Electronic Supplementary Information

Diverse diaryl sulfide synthesis through consecutive aryne reactions

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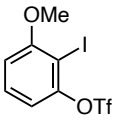
Contents

General Remarks

All reactions were performed in a dry glassware under atmosphere of argon otherwise noted. Analytical thin-layer chromatography (TLC) was performed on precoated (0.25 mm) silica-gel plates (Merck Chemicals, Silica Gel 60 F_{254}, 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. 37563-85 or particle size 63–210 μm, Cat. No. 37565-85). Preparative thin-layer chromatography (PTLC) was performed on silica-gel (Wako Pure Chemical Industries Ltd., Wakogel B5-F, Cat. No. 230-00043). Melting points (Mp) were measured on a YANACO MP-J3 instrument or an OptiMelt MPA100 (Stanford Research Systems), and are uncorrected. ^{1}H and ^{13}C NMR spectra were obtained with a Bruker AVANCE 500 spectrometer at 500 or 126 MHz, respectively. ^{19}F NMR spectra were obtained with a Bruker AVANCE 400 spectrometer at 376 MHz. Chemical shifts (δ) are given in parts per million (ppm) downfield from $(CH_3)_4Si$ (δ 0.00 for ^{1}H NMR in $CDCl_3$) or the solvent peak (δ 77.0 for ^{13}C NMR in $CDCl_3$ and δ 4.87 for ^{1}H NMR in CD_3OD) as an internal reference, or α,α,α-trifluorotoluene (δ –63.0 ppm for ^{19}F NMR in $CDCl_3$) as an external standard with coupling constants (*J*) in hertz (Hz). The abbreviations s, d, t, q, sept, m, and br signify singlet, doublet, triplet, quartet, septet, multiplet, and broad, respectively. IR spectra were measured by diffuse reflectance method on a Shimadzu IRPrestige-21 spectrometer attached with DRS-8000A with the absorption band given in cm^{-1}. High-resolution mass spectra (HRMS) were measured on a Bruker micrOTOF mass spectrometer under positive electrospray ionization (ESI^+) conditions. Elemental analyses were carried out at A Rabbit Science Japan Co., Ltd.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. 2-Iodo-3-methoxyphenyl triflate (**1a**),[S1] 2-iodo-4,5-dimethoxyphenyl triflate (**1b**),[S2] 2-iodo-3-(propargyl)phenyl triflate (**1c**),[S3] 5-bromo-2-iodo-3-(propargyl)phenyl triflate (**1d**),[S4] 1-iodo-2,6-bis(triflyloxy)benzene (**1f**),[S5] 3-chloro-2-iodo-5-methylphenyl triflate (**1g**),[S6] 1-iodo-2-naphthyl triflate (**1h**),[S2] 4-iodo-2-methyl-5-(triflyloxy)benzo[*d*]thiazole (**1i**),[S7] 7-iodo-2-(methylthio)-3-(trifluoromethyl)-6-(triflyloxy)benzo[*b*]thiophene (**1j**),[S8] 3-methoxy-5-methylthio-2-(trimethylsilyl)phenyl triflate (**2a**),[S9] 3-(trideuteriomethyloxy)-5-(methylthio)-2-(trimethylsilyl)phenyl triflate (**2a-*d***),[S9] 2-iodo-3-methoxy-5-(methylthio)phenyl triflate (**5**),[S2] 2-bromo-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(trimethylsilyl)phenyl triflate,[S2] 2-chloro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(trimethylsilyl)phenyl triflate,[S2] 3-morpholino-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trimethylsilyl)phenyl triflate,[S2] *S*-(methyl) 4-toluenethiosulfonate,[S9] and 3-hydroxy-2-iodophenyl triflate[S1] were prepared according to the reported procedure. Organolithium and organomagnesium reagents were used after titrimetric determination of the concentration by the 1,10-phenanthroline method.[S10]

Structures of *o*-Iodoaryl Triflates 1 and *o*-Silylaryl Triflates 2



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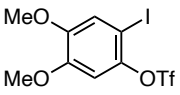

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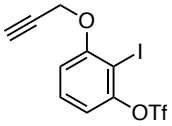

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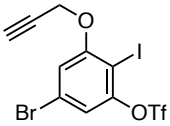

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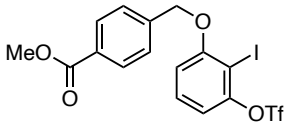

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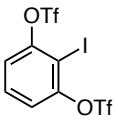

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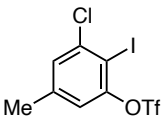

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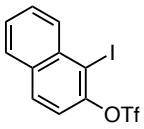

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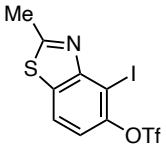

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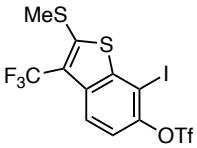

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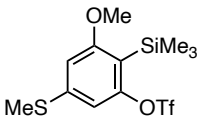
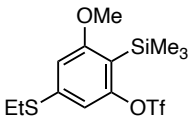


2a



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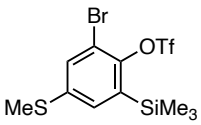

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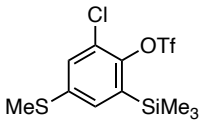

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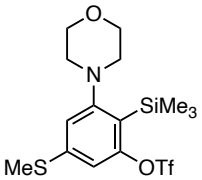
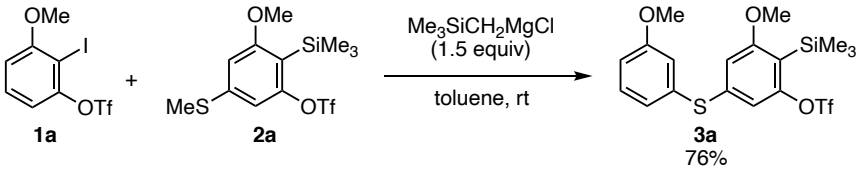


2e

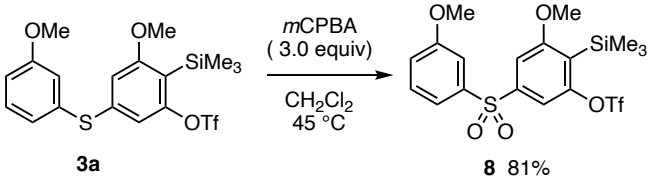
Experimental Procedures

*A typical procedure for the reaction of o-iodoaryl triflates **1** and methylthio-substituted o-silylaryltriflates **2***



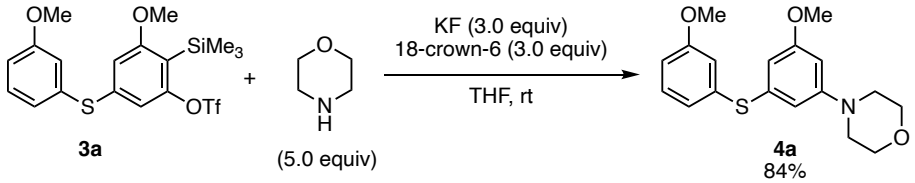
To a solution of 2-iodo-3-methoxyphenyl triflate (**1a**) (76.8 mg, 0.200 mmol, 1.0 equiv) and 3-methoxy-5-methylthio-2-(trimethylsilyl)phenyl triflate (**2a**) (74.4 mg, 0.199 mmol, 1.0 equiv) dissolved in toluene (2.0 mL) was added (trimethylsilylmethyl)magnesium chloride (1.01 M in THF, 297 μL, 0.300 mmol, 1.5 equiv) at room temperature. After stirring for 1h at the same temperature, to the mixture was added phosphate buffer solution (pH 7, 10 mL). The mixture was extracted with EtOAc (10 mL × 5). 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/toluene = 4/1) to give 3-methoxy-5-(3-methoxyphenylthio)-2-(trimethylsilyl)phenyl triflate (**3a**) (70.5 mg, 0.151 mmol, 76%) as a colorless oil.

*Synthesis of 3-methoxy-5-(3-methoxyphenylsulfonyl)-2-(trimethylsilyl)phenyl triflate (**8**)*



In a 5 mL screw-top V-vial® with a solid-top cap (Sigma-Aldrich, Cat. No. Z115118), to a solution of 3-methoxy-5-(3-methoxyphenylthio)-2-(trimethylsilyl)phenyl triflate (**3a**) (18.8 mg, 40.0 μmol, 1.0 equiv) dissolved in dichloromethane (0.60 mL) was added *m*-chloroperoxybenzoic acid (ca. 65%) (31.8 mg, ca. 0.12 mmol, 3.0 equiv) at room temperature. After stirring for 24 h at 45 °C, to the mixture was added saturated aqueous potassium carbonate (5 mL) and saturated aqueous sodium thiosulfate (5 mL). The mixture was extracted with CH_2Cl_2 (5 mL × 3). The combined organic extract was washed with brine (5 mL) and dried with Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified preparative TLC (*n*-hexane/EtOAc = 2/1) to give 3-methoxy-5-(3-methoxyphenylsulfonyl)-2-(trimethylsilyl)phenyl triflate (**8**) (16.2 mg, 32.5 μmol, 81%) as a colorless solid.

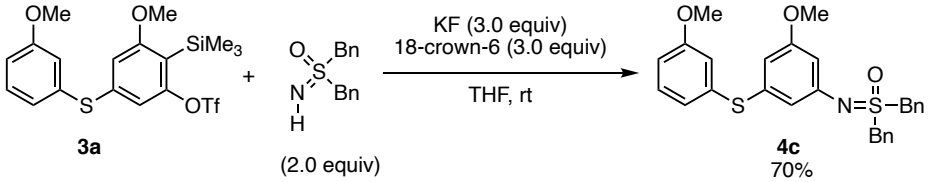
*Synthesis of N-(3-methoxy-5-(3-methoxyphenylsulfinyl)phenyl)morpholine (**4a**)*



In a 5 mL screw-top V-vial® with a solid-top cap (Sigma-Aldrich, Cat. No. Z115118), to a solution of 3-methoxy-5-(3-methoxyphenylthio)-2-(trimethylsilyl)phenyl triflate (**3a**) (23.4 mg, 50.0 μmol, 1.0 equiv) and morpholine (21.3 mg, 0.250 mmol, 5.0 equiv) dissolved in THF (0.50 mL) were added potassium fluoride (8.7 mg, 0.15 mmol, 3.0 equiv) and 18-crown-6 (40.2 mg, 0.150 mmol, 3.0 equiv) at room temperature. After stirring for 24 h at the same temperature, to the mixture was added phosphate buffer solution (pH 7, 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 preparative TLC (*n*-hexane/EtOAc = 4/1) to give *N*-(3-methoxy-5-(3-methoxyphenylthio)phenyl)morpholine (**4a**) (13.9 mg, 41.9 μmol, 84%) as a colorless oil.

Similarly, 5-methoxy-7-(3-methoxyphenylthio)-1,4-dimethyl-1,4-dihydro-1,4-epoxynaphthalene (**4d**), 1-benzyl-4-methoxy-6-((3-methoxyphenyl)thio)-1*H*-benzo[*d*][1,2,3]triazole (**4e**), and 4-(3-methoxyphenyl)-2,8,8-trimethoxybicyclo[4.2.0]octa-1,3,5-triene (**4f**) were prepared from *o*-silylaryl triflate **3a** and with 2,5-dimethylfuran, benzyl azide, or 1,1-dimethoxyethene.

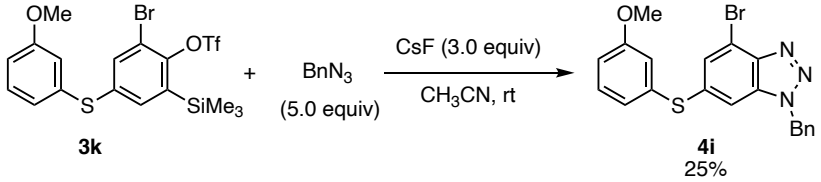
*Synthesis of S,S-dibenzyl-N-(3-methoxy-5-(3-methoxyphenylthio)phenyl)slfoximine (**4c**)*



To a solution of 3-methoxy-5-(3-methoxyphenylthio)-2-(trimethylsilyl)phenyl triflate (**3a**) (93.4 mg, 0.20 mmol, 1.0 equiv) and *S*,*S*-di(benzyl)sulfoximine (98.0 mg, 0.400 mmol, 2.0 equiv) dissolved in THF (2.0 mL) were added potassium fluoride (34.4 mg, 0.592 mmol, 3.0 equiv) and 18-crown-6 (159 mg, 0.602 mmol, 3.0 equiv) at room temperature. After stirring for 24 h at the same temperature, to the mixture was added phosphate buffer solution (pH 7, 10 mL). The mixture was extracted with CH_2Cl_2 (10 mL × 5). 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 19 g, *n*-hexane/EtOAc = 3/1) to give *S*,*S*-dibenzyl-*N*-(3-methoxy-5-(3-methoxyphenylthio)phenyl)sulfoximine (**4c**) (69.0 mg, 0.141 mmol, 70%) as a brown oil.

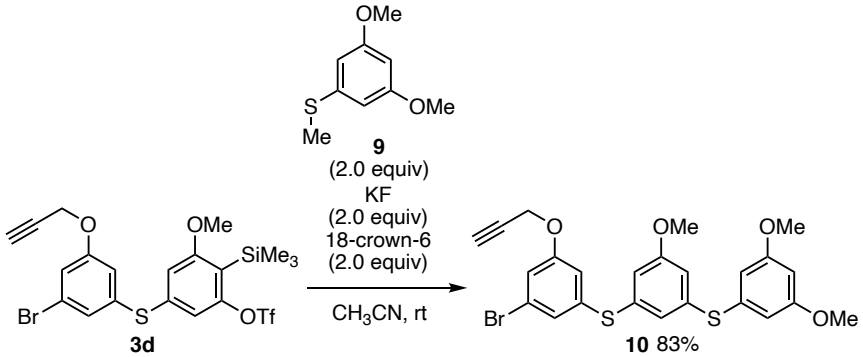
Similarly, dodecyl 3-methoxy-5-(3-methoxyphenylsulfinyl)phenyl sulfide (**4b**), 1-benzyl-6-((3,4-dimethoxyphenyl)thio)-4-methoxy-1*H*-benzo[*d*][1,2,3]triazole (**4g**), 1-benzyl-6-((2-(methylthio)-3-trifluoromethylbenzo[*b*]thiophen-6-yl)thio)-4-methoxy-1*H*-benzo[*d*][1,2,3]triazole (**4h**), and 1-benzyl-6-((3-methoxyphenyl)thio)-4-morpholino-1*H*-benzo[*d*][1,2,3]triazole (**4j**) were prepared from *o*-silylaryl triflates **3a**, **3b**, **3j**, or **3m** with dodecanethiol or benzyl azide.

*Synthesis of 1-benzyl-4-bromo-6-((3-methoxyphenyl)thio)-1H-benzo[d][1,2,3]triazole (**4i**)*



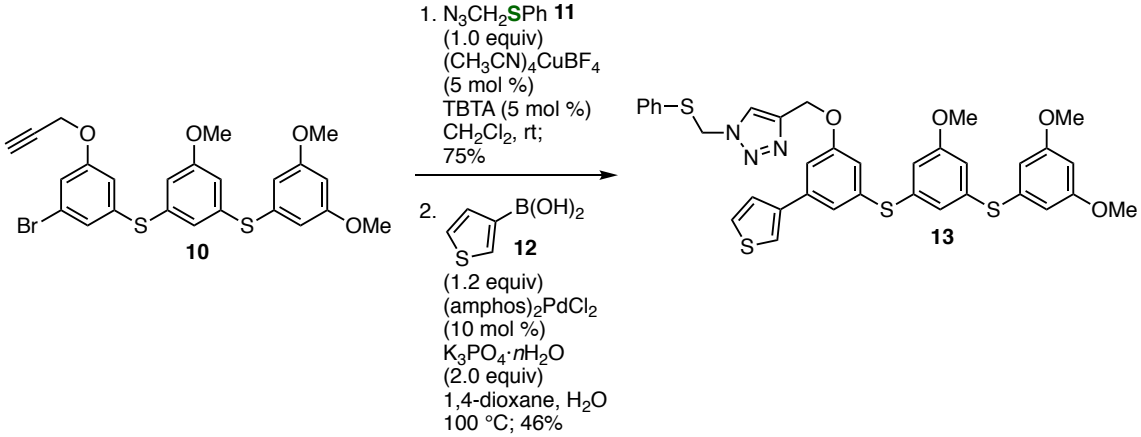
To a solution of 2-bromo-4-(3-methoxyphenylthio)-6-(trimethylsilyl)phenyl triflate (**3k**) (16.4 mg, 32.8 μmol, 1.0 equiv) and benzyl azide (21.1 mg, 0.159 mmol, 5.0 equiv) dissolved in CH_3CN (1.0 mL) was added cesium fluoride (15.5 mg, 95.3 μmol, 3.0 equiv) at room temperature. After stirring for 24 h at the same temperature, to the mixture was added phosphate buffer solution (pH 7, 10 mL). The mixture was extracted with CH_2Cl_2 (5 mL × 3). The combined organic extract was washed with brine (5 mL) and dried with Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified preparative TLC (*n*-hexane/EtOAc = 3/1) to give 1-benzyl-4-bromo-6-((3-methoxyphenyl)thio)-1*H*-benzo[*d*][1,2,3]triazole (**4i**) (3.4 mg, 8.0 μmol, 25%) as a colorless oil.

*Synthesis of 3-(3-(3,5-dimethoxyphenylthio)-5-methoxyphenylthio)-5-(propargyloxy)-1-bromobenzene (**10**)*



In a 5 mL screw-top V-vial® with a solid-top cap (Sigma-Aldrich, Cat. No. Z115118), to a solution of 5-(3-bromo-5-(propargyloxy)phenylthio)-3-methoxy-2-(trimethylsilyl)phenyl triflate (**3d**) (45.1 mg, 79.2 μmol, 1.0 equiv) and 3,5-dimethoxyphenyl methyl sulfide (**9**) (42.2 mg, 0.158 mmol, 2.0 equiv) dissolved in CH_3CN (2.0 mL) were added potassium fluoride (9.2 mg, 0.158 mmol, 2.0 equiv) and 18-crown-6 (41.7 mg, 0.158 mmol, 2.0 equiv) at room temperature. After stirring for 24 h at the same temperature, to the mixture was added water (4 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 preparative TLC (*n*-hexane/EtOAc = 4/1) to give 3-(3-(3,5-dimethoxyphenylthio)-5-methoxyphenylthio)-5-(propargyloxy)-1-bromobenzene (**10**) (33.9 mg, 65.6 μmol, 83%) as a pale yellow oil.

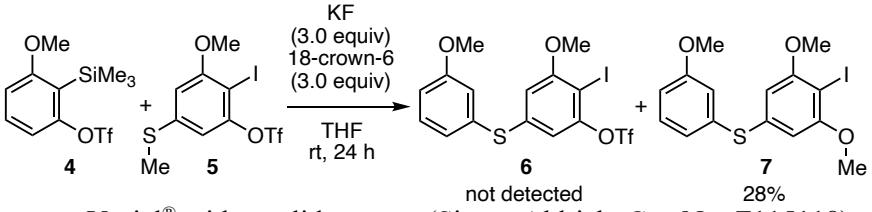
*Synthesis of 3-(3-(3,5-dimethoxyphenylthio)-5-methoxyphenylthio)-5-((1-(phenylthiomethyl)-1,2,3-triazol-4-yl)methyloxy)-1-(3-thienyl)benzene (**13**)*



In a 5 mL screw-top V-vial® with a solid-top cap (Sigma-Aldrich, Cat. No. Z115118), to a solution of 3-(3-(3,5-dimethoxyphenylthio)-5-methoxyphenylthio)-5-(propargyloxy)-1-bromobenzene (**10**) (16.8 mg, 32.5 μmol, 1.0 equiv) and (phenylthiol)methyl azide (**11**) (5.51 mg, 32.5 μmol, 1.0 equiv) dissolved in *t*-BuOH (1.0 mL) and water (1.0 mL) were added tris[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl]amine (TBTA) (0.89 mg, 1.6 μmol, 5 mol %) and $(CH_3CN)_4CuBF_4$ (0.60 mg, 1.6 μmol, 5 mol %) at room temperature. After stirring for 24 h at the same temperature, to the mixture was added water (3 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 preparative TLC (*n*-hexane/EtOAc = 3/2) to give 3-(3-(3,5-dimethoxyphenylthio)-5-methoxyphenylthio)-5-((1-(phenylthiomethyl)-1,2,3-triazol-4-yl)methyloxy)-1-bromobenzene (**S1**) (16.7 mg, 24.5 μmol, 75%) as a colorless oil.

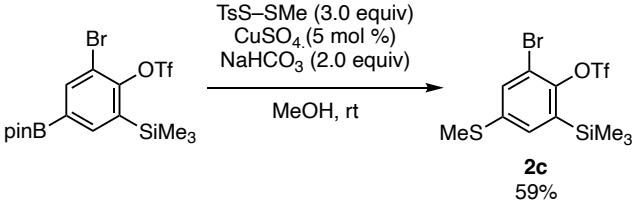
In a 5 mL screw-top V-vial® with a solid-top cap (Sigma-Aldrich, Cat. No. Z115118), to a mixture of 3-(3-(3,5-dimethoxyphenylthio)-5-methoxyphenylthio)-5-((1-(phenylthiomethyl)-1,2,3-triazol-4-yl)methyloxy)-1-bromobenzene (**S1**) (6.26 mg, 9.17 μmol, 1.0 equiv), 3-thienylboronic acid (**12**) (1.46 mg, 11.4 μmol, 1.2 equiv), $(amphos)_2PdCl_2$ (0.65 mg, 0.92 μmol, 10 mol %), and $K_3PO_4{\cdot}nH_2O$ (4.12 mg, 18.3 μmol, 2.0 equiv) were added 1,4-dioxane (45 μL) and water (15 μL) at room temperature. After stirring for 17 h at 100 °C, to the mixture was added water (5 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 preparative TLC (*n*-hexane/EtOAc = 3/2) to give 3-(3-(3,5-dimethoxyphenylthio)-5-methoxyphenylthio)-5-((1-(phenylthiomethyl)-1,2,3-triazol-4-yl)methyloxy)-1-(3-thienyl)benzene (**13**) (2.9 mg, 4.2 μmol, 46%) as a colorless oil.

*An initial attempt of hydrothiolation of 3-methoxybenzyne using **4** and **5***



In a 5 mL screw-top V-vial® with a solid-top cap (Sigma-Aldrich, Cat. No. Z115118), to a solution of 3-methoxy-2-(trimethylsilyl)phenyl triflate (**4**) (33.1 mg, 97.9 μmol, 1.0 equiv), 2-iodo-3-methoxy5-(methylthio)phenyl triflate (**5**) (43.2 mg, 0.101 mmol, 1.0 equiv) in THF (1.0 mL) were added KF (17.6 mg, 0.303 mol, 3.1 equiv) and 18-crown-6 (80.1 mg, 0.303 mmol, 3.1 equiv) at room temperature. After stirring for 24 h at the same temperature, to the mixture was added phosphate buffer solution (pH 7, 2 mL). The mixture was extracted with CH_2Cl_2 (10 mL × 3). The combined organic 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 = 9/1) to give 2,6-Dimethoxy-4-(3-methoxyphenylthio)phenyl iodide (**7**) (11.2 mg, 27.8 μmol, 28%) as a colorless oil.

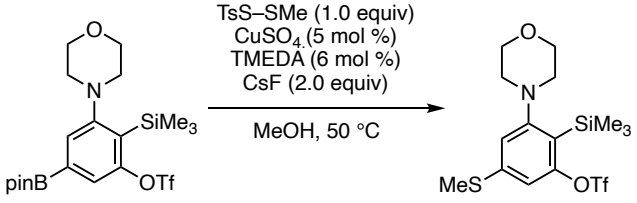
Typical procedure for the synthesis of methylthio-substituted o-silylaryl triflates ***2***



To a mixture of copper(II) sulfate (8.0 mg, 50 μmol, 5 mol %) and sodium bicarbonate (168 mg, 2.00 mmol, 2.0 equiv) were added a solution of *S*-(methyl) 4-toluenethiosulfonate (607 mg, 3.00 mmol, 3.0 equiv) and 2-bromo-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(trimethylsilyl)phenyl triflate (506 mg, 1.01 mmol, 1.0 equiv) dissolved in methanol (15 mL) at room temperature. After stirred for 20 h at the same temperature, the mixture was concentrated under reduced pressure. To the mixture was added saturated aqueous ammonium chloride (20 mL). The mixture was extracted with EtOAc (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 = 15/1). To remove a small amount of impurity, further purification was carried out by recycling preparative HPLC system (JAI, LC9210) equipped with a refractive index detector and JAIGEL1H and 2H columns (GPC) using $CHCl_3$ as an eluent, which provided 2-bromo-5-methylthio-6-(trimethylsilyl)phenyl triflate (**2c**) (217 mg, 0.513 mmol, 51%) as a colorless oil.

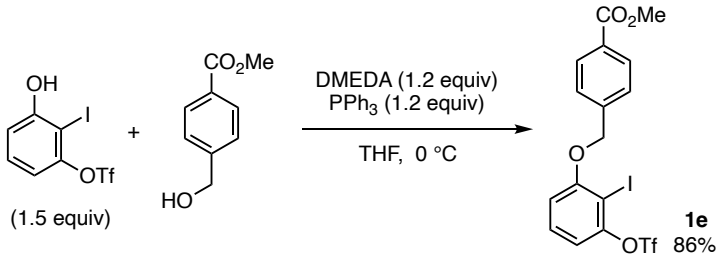
Similarly, 3-(trideuteriomethyloxy)-5-(methylthio)-2-(trimethylsilyl)phenyl triflate (**2a**), 3-(trideuteriomethyloxy)-5-methylthio-2-(trimethylsilyl)phenyl triflate (**2a-*d***), 3-(trideuteriomethyloxy)-5-(ethylthio)-2-(trimethylsilyl)phenyl triflate (**2b**), 2-chloro-5-methylthio-6-(trimethylsilyl)phenyl triflate (**2d**) were prepared from the corresponding *o*-silylaryl triflates.

Synthesis of o-silylaryl triflates ***2d***



In a 5 mL screw-top V-vial® with a solid-top cap (Sigma-Aldrich, Cat. No. Z115118) was placed a solution of *S*-(methyl) 4-toluenethiosulfonate (40.7 mg, 0.201 mmol, 1.0 equiv), 3-morpholino-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trimethylsilyl)phenyl triflate (150 mg, 0.294 mmol, 1.5 equiv), copper(Ⅱ) sulfate (1.6 mg, 10 μmol, 5 mol %) and sodium bicarbonate (61.1 mg, 0.40 mmol, 2.0 equiv) were added methanol (2.0 mL) and *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TMEDA) (1.8 μL, 12 μmol, 6 mol %) at room temperature. After stirred for 24 h at 50 °C, the mixture was passed through a pad of celite. To the mixture was added EtOAc (10 mL). The mixture 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/toluene = 4/1) to give 5-methylthio-3-morpholino-2-(trimethylsilyl)phenyl triflate (**2d**) (69.0 mg, 0.149 mmol, 74%) as a colorless solid.

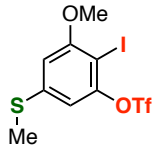
*Synthesis of 3-(4-(methoxycarbonyl)benzyloxy)-2-iodophenyl triflate (**1e**)*



To a solution of 3-hydroxy-2-iodophenyl triflate (1.66 g, 4.51 mmol, 1.5 equiv), 4-(methoxycarbonyl)benzyl alcohol (499 mg, 3.00 mmol, 1.0 equiv), and triphenylphosphine (944 mg, 3.60 mmol, 1.2 equiv) in tetrahydrofuran (15 mL) was added bis(2-methoxyethyl) azodicarboxylate (DMEAD) (843 mg, 3.60 mmol, 1.2 equiv) at 0 °C. After stirred for 8 h at the same temperature, to the mixture was added water (20 mL). The mixture was extracted with diethyl ether (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 flash column chromatography (silica-gel 90 g, *n*-hexane/EtOAc = 5/1) to give 3-(4-(methoxycarbonyl)benzyloxy)-2-iodophenyl triflate (**1e**) (1.33 g, 2.57 mmol, 86%) as a colorless solid.

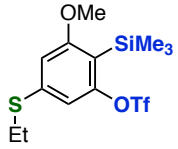
Characterization Data of New Compounds

2-Iodo-3-methoxy-5-(methylthio)phenyl triflate (**5**)



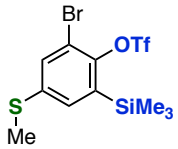
Colorless solid; Mp 90−92 °C; TLC R_f 0.29 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.51 (s, 3H), 3.91 (s, 3H), 6.67 (d, 1H, J = 1.8 Hz), 6.78 (d, 1H, J = 1.8 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 15.5 (1C), 57.0 (1C), 108.0 (1C), 111. 2 (1C), 114.9 (1C), 118.6 (q, 1C, $J_{C–F}$ = 321.4 Hz), 142.9 (1C), 151.4 (1C), 159.9 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –73.3 (s); IR (KBr, cm^{-1}) 912, 947, 1072, 1138, 1217, 1395, 1425, 1581; HRMS (ESI$^+$) *m/z* 450.8753 ([M+Na]$^+$, $C_9H_8F_3INaO_4S_2^+$ requires 450.8753).

5-Ethylthio-3-methoxy-2-(trimethylsilyl)phenyl triflate (**2b**)



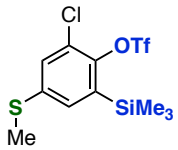
Colorless oil; TLC R_f 0.57 (*n*-hexane/EtOAc = 9/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.34 (s, 9H), 1.36 (t, 3H, J = 7.5 Hz), 2.96 (q, 2H, J = 7.5 Hz), 3.80 (s, 3H), 6.71 (s, 1H), 6.82 (s, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 0.72 (3C), 13.9 (1C), 26.7 (1C), 55.6 (1C), 108.8 (1C), 111.1 (1C), 117.5 (1C), 118.6 (q, 1C, $J_{C–F}$ = 321.4 Hz), 142.2 (1C), 154.8 (1C), 165.3 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –73.0 (s); IR (KBr, cm^{-1}) 1045, 1140, 1211, 1389, 1420, 1589; HRMS (ESI$^+$) *m/z* 411.0331 ([M+Na]$^+$, $C_{13}H_{19}F_3NaO_4S_2Si^+$ requires 411.0338).

2-Bromo-4-(methylthio)-6-(trimethylsilyl)phenyl triflate (**2c**)



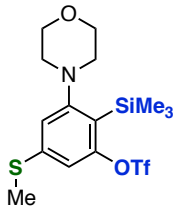
Colorless oil; TLC R_f 0.57 (*n*-hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.39 (s, 9H), 2.49 (s, 3H), 7.29 (d, 1H, J = 2.4 Hz), 7.46 (d, 1H, J = 2.4 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 0.0 (3C), 15.7 (1C), 117.0 (1C), 118.6 (q, 1C, $J_{C–F}$ = 321 Hz), 132.0 (1C), 132.9 (1C), 137.7 (1C), 140.7 (1C), 146.0 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –71.9 (s); IR (KBr, cm^{-1}) 620, 765, 812, 843, 847, 881, 1137, 1213, 1256, 1407; HRMS (ESI$^+$) *m/z* 444.9171 ([M+Na]$^+$, $C_{11}H_{14}{}^{79}BrF_3NaO_3S_2Si^+$ requires 444.9181).

2-Chloro-4-(methylthio)-6-(trimethylsilyl)phenyl triflate (**2d**)



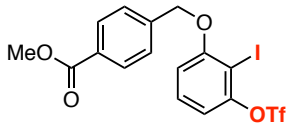
Colorless oil; TLC R_f 0.41 (*n*-hexane/EtOAc = 15/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.40 (s, 9H), 2.50 (s, 3H), 7.24 (d, 1H, J = 2.4 Hz), 7.29 (d, 1H, J = 2.4 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ –0.2 (3C), 15.6 (1C), 118.6 (q, 1C, $^1J_{C–F}$ = 322 Hz), 127.9 (1C), 128.7 (1C), 132.0 (1C), 137.6 (1C), 140.5 (1C), 145.3 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –71.8 (s); IR (KBr, cm^{-1}) 621, 820, 849, 885, 1127, 1136, 1178, 1211, 1255; HRMS (ESI$^+$) *m/z* 400.9672 ([M+Na]$^+$, $C_{11}H_{14}{}^{35}ClF_3NaO_3S_2Si^+$ requires 400.9686).

5-(Methylthio)-3-morpholino-2-(trimethylsilyl)phenyl triflate (**2e**)



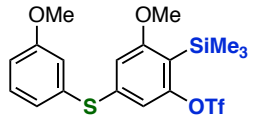
Colorless solid; Mp 84−86 °C; TLC R_f 0.43 (*n*-hexane/acetone = 10/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.39 (s, 9H), 2.49 (s, 3H), 2.75–2.98 (br, 4H), 3.74–3.93 (br, 4H), 6.96 (d, 1H, J = 1.5 Hz), 7.15 (d, 1H, J = 1.5 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 1.9 (3C), 15.0 (1C), 54.5 (2C), 66.7 (2C), 114.9 (1C), 118.6 (q, 1C, $J_{C–F}$ = 321.4 Hz), 119.8 (1C), 126.7 (1C), 143.6 (1C), 155.1 (1C), 161.7 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –72.9 (s); IR (KBr, cm^{-1}) 982, 1111, 1138, 1215, 1274, 1393, 1580; HRMS (ESI$^+$) *m/z* 430.0786 ([M+H]$^+$, $C_{15}H_{23}F_3NO_4S_2Si^+$ requires 430.0784).

3-(4-(Methoxycarbonyl)benzyl)oxy-2-iodophenyl triflate (**S2**)



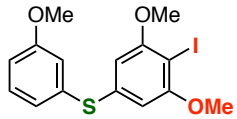
Colorless solid; Mp 128−130 °C; TLC R_f 0.57 (*n*-hexane/EtOAc = 3/2); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.93 (s, 3H), 5.24 (s, 2H), 6.83 (d, 1H, J = 8.4 Hz), 6.99 (d, 1H, J = 8.4 Hz), 7.36 (d, 1H, J = 8.4, 8.4 Hz), 7.53–7.61 (m, 2H), 8.03–8.13 (m, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 52.2 (1C), 70.9 (1C), 83.4 (1C), 111.5 (1C), 114.7 (1C), 118.7 (q, 1C, $J_{C–F}$ = 320.0 Hz), 126.7 (2C), 130.0 (2C+1C, two signals overlapped), 130.4 (1C), 140.7 (1C), 151.4 (1C), 159.1 (1C), 166.7 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –73.4 (s); IR (KBr, cm^{-1}) 949, 1063, 1136, 1209, 1279, 1422, 1589, 1719; HRMS (ESI$^+$) *m/z* 538.9243 ([M+Na]$^+$, $C_{16}H_{12}F_3INaO_6S^+$ requires 538.9244).

3-Methoxy-5-(3-methoxyphenylthio)-2-(trimethylsilyl)phenyl triflate (**3a**)



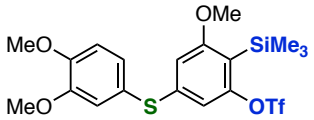
Pale brown oil; TLC R_f 0.26 (*n*-hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.33 (s, 9H), 3.74 (s, 3H), 3.80 (s, 3H), 6.65 (d, 1H, J = 1.1 Hz), 6.69 (d, 1H, J = 1.1 Hz), 6.92 (ddd, 1H, J = 8.0, 2.4, 0.6 Hz), 7.00 (dd, 1H, J = 2.4, 1.9 Hz), 7.05 (ddd, 1H, J = 8.0, 1.9, 0.6 Hz), 7.30 (dd, 1H, J = 8.0, 8.0 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 0.7 (3C), 55.4 (1C), 55.6 (1C), 109.3 (1C), 112.5 (1C), 114.9 (1C), 118.3 (1C), 118.46 (q, 1C, $J_{C–F}$ = 322 Hz), 118.52 (1C), 125.6 (1C), 130.4 (1C), 133.0 (1C), 142.3 (1C), 154.8(1C), 160.3 (1C), 165.5 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –73.0 (s); IR (KBr, cm^{-1}) 813, 844, 884, 1046, 1139, 1209, 1249, 1419, 1575, 1586; HRMS (ESI$^+$) *m/z* 489.0428 ([M+Na]$^+$, $C_{18}H_{21}F_3NaO_5S_2Si^+$ requires 489.0444).

2,6-Dimethoxy-4-(3-methoxyphenylthio)phenyl iodide (**7**)



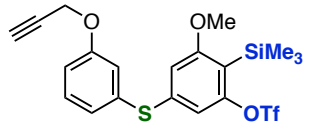
Colorless oil; TLC R_f 0.57 (*n*-hexane/acetone = 4/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.78 (s, 3H), 3.81 (s, 6H), 6.50 (s, 2H), 6.81 (ddd, 1H, J = 8.3, 2.4, 0.7 Hz), 6.90 (dd, 1H, J = 2.4, 2.4 Hz), 6.94 (ddd, 1H, J = 8.3, 2.4, 0.7 Hz), 7.24 (dd, 1H, J = 8.3, 8.3 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 55.3 (1C), 56.6 (2C), 76.3 (1C), 106.7 (2C), 113.2 (1C), 116.2 (1C), 123.2 (1C), 130.1 (1C), 136.1 (1C), 137.8 (1C), 159.7 (2C), 160.1 (1C); IR (KBr, cm^{-1}) 1016, 1039, 1119, 1231, 1392, 1462, 1566, 1589; HRMS (ESI$^+$) *m/z* 424.9679 ([M+Na]$^+$, $C_{15}H_{15}INaO_3S^+$ requires 424.9679).

3-Methoxy-5-(3,4-dimethoxyphenylthio)-2-(trimethylsilyl)phenyl triflate (**3b**)



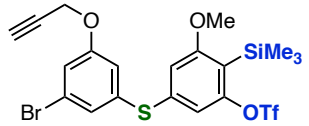
Colorless oil; TLC R_f 0.35 (*n*-hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.31 (s, 9H), 3.72 (s, 3H), 3.87 (s, 3H), 3.93 (s, 3H), 6.51 (d, 1H, J = 1.3 Hz), 6.59 (d, 1H, J = 1.3 Hz), 6.91 (d, 1H, J = 8.3 Hz), 7.03 (d, 1H, J = 2.1 Hz), 7.14 (dd, 1H, J = 8.3, 2.1 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 0.7 (3C), 55.6 (1C), 56.0 (2C), 107.3 (1C), 110.6 (1C), 111.8 (1C), 117.4 (1C), 117.6 (1C), 118.4 (q, 1C, $J_{C–F}$ = 321.9 Hz), 121.1 (1C), 128.3 (1C), 144.6 (1C), 149.7 (1C), 150.4 (1C), 154.9 (1C), 165.4 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –73.0 (s); IR (KBr, cm^{-1}) 937, 1045, 1138, 1211, 1253, 1389, 1320, 1504, 1587; HRMS (ESI$^+$) *m/z* 497.0730 ([M+H]$^+$, $C_{19}H_{24}F_3O_6S_2Si^+$ requires 497.0730).

3-Methoxy-5-(3-(propargyloxy)phenylthio)-2-(trimethylsilyl)phenyl triflate (**3c**)



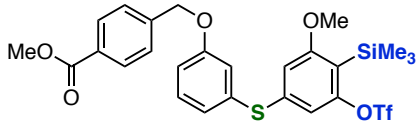
Colorless oil; TLC R_f 0.11 (*n*-hexane/toluene = 5/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.33 (s, 9H), 2.50 (dd, 1H, J = 2.4, 2.4 Hz), 4.68 (d, 2H, J = 2.4 Hz), 3.74 (s, 3H), 6.67 (d, 1H, J = 1.2 Hz), 6.70 (d, 1H, J = 1.2 Hz), 6.98 (ddd, 1H, J = 8.0, 2.5, 0.9 Hz), 7.06 (dd, 1H, J = 2.5, 1.8 Hz), 7.09 (ddd, 1H, J = 8.0, 1.8, 0.9 Hz), 7.32 (dd, 1H, J = 8.0, 8.0 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 0.7 (3C), 55.6 (1C), 55.9 (1C), 75.8 (1C), 78.0 (1C), 109.7 (1C), 112.9 (1C), 115.6 (1C), 117.5 (q, 1C, $J_{C–F}$ = 322 Hz), 118.8 (1C), 119.2 (1C), 126.2 (1C), 130.4 (1C), 133.4 (1C), 141.9 (1C), 154.8 (1C), 158.2 (1C), 165.5 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –73.0 (s); IR (KBr, cm^{-1}) 812, 843, 847, 883, 1045, 1139, 1210, 1215, 1418, 1586; HRMS (ESI$^+$) *m/z* 513.0437 ([M+Na]$^+$, $C_{20}H_{21}F_3NaO_5S_2Si^+$ requires 513.0444).

5-(5-Bromo-3-(propargyloxy)phenylthio)-3-methoxy-2-(trimethylsilyl)phenyl triflate (**3d**)



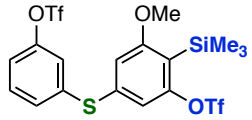
Colorless oil; TLC R_f 0.43 (*n*-hexane/CH_2Cl_2 = 4/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.37 (s, 9H), 2.55 (s, 1H), 3.80 (s, 3H), 4.68 (s, 2H), 6.78 (s, 1H), 6.81 (s, 1H), 6.95 (s, 1H), 7.12 (s, 1H), 7.22 (s, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 0.7 (3C), 55.7 (1C), 56.1 (1C), 76.3 (1C), 77.4 (1C), 110.8 (1C), 114.2 (1C), 117.0 (1C), 118.2 (1C), 118.5 (q, 1C, $J_{C–F}$ = 321.6 Hz), 120.0 (1C), 123.3 (1C), 127.4 (1C), 136.2 (1C), 139.7 (1C), 154.7 (1C), 158.5 (1C), 165.6 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –72.9 (s); IR (KBr, cm^{-1}) 1045, 1140, 1213, 1253, 1389, 1418, 1570, 3300; HRMS (ESI$^+$) *m/z* 590.9549 ([M+Na]$^+$, $C_{20}H_{20}{}^{79}BrF_3NaO_5S_2Si^+$ requires 590.9549).

3-Methoxy-5-(3-(4-(methoxycarbonyl)benzyloxy)phenylthio)-2-(trimethylsilyl)phenyl triflate (**3e**)



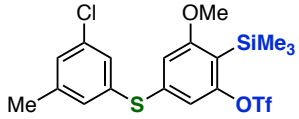
Colorless oil; TLC R_f 0.41 (*n*-hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.33 (s, 9H), 3.73 (s, 3H), 3.92 (s, 3H), 5.11 (s, 2H), 6.67 (d, 1H, J = 1.2 Hz), 6.69 (d, 1H, J = 1.2 Hz), 6.92–7.00 (m, 1H), 7.03–7.10 (m, 2H), 7.30 (dd, 1H, J = 8.0, 8.0 Hz), 7.43–7.51 (m, 2H), 8.00–8.09 (m, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 0.7 (3C), 52.2 (1C), 55.6 (1C), 69.4 (1C), 109.6 (1C), 112.8 (1C), 115.5 (1C), 118.5 (q, 1C, $J_{C–F}$ = 321.8 Hz), 118.8 (1C), 118.9 (1C), 125.8 (1C), 127.0 (2C), 129.8 (1C), 129.9 (2C), 130.5 (1C), 133.5 (1C), 141.6 (1C), 141.9 (1C), 154.8 (1C), 159.2 (1C), 165.5 (1C), 166.8 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –73.0 (s); IR (KBr, cm^{-1}) 1045, 1140, 1211, 1280, 1388, 1416, 1585, 1722; HRMS (ESI$^+$) *m/z* 623.0812 ([M+Na]$^+$, $C_{26}H_{27}F_3NaO_7S_2Si^+$ requires 623.0812).

3-Methoxy-5-(3-(triflyloxy)phenylthio)-2-(trimethylsilyl)phenyl triflate (**3f**)



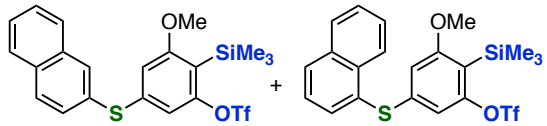
Colorless oil; TLC R_f 0.36 (*n*-hexane/EtOAc = 20/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.35 (s, 9H), 3.76 (s, 3H), 6.75 (d, 1H, J = 1.2 Hz), 6.79 (d, 1H, J = 1.2 Hz), 7.23 (ddd, 1H, J = 8.0, 2.1, 1.3 Hz), 7.28 (dd, 1H, J = 2.1, 2.1 Hz), 7.40 (ddd, 1H, J = 8.0, 2.1, 1.3 Hz), 7.45 (dd, 1H, J = 8.0, 8.0 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 0.64 (3C), 55.7 (1C), 111.0 (1C), 114.5 (1C), 118.5 (q, 1C, $J_{C–F}$ = 321.4 Hz), 118.6 (q, 1C, $J_{C–F}$ = 321.4 Hz), 120.6 (1C), 120.7 (1C), 124.2 (1C), 131.0 (1C), 131.3 (1C), 136.9 (1C), 139.0 (1C), 149.8 (1C), 154.8 (1C), 165.8 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –73.06 (s, 3F), –73.07 (s, 3F); IR (KBr, cm^{-1}) 1047, 1140, 1213, 1249, 1423, 1585; HRMS (ESI$^+$) *m/z* 606.9780 ([M+Na]$^+$, $C_{18}H_{18}F_6NaO_7S_3Si^+$ requires 606.9780).

5-(3-Chloro-5-methylphenylthio)-3-methoxy-2-(trimethylsilyl)phenyl triflate (**3g**)



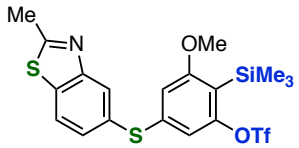
Pale yellow oil; TLC R_f 0.44 (*n*-hexane/toluene = 5/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.34 (s, 9H), 2.33 (s, 3H), 3.76 (s, 3H), 6.69 (d, 1H, J = 1.1 Hz), 6.71 (d, 1H, J = 1.1 Hz), 7.12–7.18 (m, 2H), 7.23 (s, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 0.7 (3C), 21.0 (1C), 55.7 (1C), 109.9 (1C), 113.2 (1C), 118.5 (q, 1C, $J_{C–F}$ = 322 Hz), 119.2 (1C), 129.3 (2C), 131.4 (1C), 134.0 (1C), 134.8 (1C), 141.0 (1C), 141.1 (1C), 154.8(1C), 165.5 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –73.0 (s); IR (KBr, cm^{-1}) 811, 845, 885, 1046, 1067, 1142, 1215, 1251, 1419, 1586; HRMS (ESI$^+$) *m/z* 507.0093 ([M+Na]$^+$, $C_{18}H_{20}{}^{35}ClF_3NaO_4S_2Si^+$ requires 507.0105).

5-(2-Naphthyl)-3-methoxy-2-(trimethylsilyl)phenyl triflate (**3h**) + 5-(1-Naphthyl)-3-methoxy-2-(trimethylsilyl)phenyl triflate (**3h'**)



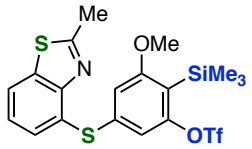
Colorless oil; TLC R_f 0.41 (*n*-hexane/EtOAc = 20/1); ^{1}H NMR for **3h** ($CDCl_3$, 500 MHz) δ 0.33 (s, 9H), 3.69 (s, 3H), 6.70 (s, 1H), 6.73 (s, 1H), 7.47 (dd, 1H, J = 8.6, 1.8 Hz), 7.50–7.56 (m, 2H), 7.78–7.82 (m, 1H), 7.83–7.88 (m, 2H), 8.00 (s, 1H); ^{13}C NMR for **3h** ($CDCl_3$, 126 MHz) δ 0.7 (3C), 55.6 (1C), 109.4 (1C), 112.7 (1C), 118.4 (q, 1C, $J_{C–F}$ = 321.5 Hz), 118.7 (1C), 126.8 (1C), 127.0 (1C), 127.7 (1C), 127.8 (1C), 129.2 (1C), 129.3 (1C), 129.9 (1C), 132.7 (1C), 132.9 (1C), 135.0 (1C), 142.3 (1C), 154.8 (1C), 165.5 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –73.0 (s, for **3h**), –73.1 (s, for **3h'**); IR (KBr, cm^{-1}) 1045, 1155, 1203, 1258, 1420, 1560, 1579; HRMS (ESI$^+$) *m/z* 509.0495 ([M+Na]$^+$, $C_{21}H_{21}F_3NaO_4S_2Si^+$ requires 509.0495).

5-(3-Methoxy-5-(triflyloxy)-4-(trimethylsilyl)phenylthio)-2-methylbenzo[*d*]thiazole (**3i**)



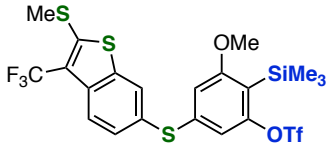
Colorless oil; TLC R_f 0.25 (*n*-hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.33 (s, 9H), 2.85 (s, 3H), 3.71 (s, 3H), 6.64–6.72 (m, 2H), 7.43 (dd, 1H, J = 8.2, 1.8 Hz), 7.83 (d, 1H, J = 8.2 Hz), 8.03 (d, 1H, J = 1.8 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 0.7 (3C), 20.2 (1C), 55.6 (1C), 109.7 (1C), 113.0 (1C), 118.4 (q, 1C, $J_{C–F}$ = 322 Hz), 118.9 (1C), 122.3 (1C), 126.9 (1C), 129.3 (1C), 130.1 (1C), 136.1 (1C), 142.0 (1C), 154.2 (1C), 154.8 (1C), 165.5 (1C), 168.6 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –73.0 (s); IR (KBr, cm^{-1}) 812, 846, 883, 1046, 1068, 1140, 1212, 1251, 1419, 1587; HRMS (ESI$^+$) *m/z* 530.0160 ([M+Na]$^+$, $C_{19}H_{20}F_3NNaO_4S_3Si^+$ requires 530.0168).

4-(3-Methoxy-5-(triflyloxy)-4-(trimethylsilyl)phenylthio)-2-methylbenzo[*d*]thiazole (**3i'**)



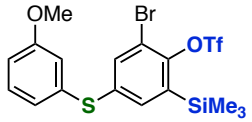
Pale brown oil; TLC R_f 0.24 (*n*-hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.33 (s, 9H), 2.86 (s, 3H), 3.76 (s, 3H), 6.71 (d, 1H, J = 1.2 Hz), 6.89 (d, 1H, J = 1.2 Hz), 7.31 (dd, 1H, J = 7.7, 7.7 Hz), 7.35 (dd, 1H, J = 7.7, 1.3 Hz), 7.80 (dd, 1H, J = 7.7, 1.3 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 0.7 (3C), 20.3 (1C), 55.7 (1C), 111.1 (1C), 114.3 (1C), 118.4 (q, 1C, $J_{C–F}$ = 322 Hz), 119.4 (1C), 121.4 (1C), 125.2 (1C), 126.9 (1C), 129.1 (1C), 136.4 (1C), 140.0 (1C), 152.8 (1C), 154.8 (1C), 165.5 (1C), 168.3 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –73.0 (s); IR (KBr, cm^{-1}) 812, 845, 884, 1046, 1140, 1213, 1251, 1397, 1419, 1587; HRMS (ESI$^+$) *m/z* 530.0147 ([M+Na]$^+$, $C_{19}H_{20}F_3NNaO_4S_3Si^+$ requires 530.0168).

4-(3-Methoxy-5-(triflyloxy)-4-(trimethylsilyl)phenylthio)-2-(methylthio)-3-(trifluoromethyl)benzo[*b*]thiophene (**3j**)



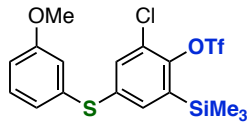
Colorless solid; Mp 77−80 °C; TLC R_f 0.35 (*n*-hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.36 (s, 9H), 2.71 (s, 3H), 3.75 (s, 3H), 6.70 (s, 1H), 6.71 (s, 1H), 7.49 (dd, 1H, J = 8.6, 1.7 Hz), 7.83 (d, 1H, J = 8.6 Hz), 7.86 (dd, 1H, J = 1.7 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 0.7 (3C), 18.4 (q, 1C, $J_{C–F}$ = 1.3 Hz), 55.7 (1C), 109.5 (1C), 112.8 (q, 1C, $J_{C–F}$ = 1.2 Hz), 118.5 (q, 1C, $J_{C–F}$ = 321.4 Hz), 119.1 (1C), 119.3 (q, 1C, $J_{C–F}$ = 34.2 Hz), 122.5 (q, 1C, $J_{C–F}$ = 2.4 Hz), 123.0 (q, 1C, $J_{C–F}$ = 272.7 Hz), 125.8 (1C), 128.2 (1C), 130.4 (1C), 137.1 (1C), 138.5 (1C), 141.8 (1C), 147.7 (q, 1C, $J_{C–F}$ = 2.5 Hz), 154.8 (1C), 165.6 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –56.7 (s, 3F), –72.9 (s, 3F); IR (KBr, cm^{-1}) 1045, 1140, 1217, 1360, 1389, 1420, 1452, 1587; HRMS (ESI$^+$) *m/z* 628.9809 ([M+Na]$^+$, $C_{21}H_{20}F_6NaO_4S_4Si^+$ requires 628.9810).

2-Bromo-4-(3-methoxyphenylthio)-6-(trimethylsilyl)phenyl triflate (**3k**)



Colorless oil; TLC R_f 0.41 (*n*-hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.33 (s, 9H), 3.81 (s, 3H), 6.92 (ddd, 1H, J = 8.0, 2.5, 0.8 Hz), 6.99 (dd, 1H, J = 2.5, 1.6 Hz), 7.04 (ddd, 1H, J = 8.0, 1.6, 0.8 Hz), 7.28 (d, 1H, J = 2.4 Hz), 7.32 (dd, 1H, J = 8.0, 8.0 Hz), 7.43 (d, 1H, J = 2.4 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ –0.1 (3C), 55.4 (1C), 114.8 (1C), 117.1 (1C), 118.2 (1C), 118.6 (q, 1C, $J_{C–F}$ = 322 Hz), 125.4 (1C), 130.6 (1C), 133.3 (1C), 134.8 (1C), 135.2 (1C), 138.1 (1C), 139.4 (1C), 146.9 (1C), 160.4 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –72.0 (s); IR (KBr, cm^{-1}) 807, 847, 881, 1020, 1040, 1055, 1136, 1212, 1227, 1259; HRMS (ESI$^+$) *m/z* 536.9437 ([M+Na]$^+$, $C_{17}H_{18}{}^{79}BrF_3NaO_4S_2Si^+$ requires 536.9443).

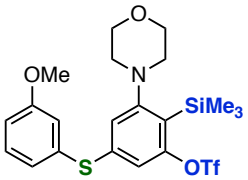
2-Chloro-4-(3-methoxyphenylthio)-6-(trimethylsilyl)phenyl triflate (**3l**)



Colorless oil; TLC R_f 0.31 (*n*-hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.34 (s, 9H), 3.81 (s, 3H), 6.93 (ddd, 1H, J = 8.0, 2.5, 0.8 Hz), 6.99 (dd, 1H, J = 2.5, 1.6 Hz), 7.04 (ddd, 1H, J = 8.0, 1.6, 0.8 Hz), 7.22−7.26 (m, 2H), 7.32 (dd, 1H, J = 8.0, 8.0 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ –0.2 (3C), 55.4 (1C), 114.9 (1C), 118.3 (1C), 118.6 (q, 1C, $J_{C–F}$ = 321 Hz), 125.5 (1C), 128.0 (1C), 130.6

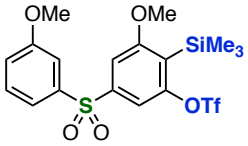
(1C), 131.4 (1C), 133.2 (1C), 134.2 (1C), 137.9 (1C), 139.3 (1C), 146.1 (1C), 160.4 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –71.8 (s); IR (KBr, cm^{-1}) 817, 845, 851, 884, 1137, 1210, 1213, 1227, 1252, 1411; HRMS (ESI$^+$) *m/z* 492.9962 ([M+Na]$^+$, $C_{17}H_{18}{}^{35}ClF_3NaO_4S_2Si^+$ requires 492.9949).

5-(3-Methoxyphenylthio)-3-morpholino-2-(trimethylsilyl)phenyl triflate (**3m**)



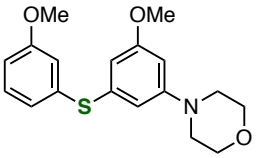
Colorless oil; TLC R_f 0.53 (*n*-hexane/EtOAc = 3/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.38 (s, 9H), 2.72−2.92 (br, 4H), 3.74−3.89 (m, 7H), 6.83 (d, 1H, *J* = 1.5 Hz), 6.95 (ddd, 1H, *J* = 8.3, 2.4, 1.0 Hz), 7.02 (dd, 1H, *J* = 2.4, 2.4 Hz), 7.07 (ddd, 1H, *J* = 8.3, 2.4, 1.0 Hz), 7.12 (d, 1H, *J* = 1.5 Hz), 7.32 (dd, 1H, *J* = 8.3, 8.3 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 1.9 (3C), 54.5 (2C), 55.4 (1C), 66.7 (2C), 115.1 (1C), 117.3 (1C), 118.5 (q, 1C, $J_{C–F}$ = 321.7 Hz), 118.6 (1C), 121.6 (1C), 125.8 (1C), 128.2 (1C), 130.5 (1C), 132.4 (1C), 142.6 (1C), 155.1 (1C), 160.4 (1C), 161.8 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –73.0 (s); IR (KBr, cm^{-1}) 1140, 1211, 1248, 1421, 1578; HRMS (ESI$^+$) *m/z* 522.1049 ([M+H]$^+$, $C_{21}H_{27}F_3NO_5S_2Si^+$ requires 522.1047).

3-Methoxy-5-(3-methoxyphenylsulfonyl)-2-(trimethylsilyl)phenyl triflate (**8**)



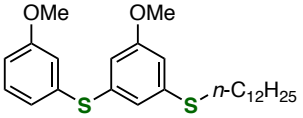
Colorless solid; Mp 102−103 °C; TLC R_f 0.50 (*n*-hexane/EtOAc = 2/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.35 (s, 9H), 3.85 (s, 3H), 3.89 (s, 3H), 7.13 (ddd, 1H, *J* = 8.3, 2.6, 0.9 Hz), 7.32 (dd, 1H, *J* = 1.2 Hz), 7.41−7.48 (m, 3H), 7.50−7.55 (m, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 0.4 (3C), 55.7 (1C), 56.1 (1C), 107.5 (1C), 112.1 (1C), 112.4 (1C), 118.5 (q, 1C, $J_{C–F}$ = 321.4 Hz), 120.0 (1C), 120.3 (1C), 127.6 (1C), 130.6 (1C), 141.5 (1C), 145.0 (1C), 154.1 (1C), 160.2 (1C), 165.9 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –72.8 (s); IR (KBr, cm^{-1}) 1045, 1140, 1153, 1213, 1244, 1317, 1386, 1423, 1479, 1589; HRMS (ESI$^+$) *m/z* 521.0342 ([M+Na]$^+$, $C_{18}H_{21}F_3NaO_7S_2Si^+$ requires 521.0342).

N-(3-Methoxy-5-(3-methoxyphenylthio)phenyl)morpholine (**4a**)



Colorless oil; TLC R_f 0.29 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.07−3.14 (m, 4H), 3.73 (s, 3H), 3.77 (s, 3H), 3.88−3.95 (m, 4H), 6.33 (dd, 1H, *J* = 2.2, 2.2 Hz), 6.43 (dd, 1H, *J* = 2.2, 2.2 Hz), 6.56 (dd, 1H, *J* = 2.2, 2.2 Hz), 6.78 (dd, 1H, *J* = 8.3, 2.4 Hz), 6.89 (dd, 1H, *J* = 2.4, 2.4 Hz), 6.93 (d, 1H, *J* = 8.3 Hz), 7.21 (dd, 1H, *J* = 8.3, 8.3 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 49.0 (2C), 55.2 (1C), 55.3 (1C), 66.7 (2C), 101.3 (1C), 107.5 (1C), 111.3 (1C), 112.8 (1C), 115.8 (1C), 122.9 (1C), 129.9 (1C), 136.7 (1C), 137.0 (1C), 152.9 (1C), 160.0 (1C), 160.9 (1C); IR (KBr, cm^{-1}) 1049, 1123, 1204, 1248, 1449, 1476, 1573, 1589; HRMS (ESI$^+$) *m/z* 332.1315 ([M+H]$^+$, $C_{18}H_{22}NO_3S^+$ requires 332.1315).

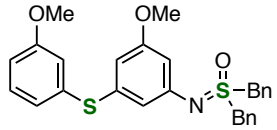
Dodecyl 3-methoxy-5-(3-methoxyphenylsulfinyl)phenyl sulfide (**4b**)



Colorless oil; TLC R_f 0.40 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.88 (t, 3H, *J* = 6.9 Hz), 1.20−1.41 (m, 18H), 1.61 (tt, 2H, *J* = 7.5, 7.5 Hz), 2.85 (t, 2H, *J* = 7.5 Hz), 3.74 (s, 3H), 3.77

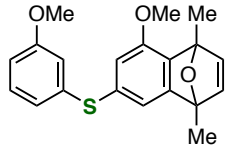
(s, 3H), 6.64 (dd, 1H, J = 1.8, 1.8 Hz), 6.70 (dd, 1H, J = 1.8, 1.8 Hz), 6.78−6.84 (m, 2H), 6.91 (dd, 1H, J = 1.8, 1.8 Hz), 6.93−6.97 (m, 1H), 7.23 (dd, 1H, J = 8.0, 8.0 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 14.1 (1C), 22.7 (1C), 28.8 (1C), 29.0 (1C), 29.1 (1C), 29.3 (1C), 29.4 (1C), 29.5 (1C), 29.62, (1C), 29.63 (1C), 31.9 (1C), 33.0 (1C), 55.2 (1C), 55.3 (1C), 112.5 (1C), 113.0 (1C), 113.3 (1C), 116.6 (1C), 121.9 (1C), 123.7 (1C), 130.0 (1C), 136.0 (1C), 137.5 (1C), 139.6 (1C), 160.1 (1C+1C, two signals overlapped); IR (KBr, cm^{-1}) 1049, 1231, 1248, 1463, 1574, 2850, 2924; HRMS (ESI$^+$) *m/z* 447.2387 ([M+H]$^+$, $C_{26}H_{39}O_2S_2^+$ requires 447.2386).

S,*S*-Dibenzyl-*N*-(3-methoxy-5-(3-methoxyphenylthio)phenyl)sulfoximine (**4c**)



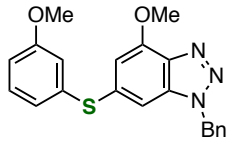
Pale brown solid; Mp 35–37 °C; TLC R_f 0.21 (*n*-hexane/EtOAc = 3/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.70 (s, 3H), 3.74 (s, 3H), 4.26 (d, 2H, J = 13.9 Hz), 4.31 (d, 2H, J = 13.9 Hz), 6.50 (dd, 1H, J = 2.1, 2.1 Hz), 6.54 (dd, 1H, J = 2.1, 2.1 Hz), 6.71 (dd, 1H, J = 2.1, 2.1 Hz), 6.77 (ddd, 1H, J = 8.0, 2.4, 0.9 Hz), 6.91 (dd, 1H, J = 2.4, 1.6 Hz), 6.94 (ddd, 1H, J = 8.0, 1.6, 0.9 Hz), 7.20 (dd, 1H, J = 8.0, 8.0 Hz), 7.29–7.42 (m, 10H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 55.25 (1C), 55.28 (1C), 57.8 (2C), 107.7 (1C), 110.4 (1C), 112.9 (1C), 116.1 (1C), 118.3 (1C), 123.3 (1C), 128.1 (2C), 128.8 (4C), 129.0 (2C), 129.8 (1C), 131.2 (4C) 136.6 (1C), 137.0 (1C), 147.4 (1C), 160.0 (1C), 160.6 (1C); IR (KBr, cm^{-1}) 1040, 1169, 1218, 1247, 1284, 1316, 1417, 1438, 1570, 1587; HRMS (ESI$^+$) *m/z* 512.1349 ([M+Na]$^+$, $C_{28}H_{27}NNaO_3S_2^+$ requires 512.1325).

5-Methoxy-7-(3-methoxyphenylthio)-1,4-dimethyl-1,4-dihydro-1,4-epoxynaphthalene (**4d**)



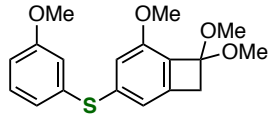
Colorless oil; TLC R_f 0.36 (*n*-hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.81 (s, 3H), 1.99 (s, 3H), 3.74 (s, 3H), 3.75 (s, 3H), 6.69 (d, 1H, J = 1.1 Hz), 6.72 (d, 1H, J = 5.3 Hz), 6.74 (ddd, 1H, J = 8.3, 2.5, 0.7 Hz), 6.79−6.89 (m, 4H), 7.18 (dd, 1H, J = 8.3, 8.3 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 15.3 (1C), 17.0 (1C), 55.3 (1C), 55.6 (1C), 88.6 (1C), 89.3 (1C), 112.3 (1C), 114.3 (1C), 114.8 (1C), 116.1 (1C), 121.8 (1C), 129.9 (1C), 132.4 (1C), 137.9 (1C), 138.0 (1C), 146.3 (1C), 147.3 (1C), 153.4 (1C), 157.0 (1C), 160.0 (1C); IR (KBr, cm^{-1}) 1042, 1250, 1283, 1301, 1458, 1477, 1587; HRMS (ESI$^+$) *m/z* 341.1205 ([M+H]$^+$, $C_{20}H_{21}O_3S^+$ requires 341.1206).

1-Benzyl-4-methoxy-6-((3-methoxyphenyl)thio)-1*H*-benzo[*d*][1,2,3]triazole (**4e**)



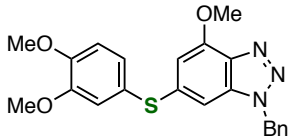
Colorless solid; Mp 77−80 °C; TLC R_f 0.38 (*n*-hexane/EtOAc = 2/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.74 (s, 3H), 4.02 (s, 3H), 5.69 (s, 2H), 6.60 (d, 1H, J = 1.1 Hz), 6.73 (d, 1H, J = 1.1 Hz), 6.84−6.90 (m, 2H), 6.91−6.96 (m, 1H), 7.15−7.21 (m, 2H), 7.22−7.32 (m, 4H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 52.3 (1C), 55.3 (1C), 56.4 (1C), 102.5 (1C), 105.7 (1C), 114.1 (1C), 117.0 (1C), 124.3 (1C), 127.7 (2C), 128.4 (1C), 128.9 (2C), 130.2 (1C), 134.4 (1C), 135.0 (1C), 135.1 (1C), 137.5 (1C), 138.1 (1C), 151.5 (1C), 160.2 (1C); IR (KBr, cm^{-1}) 1087, 1249, 1282, 1479, 1496, 1575, 1589; HRMS (ESI$^+$) *m/z* 378.1280 ([M+H]$^+$, $C_{21}H_{20}N_3O_2S^+$ requires 378.1271).

4-(3-Methoxyphenyl)-2,8,8-trimethoxybicyclo[4.2.0]octa-1,3,5-triene (**4f**)



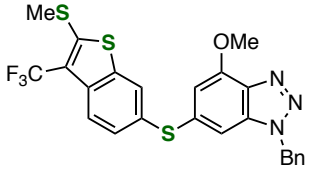
Colorless oil; TLC R_f 0.33 (*n*-hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.25 (s, 2H), 3.46 (s, 6H), 3.77 (s, 3H), 3.80 (s, 3H), 6.77−6.82 (m, 3H), 6.90−6.95 (m, 2H), 7.22 (dd, 1H, *J* = 8.0, 8.0 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 42.4 (1C), 52.2 (2C), 55.3 (1C), 55.7 (1C), 105.3 (1C), 113.01 (1C), 113.04 (1C), 116.2 (1C), 119.0 (1C), 123.3 (1C), 130.0 (1C), 130.3 (1C), 136.8 (1C), 139.2 (1C), 143.8 (1C), 152.9 (1C), 160.0 (1C); IR (KBr, cm^{-1}) 1081, 1107, 1239, 1276, 1464, 1575, 1589; HRMS (ESI^+) *m/z* 355.0974 ($[M+Na]^+$, $C_{18}H_{20}NaO_4S^+$ requires 355.0975).

1-Benzyl-6-((3,4-dimethoxyphenyl)thio)-4-methoxy-1*H*-benzo[*d*][1,2,3]triazole (**4g**)



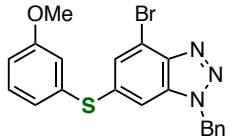
Colorless oil; TLC R_f 0.43 (*n*-hexane/EtOAc = 1/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.77 (s, 3H), 3.96 (s, 3H), 4.02 (s, 3H), 5.64 (s, 2H), 6.41 (s, 1H), 6.50 (s, 1H), 6.86−6.93 (m, 2H), 7.08 (dd, 1H, *J* = 8.3, 2.1 Hz), 7.12−7.17 (m, 2H), 7.24−7.32 (m, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 52.3 (1C), 55.9 (1C), 56.0 (1C), 56.4 (1C), 99.4 (1C), 103.5 (1C), 111.7 (1C), 117.0 (1C), 122.7 (1C), 127.7 (2C+1C, two signals overlapped), 128.4 (1C), 128.8 (2C), 134.4 (1C), 135.2 (1C), 137.1 (1C), 141.3 (1C), 149.6 (1C), 150.0 (1C), 151.4 (1C); IR (KBr, cm^{-1}) 1024, 1085, 1136, 1230, 1252, 1392, 1494, 1504, 1585; HRMS (ESI^+) *m/z* 408.1377 ($[M+H]^+$, $C_{22}H_{22}N_3O_3S^+$ requires 408.1376).

1-Benzyl-6-((2-methylthio-3-trifluoromethylbenzo[*b*]thiophen-6-yl)thio)-4-methoxy-1*H*-benzo[*d*][1,2,3]triazole (**4h**)



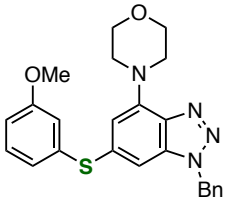
Colorless oil; TLC R_f 0.43 (*n*-hexane/EtOAc = 2/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.72 (s, 3H), 4.05 (s, 3H), 5.70 (s, 2H), 6.61 (d, 1H, *J* = 1.2 Hz), 6.63 (d, 1H, *J* = 1.2 Hz), 7.13−7.19 (m, 2H), 7.22−7.28 (m, 3H), 7.37 (dd, 1H, *J* = 8.6, 1.7 Hz), 7.72−7.78 (m, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 18.4 (q, 1C, J_{C-F} = 1.5 Hz), 52.4 (1C), 56.5 (1C), 102.3 (1C), 105.4 (1C), 119.3 (q, 1C, J_{C-F} = 33.2 Hz), 122.4 (q, 1C, J_{C-F} = 2.4 Hz), 123.1 (q, 1C, J_{C-F} = 272.4 Hz), 125.1 (1C), 127.7 (2C), 128.4 (1C), 128.9 (2C), 129.84 (1C), 129.85 (1C), 134.2 (1C), 135.1 (1C), 136.7 (q, 1C, J_{C-F} = 1.2 Hz), 137.6 (1C), 138.4 (1C), 138.5 (1C), 147.3 (q, 1C, J_{C-F} = 2.5 Hz), 151.7 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –56.7 (s); IR (KBr, cm^{-1}) 1111, 1219, 1252, 1359, 1392, 1452, 1494, 1587, 1605; HRMS (ESI^+) *m/z* 518.0636 ($[M+H]^+$, $C_{24}H_{19}F_3N_3OS_3^+$ requires 518.0637).

1-Benzyl-4-bromo-6-((3-methoxyphenyl)thio)-1*H*-benzo[*d*][1,2,3]triazole (**4i**)



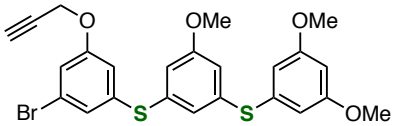
Colorless oil; TLC R_f 0.57 (*n*-hexane/EtOAc = 3/2); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.76 (s, 3H), 5.72 (s, 2H), 6.87−6.89 (m, 1H), 6.90−6.97 (m, 2H), 7.03 (d, 1H, *J* = 1.3 Hz), 7.15−7.20 (m, 2H), 7.26−7.33 (m, 4H), 7.41 (d, 1H, *J* = 1.3 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 52.8 (1C), 55.4 (1C), 108.6 (1C), 113.8 (1C), 114.7 (1C), 117.8 (1C), 125.0 (1C), 127.7 (2C), 128.1 (1C), 128.7 (1C), 129.1 (2C), 130.5 (1C), 133.8 (1C), 133.9 (1C+1C, two signals overlapped), 139.0 (1C), 144.3 (1C), 160.3 (1C); IR (KBr, cm^{-1}) 1040, 1248, 1282, 1421, 1475, 1573, 1589; HRMS (ESI^+) *m/z* 448.0094 ($[M+Na]^+$, $C_{20}H_{16}{}^{79}BrN_3NaOS^+$ requires 448.0090).

1-Benzyl-6-((3-methoxyphenyl)thio)-4-morpholino-1*H*-benzo[*d*][1,2,3]triazole (**4j**)



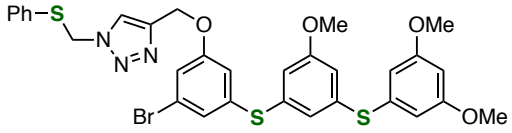
Colorless oil; TLC R_f 0.29 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.65−3.71 (m, 4H), 3.73 (s, 3H), 3.90−3.96 (m, 4H), 5.66 (s, 2H), 6.44 (d, 1H, *J* = 1.1 Hz), 6.64 (d, 1H, *J* = 1.1 Hz), 6.83−6.88 (m, 2H), 6.89−6.95 (m, 1H), 7.14−7.20 (m, 2H), 7.23 (dd, 1H, *J* = 7.9, 7.9 Hz), 7.26−7.31 (m, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 49.4 (2C), 52.0 (1C), 55.3 (1C), 66.8 (2C), 101.2 (1C), 108.0 (1C), 113.8 (1C), 116.7 (1C), 124.0 (1C), 127.6 (2C), 128.4 (1C), 128.9 (2C), 130.1 (1C), 134.6 (1C), 135.2 (1C), 135.5 (1C), 137.7 (1C), 138.2 (1C), 143.2 (1C), 160.1 (1C); IR (KBr, cm^{-1}) 1020, 1121, 1236, 1450, 1477, 1494, 1573, 1587; HRMS (ESI^+) *m/z* 433.1694 ($[M+H]^+$, $C_{24}H_{25}N_4O_2S^+$ requires 433.1693).

3-(3-(3,5-Dimethoxyphenylthio)-5-methoxyphenylthio)-5-(propargyloxy)-1-bromobenzene (**10**)



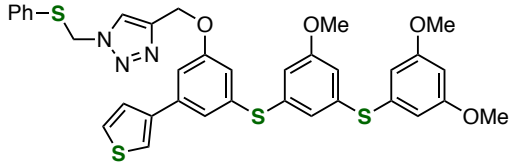
Pale yellow oil; TLC R_f 0.33 (*n*-hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.54 (t, 1H, *J* = 2.4 Hz), 3.74 (s, 3H), 3.75 (s, 6H), 4.61 (d, 2H, *J* = 2.4 Hz), 6.37 (dd, 1H, *J* = 2.2, 2.2 Hz), 6.51 (d, 2H, *J* = 2.2 Hz), 6.76 (dd, 1H, *J* = 1.6, 1.6 Hz), 6.78 (dd, 1H, *J* = 1.6, 1.6 Hz), 6.81 (dd, 1H, *J* = 1.6, 1.6 Hz), 6.88 (dd, 1H, *J* = 1.6, 1.6 Hz), 6.99 (dd, 1H, *J* = 1.6, 1.6 Hz), 7.07 (dd, 1H, *J* = 1.6, 1.6 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 55.4 (2C), 55.5 (1C), 56.1 (1C), 76.4 (1C), 77.6 (1C), 100.3 (1C), 109.5 (2C), 115.1 (1C), 115.5 (1C), 115.6 (1C), 117.2 (1C), 123.0 (1C), 125.1 (1C), 126.1 (1C), 135.7 (1C), 136.0 (1C), 138.4 (1C), 138.5 (1C), 158.3 (1C), 160.4 (1C), 161.1 (2C); IR (KBr, cm^{-1}) 1042, 1155, 1203, 1417, 1587, 3289; HRMS (ESI^+) *m/z* 517.0130 ($[M+H]^+$, $C_{24}H_{22}{}^{79}BrO_4S_2^+$ requires 517.0137).

3-(3-(3,5-Dimethoxyphenylthio)-5-methoxyphenylthio)-5-((1-(phenylthiomethyl)-1,2,3-triazol-4-yl)methyloxy)-1-bromobenzene (**S1**)



Colorless oil; TLC R_f 0.33 (*n*-hexane/EtOAc = 3/2); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.73 (s, 6H), 3.74 (s, 3H), 5.09 (s, 2H), 5.62 (s, 2H), 6.36 (dd, 1H, *J* = 2.2, 2.2 Hz), 6.51 (d, 2H, *J* = 2.2 Hz), 6.75 (dd, 1H, *J* = 1.8, 1.8 Hz), 6.78 (dd, 1H, *J* = 1.8, 1.8 Hz), 6.79 (dd, 1H, *J* = 1.8, 1.8 Hz), 6.86 (dd, 1H, *J* = 1.8, 1.8 Hz), 6.97 (dd, 1H, *J* = 1.8, 1.8 Hz), 7.03 (dd, 1H, *J* = 1.8, 1.8 Hz), 7.27−7.33 (m, 5H), 7.57 (s, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 54.0 (1C), 55.4 (2C), 55.5 (1C), 62.1 (1C), 100.4 (1C), 109.6 (2C), 115.1 (1C), 115.5 (1C), 115.6 (1C), 116.9 (1C), 122.3 (1C), 123.2 (1C), 125.1 (1C), 125.8 (1C), 128.8 (1C), 129.5 (2C), 131.6 (1C), 132.3 (2C), 135.7 (1C), 136.0 (1C), 138.5 (1C), 138.6 (1C), 143.8 (1C), 159.0 (1C), 160.4 (1C), 161.1 (2C); IR (KBr, cm^{-1}) 1045, 1155, 1258, 1420, 1560, 1579; HRMS (ESI^+) *m/z* 682.0497 ($[M+H]^+$, $C_{31}H_{29}{}^{79}BrN_3O_4S_3^+$ requires 682.0498).

3-(3-(3,5-Dimethoxyphenylthio)-5-methoxyphenylthio)-5-((1-(phenylthiomethyl)-1,2,3-triazol-4-yl)methyloxy)-1-(3-thienyl)benzene (**13**)



Colorless oil; TLC R_f 0.33 (*n*-hexane/EtOAc = 3/2); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.69 (s, 6H), 3.72 (s, 3H), 5.17 (s, 2H), 5.62 (s, 2H), 6.32 (dd, 1H, *J* = 2.3, 2.3 Hz), 6.49 (d, 2H, *J* = 2.3 Hz), 6.74 (d, 2H, *J* = 1.5 Hz), 6.83−6.87 (m, 2H), 7.09 (dd, 1H, *J* = 1.5, 1.5 Hz), 7.23 (dd, 1H, *J* = 1.5, 1.5 Hz), 7.24−7.32 (m, 6H), 7.34−7.39 (m, 1H), 7.40−7.43 (m, 1H), 7.60 (s, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 54.0 (1C), 55.4 (2C), 55.5 (1C), 62.0 (1C), 100.0 (1C), 100.2 (1C), 109.4 (2C), 112.6 (1C), 114.4 (1C), 114.5 (1C), 116.2 (1C), 121.2 (1C), 122.3 (1C), 122.7 (1C), 124.1 (1C), 126.2 (1C), 126.4 (1C), 128.8 (1C), 129.5 (2C), 131.6 (1C), 132.3 (2C), 136.0 (1C), 136.1 (1C), 137.9 (1C), 138.0 (1C), 141.0 (1C), 144.3 (1C), 158.9 (1C), 160.3 (1C), 161.1 (2C); IR (KBr, cm^{-1}) 1045, 1155, 1203, 1279, 1454, 1573; HRMS (ESI^+) *m/z* 686.1269 ($[M+H]^+$, $C_{35}H_{32}N_3O_4S_4^+$ requires 686.1270).

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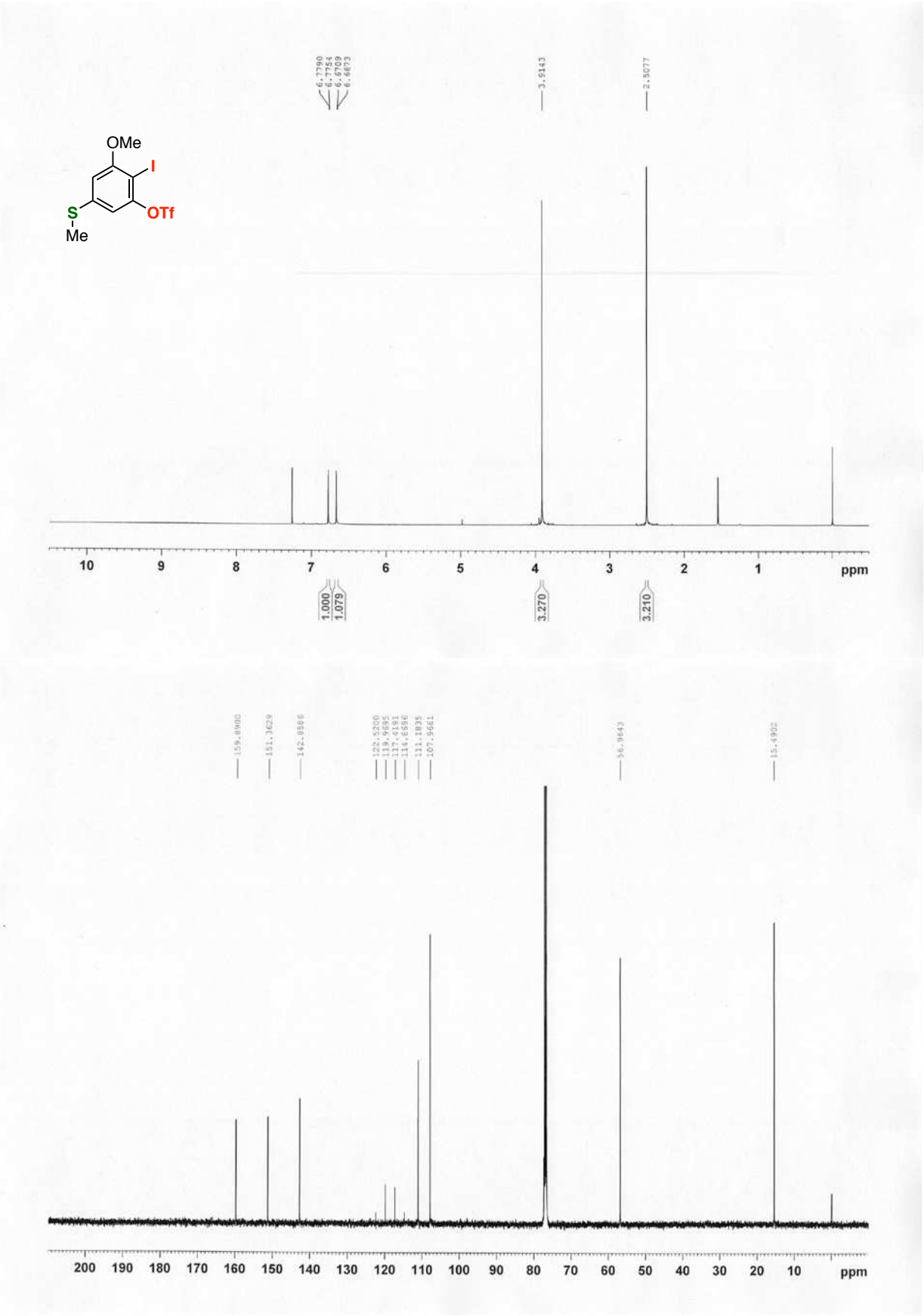
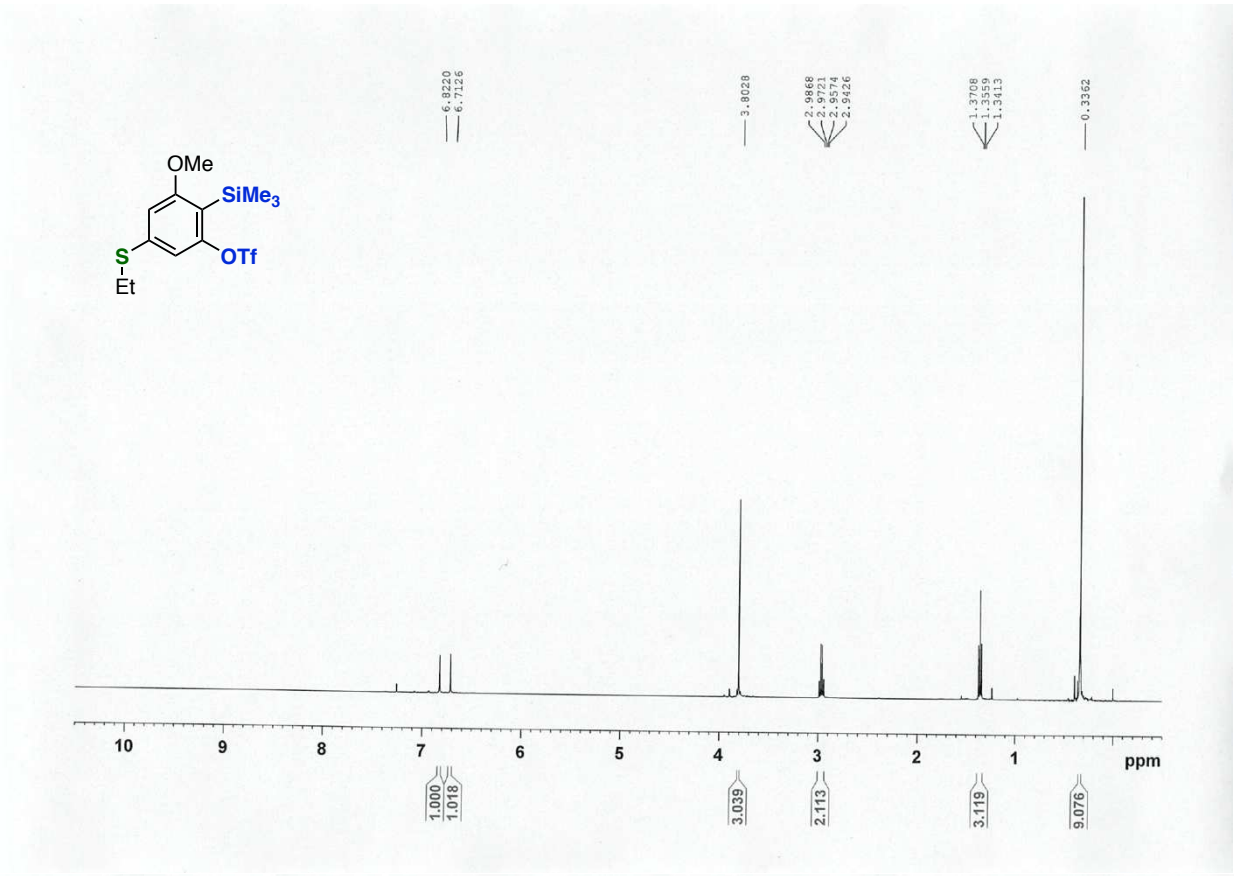
S10) D. E. Bergbreiter and E. Pendergrass, *J. Org. Chem.*, 1981, **46**, 219.

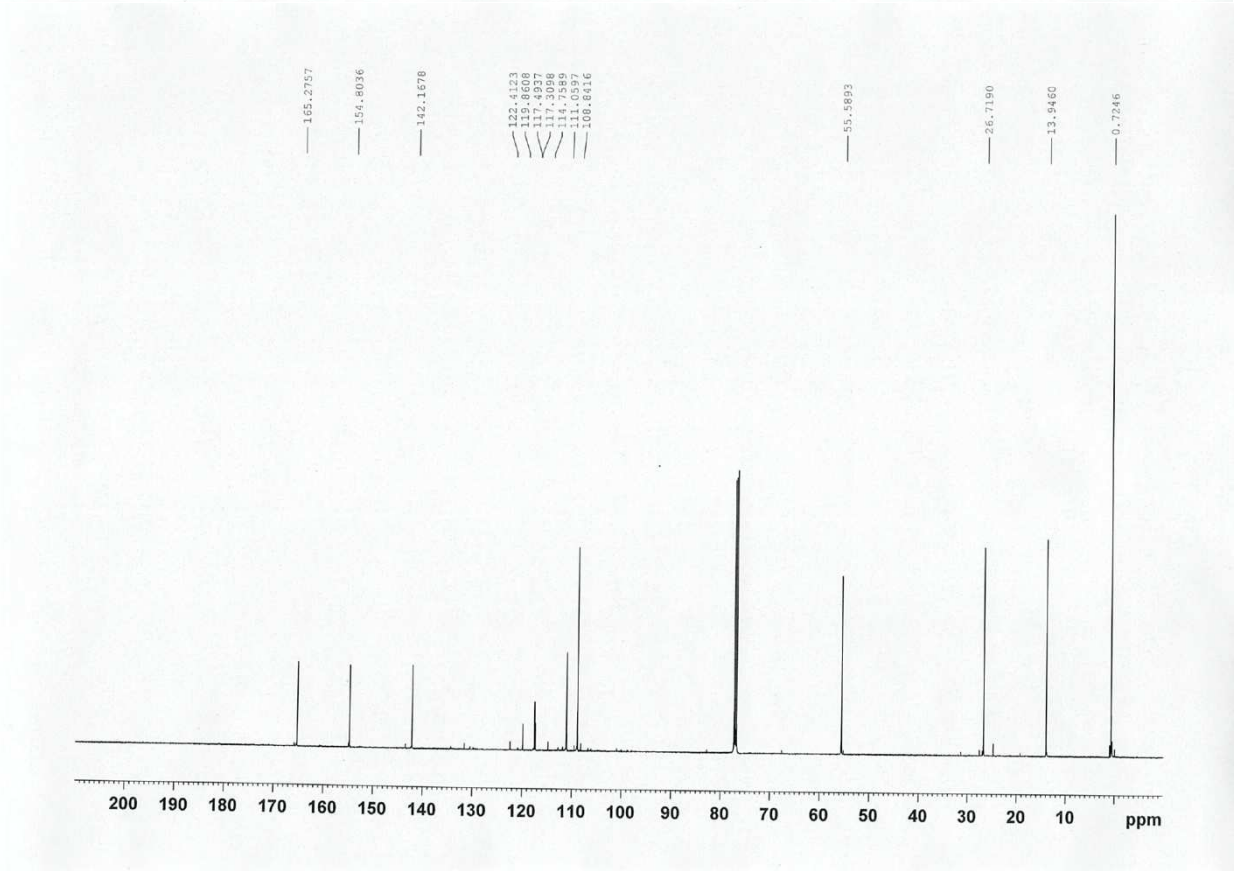
NMR Spectra of New Compounds

^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 2-iodo-3-methoxy-5-(methylthio)phenyl triflate (**5**) ($CDCl_3$)

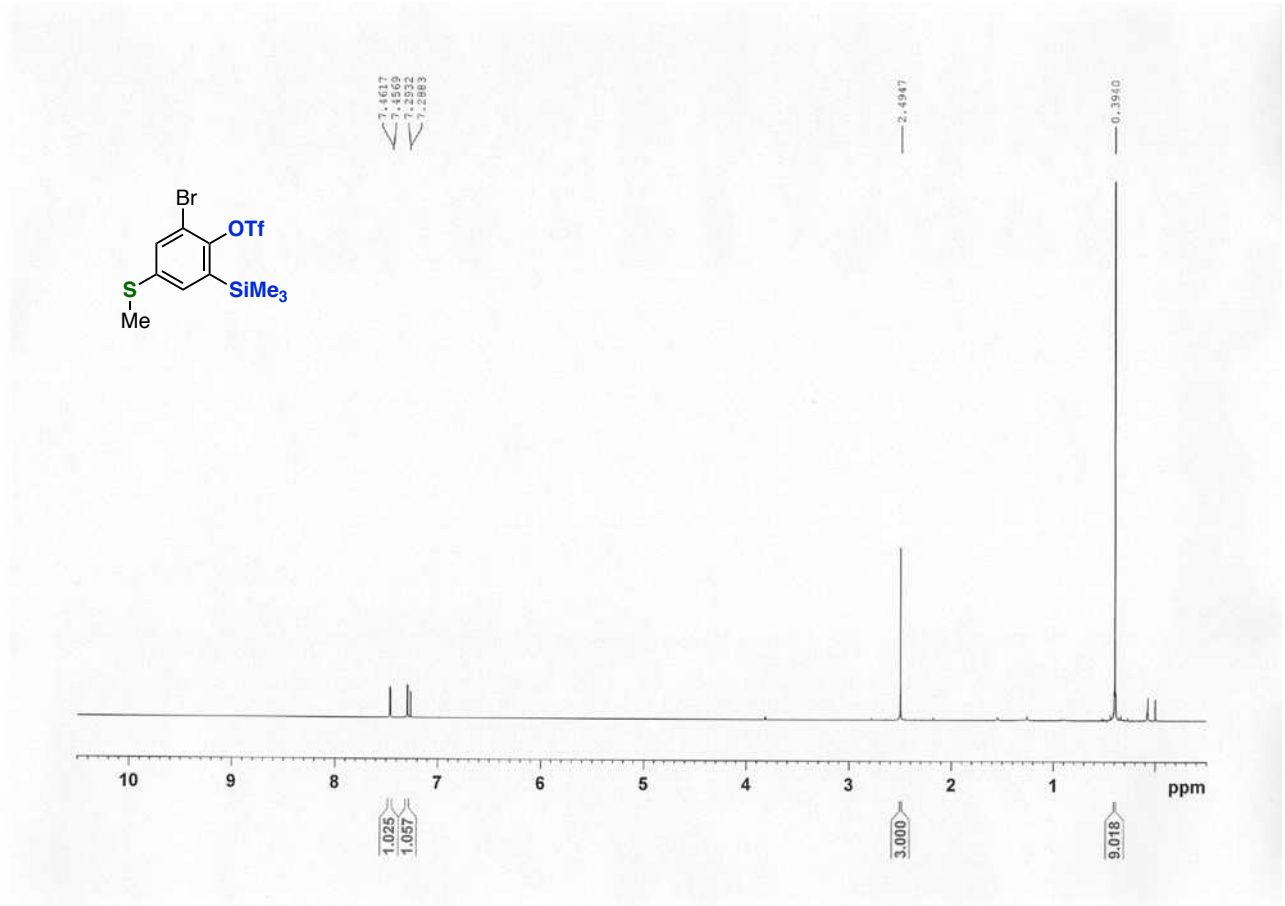


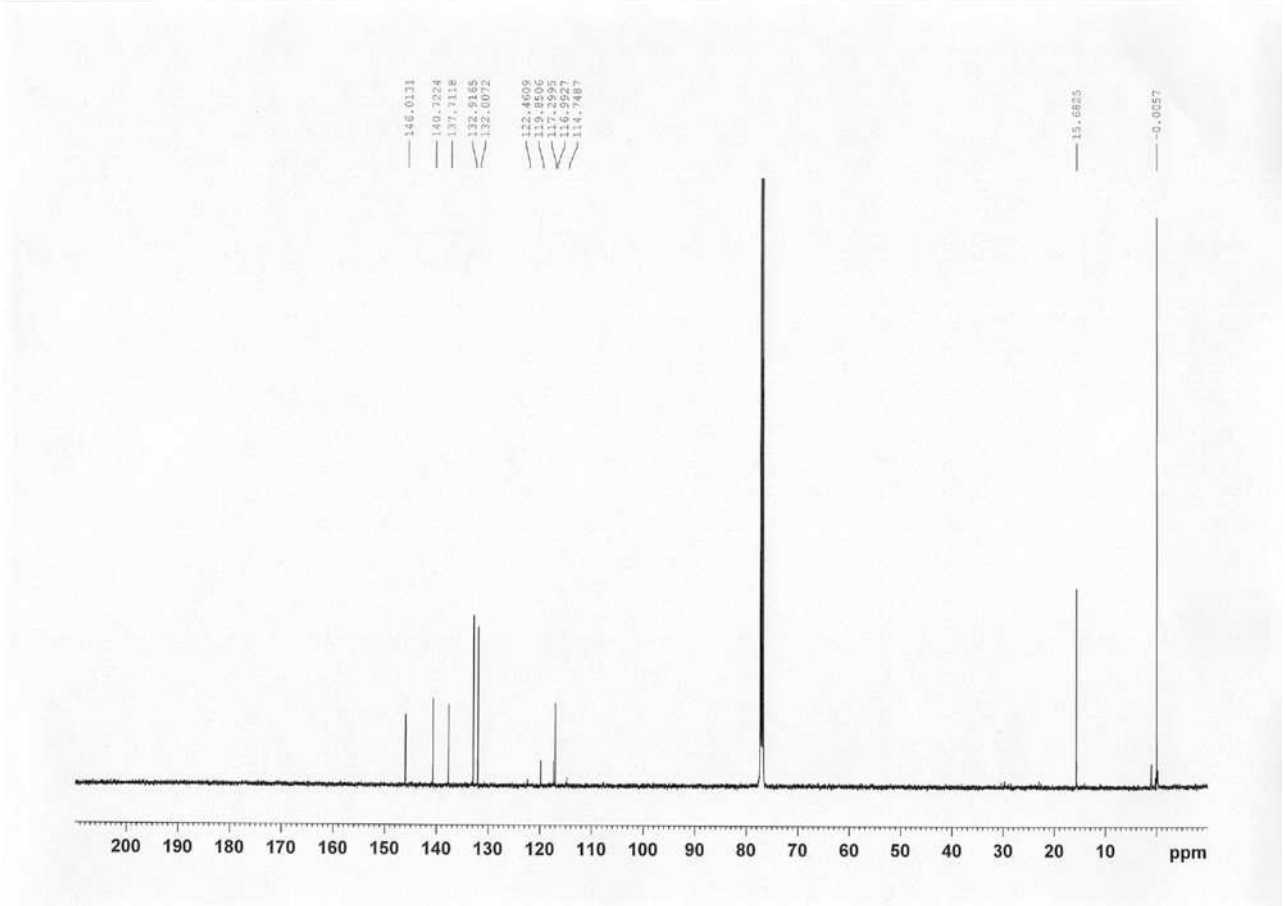
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 5-ethylthio-3-methoxy-2-(trimethylsilyl)phenyl triflate (**2b**) ($CDCl_3$)



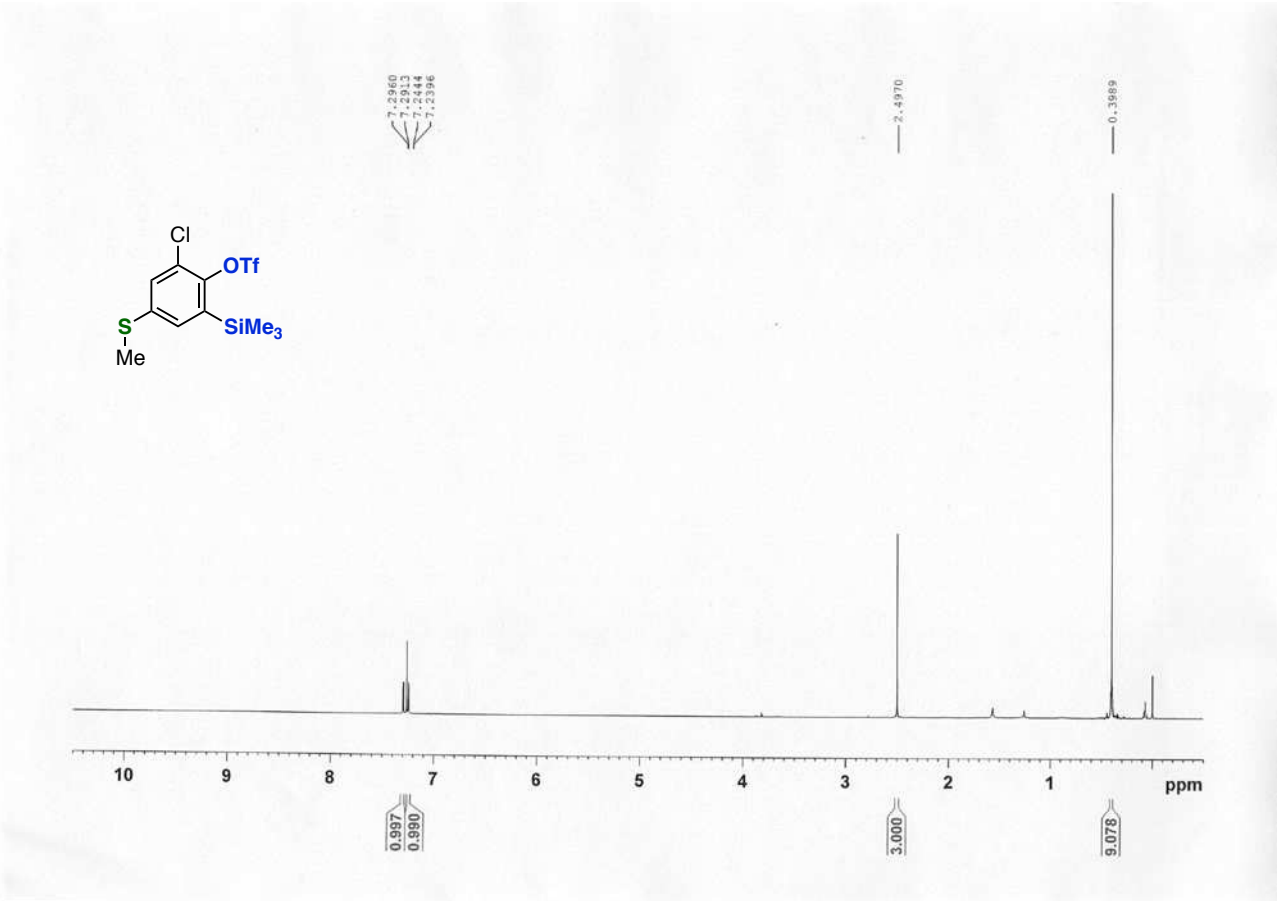


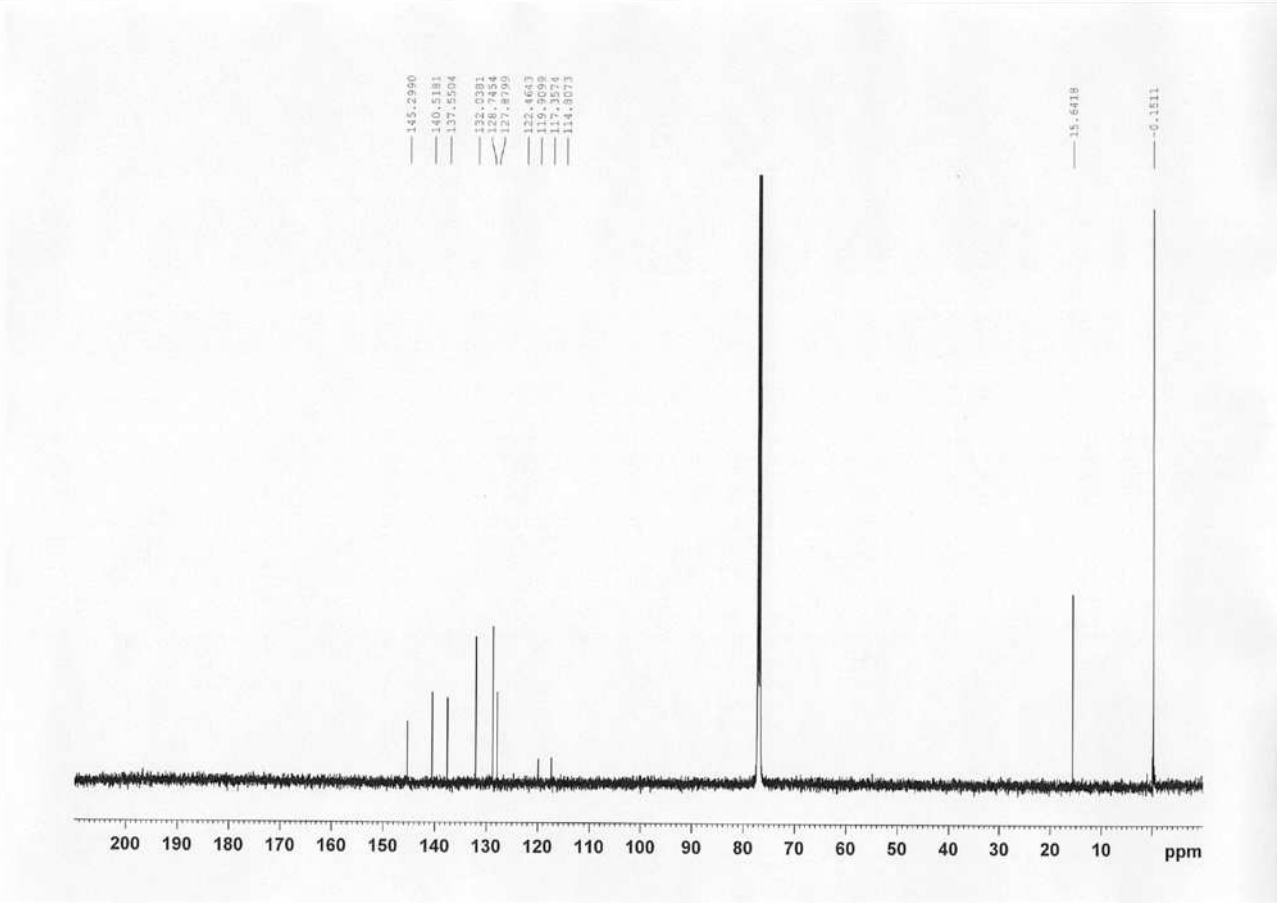
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 2-bromo-4-(methylthio)-6-(trimethylsilyl)phenyl triflate (**2c**) ($CDCl_3$)



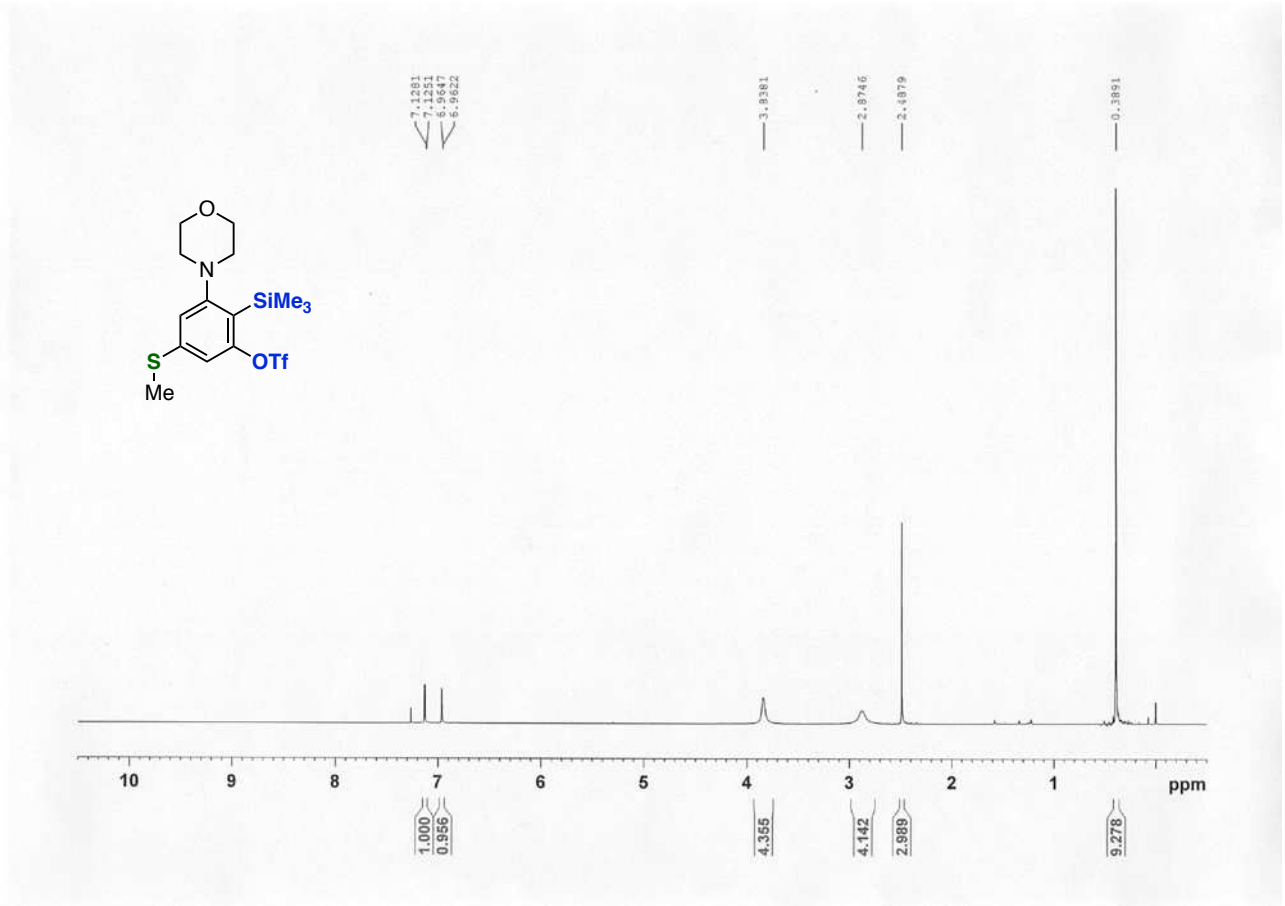


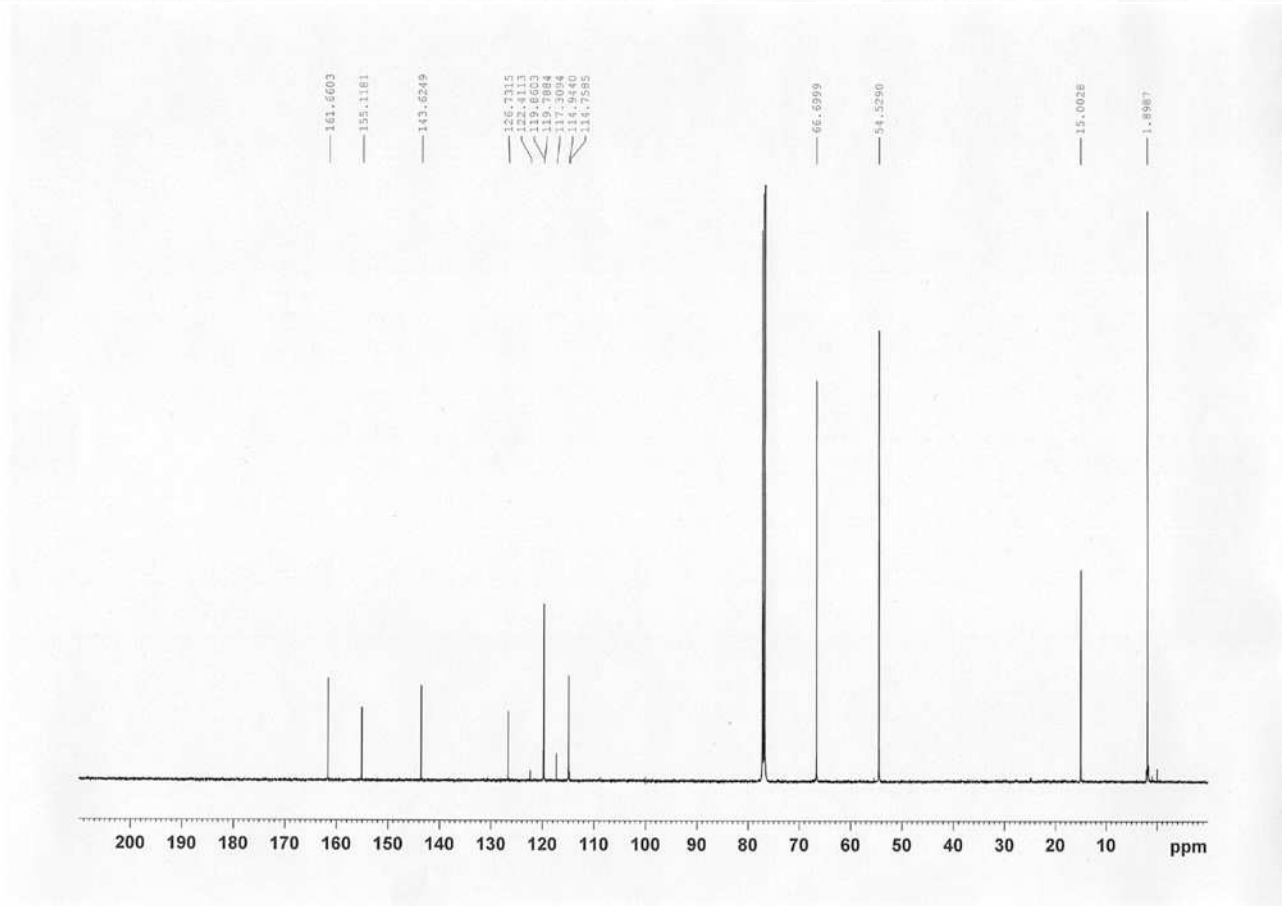
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 2-chloro-4-(methylthio)-6-(trimethylsilyl)phenyl triflate (**2d**) ($CDCl_3$)



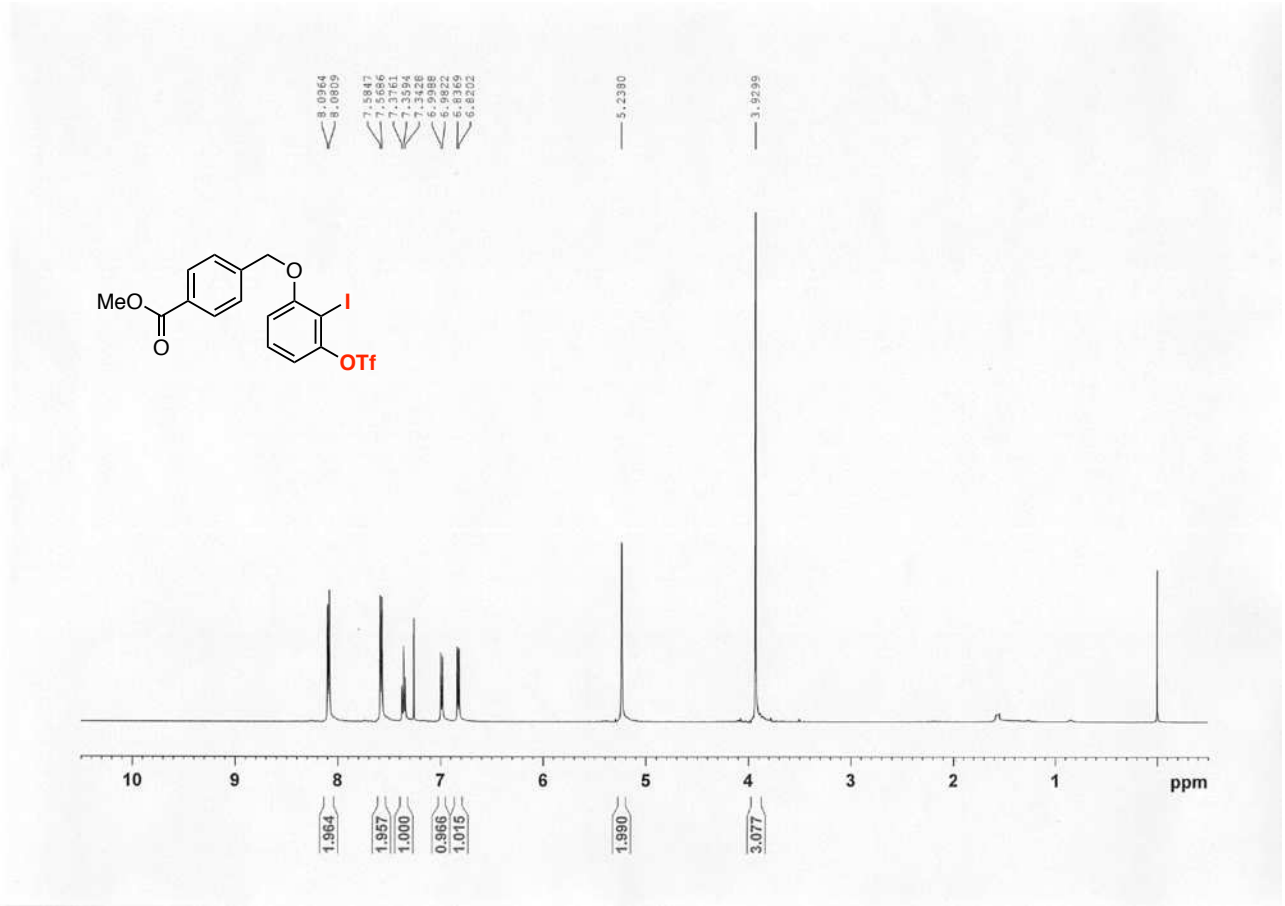


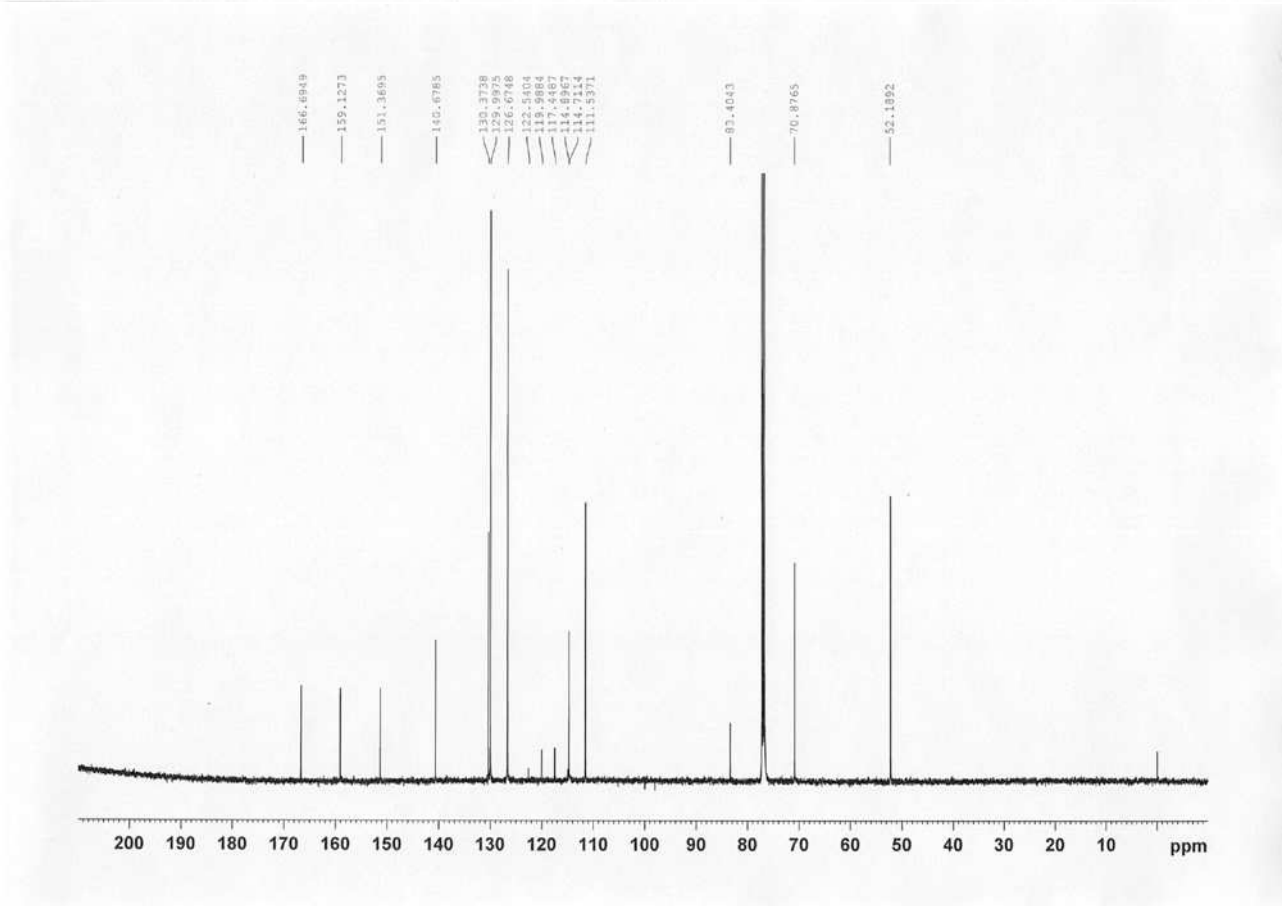
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 5-(methylthio)-3-morpholino-2-(trimethylsilyl)phenyl triflate (**2e**) ($CDCl_3$)



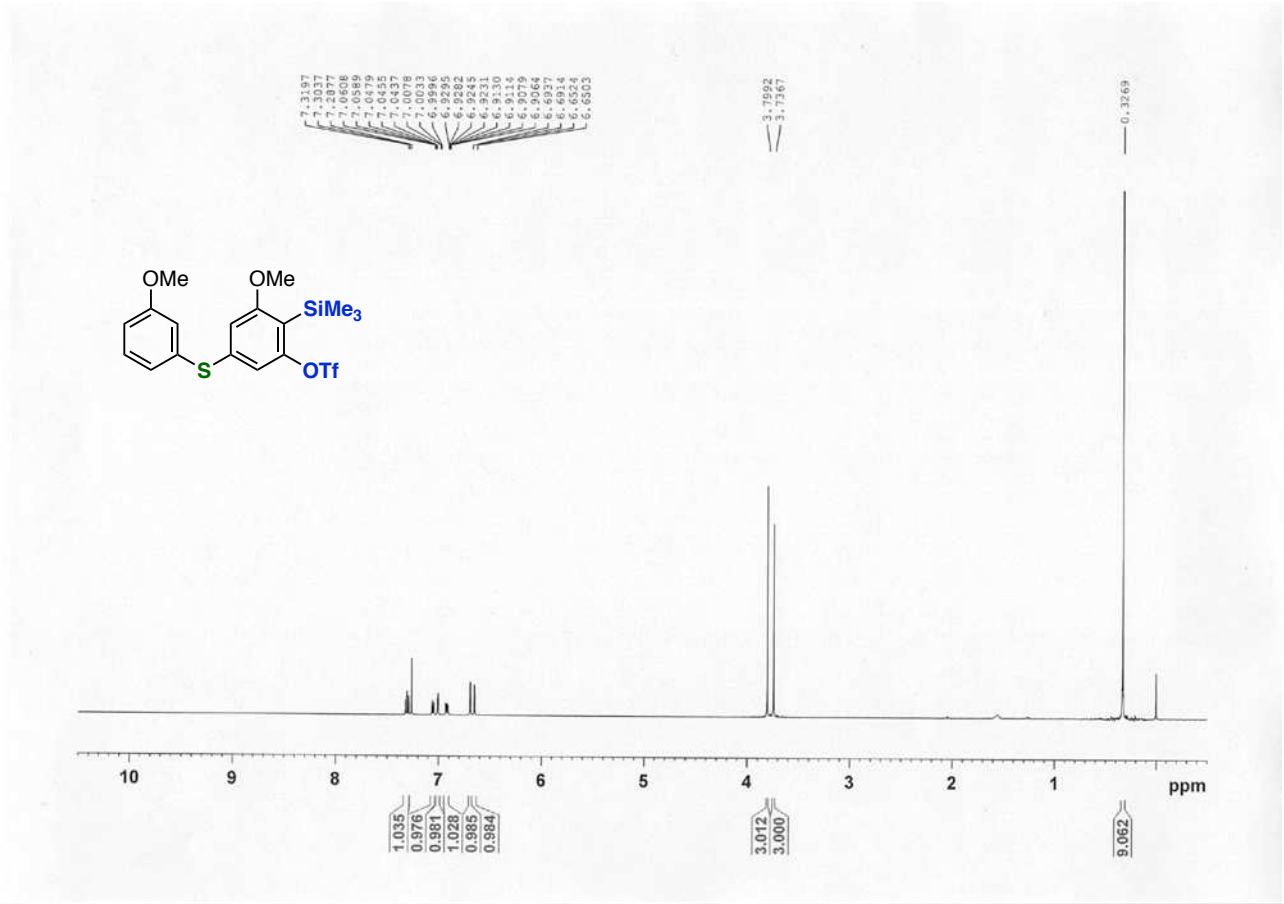


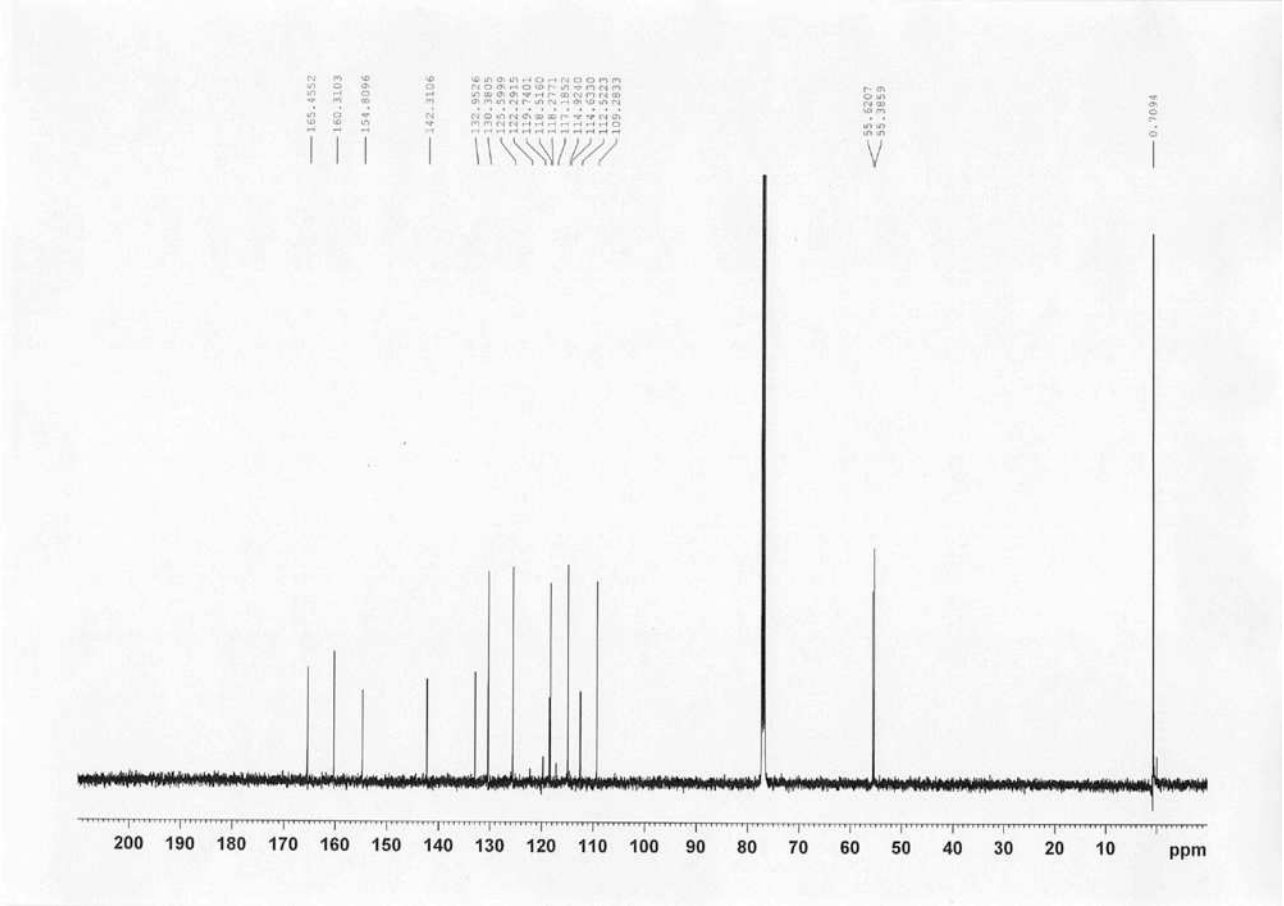
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 3-(4-(methoxycarbonyl)benzyl)oxy-2-iodophenyl triflate (**S2**) ($CDCl_3$)



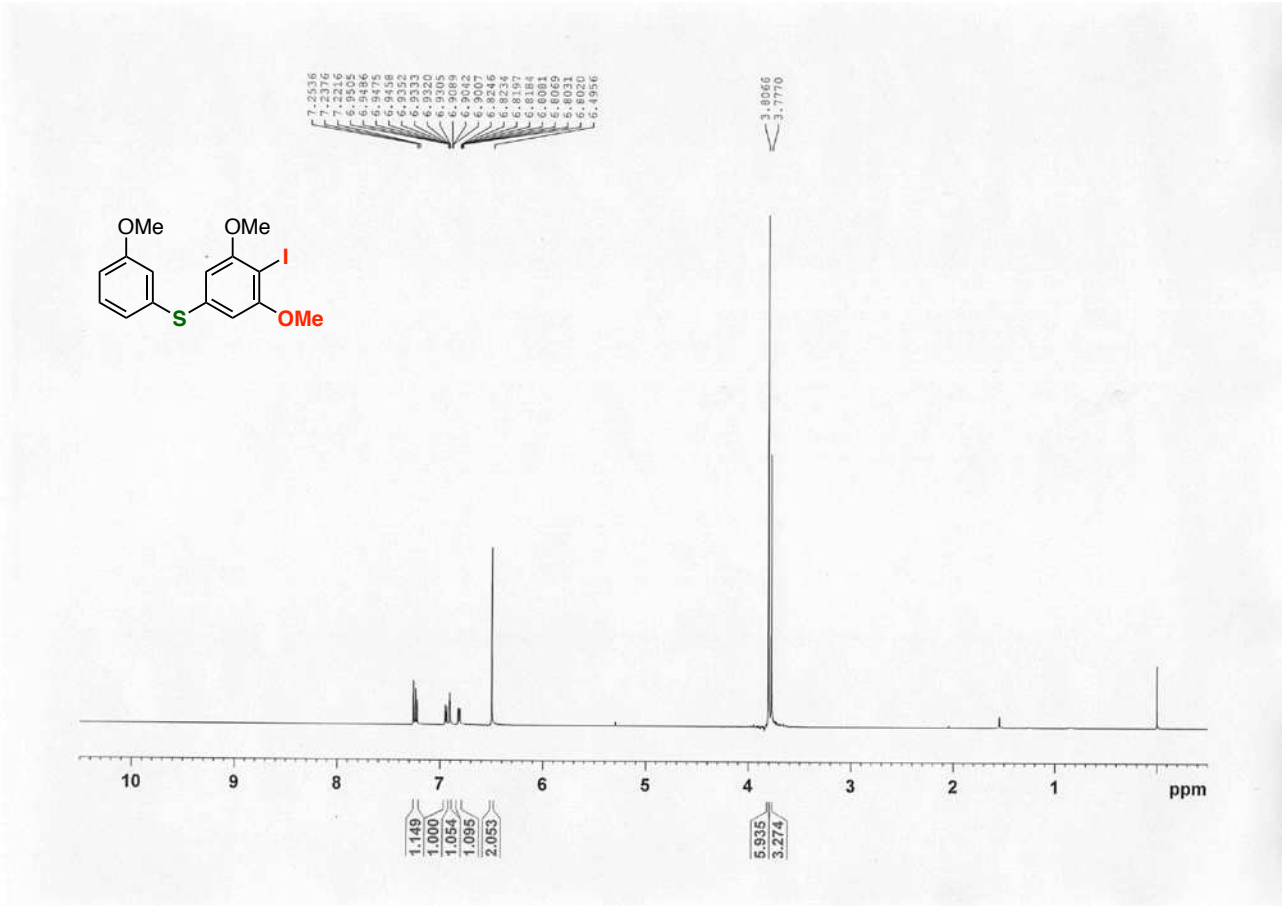


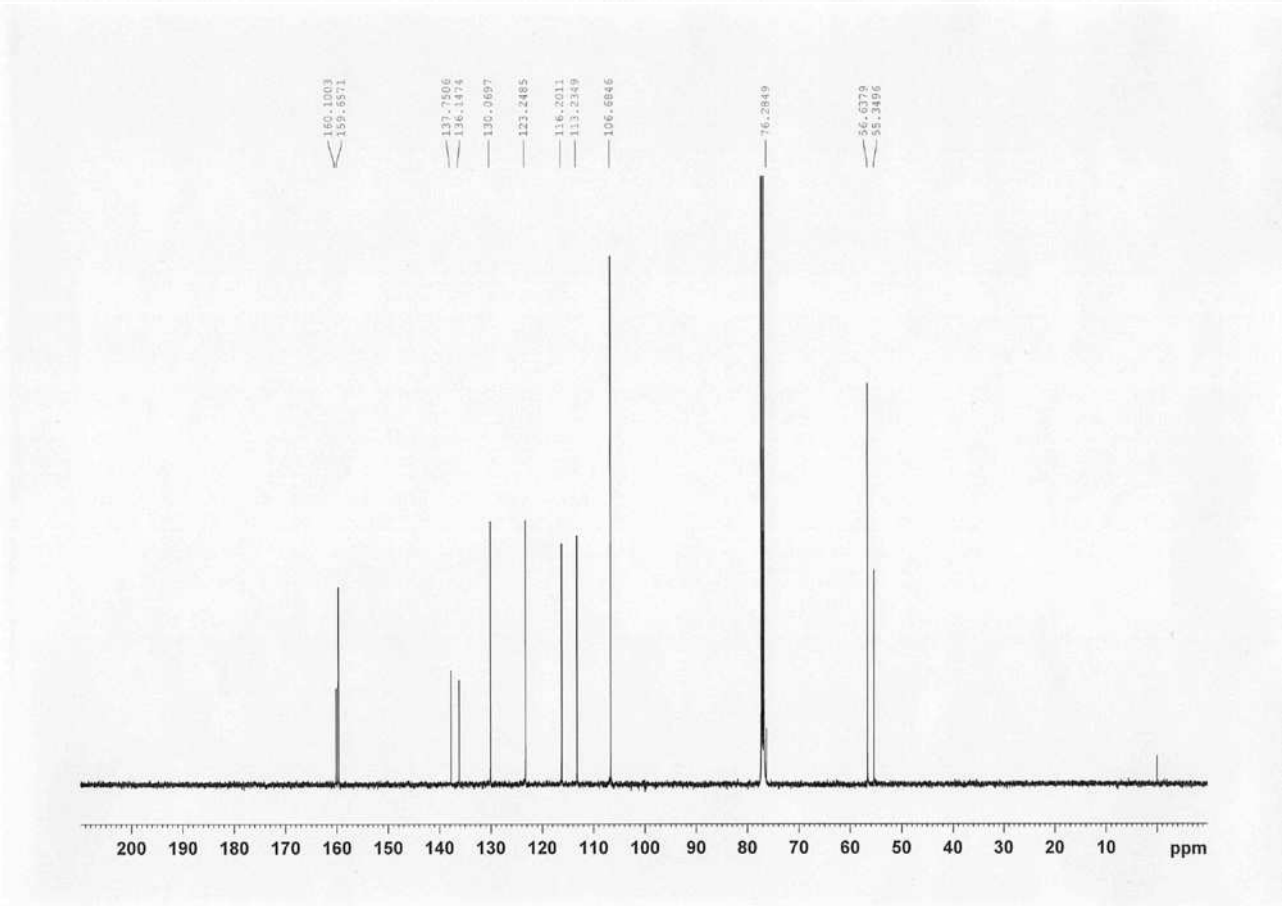
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 3-methoxy-5-(3-methoxyphenylthio)-2-(trimethylsilyl)phenyl triflate (**3a**) ($CDCl_3$)



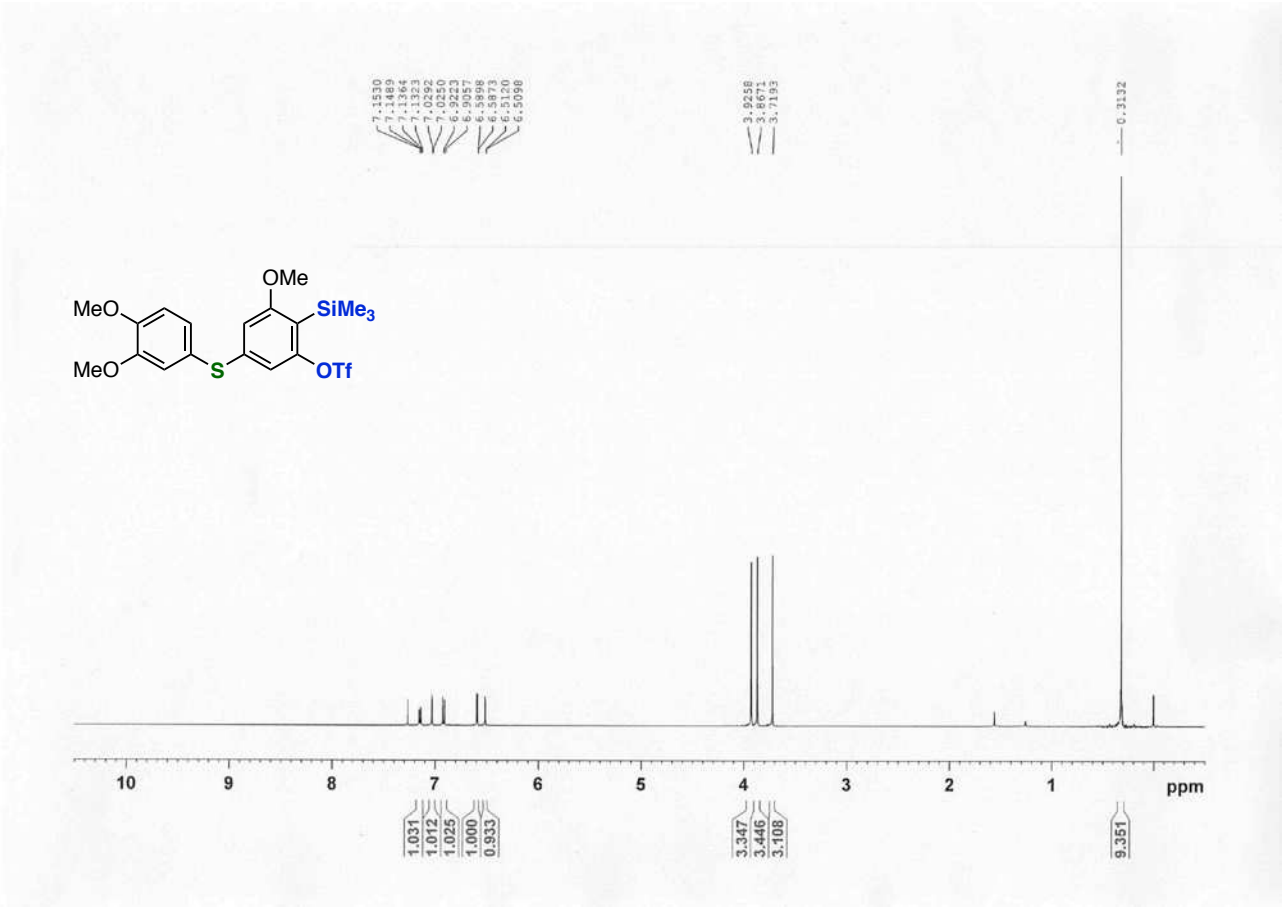


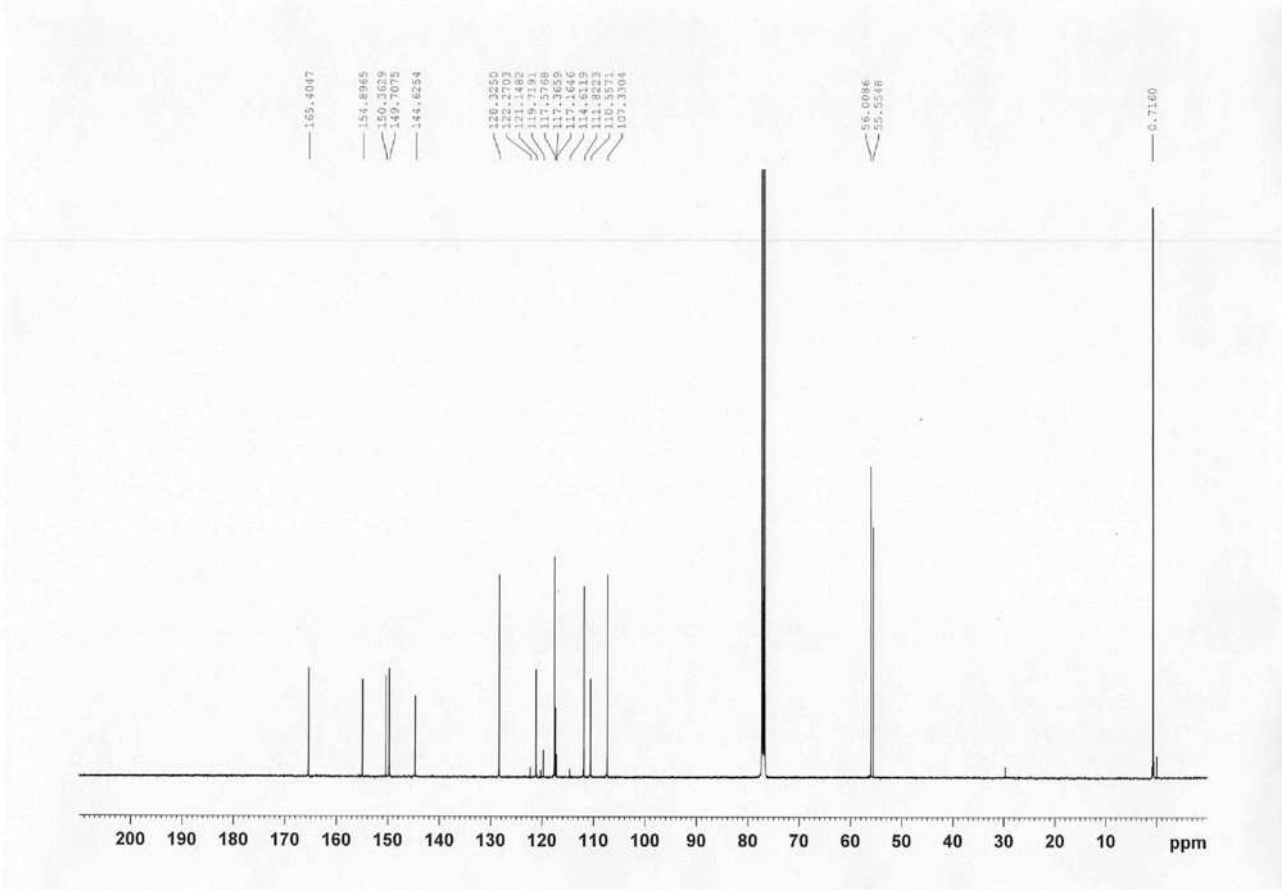
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 2,6-dimethoxy-4-(3-methoxyphenylthio)phenyl iodide (**7**) ($CDCl_3$)



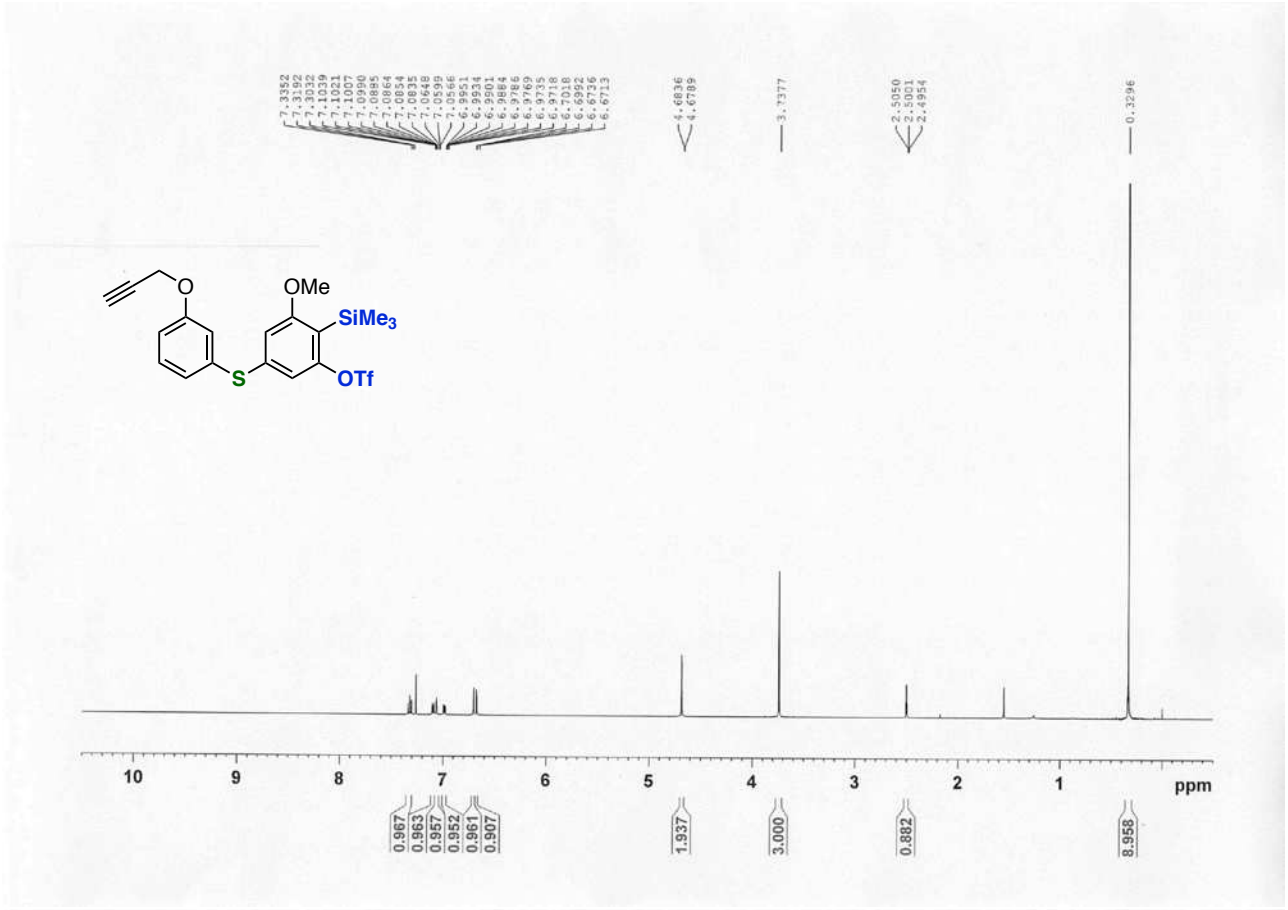


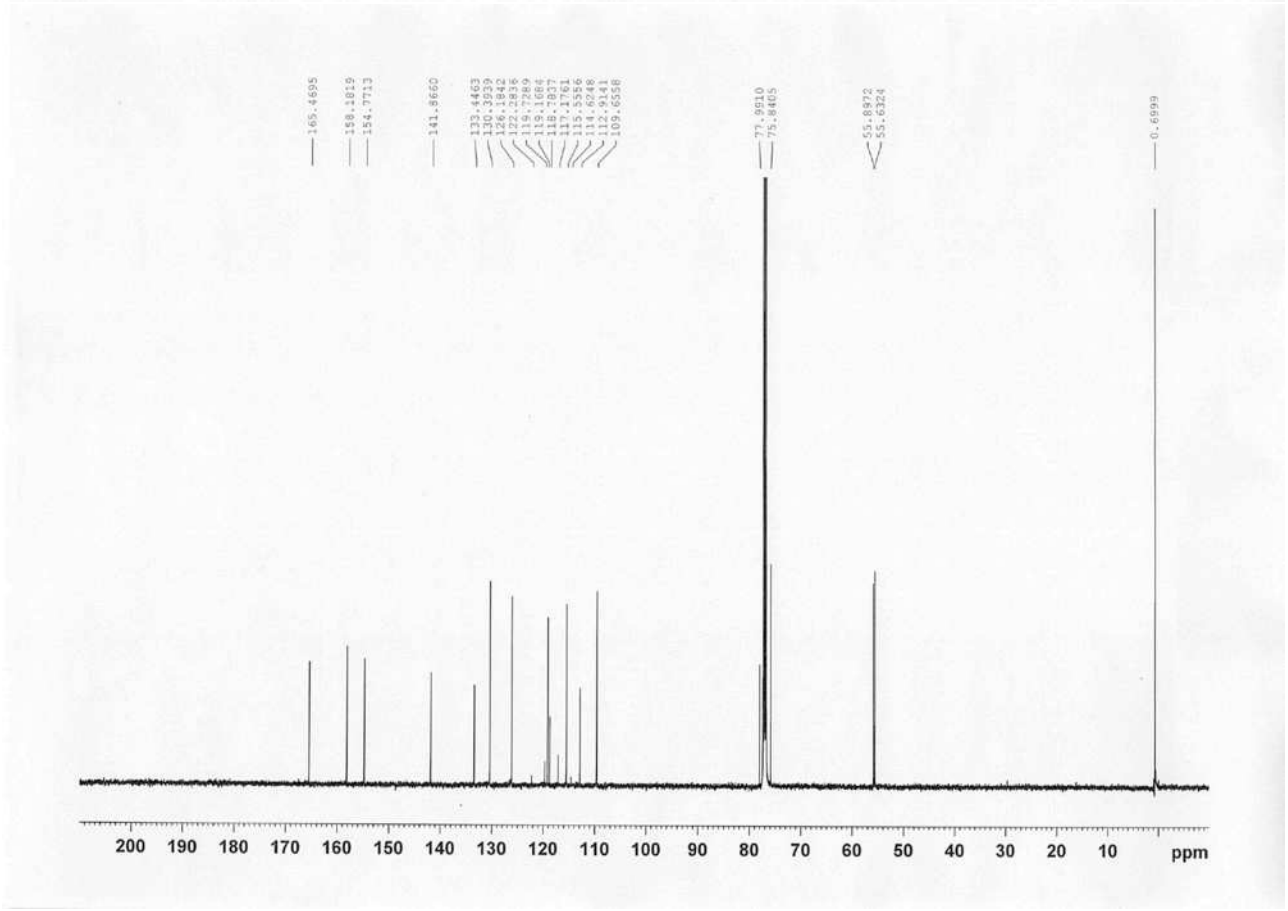
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 3-methoxy-5-(3,4-dimethoxyphenylthio)-2-(trimethylsilyl)phenyl triflate (**3b**) ($CDCl_3$)



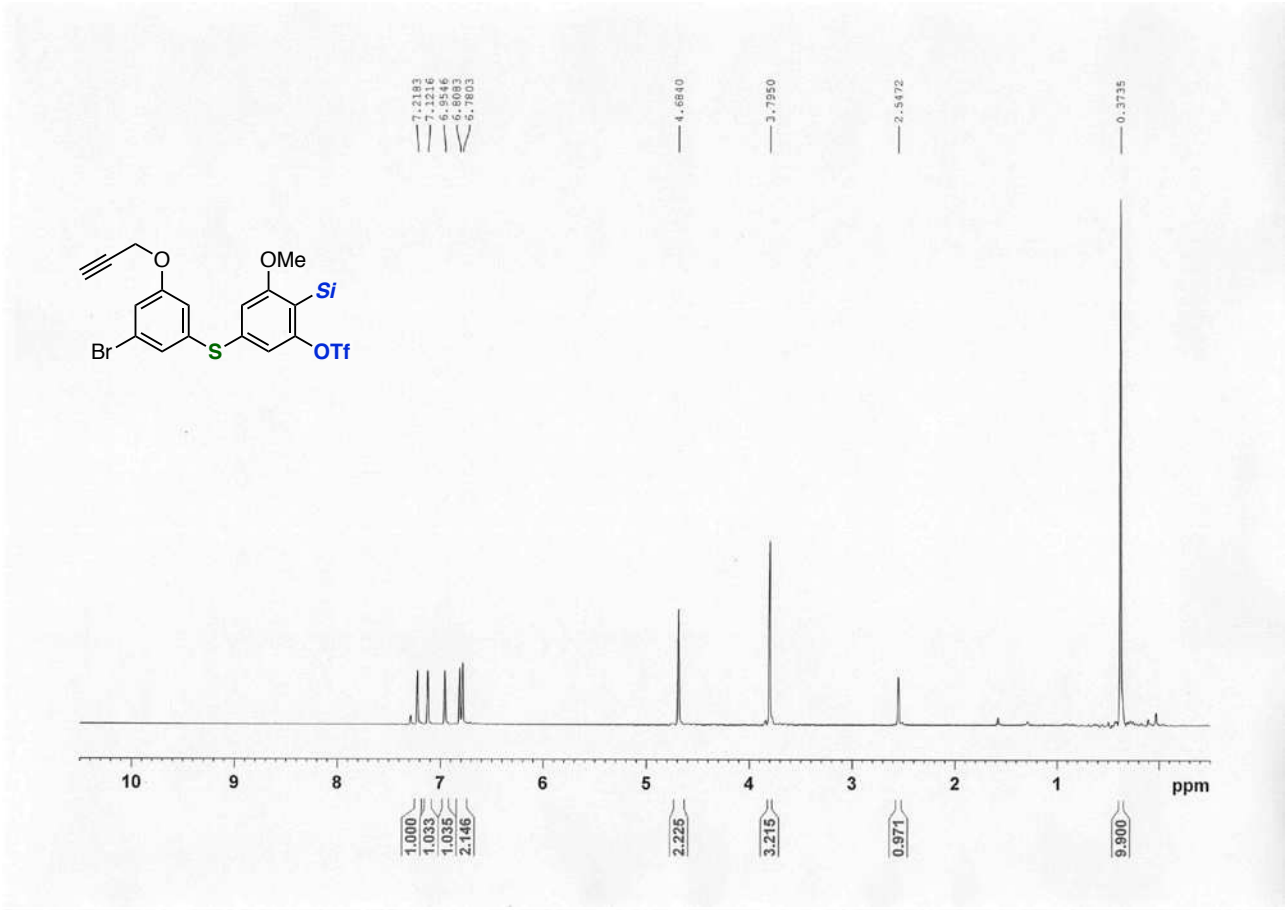


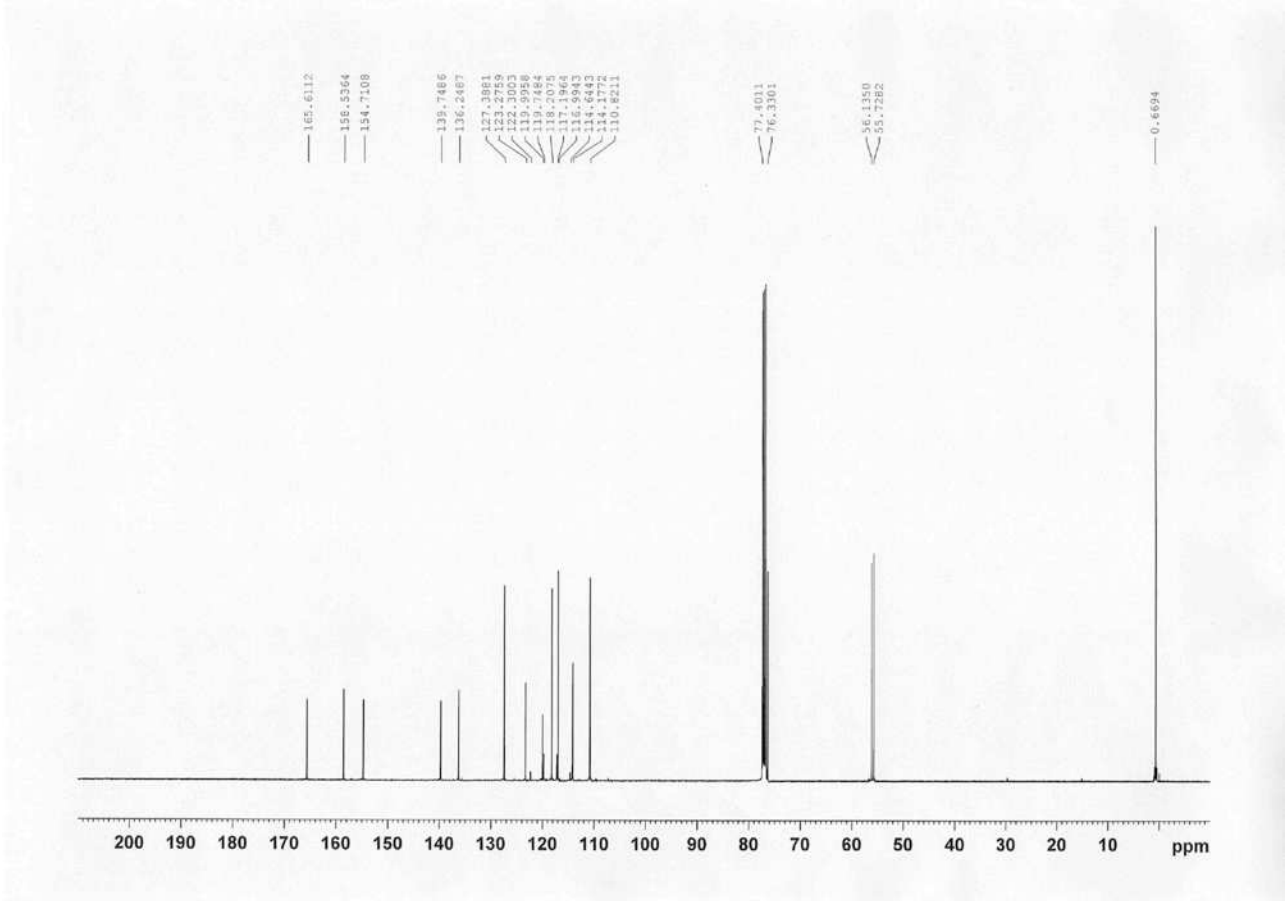
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 3-methoxy-5-(3-(propargyloxy)phenylthio)-2-(trimethylsilyl)phenyl triflate (**3c**) ($CDCl_3$)



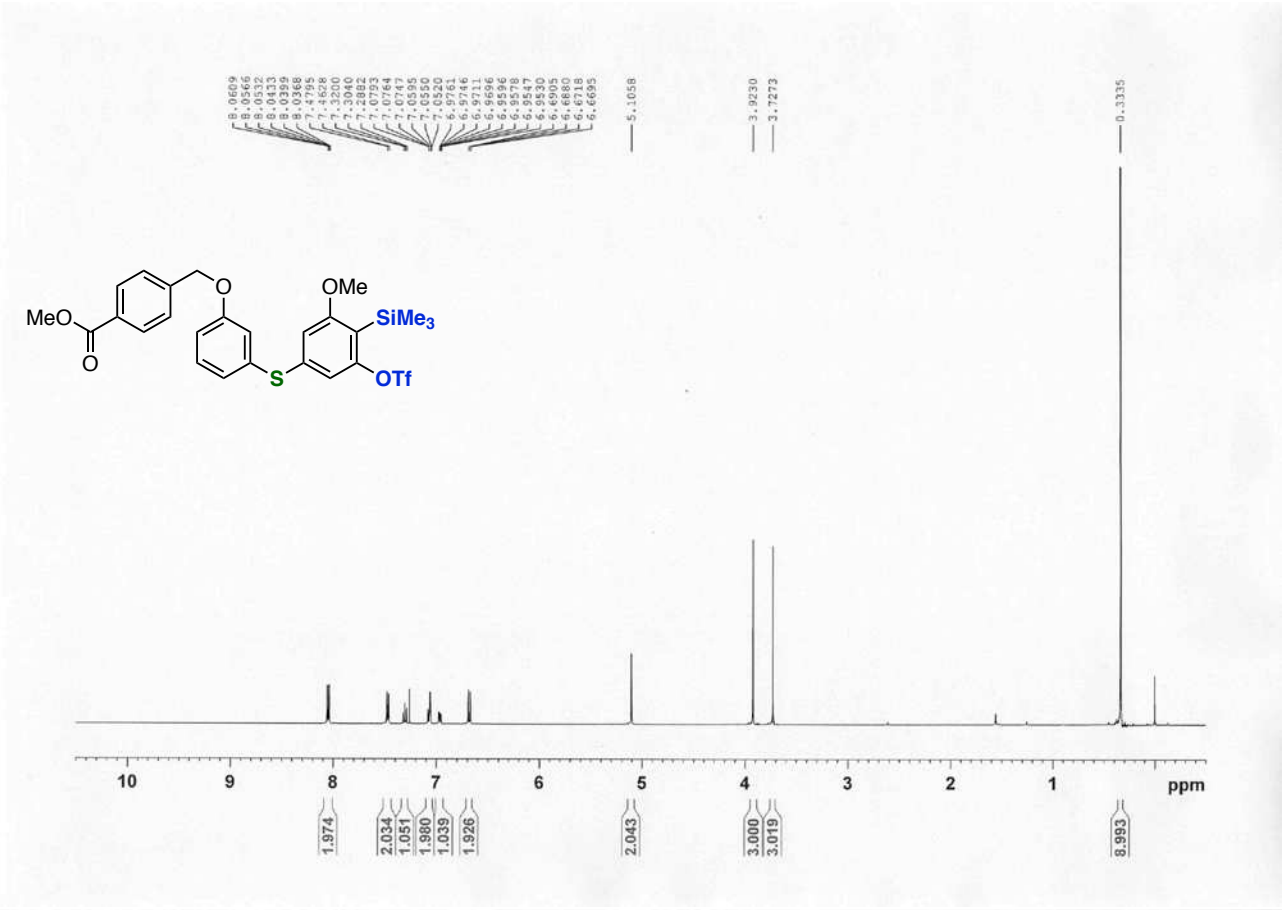


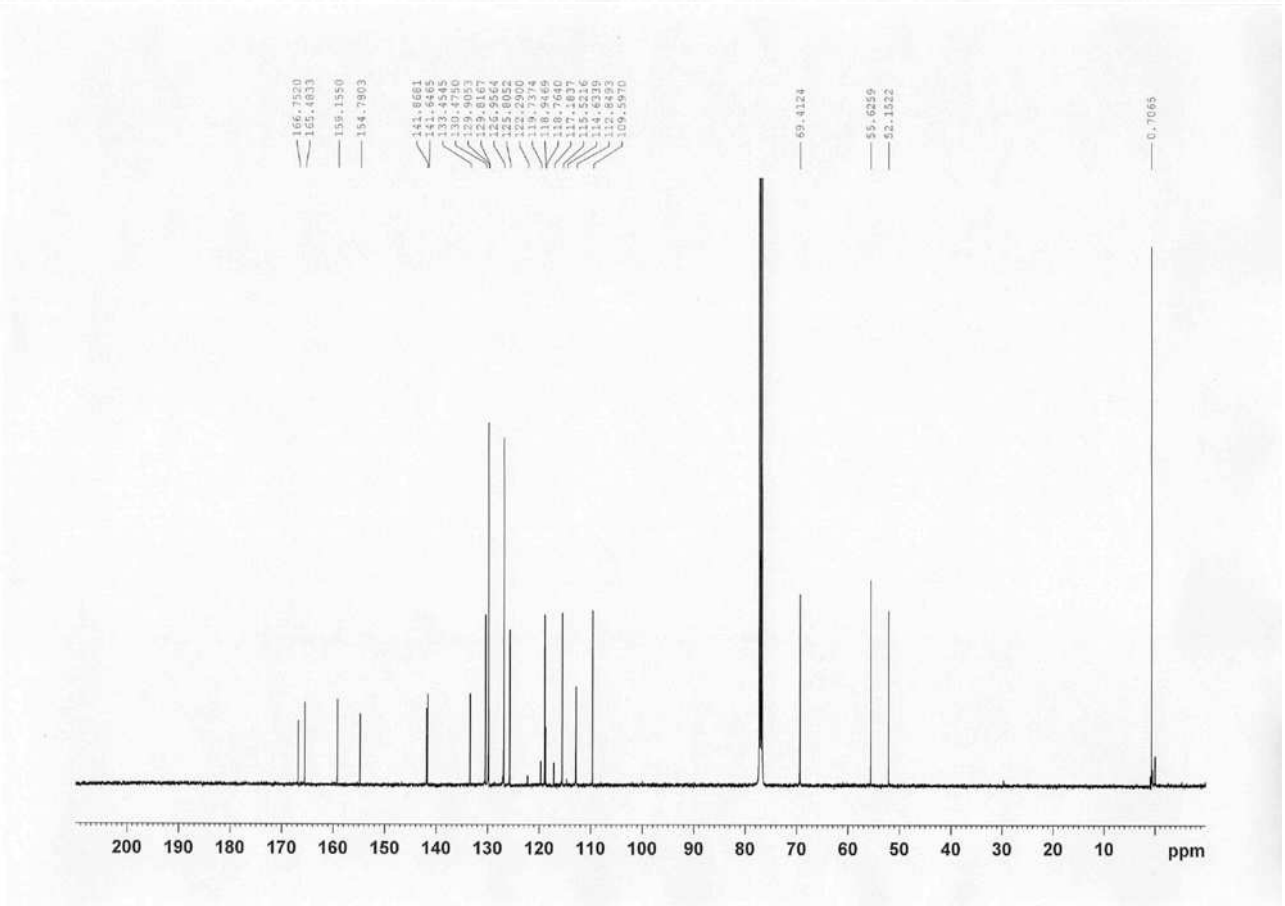
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 5-(5-Bromo-3-(propargyloxy)phenylthio)-3-methoxy-2-(trimethylsilyl)phenyl triflate (**3d**) ($CDCl_3$)



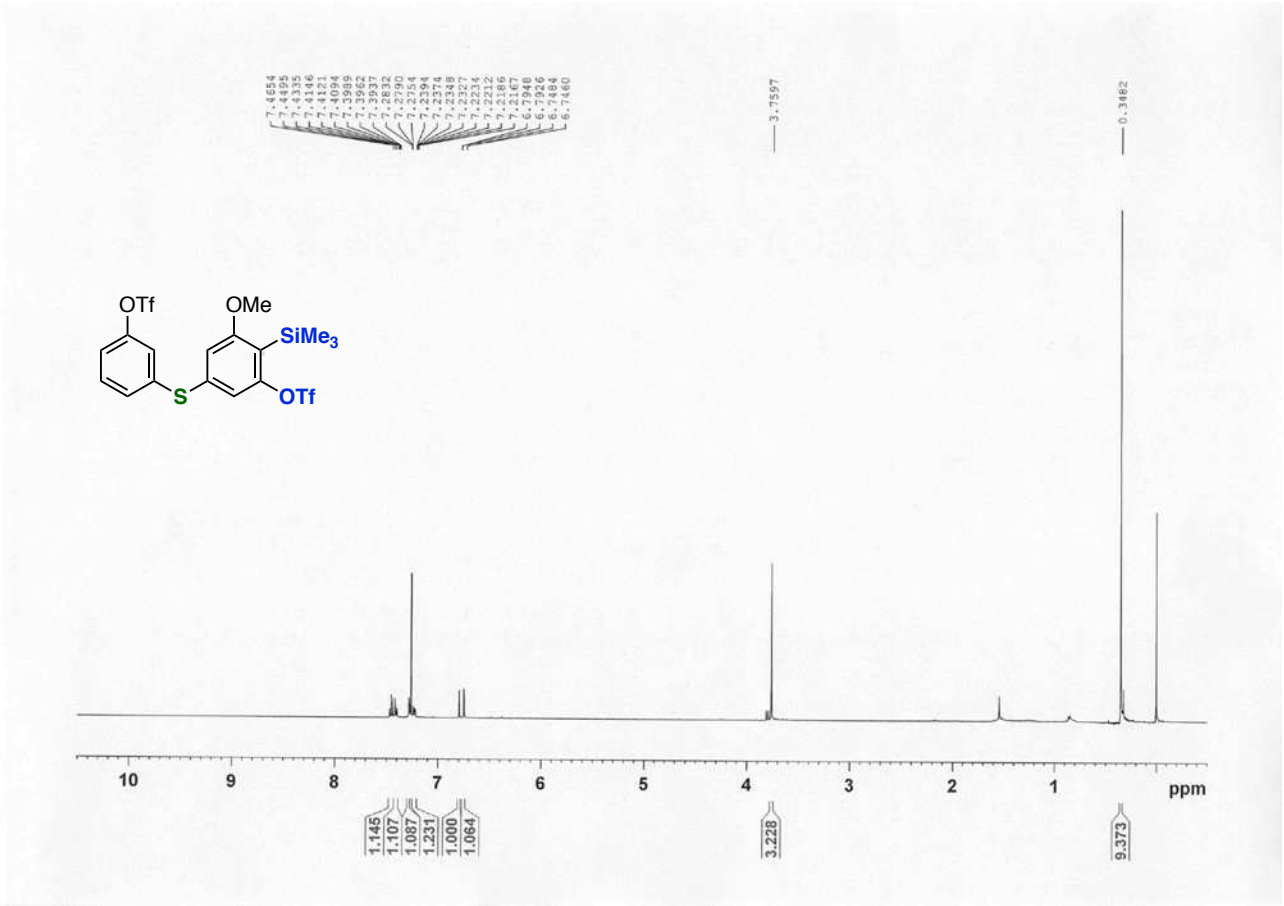


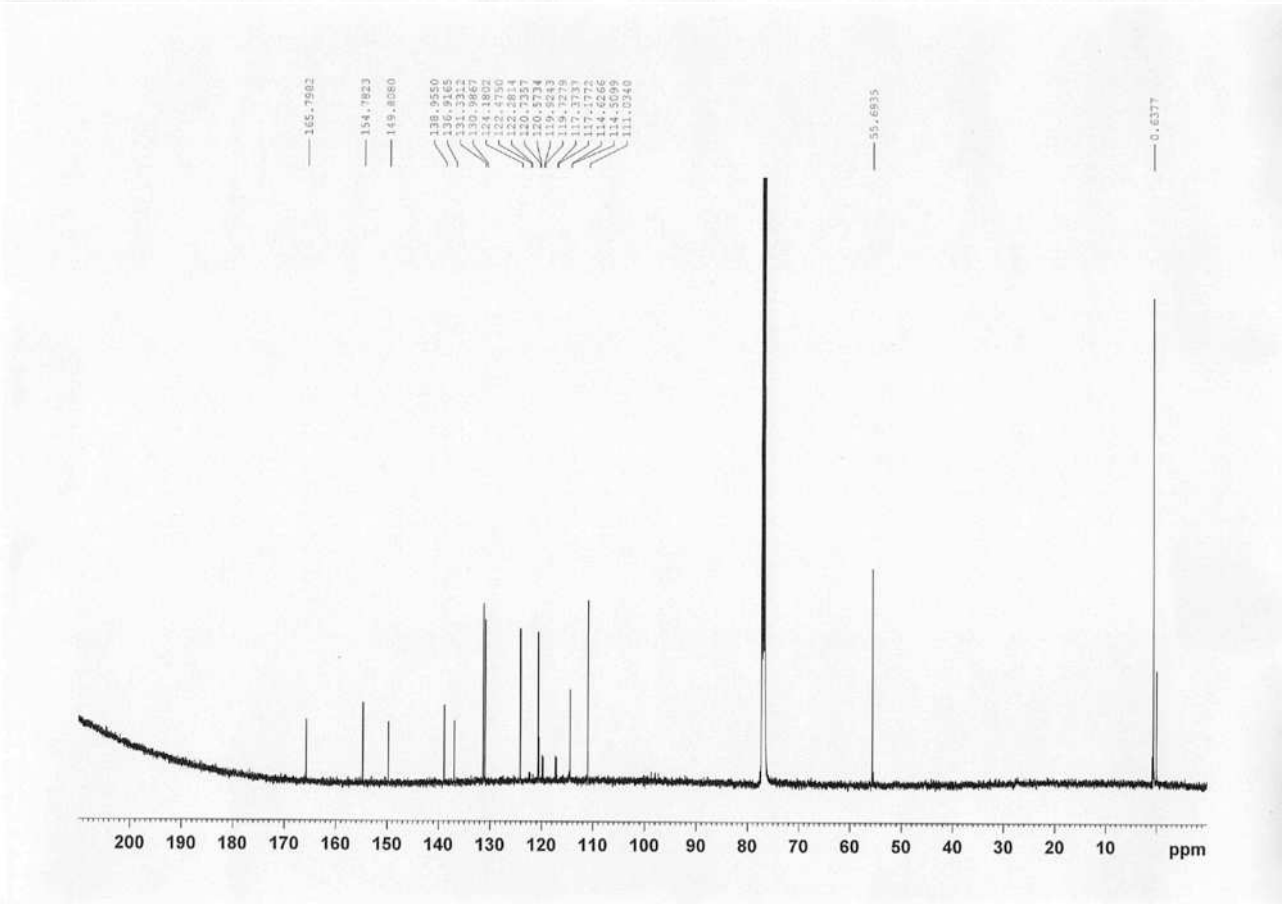
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 3-methoxy-5-(3-(4-(methoxycarbonyl)benzyloxy)phenylthio)-2-(trimethylsilyl)phenyl triflate (**3e**) ($CDCl_3$)



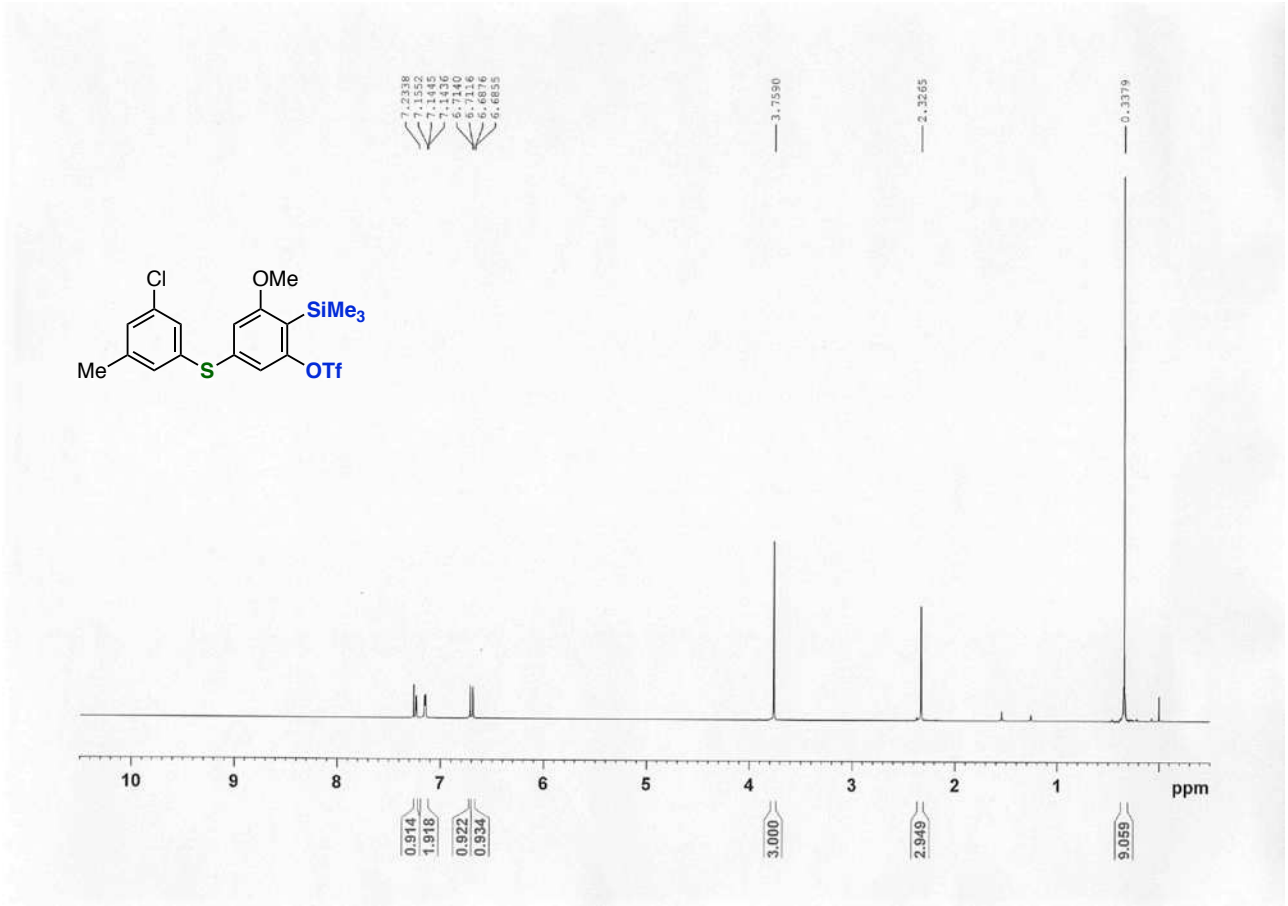


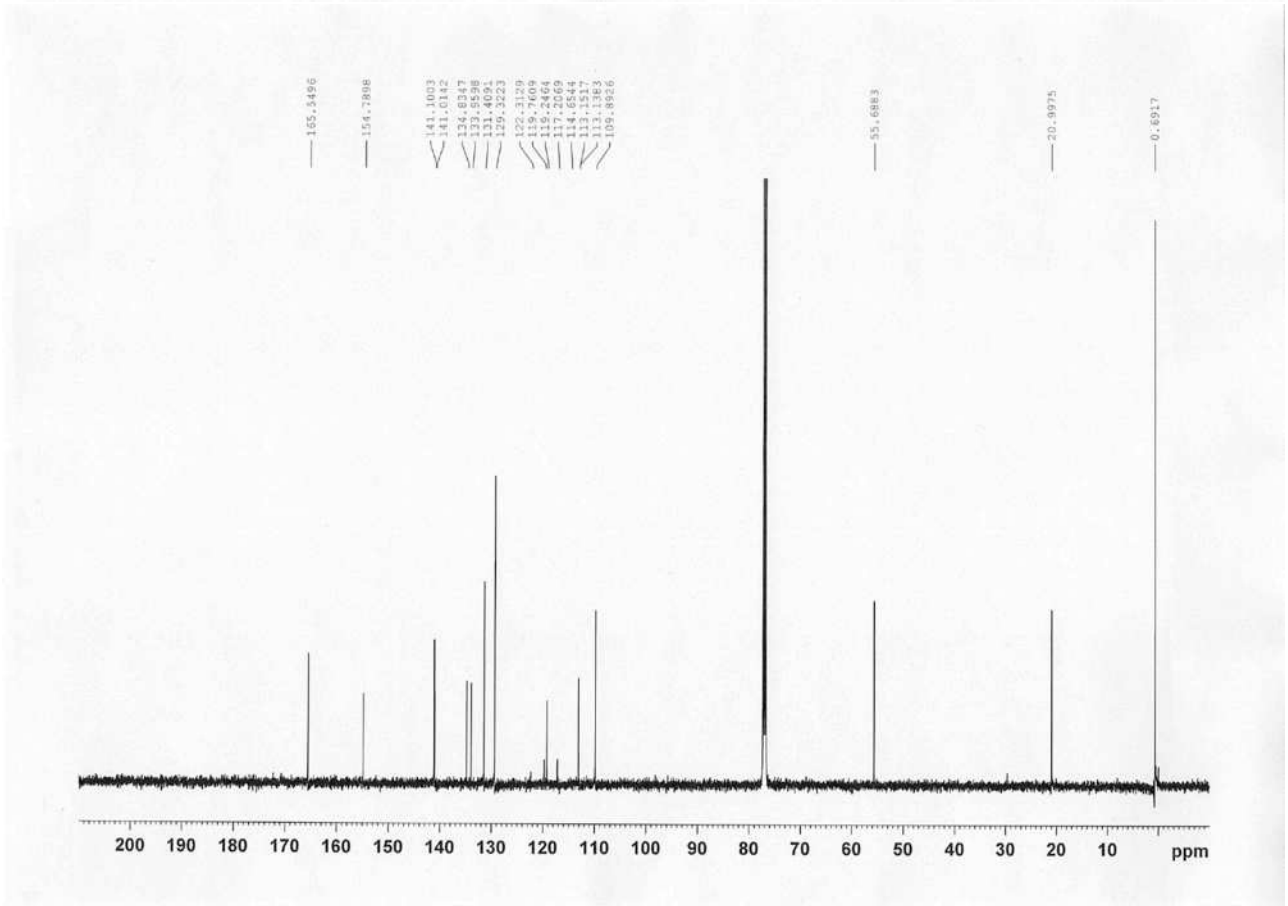
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 3-methoxy-5-(3-(triflyloxy)phenylthio)-2-(trimethylsilyl)phenyl triflate (**3f**) ($CDCl_3$)



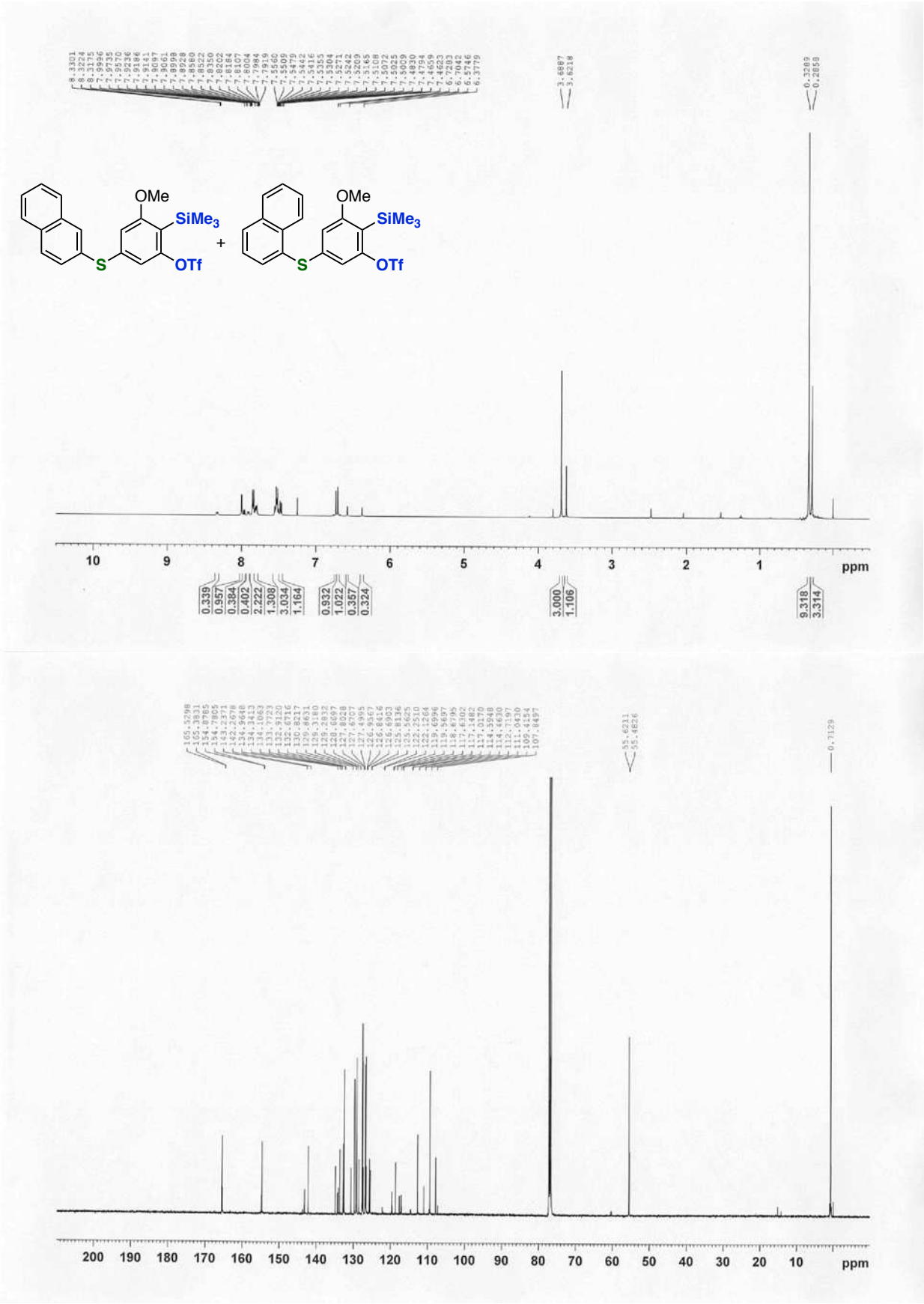


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 5-(3-chloro-5-methylphenylthio)-3-methoxy-2-(trimethylsilyl)phenyl triflate (**3g**) ($CDCl_3$)

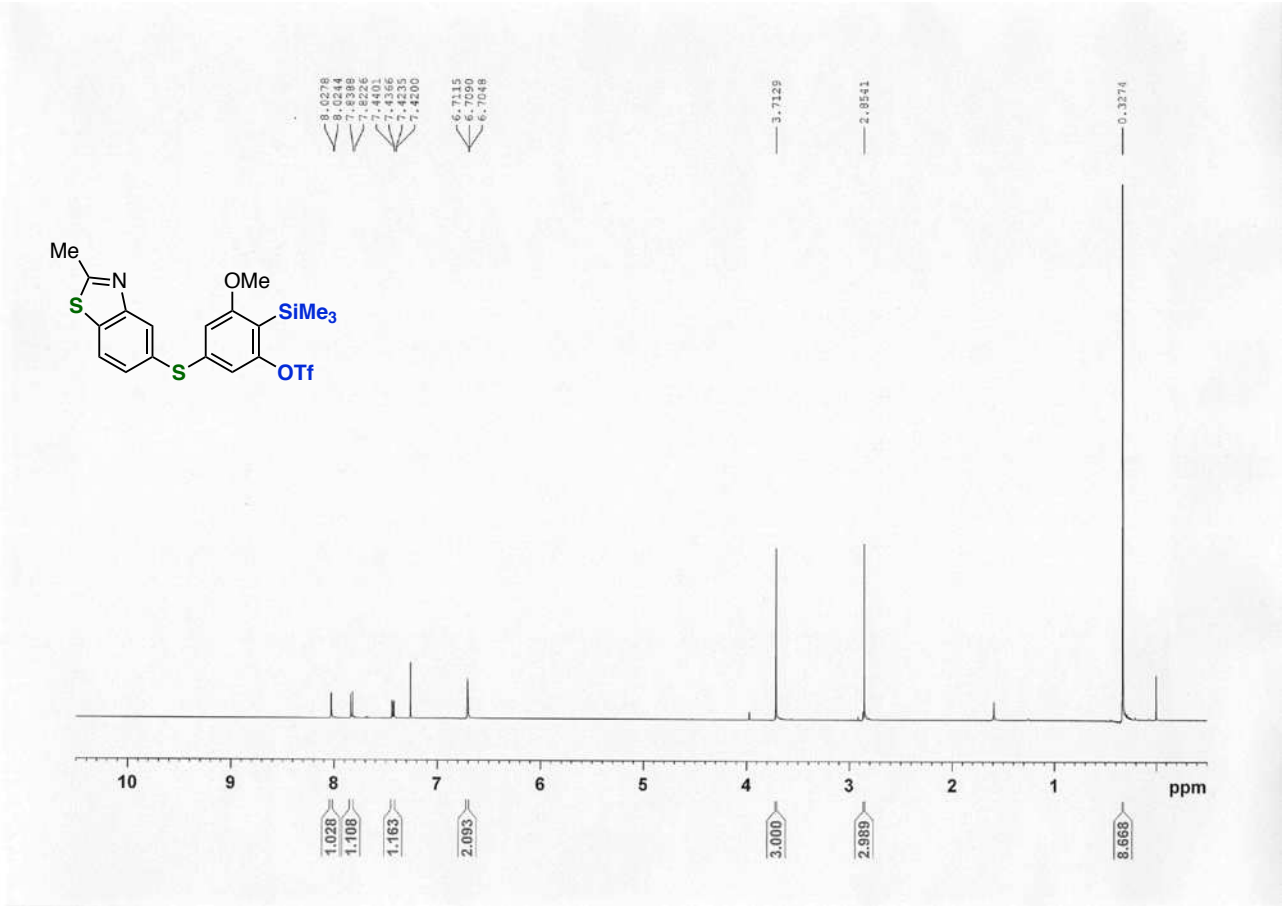


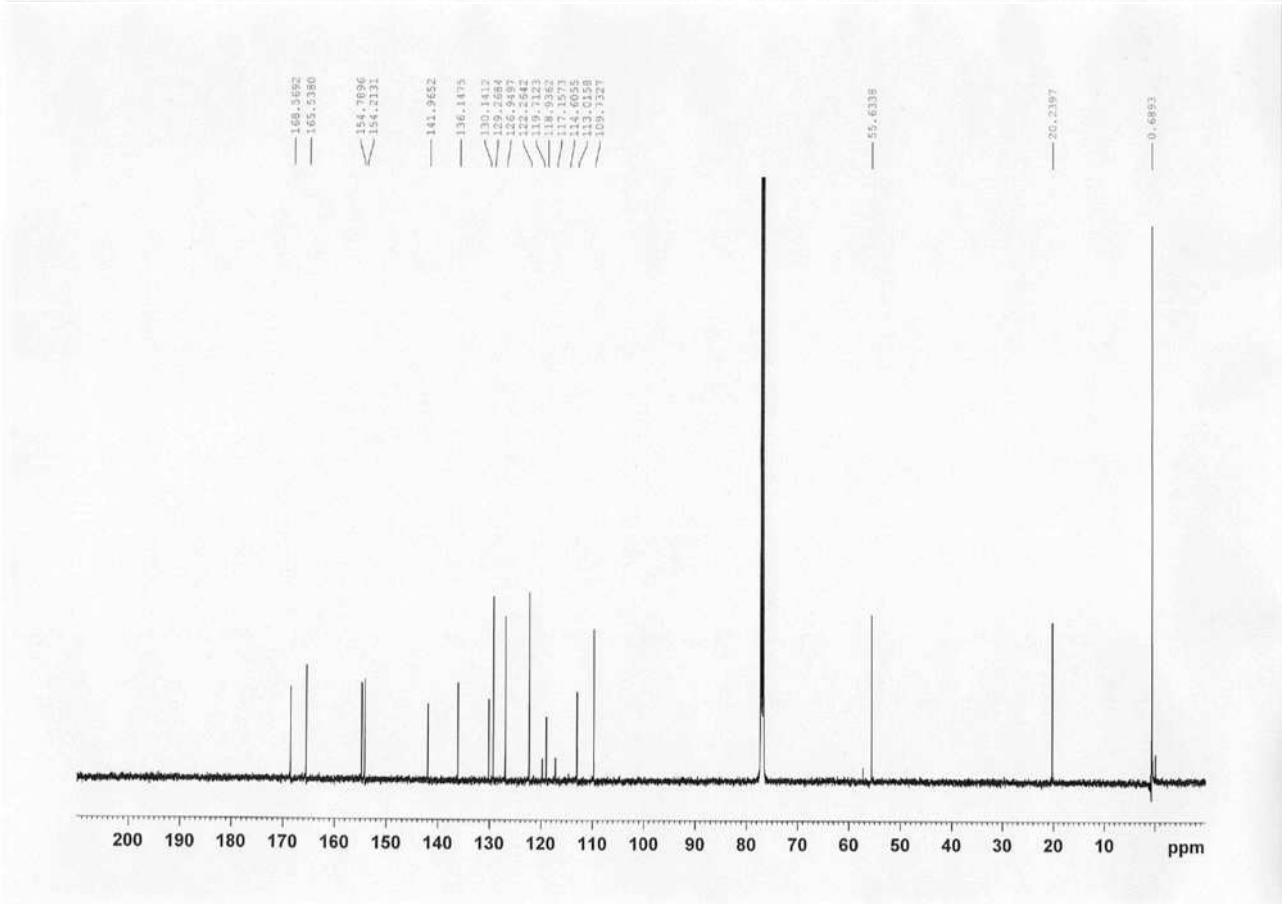


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 5-(2-naphthyl)-3-methoxy-2-(trimethylsilyl)phenyl triflate (**3h**) + 5-(1-naphthyl)-3-methoxy-2-(trimethylsilyl)phenyl triflate (**3h'**) ($CDCl_3$)

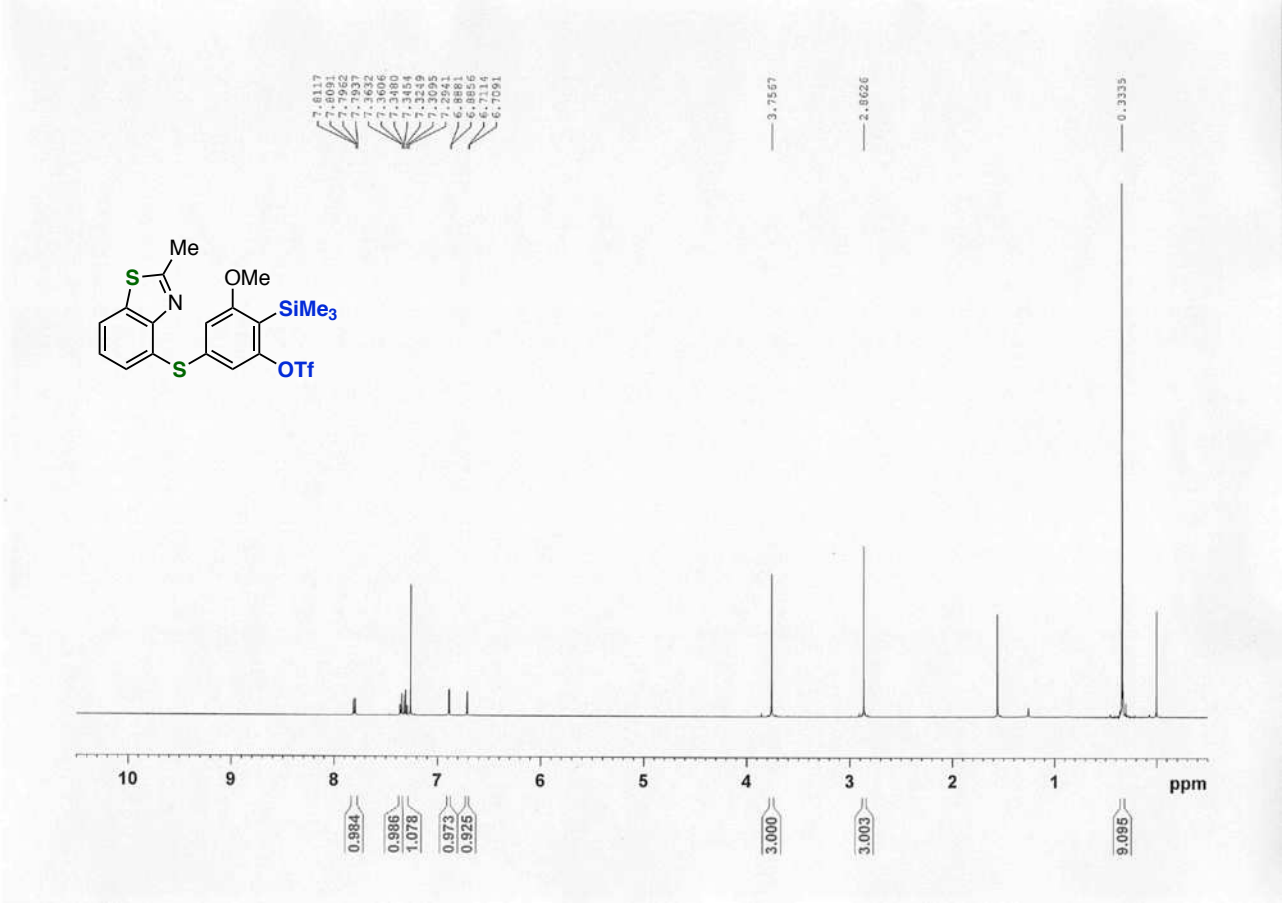


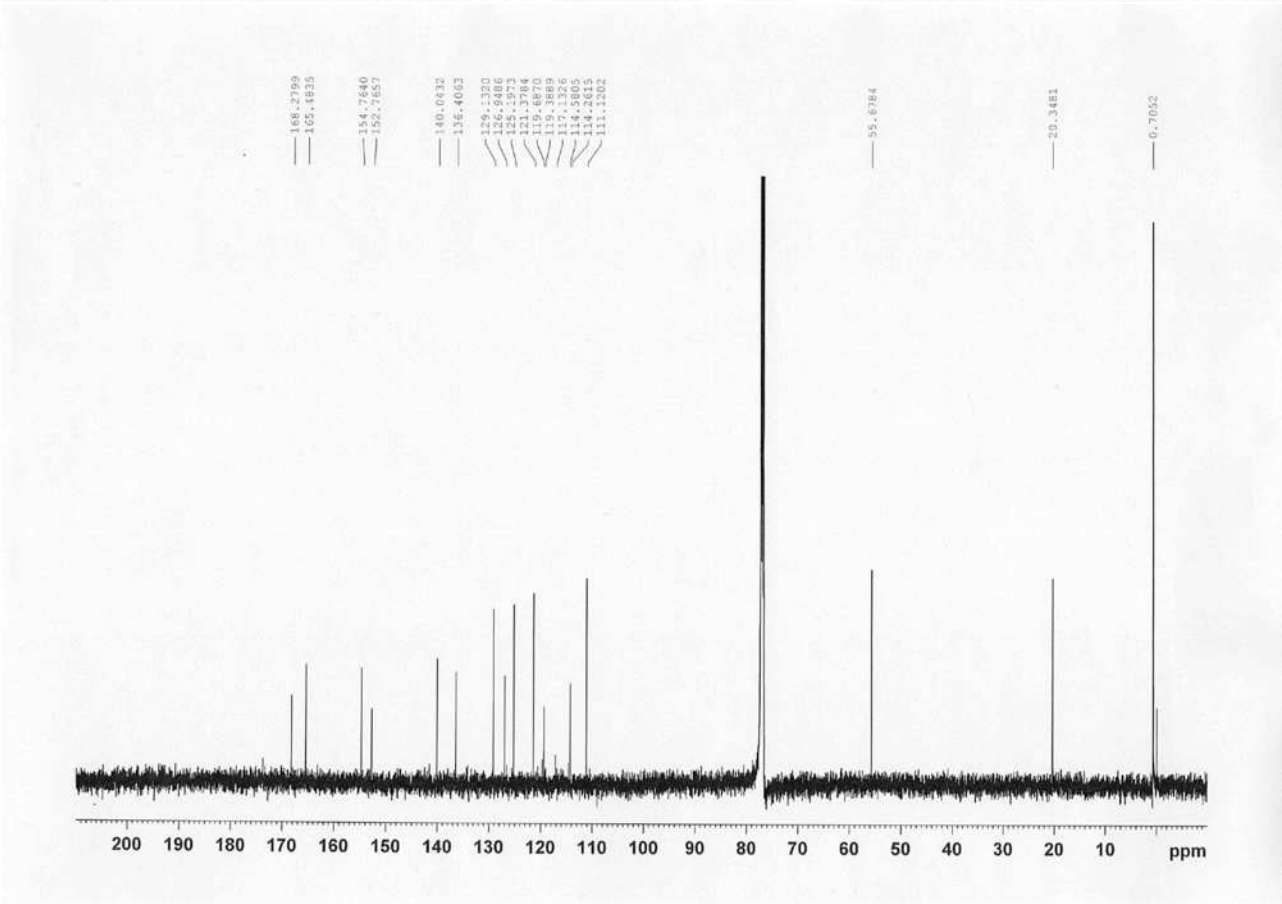
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 5-(3-methoxy-5-(triflyloxy)-4-(trimethylsilyl)phenylthio)-2-methylbenzo[*d*]thiazole (**3i**) ($CDCl_3$)



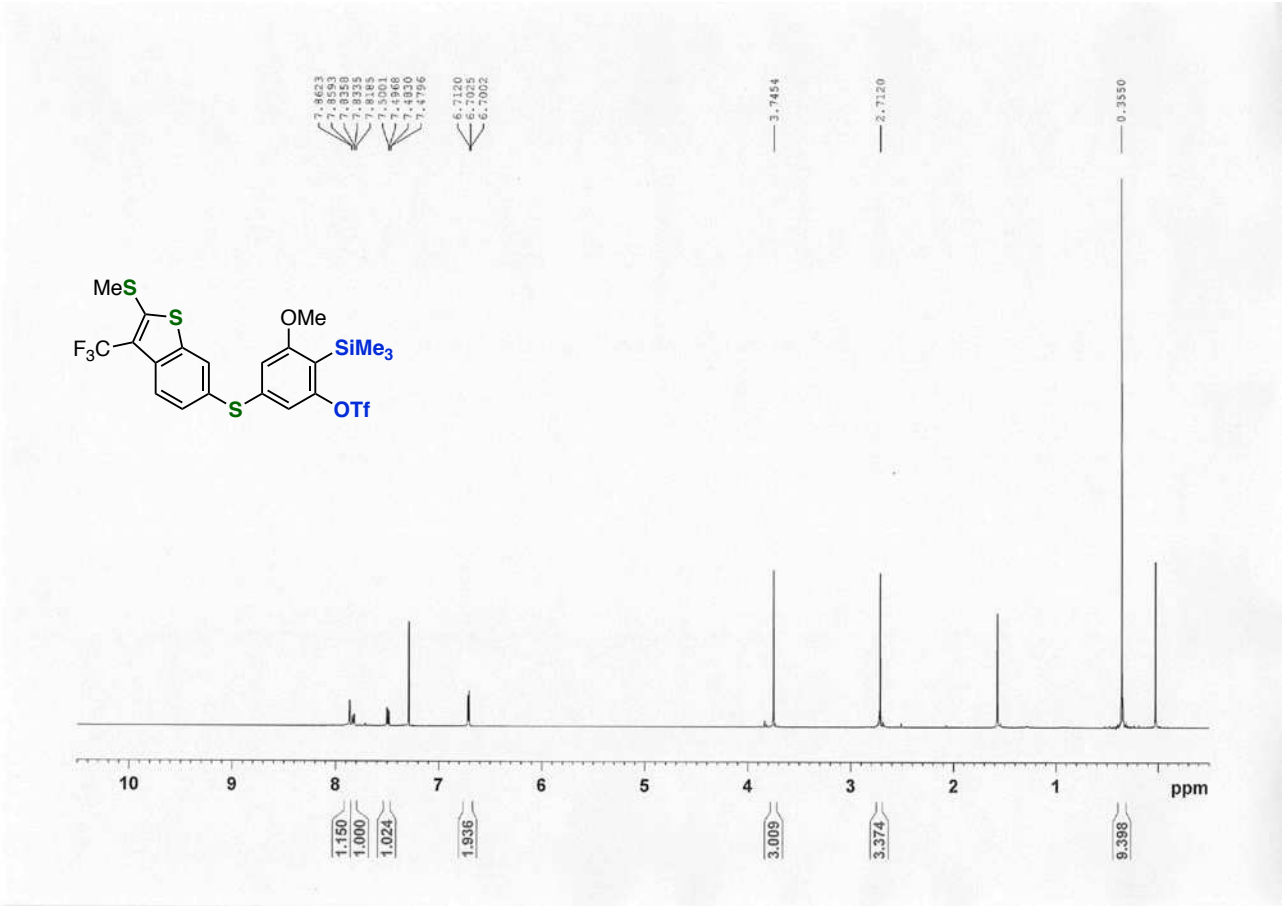


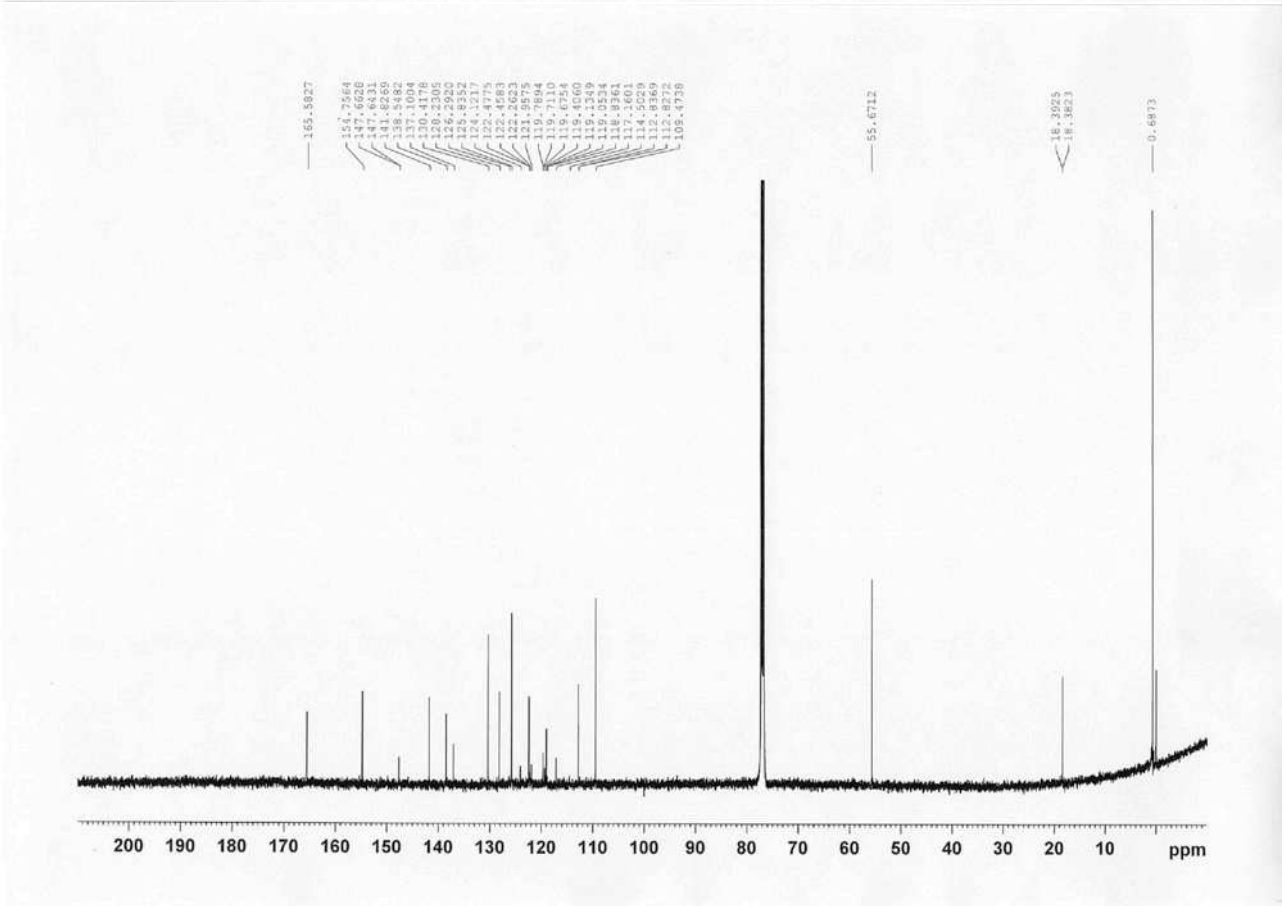
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 4-(3-methoxy-5-(triflyloxy)-4-(trimethylsilyl)phenylthio)-2-methylbenzo[*d*]thiazole (**3i'**) ($CDCl_3$)



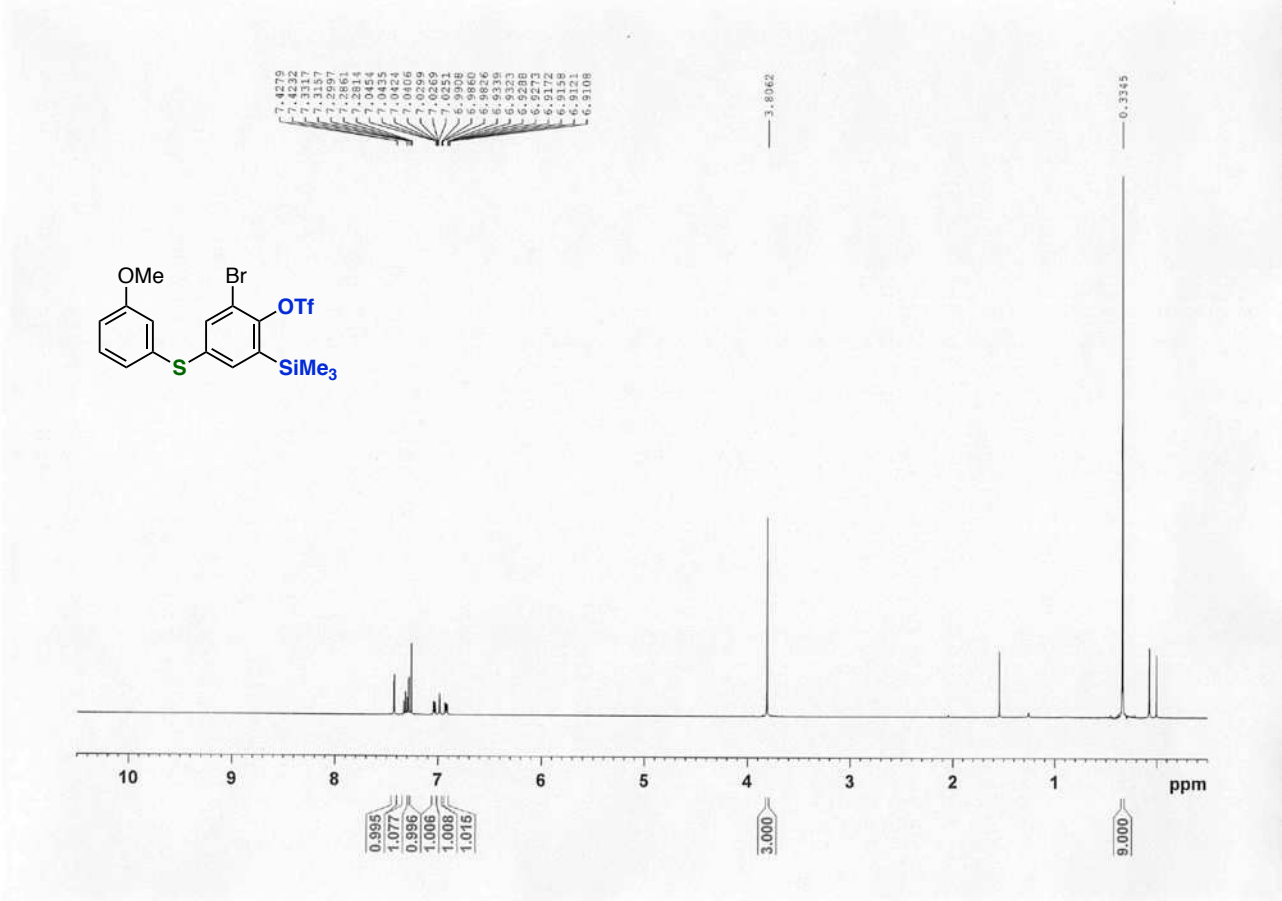


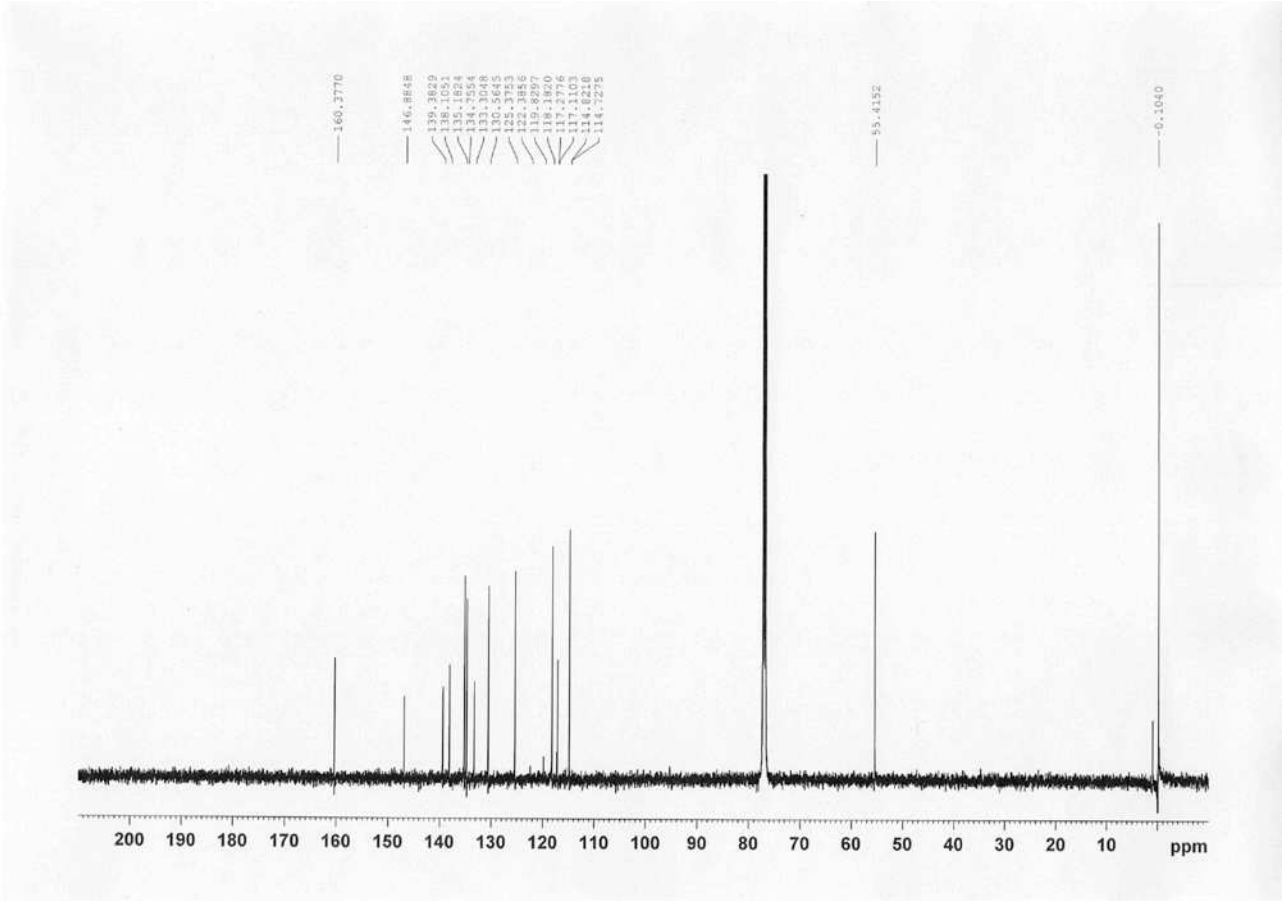
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 4-(3-methoxy-5-(triflyloxy)-4-(trimethylsilyl)phenylthio)-2-(methylthio)-3-(trifluoromethyl)benzo[*b*]thiophene (**3j**) ($CDCl_3$)



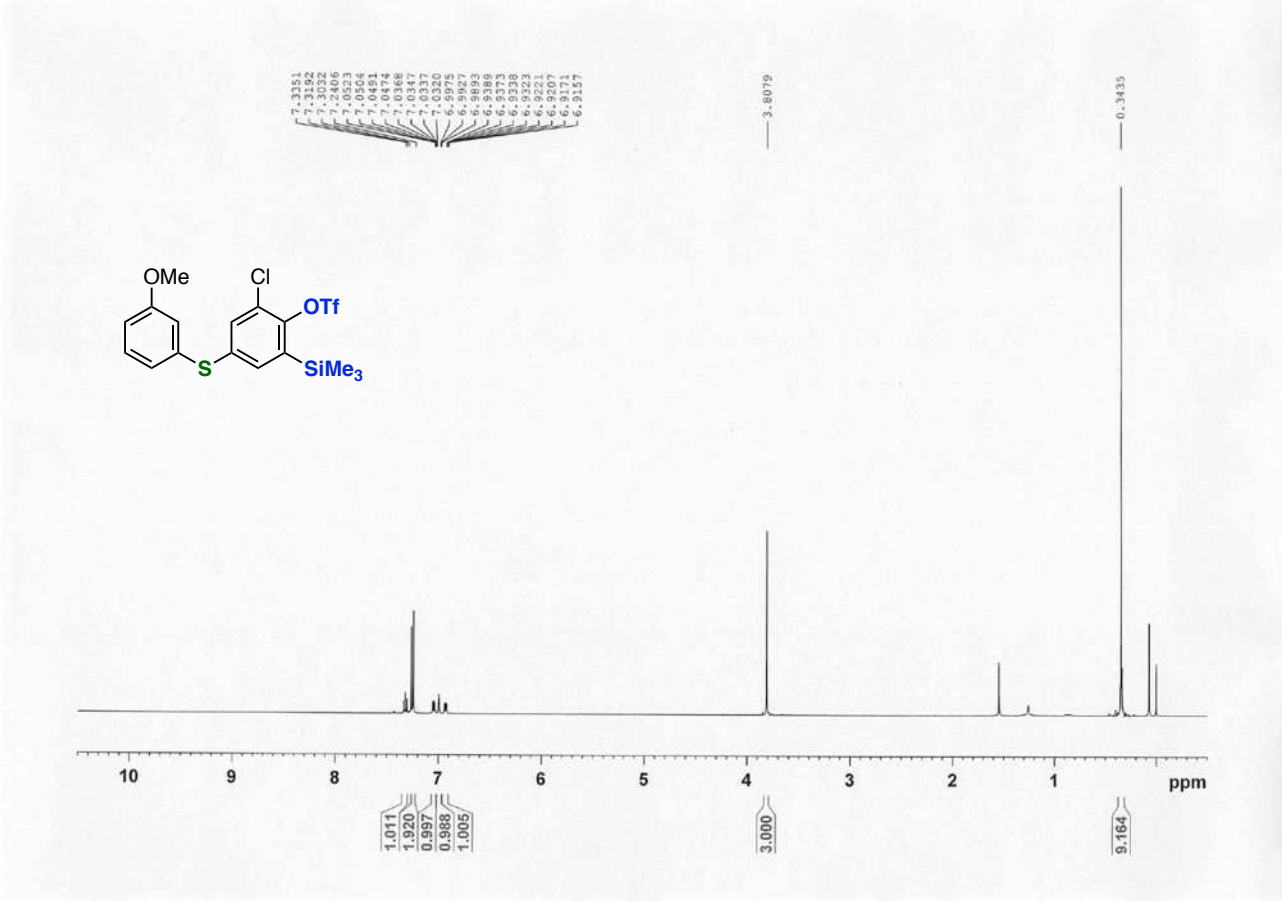


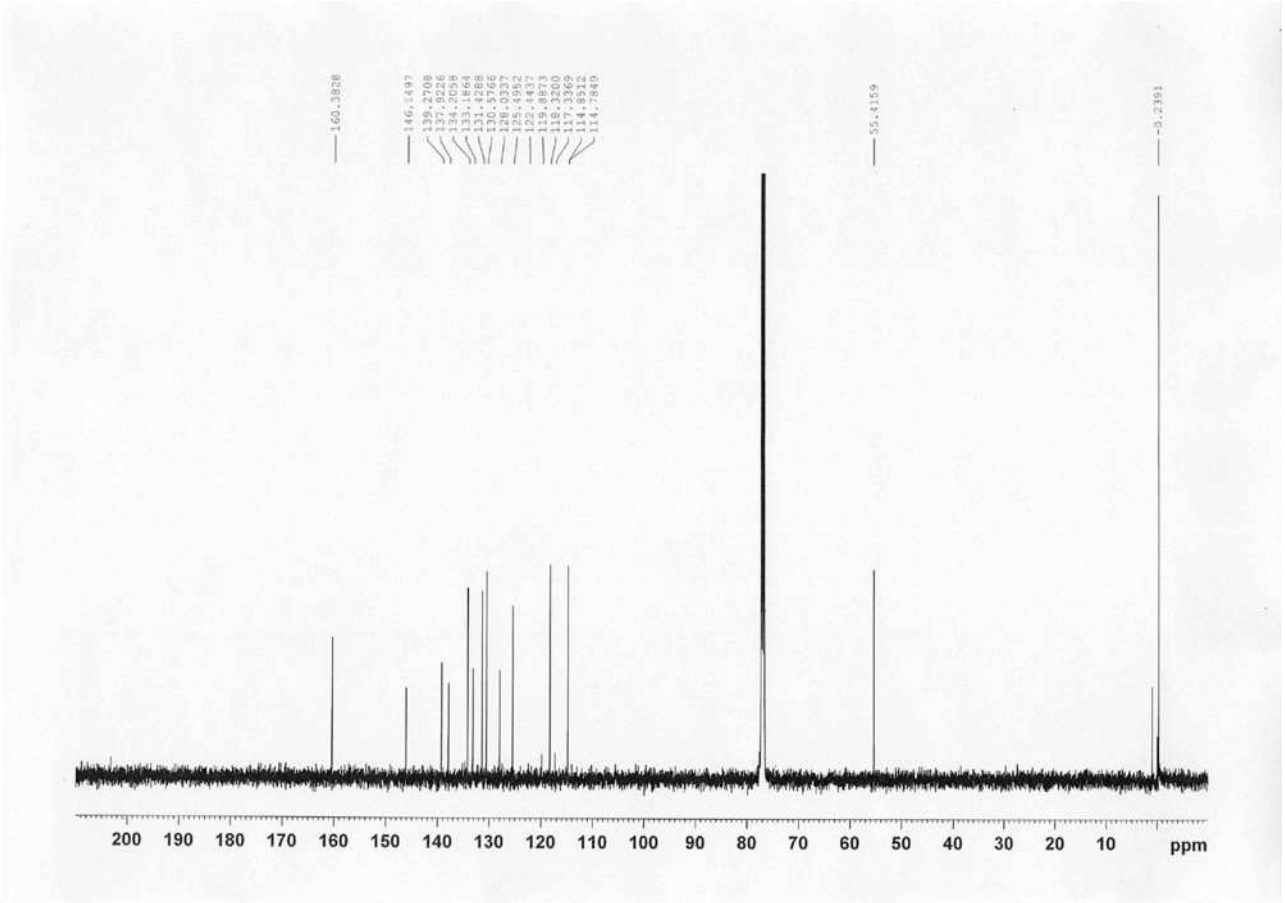
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 2-bromo-4-(3-methoxyphenylthio)-6-(trimethylsilyl)phenyl triflate (**3k**) ($CDCl_3$)



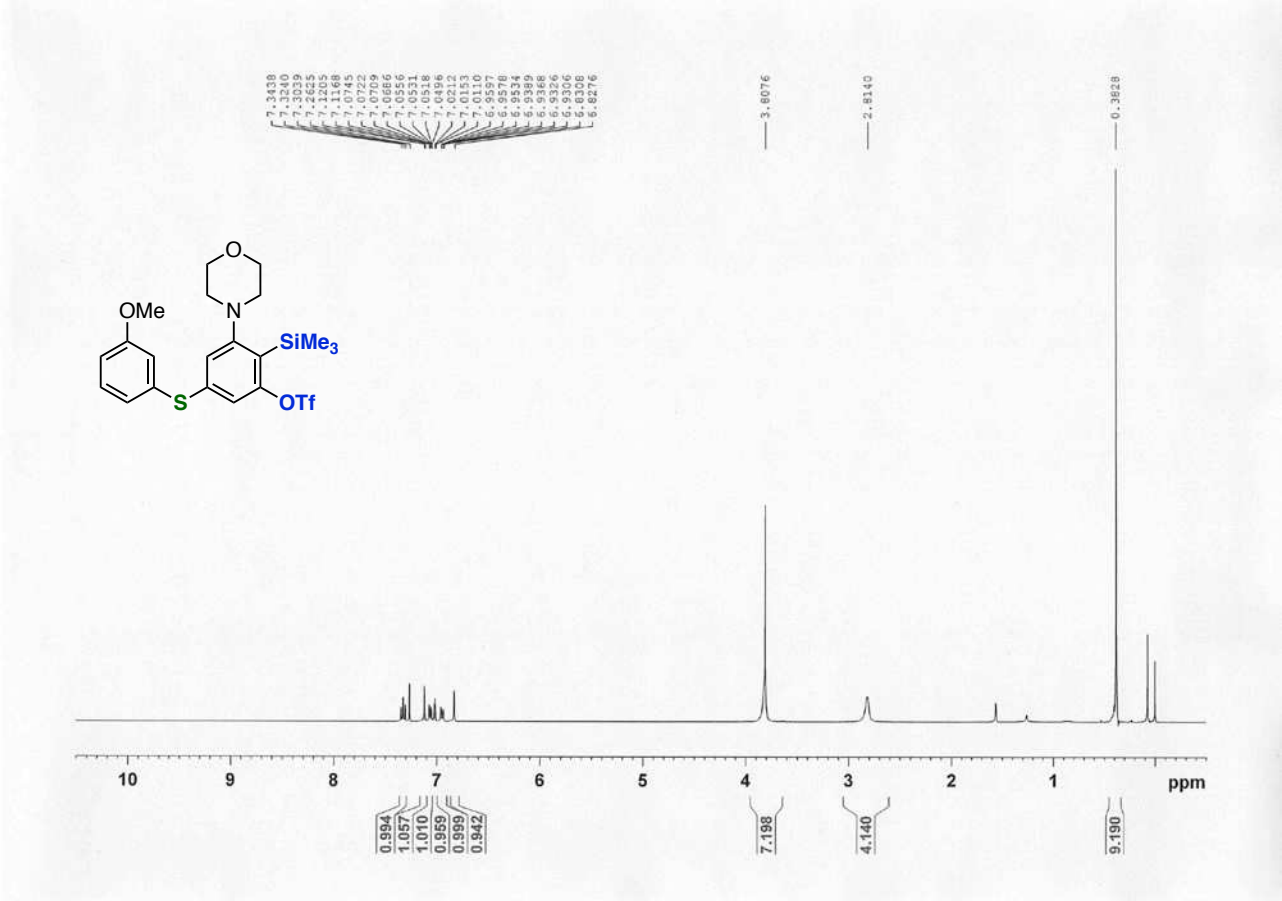


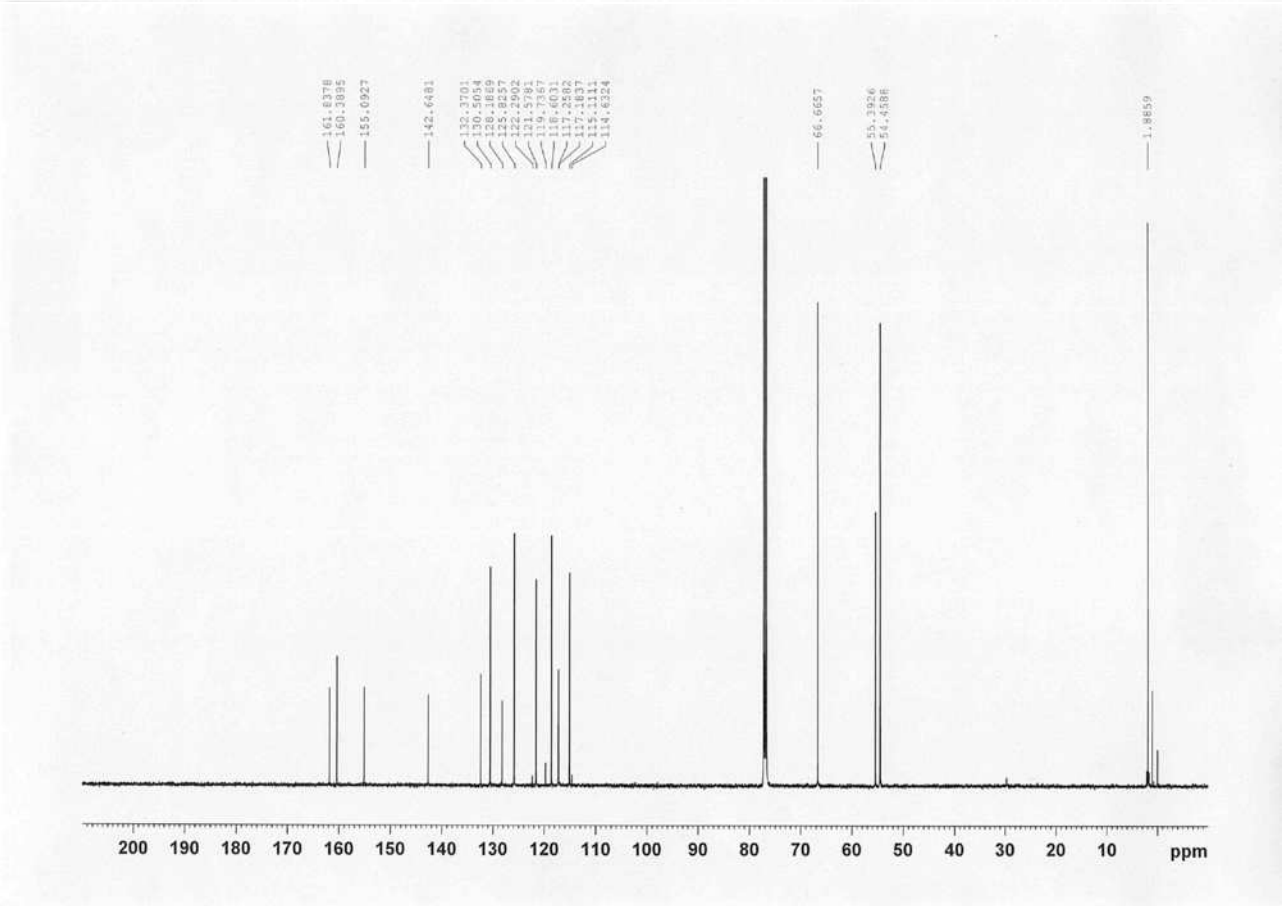
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 2-chloro-4-(3-methoxyphenylthio)-6-(trimethylsilyl)phenyl triflate (**3l**) ($CDCl_3$)



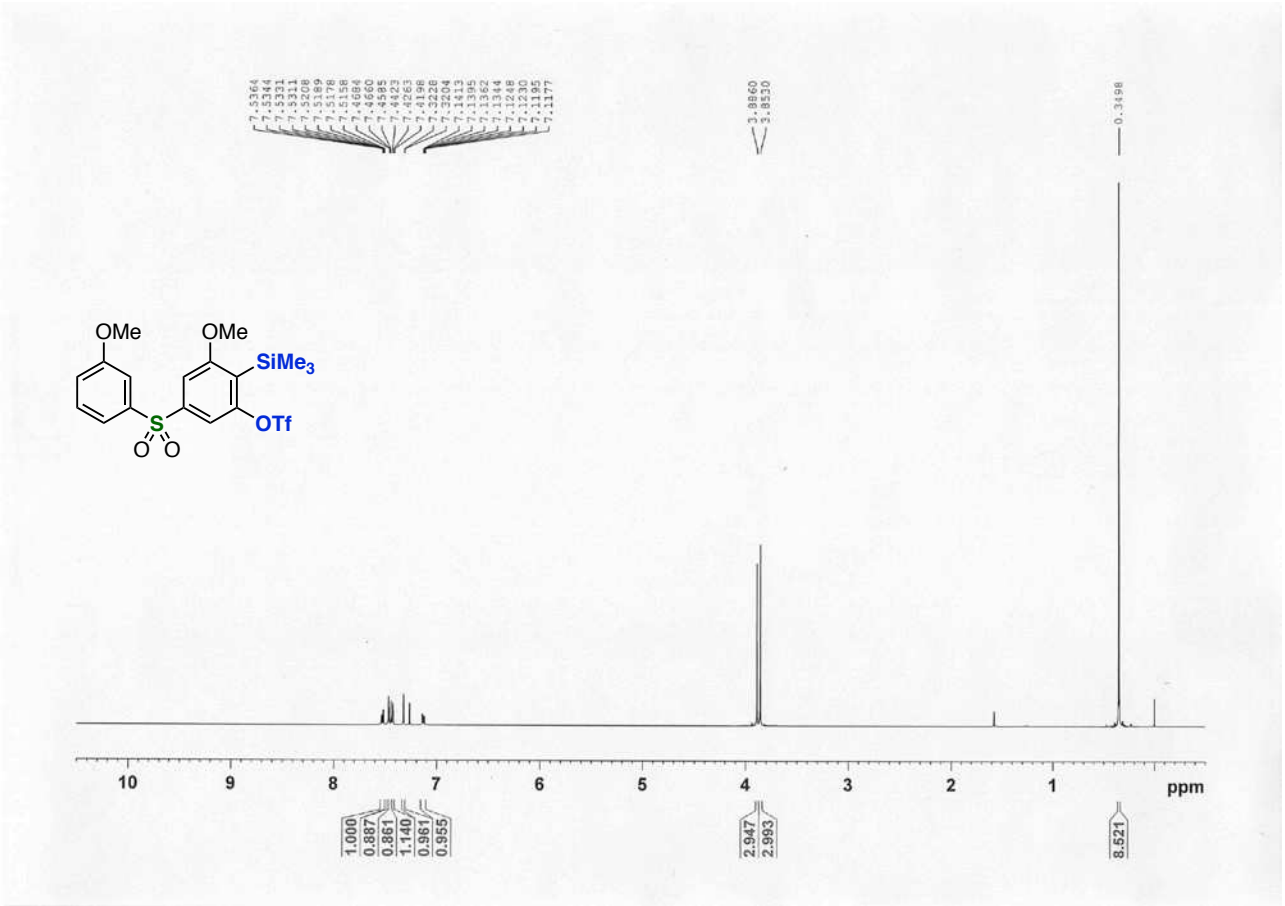


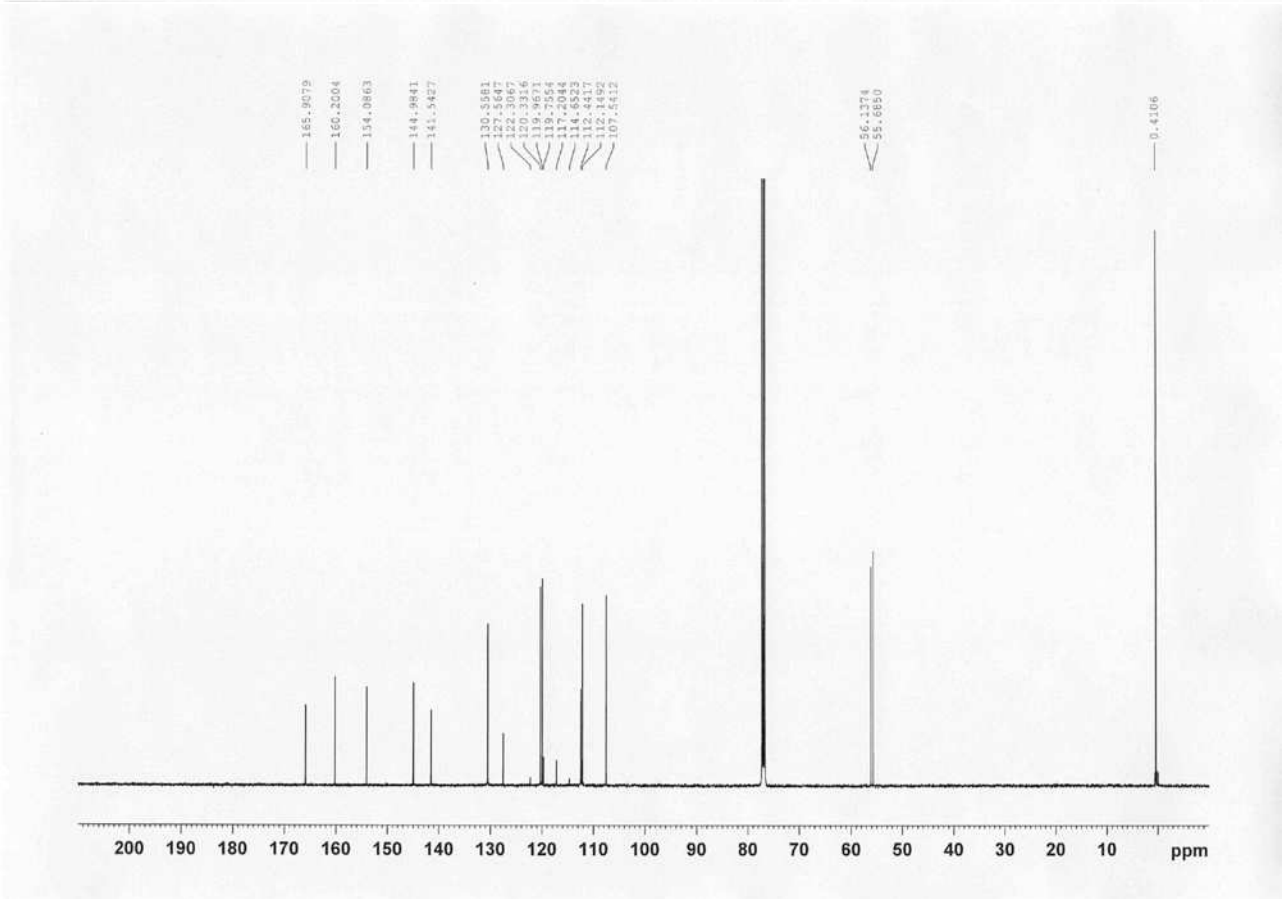
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 5-(3-methoxyphenylthio)-3-morpholino-2-(trimethylsilyl)phenyl triflate (**3m**) ($CDCl_3$)



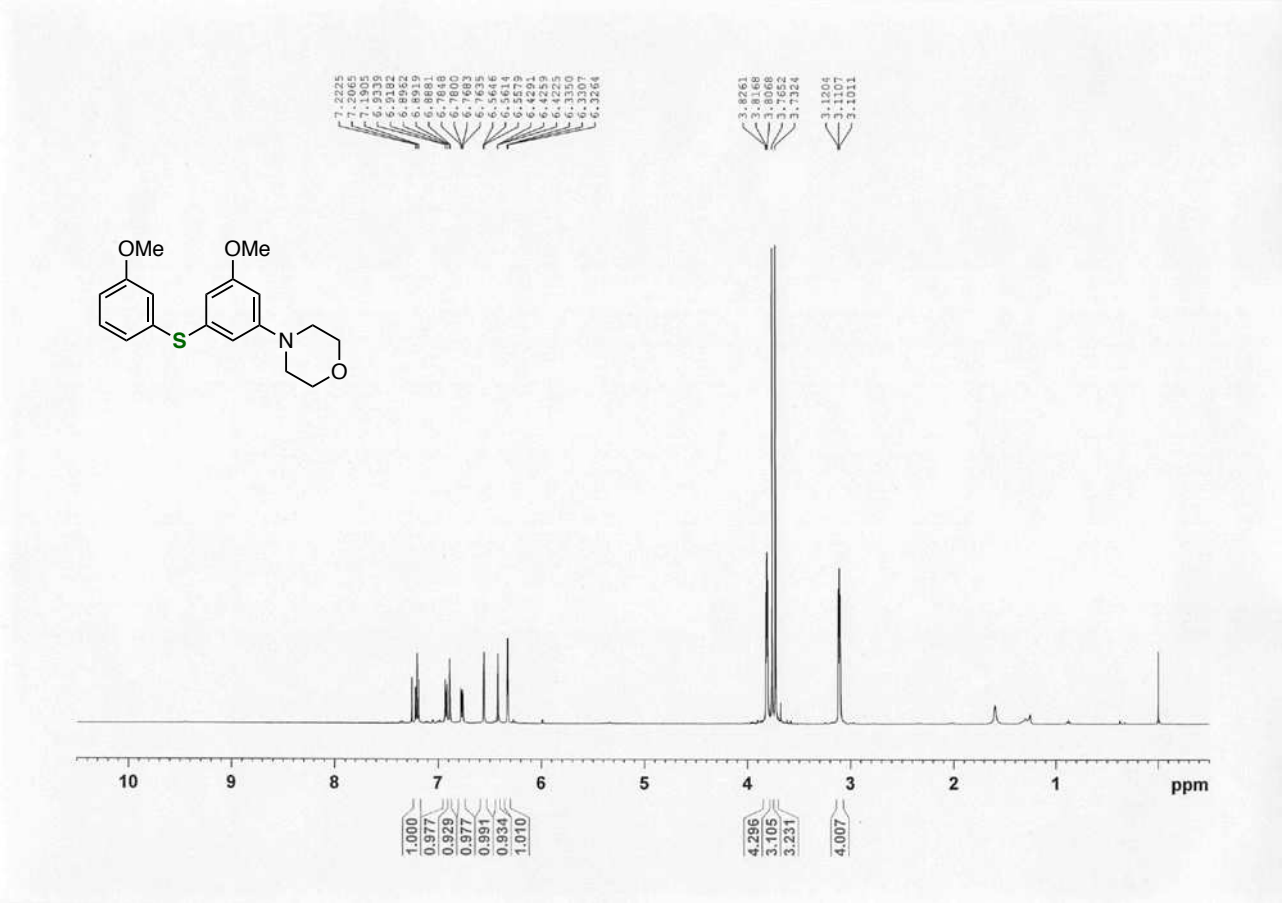


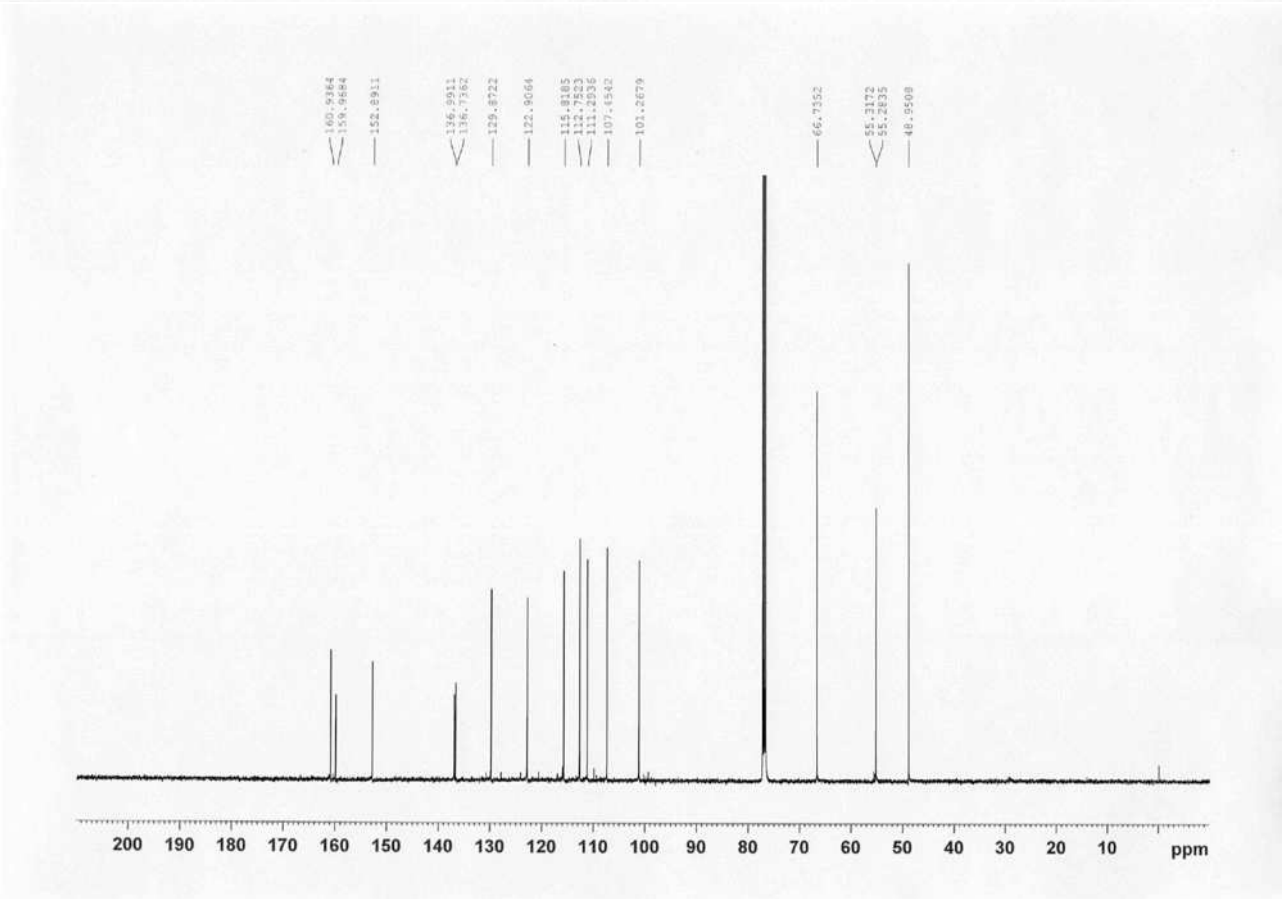
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 3-methoxy-5-(3-methoxyphenylsulfinyl)-2-(trimethylsilyl)phenyl triflate (**8**) ($CDCl_3$)



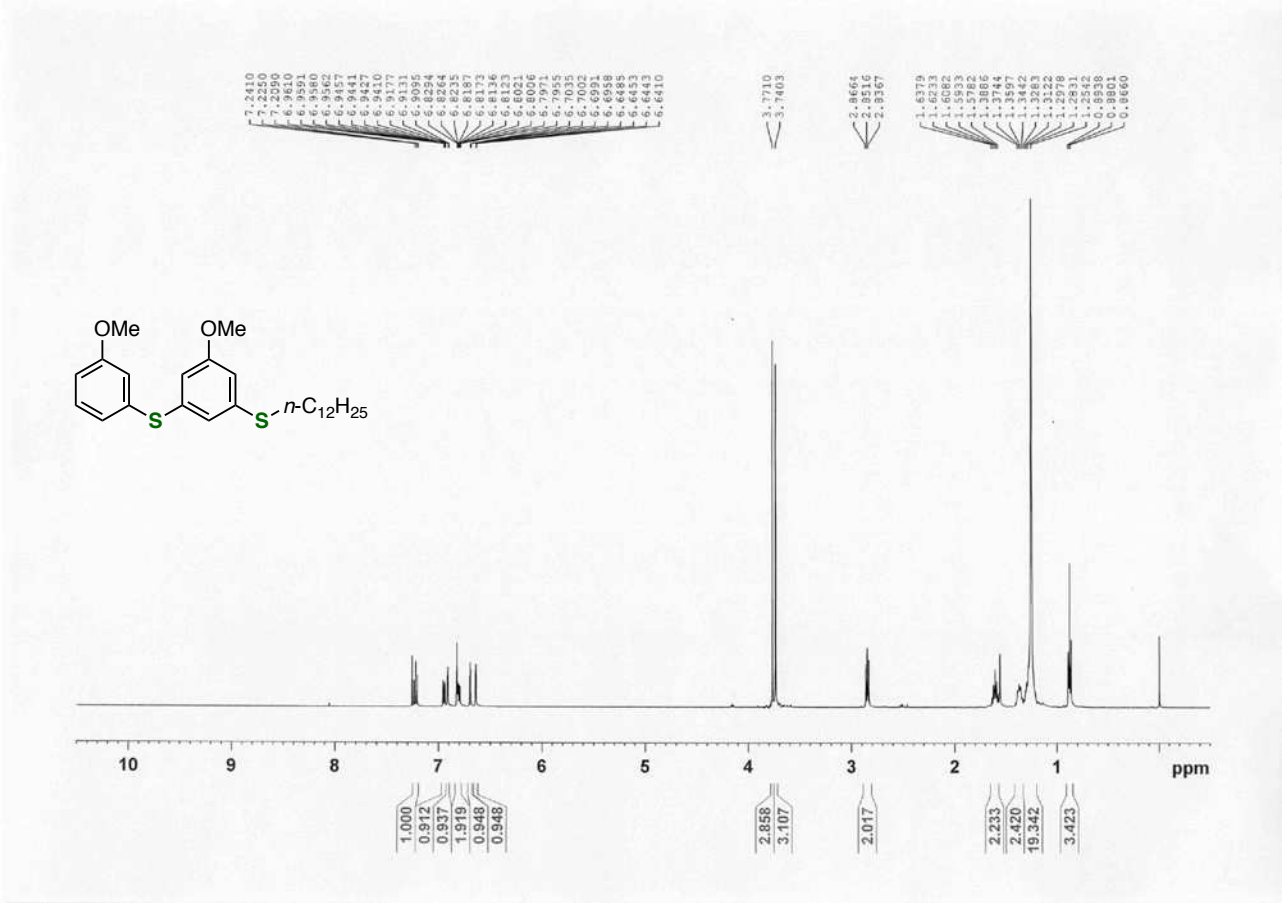


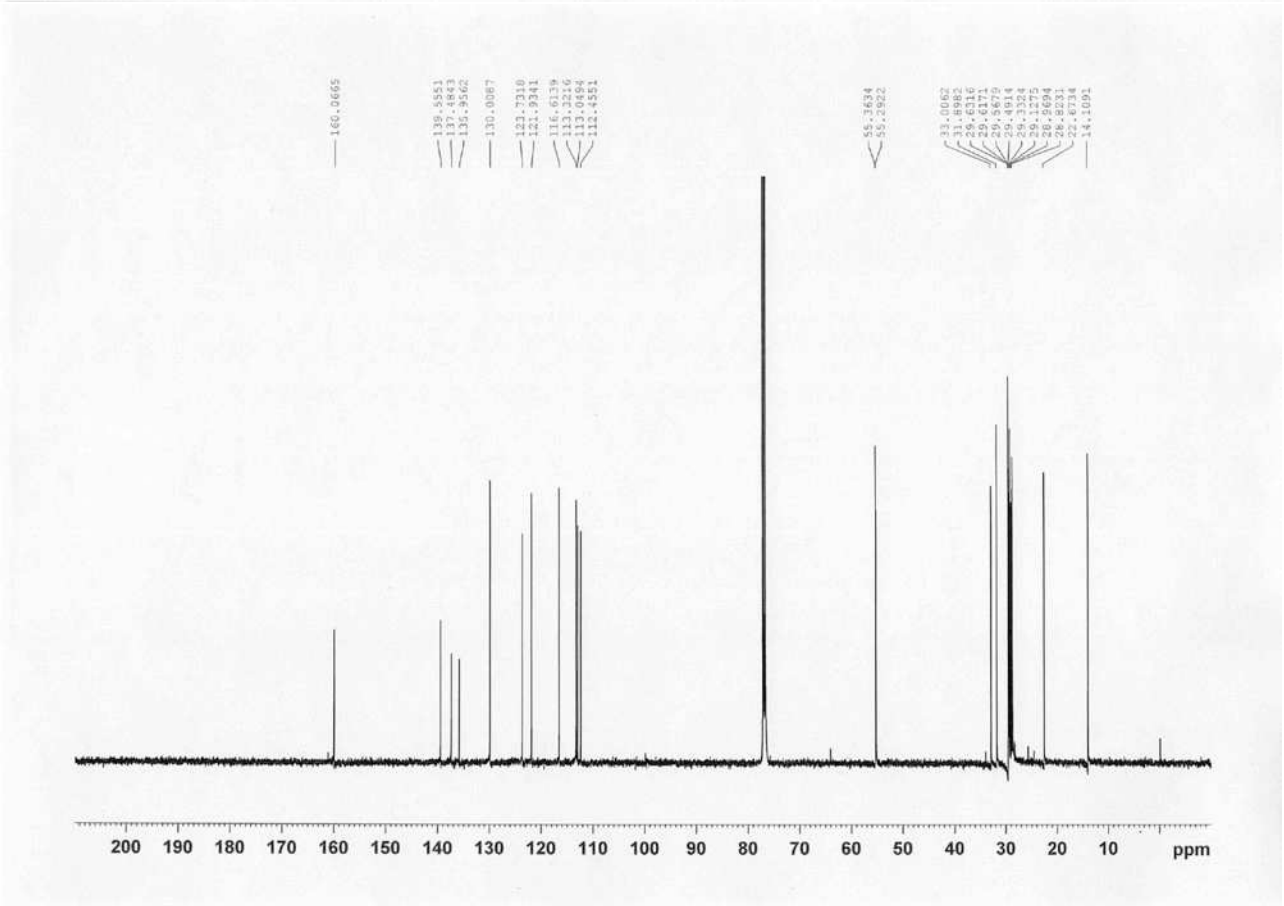
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of *N*-(3-methoxy-5-(3-methoxyphenylthio)phenyl)morpholine (**4a**) ($CDCl_3$)



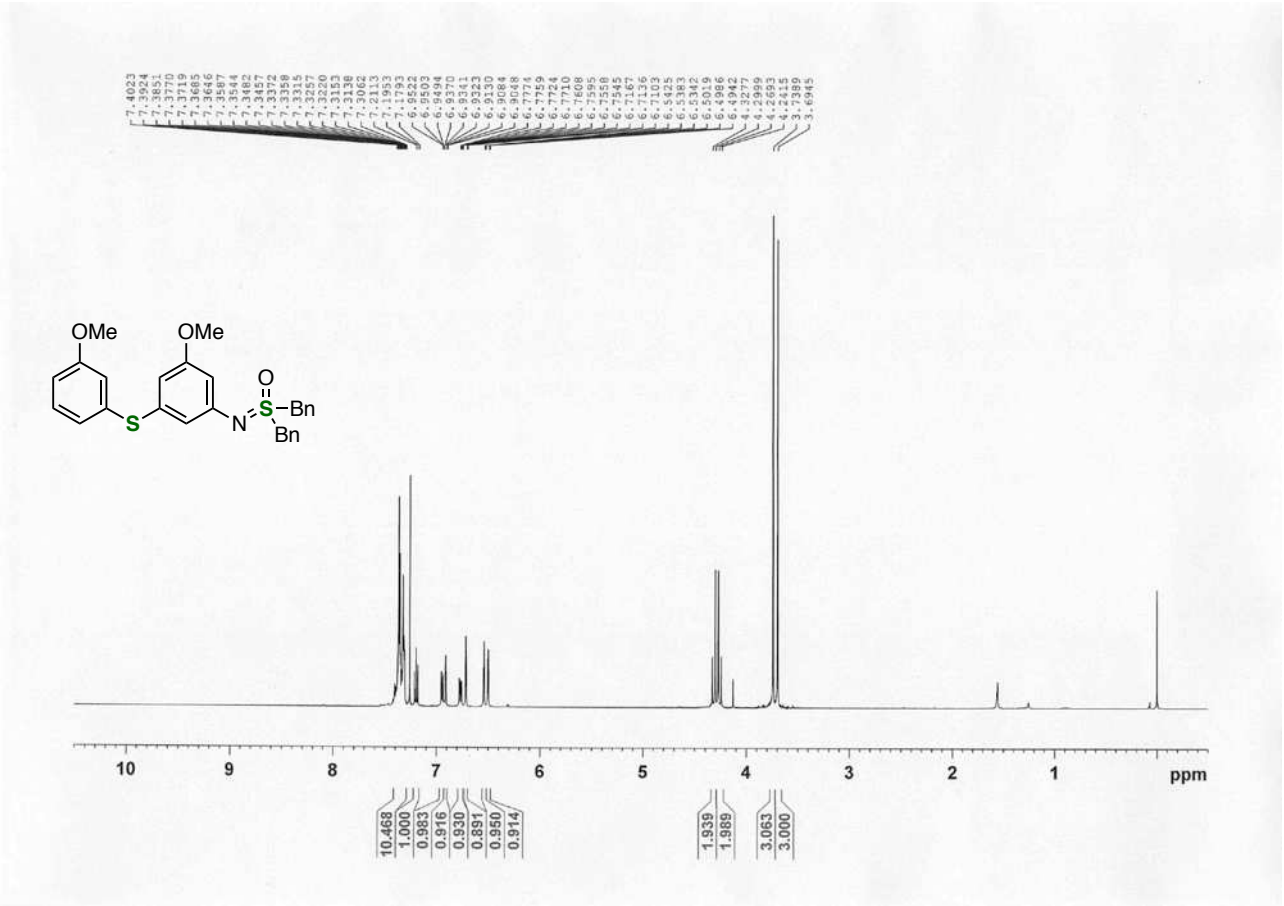


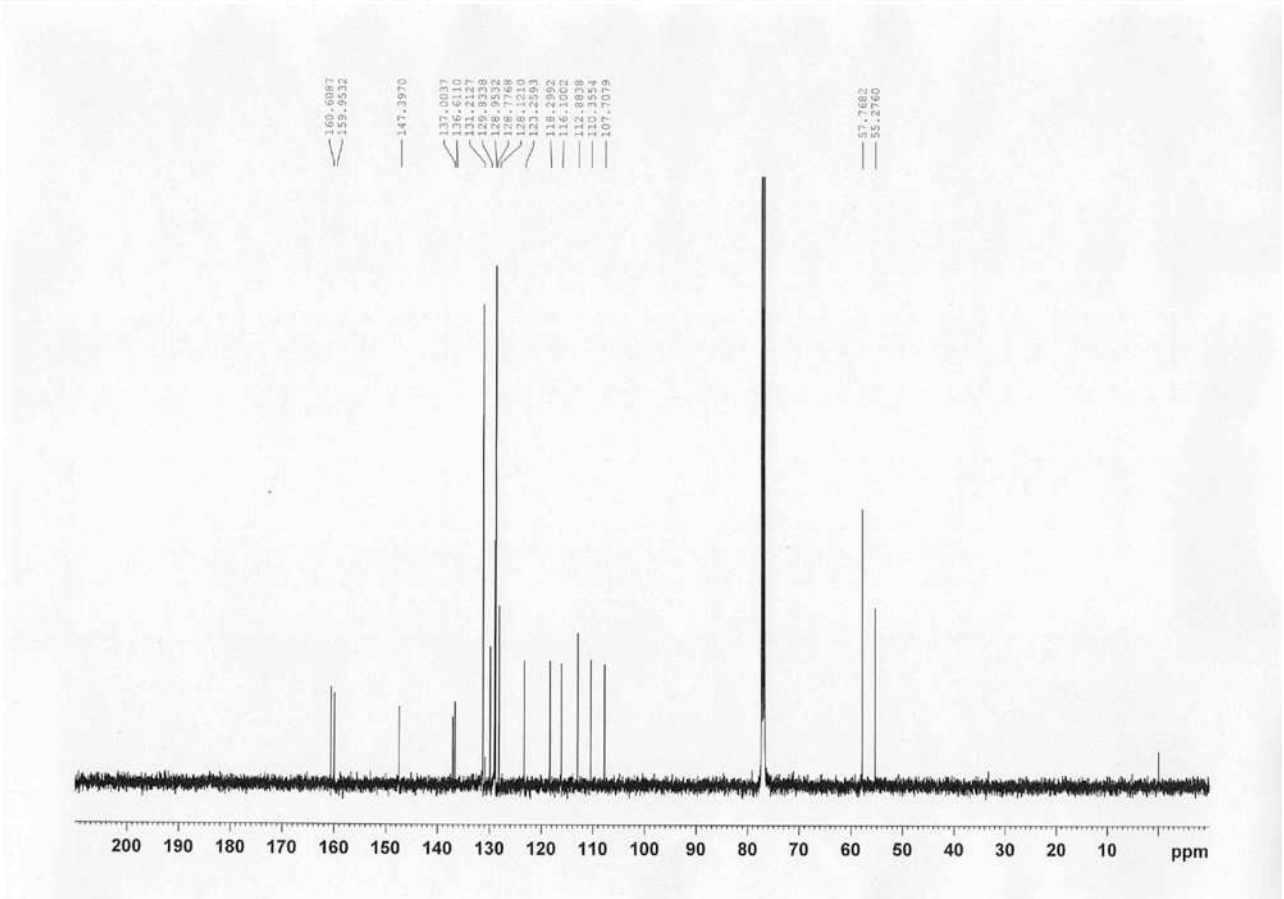
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of dodecyl 3-methoxy-5-(3-methoxyphenylsulfinyl)phenyl sulfide (**4b**) ($CDCl_3$)



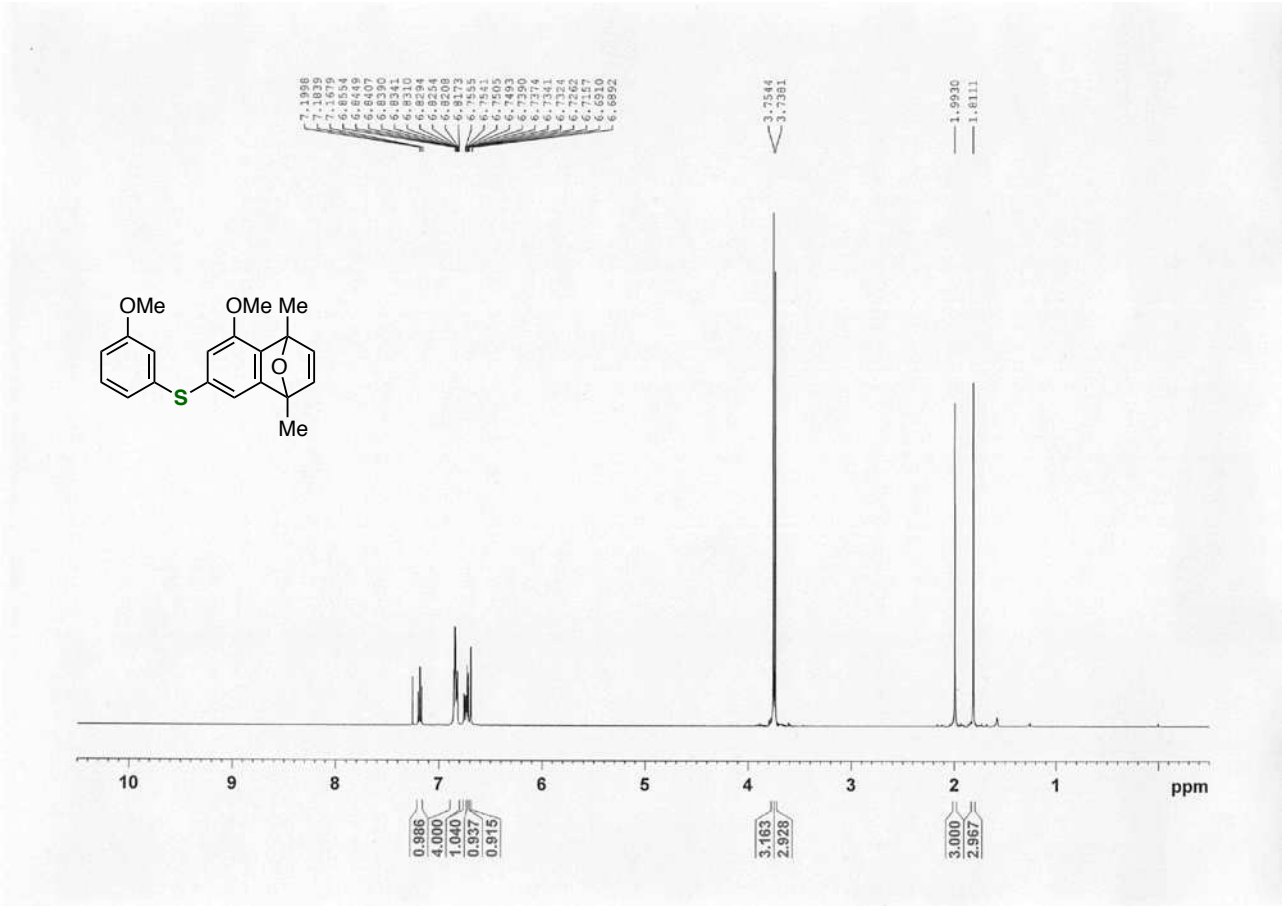


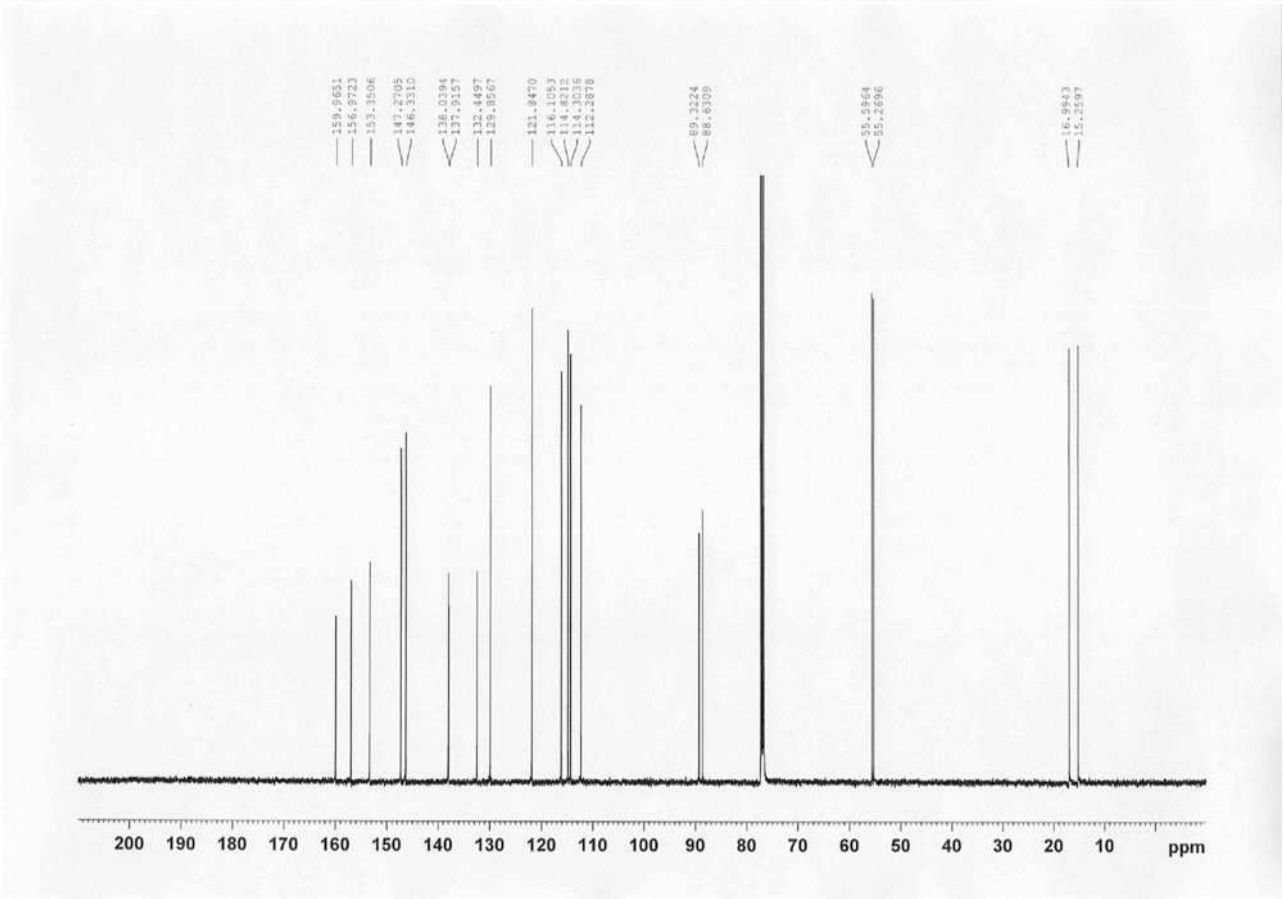
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of *S*,*S*-dibenzyl-*N*-(3-methoxy-5-(3-methoxyphenylthio)phenyl)sulfoximine (**4c**) ($CDCl_3$)



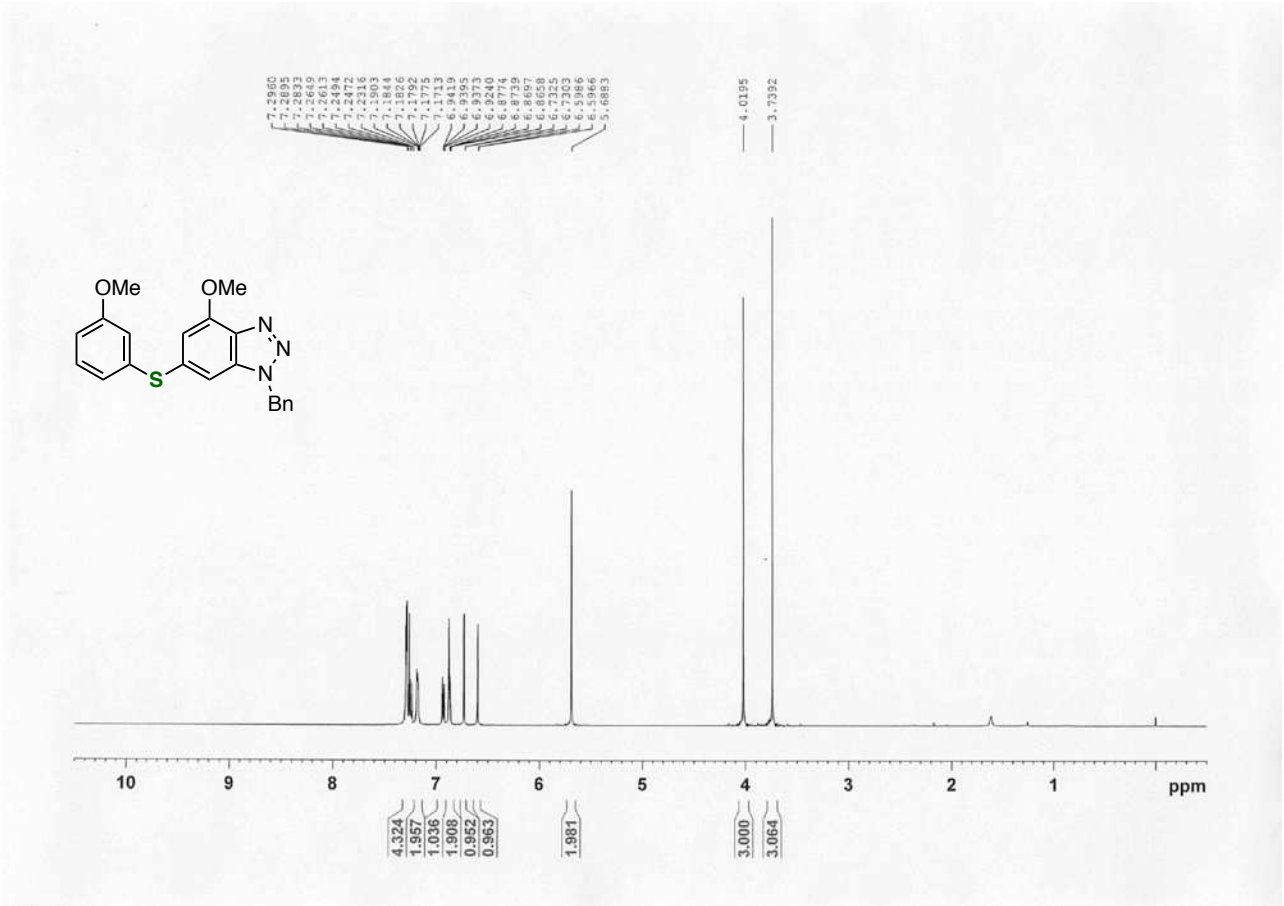


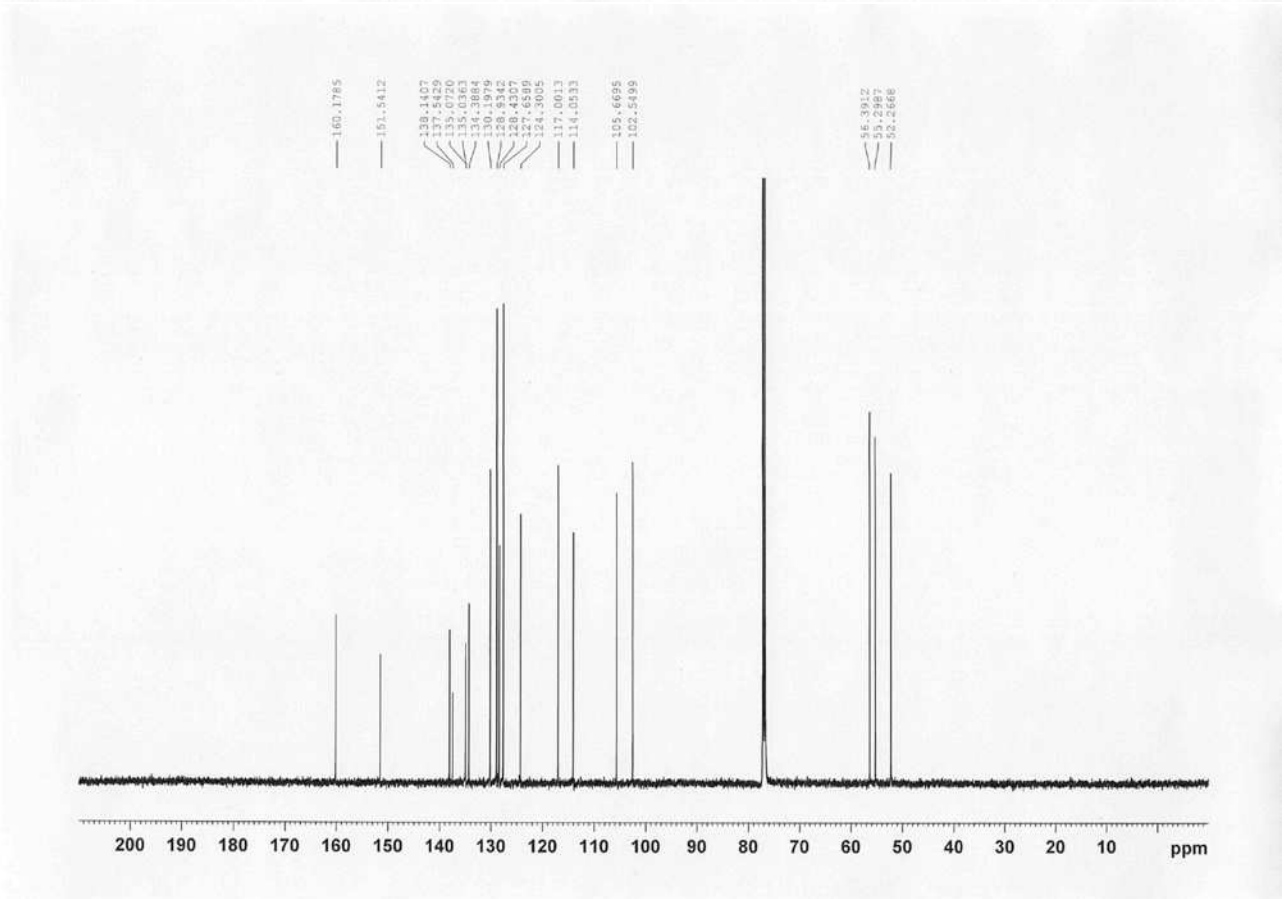
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 5-methoxy-7-(3-methoxyphenylthio)-1,4-dimethyl-1,4-dihydro-1,4-epoxynaphthalene (**4d**) ($CDCl_3$)



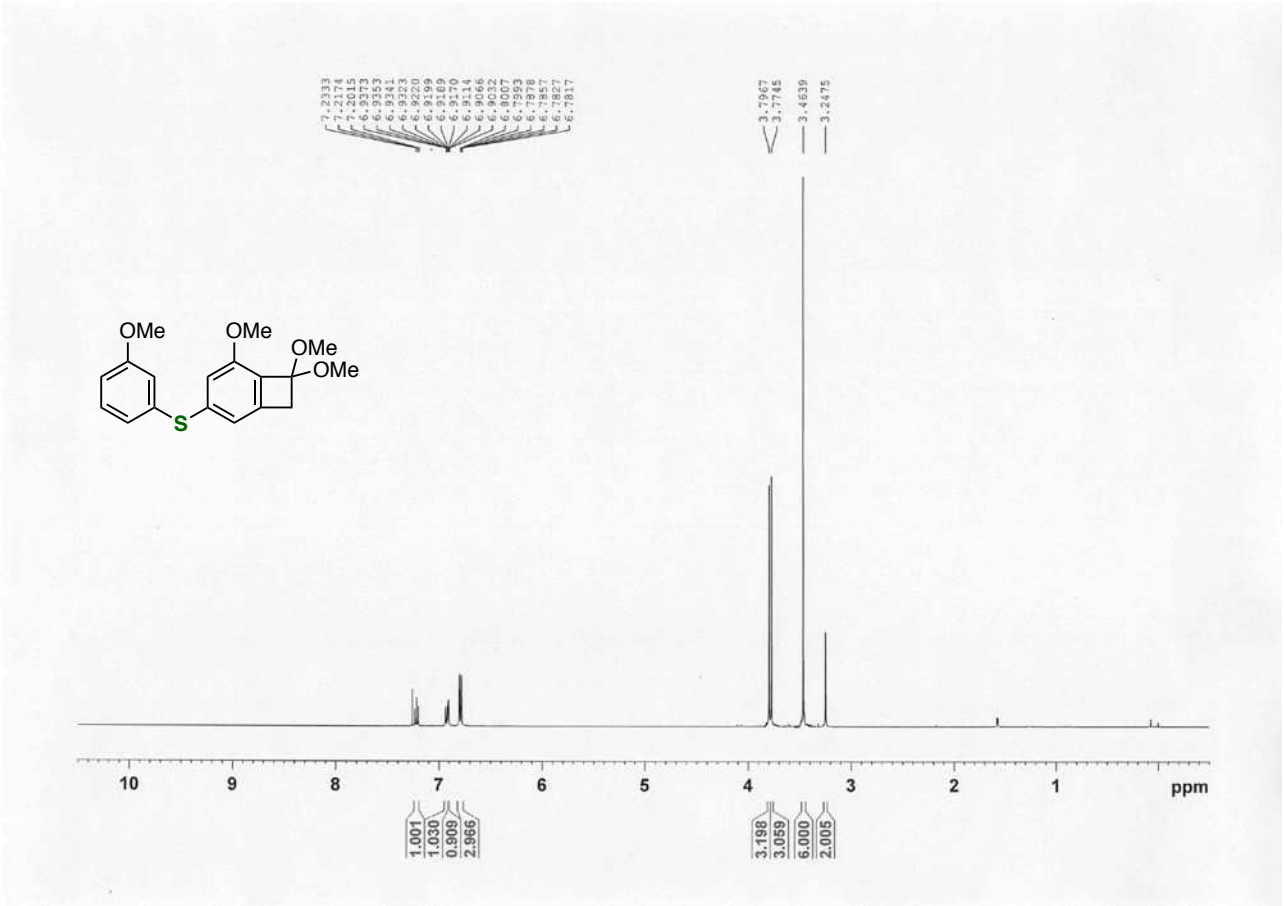


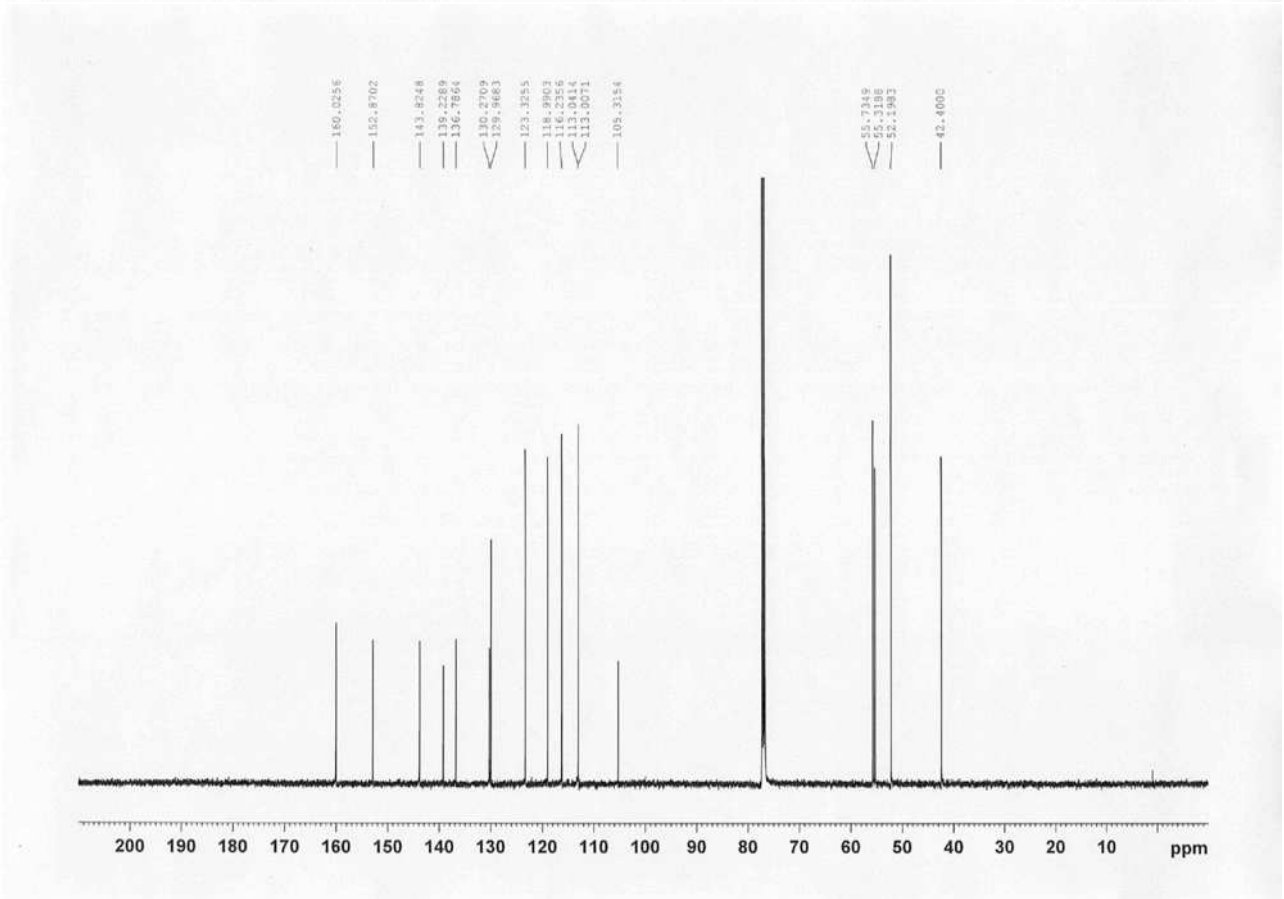
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 1-benzyl-4-methoxy-6-((3-methoxyphenyl)thio)-1*H*-benzo[*d*][1,2,3]triazole (**4e**) ($CDCl_3$)



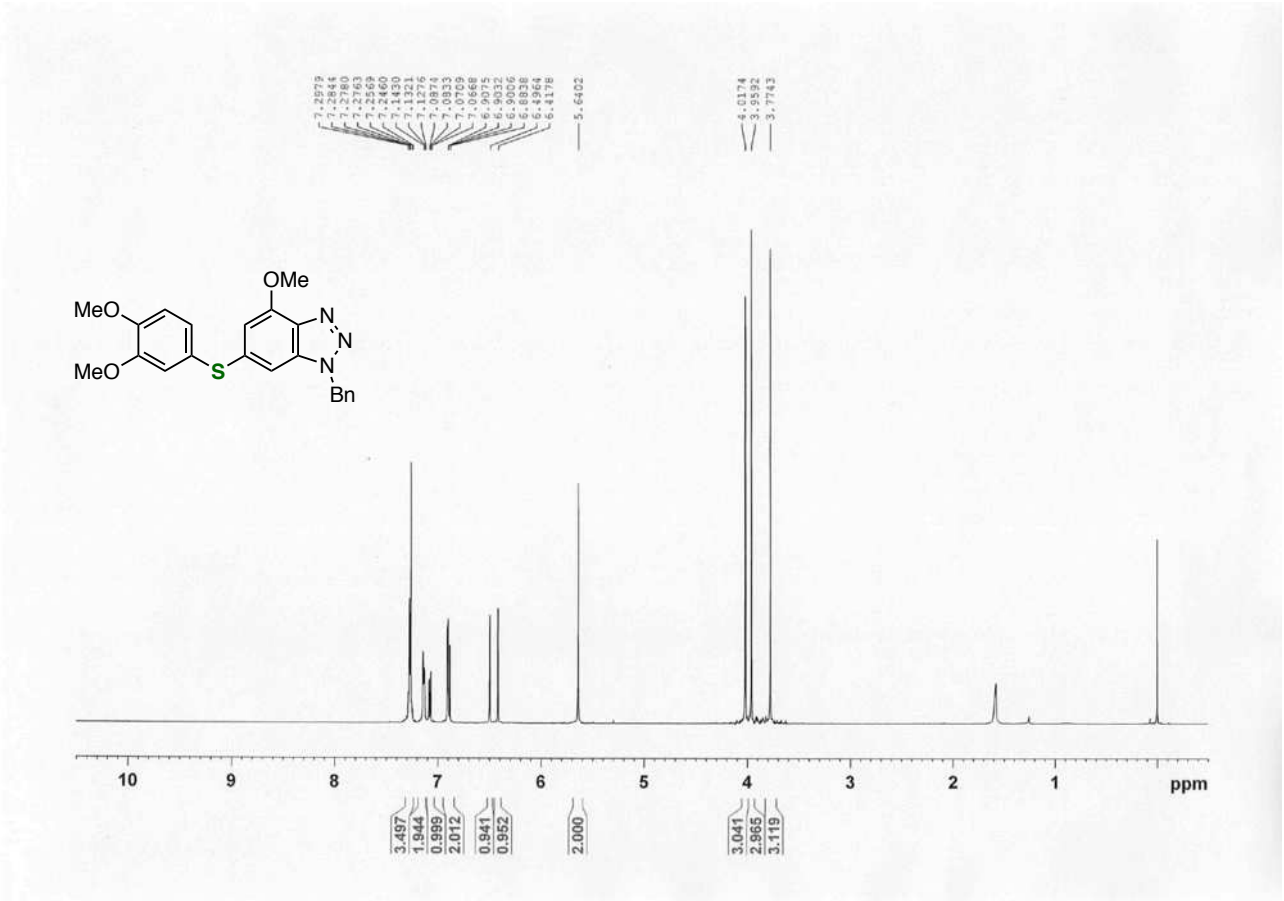


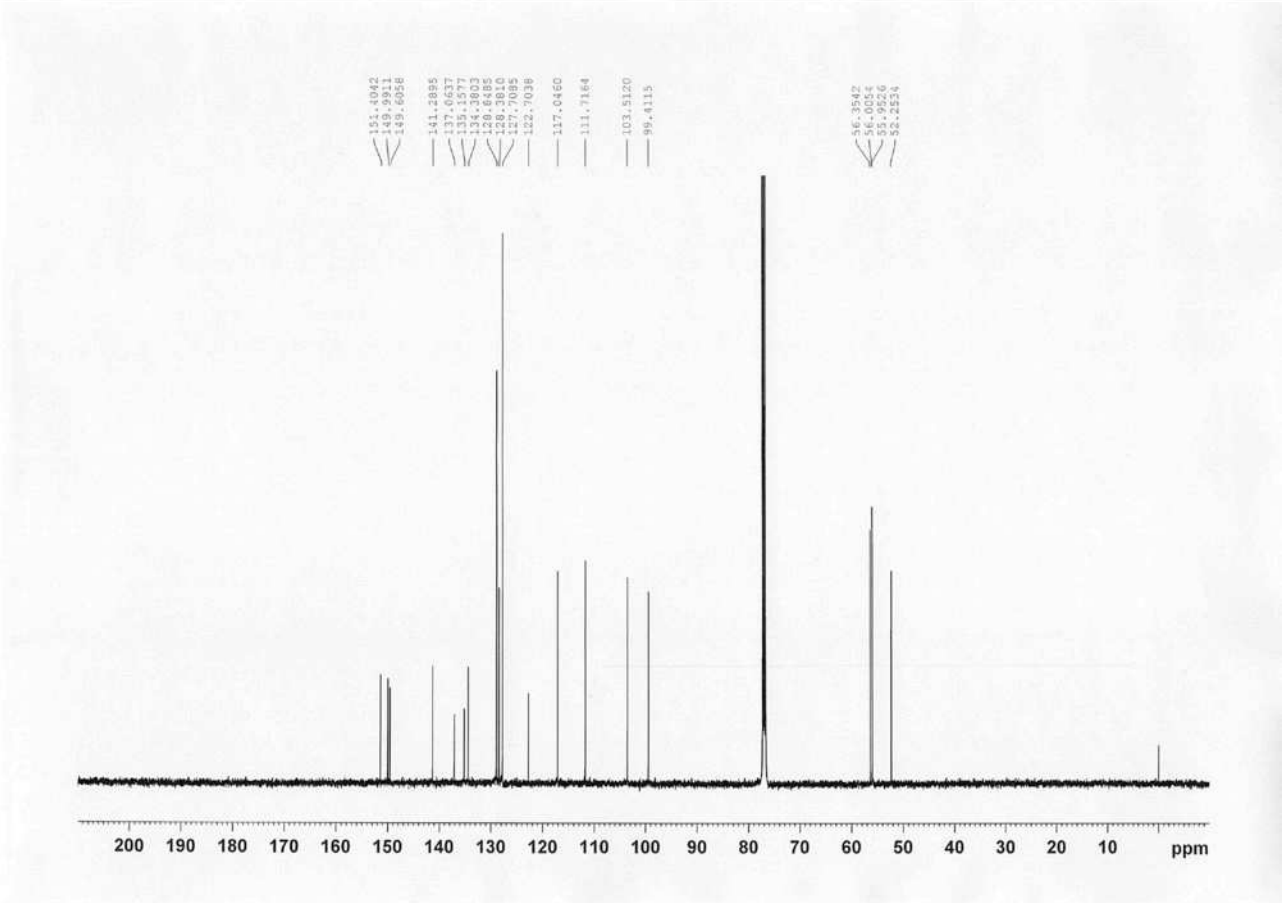
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 4-(3-methoxyphenyl)-2,8,8-trimethoxybicyclo[4.2.0]octa-1,3,5-triene (**4f**) ($CDCl_3$)



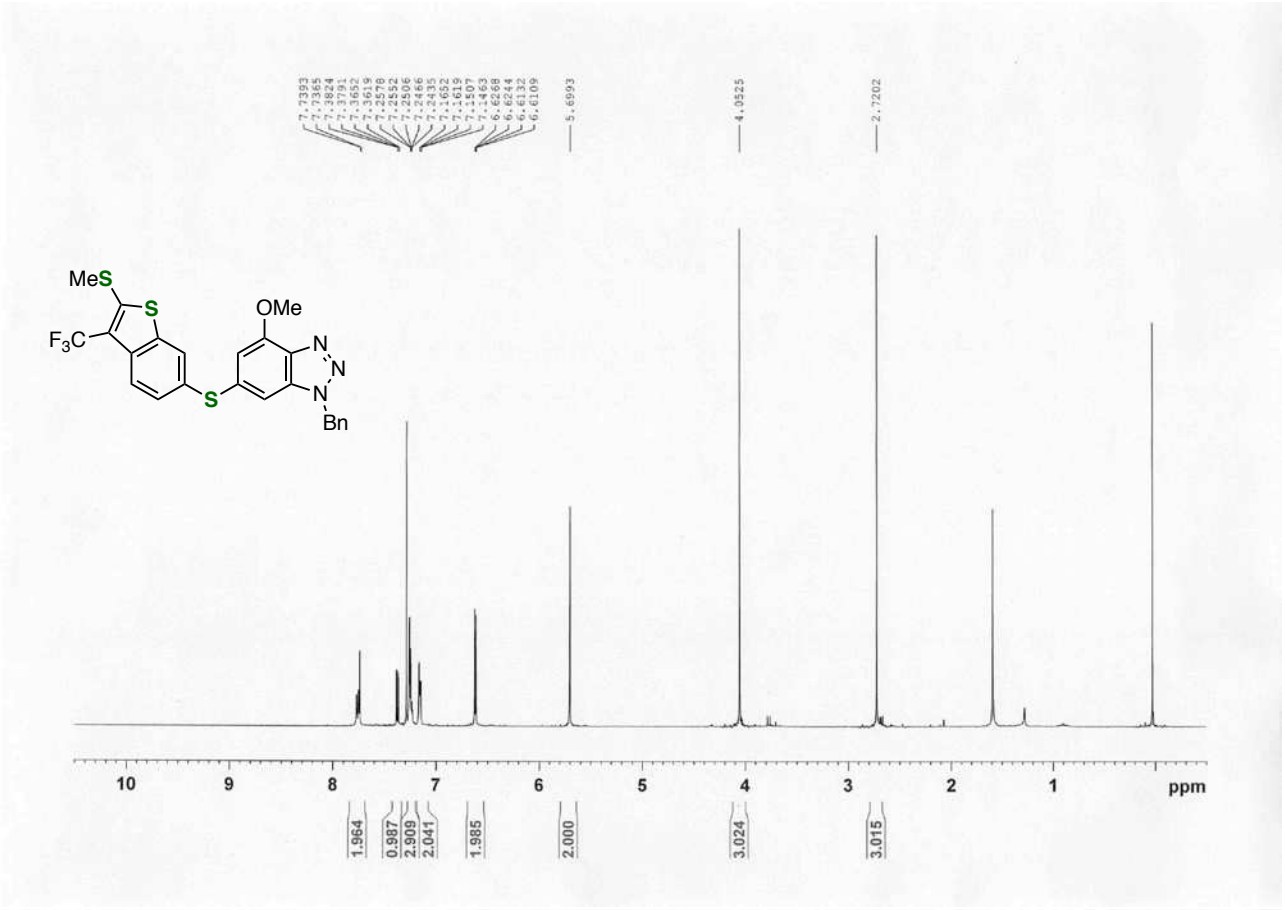


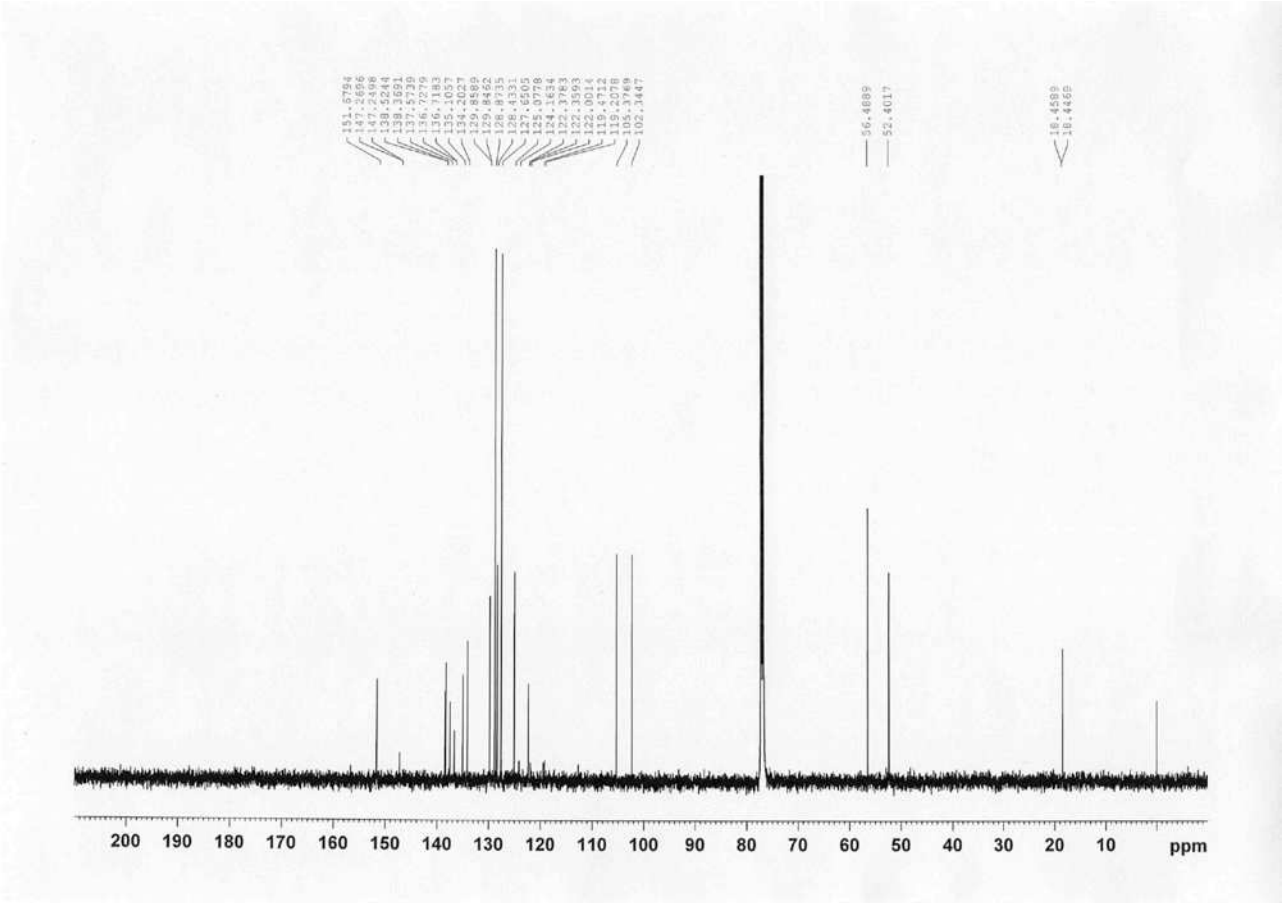
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 1-benzyl-6-((3,4-dimethoxyphenyl)thio)-4-methoxy-1*H*-benzo[*d*][1,2,3]triazole (**4g**) ($CDCl_3$)



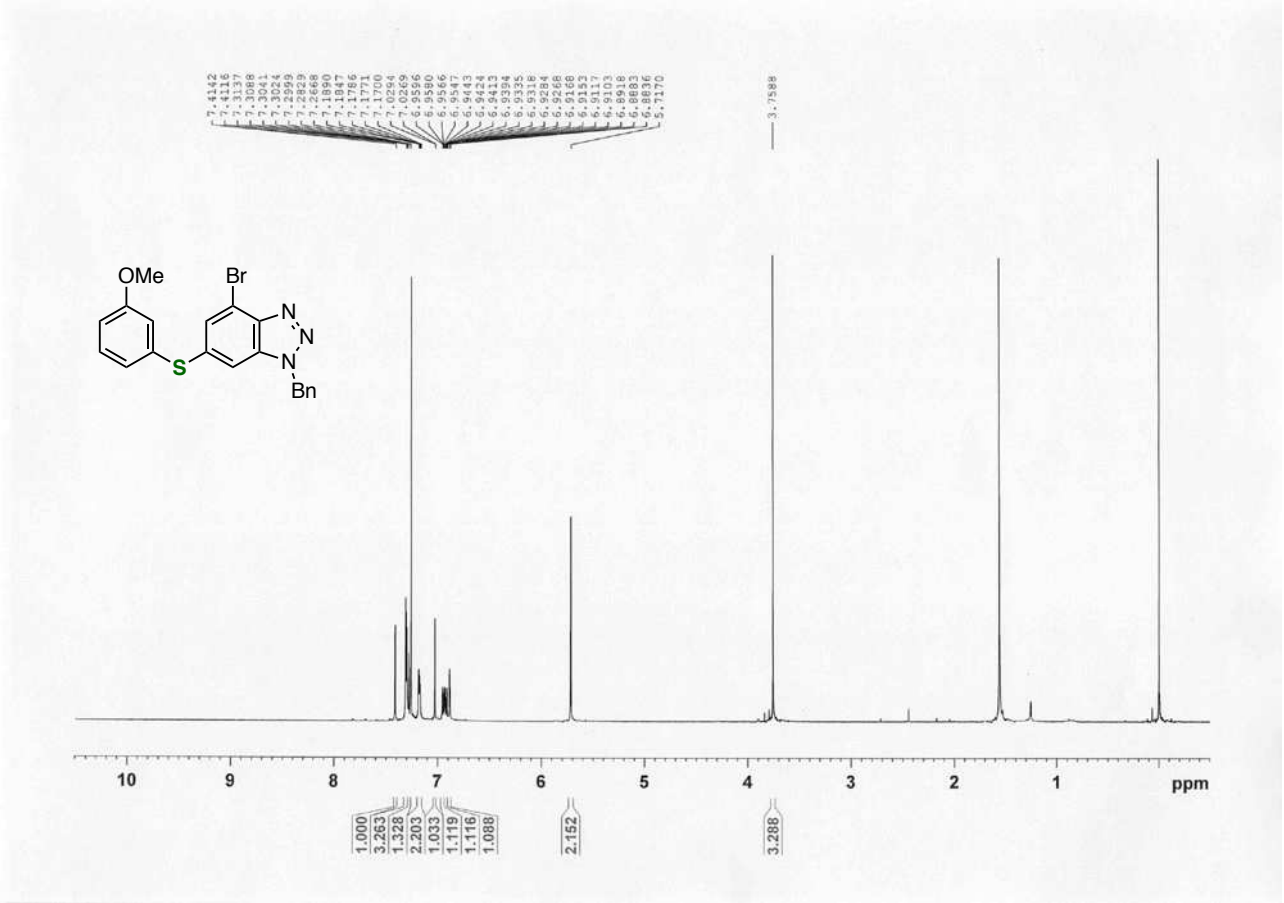


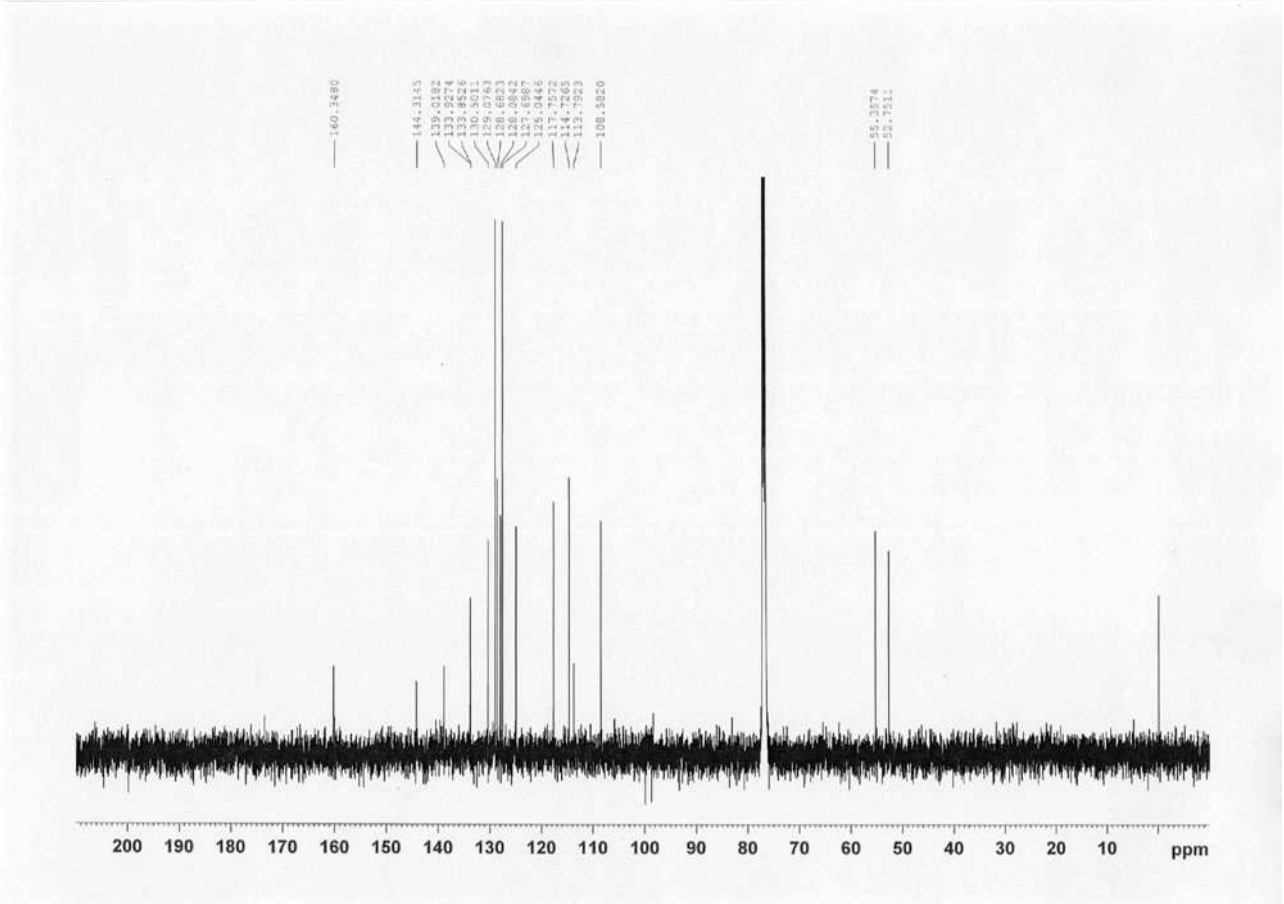
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 1-benzyl-6-((2-methylthio-3-trifluoromethylbenzo[*b*]thiophen-6-yl)thio)-4-methoxy-1*H*-benzo[*d*][1,2,3]triazole (**4h**) ($CDCl_3$)



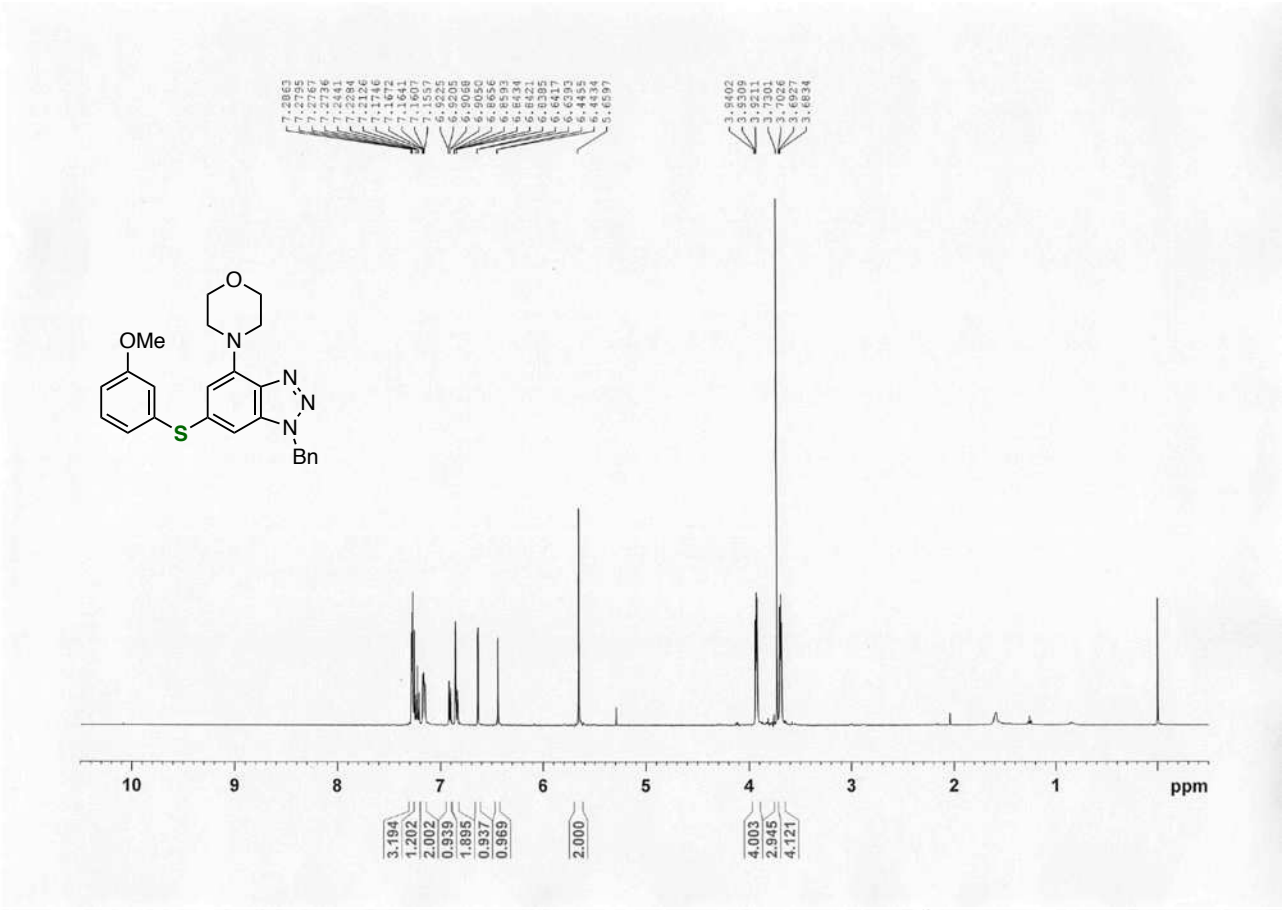


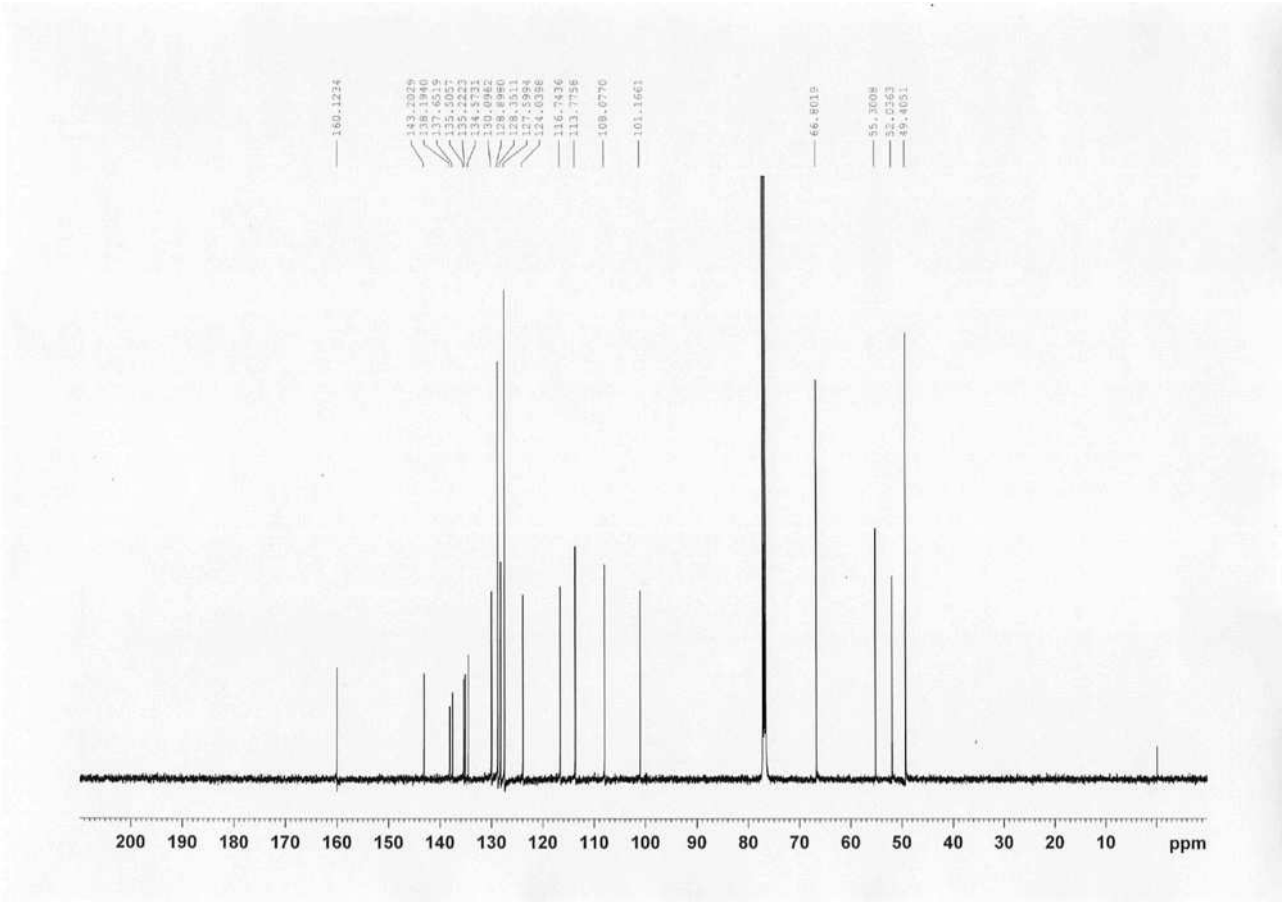
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 1-benzyl-4-bromo-6-((3-methoxyphenyl)thio)-1*H*-benzo[*d*][1,2,3]triazole (**4i**) ($CDCl_3$)



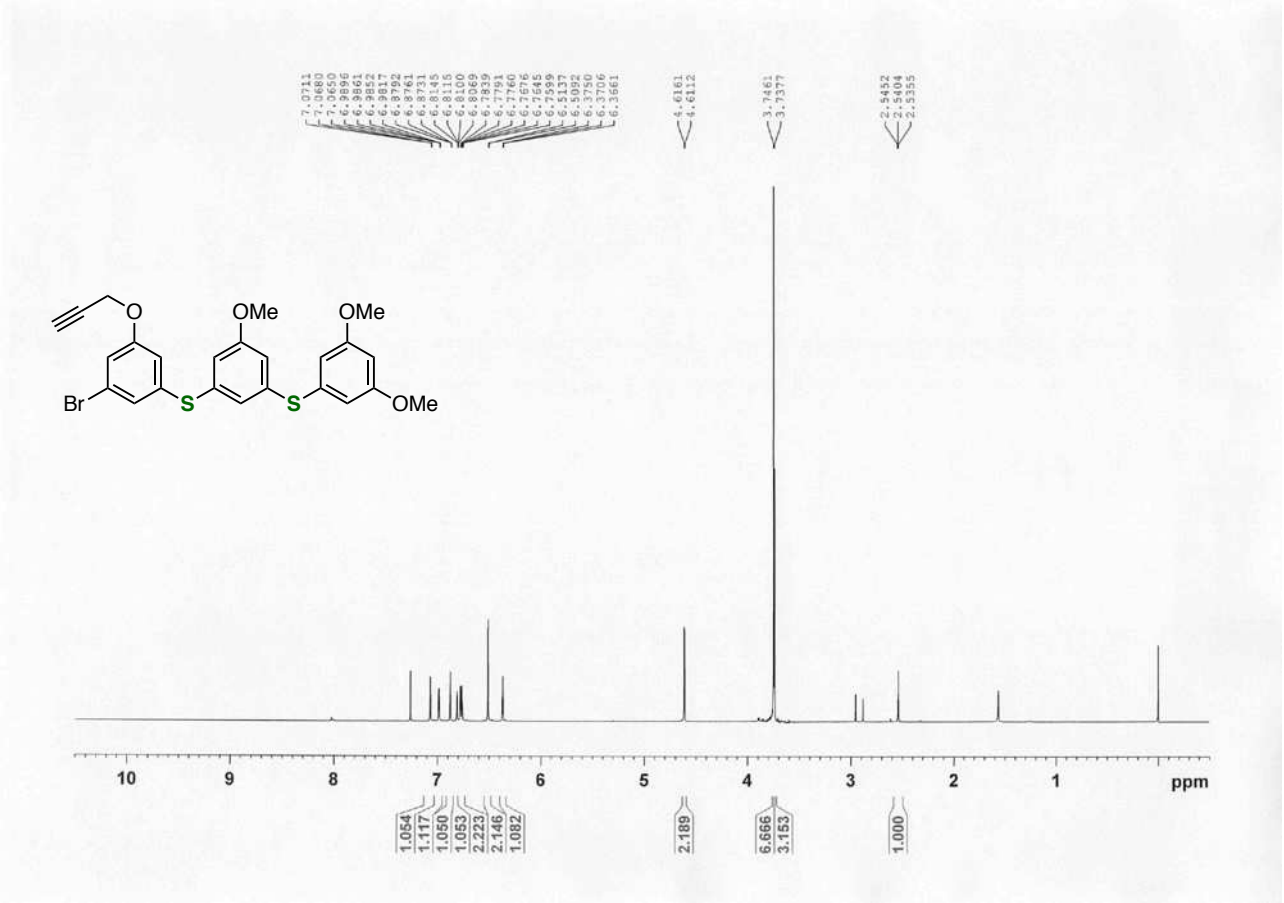


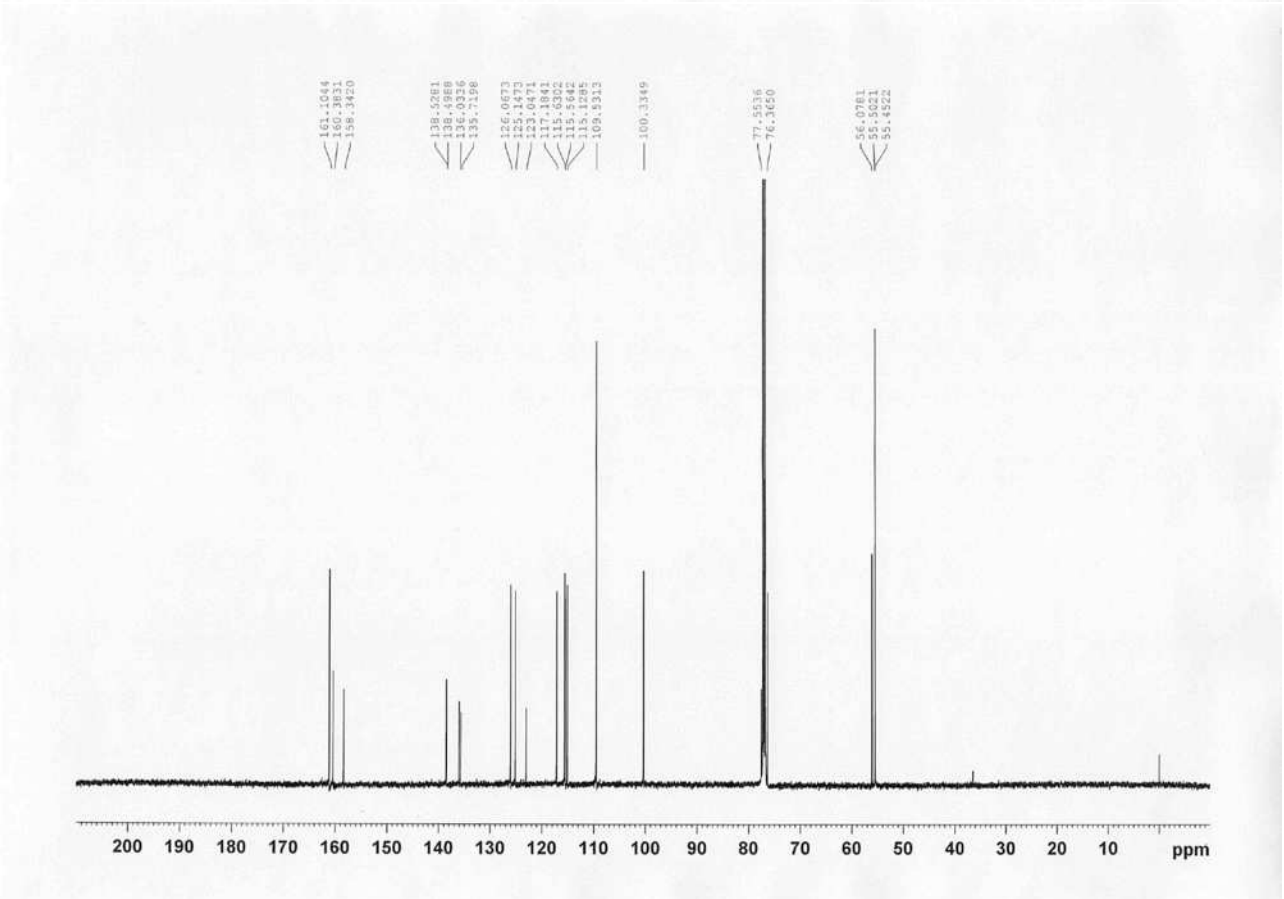
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 1-benzyl-6-((3-methoxyphenyl)thio)-4-morpholino-1*H*-benzo[*d*][1,2,3]triazole (**4j**) ($CDCl_3$)



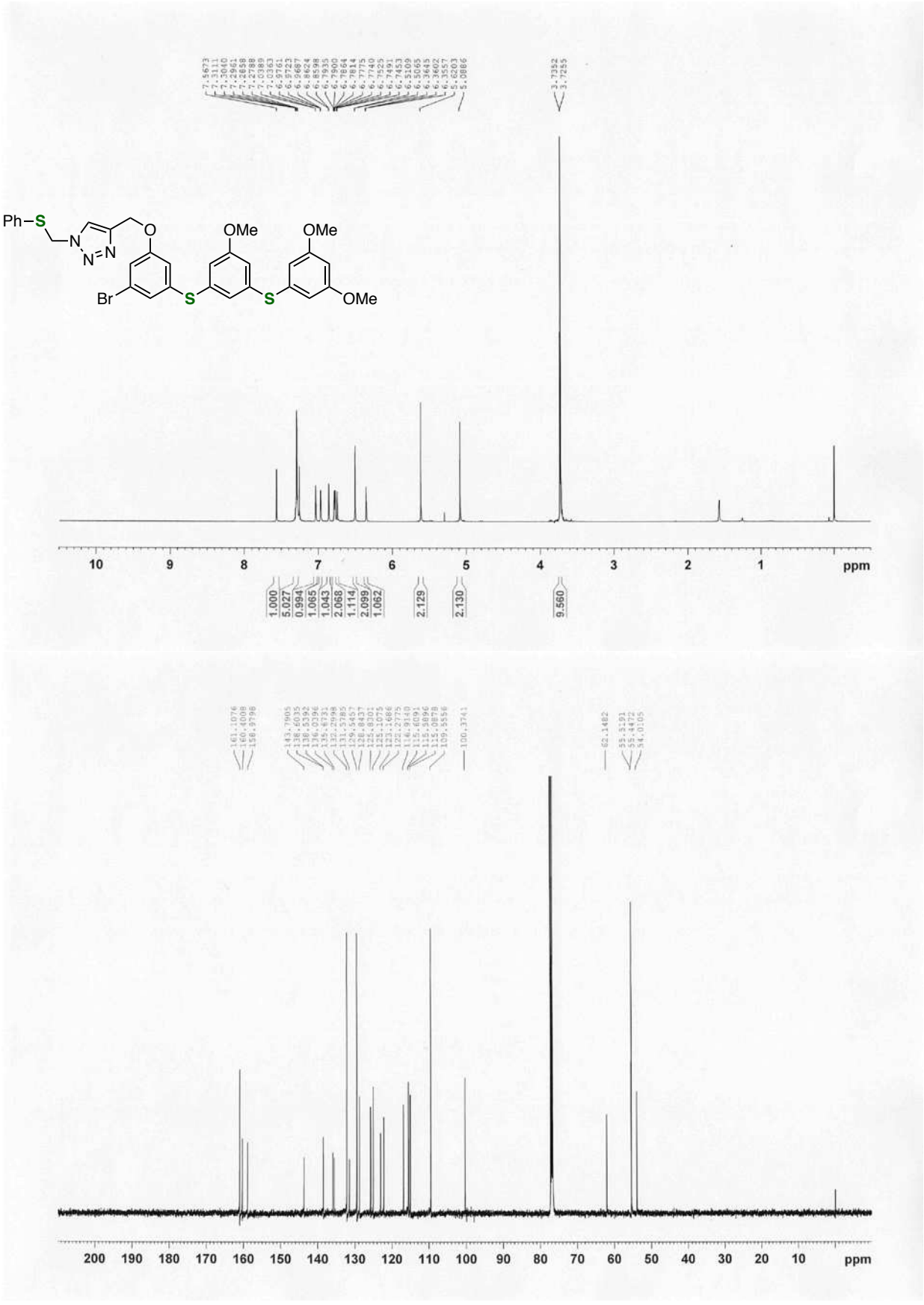


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 3-(3-(3,5-dimethoxyphenylthio)-5-methoxyphenylthio)-5-(propargyloxy)-1-bromobenzene (**10**) ($CDCl_3$)





^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 3-(3-(3,5-dimethoxyphenylthio)-5-methoxyphenylthio)-5-((1-(phenylthiomethyl)-1,2,3-triazol-4-yl)methyloxy)-1-bromobenzene (**S1**) ($CDCl_3$)



^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 3-(3-(3,5-dimethoxyphenylthio)-5-methoxyphenylthio)-5-((1-(phenylthiomethyl)-1,2,3-triazol-4-yl)methyloxy)-1-(3-thienyl)benzene (**13**) ($CDCl_3$)