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Supporting Information

Direct Sulfoxidation of Aromatic Methyl Thioethers with Aryl Halides by Copper-Catalyzed C(sp^3)-H Bond Activation

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Contents

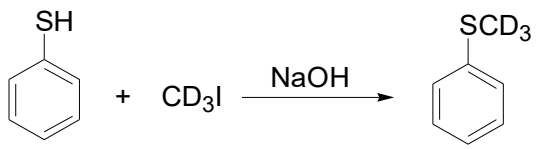
Experimental Details

General Information

All reagents used in experiment were obtained from commercial sources and used without further purification. Solvents for chromatography were technical grade and distilled prior for using. Solvent mixtures were understood as volume/volume. Chemical yields refer to pure isolated substances. Catalysts were purchased from Alfa Aesar (Analytical reagent). Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates with F-254 indicator, visualized by irradiation with UV light.

The NMR spectra were recorded on Bruker AVANCE III-400 spectrometry at 400 MHz and 100 MHz for ^{1}H and ^{13}C NMR in $CDCl_3$, respectively. The NMR chemical shift was reported in ppm relative to 7.26 and 77 ppm of $CDCl_3$ as the standards of ^{1}H and ^{13}C NMR, respectively. The NMR spectra were reported in delta (δ) units, parts per million (ppm) downfield from the internal standard and coupling constants were reported in Hertz (Hz). Multiplicities were indicated s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). The mass spectra were performed on a Bruker Esquire 3000plus mass spectrometer equipped with ESI interface and ion trap analyzer. The ESI-HRMS were tested on Bruker 7-tesla FT-ICR MS equipped with an electrospray source.

Synthesis of trideuteromethylsulfanylbenzene

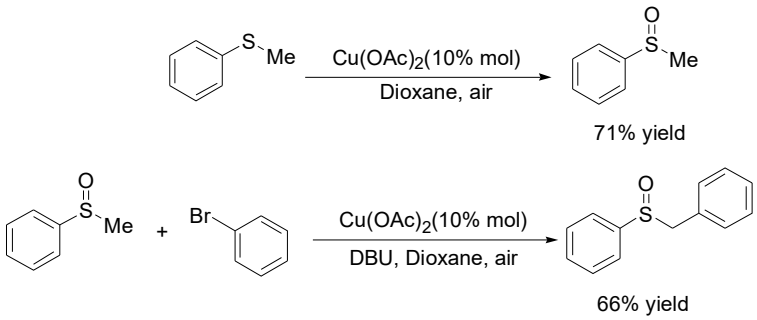


To a solution of Benzenethiol (1.10 g, 10 mmol) was added NaOH (600 mg, 15 mmol) and dry THF (10 mL). The resulting mixture was cooled to 0 °C, CD_3I (1.45 g, 10 mmol, diethyl ether, 99 atom% D) was slowly added. The resulting mixture was

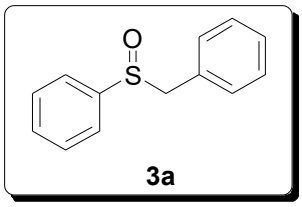
stirred overnight at room temperature. Saturated NH_4Cl was added, and the resulting solution was extracted with Et_2O for three times, combined the organic layers, dried over Na_2SO_4, distillation to give colorless oil (0.851 g, 67%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.33-7.21 (m, 3 H), 7.19-7.04 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 129.1, 128.3, 125.3, 21.4. ESI-HRMS *m*/*z*: Calcd for $C_7H_5SD_2^-$ $[M-D]^-$ 127.0532, found 127.0534.

The Two Controlled Experiments

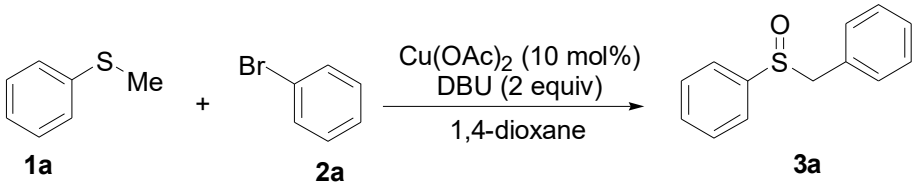
The two controlled experiments as the referee quested. The results showed both the two reaction proceeded smoothly.



Analytical Datas



Benzylsulfinylbenzene (3a):



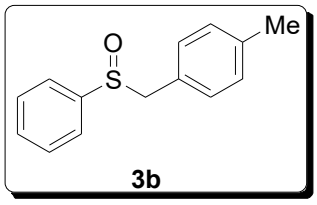
A solution of methylsulfanylbenzene **1a** (0.5 mmol, 62.1 mg), bromobenzene **2a** (0.6 mmol, 94.2 mg), $Cu(OAc)_2$ (10 mol%, 9.1 mg), and DBU (2 equiv, 152.2 mg) in 1,4-dioxane (3 mL) was stirred under air. After stirred at 110 °C for 10 h, it was cooled to room temperature. Then the reaction mixture was quenched with saturated salt water (10 mL). After that, the solution was extracted with ethyl acetate (3 × 10 mL), and then washed with saturated Na_2CO_3 solution. The organic layers were combined

and dried by Na_2SO_4 and concentrated in vacuo. The pure product benzylsulfinylbenzene **3a** (94.1 mg, 87% yield) was afforded by flash column chromatography on silica gel (cyclohexane/ethyl acetate = 5:1).

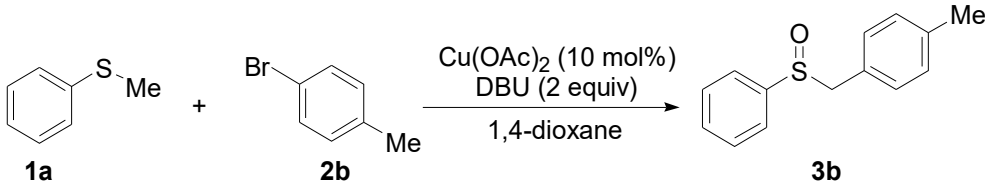
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.37 (m, 5 H), 7.34-7.23 (m, 3 H), 7.05-6.94 (m, 2 H), 4.11 (d, *J* = 12.6 Hz, 1 H), 4.02 ppm (d, *J* = 12.6 Hz, 1 H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 131.3, 130.5, 129.2, 128.9, 128.5, 128.3, 124.5, 63.7;

ESI-HRMS *m*/*z*: Calcd for $C_{13}H_{12}NaOS^+$ $[M+Na]^+$ 239.0507, found 239.0508.



1-Benzenesulfinylmethyl-4-methylbenzene (3b):

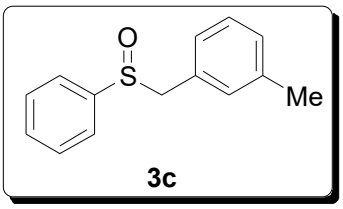


A solution of methylsulfanylbenzene **1a** (0.5 mmol, 62.1 mg), 1-bromo-4-methylbenzene **2b** (0.6 mmol, 102.6 mg), $Cu(OAc)_2$ (10 mol%, 9.1 mg), and DBU (2 equiv, 152.2 mg) in 1,4-dioxane (3 mL) was stirred under air. After stirred at 110 °C for 10 h, it was cooled to room temperature. Then the reaction mixture was quenched with saturated salt water (10 mL). After that, the solution was extracted with ethyl acetate (3 × 10 mL), and then washed with saturated Na_2CO_3 solution. The organic layers were combined and dried by Na_2SO_4 and concentrated in vacuo. The pure product 1-benzenesulfinylmethyl-4-methylbenzene **3b** (95.6 mg, 83% yield) was afforded by flash column chromatography on silica gel (cyclohexane/ethyl acetate = 5:1).

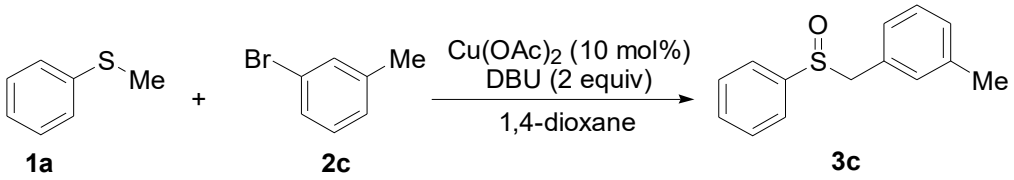
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.34 (m, 5 H), 7.06 (d, *J* = 7.9 Hz, 2 H), 6.87 (d, *J* = 7.9 Hz, 2 H), 4.08 (d, *J* = 12.6 Hz, 1 H), 3.97 (d, *J* = 12.6 Hz, 1 H), 2.32 (s, H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 138.3, 131.3, 130.4, 129.3, 128.9, 126.1, 124.6, 63.5, 21.3;

ESI-HRMS *m*/*z*: Calcd for $C_{14}H_{14}NaOS^+$ $[M+Na]^+$ 253.0663, found 253.0661.



1-Benzenesulfinylmethyl-3-methylbenzene (3c):

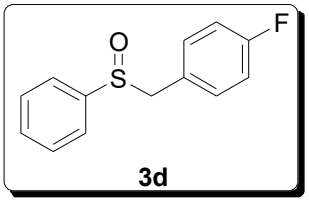


A solution of methylsulfanylbenzene **1a** (0.5 mmol, 62.1 mg), 1-bromo-3-methylbenzene **2c** (0.6 mmol, 102.6 mg), $Cu(OAc)_2$ (10 mol%, 9.1 mg), and DBU (2 equiv, 152.2 mg) in 1,4-dioxane (3 mL) was stirred under air. After stirred at 110 °C for 10 h, it was cooled to room temperature. Then the reaction mixture was quenched with saturated salt water (10 mL). After that, the solution was extracted with ethyl acetate (3 × 10 mL), and then washed with saturated Na_2CO_3 solution. The organic layers were combined and dried by Na_2SO_4 and concentrated in vacuo. The pure product 1-benzenesulfinylmethyl-3-methylbenzene **3c** (96.7 mg, 84% yield) was afforded by flash column chromatography on silica gel (cyclohexane/ethyl acetate = 5:1).

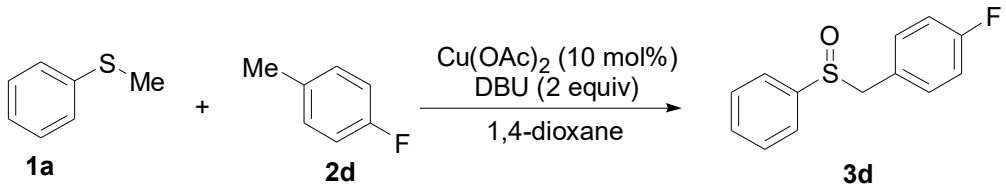
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.33 (m, 5 H), 7.17-7.03 (m, 2 H), 6.79 (m, 2 H), 4.07 (d, *J* = 12.5 Hz, 1 H), 3.93 (d, *J* = 12.5 Hz, 1 H), 2.26 (s, 3 H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 138.3, 131.2, 131.2, 129.2, 129.1, 128.9, 128.5, 127.4, 124.6, 63.9, 21.4;

ESI-HRMS *m*/*z*: Calcd for $C_{14}H_{14}NaOS^+$ $[M+Na]^+$ 253.0663, found 253.0661.



1-Benzenesulfinylmethyl-4-fluorobenzene (3d):



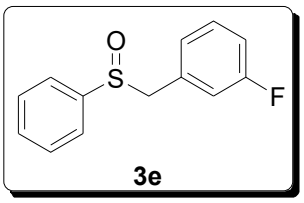
1a **2d** **3d**

A solution of methylsulfanylbenzene **1a** (0.5 mmol, 62.1 mg), 1-bromo-4-fluorobenzene **2d** (0.6 mmol, 105.0 mg), $Cu(OAc)_2$ (10 mol%, 9.1 mg), and DBU (2 equiv, 152.2 mg) in 1,4-dioxane (3 mL) was stirred under air. After stirred at 110 °C for 10 h, it was cooled to room temperature. Then the reaction mixture was quenched with saturated salt water (10 mL). After that, the solution was extracted with ethyl acetate (3 × 10 mL), and then washed with saturated Na_2CO_3 solution. The organic layers were combined and dried by Na_2SO_4 and concentrated in vacuo. The pure product 1-benzenesulfinylmethyl-4-fluorobenzene **3d** (108.9 mg, 93% yield) was afforded by flash column chromatography on silica gel (cyclohexane/ethyl acetate = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.39 (m, 3 H), 7.35 (m, 2 H), 6.92 (d, *J* = 7.0 Hz, 4 H), 4.01 (d, *J* = 12.9 Hz, 1 H), 3.98 (d, *J* = 12.9 Hz, 1 H);

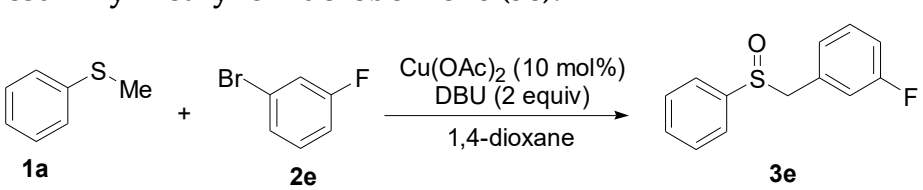
^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9 (d, *J* = 247.5 Hz), 142.5, 132.1 (d, *J* = 8.3 Hz), 131.4, 129.0, 124.9 (d, *J* = 3.3 Hz), 124.5, 115.5 (d, *J* = 21.6 Hz), 62.4;

ESI-HRMS *m*/*z*: Calcd for $C_{13}H_{11}FNaOS^+$ $[M+Na]^+$ 257.0412, found 257.0410.



3e

1-Benzenesulfinylmethyl-3-fluorobenzene (3e):



1a **2e** **3e**

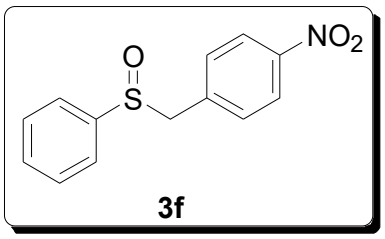
A solution of methylsulfanylbenzene **1a** (0.5 mmol, 62.1 mg), 1-bromo-3-fluorobenzene **2e** (0.6 mmol, 105.0 mg), $Cu(OAc)_2$ (10 mol%, 9.1 mg), and DBU (2 equiv, 152.2 mg) in 1,4-dioxane (3 mL) was stirred under air. After stirred at 110 °C for 10 h, it was cooled to room temperature. Then the reaction mixture was quenched

with saturated salt water (10 mL). After that, the solution was extracted with ethyl acetate (3 × 10 mL), and then washed with saturated Na_2CO_3 solution. The organic layers were combined and dried by Na_2SO_4 and concentrated in vacuo. The pure product 1-benzenesulfinylmethyl-3-fluorobenzene **3e** (103.1 mg, 88% yield) was afforded by flash column chromatography on silica gel (cyclohexane/ethyl acetate = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.36 (m, 5 H), 7.21 (m, 1 H), 6.98 (td, *J* = 7.9, 2.2 Hz, 1 H), 6.78 (d, *J* = 7.9 Hz, 1 H), 6.68 (m, 1 H), 4.03-3.99 (q, *J* = 12.5 Hz, 2 H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6 (d, *J* = 246.9 Hz), 142.6, 131.5 (d, *J* = 7.9 Hz), 131.5, 130.0 (d, *J* = 8.3 Hz), 129.1, 126.2 (d, *J* = 3.0 Hz), 124.4, 117.3 (d, *J* = 21.9 Hz), 115.3 (d, *J* = 21.0 Hz), 63.0;

ESI-HRMS *m*/*z*: Calcd for $C_{13}H_{11}FNaOS^+$ $[M+Na]^+$ 257.0412, found 257.0410.



1-Benzenesulfinylmethyl-4-nitrobenzene (3f):

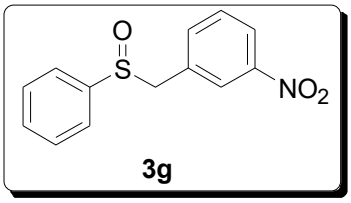
A solution of methylsulfanylbenzene **1a** (0.5 mmol, 62.1 mg), 1-Bromo-4-nitrobenzene **2f** (0.6 mmol, 121.2 mg), $Cu(OAc)_2$ (10 mol%, 9.1 mg), and DBU (2 equiv, 152.2 mg) in 1,4-dioxane (3 mL) was stirred under air. After stirred at 110 °C for 10 h, it was cooled to room temperature. Then the reaction mixture was quenched with saturated salt water (10 mL). After that, the solution was extracted with ethyl acetate (3 × 10 mL), and then washed with saturated Na_2CO_3 solution. The organic layers were combined and dried by Na_2SO_4 and concentrated in vacuo. The pure product 1-benzenesulfinylmethyl-4-nitrobenzene **3f** (117.6 mg, 90% yield) was

afforded by flash column chromatography on silica gel (cyclohexane/ethyl acetate = 5:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50-7.40 (m, 3 H), 7.39-7.34 (m, 2 H), 7.23-7.18 (m, 2 H), 6.88 (d, *J* = 8.4 Hz, 2 H), 4.01 (d, *J* = 12.8 Hz, 1 H), 3.96 (d, *J* = 12.8 Hz, 1 H);

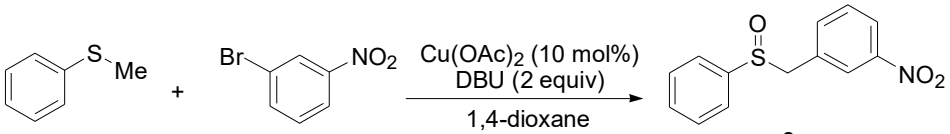
^{13}C NMR (126 MHz, $CDCl_3$) δ 142.6, 134.5, 131.7, 131.4, 129.0, 128.7, 127.6, 124.4, 62.5;

ESI-HRMS *m*/*z*: Calcd for $C_{13}H_{11}NO_3S^+$ $[M+Na]^+$ 284.0357, found 284.0355.



3g

1-Benzenesulfinylmethyl-3-nitrobenzene (3g):



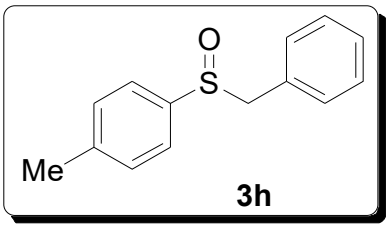
1a **2g** **3g**

A solution of methylsulfanylbenzene **1a** (0.5 mmol, 62.1 mg), 1-benzenesulfinylmethyl-3-nitrobenzene **2g** (0.6 mmol, 121.2 mg), $Cu(OAc)_2$ (10 mol%, 9.1 mg), and DBU (2 equiv, 152.2 mg) in 1,4-dioxane (3 mL) was stirred under air. After stirred at 110 °C for 10 h, it was cooled to room temperature. Then the reaction mixture was quenched with saturated salt water (10 mL). After that, the solution was extracted with ethyl acetate (3 × 10 mL), and then washed with saturated Na_2CO_3 solution. The organic layers were combined and dried by Na_2SO_4 and concentrated in vacuo. The pure product 1-benzenesulfinylmethyl-3-nitrobenzene **3g** (113.7 mg, 87% yield) was afforded by flash column chromatography on silica gel (cyclohexane/ethyl acetate = 5:1).

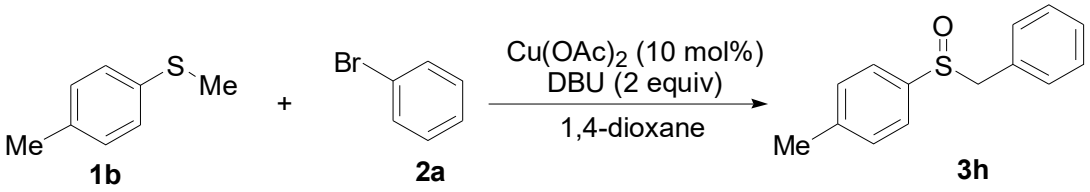
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.42 (m, 3 H), 7.38 (dd, *J* = 8.0, 1.4 Hz, 2 H), 7.29 - 7.24 (m, 1 H), 7.18 (t, *J* = 8.0 Hz, 1 H), 6.93-6.86 (m, 2 H), 3.98 (s, 2 H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 134.3, 131.5, 131.1, 130.4, 129.7, 129.0, 128.6, 128.5, 124.4, 62.8;

ESI-HRMS *m*/*z*: Calcd for $C_{13}H_{11}NO_3S^+$ $[M+Na]^+$ 284.0357, found 284.0355.



1-Methyl-4-phenylmethanesulfinylbenzene (3h):

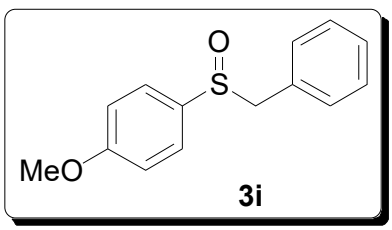


A solution of 1-methyl-4-methylsulfanyl-benzene **1b** (0.5 mmol, 69.1 mg), bromobenzene **2a** (0.6 mmol, 94.2 mg), $Cu(OAc)_2$ (10 mol%, 9.1 mg), and DBU (2 equiv, 152.2 mg) in 1,4-dioxane (3 mL) was stirred under air. After stirred at 110 °C for 10 h, it was cooled to room temperature. Then the reaction mixture was quenched with saturated salt water (10 mL). After that, the solution was extracted with ethyl acetate (3 × 10 mL), and then washed with saturated Na_2CO_3 solution. The organic layers were combined and dried by Na_2SO_4 and concentrated in vacuo. The pure product 1-methyl-4-phenylmethanesulfinylbenzene **3h** (93.3 mg, 81% yield) was afforded by flash column chromatography on silica gel (cyclohexane/ethyl acetate = 5:1).

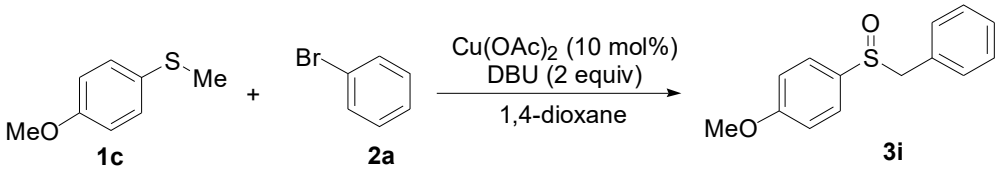
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.21 (m, 7 H), 7.02 (dd, *J* = 12.3, 6.1 Hz, 2 H), 4.10 (d, *J* = 12.5 Hz, 1 H), 3.98 (d, *J* = 12.5 Hz, 1 H), 2.41 (s, 3 H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 139.6, 130.4, 129.6, 129.4, 128.5, 128.2, 124.5, 63.8, 21.5;

ESI-HRMS *m*/*z*: Calcd for $C_{14}H_{14}NaOS^+$ $[M+Na]^+$ 253.0663, found 253.0661.



1-Methoxy-4-phenylmethanesulfinylbenzene (3i):

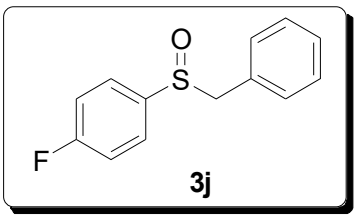


A solution of 1-methoxy-4-methylsulfanyl-benzene **1c** (0.5 mmol, 77.1 mg), bromobenzene **2a** (0.6 mmol, 94.2 mg), $Cu(OAc)_2$ (10 mol%, 9.1 mg), and DBU (2 equiv, 152.2 mg) in 1,4-dioxane (3 mL) was stirred under air. After stirred at 110 °C for 10 h, it was cooled to room temperature. Then the reaction mixture was quenched with saturated salt water (10 mL). After that, the solution was extracted with ethyl acetate (3 × 10 mL), and then washed with saturated Na_2CO_3 solution. The organic layers were combined and dried by Na_2SO_4 and concentrated in vacuo. The pure product 1-methoxy-4-phenylmethanesulfinylbenzene **3i** (104.7 mg, 85% yield) was afforded by flash column chromatography on silica gel (cyclohexane/ethyl acetate = 4:1).

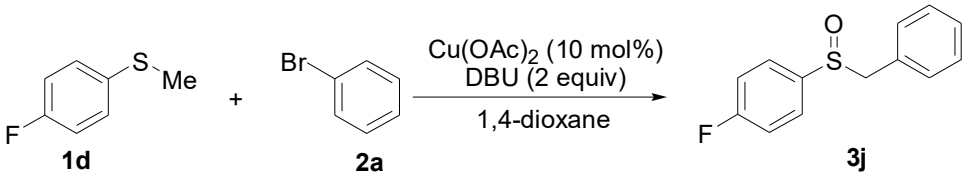
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.34 (m, 5 H), 7.06 (d, *J* = 7.9 Hz, 2 H), 6.87 (d, *J* = 7.9 Hz, 2 H), 4.08 (d, *J* = 12.6 Hz, 1 H), 3.97 (d, *J* = 12.6 Hz, 1 H), 2.32 (s, 3 H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 138.2, 131.2, 130.3, 129.3, 128.9, 26.1, 124.6, 63.5, 21.3;

ESI-HRMS *m*/*z*: Calcd for $C_{14}H_{14}NaO_2S^+$ $[M+Na]^+$ 269.0612, found 269.0611.



1-Fluoro-4-phenylmethanesulfinylbenzene (3j):



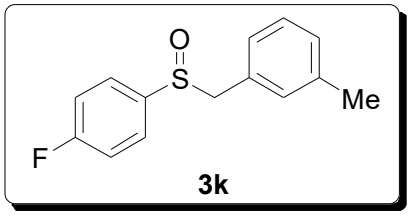
A solution of 1-fluoro-4-methylsulfanylbenzene **1d** (0.5 mmol, 71.1 mg), bromobenzene **2a** (0.6 mmol, 94.2 mg), $Cu(OAc)_2$ (10 mol%, 9.1 mg), and DBU (2 equiv, 152.2 mg) in 1,4-dioxane (3 mL) was stirred under air. After stirred at 110 °C for 10 h, it was cooled to room temperature. Then the reaction mixture was quenched

with saturated salt water (10 mL). After that, the solution was extracted with ethyl acetate (3 × 10 mL), and then washed with saturated Na_2CO_3 solution. The organic layers were combined and dried by Na_2SO_4 and concentrated in vacuo. The pure product 1-fluoro-4-phenylmethanesulfinyl-3-methylbenzene **3j** (99.3 mg, 80% yield) was afforded by flash column chromatography on silica gel (cyclohexane/ethyl acetate = 5:1).

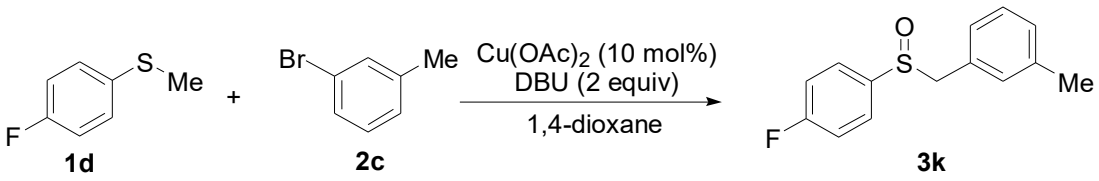
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.5 Hz, 2 H), 7.35-7.25 (m, 3 H), 7.22 (d, *J* = 8.5 Hz, 2 H), 7.04-6.94 (m, 2 H), 4.11 (d, *J* = 12.6 Hz, 1 H), 4.00 (d, *J* = 12.6 Hz, 1 H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 132.1, 130.4, 128.6, 128.5, 26.15, 25.7, 63.5;

ESI-HRMS *m*/*z*: Calcd for $C_{13}H_{11}FNaOS^+$ $[M+Na]^+$ 257.0412, found 257.0410.



1-(3-Methylphenylmethanesulfinyl)-4-fluoromethylbenzene (3k):

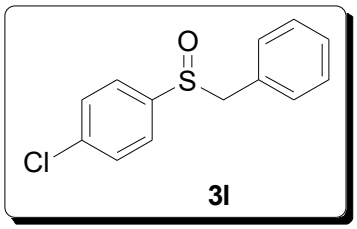


A solution of 1-fluoro-4-methylsulfanyl-benzene **1d** (0.5 mmol, 71.1 mg), 1-bromo-3-methyl-benzene **2c** (0.6 mmol, 102.6 mg), $Cu(OAc)_2$ (10 mol%, 9.1 mg), and DBU (2 equiv, 152.2 mg) in 1,4-dioxane (3 mL) was stirred under air. After stirred at 110 °C for 10 h, it was cooled to room temperature. Then the reaction mixture was quenched with saturated salt water (10 mL). After that, the solution was extracted with ethyl acetate (3 × 10 mL), and then washed with saturated Na_2CO_3 solution. The organic layers were combined and dried by Na_2SO_4 and concentrated in vacuo. The pure product 1-(3-methylphenylmethanesulfinyl)-4-fluoromethylbenzene **3k** (93.1 mg, 75% yield) was afforded by flash column chromatography on silica gel (cyclohexane/ethyl acetate = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.5 Hz, 2 H), 7.22 (d, *J* = 8.5 Hz, 2 H), 7.13 (m, 2 H), 6.80-6.74 (m, 2 H), 4.07 (d, *J* = 12.5 Hz, 1 H), 3.92 (d, *J* = 12.5 Hz, 1 H), 2.28 (s, 3 H);

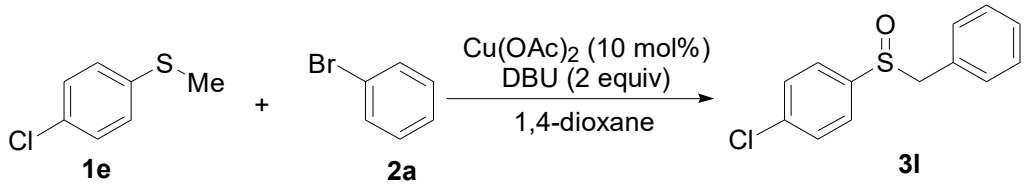
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 138.4, 132.0, 131.1, 129.3, 128.6, 128.5, 127.4, 126.1, 125.7, 63.8, 21.3;

ESI-HRMS *m*/*z*: Calcd for $C_{14}H_{13}FNaOS^+$ $[M+Na]^+$ 257.0412, found 257.0410.



3l

1-Chloro-4-phenylmethanesulfinylbenzene (3l):



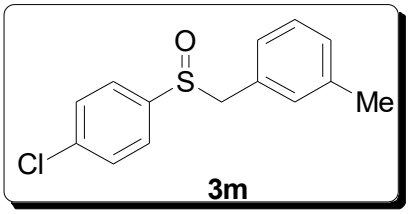
1e **2a** **3l**

A solution of 1-chloro-4-methylsulfanyl-benzene **1e** (0.5 mmol, 79.3 mg), bromobenzene **2a** (0.6 mmol, 94.2 mg), $Cu(OAc)_2$ (10 mol%, 9.1 mg), and DBU (2 equiv, 152.2 mg) in 1,4-dioxane (3 mL) was stirred under air. After stirred at 110 °C for 10 h, it was cooled to room temperature. Then the reaction mixture was quenched with saturated salt water (10 mL). After that, the solution was extracted with ethyl acetate (3 × 10 mL), and then washed with saturated Na_2CO_3 solution. The organic layers were combined and dried by Na_2SO_4 and concentrated in vacuo. The pure product 1-chloro-4-phenylmethanesulfinylbenzene **3l** (99.0 mg, 79% yield) was afforded by flash column chromatography on silica gel (cyclohexane/ethyl acetate = 5:1).

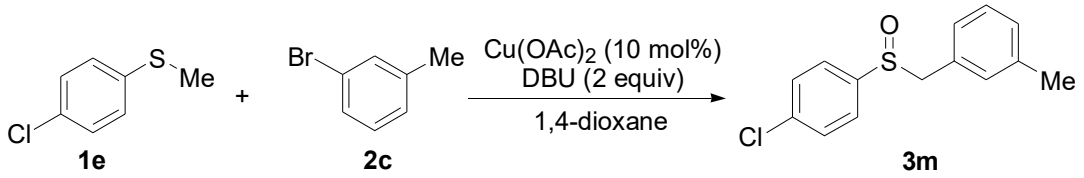
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.5 Hz, 2 H), 7.36-7.21 (m, 5 H), 7.05-6.92 (m, 2 H), 4.12 (d, *J* = 12.6 Hz, 1 H), 4.00 (d, *J* = 12.6 Hz, 1 H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 137.4, 130.4, 129.2, 128.7, 128.6, 128.5, 125.9, 63.5;

ESI-HRMS *m*/*z*: Calcd for $C_{13}H_{11}ClNaOS^+$ $[M+Na]^+$ 273.0117, found 273.0114.



1-Chloro-4-phenylmethanesulfinyl-3-methylbenzene (3m):

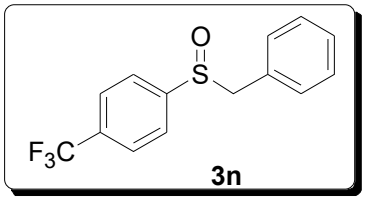


A solution of 1-chloro-4-methylsulfanyl-benzene **1e** (0.5 mmol, 79.3 mg), 1-bromo-3-methyl-benzene **2c** (0.6 mmol, 102.6 mg), $Cu(OAc)_2$ (10 mol%, 9.1 mg), and DBU (2 equiv, 152.2 mg) in 1,4-dioxane (3 mL) was stirred under air. After stirred at 110 °C for 10 h, it was cooled to room temperature. Then the reaction mixture was quenched with saturated salt water (10 mL). After that, the solution was extracted with ethyl acetate (3 × 10 mL), and then washed with saturated Na_2CO_3 solution. The organic layers were combined and dried by Na_2SO_4 and concentrated in vacuo. The pure product 1-chloro-4-phenylmethanesulfinyl-3-methylbenzene **3m** (98.0 mg, 74% yield) was afforded by flash column chromatography on silica gel (cyclohexane/ethyl acetate = 4:1).

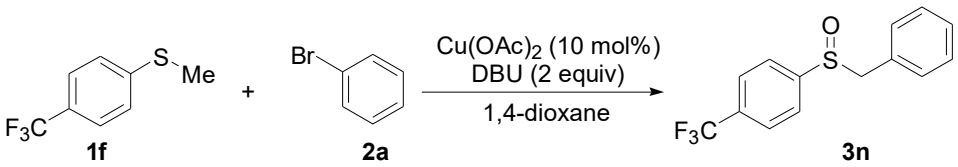
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.5 Hz, 2 H), 7.29 (d, *J* = 8.5 Hz, 2 H), 7.13 (m, 2 H), 6.80-6.74 (m, 2 H), 4.08 (d, *J* = 12.5 Hz, 1 H), 3.92 (d, *J* = 12.5 Hz, 1 H), 2.28 (s, 3 H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 138.4, 137.4, 131.2, 129.3, 129.1, 128.7, 128.5, 127.5, 126.0, 63.8, 21.3;

ESI-HRMS *m*/*z*: Calcd for $C_{14}H_{13}ClNaOS^+$ $[M+Na]^+$ 287.0273, found 287.0271.



1-Phenylmethanesulfinyl-4-trifluoromethylbenzene (3n):

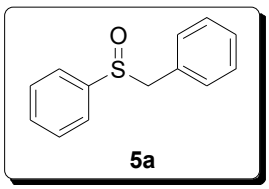


A solution of 1-methylsulfanyl-4-trifluoromethyl-benzene **1f** (0.5 mmol, 96.1 mg), bromo-benzene **2a** (0.6 mmol, 94.2 mg), $Cu(OAc)_2$ (10 mol%, 9.1 mg), and DBU (2 equiv, 152.2 mg) in 1,4-dioxane (3 mL) was stirred under air. After stirred at 110 °C for 10 h, it was cooled to room temperature. Then the reaction mixture was quenched with saturated salt water (10 mL). After that, the solution was extracted with ethyl acetate (3 × 10 mL), and then washed with saturated Na_2CO_3 solution. The organic layers were combined and dried by Na_2SO_4 and concentrated in vacuo. The pure product 1-phenylmethanesulfinyl-4-trifluoromethylbenzene **3n** (102.3 mg, 72% yield) was afforded by flash column chromatography on silica gel (cyclohexane/ethyl acetate = 4:1).

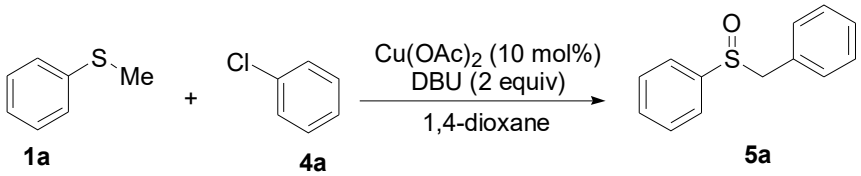
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.2 Hz, 2 H), 7.48 (d, *J* = 8.2 Hz, 2 H), 7.37-7.23 (m, 3 H), 6.99 (d, *J* = 6.9 Hz, 2 H), 4.13 (d, *J* = 12.7 Hz, 1 H), 4.05 (d, *J* = 12.7 Hz, 1 H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.2, 133.1 (q, *J* = 31.5 Hz), 130.4, 128.7, 128.7, 128.5, 125.8 (q, *J* = 3.7 Hz), 125.0, 122.2, 63.4;

ESI-HRMS *m*/*z*: Calcd for $C_{14}H_{11}F_3NaOS^+$ $[M+Na]^+$ 307.0380, found 307.0381.



Benzylsulfinylbenzene (5a):



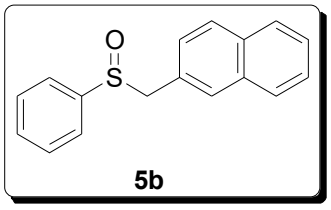
A solution of methylsulfanylbenzene **1a** (0.5 mmol, 62.1 mg), chlorobenzene **4a** (0.6 mmol, 67.6 mg), $Cu(OAc)_2$ (10 mol%, 9.1 mg), and DBU (2 equiv, 152.2 mg) in 1,4-dioxane (3 mL) was stirred under air. After stirred at 110 °C for 10 h, it was cooled

to room temperature. Then the reaction mixture was quenched with saturated salt water (10 mL). After that, the solution was extracted with ethyl acetate (3 × 10 mL), and then washed with saturated Na_2CO_3 solution. The organic layers were combined and dried by Na_2SO_4 and concentrated in vacuo. The pure product benzylsulfinylbenzene **5a** (85.4 mg, 79% yield) was afforded by flash column chromatography on silica gel (cyclohexane/ethyl acetate = 5:1).

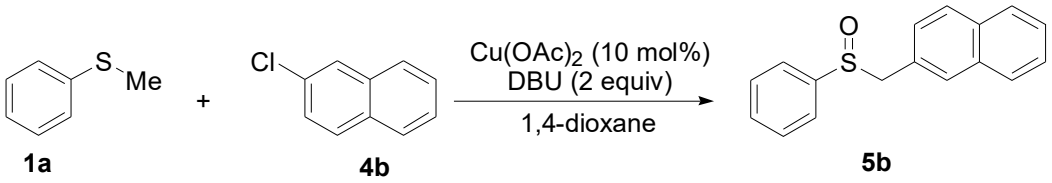
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.37 (m, 5 H), 7.34-7.23 (m, 3 H), 7.05-6.94 (m, 2 H), 4.11 (d, *J* = 12.6 Hz, 1 H), 4.02 ppm (d, *J* = 12.6 Hz, 1 H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 131.3, 130.5, 129.2, 128.9, 128.5, 128.3, 124.5, 63.7;

ESI-HRMS *m*/*z*: Calcd for $C_{13}H_{12}NaOS^+$ $[M+Na]^+$ 239.0508, found 239.0507.



2-Benzenesulfinylmethylnaphthalene (5b):

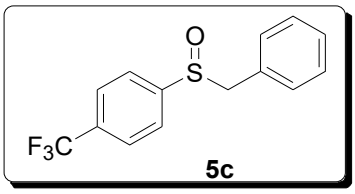


A solution of methylsulfanyl-benzene **1a** (0.5 mmol, 62.1 mg), 2-chloro-naphthalene **4b** (0.6 mmol, 97.6 mg), $Cu(OAc)_2$ (10 mol%, 9.1 mg), and DBU (2 equiv, 152.2 mg) in 1,4-dioxane (3 mL) was stirred under air. After stirred at 110 °C for 10 h, it was cooled to room temperature. Then the reaction mixture was quenched with saturated salt water (10 mL). After that, the solution was extracted with ethyl acetate (3 × 10 mL), and then washed with saturated Na_2CO_3 solution. The organic layers were combined and dried by Na_2SO_4 and concentrated in vacuo. The pure product 2-benzenesulfinylmethylnaphthalene **5b** (115.9 mg, 87% yield) was afforded by flash column chromatography on silica gel (cyclohexane/ethyl acetate = 3:1).

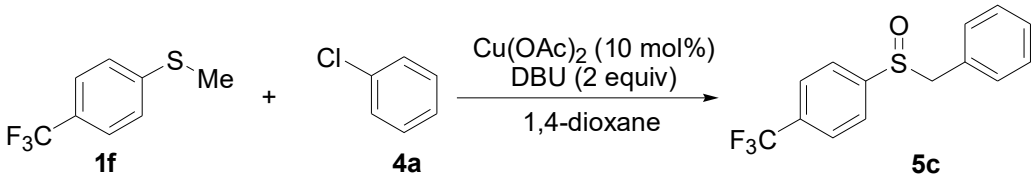
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-7.93 (m, 1 H), 7.90-7.84 (m, 1 H), 7.81 (d, *J* = 8.3 Hz, 1 H), 7.56-7.47 (m, 2 H), 7.47-7.34 (m, 5 H), 7.33-7.28 (m, 1 H), 7.02 (d, *J* = 7.0 Hz, 1 H), 4.73 (d, *J* = 12.6 Hz, 1 H), 4.36 (d, *J* = 12.6 Hz, 1 H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 133.8, 132.0, 131.3, 129.8, 129.3, 128.9, 128.9, 126.7, 126.1, 125.9, 125.3, 124.4, 123.5, 62.4;

ESI-HRMS *m*/*z*: Calcd for $C_{17}H_{14}NaOS^+$ $[M+Na]^+$ 289.0663, found 289.0663.



1-Phenylmethanesulfinyl-4-trifluoromethylbenzene (5c):

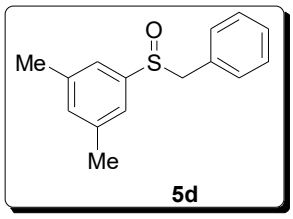


A solution of 1-methylsulfanyl-4-trifluoromethyl-benzene **1f** (0.5 mmol, 96.1 mg), chlorobenzene **4a** (0.6 mmol, 67.6 mg), $Cu(OAc)_2$ (10 mol%, 9.1 mg), and DBU (2 equiv, 152.2 mg) in 1,4-dioxane (3 mL) was stirred under air. After stirred at 110 °C for 10 h, it was cooled to room temperature. Then the reaction mixture was quenched with saturated salt water (10 mL). After that, the solution was extracted with ethyl acetate (3 × 10 mL), and then washed with saturated Na_2CO_3 solution. The organic layers were combined and dried by Na_2SO_4 and concentrated in vacuo. The pure product 1-phenylmethanesulfinyl-4-trifluoromethylbenzene **5c** (89.5 mg, 63% yield) was afforded by flash column chromatography on silica gel (cyclohexane/ethyl acetate = 4:1).

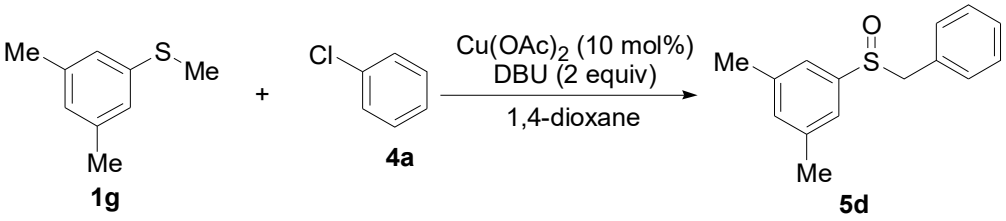
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.2 Hz, 2 H), 7.48 (d, *J* = 8.2 Hz, 2 H), 7.37-7.23 (m, 3 H), 6.99 (d, *J* = 6.9 Hz, 2 H), 4.13 (d, *J* = 12.7 Hz, 1 H), 4.05 (d, *J* = 12.7 Hz, 1 H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.2, 133.1 (q, *J* = 31.5 Hz), 130.4, 128.7, 128.7, 128.5, 125.8 (q, *J* = 3.7 Hz), 125.0, 122.2, 63.4;

ESI-HRMS *m*/*z*: Calcd for $C_{14}H_{11}F_3NaOS^+$ [M+Na]$^+$ 307.0380, found 307.0378.



1,3-Dimethyl-5-phenylmethanesulfinylbenzene (5d):

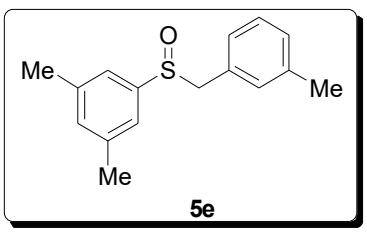


A solution of 1,3-dimethyl-5-methylsulfanyl-benzene **1g** (0.5 mmol, 76.2 mg), chlorobenzene **4a** (0.6 mmol, 67.6 mg), $Cu(OAc)_2$ (10 mol%, 9.1 mg), and DBU (2 equiv, 152.2 mg) in 1,4-dioxane (3 mL) was stirred under air. After stirred at 110 °C for 10 h, it was cooled to room temperature. Then the reaction mixture was quenched with saturated salt water (10 mL). After that, the solution was extracted with ethyl acetate (3 × 10 mL), and then washed with saturated Na_2CO_3 solution. The organic layers were combined and dried by Na_2SO_4 and concentrated in vacuo. The pure product 1,3-dimethyl-5-phenylmethanesulfinylbenzene **5d** (110.0 mg, 90% yield) was afforded by flash column chromatography on silica gel (cyclohexane/ethyl acetate = 4:1).

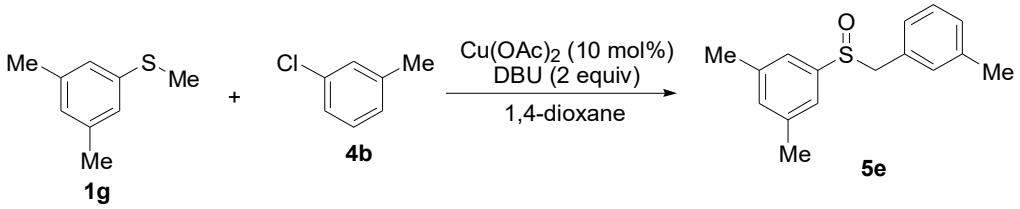
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.25 (m, 3 H), 7.09 (s, 1 H), 7.03 (dd, *J* = 7.5, 1.6 Hz, 2 H), 6.99 (s, 2 H), 4.08 (d, *J* = 12.5 Hz, 1 H), 3.97 (d, *J* = 12.5 Hz, 1 H), 2.32 (s, 6 H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 138.8, 132.9, 130.5, 129.6, 128.4, 128.3, 121.9, 63.9, 21.3;

ESI-HRMS *m*/*z*: Calcd for $C_{15}H_{16}NaOS^+$ [M+Na]$^+$ 267.0820, found 267.0821.



1,3-Dimethyl-5-m-tolylmethanesulfinylbenzene (5e):

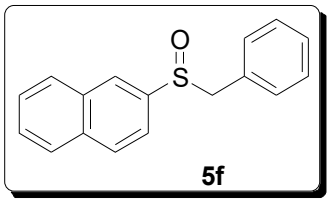


A solution of 1,3-dimethyl-5-methylsulfanyl-benzene **1g** (0.5 mmol, 76.2 mg), 1-chloro-3-methyl-benzene **4b** (0.6 mmol, 76.0 mg), $Cu(OAc)_2$ (10 mol%, 9.1 mg), and DBU (2 equiv, 152.2 mg) in 1,4-dioxane (3 mL) was stirred under air. After stirred at 110 °C for 10 h, it was cooled to room temperature. Then the reaction mixture was quenched with saturated salt water (10 mL). After that, the solution was extracted with ethyl acetate (3 × 10 mL), and then washed with saturated Na_2CO_3 solution. The organic layers were combined and dried by Na_2SO_4 and concentrated in vacuo. The pure product 1,3-dimethyl-5-m-tolylmethanesulfinylbenzene **5e** (104.6 mg, 81% yield) was afforded by flash column chromatography on silica gel (cyclohexane/ethyl acetate = 4:1).

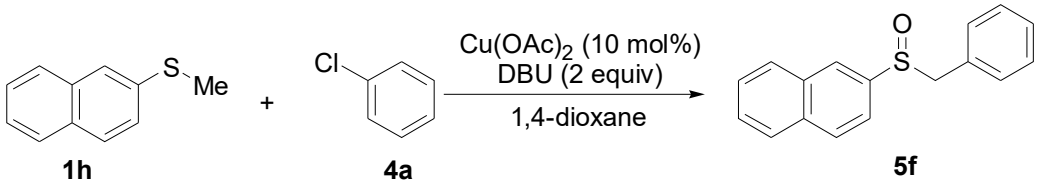
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (t, *J* = 7.5 Hz, 1 H), 7.12-7.06 (m, 2 H), 7.00 (s, 2 H), 6.85 (s, 1 H), 6.82 (s, 1 H), 4.04 (d, *J* = 12.4 Hz, 1 H), 3.89 (d, *J* = 12.4 Hz, 1 H), 2.31 (s, 6 H), 2.28 (s, 3 H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 138.8, 138.2, 132.9, 131.2, 129.5, 129.0, 128.4, 127.5, 122.0, 64.1, 21.3, 21.3;

ESI-HRMS *m*/*z*: Calcd for $C_{16}H_{18}NaOS^+$ $[M+Na]^+$ 281.0976, found 281.0974.



2-Phenylmethanesulfinylnaphthalene (5f):



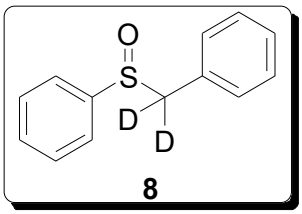
A solution of 2-methylsulfanyl-naphthalene **1h** (0.5 mmol, 87.2 mg), chlorobenzene **4a** (0.6 mmol, 67.6 mg), $Cu(OAc)_2$ (10 mol%, 9.1 mg), and DBU (2 equiv, 152.2 mg) in

1,4-dioxane (3 mL) was stirred under air. After stirred at 110 °C for 10 h, it was cooled to room temperature. Then the reaction mixture was quenched with saturated salt water (10 mL). After that, the solution was extracted with ethyl acetate (3 × 10 mL), and then washed with saturated Na_2CO_3 solution. The organic layers were combined and dried by Na_2SO_4 and concentrated in vacuo. The pure product 2-phenylmethanesulfinylnaphthalene **5f** (106.6 mg, 86% yield) was afforded by flash column chromatography on silica gel (cyclohexane/ethyl acetate = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-7.87 (m, 3 H), 7.84 (d, *J* = 8.6 Hz, 1 H), 7.64-7.53 (m, 2 H), 7.44 (dd, *J* = 8.6, 1.6 Hz, 1 H), 7.28 (m, 3 H), 7.01 (d, *J* = 7.0 Hz, 2 H), 4.18 (d, *J* = 12.6 Hz, 1 H), 4.11 (d, *J* = 12.6 Hz, 1 H);

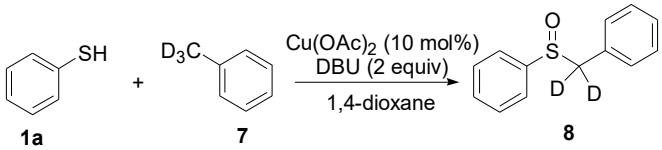
^{13}C NMR (100 MHz, $CDCl_3$) δ 139.9, 134.6, 132.7, 130.5, 129.2, 129.0, 128.5, 128.3, 128.1, 127.8, 127.2, 125.3, 120.3, 63.5.;

ESI-HRMS *m*/*z*: Calcd for $C_{17}H_{14}NaOS^+$ $[M+Na]^+$ 289.0663, found 289.0661.



8

Dideuterobenzylsulfinylbenzene (8):



1a **7** **8**

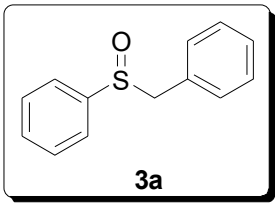
A solution of thiophenol **1a** (0.5 mmol, 55.1 mg), trideuteromethylbenzene **7** (0.6 mmol, 57.1 mg), $Cu(OAc)_2$ (10 mol%, 9.1 mg), and DBU (2 equiv, 152.2 mg) in 1,4-dioxane (3 mL) was stirred under air. After stirred at 110 °C for 10 h, it was cooled to room temperature. Then the reaction mixture was quenched with saturated salt water (10 mL). After that, the solution was extracted with ethyl acetate (3×10 mL), and then washed with saturated Na_2CO_3 solution. The organic layers were combined and dried by Na_2SO_4 and concentrated in vacuo. The pure product dideuterobenzylsulfinylbenzene **8** (91.7 mg, 84% yield) was afforded by flash column chromatography on silica gel (cyclohexane/ethyl acetate = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.36 (m, 5 H), 7.33-7.22 (m, 3 H), 7.04-6.93 (m, 2 H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 131.2, 130.4, 129.2, 128.9, 128.5, 128.3, 124.5, 63.6;

ESI-HRMS *m*/*z*: Calcd for $C_{13}H_{10}D_2NaOS^+$ $[M+Na]^+$ 241.0630, found 241.0633.

Spectrums



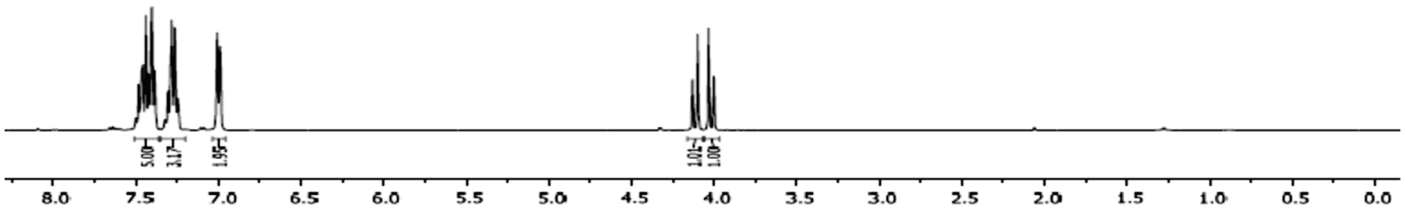


Figure S1. ^{1}H-NMR **3a**

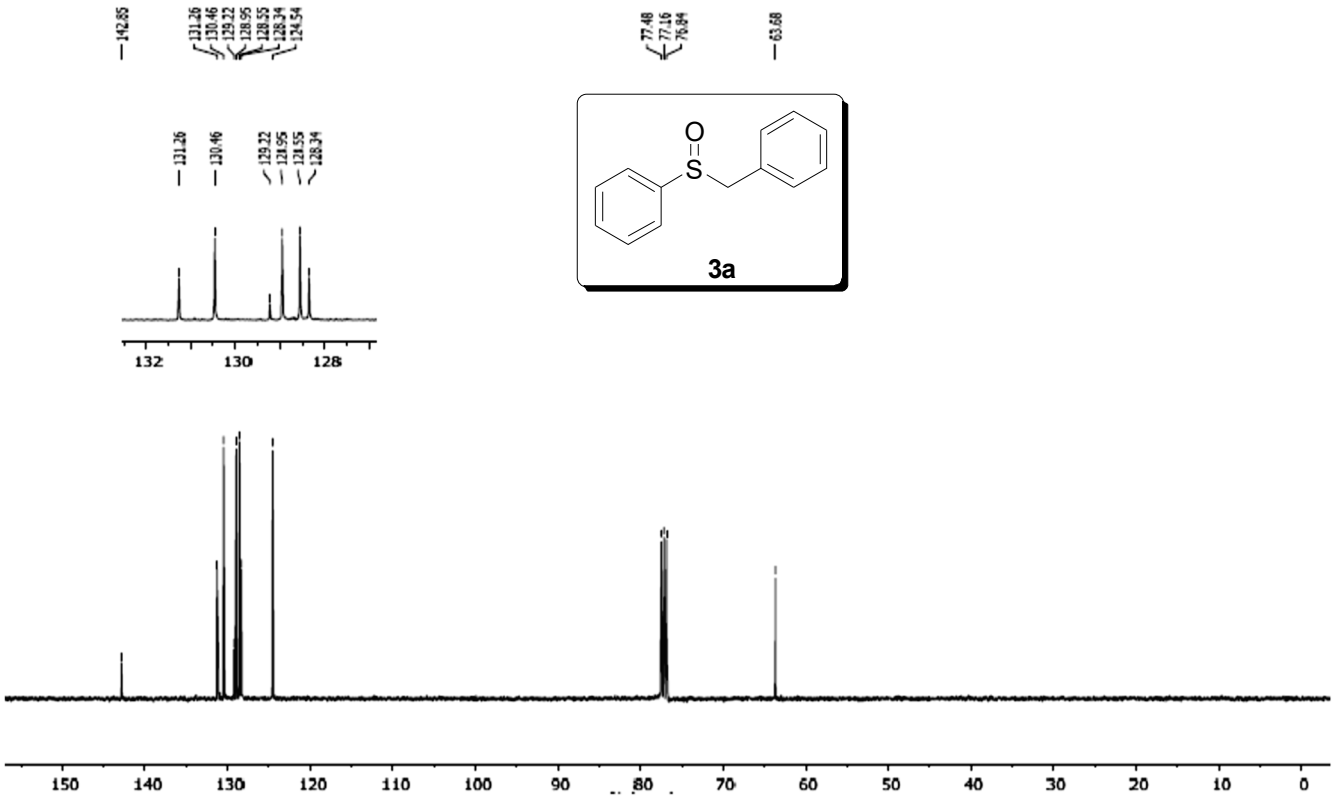


Figure S2. ^{13}C-NMR **3a**

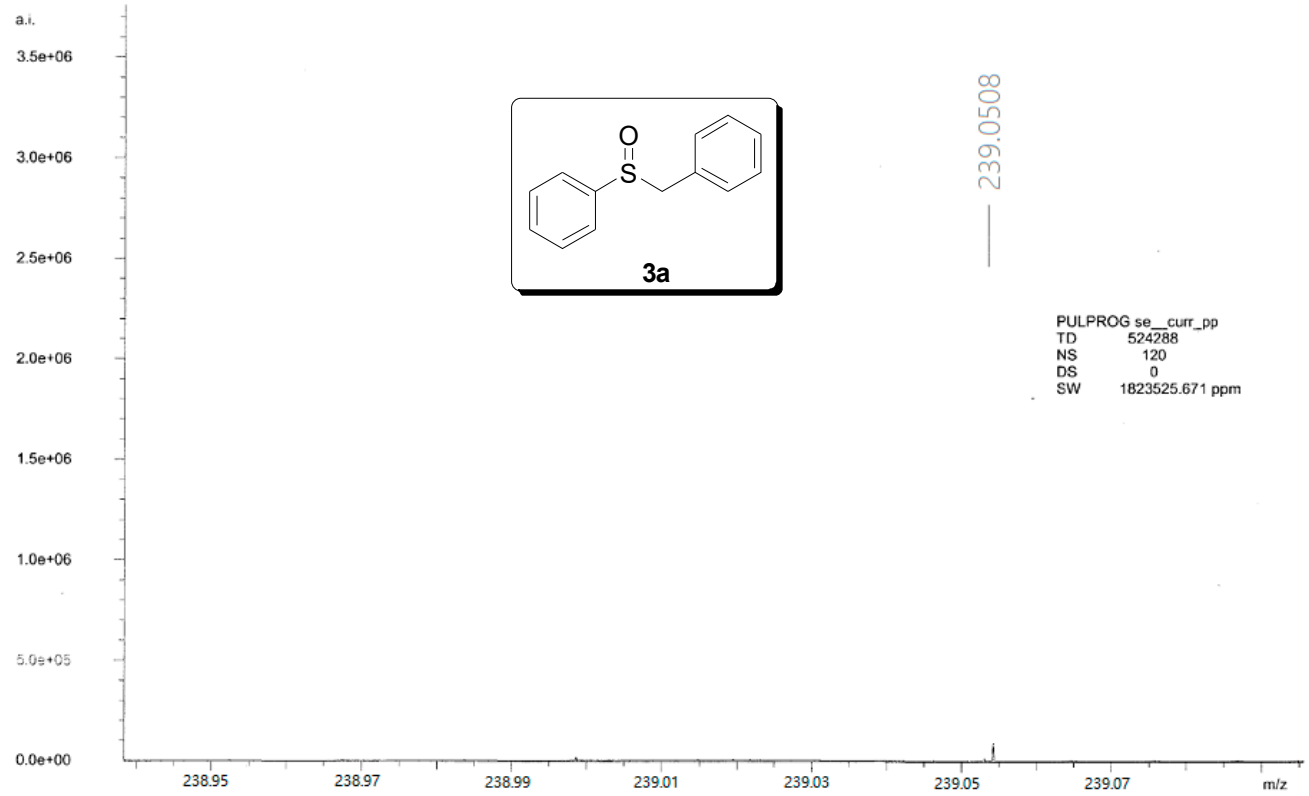


Figure S3. ESI-HRMS **3a**

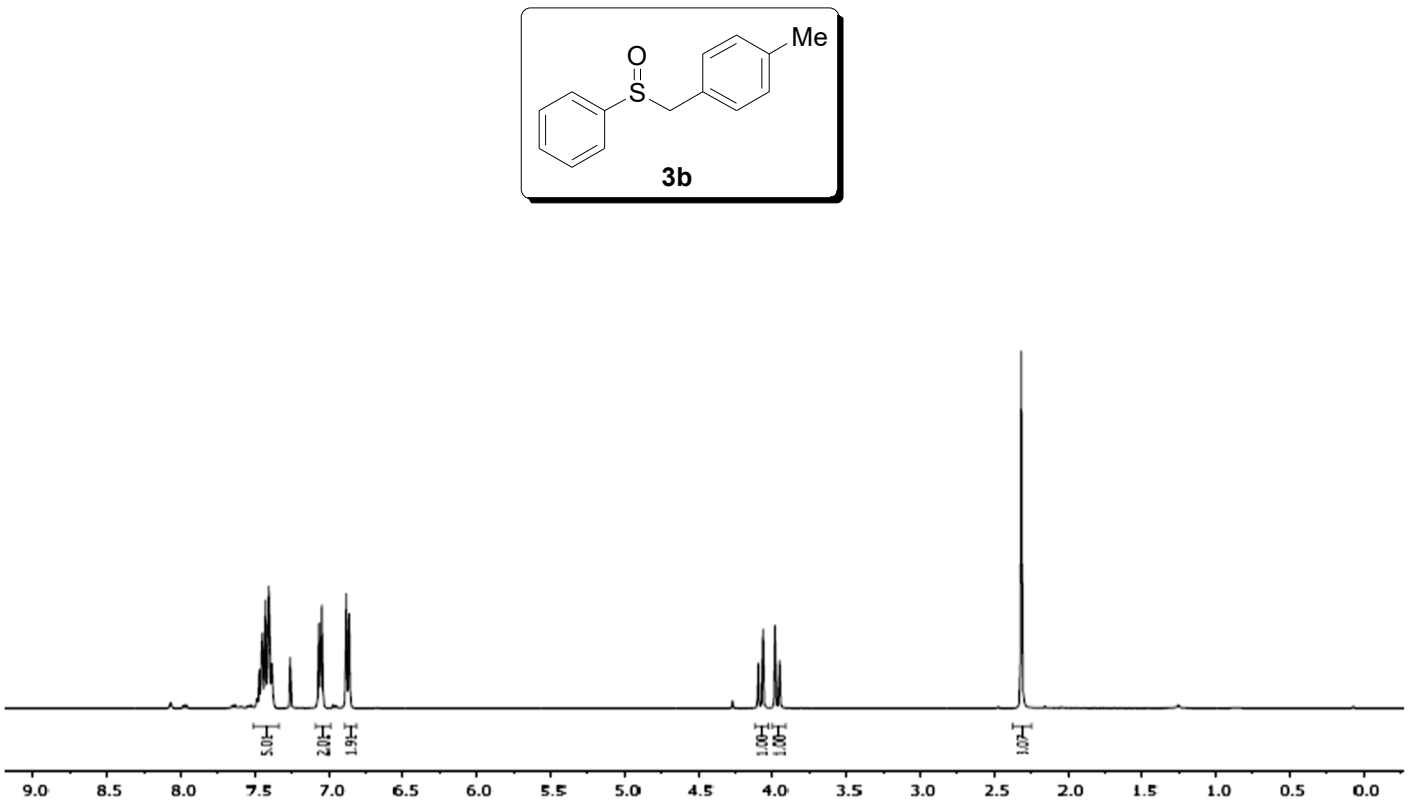


Figure S4. ^{1}H-NMR **3b**

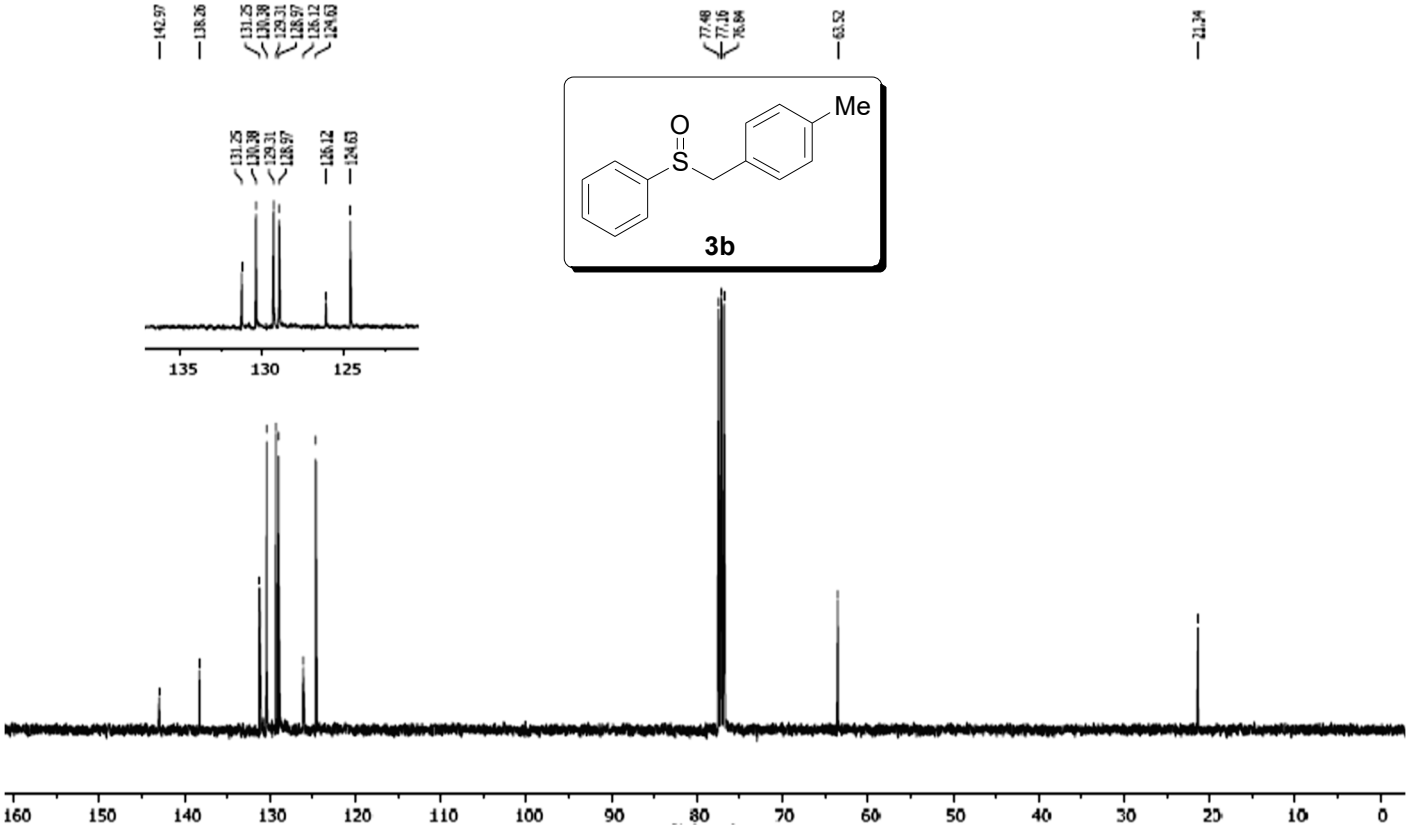


Figure S5. ^{13}C-NMR **3b**

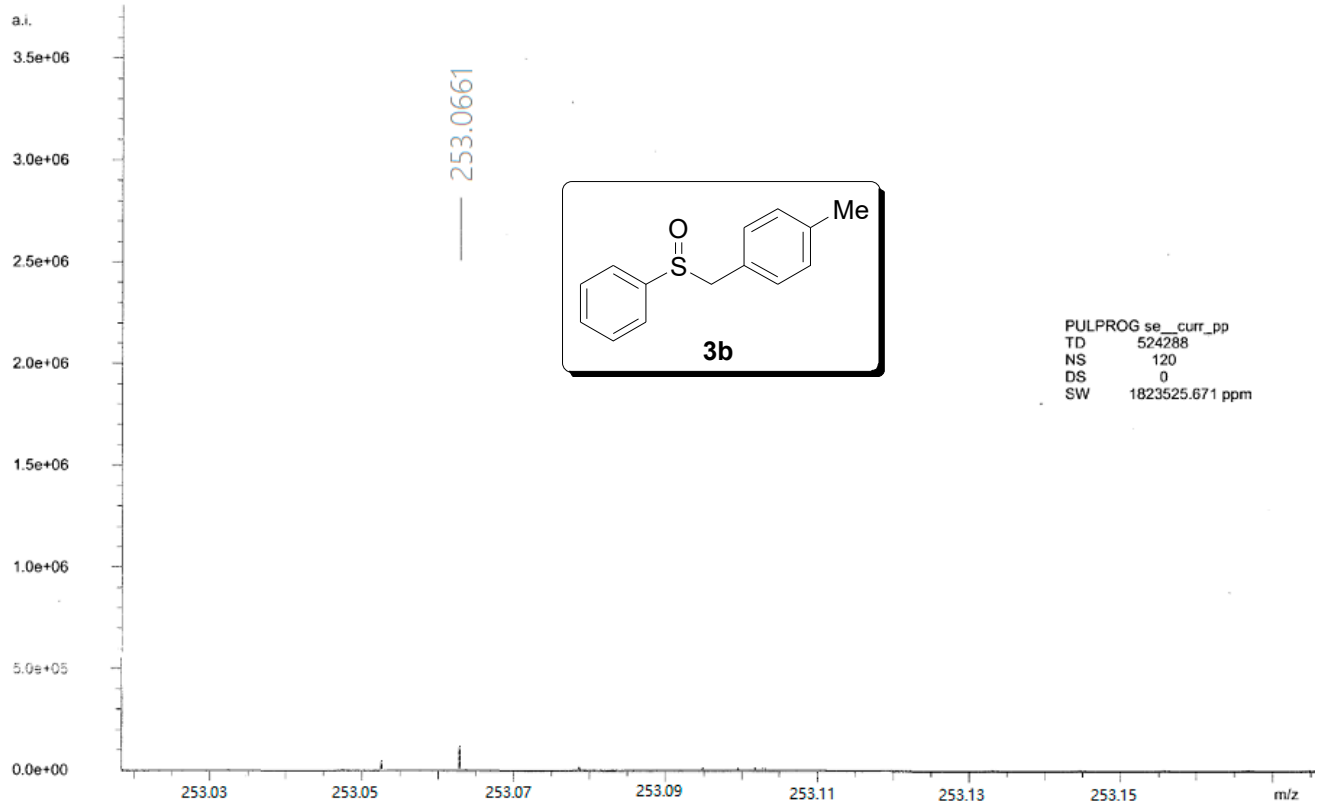


Figure S6. ESI-HRMS **3b**

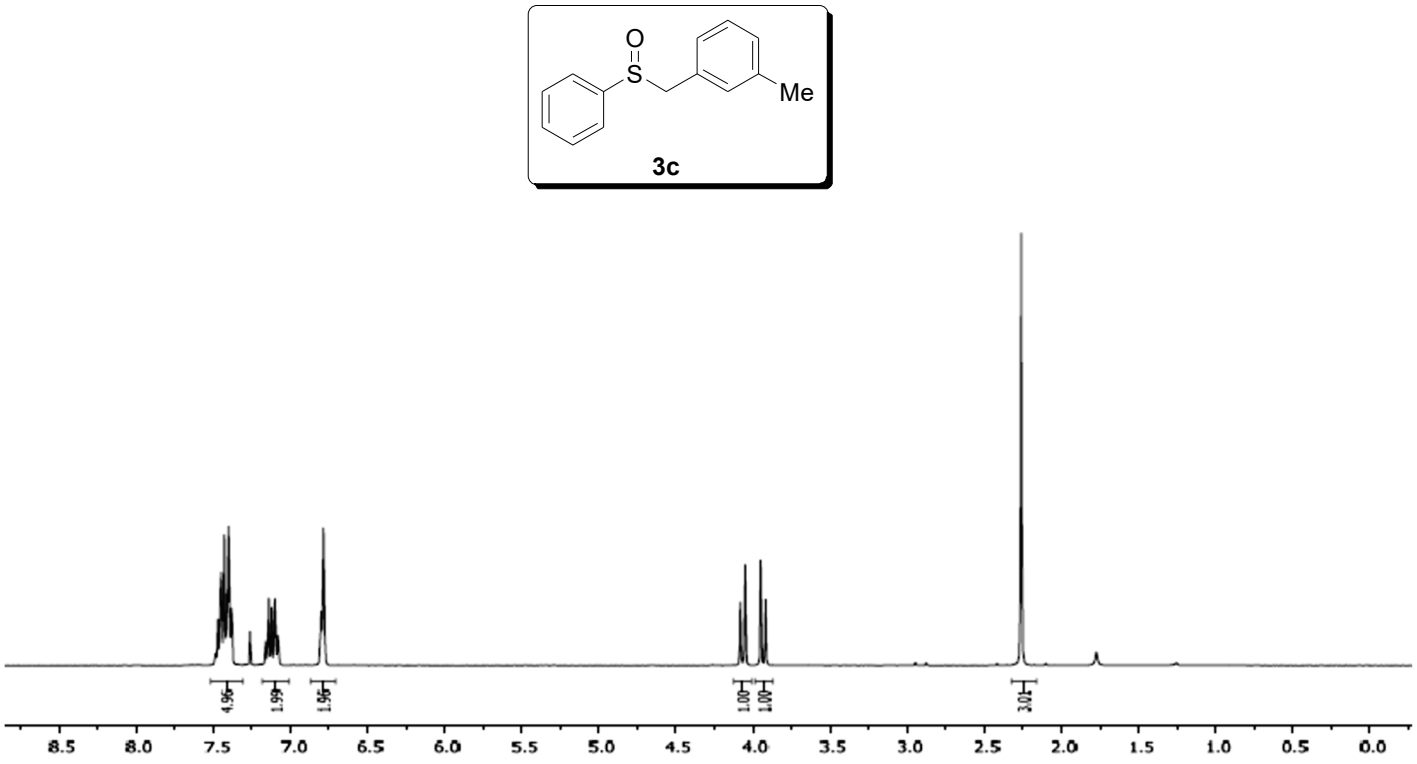


Figure S7. ^{1}H-NMR **3c**

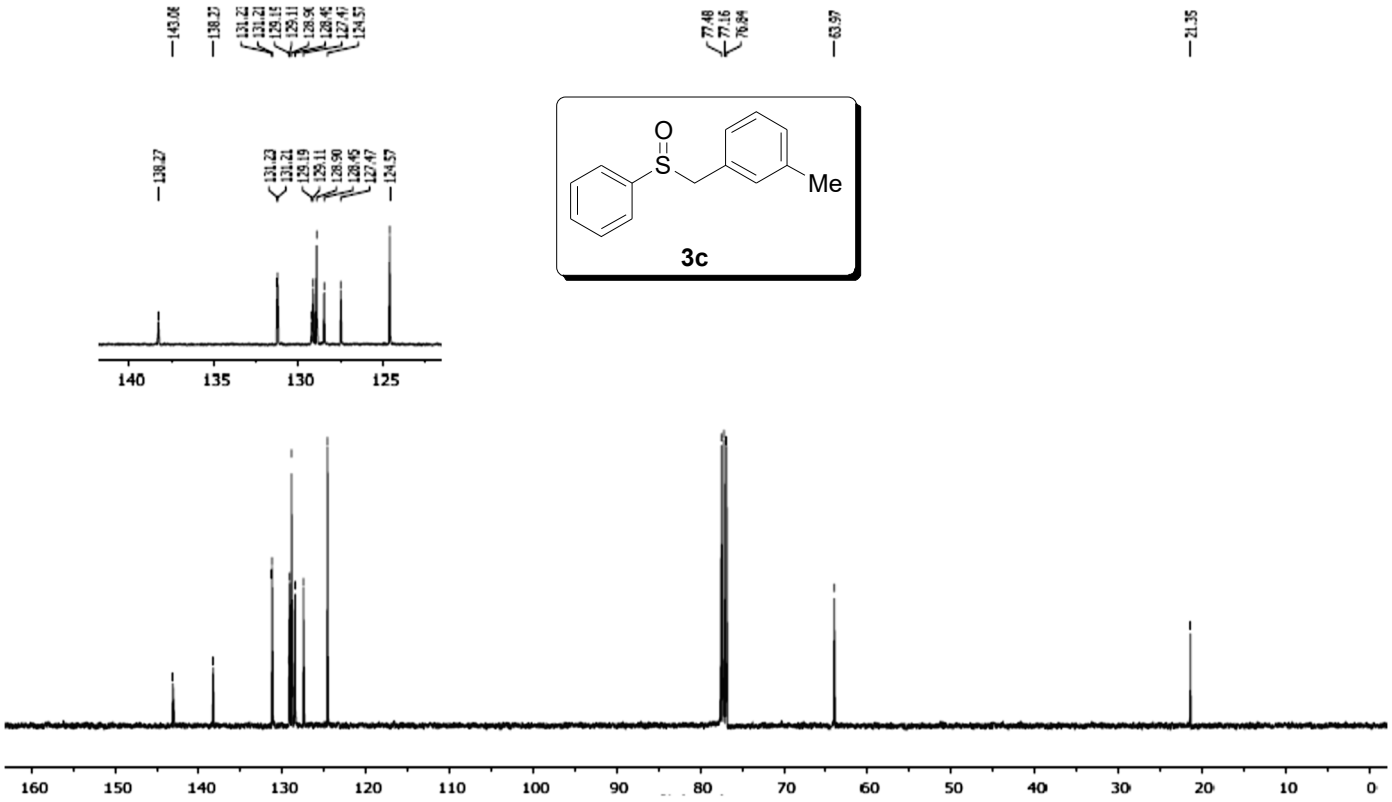


Figure S8. ^{13}C-NMR **3c**

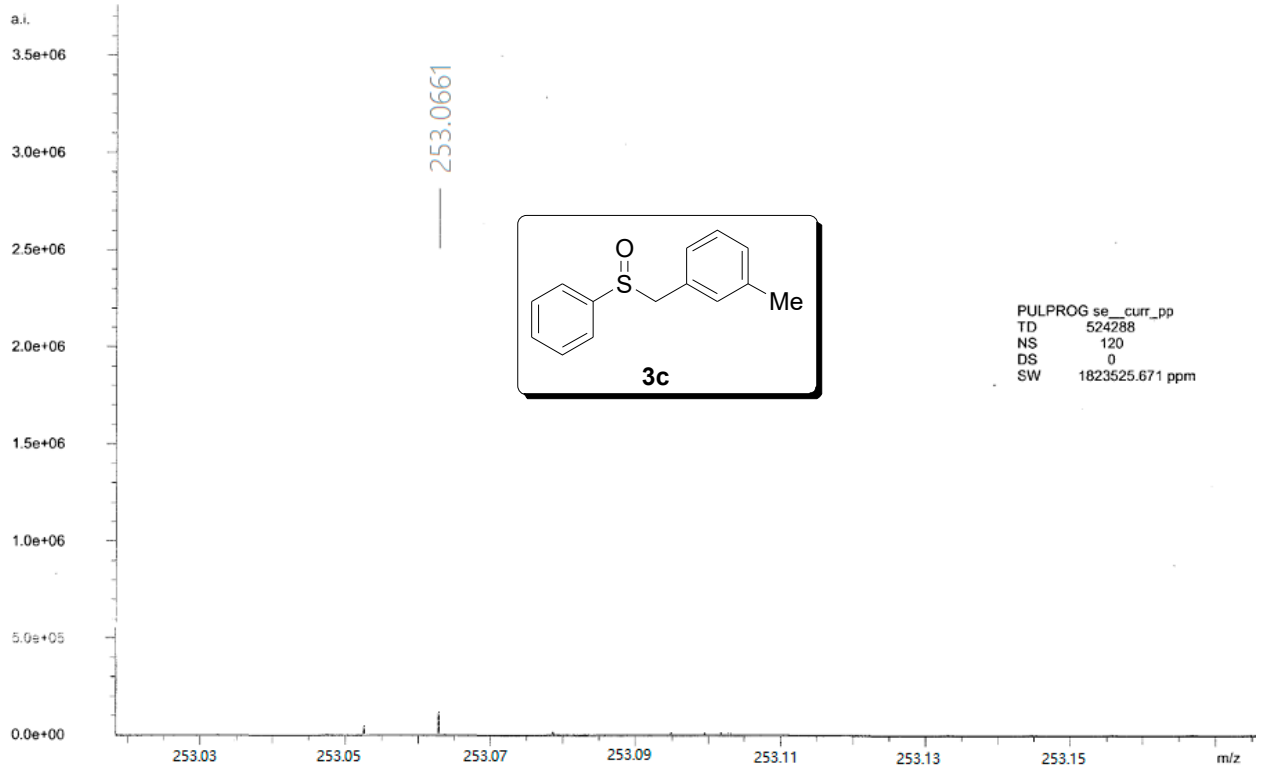


Figure S9. ESI-HRMS **3c**

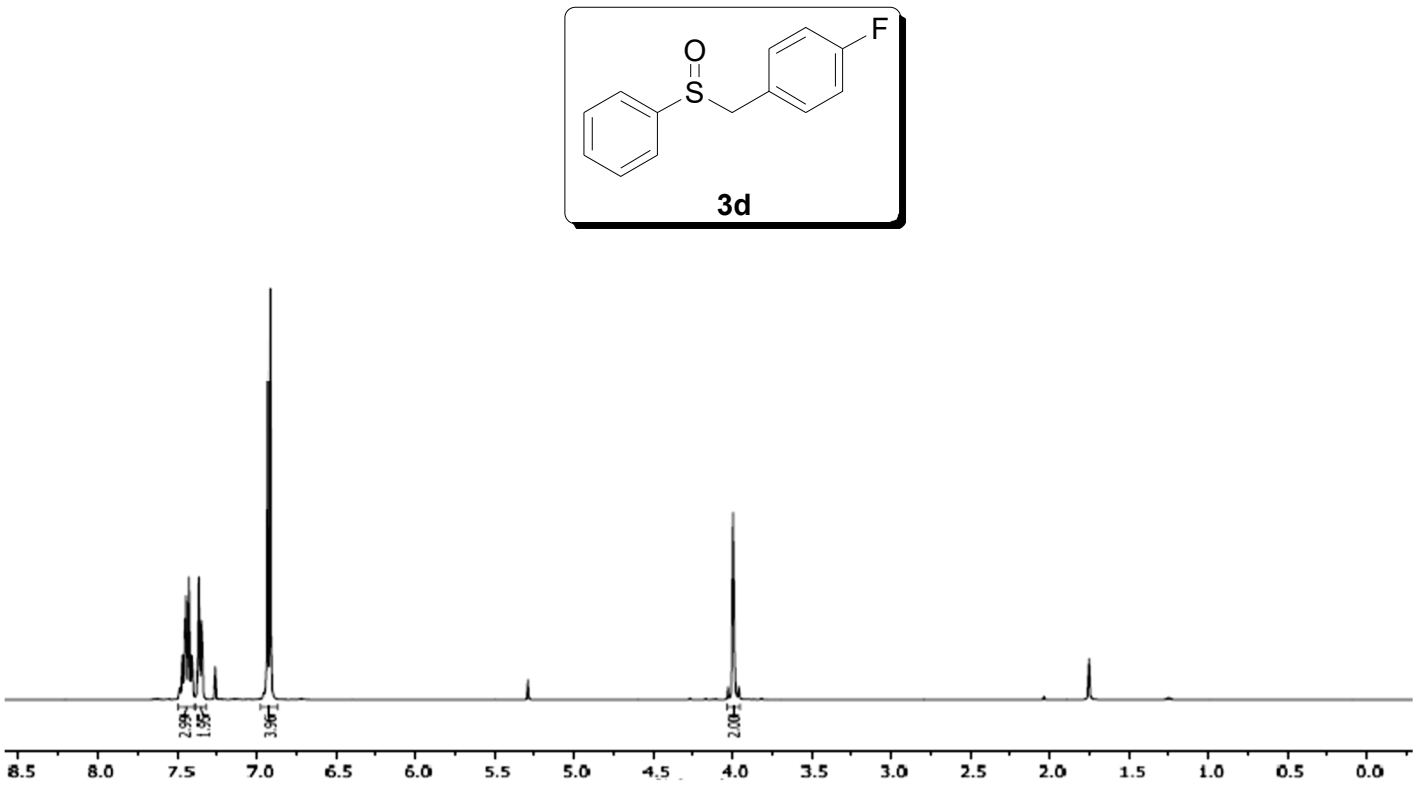


Figure S10. [1]H-NMR **3d**

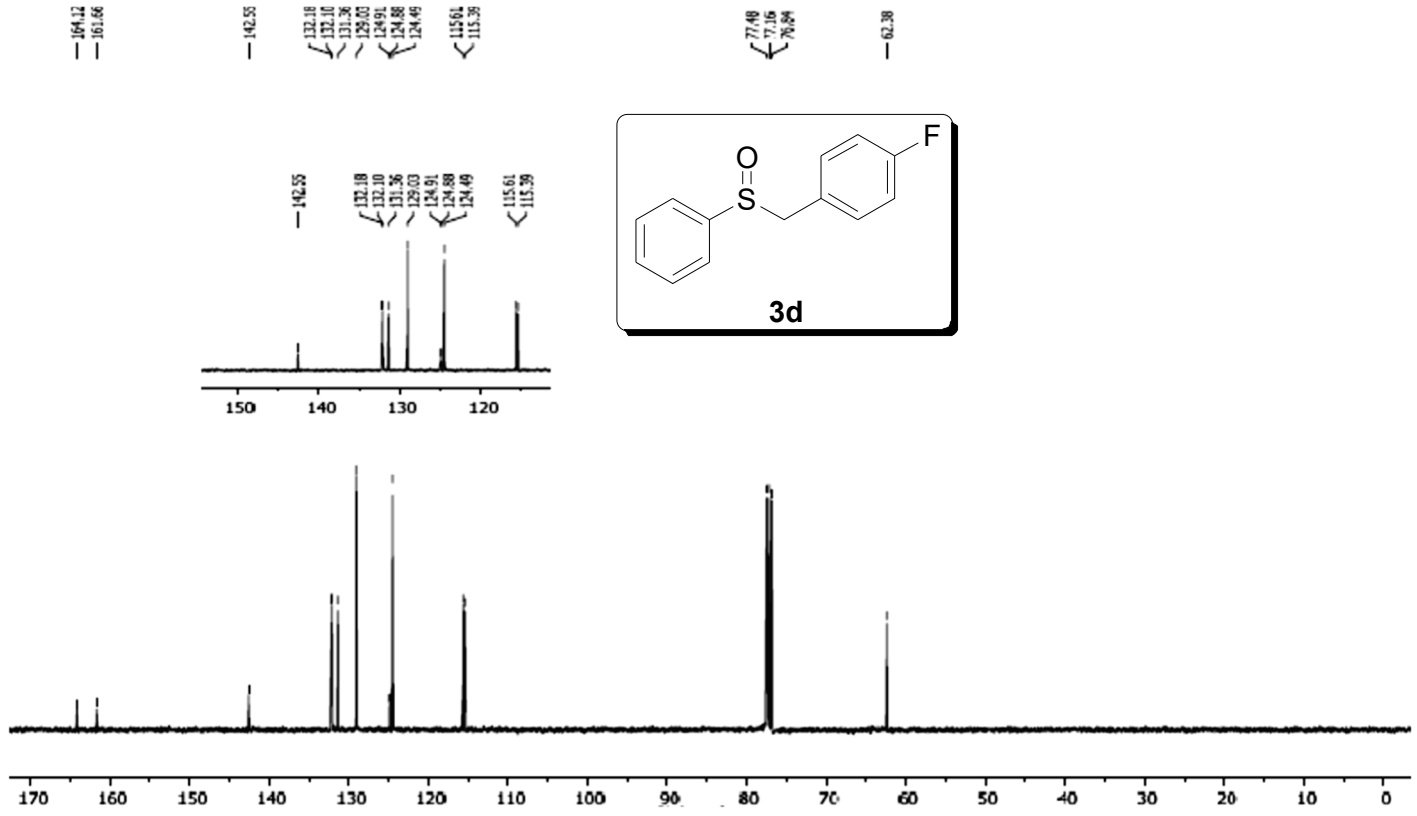


Figure S11. [13]C-NMR **3d**

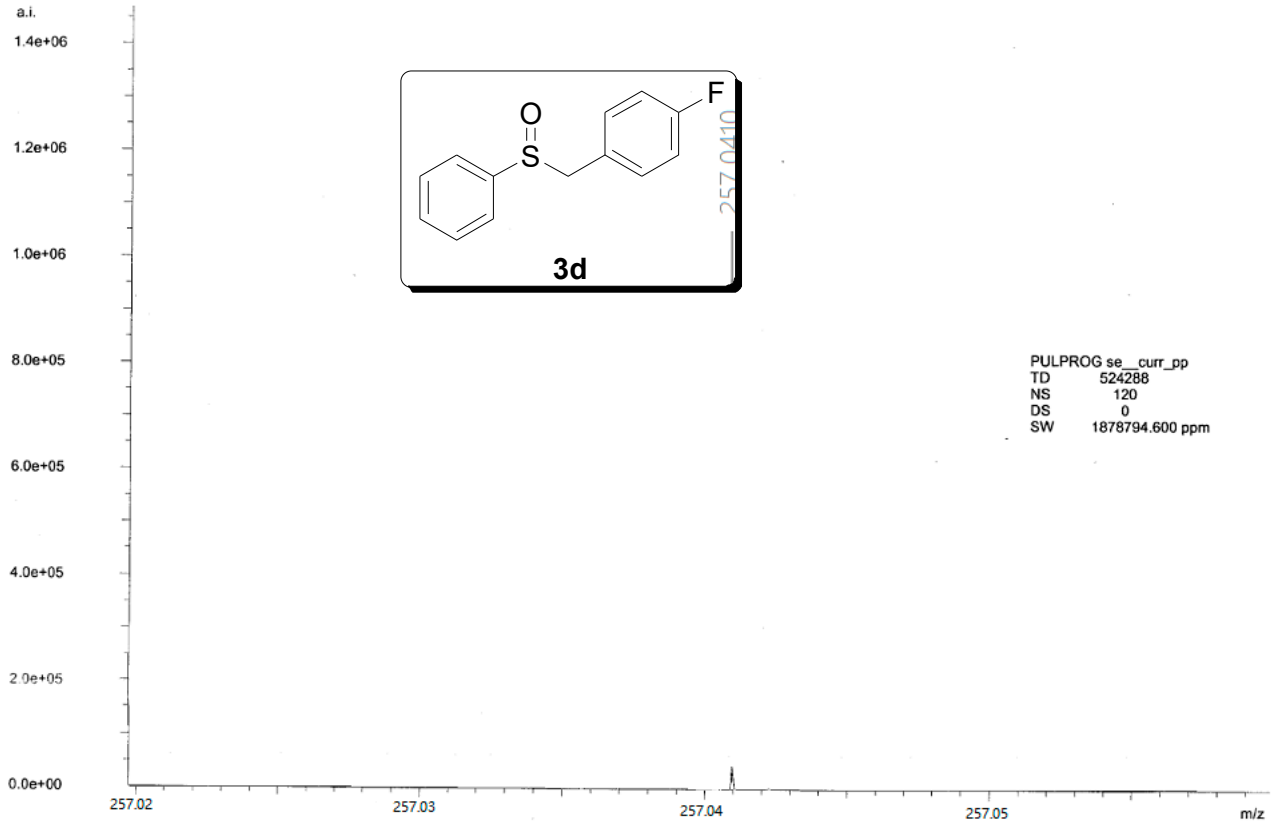
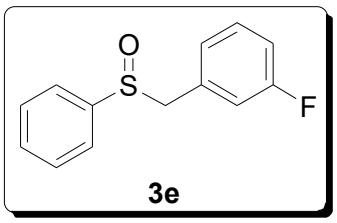


Figure S12. ESI-HRMS **3d**



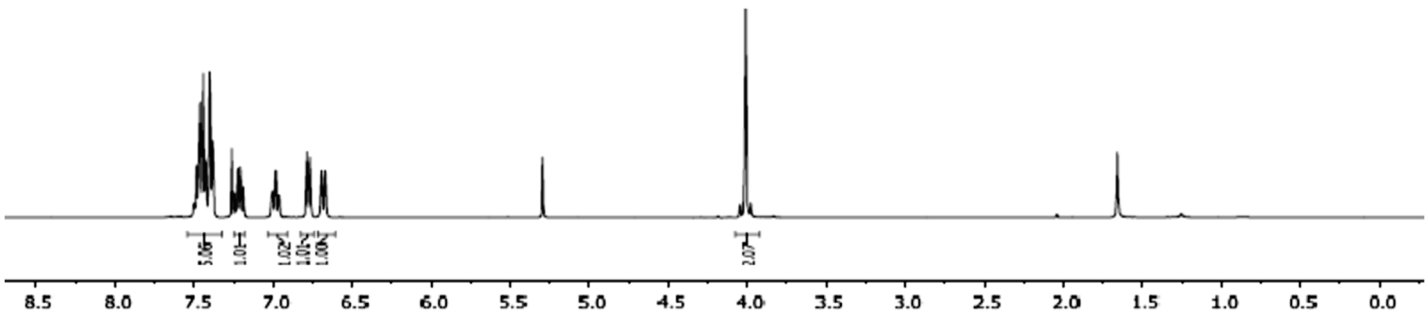


Figure S13. ^{1}H-NMR **3e**

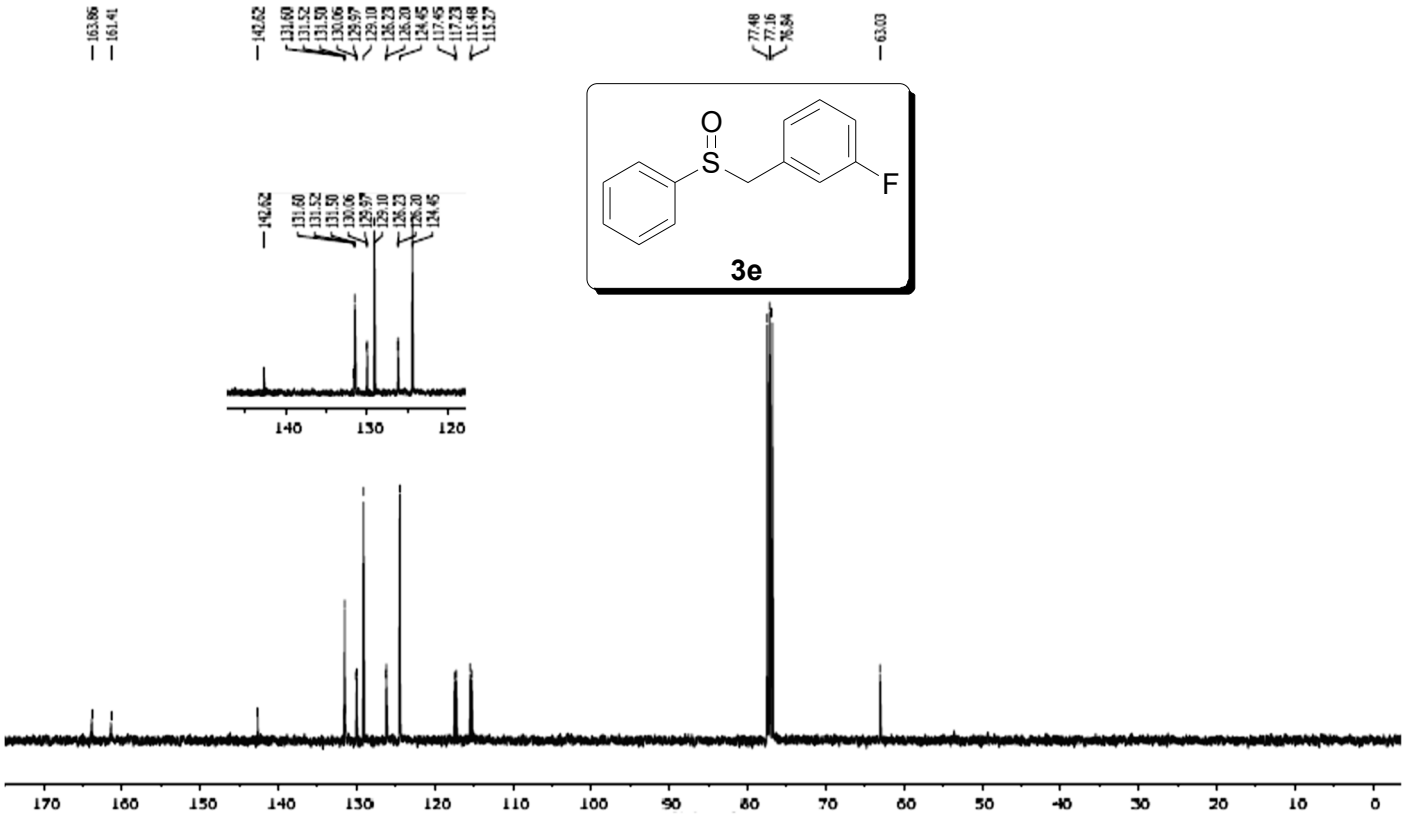


Figure S14. ^{13}C-NMR **3e**

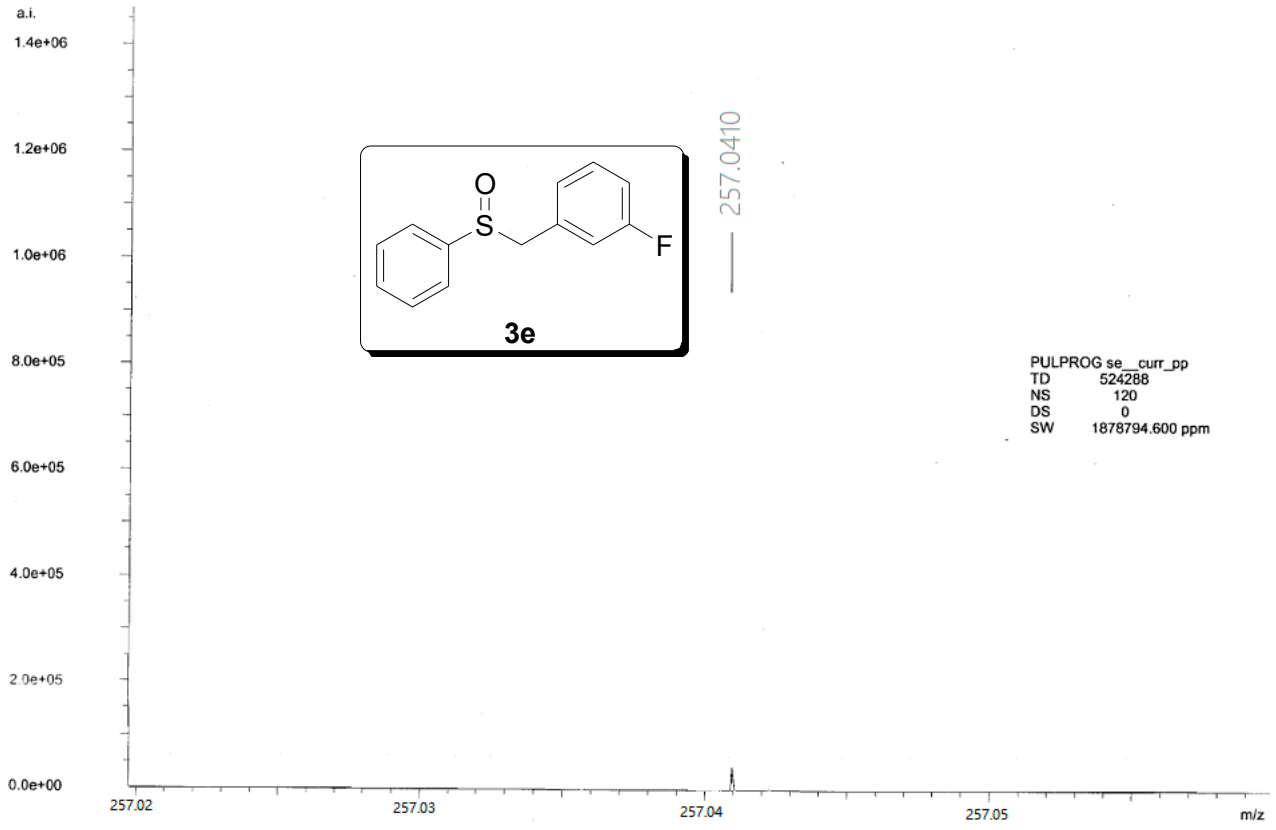
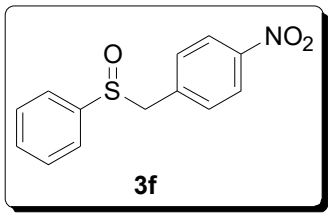


Figure S15. ESI-HRMS **3e**



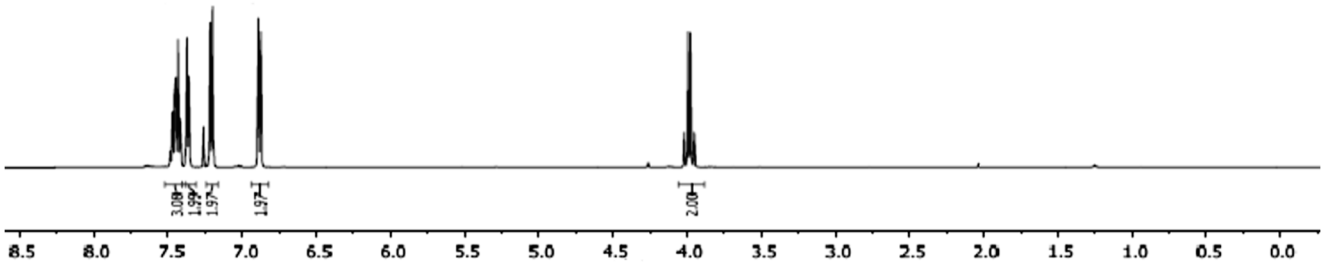


Figure S16. [1]H-NMR **3f**

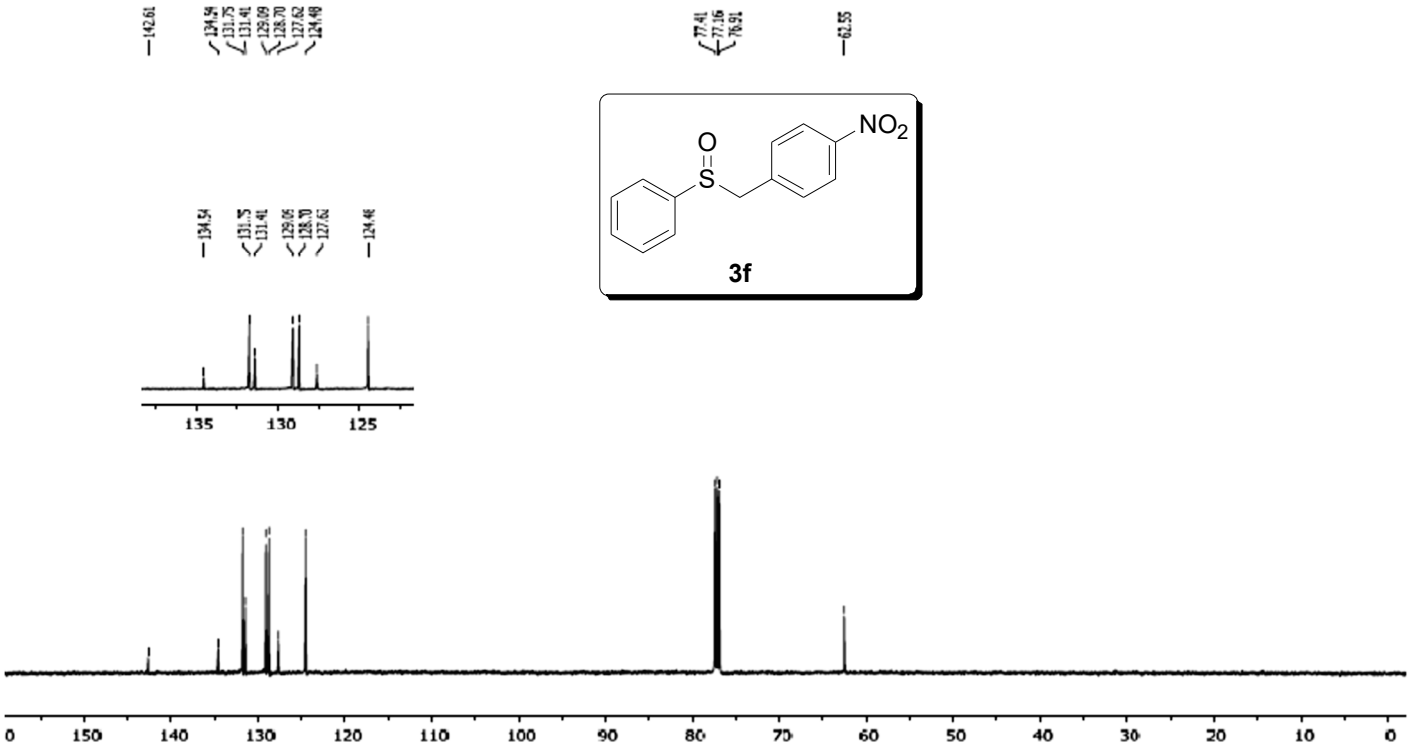


Figure S17. [13]C-NMR **3f**

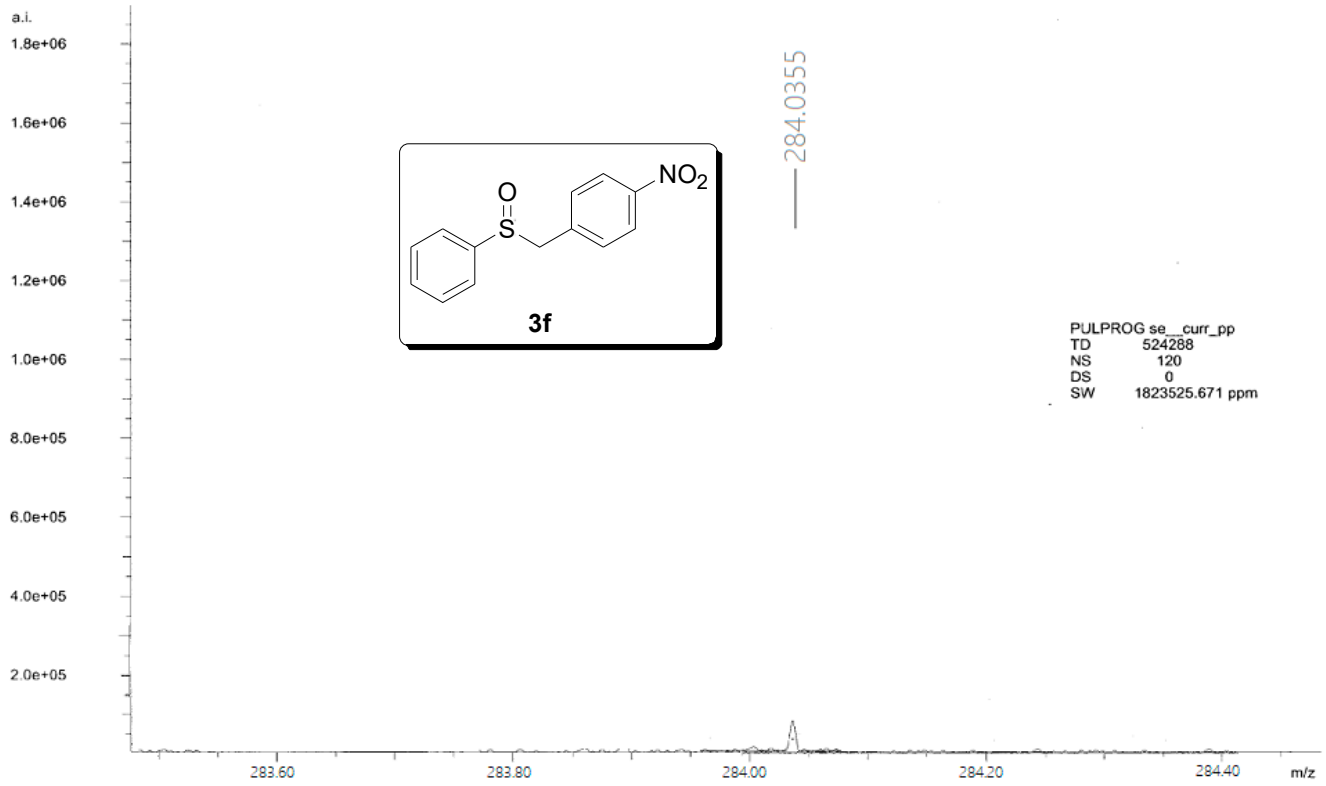
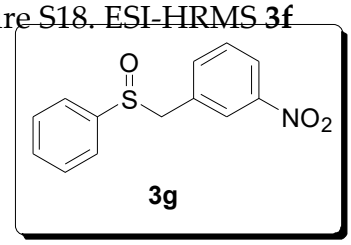


Figure S18. ESI-HRMS **3f**



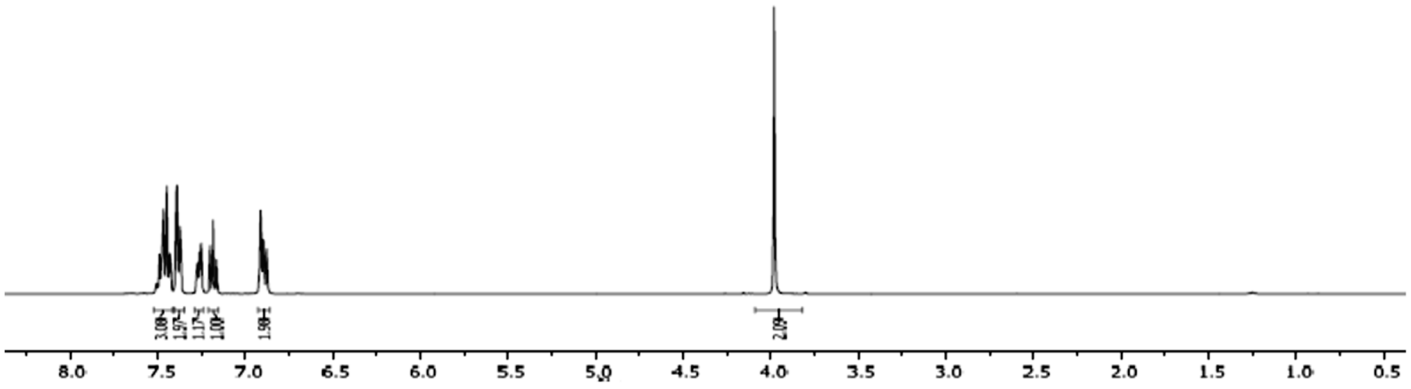


Figure S19. ^{1}H-NMR **3g**

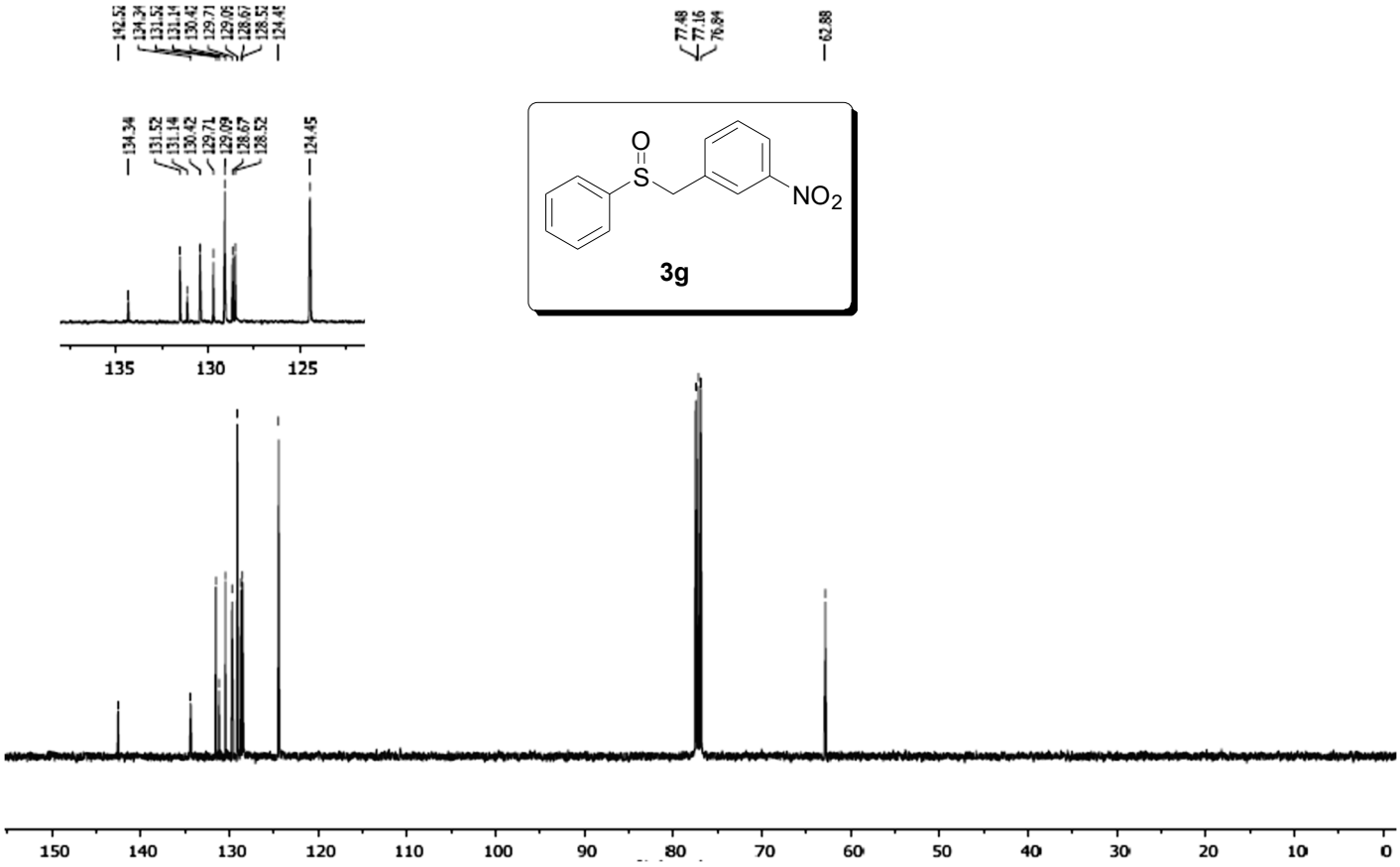


Figure S20. ^{13}C-NMR **3g**

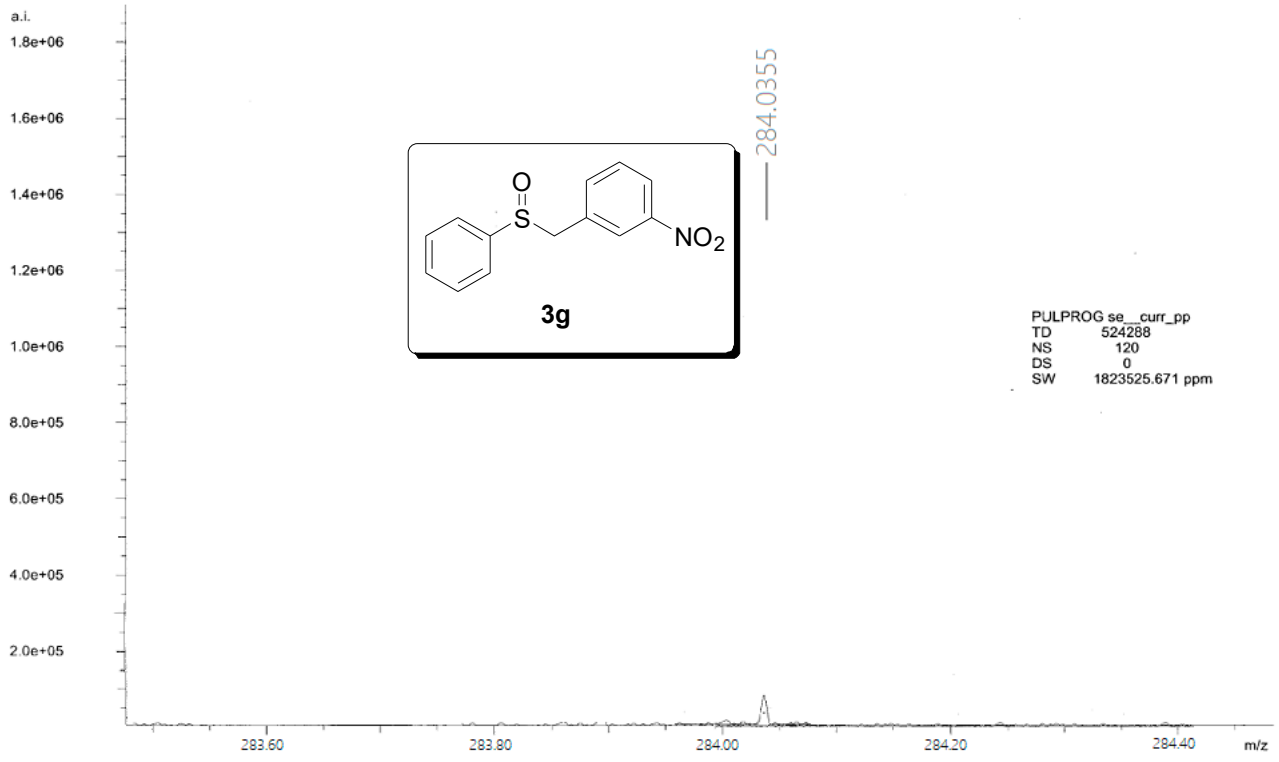
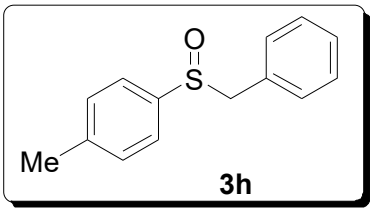


Figure S21. ESI-HRMS **3g**



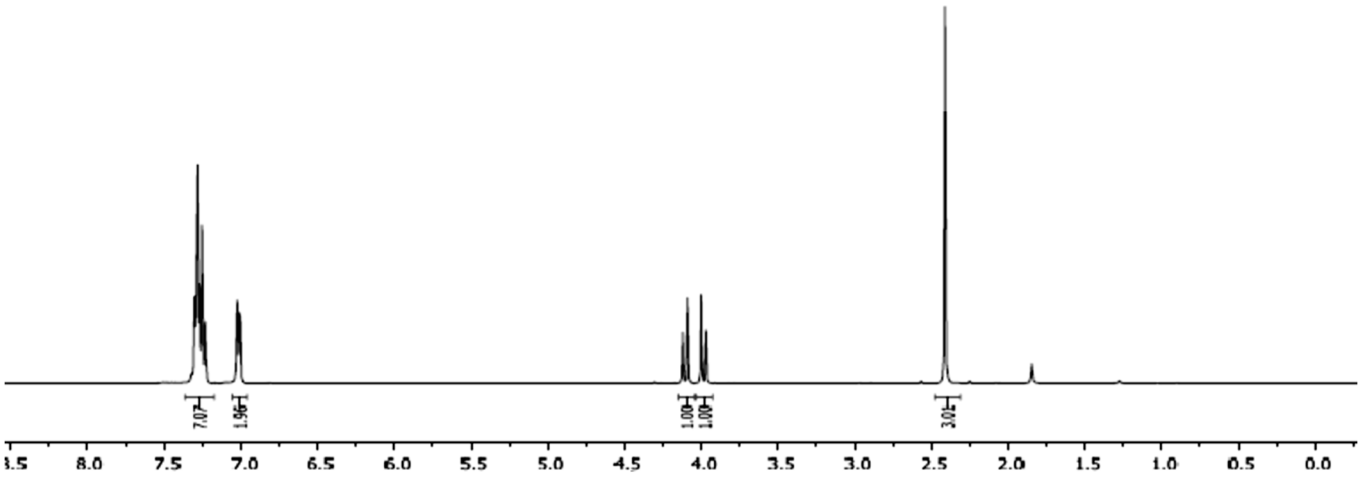


Figure S22. [1]H-NMR **3h**

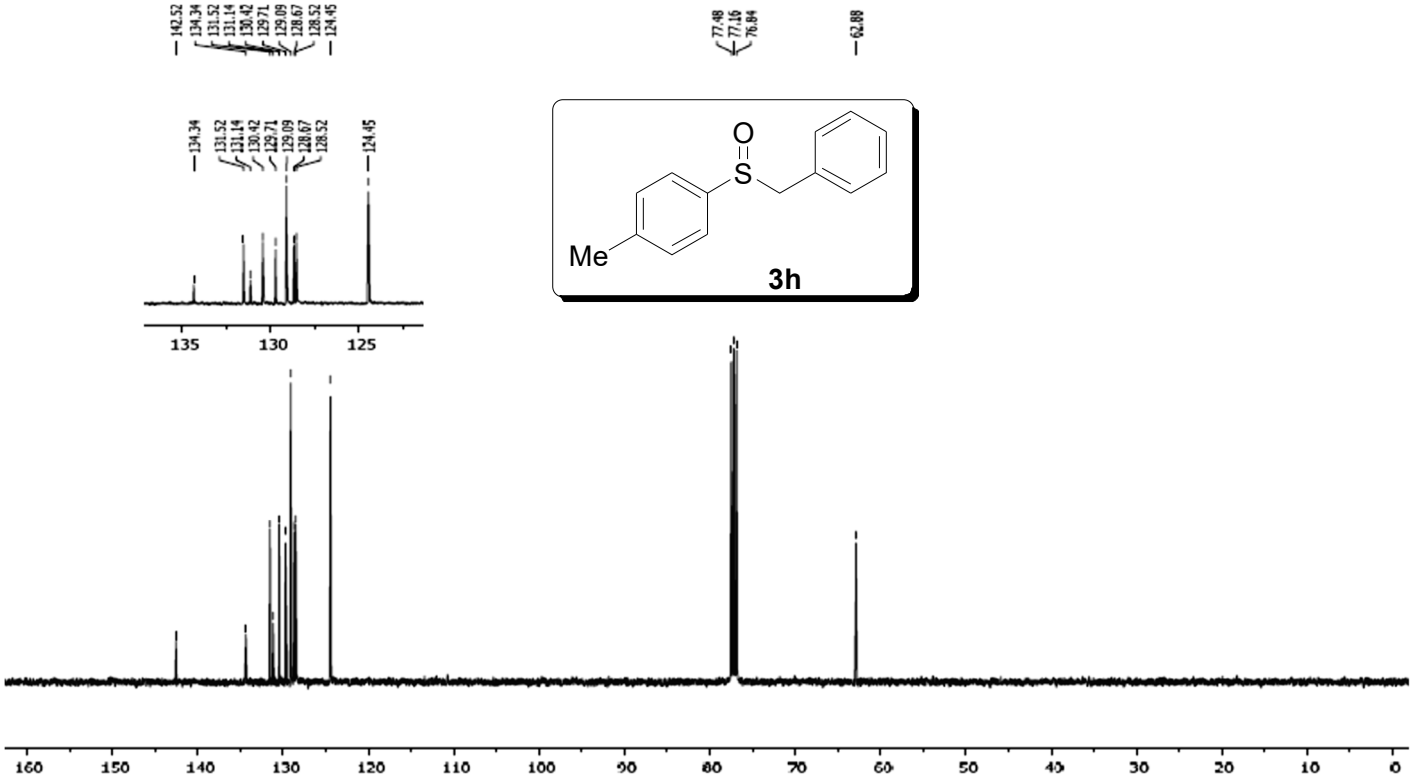


Figure S23. [13]C-NMR **3h**

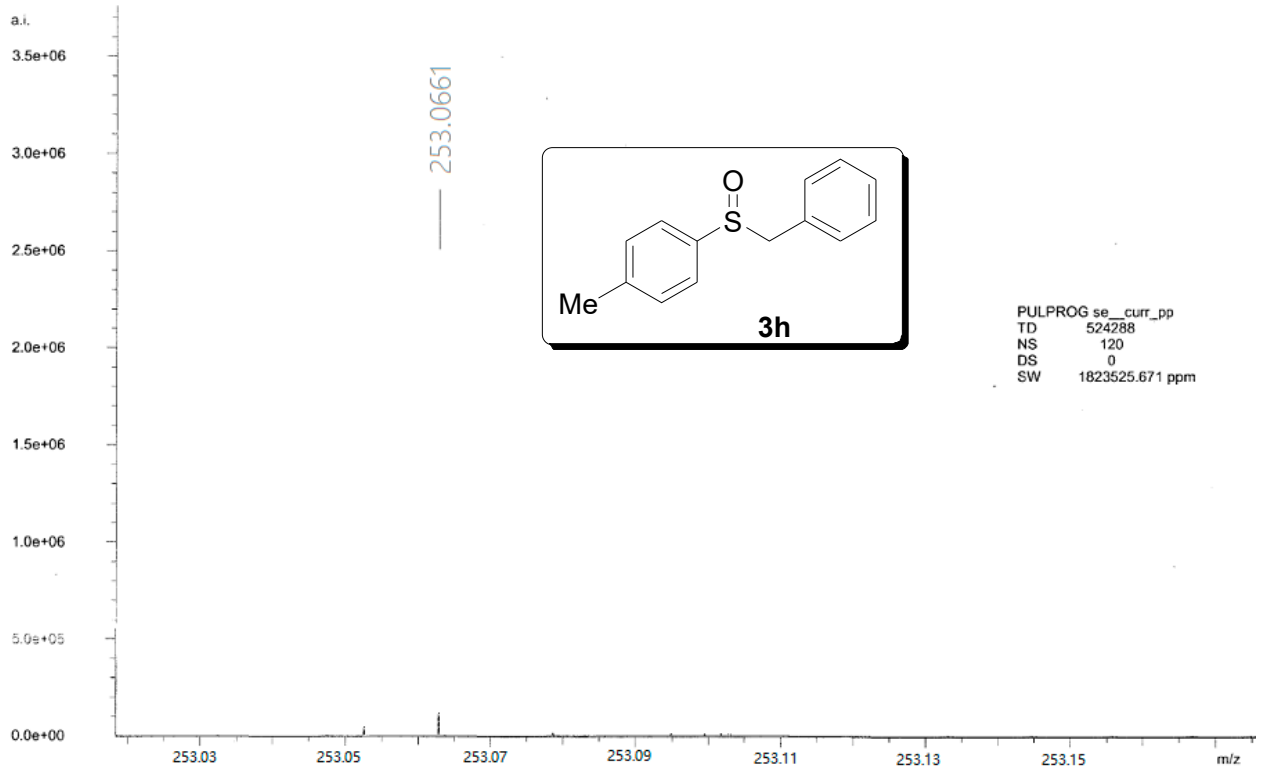


Figure 24. ESI-HRMS **3h**

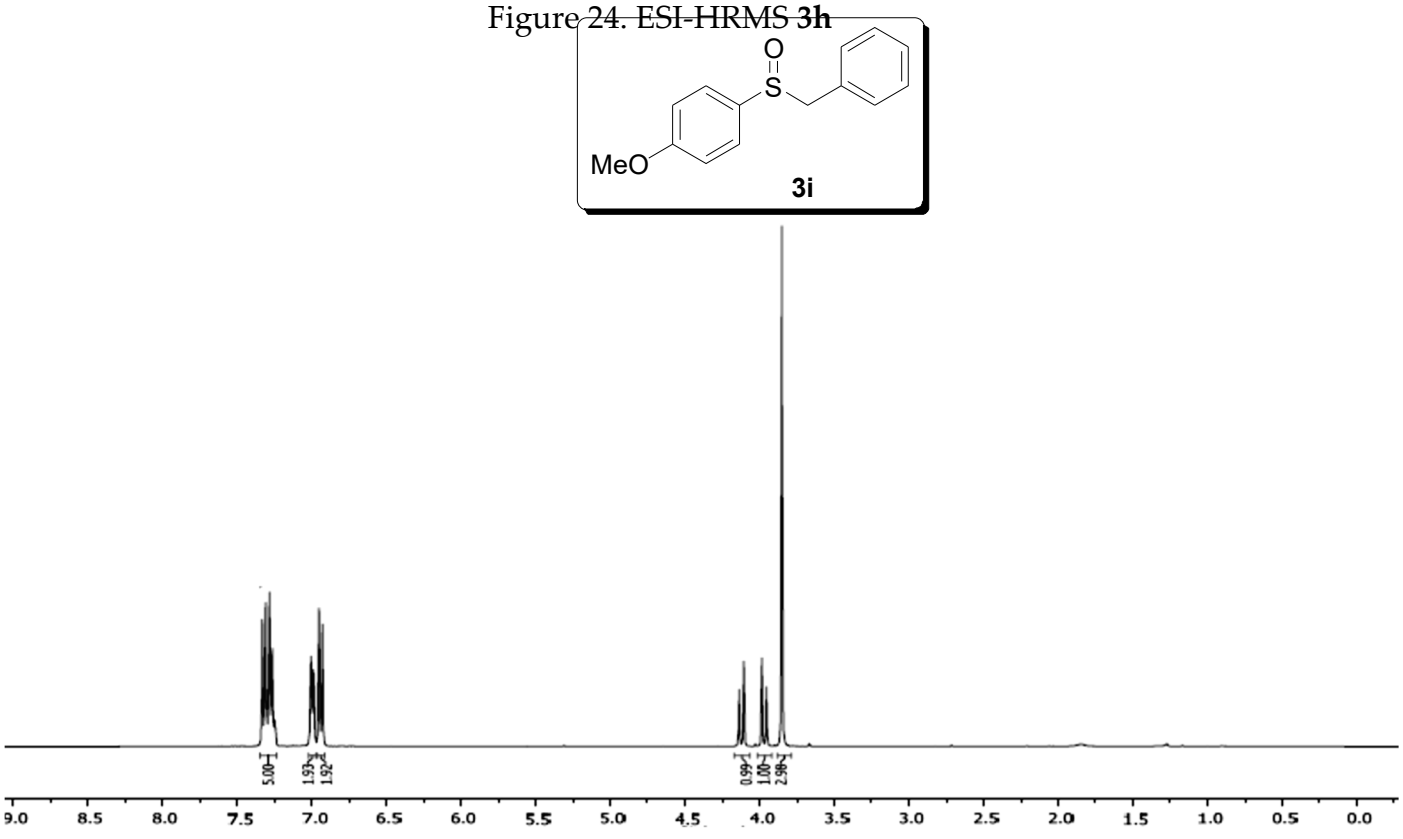


Figure S25. ^{1}H-NMR **3i**

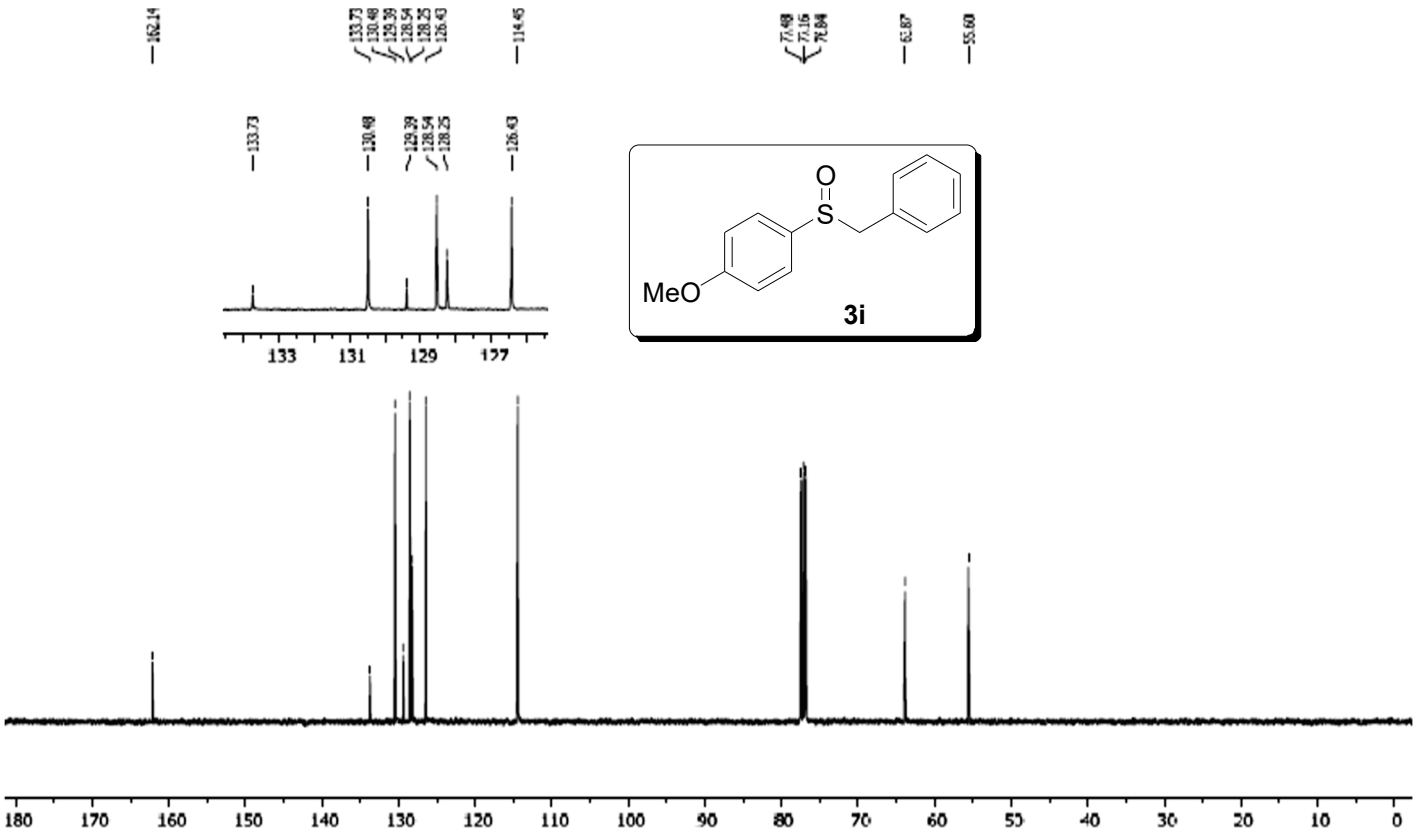


Figure S26. ^{13}C-NMR **3i**

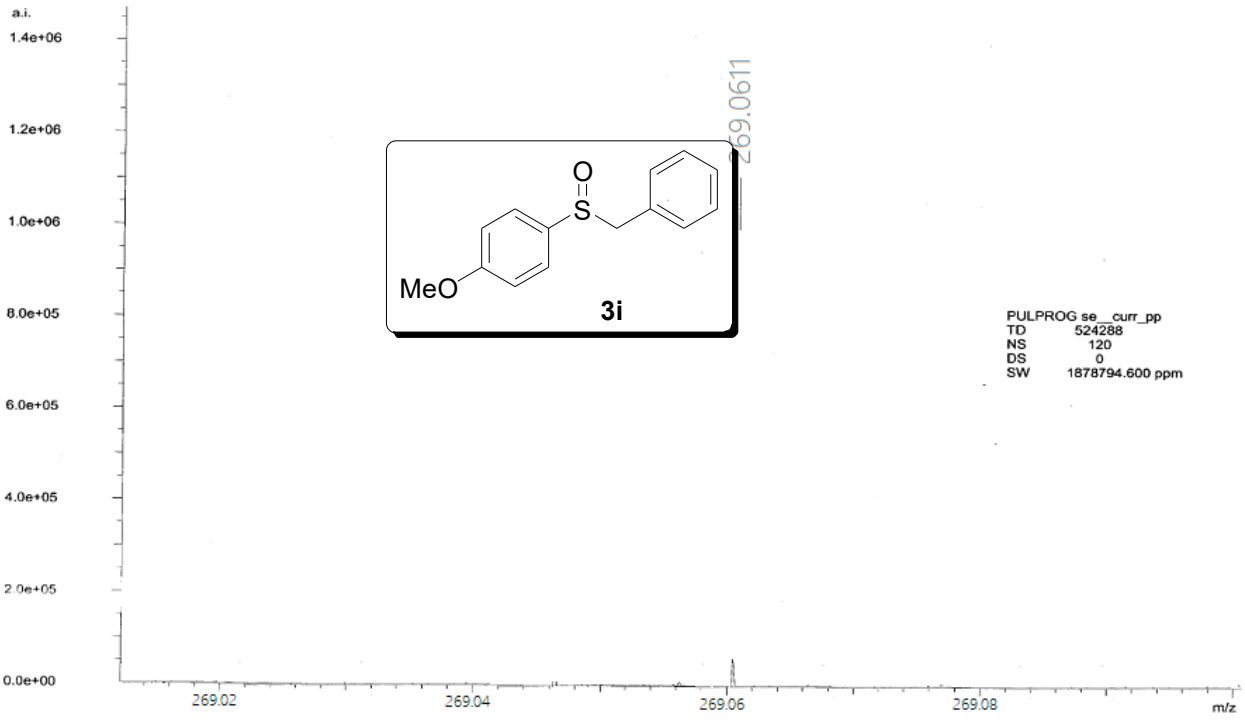
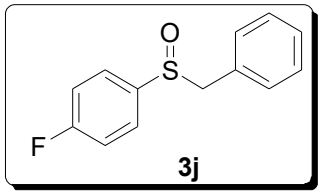


Figure S27. ESI-HRMS **3i**



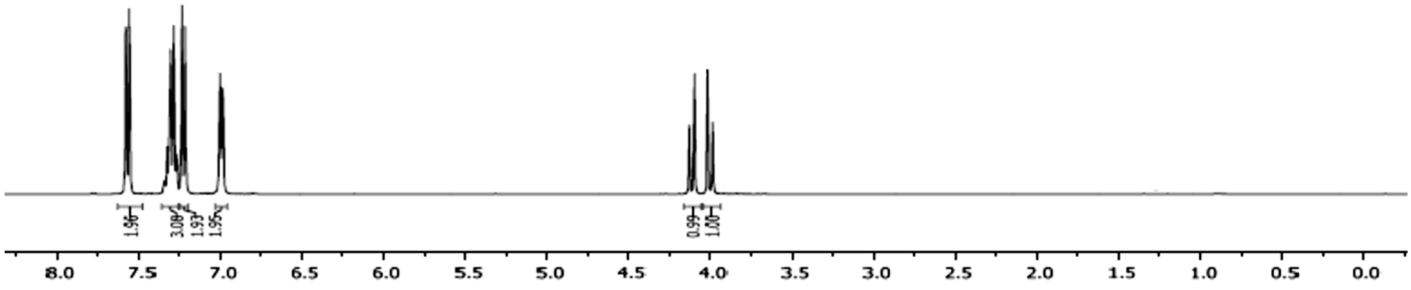


Figure S28. [1]H-NMR **3j**

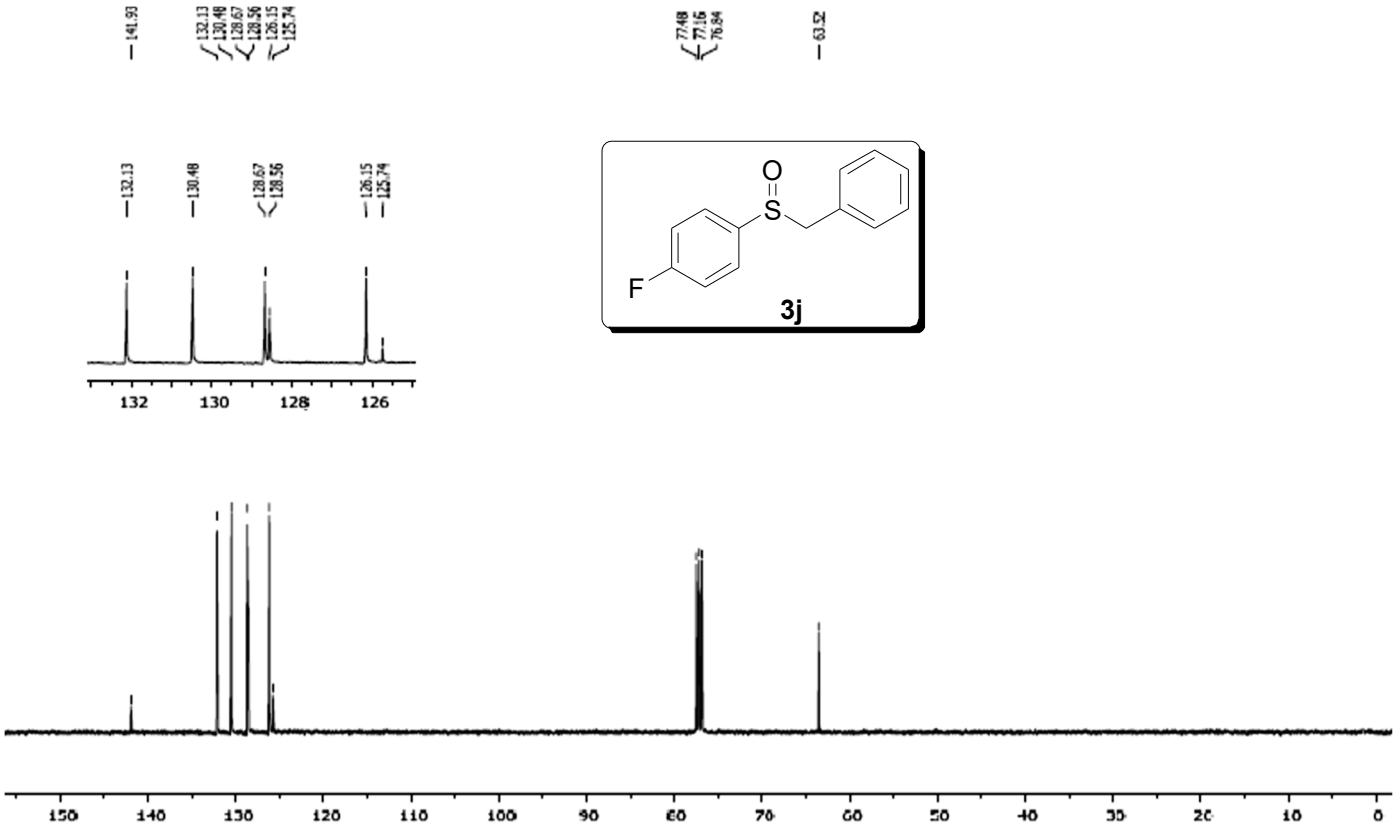


Figure S29. [13]C-NMR **3j**

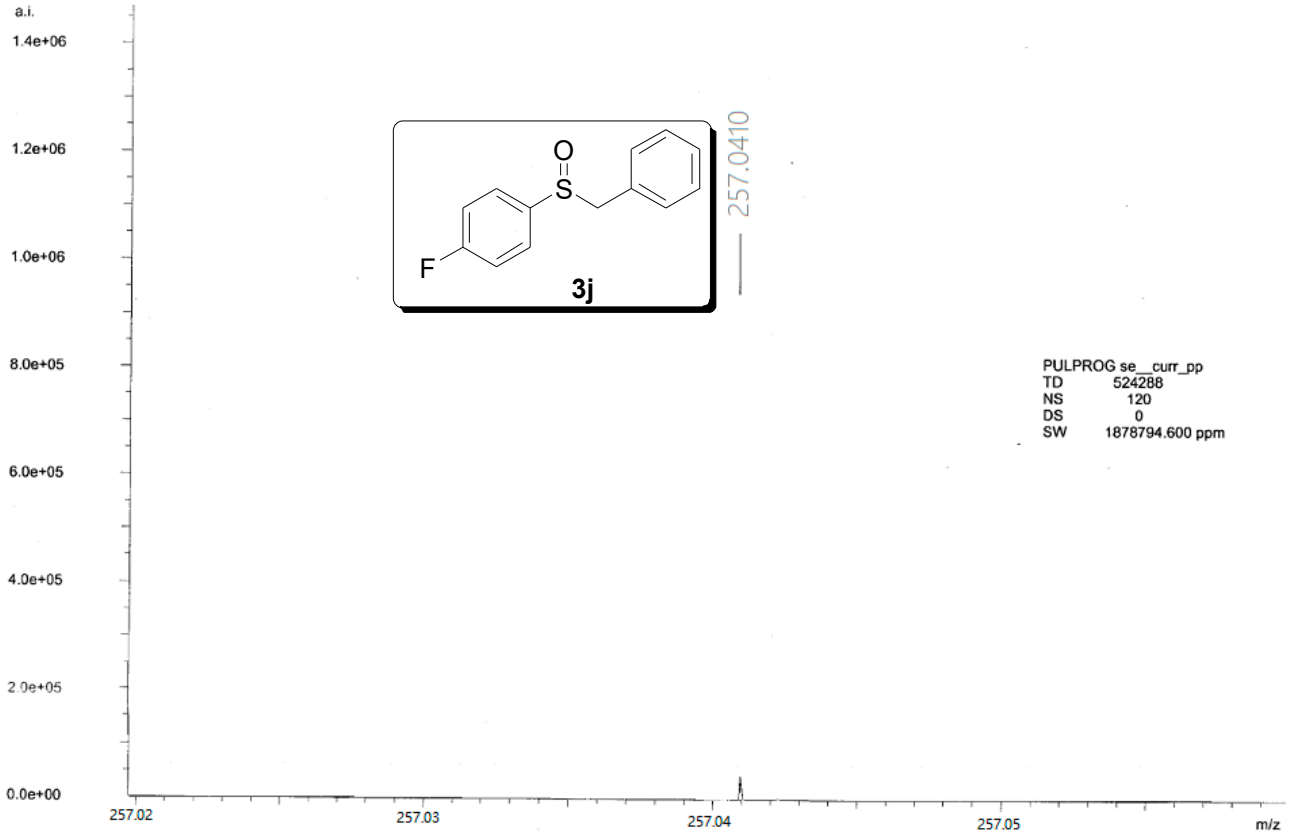


Figure S30. ESI-HRMS **3j**

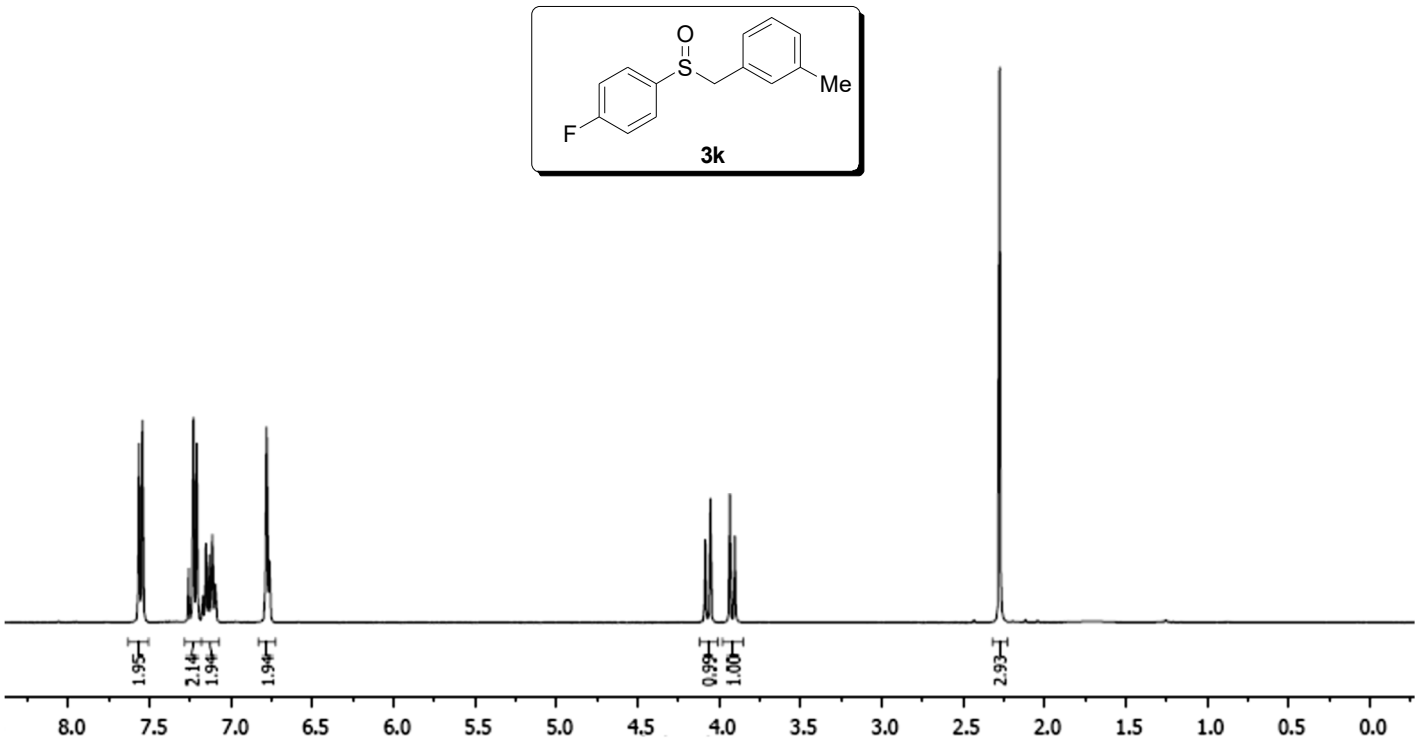


Figure S31. ^{1}H-NMR **3k**

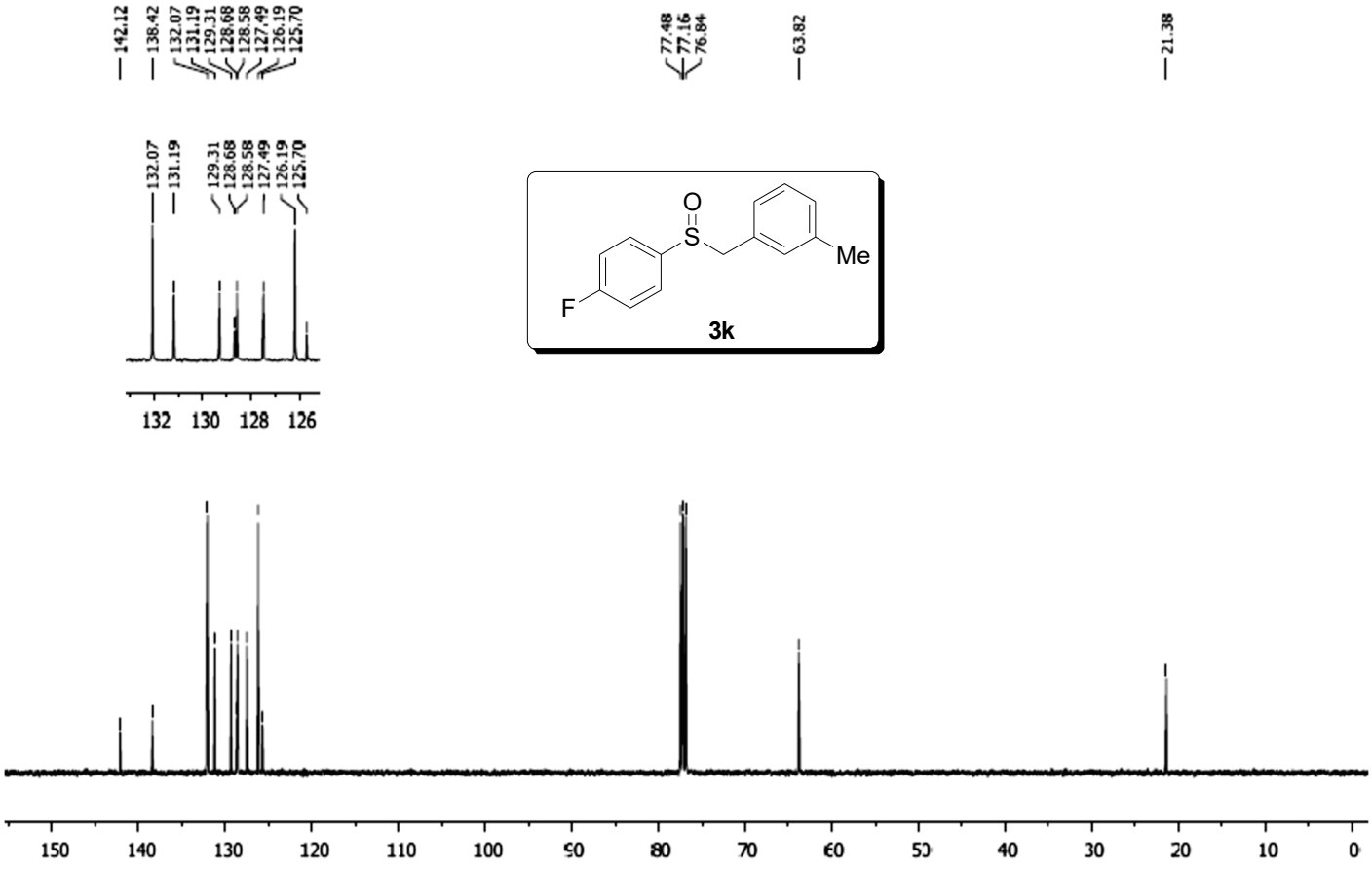


Figure S32. ^{13}C-NMR **3k**

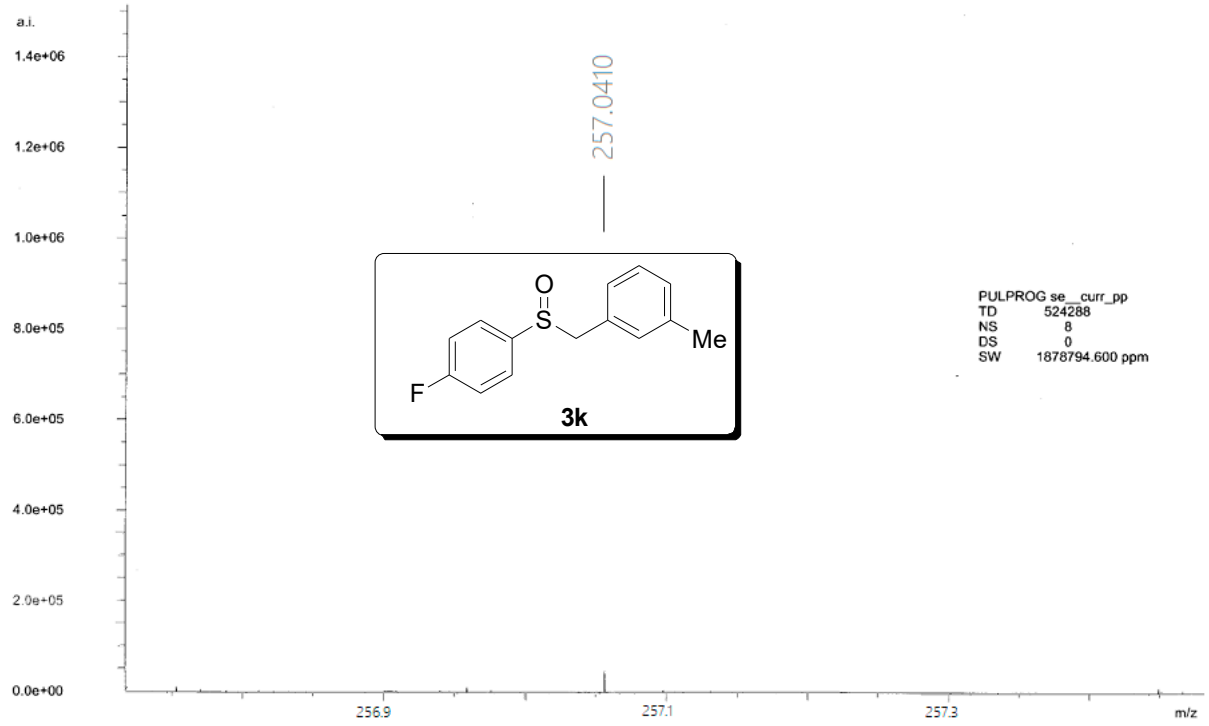
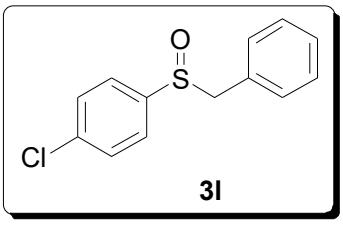


Figure S33. ESI-HRMS **3k**



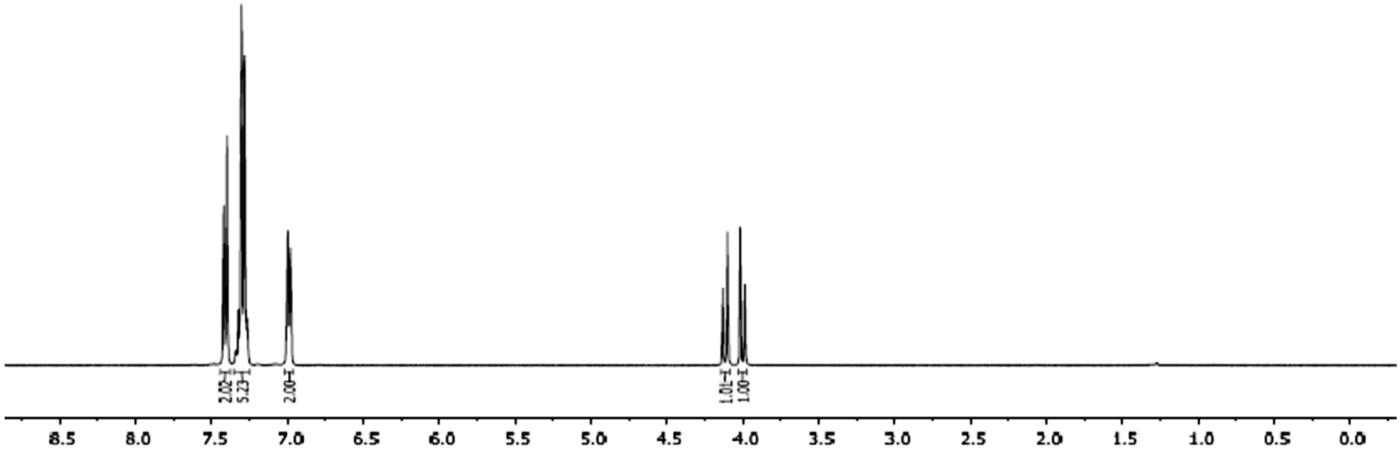


Figure S34. ^{1}H-NMR **3l**

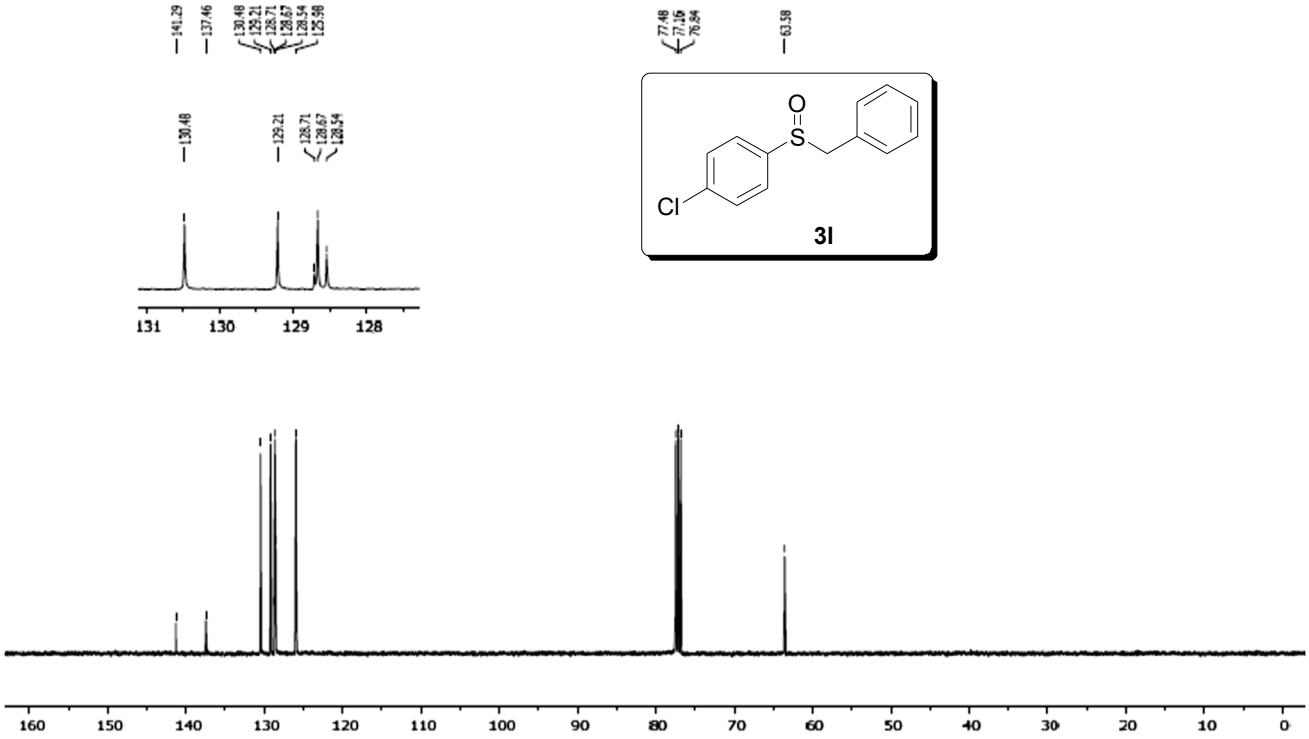
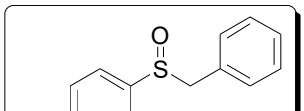


Figure S35. ^{13}C-NMR **3l**



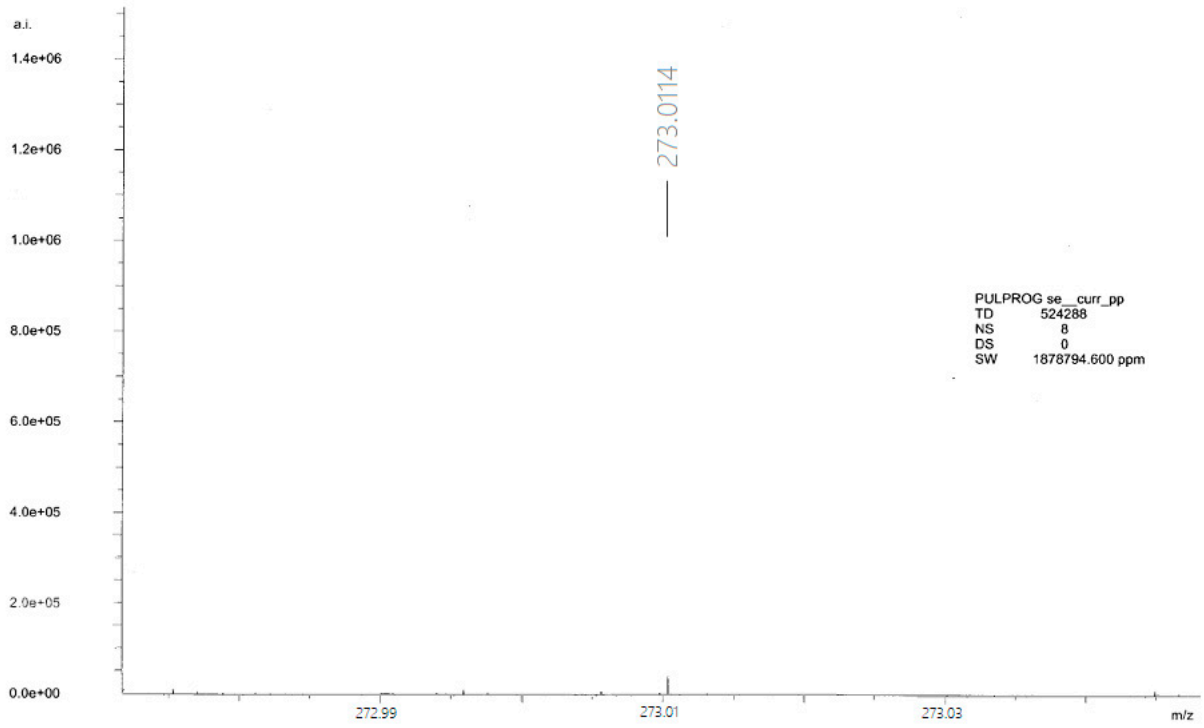
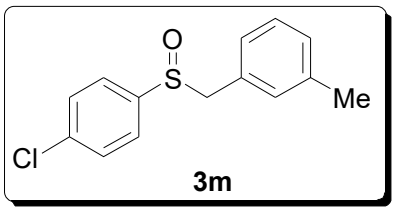


Figure S36. ESI-HRMS **3l**



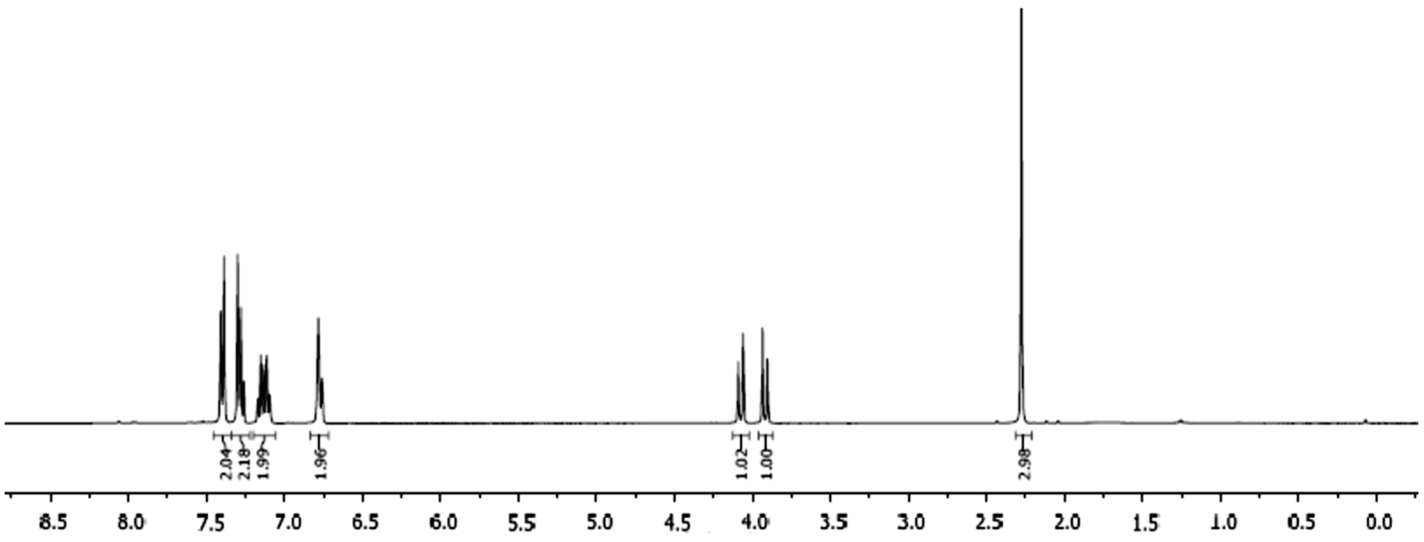


Figure S37. ^{1}H-NMR **3m**

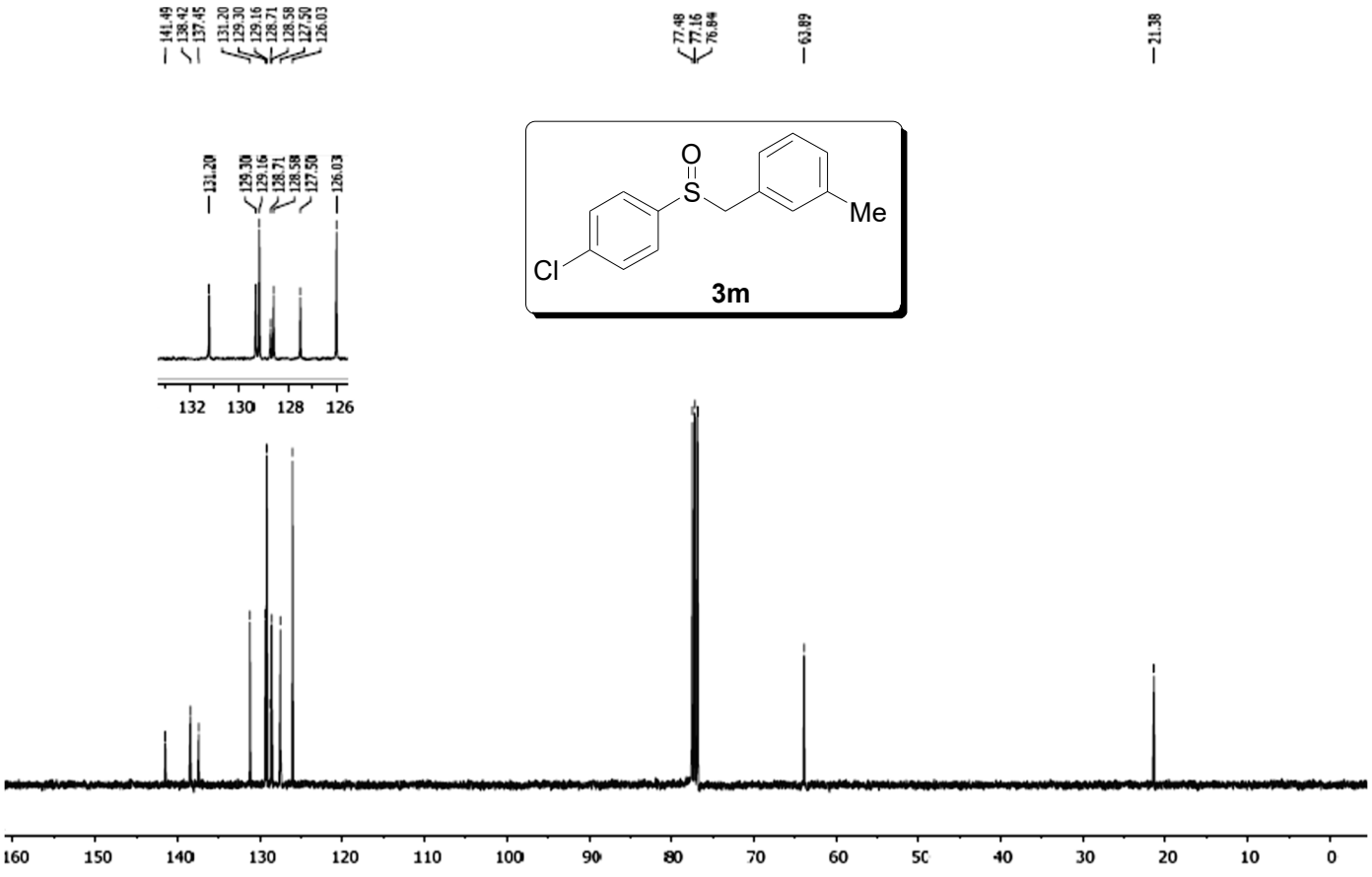


Figure S38. ^{13}C-NMR **3m**

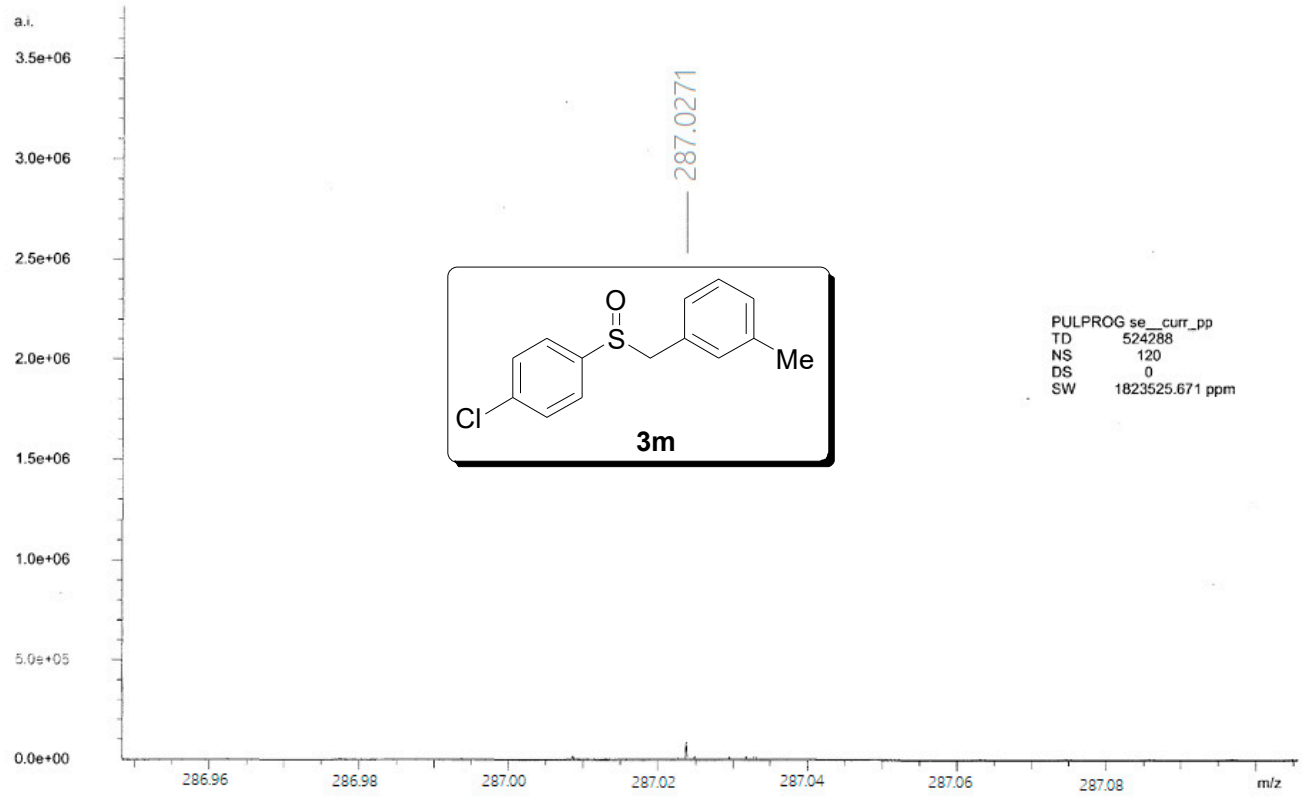
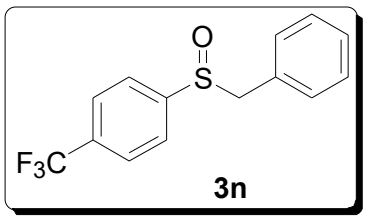


Figure S39. ESI-HRMS **3m**



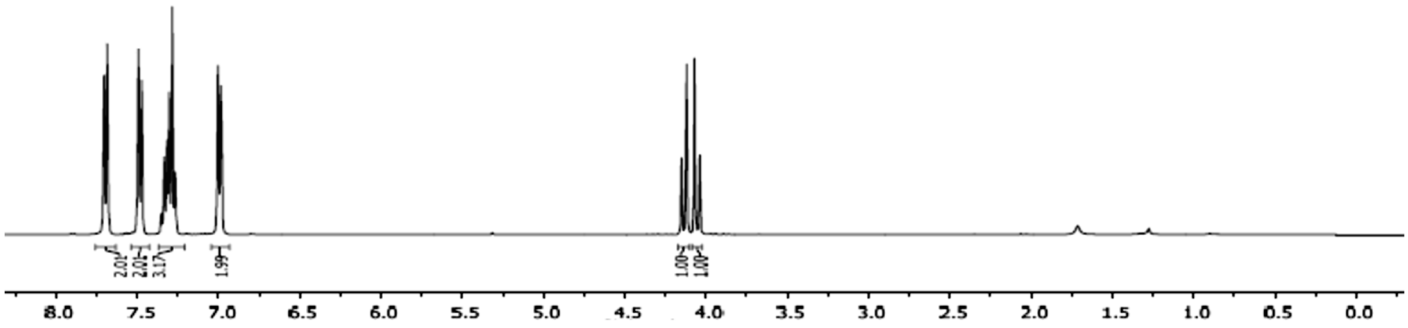
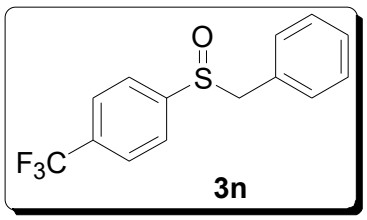


Figure S40. [1]H-NMR **3n**



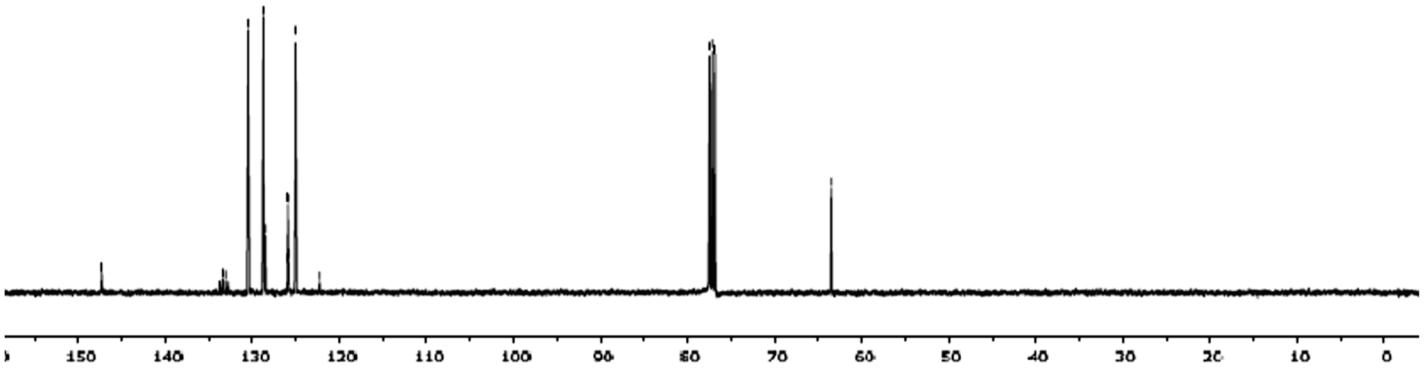


Figure S41. [1]C-NMR **3n**

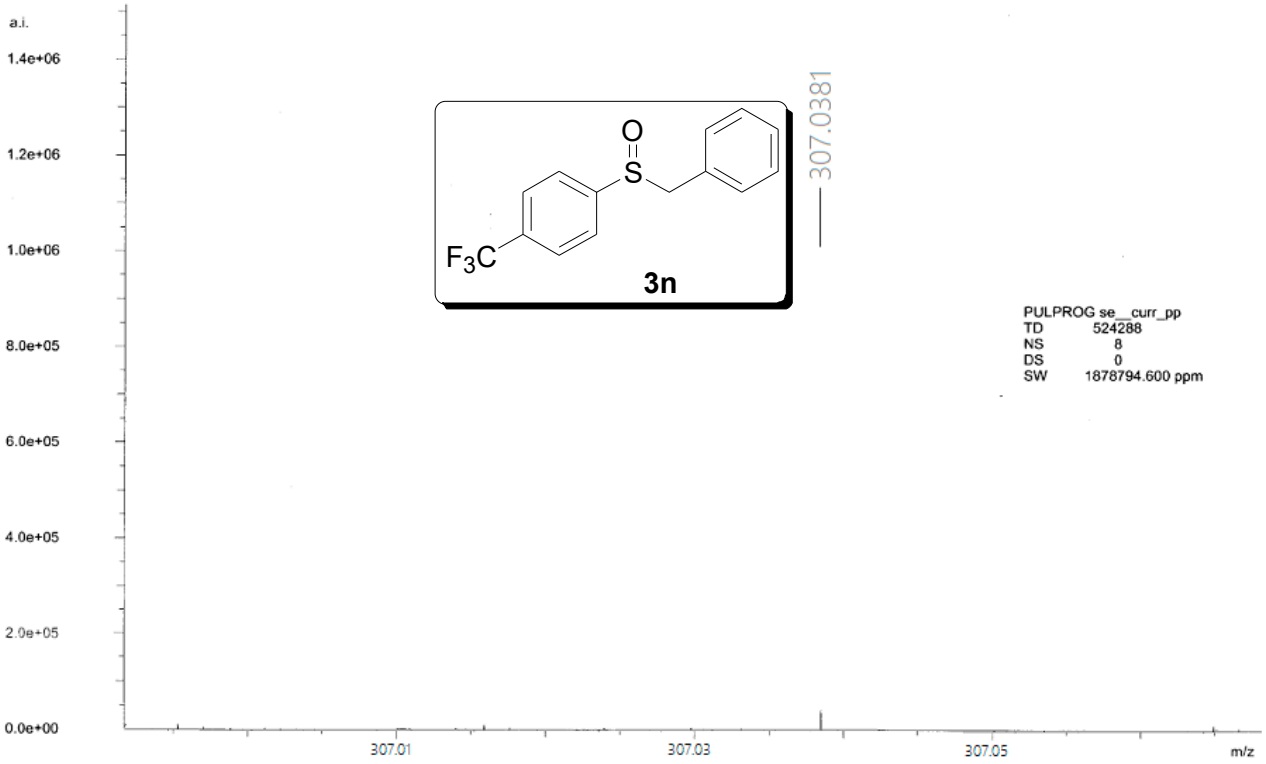
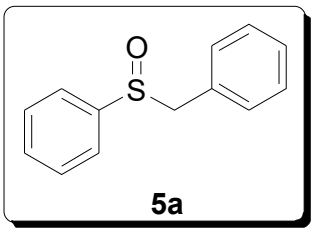


Figure S42. ESI-HRMS **3n**



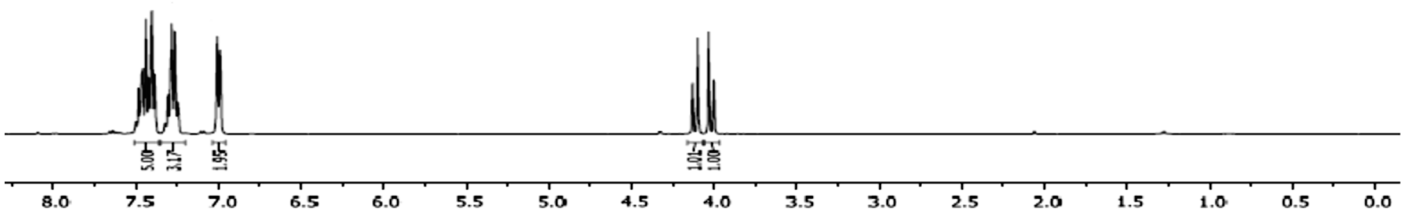


Figure S43. ^{1}H-NMR **5a**

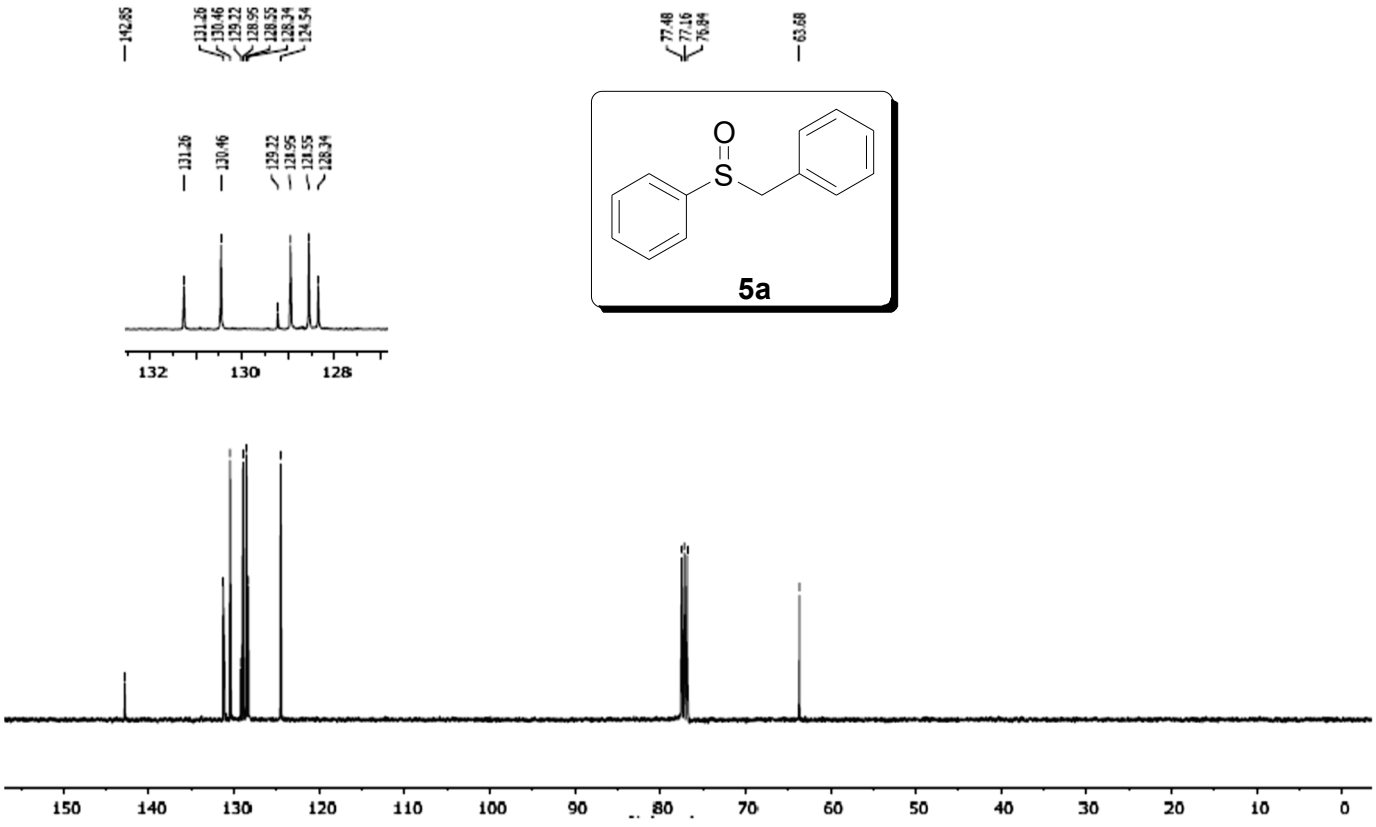


Figure S44. ^{13}C-NMR **5a**

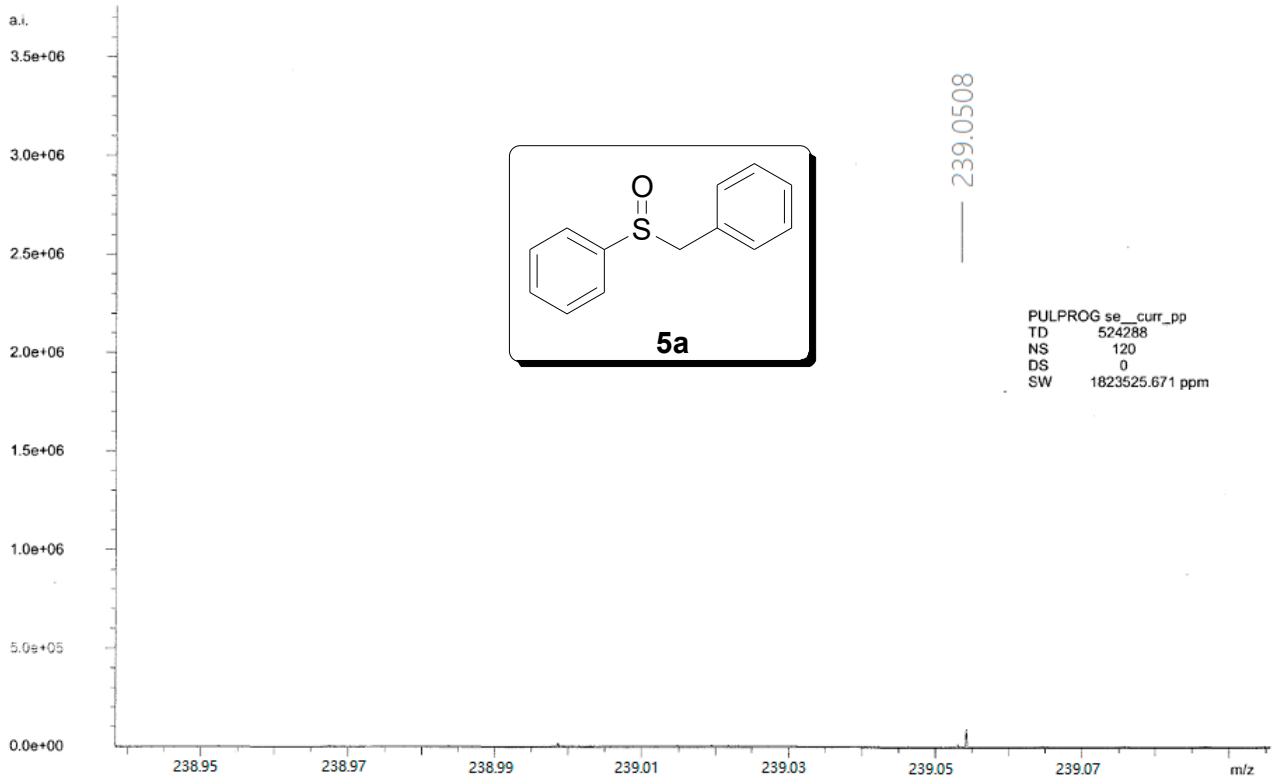
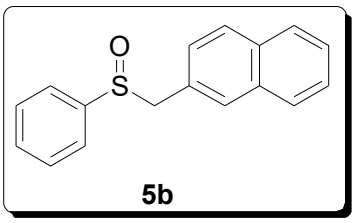


Figure S45. ESI-HRMS **5a**



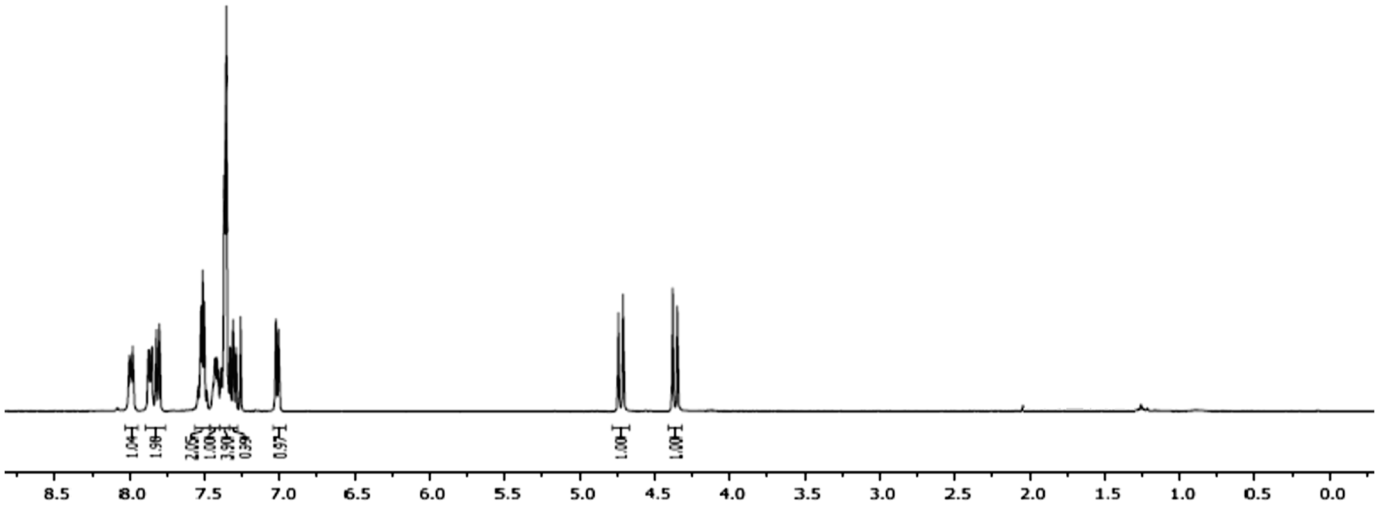


Figure S46. ^{1}H-NMR **5b**

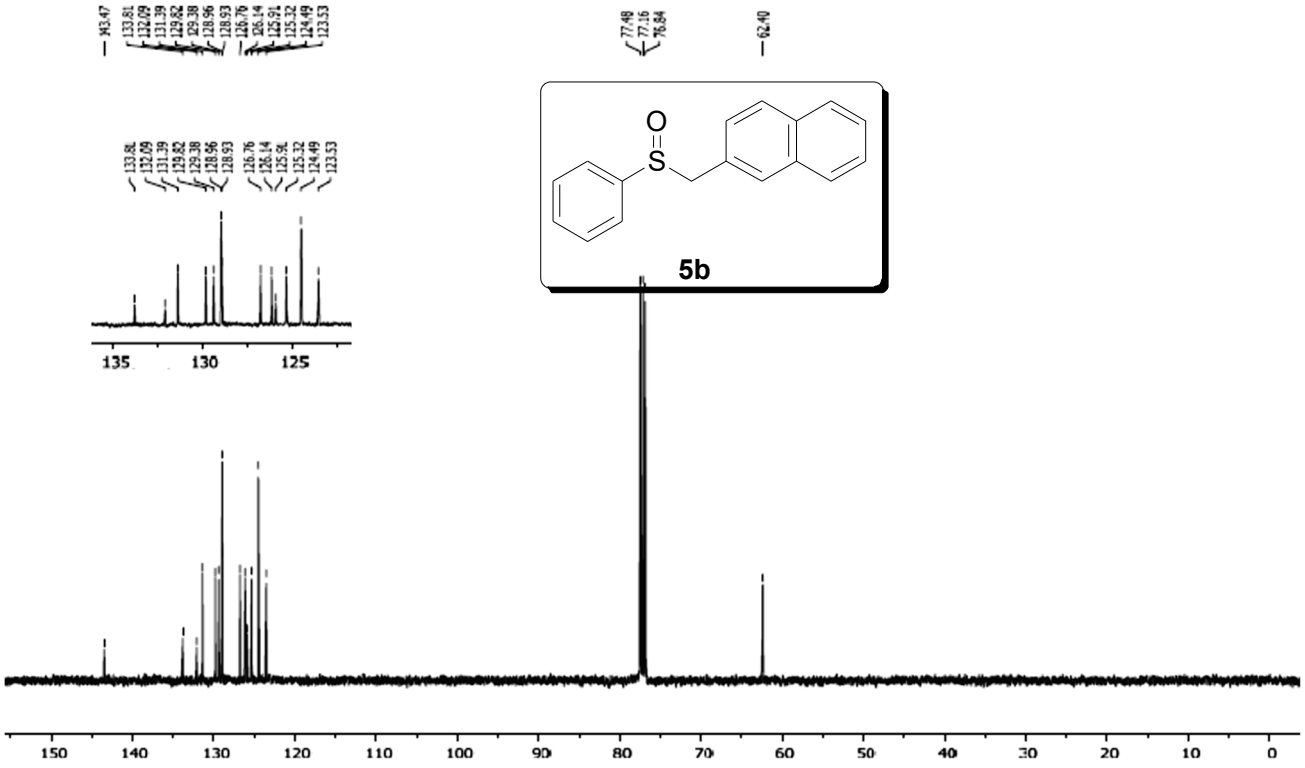


Figure S47. ^{1}C-NMR **5b**

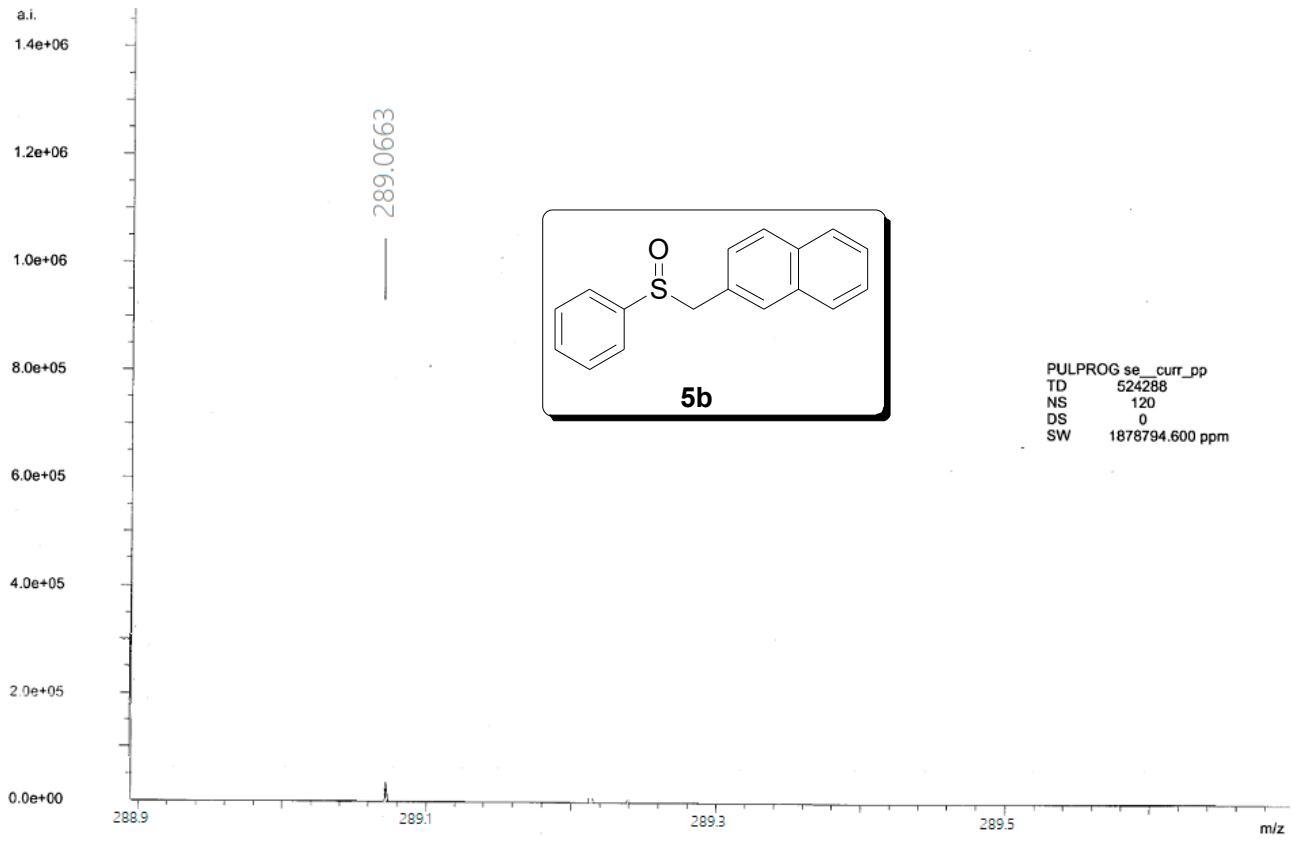
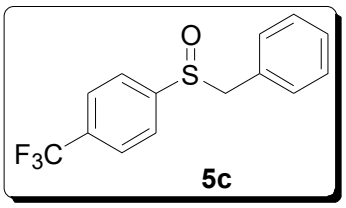


Figure S48. ESI-HRMS **5b**



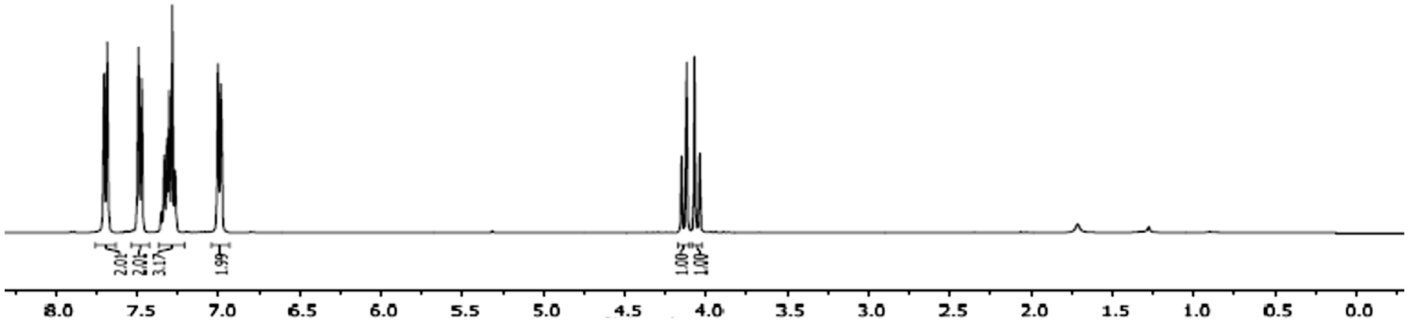


Figure S49. ^{1}H-NMR **5c**

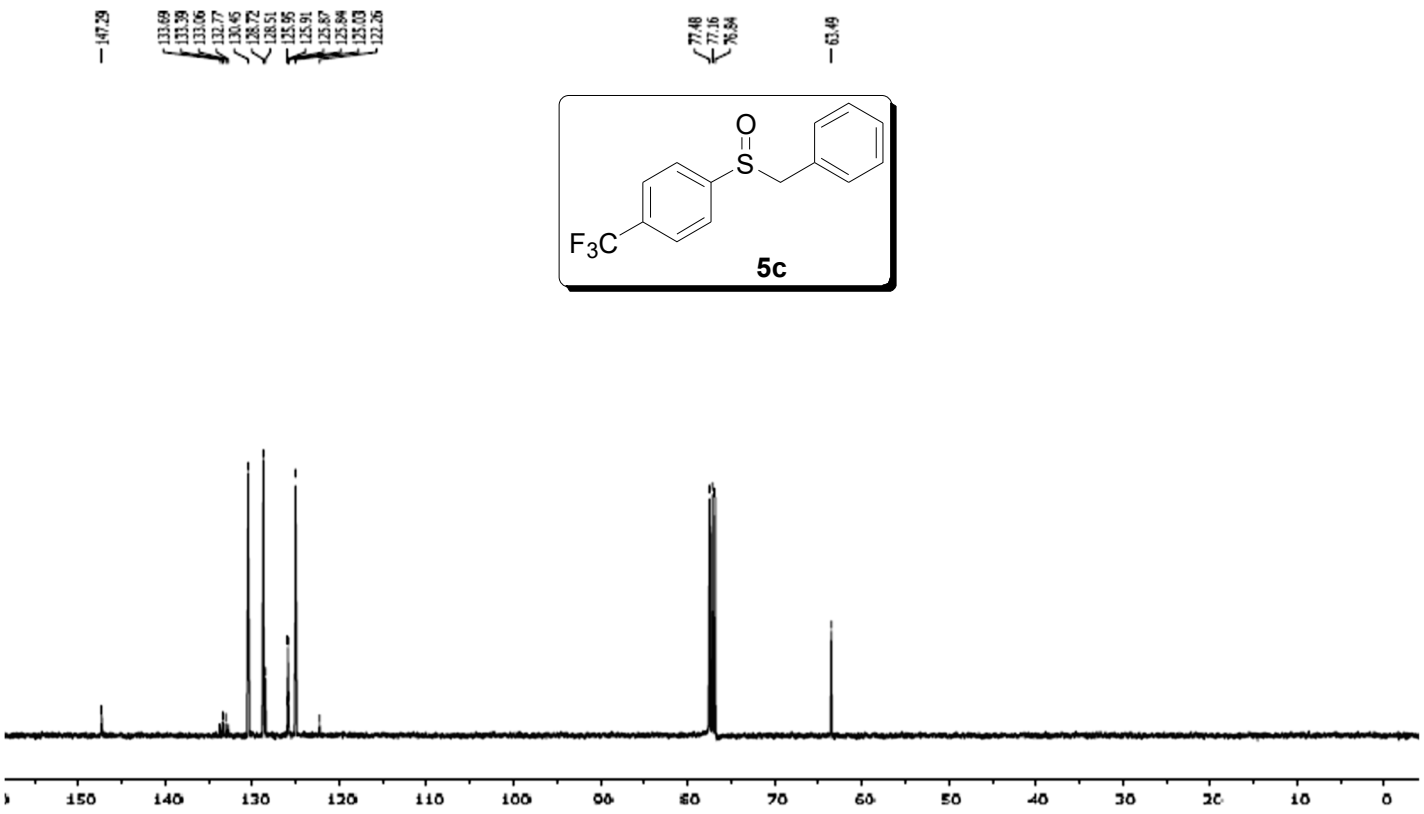


Figure S50. ^{1}C-NMR **5c**

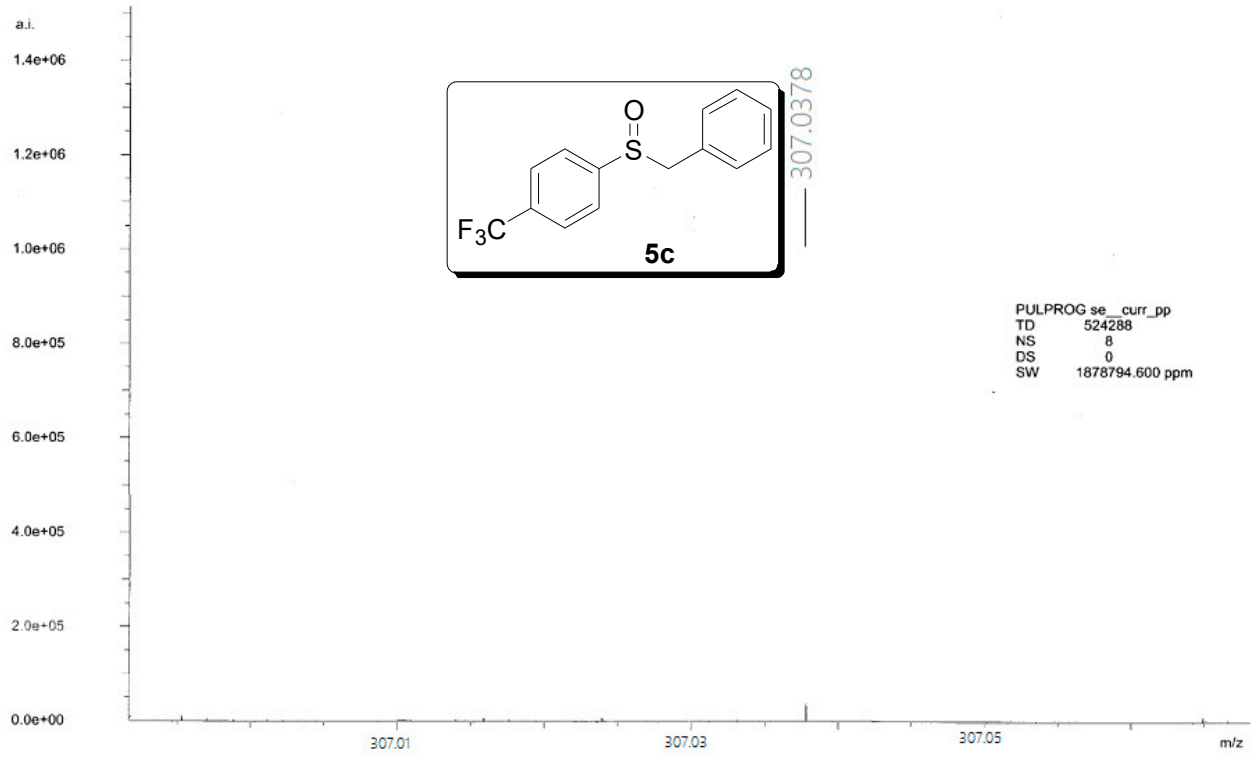


Figure S51. ESI-HRMS **5c**

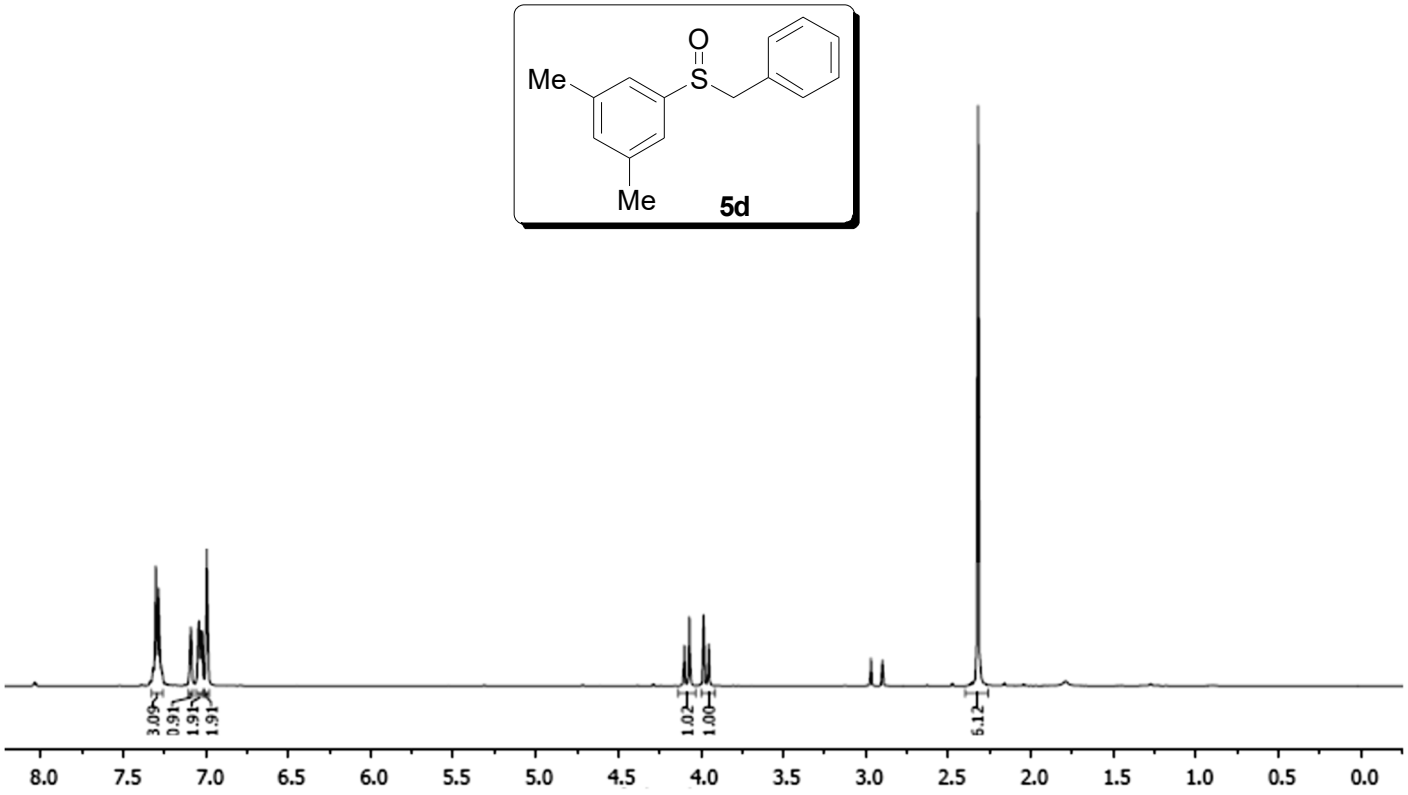


Figure S52. ^{1}H-NMR **5d**

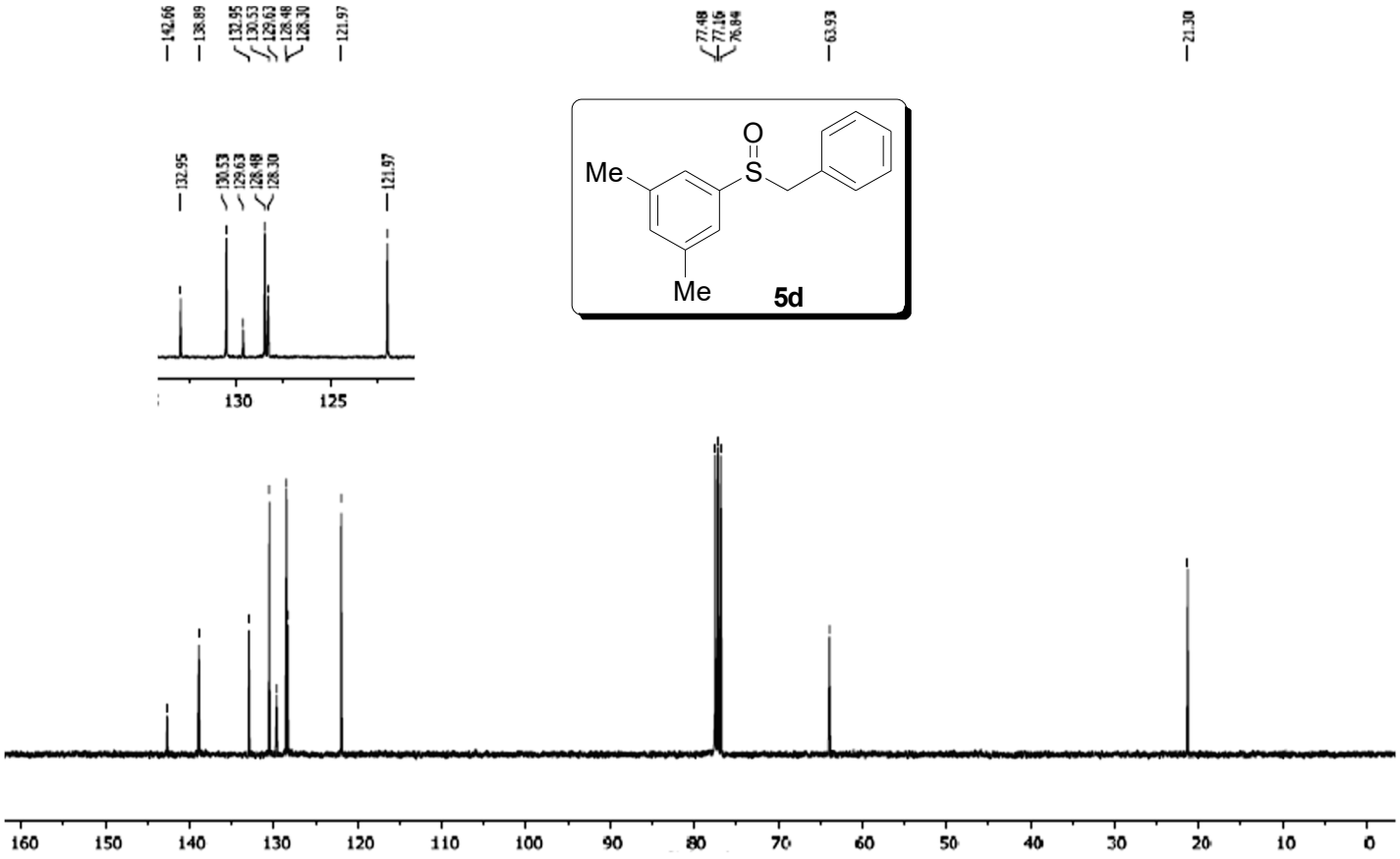


Figure S53. ^{1}C-NMR **5d**

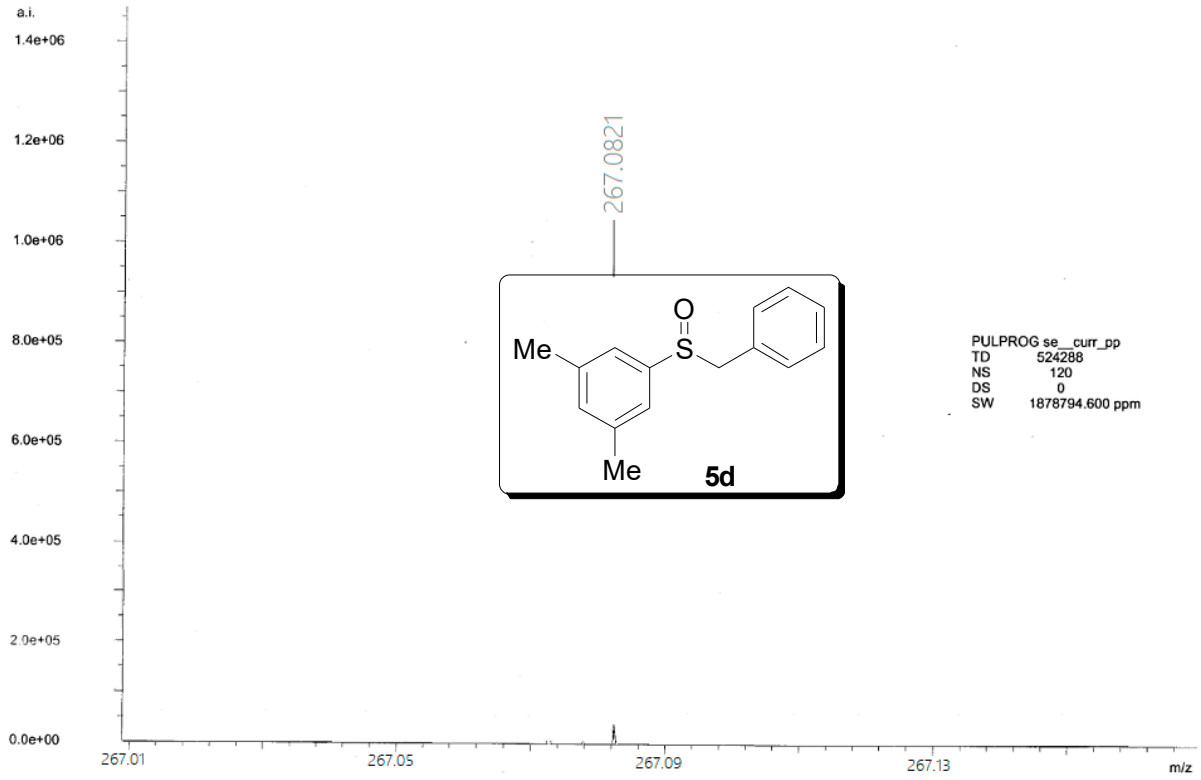


Figure S54. ESI-HRMS **5d**

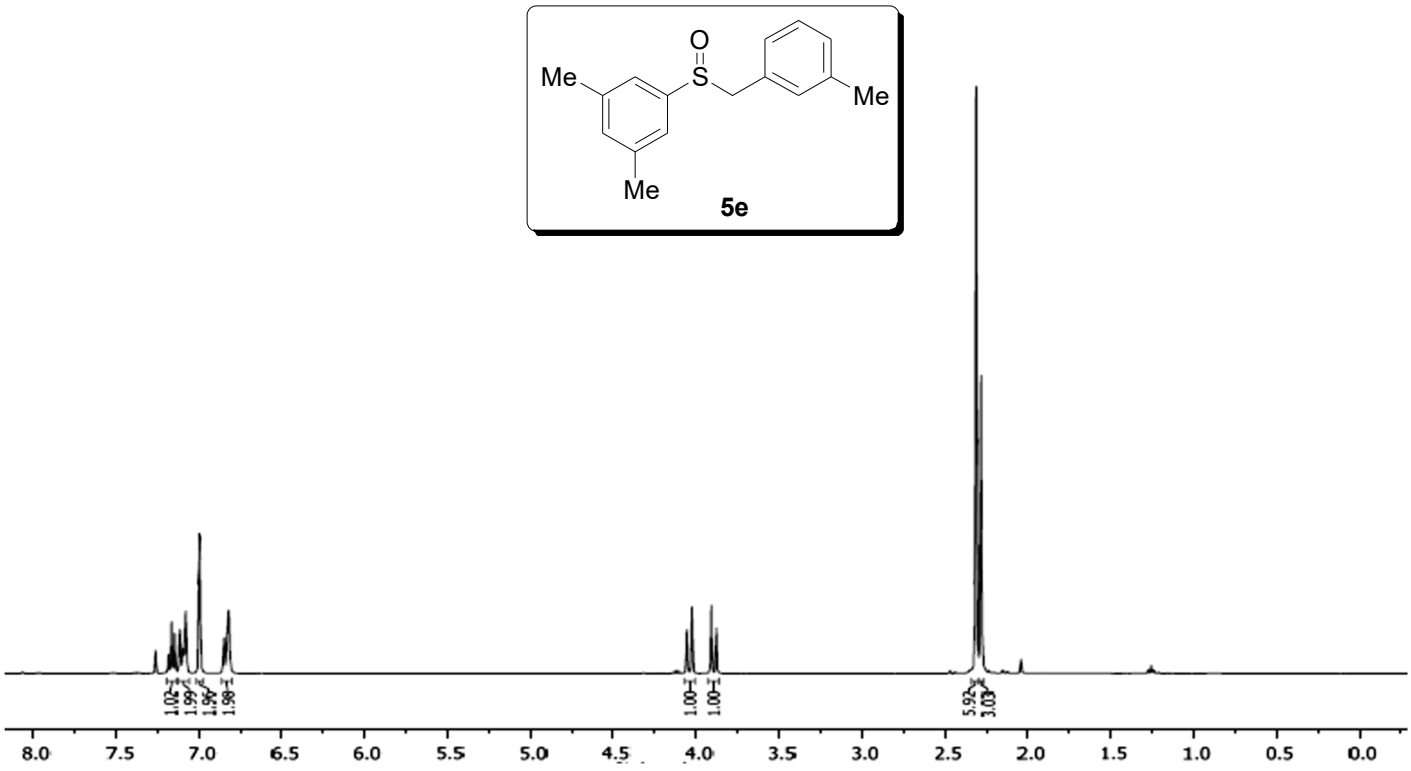


Figure S55. ^{1}H-NMR **5e**

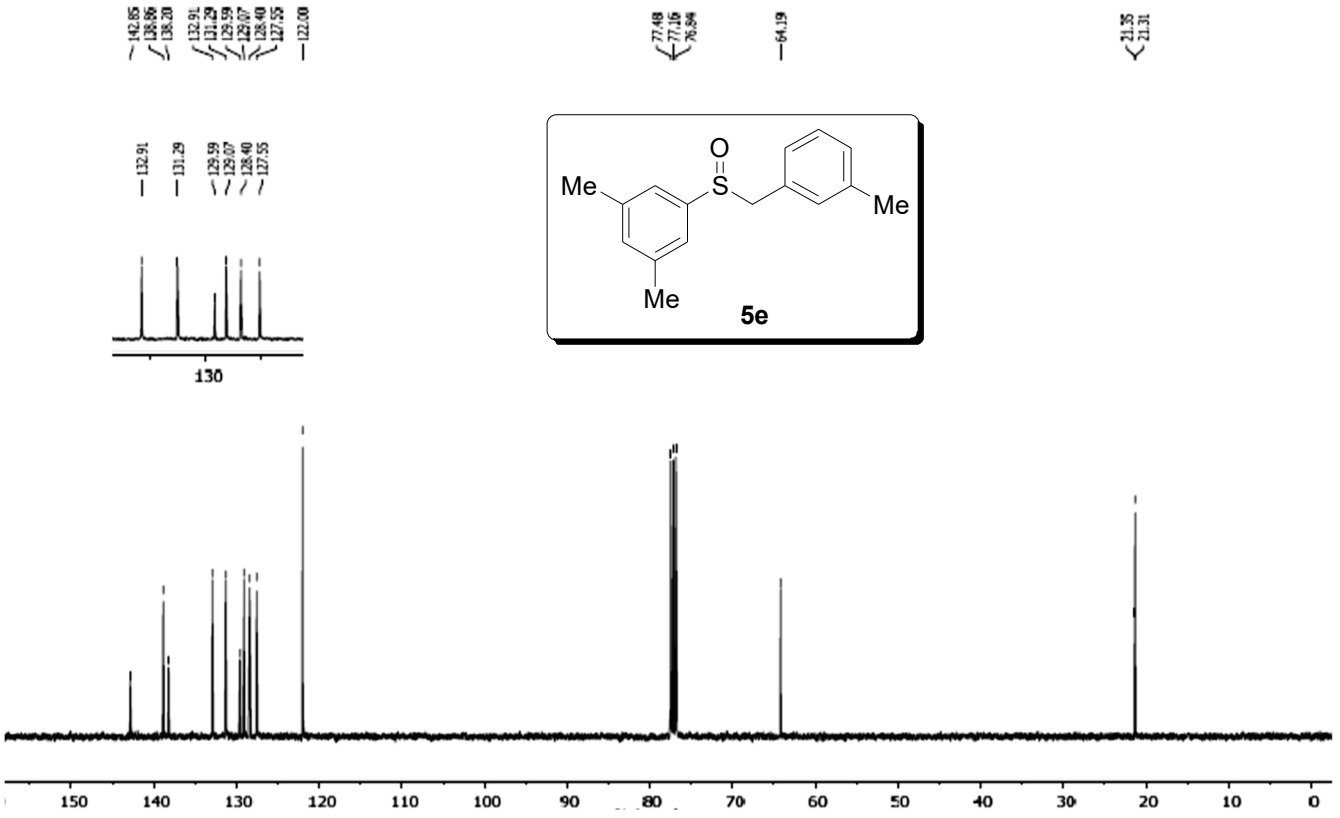


Figure S56. ^{1}C-NMR **5e**

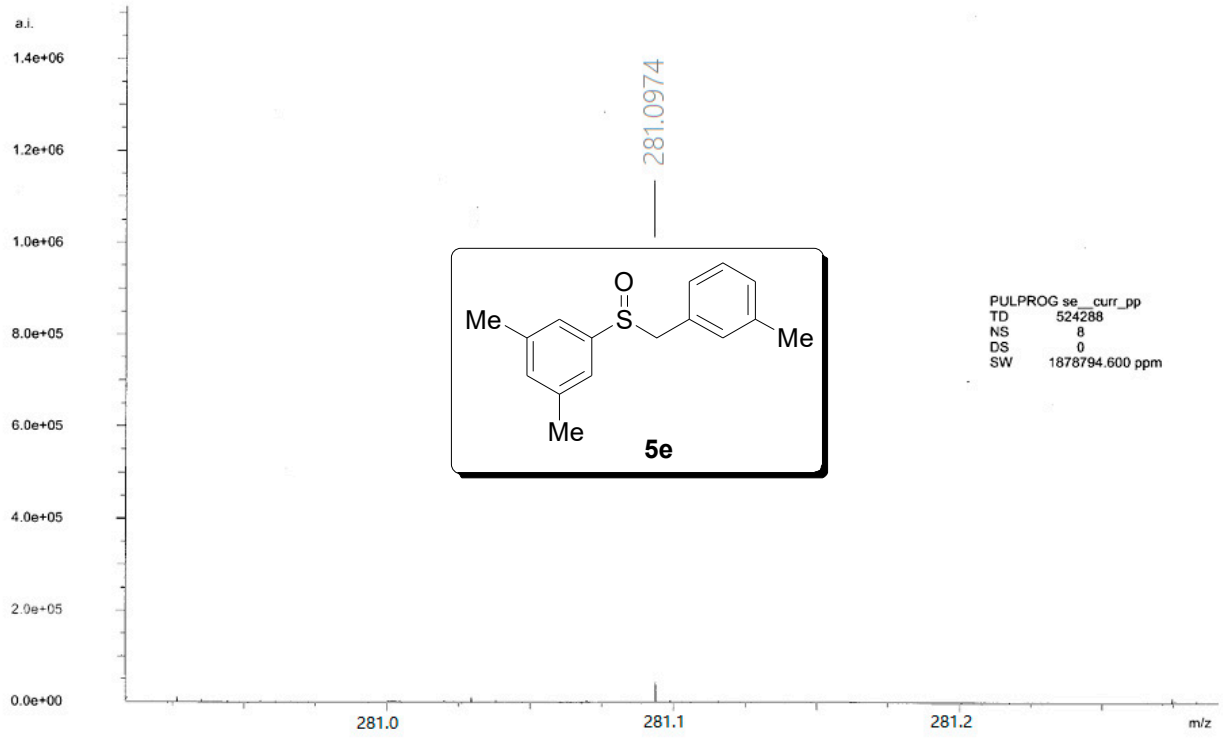
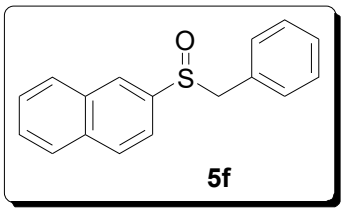


Figure S57. ESI-HRMS **5e**



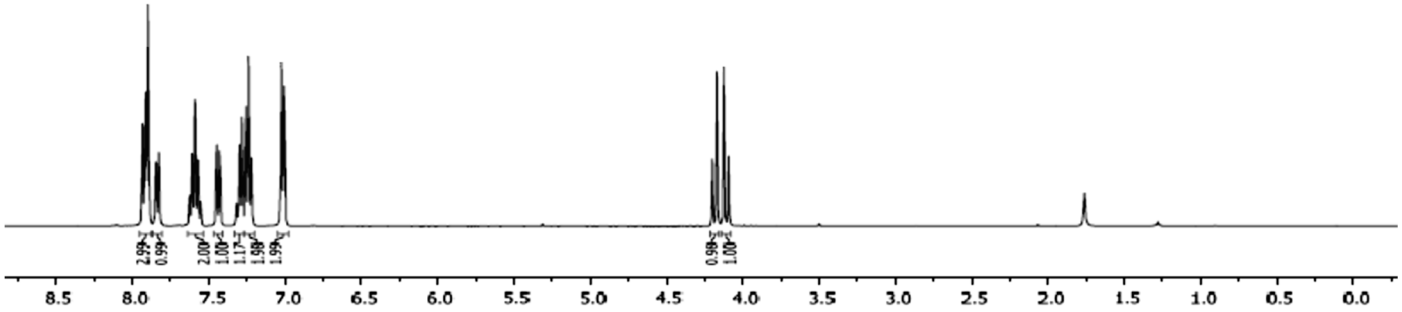


Figure S58. ^{1}H-NMR **5f**

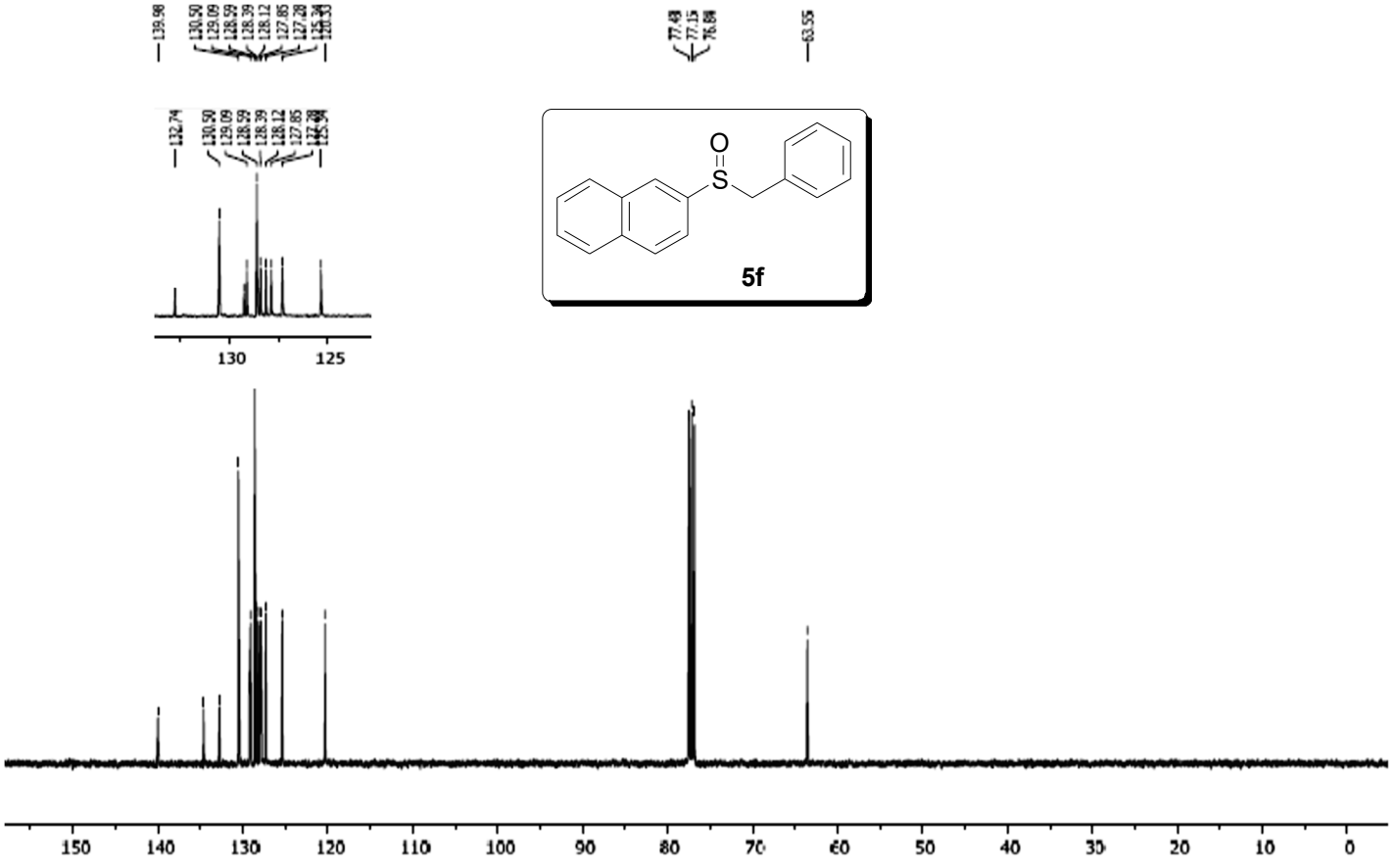


Figure S59. ^{1}C-NMR **5f**

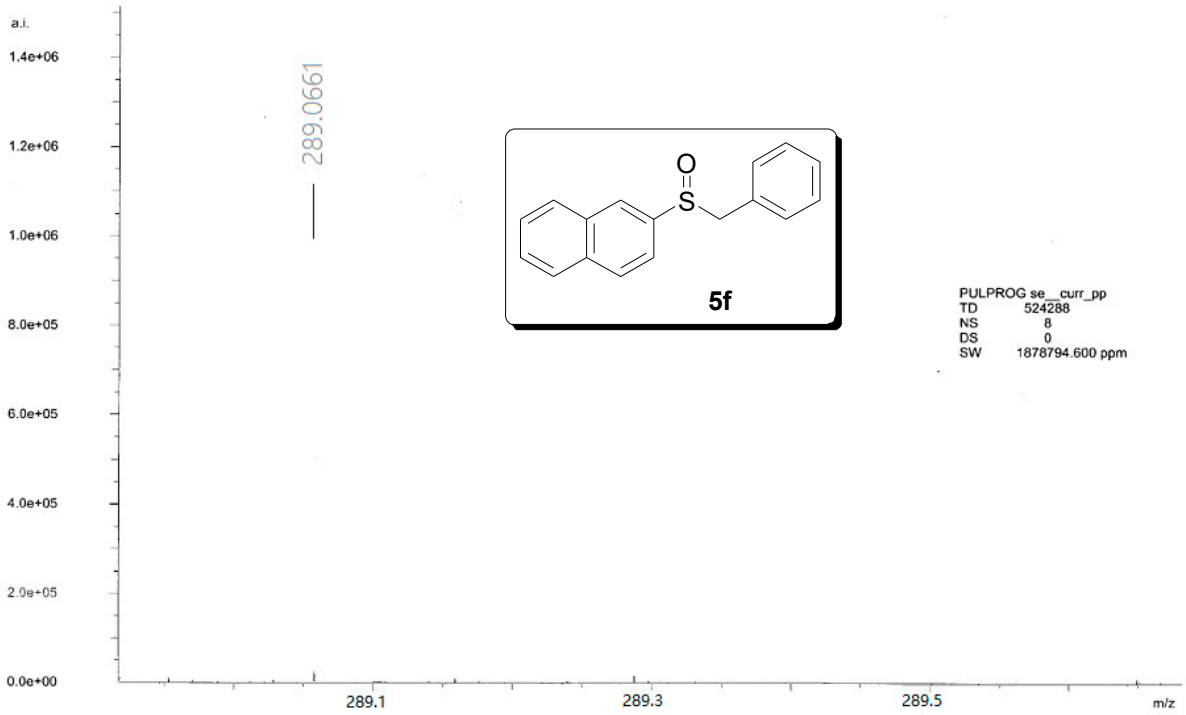


Figure60. ESI-HRMS **5f**