Supporting Information

Thiosulfonate synthesis via halothiolation of aryne intermediates followed by oxidative *S*-sulfonylation

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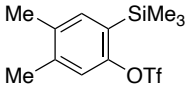
General Information

All reactions were performed with dry glassware under an 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. $CDCl_3$ or acetone-d_6 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 $CDCl_3$; δ 2.04 for ^{1}H NMR in acetone-d_6, δ 29.8 for ^{13}C NMR in acetone-d_6, or α,α,α-trifluorotoluene (δ –63.0 ppm for ^{19}F NMR in $CDCl_3$) as an internal reference with coupling constants (*J*) in hertz (Hz). The abbreviations s, d, t, q, m, and br signify singlet, doublet, triplet, quartet, multiplet, and broad, respectively. IR spectra were measured on a Shimadzu IRSpirit spectrometer with the absorption band given in cm^{-1}. High-resolution mass spectra (HRMS) were measured on a JEOL JMS-T100CS "AccuTOF CS" mass spectrometer under positive electrospray ionization (ESI^+) conditions or negative 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. 4,5-dimethyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**1a**),[S1] 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**1b**),[S1] 4,5-difluoro-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**1c**),[S1] 4,5-dimethoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**1d**),[S1] 6-(trimethylsilyl)benzo[*d*][1,3]dioxol-5-yl trifluoromethanesulfonate (**1e**),[S2] 3-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**1f**),[S3] 3-((4-methoxyphenyl)thio)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**1g**),[S4] 3-morpholino-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**1h**),[S5] 5-azido-3-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate,[S6] 3-fluoro-2-iodophenyl trifluoromethanesulfonate (**19a**),[S7] 3-(benzyloxy)-2-iodophenyl trifluoromethanesulfonate (**19b**),[S8] and 4-iododibenzo[*b*,*d*]furan-3-yl trifluoromethanesulfonate (**19c**)[S9] were prepared according to the reported methods.

Structures of Aryne Precursors 1 and 19



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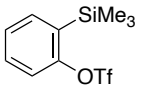

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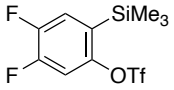

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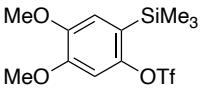

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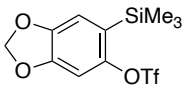

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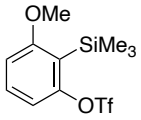

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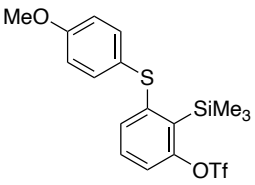

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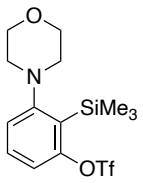

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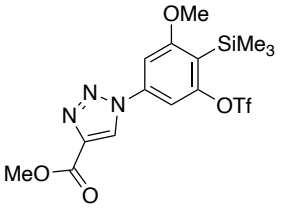

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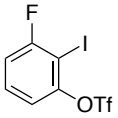
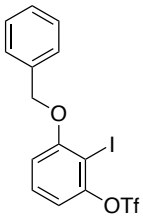


19a



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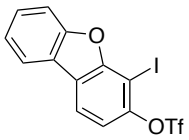
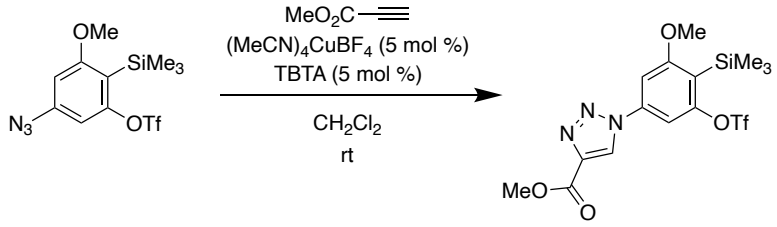


19c

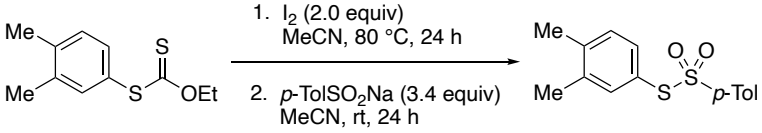
Experimental Procedures

*Synthesis of methyl 1-(3-methoxy-5-(((trifluoromethyl)sulfonyl)oxy)-4-(trimethylsilyl)phenyl)-1H-1,2,3-triazole-4-carboxylate (**1j**)*



To a solution of 5-azido-3-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (670 mg, 1.82 mmol) and methyl propiolate (302 mg, 3.60 mmol, 2.0 equiv) in CH_2Cl_2 (19.0 mL) were added $(MeCN)_4CuBF_4$ (28.2 mg, 89.6 μmol, 5 mol %) and tris((1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl)amine (TBTA) (47.4 mg, 89.3 μmol, 5 mol %) at room temperature. After stirring for 12 h at the same temperature, to the mixture was added water (20 mL). The mixture was extracted with CH_2Cl_2 (20 mL × 3). The combined organic extract was washed with brine (10 mL) and dried with Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica-gel 50 g, *n*-hexane/EtOAc = 5/1) to give methyl 1-(3-methoxy-5-(((trifluoromethyl)sulfonyl)oxy)-4-(trimethylsilyl)phenyl)-1*H*-1,2,3-triazole-4-carboxylate (**1j**) (806 mg, 1.78 mmol, 98%) as a colorless solid.

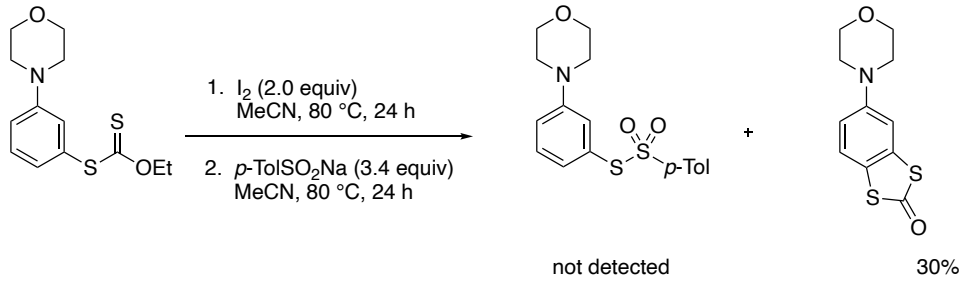
A typical procedure for thiosulfonate synthesis from aryl xanthates



In a 5 mL screw-top V-vial® with a solid-top cap (Sigma–Aldrich, Cat. No. Z115118), to a mixture of *S*-(3,4-dimethylphenyl) *O*-ethyl carbonodithioate (**2a**) (11.3 mg, 50.0 μmol, 1.00 equiv) and CH_3CN (0.50 mL) was added I_2 (25.4 mg, 0.100 mmol, 2.00 equiv) at room temperature. The mixture was stirred at 80 °C for 24 h. After the resulting mixture was cooled to room temperature, to the mixture was added sodium *p*-toluenesulfinate (30.3 mg, 0.170 mmol, 3.40 equiv) at the same temperature. After stirring for 24 h at the same temperature, to the mixture were added an aqueous saturated $Na_2S_2O_3$ (2 mL + 10 mL) and EtOAc (10 mL). The mixture was extracted with EtOAc (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/EtOAc = 4/1) to give *S*-(3,4-dimethylphenyl) 4-methylbenzenesulfonothioate (**3a**) (12.7 mg, 43.5 μmol, 87%) as a colorless solid.

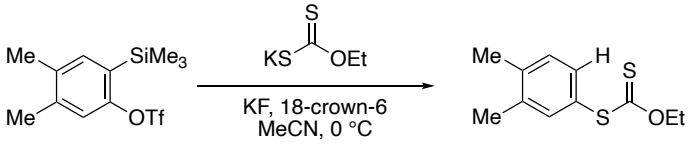
According to the procedure for preparing *S*-(3,4-dimethylphenyl) 4-methylbenzenesulfonothioate, *S*-(3,4-difluorophenyl) 4-methylbenzenesulfonothioate (**3c**) (7.7 mg, 51%), *S*-(3,4-dimethoxyphenyl) 4-methylbenzenesulfonothioate (**3d**) (12.7 mg, 80%), *S*-(3-((4-methoxyphenyl)thio)phenyl) 4-methylbenzenesulfonothioate (**3g**) (12.1 mg, 60%), methyl 1-(3-methoxy-5-(tosylthio)phenyl)-1*H*-1,2,3-triazole-4-carboxylate (**3j**) (4.7 mg, 52%), *S*-(2-bromo-4,5-dimethylphenyl) 4-methylbenzenesulfonothioate (**5a**) (14.8 mg, 80%), *S*-(2-bromo-4,5-difluorophenyl) 4-methylbenzenesulfonothioate (**5c**) (10.9 mg, 57%), *S*-(2-bromo-3-methoxyphenyl) 4-methylbenzenesulfonothioate (**5f**) (15.4 mg, 84%), *S*-(2-chloro-4,5-dimethylphenyl) 4-methylbenzenesulfonothioate (**9a**) (12.3 mg, 74%), *S*-(2-iodo-4,5-dimethylphenyl) 4-methylbenzenesulfonothioate (**10a**) (7.9 mg, 76%), *S*-(2-iodophenyl) 4-methylbenzenesulfonothioate (**10b**) (19.5 mg, 98%), *S*-(2-iodo-4,5-dimethoxyphenyl) 4-methylbenzenesulfonothioate (**10d**) (18.5 mg, 75%), *S*-(6-iodobenzo[d][1,3]dioxol-5-yl) 4-methylbenzenesulfonothioate (**10e**) (20.4 mg, 71%), *S*-(2-iodo-3-methoxyphenyl) 4-methylbenzenesulfonothioate (**10f**) (10.7 mg, 51%), and *S*-(2-iodo-3-((4-methoxyphenyl)thio)phenyl) 4-methylbenzenesulfonothioate (**10g**) (13.8 mg, 67%) were prepared from the corresponding aryl xanthates.

*Synthesis of 5-morpholinobenzo[d][1,3]dithiol-2-one (**4**)*



In a 5 mL screw-top V-vial® with a solid-top cap (Sigma–Aldrich, Cat. No. Z115118), to a mixture of *O*-ethyl *S*-(3-morpholinophenyl) carbonodithioate (**2h**) (44.5 mg, 0.157 mmol, 1.00 equiv) and CH_3CN (1.50 mL) was added I_2 (159.9 mg, 0.630 mmol, 4.01 equiv) at room temperature. The mixture was stirred at 80 °C for 24 h. After the resulting mixture was cooled to room temperature, to the mixture was added sodium *p*-toluenesulfinate (30.3 mg, 0.170 mmol, 3.40 equiv) at room temperature. After stirring at 80 °C for 24 h, to the mixture was added an aqueous saturated $Na_2S_2O_3$ (2 mL + 10 mL) and EtOAc (10 mL) at room temperature. The mixture was extracted with EtOAc (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/EtOAc = 4/1) to give 5-morpholinobenzo[*d*][1,3]dithiol-2-one (**4**) (11.9 mg, 47.0 μmol, 30%) as a colorless solid.

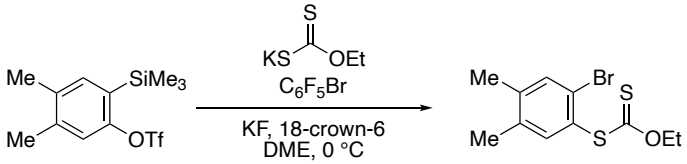
A typical procedure for the hydrothiolation of arynes from potassium xanthate



In a 5 mL screw-top V-vial® with a solid-top cap (Sigma–Aldrich, Cat. No. Z115118), to a mixture of 4,5-dimethyl-2-trimethylsilylphenyl triflate (**1a**) (48.8 mg, 0.150 mmol, 1.50 equiv) and potassium *O*-ethyl dithiocarbonate (16.0 mg, 99.8 μmol) dissolved in CH_3CN (1.30 mL) were added 18-crown-6-ether (105 mg, 0.400 mmol, 4.01 equiv) and potassium fluoride (17.4 mg, 0.300 mmol, 3.01 equiv) at 0 ºC. After stirring for 24 h at the same temperature, the mixture was warmed to room temperature. To the mixture were added water (2 mL + 10 mL) and EtOAc (10 mL). The mixture was extracted with EtOAc (10 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/EtOAc = 4/1) to give *S*-(3,4-dimethylphenyl) *O*-ethyl carbonodithioate (**2a**) (18.7 mg, 82.8 μmol, 83%) as a yellow oil.

Similarly, *S*-aryl *O*-ethyl carbonodithioates **2b**–**j** were prepared from the corresponding *o*-silylaryl triflates.

A typical procedure for the bromothiolation of arynes from potassium xanthate and bromopentafluorobenzene

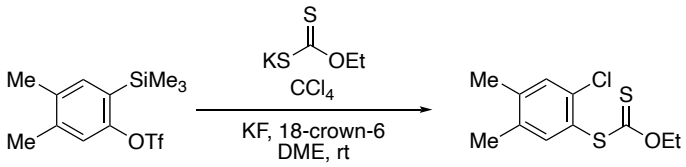


In a 5 mL screw-top V-vial® with a solid-top cap (Sigma–Aldrich, Cat. No. Z115118), to a mixture of 4,5-dimethyl-2-trimethylsilylphenyl triflate (**1a**) (48.8 mg, 0.150 mmol, 1.50 equiv) and potassium *O*-ethyl dithiocarbonate (16.0 mg, 99.8 μmol) dissolved in 1,2-dimethoxyethane (1.30 mL) were added bromopentafluorobenzene (63.3 μL, 0.500 mmol, 5.01 equiv), 18-crown-6-ether (105 mg, 0.400 mmol, 4.01

equiv), and potassium fluoride (17.4 mg, 0.300 mmol, 3.01 equiv) at 0 °C. After stirring for 24 h at the same temperature, the mixture was warmed to room temperature. To the mixture were added water (2 mL + 10 mL) and EtOAc (10 mL). The mixture was extracted with EtOAc (10 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/EtOAc = 4/1) to give *S*-(2-bromo-4,5-dimethylphenyl) *O*-ethyl carbonodithioate (**6a**) (20.9 mg, 68.6 μmol, 69%) as a yellow solid.

Similarly, *S*-aryl *O*-ethyl carbonodithioates **6b**, **6c**, and **6f** were prepared from the corresponding *o*-silylaryl triflates.

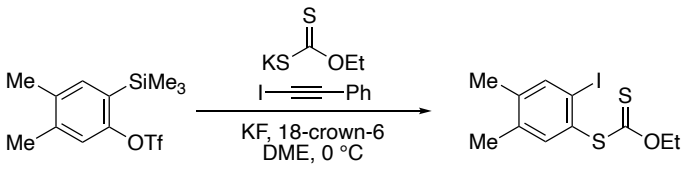
A typical procedure for the chlorothiolation of arynes from potassium xanthate and tetrachloromethane



In a 5 mL screw-top V-vial® with a solid-top cap (Sigma–Aldrich, Cat. No. Z115118), to a mixture of 4,5-dimethyl-2-trimethylsilylphenyl triflate (**1a**) (49.0 mg, 150 μmol, 1.50 equiv) and potassium *O*-ethyl dithiocarbonate (16.0 mg, 99.8 μmol) dissolved in 1,2-dimethoxyethane (1.30 mL) were added tetrachloromethane (48.4 μL, 0.500 mmol, 5.01 equiv), 18-crown-6-ether (105 mg, 0.400 mmol, 4.01 equiv), and potassium fluoride (17.4 mg, 0.300 mmol, 3.01 equiv) at room temperature. After stirring for 24 h at the same temperature, to the mixture were added water (2 mL + 10 mL) and EtOAc (10 mL). The mixture was extracted with EtOAc (10 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/EtOAc = 4/1) to give *S*-(2-chloro-4,5-dimethylphenyl) *O*-ethyl carbonodithioate (**7a**) (22.7 mg, 87.2 μmol, 87%) as a colorless solid.

Similarly, *S*-aryl *O*-ethyl carbonodithioate **7b** was prepared from the corresponding *o*-silylaryl triflate.

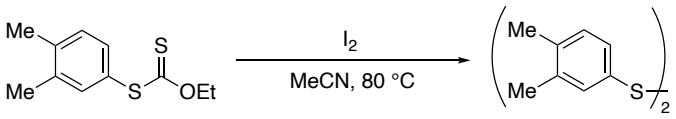
A typical procedure for the iodination of arynes from potassium xanthate and (iodoethynyl)benzene



In a 5 mL screw-top V-vial® with a solid-top cap (Sigma–Aldrich, Cat. No. Z115118), to a mixture of 4,5-dimethyl-2-trimethylsilylphenyl triflate (**1a**) (49.0 mg, 150 μmol, 1.50 equiv) and potassium *O*-ethyl dithiocarbonate (16.0 mg, 99.8 μmol) dissolved in 1,2-dimethoxyethane (1.30 mL) were added (iodoethynyl)benzene (63.3 μL, 0.500 mmol, 5.01 equiv), 18-crown-6-ether (105 mg, 0.400 mmol, 4.01 equiv), and potassium fluoride (17.4 mg, 0.300 mmol, 3.01 equiv) at 0 °C. After stirring for 24 h at the same temperature, the mixture was warmed to room temperature. To the mixture were added water (2 mL + 10 mL) and EtOAc (10 mL). The mixture was extracted with EtOAc (10 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/EtOAc = 4/1) to give *S*-(2-iodo-4,5-dimethylphenyl) *O*-ethyl carbonodithioate (**8a**) (24.6 mg, 69.9 μmol, 70%) as a yellow solid.

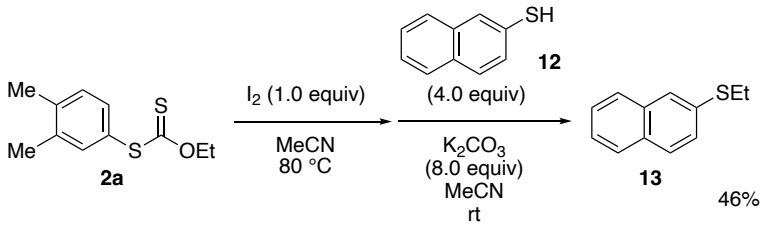
Similarly, *S*-aryl *O*-alkyl carbonodithioates **8b** and **8d**–**g** were prepared from the corresponding *o*-silylaryl triflates.

*Synthesis of bis(3,4-dimethylphenyl) disulfide (**11a**)*



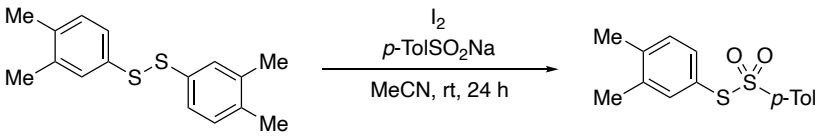
In a 5 mL screw-top V-vial® with a solid-top cap (Sigma–Aldrich, Cat. No. Z115118), to a mixture of *S*-(3,4-dimethylphenyl) *O*-ethyl carbonodithioate (**2a**) (11.3 mg, 50.0 μmol) and CH_3CN (0.50 mL) was added I_2 (25.4 mg, 0.100 mmol, 2.00 equiv) at room temperature. The mixture was stirred at 80 °C for 24 h. After the resulting mixture was cooled to room temperature, to the mixture were added an aqueous saturated $Na_2S_2O_3$ (2 mL + 10 mL) and EtOAc (10 mL). The mixture was extracted with EtOAc (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/EtOAc = 20/1) to give 1,2-bis(3,4-dimethylphenyl)disulfane (**11a**) (6.9 mg, 25 μmol, quant) as a colorless solid.

*Synthesis of ethyl(naphthalen-2-yl)sulfane (**13**)*



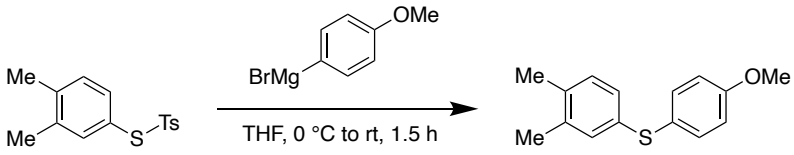
In a 5 mL screw-top V-vial® with a solid-top cap (Sigma–Aldrich, Cat. No. Z115118), to a mixture of *S*-(3,4-dimethylphenyl) *O*-ethyl carbonodithioate (**2a**) (58.9 mg, 0.182 mmol) and CH_3CN (1.80 mL) was added I_2 (46.0 mg, 0.181 mmol, 1.00 equiv) at room temperature. The mixture was stirred at 80 °C for 24 h. After the resulting mixture was cooled to room temperature, to the mixture was added a solution of naphthalene-2-thiol (**12**) (116.8 mg, 0.730 mmol, 4.01 equiv) and potassium carbonate (201.2 mg, 1.456 mmol, 8.00 equiv) dissolved in MeOH (2.0 mL) at room temperature. After stirring for 24 h at the same temperature, to the mixture was added an aqueous saturated $Na_2S_2O_3$ (2 mL + 10 mL) and EtOAc (10 mL). The mixture was extracted with EtOAc (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/CH_2Cl_2 = 4/1) to give ethyl(naphthalen-2-yl)sulfane (**13**) (15.8 mg, 83.9 μmol, 46%) as a colorless oil.

*Synthesis of S-(3,4-dimethylphenyl) 4-methylbenzenesulfonothioate from bis(3,4-dimethylphenyl) disulfide (**3a**)*



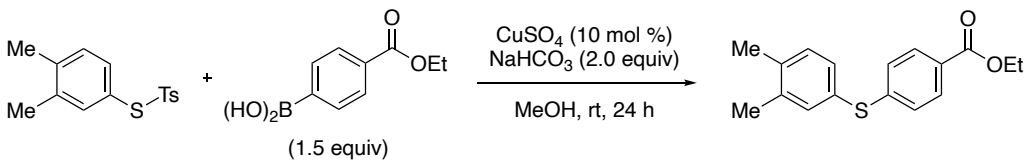
In a 5 mL screw-top V-vial® with a solid-top cap (Sigma–Aldrich, Cat. No. Z115118), to a mixture of 1,2-bis(3,4-dimethylphenyl) disulfide (**11a**) (6.9 mg, 25 μmol) and CH_3CN (0.50 mL) were added I_2 (12.7 mg, 50.0 μmol, 2.00 equiv) and sodium *p*-toluenesulfinate (30.3 mg, 0.170 mmol, 6.80 equiv) at room temperature. The mixture was stirred at 80 °C for 24 h. After the resulting mixture was cooled to room temperature, to the mixture were added an aqueous saturated $Na_2S_2O_3$ (2 mL + 10 mL) and EtOAc (10 mL). The mixture was extracted with EtOAc (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/EtOAc = 4/1) to give *S*-(3,4-dimethylphenyl) 4-methylbenzenesulfonothioate (**3a**) (12.1 mg, 41.4 μmol, 83%) as a colorless solid.

*Synthesis of 3,4-dimethylphenyl 4-methoxyphenyl sulfide (**15a**)*



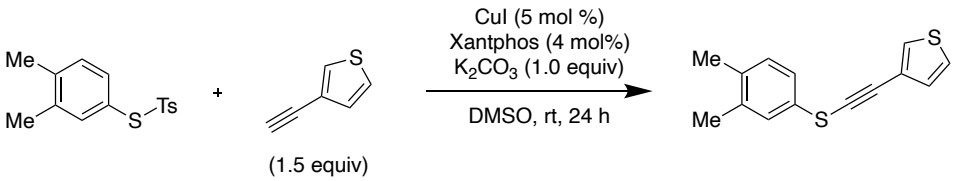
To a solution of *S*-(3,4-dimethylphenyl) 4-methylbenzenesulfonothioate (**3a**) (10.5 mg, 35.9 μmol) dissolved in THF (2.0 mL) was slowly added (4-methoxyphenyl)magnesium bromide (**14**) (2.0 M, THF solution, 35.9 μL, 72 μmol, 2.0 equiv) at 0 °C. After the addition was complete, the mixture was allowed to warm to room temperature and stirred for 1.5 h at the same temperature. Then, to the mixture was added an aqueous saturated ammonium chloride (5 mL). The mixture was extracted with EtOAc (5 mL × 3), and the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 4/1) to give 3,4-dimethylphenyl 4-methoxyphenyl sulfide (**15a**) (8.2 mg, 34 μmol, 94%) as a yellow solid.

*Synthesis of ethyl 4-((3,4-dimethylphenyl)thio)benzoate (**15b**)*



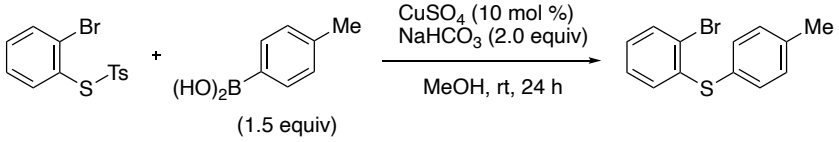
In a 5 mL screw-top V-vial® with a solid-top cap (Sigma–Aldrich, Cat. No. Z115118), to a mixture of $CuSO_4$ (0.8 mg, 5 μmol, 10 mol %) and $NaHCO_3$ (8.4 mg, 0.10 mmol, 2.0 equiv) was added a solution of (4-(ethoxycarbonyl)phenyl)boronic acid (**16a**) (10.2 mg, 75.0 μmol, 1.50 equiv) and *S*-(3,4-dimethylphenyl) 4-methylbenzenesulfonothioate (17.1 mg, 50.0 μmol) dissolved in MeOH (0.50 mL) at room temperature. After stirring for 24 h at the same temperature, to the mixture was added an aqueous saturated ammonium chloride (2 mL + 10 mL). The mixture was extracted with EtOAc (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/EtOAc = 10/1) to give ethyl 4-((3,4-dimethylphenyl)thio)benzoate (**15b**) (13.3 mg, 46.4 μmol, 93%) as a colorless oil.

*Synthesis of 3-(((3,4-dimethylphenyl)thio)ethynyl)thiophene (**15c**)*



In a 5 mL screw-top V-vial® with a solid-top cap (Sigma–Aldrich, Cat. No. Z115118), to a mixture of CuI (0.6 mg, 3 μmol, 5 mol %), Xantphos (1.5 mg, 2.6 μmol, 4.0 mol %), and K_2CO_3 (8.9 mg, 64 μmol, 1.0 equiv) was added a solution of *S*-(3,4-dimethylphenyl) 4-methylbenzenesulfonothioate (**3a**) (18.9 mg, 64.5 μmol) and 3-ethynylthiophene (**17**) (10.5 mg, 96.8 μmol, 1.50 equiv) dissolved in DMSO (0.43 mL) at room temperature. After stirring for 24 h at the same temperature, the mixture was filtrated through a pad of Celite and washed with EtOAc (5 mL). The filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 10/1) to give 3-(((3,4-dimethylphenyl)thio)ethynyl)thiophene (**15c**) (14.4 mg, 58.9 μmol, 91%) as a colorless oil.

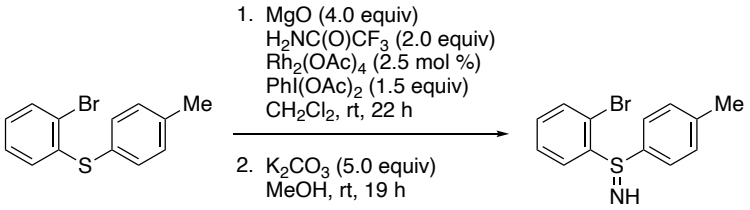
Synthesis of 2-bromophenyl p-tolyl sulfide



In a 5 mL screw-top V-vial® with a solid-top cap (Sigma–Aldrich, Cat. No. Z115118), to a mixture of $CuSO_4$ (0.8 mg, 5 μmol, 10 mol %) and $NaHCO_3$ (8.4 mg, 0.10 mmol, 2.0 equiv) was added a solution of *p*-tolylboronic acid (**16b**) (10.2 mg, 75.0 μmol, 1.50 equiv) and *S*-(2-bromophenyl) 4-methylbenzenesulfonothioate (17.1 mg, 50.0 μmol) dissolved in MeOH (0.50 mL) at room temperature. After stirring for 24 h at the same temperature, to the mixture was added an aqueous saturated ammonium chloride (2 mL + 10 mL). The mixture was extracted with EtOAc (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/EtOAc = 10/1) to give 2-bromophenyl *p*-tolyl sulfide (8.9 mg, 25 μmol, 64%) as a colorless solid.

According to the procedure for preparing *S*-(3,4-dimethylphenyl) 4-methylbenzenesulfonothioate, 2-bromo-4,5-difluorophenyl 3,5-dimethoxyphenyl sulfide (12.9 mg, 71%) was prepared from *S*-(2-bromo-4,5-difluorophenyl) 4-methylbenzenesulfonothioate (**5c**) and (3,5-dimethoxyphenyl)boronic acid (**16c**).

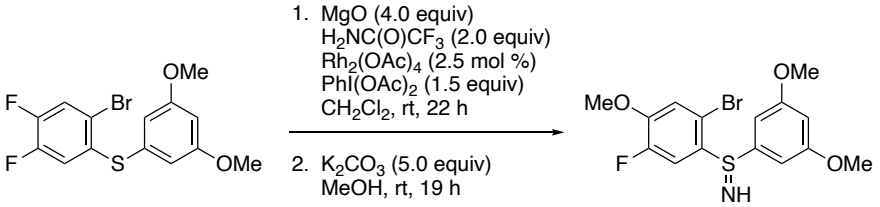
*Synthesis of S-(2-bromophenyl)-S-(4-tolyl)sulfilimine (**18a**)*



To a mixture of 2-bromophenyl 4-tolyl sulfide (1.14 g, 3.31 mmol), MgO (532 mg, 13.2 mmol, 3.99 equiv), $H_2NC(O)CF_3$ (0.748 g, 6.62 mmol, 2.00 equiv), and $Rh_2(OAc)_4$ (36.6 mg, 82.8 μmol, 2.50 mol %) in CH_2Cl_2 (15.0 mL) was added $PhI(OAc)_2$ (1.60 g, 4.97 mmol, 1.50 equiv) at room temperature. After stirring for 22 h at the same temperature, the mixture was filtered through a pad of Celite and washed with EtOAc (20 mL). The filtrate was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (CH_2Cl_2) to give *N*-((2-bromophenyl)(*p*-tolyl)-λ^4-sulfaneylidene)-2,2,2-trifluoroacetamide (1.19 g, 3.04 mmol, 92%) as a colorless solid.

To a solution of the residue prepared above in MeOH (6.5 mL) was added K_2CO_3 (2.10 g, 15.2 mmol, 5.00 equiv) at room temperature. After stirring for 19 h at the same temperature, to the mixture was added water (10 mL). The mixture was extracted with CH_2Cl_2 (10 mL × 3). The combined organic extract was washed with brine (20 mL) and dried with Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica-gel 50.0 g, CH_2Cl_2/MeOH = 5/1) to give (2-bromophenyl)(*p*-tolyl)-λ^4-sulfanimine (**18a**) (830.9 mg, 2.82 mmol, 93%) as a pale yellow solid.

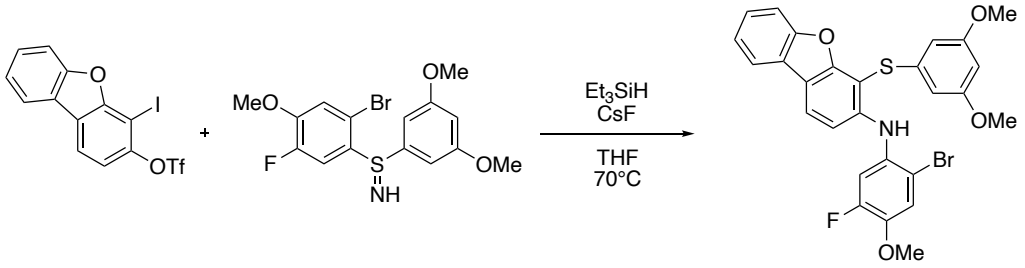
*Synthesis of (2-bromo-5-fluoro-4-methoxyphenyl)(3,5-dimethoxyphenyl)-λ⁴-sulfanimine (**18b**)*



In a 5 mL screw-top V-vial® with a solid-top cap (Sigma–Aldrich, Cat. No. Z115118), to a mixture of 2-bromo-4,5-difluorophenyl 3,5-dimethoxyphenyl sulfide (33.7 mg, 93.3 μmol), MgO (15.0 mg, 0.372 mmol, 3.99 equiv), $H_2NC(O)CF_3$ (21.0 mg, 0.186 mmol, 2.0 equiv), and $Rh_2(OAc)_4$ (1.0 mg, 2.3 μmol, 2.5 mol %) in CH_2Cl_2 (0.45 mL) was added $PhI(OAc)_2$ (45.0 mg, 0.135 mmol, 1.47 equiv) at room temperature. After stirring for 22 h at the same temperature, the mixture was filtered through a pad of Celite and washed with EtOAc (5 mL). The filtrate was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (CH_2Cl_2) to give *N*-((2-bromo-4,5-difluorophenyl)(3,5-dimethoxyphenyl)-λ⁴-sulfaneylidene)-2,2,2-trifluoroacetamide (23.9 mg, 50.6 μmol, 54%) as yellow solid.

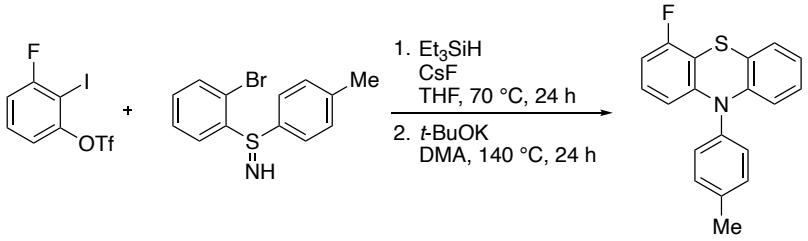
To a solution of the residue prepared above in MeOH (0.50 mL) was added K_2CO_3 (35.0 mg, 0.253 mmol, 5.00 equiv) at room temperature. After stirring for 19 h at the same temperature, to the mixture was added water (10 mL). The mixture was extracted with CH_2Cl_2 (10 mL × 3). The combined organic extract was washed with brine (20 mL) and dried with Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (CH_2Cl_2/MeOH = 5/1) to give (2-bromo-5-fluoro-4-methoxyphenyl)(3,5-dimethoxyphenyl)-λ⁴-sulfanimine (**18b**) (15.8 mg, 42.0 μmol, 83%) as a yellow solid.

*Synthesis of N-(2-bromo-5-fluoro-4-methoxyphenyl)-4-((3,5-dimethoxyphenyl)thio)dibenzo[b,d]furan-3-amine (**20d**)*



In a 5 mL screw-top V-vial® with a solid-top cap (Sigma–Aldrich, Cat. No. Z115118), to a mixture of 4-iododibenzo[*b*,*d*]furan-3-yl trifluoromethanesulfonate (**19c**) (208 mg, 0.471 mmol, 1.50 equiv) and (2-bromo-5-fluoro-4-methoxyphenyl)(3,5-dimethoxyphenyl)-λ⁴-sulfanimine (**18b**) (0.122 g, 0.314 mmol, 1.00 equiv) dissolved in THF (3.0 mL) were added triethylsilane (225 μL, 1.41 mmol, 4.49 equiv) and cesium fluoride (0.215 g, 1.41 mmol, 4.49 equiv) at room temperature. After stirring for 24 h at 70 ºC, the mixture was cooled to room temperature. To the mixture was added 0.1 M phosphate buffer solution (pH 7.2) (2 mL + 10 mL). The mixture was extracted with EtOAc (10 mL × 3). The combined organic extract was washed with brine (10 mL) and dried with Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (n-hexane/EtOAc =4/1) to give *N*-(2-bromo-5-fluoro-4-methoxyphenyl)-4-((3,5-dimethoxyphenyl)thio)dibenzo[*b*,*d*]furan-3-amine (**20d**) (63.4 mg, 114 μmol, 36%) as a pale yellow oil.

A typical procedure for the synthesis of N-arylphenothiazines from o-arylthio-N-arylanilines



In a 5 mL screw-top V-vial® with a solid-top cap (Sigma–Aldrich, Cat. No. Z115118), to a mixture of 3-fluoro-2-iodophenyl trifluoromethanesulfonate (**19a**) (111 mg, 0.300 mmol, 1.50 equiv) and (2-bromophenyl)(*p*-tolyl)-λ^4-sulfanimine (**18a**) (58.8 mg, 0.200 mmol) dissolved in THF (2.0 mL) were added triethylsilane (91.7 μL, 0.900 mmol, 4.50 equiv) and cesium fluoride (137 mg, 0.900 mmol, 4.50 equiv) at room temperature. After stirring for 24 h at 70 ºC, the mixture was cooled to room temperature. To the mixture was added 0.1 M phosphate buffer solution (pH 7.2) (2 mL + 10 mL). The mixture was extracted with EtOAc (10 mL × 3). The combined organic extract was washed with brine (10 mL) and dried with Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc =7/1) to give *N*-(2-bromophenyl)-3-fluoro-2-(*p*-tolylthio)aniline (**20a**) (43.5 mg, 0.112 mmol, 56%) as a colorless solid.

To a solution of the residue prepared above in *N*, *N*-dimethylacetamide (DMA) (1.5 mL) was added *t*-BuOK (62.8 mg, 0.560 mmol, 5.0 equiv) at room temperature. After stirring for 24 h at 140 °C, to the mixture was added water (10 mL). The mixture was extracted with CH_2Cl_2 (10 mL × 3), and the combined organic extract was washed with brine (20 mL) and dried with Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (n-hexane/EtOAc =5/1) to give 4-fluoro-10-(*p*-tolyl)-10*H*-phenothiazine (**21a**) (21.0 mg, 68.4 μmol, 61%) as a colorless solid.

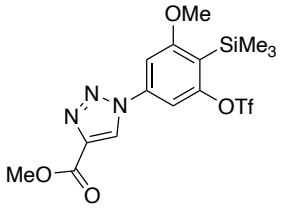
According to the procedure for preparing 4-fluoro-10-(*p*-tolyl)-10*H*-phenothiazine (**21a**), 4-(benzyloxy)-10-(*p*-tolyl)-10*H*-phenothiazine (**21b**) (25.1 mg, 73%) and 5-(*p*-tolyl)-5*H*-benzofuro[3,2-*c*]phenothiazine (**21c**) (56.6 mg, 42%) were prepared from the corresponding sulfides **20**.

Characterization Data of New Compounds

O-Ethyl *S*-(4-methoxyphenyl) carbonodithioate (**2i**),[S10] *O*-ethyl *S*-(3-methoxyphenyl) carbonodithioate (**2i'**),[S11] *S*-(2-chlorophenyl) *O*-ethyl carbonodithioate (**7b**),[S10] *S*-phenyl 4-methylbenzenesulfonothioate (**3b**),[S12] *S*-(benzo[*d*][1,3]dioxol-5-yl) 4-methylbenzenesulfonothioate (**3e**),[S13] *S*-(3-methoxyphenyl) 4-methylbenzenesulfonothioate (**3f**),[S14] *S*-(4-methoxyphenyl) 4-methylbenzenesulfonothioate (**3i**),[S12] *S*-(2-bromophenyl) 4-methylbenzenesulfonothioate (**5b**),[S14] *S*-(2-chlorophenyl) 4-methylbenzenesulfonothioate (**9b**),[S12] 3,4-dimethylphenyl 4-methoxyphenyl sulfide (**15a**),[S15] 2-bromophenyl *p*-tolyl sulfide,[S16] and *S*-(2-bromophenyl)-*S*-(4-tolyl)sulfilimine (**18a**)[S15] were identical with the spectral data reported in the literature.

Characterization Data of a New Aryne Precursor

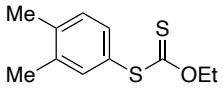
Methyl 1-(3-methoxy-5-(((trifluoromethyl)sulfonyl)oxy)-4-(trimethylsilyl)phenyl)-1*H*-1,2,3-triazole-4-carboxylate (**1j**)



Yield: 98% (15.8 mg, 1.78 mmol); Colorless solid; Mp 112–115 ºC; TLC R_f 0.43 (*n*-hexane/EtOAc = 1/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.51 (s, 1H), 7.38 (d, 1H, J = 1.7 Hz), 7.26–7.25 (m, 1H), 4.01 (s, 3H), 3.94 (s, 3H), 0.39 (s, 9H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 166.5, 160.7, 154.6, 140.9, 138.6, 125.5, 122.7, 118.5 (q, J = 321 Hz), 104.8, 102.2, 56.2, 52.5, 0.6; ^{19}F{^{1}H} NMR ($CDCl_3$, 377 MHz): δ –72.6 (s); IR (NaCl, cm^{-1}) 847, 940, 1049, 1140, 1216, 1425, 1605, 1736; HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{19}F_3N_3O_6SSi^+$ 454.0710; Found 454.0710.

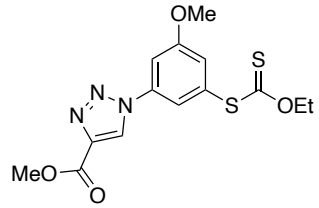
Characterization Data of New Xanthates

S-(3,4-Dimethylphenyl) *O*-ethyl carbonodithioate (**2a**)



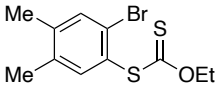
Yield: 70% (15.8 mg, 69.9 μmol); Pale yellow oil; TLC R_f 0.21 (*n*-hexane); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.27–7.26 (m, 1H), 7.25–7.23 (m, 1H), 7.19 (d, 1H, J = 7.8 Hz), 4.62 (q, 2H, J = 7.1 Hz), 2.30 (s, 3H), 2.29 (s, 3H), 1.35 (t, 3H, J = 7.1 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 214.3, 139.0, 137.7, 135.9, 132.5, 130.5, 126.9, 70.2, 19.7, 19.6, 13.6; IR (NaCl, cm^{-1}) 813, 851, 884, 996, 1042, 1110, 1148, 1225, 1366, 1385, 1447, 1487, 1597, 2980; HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{11}H_{14}NaOS_2^+$ 249.0384; Found 249.0385.

Methyl 1-(3-((ethoxycarbonothioyl)thio)-5-methoxyphenyl)-1*H*-1,2,3-triazole-4-carboxylate (**2j**)



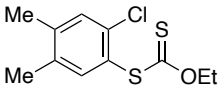
Yield: 33% (22.4 mg involving a small amount of impurity, <64 μmol; ^{1}H NMR yield); To obtain an authentic sample of **2j**, further purification was carried out by recycling preparative HPLC system (SHIMADZU) equipped with a refractive index detector and a YMC-GPC T2000 (600 mm × 20 φ) column (YMC Co., Ltd.) using $CHCl_3$ as an eluent, followed by recrystallization from EtOH/*n*-hexane (v/v = 3/1). Colorless solid; Mp 121–124 ºC; TLC R_f 0.40 (*n*-hexane/EtOAc = 1/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.52 (s, 1H), 7.48–7.47 (m, 1H), 7.46–7.45 (m, 1H), 7.41 (dd, 1H, J = 2.3, 1.4 Hz), 4.64 (q, 2H, J = 7.1 Hz), 4.00 (s, 3H), 3.92 (s, 3H), 1.37 (t, 3H, J = 7.1 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 211.0, 160.9, 160.8, 140.7, 137.5, 133.3, 125.5, 121.4, 118.8, 108.2, 70.8, 56.1, 52.4, 13.6; IR (NaCl, cm^{-1}) 1036, 1149, 1232, 1368, 1429, 1554, 1603, 1739; HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{16}N_3O_4S_2^+$ 354.0577; Found 354.0578.

S-(2-Bromo-4,5-dimethylphenyl) *O*-ethyl carbonodithioate (**6a**)



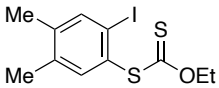
Yield: 69% (21.0 mg, 69.1 μmol); Colorless solid; Mp 64–67 ºC; TLC R_f 0.64 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.48 (s, 1H), 7.35 (s, 1H), 4.61 (q, 2H, *J* = 7.1 Hz), 2.27 (s, 3H), 2.23 (s, 3H), 1.34 (t, 3H, *J* = 7.1 Hz);^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 211.4, 141.3, 137.8, 136.9, 134.2, 127.9, 127.0, 70.3, 19.5, 19.1, 13.6; IR (NaCl, cm^{-1}) 917, 999, 1043, 1110, 1228, 1365, 1445, 2979; HRMS (ESI) *m/z*: [M+Na]$^+$ Calcd for $C_{11}H_{13}BrNaOS_2^+$ 326.9489; Found 326.9489.

S-(2-Chloro-4,5-dimethylphenyl) *O*-ethyl carbonodithioate (**7a**)



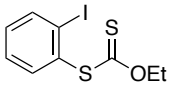
Yield: 87% (22.6 mg, 86.9 μmol); Colorless solid; Mp 111–114 ºC; TLC R_f 0.43 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.33 (s, 1H), 7.30 (s, 1H), 4.61 (q, 2H, *J* = 7.1 Hz), 2.28 (s, 3H), 2.24 (s, 3H), 1.34 (t, 3H, *J* = 7.1 Hz);^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 211.6, 141.3, 137.8, 136.3, 136.2, 131.0, 125.8, 70.4, 19.6, 19.1, 13.6; IR (NaCl, cm^{-1}) 999, 1045, 1110, 1228, 1447, 1455, 1464, 1471, 2922; HRMS (ESI) *m/z*: [M+Na]$^+$ Calcd for $C_{11}H_{13}ClNaOS_2^+$ 282.9994; Found 282.9990.

O-Ethyl *S*-(2-iodo-4,5-dimethylphenyl) carbonodithioate (**8a**)



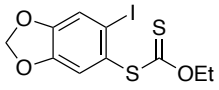
Yield: 70% (15.8 mg, 69.9 μmol); Pale yellow oil; TLC R_f 0.66 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.75 (s, 1H), 7.40 (s, 1H), 4.62 (q, 2H, *J* = 7.1 Hz), 2.25 (s, 3H), 2.22 (s, 3H), 1.35 (t, 3H, *J* = 7.1 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 211.7, 141.1, 140.9, 138.0, 137.2, 132.4, 104.4, 70.4, 19.3, 19.2, 13.7; IR (NaCl, cm^{-1}) 904, 1040, 1110, 1149, 1226, 1339, 1366, 1442, 1583, 1739, 2925; HRMS (ESI) *m/z*: [M+Na]$^+$ Calcd for $C_{11}H_{13}INaOS_2^+$ 374.9350; Found 374.9345.

O-Ethyl *S*-(2-iodophenyl) carbonodithioate (**8b**)



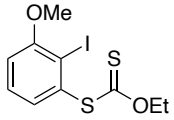
Yield: 80% (25.9 mg, 80.0 μmol); Brown oil; TLC R_f 0.63 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.00 (dd, 1H, *J* = 7.7, 1.3 Hz), 7.65 (dd, 1H, *J* = 7.7, 1.6 Hz), 7.41 (ddd, 1H, *J* = 7.7, 7.7, 1.3 Hz), 7.12 (ddd, 1H, *J* = 7.7, 7.7, 1.6 Hz), 4.61 (q, 2H, *J* = 7.1 Hz), 1.33 (t, 3H, *J* = 7.1 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 210.7, 140.2, 136.4, 135.7, 131.4, 129.1, 108.2, 70.5, 13.6; IR (NaCl, cm^{-1}) 849, 1010, 1043, 1109, 1149, 1226, 1365, 1444, 2978; HRMS (ESI) *m/z*: [M+Na]$^+$ Calcd for $C_9H_9INaOS_2^+$ 346.9037; Found 346.9036.

O-Ethyl *S*-(6-iodobenzo[*d*][1,3]dioxol-5-yl) carbonodithioate (**8e**)



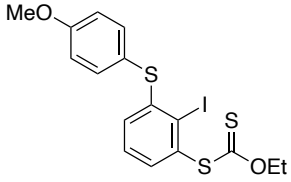
Yield: 73% (26.7 mg, 72.5 μmol); Pale yellow oil; TLC R_f 0.48 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.34 (s, 1H), 7.11 (s, 1H), 6.06 (s, 2H), 4.63 (q, 2H, *J* = 7.1 Hz), 1.37 (t, 3H, *J* = 7.1 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 211.6, 150.1, 148.9, 127.8, 119.4, 115.6, 102.4, 98.3, 70.6, 13.7; IR (NaCl, cm^{-1}) 861, 933, 1000, 1036, 1110, 1143, 1232, 1319, 1365, 1464, 1470, 1501, 2899; HRMS (ESI) *m/z*: [M+H]$^+$ Calcd for $C_{10}H_{10}IO_3S_2^+$ 368.9111; Found 368.9114.

O-Ethyl *S*-(2-iodo-3-methoxyphenyl) carbonodithioate (**8f**)



Yield: 68% (24.1 mg, 68.1 μmol); Pale yellow solid; Mp 66–69 ºC; TLC R_f 0.69 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36 (dd, 1H, *J* = 8.1, 8.1 Hz), 7.29 (dd, 1H, *J* = 8.1, 1.4 Hz), 6.86 (dd, 1H, *J* = 8.1, 1.4 Hz), 4.61 (q, 2H, *J* = 7.1 Hz), 3.92 (s, 3H), 1.32 (t, 3H, *J* = 7.1 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 210.8, 159.4, 137.2, 129.6, 128.5, 111.9, 100.4, 70.4, 56.8, 13.6; IR (NaCl, cm^{-1}) 1013, 1035, 1112, 1149, 1225, 1262, 1408, 1428, 1455, 1564; HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{10}H_{12}IO_2S_2^+$ 354.9318; Found 354.9318.

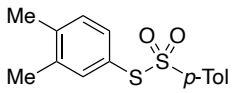
O-Ethyl *S*-(2-iodo-3-((4-methoxyphenyl)thio)phenyl) carbonodithioate (**8g**)



Yield: 91% (41.9 mg, 90.6 μmol); Pale yellow oil; TLC R_f 0.38 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.50–7.48 (AA'BB', 2H), 7.37 (dd, 1H, *J* = 7.5 Hz, 1.5 Hz), 7.16 (dd, 1H, *J* = 7.8, 7.8 Hz), 6.99–6.97 (AA'BB', 2H), 6.62 (dd, 1H, *J* = 8.0, 1.5 Hz), 4.62 (q, 2H, *J* = 7.1 Hz), 3.86 (s, 3H), 1.34 (t, 3H, *J* = 7.1 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz):δ 210.5, 160.8, 147.8, 137.0, 132.2, 128.8, 127.5, 123.4, 115.6, 115.0, 109.1, 70.4, 55.4, 13.6; IR (NaCl, cm^{-1}) 830, 1006, 1039, 1107, 1172, 1231, 1251, 1372, 1424, 1494, 1590; HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{16}IO_2S_3^+$ 462.9352; Found 462.9358.

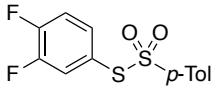
Characterization Data of New Thiosulfonates

S-(3,4-Dimethylphenyl) 4-methylbenzenesulfonothioate (**3a**)



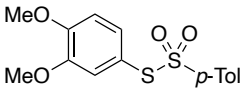
Yield: 87% (12.7 mg, 43.5 μmol); Colorless solid; Mp 75–78 ºC; TLC R_f 0.41 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.48–7.46 (AA'BB', 2H), 7.23–7.21 (AA'BB', 2H), 7.13−7.11 (br, 1H), 7.08 (d, 1H, *J* = 7.8 Hz), 7.04 (dd, 1H, *J* = 7.8, 1.7 Hz), 2.43 (s, 3H), 2.27 (s, 3H), 2.19 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 144.5, 140.7, 140.4, 138.0, 137.5, 133.9, 130.6, 129.3, 127.7, 124.5, 21.6, 19.8, 19.6; IR (NaCl, cm^{-1}) 813, 1079, 1143, 1328, 1455, 1488, 1594, 2920; HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{15}H_{16}NaO_2S_2^+$ 315.0489; Found 315.0491.

S-(3,4-Difluorophenyl) 4-methylbenzenesulfonothioate (**3c**)



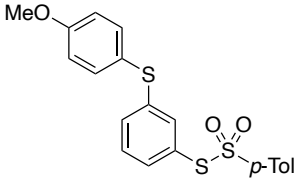
Yield: 51% (7.7 mg, 26 μmol); Colorless solid; Mp 48–51 ºC; TLC R_f 0.40 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.50–7.48 (AA'BB', 2H), 7.27–7.25 (m, 2H), 7.23–7.18 (m, 1H), 7.16–7.13 (m, 2H), 2.44 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 152.7 (dd, *J* = 256, 11.9 Hz), 150.1 (dd, *J* = 254, 13.0 Hz), 145.3, 139.9, 133.4 (dd, *J* = 7.0, 3.6 Hz), 129.6, 127.6, 125.5 (dd, *J* = 17.4, 1.7 Hz), 124.2 (dd, *J* = 6.6, 4.4 Hz), 118.2 (d, *J* = 17.9 Hz), 21.7; ^{19}F{^{1}H} NMR ($CDCl_3$, 377 MHz): δ –131.6 (d, 1F, *J* = 21.2 Hz), –134.4 (d, 1F, *J* = 21.2 Hz); IR (NaCl, cm^{-1}) 814, 1079, 1118, 1145, 1275, 1332, 1407, 1502, 1603; HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{13}H_{10}F_2NaO_2S_2^+$ 322.9982; Found 322.9982.

S-(3,4-Dimethoxyphenyl) 4-methylbenzenesulfonothioate (**3d**)



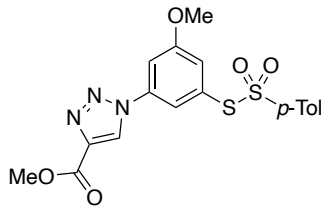
Yield: 80% (12.7 mg, 43.5 μmol); Colorless solid; Mp 101–104 ºC; TLC R_f 0.32 (*n*-hexane/EtOAc = 2/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.49–7.47 (AA'BB', 2H), 7.24–7.22 (AA'BB', 2H), 6.98 (dd, 1H, *J* = 8.4, 2.1 Hz), 6.81 (d, 1H, *J* = 8.4 Hz), 6.74 (d, 1H, *J* = 2.1 Hz), 3.91 (s, 3H), 3.72 (s, 3H), 2.42 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 151.8, 149.0, 144.6, 140.2, 130.4, 129.4, 127.8, 118.8, 118.7, 111.3, 56.0, 55.9, 21.7; IR (NaCl, cm^{-1}) 1022, 1139, 1233, 1258, 1324, 1505, 1583; HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{15}H_{16}NaO_4S_2^+$ 347.0388; Found 347.0386.

S-(3-((4-Methoxyphenyl)thio)phenyl) 4-methylbenzenesulfonothioate (**3g**)



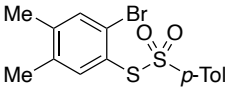
Yield: 60% (12.1 mg, 30.1 μmol); Brown oil; TLC R_f 0.24 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.44–7.42 (AA'BB', 2H), 7.37–7.33 (AA'BB', 2H), 7.23–7.21 (AA'BB', 2H), 7.21–7.14 (m, 3H), 6.99–6.98 (m, 1H), 6.92–6.89 (AA'BB', 2H), 3.84 (s, 3H), 2.45 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz):δ 160.3, 144.8, 141.0, 140.1, 136.0, 134.6, 133.4, 130.0, 129.7, 129.4, 128.8, 127.7, 122.3, 115.2, 55.4, 21.8; IR (NaCl, cm^{-1}) 830, 1030, 1079, 1145, 1173, 1246, 1291, 1329, 1395, 1458, 1491, 1570, 1593, 2925; HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{20}H_{18}NaO_3S_3^+$ 425.0316; Found 425.0313.

Methyl 1-(3-methoxy-5-(tosylthio)phenyl)-1*H*-1,2,3-triazole-4-carboxylate (**3j**)



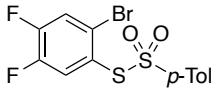
Yield: 52% (4.7 mg, 11 μmol); Colorless solid; Mp 171–176 ºC; TLC R_f 0.40 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.34 (s, 1H), 7.56–7.54 (AA'BB', 2H), 7.52 (dd, 1H, *J* = 1.9, 1.9 Hz), 7.27–7.25 (m, 2H), 7.14 (dd, 1H, *J* = 1.9, 1.9 Hz), 7.06 (dd, 1H, *J* = 1.9, 1.9 Hz), 4.00 (s, 3H), 3.86 (s, 3H), 2.43 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 160.9, 160.7, 145.6, 140.8, 139.9, 137.4, 131.1, 129.7, 127.9, 125.5, 122.3, 119.5, 109.9, 56.1, 52.5, 21.7; IR (NaCl, cm^{-1}) 811, 1036, 1143, 1232, 1331, 1429, 1457, 1557, 1600, 1743; HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{18}N_3O_5S_2^+$ 420.0682; Found 420.0682.

S-(2-Bromo-4,5-dimethylphenyl) 4-methylbenzenesulfonothioate (**5a**)



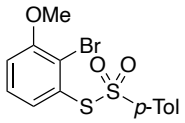
Yield: 80% (14.8 mg, 40.0 μmol); Colorless solid; Mp 104–107 ºC; TLC R_f 0.43 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.50–7.48 (AA'BB', 2H), 7.42 (s, 1H), 7.34 (s, 1H), 7.24–7.22 (AA'BB', 2H), 2.43 (s, 3H), 2.26 (s, 3H), 2.21 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 144.8, 142.8, 140.9, 140.2, 137.3, 134.3, 129.5, 127.8, 127.7, 125.8, 21.7, 19.6, 19.1; IR (NaCl, cm^{-1}) 811, 1079, 1143, 1331, 1457, 1517, 1541; HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{15}H_{15}BrNaO_2S_2^+$ 392.9595; Found 392.9593.

S-(2-Bromo-4,5-difluorophenyl) 4-methylbenzenesulfonothioate (**5c**)



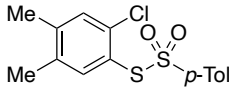
Yield: 57% (10.9 mg, 28.7 μmol); Colorless solid; Mp 126–129 ºC; TLC R_f 0.39 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.58 (dd, 1H, *J* = 9.6, 8.0 Hz), 7.52–7.50 (AA'BB', 2H), 7.42 (dd, 1H, *J* = 9.4, 7.4 Hz), 7.28–7.26 (m, 2H), 2.4 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 152.1 (dd, *J* = 261, 13.3 Hz), 149.3 (dd, *J* = 255, 12.9 Hz), 145.6, 140.4, 129.8, 127.6, 127.4 (dd, *J* = 17.1, 1.4 Hz), 126.0−125.8 (m), 122.3 (d, *J* = 20.3 Hz), 21.7; ^{19}F{^{1}H} NMR ($CDCl_3$, 377 MHz): δ –128.4 (d, 1F, *J* = 20.8 Hz), –135.2 (d, 1F, *J* = 20.8 Hz); IR (NaCl, cm^{-1}) 813, 884, 1079, 1146, 1182, 1281, 1334, 1362, 1478, 1593; HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{13}H_9BrF_2NaO_2S_2^+$ 400.9088; Found 400.9086.

S-(2-Bromo-3-methoxyphenyl) 4-methylbenzenesulfonothioate (**5f**)



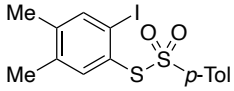
Yield: 84% (15.4 mg, 41.4 μmol); Off-white solid; Mp 71–74 ºC; TLC R_f 0.38 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.51–7.51 (AA'BB', 2H), 7.35–7.30 (m, 2H), 7.23–7.21 (AA'BB', 2H), 6.99 (dd, 1H, *J* = 7.0, 2.7 Hz), 3.89 (s, 3H), 2.42 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 156.9, 145.0, 140.9, 130.9, 130.8, 129.6, 128.4, 127.5, 120.5, 114.5, 56.7, 21.7; IR (NaCl, cm^{-1}) 813, 1045, 1079, 1143, 1268, 1331, 1414, 1432, 1461, 1567, 2939; HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{14}H_{13}BrNaO_3S_2^+$ 394.9387; Found 394.9383.

S-(2-Chloro-4,5-dimethylphenyl) 4-methylbenzenesulfonothioate (**9a**)



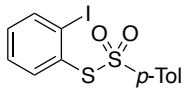
Yield: 74% (12.3 mg, 37.6 μmol); Colorless solid; Mp 111–114 ºC; TLC R_f 0.43 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.51–7.49 (AA'BB', 2H), 7.38 (s, 1H), 7.24–7.22 (AA'BB', 2H), 7.16 (s, 1H), 2.43 (s, 3H), 2.26 (s, 3H), 2.22 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 144.8, 142.8, 141.0, 140.2, 137.1, 136.6, 131.0, 129.5, 127.6, 123.4, 21.7, 19.7, 19.0; IR (NaCl, cm^{-1}) 813, 1079, 1145, 1304, 1331, 1447, 1464, 1593, 2923; HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{15}H_{15}ClNaO_2S_2^+$ 349.0100; Found 349.0093.

S-(2-Iodo-4,5-dimethylphenyl) 4-methylbenzenesulfonothioate (**10a**)



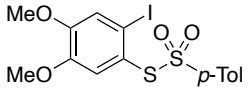
Yield: 76% (7.9 mg, 19 μmol); Colorless solid; Mp 94–97 ºC; TLC R_f 0.39 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.61 (s, 1H), 7.48–7.46 (m, 3H), 7.25–7.23 (AA'BB', 2H), 2.44 (s, 3H), 2.24 (s, 3H), 2.21 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 145.0, 142.6, 141.0, 140.8, 139.3, 138.4, 130.2, 129.7, 127.8, 104.9, 21.8, 19.4, 19.3; IR (NaCl, cm^{-1}) 811, 904, 1079, 1143, 1329, 1447, 1451, 1594, 2919; HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{15}H_{15}INaO_2S_2^+$ 440.9456; Found 440.9454.

S-(2-Iodophenyl) 4-methylbenzenesulfonothioate (**10b**)



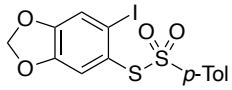
Yield: 98% (19.5 mg, 50.0 μmol); Pale yellow solid; Mp 109–112 ºC; TLC R_f 0.37 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.85 (dd, 1H, *J* = 7.8, 1.6 Hz), 7.78 (dd, 1H, *J* = 7.8, 1.6 Hz), 7.45–7.40 (m, 3H), 7.24–7.22 (AA'BB', 2H), 7.12 (ddd, 1H, *J* = 7.8, 7.8, 1.6 Hz), 2.44 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 145.2, 140.7, 140.3, 138.4, 133.7, 132.4, 129.7, 129.3, 127.7, 108.7, 21.8; IR (NaCl, cm^{-1}) 811, 1013, 1079, 1143, 1252, 1331, 1442, 1565, 1594, 2923, 3058; HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{13}H_{11}INaO_2S_2^+$ 412.9143; Found 412.9142.

S-(2-Iodo-4,5-dimethoxyphenyl) 4-methylbenzenesulfonothioate (**10d**)



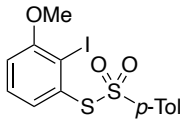
Yield: 75% (18.5 mg, 41.1 μmol); Colorless solid; Mp 134–137 ºC; TLC R_f 0.39 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.50–7.48 (AA'BB', 2H), 7.26–7.23 (m, 2H), 7.22 (s, 1H), 7.14 (s, 1H), 3.89 (s, 3H), 3.81 (s, 3H), 2.44 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 151.7, 149.5, 145.0, 140.5, 129.7, 127.8, 124.6, 121.9, 119.8, 98.4, 56.3, 56.1, 21.7; IR (NaCl, cm^{-1}) 859, 1020, 1077, 1142, 1211, 1253, 1325, 1437, 1461, 1494, 1577; HRMS (ESI) *m/z*: $[M+NH_4]^+$ Calcd for $C_{15}H_{19}INO_4S_2^+$467.9795; Found 467.9797.

S-(6-Iodobenzo[*d*][1,3]dioxol-5-yl) 4-methylbenzenesulfonothioate (**10e**)



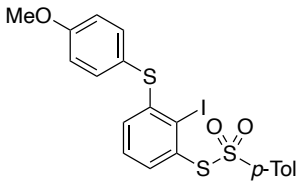
Yield: 71% (20.4 mg, 47.0 μmol); Colorless solid; Mp 69–73 ºC; TLC R_f 0.48 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.51–7.49 (AA'BB', 2H), 7.27–7.24 (m, 4H), 6.07 (s, 2H), 2.44 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 151.1, 149.0, 145.1, 140.6, 129.7, 127.7, 125.5, 119.3, 117.2, 102.7, 99.3, 21.7; IR (NaCl, cm^{-1}) 813, 863, 933, 1036, 1079, 1143, 1236, 1328, 1464, 1471, 1475, 1480, 1504, 1594, 2910; HRMS (ESI) *m/z*: $[M+NH_4]^+$ Calcd for $C_{14}H_{15}INO_4S_2^+$ 451.9482; Found 451.9482.

S-(2-Iodo-3-methoxyphenyl) 4-methylbenzenesulfonothioate (**10f**)



Yield: 51% (10.7 mg, 25.5 μmol); Pale yellow solid; Mp 81–84 ºC; TLC R_f 0.32 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.50–7.48 (AA'BB', 2H), 7.41–7.33 (m, 2H), 7.23–7.21 (AA'BB', 2H), 6.87 (dd, 1H, J = 8.0, 1.5 Hz), 3.87 (s, 3H), 2.42 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 159.4, 145.0, 140.9, 135.1, 130.4, 129.7, 129.6, 127.6, 113.0, 100.9, 56.9, 21.7; IR (NaCl, cm^{-1}) 811, 1016, 1040, 1079, 1143, 1263, 1329, 1429, 1455, 1563, 2923; HRMS (ESI) *m/z*: $[M+NH_4]^+$ Calcd for $C_{14}H_{17}INO_3S_2^+$ 437.9689; Found 437.9689.

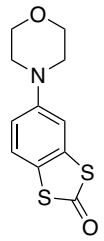
S-(2-Iodo-3-((4-methoxyphenyl)thio)phenyl) 4-methylbenzenesulfonothioate (**10g**)



Yield: 67% (13.8 mg, 26.1 μmol); Colorless solid; Mp 73–76 ºC; TLC R_f 0.28 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.50–7.44 (m, 5H), 7.26–7.24 (m, 2H), 7.15 (dd, 1H, J = 7.8, 7.8 Hz), 7.00–6.97 (AA'BB', 2H), 6.61 (dd, 1H, J = 7.8, 1.4 Hz), 3.87 (s, 3H), 2.45 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz):δ 160.9, 148.2, 145.2, 140.8, 137.2, 135.1, 134.1, 129.7, 129.0, 128.5, 127.7, 123.2, 115.7, 109.4, 55.5, 21.8; IR (NaCl, cm^{-1}) 811, 829, 1030, 1079, 1143, 1173, 1252, 1291, 1331, 1424, 1494, 1591, 1729, 2928; HRMS (ESI) *m/z*: $[M+NH_4]^+$ Calcd for $C_{20}H_{21}INO_3S_3^+$ 545.9723; Found 545.9725.

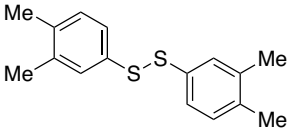
Characterization Data of Other New Compounds

5-Morpholinobenzo[*d*][1,3]dithiol-2-one (**4**)



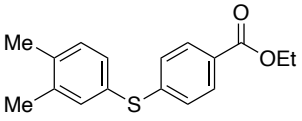
Yield: 30% (11.9 mg, 47.0 μmol); Colorless solid; Mp 147–150 ºC; TLC R_f 0.30 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.34 (d, 1H, *J* = 8.8 Hz), 6.99 (d, 1H, *J* = 2.5 Hz), 6.91 (dd, 1H, *J* = 8.8, 2.5 Hz), 3.88–3.86 (AA'BB', 4H), 3.17–3.15 (AA'BB', 4H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 190.9, 150.6, 133.9, 123.5, 122.3, 115.6, 109.5, 66.7, 49.1; IR (NaCl, cm^{-1}) 1012, 1242, 1478, 1590, 1630, 2958; HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{11}H_{12}NO_2S_2^+$ 254.0304; Found 254.0303.

1,2-Bis(3,4-dimethylphenyl) disulfide (**11a**)



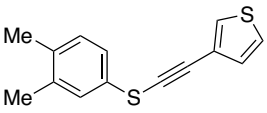
Yield: quant. (6.9 mg, 25 μmol); Colorless solid; Mp 43–46 ºC; TLC R_f 0.69 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.27–7.26 (m, 2H), 7.23 (dd, 2H, *J* = 7.9, 2.0 Hz), 7.06 (d, 2H, *J* = 7.9 Hz), 2.22 (s, 6H + 6H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 137.5, 136.1, 134.1, 130.2, 129.5, 125.9, 19.8, 19.4; IR (NaCl, cm^{-1}) 808, 877, 1128, 1382, 1448, 1485, 1595, 2920; HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{16}H_{18}NaS_2^+$ 297.0748; Found 297.0748.

Ethyl 4-((3,4-dimethylphenyl)thio)benzoate (**15b**)



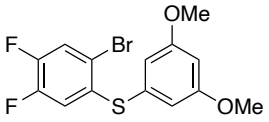
Yield: 93% (10.3 mg, 35.9 μmol); Colorless oil; TLC R_f 0.52 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.89–7.86 (AA'BB', 2H), 7.30–7.28 (br, 1H), 7.26–7.24 (m, 1H), 7.18–7.13 (m, 3H), 4.34 (q, 2H, *J* = 7.1 Hz), 2.29 (s, 3H), 2.26 (s, 3H), 1.37 (t, 3H, *J* = 7.1 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 166.3, 145.4, 138.3, 137.9, 135.4, 131.9, 130.9, 130.0, 128.3, 127.3, 126.7, 60.9, 19.7, 19.6, 14.4; IR (NaCl, cm^{-1}) 816, 827, 1017, 1106, 1177, 1274, 1401, 1487, 1593, 1714; HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{19}O_2S^+$ 287.1100; Found 287.1099.

3-(((3,4-Dimethylphenyl)thio)ethynyl)thiophene (**15c**)



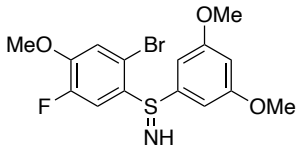
Yield: 91% (14.4 mg, 58.9 μmol); Colorless oil; TLC R_f 0.71 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.54 (dd, 1H, *J* = 3.0, 1.2 Hz), 7.29 (dd, 1H, *J* = 5.0, 3.0 Hz), 7.23–7.21 (m, 2H), 7.18 (dd, 1H, *J* = 7.6 Hz), 7.11(d, 1H, *J* = 7.6 Hz), 2.26 (s, 3H), 2.24 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 137.9, 135.4, 130.5, 130.2, 129.9, 129.2, 127.8, 125.4, 124.2, 122.2, 91.9, 75.8, 19.9, 19.4; IR (NaCl, cm^{-1}) 804, 873, 1020, 1080, 1261, 1447, 1488, 1597, 2163, 2358, 2920, 3106; HRMS (EI) *m/z*: $[M]^{\bullet+}$ Calcd for $C_{14}H_{12}S_2^{\bullet+}$ 244.0380; Found 244.0381.

2-Bromo-4,5-difluorophenyl 3,5-dimethoxyphenyl sulfide



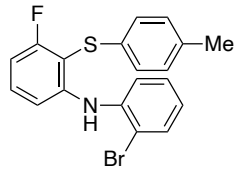
Yield: 71% (12.9 mg, 35.7 μmol); Colorless solid; Mp 53–56 °C; TLC R_f 0.50 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.41 (dd, 1H, *J* = 9.4, 7.4 Hz), 6.81 (dd, 1H, *J* = 10.8, 7.9 Hz), 6.59 (d, 2H, *J* = 2.6 Hz), 6.48 (t, 1H, *J* = 2.6 Hz), 3.79 (s, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 161.5, 150.5 (dd, *J* = 251, 12.9 Hz), 148.0 (dd, *J* = 252, 13.7 Hz), 135.3 (dd, *J* = 5.4, 3.8 Hz), 133.7, 121.7 (d, *J* = 20.4 Hz), 118.1 (d, *J* = 20.7 Hz), 116.3 (dd, *J* = 7.3, 3.7 Hz), 111.1, 101.4, 55.5; ^{19}F{^{1}H} NMR ($CDCl_3$, 377 MHz): δ –136.9 (d, 1F, *J* = 20.9 Hz), –138.1 (d, 1F, *J* = 20.9 Hz); IR (NaCl, cm^{-1}) 838, 1063, 1158, 1205, 1281, 1366, 1422, 1480, 1590; HRMS (EI) *m/z*: $[M]^{\bullet+}$ Calcd for $C_{14}H_{11}BrF_2S^{\bullet+}$ 359.9631; Found 359.9632.

(2-Bromo-5-fluoro-4-methoxyphenyl)(3,5-dimethoxyphenyl)-λ^4-sulfanimine (**18d**)



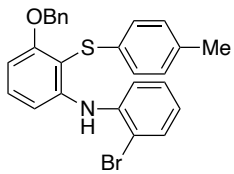
Yield: 80% (15.8 mg, 40.7 μmol); Pale yellow solid; Mp 101–104 °C; TLC R_f 0.39 (CH_2Cl_2/MeOH = 10/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.56 (d, 1H, *J* = 10.4 Hz), 7.11 (d, 1H, *J* = 7.2 Hz), 6.72 (d, 2H, *J* = 2.2 Hz), 6.46 (t, 1H, *J* = 2.2 Hz), 3.90 (s, 3H), 3.78 (s, 6H), 1.92 (s, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 161.3, 152.4 (d, *J* = 253 Hz), 150.3 (d, *J* = 11.7 Hz), 146.3, 136.8 (d, *J* = 2.6 Hz), 117.5, 115.7 (d, *J* = 3.8 Hz), 115.1 (d, *J* = 21.9 Hz), 103.8, 102.6, 56.7, 55.6; ^{19}F{^{1}H} NMR ($CDCl_3$, 377 MHz): δ –132.1 (s); IR (NaCl, cm^{-1}) 1020, 1158, 1205, 1269, 1435, 1455, 1488, 1495, 1600; HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{16}BrFNO_3S^+$ 388.0013; Found 388.0015.

N-(2-Bromophenyl)-3-fluoro-2-(*p*-tolylthio)aniline (**20a**)



Yield: 56% (28.9 mg, 74.8 μmol); Colorless oil; TLC R_f 0.49 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.56 (dd, 1H, *J* = 8.0, 1.4 Hz), 7.39 (dd, 1H, *J* = 8.0, 1.4 Hz), 7.28–7.22 (m, 3H), 7.16–7.14 (AA'BB', 2H), 7.05–7.03 (m, 3H), 6.88 (ddd, 1H, *J* = 8.0, 8.0, 1.4 Hz), 6.69 (ddd, 1H, *J* = 8.0, 8.0, 1.4 Hz), 2.27 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 164.3 (d, *J* = 247 Hz), 146.4 (d, *J* = 2.7 Hz), 139.3, 136.3, 133.3, 131.4, 131.3 (d, *J* = 10.7 Hz), 129.9, 128.0, 127.9, 123.7, 120.3, 116.0, 109.9 (d, *J* = 3.0 Hz), 107.10 (d, *J* = 21.3 Hz), 107.06 (d, *J* = 24.1 Hz), 21.0; ^{19}F{^{1}H} NMR ($CDCl_3$, 377 MHz): δ –103.4 (s); IR (NaCl, cm^{-1}) 1025, 1119, 1182, 1246, 1325, 1398, 1447, 1520, 1605, 3360; HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{16}BrFNS^+$ 388.0165; Found 388.0614.

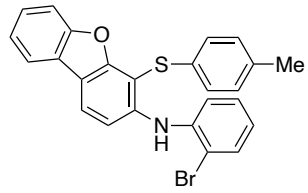
3-(Benzyloxy)-*N*-(2-bromophenyl)-2-(*p*-tolylthio)aniline (**20b**)



Yield: 69% (41.3 mg, 86.9 μmol); Colorless oil; TLC R_f 0.53 (*n*-hexane/CH_2Cl_2 = 1/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.54 (dd, 1H, *J* = 8.0, 1.5 Hz), 7.43–7.41 (m, 2H), 7.30–7.20 (m, 7H), 7.14–7.11 (AA'BB', 2H), 7.03–7.01 (AA'BB', 2H), 6.94 (dd, 1H, *J* = 8.3, 1.0 Hz), 6.84 (ddd, 1H, *J* = 8.0, 8.0, 1.5 Hz), 5.12 (s, 3H), 2.28 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 160.5, 146.3, 139.9, 136.9, 135.5, 133.2, 133.0, 130.9, 129.7, 128.4, 127.9,

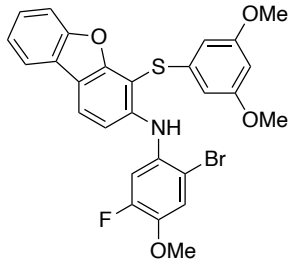
127.7, 127.6, 126.9, 123.0, 119.8, 115.7, 108.2, 108.0, 104.7, 70.4, 21.0; IR (NaCl, cm^{-1}) 1023, 1066, 1263, 1293, 1377, 1446, 1463, 1490, 1515, 1582; HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{26}H_{23}BrNOS^+$ 476.0678; Found 476.0678.

N-(2-Bromophenyl)-4-(*p*-tolylthio)dibenzo[*b*,*d*]furan-3-amine (**20c**)



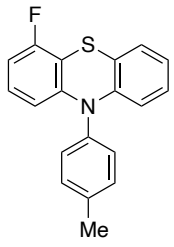
Yield: 45% (28.7 mg, 62.6 μmol); Colorless oil; TLC R_f 0.34 (*n*-hexane/CH_2Cl_2 = 1/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.86–7.84 (m, 2H), 7.59–7.55 (m, 2H), 7.44 (dd, 1H, *J* = 8.0, 1.4 Hz), 7.40–7.36 (m, 1H), 7.34–7.29 (m, 3H), 7.25–7.21 (m, 1H), 7.19–7.16 (AA'BB', 2H), 7.01–6.99 (AA'BB', 2H), 6.87 (ddd, 1H, *J* = 8.0, 8.0, 1.4 Hz), 2.24 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 159.1, 156.2, 144.5, 139.9, 136.2, 133.3, 131.5, 129.9, 128.0, 127.9, 126.0, 124.8, 123.2, 123.1, 122.3, 119.7, 119.3, 117.5, 115.5, 111.8, 111.3, 103.0, 20.9; IR (NaCl, cm^{-1}) 1143, 1186, 1322, 1417, 1447, 1520, 1585; HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{25}H_{18}BrNNaOS^+$ 484.0170; Found 484.0172.

N-(2-Bromo-5-fluoro-4-methoxyphenyl)-4-((3,5-dimethoxyphenyl)thio)dibenzo[*b*,*d*]furan-3-amine (**20d**)



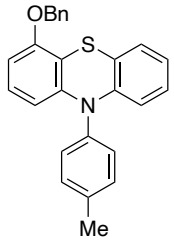
Yield: 48% (6.5 mg, 12 μmol); Pale yellow oil; TLC R_f 0.34 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.87–7.84 (m, 2H), 7.58–7.56 (m, 1H), 7.40–7.30 (m, 2H), 7.22 (d, 1H, *J* = 12.4 Hz), 7.17 (d, 1H, *J* = 8.6 Hz), 7.11 (d, 1H, *J* = 8.6 Hz), 6.96 (s, 1H), 6.37 (d, 2H, *J* = 2.2 Hz), 6.22 (d, 1H, *J* = 2.2 Hz), 3.88 (s, 3H), 3.67 (s, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 161.2, 159.2, 156.1, 147.9 (d, *J* = 247 Hz), 145.3, 144.0 (d, *J* = 12.0 Hz), 137.2, 133.2 (d, *J* = 8.8 Hz), 126.0, 124.8, 123.0 (d, *J* = 17.6 Hz), 119.7, 118.0 (d, *J* = 2.3 Hz), 117.4, 111.8, 110.62, 110.59, 110.2, 109.7 (d, *J* = 22.1 Hz), 105.0, 100.6, 98.5, 56.9, 55.4; ^{19}F{^{1}H} NMR ($CDCl_3$, 377 MHz): δ –133.2 (s); IR (NaCl, cm^{-1}) 810, 1040, 1156, 1205, 1251, 1295, 1418, 1455, 1505, 1593, 2936, 3351; HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{27}H_{22}BrFNO_4S^+$ 554.0431; Found 554.0432.

4-Fluoro-10-(*p*-tolyl)-10*H*-phenothiazine (**21a**)



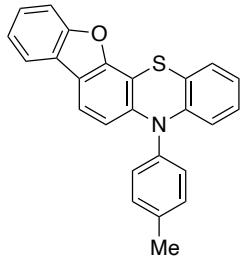
Yield: 61% (14.0 mg, 45.6 μmol); Colorless solid; Mp 146–149 ºC; TLC R_f 0.66 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.41–7.39 (AA'BB', 2H), 7.25–7.23 (m, 2H), 6.99 (m, 1H), 6.84–6.70 (m, 3H), 6.55 (dd, 1H, *J* = 8.4, 1.0 Hz), 6.12 (d, 1H, *J* = 8.1, 1.3 Hz), 5.90 (d, 1H, *J* = 8.4 Hz), 2.46 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 158.1 (d, *J* = 241 Hz), 145.7 (d, *J* = 4.5 Hz), 143.8, 138.6, 137.9, 131.6, 130.8, 127.1, 126.9, 126.7 (d, *J* = 9.5 Hz), 122.5, 117.8, 115.9, 111.2 (d, *J* = 2.5 Hz), 108.5 (d, *J* = 21.7 Hz), 107.6 (d, *J* = 22.9 Hz), 21.3; ^{19}F{^{1}H} NMR ($CDCl_3$, 400 MHz); δ –113.9 (s); IR (NaCl, cm^{-1}) 1023 1047, 1211, 1239, 1316, 1455, 1483, 1512, 1600; HRMS (EI) *m/z*: $[M]^{\bullet+}$ Calcd for $C_{19}H_{14}FNS^{\bullet+}$ 307.0831; Found 307.0831.

4-(Benzyloxy)-10-(*p*-tolyl)-10*H*-phenothiazine (**21b**)



Yield: 73% (25.1 mg, 63.4 μmol); Brown solid; Mp 160–163 ºC; TLC R_f 0.71 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.49–7.47 (AA'BB', 2H), 7.43–7.33 (m, 5H), 7.26–7.23 (m, 2H), 6.99–6.97 (m, 1H), 6.76–6.66 (m, 3H), 6.39 (d, 1H, *J* = 8.2 Hz), 6.06–6.04 (m, 1H), 5.74 (d, 1H, *J* = 8.4 Hz), 5.12 (s, 2H), 2.45 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 153.9, 144.7, 143.7, 138.4, 138.2, 136.9, 131.5, 130.9, 128.6, 127.9, 127.0, 126.8, 126.7, 126.3, 122.0, 119.1, 115.6, 109.4, 108.6, 106.0, 70.7, 21.3; IR (NaCl, cm^{-1}) 1067, 1087, 1249, 1299, 1451, 1573, 1594, 3029; HRMS (EI) *m/z*: $[M]^{\bullet+}$ Calcd for $C_{26}H_{21}NOS^{\bullet+}$ 395.1338; Found 395.1339.

5-(*p*-Tolyl)-5*H*-benzofuro[3,2-*c*]phenothiazine (**21c**)



Yield: 42% (56.6 mg, 149 μmol); Yellow solid; Mp 136–139 ºC; TLC R_f 0.36 (*n*-hexane/CH_2Cl_2 = 5/1); ^{1}H NMR (Acetone-d_6, 400 MHz): δ 7.90 (d, 1H, *J* = 7.6 Hz), 7.60 (d, 1H, *J* = 8.2 Hz), 7.55–7.52 (m, 3H), 7.44 (dd, 1H, *J* = 7.4, 1.3 Hz), 7.37–7.31 (m, 3H), 7.10 (dd, 1H, *J* = 7.4, 1.7 Hz), 6.94–6.84 (m, 2H), 6.25 (d, 1H, *J* = 8.6 Hz), 6.22 (dd, 1H, *J* = 8.2, 1.3 Hz), 2.48 (s, 3H); ^{13}C{^{1}H} NMR (Acetone-d_6, 101 MHz): δ 157.1, 153.1, 145.0, 144.6, 139.5, 139.2, 132.5, 131.6, 128.3, 127.8, 127.3, 124.9, 124.2, 123.7, 121.2, 119.6, 119.0, 118.6, 117.3, 112.9, 112.3, 103.3, 21.2; IR (NaCl, cm^{-1}) 871, 927, 1025, 1046, 1192, 1283, 1311, 1349, 1412, 1451, 1600, 3058; HRMS (EI) *m/z*: $[M+Na]^+$ Calcd for $C_{25}H_{17}NNaOS^{\bullet+}$ 402.0928; Found 402.0928.

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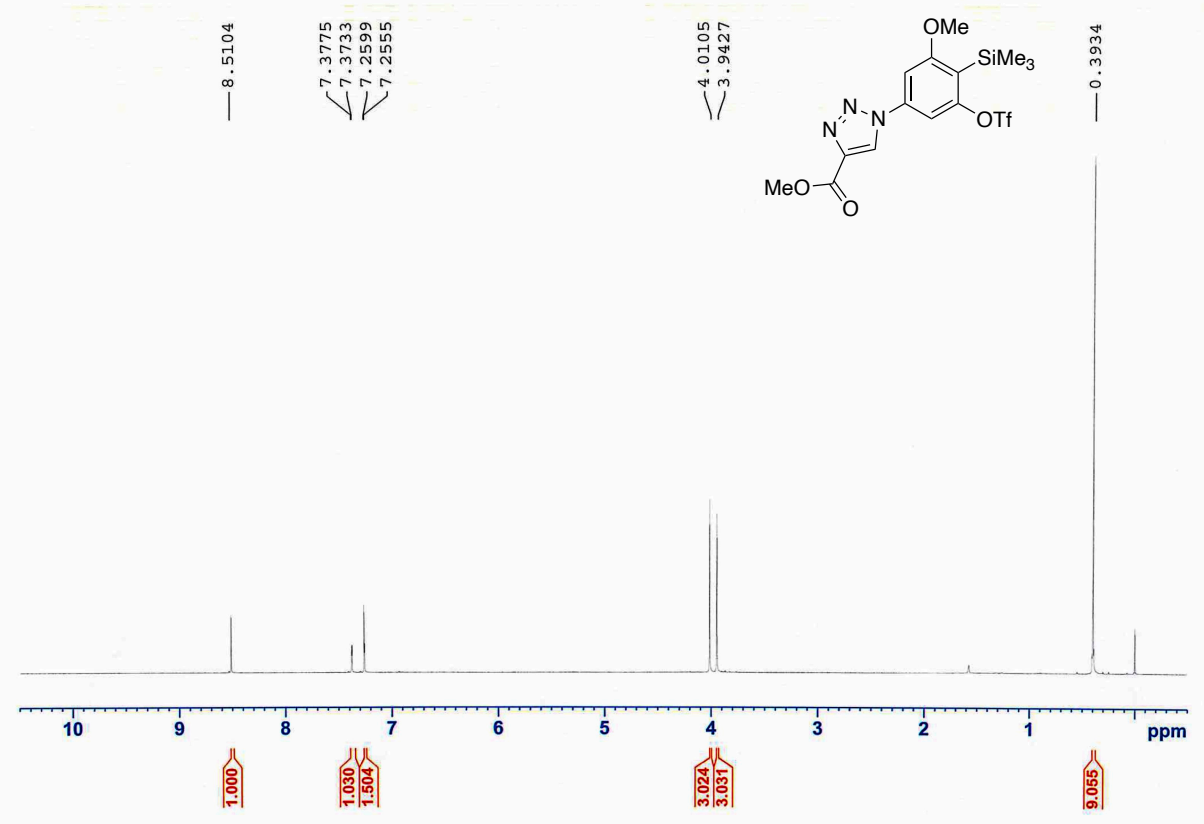
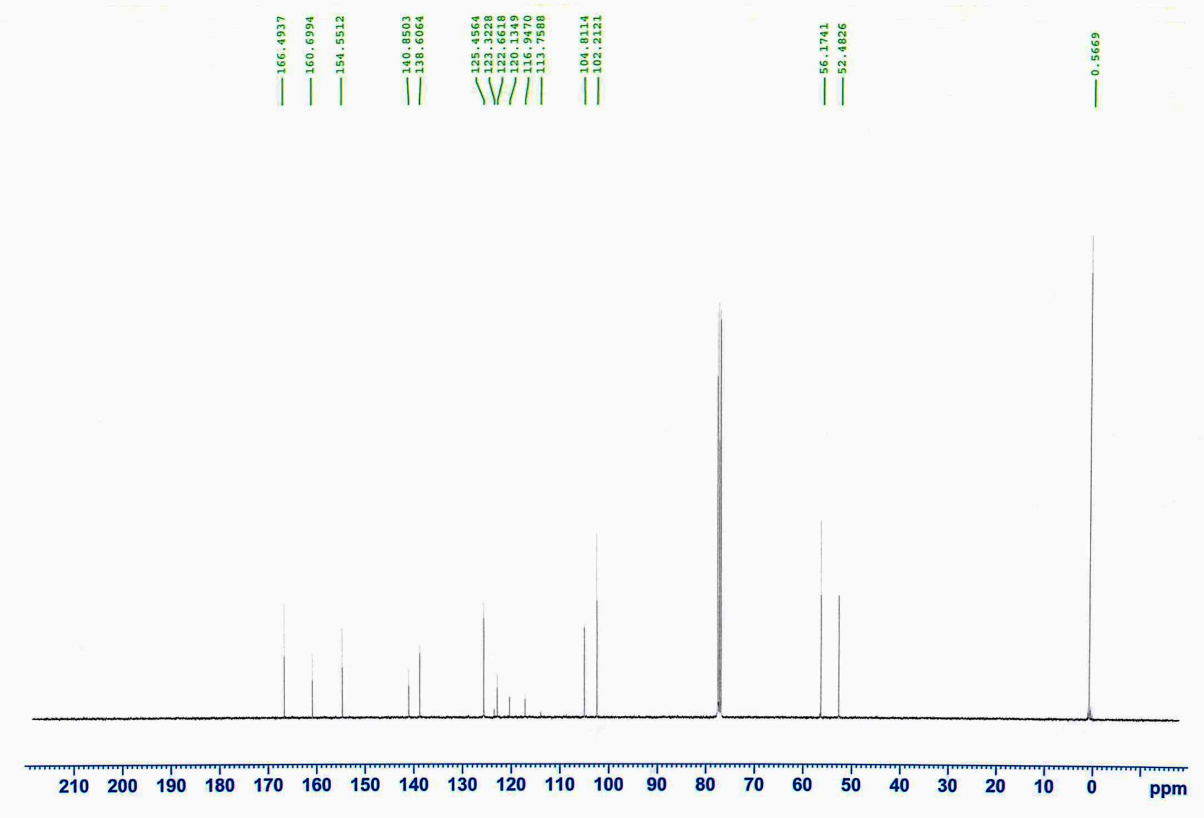
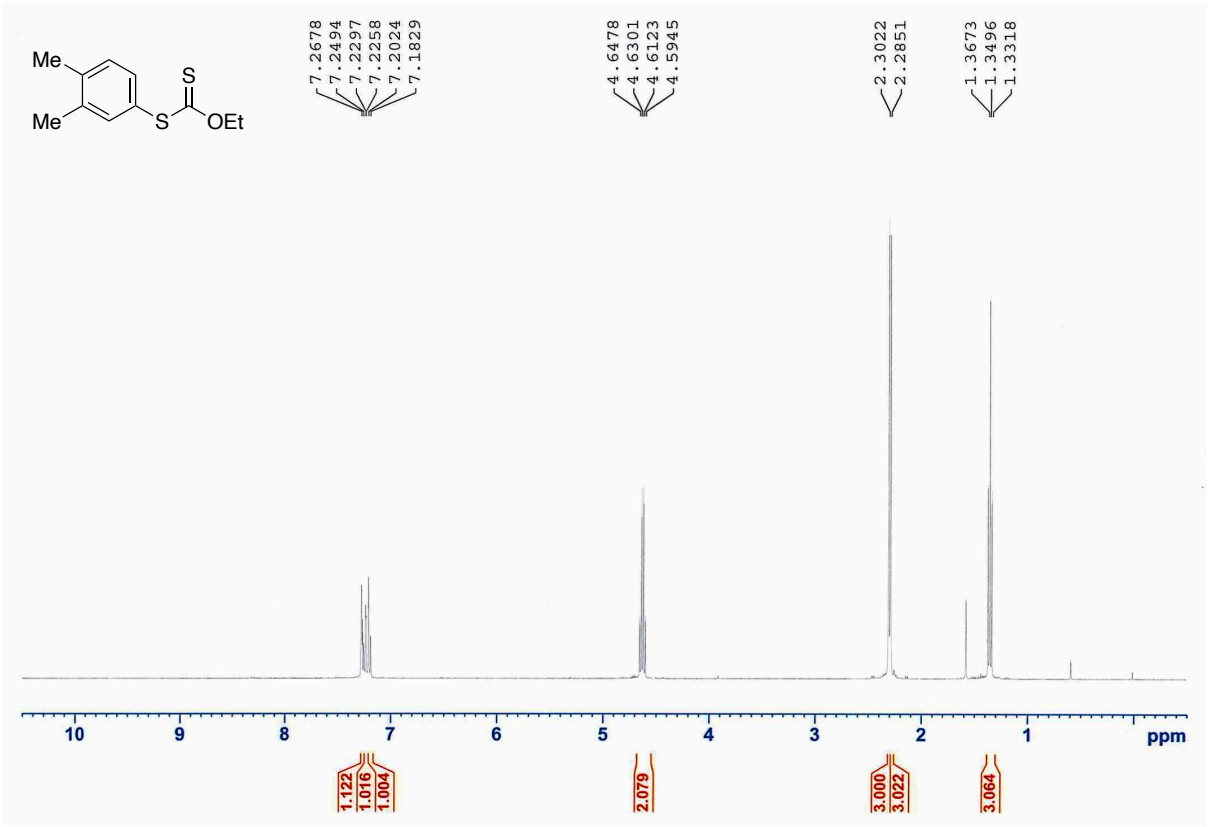
^{1}H and ^{13}C NMR Spectra of New Compounds

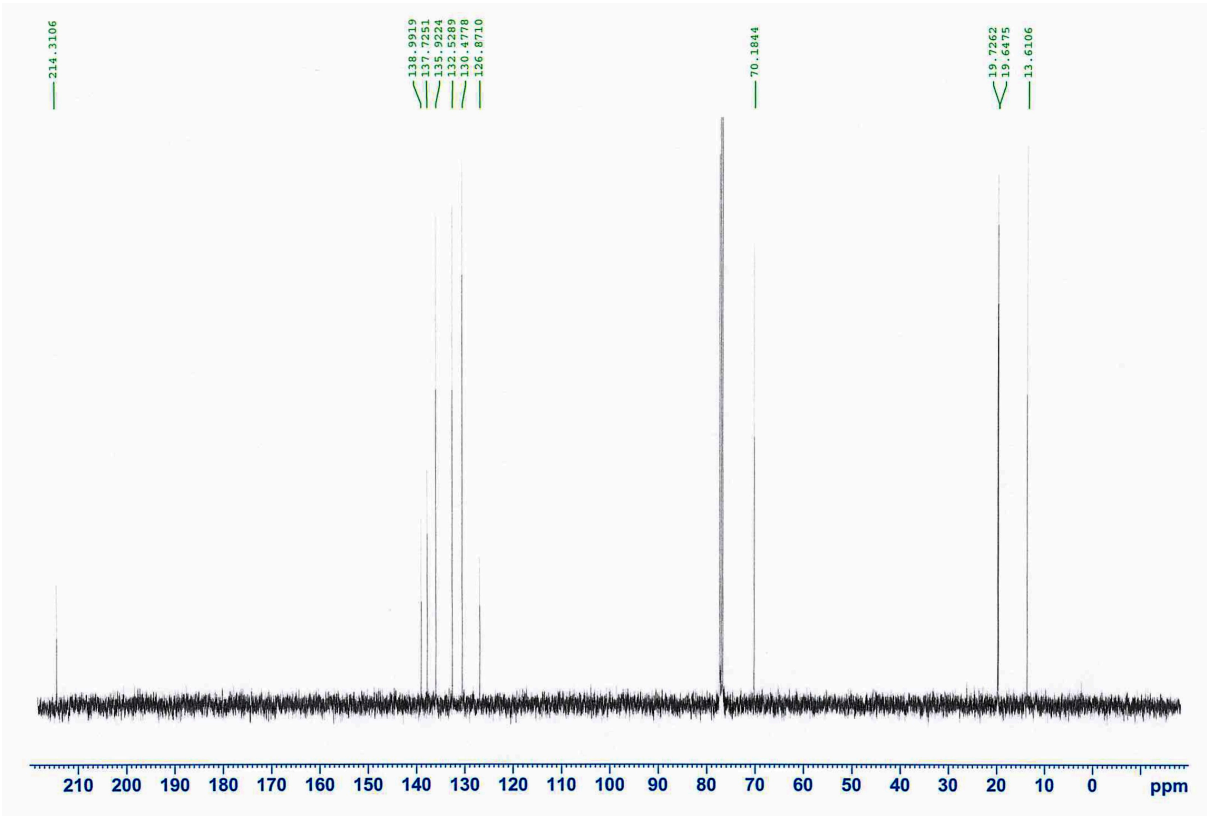
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of methyl 1-(3-methoxy-5-((((trifluoromethyl)sulfonyl)oxy)-4-(trimethylsilyl)phenyl)-1*H*-1,2,3-triazole-4-carboxylate (**1j**) ($CDCl_3$)



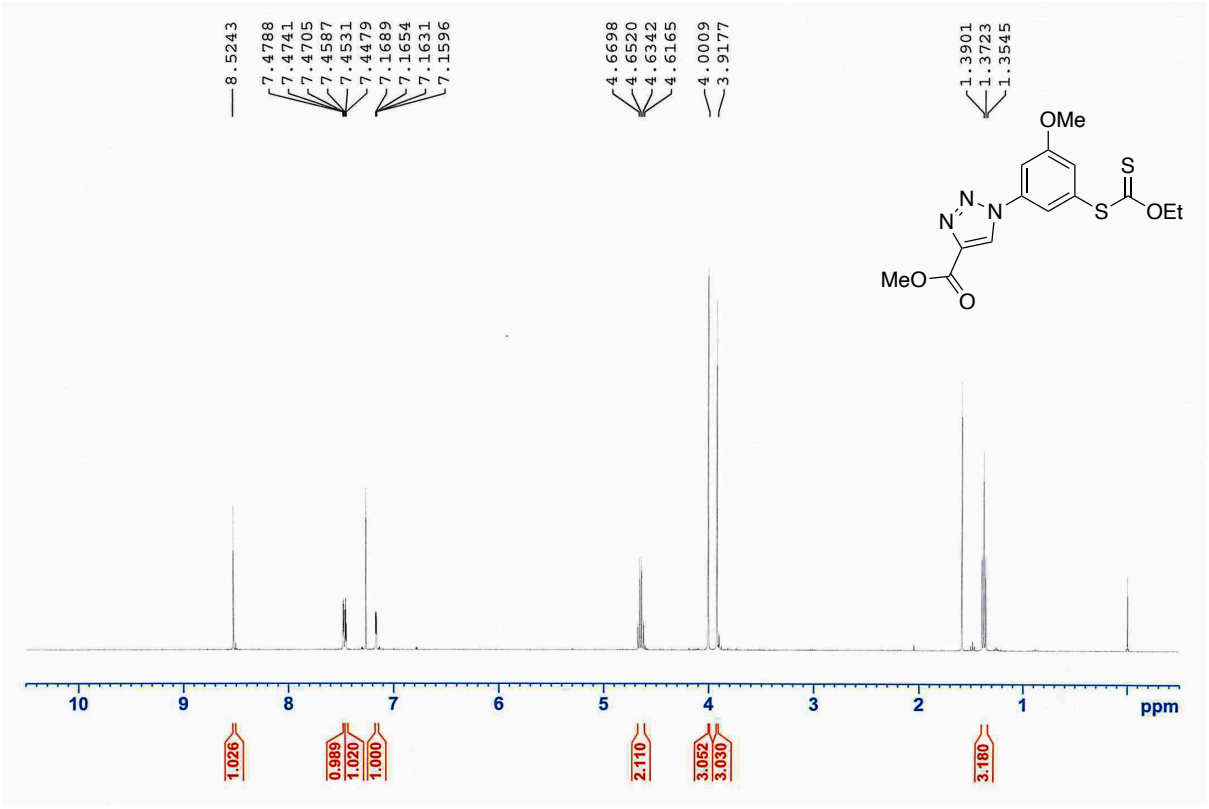


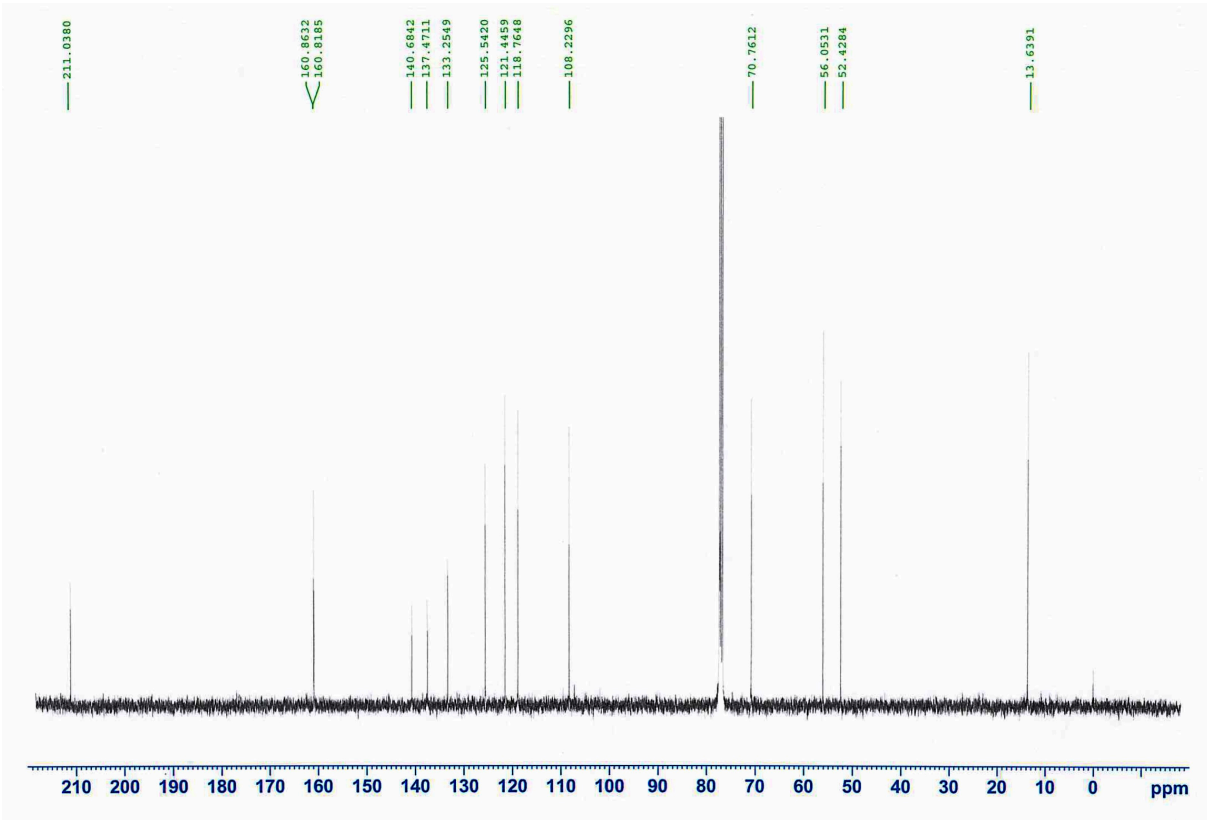
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of *S*-(3,4-dimethylphenyl) *O*-ethyl carbonodithioate (**2a**) ($CDCl_3$)



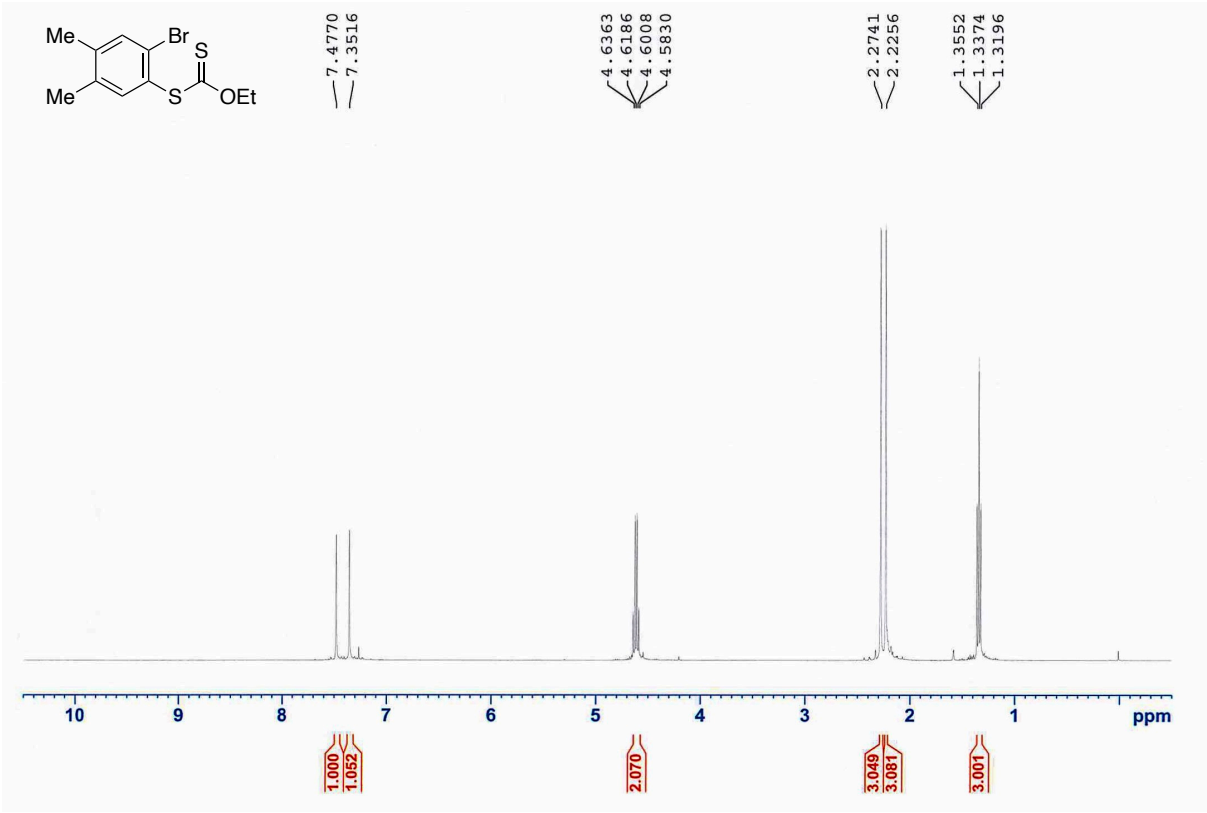


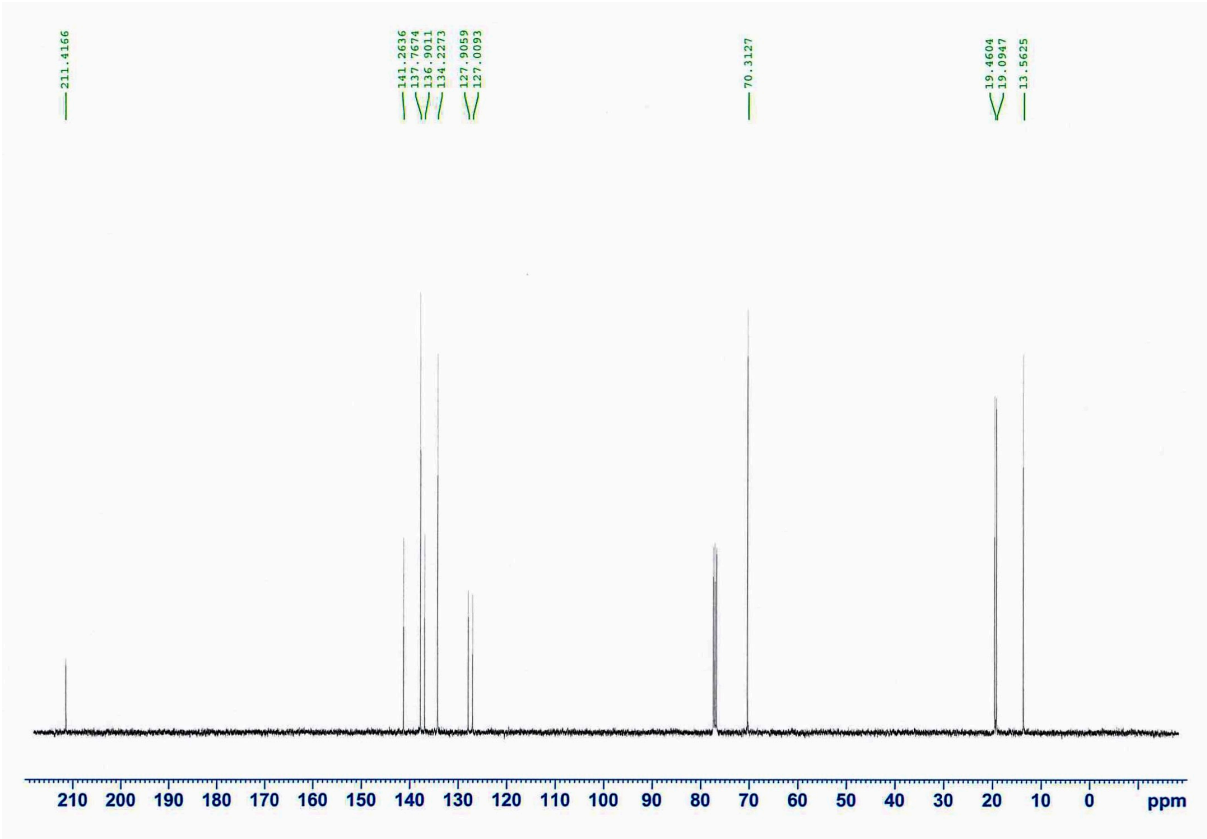
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of *S*-(3,4-dimethylphenyl) *O*-ethyl carbonodithioate (**2j**) ($CDCl_3$)



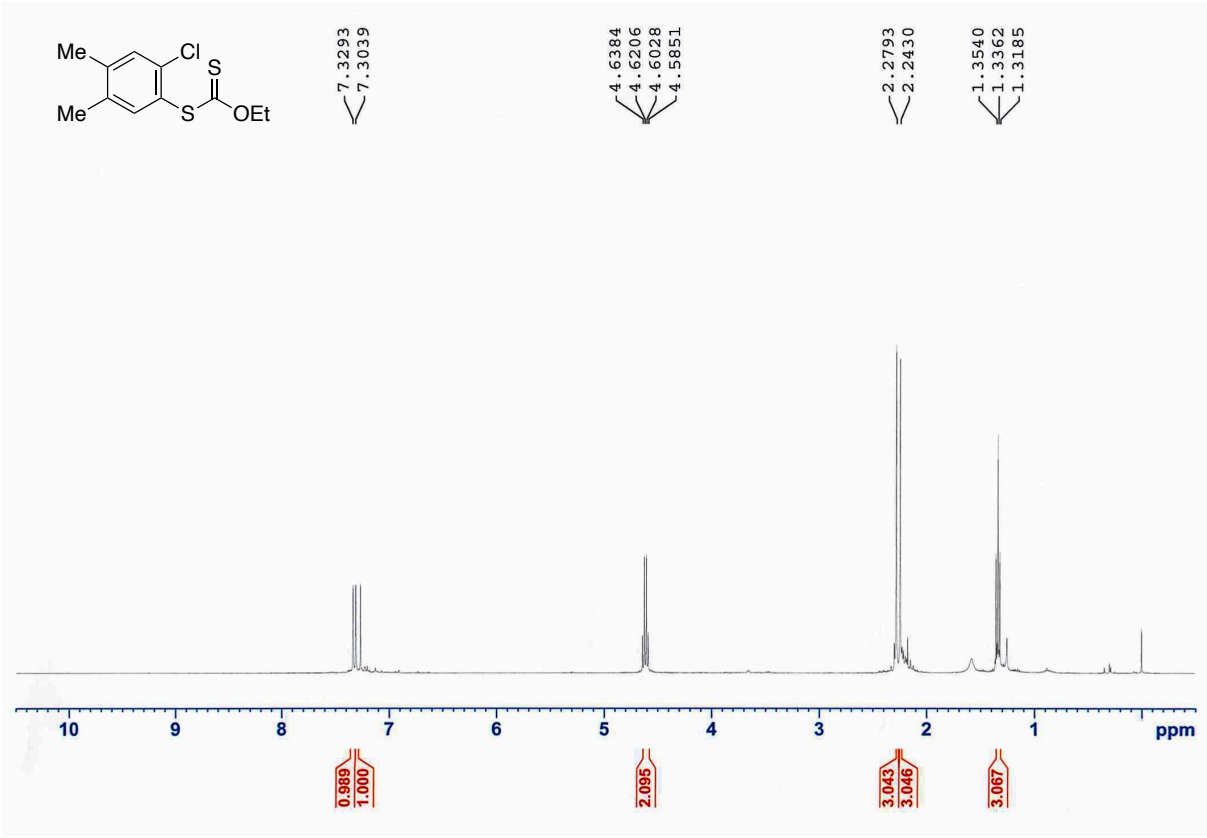


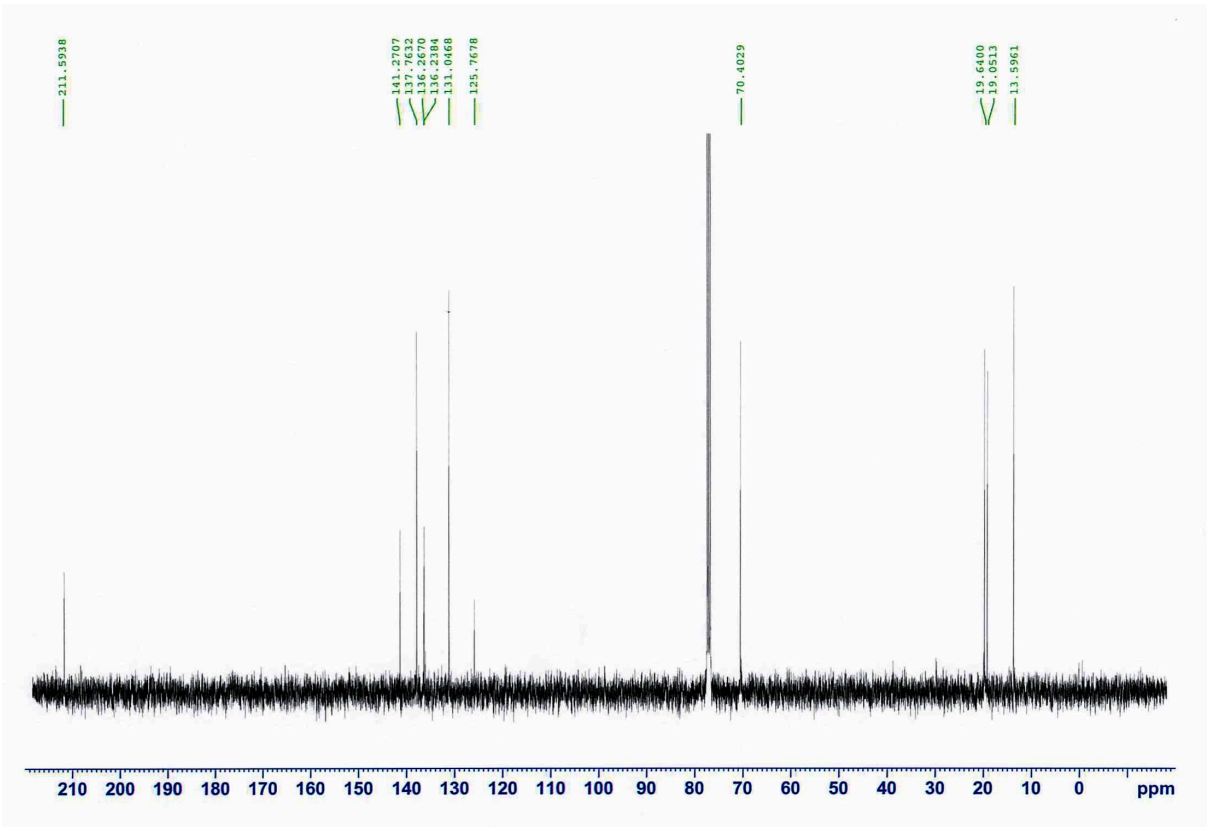
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of *S*-(2-bromo-4,5-dimethylphenyl) *O*-ethyl carbonodithioate (**6a**) ($CDCl_3$)



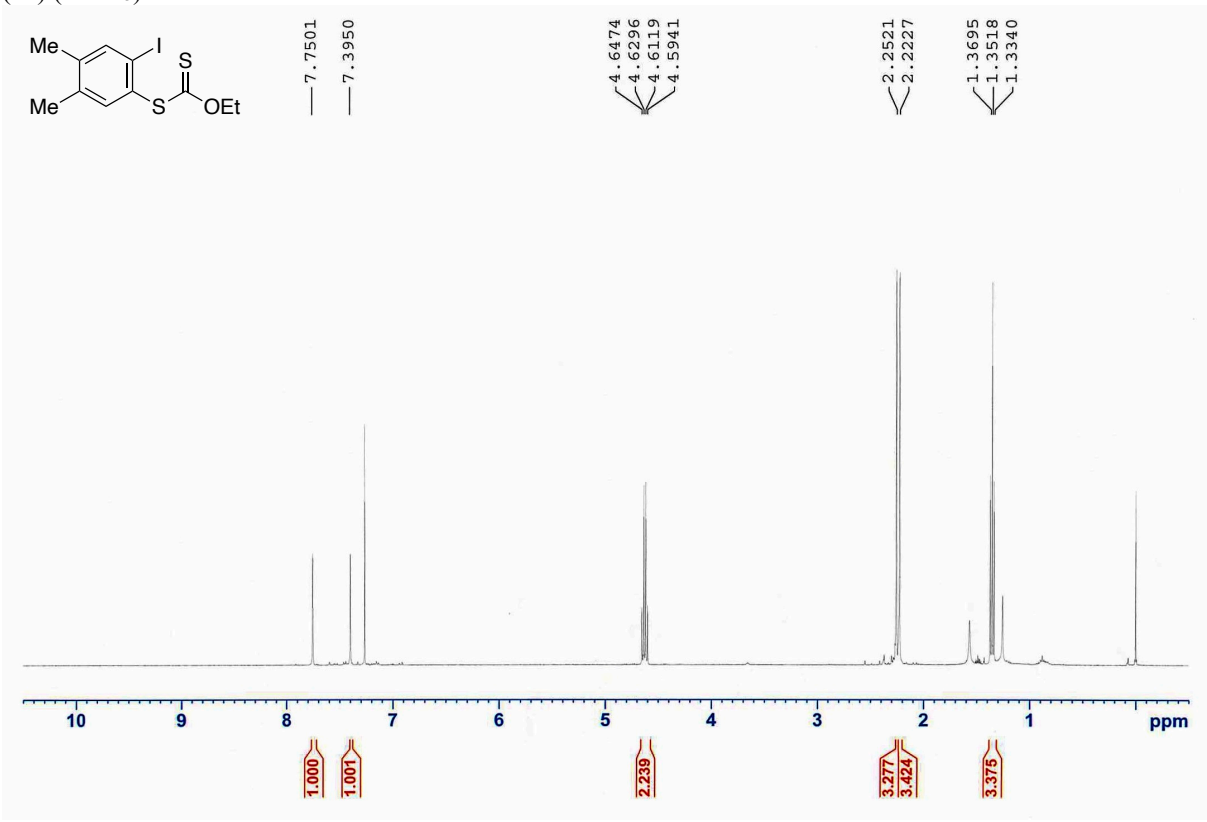


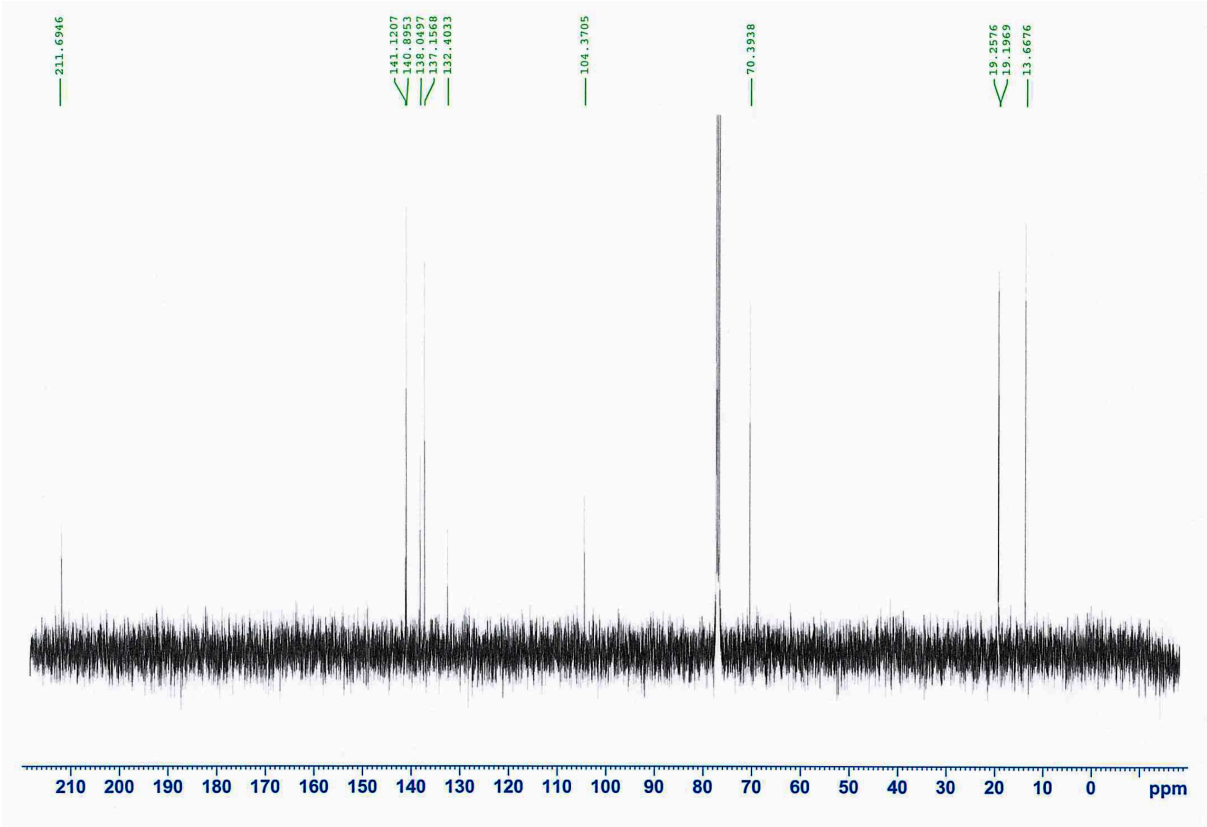
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of *S*-(2-chloro-4,5-dimethylphenyl) *O*-ethyl carbonodithioate (**7a**) ($CDCl_3$)



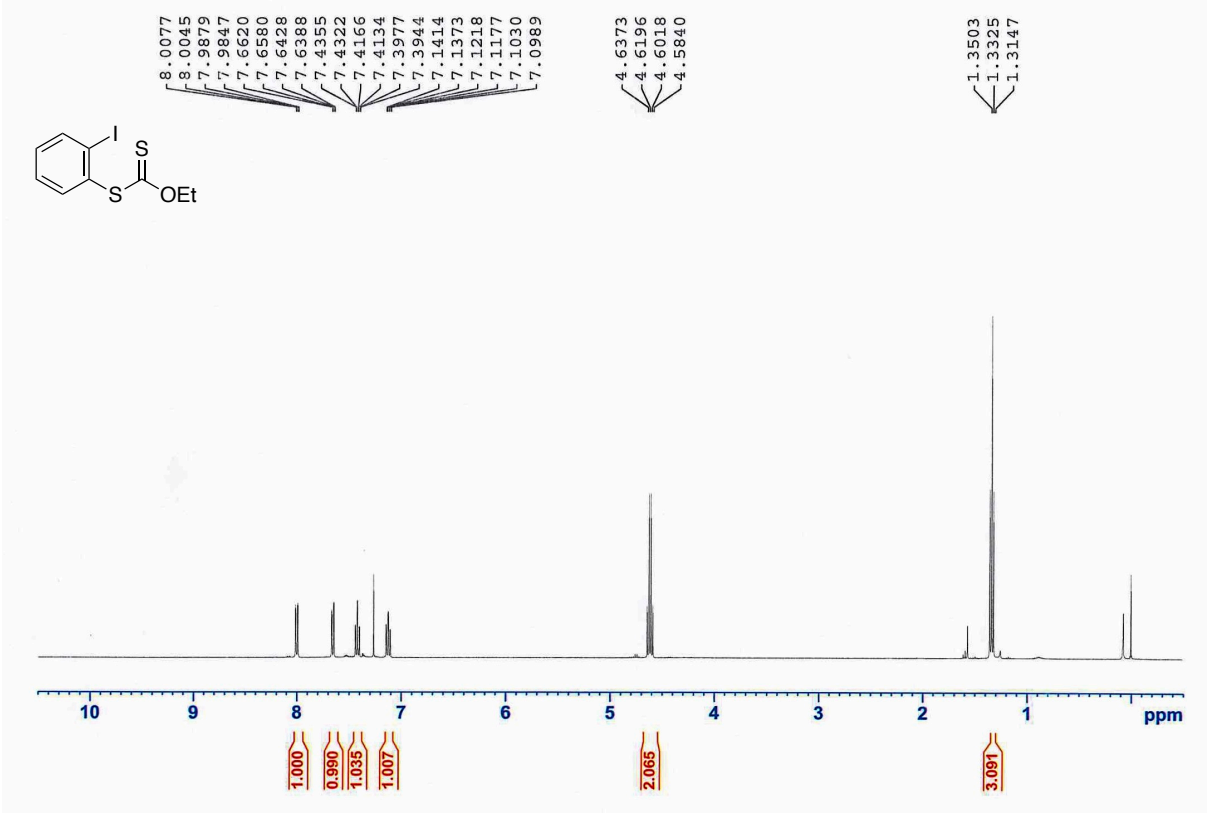


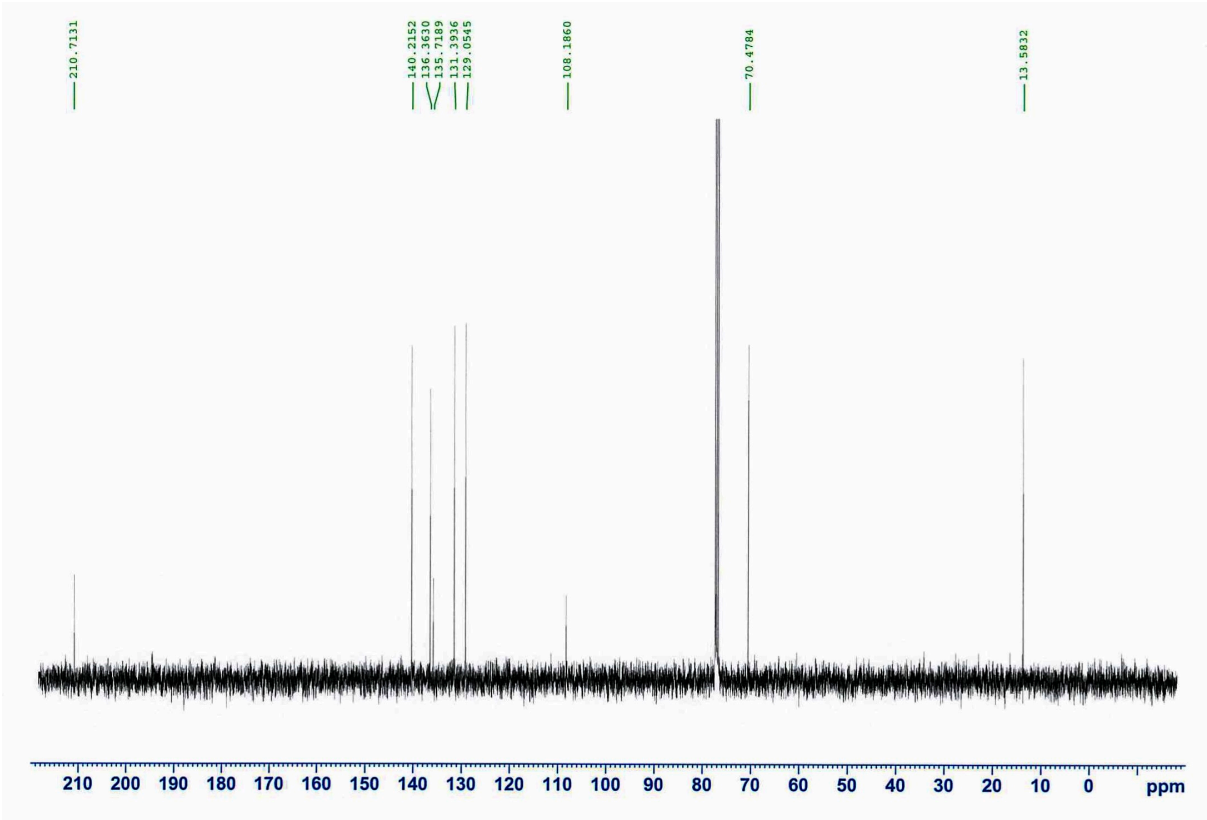
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of *O*-ethyl *S*-(2-iodo-4,5-dimethylphenyl) carbonodithioate (**8a**) ($CDCl_3$)



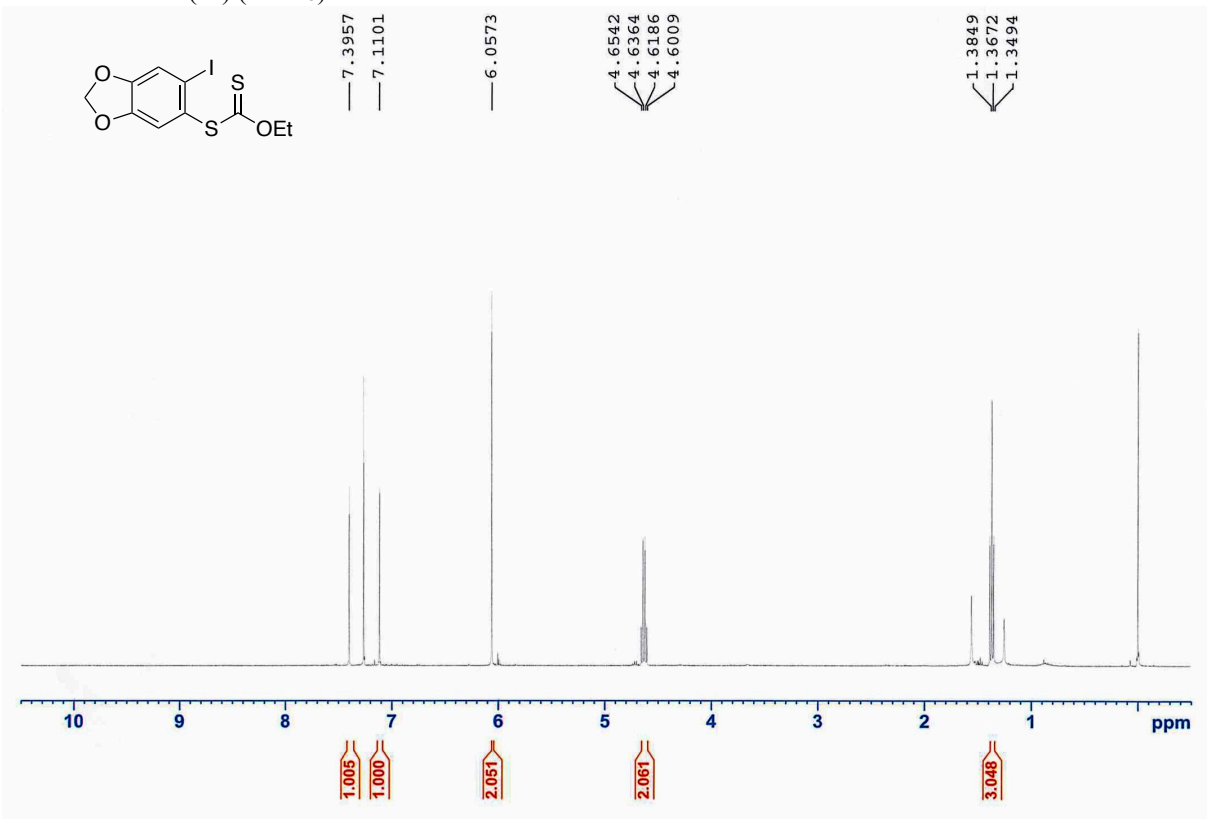


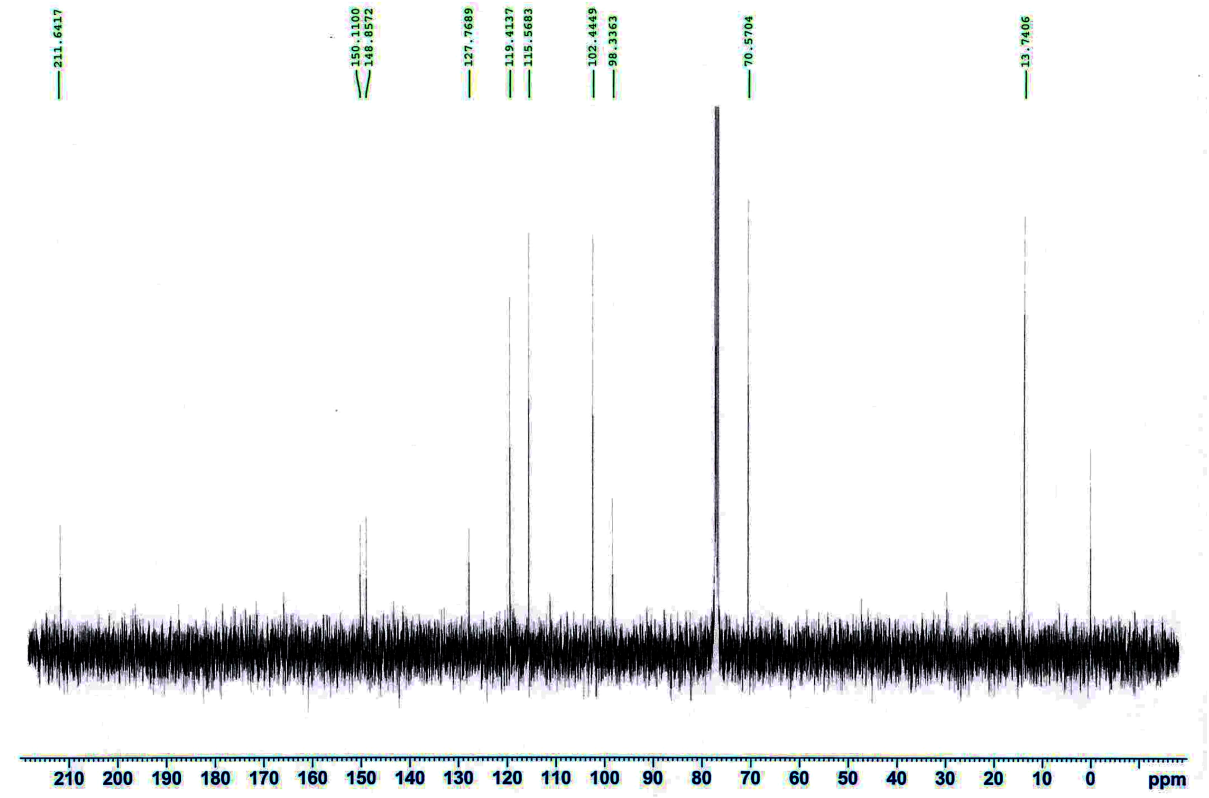
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of *O*-ethyl *S*-(2-iodophenyl) carbonodithioate (**8b**) ($CDCl_3$)



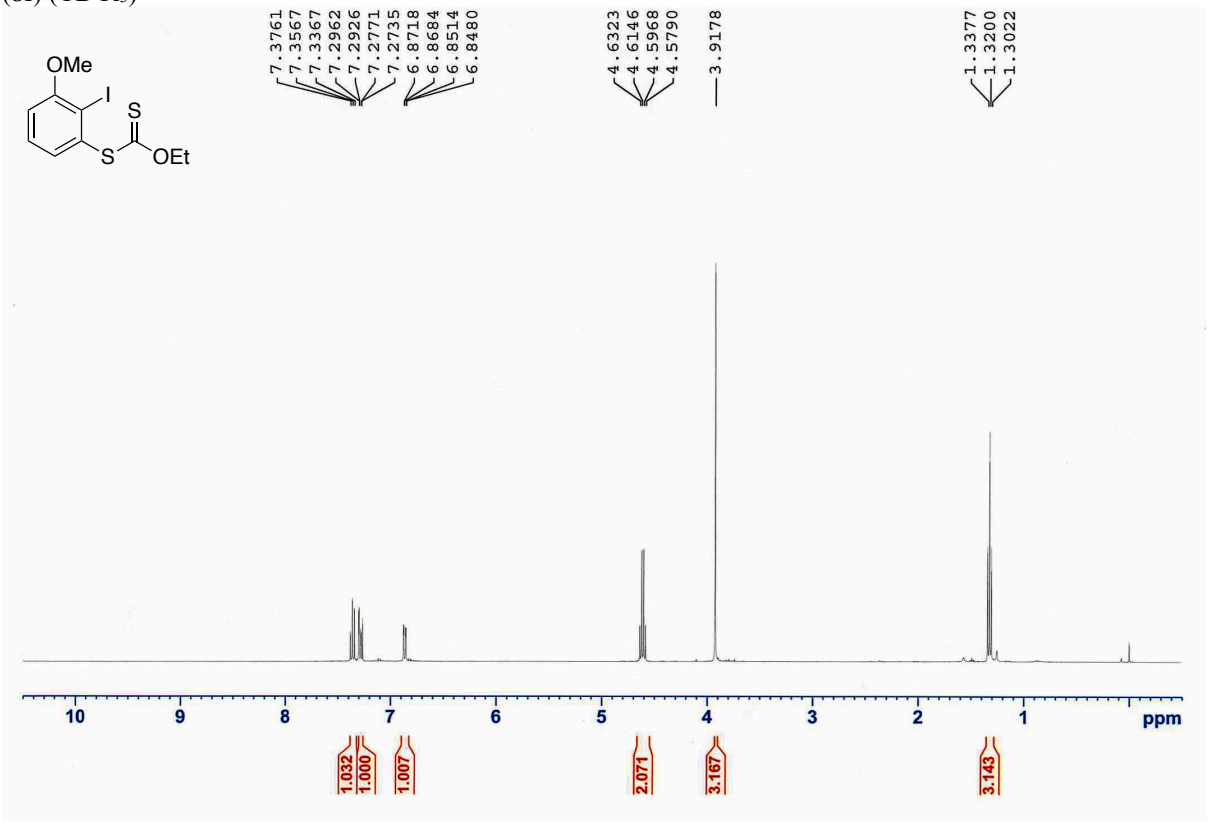


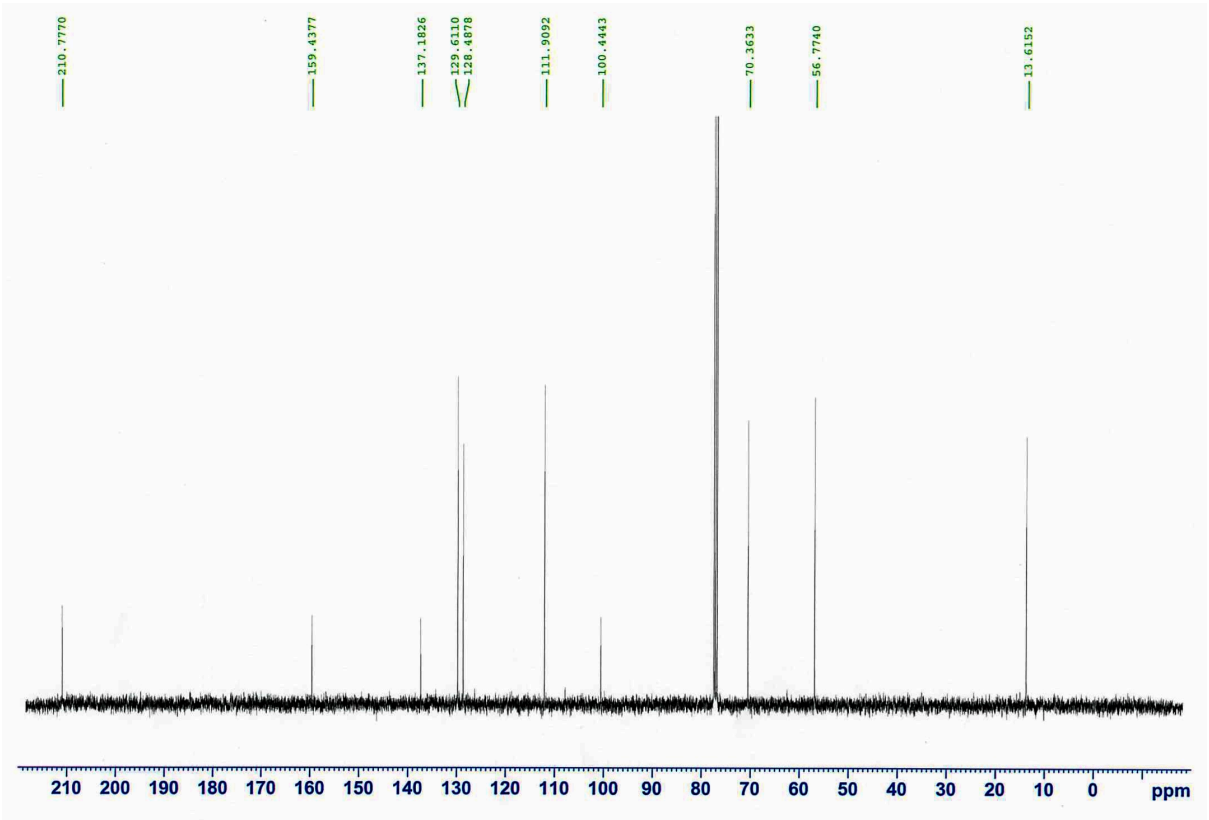
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of *O*-ethyl *S*-(6-iodobenzo[*d*][1,3]dioxol-5-yl) carbonodithioate (**8e**) ($CDCl_3$)



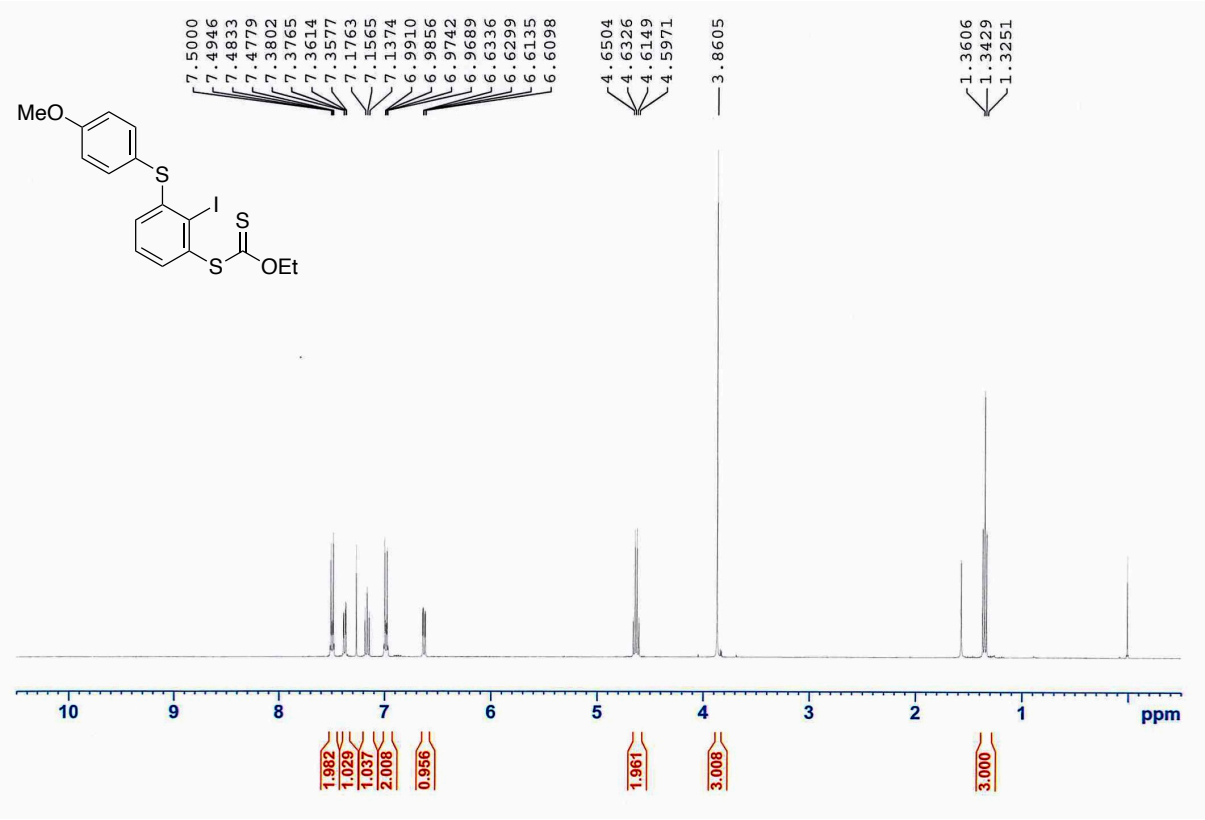


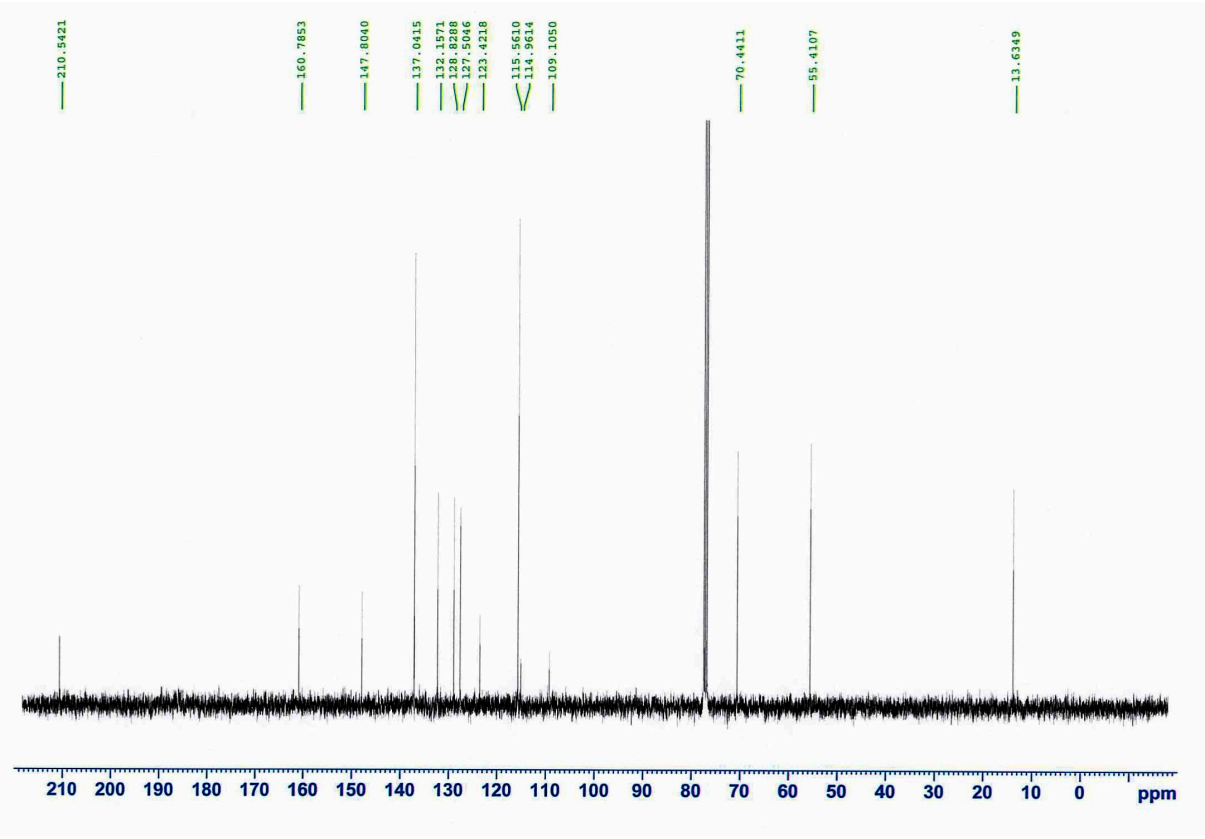
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of *O*-ethyl *S*-(2-iodo-3-methoxyphenyl) carbonodithioate (**8f**) ($CDCl_3$)



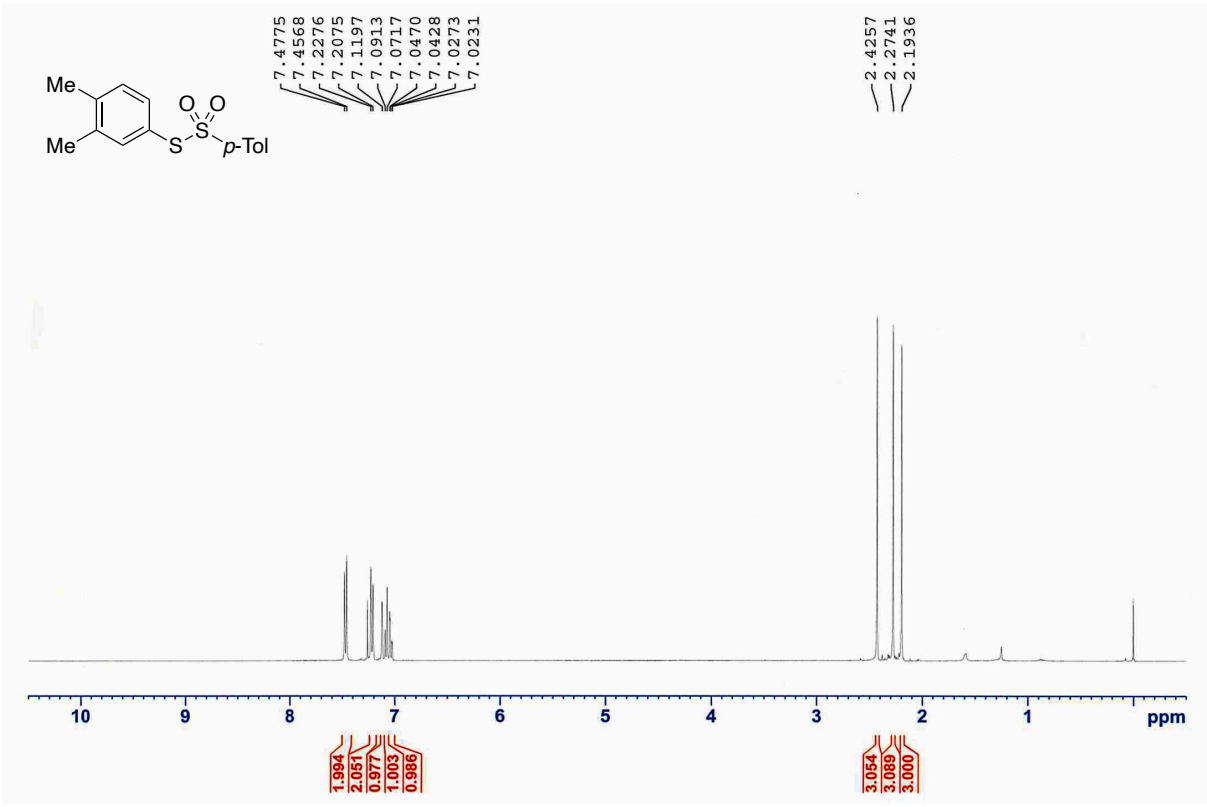


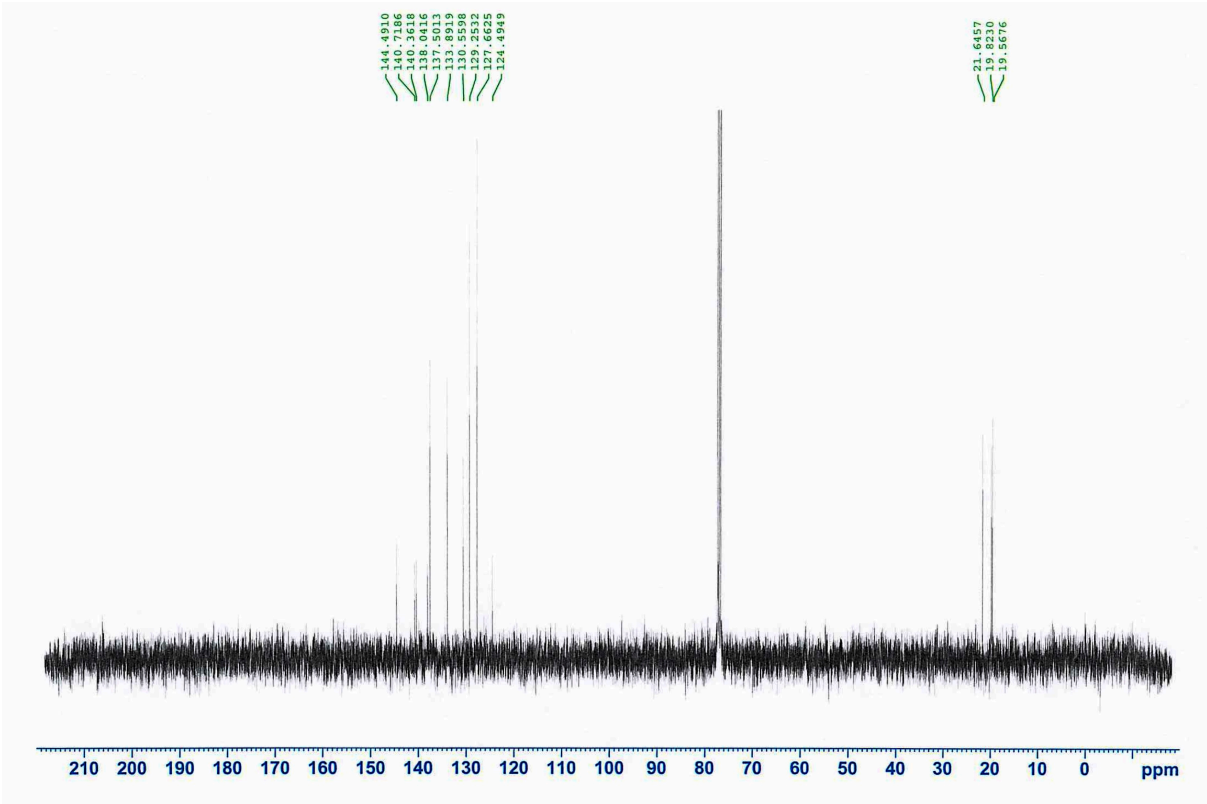
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of *O*-ethyl *S*-(2-iodo-3-((4-methoxyphenyl)thio)phenyl) carbonodithioate (**8g**) ($CDCl_3$)



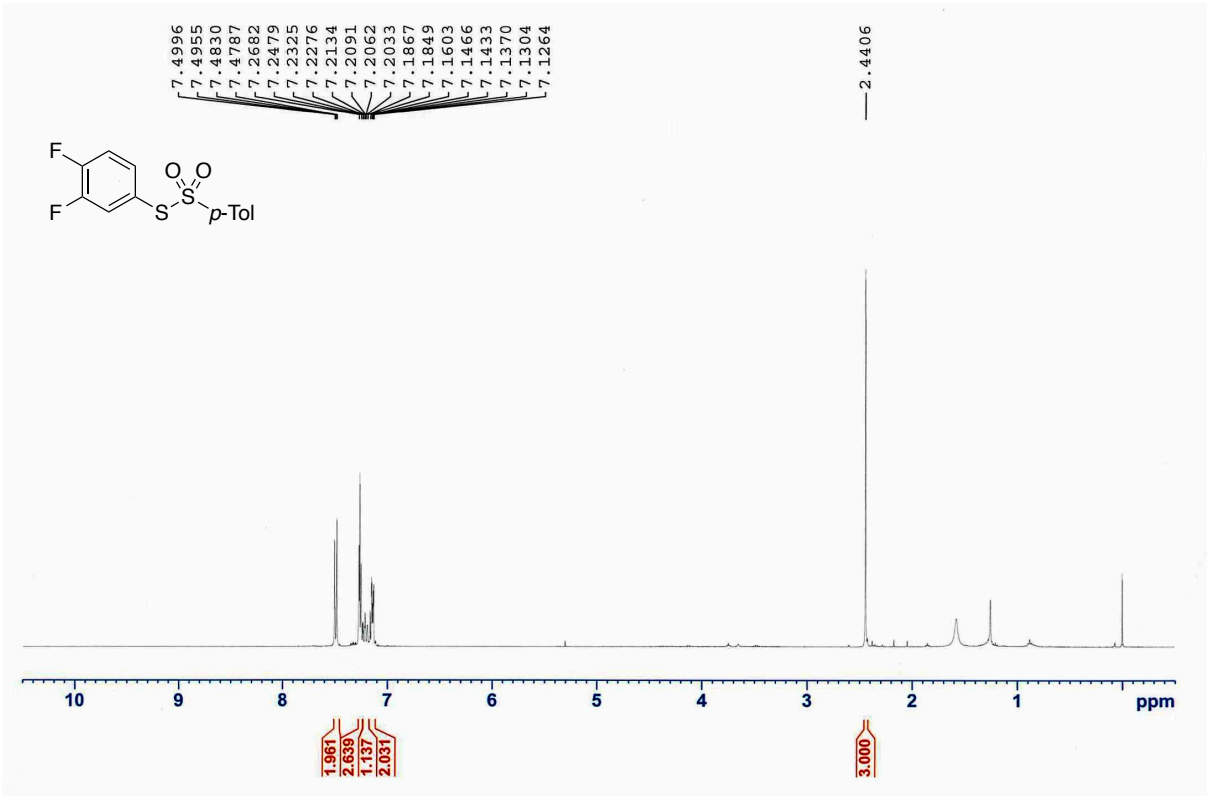


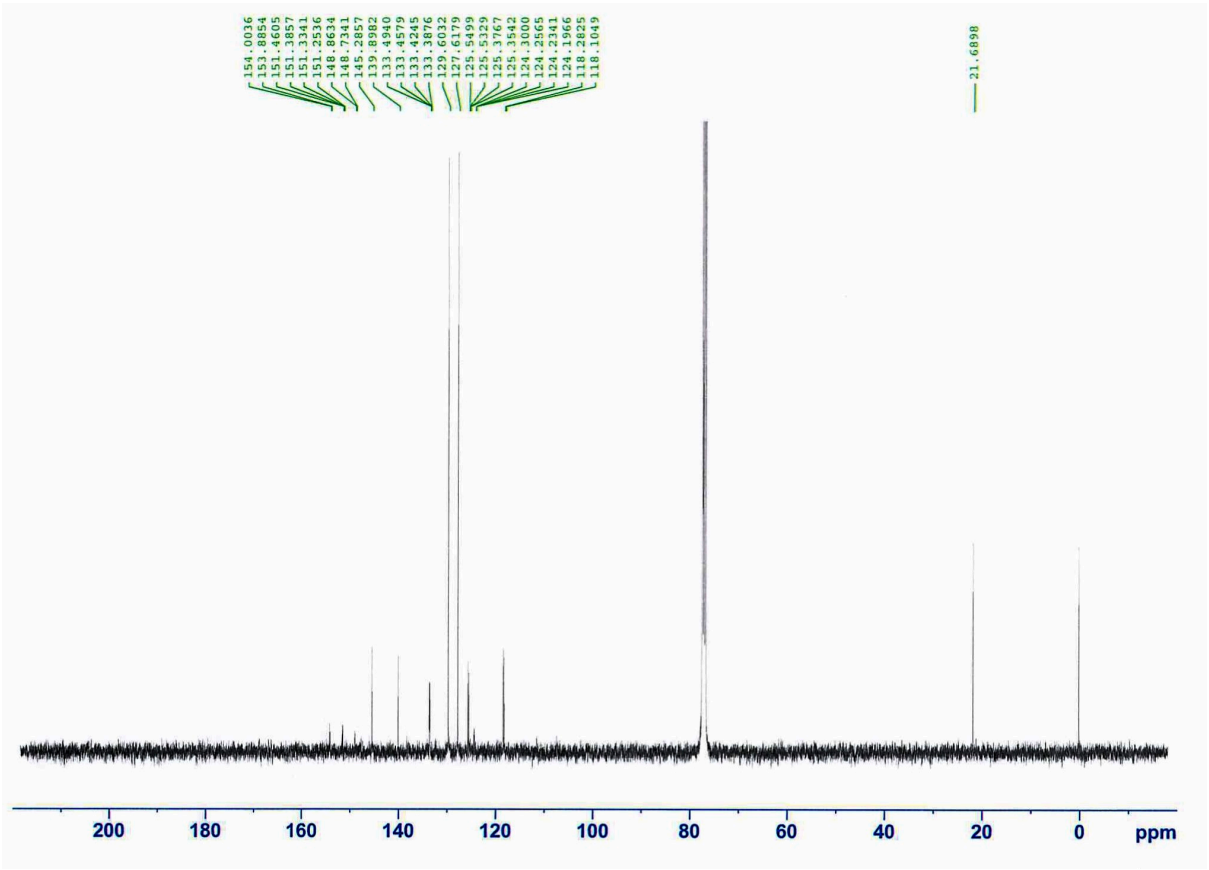
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of *S*-(3,4-dimethylphenyl) 4-methylbenzenesulfonothioate (**3a**) ($CDCl_3$)



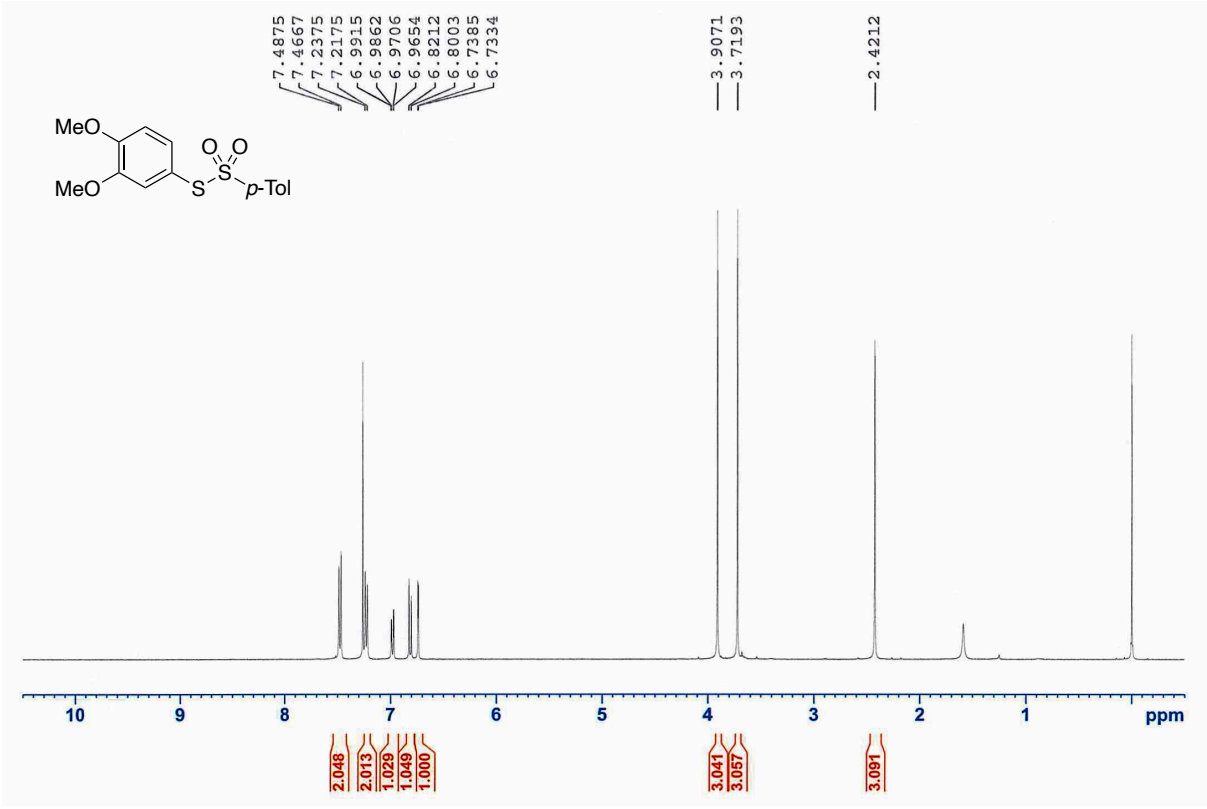


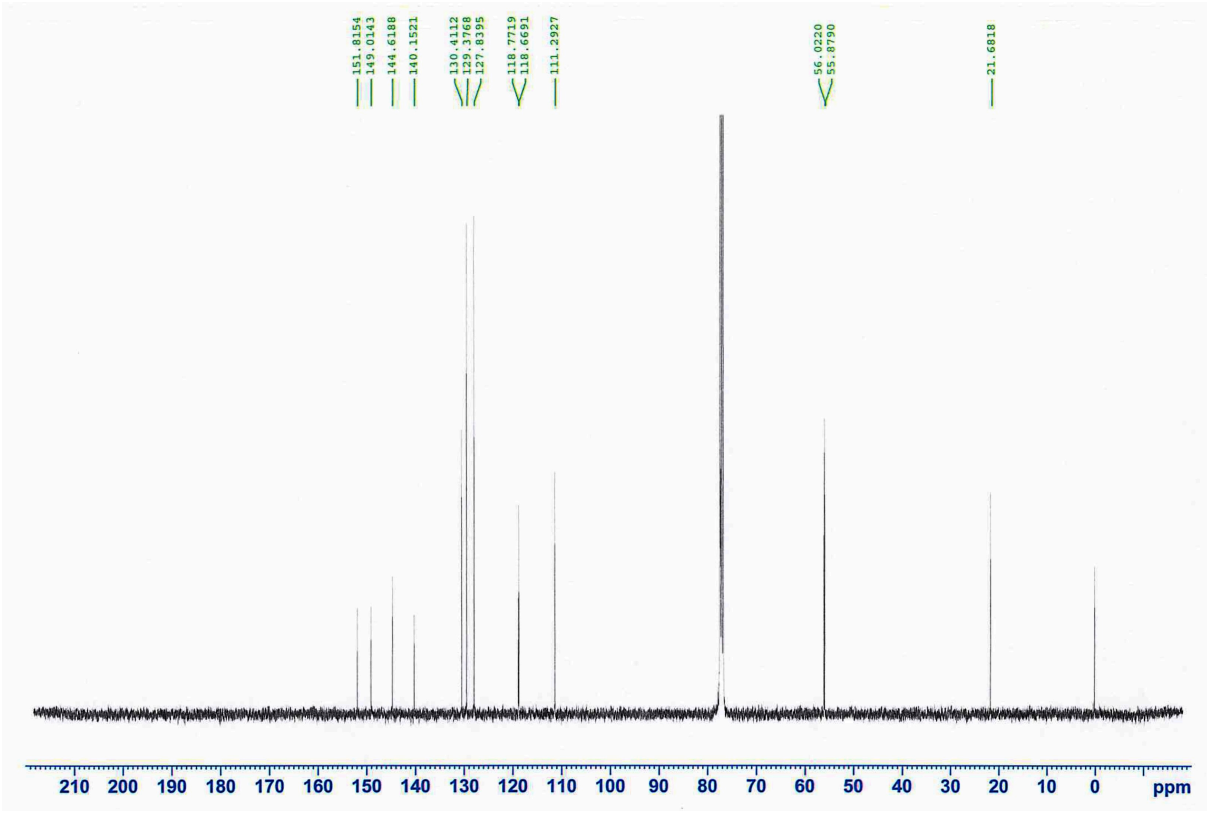
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of *S*-(3,4-difluorophenyl) 4-methylbenzenesulfonothioate (**3c**) ($CDCl_3$)



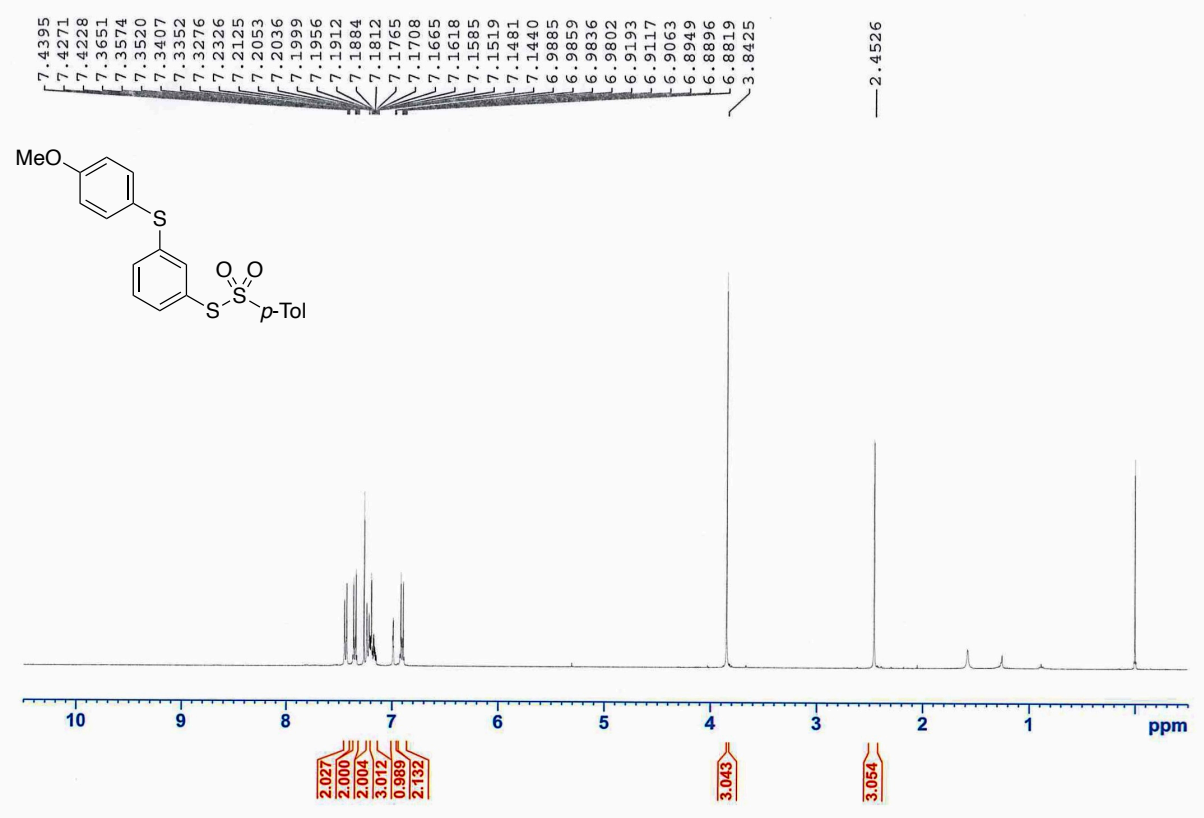


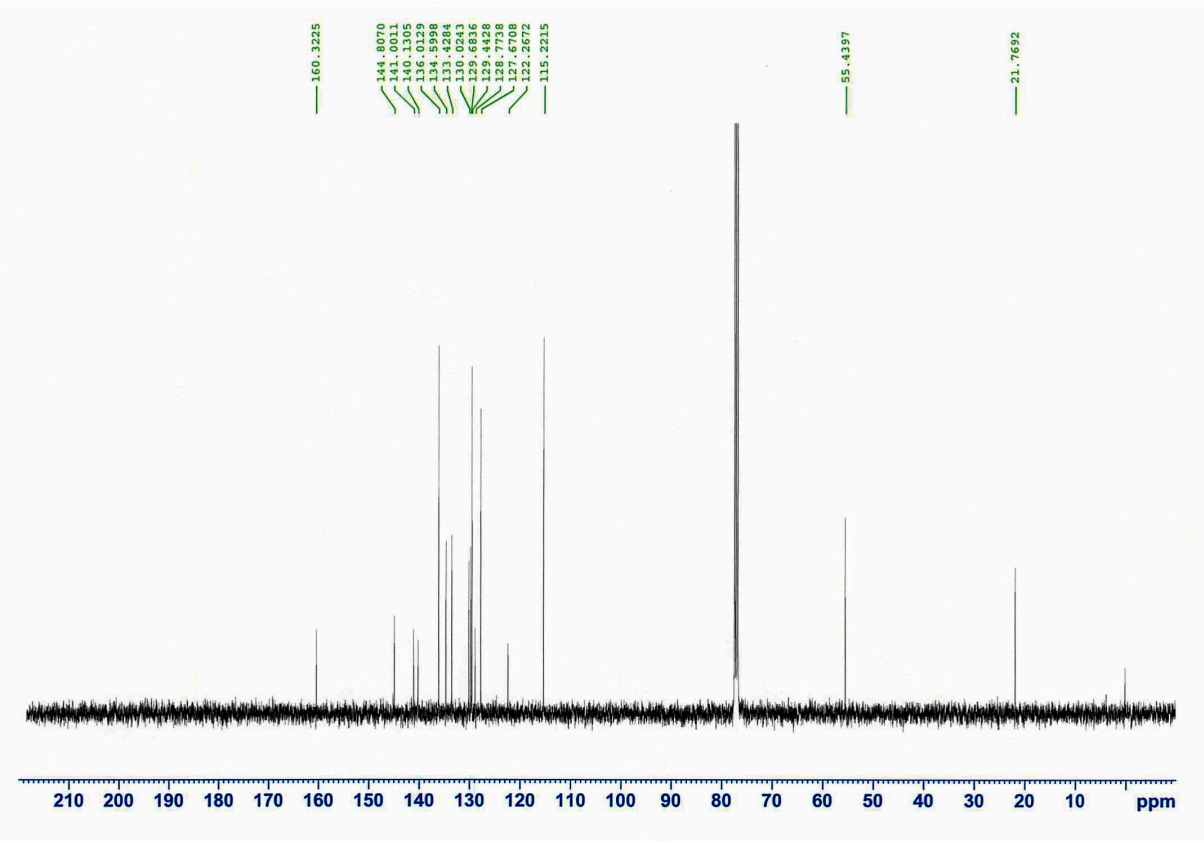
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of *S*-(3,4-dimethoxyphenyl) 4-methylbenzenesulfonothioate (**3d**) ($CDCl_3$)



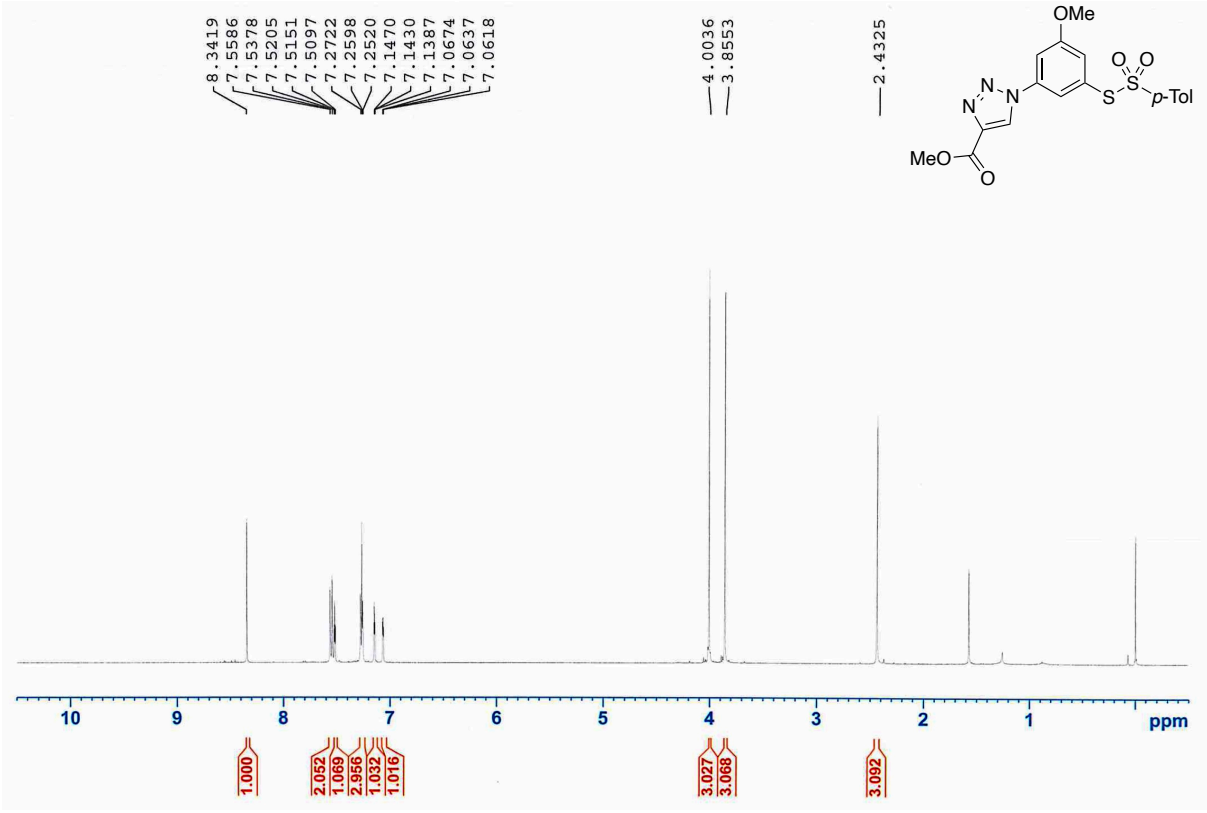


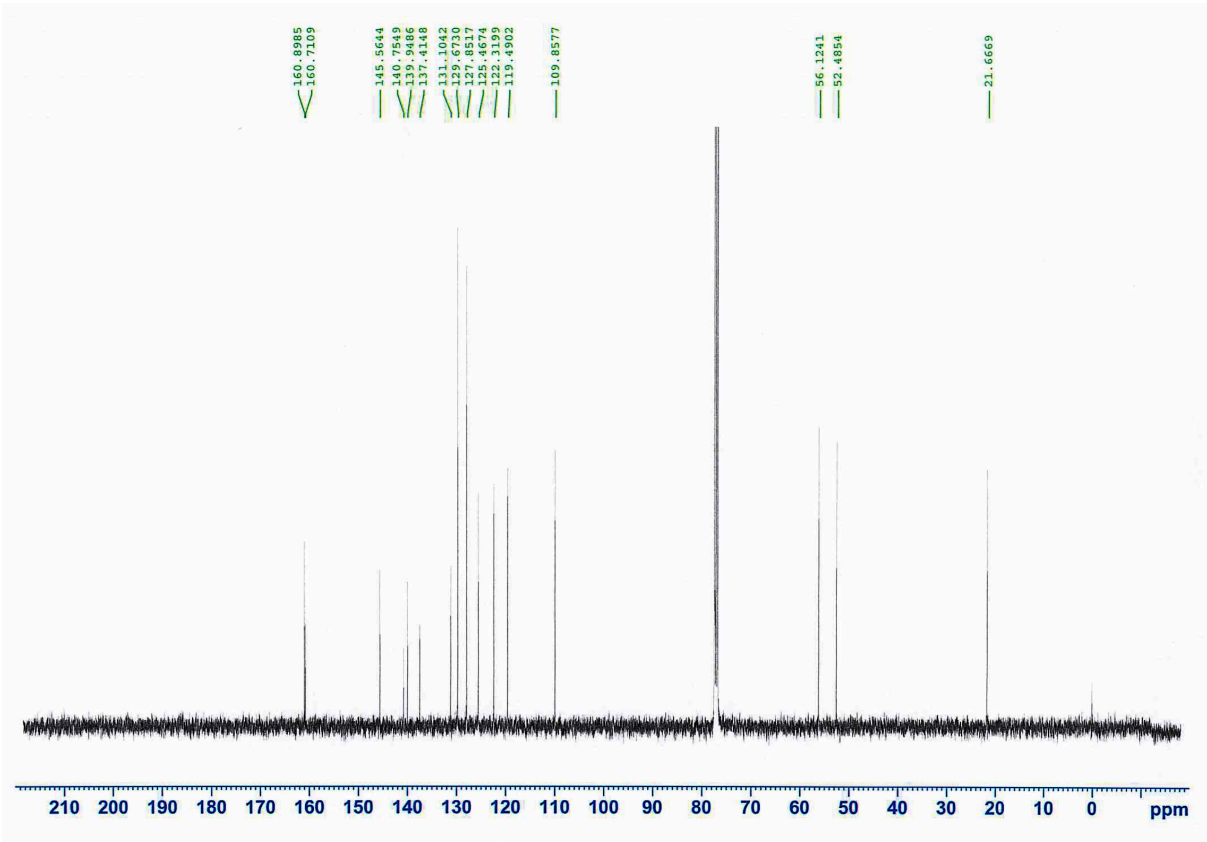
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of *S*-(3-((4-methoxyphenyl)thio)phenyl) 4-methylbenzenesulfonothioate (**3g**) ($CDCl_3$)



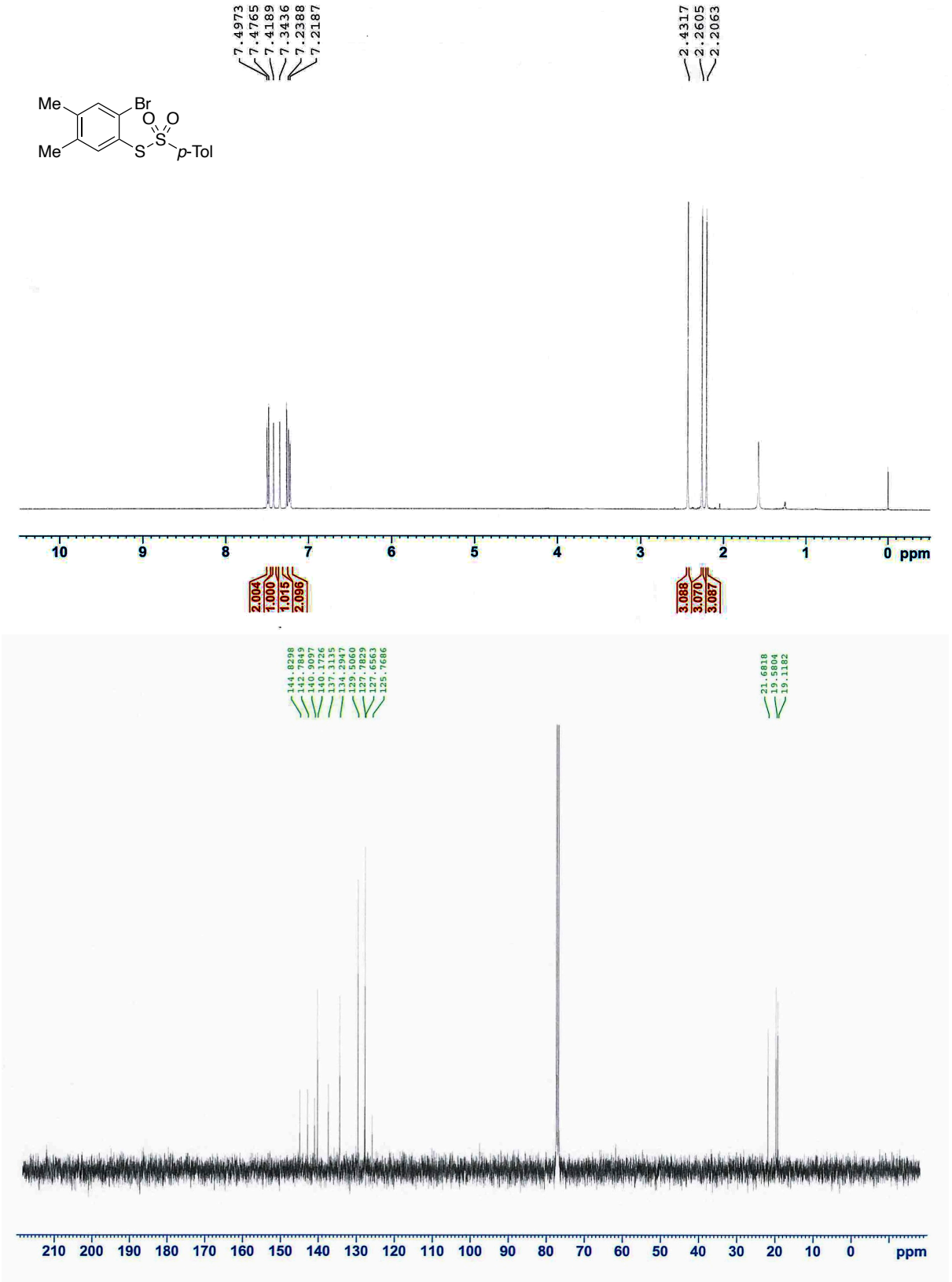


^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of methyl 1-(3-methoxy-5-(tosylthio)phenyl)-1*H*-1,2,3-triazole-4-carboxylate (**3j**) ($CDCl_3$)

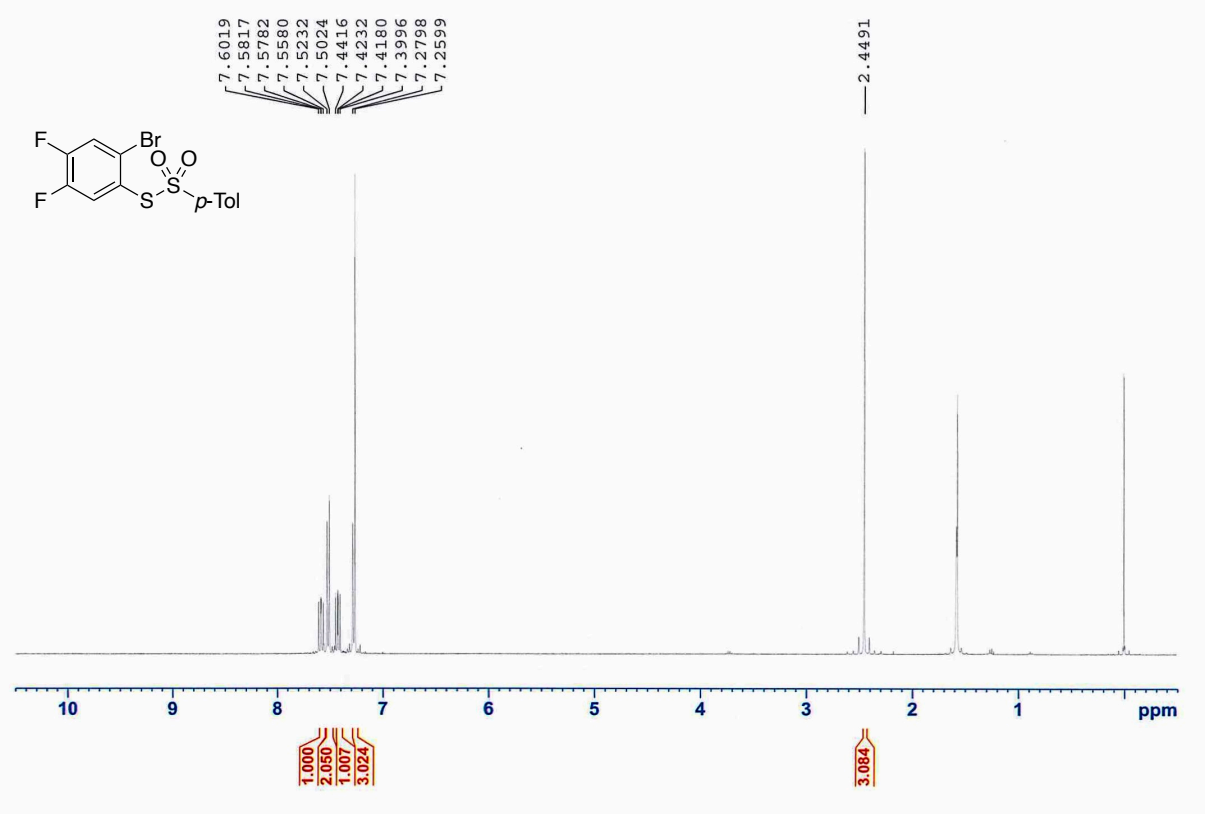


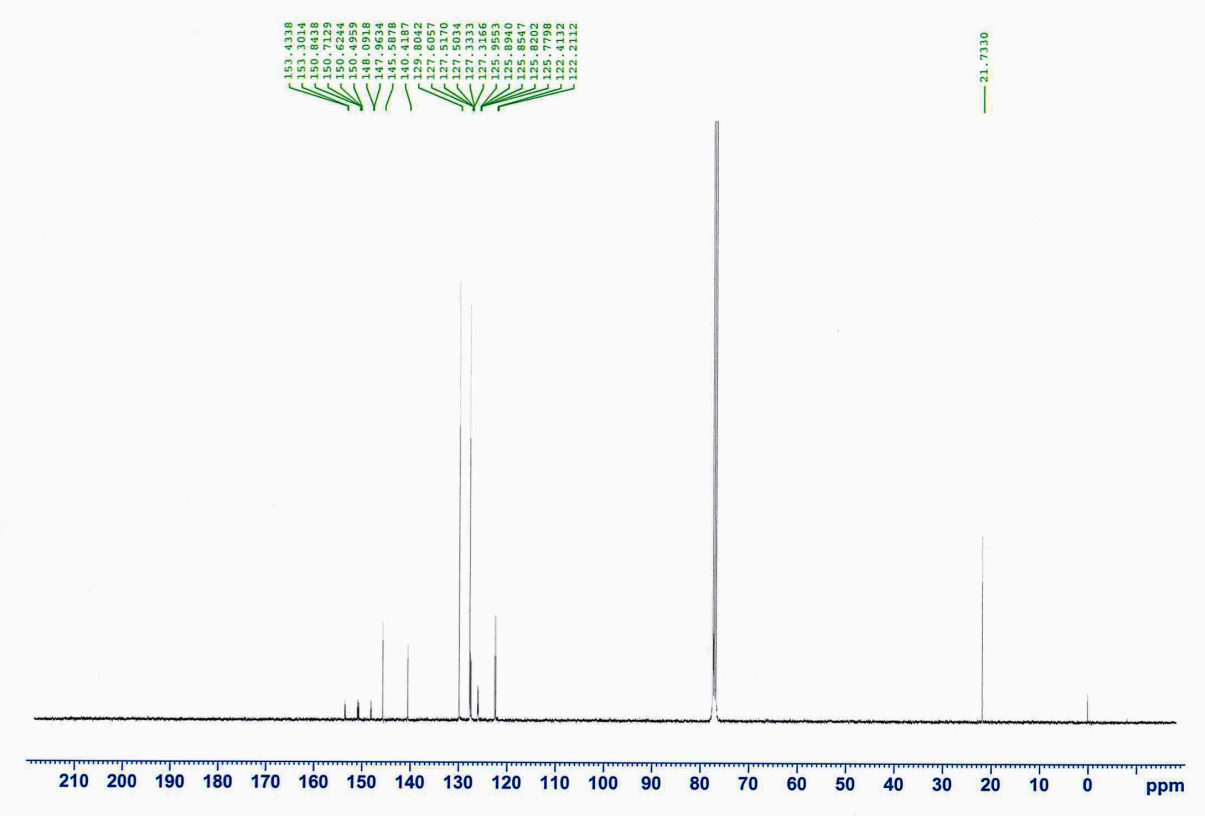


^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of *S*-(2-bromo-4,5-dimethylphenyl) 4-methylbenzenesulfonothioate (**5a**) ($CDCl_3$)

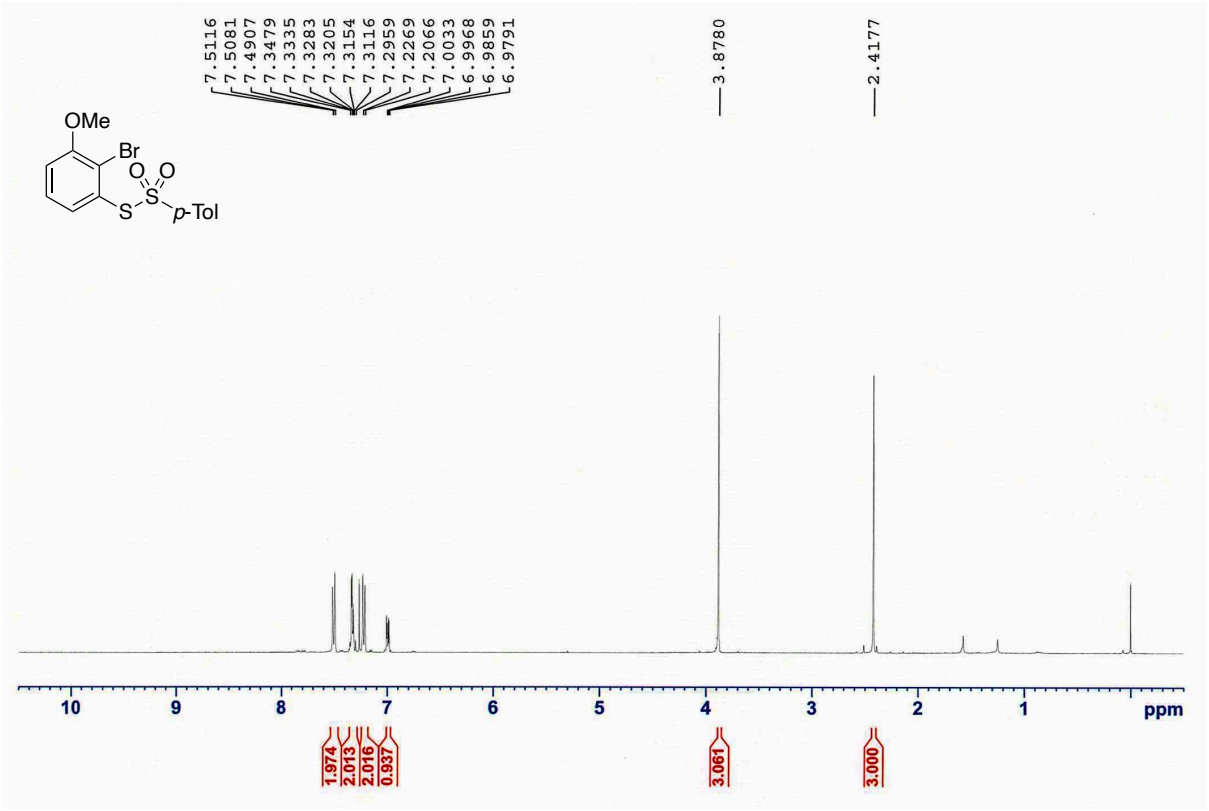


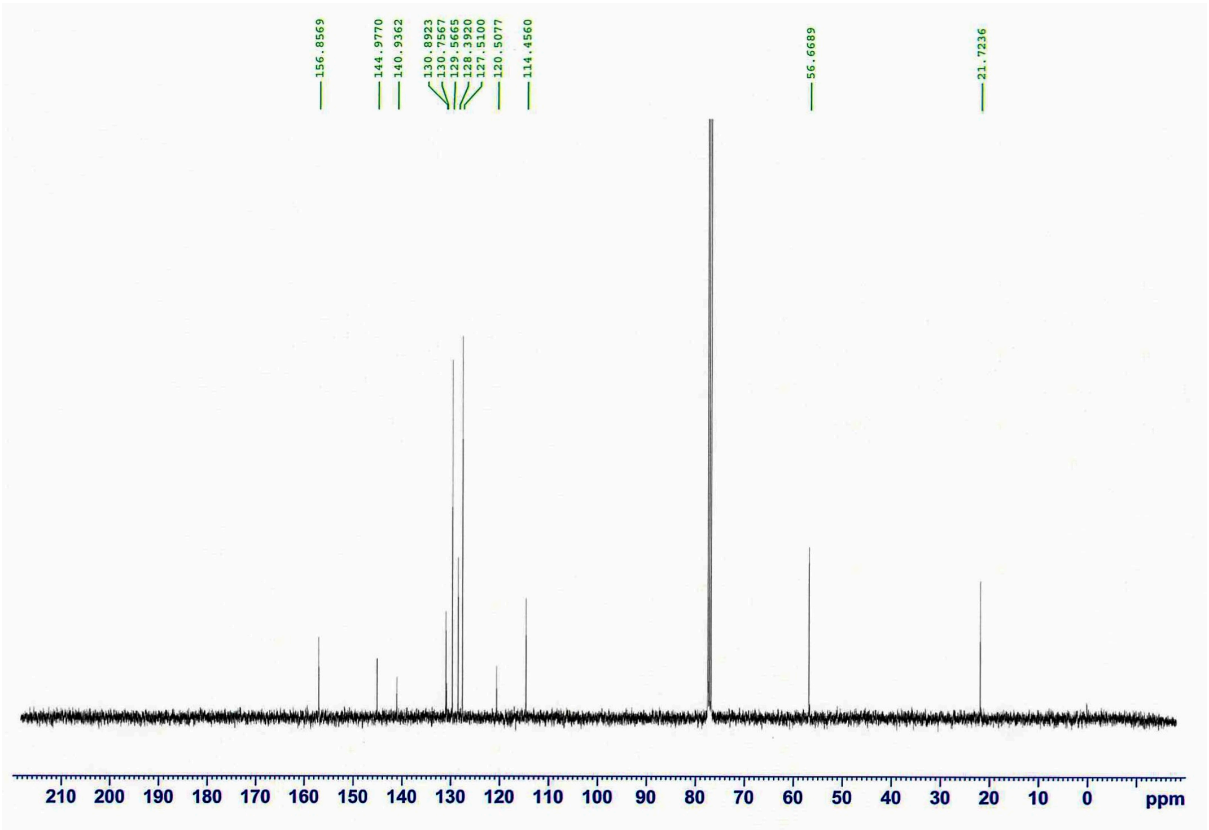
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of *S*-(2-bromo-4,5-difluorophenyl) 4-methylbenzenesulfonothioate (**5c**) ($CDCl_3$)



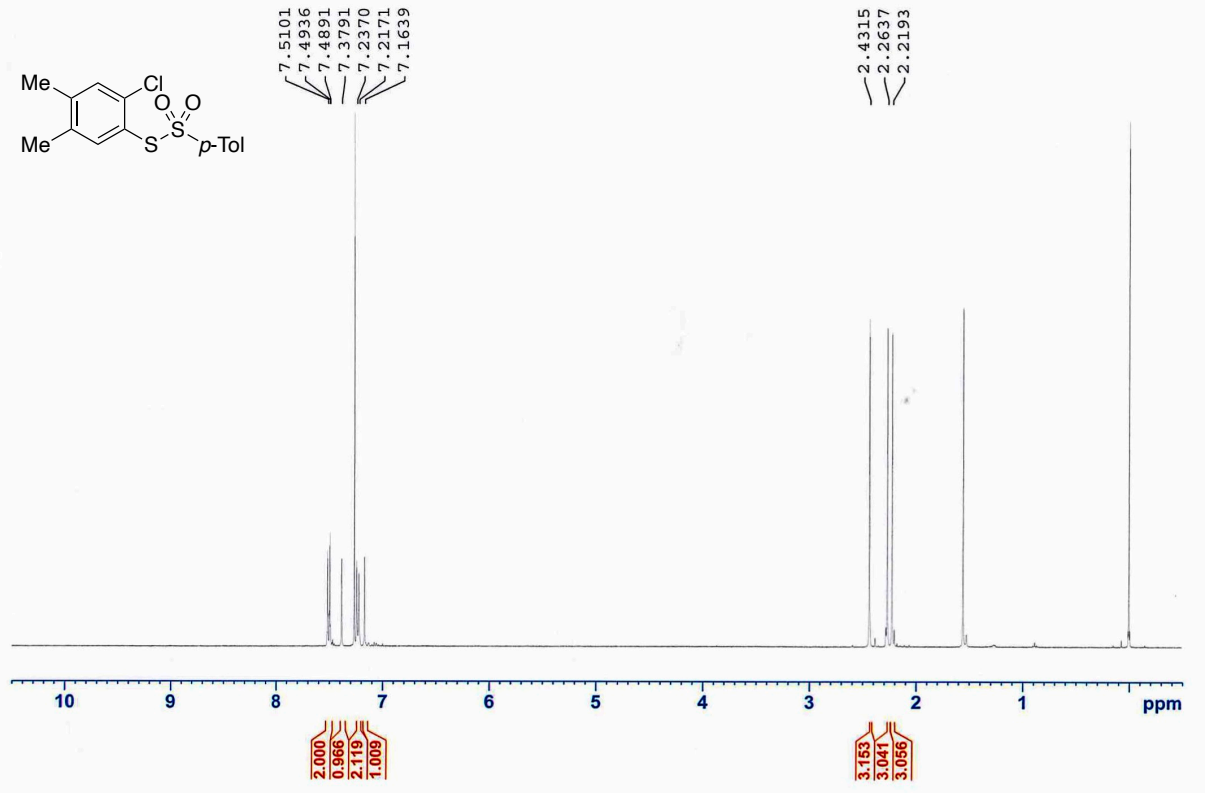


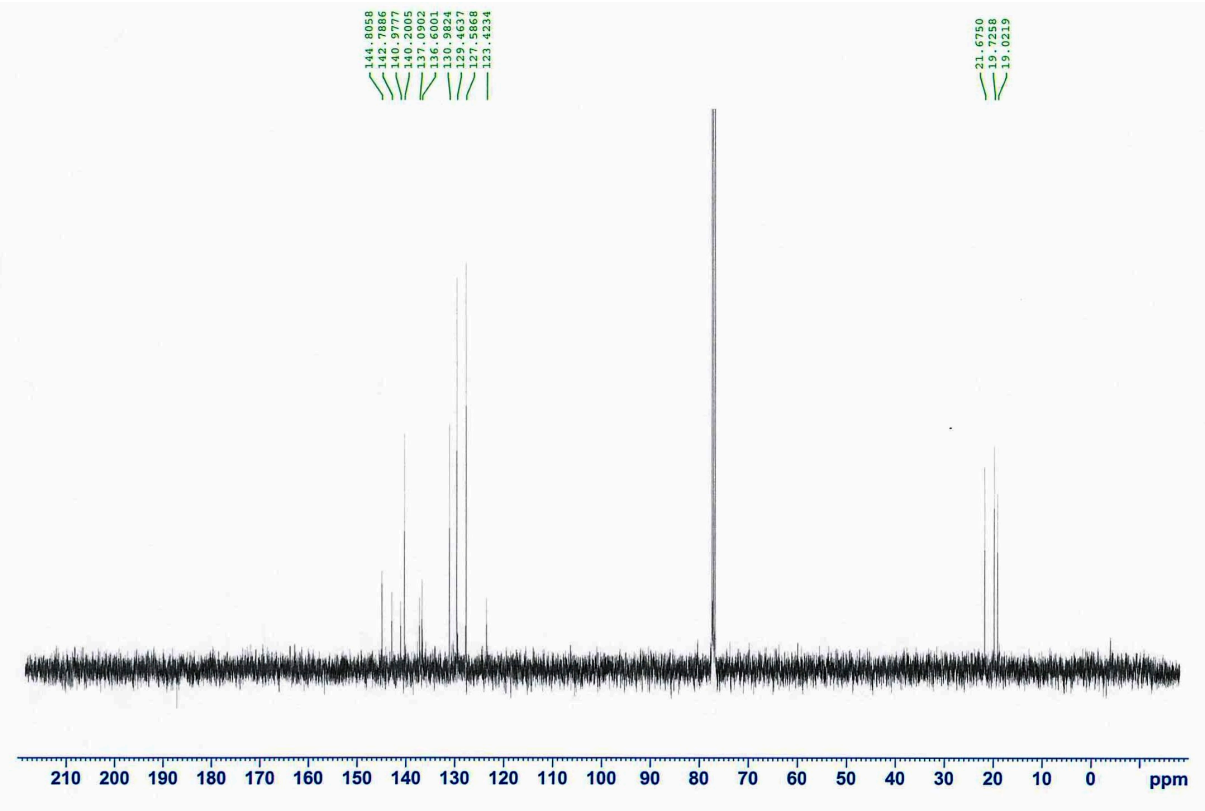
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of *S*-(2-bromo-3-methoxyphenyl) 4-methylbenzenesulfonothioate (**5f**) ($CDCl_3$)



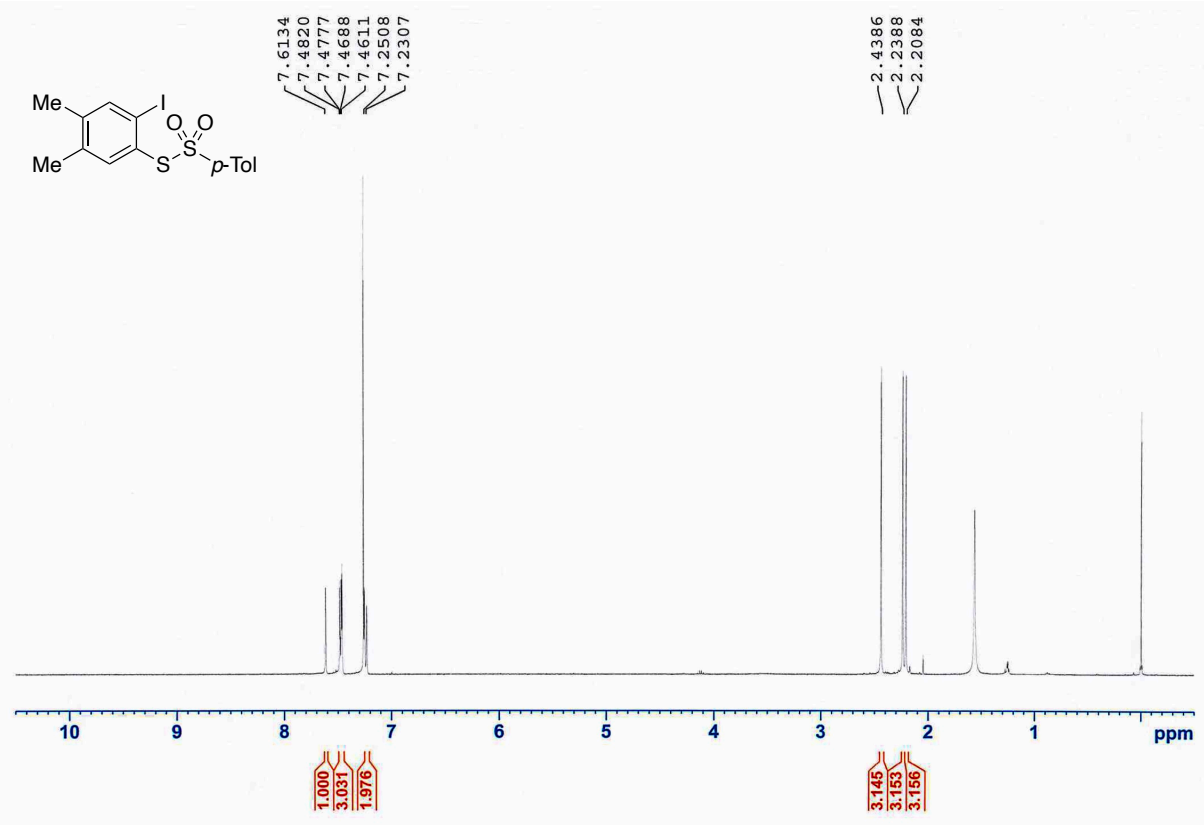


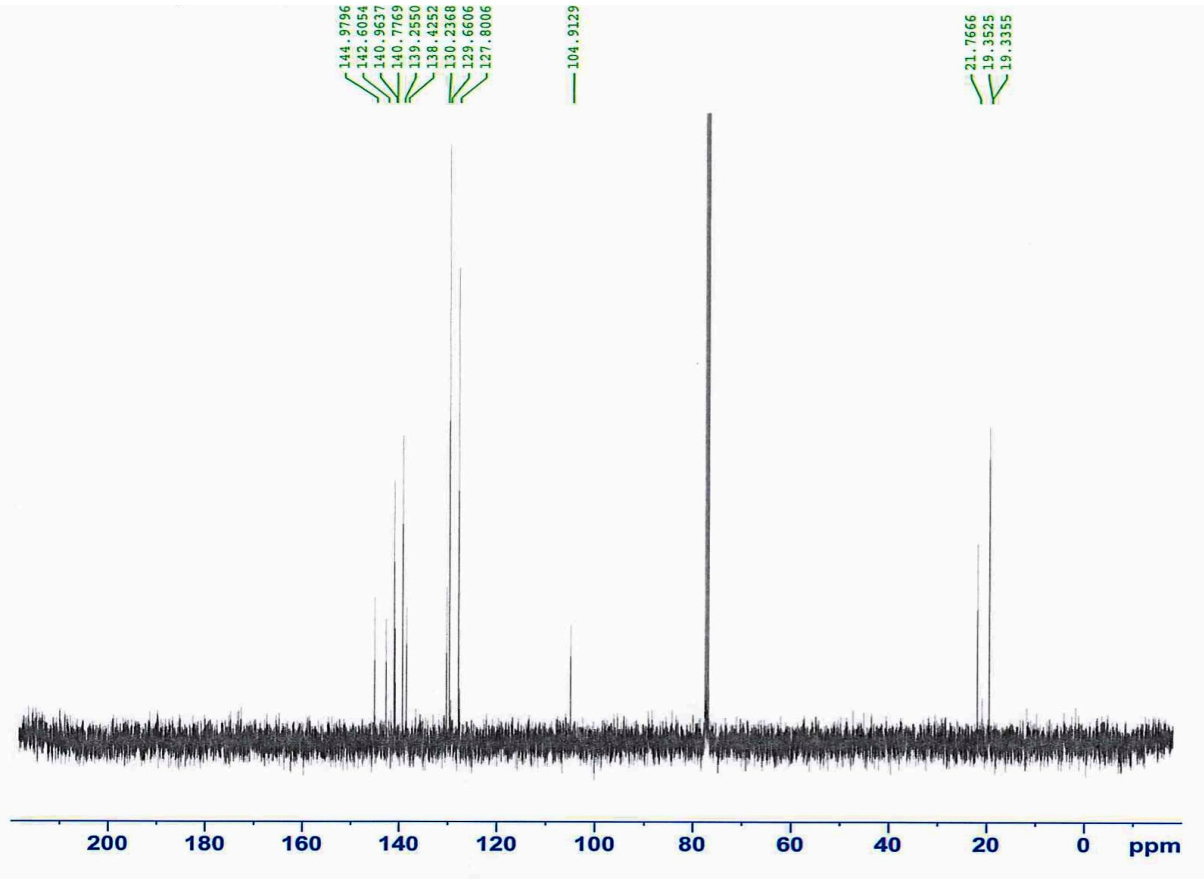
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of *S*-(2-chloro-4,5-dimethylphenyl) 4-methylbenzenesulfonothioate (**9a**) ($CDCl_3$)



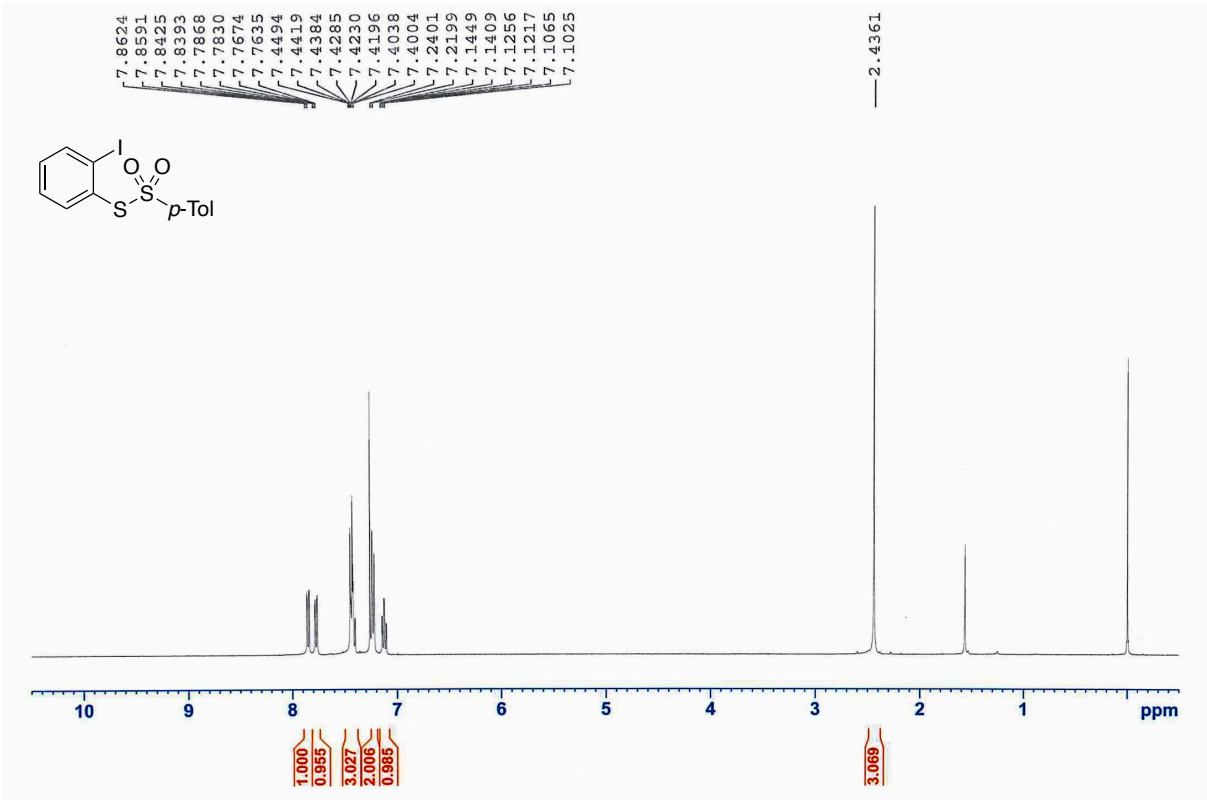


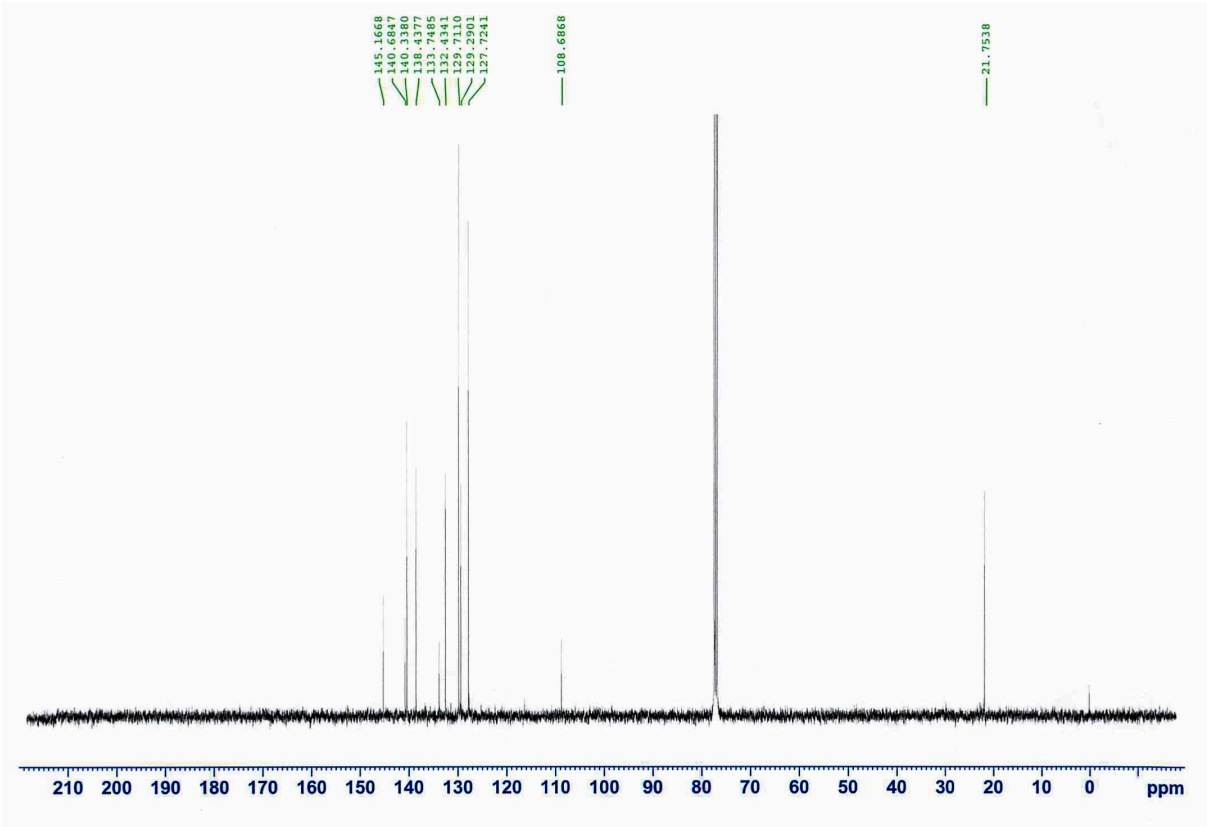
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of *S*-(2-iodo-4,5-dimethylphenyl) 4-methylbenzenesulfonothioate (**10a**) ($CDCl_3$)



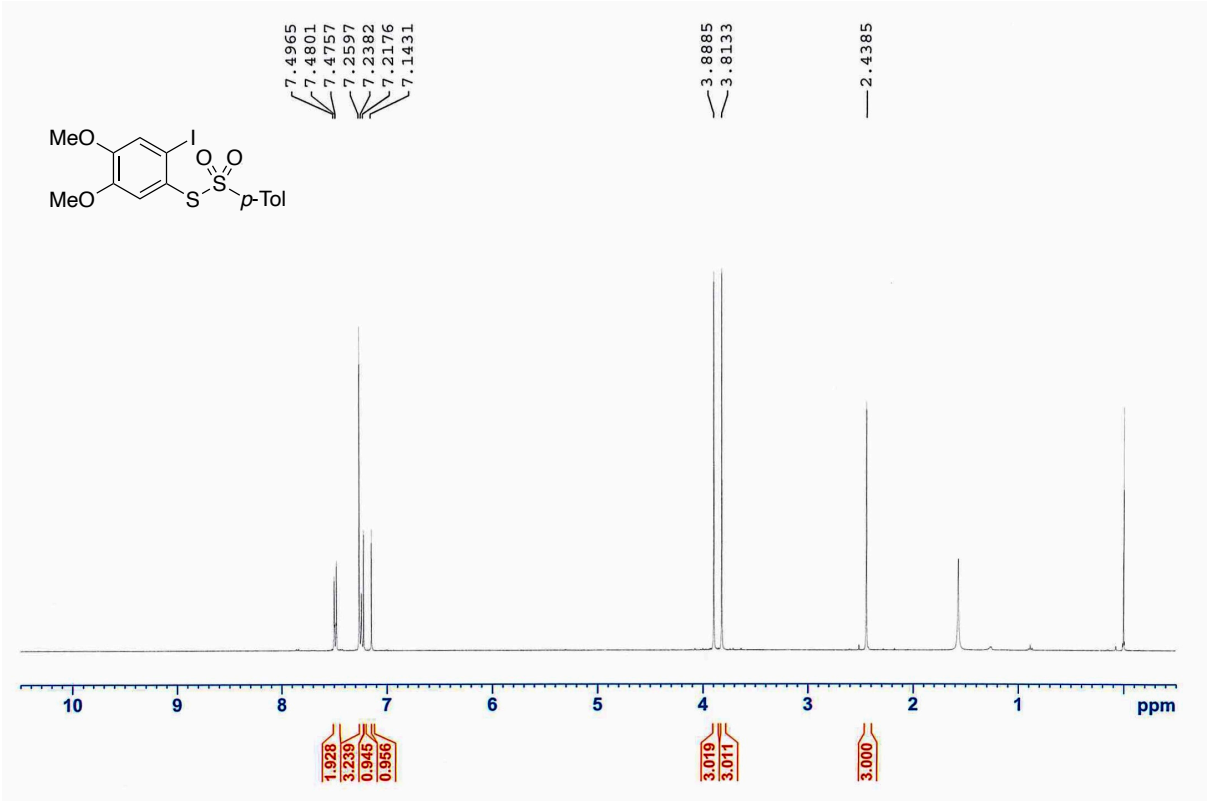


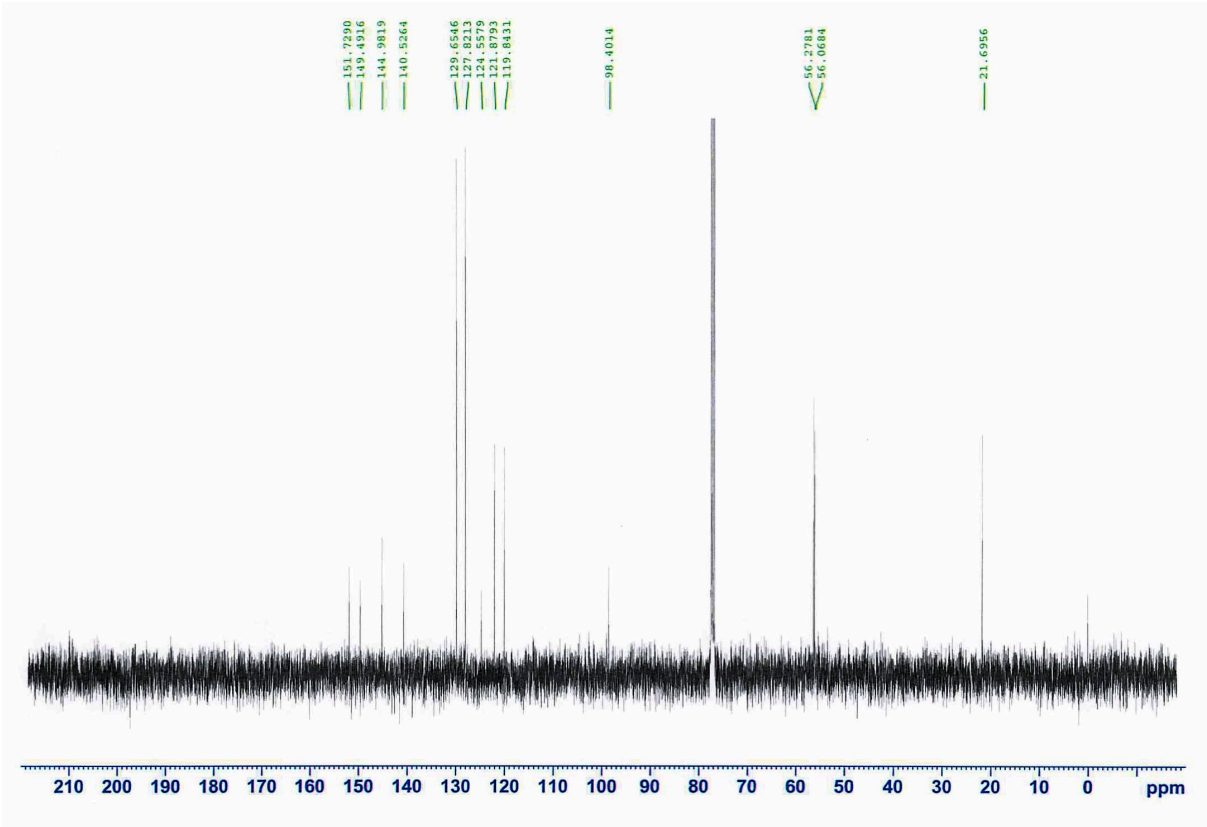
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of *S*-(2-iodophenyl) 4-methylbenzenesulfonothioate (**10b**) ($CDCl_3$)



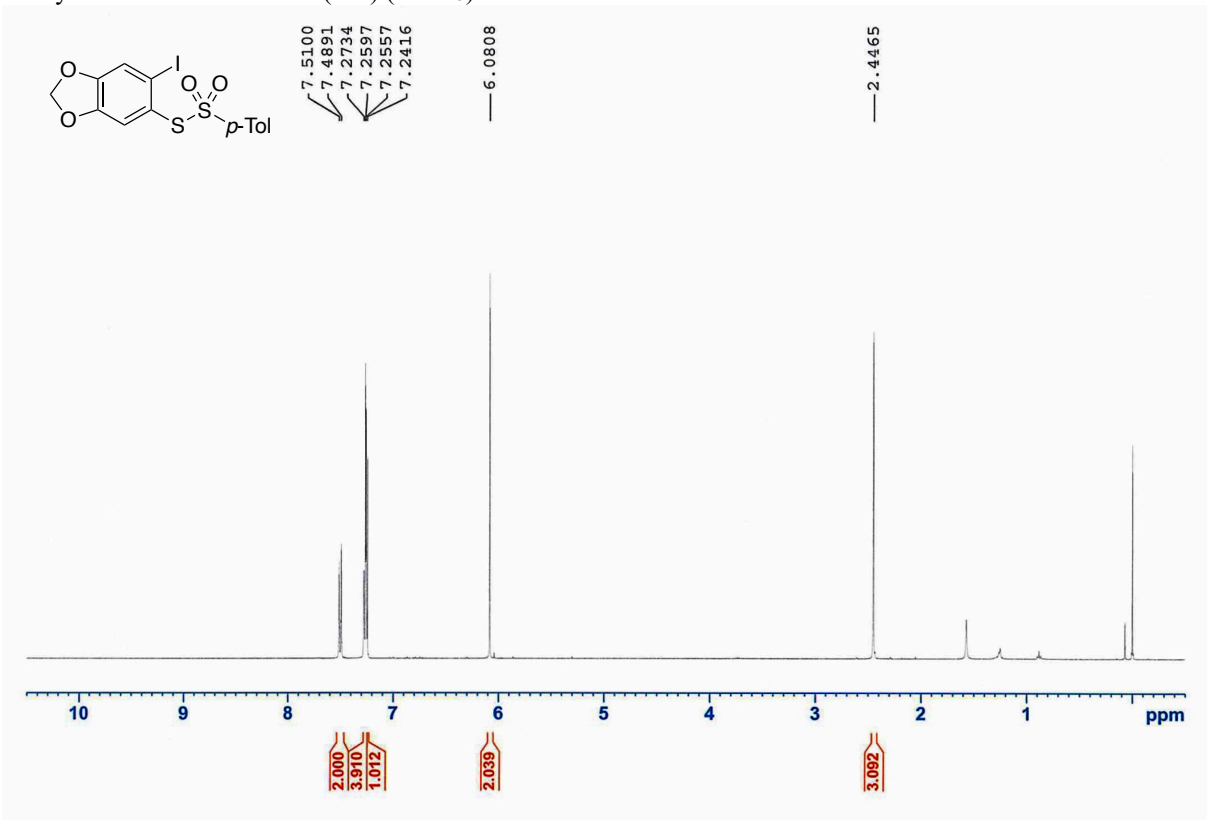


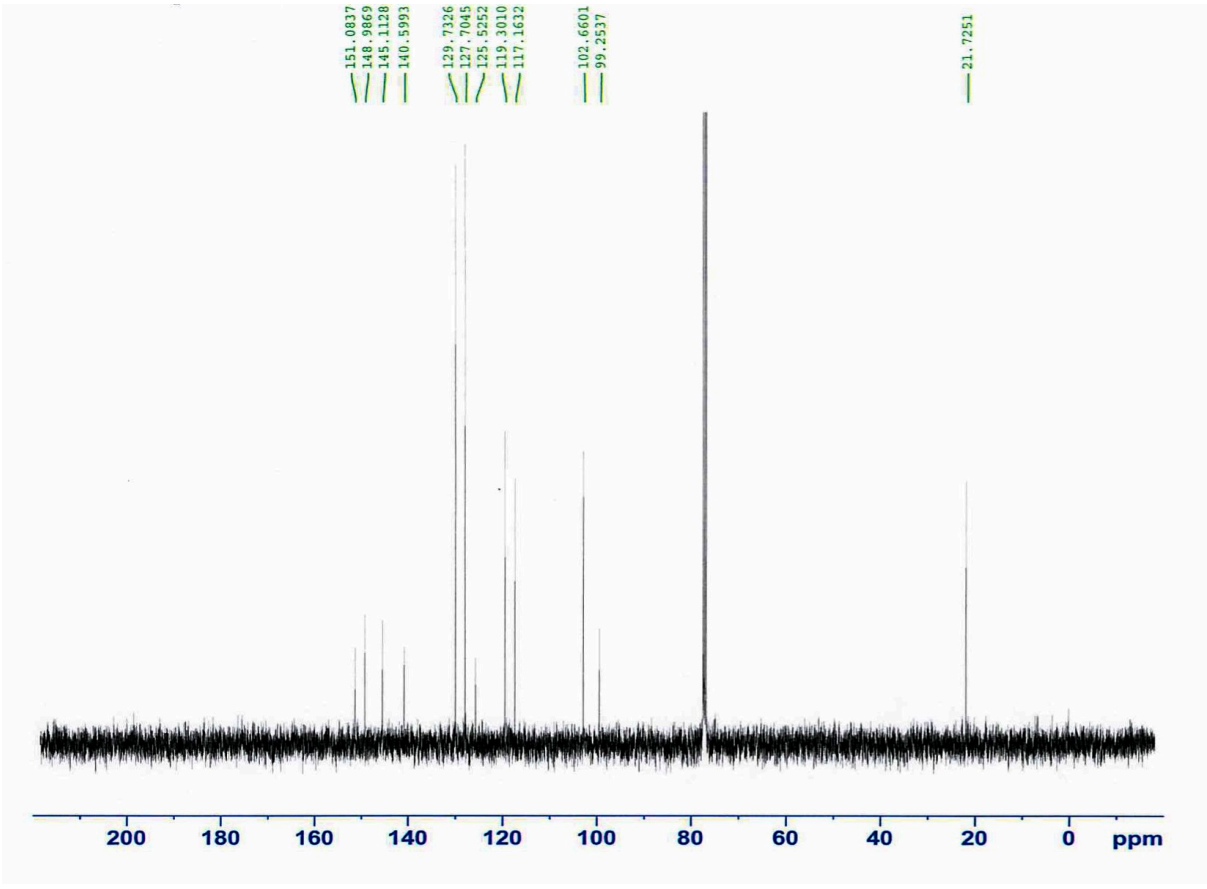
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of *S*-(2-iodo-4,5-dimethoxyphenyl) 4-methylbenzenesulfonothioate (**10d**) ($CDCl_3$)



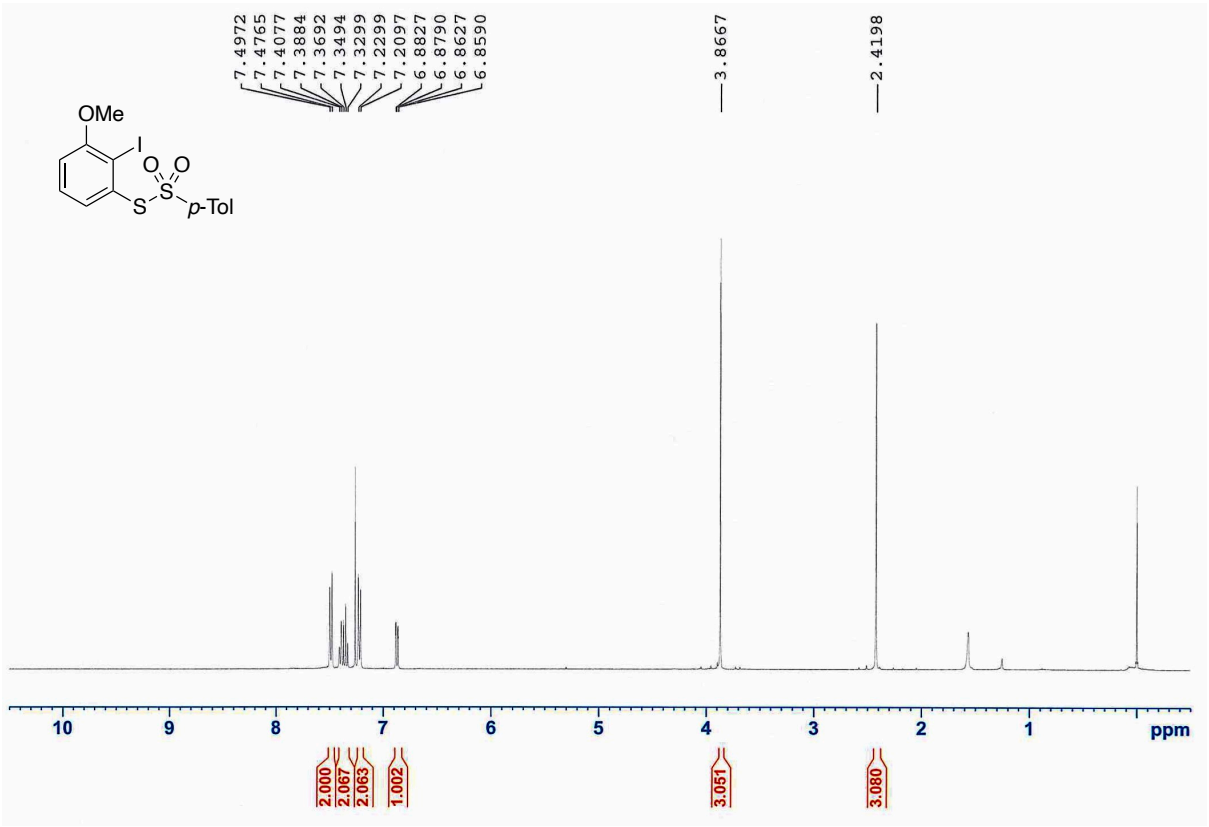


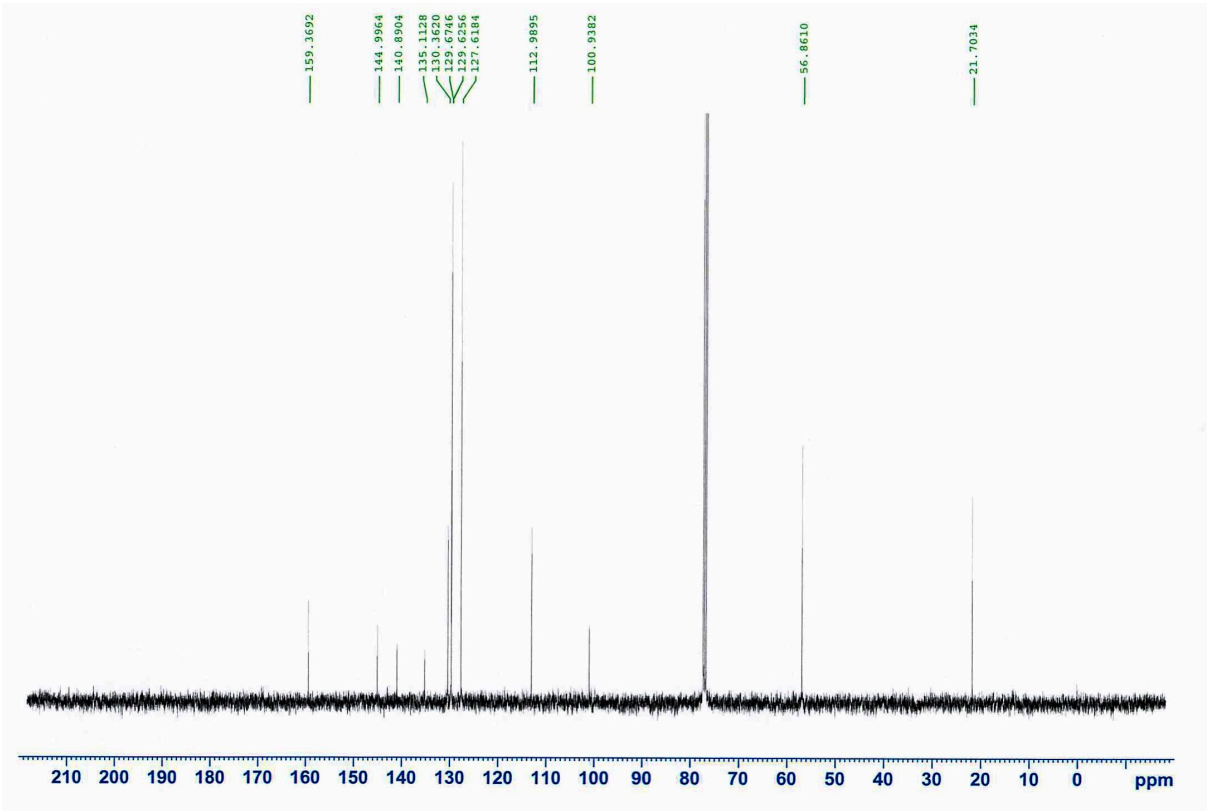
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of *S*-(6-iodobenzo[*d*][1,3]dioxol-5-yl) 4-methylbenzenesulfonothioate (**10e**) ($CDCl_3$)



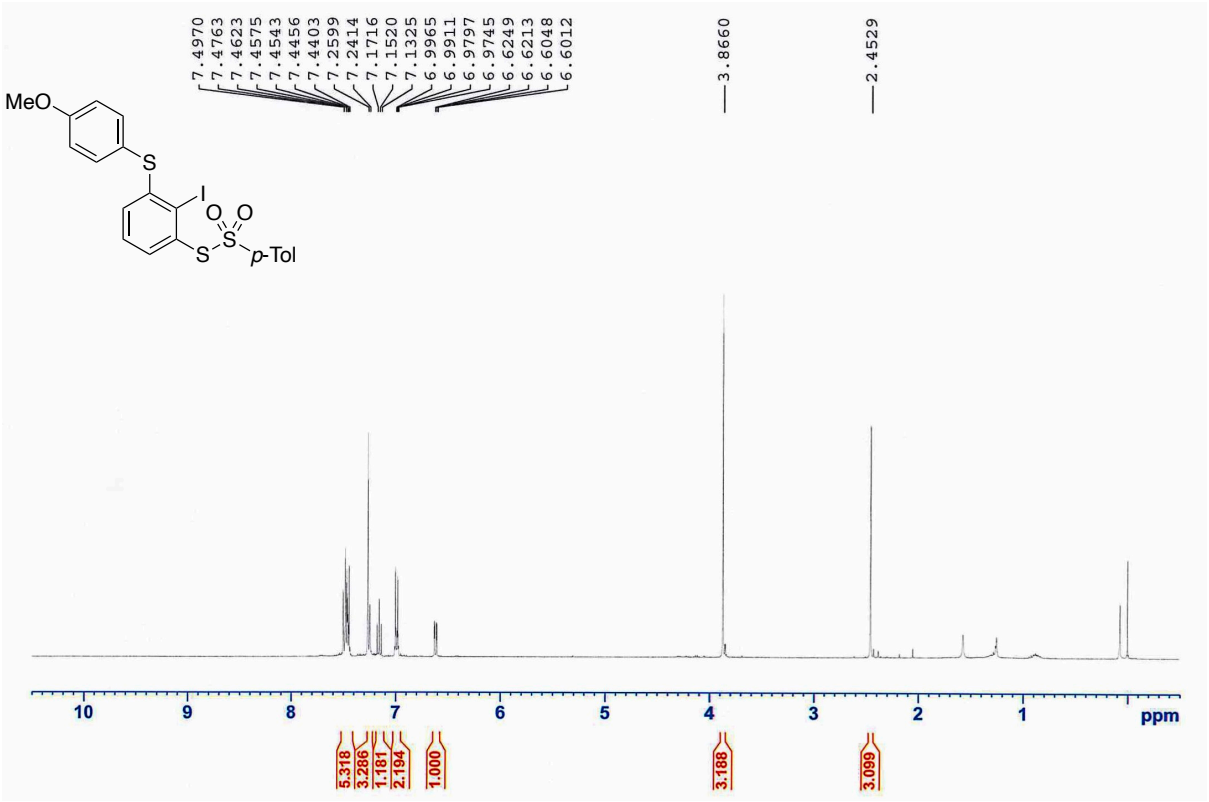


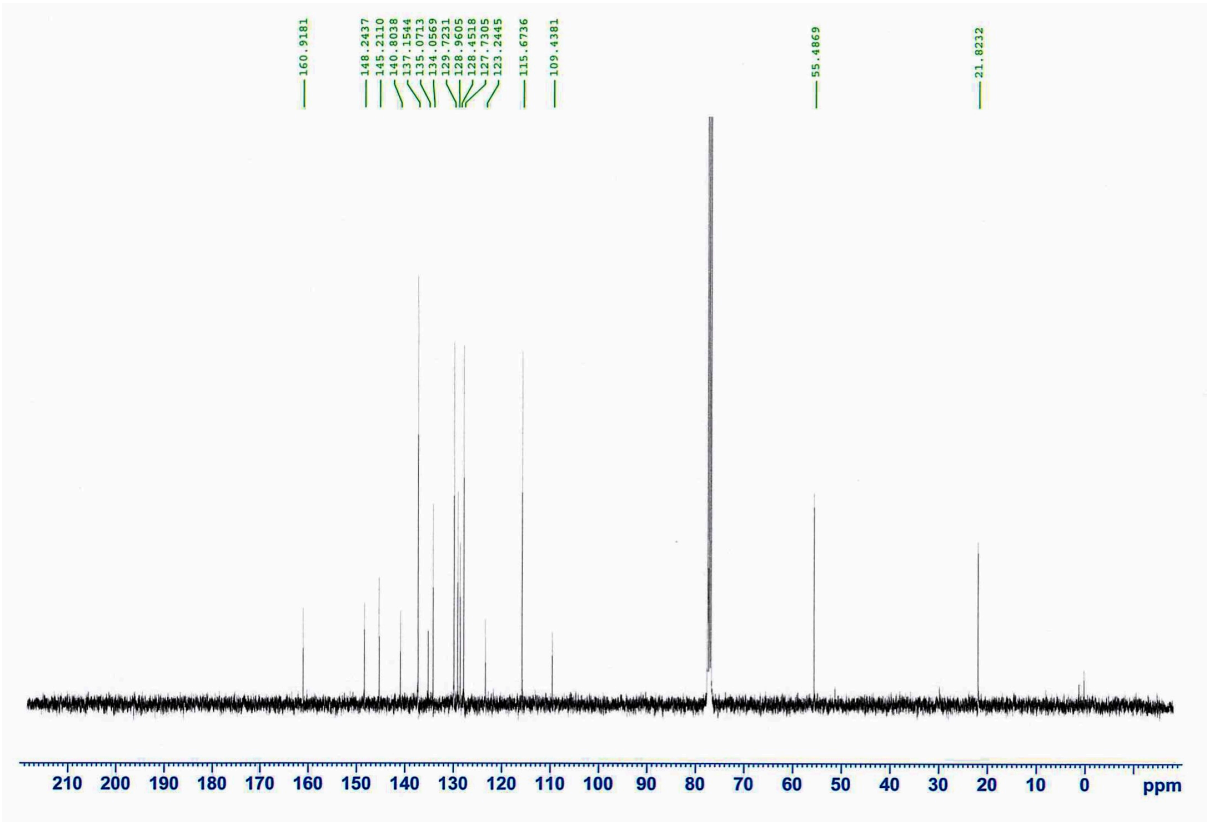
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of *S*-(2-iodo-3-methoxyphenyl) 4-methylbenzenesulfonothioate (**10f**) ($CDCl_3$)



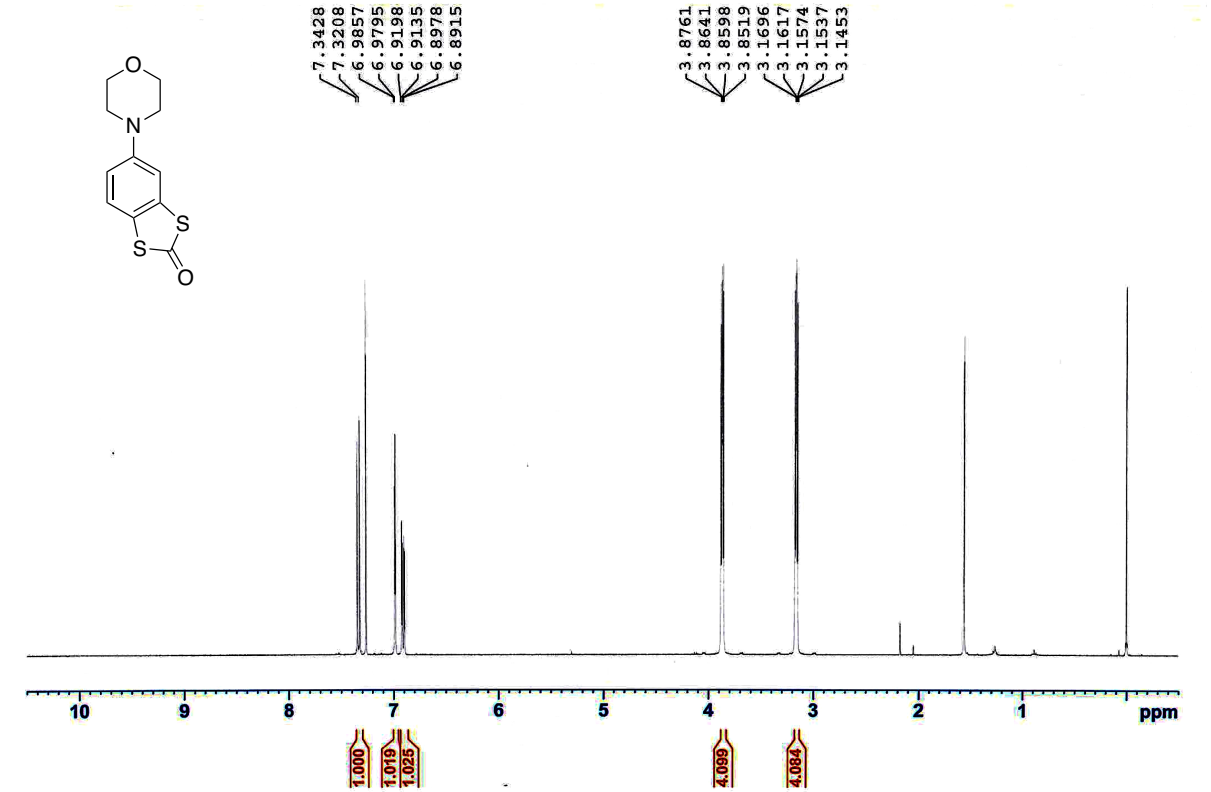


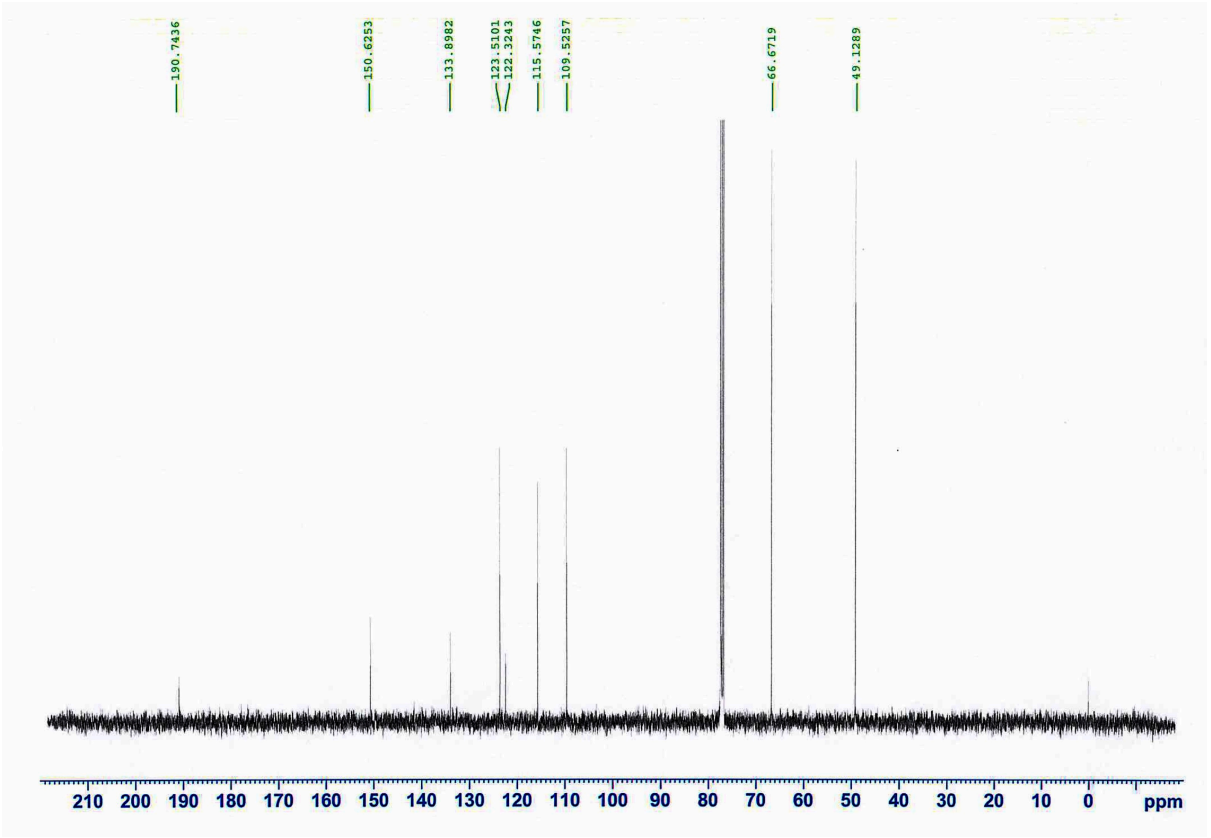
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of *S*-(2-iodo-3-((4-methoxyphenyl)thio)phenyl) 4-methylbenzenesulfonothioate (**10g**) ($CDCl_3$)



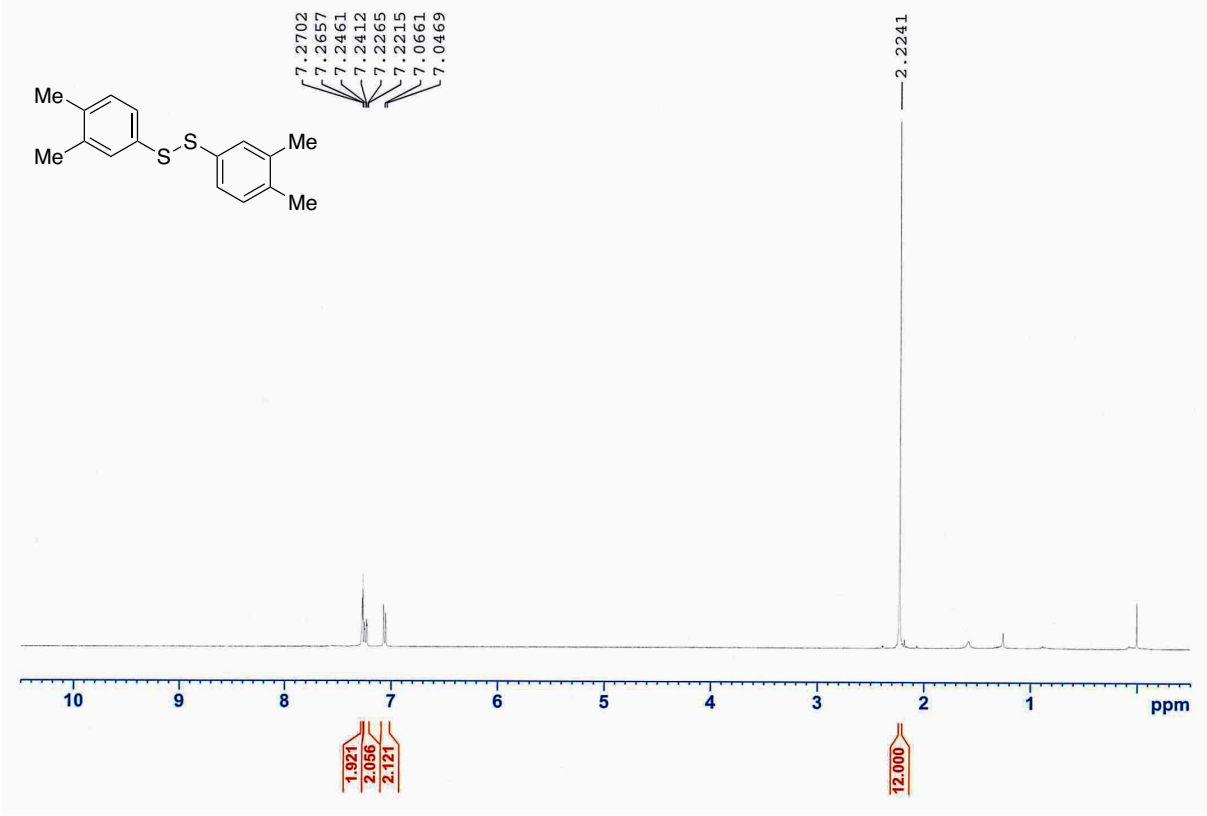


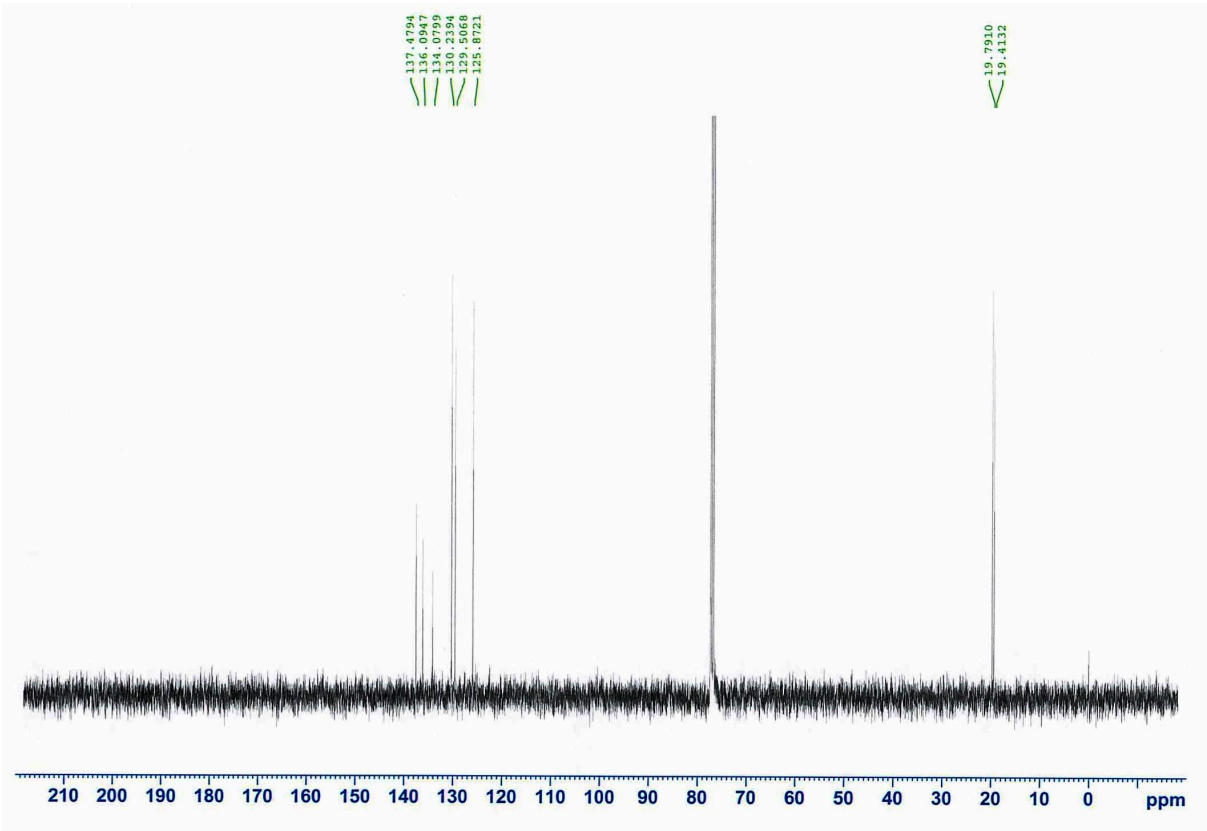
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 3,8-dimorpholinodibenzo[*c*,*e*][1,2]dithiine (**4**) ($CDCl_3$)



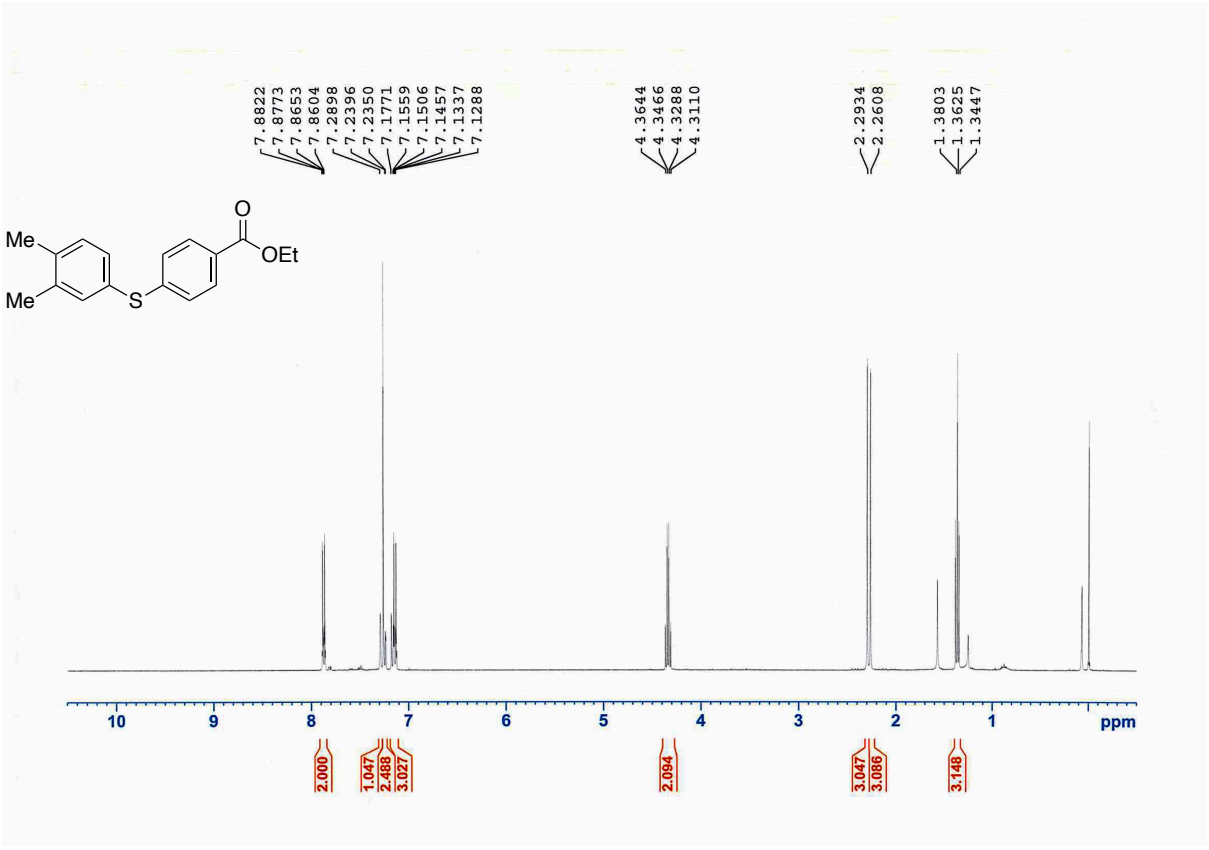


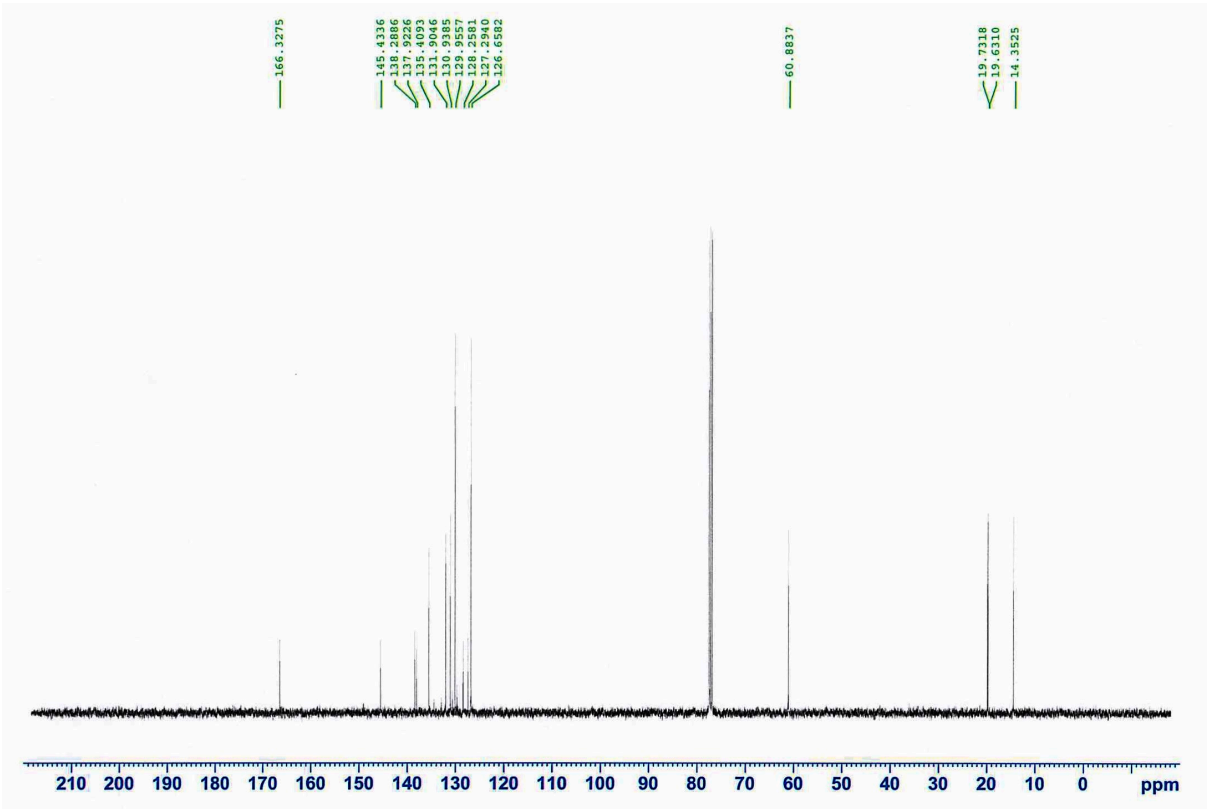
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 1,2-bis(3,4-dimethylphenyl) disulfide (**11a**) ($CDCl_3$)



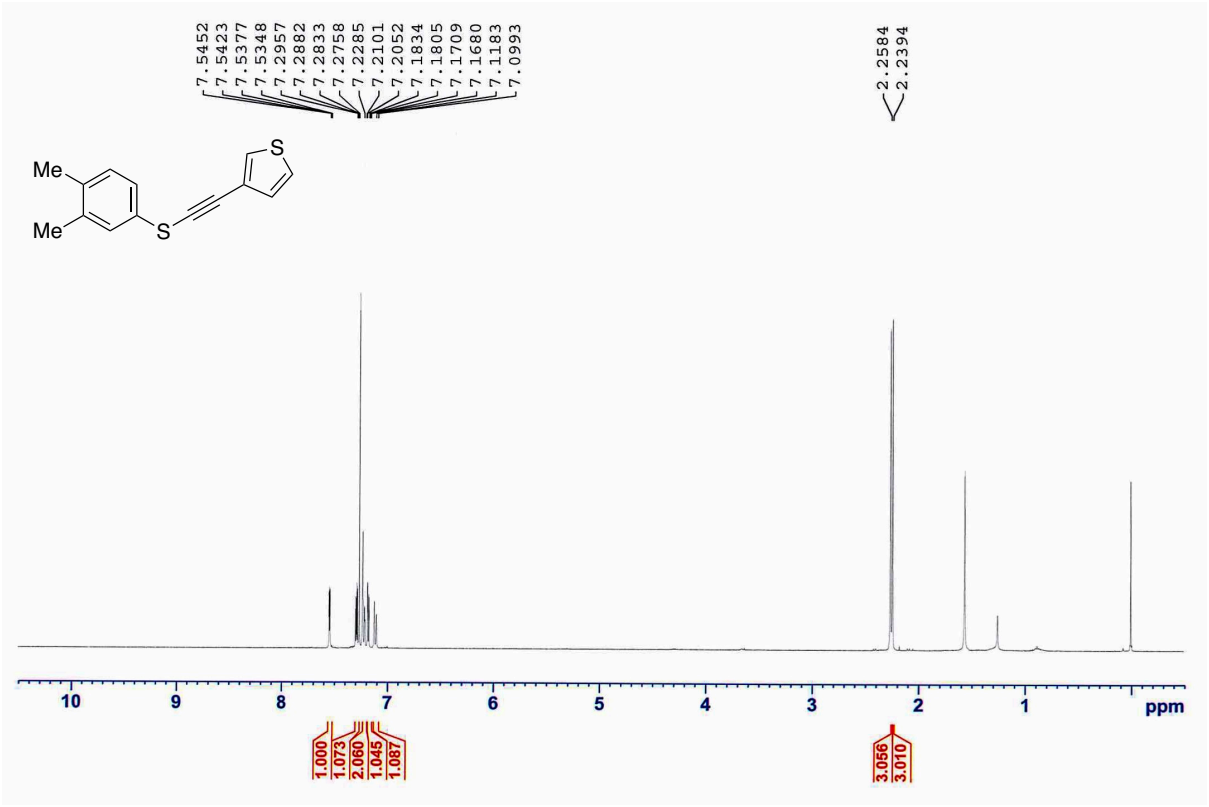


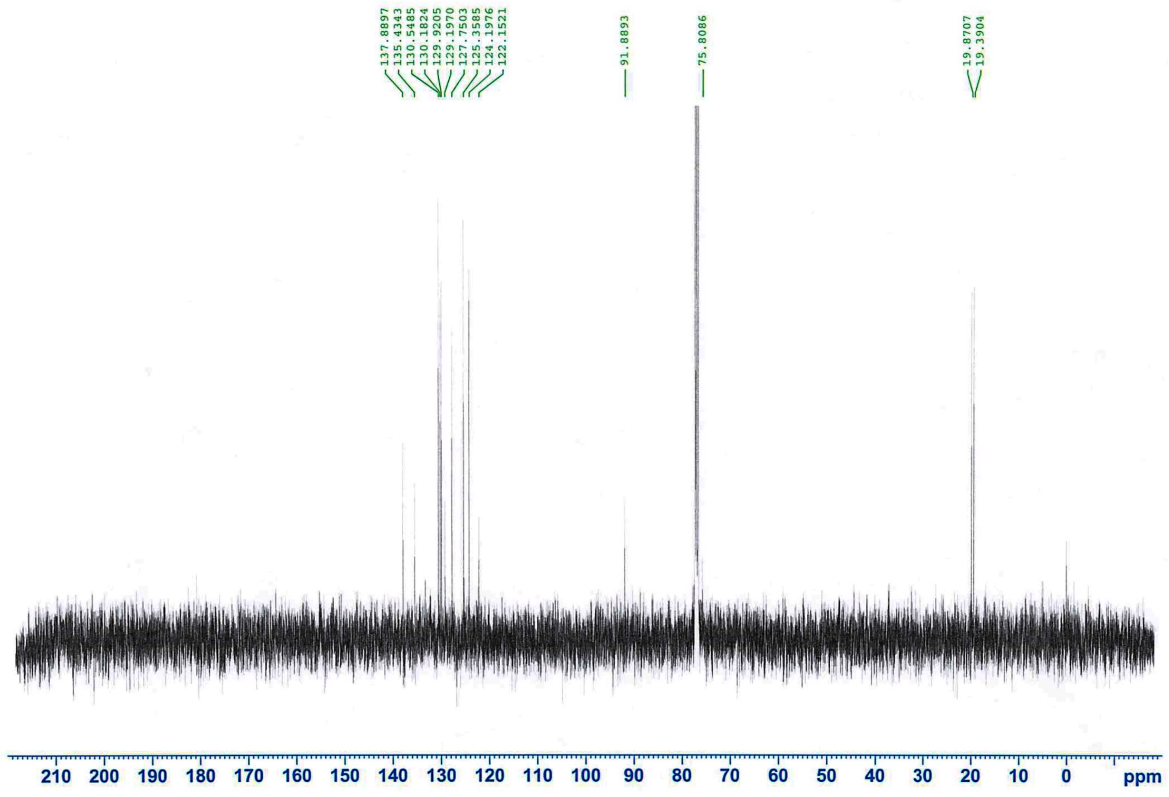
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of ethyl 4-((3,4-dimethylphenyl)thio)benzoate (**15b**) ($CDCl_3$)



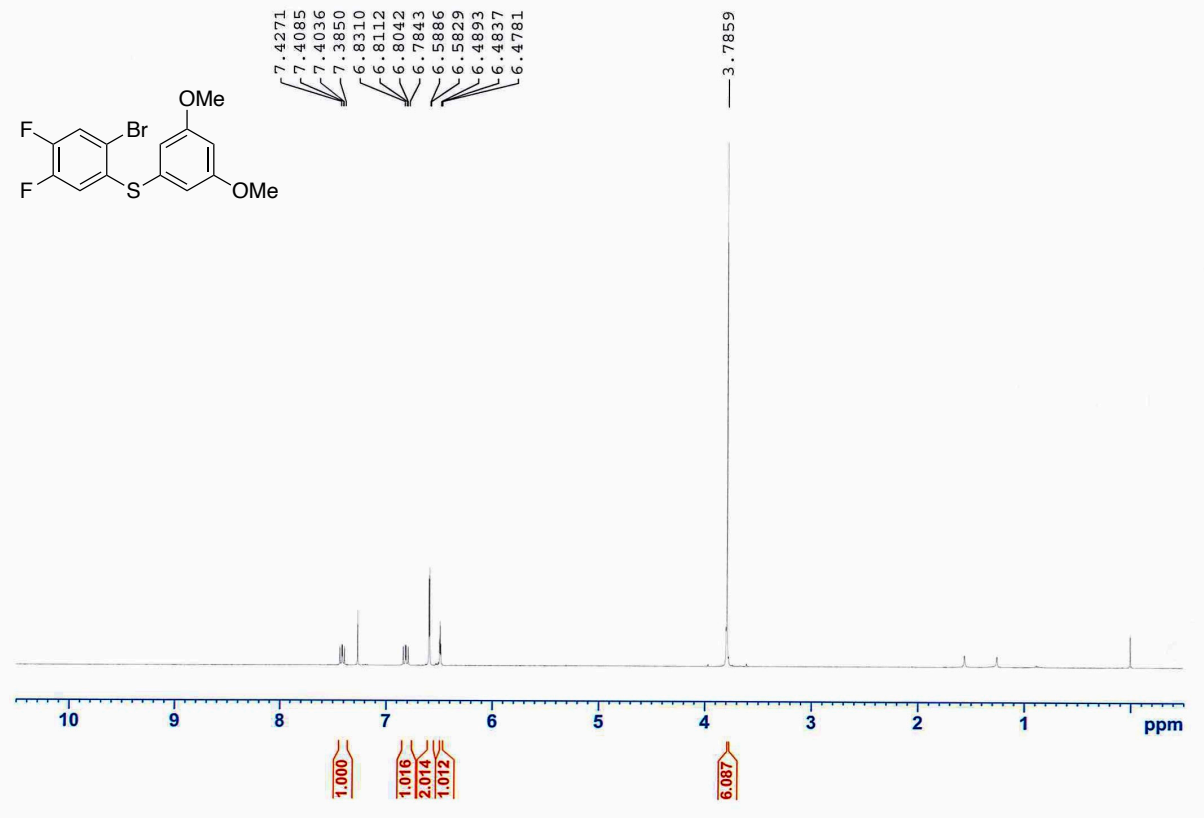


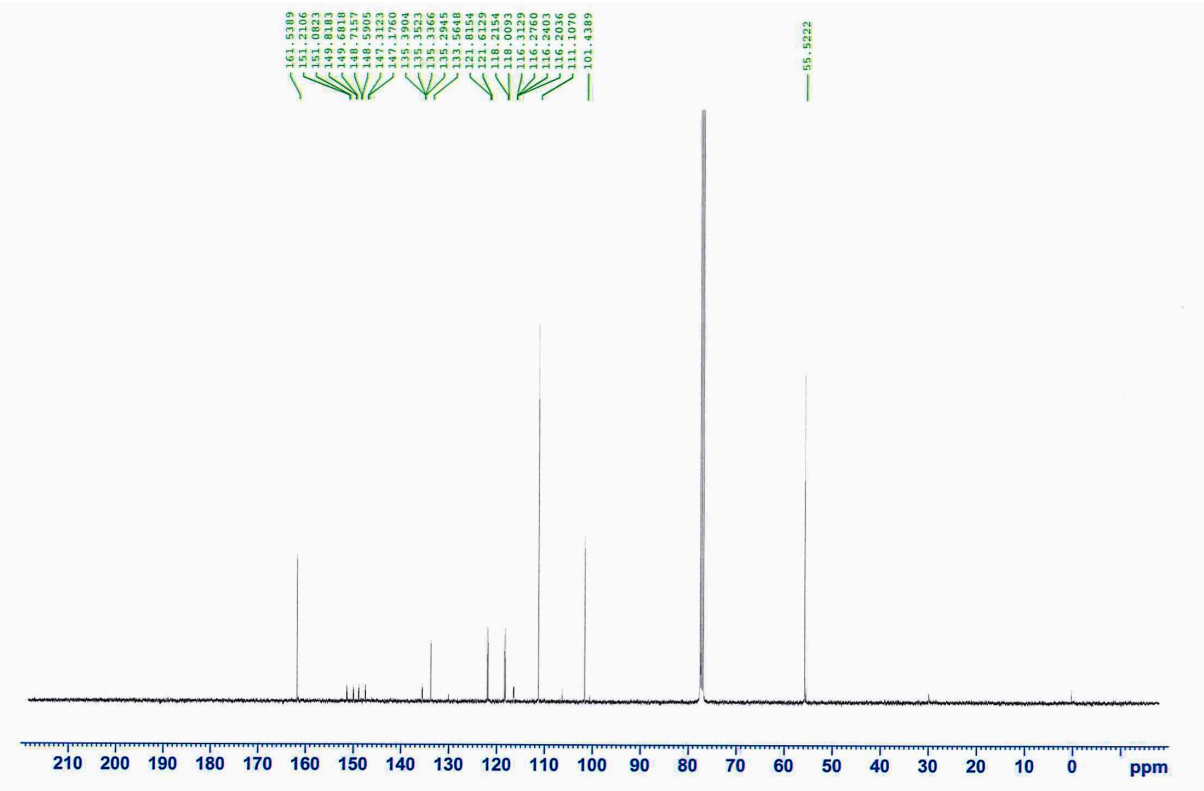
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 3-(((3,4-dimethylphenyl)thio)ethynyl)thiophene (**15c**) ($CDCl_3$)



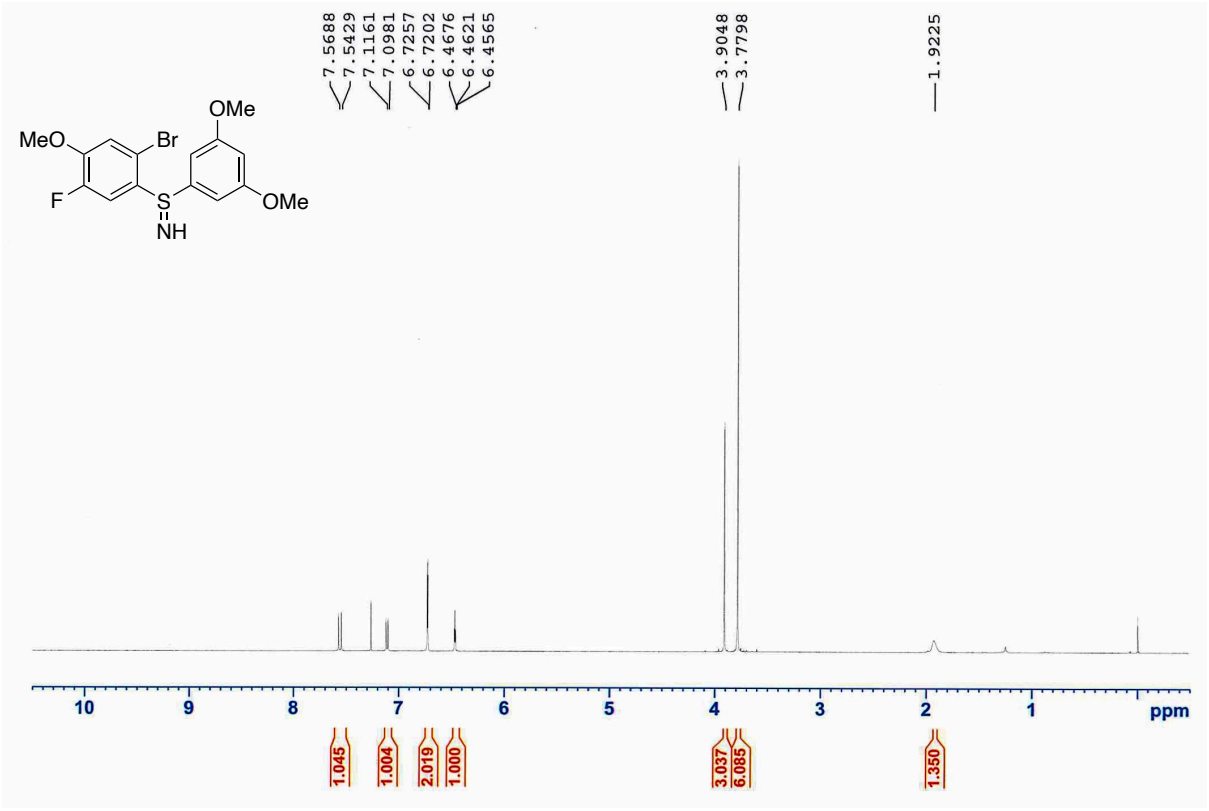


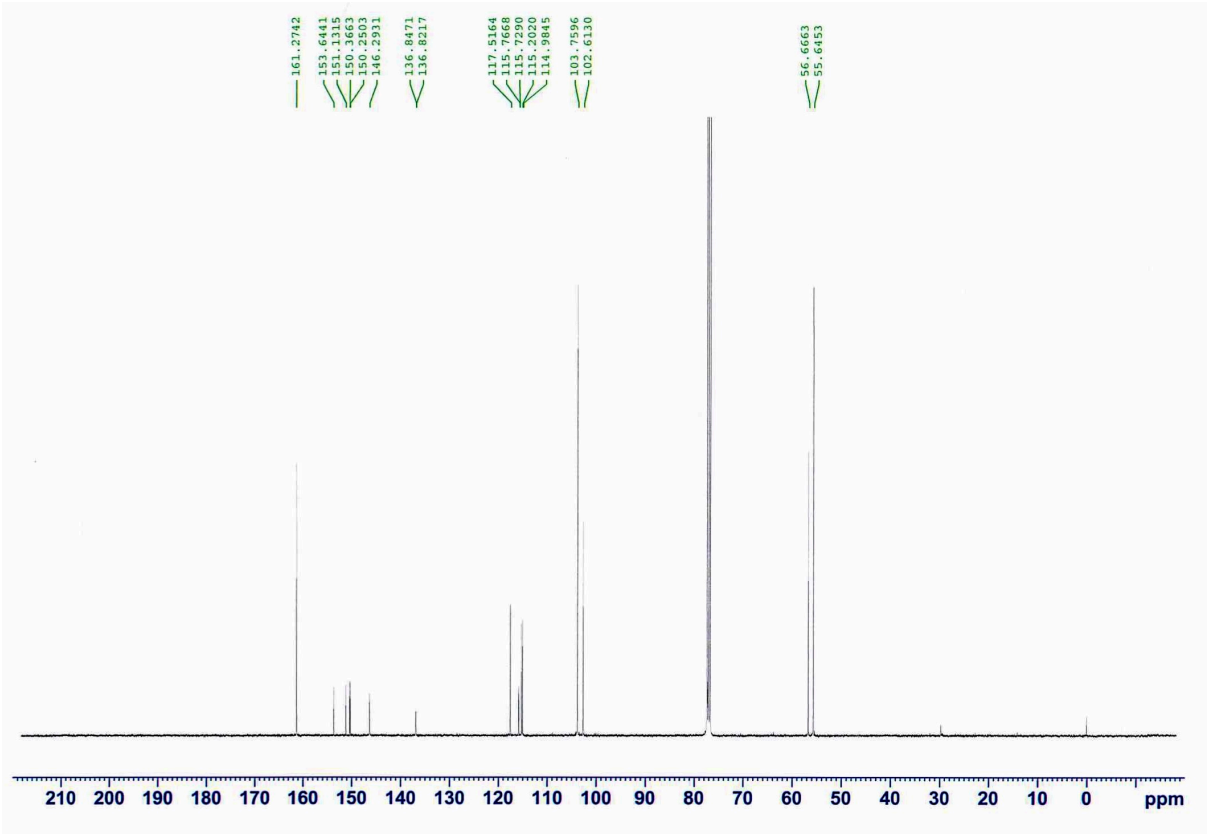
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 2-bromo-4,5-difluorophenyl 3,5-dimethoxyphenyl sulfide ($CDCl_3$)



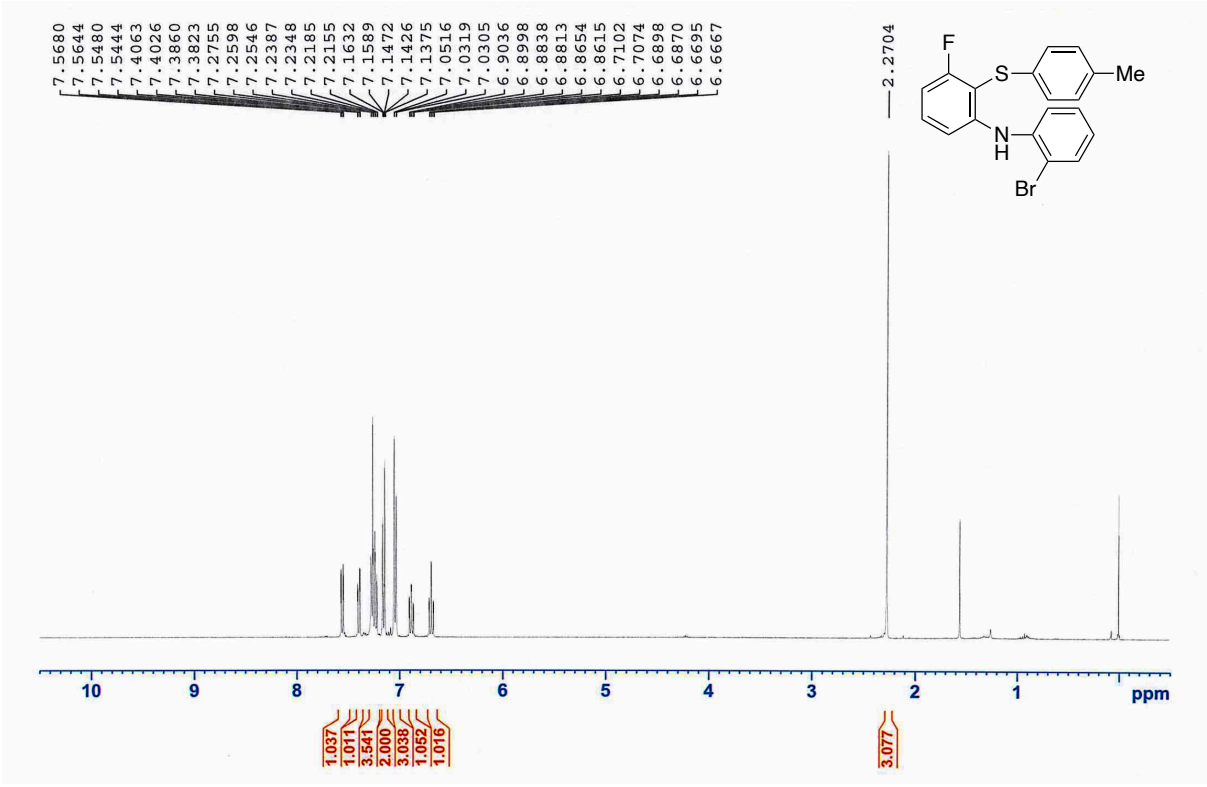


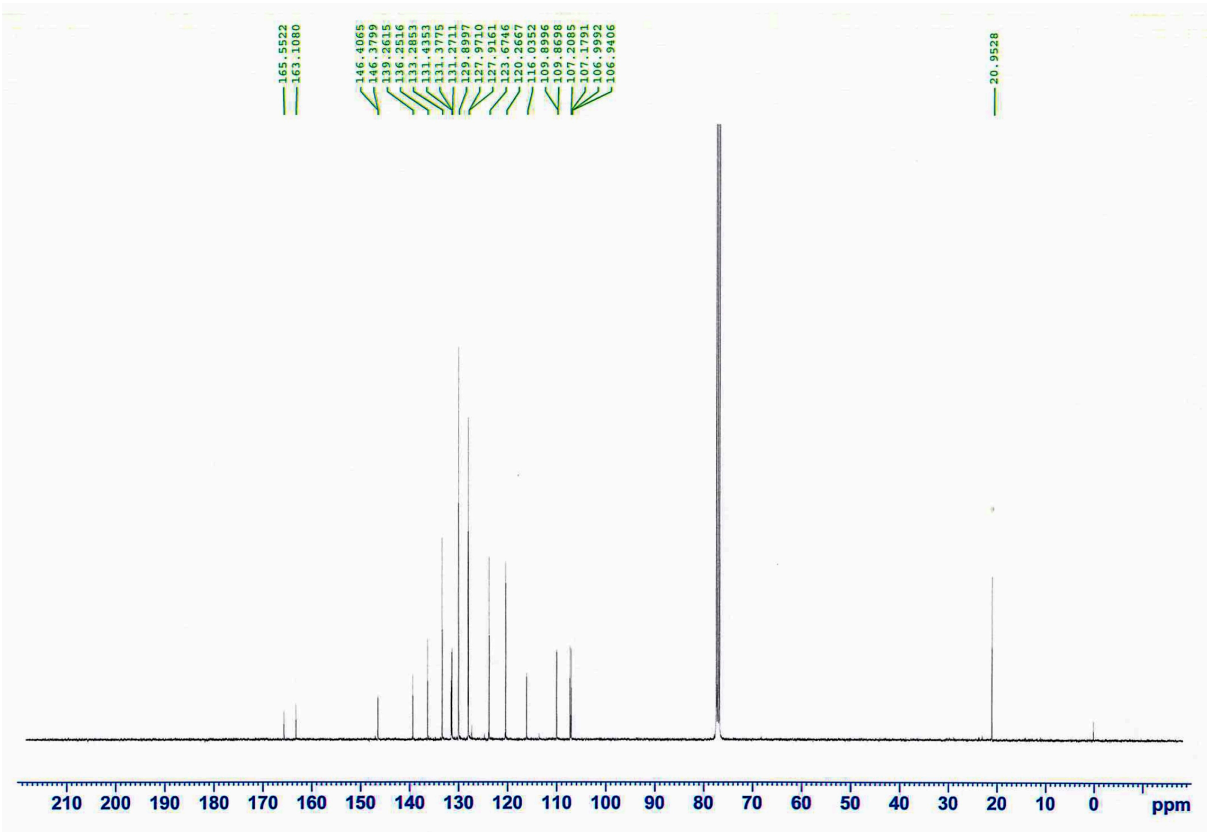
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of (2-bromo-5-fluoro-4-methoxyphenyl)(3,5-dimethoxyphenyl)-λ^{4}-sulfanimine (**18d**) ($CDCl_3$)



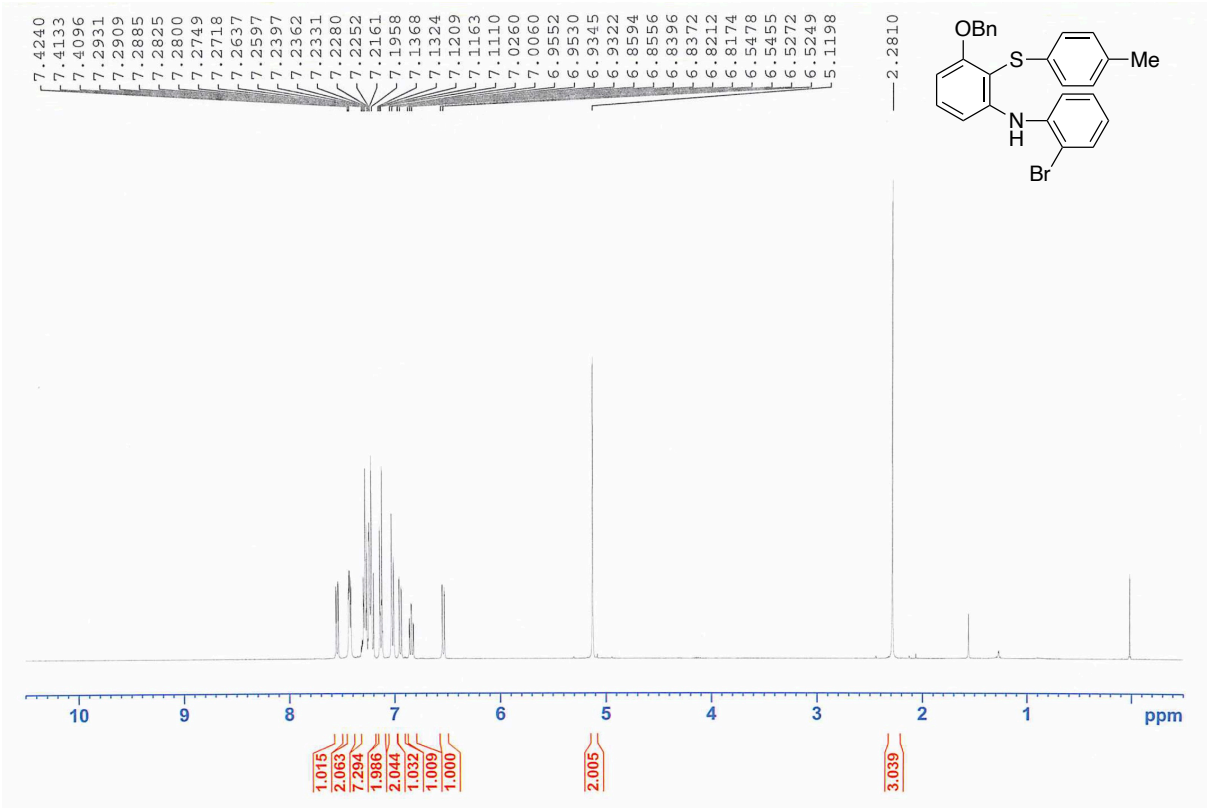


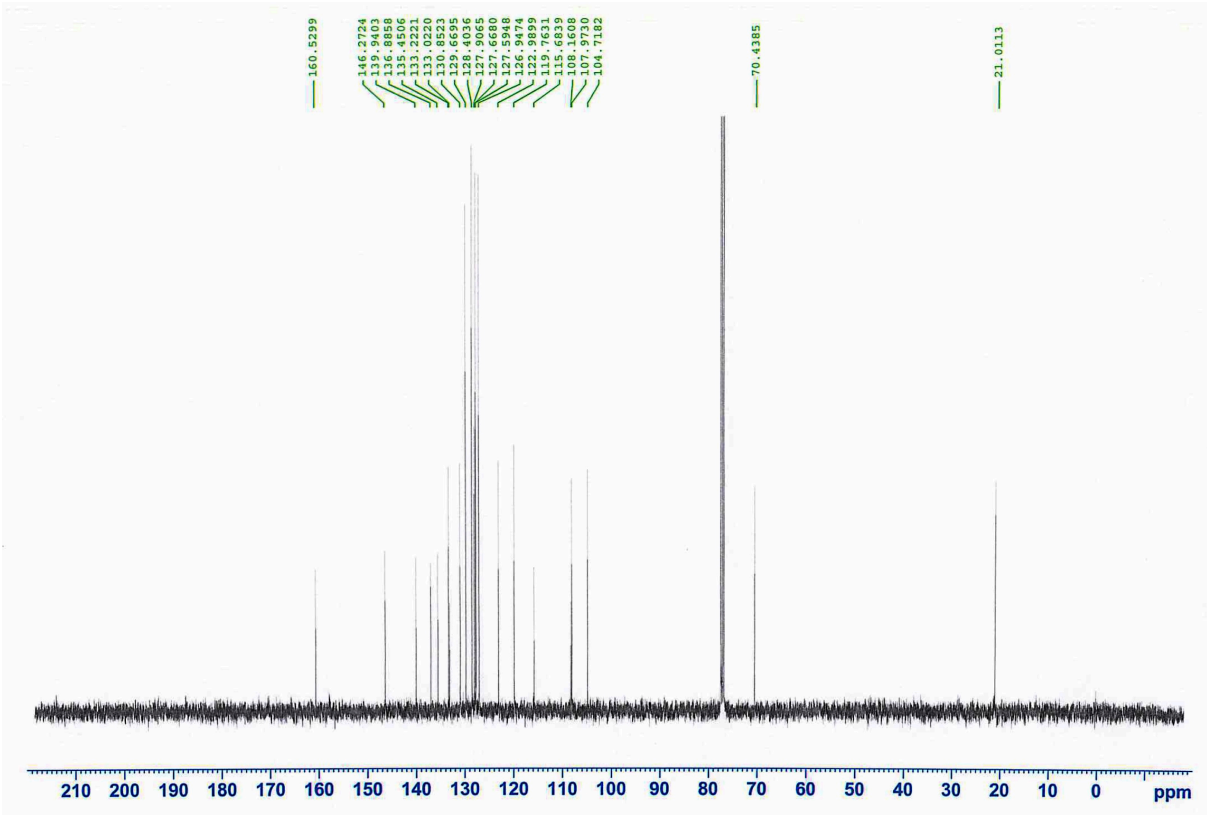
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of *N*-(2-Bromophenyl)-3-fluoro-2-(*p*-tolylthio)aniline (**20a**) ($CDCl_3$)



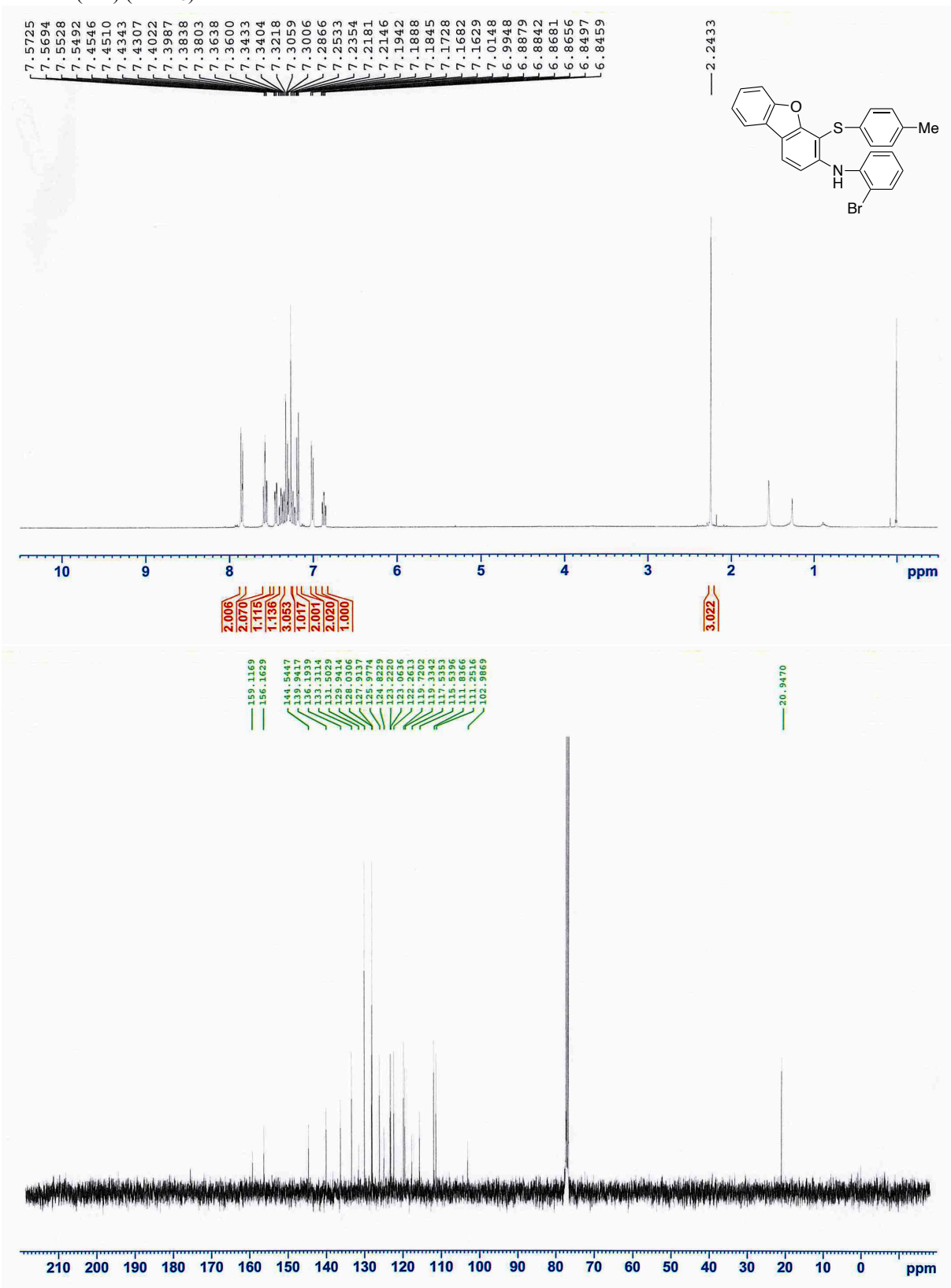


^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 3-(Benzyloxy)-*N*-(2-bromophenyl)-2-(*p*-tolylthio)aniline (**20b**) ($CDCl_3$)

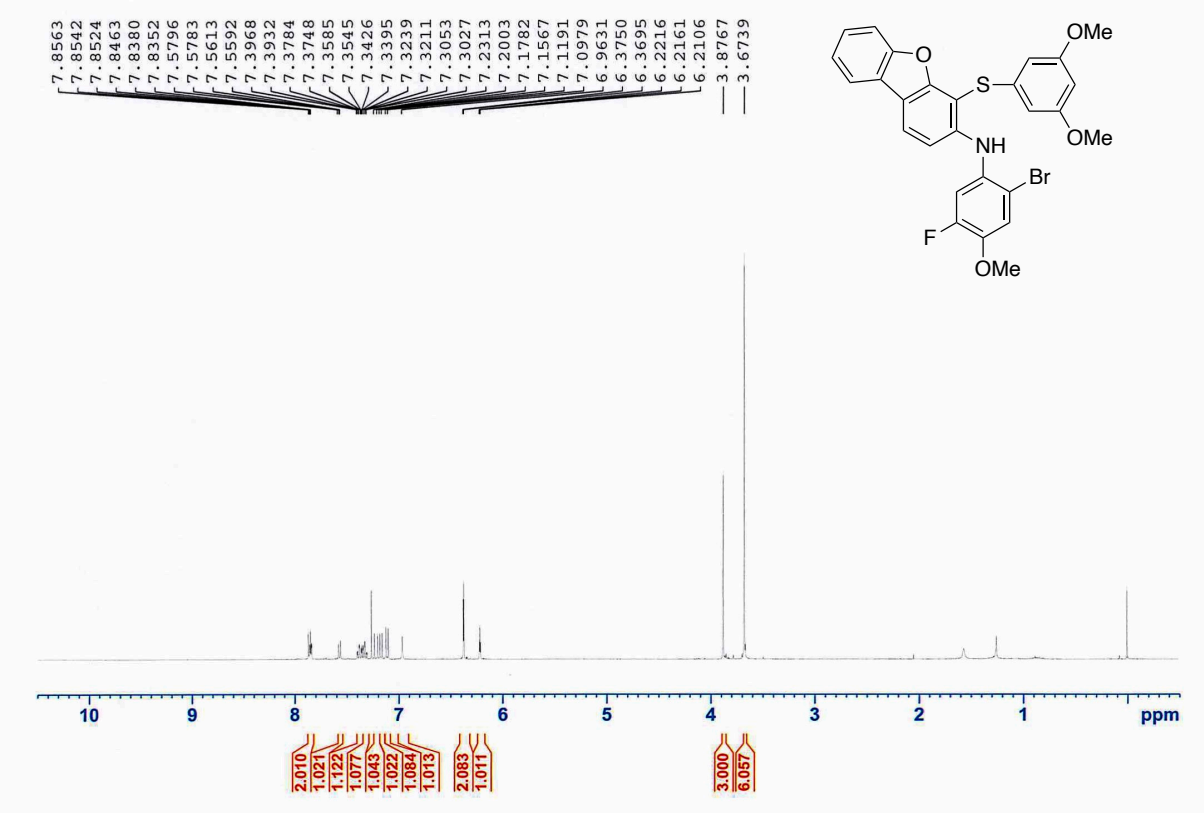


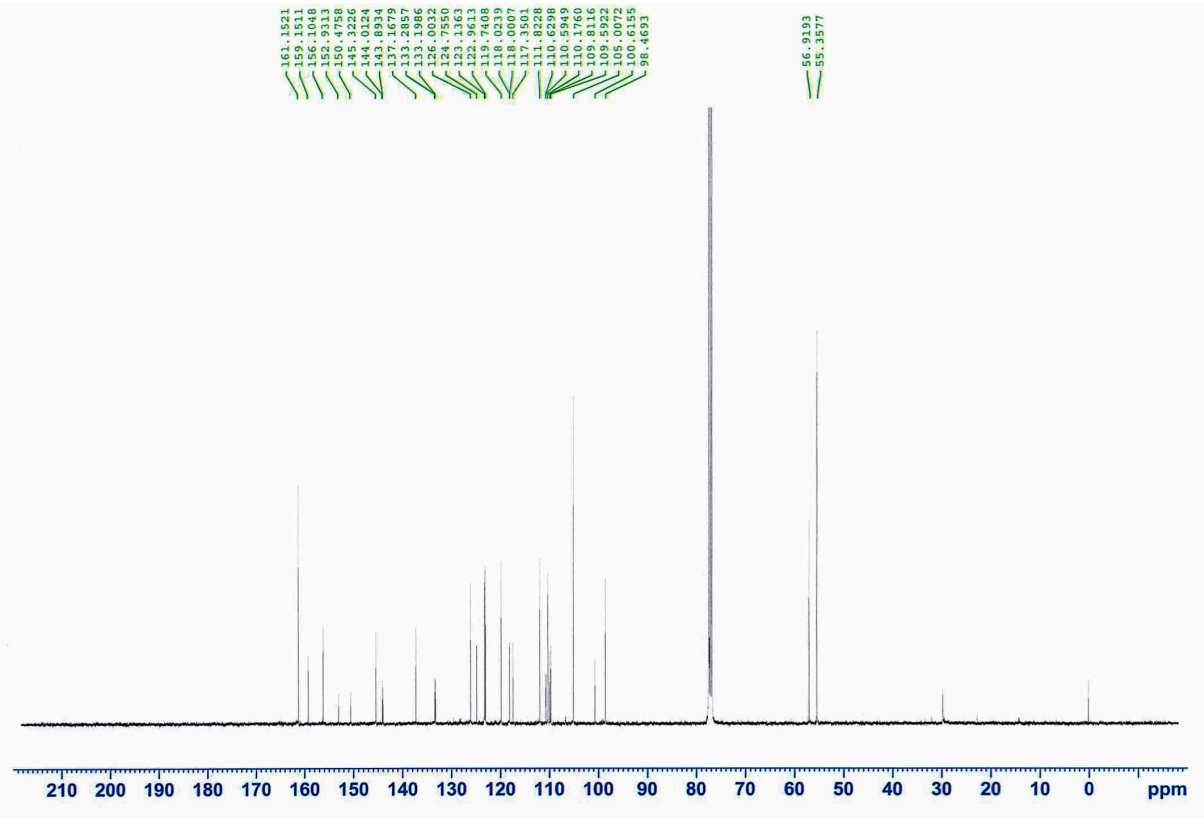


^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of *N*-(2-Bromophenyl)-4-(*p*-tolylthio)dibenzo[*b*,*d*]furan-3-amine (**20c**) ($CDCl_3$)

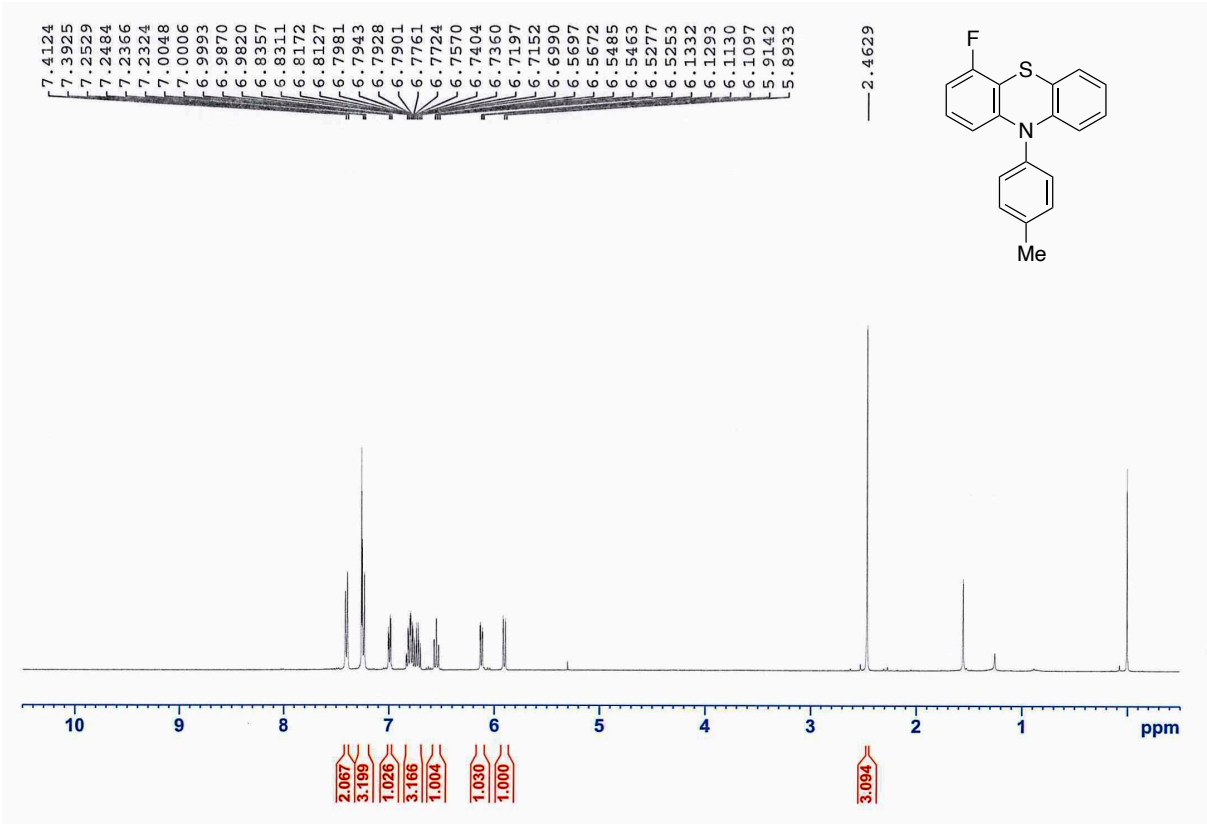


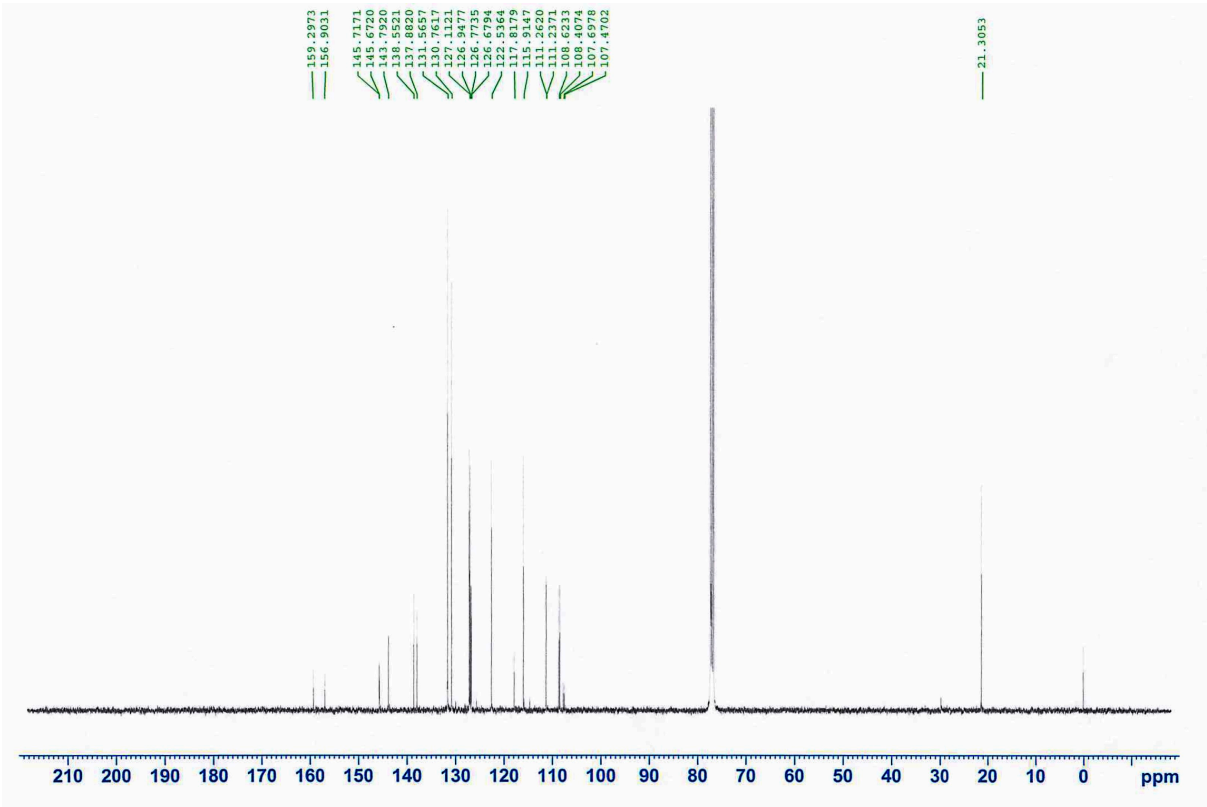
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of *N*-(2-bromo-5-fluoro-4-methoxyphenyl)-4-((3,5-dimethoxyphenyl)thio)dibenzo[*b*,*d*]furan-3-amine (**20d**) ($CDCl_3$)



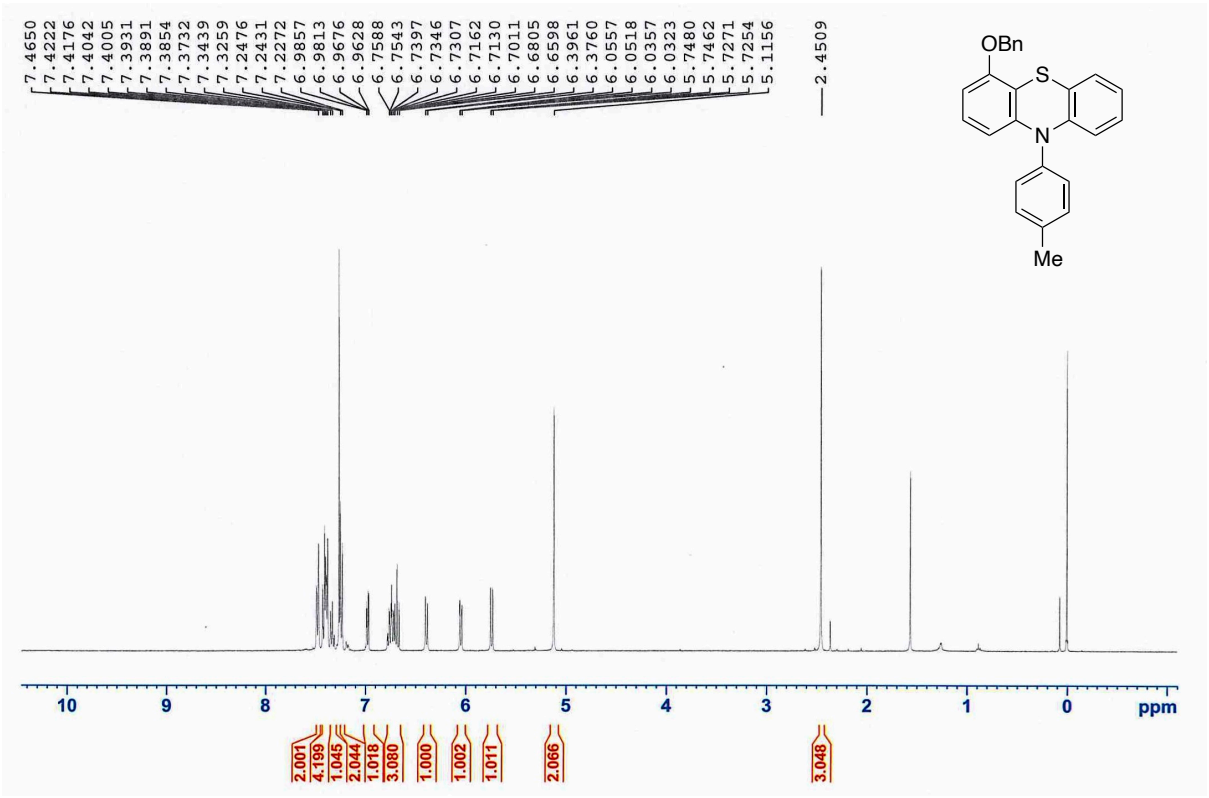


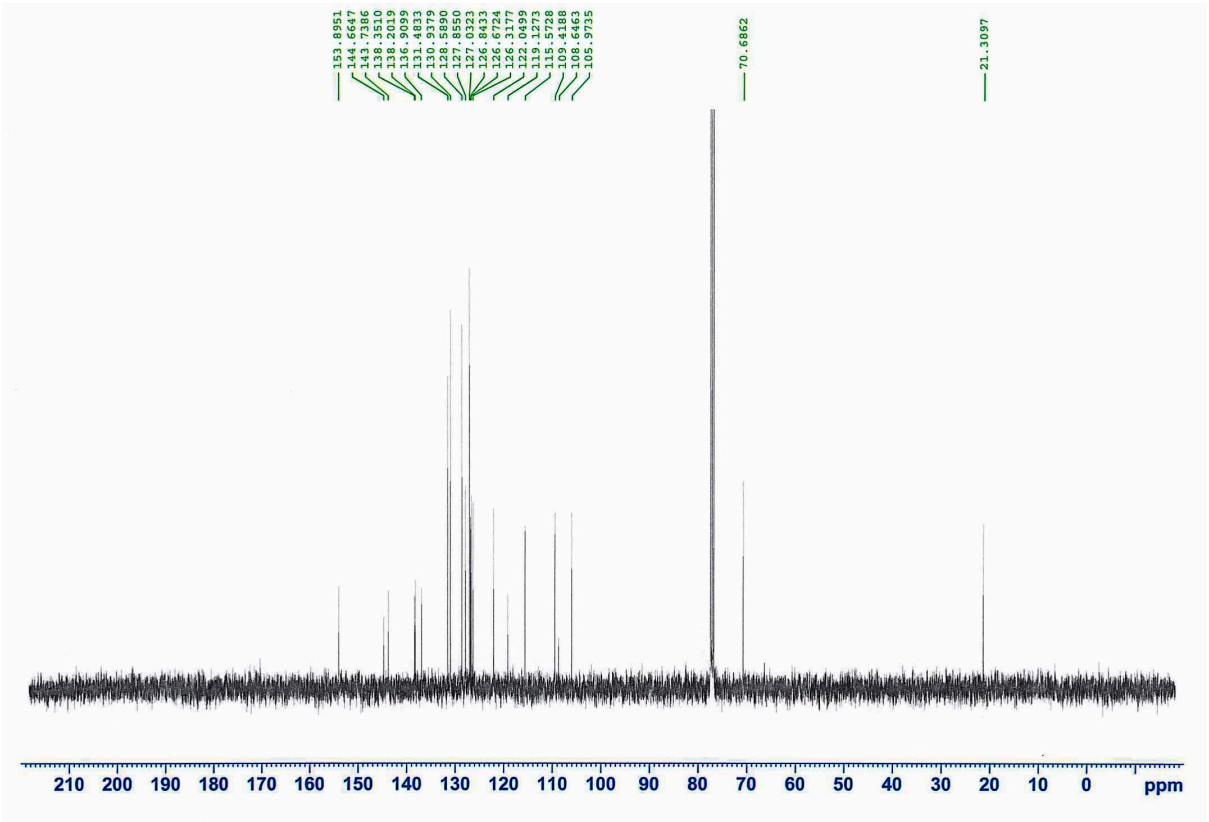
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 4-fluoro-10-(*p*-tolyl)-10*H*-phenothiazine (**21a**) ($CDCl_3$)





^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 4-(benzyloxy)-10-(*p*-tolyl)-10*H*-phenothiazine (**21b**) ($CDCl_3$)





^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 5-(*p*-tolyl)-5*H*-benzofuro[3,2-*c*]phenothiazine (**21c**) (acetone-d_6)