

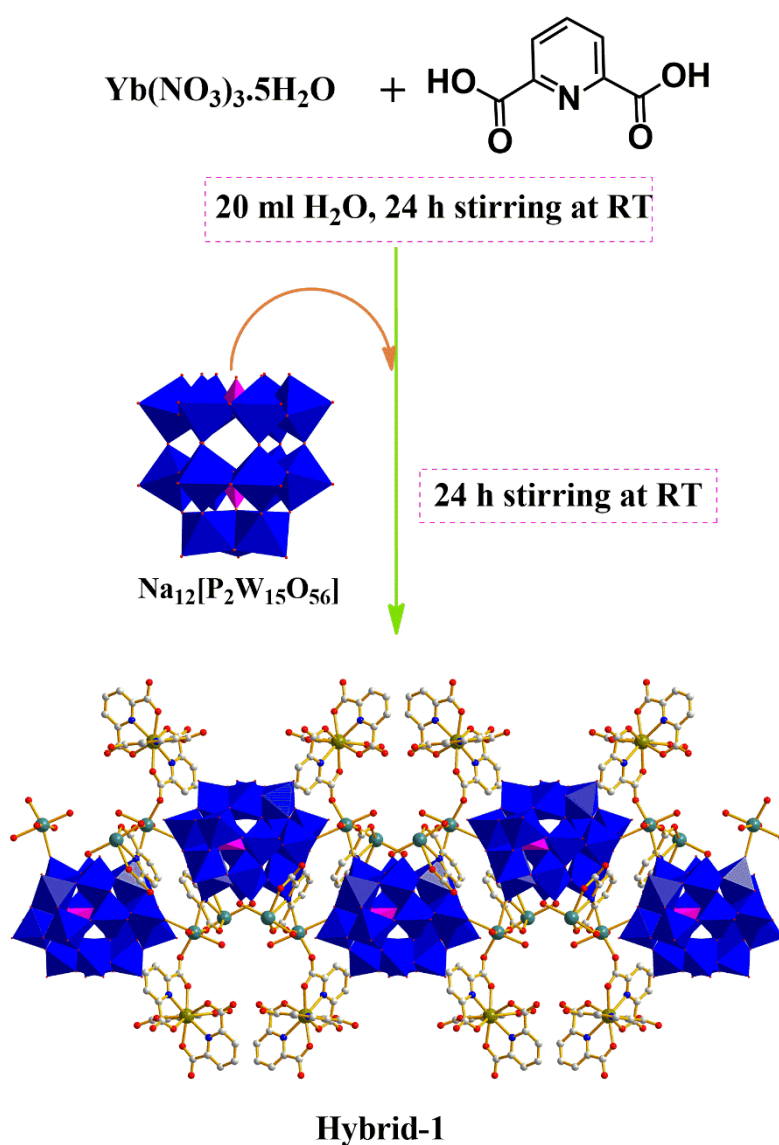
Electronic Supporting Information

An organic-inorganic hybrid supramolecular framework material based on $[P_2W_{18}O_{62}]^{6-}$ cluster and Yb & Na complexes of pyridine 2,6-dicarboxylic acid: a catalyst for selective oxidation of sulfides in water with H_2O_2

Pulikanti Guruprasad Reddy, Narsimha Mamidi and Chullikkattil P. Pradeep*

School of Basic Sciences, Indian Institute of Technology Mandi, Mandi - 175001, Himachal Pradesh, India.

E-mail: pradeep@iitmandi.ac.in; Fax: (+91) 1905 267 009.



Scheme 1. Synthetic scheme of hybrid 1. Colour code: WO_6 - dark blue polyhedra, PO_4 - pink polyhedra, Na - cyan, Yb - pale green, C - grey, O - red and N - blue.

Materials and methods

$\text{Na}_{12}[\text{P}_2\text{W}_{15}\text{O}_{59}]\cdot 14\text{H}_2\text{O}$,¹ 2-(ethylthio)aniline,² 2-(propylthio)aniline,² 2-(butylthio)aniline,² 4-(methylthio)phenylmethanol,³ 4-(methylthio)phenyl methacrylate⁴ and 4-(methylthio)phenyl benzoate⁵ were prepared according to the reported procedures. Pyridine 2,6-dicarboxylic acid, ytterbium (iii) nitrate pentahydrate, 4-(methylthio)phenol, 4-(methylthio)aniline, ferrocene carboxaldehyde, 4-(methylthio)benzoic acid, 4-(methylthio)benzaldehyde, methyl(4-nitrophenyl)sulfane and methyl(p-tolyl)sulfane were purchased from Sigma Aldrich. FT-IR spectra were recorded on a Perkin Elmer Spectrum 2 spectrophotometer using KBr pellets. ¹H and ¹³C NMR spectra were recorded on Jeol JNM ECX 500 MHz spectrometer in CDCl_3 . TGA measurements were performed on NETZSCH STA 449 F1 JUPITER Series instrument. The heating rate employed was 10 °C/min under N_2 atmosphere over a temperature range of 25-1000 °C. HR-MS spectra of compounds were recorded on Bruker HD compact instrument. UV-Vis studies were carried out on SHIMADZU UV-2450 spectrophotometer using quartz cuvettes. Energy-dispersive X-ray spectroscopy (EDX) analyses of hybrid **1** were conducted on FEI-Nova nano SEM-450.

X-ray crystallography

Single crystal X-ray data were collected on Agilent Super Nova diffractometer, equipped with multilayer optics monochromatic dual source (Cu and Mo) and Eos CCD detector, using Mo-K α (0.71073 Å) radiation at temperature 150 K. Data acquisition, data reduction and analytical face-index based absorption correction were performed using the program CrysAlisPRO.⁶ The structure was solved by Direct methods with ShelXS⁷ program and refined on F^2 by full matrix least-squares techniques with ShelXL⁷ program in Olex² (v.1.2) program package.⁸ Anisotropic displacement parameters were applied for all the atoms, except for hydrogen atoms and some less intensely scattered atoms. The crystal and refinement data are summarized in Table 1. CCDC 1444174 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cifdata.

Experimental section

1. Synthesis and characterization of hybrid **1**

Pyridine-2,6-dicarboxylic acid (0.02321 g, 0.13904 mmol) and $\text{Yb}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$ (0.0534 g, 0.13904 mmol) were stirred together in 20 ml of distilled water for 24 hrs at room temperature. To the resultant turbid solution was added $\text{Na}_{12}[\text{P}_2\text{W}_{15}\text{O}_{56}]$ (0.300 gm, 0.06952 mmol) and stirred again for 24 hrs. The clear solution thus obtained was kept for crystallization by slow evaporation. After 7 days, block color-less crystals were collected and dried overnight in desiccator. Yield: 0.170 gm (75 %) based on $\text{Na}_{12}[\text{P}_2\text{W}_{15}\text{O}_{56}]$ used. FT-IR: ν max/ cm^{-1} 3565, 1615, 1435, 1386, 1283, 1195, 1080, 1055, 1024, 939, 903, 824, 694 cm^{-1} .

(a) Infrared spectroscopy

The infrared spectrum of hybrid **1** agrees well with the proposed structure (see Figure S1). The broad bands at 3140 cm^{-1} are ascribed to the presence of hydrogen bonded O-H functional groups of PDCH₂ and lattice water molecules.⁹ The appearance of vibrational peaks at 1613, 1575 and 1386 cm^{-1} are due to the anti-symmetric and symmetric vibrations of carbonyl groups respectively. The peaks at 1435 and 1283 cm^{-1} are due to the stretching vibrations of C=C and C-O groups.¹⁰ The bands at 1086 (P-O) and 950 (W=O), 907 and 700 (W-O-W) cm^{-1} are due to the presence of $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ POM units in hybrid **1**.¹¹

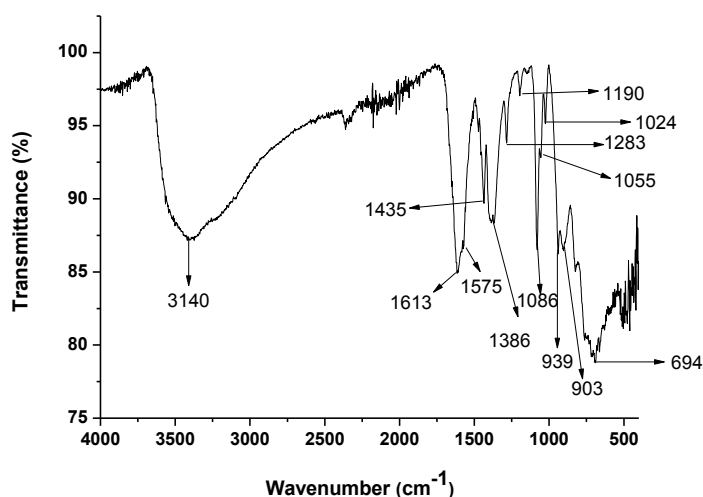


Figure S1. Infrared spectrum of hybrid **1**

(b) UV-visible spectroscopy

The electronic properties of hybrid **1** were studied by UV-visible measurements on 10^{-5} M aqueous solutions (see Figure S2). The maximum absorption of hybrid **1**, $\lambda_{\text{max}} = 269, 277$ nm, are due to the presence of $(\text{Yb}(\text{PDCH}_2)_2(\text{PDCH}))^{2+}$ complex in the hybrid **1**.¹²

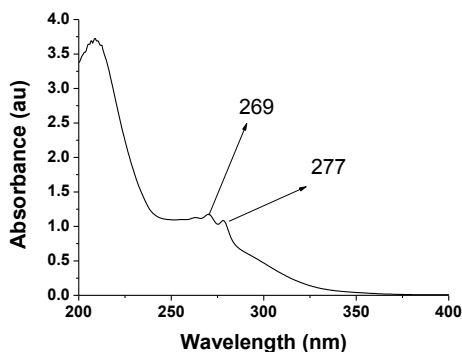


Figure S2. UV-Visible spectra of hybrid **1** at 10^{-5} M aqueous solution

(c) TGA analysis

To investigate the thermal stability of hybrid **1**, thermo gravimetric analysis was carried out and results are shown in Figure S3. The hybrid **1** shows two major weight losses in the temperature range between 25 °C to 650 °C. The first weight loss of 6.08 % (calcd. 6.12 %) was observed at 25-200 °C due to the loss of lattice water molecules and water molecules coordinated to the Na1 and Na2 atoms. The second weight loss of 20.34 % (calcd. 20.47 %) occurred between 200-650 °C due to the loss of four PDCH₂ based ligands present in the cationic unit. The TGA data is therefore in good agreement with other spectroscopic data and XRD analysis.

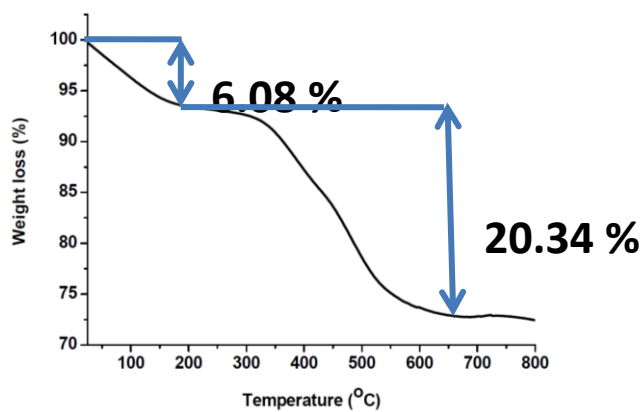


Figure S3. TGA profile of hybrid 1

(d) EDX analysis

EDX analyses of hybrid 1 were carried out to confirm the presence of Yb, Na etc elements. EDX analyses revealed that the hybrid 1 consists of following elements: W, O, Yb, P, C, Na and N elements (see Figure S4) as expected in agreement with other characterization data.

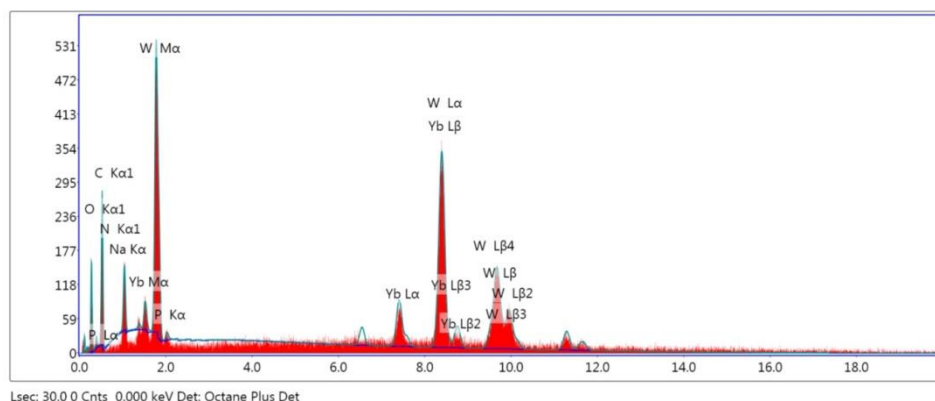
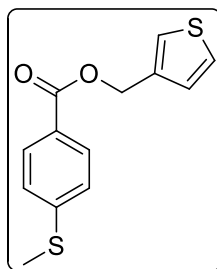


Figure S4. EDX data of hybrid 1

2. General procedure for the esterification (I)¹³

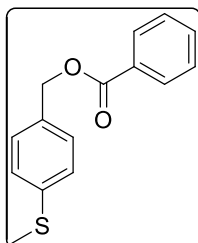
Carboxylic acid (1.0 equiv), dicyclohexylcarbodiimide (1.5 equiv) and *N,N*-dimethylaminopyridine (0.1 equiv) were added to a solution of alcohol (1.0 equiv) in anhydrous dichloromethane under N_2 atmosphere. Stirring was continued for 16 h at room temperature. Upon completion of reaction (monitored by TLC), the reaction mixture was filtered and washed with dichloromethane (5 mL X 3). The crude reaction mixture was concentrated under reduced pressure and the residue was purified using column chromatography on silica gel with EtOAc/hexane (1-3%) as an eluent to afford corresponding esters. The average yields were 76 to 78%.

(a) Thiophene-3-ylmethyl 4-(methylthio)benzoate



Using the general procedure (I) and starting from 4-(methylthio)benzoic acid (500 mg, 2.98 mmol), thiophene-3-ylmethyl 4-(methylthio)benzoate (595 mg, 2.25 mmol, 76%) was isolated as a yellow oil. ^1H NMR (500 MHz, CDCl_3) δ_{ppm} 7.95 (d, $J = 8.9$ Hz, 2H), 7.36 (s, 1H), 7.33 (d, $J = 8.25$ Hz, 1H), 7.28 (d, $J = 8.95$ Hz, 2H), 7.16 (d, $J = 4.1$ Hz, 1H), 5.34 (s, 2H), 2.50 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ_{ppm} 166.16, 145.60, 136.89, 129.94, 127.57, 126.22, 126.10, 124.84, 124.22, 61.71, 14.77; ESI-MS: m/z [M+H] calcd. for $\text{C}_{13}\text{H}_{12}\text{O}_2\text{S}_2$: 264.36; found: 265.18.

(b) 4-(Methylthio)benzyl benzoate

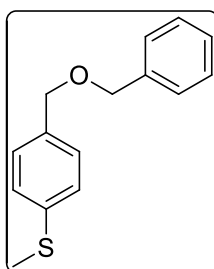


Using the general procedure (I) and starting from (4-(methylthio)phenyl)methanol (500 mg, 3.25 mmol), 4-(methylthio)benzyl benzoate (600 mg, 2.52 mmol, 78%) was isolated as a yellow oil. ^1H NMR (500 MHz, CDCl_3) δ_{ppm} 8.06 (d, $J = 8.95$ Hz, 2H), 7.55 (t, $J = 7.55$ Hz, 1H), 7.43 (t, $J = 7.9$ Hz, 2H), 7.37 (d, $J = 8.2$ Hz, 2H), 7.26 (d, $J = 8.2$ Hz, 2H), 5.31 (s, 2H), 2.48 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ_{ppm} 166.40, 138.75, 133.02, 132.69, 130.03, 129.64, 128.88, 128.34, 126.49, 66.32, 15.69; ESI-MS: m/z [M+Na] calcd. for $\text{C}_{15}\text{H}_{14}\text{O}_2\text{S}$: 258.335; found: 281.05.

3. General procedure for the etherification (II)¹³

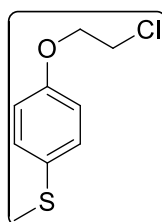
Sodium hydride (60% in mineral oil, 2.0 equiv) was taken into a flame-dried round-bottom flask under N_2 atmosphere and washed thrice with anhydrous hexane to remove mineral oil. Alcohol (1.0 equiv) in anhydrous THF (5 mL) was added drop wise to a stirred suspension of NaH in anhydrous THF (15 mL) at 0°C and stirred for 1 h. Then aryl bromide or chloro bromo ethane or 1-bromohexane (1.1 equiv) was added drop wise to the reaction mixture and stirred overnight at room temperature. The reaction was quenched by a saturated solution of ammonium chloride and extracted with diethyl ether (3×10 ml). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with EtOAc/hexane (1-2%) as the eluent to afford corresponding ethers. The average yields were 75 - 85%.

(a) 4-((Benzyloxy)methyl)phenyl(methyl)sulfane



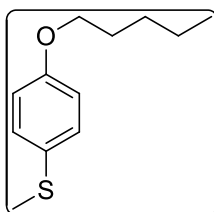
Using the general procedure (II) and starting from 4-(methylthio)phenylmethanol (500 mg, 3.25 mmol) 4-((benzyloxy)methyl)phenyl(methyl)sulfane (620 mg, 2.54 mmol, 78%) was isolated as a yellow oil. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ_{ppm} 7.35 (d, $J = 4.5$ Hz, 4H), 7.29 (d, $J = 8.6$ Hz, 2H), 7.24 (t, $J = 4.1$ Hz, 3H), 4.53 (s, 2H), 4.51 (s, 2H), 2.24 (s, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ_{ppm} 138.14, 137.70, 135.09, 128.39, 127.77, 127.63, 126.62, 71.97, 71.62, 15.92; ESI-MS: m/z [M+2H] calcd. for $\text{C}_{15}\text{H}_{16}\text{OS}$: 244.352; found: 246.23.

(b) 4-(2-Chloroethoxy)phenyl(methyl)sulfane



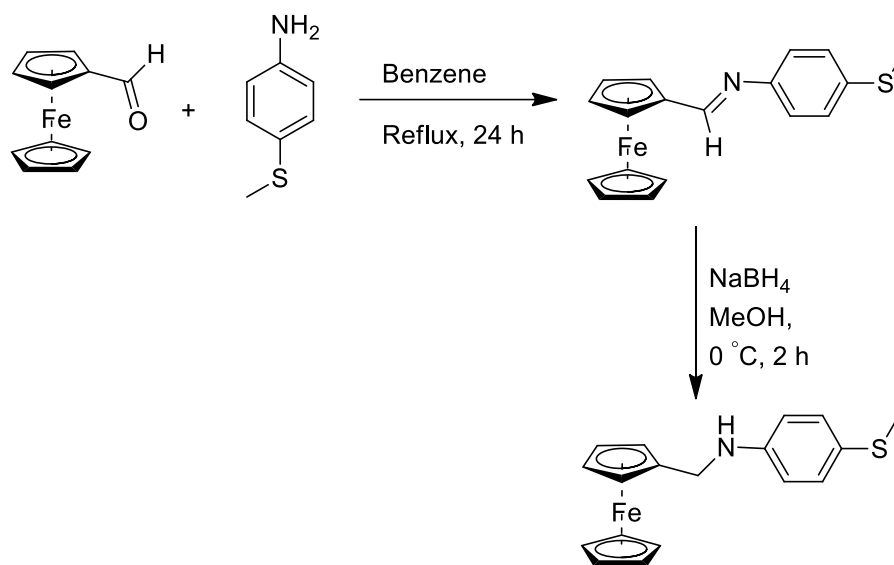
Using the general procedure (II) and starting from 4-(methylthio)phenol (500 mg, 3.57 mmol), 4-(2-chloroethoxy)phenyl(methyl)sulfane (600 mg, 2.97 mmol, 83%) was isolated as a white solid. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ_{ppm} 7.26 (d, $J = 8.5$ Hz, 2H), 6.86 (d, $J = 8.9$ Hz, 2H), 4.20 (t, $J = 5.85$ Hz, 2H), 3.80 (t, $J = 6.0$ Hz, 2H), 2.44 (s, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ_{ppm} 156.61, 129.85, 129.75, 115.41, 68.15, 41.83, 17.74; ESI-MS: m/z [M] calcd. for $\text{C}_9\text{H}_{11}\text{ClOS}$: 202.701; found: 202.03.

(c) Methyl 4-(pentyloxy)phenylsulfane



Using the general procedure (II) and starting from 4-(methylthio)phenol (500 mg, 3.57 mmol), methyl 4-(pentyloxy)phenylsulfane (600 mg, 2.86 mmol, 80%) was isolated as a yellow oil. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ_{ppm} 7.25 (d, $J = 8.9$ Hz, 2H), 6.83 (d, $J = 8.9$ Hz, 2H), 3.92 (t, $J = 6.5$ Hz, 2H), 2.43 (s, 3H), 1.78-1.75 (m, 2H), 1.43-1.36 (m, 4H), 0.92 (t, $J = 7.2$, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ_{ppm} 157.72, 130.18, 128.38, 115.14, 68.09, 28.90, 28.15, 22.43, 18.10, 14.00; ESI-MS: m/z [M] calcd. for $\text{C}_{12}\text{H}_{18}\text{OS}$: 210.33; found: 210.14.

4. Procedure for the synthesis of ferrocene-4-(methylthio)aniline



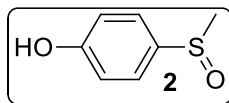
Scheme 2. Synthetic route of ferrocene-4-(methylthio)aniline

Ferrocene carboxaldehyde (1 gm, 4.67 mmol, 1.0 equiv) and 4-(methylthio)aniline (0.650 gm, 4.67 mmol, 1.0 equiv) were dissolved in 50 ml of benzene in a 100 mL round bottom flask and refluxed the reaction mixture at 100 °C for 24 hrs using dean stark apparatus. After completion of the reaction (monitored by TLC), evacuated the benzene under reduced pressure (use fume hood for all these steps). After that, 40 mL of methanol was added into the same round bottom flask and dissolved the reaction mixture while stirring at room temperature. The reaction temperature was maintained at 0°C using an ice bath and sodium borohydride (0.621 gm, 16.35 mmol, 3.5 equiv) was added portion wise in 15 min duration and finally stirred for 2 hours. After completion of the reaction (monitored by TLC), reaction mixture was cautiously quenched by addition of 3 mL of water and extracted with dichloromethane (3×10 mL). The combined organic phases were dried with anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified using column chromatography on silica gel with EtOAc/hexane (1:4) as the eluent to afford ferrocene-4-(methylthio)aniline (C₁₈H₁₉FeNS) as a yellow solid (0.947 gm, 60%). ¹H NMR (500 MHz, CDCl₃) δ_{ppm}7.16 (d, *J* = 8.2 Hz, 2H), 6.52 (d, *J* = 8.2 Hz, 2H), 4.15 (s, 2H), 4.09 (s, 4H), 4.06 (s, 2H), 3.8 (s, 2H), 2.33 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ_{ppm}146.99, 131.46, 124.17, 113.17, 86.03, 68.42, 68.03, 67.87, 43.28, 19.15; ESI-MS: *m/z*[M] calcd. for C₁₈H₁₉FeNS: 337.26; found:337.07.

5. General procedure for the oxidation of sulfides using hybrid **1** (III)

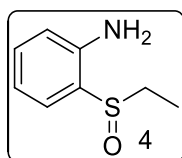
To a 10 mL Ace pressure tube were added sulfide (1.0 equiv), H₂O₂ (1.2 equiv), catalytic amount of hybrid **1** (0.012 mol%) and dissolved in 3 mL of recommended solvent (see main manuscript Table 1). Then the reaction mixture was stirred on a pre-heated hot plate at 85 °C for the mentioned time. After completion of the reaction (monitored by TLC), the reaction mixture was extracted with dichloromethane (3×5 mL). The combined organic phases were dried with anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified using column chromatography on silica gel with DCM/MeOH as an eluent to afford desired sulfoxides.

(a) 4-(Methylsulfinyl)phenol (2)



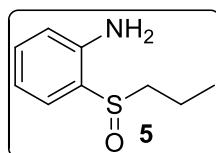
Using the general procedure (III) and starting from 4-(methylthio)phenol (25 mg, 0.178 mmol), 4-(methylsulfinyl)phenol (28 mg, 0.179 mmol, 100 %) was isolated as a white solid; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ_{ppm} 7.52 (d, $J = 8.9$ Hz, 2H), 6.96 (d, $J = 8.9$ Hz, 2H), 3.63 (s, 1H), 2.74 (s, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ_{ppm} 159.5, 148.0, 126.0, 116.6, 43.4; ESI-MS: m/z [M+H] calcd. for $\text{C}_7\text{H}_8\text{O}_2\text{S}$: 156.20; found: 157.03.

(b) 2-(Ethylsulfinyl)aniline (4)



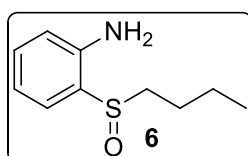
Using the general procedure (III) and starting from 2-(ethylthio)aniline (25 mg, 0.163 mmol), 2-(ethylsulfinyl)aniline (22.6 mg, 0.134 mmol, 85%) was isolated as a yellow oil; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ_{ppm} 7.23 (d, $J = 9.0$ Hz, 1H), 7.20 (t, $J = 7.2$ Hz, 1H), 6.74 (t, $J = 7.6$ Hz, 1H), 6.68 (d, $J = 8.3$ Hz, 1H), 5.06 (brs, 2H), 3.24-3.21 (m, 1H), 3.14-3.12 (m, 1H), 1.21 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ_{ppm} 147.7, 132.3, 127.3, 121.4, 117.3, 117.2, 45.0, 7.6; ESI-MS: m/z [M+H] calcd. for $\text{C}_8\text{H}_{11}\text{NOS}$: 169.24; found: 170.04.

(c) 2-(Propylsulfinyl)aniline (5)



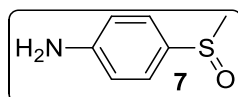
Using the general procedure (III) and starting from 2-(propylthio)aniline (25 mg, 0.150 mmol), 2-(propylsulfinyl)aniline (20 mg, 0.109 mmol, 73%) was isolated as a yellow oil; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ_{ppm} 7.24 (d, $J = 8.9$ Hz, 1H), 7.20 (t, $J = 6.5$ Hz, 1H), 6.73 (t, $J = 7.6$ Hz, 1H), 6.00 (d, $J = 7.9$ Hz, 1H), 5.07 (brs, 2H), 3.31-3.25 (m, 1H), 3.03-2.97 (m, 1H), 1.74-1.62 (m, 2H), 1.06 (t, $J = 7.5$ Hz, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ_{ppm} 147.7, 132.3, 127.1, 121.9, 117.4, 117.3, 53.2, 16.8, 13.1; ESI-MS: m/z [M+H] calcd. for $\text{C}_9\text{H}_{13}\text{NOS}$: 183.271; found: 184.06.

(d) 2-(Butylsulfinyl)aniline (6)



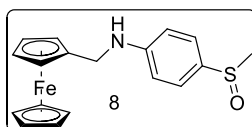
Using the general procedure (III) and starting from 2-(butylthio)aniline (25 mg, 0.138 mmol), 2-(butylsulfinyl)aniline (12.1 mg, 0.0614 mmol, 45%) was isolated as a yellow oil; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ_{ppm} 7.24 (d, $J = 8.9$ Hz, 1H), 7.20 (t, $J = 6.5$ Hz, 1H), 6.74 (t, $J = 7.2$ Hz, 1H), 6.68 (d, $J = 8.3$ Hz, 1H), 5.06 (brs, 2H), 3.32-3.26 (m, 1H), 3.06-3.00 (m, 1H), 1.68-1.66 (m, 1H), 1.63-1.56 (m, 1H), 1.49-1.42 (m, 2H), 0.93 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ_{ppm} 147.7, 132.3, 127.3, 121.4, 117.3, 117.2, 51.10, 25.19, 21.78, 13.62; ESI-MS: m/z $[\text{M}+\text{H}]$ calcd. for $\text{C}_{10}\text{H}_{15}\text{NOS}$: 197.297; found: 198.09.

(e) 4-(Methylsulfinyl)aniline (7)



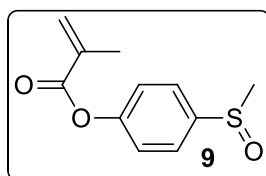
Using the general procedure (III) and starting from 4-(methylthio)aniline (25 mg, 0.180 mmol), 4-(methylsulfinyl)aniline (26.3 mg, 0.169 mmol, 94%) was isolated as a yellow oil; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ_{ppm} 7.45 (d, $J = 9.5$ Hz, 2H), 6.75 (d, $J = 8.3$ Hz, 2H), 4.06 (brs, 2H), 2.69 (s, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ_{ppm} 149.6, 133.02, 125.6, 115.0, 43.7; ESI-MS: m/z $[\text{M}+\text{H}]$ calcd. for $\text{C}_7\text{H}_9\text{NOS}$: 155.217; found: 156.06.

(f) Ferrocene-4-(methylsulfinyl)aniline (8)



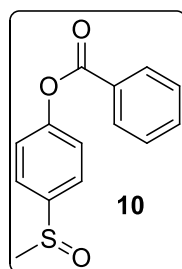
Using the general procedure (III) and starting from ferrocene-4-(methylthio)aniline ($\text{C}_{18}\text{H}_{19}\text{FeNS}$) (50 mg, 0.148 mmol), ferrocene-4-(methylsulfinyl)aniline ($\text{C}_{18}\text{H}_{19}\text{FeNOS}$) (19 mg, 0.053 mmol, 36%) was isolated as a yellow solid; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ_{ppm} 7.50 (d, $J = 8.9$ Hz, 2H), 6.71 (d, $J = 9.0$ Hz, 2H), 4.24 (s, 2H), 4.19 (s, 4H), 4.17 (s, 2H), 4.0 (s, 2H), 2.70 (s, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ_{ppm} 150.6, 131.6, 125.8, 115.0, 112.6, 85.3, 68.5, 68.2, 68.1, 43.6, 42.9; ESI-MS: m/z $[\text{M}+\text{H}]$ calcd. for $\text{C}_{18}\text{H}_{19}\text{FeNOS}$: 353.260; found: 353.05.

(g) 4-(Methylsulfinyl)phenyl methacrylate (9)



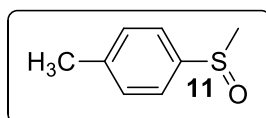
Using the general procedure (III) and starting from 4-(methylthio)phenyl methacrylate (25 mg, 0.120 mmol), 4-(methylsulfinyl)phenyl methacrylate (24.4 gm, 0.109 mmol, 91%) was isolated as a white solid; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ_{ppm} 7.67 (d, $J = 9.0$ Hz, 2H), 7.30 (d, $J = 9.0$ Hz, 2H), 6.36 (s, 1H), 5.79 (s, 1H), 2.72 (s, 3H), 2.05 (s, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ_{ppm} 165.4, 153.0, 142.7, 135.4, 128.0, 125.0, 122.8, 44.1, 18.3; ESI-MS: m/z $[\text{M}+\text{H}]$ calcd. for $\text{C}_{11}\text{H}_{12}\text{O}_3\text{S}$: 224.276; found: 225.06.

(h) 4-(Methylsulfinyl)phenyl benzoate (10)



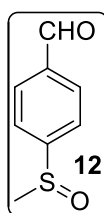
Using the general procedure (III) and starting from 4-(methylthio)phenyl benzoate (50 mg, 0.205 mmol), 4-(methylsulfinyl)phenyl benzoate (44.1 mg, 0.170 mmol, 83%) was isolated as a white solid; ^1H NMR (500 MHz, CDCl_3) δ_{ppm} 8.22 (d, $J = 9.0$ Hz, 2H), 7.74 (d, $J = 9.0$ Hz, 2H), 7.67 (t, $J = 7.6$ Hz, 1H), 7.55 (t, $J = 7.9$ Hz, 2H), 7.42 (d, $J = 8.6$ Hz, 2H), 2.77 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ_{ppm} 164.8, 153.0, 142.9, 134, 130.3, 128.9, 128.7, 125.0, 122.9, 44.1; ESI-MS: m/z [M+H] calcd. for $\text{C}_{14}\text{H}_{12}\text{O}_3\text{S}$: 260.308; found: 261.04.

(i) 1-Methyl-4-(methylsulfinyl)benzene (11)



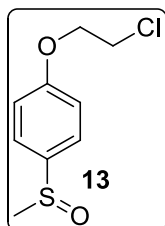
Using the general procedure (III) and starting from methyl(p-tolyl)sulfane (50 mg, 0.362 mmol), 1-methyl-4-(methylsulfinyl)benzene (56 mg, 0.362 mmol, 100%) was isolated as a colorless liquid; ^1H NMR (500 MHz, CDCl_3) δ_{ppm} 7.54 (d, $J = 8.25$ Hz, 2H), 7.33 (d, $J = 8.25$ Hz, 2H), 2.70 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ_{ppm} 142.26, 141.35, 129.43, 123.37, 43.81, 21.23; ESI-MS: m/z [M+H] calcd. for $\text{C}_8\text{H}_{10}\text{O}_2\text{S}$: 154.22; found: 155.04.

(j) 4-(Methylsulfinyl)benzaldehyde (12)



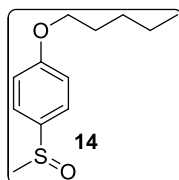
Using the general procedure (III) and starting from 4-(methylthio)benzaldehyde (50 mg, 0.329 mmol) 4-(methylsulfinyl)benzaldehyde (31.3 mg, 0.186 mmol, 57 %) was isolated as a yellow colored oil; ^1H NMR (500 MHz, CDCl_3) δ_{ppm} 10.1 (s, 1H), 8.06 (d, $J = 8.3$ Hz, 2H), 7.83 (d, $J = 8.3$ Hz, 2H), 2.80 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ_{ppm} 191.1, 152.3, 138.0, 130.3, 124.1, 43.7; ESI-MS: m/z [M+H] calcd. for $\text{C}_8\text{H}_8\text{O}_2\text{S}$: 168.213; found: 169.09.

(k) 1-(2-Chloroethoxy)-4-(methylsulfinyl)benzene (13)



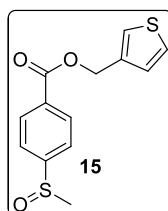
Using the general procedure (III) and starting from (4-(2-chloroethoxy)phenyl)(methyl)sulfane (50 mg, 0.248 mmol), 1-(2-chloroethoxy)-4-(methylsulfinyl)benzene (32.4 mg, 0.149 mmol, 60%) was isolated as a yellow liquid; ^1H NMR (500 MHz, CDCl_3) δ_{ppm} 7.61 (d, $J = 8.9$ Hz, 2H), 7.06 (d, $J = 8.3$ Hz, 2H), 4.28 (t, $J = 5.5$ Hz, 2H), 3.85 (t, $J = 5.8$ Hz, 2H), 2.71 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ_{ppm} 160.5, 137.2, 125.5, 115.4, 68.1, 43.9, 41.6; ESI-MS: m/z [M+H] calcd. for $\text{C}_9\text{H}_{11}\text{ClO}_2\text{S}$: 218.70; found: 219.01.

(l) 1-(Methylsulfinyl)-4-(pentyloxy)benzene (14)



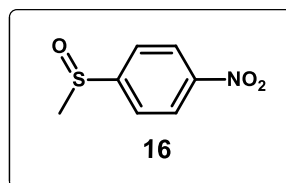
Using the general procedure (III) and starting from methyl(4-(pentyloxy)phenyl)sulfane (25 mg, 0.119 mmol), 1-(methylsulfinyl)-4-(pentyloxy)benzene (24.5 mg, 0.108 mmol, 91%) was isolated as a yellow liquid; ^1H NMR (500 MHz, CDCl_3) δ_{ppm} 7.58 (d, $J = 8.3$ Hz, 2H), 7.30 (d, $J = 9.0$ Hz, 2H), 4.00 (t, $J = 6.53$ Hz, 2H), 2.70 (s, 3H), 1.83-1.78 (m, 2H), 1.46-1.38 (m, 4H), 0.94 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ_{ppm} 161.5, 136.0, 125.3, 115.2, 68.2, 43.8, 28.7, 28.0, 22.3, 13.9; ESI-MS: m/z [M+H] calcd. for $\text{C}_{12}\text{H}_{18}\text{O}_2\text{S}$: 226.335; found: 227.11.

(m) Thiophen-2-ylmethyl 4-(methylsulfinyl)benzoate (15)



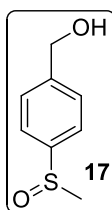
Using the general procedure (III) and starting from thiophen-2-ylmethyl 4-(methylthio)benzoate (50 mg, 0.189 mmol), thiophen-2-ylmethyl 4-(methylsulfinyl)benzoate (40 mg, 0.142 mmol, 75%) was isolated as a yellow liquid; ^1H NMR (500 MHz, CDCl_3) δ_{ppm} 8.21 (d, $J = 8.3$ Hz, 2H), 7.72 (d, $J = 9.0$ Hz, 2H), 7.40 (s, 1H), 7.35 (d, $J = 7.3$ Hz, 1H), 7.18 (d, $J = 5.5$ Hz, 1H), 5.40 (s, 2H), 2.75 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ_{ppm} 165.2, 150.8, 136.3, 132.5, 130.5, 127.6, 126.4, 124.7, 123.4, 62.1, 43.7; ESI-MS: m/z [M+H] calcd. for $\text{C}_{13}\text{H}_{12}\text{O}_3\text{S}_2$: 280.363; found: 281.02.

(n) 1-(Methylsulfinyl)-4-nitrobenzene (16)



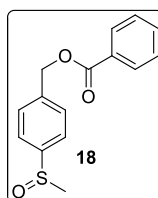
Using the general procedure (III) and starting from methyl(4-nitrophenyl)sulfane (50 mg, 0.296 mmol), 1-(methylsulfinyl)-4-nitrobenzene (39.5 mg, 0.214 mmol, 72%) was isolated as a light yellow solid; ^1H NMR (500 MHz, CDCl_3) δ_{ppm} 8.40 (d, $J = 8.95$ Hz, 2H), 7.84 (d, $J = 8.25$ Hz, 2H), 2.80 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ_{ppm} : 153.19, 149.47, 124.63, 124.47, 43.84; ESI-MS: m/z [M+H] calcd. for $\text{C}_{15}\text{H}_{11}\text{NO}_3\text{S}$: 185.20; found: 186.01.

(o) (4-(Methylsulfinyl)phenyl)methanol (17)



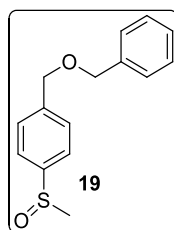
Using the general procedure (III) and starting from 4-(methylthio)phenylmethanol (50 mg, 0.325 mmol) 4-(methylsulfinyl)phenylmethanol (55.3 mg, 0.325 mmol, 100%) was isolated as a colorless oil; ^1H NMR (500 MHz, CDCl_3) δ_{ppm} 7.55 (d, $J = 8.3$ Hz, 2H), 7.49 (d, $J = 8.3$ Hz, 2H), 4.70 (s, 2H), 2.70 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ_{ppm} 145.0, 143.7, 127.5, 123.6, 64.1, 43.6; ESI-MS: m/z [M+H] calcd. for $\text{C}_8\text{H}_{10}\text{O}_2\text{S}$: 170.229; found: 171.05.

(p) (4-(Methylsulfinyl)benzyl benzoate (18)



Using the general procedure (III) and starting from 4-(methylthio)benzyl benzoate (50 mg, 0.194 mmol), 4-(methylsulfinyl)benzyl benzoate (46 mg, 0.167 mmol, 86%) was isolated as a yellow oil; ^1H NMR (500 MHz, CDCl_3) δ_{ppm} 8.08 (d, $J = 7.55$ Hz, 2H), 7.67 (d, $J = 8.2$ Hz, 2H), 7.62-7.56 (m, 3H), 7.45 (t, $J = 7.9$ Hz, 2H), 5.42 (s, 2H), 2.74 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ_{ppm} 166.2, 145.4, 139.3, 133.2, 129.6, 128.8, 128.4, 123.8, 65.7, 43.9; ESI-MS: m/z [M+H] calcd. for $\text{C}_{15}\text{H}_{14}\text{O}_3\text{S}$: 274.335; found: 275.06.

(q) 1-((Benzyloxy)methyl)-4-(methylsulfinyl)benzene (19)



Using the general procedure (III) and starting from (4-((benzyloxy)methyl)phenyl)(methyl)sulfane (50 mg, 0.205 mmol), 1-((benzyloxy)methyl)-4-(methylsulfinyl)benzene (42 mg, 0.162 mmol, 79%) was isolated as a yellow oil; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ_{ppm} 7.64 (d, $J = 8.3$ Hz, 2H), 7.53 (d, $J = 8.3$ Hz, 2H), 7.37 (d, $J = 4.8$ Hz, 4H), 7.34-7.31 (m, 1H), 4.60, (s, 2H), 4.59 (s, 2H), 2.72 (s, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ_{ppm} 144.7, 141.7, 137.7, 128.4, 128.3, 127.8, 127.7, 123.6, 72.5, 71.2, 43.9; ESI-MS: m/z $[\text{M}+\text{H}]$ calcd. for $\text{C}_{15}\text{H}_{16}\text{O}_2\text{S}$: 260.351; found: 261.09.

Table S1. Crystal and structure refinement data for hybrid 1

Empirical formula	$\text{C}_{28}\text{H}_{40}\text{N}_4\text{Na}_2\text{O}_{58}\text{P}\text{W}_9\text{Yb}$
Formula weight	3265.28
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C 2/c
Unit cell dimensions	$a = 18.2405(16)$ Å $b = 35.036(2)$ Å $c = 22.8447(14)$ Å $\beta = 101.071(8)^\circ$
Volume	$14327.7(18)$ Å ³
Z	8
Density (calculated)	3.027 Mg/m ³
Absorption coefficient	15.827 mm ⁻¹
F(000)	11784
Crystal size	$0.4668 \times 0.0692 \times 0.0437$ mm ³
Theta range for data collection	1.817 to 28.401°
Index ranges	$-24 \leq h \leq 24$, $-44 \leq k \leq 17$, $-10 \leq l \leq 29$
Reflections collected	23691
Independent reflections	15635 [R(int) = 0.0566]
Completeness to theta = 25.242°	98.9 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	15635 / 0 / 864
Goodness-of-fit on F^2	1.048
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0849, wR2 = 0.2288
R indices (all data)	R1 = 0.1233, wR2 = 0.2872
Extinction coefficient	n/a
Largest diff. peak and hole	7.785 and -4.047 e.Å ⁻³

Table S2. Bond lengths [\AA] and angles [$^\circ$] for hybrid 1

W(6)-O(15)	1.688(18)	W(3)-O(1)	1.693(16)
W(6)-O(20)	1.832(18)	W(3)-O(27)#1	1.877(19)
W(6)-O(14)	1.871(15)	W(3)-O(6)	1.901(17)
W(6)-O(16)	1.940(16)	W(3)-O(2)	1.914(17)
W(6)-O(9)	2.033(15)	W(3)-O(4)	1.951(16)
W(6)-O(17)	2.355(14)	W(3)-O(7)	2.369(16)
W(5)-O(12)	1.692(14)	Yb(1)-O(30)	2.30(2)
W(5)-O(10)	1.894(15)	Yb(1)-O(40)	2.310(16)
W(5)-O(14)	1.906(15)	Yb(1)-O(32)	2.330(17)
W(5)-O(13)	1.912(15)	Yb(1)-O(34)	2.356(17)
W(5)-O(19)	1.924(14)	Yb(1)-O(38)	2.363(17)
W(5)-O(11)	2.372(14)	Yb(1)-N(1)	2.427(19)
W(4)-O(50)#1	1.716(15)	Yb(1)-N(2)	2.428(18)
W(4)-O(13)#1	1.856(15)	Yb(1)-O(36)	2.435(17)
W(4)-O(22)#1	1.874(15)	Yb(1)-N(3)	2.44(2)
W(4)-O(19)	1.912(13)	Yb(1)-C(1)	3.19(3)
W(4)-O(8)	1.957(16)	Yb(1)-C(7)	3.21(3)
W(4)-O(11)	2.351(14)	P(1)-O(17)	1.512(15)
W(8)-O(23)	1.690(16)	P(1)-O(11)	1.520(15)
W(8)-O(25)	1.889(16)	P(1)-O(24)#1	1.529(13)
W(8)-O(28)	1.892(18)	P(1)-O(7)	1.576(18)
W(8)-O(22)	1.894(16)	O(15)-Na(1)	2.34(2)
W(8)-O(20)	1.933(18)	O(36)-C(14)	1.18(3)
W(8)-O(24)	2.373(13)	O(40)-C(21)	1.29(3)
W(7)-O(41)#2	1.706(15)	O(35)-C(14)	1.28(3)
W(7)-O(16)	1.860(15)	O(35)-H(35)	0.8200
W(7)-O(6)	1.893(16)	O(31)-C(7)	1.24(3)
W(7)-O(18)	1.920(14)	O(31)-Na(1)	2.29(3)
W(7)-O(21)	1.931(17)	O(27)-W(3)#1	1.877(19)
W(7)-O(17)	2.375(14)	O(41)-W(7)#2	1.706(15)
W(1)-O(5)	1.690(16)	O(41)-Na(1)	2.38(2)
W(1)-O(9)	1.785(15)	O(22)-W(4)#1	1.874(15)
W(1)-O(10)	1.891(14)	O(28)-W(2)#1	1.937(18)
W(1)-O(4)	1.916(16)	O(13)-W(4)#1	1.855(14)
W(1)-O(3)	1.956(17)	N(3)-C(16)	1.34(3)
W(1)-O(7)	2.388(14)	N(3)-C(20)	1.36(3)
W(9)-O(26)	1.709(16)	O(18)-W(9)#1	1.876(14)
W(9)-O(21)	1.839(17)	Na(1)-O(42)	2.27(4)
W(9)-O(18)#1	1.876(14)	Na(1)-O(43)	2.40(5)
W(9)-O(25)	1.917(15)	Na(1)-O(44)	2.61(5)
W(9)-O(27)	1.941(19)	O(33)-C(8)	1.26(3)
W(9)-O(24)	2.340(14)	O(33)-H(33)	0.8200
W(2)-O(51)#1	1.683(16)	O(37)-C(15)	1.29(3)
W(2)-O(8)	1.845(16)	O(37)-H(37)	0.8200
W(2)-O(3)	1.875(15)	N(2)-C(13)	1.33(4)
W(2)-O(28)#1	1.937(18)	N(2)-C(9)	1.34(3)
W(2)-O(2)	1.958(17)	O(32)-C(7)	1.26(3)
W(2)-O(7)	2.367(17)	O(34)-C(8)	1.27(3)

O(38)-C(15)	1.28(3)	C(24)-C(25)	1.46(5)
O(39)-C(21)	1.25(3)	C(24)-H(24)	0.9300
O(39)-H(39)	0.8200	O(45)-C(28)	1.30(5)
N(1)-C(6)	1.30(3)	O(45)-Na(2)	2.45(6)
N(1)-C(2)	1.34(3)	O(56)-H(56A)	0.8501
O(30)-C(1)	1.27(4)	O(56)-H(56B)	0.8501
C(9)-C(10)	1.38(4)	C(25)-H(25)	0.9300
C(9)-C(8)	1.49(4)	N(4)-C(23)	1.27(5)
O(29)-C(1)	1.28(4)	N(4)-C(27)	1.37(5)
O(29)-H(29)	0.8200	N(4)-Na(2)	2.54(4)
C(12)-C(11)	1.40(4)	O(54)-H(54A)	0.8498
C(12)-C(13)	1.43(4)	O(54)-H(54B)	0.8499
C(12)-H(12)	0.9300	O(47)-H(47)	0.8200
C(10)-C(11)	1.35(4)	O(46)-Na(2)	2.57(4)
C(10)-H(10)	0.9300	C(27)-C(28)	1.53(6)
C(13)-C(14)	1.45(4)	O(53)-H(53A)	0.8501
C(18)-C(19)	1.35(4)	O(53)-H(53B)	0.8498
C(18)-C(17)	1.39(4)	Na(2)-O(49)	2.27(5)
C(18)-H(18)	0.9300	Na(2)-O(48)	2.45(7)
C(6)-C(5)	1.39(4)	O(57)-H(57A)	0.8505
C(6)-C(7)	1.46(4)	O(57)-H(57B)	0.8492
C(2)-C(3)	1.35(4)	O(52)-H(52A)	0.8498
C(2)-C(1)	1.49(4)	O(52)-H(52B)	0.8503
C(5)-C(4)	1.35(5)		
C(5)-H(5)	0.9300	O(15)-W(6)-O(20)	99.1(8)
C(11)-H(11)	0.9300	O(15)-W(6)-O(14)	102.8(7)
C(4)-C(3)	1.38(4)	O(20)-W(6)-O(14)	91.6(7)
C(4)-H(4)	0.9300	O(15)-W(6)-O(16)	99.9(7)
C(19)-C(20)	1.41(3)	O(20)-W(6)-O(16)	92.3(7)
C(19)-H(19)	0.9300	O(14)-W(6)-O(16)	156.1(6)
O(24)-P(1)#1	1.529(13)	O(15)-W(6)-O(9)	96.2(8)
C(21)-C(20)	1.46(3)	O(20)-W(6)-O(9)	164.7(6)
C(15)-C(16)	1.44(4)	O(14)-W(6)-O(9)	84.0(6)
C(3)-H(3)	0.9300	O(16)-W(6)-O(9)	86.0(6)
C(17)-C(16)	1.37(4)	O(15)-W(6)-O(17)	172.1(7)
C(17)-H(17)	0.9300	O(20)-W(6)-O(17)	84.3(6)
O(44)-C(28)	1.30(6)	O(14)-W(6)-O(17)	84.2(6)
O(50)-W(4)#1	1.716(15)	O(16)-W(6)-O(17)	72.7(6)
O(51)-W(2)#1	1.683(16)	O(9)-W(6)-O(17)	80.7(6)
C(22)-O(47)	1.24(8)	O(12)-W(5)-O(10)	98.8(7)
C(22)-O(46)	1.40(8)	O(12)-W(5)-O(14)	103.1(7)
C(22)-C(23)	1.55(8)	O(10)-W(5)-O(14)	85.8(6)
O(55)-H(55A)	0.8497	O(12)-W(5)-O(13)	98.4(7)
O(55)-H(55B)	0.8503	O(10)-W(5)-O(13)	162.2(6)
C(26)-C(25)	1.28(5)	O(14)-W(5)-O(13)	86.0(6)
C(26)-C(27)	1.37(5)	O(12)-W(5)-O(19)	100.2(7)
C(26)-H(26)	0.9300	O(10)-W(5)-O(19)	92.8(6)
O(58)-H(58A)	0.8500	O(14)-W(5)-O(19)	156.6(6)
O(58)-H(58B)	0.8499	O(13)-W(5)-O(19)	88.5(6)
C(24)-C(23)	1.33(5)	O(12)-W(5)-O(11)	172.9(6)

O(10)-W(5)-O(11)	81.8(6)	O(5)-W(1)-O(10)	101.6(7)
O(14)-W(5)-O(11)	84.0(6)	O(9)-W(1)-O(10)	87.4(7)
O(13)-W(5)-O(11)	81.7(6)	O(5)-W(1)-O(4)	101.4(8)
O(19)-W(5)-O(11)	72.7(5)	O(9)-W(1)-O(4)	92.5(7)
O(50)#1-W(4)-O(13)#1	99.3(8)	O(10)-W(1)-O(4)	156.6(6)
O(50)#1-W(4)-O(22)#1	102.0(7)	O(5)-W(1)-O(3)	101.1(8)
O(13)#1-W(4)-O(22)#1	90.6(7)	O(9)-W(1)-O(3)	158.6(7)
O(50)#1-W(4)-O(19)	99.2(7)	O(10)-W(1)-O(3)	86.5(6)
O(13)#1-W(4)-O(19)	90.9(6)	O(4)-W(1)-O(3)	85.1(7)
O(22)#1-W(4)-O(19)	158.2(6)	O(5)-W(1)-O(7)	172.0(8)
O(50)#1-W(4)-O(8)	97.3(8)	O(9)-W(1)-O(7)	86.4(6)
O(13)#1-W(4)-O(8)	163.3(6)	O(10)-W(1)-O(7)	82.9(6)
O(22)#1-W(4)-O(8)	84.1(7)	O(4)-W(1)-O(7)	73.8(6)
O(19)-W(4)-O(8)	88.3(6)	O(3)-W(1)-O(7)	72.4(6)
O(50)#1-W(4)-O(11)	172.1(7)	O(26)-W(9)-O(21)	99.5(8)
O(13)#1-W(4)-O(11)	83.9(6)	O(26)-W(9)-O(18)#1	101.1(8)
O(22)#1-W(4)-O(11)	85.1(6)	O(21)-W(9)-O(18)#1	89.0(7)
O(19)-W(4)-O(11)	73.4(5)	O(26)-W(9)-O(25)	100.7(8)
O(8)-W(4)-O(11)	79.9(6)	O(21)-W(9)-O(25)	92.7(7)
O(23)-W(8)-O(25)	98.8(7)	O(18)#1-W(9)-O(25)	157.5(6)
O(23)-W(8)-O(28)	99.6(8)	O(26)-W(9)-O(27)	95.7(8)
O(25)-W(8)-O(28)	91.9(8)	O(21)-W(9)-O(27)	164.6(7)
O(23)-W(8)-O(22)	104.5(7)	O(18)#1-W(9)-O(27)	85.4(7)
O(25)-W(8)-O(22)	156.5(6)	O(25)-W(9)-O(27)	87.1(7)
O(28)-W(8)-O(22)	87.3(7)	O(26)-W(9)-O(24)	173.1(7)
O(23)-W(8)-O(20)	97.8(7)	O(21)-W(9)-O(24)	84.3(6)
O(25)-W(8)-O(20)	87.6(7)	O(18)#1-W(9)-O(24)	84.7(6)
O(28)-W(8)-O(20)	162.5(6)	O(25)-W(9)-O(24)	73.2(6)
O(22)-W(8)-O(20)	86.3(6)	O(27)-W(9)-O(24)	80.9(6)
O(23)-W(8)-O(24)	171.3(6)	O(51)#1-W(2)-O(8)	102.1(8)
O(25)-W(8)-O(24)	72.9(5)	O(51)#1-W(2)-O(3)	101.5(8)
O(28)-W(8)-O(24)	83.6(6)	O(8)-W(2)-O(3)	94.1(7)
O(22)-W(8)-O(24)	83.7(6)	O(51)#1-W(2)-O(28)#1	100.1(7)
O(20)-W(8)-O(24)	79.5(5)	O(8)-W(2)-O(28)#1	85.0(7)
O(41)#2-W(7)-O(16)	100.4(7)	O(3)-W(2)-O(28)#1	158.1(8)
O(41)#2-W(7)-O(6)	99.1(8)	O(51)#1-W(2)-O(2)	100.1(8)
O(16)-W(7)-O(6)	90.6(7)	O(8)-W(2)-O(2)	157.1(7)
O(41)#2-W(7)-O(18)	102.5(7)	O(3)-W(2)-O(2)	87.3(7)
O(16)-W(7)-O(18)	157.0(6)	O(28)#1-W(2)-O(2)	85.3(7)
O(6)-W(7)-O(18)	88.4(7)	O(51)#1-W(2)-O(7)	172.3(7)
O(41)#2-W(7)-O(21)	97.3(8)	O(8)-W(2)-O(7)	84.8(6)
O(16)-W(7)-O(21)	88.4(7)	O(3)-W(2)-O(7)	74.2(7)
O(6)-W(7)-O(21)	163.5(6)	O(28)#1-W(2)-O(7)	83.9(6)
O(18)-W(7)-O(21)	86.1(7)	O(2)-W(2)-O(7)	73.6(6)
O(41)#2-W(7)-O(17)	173.7(7)	O(1)-W(3)-O(27)#1	102.0(8)
O(16)-W(7)-O(17)	73.5(6)	O(1)-W(3)-O(6)	102.6(8)
O(6)-W(7)-O(17)	82.6(6)	O(27)#1-W(3)-O(6)	87.5(7)
O(18)-W(7)-O(17)	83.6(6)	O(1)-W(3)-O(2)	100.4(8)
O(21)-W(7)-O(17)	81.3(6)	O(27)#1-W(3)-O(2)	91.0(7)
O(5)-W(1)-O(9)	100.2(8)	O(6)-W(3)-O(2)	156.7(7)

O(1)-W(3)-O(4)	100.7(8)	N(1)-Yb(1)-C(1)	47.6(7)
O(27)#1-W(3)-O(4)	157.2(7)	N(2)-Yb(1)-C(1)	138.8(7)
O(6)-W(3)-O(4)	85.1(6)	O(36)-Yb(1)-C(1)	156.9(7)
O(2)-W(3)-O(4)	87.4(7)	N(3)-Yb(1)-C(1)	90.9(8)
O(1)-W(3)-O(7)	172.1(7)	O(30)-Yb(1)-C(7)	112.8(7)
O(27)#1-W(3)-O(7)	84.0(6)	O(40)-Yb(1)-C(7)	76.1(6)
O(6)-W(3)-O(7)	82.5(6)	O(32)-Yb(1)-C(7)	19.0(7)
O(2)-W(3)-O(7)	74.2(6)	O(34)-Yb(1)-C(7)	83.6(7)
O(4)-W(3)-O(7)	73.6(6)	O(38)-Yb(1)-C(7)	152.8(7)
O(30)-Yb(1)-O(40)	87.1(6)	N(1)-Yb(1)-C(7)	46.2(7)
O(30)-Yb(1)-O(32)	131.7(7)	N(2)-Yb(1)-C(7)	86.3(7)
O(40)-Yb(1)-O(32)	78.7(6)	O(36)-Yb(1)-C(7)	91.1(7)
O(30)-Yb(1)-O(34)	80.0(7)	N(3)-Yb(1)-C(7)	140.7(7)
O(40)-Yb(1)-O(34)	149.5(6)	C(1)-Yb(1)-C(7)	93.8(7)
O(32)-Yb(1)-O(34)	89.4(7)	O(17)-P(1)-O(11)	112.0(8)
O(30)-Yb(1)-O(38)	77.9(7)	O(17)-P(1)-O(24)#1	112.9(8)
O(40)-Yb(1)-O(38)	130.7(6)	O(11)-P(1)-O(24)#1	112.0(8)
O(32)-Yb(1)-O(38)	143.3(7)	O(17)-P(1)-O(7)	106.5(9)
O(34)-Yb(1)-O(38)	73.4(6)	O(11)-P(1)-O(7)	107.2(8)
O(30)-Yb(1)-N(1)	66.8(7)	O(24)#1-P(1)-O(7)	105.7(8)
O(40)-Yb(1)-N(1)	77.4(6)	P(1)-O(17)-W(6)	129.9(8)
O(32)-Yb(1)-N(1)	65.1(6)	P(1)-O(17)-W(7)	126.9(9)
O(34)-Yb(1)-N(1)	72.2(6)	W(6)-O(17)-W(7)	90.1(5)
O(38)-Yb(1)-N(1)	134.0(7)	P(1)-O(7)-W(2)	125.1(8)
O(30)-Yb(1)-N(2)	139.4(7)	P(1)-O(7)-W(3)	125.8(8)
O(40)-Yb(1)-N(2)	133.1(6)	W(2)-O(7)-W(3)	90.9(6)
O(32)-Yb(1)-N(2)	72.0(6)	P(1)-O(7)-W(1)	123.6(9)
O(34)-Yb(1)-N(2)	66.4(7)	W(2)-O(7)-W(1)	90.2(5)
O(38)-Yb(1)-N(2)	71.4(7)	W(3)-O(7)-W(1)	90.6(5)
N(1)-Yb(1)-N(2)	119.3(6)	W(6)-O(15)-Na(1)	154.0(12)
O(30)-Yb(1)-O(36)	144.6(6)	W(6)-O(14)-W(5)	152.9(9)
O(40)-Yb(1)-O(36)	73.2(6)	W(2)-O(3)-W(1)	123.1(10)
O(32)-Yb(1)-O(36)	73.7(6)	W(6)-O(20)-W(8)	162.5(9)
O(34)-Yb(1)-O(36)	130.4(7)	W(1)-O(9)-W(6)	150.3(9)
O(38)-Yb(1)-O(36)	92.7(6)	W(8)-O(25)-W(9)	123.3(7)
N(1)-Yb(1)-O(36)	133.0(6)	C(14)-O(36)-Yb(1)	122.0(18)
N(2)-Yb(1)-O(36)	64.0(6)	C(21)-O(40)-Yb(1)	126.0(15)
O(30)-Yb(1)-N(3)	73.7(7)	W(1)-O(10)-W(5)	151.1(9)
O(40)-Yb(1)-N(3)	65.4(7)	C(14)-O(35)-H(35)	109.5
O(32)-Yb(1)-N(3)	135.5(7)	W(4)-O(19)-W(5)	122.8(7)
O(34)-Yb(1)-N(3)	134.6(7)	W(9)-O(21)-W(7)	163.1(10)
O(38)-Yb(1)-N(3)	65.3(7)	W(2)-O(8)-W(4)	154.0(10)
N(1)-Yb(1)-N(3)	126.2(7)	C(7)-O(31)-Na(1)	131(2)
N(2)-Yb(1)-N(3)	114.5(7)	W(3)#1-O(27)-W(9)	151.6(9)
O(36)-Yb(1)-N(3)	71.4(7)	W(7)#2-O(41)-Na(1)	172.0(10)
O(30)-Yb(1)-C(1)	19.4(7)	W(7)-O(16)-W(6)	123.5(8)
O(40)-Yb(1)-C(1)	86.1(7)	W(4)#1-O(22)-W(8)	151.8(8)
O(32)-Yb(1)-C(1)	112.8(7)	W(8)-O(28)-W(2)#1	148.7(9)
O(34)-Yb(1)-C(1)	72.7(8)	W(4)#1-O(13)-W(5)	163.6(9)
O(38)-Yb(1)-C(1)	93.1(7)	C(16)-N(3)-C(20)	121(2)

C(16)-N(3)-Yb(1)	120.3(18)	N(1)-C(6)-C(5)	120(3)
C(20)-N(3)-Yb(1)	118.7(16)	N(1)-C(6)-C(7)	114(2)
W(3)-O(2)-W(2)	121.3(9)	C(5)-C(6)-C(7)	125(3)
W(9)#1-O(18)-W(7)	150.8(9)	N(1)-C(2)-C(3)	120(3)
O(42)-Na(1)-O(31)	99.3(13)	N(1)-C(2)-C(1)	114(2)
O(42)-Na(1)-O(15)	176(2)	C(3)-C(2)-C(1)	126(3)
O(31)-Na(1)-O(15)	82.7(9)	C(4)-C(5)-C(6)	118(3)
O(42)-Na(1)-O(41)	98.5(12)	C(4)-C(5)-H(5)	120.9
O(31)-Na(1)-O(41)	155.0(13)	C(6)-C(5)-H(5)	120.7
O(15)-Na(1)-O(41)	80.5(7)	C(10)-C(11)-C(12)	122(3)
O(42)-Na(1)-O(43)	88(2)	C(10)-C(11)-H(11)	119.1
O(31)-Na(1)-O(43)	109.5(15)	C(12)-C(11)-H(11)	119.2
O(15)-Na(1)-O(43)	88.2(13)	C(5)-C(4)-C(3)	120(3)
O(41)-Na(1)-O(43)	88.4(14)	C(5)-C(4)-H(4)	119.9
O(42)-Na(1)-O(44)	85(2)	C(3)-C(4)-H(4)	120.0
O(31)-Na(1)-O(44)	80.6(13)	O(29)-C(1)-O(30)	125(3)
O(15)-Na(1)-O(44)	98.5(13)	O(29)-C(1)-C(2)	118(3)
O(41)-Na(1)-O(44)	83.7(12)	O(30)-C(1)-C(2)	117(3)
O(43)-Na(1)-O(44)	168.6(16)	O(29)-C(1)-Yb(1)	161(2)
C(8)-O(33)-H(33)	109.4	O(30)-C(1)-Yb(1)	37.0(14)
W(7)-O(6)-W(3)	149.1(9)	C(2)-C(1)-Yb(1)	80.4(16)
C(15)-O(37)-H(37)	109.5	C(18)-C(19)-C(20)	120(3)
C(13)-N(2)-C(9)	120(2)	C(18)-C(19)-H(19)	119.8
C(13)-N(2)-Yb(1)	120.5(16)	C(20)-C(19)-H(19)	119.9
C(9)-N(2)-Yb(1)	119.0(18)	P(1)-O(11)-W(4)	128.9(8)
C(7)-O(32)-Yb(1)	123.9(17)	P(1)-O(11)-W(5)	127.3(8)
C(8)-O(34)-Yb(1)	123.0(18)	W(4)-O(11)-W(5)	91.0(5)
C(15)-O(38)-Yb(1)	121.8(16)	P(1)#1-O(24)-W(9)	128.9(8)
C(21)-O(39)-H(39)	109.5	P(1)#1-O(24)-W(8)	127.5(8)
C(6)-N(1)-C(2)	122(2)	W(9)-O(24)-W(8)	90.5(4)
C(6)-N(1)-Yb(1)	119.8(17)	O(39)-C(21)-O(40)	125(2)
C(2)-N(1)-Yb(1)	118.2(15)	O(39)-C(21)-C(20)	120(2)
W(1)-O(4)-W(3)	122.0(8)	O(40)-C(21)-C(20)	115(2)
C(1)-O(30)-Yb(1)	123.6(19)	O(33)-C(8)-O(34)	122(3)
N(2)-C(9)-C(10)	122(3)	O(33)-C(8)-C(9)	120(3)
N(2)-C(9)-C(8)	114(2)	O(34)-C(8)-C(9)	117(2)
C(10)-C(9)-C(8)	124(2)	O(31)-C(7)-O(32)	123(3)
C(1)-O(29)-H(29)	109.5	O(31)-C(7)-C(6)	120(3)
C(11)-C(12)-C(13)	117(3)	O(32)-C(7)-C(6)	117(3)
C(11)-C(12)-H(12)	121.6	O(31)-C(7)-Yb(1)	160(2)
C(13)-C(12)-H(12)	121.6	O(32)-C(7)-Yb(1)	37.1(12)
C(11)-C(10)-C(9)	118(2)	C(6)-C(7)-Yb(1)	79.6(15)
C(11)-C(10)-H(10)	120.8	N(3)-C(20)-C(19)	119(2)
C(9)-C(10)-H(10)	120.8	N(3)-C(20)-C(21)	114(2)
N(2)-C(13)-C(12)	120(2)	C(19)-C(20)-C(21)	126(2)
N(2)-C(13)-C(14)	113(3)	O(36)-C(14)-O(35)	126(2)
C(12)-C(13)-C(14)	127(3)	O(36)-C(14)-C(13)	120(3)
C(19)-C(18)-C(17)	118(3)	O(35)-C(14)-C(13)	113(2)
C(19)-C(18)-H(18)	120.9	O(38)-C(15)-O(37)	123(2)
C(17)-C(18)-H(18)	120.8	O(38)-C(15)-C(16)	120(2)

O(37)-C(15)-C(16)	117(2)	C(23)-N(4)-Na(2)	125(3)
C(2)-C(3)-C(4)	119(3)	C(27)-N(4)-Na(2)	120(3)
C(2)-C(3)-H(3)	120.5	H(54A)-O(54)-H(54B)	109.5
C(4)-C(3)-H(3)	120.5	N(4)-C(23)-C(24)	131(4)
C(16)-C(17)-C(18)	121(3)	N(4)-C(23)-C(22)	116(5)
C(16)-C(17)-H(17)	119.3	C(24)-C(23)-C(22)	113(5)
C(18)-C(17)-H(17)	119.4	C(22)-O(47)-H(47)	109.1
N(3)-C(16)-C(17)	120(3)	C(22)-O(46)-Na(2)	121(4)
N(3)-C(16)-C(15)	113(2)	C(26)-C(27)-N(4)	119(4)
C(17)-C(16)-C(15)	127(2)	C(26)-C(27)-C(28)	126(4)
C(28)-O(44)-Na(1)	161(4)	N(4)-C(27)-C(28)	115(4)
O(47)-C(22)-O(46)	124(7)	O(44)-C(28)-O(45)	128(5)
O(47)-C(22)-C(23)	118(7)	O(44)-C(28)-C(27)	117(4)
O(46)-C(22)-C(23)	114(6)	O(45)-C(28)-C(27)	115(4)
H(55A)-O(55)-H(55B)	109.5	H(53A)-O(53)-H(53B)	109.5
C(25)-C(26)-C(27)	125(4)	O(49)-Na(2)-O(48)	171(2)
C(25)-C(26)-H(26)	117.7	O(49)-Na(2)-O(45)	83.4(17)
C(27)-C(26)-H(26)	117.7	O(48)-Na(2)-O(45)	89.7(18)
H(58A)-O(58)-H(58B)	109.5	O(49)-Na(2)-N(4)	88.0(16)
C(23)-C(24)-C(25)	114(4)	O(48)-Na(2)-N(4)	93.8(18)
C(23)-C(24)-H(24)	123.2	O(45)-Na(2)-N(4)	64.5(13)
C(25)-C(24)-H(24)	123.1	O(49)-Na(2)-O(46)	94.1(15)
C(28)-O(45)-Na(2)	126(3)	O(48)-Na(2)-O(46)	94.3(18)
H(56A)-O(56)-H(56B)	109.5	O(45)-Na(2)-O(46)	128.0(13)
C(26)-C(25)-C(24)	117(4)	N(4)-Na(2)-O(46)	63.6(11)
C(26)-C(25)-H(25)	121.6	H(57A)-O(57)-H(57B)	109.5
C(24)-C(25)-H(25)	121.5	H(52A)-O(52)-H(52B)	109.5
C(23)-N(4)-C(27)	115(4)		

Symmetry transformations used to generate equivalent atoms:

#1 -x,y,-z+3/2 #2 -x,-y+1,-z+1

Table S3. Details of hydrogen bonds in hybrid **1**

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(35)-H(35)...O(39)#3	0.82	1.75	2.55(2)	165.4
O(37)-H(37)...O(52)#5	0.82	1.84	2.63(4)	162.3
O(39)-H(39)...O(58)#6	0.82	1.92	2.63(5)	143.9
O(39)-H(39)...O(53)#6	0.82	2.64	3.36(8)	147.0
O(29)-H(29)...O(43)#7	0.82	2.26	2.93(4)	139.0
C(12)-H(12)...O(19)#4	0.93	2.61	3.46(3)	151.7
C(19)-H(19)...O(51)#7	0.93	2.41	3.05(3)	125.7
C(3)-H(3)...O(40)#7	0.93	2.66	3.44(3)	141.4
O(55)-H(55A)...O(44)#8	0.85	2.46	3.26(6)	159.2
C(26)-H(26)...O(41)	0.93	2.60	3.42(4)	146.7
O(58)-H(58A)...O(39)#6	0.85	1.89	2.63(5)	144.5

O(56)-H(56B)...O(40)#8	0.85	2.82	3.39(4)	126.4
O(54)-H(54A)...O(43)	0.85	2.50	3.10(11)	128.3
O(47)-H(47)...O(37)#10	0.82	2.65	3.35(5)	145.1
O(53)-H(53B)...O(58)	0.85	1.81	2.61(7)	154.7
O(53)-H(53A)...O(29)#11	0.85	1.89	2.70(7)	159.6
O(57)-H(57B)...O(27)#12	0.85	2.68	3.21(6)	121.4
O(57)-H(57B)...O(2)#13	0.85	2.35	3.16(6)	160.6
O(57)-H(57B)...O(28)#12	0.85	2.86	3.16(6)	103.3
O(52)-H(52B)...O(49)#7	0.85	2.16	2.72(6)	123.0

Symmetry transformations used to generate equivalent atoms:

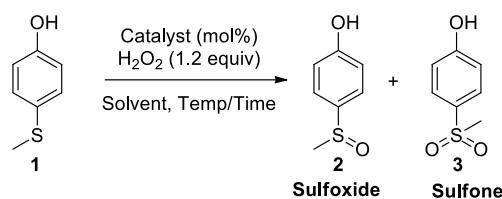
#1 -x,y,-z+3/2 #2 -x,-y+1,-z+1 #3 -x,y,-z+1/2

#4 -x-1/2,-y+3/2,-z+1 #5 x-1,y,z #6 -x+1,y,-z+1/2

#7 -x+1/2,-y+3/2,-z+1 #8 x+1,y,z #9 -x+2,y,-z+1/2

#10 x-1/2,y-1/2,z #11 x+1/2,-y+3/2,z-1/2 #12 -x+1,-y+1,-z+1

Table S4. Screening of catalyst and solvent system for oxidation of sulfide^a



S. No.	Catalyst (mol%)	H ₂ O ₂ (equiv)	Solvent	Temp (°C)/Time (min.)	Yield (%) ^b		Sulfoxide Selectivity
					2	3	
1.	0.012	1.2	H ₂ O	85/30	56.0	44.0	56%
2.	0.012	1.2	H ₂ O	85/20	61.0	39.0	61%
3.	0.012	1.2	H ₂ O	85/15	64.0	36.0	64%
4.	0.012	1.2	H ₂ O	85/10	85.0	15.0	85%
5.	0.012	1.2	H₂O	85/5	100	ND	100%
6.	0.006	1.2	H ₂ O	85/10	65	ND	100%
7.	0.024	1.2	H ₂ O	85/5	100	ND	100%
8.	0.012	1.2	H ₂ O	r.t/60	ND	ND	-
9.	0.012	1.2	H ₂ O	60/60	70	ND	100%
10.	0.012	-	H ₂ O	85/5	ND	ND	-
11.	-	1.2	H ₂ O	85/5	29.0	ND	100%
12.	0.012	1.2	CH ₃ CN	85/60	23.0	ND	100%
13.	0.012	1.2	EtOH	85/60	20.0	20.0	50%
14.	0.012	1.2	Isopropanol	85/60	3.0	ND	100%
15.	0.012	1.2	MeOH	85/60	9.0	ND	100%
16.	0.012	1.2	THF	85/60	6.0	ND	100%
17.	Na ₁₂ [P ₂ W ₁₅ O ₅₆] (0.012%)	1.2	H ₂ O	85/5	20.0	34	37%
18.	PDCH ₂ (0.012%)	1.2	H ₂ O	85/5	23.0	ND	100%
19.	Yb(NO ₃) ₃ ·5H ₂ O (0.012%)	1.2	H ₂ O	85/5	36.0	ND	100%
20.	K ₆ [P ₂ W ₁₈ O ₆₂]	1.2	H ₂ O	85/5	38.8	24.5	61%
21.	Na ₁₂ [P ₂ W ₁₅ O ₅₆] + PDCH ₂ (0.012%)	1.2	H ₂ O	85/5	24.3	16.7	59.6%

^aPerformed with sulfide (1.0 equiv), H₂O₂ (1.2 equiv), hybrid **1** catalyst (0.012 mol%) in water. ^b Isolated yield. ND: Not detected.

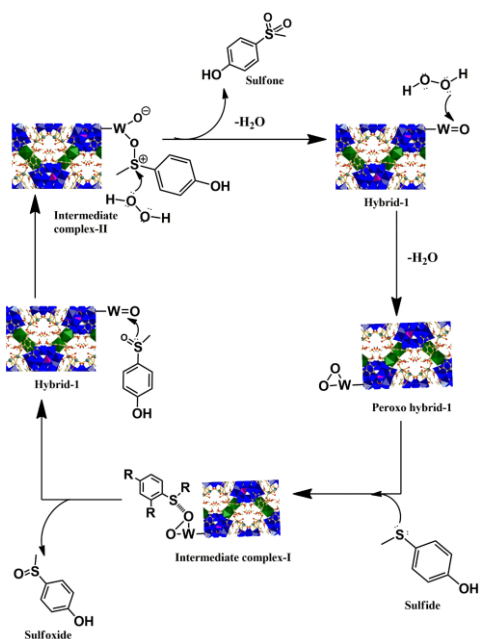


Figure S5. Proposed mechanism for the oxidation of sulfides using hybrid **1** with H₂O₂ as oxidant

Recyclability and stability studies on hybrid **1** as catalyst

The recyclability studies on hybrid **1** in the oxidation of 4-(methylthio)phenol was investigated. In a simple process, the 4-(methylsulfinyl)phenol product was extracted by adding dichloromethane after first cycle of the oxidation reaction and the remaining aqueous solutions containing hybrid **1** catalyst was reused directly for the next round of reactions. In this way, hybrid **1** could be reused for at least three times without any significant reduction in catalytic activity (see Table S5). The isolated sulfoxide yields from 1-3 cycles are given in Table S5. After completion of the catalytic cycles, hybrid **1** was isolated by evaporating the aqueous layer under reduced pressure. The stability of recycled hybrid **1** (after three catalytic cycles) were checked by using IR spectroscopy, which was almost similar to that of the fresh hybrid **1** (see Figure S6). This suggested that the structural framework of hybrid **1** is stable even after three catalytic cycles.

Table S5. Recyclability of hybrid **1** catalyst in the oxidation of 4-(methylthio)phenol by H₂O₂

Run	Sulfoxide %
1	100
2	98.42
3	95.18

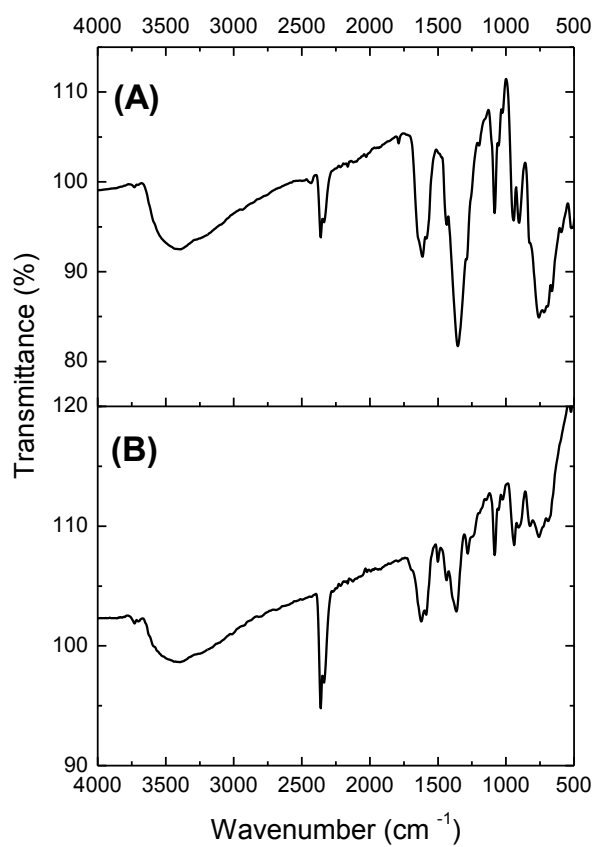


Figure S6. Comparison of IR spectra of hybrid **1**: fresh catalyst (A) and recycled hybrid **1** catalyst after third cycle of catalytic oxidation (B)

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^1H and ^{13}C NMR spectra for new compounds

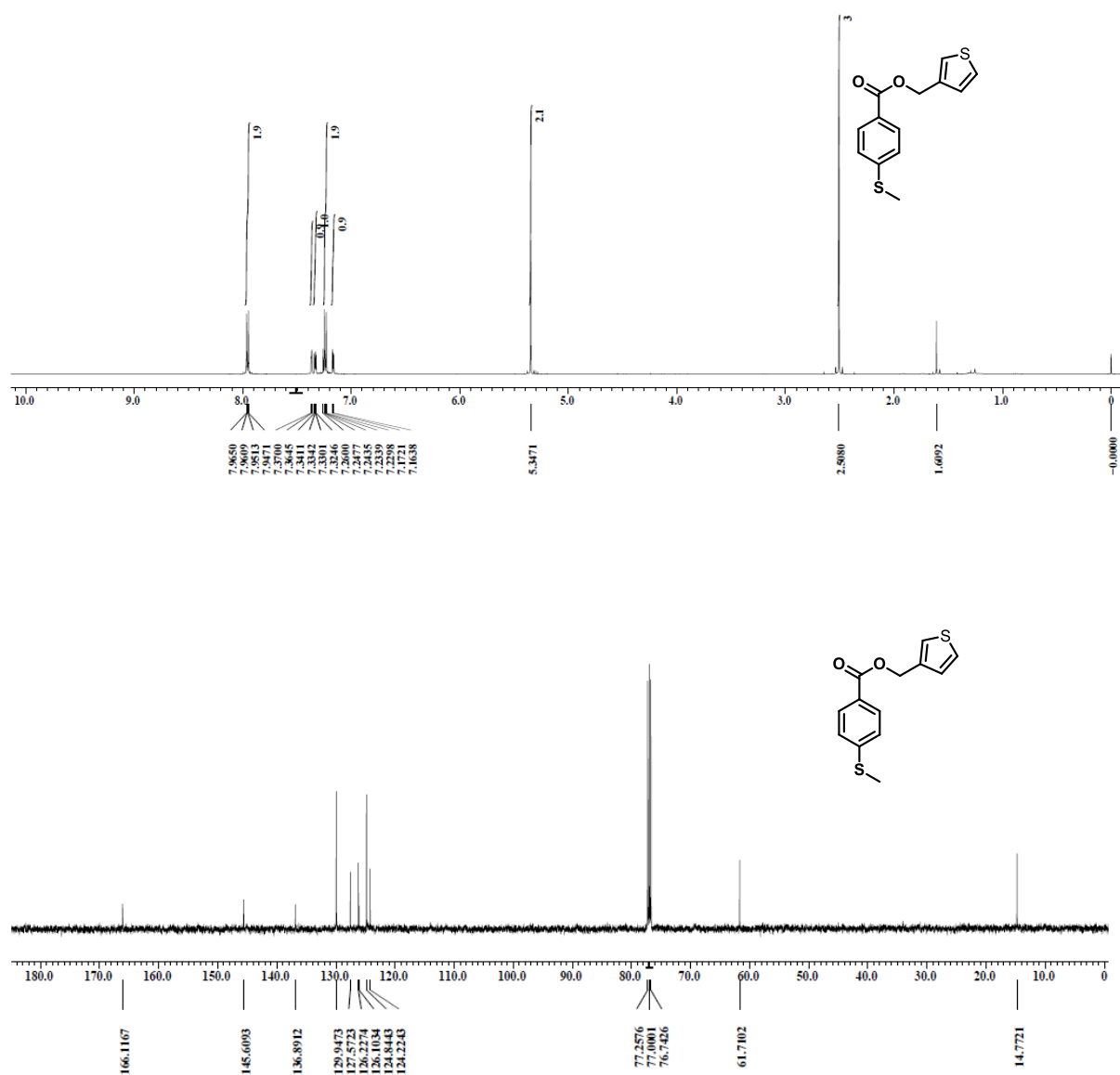


Figure S7. ^1H and ^{13}C NMR of thiophene-3-ylmethyl 4-(methylthio)benzoate

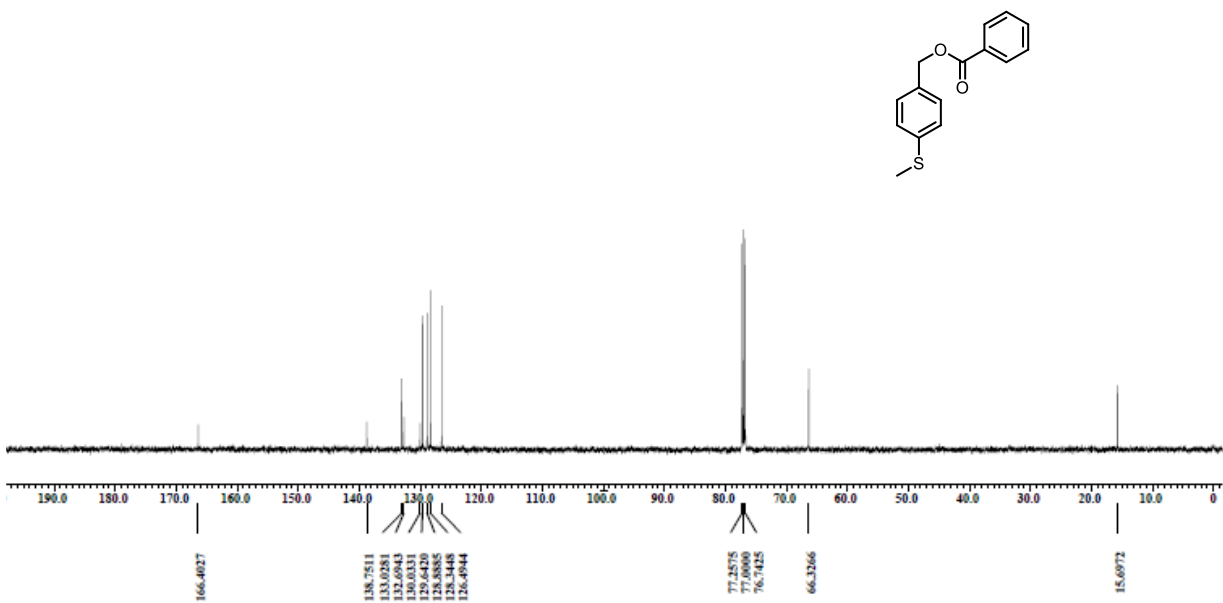
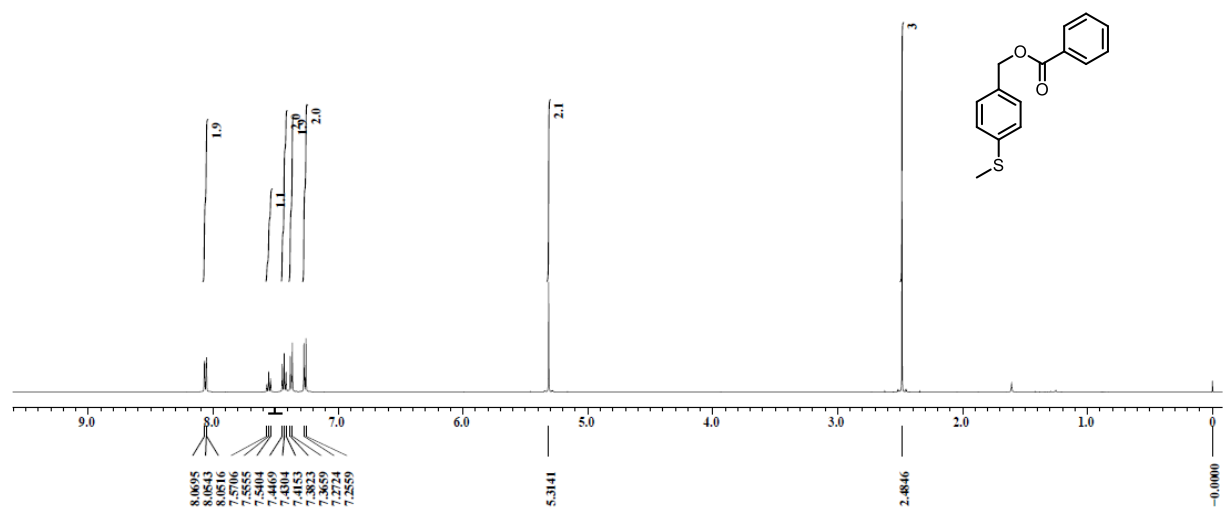


Figure S8. ^1H and ^{13}C NMR of 4-(methylthio)benzyl benzoate

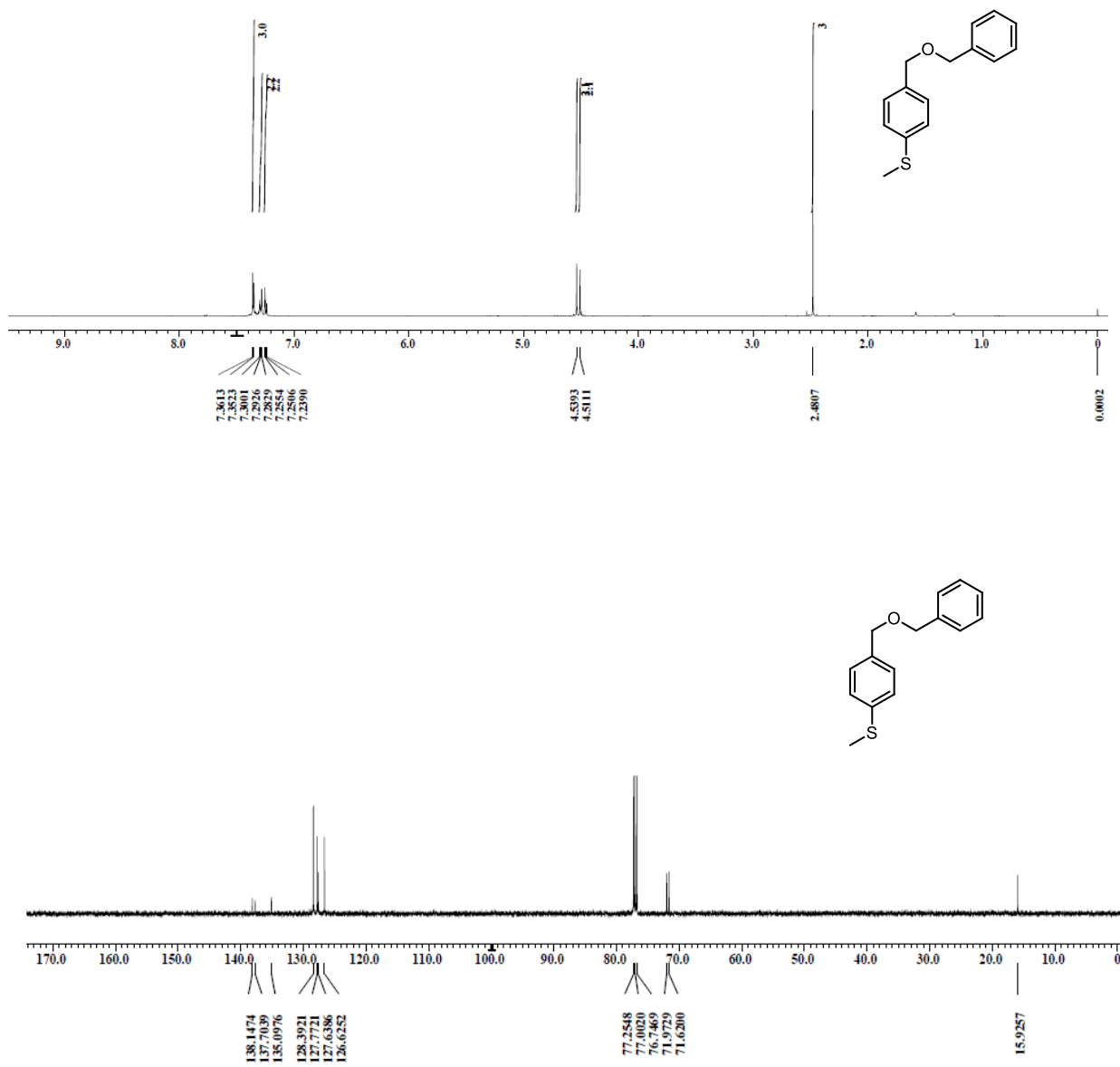


Figure S9. ^1H and ^{13}C NMR spectra of 4-((benzyloxy)methyl)phenyl(methyl)sulfane

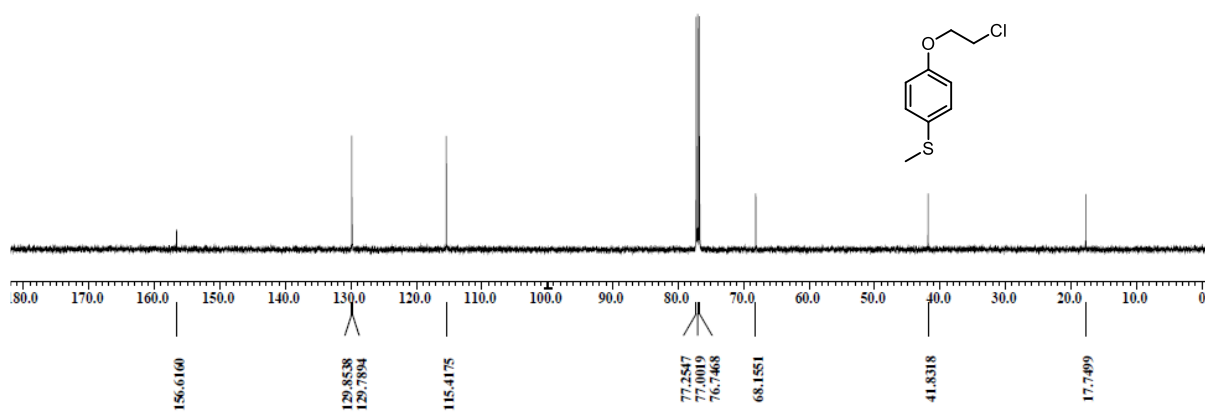
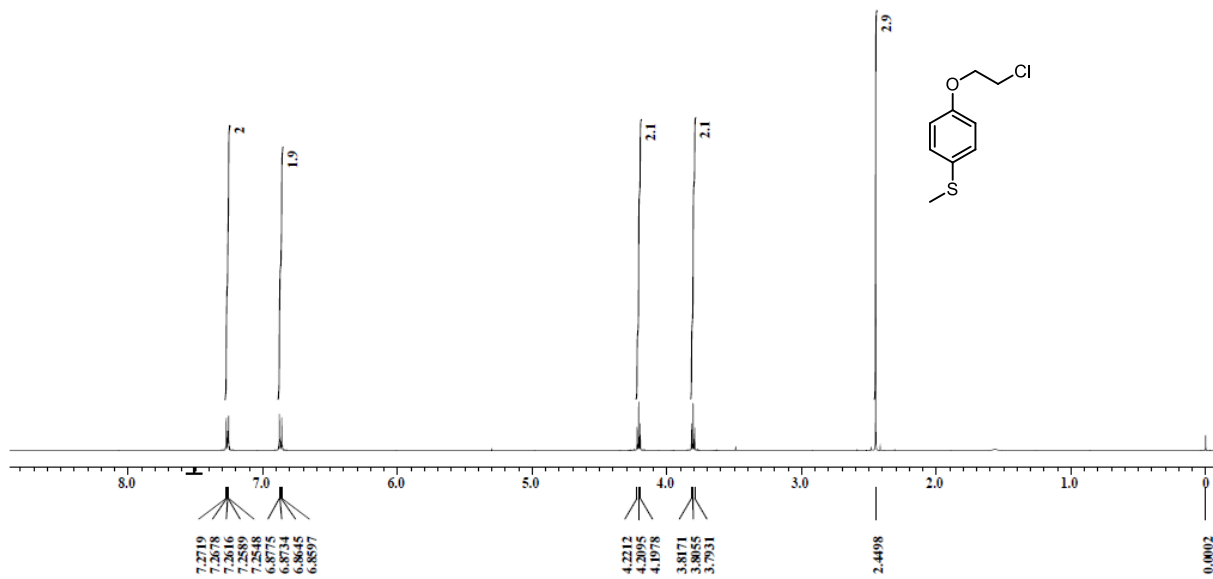


Figure S10. ^1H and ^{13}C NMR of (4-(2-chloroethoxy)phenyl)(methyl)sulfane

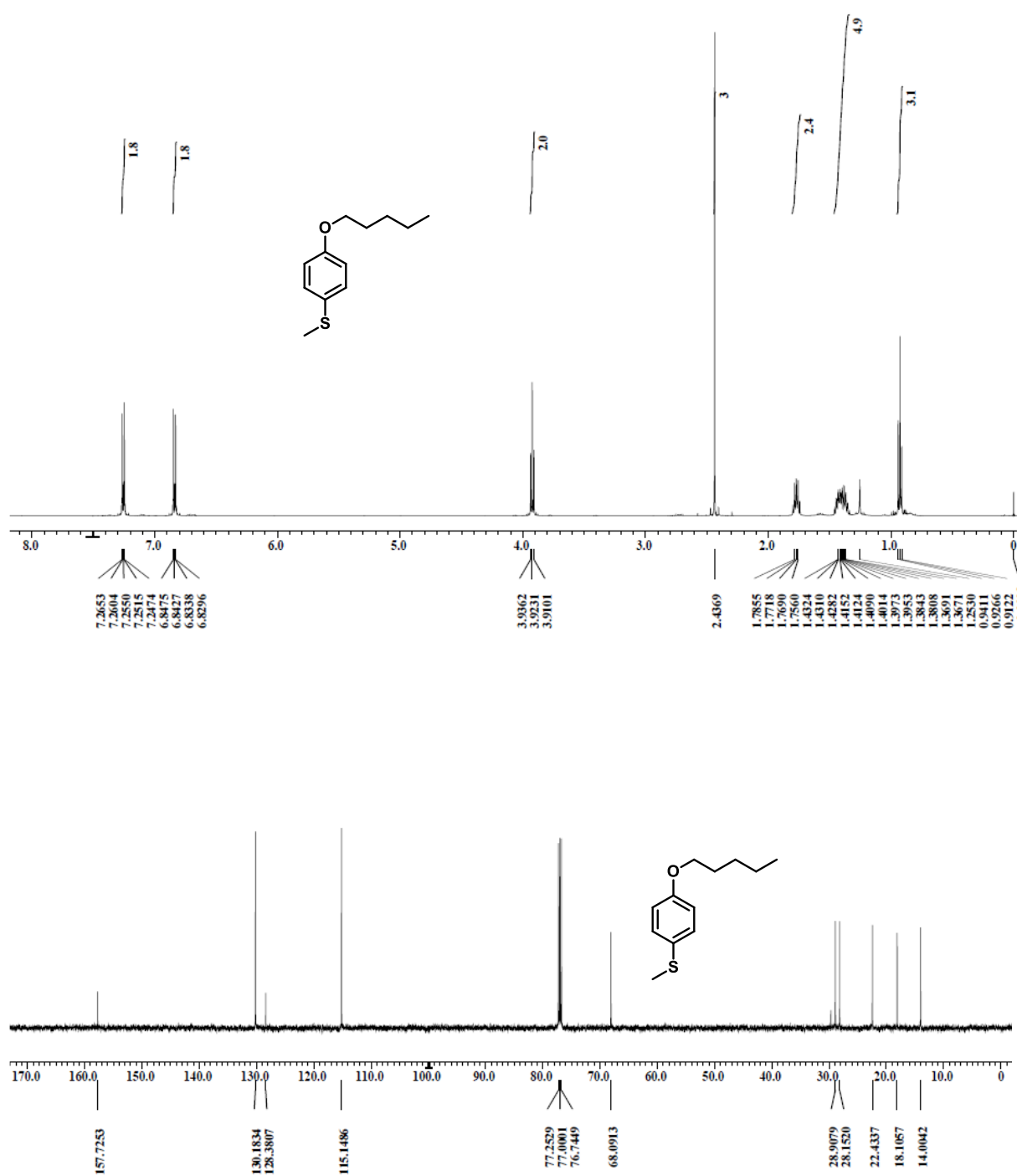


Figure S11. ¹H and ¹³C NMR of methyl(4-(pentyloxy)phenyl)sulfane

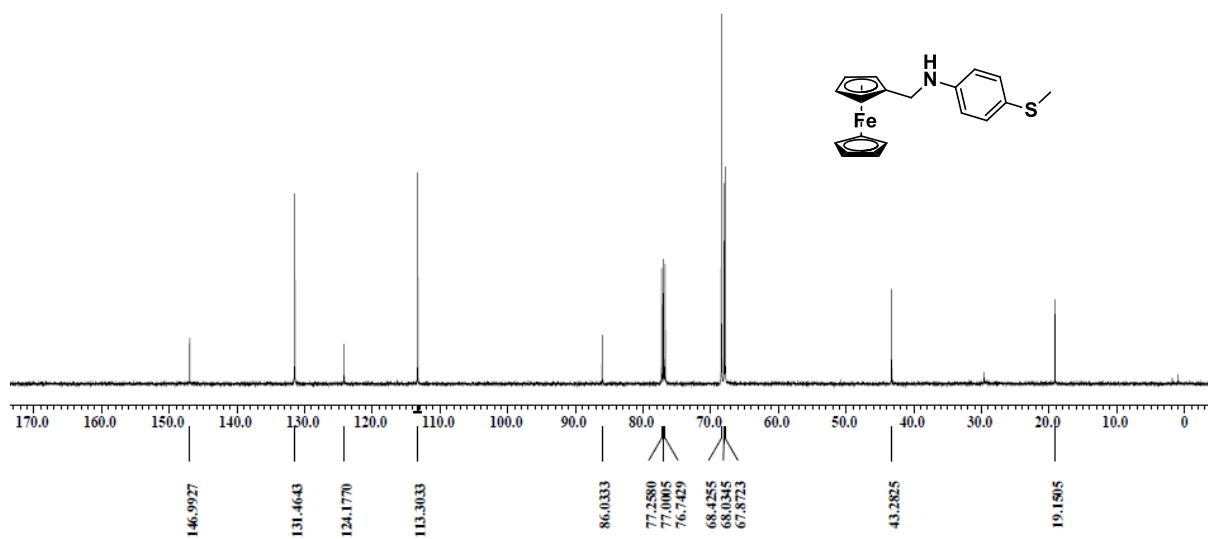
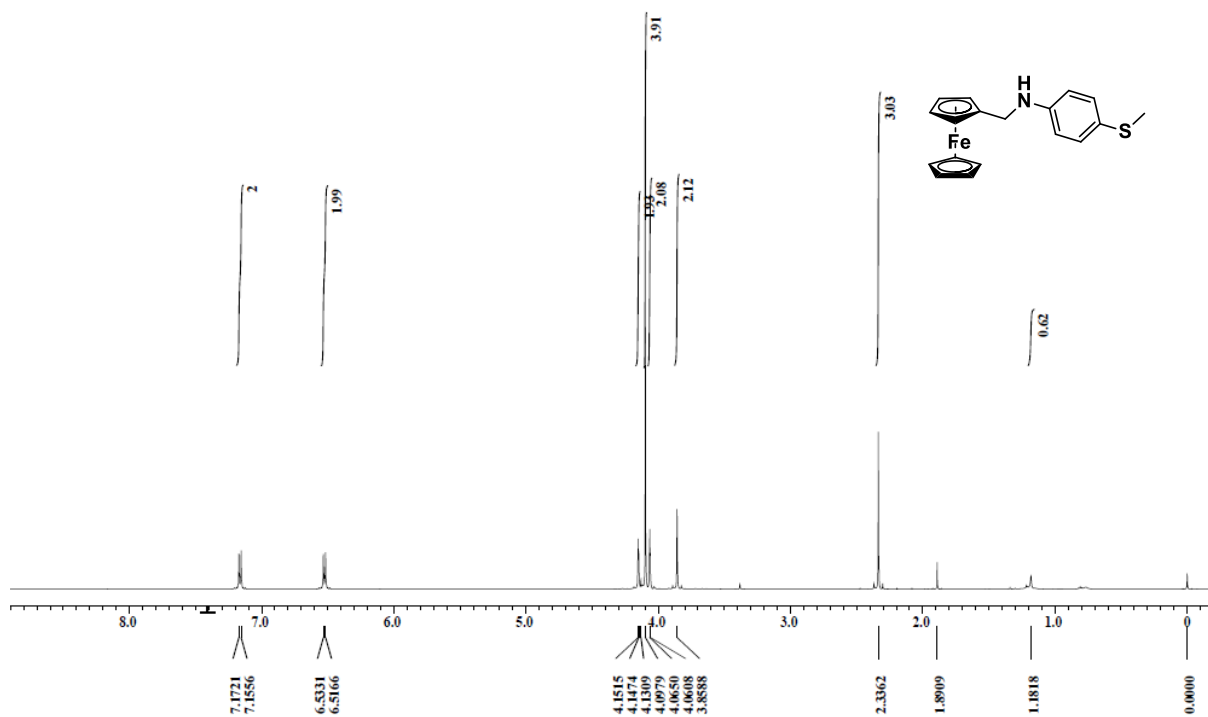


Figure S12. ^1H and ^{13}C NMR of ferrocene-4-(methylthio)aniline

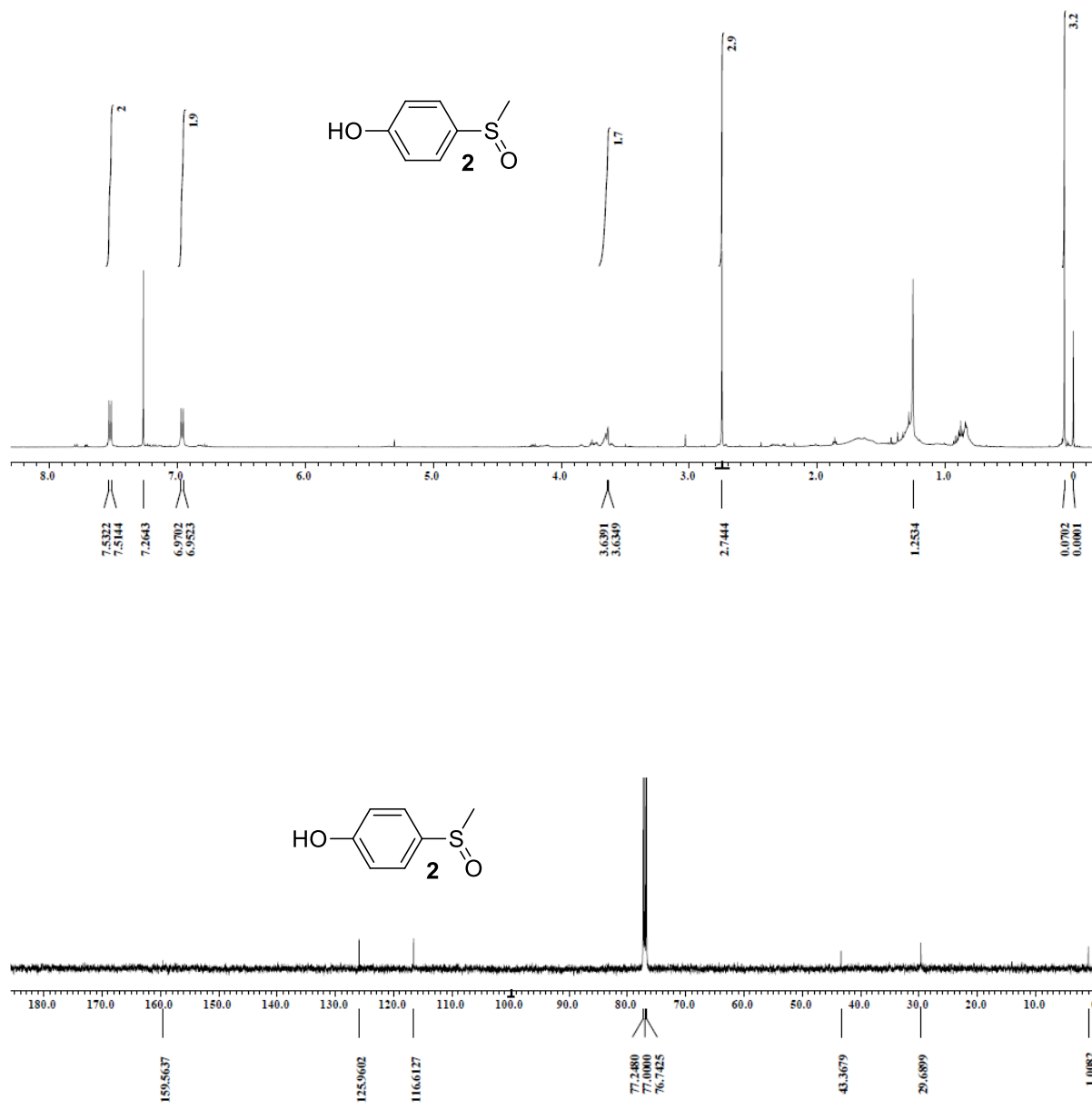


Figure S13. ¹H and ¹³C NMR of 4-(methylsulfinyl)phenol (2)

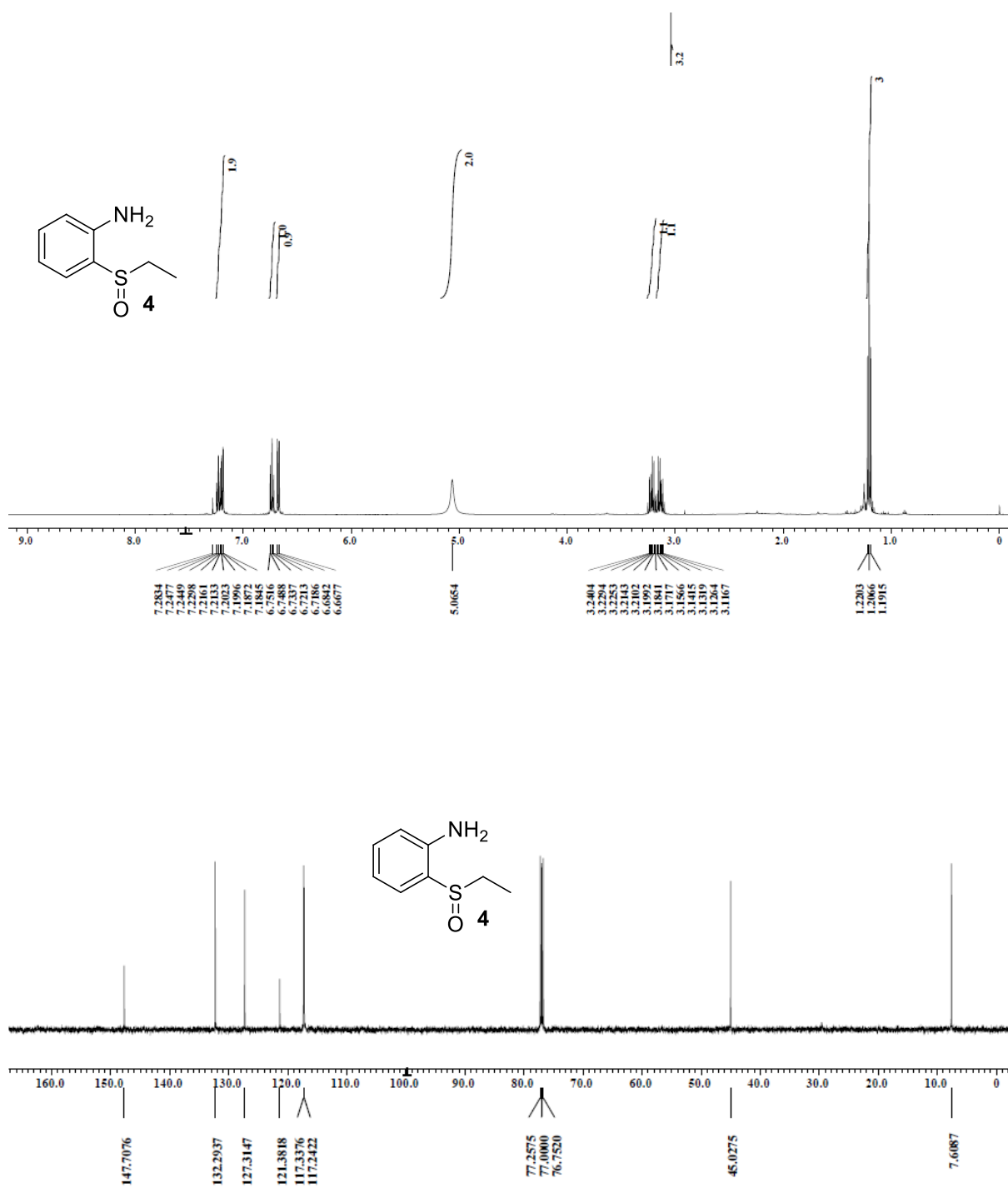


Figure S14. ¹H and ¹³C NMR of 2-(ethylsulfinyl)aniline (4)

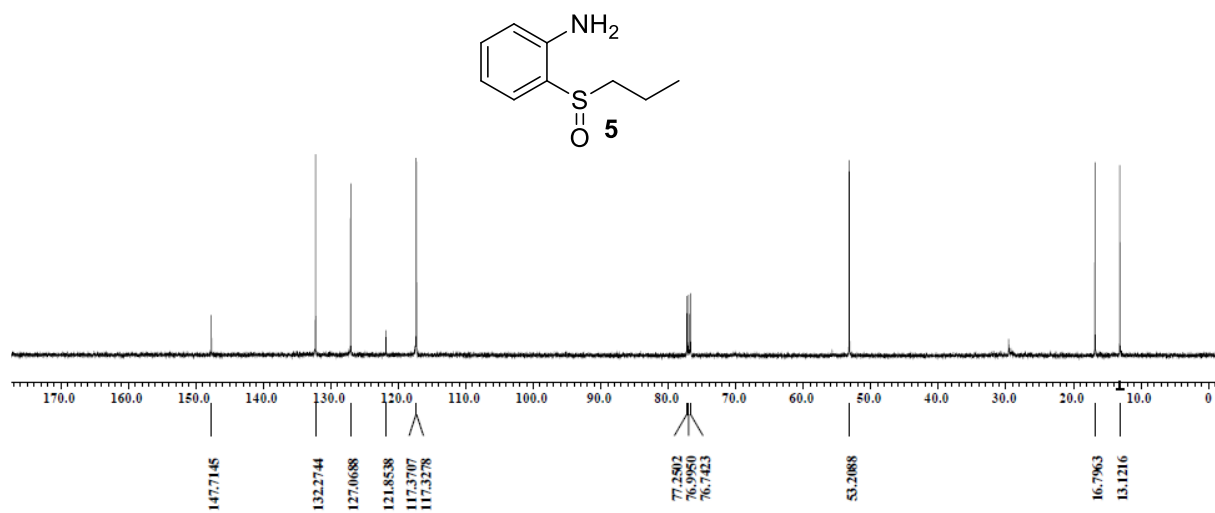
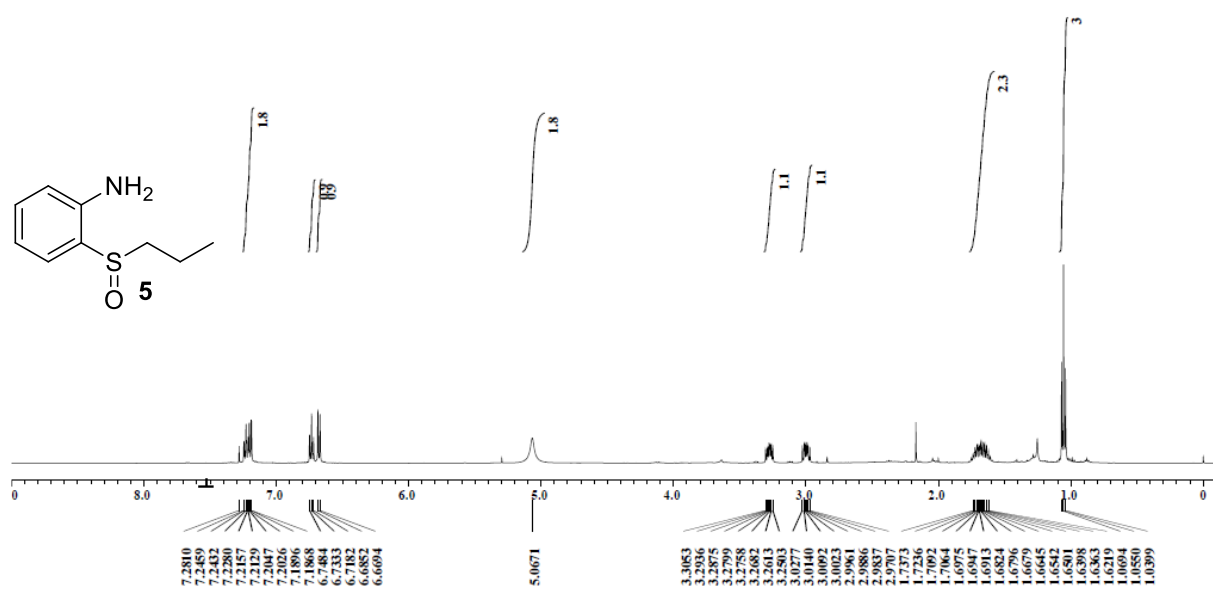


Figure S15. ¹H and ¹³C NMR of 2-(propylsulfonyl)aniline (5)

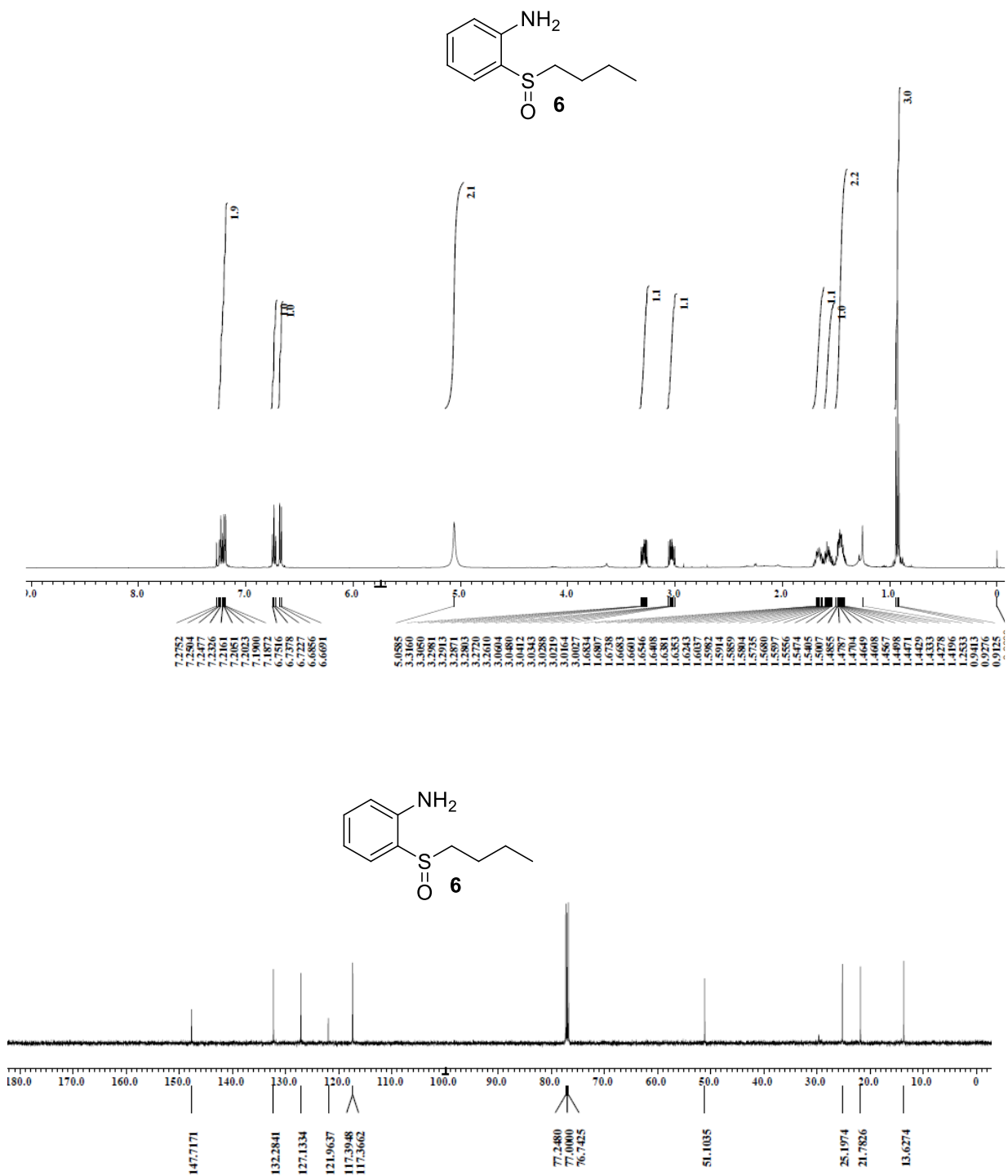


Figure S16. ¹H and ¹³C NMR of 2-(butylsulfinyl)aniline (6)

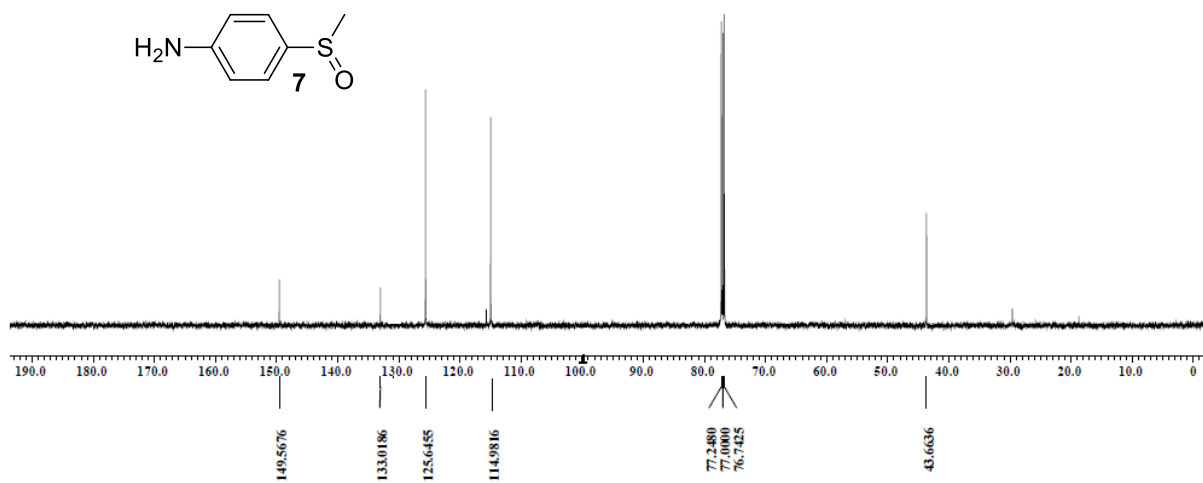
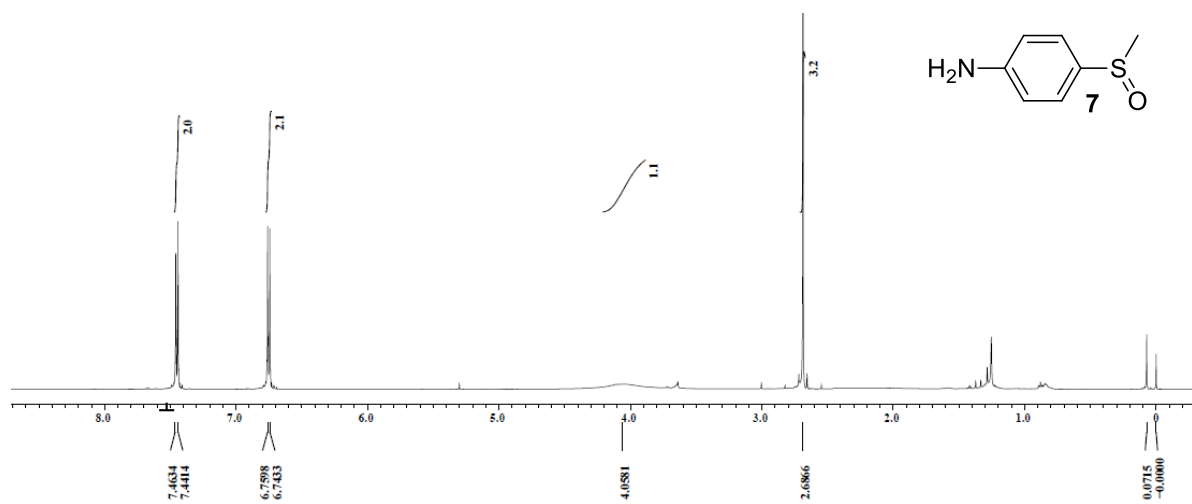


Figure S17. ^1H and ^{13}C NMR of 4-(methylsulfinyl)aniline (7)

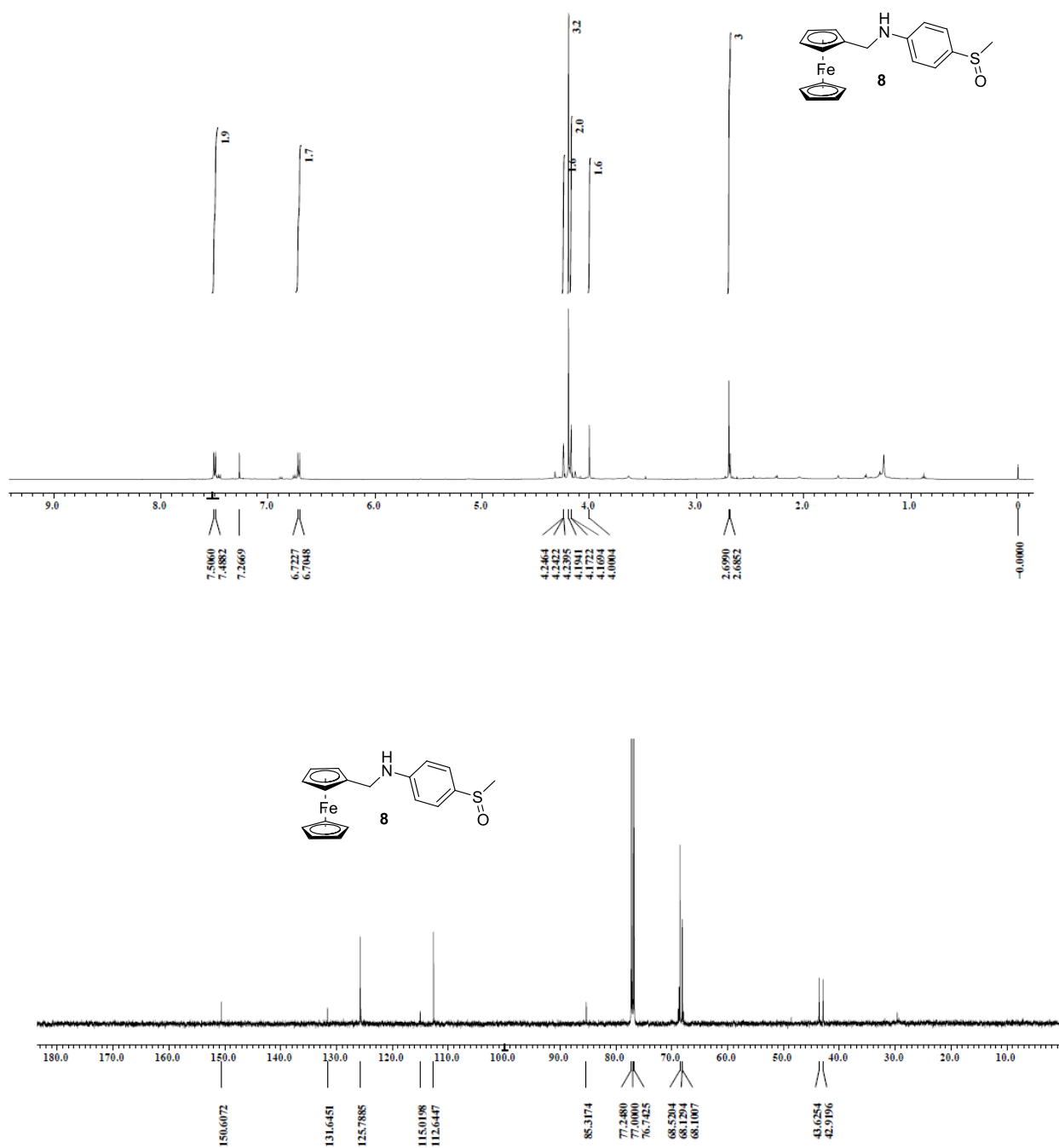


Figure S18. ¹H and ¹³C NMR of ferrocene-4-(methylsulfinyl)aniline (**8**)

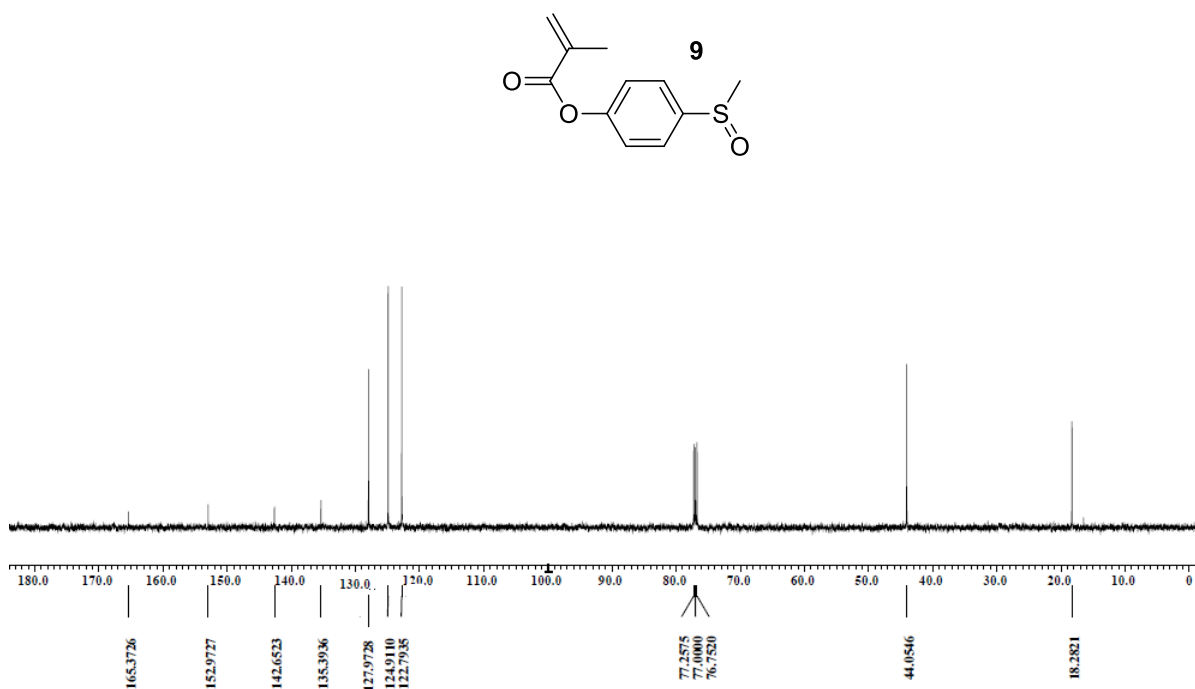
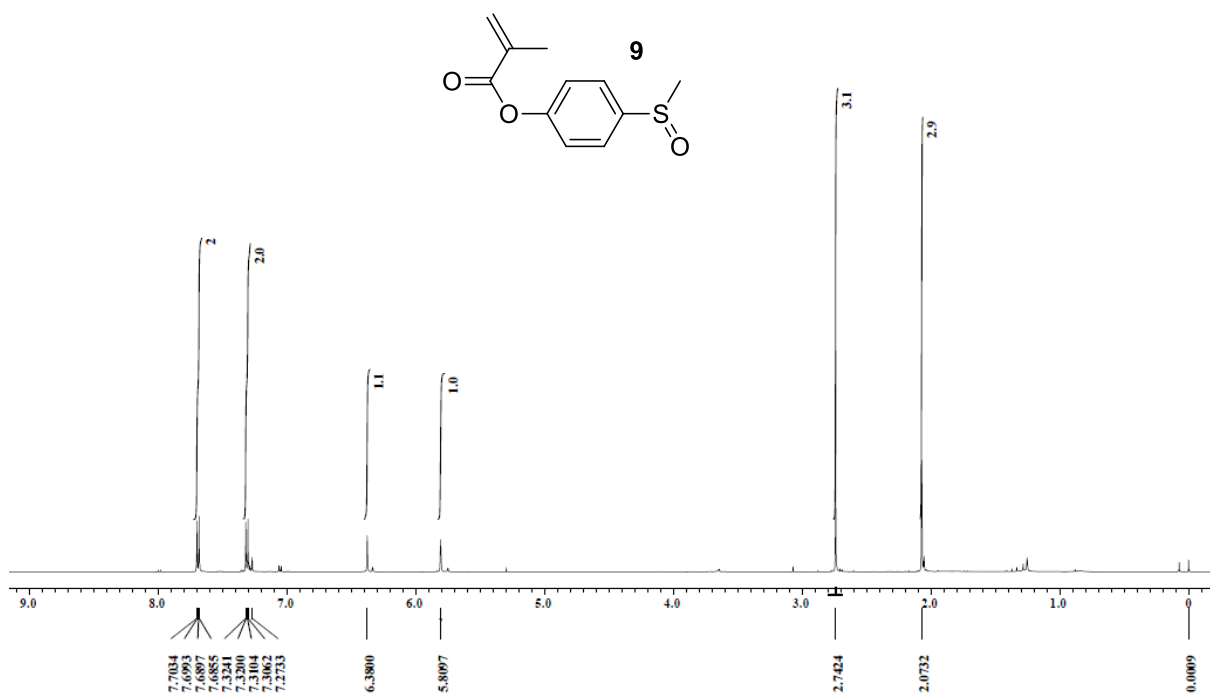


Figure S19. ¹H and ¹³C NMR of 4-(methylsulfinyl)phenyl methacrylate (**9**)

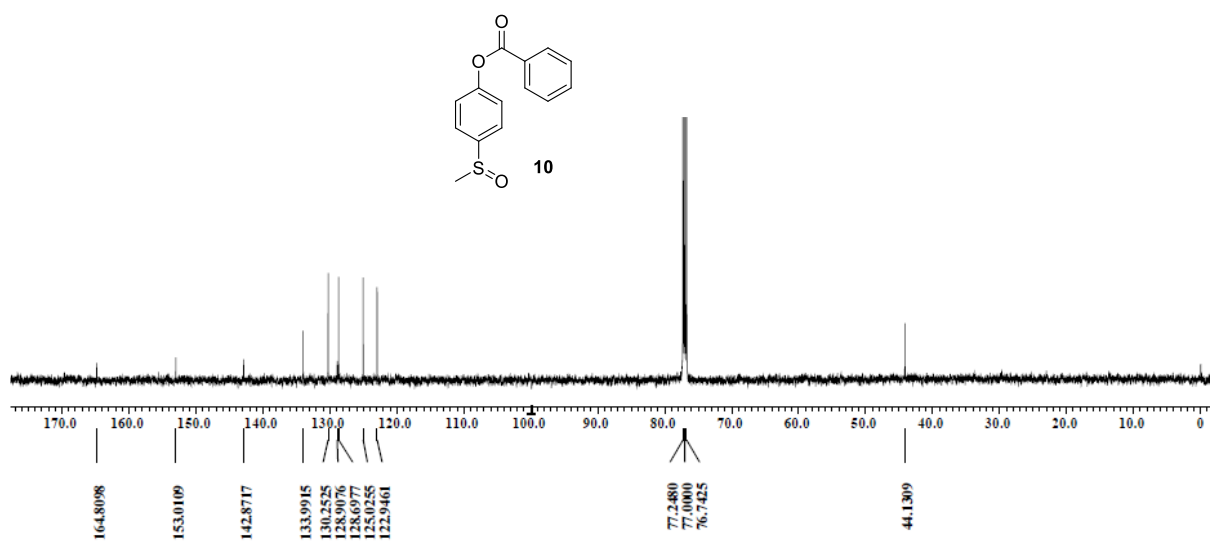
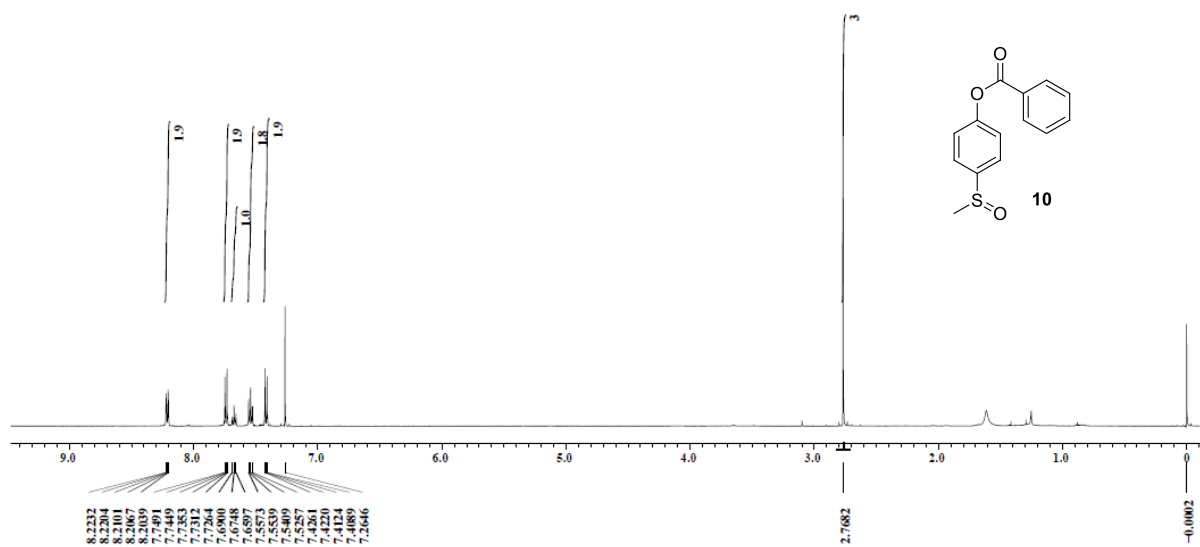


Figure S20. ¹H and ¹³C NMR of 4-(methylsulfinyl)phenyl benzoate (10)

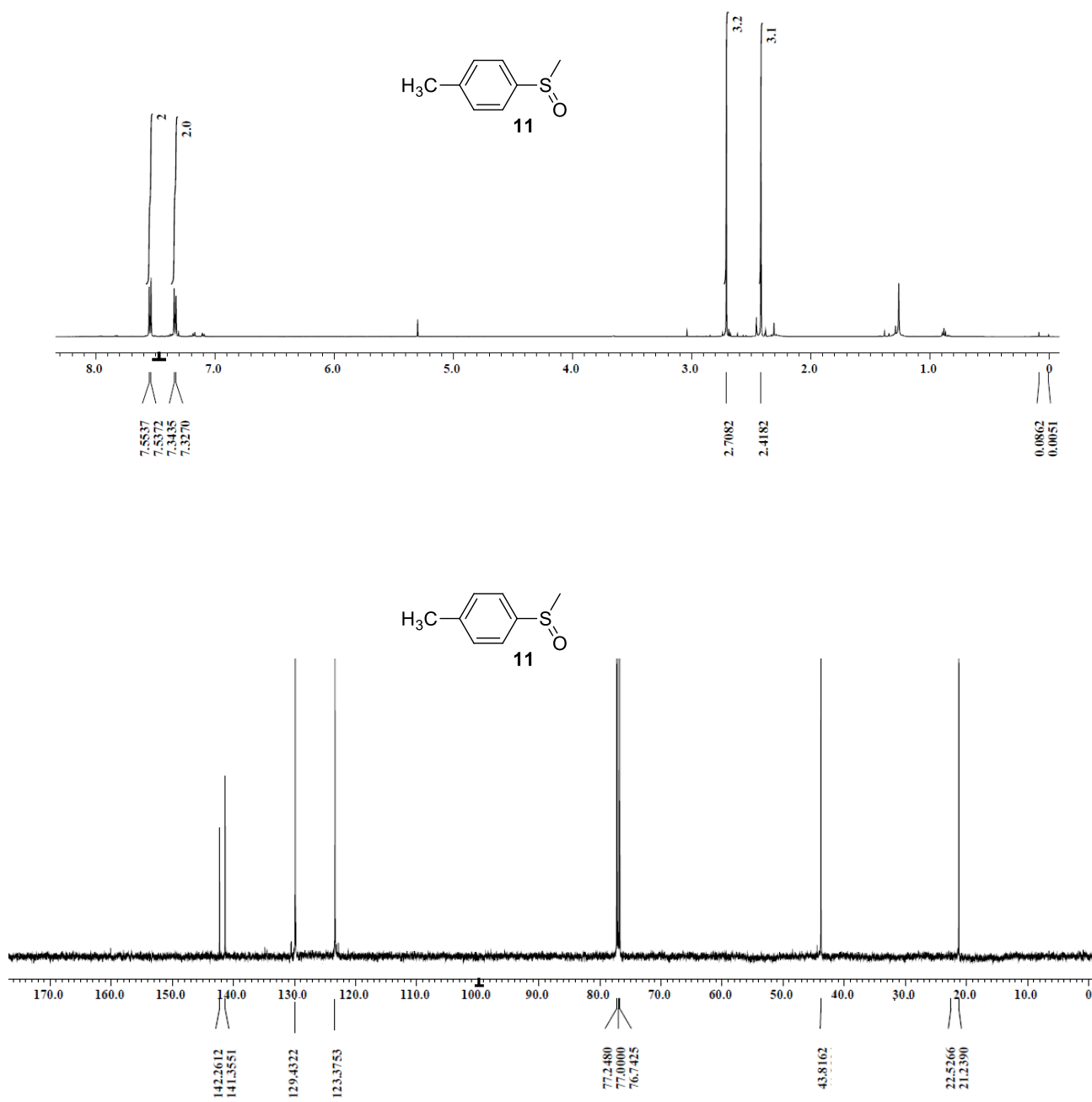


Figure S21. ¹H and ¹³C NMR of 1-methyl-4-(methylsulfinyl)benzene (11)

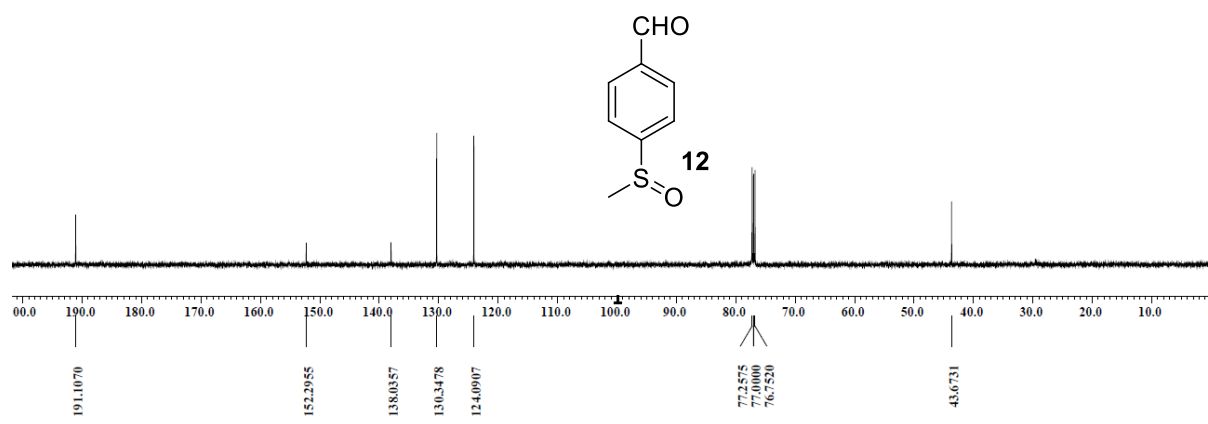
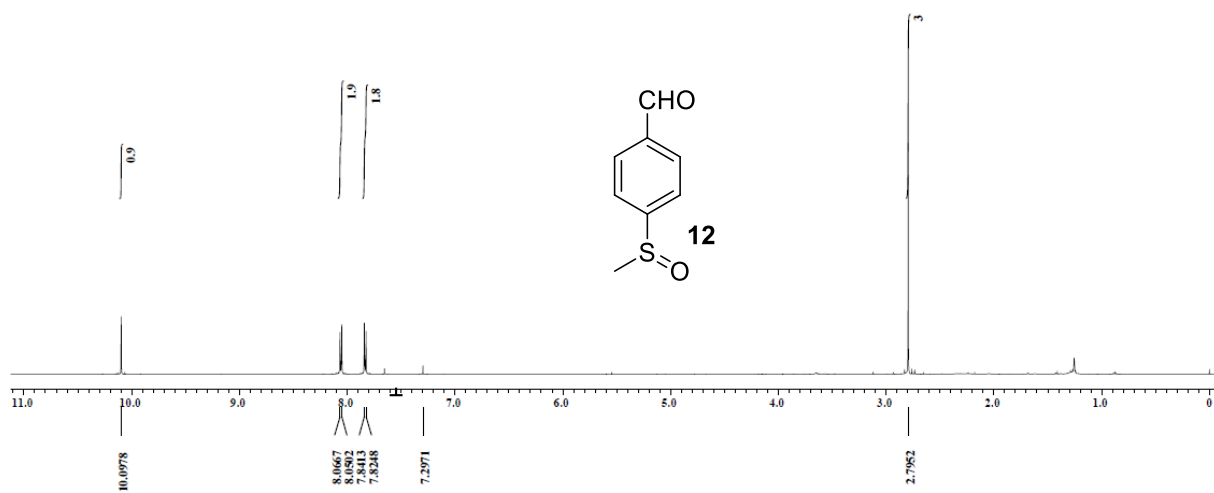


Figure S22. ¹H and ¹³C NMR of 4-(methylsulfinyl)benzaldehyde (**12**)

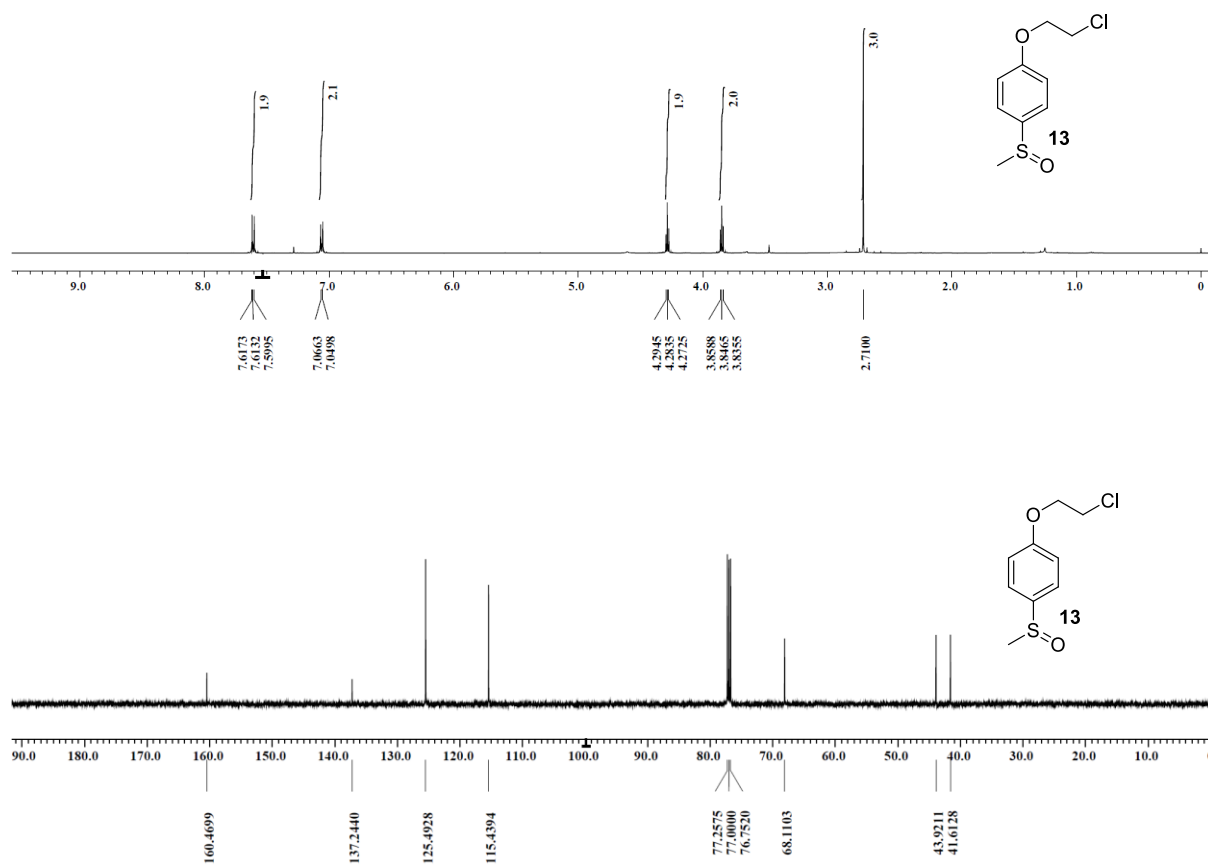


Figure S23. ¹H and ¹³C NMR of 1-(2-chloroethoxy)-4-(methylsulfinyl)benzene (13)

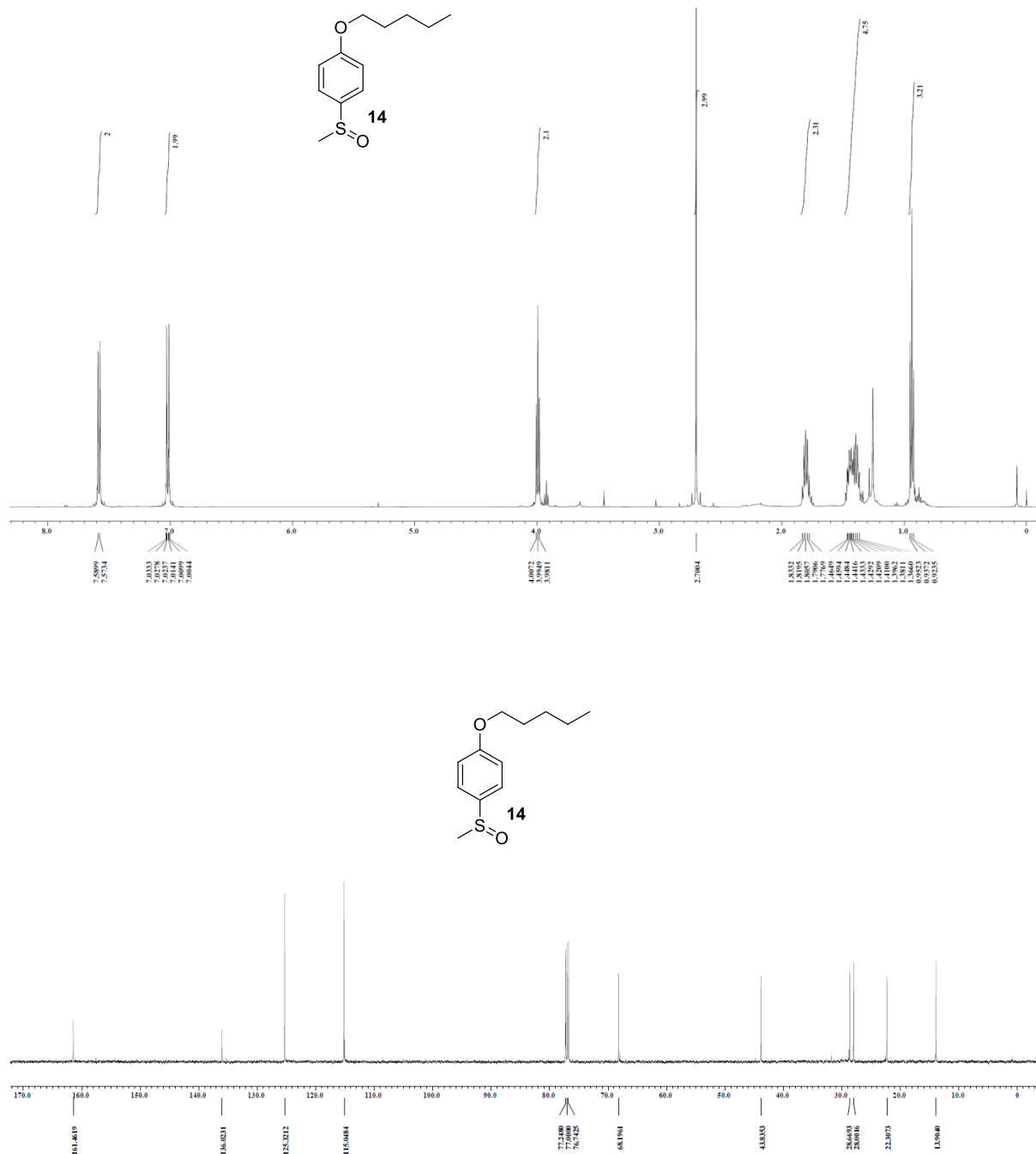


Figure S24. ¹H and ¹³C NMR of 1-(methylsulfinyl)-4-(pentyloxy)benzene (**14**)

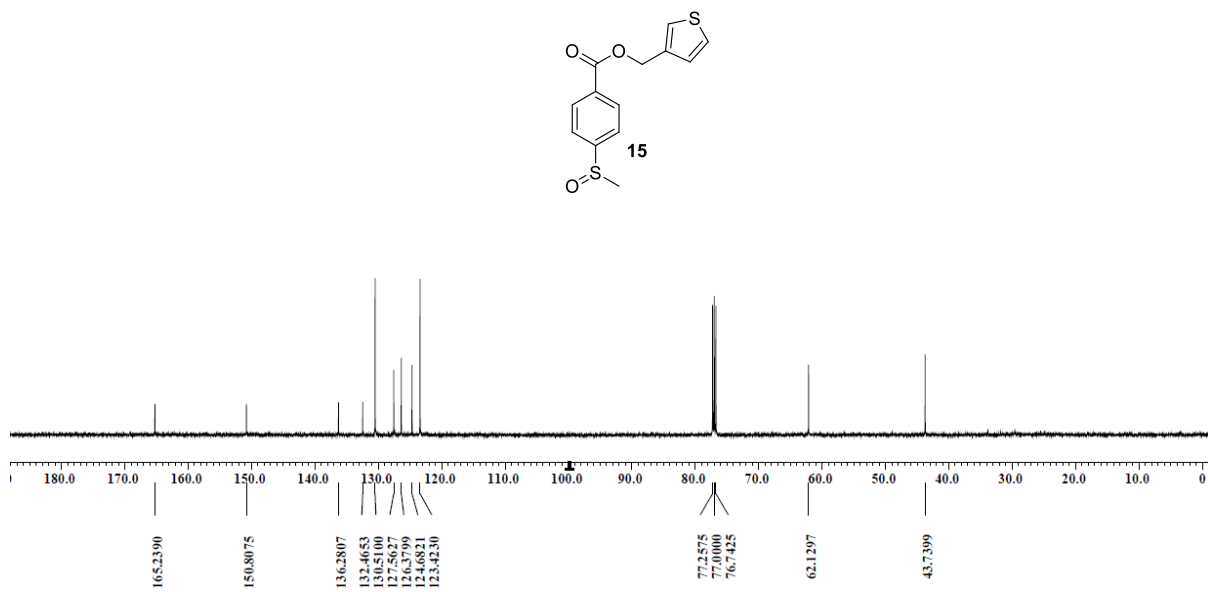
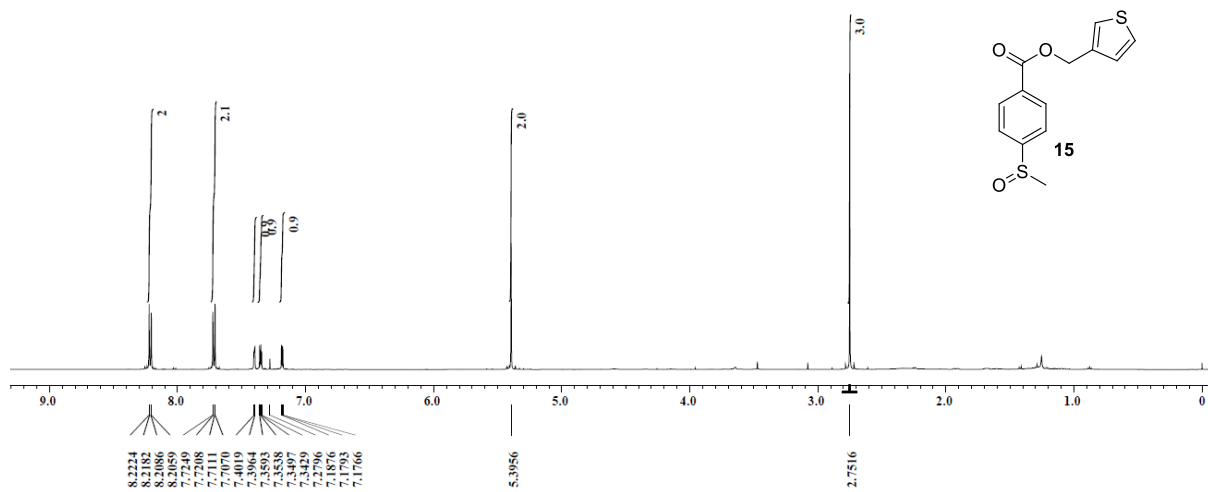


Figure S25. ¹H and ¹³C NMR of thiophen-3-ylmethyl 4-(methylsulfinyl)benzoate (15)

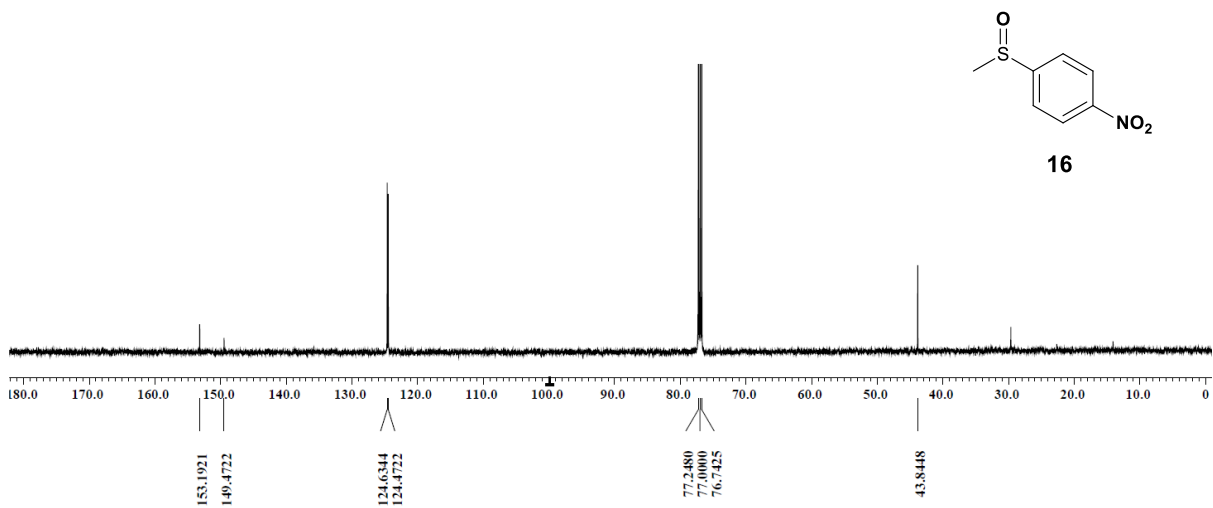
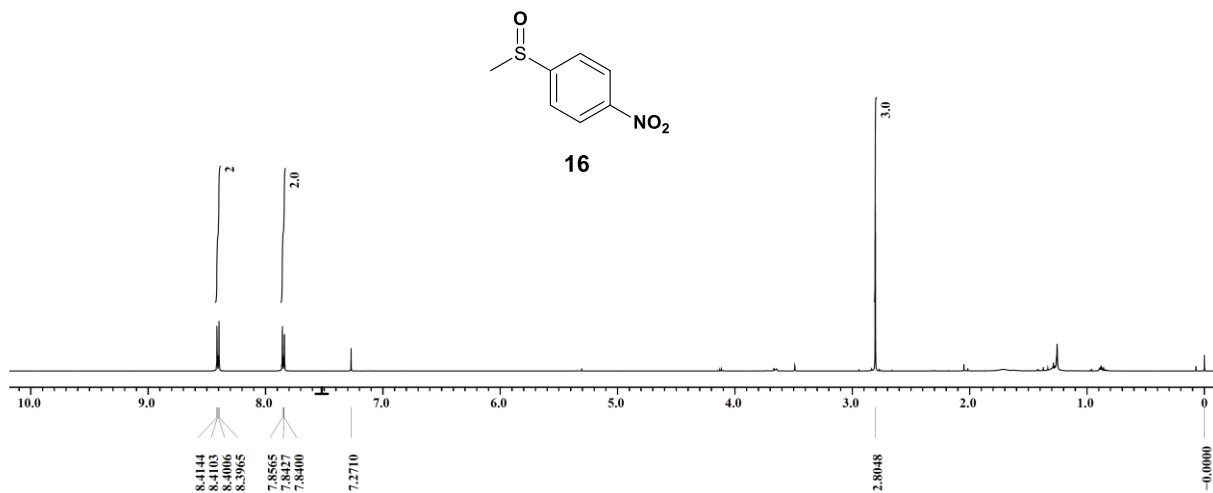


Figure S26. ^1H and ^{13}C NMR of 1-(methylsulfinyl)-4-nitrobenzene (**16**)

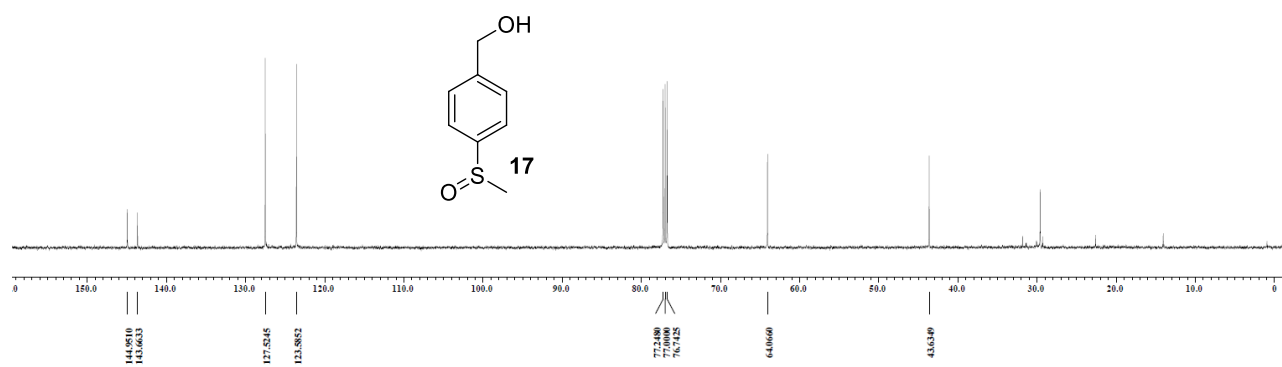
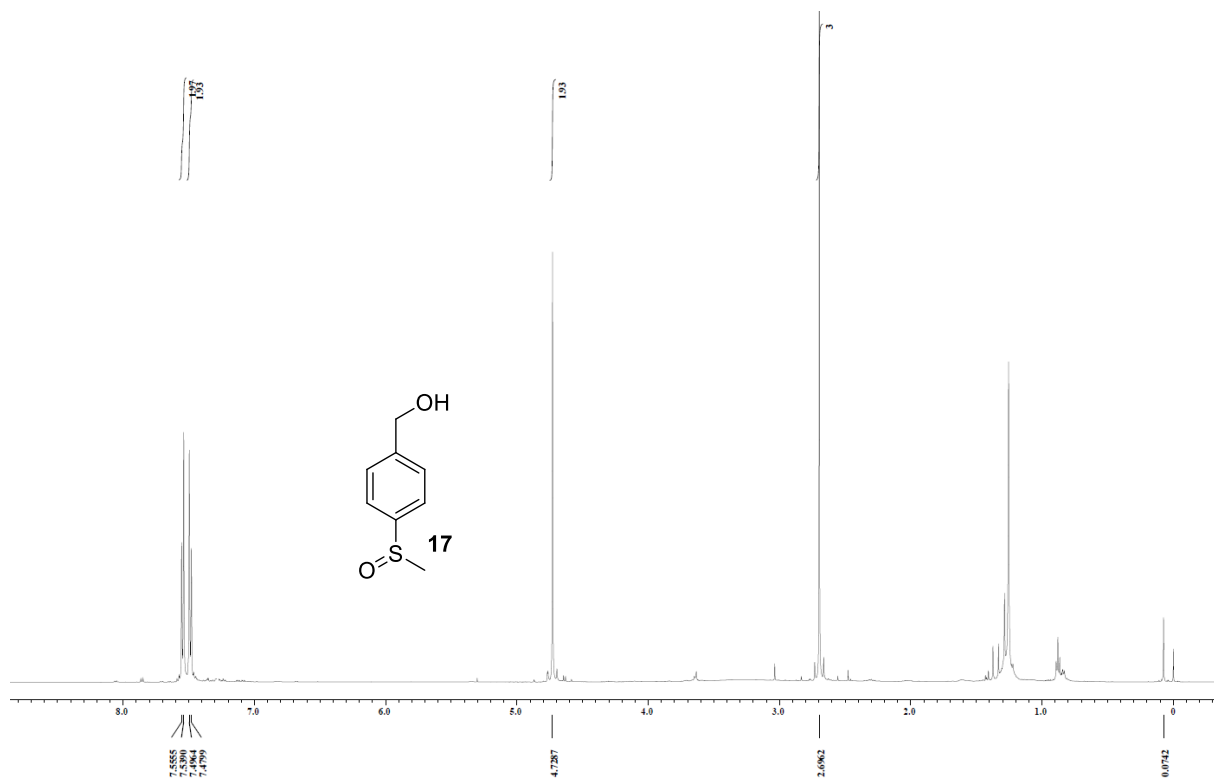


Figure S27. ¹H and ¹³C NMR of (4-(methylsulfinyl)phenyl)methanol (17)

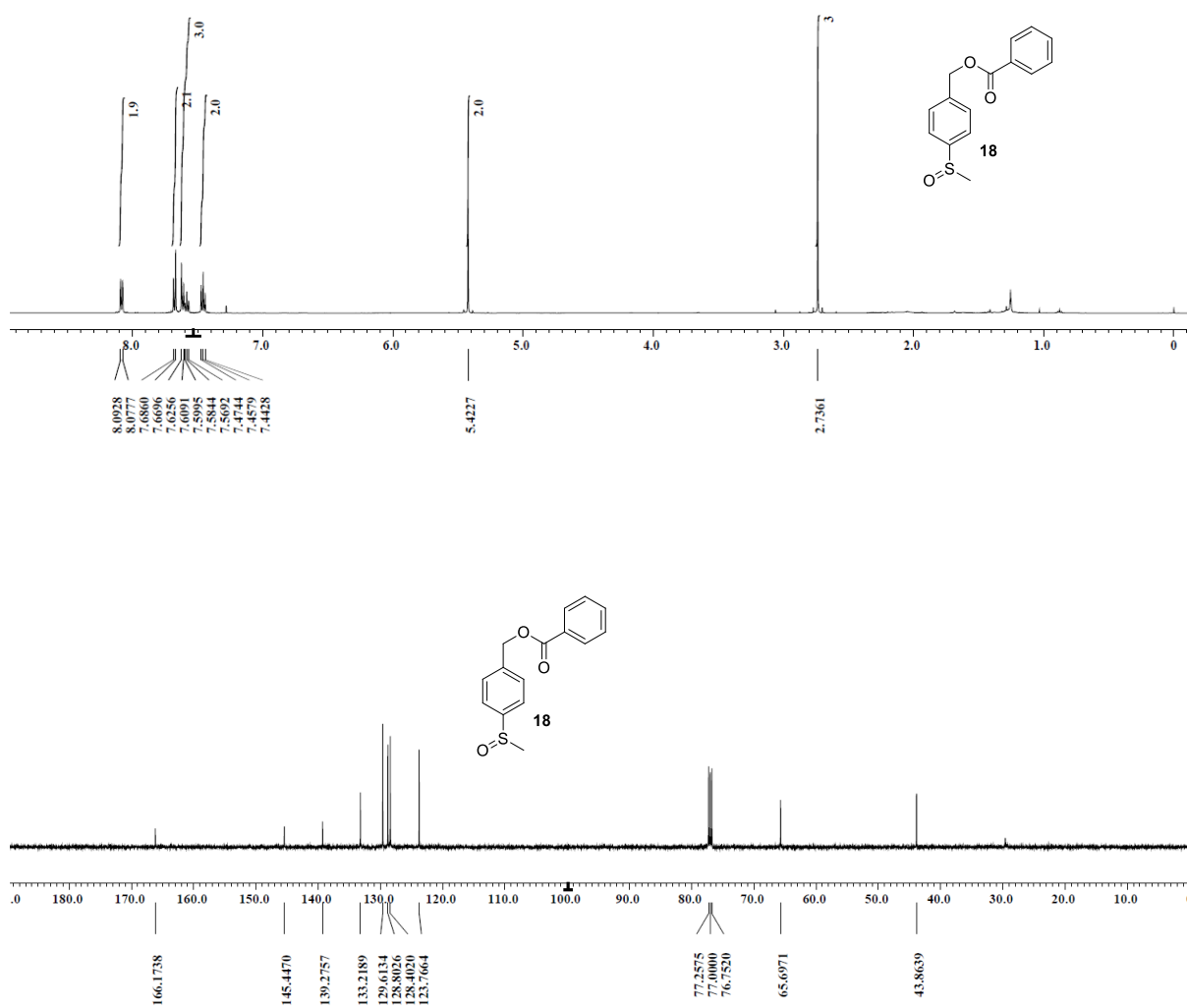


Figure S28. ¹H and ¹³C NMR of (4-(methylsulfinyl)benzyl) benzoate (**18**)

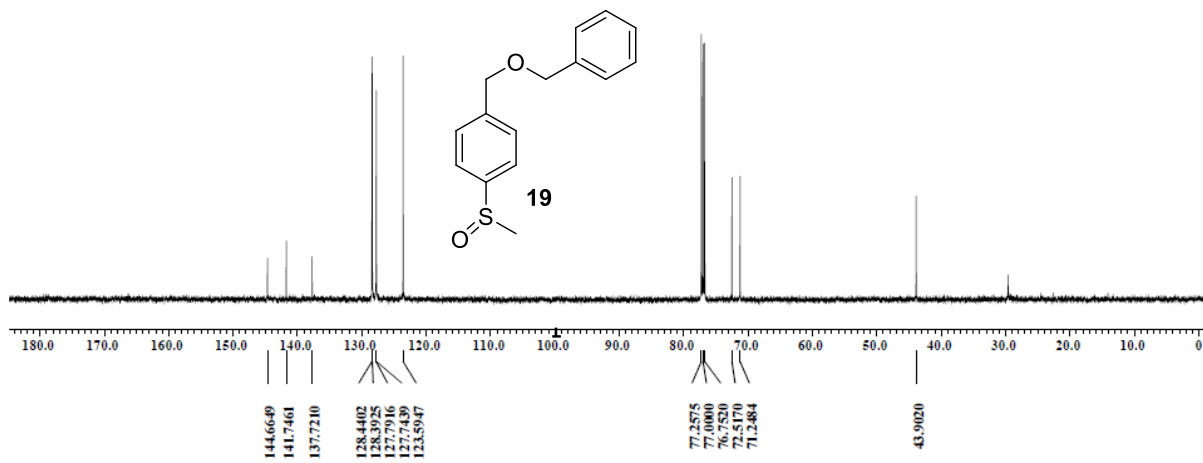
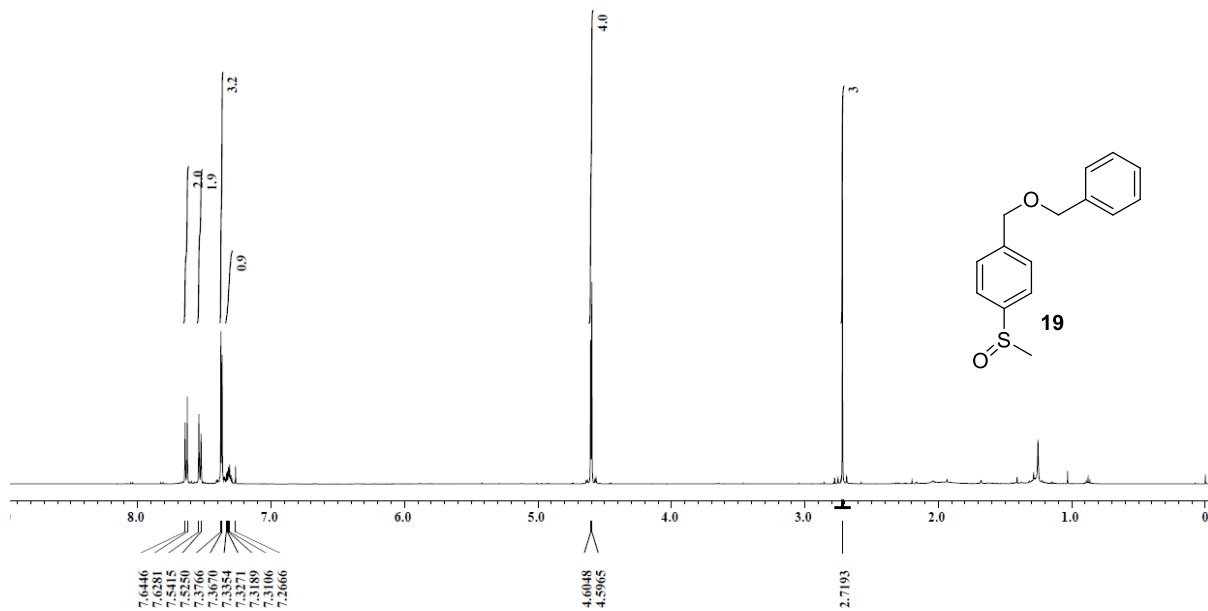


Figure S29. ¹H and ¹³C of 1-((benzyloxy)methyl)-4-(methylsulfinyl)benzene (**19**)

HR-MS spectra of new compounds

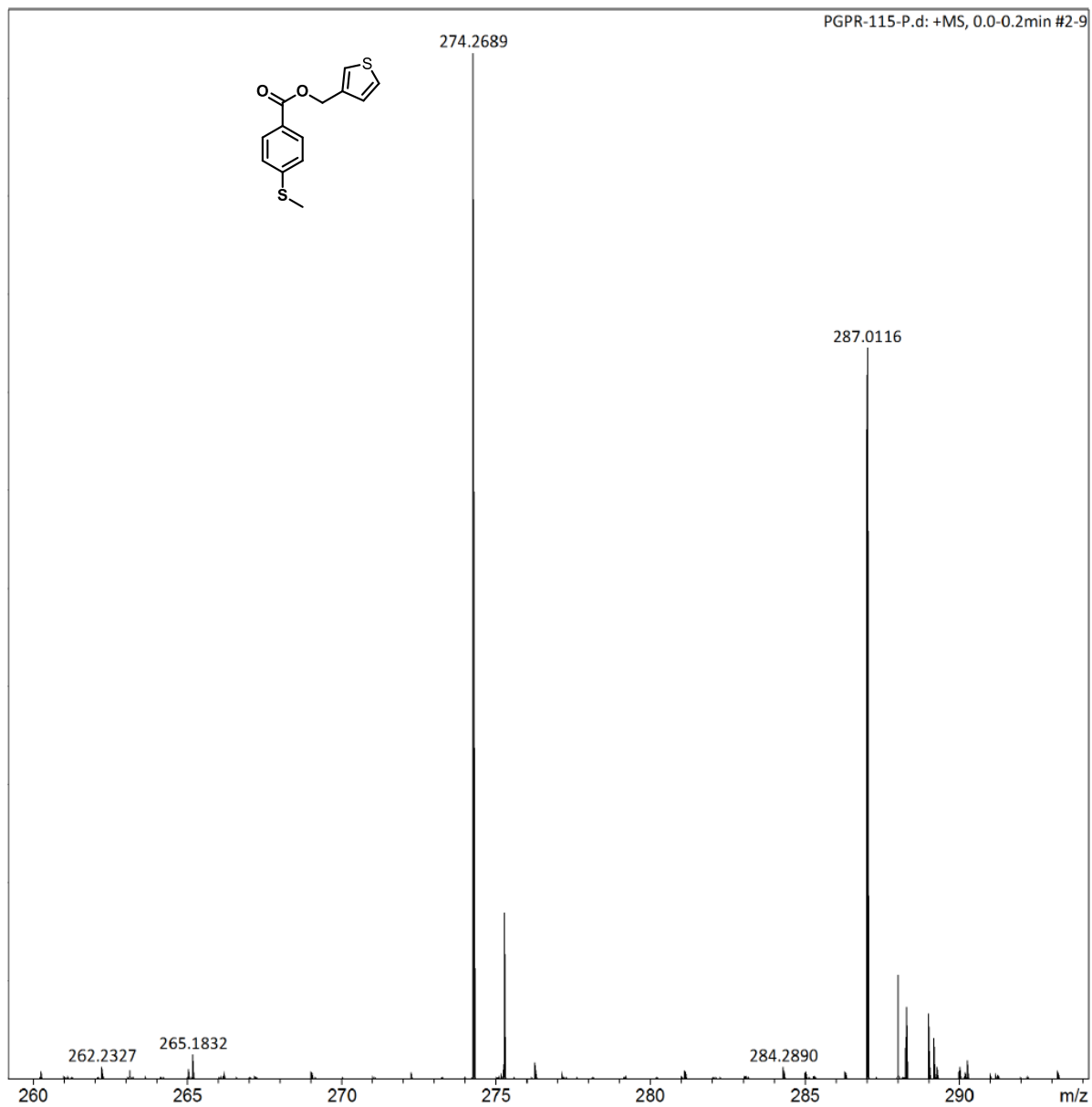


Figure S30. HR-MS of thiophene-3-ylmethyl 4-(methylthio)benzoate

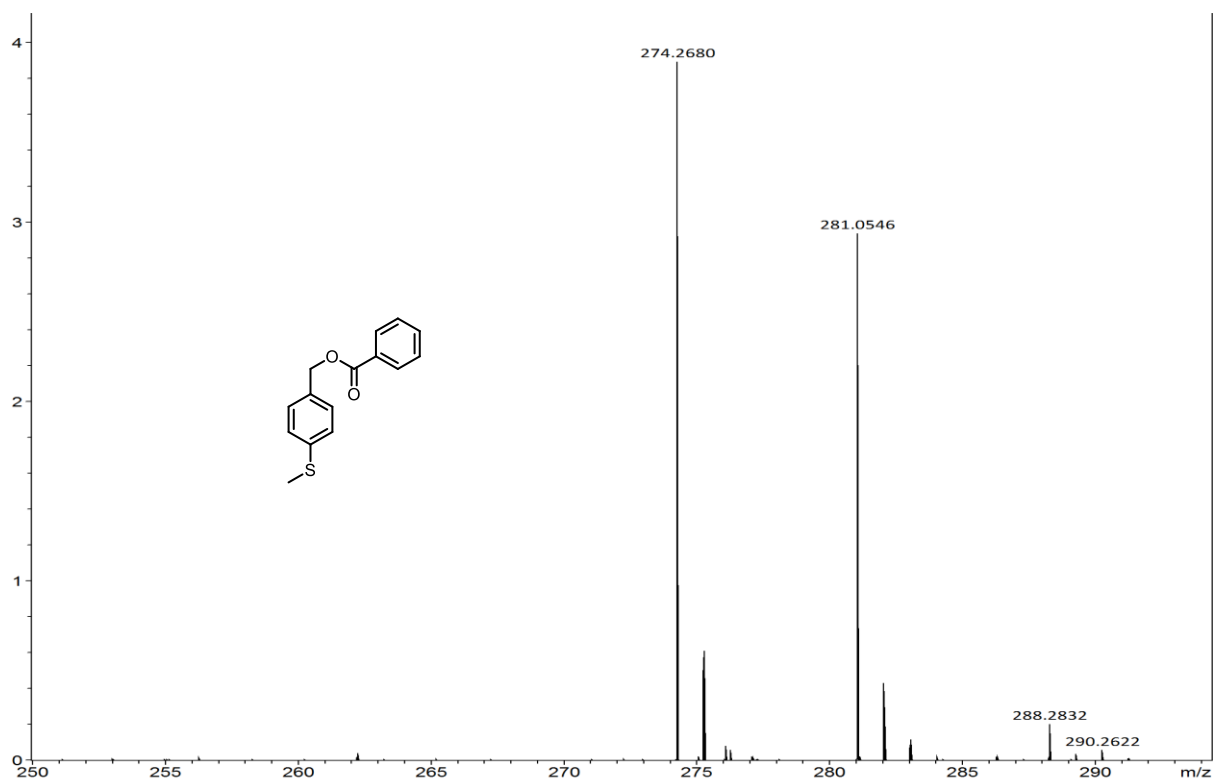


Figure S31. HR-MS of 4-(methylthio)benzyl benzoate

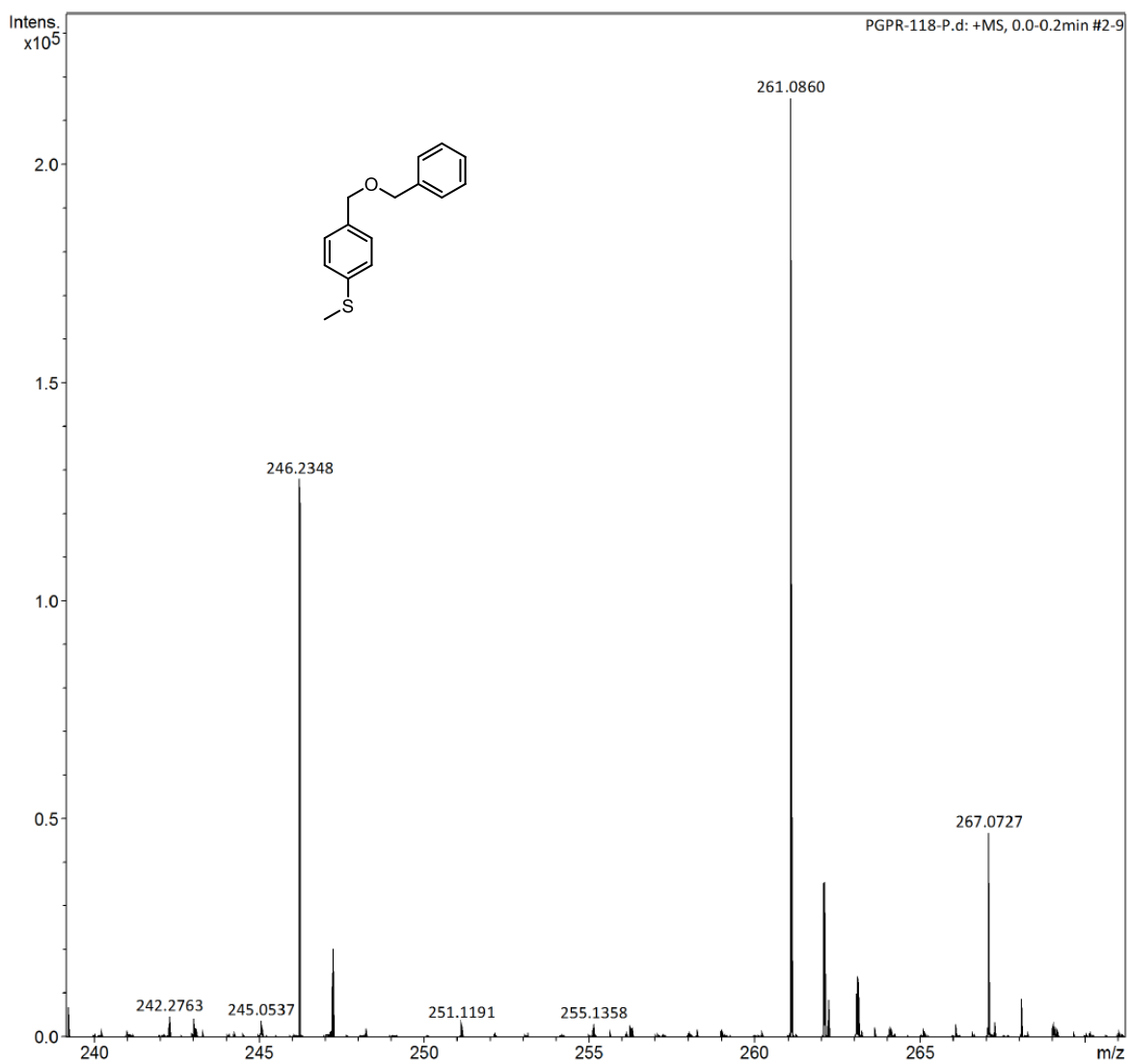


Figure S32. HR-MS of 4-((benzyloxy)methyl)phenyl(methyl)sulfane

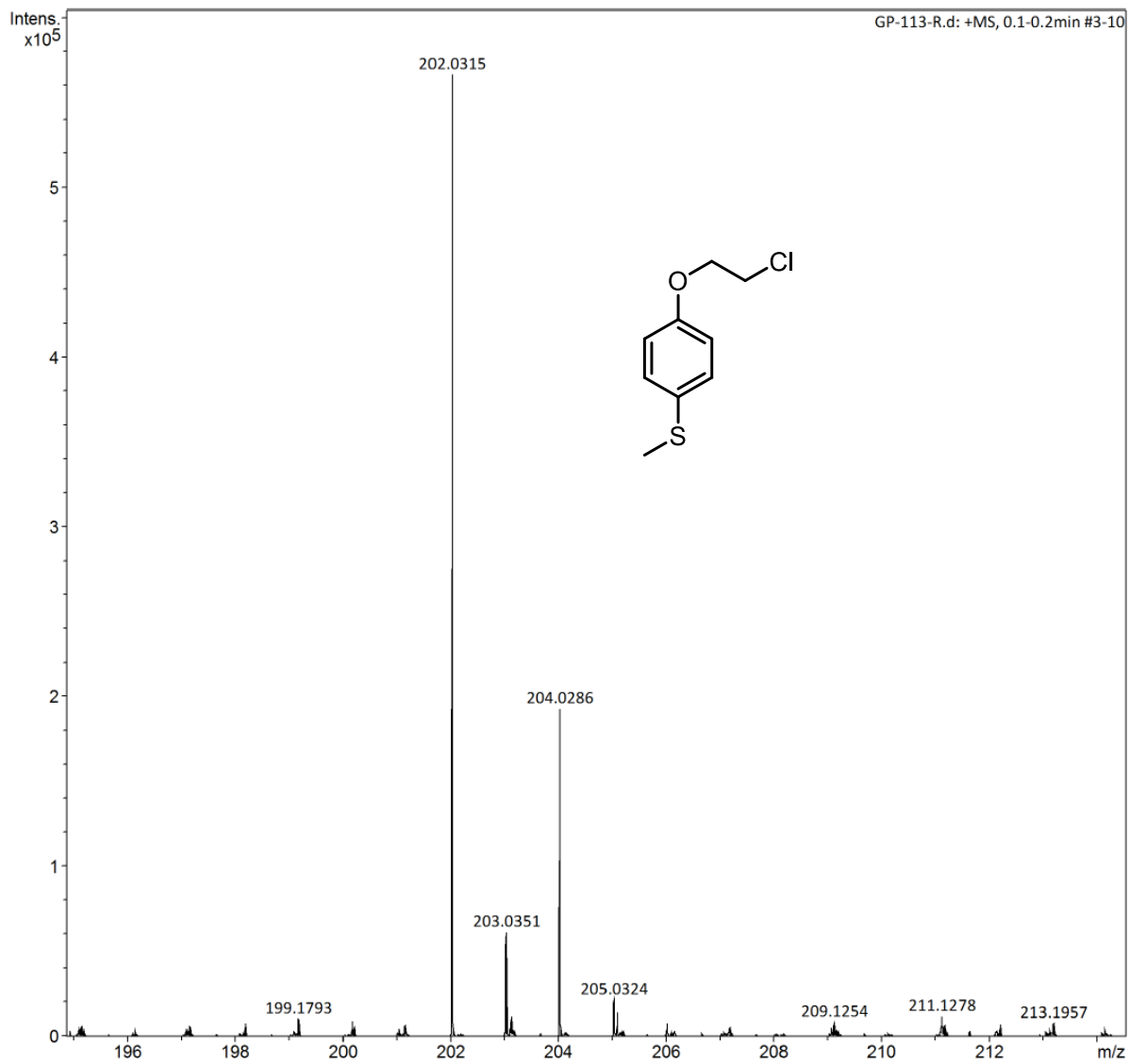


Figure S33. HR-MS of ((4-(2-chloroethoxy)phenyl)(methyl)sulfane

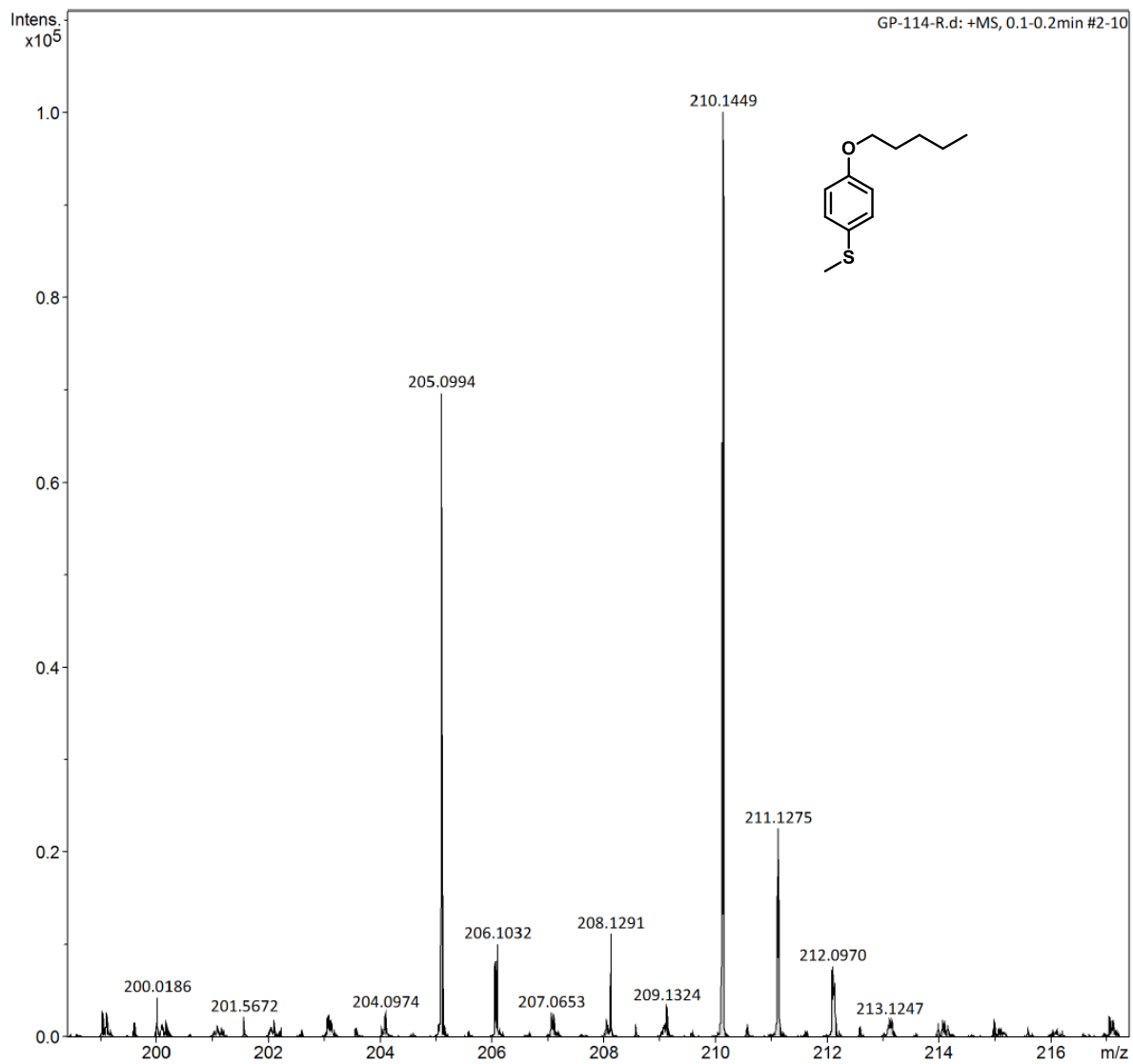


Figure S34. HR-MS of methyl(4-(pentyloxy)phenyl)sulfane

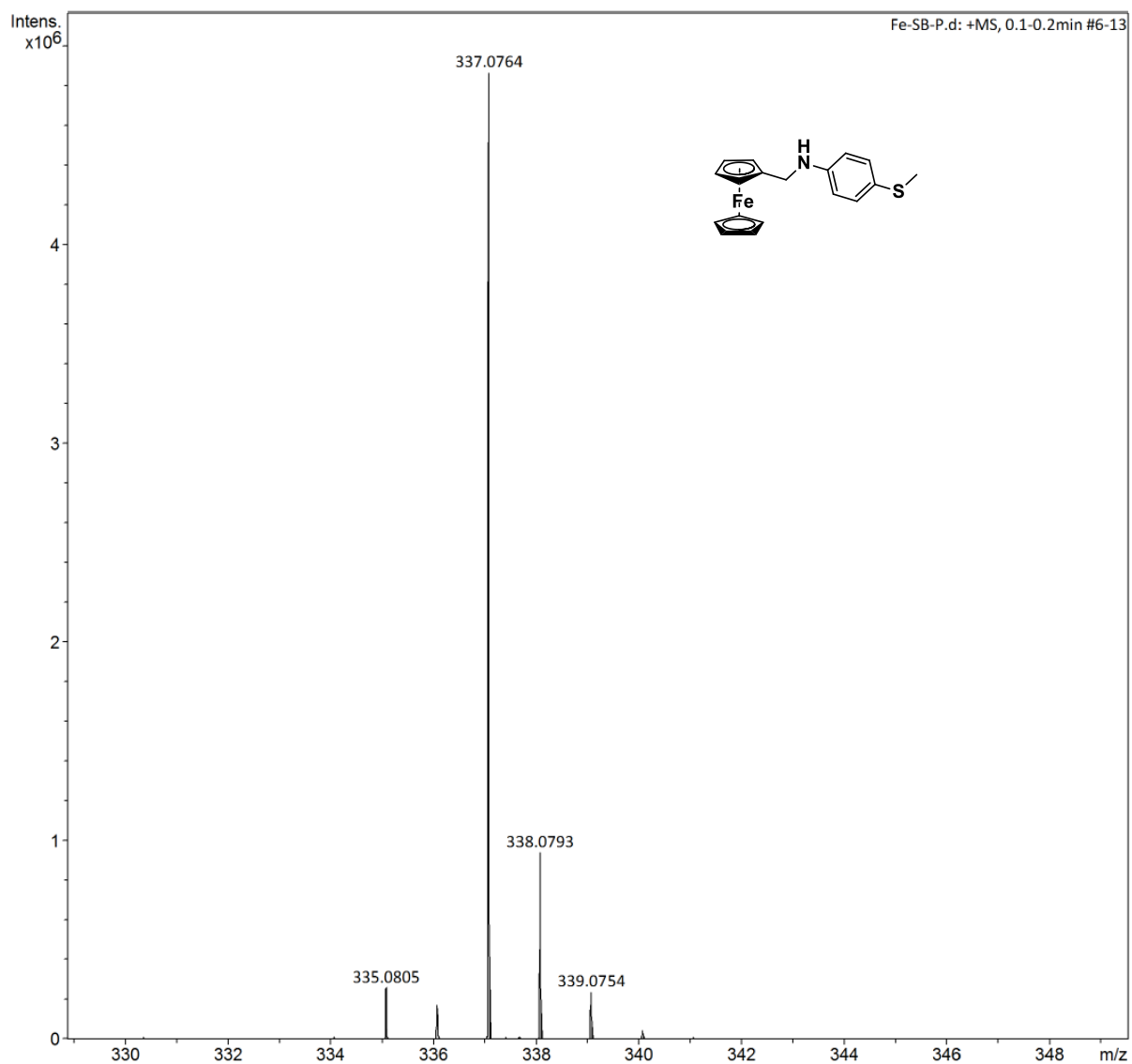


Figure S35. HR-MS of ferrocene-4-(methylthio)aniline

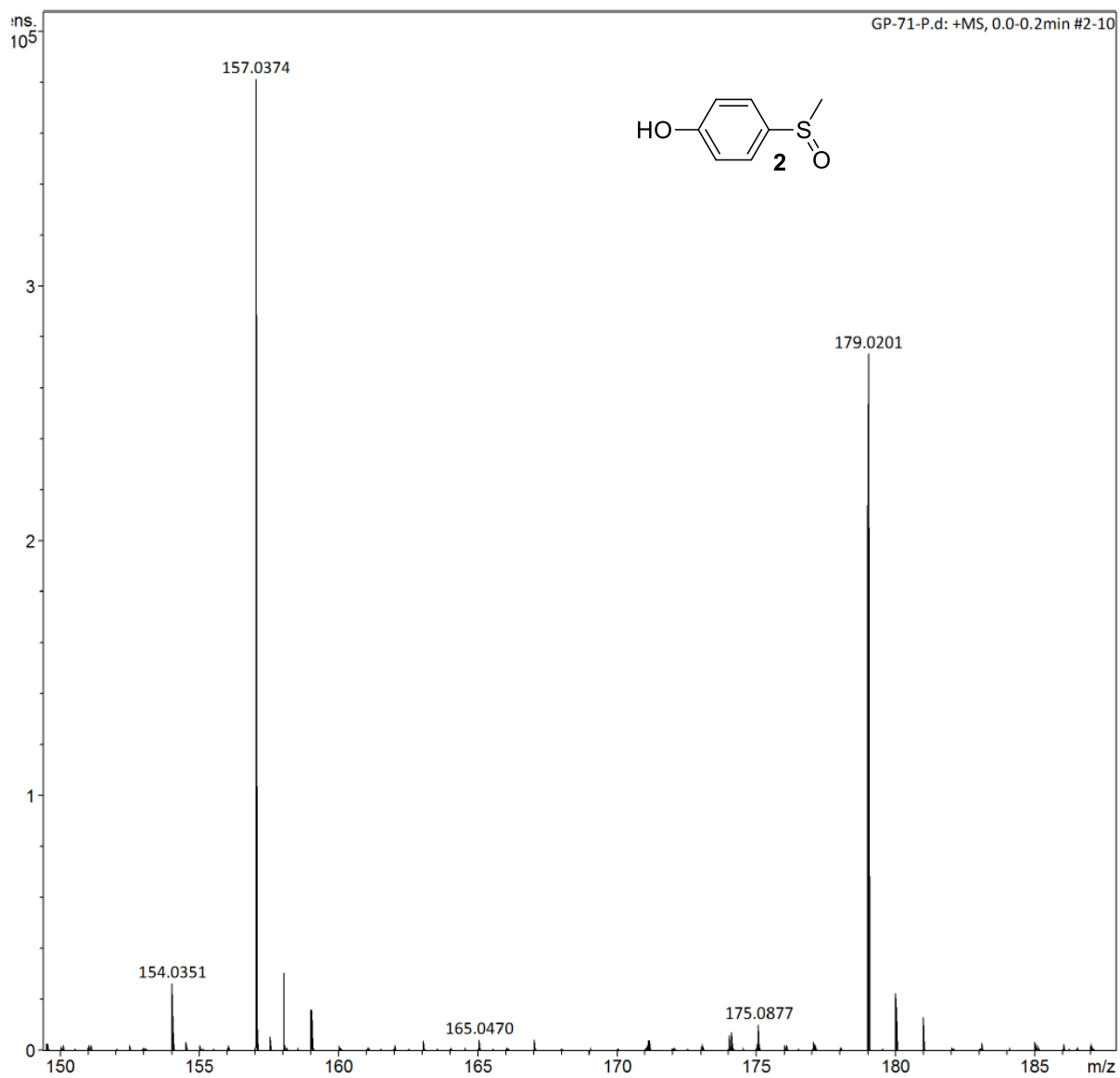


Figure S36. HR-MS of 4-(methylsulfinyl)phenol

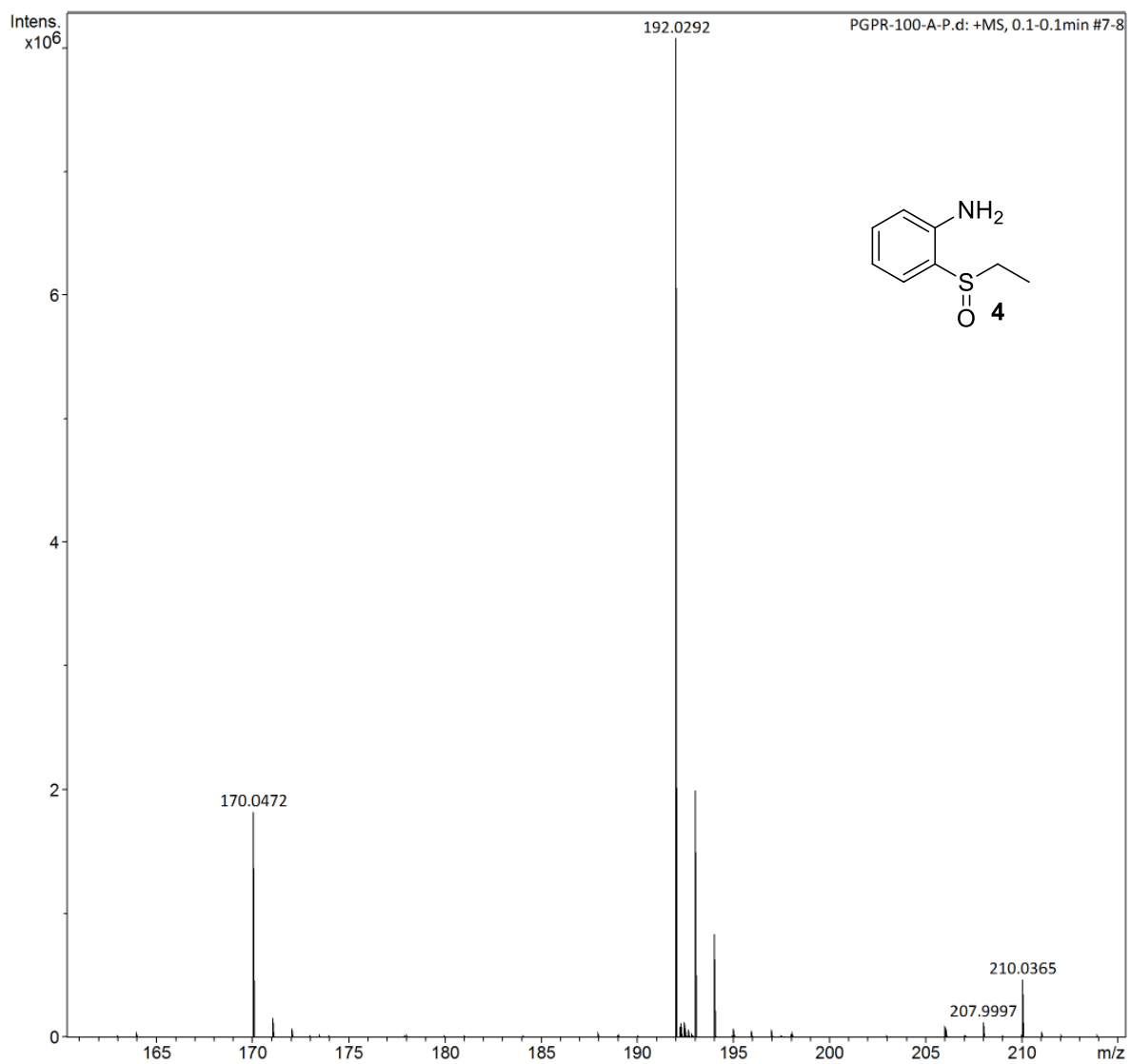


Figure S37. HR-MS of 2-(ethylsulfinyl)aniline

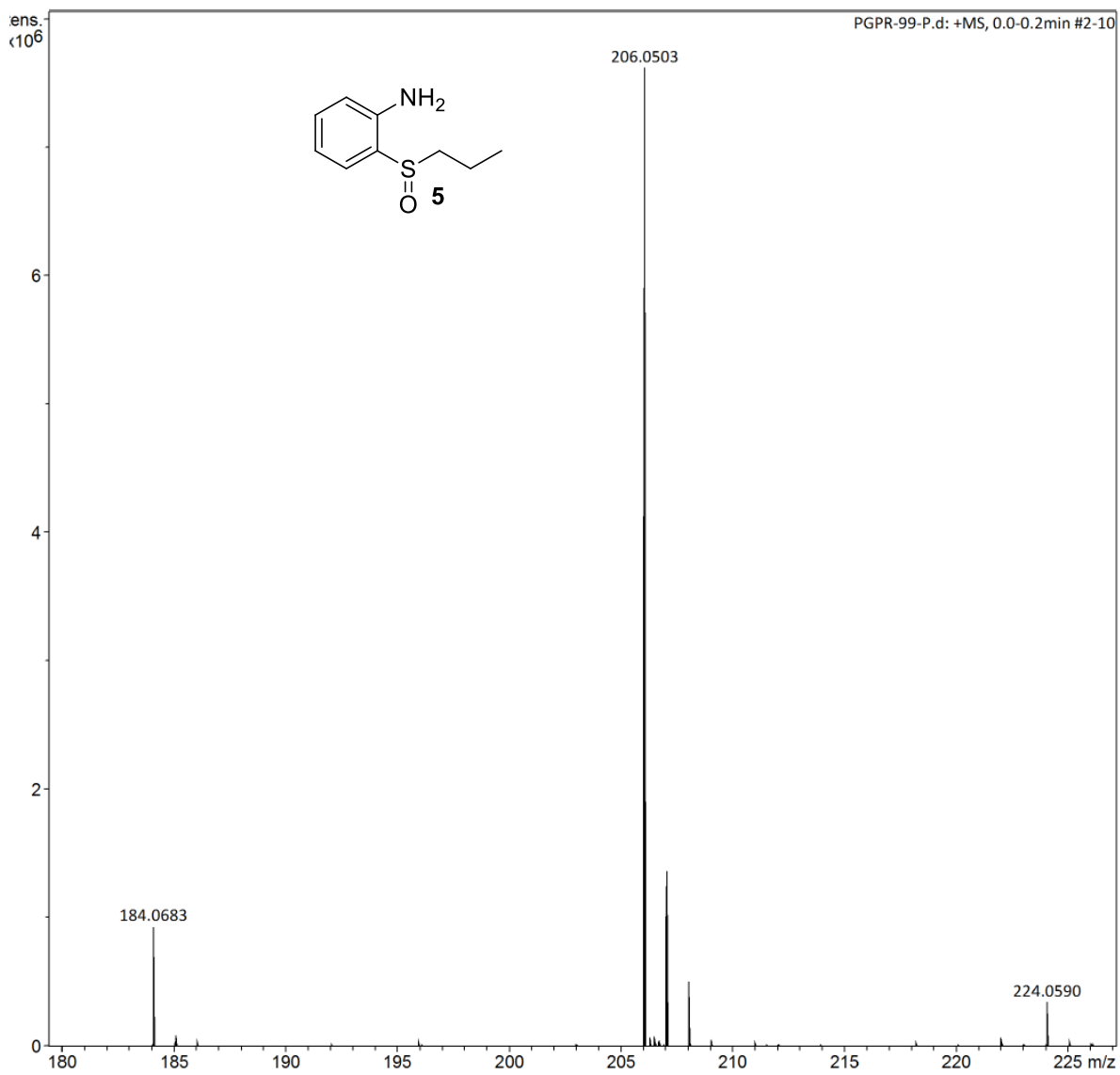


Figure S38. HR-MS of 2-(propylsulfinyl)aniline

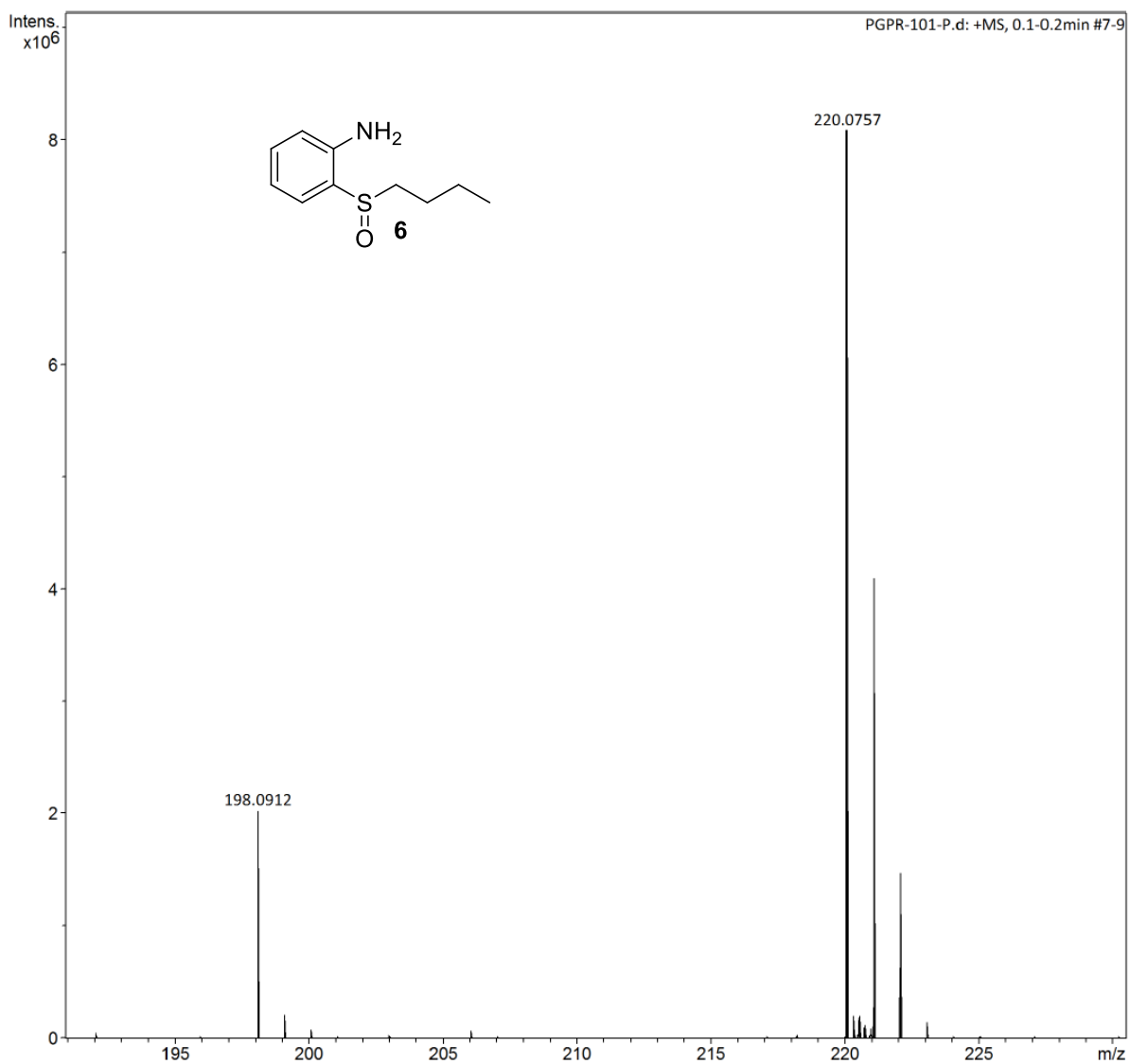


Figure S39. HR-MS of 2-(butylsulfinyl)aniline

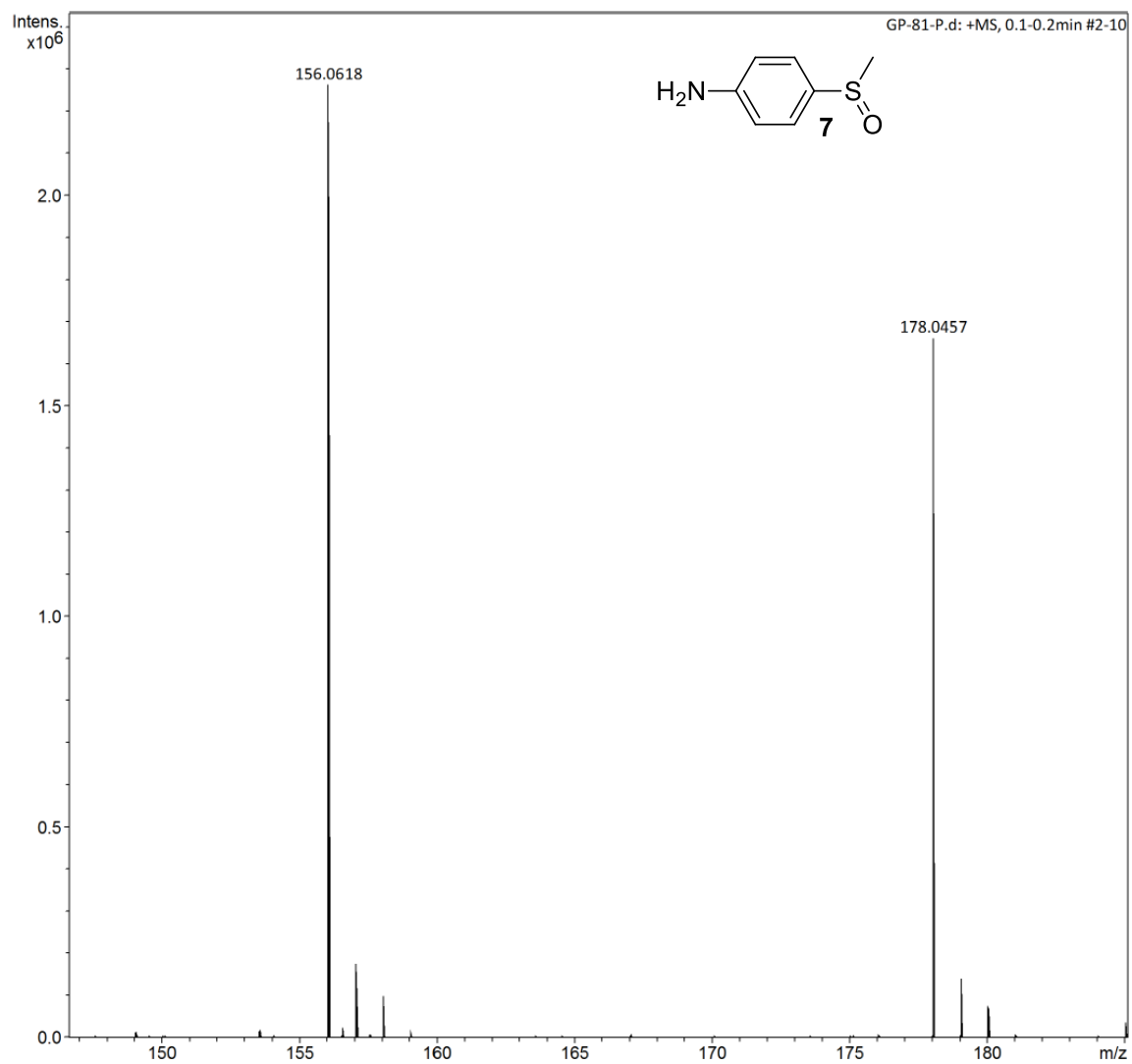


Figure S40. HR-MS of 4-(methylsulfinyl)aniline

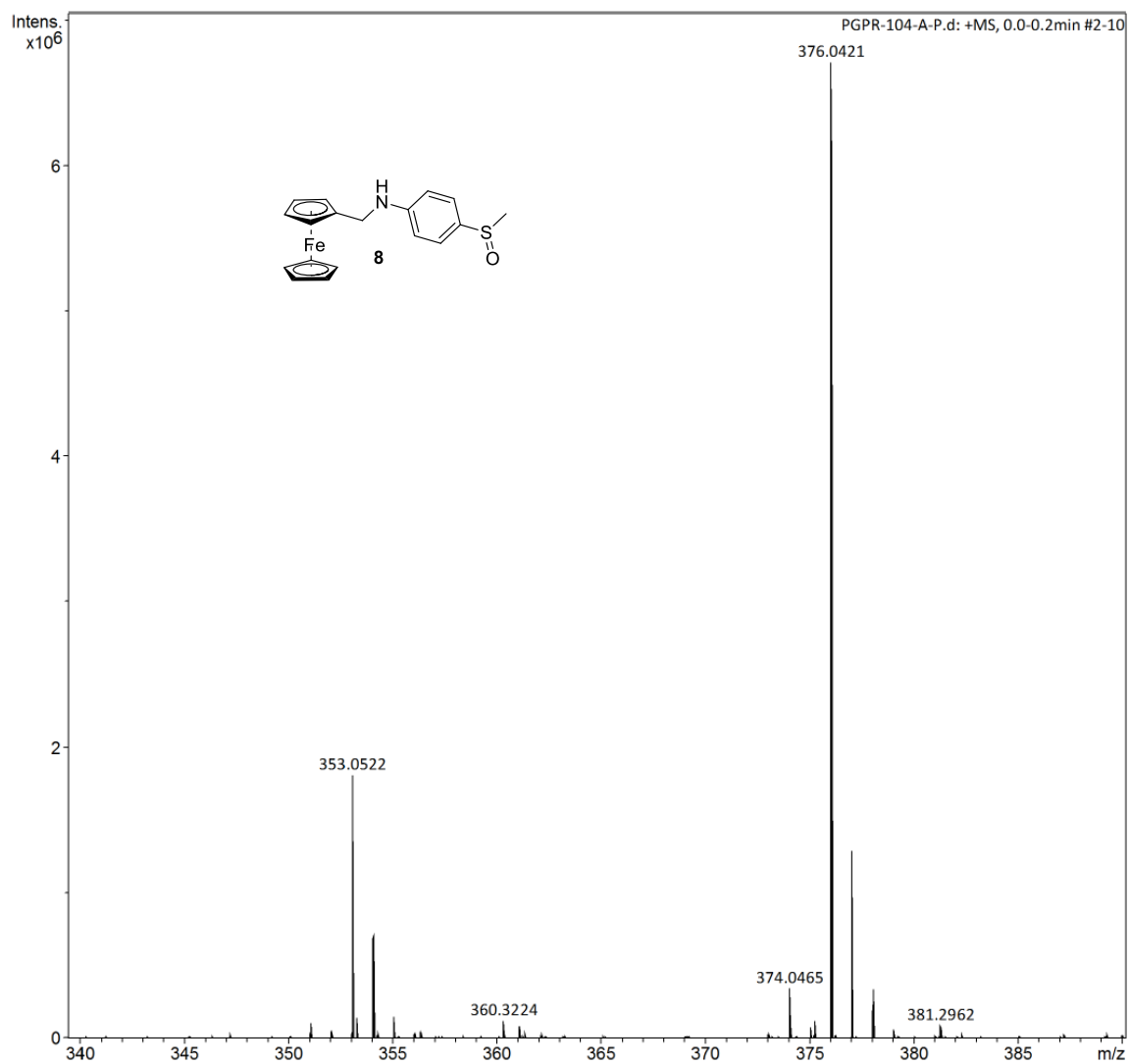


Figure S41. HR-MS of ferrocene-4-(methylsulfinyl)aniline

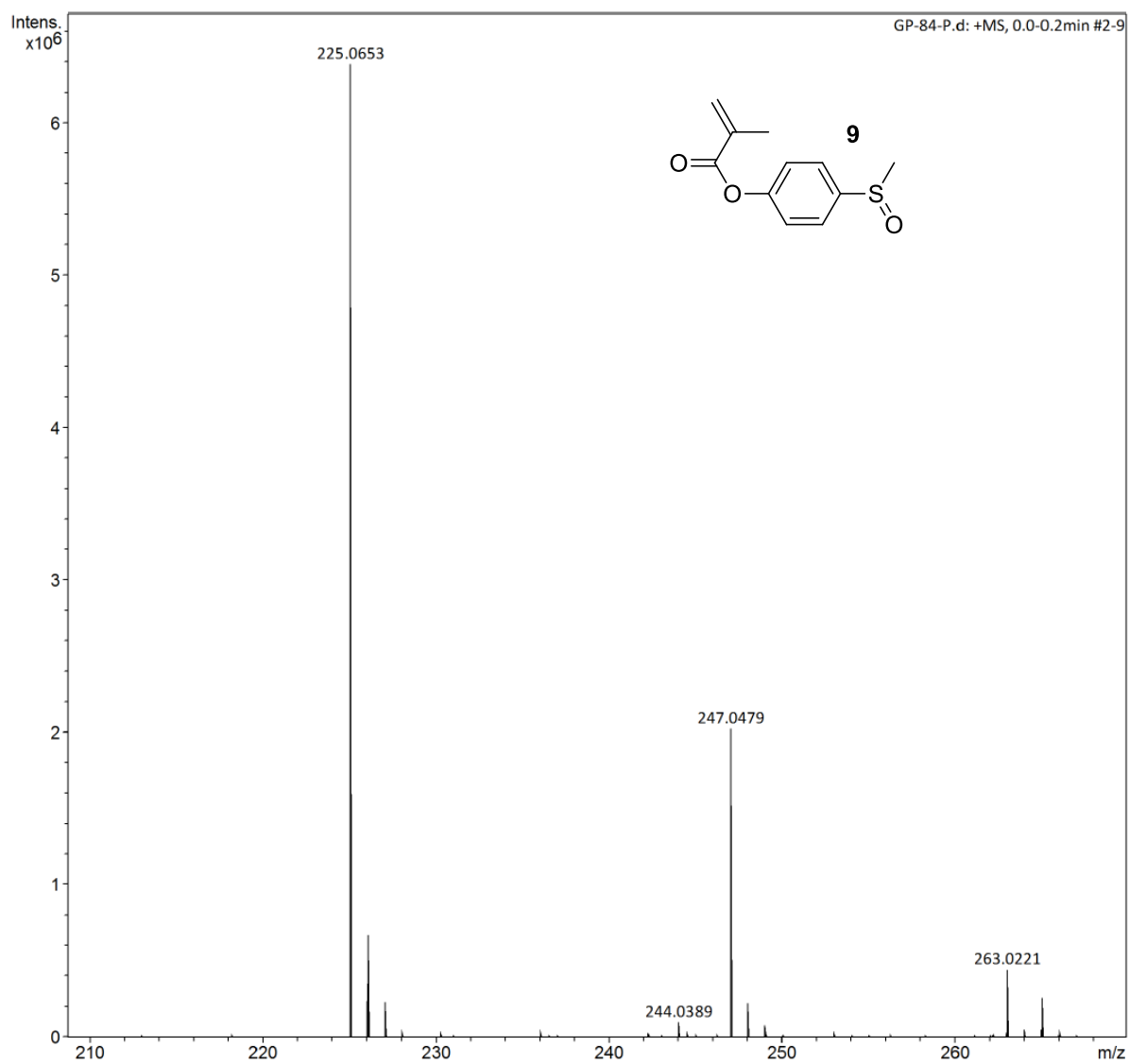


Figure S42. HR-MS of 4-(methylsulfinyl)phenyl methacrylate

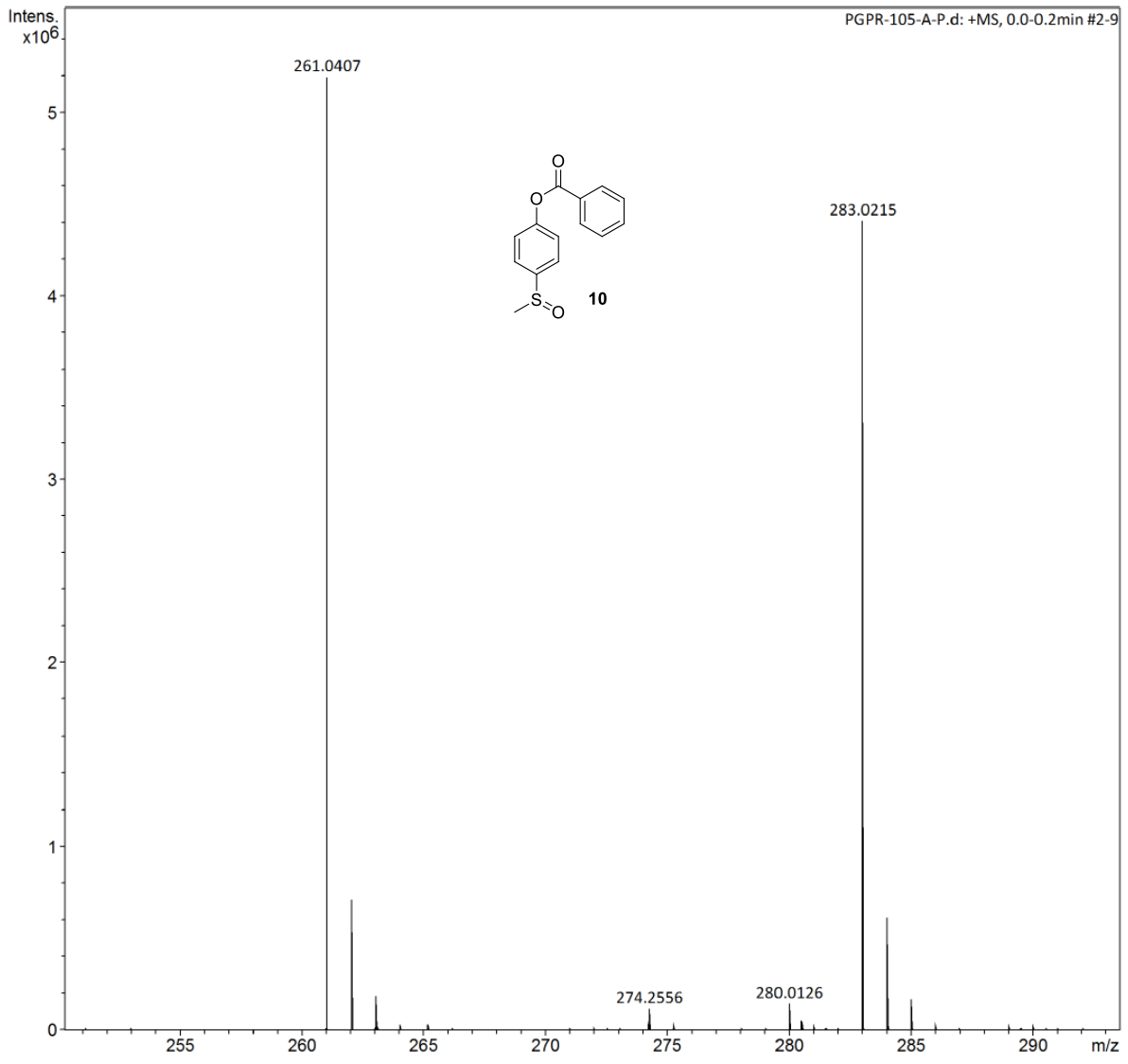


Figure S43. HR-MS of 4-(methylsulfinyl)phenyl benzoate

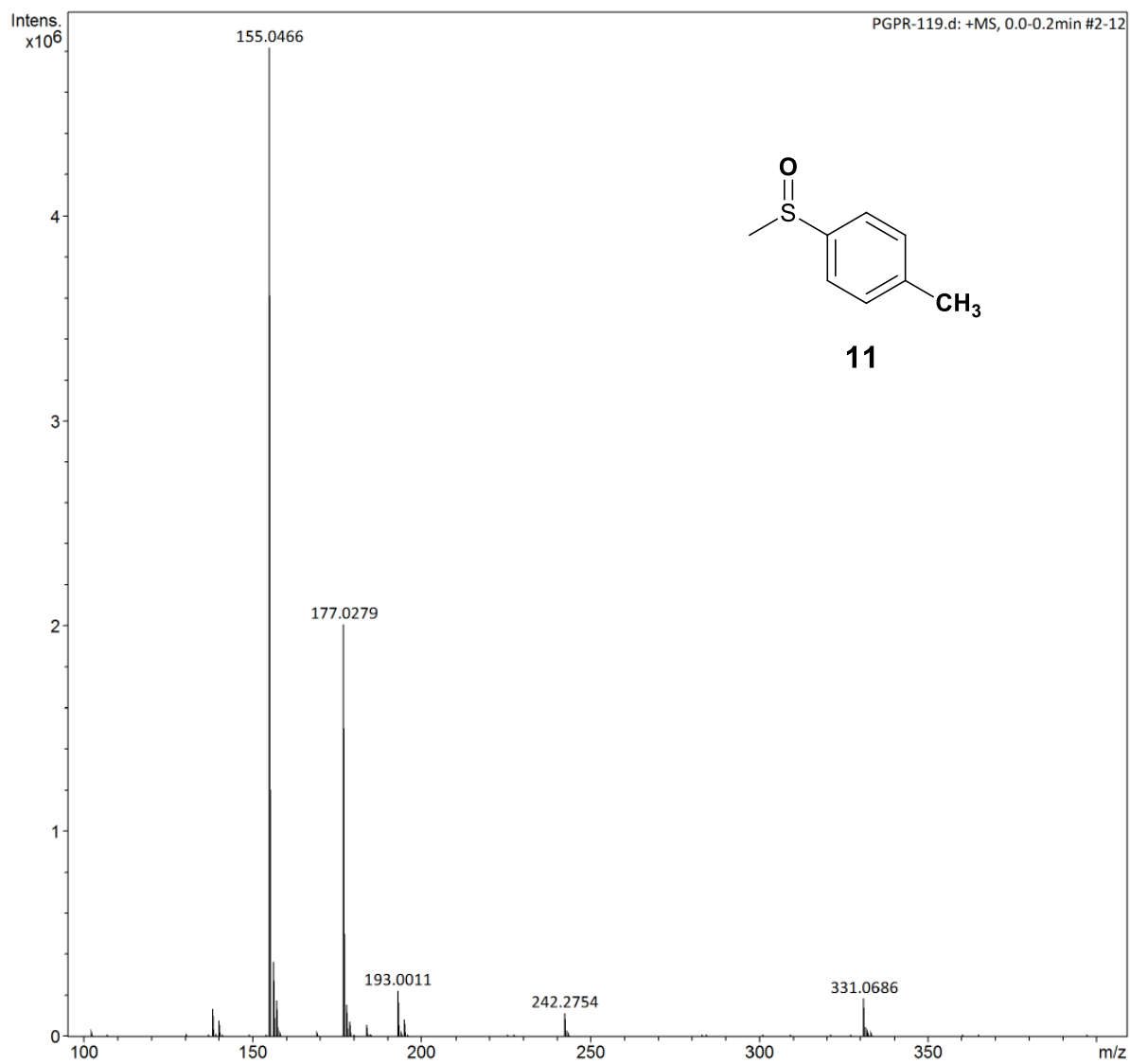


Figure S44. HR-MS of 1-methyl-4-(methylsulfinyl)benzene

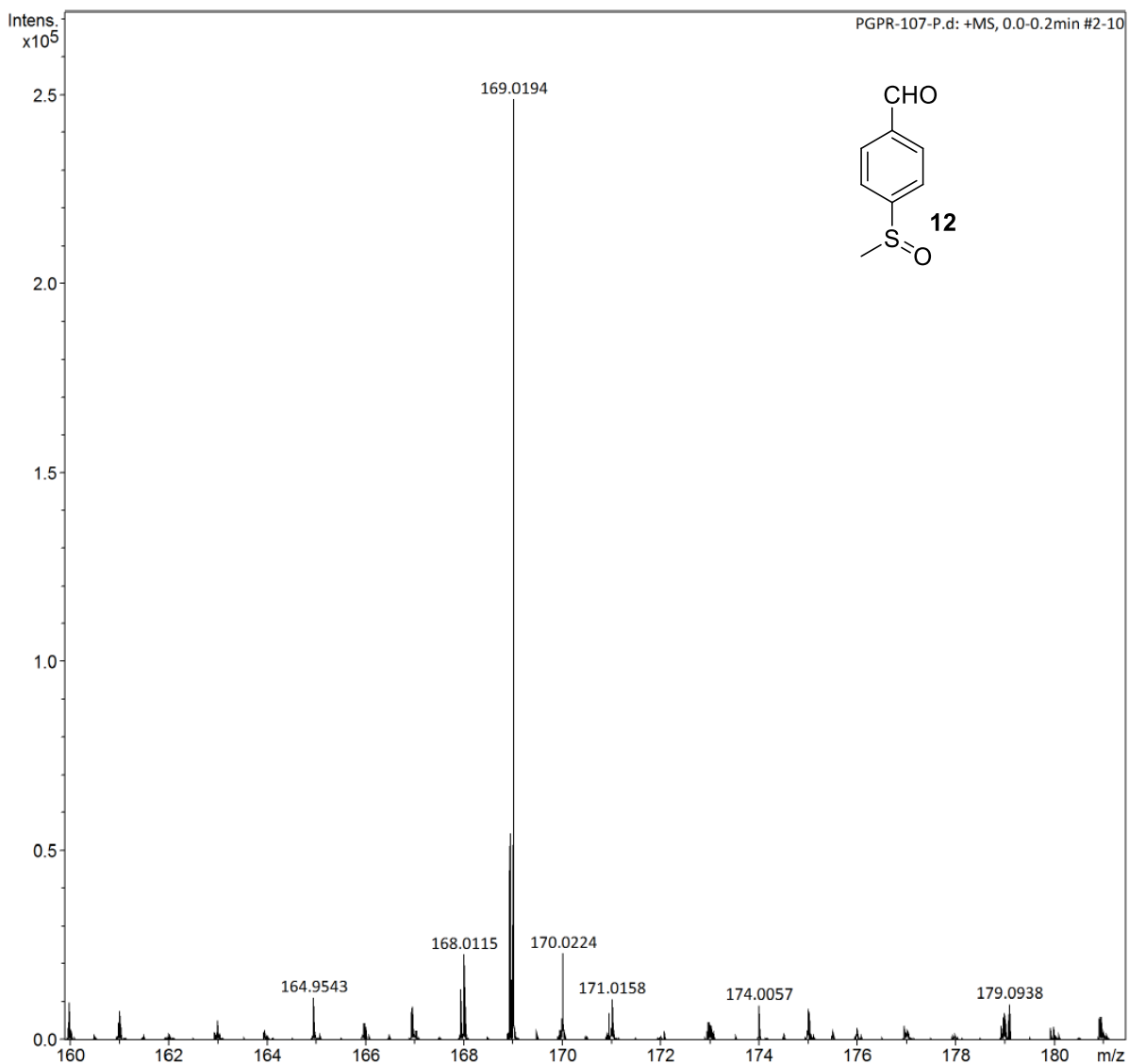


Figure S45. HR-MS of 4-(methylsulfinyl)benzaldehyde

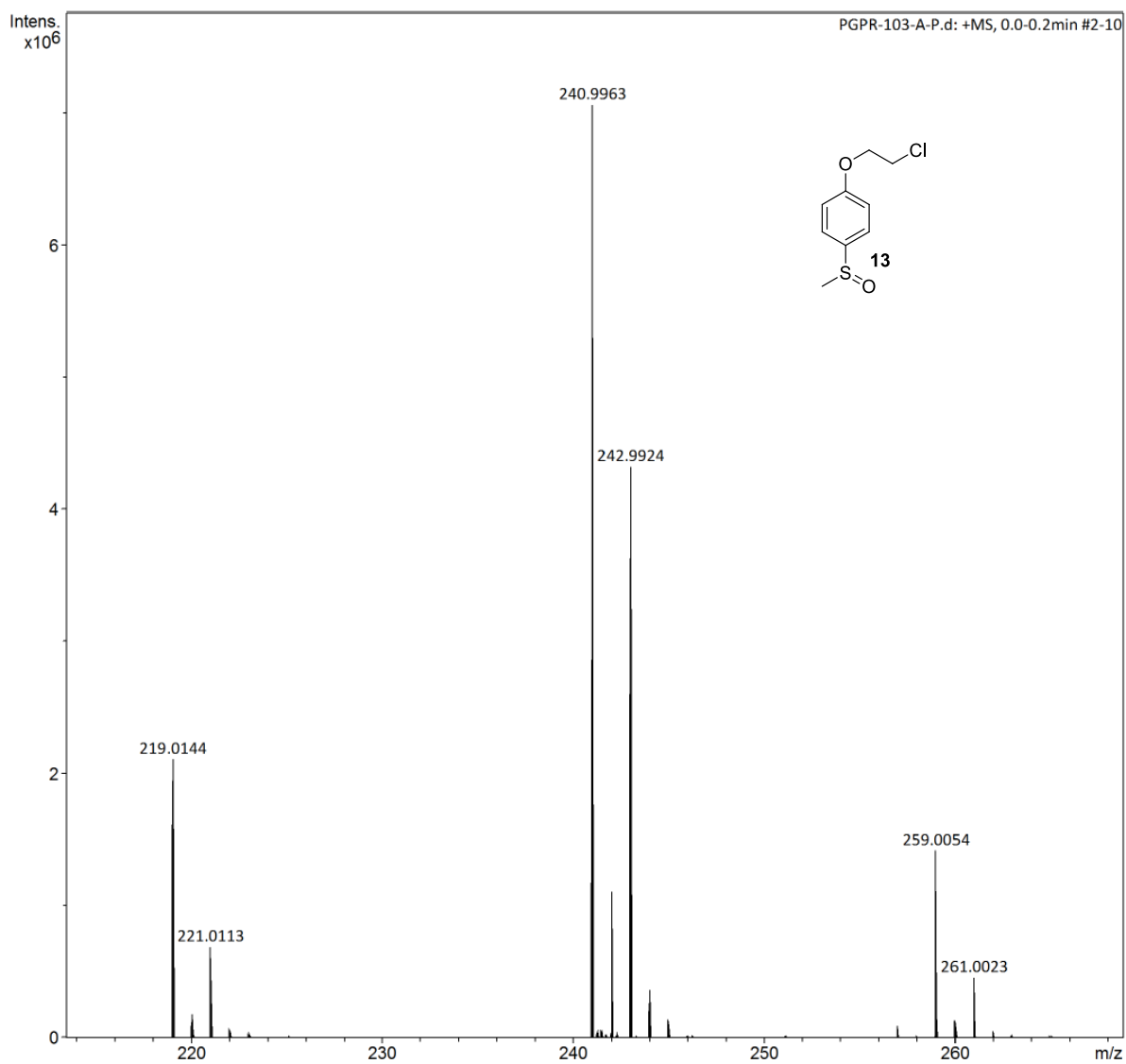


Figure S46. HR-MS of 1-(2-chloroethoxy)-4-(methylsulfinyl)benzene

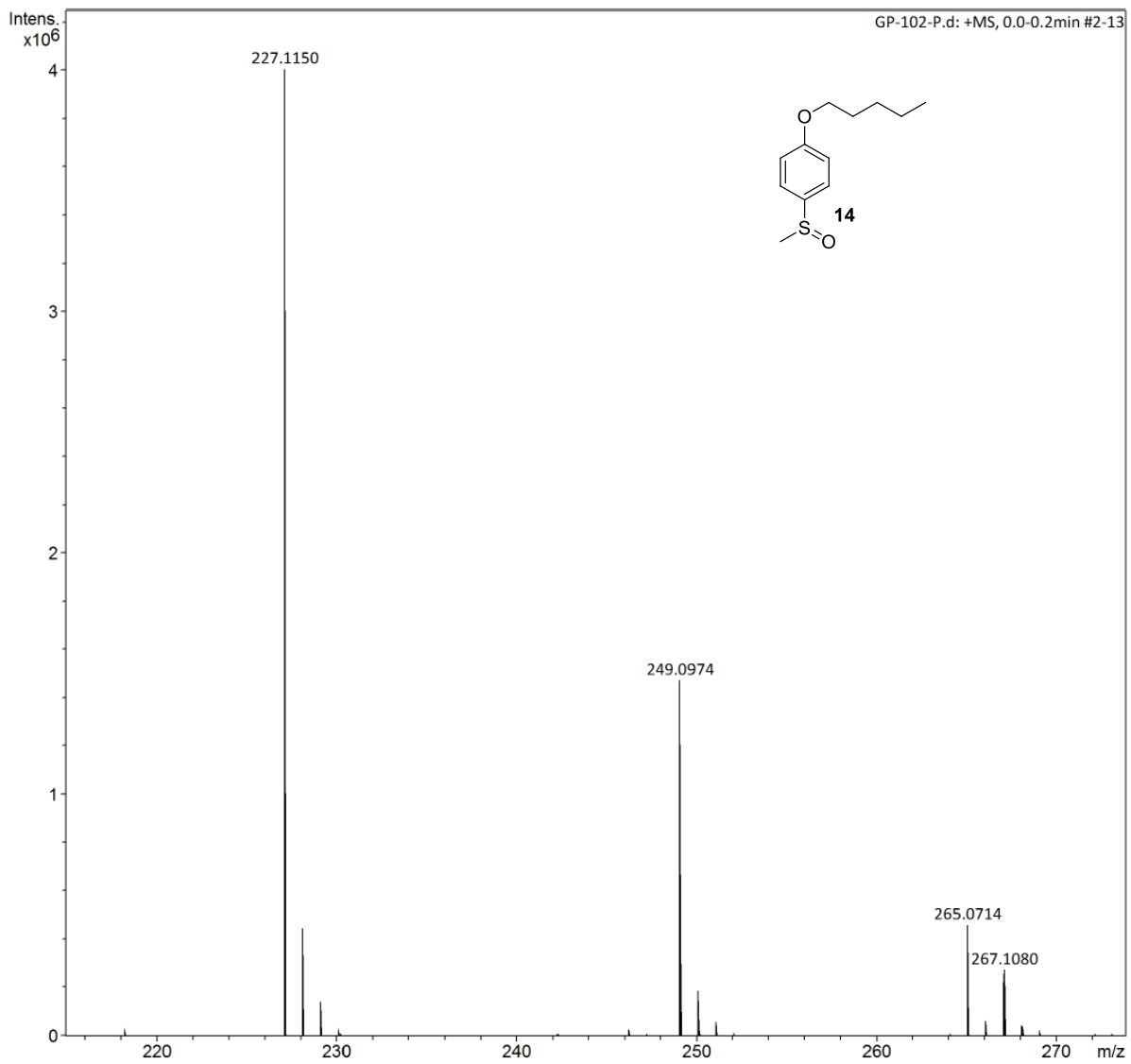


Figure S47. HR-MS of 1-(methylsulfinyl)-4-(pentyloxy)benzene

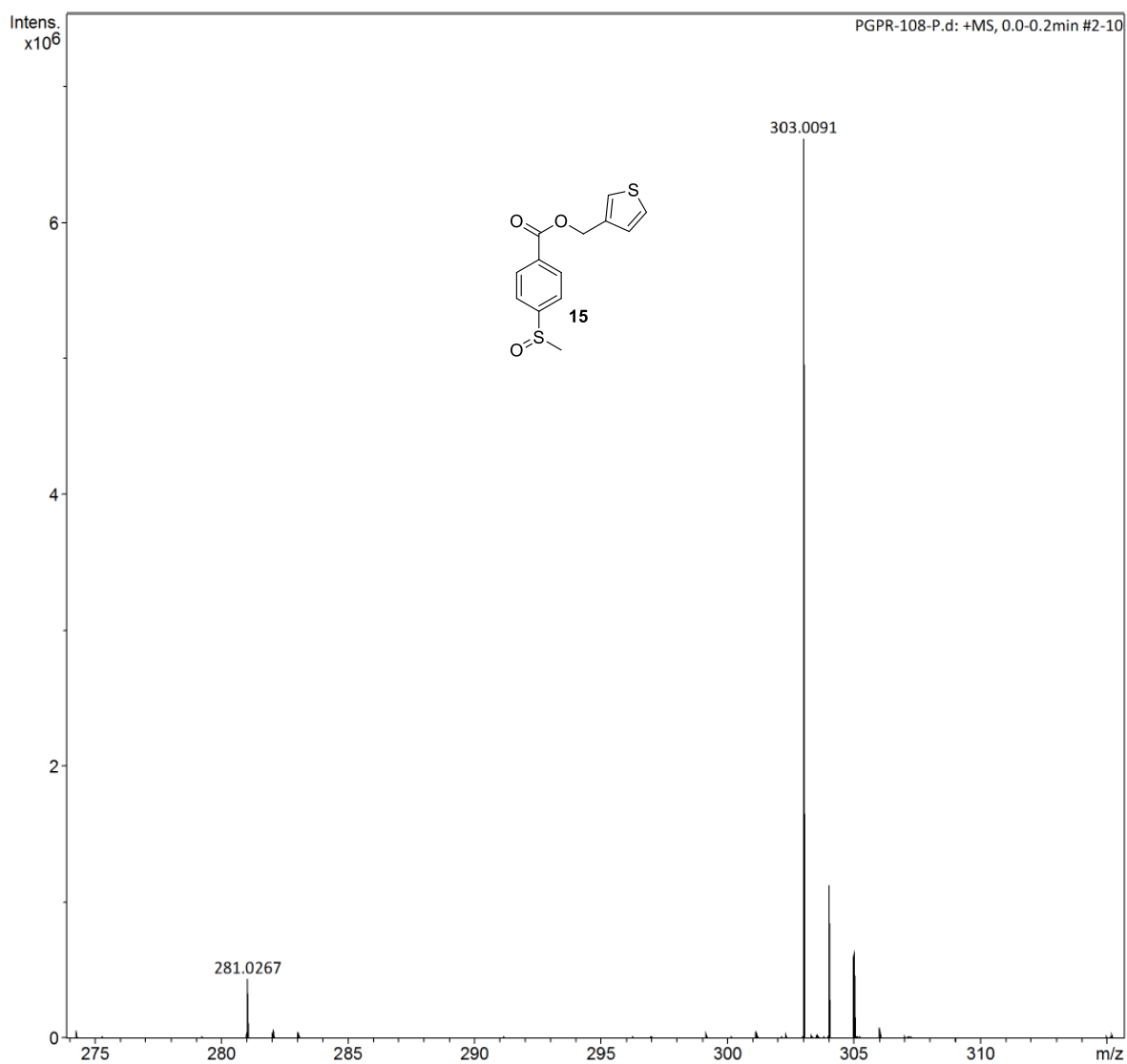


Figure S48. HR-MS of thiophen-3-ylmethyl 4-(methylsulfinyl)benzoate

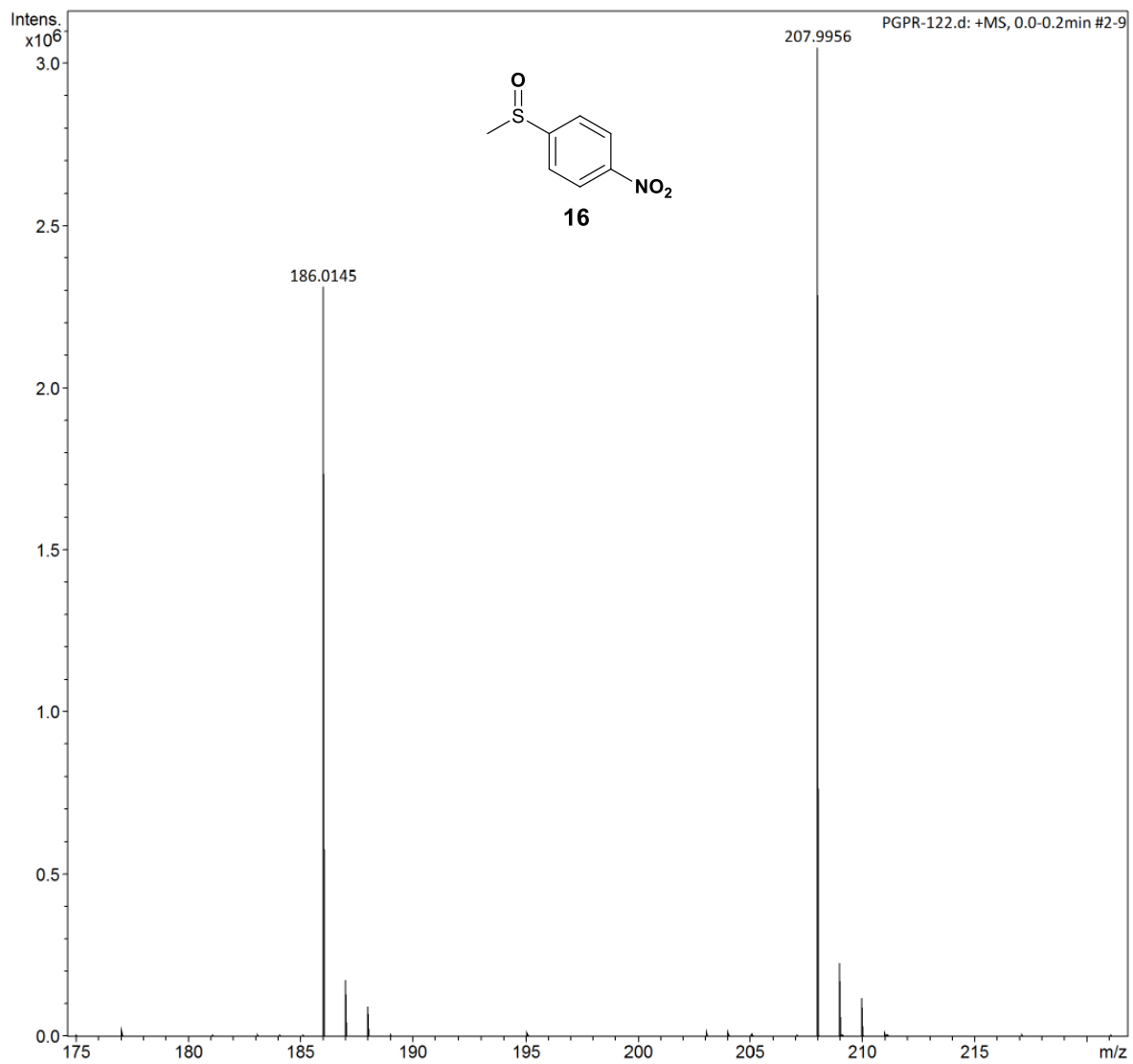


Figure S49. HR-MS of 1-(methylsulfinyl)-4-nitrobenzene

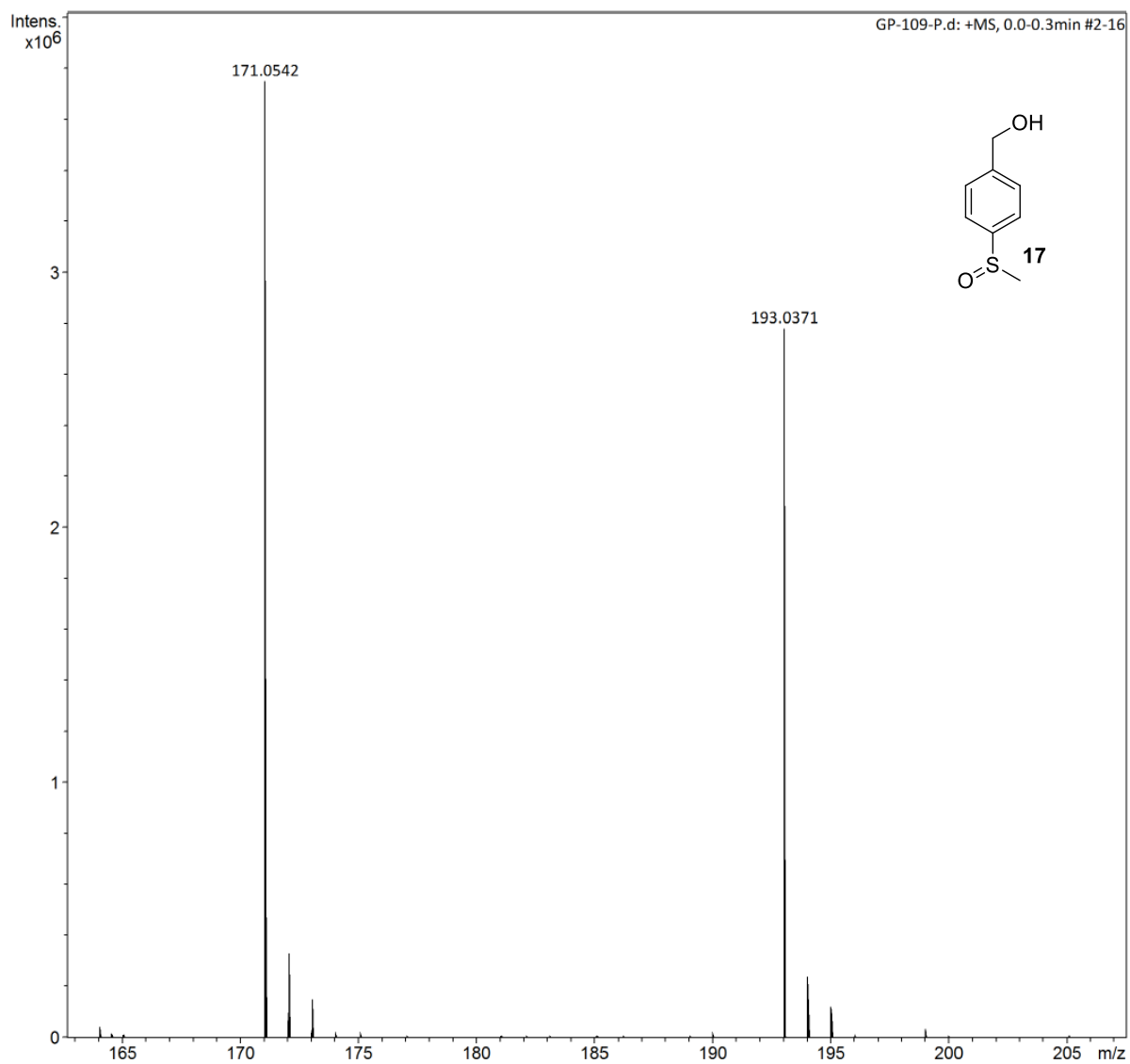


Figure S50. HR-MS of (4-(methanesulfinyl)phenyl)methanol

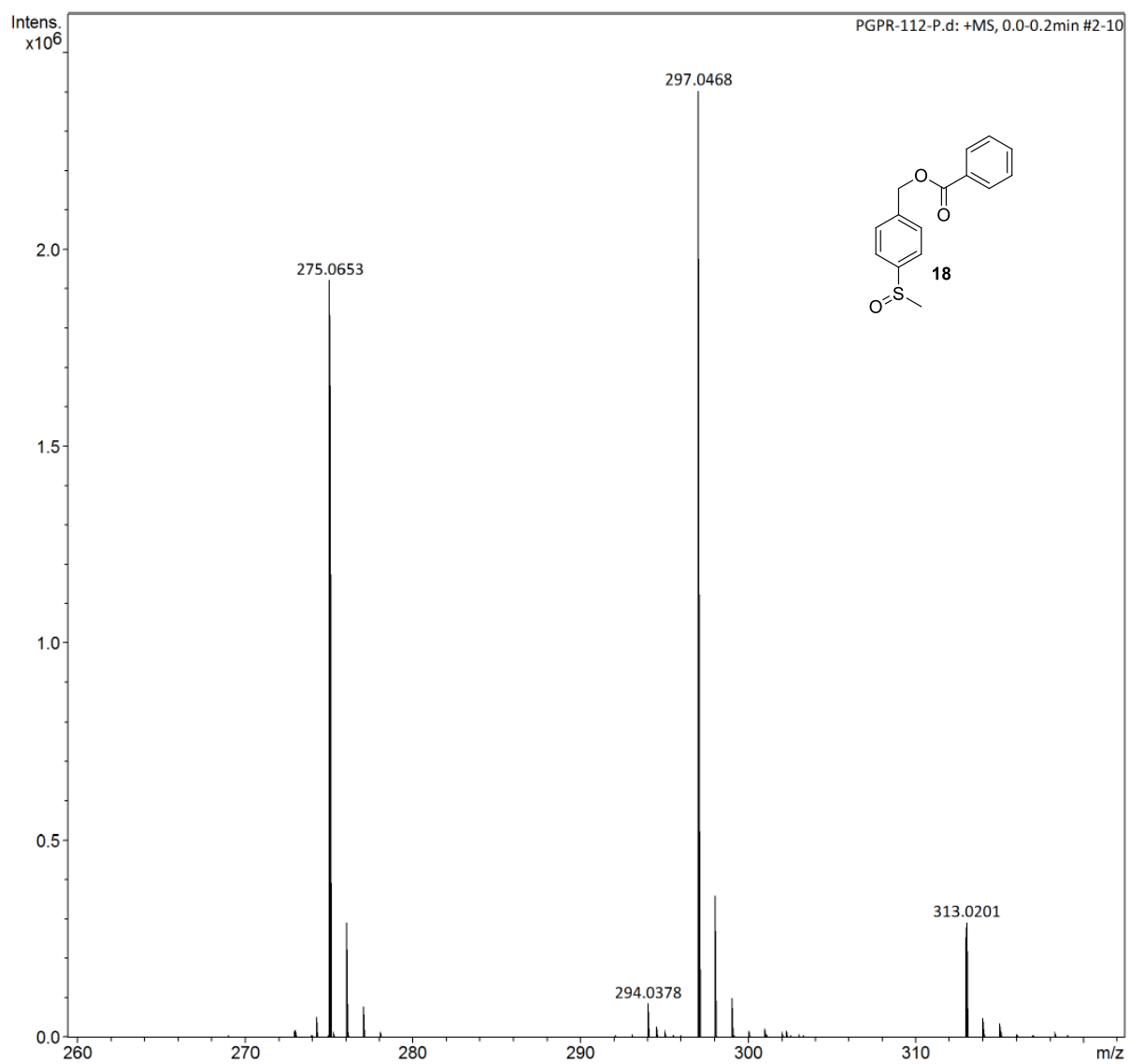


Figure S51. HR-MS of (4-(methanesulfinyl)benzyl) benzoate

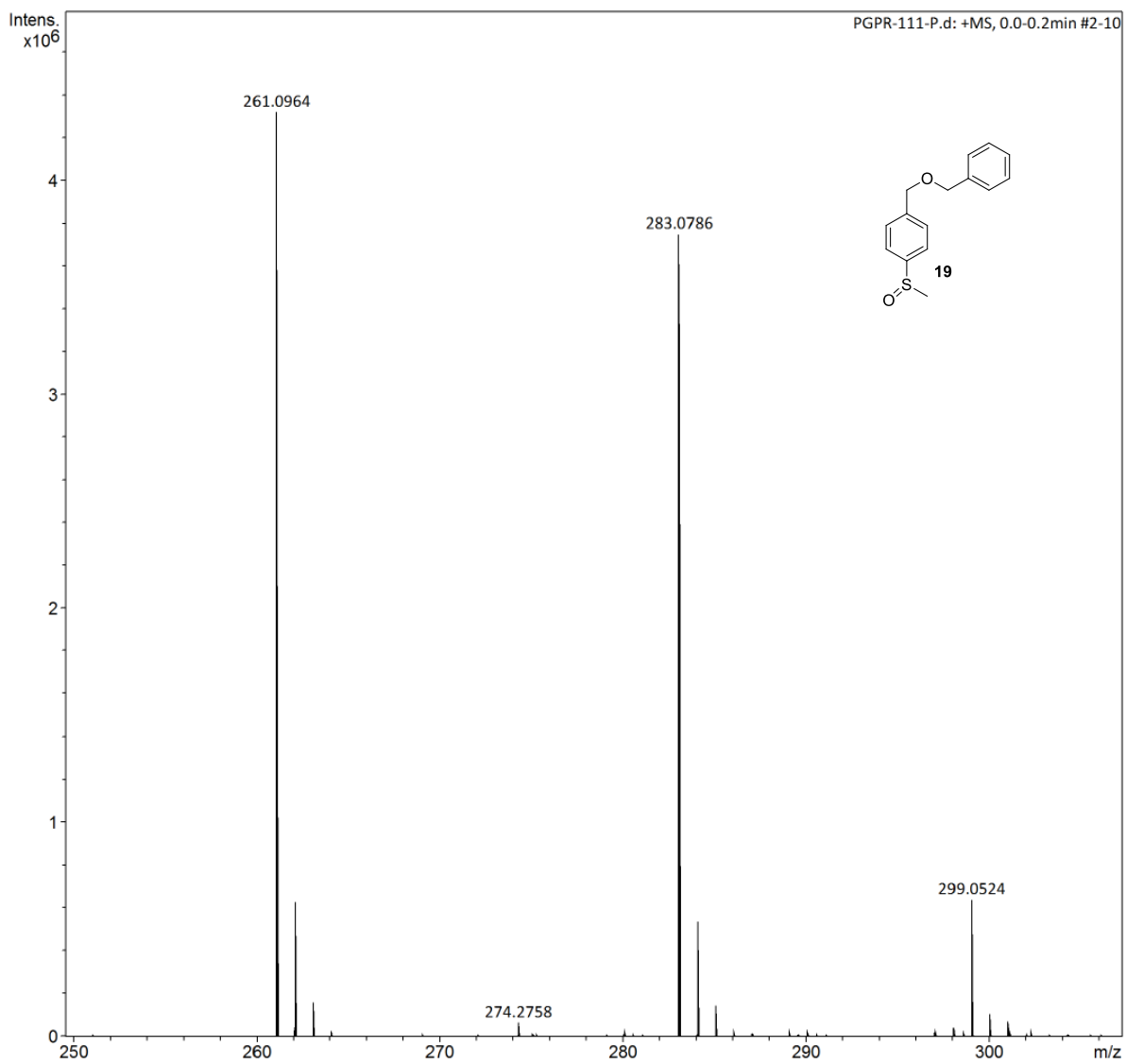


Figure S52. HR-MS of 1-((benzyloxy)methyl)-4-(methylsulfinyl)benzene