Supporting Information

Facile Synthesis of Dibenzothiophene *S*-Oxides from Sulfinate Esters

Yukiko Kumagai,[a] Akihiro Kobayashi,[a,b] Keisuke Nakamura,[a] and Suguru Yoshida*[a]

[a]*Department of Biological Science and Technology, Faculty of Advanced Engineering, Tokyo University of Science, 6-3-1 Niijuku, Katsushika-ku Tokyo 125-8585*
[b]*Laboratory of Chemical Bioscience, Institute of Biomaterials and Bioengineering, Tokyo Medical and Dental University (TMDU), 2-3-10 Kanda-Surugadai, Chiyoda-ku, Tokyo 101-0062, Japan*

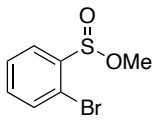
Contents

General Information

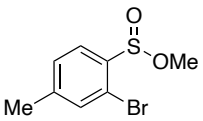
All reactions were performed with dry glassware under atmosphere of argon, unless otherwise noted. Analytical thin-layer chromatography (TLC) was performed on precoated (0.25 mm) silica-gel plates (Merck Chemicals, Silica Gel 60 F254, Cat. No. 1.05715). Column chromatography was conducted using silica-gel (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). 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 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 or JMS-700 (JEOL, Tokyo, Japan) mass spectrometer under electron impact ionization (EI) conditions.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Methyl 2-bromobenzenesulfinate (**1a**),[S1] methyl 2-bromo-4-methylbenzenesulfinate (**1b**),[S2] methyl 2-bromo-4,6-dimethylbenzenesulfinate (**1c**),[S2] methyl 6-bromobenzo[*d*][1,3]dioxole-5-sulfinate (**1d**),[S2] methyl 2-bromo-4-chlorobenzenesulfinate (**1e**),[S2] methyl 2-bromo-4-(trifluoromethyl)benzenesulfinate (**1f**),[S2] and 3-methoxy-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**2l**)[S3] were prepared according to reported methods. According to the procedure for the preparation of methyl 2-bromobenzenesulfinate (**1a**),[S1] ethyl 3-bromo-4-(methoxysulfinyl)benzoate (**1r**) was prepared from ethyl 3-bromo-4-iodobenzoate.

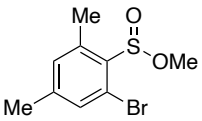
Structures of Sulfinate Esters 1 and Arylboronic Acids 2



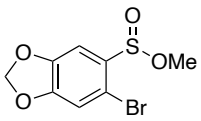
1a



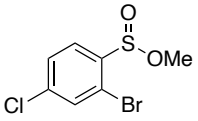
1b



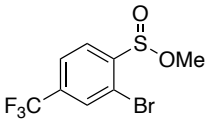
1c



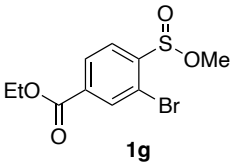
1d



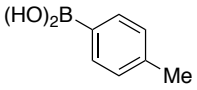
1e



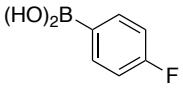
1f



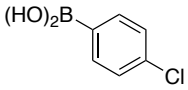
1g



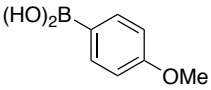
2a



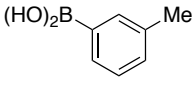
2b



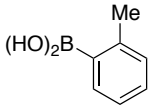
2c



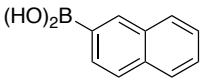
2d



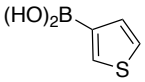
2e



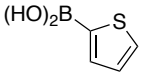
2f



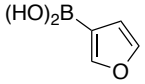
2g



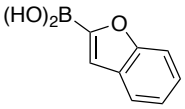
2h



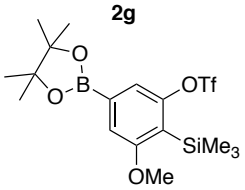
2i



2j



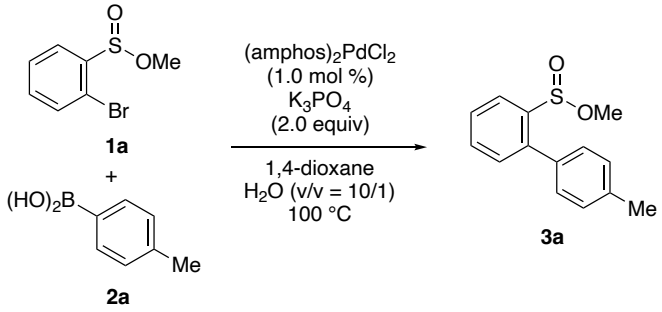
2k



2l

Experimental Procedures

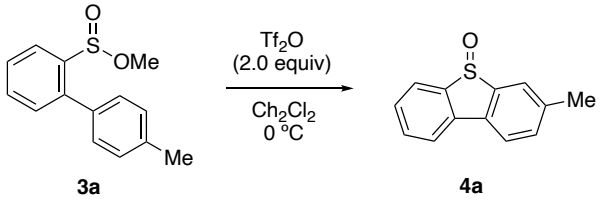
A typical procedure for the synthesis of biarylsulfinate esters from arylsulfinate esters with arylboronic acids



To a mixture of methyl 2-bromobenzenesulfinate (**1a**) (1.17 g, 4.98 mmol) and *p*-tolylboronic acid (**2a**) (1.02 g, 7.50 mmol, 1.5 equiv) in 1,4-dioxane (20 mL) and water (2.0 mL) were added potassium phosphate (2.12 g, 10.0 mmol, 2.0 equiv) and $(amphos)_2PdCl_2$ (35.4 mg, 50.0 μmol, 1.0 mol %) at room temperature. After stirring at 100 °C (oil bath) for 5 h, the mixture was added to water (10 mL). The reaction mixture was extracted with CH_2Cl_2 (20 mL × 3). The combined organic extract was washed with brine (5 mL). The extract was then dried with Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica-gel 60 g, *n*-hexane/EtOAc = 4/1) to give methyl 4'-methyl-[1,1'-biphenyl]-2-sulfinate (**3a**) (1.22 g, 4.96 mmol, 99%) as a black solid.

According to the procedure for preparing 4'-methyl-[1,1'-biphenyl]-2-sulfinate (**3a**), methyl 4'-fluoro-[1,1'-biphenyl]-2-sulfinate (**3b**), methyl 4'-chloro-[1,1'-biphenyl]-2-sulfinate (**3c**), methyl 4'-methoxy-[1,1'-biphenyl]-2-sulfinate (**3d**), methyl 3'-methyl-[1,1'-biphenyl]-2-sulfinate (**3e**), methyl 2'-methyl-[1,1'-biphenyl]-2-sulfinate (**3f**), methyl 2-(naphthalen-2-yl)benzenesulfinate (**3g**), methyl 2-(thiophen-3-yl)benzenesulfinate (**3h**), methyl 2-(thiophen-2-yl)benzenesulfinate (**3i**), methyl 2-(furan-3-yl)benzenesulfinate (**3j**), methyl 2-(benzofuran-2-yl)benzenesulfinate (**3k**), methyl 4',5-dimethyl-[1,1'-biphenyl]-2-sulfinate (**3l**), methyl 3,4',5-trimethyl-[1,1'-biphenyl]-2-sulfinate (**3m**), methyl 6-(*p*-tolyl)benzo[*d*][1,3]dioxole-5-sulfinate (**3n**), methyl 5-chloro-4'-methyl-[1,1'-biphenyl]-2-sulfinate (**3o**), methyl 4'-methyl-5-(trifluoromethyl)-[1,1'-biphenyl]-2-sulfinate (**3p**), ethyl 6-(methoxysulfinyl)-4'-methyl-[1,1'-biphenyl]-3-carboxylate (**3q**), methyl (*E*)-2-styrylbenzenesulfinate (**3r**), and methyl 2-(5-methoxy-3-(triflyloxy)-4-(trimethylsilyl)phenyl)benzenesulfinate (**3s**) were prepared from the corresponding sulfinate esters and boronic acid derivatives.

A typical procedure for the synthesis of dibenzothiophene S-oxides from biaryl sulfinate esters

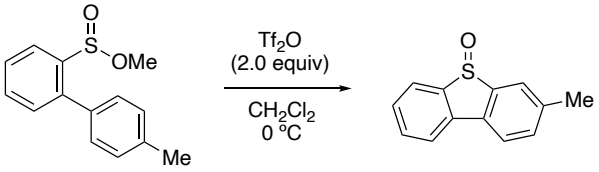


To a solution of methyl 4'-methyl-[1,1'-biphenyl]-2-sulfinate (**3a**) (49.7 mg, 0.202 mmol) in dichloromethane (2.0 mL) was added trifluoromethanesulfonic anhydride (67.2 μL, 0.400 mmol, 2.0 equiv) at 0 ºC. After stirring for 1 h at the same temperature, to the mixture was added an aqueous saturated solution of sodium bicarbonate (3 mL). The mixture was extracted with dichloromethane (15 mL × 3). The combined organic extract was washed with brine (20 mL). The extract was dried with Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 2/1) to give 3-methyldibenzo[*b*,*d*]thiophene 5-oxide (**4a**) (41.4 mg, 0.193 mmol, 97%) as a colorless solid.

According to the procedure for preparing 3-fluorodibenzo[*b*,*d*]thiophene 5-oxide (**4b**), 3-chlorodibenzo[*b*,*d*]thiophene 5-oxide (**4c**), 2-methyldibenzo[*b*,*d*]thiophene 5-oxide (**4e**) (with 4-methyldibenzo[*b*,*d*]thiophene 5-oxide (**4e'**)), 1-methyldibenzo[*b*,*d*]thiophene 5-oxide (**4f**), benzo[*b*]naphtho[2,1-*d*]thiophene 11-oxide (**4g**), benzo[*b*]thieno[3,2-*d*]thiophene 8-oxide (**4h**), 2,7-dimethyldibenzo[*b*,*d*]thiophene 5-oxide (**4l**), 2,4,7-trimethyldibenzo[*b*,*d*]thiophene 5-oxide (**4m**), 2-chloro-7-methyldibenzo[*b*,*d*]thiophene 5-oxide (**4o**), 7-methyl-2-(trifluoromethyl)dibenzo[*b*,*d*]thiophene 5-oxide (**4p**), 2-(ethoxycarbonyl)-7-

methyldibenzo[*b*,*d*]thiophene 5-oxide (**4q**), 2-methoxy-4-(triflyloxy)-3-(trimethylsilyl)dibenzo[*b*,*d*]thiophene 5-oxide (**4r**), and 2-phenylbenzo[*b*]thiophene 1-oxide (**6**) were prepared from the corresponding sulfinate ester derivatives **3**.

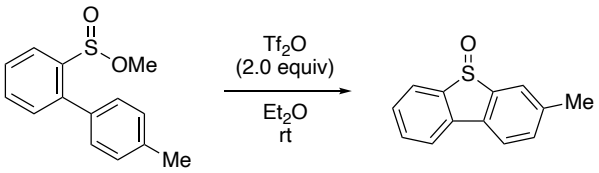
*Gram-scale synthesis of dibenzothiophene S-oxide (**4a**)*



3a **4a**

To a mixture of methyl 4'-methyl-[1,1'-biphenyl]-2-sulfinate (**3a**) (1.00 g, 4.34 mmol) in dichloromethane (43.4 mL) was added trifluoromethanesulfonic anhydride (1.46 mL, 8.68 mmol, 2.0 equiv) at 0 ºC. After stirring for 1 h at the same temperature, to the mixture was added an aqueous saturated solution of sodium bicarbonate (50 mL). The mixture was extracted with dichloromethane (30 mL × 3). The combined organic extract was washed with brine (20 mL). The extract was dried with Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica-gel 25 g, *n*-hexane/EtOAc = 2/1) to give 3-methyldibenzo[*b*,*d*]thiophene 5-oxide (**4a**) (778.1 mg, 3.63 mmol, 83%) as a colorless solid.

A typical procedure for the synthesis of dibenozothiophene S-oxides in diethyl ether

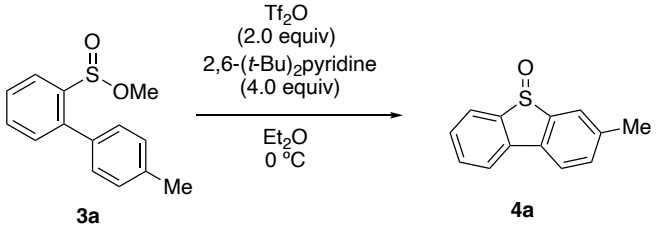


3a **4a**

To a mixture of methyl 4'-methyl-[1,1'-biphenyl]-2-sulfinate (**3a**) (50.0 mg, 0.203 mmol) in diethyl ether (2.0 mL) was added trifluoromethanesulfonic anhydride (67.2 µL, 0.400 mmol, 2.0 equiv) at room temperature. After stirring for 1 h at the same temperature, to the mixture was added an aqueous saturated solution of sodium bicarbonate (3 mL) and the mixture was extracted with dichloromethane (15 mL × 3). The combined organic extract was washed with brine (20 mL). The extract was dried with Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 2/1) to give 3-methyldibenzo[*b*,*d*]thiophene 5-oxide (**4a**) (41.8 mg, 0.195 mmol, 98%) as a colorless solid.

According to the procedure for preparing 3-methoxydibenzo[*b*,*d*]thiophene 5-oxide (**4d**), benzo[*b*]thieno[2,3-*d*]thiophene 4-oxide (**4i**) and 7-methylbenzo[4',5']thieno[2',3':4,5]benzo[1,2-*d*][1,3]dioxole 5-oxide (**4n**) were prepared from the corresponding sulfinate esters.

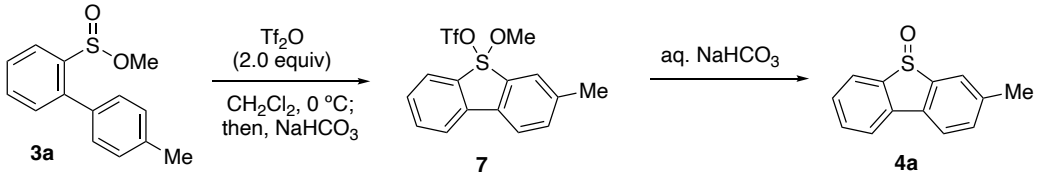
A typical procedure for the synthesis of dibenozothiophene S-oxides in the presence of 2,6-di(tert-butyl)pyridine



To a mixture of methyl 4'-methyl-[1,1'-biphenyl]-2-sulfinate (**3a**) (24.4 mg, 99.1 μmol) in diethyl ether (1.0 mL) was added 2,6-di(*tert*-butyl)pyridine (87.9 μL, 0.400 mmol, 4.0 equiv) and trifluoromethanesulfonic anhydride (33.6 μL, 0.200 mmol, 2.0 equiv) at 0 ºC. After stirring for 1 h at the same temperature, to the mixture was added an aqueous saturated solution of sodium bicarbonate (3 mL). The mixture was extracted with dichloromethane (15 mL × 3). The combined organic extract was washed with brine (20 mL). The extract was dried with Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 2/1) to give 3-methyldibenzo[*b*,*d*]thiophene 5-oxide (**4a**) (21.3 mg, 99.1 μmol, quant.) as a colorless solid.

According to the procedure for preparing benzo[4,5]thieno[2,3-*b*]furan 8-oxide (**4j**), benzo[4,5]thieno[3,2-*b*]benzofuran 10-oxide (**4k**) was prepared from the corresponding sulfinate ester **3k**.

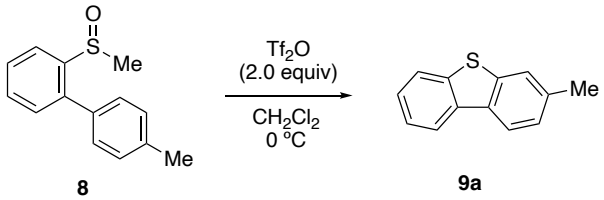
*Procedure for the synthesis of dibenzo thiophene S-oxide **4a** from biaryl sulfinate ester **3a** via the isolation of 5-methoxy-3-methyl-5H-5λ⁴-dibenzo[b,d]thiophen-5-yl trifluoromethanesulfonate (7)*



To a mixture of methyl 4'-methyl-[1,1'-biphenyl]-2-sulfinate (**3a**) (24.6 mg, 0.100 mmol) in dichloromethane (1.0 mL) was added trifluoromethanesulfonic anhydride (33.6 μL, 0.200 mmol, 2.0 equiv) at 0 ºC. After stirring for 1 h at the same temperature, to the mixture was added sodium bicarbonate (42.0 mg, 0.500 mmol, 5.0 equiv). After stirring for 5 min at the same temperature, the mixture was filtrated. The resulting filtrate was concentrated under reduced pressure. The resulting yellow solid was washed with Et_2O (5.0 mL × 3) and dried under reduced pressure to give 5-methoxy-3-methyl-5*H*-5λ⁴-dibenzo[*b*,*d*]thiophen-5-yl trifluoromethanesulfonate (**7**) (38.1 mg, 0.100 mmol, quant.) as a yellow solid.

To a mixture of 5-methoxy-3-methyl-5*H*-5λ⁴-dibenzo[*b*,*d*]thiophen-5-yl trifluoromethanesulfonate (**5**) (10.7 mg, 28.0 μmol) in dichloromethane (280 μL) was added an aqueous saturated solution of sodium bicarbonate (3 mL) and the mixture was extracted with dichloromethane (15 mL × 3). The combined organic extract was washed with brine (20 mL). The extract was dried with Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 2/1) to give 3-methyldibenzo[*b*,*d*]thiophene 5-oxide (**4a**) (6.1 mg, 28 μmol, quant.) as a colorless solid.

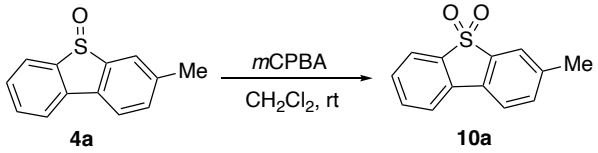
*Synthesis of dibenzothiophene **9a** from sulfoxide **8***



8 **9a**

To a mixture of 4'-methyl-2-(methylsulfinyl)-1,1'-biphenyl (**8**) (23.1 mg, 0.100 mmol) in dichloromethane (1.0 mL) was added trifluoromethanesulfonic anhydride (33.6 µL, 0.200 mmol, 2.0 equiv) at 0 ºC. After stirring for 1 h at the same temperature, to the mixture was added an aqueous saturated solution of sodium bicarbonate (3 mL). The mixture was extracted with dichloromethane (15 mL × 3). The combined organic extract was washed with brine (20 mL). The extract was dried with Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 2/1) to give 3-methyldibenzo[*b*,*d*]thiophene (**9a**) (17.2 mg, 86.7 µmol, 87%) as a colorless solid.

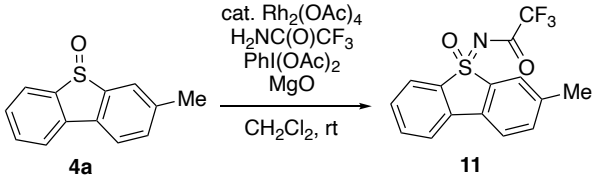
*Synthesis of 3-methyldibenzo[b,d]thiophene 5,5-dioxide **(10a)***



4a **10a**

To a mixture of 3-methyldibenzo[*b*,*d*]thiophene 5-oxide (**4a**) (42.9 mg, 0.200 mmol) in dichloromethane (2.0 mL) was added *m*-chloroperbenzoic acid (*m*CPBA) (69.4 mg, 77%, 0.154 mmol, 1.54 equiv) at room temperature. After stirring for 12 h at room temperature, to the mixture was added an aqueous saturated solution of sodium bicarbonate (3 mL). The mixture was extracted with dichloromethane (15 mL × 3). The combined organic extract was washed with brine (20 mL). The extract was dried with Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 2/1) to give 3-methyldibenzo[*b*,*d*]thiophene 5,5-dioxide (**10a**) (38.3 mg, 0.166 mmol, 83%) as a colorless solid.

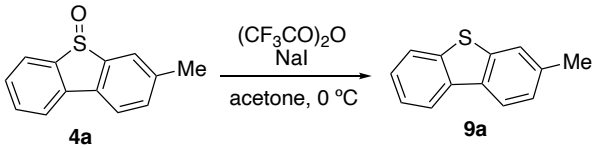
*Synthesis of 2,2,2-trifluoro-N-(3-methyl-5-oxido-5λ^4-dibenzo[b,d]thiophen-5-ylidene)acetamide **(8)***



4a **11**

To a mixture of 3-methyldibenzo[*b*,*d*]thiophene 5-oxide (**4a**) (21.8 mg, 0.102 mmol), trifluoroacetamide (23.0 mg, 0.203 mmol, 2.0 equiv), MgO (16.5 mg, 0.401 mmol. 4.0 equiv), and $Rh_2(OAc)_4$ (1.10 mg, 2.5 µmol, 2.5 mol %) in CH_2Cl_2 (2.0 mL) was added $PhI(OAc)_2$ (48.3 mg, 0.150 mmol, 1.5 equiv) at room temperature. After stirring for 6 h at the same temperature, the mixture was concentrated under reduced pressure. The resulting residue was purified by preparative TLC (*n*-hexane/EtOAc = 1/2) to give 2,2,2-trifluoro-*N*-(3-methyl-5-oxido-5λ^4-dibenzo[*b*,*d*]thiophen-5-ylidene)acetamide *S*-oxide (**11**) (23.6 mg, 72.5 µmol, 72%) as a colorless solid.

*Synthesis of dibenzothiophenes **9***

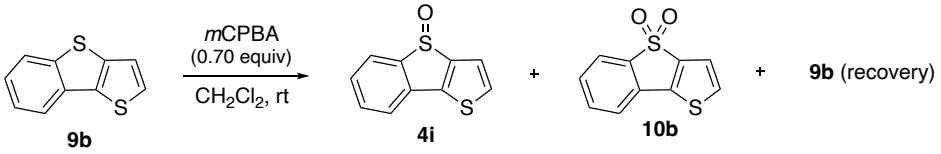


4a **9a**

To a solution of 3-methyldibenzo[*b*,*d*]thiophene 5-oxide (**4a**) (42.9 mg, 0.200 mmol) and NaI (71.9 mg, 0.48 mmol, 2.4 equiv) in acetone (1.0 mL) was added dropwise a solution of TFAA (67.2 μL, 0.48 mmol, 2.4 equiv) in acetone (400 μL) at 0 °C. After stirring for 1 h at the same temperature, the resulting brown solution was diluted with Et_2O (10 mL). The mixture was extracted with a saturated solution of $Na_2S_2O_3$ (15 mL × 3). The combined organic extract was washed with brine (20 mL). The extract was dried with Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane) to give 3-methyldibenzo[*b*,*d*]thiophene (**9a**) (29.8 mg, 0.150 mmol, 75%) as a colorless solid.

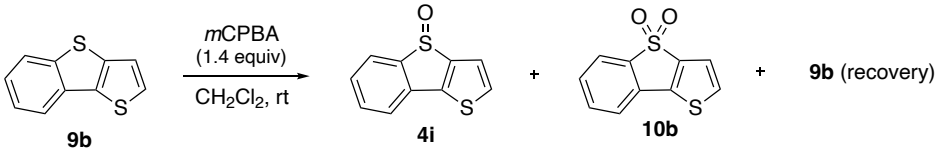
According to the procedure for preparing 3-methyldibenzo[*b*,*d*]thiophene (**9a**), benzo[*b*]thieno[2,3-*d*]thiophene (**9b**) and benzo[4,5]thieno[2,3-*b*]furan (**9c**) were prepared from the corresponding sulfoxides.

*Oxidation of **9b** with mCPBA*



9b **4i** **10b**

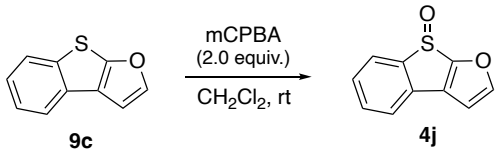
To a mixture of benzo[*b*]thieno[2,3-*d*]thiophene (**9b**) (19.0 mg, 0.100 mmol) in dichloromethane (1.0 mL) was added *m*-chloroperbenzoic acid (*m*CPBA) (17.3 mg, 77%, 77 μmol, 0.77 equiv) at room temperature. After stirring for 12 h at room temperature, to the mixture was added an aqueous saturated solution of sodium bicarbonate (3 mL). The mixture was extracted with dichloromethane (15 mL × 3). The combined organic extract was washed with brine (20 mL). The extract was dried with Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 1/2) to give benzo[*b*]thieno[2,3-*d*]thiophene 4-oxide (**4i**) (9.1 mg, 44 μmol, 44%), benzo[*b*]thieno[2,3-*d*]thiophene 4,4-dioxide (**10b**) (2.6 mg, 12 μmol, 12%), and benzo[*b*]thieno[2,3-*d*]thiophene (**9b**) (3.1 mg, 16 μmol, 16%) as a colorless solid.



9b **4i** **10b**

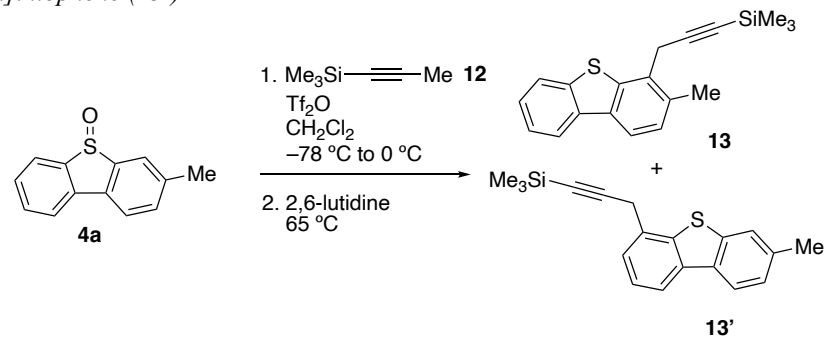
To a mixture of benzo[*b*]thieno[2,3-*d*]thiophene (**9b**) (19.0 mg, 0.100 mmol) in dichloromethane (1.0 mL) was added *m*-chloroperbenzoic acid (*m*CPBA) (34.5 mg, 77%, 0.154 mmol, 1.54 equiv) at room temperature. After stirring for 12 h at room temperature, to the mixture was added an aqueous saturated solution of sodium bicarbonate (3 mL). The mixture was extracted with dichloromethane (15 mL × 3). The combined organic extract was washed with brine (20 mL). The extract was dried with Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 1/2) to give benzo[*b*]thieno[2,3-*d*]thiophene 4-oxide (**4i**) (9.6 mg, 47 μmol, 47%) and benzo[*b*]thieno[2,3-*d*]thiophene 4,4-dioxide (**10b**) (7.9 mg, 36 μmol, 36%) as a colorless solid, in which benzo[*b*]thieno[2,3-*d*]thiophene was not detected.

*Oxidation of **9c** with mCPBA*



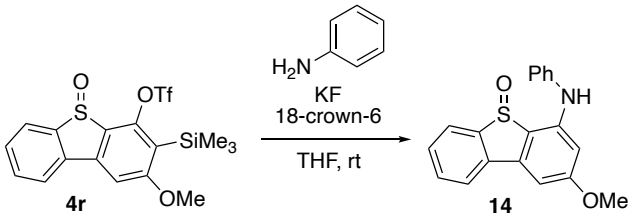
To a mixture of benzo[4,5]thieno[2,3-*b*]furan (**6c**) (1.7 mg, 10 μmol) in dichloromethane (100 μL) was added *m*-chloroperbenzoic acid (*m*CPBA) (3.5 mg, 77%, 15 μmol, 1.54 equiv) at room temperature. After stirring for 12 h at room temperature, to the mixture was added an aqueous saturated solution of sodium bicarbonate (3 mL). The mixture was extracted with dichloromethane (5 mL × 3). The combined organic extract was washed with brine (10 mL). The extract was dried with Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. Benzo[4,5]thieno[2,3-*b*]furan 8-oxide (**4j**) was not detected, and a complex mixture of products was observed in the analysis of the resulting residue by ^{1}H NMR ($CDCl_3$).

*Ssynthesis of 4-(but-2-yn-1-yl)-3-methyldibenzo[b,d]thiophene (**13**) and 6-(but-2-yn-1-yl)-3-methyldibenzo[b,d]thiophene (**13'**)*



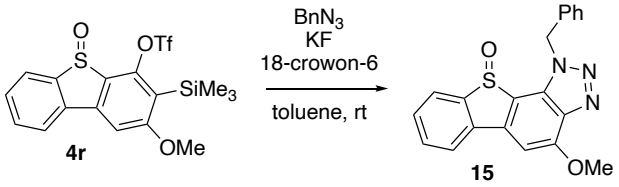
To a solution of dibenzothiophene *S*-oxide (32.1 mg, 0.150 mmol) in CH_2Cl_2 (0.75 mL) was slowly added Tf_2O (32.7 μL, 0.195 mmol, 1.3 equiv) and propargyltrimethylsilane (28.9 μL, 0.195 mmol, 1.3 equiv) at –78 ºC. After stirring 15 min at the same temperature, the reaction was warmed to 0 ºC. After stirring 30 min at the same temperature, 2,6-lutidine (52.4 μL, 0.452 mmol, 3.0 equiv) was added at room temperature. After stirring for 12 h at 65 ºC, to the mixture was added water (3 mL). The mixture was extracted with dichloromethane (5 mL × 3). The combined organic extract was washed with brine (10 mL). The extract was dried with Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane) to give a mixture of 4-(but-2-yn-1-yl)-3-methyldibenzo[*b*,*d*]thiophene (**13**) and 6-(but-2-yn-1-yl)-3-methyldibenzo[*b*,*d*]thiophene (**13'**) (40.2 mg, 0.13 mmol, **13**:**13'** = 4:1) as a pale yellow solid.

*Synthesis of 2-methoxy-4-(phenylamino)dibenzo[b,d]thiophene 5-oxide (**14**)*



To a mixture of 2-methoxy-5-oxido-3-(trimethylsilyl)dibenzo[*b*,*d*]thiophen-4-yl trifluoromethanesulfonate (**4r**) (9.0 mg, 20 μmol) and aniline (9.3 mg, 0.10 mmol, 5.0 equiv.) in THF (100 μL) was added KF (3.5 mg, 60.0 μmol, 3.0 equiv) and 18-crown-6 (15.9 mg, 60.0 μmol, 3.0 equiv) at room temperature. After stirring for 48 h at the same temperature, to the mixture was added water (1 mL). The mixture was extracted with EtOAc (5 mL × 3). The combined organic extract was washed with brine (2 mL). The extract was dried with Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 2/1) to give 2-methoxy-4-(phenylamino)dibenzo[*b*,*d*]thiophene 5-oxide (**14**) (3.5 mg, 11 μmol, 55%) as a yellow oil.

*Synthesis of 1-benzyl-4-methoxy-1H-benzo[4',5']thieno[2',3':3,4]benzo[1,2-d][1,2,3]triazole 10-oxide (**15**)*

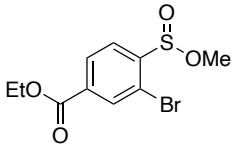


To a mixture of 2-methoxy-5-oxido-3-(trimethylsilyl)dibenzo[*b*,*d*]thiophen-4-yl trifluoromethanesulfonate (**12b**) (9.0 mg, 20 μmol) in toluene (120 μL) was added BnN_3 (13.2 mg, 0.10 mmol, 5.0 equiv), KF (9.3 mg, 0.16 mmol, 8.0 equiv), and 18-crown-6 (43.2 mg, 0.16 mmol, 8.0 equiv) at room temperature. After stirring for 12 h at the same temperature, to the mixture was added water (1 mL). The mixture was extracted with EtOAc (5 mL × 3). The combined organic extract was washed with brine (2 mL). The extract was dried with Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 2/1) to give 1-benzyl-4-methoxy-1*H*-benzo[4',5']thieno[2',3':3,4]benzo[1,2-*d*][1,2,3]triazole 10-oxide (**15**) (2.8 mg, 7.8 μmol, 39%) as a colorless solid.

Characterization Data of New Compounds

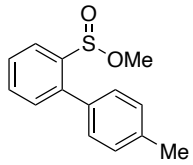
3-Methyldibenzo[*b*,*d*]thiophene 5-oxide (**4a**),[S4] 3-methoxydibenzo[*b*,*d*]thiophene 5-oxide (**4d**),[S4] benzo[*b*]thieno[2,3-*d*]thiophene 4-oxide (**4i**),[S4] and benzo[4,5]thieno[3,2-*b*]benzofuran 10-oxide (**4k**)[S5] were identical in spectra data with those reported in the literature.

Ethyl 3-bromo-4-(methoxysulfinyl)benzoate (**1r**)



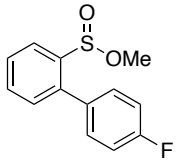
Yield: 75% (1.15 g, 3.74 mmol); Colorless oil; TLC R_f 0.30 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.41 (t, 3H, *J* = 7.1 Hz), 3.61 (s, 3H), 4.42 (q, 2H, *J* = 7.1 Hz), 7.99 (d, 1H, *J* = 8.0 Hz), 8.17 (dd, 1H, *J* = 8.0, 1.5 Hz), 8.28 (d, 1H, *J* = 1.5 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 14.2, 51.8, 61.9, 120.9, 127.0, 128.6, 134.5, 135.4, 146.7, 164.3; IR (NaCl, cm^{-1}) 966, 1025, 1110, 1138, 1239, 1275, 1378, 1455, 1459, 1561, 1724, 1727, 2942, 2985; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{10}H_{11}BrNaO_4S^+$ 328.9459; Found 328.9458.

Methyl 4'-methyl-[1,1'-biphenyl]-2-sulfinate (**3a**)



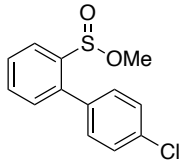
Yield: 94% (235 mg, 0.956 mmol); Pale yellow oil; TLC R_f 0.54 (*n*-hexane/CH_2Cl_2 = 1/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.42 (s, 3H), 3.39 (s, 3H), 7.24–7.31 (m, 4H), 7.33–7.39 (m, 1H), 7.53–7.61 (m, 2H), 8.05–8.13 (m, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 21.2, 51.2, 124.2, 127.6, 129.0, 129.3, 130.7, 132.0, 134.8, 138.0, 141.5, 142.2; IR (NaCl, cm^{-1}) 820, 967, 1004, 1129, 1435, 1464, 2938; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{14}H_{14}NaO_2S^+$ 269.0612; Found 269.0612.

Methyl 4'-fluoro-[1,1'-biphenyl]-2-sulfinate (**3b**)



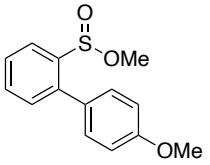
Yield: 98% (1.22 g, 4.90 mmol); Colorless oil; TLC R_f 0.51 (*n*-hexane/EtOAc = 3/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.40 (s, 3H), 7.11–7.18 (m, 2H), 7.31–7.39 (m, 3H), 7.56–7.62 (m, 2H), 8.06–8.12 (m, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 51.3, 115.4 (d, *J* = 21.7 Hz), 124.4, 128.0, 130.8, 131.1 (d, *J* = 8.4 Hz), 132.1, 133.7 (d, *J* = 3.3 Hz), 140.4, 142.3, 162.7 (d, *J* = 248 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz): δ −113.7 (s); IR (NaCl, cm^{-1}) 820, 838, 967, 1096, 1130, 1160, 1223, 1464, 1514, 1605; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{13}H_{11}FNaO_2S^+$ 273.0362; Found 273.0362

Methyl 4'-chloro-[1,1'-biphenyl]-2-sulfinate (**3c**)



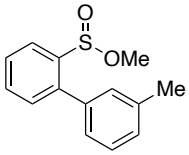
Yield: 67% (892 mg, 3.35 mmol); Pale yellow oil; TLC R_f 0.52 (*n*-hexane/EtOAc = 3/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.40 (s, 3H), 7.30–7.36 (m, 3H), 7.40–7.45 (AA'BB', 2H), 7.57–7.62 (m, 2H), 8.06–8.12 (m, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 51.3, 124.4, 128.1, 128.6, 130.6, 130.7, 132.2, 134.4, 136.2, 140.1, 142.2; IR (NaCl, cm^{-1}) 830, 967, 1004, 1062, 1092, 1102, 1126, 1462, 1644, 1651; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{13}H_{11}ClNaO_2S^+$ 289.0066; Found 289.0065.

Methyl 4'-methoxy-[1,1'-biphenyl]-2-sulfinate (**3d**)



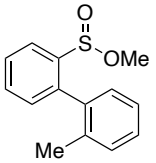
Yield: 87% (239 mg, 0.867 mmol); Pink solid; Mp 65–67 °C; TLC R_f 0.54 (*n*-hexane/EtOAc = 3/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.41 (s, 3H), 3.86 (s, 3H), 6.95–7.00 (AA'BB' 2H), 7.29–7.37 (m, 3H), 7.52–7.61 (m, 2H), 8.04–8.12 (m, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 51.4, 55.3, 113.8, 124.3, 127.5, 130.1, 130.7, 130.9, 132.1, 141.2, 142.4, 159.5; IR (NaCl, cm^{-1}) 1435, 1447, 1455, 1471, 1515, 2820, 2872, 2912, 3039, 3043; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{14}H_{14}NaO_3S^+$ 285.0561; Found 285.0561.

Methyl 3'-methyl-[1,1'-biphenyl]-2-sulfinate (**3e**)



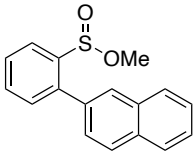
Yield: 86% (1.05 g, 4.28 mmol); Pale yellow oil; TLC R_f 0.47 (*n*-hexane/EtOAc = 3/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.40 (s, 3H), 3.38 (s, 3H), 7.15–7.25 (m, 3H), 7.28–7.38 (m, 2H), 7.52–7.59 (m, 2H), 8.05–8.12 (m, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 21.3, 51.3, 124.1, 126.4, 127.6, 128.1, 128.7, 130.0, 130.5, 131.9, 137.6, 137.9, 141.5, 142.2; IR (NaCl, cm^{-1}) 969, 1067, 1096, 1123, 1159, 1438, 1462, 1591, 2938; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{14}H_{14}NaO_2S^+$ 269.0612; Found 269.0612.

Methyl 2'-methyl-[1,1'-biphenyl]-2-sulfinate (**3f**)



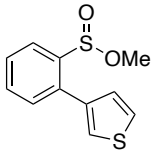
Methyl 2'-methyl-[1,1'-biphenyl]-2-sulfinate was observed as a 1:1 diastereomeric mixture in ^{1}H and ^{13}C NMR analyses due to the chiral sulfur atom and axial chirality at the biphenyl moiety. Yield: 97% (1.20 g, 4.87 mmol); Black oil; TLC R_f 0.41 (*n*-hexane/EtOAc = 3/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.01 (s, 3H), 2.07 (s, 3H), 3.30 (s, 3H), 3.36 (s, 3H), 7.12 (d, 1H, J = 1.3 Hz), 7.17–7.35 (m, 9H), 7.53–7.62 (m, 4H), 8.04–8.11 (m, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 19.9, 20.1, 51.5, 51.9, 123.6, 124.0, 125.2, 125.3, 127.6, 127.7, 128.29, 128.33, 129.6, 129.8, 130.0, 130.2, 130.3, 130.6, 131.5, 132.1,135.6, 136.5, 136.8, 136.9, 140.5, 140.8, 142.3, 142.6; IR (NaCl, cm^{-1}) 969, 982, 1006, 1036, 1049, 1063, 1125, 1432, 1464, 1493, 2938; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{14}H_{14}NaO_2S^+$ 269.0612; Found 269.0611.

Methyl 2-(naphthalen-2-yl)benzenesulfinate (**3g**)



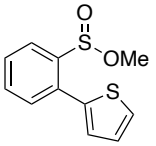
Yield: 81% (1.14 g, 4.03 mmol); Pale yellow solid; Mp 61–63 °C; TLC R_f 0.50 (*n*-hexane/EtOAc = 3/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.38 (s, 3H), 7.45–7.50 (m, 1H), 7.50–7.58 (m, 3H), 7.59–7.67 (m, 2H), 7.85–7.96 (m, 4H), 8.11–8.18 (m, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 51.6, 124.3, 126.57, 126.64, 127.2, 127.8, 127.9, 128.0, 128.2, 128.6, 130.9, 132.1, 132.7, 132.9, 135.2, 141.4, 142.6; IR (NaCl, cm^{-1}) 823, 860, 967, 1126, 3421, 3591; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{17}H_{14}NaO_2S^+$ 305.0612; Found 305.0611.

Methyl 2-(thiophen-3-yl)benzenesulfinate (**3h**)



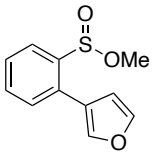
Yield: 95% (1.13 g, 4.73 mmol); Pale yellow oil; TLC R_f 0.57 (*n*-hexane/EtOAc = 3/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.46 (s, 3H), 7.20 (dd, 1H, *J* = 4.9, 1.3 Hz), 7.36–7.40 (m, 1H), 7.40–7.47 (m, 2H), 7.52–7.61 (m, 2H), 8.06–8.12 (m, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 51.1, 124.4, 124.6, 125.9, 127.7, 128.8, 130.6, 132.1, 136.0, 137.8, 142.1; IR (NaCl, cm^{-1}) 820, 860, 969, 1065, 1086, 1128, 1160, 1193, 1435, 1464; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{11}H_{10}NaO_2S_2^+$ 261.0020; Found 261.0019.

Methyl 2-(thiophen-2-yl)benzenesulfinate (**3i**)



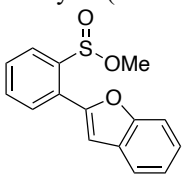
Yield: 88% (21.4 mg, 89.8 μmol); Brown oil; TLC R_f 0.45 (*n*-hexane/EtOAc = 3/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.49 (s, 3H), 7.12 (dd, 1H, *J* = 5.1, 3.6 Hz), 7.21 (dd, 1H, *J* = 3.6, 1.2 Hz), 7.44 (dd, 1H, *J* = 5.1, 1.2 Hz), 7.48–7.54 (m, 1H), 7.54–7.60 (m, 2H), 8.08–8.14 (m, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 51.2, 124.7, 127.1, 127.5, 128.2, 128.5, 131.4, 132.1, 133.7, 138.3, 142.4; IR (NaCl, cm^{-1}) 801, 1633, 1644, 1657; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{11}H_{10}NaO_2S_2^+$ 261.0020; Found 261.0018.

Methyl 2-(furan-3-yl)benzenesulfinate (**3j**)



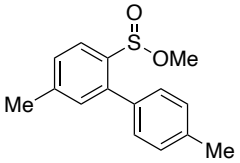
Yield: 94% (210 mg, 0.943 mmol); Black oil; TLC R_f 0.56 (*n*-hexane/EtOAc = 3/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.47 (s, 3H), 6.57–6.63 (m, 1H), 7.43 (dd, 1H, *J* = 7.3, 1.6 Hz), 7.48–7.59 (m, 3H), 7.63 (s, 1H), 8.08 (dd, 1H, *J* = 7.3, 1.6 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 50.2, 111.5, 122.0, 124.6, 127.5, 130.4, 131.9, 132.2, 141.2, 141.5, 143.2; IR (NaCl, cm^{-1}) 874, 921, 967, 1016, 1033, 1046, 1102, 1126, 1163, 1461, 1508; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{11}H_{10}NaO_3S^+$ 245.0248; Found 245.0249.

Methyl 2-(benzofuran-2-yl)benzenesulfinate (**3k**)



Yield: 92% (251 mg, 0.922 mmol); Brown oil; TLC R_f 0.59 (*n*-hexane/EtOAc = 3/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.52 (s, 3H), 7.14 (d, 1H, *J* = 0.8 Hz), 7.28 (ddd, 1H, *J* = 7.2, 7.2, 1.1 Hz), 7.36 (ddd, 1H, *J* = 7.2, 7.2, 1.2 Hz), 7.55 (dd, 1H, *J* = 7.2, 0.8 Hz), 7.60 (ddd, 1H, *J* = 7.6, 7.6, 1.5 Hz), 7.62–7.68 (m, 2H), 7.93 (dd, 1H *J* = 7.6, 1.6 Hz), 8.20 (dd, 1H, *J* = 7.6, 1.5 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 50.9, 107.0, 111.2, 121.5, 123.2, 125.1, 125.2, 128.5, 128.65, 128.66, 129.1, 132.2, 141.3, 152.1, 155.0; IR (NaCl, cm^{-1}) 803, 921, 966, 1020, 1125, 1165, 1258, 1431, 1447; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{15}H_{12}NaO_3S^+$ 295.0405; Found 295.0404.

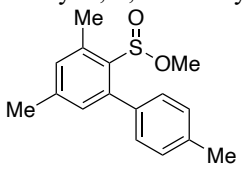
Methyl 4',5-dimethyl-[1,1'-biphenyl]-2-sulfinate (**3l**)



Yield: 88% (92.1 mg, 0.354 mmol); Brown oil; TLC R_f 0.50 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.41 (s, 3H), 2.44 (s, 3H), 3.38 (s, 3H), 7.16 (s, 1H), 7.22–7.29 (m, 4H), 7.36 (d, 1H, *J* = 8.0 Hz), 7.96 (d, 1H, *J* = 8.0 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 21.3, 21.5, 51.0, 124.5, 128.3, 129.0, 129.3, 131.5, 135.0,

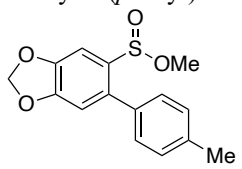
137.9, 139.4, 141.4, 142.6; IR (NaCl, cm^{-1}) 818, 969, 1072, 1125, 1455, 1462, 1515, 1597, 2938; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{15}H_{16}NaO_2S^+$ 283.0769; Found 283.0768.

Methyl 3,4',5-trimethyl-[1,1'-biphenyl]-2-sulfinate (**3m**)



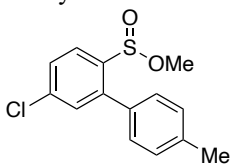
Yield: quant. (6.7 mg, 25 μmol); Yellow oil; TLC R_f 0.30 (*n*-hexane/CH_2Cl_2 = 1/1); ^1H NMR ($CDCl_3$, 400 MHz): δ 2.35 (s, 3H), 2.41 (s, 3H), 2.77 (s, 3H), 3.72 (s, 3H), 6.92 (s, 1H), 7.07 (s, 1H), 7.19–7.22 (m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 18.8, 21.1 (two signals overlapped), 54.8, 128.5, 128.8, 129.5, 132.8, 135.7, 137.4, 138.2, 138.6, 141.4, 142.3; IR (NaCl, cm^{-1}) 820, 986, 1128, 1452, 1459, 1512, 1595, 2933; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{16}H_{18}NaO_2S^+$ 297.0925; Found 297.0923.

Methyl 6-(*p*-tolyl)benzo[*d*][1,3]dioxole-5-sulfinate (**3n**)



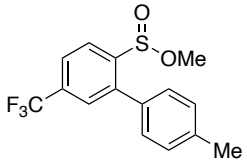
Yield: 67% (77.5 mg, 0.267 mmol); Colorless solid; Mp 86–88 °C; TLC R_f 0.50 (*n*-hexane/EtOAc = 2/1); ^1H NMR ($CDCl_3$, 400 MHz): δ 2.40 (s, 3H), 3.43 (s, 3H), 6.06–6.10 (m, 2H), 6.78 (s, 1H), 7.23 (s, 4H), 7.53 (s, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 21.2, 51.1, 102.0, 104.2, 110.5, 129.0, 129.4, 134.4, 136.3, 137.0, 138.0, 147.4, 150.6; IR (NaCl, cm^{-1}) 970, 1037, 1120, 1228, 1475, 2918, 2935, 3852; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{15}H_{14}NaO_4S^+$ 313.0511; Found 313.0512.

Methyl 5-chloro-4'-methyl-1,1'-biphenyl-2-sulfinate (**3o**)



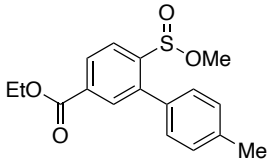
Yield: 70% (39.6 mg, 0.141 mmol); Pale yellow oil; TLC R_f 0.45 (*n*-hexane/EtOAc = 4/1); ^1H NMR ($CDCl_3$, 400 MHz): δ 2.42 (s, 3H), 3.38 (s, 3H), 7.23–7.28 (m, 4H), 7.35 (d, 1H, *J* = 2.1 Hz), 7.52 (dd, 1H, *J* = 8.4, 2.1 Hz), 8.01 (d, 1H, *J* = 8.4 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 21.2, 51.3, 126.1, 127.7, 129.1, 129.2, 130.6, 133.5, 138.2, 138.6, 140.8, 143.0; IR (NaCl, cm^{-1}) 818, 911, 969, 1016, 1059, 1093, 1129, 1452, 1551, 1581; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{14}H_{13}ClNaO_2S^+$ 303.0223; Found 303.0222.

Methyl 4'-methyl-5-(trifluoromethyl)-1,1'-biphenyl-2-sulfinate (**3p**)



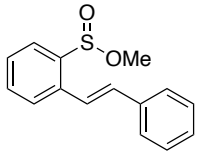
Yield: 87% (101 mg, 0.323 mmol); Brown solid; Mp 48–49 °C; TLC R_f 0.55 (*n*-hexane/EtOAc = 4/1); ^1H NMR ($CDCl_3$, 400 MHz): δ 2.43 (s, 3H), 3.41 (s, 3H), 7.25–7.35 (m, 4H), 7.62 (s, 1H), 7.81 (dd, 1H, *J* = 8.1, 1.1 Hz), 8.21 (d, 1H, *J* = 8.1 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 21.2, 51.8, 123.4 (q, *J* = 273 Hz), 124.4 (q, *J* = 3.7 Hz), 125.2, 127.7 (q, *J* = 3.6 Hz), 129.1, 129.3, 133.5, 133.8 (q, *J* = 32.8 Hz), 138.8, 142.3, 146.0; ^{19}F NMR ($CDCl_3$, 376 MHz): δ −62.9 (s) IR (NaCl, cm^{-1}) 818, 969, 1053, 1082, 1128, 1170, 1258, 1292, 1335, 1414; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{15}H_{13}F_3NaO_2S^+$ 337.0486; Found 337.0488.

Ethyl 6-(methoxysulfinyl)-4'-methyl-[1,1'-biphenyl]-3-carboxylate (**3q**)



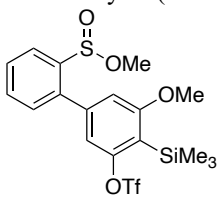
Yield: quant. (161 mg, 0.504 mmol); Pale yellow oil; TLC R_f 0.26 (*n*-hexane/EtOAc = 7/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.40 (t, 3H, *J* = 7.1 Hz), 2.43 (s, 3H), 3.40 (s, 3H), 4.41 (q, 2H, *J* = 7.1 Hz), 7.25–7.32 (m, 4H), 8.03 (d, 1H, *J* = 1.6 Hz), 8.15 (d, 1H, *J* = 8.2 Hz), 8.20 (dd, 1H, *J* = 8.2, 1.6 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 14.1, 21.1, 51.4, 61.4, 124.5, 128.3, 129.06, 129.11, 131.7, 133.5, 133.9, 138.2, 141.5, 146.2, 165.3; IR (NaCl, cm^{-1}) 821, 969, 1106, 1132, 1245, 1276, 1285, 1305, 1723; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{17}H_{18}NaO_4S^+$ 341.0824; Found 341.0823.

Methyl (*E*)-2-styrylbenzenesulfinate (**3r**)



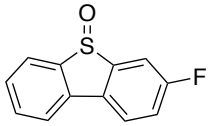
Yield: 38% (95.1 mg, 0.368 mmol); Pale yellow solid; Mp 44–45 °C; TLC R_f 0.57 (*n*-hexane/EtOAc = 3/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.48 (s, 3H), 7.13 (d, 1H, *J* = 16.0 Hz), 7.29–7.35 (AA'BB'C, 1H), 7.36–7.43 (AA'BB'C, 2H), 7.48 (ddd, 1H, *J* = 7.6, 7.6, 1.2 Hz), 7.51–7.59 (m, 4H), 7.75 (d, 1H, *J* = 7.6 Hz), 7.98 (dd, 1H, *J* = 7.6, 1.2 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 49.8, 122.2, 125.0, 126.1, 126.9, 127.7, 128.5, 128.8, 132.4, 132.8, 136.5, 136.6, 140.2; IR (NaCl, cm^{-1}) 963, 1050, 1129, 1158, 1449, 1464, 1495, 2939, 3058; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{15}H_{14}NaO_2S^+$ 281.0612; Found 281.0614.

5-Methoxy-2'-(methoxysulfinyl)-4-(trimethylsilyl)-[1,1'-biphenyl]-3-yl trifluoromethanesulfonate (**3s**)



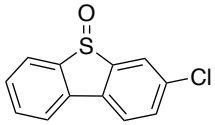
Yield: 93% (224 mg, 0.464 mmol); Pale yellow oil; TLC R_f 0.58 (*n*-hexane/EtOAc = 2/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.40 (s, 9H), 3.43 (s, 3H), 3.85 (s, 3H), 6.86 (d, 1H, *J* = 1.1 Hz), 6.97 (d, 1H, *J* = 1.1 Hz), 7.34–7.39 (m, 1H), 7.59–7.66 (m, 2H), 8.09–8.14 (m, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 0.7, 51.1, 55.7, 110.8, 113.8, 118.5 (q, *J* = 320 Hz), 120.6, 124.7, 128.6, 130.4, 132.3, 139.4, 141.5, 142.2, 154.3, 165.1; ^{19}F NMR ($CDCl_3$, 376 MHz): δ –72.8 (s); IR (NaCl, cm^{-1}) 847, 940, 1046, 1065, 1140, 1216, 1249, 1395, 1418, 1422; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{18}H_{21}F_3NaO_6S_2Si^+$ 505.0399; Found 505.0396.

3-Fluorodibenzo[*b*,*d*]thiophene 5-oxide (**4b**)



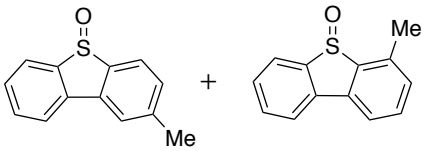
Yield: 85% (37.2 mg, 0.171 mmol); Pale yellow solid; Mp 176–179 °C; TLC R_f 0.40 (CH_2Cl_2/MeOH = 10/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.25 (ddd, 1H, *J* = 8.5, 8.5, 2.4 Hz), 7.47 (ddd, 1H, *J* = 7.5, 7.5, 1.1 Hz), 7.58 (ddd, 1H, *J* = 7.5, 7.5, 1.1 Hz), 7.67 (dd, 1H, *J* = 8.5, 2.4 Hz), 7.71–7.79 (m, 2H), 7.96 (d, 1H, *J* = 7.5 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 115.0 (d, *J* = 22.9 Hz), 119.9 (d, *J* = 22.9 Hz), 121.6, 123.2 (d, *J* = 7.2 Hz), 127.5, 129.1, 132.7, 133.1 (d, *J* = 3.1 Hz), 136.2, 145.0, 146.8 (d, *J* = 7.2 Hz), 163.1 (d, *J* = 253 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz); δ −109.7 (s); IR (NaCl, cm^{-1}) 873, 1025, 1052, 1069, 1196, 1261, 1445, 1459, 1491; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{12}H_7FNaOS^+$ 241.0099; Found 241.0097.

3-Chlorodibenzo[*b*,*d*]thiophene 5-oxide (**4c**)



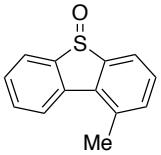
Yield: 71% (33.4 mg, 0.142 mmol); Colorless solid; Mp 192–194 °C; TLC R_f 0.29 (*n*-hexane/EtOAc = 2/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.52 (ddd, 1H, *J* = 7.5, 7.5, 1.1 Hz), 7.57 (dd, 1H, *J* = 8.2, 1.9 Hz), 7.62 (ddd, 1H, *J* = 7.5, 7.5, 1.1 Hz), 7.74 (d, 1H, *J* = 8.2 Hz), 7.78 (d, 1H, *J* = 7.5 Hz), 7.95–8.01 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 121.9, 122.8, 127.6, 127.8, 129.8, 132.8 (two signals overlapped), 135.50, 135.53, 136.2, 145.1, 146.6; IR (NaCl, cm^{-1}) 1018, 1063, 1092, 1392, 1435, 1455; HRMS (EI) *m/z*: $[M + Na]^+$ Calcd for $C_{12}H_7ClNaOS^+$ 256.9804; Found 256.9809.

2-Methyldibenzo[*b*,*d*]thiophene 5-oxide (**4e**) and 4-Methyldibenzo[*b*,*d*]thiophene 5-oxide (**4e'**)



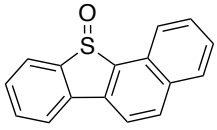
2-Methyldibenzo[*b*,*d*]thiophene 5-oxide was isolated with a small amount of 4-methyldibenzo[*b*,*d*]thiophene 5-oxide. The ratio **4e**/**4e'** was judged from ^{1}H NMR analysis of the isolated product. Yield: 76% (83.0 mg, 0.388 mmol); Pale yellow solid; Mp 102–104 °C; TLC R_f 0.43 (*n*-hexane/EtOAc = 1/2); For **4e**: ^{1}H NMR (MeOD, 400 MHz): δ 2.46 (s, 3H), 7.27 (dd, 1H, *J* = 7.8, 0.7 Hz), 7.46 (ddd, 1H, *J* = 7.5, 7.5, 1.0 Hz), 7.53–7.60 (m, 2H), 7.75 (d, 1H, *J* = 7.5 Hz), 7.83 (d, 1H, *J* = 7.8 Hz), 7.95 (dd, 1H, *J* = 7.5 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 21.7, 123.5, 124.0, 128.3, 128.4, 130.9, 131.7, 134.2, 138.5, 138.7, 142.2, 145.59, 145.65; For **4e'**: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.72 (s, 3H), 7.21 (d, 1H, *J* = 7.5 Hz), 7.42–7.49 (m, 2H), 7.53–7.60 (m, 2H), 7.75 (d, 1H, *J* = 7.5 Hz), 7.95 (d, 1H, *J* = 7.5 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 18.6, 121.1, 123.6, 128.3, 132.4, 134.2, 134.7, 138.6, 138.7, 140.3, 143.1, 144.7, 145.6; IR (NaCl, cm^{-1}) 814, 1023, 1066, 1435, 1441, 1447, 1451, 1455, 1600; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{13}H_{10}OS^+$ 237.0350; Found 237.0356.

1-Methyldibenzo[*b*,*d*]thiophene 5-oxide (**4f**)



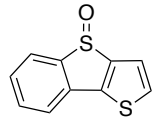
Yield: 79% (33.6 mg, 0.157 mmol); Colorless solid; Mp 123–125 °C; TLC R_f 0.58 (*n*-hexane/EtOAc = 1/3); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.74 (s, 3H), 7.36–7.43 (m, 2H), 7.50 (ddd, 1H, *J* = 7.6, 7.6, 1.0 Hz), 7.61 (ddd, 1H, *J* = 7.6, 7.6, 1.2 Hz), 7.85–7.89 (m, 1H), 7.98 (d, 1H, *J* = 7.9 Hz), 8.03 (dd, 1H, *J* = 7.6, 1.2 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 21.8, 125.39, 125.42, 127.9, 128.8, 129.0, 132.5, 135.0, 135.4, 135.5, 138.3, 145.2, 145.6; IR (NaCl, cm^{-1}) 1435, 1447, 1455, 1471, 2730, 2893, 2910; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{13}H_{10}NaOS^+$ 237.0351; Found 237.0350.

Benzo[*b*]naphtho[2,1-*d*]thiophene 11-oxide (**4g**)



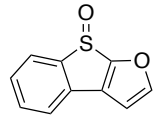
Yield: 82% (41.0 mg, 0.164 mmol); Yellow solid; Mp 175–176 °C; TLC R_f 0.43 (*n*-hexane/EtOAc = 1/2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.51 (ddd, 1H, *J* = 7.5, 7.5, 1.1 Hz), 7.54–7.63 (m, 2H), 7.68 (ddd, 1H, *J* = 8.2, 7.0, 1.2 Hz), 7.81–7.85 (m, 2H), 7.92 (d, 1H, *J* = 8.2 Hz), 8.01–8.05 (m, 2H), 8.51 (dd, 1H, *J* = 8.2, 0.8 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 118.7, 122.0, 123.9, 127.25, 127.32, 128.8, 129.0, 129.3, 130.6, 132.4, 133.7, 133.9, 135.5, 137.3, 140.3, 145.2; IR (NaCl, cm^{-1}) 820, 863, 1019, 1053, 1140, 1472; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{16}H_{10}NaOS^+$ 273.0350; Found 273.0350.

Benzo[*b*]thieno[3,2-*d*]thiophene 8-oxide (**4h**)



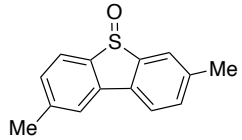
Yield: 82% (33.7 mg, 0.163 mmol); Brown solid; Mp 114–115 °C; TLC R_f 0.57 (*n*-hexane/EtOAc = 1/2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.34 (d, 1H, *J* = 5.0 Hz), 7.43 (ddd, 1H, *J* = 7.5, 7.5, 1.3 Hz), 7.54 (ddd, 1H, *J* = 7.5, 7.5, 1.1 Hz), 7.60 (d, 1H, *J* = 7.5 Hz), 7.73 (d, 1H, *J* = 5.0 Hz), 7.90 (d, 1H, *J* = 7.5 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 119.6, 121.8, 127.4, 128.1, 132.2, 133.6, 136.7, 144.1, 147.9, 151.4; IR (NaCl, cm^{-1}) 1374, 1435, 1447, 1455, 1471, 2724, 2923, 3048, 3053; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{10}H_6NaOS_2^+$ 228.9753; Found 228.9758.

Benzo[4,5]thieno[2,3-*b*]furan 8-oxide (**4j**)



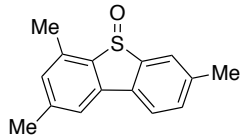
Yield: 72% (31.4 mg, 0.143 mmol); Brown solid; Mp 67–69 °C; TLC R_f 0.52 (*n*-hexane/EtOAc = 1/2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.74 (d, 1H, *J* = 1.9 Hz), 7.40 (ddd, 1H, *J* = 7.6, 7.6, 1.7 Hz), 7.45–7.53 (m, 2H), 7.68 (d, 1H, *J* = 1.9 Hz), 7.81 (d, 1H *J* = 7.6 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 106.2, 122.0, 127.6, 128.5, 130.7, 132.2, 133.5, 149.1, 152.2, 158.6; IR (NaCl, cm^{-1}) 1029, 1085, 1125, 1261, 1447, 1455; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{10}H_6NaO_2S^+$ 212.9985; Found 212.9986.

2,7-Dimethyldibenzo[*b*,*d*]thiophene 5-oxide (**4l**)



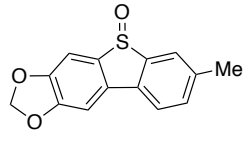
Yield: 83% (18.9 mg, 82.7 μmol); Colorless solid; Mp 152–153 °C; TLC R_f 0.60 (*n*-hexane/EtOAc = 1/2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.45–2.46 (br, 3H), 2.47 (s, 3H), 7.24–7.27 (m, 1H), 7.38 (dq, 1H, *J* = 7.8, 0.7 Hz), 7.56 (s, 1H), 7.66 (d, 1H, *J* = 7.8 Hz), 7.78 (s, 1H), 7.83 (d, 1H, *J* = 7.8 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 21.4, 21.8, 121.5, 122.1, 127.2, 127.9, 129.8, 133.2, 134.5, 137.4, 140.0, 142.0, 143.2, 145.6; IR (NaCl, cm^{-1}) 821, 1027, 1065, 1447, 1451, 1603; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{14}H_{12}NaOS^+$ 251.0507; Found 251.0504.

2,4,7-Trimethyldibenzo[*b*,*d*]thiophene 5-oxide (**4m**)



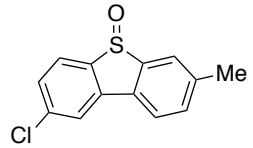
Yield: 57% (3.3 mg, 14 μmol); Pale yellow solid; Mp 132–134 °C; TLC R_f 0.71 (*n*-hexane/EtOAc = 2/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.41 (s, 3H), 2.45 (s, 3H), 2.68 (s, 3H), 7.01 (s, 1H), 7.32–7.40 (m, 2H), 7.61 (d, 1H, *J* = 7.8 Hz), 7.75 (s, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 18.6, 21.4, 21.6, 119.7, 121.5, 127.7, 131.3, 133.0, 134.7, 137.6, 138.9, 139.8, 140.1, 143.3, 145.2; IR (NaCl, cm^{-1}) 821, 1027, 1065, 1437, 1447, 1455, 1490, 1603; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{15}H_{14}NaOS^+$ 265.0663; Found 265.0662.

7-Methylbenzo[4',5']thieno[2',3':4,5]benzo[1,2-*d*][1,3]dioxole 5-oxide (**4n**)



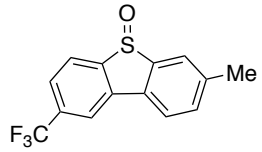
Yield: 82% (5.3 mg, 21 μmol); Pale yellow solid; Mp 180–182 °C; TLC R_f 0.43 (*n*-hexane/EtOAc = 1/2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.44 (s, 3H), 6.10 (s, 2H), 7.15 (s, 1H), 7.32–7.38 (m, 2H), 7.51 (d, 1H, *J* = 7.8 Hz), 7.72 (s, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 21.3, 101.8, 102.4, 107.5, 120.8, 127.7, 132.7, 137.2, 134.3, 138.3, 139.0, 145.6, 148.8, 151.8; IR (NaCl, cm^{-1}) 924, 1020, 1036, 1057, 1223, 1261, 1470; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{14}H_{10}NaO_3S^+$ 281.0248; Found 281.0249.

2-Chloro-7-methyldibenzo[*b*,*d*]thiophene 5-oxide (**4o**)



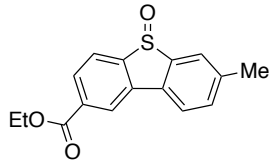
Yield: 85% (21.1 mg, 84.8 μmol); Colorless solid; Mp 174–176 °C; TLC R_f 0.26 (*n*-hexane/EtOAc = 1/2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.48 (s, 3H), 7.39–7.45 (m, 2H), 7.66 (d, 1H, J = 7.8 Hz), 7.73 (d, 1H, J = 1.9 Hz), 7.79 (s, 1H), 7.88 (d, 1H, J = 8.2 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 21.5, 121.88, 121.93, 128.1, 128.6, 129.0, 133.3, 133.5, 139.1 (two signals overlapped), 141.0, 143.1, 145.9; IR (NaCl, cm^{-1}) 823, 1014, 1029, 1057, 1086, 1448, 1488, 1565, 1585; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{13}H_9ClNaOS^+$ 270.9960; Found 270.9964.

7-Methyl-2-(trifluoromethyl)dibenzo[*b*,*d*]thiophene 5-oxide (**4p**)



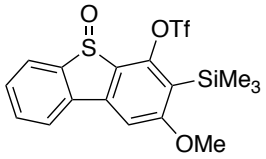
Yield: 68% (38.3 mg, 0.136 mmol); Colorless solid; Mp 146–148 °C; TLC R_f 0.39 (*n*-hexane/EtOAc = 2/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.48 (s, 3H), 7.44 (d, 1H, J = 7.8 Hz), 7.67–7.77 (m, 2H), 7.81 (s, 1H), 7.97 (s, 1H), 8.07 (d, 1H, J = 8.0 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 21.5, 118.0 (q, J = 3.7 Hz), 122.1, 123.4 (q, J = 273 Hz), 125.7 (q, J = 3.7 Hz), 127.9, 128.1, 133.0, 133.7, 134.6 (q, J = 32.9 Hz), 138.1, 141.3, 145.5, 148.2; ^{19}F NMR ($CDCl_3$, 376 MHz): δ −62.9 (s) IR (NaCl, cm^{-1}) 826, 1033, 1055, 1128, 1170, 1641, 1656, 3421; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{14}H_9F_3NaOS^+$ 305.0224; Found 305.0222.

Ethyl 7-methyldibenzo[*b*,*d*]thiophene-2-carboxylate 5-oxide (**4q**)



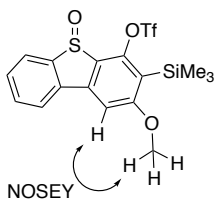
Yield: 70% (22.7 mg, 79.3 μmol); Pale yellow solid; Mp 171–173 °C; TLC R_f 0.47 (*n*-hexane/EtOAc = 2/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.45 (t, 3H, J = 7.1 Hz), 2.49 (s, 3H), 4.45 (q, 2H, J = 7.1 Hz), 7.44 (d, 1H, J = 7.8 Hz), 7.77–7.83 (m, 2H), 8.03 (d, 1H, J = 7.9 Hz), 8.14 (dd, 1H, J = 7.9, 1.0 Hz), 8.41 (d, 1H, J = 1.0 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 14.3, 21.5, 61.7, 122.1, 122.6, 127.4, 128.0, 130.0, 133.59, 133.63, 134.4, 137.6, 140.8, 145.3, 148.8, 165.4; IR (NaCl, cm^{-1}) 1028, 1246, 1273, 1417, 1714; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{16}H_{14}NaO_3S$ 309.0561; Found 309.0563.

2-Methoxy-5-oxido-3-(trimethylsilyl)dibenzo[*b*,*d*]thiophen-4-yl trifluoromethanesulfonate (**4r**)

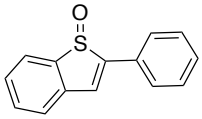


Yield: 76% (16.5 mg, 38.0 mmol); Colorless solid; Mp 224–226 °C; TLC R_f 0.51 (*n*-hexane/EtOAc = 1/2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.40 (s, 9H), 3.99 (s, 3H), 7.19 (s, 1H), 7.55 (ddd, 1H, J = 7.4, 7.4, 1.0 Hz), 7.62 (ddd, 1H, J = 7.4. 7.4, 0.8 Hz), 7.79 (d, 1H, J = 7.4 Hz), 7.95 (d, 1H, J = 7.4 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 0.4, 56.1, 103.0, 118.4 (q, J = 321 Hz), 122.2, 125.0, 127.4, 130.5, 130.7, 132.6, 136.1, 143.3, 146.0, 150.1, 169.7; ^{19}F NMR ($CDCl_3$, 376 MHz): δ −72.8 (s); IR (NaCl, cm^{-1}) 810, 1030, 1062, 1136, 1216, 1222, 1378; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{17}H_{17}F_3NaO_5S_2Si^+$ 473.0131; Found 473.0123.

The regiochemistry of **4r** was determined by the NOESY experiment.

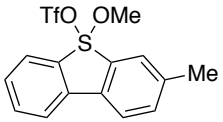


2-Phenylbenzo[*b*]thiophene 1-oxide (**6**)



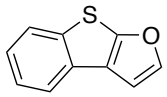
Yield: 59% (13.4 mg, 59.2 μmol); Pale yellow solid; Mp 132–134 °C; TLC R_f 0.34 (*n*-hexane/EtOAc = 2/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.29 (s, 1H), 7.39–7.56 (m, 6H), 7.78–7.83 (m, 2H), 7.95 (d, 1H, J = 7.5 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 124.5, 126.4, 126.6, 127.0, 128.4, 129.2, 129.5, 130.8, 132.3, 137.8, 144.1, 152.4; IR (NaCl, cm^{-1}) 1025, 1063, 2852, 2923, 3048, 3056, 3852; HRMS (EI) *m/z*: $[M + Na]^+$ Calcd for $C_{14}H_{10}NaOS^+$ 249.0350; Found 249.0352.

5-Methoxy-3-methyl-5*H*-5λ^4-dibenzo[*b*,*d*]thiophen-5-yl trifluoromethanesulfonate (**7**)



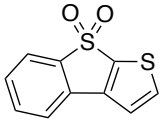
Yield: quant. (38.1 mg, 0.101 mmol); Yellow solid; Mp 89–90 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.54 (s, 3H), 3.64 (s, 3H), 7.64–7.70 (m, 2H), 7.84–7.90 (m, 2H), 7.95 (d, 1H, J = 7.6 Hz), 8.13 (s, 1H), 8.29 (d, 1H, J = 7.8 Hz); $^{13}C\{^1H\}$ NMR (CD_3CN, 101 MHz): δ 21.4, 58.4, 121.7 (q, J = 319.7 Hz), 124.8, 124.9, 128.8, 128.9, 131.6, 131.8, 132.2, 138.6, 139.2 (two signals overlapped), 142.0, 144.1; ^{19}F NMR ($CDCl_3$, 376 MHz): δ –78.4 (s); IR (NaCl, cm^{-1}) 1029, 1062, 1173, 1232, 1259, 1455. Gradual decomposition was observed in $CDCl_3$.

Benzo[4,5]thieno[2,3-*b*]furan (**9c**)



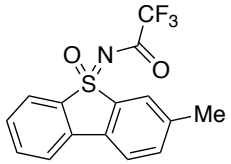
Yield: 66% (11.5 mg, 66.0 μmol); Brown oil; TLC R_f 0.44 (*n*-hexane); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.95 (d, 1H, J = 2.0 Hz), 7.27–7.33 (m, 1H), 7.37–7.43 (m, 1H), 7.68 (d, 1H, J = 2.0 Hz), 7.77 (d, 1H, J = 7.8 Hz), 7.80 (d, 1H, J = 7.8 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 106.0, 121.3, 123.7, 123.9, 124.2, 124.9, 130.0, 139.4, 148.0, 154.6; IR (NaCl, cm^{-1}) 1009, 1050, 1119, 1236, 1259, 1328, 1435, 1488; HRMS (EI) *m/z*: $[M]^{\cdot+}$ Calcd for $C_{10}H_6OS^{\cdot+}$ 174.0139; Found 174.0139.

Benzo[*b*]thieno[2,3-*d*]thiophene 4,4-dioxide (**10b**)



Yield: 36% (7.9 mg, 0.0355 mmol); Colorless solid; Mp 300 °C over; TLC R_f 0.66 (*n*-hexane/EtOAc = 2/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.30 (s, 1H), 7.43–7.49 (m, 3H), 7.56 (ddd, 1H, J = 7.6, 7.6, 1.1 Hz), 7.71–7.75 (m, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 120.0, 121.4, 122.2, 128.1, 129.6, 131.1, 133.7, 139.9, 142.1, 142.8; IR (NaCl, cm^{-1}) 1027, 1093, 1146, 1261, 1288, 1634, 1646, 1651, 2963; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{10}H_6NaO_2S_2^+$ 244.9707; Found 244.9705.

2,2,2-Trifluoro-*N*-(3-methyl-5-oxido-5λ^4-dibenzo[*b*,*d*]thiophen-5-ylidene)acetamide (**11**)

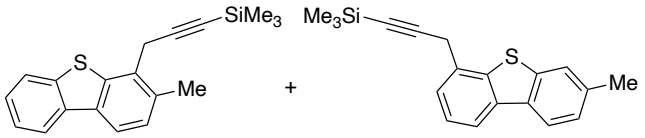


Yield: 73% (23.6 mg, 72.5 μmol); Colorless solid; Mp 198–200 °C; TLC R_f 0.59 (*n*-hexane/EtOAc = 1/2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.50 (s, 3H), 7.52–7.60 (m, 2H), 7.71–7.76 (m, 2H), 7.81(d, 1H, J = 7.7 Hz), 8.02 (s, 1H), 8.21 (d, 1H, J = 7.8 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 21.6, 116.0 (q, J = 287 Hz), 121.7, 121.8, 125.7, 125.8, 130.5, 130.6, 133.5, 135.1, 135.2, 135.5, 136.3, 142.2, 165.1 (q, J = 38.4 Hz); ^{19}F NMR ($CDCl_3$,

376 MHz): δ −75.3 (s); IR (NaCl, cm^{-1}) 820, 1155, 1169, 1202, 1231, 1671; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{15}H_{10}F_3NNaO_2S^+$ 348.0282; Found 348.0283.

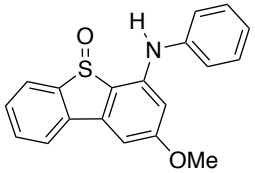
Trimethyl(3-(3-methyldibenzo[*b*,*d*]thiophen-4-yl)prop-1-yn-1-yl)silane (**13**) and

Trimethyl(3-(7-methyldibenzo[*b*,*d*]thiophen-4-yl)prop-1-yn-1-yl)silane (**13'**)



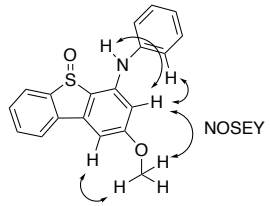
Trimethyl(3-(3-methyldibenzo[*b*,*d*]thiophen-4-yl)prop-1-yn-1-yl)silane and trimethyl(3-(7-methyldibenzo[*b*,*d*]thiophen-4-yl)prop-1-yn-1-yl)silane were isolated as an inseparable mixture. The ratio **13**/**13'** was judged from ^{1}H NMR analysis. Yield: 87% (40.2 mg, 0.130 mmol); Pale yellow solid; Mp 119–120 °C; TLC R_f 0.35 (*n*-hexane); For **13**: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.12 (s, 9H), 2.56 (s, 3H), 3.82 (s, 2H), 7.30 (d, 1H, *J* = 9.2 Hz), 7.40–7.46 (m, 2H), 7.83–7.89 (m, 1H), 7.96 (d, 1H *J* = 7.9 Hz), 8.07–8.13 (m, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ –0.01, 19.5, 23.5, 86.0, 102.0, 119.9, 121.3, 122.7, 124.3, 126.3, 127.5, 128.9, 134.0, 135.0, 136.2, 139.1, 140.0; For **13'**: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.22 (s, 9H), 2.52 (s, 3H), 3.86 (s, 2H), 7.25–7.27 (m, 1H), 7.47 (d, 1H, *J* = 7.6 Hz), 7.58 (dd, 1H, *J* = 7.3, 0.9 Hz), 7.67 (s, 1H), 8.00–8.05 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 0.04, 21.7, 25.4, 88.3, 102.2, 119.8, 121.4, 122.8, 124.8, 125.3, 126.0, 130.6, 133.5, 135.7, 136.9, 138.0, 139.3; IR (NaCl, cm^{-1}) 816, 841, 1019, 1249, 1448, 2172, 2959; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{19}H_{20}NaOSSi^+$ 347.0902; Found 347.0909.

2-Methoxy-4-(phenylamino)dibenzo[*b*,*d*]thiophene 5-oxide (**14**)

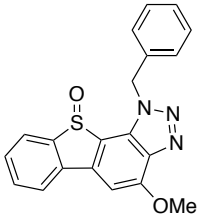


Yield: 55% (3.5 mg, 11 μmol); Yellow oil; TLC R_f 0.47 (*n*-hexane/EtOAc = 2/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.86 (s, 3H), 6.82 (d, 1H, *J* = 2.1 Hz), 6.87–6.91 (m, 2H), 7.08–7.14 (AA'BB'C, 1H), 7.24–7.30 (m, 2H), 7.35–7.42 (AA'BB'C, 2H), 7.54 (ddd, 1H, *J* = 7.5, 7.5, 1.1 Hz), 7.62 (ddd, 1H, *J* = 7.5, 7.5, 1.1 Hz), 7.79 (d, 1H, *J* = 7.5 Hz), 8.00 (d, 1H, *J* = 7.5 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 55.8, 99.9, 100.8, 120.7, 121.7, 122.1, 123.2, 127.1, 129.5, 129.6, 132.2, 136.9, 139.7, 140.5, 145.5, 146.0, 164.9; IR (NaCl, cm^{-1}) 1090, 1205, 1434, 1497, 1575, 1578, 1593; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{19}H_{15}NNaO_2S^+$ 344.0721; Found 344.0723.

The regiochemistry of **14** was determined by the NOESY experiment.



1-Benzyl-4-methoxy-1*H*-benzo[4',5']thieno[2',3':3,4]benzo[1,2-*d*][1,2,3]triazole 10-oxide (**15**)



Yield: 28% (2.1 mg, 5.6 μmol); Colorless solid; Mp 228–230 °C; TLC R_f 0.31 (*n*-hexane/EtOAc = 2/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.28 (s, 3H), 6.12 (d, 1H, *J* = 15.9 Hz), 6.29 (d, 1H, *J* = 15.9 Hz), 7.08 (s, 1H), 7.30–7.39 (m, 3H), 7.42–7.47 (m, 2H), 7.53 (ddd, 1H, *J* = 7.5, 7.5, 1.1 Hz), 7.62 (ddd, 1H, *J* = 7.5, 7.5, 1.1 Hz), 7.82 (d, 1H, *J* = 7.5 Hz), 7.95 (d, 1H, *J* = 7.5 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 29.7, 53.7, 57.1, 97.5, 118.0, 122.4,

127.3, 127.5, 128.5, 129.0, 130.0, 132.5, 133.3, 135.2, 136.5, 140.1, 145.9, 156.0; IR (NaCl, cm^{-1}) 1036, 1173, 1232, 1259, 2849, 2918; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{15}N_3NaO_2S^+$ 384.0783; Found 384.0785.

The regiochemistry of **15** was determined by the NOESY experiment and ^1H NMR analysis. NOESY experiment showed no correlation between the benzyl and methoxy protons. In ^1H NMR analysis, it was shown that the benzylic protons close to the sulfoxide moiety appeared at 6.22–6.33 ppm, while the benzylic protons far from the sulfoxide appeared at 5.79–5.85 ppm.[S6] According to this low-field shift by the neighboring sulfoxide moiety, the regiochemistry of **15** was judged from the benzylic protons at 6.12 and 6.29 ppm.

References for the Supporting Information

S1 A. Kobayashi, T. Matsuzawa, T. Hosoya, S. Yoshida, *Chem. Commun.* **2020**, 56, 5429

S2 K. Nakamura, Y. Kumagai, A. Kobayashi, S. Yoshida, *Org. Biomol. Chem.* **2023**, 21, 6886.

S3 S. Yoshida, K. Shimomori, T. Nonaka, T. Hosoya, *Chem. Lett.,* **2015**, 44, 1324.

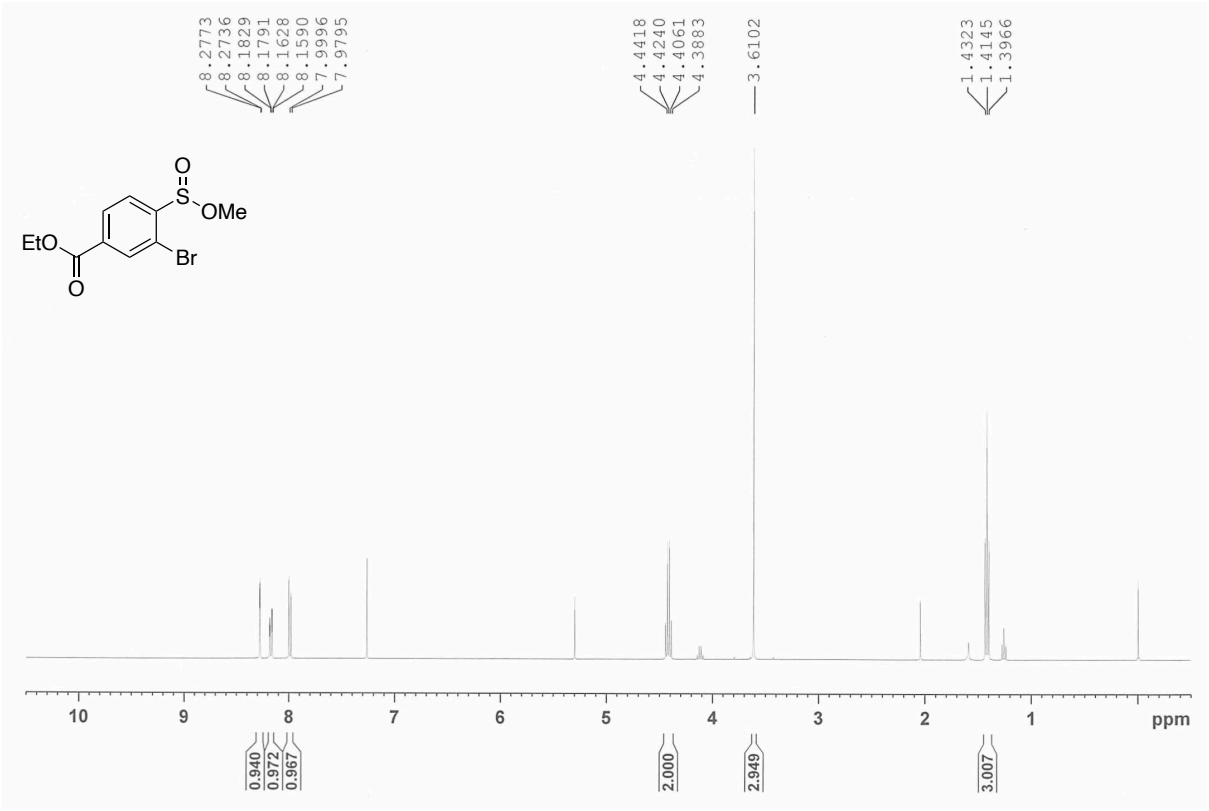
S4 R. Wada, S. Kaga, Y. Kawai, K. Futamura, T. Murai, F. Shibahara, *Tetrahedron* **2021**, 83, 131978.

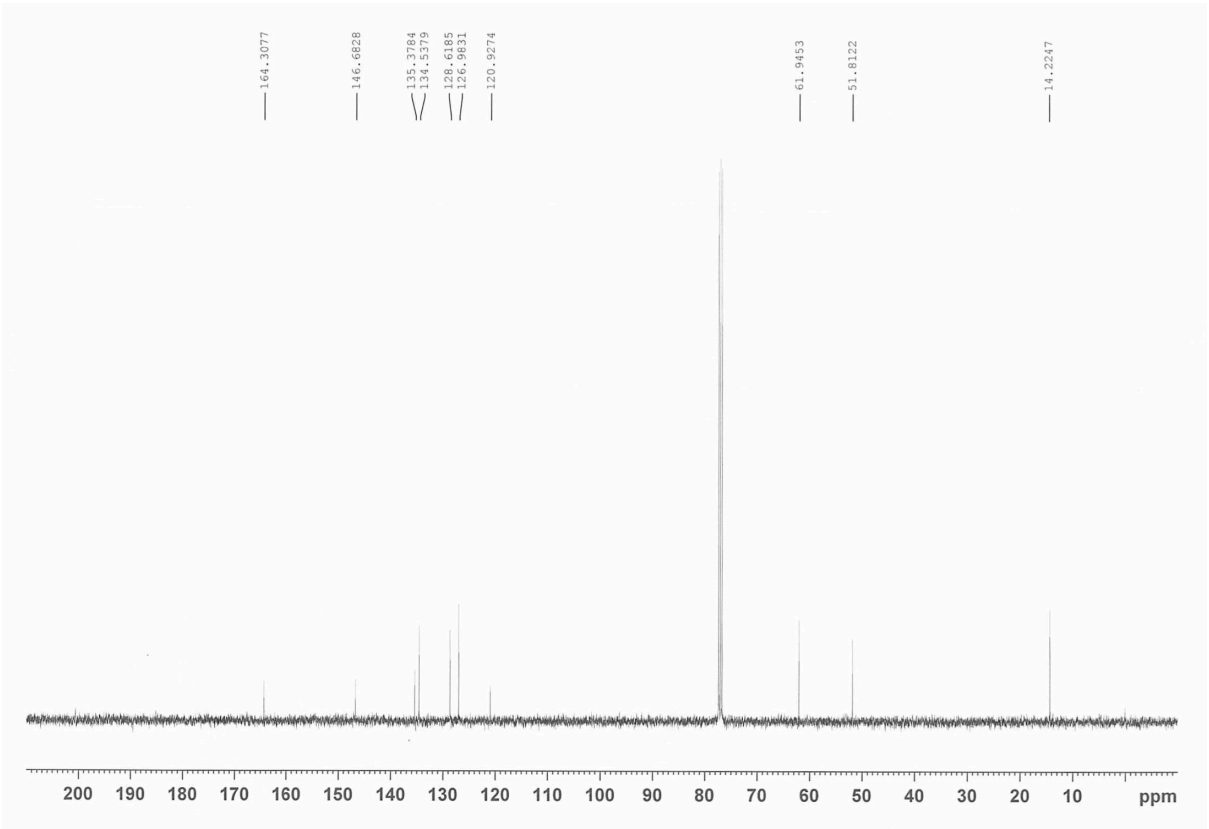
S5 Z. He, H. J. Shrives, J. A. Fernµndez-Salas, A. Abengózar, J. Neufeld, K. Yang, A. P. Pulis, D. J. Procter, *Angew. Chem. Int. Ed.* **2018**, 57, 5759.

S6 Y. Nakamura, Y. Miyata, K. Uchida, S. Yoshida, T. Hosoya, *Org. Lett.* **2019**, 21, 5252.

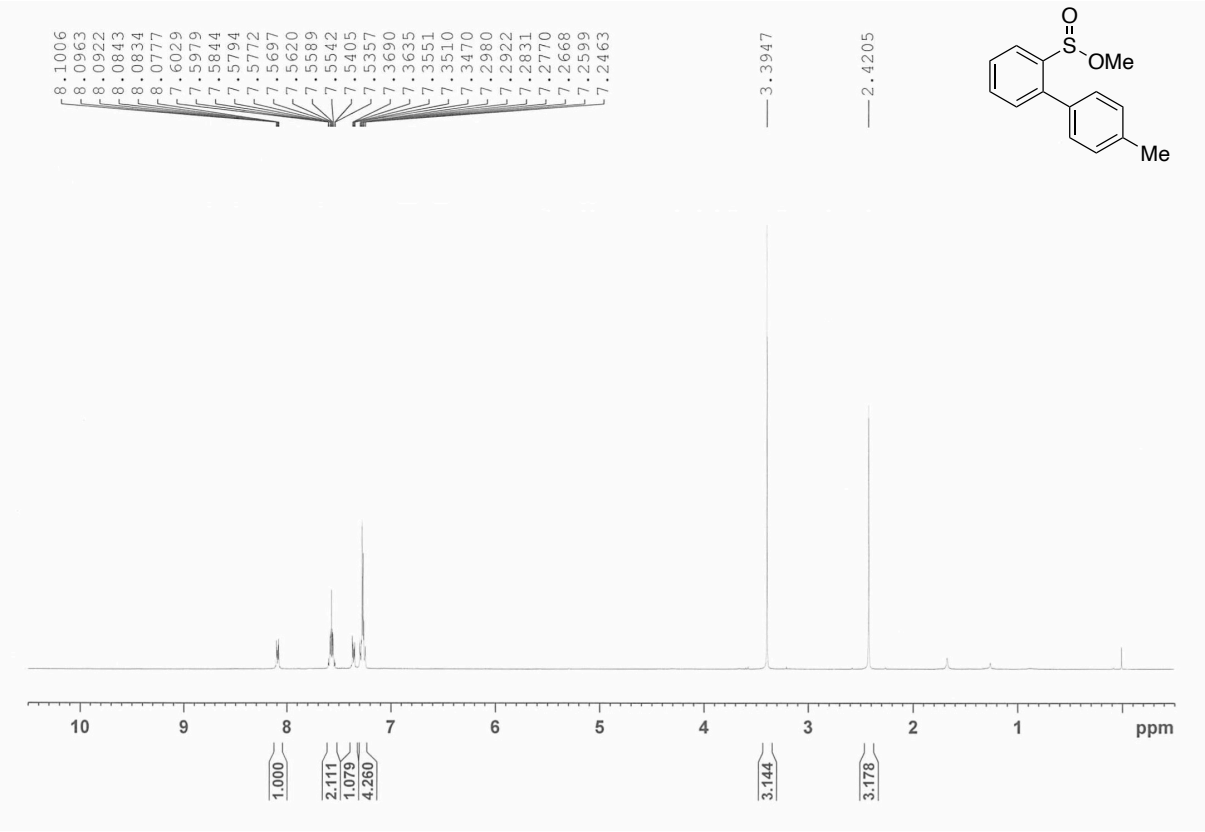
^{1}H and ^{13}C NMR Spectra of Compounds

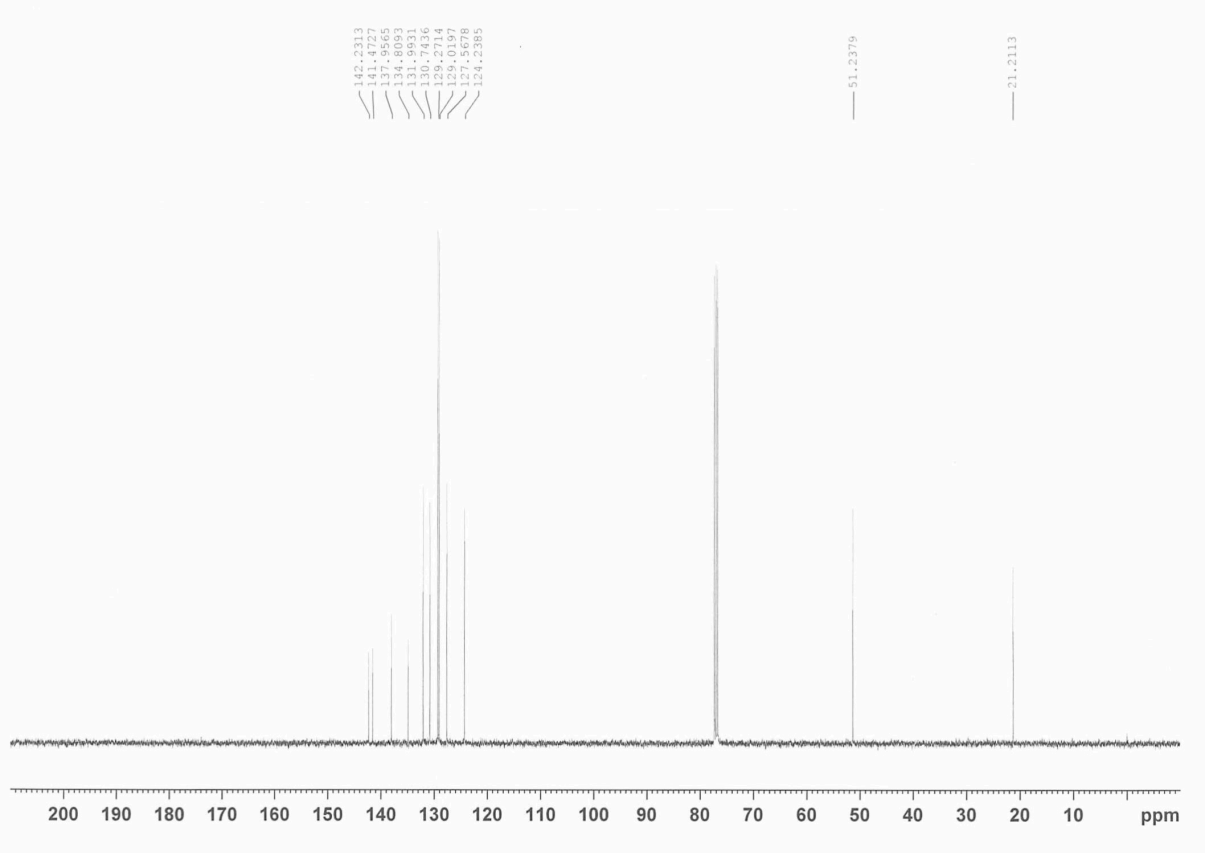
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of ethyl 3-bromo-4-(methoxysulfinyl)benzoate (**1r**) ($CDCl_3$)



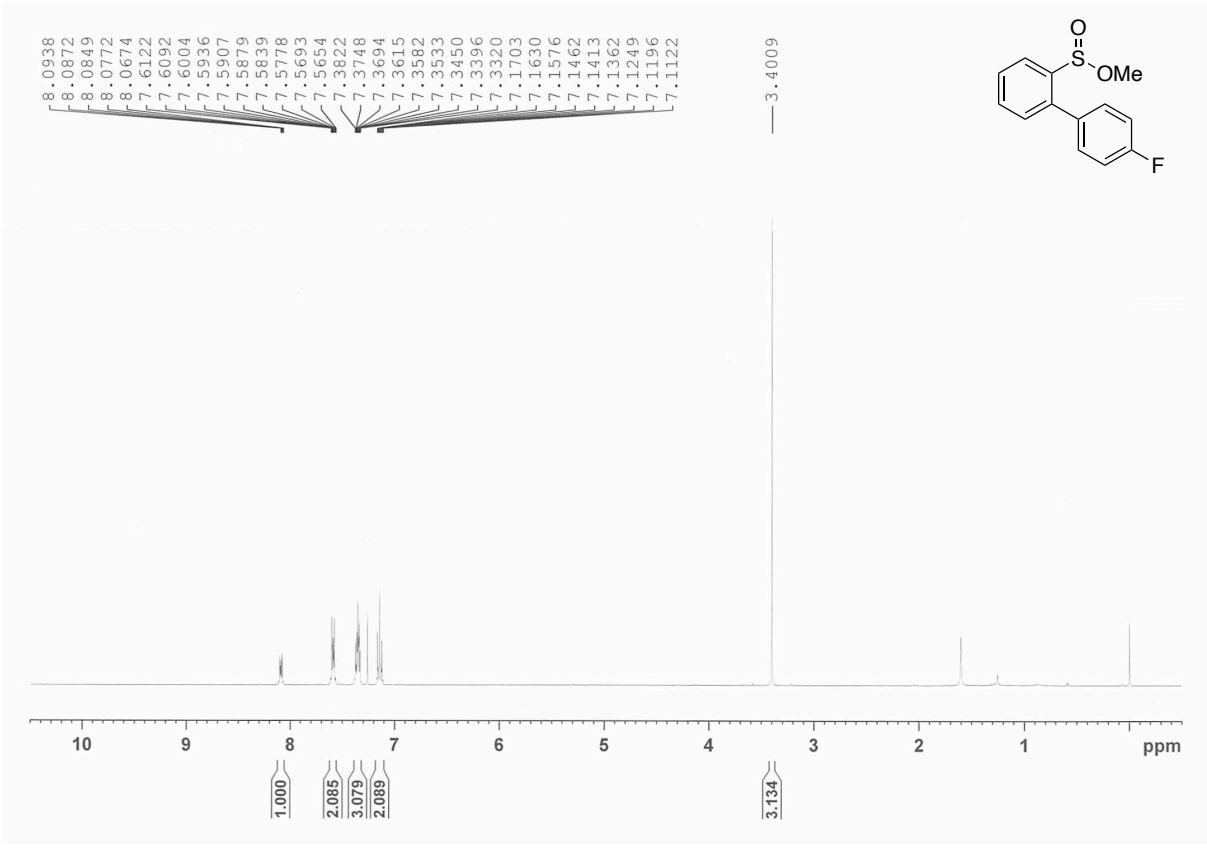


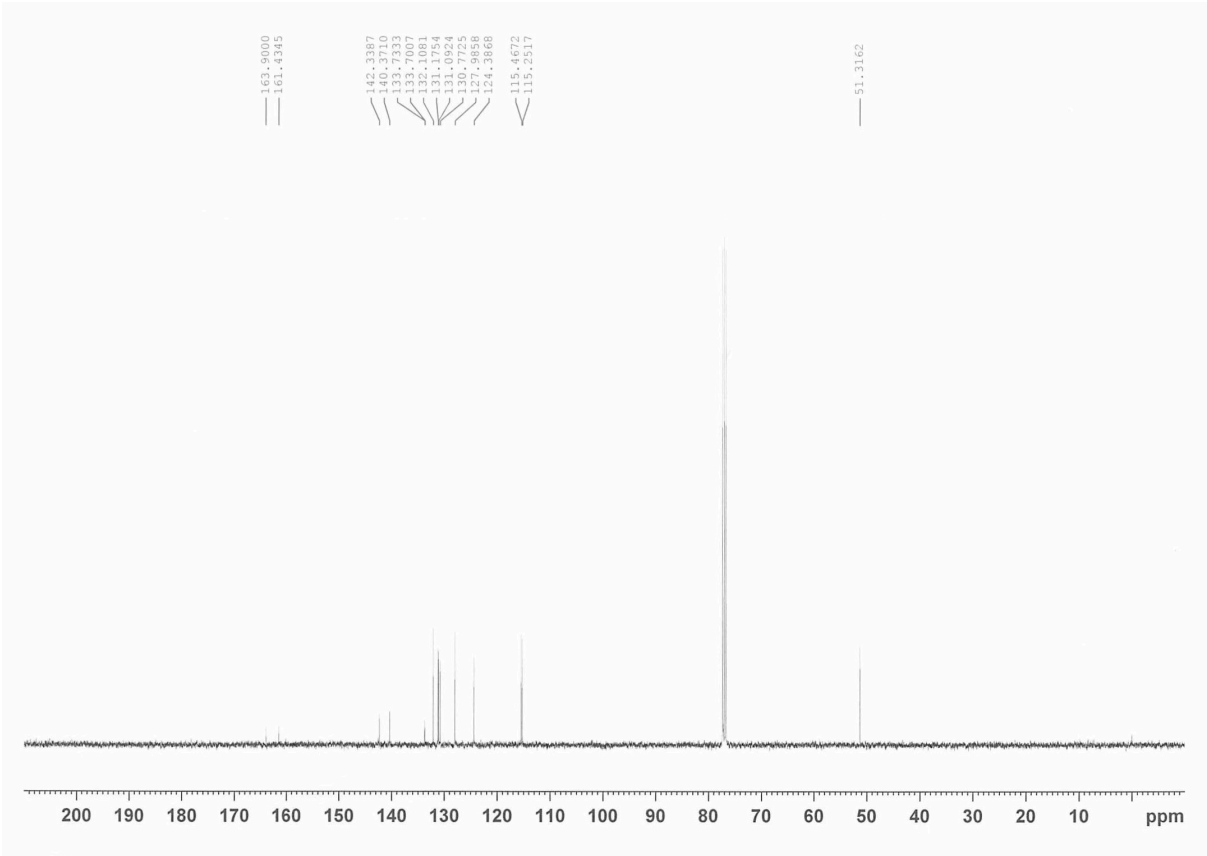
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of methyl 4'-methyl-[1,1'-biphenyl]-2-sulfinate (**3a**) ($CDCl_3$)



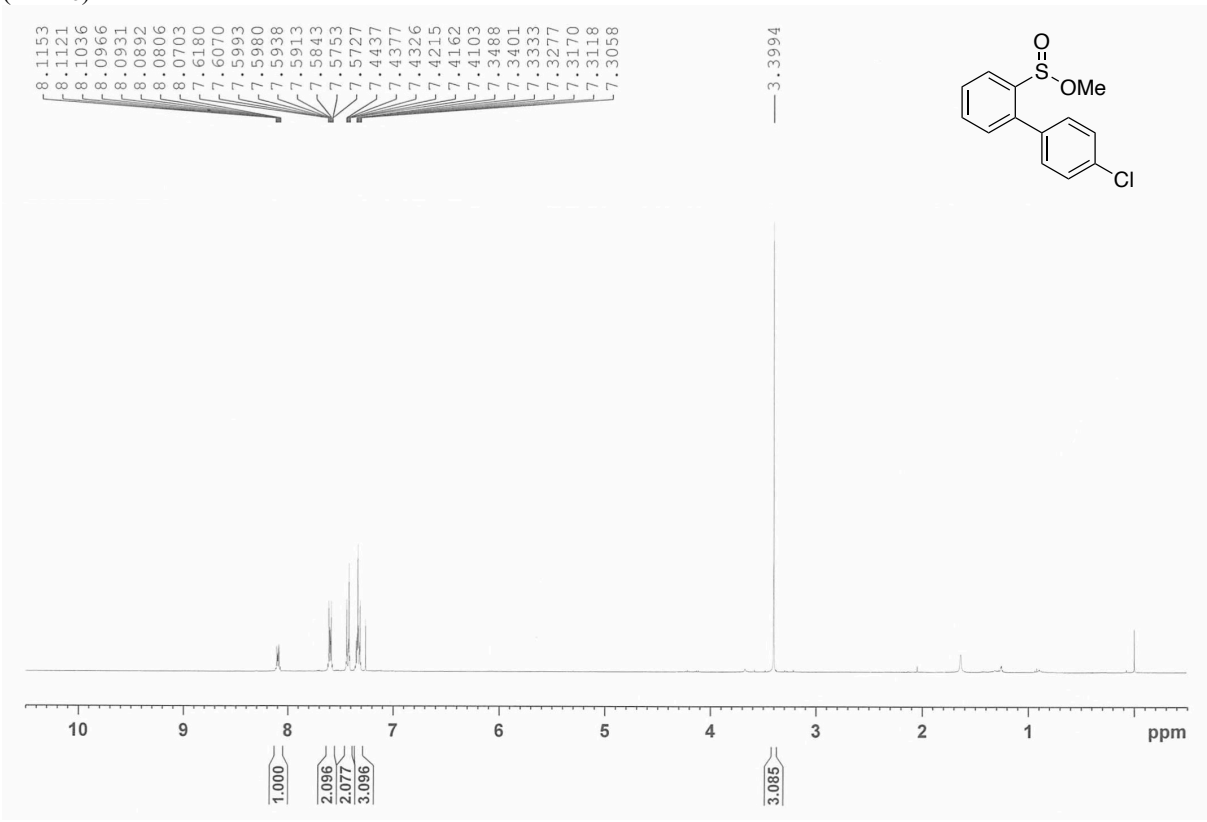


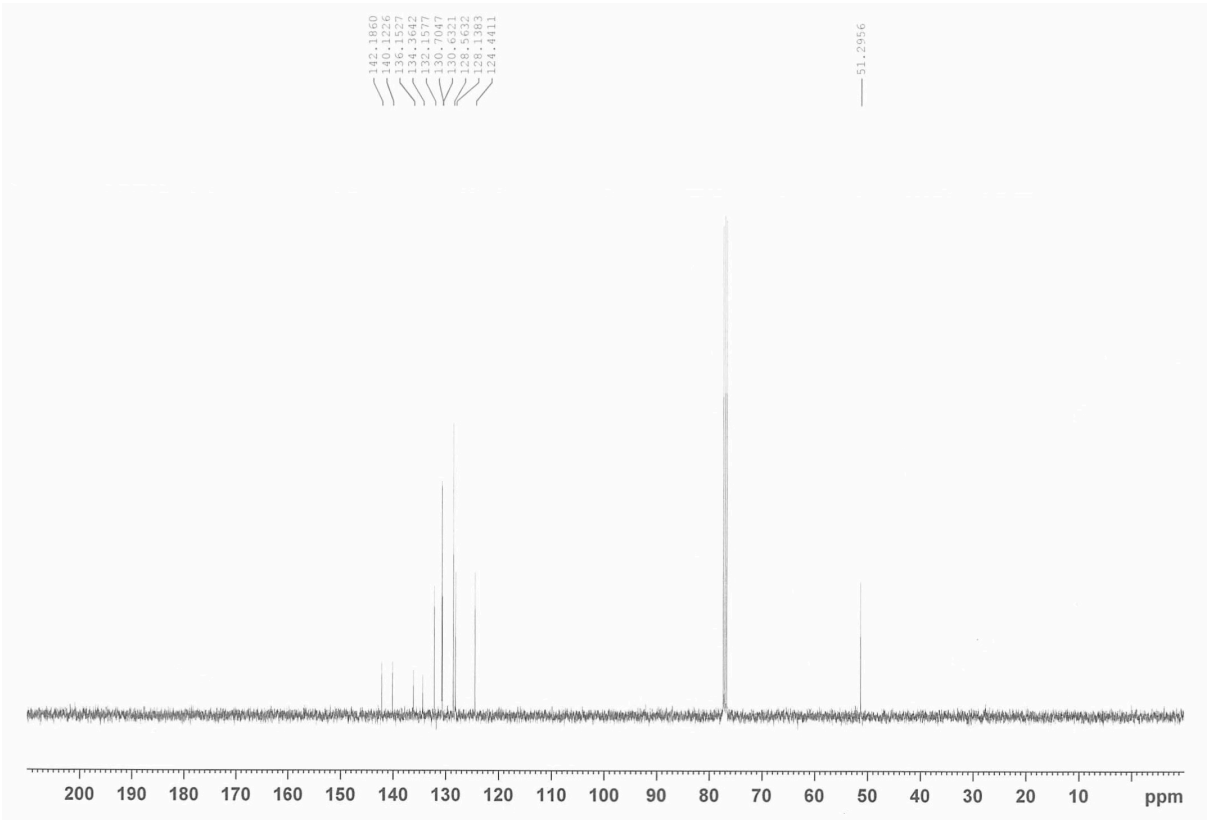
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of methyl 4'-fluoro-[1,1'-biphenyl]-2-sulfinate (**3b**) ($CDCl_3$)



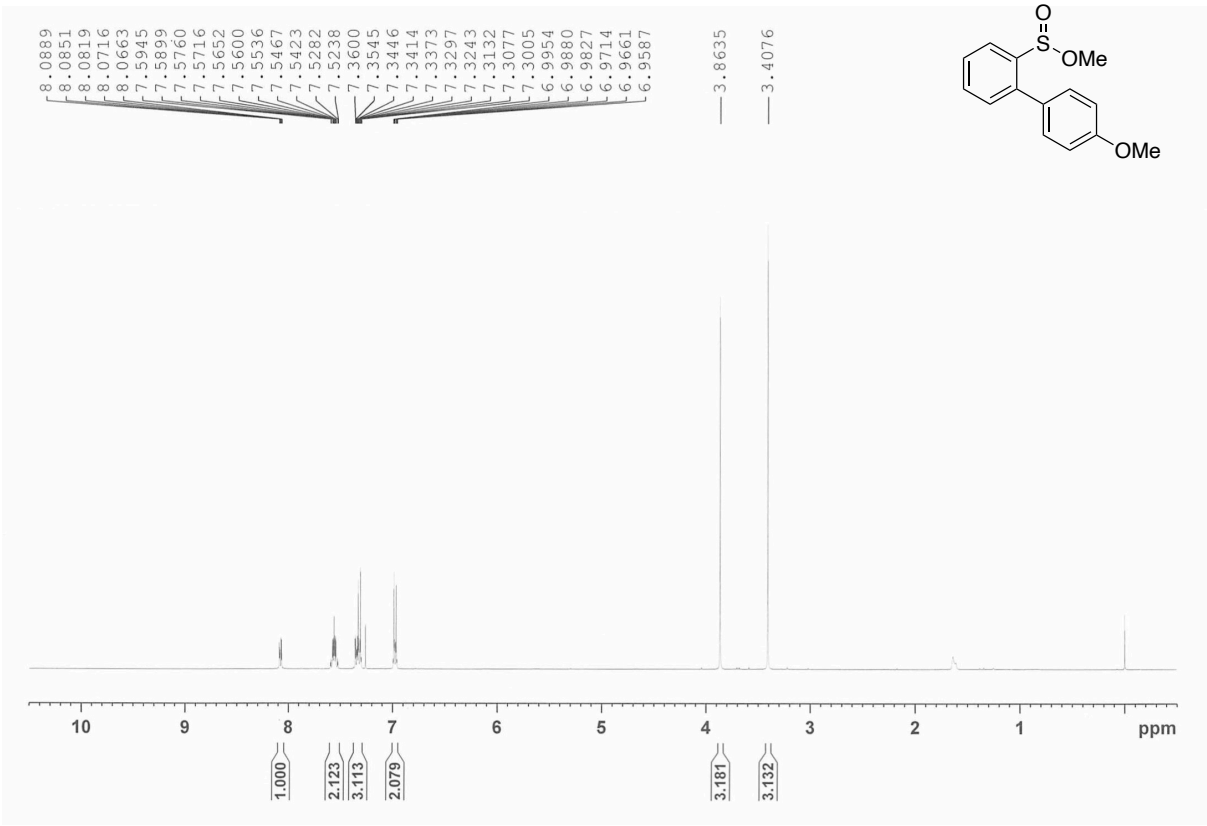


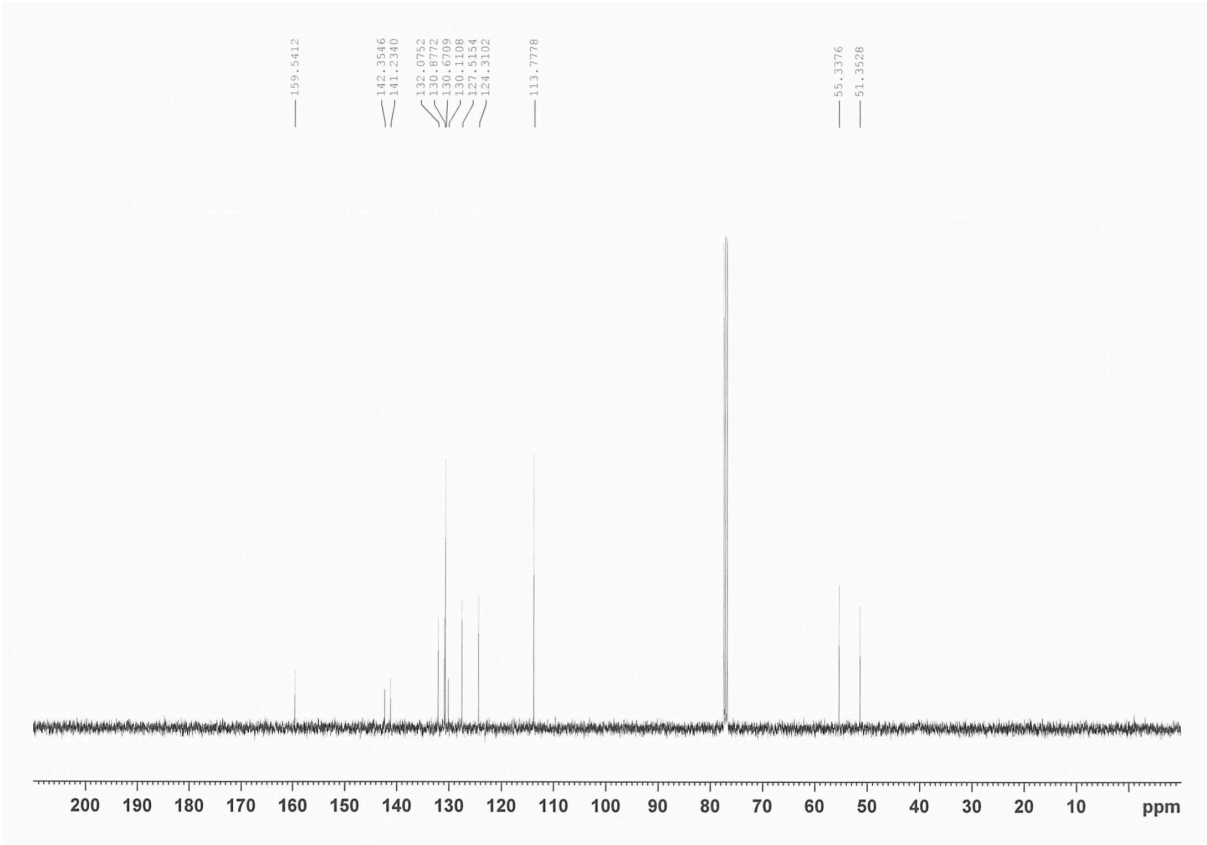
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of methyl 4'-chloro-[1,1'-biphenyl]-2-sulfinate (**3c**) ($CDCl_3$)



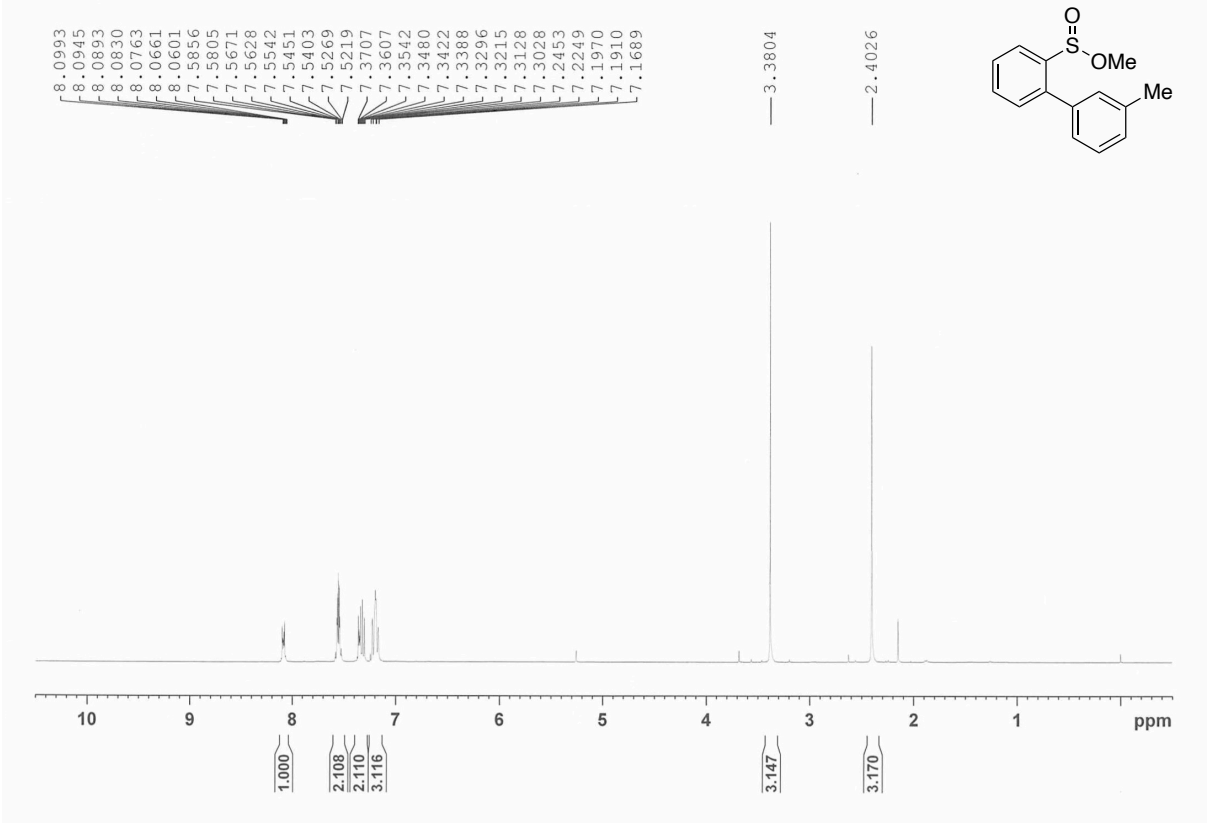


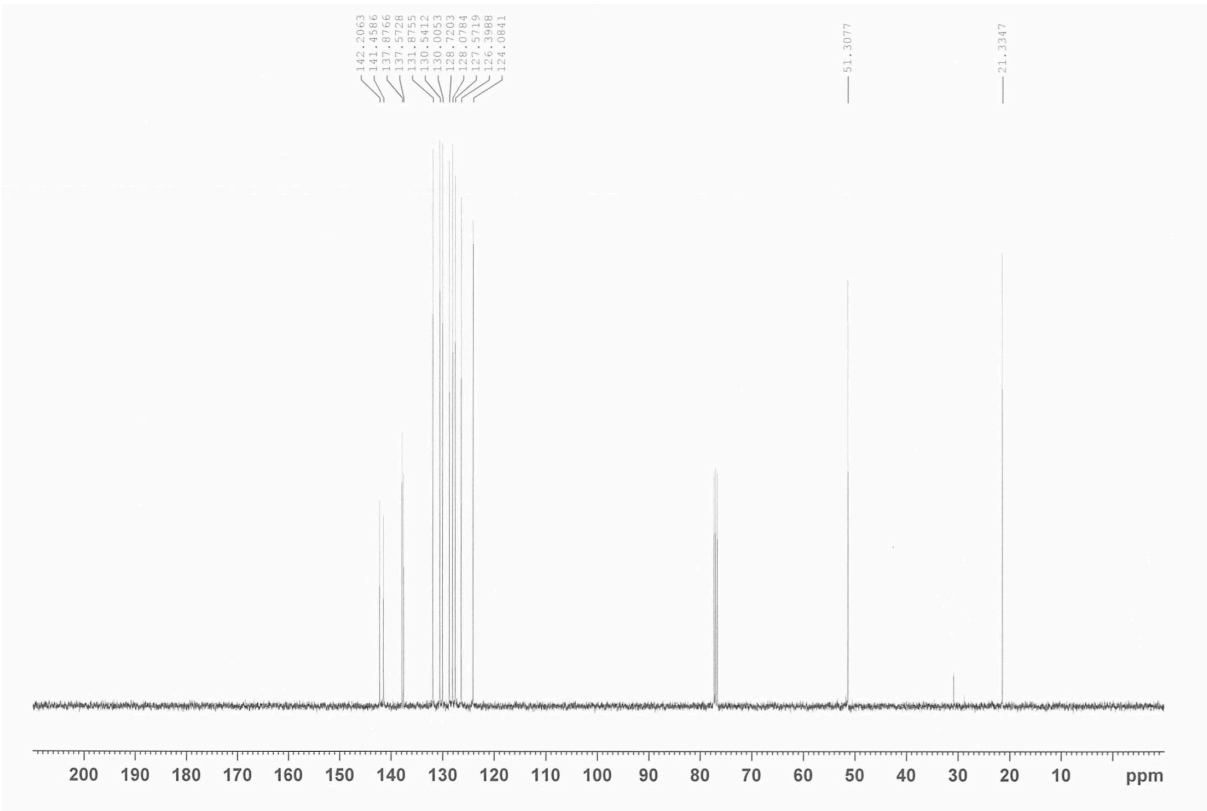
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of methyl 4'-methoxy-[1,1'-biphenyl]-2-sulfinate (**3d**) ($CDCl_3$)



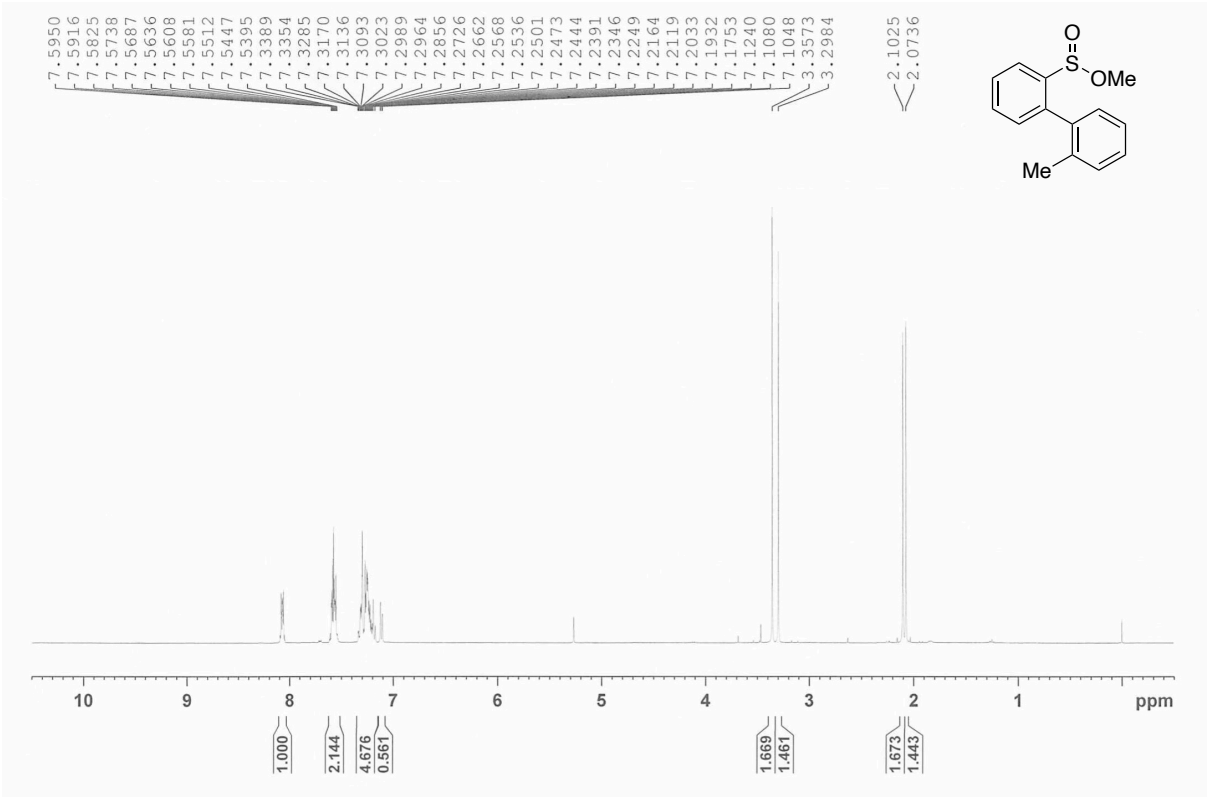


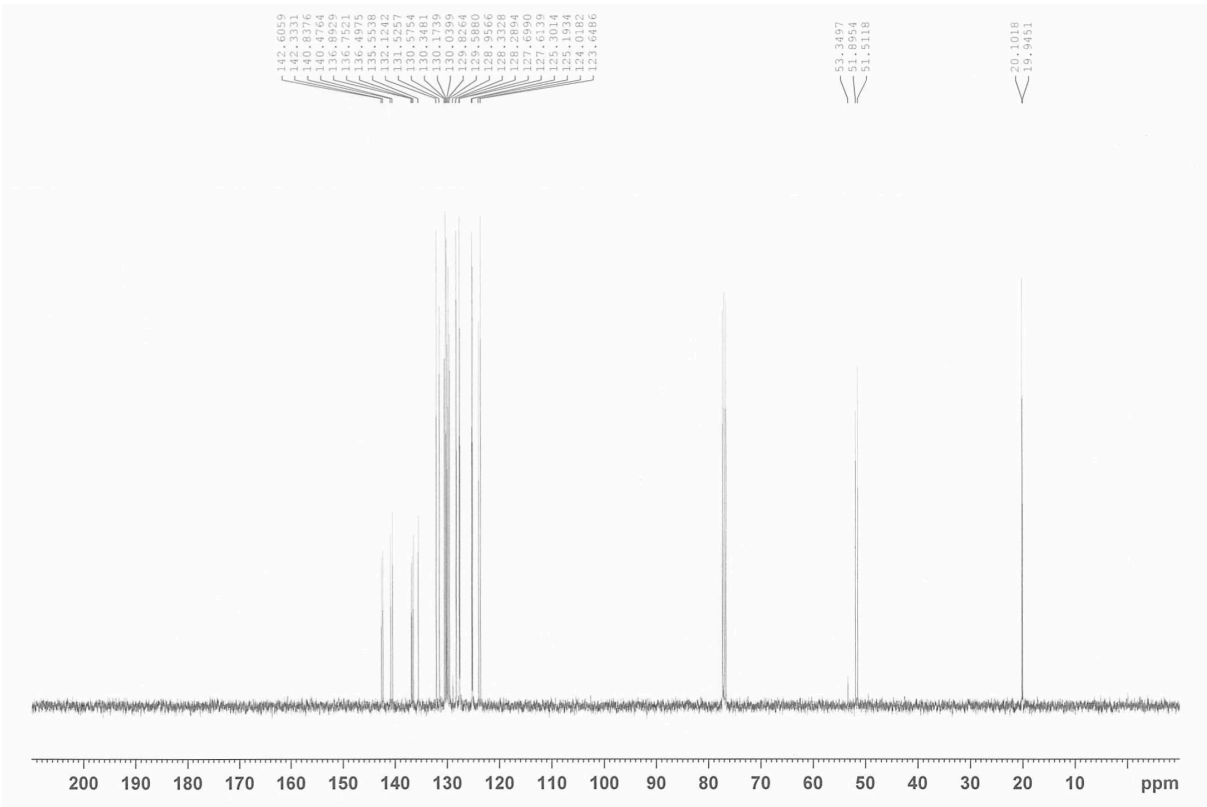
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of methyl 3'-methyl-[1,1'-biphenyl]-2-sulfinate (**3e**) ($CDCl_3$)



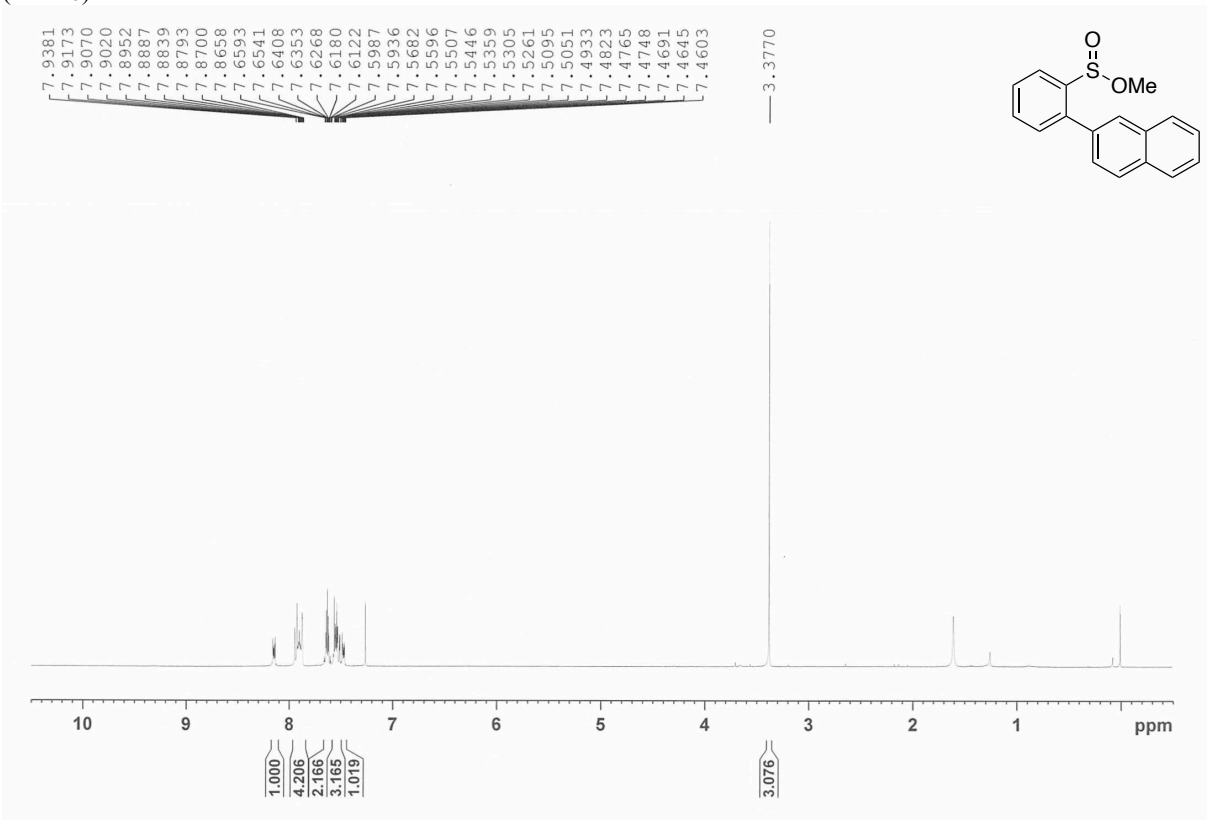


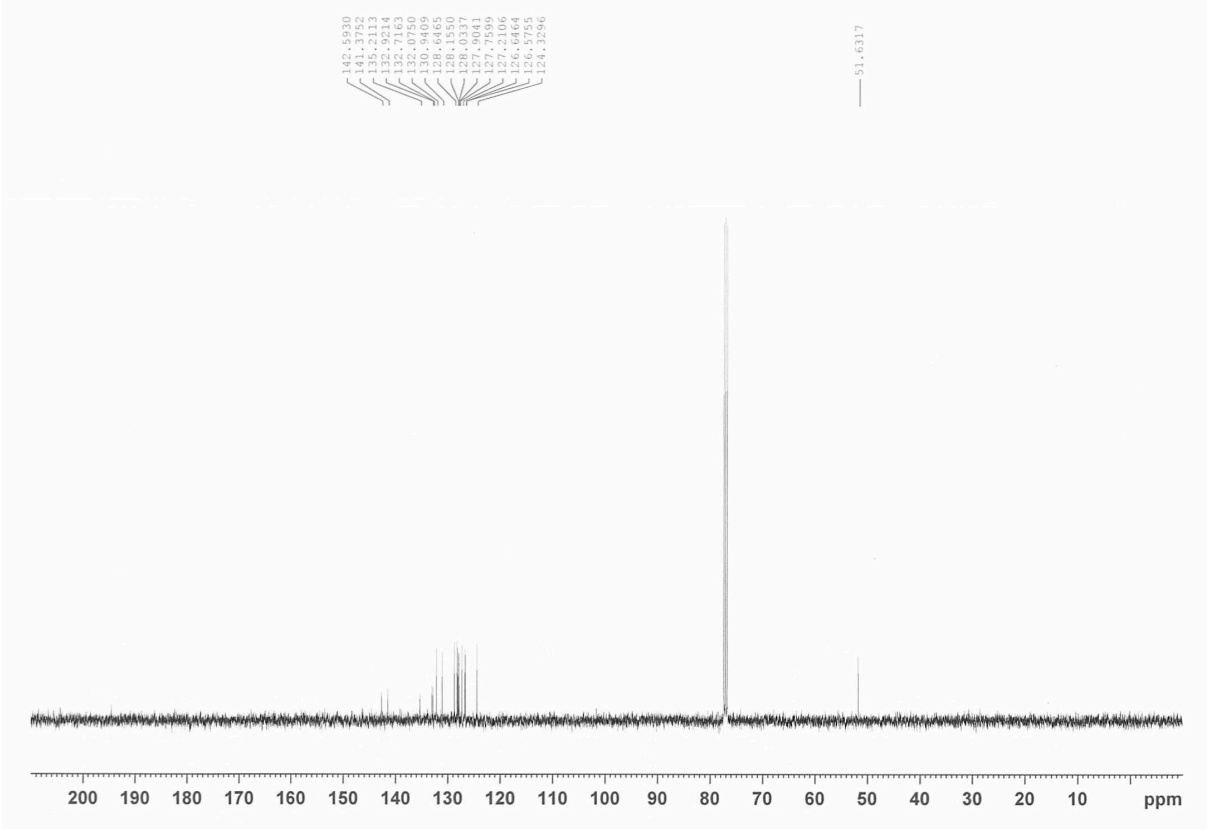
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of methyl 2'-methyl-[1,1'-biphenyl]-2-sulfinate (**3f**) ($CDCl_3$)



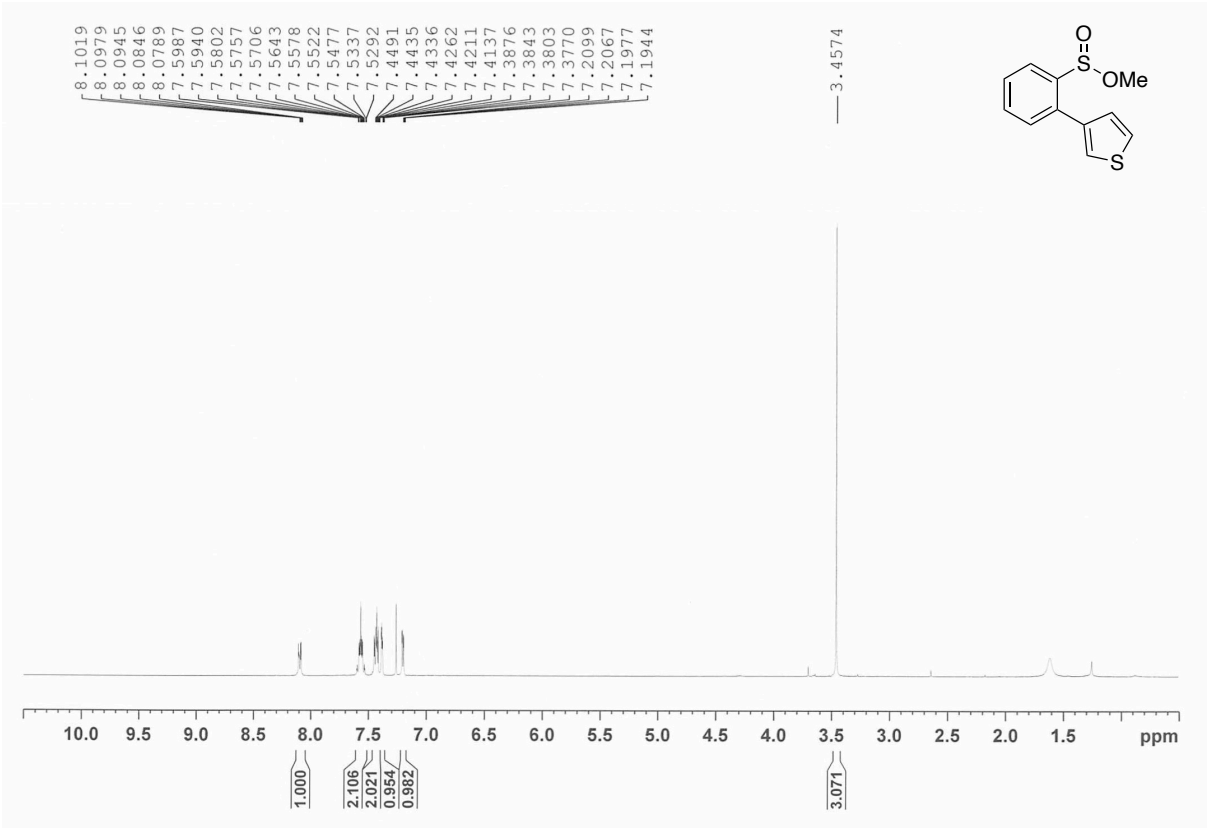


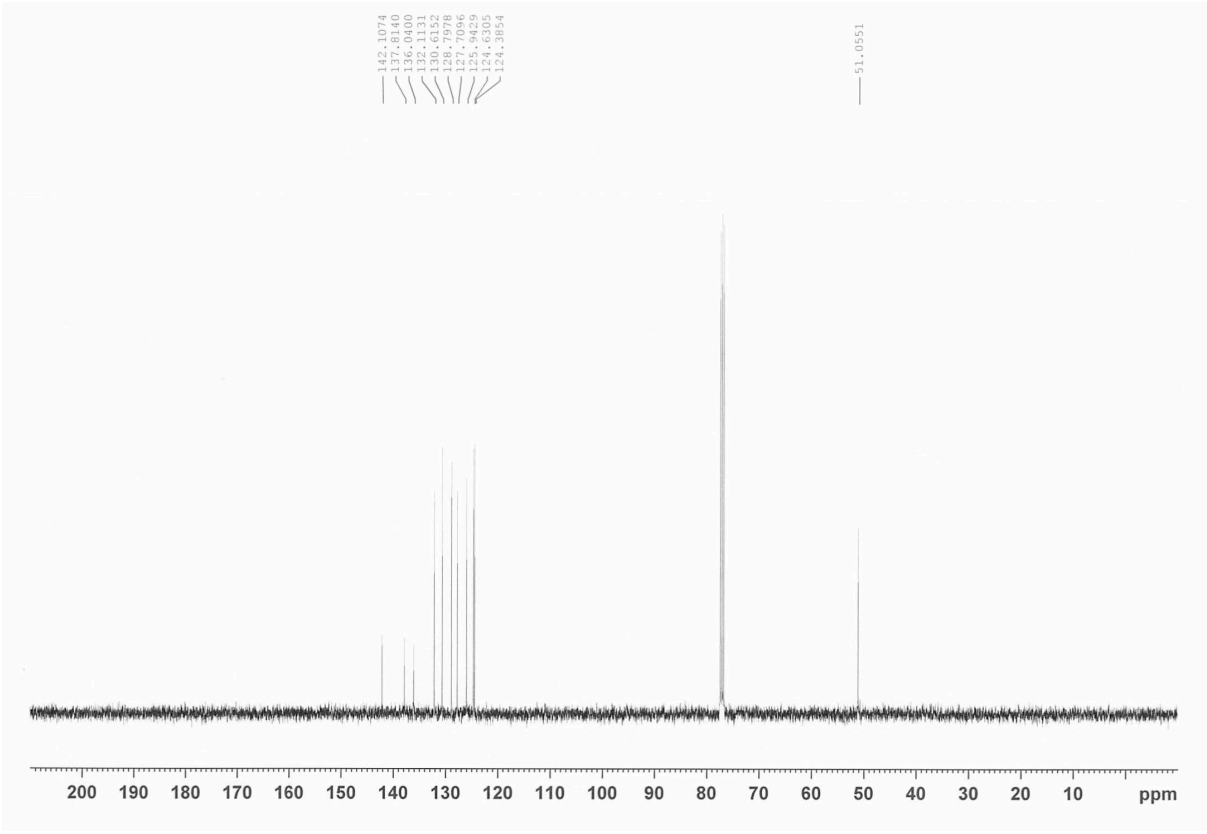
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of methyl 2-(naphthalen-2-yl)benzenesulfinate (**3g**) ($CDCl_3$)



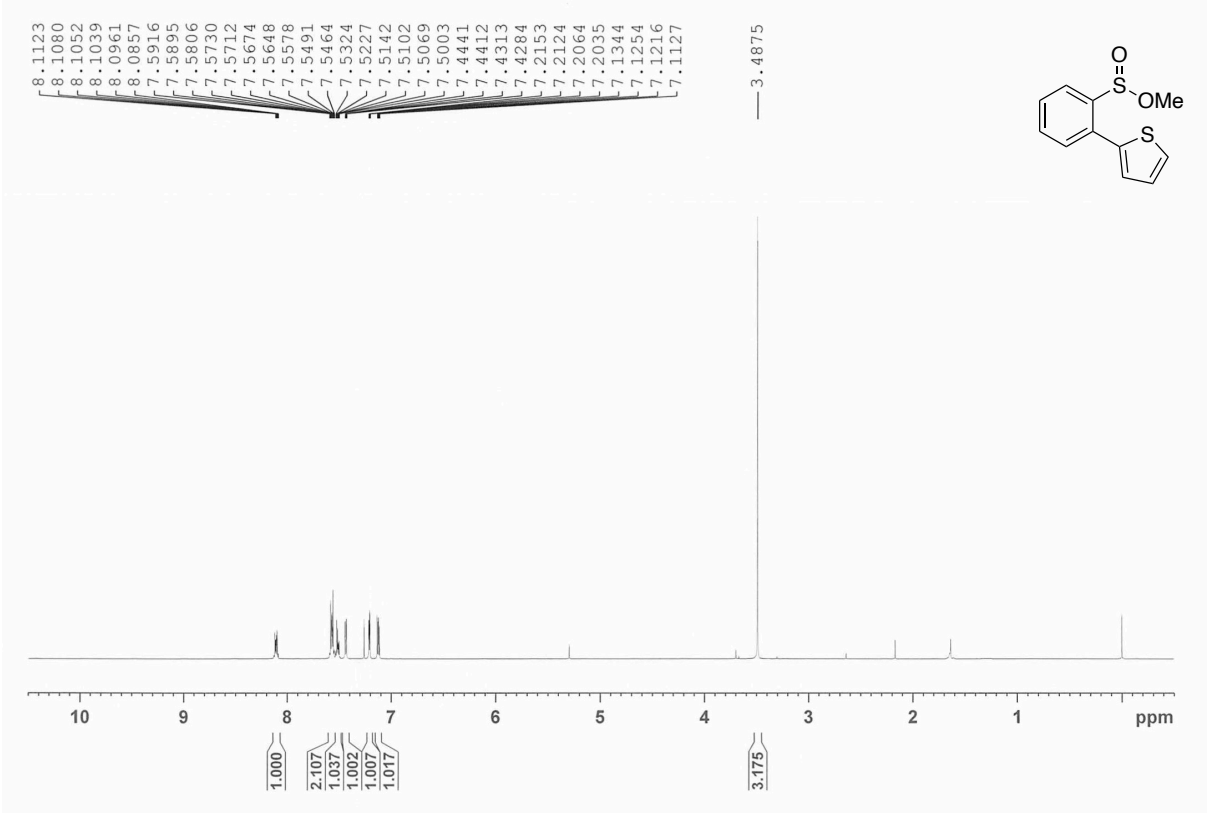


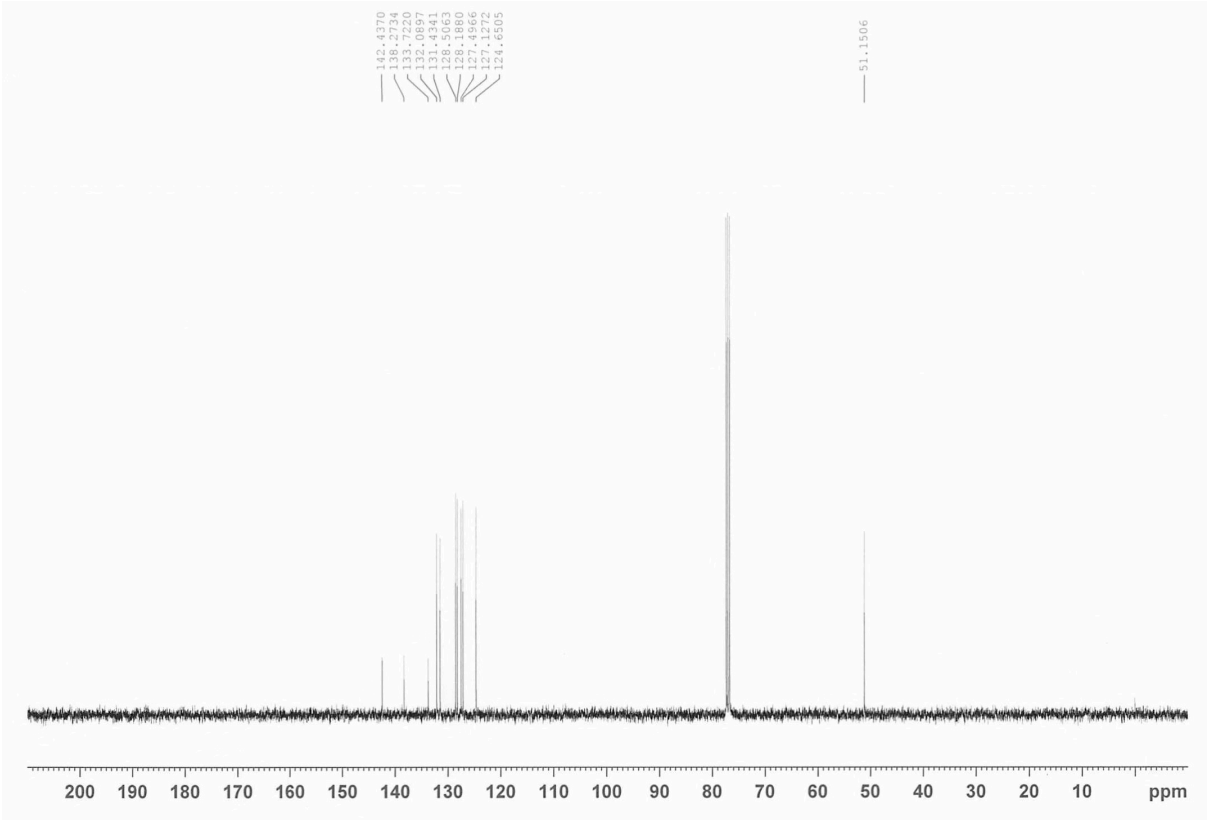
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of Methyl 2-(thiophen-3-yl)benzenesulfinate (**3h**) ($CDCl_3$)



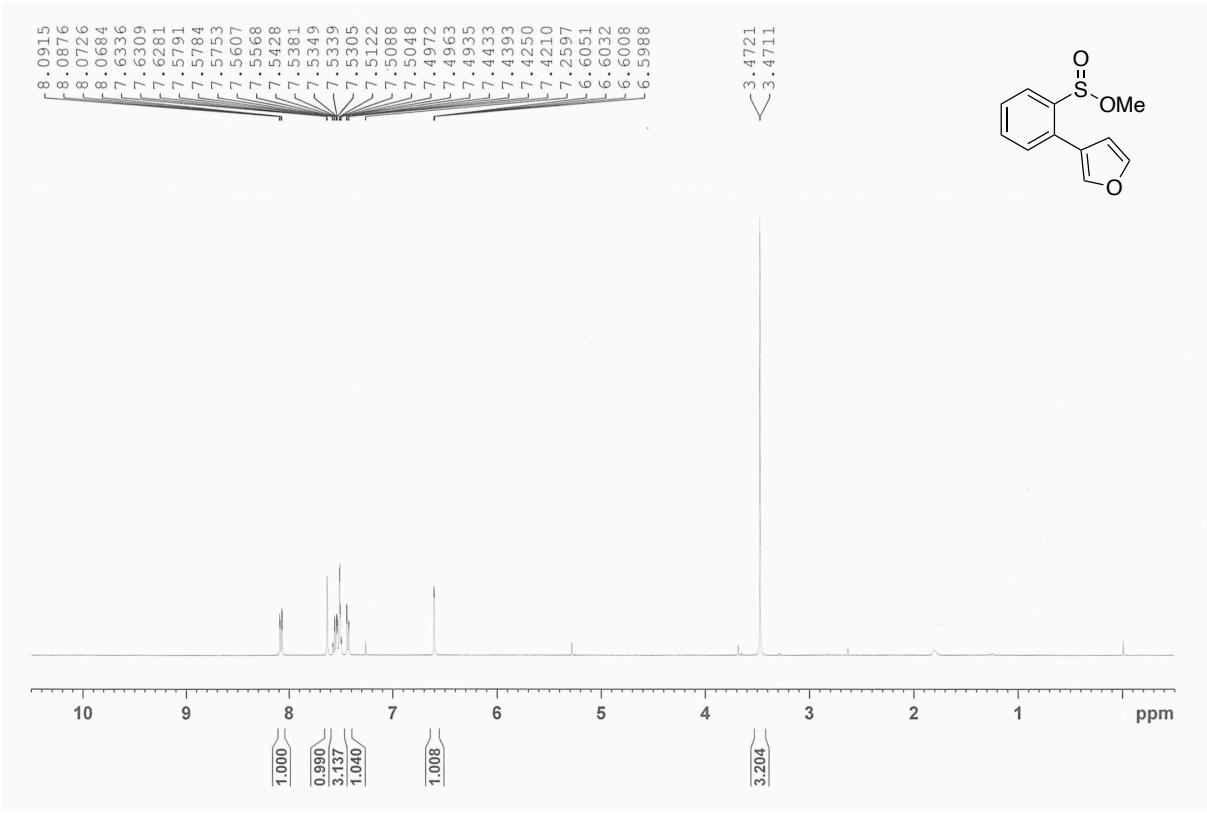


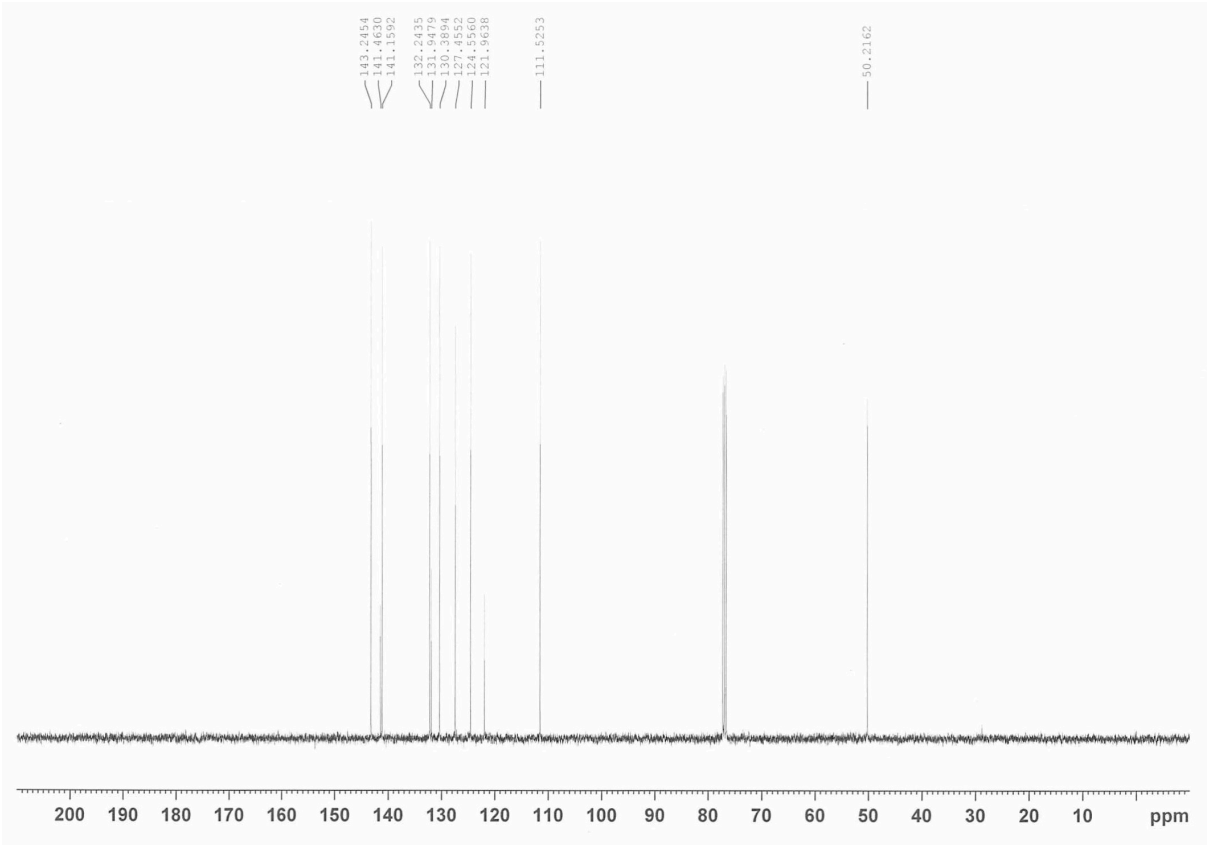
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of methyl 2-(thiophen-2-yl)benzenesulfinate (**3i**) ($CDCl_3$)



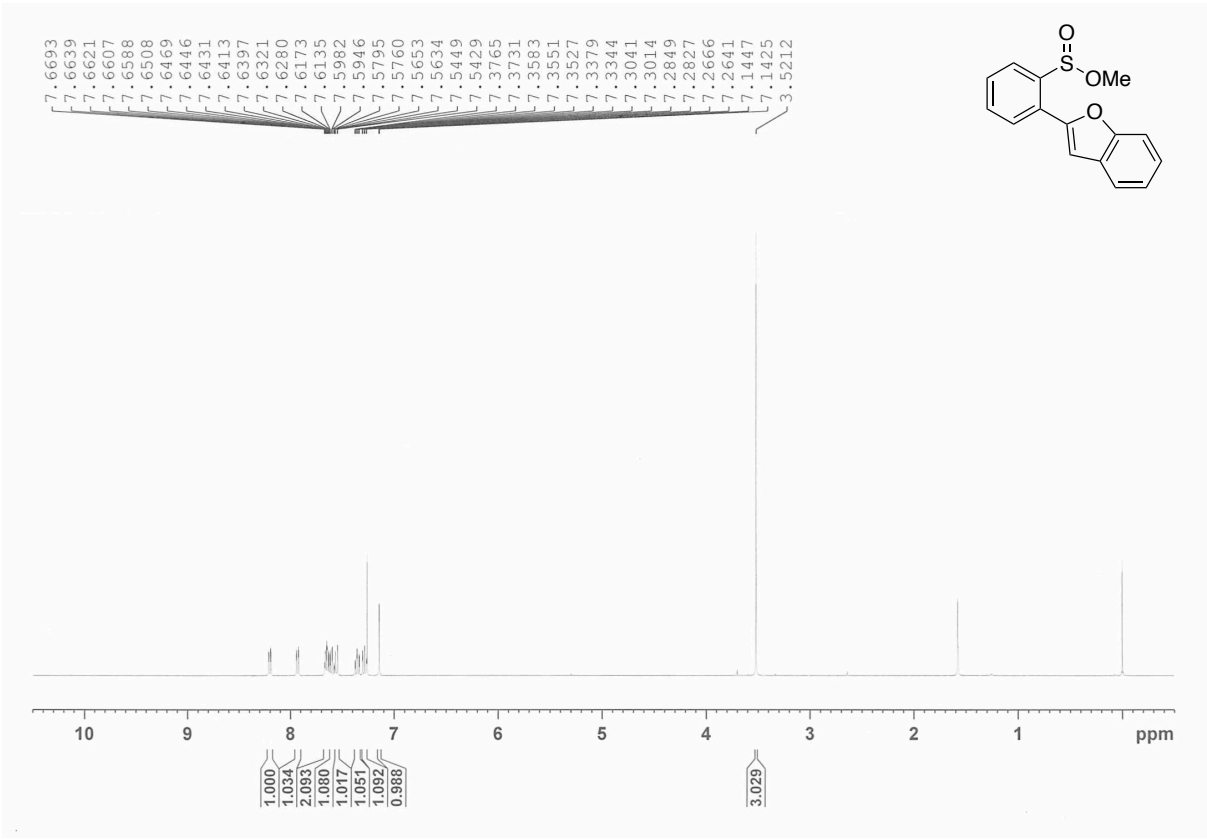


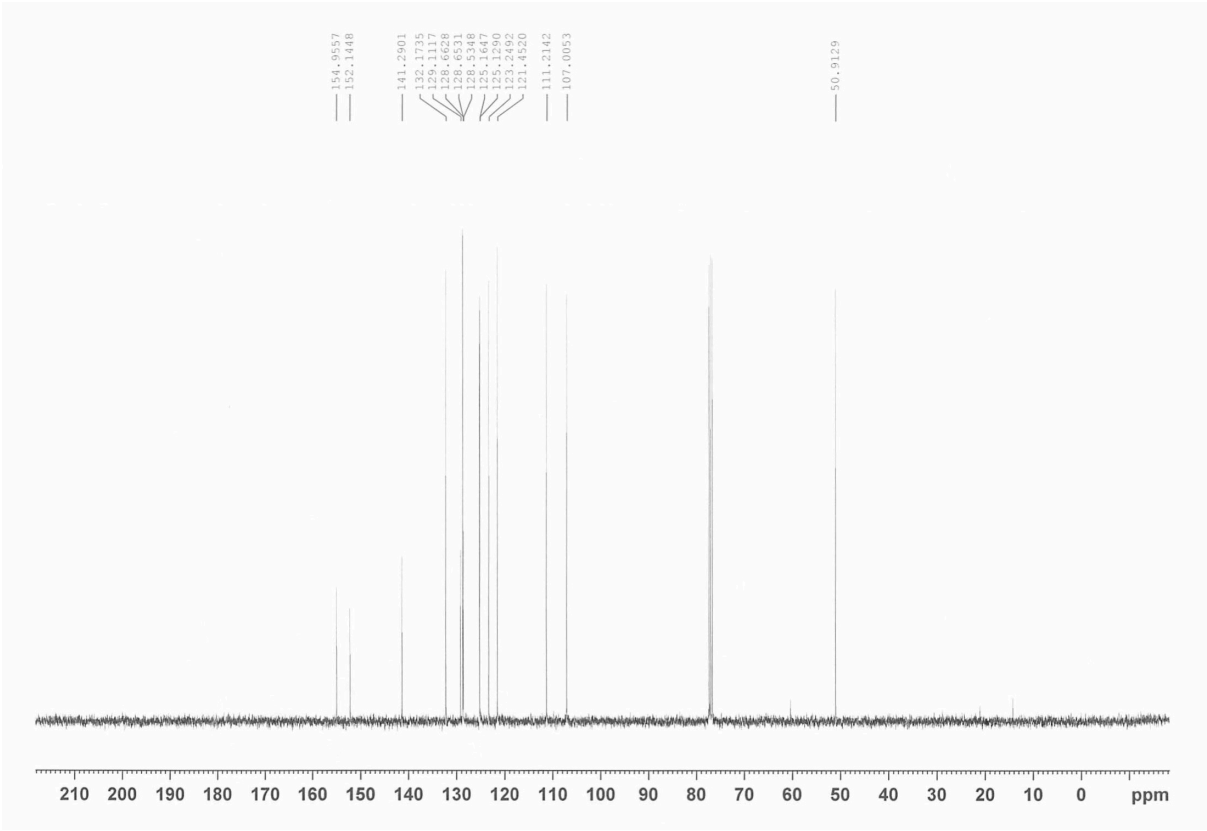
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of methyl 2-(furan-3-yl)benzenesulfinate (**3j**) ($CDCl_3$)



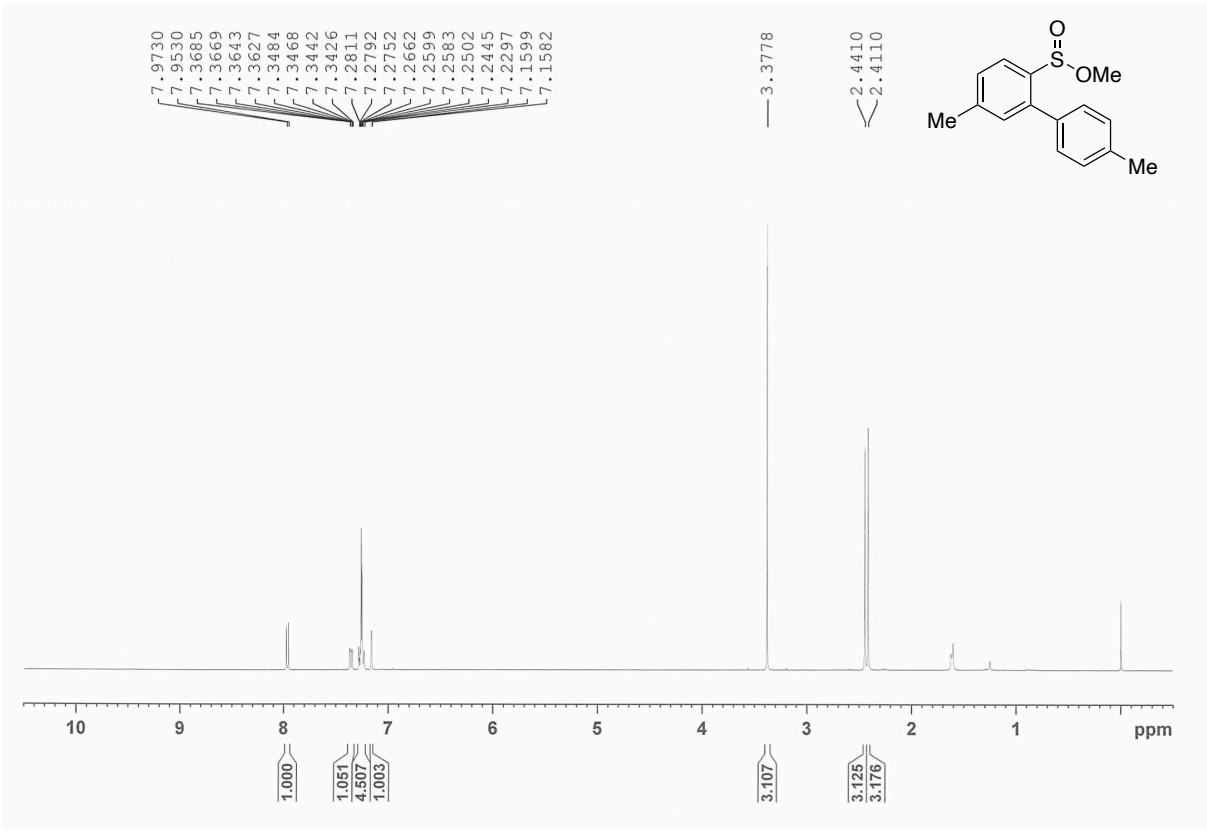


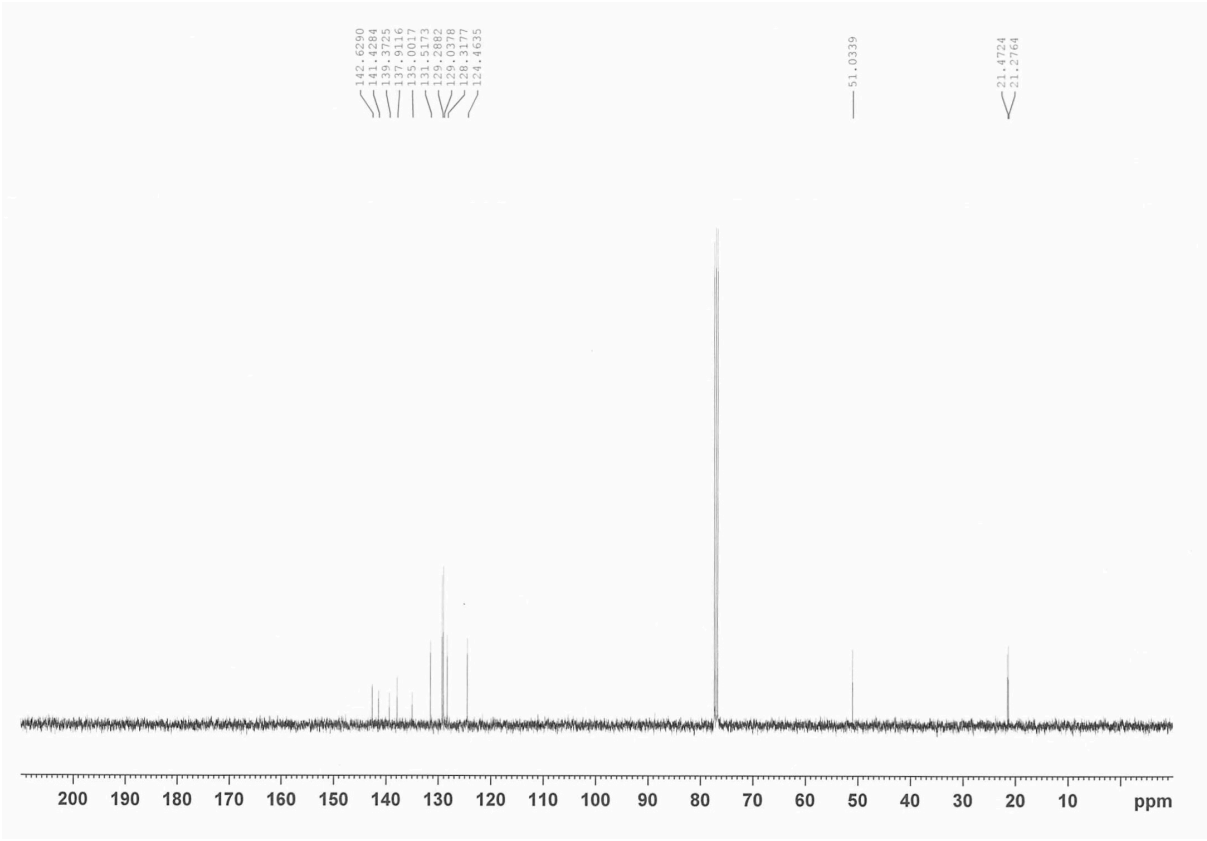
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of methyl 2-(benzofuran-2-yl)benzenesulfinate (**3k**) ($CDCl_3$)



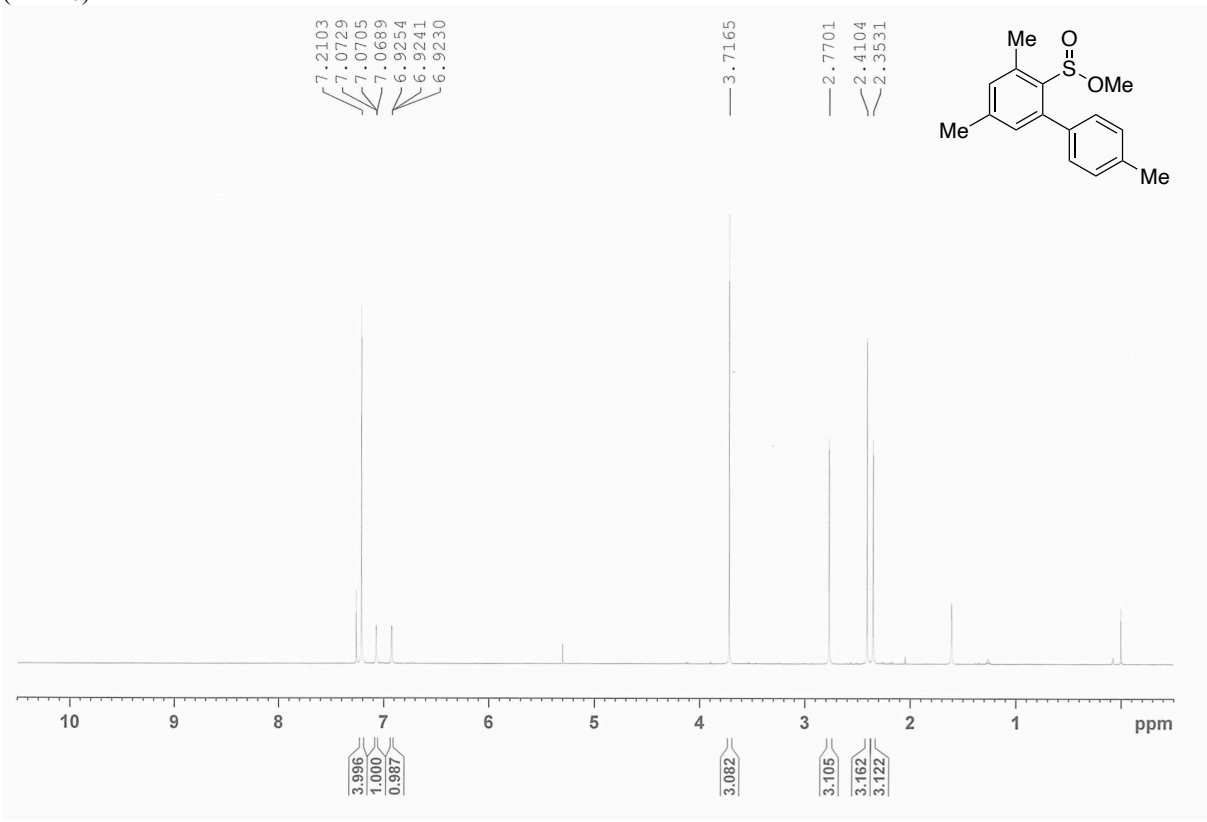


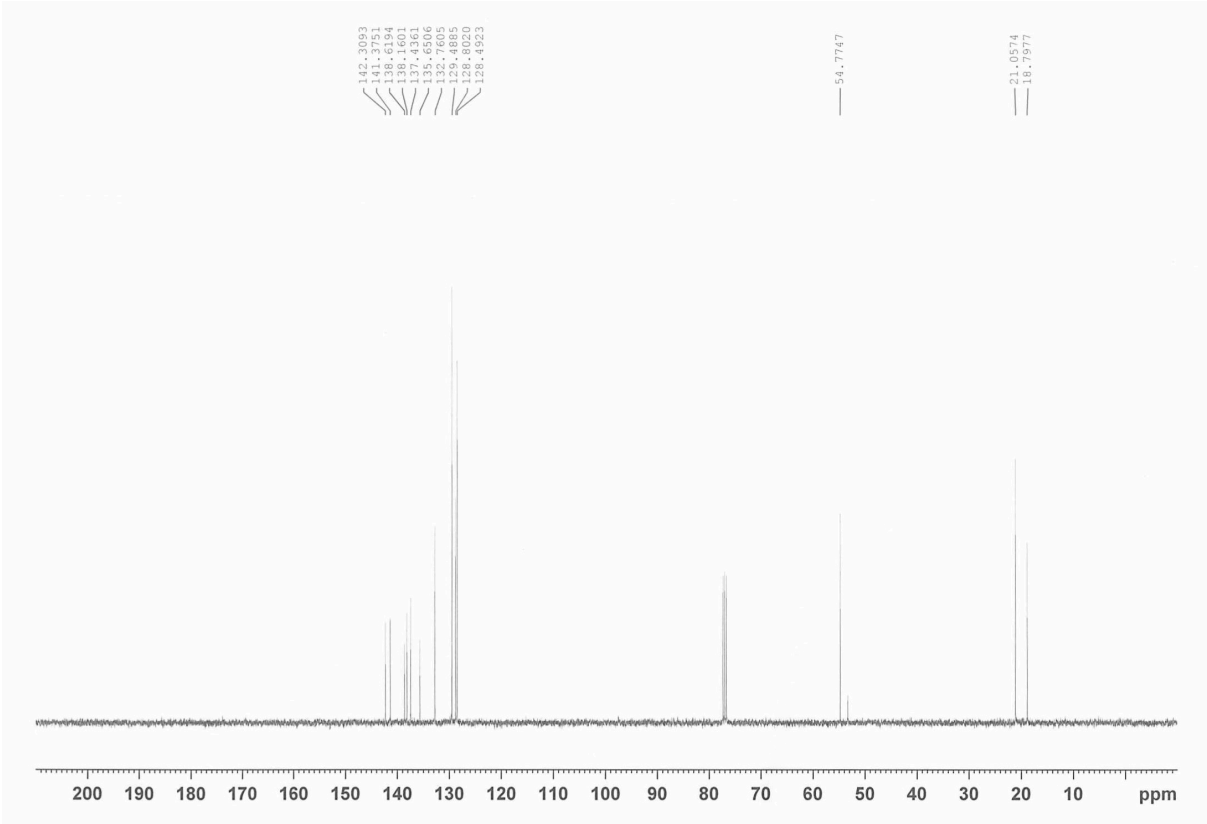
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of methyl 4',5-dimethyl-[1,1'-biphenyl]-2-sulfinate (**3l**) ($CDCl_3$)



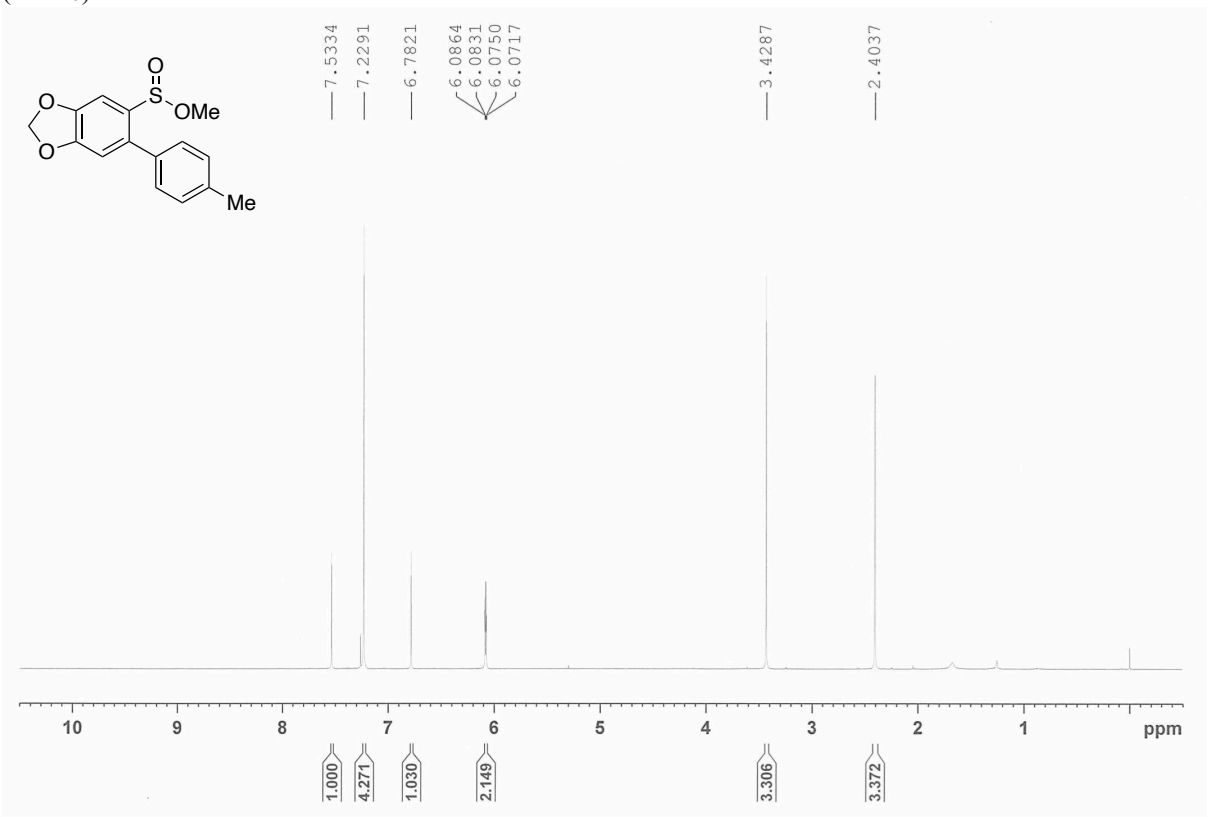


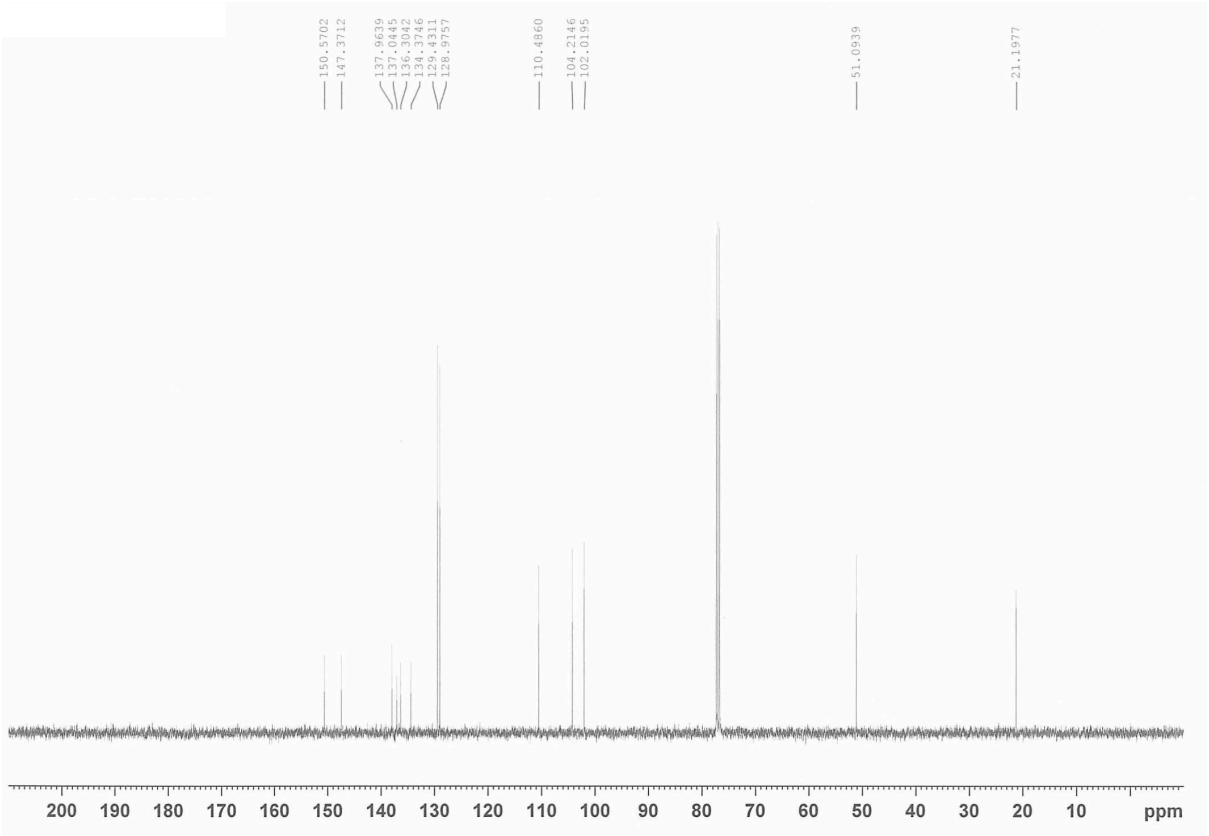
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of methyl 3,4',5-trimethyl-[1,1'-biphenyl]-2-sulfinate (**3m**) ($CDCl_3$)



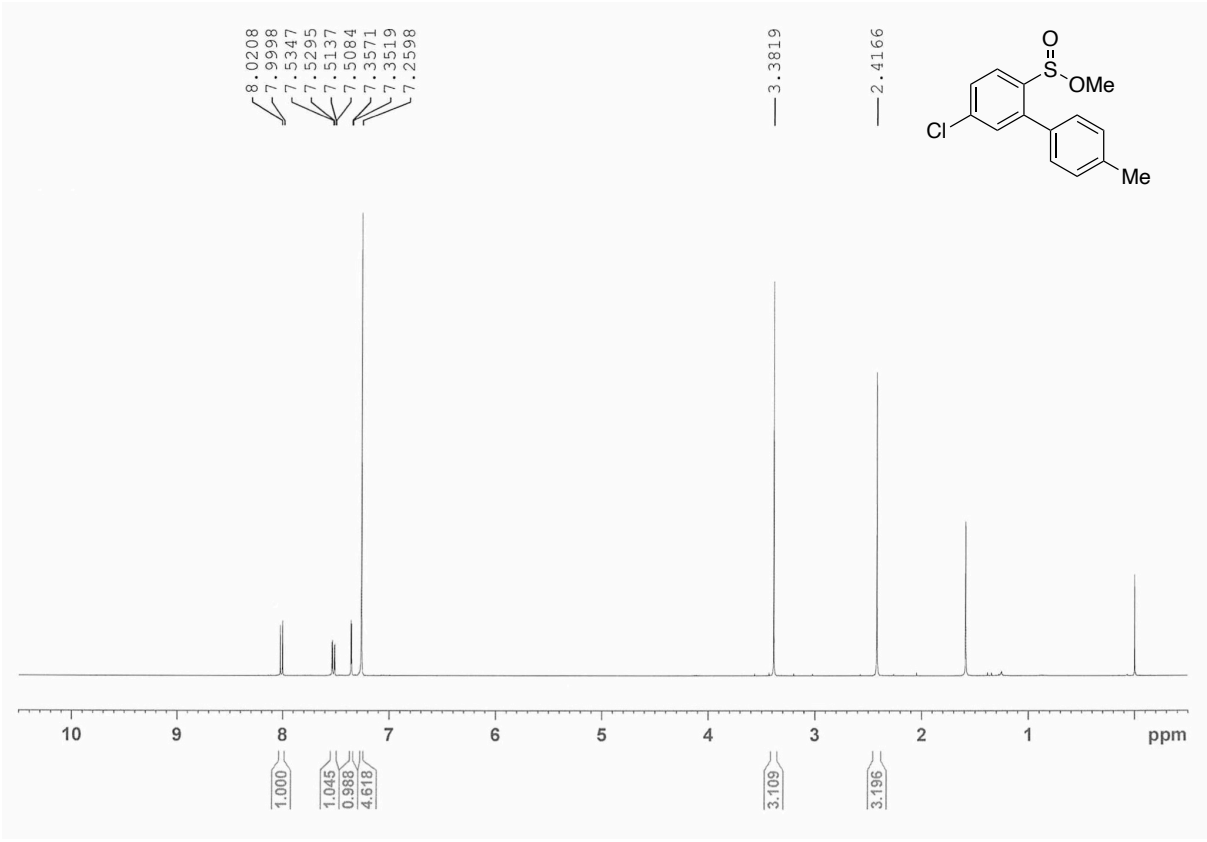


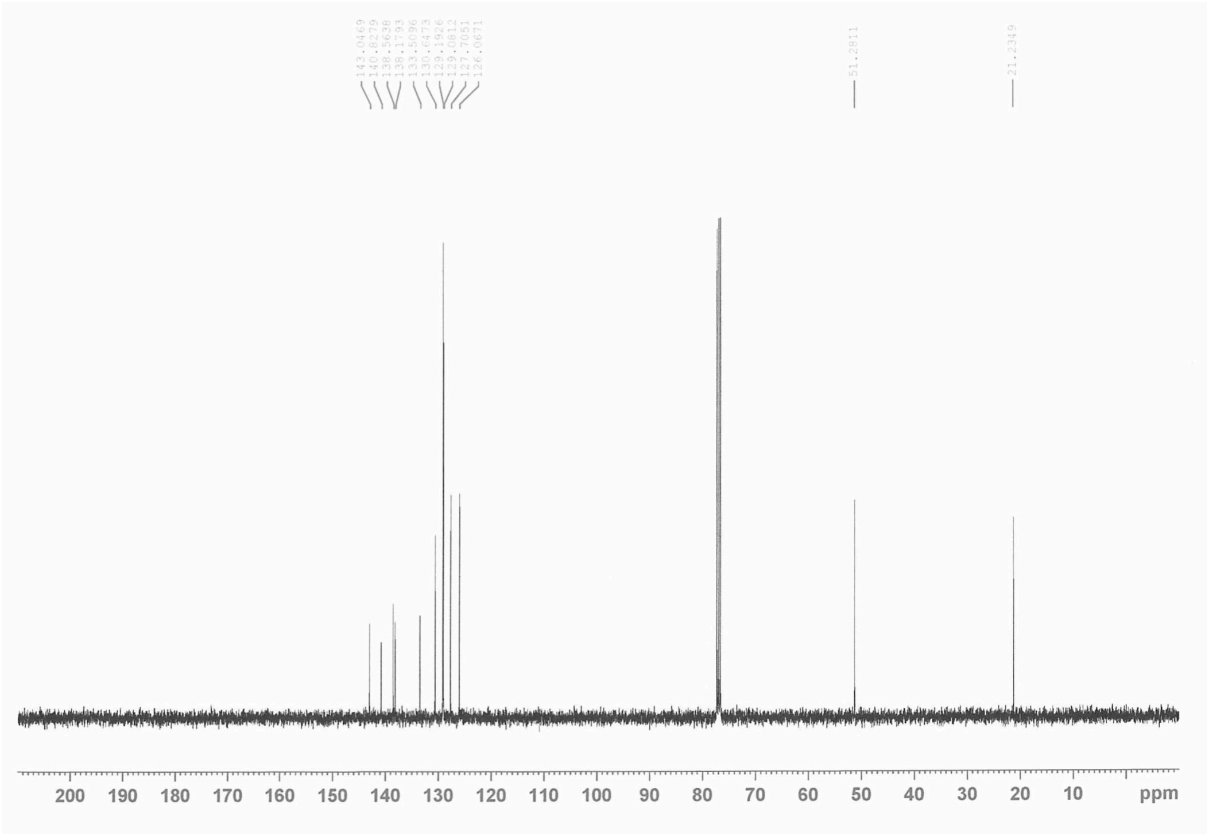
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of methyl 6-(*p*-tolyl)benzo[*d*][1,3]dioxole-5-sulfinate (**3n**) ($CDCl_3$)



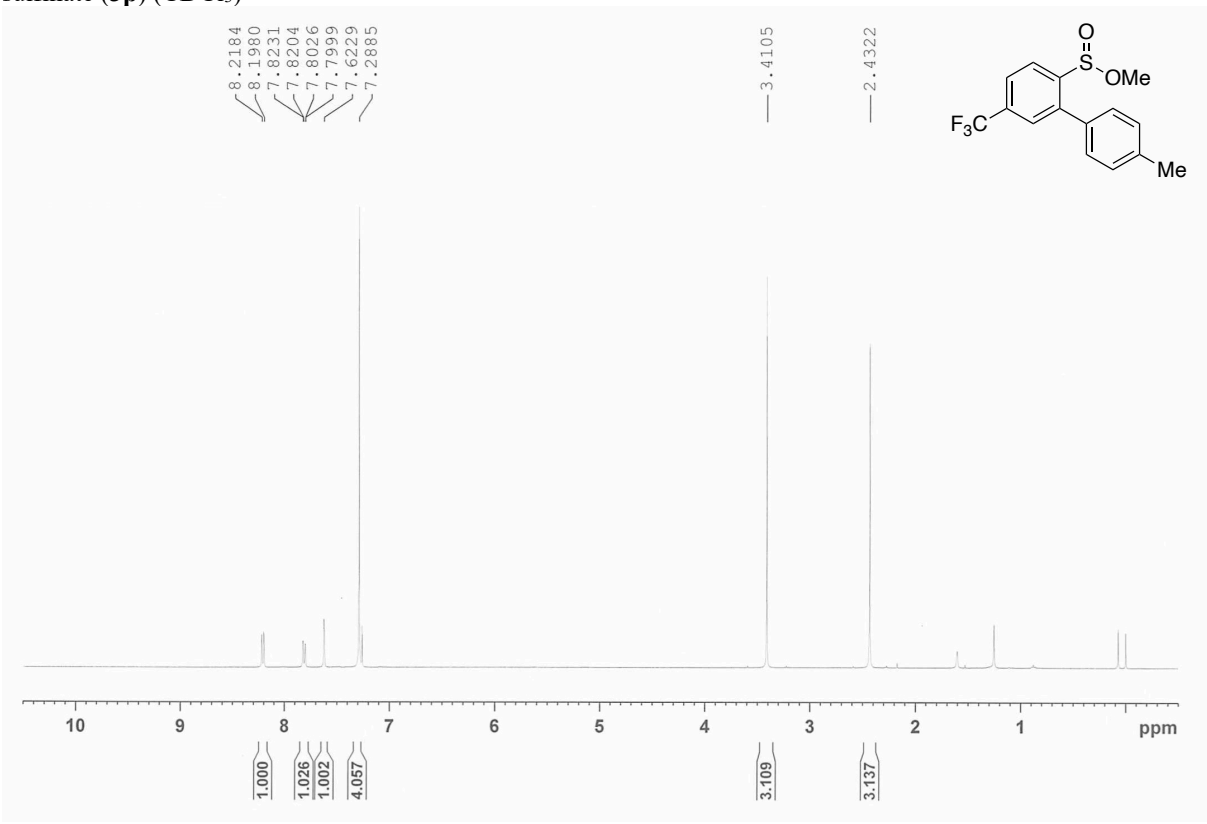


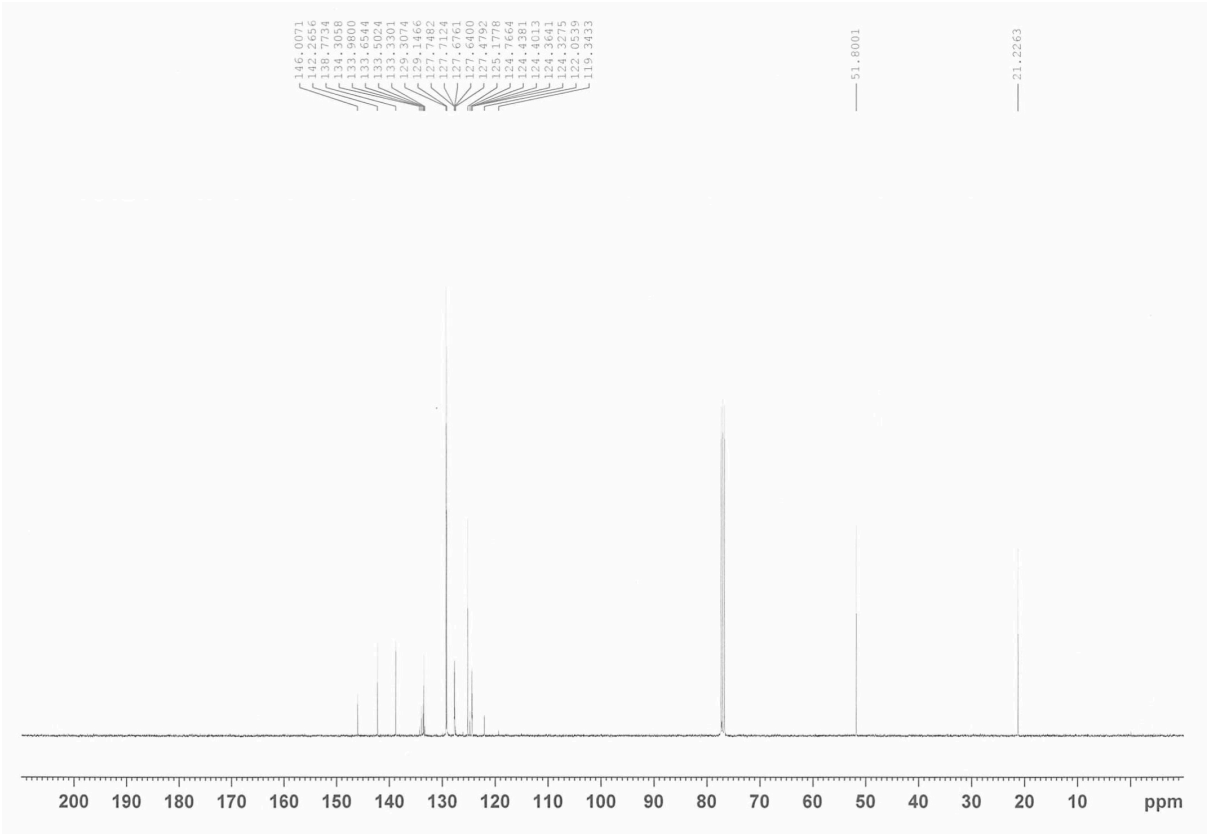
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of methyl 5-chloro-4'-methyl-1,1'-biphenyl-2-sulfinate (**3o**) ($CDCl_3$)



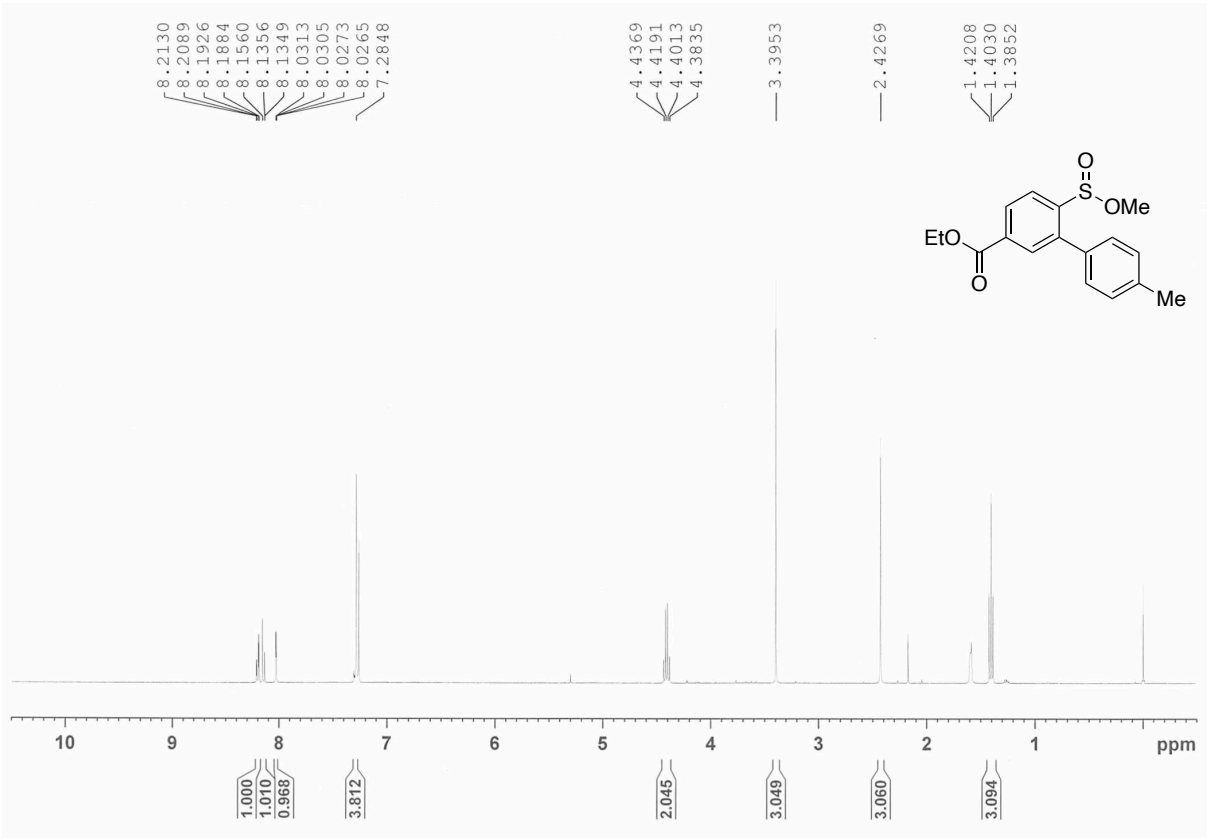


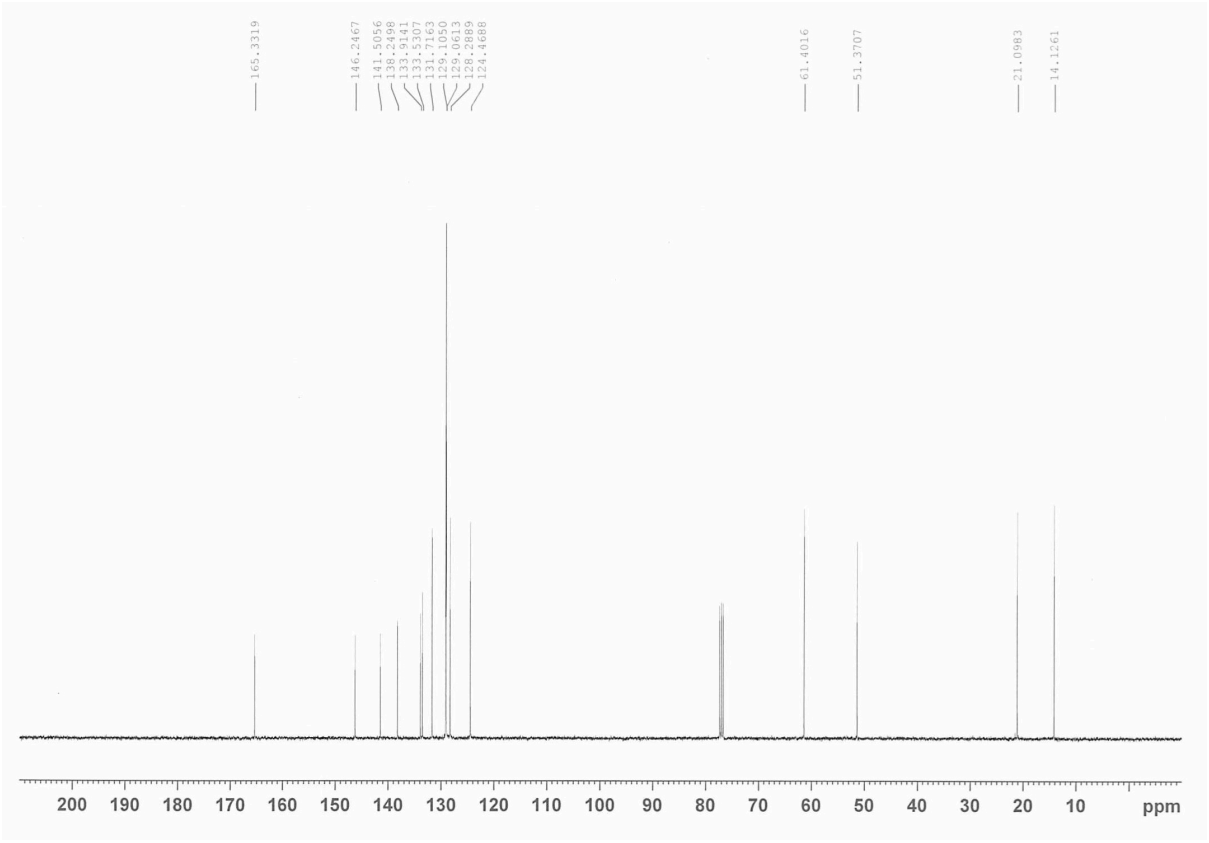
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of methyl 4'-methyl-5-(trifluoromethyl)-1,1'-biphenyl-2-sulfinate (**3p**) ($CDCl_3$)



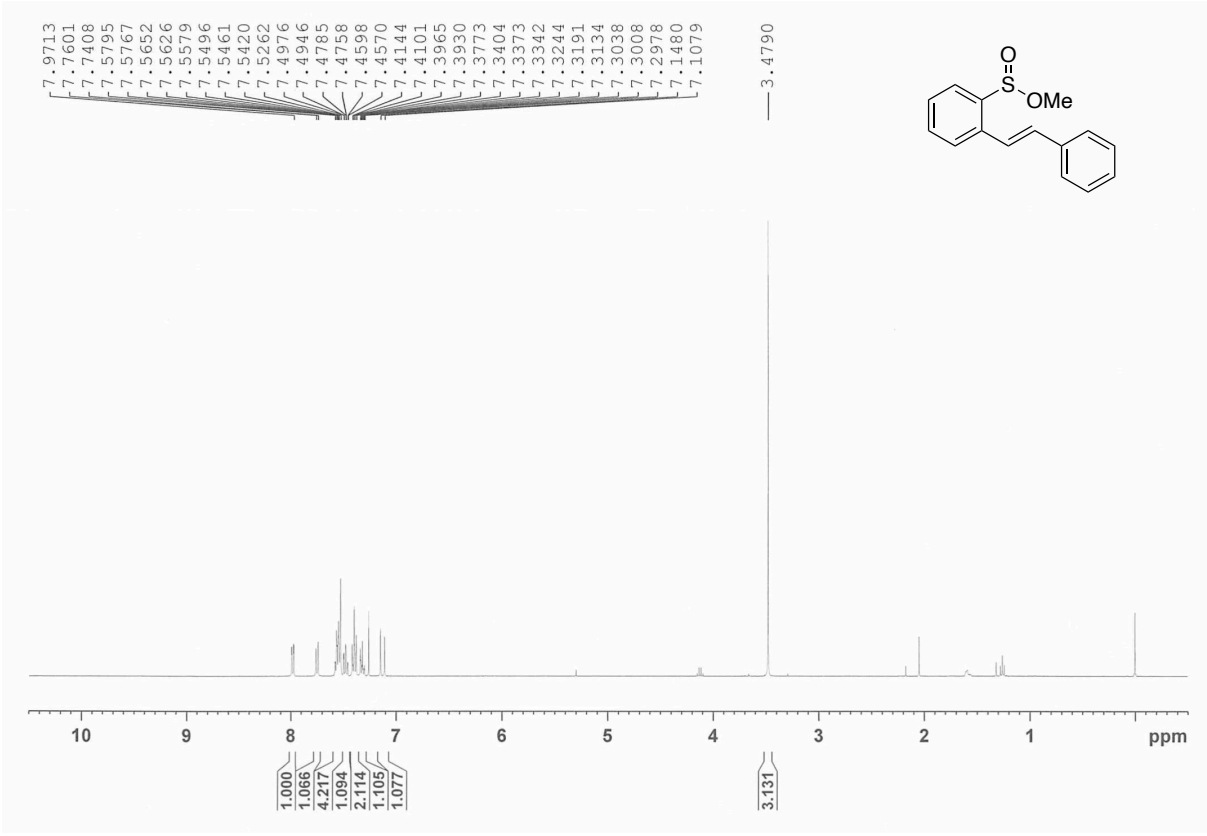


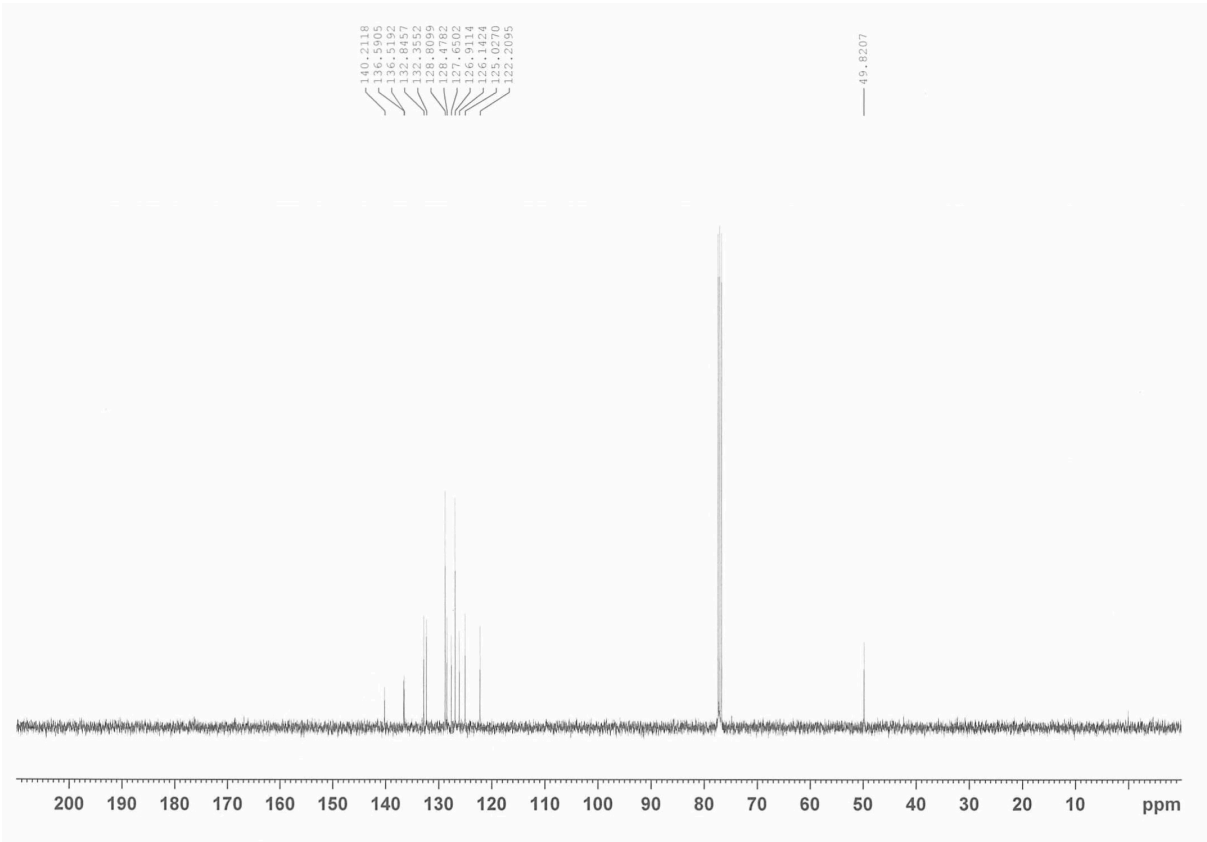
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of ethyl 6-(methoxysulfinyl)-4'-methyl-[1,1'-biphenyl]-3-carboxylate (**3q**) ($CDCl_3$)



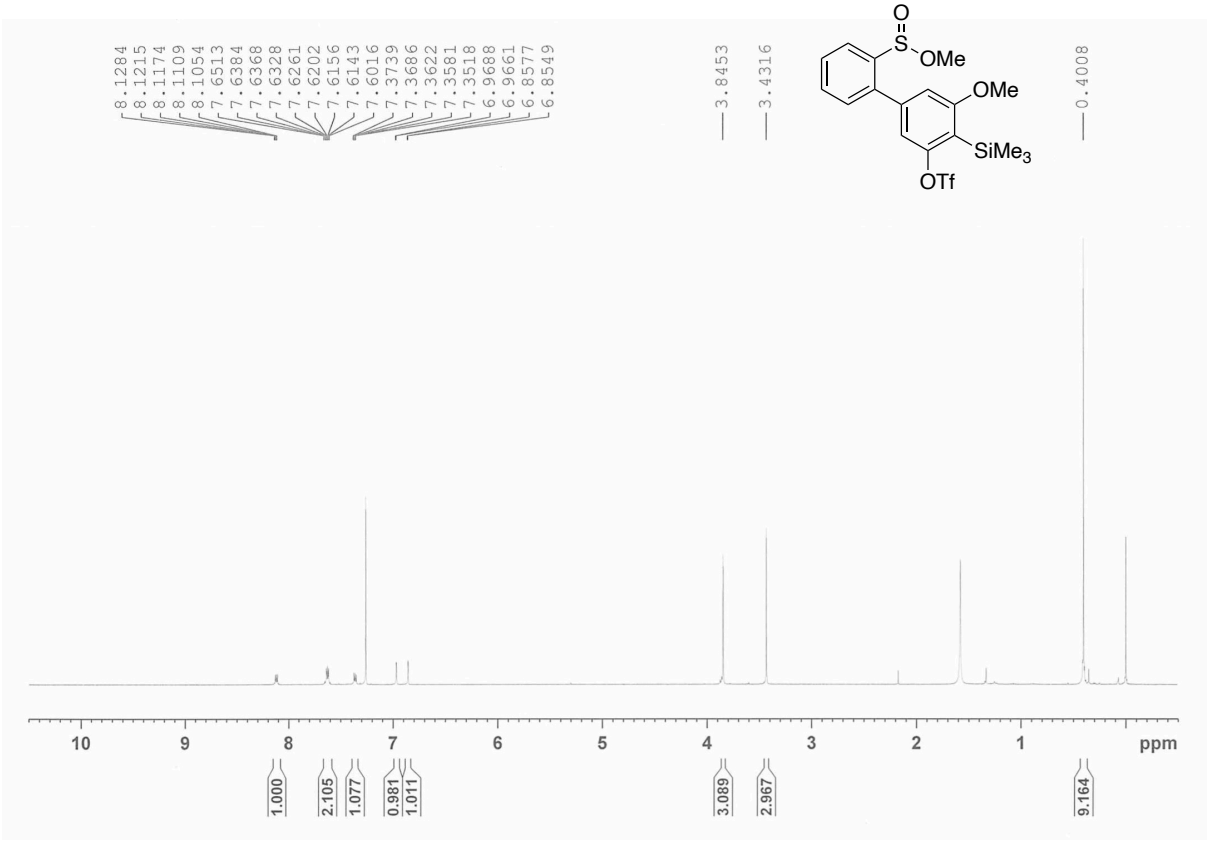


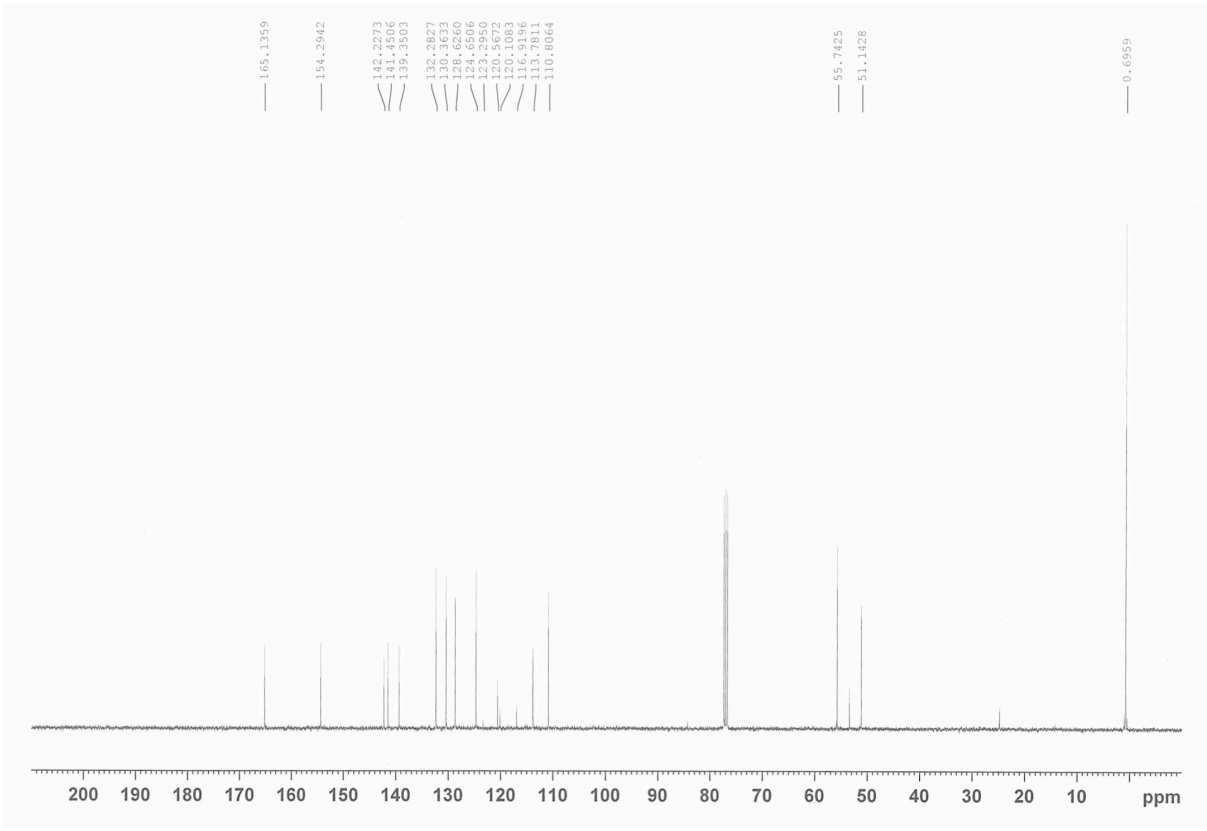
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of methyl (*E*)-2-styrylbenzenesulfinate (**3r**) ($CDCl_3$)



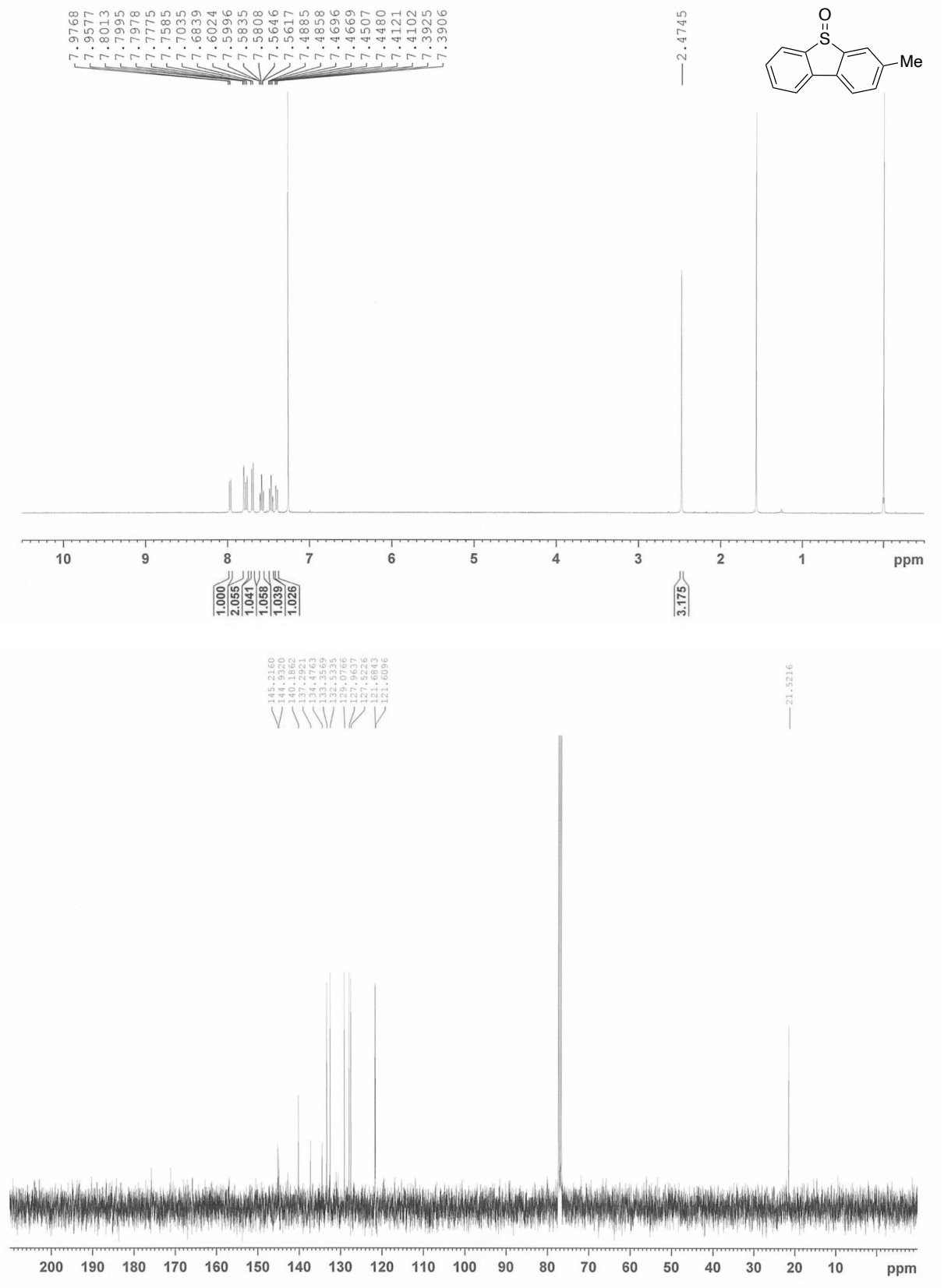


^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 5-methoxy-2'-(methoxysulfinyl)-4-(trimethylsilyl)-[1,1'-biphenyl]-3-yl trifluoromethanesulfonate (**3s**) ($CDCl_3$)

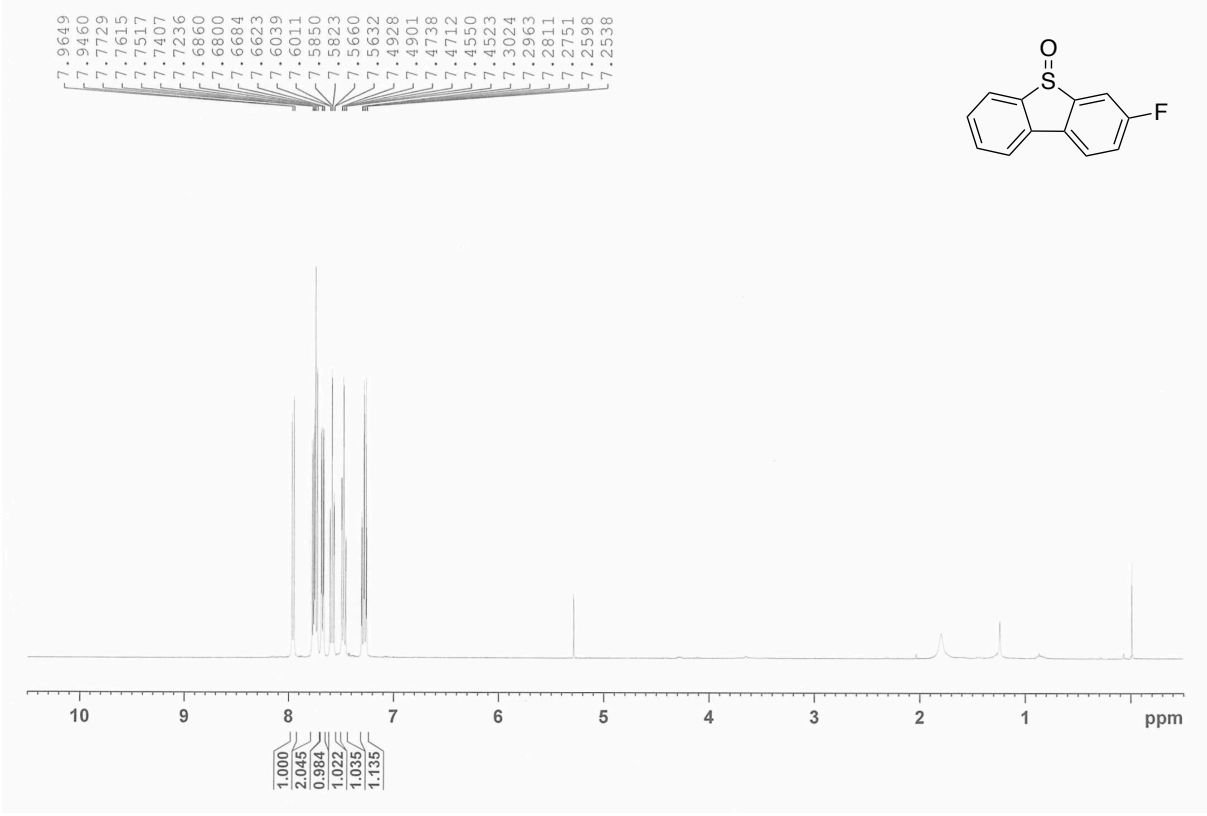


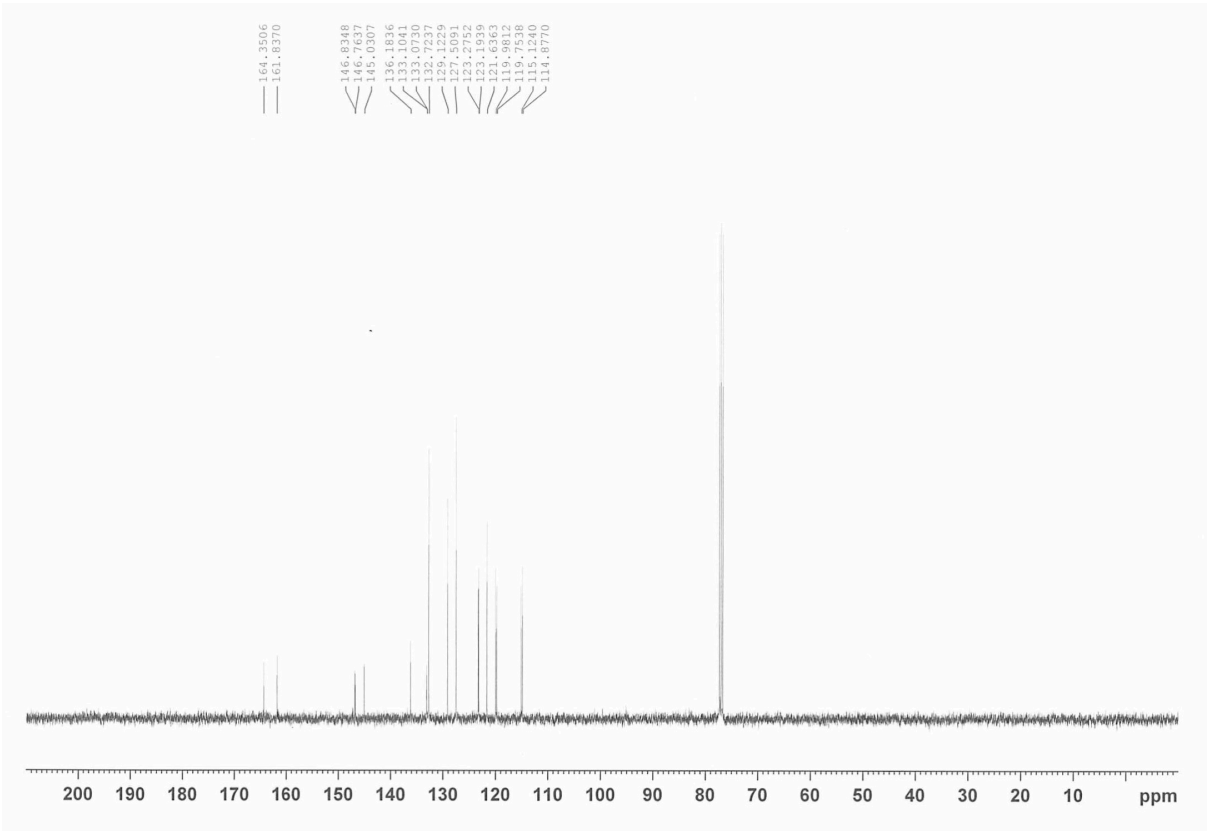


^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 3-methyldibenzo[*b*,*d*]thiophene 5-oxide (**4a**) ($CDCl_3$)

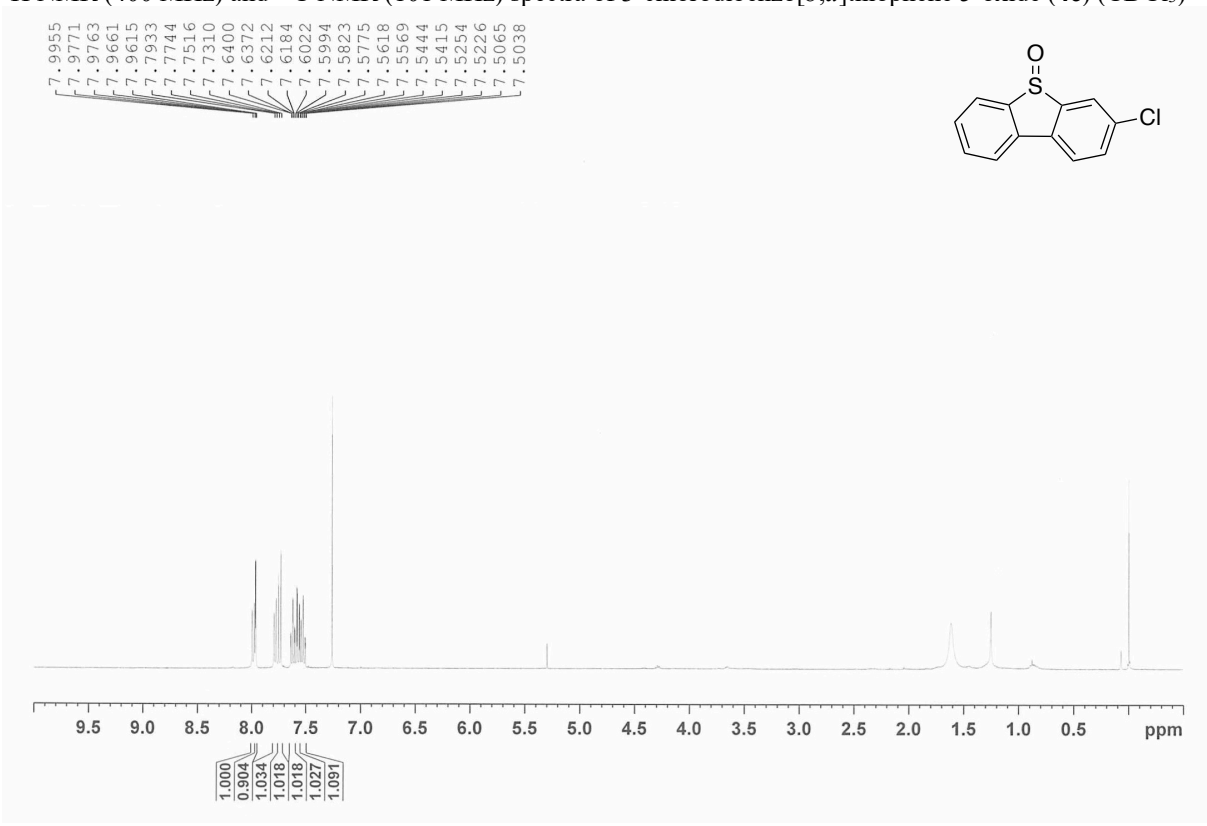


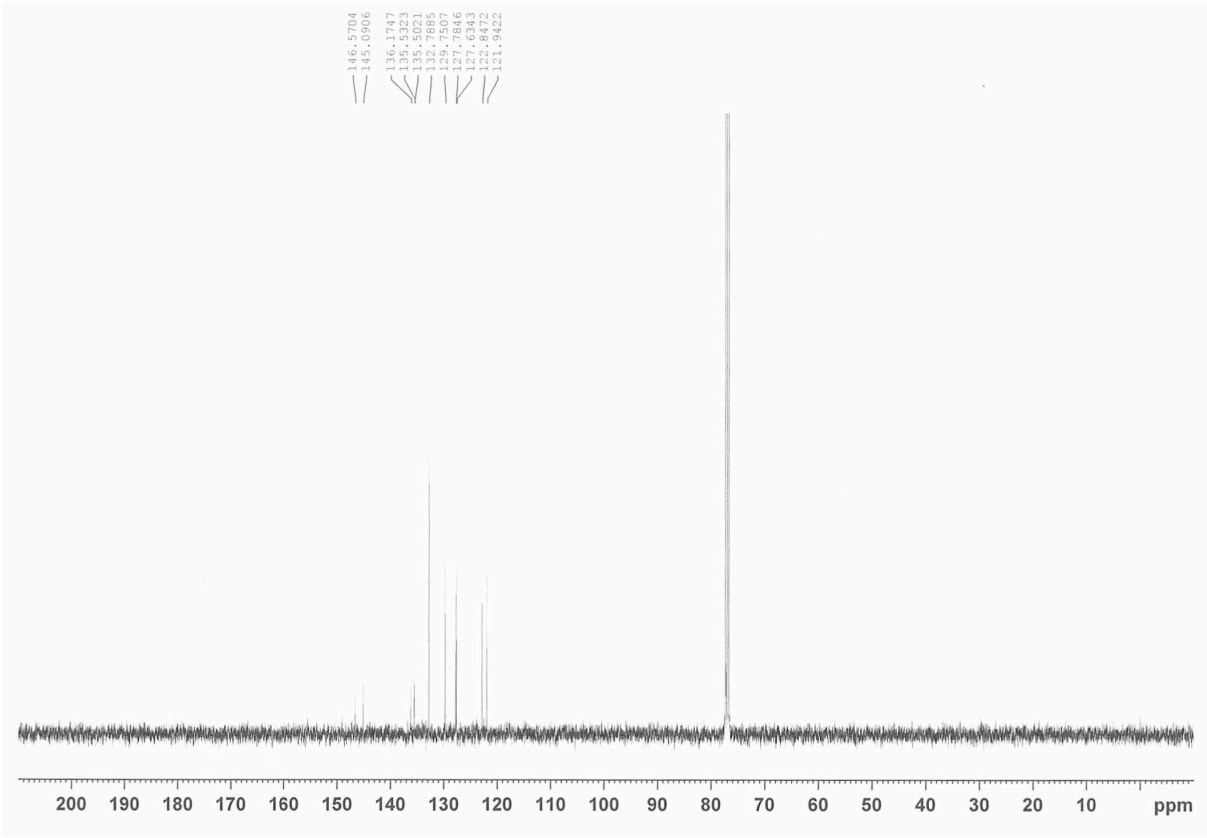
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 3-fluorodibenzo[*b*,*d*]thiophene 5-oxide (**4b**) ($CDCl_3$)



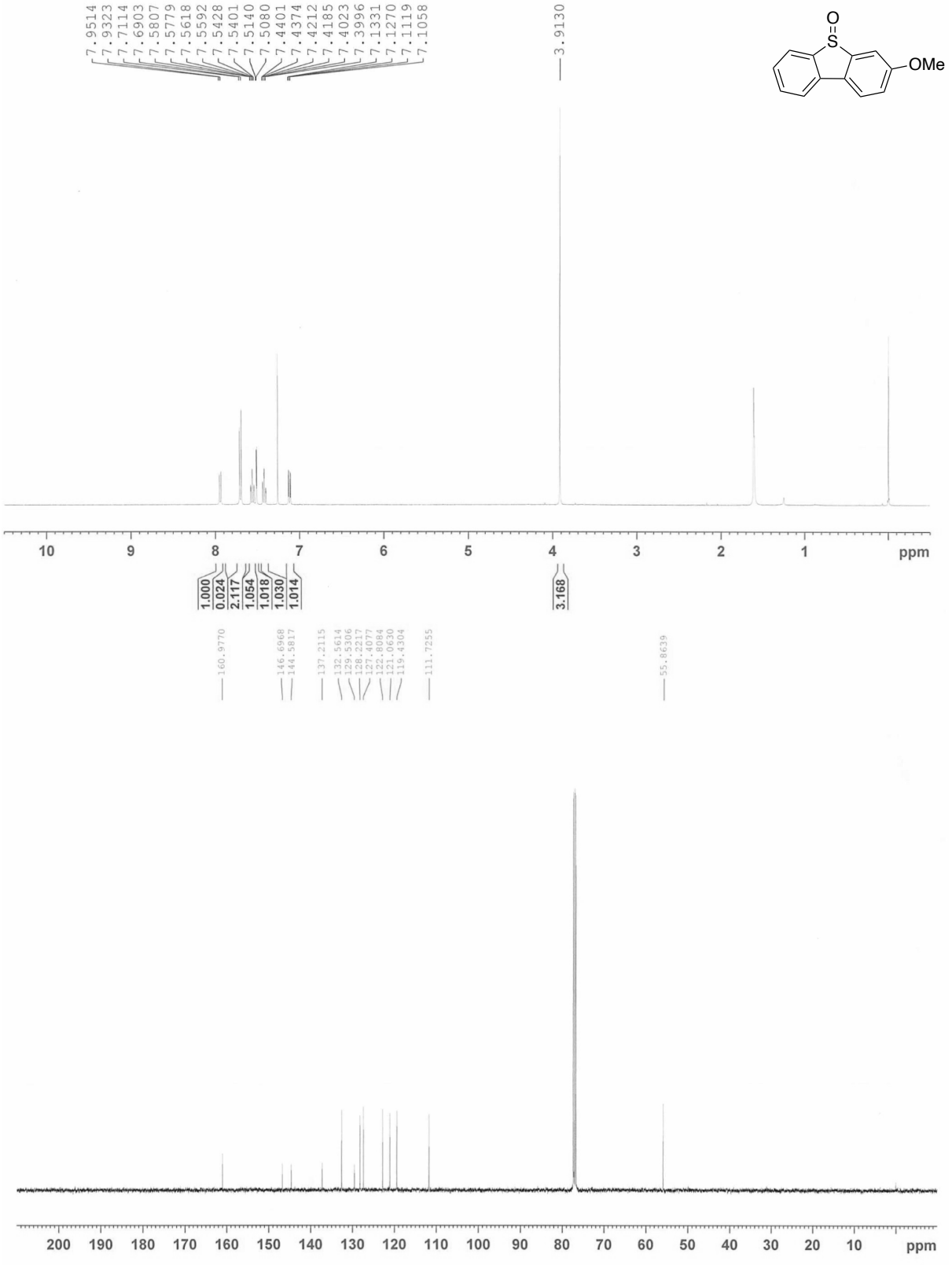


^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 3-chlorodibenzo[*b*,*d*]thiophene 5-oxide (**4c**) ($CDCl_3$)

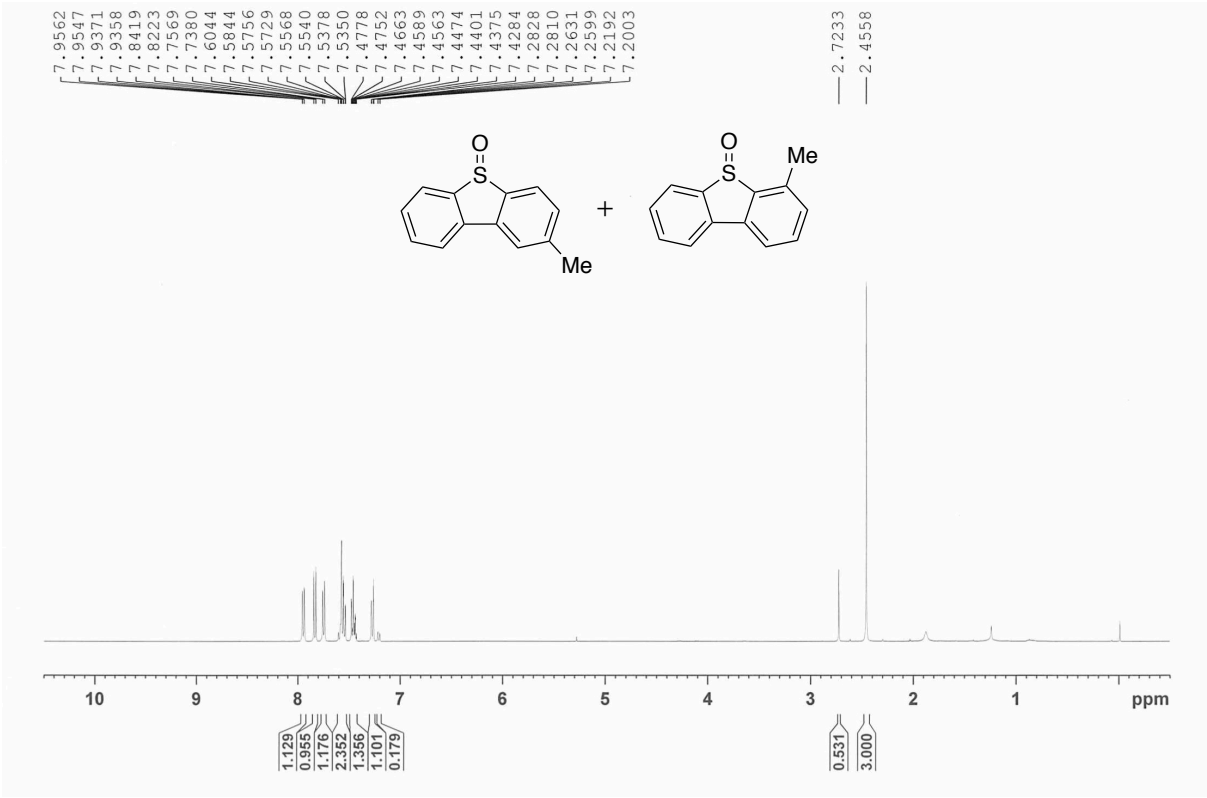


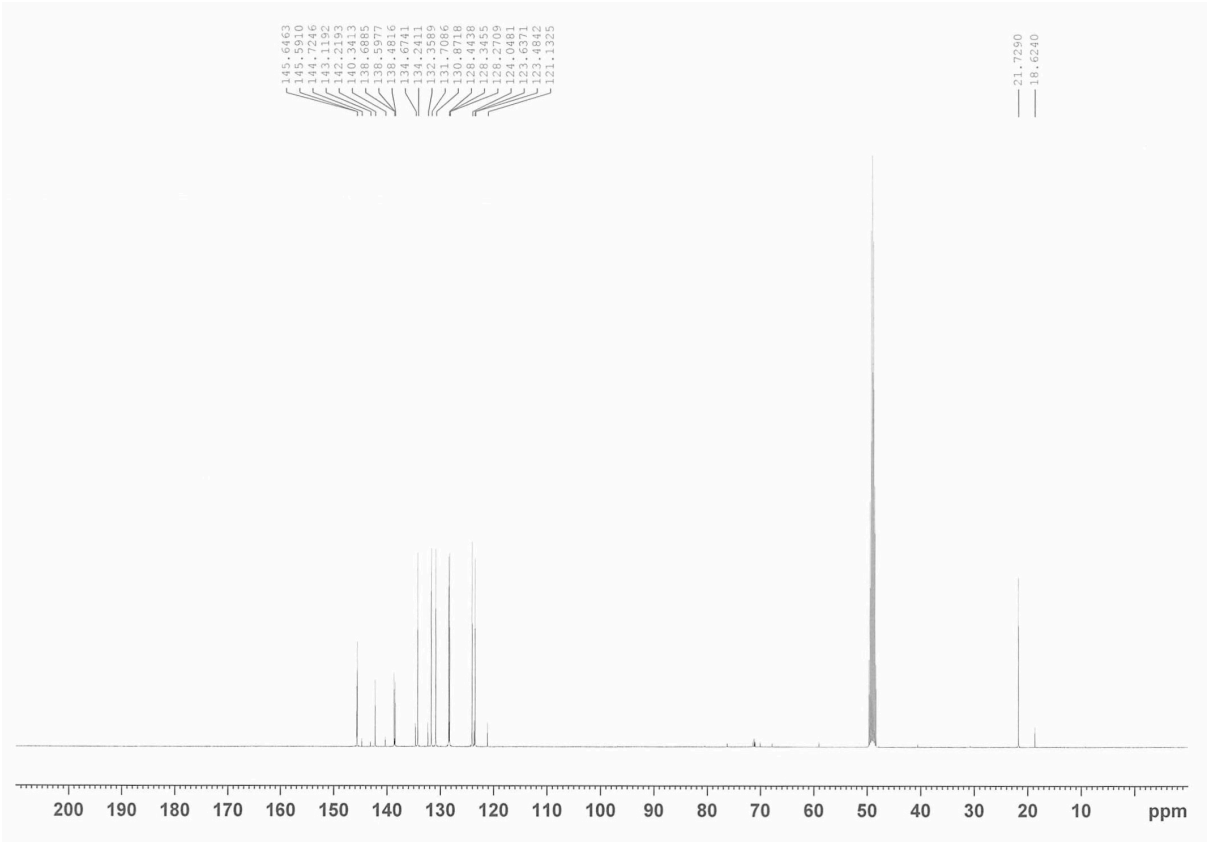


^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 3-methoxydibenzo[*b*,*d*]thiophene 5-oxide (**4d**) ($CDCl_3$)

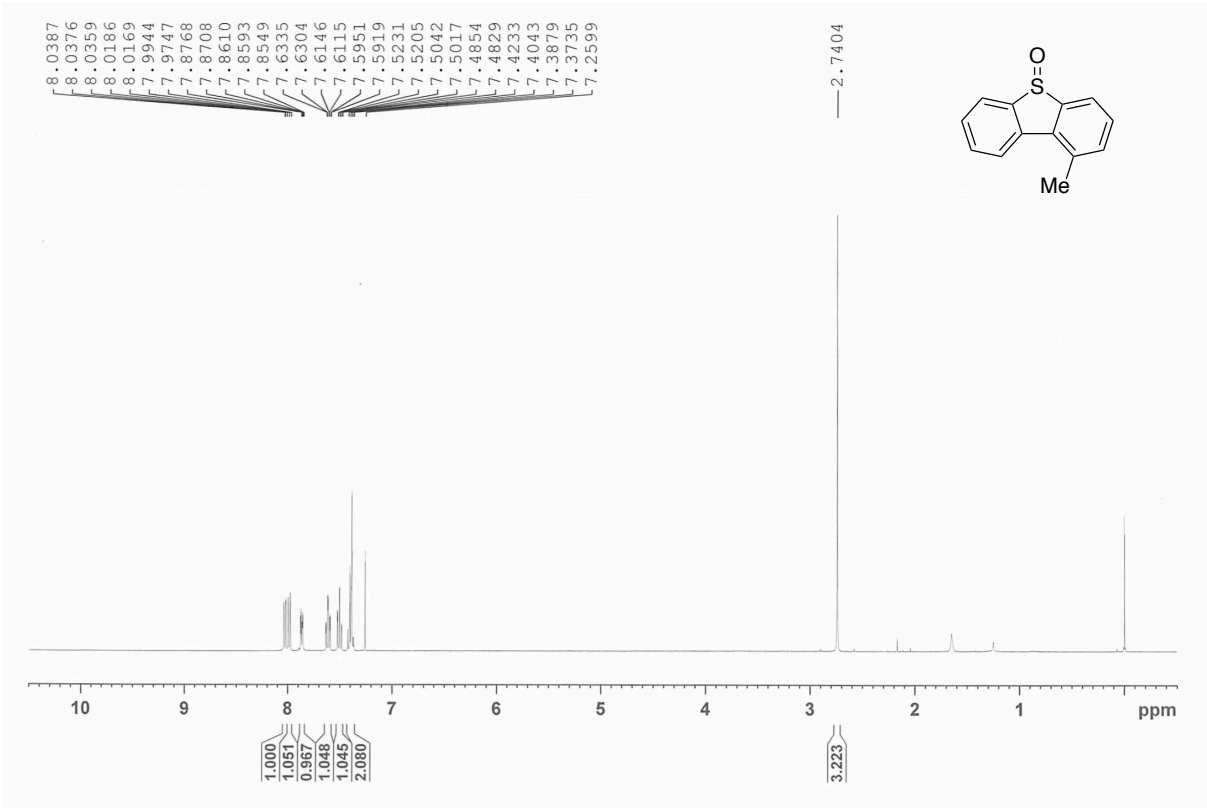


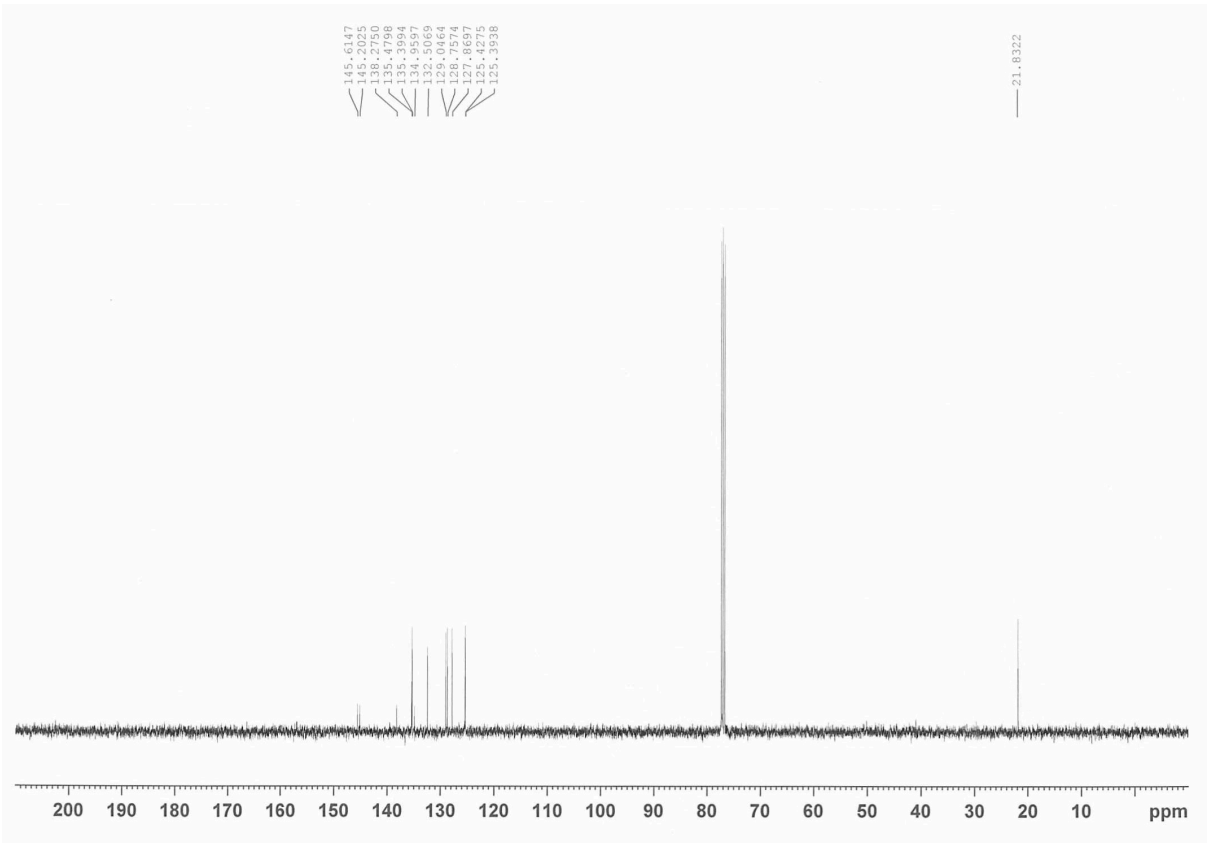
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 2-methyldibenzo[*b*,*d*]thiophene 5-oxide (**4e**) and 4-methyldibenzo[*b*,*d*]thiophene 5-oxide (**4e'**) ($CDCl_3$)



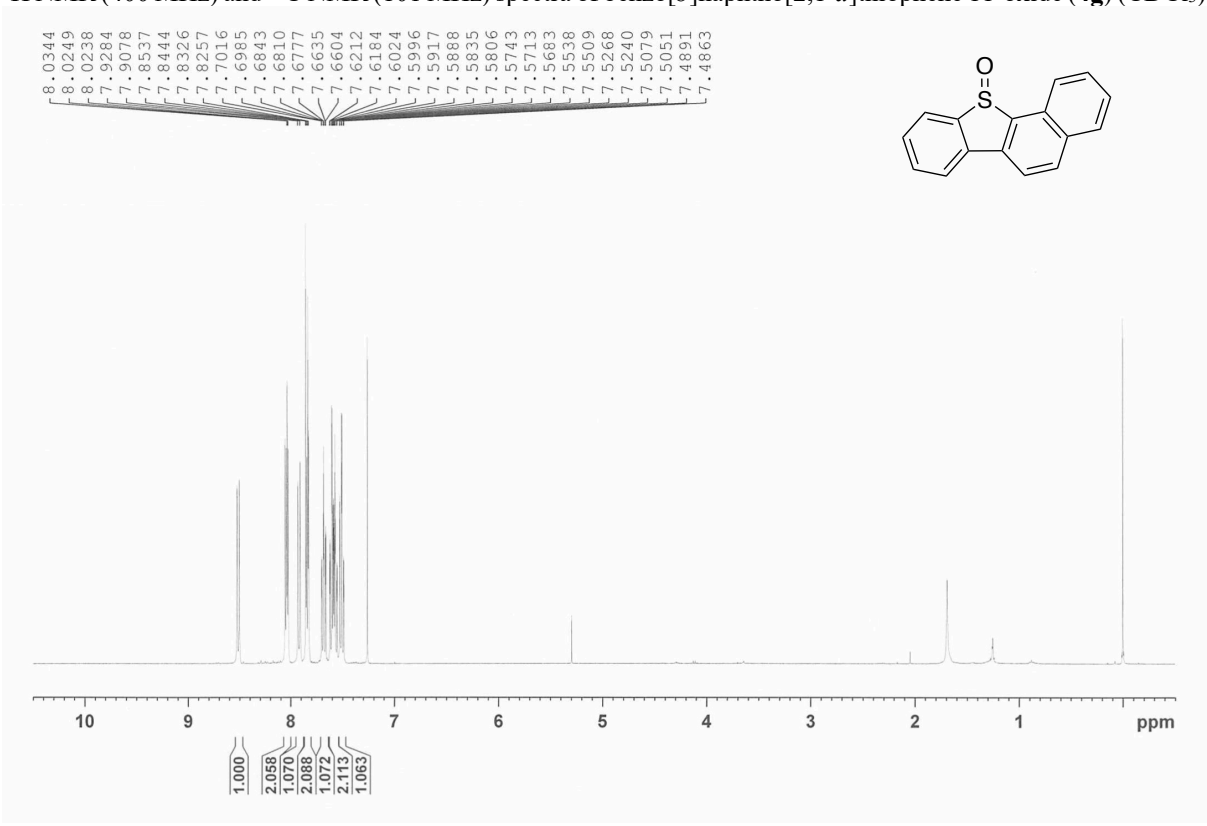


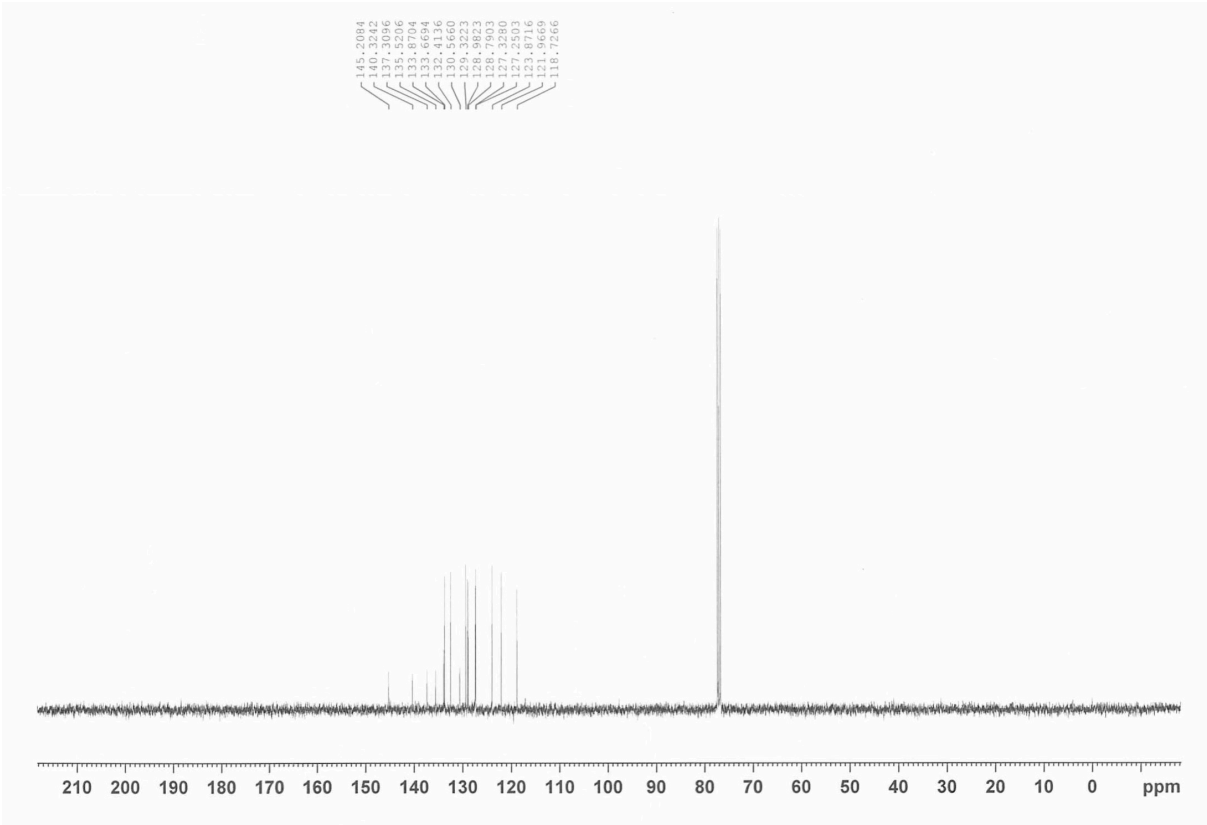
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 1-methyldibenzo[*b*,*d*]thiophene 5-oxide (**4f**) ($CDCl_3$)



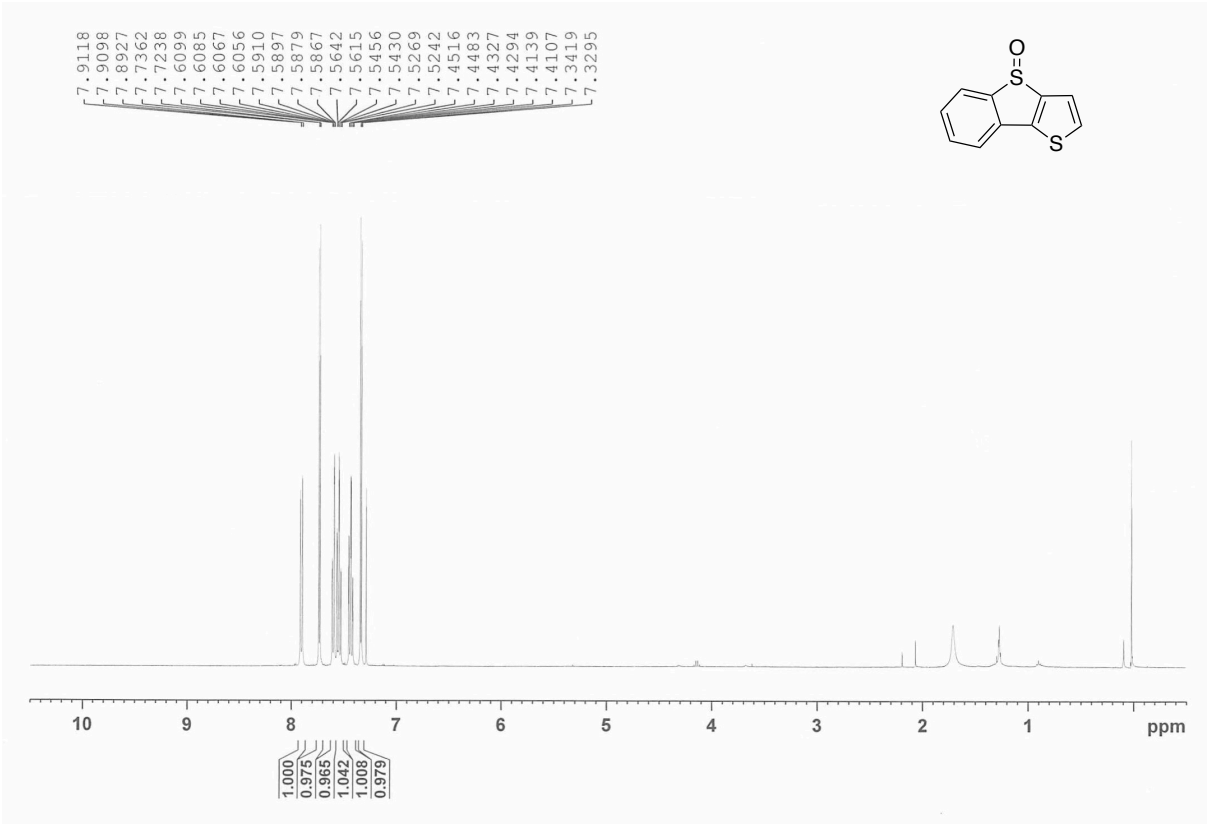


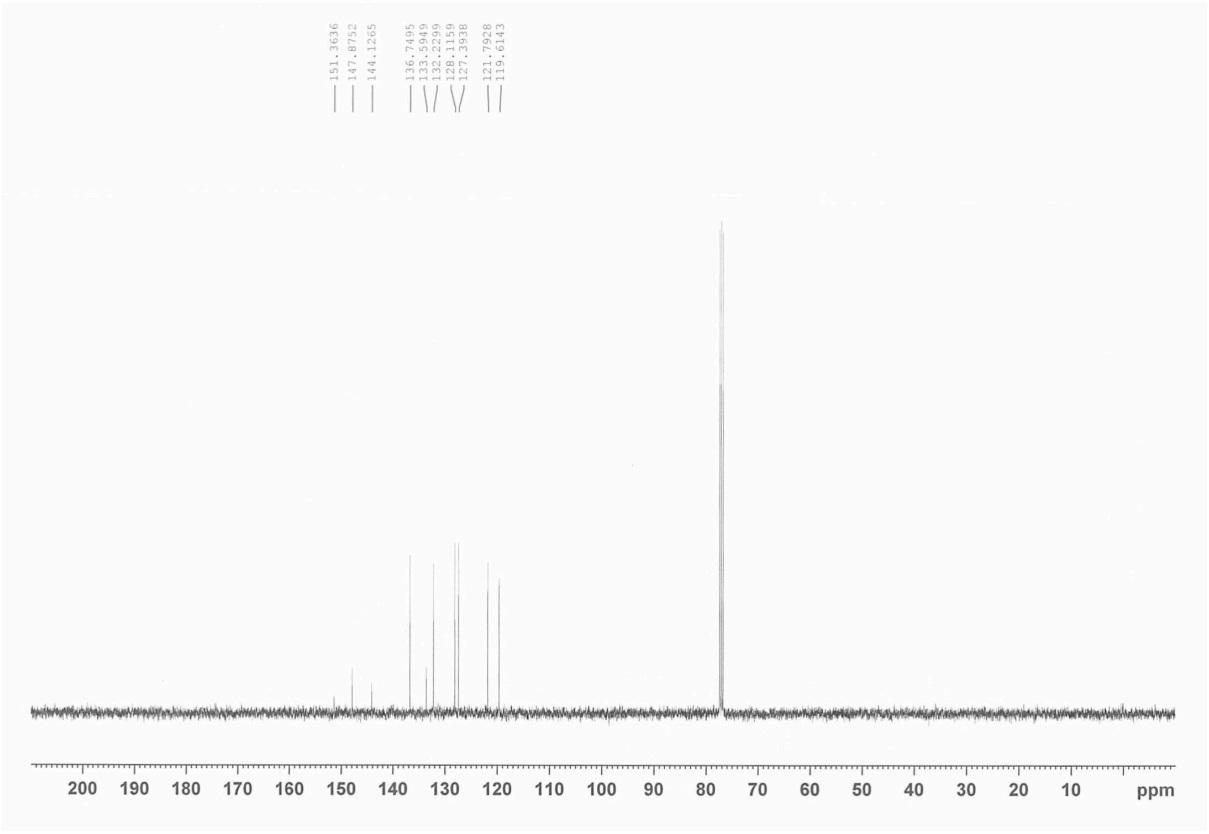
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of benzo[*b*]naphtho[2,1-*d*]thiophene 11-oxide (**4g**) ($CDCl_3$)



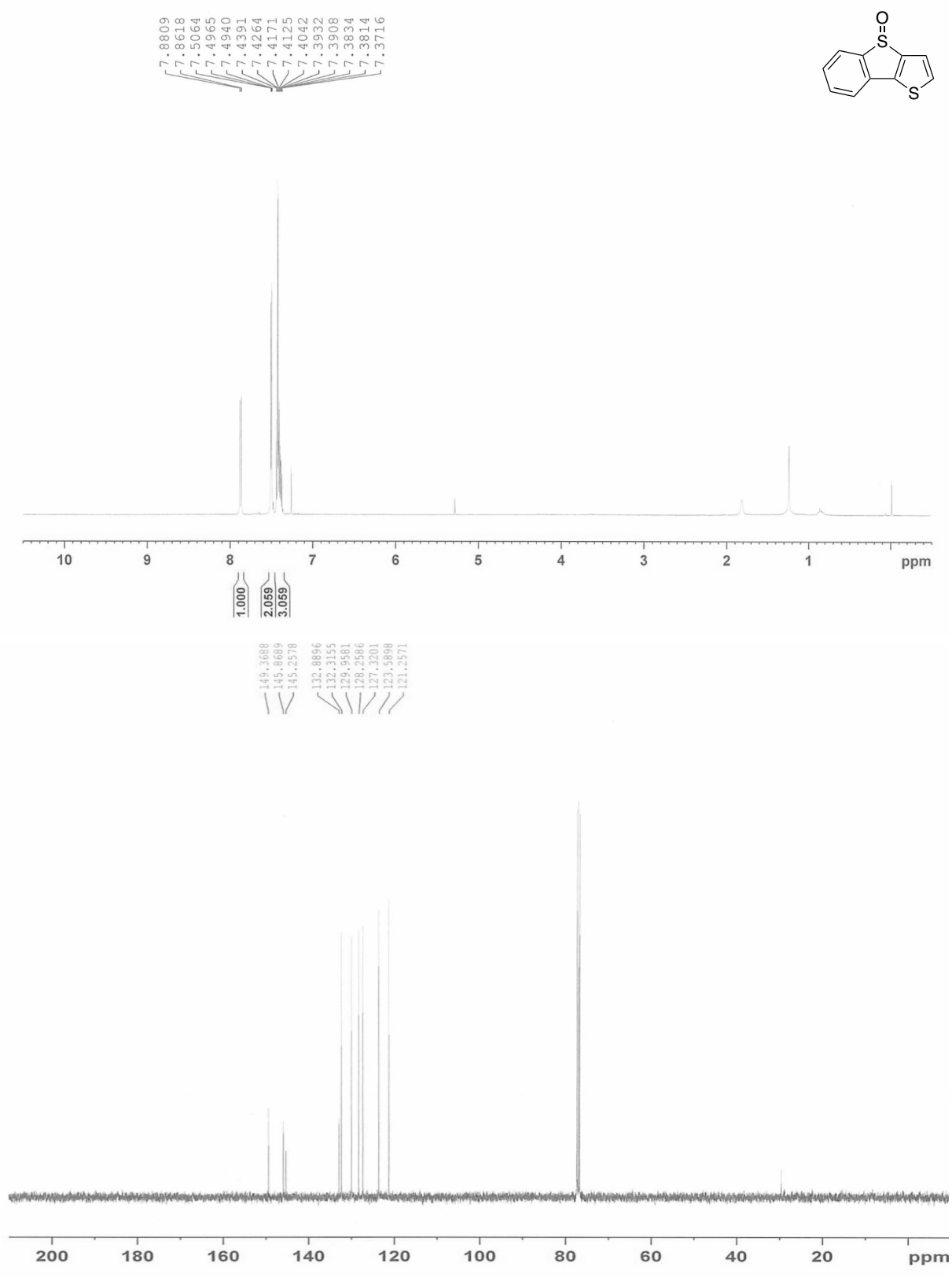


^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of benzo[*b*]thieno[3,2-*d*]thiophene 8-oxide (**4h**) ($CDCl_3$)

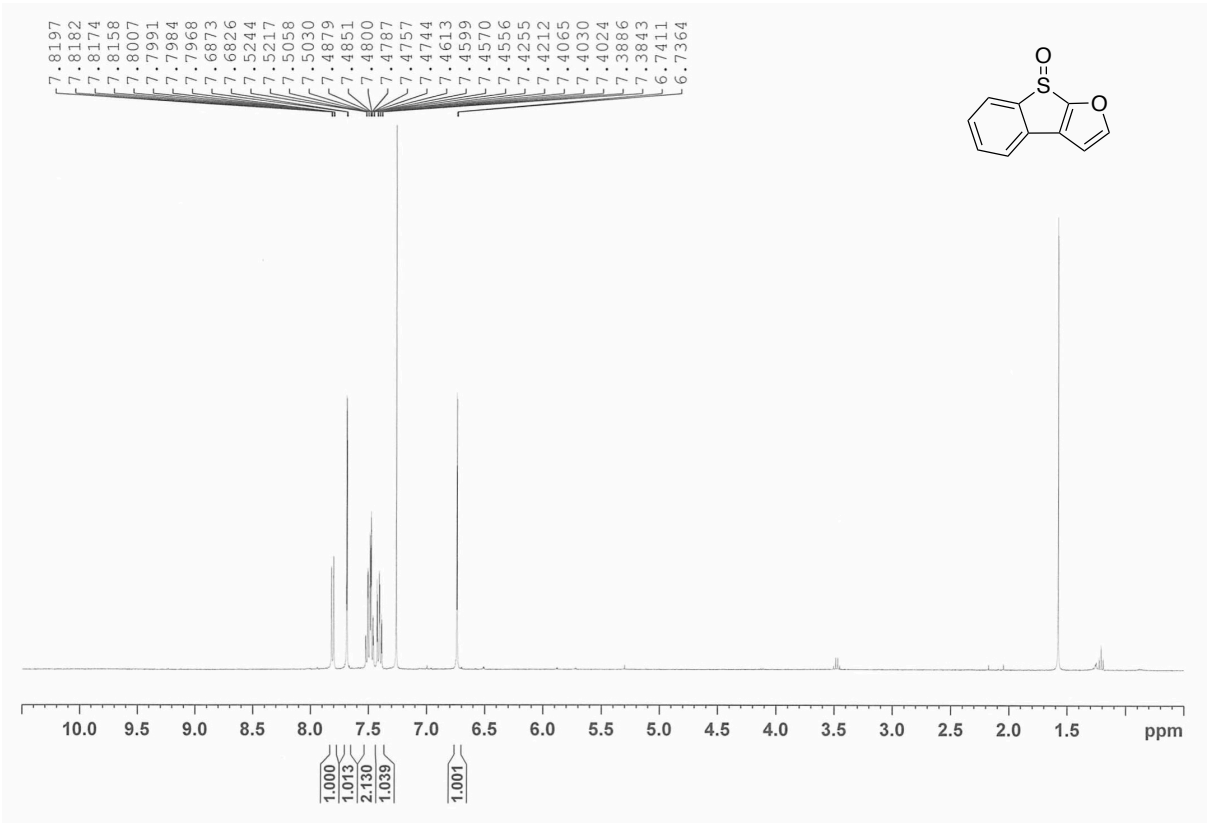


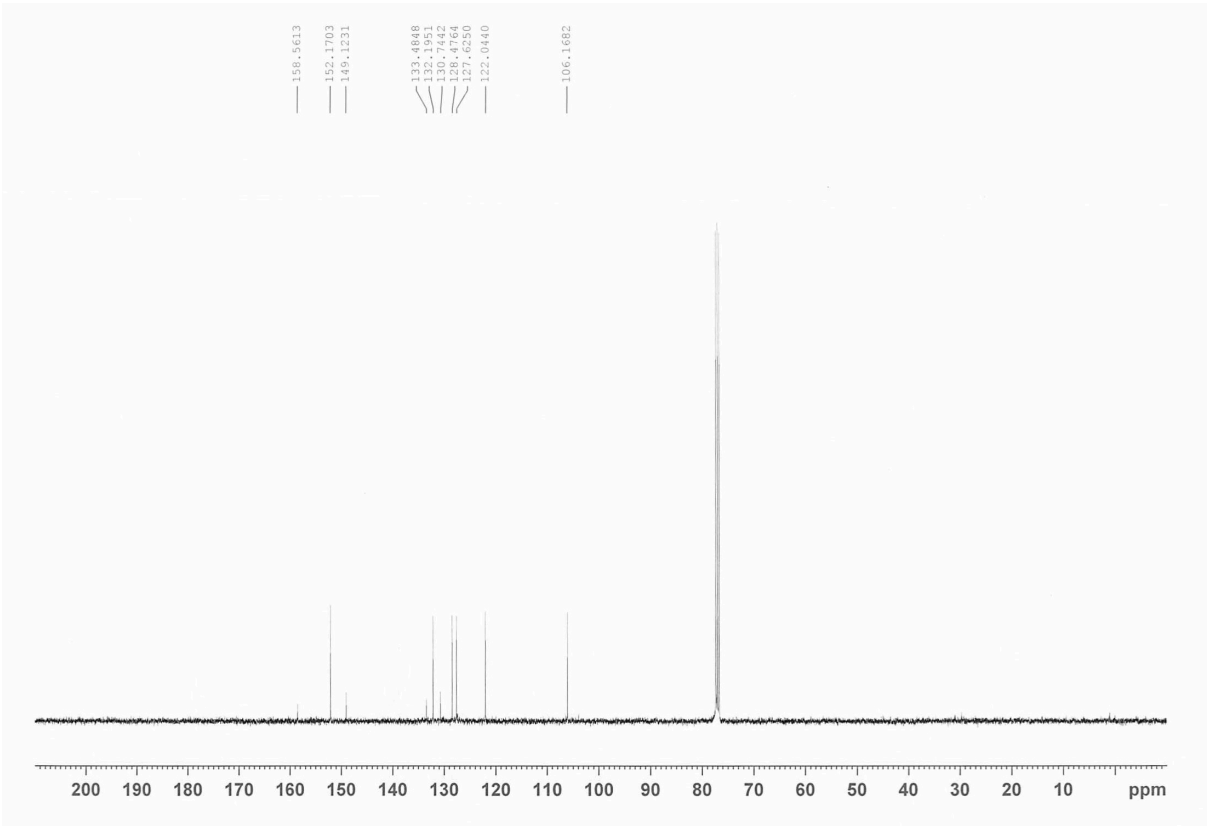


^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of benzo[*b*]thieno[2,3-*d*]thiophene 4-oxide (**4i**) ($CDCl_3$)

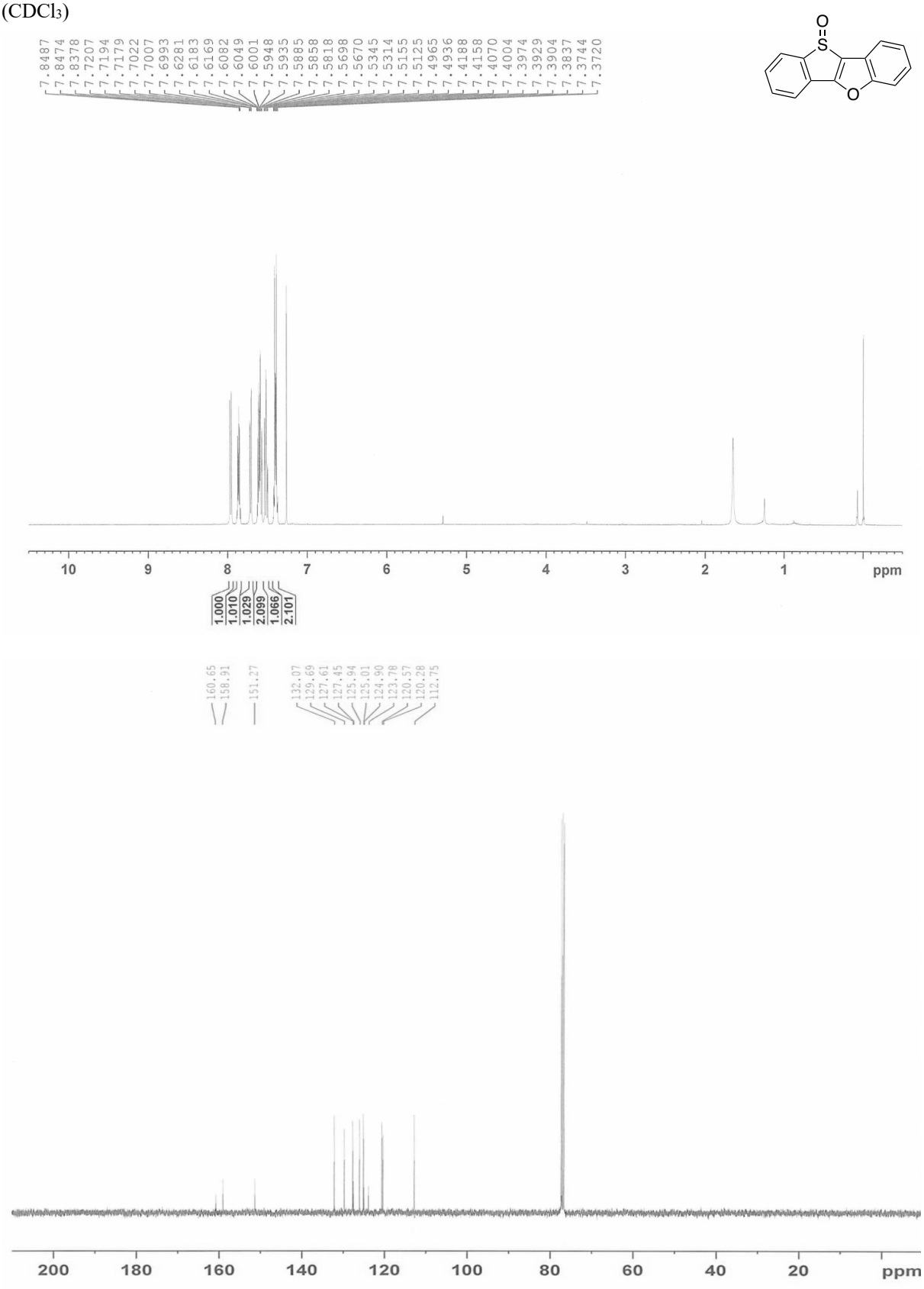


^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of benzo[4,5]thieno[2,3-*b*]furan 8-oxide (**4j**) ($CDCl_3$)

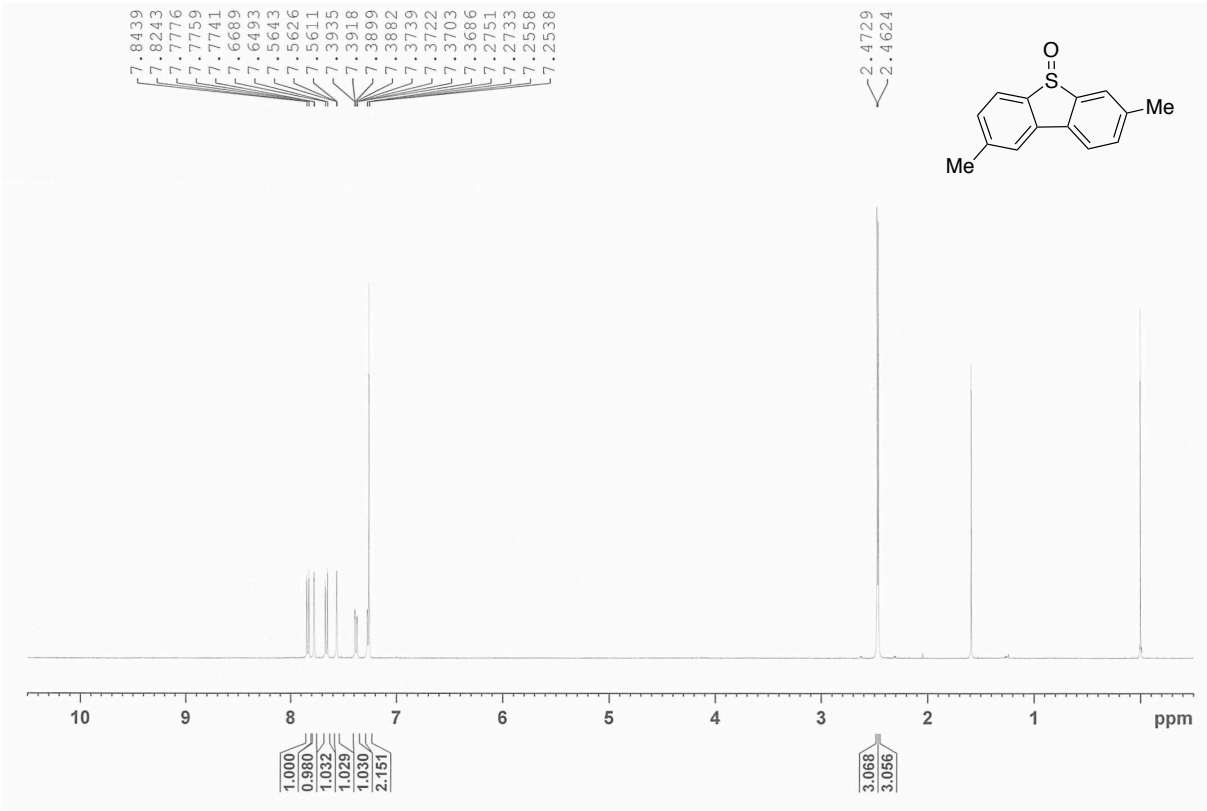


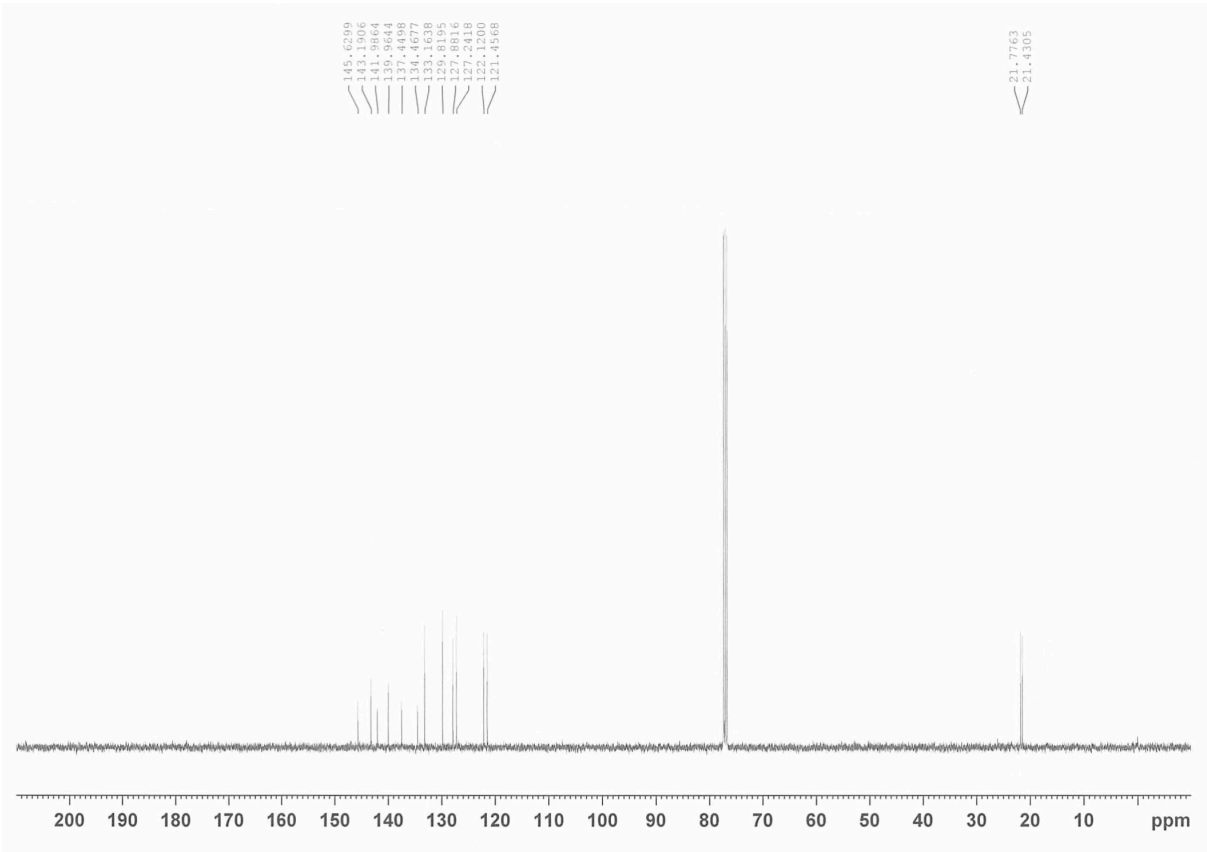


^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of benzo[4,5]thieno[3,2-*b*]benzofuran 10-oxide (**4k**) ($CDCl_3$)

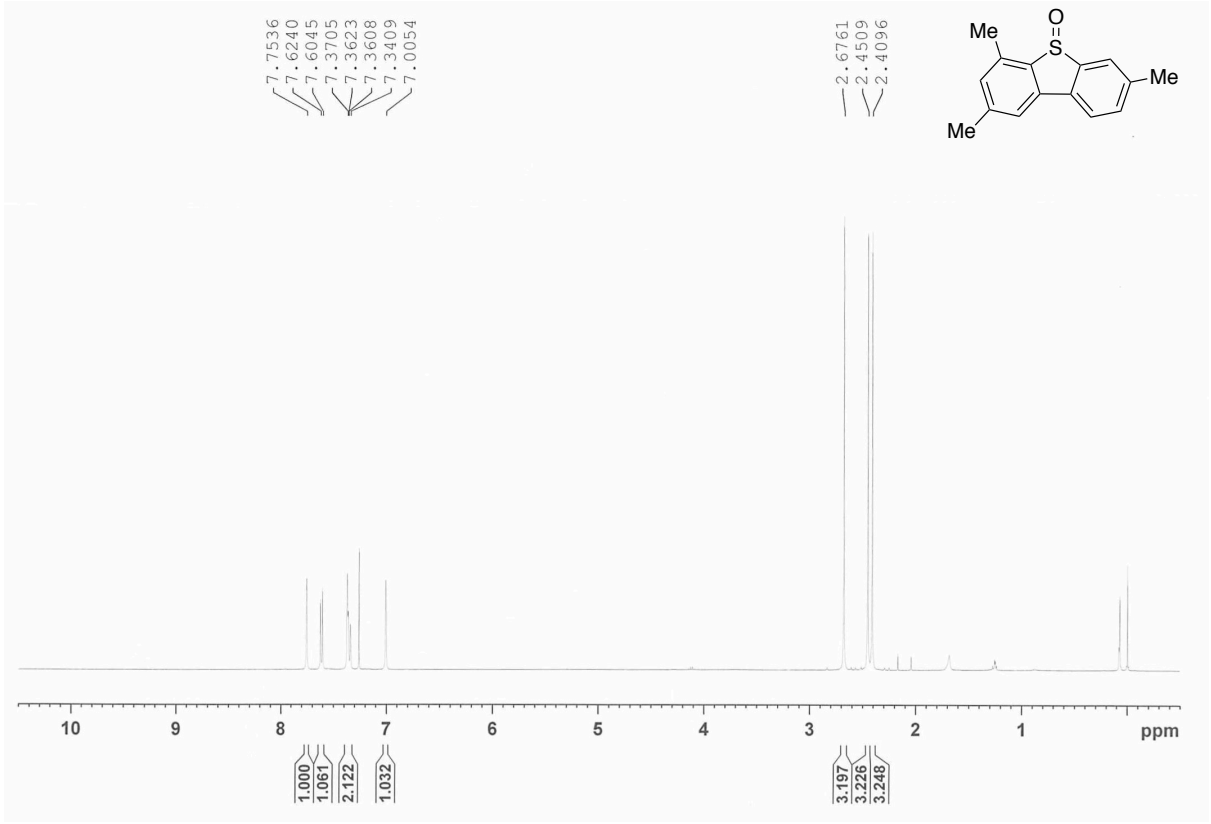


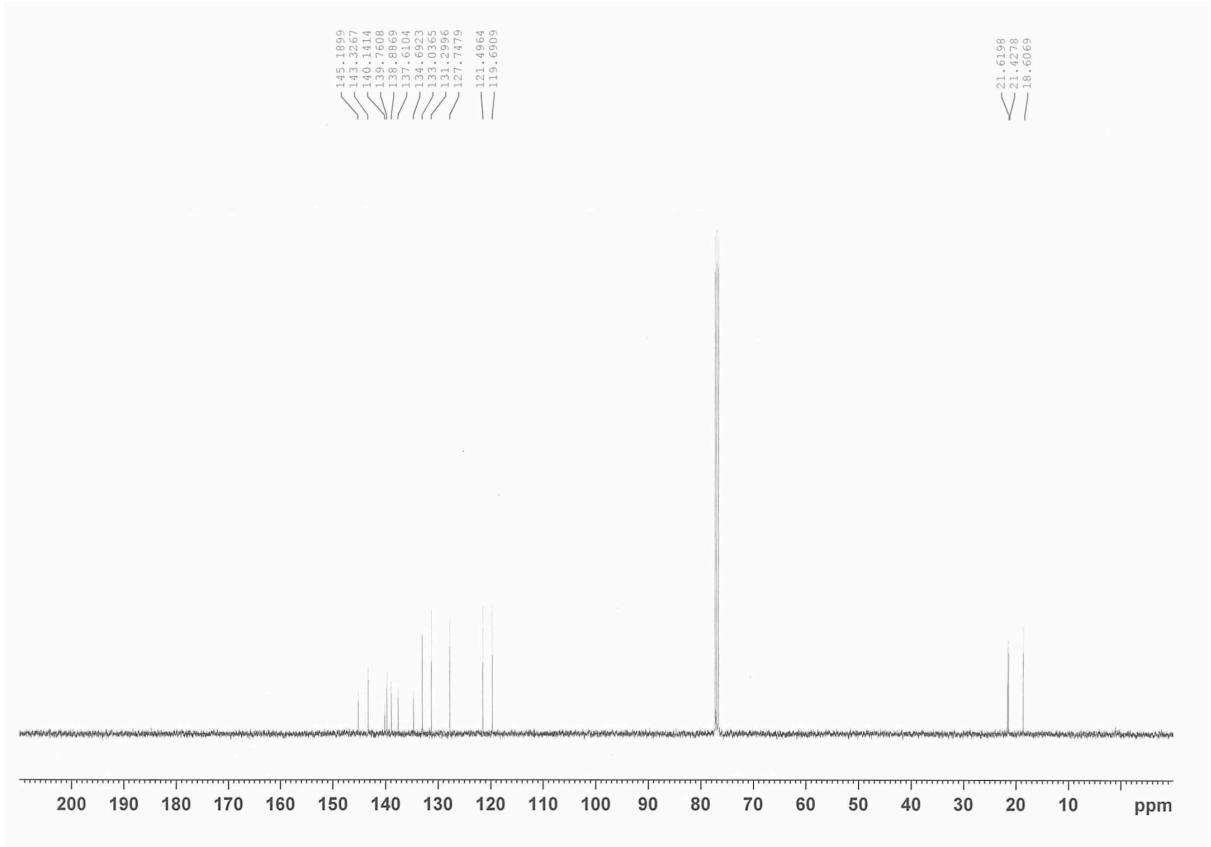
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 2,7-dimethyldibenzo[*b*,*d*]thiophene 5-oxide (**4l**) ($CDCl_3$)



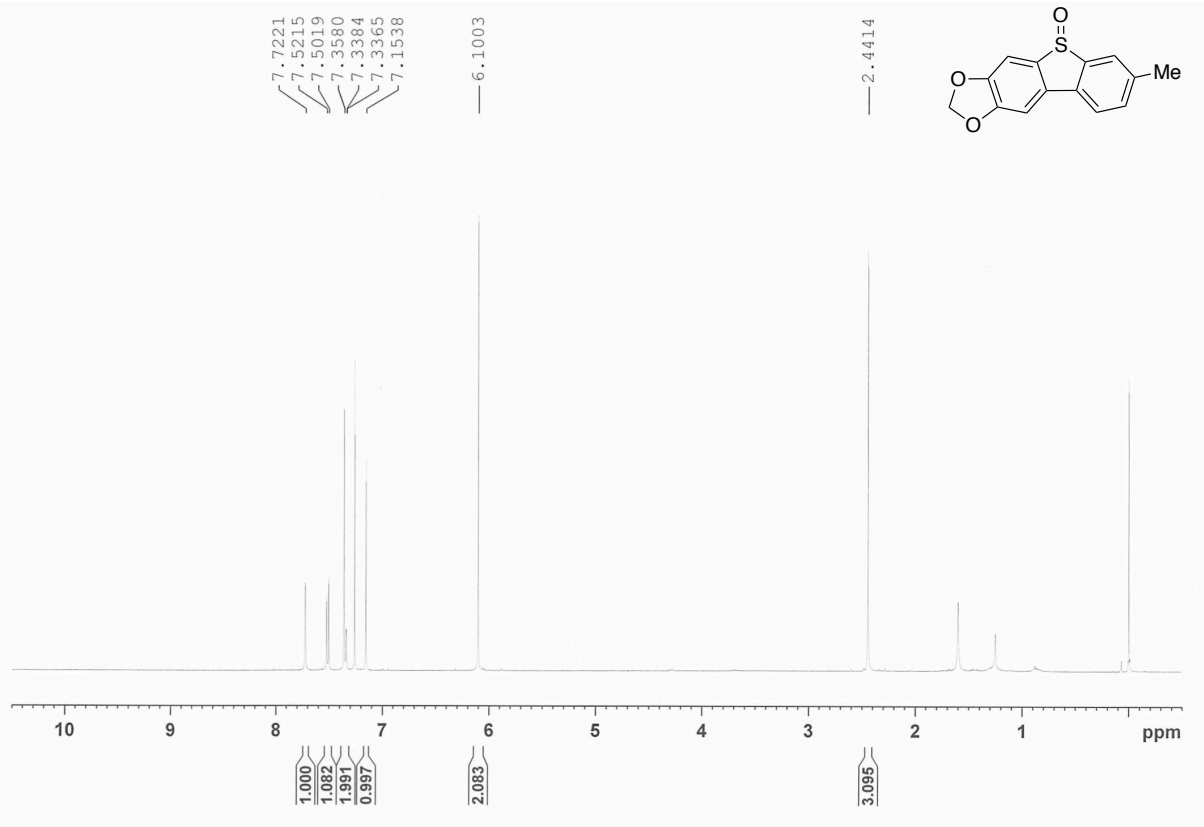


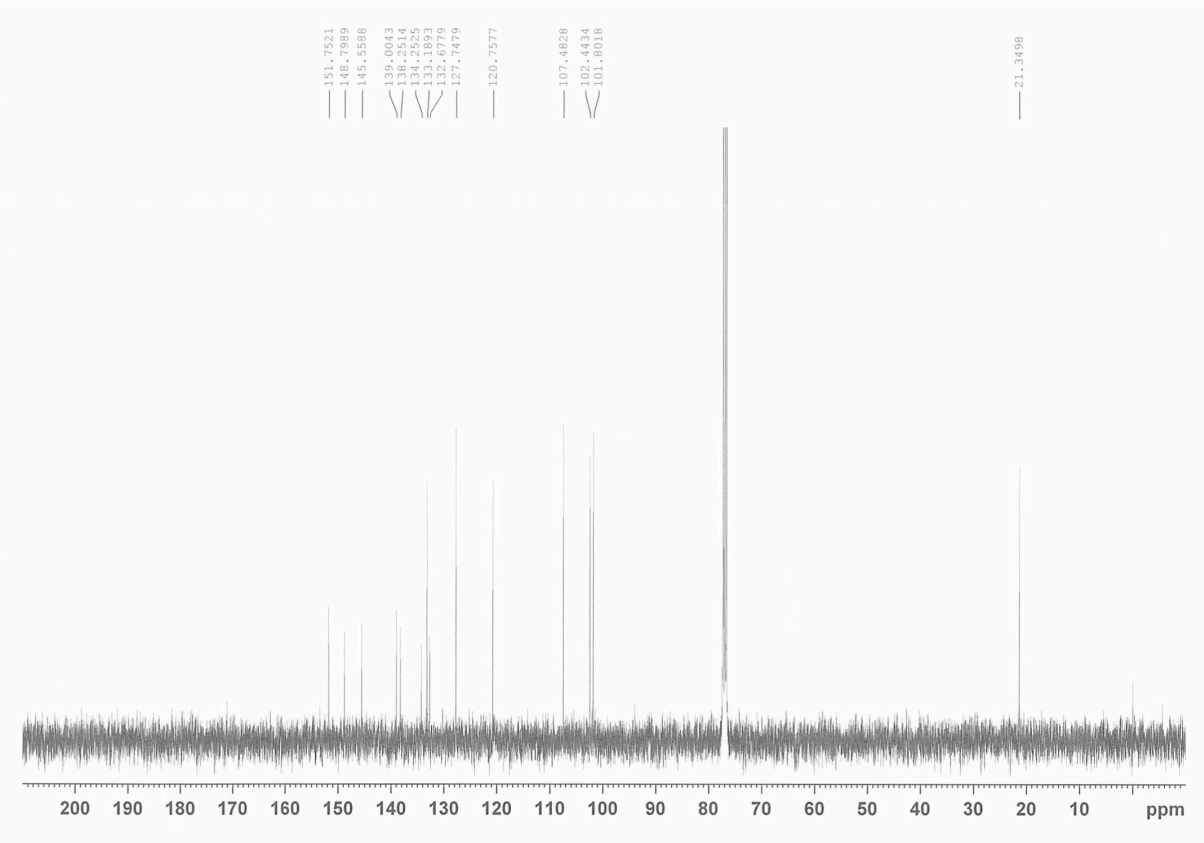
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 2,4,7-trimethyldibenzo[*b*,*d*]thiophene 5-oxide (**4m**) ($CDCl_3$)



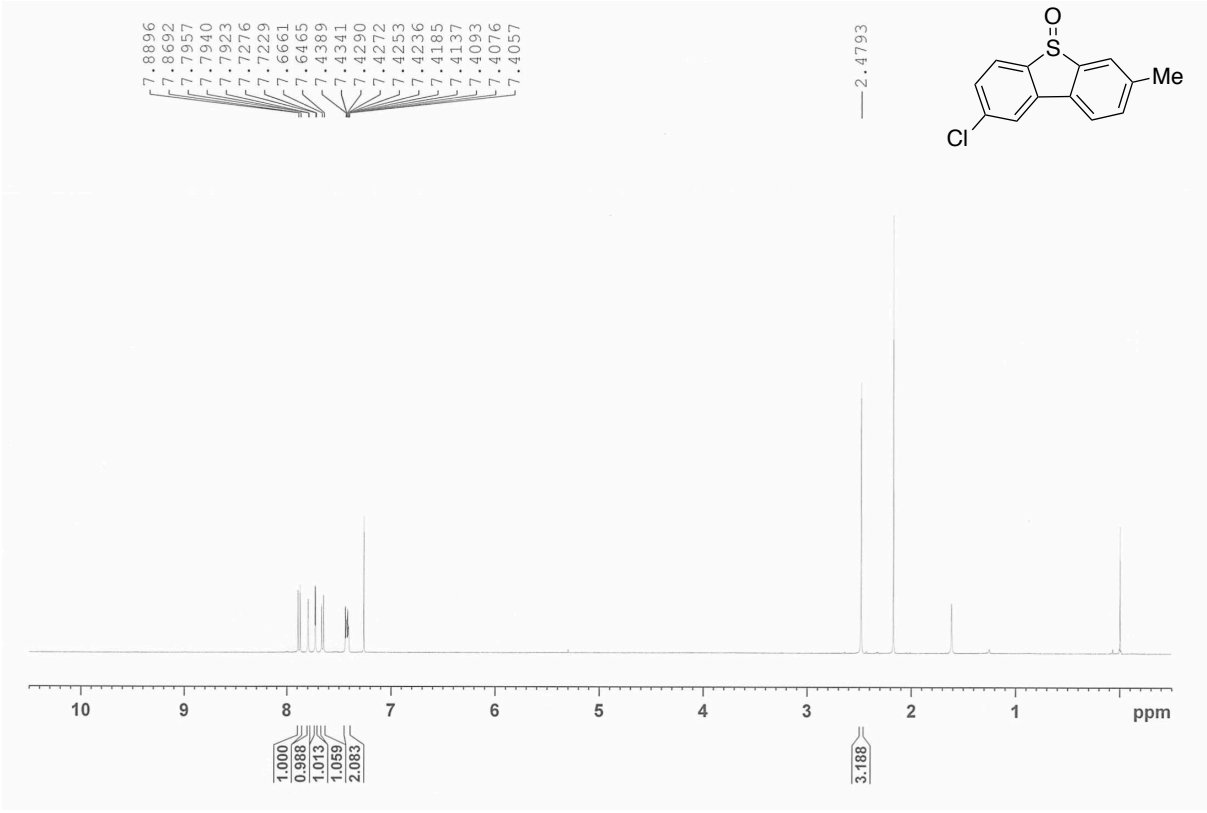


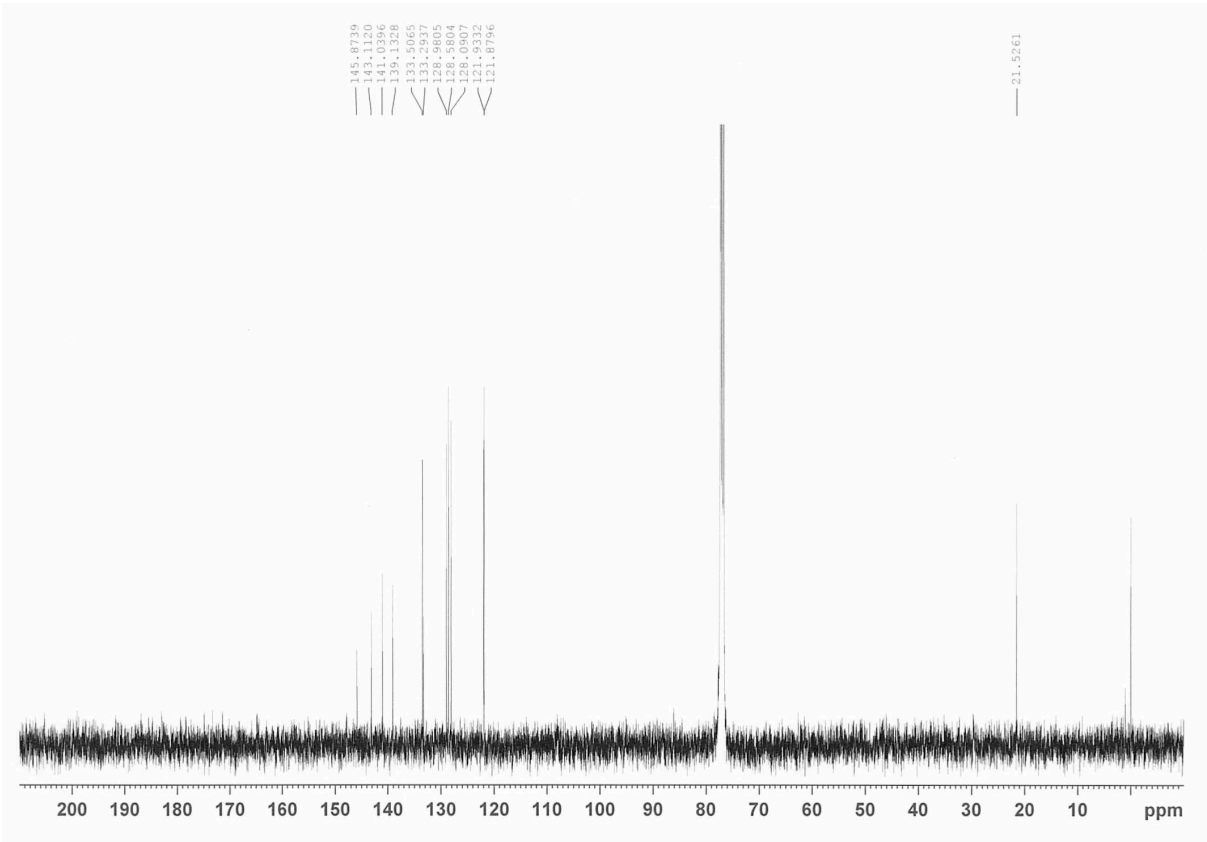
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 7-methylbenzo[4',5']thieno[2',3':4,5]benzo[1,2-*d*][1,3]dioxole 5-oxide (**4n**) ($CDCl_3$)



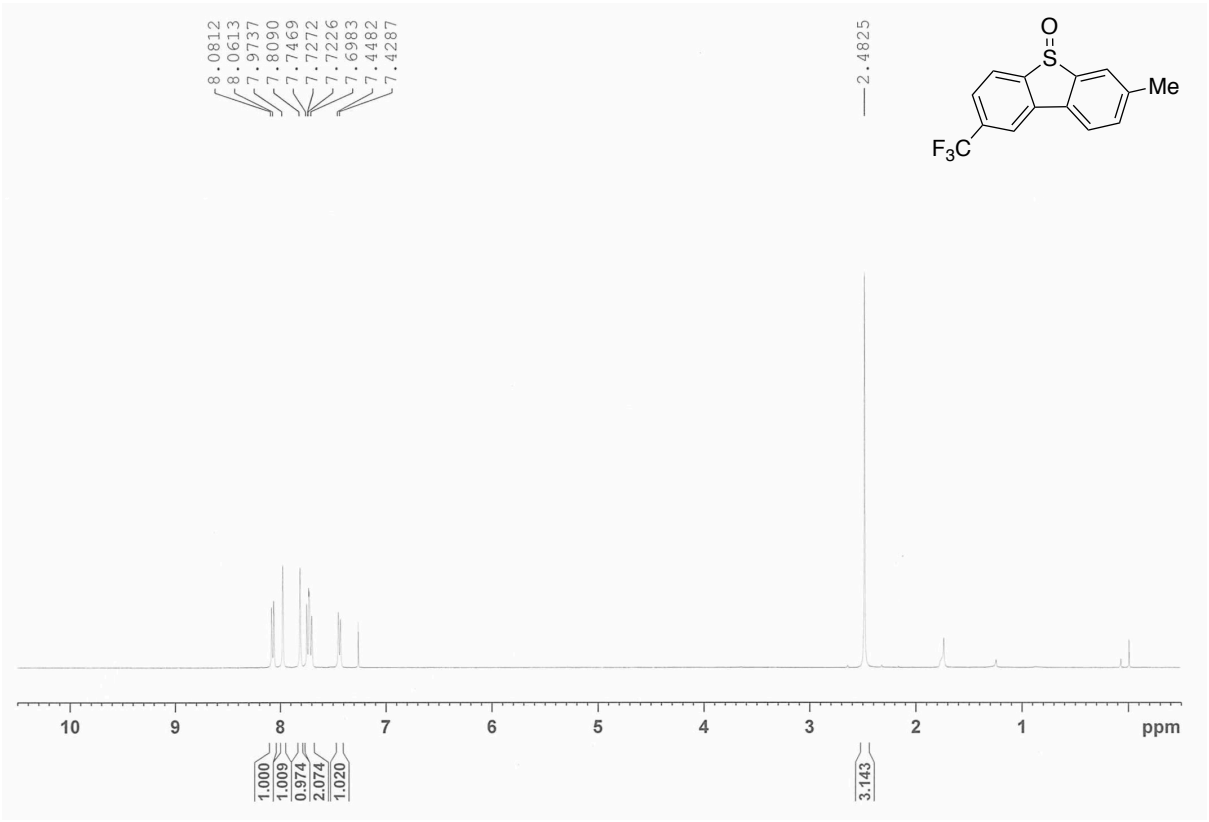


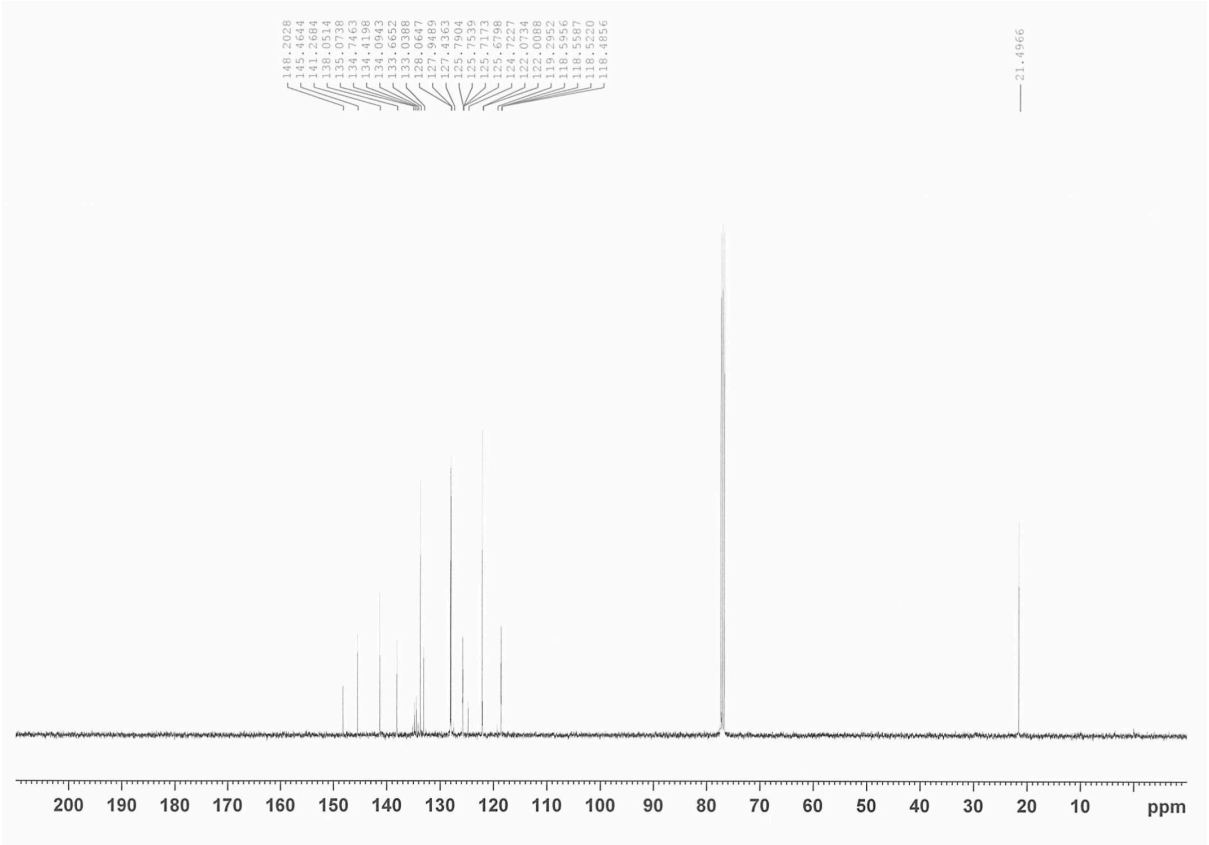
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 2-chloro-7-methyldibenzo[*b*,*d*]thiophene 5-oxide (**4o**) ($CDCl_3$)



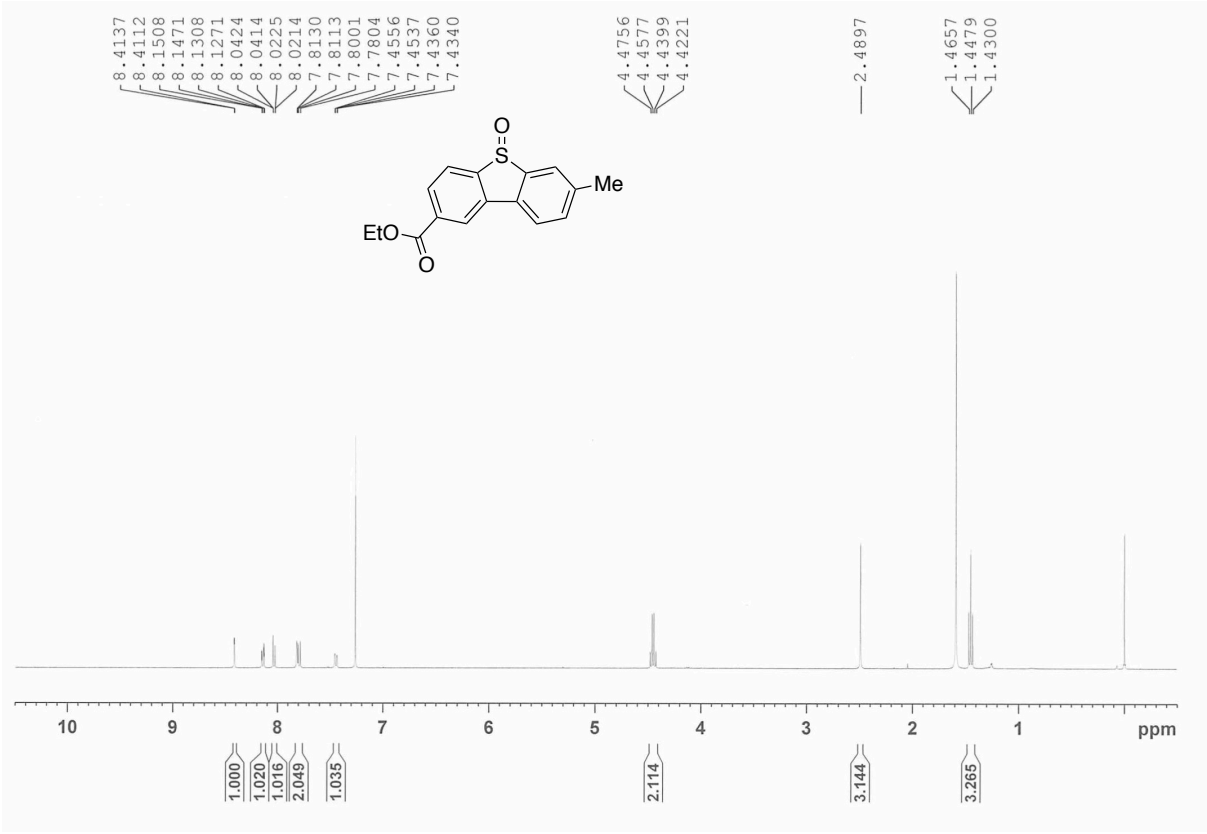


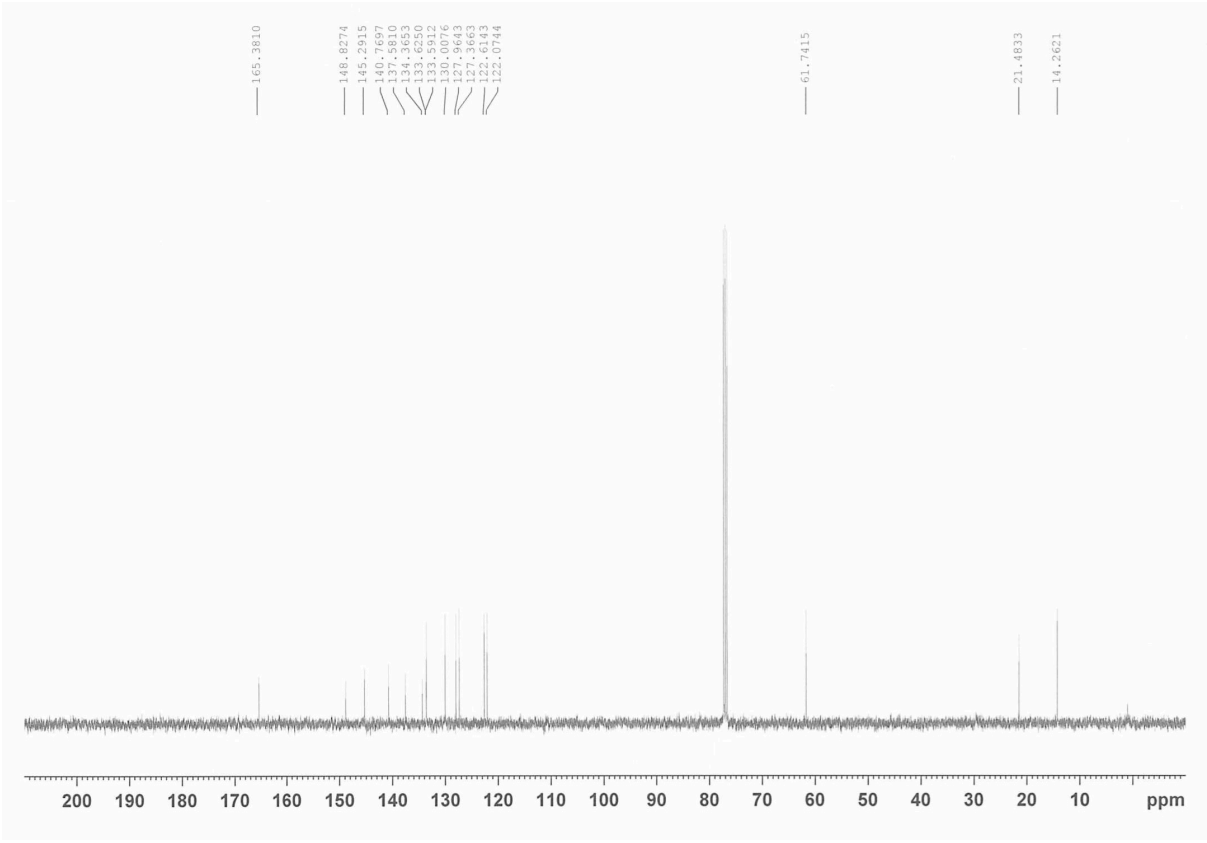
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 7-methyl-2-(trifluoromethyl)dibenzo[*b*,*d*]thiophene 5-oxide (**4p**) ($CDCl_3$)



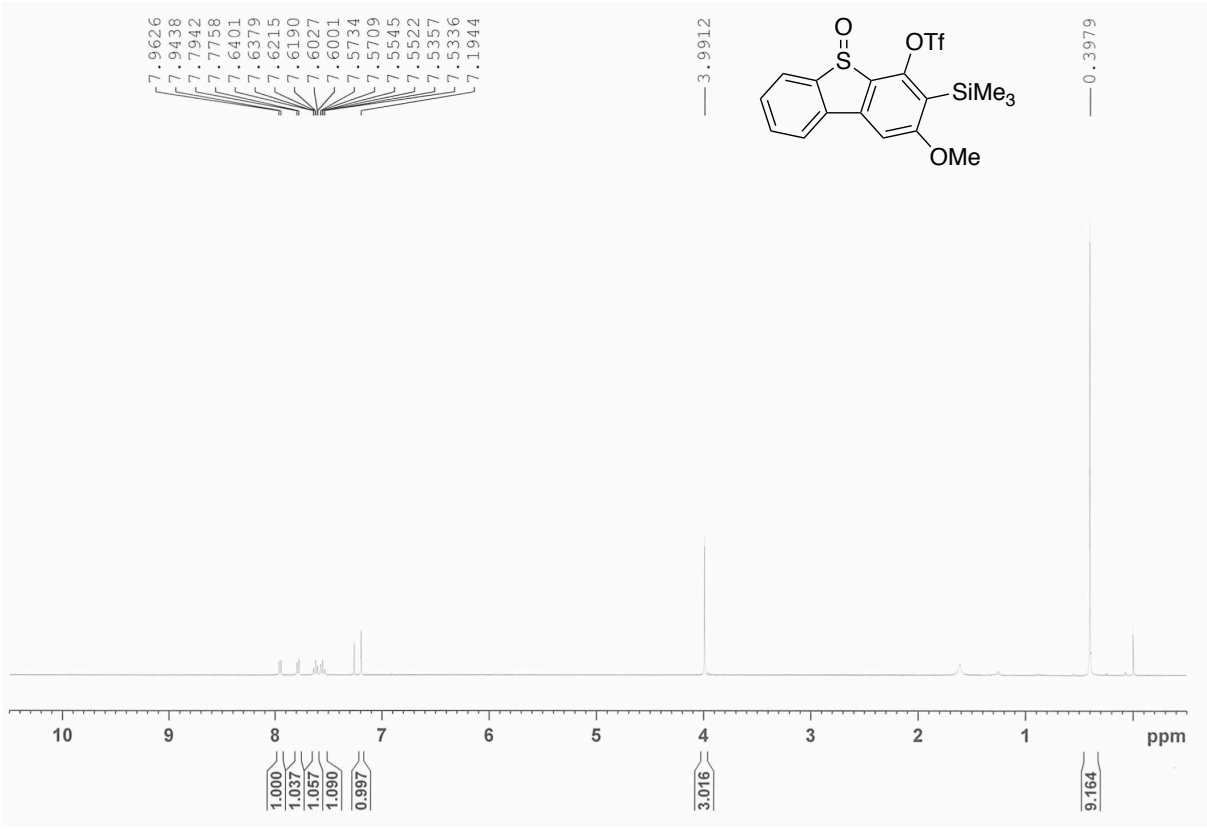


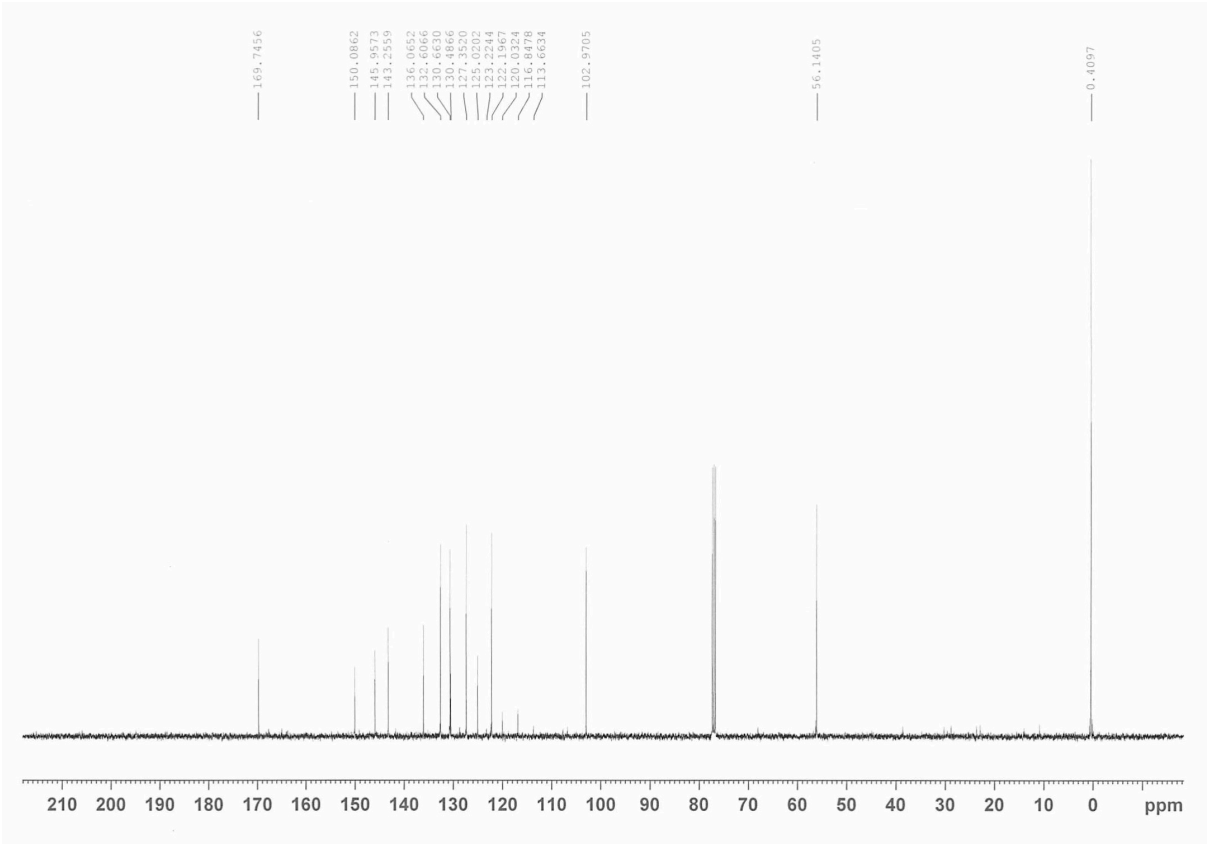
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of ehyl 7-methyldibenzo[*b*,*d*]thiophene-2-carboxylate 5-oxide (**4q**) ($CDCl_3$)



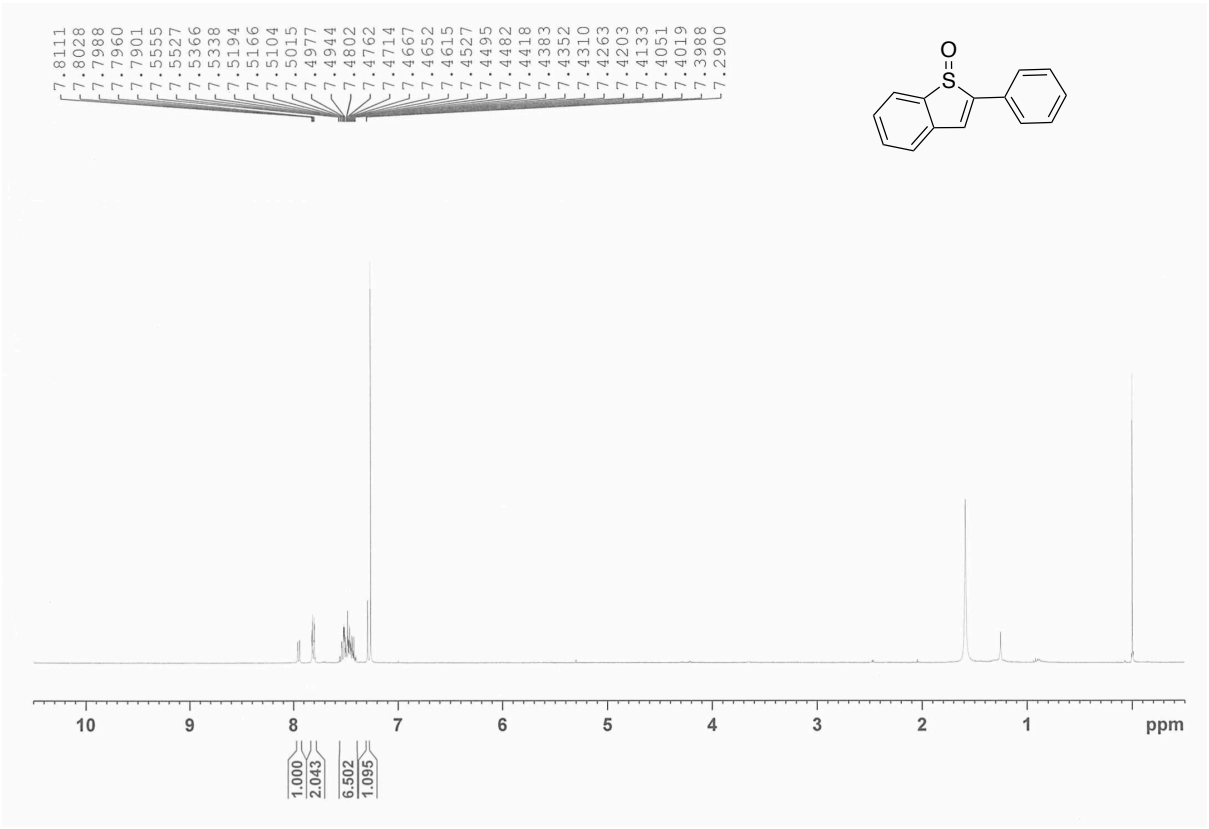


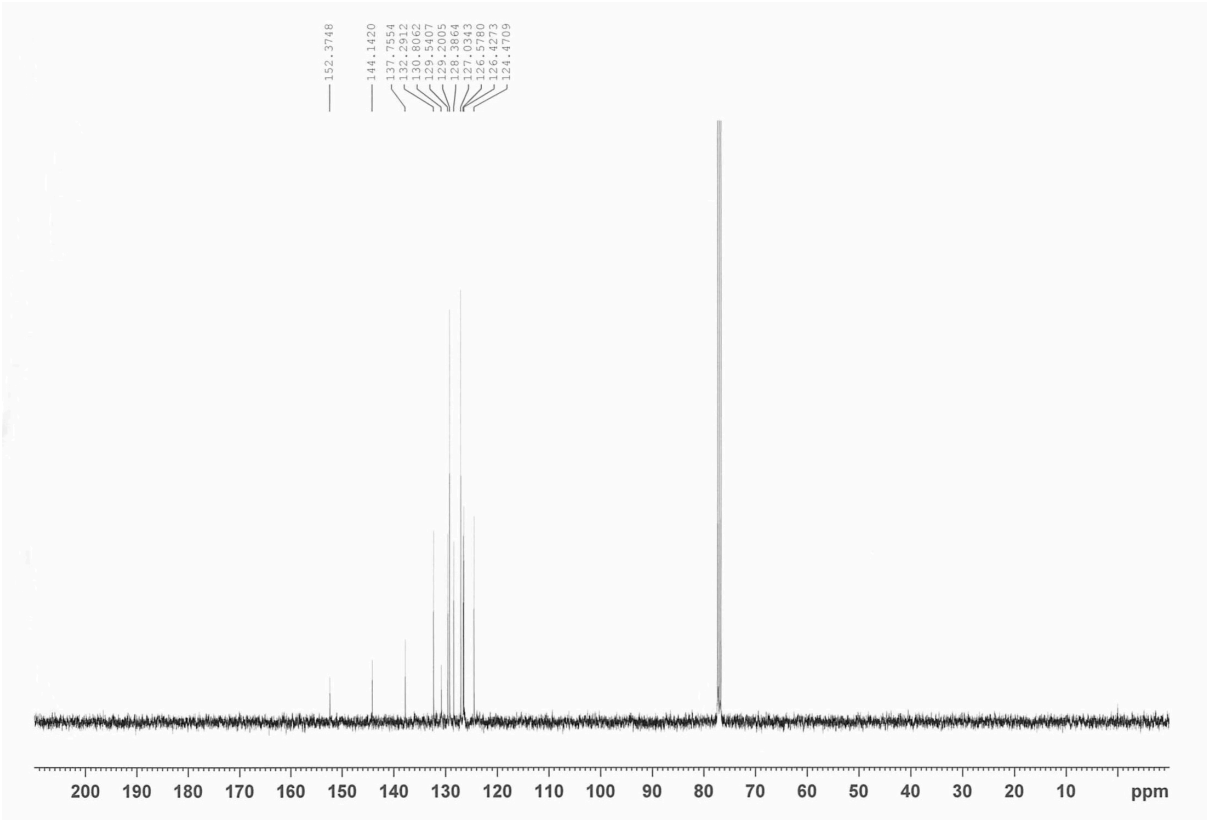
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 2-methoxy-5-oxido-3-(trimethylsilyl)dibenzo[*b*,*d*]thiophen-4-yl trifluoromethanesulfonate (**4r**) ($CDCl_3$)



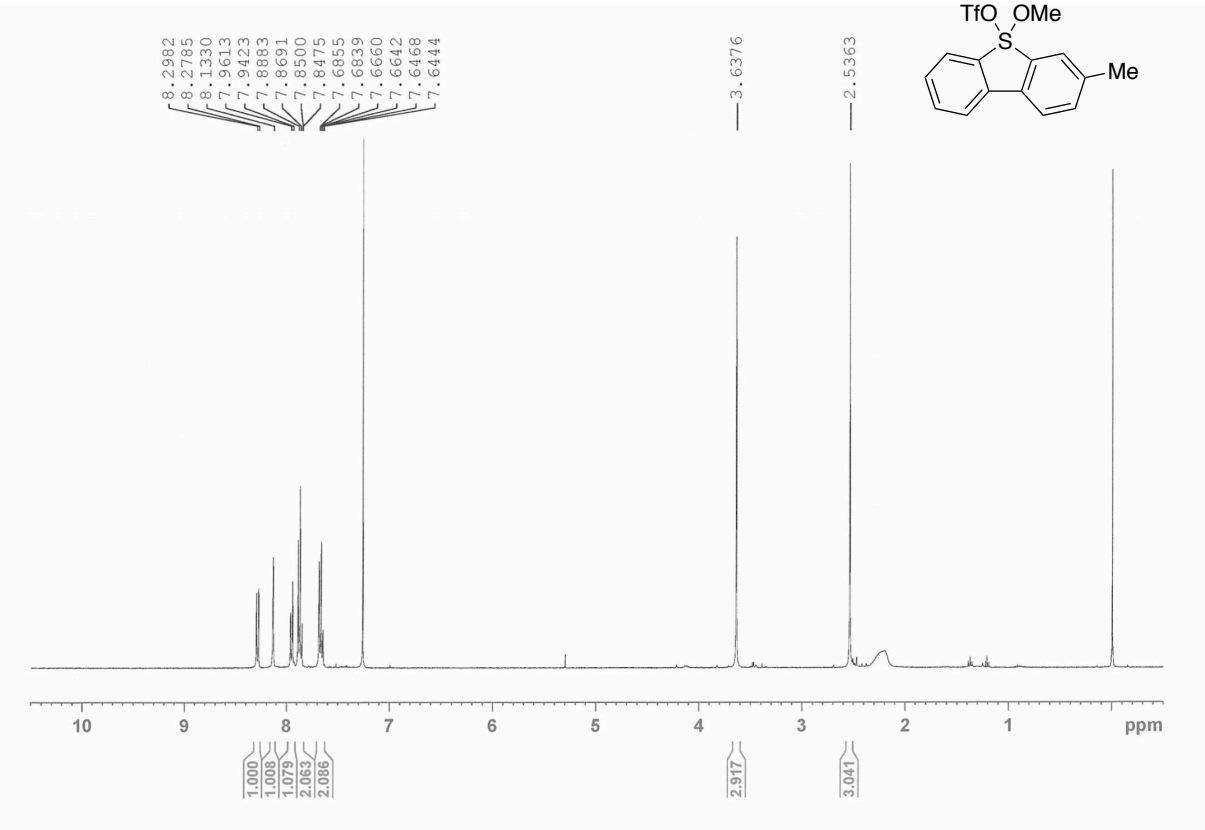


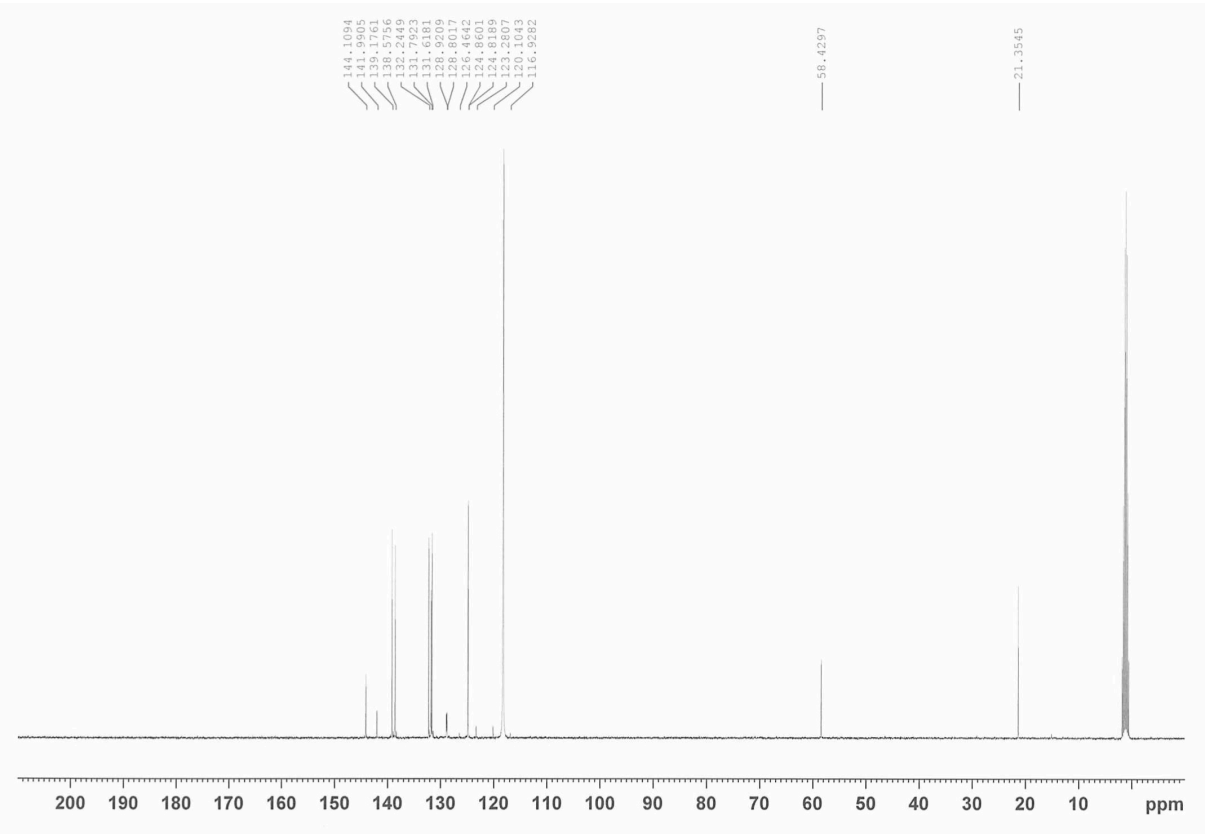
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 2-phenylbenzo[*b*]thiophene 1-oxide (**6**) ($CDCl_3$)



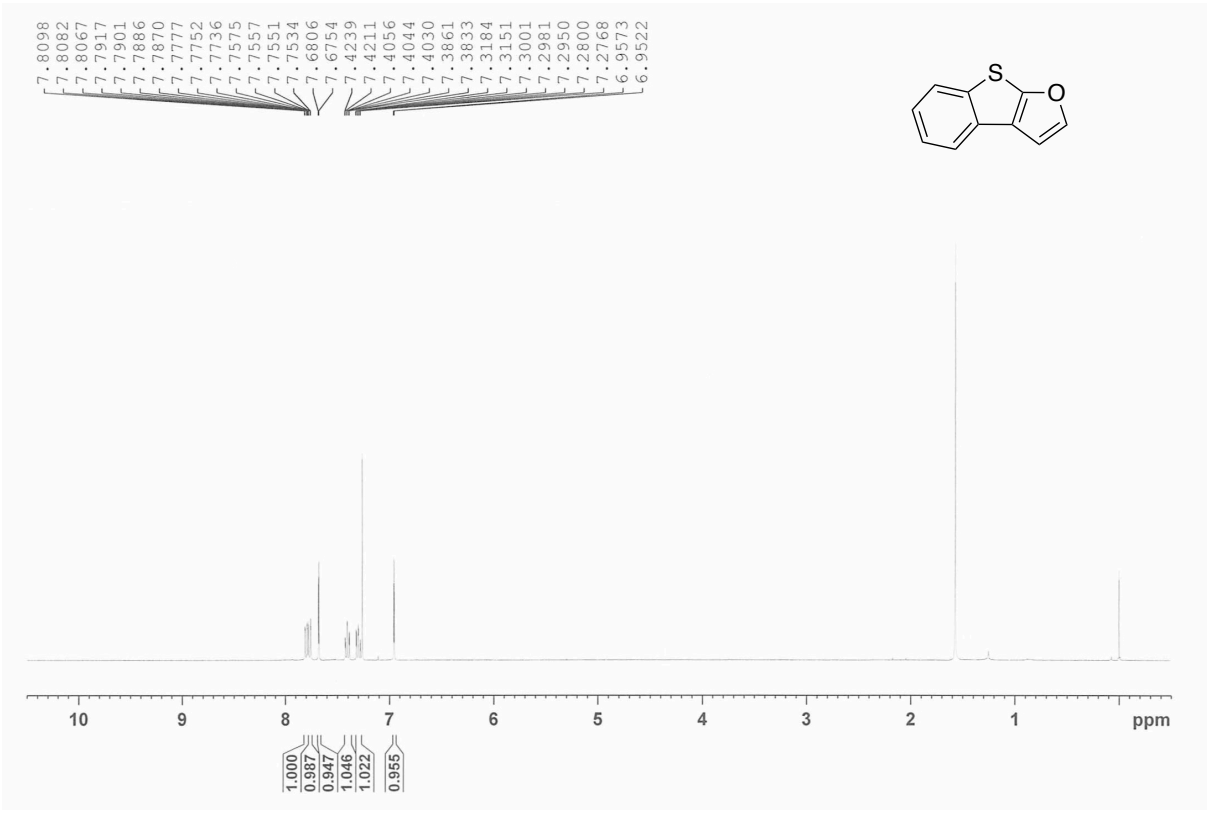


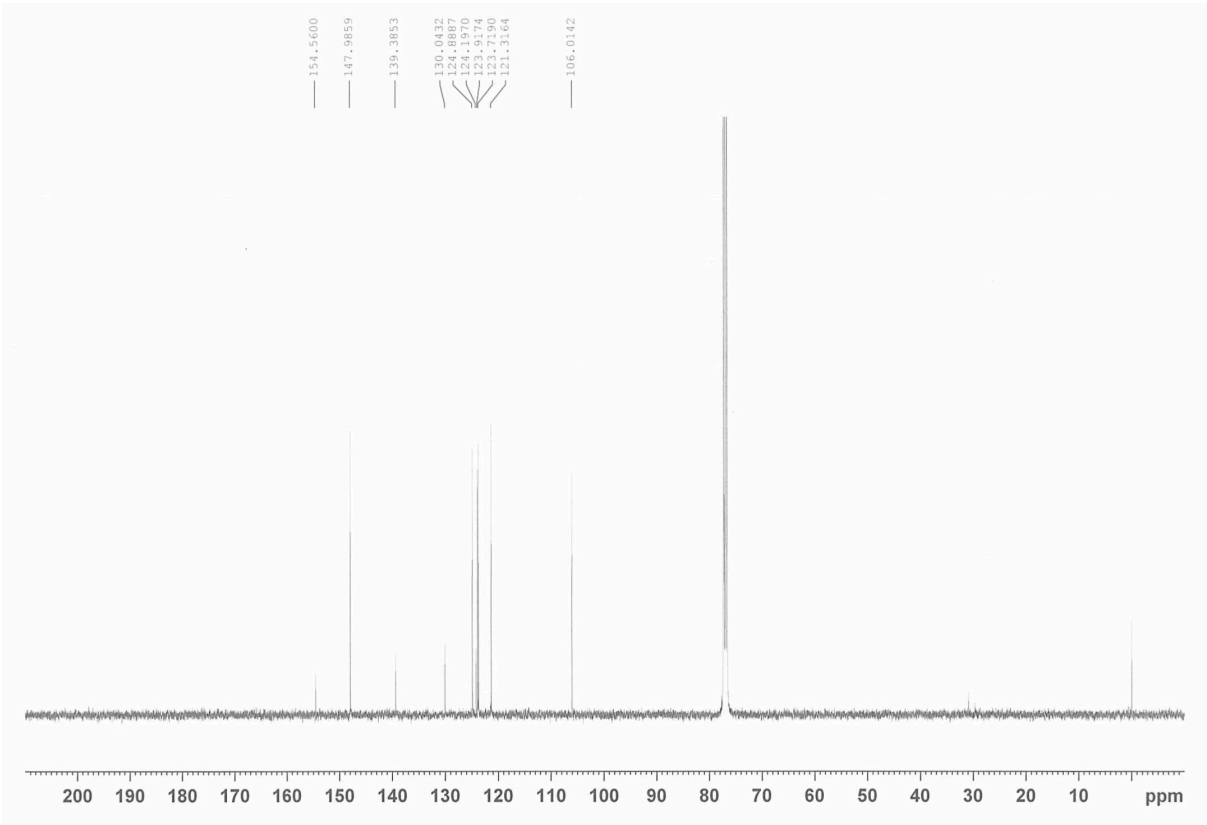
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, CD_3CN) spectra of 5-Methoxy-3-methyl-5*H*-5λ^{4}-dibenzo[*b*,*d*]thiophen-5-yl trifluoromethanesulfonate (**7**)



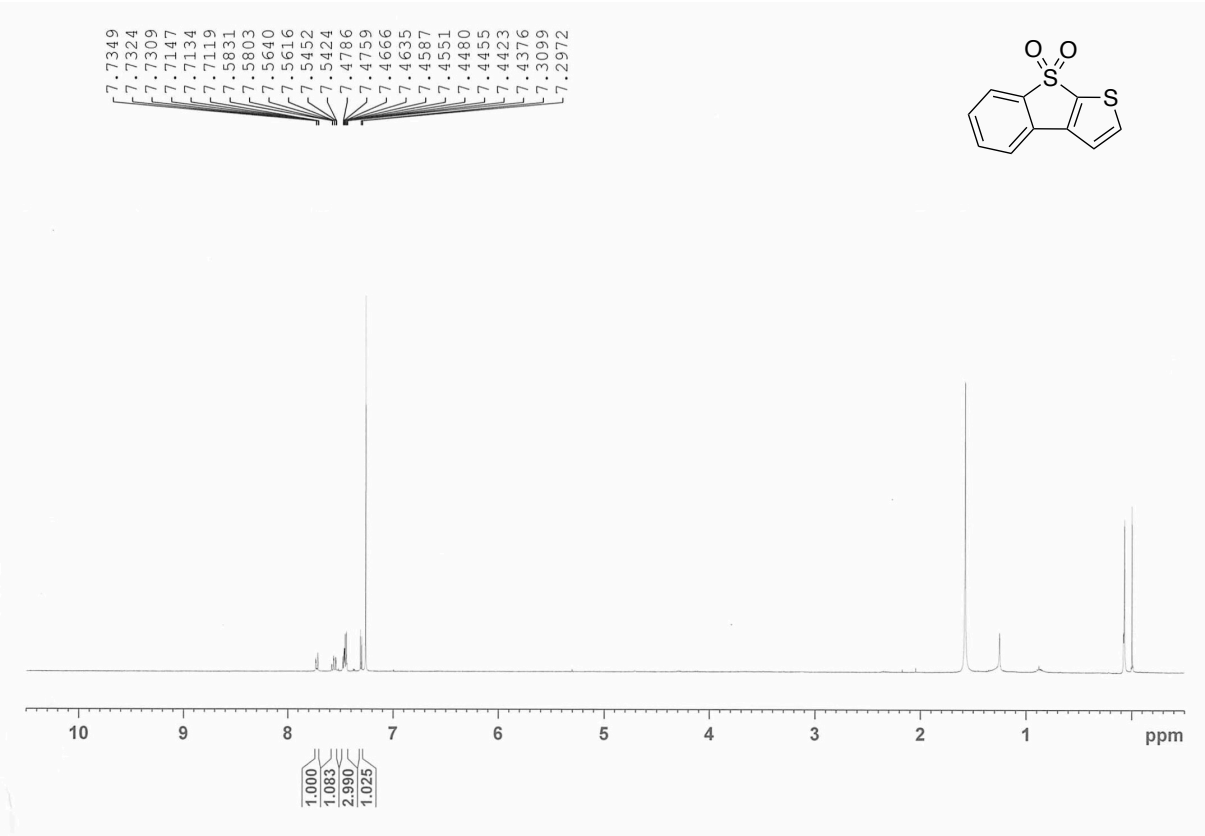


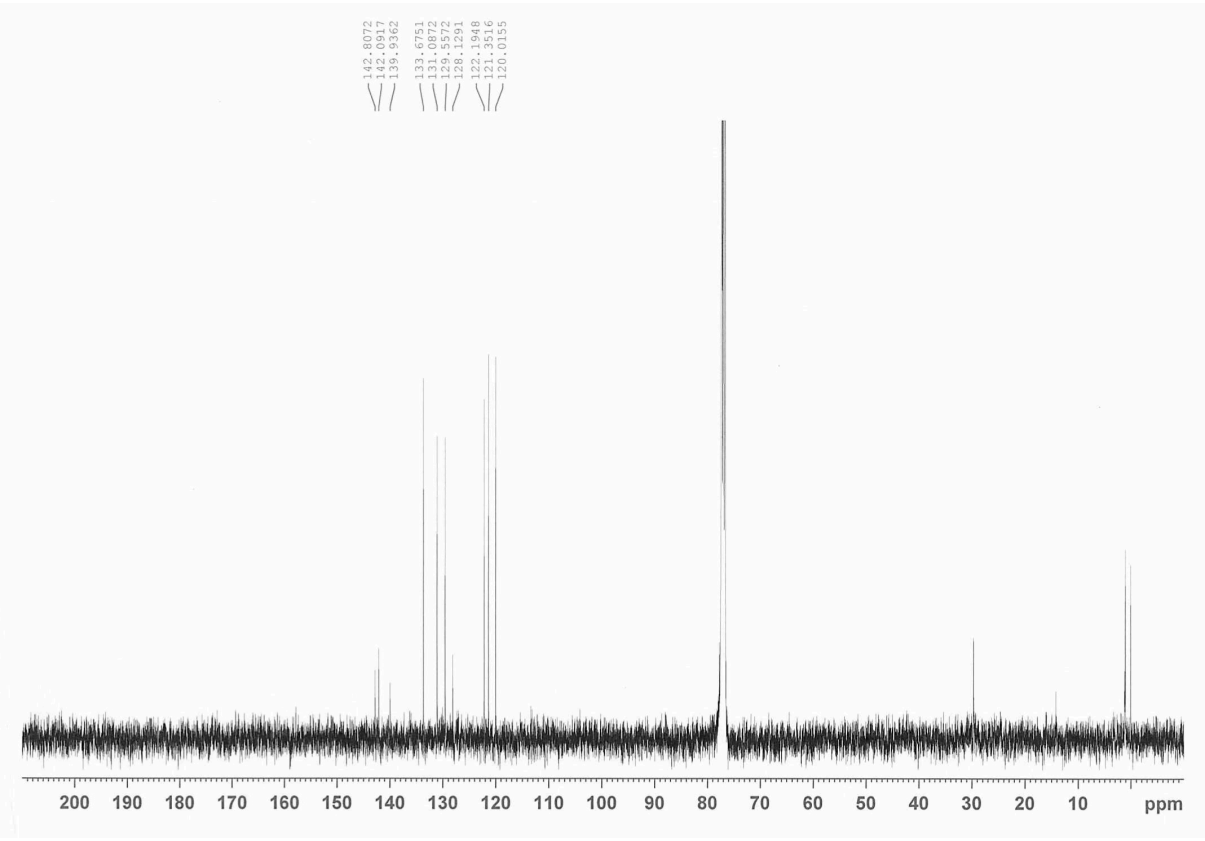
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of benzo[4,5]thieno[2,3-*b*]furan (**9c**) ($CDCl_3$)



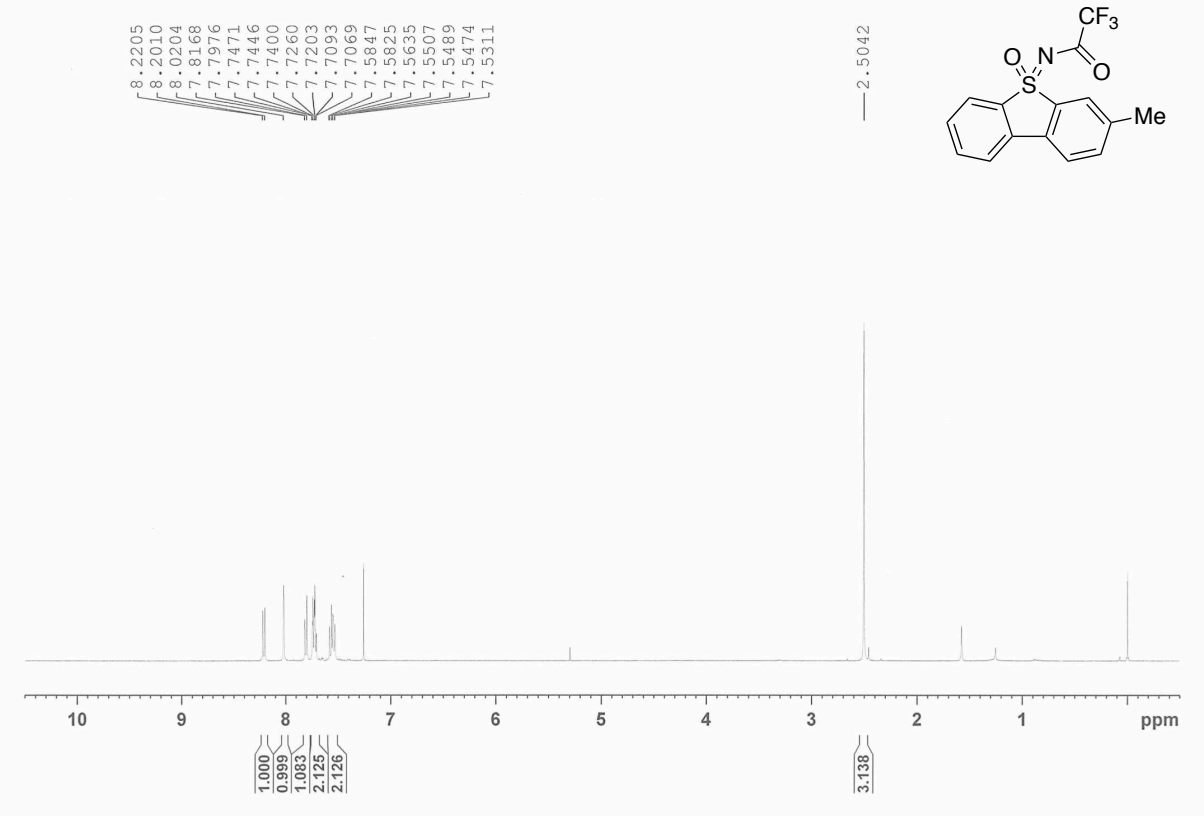


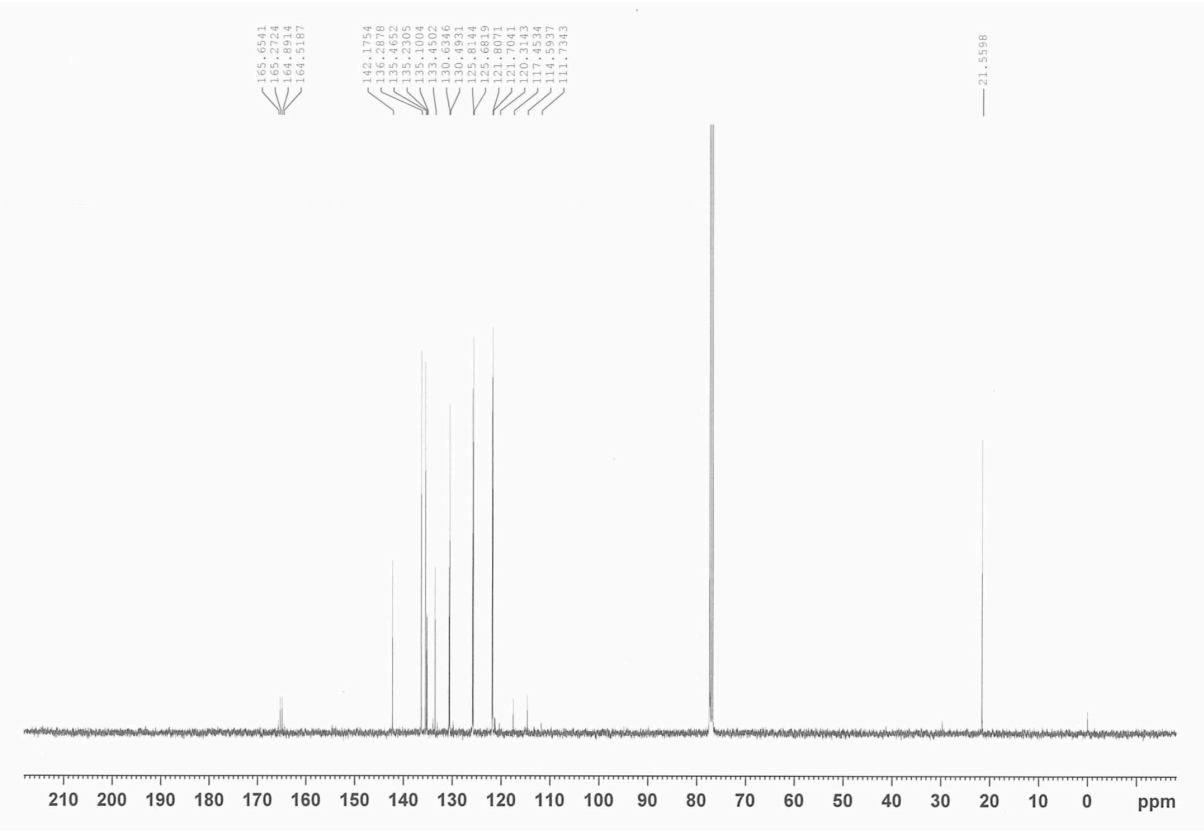
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of benzo[*b*]thieno[2,3-*d*]thiophene 4,4-dioxide (**10b**) ($CDCl_3$)



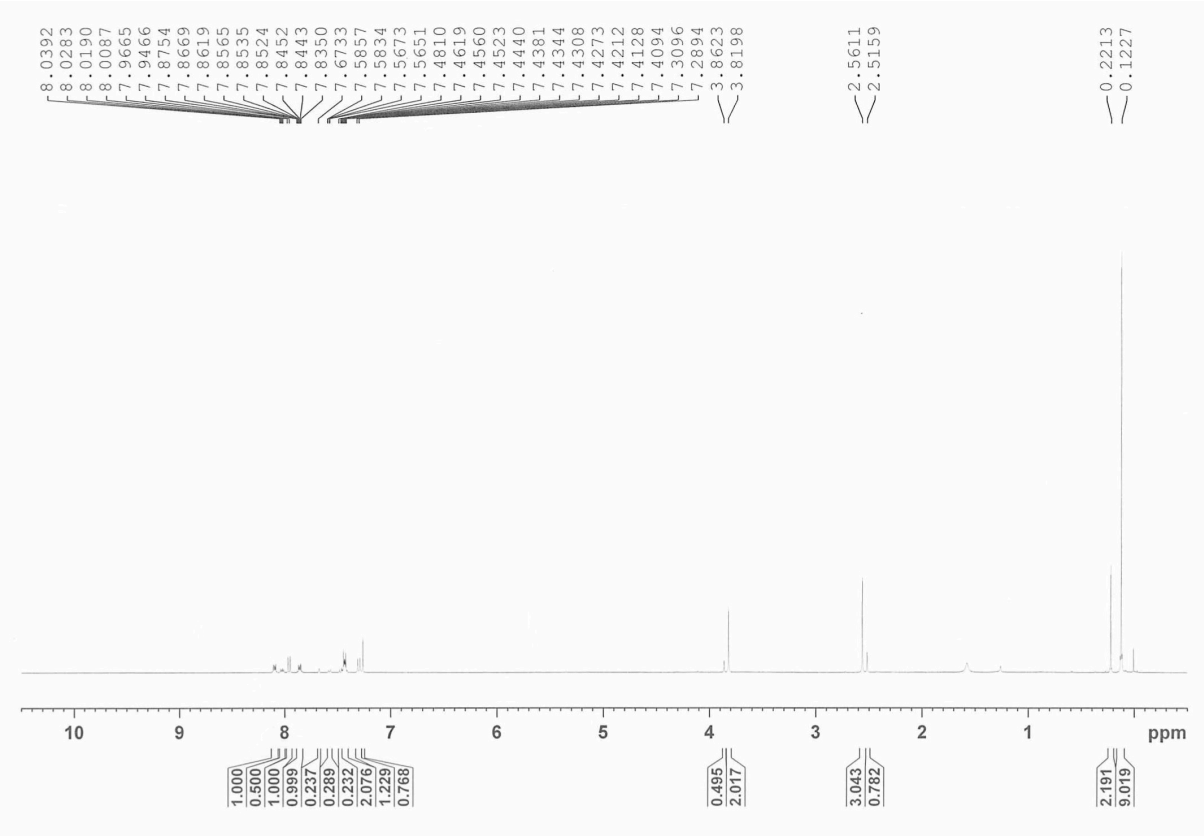


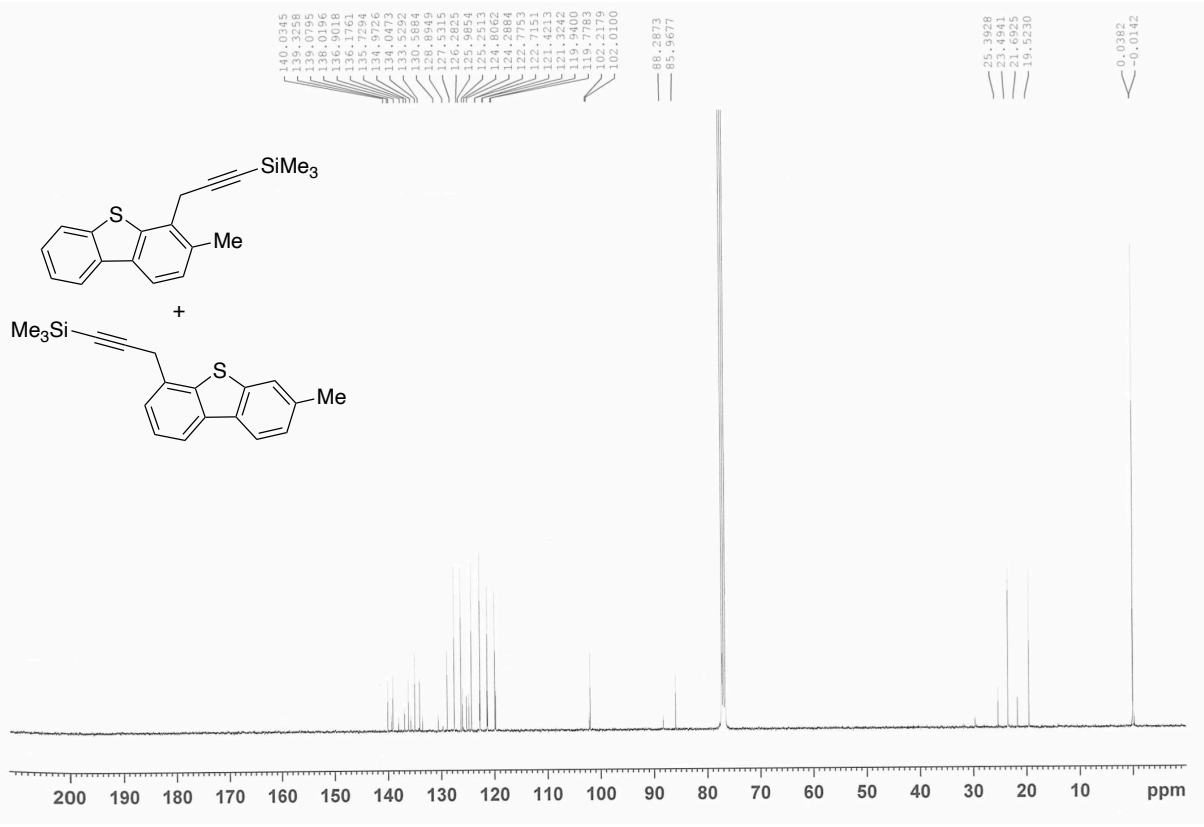
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 2,2,2-trifluoro-*N*-(3-methyl-5-oxido-5λ^{4}-dibenzo[*b*,*d*]thiophen-5-ylidene)acetamide (**11**) ($CDCl_3$)



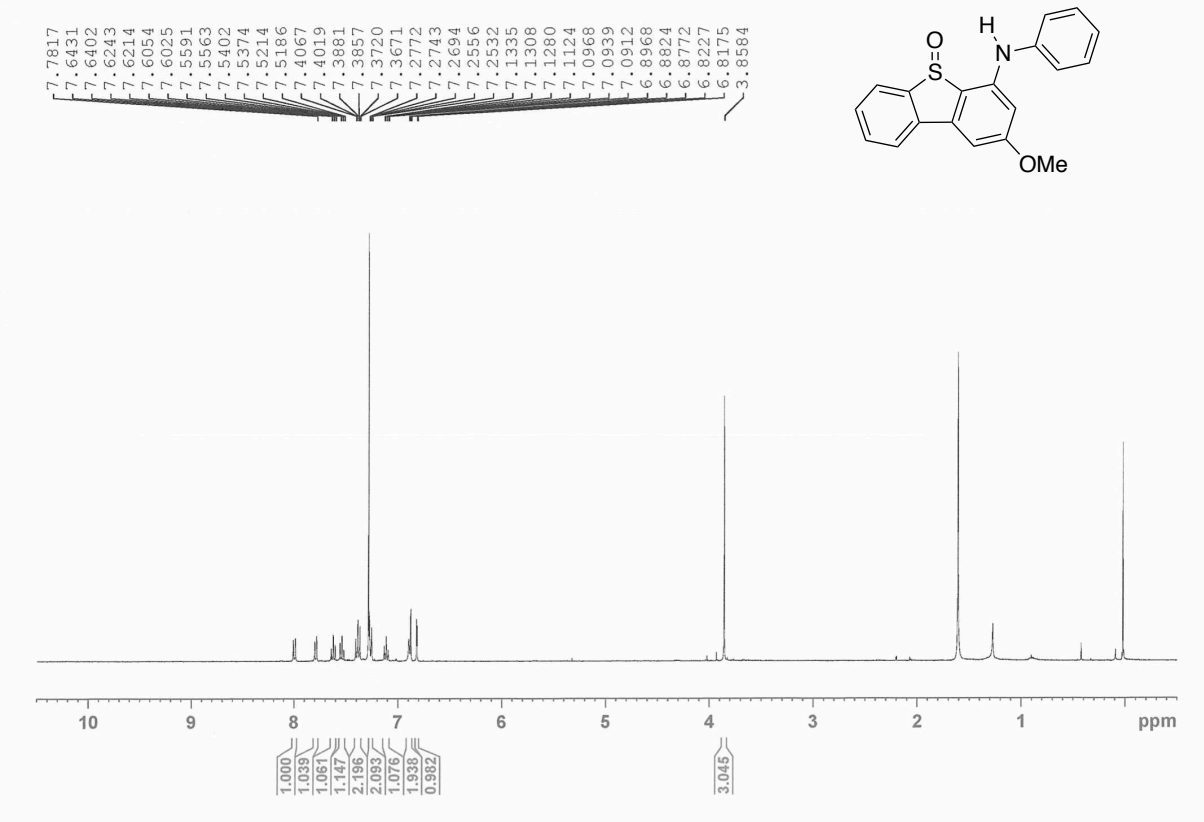


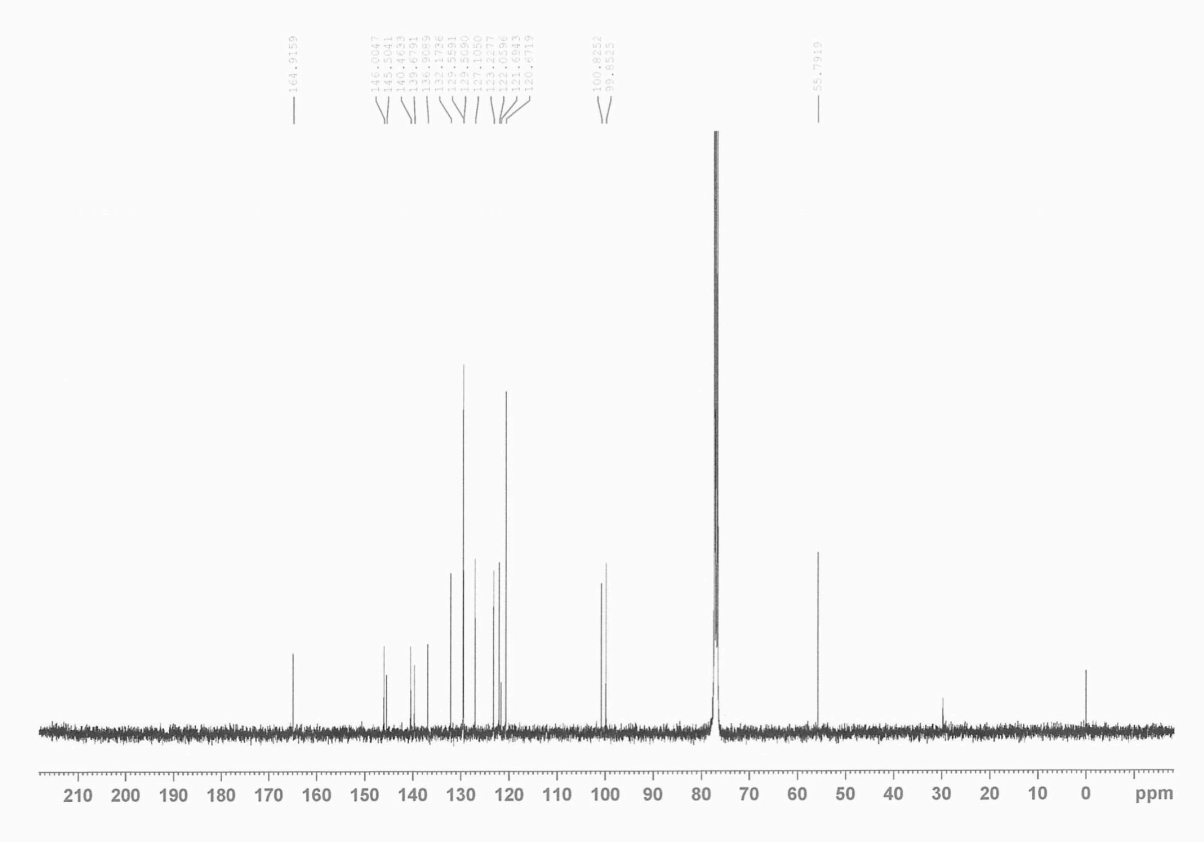
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of trimethyl(3-(3-methyldibenzo[*b*,*d*]thiophen-4-yl)prop-1-yn-1-yl)silane (**13**) and trimethyl(3-(7-methyldibenzo[*b*,*d*]thiophen-4-yl)prop-1-yn-1-yl)silane (**13'**) ($CDCl_3$)

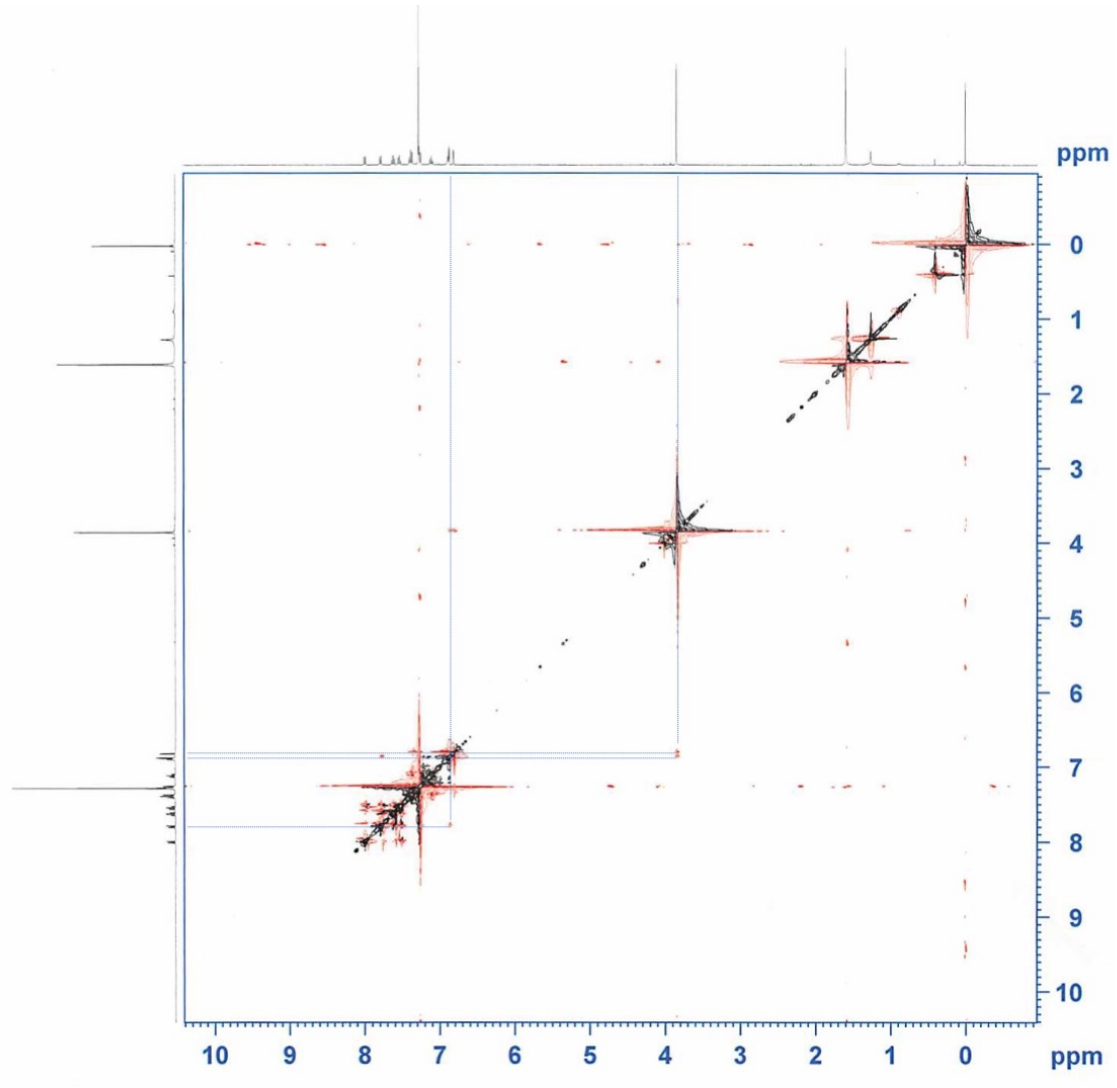




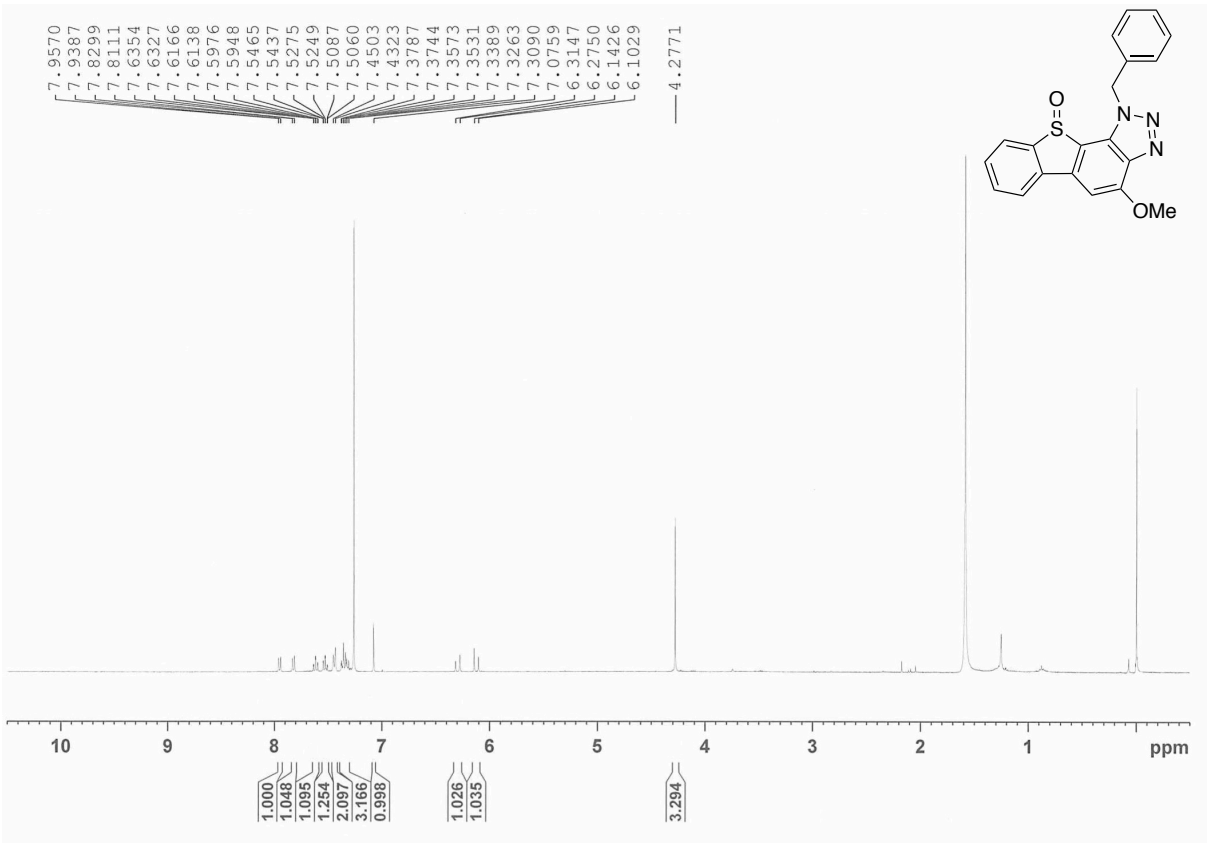
^{1}H NMR (400 MHz), ^{13}C NMR (101 MHz), and NOESY spectra of 2-methoxy-4-(phenylamino)dibenzo[*b*,*d*]thiophene 5-oxide (**14**) ($CDCl_3$)

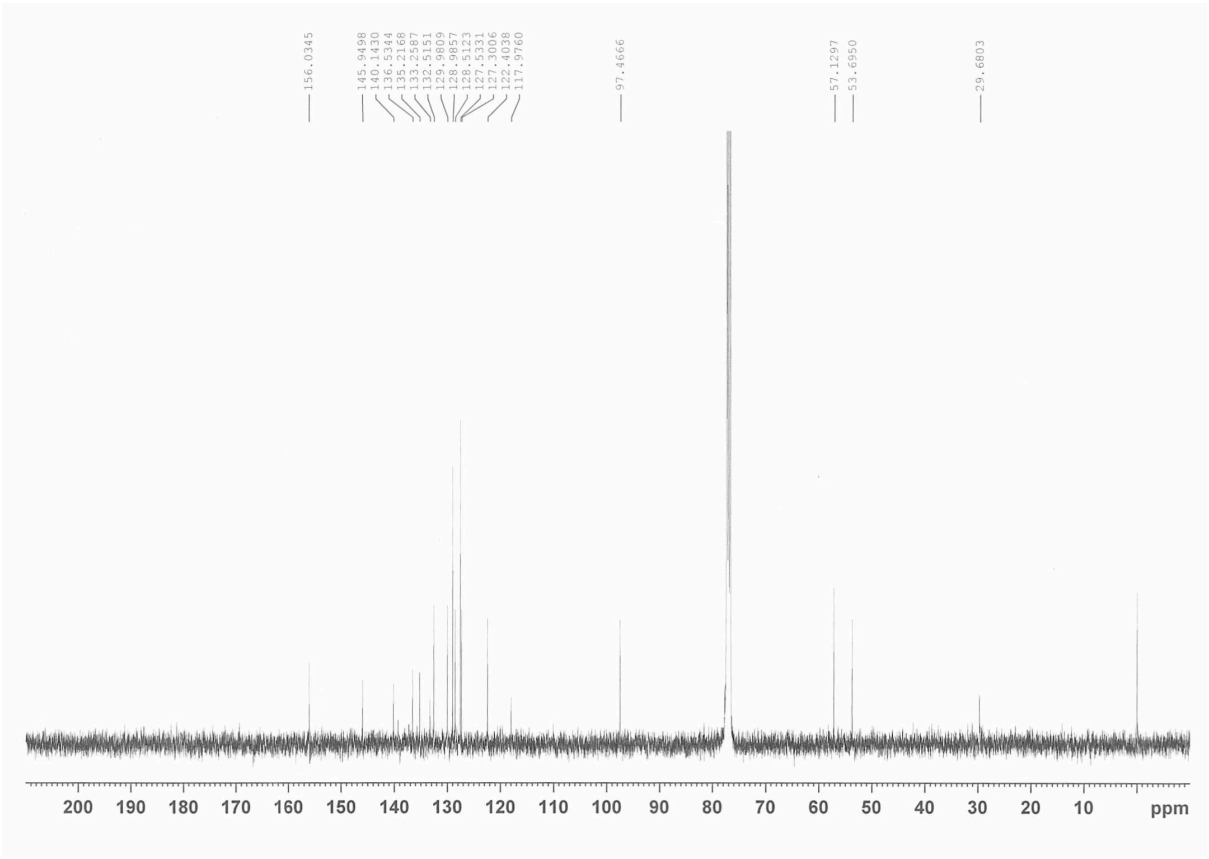


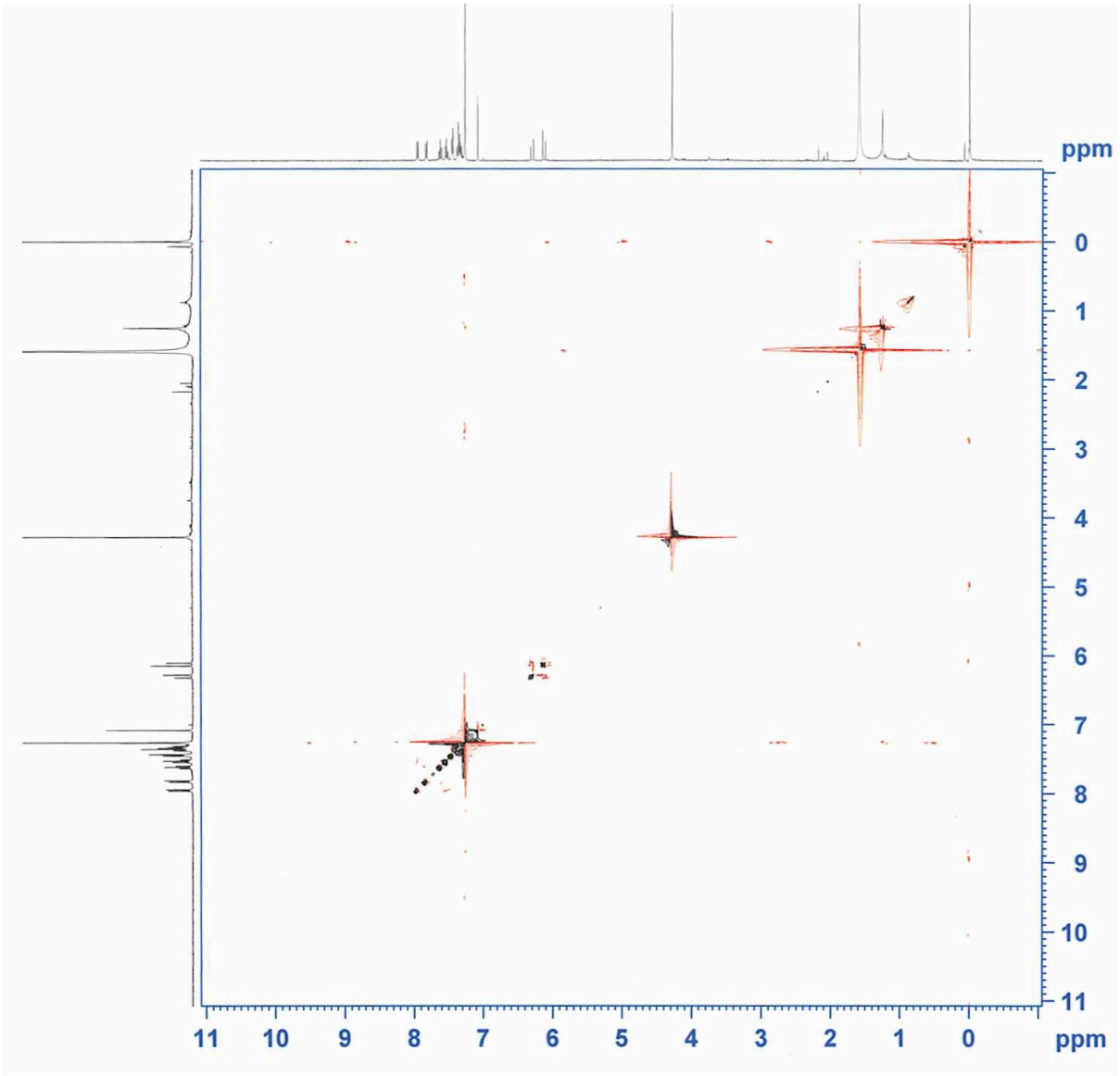



ppm
0
1
2
3
4
5
6
7
8
9
10
10
9
8
7
6
5
4
3
2
1
0
ppm

^{1}H NMR (400 MHz), ^{13}C NMR (101 MHz), and NOESY spectra of 1-benzyl-4-methoxy-1*H*-benzo[4',5']thieno[2',3':3,4]benzo[1,2-*d*][1,2,3]triazole 10-oxide (**15**) ($CDCl_3$)






ppm
0
1
2
3
4
5
6
7
8
9
10
11
11 10 9 8 7 6 5 4 3 2 1 0
ppm