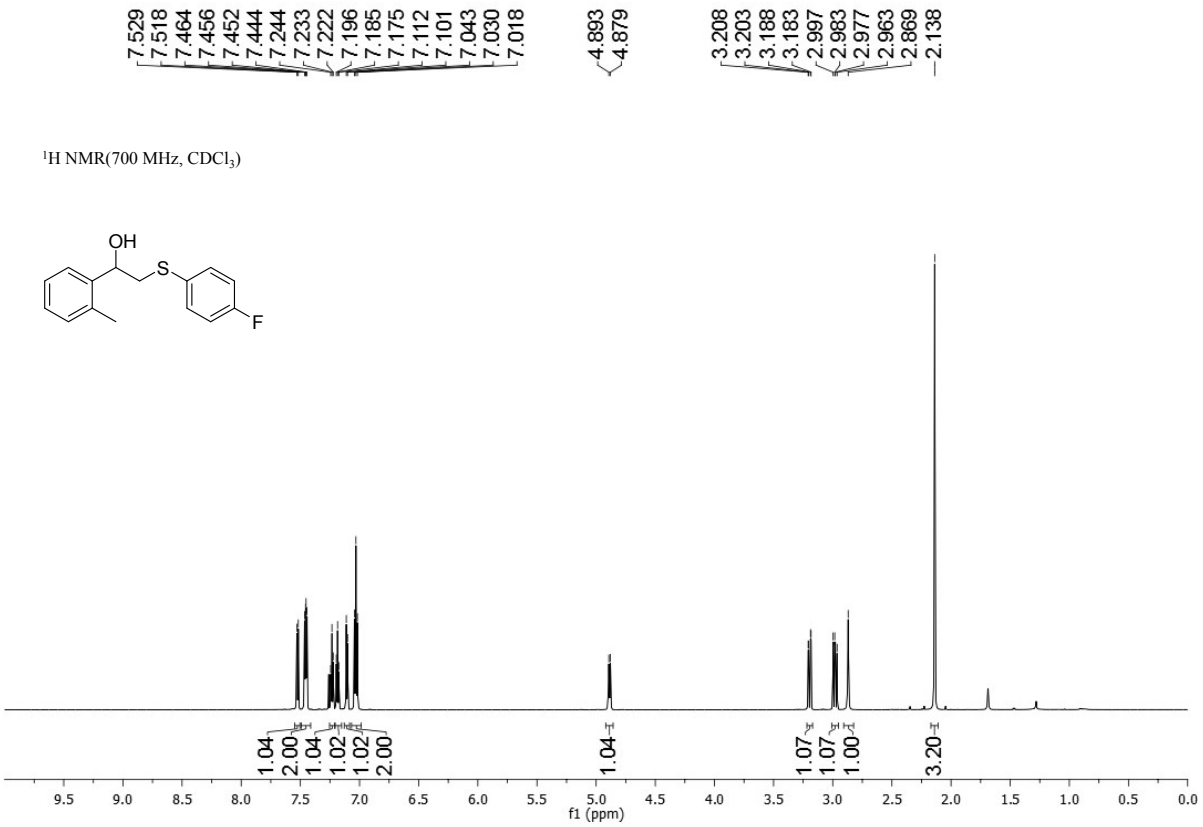


Fig. S49. ^{1}H NMR spectrum of 2-((4-fluorophenyl)thio)-1-(o-tolyl)ethanol **(4cc)**

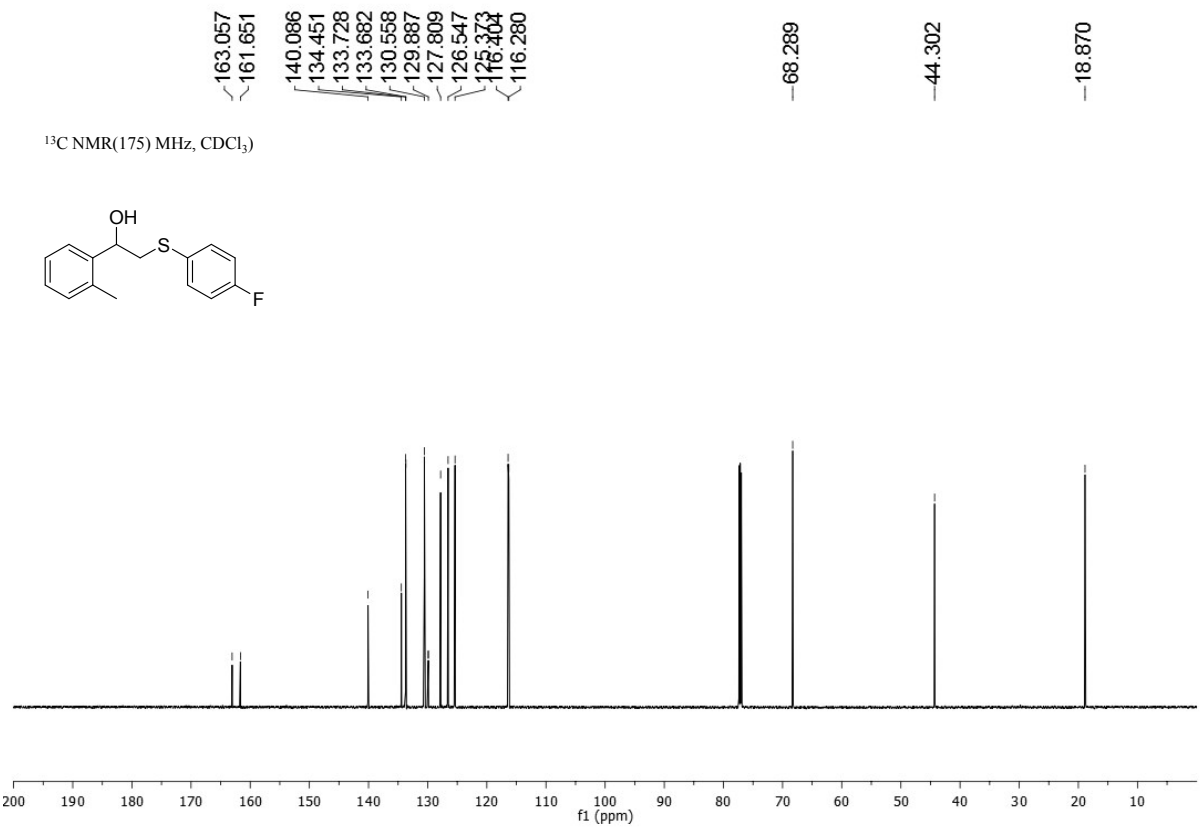


Fig. S50. ^{13}C NMR spectrum of 2-((4-fluorophenyl)thio)-1-(o-tolyl)ethanol **(4cc)**

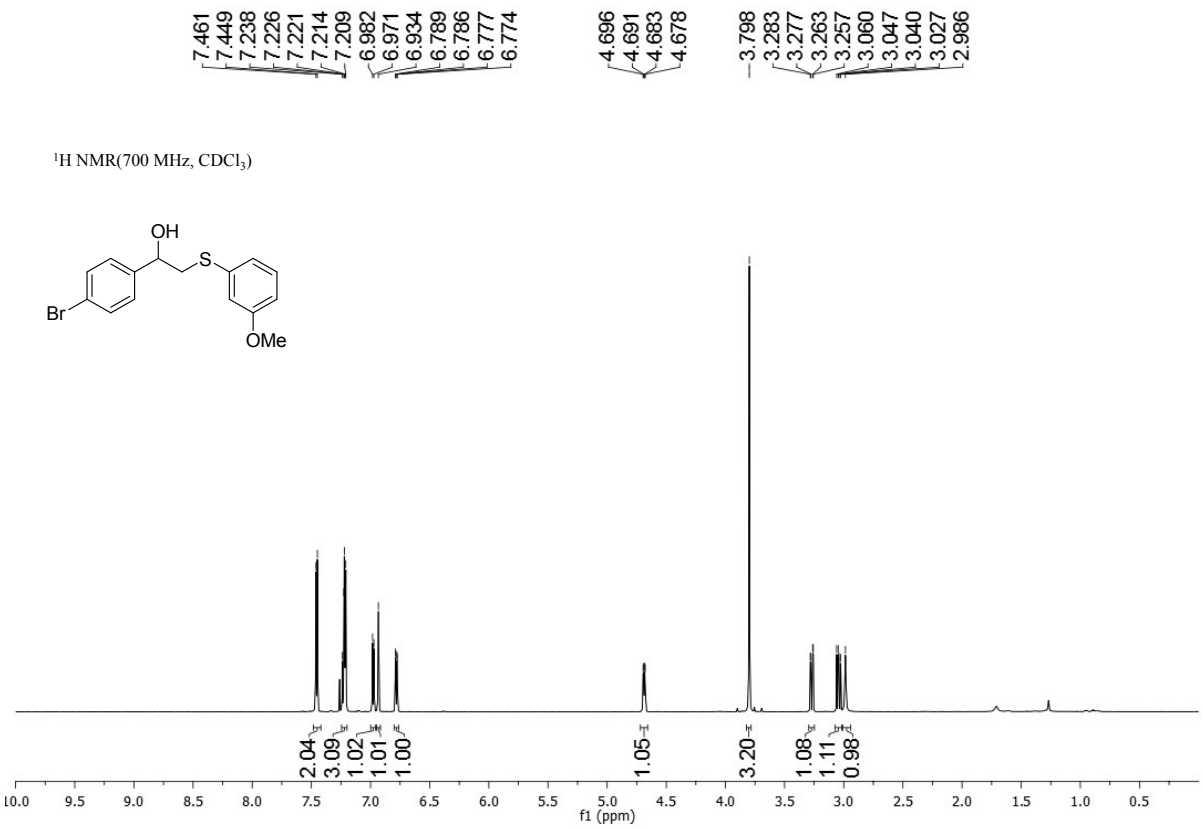


Fig. S51. ^{1}H NMR spectrum of 1-(4-bromophenyl)-2-((3-methoxyphenyl)thio)ethanol **(4te)**

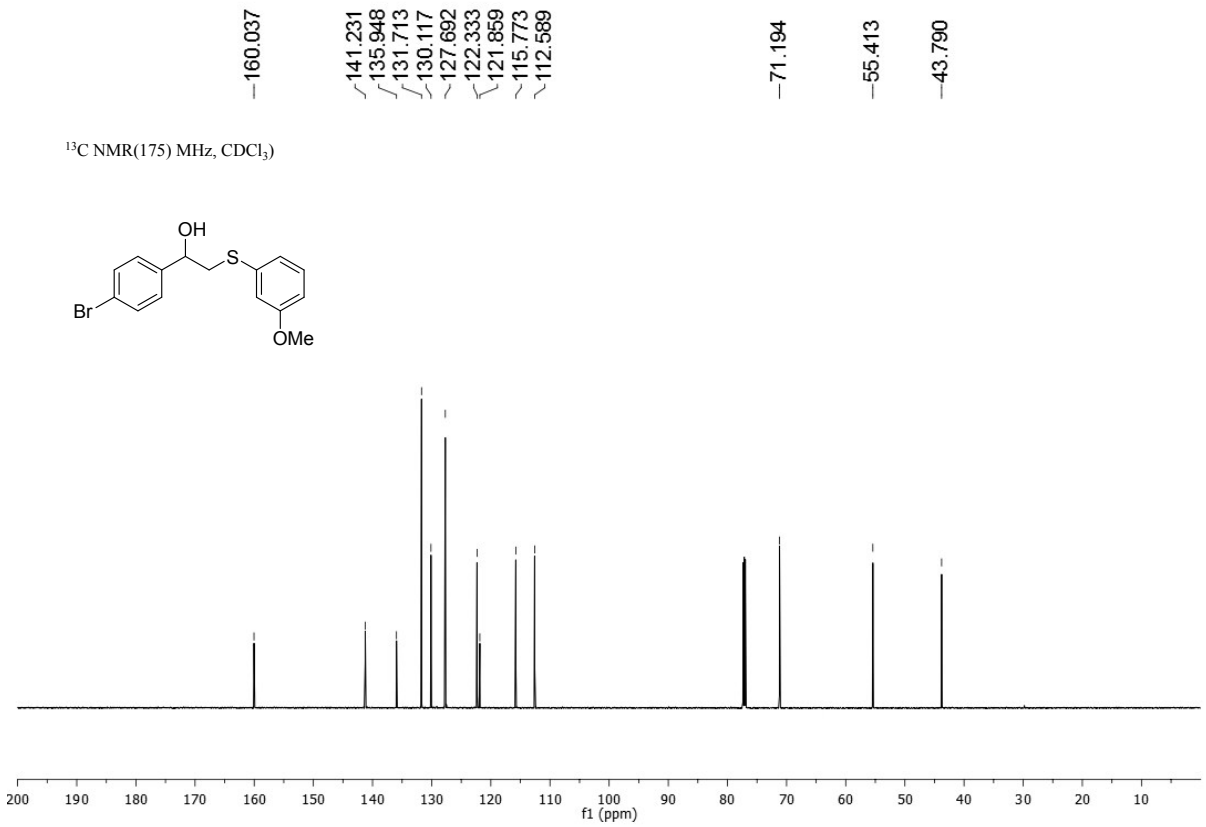


Fig. S52. ^{13}C NMR spectrum of 1-(4-bromophenyl)-2-((3-methoxyphenyl)thio)ethanol **(4te)**

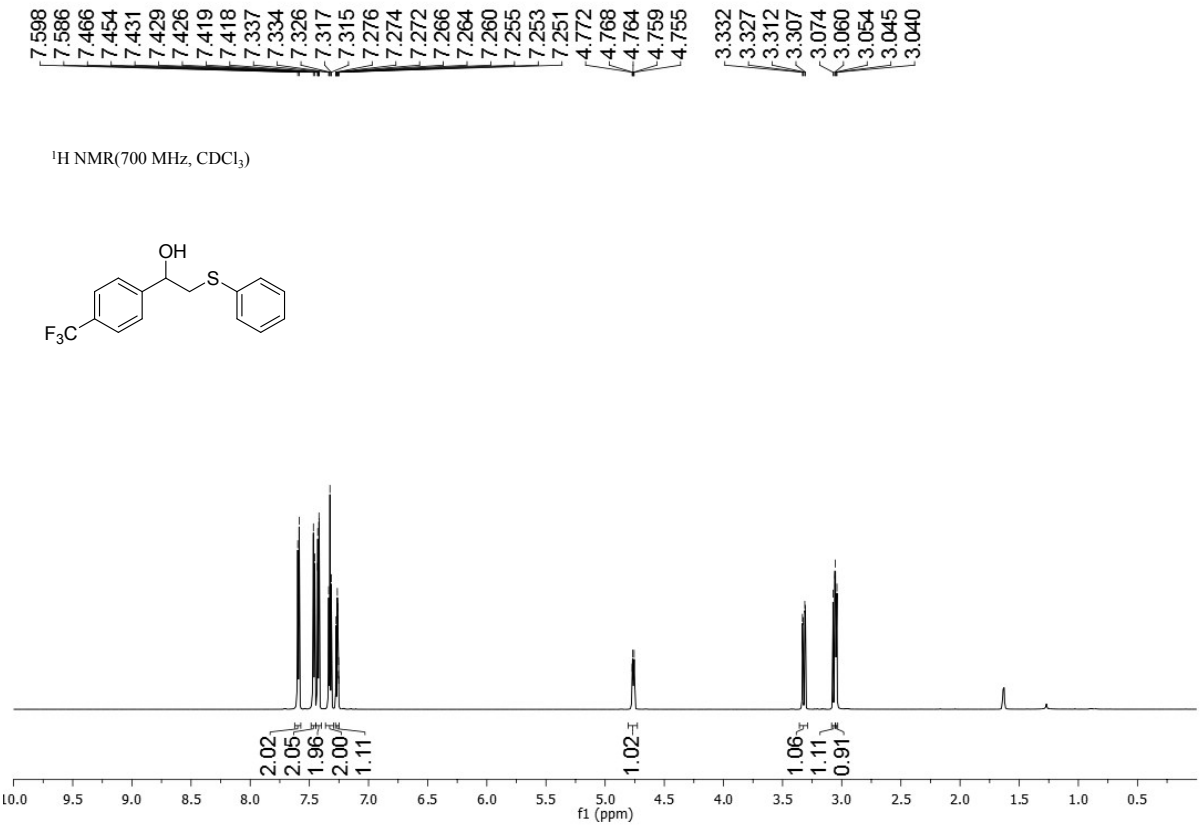


Fig. S53. ^{1}H NMR spectrum of 2-(phenylthio)-1-(4-(trifluoromethyl)phenyl)ethanol **(4la)**

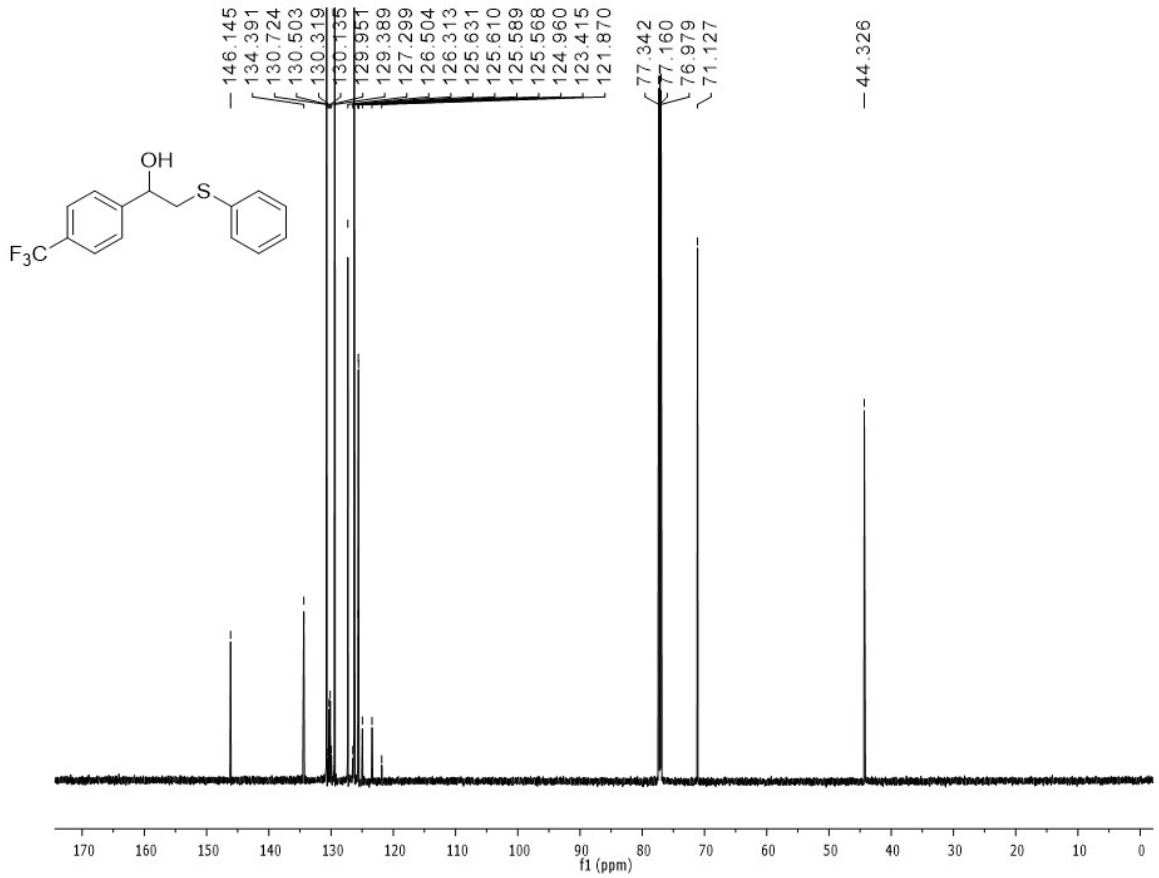


Fig. S54. ^{13}C NMR spectrum of 2-(phenylthio)-1-(4-(trifluoromethyl)phenyl)ethanol **(4la)**

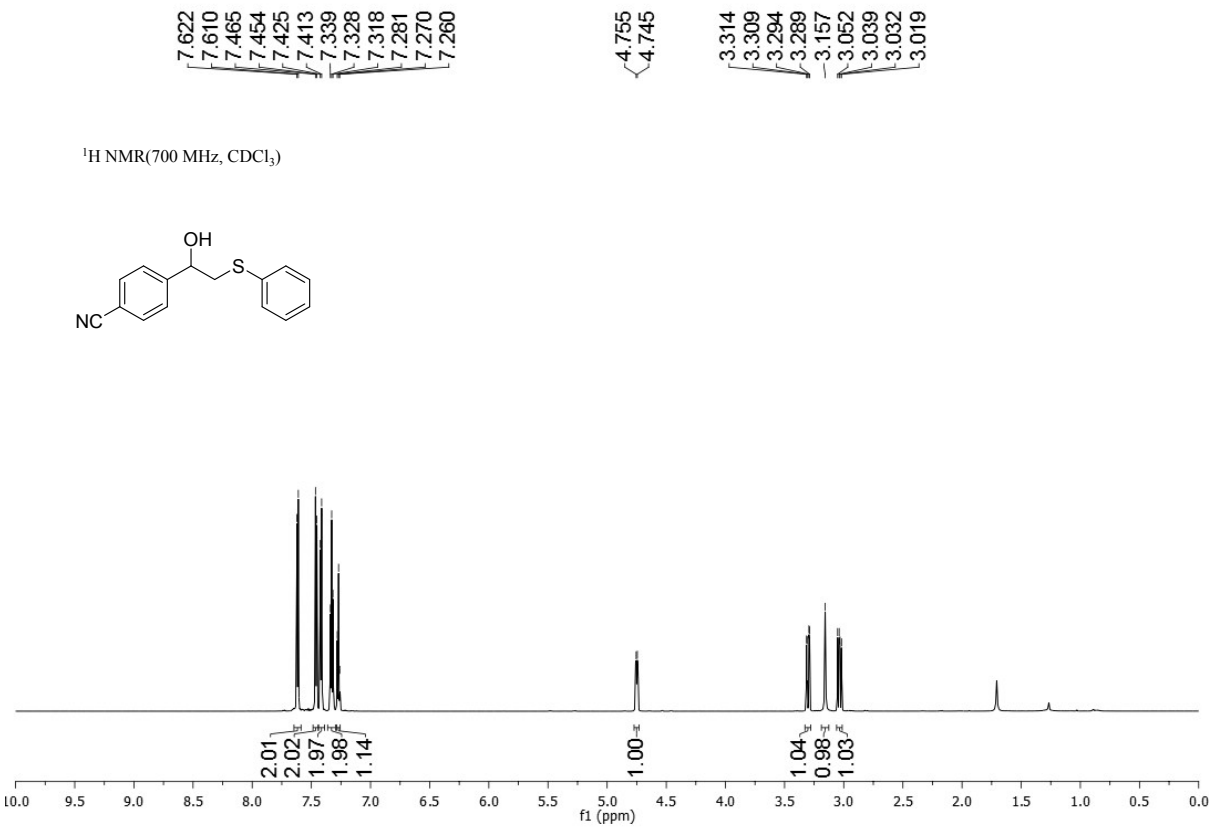


Fig. S55. ^{1}H NMR spectrum of 4-(1-hydroxy-2-(phenylthio)ethyl)benzonitrile **(4da)**

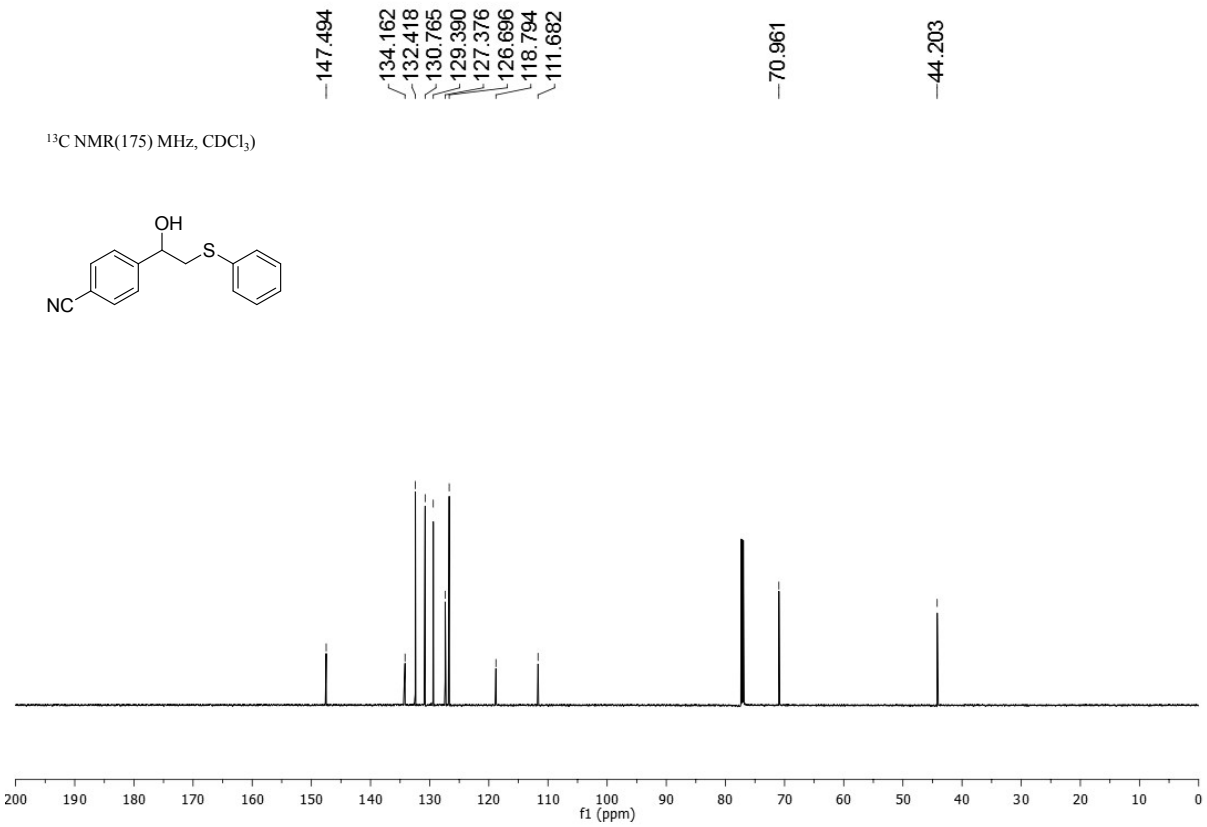


Fig. S56. ^{13}C NMR spectrum of 4-(1-hydroxy-2-(phenylthio)ethyl)benzonitrile **(4da)**

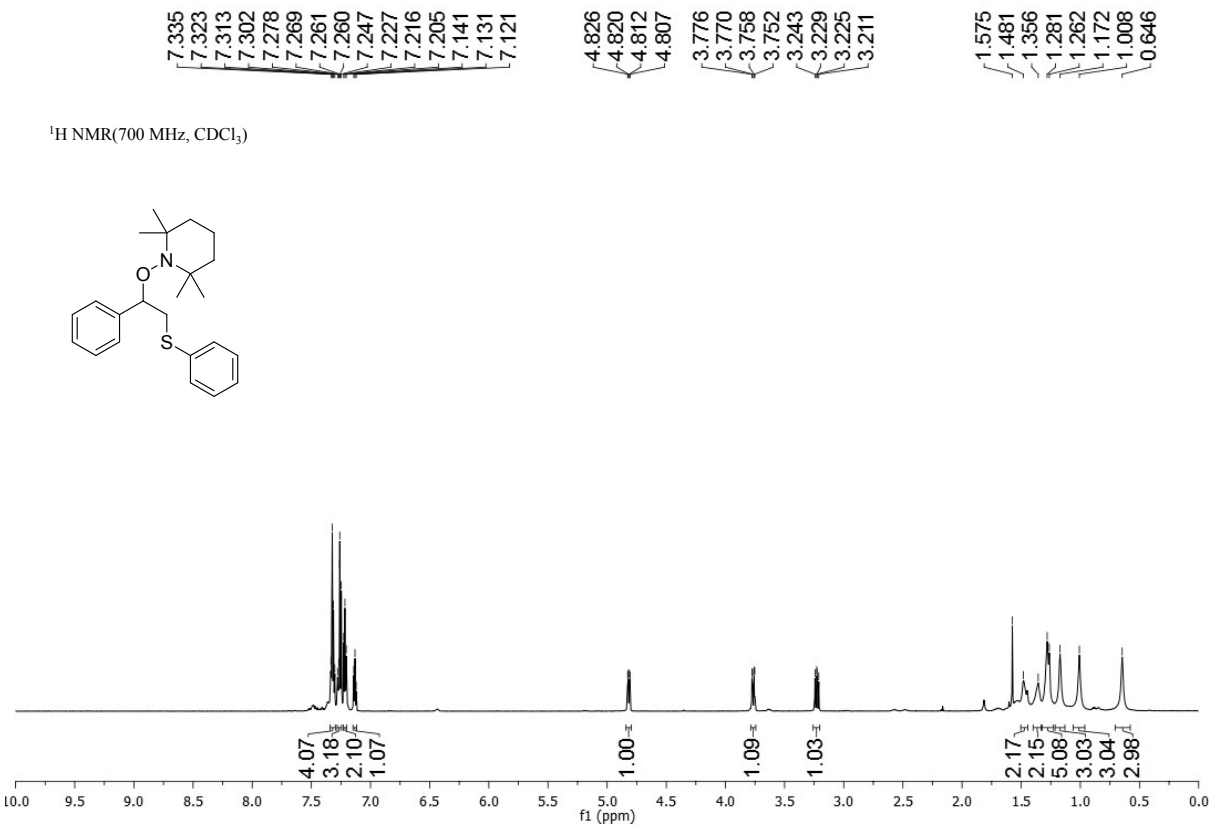


Fig. S57. ^{13}C NMR spectrum of 2,2,6,6-tetramethyl-1-(1-phenyl-2-(phenylthio)ethoxy)piperidine

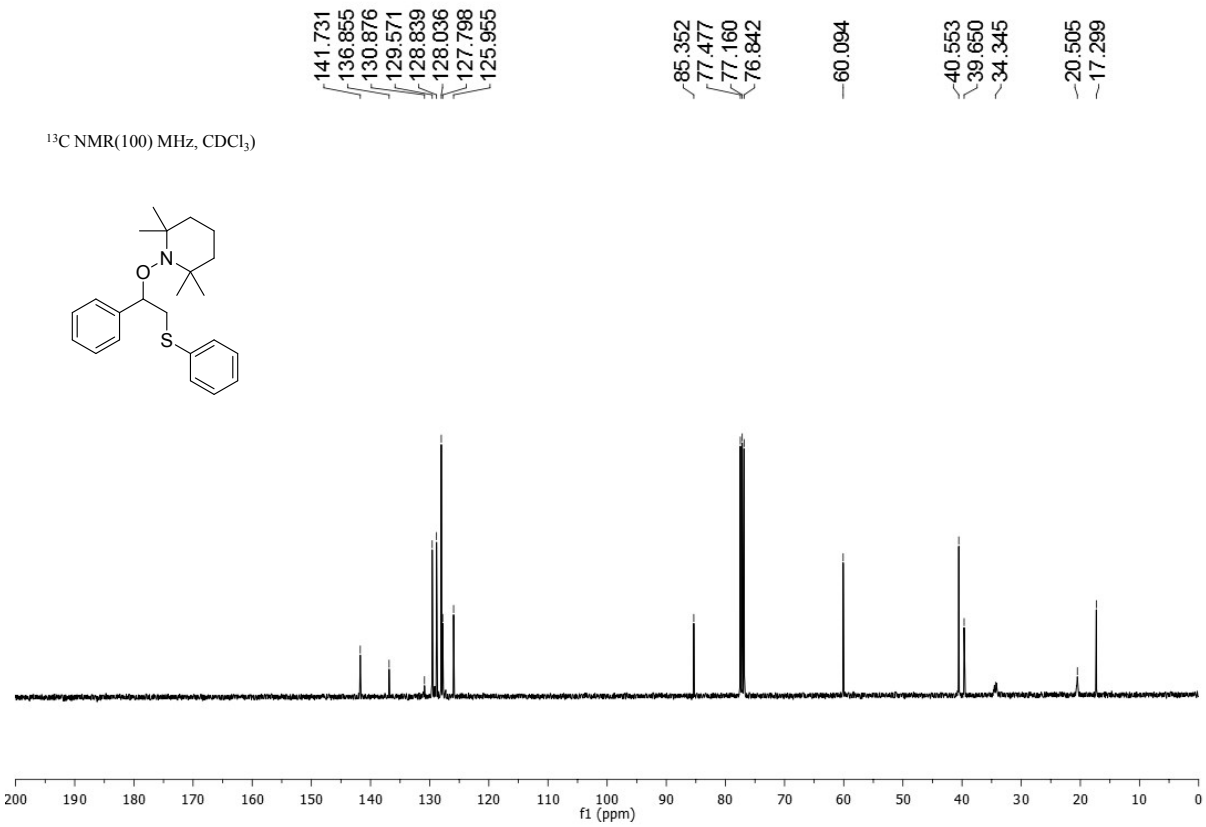


Fig. S58. ^{13}C NMR spectrum of 2,2,6,6-tetramethyl-1-(1-phenyl-2-(phenylthio)ethoxy)piperidine

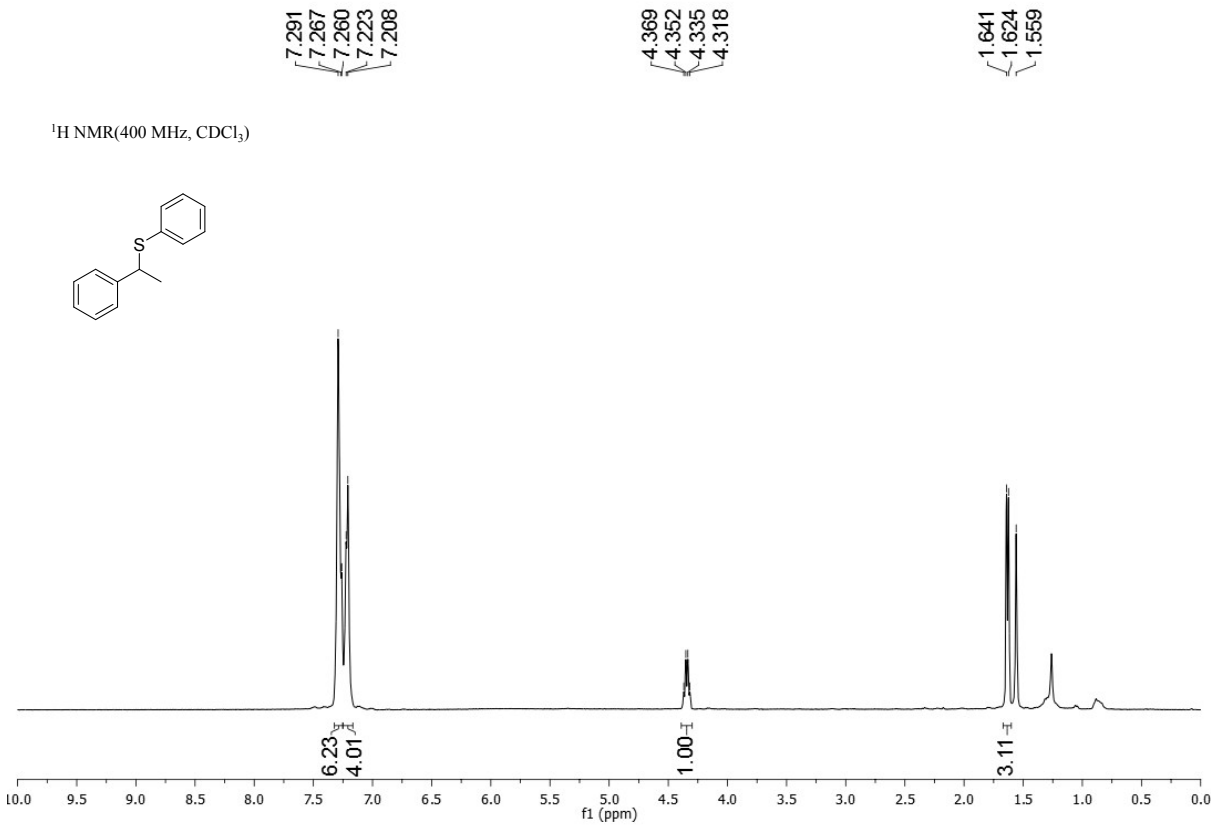


Fig. S59. ^{1}H NMR spectrum of phenyl(1-phenylethyl)sulfane

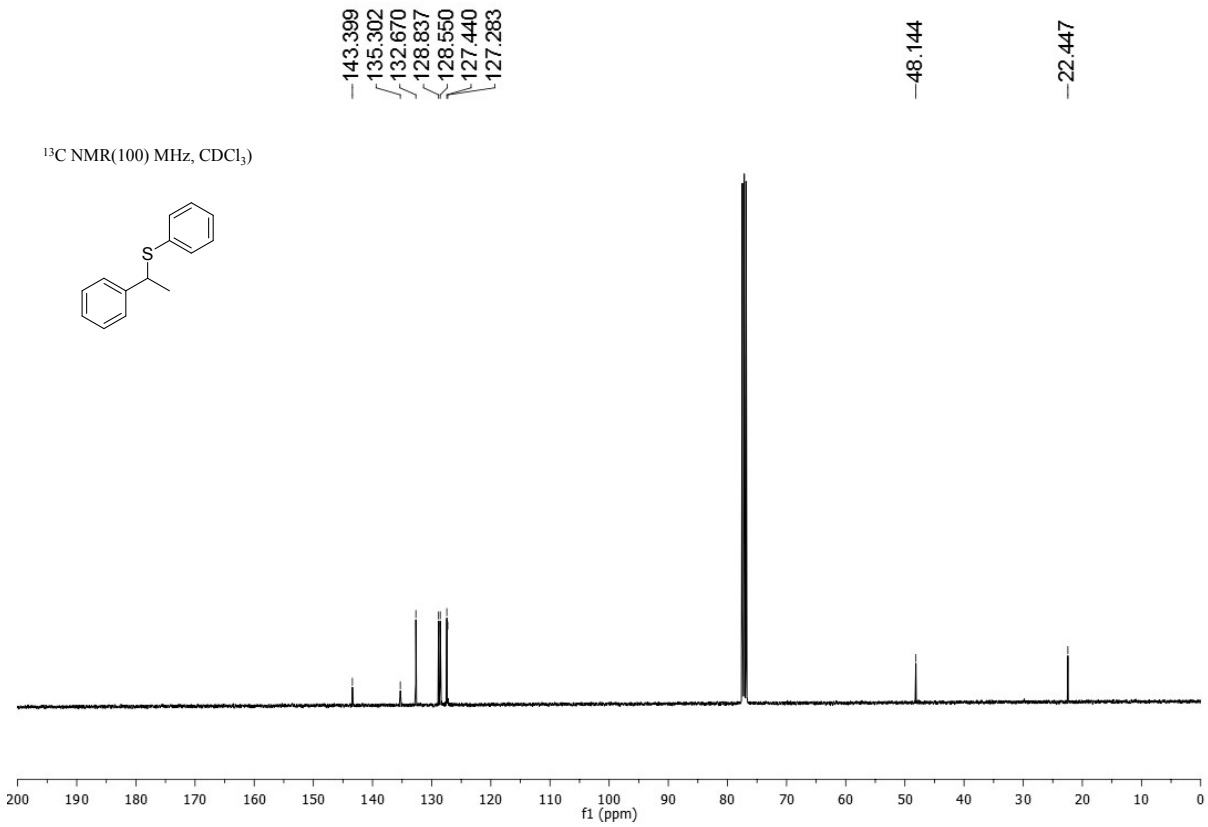


Fig. S60. ^{13}C NMR spectrum of phenyl(1-phenylethyl)sulfane