Supporting Information

Efficient generation method and remarkable reactivities of 3-triflyloxybenzyne

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Contents

General Remarks

All reactions were performed in a dry glassware under atmosphere of argon otherwise noted. Analytical thin-layer chromatography (TLC) was performed on precoated (0.25 mm) silica-gel plates (Merck Chemicals, Silica Gel 60 F_{254}, Cat. No. 1.05715). Column chromatography was conducted using silica-gel (Kanto Chemical Co., Inc., Silica Gel 60N, spherical neutral, particle size 40–50 μm, Cat. No. 37563-85 or particle size 63–210 μm, Cat. No. 37565-85). Preparative thin-layer chromatography (PTLC) was performed on silica-gel (Wako Pure Chemical Industries Ltd., Wakogel B5-F, Cat. No. 230-00043). Melting points (Mp) were measured on a YANACO MP-J3 instrument or an OptiMelt MPA100 (Stanford Research Systems), and are uncorrected. ^{1}H and ^{13}C NMR spectra were obtained with a Bruker AVANCE 500 spectrometer at 500 or 126 MHz, respectively. ^{19}F NMR spectra were obtained with a Bruker AVANCE 400 spectrometer at 376 MHz. ^{31}P NMR spectra were obtained with a Bruker AVANCE 400 spectrometer at 162 MHz. $CDCl_3$ (Acros Organics, Cat. No. 368651000) or C_6D_6 (Kanto Chemical Co. Inc., Cat. No. 05081-43) was used as a solvent for obtaining NMR spectra. Chemical shifts (δ) are given in parts per million (ppm) downfield from $(CH_3)_4Si$ (δ 0.00 for ^{1}H NMR in $CDCl_3$) or the solvent peak (δ 77.0 for ^{13}C NMR in $CDCl_3$, and δ 7.15 for ^{1}H NMR and δ 128.0 for ^{13}C NMR in C_6D_6) as an internal reference, or α,α,α-trifluorotoluene (δ –63.0 ppm for ^{19}F NMR in $CDCl_3$) or phosphoric acid as (δ 0.00 ppm for ^{31}P NMR in D_2O) as an external standard with coupling constants (J) in hertz (Hz). The abbreviations s, d, t, q, m, and br signify singlet, doublet, triplet, quartet, multiplet, and broad, respectively. IR spectra were measured by diffuse reflectance method on a Shimadzu IRPrestige-21 spectrometer attached with DRS-8000A with the absorption band given in cm^{-1}. High-resolution mass spectra (HRMS) were measured on a Bruker micrOTOF mass spectrometer under positive electrospray ionization (ESI^+) conditions. Elemental analyses were carried out at A Rabbit Science Japan Co., Ltd. X-ray crystallographic data was collected on a Rigaku R-AXIS RAPID diffractometer with graphite monochromated Cu-Kα radiation (λ = 1.54187 Å) at 123 K. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre (CCDC) via www.ccdc.cam.ac.uk/data_request/cif.

Tetrahydrofuran (THF) (Cat. No. 41001-84), diethyl ether (Et_2O) (Cat. No. 14547-84), tripotassium phosphate *n*-hydrate (Cat. No. 32380-30) and *n*-butyllithium (1.6 M, hexane solution, Cat. No. 04937-05) were purchased from Kanto Chemical Co. Inc. Magnesium turnings (19108-5000) was purchased from Acros Organics. Tetraphenylcyclopentadienone (**10**) (Cat. No. 326-46632), benzyl azide (**12**) (Cat. No. 327-79632), 4-methylphenylboronic acid (Cat. No. 321-63302), diphenyl sulfide (Cat. No. 162-12562), triphenylphosphine (Cat. No. 204-03061), isopropylmagnesium chloride lithium chloride complex (abt. 14%, THF solution, Cat. No. 095-06431) and 1,4-dioxane (Cat. No. 042-03766) were purchased from Wako Pure Chemical Industries Ltd. 1-Phenylpyrrole (**8**) (Cat. No. 131474), 1-(*tert*-butyldimethylsilyloxy)-1-

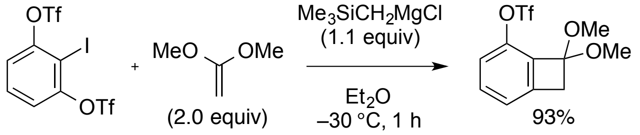
methoxyethene (**4**) (Cat. No. 519324), bromobenzene (Cat. No. 16350), ethylmagnesium bromide (3.0 M, Et_2O solution, Cat. No. 189871) and isopropylmagnesium chloride (2.0 M, THF solution, Cat. No. 230111) were purchased from Sigma–Aldrich Japan. *N*-*tert*–Butyl-α-phenylnitrone (**16**) (Cat. No. B1701), methyl 4-(bromomethyl)benzoate (Cat. No. B2053), 2,5-dimethylfuran (**6**) (Cat. No. D0725), dibenzyl sulfide (Cat. No. B0440) and trimethylsilylmethyl chloride (Cat. No. C0862) were purchased from Tokyo Chemical Industry Co., Ltd. Bis(di-*tert*-butyl(4-dimethylaminophenyl)phosphine)dichloropalladium(II) (Pd(amphos)$_2$Cl$_2$) (Cat. No. 68 1844 5415) was purchased from Umicore AG & Co. KG.

Phenylmagnesium bromide (1.01 M in Et_2O or 1.05 M in THF) was prepared from bromobenzene and magnesium in the conventional way. (Trimethylsilyl)methylmagnesium chloride (1.07 M in Et_2O or 0.968 M in THF) was prepared from trimethylsilylmethyl chloride and magnesium in the conventional way. Phenylmagnesium bromide (1.05 M, THF solution), (trimethylsilyl)methylmagnesium chloride (1.07 M, Et_2O or THF solution) and commercial Grignard reagents were used after titrimetric determination of the concentration by the 1,10-phenanthroline method.[S1]

1,3-Bis(triflyloxy)-2-iodobenzene[S2] (**1**), methyl 4-(azidomethyl)benzoate[S3] (**14**) and 2-iodo-3-methoxyphenyl triflate[S2] (**18**) were prepared according to the reported methods.

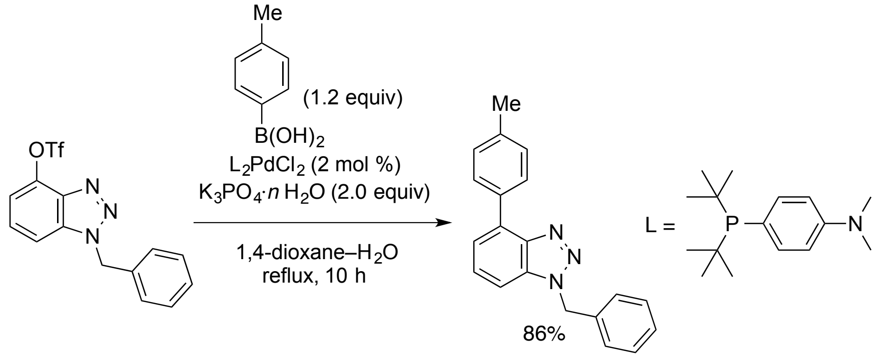
Experimental Procedures

A typical procedure for the cycloaddition of 3-triflyloxybenzyne



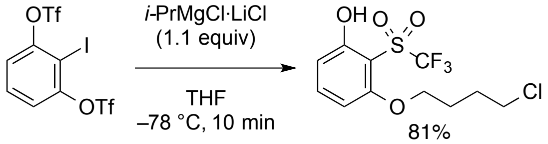
To a mixture of 1,3-bis(triflyloxy)-2-iodobenzene (**1**) (100 mg, 0.200 mmol) and 1,1-dimethoxyethylene (**2**) (37.9 µL, 0.400 mmol, 2.00 equiv) dissolved in Et_2O (3.0 mL) was slowly added (trimethylsilyl)-methylmagnesium chloride (1.07 M, Et_2O solution, 0.206 mL, 0.220 mmol, 1.10 equiv) at –30 °C. After stirring for 1 h at the same temperature, to the mixture was added an aqueous phosphate buffer solution (pH 7, 10 mL). The mixture was extracted with EtOAc (10 mL × 3), and the combined organic extract was washed with brine (5 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica-gel 600 mg, *n*-hexane/EtOAc = 20/1) to give 8,8-dimethoxy-2-triflyloxybicyclo[4.2.0]octa-1,3,5-triene (**3**) (57.9 mg, 0.185 mmol, 92.5%) as a colorless oil.

*Palladium catalyzed cross-coupling reaction of cycloadduct **13***



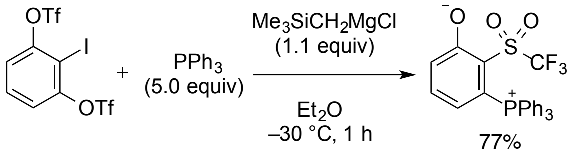
To a mixture of 1-benzyl-4-triflyloxy-1*H*-benzo[*d*][1,2,3]triazole (**13**) (71.5 mg, 0.200 mmol), 4-methylphenylboronic acid (32.6 mg, 0.240 mmol, 1.20 equiv), Pd(amphos)$_2$Cl$_2$ (2.8 mg, 4.0 µmol, 2.0 mol %), and tripotassium phosphate *n*-hydrate (106 mg, ca. 0.40 mmol, ca. 2.0 equiv) were added 1,4-dioxane (2.0 mL) and H_2O (0.20 mL) at room temperature and the mixture was heated at 100 °C with stirring for 10 h. After cooling to room temperature, to the mixture was added water (10 mL). The mixture was extracted with EtOAc (50 mL × 3), and the combined organic extract was washed with aqueous saturated solution of sodium bicarbonate, brine (5 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 5/1) to give 1-benzyl-4-(4-tolyl)-1*H*-benzo[*d*][1,2,3]triazole (**20**) (51.5 mg, 0.172 mmol, 86.0%) as a colorless oil.

A typical procedure for the synthesis of aryl triflone via nucleophilic addition of tetrahydrofuran to 3-triflyloxybenzyne followed by thia-Fries rearrangement



To a solution of 1,3-bis(triflyloxy)-2-iodobenzene (**1**) (100 mg, 0.200 mmol) in THF (3.0 mL) was slowly added isopropylmagnesium chloride lithium chloride complex (1.37 M, THF solution, 0.220 mmol, 1.10 equiv) at –78 °C. After stirring for 10 min at the same temperature, to the mixture was added an aqueous phosphate buffer solution (pH 7, 10 mL). The mixture was extracted with EtOAc (10 mL × 3), and the combined organic extract was washed with brine (5 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 5/1) to give 3-(4-chlorobutoxy)-2-triflylphenol (**23**) (54.0 mg, 0.162 mmol, 81.0%) as a colorless solid.

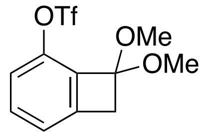
A typical procedure for the synthesis of aryl triflone via nucleophilic addition of nucleophiles to 3-triflyloxybenzyne followed by thia-Fries rearrangement



To a mixture of 1,3-bis(triflyloxy)-2-iodobenzene (**1**) (100 mg, 0.200 mmol) and triphenylphosphine (262 mg, 1.00 mmol, 5.00 equiv) dissolved in Et_2O (3.0 mL) was slowly added (trimethylsilyl)methylmagnesium chloride (1.07 M, Et_2O solution, 0.206 mL, 0.220 mmol, 1.10 equiv) at –30 °C. After stirring for 1 h at the same temperature, to the mixture was added an aqueous phosphate buffer solution (pH 7, 10 mL). The mixture was extracted with EtOAc (10 mL × 3), and the combined organic extract was washed with brine (5 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (dichloromethane/methanol = 10/1) to give 2-triflyl-3-(triphenylphosphonio)phenolate (**25**) (74.7 mg, 0.154 mmol, 77.0%) as a pale yellow solid.

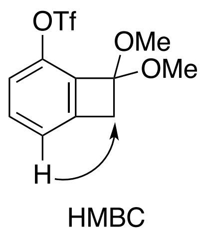
Characterization Data of New Compounds

8,8-Dimethoxy-2-triflyloxybicyclo[4.2.0]octa-1,3,5-triene (**3**)

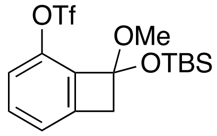


Colorless oil; TLC R_f 0.37 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.40 (s, 2H, CH_2), 3.46 (s, 6H, $2CH_3$), 7.16 (d, 1H, *J* = 8.5 Hz, aromatic), 7.25 (d, 1H, *J* = 7.5 Hz, aromatic), 7.41 (dd, 1H, *J* = 7.5, 8.5 Hz, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 43.5 (1C), 51.9 (2C), 105.1 (1C), 118.5 (q, 1C, $J^{1}_{\text{C–F}}$ = 321 Hz), 119.5 (1C), 124.2 (1C), 132.1 (1C), 136.4 (1C), 140.6 (1C), 144.9 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –73.9 (s); IR (KBr, cm^{-1}) 840, 913, 992, 1065, 1142, 1217, 1245, 1424, 2942; HRMS (ESI$^+$) *m*/*z* 335.0183 ($[M+Na]^+$, $C_{11}H_{11}F_3NaO_5S^+$ requires 335.0171).

The regiochemistry was determined by HMBC analysis (500 MHz ^{1}H NMR/126 MHz ^{13}C NMR in $CDCl_3$).

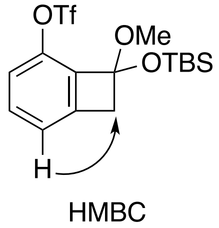


8-(*tert*-Butyldimethylsilyl)oxy-8-methoxy-2-triflyloxybicyclo[4.2.0]octa-1,3,5-triene (**5**)

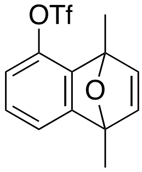


Colorless oil; TLC R_f 0.52 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR (CDCl$_3$, 500 MHz) δ 0.17 (s, 3H, SiCH$_3$), 0.19 (s, 3H, SiCH$_3$), 0.91 (s, 9H, 3CH$_3$), 3.45 (d, 1H, J = 13.5 Hz, methylene CH), 3.49 (s, 3H, OCH$_3$), 3.50 (d, 1H, J = 13.5 Hz, methylene CH), 7.13 (d, 1H, J = 8.5 Hz , aromatic), 7.22 (d, 1H, J = 7.0 Hz, aromatic), 7.38 (dd, 1H, J = 7.0, 8.5 Hz, aromatic); ^{13}C NMR (CDCl$_3$, 126 MHz) δ –3.9 (1C), –3.5 (1C), 17.9 (1C), 25.5 (3C), 48.9 (1C), 53.2 (1C), 102.8 (1C), 118.6 (q, 1C, $J^1_{\mathrm{C–F}}$ = 321 Hz), 119.3 (1C), 124.1 (1C), 131.8 (1C), 138.8 (1C), 140.3 (1C), 144.4 (1C); ^{19}F NMR (CDCl$_3$, 376 MHz) δ –74.1 (s); IR (KBr, cm^{-1}) 840, 1000, 1065, 1144, 1216, 1245, 1426, 2934; HRMS (ESI$^+$) *m*/*z* 435.0867 ([M+Na]$^+$, $C_{16}H_{23}F_3NaO_5SSi^+$ requires 435.0880).

The regiochemistry was determined by HMBC analysis (500 MHz ^{1}H NMR/126 MHz ^{13}C NMR in C$_6$D$_6$).

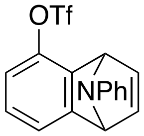


1,4-Dihydro-1,4-dimethyl-5-triflyloxy-1,4-epoxynaphthalene (**7**)



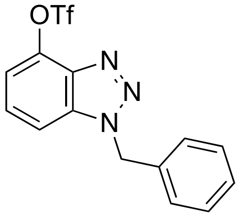
Colorless oil; TLC R_f 0.37 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR (CDCl$_3$, 500 MHz) δ 1.91 (s, 3H, CH$_3$), 2.03 (s, 3H, CH$_3$), 6.79 (d, 1H, J = 5.0 Hz, alkenic), 6.83 (d, 1H, J = 8.0 Hz, aromatic), 6.88 (d, 1H, J = 5.0 Hz, alkenic), 7.05 (dd, 1H, J = 7.0, 8.0 Hz, aromatic), 7.11 (d, 1H, J = 7.0 Hz, aromatic); ^{13}C NMR (CDCl$_3$, 126 MHz) δ 15.1 (1C), 16.4 (1C), 88.8 (1C), 89.3 (1C), 118.1 (1C), 118.4 (1C), 118.6 (q, 1C, $J^1_{\mathrm{C–F}}$ = 321 Hz), 127.7 (1C), 142.3 (1C), 144.1 (1C), 146.4 (1C), 146.8 (1C), 157.5 (1C); ^{19}F NMR (CDCl$_3$, 376 MHz) δ –73.3 (s); IR (KBr, cm^{-1}) 932, 1141, 1221, 1423, 2936, 2984; HRMS (ESI$^+$) *m*/*z* 343.0209 ([M+Na]$^+$, $C_{13}H_{11}F_3NaO_4S^+$ requires 343.0222).

1,4-Dihydro-9-phenyl-5-triflyloxynaphthalen-1,4-imine (**9**)



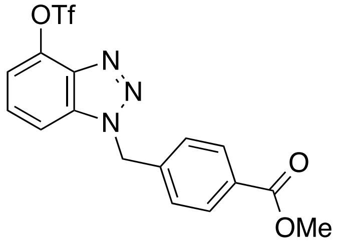
Pale brown solid; Mp 60–62 °C; TLC R_f 0.44 (*n*-hexane/EtOAc = 5/1); ^{1}H NMR (CDCl$_3$, 500 MHz) δ 5.50 (s, 1H), 5.65 (s, 1H), 6.77–6.83 (m, 3H), 6,86 (dd, 1H, J = 7.5, 7.5 Hz), 6.97–7.03 (m, 3H), 7.15–7.20 (AA'BB', 2H), 7.25 (d, 1H, J = 7.5 Hz); ^{13}C NMR (CDCl$_3$, 126 MHz) δ 67.0 (1C), 69.6 (1C), 117.8 (2C), 118.1 (1C), 118.7 (q, 1C, $J^1_{\mathrm{C–F}}$ = 321 Hz), 121.3 (1C), 121.4 (1C), 127.6 (1C), 129.0 (2C), 140.8 (1C), 141.5 (1C), 142.1 (1C), 143.9 (1C), 145.9 (1C), 152.9 (1C); ^{19}F NMR (CDCl$_3$, 376 MHz) δ –73.1 (s); IR (KBr, cm^{-1}) 866, 1119, 1142, 1213, 1422, 1495, 1601; HRMS (ESI$^+$) *m*/*z* 390.0395 ([M+Na]$^+$, $C_{17}H_{12}F_3NNaO_3S^+$ requires 390.0382).

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

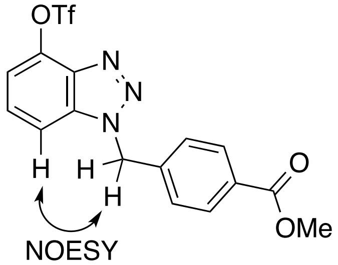


Colorless solid; Mp 84–85 °C; TLC R_f 0.29 (*n*-hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.88 (s, 2H, CH_2), 7.25–7.32 (m, 3H, aromatic), 7.32–7.40 (m, 4H, aromatic), 7.43 (dd, 1H, J = 8.5, 8.5 Hz, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 52.8 (1C), 110.4 (1C), 116.2 (1C), 118.8 (q, 1C, $J^1_{C–F}$ = 321 Hz), 127.70 (2C), 127.74 (1C), 128.9 (1C), 129.2 (2C), 133.8 (1C), 135.3 (1C), 139.1 (1C), 139.6 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –72.9 (s); IR (KBr, cm^{-1}) 822, 1015, 1139, 1168, 1219, 1428, 1505, 3035; Anal. calcd. for $C_{14}H_{10}F_3N_3O_3S$: C, 47.06; N, 11.76; H, 2.82%; Found: C, 47.09; N, 11.96; H, 2.79%.

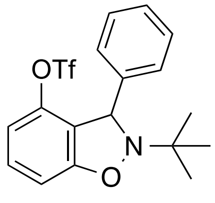
1-[4-(Methoxycarbonyl)benzyl]-4-triflyloxy-1*H*-benzo[*d*][1,2,3]triazole (**15**)



Colorless solid; Mp 1 1 1–1 12 °C; TLC R_f 0.46 (*n*-hexane/EtOAc = 1/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.91 (s, 3H, CH_3), 5.94 (s, 2H, CH_2), 7.30 (d, 1H, J = 8.0 Hz, aromatic), 7.32–7.37 (m, 3H, aromatic), 7.46 (dd, 1H, J = 8.0, 8.0 Hz, aromatic), 8.01–8.05 (AA'BB', 2H, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 52.3 (1C+1C, two signals overlapped), 1 10.1 (1C), 1 16.4 (1C), 1 18.8 (q, 1C, $J^1_{C–F}$ = 321 Hz), 127.5 (2C), 128.1 (1C), 130.5 (2C), 130.7 (1C), 135.2 (1C), 138.6 (1C), 139.2 (1C), 139.7 (1C), 166.3 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –72.9 (s); IR (KBr, cm^{-1}) 827, 1018, 1139, 1216, 1283, 1424, 1505, 1728; Anal. calcd. for $C_{16}H_{12}F_3N_3O_5S$: C, 46.27; N, 10.12; H, 2.91%; Found: C, 46.07; N, 10.41; H, 2.84%.
The regiochemistry was determined by the NOESY experiment (500 MHz ^{1}H NMR in C_6D_6).



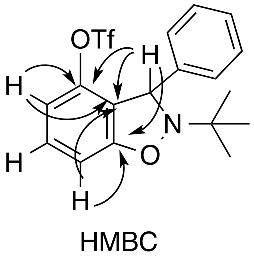
2-*tert*-Butyl-2,3-dihydro-3-phenyl-4-triflyloxy-1,2-benzoisoxazole (**17**)



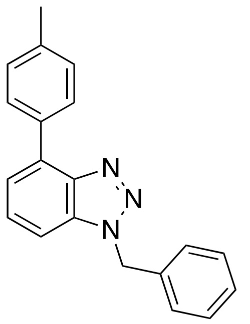
Colorless solid; Mp 48–49 °C; TLC R_f 0.40 (*n*-hexane/EtOAc = 20/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.19 (s, 9H, CH_3), 5.79 (s, 1H, sp^{3}CH), 6.72 (d, 1H, J = 8.5 Hz, aromatic), 6.88 (d, 1H, J = 8.0 Hz, aromatic), 7.22–7.36 (m, 6H, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 25.2 (3C), 61.9 (1C), 65.5 (1C), 107.2 (1C), 113.3 (1C), 118.5 (q, 1C, $J^1_{C–F}$ = 321 Hz), 122.8 (1C), 127.5 (2C), 128.0 (1C), 128.7 (2C), 130.8 (1C), 141.1 (1C), 144.4 (1C), 159.6 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –73.4 (s); IR (KBr, cm^{-1}) 855, 1009, 1140, 1215, 1249, 1423, 1457, 2976; Anal. calcd. $C_{18}H_{18}F_3NO_4S$: C, 53.86; N, 3.49; H, 4.52%; Found: C, 53.86; N, 3.50;

H, 4.56%.

The regiochemistry was determined by HMBC analysis (500 MHz ^{1}H NMR/126 MHz ^{13}C NMR in $CDCl_3$).

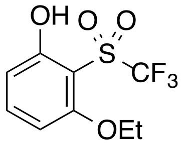


1-Benzyl-4-(4-tolyl)-1*H*-benzo[*d*][1,2,3]triazole (**20**)



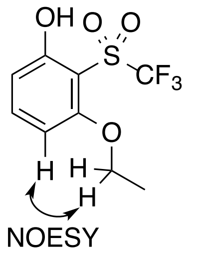
Colorless oil; TLC R_f 0.38 (*n*-hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.46 (s, 3H, CH_3), 5.91 (s, 2H, CH_2), 7.29–7.39 (m, 8H, aromatic), 7.46 (dd, 1H, J = 7.5, 8.0 Hz, aromatic), 7.50 (d, 1H, J = 7.5 Hz, aromatic), 8.04–8.08 (AA’BB’, 2H, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 21.3 (1C), 52.2 (1C), 108.1 (1C), 122.0 (1C), 127.5 (2C), 127.6 (1C), 128.4 (1C), 128.9 (2C), 129.0 (2C), 129.4 (2C), 133.4 (1C), 133.5 (1C), 133.8 (1C), 134.8 (1C), 138.1 (1C), 144.4 (1C); IR (KBr, cm^{-1}) 824, 1097, 1159, 1245, 1257, 1455, 1496, 1606, 2921, 3032; HRMS (ESI^{+}) *m*/*z* 322.1313 ([M+Na]$^{+}$, $C_{20}H_{17}N_3Na^{+}$ requires 322.1315).

3-Ethoxy-2-triflylphenol (**22**)

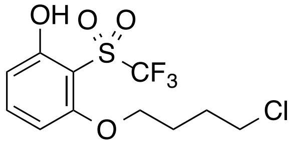


Colorless oil; TLC R_f 0.44 (*n*-hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.45 (t, 3H, J = 7.0 Hz, CH_3), 4.14 (q, 2H, J = 7.0 Hz, CH_2), 6.48 (dd, 1H, J = 0.50, 8.5 Hz, aromatic), 6.63 (dd, 1H, J = 0.50, 8.5 Hz, aromatic), 7.51 (dd, 1H, J = 8.5, 8.5 Hz, aromatic), 9.55 (1H, OH); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 14.0 (1C), 65.6 (1C), 103.6 (1C), 103.7 (q, 1C, $J^{3}_{\mathrm{C–F}}$ = 4.9 Hz), 111.4 (1C), 119.9 (q, 1C, $J^{1}_{\mathrm{C–F}}$ = 328 Hz), 139.3 (1C), 159.9 (1C), 160.7 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –76.5 (s); IR (KBr, cm^{-1}) 1092, 1122, 1218, 1334, 1495, 1580, 1607, 3340; Anal. calcd. for $C_9H_9F_3O_4S$: C, 40.00; H, 3.36%; Found: C, 40.10; H, 3.38%.

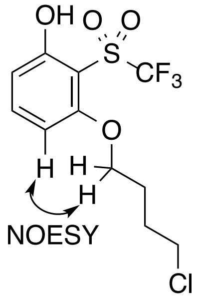
Regiochemistry was determined by the NOESY experiment (500 MHz ^{1}H NMR in $CDCl_3$).



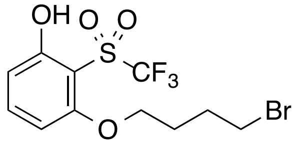
3-(4-Chlorobutoxy)-2-triflylphenol (**23**)



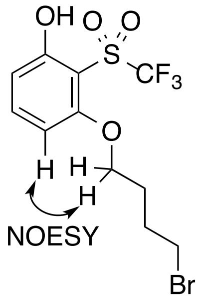
Colorless solid; Mp 31–32 °C; TLC R_f 0.38 (*n*-hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.94–2.08 (m, 4H, $2CH_2$), 3.63 (t, 2H, J = 6.0 Hz, CH_2), 4.10 (t, 2H, J = 5.5 Hz, CH_2), 6.49 (dd, 1H, J = 0.8, 8.5 Hz, aromatic), 6.66 (dd, 1H, J = 0.8, 8.5 Hz, aromatic), 7.53 (dd, 1H, J = 8.5, 8.5 Hz, aromatic), 9.55 (s, 1H, OH); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 26.0 (1C), 28.6 (1C), 44.6 (1C), 68.9 (1C), 103.3 (1C), 103.5 (1C), 111.6 (1C), 119.9 (q, 1C, $J^1_{C\text{–}F}$ = 328 Hz), 139.4 (1C), 159.8 (1C), 160.9 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –77.0 (s); IR (KBr, cm^{-1}) 1039, 1220, 1335, 1495, 1568, 1575, 1606, 2956, 3314; Anal. calcd. for $C_{11}H_{12}ClF_3O_4S$: C, 39.71; H, 3.64%; Found: C, 39.84; H, 3.59%.
Regiochemistry was determined by the NOESY experiment (500 MHz ^{1}H NMR in $CDCl_3$).



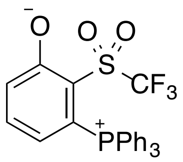
3-(4-Bromobutyloxy)-2-triflylphenol (**24**)



Colorless solid; Mp 32–33 °C; TLC R_f 0.35 (*n*-hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.00 (tt, 2H, J = 6.5, 6.5 Hz, CH_2), 2.10 (tt, 2H, J = 6.5, 6.5 Hz, CH_2), 3.49 (t, 2H, J = 6.5 Hz, CH_2), 4.10 (t, 2H, J = 6.5 Hz, CH_2), 6.49 (d, 1H, J = 8.5 Hz, aromatic), 6.66 (d, 1H, J = 8.5 Hz, aromatic), 7.53 (dd, 1H, J = 8.5, 8.5 Hz, aromatic), 9.55 (s, 1H, OH); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 27.2 (1C), 28.7 (1C), 33.3 (1C), 68.7 (1C), 103.3 (1C), 103.5 (1C), 111.7 (1C), 119.9 (q, 1C, $J^1_{C\text{–}F}$ = 328 Hz) 139.4 (1C), 159.8 (1C), 160.9 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –77.0 (s); IR (KBr, cm^{-1}) 1072, 1121, 1208, 1335, 1450, 1492, 1578, 1607, 2925, 3335; Anal. calcd. for $C_{11}H_{12}BrF_3O_4S$: C, 35.03; H, 3.21%; Found: C, 35.23; H, 3.15%.
Regiochemistry was determined by the NOESY experiment (500 MHz ^{1}H NMR in $CDCl_3$).



2-Triflyl-3-(triphenylphosphonio)phenolate (**25**)



Pale yellow solid; Mp 261–262 °C; TLC R_f 0.56 (CH_2Cl_2/MeOH = 5/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.86 (dd, 1H, J = 6.5 Hz, $J_{H–P}$ = 19.0 Hz, aromatic), 7.08 (d, 1H, J = 8.5 Hz, aromatic), 7.11–7.18 (m, 1H, aromatic), 7.40–7.90 (m, 15H, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 116.0 (br s, 1C), 116.6 (d, 1C, $J_{C–P}$ = 38.4 Hz), 120.1 (q, 1C, $J^1_{C–F}$ = 330 Hz), 122.7–123.2 (br, 1C), 123.7 (br s, 1C), 129.5 (d, 6C, $J_{C–P}$ = 13.2 Hz), 133.6 (br, d, 3C, $J_{C–P}$ = 8.1 Hz), 133.7 (d, 6C, $J_{C–P}$ = 3.0 Hz), 134.1 (d, 3C, $J_{C–P}$ = 19.3 Hz), 135.1 (1C), 175.7 (d, 1C, $J_{C–P}$ = 4.8 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –72.3 (s); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 27.1 Hz (s); IR (KBr, cm^{-1}) 1109, 1174, 1185, 1211, 1328, 1437, 1524, 1595, 3061; HRMS (ESI$^+$) m/z 487.0728 ($[M+H]^+$, $C_{25}H_{19}F_3O_3PS^+$ requires 487.0739).

Crystallographic analysis

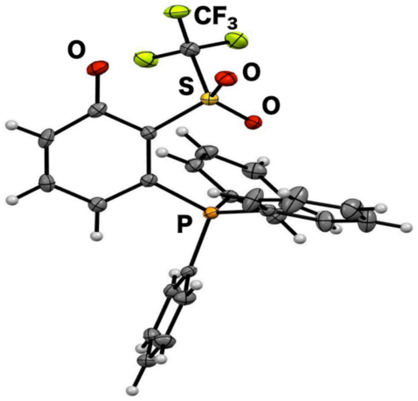
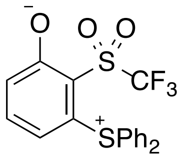


Figure S1. ORTEP drawing of phosphonium salt **25** (ellipsoids set at 40% probability level).

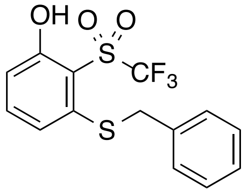
Selected crystal data: Crystal System; monoclinic, Space Group; $P2_1/n$ (No. 14), a = 9.528(2) Å, b = 17.804(3) Å, c = 13.794(2) Å, β = 104.385(9)°, V = 2266.6(6) Å^3, Z = 4, R_1 = 0.0316, wR_2 = 0.0836. CCDC 1014336 contains the supplementary crystallographic data for this compound. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3-(Diphenylsulfonio)-2-triflylphenolate (**26**)



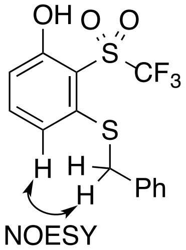
Pale yellow solid; Mp 176–177 °C; TLC R_f 0.59 (CH_2Cl_2/MeOH = 5/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.63 (d, 1H, J = 7.5 Hz, aromatic), 6.87 (d, 1H, J = 9.0 Hz, aromatic), 7.10 (dd, 1H, J = 7.5, 9.0 Hz, aromatic), 7.48 (d, 4H, J = 8.0 Hz, aromatic), 7.66 (dd, 4H, J = 7.5, 8.0 Hz, aromatic), 7.74 (t, 2H, J = 7.5 Hz, aromatic); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 110.2 (1C), 114.6 (1C), 120.3 (q, 1C, $J^1_{C–F}$ = 329 Hz), 123.2 (1C), 125.7 (1C), 130.7 (4C), 131.2 (4C), 133.3 (1C), 133.9 (1C), 134.1 (2C), 175.8 (1C); ^{19}F NMR ($CDCl_3$, 376 MHz) δ –75.4 (s); IR (KBr, cm^{-1}) 1011, 1108, 1196, 1333, 1447, 1484, 1535, 1600, 3060; HRMS (ESI$^+$) m/z 411.0325 ($[M+H]^+$, $C_{19}H_{14}F_3O_3S_2^+$ requires 411.0331).

3-Benzylthio-2-triflylphenol (**27**)



Colorless solid; Mp 112–113 °C; TLC R_f 0.41 (*n*-hexane/EtOAc = 5/1); ^{1}H NMR (CDCl$_3$, 500 MHz) δ 4.18 (s, 2H, CH$_2$), 6.85 (d, 1H, J = 8.0 Hz, aromatic), 6.94 (d, 1H, J = 8.0 Hz, aromatic), 7.26–7.43 (m, 5H, aromatic), 7.44 (dd, 1H, J = 8.0, 8.0 Hz, aromatic), 9.43 (s, 1H, OH); ^{13}C NMR (CDCl$_3$, 126 MHz) δ 38.9 (1C), 110.6 (1C), 116.6 (1C), 120.2 (q, 1C, $J^1_{\text{C–F}}$ = 329 Hz), 120.4 (1C), 127.8 (1C), 128.8 (2C), 129.0 (2C), 134.8 (1C), 137.8 (1C), 144.5 (1C), 161.3 (1C); ^{19}F NMR (CDCl$_3$, 376 MHz) δ –77.3 (s); IR (KBr, cm^{-1}) 1033, 1095, 1137, 1206, 1221, 1357, 1464, 1585, 3370; Anal. calcd. for $C_{14}H_{11}F_3O_3S_2$: C, 48.27; H, 3.18%; Found: C, 48.27; H, 3.25%.

Regiochemistry was determined by the NOESY experiment (500 MHz ^{1}H NMR in C_6D_6).



References for Supporting Information

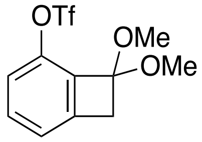
(S1) D. E. Bergbreiter and E. Pendergrass, *J. Org. Chem.*, 1981, **46**, 219.

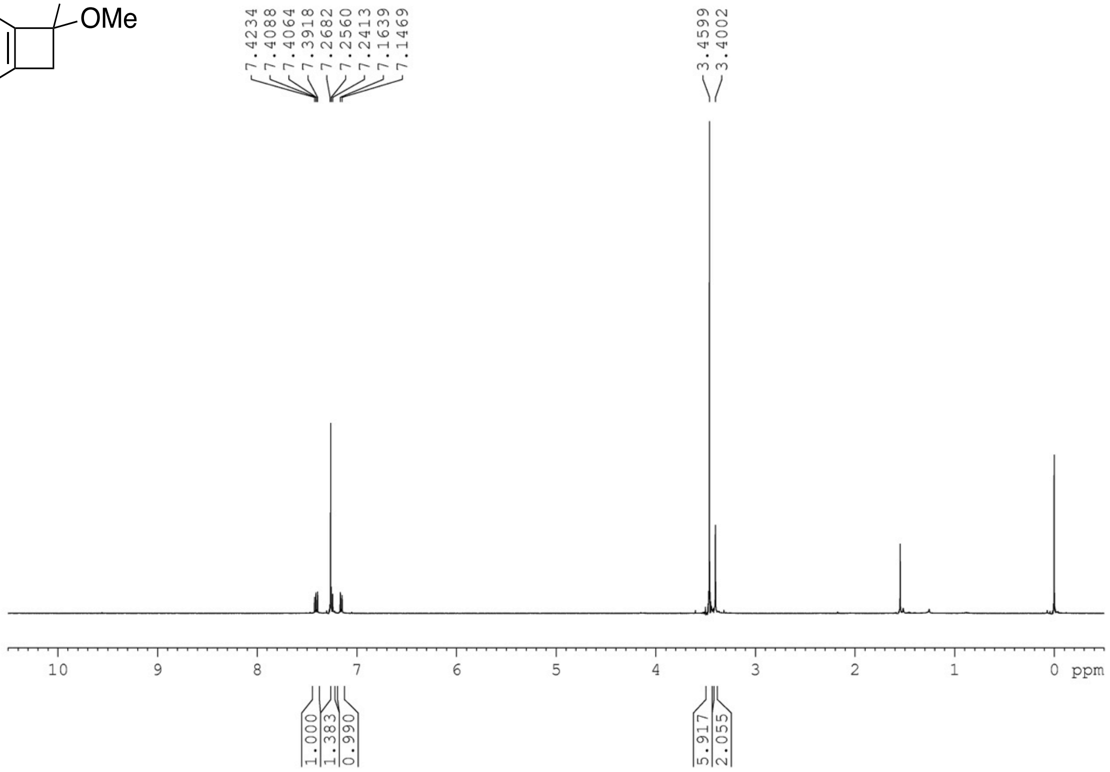
(S2) T. Hamura, T. Hosoya, H. Yamaguchi, Y. Kuriyama, M. Tanabe, M. Miyamoto, Y. Yasui, T. Matsumoto and K. Suzuki, *Helv. Chim. Acta*, 2002, **85**, 3589.

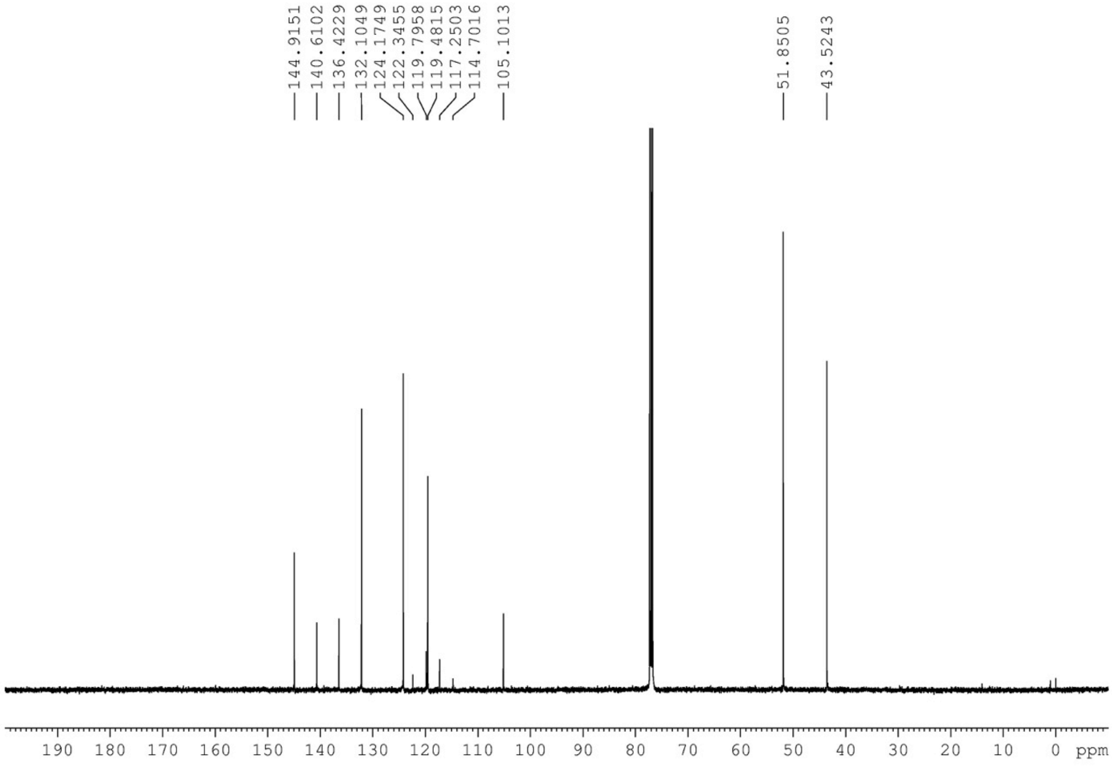
(S3) E. A. Wydysh, S. M. Medghalchi, A. Vadlamudi and C. A. Townsend, *J. Med. Chem.* 2009, **52**, 3317.

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

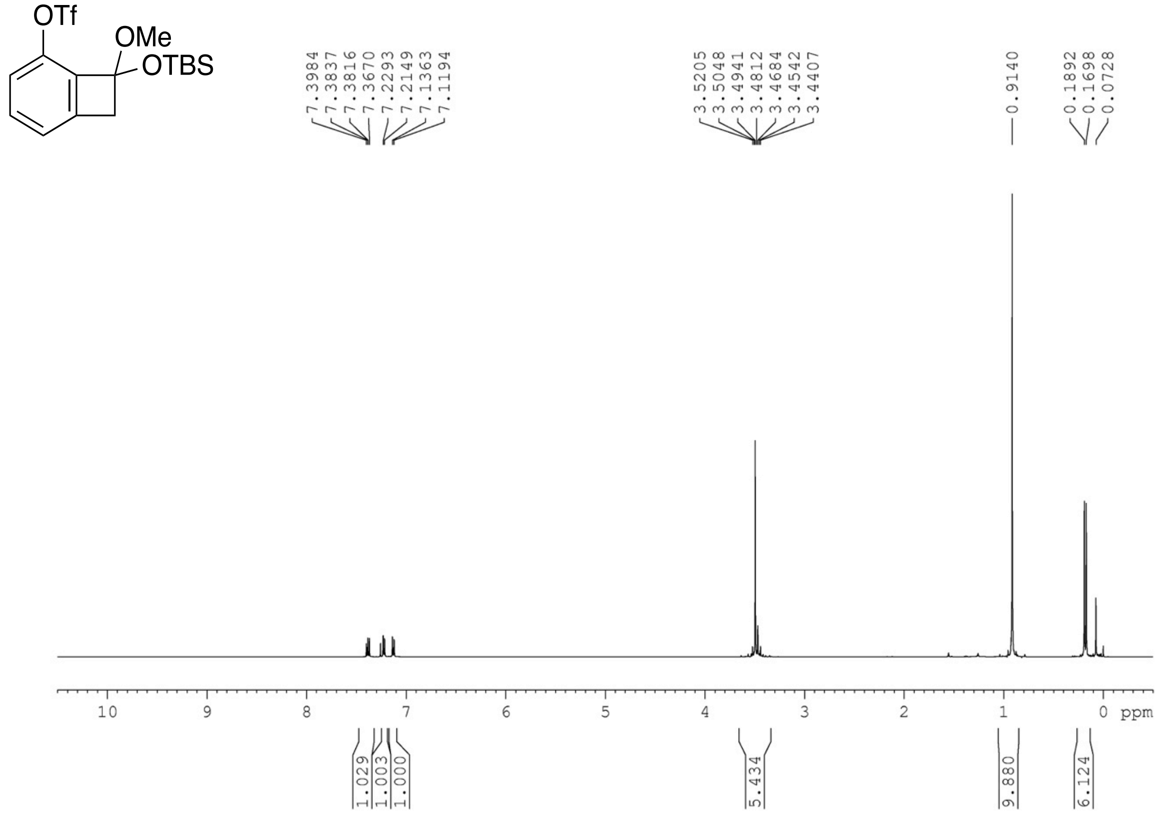
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **3** ($CDCl_3$)

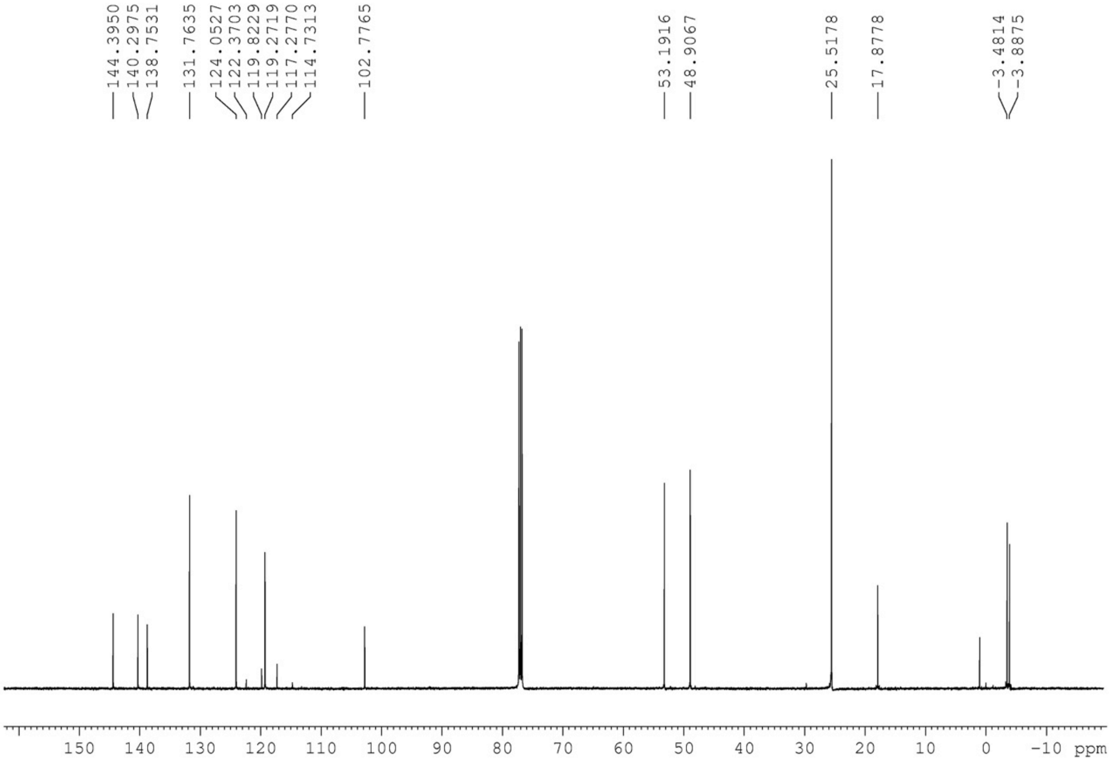




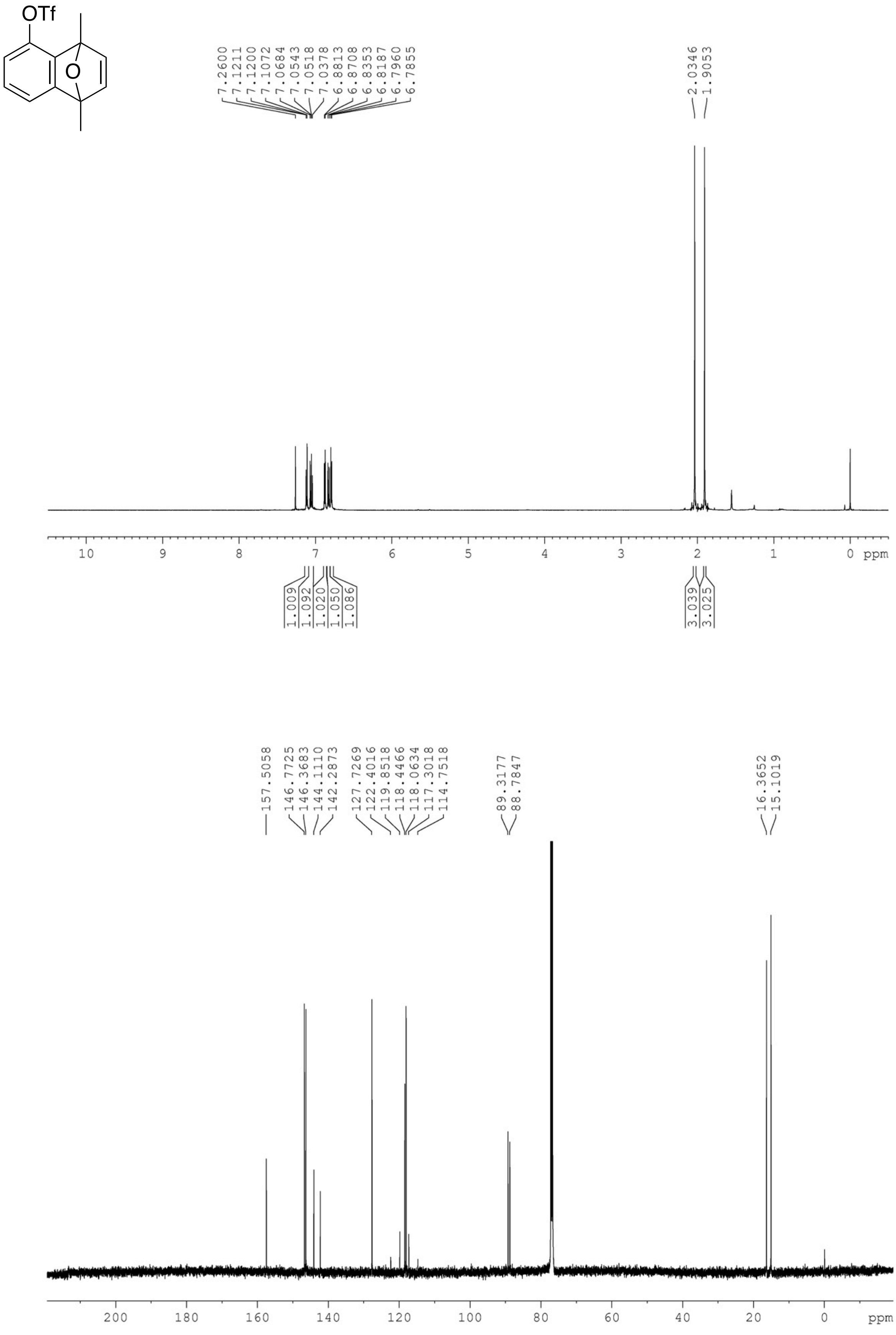


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **5** ($CDCl_3$)

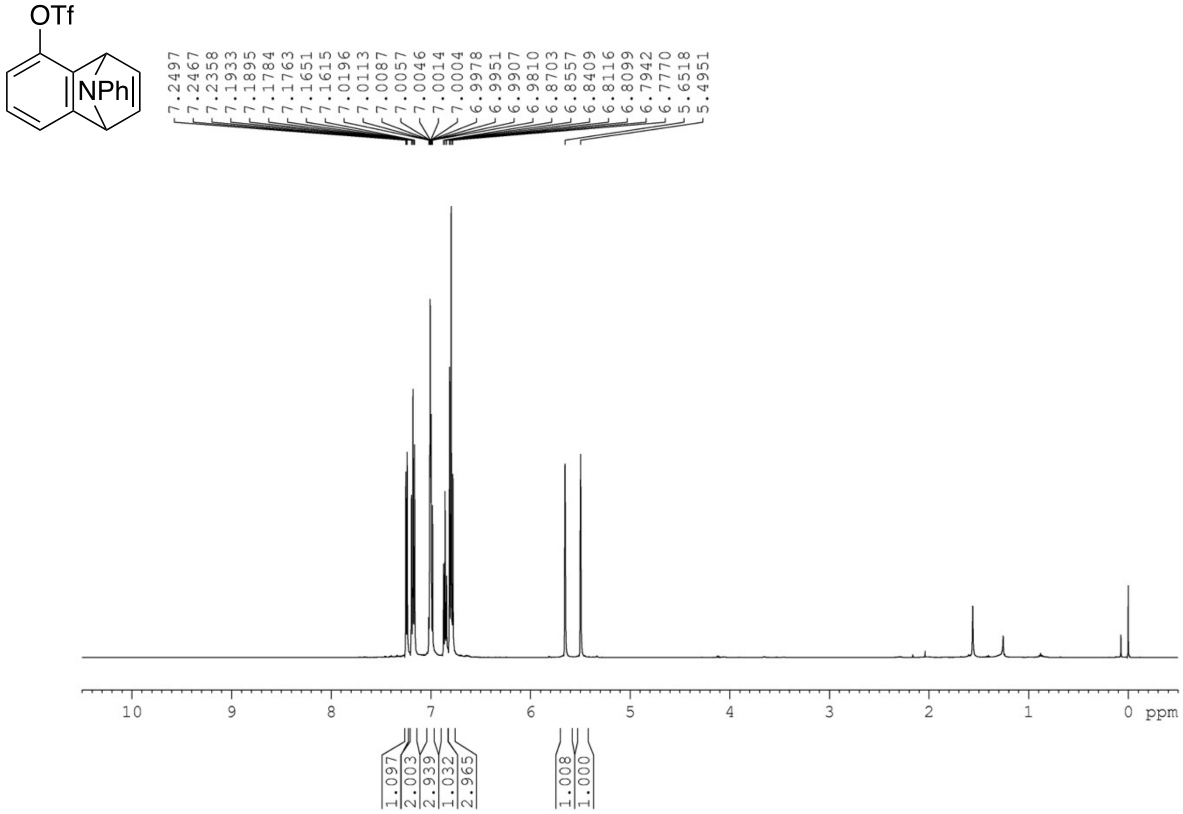


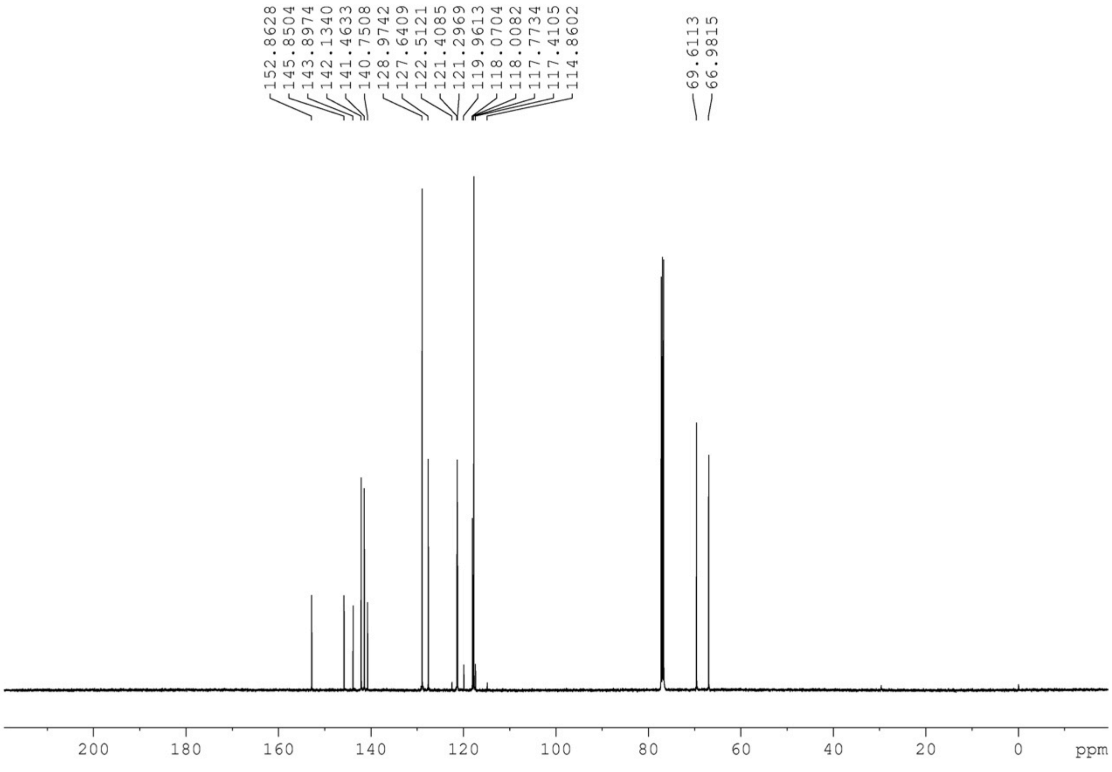


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **7** ($CDCl_3$)

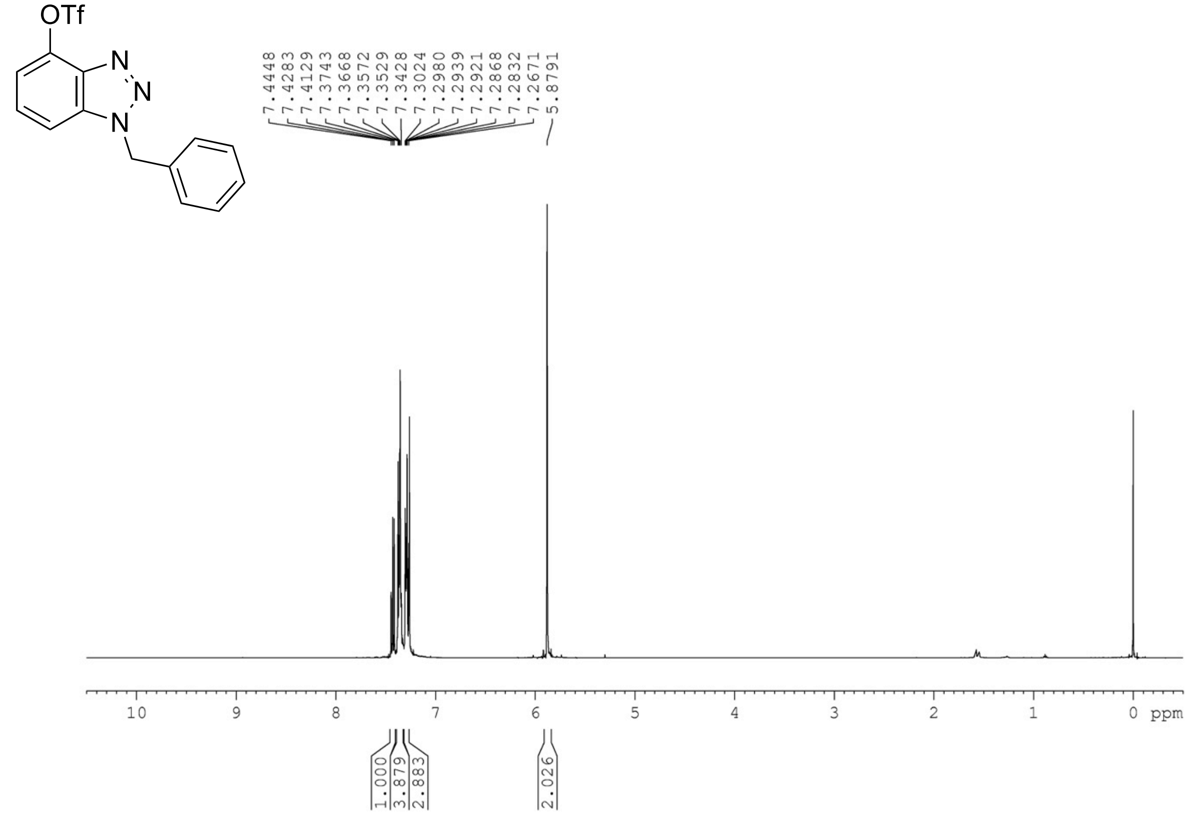


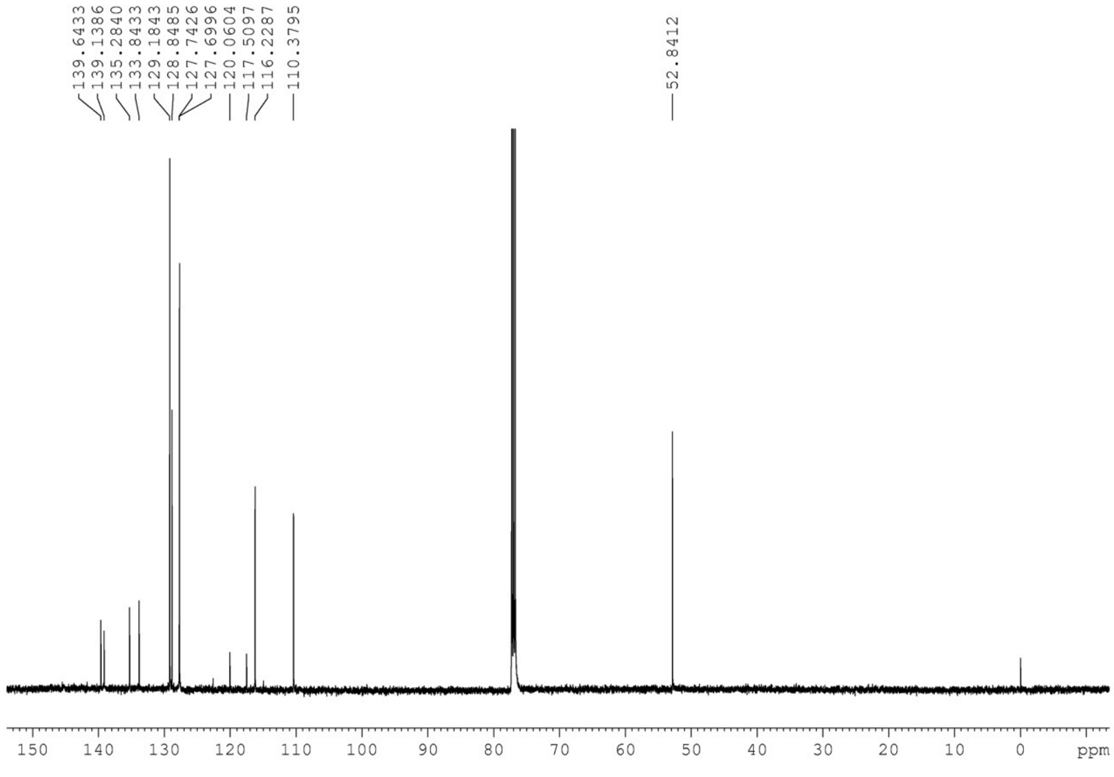
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **9** ($CDCl_3$)



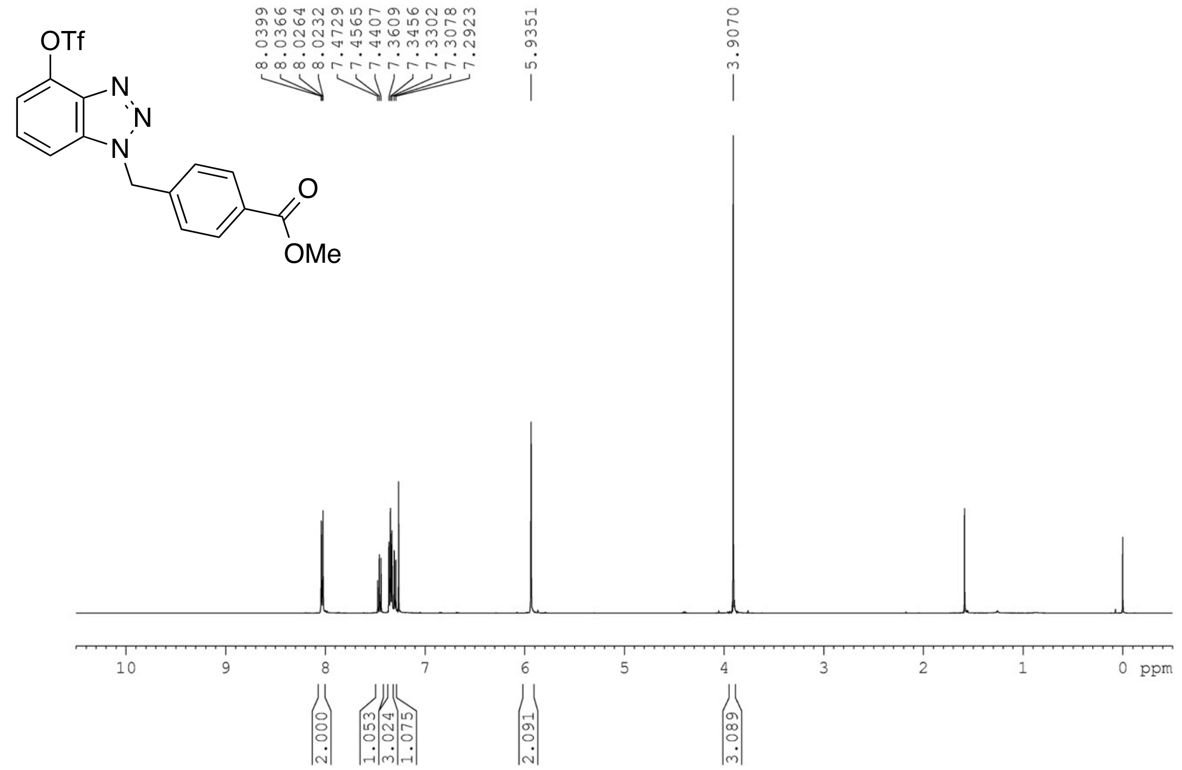


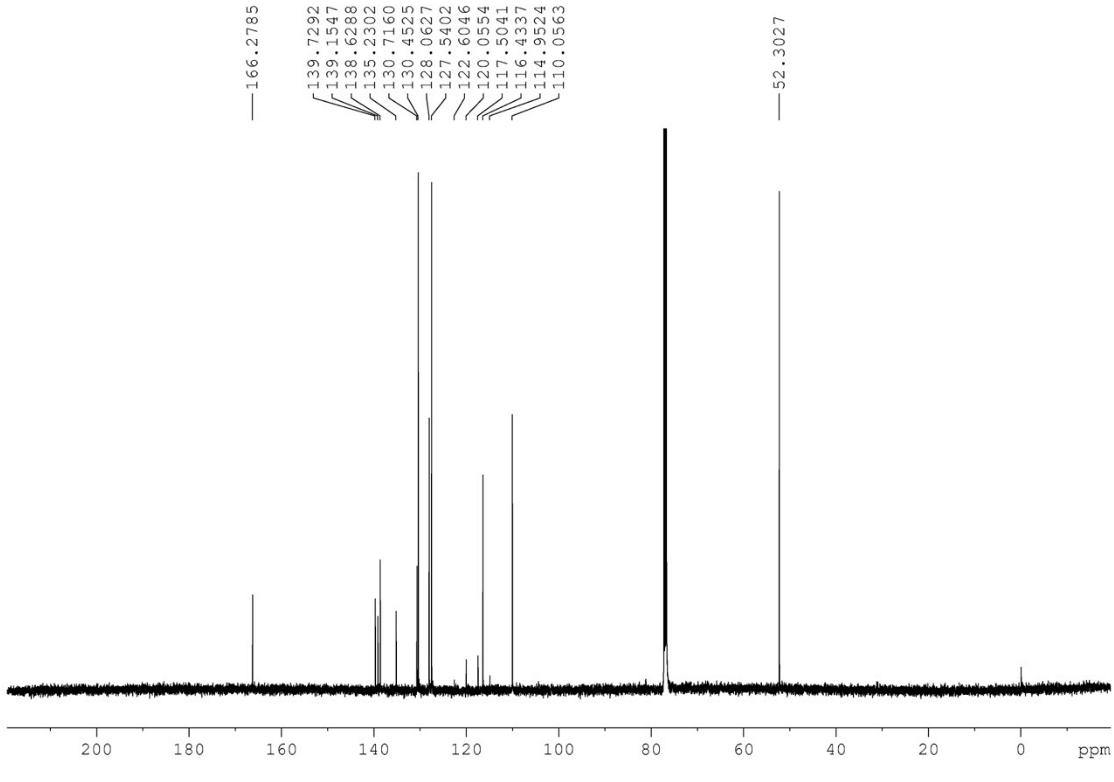
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **13** (CDCl$_3$)



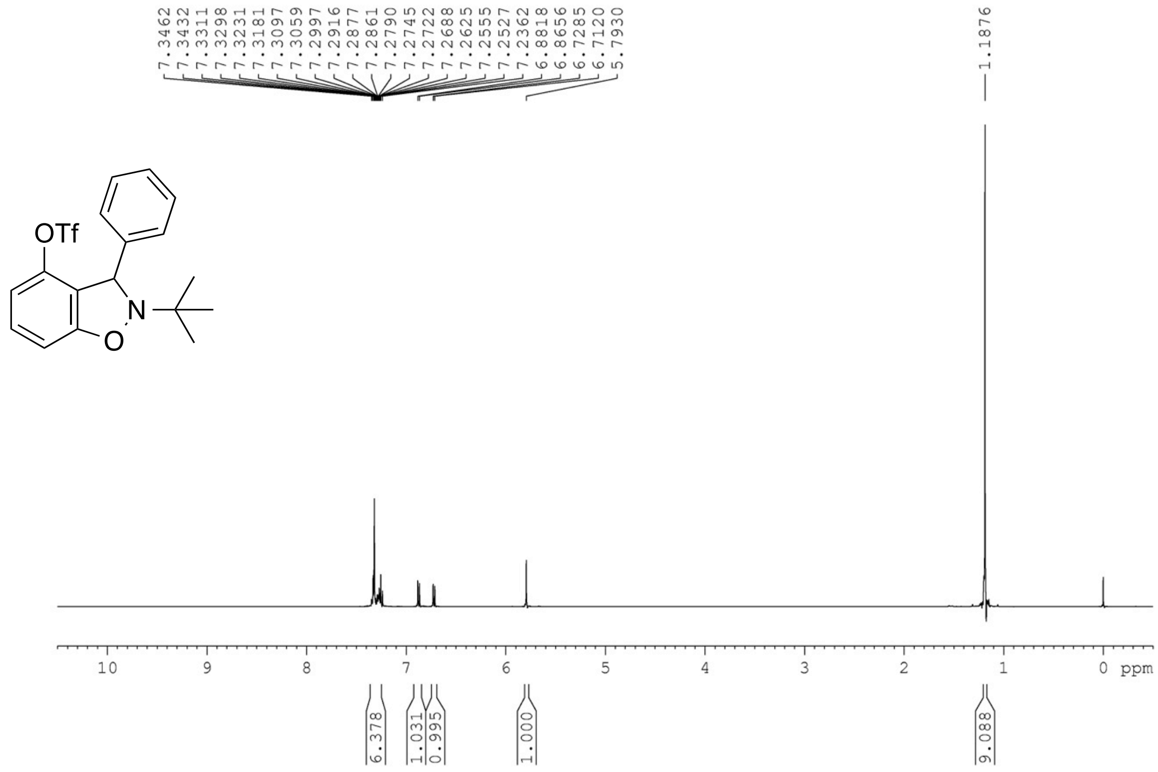


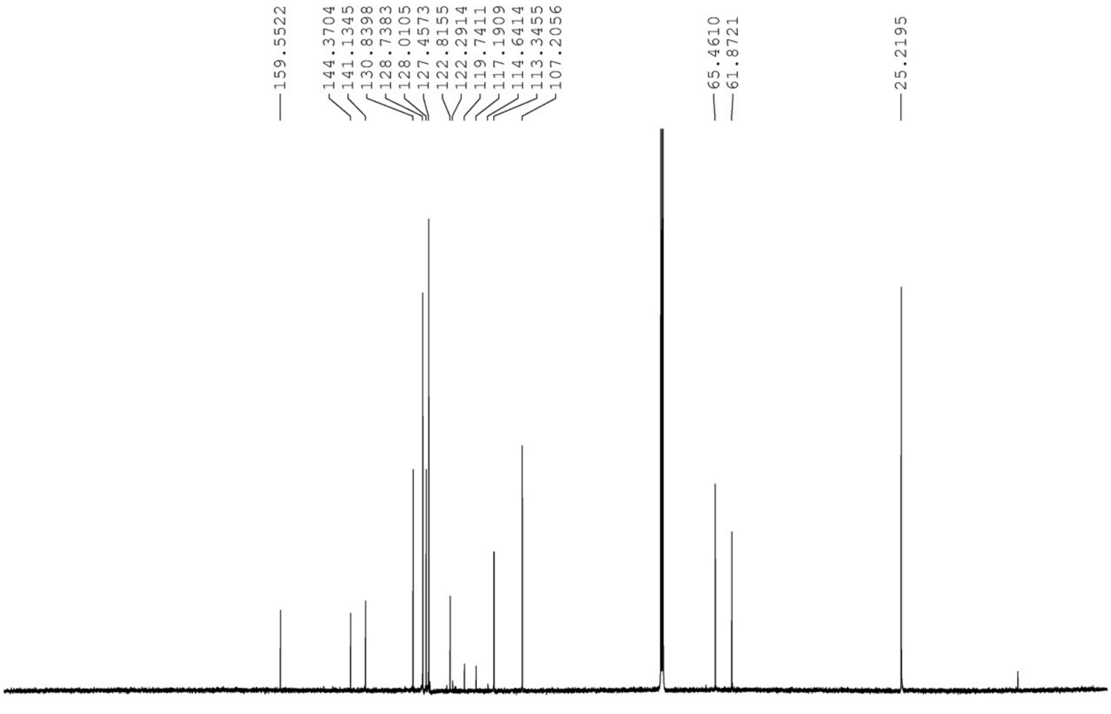
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **15** (CDCl$_3$)



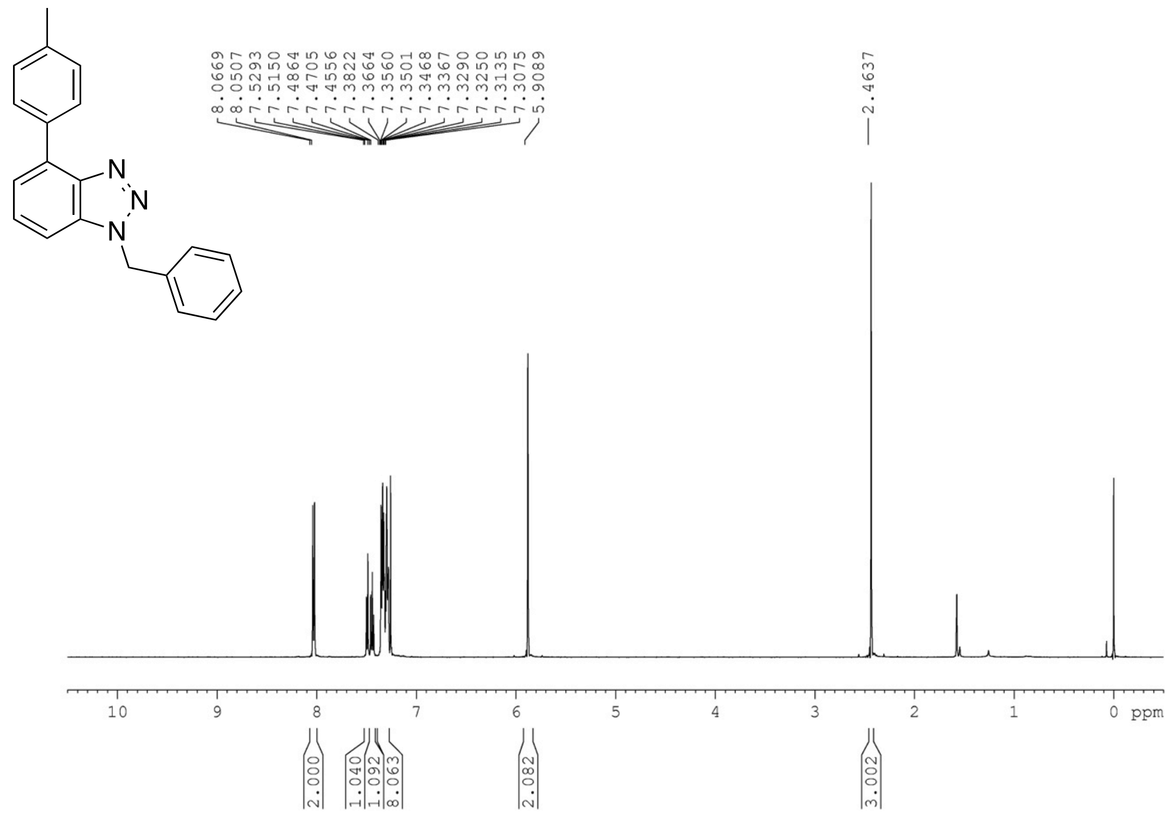


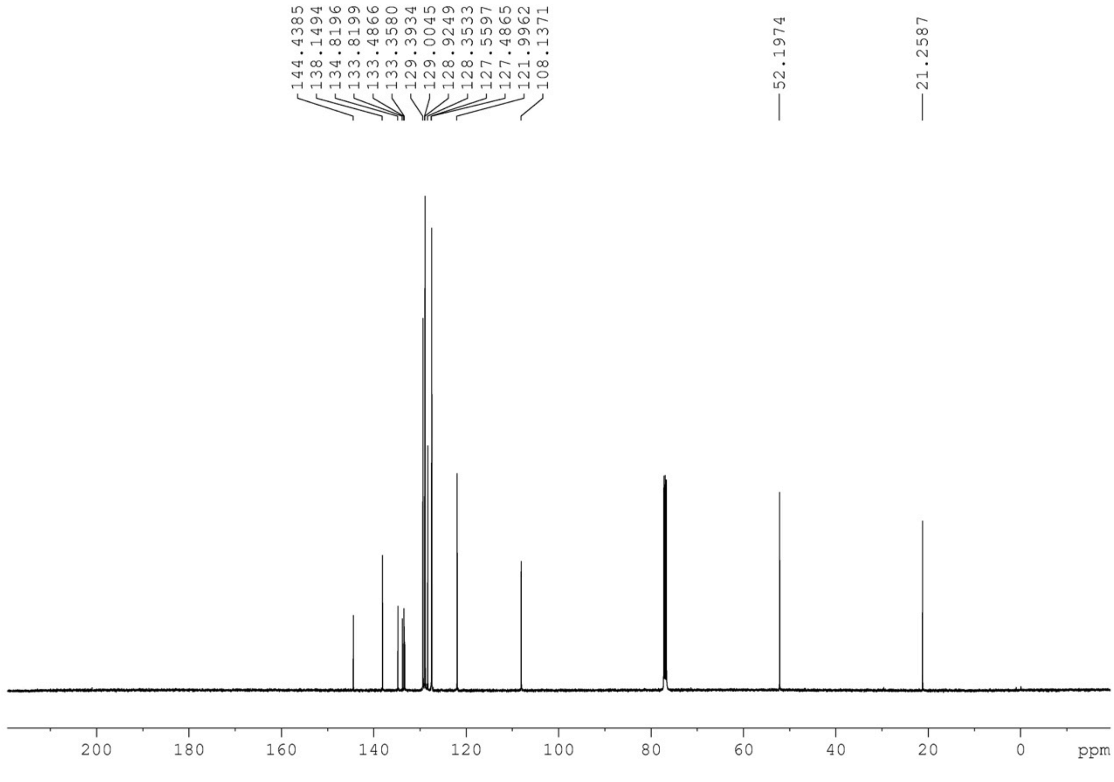
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **17** ($CDCl_3$)



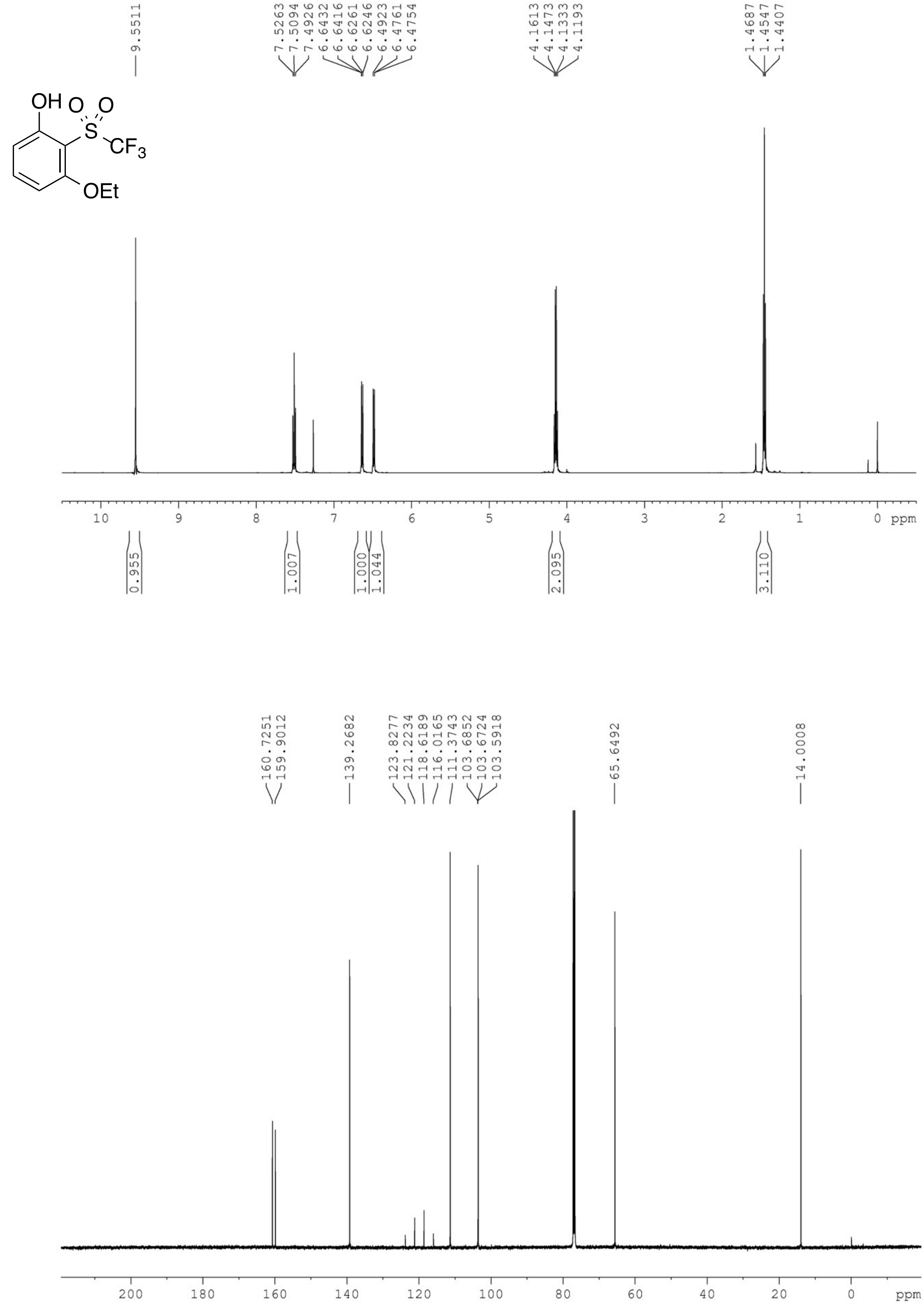


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **20** ($CDCl_3$)

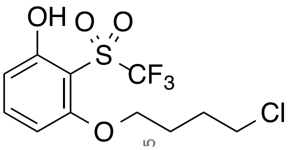


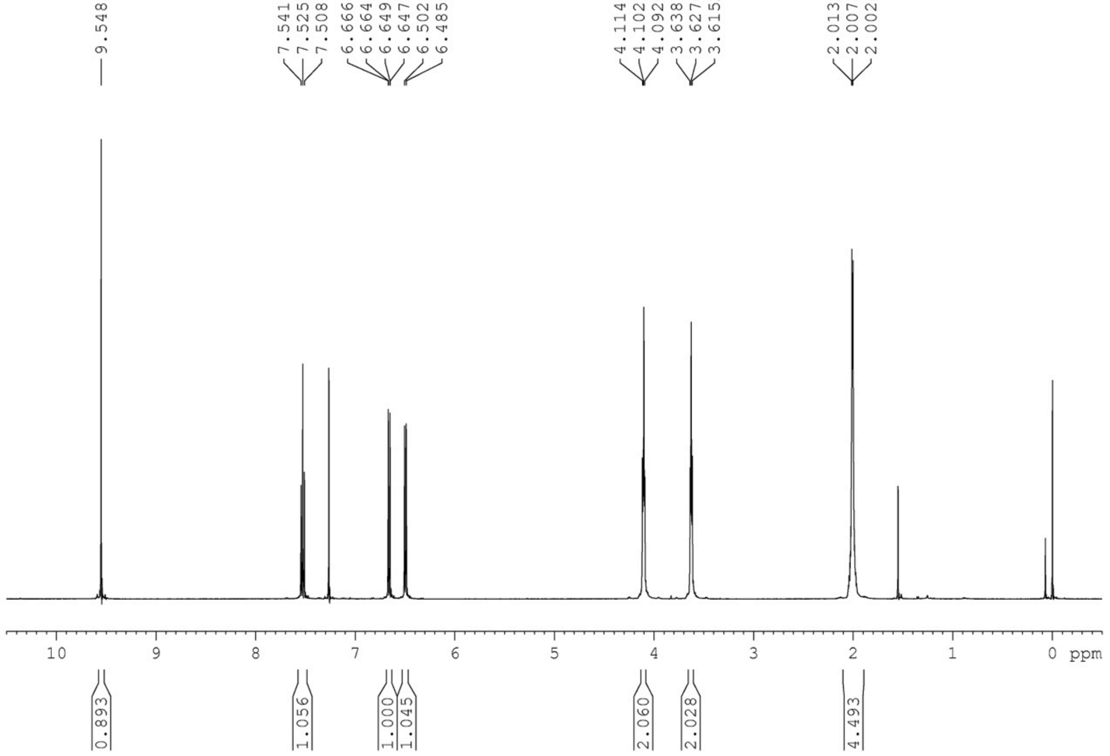


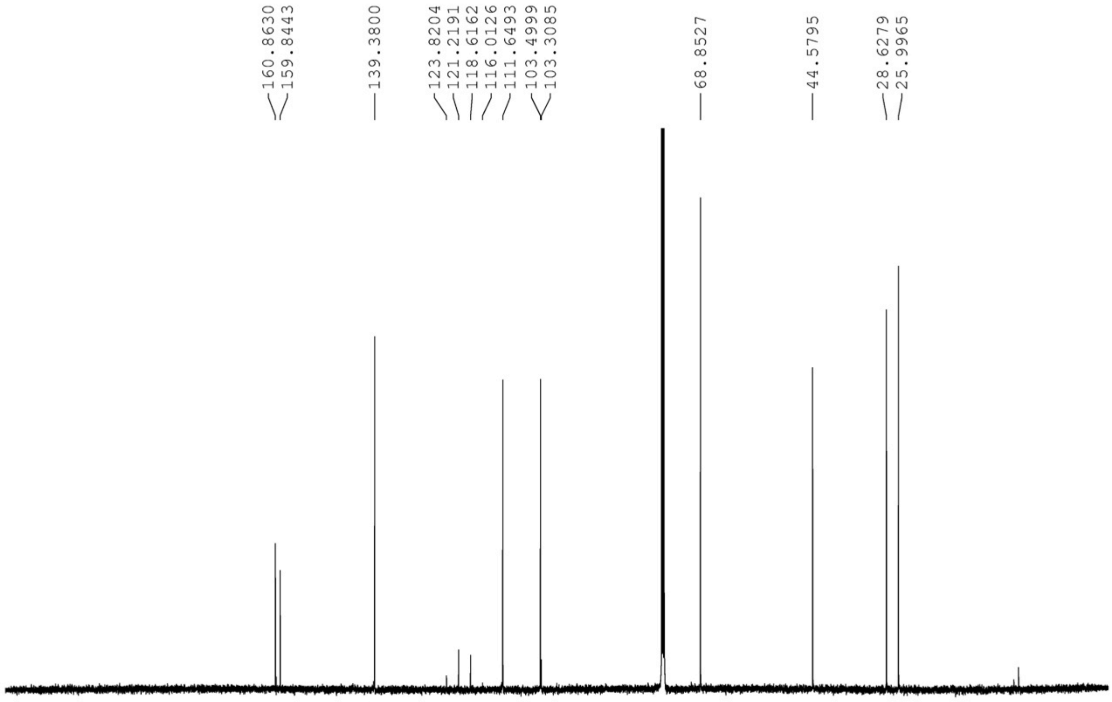
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **22** ($CDCl_3$)



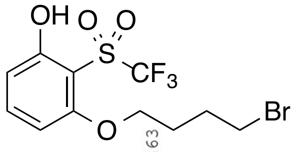
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **23** ($CDCl_3$)

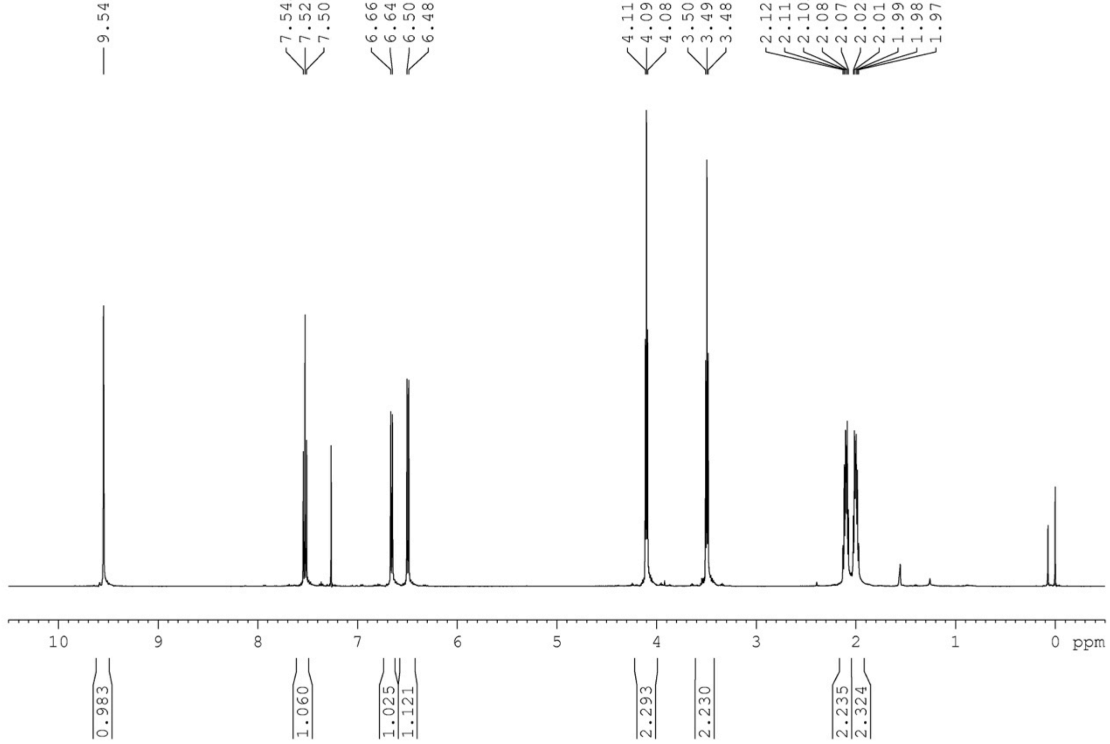


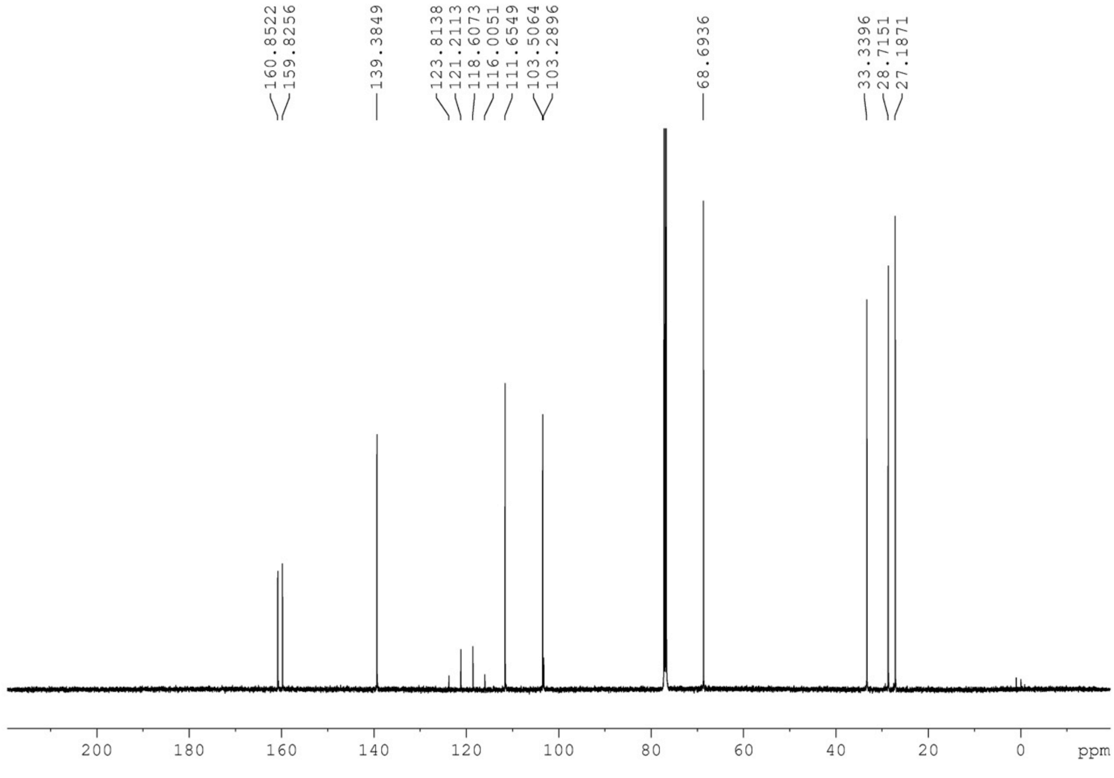




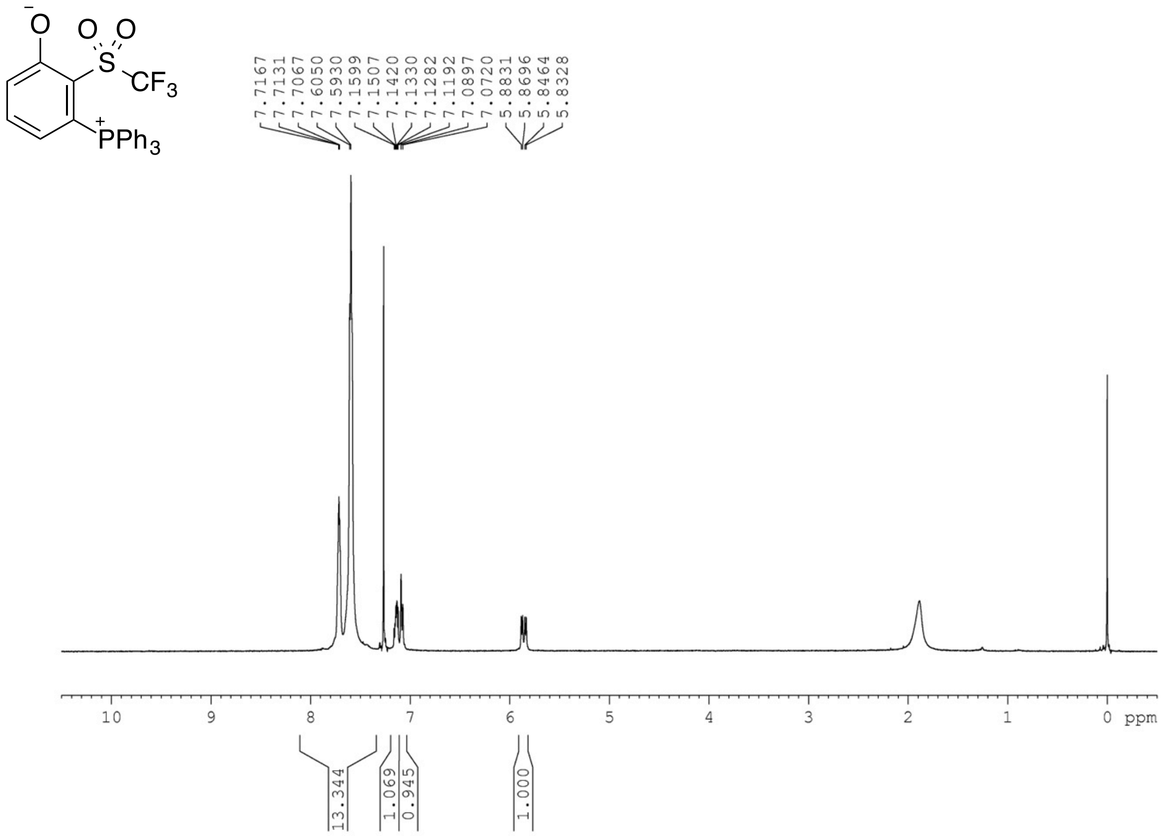
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **24** ($CDCl_3$)

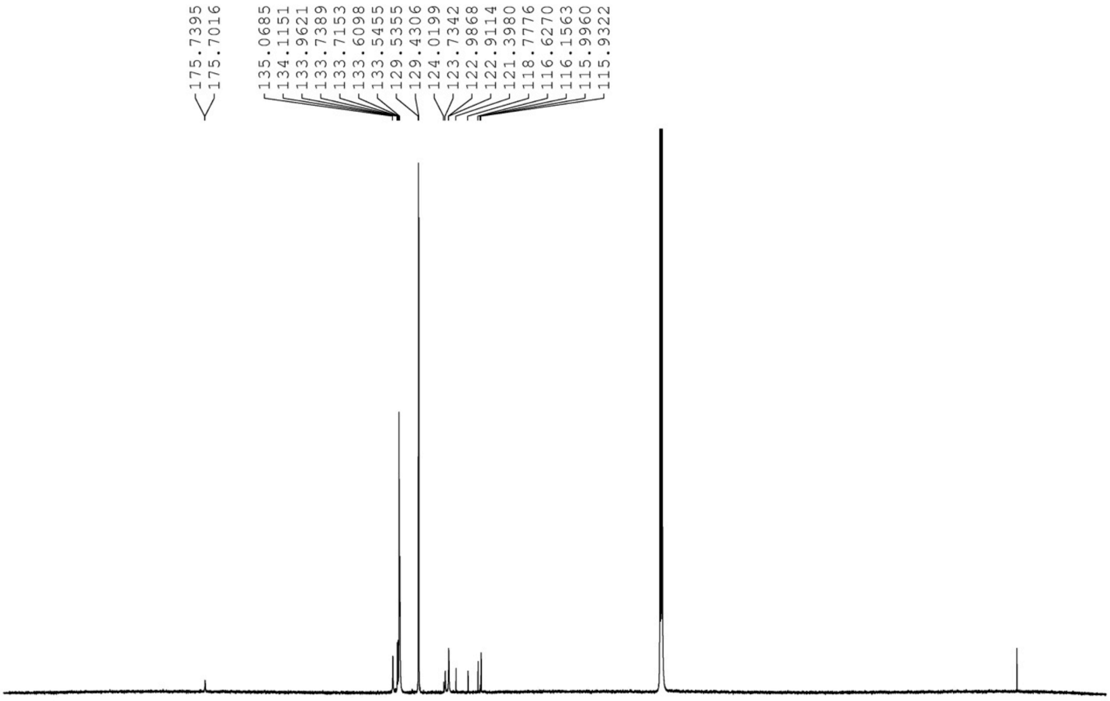




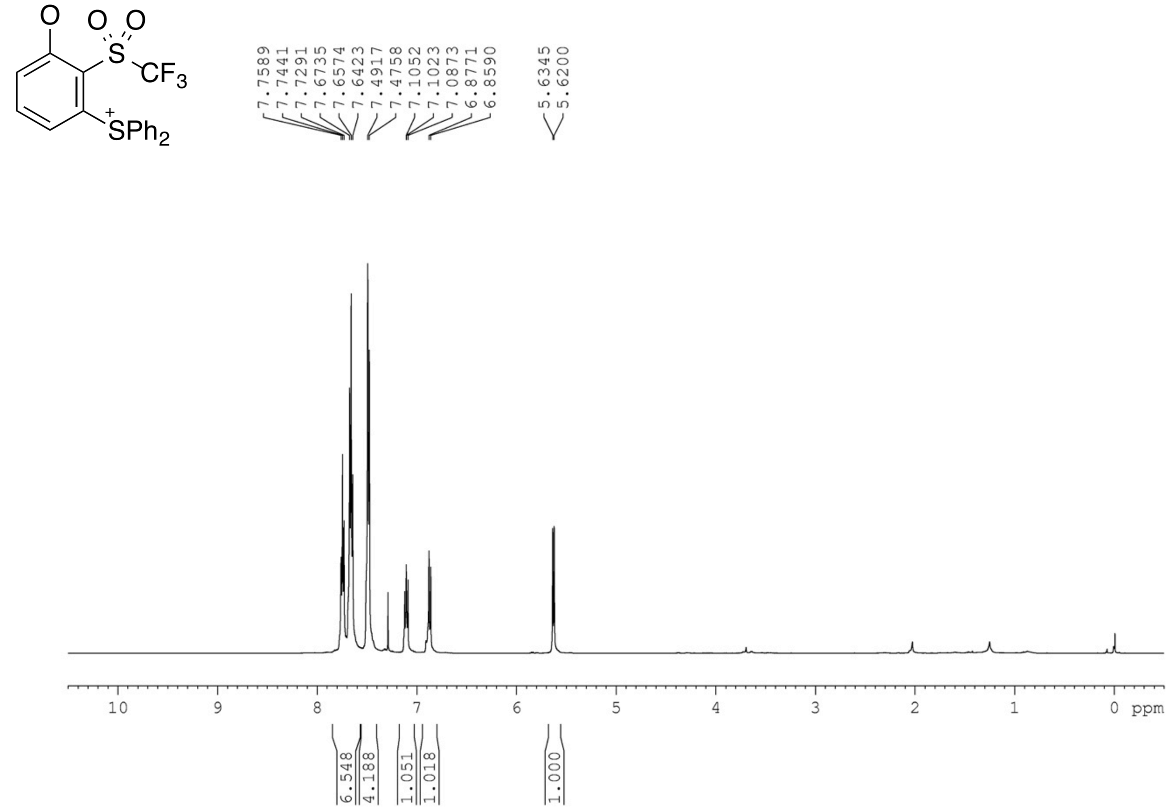


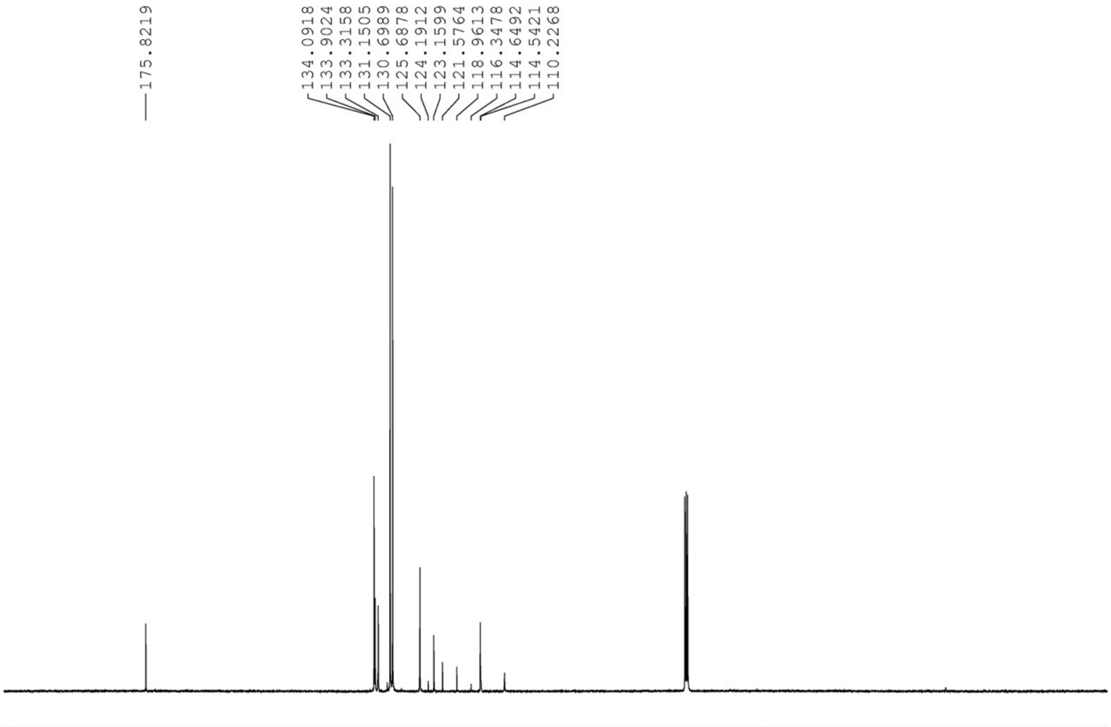
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **25** (CDCl$_3$)





^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of **26** ($CDCl_3$)





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