

Supporting Information

3-Thioaryne Intermediates for the Synthesis of Diverse Thioarenes

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General Remarks

All reactions were performed with dry glassware under atmosphere of argon unless otherwise noted. Analytical thin-layer chromatography (TLC) was performed on precoated (0.25 mm) silica-gel plates (Merck Chemicals, Silica Gel 60 F₂₅₄, Cat. No. 1.05715). Column chromatography was conducted using silica-gel (Kanto Chemical Co., Inc., Silica Gel 60, spherical neutral, particle size 40–50 μm, Cat. No. 37562-85). Preparative thin-layer chromatography (PTLC) was performed on silica-gel (FUJIFILM Wako Pure Chemical Corporation, Wakogel® B-5F, Cat. No. 230-00043). ¹H and ¹³C NMR spectra were obtained with a Bruker AVANCE 500 spectrometer at 500 and 126 MHz, respectively. ¹⁹F NMR spectra were obtained with a Bruker AVANCE 400 spectrometer at 376 MHz. All NMR measurements were carried out at 25 °C. CDCl₃ (Kanto Chemical Co. Inc., Cat. No. 07663-23), benzene-*d*₆ (FUJIFILM Wako Pure Chemical Corporation, Cat. No. 024-19091), and acetone-*d*₆ (Sigma–Aldrich Japan, Cat. No. 151793) were 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 ¹H NMR and δ 77.2 for ¹³C NMR in CDCl₃, δ 7.16 for ¹H NMR and δ 128.4 for ¹³C NMR in benzene-*d*₆, and δ 2.05 for ¹H NMR and δ 29.9 for ¹³C NMR in acetone-*d*₆) as an internal reference or α,α,α-trifluorotoluene (δ –63.0 ppm for ¹⁹F NMR in CDCl₃) 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}. Elemental analyses were carried out

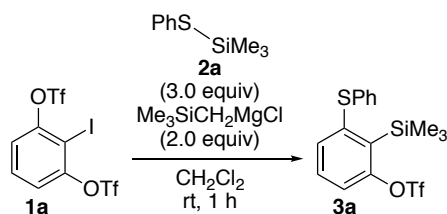
at A Rabbit Science Japan Co. Ltd. High-resolution mass spectra (HRMS) were measured on a Bruker micrOTOF mass spectrometer under positive electrospray ionization (ESI⁺) conditions. The absorbance spectra (UV/Vis) and fluorescence spectra (FL) were measured with a JASCO UV-650 spectrophotometer and a JASCO FP-8500 spectrofluorophotometer, respectively, at 25 °C using a quartz cuvette (10 mm light path). Fluorescence quantum yields were estimated by using 9,10-diphenylanthracene (9,10-DPA) in cyclohexane as a standard (Φ_F = 0.95).

Tetrahydrofuran (THF) (Cat. No. 41001-84), diethyl ether (Et₂O) (Cat. No. 14547-84), *m*-chloroperoxybenzoic acid (*m*CPBA) (Cat. No. 07938-02), *n*-butyllithium (1.6 M, hexane solution, Cat. No. 04937-05), magnesium turnings (Cat. No. 26000-25), and potassium acetate (Cat. No. 32299-30) were purchased from Kanto Chemical Co. Diethyl malonate (**14**) (Cat. No. 057-01436), benzyl azide (**12**) (Cat. No. 327-79632), potassium fluoride (Cat. No. 169-03765), 18-crown-6-ether (Cat. No. 031-12542), dichloromethane (Cat. No. 044-31235), sodium iodide (Cat. No. 196-02271), aniline (**6**) (Cat. No. 019-03991), 2-aminoethanol (Cat. No. 016-12453), acetonitrile (Cat. No. 014-00381), *N,N*-dimethylacetamide (Cat. No. 042-18656), cesium fluoride (Cat. No. 031-17162), toluene (Cat. No. 204-17915), *N,N*-dimethylformamide (Cat. No. 045-32365), isopropylmagnesium chloride–lithium complex (1.3 M, THF solution, Cat. No. 095-06431), and bromobenzene (Cat. No. 020-02545) were purchased from FUJIFILM Wako Pure Chemical Corporation. Chloro(trimethyl)silane (Cat. No. C0306), 4-methoxybenzenethiol (Cat. No. M1333), 1-dodecanethiol (Cat. No. D0970), 2,5-dimethylfuran (**8**) (Cat. No. D0725), 3-methoxy-2-(trimethylsilyl)phenyl triflate (**4a**) (Cat. No. M1884), (trimethylsilyl)methyl chloride (Cat. No. C0862), 2-bromobenzenethiol (Cat. No. B2347), *N*-*tert*-butyl- α -phenylnitrone (**10**) (Cat. No. B1701), benzo[*b*]thiophene (Cat. No. B0093), chlorodimethylsilane (Cat. No. C0778), chlorodimethylphenylsilane (Cat. No. D1147), trifluoroacetic anhydride (Cat. No. T0433), and bis(trimethylsilyl) sulfide (**2g**) (Cat. No. H0871) were purchased from Tokyo Chemical Industry Co., Ltd. Phenyl trimethylsilyl sulfide (**2a**) (Cat. No. 226467), methyl trimethylsilyl sulfide (**2c**) (Cat. No. 359491), tetrabutylammonium difluorotriphenylsilicate (Cat. No. 441457), and palladium(II) acetate (Cat. No. 379875) were purchased from Sigma–Aldrich Japan.

(Trimethylsilyl)methylmagnesium chloride (1.23 M in Et₂O) was prepared from (trimethylsilyl)methyl chloride and magnesium in the conventional way. Phenylmagnesium bromide (2.62 M in Et₂O) was prepared from bromobenzene and magnesium in the conventional way. (Trimethylsilyl)methylmagnesium chloride (1.23 M, Et₂O), phenylmagnesium bromide (2.62 M, Et₂O solution), and commercial Grignard reagents were used after titrimetric determination of the concentration by the 1,10-phenanthroline method.^{S1} 2-Iodo-3-methoxyphenyl triflate (**4b**),^{S2} 1,3-bis(triflyloxy)-2-iodobenzene (**1a**),^{S3} 1,3-bis(triflyloxy)-2-iodo-5-(4-methoxyphenyl)benzene (**1b**),^{S4} 1,3-bis(triflyloxy)-5-bromo-2-iodobenzene (**1c**),^{S4} 1,3-bis(triflyloxy)-5-chloro-2-iodobenzene (**1d**),^{S4} 1,3-bis(triflyloxy)-5-(methoxycarbonyl)-2-iodobenzene (**1e**),^{S5} 1,3-bis(triflyloxy)-4,6-di(*tert*-butyl)-2-iodobenzene (**1f**),^{S4} 1,3-bis(triflyloxy)-4-(*n*-hexyl)-2-iodobenzene (**1g**),^{S4} 4-methoxyphenyl trimethylsilyl sulfide (**2b**),^{S6} *S*-(4-tolyl)-*S*-(4-(trifluoromethyl)phenyl)sulfilimine (**16**),^{S7} 2-bromophenyl 4-tolyl sulfoxide (**18**),^{S8} and 2-benzothieryl methyl sulfoxide (**26**)^{S9} were prepared according to the reported methods. All other chemical reagents used were commercial grade and used as received.

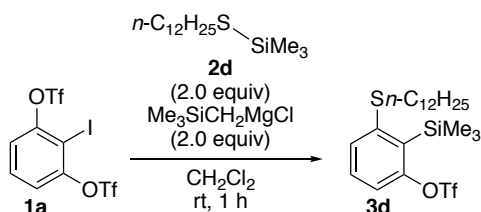
Experimental Procedures

A typical procedure for the synthesis of 3-sulfanyl-2-silylphenyl triflates 3



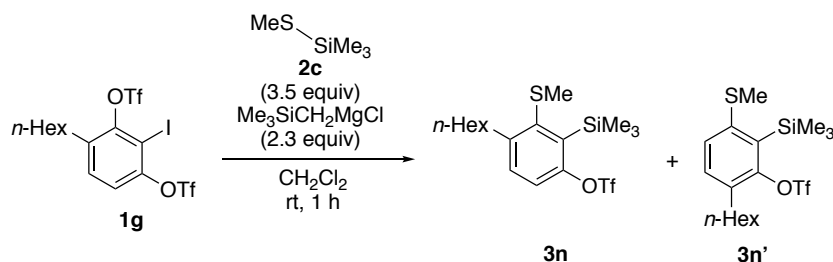
To a solution of 1,3-bis(triflyloxy)-2-iodobenzene (**1a**) (500 mg, 1.00 mmol) and phenyl trimethylsilyl sulfide (**2a**) (0.564 mL, 3.00 mmol, 3.0 equiv) dissolved in CH₂Cl₂ (1.0 mL) was slowly added (trimethylsilyl)methylmagnesium chloride (1.23 M, Et₂O solution, 1.63 mL, 2.00 mmol, 2.0 equiv) at room temperature. After stirring for 1 h at the same temperature, to the mixture was added an aqueous saturated solution of ammonium chloride (10 mL). The mixture was extracted with CH₂Cl₂ (10 mL \times 3), and the combined organic extract was washed with brine (5 mL), dried (Na₂SO₄), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica-gel 61 g, *n*-hexane) to give 3-(phenylthio)-2-(trimethylsilyl)phenyl triflate (**3a**) (321 mg, 0.790 mmol, 79.0%) as a colorless oil.

A gram-scale synthesis of 3-(dodecylthio)-2-(trimethylsilyl)phenyl triflate (3d)



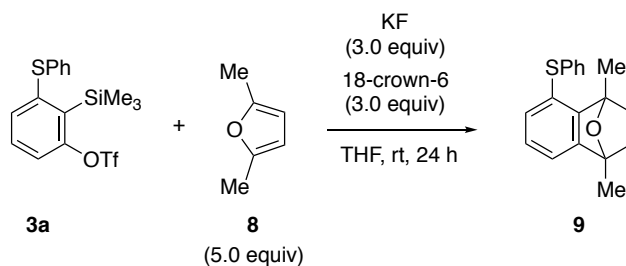
To a solution of 1,3-bis(triflyloxy)-2-iodobenzene (**1a**) (5.01 g, 10.0 mmol) and dodecyl trimethylsilyl sulfide (**2d**) (6.53 mL, 20.0 mmol, 2.0 equiv) dissolved in CH₂Cl₂ (50 mL) was slowly added (trimethylsilyl)methylmagnesium chloride (1.19 M, Et₂O solution, 16.8 mL, 20.0 mmol, 2.0 equiv) at room temperature. After stirring for 1 h at the same temperature, to the mixture was added an aqueous saturated solution of ammonium chloride (30 mL). The mixture was extracted with CH₂Cl₂ (30 mL \times 3), and the combined organic extract was washed with brine (10 mL), dried (Na₂SO₄), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica-gel 250 g, *n*-hexane) to give 3-(dodecylthio)-2-(trimethylsilyl)phenyl triflate (**3d**) (3.08 g, 6.17 mmol, 61.7%) as a colorless oil.

*Synthesis of 4-(n-hexyl)-3-(methylthio)-2-(trimethylsilyl)phenyl triflate (**3n**) and 6-(n-hexyl)-3-(methylthio)-2-(trimethylsilyl)phenyl triflate (**3n'**)*



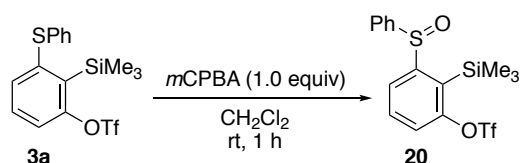
To a solution of 1,3-bis(triflyloxy)-4-(n-hexyl)-2-iodobenzene (**1g**) (101 mg, 0.173 mmol) and methyl trimethylsilyl sulfide (**2c**) (85.1 μ L, 0.600 mmol, 3.5 equiv) dissolved in CH₂Cl₂ (0.20 mL) was slowly added (trimethylsilyl)methylmagnesium chloride (1.49 M, Et₂O solution, 0.269 mL, 0.400 mmol, 2.3 equiv) at room temperature. After stirring for 1 h at the same temperature, to the mixture was added an aqueous saturated solution of ammonium chloride (2 mL). The mixture was extracted with CH₂Cl₂ (10 mL \times 3), and the combined organic extract was washed with brine (5 mL), dried (Na₂SO₄), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 100/1) to give 4-(n-hexyl)-3-(methylthio)-2-(trimethylsilyl)phenyl triflate (**3n**) (41.9 mg, 97.8 μ mol, 56.5%) as a colorless oil and 6-(n-hexyl)-3-(methylthio)-2-(trimethylsilyl)phenyl triflate (**3n'**) (13.3 mg, 31.0 μ mol, 17.9%) as a colorless oil.

A typical procedure for generation of 3-thiobenzynes from 3-sulfanyl-2-(trimethylsilyl)phenyl triflate



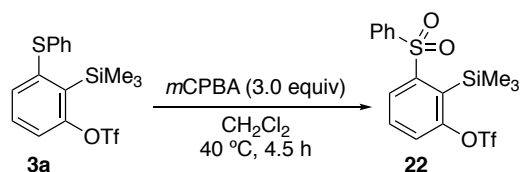
To a solution of 3-(phenylthio)-2-(trimethylsilyl)phenyl triflate (**3a**) (83.2 mg, 0.205 mmol) and 2,5-dimethylfuran (**8**) (96.1 mg, 1.00 mmol, 5.0 equiv) dissolved in THF (1.0 mL) were added potassium fluoride (34.9 mg, 0.600 mmol, 3.0 equiv) and 18-crown-6-ether (159 mg, 0.600 mmol, 3.0 equiv) at room temperature. After stirring for 24 h at the same temperature, to the mixture was added water (10 mL). The mixture was extracted with EtOAc (10 mL \times 3), and the combined organic extract was washed with brine (5 mL), dried (Na₂SO₄), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 20/1) to give 1,4-dimethyl-5-(phenylthio)-1,4-dihydro-1,4-epoxynaphthalene (**9**) (51.8 mg, 0.185 mmol, 90.3%) as a pale yellow oil.

Oxidation of 3-(phenylthio)-2-(trimethylsilyl)phenyl triflate (3a) for the synthesis of 3-(phenylsulfinyl)-2-(trimethylsilyl)phenyl triflate (20)



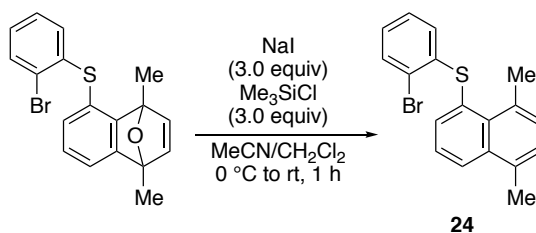
To a solution of 3-(phenylthio)-2-(trimethylsilyl)phenyl triflate (**3a**) (61.1 mg, 0.150 mmol) dissolved in CH₂Cl₂ (2.3 mL) was slowly added *m*-chloroperbenzoic acid (ca. 65%, 39.7 mg, ca. 0.15 mmol, ca. 1.0 equiv) at room temperature. After stirring for 1 h at the same temperature, to the mixture was added an aqueous saturated solution of potassium carbonate (5 mL) and an aqueous saturated solution of sodium thiosulfate (5 mL). The mixture was extracted with CH₂Cl₂ (10 mL × 3), and the combined organic extract was washed with brine (5 mL), dried (Na₂SO₄), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 1/1) to give 3-(phenylsulfinyl)-2-(trimethylsilyl)phenyl triflate (**20**) (60.7 mg, 0.144 mmol, 95.8%) as a colorless oil.

Oxidation of 3-(phenylthio)-2-(trimethylsilyl)phenyl triflate (3a) for the synthesis of 3-(phenylsulfonyl)-2-(trimethylsilyl)phenyl triflate (22)



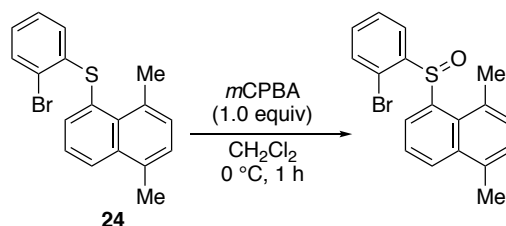
To a solution of 3-(phenylthio)-2-(trimethylsilyl)phenyl triflate (**3a**) (637 mg, 1.57 mmol) dissolved in CH₂Cl₂ (24 mL) was slowly added *m*-chloroperbenzoic acid (ca. 65%, 1.25 g, ca. 4.7 mmol, ca. 3.0 equiv) at 40 °C. After stirring for 4.5 h at the same temperature, the mixture was allowed to cool to room temperature, and to this was added an aqueous saturated solution of potassium carbonate (5 mL) and an aqueous saturated solution of sodium thiosulfate (5 mL). The mixture was extracted with CH₂Cl₂ (20 mL × 3) and the combined organic extract was washed with brine (5 mL), dried (Na₂SO₄), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica-gel 33 g, *n*-hexane/EtOAc = 5/1) to give 3-(phenylsulfonyl)-2-(trimethylsilyl)phenyl triflate (**22**) (525 mg, 1.20 mmol, 76.0%) as a colorless oil.

Synthesis of 5-((2-bromophenyl)thio)-1,4-dimethylnaphthalene (**24**)^{S10}



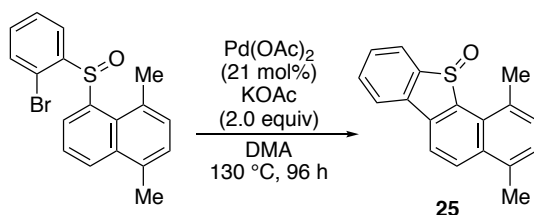
To a solution of 5-((2-bromophenyl)thio)-1,4-dimethyl-1,4-dihydro-1,4-epoxynaphthalene (105 mg, 0.292 mmol) and sodium iodide (131 mg, 0.874 mmol, 3.00 equiv) dissolved in MeCN (8.7 mL) and CH₂Cl₂ (1.0 mL) was added chloro(trimethyl)silane (0.110 mL, 0.870 mmol, 3.0 equiv) at 0 °C. After warming to room temperature, the mixture was stirred for 1 h. To this was added water (15 mL) and the mixture was extracted with CH₂Cl₂ (20 mL × 3). The combined organic extract was washed with brine (5 mL), dried (Na₂SO₄), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/CH₂Cl₂/CHCl₃ = 10/1/1) to give 5-((2-bromophenyl)thio)-1,4-dimethylnaphthalene (**24**) (95.4 mg, 0.278 mmol, 95.0%) as a colorless solid.

Oxidation of 5-((2-bromophenyl)thio)-1,4-dimethylnaphthalene (**24**) for the synthesis of 5-((2-bromophenyl)sulfinyl)-1,4-dimethylnaphthalene



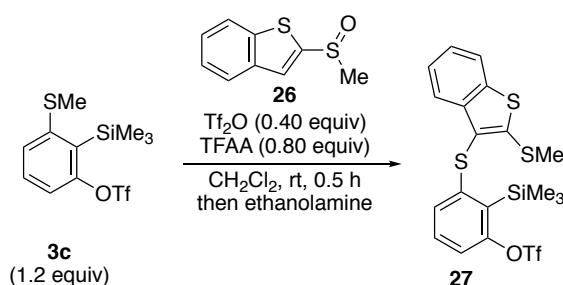
To a solution of 5-((2-bromophenyl)thio)-1,4-dimethylnaphthalene (**24**) (19.4 mg, 56.5 μmol) dissolved in CH₂Cl₂ (0.9 mL) was slowly added *m*-chloroperbenzoic acid (ca. 65%, 15.2 mg, ca. 57 μmol, ca. 1.0 equiv) at 0 °C. After stirring for 1 h at the same temperature, the mixture was allowed to warm to room temperature, and to this was added an aqueous saturated solution of potassium carbonate (5 mL) and an aqueous saturated solution of sodium thiosulfate (5 mL). The mixture was extracted with CH₂Cl₂ (10 mL × 3), and the combined organic extract was washed with brine (5 mL), dried (Na₂SO₄), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 2/1) to give 5-((2-bromophenyl)sulfinyl)-1,4-dimethylnaphthalene (19.5 mg, 54.2 μmol, 95.9%) as a yellow solid.

*Palladium-catalyzed cyclization for the synthesis of 1,4-dimethylbenzo[*b*]naphtho[2,1-*d*]thiophene 11-oxide (**25**)^{S11}*



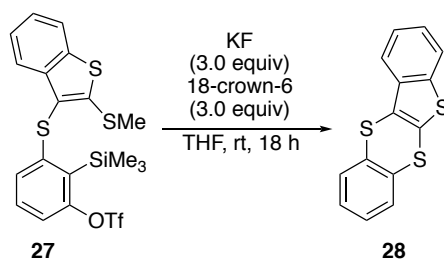
To a solution of 5-((2-bromophenyl)sulfinyl)-1,4-dimethylnaphthalene (21.8 mg, 60.7 μ mol) and potassium acetate (11.9 mg, 0.121 mmol, 2.0 equiv) dissolved in dimethylacetamide (0.60 mL) was added palladium(II) acetate (2.87 mg, 12.8 μ mol, 21 mol %) at 130 °C. After stirring for 96 h at the same temperature, the mixture was allowed to cool to room temperature, and this was filtered through a pad of Celite. The filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (CHCl₃) to give 1,4-dimethylbenzo[*b*]naphtho[2,1-*d*]thiophene 11-oxide (**25**) (10.7 mg, 38.3 μ mol, 63.1%) as a colorless solid.

*Synthesis of 3-((2-(methylthio)benzo[*b*]thiophen-3-yl)thio)-2-(trimethylsilyl)phenyl triflate (**27**)^{S9}*



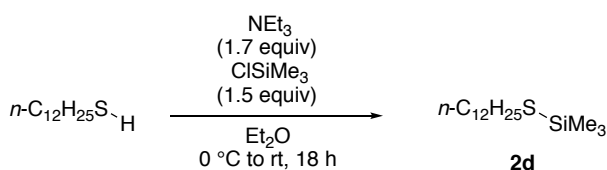
To a solution of 3-(methylthio)-2-(trimethylsilyl)phenyl triflate (**3c**) (83.2 mg, 0.242 mmol, 1.2 equiv) and 2-benzothienyl methyl sulfoxide (**26**) (39.5 mg, 0.201 mmol) dissolved in CH₂Cl₂ (1.0 mL) was added a solution of trifluoromethanesulfonic anhydride (13.1 μ L, 80.0 μ mol, 0.40 equiv) and trifluoroacetic anhydride (22.1 μ L, 160 μ mol, 0.80 equiv) dissolved in CH₂Cl₂ (1.0 mL) at room temperature. After stirring for 30 min at the same temperature, to the mixture was added ethanolamine (60.4 μ L, 1.00 mmol, 5.0 equiv). After stirring for 3 h at the same temperature, the resulting mixture was filtered through a pad of Celite. The filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane) to give 3-((2-(methylthio)benzo[*b*]thiophen-3-yl)thio)-2-(trimethylsilyl)phenyl triflate (**27**) (35.1 mg, 69.0 μ mol, 34.3%) as a pale yellow oil.

*Synthesis of 1,4-benzodithiino[2,3-*d*]benzo[*b*]thiophene (**28**)*



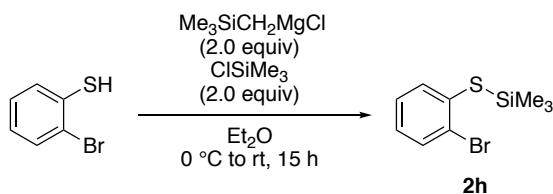
To a solution of 3-((2-(methylthio)benzo[*b*]thiophen-3-yl)thio)-2-(trimethylsilyl)phenyl triflate (**27**) (59.4 mg, 0.117 mmol) dissolved in THF (1.5 mL) were added potassium fluoride (20.4 mg, 0.351 mmol, 3.0 equiv) and 18-crown-6-ether (92.8 mg, 0.351 mmol, 3.0 equiv) at room temperature. After stirring for 18 h at the same temperature, to the mixture was added water (30 mL). The mixture was extracted with EtOAc (10 mL \times 3), and the combined organic extract was washed with brine (5 mL), dried (Na₂SO₄), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane) to give 1,4-benzodithiino[2,3-*d*]benzo[*b*]thiophene (**28**) (22.1 mg, 81.3 μ mol, 69.5%) as a colorless solid.

*A typical procedure for the preparation of dodecyl silyl sulfides **2d–f***



To a solution of 1-dodecanethiol (10.7 mL, 45.0 mmol) and triethylamine (10.6 mL, 76.5 mmol, 1.7 equiv) dissolved in Et₂O (180 mL) was added chlorotrimethylsilane (8.52 mL, 67.5 mmol, 1.5 equiv) at 0 °C. The mixture was allowed to warm to room temperature and stirred for 18 h. The resulting mixture was filtered through a pad of Celite and the filtrate was concentrated under reduced pressure to give dodecyl trimethylsilyl sulfide (**2d**) (12.2 g, 44.4 mmol, 98.7%) as a colorless oil, which was used for the silylthiolation of 3-(triflyloxy)arynes without further purification.

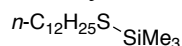
Preparation of 2-bromophenyl trimethylsilyl sulfide (2h)



To a solution of 2-bromobenzenethiol (294 μL , 2.50 mmol) dissolved in Et_2O (25 mL) was slowly added (trimethylsilyl)methylmagnesium chloride (1.56 M, Et_2O solution, 3.21 mL, 5.00 mmol, 2.0 equiv) at $0\text{ }^\circ\text{C}$. After stirring for 15 min at the same temperature, to this was slowly added chlorotrimethylsilane (632 μL , 5.00 mmol, 2.0 equiv) at $0\text{ }^\circ\text{C}$. The mixture was allowed to warm to room temperature and stirred for 15 h. The resulting mixture was filtered through a pad of Celite and the filtrate was concentrated under reduced pressure to give 2-bromophenyl trimethylsilyl sulfide (**2h**) that contained remaining 2-bromobenzenethiol (623 mg; **2h**:thiol = 81:19 as judged from ^1H NMR analysis; 2.04 mmol of **2h**, 81.6%) as a brown oil, which was used for the silylthiolation of 3-(triflyloxy)arynes without further purification.

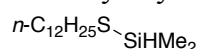
Characterization Data of New Compounds

Dodecyl trimethylsilyl sulfide (**2d**)



Colorless oil; ^1H NMR (CDCl_3 , 500 MHz) δ 0.31 (s, 9H, SiCH_3), 0.88 (t, 3H, $J = 7.1$ Hz, CH_3), 1.19–1.33 (br, 16H, aliphatic), 1.34–1.42 (br, 2H, aliphatic), 1.59 (tt, 2H, $J = 7.4$, 7.4 Hz, aliphatic), 2.48 (t, 2H, $J = 7.4$ Hz, SCH_2); ^{13}C NMR (CDCl_3 , 126 MHz) δ 0.9 (3C), 14.1 (1C), 22.7 (1C), 26.4 (1C), 28.8 (1C), 29.2 (1C), 29.3 (1C), 29.5 (1C), 29.58 (1C), 29.61 (1C), 29.64 (1C), 31.9 (1C), 33.1 (1C); IR (KBr, cm^{-1}) 633, 750, 841, 1248, 1466, 2853, 2924, 2953. Neither the elemental analysis nor HRMS analysis was conducted due to the instability of **2d**.

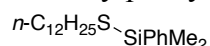
Dimethylsilyl dodecyl sulfide (**2e**)



According to the procedure for preparation of silyl sulfide **2d** using chlorodimethylsilane instead of chloro(trimethyl)silane, almost pure sulfide **2e** was obtained and used without further purification.

Yield: 50% (3.47 g, 10.0 mmol); Pale purple oil; ^1H NMR (CDCl_3 , 500 MHz) δ 0.37 (d, 6H, $J = 3.5$ Hz, SiCH_3), 0.88 (t, 3H, $J = 7.1$ Hz, CH_3), 1.19–1.32 (m, 16H, aliphatic), 1.33–1.41 (m, 2H, aliphatic), 1.61 (tt, 2H, $J = 7.4$, 7.4 Hz, aliphatic), 2.53 (t, 2H, $J = 7.4$ Hz, SCH_2), 4.61 (sept, 1H, $J = 3.5$, 3.5 Hz, SiH); ^{13}C NMR (CDCl_3 , 126 MHz) δ -1.3 (2C), 14.3 (1C), 22.9 (1C), 27.8 (1C), 29.0 (1C), 29.4 (1C), 29.6 (1C), 29.75 (1C), 29.82 (1C), 29.85 (1C), 29.9 (1C), 32.1 (1C), 33.1 (1C); IR (KBr, cm^{-1}) 764, 837, 870, 895, 1248, 1466, 2122, 2853, 2922, 2953. Neither the elemental analysis nor HRMS analysis was conducted due to the instability of **2e**.

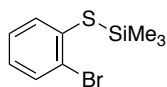
Dimethylphenylsilyl dodecyl sulfide (**2f**)



According to the procedure for preparation of silyl sulfide **2d** using chlorodimethylphenylsilane instead of chloro(trimethyl)silane, a mixture of **2f** and 1,1-dimethyl-1-phenyl-silanol 2.05 g (72:28 as judged from ^1H NMR analysis) was obtained and used without further purification.

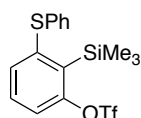
Yield: 85% (4.25 mmol); Colorless oil; ^1H NMR (CDCl_3 , 500 MHz) δ 0.56 (s, 6H, SiCH_3), 0.88 (t, 3H, $J = 7.2$ Hz, CH_3), 1.15–1.34 (m, 18H, aliphatic), 1.50 (tt, 2H, $J = 7.4$, 7.4 Hz, aliphatic), 2.39 (t, 2H, $J = 7.4$ Hz, SCH_2), 7.36–7.41 (m, 3H, aromatic), 7.61–7.65 (AA'BB'C, 2H, aromatic); ^{13}C NMR (CDCl_3 , 126 MHz) δ -0.2 (2C), 14.3 (1C), 22.88 (1C), 22.91 (1C), 27.1 (1C), 28.9 (1C), 29.3 (1C), 29.6 (1C), 29.7 (1C), 29.80 (1C), 29.85 (1C), 32.1 (1C), 32.9 (1C), 128.1 (2C), 129.9 (1C), 134.0 (2C), 137.3 (1C); IR (KBr, cm^{-1}) 700, 808, 833, 1065, 1111, 1252, 1427, 2853, 2924, 2955. Analyzed as a crude mixture. Neither the elemental analysis nor HRMS analysis was conducted due to the instability of **2f**.

2-Bromophenyl trimethylsilyl sulfide (**2h**)



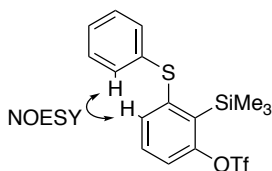
Brown oil; ^1H NMR (CDCl_3 , 500 MHz) δ 0.31 (s, 9H, SiCH_3), 7.09 (ddd, 1H, $J = 7.6, 7.6, 1.7$ Hz, aromatic), 7.20 (ddd, 1H, $J = 7.6, 7.6, 1.7$ Hz, aromatic), 7.53 (dd, 1H, $J = 7.6, 1.7$ Hz, aromatic), 7.62 (dd, 1H, $J = 7.6, 1.7$ Hz, aromatic); ^{13}C NMR (CDCl_3 , 126 MHz) δ 1.2 (3C), 127.6 (1C), 128.6 (1C), 130.4 (1C), 133.6 (1C+1C, two signals overlapped), 137.2 (1C); IR (KBr, cm^{-1}) 424, 631, 719, 748, 841, 1022, 1250, 1427, 1447, 2955. Analyzed as a crude mixture. Neither the elemental analysis nor HRMS analysis was conducted due to the instability of **2h**.

3-(Phenylthio)-2-(trimethylsilyl)phenyl triflate (**3a**)

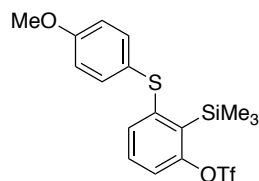


Yield: 79% (321 mg, 0.790 mmol); Colorless oil; TLC R_f 0.38 (*n*-hexane); ^1H NMR (benzene- d_6 , 500 MHz) δ 0.56 (s, 9H, SiCH_3), 6.57 (dd, 1H, $J = 8.1, 8.1$ Hz, aromatic), 6.85–6.89 (AA'BB'C, 1H, aromatic), 6.89–6.94 (AA'BB'C, 2H, aromatic), 6.97 (d, 1H, $J = 8.1$ Hz, aromatic), 7.02 (d, 1H, $J = 8.1$ Hz, aromatic), 7.04–7.08 (AA'BB'C, 2H, aromatic); ^{13}C NMR (benzene- d_6 , 126 MHz) δ 2.8 (3C), 119.7 (q, 1C, $^1J_{\text{C-F}} = 321.2$ Hz), 120.2 (1C), 127.8 (1C), 130.2 (2C), 131.1 (2C), 131.8 (1C), 134.1 (1C), 136.2 (1C), 137.8 (1C), 146.5 (1C), 155.6 (1C); ^{19}F NMR (benzene- d_6 , 376 MHz) δ -73.3 (s); IR (KBr, cm^{-1}) 608, 847, 899, 1140, 1213, 1248, 1422; HRMS (ESI $^+$) m/z 429.0238 ($[\text{M}+\text{Na}]^+$, $\text{C}_{16}\text{H}_{17}\text{F}_3\text{NaO}_3\text{S}_2\text{Si}^+$ requires 429.0233).

The regiochemistry of **3a** was determined by the NOESY experiment.

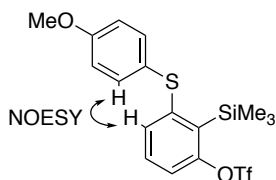


3-(4-Methoxyphenylthio)-2-(trimethylsilyl)phenyl triflate (**3b**)

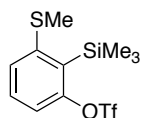


Yield: 69% (299 mg, 0.686 mmol); Colorless oil; TLC R_f 0.39 (n -hexane/EtOAc = 20/1); ^1H NMR (CDCl_3 , 500 MHz) δ 0.57 (s, 9H, SiCH_3), 3.83 (s, 3H, OCH_3), 6.89–6.96 (AA'BB', 2H, aromatic), 7.03 (d, 1H, $J = 8.1$ Hz, aromatic), 7.13 (d, 1H, $J = 8.1$ Hz, aromatic), 7.20 (dd, 1H, $J = 8.1, 8.1$ Hz, aromatic), 7.31–7.37 (AA'BB', 2H, aromatic); ^{13}C NMR (CDCl_3 , 126 MHz) δ 2.1 (3C), 55.3 (1C), 115.2 (2C), 117.7 (1C), 118.6 (q, 1C, $^1J_{\text{C-F}} = 321.0$ Hz), 125.3 (1C), 129.8 (1C), 130.6 (1C), 132.3 (1C), 134.8 (2C), 148.7 (1C), 154.7 (1C), 159.9 (1C); ^{19}F NMR (CDCl_3 , 376 MHz) δ -73.0 (s); IR (KBr, cm^{-1}) 829, 847, 903, 1140, 1155, 1211, 1248, 1422, 1493; HRMS (ESI^+) m/z 459.0352 ($[\text{M}+\text{Na}]^+$, $\text{C}_{17}\text{H}_{19}\text{F}_3\text{NaO}_4\text{S}_2\text{Si}^+$ requires 459.0338).

The regiochemistry of **3b** was determined by the NOESY experiment.

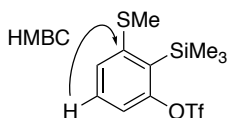


3-(Methylthio)-2-(trimethylsilyl)phenyl triflate (**3c**)



Yield: 58% (182 mg, 0.583 mmol); Brown oil; TLC R_f 0.27 (n -hexane/EtOAc = 20/1); ^1H NMR (CDCl_3 , 500 MHz) δ 0.50 (s, 9H, SiCH_3), 2.50 (s, 3H, SCH_3), 7.13 (d, 1H, $J = 8.1$ Hz, aromatic), 7.30 (d, 1H, $J = 8.1$ Hz, aromatic), 7.35 (dd, 1H, $J = 8.1, 8.1$ Hz, aromatic); ^{13}C NMR (CDCl_3 , 126 MHz) δ 2.0 (3C), 18.5 (1C), 117.4 (1C), 118.6 (q, 1C, $^1J_{\text{C-F}} = 320.9$ Hz), 127.3 (1C), 130.7 (1C), 132.3 (1C), 148.6 (1C), 154.5 (1C); ^{19}F NMR (CDCl_3 , 376 MHz) δ -73.0 (s); IR (KBr, cm^{-1}) 608, 845, 905, 1140, 1155, 1211, 1248, 1422; HRMS (ESI^+) m/z 367.0067 ($[\text{M}+\text{Na}]^+$, $\text{C}_{11}\text{H}_{15}\text{F}_3\text{NaO}_3\text{S}_2\text{Si}^+$ requires 367.0076).

The regiochemistry of **3c** was determined by the HMBC experiment.

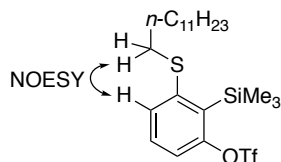


3-(Dodecylthio)-2-(trimethylsilyl)phenyl triflate (**3d**)

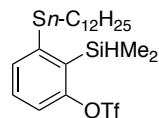


Yield: 66% (328 mg, 0.657 mmol from 1.00 mmol of **1a**), 62% (3.08 g, 6.17 mmol from 10.0 mmol of **1a**); Colorless oil; TLC R_f 0.38 (*n*-hexane); ^1H NMR (CDCl_3 , 500 MHz) δ 0.49 (s, 9H, SiCH_3), 0.88 (t, 3H, $J = 7.1$ Hz, CH_3), 1.21–1.35 (m, 16H, aliphatic), 1.41 (tt, 2H, $J = 7.6$, 7.6 Hz, aliphatic), 1.66 (tt, 2H, $J = 7.6$, 7.6 Hz, aliphatic), 2.93 (t, 2H, $J = 7.6$ Hz, SCH_2), 7.13 (dd, 1H, $J = 7.8$, 1.3 Hz, aromatic), 7.32 (dd, 1H, $J = 7.8$, 7.8 Hz, aromatic), 7.35 (dd, 1H, $J = 7.8$, 1.3 Hz, aromatic); ^{13}C NMR (CDCl_3 , 126 MHz) δ 2.4 (3C), 14.3 (1C), 22.9 (1C), 29.1 (1C), 29.2 (1C), 29.4 (1C), 29.6 (1C), 29.7 (1C), 29.79 (1C), 29.85 (1C+1C, two signals overlapped), 32.1 (1C), 36.3 (1C), 117.9 (1C), 118.8 (q, 1C, $^1J_{\text{C-F}} = 321.0$ Hz), 129.3 (1C), 130.7 (1C), 133.7 (1C), 147.9 (1C), 154.8 (1C); ^{19}F NMR (CDCl_3 , 376 MHz) δ -72.7 (s); IR (KBr, cm^{-1}) 608, 847, 903, 1142, 1211, 1248, 1422, 2853, 2926, 2953; Anal. calcd. for $\text{C}_{22}\text{H}_{37}\text{F}_3\text{O}_3\text{S}_2\text{Si}$: C, 52.98; H, 7.48; N, 0.00%; Found: C, 52.77; H, 7.32; N, 0.00%.

The regiochemistry of **3d** was determined by the NOESY experiment.

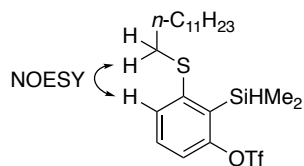


2-(Dimethylsilyl)-3-(dodecylthio)phenyl triflate (**3e**)

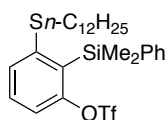


Yield: 57% (278 mg, 0.573 mmol); Colorless oil; TLC R_f 0.29 (*n*-hexane); ^1H NMR (CDCl_3 , 500 MHz) δ 0.51 (d, 6H, $J = 3.9$ Hz, SiCH_3), 0.88 (t, 3H, $J = 7.1$ Hz, CH_3), 1.18–1.34 (m, 16H, aliphatic), 1.42 (tt, 2H, $J = 7.5$, 7.5 Hz, aliphatic), 1.67 (tt, 2H, $J = 7.5$, 7.5 Hz, aliphatic), 2.94 (t, 2H, $J = 7.5$, 7.5 Hz, SCH_2), 4.79 (sept, 1H, $J = 3.9$ Hz, SiH), 7.08 (dd, 1H, $J = 7.2$, 1.9 Hz, aromatic), 7.32–7.38 (m, 2H, aromatic); ^{13}C NMR (CDCl_3 , 126 MHz) δ -2.9 (2C), 14.3 (1C), 22.9 (1C), 29.1 (1C), 29.2 (1C), 29.4 (1C), 29.6 (1C), 29.7 (1C), 29.8 (1C), 29.9 (1C+1C, two signals overlapped), 32.1 (1C), 35.8 (1C), 118.3 (1C), 118.8 (q, 1C, $^1J_{\text{C-F}} = 320.8$ Hz), 128.8 (1C), 131.3 (1C), 132.4 (1C), 147.7 (1C), 154.6 (1C); ^{19}F NMR (CDCl_3 , 376 MHz) δ -72.9 (s); IR (KBr, cm^{-1}) 606, 883, 908, 1142, 1211, 1248, 1422, 2853, 2924; Anal. calcd. for $\text{C}_{21}\text{H}_{35}\text{F}_3\text{O}_3\text{S}_2\text{Si}$: C, 52.04; H, 7.28; N, 0.00%; Found: C, 51.93; H, 7.40; N, 0.00%.

The regiochemistry of **3e** was determined by the HMBC experiment.

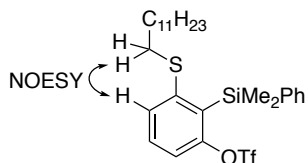


2-(Dimethylphenylsilyl)-3-(dodecylthio)phenyl triflate (**3f**)

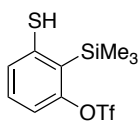


Yield: 64% (357 mg, 0.637 mmol); Colorless oil; TLC R_f 0.22 (*n*-hexane); ^1H NMR (CDCl_3 , 500 MHz) δ 0.73 (s, 6H, SiCH_3), 0.89 (t, 3H, $J = 7.1$ Hz, CH_3), 1.09–1.37 (m, 20H, aliphatic), 2.54 (t, 2H, $J = 7.7$ Hz, CH_2), 7.21 (dd, 1H, $J = 7.0, 2.3$ Hz, aromatic), 7.27–7.33 (m, 3H, aromatic), 7.34–7.40 (m, 2H, aromatic), 7.44–7.48 (AA'BB'C, 2H, aromatic); ^{13}C NMR (CDCl_3 , 126 MHz) δ 1.6 (2C), 14.3 (1C), 22.9 (1C), 28.9 (1C), 29.1 (1C), 29.3 (1C), 29.57 (1C), 29.64 (1C), 29.77 (1C), 29.85 (1C+1C, two signals overlapped), 32.1 (1C), 36.7 (1C), 118.4 (1C), 118.8 (q, 1C, $^1J_{\text{C-F}} = 321.0$ Hz), 127.8 (2C), 128.9 (1C), 130.9 (1C), 131.3 (1C), 132.7 (1C), 133.7 (2C), 139.9 (1C), 148.3 (1C), 155.3 (1C); ^{19}F NMR (CDCl_3 , 376 MHz) δ -73.0 (s); IR (KBr, cm^{-1}) 610, 820, 903, 1140, 1211, 1248, 1422, 2853, 2924; Anal. calcd. for $\text{C}_{27}\text{H}_{39}\text{F}_3\text{O}_3\text{S}_2\text{Si}$: C, 57.83; H, 7.01; N, 0.00%; Found: C, 57.78; H, 6.91; N, 0.00%.

The regiochemistry of **3f** was determined by the NOESY experiment.

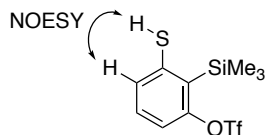


3-Mercapto-2-(trimethylsilyl)phenyl triflate (**3g**)

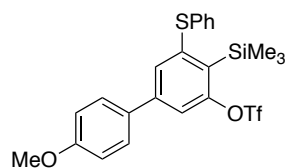


Yield: 59% (196 mg, 0.594 mmol); Colorless oil; TLC R_f 0.46 (*n*-hexane/EtOAc = 99/1); ^1H NMR (CDCl_3 , 500 MHz) δ 0.51 (s, 9H, SiCH_3), 3.70 (s, 1H, SH), 7.13 (d, 1H, $J = 8.2$ Hz, aromatic), 7.22 (dd, 1H, $J = 8.2, 8.2$ Hz, aromatic), 7.26 (d, 1H, $J = 8.2$ Hz, aromatic); ^{13}C NMR (CDCl_3 , 126 MHz) δ 1.8 (3C), 117.8 (1C), 118.8 (q, 1C, $^1J_{\text{C-F}} = 320.7$ Hz), 130.8 (1C), 131.5 (1C), 131.7 (1C), 141.4 (1C), 155.3 (1C); ^{19}F NMR (CDCl_3 , 376 MHz) δ -73.1 (s); IR (KBr, cm^{-1}) 608, 710, 758, 783, 797, 847, 903, 1105, 1140, 1155; Anal. calcd. for $\text{C}_{10}\text{H}_{13}\text{F}_3\text{O}_3\text{S}_2\text{Si}$: C, 36.35; H, 3.97; N, 0.00%; Found: C, 36.51; H, 4.16; N, 0.00%.

The regiochemistry of **3g** was determined by the NOESY experiment.

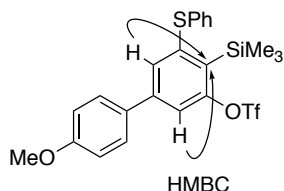


5-(4-Methoxyphenyl)-3-(phenylthio)-2-(trimethylsilyl)phenyl triflate (**3h**)

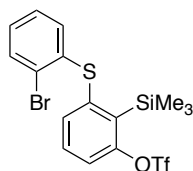


Yield: 78% (321 mg, 0.626 mmol); Colorless oil; TLC R_f 0.30 (n -hexane/EtOAc = 20/1); ^1H NMR (CDCl_3 , 500 MHz) δ 0.52 (s, 9H, SiCH_3), 3.81 (s, 3H, OCH_3), 6.88–6.97 (AA'BB', 2H, aromatic), 7.20–7.28 (m, 3H, aromatic), 7.28–7.38 (m, 4H, aromatic), 7.40 (s, 1H, aromatic), 7.47 (s, 1H, aromatic); ^{13}C NMR (CDCl_3 , 126 MHz) δ 2.4 (3C), 55.6 (1C), 114.7 (2C), 117.7 (1C), 118.9 (q, 1C, $^1J_{\text{C-F}} = 321.0$ Hz), 127.2 (1C), 128.2 (2C), 129.6 (2C), 130.1 (2C), 130.7 (1C), 131.6 (1C), 133.1 (1C), 137.3 (1C), 144.1 (1C), 145.6 (1C), 155.4 (1C), 160.3 (1C); ^{19}F NMR (CDCl_3 , 376 MHz) δ -72.7 (s); IR (KBr, cm^{-1}) 610, 829, 847, 920, 1140, 1180, 1211, 1250, 1416, 1514; HRMS (ESI $^+$) m/z 535.0633 ($[\text{M}+\text{Na}]^+$, $\text{C}_{23}\text{H}_{23}\text{F}_3\text{NaO}_4\text{S}_2\text{Si}^+$ requires 535.0651).

The regiochemistry of **3h** was determined by the HMBC experiment.

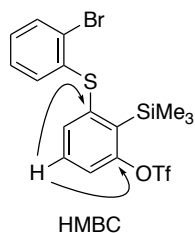


3-(2-Bromophenylthio)-2-(trimethylsilyl)phenyl triflate (**3i**)

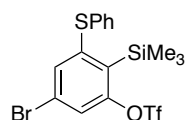


Yield: 70% (340 mg, 0.700 mmol); Colorless oil; TLC R_f 0.25 (n -hexane/EtOAc = 20/1); ^1H NMR (CDCl_3 , 500 MHz) δ 0.46 (s, 9H, SiCH_3), 6.74 (d, 1H, $J = 7.8$ Hz, aromatic), 7.05 (dd, 1H, $J = 7.8, 7.8$ Hz, aromatic), 7.17 (dd, 1H, $J = 7.8, 7.8$ Hz, aromatic), 7.32–7.36 (m, 2H, aromatic), 7.39 (dd, 1H, $J = 7.8, 7.8$ Hz, aromatic), 7.57 (d, 1H, $J = 7.8$ Hz, aromatic); ^{13}C NMR (CDCl_3 , 126 MHz) δ 2.3 (3C), 118.8 (q, 1C, $^1J_{\text{C-F}} = 320.9$ Hz), 120.7 (1C), 123.1 (1C), 127.8 (1C), 128.3 (1C), 129.8 (1C), 131.6 (1C), 133.4 (1C), 135.3 (1C), 137.6 (1C), 139.3 (1C), 143.1 (1C), 155.3 (1C); ^{19}F NMR (CDCl_3 , 376 MHz) δ -72.9 (s); IR (KBr, cm^{-1}) 608, 746, 847, 901, 1140, 1211, 1250, 1422, 1447; Anal. calcd. for $\text{C}_{16}\text{H}_{16}\text{BrF}_3\text{O}_3\text{S}_2\text{Si}$: C, 39.59; H, 3.32; N, 0.00%; Found: C, 39.87; H, 3.30; N, 0.00%.

The regiochemistry of **3i** was determined by the HMBC experiment.

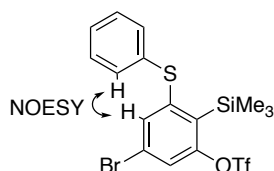


5-Bromo-3-(phenylthio)-2-(trimethylsilyl)phenyl triflate (**3j**)

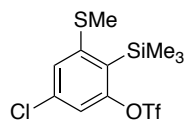


Yield: 58% (279 mg, 0.575 mmol); Brown oil; TLC R_f 0.67 (*n*-hexane); ^1H NMR (benzene- d_6 , 500 MHz) δ 0.53 (s, 9H, SiCH₃), 6.77–6.88 (m, 3H, aromatic), 6.99–7.04 (AA'BB'C, 2H, aromatic), 7.24 (d, 1H, J = 1.6 Hz, aromatic), 7.31 (d, 1H, J = 1.6 Hz, aromatic); ^{13}C NMR (CDCl₃, 126 MHz) δ 2.2 (3C), 118.8 (q, 1C, $^1J_{\text{C-F}}$ = 321.1 Hz), 122.2 (1C), 124.2 (1C), 128.3 (1C), 130.0 (2C), 131.7 (2C), 133.3 (1C), 134.4 (1C), 135.2 (1C), 148.3 (1C), 154.4 (1C); ^{19}F NMR (benzene- d_6 , 376 MHz) δ -73.2 (s); IR (KBr, cm⁻¹) 608, 800, 849, 914, 1140, 1177, 1213, 1250, 1360, 1427; Anal. calcd. for C₁₆H₁₆BrF₃O₃S₂Si: C, 39.59; H, 3.32; N, 0.00%; Found: C, 39.71; H, 3.46; N, 0.00%.

The regiochemistry of **3j** was determined by the NOESY experiment.

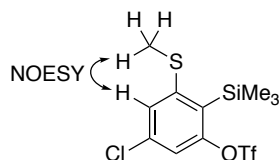


5-Chloro-3-(methylthio)-2-(trimethylsilyl)phenyl triflate (**3k**)

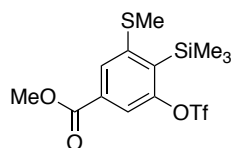


Yield: 53% (39.7 mg, 0.105 mmol); Colorless oil; TLC R_f 0.47 (*n*-hexane); ^1H NMR (CDCl₃, 500 MHz) δ 0.48 (s, 9H, SiCH₃), 2.51 (s, 3H, SCH₃), 7.13 (d, 1H, J = 1.7 Hz, aromatic), 7.21 (d, 1H, J = 1.7 Hz, aromatic); ^{13}C NMR (CDCl₃, 126 MHz) δ 1.9 (3C), 17.9 (1C), 117.4 (1C), 118.5 (q, 1C, $^1J_{\text{C-F}}$ = 320.9 Hz), 125.9 (1C), 130.0 (1C), 136.2 (1C), 150.2 (1C), 154.2 (1C); ^{19}F NMR (CDCl₃, 376 MHz) δ -72.9 (s); IR (KBr, cm⁻¹) 650, 762, 912, 1138, 1217, 1261, 1368, 1422, 1537, 1574; HRMS (ESI⁺) m/z 400.9696 ([M+Na]⁺, C₁₁H₁₄³⁵ClF₃NaO₃S₂Si⁺ requires 400.9686).

The regiochemistry of **3k** was determined by the NOESY experiment.

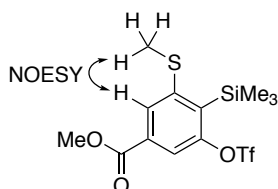


5-(Methoxycarbonyl)-3-(methylthio)-2-(trimethylsilyl)phenyl triflate (**3l**)

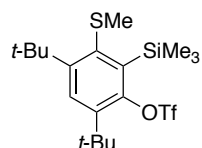


Yield: 23% (18.6 mg, 46.2 μ mol); Colorless oil; TLC R_f 0.19 (*n*-hexane/EtOAc = 50/1); ^1H NMR (CDCl_3 , 500 MHz) δ 0.51 (s, 9H, SiCH_3), 2.56 (s, 3H, SCH_3), 3.94 (s, 3H, OCH_3), 7.71 (d, 1H, $J = 1.3$ Hz, aromatic), 7.90 (d, 1H, $J = 1.3$ Hz, aromatic); ^{13}C NMR (CDCl_3 , 126 MHz) δ 1.8 (3C), 18.1 (1C), 52.7 (1C), 117.9 (1C), 118.5 (q, 1C, $^1J_{\text{C-F}} = 321.0$ Hz), 126.8 (1C), 132.6 (1C), 137.6 (1C), 149.6 (1C), 154.2 (1C), 165.1 (1C); ^{19}F NMR (CDCl_3 , 376 MHz) δ -72.9 (s); IR (KBr, cm^{-1}) 764, 849, 1140, 1213, 1277, 1423, 1730; HRMS (ESI^+) m/z 425.0133 ($[\text{M}+\text{Na}]^+$, $\text{C}_{13}\text{H}_{17}\text{F}_3\text{NaO}_5\text{S}_2\text{Si}^+$ requires 425.0131).

The regiochemistry of **3l** was determined by the NOESY experiment.

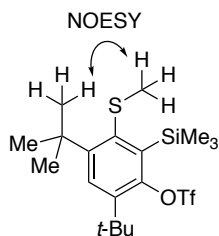


4,6-Di(*tert*-butyl)-3-(methylthio)-2-(trimethylsilyl)phenyl triflate (**3m**)

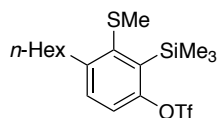


Yield: 52% (47.1 mg, 0.103 mmol); Colorless solid; Mp 98–99 $^{\circ}\text{C}$; TLC R_f 0.63 (*n*-hexane); ^1H NMR (CDCl_3 , 500 MHz) δ 0.41 (s, 9H, SiCH_3), 1.40 (s, 9H, CH_3), 1.54 (s, 9H, CH_3), 2.25 (s, 3H, SCH_3), 7.52 (s, 1H, aromatic); ^{13}C NMR (CDCl_3 , 126 MHz) δ 4.0 (3C), 26.9 (1C), 31.1 (3C), 31.2 (3C), 35.9 (1C), 37.3 (1C), 118.4 (q, 1C, $^1J_{\text{C-F}} = 320.1$ Hz), 129.2 (1C), 141.9 (1C), 146.2 (1C), 146.7 (1C), 147.6 (1C), 152.7 (1C); ^{19}F NMR (CDCl_3 , 376 MHz) δ -72.7 (s); IR (KBr, cm^{-1}) 866, 1074, 1140, 1211, 1244, 1396; HRMS (ESI^+) m/z 479.1333 ($[\text{M}+\text{Na}]^+$, $\text{C}_{19}\text{H}_{31}\text{F}_3\text{NaO}_3\text{S}_2\text{Si}^+$ requires 479.1328).

The regiochemistry of **3m** was determined by the NOESY experiment.

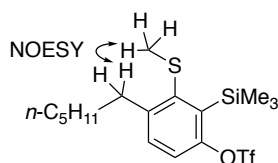


4-(*n*-Hexyl)-3-(methylthio)-2-(trimethylsilyl)phenyl triflate (**3n**)

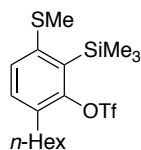


Yield: 57% (41.9 mg, 97.8 μ mol); Colorless oil; TLC R_f 0.41 (*n*-hexane); ^1H NMR (CDCl_3 , 500 MHz) δ 0.49 (s, 9H, SiCH_3), 0.90 (t, 3H, $J = 7.1$ Hz, aliphatic), 1.29–1.36 (m, 4H, aliphatic), 1.36–1.41 (m, 2H, aliphatic), 1.63 (tt, 2H, $J = 8.0, 8.0$ Hz, aliphatic), 2.24 (s, 3H, SCH_3), 2.91 (t, 2H, $J = 8.0$ Hz, aliphatic), 7.21 (d, 1H, $J = 8.6$ Hz, aromatic), 7.31 (d, 1H, $J = 8.6$ Hz, aromatic); ^{13}C NMR (CDCl_3 , 126 MHz) δ 3.0 (3C), 14.1 (1C), 21.9 (1C), 22.6 (1C), 29.4 (1C), 31.4 (1C), 31.7 (1C), 33.7 (1C), 118.6 (q, 1C, $^1J_{\text{C-F}} = 320.9$ Hz), 121.0 (1C), 131.6 (1C), 139.3 (1C), 144.8 (1C), 147.7 (1C), 152.1 (1C); ^{19}F NMR (CDCl_3 , 376 MHz) δ -72.9 (s); IR (KBr, cm^{-1}) 764, 847, 914, 1140, 1215, 1261, 1416; HRMS (ESI^+) m/z 451.1015 ($[\text{M}+\text{Na}]^+$, $\text{C}_{17}\text{H}_{27}\text{F}_3\text{NaO}_3\text{S}_2\text{Si}^+$ requires 451.1015).

The regiochemistry of **3n** was determined by the NOESY experiment.

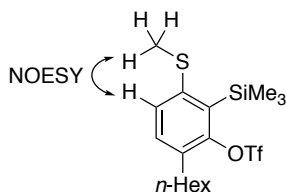


6-(*n*-Hexyl)-3-(methylthio)-2-(trimethylsilyl)phenyl triflate (**3n'**)

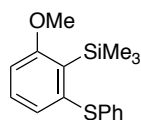


Yield: 18% (13.3 mg, 31.0 μ mol); Colorless oil; TLC R_f 0.37 (*n*-hexane); ^1H NMR (CDCl_3 , 500 MHz) δ 0.48 (s, 9H, SiCH_3), 0.88 (t, 3H, $J = 6.9$ Hz, aliphatic), 1.24–1.37 (m, 6H, aliphatic), 1.53–1.61 (m, 2H, aliphatic), 2.48 (s, 3H, SCH_3), 2.66 (t, 2H, $J = 8.0$ Hz, aliphatic), 7.26 (d, 1H, $J = 8.0$ Hz, aromatic), 7.34 (d, 1H, $J = 8.0$ Hz, aromatic); ^{13}C NMR (CDCl_3 , 126 MHz) δ 2.1 (3C), 14.0 (1C), 19.5 (1C), 22.5 (1C), 29.1 (1C), 29.9 (1C), 30.0 (1C), 31.5 (1C), 118.5 (q, 1C, $^1J_{\text{C-F}} = 320.0$ Hz), 130.0 (1C), 132.0 (1C), 134.3 (1C), 136.0 (1C), 145.2 (1C), 149.2 (1C); ^{19}F NMR (CDCl_3 , 376 MHz) δ -73.7 (s); IR (KBr, cm^{-1}) 764, 872, 1086, 1140, 1215, 1261, 1416; HRMS (ESI^+) m/z 451.1015 ($[\text{M}+\text{Na}]^+$, $\text{C}_{17}\text{H}_{27}\text{F}_3\text{NaO}_3\text{S}_2\text{Si}^+$ requires 451.1015).

The regiochemistry of **3n'** was determined by the NOESY experiment.

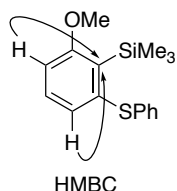


3-Methoxy-2-(trimethylsilyl)phenyl phenyl sulfide (**5**)

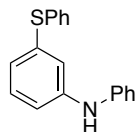


Yield: 37% (27.2 mg, 94.4 μ mol); Colorless oil; TLC R_f 0.39 (*n*-hexane); ^1H NMR (benzene- d_6 , 500 MHz) δ 0.60 (s, 9H, SiCH₃), 3.20 (s, 3H, OCH₃), 6.34 (d, 1H, J = 8.2 Hz, aromatic), 6.84–6.89 (AA'BB'C, 1H, aromatic), 6.90–6.98 (m, 3H, aromatic), 7.08 (d, 1H, J = 8.2 Hz, aromatic), 7.18–7.22 (AA'BB'C, 2H, aromatic); ^{13}C NMR (benzene- d_6 , 126 MHz) δ 3.4 (3C), 55.1 (1C), 100.7 (1C), 110.0 (1C), 126.5 (1C), 129.7 (2C), 129.8 (2C), 131.5 (1C), 131.8 (1C), 139.7 (1C), 143.0 (1C), 165.9 (1C); IR (KBr, cm⁻¹) 689, 737, 785, 849, 1043, 1244, 1422, 1450, 1557, 2953; Anal. calcd. for C₁₆H₂₀OSSi: C, 66.62; H, 6.99; N, 0.00%; Found: C, 66.41; H, 6.83; N, 0.00%.

The regiochemistry of **5** was determined by the HMBC experiment.

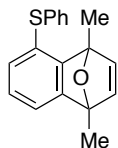


Phenyl 2-(phenylamino)phenyl sulfide (**7**)



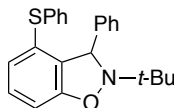
Yield: 80% (44.8 mg, 0.162 mmol); Brown oil; TLC R_f 0.24 (*n*-hexane/EtOAc = 20/1); ^1H NMR (benzene- d_6 , 500 MHz) δ 4.88 (br s, 1H, NH), 6.67–6.71 (AA'BB'C, 1H, aromatic), 6.75–6.82 (m, 3H, aromatic), 6.87–6.99 (m, 6H, aromatic), 7.02–7.07 (AA'BB'C, 2H, aromatic), 7.35–7.40 (AA'BB'C, 2H, aromatic); ^{13}C NMR (benzene- d_6 , 126 MHz) δ 116.1 (1C), 119.1 (2C), 120.2 (1C), 122.0 (1C), 123.4 (1C), 127.6 (1C), 129.8 (2C), 129.9 (2C), 130.5 (1C), 132.1 (2C), 136.7 (1C), 138.0 (1C), 143.1 (1C), 144.9 (1C); IR (KBr, cm⁻¹) 610, 829, 847, 920, 1140, 1180, 1211, 1250, 1416, 1514; HRMS (ESI⁺) m/z 278.0998 ([M+H]⁺, C₁₈H₁₆NS⁺ requires 278.0998).

1,4-Dimethyl-5-(phenylthio)-1,4-dihydro-1,4-epoxynaphthalene (**9**)



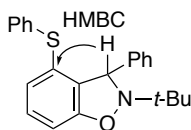
Yield: 90% (51.8 mg, 0.185 mmol); Pale yellow oil; TLC R_f 0.30 (*n*-hexane/EtOAc = 20/1); ^1H NMR (CDCl_3 , 500 MHz) δ 1.89 (s, 3H, CH_3), 2.02 (s, 3H, CH_3), 6.66 (d, 1H, $J = 5.3$ Hz, olefinic), 6.75 (d, 1H, $J = 5.3$ Hz, olefinic), 6.90–6.96 (m, 2H, aromatic), 7.07 (dd, 1H, $J = 6.3$, 1.8 Hz, aromatic), 7.08–7.12 (AA'BB'C, 2H, aromatic), 7.13–7.19 (AA'BB'C, 1H, aromatic), 7.22–7.27 (m, 2H, aromatic); ^{13}C NMR (CDCl_3 , 126 MHz) δ 15.2 (1C), 17.4 (1C), 88.1 (1C), 90.7 (1C), 118.1 (1C), 125.8 (1C), 126.0 (1C), 126.2 (1C), 128.6 (2C), 129.1 (2C), 131.3 (1C), 137.5 (1C), 146.7 (1C), 146.9 (1C), 154.3 (1C), 154.6 (1C); IR (KBr, cm^{-1}) 691, 723, 739, 758, 858, 1134, 1300, 1381, 1439, 1477; HRMS (ESI^+) m/z 303.0812 ($[\text{M}+\text{Na}]^+$, $\text{C}_{18}\text{H}_{16}\text{NaOS}^+$ requires 303.0814).

2-*tert*-Butyl-2,3-dihydro-3-phenyl-4-(phenylthio)-1,2-benzisoxazole (**11**)

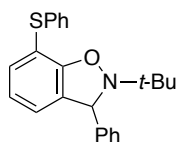


Yield: 86% (mixture of **11** and **11'**, 62.0 mg, 0.172 mmol, **11**:**11'** = 87:13. The yield was determined as a purified mixture of **11** and **11'**. The ratio of regioisomers were determined on the basis ^1H NMR analysis of this mixture. The regioisomers were separated before characterization.); Colorless solid; Mp 133–135 °C; TLC R_f 0.38 (*n*-hexane/EtOAc = 20/1); ^1H NMR (CDCl_3 , 500 MHz) δ 1.10 (s, 9H, CH_3), 5.36 (s, 1H, CH), 6.73 (d, 1H, $J = 7.7$ Hz, aromatic), 6.76 (d, 1H, $J = 7.7$ Hz, aromatic), 7.09–7.16 (m, 3H, aromatic), 7.16–7.28 (m, 8H, aromatic); ^{13}C NMR (CDCl_3 , 126 MHz) δ 25.5 (3C), 61.7 (1C), 66.6 (1C), 106.0 (1C), 124.4 (1C), 127.3 (1C), 127.6 (1C), 128.3 (2C), 128.6 (2C), 129.3 (2C), 129.9 (1C), 130.3 (1C), 131.4 (2C), 131.6 (1C), 134.9 (1C), 142.4 (1C), 158.2 (1C); IR (KBr, cm^{-1}) 692, 743, 930, 1207, 1256, 1364, 1441, 1477, 1578, 2972; Anal. calcd. for $\text{C}_{23}\text{H}_{23}\text{NOS}$: C, 76.42; H, 6.41; N, 3.87%; Found: C, 76.37; H, 6.42; N, 3.85%.

The regiochemistry of **11** was determined by the HMBC experiment.

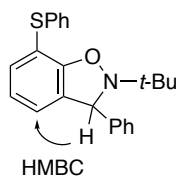


2-*tert*-Butyl-2,3-dihydro-3-phenyl-7-(phenylthio)-1,2-benzisoxazole (**11'**)

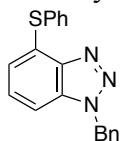


Yellow solid; Mp 62–63 °C; TLC R_f 0.41 (*n*-hexane/EtOAc = 20/1); ^1H NMR (CDCl_3 , 500 MHz) δ 1.01 (s, 9H, CH_3), 5.58 (s, 1H, CH), 6.77 (dd, 1H, $J = 7.6$, 7.6 Hz, aromatic), 6.82–6.86 (AA'BB'C, 1H, aromatic), 7.17–7.37 (m, 9H, aromatic), 7.38–7.42 (AA'BB'C, 2H, aromatic); ^{13}C NMR (CDCl_3 , 126 MHz) δ 25.2 (3C), 61.1 (1C), 67.4 (1C), 113.2 (1C), 121.4 (1C), 123.6 (1C), 126.6 (1C), 127.2 (2C), 127.5 (1C), 128.6 (2C), 128.9 (2C), 130.3 (2C), 130.6 (1C), 133.0 (1C), 135.5 (1C), 143.6 (1C), 156.0 (1C); IR (KBr, cm^{-1}) 698, 727, 741, 1209, 1227, 1364, 1435, 1477, 1582, 2972; HRMS (ESI^+) m/z 384.1386 ($[\text{M}+\text{Na}]^+$, $\text{C}_{23}\text{H}_{23}\text{NNaOS}^+$ requires 384.1393).

The regiochemistry of **11'** was determined by the HMBC experiment.

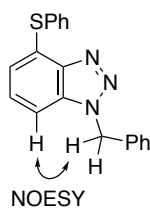


1-Benzyl-4-(phenylthio)-1*H*-benzo[*d*][1,2,3]triazole (**13**)

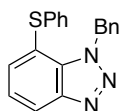


Yield: 90% (mixture of **13** and **13'**, 28.7 mg, 90.4 μmol , **13**:**13'** = 88:12. The yield was determined as a purified mixture of **13** and **13'**. The ratio of regioisomers were determined on the basis ^1H NMR analysis of this mixture. The regioisomers were separated before characterization.); Brown solid; Mp 112–113 °C; TLC R_f 0.22 (*n*-hexane/EtOAc = 5/1); ^1H NMR (CDCl_3 , 500 MHz) δ 5.84 (s, 2H, NCH_2), δ 6.82 (d, 1H, $J = 7.7$ Hz, aromatic), 7.11 (d, 1H, $J = 7.7$ Hz, aromatic), 7.19 (dd, 1H, $J = 7.7$, 7.7 Hz, aromatic), 7.24–7.28 (AA'BB'C, 2H, aromatic), 7.30–7.36 (m, 3H, aromatic), 7.37–7.43 (m, 3H, aromatic), 7.56–7.61 (AA'BB'C, 2H, aromatic); ^{13}C NMR (CDCl_3 , 126 MHz) δ 52.7 (1C), 107.2 (1C), 122.3 (1C), 127.8 (2C), 128.0 (1C), 128.7 (1C), 128.9 (1C), 129.2 (2C), 129.8 (2C), 131.3 (1C), 131.7 (1C), 133.2 (1C), 134.5 (2C), 134.8 (1C), 144.7 (1C); IR (KBr, cm^{-1}) 692, 727, 748, 964, 1094, 1439, 1477, 1489, 2849, 2922; Anal. calcd. for $\text{C}_{19}\text{H}_{15}\text{N}_3\text{S}$: C, 71.90; H, 4.76; N, 13.24%; Found: C, 72.01; H, 4.97; N, 12.96%.

The regiochemistry of **13** was determined by the NOESY experiment.

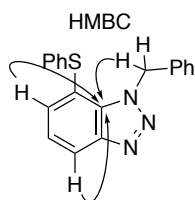


1-Benzyl-7-(phenylthio)-1*H*-benzo[*d*][1,2,3]triazole (**13'**)

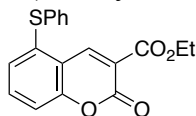


Pale yellow solid; Mp 85–86 °C; TLC R_f 0.36 (*n*-hexane/EtOAc = 5/1); ^1H NMR (CDCl_3 , 500 MHz) δ 6.09 (s, 2H, NCH_2), 6.97–7.01 (AA'BB'C, 2H, aromatic), 7.12–7.24 (m, 8H, aromatic), 7.35 (dd, 1H, $J = 7.8, 7.8$ Hz, aromatic), 7.54 (d, 1H, $J = 7.8$ Hz, aromatic), 8.11 (d, 1H, $J = 7.8$ Hz, aromatic); ^{13}C NMR (CDCl_3 , 126 MHz) δ 52.8 (1C), 115.6 (1C), 121.1 (1C), 124.8 (1C), 126.6 (1C), 127.2 (2C), 127.9 (1C), 128.1 (2C), 128.6 (2C), 129.4 (1C), 130.1 (2C), 133.1 (1C), 135.7 (1C), 136.3 (1C), 147.1 (1C); IR (KBr, cm^{-1}) 691, 723, 745, 1069, 1092, 1244, 1439, 1454, 1477, 2918; HRMS (ESI^+) m/z 340.0870 ($[\text{M}+\text{Na}]^+$, $\text{C}_{19}\text{H}_{15}\text{N}_3\text{NaS}^+$ requires 340.0879).

The regiochemistry of **13'** was determined by the HMBC experiment.

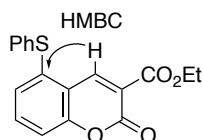


3-(Ethoxycarbonyl)-5-(phenylthio)coumarin (**15**)

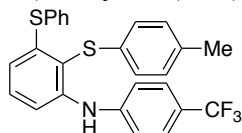


Yield: 78% (51.0 mg, 0.156 mmol); Yellow solid; Mp 127–128 °C; TLC R_f 0.38 (*n*-hexane/EtOAc = 5/1); ^1H NMR (benzene- d_6 , 500 MHz) δ 1.02 (t, 3H, $J = 7.1$ Hz, CH_3), 4.08 (q, 2H, $J = 7.1$ Hz, CH_2), 6.59–6.67 (m, 2H, aromatic), 6.77 (dd, 1H, $J = 6.5, 2.0$ Hz, aromatic), 6.86–6.96 (m, 3H, aromatic), 7.09–7.14 (AA'BB'C, 2H, aromatic), 8.86 (s, 1H, olefinic); ^{13}C NMR (CDCl_3 , 126 MHz) δ 14.4 (1C), 62.2 (1C), 115.9 (1C), 118.1 (1C), 118.4 (1C), 128.0 (1C), 128.5 (1C), 130.0 (2C), 132.1 (2C), 133.6 (1C), 134.2 (1C), 138.3 (1C), 145.7 (1C), 156.2 (1C), 156.6 (1C), 163.1 (1C); IR (KBr, cm^{-1}) 422, 1026, 1192, 1233, 1244, 1287, 1445, 1589, 1607, 1713; Anal. calcd. for $\text{C}_{18}\text{H}_{14}\text{O}_4\text{S}$: C, 66.24; H, 4.32; N, 0.00%; Found: C, 66.28; H, 4.50; N, 0.00%.

The regiochemistry of **15** was determined by the HMBC experiment.

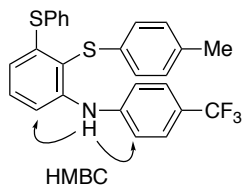


3-(Phenylthio)-2-(4-tolylthio)-*N*-(4-(trifluoromethyl)phenyl)aniline (**17**)

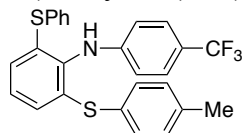


Yield: 58% (mixture of **17** and **17'**, 54.1 mg, 0.116 mmol, **17**:**17'** = 92:8. The yield was determined as a purified mixture of **17** and **17'**. The ratio of regioisomers were determined on the basis ^1H NMR analysis of this mixture. The regioisomers were separated before characterization.); Pale red solid; Mp 92–93 °C; TLC R_f 0.23 (*n*-hexane/toluene = 10/1); ^1H NMR (acetone- d_6 , 500 MHz) δ 2.22 (s, 3H, CH₃), 6.45 (dd, 1H, J = 7.4, 1.8 Hz, aromatic), 7.04–7.07 (AA'BB', 2H, aromatic), 7.07–7.11 (AA'BB', 2H, aromatic), 7.22–7.29 (m, 4H, aromatic), 7.45–7.55 (m, 7H, aromatic), 7.69 (s, 1H, NH); ^{13}C NMR (acetone- d_6 , 126 MHz) δ 20.9 (1C), 115.6 (1C), 118.6 (2C), 118.9 (1C), 121.2 (1C), 122.8 (q, 1C, $^2J_{\text{C-F}}$ = 32.5 Hz), 125.8 (q, 1C, $^1J_{\text{C-F}}$ = 270.3 Hz), 127.3 (q, 2C, $^3J_{\text{C-F}}$ = 3.8 Hz), 127.9 (2C), 129.9 (1C), 130.8 (4C), 131.8 (1C), 132.9 (1C), 133.9 (1C), 135.6 (2C), 136.7 (1C), 146.5 (1C), 147.3 (1C), 149.1 (1C); ^{19}F NMR (acetone- d_6 , 376 MHz) δ –62.3 (s); IR (KBr, cm^{-1}) 1067, 1115, 1161, 1179, 1323, 1143, 1491, 1524, 1566, 1616; Anal. calcd. for C₂₆H₂₀F₃NS₂: C, 66.79; H, 4.31; N, 3.00%; Found: C, 66.77; H, 4.50; N, 2.99%.

The regiochemistry of **17** was determined by the HMBC experiment.

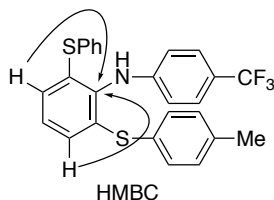


2-(Phenylthio)-6-(4-tolylthio)-*N*-(4-(trifluoromethyl)phenyl)aniline (**17'**)

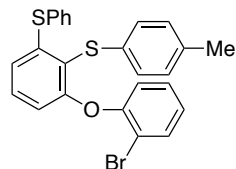


Brown solid; Mp 69–70 °C; TLC R_f 0.15 (*n*-hexane/toluene = 10/1); ^1H NMR (CDCl_3 , 500 MHz) δ 2.34 (s, 3H, CH_3), 5.80 (s, 1H, NH), 6.57–6.62 (AA'BB', 2H, aromatic), 6.90 (dd, 1H, $J = 7.8$, 1.5 Hz, aromatic), 6.95 (dd, 1H, $J = 7.8$, 1.5 Hz, aromatic), 7.01 (dd, 1H, $J = 7.8$, 7.8 Hz, aromatic), 7.10–7.15 (AA'BB', 2H, aromatic), 7.27–7.36 (m, 7H, aromatic), 7.37–7.42 (AA'BB', 2H, aromatic); ^{13}C NMR (CDCl_3 , 126 MHz) δ 21.4 (1C), 114.1 (2C), 121.3 (q, 1C, $^2J_{\text{C-F}} = 32.5$ Hz), 125.0 (q, 1C, $^1J_{\text{C-F}} = 270.7$ Hz), 126.6 (q, 2C, $^3J_{\text{C-F}} = 3.7$ Hz), 127.4 (1C), 128.0 (1C), 128.2 (1C), 128.4 (1C), 129.2 (1C), 129.7 (2C), 130.6 (2C), 133.0 (2C), 133.5 (1C), 133.9 (2C), 135.9 (1C), 137.4 (1C), 138.6 (1C), 138.9 (1C), 147.9 (1C); ^{19}F NMR (CDCl_3 , 376 MHz) δ -61.5 (s); IR (KBr, cm^{-1}) 826, 1065, 1111, 1159, 1182, 1325, 1439, 1522, 1614, 2924, 3371; HRMS (ESI $^+$) m/z 490.0869 ($[\text{M}+\text{Na}]^+$, $\text{C}_{26}\text{H}_{20}\text{F}_3\text{NNaS}_2^+$ requires 490.0881).

The regiochemistry of **17'** was determined by the HMBC experiment.

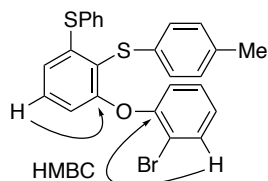


2-Bromophenyl 3-(phenylthio)-2-(4-tolylthio)phenyl ether (**19**)

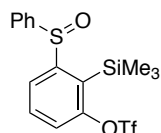


Yield: 41% (40.9 mg, 85.3 μmol); Colorless solid; Mp 116–117 °C; TLC R_f 0.38 (*n*-hexane/toluene = 10/1); ^1H NMR (CDCl_3 , 500 MHz) δ 2.28 (s, 3H, CH_3), 6.50 (d, 1H, $J = 8.1$ Hz, aromatic), 6.54 (d, 1H, $J = 8.1$ Hz, aromatic), 6.72 (dd, 1H, $J = 8.1$, 1.4 Hz, aromatic), 6.97 (ddd, 1H, $J = 8.1$, 8.1, 1.4 Hz, aromatic), 7.00–7.04 (AA'BB', 2H, aromatic), 7.06 (dd, 1H, $J = 8.1$, 8.1 Hz, aromatic), 7.17 (ddd, 1H, $J = 8.1$, 8.1, 1.4 Hz, aromatic), 7.22–7.27 (AA'BB', 2H, aromatic), 7.38–7.43 (m, 3H, aromatic), 7.51–7.55 (AA'BB'C, 2H, aromatic), 7.57 (dd, 1H, $J = 8.1$, 1.4 Hz, aromatic); ^{13}C NMR (CDCl_3 , 126 MHz) δ 21.2 (1C), 114.7 (1C), 115.0 (1C), 120.5 (1C), 121.2 (1C), 122.2 (1C), 125.3 (1C), 128.8 (1C), 129.1 (2C), 129.2 (1C), 129.8 (2C), 129.9 (2C), 130.6 (1C), 132.7 (1C), 133.0 (1C), 133.9 (1C), 135.4 (2C), 136.1 (1C), 149.0 (1C), 153.5 (1C), 158.6 (1C); IR (KBr, cm^{-1}) 403, 419, 750, 916, 1244, 1437, 1470, 1558; Anal. calcd. for $\text{C}_{25}\text{H}_{19}\text{BrOS}_2$: C, 62.63; H, 3.99; N, 0.00%; Found: C, 62.69; H, 3.98; N, 0.00%.

The regiochemistry of **19** was determined by the HMBC experiment.

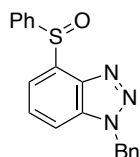


3-(Phenylsulfinyl)-2-(trimethylsilyl)phenyl triflate (**20**)



Yield: 96% (60.7 mg, 0.144 mmol); Colorless oil; TLC R_f 0.30 (*n*-hexane/EtOAc = 4/1); ^1H NMR (CDCl_3 , 500 MHz) δ 0.58 (s, 9H, SiCH_3), 7.41–7.50 (m, 6H, aromatic), 7.55 (dd, 1H, $J = 8.0, 8.0$ Hz, aromatic), 7.80 (dd, 1H, $J = 8.0, 1.0$ Hz, aromatic); ^{13}C NMR (CDCl_3 , 126 MHz) δ 3.0 (3C), 118.7 (q, 1C, $^1J_{\text{C-F}} = 320.9$ Hz), 123.3 (1C), 125.2 (2C), 126.9 (1C), 129.6 (2C), 130.9 (1C), 132.6 (1C), 133.7 (1C), 145.3 (1C), 154.1 (1C), 155.4 (1C); ^{19}F NMR (CDCl_3 , 376 MHz) δ -73.1 (s); IR (KBr, cm^{-1}) 752, 845, 899, 1053, 1099, 1125, 1140, 1215, 1250, 1423; Anal. calcd. for $\text{C}_{16}\text{H}_{17}\text{F}_3\text{O}_4\text{S}_2\text{Si}$: C, 45.48; H, 4.06; N, 0.00%; Found: C, 45.65; H, 4.05; N, 0.00%.

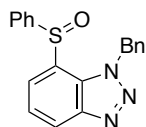
1-Benzyl-4-(phenylsulfinyl)-1*H*-benzo[*d*][1,2,3]triazole (**21**)



Yield: 51% (mixture of **21** and **21'**, 17.1 mg, 51.3 μmol , **21**:**21'** = 95:5. The yield was determined as a purified mixture of **21** and **21'**. The ratio of regioisomers were determined on the basis ^1H NMR analysis of this mixture. The regioisomers were separated before characterization.); Pale yellow oil; TLC R_f 0.30 (*n*-hexane/EtOAc = 3/2); ^1H NMR (CDCl_3 , 500 MHz) δ 5.79 (d, 1H, $J = 15.5$ Hz, CH), 5.85 (d, 1H, $J = 15.5$ Hz, CH), 7.24–7.29 (AA'BB'C, 2H, aromatic), 7.30–7.36 (m, 3H, aromatic), 7.37–7.45 (m, 4H, aromatic), 7.54 (dd, 1H, $J = 7.3, 7.3$ Hz, aromatic), 7.97 (d, 1H, $J = 7.3$ Hz, aromatic), 7.98–8.02 (AA'BB'C, 2H, aromatic); ^{13}C NMR (CDCl_3 , 126 MHz) δ 52.9 (1C), 112.4 (1C), 119.0 (1C), 125.2 (2C), 127.9 (1C), 128.0 (2C), 129.0 (1C), 129.3 (2C), 129.4 (2C), 131.4 (1C), 133.5 (1C), 134.2 (1C), 137.3 (1C), 141.8 (1C), 144.8 (1C); IR (KBr, cm^{-1}) 696, 727, 750, 1036, 1053, 1069, 1082, 1240, 1443, 2359; HRMS (ESI $^+$) m/z 356.0826 ($[\text{M}+\text{Na}]^+$, $\text{C}_{19}\text{H}_{15}\text{N}_3\text{NaOS}^+$ requires 356.0828).

The regiochemistry of **21** was determined by preparing the authentic sample by oxidation of 1-benzyl-4-(phenylthio)-1*H*-benzo[*d*][1,2,3]triazole (**13**).

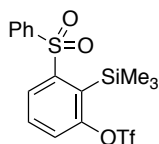
1-Benzyl-7-(phenylsulfinyl)-1*H*-benzo[*d*][1,2,3]triazole (**21'**)



Colorless solid; Mp 108–109 °C; TLC R_f 0.20 (*n*-hexane/EtOAc = 2/1); ^1H NMR (acetone- d_6 , 500 MHz) δ 6.22 (d, 1H, J = 16.2 Hz, CH), 6.33 (d, 1H, J = 16.2 Hz, CH), 7.07–7.12 (AA'BB'C, 2H, aromatic), 7.28–7.33 (m, 3H, aromatic), 7.35–7.47 (m, 5H, aromatic), 7.62 (dd, 1H, J = 8.3, 7.4 Hz, aromatic), 7.97 (dd, 1H, J = 7.4, 0.9 Hz, aromatic), 8.28 (dd, 1H, J = 8.3, 0.9 Hz, aromatic); ^{13}C NMR (acetone- d_6 , 126 MHz) δ 55.0 (1C), 124.6 (1C), 125.4 (1C), 126.0 (2C), 127.8 (1C), 127.9 (2C), 128.9 (1C), 129.8 (2C), 130.5 (2C), 130.7 (1C), 131.0 (1C), 132.1 (1C), 137.3 (1C), 145.9 (1C), 148.4 (1C); IR (KBr, cm^{-1}) 694, 727, 746, 800, 1043, 1082, 1244, 1418, 1443; HRMS (ESI $^+$) m/z 356.0818 ([M+Na] $^+$, $\text{C}_{19}\text{H}_{15}\text{N}_3\text{NaOS}^+$ requires 356.0828).

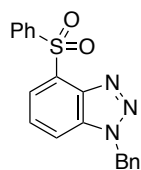
The regiochemistry of **21'** was determined by preparing the authentic sample by oxidation of 1-benzyl-7-(phenylthio)-1*H*-benzo[*d*][1,2,3]triazole (**13'**).

3-(Phenylsulfonyl)-2-(trimethylsilyl)phenyl triflate (**22**)



Yield: 76% (525 mg, 1.20 mmol); Colorless oil; TLC R_f 0.31 (*n*-hexane/EtOAc = 5/1); ^1H NMR (CDCl_3 , 500 MHz) δ 0.58 (s, 9H, SiCH_3), 7.38–7.45 (m, 3H, aromatic), 7.53–7.58 (AA'BB'C, 2H, aromatic), 7.62–7.67 (AA'BB'C, 1H, aromatic), 7.83–7.87 (AA'BB'C, 2H, aromatic); ^{13}C NMR (CDCl_3 , 126 MHz) δ 3.2 (3C), 118.7 (q, 1C, $^1J_{\text{C-F}}$ = 320.6 Hz), 124.8 (1C), 128.2 (2C), 129.4 (1C), 129.5 (2C), 131.0 (1C), 133.9 (1C), 134.9 (1C), 141.3 (1C), 150.0 (1C), 155.1 (1C); ^{19}F NMR (CDCl_3 , 376 MHz) δ -73.5 (s); IR (KBr, cm^{-1}) 584, 793, 849, 1105, 1138, 1150, 1215, 1250, 1410, 1427; HRMS (ESI $^+$) m/z 461.0129 ([M+Na] $^+$, $\text{C}_{16}\text{H}_{17}\text{F}_3\text{NaO}_5\text{S}_2\text{Si}^+$ requires 461.0131).

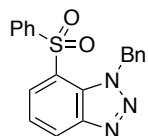
1-Benzyl-4-(phenylsulfonyl)-1*H*-benzo[*d*][1,2,3]triazole (**23**)



Yield: 70% (mixture of **23** and **23'**, 49.3 mg, 0.141 mmol, **23**:**23'** = 97:3. The yield was determined as a purified mixture of **23** and **23'**. The ratio of regioisomers were determined on the basis ¹H NMR analysis of this mixture. The regioisomers were separated before characterization.); Pale yellow oil; TLC *R*_f 0.20 (*n*-hexane/EtOAc = 2/1); ¹H NMR (CDCl₃, 500 MHz) δ 5.84 (s, 2H, CH₂), 7.23–7.28 (m, 2H, aromatic), 7.31–7.36 (m, 3H, aromatic), 7.48–7.54 (m, 3H, aromatic), 7.54–7.59 (m, 2H, aromatic), 8.11 (d, 1H, *J* = 7.2 Hz, aromatic), 8.33–8.38 (AA'BB'C, 2H, aromatic); ¹³C NMR (CDCl₃, 126 MHz) δ 53.0 (1C), 115.9 (1C), 125.1 (1C), 127.0 (1C), 127.9 (2C), 129.08 (1C), 129.13 (2C), 129.2 (2C), 129.4 (2C), 132.6 (1C), 133.8 (1C), 134.0 (1C), 134.2 (1C), 141.0 (1C), 141.7 (1C); IR (KBr, cm⁻¹) 554, 646, 687, 727, 1084, 1134, 1157, 1244, 1310, 1321, 1447; HRMS (ESI⁺) *m/z* 372.0777 ([M+Na]⁺, C₁₉H₁₅N₃NaO₂S⁺ requires 372.0777).

The regiochemistry of **23** was determined by preparing the authentic sample by oxidation of 1-benzyl-4-(phenylsulfinyl)-1*H*-benzo[*d*][1,2,3]triazole (**13**).

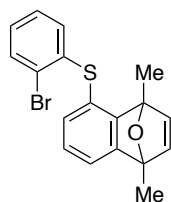
1-Benzyl-7-(phenylsulfonyl)-1*H*-benzo[*d*][1,2,3]triazole (**23'**)



Colorless solid; Mp 145–146 °C; TLC *R*_f 0.36 (*n*-hexane/EtOAc = 2/1); ¹H NMR (CDCl₃, 500 MHz) δ 6.36 (s, 2H, CH₂), 6.87–6.92 (AA'BB'C, 2H, aromatic), 7.14–7.20 (m, 3H, aromatic), 7.29–7.34 (AA'BB'C, 2H, aromatic), 7.44–7.49 (AA'BB'C, 1H, aromatic), 7.52 (dd, 1H, *J* = 8.2, 7.6 Hz, aromatic), 7.60–7.65 (AA'BB'C, 2H, aromatic), 8.13 (dd, 1H, *J* = 7.6, 1.0 Hz, aromatic), 8.40 (dd, 1H, *J* = 8.2, 1.0 Hz, aromatic); ¹³C NMR (CDCl₃, 126 MHz) δ 54.4 (1C), 123.4 (1C), 125.3 (1C), 126.9 (2C), 127.0 (1C), 127.4 (2C), 127.9 (1C), 128.8 (2C), 129.1 (1C), 129.5 (2C), 131.4 (1C), 133.8 (1C), 136.6 (1C), 140.3 (1C), 148.4 (1C); IR (KBr, cm⁻¹) 407, 581, 596, 619, 687, 723, 1078, 1140, 1155, 1308, 1447; HRMS (ESI⁺) *m/z* 372.0777 ([M+Na]⁺, C₁₉H₁₅N₃NaO₂S⁺ requires 372.0777).

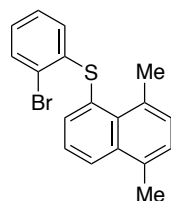
The regiochemistry of **23'** was determined by preparing the authentic sample by oxidation of 1-benzyl-7-(phenylthio)-1*H*-benzo[*d*][1,2,3]triazole (**13'**).

5-((2-Bromophenyl)thio)-1,4-dimethyl-1,4-dihydro-1,4-epoxynaphthalene



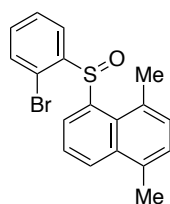
Yield: 89% (65.0 mg, 0.181 mmol); Brown oil; TLC R_f 0.38 (*n*-hexane/EtOAc = 20/1); ^1H NMR (CDCl_3 , 500 MHz) δ 1.91 (s, 3H, CH_3), 1.95 (s, 3H, CH_3), 6.57 (dd, 1H, $J = 7.9, 1.5$ Hz, aromatic), 6.67 (d, 1H, $J = 5.3$ Hz, olefinic), 6.76 (d, 1H, $J = 5.3$ Hz, olefinic), 6.96–7.04 (m, 3H, aromatic), 7.09 (ddd, 1H, $J = 7.5, 7.5, 1.2$ Hz, aromatic), 7.16 (dd, 1H, $J = 6.0, 2.1$ Hz, aromatic), 7.53 (dd, 1H, $J = 7.9, 1.5$ Hz, aromatic); ^{13}C NMR (CDCl_3 , 126 MHz) δ 15.4 (1C), 17.1 (1C), 88.3 (1C), 90.9 (1C), 119.3 (1C), 121.2 (1C), 124.0 (1C), 126.7 (1C), 126.8 (1C), 128.0 (1C), 128.4 (1C), 132.9 (1C), 133.1 (1C), 140.1 (1C), 146.9 (1C), 147.2 (1C), 155.3 (1C), 156.3 (1C); IR (KBr, cm^{-1}) 662, 723, 746, 856, 1018, 1134, 1300, 1381, 1427, 1445; HRMS (ESI^+) m/z 380.9910 ($[\text{M}+\text{Na}]^+$, $\text{C}_{18}\text{H}_{15}\text{BrNaOS}^+$ requires 380.9919).

5-((2-Bromophenyl)thio)-1,4-dimethylnaphthalene (**24**)



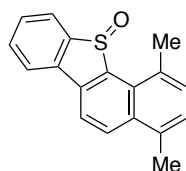
Yield: 95% (95.4 mg, 0.278 mmol); Colorless solid; Mp 104–105 °C; TLC R_f 0.39 (*n*-hexane); ^1H NMR (CDCl_3 , 500 MHz) δ 2.69 (s, 3H, CH_3), 2.94 (s, 3H, CH_3), 6.41 (d, 1H, $J = 7.6$ Hz, aromatic), 6.91 (dd, 1H, $J = 7.6, 7.6$ Hz, aromatic), 6.97 (dd, 1H, $J = 7.6, 7.6$ Hz, aromatic), 7.20 (d, 1H, $J = 7.1$ Hz, aromatic), 7.24 (d, 1H, $J = 7.1$ Hz, aromatic), 7.56 (dd, 1H, $J = 7.8, 7.8$ Hz, aromatic), 7.52 (d, 1H, $J = 7.6$ Hz, aromatic), 7.80 (d, 1H, $J = 7.8$ Hz, aromatic), 8.14 (d, 1H, $J = 7.8$ Hz, aromatic); ^{13}C NMR (CDCl_3 , 126 MHz) δ 20.4 (1C), 25.4 (1C), 120.2 (1C), 125.3 (1C), 126.0 (1C), 127.1 (1C), 127.6 (1C), 127.7 (1C), 127.9 (1C), 128.9 (1C), 130.9 (1C), 132.7 (1C), 133.5 (1C), 133.9 (1C), 134.4 (1C), 135.3 (1C), 138.3 (1C), 142.0 (1C); IR (KBr, cm^{-1}) 745, 824, 1020, 1038, 1427, 1445, 1460, 1574, 2926, 2965; Anal. calcd. for $\text{C}_{18}\text{H}_{15}\text{BrS}$: C, 62.98; H, 4.40; N, 0.00%; Found: C, 62.89; H, 4.32; N, 0.00%.

5-((2-Bromophenyl)sulfinyl)-1,4-dimethylnaphthalene



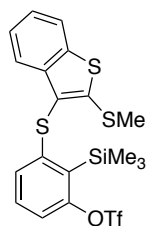
Yield: 96% (19.5 mg, 54.2 μmol); Yellow solid; Mp 153–154 $^{\circ}\text{C}$; TLC R_f 0.25 (*n*-hexane/EtOAc = 5/1); ^1H NMR (CDCl_3 , 500 MHz) δ 2.68 (s, 3H, CH_3), 2.97 (s, 3H, CH_3), 7.23–7.31 (m, 3H, aromatic), 7.38 (dd, 1H, $J = 7.8, 7.8$ Hz, aromatic), 7.43 (d, 1H, $J = 7.8$ Hz, aromatic), 7.55 (d, 1H, $J = 7.8$ Hz, aromatic), 7.60 (dd, 1H, $J = 8.1, 8.1$ Hz, aromatic), 8.12 (d, 1H, $J = 8.1$ Hz, aromatic), 8.21 (d, 1H, $J = 8.1$ Hz, aromatic); ^{13}C NMR (CDCl_3 , 126 MHz) δ 20.5 (1C), 26.1 (1C), 122.6 (1C), 125.1 (1C), 127.6 (1C), 127.9 (1C), 128.6 (1C), 128.7 (1C), 129.5 (1C), 131.3 (1C), 132.0 (1C), 132.5 (1C), 133.6 (1C), 133.7 (1C+1C, two signals overlapped), 134.3 (1C), 141.7 (1C), 145.7 (1C); IR (KBr, cm^{-1}) 449, 754, 826, 1015, 1049, 1076, 1092, 1445, 1462; Anal. calcd. for $\text{C}_{18}\text{H}_{15}\text{BrOS}$: C, 60.18; H, 4.21; N, 0.00%; Found: C, 60.13; H, 4.26; N, 0.00%.

1,4-Dimethylbenzo[*b*]naphtho[2,1-*d*]thiophene 11-oxide (25)



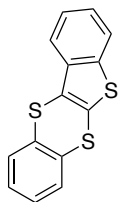
Yield: 63% (10.7 mg, 38.3 μmol); Colorless solid; Mp 209–210 $^{\circ}\text{C}$; TLC R_f 0.26 (*n*-hexane/EtOAc = 7/3); ^1H NMR (CDCl_3 , 500 MHz) δ 2.69 (s, 3H, CH_3), 3.30 (s, 3H, CH_3), 7.27 (d, 1H, $J = 7.2$ Hz, aromatic), 7.37 (d, 1H, $J = 7.2$ Hz, aromatic), 7.51 (dd, 1H, $J = 7.6, 7.6$ Hz, aromatic), 7.61 (dd, 1H, $J = 7.6, 7.6$ Hz, aromatic), 7.87 (d, 1H, $J = 7.6$ Hz, aromatic), 7.90 (d, 1H, $J = 8.7$ Hz, aromatic), 7.99 (d, 1H, $J = 7.6$ Hz, aromatic), 8.27 (d, 1H, $J = 8.7$ Hz, aromatic); ^{13}C NMR (CDCl_3 , 126 MHz) δ 20.4 (1C), 23.7 (1C), 118.5 (1C), 122.1 (1C), 127.1 (1C), 128.0 (1C), 129.6 (1C), 131.1 (1C), 131.2 (1C), 131.6 (1C), 132.5 (1C), 132.7 (1C), 133.6 (1C), 134.8 (1C), 137.1 (1C), 137.7 (1C), 141.5 (1C), 145.1 (1C); IR (KBr, cm^{-1}) 735, 752, 831, 1022, 1040, 1454, 1468; Anal. calcd. for $\text{C}_{18}\text{H}_{14}\text{OS}$: C, 77.67; H, 5.07; N, 0.00%; Found: C, 77.54; H, 5.26; N, 0.00%.

3-((2-(Methylthio)benzo[*b*]thiophen-3-yl)thio)-2-(trimethylsilyl)phenyl triflate (**27**)



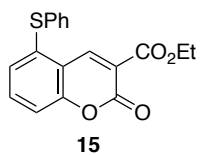
Yield: 34% (35.1 mg, 69.0 μmol); Pale yellow oil; TLC R_f 0.34 (*n*-hexane/EtOAc = 20/1); ^1H NMR (CDCl_3 , 500 MHz) δ 0.67 (s, 9H, SiCH_3), 2.64 (s, 3H, SCH_3), 6.63 (dd, 1H, $J = 6.3, 2.2$ Hz, aromatic), 7.02–7.08 (m, 2H, aromatic), 7.28–7.37 (m, 2H, aromatic), 7.57 (d, 1H, $J = 7.2$ Hz, aromatic), 7.79 (d, 1H, $J = 7.2$ Hz, aromatic); ^{13}C NMR (CDCl_3 , 126 MHz) δ 2.5 (3C), 18.4 (1C), 117.3 (1C), 118.9 (q, 1C, $^1J_{\text{C-F}} = 320.8$ Hz), 119.6 (1C), 122.29 (1C), 122.32 (1C), 124.6 (1C), 125.8 (1C), 126.0 (1C), 130.4 (1C), 131.0 (1C), 138.8 (1C), 140.7 (1C), 147.1 (1C), 149.6 (1C), 155.3 (1C); ^{19}F NMR (CDCl_3 , 376 MHz) δ -73.1 (s); IR (KBr, cm^{-1}) 754, 847, 901, 1140, 1213, 1250, 1269, 1420, 1726; HRMS (ESI $^+$) m/z 530.9816 ($[\text{M}+\text{Na}]^+$, $\text{C}_{19}\text{H}_{19}\text{F}_3\text{NaO}_3\text{S}_4\text{Si}^+$ requires 530.9831).

1,4-Benzodithiino[2,3-*d*]benzo[*b*]thiophene (**28**)



Yield: 70% (22.1 mg, 81.3 μmol); Colorless solid; Mp 110–111 $^\circ\text{C}$; TLC R_f 0.45 (*n*-hexane); ^1H NMR (acetone- d_6 , 500 MHz) 7.34–7.41 (m, 2H, aromatic), 7.44 (dd, 1H, $J = 7.6, 7.6$ Hz, aromatic), 7.50 (dd, 1H, $J = 7.6, 7.6$ Hz, aromatic), 7.54–7.59 (m, 1H, aromatic), 7.59–7.64 (m, 1H, aromatic), 7.79 (d, 1H, $J = 8.0$ Hz, aromatic), 7.95 (d, 1H, $J = 8.0$ Hz, aromatic); ^{13}C NMR (acetone- d_6 , 126 MHz) δ 121.7 (1C), 123.9 (1C), 126.25 (1C), 126.30 (1C+1C, two signals overlapped), 128.0 (1C), 129.2 (1C), 129.6 (1C), 129.9 (1C), 130.3 (1C), 131.8 (1C), 135.1 (1C), 137.6 (1C), 141.6 (1C); IR (KBr, cm^{-1}) 725, 748, 926, 1016, 1109, 1252, 1422, 1447, 2849, 2920; HRMS (ESI $^+$) m/z 294.9681 ($[\text{M}+\text{Na}]^+$, $\text{C}_{14}\text{H}_8\text{NaS}_3^+$ requires 294.9680).

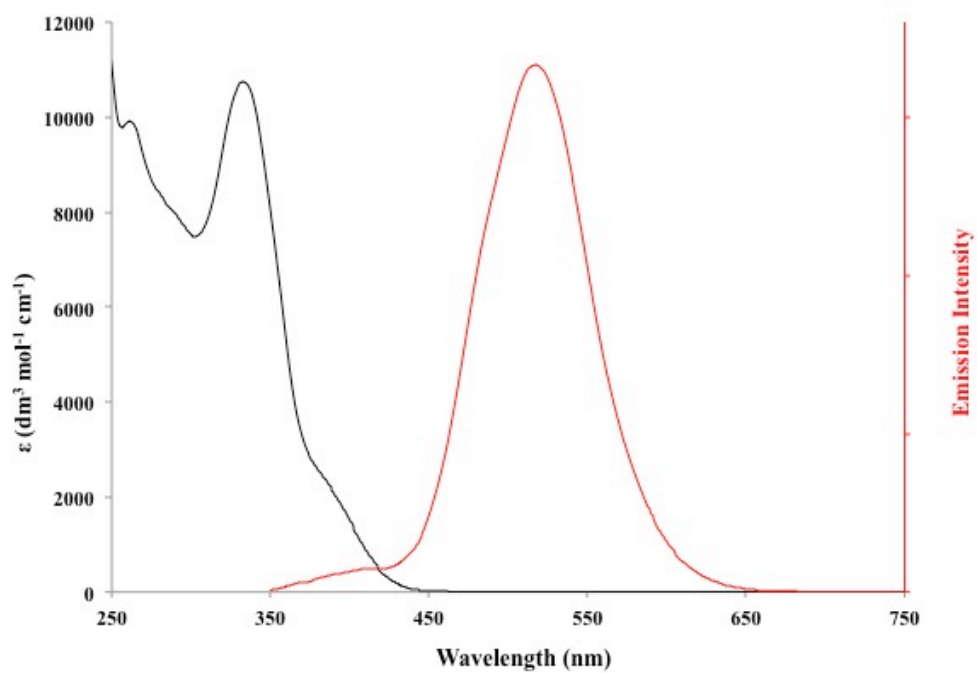
Absorption and fluorescent properties and spectra of 5-thiocoumarin (15)



In CH₂Cl₂

UV/Vis (100 μM): λ_{max} (log ϵ) = 333 (4.03), 374 (3.47) nm.

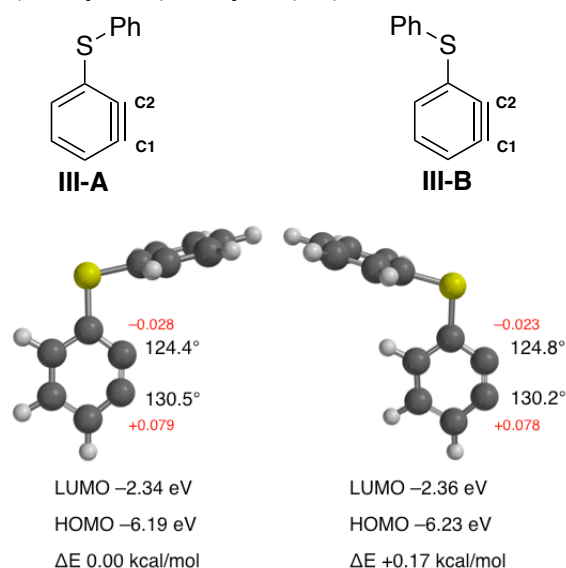
FL (1 μM): λ_{max} = 518 nm; Φ_F = 0.011 (reference to 9,10-DPA; excited at 420 nm).



Computational Methods

The optimized structures of 3-(phenylthio)benzyne (**III**), 3-(phenylsulfinyl)benzyne (**IV**), and 3-(phenylsulfonyl)benzyne (**V**) (Figure 3) were computed in Spartan '16^{S12} using density functional theory (B3LYP/6-311+G(d,p)). Calculated internal angles (black numbers) and charge distribution of C1 and C2 (red numbers) are shown.

3-(Phenylthio)benzyne (**III**)



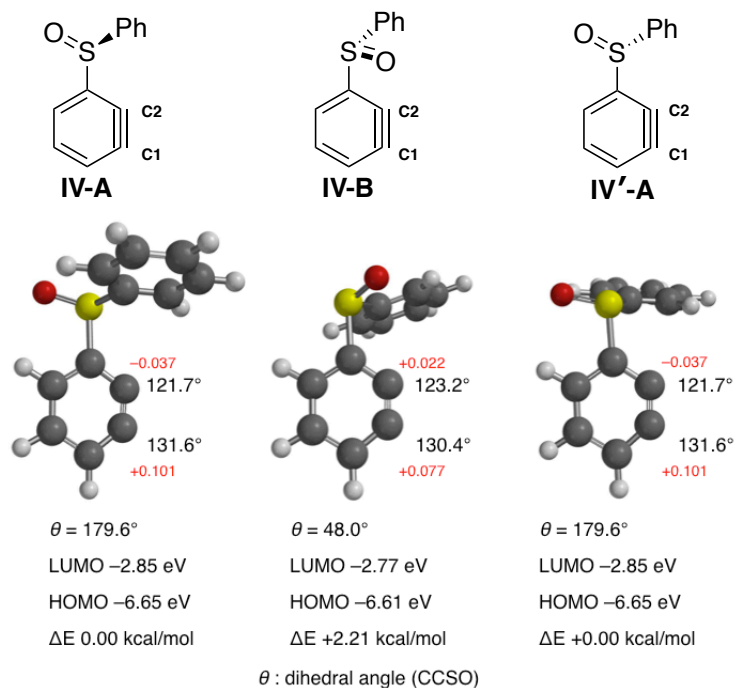
for **III-A**

Cartesian Coordinates (Angstroms)			
C	-1.4981711	0.6909963	-0.0275373
C	-3.7355257	-1.1877670	-0.0594838
C	-1.4096708	-0.6854933	-0.1501741
C	-2.8463552	1.1129468	0.0859483
C	-3.9169087	0.2085283	0.0671710
C	-2.3875089	-1.4549337	-0.1559399
S	-0.1682372	1.8790650	-0.0209067
C	1.2676408	0.7992970	-0.0117397
C	3.5462532	-0.8065963	0.0039242
C	1.9695403	0.5737605	-1.1979040
C	1.7092838	0.2270008	1.1843943
C	2.8441304	-0.5804941	1.1873621
C	3.1093388	-0.2287832	-1.1864495
H	-4.5557799	-1.8916505	-0.0707548
H	-3.0564133	2.1724888	0.1948735
H	-4.9276401	0.5947555	0.1576161
H	4.4325559	-1.4309519	0.0102761
H	1.6207634	1.0216413	-2.1204427
H	1.1664405	0.4155914	2.1027532
H	3.1833576	-1.0267448	2.1153556
H	3.6529061	-0.4026571	-2.1083419

for **III-B**

Cartesian Coordinates (Angstroms)			
C	1.7081615	1.0244574	0.2990120
C	4.1365903	-0.3611185	-0.5665426
C	3.0027320	1.5234860	0.3417999
C	1.6862424	-0.2880040	-0.2310690
C	2.8548112	-0.9466389	-0.6449608
C	4.0134309	0.9060793	-0.0357710
S	0.3096246	1.9727938	0.8646056
C	-1.0873728	0.8987389	0.5042092
C	-3.3214111	-0.6882864	-0.0193573
C	-1.5591595	0.0130883	1.4772334
C	-1.7407204	0.9961842	-0.7274693
C	-2.8551689	0.2006752	-0.9870412
C	-2.6738888	-0.7805743	1.2116531
H	5.0385198	-0.8643964	-0.8848280
H	0.7380748	-0.8043332	-0.3217107
H	2.7683251	-1.9531675	-1.0432452
H	-4.1908634	-1.3035435	-0.2221876
H	-1.0543891	-0.0496296	2.4338433
H	-1.3761228	1.6928670	-1.4728718
H	-3.3601224	0.2785288	-1.9433203
H	-3.0372934	-1.4672067	1.9680182

3-(Phenylsulfinyl)benzyne (**IV**)



for IV-A

	Cartesian Coordinates (Angstroms)		
C	-1.5151227	0.4944590	-0.6056469
C	-3.7663530	-1.1333397	0.1918681
C	-1.8263790	-0.7413108	-1.1502472
C	-2.4163037	0.9250314	0.3816593
C	-3.5052385	0.1282819	0.7704358
C	-2.8041715	-1.4029070	-0.7539746
S	-0.1538750	1.5968850	-1.1436617
C	1.2295175	0.5556717	-0.5418273
C	3.3761257	-0.9358976	0.3594870
C	1.6508371	-0.5431205	-1.2861959
C	1.8722766	0.9380139	0.6291114
C	2.9523385	0.1801867	1.0802809
C	2.7277230	-1.2964321	-0.8221373
O	-0.2218332	2.8098015	-0.2393642
H	-4.6023859	-1.7533957	0.4833493
H	-2.2462041	1.8943890	0.8381979
H	-4.1758174	0.4904015	1.5430933
H	4.2180224	-1.5201792	0.7129913
H	1.1518244	-0.8122328	-2.2106976
H	1.5264637	1.8190830	1.1576512
H	3.4644204	0.4649928	1.9924673
H	3.0641347	-2.1583822	-1.3868400

for IV-B

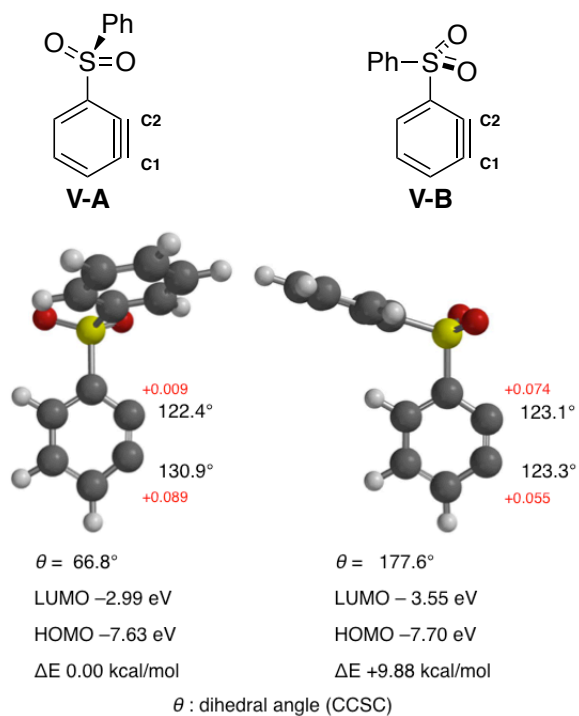
	Cartesian Coordinates (Angstroms)		
C	-1.5249771	0.5367461	-0.3422194
C	-3.7090891	-1.2218408	0.3922084
C	-1.8313861	0.1332160	0.9477090
C	-2.4125358	0.0123236	-1.3010013
C	-3.4668482	-0.8471096	-0.9450472
C	-2.7764617	-0.6285726	1.2164405
S	-0.2294790	1.7293004	-0.8348211
C	1.1938036	0.7828360	-0.1818762
C	3.4071459	-0.5519757	0.8045201
C	1.6912455	-0.3159356	-0.8795366
C	1.7917455	1.2380192	0.9860965
C	2.9042416	0.5576060	1.4815926
C	2.8022347	-0.9880758	-0.3756262
O	-0.3770421	2.9420805	0.0563100
H	-4.5188777	-1.8785336	0.6795883
H	-2.2805637	0.2842073	-2.3434709
H	-4.1231450	-1.2281373	-1.7206799
H	4.2746001	-1.0750445	1.1908114

H	1.2208547	-0.6471220	-1.7995747
H	1.3861331	2.1138168	1.4802462
H	3.3799336	0.8989764	2.3940241
H	3.1984673	-1.8467809	-0.9056935

for IV'-A

	Cartesian Coordinates (Angstroms)		
C	1.5151227	0.4944592	-0.6056471
C	3.7663532	-1.1333397	0.1918669
C	1.8263795	-0.7413102	-1.1502483
C	2.4163033	0.9250308	0.3816598
C	3.5052380	0.1282812	0.7704358
C	2.8041721	-1.4029066	-0.7539762
S	0.1538749	1.5968854	-1.1436613
C	-1.2295174	0.5556720	-0.5418271
C	-3.3761257	-0.9358974	0.3594872
C	-1.6508363	-0.5431208	-1.2861951
C	-1.8722774	0.9380147	0.6291110
C	-2.9523392	0.1801874	1.0802805
C	-2.7277222	-1.2964325	-0.8221365
O	0.2218332	2.8098017	-0.2393635
H	4.6023862	-1.7533958	0.4833478
H	2.2462034	1.8943880	0.8381992
H	4.1758166	0.4904002	1.5430939
H	-4.2180223	-1.5201792	0.7129914
H	-1.1518230	-0.8122337	-2.2106964
H	-1.5264649	1.8190843	1.1576504
H	-3.4644218	0.4649940	1.9924664
H	-3.0641332	-2.1583831	-1.3868388

3-(Phenylsulfonyl)benzyne (**V**)



for **V-A**

	Cartesian Coordinates (Angstroms)		
C	0.4613053	-1.4151403	0.7789028
C	1.7443467	-1.4112720	3.3669634
C	1.7675657	-1.0249608	1.0144761
C	-0.2222303	-1.8265729	1.9376122
C	0.4057621	-1.8260325	3.1929313
C	2.2722015	-1.0391524	2.1516432
S	-0.3397570	-1.4648323	-0.8447572
C	-0.4395661	0.2673324	-1.3330344
C	-0.5825031	2.9262237	-2.0714707
C	0.6064147	0.8235161	-2.0661662
C	-1.5600236	1.0118001	-0.9700952
C	-1.6258241	2.3512462	-1.3455367
C	0.5286311	2.1650611	-2.4331444
O	0.5721729	-2.1382035	-1.7713348
O	-1.7034153	-1.9563513	-0.6150418
H	2.2359468	-1.4056694	4.3300660
H	-1.2509558	-2.1545057	1.8405114
H	-0.1520051	-2.1570312	4.0626328
H	-0.6388237	3.9692817	-2.3617028
H	1.4497443	0.2091478	-2.3558372
H	-2.3673624	0.5410983	-0.4229074
H	-2.4936921	2.9427188	-1.0778905
H	1.3320674	2.6122981	-3.0068199

for **V-B**

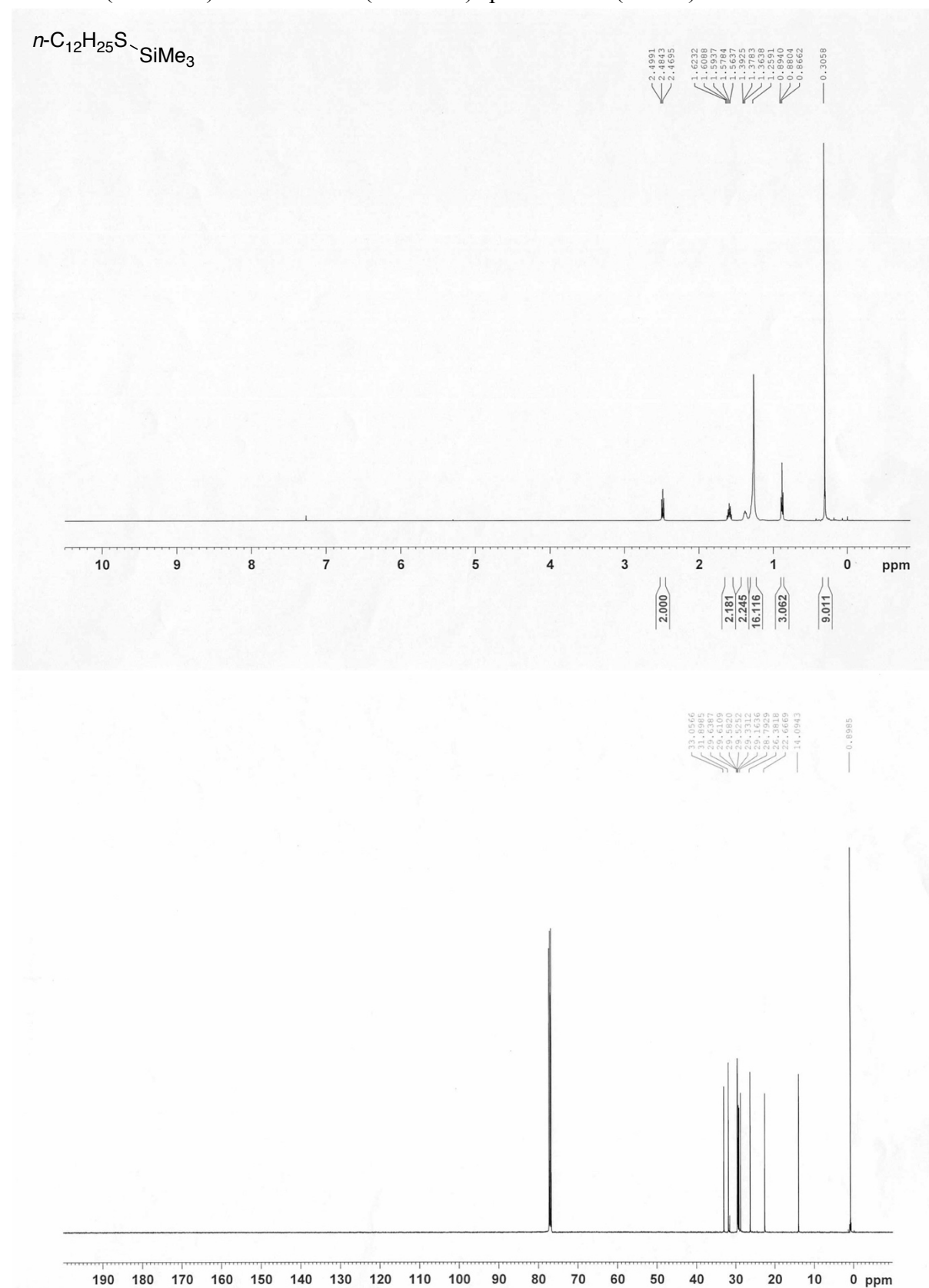
	Cartesian Coordinates (Angstroms)		
C	1.3747296	1.3304509	0.3616616
C	2.5963198	1.3607772	2.9102098
C	2.3424980	2.2855109	0.7445837
C	1.0218295	0.3733269	1.3326760
C	1.6344040	0.3886895	2.5993415
C	2.8970714	2.2956370	1.8998190
S	0.5614163	1.3122035	-1.2101386
C	-0.6125964	-0.0235438	-1.1987142
C	-2.4551021	-2.1054785	-1.2238017
C	-1.9447227	0.2291917	-0.8577697
C	-0.2000738	-1.3065838	-1.5718476
C	-1.1268885	-2.3487829	-1.5783266
C	-2.8643092	-0.8193515	-0.8667581
O	-0.1829685	2.5550088	-1.3134729
O	1.5672481	0.9771497	-2.2052188
H	3.0947047	1.4120428	3.8701127
H	0.2728504	-0.3826794	1.1047731
H	1.3611305	-0.3554336	3.3433223
H	-3.1756883	-2.9201024	-1.2314481
H	-2.2733445	1.2298930	-0.5856171
H	0.8302501	-1.5022349	-1.8602413
H	-0.8167849	-3.3511063	-1.8642417
H	-3.9019734	-0.6345847	-0.5989034

References for Supporting Information

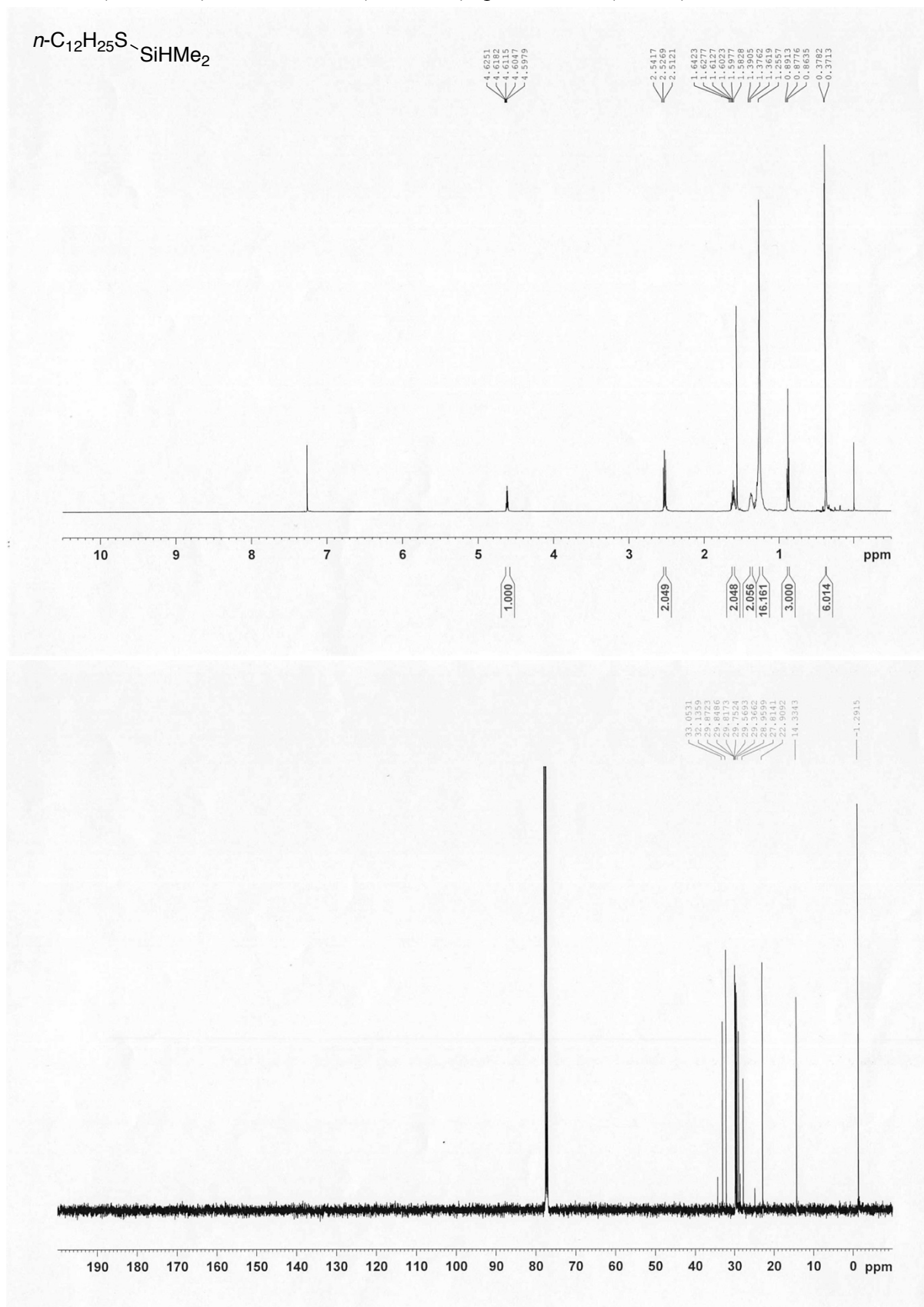
- S1 Bergbreiter, D. E.; Pendergrass, E. *J. Org. Chem.* **1981**, *46*, 219.
- S2 Hamura, T.; Hosoya, T.; Yamaguchi, H.; Kuriyama, Y.; Tanabe, M.; Miyamoto, M.; Yasui, Y.; Matsumoto, T.; Suzuki, K. *Helv. Chim. Acta* **2002**, *85*, 3589.
- S3 Yoshida, S.; Uchida, K.; Igawa, K.; Tomooka, K.; Hosoya, T. *Chem. Commun.* **2014**, *50*, 15059.
- S4 Uchida, K.; Yoshida, S.; Hosoya, T. *Synthesis* **2016**, *48*, 4099.
- S5 Chen, P.-h.; Xu, T.; Dong, G. *Angew. Chem., Int. Ed.* **2014**, *53*, 1674.
- S6 Saadi, J.; Wennemers, H. *Nat. Chem.* **2016**, *8*, 276.
- S7 Yoshida, S.; Yano, T.; Misawa, Y.; Sugimura, Y.; Igawa, K.; Shimizu, S.; Tomooka, K.; Hosoya, T. *J. Am. Chem. Soc.* **2015**, *137*, 14071.
- S8 Matsuzawa, T.; Uchida, K.; Yoshida, S.; Hosoya, T. *Org. Lett.* **2017**, *19*, 5521.
- S9 Kawashima, H.; Yanagi, T.; Wu, C.-C.; Nogi, K.; Yorimitsu, H. *Org. Lett.* **2017**, *19*, 4552.
- S10 Jung, K.-Y.; Koreeda, M. *J. Org. Chem.* **1989**, *54*, 5667.
- S11 Wesch, T.; Berthelot-Bréhier, A.; Leroux, F. R.; Colobert, F. *Org. Lett.* **2013**, *15*, 2490.
- S12 Spartan '16; Wavefunction, Inc: Irvine, CA, 2016.

¹H and ¹³C NMR Spectra of Compounds

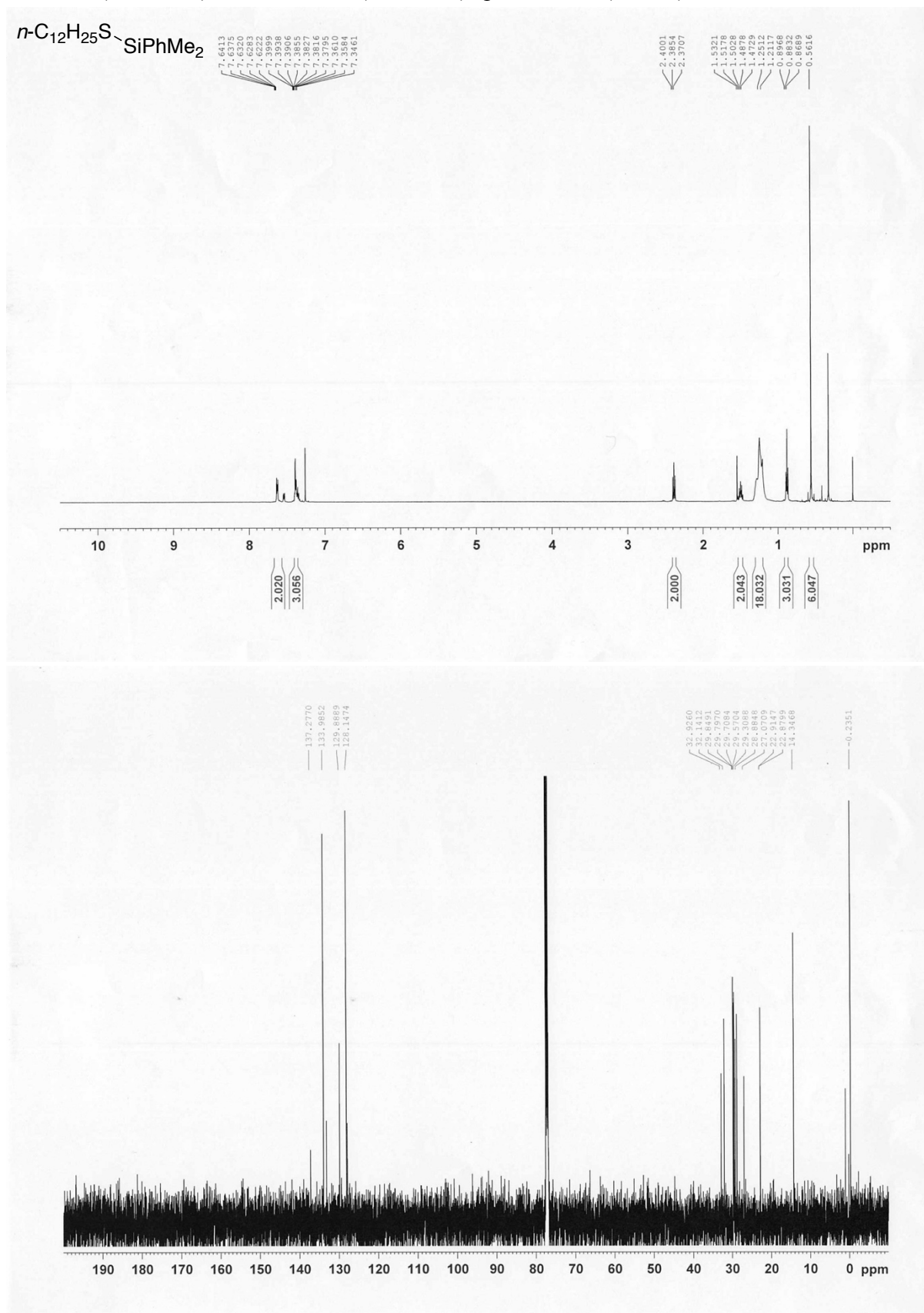
¹H NMR (500 MHz) and ¹³C NMR (126 MHz) spectra of **2d** (CDCl₃)



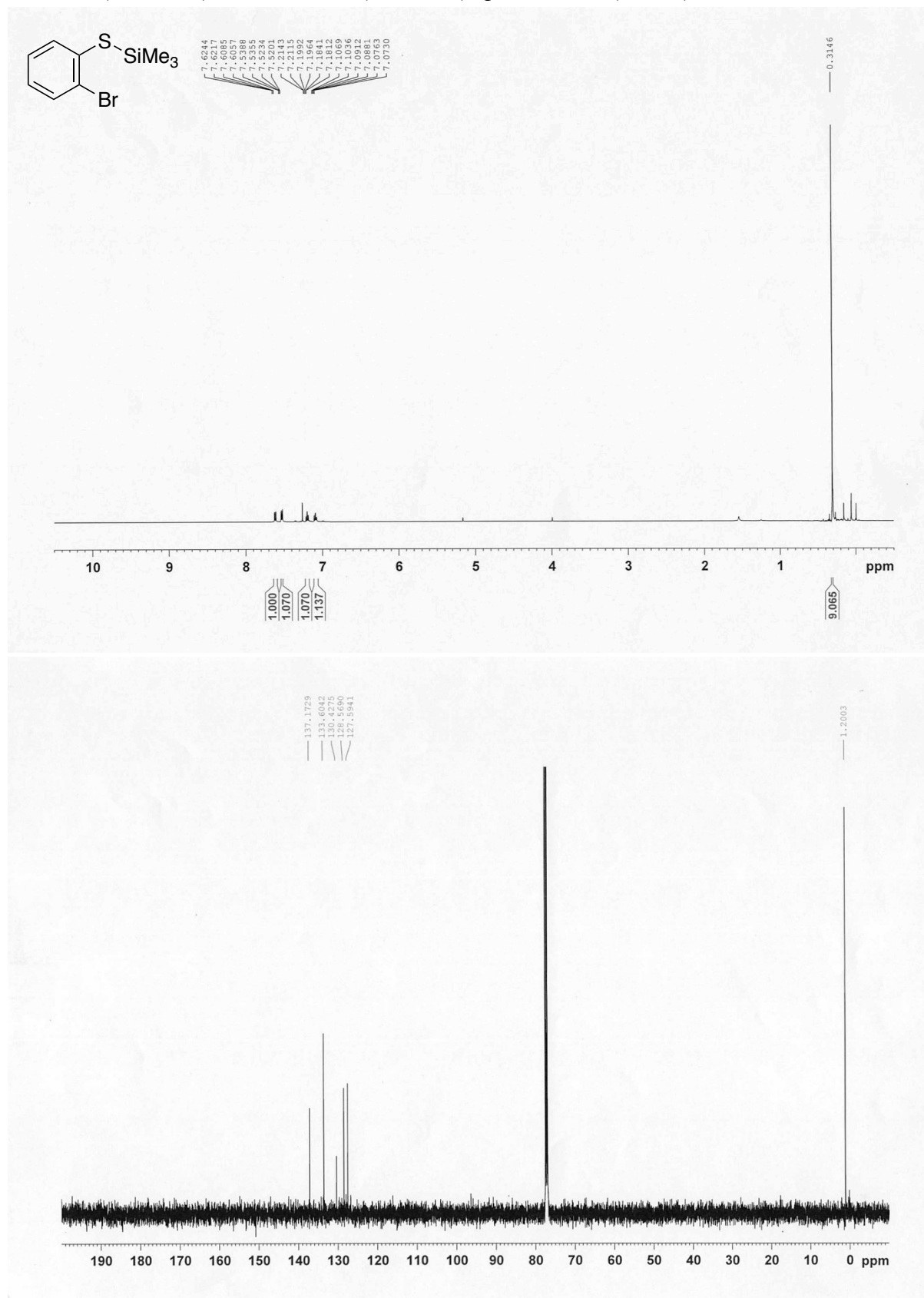
^1H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **2e** (CDCl_3)



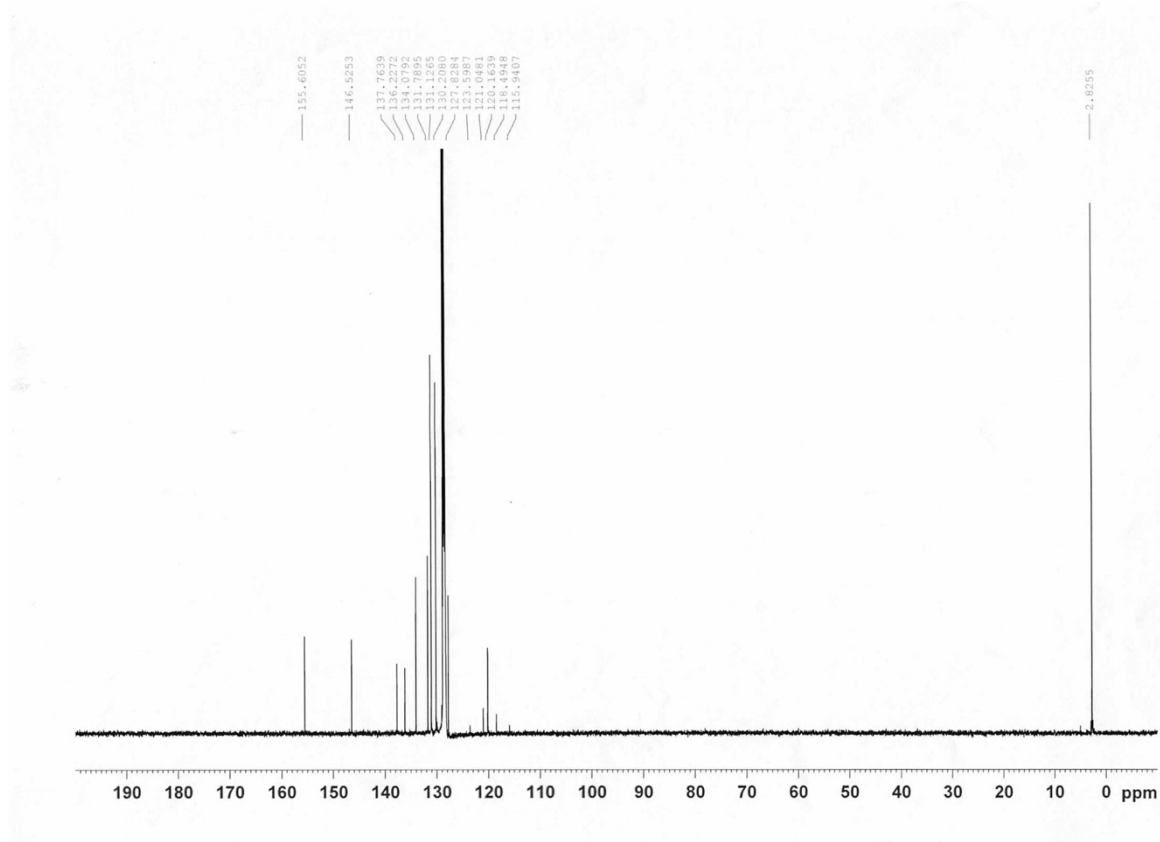
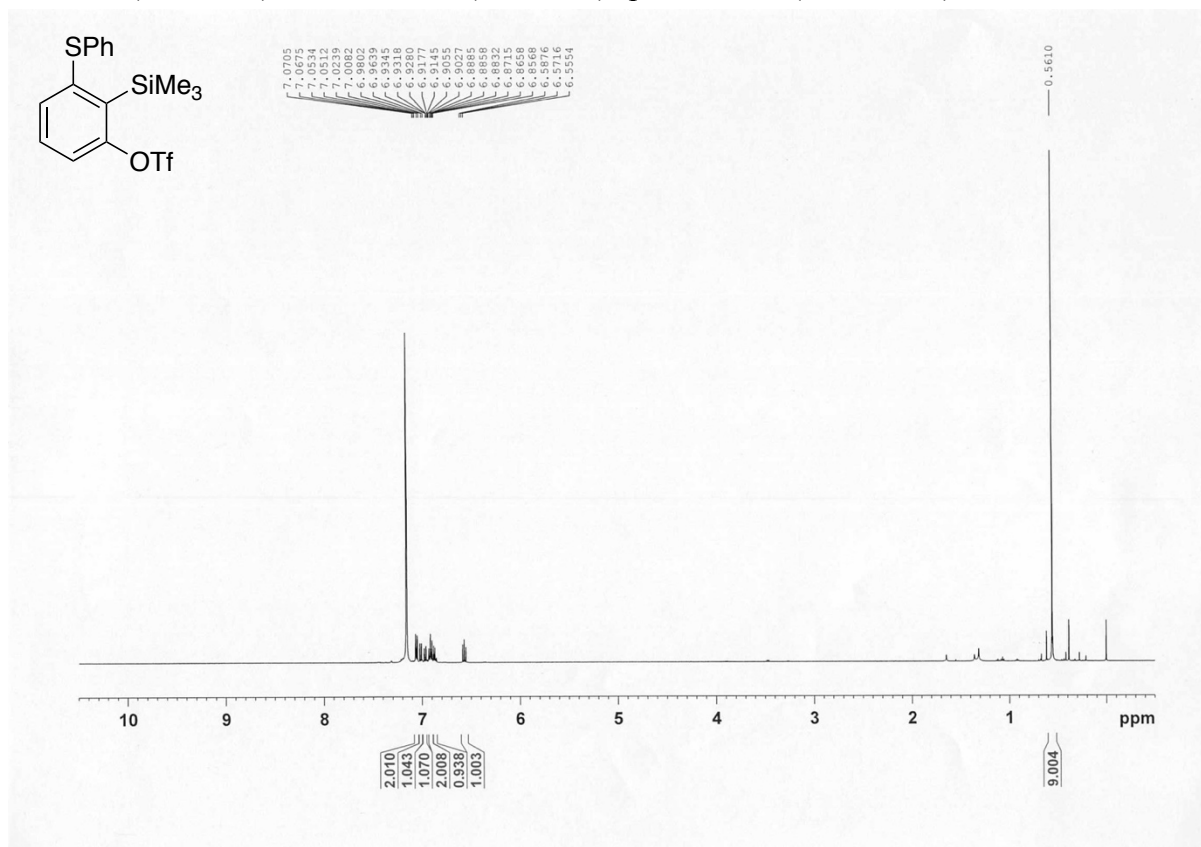
^1H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **2f** (CDCl_3)



^1H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **2h** (CDCl_3)



^1H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **3a** (benzene- d_6)

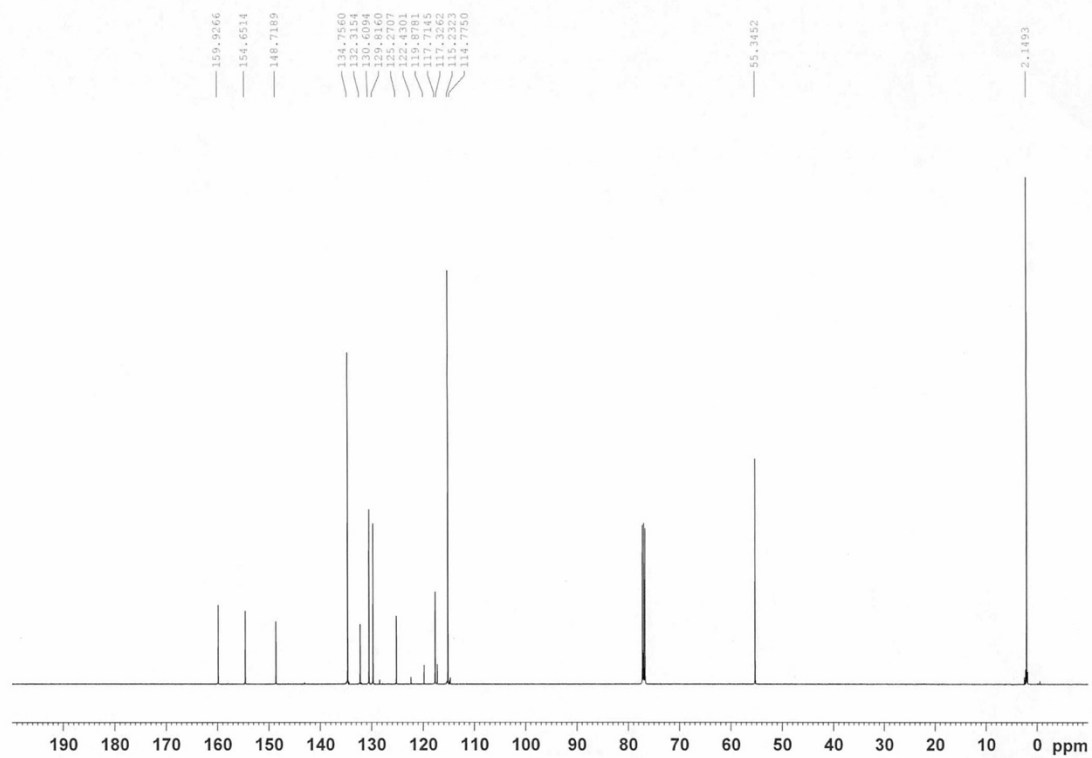


COc1ccc(cc1)S(=O)(=O)c2ccccc2C(F)(F)F

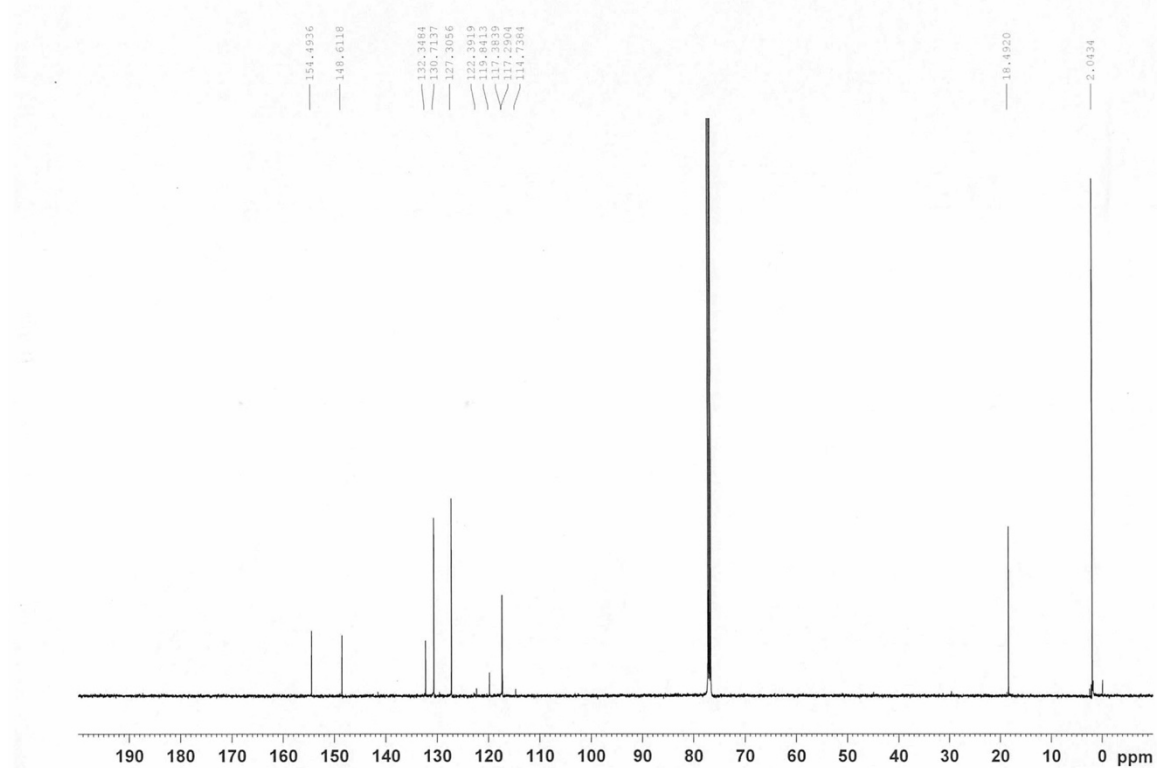
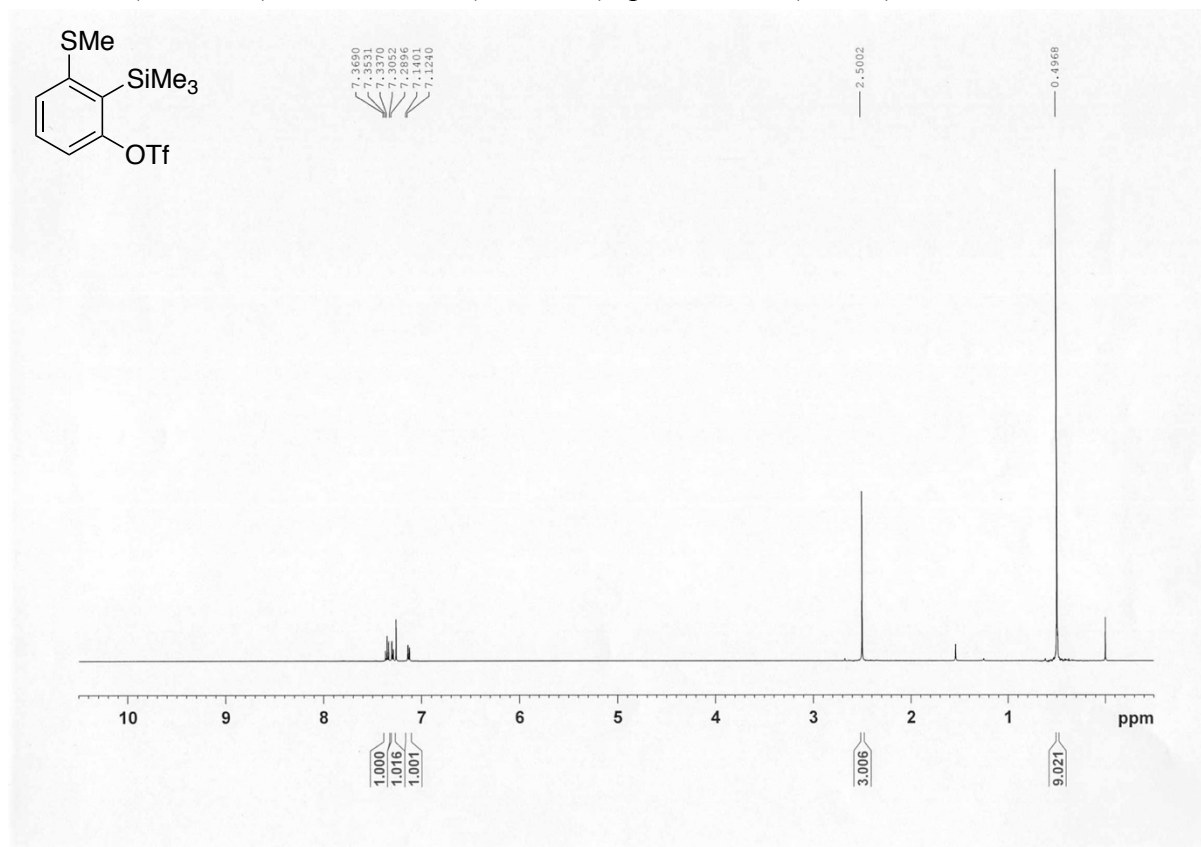
Chemical Structure: 4-methoxyphenyl 4-(trimethylsilyl)phenyl sulfonate

¹H NMR Data (CDCl₃):

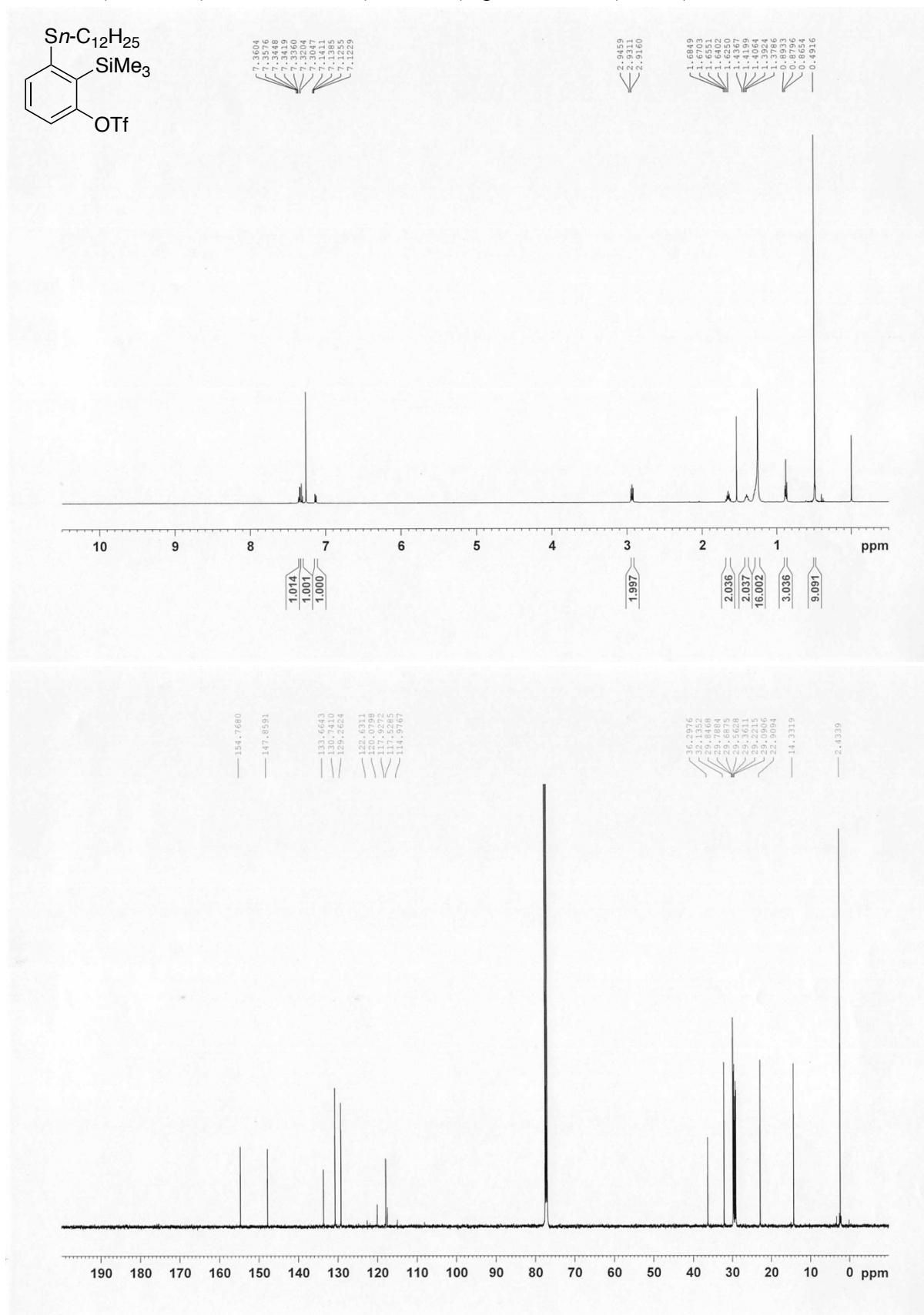
Chemical Shift (ppm)	Integration
7.3429, 7.3290, 7.3250, 7.3195, 7.3154, 7.2183, 7.2021, 7.1971, 7.1371, 7.1209, 7.0398, 6.9922, 6.9865, 6.9223, 6.9131, 6.9088	2.022, 1.004, 1.018, 1.000, 2.024
3.8304	3.014
0.5745	9.004



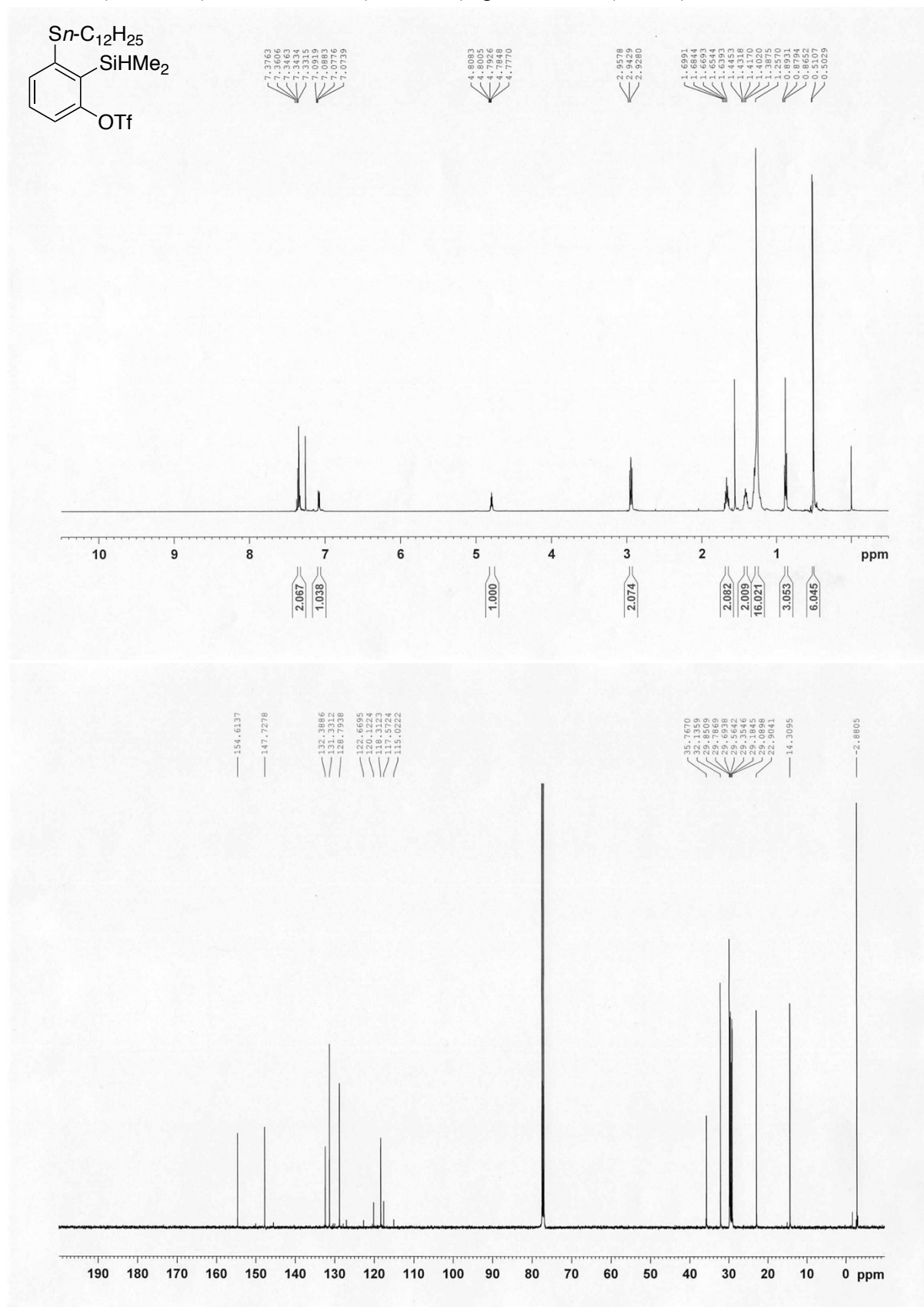
^1H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **3c** (CDCl_3)



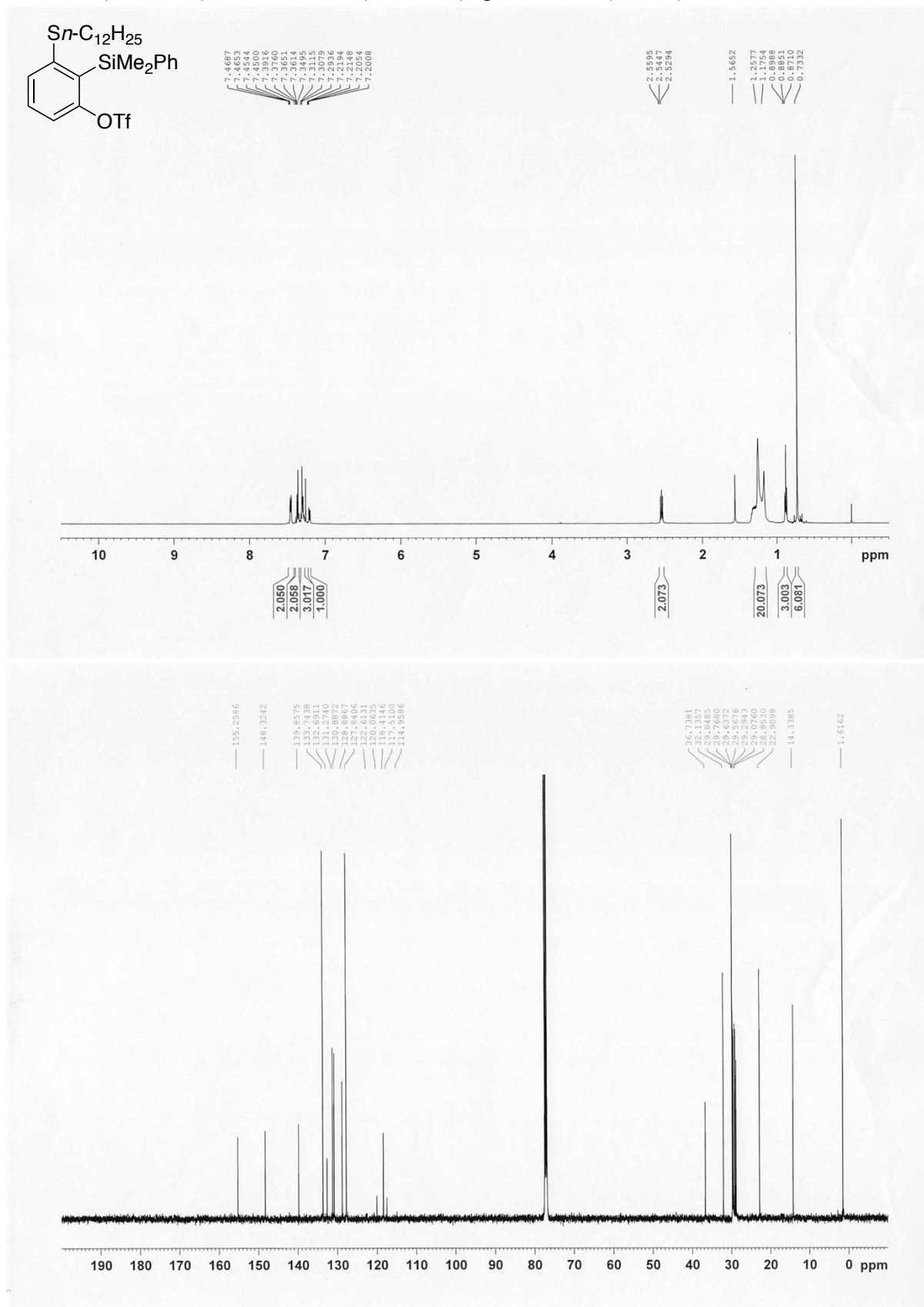
^1H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **3d** (CDCl_3)



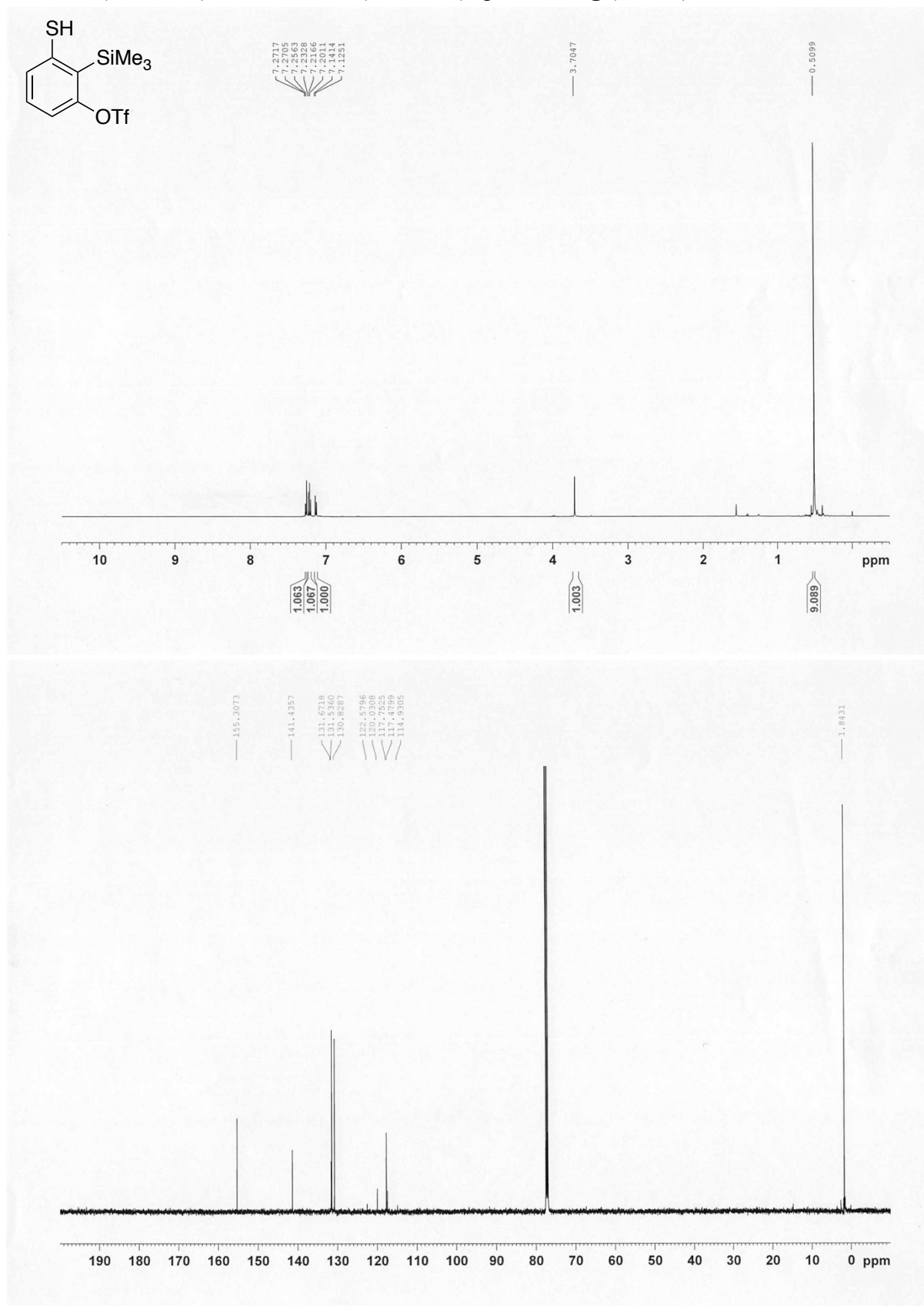
^1H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **3e** (CDCl_3)



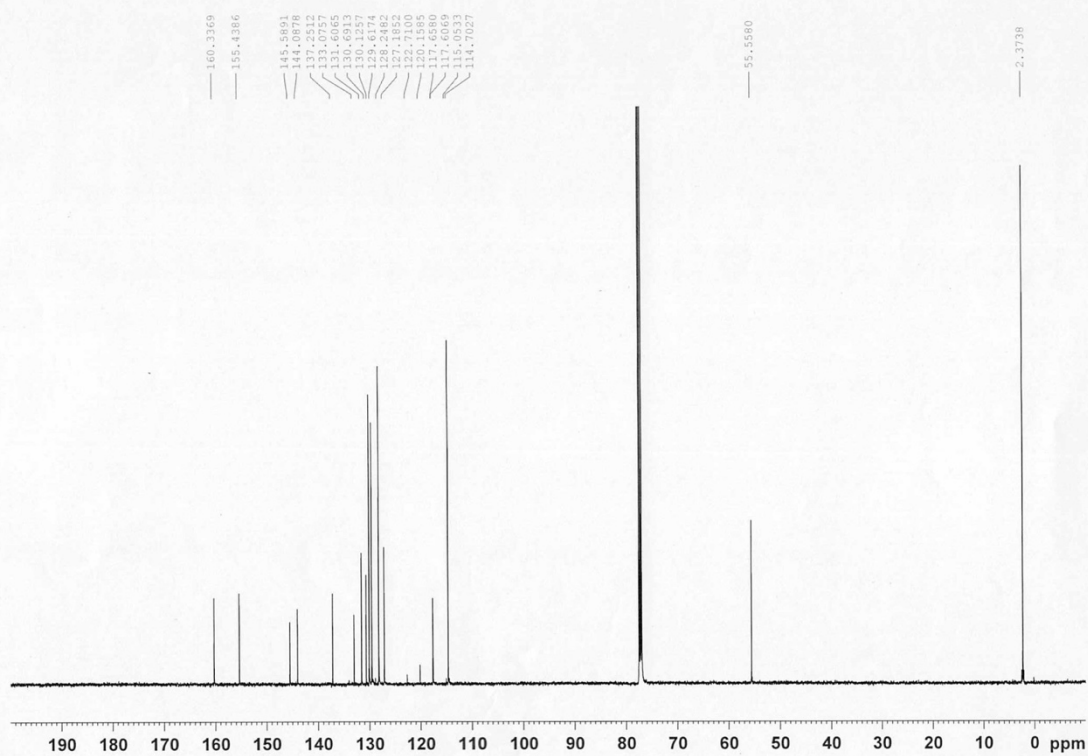
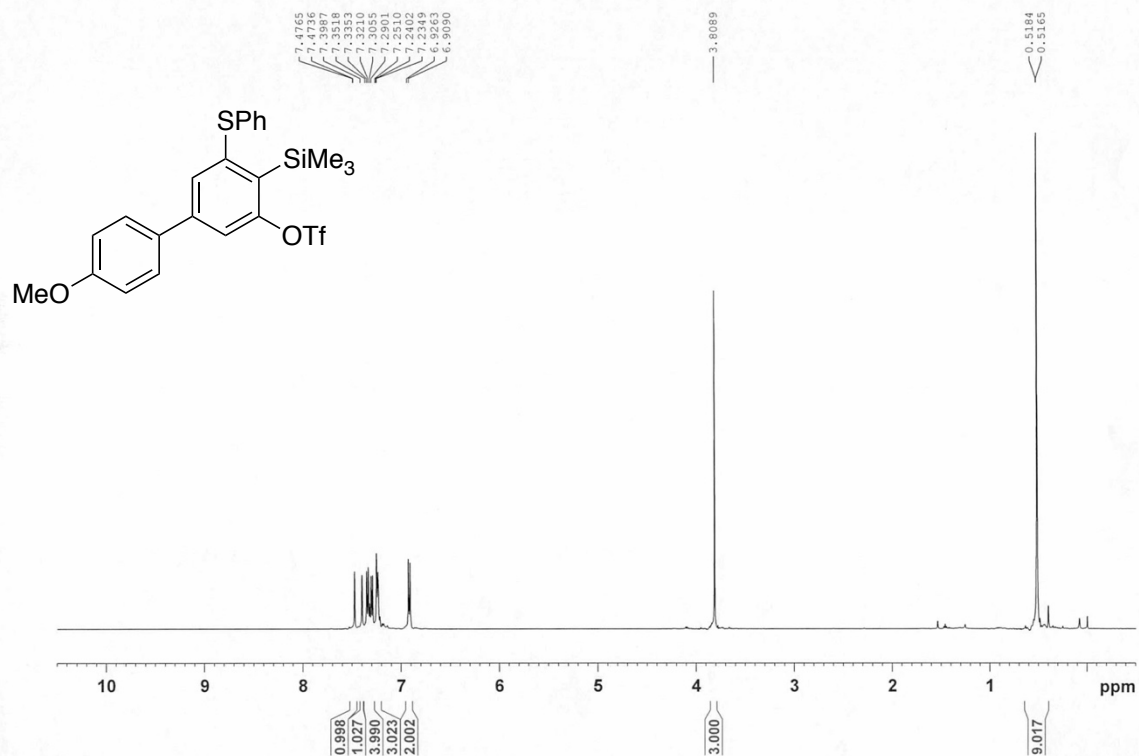
^1H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **3f** (CDCl_3)



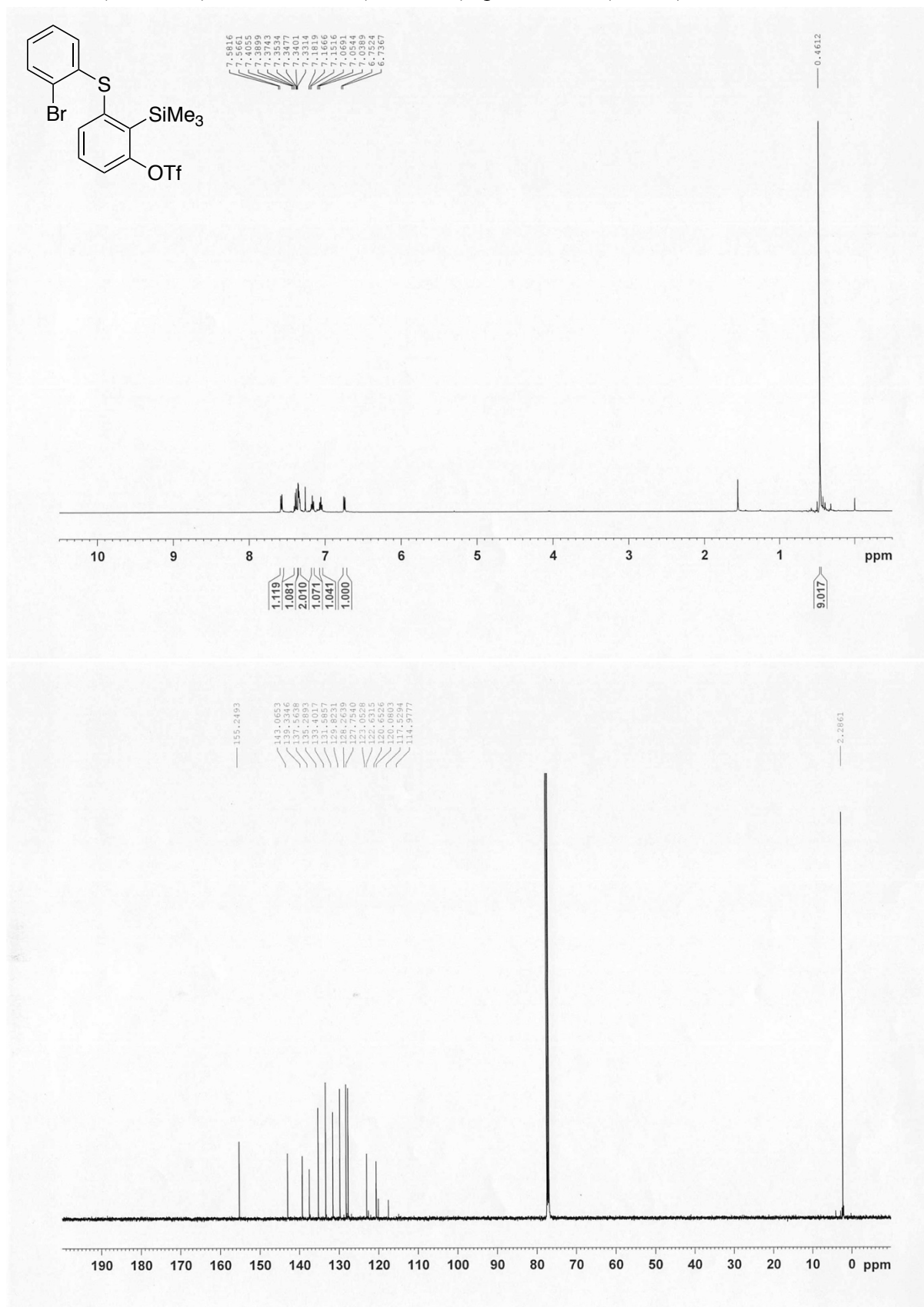
^1H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **3g** (CDCl_3)



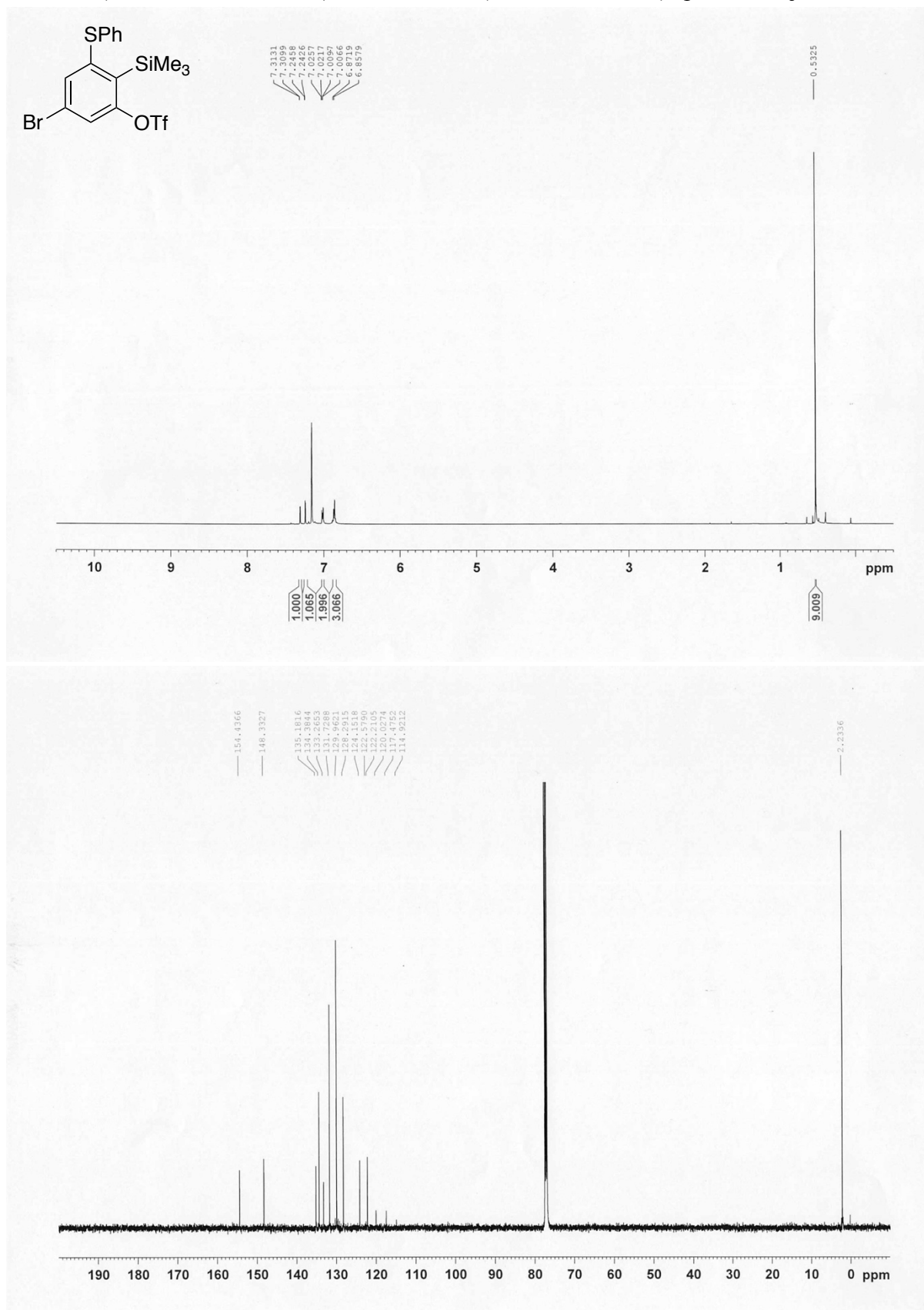
^1H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **3h** (CDCl_3)



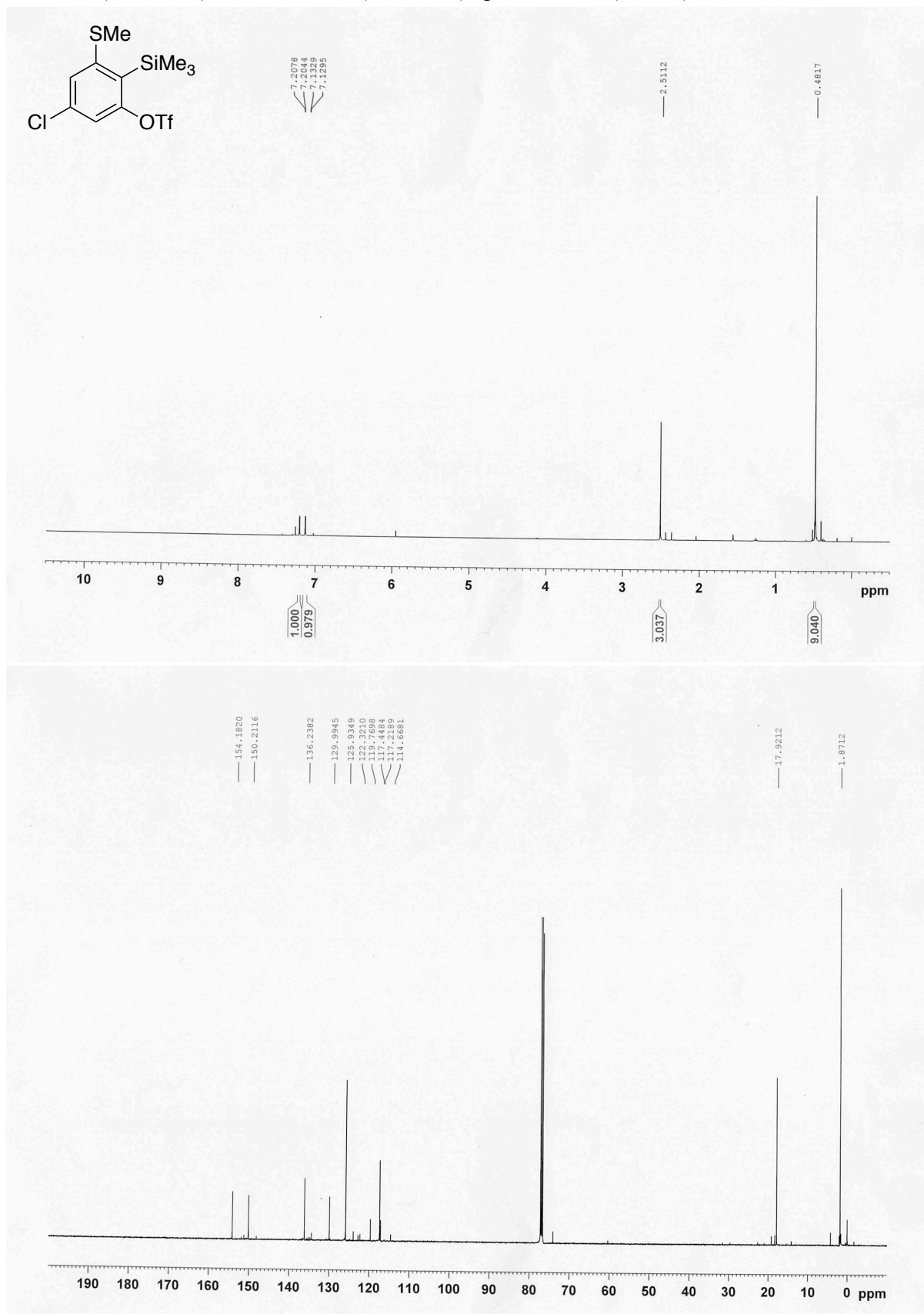
^1H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **3i** (CDCl_3)



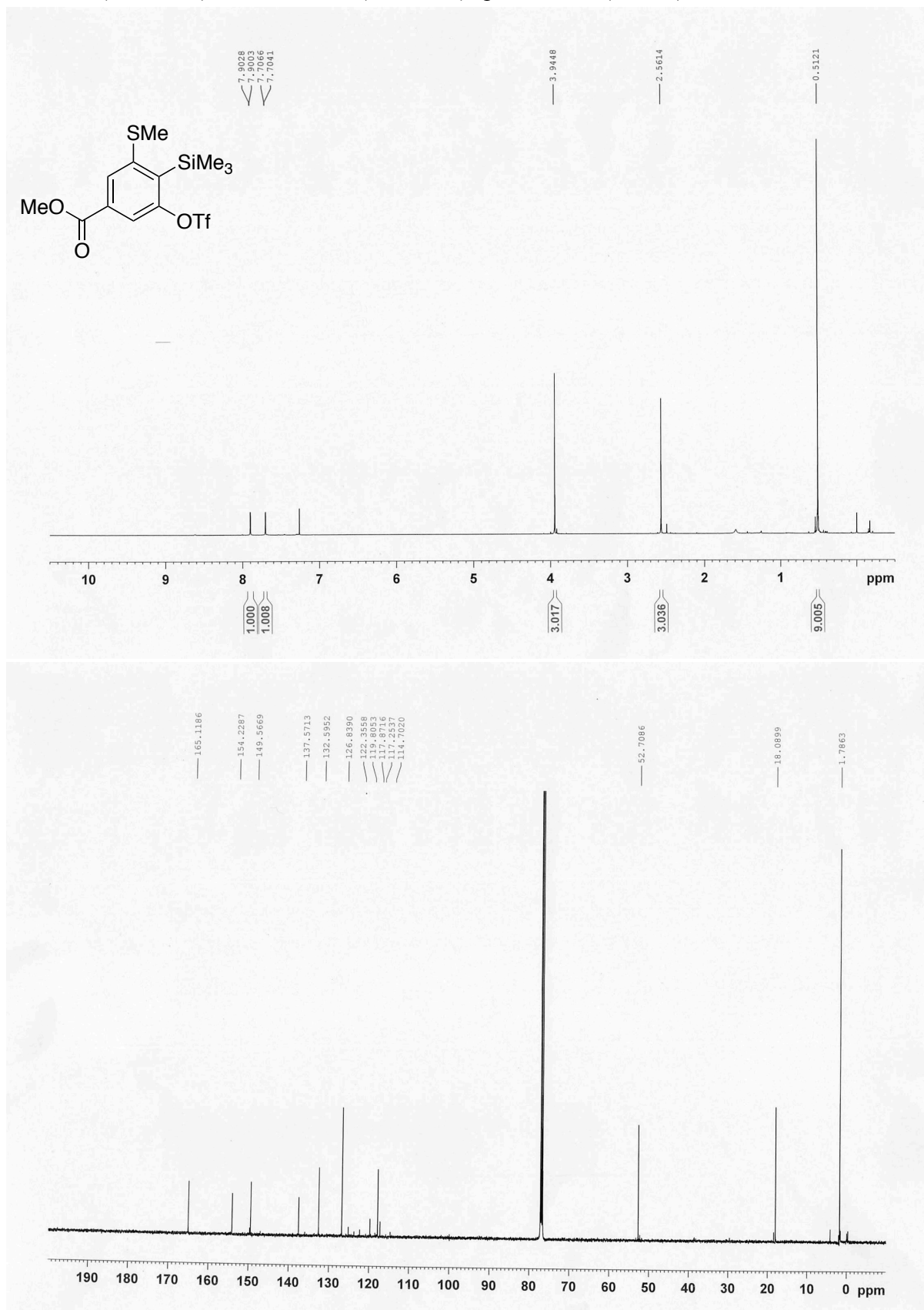
^1H NMR (500 MHz, benzene- d_6) and ^{13}C NMR (126 MHz, CDCl_3) spectra of **3j**



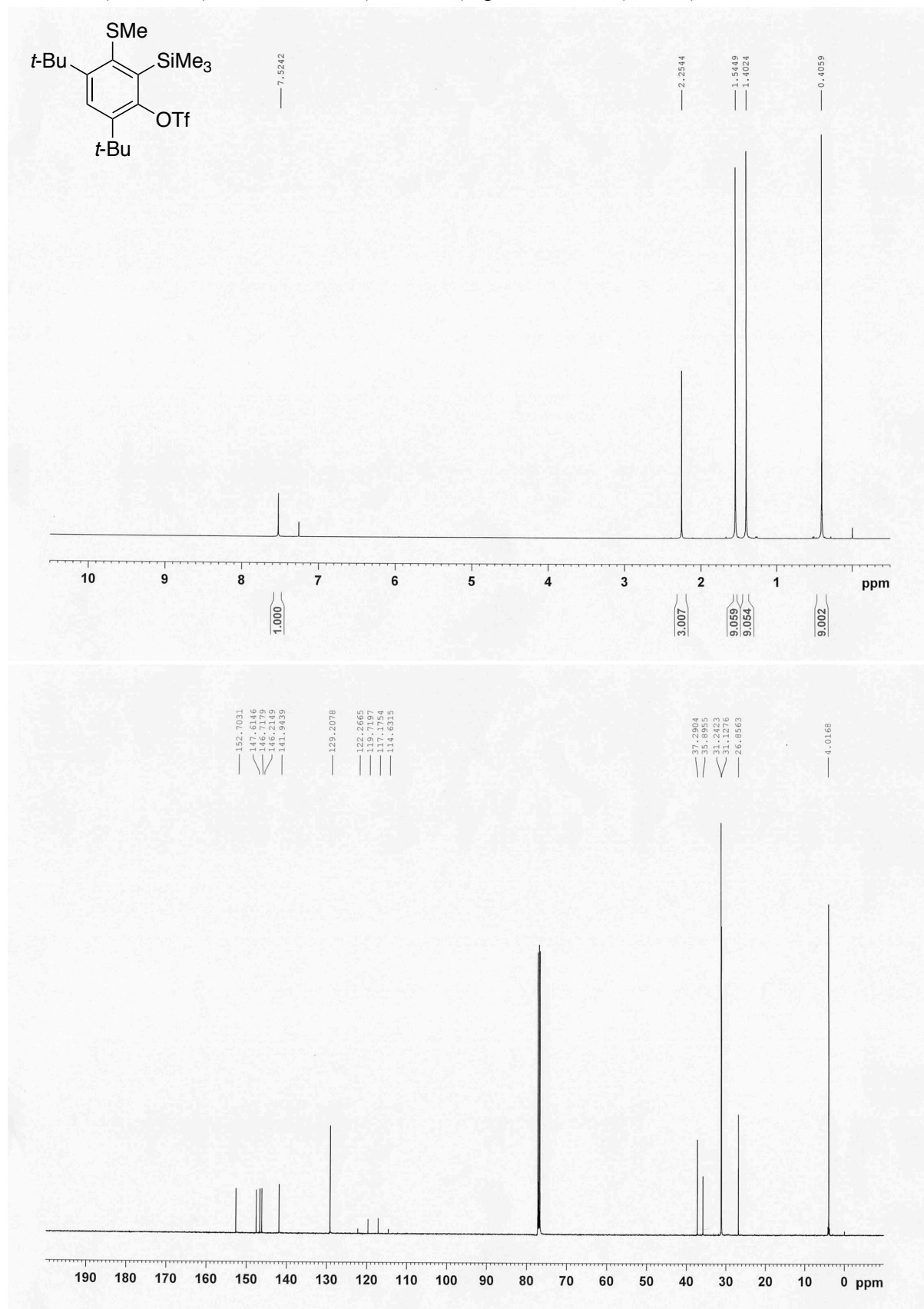
^1H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **3k** (CDCl_3)



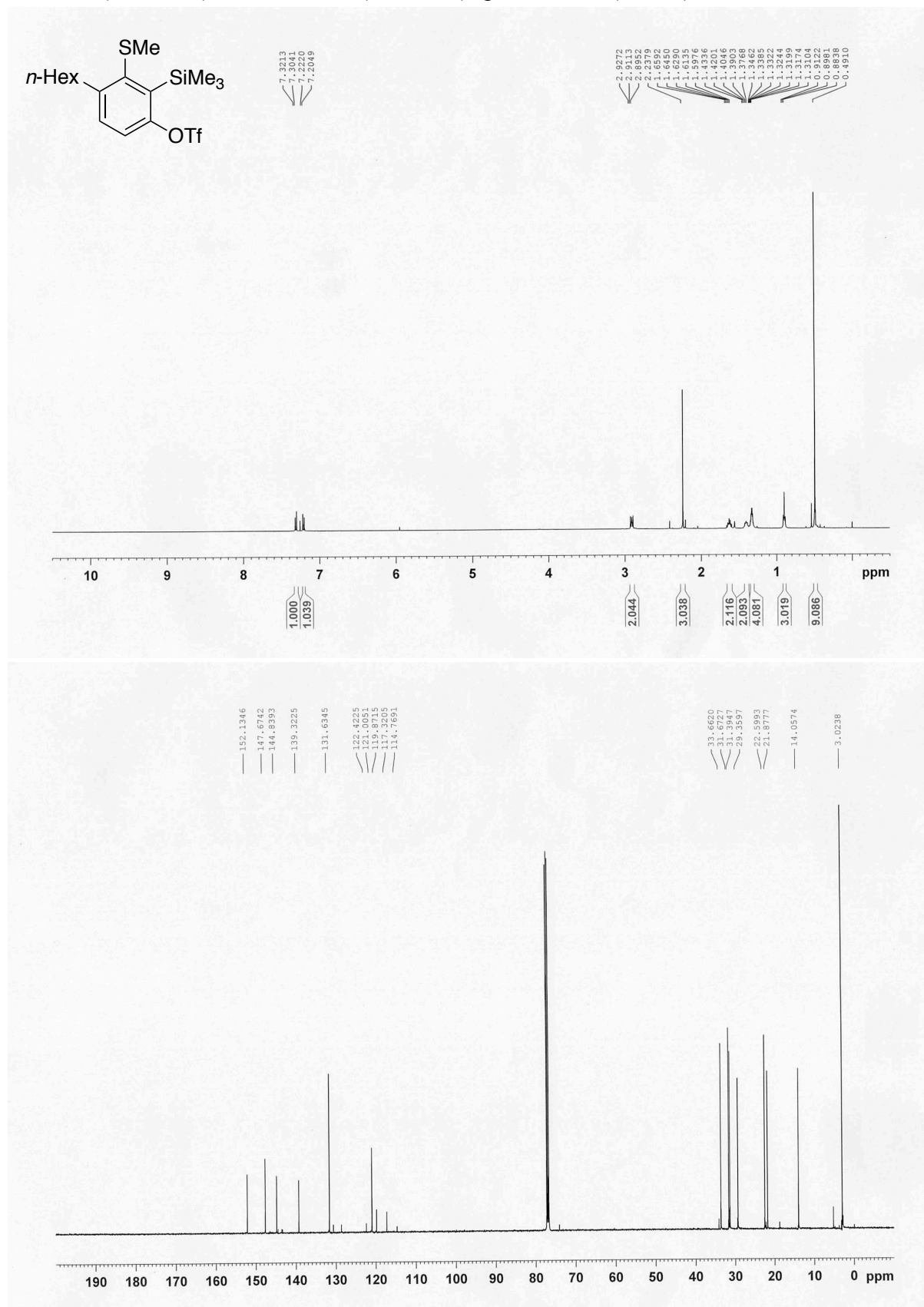
^1H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **3I** (CDCl_3)



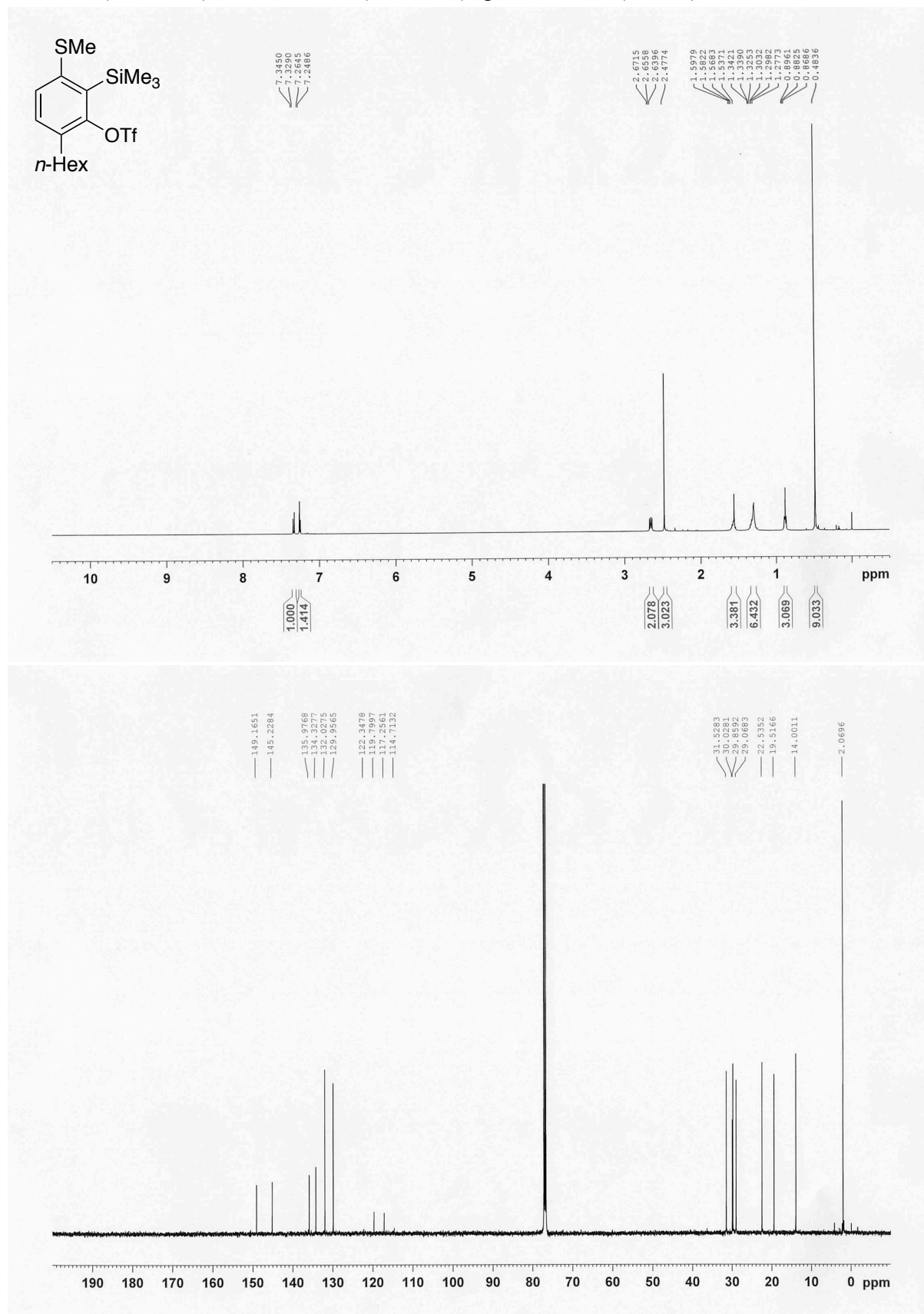
^1H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **3m** (CDCl_3)



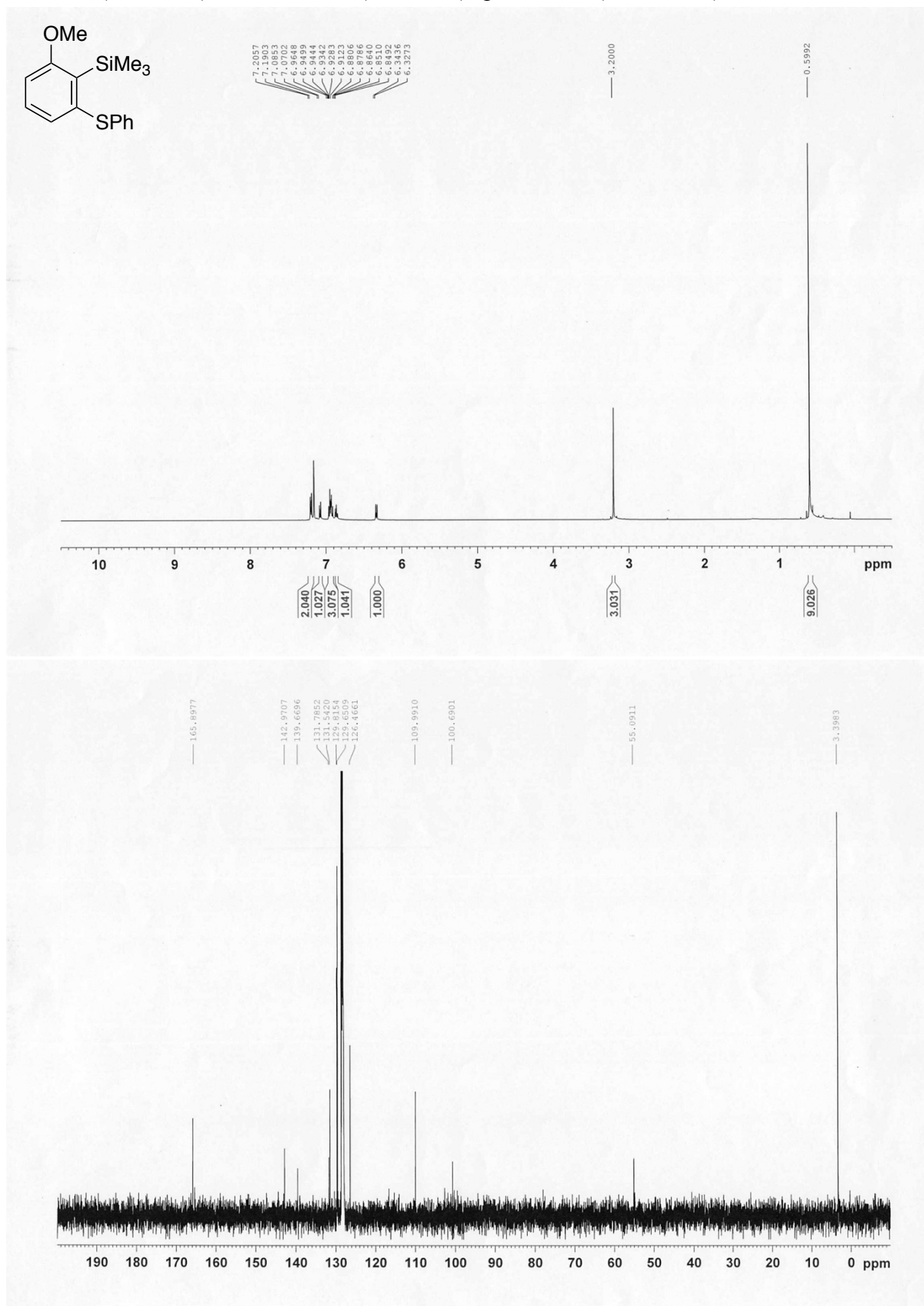
^1H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **3n** (CDCl_3)



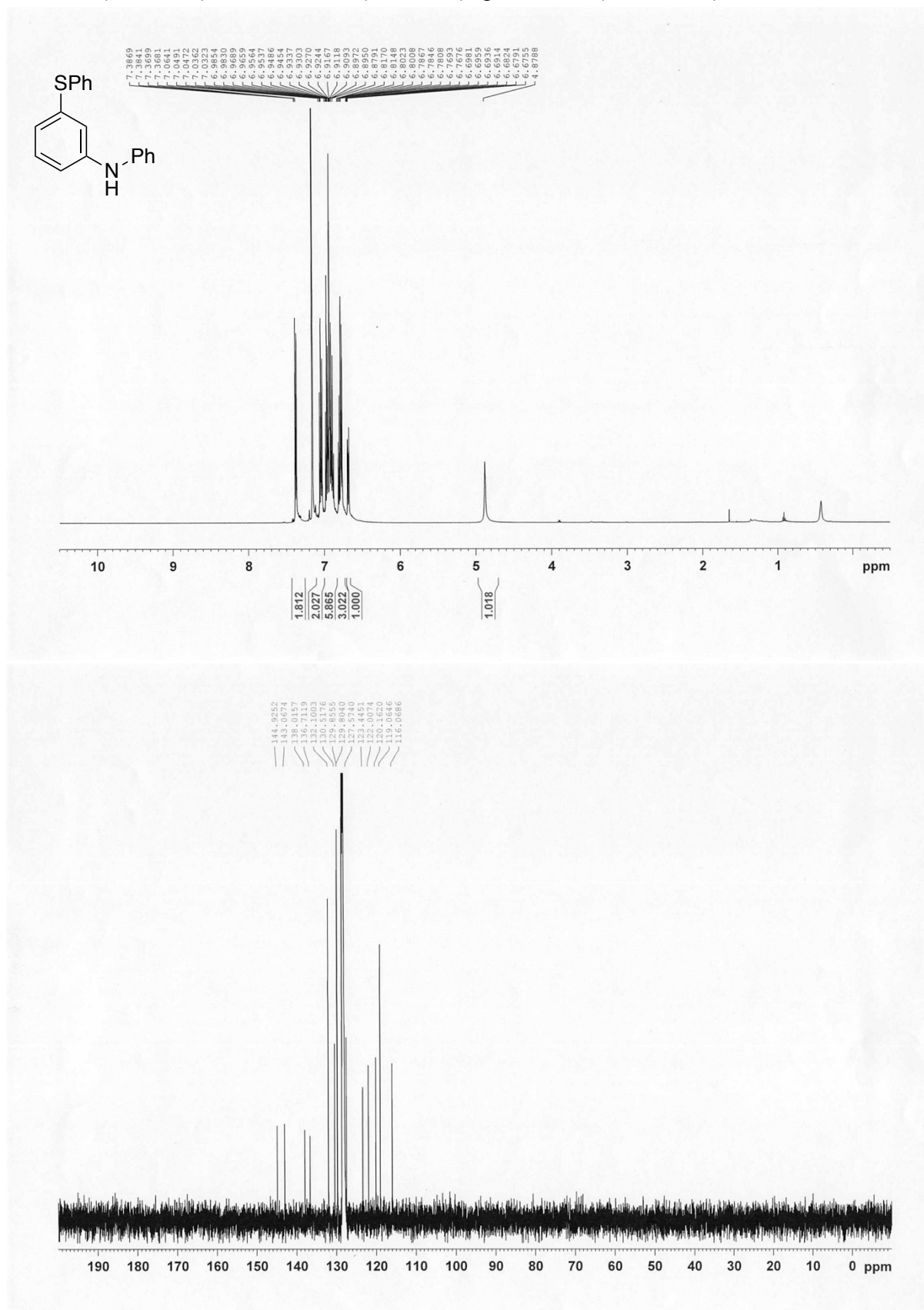
^1H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **3n'** (CDCl_3)



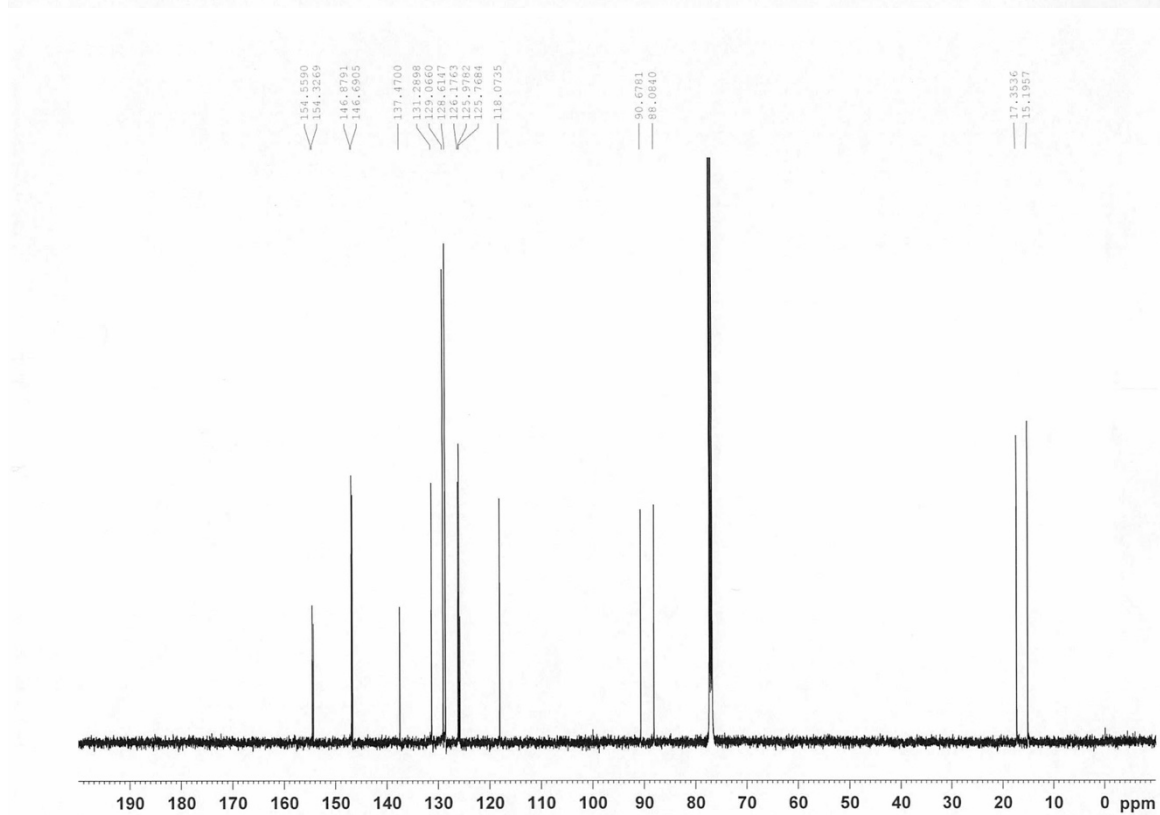
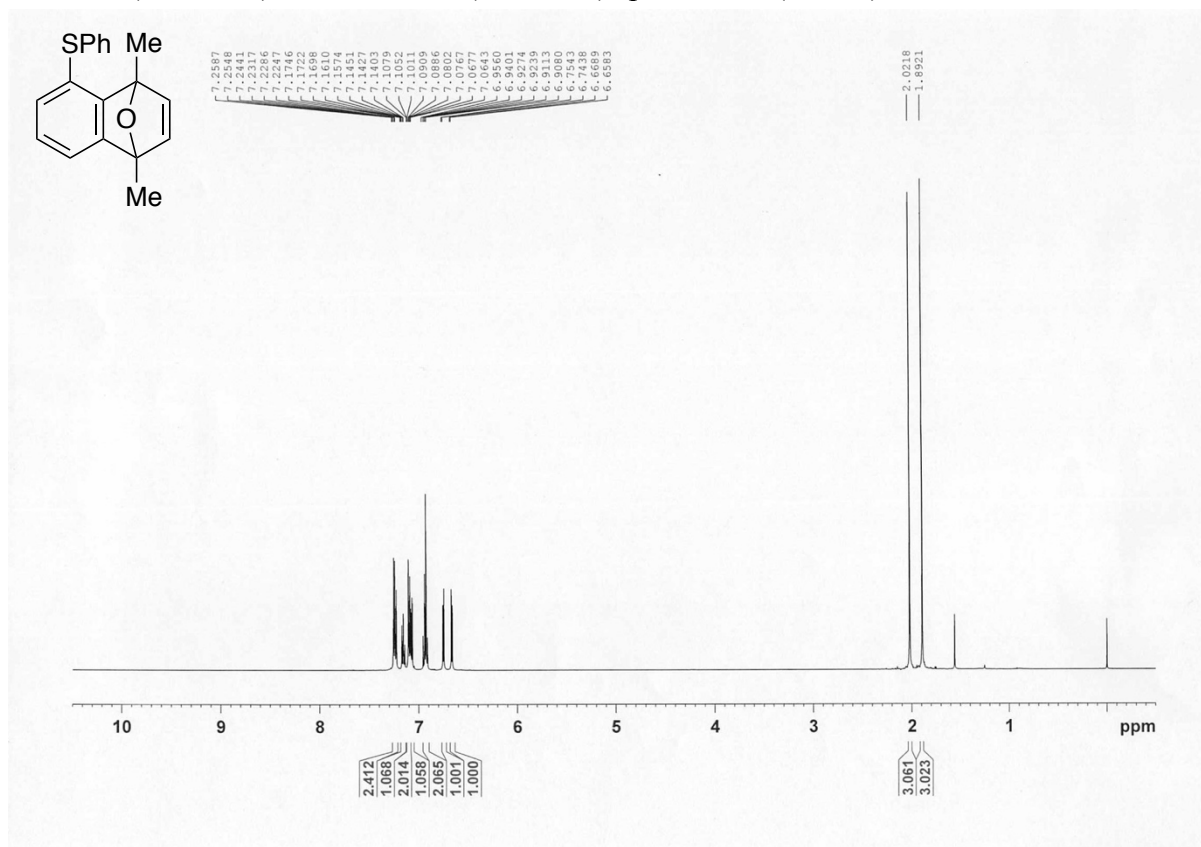
^1H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **5** (benzene- d_6)



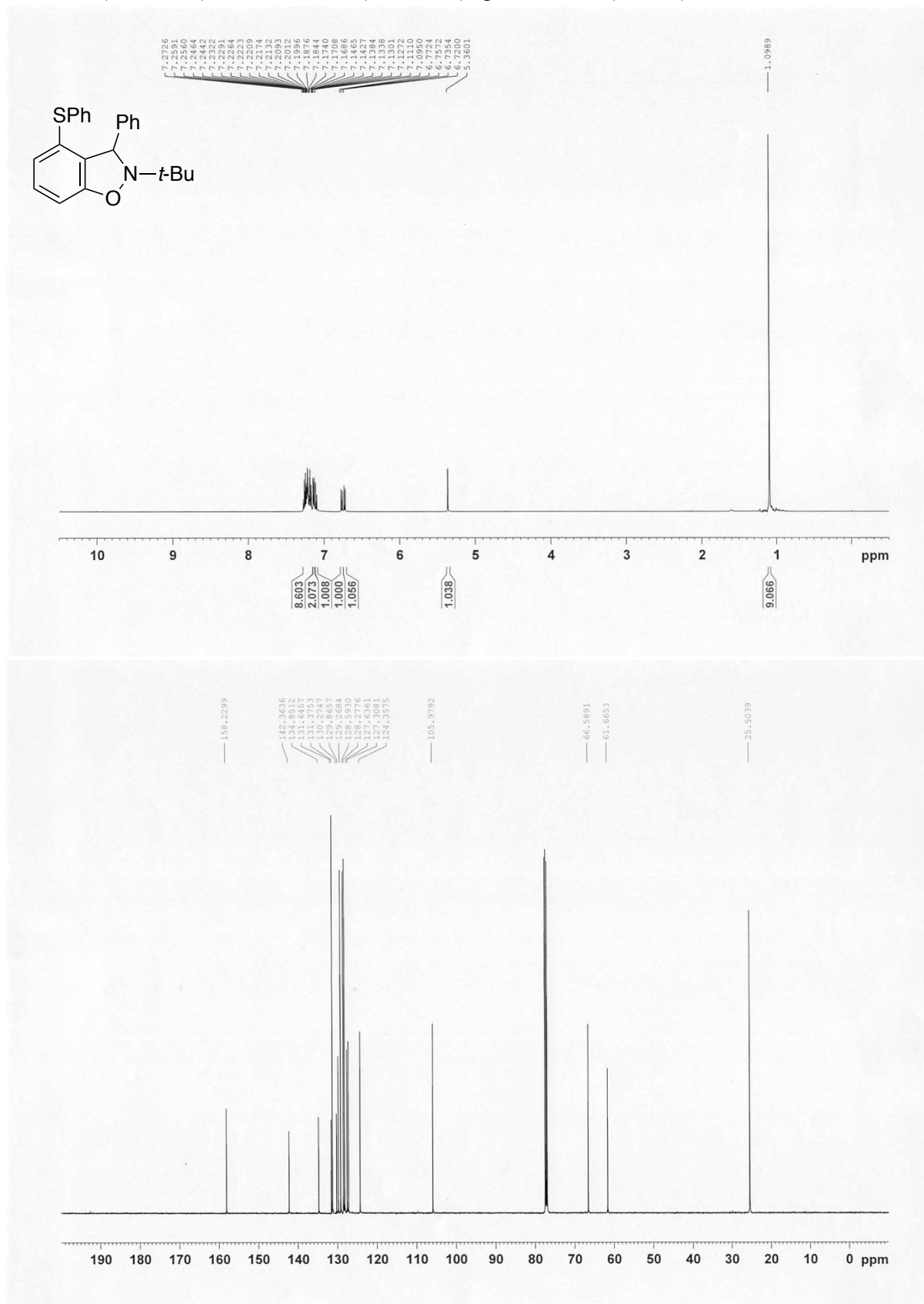
^1H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **7** (benzene- d_6)



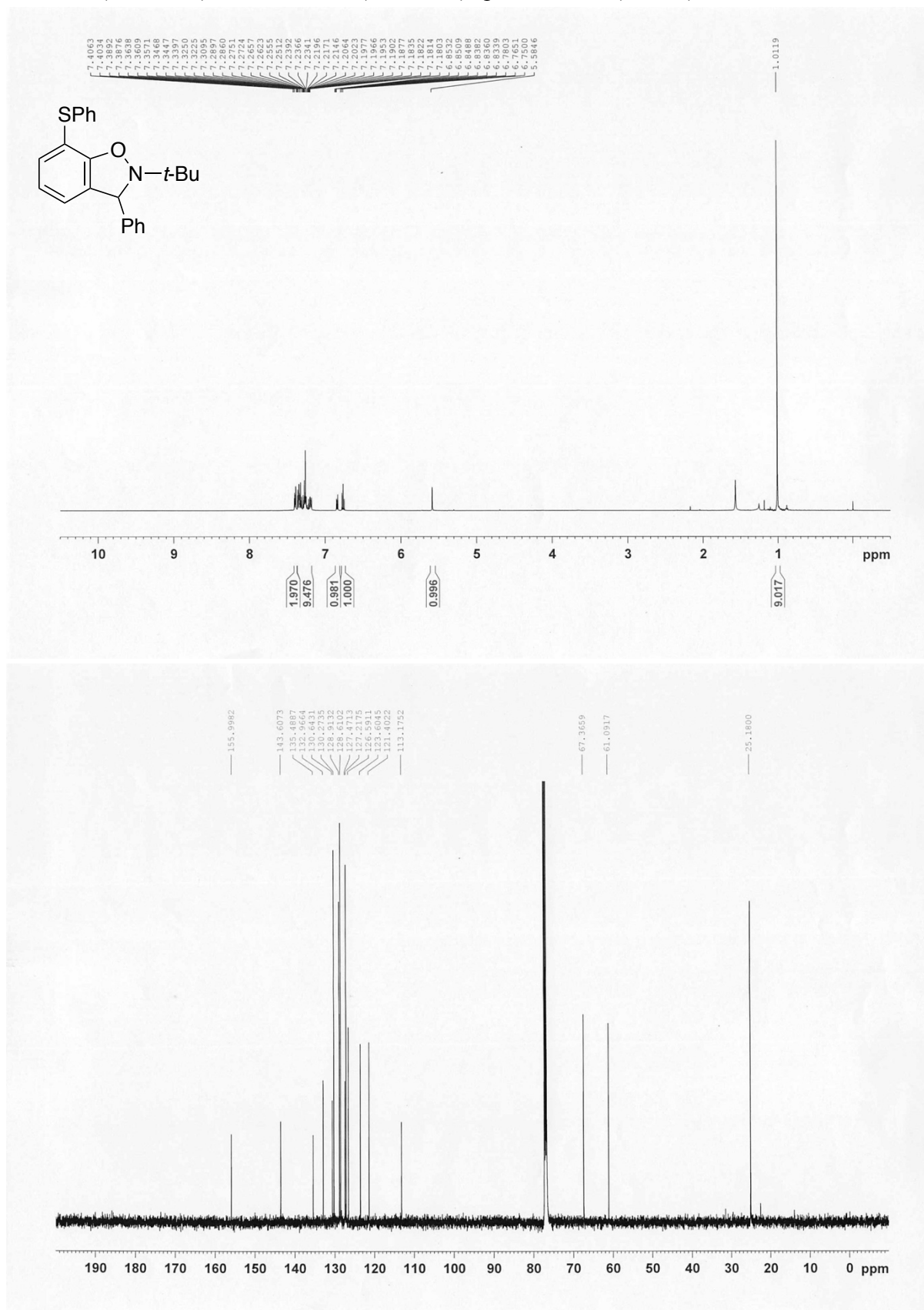
^1H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **9** (CDCl_3)



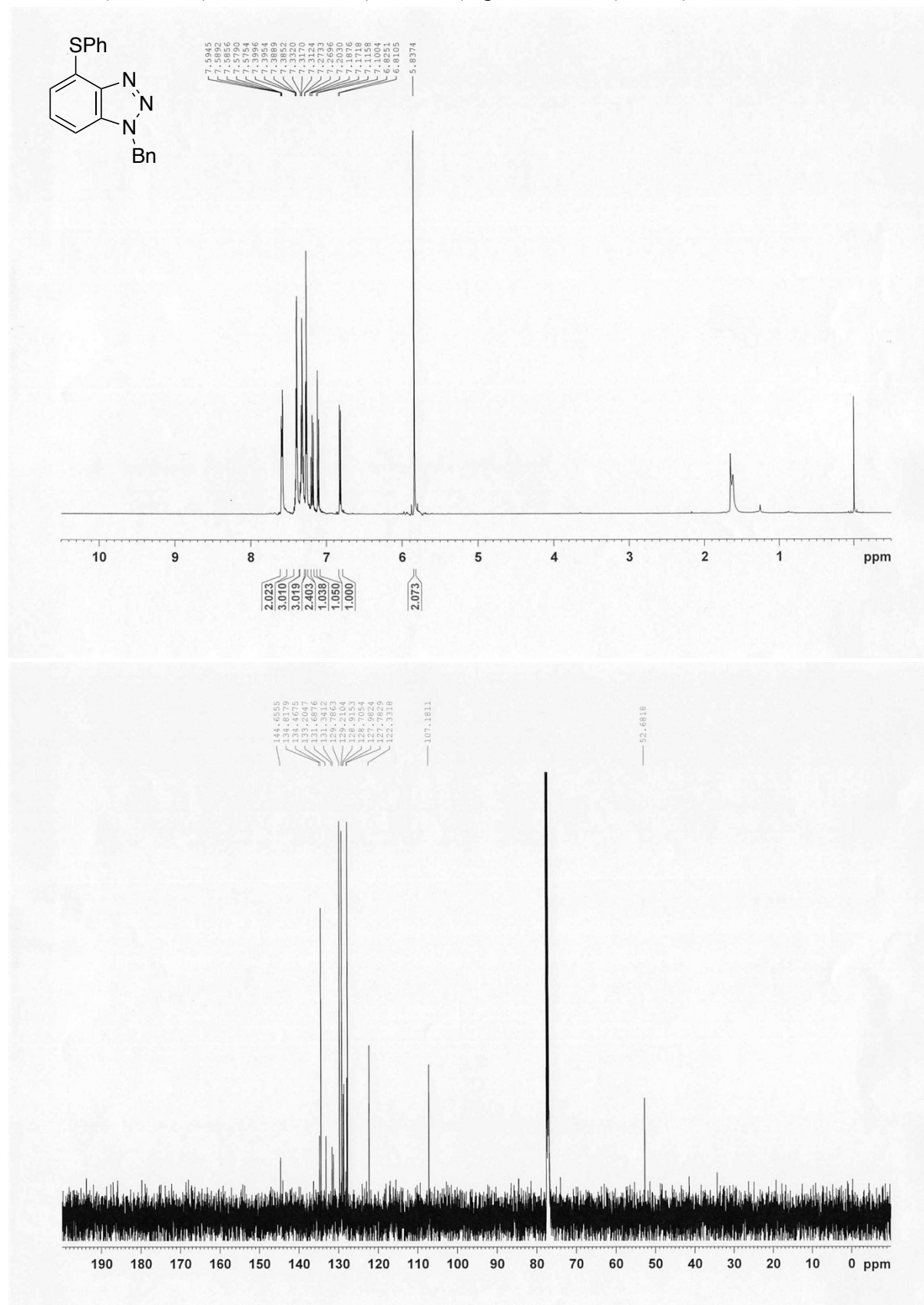
^1H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **11** (CDCl_3)



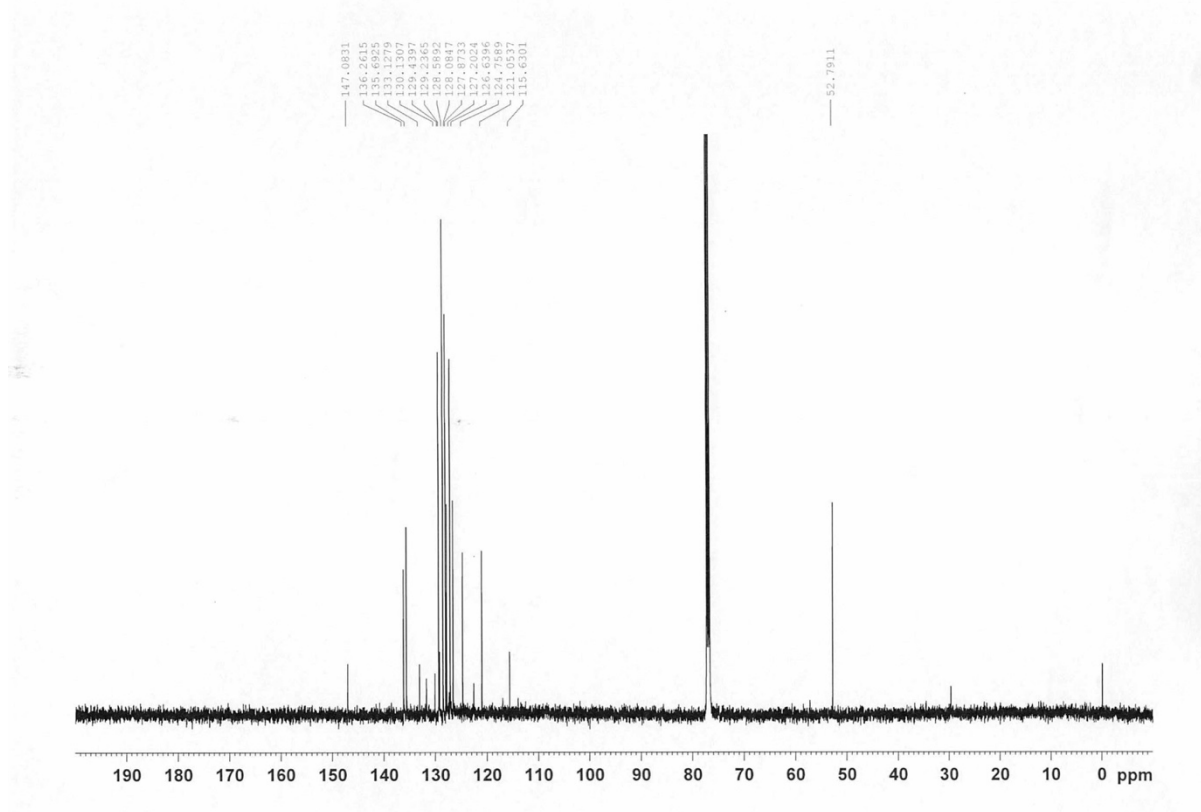
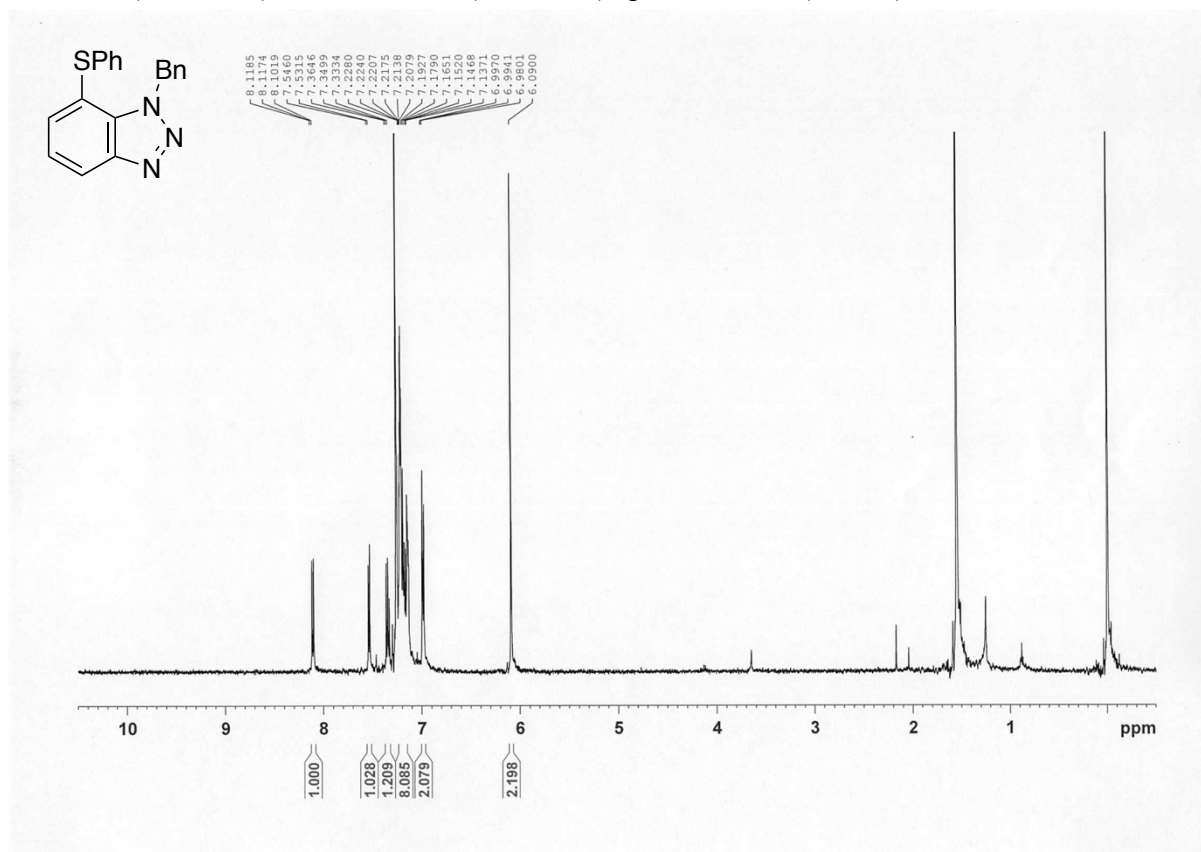
^1H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **11'** (CDCl_3)



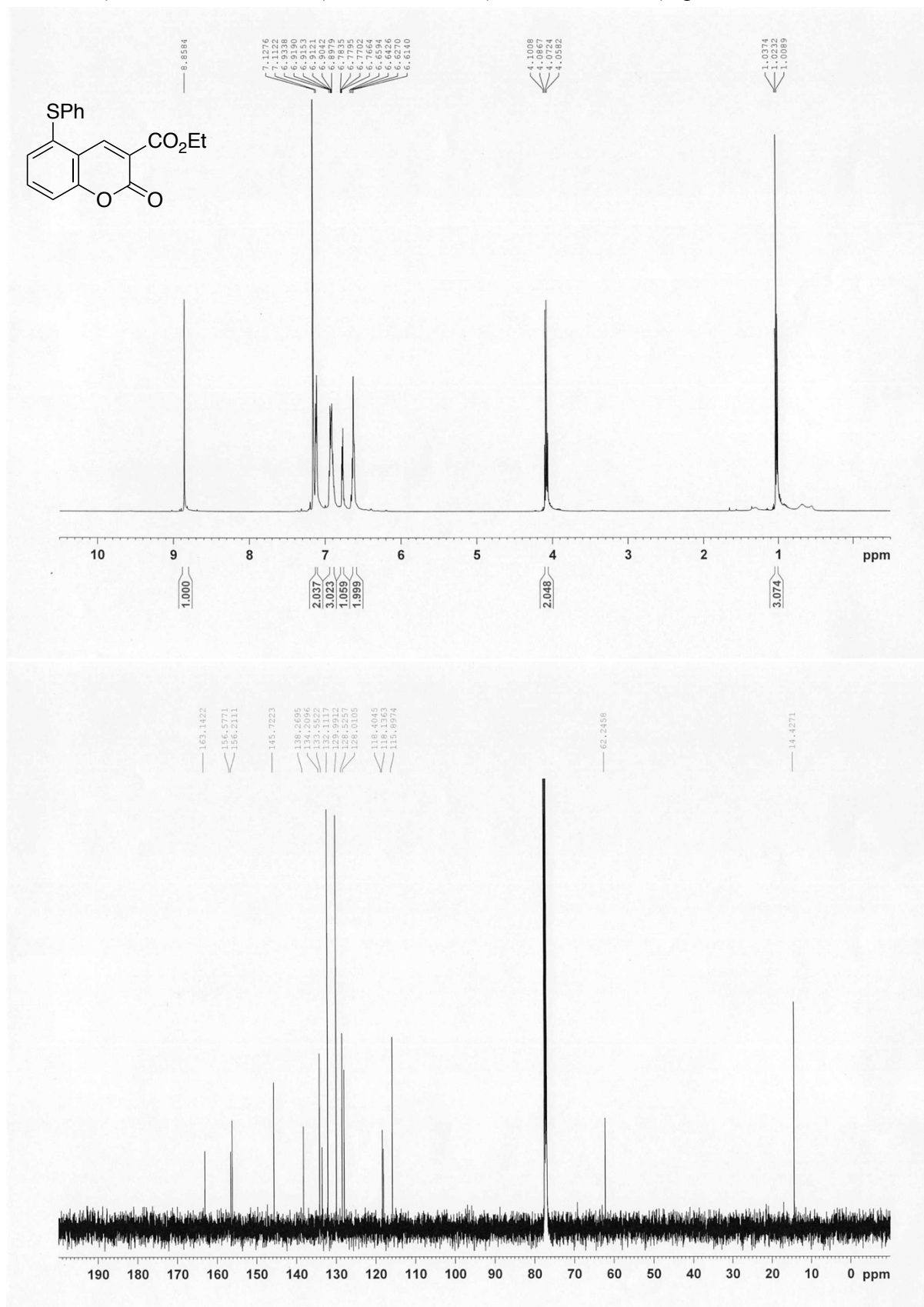
^1H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **13** (CDCl_3)



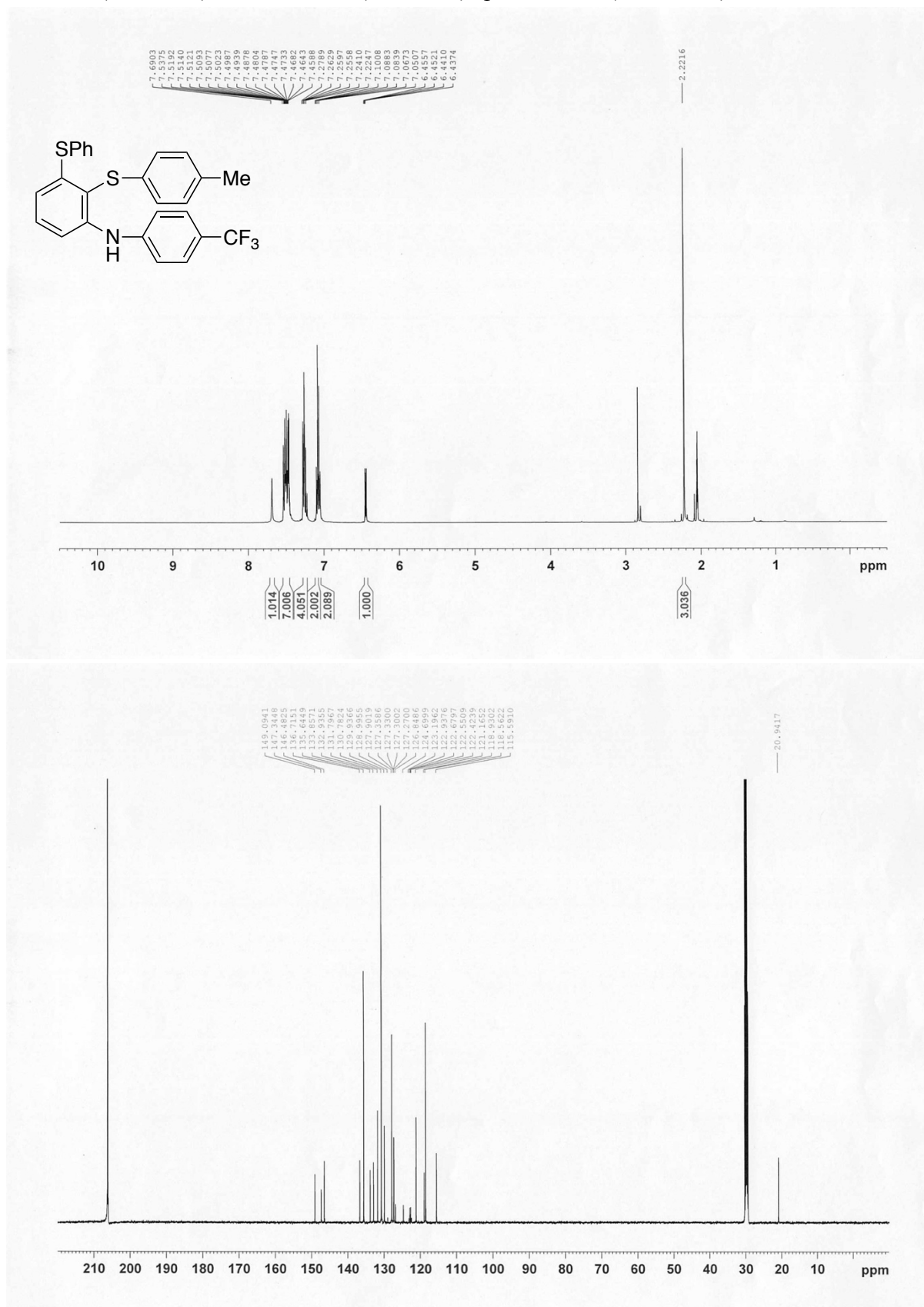
^1H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **13'** (CDCl_3)



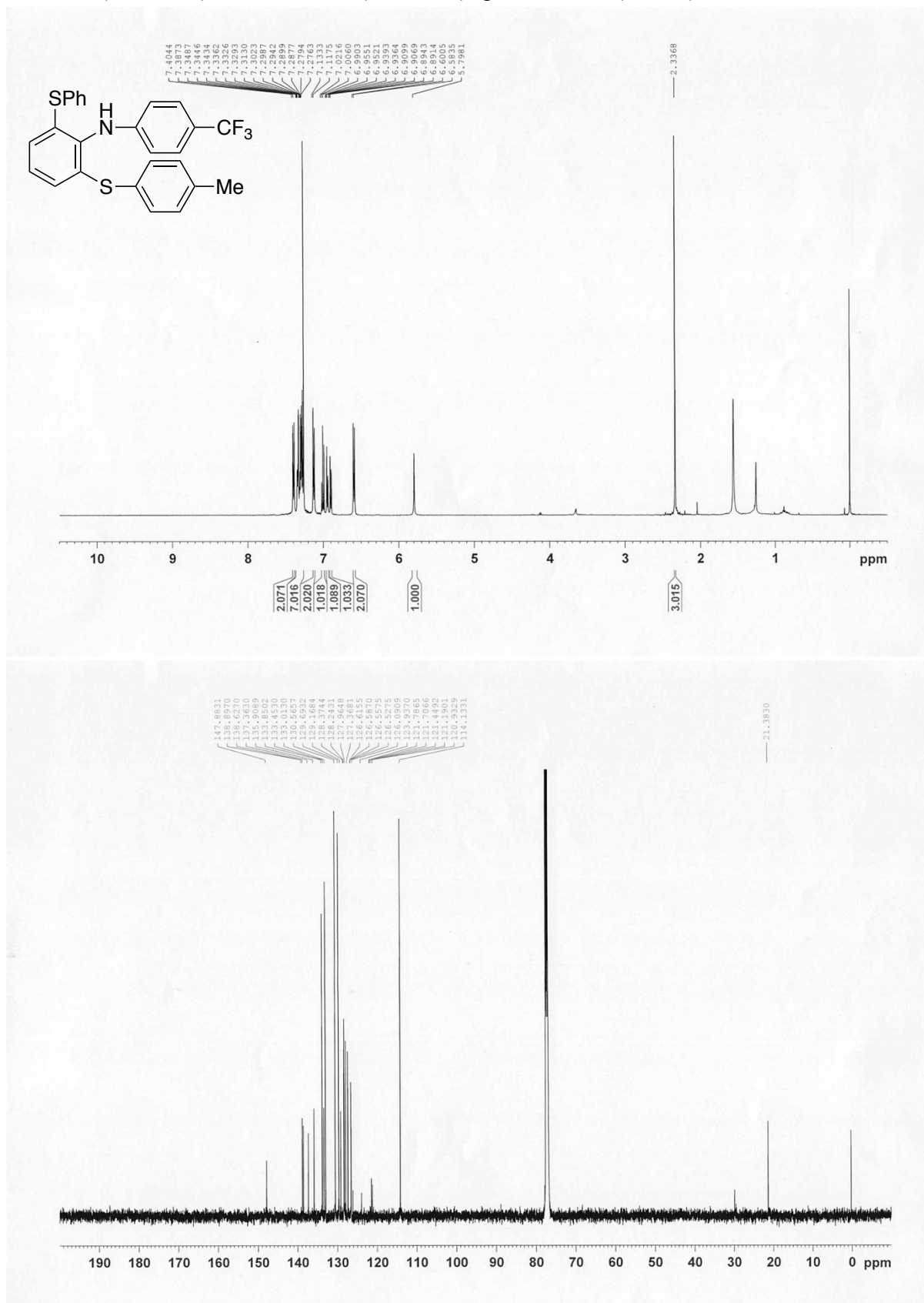
^1H NMR (500 MHz, benzene- d_6) and ^{13}C NMR (126 MHz, CDCl_3) spectra of **15**



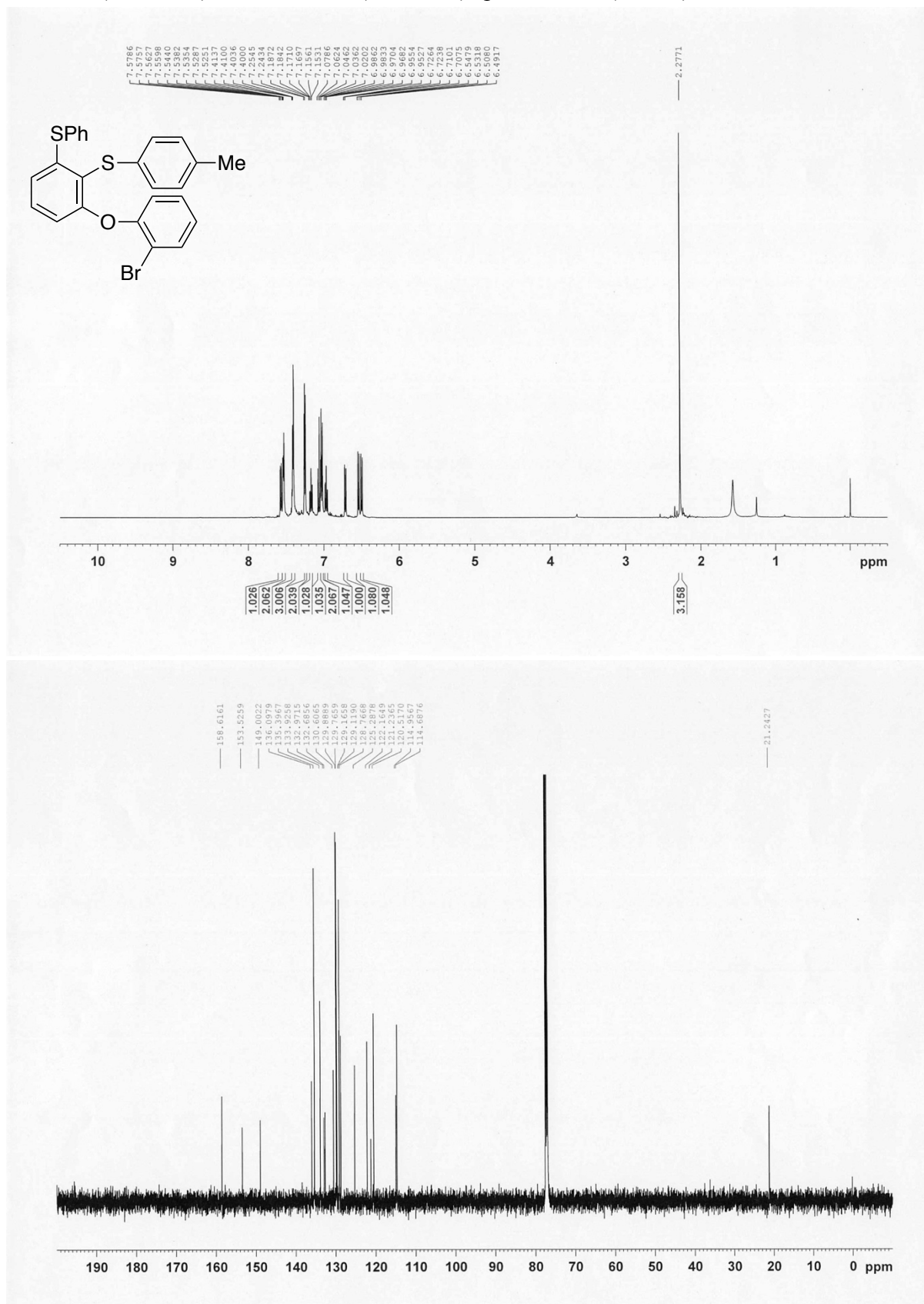
^1H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **17** (acetone- d_6)



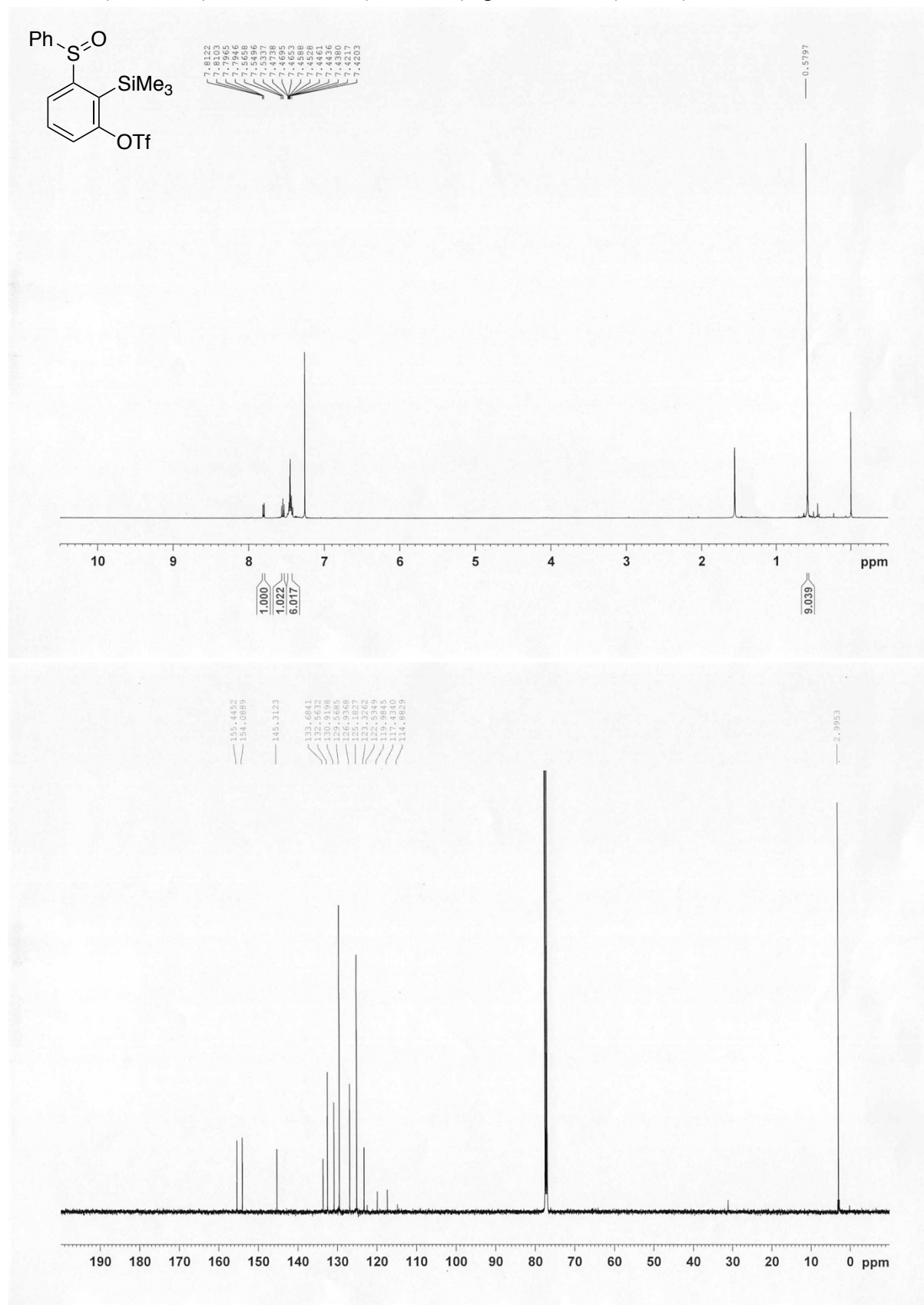
^1H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **17'** (CDCl_3)



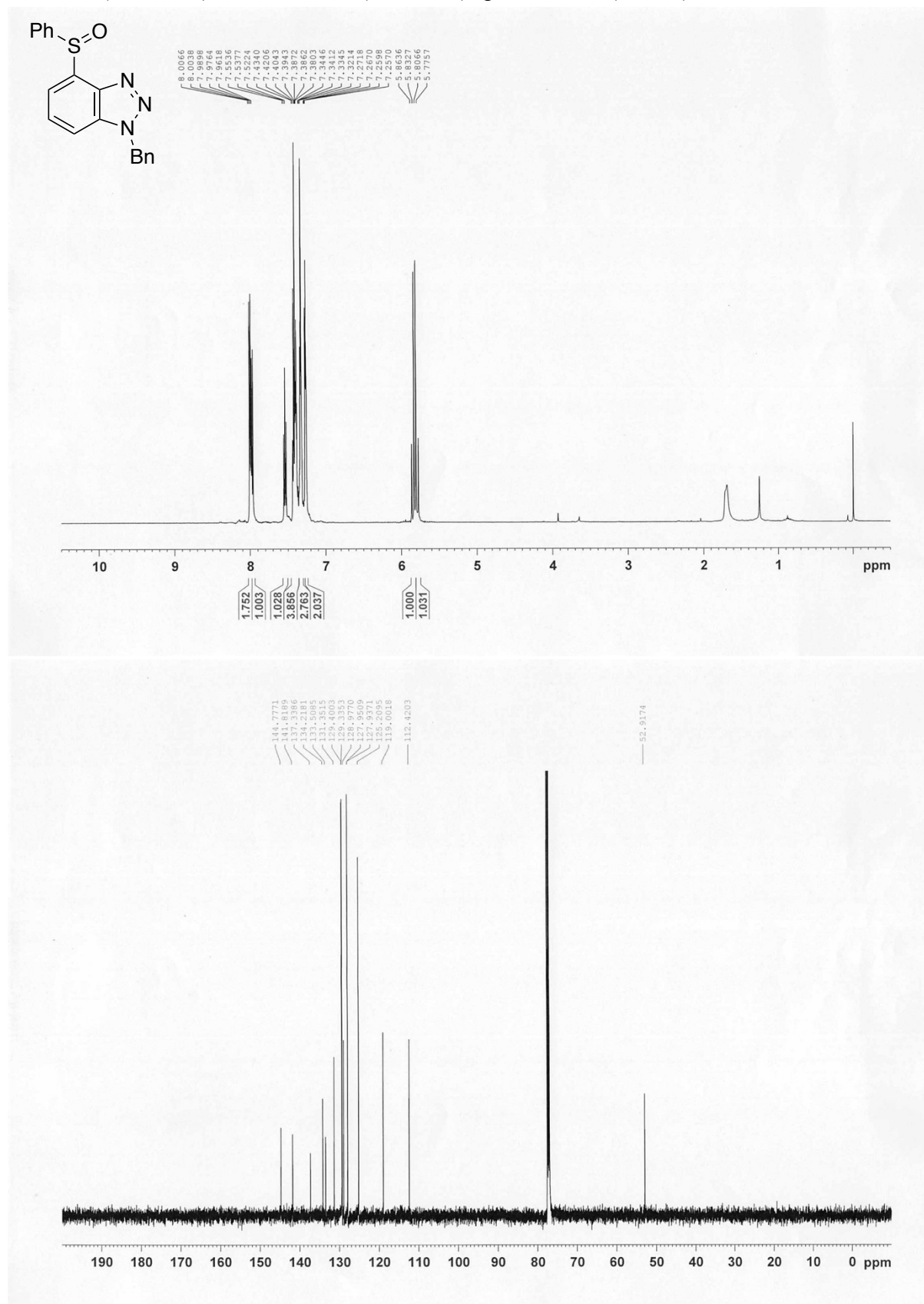
^1H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **19** (CDCl_3)



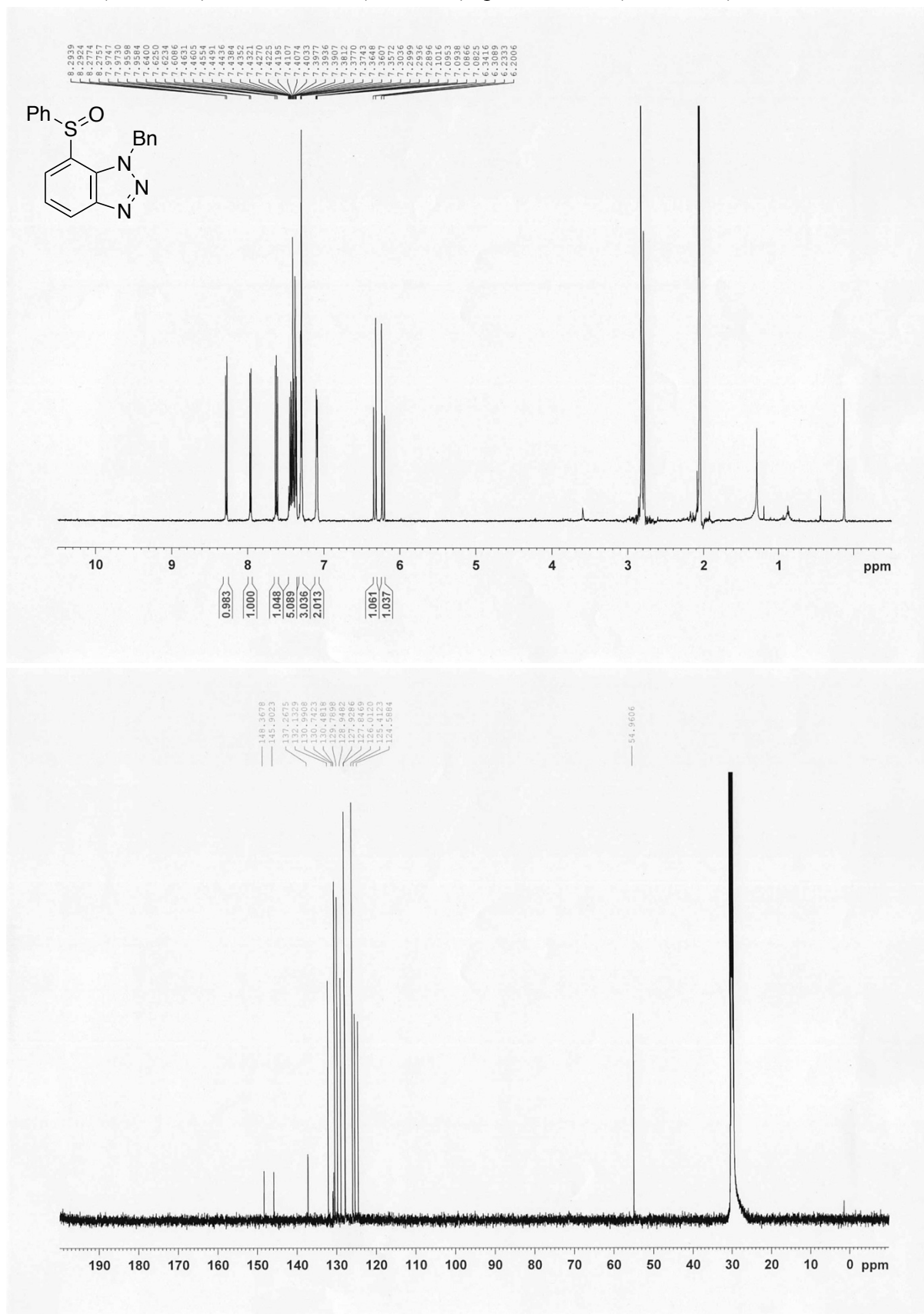
^1H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **20** (CDCl_3)



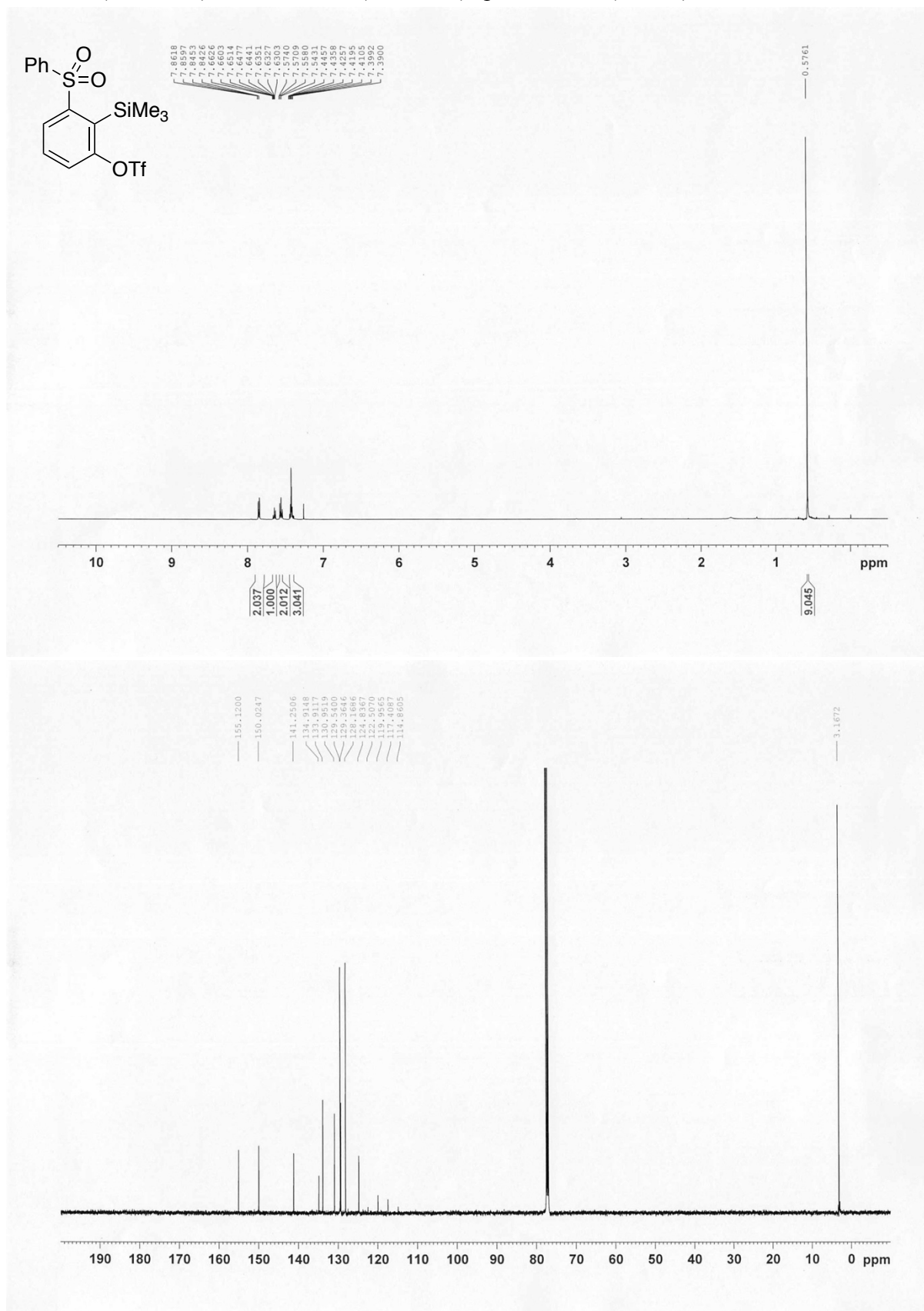
^1H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **21** (CDCl_3)



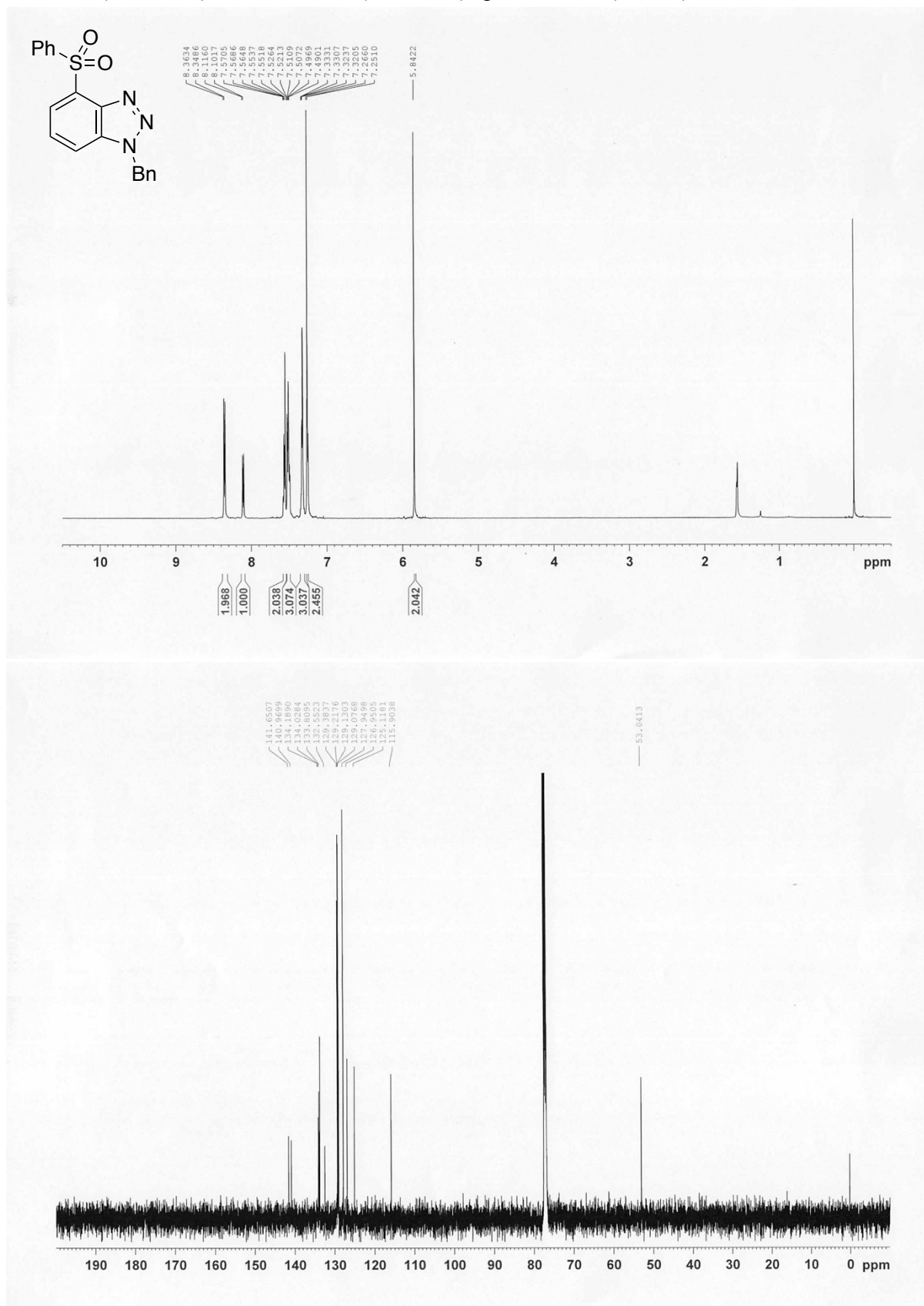
^1H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **21'** (acetone- d_6)



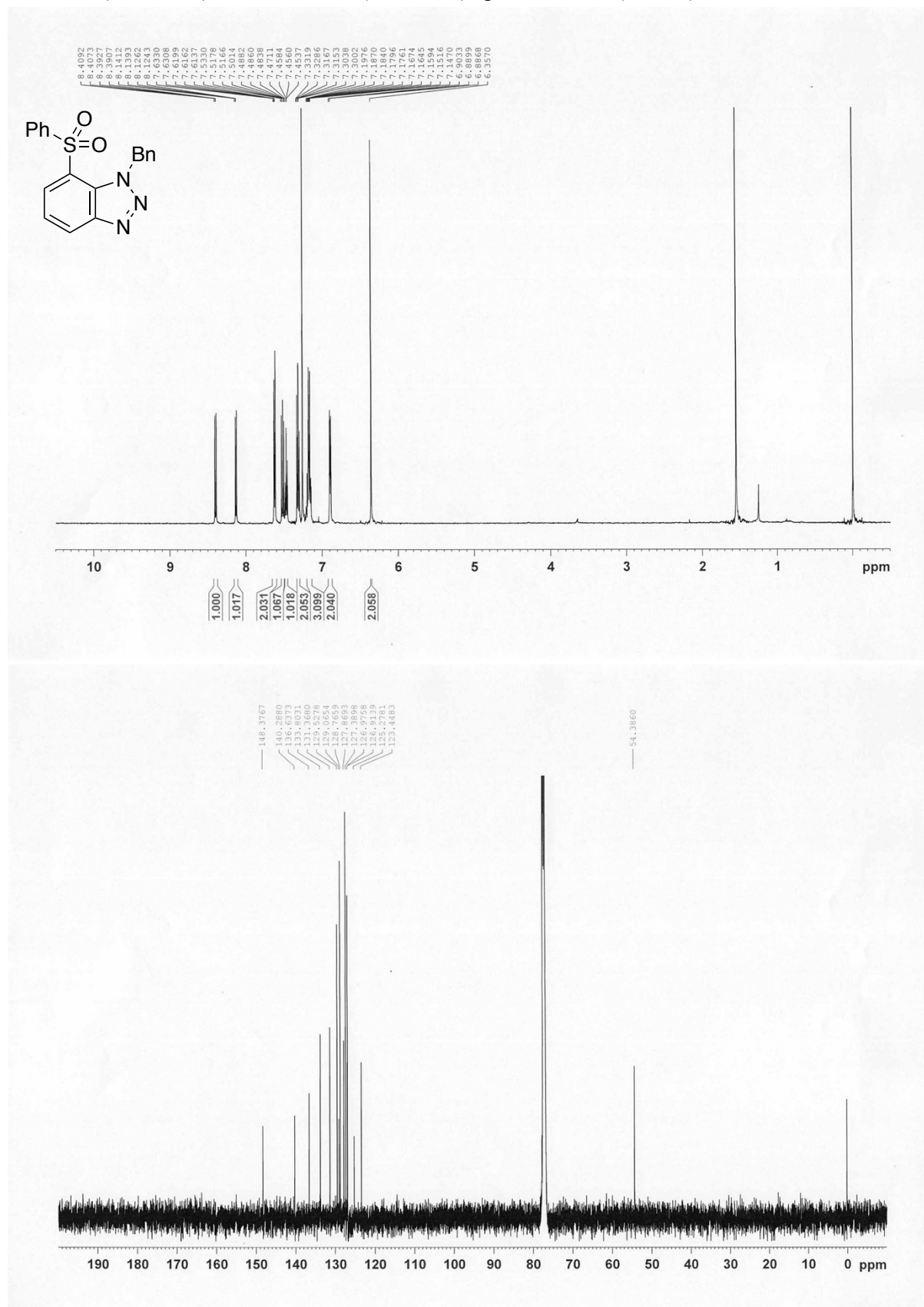
^1H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **22** (CDCl_3)



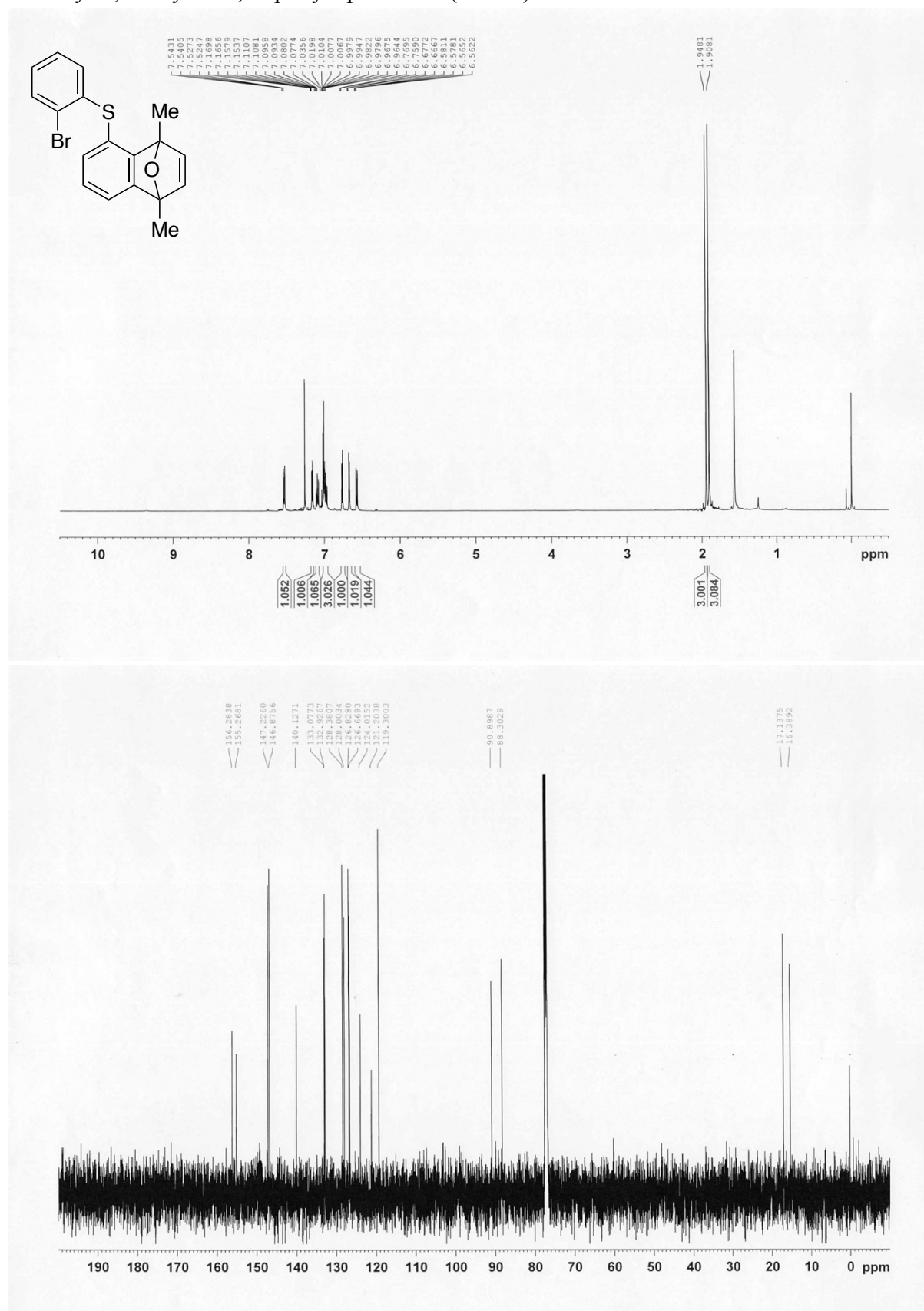
^1H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **23** (CDCl_3)



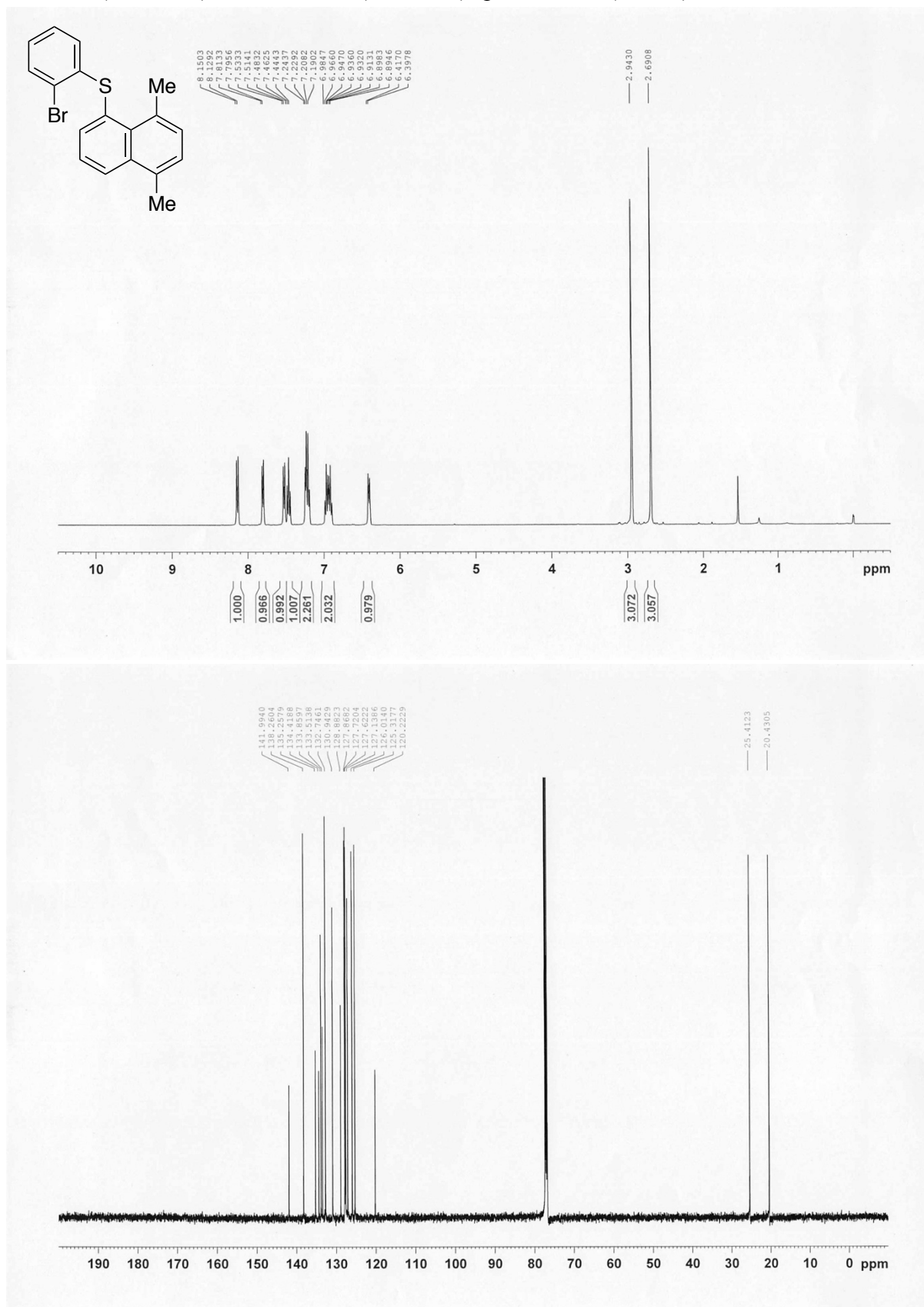
^1H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **23'** (CDCl_3)



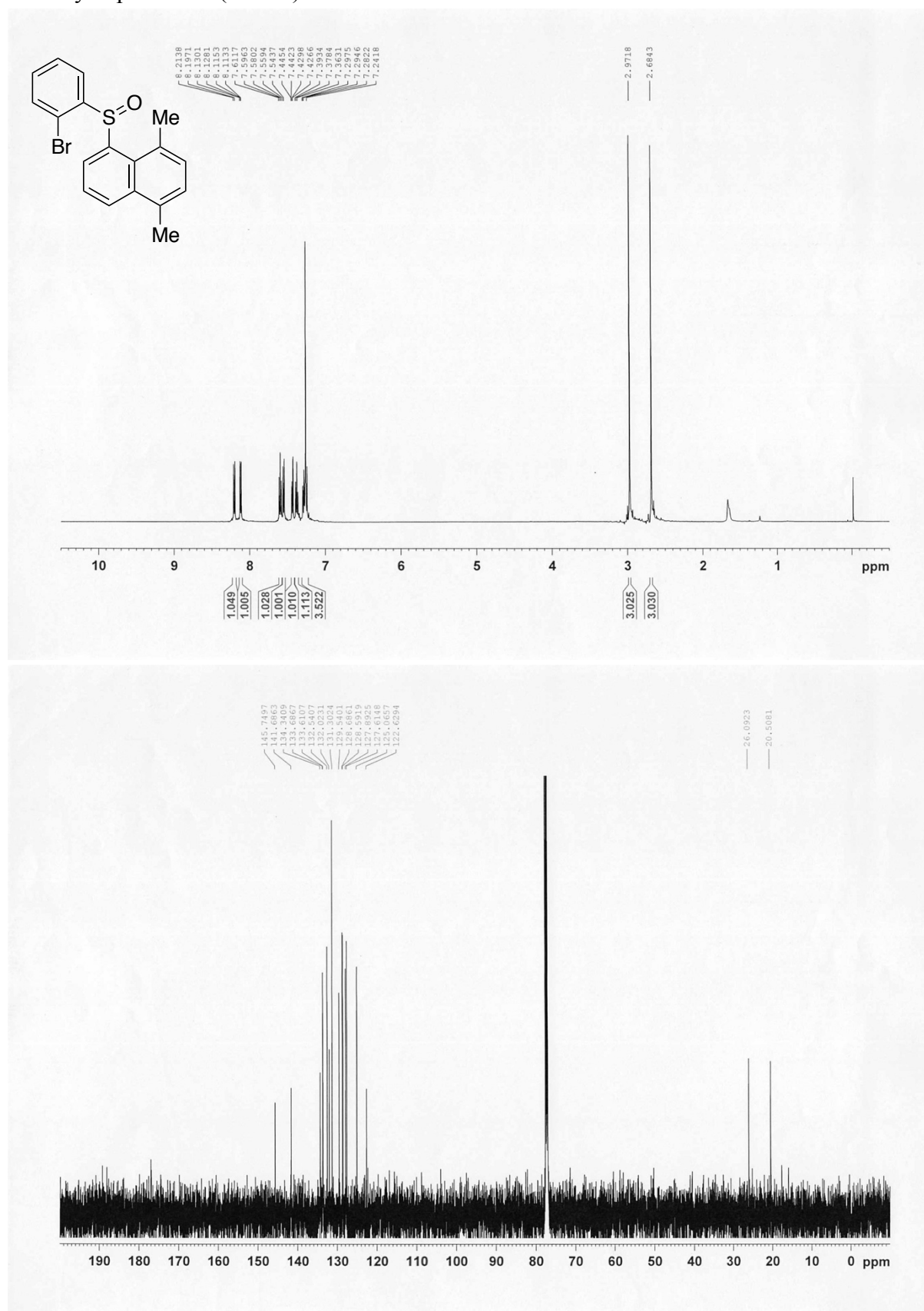
^1H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 5-((2-bromophenyl)thio)-1,4-dimethyl-1,4-dihydro-1,4-epoxynaphthalene (CDCl_3)



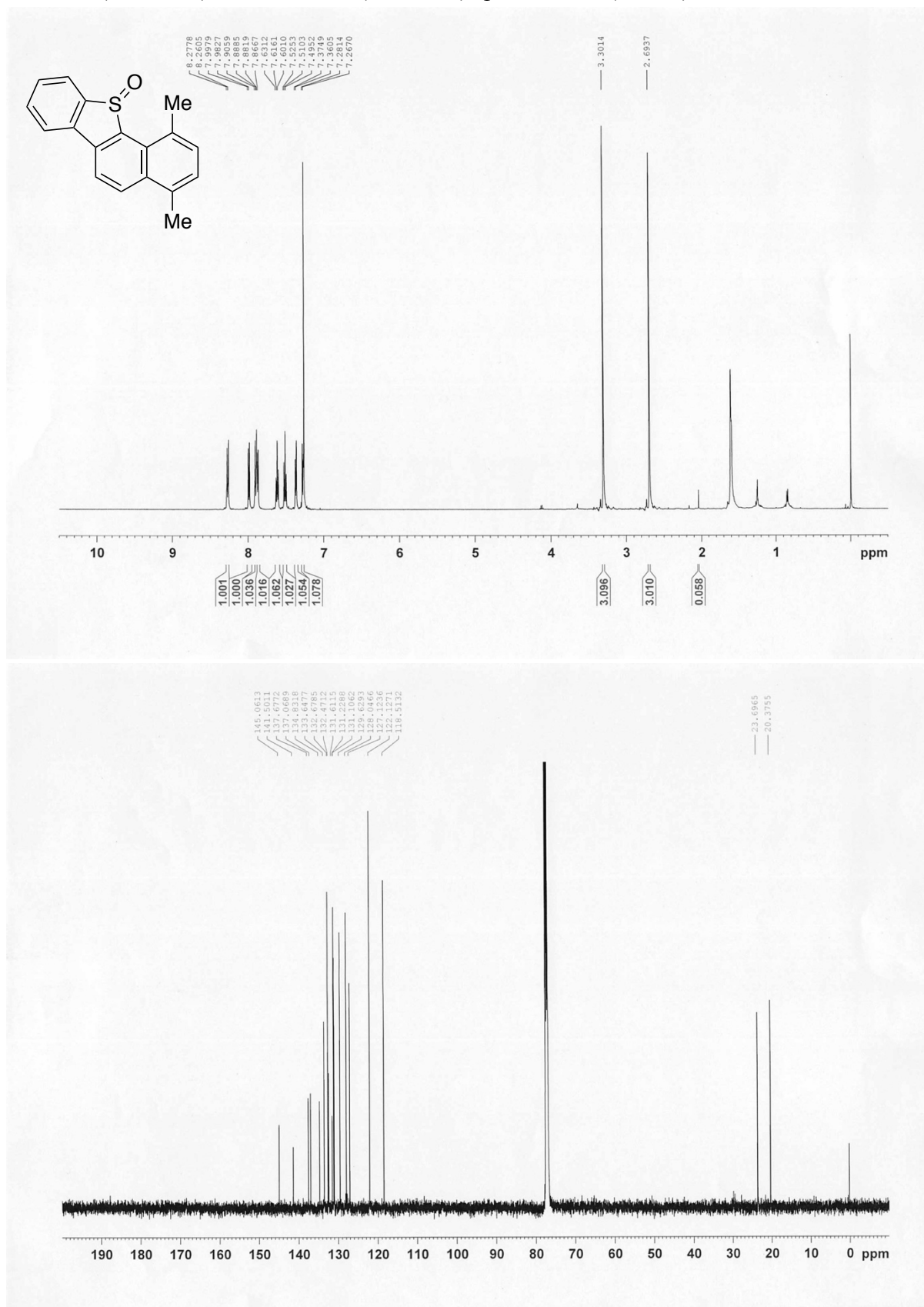
^1H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **24** (CDCl_3)



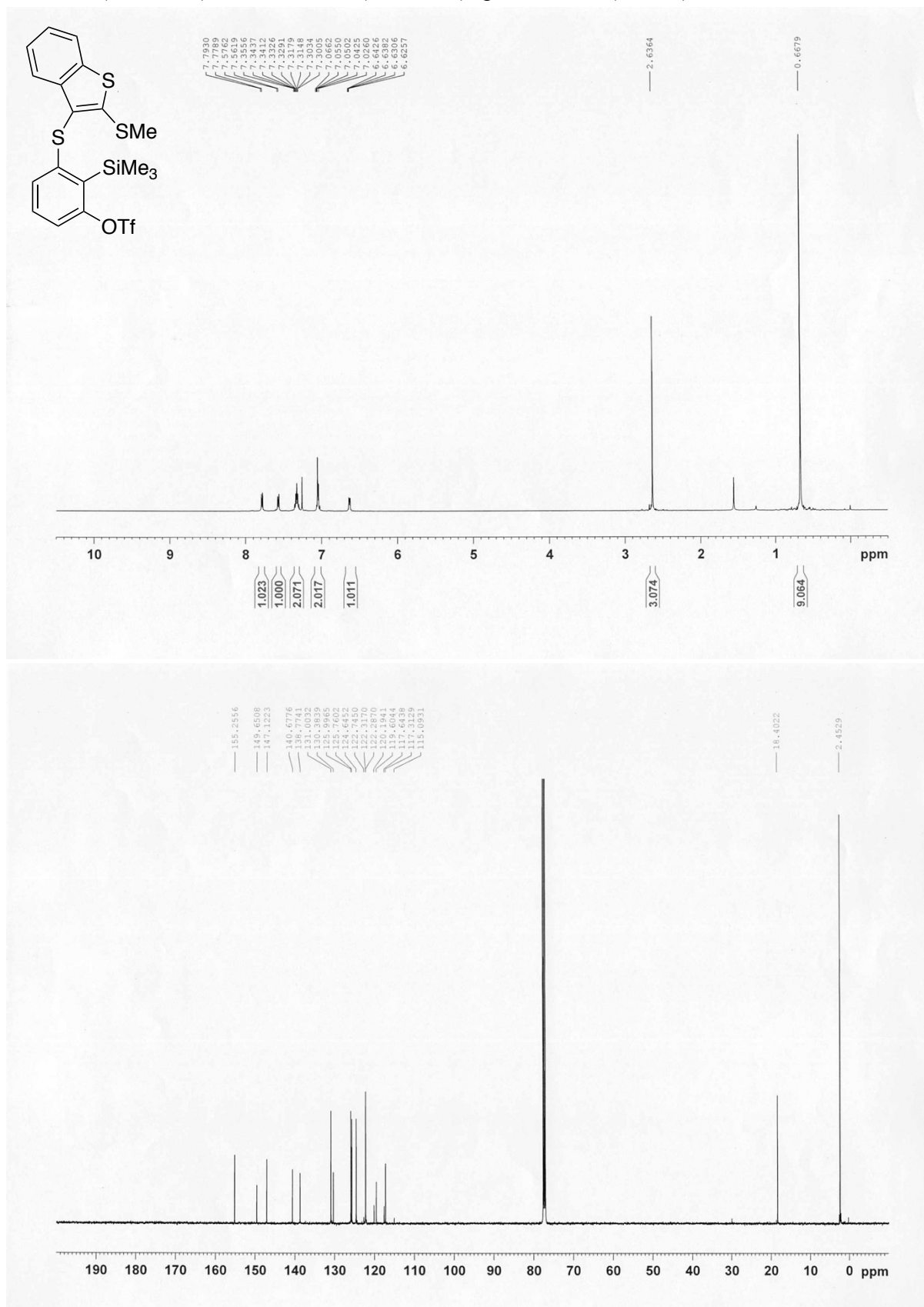
^1H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 5-((2-bromophenyl)sulfinyl)-1,4-dimethylnaphthalene (CDCl_3)



^1H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **25** (CDCl_3)



^1H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **27** (CDCl_3)



^1H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **28** (acetone- d_6)

