Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Visible-Light Mediated Sulfonylation of Thiols *via* Insertion of Sulfur Dioxide

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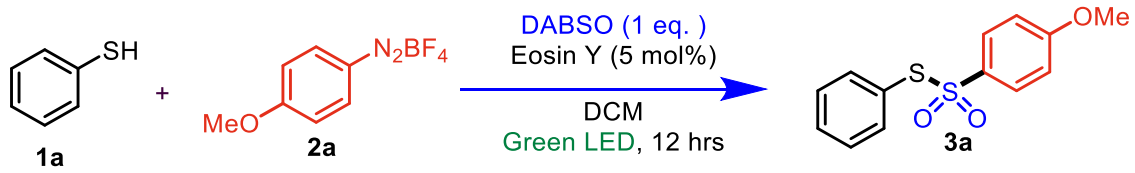
Experimental Section

General Experimental

^{1}H and ^{13}C spectra were recorded on Bruker Avance 400 and 500 MHz spectrophotometers. The chemical shifts (δ ppm) and coupling constants (Hz) are reported in the standard fashion with reference to internal chloroform. High resolution mass measurements were carried out using Micromass Q-ToF ESI instrument using direct inlet mode. Analytical thin-layer chromatography (TLC) was performed on pre-coated 0.2 mm thick Merck 60 F_{245} silica plates and various combinations of diethyl ether and Petroleum ether were used as eluent. Visualization of the spots were accomplished by exposure to UV or iodine vapors. All compounds were purified using silica gel (100-200 mesh) column chromatography and gave spectroscopic data consistent with being ≥95% the assigned structure.. Thiols and Thiophenols were purchased from either Sigma-Aldrich and TCI and were used as such without further purification. Aryl diazonium salts[1] and DABSO[2] were prepared as per the previous reports.

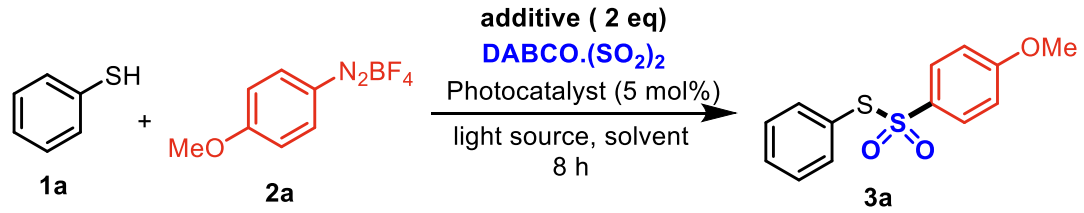
1. General procedure for the visible-light mediated three component synthesis of thiosulfonates.



In a reaction vial equipped with magnetic stirring bar, was added thiol **1** (22.0 mg, 0.2 mmol), aryldiazonium salt **2a (**66.0 mg, 0.3 mmol), DABSO (48.0 mg, 0.2 mmol) and Eosin Y (6.5 mg, 5.0 mol%) followed by DCM (2 mL). The reaction was then irradiated by green LED for 8 hrs. The reaction mass was then diluted with sat. $NaHCO_3$ solution (5 mL) and extracted with DCM (3 x 5 mL). Organic layer was dried over Na_2SO_4, evaporated under reduced pressure and chromatographed with EtOAc in Petroleum ether (1:19) to give 47.1 mg, 84% yield of the desired product **3a**.

2. Control studies.

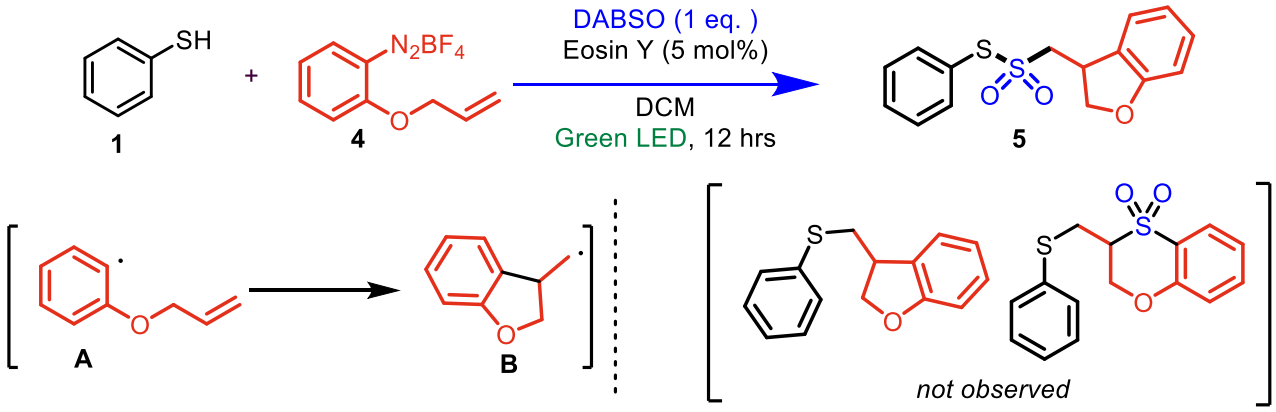
control studies



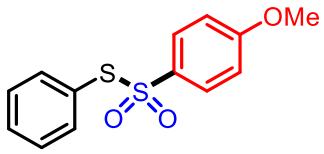
Additive	Role	Yield of **3a**
TEMPO	radical quencher	traces
BHT	radical quencher	traces
$CuCl_2$	Single electron quencher	traces

We subsequently carried out a few control studies to shed light onto the reaction mechanism (Table 5). The complete termination of the reaction in the presence of radical scavengers like TEMPO and BHT suggests that the reaction proceeds via a stable radical intermediate. When a known single electron quencher $CuCl_2$ was used, no formation of **3a** was observed which suggests that the reaction proceeds through a single electron pathway.

3. Synthesis of dihydrobenzofuran derived thiosulfonates and basic insights into the mechanism.



The exclusive formation of the product **5** confirms the formation of the aryl radical **A** and it also indicates that the formation of arylsulfonyl radical from DABSO and aryl diazonium salt occurs in two steps i.e. formation of aryl radical and capture of SO_2 by the aryl radical.



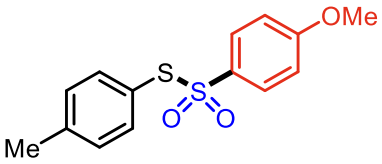
***S*-phenyl 4-methoxybenzenesulfonothioate (3a)**

Yellow oil, 0.63 RF in EtOAc:Heaxane (1:9), 47.1 mg, 84% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.42 (m, 3H), 7.40 – 7.30 (m, 4H), 6.89 – 6.81 (m, 2H), 3.86 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.7, 136.8, 135.1, 131.4, 130.0, 129.5, 128.4, 114.0, 55.84.

HRMS (ESI): $C_{13}H_{12}NaO_3S_2$ $[M+Na]^+$ calculated = 303.0120; found = 303.0122.



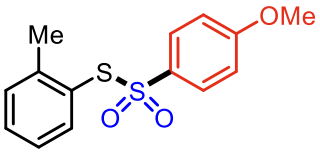
***S*-(*p*-tolyl) 4-methoxybenzenesulfonothioate (3b)**

Yellow oil, 0.53 RF in EtOAc:Heaxane (1:9), 50.0 mg, 85% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, J = 8.6 Hz, 2H), 7.16 (d, J = 7.7 Hz, 2H), 7.06 (d, J = 7.7 Hz, 2H), 6.79 (d, J = 8.6 Hz, 1H), 3.79 (s, 3H), 2.30 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.7, 142.1, 136.6, 135.2, 130.3, 130.0, 124.9, 113.9, 55.8, 21.6.

HRMS (ESI): $C_{14}H_{14}NaO_3S_2$ $[M+Na]^+$ calculated = 317.0277; found = 317.0274.



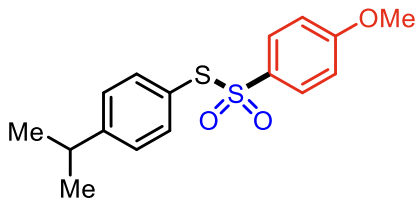
***S*-(*o*-tolyl) 4-methoxybenzenesulfonothioate (3c)**

Yellow oil, 0.55 RF in EtOAc:Heaxane (1:9), 51.2 mg, 87% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.44 (m, 2H), 7.36 – 7.30 (m, 2H), 7.23 (d, J = 7.5 Hz, 1H), 7.16 (dd, J = 7.5 Hz, 1H), 6.90 – 6.82 (m, 2H), 3.86 (s, 3H), 2.18 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.8, 144.3, 138.5, 135.5, 131.9, 131.1, 129.9, 127.6, 127.0, 114.0, 55.9, 20.8.

HRMS (ESI): $C_{14}H_{14}NaO_3S_2$ $[M+Na]^+$ calculated = 317.0277; found = 317.0281.



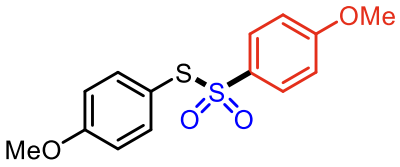
***S*-(4-isopropylphenyl) 4-methoxybenzenesulfonothioate (3d)**

Yellow oil, 0.65 RF in EtOAc:Heaxane (1:9), 53.5 mg, 87% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 2H), 7.31 – 7.23 (m, 2H), 7.19 (d, *J* = 8.2 Hz, 2H), 6.89 – 6.82 (m, 2H), 3.86 (s, 3H), 3.07 – 2.71 (m, 1H), 1.24 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.7, 152.9, 136.8, 135.1, 130.0, 127.7, 125.1, 113.9, 55.8, 34.1, 23.9.

HRMS (ESI): $C_{16}H_{18}NaO_3S_2$ $[M+Na]^+$ calculated = 345.0590; found = 345.0597.



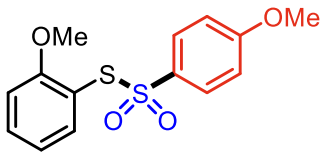
***S*-(4-methoxyphenyl) 4-methoxybenzenesulfonothioate (3e)**

White sticky semisolid, 0.2 RF in EtOAc:Heaxane (1:9), 51.5 mg, 83% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.9 Hz, 2H), 7.25 (d, *J* = 8.8 Hz, 2H), 6.85 (d, 8.8 Hz, 4H), 3.85 (s, 3H), 3.81 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6, 162.3, 138.4, 134.9, 130.0, 118.9, 115.0, 113.9, 55.8, 55.6.

HRMS (ESI): $C_{14}H_{14}NaO_4S_2$ $[M+Na]^+$ calculated = 333.0226; found = 333.0229.



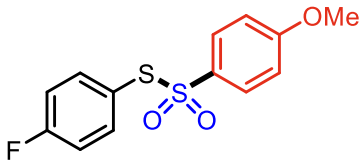
_S_-(2-methoxyphenyl) 4-methoxybenzenesulfonothioate (3f)

White sticky semisolid, 0.30 RF in EtOAc:Heaxane (1:9), 49.6 mg, 80% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 9.5, 2.3 Hz, 2H), 7.50 – 7.38 (m, 2H), 7.00 – 6.93 (m, 1H), 6.89 – 6.83 (m, 2H), 6.79 (d, *J* = 8.1 Hz, 1H), 3.85 (s, 3H), 3.50 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5, 160.3, 139.6, 136.3, 133.87, 130.0, 121.4, 115.8, 113.7, 111.4, 55.9, 55.6.

HRMS (ESI): $C_{14}H_{14}NaO_4S_2$ $[M+Na]^+$ calculated = 333.0226; found = 333.0231.



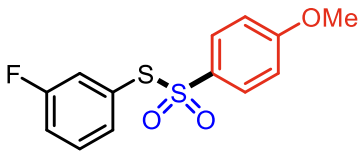
_S_-(4-fluorophenyl) 4-methoxybenzenesulfonothioate (3g)

Yellow oil, 0.52 RF in EtOAc:Heaxane (1:9), 48.3 mg, 81% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.46 (m, 2H), 7.39 – 7.31 (m, 2H), 7.08 – 6.99 (m, 2H), 6.91 – 6.85 (m, 2H), 3.87 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.2 (d, *J*= 253.6 Hz), 163.9, 138.9 (d, *J* = 9.1 Hz), 134.8, 130.1, 123.8 (d, *J* = 3.1 Hz), 116.7 (d, *J* = 22.2 Hz), 114.1, 55.9.

HRMS (ESI): $C_{13}H_{11}FNaO_3S_2$ $[M+Na]^+$ calculated = 321.0026; found = 321.0033.



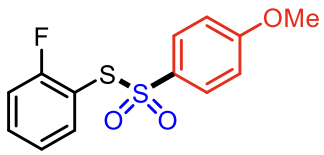
_S_-(3-fluorophenyl) 4-methoxybenzenesulfonothioate (3h)

Yellow oil, 0.55 RF in EtOAc:Heaxane (1:9), 46.5mg, 78% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.45 (m, 2H), 7.32 (td, *J* = 8.1, 5.8 Hz, 1H), 7.22 – 7.13 (m, 1H), 7.10 (ddd, *J* = 8.4, 2.3, 1.8 Hz, 1H), 6.96 – 6.78 (m, 2H), 3.87 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0, 162.4 (d, *J* = 250.9 Hz), 134.8, 132.4 (d, *J* = 3.3 Hz), 130.7 (d, *J* = 8.1 Hz), 130.0, 123.3 (d, *J* = 22.2 Hz), 118.6 (d, *J* = 21.0 Hz), 114.1, 55.9.

HRMS (ESI): $C_{13}H_{11}FNaO_3S_2$ $[M+Na]^+$ calculated = 321.0026; found = 321.0029.



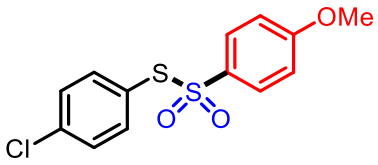
***S*-(2-fluorophenyl) 4-methoxybenzenesulfonothioate (3i)**

Brown oil, 0.50 RF in EtOAc:Heaxane (1:9), 47.7mg, 78% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.44 (m, 4H), 7.18 (td, *J* = 7.6, 1.1 Hz, 1H), 7.06 (dd, *J* = 12.4, 4.5 Hz, 1H), 6.92 – 6.83 (m, 2H), 3.87 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9 (s), 162.9 (d, *J* = 253.4 Hz), 139.1 (s), 135.3 (s), 134.1 (d, *J* = 8.3 Hz), 129.9 (s), 125.0 (d, *J* = 4.0 Hz), 116.4 (d, *J* = 22.7 Hz), 115.5 (d, *J* = 17.9 Hz), 114.0 (s), 55.9.

HRMS (ESI): $C_{13}H_{11}FNaO_3S_2$ $[M+Na]^+$ calculated = 321.0026; found = 321.0023.



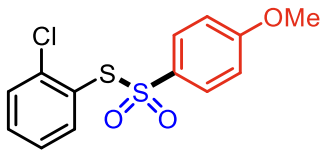
***S*-(4-chlorophenyl) 4-methoxybenzenesulfonothioate (3j)**

Colorless oil, 0.55 RF in EtOAc:Heaxane (1:9), 50.8 mg, 81% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.50 (m, 2H), 7.35 – 7.27 (m, 4H), 6.88 (dd, *J* = 12.1, 5.0 Hz, 2H), 3.87 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9, 138.3, 137.9, 134.9, 130.1, 129.8, 126.9, 114.1, 55.9.

HRMS (ESI): $C_{13}H_{11}NaO_3S_2$ $[M+Na]^+$ calculated = 336.9730; found = 336.9733.



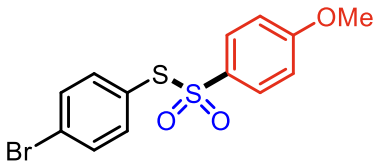
***S*-(2-chlorophenyl) 4-methoxybenzenesulfonothioate (3k)**

Colorless oil, 0.67 RF in EtOAc:Heaxane (1:9), 48.4 mg, 77% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.65 (m, 1H), 7.54 – 7.47 (m, 3H), 7.44 – 7.36 (m, 2H), 7.34 – 7.27 (m, 1H), 6.91 – 6.79 (m, 2H), 3.86 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1, 140.4, 139.7, 135.4, 132.9, 130.4, 130.0, 127.8, 127.5, 114.2, 55.9.

HRMS (ESI): $C_{13}H_{11}NaO_3S_2$ $[M+Na]^+$ calculated = 336.9730; found = 336.9729.



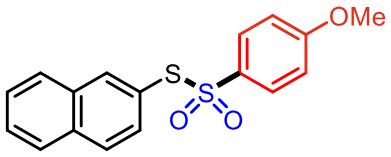
***S*-(4-bromophenyl) 4-methoxybenzenesulfonothioate (3l)**

Brown oil, 0.63 RF in EtOAc:Heaxane (1:9), 55.1 mg, 77% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.41 (m, 4H), 7.25 – 7.15 (m, 2H), 6.94 – 6.84 (m, 2H), 3.87 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9, 138.0, 134.9, 132.8, 130.1, 127.4, 126.7, 114.1, 55.9

HRMS (ESI): $C_{13}H_{11}BrNaO_3S_2$ $[M+Na]^+$ calculated = 380.9225; found = 380.9232.



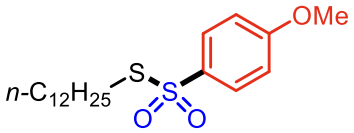
***S*-(naphthalen-2-yl) 4-methoxybenzenesulfonothioate (3m)**

Colorless oil, 0.54 RF in EtOAc:Heaxane (1:9), 48.8 mg, 74% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.85 (m, 2H), 7.81 – 7.76 (m, 2H), 7.62 – 7.51 (m, 2H), 7.51 – 7.44 (m, 2H), 7.40 (dd, J = 8.5, 1.8 Hz, 1H), 6.89 – 6.70 (m, 2H), 3.83 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.8, 137.7, 135.1, 134.2, 133.4, 132.1, 130.1, 129.2, 128.6, 128.3, 127.9, 127.0, 125.5, 114.0, 55.84.

HRMS (ESI): $C_{17}H_{14}NaO_3S_2$ $[M+Na]^+$ calculated = 353.0277; found = 353.0283.



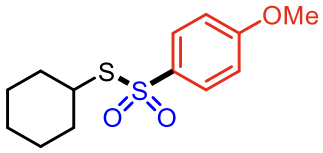
_S_-dodecyl 4-methoxybenzenesulfonothioate (3o)

Colorless oil, 0.66 RF in EtOAc:Heaxane (1:19), 64.9 mg, 87% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.83 (m, 2H), 7.01 – 6.96 (m, 2H), 3.88 (s, 3H), 2.96 (t, *J* = 7.4 Hz, 2H), 1.63 – 1.48 (m, 2H), 1.41 – 1.07 (m, 18H), 0.87 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.7, 136.8, 129.4, 114.4, 55.9, 36.1, 32.0, 29.7, 29.6, 29.4, 29.4, 29.0, 28.6, 28.6, 22.8, 14.2.

HRMS (ESI): $C_{19}H_{32}NaO_3S_2$ $[M+Na]^+$ calculated = 395.1685; found = 395.1692.



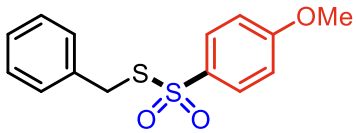
_S_-cyclohexyl 4-methoxybenzenesulfonothioate (3p)

Colorless oil, 0.50 RF in EtOAc:Heaxane (1:19), 50.9 mg, 89% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.74 (m, 2H), 7.08 – 6.87 (m, 2H), 3.88 (s, 3H), 3.38 – 3.24 (m, 2H), 2.01 – 1.80 (m, 2H), 1.66 – 1.62 (m, 2H), 1.57 – 1.18 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6, 137.5, 129.3, 114.5, 55.9, 50.3, 33.5, 25.8, 25.3.

HRMS (ESI): $C_{13}H_{18}NaO_3S_2$ $[M+Na]^+$ calculated = 309.0590; found = 309.0593.



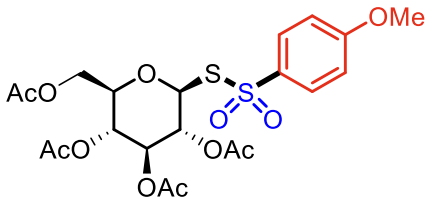
_S_-benzyl 4-methoxybenzenesulfonothioate (3q)

Colorless oil, 0.45 RF in EtOAc:Heaxane (1:19), 41.7 mg, 71% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.73 (m, 2H), 7.28 – 7.15 (m, 5H), 6.97 – 6.88 (m, 2H), 4.25 (s, 2H), 3.88 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.7, 136.7, 133.9, 129.4, 129.2, 128.9, 128.1, 114.345, 55.9, 40.47.

HRMS (ESI): $C_{14}H_{14}NaO_3S_2$ $[M+Na]^+$ calculated = 317.0277; found = 317.0270.



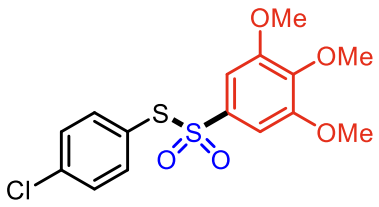
(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(((4-methoxyphenyl)sulfonyl)thio) tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3r)

White sticky semisolid, 0.42 RF in EtOAc:Heaxane (1:2), 43.8 mg (reaction performed at 0.1 mmol scale of the thiol), 82% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.84 (m, 2H), 7.02 – 6.93 (m, 2H), 5.30 – 5.20 (m, 2H), 5.03 (dd, *J* = 19.5, 10.1 Hz, 2H), 4.12 (dd, *J* = 12.5, 4.4 Hz, 1H), 3.97 (dd, *J* = 12.5, 2.4 Hz, 1H), 3.89 (s, 3H), 3.77 – 3.69 (m, 1H), 2.05 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H), 1.99 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 169.9, 169.4, 164.0, 164.1, 137.6, 129.6, 114.4, 86.7, 76.5, 73.6, 68.9, 68.0, 61.7, 56.0, 20.8, 20.7.

HRMS (ESI): $C_{21}H_{26}NaO_{12}S_2$ $[M+Na]^+$ calculated = 557.0758; found = 557.0757.



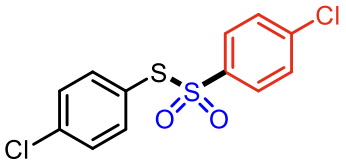
***S*-(4-chlorophenyl) 3,4,5 trimethoxybenzenesulfonothioate (3s)**

White semisolid, 0.45 RF in EtOAc:Heaxane (1:4), 64.3 mg, 86% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 3.8 Hz, 4H), 6.72 (d, *J* = 4.1 Hz, 2H), 3.91 – 3.86 (s, 3H), 3.74 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.0, 142.6, 138.4, 138.0, 137.2, 129.8, 126.9, 104.9, 77.5, 77.2, 76.8, 61.2, 56.4, 31.0.

HRMS (ESI): $C_{15}H_{15}ClNaO_5S_2$ $[M+Na]^+$ calculated = 396.9942; found = 396.9937.



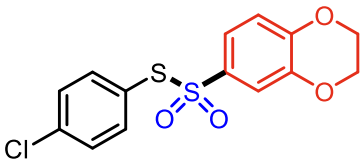
***S*-(4-chlorophenyl) 4-chlorobenzenesulfonothioate (3t)**

Yellow oil, 0.34 RF in EtOAc:Heaxane (1:9), 49.5 mg, 78% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.48 (m, 2H), 7.47 – 7.40 (m, 2H), 7.38 – 7.29 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4, 140.7, 138.7, 137.8, 130.1, 129.4, 129.1, 126.2.

HRMS (ESI): $C_{12}H_8Cl_2NaO_3S_2$ $[M+Na]^+$ calculated = 340.9235; found = 340.9241.



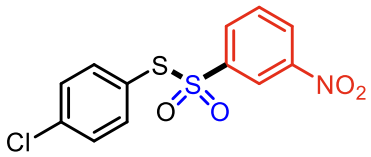
***S*-(4-chlorophenyl) 2,3-dihydrobenzo[*b*][1,4]dioxine-6-sulfonothioate (3u)**

White semisolid, 0.4 RF in EtOAc:Heaxane (1:4), 59.5 mg, 87% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (s, 4H), 7.16 (d, J = 2.3 Hz, 1H), 7.03 (dd, J = 8.6, 2.3 Hz, 1H), 6.87 – 6.84 (m, 1H), 4.36 – 4.25 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.5, 143.5, 138.3, 137.9, 129.8, 126.8, 121.7, 117.5, 117.3, 64.8, 64.2.

HRMS (ESI): $C_{14}H_{11}ClNaO_4S_2$ $[M+Na]^+$ calculated = 364.9679; found = 364.9684.



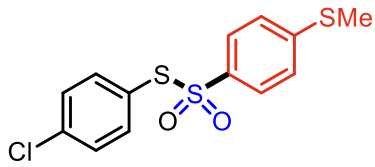
***S*-(4-chlorophenyl) 3-nitrobenzenesulfonothioate (3v)**

Greenish yellow oil, 0.5 RF in EtOAc:Heaxane (1:9), 36.8 mg, 87% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (ddd, J = 8.2, 2.2, 1.0 Hz, 1H), 8.44 (t, J = 1.9 Hz, 1H), 7.95 – 7.85 (m, 1H), 7.70 (dd, J = 16.2, 8.2 Hz, 1H), 7.46 – 7.32 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 139.3, 137.8, 132.8, 130.5, 130.4, 128.3, 125.5, 122.9.

HRMS (ESI): $C_{13}H_{11}NaO_3S_2$ $[M+Na]^+$ calculated = 336.9733; found = 336.9730.



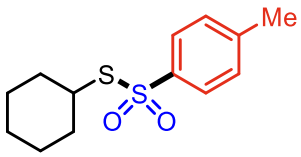
***S*-(4-chlorophenyl) 4-(methylthio)benzenesulfonothioate (3w)**

Colorless oil, 0.55 RF in EtOAc:Heaxane (1:9), 47.5 mg, 72% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.42 (m, 2H), 7.37 – 7.28 (m, 4H), 7.24 – 7.18 (m, 2H), 2.52 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.9, 138.8, 138.4, 137.9, 129.9, 127.9, 126.6, 124.9.

HRMS (ESI): $C_{13}H_{11}ClNaO_2S_3$ $[M+Na]^+$ calculated = 352.9502; found = 352.9509.



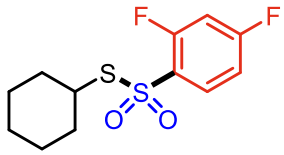
***S*-cyclohexyl 4-methylbenzenesulfonothioate (3x)**

Colorless oil, 0.45 RF in EtOAc:Heaxane (1:19), 43.8 mg, 81% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.77 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 3.41 – 3.28 (m, 1H), 2.44 (s, 3H), 1.98 – 1.85 (m, 3H), 1.71 – 1.57 (m, 2H), 1.55 – 1.19 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.6, 143.0, 129.9, 127.0, 50.4, 33.5, 25.8, 25.3, 21.8.

HRMS (ESI): $C_{13}H_{18}NaO_2S_2$ $[M+Na]^+$ calculated = 293.0640; found = 293.0643.

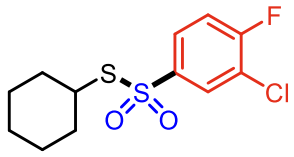


***S*-cyclohexyl 2,4-difluorobenzenesulfonothioate (3y)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.92 (m, 1H), 7.10 – 6.91 (m, 2H), 3.62 – 3.36 (m, 1H), 1.97-1.94 (m, 2H), 1.78 – 1.11 (m, 8H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3 (dd, *J* = 259.0, 11.4 Hz), 159.8 (d, *J* = 261.4 Hz), 131.1 (d, *J* = 10.6 Hz), 130.5 (dd, *J* = 14.1, 4.0 Hz), 111.9 (dd, *J* = 22.1, 3.9 Hz), 106.3 (t, *J* = 25.4 Hz). 51.4, 33.7, 25.8, 25.2.

HRMS (ESI): $C_{12}H_{14}F_2NaO_2S_2$ $[M+Na]^+$ calculated = 315.0295; found = 315.0295.



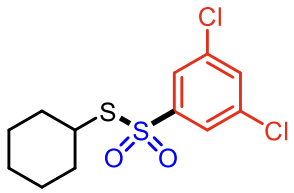
_S_-cyclohexyl 3-chloro-4-fluorobenzenesulfonothioate (3z)

Colorless oil, 0.40 RF in EtOAc:Heaxane (1:19), 47.4 mg, 77% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.93 (m, 1H), 7.89 – 7.76 (m, 1H), 7.39 – 7.27 (m, 1H), 3.42 – 3.29 (m, 1H), 1.99 – 1.83 (m, 2H), 1.77 – 1.17 (m, 8H).

^{13}C NMR (101 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0 (d, J = 258.6 Hz), 142.7 (d, J = 3.9 Hz), 129.9 (s), 127.4 (d, J = 8.7 Hz), 122.7 (d, J = 18.9 Hz), 117.6 (d, J = 22.5 Hz), 51.0, 33.5, 25.7, 25.2.

HRMS (ESI): $C_{12}H_{14}ClFNaO_2S_2$ $[M+Na]^+$ calculated = 331.0000; found = 331.0011.



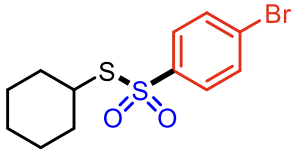
_S_-cyclohexyl 3,5-dichlorobenzenesulfonothioate (3aa)

Colorless oil, 0.43 RF in EtOAc:Heaxane (1:19), 53.1 mg, 82% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 1.7 Hz, 2H), 7.58 (t, J = 1.7 Hz, 1H), 3.41 (ddd, J = 13.6, 9.7, 3.7 Hz, 1H), 2.10 – 1.82 (m, 2H), 1.79 – 1.14 (m, 8H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.3, 136.3, 133.5, 125.2, 51.3, 33.5, 25.7, 25.2.

HRMS (ESI): $C_{12}H_{14}Cl_2NaO_2S_2$ $[M+Na]^+$ calculated = 346.9704; found = 346.9699.



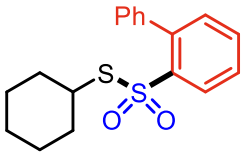
_S_-cyclohexyl 4-bromobenzenesulfonothioate (3ab)

Yellow oil, 0.45 RF in EtOAc:Heaxane (1:19), 53.4 mg, 80% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.74 (m, 2H), 7.73 – 7.64 (m, 2H), 3.56 – 3.05 (m, 1H), 2.02 – 1.83 (m, 2H), 1.82 – 1.03 (m, 8H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 132.6, 128.7, 128.4, 50.8, 33.5, 25.7, 25.2.

HRMS (ESI): $C_{12}H_{15}BrNaO_2S_2$ $[M+Na]^+$ calculated = 356.9589; found = 356.9582.



***S*-cyclohexyl [1,1'-biphenyl]-2-sulfonothioate (3ac)**

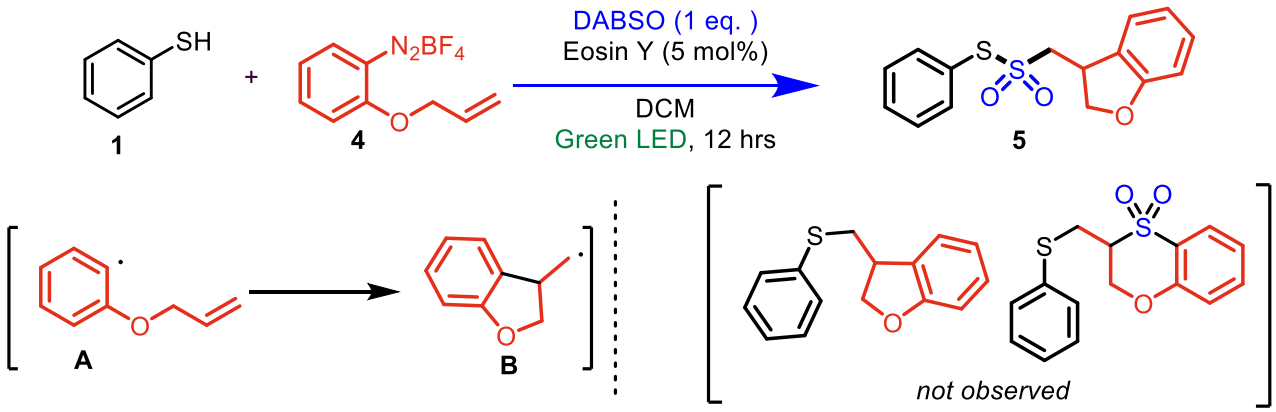
Yellow oil, 0.40 RF in EtOAc:Heaxane (1:19), 35.9 mg, 54% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.66 – 7.60 (m, 1H), 7.52 (td, *J* = 7.8, 1.4 Hz, 1H), 7.47 – 7.39 (m, 5H), 7.36 (dd, *J* = 7.5, 1.3 Hz, 1H), 3.25 – 2.93 (m, 1H), 1.75 (ddd, *J* = 21.9, 13.5, 8.9 Hz, 2H), 1.65 – 1.06 (m, 8H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.1, 141.5, 138.6, 133.4, 133.1, 130.2, 128.4, 128.1, 127.7, 127.6, 50.9, 33.5, 25.8, 25.2.

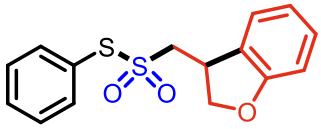
HRMS (ESI): $C_{18}H_{20}NaO_2S_2$ $[M+Na]^+$ calculated = 355.0797; found = 355.0802.

4. Synthesis of dihydrobenzofuran derived thiosulfonates and basic insights into the mechanism.



In a reaction vial equipped with magnetic stirring bar, was added thiol **1a** (22 mg, 0,2 mmol), aryldiazonium salt **4a (**74.4 mg, 0.3 mmol), DABSO (48 mg, 0.2 mmol, 1.0 equiv.) and Eosin Y (6.5 mg, 5.0 mol%) followed by DCM (2 mL). The reaction was then irradiated by green LED for 8 hrs. The reaction mass was then diluted with sat. $NaHCO_3$ solution (5 mL) and extracted with DCM (3 x 5 mL). Organic layer was dried over Na_2SO_4, evaporated under reduced pressure

and chromatographed with EtOAc in Petroleum ether (1:19) to give 48.4 mg (79 %) of the desired product **5a**.



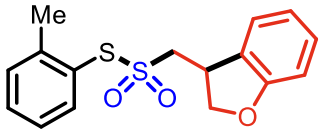
***S*-phenyl (*S*)-(2,3-dihydrobenzofuran-3-yl)methanesulfonothioate (5a)**

Colorless oil, 0.35 RF in EtOAc:Hexane (1:19), 48.4 mg, 79% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.2 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.4 Hz, 2H), 7.21 (t, *J* = 7.7 Hz, 1H), 7.13 (d, *J* = 7.4 Hz, 1H), 6.92 (t, *J* = 7.4 Hz, 1H), 6.84 (d, *J* = 8.1 Hz, 1H), 4.78 – 4.65 (m, 1H), 4.61 – 4.45 (m, 1H), 4.25 – 4.05 (m, 1H), 3.64 (dd, *J* = 14.0, 2.7 Hz, 1H), 3.42 (dt, *J* = 21.7, 10.8 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.9, 136.3, 132.0, 130.2, 129.7, 127.6, 126.4, 124.2, 121.1, 110.3, 75.8, 63.1, 37.8.

HRMS (ESI): $C_{15}H_{14}NaO_3S_2$ $[M+Na]^+$ calculated = 329.0277; found = 329.0282.



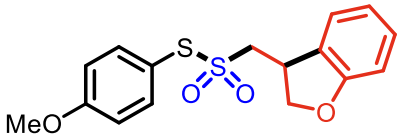
***S*-*o*-tolyl (*S*)-(2,3-dihydrobenzofuran-3-yl)methanesulfonothioate (5b)**

Colorless oil, 0.4 RF in EtOAc:Hexane (1:19), 50.6 mg, 79% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.7 Hz, 1H), 7.49 (td, *J* = 7.5, 1.1 Hz, 1H), 7.46 – 7.40 (m, 1H), 7.34 (dd, *J* = 11.0, 4.0 Hz, 1H), 7.21 (t, *J* = 7.7 Hz, 1H), 7.16 (d, *J* = 7.4 Hz, 1H), 6.97 – 6.90 (m, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 4.75 (dd, *J* = 21.6, 12.1 Hz, 1H), 4.60 – 4.48 (m, 1H), 4.18 (ddd, *J* = 10.9, 9.9, 2.6 Hz, 1H), 3.72 – 3.64 (m, 1H), 3.46 (dd, *J* = 13.9, 10.9 Hz, 1H), 2.64 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 160.0, 144.3, 137.7, 132.5, 131.9, 129.7, 127.5, 126.9, 126.4, 124.2, 121.1, 110.4, 75.9, 63.6, 37.6, 21.6.

HRMS (ESI): $C_{16}H_{16}NaO_3S_2$ $[M+Na]^+$ calculated = 343.0433; found = 343.0437.



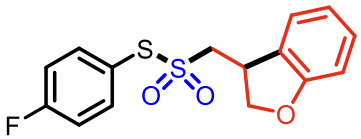
***S*-(4-methoxyphenyl) (*S*)-(2,3-dihydrobenzofuran-3-yl)methanesulfonothioate (5c)**

Colorless oil, 0.2 RF in EtOAc:Hexane (1:19), 56.5 mg, 84% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 – 7.58 (m, 1H), 7.25 – 7.17 (m, 1H), 7.14 (d, *J* = 7.4 Hz, 1H), 7.06 – 7.00 (m, 1H), 6.92 (td, *J* = 7.4, 0.6 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 4.72 (t, *J* = 9.2 Hz, 1H), 4.53 (dd, *J* = 9.8, 6.1 Hz, 1H), 4.16 (ddd, *J* = 10.6, 9.8, 2.5 Hz, 1H), 3.90 (s, 2H), 3.62 (dd, *J* = 14.0, 2.7 Hz, 1H), 3.48 – 3.33 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.7, 159.9, 138.1, 129.6, 126.5, 124.2, 121.1, 118.1, 115.7, 110.3, 75.8, 62.6, 55.7, 37.7.

HRMS (ESI): $C_{16}H_{16}NaO_4S_2$ $[M+Na]^+$ calculated = 359.0382; found = 359.0383.



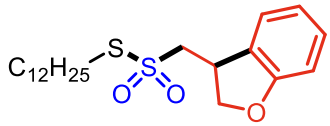
***S*-(4-fluorophenyl) (*S*)-(2,3-dihydrobenzofuran-3-yl)methanesulfonothioate (5d)**

Yellow oil, 0.54 RF in EtOAc:Hexane (1:19), 52.5 mg, 81% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 – 7.68 (m, 1H), 7.26 – 7.18 (m, 2H), 7.13 (d, *J* = 7.5 Hz, 1H), 6.92 (td, *J* = 7.5, 0.8 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 4.79 – 4.65 (m, 1H), 4.53 (dd, *J* = 9.8, 5.9 Hz, 1H), 4.25 – 4.07 (m, 1H), 3.62 (dd, *J* = 14.0, 2.8 Hz, 1H), 3.44 (dd, *J* = 14.0, 10.8 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.1 (d, *J* = 254.9 Hz), 159.9 (s), 138.6 (d, *J* = 9.1 Hz), 129.8 (s), 126.3 (s), 124.2 (s), 123.1 (d, *J* = 3.4 Hz), 121.2 (s), 117.6 (d, *J* = 22.4 Hz), 110.4 (s)., 75.7, 63.2, 37.7.

HRMS (ESI): $C_{15}H_{13}NaO_3FS_2$ $[M+Na]^+$ calculated = 347.0182; found = 347.0183.



***S*-dodecyl (*S*)-(2,3-dihydrobenzofuran-3-yl)methanesulfonothioate (5e)**

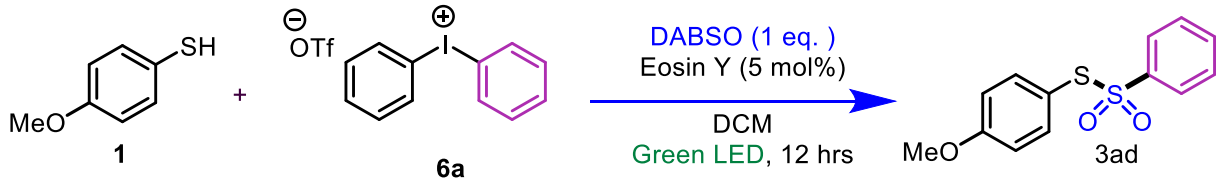
Colorless oil, 0.6 RF in EtOAc:Hexane (1:19), 65.3 mg, 82% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (t, *J* = 7.4 Hz, 2H), 6.91 (t, *J* = 7.4 Hz, 1H), 6.84 (d, *J* = 8.2 Hz, 1H), 4.76 (t, *J* = 9.2 Hz, 1H), 4.62 (dd, *J* = 9.6, 6.1 Hz, 1H), 4.25 – 4.04 (m, 1H), 3.69 (dd, *J* = 13.9, 2.5 Hz, 1H), 3.55 (dd, *J* = 13.8, 10.8 Hz, 1H), 3.18 (t, *J* = 7.4 Hz, 2H), 1.88 – 1.69 (m, 2H), 1.47 – 1.37 (m, 2H), 1.26 (br, 16H), 0.88 (t, *J* = 6.6 Hz, 2H).

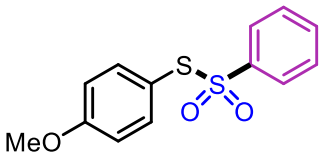
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9, 129.7, 126.6, 124.3, 121.1, 110.4, 75.9, 66.6, 37.9, 36.8, 32.0, 29.7, 29.7, 29.5, 29.5, 29.1, 28.7, 22.8, 14.3.

HRMS (ESI): $C_{21}H_{34}NaO_3S_2$ $[M+Na]^+$ calculated = 421.1842; found = 421.1844.

5. Three component coupling of thiols, iodinium salts and SO_2



In a reaction vial equipped with magnetic stirring bar, was added thiol **1a** (28 mg, 0.2 mmol), aryldiazonium salt **2a (**141.6 mg, 0.3 mmol), DABSO (48 mg, 0.2 mmol, 1.0 equiv.) and Eosin Y (6.5 mg, 5.0 mol %) followed by DCM (2 mL). The reaction was then irradiated by green LED for 8 hrs. The reaction mass was then diluted with sat. $NaHCO_3$ solution (5 mL) and extracted with DCM (3 x 5 mL). Organic layer was dried over Na_2SO_4, evaporated under reduced pressure and chromatographed with EtOAc in Petroleum ether (1:19) to give 26.3 mg, 47% yield of the desired product **3ad**.



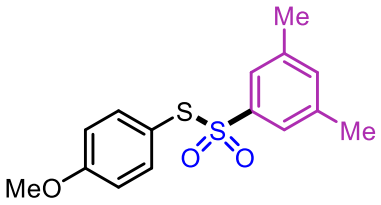
***S*-(4-methoxyphenyl) benzenesulfonothioate (3ad)**

Colorless oil, 0.4 RF in EtOAc:Hexane (1:19), 26.3 mg, 47% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 – 7.58 (m, 3H), 7.53 – 7.41 (m, 2H), 7.35 – 7.23 (m, 2H), 6.94 – 6.78 (m, 2H), 3.86 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.5, 143.1, 138.5, 133.6, 128.9, 127.7, 118.7, 115.1, 55.6.

HRMS (ESI): $C_{13}H_{12}NaO_3S_2$ $[M+Na]^+$ calculated = 303.0120; found = 303.0123.



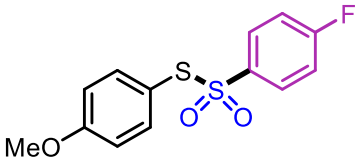
S-(4-methoxyphenyl) 3,5-dimethylbenzenesulfonothioate (3ae)

Colorless oil, 0.55 RF in EtOAc:Hexane (1:19), 34.5 mg, 56% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 2H), 7.19 (s, 1H), 7.15 (d, *J* = 0.5 Hz, 2H), 6.88 – 6.82 (m, 2H), 3.84 (s, 3H), 2.30 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4, 142.7, 139.0, 138.6, 135.3, 125.3, 119.0, 115.0, 55.6, 21.2.

HRMS (ESI): $C_{15}H_{16}NaO_3S_2$ $[M+Na]^+$ calculated = 331.0433; found = 331.0434.



S-(4-methoxyphenyl) 4-fluorobenzenesulfonothioate (3af)

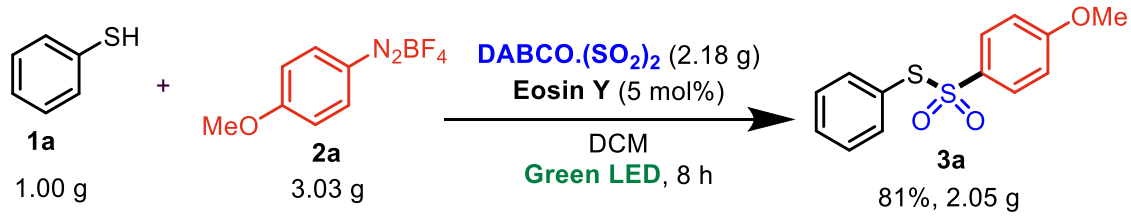
Colorless oil, 0.6 RF in EtOAc:Hexane (1:19), 20.3 mg, 34% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.55 (m, 2H), 7.31 – 7.22 (m, 2H), 7.10 (t, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.9 Hz, 2H), 3.84 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6 (d, *J* = 256.6 Hz), 162.6 (s), 139.2 (d, *J* = 3.1 Hz), 138.5 (s), 130.6 (d, *J* = 9.6 Hz), 118.5 (s), 116.2 (d, *J* = 22.8 Hz), 115.2 (s), 55.6 (s).

HRMS (ESI): $C_{13}H_{11}FNaO_3S_2$ $[M+Na]^+$ calculated = 321.0026; found = 321.0024.

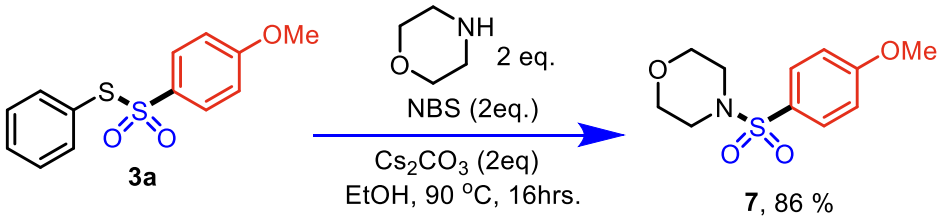
6. Gram scale synthesis



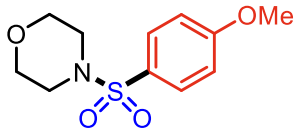
In a 250 mL round bottom flask equipped with magnetic stirring bar, was added thiol **1a** (1.0 g, 9.1 mmol), aryldiazonium salt **2a** (1.67 g, 13.7 mmol, 1.5 eq.), DABSO (2.18 g, 9.1 mmol, 1.0

equiv.) and Eosin Y (294.4 mg, 5.0 mol%) followed by DCM (90 mL). The reaction was then irradiated by green LED for 8 hrs. The reaction mass was then diluted with sat. $NaHCO_3$ solution (200 mL) and extracted with DCM (3 x 200 mL). Organic layer was dried over Na_2SO_4, evaporated under reduced pressure and chromatographed with EtOAc in Petroleum ether (1:19) to give 2.05g (81%) of the desired product.

7. Functionalizations of 3a



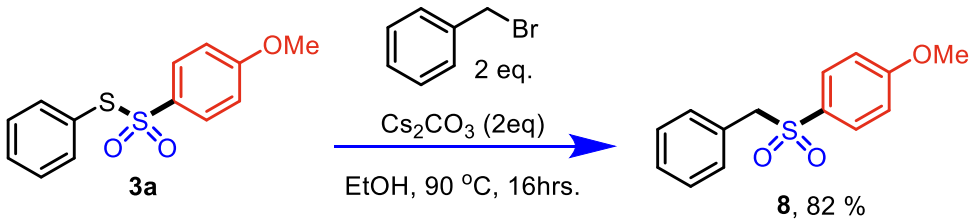
Compound synthesized as per the procedure reported by Jang and group, the spectral data were found be in accordance to the reported ones.[4]



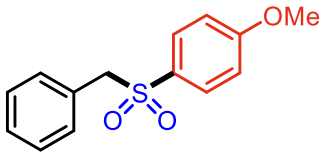
4-((4-methoxyphenyl)sulfonyl)morpholine (7)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.7 Hz, 1H), 6.99 (d, *J* = 8.7 Hz, 1H), 3.86 (s, 2H), 3.74 – 3.68 (m, 2H), 2.97 – 2.91 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3, 130.0, 126.6, 114.4, 66.1, 55.7, 46.1.



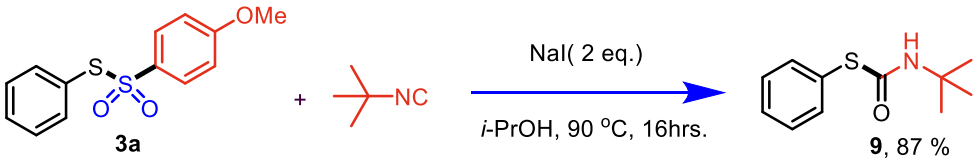
Compound synthesized as per the procedure reported by Jang and group, the spectral data were found be in accordance to the reported ones.[4]



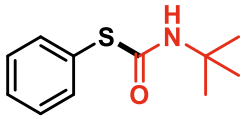
1-(benzylsulfonyl)-4-methoxybenzene (8)[3]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 24.8, 7.9 Hz, 2H), 7.37 – 7.20 (m, 3H), 7.11 (t, *J* = 17.1 Hz, 2H), 6.96 – 6.82 (m, 2H), 4.29 (s, 2H), 3.84 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.7, 130.8, 130.8, 129.4, 128.7, 128.5, 128.5, 114.1, 63.1, 55.7.



Compound synthesized as per the procedure reported by Maes and group, the spectral data were found be in accordance to the reported ones.[5]



S-phenyl tert-butylcarbamothioate (9)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 – 7.50 (m, 2H), 7.45 – 7.39 (m, 3H), 5.26 (bs, 1H), 1.35 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.1, 135.5, 129.4, 129.3, 129.2, 53.6, 28.9.

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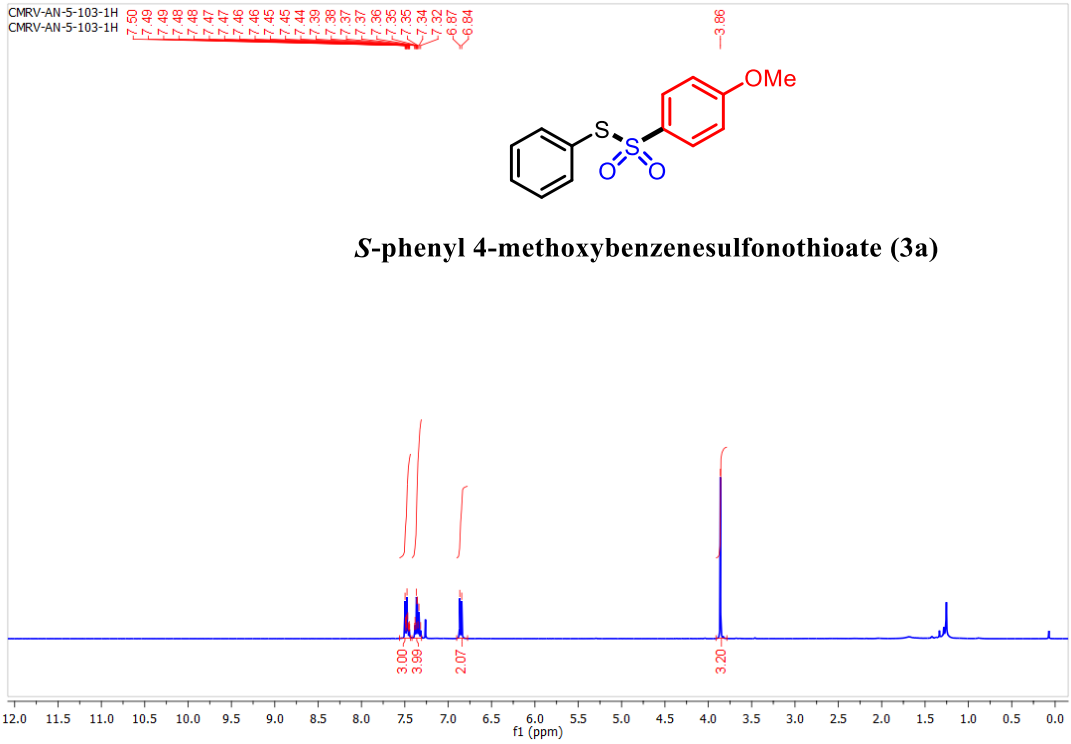
1) A. P. Colleville, R. A. J. Horan and N. C. O. Tomkinson, *Org. Process Res. Dev*. 2014, **18**, 1128.

2) S. V. Mileghem and W. M. De Borggraeve, *Org. Process Res. Dev*. 2017, **21**, 785.

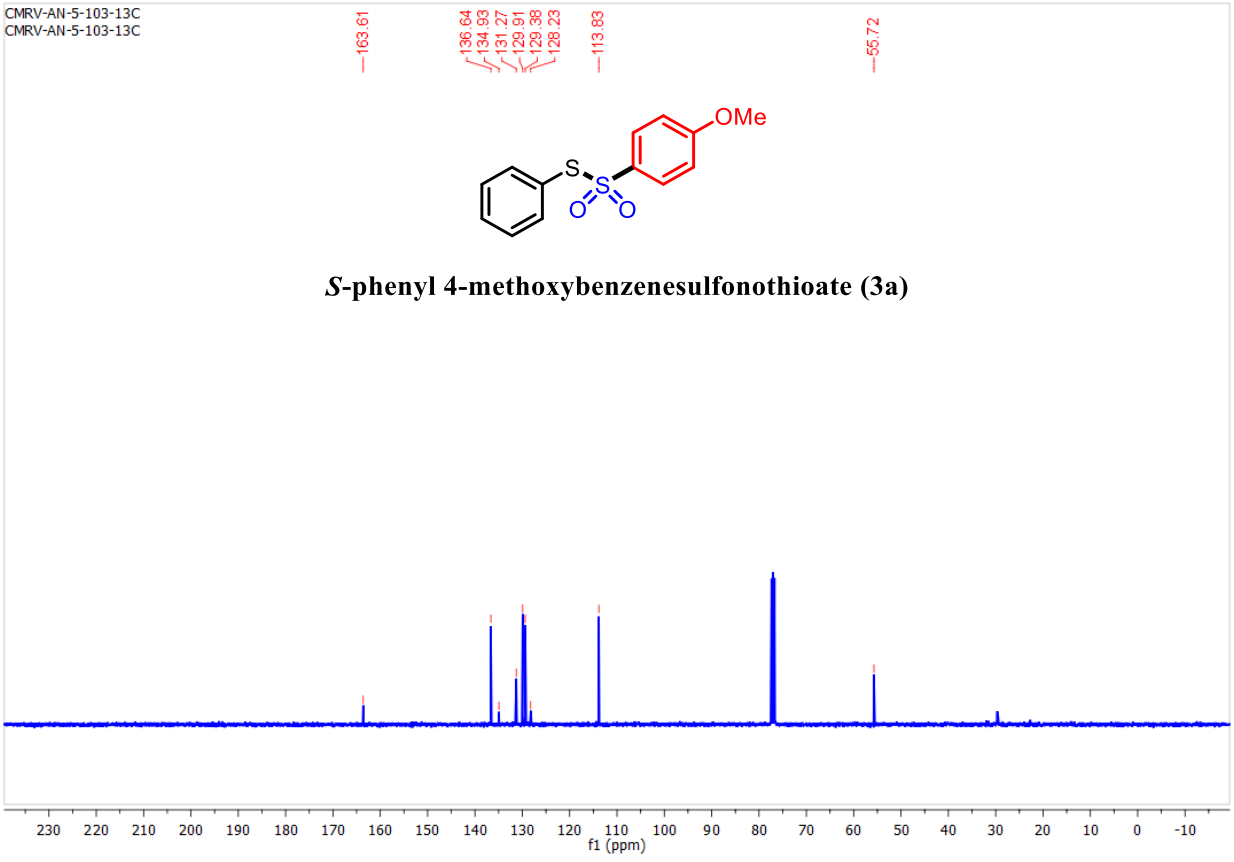
3) R. Cai, M. Lu, E. Y. Aguilera, Y. Xi, N. G. Akhmedov, J. L. Petersen, H. Chen, and X. Shi, *Angew. Chem. Int. Ed*. 2015, **54**, 8, 772.

4) P. K. Shyam and H.-Y. Jang, *J. Org. Chem*. 2017, **82**, 1761.

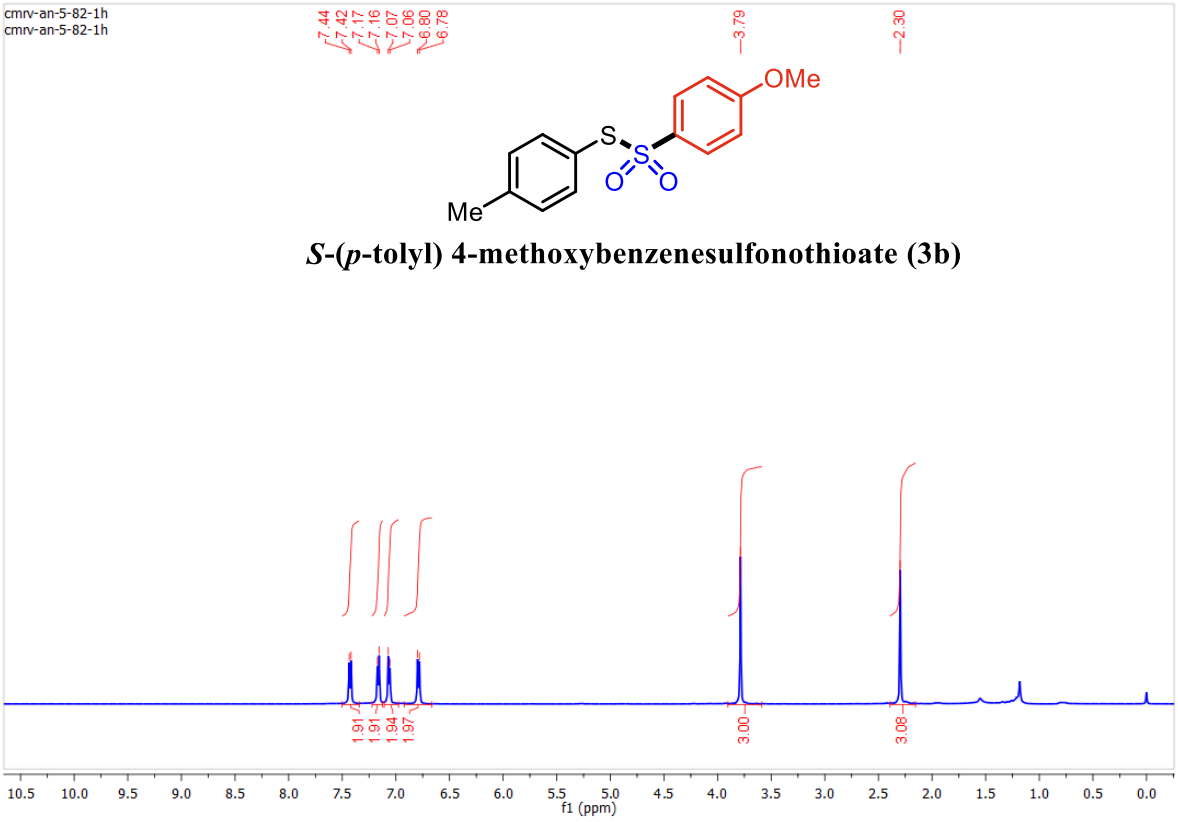
5) P. Mampuys, Y. Zhu, S. Sergeyev, E. Ruijter, R. V. A. Orru, S. V. Doorslaer, and B. U. W. Maes, *Org. Lett*. 2016, **18**, 2808.



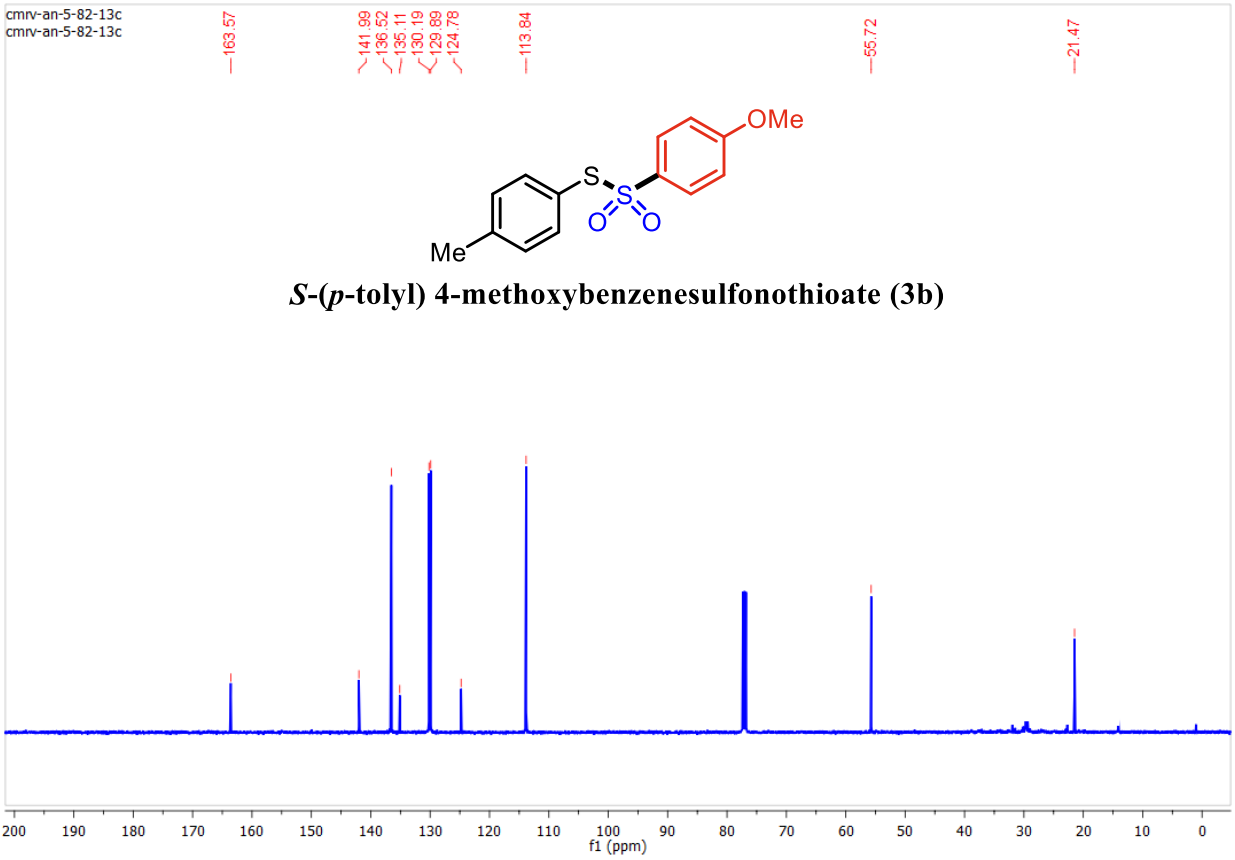
***S*-phenyl 4-methoxybenzenesulfonothioate (3a)**



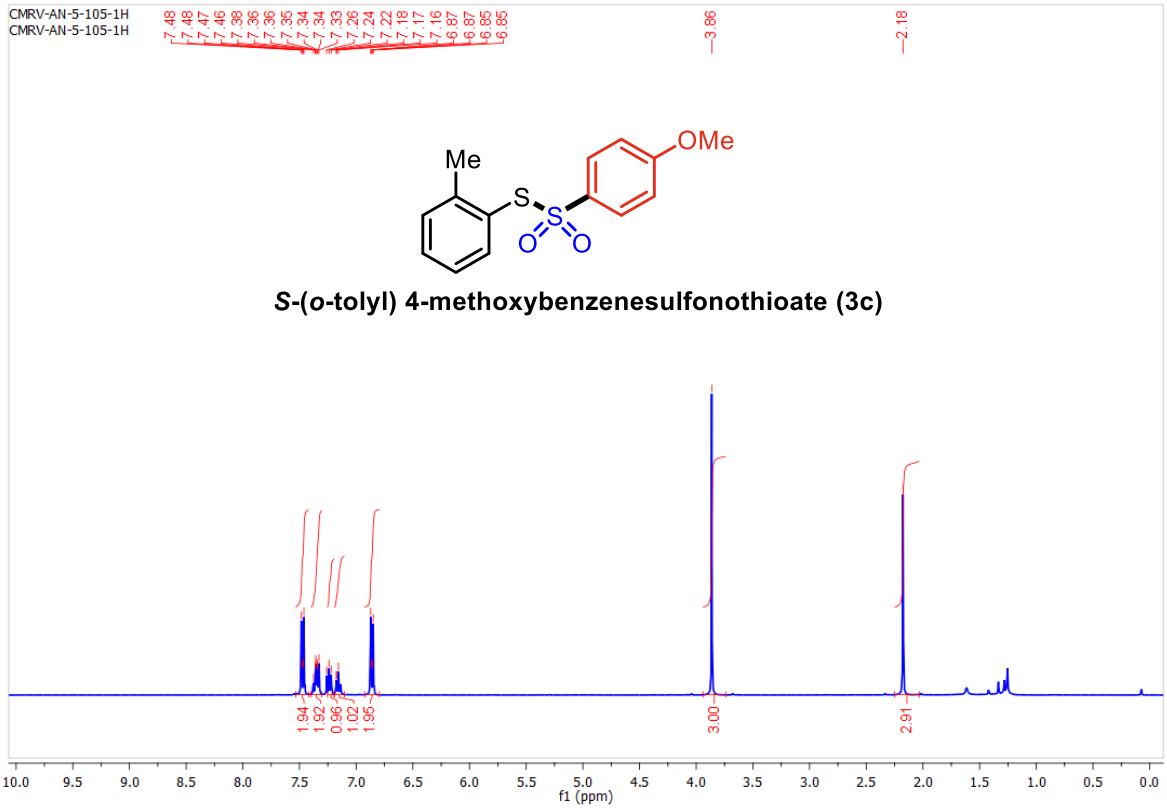
***S*-phenyl 4-methoxybenzenesulfonothioate (3a)**



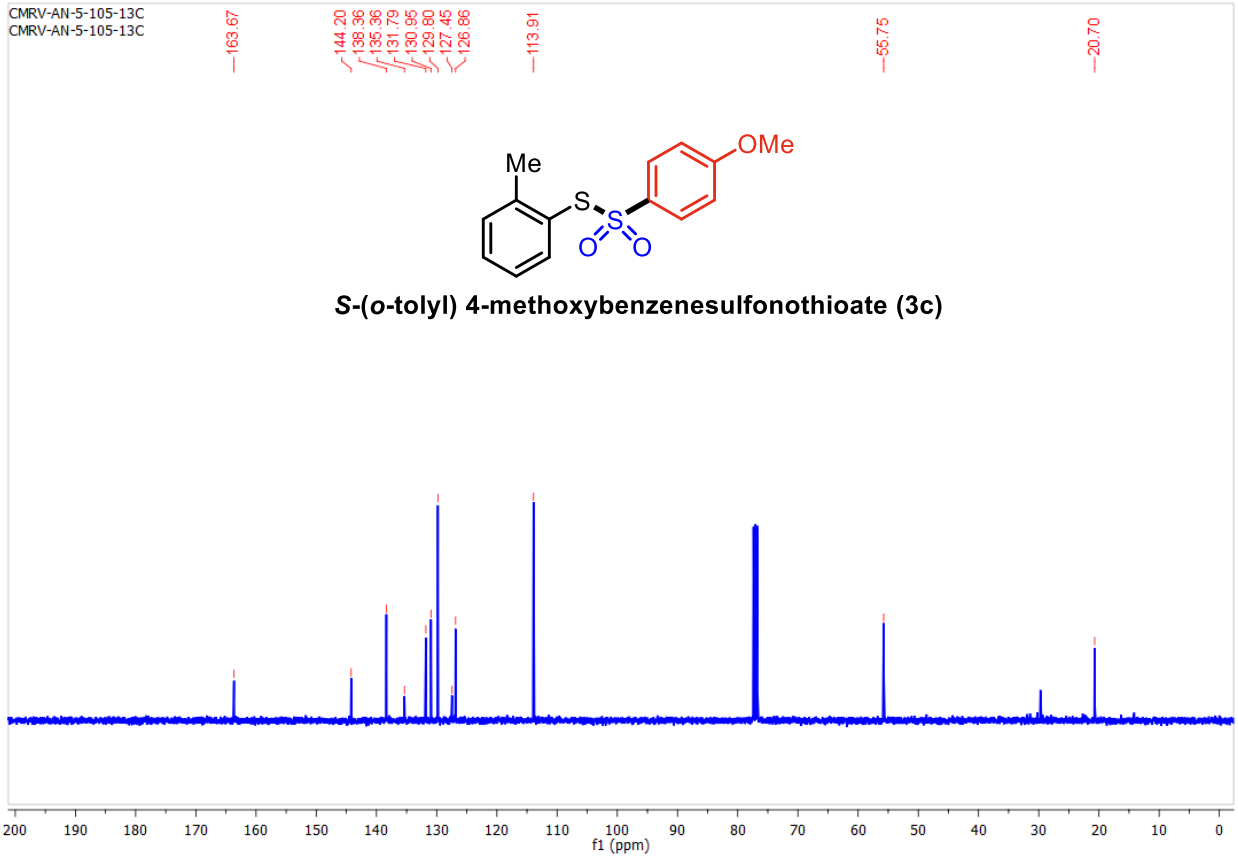
***S*-(*p*-tolyl) 4-methoxybenzenesulfonothioate (3b)**



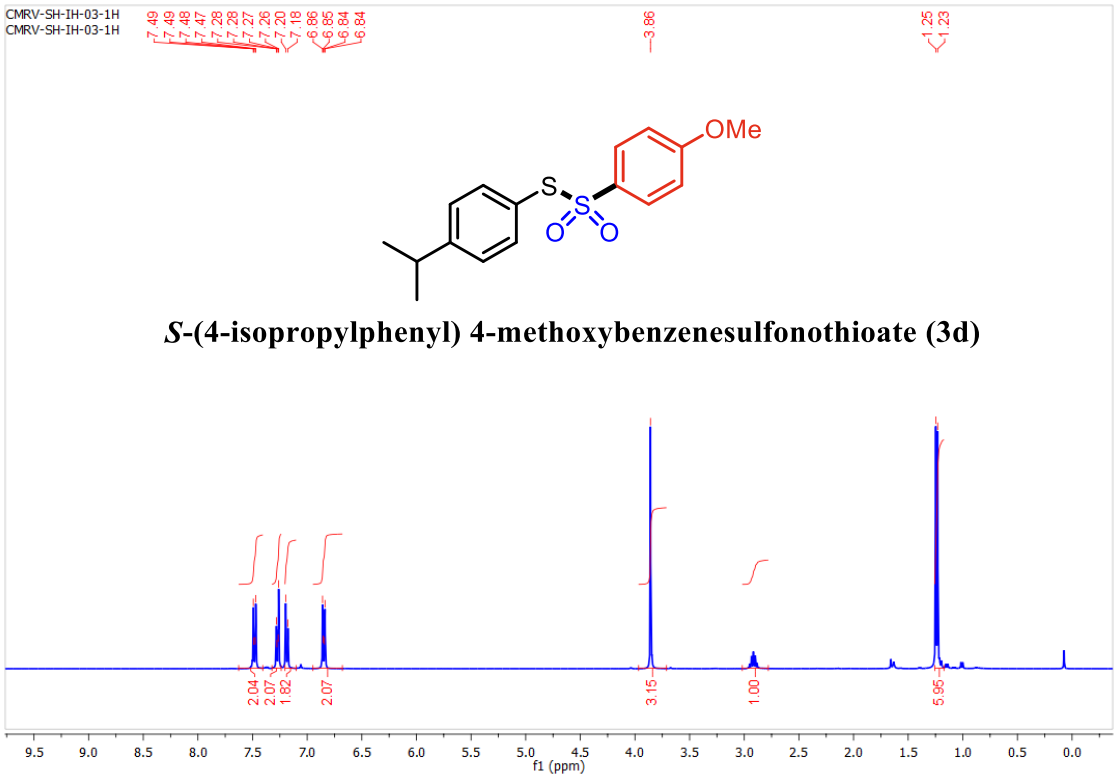
***S*-(*p*-tolyl) 4-methoxybenzenesulfonothioate (3b)**



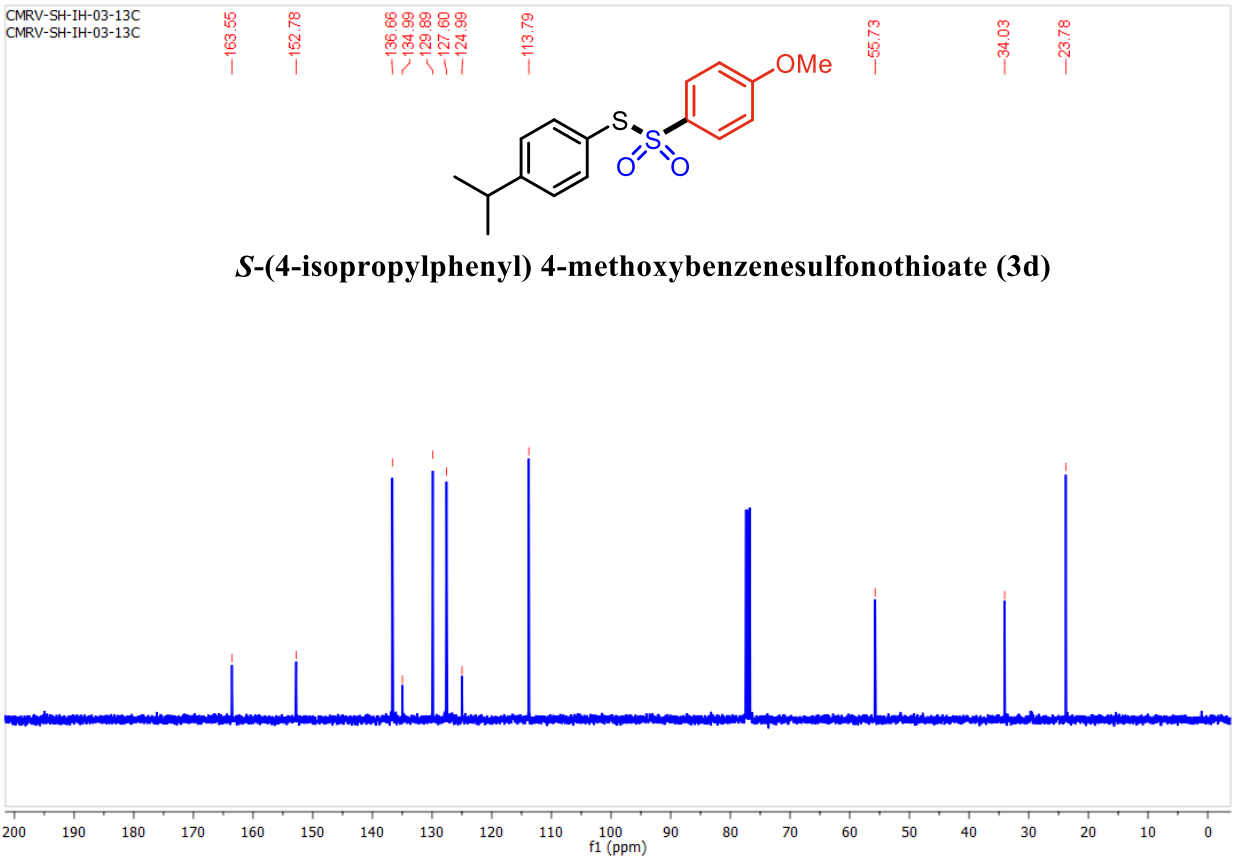
***S*-(*o*-tolyl) 4-methoxybenzenesulfonothioate (3c)**



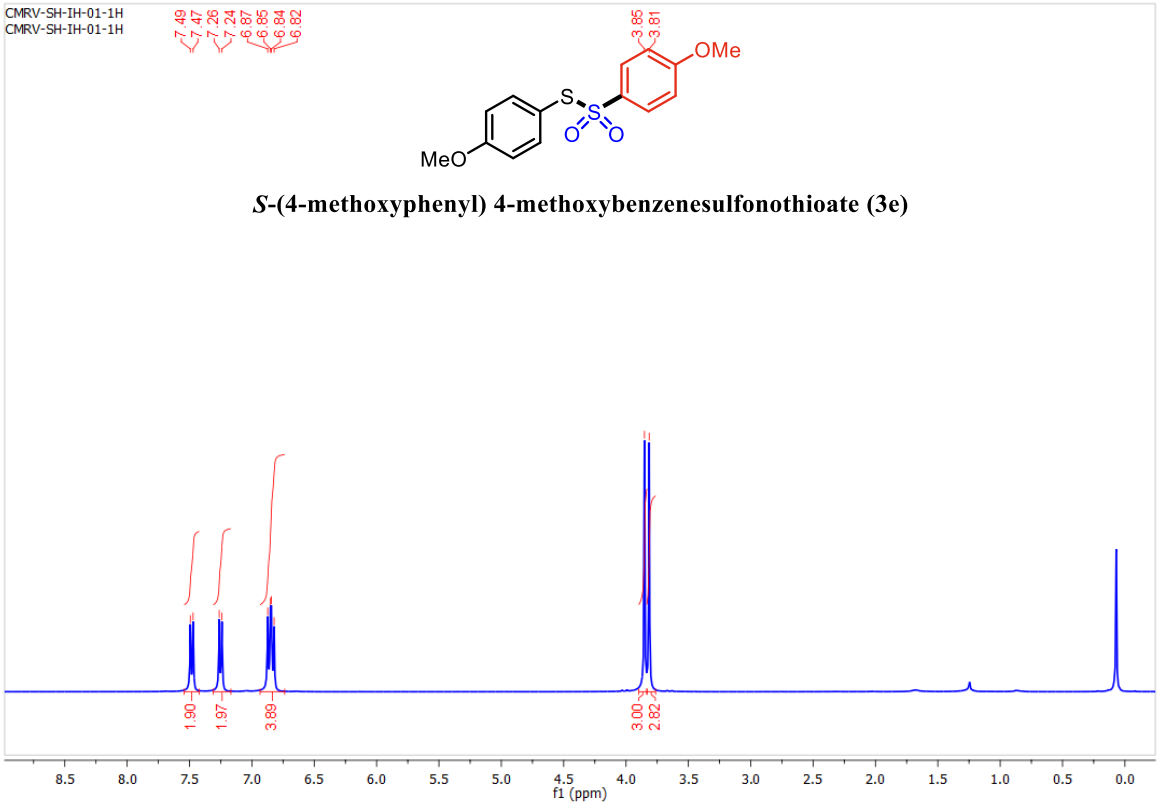
***S*-(*o*-tolyl) 4-methoxybenzenesulfonothioate (3c)**



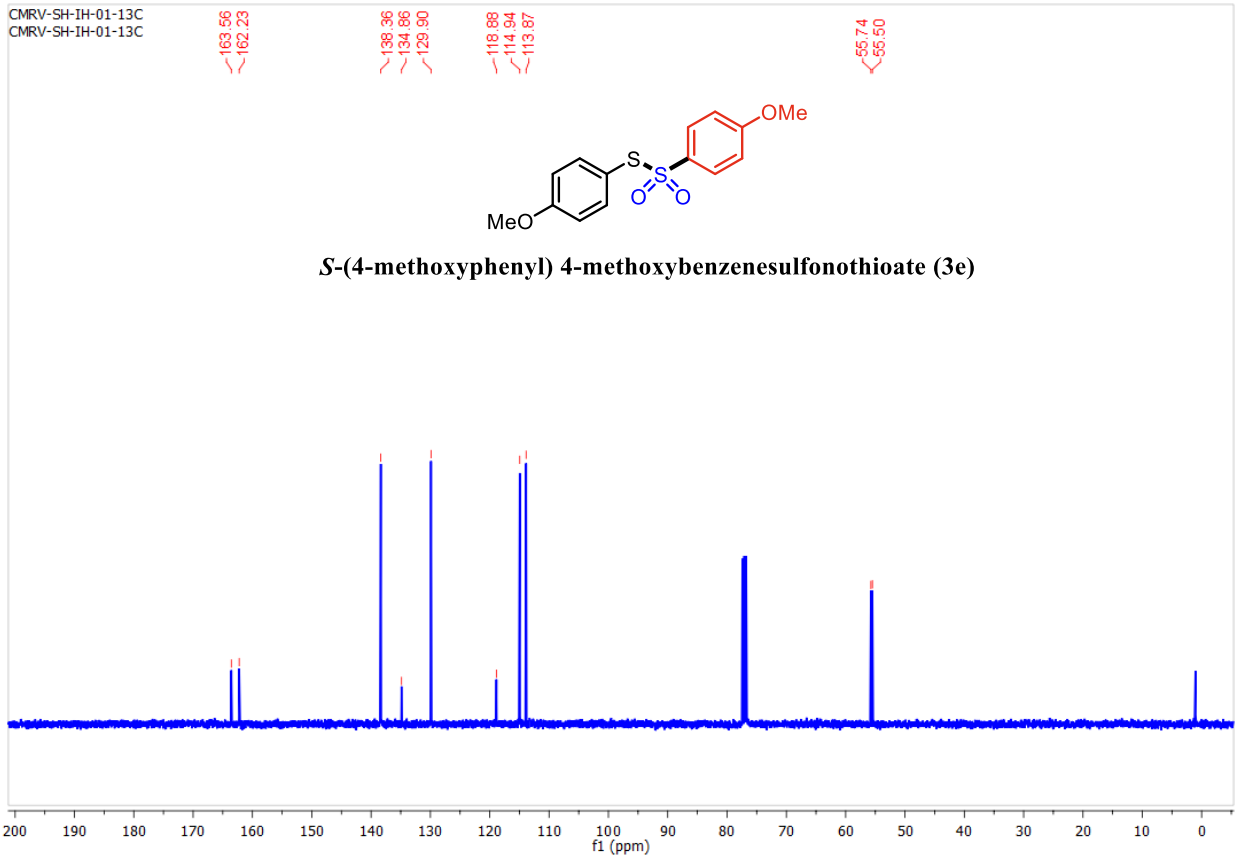
***S*-(4-isopropylphenyl) 4-methoxybenzenesulfonothioate (3d)**



***S*-(4-isopropylphenyl) 4-methoxybenzenesulfonothioate (3d)**



***S*-(4-methoxyphenyl) 4-methoxybenzenesulfonothioate (3e)**



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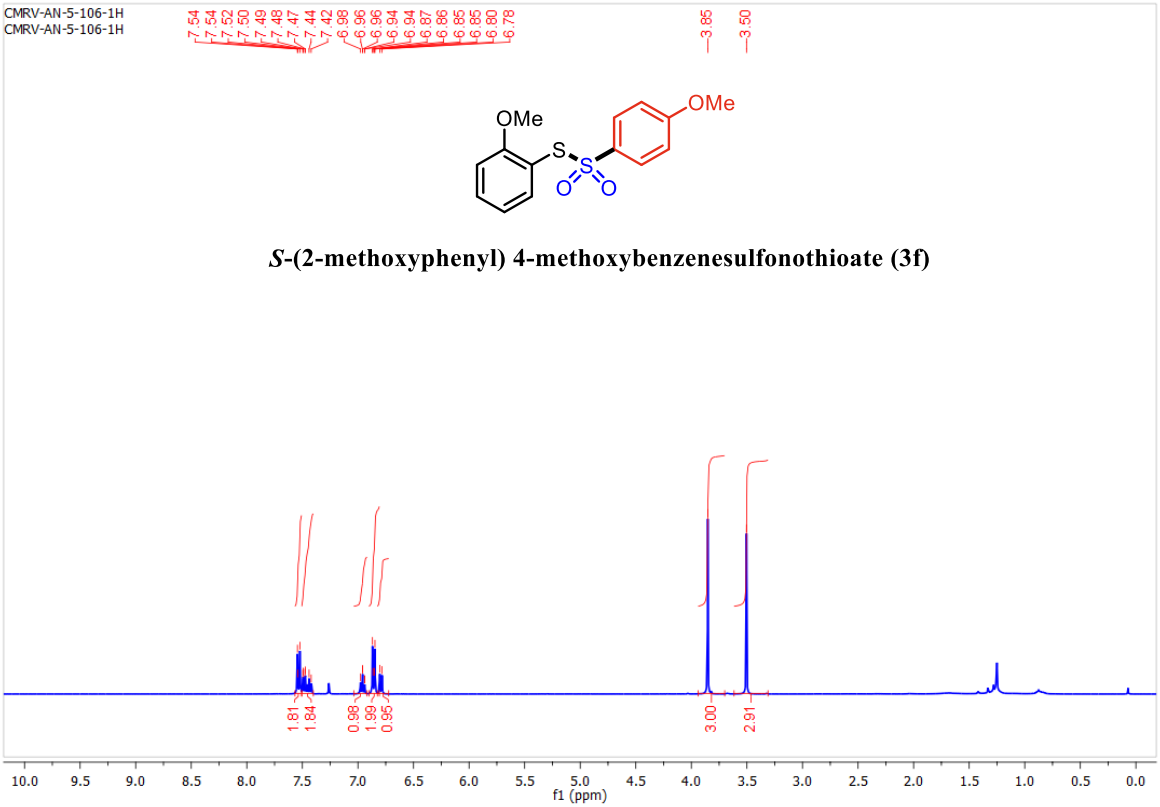
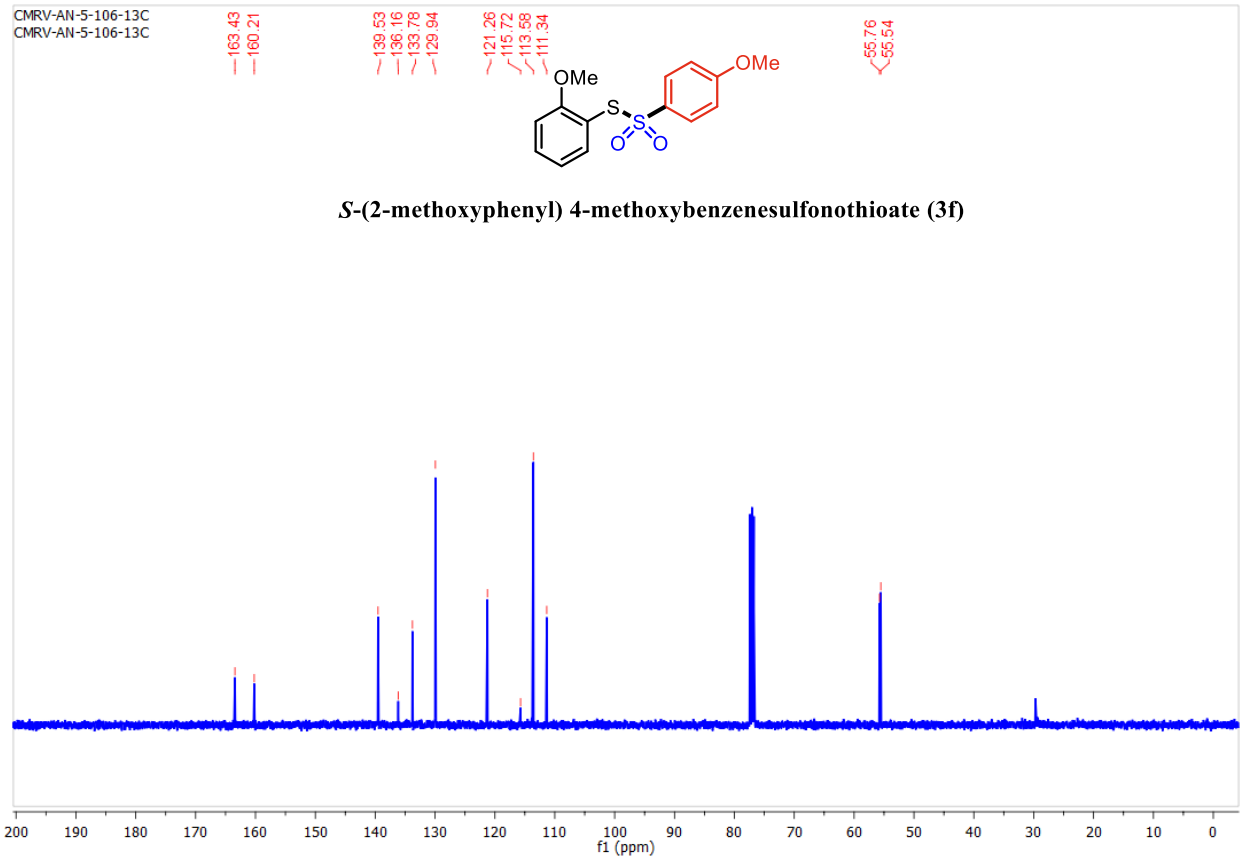
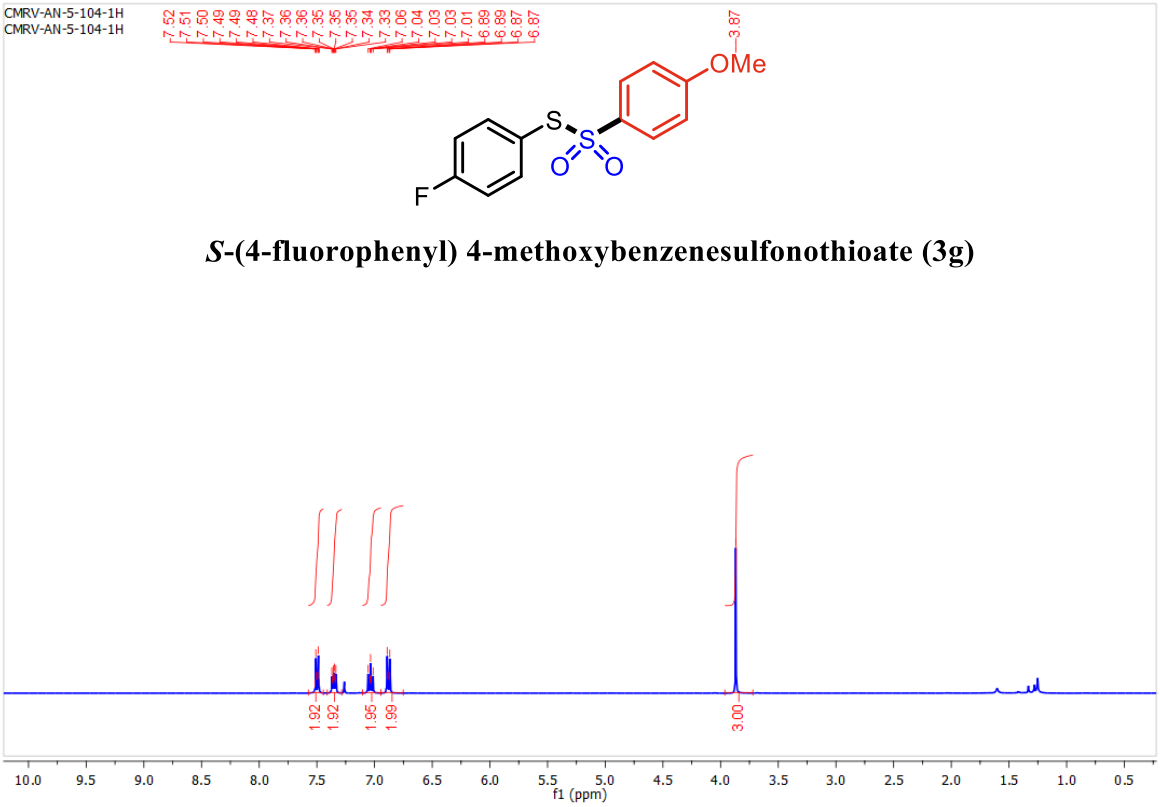


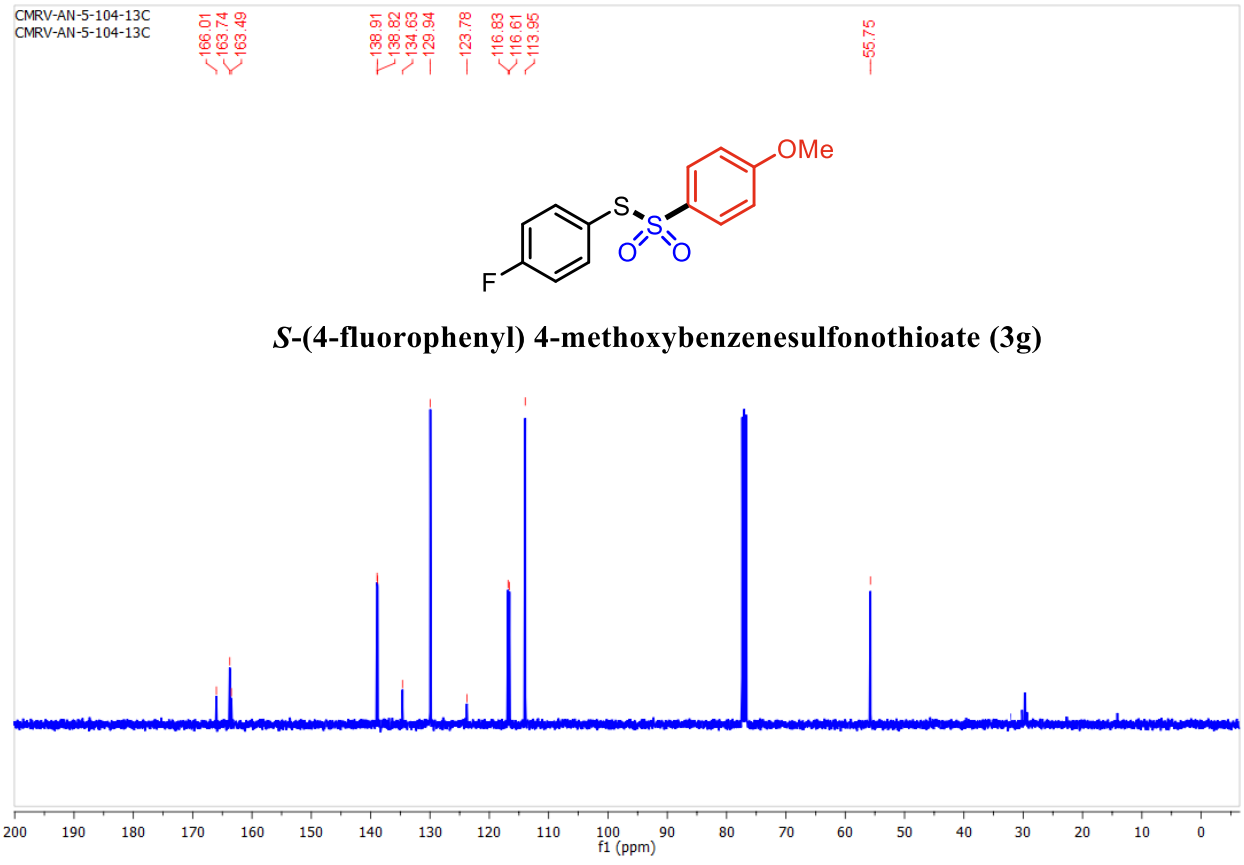
***S*-(2-methoxyphenyl) 4-methoxybenzenesulfonothioate (3f)**



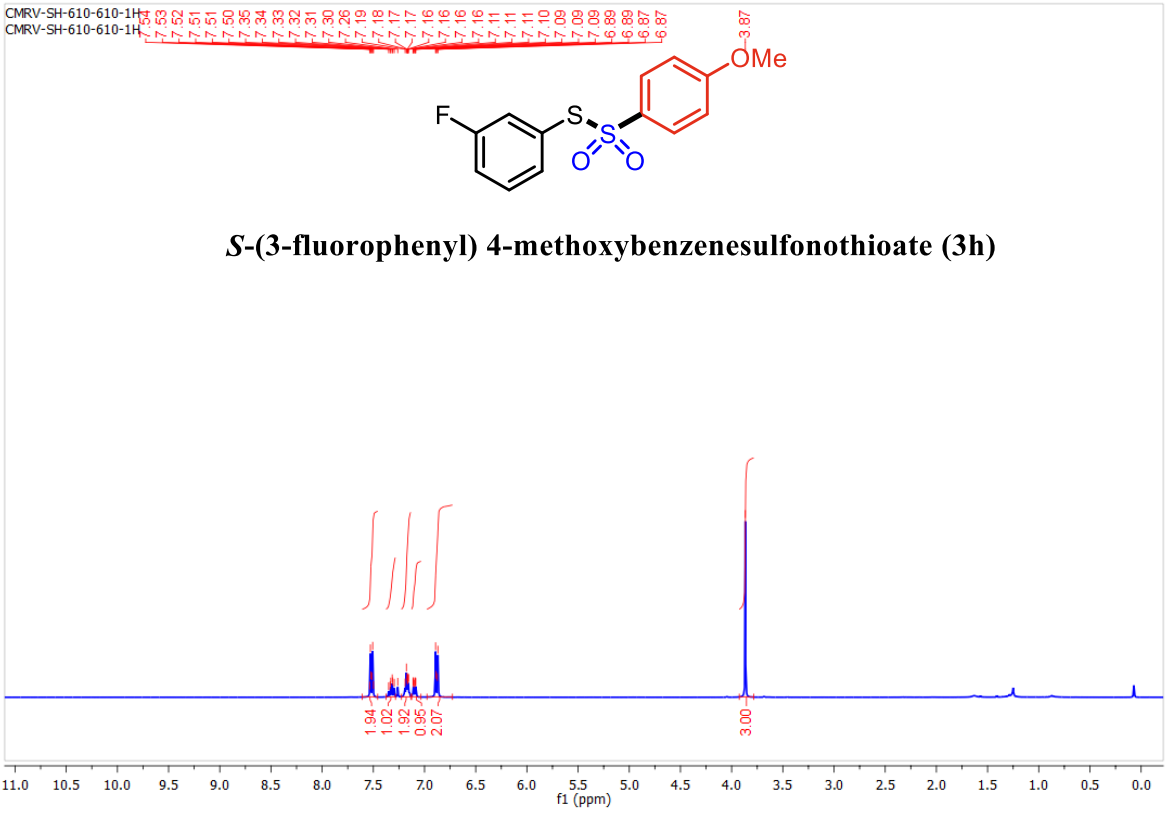
***S*-(2-methoxyphenyl) 4-methoxybenzenesulfonothioate (3f)**



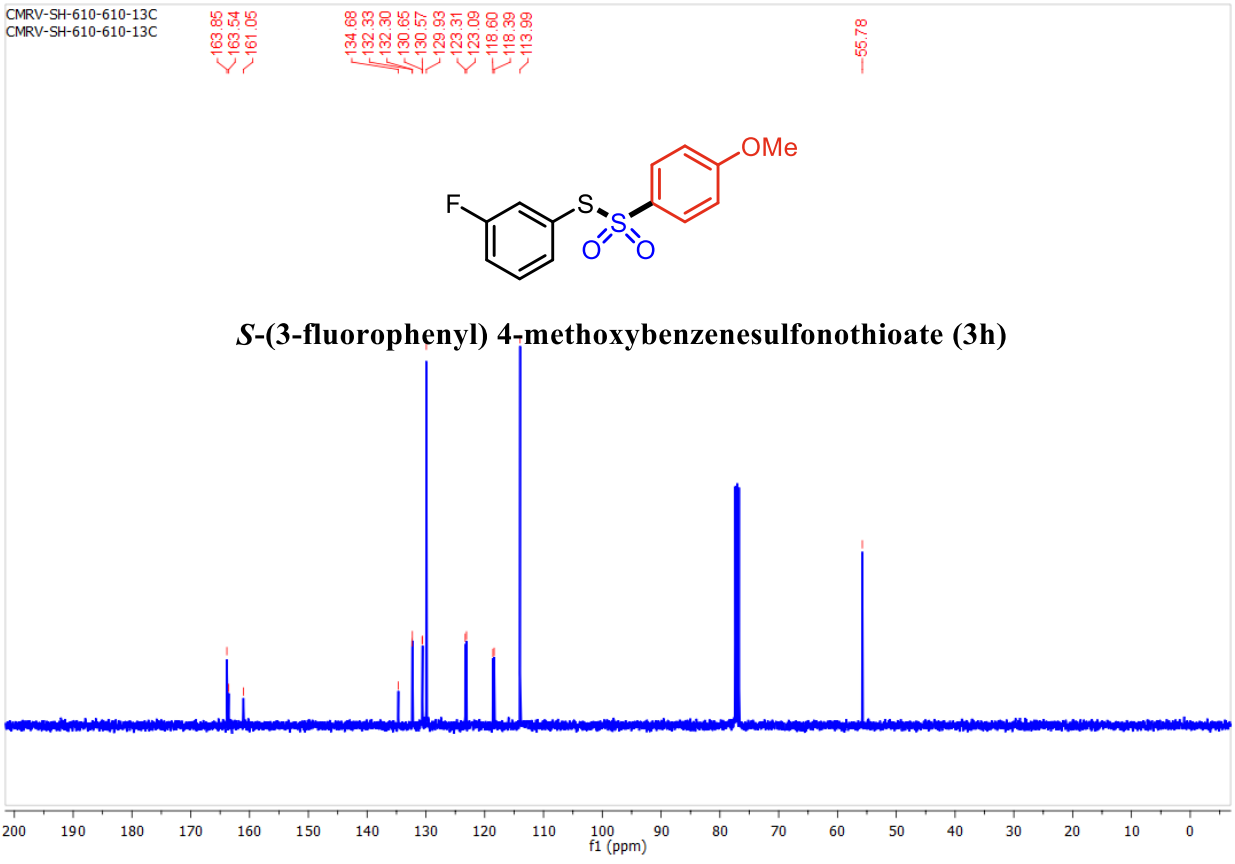
***S*-(4-fluorophenyl) 4-methoxybenzenesulfonothioate (3g)**



***S*-(4-fluorophenyl) 4-methoxybenzenesulfonothioate (3g)**



***S*-(3-fluorophenyl) 4-methoxybenzenesulfonothioate (3h)**



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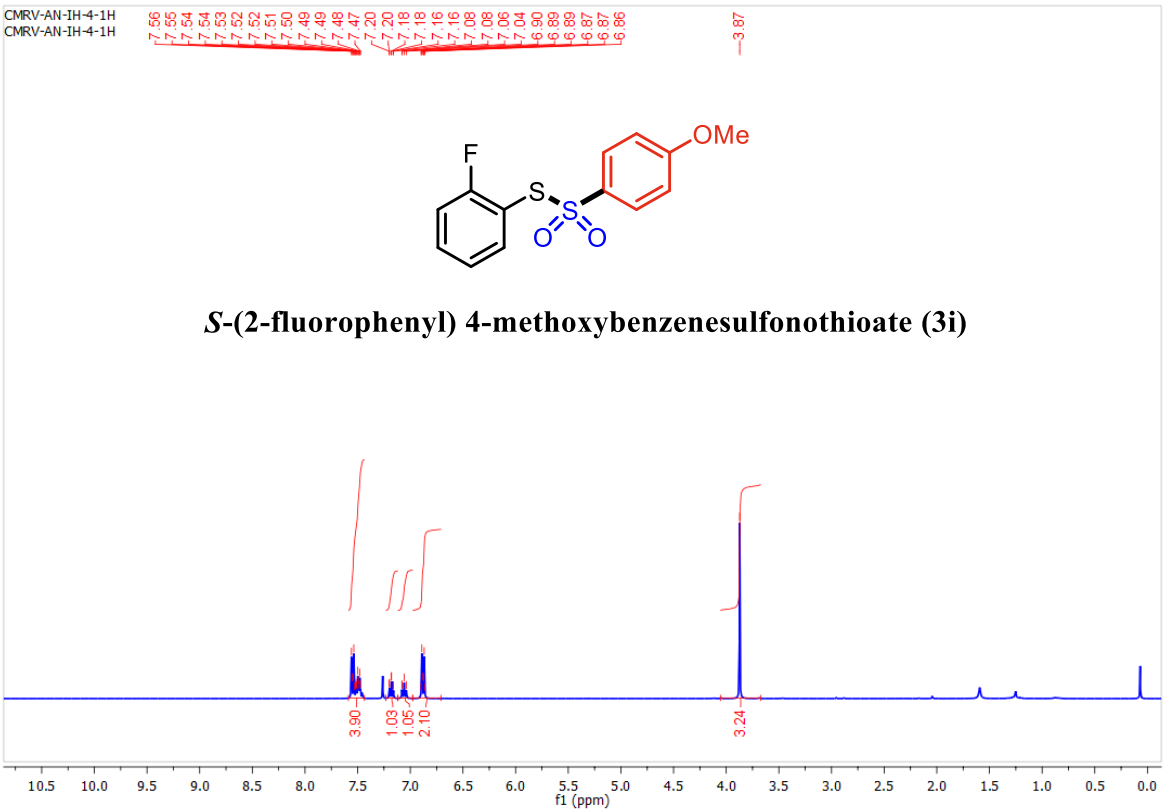
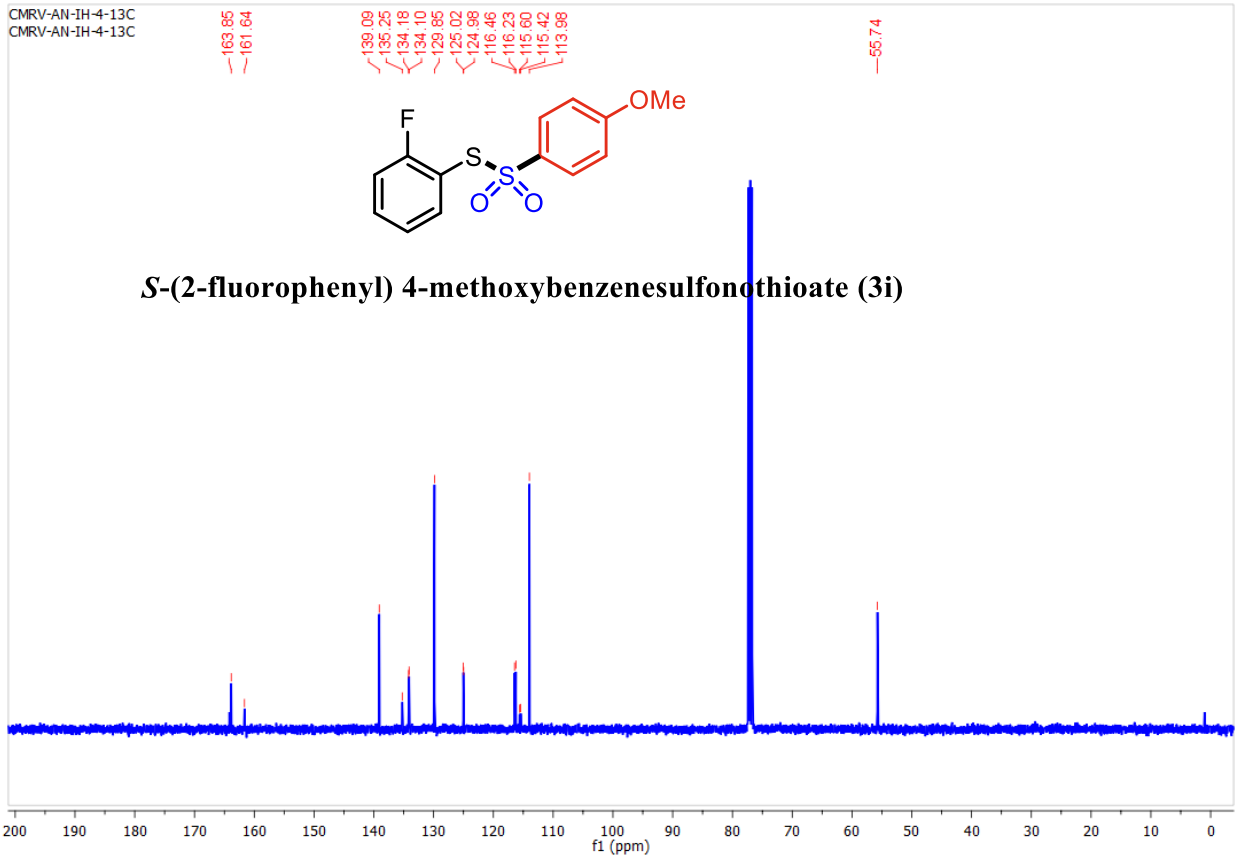
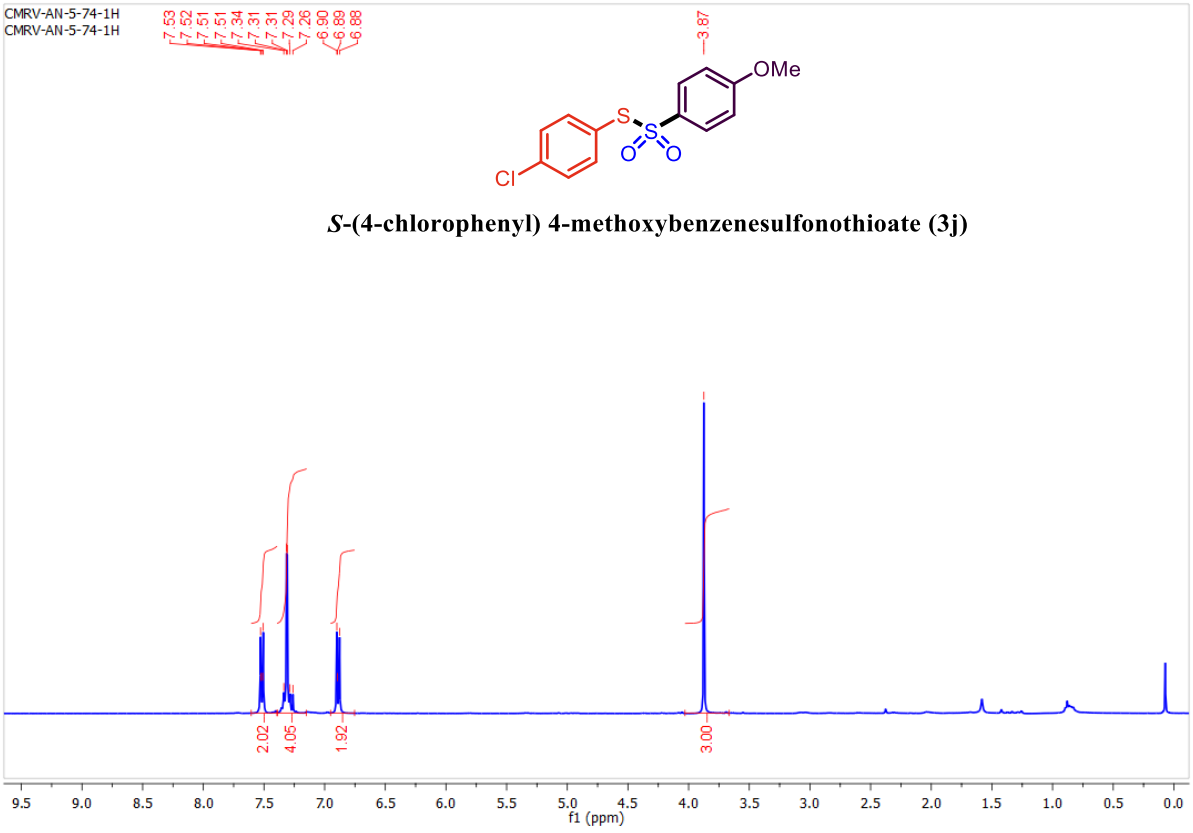


_S_-(2-fluorophenyl) 4-methoxybenzenesulfonothioate (3i)



_S_-(2-fluorophenyl) 4-methoxybenzenesulfonothioate (3i)



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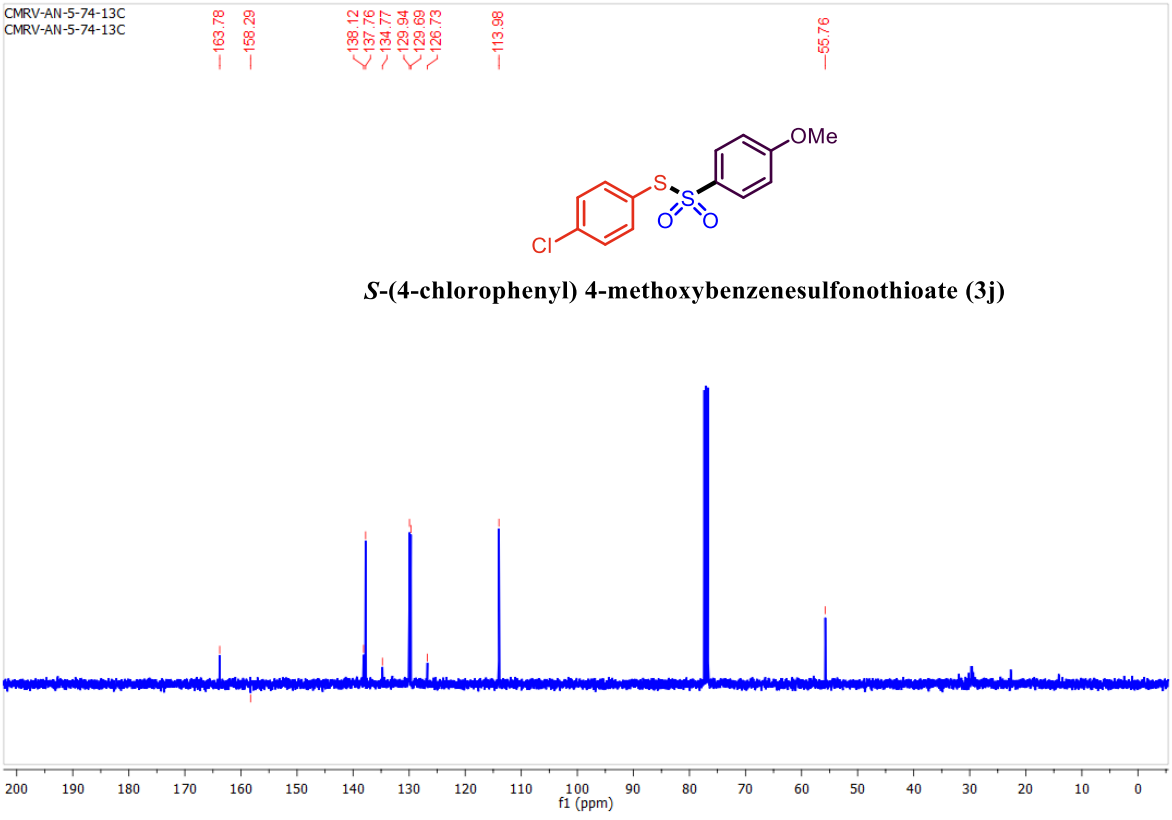

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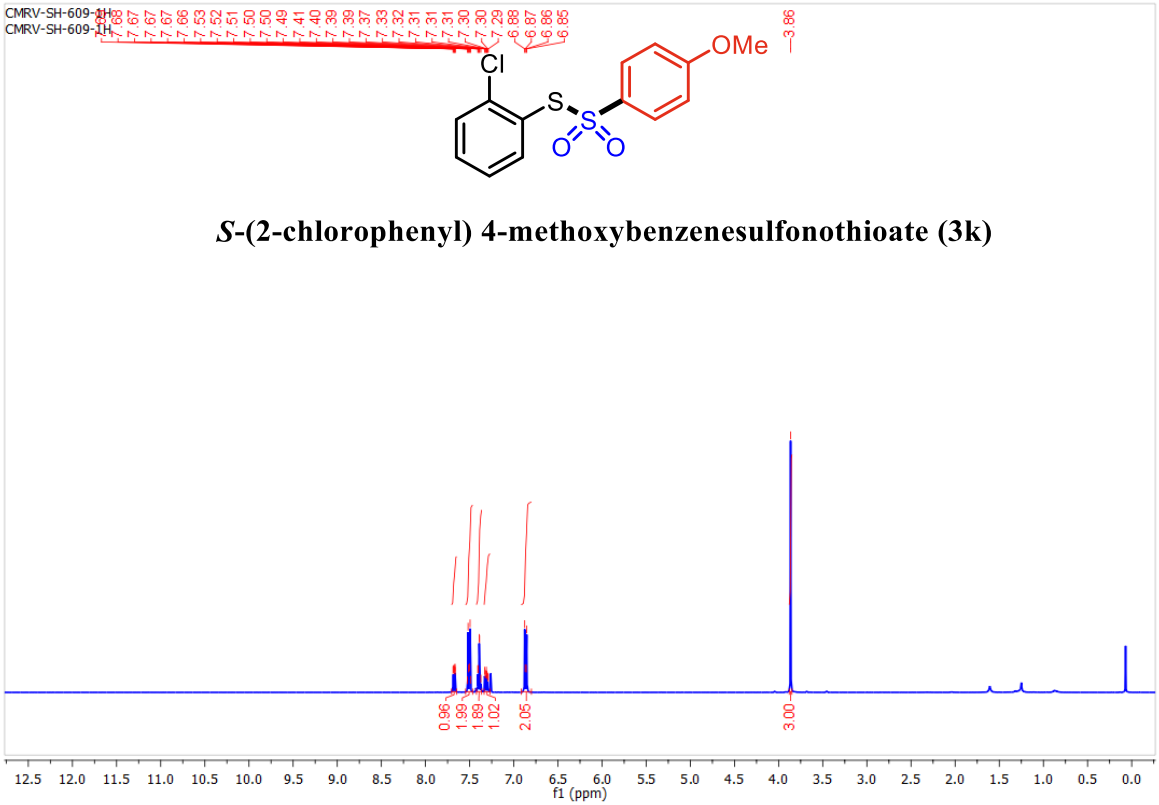

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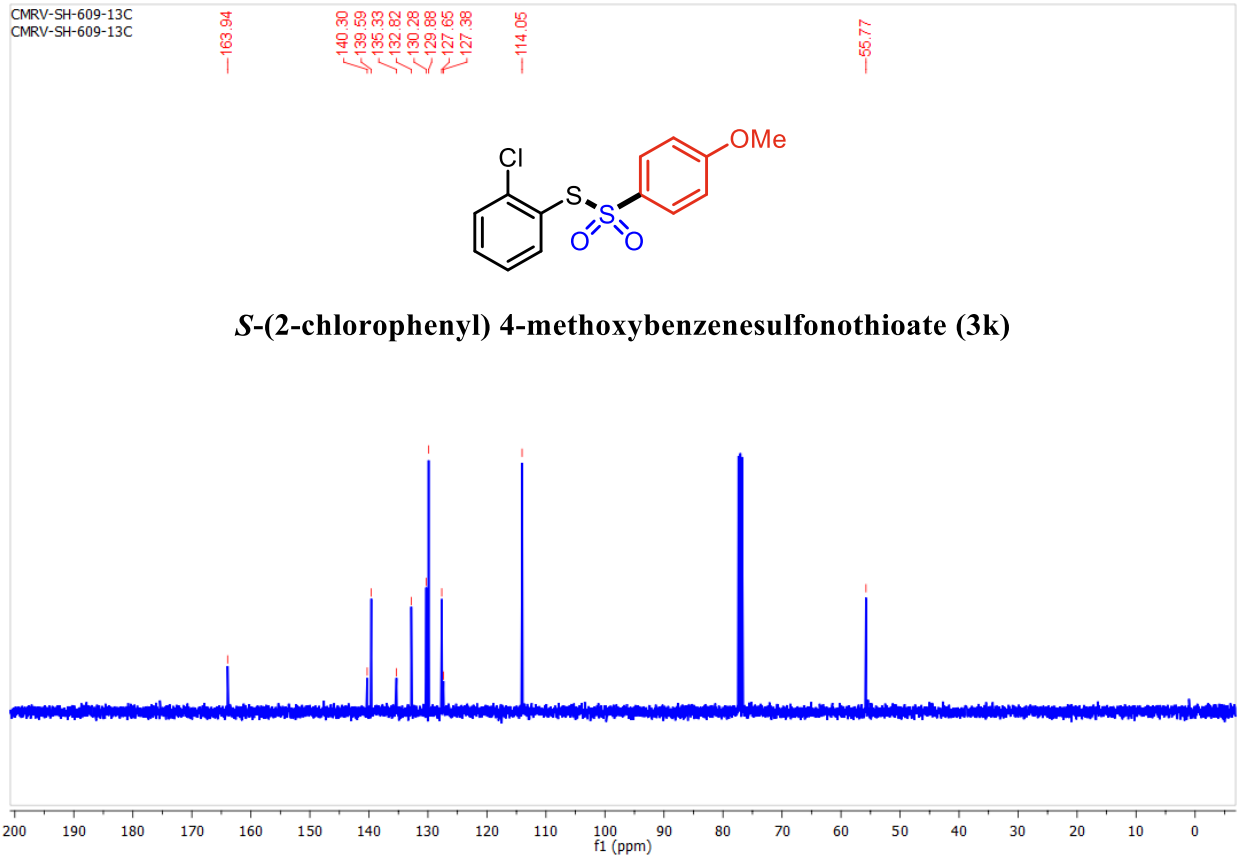

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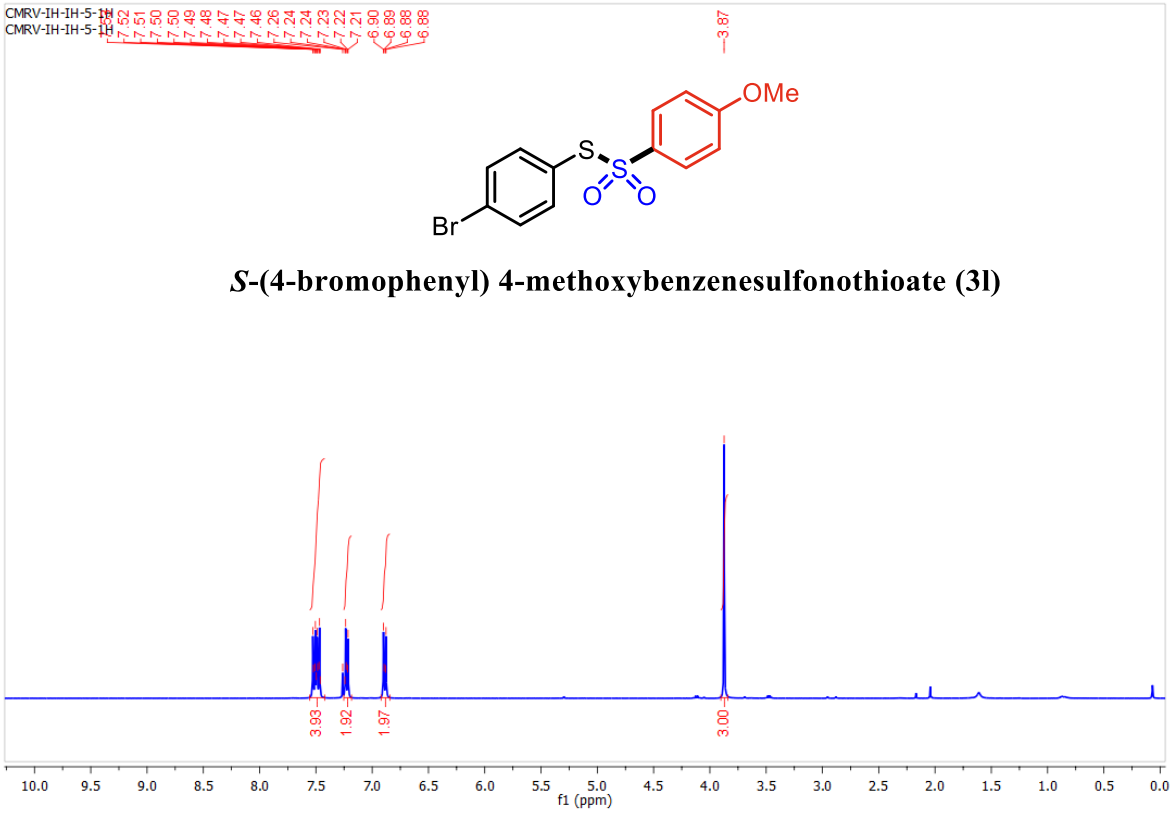
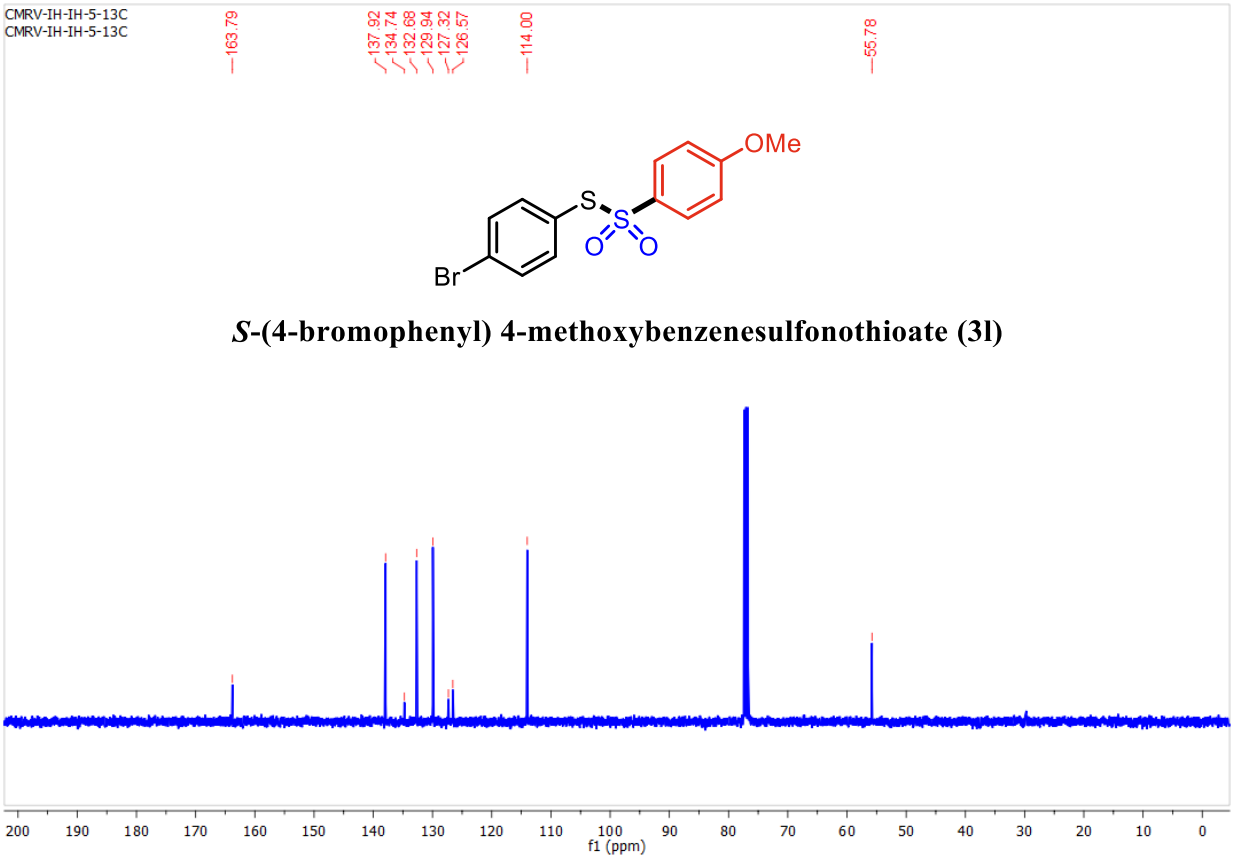


***S*-(4-bromophenyl) 4-methoxybenzenesulfonothioate (3l)**



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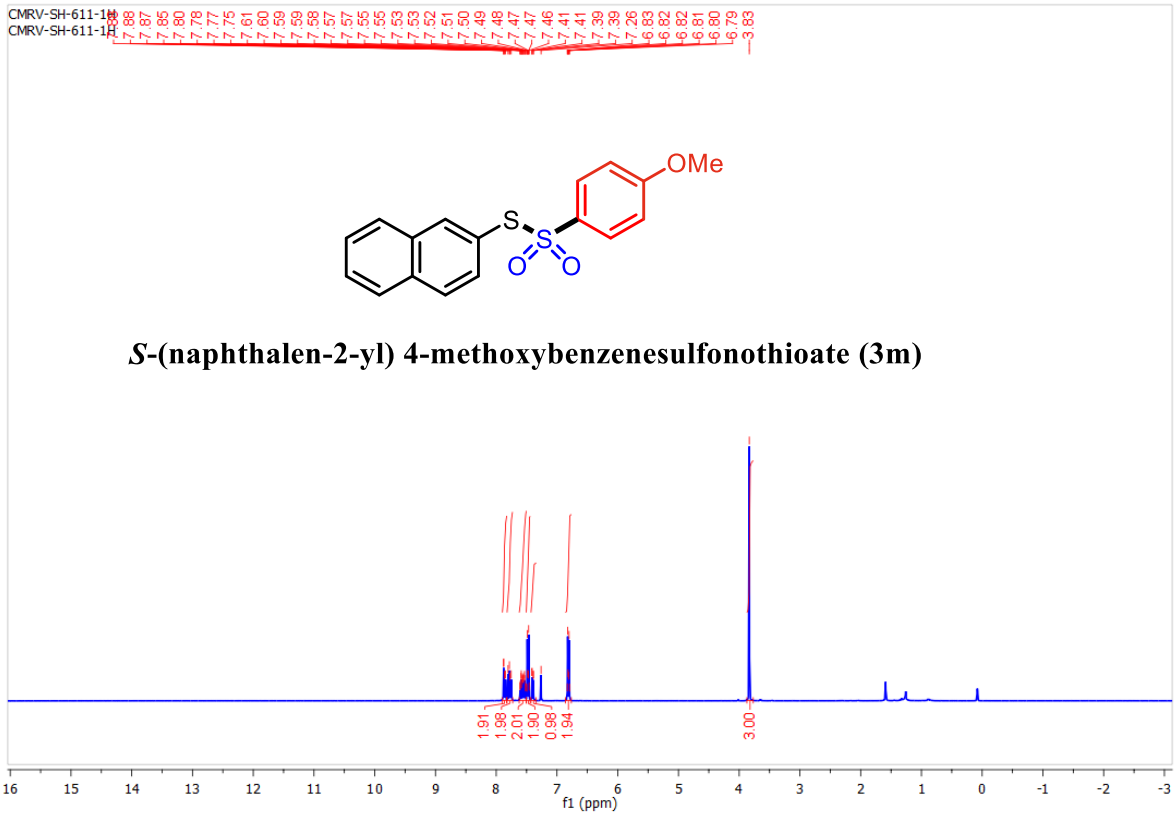
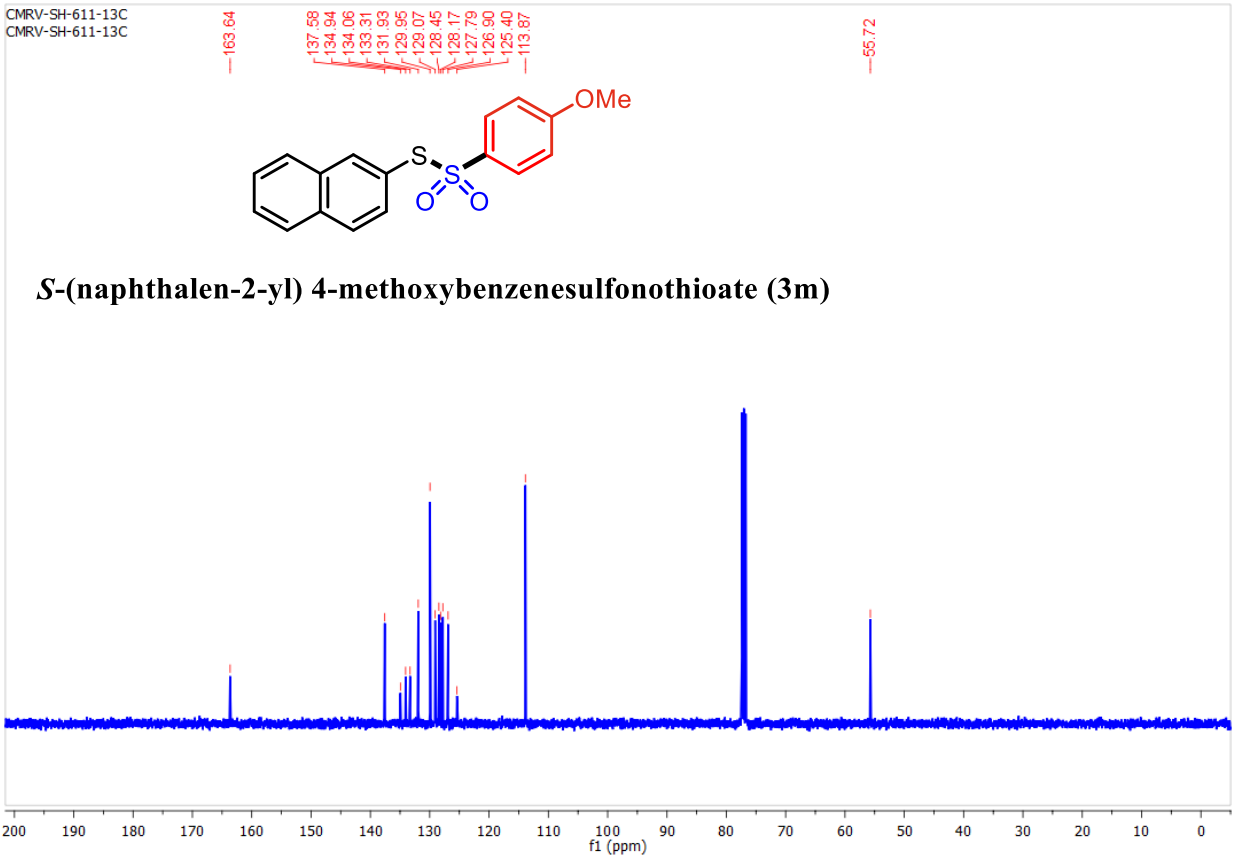
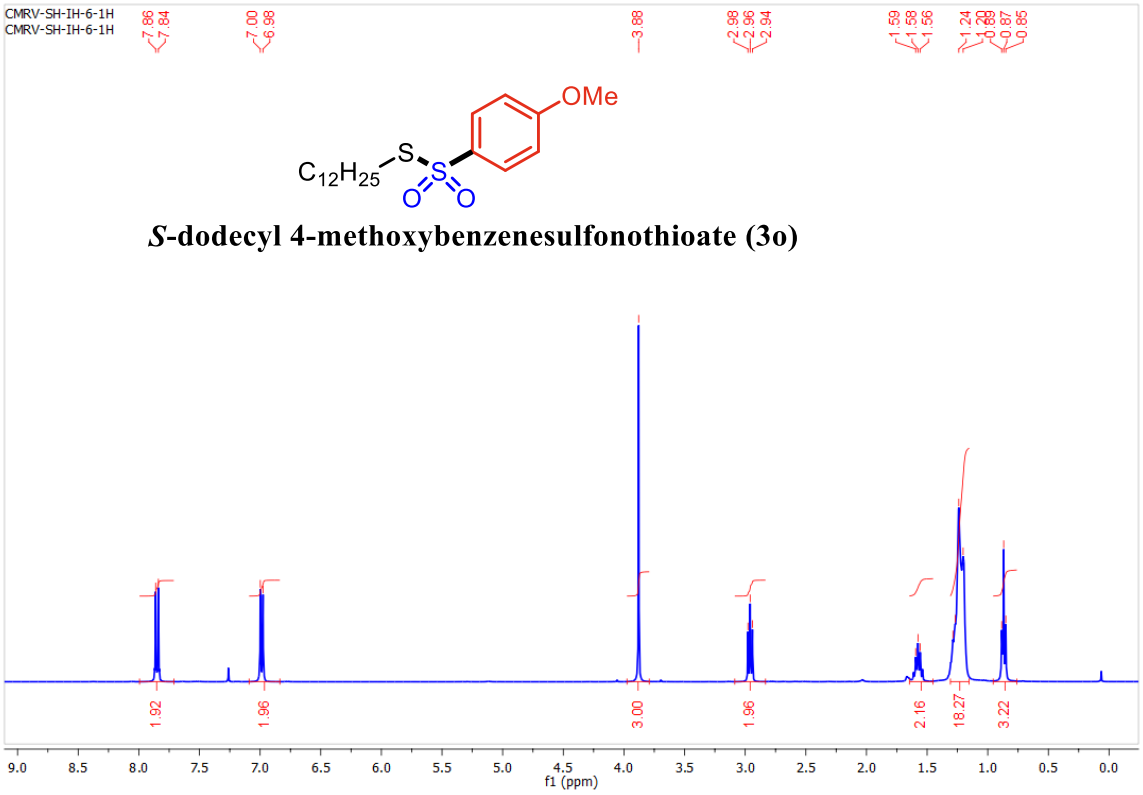


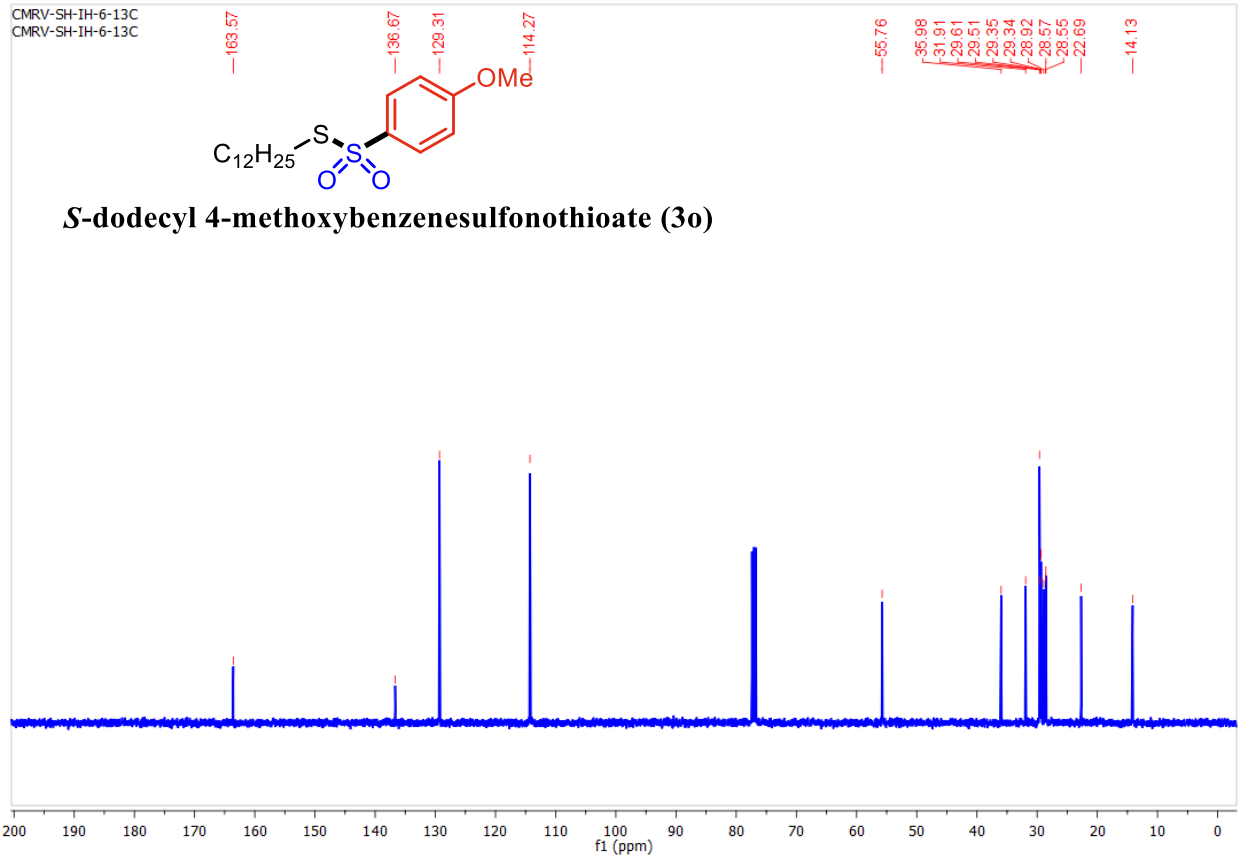
***S*-(naphthalen-2-yl) 4-methoxybenzenesulfonothioate (3m)**



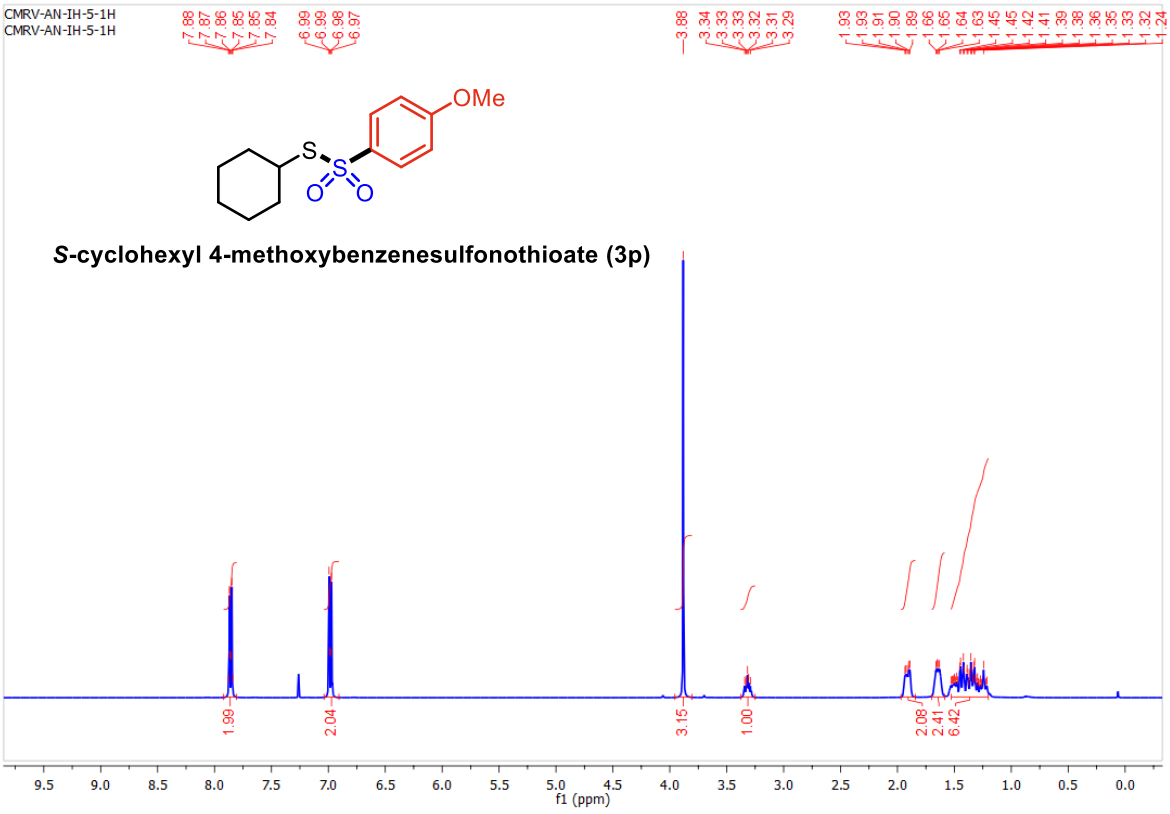
***S*-(naphthalen-2-yl) 4-methoxybenzenesulfonothioate (3m)**



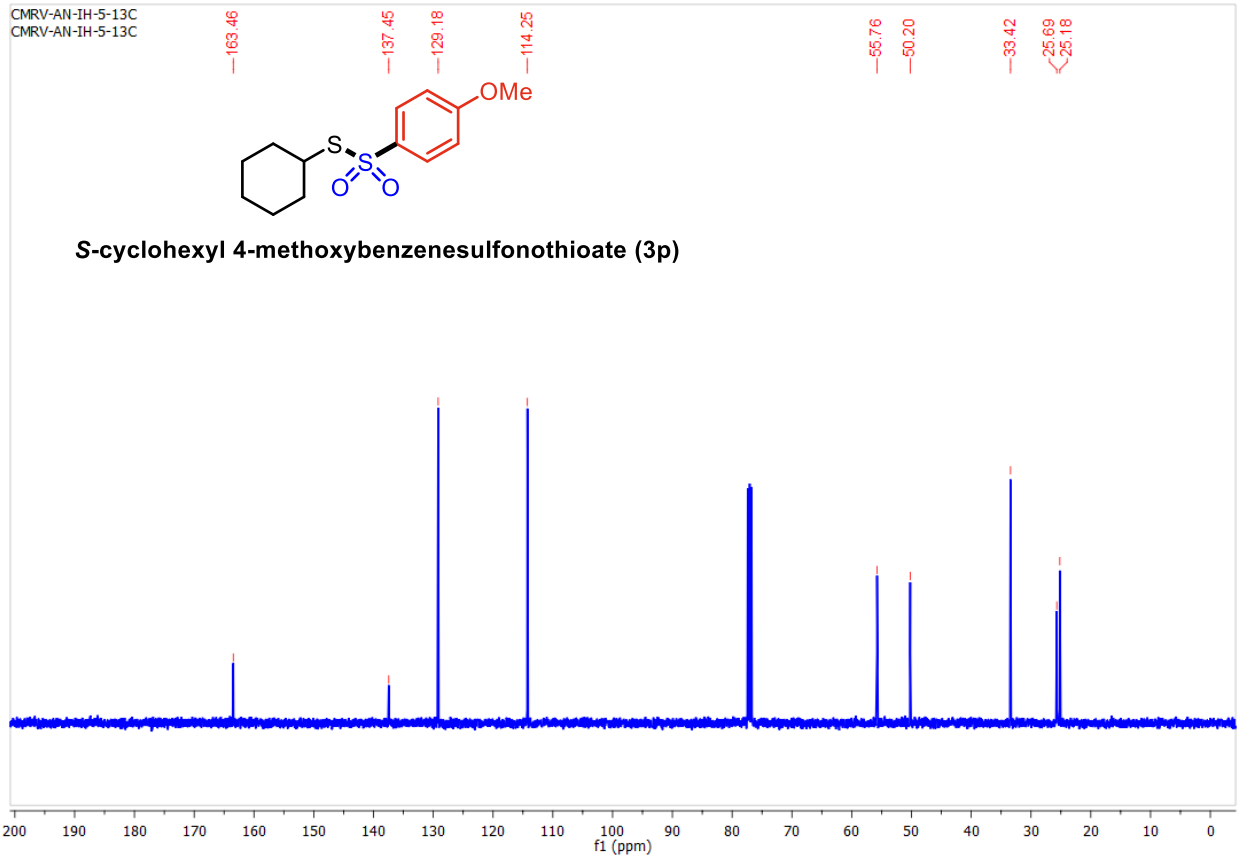
***S*-dodecyl 4-methoxybenzenesulfonothioate (3o)**



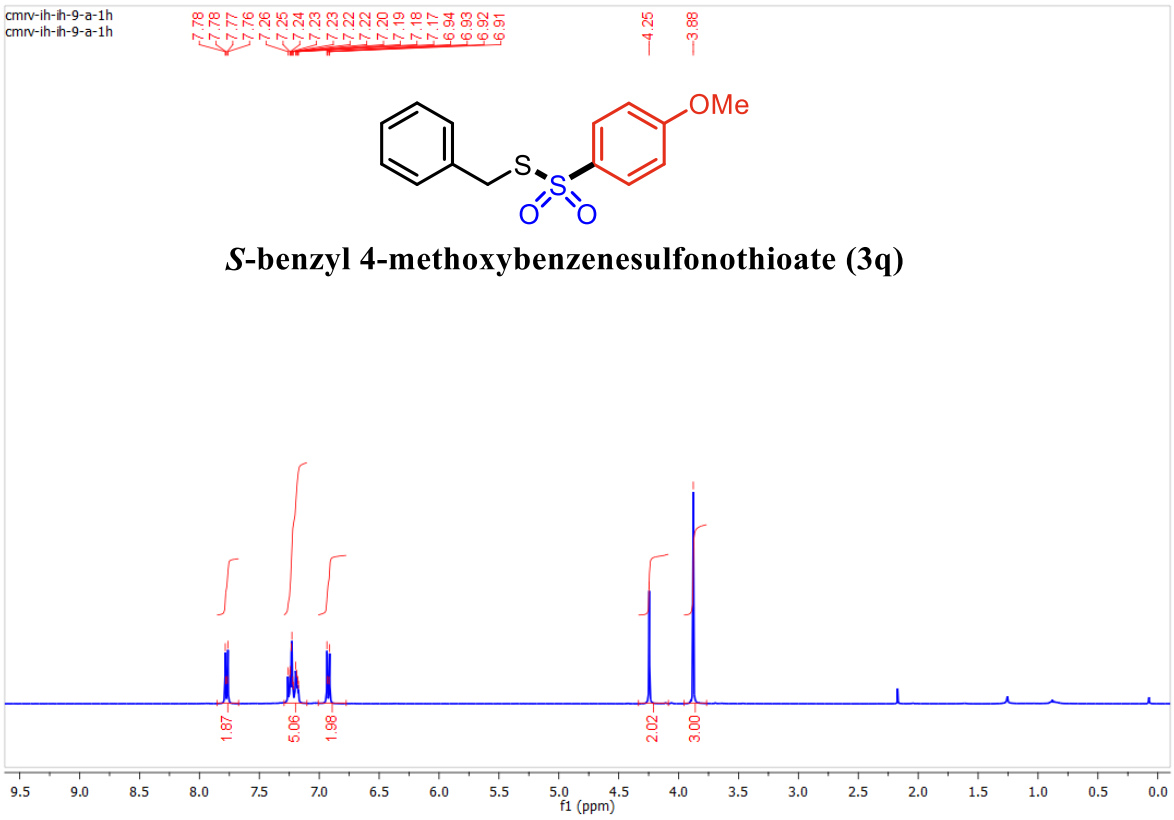
***S*-dodecyl 4-methoxybenzenesulfonothioate (3o)**



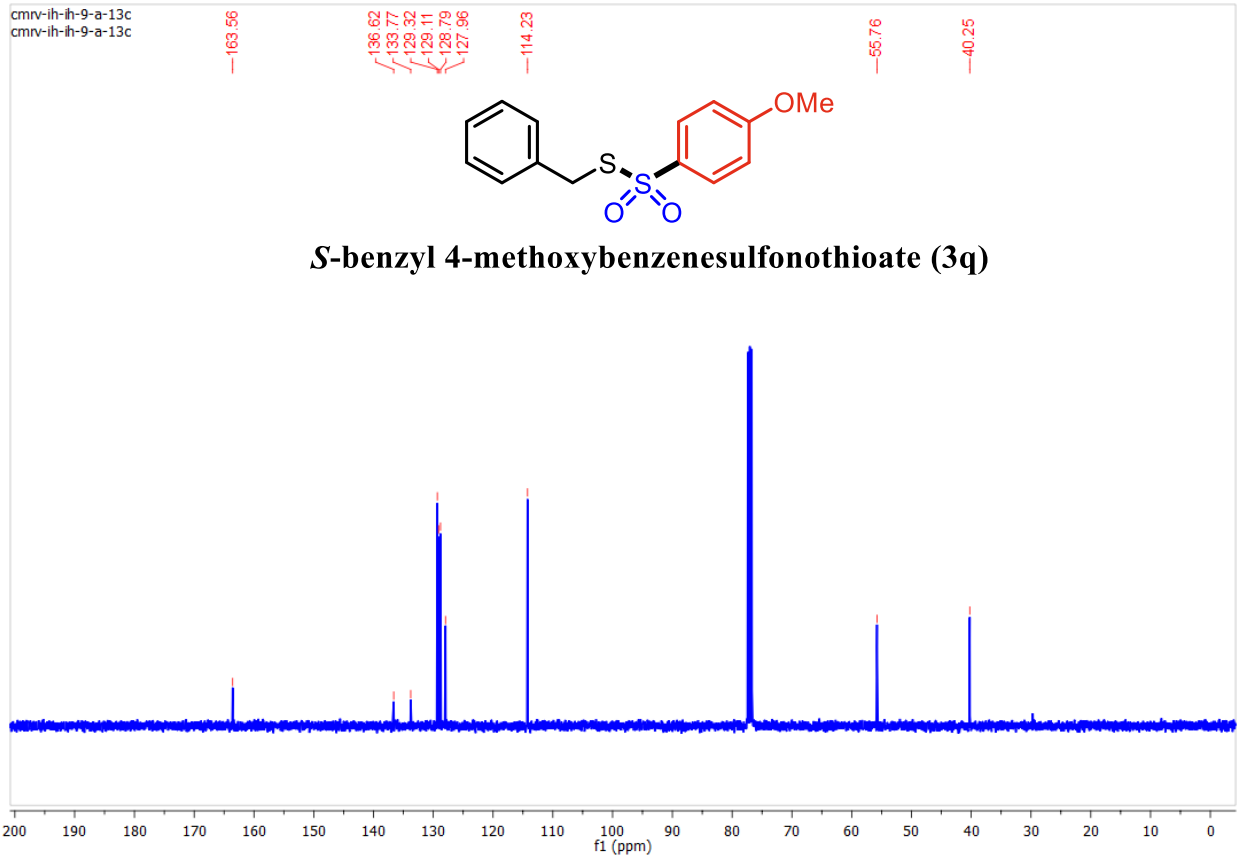
***S*-cyclohexyl 4-methoxybenzenesulfonothioate (3p)**



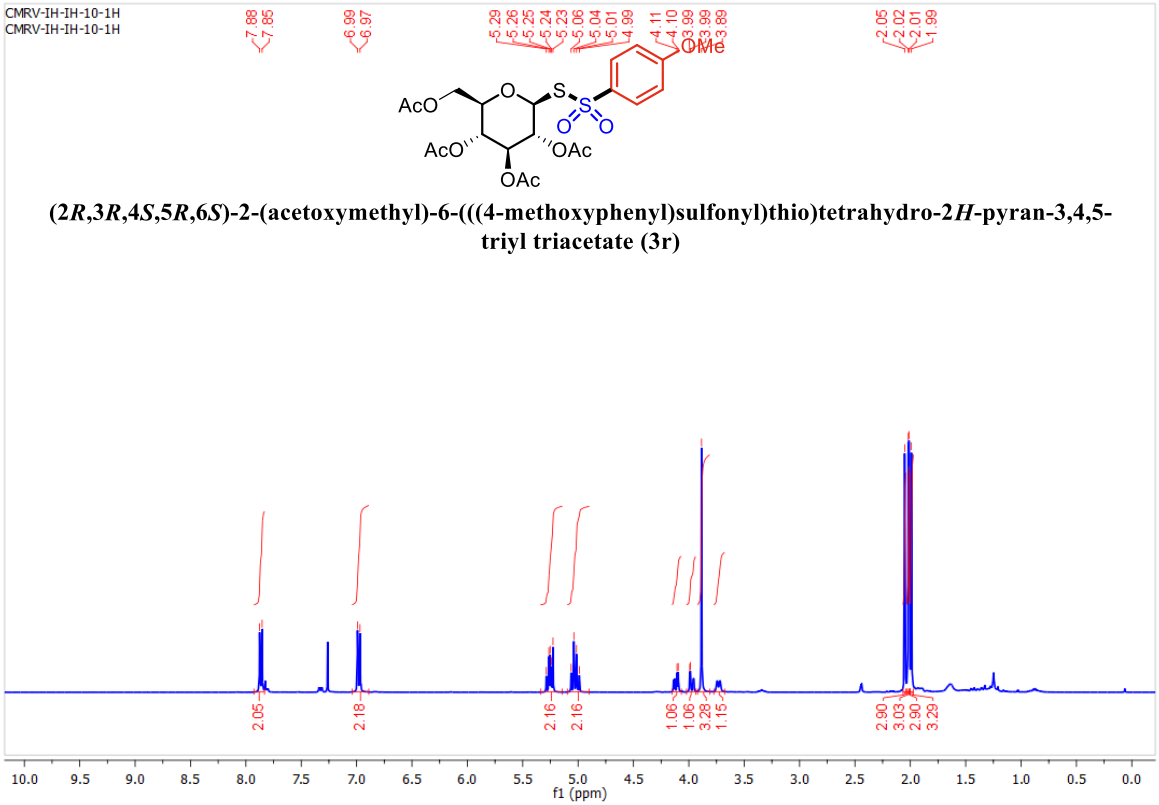
***S*-cyclohexyl 4-methoxybenzenesulfonothioate (3p)**



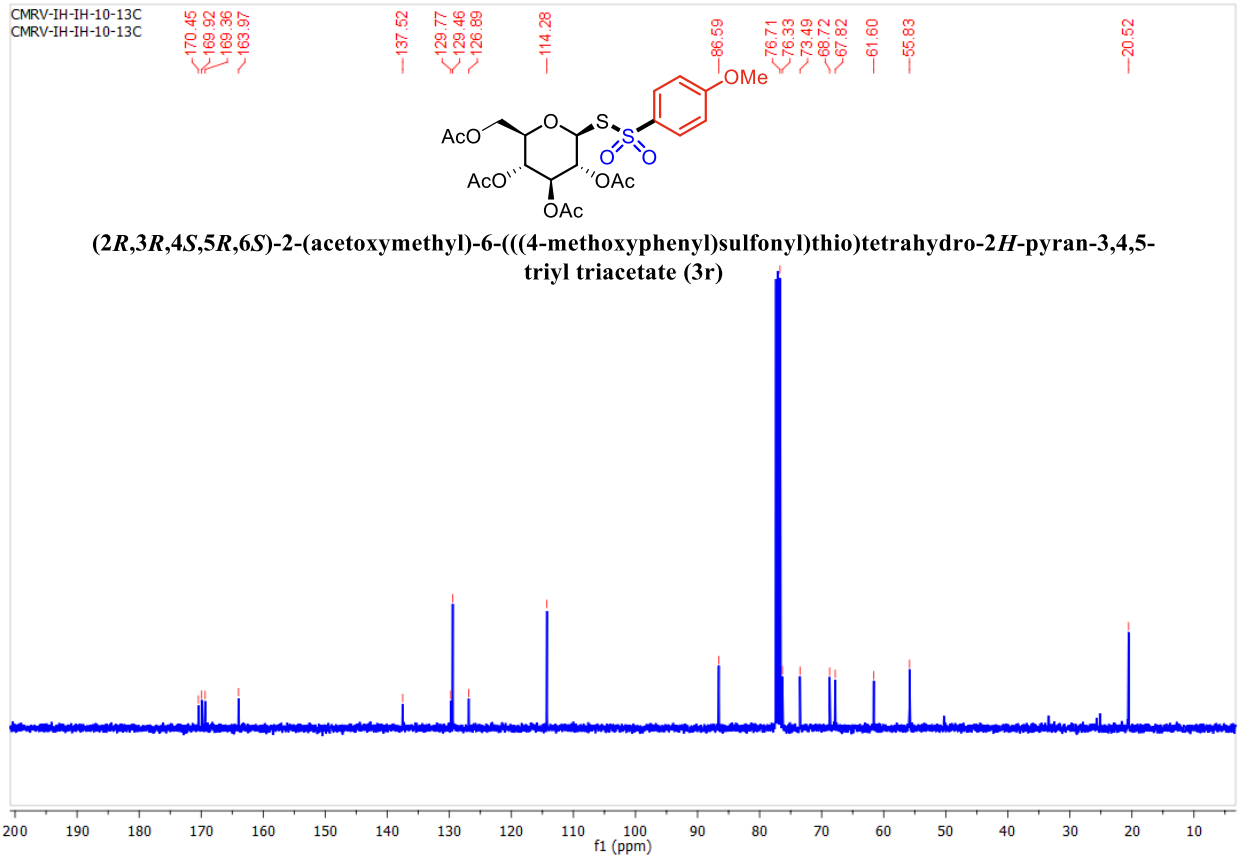
_S_-benzyl 4-methoxybenzenesulfonothioate (3q)



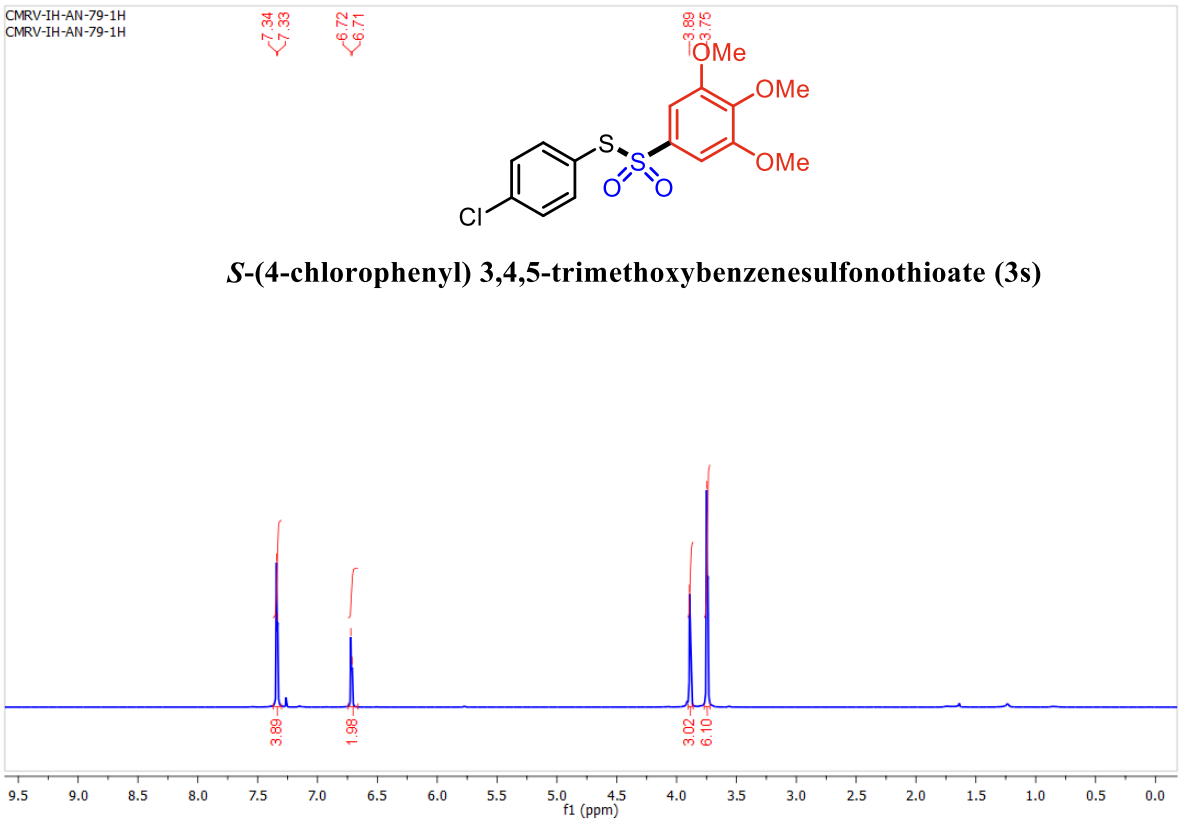
_S_-benzyl 4-methoxybenzenesulfonothioate (3q)



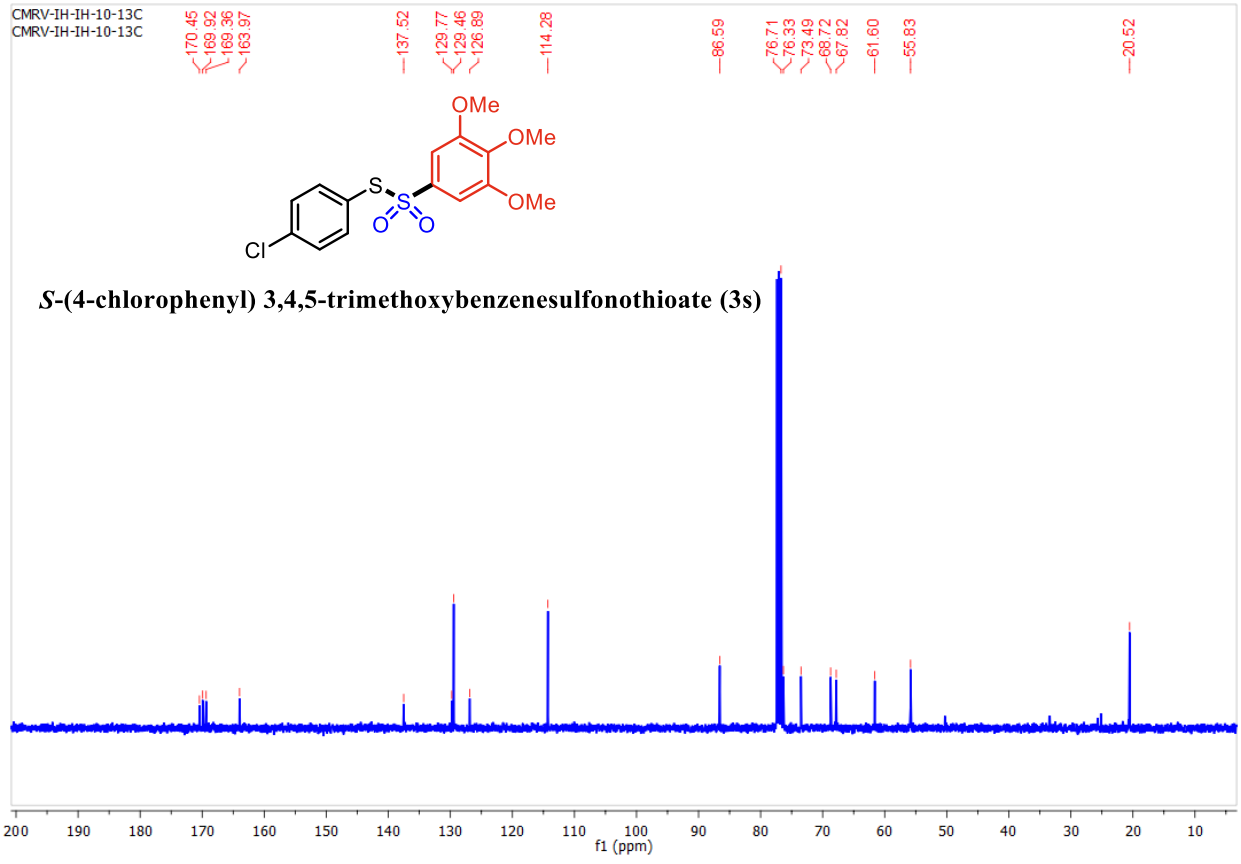
(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(((4-methoxyphenyl)sulfonyl)thio)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3r)



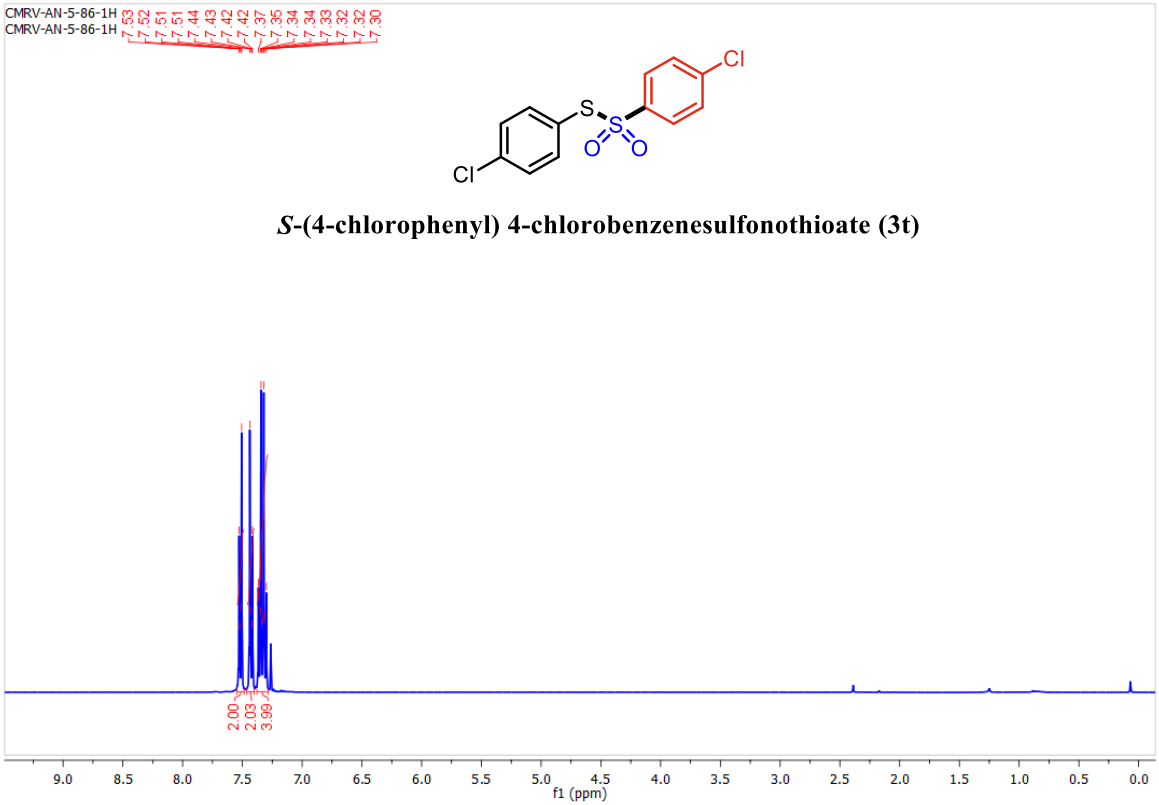
(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(((4-methoxyphenyl)sulfonyl)thio)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3r)



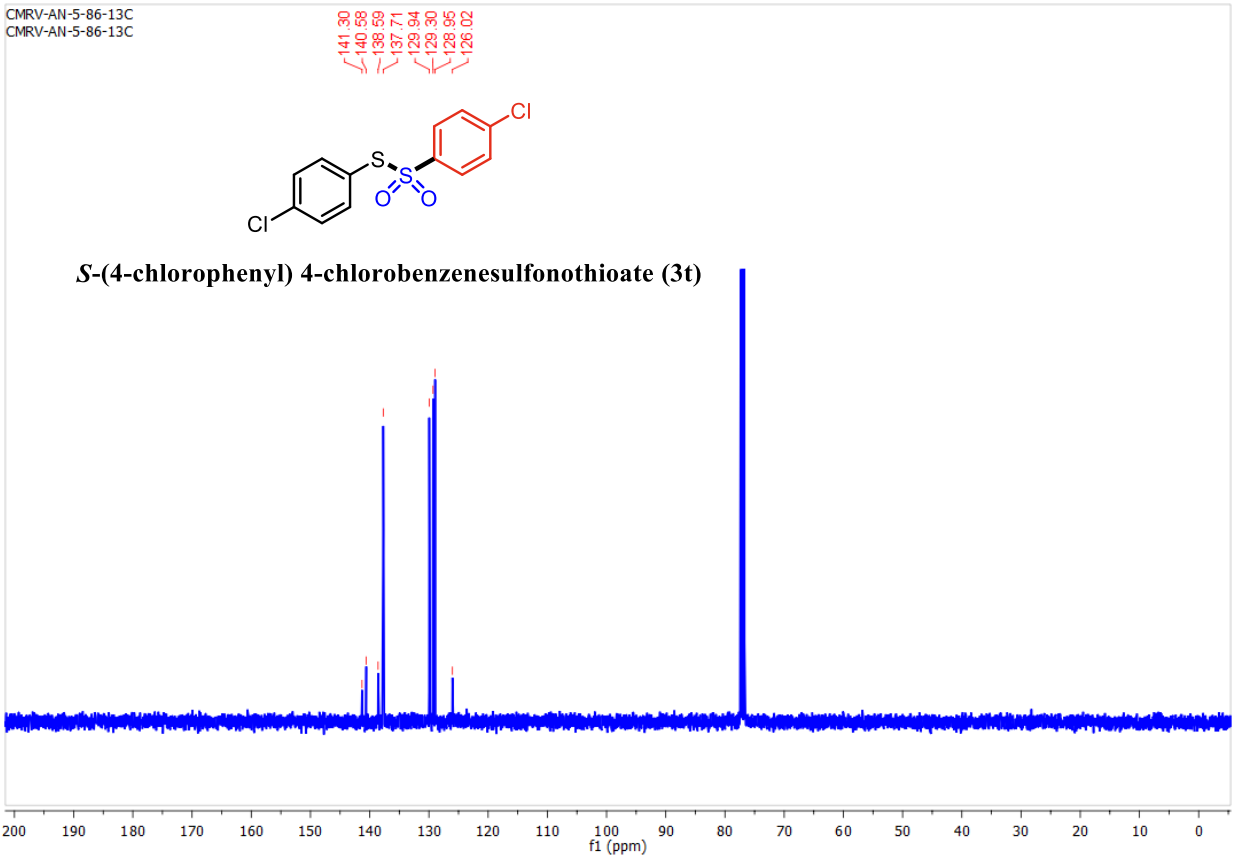
***S*-(4-chlorophenyl) 3,4,5-trimethoxybenzenesulfonothioate (3s)**



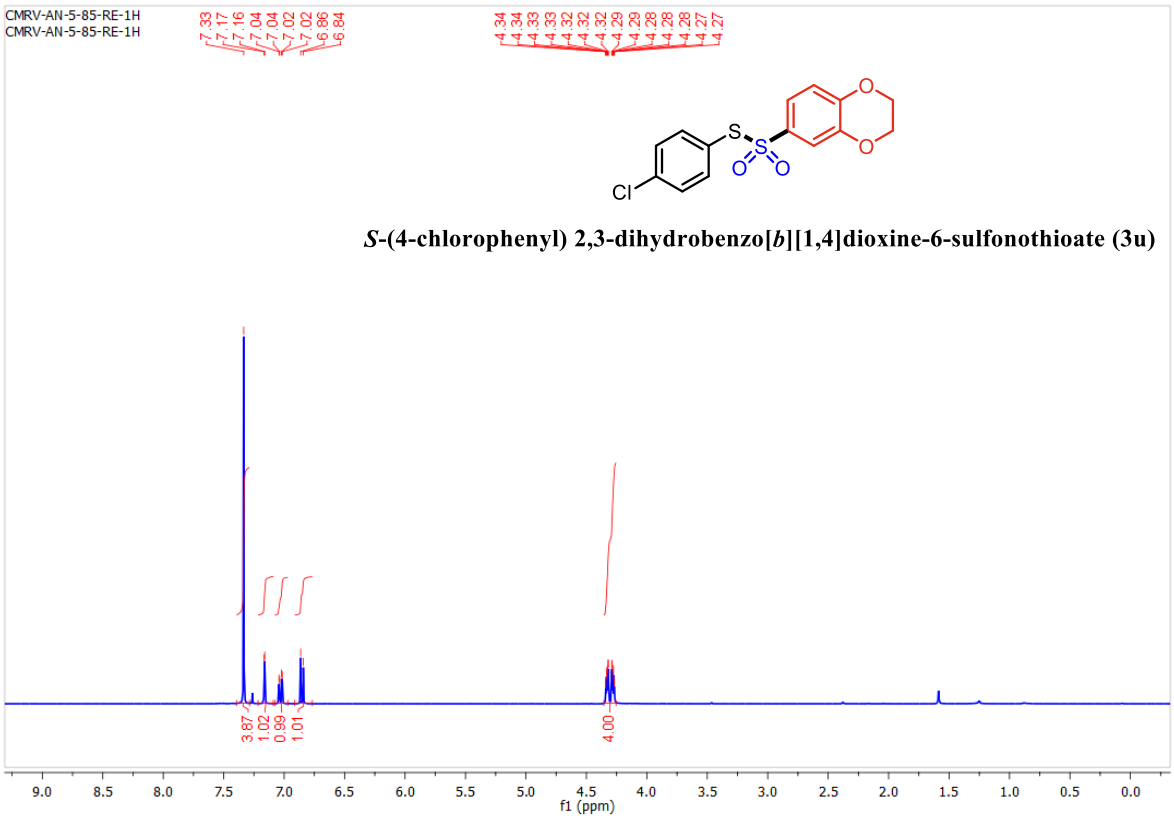
***S*-(4-chlorophenyl) 3,4,5-trimethoxybenzenesulfonothioate (3s)**



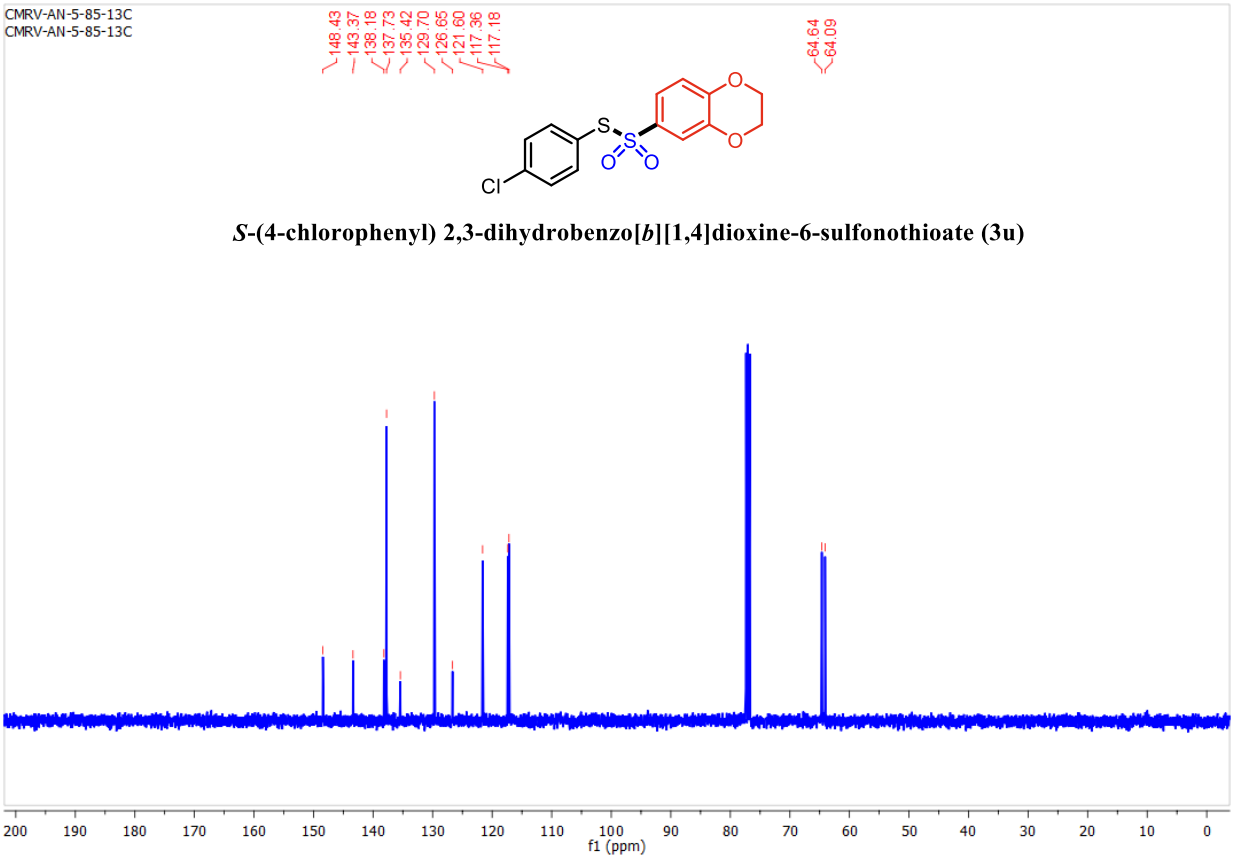
***S*-(4-chlorophenyl) 4-chlorobenzenesulfonothioate (3t)**



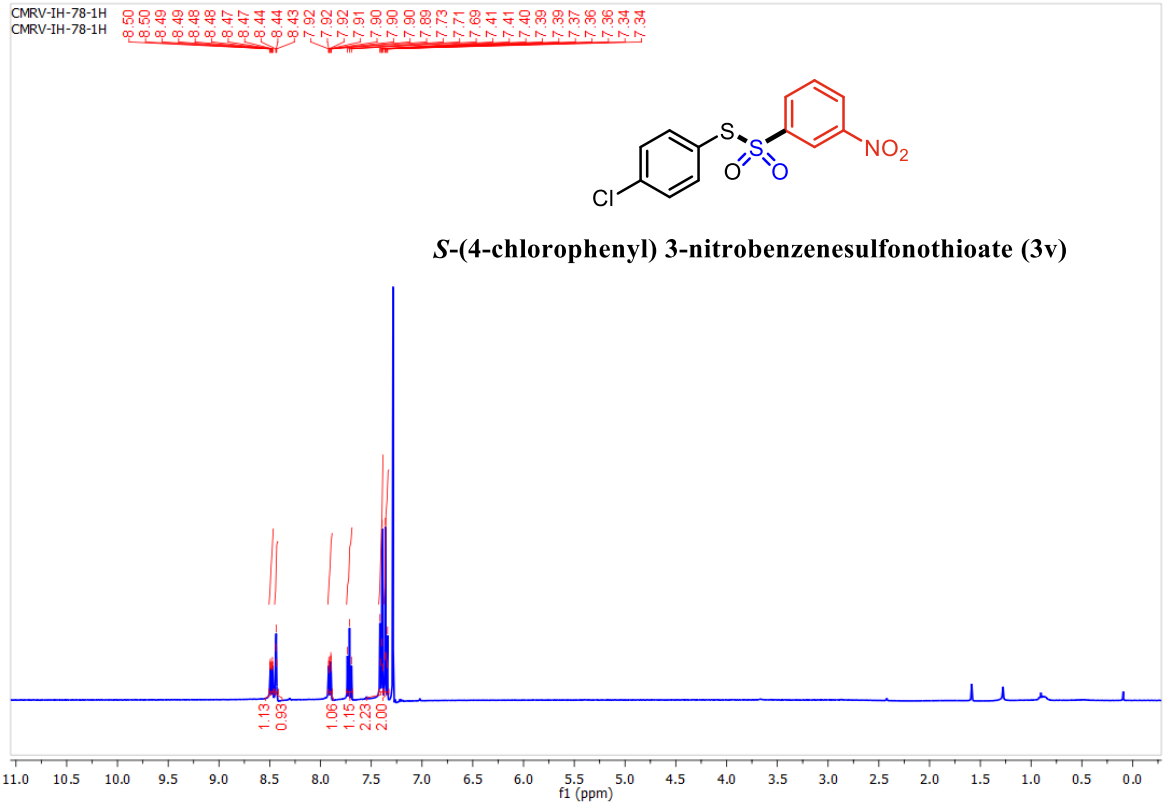
***S*-(4-chlorophenyl) 4-chlorobenzenesulfonothioate (3t)**



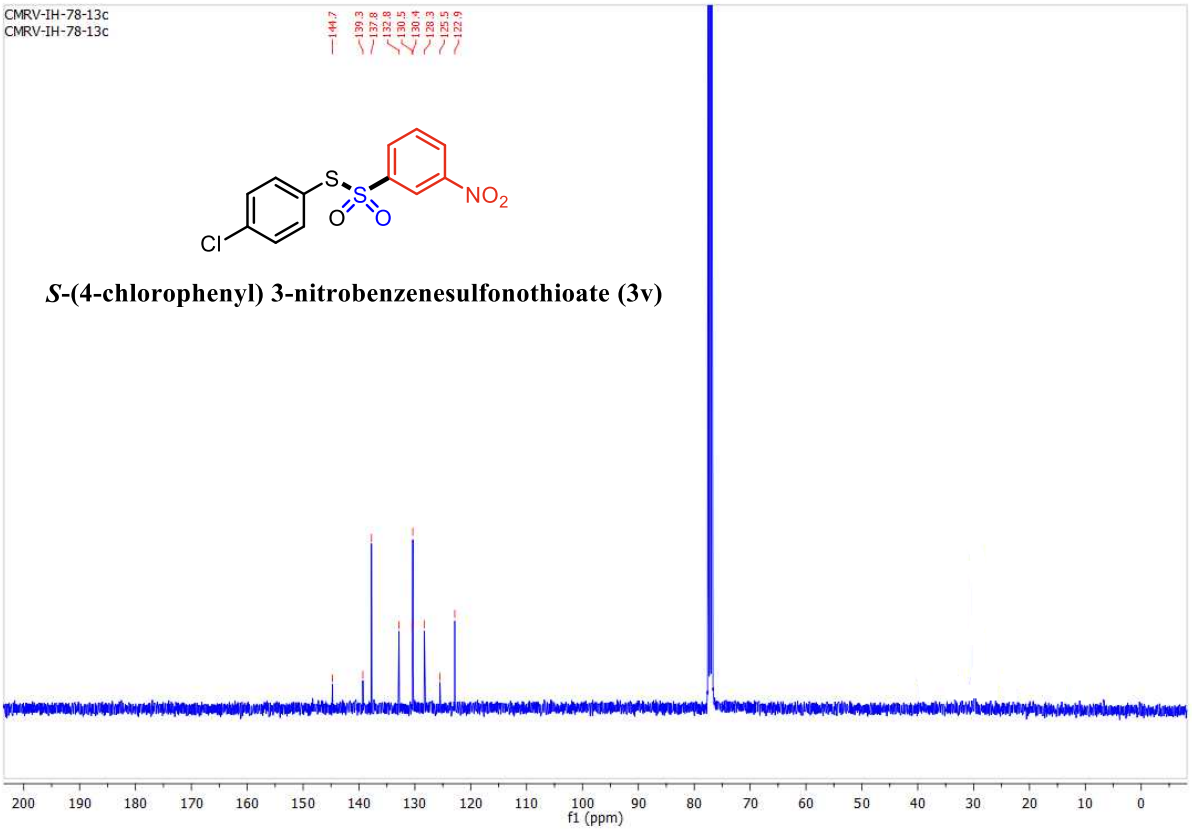
***S*-(4-chlorophenyl) 2,3-dihydrobenzo[*b*][1,4]dioxine-6-sulfonothioate (3u)**



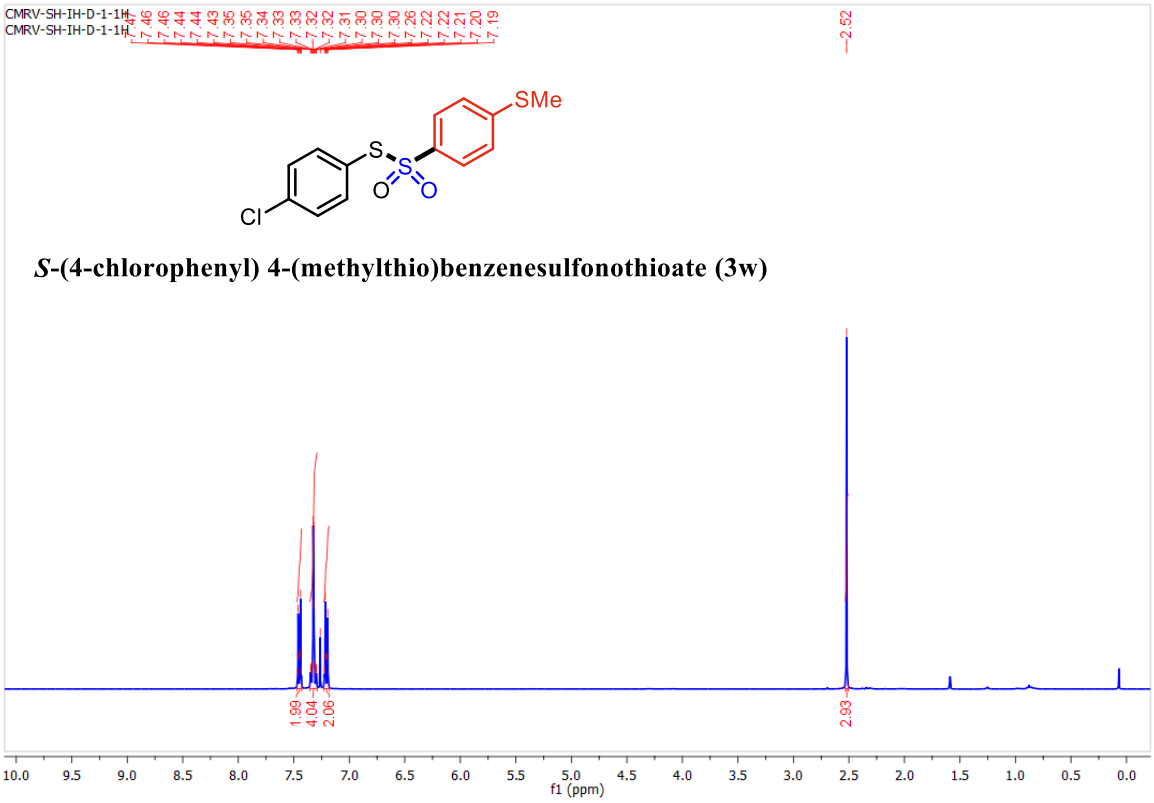
***S*-(4-chlorophenyl) 2,3-dihydrobenzo[*b*][1,4]dioxine-6-sulfonothioate (3u)**



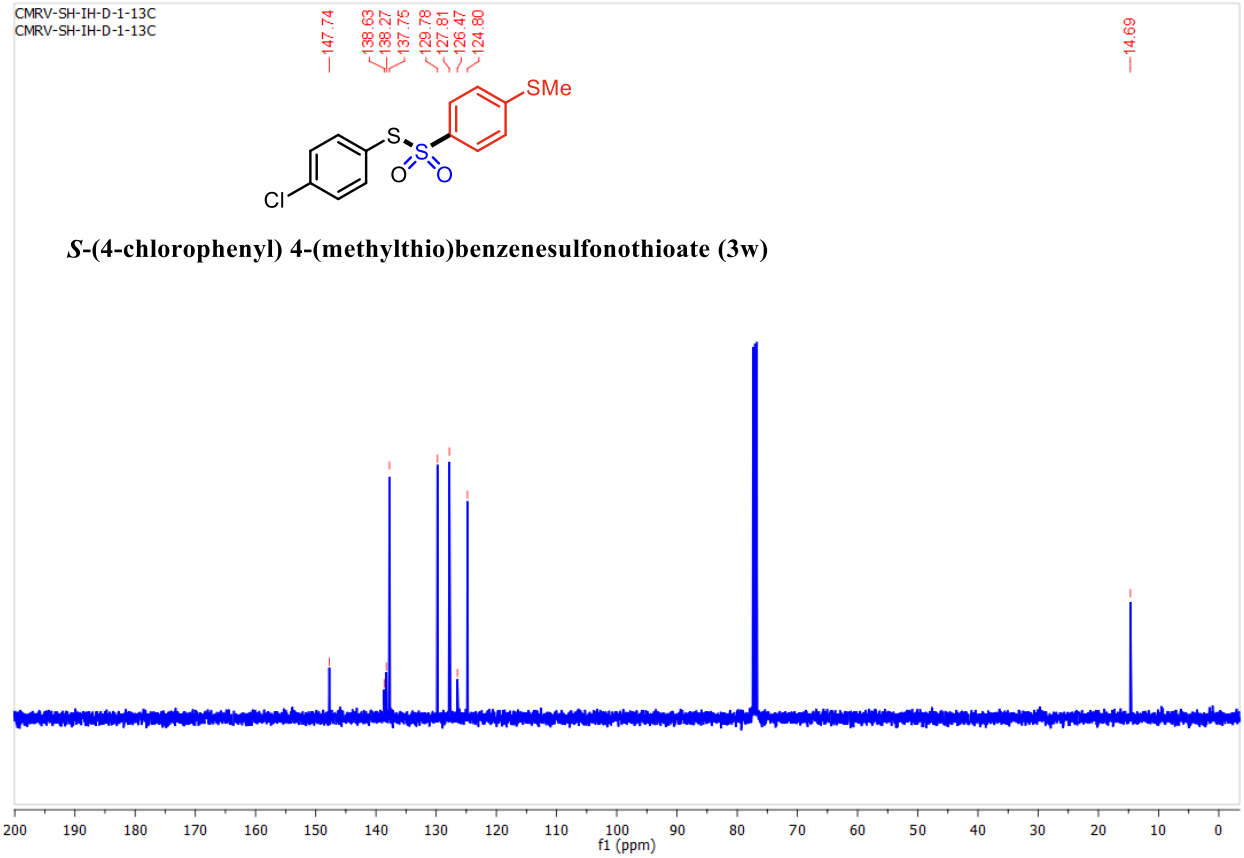
***S*-(4-chlorophenyl) 3-nitrobenzenesulfonothioate (3v)**



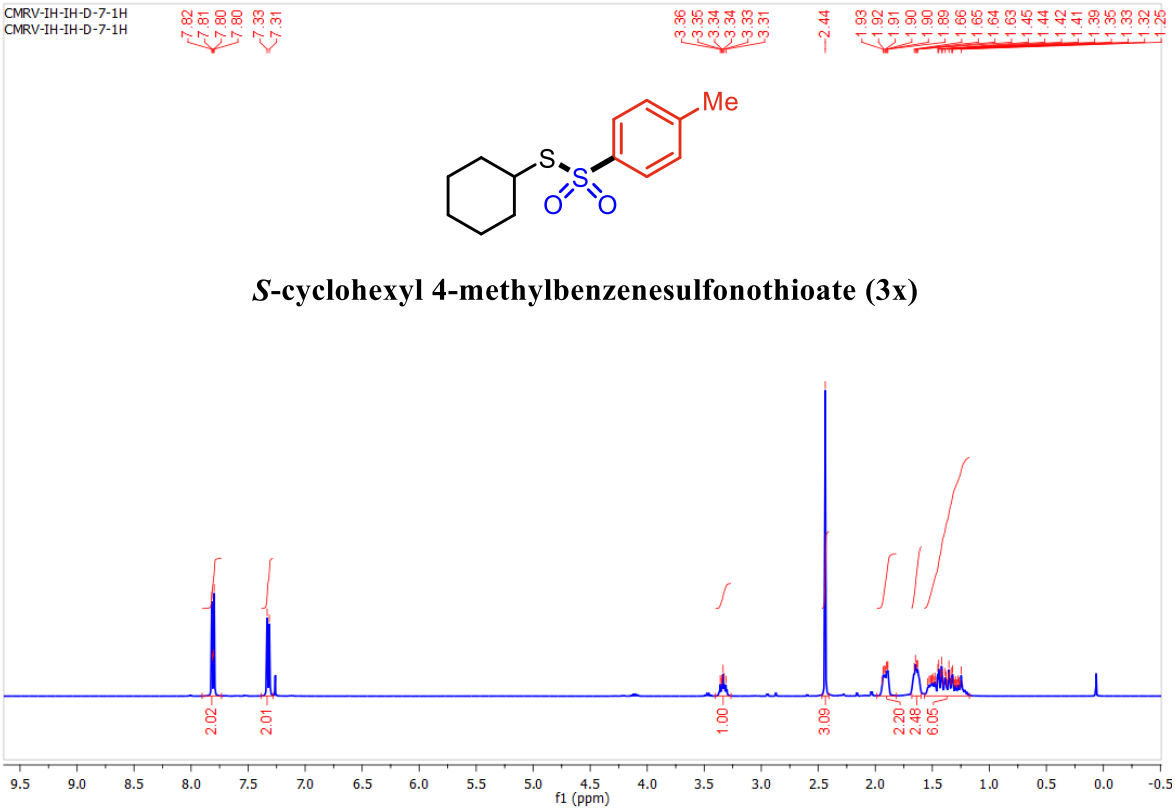
***S*-(4-chlorophenyl) 3-nitrobenzenesulfonothioate (3v)**



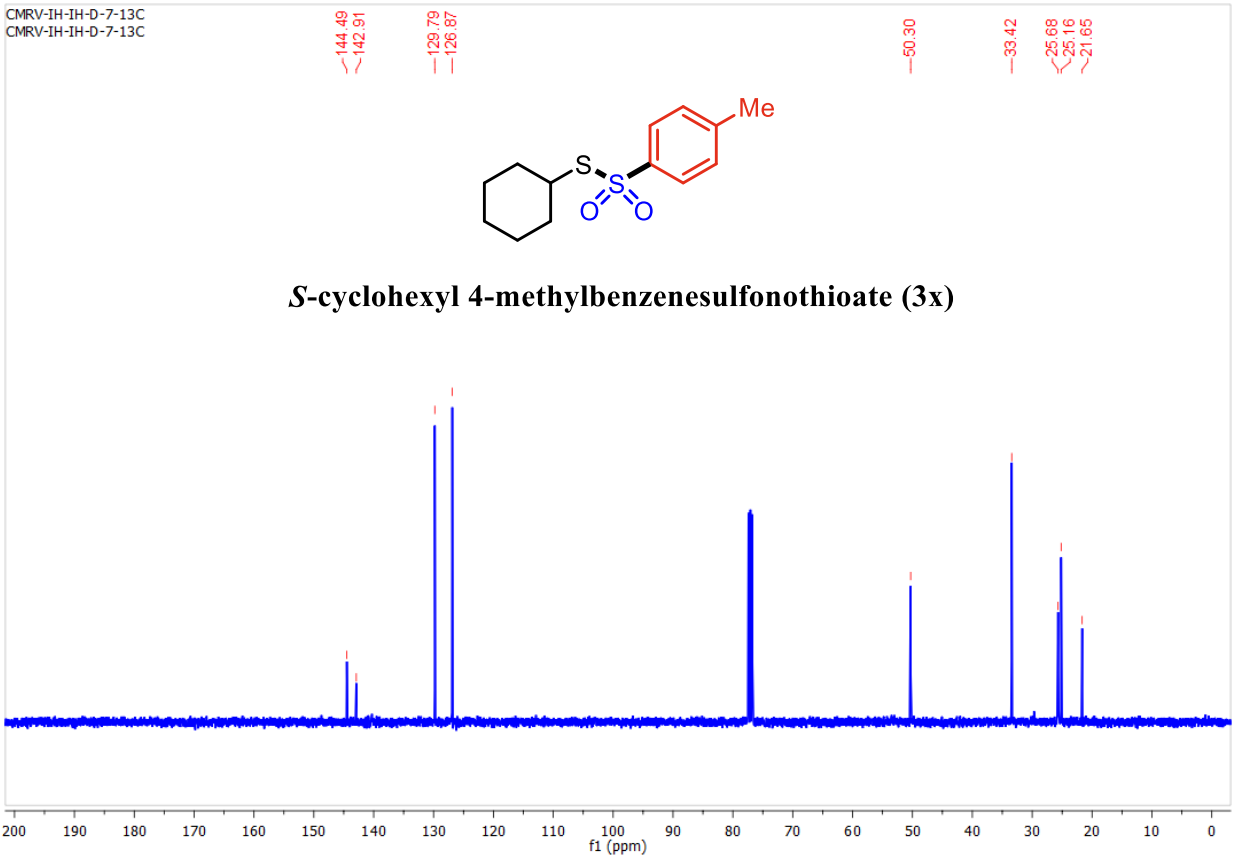
***S*-(4-chlorophenyl) 4-(methylthio)benzenesulfonothioate (3w)**



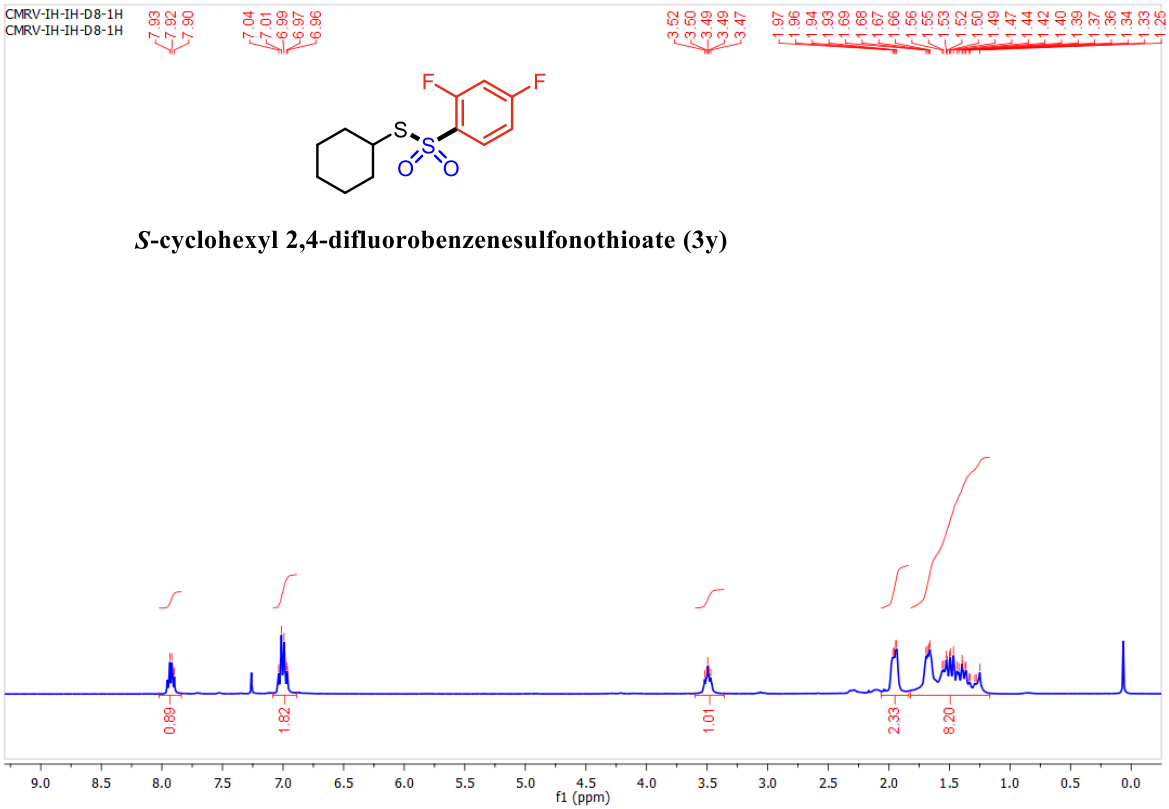
***S*-(4-chlorophenyl) 4-(methylthio)benzenesulfonothioate (3w)**



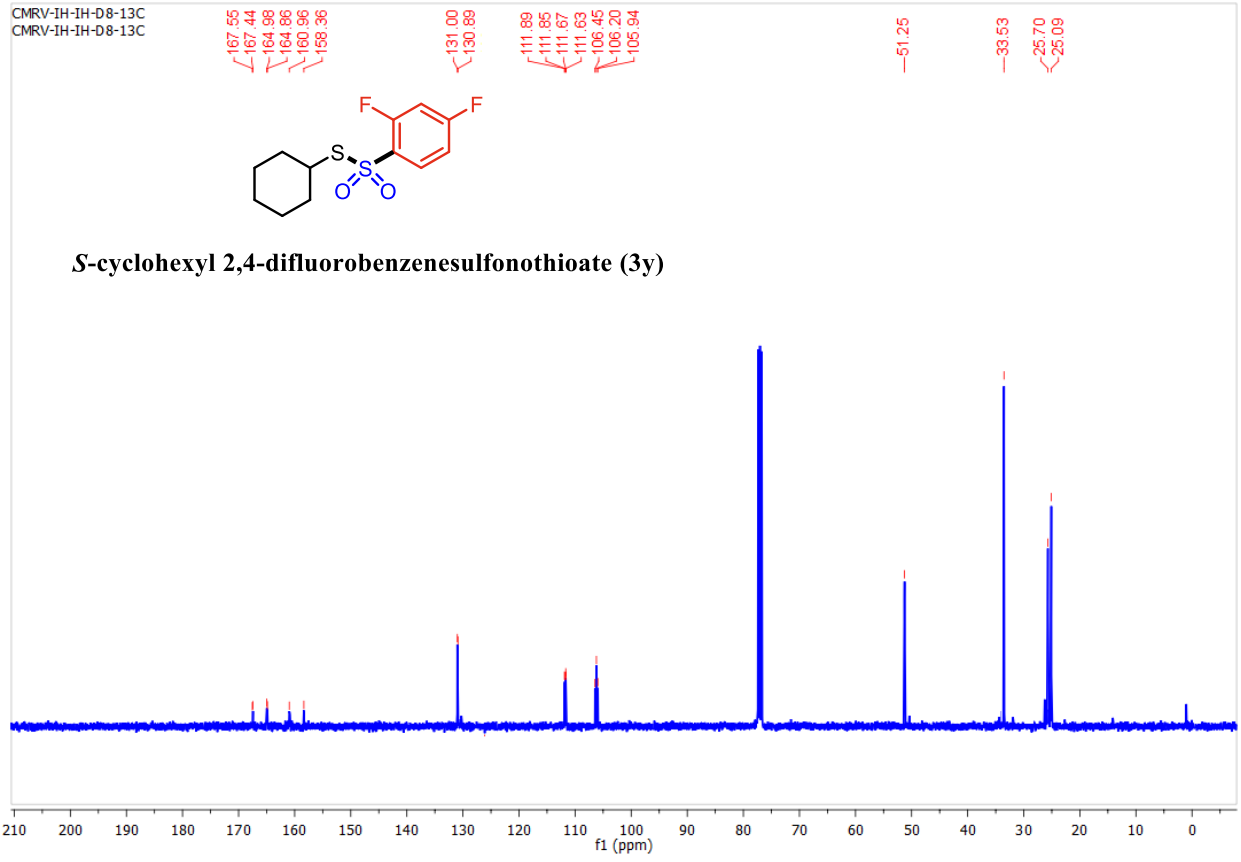
***S*-cyclohexyl 4-methylbenzenesulfonothioate (3x)**



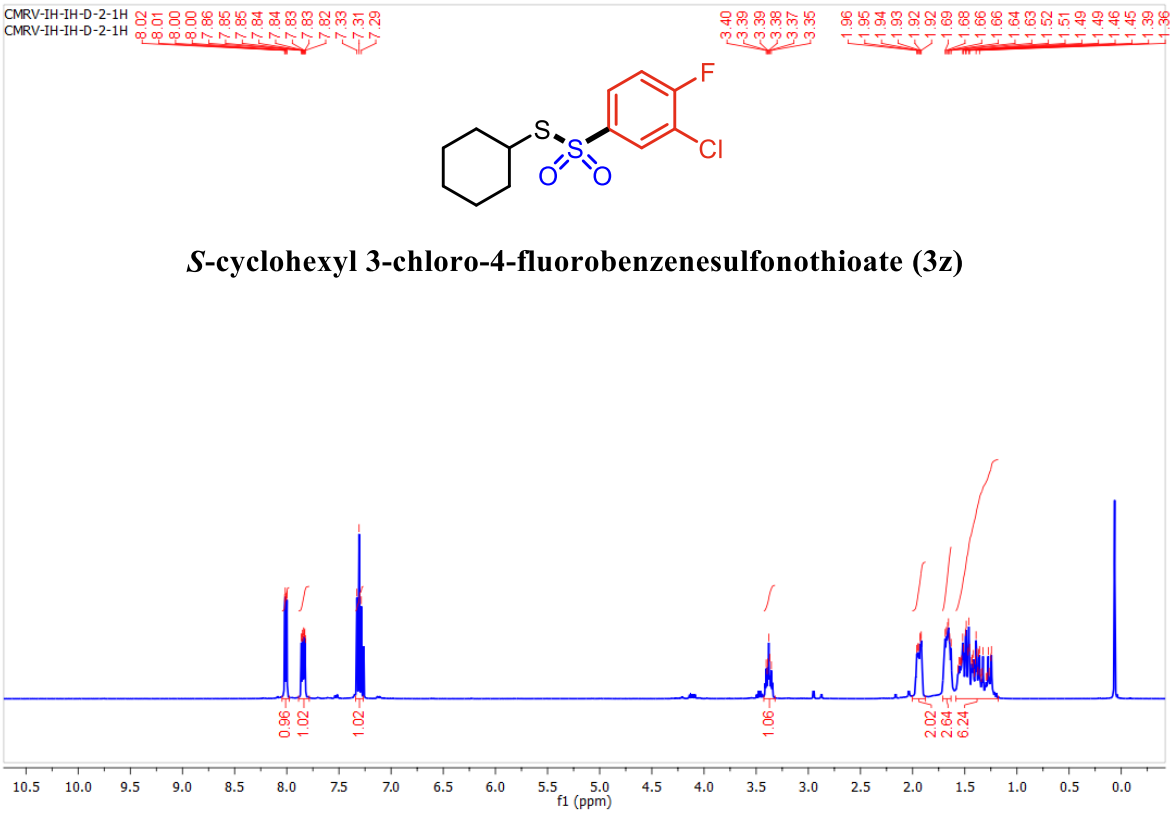
***S*-cyclohexyl 4-methylbenzenesulfonothioate (3x)**



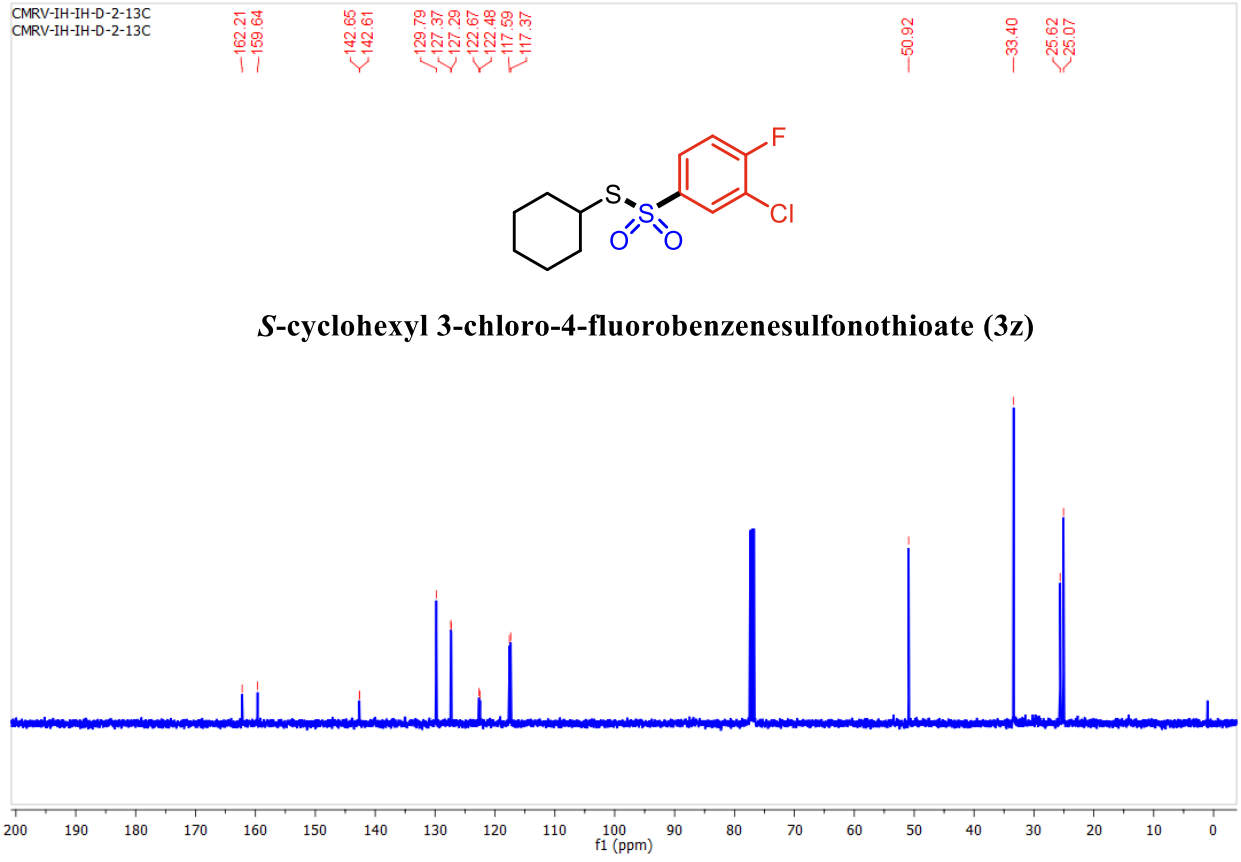
***S*-cyclohexyl 2,4-difluorobenzenesulfonothioate (3y)**



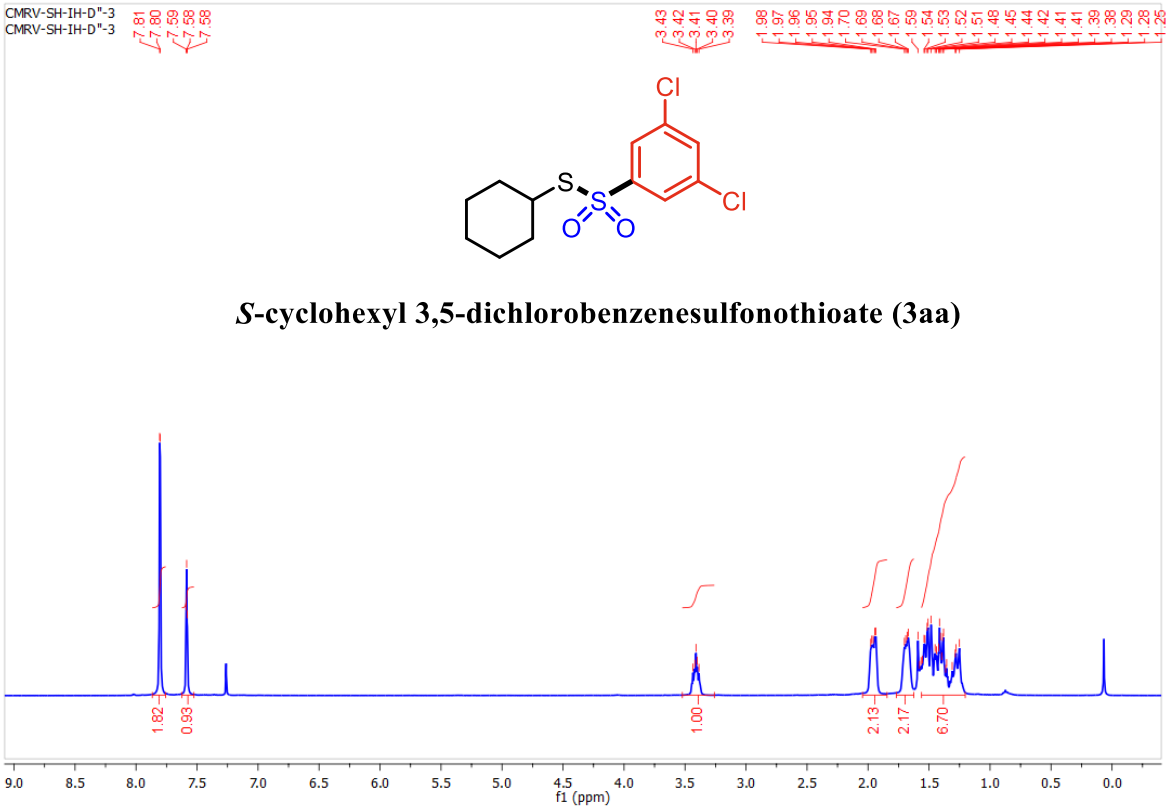
***S*-cyclohexyl 2,4-difluorobenzenesulfonothioate (3y)**



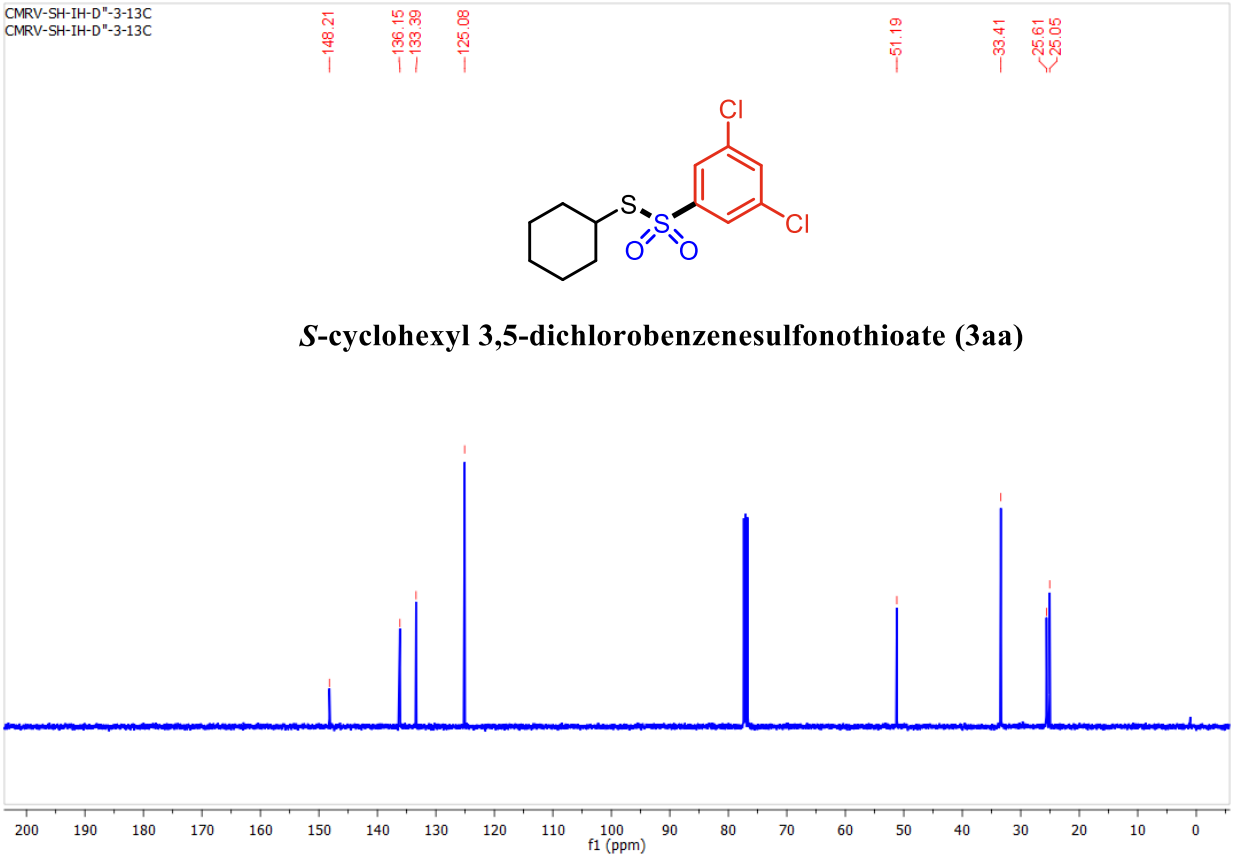
***S*-cyclohexyl 3-chloro-4-fluorobenzenesulfonothioate (3z)**



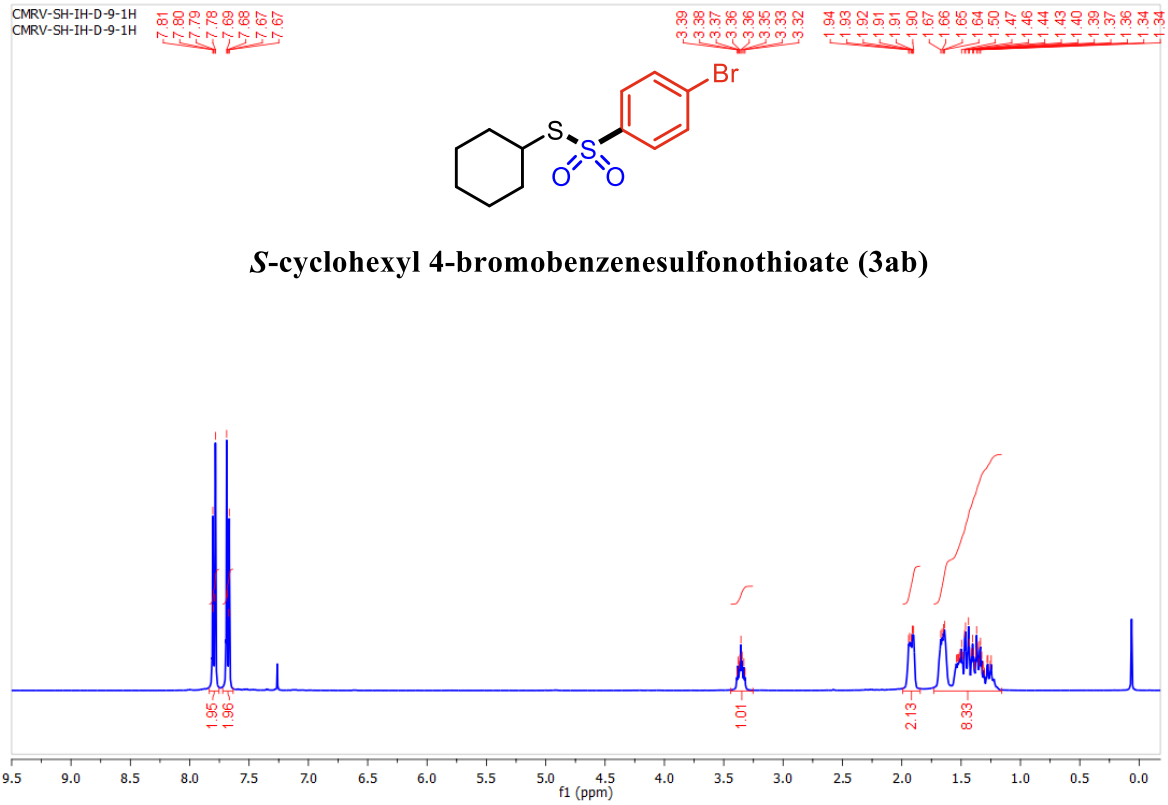
***S*-cyclohexyl 3-chloro-4-fluorobenzenesulfonothioate (3z)**



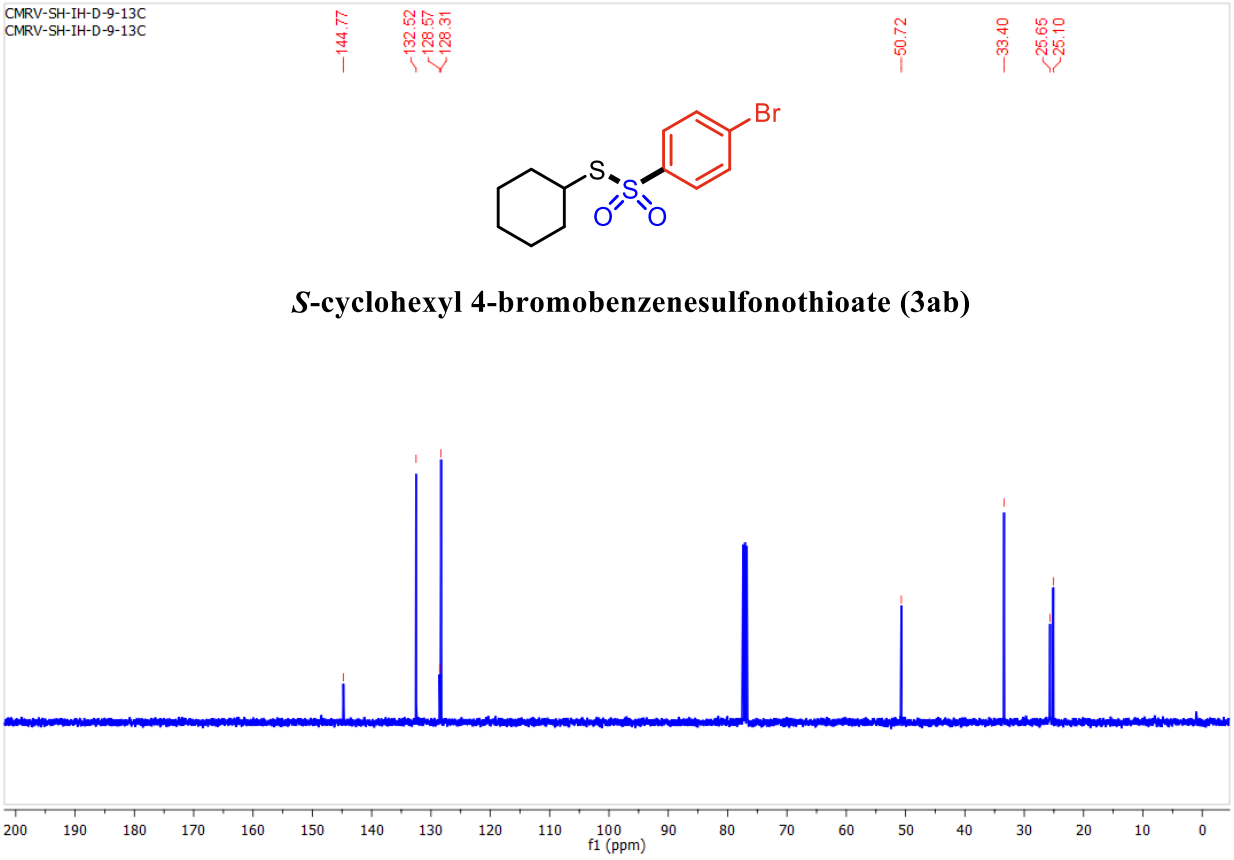
***S*-cyclohexyl 3,5-dichlorobenzenesulfonothioate (3aa)**



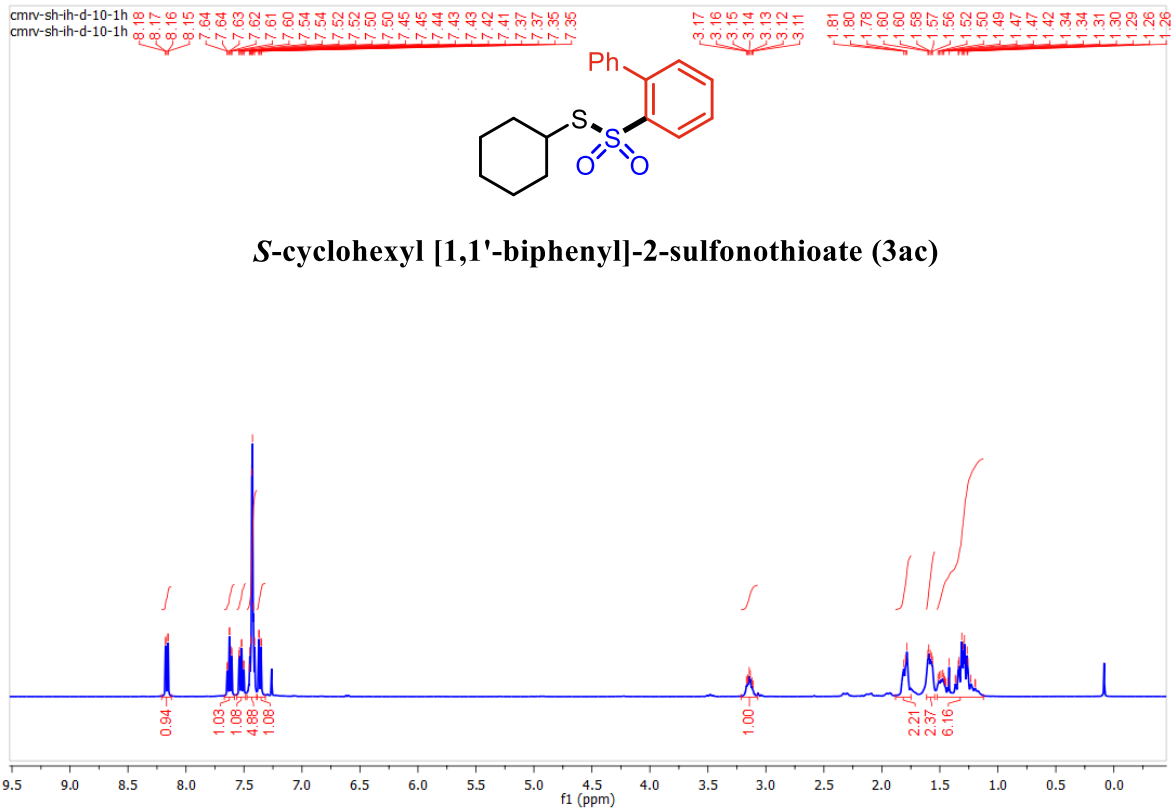
***S*-cyclohexyl 3,5-dichlorobenzenesulfonothioate (3aa)**



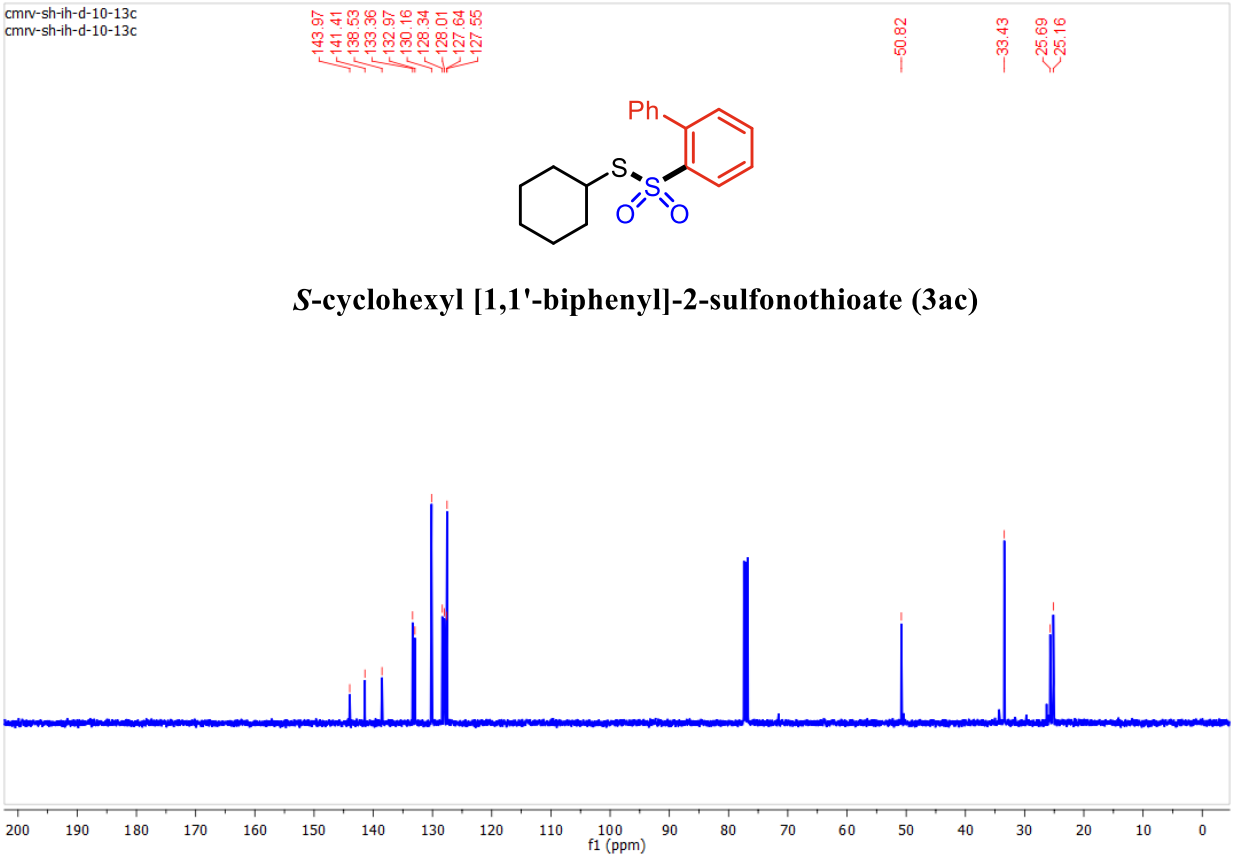
***S*-cyclohexyl 4-bromobenzenesulfonothioate (3ab)**



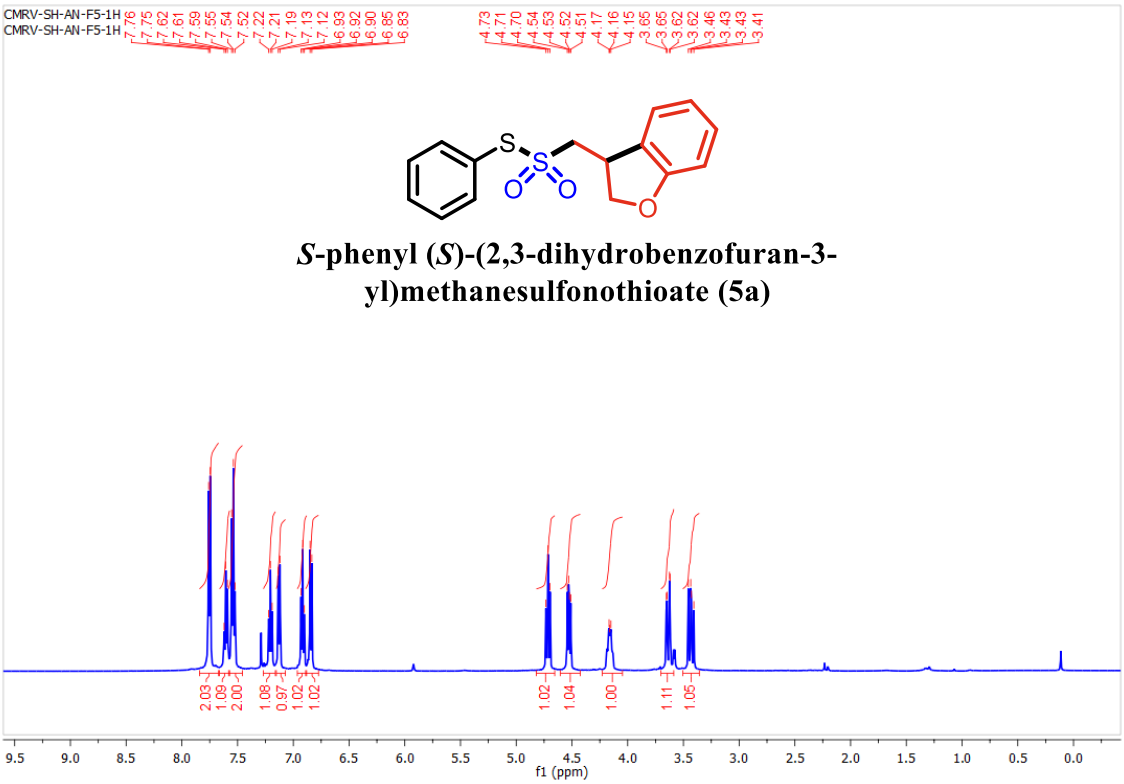
***S*-cyclohexyl 4-bromobenzenesulfonothioate (3ab)**



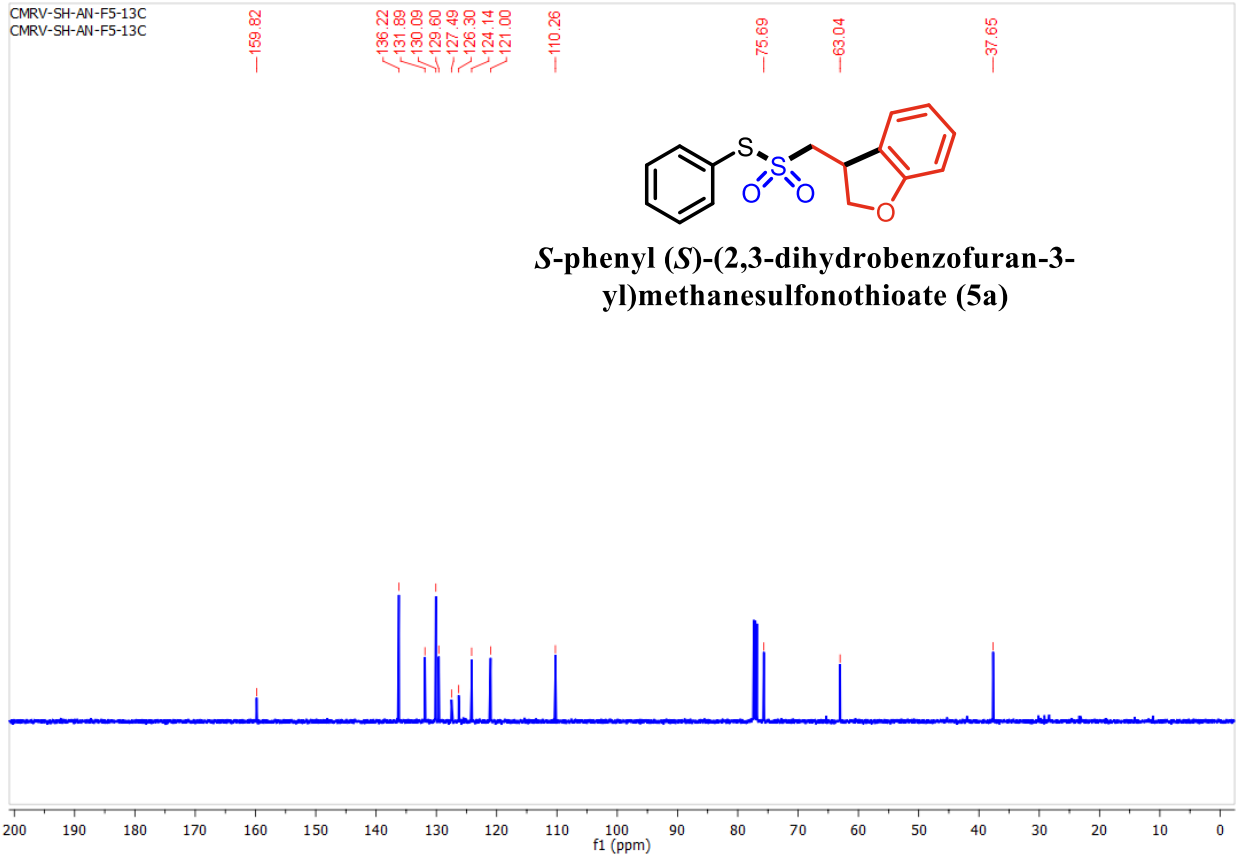
***S*-cyclohexyl [1,1'-biphenyl]-2-sulfonothioate (3ac)**



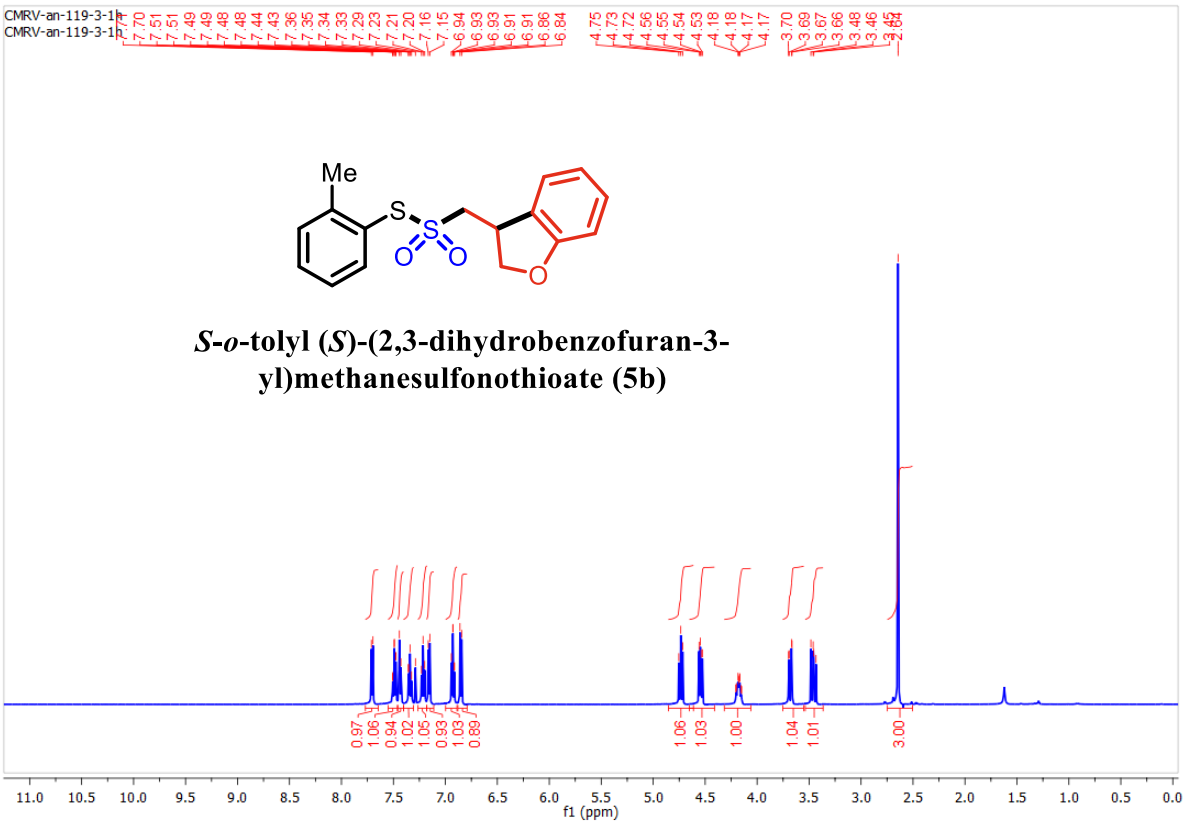
***S*-cyclohexyl [1,1'-biphenyl]-2-sulfonothioate (3ac)**



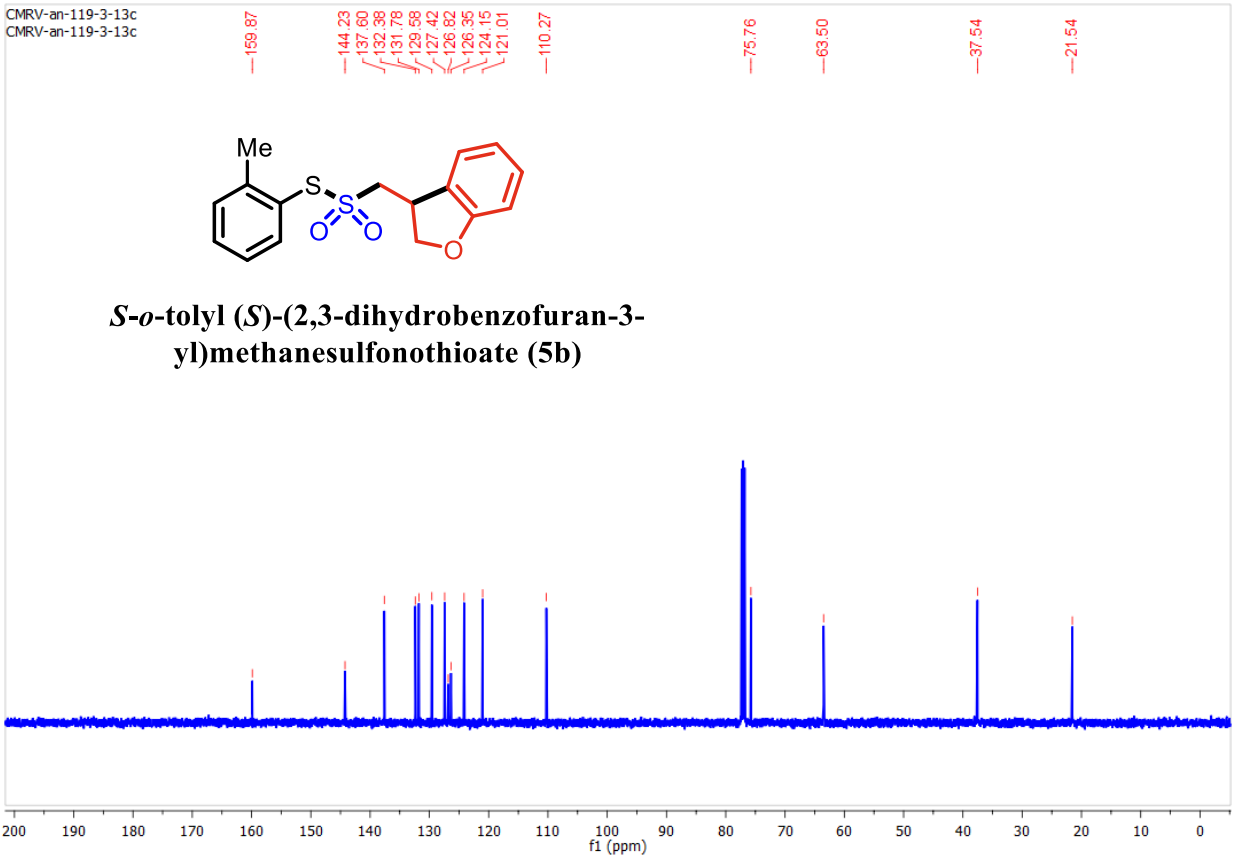
_S_-phenyl (_S_)-(2,3-dihydrobenzofuran-3-yl)methanesulfonothioate (5a)



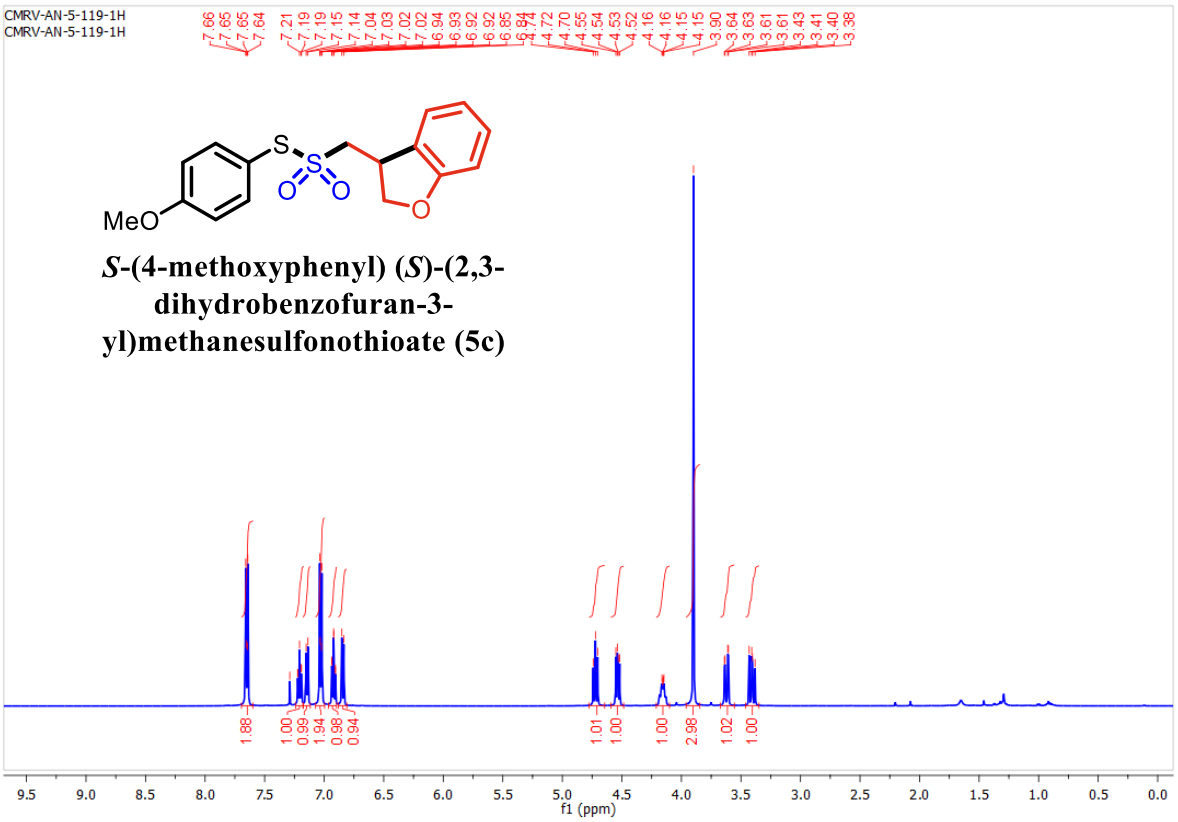
_S_-phenyl (_S_)-(2,3-dihydrobenzofuran-3-yl)methanesulfonothioate (5a)



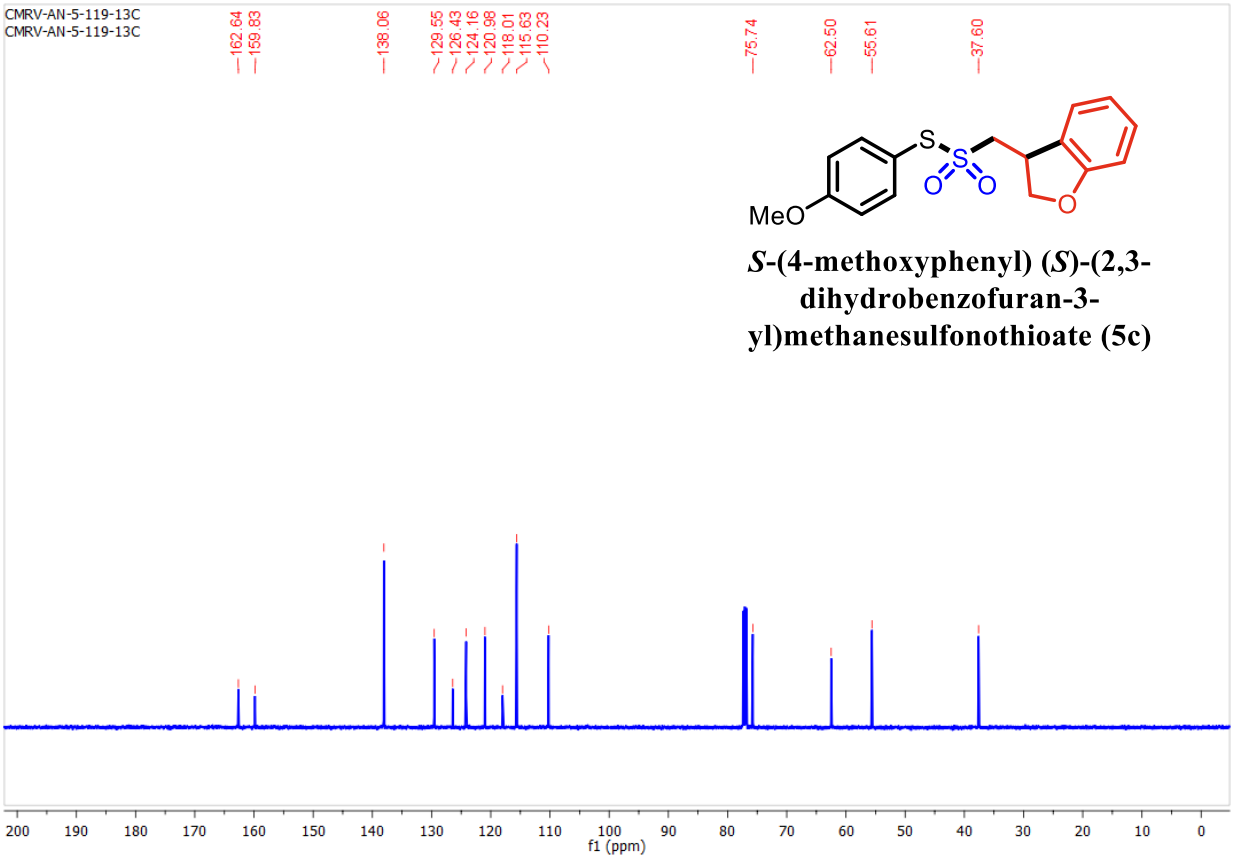
***S*-*o*-tolyl (*S*)-(2,3-dihydrobenzofuran-3-yl)methanesulfonothioate (5b)**



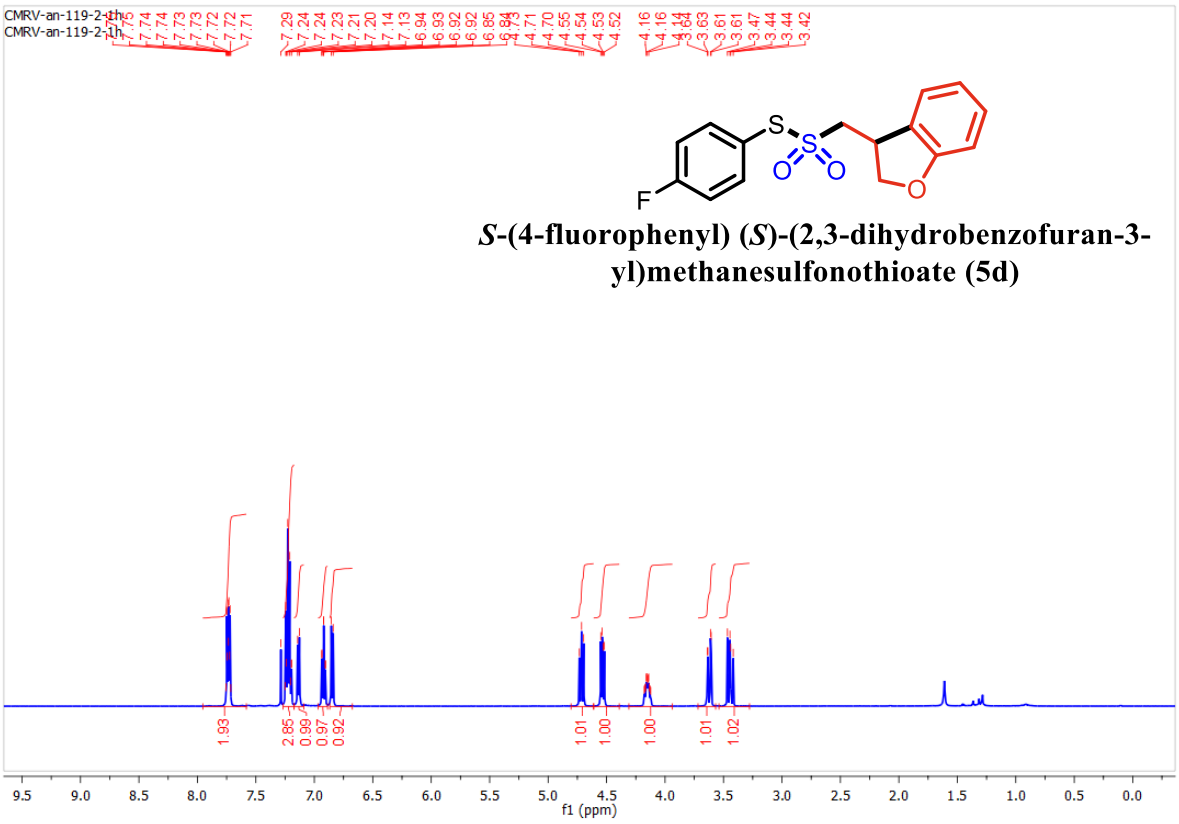
***S*-*o*-tolyl (*S*)-(2,3-dihydrobenzofuran-3-yl)methanesulfonothioate (5b)**



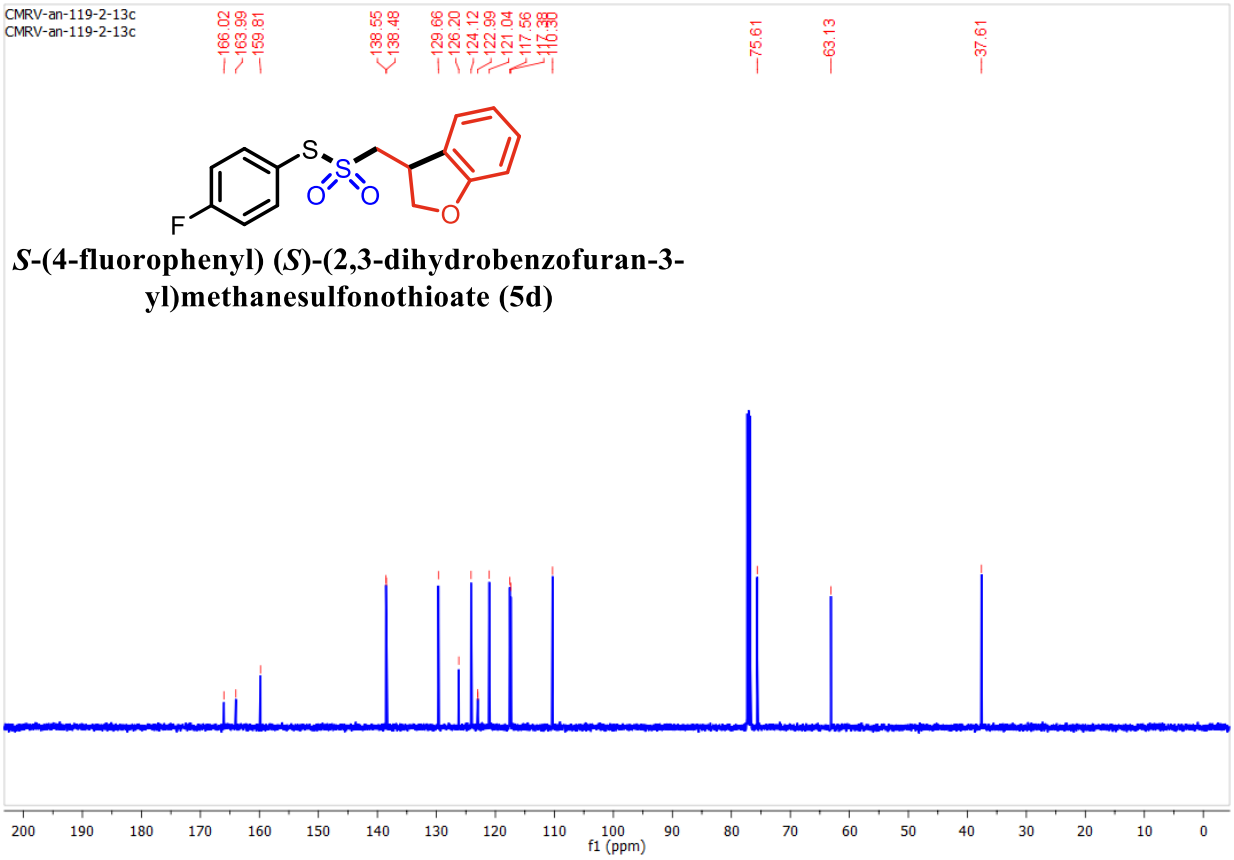
***S*-(4-methoxyphenyl) (*S*)-(2,3-dihydrobenzofuran-3-yl)methanesulfonothioate (5c)**



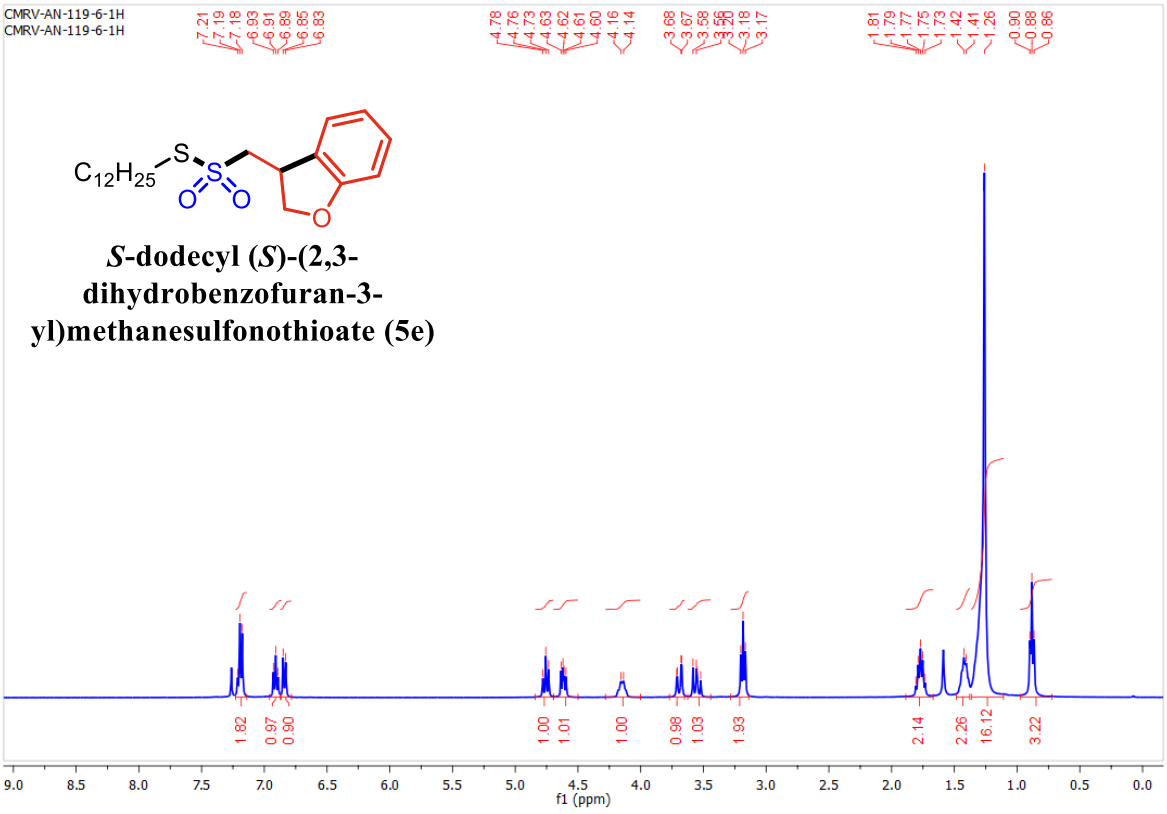
***S*-(4-methoxyphenyl) (*S*)-(2,3-dihydrobenzofuran-3-yl)methanesulfonothioate (5c)**

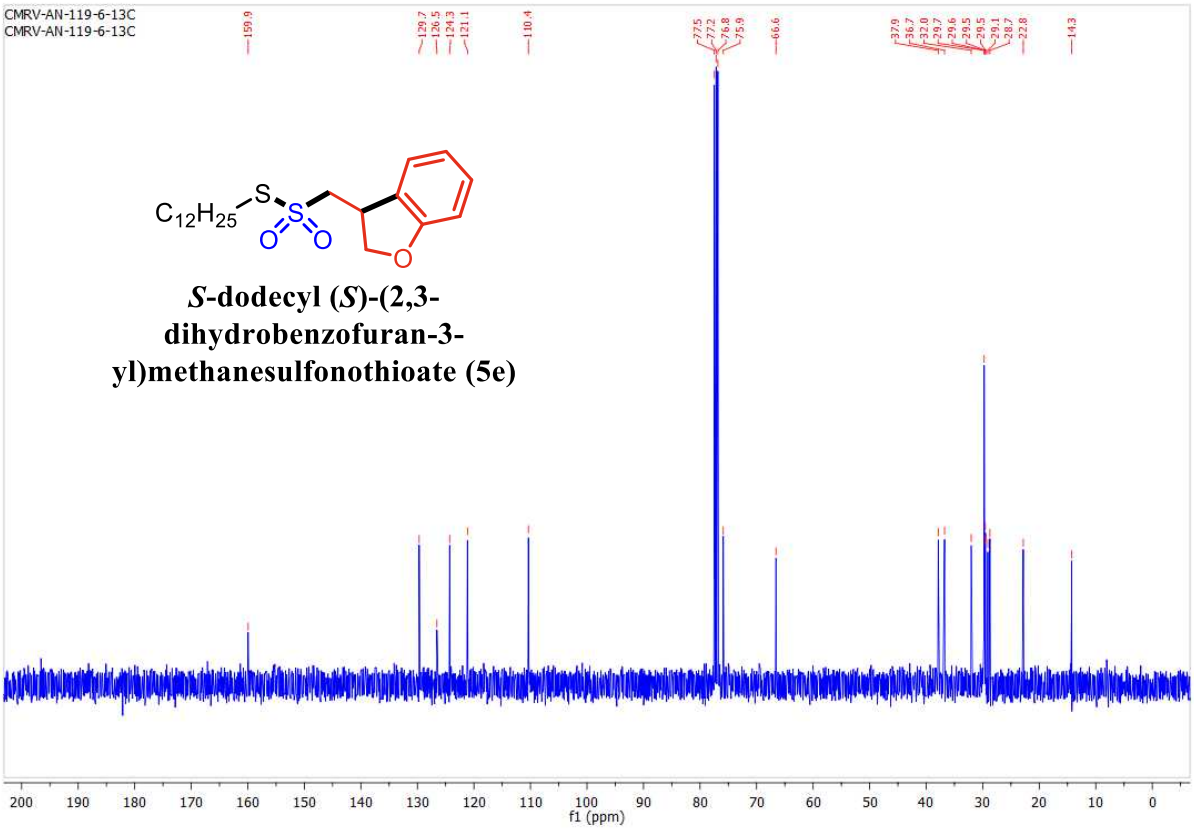


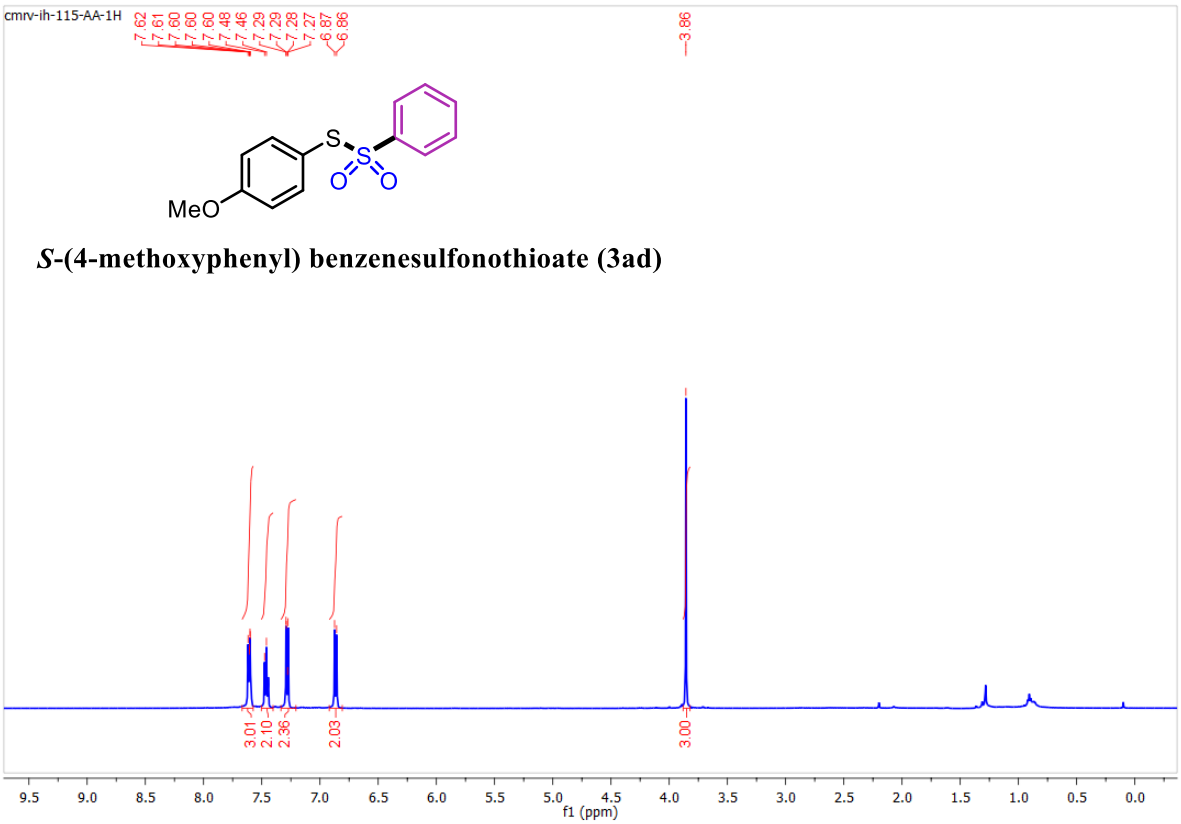
***S*-(4-fluorophenyl) (*S*)-(2,3-dihydrobenzofuran-3-yl)methanesulfonothioate (5d)**



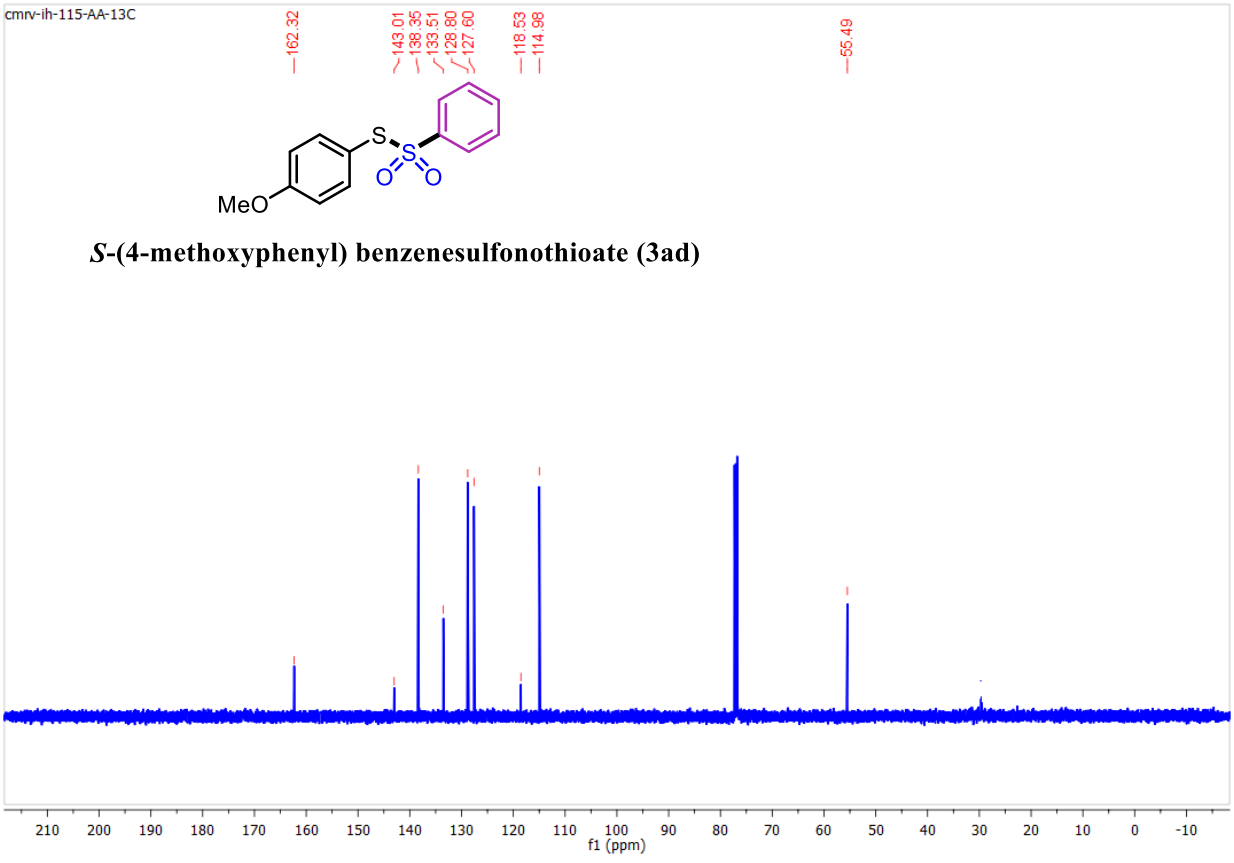
***S*-(4-fluorophenyl) (*S*)-(2,3-dihydrobenzofuran-3-yl)methanesulfonothioate (5d)**


CMRV-AN-119-6-1H
CMRV-AN-119-6-1H
7.21
7.19
7.18
6.93
6.91
6.89
6.85
6.83
4.78
4.76
4.73
4.63
4.62
4.61
4.60
4.16
4.14
3.68
3.67
3.58
3.56
3.20
3.18
3.17
1.81
1.79
1.77
1.75
1.73
1.42
1.41
1.26
0.90
0.88
0.86
C12H25
S
S
O
O
O
S-dodecyl (S)-(2,3-dihydrobenzofuran-3-yl)methanesulfonothioate (5e)
1.82
0.97
0.90
1.00
1.01
1.00
0.98
1.03
1.93
2.14
2.26
16.12
3.22
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

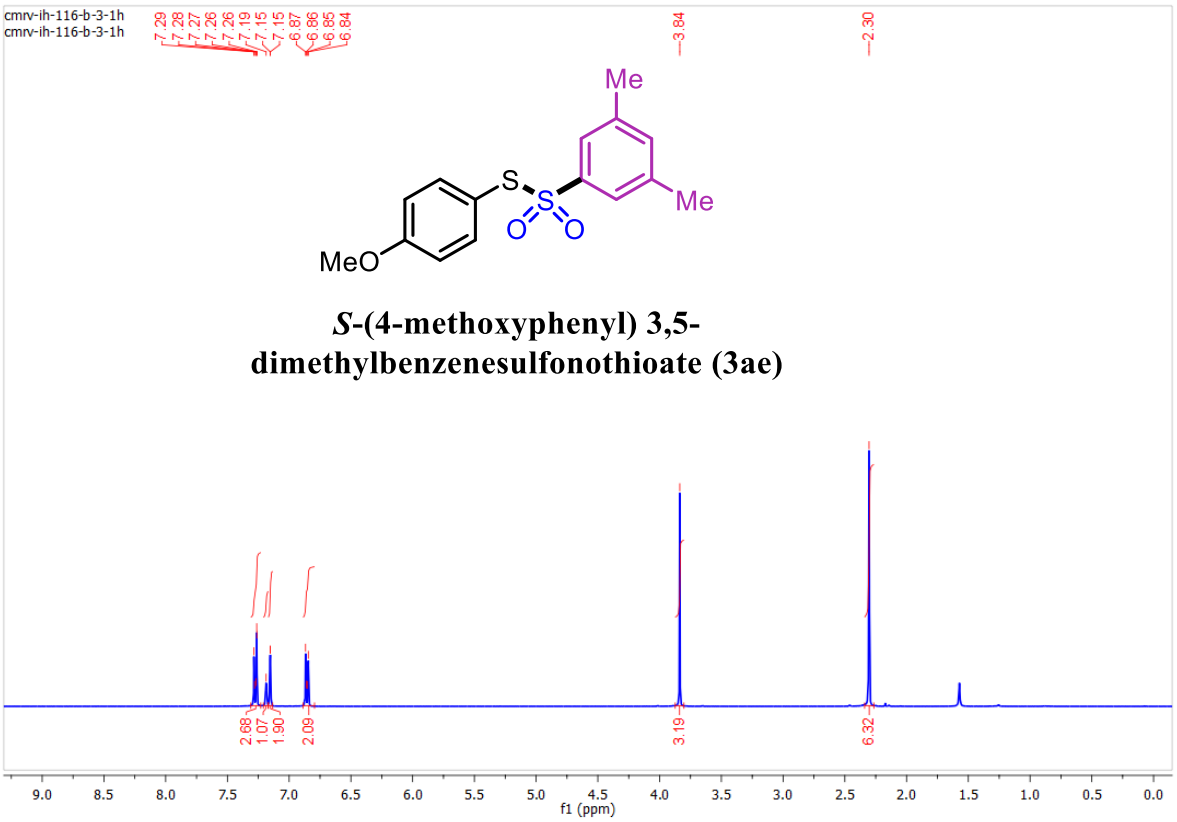

CMRV-AN-119-6-13C
CMRV-AN-119-6-13C
159.9
129.7
126.5
124.3
121.1
110.4
77.5
77.2
76.8
75.9
66.6
37.9
36.7
32.0
29.7
29.6
29.5
29.5
29.1
28.7
22.8
14.3
C12H25
S
S
O
O
O
S-dodecyl (S)-(2,3-dihydrobenzofuran-3-yl)methanesulfonothioate (5e)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



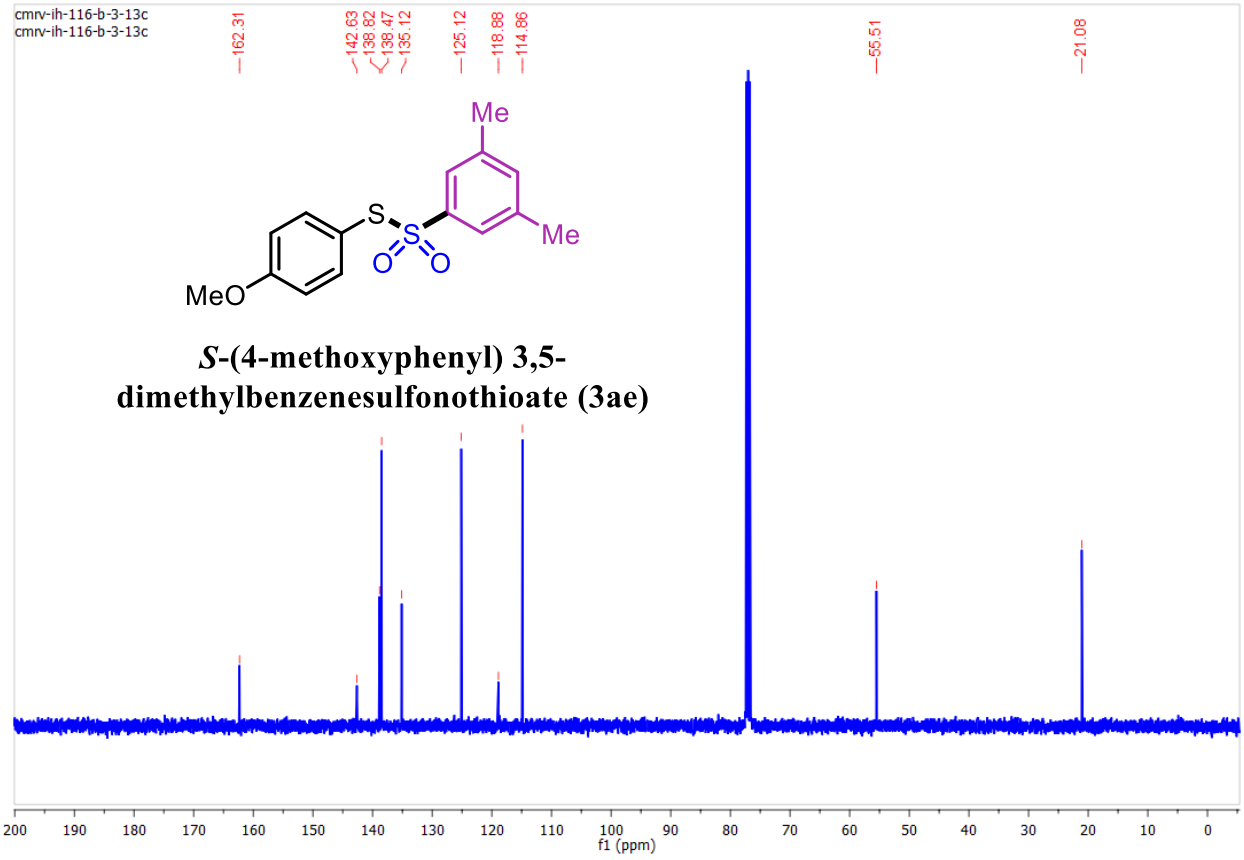
***S*-(4-methoxyphenyl) benzenesulfonothioate (3ad)**



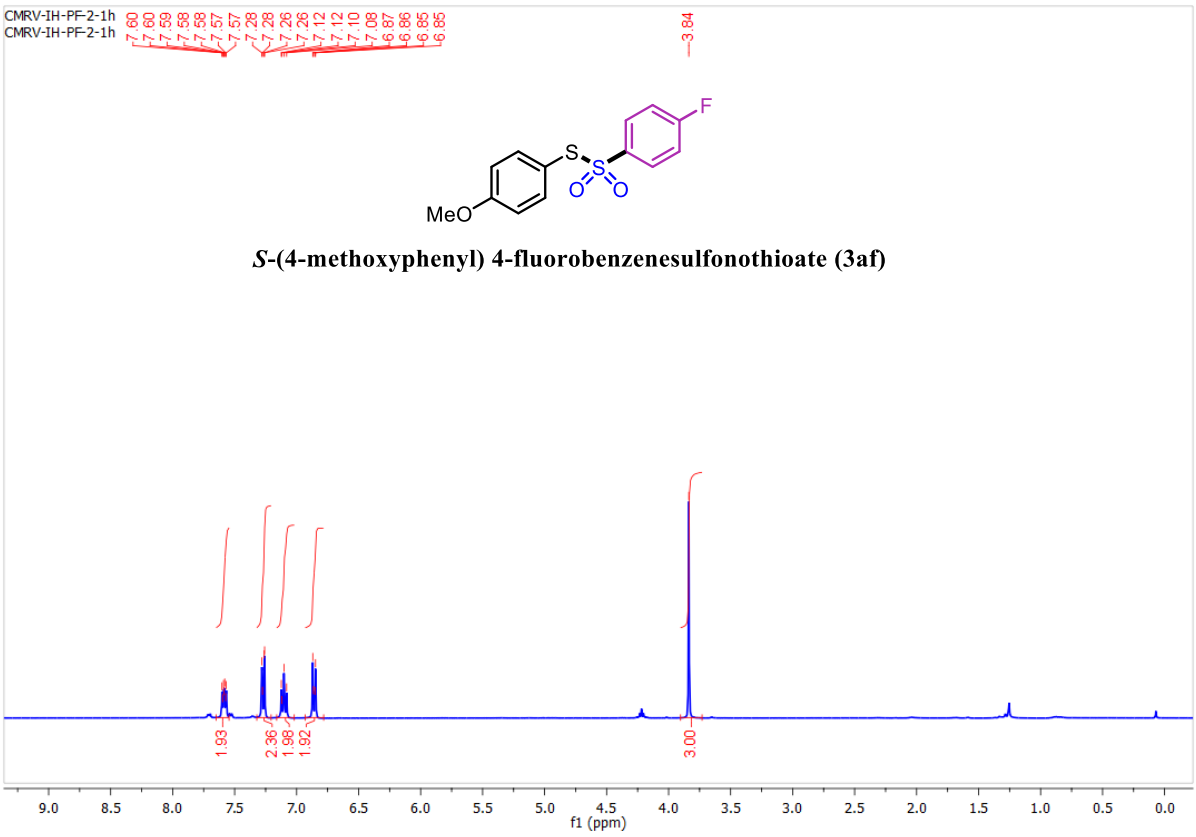
***S*-(4-methoxyphenyl) benzenesulfonothioate (3ad)**



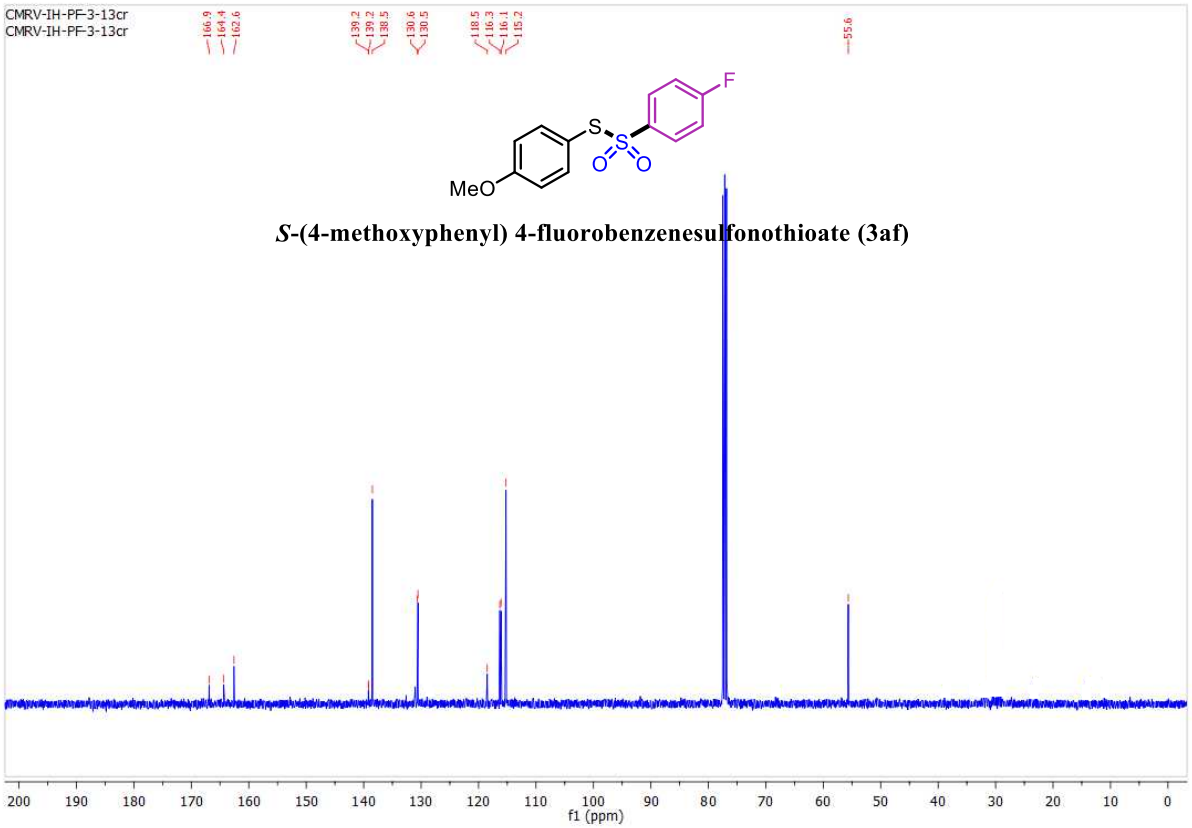
_S_-(4-methoxyphenyl) 3,5-dimethylbenzenesulfonothioate (3ae)



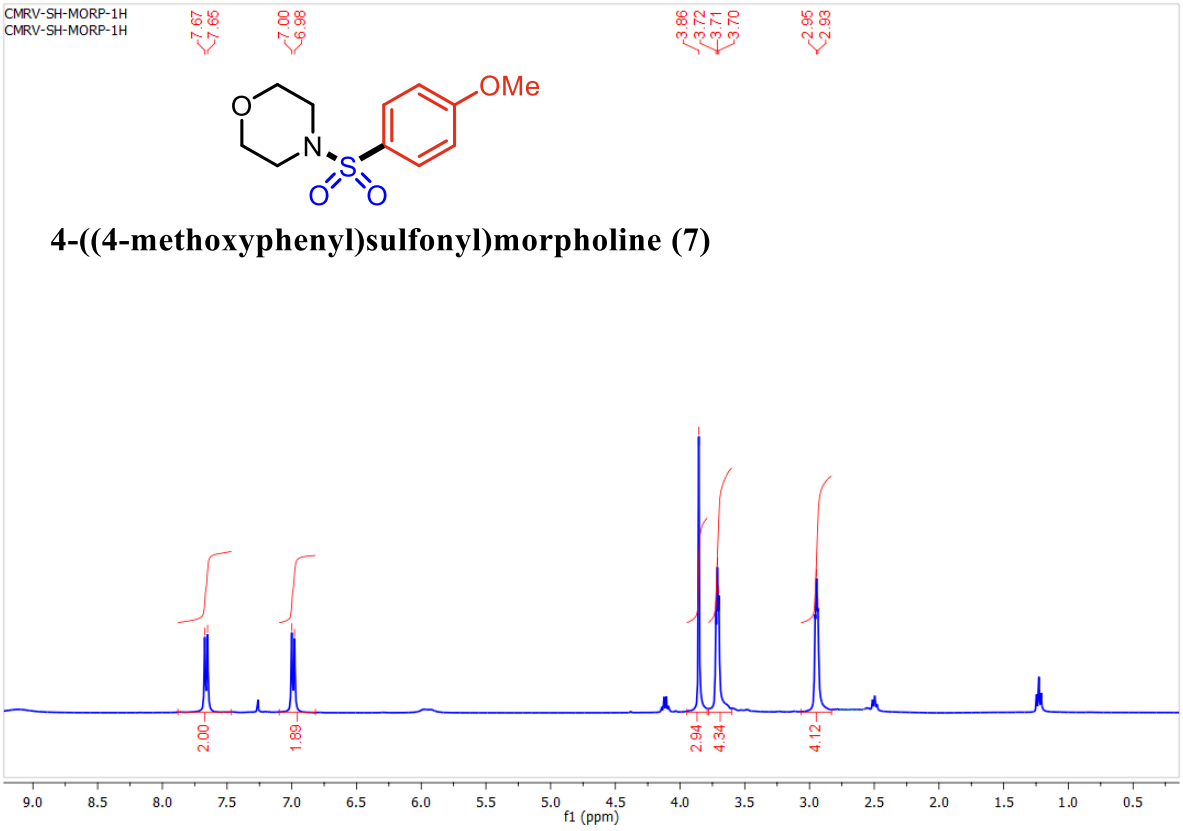
_S_-(4-methoxyphenyl) 3,5-dimethylbenzenesulfonothioate (3ae)



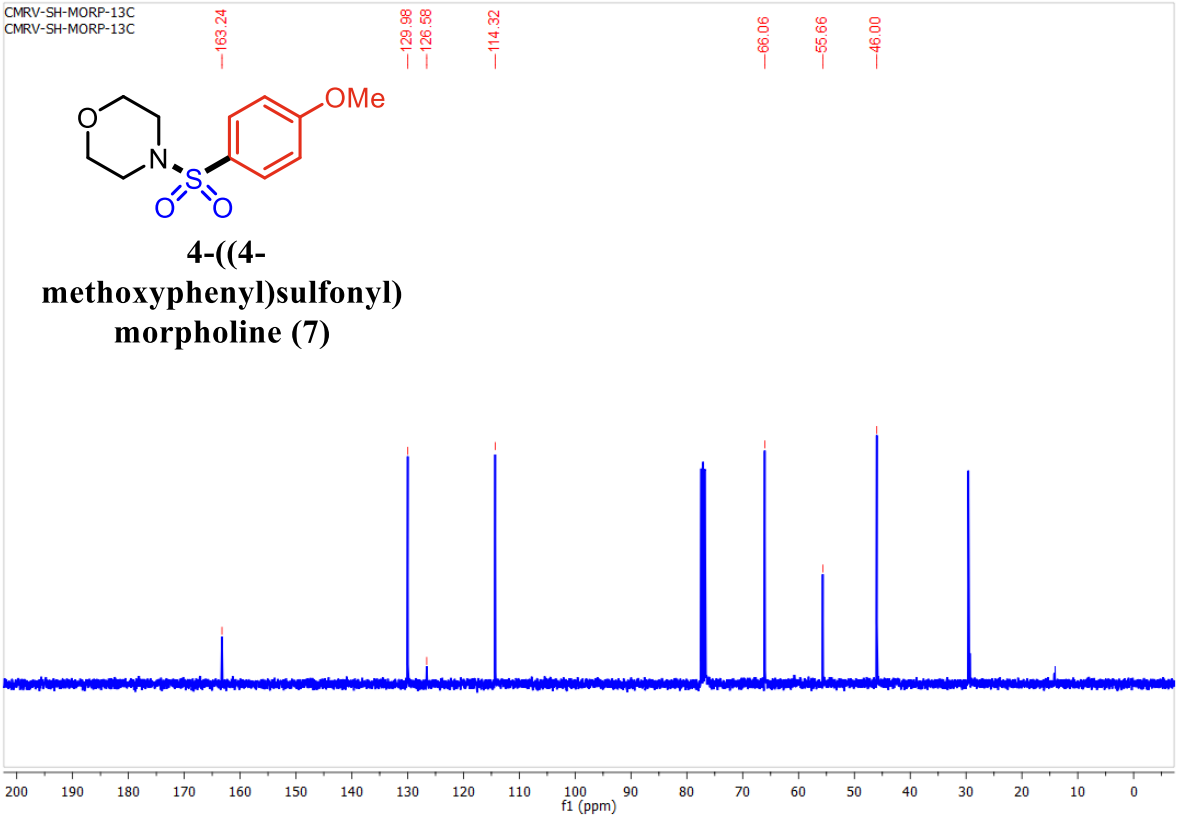
***S*-(4-methoxyphenyl) 4-fluorobenzenesulfonothioate (3af)**



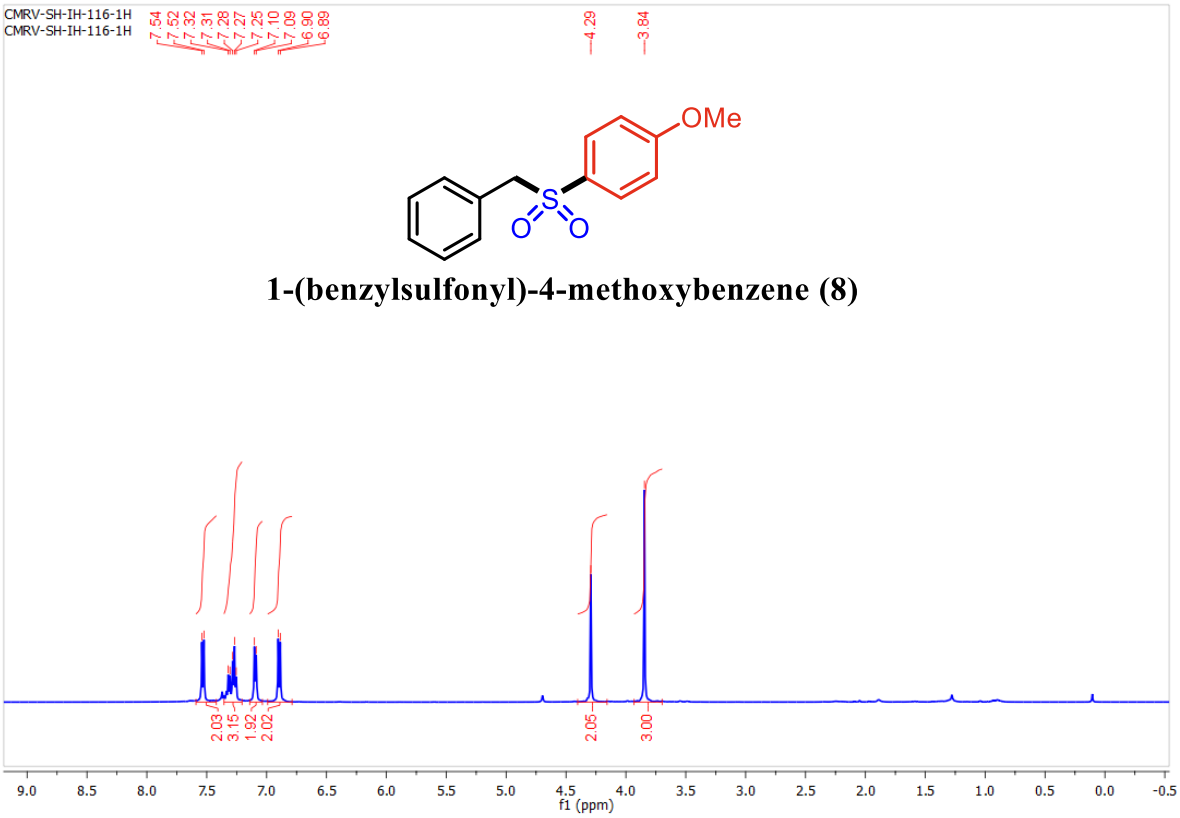
***S*-(4-methoxyphenyl) 4-fluorobenzenesulfonothioate (3af)**



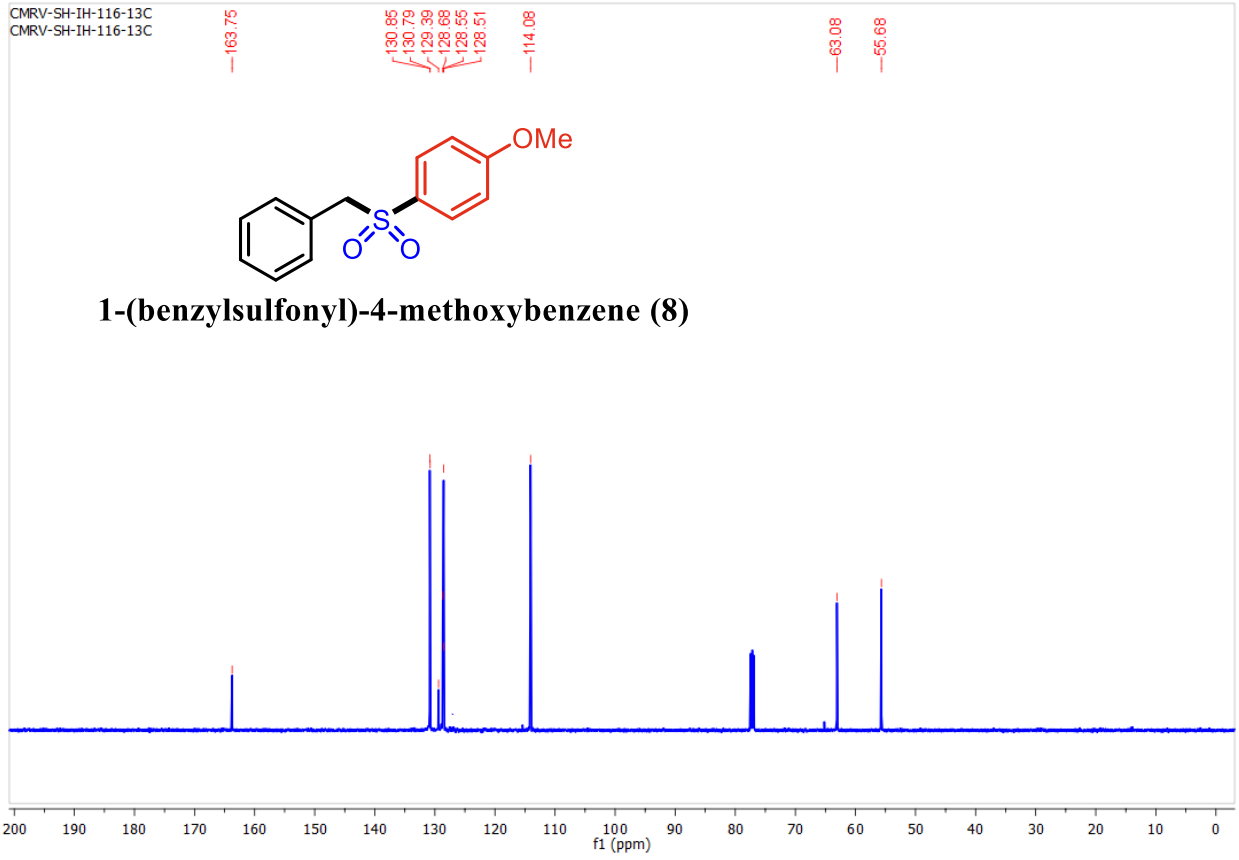
4-((4-methoxyphenyl)sulfonyl)morpholine (7)



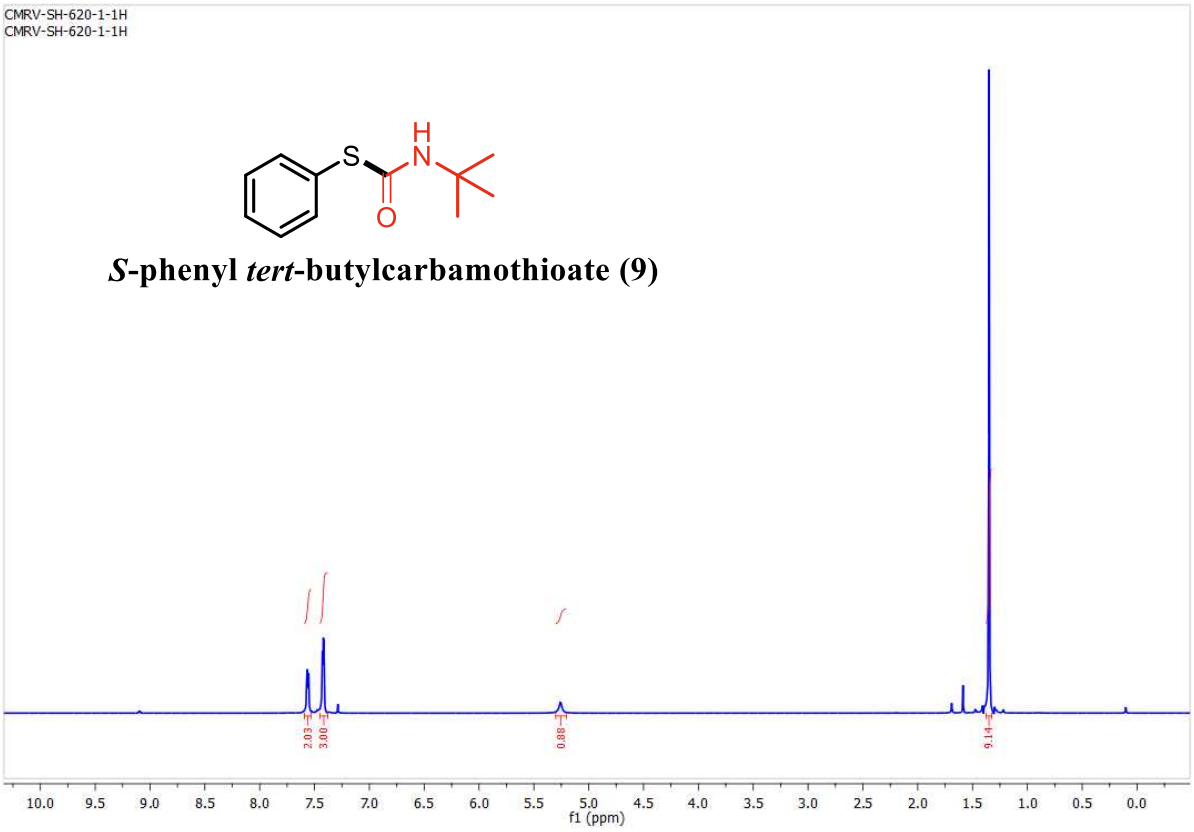
4-((4-methoxyphenyl)sulfonyl) morpholine (7)



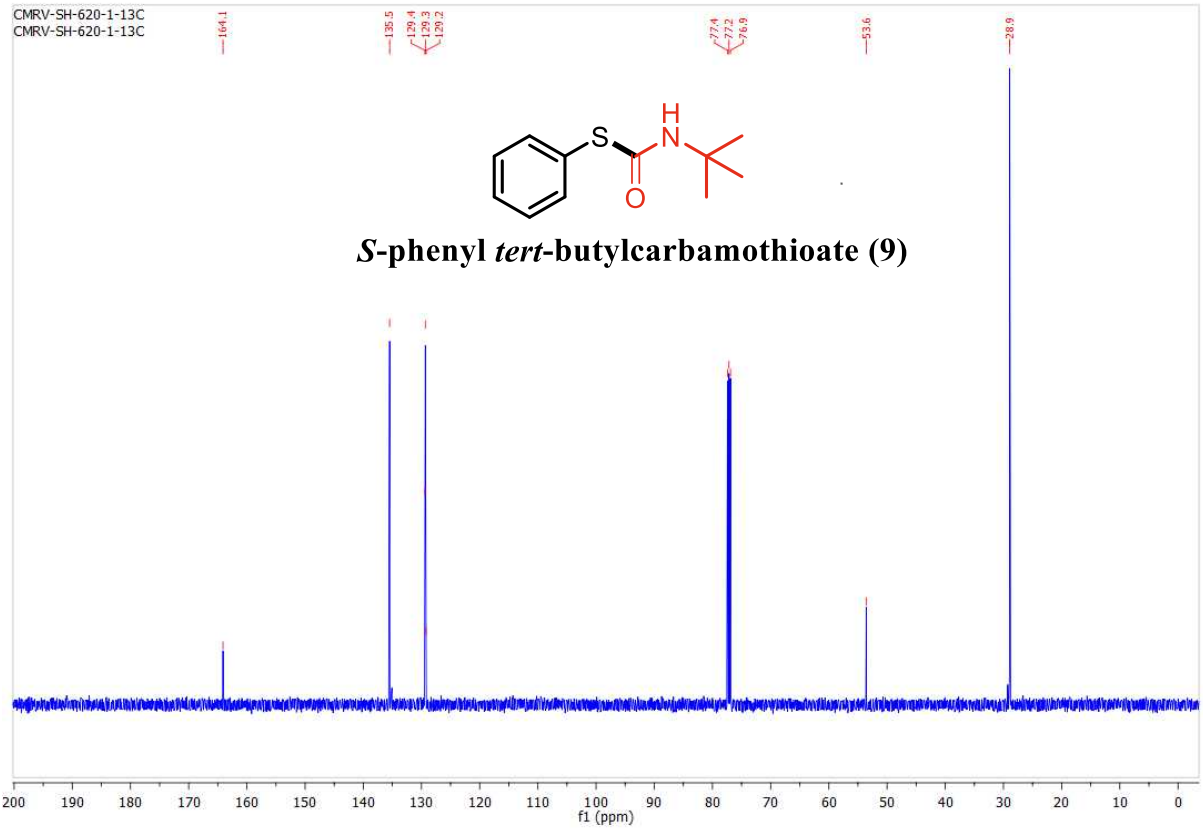
1-(benzylsulfonyl)-4-methoxybenzene (8)



1-(benzylsulfonyl)-4-methoxybenzene (8)



***S*-phenyl *tert*-butylcarbamothioate (9)**



***S*-phenyl *tert*-butylcarbamothioate (9)**