Electronic Supplementary Information

Facile Synthesis of Sulfinate Esters from Aryl Iodides via Direct Oxidation of Thioesters

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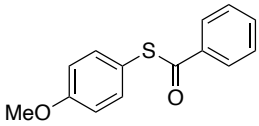
General Information

All reactions were performed with dry glassware under atmosphere of argon, unless otherwise noted. Analytical thin-layer chromatography (TLC) was performed on precoated (0.25 mm) silica-gel plates (Merck Chemicals, Silica Gel 60 F254, Cat. No. 1.05715) or NH TLC plates (Fuji Silysia Chemical Ltd., Chromatorex, NH-TLC plate). Column chromatography was conducted using silica-gel (Kanto Chemical Co., Inc., Silica Gel 60N, spherical neutral, particle size 40–50 μm, Cat. No. 37562-85 or particle size 63–210 μm, Cat. No. 37565-85) or amino silica-gel (Kanto Chemical Co., Inc., Silica Gel 60 NH_2, spherical, particle size 40–50 μm, Cat. No. 37568-08). Preparative TLC (PTLC) was performed on silica gel (Wako Pure Chemical Industries Ltd., Wakogel B-5F, Cat. No. 230-00043). Melting points (Mp) were measured on an OptiMelt MPA100 (Stanford Research Systems), and are uncorrected. ^{1}H NMR spectra were obtained with a Bruker AVANCE 400 spectrometer at 400 MHz. ^{13}C NMR spectra were obtained with a Bruker AVANCE 400 spectrometer at 101 MHz. ^{19}F NMR spectra were obtained with a Bruker AVANCE 400 spectrometer at 376 MHz. All NMR measurements were carried out at 25 ºC. $CDCl_3$ (Kanto Chemical Co. Inc., Cat. No. 07663-23) was used as a solvent for obtaining NMR spectra. Chemical shifts (δ) are given in parts per million (ppm) downfield from the solvent peak (δ 7.26 for ^{1}H NMR in $CDCl_3$, δ 77.0 for ^{13}C NMR in $CDCl_3$) as an internal reference or α,α,α-trifluorotoluene (δ –63.0 ppm for ^{19}F NMR in $CDCl_3$) as an external standard with coupling constants (*J*) in hertz (Hz). The abbreviations s, d, t, q, and m signify singlet, doublet, triplet, quartet, and multiplet, respectively. High-resolution mass spectra (HRMS) were measured on a JEOL JMS-T100CS "AccuTOF CS" mass spectrometer under positive electrospray ionization (ESI^+) conditions.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. 6-Bromo-5-iodobenzo[*d*][1,3]dioxole (**5m**) was prepared according to the reported methods.[S1]

Structures of Benzothioates 4, Aryl Iodides 5, and Alkyl Iodide 11



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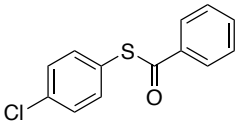

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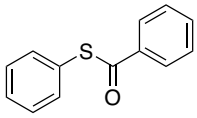

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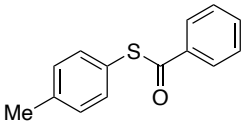

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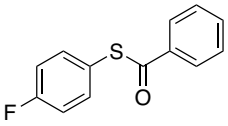

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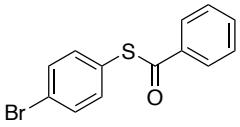

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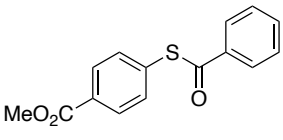

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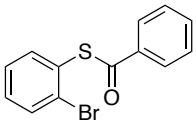

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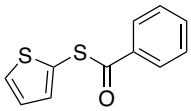

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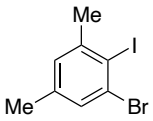

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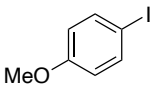

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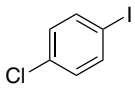

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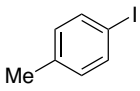

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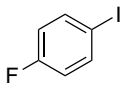

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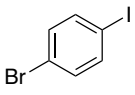

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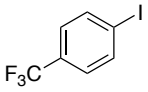

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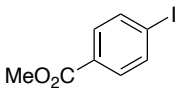

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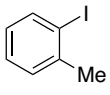

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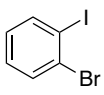

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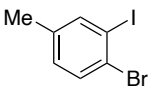

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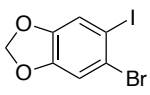

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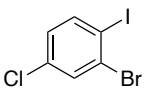

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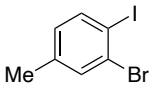

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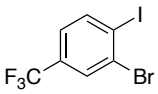

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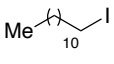

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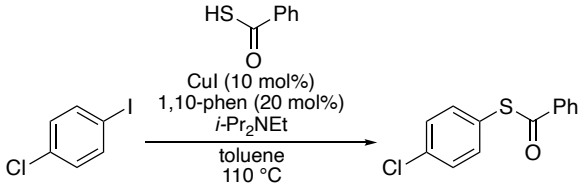
Experimental Procedures

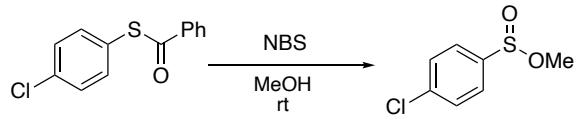
A typical procedure for the synthesis of S-Aryl benzothioates



To a mixture of 4-chlorophenyl iodide (**5c**) (1.19 g, 5.00 mmol, 1.0 equiv), 1,10-phenanthroline (1,10-phen) (181 mg, 1.00 mmol, 20 mol %), and CuI (95.8 mg, 0.531 mmol, 10 mol %) in toluene (10 mL) were added thiobenzoic acid (706 μL, 6.00 mmol, 1.2 equiv) and *N,N*-diisopropylethylamine (1.74 mL, 10.0 mmol, 2.0 equiv) at room temperature. After stirring for 19 h at 110 ℃ (oil bath), the mixture was cooled to room temperature and quenched with water (20 mL). The mixture was extracted with EtOAc (15 mL × 3). The combined organic extract was washed with brine (20 mL) and dried (Na_2SO_4). After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (*n*-hexane/EtOAc = 15/1) to give *S*-(4-chlorophenyl) benzothioate (**4c**) (1.17 g, 4.71 mmol, 94%) as a colorless solid.

According to the procedure for preparing *S*-(4-chlorophenyl) benzothioate (**4c**), *S*-(4-methoxyphenyl) benzothioate (**4b**) (556 mg, 45%; reaction time: 6 h), *S*-phenyl benzothioate (**4d**) (1.02 g, 88%), *S*-(4-tolyl) benzothioate (**4e**) (1.03 g, 90%), *S*-(4-fluorophenyl) benzothioate (**4f**) (1.10 g, 95%), *S*-(4-bromophenyl) benzothioate (**4g**) (1.20 g, 82%), methyl 4-(benzoylthiol) benzoate (**4i**) (1.05 g, 77%), *S*-(2-bromophenyl) benzothioate (**4k)** (1.47 g, 86%), *S*-(2-thienyl) benzothioate (**4n**) (971 mg, 88%) were prepared from the corresponding aryl iodides.

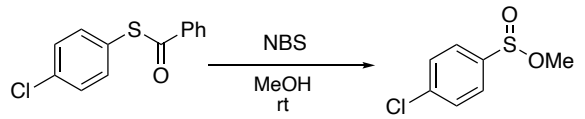
A typical procedure for the synthesis of sulfinate esters from thioesters



To a mixture of *S*-(4-chlorophenyl) benzothioate (**4c**) (125 mg, 0.501 mmol, 1.0 equiv) and MeOH (2.5 mL) in 5 mL screw-top V-vial® (Sigma-Aldrich, Cat. No. Z115118) was added *N*-bromosuccinimide (NBS) (267 mg, 1.50 mmol, 3.0 equiv) at room temperature. After stirring for 1 h at the same temperature, to the mixture were added an aqueous saturated sodium bicarbonate (10 mL) and an aqueous saturated sodium thiosulfate (10 mL). The reaction mixture was extracted with dichloromethane (10 mL × 3). The combined organic extract was washed with brine (10 mL) and dried (Na_2SO_4). After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (*n*-hexane/dichloromethane = 1/1) to give methyl 4-chlorobenzenesulfinate (**3c**) (94.9 mg, 0.498 mmol, 99%) as a colorless oil.

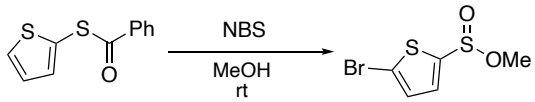
According to the procedure for preparing methyl 4-chlorobenzenesulfinate (**3c**), methyl benzenesulfinate (**3d**) (67.2 mg, 86%), methyl 4-methylbenzenesulfinate (**3e**) (79.5 mg, 93%), methyl 4-fluorobenzenesulfinate (**3f**) (76.8 mg, 88%), methyl 4-bromobenzenesulfinate (**3g**) (116 mg, 99%), methyl 4-(methoxycarbonyl)benzenesulfinate (**3i**) (106 mg, 99%), and methyl 2-bromobenzenesulfinate (**3k**) (108 mg, 90%) were prepared from the corresponding thioesters.

*Gram-scale synthesis of methyl 4-chlorobenzenesulfinate (**3c**)*



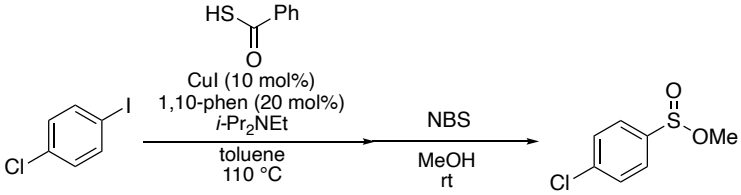
To a mixture of *S*-(4-chlorophenyl) benzothioate (**4c**) (1.49 g, 6.00 mmol, 1.0 equiv) and MeOH (30 mL) was added *N*-bromosuccinimide (3.20 g, 18.0 mmol, 3.0 equiv) at room temperature. After stirring for 1 h at the same temperature, to the mixture were added an aqueous saturated sodium bicarbonate (20 mL) and an aqueous saturated sodium thiosulfate (20 mL) and extracted with dichloromethane (20 mL × 3). The combined organic extract was washed with brine (20 mL) and dried (Na_2SO_4). After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (*n*-hexane/EtOAc = 9/1) to give methyl 4-chlorobenzenesulfinate (**3c**) (1.13 g, 5.92 mmol, 99%) as a colorless oil.

*Synthesis of 5-bromothiophene-2-sulfinate (**3n**)*



To a mixture of *S*-(2-thienyl) benzothioate (**4n**) (110 mg, 0.501 mmol, 1.0 equiv) and MeOH (2.5 mL) in 5 mL screw-top V-vial® (Sigma-Aldrich, Cat. No. Z115118) was added *N*-bromosuccinimide (356 mg, 2.00 mmol, 4.0 equiv) at room temperature. After stirring for 1 h at the same temperature, to the mixture were added an aqueous saturated sodium bicarbonate (10 mL) and an aqueous saturated sodium thiosulfate (10 mL) and extracted with dichloromethane (10 mL × 3). The combined organic extract was washed with brine (10 mL) and dried (Na_2SO_4). After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (*n*-hexane/EtOAc = 15/1) to give methyl 5-bromothiophene-2-sulfinate (**3n**) (72.7 mg, 0.302 mmol, 60%) as a colorless oil.

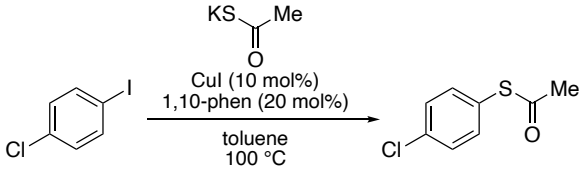
A typical procedure for the synthesis of sulfinate esters from aryl iodides via S-Aryl benzothioate



To a mixture of 4-chlorophenyl iodide (**5c**) (119 mg, 0.500 mmol, 1.0 equiv), 1,10-phenanthroline (18.2 mg, 0.101 mmol, 20 mol %) and CuI (9.6 mg, 50 μmol, 10 mol %) in toluene (1 mL) were added thiobenzoic acid (70.6 μL, 0.600 mmol, 1.2 equiv) and *N,N*-diisopropylethylamine (170 μL, 1.00 mmol, 2.0 equiv) at room temperature. After stirring for 19 h at 110 °C (oil bath), the mixture was cooled to room temperature and quenched with water (20 mL). The mixture was extracted with EtOAc (10 mL × 3). The combined organic extract was washed with brine (20 mL) and dried (Na_2SO_4). After filtration, the filtrate was concentrated under reduced pressure. To the resulting mixture in MeOH (500 μL) was added *N*-bromosuccinimide (267 mg, 1.50 mmol, 3.0 equiv) at room temperature. After stirring for 1 h at the same temperature, to the mixture were added an aqueous saturated sodium bicarbonate (10 mL) and an aqueous saturated sodium thiosulfate (10 mL) and extracted with dichloromethane (10 mL × 3). The combined organic extract was washed with brine (10 mL) and dried (Na_2SO_4). After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (*n*-hexane/EtOAc = 10/1) to give methyl 4-chlorobenzenesulfinate (**3c**) (92.9 mg, 0.487 mmol. 97%) as a colorless oil.

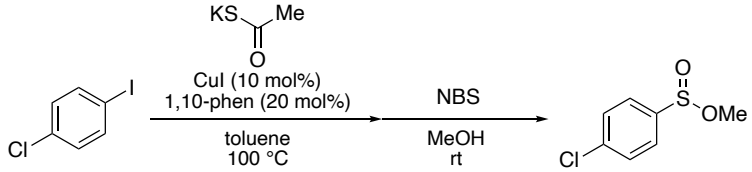
According to the procedure for preparing methyl 4-chlorobenzenesulfinate (**3c**), methyl 2-bromo-4,6-dimethylbenzenesulfinate (**3a**) (50.8 mg, 19%), methyl 4-(trifluoromethyl)benzenesulfinate (**3h**) (94.6 mg, 84%), methyl 4-(methoxycarbonyl)benzenesulfinate (**3i**) (82.9 mg, 77%), methyl 2-methylbenzenesulfinate (**3j**) (67.3 mg, 79%; reaction time for the thioester formation was 7 h), methyl 2-bromo-5-methylbenzenesulfinate (**3l**) (105 mg, 42%), methyl 6-bromobenzo[*d*][1,3]dioxole-5-sulfinate (**3m**) (92.9 mg, 67%; reaction time for the thioester formation was 7 h), methyl 2-bromo-4-chlorobenzenesulfinate (**3o**) (199 mg, 74%), methyl 2-bromo-4-methylbenzenesulfinate (**3p**) (166 mg, 67%), and methyl 2-bromo-4-(trifluoromethyl)benzenesulfinate (**3q**) (81.2 mg, 53%) were prepared from the corresponding aryl iodides.

A typical procedure for the synthesis of S-Aryl ethanethioate



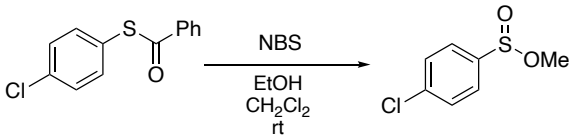
To a mixture of 4-chlorophenyl iodides (**5c**) (1.19 g, 5.01 mmol, 1.0 equiv), potassium thioacetate (857 mg, 7.50 mmol, 1.5 equiv), 1,10-phenanthroline (181 mg, 1.00 mmol, 20 mol %), and CuI (95.2 mg, 0.500 mmol, 10 mol %) was added toluene (40 mL) at room temperature. After stirring for 24 h at 100 °C (oil bath), the mixture was cooled to room temperature and quenched with water (20 mL). The mixture was extracted with EtOAc (15 mL × 3). The combined organic extract was washed with brine (20 mL) and dried (Na_2SO_4). After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (*n*-hexane/EtOAc = 10/1) to give *S*-(4-chlorophenyl) ethanethioate (**8**) (906 mg, 4.86 mmol, 97%) as a pale red solid.

One-pot synthesis of S-(4-chlorophenyl) thioacetate



To a mixture of 4-chlorophenyl iodides (**5c**) (119 mg, 0.499 mmol, 1.0 equiv), potassium thioacetate (85.9 mg, 0.750 mmol, 1.5 equiv), 1,10-phenanthroline (18.4 mg, 0.10 mmol, 20 mol %), and CuI (9.7 mg, 51 μmol, 10 mol %) was added toluene (4 mL) at room temperature. After stirring for 24 h at 100 °C (oil bath), to the resulting mixture were added MeOH (2.5 mL) and *N*-bromosuccinimide (444 mg, 2.49 mmol, 5.0 equiv) at room temperature. After stirring for 1 h at the same temperature, to the mixture were added an aqueous saturated sodium bicarbonate (10 mL) and an aqueous saturated sodium thiosulfate (10 mL) and extracted with dichloromethane (10 mL × 3). The combined organic extract was washed with brine (10 mL) and dried (Na_2SO_4). After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (*n*-hexane/EtOAc = 4/1) to give methyl 4-chlorobenzenesulfinate (**3c**) (51.8 mg, 0.272 mmol, 54%) as a colorless oil.

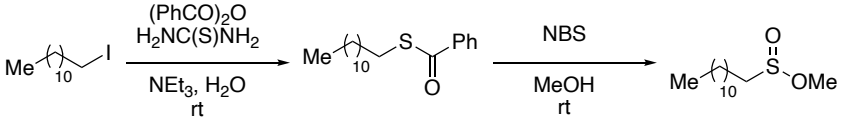
A typical procedure for the synthesis sulfinate esters with various alcohol



To a mixture of *S*-(4-chlorophenyl) benzothioate (**4c**) (24.8 mg, 99.7 μmol, 1.0 equiv) and EtOH (58.2 μL, 1.00 mmol, 10 equiv) in dichloromethane (0.50 mL) in 5 mL screw-top V-vial® (Sigma-Aldrich, Cat. No. Z115118) was added *N*-bromosuccinimide (53.2 mg, 0.299 mmol, 3.0 equiv) at room temperature. After stirring for 1 h at the same temperature, to the mixture were added an aqueous saturated sodium bicarbonate (10 mL) and an aqueous saturated sodium thiosulfate (10 mL). The reaction mixture was extracted with dichloromethane (10 mL × 3). The combined organic extract was washed with brine (10 mL) and dried (Na_2SO_4). After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 4/1) to give ethyl 4-chlorobenzenesulfinate (**9a**) (19.1 mg, 93.3 μmol, 94%) as a colorless oil.

According to the procedure for preparing ethyl 4-chlorobenzenesulfinate (**9a**), 2-methoxyethyl 4-chlorobenzenesulfinate (**9b**) (16.4 mg, 70%), and isopropyl 4-chlorobenzenesulfinate (**9c**) (3.4 mg, 16%; 2-propanol was used as a solvent) [8.8 mg, 40% when *S*-(4-chlorophenyl) thioacetate (**8**) was used instead of thioester **4c** and 2-propanol was used as a solvent] were prepared from the corresponding alcohols.

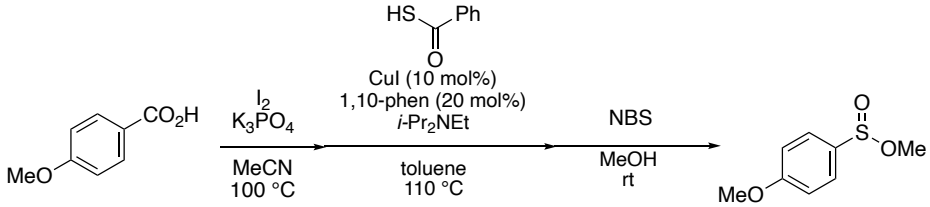
*Synthesis of methyl dodecane-1-sulfinate (**12**)*



To a mixture of benzoic anhydride (543 mg, 2.40 mmol, 1.2 equiv), thiourea (198 mg, 2.60 mmol, 1.3 equiv), was added triethylamine (1.00 mL) at room temperature. After stirring for 30 min at 40 °C, the mixture was cooled to room temperature. To the resulting mixture were added water (2.0 mL) and 1-iododododecane (**10**) (593 mg, 2.00 mmol, 1.0 equiv) at room temperature. After stirring for 3 h at the same temperature, to the reaction mixture was added water (10 mL). The mixture was extracted with EtOAc (15 mL × 3). The combined organic extract was washed with brine (15 mL) and dried (Na_2SO_4). After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (*n*-hexane/EtOAc = 30/1) to give *S*-(4-chlorophenyl) *S*-dodecyl benzothioate (201 mg, 0.684 mmol, 34%) (**11**) as a colorless solid.

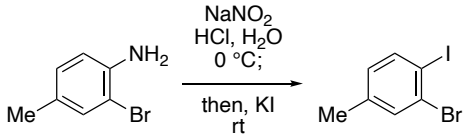
To a mixture of *S*-dodecyl benzothioate (**11**) (30.8 mg, 0.100 mmol, 1.0 equiv) and MeOH (2.5 mL) in 5 mL screw-top V-vial® (Sigma-Aldrich, Cat. No. Z115118) was added *N*-bromosuccinimide (35.6 mg, 0.200 mmol, 2.0 equiv) at room temperature. After stirring for 1 h at the same temperature, to the mixture were added an aqueous saturated sodium bicarbonate (10 mL) and an aqueous saturated sodium thiosulfate (10 mL) and extracted with dichloromethane (10 mL × 3). The combined organic extract was washed with brine (10 mL) and dried (Na_2SO_4). After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (*n*-hexane/EtOAc = 15/1) to give methyl dodecane-1-sulfinate (**12**) (24.5 mg, 98.6 μmol, 98%) as a colorless oil.

*Synthesis of methyl 4-methoxybenzenesulfinate (**3b**) from 4-methoxybenzoic acid (**15**)*



To a mixture of 4-methoxybenzoic acid (**1a**) (38.2 mg, 0.251 mmol, 1.0 equiv) and tripotassium phosphate (53.2 mg, 0.251 mmol, 1.0 equiv) in acetonitrile (2.5 mL) was added iodine (255 mg, 1.00 mmol, 4.0 equiv) at room temperature. After stirring for 2 h at 100 ℃ (oil bath), the mixture was cooled to room temperature. To the mixture was added iodine (254 mg, 1.00 mmol, 4.0 equiv) at room temperature. After stirring for 2 h at 100℃ (oil bath), the mixture was cooled to room temperature. To the mixture was added an aqueous saturated potassium carbonate (10 mL) and an aqueous saturated sodium thiosulfate (10 ml). The solution was extracted with dichloromethane (10 mL × 3). The combined organic extract was washed with brine (10 mL) and dried (Na_2SO_4). After filtration, the filtrate was concentrated under reduced pressure. To the resulting mixture involving 1-iodo-4-methoxybenzene (ca. 56.2 mg, 0.240 mmol, 96%). To the resulting mixture in toluene (500 μL) was added 1,10-phenanthroline (8.8 mg, 48 μmol, 20 mol %), CuI (4.8 mg, 25 μmol, 10 mol %) thiobenzoic acid (33.9 μL, 0.288 mmol, 1.2 equiv) and *i*-Pr_2NEt (83.6 μL, 0.48 mmol, 2.0 equiv) at room temperature. After stirring for 7 h at 110 ℃, the mixture was cooled to room temperature and quenched with water. The mixture was extracted with EtOAc (10 mL × 3). The combined organic extract was washed with brine (10 mL) and dried (Na_2SO_4). After filtration, the filtrate was concentrated under reduced pressure. To the resulting mixture in MeOH (1.25 mL) was added *N*-bromosuccinimide (128 mg, 0.719 mmol, 3.0 equiv) at room temperature. After stirring for 1 h at the same temperature, to the mixture were added an aqueous saturated sodium bicarbonate (10 mL) and an aqueous saturated sodium thiosulfate (10 mL) and extracted with dichloromethane (10 mL × 3). The combined organic extract was washed with brine (10 mL) and dried (Na_2SO_4). After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/dichloromethane = 4/1) to give 4-methoxybenzenesulfinate (27.6 mg, 0.148 mmol. 59%) as a colorless oil.

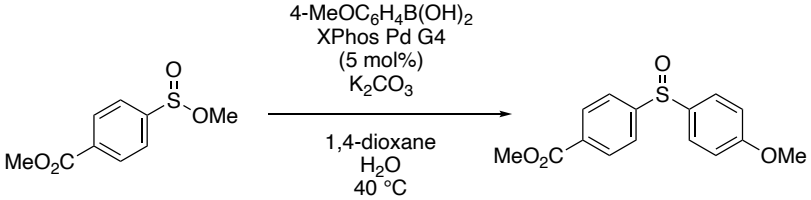
A typical procedure for the synthesis of Aryl iodides from aniline



To a mixture of 2-bromo-4-methylaniline (1.01 g, 5.41 mmol, 1.0 equiv) and 12 M aqueous HCl (2.5 mL) was added sodium nitrite (407 mg, 5.90 mmol, 1.1 equiv) in water (4 mL) dropwise at 0 ℃ and stirred for 15 min at the same temperature. Potassium iodide (9.52 g, 57.4 mmol, 10 equiv) dissolved in water (9.4 mL) was added dropwise to the mixture at 0 ℃. After stirring for 15 h at room temperature, the mixture was added an aqueous saturated sodium thiosulfate (10 mL) and extracted with EtOAc (15 mL × 3). The combined organic extract was washed with an aqueous 10 wt% sodium hydroxide (5 mL), brine (5 mL) and an aqueous saturated $NaHCO_3$ (5 mL). The mixture was dried with Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (*n*-hexane only) to give 2-bromo-1-iodo-4-methylbenzene (**5p**) (1.07 g, 3.62 mmol, 67%) as a colorless solid.

According to the procedure for preparing 2-bromo-1-iodo-4-methylbenzene (**5p**), 2-bromo-4-chloro-1-iodo-benzene (**5o**) (1.20 g, 70%), 2-bromo-1-iodo-4-(trifluoromethyl)benzene (**5q**) (1.18 g, 62%), and 2-bromo-1-iodo-4,6-dimethylbenzene (**5a**) (1.05 g, 63%) were prepared from the corresponding anilines.

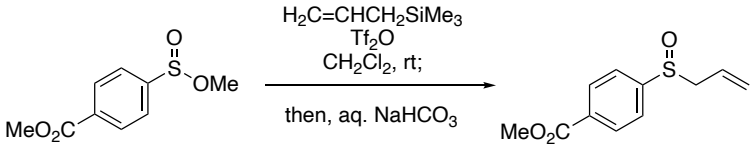
*Synthesis of methyl 4-((4-methoxyphenyl)sulfinyl)benzoate (**16**)*



In a 5 mL screw-top V-vial® (Sigma-Aldrich, Cat. No. Z115118) with a solid-top cap were placed methyl 4-(methoxycarbonyl)benzenesulfinate (**3i**) (21.4 mg, 99.9 μmol, 1.0 equiv), 4-methoxyphenyl boronic acid (30.5 mg, 0.201 mmol, 2.0 equiv), XPhos Pd G4 (4.5 mg, 5.2 μmol, 5 mol %), and potassium carbonate (20.7 mg, 0.150 mmol, 1.5 equiv) in 1,4-dioxane (1.6 mL) and H_2O (0.32 μL) at room temperature. The mixture was stirred with

heating at 40 °C (aluminium heating block) for 24 h. After cooling to room temperature, the mixture was filtrated through Na_2SO_4 and washed with EtOAc. The filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 1/1) to give methyl 4-((4-methoxyphenyl)sulfinyl)benzoate (**16**) (15.1 mg, 52.0 μmol, 52%) as a colorless solid.

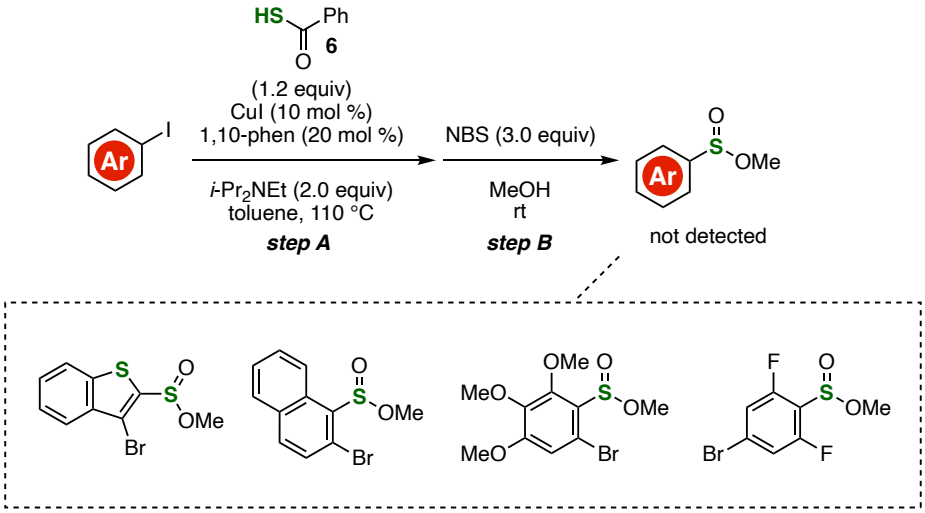
*Synthesis of methyl 4-(allylsulfinyl)benzoate (**17**)*



To a mixture of methyl 4-(methoxycarbonyl)benzenesulfinate (**3i**) (21.4 mg, 99.9 μmol, 1.0 equiv) and allyltrimethylsilane (47.7 μL, 0.300 mmol, 3.0 equiv) in dichloromethane (1 mL) was added trifluoromethanesulfonic anhydride (Tf_2O) (25.2 μL, 0.150 mmol, 1.5 equiv) at room temperature. After stirring for 1 h at the same temperature, the mixture was quenched with an aqueous saturated solution of sodium bicarbonate (10 mL) and extracted with dichloromethane (10 mL × 3). The combined organic extract was washed with brine (10 mL) and dried (Na_2SO_4). After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 1/1) to give methyl 4-(allylsulfinyl)benzoate (**17**) (20.4 mg, 91.0 μmol, 91%) as a colorless solid.

Limitations in the Sulfinate Ester Synthesis from Aryl Iodides

When sulfinate ester synthesis was conducted using 2-iodo-3-bromobenzo[*b*]thiophene or 1-iodo-2-bromonaphthalene, the corresponding sulfinate esters were not obtained along with complex mixtures of products. Sulfinate ester synthesis also resulted in failure when 1-bromo-2-iodo-3,4,5-trimethoxy-benzene and 1-bromo-3,5-difluoro-4-iodobenzene were used as starting materials.

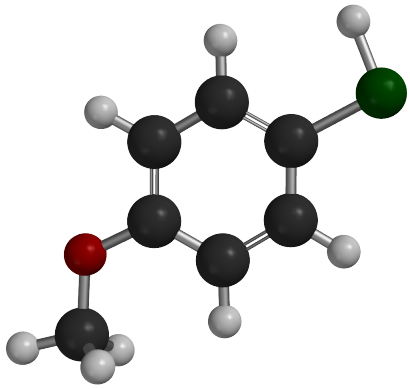


Computational Methods

Geometry optimizations and frequency calculations were performed at B3LYP/6-311+G(d,p) level of theory with Spartan 18 program (Wavefunction,. Inc. Irvine, CA) in the gas phase. Cartesian coordinates obtained by the DFT calculation were shown as calculated geometries described below. All the stationary geometries were confirmed to be energy minima by achieving vibrational frequency analyses.

Calculated Geometries

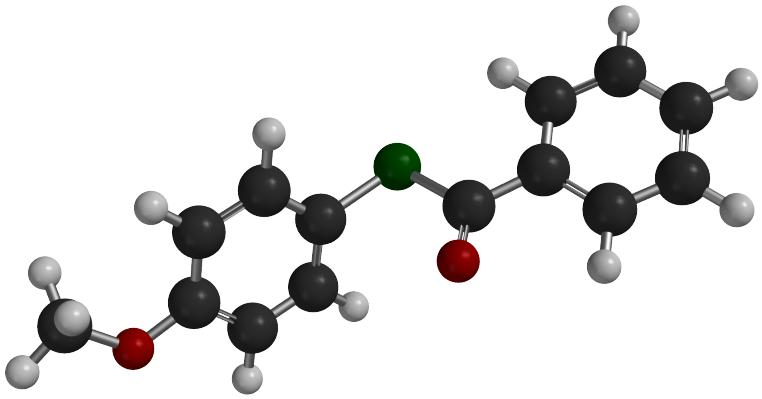
Optimized structure of **2b**



black: carbon, grey: hydrogen, red: oxygen, green: sulfur
E = –745.080221 hartrees
LUMO: –0.68 eV
HOMO: –5.75 eV

H	-2.083025	-0.000000	-1.679929
C	-1.090281	-0.000000	-1.243647
C	1.435313	-0.000000	-0.089732
C	0.035376	0.000000	-2.065240
C	-0.964443	-0.000001	0.146673
C	0.303029	-0.000001	0.732306
C	1.303370	-0.000000	-1.470258
H	-1.860970	-0.000001	0.752039
H	2.196544	-0.000000	-2.084937
H	2.414980	-0.000000	0.372835
S	-0.207867	0.000000	-3.839952
H	1.095536	0.000001	-4.175104
O	0.540108	-0.000001	2.077823
C	-0.574349	0.000001	2.958835
H	-1.191945	0.894505	2.821172
H	-0.159427	0.000001	3.965942
H	-1.191946	-0.894505	2.821174

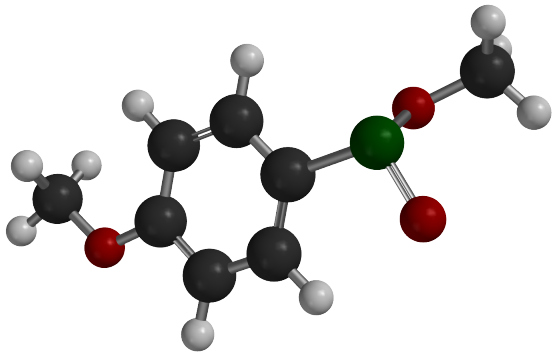
Optimized structure of **4b**



black: carbon, grey: hydrogen, red: oxygen, green: sulfur
E = –1089.558821 hartrees
LUMO: –1.88 eV
HOMO: –6.32 eV

H	0.205261	1.550145	-2.083886
C	0.082297	1.948243	-1.083846
C	-0.218595	2.971588	1.485562
C	-0.600154	1.208082	-0.122159
C	0.613862	3.200840	-0.775511
C	0.468209	3.714009	0.515979
C	-0.752303	1.734067	1.167790
H	1.136874	3.754893	-1.542559
H	-1.285000	1.169089	1.922419
H	-0.322759	3.387004	2.480325
O	0.952597	4.918410	0.927297
C	1.640380	5.737783	-0.009979
H	2.547163	5.247403	-0.380925
H	1.914991	6.640513	0.531951
H	0.996200	6.004906	-0.855247
S	-1.313370	-0.372991	-0.551261
C	-0.091777	-1.517119	0.190108
O	0.840035	-1.118512	0.841149
C	-0.371369	-2.968618	-0.041837
C	-0.802213	-5.708469	-0.379728
C	-1.250645	-3.427160	-1.029973
C	0.296000	-3.894438	0.771993
C	0.076338	-5.256738	0.606189
C	-1.462160	-4.792586	-1.198212
H	-1.759935	-2.723161	-1.676088
H	0.978704	-3.526620	1.528340
H	0.590716	-5.967391	1.242905
H	-2.138859	-5.141422	-1.970021
H	-0.970488	-6.771749	-0.510776

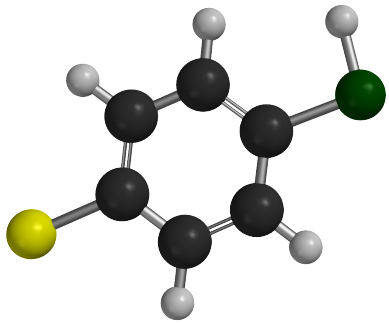
Optimized structure of **3b**



black: carbon, grey: hydrogen, red: oxygen, green: sulfur
E = –934.836782 hartrees
LUMO: –1.23 eV
HOMO: –6.61 eV

H	-0.271245	0.101982	-1.949483
C	0.066822	0.270180	-0.934181
C	0.933541	0.701049	1.681110
C	0.580195	-0.775677	-0.178822
C	-0.028429	1.545733	-0.380917
C	0.405378	1.762465	0.932211
C	1.023352	-0.564821	1.126063
H	-0.439388	2.351841	-0.973825
H	1.432799	-1.397569	1.687282
H	1.265852	0.895400	2.693487
O	0.359239	2.964845	1.564653
C	-0.168713	4.089576	0.870038
H	0.419606	4.317808	-0.025193
H	-0.104136	4.923768	1.565478
H	-1.215827	3.928966	0.592315
S	0.763636	-2.419179	-0.907427
O	1.396200	-3.274654	0.138087
O	-0.922880	-2.694455	-0.933389
C	-1.288390	-3.949043	-1.530091
H	-0.961909	-4.787634	-0.909865
H	-0.869333	-4.047535	-2.537634
H	-2.376369	-3.943044	-1.589896

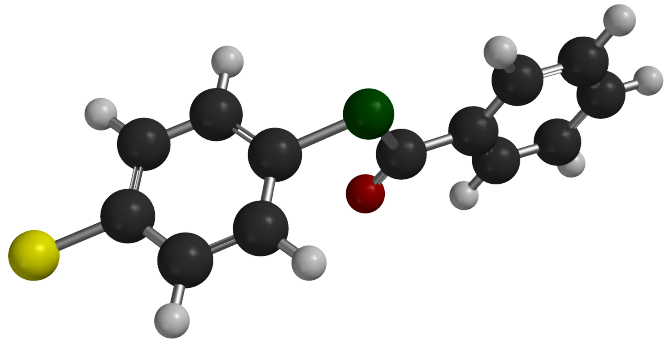
Optimized structure of **2c**



black: carbon, grey: hydrogen, yellow: chlorine, green: sulfur
E = –1090.147301 hartrees
LUMO: –1.05 eV
HOMO: –6.32 eV

H	-2.247018	0.000000	0.946393
C	-1.298731	0.000000	0.421052
C	1.125355	0.000000	-0.952955
C	-0.097440	0.000000	1.138164
C	-1.291893	0.000000	-0.970014
C	-0.077907	0.000000	-1.649292
C	1.113159	0.000000	0.439358
H	-2.223691	0.000000	-1.520748
H	2.056526	0.000000	0.972730
H	2.065363	0.000000	-1.489817
Cl	-0.065199	0.000000	-3.408955
S	-0.192375	0.000000	2.921579
H	1.133850	0.000000	3.152504

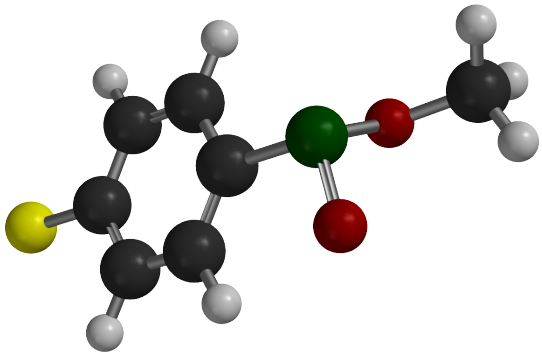
Optimized structure of **4c**



black: carbon, grey: hydrogen, yellow: chlorine, red: oxygen, green: sulfur
E = –1434.624458 hartrees
LUMO: –2.10 eV
HOMO: –7.00 eV

H	1.163575	2.005679	-2.107668
C	1.057562	2.559188	-1.182900
C	0.779899	3.986502	1.201661
C	0.114970	2.158313	-0.234496
C	1.865219	3.667216	-0.943903
C	1.717298	4.369772	0.247701
C	-0.021845	2.875550	0.955010
H	2.600581	3.981308	-1.673455
H	-0.752764	2.564798	1.691482
H	0.680950	4.544887	2.123635
Cl	2.737344	5.768750	0.553904
S	-0.954932	0.760323	-0.559765
C	0.098905	-0.606026	0.065414
O	1.203839	-0.398874	0.496547
C	-0.516501	-1.966024	-0.010491
C	-1.546574	-4.563071	-0.092777
C	-1.823364	-2.192978	-0.458699
C	0.269711	-3.052465	0.397659
C	-0.243842	-4.343402	0.355576
C	-2.334294	-3.486769	-0.498996
H	-2.448991	-1.366417	-0.773093
H	1.278325	-2.863745	0.743853
H	0.370068	-5.178529	0.673123
H	-3.347555	-3.653976	-0.845028
H	-1.947585	-5.570009	-0.124293

Optimized structure of **3c**



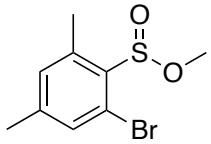
black: carbon, grey: hydrogen, yellow: chlorine, red: oxygen, green: sulfur
E = –1279.901303 hartrees
LUMO: –1.73 eV
HOMO: –7.14 eV

H	-0.520759	1.035776	-1.728803
C	-0.151196	1.214377	-0.725198
C	0.796124	1.664945	1.870360
C	0.501915	0.208826	-0.016277
C	-0.340350	2.456925	-0.128649
C	0.134904	2.666865	1.164308
C	0.984461	0.423383	1.268020
H	-0.847783	3.253513	-0.656890
H	1.499406	-0.379017	1.783060
H	1.159456	1.854320	2.872648
Cl	-0.099499	4.236443	1.914950
S	0.825444	-1.396764	-0.799807
O	1.564089	-2.206863	0.207481
O	-0.825097	-1.819466	-0.786220
C	-1.100863	-3.070802	-1.439998
H	-0.660050	-3.904040	-0.886804
H	-0.734344	-3.070628	-2.471374
H	-2.185859	-3.167792	-1.440806

Characterization Data of New Compounds

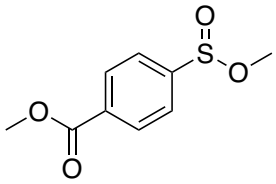
Methyl 4-methoxybenzenesulfinate (**3b**),[S2] methyl 4-chlorobenzenesulfinate (**3c**),[S2] methyl benzenesulfinate (**3d**),[S3] methyl 4-methylbenzenesulfinate (**3e**),[S2] methyl 4-fluorobenzenesulfinate (**3f**),[S2] methyl 4-bromobenzenesulfinate (**3g**),[S2] methyl 4-(trifluoromethyl)benzenesulfinate (**3h**),[S3] methyl 2-methylbenzenesulfinate (**3j**),[S3] methyl 2-bromobenzenesulfinate (**3k**),[S2] methyl 5-bromothiophene-2-sulfinate (**3n**),[S4] *S*-(4-methoxyphenyl) benzothioate (**4b**),[S5] *S*-(4-chlorophenyl) benzothioate (**4c**),[S5] *S*-phenyl benzothioate (**4d**),[S5] *S*-(4-methylphenyl) benzothioate (**4e**),[S5] *S*-(4-fluorophenyl) benzothioate (**4f**),[S5] *S*-(4-bromophenyl) benzothioate (**4g**),[S5] *S*-(2-bromophenyl) benzothioate (**4k**),[S6] *S*-(2-thienyl) benzothioate (**4n**),[S7] 2-bromo-4,6-dimethyl-1-iodobenzene (**5a**),[S8] 2-bromo-4-chloro-1-iodobenzene (**5o**),[S8] 2-bromo-1-iodo-4-methylbenzene (**5p**),[S9] 2-bromo-1-iodo-4-(trifluoromethyl)benzene (**5q**),[S10] *S*-(4-chlorophenyl) thioacetate (**8**),[S11] ethyl 4-chlorobenzene sulfinate (**9a**),[S2] *S*-*n*-decyl benzoate (**11**),[S12] methyl 4-chlorobenzenesulfonate (**13**),[S13] methyl benzoate (**14**),[S14] and allyl 4-(methoxycarbonyl)phenyl sulfoxide (**17**)[S15] were identical in spectra data with those reported in the literature.

Methyl 2-bromo-4,6-dimethylbenzenesulfinate (**3a**)



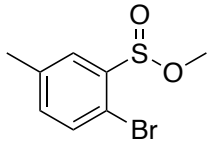
Colorless oil; TLC R_f 0.50 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.23 (s, 1H), 6.99 (s, 1H), 3.85 (s, 3H), 2.68 (s, 3H), 2.31 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 143.4, 140.6, 138.5, 133.3, 131.7, 121.9, 55.0, 20.9, 18.6; IR (NaCl, cm^{-1}) 1595, 1547, 1452, 1421, 1215, 1138, 1055, 1036, 982, 851, 804; HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_9H_{11}{}^{79}BrNaO_2S^+$ 284.9561; Found 284.9561.

Methyl 4-(methoxycarbonyl)benzene sulfinate (**3i**)



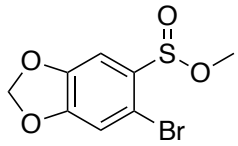
Colorless solid; Mp 36–38 °C; TLC R_f 0.42 (*n*-hexane/EtOAc = 2/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.22–8.19 (AA'BB', 2H), 7.80–7.77 (AA'BB', 2H), 3.96 (s, 3H), 3.50 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 165.8, 148.1, 133.5, 130.1, 125.5, 52.5, 49.9; IR (NaCl, cm^{-1}) 1728, 1395, 1276. 1142. 962, 856, 827; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_9H_{10}NaO_4S^+$ 237.0198; Found 237.0196.

Methyl 2-bromo-5-methylbenzenesulfinate (**3l**)



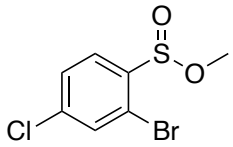
Pale yellow oil; TLC R_f 0.54 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.72 (d, 1H, J = 2.0 Hz), 7.48 (d, 1H J = 8.0 Hz), 7.21 (dd, 1H, J = 8.0, 2.0 Hz), 3.60 (s, 3H), 2.40 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 142.0, 138.2, 134.4, 133.3, 127.2, 117.5, 51.6, 21.0; IR (NaCl, cm^{-1}) 2939, 1455, 1382, 1252, 1130, 1093, 1040, 1019, 967, 860, 818; HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_8H_9{}^{79}BrNaO_2S^+$ 270.9404; Found 270.9404.

Methyl 6-bromobenzo[*d*][1,3]dioxole-5-sulfinate (**3m**)



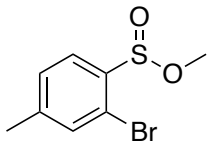
Colorless solid; Mp 76–78 °C; TLC R_f 0.43 (*n*-hexane/EtOAc = 3/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.39 (s, 1H), 7.04 (s, 1H), 6.10–6.07 (m, 2H), 3.58 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 151.7, 147.9, 136.1, 113.3, 113.1, 106.6, 102.7, 51.0; IR (NaCl, cm^{-1}) 1598, 1495, 1376, 1245, 1112, 1036, 963, 916, 886; HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_8H_7{}^{79}BrNaO_4S^+$ 300.9146; Found 300.9147.

Methyl 2-bromo-4-chlorobenzenesulfinate (**3o**)



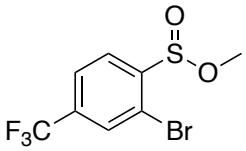
Pale yellow oil; TLC R_f 0.48 (*n*-hexane/EtOAc = 7/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.86 (d, 1H, J = 8.4 Hz), 7.64 (d, 1H, J = 1.9 Hz), 7.51 (dd, 1H, J = 8.4, 1.9 Hz), 3.59 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 141.3, 139.3, 133.2, 128.1, 128.0, 121.5, 51.5; IR (NaCl, cm^{-1}) 1567, 1557, 1447, 1365, 1139, 1102, 1025, 967, 869, 828; HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_7H_6{}^{79}Br^{35}ClNaO_2S^+$ 290.8858; Found 290.8858.

Methyl 2-bromo-4-methylbenzenesulfinate (**3p**)



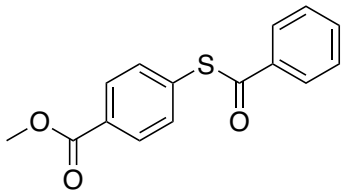
Colorless solid; Mp 77–79 °C; TLC R_f 0.35 (*n*-hexane/EtOAc = 7/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.80 (d, 1H, J = 7.9 Hz), 7.45 (d, 1H, J = 0.7 Hz), 7.32 (dd, 1H, J = 7.9, 0.7 Hz), 3.57 (s, 3H), 2.41 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 144.7, 139.5, 134.0, 128.5, 126.8, 120.8, 51.1, 21.1; IR (NaCl, cm^{-1}) 1468, 1455, 1447, 1435, 970, 821; HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_8H_9{}^{79}BrNaO_2S^+$ 270.9404; Found 270.9405.

Methyl 2-bromo-4-(trifluoromethyl)benzenesulfinate (**3q**)



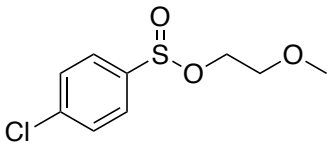
Pale yellow oil; TLC R_f 0.58 (*n*-hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.08 (dd, 1H, J = 8.1, 0.4 Hz), 7.91 (d, 1H, J = 0.4 Hz), 7.84–7.81 (m, 1H), 3.66 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 146.5, 135.4 (q, JC–F = 34.2 Hz), 130.6, 127.6, 124.7, 122.5 (q, JC–F = 273 Hz), 121.4, 52.0; ^{19}F NMR ($CDCl_3$, 367 MHz): δ −63.0 (s); IR (NaCl, cm^{-1}) 1387, 1321, 1175, 1135, 1073, 1029, 969, 891, 846, 816; HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_8H_6{}^{79}BrF_3NaO_2S^+$ 324.9122; Found 324.9123.

Methyl 4-(benzoylthio)benzoate (**4i**)



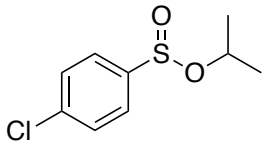
Colorless solid; Mp 119–121 °C; TLC R_f 0.30 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.13–8.10 (AA'BB', 2H), 8.04–8.01 (AA'BB'C, 2H), 7.66–7.59 (m, 3H), 7.53–7.49 (AA'BB'C, 2H), 3.95 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 189.0, 166.5, 136.3, 134.7, 133.9, 133.2, 130.9, 130.1, 128.8, 127.5, 52.3; IR (NaCl, cm^{-1}) 1727, 1664, 1397, 1276, 1209, 1192, 1180, 1107, 901, 856; HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{15}H_{12}NaO_3S^+$ 295.0405; Found 295.0405.

2-Methoxyethyl 4-chlorobenzenesulfinate (**9b**)



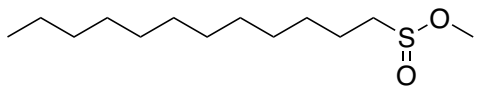
Colorless oil; TLC R R_f 0.31 (*n*-hexane/EtOAc = 3/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.69–7.65 (AA'BB', 2H), 7.53–7.49 (AA'BB', 2H), 4.20–4.15 (m, 1H), 3.75–3.69 (m, 1H), 3.61–3.52 (m, 2H), 3.35 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 143.0, 138.6, 129.3, 126.9, 71.0, 63.5, 59.0; IR (NaCl, cm^{-1}) 2933, 2887, 1574, 1475, 1392, 1362, 1199, 1132, 1087, 1026, 889, 828; HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_9H_{11}{}^{35}ClNaO_3S^+$ 257.0015; Found 257.0015.

Isopropyl 4-chlorobenzenesulfinate (**9c**)



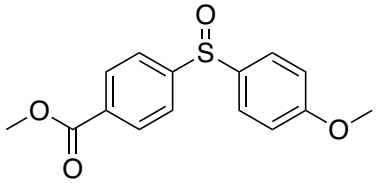
Colorless oil; TLC R_f 0.42 (*n*-hexane/EtOAc = 8/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.66–7.63 (AA'BB', 2H), 7.52–7.48 (AA'BB', 2H), 4.61 (qq, 1H, J = 6.2, 6.2 Hz), 1.39 (d, 3H, J = 6.2 Hz), 1.26 (d, 3H, J = 6.2 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 144.1, 138.4, 129.2, 126.6, 73.3, 23.9, 23.7; IR (NaCl, cm^{-1}) 2979, 1578, 1475, 1389, 1374, 1143, 1087, 1013, 916, 843; HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_9H_{11}{}^{35}ClNaO_2S^+$ 241.0066; Found 241.0065.

Methyl dodecane-1-sulfinate (**12**)



Colorless oil; TLC R_f 0.41 (*n*-hexane/EtOAc = 8/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.76 (s, 3H), 2.80–2.64 (m, 2H), 1.68 (tt, 2H, J = 7.6, 7.6 Hz), 1.43–1.36 (m, 2H), 1.29–1.25 (m, 16H), 0.87 (t, 3H, J = 6.8 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 56.9, 54.4, 31.9, 29.6 (two signals overlapped), 29.5, 29.29, 29.28, 29.2, 28.7, 22.6, 21.2, 14.1; IR (NaCl, cm^{-1}) 3019, 2963, 1597, 1582, 1440, 1398, 1219, 1140, 1024, 945, 856; HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{13}H_{28}NaO_2S^+$ 271.1708; Found 271.1704.

Methyl 4-((4-methoxyphenyl)sulfinyl)benzoate (**16**)



Colorless solid; Mp 89–91 °C; TLC R_f 0.51 (*n*-hexane/EtOAc = 1/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.12–8.09 (AA'BB', 2H), 7.69–7.66 (AA'BB', 2H), 7.59–7.55 (AA'BB', 2H), 6.97–6.94 (AA'BB', 2H), 3.92 (s, 3H), 3.82 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 166.0, 162.3, 150.7, 136.0, 132.0, 130.3, 127.5, 124.3, 115.0, 55.5, 52.4; IR (NaCl, cm^{-1}) 2855, 1726, 1457, 1278, 1253, 1107, 1089, 1042, 1014; HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{15}H_{14}NaO_4S^+$ 313.0511; Found 313.0511.

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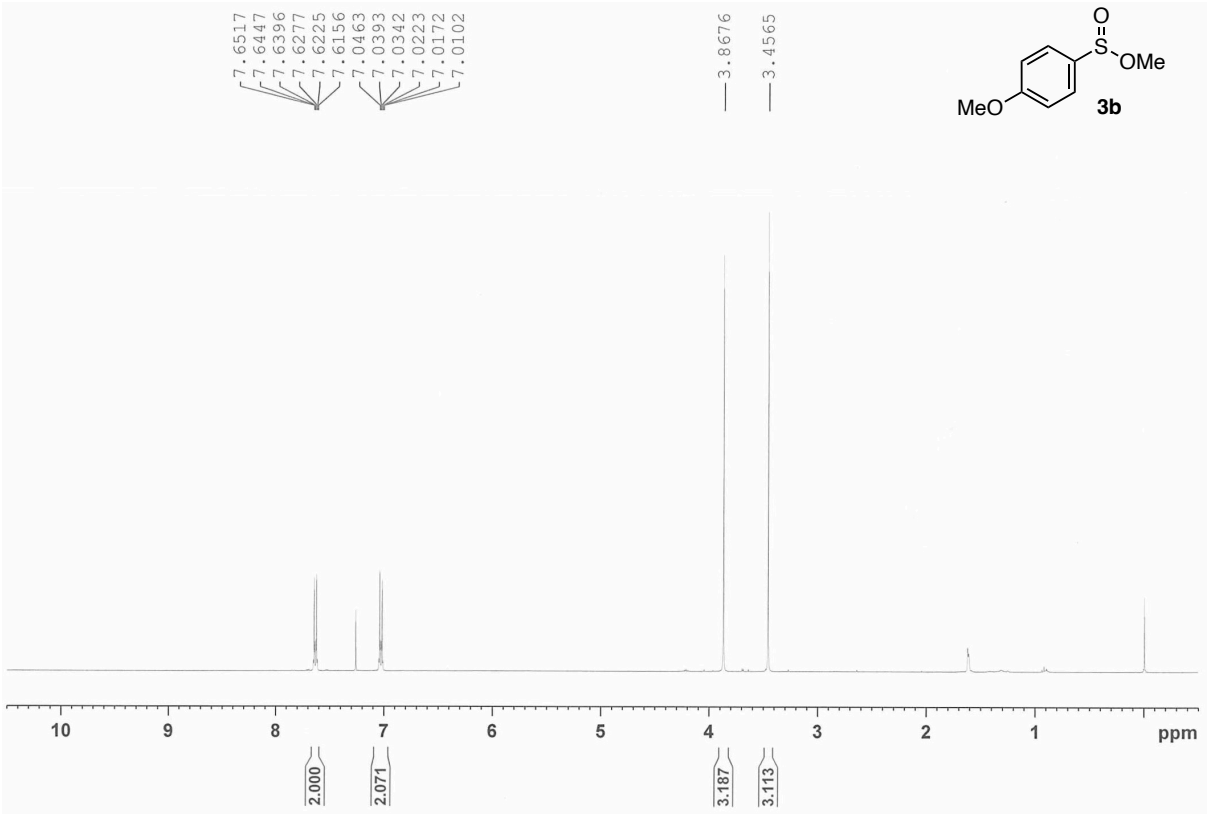
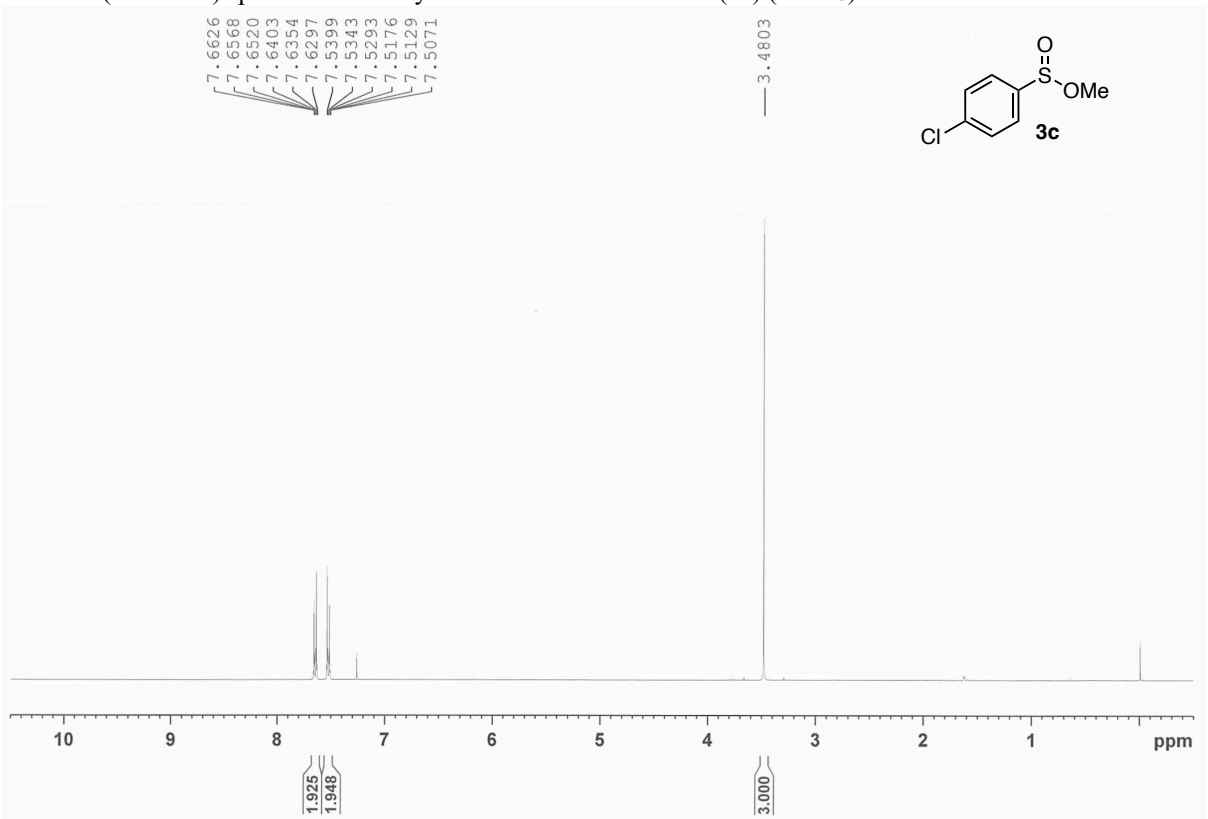
^{1}H NMR Spectra of Known Compounds

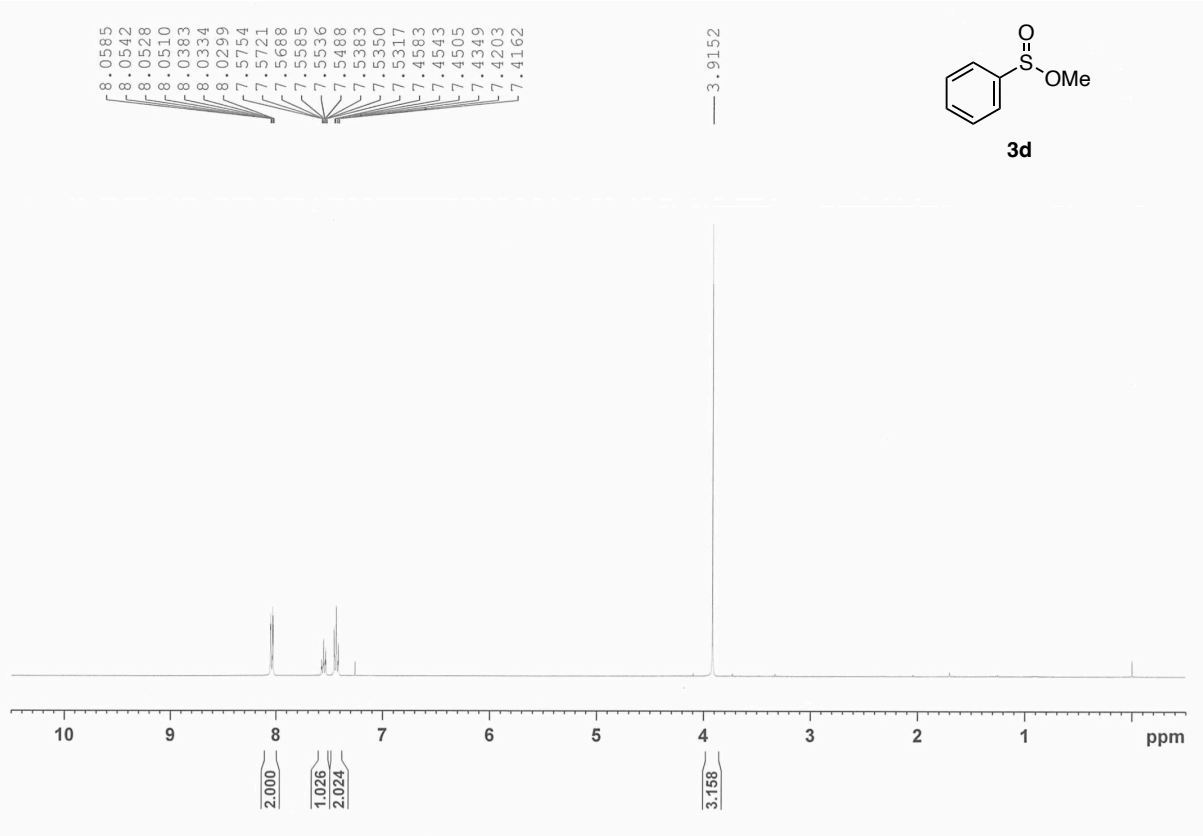
^{1}H NMR (400 MHz) spectrum of methyl 4-methoxybenzenesulfinate (**3b**) ($CDCl_3$)



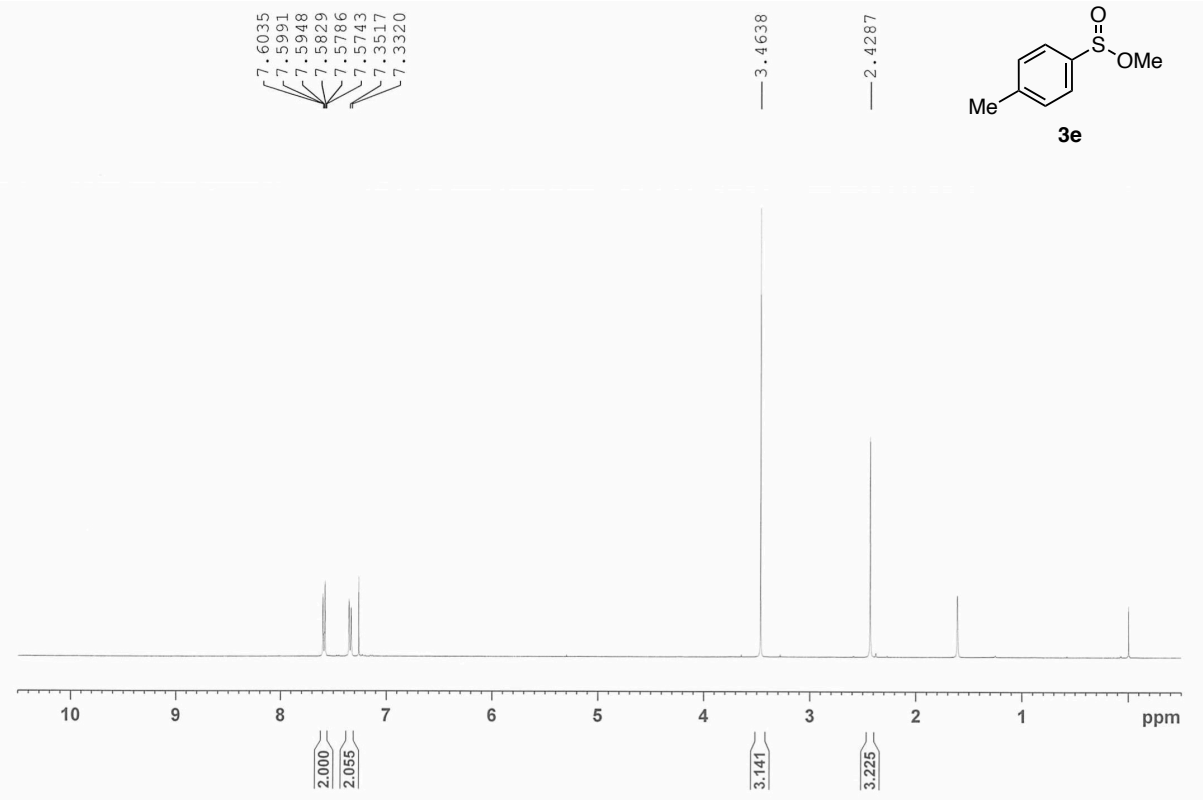
^{1}H NMR (400 MHz) spectrum of methyl 4-chlorobenzenesulfinate (**3c**) ($CDCl_3$)



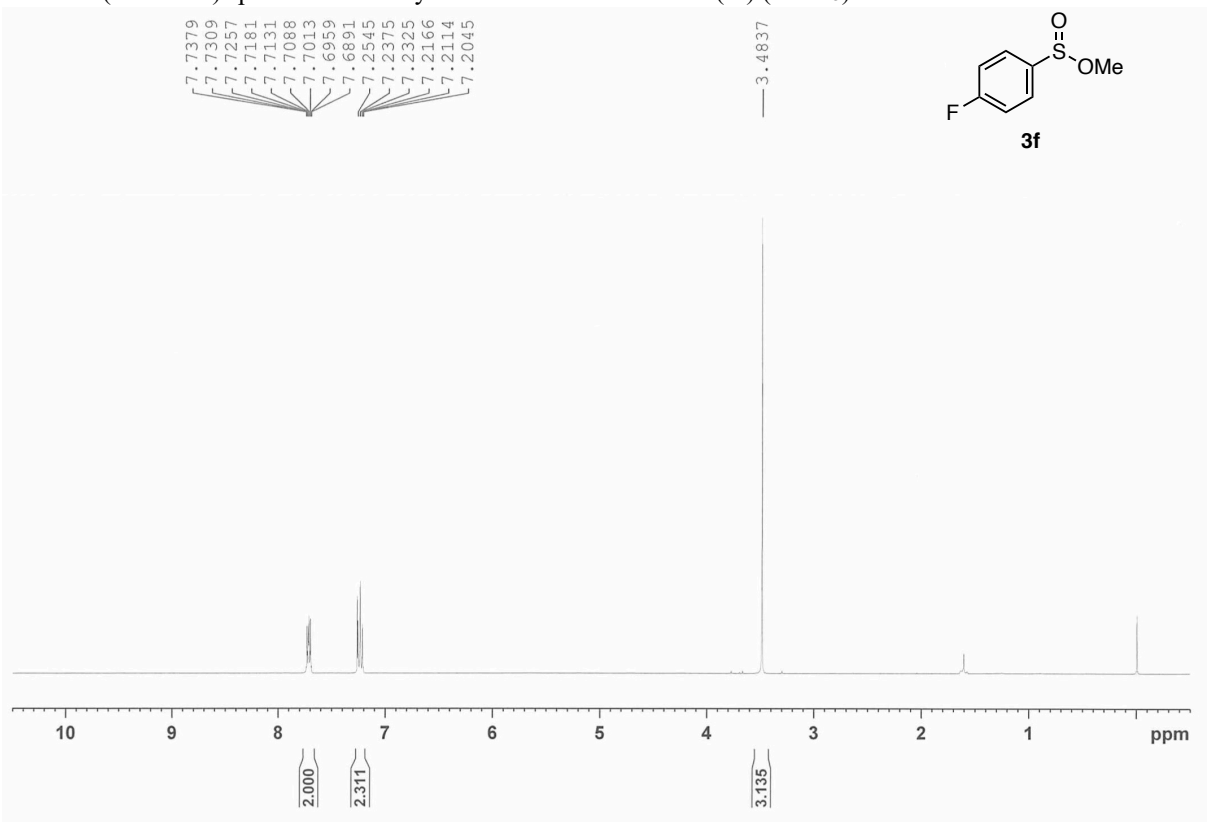
^{1}H NMR (400 MHz) spectrum of methyl benzenesulfinate (**3d**) ($CDCl_3$)



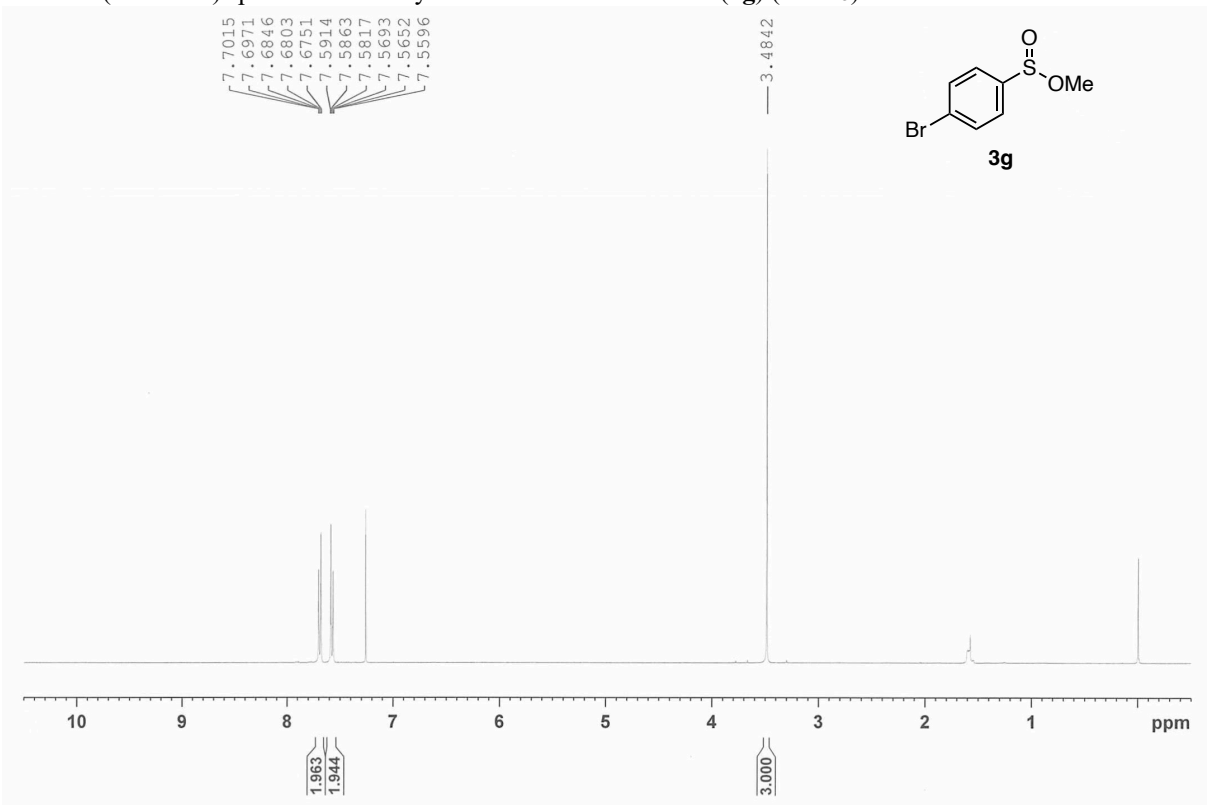
^{1}H NMR (400 MHz) spectrum of methyl 4-methylbenzenesulfinate (**3e**) ($CDCl_3$)



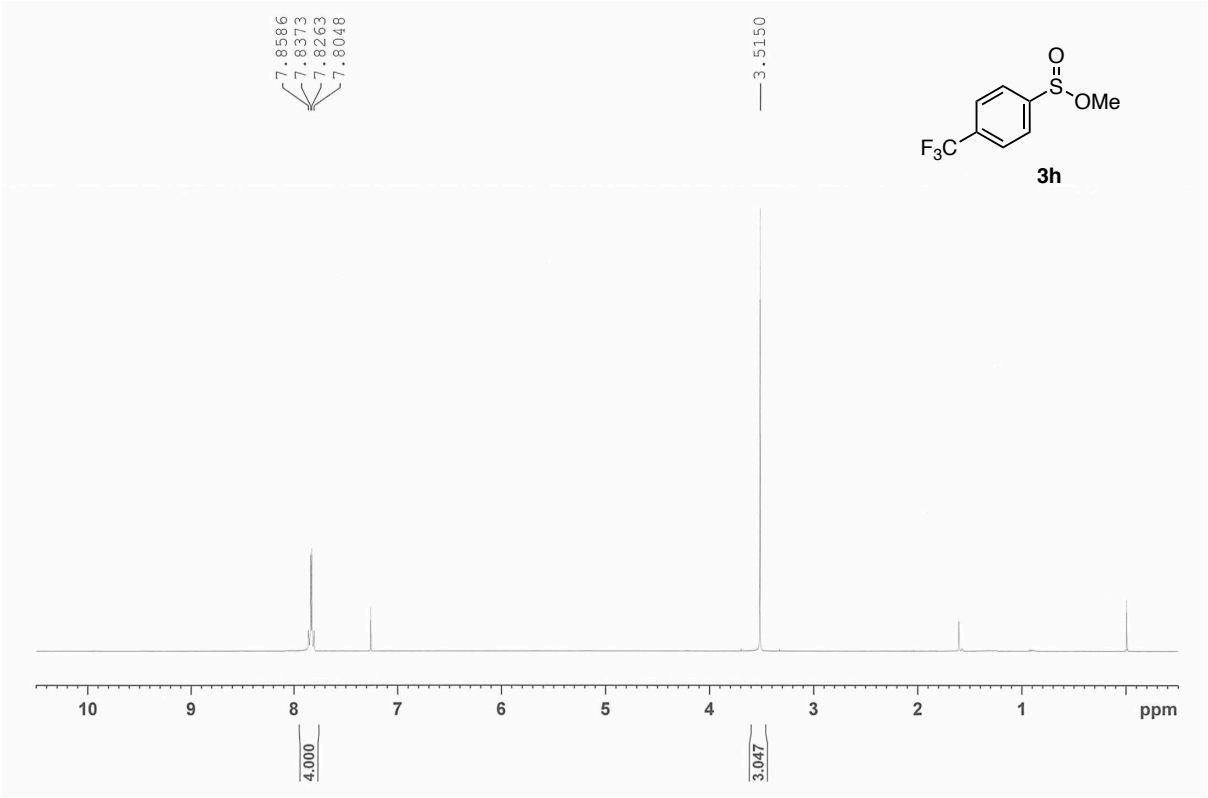
^{1}H NMR (400 MHz) spectrum of methyl 4-fluorobenzenesulfinate (**3f**) ($CDCl_3$)



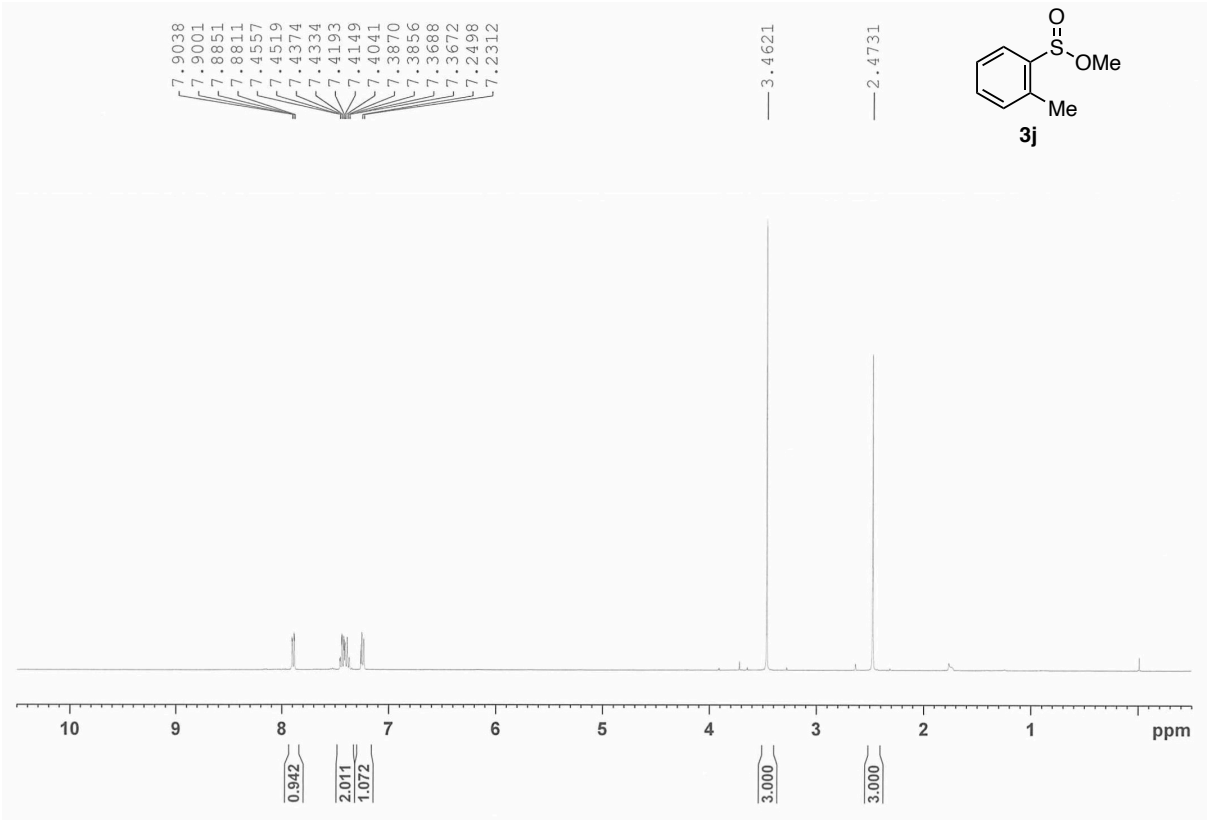
^{1}H NMR (400 MHz) spectrum of methyl 4-bromobenzenesulfinate (**3g**) ($CDCl_3$)



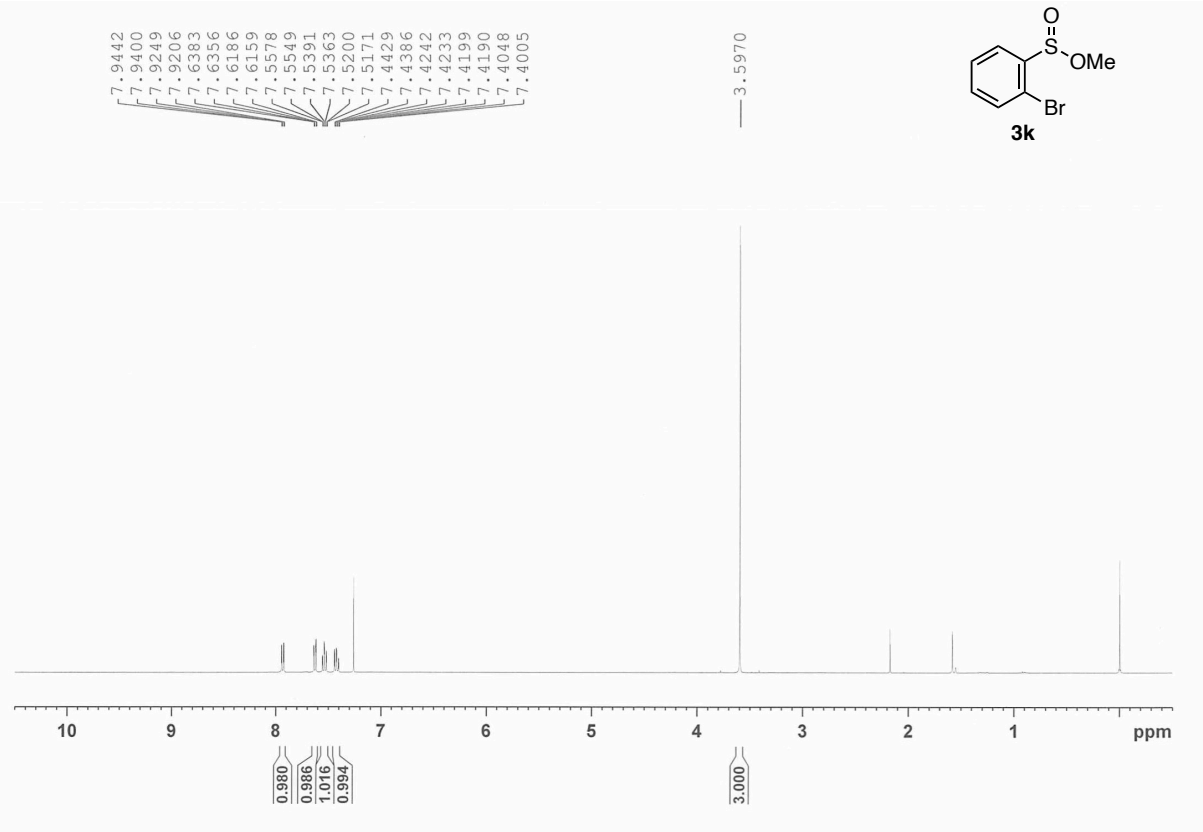
^{1}H NMR (400 MHz) spectrum of methyl 4-(trifluoromethyl)benzenesulfinate (**3h**) ($CDCl_3$)



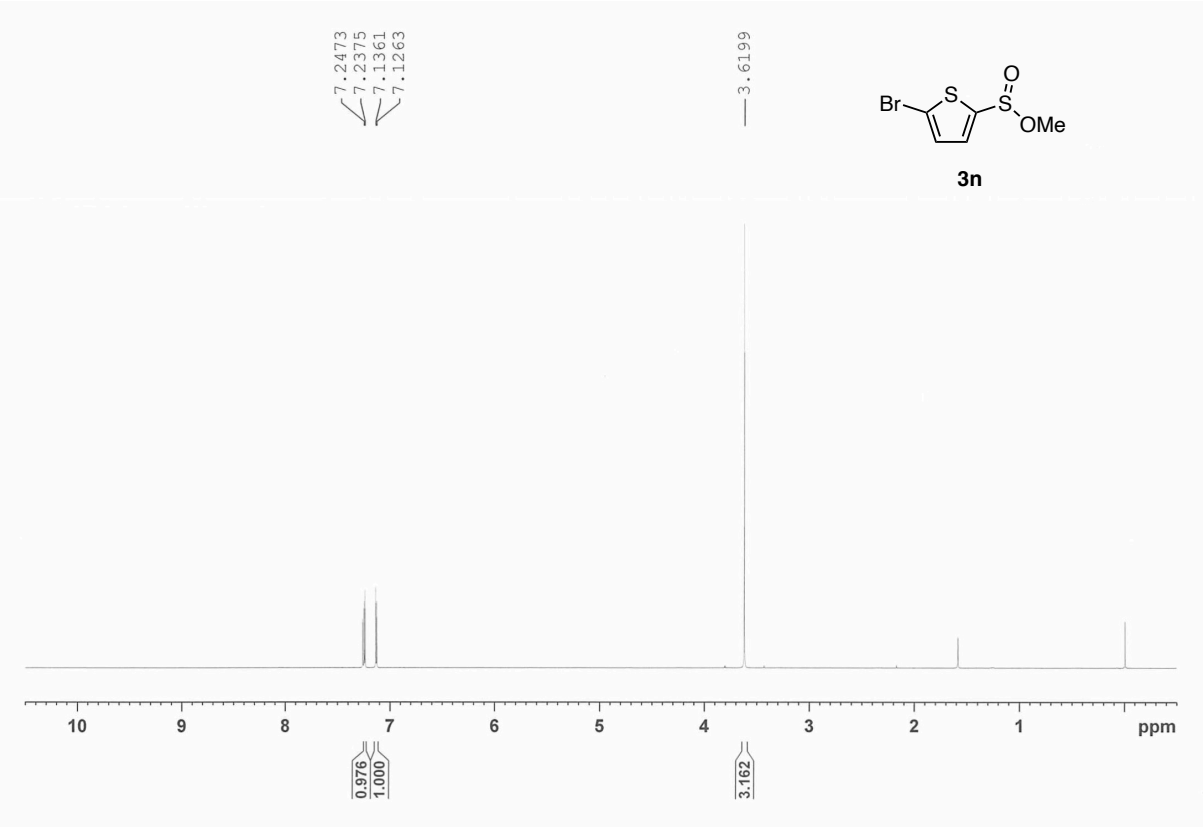
^{1}H NMR (400 MHz) spectrum of methyl 2-methylbenzenesulfinate (**3j**) ($CDCl_3$)



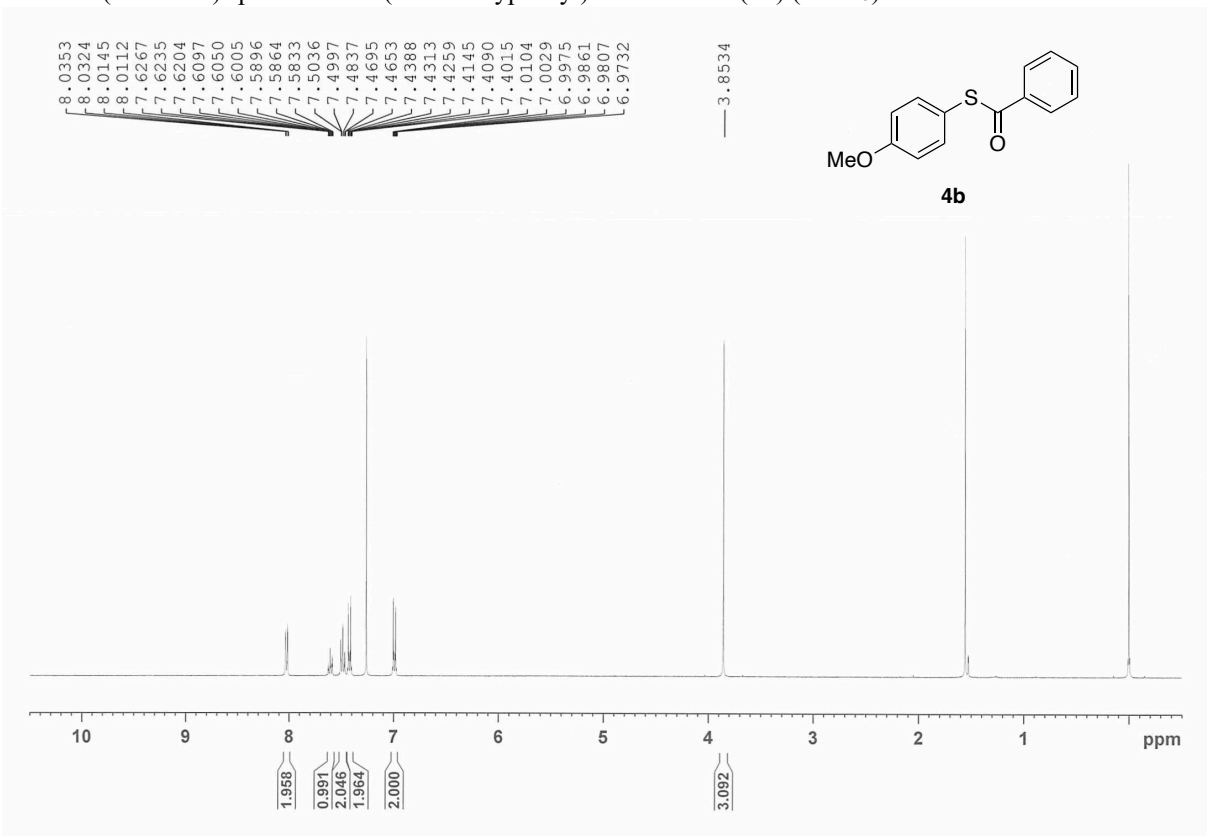
^{1}H NMR (400 MHz) spectrum of methyl 2-bromobenzenesulfinate (**3k**) ($CDCl_3$)



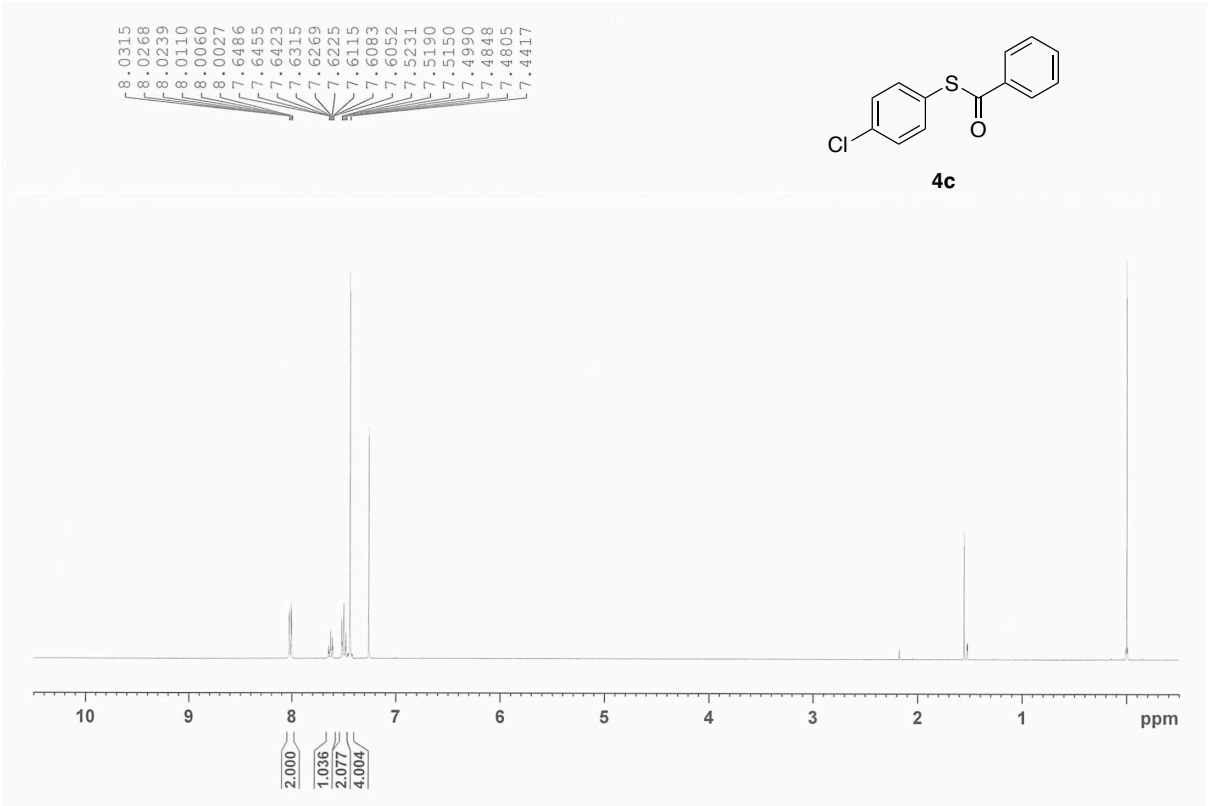
^{1}H NMR (400 MHz) spectrum of methyl 5-bromothiophene-2-sulfinate (**3n**) ($CDCl_3$)



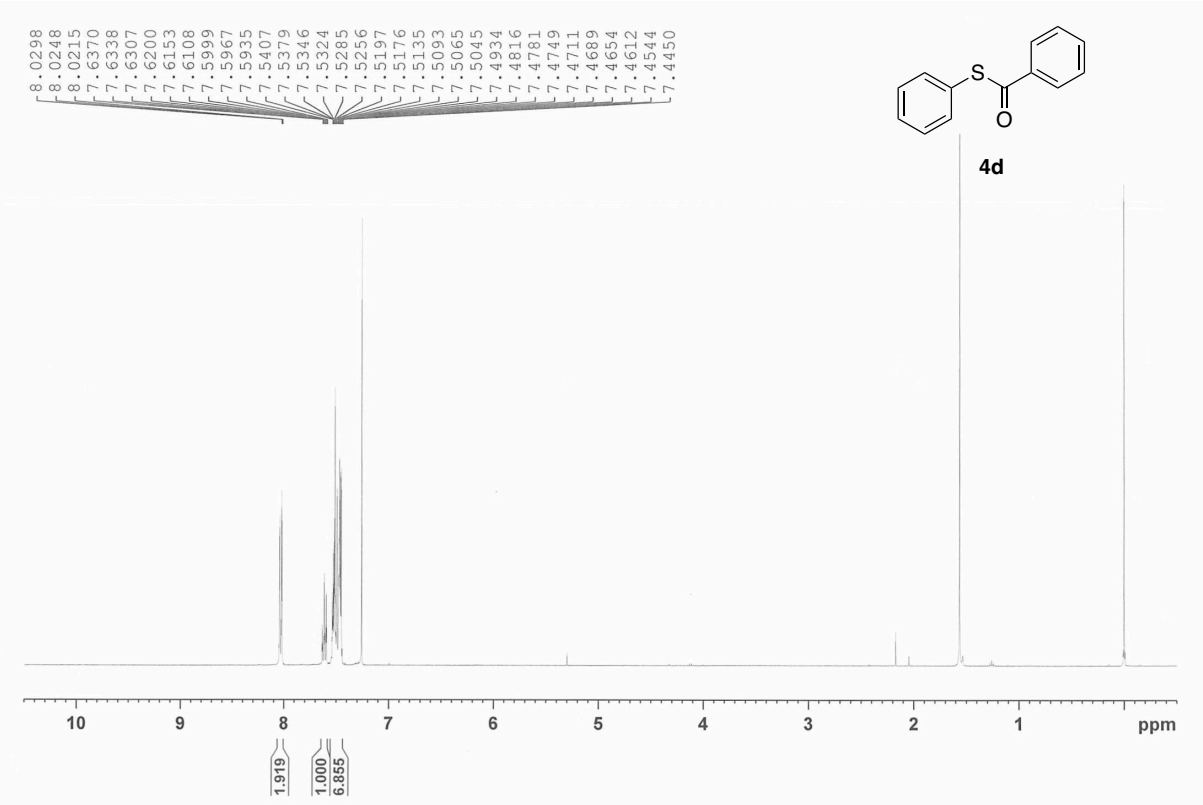
^{1}H NMR (400 MHz) spectrum of *S*-(4-methoxyphenyl) benzothioate (**4b**) ($CDCl_3$)



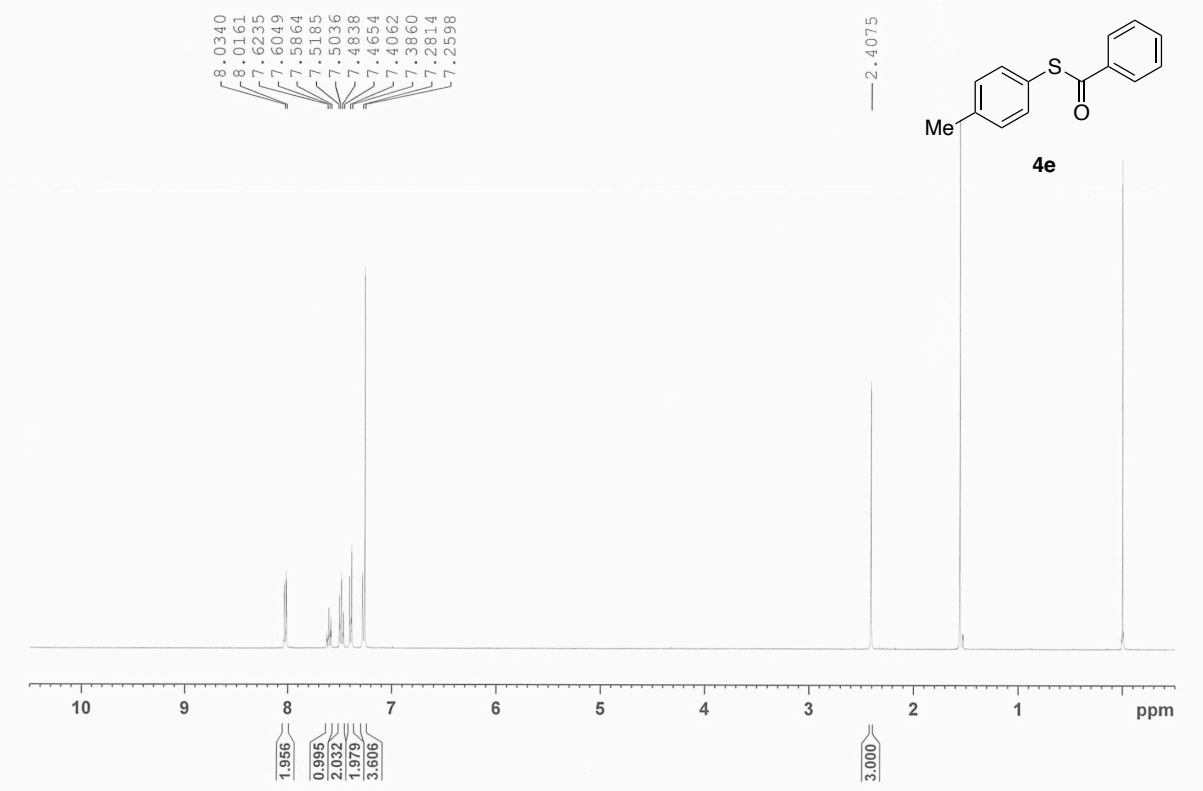
^{1}H NMR (400 MHz) spectrum of *S*-(4-chlorophenyl) benzothioate (**4c**) ($CDCl_3$)



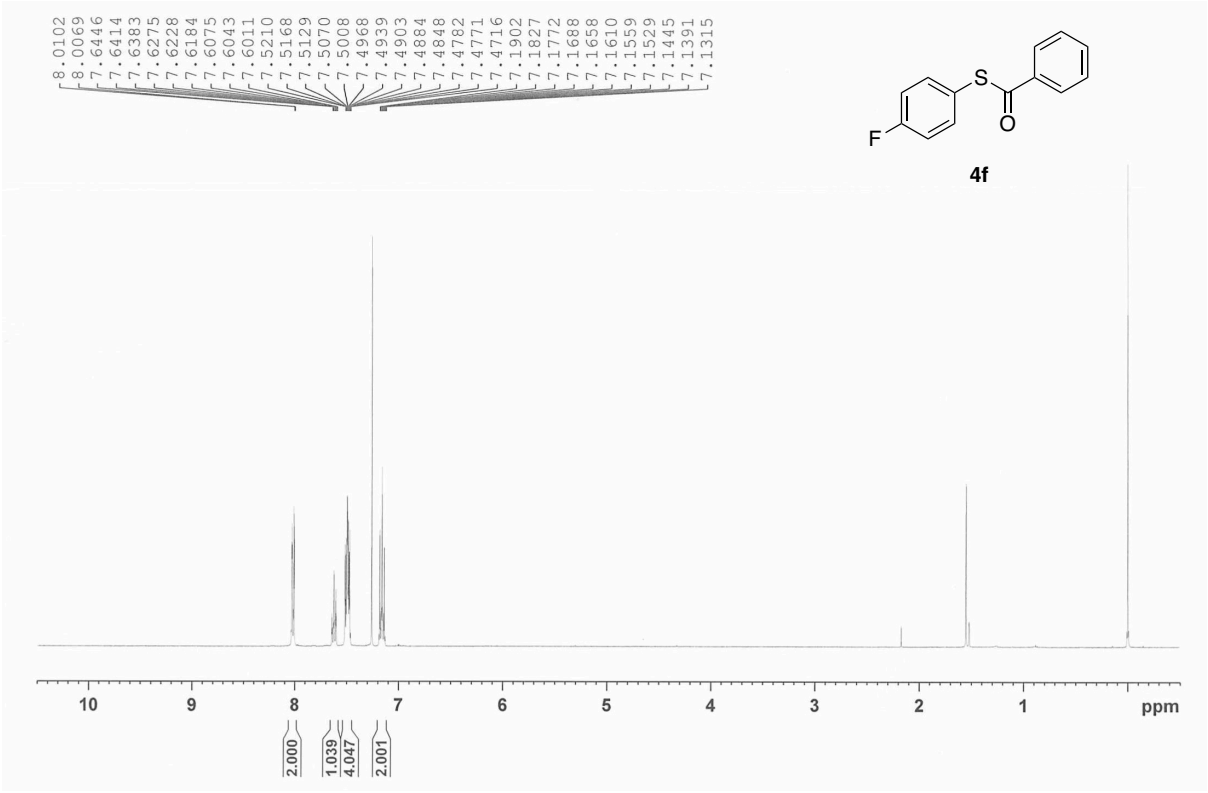
^{1}H NMR (400 MHz) spectrum of *S*-phenyl benzothioate (**4d**) ($CDCl_3$)



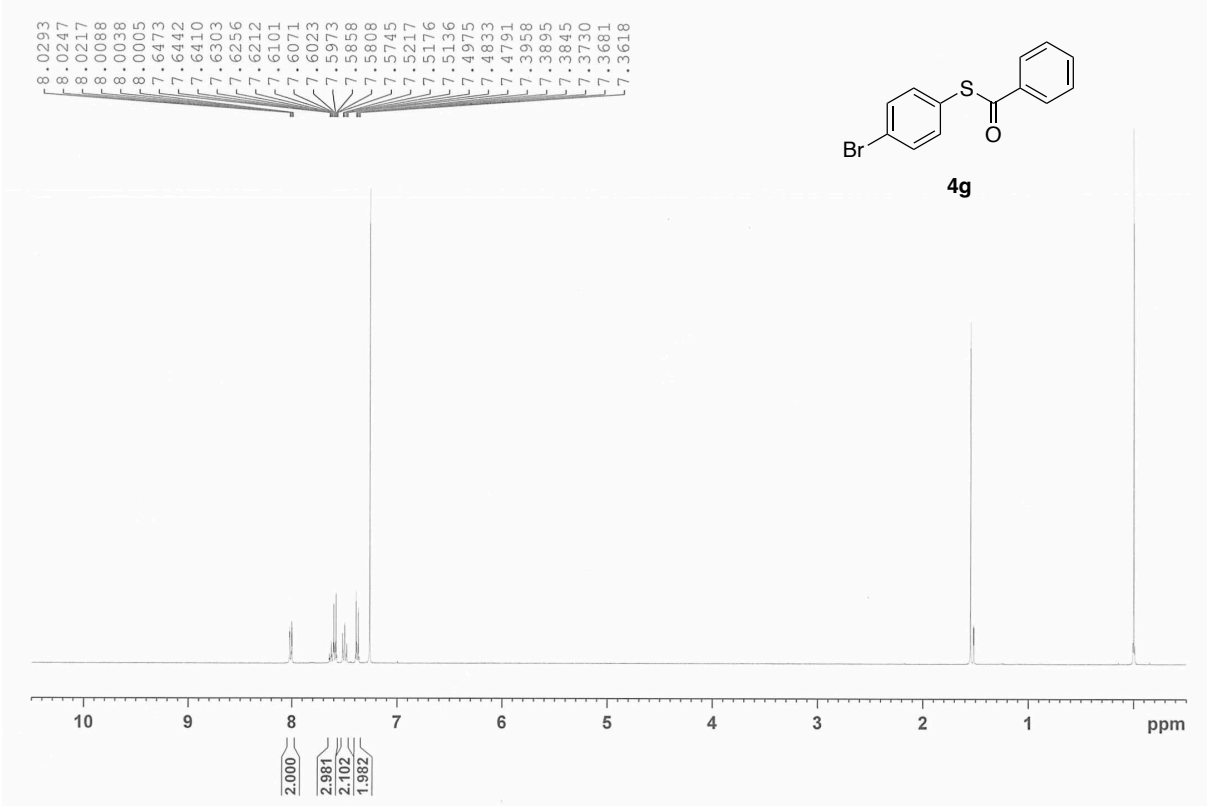
^{1}H NMR (400 MHz) spectrum of *S*-(4-methylphenyl) benzothioate (**4e**) ($CDCl_3$)



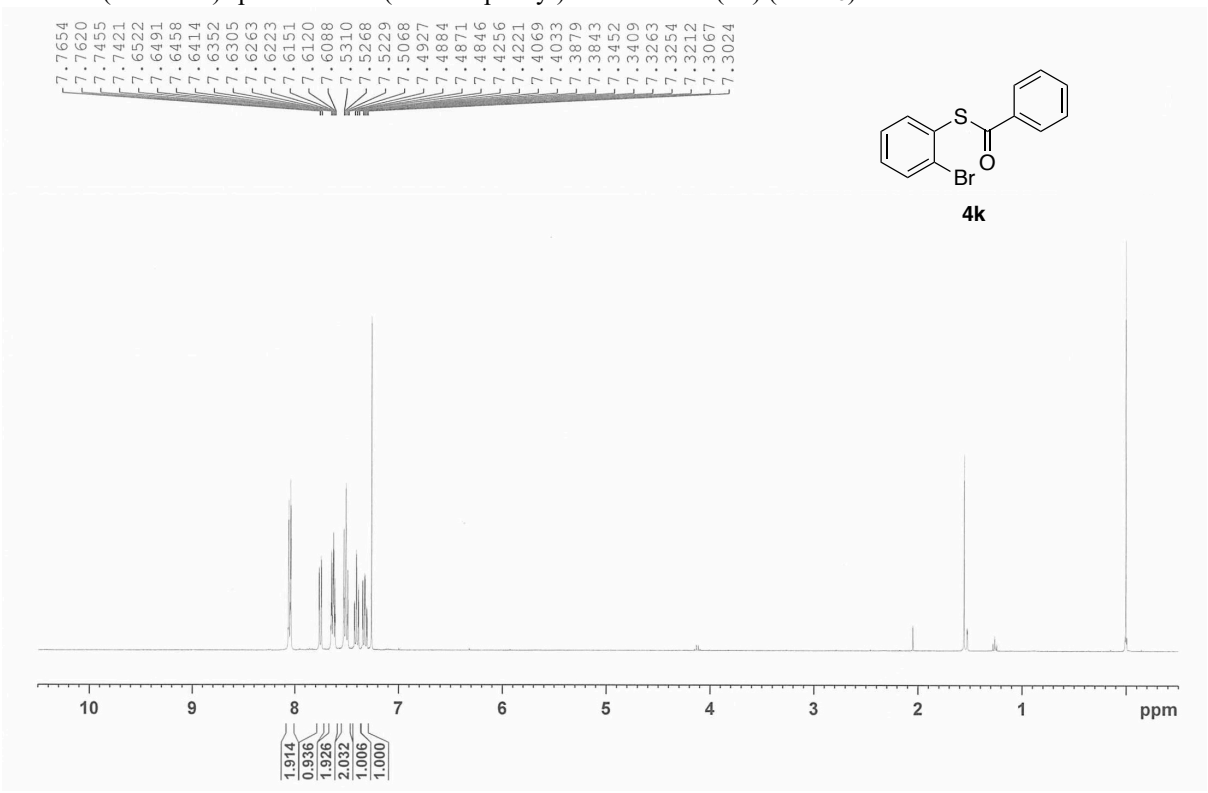
^{1}H NMR (400 MHz) spectrum of *S*-(4-fluorophenyl) benzothioate (**4f**) ($CDCl_3$)



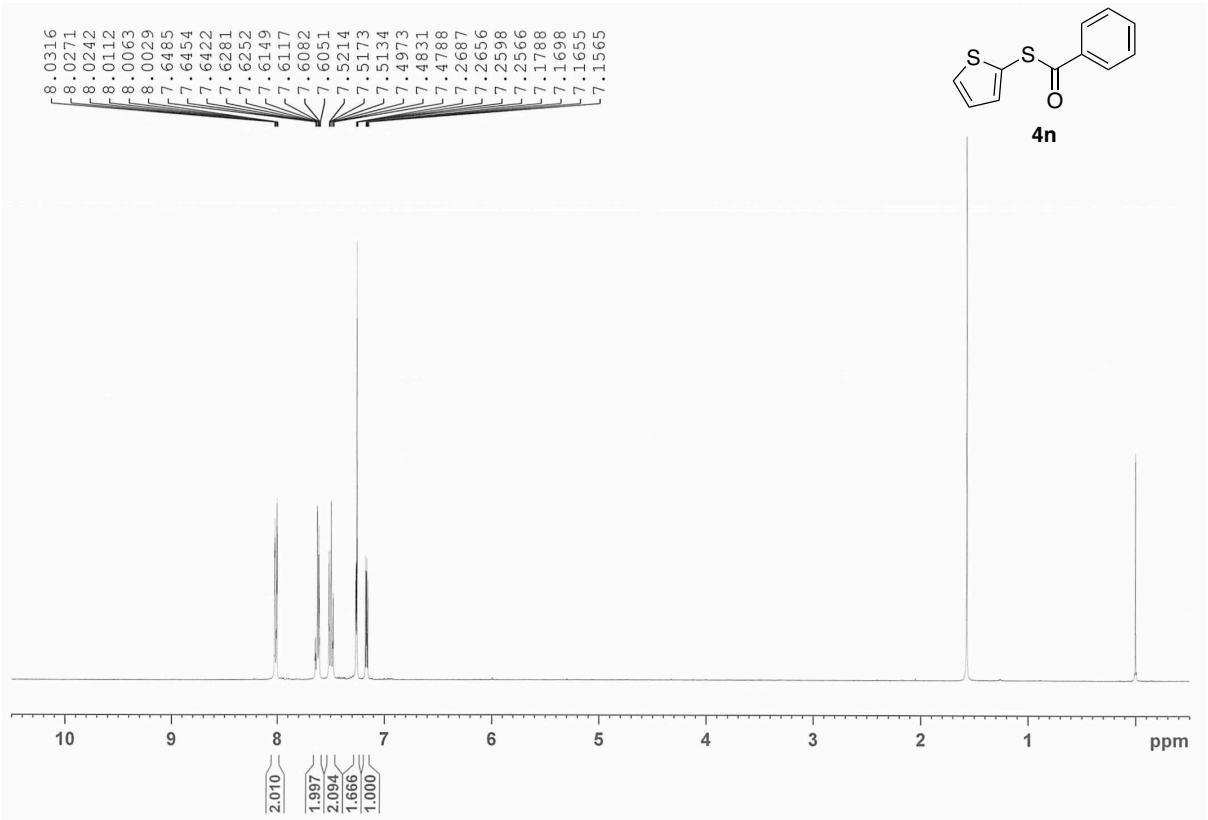
^{1}H NMR (400 MHz) spectrum of *S*-(4-bromophenyl) benzothioate (**4g**) ($CDCl_3$)



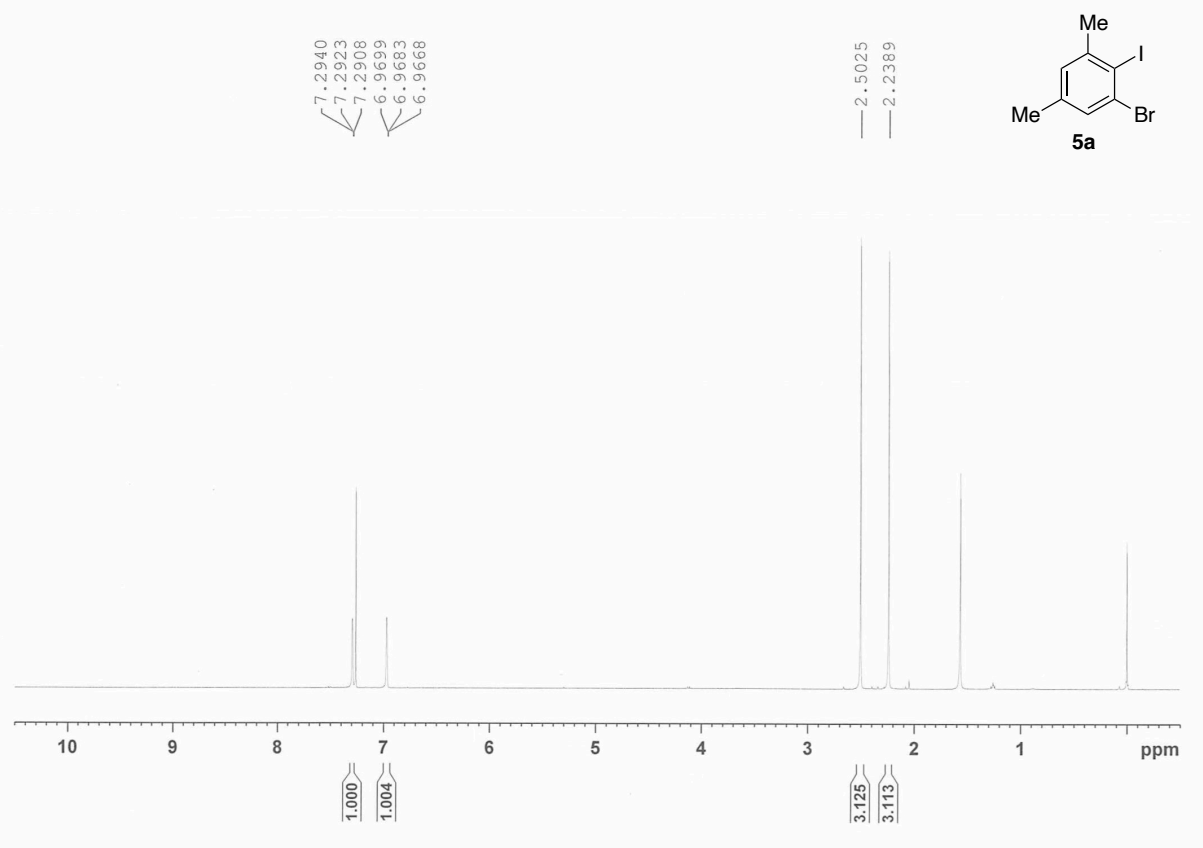
^{1}H NMR (400 MHz) spectrum of *S*-(2-bromophenyl) benzothioate (**4k**) ($CDCl_3$)



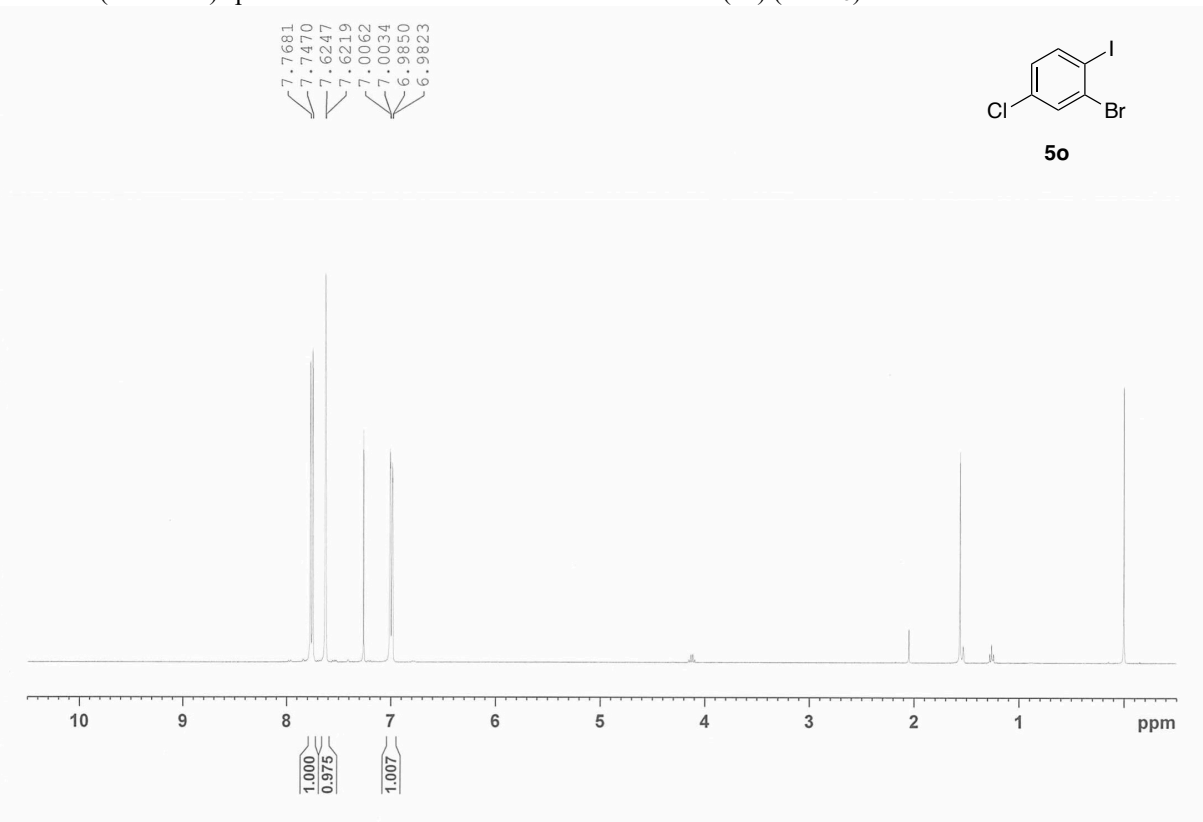
^{1}H NMR (400 MHz) spectrum of *S*-(2-thienyl) benzothioate (**4n**) ($CDCl_3$)



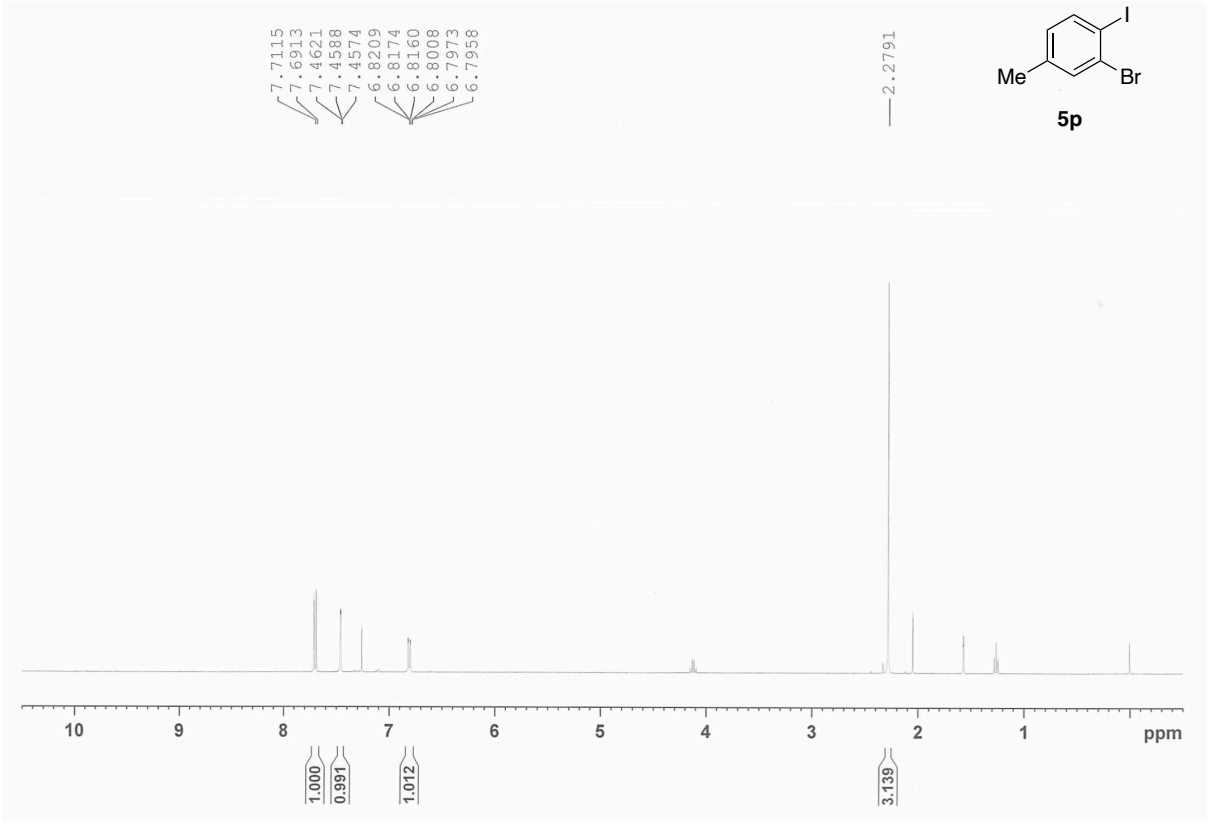
^{1}H NMR (400 MHz) spectrum of 2-bromo-4,6-dimethyl-1-iodobenzene (**5a**) ($CDCl_3$)



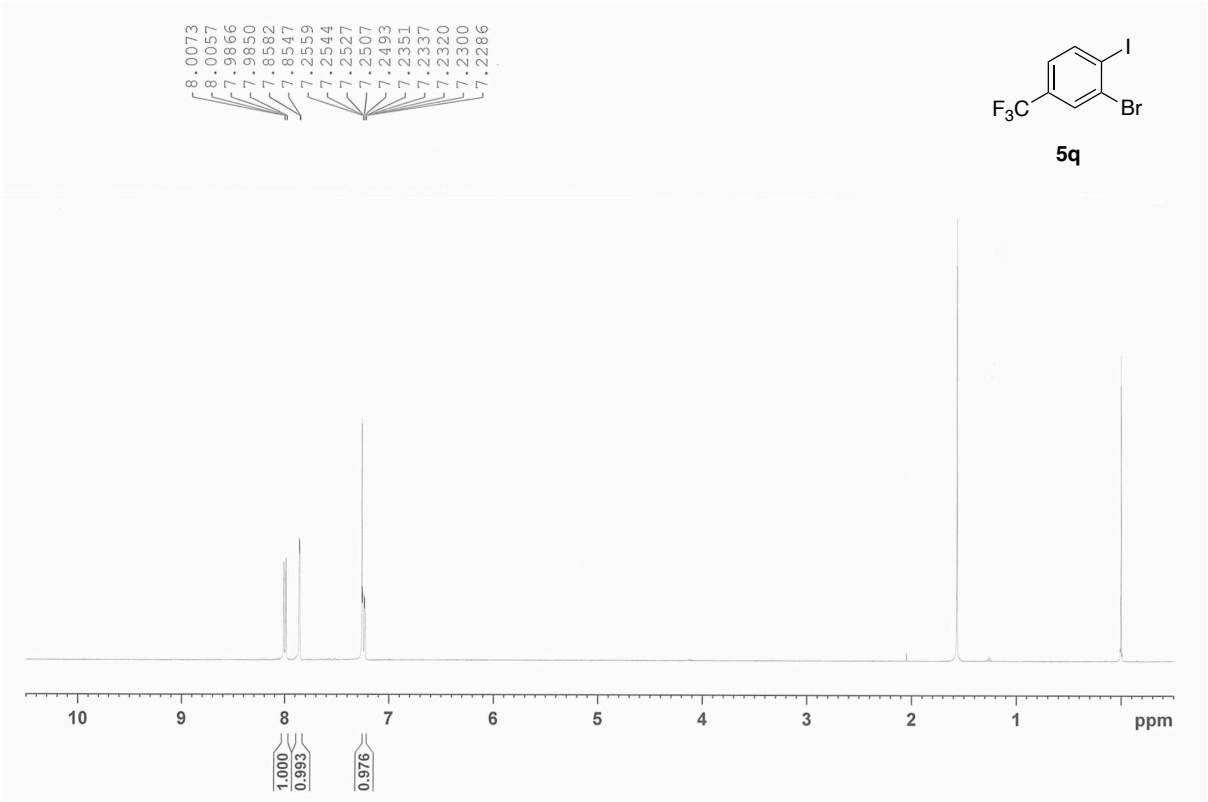
^{1}H NMR (400 MHz) spectrum of 2-bromo-4-chloro-1-iodobenzene (**5o**) ($CDCl_3$)



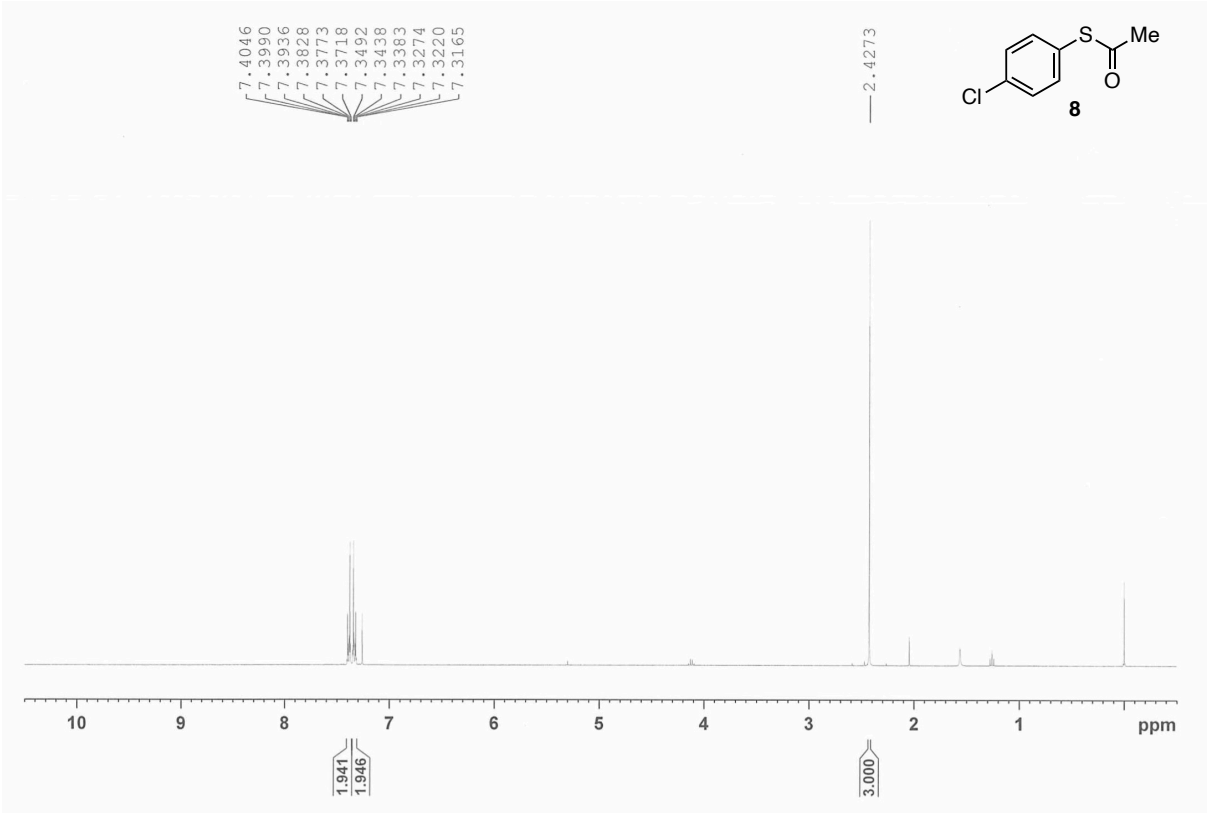
^{1}H NMR (400 MHz) spectrum of 2-bromo-1-iodo-4-methylbenzene (**5p**) ($CDCl_3$)



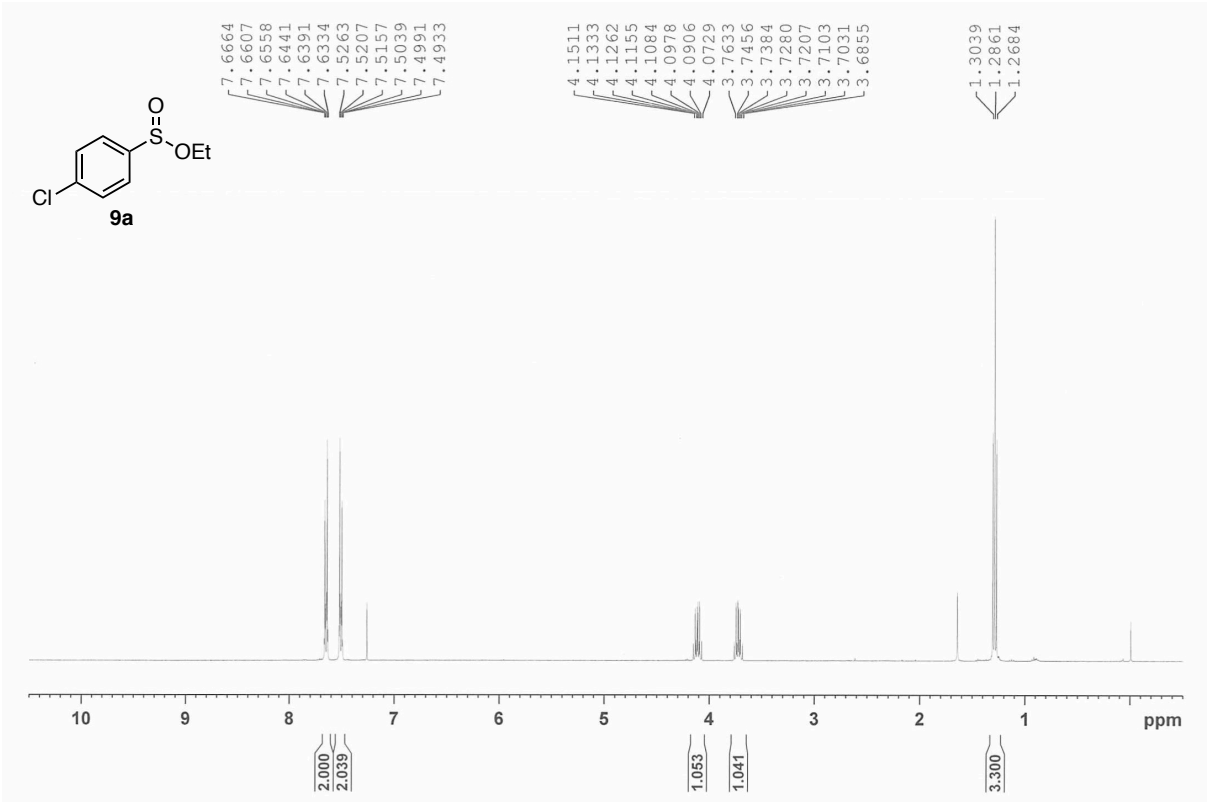
^{1}H NMR (400 MHz) spectrum of 2-bromo-1-iodo-4-(trifluoromethyl)benzene (**5q**) ($CDCl_3$)



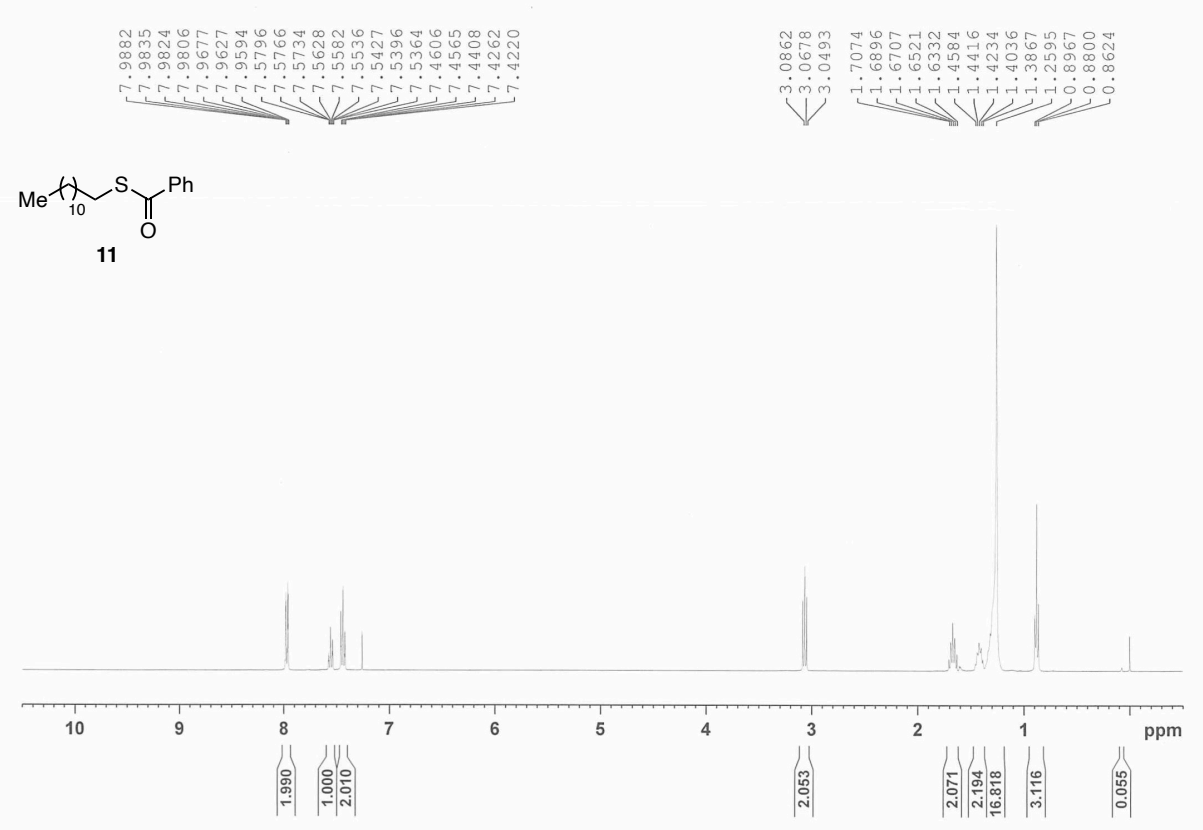
^{1}H NMR (400 MHz) spectrum of *S*-(4-chlorophenyl) thioacetate (**8**) ($CDCl_3$)



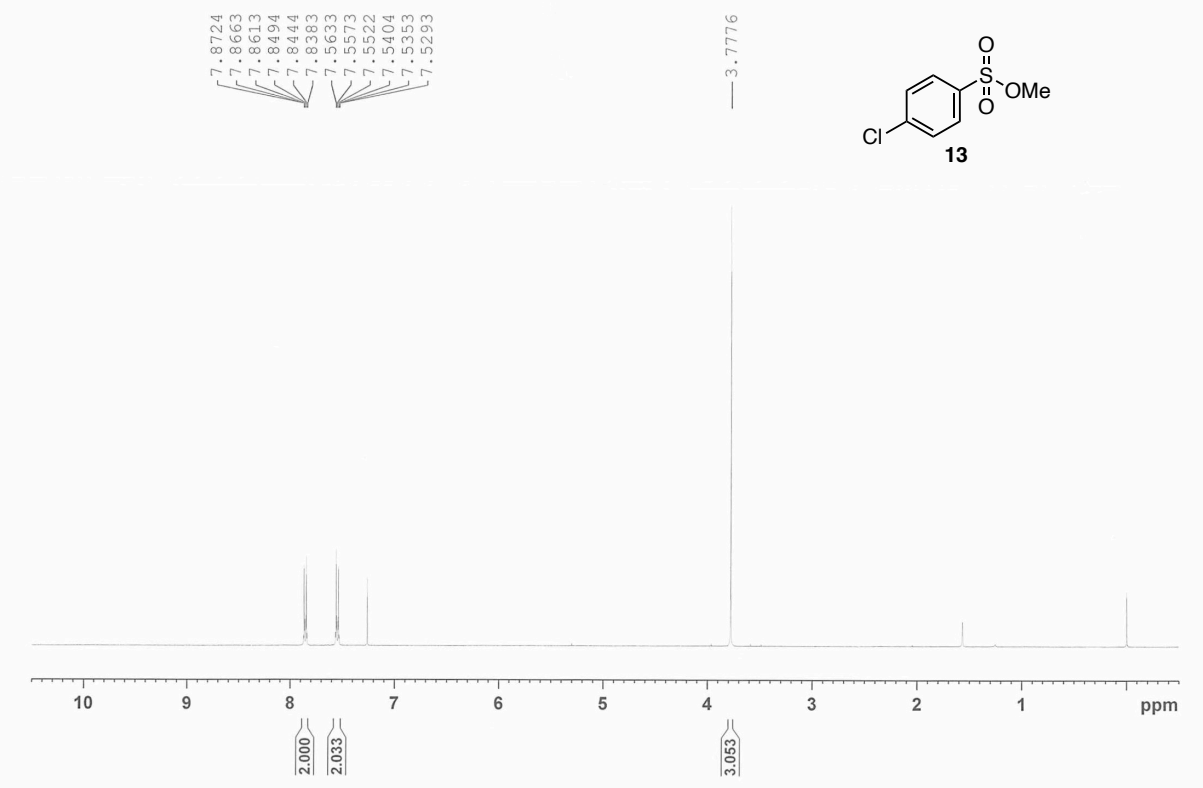
^{1}H NMR (400 MHz) spectrum of ethyl 4-chlorobenzene sulfinate (**9a**) ($CDCl_3$)



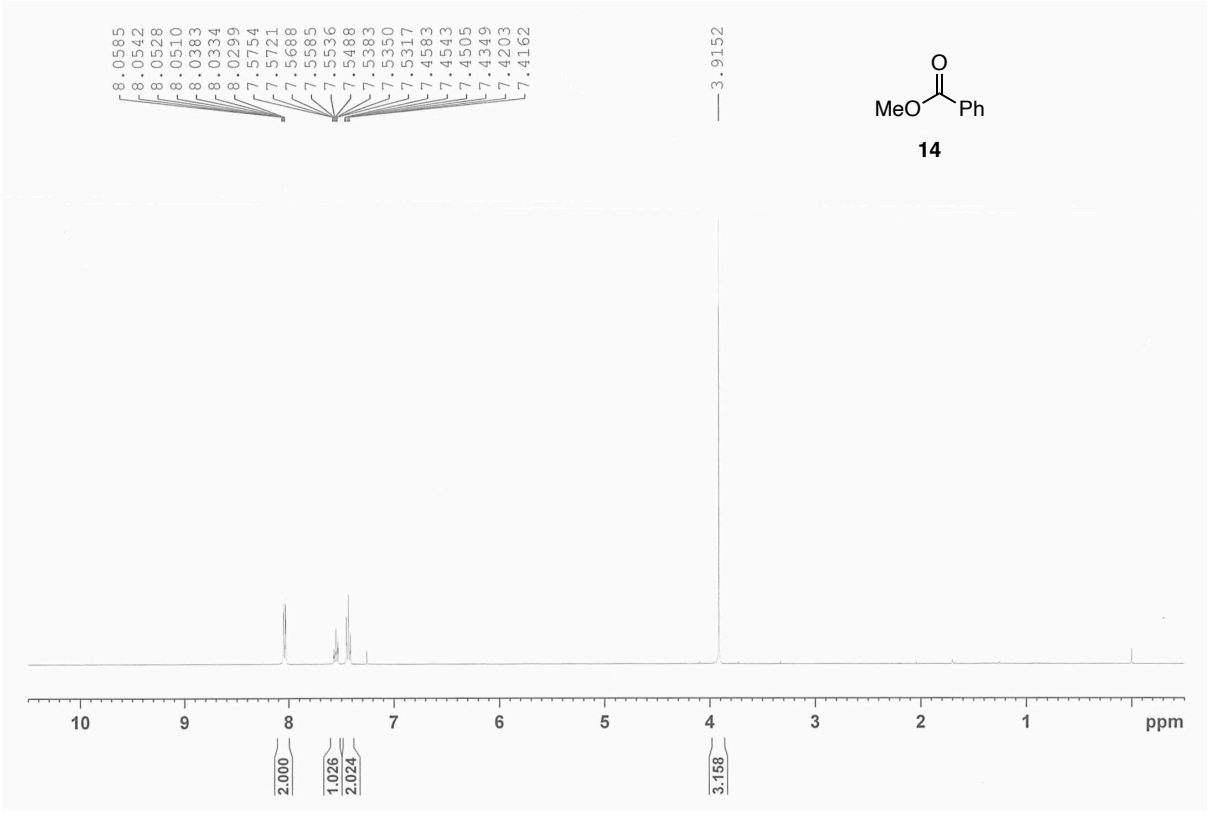
^{1}H NMR (400 MHz) spectrum of *S*-*n*-decyl benzoate (**11**) ($CDCl_3$)



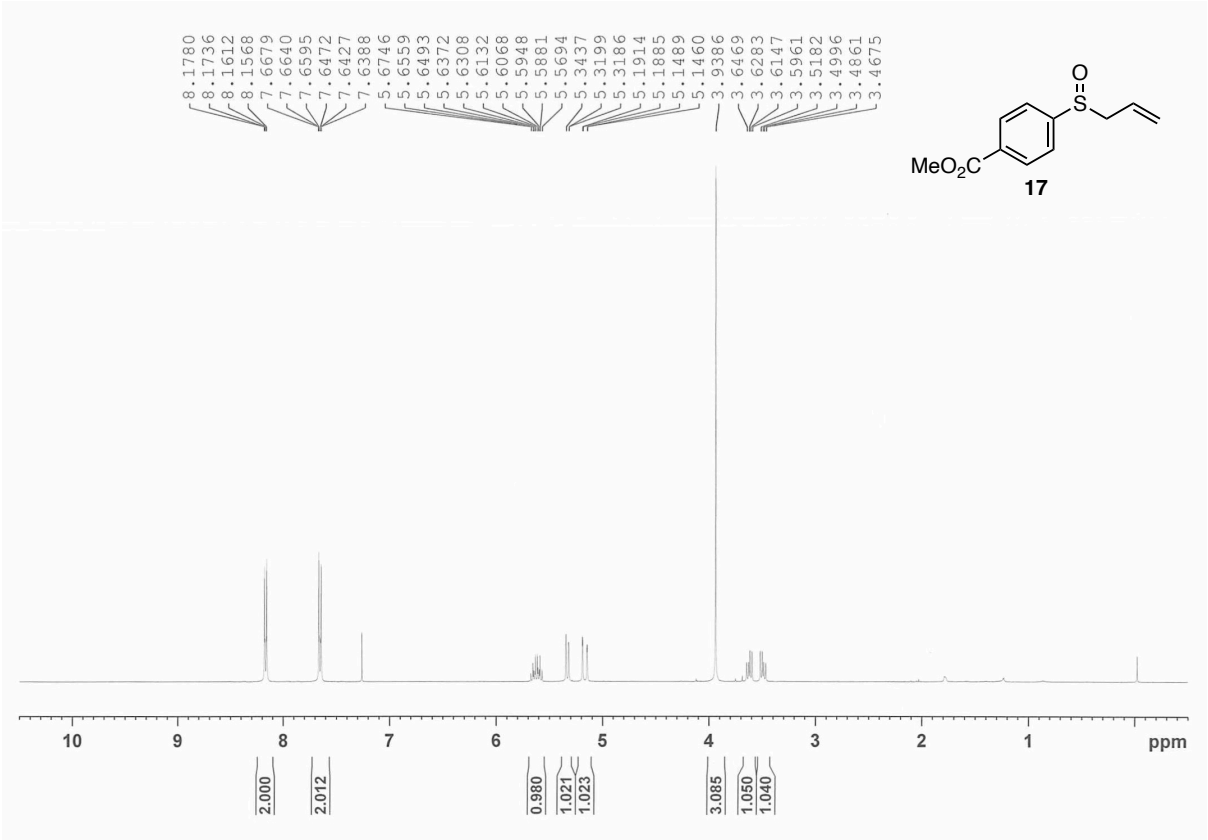
^{1}H NMR (400 MHz) spectrum of methyl 4-chlorobenzenesulfonate (**13**) ($CDCl_3$)



^{1}H NMR (400 MHz) spectrum of methyl benzoate (**14**) ($CDCl_3$)

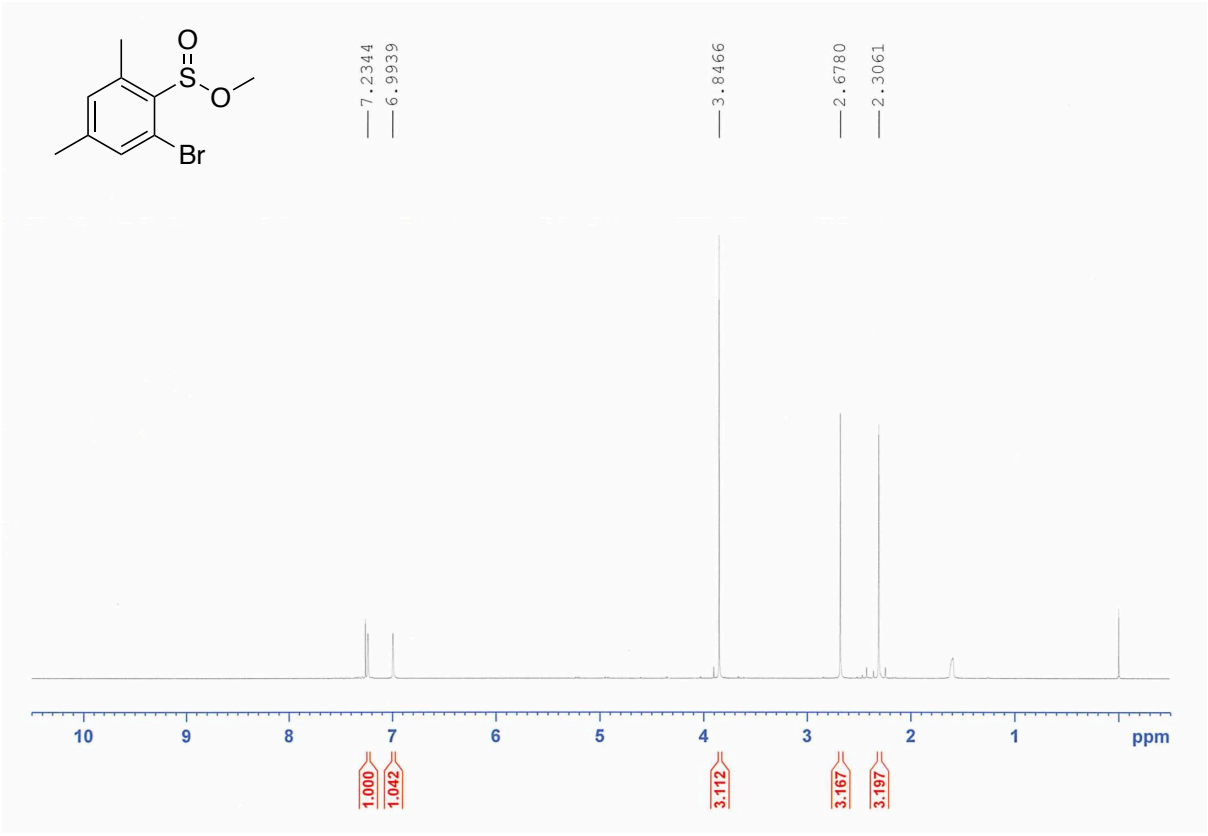


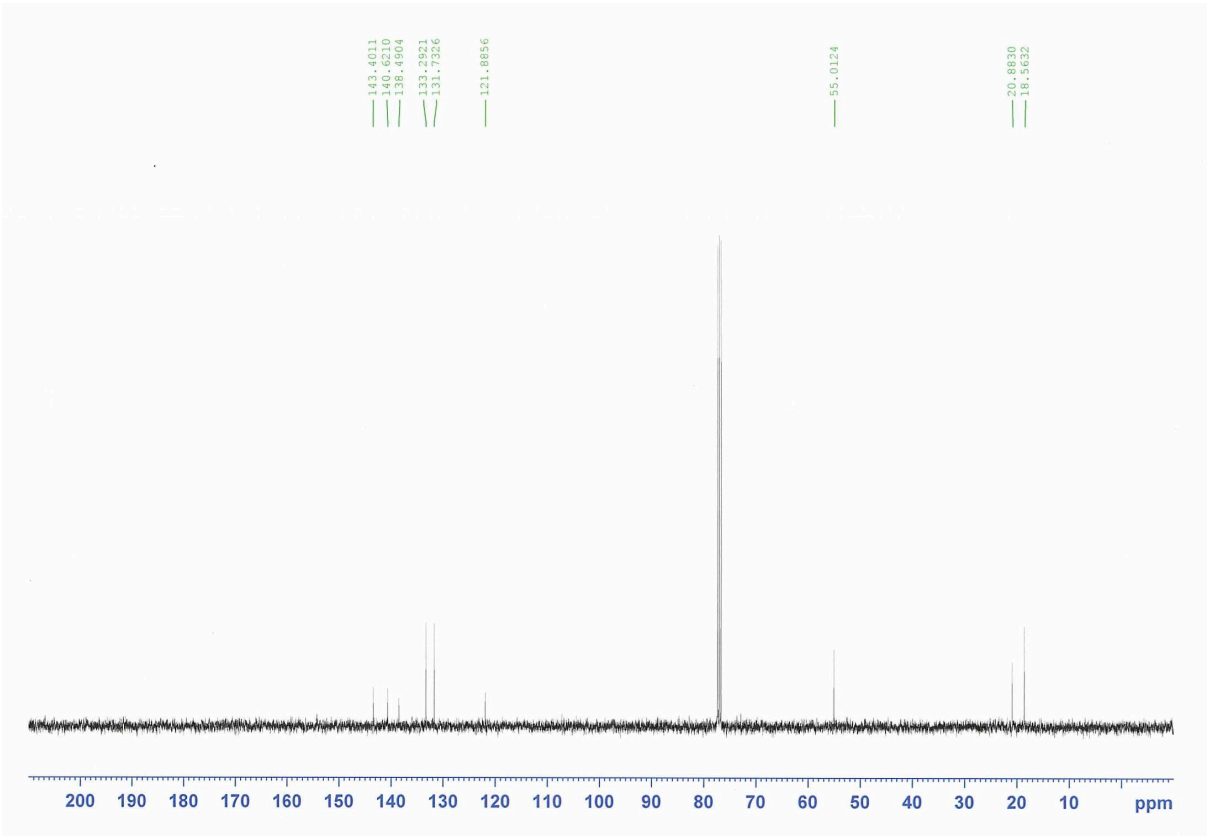
^{1}H NMR (400 MHz) spectrum of allyl 4-(methoxycarbonyl)phenyl sulfoxide (**17**) ($CDCl_3$)



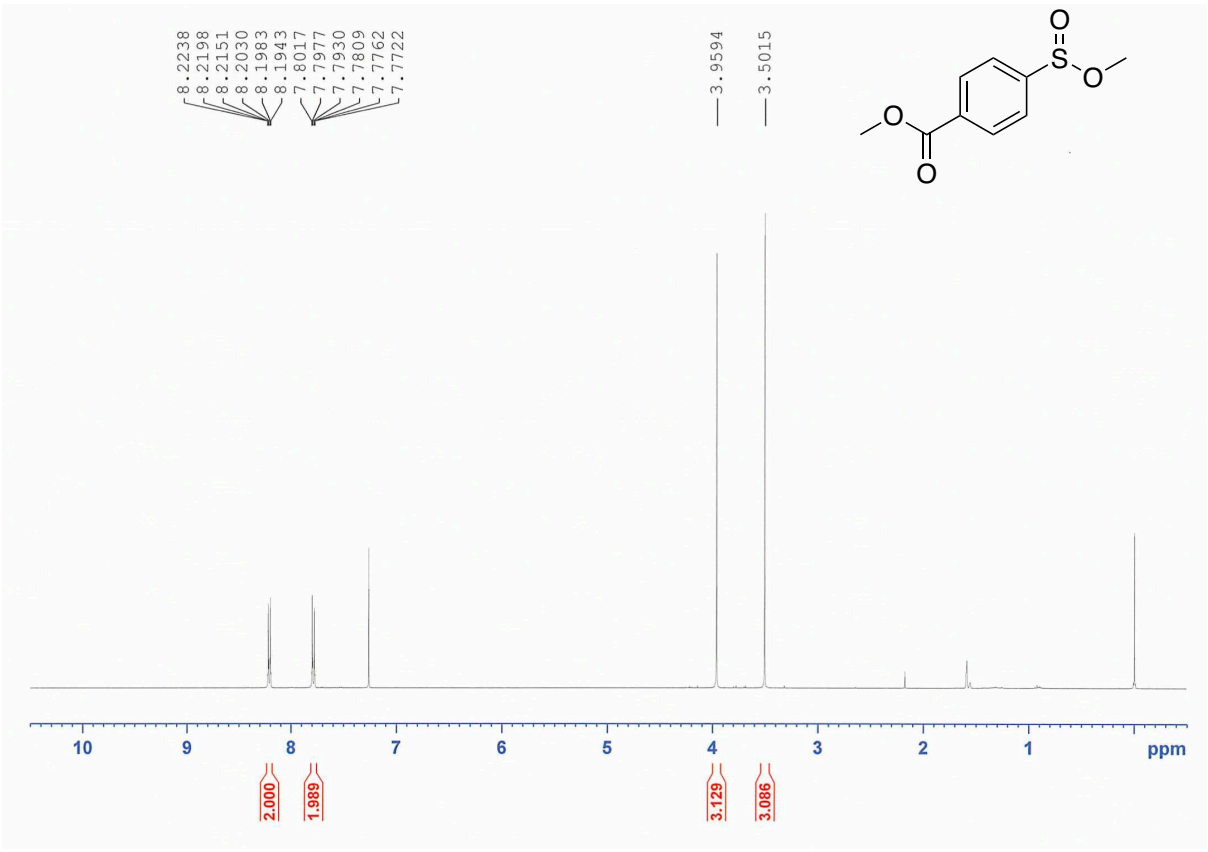
^{1}H and ^{13}C NMR Spectra of Compounds

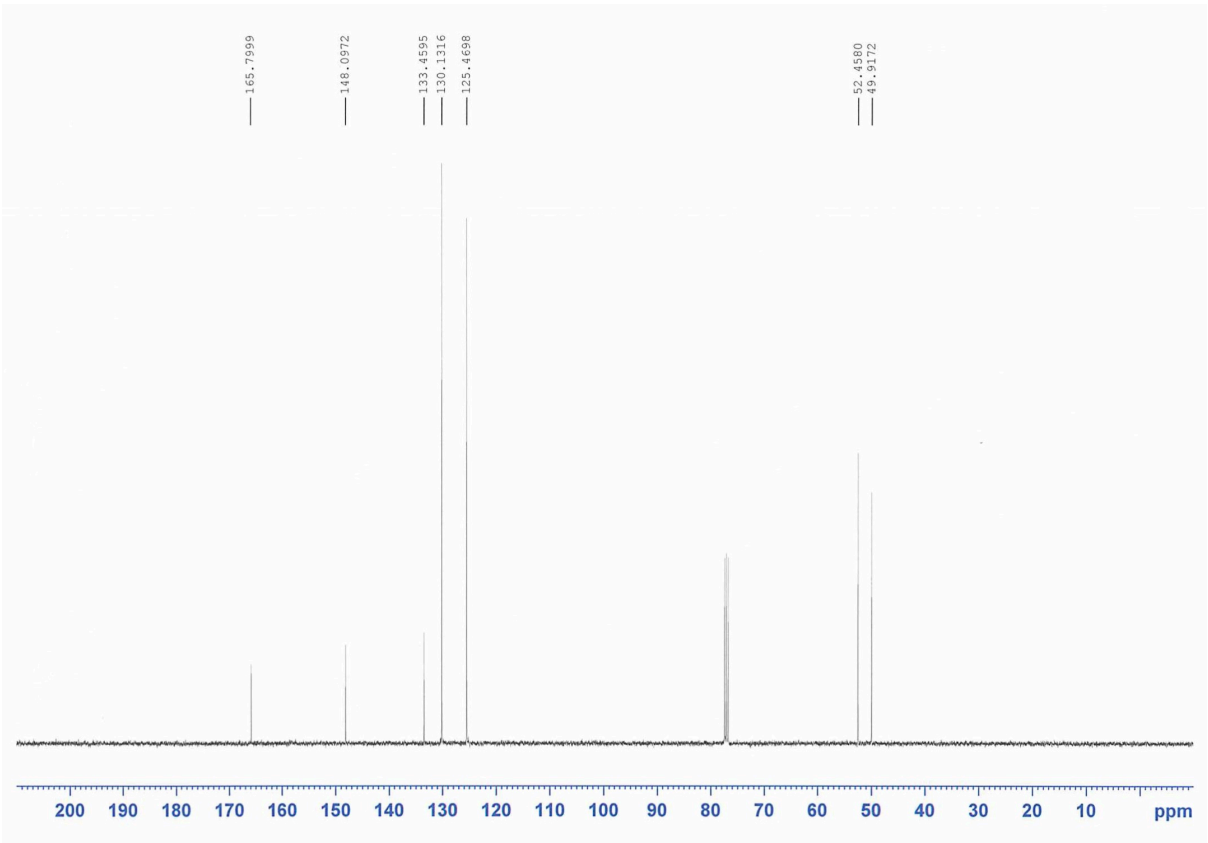
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of methyl 2-bromo-4,6-dimethylbenzenesulfinate (**3a**) ($CDCl_3$)



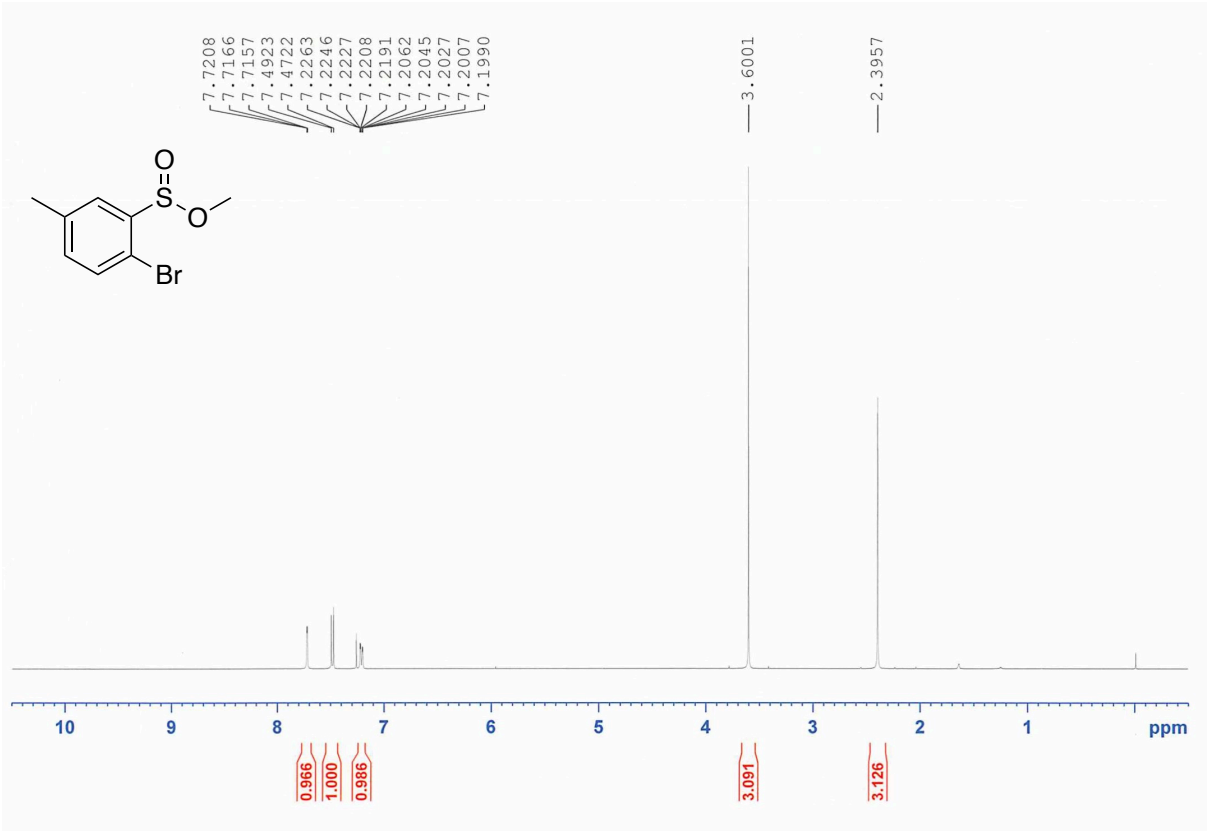


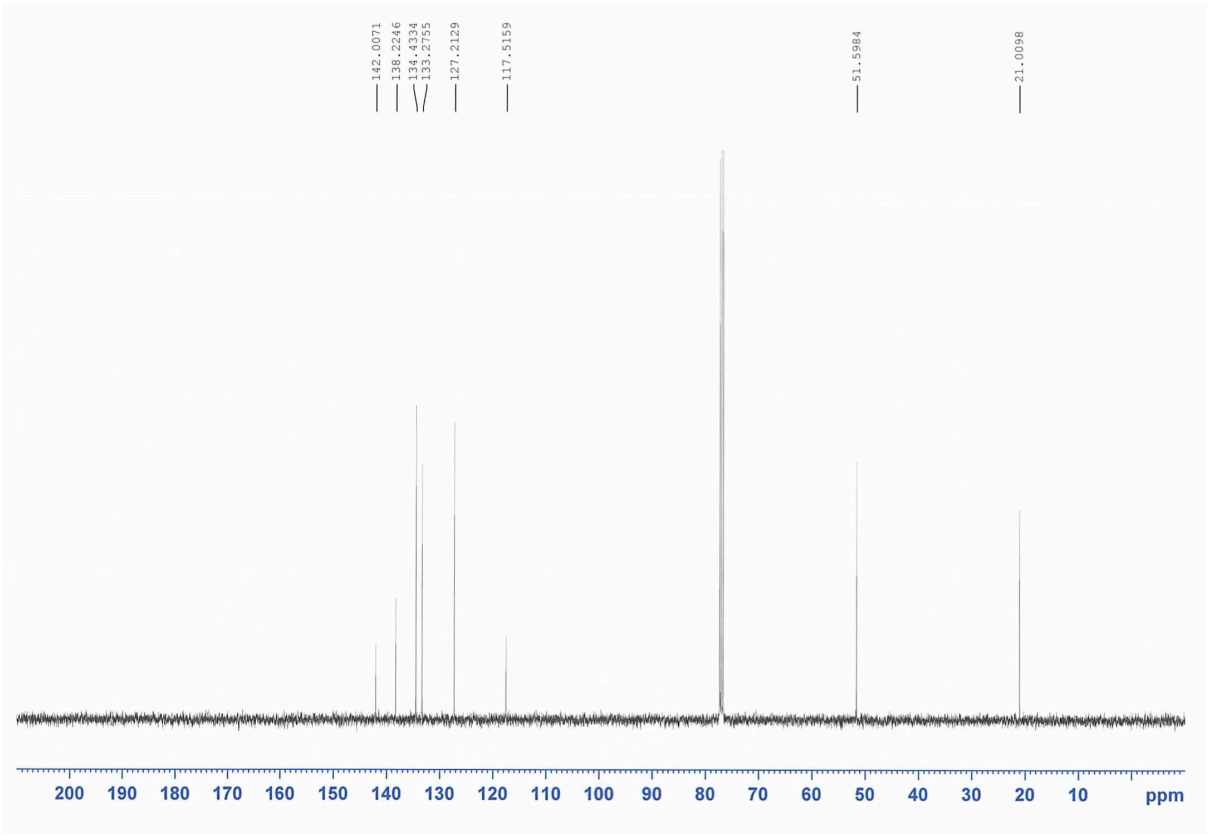
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of methyl 4-(methoxycarbonyl)benzene sulfinate (**3i**) ($CDCl_3$)



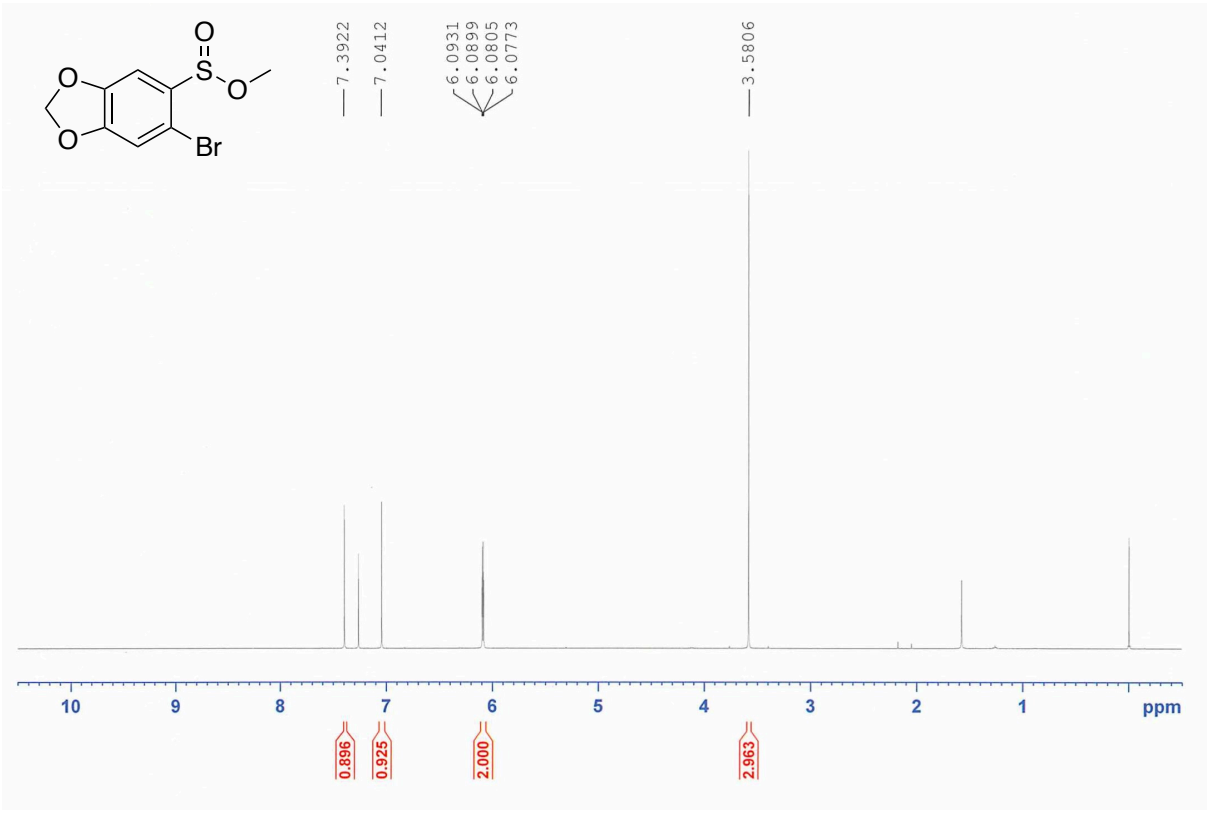


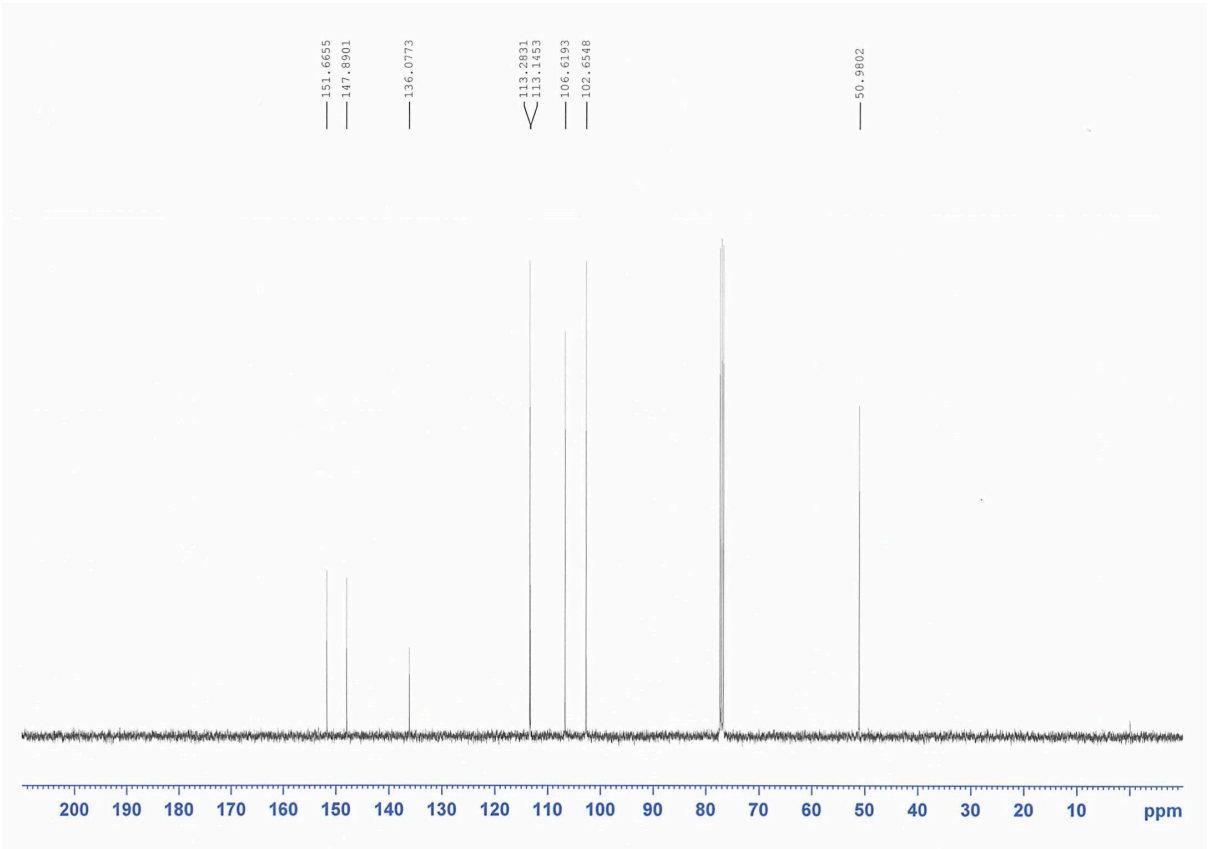
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of methyl 2-bromo-5-methylbenzenesulfinate (**3l**) ($CDCl_3$)



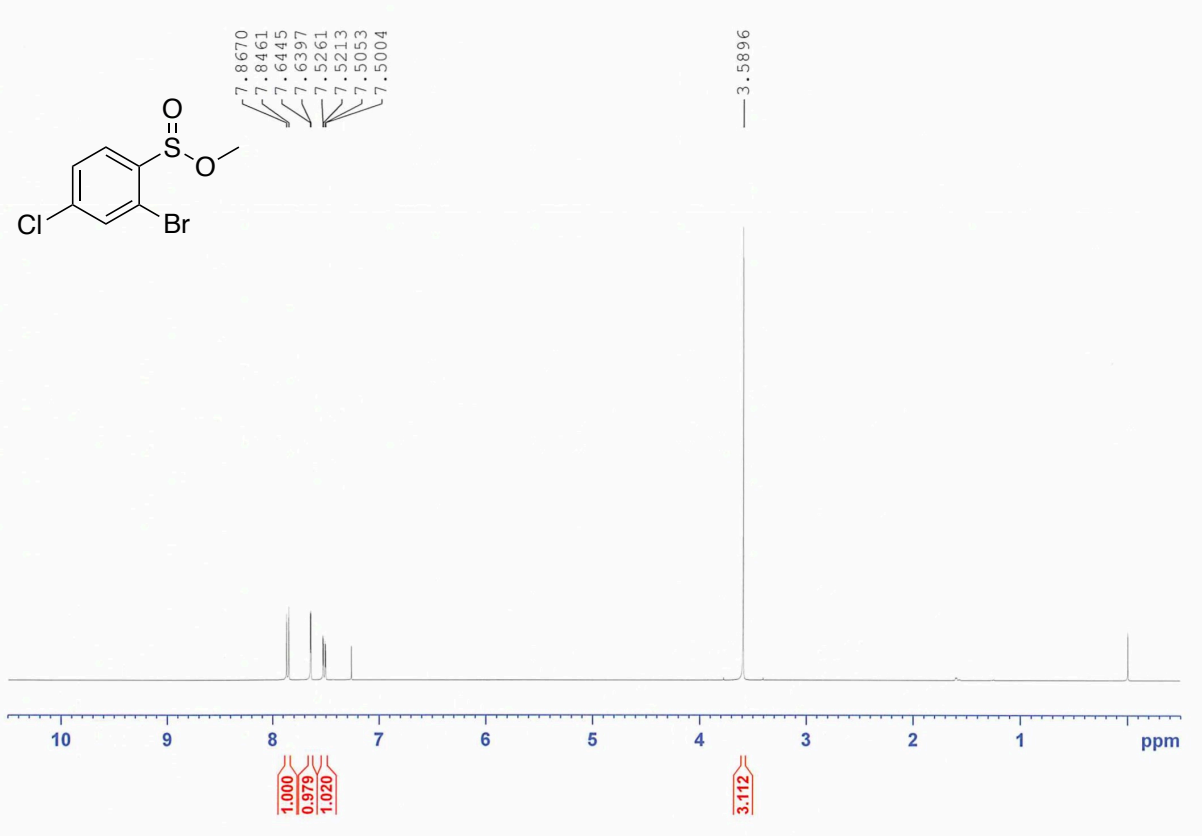


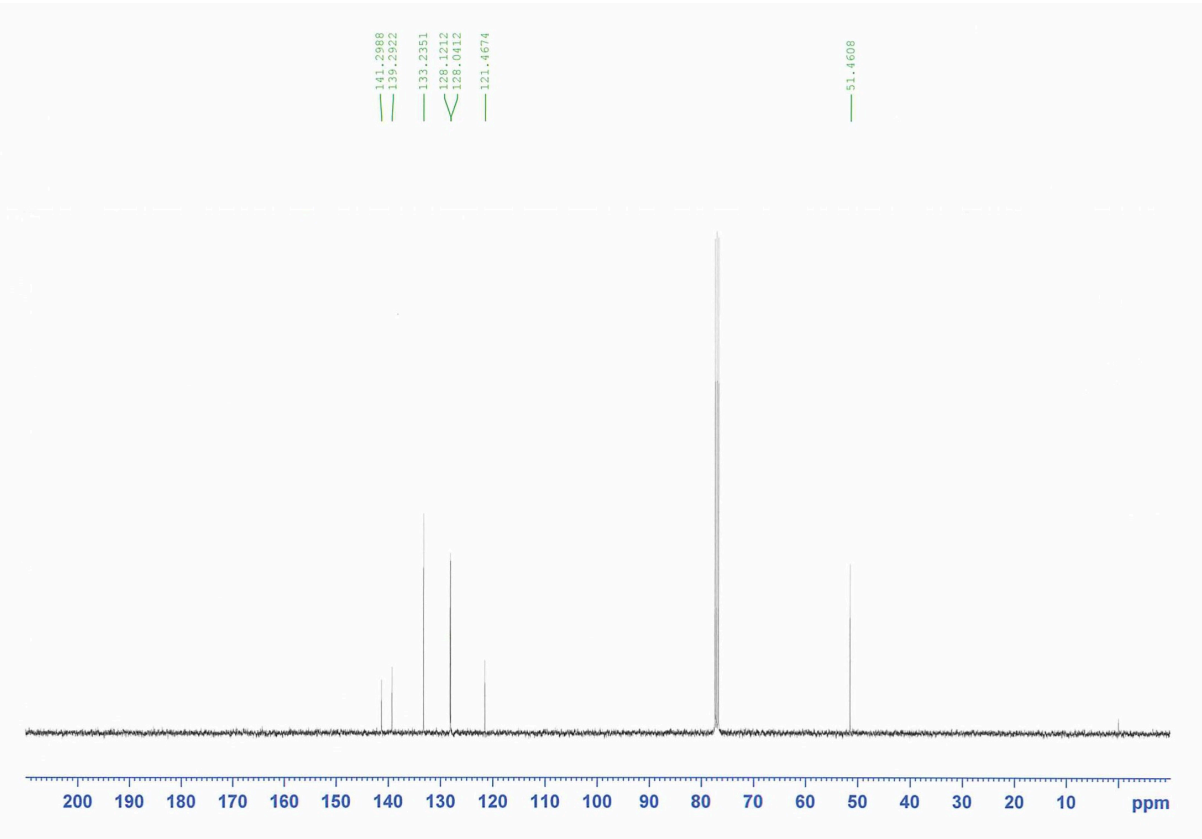
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of methyl 6-bromobenzo[*d*][1,3]dioxole-5-sulfinate (**3m**) ($CDCl_3$)



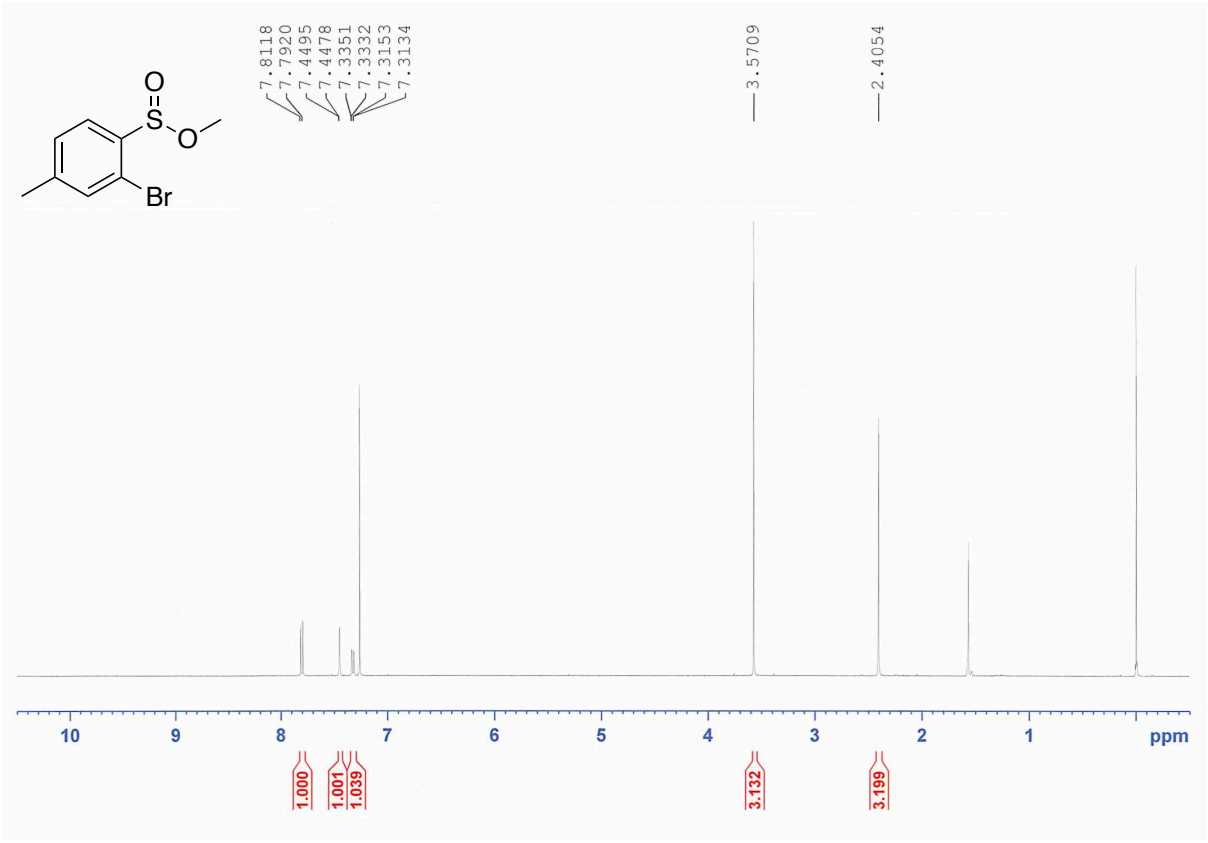


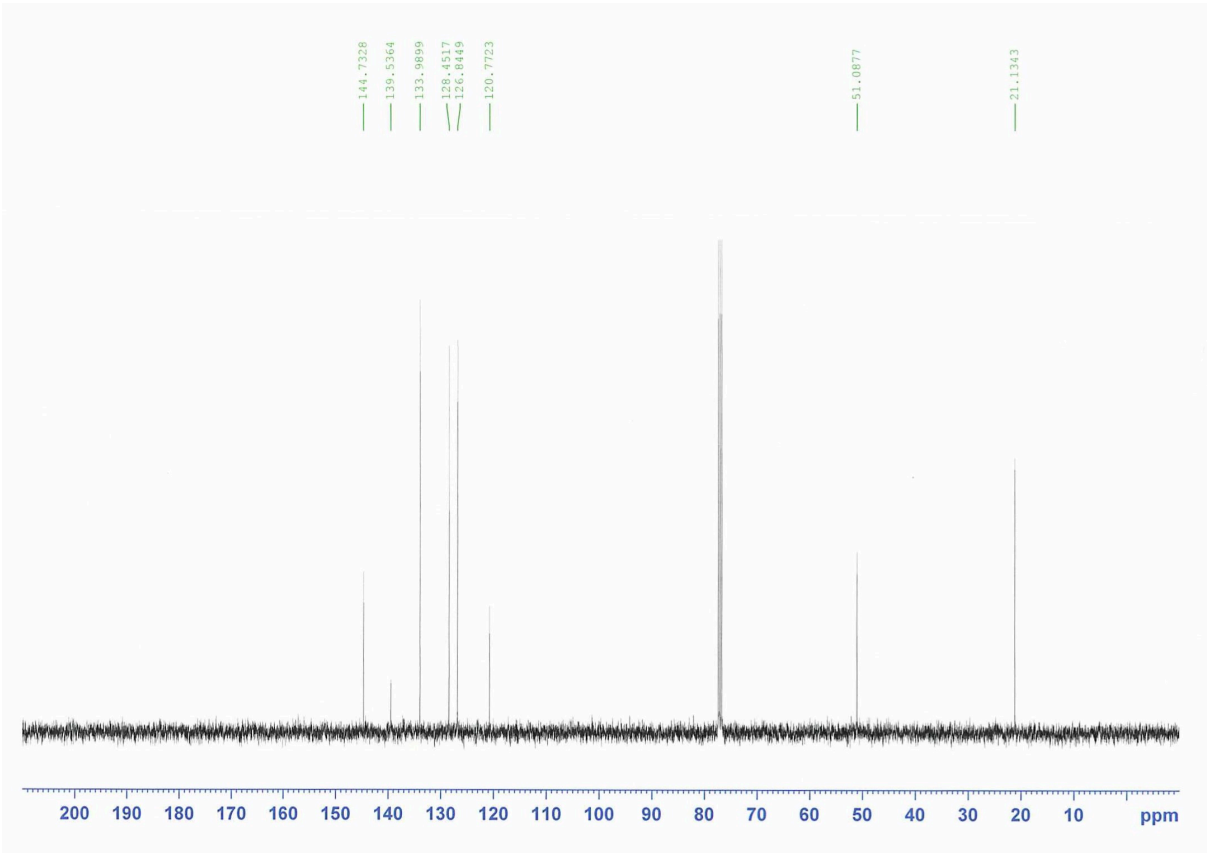
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of methyl 2-bromo-4-chlorobenzenesulfinate (**3o**) ($CDCl_3$)



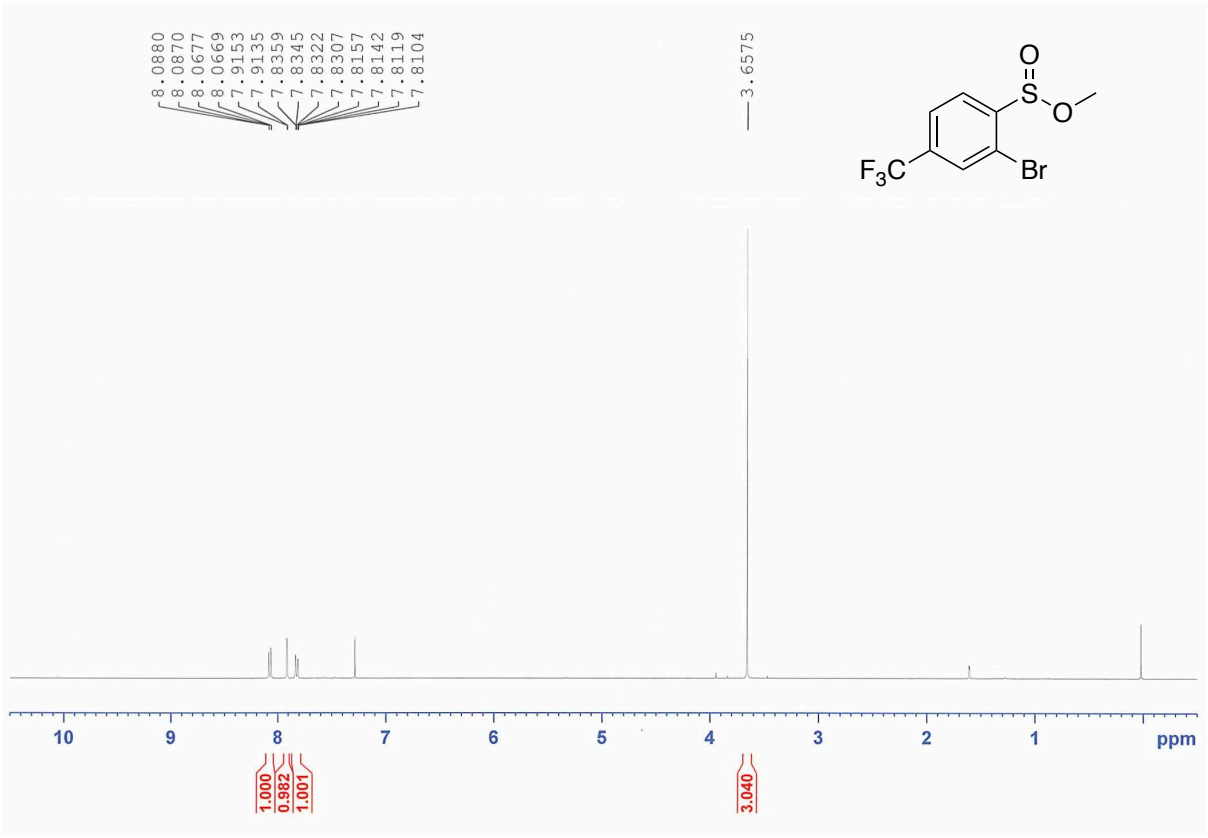


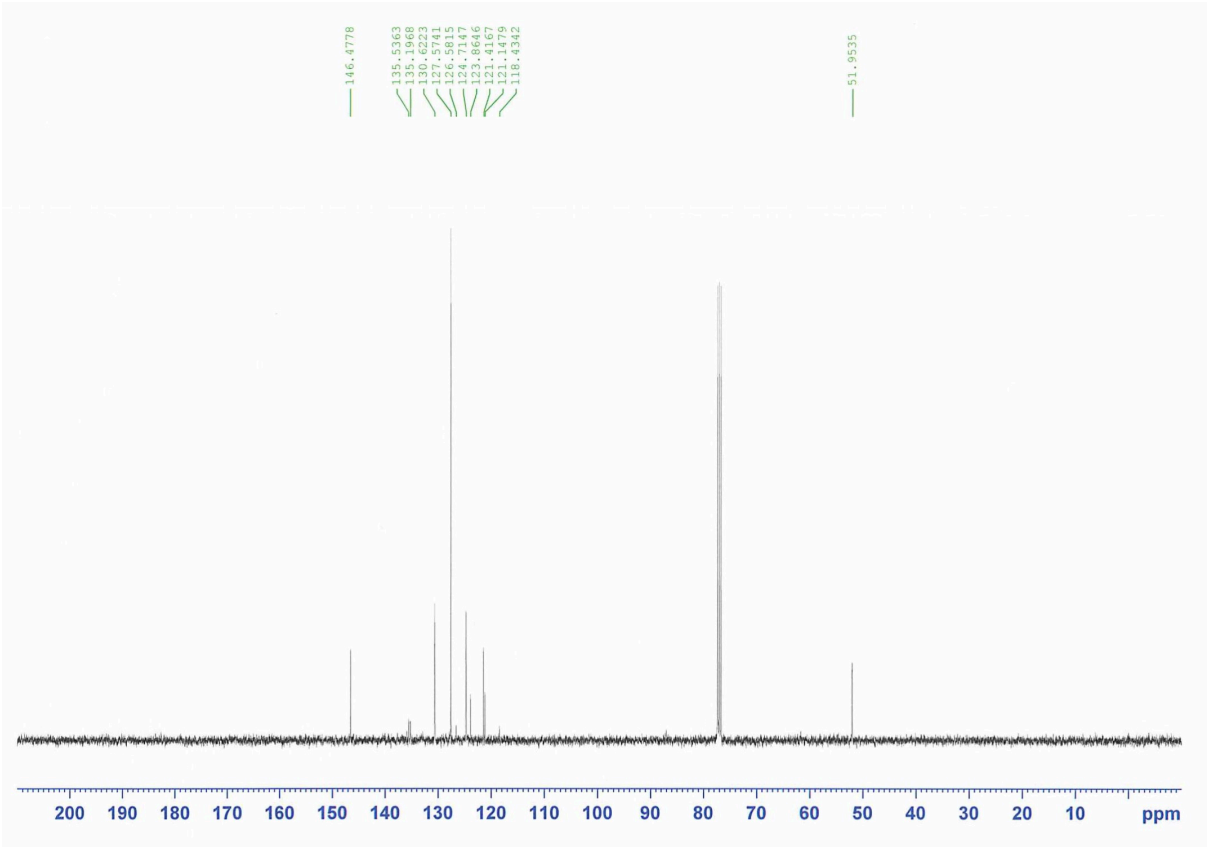
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of methyl 2-bromo-4-methylbenzenesulfinate (**3p**) ($CDCl_3$)



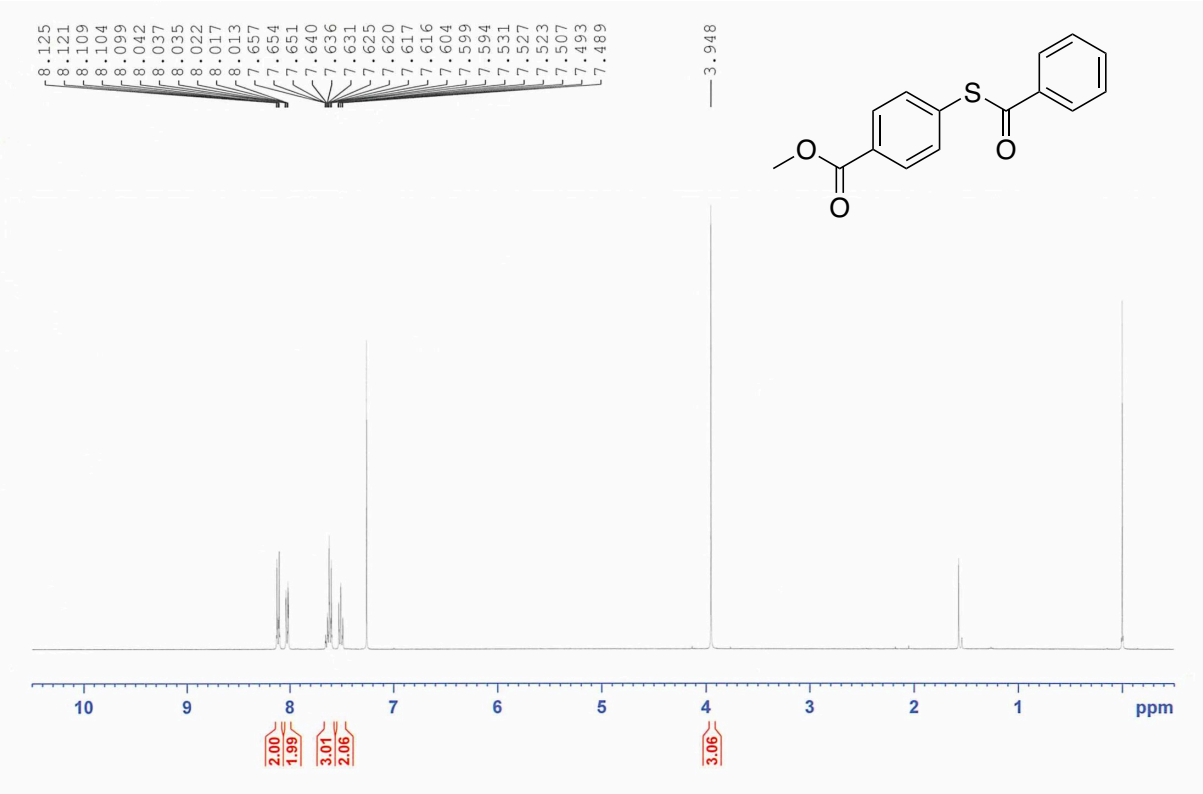


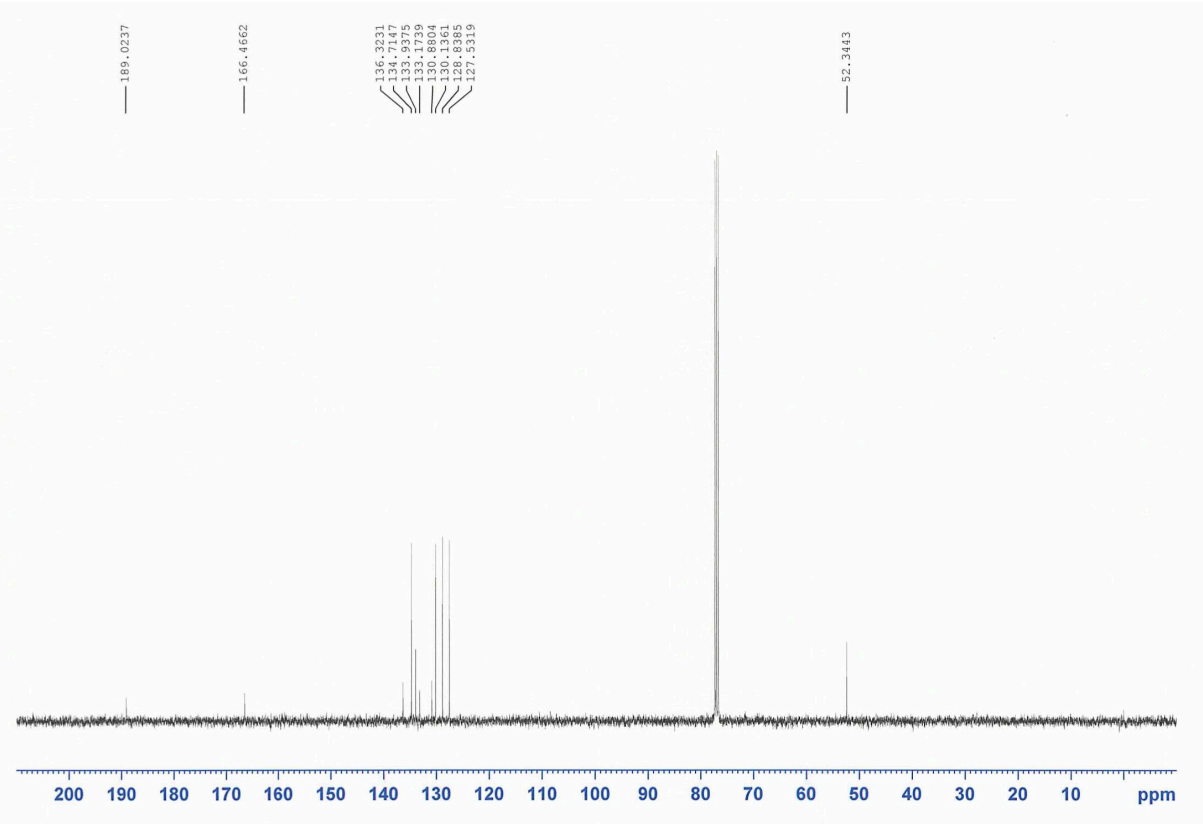
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of methyl 2-bromo-4-(trifluoromethyl)benzenesulfinate (**3q**) ($CDCl_3$)



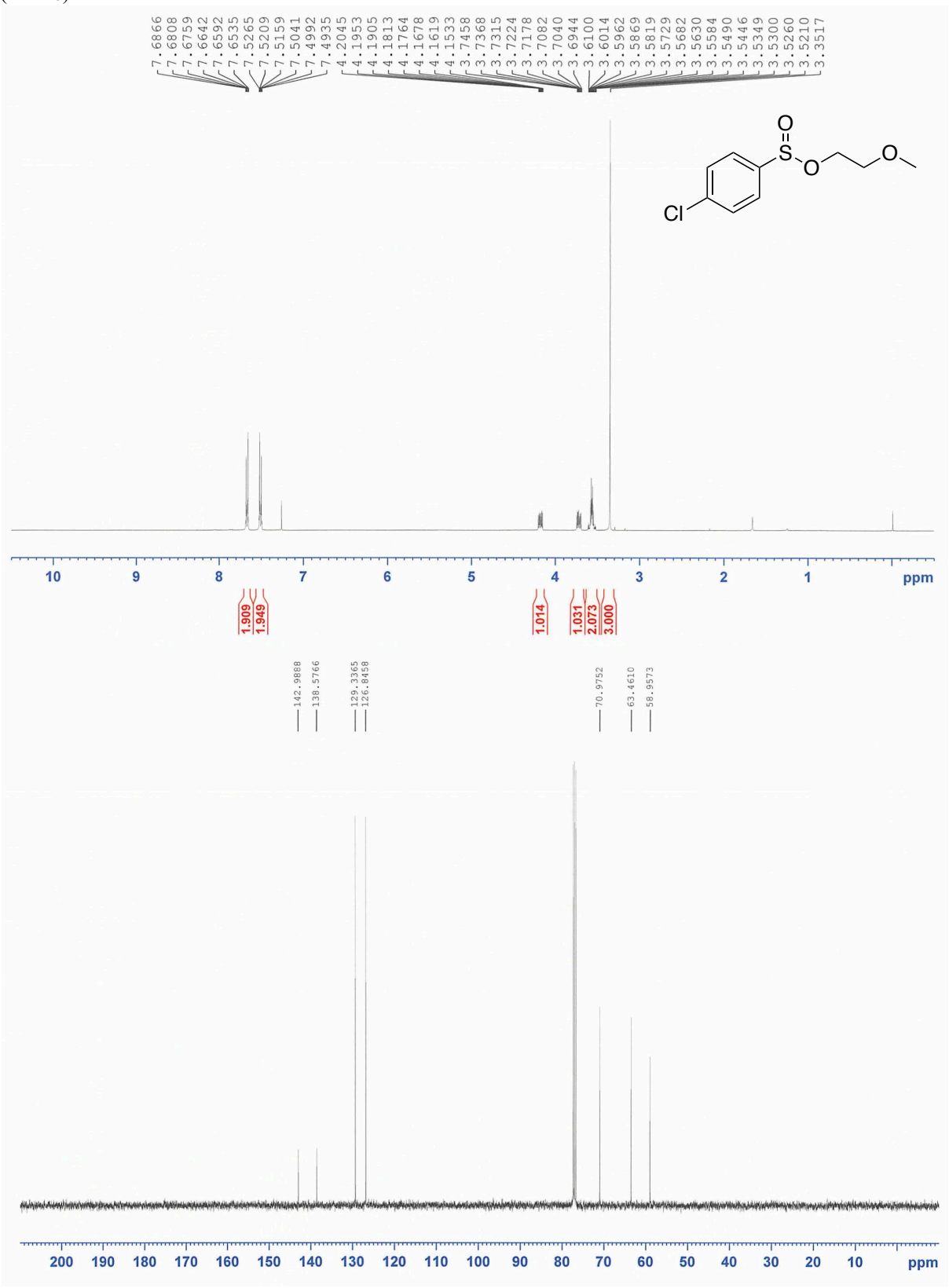


^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of methyl 4-(benzoylthio)benzoate (**4i**) ($CDCl_3$)

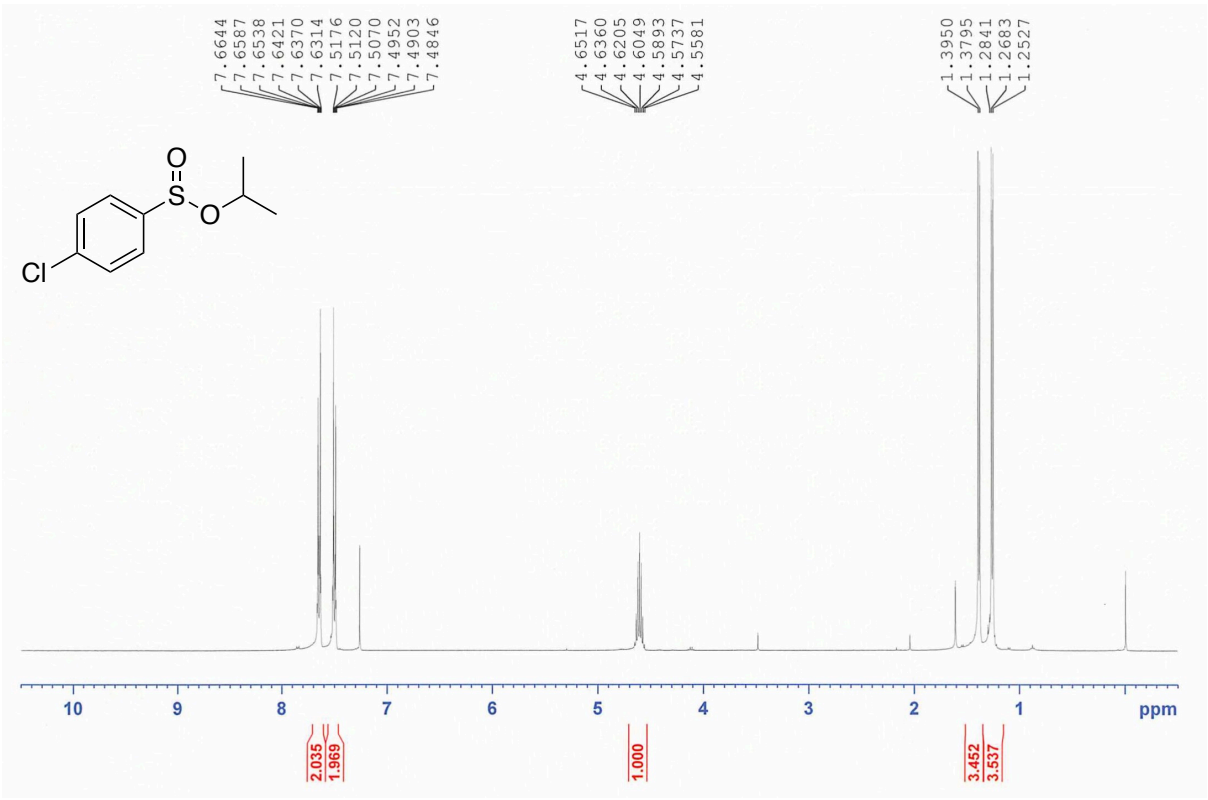


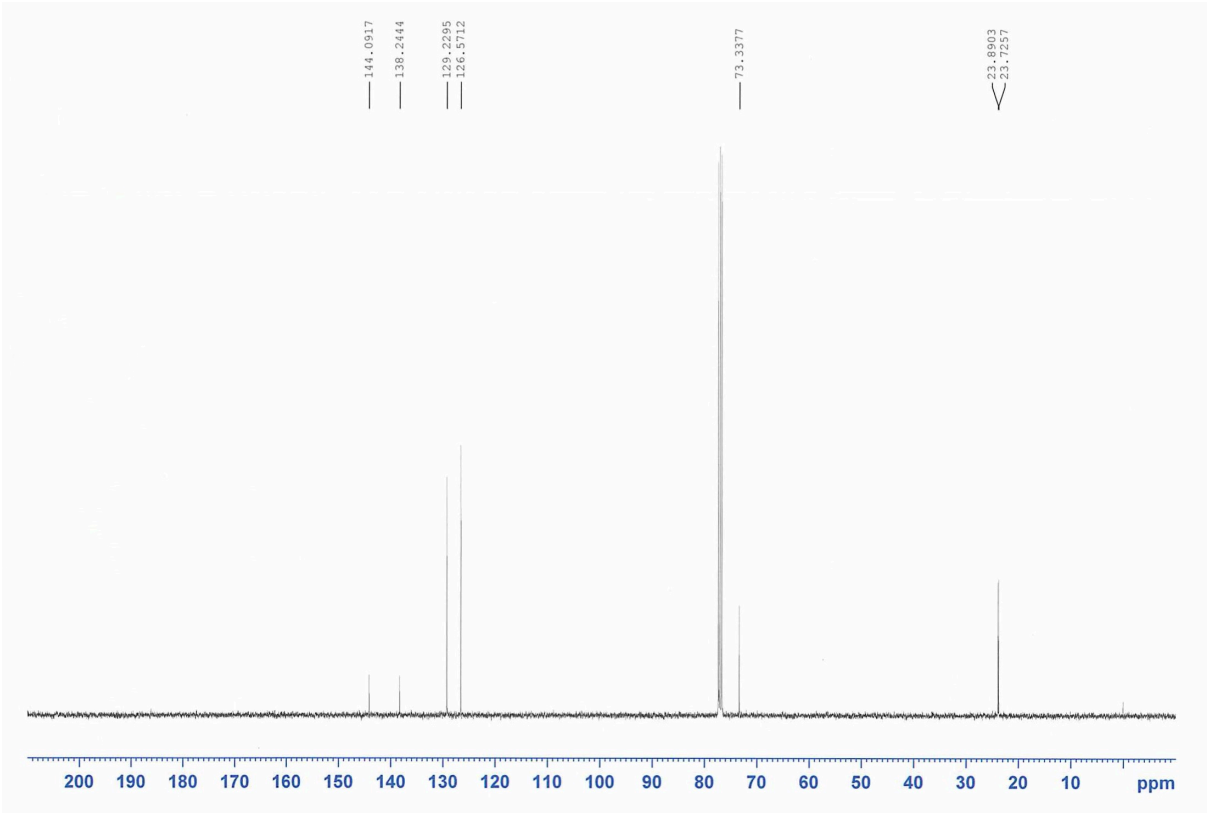


^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 2-methoxyethyl 4-chlorobenzenesulfinate (**9b**) ($CDCl_3$)

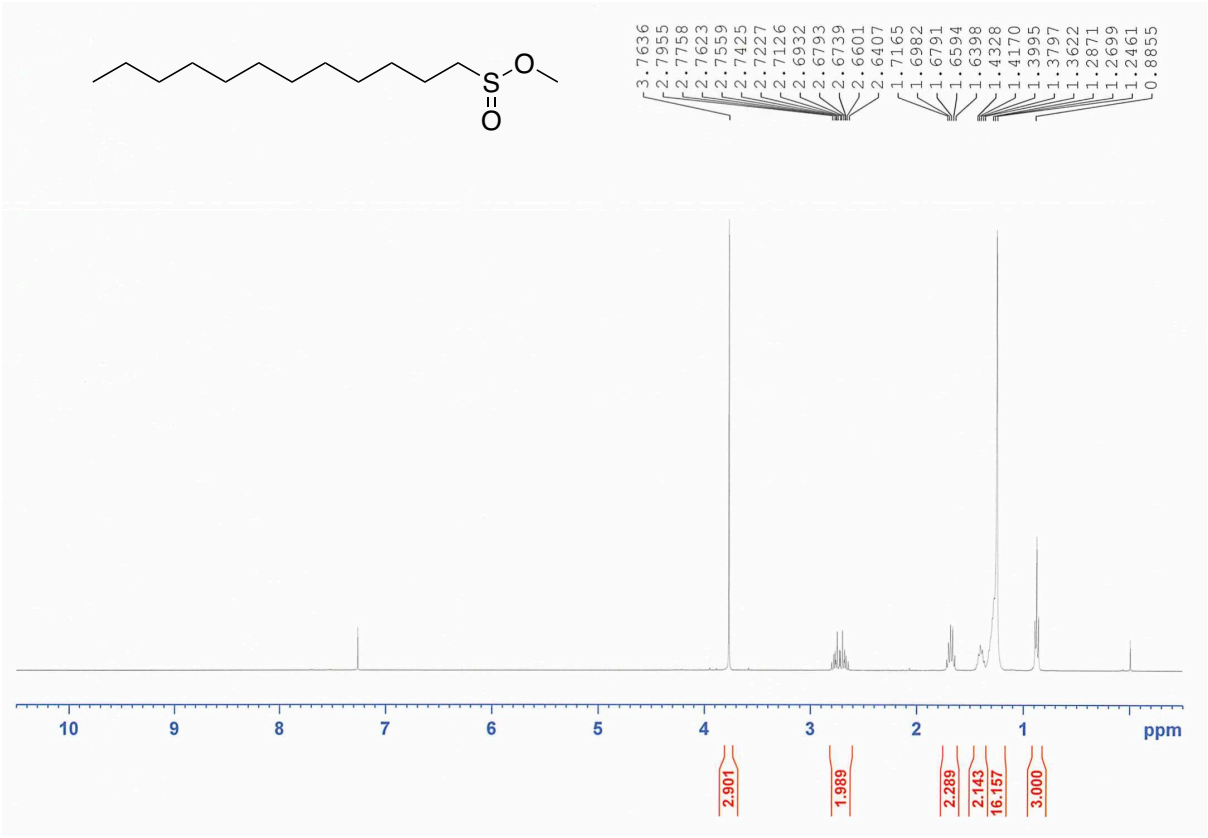


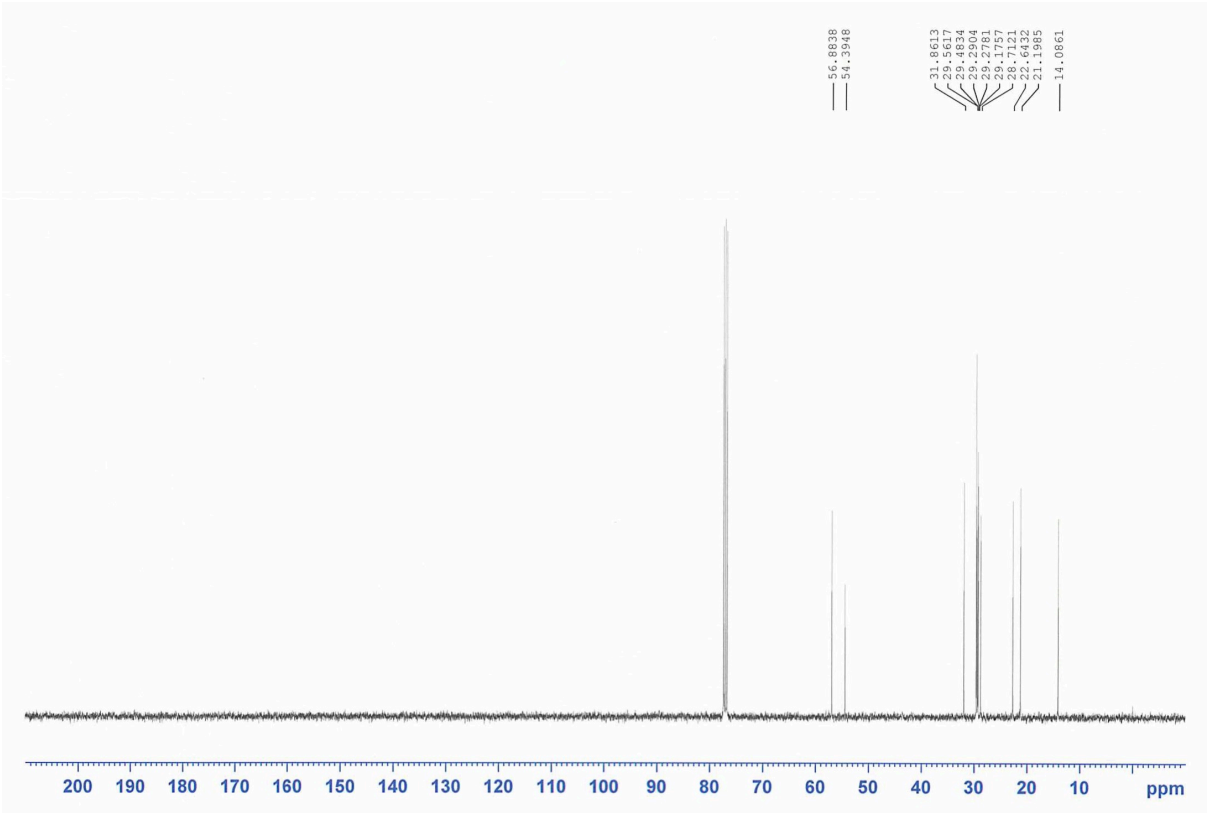
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of isopropyl 4-chlorobenzenesulfinate (**9c**) ($CDCl_3$)





^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of methyl dodecane-1-sulfinate (**12**) ($CDCl_3$)





^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of methyl 4-((4-methoxyphenyl)sulfinyl)benzoate (**16**) ($CDCl_3$)