Supporting Information

Boron-selective Biaryl Coupling Approach to Versatile Dibenzoxaborins and Application to Concise Synthesis of Defucogilvocarcin M

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Contents

Instrumentation and chemicals

All reactions were performed using a flame-dried glassware under atmosphere of argon unless otherwise indicated.

Analytical thin-layer chromatography (TLC) was performed on precoated (0.25 mm) silica-gel plates (Merck, Merck Silica Gel 60 F_{254}, Cat. No. 1.05715.0009). Preparative TLC was carried out using silica-gel (Wako Pure Chemical Co., Wakogel B-5F, Cat. No. 230-00043 or Merck Millipore Japan inc., Merck Silica gel 60 PF_{254}, Cat. No. 1.07787.2500). Column chromatography was conducted using silica-gel (Kanto Chemical Co., Inc., Silica Gel 60N, Cat. No. 37563-84, neutral or Kanto Chemical Co., Inc., Silica Gel 60, Cat. No. 37562-85, acidic).

Melting points (mp) were measured with a Micro Melting Point System MP-J3 (Yanaco New Science Inc.) or an OptiMelt MPA100 automated melting point apparatus (Stanford Research Systems) and are uncorrected.

^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra were obtained with a Bruker AVANCE 500 spectrometer. ^{19}F NMR (376 MHz) spectra were obtained with a Bruker AVANCE 400 spectrometer. ^{11}B NMR (128 MHz) spectra were obtained with a Bruker AVANCE 400 spectrometer or a JEOL JNM-ECS 400 spectrometer. Chloroform-d_1 ($CDCl_3$) containing 0.03% tetramethylsilane (TMS) (>99.8%D, Acros Organics, Cat. No. 368651000) or acetone-d_6 (99.96%D, Cambridge Isotope Laboratories, Inc., Cat. No. DLM-38) were used as solvents for NMR measurements at ambient temperature. Chemical shifts (δ) for ^{1}H NMR are given in parts per million (ppm) relative to TMS (δ 0.00 ppm in $CDCl_3$), or residual acetone (δ 2.07 ppm). Chemical shifts (δ) for ^{13}C NMR are given in ppm relative to residual $CHCl_3$ (δ 77.0 ppm), or residual acetone (δ 205.9 ppm). Chemical shifts (δ) for ^{19}F NMR are given in ppm relative to α,α,α-trifluorotoluene (δ –63.0 ppm in $CDCl_3$) used as the external standard. Chemical shifts (δ) for ^{11}B NMR are given in ppm relative to $BF_3{\cdot}OEt_2$ (δ 0.0 ppm in $CDCl_3$) used as the external standard. The abbreviations s, d, t, q, m and br signify singlet, doublet, triplet, quartet, multiplet and broad, respectively.

Specific optical rotations were measured on a Jasco P-2100 digital polarimeter with a sodium lamp and reported as follows; $[\alpha]_D^{T\,°C}$ (c = g/100 mL, solvent).

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 at Institute of Biomaterials and Bioengineering, Tokyo Medical and Dental University, or on a QFT-7 (Varian) Fourier transform ion cyclotron resonance mass spectrometer under positive electrospray ionization (ESI^+) conditions or a JEOL JMS-700V magnetic sector mass spectrometer under electron impact (EI^+) conditions at Molecular Characterization, Collaboration Promotion Unit, RIKEN.

Elemental analyses were carried out at the Elemental Analysis Center of Tokyo Institute of Technology or A Rabbit Science Japan Co., Ltd.

Intensity data of X-ray crystallographical analyses were collected on a Rigaku R-AXIS RAPID II diffractometer. The structures were solved by direct methods (SHELXS-2013) and refined by the full-matrix least-squares on F^2 (SHELXL-2013). CCDC 1020935 (compound **2n**) and CCDC 1020936 (compound **11**) contain the supplementary crystallographic data for these structure. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre (CCDC) via www.ccdc.cam.ac.uk/data_request/cif.

(2-Hydroxy-5-nitrophenyl)boronic acid (**3d**),[S1] potassium (2-hydroxy-[1,1'-biphenyl]-3-yl)-trifluoroborate (**3h**),[S2] 2,3-dihydro-1*H*-naphtho[1,8-*de*]-1,3,2-diazaborinyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (**7**),[S3] 2-methoxy-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl trifluoromethanesulfonate,[S4] and 3-benzyloxy-2-iodophenyl trifluoromethanesufonate[S5] 2-(benzyloxy)phenol (**13**) [S6] were prepared in conventional ways according to the literatures. Distilled water was prepared by SA-2100A automatic water distillation apparatus (EYELA).

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

Wako Pure Chemical Co.

1-Methoxy-4-methylbenzene (Cat. No. 032-09723), acetone (Cat. No. 011-00357), ethyl acetate (Cat. No. 056-00367), *n*-hexane (Cat. No. 080-00427), toluene (Cat. No. 204-01866), dichloromethane (Cat. No. 130-02457), methanol (Cat. No. 136-01837), benzene (super dehydrated, Cat. No. 023-16945), 1,4-dioxane (super dehydrated, Cat. No. 042-31655), *N,N*-dimethylformamide (DMF) (super dehydrated, Cat. No. 045-32365), 1,2-dimethoxyethane (DME) (Cat. No. 046-21785), dimethylsulfoxide (Cat. No. 043-07216), *N*-bromosuccinimide (Cat. No. 025-07235), triisopropyl borate (Cat. No. 324-41535), sodium periodate (Cat. No. 199-02401), conc aqueous HCl (Cat. No. 080-01066), cesium fluoride (Cat. No. 031-17162), sodium hydroxide (Cat. No. 198-13765), sodium carbonate monohydrate (Cat. No. 193-04925), sodium thiosulfate pentahydrate (Cat. No. 194-03595), 1,8-diaminonaphthalene (Cat. No. 049-00792), diisopropylethylamine (Cat. No. 053-05355), (2-chloro-4-methylphenyl)boronic acid (Cat. No. 321-90831), (2-chloropyridin-3-yl)boronic acid (Cat. No. 323-99193), (2-chloro-4-fluorophenyl)boronic acid (Cat. No. 329-84881), (2-chloro-4-methoxyphenyl)boronic acid (Cat. No. 328-90863), (2-(acetylamino)phenyl)boronic acid (**8b**, Cat. No. 329-56931), iodine (Cat. No. 096-05425), 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (HBpin, Cat. No. 323-59832), bis(1,5-cyclooctadiene)diiridium(I) dichloride ($[Ir(cod)Cl]_2$) (Cat. No. 047-31443), 2-methoxy-4-methylphenol (**17**, 4-methylguaiacol, Cat. No. 323-23562), dichloromethane (super dehydrated, Cat. No. 044-31235), molecular sieves 4A (MS4A, Cat. No. 137-06085), potassium carbonate (162-03495), (2-aminophenyl)boronic acid (**8a**, Cat. No. 350-19121), Celite (Cat. No. 537-02305) and triethylamine (Cat. No. 202-02646).

Ark Pharma Inc.

Bis(pinacolato)diboron ($(Bpin)_2$) (Cat. No. AK-47583).

Umicore

Bis(di-*tert*-butyl(4-dimethylaminophenyl)phosphine)dichloropalladium(II) ($Pd(amphos)_2Cl_2$) (Cat. No. 68 1844 5415).

(S1) Ni, W.; Fang, H.; Springsteen, G.; Wang, B. *J. Org. Chem.* **2004**, *69*, 1999–2007.
(S2) Boebel, T. A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2008**, *130*, 7534–7535.
(S3) Noguchi, H.; Shioda, T.; Chou, C.-M.; Suginome, M. *Org. Lett*. **2008**, *10*, 377–380.
(S4) Sumida, Y.; Kato, T.; Hosoya, T. *Org. Lett*. **2013**, *15*, 2806–2809.
(S5) Hamura, T.; Hosoya, T.; Yamaguchi, H.; Kuriyama, Y.; Tanabe, M.; Miyamoto, M.; Yasui, Y.; Matsumoto, T.; Suzuki, K. *Helv Chim Acta*. **2002**, *85*, 3589–3604.
(S6) Li, Y.; Chen, S.-H.; Ou, T.-M.; Tan, J.-H.; Li, D.; Gu, L.-Q.; Huang, Z.-S. *Bioorg. Med. Chem.* **2011**, *19*, 2074–2083.

Acros Organics

Phenylboronic acid (Cat. No. 130360100).

Merck Millipore

10% Pd/C (Cat. No. 8071040010).

Sigma–Aldrich Japan Inc.

Bis(1,5-cyclooctadiene)diiridium(I) dichloride ($[Ir(cod)Cl]_2$) (Cat. No. 683094), dichlorobis(triphenylphosphine)palladium(II) (Cat. No. 412740), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (dtbpy, Cat. No. 515477), boron tribromide (BBr_3, 1.0 M in dichloromethane, Cat. No. 211222) methyl 4-hydroxy-3-iodobenzoate (Cat. No. 631949), isopropylmagnesium chloride lithium chloride complex (*i*PrMgCl·LiCl, 1.3 M in THF, Cat. No. 656984), potassium phosphate tribasic (anhydrous, Cat. No. P5629), tetrakis(triphenylphosphine)palladium(0) (Cat. No. 216666), palladium(II) acetate (recrystallized, Cat. No. 720070), 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl (XPhos, Cat. No. 638064), 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (SPhos, Cat. No. 638072), di(1-adamantyl)-*n*-butylphosphine ($P(1\text{-}Ad)_2(n\text{-}Bu)$, cataCXium® A, Cat. No. 671479), [1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene](3-chloropyridyl)palladium(II) dichloride (PEPPSI-IPr, Cat. No. 669032), (2,6-dibromophenyl)boronic acid (Cat. No. 704407), and 2-methoxyfuran (Cat. No. 138274). 2-Methoxyfuran was distilled before used.

Tokyo Chemical Industry Co., Ltd.

Pinacol (Cat. No. D0691), 1,1′-bis(diphenylphosphino)ferrocene (dppf, Cat. No. B2027), (2-hydroxyphenyl)boronic acid (**3a**, Cat. No. H1184), 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl trifluoromethanesulfonate (**3b**, Cat. No. T1952), 1-heptyne (Cat. No. H0048), 2-(dicyclohexylphosphino)biphenyl (CyJohnPhos) (Cat. No. D3388), diethylsilane (Cat. No. D3761), chloromethyl methyl ether (Cat. No. C0202), 4-hydroxybenzotrifluoride (Cat. No. H0644), 3-hydroxybenzotrifluoride (Cat. No. T0436), and (1*R*)-3,3′-dibromo-[1,1′-binaphthalene]-2,2′-diol (**6**) ((*R*)-3,3'-dibromo-1,1'-bi-2-naphthol, Cat. No. D2810).

Kanto Chemical Co.

Guaiacol (Cat. No. 17047-30), *s*-butyllithium (1.0 M in cyclohexane/*n*-hexane, Cat. No. 04938-25), *n*-butyllithium (1.6 M in *n*-hexane, Cat. No. 04937-05), *n*-butyllithium (2.6 M in *n*-hexane, Cat. No. 04935-25), diethyl ether (dehydrated, Cat. No. 14547-84), tri-potassium phosphate *n*-hydrate (Cat. No. 32380-30), ammonium chloride (Cat. No. 9287-01), (1*S*)-[1,1′-binaphthalene]-2,2′-diol ((*S*)-(–)-1,1′-bi-2-naphthol, Cat. No. 05057-35), and tetrahydrofuran (THF) (dehydrated, Cat. No. 41001-84).

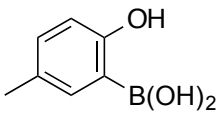
Taiyo Nippon Sanso Gas Co., Ltd.

Hydrogen gas and carbon monoxide gas.

Trifluoromethanesulfonic anhydride was kindly provided from Central Glass Co., Ltd.

Synthetic procedures and characterization data

(2-Hydroxy-5-methylphenyl)boronic acid (3c)[S7]



To a solution of 1-methoxy-4-methylbenzene (1.26 mL, 10.0 mmol) in THF (dehydrated, 20 mL) was slowly added *n*-BuLi (2.6 M in hexane, 4.2 mL, 11 mmol) at room temperature. To the solution was added triisopropyl borate (2.8 mL, 12 mmol) at –78 ºC and the mixture was gradually warmed to room temperature with stirring overnight. To the reaction mixture was added water and extracted with ether (×3). The combined organic extracts was washed with water (×1) and brine (×1), dried over Na_2SO_4, and after filtration, the filtrate was concentrated under reduced pressure.

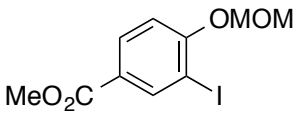
The residual oil was dissolved in dichloromethane (dehydrated, 20 mL) and to the solution was added BBr_3 (1.0 M in dichloromethane, 20 mL, 20 mmol) at –78 ºC and the mixture was gradually warmed to room temperature with stirring overnight. To the mixture was added water and extracted with ether (×3). The combined organic extracts was washed with water (×1) and brine (×2), dried over Na_2SO_4, and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (50 g of silica-gel, *n*-hexane/ethyl acetate = 5/1) to give **3c** (1.05 g, 6.93 mmol, 69.3%, 2 steps) as a colorless solid.

^{1}H NMR (1 M D_2O in acetone-d_6) δ 7.53 (d, J = 2.0 Hz, 1H, aromatic), 7.10 (dd, J = 8.0, 2.0 Hz, 1H, aromatic), 6.72 (d, J = 8.0 Hz, 1H, aromatic), 2.22 (s, 3H, ArCH_3) (the signals for the protons of boronic acid and phenolic hydroxy group were not observed);

^{13}C NMR (1 M D_2O in acetone-d_6) δ 161.7, 136.2, 133.2, 127.9, 115.0, 19.8 (the signal for the carbon which is attached to the boron atom was not observed);

^{11}B NMR (1 M D_2O in acetone-d_6) δ 28.4.

Methyl 3-iodo-4-(methoxymethoxy)benzoate



To a solution of methyl 4-hydroxy-3-iodobenzoate (1.39 g, 5.00 mmol) in dichloromethane (dehydrated, 4 mL) was added Et_3N (1.4 mL, 10 mmol) at room temperature. To the solution was added chloromethyl methyl ether (760 μL, 10.0 mmol) at 0 ºC and the mixture was stirred for 1 h at the same temperature. To the mixture was added water,and extracted with dichloromethane (×3).

(S7) Ohrui, H.; Okada, S.; Senoo, A.; Yamada, N.; Muratsubaki, M. Patent WO/2008/016166, 2008.

The combined organic extracts was washed with water (×1) and brine (×1), dried over Na_2SO_4, and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (50 g of silica-gel, *n*-hexane/ethyl acetate = 5/1) to give methyl 3-iodo-4-(methoxymethoxy)benzoate (1.22 g, 3.79 mmol, 75.8%) as a colorless solid.

TLC R_f = 0.50 (*n*-hexane/ethyl acetate = 5/1);

mp 64–65 ºC;

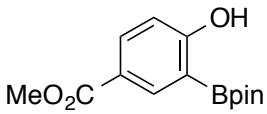
^{1}H NMR ($CDCl_3$) δ 8.47 (d, *J* = 2.0 Hz, 1H, aromatic), 7.98 (dd, *J* = 8.5, 2.0 Hz, 1H, aromatic), 7.08 (d, *J* = 8.5 Hz, 1H, aromatic), 5.30 (s, 2H, ArOC*H*$_2$OCH$_3$), 3.89 (s, 3H, ArCO$_2$C*H*$_3$), 3.51 (s, 3H, ArOCH$_2$OC*H*$_3$);

^{13}C NMR ($CDCl_3$) δ 165.7, 159.7, 141.3, 131.6, 125.5, 113.6, 94.9, 86.4, 56.8, 52.4;

IR (KBr, cm^{-1}) 1718, 1593, 1488, 1435, 1289, 1257, 1116, 1037, 978;

HRMS (EI$^+$) *m*/*z* 321.9715 (321.9702 calcd for $C_{10}H_{11}IO_4$, $[M]^+$).

Methyl 4-hydroxy-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (3e)



To a solution of methyl 3-iodo-4-(methoxymethoxy)benzoate (1.21 g, 3.76 mmol) in THF (dehydrated, 4 mL) was slowly added *i*PrMgCl·LiCl (0.67 M in THF, 6.2 mL, 4.1 mmol) at –78 ºC. After stirring for 1 h at the same temperature, to the mixture was added triisopropyl borate (3.9 mL, 17 mmol) in one portion and the mixture was warmed to room temperature. After stirring overnight, to the mixture was added aqueous HCl (2 M, 10 mL), and after stirring for 5 h at the same temperature, to the mixture was added water and extracted with ethyl acetate (×3). The combined organic extracts was dried over Na_2SO_4, and after filtration, the filtrate was concentrated under reduced pressure.

The residual oil was dissolved in ethyl acetate (10 mL) and to the solution was added pinacol (890 mg, 7.53 mmol) at room temperature. After stirring for 2 h, to the mixture was added water and extracted with ethyl acetate (×3). The combined organic extracts was washed with water (×1) and brine (×1), dried over Na_2SO_4, and after filtration, the filtrate was concentrated under reduced pressure. The resultant solid was washed with a small amount of ethyl acetate on a funnel to give **3e** (356 mg, 1.28 mmol, 34.0%) as a colorless solid.

TLC R_f = 0.33 (*n*-hexane/ethyl acetate = 5/1);

mp 157–159 ºC;

^{1}H NMR ($CDCl_3$) δ 8.33 (d, *J* = 2.5 Hz, 1H, aromatic), 8.24 (s, 1H, ArO*H*), 8.05 (dd, *J* = 8.5, 2.5 Hz, 1H, aromatic), 6.90 (d, *J* = 8.5 Hz, 1H, aromatic), 3.87 (s, 3H, ArCO$_2$C*H*$_3$), 1.38 (s, 12H,

$ArBO_2C_2(CH_3)_4$);

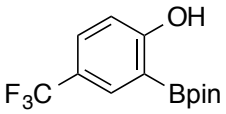
^{13}C NMR ($CDCl_3$) δ 167.6, 166.9, 138.4, 135.6, 121.9, 115.8, 85.0, 51.9 (2C), 25.0 (4C) (the signal for the carbon which is attached to the boron atom was not observed);

^{11}B NMR ($CDCl_3$) δ 30.5;

IR (KBr, cm^{-1}) 3416, 1713, 1620, 1582, 1401, 1356, 1265, 1142, 1106, 850;

HRMS (ESI^+) *m*/*z* 279.1401 (279.1398 calcd for $C_{14}H_{20}BO_5^+$, $[M+H]^+$).

2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(trifluoromethyl)phenol (3f)



To a solution of 4-(trifluoromethyl)phenol (811 mg, 5.00 mmol) and $[Ir(cod)Cl]_2$ (16.8 mg, 25.0 μmol) in benzene (dehydrated, 2.5 mL) was added diethylsilane (0.96 mL, 7.5 mmol) at room temperature. Generation of hydrogen gas was observed during the addition of diethylsilane, which ceased after stirring the mixture overnight at room temperature. After concentration of the mixture under high vacuum, the residual oil was dissolved in THF (dehydrated, 10 mL) and to the solution was added bis(pinacolato)diboron ($(Bpin)_2$) (1.27 g, 5.00 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (dtbpy) (26.8 mg, 0.100 mmol), $[Ir(cod)Cl]_2$ (33.6 mg, 50.0 μmol), and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (HBpin) (36 μL, 0.25 mmol) at room temperature. The resultant dark solution was refluxed at 80 °C (oil bath temperature) with stirring for 2 h. After cooling to room temperature, to the reaction mixture was added aqueous HCl (2 M, 10 mL), which caused the gas evolution. The biphasic mixture was stirred overnight at room temperature and extracted with ethyl acetate (×3). The combined organic extracts was dried over Na_2SO_4, and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (25 g of silica-gel, *n*-hexane/ethyl acetate = 20/1 to 10/1, the outside of the column was cooled by dry ice and covered with aluminum foil to protect from the light) to give **3f** (495 mg, 1.72 mmol, 34.4%) as a colorless solid.

TLC R_f = 0.51 (*n*-hexane/ethyl acetate = 5/1);

mp 72–74 ºC;

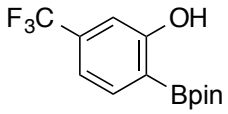
^1H NMR ($CDCl_3$) δ 8.14 (s, 1H, ArO*H*), 7.88 (d, *J* = 2.0 Hz, 1H, aromatic), 7.60 (dd, *J* = 2.0, 8.5 Hz, 1H, aromatic), 6.94 (d, *J* = 8.5 Hz, 1H, aromatic), 1.38 (s, 12H, $ArBO_2C_2(CH_3)_4$);

^{13}C NMR ($CDCl_3$) δ 166.3, 133.4 (q, *J* = 3.8 Hz), 130.9 (q, *J* = 3.8 Hz), 124.4 (q, *J* = 271.6 Hz), 122.2 (q, *J* = 32.7 Hz), 116.1, 85.3 (2C), 25.0 (4C) (the signal for the carbon which is attached to the boron atom was not observed);

^{19}F NMR ($CDCl_3$) δ –61.8;

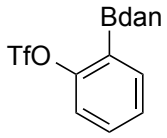
^{11}B NMR ($CDCl_3$) δ 30.4;
IR (KBr, cm^{-1}) 2983, 1620, 1630, 1314, 1265, 1274, 1140, 1117;
HRMS (EI^+) *m*/*z* 288.1155 (288.1145 calcd for $C_{13}H_{16}BF_3O_3$, $[M]^+$).

2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(trifluoromethyl)phenol (3g)



To a solution of 3-(trifluoromethyl)phenol (811 mg, 5.00 mmol) and $[Ir(cod)Cl]_2$ (16.8 mg, 25.0 μmol) in benzene (dehydrated, 2.5 mL) was added diethylsilane (0.96 mL, 7.5 mmol) at room temperature. Generation of hydrogen gas was observed during the addition of diethylsilane, which ceased after stirring the mixture overnight at room temperature. After concentration of the mixture under high vacuum, the residual oil was dissolved in THF (dehydrated, 10 mL) and to the solution was added bis(pinacolato)diboron ($(Bpin)_2$) (1.27 g, 5.00 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (dtbpy) (26.8 mg, 0.100 mmol), $[Ir(cod)Cl]_2$ (33.6 mg, 50.0 μmol), and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (HBpin) (36 μL, 0.25 mmol) at room temperature. The resultant dark solution was refluxed at 80 °C (oil bath temperature) with stirring for 2 h. After cooling to room temperature, to the reaction mixture was added aqueous HCl (2 M, 10 mL), which caused the gas evolution. The biphasic mixture was stirred overnight at room temperature and extracted with ethyl acetate (×3). The combined organic extracts was dried over Na_2SO_4, and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (25 g of silica-gel, *n*-hexane/ethyl acetate = 20/1 to 10/1, the outside of the column was cooled by dry ice and covered with aluminum foil to protect from the light) to give **3g** (973 mg, 3.38 mmol, 67.6%) as a colorless oil.
TLC R_f = 0.57 (*n*-hexane/ethyl acetate = 5/1);
^{1}H NMR ($CDCl_3$) δ 7.99 (s, 1H, ArO*H*), 7.70 (d, *J* = 7.0 Hz, 1H, aromatic), 7.122 (s, 1H, aromatic), 7.115 (d, *J* = 7.0 Hz, 1H, aromatic), 1.38 (s, 12H, $ArBO_2C_2(CH_3)_4$);
^{13}C NMR ($CDCl_3$) δ 163.8, 136.6, 135.6 (q, *J* = 31.4 Hz), 124.0 (q, *J* = 272.9 Hz), 116.1 (q, *J* = 3.8 Hz), 112.7 (q, *J* = 3.8 Hz), 85.2 (2C), 25.0 (4C) (the signal for the carbon which is attached to the boron atom was not observed);
^{19}F NMR ($CDCl_3$) δ –63.7;
^{11}B NMR ($CDCl_3$) δ 30.3;
IR (KBr, cm^{-1}) 3439, 2982, 1448, 1416, 1387, 1331, 1209, 1169, 1127, 1082, 918, 854;
HRMS (EI^+) *m*/*z* 288.1152 (288.1145 calcd for $C_{13}H_{16}BF_3O_3$, $[M]^+$).

2-(1*H*-Naphtho[1,8-*de*]-1,3,2-diazaborin-2(3*H*)-yl)phenyl trifluoromethanesulfonate (4a)



To a solution of (2-hydroxyphenyl)boronic acid (**3a**) (3.36 g, 24.4 mmol) in toluene (80 mL), placed in a two-necked round-bottomed flask equipped with a Dean–Stark apparatus, was added 1,8-diaminonaphthalene (3.95 g, 25.0 mmol) at room temperature. The mixture was refluxed at 130 °C (oil bath temperature) for 2 h with azeotropic removal of water. After cooling to room temperature, the mixture was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (100 g of silica-gel, *n*-hexane/ethyl acetate = 10/1) to give a colorless solid.

The obtained colorless solid was dissolved in dichloromethane (100 mL) and to the solution was added diisopropylethylamine (8.1 mL, 47 mmol) at room temperature. After stirring for 20 min at the same temperature, to the mixture was slowly added trifluoromethanesulfonic anhydride (5.90 mL, 35.7 mmol) at –78 ºC and the mixture was warmed to room temperature. After stirring for 2 h. to the mixture was added saturated aqueous $NaHCO_3$ and extracted with diethyl ether (×3). The combined organic extracts was washed with water (×1) and brine (×1), dried over Na_2SO_4, and,after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (100 g of silica-gel, *n*-hexane/ethyl acetate = 10/1) to give **4a** (7.56 g, 19.3 mmol, 79.1 % from **3a**) as a brown solid.

TLC R_f = 0.38 (*n*-hexane/ethyl acetate = 5/1);

mp 91–93 ºC;

^{1}H NMR ($CDCl_3$) δ 7.67 (dd, *J* = 7.0, 1.0 Hz, 1H, aromatic), 7.53 (ddd, *J* = 8.0, 7.5, 1.0 Hz, 1H, aromatic), 7.45 (dd, *J* = 7.5, 7.0 Hz, 1H, aromatic), 7.35 (d, *J* = 8.0 Hz, 1H, aromatic), 7.14 (dd, *J* = 8.0, 7.5 Hz, 2H, aromatic), 7.08 (d, *J* = 8.0 Hz, 2H, aromatic), 6.40 (d, *J* = 7.5 Hz, 2H, aromatic), 6.07 (br s, 2H, N*H*×2);

^{13}C NMR ($CDCl_3$) δ 152.5, 140.6 (2C), 136.4, 134.5, 132.0, 128.5, 127.8 (2C), 122.6, 120.1, 118.5 (2C), 118.3 (q, *J* = 320.7 Hz), 106.5 (2C) (the signal for the carbon which is attached to the boron atom was not observed);

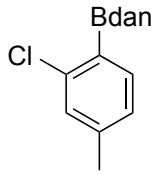
^{19}F NMR ($CDCl_3$) δ –73.5;

^{11}B NMR ($CDCl_3$) δ 28.6;

IR (KBr, cm^{-1}) 3430, 1629, 1603, 1591, 1513, 1412, 1246, 1213, 1140, 892, 820;

Anal. calcd for $C_{17}H_{12}BF_3N_2O_3S$: C, 52.07; H, 3.08; N, 7.14; S, 8.18%. Found: C, 51.94; H, 3.38; N, 6.94; S, 8.00%.

2-(2-Chloro-4-methylphenyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*]-1,3,2-diazaborine (4b)



Under air, to a solution of (2-chloro-4-methylphenyl)boronic acid (341 mg, 2.00 mmol) in dichloromethane (dehydrated, 10 mL) was added 1,8-diaminonaphthalene (316 mg, 2.00 mmol) and molecular sieves 4A (ca. 300 mg) at room temperature. After stirring for 30 min, the mixture was filtered and the filtrate was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (50 g of silica-gel, *n*-hexane/ethyl acetate = 10/1) to give **4b** (575 mg, 1.97 mmol, 98.3%) as a gray solid.

TLC R_f = 0.57 (*n*-hexane/ethyl acetate = 5/1);

mp 120–122 ºC;

^{1}H NMR ($CDCl_3$) δ 7.38 (d, *J* = 7.5 Hz, 1H, aromatic), 7.21 (s, 1H, aromatic), 7.13–7.06 (m, 3H, aromatic), 7.03 (d, *J* = 7.5 Hz, 2H, aromatic), 6.34 (dd, *J* = 7.5, 1.0 Hz, 2H, aromatic), 6.06 (s, 2H, N*H*×2), 2.33 (s, 3H, ArC*H*$_3$);

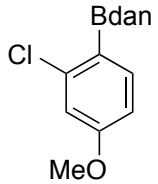
^{13}C NMR ($CDCl_3$) δ 141.7, 141.1 (2C), 137.9, 136.4, 133.9, 130.3, 127.7 (2C), 127.5, 119.9, 117.9 (2C), 106.1 (2C), 21.2 (the signal for the carbon which is attached to the boron atom was not observed);

^{11}B NMR ($CDCl_3$) δ 29.4;

IR (KBr, cm^{-1}) 3424, 1629, 1600, 1513, 1482, 1409, 1383, 1331, 1095, 819;

Anal. calcd for $C_{17}H_{14}BClN_2$: C, 69.79; H, 4.82; N, 9.58%. Found: C, 69.82; H, 5.08; N, 9.47%.

2-(2-Chloro-4-methoxyphenyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*]-1,3,2-diazaborine (4c)



Under air, to a solution of (2-chloro-4-methoxyphenyl)boronic acid (373 mg, 2.00 mmol) in dichloromethane (dehydrated, 10 mL) was added 1,8-diaminonaphthalene (316 mg, 2.00 mmol) and molecular sieves 4A (ca. 300 mg) at room temperature. After stirring for 30 min, the mixture was filtered and the filtrate was concentrated under reduced pressure. The residue was purified by recrystallization (*n*-hexane/ethyl acetate = 10/1) to give **4c** (441 mg, 1.43 mmol, 71.5%) as colorless plates.

TLC R_f = 0.33 (*n*-hexane/ethyl acetate = 5/1);

mp 194–196 ºC;

^{1}H NMR ($CDCl_3$) δ 7.45 (d, *J* = 8.5 Hz, 1H, aromatic), 7.12 (dd, *J* = 8.0, 7.5 Hz, 2H, aromatic), 7.04 (d, *J* = 8.0 Hz, 2H, aromatic), 6.95 (d, *J* = 2.5 Hz, 1H, aromatic), 6.85 (dd, *J* = 8.5, 2.5 Hz, 1H, aromatic), 6.37 (d, *J* = 7.5 Hz, 2H, aromatic), 6.09 (br s, 2H, N*H*×2), 3.83 (s, 3H, ArOC*H*$_3$);

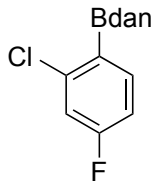
^{13}C NMR ($CDCl_3$) δ 161.6, 141.3 (2C), 139.2, 136.6, 135.0, 127.9 (2C), 120.0, 118.0 (2C), 115.5, 113.0, 106.2 (2C), 55.7 (the signal for the carbon which is attached to the boron atom was not observed);

^{11}B NMR ($CDCl_3$) δ 28.9;

IR (KBr, cm^{-1}) 3423, 3375, 1627, 1598, 1514, 1486, 1410, 1278, 1095, 1034, 821;

HRMS (EI$^+$) *m*/*z* 308.0881 (308.0888 calcd for $C_{17}H_{14}BClN_2O$, $[M]^+$).

2-(2-Chloro-4-fluorophenyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*]-1,3,2-diazaborine (4d)



Under air, to a solution of (2-chloro-4-fluorophenyl)boronic acid (348 mg, 2.00 mmol) in dichloromethane (dehydrated, 10 mL) was added 1,8-diaminonaphthalene (316 mg, 2.00 mmol) and molecular sieves 4A (ca. 300 mg) at room temperature. After stirring for 30 min, the mixture was filtered and the filtrate was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (15 g of silica-gel, *n*-hexane/ethyl acetate = 10/1) to give **4d** (594 mg, 2.00 mmol, quantitative) as a colorless solid.

TLC R_f = 0.59 (*n*-hexane/ethyl acetate = 5/1);

mp 111–113 ºC;

^{1}H NMR ($CDCl_3$) δ 7.50 (dd, *J* = 8.5, 6.5 Hz, 1H, aromatic), 7.18–7.10 (m, 3H, aromatic), 7.08–7.00 (m, 3H, aromatic), 6.37 (d, *J* = 7.5 Hz, 2H, aromatic), 6.02 (br s, 2H, N*H*×2);

^{13}C NMR ($CDCl_3$) δ 163.6 (d, *J* = 251.5 Hz), 140.9 (2C), 138.9 (d, *J* = 10.1 Hz), 136.5, 135.3 (d, *J* = 8.8 Hz), 127.8 (2C), 120.0, 118.2 (2C), 117.3 (d, *J* = 23.9 Hz), 114.2 (d, *J* = 20.1 Hz), 106.3 (2C) (the signal for the carbon which is attached to the boron atom was not observed);

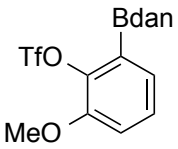
^{19}F NMR ($CDCl_3$) δ –109.3;

^{11}B NMR ($CDCl_3$) δ 29.0;

IR (KBr, cm^{-1}) 3438, 3406, 3054, 1599, 1514, 1480, 1409, 1374, 1090, 819;

HRMS (EI$^+$) *m*/*z* 296.0682 (296.0689 calcd for $C_{16}H_{11}BClFN_2$, $[M]^+$).

2-Methoxy-6-(1*H*-naphtho[1,8-*de*]-1,3,2-diazaborin-2(3*H*)-yl)phenyl trifluoromethanesulfonate (4e)



Under air, to a solution of 2-methoxy-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl trifluoromethanesulfonate[S4] (413 mg, 1.03 mmol) in THF (5 mL) and distilled water (1 mL) was added sodium periodate (856 mg, 4.00 mmol) at room temperature. After stirring for 30 min, to the mixture was added aqueous HCl (1 M, 0.6 mL). After stirring for 5 h at room temperature, the mixture was diluted with water (ca. 5 mL) and extracted with ethyl acetate (ca. 5 mL×3). The combined organic extracts was washed with brine (×1), dried over Na_2SO_4, and after filtration, the filtrate was concentrated under reduced pressure.

The residue was dissolved in dichloromethane (dehydrated, 10 mL) and to the solution was added 1,8-diaminonaphthalene (316 mg, 2.00 mmol) and molecular sieves 4A (ca. 300 mg) at room temperature. After stirring for 30 min, the mixture was filtered and the filtrate was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (25 g of silica-gel, *n*-hexane/ethyl acetate = 10/1) to give **4e** (306 mg, 0.720 mmol, 72.5%) as a colorless solid.

TLC R_f = 0.24 (*n*-hexane/ethyl acetate = 5/1);

mp 144–148 ºC;

^{1}H NMR ($CDCl_3$) δ 7.36 (dd, *J* = 8.0, 7.5 Hz, 1H, aromatic), 7.17–7.05 (m, 6H, aromatic), 6.38 (dd, *J* = 7.5, 1.0 Hz, 2H, aromatic), 6.01 (br s, 2H, N*H*×2), 3.92 (s, 3H, ArOC*H*$_3$);

^{13}C NMR ($CDCl_3$) δ 151.3, 141.8, 140.6 (2C), 136.4, 129.3, 127.8 (2C), 124.9, 120.1, 118.8 (q, *J* = 320.7 Hz), 118.4 (2C), 114.8, 106.4 (2C), 56.3 (the signal for the carbon which is attached to the boron atom was not observed);

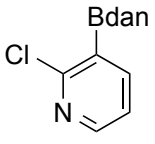
^{19}F NMR ($CDCl_3$) δ –74.0;

^{11}B NMR ($CDCl_3$) δ 28.7;

IR (KBr, cm^{-1}) 3422, 1600, 1511, 1063, 1139, 1207, 1313, 1410, 1431, 881, 821;

Anal. calcd for $C_{18}H_{14}BF_3N_2O_4S$: C, 51.21; H, 3.34; N, 6.64%. Found: C, 51.19; H, 3.38; N, 6.43%.

2-(2-Chloropyridin-3-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*]-1,3,2-diazaborine (4f)



Under air, to a solution of (2-chloropyridin-3-yl)boronic acid (787 mg, 5.00 mmol) in

dichloromethane (dehydrated, 10 mL) was added 1,8-diaminonaphthalene (791 mg, 5.00 mmol) and molecular sieves 4A (ca. 500 mg) at room temperature. After stirring for 30 min, the mixture was filtered and the filtrate was concentrated under reduced pressure. The residue was purified by recrystallization (ethyl acetate) to give **4f** (1.03 g, 3.69 mmol, 73.8%) as dark green plates.

TLC R_f = 0.24 (*n*-hexane/ethyl acetate = 5/1);

mp 204–205 ºC;

^{1}H NMR ($CDCl_3$) δ 8.44 (dd, *J* = 4.5, 2.0 Hz, 1H, aromatic), 7.86 (dd, *J* = 7.0, 2.0 Hz, 1H, aromatic), 7.28 (dd, *J* = 7.0, 4.5 Hz, 1H, aromatic), 7.14 (dd, *J* = 8.0, 7.0 Hz, 2H, aromatic), 7.08 (d, *J* = 8.0 Hz, 2H, aromatic), 6.40 (d, *J* = 7.0 Hz, 2H, aromatic), 6.06 (br s, 2H, N*H*×2);

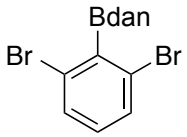
^{13}C NMR ($CDCl_3$) δ 154.3, 150.8, 143.2, 140.6 (2C), 136.4, 127.8 (2C), 122.4, 120.1, 118.5 (2C), 106.5 (2C) (the signal for the carbon which is attached to the boron atom was not observed);

^{11}B NMR ($CDCl_3$) δ 29.1;

IR (KBr, cm^{-1}) 3440, 3317, 1602, 1575, 1516, 1406, 1375, 1335, 1062, 817;

HRMS (EI^+) *m*/*z* 279.0739 (279.0735 calcd for $C_{15}H_{11}BClN_3$, $[M]^+$).

2-(2,6-Dibromophenyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*]-1,3,2-diazaborine (4g)



Under air, to a solution of (2,6-dibromophenyl)boronic acid (588 mg, 1.99 mmol) in toluene (50 mL), placed in a two-necked round-bottomed flask equipped with a Dean–Stark apparatus, was added 1,8-diaminonaphthalene (316 mg, 2.00 mmol). The mixture was refluxed at 130 ºC (oil bath temperature) for 3 h with azeotropic removal of water. After cooling to room temperature, the mixture was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (25 g of silica-gel, *n*-hexane/ethyl acetate/acetic acid = 100/10/1) to give **4g** (770 mg, 1.92 mmol, 95.8%) as a colorless solid.

TLC R_f = 0.15 (*n*-hexane/ethyl acetate = 10/1);

mp 168–170ºC;

^{1}H NMR ($CDCl_3$) δ 7.51 (d, *J* = 8.0 Hz, 2H, aromatic), 7.17–7.05 (m, 5H, aromatic), 6.38 (dd, *J* = 7.0, 1.0 Hz, 2H, aromatic), 5.79 (br s, 2H, N*H*×2);

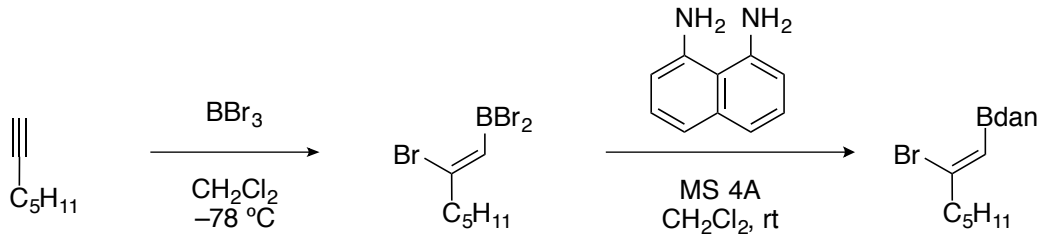
^{13}C NMR ($CDCl_3$) δ 140.8 (2C), 136.5, 131.8 (2C), 130.9 (2C), 127.7 (2C), 127.2, 120.2, 118.3 (2C), 106.4 (2C) (the signal for the carbon which is attached to the boron atom was not observed);

^{11}B NMR ($CDCl_3$) δ 29.2;

IR (KBr, cm^{-1}) 3415, 2983, 1613, 1382, 1335, 1247, 1119, 1059, 856, 780;

HRMS (EI^+) *m*/*z* 399.9378 (399.9382 calcd for $C_{16}H_{11}BBr_2N_2$, $[M]^+$).

2-[(1*Z*)-2-Bromo-1-hepten-1-yl]-2,3-dihydro-1*H*-naphtho[1,8-*de*]-1,3,2-diazaborine (4h)



According to the literature,[S8] to a solution of 1-heptyne (1.3 mL, 10 mmol) in dichloromethane (dehydrated, 5 mL) was added BBr_3 (1.0 M in dichloromethane, 11 mL, 11 mmol) at –78 ºC. After stirring for 1 h at the same temperature, to the mixture was added aqueous Na_2CO_3 (1 M, 10 mL, 10 mmol) and extracted with ethyl acetate (ca. 5 mL×3). The combined organic extracts was washed with water (×1) and brine (×2), dried over Na_2SO_4, and after filtration, the filtrate was concentrated under reduced pressure.

The residue was dissolved in dichloromethane (dehydrated, 10 mL) and to the mixture was added 1,8-diaminonaphthalene (1.58 g, 9.99 mmol) and molecular sieves 4A (ca. 300 mg) at room temperature. After stirring for 30 min, the mixture was filtered and the filtrate was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (50 g of silica-gel, *n*-hexane/ethyl acetate = 10/1) to give **4h** (1.25 g, 3.63 mmol, 36.4%) as a gray solid.

TLC R_f = 0.58 (*n*-hexane/ethyl acetate = 5/1);

mp 53–54 ºC;

^{1}H NMR ($CDCl_3$) δ 7.09 (dd, *J* = 8.0, 7.5 Hz, 2H, aromatic), 7.00 (d, *J* = 8.0 Hz, 2H, aromatic), 6.31 (d, *J* = 7.5 Hz, 2H, aromatic), 6.10 (s, 2H, N*H*×2), 5.86 (s, 1H, olefinic), 2.55 (dd, *J* = 7.5, 7.5 Hz, 2H, C*H*$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 1.61 (q, *J* = 7.5 Hz, 2H, CH$_2$C*H*$_2$CH$_2$CH$_2$CH$_3$), 1.40–1.24 (m, 4H, CH$_2$CH$_2$C*H*$_2$C*H*$_2$CH$_3$), 0.91 (t, *J* = 7.0 Hz, 3H, CH$_2$CH$_2$CH$_2$CH$_2$C*H*$_3$);

^{13}C NMR ($CDCl_3$) δ 143.5, 141.0 (2C), 136.5, 127.7 (2C), 122.4 (broad), 120.1, 117.8 (2C), 106.0 (2C), 45.9, 30.7, 28.0, 22.6, 14.1;

^{11}B NMR ($CDCl_3$) δ 26.9;

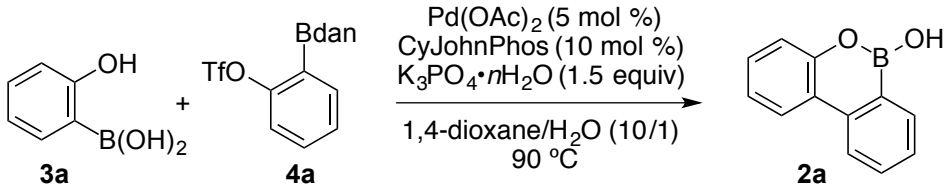
IR (KBr, cm^{-1}) 3423, 1629, 1602, 1506, 1410, 819;

HRMS (EI$^+$) *m*/*z* 342.0901 (342.0903 calcd for $C_{17}H_{20}BBrN_2$, $[M]^+$).

(S8) Wang, C.; Tobrman, T.; Xu, Z.; Negishi, E. *Org. Lett.* **2009**, *11*, 4092–4095.

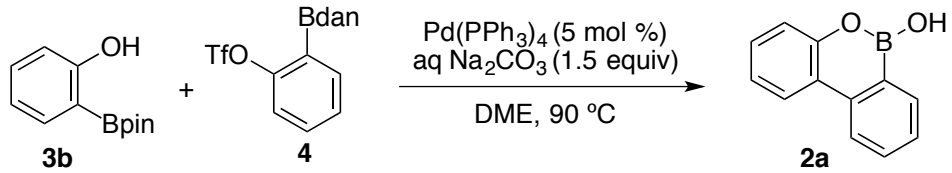
6-Hydroxy-6*H*-dibenz[*c*,*e*][1,2]oxaborin (2a)

*Under $Pd(OAc)_2$/CyJohnPhos conditions using boronic acid **3a** (Table S1, entry 7)*



A suspension of (2-hydroxyphenyl)boronic acid (**3a**) (41.4 mg, 0.300 mmol), **4a** (78.4 mg, 0.200 mmol), $Pd(OAc)_2$ (2.2 mg, 10 μmol), CyJohnPhos (7.0 mg , 20 μmol), and $K_3PO_4{\cdot}nH_2O$ (80 wt% of K_3PO_4, 79.6 mg, 0.300 mmol) in 1,4-dioxane (1.5 mL) and distilled water (0.15 mL) was stirred for 4 h at 90 ºC (oil bath temperature). After cooling to room temperature, to the mixture was added aqueous NH_4Cl (saturated, ca. 2 mL) and extracted with ethyl acetate (ca. 2 mL×3). The combined organic extracts was washed with water (×1) and brine (×2), dried over Na_2SO_4, and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by silica-gel flash column chromatography (10 g of silica-gel, *n*-hexane/ethyl acetate = 5/1) to give **2a** (40.0 mg, 0.204 mmol, quantitative) as a colorless solid.

*Under $Pd(PPh_3)_4$ conditions using boronic acid pinacol ester **3b** (Table S1, entry 17)*



A suspension of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (**3b**) (66.0 mg, 0.300 mmol), **4a** (78.4 mg, 0.200 mmol), $Pd(PPh_3)_4$ (11.6 mg, 10.0 μmol), and aqueous Na_2CO_3 (2 M, 150 μL, 0.300 mmol), in 1,2-dimethoxyethane (2.0 mL) was stirred for 5 h at 90 ºC (oil bath temperature). After cooling to room temperature, to the mixture was added aqueous NH_4Cl (saturated, ca. 2 mL) and extracted with ethyl acetate (ca. 2 mL×3). The combined organic extracts was washed with water (×1) and brine (×2), dried over Na_2SO_4, and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/ethyl acetate = 5/1) to give **2a** (38.4 mg, 0.196 mmol, 97.8%) as a colorless solid.

TLC R_f = 0.45 (*n*-hexane/ethyl acetate = 5/1);

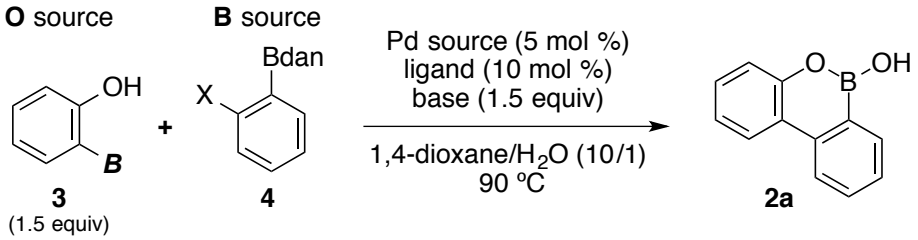
^{1}H NMR ($CDCl_3$) δ 8.15 (d, *J* = 8.0 Hz, 1H, aromatic), 8.13 (dd, *J* = 6.5, 1.5 Hz, 1H, aromatic), 8.07 (dd, *J* = 8.0, 1.0 Hz, 1H, aromatic), 7.71 (ddd, *J* = 8.0, 8.0, 1.5 Hz, 1H, aromatic), 7.48 (ddd, *J* = 6.5, 6.5, 1.0 Hz, 1H, aromatic), 7.39 (ddd, *J* = 8.0, 8.0, 1.5 Hz, 1H, aromatic), 7.29–7.21 (m, 2H, aromatic), 4.82 (s, 1H, BO*H*). The chemical shifts were consistent with those reported in the

literature;[S9]

^{13}C NMR ($CDCl_3$) δ 151.3, 140.5, 133.6, 132.8, 129.2, 127.4, 123.8, 123.2, 122.9, 121.8, 119.8 (the signal for the carbon which is attached to the boron atom was not observed);

^{11}B NMR ($CDCl_3$) δ 28.3.

Table S1. Detailed results for optimization of the reaction conditions

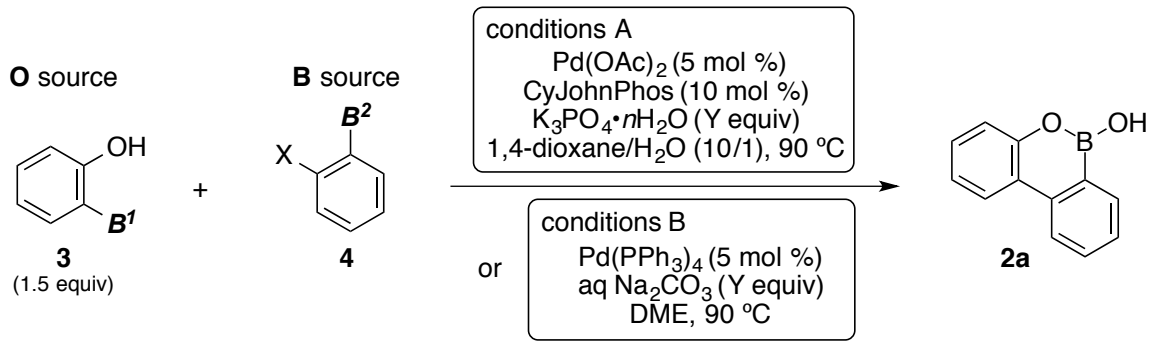


entry	***B***	X	Pd source	ligand	base	time (h)	yield (%)[a]
1	$B(OH)_2$	OTf	$Pd(OAc)_2$	PPh_3	$K_3PO_4{\cdot}nH_2O$[b]	10	68
2	$B(OH)_2$	OTf	$Pd(PPh_3)_2Cl_2$	–	$K_3PO_4{\cdot}nH_2O$[b]	10	64
3	$B(OH)_2$	OTf	PEPPSI-IPr	–	$K_3PO_4{\cdot}nH_2O$[b]	10	43
4	$B(OH)_2$	OTf	$Pd(OAc)_2$	dppf[c]	$K_3PO_4{\cdot}nH_2O$[b]	10	76
5	$B(OH)_2$	OTf	$Pd(OAc)_2$	XPhos	$K_3PO_4{\cdot}nH_2O$[b]	10	59
6	$B(OH)_2$	OTf	$Pd(OAc)_2$	SPhos	$K_3PO_4{\cdot}nH_2O$[b]	10	41
7	$B(OH)_2$	OTf	$Pd(OAc)_2$	CyJohnPhos	$K_3PO_4{\cdot}nH_2O$[b]	4	**quant**[d]
8	$B(OH)_2$	OTf	$Pd(OAc)_2$	CyJohnPhos	K_2CO_3	10	52
9	$B(OH)_2$	OTf	$Pd(OAc)_2$	CyJohnPhos	CsF	10	42
10	$B(OH)_2$	OTf	$Pd(OAc)_2$	CyJohnPhos	12 M aq NaOH	10	34
11	$B(OH)_2$	OTf	$Pd(OAc)_2$	CyJohnPhos	$K_3PO_4{\cdot}nH_2O$[b,e]	10	77
12	$B(OH)_2$	OTf	$Pd(OAc)_2$	CyJohnPhos	$K_3PO_4{\cdot}nH_2O$[b,f]	10	37
13	$B(OH)_2$	OTf	$Pd(OAc)_2$	CyJohnPhos	K_3PO_4[g]	10	**quant**[d]
14	$B(OH)_2$	Br	$Pd(OAc)_2$	CyJohnPhos	K_3PO_4[g]	10	85
15[h]	$B(OH)_2$	OTf	$Pd(PPh_3)_4$	–	2 M aq Na_2CO_3	6	68
16	Bpin[i]	OTf	$Pd(OAc)_2$	CyJohnPhos	$K_3PO_4{\cdot}nH_2O$[b]	8	**74**[d]
17[h]	Bpin[i]	OTf	$Pd(PPh_3)_4$	–	2 M aq Na_2CO_3	5	**98**[d]

[a]Determined by ^{1}H NMR unless otherwise noted. [b]Contained 80 wt% of K_3PO_4. [c]5 mol% of ligand was used. [d]Isolated yields. [e]2.0 equiv of base was used. [f]3.0 equiv of base was used. [g]Weighed under argon atmosphere in a glove box. [h]DME was used as solvent instead of 1,4-dioxane. [i]Bpin = 4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl.

(S9) Zhou, Q. J.; Worm, K.; Dolle, R. E. *J. Org. Chem.* **2004**, *69*, 5147–5149.

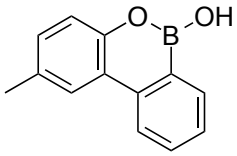
Table S2. Attempts for coupling reactions using B sources without dan protection



entry	B^1	B^2	X	conditions	base (Y equiv)	time (h)	yield (%)[a]
1	$B(OH)_2$	$B(OH)_2$	OTf	A	1.5	15	<1
2	$B(OH)_2$	$B(OH)_2$	OTf	A	3.0	9	4
3	Bpin	$B(OH)_2$	OTf	B	1.5	15	12
4	Bpin	$B(OH)_2$	OTf	B	3.0	9	7
5	Bpin	Bpin	OTf	B	1.5	15	15
6	Bpin	Bpin	OTf	B	3.0	9	13
7	$B(OH)_2$	$B(OH)_2$	Br	A	1.5	15	<1
8	$B(OH)_2$	$B(OH)_2$	Br	A	3.0	9	1

[a]Determined by ^{1}H NMR.

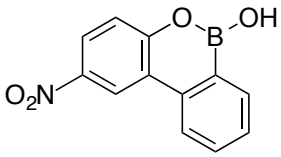
6-Hydroxy-2-methyl-6*H*-dibenz[*c*,*e*][1,2]oxaborin (2b)



A suspension of **3c** (45.6 mg, 0.300 mmol), **4a** (78.4 mg, 0.200 mmol), $Pd(OAc)_2$ (2.2 mg, 9.8 μmol), CyJohnPhos (7.0 mg, 20 μmol), and $K_3PO_4 \cdot nH_2O$ (80 wt% of K_3PO_4, 79.6 mg, 0.300 mmol) in 1,4-dioxane (1.5 mL) and distilled water (0.15 mL) was stirred for 5 h at 90 ºC (oil bath temperature). After cooling to room temperature, to the mixture was added aqueous NH_4Cl (saturated, ca. 7 mL) and extracted with ethyl acetate (ca. 5 mL×3). The combined organic extracts was washed with water (×1) and brine (×2), dried over Na_2SO_4, and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/ethyl acetate = 5/1) to give **2b** (36.8 mg, 0.175 mmol, 87.6%) as a colorless solid.

TLC R_f = 0.45 (*n*-hexane/ethyl acetate = 5/1);
^{1}H NMR ($CDCl_3$) δ 8.16 (d, *J* = 7.0 Hz, 1H, aromatic), 8.06 (d, *J* = 7.0 Hz, 1H, aromatic), 7.93 (s, 1H, aromatic), 7.71 (ddd, *J* = 8.0, 8.0, 1.5 Hz, 1H, aromatic), 7.46 (ddd, *J* = 8.0, 7.0, 0.5 Hz, 1H, aromatic), 7.20–7.16 (m, 2H, aromatic), 4.61 (br s, 1H, BO*H*), 2.44 (s, 3H, ArC*H*$_3$). The chemical shifts were consistent with those reported in the literature;[S8]
^{13}C NMR ($CDCl_3$) δ 149.3, 140.6, 133.5, 132.7, 132.1, 130.1, 127.3, 124.0, 122.8, 121.8, 119.5, 21.3 (the signal for the carbon which is attached to the boron atom was not observed);
^{11}B NMR ($CDCl_3$) δ 27.8.

6-Hydroxy-2-nitro-6*H*-dibenz[*c*,*e*][1,2]oxaborin (2c)



A suspension of **3d**[S1] (54.9 mg, 0.300 mmol) **4a** (78.4 mg, 0.200 mmol), $Pd(OAc)_2$ (2.2 mg, 9.8 μmol), CyJohnPhos (7.0 mg, 20 μmol), and $K_3PO_4 \cdot nH_2O$ (80 wt% of K_3PO_4, 79.6 mg, 0.300 mmol) in 1,4-dioxane (1.5 mL) and distilled water (0.15 mL) was stirred for 4 h at 90 ºC (oil bath temperature). After cooling to room temperature, to the mixture was added aqueous NH_4Cl (saturated, ca. 2 mL) and extracted with ethyl acetate (ca. 5 mL×3). The combined organic extracts was washed with water (×1) and brine (×2), dried over Na_2SO_4, and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/ethyl acetate/acetic acid = 50/50/1) to give **2c** (32.4 mg, 0.134 mmol, 67.2%) as a pale gray solid.
TLC R_f = 0.23–0.57, a broad spot (dichloromethane/methanol = 1/1);

mp 278–282 ºC;

^{1}H NMR (acetone-d_6) δ 9.12 (d, J = 3.0 Hz, 1H, aromatic), 8.85 (br s, 1H, BO*H*), 8.48 (d, J = 8.0 Hz, 1H, aromatic), 8.28 (dd, J = 9.0, 3.0 Hz, 1H, aromatic), 8.19 (d, J = 7.0 Hz, 1H, aromatic), 7.85 (ddd, J = 7.5, 7.0, 1.0 Hz, 1H, aromatic), 7.62 (ddd, J = 8.0, 7.5, 1.0 Hz, 1H, aromatic), 7.47 (d, J = 9.0 Hz, 1H, aromatic);

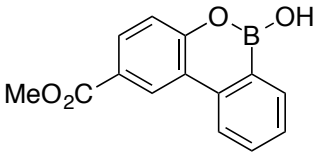
^{13}C NMR (acetone-d_6) δ 157.0, 144.0, 139.4, 134.4, 133.8, 129.4, 124.8, 124.4, 123.2, 121.4, 120.6 (the signal for the carbon which is attached to the boron atom was not observed);

^{11}B NMR (acetone-d_6) δ 27.9;

IR (KBr, cm^{-1}) 3441, 1610, 1518, 1491, 1444, 1389, 1351, 1304, 1293, 1272;

HRMS (EI$^+$) m/z 241.0539 (241.0546 calcd for $C_{12}H_8BNO_4$, $[M]^+$).

6-Hydroxy-2-methoxycarbonyl-6*H*-dibenz[*c*,*e*][1,2]oxaborin (2d)



A suspension of **3e** (417 mg, 1.50 mmol), **4a** (392 mg, 1.00 mmol), $Pd(OAc)_2$ (11.2 mg, 49.9 μmol), CyJohnPhos (35.0 mg, 99.9 μmol), and $K_3PO_4 \cdot nH_2O$ (80 wt% of K_3PO_4, 398 mg, 1.50 mmol) in 1,4-dioxane (7.5 mL) and distilled water (0.75 mL) was stirred for 5 h at 90 ºC (oil bath temperature). After cooling to room temperature, to the mixture was added aqueous NH_4Cl (saturated, ca. 7 mL) and extracted with ethyl acetate (ca. 5 mL×3). The combined organic extracts was washed with water (×1) and brine (×2), dried over Na_2SO_4, and after filtration, the filtrate was concentrated under reduced pressure. The residue was dissolved in ethyl acetate (1 mL) and to the solution was added MeOH (1 mL) to form a colorless precipitate, which was collected by filtration. The filtrate was concentrated under reduced pressure and the same operation was repeated three times and the combined solid was washed with MeOH on a funnel to give **2d** (233 mg, 0.915 mmol, 91.5%) as a colorless solid.

TLC R_f = 0.31 (*n*-hexane/ethyl acetate = 2/1);

mp 126–129 ºC;

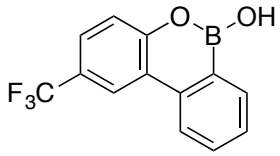
^{1}H NMR (acetone-d_6) δ 8.82 (d, J = 2.0 Hz, 1H, aromatic), 8.60 (br s, 1H, BO*H*), 8.31 (d, J = 8.0 Hz, 1H, aromatic), 8.14 (dd, J = 8.0, 1.0 Hz, 1H, aromatic), 7.99 (dd, J = 8.5, 2.0 Hz, 1H, aromatic), 7.78 (ddd, J = 7.5, 7.0, 1.0 Hz, 1H, aromatic), 7.54 (ddd, J = 8.0, 7.5, 1.0 Hz, 1H, aromatic), 7.31 (d, J = 8.5 Hz, 1H, aromatic), 3.91 (s, 3H, $ArCO_2CH_3$);

^{13}C NMR (acetone-d_6) δ 166.7, 155.7, 140.1, 134.3, 133.4, 130.6, 128.5, 126.2, 125.2, 123.5, 122.5, 120.5, 52.2 (the signal for the carbon which is attached to the boron atom was not observed);

^{11}B NMR (acetone-d_6) δ 27.9;

IR (KBr, cm^{-1}) 3402, 1704, 1615, 1438, 1393, 1300, 1295, 1274, 1234, 1113;
Anal. calcd for $C_{14}H_{11}BO_4$: C, 66.19; H, 4.36%. Found: C, 66.19; H, 4.47%.

6-Hydroxy-2-trifluoromethyl-6*H*-dibenz[*c*,*e*][1,2]oxaborin (2e)



Under $Pd(OAc)_2$/CyJohnPhos conditions

A suspension of **3f** (432 mg, 1.50 mmol), **4a** (392 mg, 1.00 mmol), $Pd(OAc)_2$ (11.2 mg, 49.9 μmol), CyJohnPhos (35.0 mg, 99.9 μmol), and $K_3PO_4 \cdot nH_2O$ (80 wt% of K_3PO_4, 398 mg, 1.50 mmol) in 1,4-dioxane (7.5 mL) and distilled water (0.75 mL) was stirred for 4 h at 90 ºC (oil bath temperature). After cooling to room temperature, to the mixture was added aqueous NH_4Cl (saturated, ca. 7 mL) and extracted with ethyl acetate (ca. 5 mL×3). The combined organic extracts was washed with water (×1) and brine (×2), dried over Na_2SO_4, and after filtration, the filtrate was concentrated under reduced pressure. The residue was roughly purified by silica-gel column chromatography (20 g, *n*-hexane/ethyl acetate = 5/1 to 1/1) followed by another silica-gel column chromatography (15 g of acidic silica-gel, *n*-hexane/ethyl acetate = 5/1) to give **2e** (206 mg, 0.780 mmol, 78.0%) as a colorless solid.

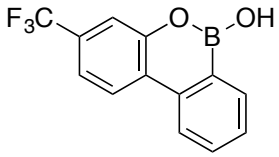
Under $Pd(PPh_3)_4$ conditions

A suspension of **3f** (86.4 mg, 0.300 mmol), **4a** (78.4 mg, 0.200 mmol), $Pd(PPh_3)_4$ (11.6 mg, 10.0 μmol), and aqueous Na_2CO_3 (2 M, 150 μL, 0.300 mmol), in 1,2-dimethoxyethane (2.0 mL) was stirred for 9 h at 90 ºC (oil bath temperature). After cooling to room temperature, to the mixture was added aqueous NH_4Cl (saturated, ca. 2 mL) and extracted with ethyl acetate (ca. 5 mL×3). The combined organic extracts was washed with water (×1) and brine (×2), dried over Na_2SO_4, and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/ethyl acetate = 5/1) to give **2e** (48.3 mg, 0.183 mmol, 91.5%) as a colorless solid.

TLC R_f = 0–0.13, a broad spot (*n*-hexane/ethyl acetate = 5/1);
mp 218–219 ºC;
^{1}H NMR (1 M D_2O in acetone-d_6) δ 8.74 (br s, 1H, BO*H*), 8.58 (s, 1H, aromatic), 8.43 (d, *J* = 8.0 Hz, 1H, aromatic), 8.17 (d, *J* = 7.0 Hz, 1H, aromatic), 7.79 (dd, *J* = 7.5, 7.0 Hz, 1H, aromatic), 7.71 (d, *J* = 8.0 Hz, 1H, aromatic), 7.56 (dd, *J* = 7.5, 7.0 Hz, 1H, aromatic), 7.43 (d, *J* = 8.0 Hz, 1H, aromatic);

^{13}C NMR (1 M D_2O in acetone-d_6) δ 155.1, 139.9, 134.5, 133.6, 129.1, 126.5 (q, J = 30.2 Hz), 125.6 (q, J = 270.4 Hz), 125.1 (q, J = 3.8 Hz), 124.4, 123.0, 122.2 (q, J = 3.8 Hz), 121.4 (the signal for the carbon which is attached to the boron atom was not observed);
^{19}F NMR (1 M D_2O in acetone-d_6) δ –62.2;
^{11}B NMR (acetone-d_6) δ 29.4;
IR (KBr, cm^{-1}) 3458, 1607, 1443, 1433, 1401, 1394, 1346, 1316, 1287, 1125, 1089, 834;
HRMS (EI$^+$) m/z 264.0570 (264.0569 calcd for $C_{13}H_8BF_3O_2$, $[M]^+$).

6-Hydroxy-3-(trifluoromethyl)-6*H*-dibenz[*c*,*e*][1,2]oxaborin (2f)



Under Pd(OAc)$_2$/CyJohnPhos conditions

A suspension of **3g** (432 mg, 1.50 mmol), **4a** (392 mg, 1.00 mmol), $Pd(OAc)_2$ (11.2 mg, 49.9 μmol), CyJohnPhos (35.0 mg, 99.9 μmol), and $K_3PO_4 \cdot nH_2O$ (80 wt% of K_3PO_4, 398 mg, 1.50 mmol) in 1,4-dioxane (7.5 mL) and distilled water (0.75 mL) was stirred for 4 h at 90 ºC (oil bath temperature). After cooling to room temperature, to the mixture was added aqueous NH_4Cl (saturated, ca. 7 mL) and extracted with ethyl acetate (ca. 5 mL×3). The combined organic extracts was washed with water (×1) and brine (×2), dried over Na_2SO_4, and after filtration, the filtrate was concentrated under reduced pressure. The residue was roughly purified by silica-gel column chromatography (20 g, *n*-hexane/ethyl acetate = 10/1 to 5/1) by another silica-gel column chromatography (15 g of acidic silica-gel, *n*-hexane/ethyl acetate = 5/1) to give **2f** (147 mg, 0.558 mmol, 55.8%) as a colorless solid.

Under Pd(PPh$_3$)$_4$ conditions

A suspension of **3g** (86.4 mg, 0.300 mmol), **4a** (78.4 mg, 0.200 mmol), $Pd(PPh_3)_4$ (11.6 mg, 10.0 μmol), and aqueous Na_2CO_3 (2 M, 150 μL, 0.300 mmol), in 1,2-dimethoxyethane (2.0 mL) was stirred for 9 h at 90 ºC (oil bath temperature). After cooling to room temperature, to the mixture was added aqueous NH_4Cl (saturated, ca. 2 mL) and extracted with ethyl acetate (ca. 5 mL×3). The combined organic extracts was washed with water (×1) and brine (×2), dried over Na_2SO_4, and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/ethyl acetate = 5/1) to give **2f** (38.8 mg, 0.147 mmol, 73.5%) as a colorless solid.

TLC R_f = 0–0.13, a broad spot (*n*-hexane/ethyl acetate = 5/1);

mp 284–286 ºC (decomposed);

^{1}H NMR (1 M D_2O in acetone-d_6) δ 8.88 (br s, 1H, BO*H*), 8.49 (d, *J* = 8.5 Hz, 1H, aromatic), 8.38 (d, *J* = 8.5 Hz, 1H, aromatic), 8.18 (d, *J* = 7.5 Hz, 1H, aromatic), 7.80 (ddd, *J* = 8.5, 7.5, 1.5 Hz, 1H, aromatic), 7.58 (ddd, *J* = 8.5, 7.5, 1.5 Hz, 1H, aromatic), 7.54 (d, *J* = 7.5 Hz, 1H, aromatic), 7.53 (s, 1H, aromatic);

^{13}C NMR (1 M D_2O in acetone-d_6) δ 152.5, 139.8, 134.6, 133.6, 130.9 (q, *J* = 32.7 Hz), 129.4, 127.4, 125.9, 125.1 (q, *J* = 271.3 Hz), 123.4, 119.7 (q, *J* = 3.8 Hz), 117.4 (q, *J* = 3.8 Hz) (the signal for the carbon which is attached to the boron atom was not observed);

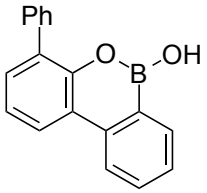
^{19}F NMR (1 M D_2O in acetone-d_6) δ –63.2;

^{11}B NMR (acetone-d_6) δ 27.9;

IR (KBr, cm^{-1}) 3474, 2926, 1607, 1486, 1392, 1370, 1337, 1295, 1125, 904;

HRMS (EI^+) *m*/*z* 264.0562 (264.0569 calcd for $C_{13}H_8BF_3O_2$, $[M]^+$).

6-Hydroxy-4-phenyl-6*H*-dibenz[*c*,*e*][1,2]oxaborin (2g)



A suspension of **3h**[S2] (82.8 mg, 0.300 mmol), **4a** (78.4 mg, 0.200 mmol,), $Pd(OAc)_2$ (2.2 mg, 9.8 μmol), CyJohnPhos (7.0 mg, 20 μmol), and $K_3PO_4 \cdot nH_2O$ (80 wt% of K_3PO_4, 79.6 mg, 0.300 mmol) in 1,4-dioxane (1.5 mL) and distilled water (0.15 mL) was stirred for 4 h at 90 ºC (oil bath temperature). After cooling to room temperature, to the mixture was added aqueous NH_4Cl (saturated, ca. 7 mL) and extracted with ethyl acetate (ca. 5 mL×3). The combined organic extracts was washed with water (×1) and brine (×2), dried over Na_2SO_4, and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/ethyl acetate/MeOH = 8/1/1) to give **2g** (38.9 mg, 0.143 mmol, 71.5%) as a colorless solid.

TLC R_f = 0.33 (*n*-hexane/ethyl acetate = 5/1);

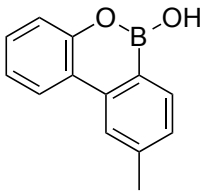
mp 176–178 ºC;

^{1}H NMR (acetone-d_6) δ 8.40 (br s, 1H, BO*H*), 8.39 (d, *J* = 7.0 Hz, 1H, aromatic), 8.33 (dd, *J* = 8.0, 1.5 Hz, 1H, aromatic), 8.15 (dd, *J* = 7.0, 1.0 Hz, 1H, aromatic), 7.78 (ddd, *J* = 9.0, 7.5, 1.5 Hz, 1H, aromatic), 7.67–7.64 (m, 2H, aromatic), 7.53 (ddd, *J* = 7.0, 6.0, 1.0 Hz, 1H, aromatic), 7.49–7.39 (m, 4H, aromatic), 7.33 (dd, *J* = 8.0, 7.5 Hz, 1H, aromatic);

^{13}C NMR (acetone-d_6) δ 149.4, 141.5, 139.6, 134.3, 133.4, 133.3, 131.3, 130.8 (2C), 128.9 (2C), 128.2, 128.0, 124.2, 123.3 (2C), 123.0 (the signal for the carbon which is attached to the boron atom was not observed);

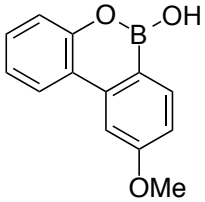
^{11}B NMR (acetone-d_6) δ 27.9;
IR (KBr, cm^{-1}) 3546, 3415, 1607, 1560, 1500, 1488, 1456, 1367, 1312;
HRMS (EI$^+$) *m*/*z* 272.1003 (272.1009 calcd for $C_{18}H_{13}BO_2$, $[M]^+$).

6-Hydroxy-9-methyl-6*H*-dibenz[*c*,*e*][1,2]oxaborin (2h)



A suspension of **3a** (41.4 mg, 0.300 mmol) **4b** (58.5 mg, 0.200 mmol), $Pd(OAc)_2$ (2.2 mg, 9.8 μmol), CyJohnPhos (7.0 mg, 20 μmol), and $K_3PO_4{\cdot}nH_2O$ (80 wt% of K_3PO_4, 79.6 mg, 0.300 mmol) in 1,4-dioxane (1.5 mL) and distilled water (0.15 mL) was stirred for 4 h at 90 ºC (oil bath temperature). After cooling to room temperature, to the mixture was added aqueous NH_4Cl (saturated, ca. 2 mL) and extracted with ethyl acetate (ca. 5 mL×3). The combined organic extracts was washed with water (×1) and brine (×2), dried over Na_2SO_4, and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/ethyl acetate = 5/1) to give **2h** (38.6 mg, 0.184 mmol, 91.9%) as a colorless solid.
TLC R_f = 0.40 (*n*-hexane/ethyl acetate = 5/1);
^{1}H NMR ($CDCl_3$) δ 8.14 (dd, *J* = 8.0, 1.0 Hz, 1H, aromatic), 7.98 (s, 1H, aromatic), 7.97 (d, *J* = 7.5 Hz, 1H, aromatic), 7.37 (ddd, *J* = 7.5, 7.0, 1.5 Hz, 1H, aromatic), 7.31 (d, *J* = 7.0 Hz, 1H, aromatic), 7.27 (dd, *J* = 8.0, 1.0 Hz, 1H, aromatic), 7.22 (ddd, *J* = 8.0, 8.0, 1.0 Hz, 1H, aromatic), 4.61 (br s, 1H, BO*H*), 2.53 (s, 3H, ArC*H*$_3$). The chemical shifts were consistent with those reported in the literature;[S9]
^{13}C NMR ($CDCl_3$) δ 151.2, 142.8, 140.4, 133.2, 128.8, 128.4, 123.5, 122.9, 122.5, 122.0, 119.5, 22.3 (the signal for the carbon which is attached to the boron atom was not observed);
^{11}B NMR ($CDCl_3$) δ 28.6.

6-Hydroxy-9-methoxy-6*H*-dibenz[*c*,*e*][1,2]oxaborin (2i)



A suspension of **3a** (207 mg, 1.50 mmol), **4c** (309 mg, 1.00 mmol), $Pd(OAc)_2$ (11.2 mg, 49.9 μmol), CyJohnPhos (35.0 mg, 99.9 μmol), and $K_3PO_4{\cdot}nH_2O$ (80 wt% of K_3PO_4, 398 mg, 1.50 mmol) in 1,4-dioxane (7.5 mL) and distilled water (0.75 mL) was stirred for 4 h at 90 ºC (oil bath

temperature). After cooling to room temperature, to the mixture was added aqueous NH_4Cl (saturated, ca. 7 mL) and extracted with ethyl acetate (ca. 5 mL×3). The combined organic extracts was washed with water (×1) and brine (×2), dried over Na_2SO_4, and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/ethyl acetate/MeOH = 8/1/1) to give **2i** (180 mg, 0.798 mmol, 79.8%) as a colorless solid.

TLC R_f = 0–0.22, a broad spot (*n*-hexane/ethyl acetate = 5/1);

mp 192–194 ºC;

^{1}H NMR (acetone-d_6) δ 8.26 (dd, J = 8.0, 1.5 Hz, 1H, aromatic), 8.06 (d, J = 8.0 Hz, 1H, aromatic), 8.03 (br s, 1H, BO*H*), 7.78 (d, J = 2.5 Hz, 1H, aromatic), 7.39 (ddd, J = 8.5, 8.0, 1.5 Hz, 1H, aromatic), 7.24–7.19 (m, 2H, aromatic), 7.08 (dd, J = 8.5, 2.5 Hz, 1H, aromatic), 3.98 (s, 3H, ArOC*H*$_3$);

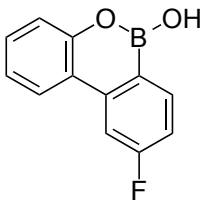
^{13}C NMR (acetone-d_6) δ 164.4, 153.0, 143.4, 136.2, 130.1, 124.9, 123.8, 123.2, 120.4, 115.6, 106.6, 55.8 (the signal for the carbon which is attached to the boron atom was not observed);

^{11}B NMR (acetone-d_6) δ 28.0;

IR (KBr, cm^{-1}) 3477, 1560, 1503, 1463, 1389, 1321, 1299, 1272, 1250, 1138, 1018;

HRMS (EI$^+$) *m*/*z* 226.0801 (226.0801 calcd for $C_{13}H_{11}BO_3$, $[M]^+$).

9-Fluoro-6-hydroxy-6*H*-dibenz[*c*,*e*][1,2]oxaborin (2j)



A suspension of **3a** (207 mg, 1.50 mmol), **4d** (297 mg, 1.00 mmol), $Pd(OAc)_2$ (11.2 mg, 49.9 μmol), CyJohnPhos (35.0 mg, 99.9 μmol,), and $K_3PO_4{\cdot}nH_2O$ (80% of K_3PO_4, 1.50 mmol, 398 mg) in 1,4-dioxane (7.5 mL) and distilled water (0.75 mL) was stirred for 2 h at 90 ºC (oil bath temperature). After cooling to room temperature, to the mixture was added aqueous NH_4Cl (saturated, ca. 7 mL) and extracted with ethyl acetate (ca. 10 mL×3). The combined organic extracts was washed with water (×1) and brine (×2), dried over Na_2SO_4, and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (50 g of silica-gel, *n*-hexane/ethyl acetate/MeOH = 8/1/1) to give **2j** (177 mg, 0.826 mmol, 82.6%) as a colorless solid.

TLC R_f = 0–0.23, a broad spot (*n*-hexane/ethyl acetate = 5/1);

mp 195–197 ºC;

^{1}H NMR (acetone-d_6) δ 8.42 (br s, 1H, BO*H*), 8.25 (dd, J = 8.0, 1.5 Hz, 1H, aromatic), 8.17 (dd, J = 8.5, 7.0 Hz, 1H, aromatic), 8.03 (dd, J = 11.5, 2.5 Hz, 1H, aromatic), 7.43 (ddd, J = 8.0, 7.0, 1.5 Hz,

1H, aromatic), 7.29–7.22 (m, 3H, aromatic);

^{13}C NMR (acetone-d_6) δ 166.8 (d, J = 249.5 Hz), 152.7, 144.1 (d, J = 8.8 Hz), 137.1 (d, J = 8.8 Hz), 130.6, 125.0, 123.3, 122.8 (d, J = 2.5 Hz), 120.3, 115.5 (d, J = 21.4 Hz), 108.9 (d, J = 22.7 Hz) (the signal for the carbon which is attached to the boron atom was not observed);

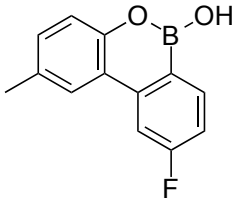
^{19}F NMR (1 M D_2O in acetone-d_6) δ –108.5;

^{11}B NMR (acetone-d_6) δ 27.6;

IR (KBr, cm^{-1}) 3454, 1608, 1590, 1554, 1418, 1396, 1289, 1181, 1094, 865, 846;

Anal. calcd for $C_{12}H_8BFO_2$: C, 67.35; H, 3.77%. Found: C, 67.32; H, 3.81%.

9-Fluoro-6-hydroxy-2-methyl-6*H*-dibenz[*c*,*e*][1,2]oxaborin (2k)



A suspension of **3c** (297 mg, 1.50 mmol), **4d** (228 mg, 1.00 mmol), $Pd(OAc)_2$ (11.2 mg, 49.9 μmol), CyJohnPhos (35.0 mg, 99.9 μmol), and K_3PO_4·$n$$H_2O$ (80 wt% of K_3PO_4, 398 mg, 1.50 mmol) in 1,4-dioxane (7.5 mL) and distilled water (0.75 mL) was stirred for 3.5 h at 90 ºC (oil bath temperature). After cooling to room temperature, to the mixture was added aqueous NH_4Cl (saturated, ca. 7 mL) and extracted with ethyl acetate (ca. 10 mL×3). The combined organic extracts was washed with water (×1) and brine (×2), dried over Na_2SO_4, and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (50 g of silica-gel, *n*-hexane/ethyl acetate/MeOH = 8/1/1) to give **2k** (204 mg, 0.890 mmol, 89.0%) as a colorless solid.

TLC R_f = 0–0.26, a broad spot (*n*-hexane/ethyl acetate = 5/1);

mp 187–189 ºC;

^{1}H NMR (acetone-d_6) δ 8.21 (br s, 1H, BO*H*), 8.15 (dd, J = 8.0, 6.5 Hz, 1H, aromatic), 8.04 (d, J = 1.5 Hz, 1H, aromatic), 8.03 (dd, J = 12.0, 2.5 Hz, 1H, aromatic), 7.27–7.22 (m, 2H, aromatic), 7.13 (d, J = 8.0 Hz, 1H, aromatic), 2.41 (s, 3H, ArCH_3);

^{13}C NMR (acetone-d_6) δ 166.9 (d, J = 285.2 Hz), 150.9, 144.4 (d, J = 8.8 Hz), 137.2 (d, J = 8.8 Hz), 132.7, 131.5, 125.2, 122.6 (d, J = 3.8 Hz), 120.1, 115.4 (d, J = 21.4 Hz), 109.0 (d, J = 22.7 Hz), 20.9 (the signal for the carbon which is attached to the boron atom was not observed);

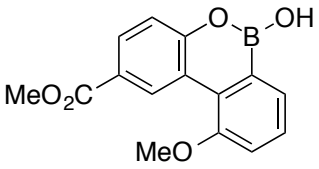
^{19}F NMR (1 M D_2O in acetone-d_6) δ –108.6;

^{11}B NMR (acetone-d_6) δ 27.6;

IR (KBr, cm^{-1}) 3419, 1613, 1569, 1361, 1348, 1287, 1277, 1247, 860, 811;

HRMS (EI$^+$) m/z 228.0765 (228.0758 calcd for $C_{13}H_{10}BFO_2$, $[M]^+$).

6-Hydroxy-2-methoxycarbonyl-10-methoxy-6*H*-dibenz[*c*,*e*][1,2]oxaborin (2l)



A suspension of **3e** (278 mg, 0.749 mmol), **4e** (211 mg, 0.500 mmol), $Pd(OAc)_2$ (5.6 mg, 25 μmol), CyJohnPhos (17.5 mg, 50.0 μmol), and $K_3PO_4 \cdot nH_2O$ (80 wt% of K_3PO_4, 199 mg, 0.75 mmol) in 1,4-dioxane (7.5 mL) and distilled water (0.75 mL) was stirred for 5 h at 90 ºC (oil bath temperature). After cooling to room temperature, to the mixture was added aqueous NH_4Cl (saturated, ca. 7 mL) and extracted with ethyl acetate (ca. 5 mL×3). The combined organic extracts was washed with water (×1) and brine (×2), dried over Na_2SO_4, and after filtration, the filtrate was concentrated under reduced pressure. To the residue was added ethyl acetate (3 mL) and the insoluble solid was collected by filtration. The filtrate was concentrated under reduced pressure and the same operation was repeated three times. The combined solid was washed with a small amount of ethyl acetate on a funnel and dried under reduced pressure to give **2l** (120 mg, 0.423 mmol, 84.7%) as a colorless solid.

TLC R_f = 0.16 (*n*-hexane/ethyl acetate = 2/1);

mp 197–199 ºC;

^{1}H NMR (acetone-d_6) δ 9.88 (d, J = 2.0 Hz, 1H, aromatic), 8.41 (br s, 1H, BO*H*), 7.99 (dd, J = 8.5, 2.0 Hz, 1H, aromatic), 7.80 (dd, J = 8.0, 1.5 Hz, 1H, aromatic), 7.54 (dd, J = 8.0, 1.5 Hz, 1H, aromatic), 7.48 (dd, J = 8.0, 1.5 Hz, 1H, aromatic), 7.31 (d, J = 8.5 Hz, 1H, aromatic), 4.11 (s, 3H, $ArCO_2CH_3$), 3.91 (s, 3H, $ArOCH_3$);

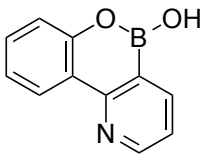
^{13}C NMR (acetone-d_6) δ 167.4, 158.7, 155.9, 132.7, 130.2, 129.8, 128.8, 126.5, 125.1, 123.6, 120.2, 116.7, 56.3, 52.3 (the signal for the carbon which is attached to the boron atom was not observed);

^{11}B NMR (acetone-d_6) δ 28.1;

IR (KBr, cm^{-1}) 3432, 1694, 1443, 1434, 1379, 1315, 1300, 1277, 1269, 1247, 1041;

Anal. calcd for $C_{15}H_{13}BO_5$: C, 63.42; H, 4.61%. Found: C, 63.23; H, 4.78%.

5-Hydroxy-5*H*-[1,2]benzoxaborino[4,3-*b*]pyridine (2m)



A suspension of **3a** (207 mg, 1.50 mmol), **4f** (280 mg, 1.00 mmol), $Pd(OAc)_2$ (11.2 mg, 49.9 μmol), CyJohnPhos (35.0 mg, 99.9 μmol), and $K_3PO_4 \cdot nH_2O$ (80 wt% of K_3PO_4, 398 mg, 1.50 mmol) in 1,4-dioxane (7.5 mL) and distilled water (0.75 mL) was stirred for 16 h at 90 ºC (oil bath

temperature). After cooling to room temperature, to the mixture was added water and ethyl acetate and extracted with aqueous Na_2CO_3 (0.1 M, ×2). The combined aqueous extracts was neutralized with aqueous HCl (1 M) to pH 7 and concentrated under reduced pressure. To the residue was added MeOH and insoluble materials were removed by filtration. The filtrate was concentrated under reduced pressure and the residue was purified by silica-gel column chromatography (25 g of silica-gel, dichloromethane/MeOH = 10/1) to give a brown oil, to which was added ethyl acetate. After removing the insoluble materials by filtration. The filtrate was concentrated under reduced pressure. To the residue was added acetone/water (100/1) and concentrated under reduced pressure to give **2m** (127 mg, 0.645 mmol, 64.5%) as a colorless solid.

TLC R_f = 0–0.20, a broad spot (ethyl acetate);

mp 156–158 ºC;

^{1}H NMR (0.2 mM DCl in D_2O) δ 8.57 (dd, J = 7.5, 1.5 Hz, 1H, aromatic), 8.48 (dd, J = 6.0, 1.5 Hz, 1H, aromatic), 7.90 (dd, J = 8.0, 1.5 Hz, 1H, aromatic), 7.76 (dd, J = 7.5, 6.0 Hz, 1H, aromatic), 7.46 (ddd, J = 8.5, 7.5, 1.5 Hz, 1H, aromatic), 7.08 (ddd, J = 8.0, 7.5, 1.0 Hz, 1H, aromatic), 7.00 (dd, J = 8.5, 1.0 Hz, 1H, aromatic) (the signal for the proton of half boronic acid was not observed);

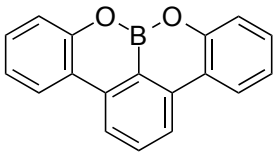
^{13}C NMR (0.2 mM DCl in D_2O) δ 155.9, 149.2, 147.6, 140.0, 134.5, 123.9, 123.7, 121.1, 120.1, 114.9 (the signal for the carbon which is attached to the boron atom was not observed);

^{11}B NMR (acetone-d_6) δ 28.2;

IR (KBr, cm^{-1}) 3352, 1613, 1440, 1381, 1258, 1152, 1135, 1003, 928, 916;

HRMS (EI$^+$) m/z 197.0641 (197.0648 calcd for $C_{11}H_8BNO_2$, $[M]^+$).

8,9-Dioxa-8a-borabenzo[*fg*]tetracene (2n)



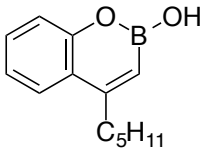
A suspension of **3a** (82.6 mg, 0.599 mmol), **4g** (58.5 mg, 0.200 mmol), $Pd(OAc)_2$ (2.2 mg, 9.8 μmol), CyJohnPhos (7.0 mg, 20 μmol), and $K_3PO_4 \cdot nH_2O$ (80 wt% of K_3PO_4, 79.6 mg, 0.300 mmol) in 1,4-dioxane (1.5 mL) and distilled water (0.15 mL) was stirred for 9 h at 90 ºC (oil bath temperature). After cooling to room temperature, to the mixture was added aqueous NH_4Cl (saturated, ca. 7 mL) and extracted with ethyl acetate (ca. 5 mL×3). The combined organic extracts was washed with water (×1) and brine (×2), dried over Na_2SO_4, and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/ethyl acetate = 5/1) to give **2n** (16.0 mg, 59.2 μmol, 29.6%) as a colorless solid.

TLC R_f = 0.50 (*n*-hexane/ethyl acetate = 5/1);

mp 203–205 ºC;

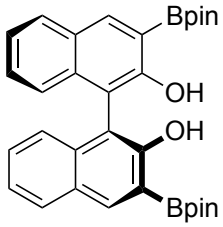
^{1}H NMR ($CDCl_3$) δ 8.14 (d, *J* = 7.5 Hz, 2H, aromatic), 8.07 (d, *J* = 8.0 Hz, 2H, aromatic), 7.89 (dd, *J* = 8.0, 8.0 Hz, 1H, aromatic), 7.45 (d, *J* = 3.5 Hz, 4H, aromatic), 7.31–7.24 (m, 2H, aromatic);
^{13}C NMR ($CDCl_3$) δ 151.8 (2C), 139.4 (2C), 133.9, 129.5 (2C), 123.9 (2C), 123.1 (2C), 123.0 (2C), 120.4 (2C), 119.6 (2C) (the signal for the carbon which is attached to the boron atom was not observed);
^{11}B NMR ($CDCl_3$) δ 28.7;
IR (KBr, cm^{-1}) 1738, 1727, 1719, 1373, 1365, 1350, 1229, 1217;
HRMS (EI^+) *m*/*z* 270.0856 (270.0852 calcd for $C_{18}H_{11}BO_2$, $[M]^+$).

2-Hydroxy-4-pentyl-2*H*-1,2-benzoxaborin (2o)



A suspension of **3a** (207 mg, 1.50 mmol), **4h** (392 mg, 1.00 mmol), $Pd(OAc)_2$ (11.2 mg, 49.9 μmol), CyJohnPhos (35.0 mg, 99.9 μmol), and $K_3PO_4{\cdot}nH_2O$ (80 wt% of K_3PO_4, 398 mg, 1.50 mmol) in 1,4-dioxane (7.5 mL) and distilled water (0.75 mL) was stirred for 5 h at 90 ºC (oil bath temperature). After cooling to room temperature, to the mixture was added aqueous NH_4Cl (saturated, ca. 7 mL) and extracted with ethyl acetate (ca. 10 mL×3). The combined organic extracts was washed with water (×1) and brine (×2), dried over Na_2SO_4, and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (50 g of silica-gel, *n*-hexane/ethyl acetate = 20/1 to 10/1) to give **2o** (174 mg, 0.807 mmol, 80.7%) as a gray solid.
TLC R_f = 0.41 (*n*-hexane/ethyl acetate = 5/1);
mp 63–65 ºC;
^{1}H NMR (acetone-d_6) δ 7.71 (dd, *J* = 7.5, 1.5 Hz, 1H, aromatic), 7.67 (br s, 1H, BO*H*), 7.38 (ddd, *J* = 8.0, 7.5, 1.5 Hz, 1H, aromatic), 7.21 (dd, *J* = 8.0, 1.5 Hz, 1H, aromatic), 7.16 (ddd, *J* = 8.0, 7.5, 1.5 Hz, 1H, aromatic), 6.00 (s, 1H, olefinic), 2.79 (dt, *J* = 1.0, 8.0 Hz, 2H, C*H*$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 1.72–1.66 (m, 2H, CH$_2$C*H*$_2$CH$_2$CH$_2$CH$_3$), 1.47–1.37 (m, 4H, CH$_2$CH$_2$C*H*$_2$C*H*$_2$CH$_3$), 0.93 (t, *J* = 7.0 Hz, 3H, CH$_2$CH$_2$CH$_2$CH$_2$C*H*$_3$).
^{13}C NMR (acetone-d_6) δ 160.3, 154.2, 130.0, 125.9, 125.2, 122.7, 119.8, 35.3, 32.6, 29.4, 23.3, 14.4 (the signal for the carbon which is attached to the boron atom was not observed);
^{11}B NMR (acetone-d_6) δ 27.7;
IR (KBr, cm^{-1}) 3396, 2360, 2341, 2333, 1601, 1376, 1342, 1270, 1053, 847;
HRMS (EI^+) *m*/*z* 216.1319 (216.1322 calcd for $C_{13}H_{17}BO_2$, $[M]^+$).

(1*S*)-3,3′-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[1,1′-binaphthalene]-2,2′-diol (21)



To a solution of (1*S*)-[1,1′-binaphthalene]-2,2′-diol (1.43 g, 4.99 mmol) and $[Ir(cod)Cl]_2$ (33.6 mg, 50.0 μmol) in THF (dehydrated, 5.0 mL) was added diethylsilane (2.00 mL, 15.6 mmol) at room temperature. Generation of hydrogen gas was observed during the addition of diethylsilane, which ceased after stirring the mixture 2 h at room temperature. After concentration of the mixture under high vacuum, the residual oil was dissolved in THF (dehydrated, 2.5 mL) and to the solution was added bispinacolatodiboron ($(Bpin)_2$) (2.54 g, 10.0 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (dtbpy) (53.7 mg, 0.200 mmol), $[Ir(cod)Cl]_2$ (67.2 mg, 0.100 mmol), and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (HBpin) (73 μL, 0.50 mmol) at room temperature. The resultant dark solution was refluxed at 80 °C (oil bath temperature) with stirring for 6 h. After cooling to room temperature, to the reaction mixture was added aqueous HCl (1 M, 15 mL) at 0 ºC, which caused the gas evolution. The biphasic mixture was stirred overnight at room temperature and extracted with Et_2O (×3). The combined organic extracts was dried over Na_2SO_4, and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (30 g of silica-gel, *n*-hexane/dichloromethane/MeOH = 5/1/1, the outside of the column was cooled by dry ice and covered with aluminum foil to protect from the light) to give **21** (1.22 g, 2.27 mmol, 45.4%) as a colorless solid.

TLC R_f = 0.20 (*n*-hexane/ethyl acetate = 5/1), 0.50 (*n*-hexane/dichloromethane/MeOH = 5/1/1);

mp 221–223 ºC;

^{1}H NMR ($CDCl_3$) δ 8.38 (s, 2H, aromatic), 7.94 (s, 2H, ArO*H*), 7.88–7.85 (m, 2H, aromatic), 7.28–7.25 (m, 4H, aromatic), 7.19–7.16 (m, 2H, aromatic), 1.39 (s, 24H, $ArBO_2C_2(CH_3)_4$×2);

^{13}C NMR ($CDCl_3$) δ 156.4 (2C), 138.2 (2C), 136.6 (2C), 128.9 (2C), 128.3 (2C), 127.9 (2C), 124.8 (2C), 123.0 (2C), 115.4 (2C), 84.8 (4C), 24.9 (8C) (the signals for the carbons which are attached to the boron atoms were not observed);

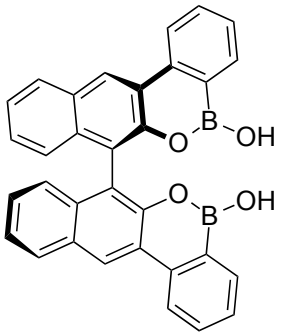
^{11}B NMR ($CDCl_3$) δ 31.0;

$[\alpha]_D^{25}$ 9.9º (*c* = 0.50, $CHCl_3$);

IR (KBr, cm^{-1}) 3444, 3055, 2934, 2556, 2250, 1606, 1575, 1497, 1209, 1044, 845;

HRMS (ESI^+) *m*/*z* 539.2768 (539.2771 calcd for $C_{32}H_{37}B_2O_6^+$, $[M+H]^+$).

(7*R*)-5,5'-Dihydroxy-5*H*,5'*H*-7,7'-bibenzo[*c*]naphth[2,3-*e*][1,2]oxaborin (2p)



A suspension of (1*R*)-3,3′-dibromo-[1,1′-binaphthalene]-2,2′-diol (**6**) (88.8 mg, 0.200 mmol), 2,3-dihydro-1*H*-naphtho[1,8-*de*]-1,3,2-diazaborinyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) benzene (**7**)[S3] (148 mg, 0.400 mmol), $Pd(OAc)_2$ (9.0 mg, 40 μmol), P(1-Ad)$_2$(*n*-Bu) (28.7 mg, 80.0 μmol), and K_2CO_3 (55.3 mg, 0.400 mmol) in DME (2.0 mL) and distilled water (0.4 mL), placed in a 5 mL screw top glass vial, was stirred for 10.5 h at 90 ºC (regulated with an aluminum heat block). After cooling to room temperature, to the mixture was added aqueous HCl (1 M, 2 mL) and extracted with ethyl acetate (ca. 5 mL×3). The combined organic extracts was washed with water (×1) and brine (×2), dried over Na_2SO_4, and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (10 g of silica-gel, *n*-hexane/ethyl acetate = 3/1, the outside of the column was cooled at –5 ºC by circulating 30 v/v% ethylene glycol in water), to give **2p** (42.3 mg, 86.3 μmol, 43.2%) as a pale yellow solid.

TLC R_f = 0.40 (*n*-hexane/ethyl acetate = 3/1);

mp 250–255 ºC (decomposed);

^{1}H NMR (acetone-d_6) δ 9.11 (s, 2H, aromatic), 8.68 (d, J = 8.0 Hz, 2H, aromatic), 8.19 (d, J = 8.0 Hz, 2H, aromatic), 8.14 (br s, 2H, BO*H*), 8.09 (dd, J = 8.0, 1.0 Hz, 2H, aromatic), 7.84 (ddd, J = 8.0, 7.5, 1.5 Hz, 2H, aromatic), 7.55 (ddd, J = 8.0, 7.5, 1.0 Hz, 2H, aromatic), 7.45 (ddd, J = 8.0, 7.5, 1.5 Hz, 2H, aromatic), 7.26 (ddd, J = 8.0, 7.5, 1.0 Hz, 2H, aromatic), 7.11 (dd, J = 8.0, 1.0 Hz, 2H, aromatic);

^{13}C NMR (acetone-d_6) δ 149.4 (2C), 142.2 (2C), 135.10 (2C), 135.08 (2C), 134.1 (2C), 131.2 (2C), 130.2 (2C), 129.2 (2C), 128.1 (2C), 126.8 (2C), 125.9 (2C), 125.4 (2C), 124.9 (2C), 123.9 (2C), 122.7 (2C) (the signals for the carbons which are attached to the boron atoms were not observed);

^{11}B NMR (acetone-d_6) δ 27.5;

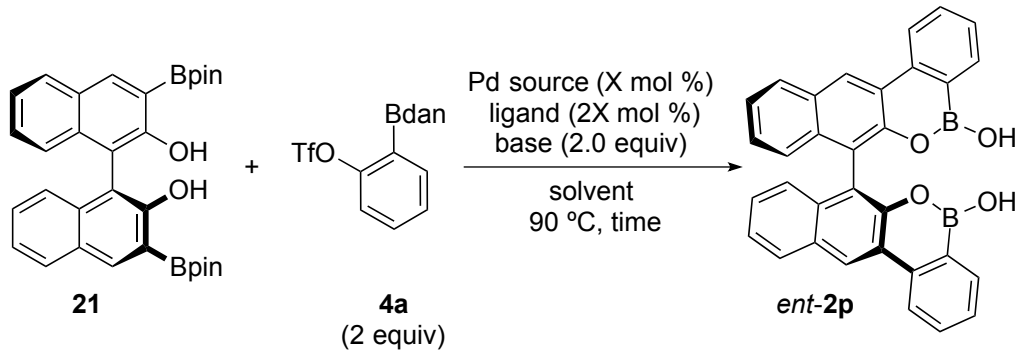
$[\alpha]_D^{25}$ –6.4º (c = 0.50, $CHCl_3$);

IR (KBr, cm^{-1}) 3339, 3058, 2360, 1695, 1562, 1446, 1042, 854;

HRMS (ESI$^+$) m/z 513.1447 (513.1440 calcd for $C_{32}H_{20}B_2O_4Na^+$, $[M+Na]^+$).

Attempts for preparation of ***2p***

Table S3.

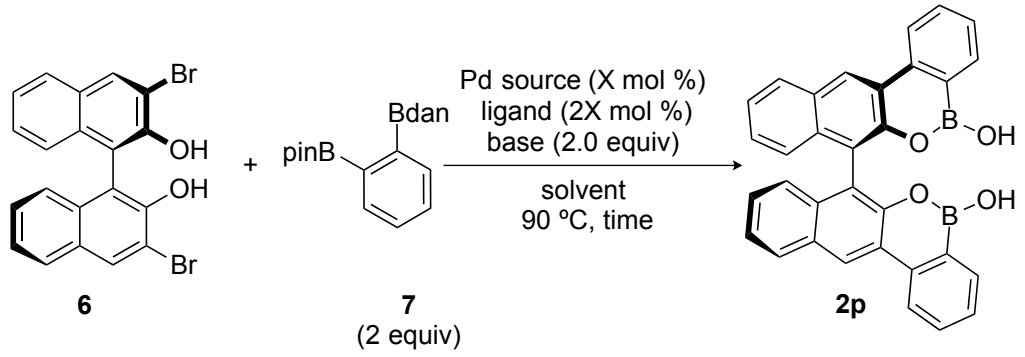


21 **4a** (2 equiv) *ent*-**2p**

entry	Pd source	X	ligand	solvent	base	time (h)	yield (%)[a]
1	$Pd(PPh_3)_4$	5	–	DME/H_2O (10/1)	$Na_2CO_3{\cdot}H_2O$	15.5	n.d.[b]
2	$Pd(OAc)_2$	5	P(1-Ad)$_2$(*n*-Bu)	DME/H_2O (5/1)	K_2CO_3	13	n.d.[b]
3	$Pd(OAc)_2$	5	CyJohnPhos	1,4-dioxane/H_2O (10/1)	$K_3PO_4{\cdot}nH_2O$	12.5	n.d.[b]
4	$Pd(OAc)_2$	20	CyJohnPhos	1,4-dioxane/H_2O (10/1)	$K_3PO_4{\cdot}nH_2O$	13	n.d.[b]

[a]Determined by ^{1}H NMR. [b]n.d. = not detected.

Table S4.

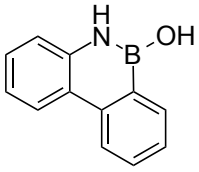


6 **7** (2 equiv) **2p**

entry	Pd source	X	ligand	solvent	base	time (h)	yield (%)[a]
1	$Pd(PPh_3)_4$	5	–	DME/H_2O (10/1)	$Na_2CO_3{\cdot}H_2O$	15.5	n.d.[b]
2	$Pd(OAc)_2$	5	P(1-Ad)$_2$(*n*-Bu)	DME/H_2O (5/1)	K_2CO_3	13	9
3	$Pd(OAc)_2$	20	P(1-Ad)$_2$(*n*-Bu)	DME/H_2O (5/1)	K_2CO_3	10.5	43[c]

[a]Determined by ^{1}H NMR unless otherwise noted. [b]n.d. = not detected. [c]An isolated yield.

5,6-Dihydro-6-hydroxydibenz[*c*,*e*][1,2]azaborine (9)



A suspension of (2-aminophenyl)boronic acid (**8a**) (41.1 mg, 0.300 mmol), **4a** (78.4 mg, 0.200 mmol), $Pd(OAc)_2$ (2.2 mg, 10 μmol), CyJohnPhos (7.0 mg, 20 μmol), and $K_3PO_4 \cdot nH_2O$ (80 wt% of K_3PO_4, 79.6 mg, 0.300 mmol) in 1,4-dioxane (1.5 mL) and distilled water (0.15 mL) was stirred for 5 h at 90 ºC (oil bath temperature). After cooling to room temperature, to the mixture was added aqueous NH_4Cl (saturated, ca. 7 mL) and extracted with ethyl acetate (ca. 10 mL×3). The combined organic extracts was washed with water (×1) and brine (×2), dried over Na_2SO_4, and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by twice of preparative TLC (dichloromethane/MeOH = 100/1) to give **9** (27.4 mg, 0.139 mmol, 69.5%) as a pale gray solid.

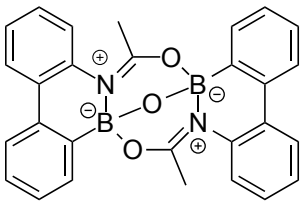
TLC R_f = 0.50 (dichloromethane/MeOH = 100/1);

^{1}H NMR (acetone-d_6) δ 8.39 (d, J = 5.5 Hz, 1H, aromatic), 8.31 (dd, J = 9.0, 1.0 Hz, 1H, aromatic), 8.21 (dd, J = 9.0, 1.0 Hz, 1H, aromatic), 7.71 (br s, 1H, N*H*), 7.65 (ddd, J = 10.5, 8.5, 2.0 Hz, 1H, aromatic), 7.48 (s, 1H, BO*H*), 7.42 (ddd, J = 9.0, 7.5, 1.0 Hz, 1H, aromatic), 7.31–7.24 (m, 2H, aromatic), 7.05 (ddd, J = 10.5, 8.0, 2.0 Hz, 1H, aromatic). The chemical shifts were consistent with those reported in the literature;[S9]

^{13}C NMR (acetone-d_6) δ 141.0, 140.5, 131.9, 130.4, 127.9, 125.6, 123.6, 122.0, 121.4, 119.4, 118.2 (the signal for the carbon which is attached to the boron atom was not observed);

^{11}B NMR (acetone-d_6) δ 28.7.

5-Acetyl-5,6-dihydro-6-hydroxydibenzo[*c*,*e*][1,2]azaborine, dehydrated dimer (11)



A suspension of (2-(acetylamino)phenyl)boronic acid (**8b**) (53.7 mg, 0.300 mmol), **4a** (78.4 mg, 0.200 mmol), $Pd(amphos)_2Cl_2$ (7.1 mg, 10 μmol), and $K_3PO_4 \cdot nH_2O$ (80 wt% of K_3PO_4, 79.6 mg, 0.300 mmol) in 1,4-dioxane (1.5 mL) and distilled water (0.15 mL) was stirred for 10 h at 90 ºC (oil bath temperature). After cooling to room temperature, to the mixture was added aqueous NH_4Cl (saturated, ca. 7 mL) and extracted with ethyl acetate (ca. 5 mL×3). The combined organic extracts was washed with water (×1) and brine (×2), dried over Na_2SO_4, and after filtration, the filtrate was

concentrated under reduced pressure to give a cross-coupling product **10**.

Before deprotection, to the residue was added 1,1,2,2-tetrachloroethane (20 μL) as an internal standard, and the mixture was dissolved in $CDCl_3$, and then ^{1}H NMR was measured. The ^{1}H NMR yield of **10** was obtained to be 87% by comparing the relative value of integration for the peak of 2 protons for dan-unit of **10** at 6.37 ppm with that of 1,1,2,2-tetrachloroethane observed at 5.91 ppm. After the measurement of ^{1}H NMR, the sample solution was recovered and concentrated under reduced pressure.

To the residue containing **10** was dissolved in THF (10 mL) and to the solution was added aqueous HCl (5 M, 0.75 mL) at room temperature. After stirring for 5 h at the same temperature, the reaction mixture was extracted with diethyl ether (×3). The combined organic extracts was washed with water (×1) and brine (×2), dried over Na_2SO_4, and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by recrystallization (ethyl acetate) to give **11** (31.8 mg, 69.7 μmol, 69.7% from **4a**) as colorless plate crystals.

TLC R_f = 0–0.27, a broad spot (*n*-hexane/ethyl acetate = 5/1);

mp >300 ºC;

^{1}H NMR (acetone-d_6) δ 8.05 (dd, J = 8.0, 1.5 Hz, 2H, aromatic), 7.90 (d, J = 8.0 Hz, 2H, aromatic), 7.86 (dd, J = 7.5, 1.5 Hz, 2H, aromatic), 7.47–7.41 (m, 4H, aromatic), 7.38–7.27 (m, 6H, aromatic), 2.27 (s, 6H, CH_3);

^{13}C NMR (acetone-d_6) δ 174.5 (2C), 137.6 (2C), 137.2 (2C), 133.7 (2C), 133.0 (2C), 129.2 (2C), 128.4 (2C), 128.0 (4C), 127.1 (2C), 126.7 (2C), 123.7 (2C), 21.4 (2C) (the signals for the carbons which are attached to the boron atoms were not observed);

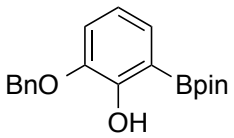
^{11}B NMR (acetone-d_6) δ 1.5;

IR (KBr, cm^{-1}) 3433, 1570, 1553, 1453, 1421, 1264, 1238, 1071, 977, 910, 843;

HRMS (EI$^+$) *m*/*z* 456.1824 (456.1817 calcd for $C_{28}H_{22}B_2N_2O_3$, $[M]^+$).

Synthesis of defucogilvocarcin M

2-Benzyloxy-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (14)



To a solution of 2-(benzyloxy)phenol (**13**) (3.00 g, 15.0 mmol) and $[Ir(cod)Cl]_2$ (50.4 mg, 75.0 μmol) in benzene (dehydrated, 7.5 mL) was added diethylsilane (2.91 mL, 22.5 mmol) at room temperature. Generation of hydrogen gas was observed during the addition of diethylsilane, which ceased after stirring the mixture overnight at room temperature. After concentration of the mixture under high vacuum, the residual oil was dissolved in THF (dehydrated, 7.5 mL) and to the solution

was added bis(pinacolato)diboron ($(Bpin)_2$) (3.81 g, 15.0 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (dtbpy) (80.5 mg, 300 μmol), $[Ir(cod)Cl]_2$ (101 mg, 150 μmol), and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (HBpin) (108 μL, 0.750 mmol) at room temperature. The dark solution was refluxed at 80 °C (oil bath temperature) with stirring for 2 h. After cooling to room temperature, to the reaction mixture was added aqueous HCl (1 M, 7.5 mL), which caused the gas evolution. The biphasic mixture was stirred overnight at room temperature and extracted with ethyl acetate (×3). The combined organic extracts was dried over Na_2SO_4, and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (100 g of silica-gel, *n*-hexane/ethyl acetate = 10/1) to give **14** (4.58 g, 14.0 mmol, 93.6%) as a colorless solid.

TLC R_f = 0.37 (*n*-hexane/ethyl acetate = 5/1);

mp 82–84 ºC;

^{1}H NMR ($CDCl_3$) δ 7.81 (s, 1H, ArO*H*), 7.46 (d, *J* = 7.5 Hz, 2H, aromatic), 7.36 (dd, *J* = 7.5, 7.0 Hz, 2H, aromatic), 7.30 (t, *J* = 7.0 Hz, 1H, aromatic), 7.23 (dd, *J* = 7.5, 1.0 Hz, 1H, aromatic), 7.00 (dd, *J* = 8.0, 1.0 Hz, 1H, aromatic), 6.79 (dd, *J* = 8.0, 7.5 Hz, 1H, aromatic), 5.14 (s, 2H, C*H*$_2$Ph), 1.37 (s, 12H, $ArBO_2C_2(CH_3)_4$);

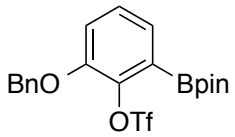
^{13}C NMR ($CDCl_3$) δ 153.7, 146.5, 137.4, 128.7 (2C), 127.94, 127.89, 127.5 (2C), 119.8, 118.5, 84.6 (2C), 71.3, 25.0 (4C) (the signal for the carbon which is attached to the boron atom was not observed);

^{11}B NMR ($CDCl_3$) δ 30.7;

IR (KBr, cm^{-1}) 3423, 2979, 1458, 1367, 1243, 1229, 1130, 1046;

HRMS (ESI$^+$) *m*/*z* 349.1589 (349.1582 calcd for $C_{19}H_{23}BNaO_6^+$, $[M+Na]^+$).

2-Benzyloxy-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl trifluoromethanesulfonate (15)



To a solution of **14** (1.63 g, 5.00 mmol) in dichloromethane (10 mL) was added diisopropylethylamine (1.70 mL, 10.0 mmol) at room temperature. After stirring for 20 min at the same temperature, to the mixture was slowly added trifluoromethanesulfonic anhydride (1.23 mL, 7.50 mmol) at –78 ºC and the mixture was warmed to room temperature. After stirring for 2 h, to the mixture was added saturated aqueous $NaHCO_3$ and extracted with diethyl ether (×3). The combined organic extracts was washed with water (×1) and brine (×1), dried over Na_2SO_4, and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (100 g of silica-gel, *n*-hexane/ethyl acetate = 10/1) to give **15**

(2.06 g, 4.50 mmol, 89.9%) as a colorless solid.

TLC R_f = 0.40 (*n*-hexane/ethyl acetate = 5/1);

mp 63–65 ºC;

^{1}H NMR ($CDCl_3$) δ 7.45–7.30 (m, 6H, aromatic), 7.25 (dd, *J* = 8.0, 7.5 Hz, 1H, aromatic), 7.12 (dd, *J* = 8.0, 1.5 Hz, 1H, aromatic), 5.14 (s, 2H, C*H*$_2$Ph), 1.36 (s, 12H, ArBO$_2$C$_2$(C*H*$_3$)$_4$);

^{13}C NMR ($CDCl_3$) δ 150.0, 143.4, 135.9, 128.7 (2C), 128.5, 128.3, 128.0, 127.5 (2C), 118.8 (q, *J* = 321.9 Hz), 117.5, 84.7 (2C), 71.3, 24.9 (4C) (the signal for the carbon which is attached to the boron atom was not observed);

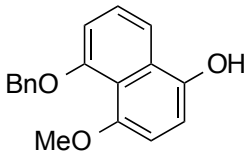
^{19}F NMR ($CDCl_3$) δ –73.9;

^{11}B NMR ($CDCl_3$) δ 29.5;

IR (KBr, cm^{-1}) 3430, 1445, 1420, 1356, 1268, 1203, 1141, 1025, 890, 854;

Anal. calcd for $C_{20}H_{22}BF_3O_6S$: C, 52.42; H, 4.84%. Found: C, 52.65; H, 4.88%.

5-Benzyloxy-4-methoxy-1-naphthalenol (16)[S10]



To a solution of **15** (458 mg, 1.00 mmol) in diethyl ether (dehydrated, 10 mL) was added *s*-butyllithium (1.06 M in cyclohexane/*n*-hexane, 1.0 mL, 1.1 mmol) at –78 ºC, and the mixture was allowed to warm to –20 ºC. To the mixture was added freshly distilled 2-methoxyfuran (276 μL, 2.99 mmol) at –20 ºC and warmed to room temperature. After stirring for 30 min at the same temperature, to the reaction mixture was added a solution of pH 7.4 aqueous phosphate buffer (ca. 2 mL) and extracted with ethyl acetate (×3). The combined organic extracts was washed with water (×1) and brine (×1), dried over Na_2SO_4, and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (60 g of silica-gel, *n*-hexane/ethyl acetate = 3/2, the outside of the column was covered with aluminum foil to protect from the light) to give **16** (239 mg, 0.853 mmol, 85.3%) as a gray solid.

TLC R_f = 0.25 (*n*-hexane/ethyl acetate = 5/1);

^{1}H NMR ($CDCl_3$) δ 7.78 (dd, *J* = 8.5, 0.5 Hz, 1H, aromatic), 7.60 (d, *J* = 7.5 Hz, 2H, aromatic), 7.43–7.38 (m, 3H, aromatic), 7.33 (t, *J* = 7.5 Hz, 1H, aromatic), 6.99 (d, *J* = 7.0 Hz, 1H, aromatic), 6.77 (d, *J* = 8.0 Hz, 1H, aromatic), 6.73 (d, *J* = 8.0 Hz, 1H, aromatic), 5.22 (s, 2H, C*H*$_2$Ph), 4.89 (s, 1H, ArO*H*), 3.89 (s, 3H, ArOC*H*$_3$);

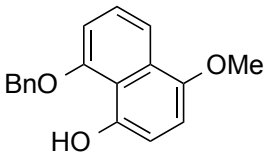
^{13}C NMR ($CDCl_3$) δ 155.9, 151.3, 145.1, 137.5, 128.3 (2C), 127.7, 127.5, 127.0 (2C), 125.9, 119.0,

(S10) Matsumoto, T.; Hosoya, T.; Katsuki, M.; Suzuki, K. *Tetrahedron Lett.* **1991**, *32*, 6735–6736.

114.8, 109.3, 108.9, 106.9, 71.5, 57.2.

Production of small amount of regioisomer of **16** was observed in this reaction. To identify the regioisomer, a separate experiment was carried out in larger scale by using 3-benzyloxy-2-iodophenyl trifluoromethanesufonate[S5] as a benzyne precursor.

8-Benzyloxy-4-methoxy-1-naphthalenol (16′, regioisomer of 16)



To a solution of 3-benzyloxy-2-iodophenyl trifluoromethanesufonate[S5] (4.58 g, 10.0 mmol) and freshly distilled 2-methoxyfuran (1.84 mL, 20.0 mmol) in THF (dehydrated, 100 mL) was added *n*-butyllithium (1.64 M in *n*-hexane, 9.14 mL, 15.0 mmol) at –78 ºC. After stirring for 10 min at the same temperature, to the reaction mixture was added a solution of pH 7.4 aqueous phosphate buffer (ca. 20 mL) and extracted with ethyl acetate (×3). The combined organic extracts was washed with water (×1) and brine (×1), dried over Na_2SO_4, and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (*n*-hexane/ethyl acetate = 5/1, the outside of the column was covered with aluminum foil to protect from the light) to give **16** (2.27 g, 8.10 mmol, 81.0%) as a gray solid and **16′** (90.3 mg, 0.322 mmol, 3.22%) as a gray solid.

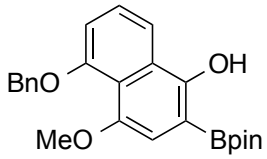
TLC R_f = 0.45 (*n*-hexane/ethyl acetate = 5/1);

^{1}H NMR ($CDCl_3$) δ 8.99 (s, 1H, ArO*H*), 7.87 (dd, *J* = 8.5, 1.0 Hz, 1H, aromatic), 7.50–7.48 (m, 2H, aromatic), 7.44–7.38 (m, 3H, aromatic), 7.32 (dd, *J* = 8.5, 8.0 Hz, 1H, aromatic), 6.92 (d, *J* = 7.5 Hz, 1H, aromatic), 6.76 (br s, 2H, aromatic), 5.26 (s, 2H, C*H*$_2$Ph), 3.93 (s, 3H, ArOC*H*$_3$);

^{13}C NMR ($CDCl_3$) δ 155.3, 148.3, 148.0, 135.4, 129.2 (2C), 129.0, 128.12, 128.06 (2C), 125.3, 116.3, 115.8, 109.3, 106.41, 106.40, 71.8, 56.1.

The chemical shifts were consistent with those reported in the literature.[S11]

5-Benzyloxy-4-methoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalen-1-ol (3i)



To a solution of **16** (1.40 g, 4.99 mmol) and $[Ir(cod)Cl]_2$ (16.8 mg, 25.0 μmol) in benzene (dehydrated, 2.5 mL), placed in a two-necked 50 mL flask covered with aluminum foil, was added

(S11) Brimble, M. A.; Brenstrum, T. J. *J. Chem. Soc*., *Perkin Trans. 1* **2001**, 1612–1623.

diethylsilane (959 μL, 7.50 mmol) at room temperature. Generation of hydrogen gas was observed during the addition of diethylsilane, which ceased after stirring the mixture overnight at room temperature. After concentration of the mixture under high vacuum, the residual oil was dissolved in THF (dehydrated, 7.5 mL) and to the solution was added bis(pinacolato)diboron ($(Bpin)_2$) (1.27 g, 5.00 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (dtbpy) (26.8 mg, 100 μmol), $[Ir(cod)Cl]_2$ (33.6 mg, 50.0 μmol), and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (HBpin) (36 μL, 0.25 mmol) at room temperature. The dark solution was refluxed at 80 °C (oil bath temperature) with stirring for 2 h. After cooling to room temperature, to the reaction mixture was slowly added aqueous HCl (2 M, 10 mL), which caused the gas evolution. The biphasic mixture was stirred overnight at room temperature and extracted with ethyl acetate (×3). The combined organic extracts was dried over Na_2SO_4, and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography by using a glass chromatographic column (50 g of silica-gel, *n*-hexane/ethyl acetate = 20/1 to 10/1 to 5/1, the outside of the column was cooled by dry ice and covered with aluminum foil to protect from the light) to give **3i** (1.62 g, 3.99 mmol, 79.9%) as a colorless solid.

TLC R_f = 0.40 (*n*-hexane/ethyl acetate = 10/1);

mp 96–97 ºC;

^{1}H NMR ($CDCl_3$) δ 8.30 (s, 1H, ArO*H*), 7.96 (dd, *J* = 8.0, 1.0 Hz, 1H, aromatic), 7.60 (d, *J* = 7.0 Hz, 2H, aromatic), 7.43–7.36 (m, 3H, aromatic), 7.32 (dd, *J* = 8.0, 7.0 Hz, 1H, aromatic), 7.05 (dd, *J* = 8.0, 1.0 Hz, 1H, aromatic), 6.95 (s, 1H, aromatic), 5.20 (s, 2H, CH_2Ph), 3.91 (s, 3H, ArOCH_3), 1.41 (s, 12H, $ArBO_2C_2(CH_3)_4$);

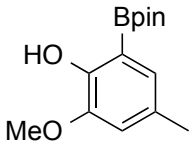
^{13}C NMR ($CDCl_3$) δ 155.8, 155.7, 149.8, 137.8, 128.5, 127.7 (2C), 127.3 (2C), 127.2, 125.9, 121.7, 116.6, 111.6, 110.4, 84.7 (2C), 72.0, 57.4, 25.0 (4C) (the signal for the carbon which is attached to the boron atom was not observed);

^{11}B NMR (acetone-d_6) δ 31.0;

IR (KBr, cm^{-1}) 3385, 1600, 1504, 1452, 1362, 1303, 1279, 1136, 969, 847;

HRMS (ESI^+) *m*/*z* 429.1842 (429.1844 calcd for $C_{24}H_{27}BNaO_5^+$, $[M+Na]^+$).

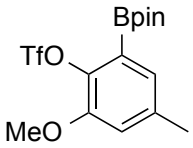
2-Methoxy-4-methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (18)



To a solution of 4-methylguaiacol (**17**) (691 mg, 5.00 mmol) and $[Ir(cod)Cl]_2$ (16.8 mg, 25.0 μmol) in benzene (dehydrated, 2.5 mL) was added diethylsilane (959 μL, 7.50 mmol) at room temperature. Generation of hydrogen gas was observed during the addition of diethylsilane, which

ceased after stirring the mixture overnight at room temperature. After concentration of the mixture under high vacuum, the residual oil was dissolved in THF (dehydrated, 7.5 mL) and to the solution was added bis(pinacolato)diboron ($(Bpin)_2$) (1.27 g, 5.00 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (dtbpy) (26.8 mg, 100 μmol), $[Ir(cod)Cl]_2$ (33.6 mg, 50.0 μmol), and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (HBpin) (36 μL, 0.25 mmol) at room temperature. The dark solution was refluxed at 80 °C (oil bath temperature) with stirring for 2 h. After cooling to room temperature, to the reaction mixture was added aqueous HCl (2 M, 10 mL), which caused the gas evolution. The biphasic mixture was stirred overnight at room temperature and extracted with ethyl acetate (×3). The combined organic extracts was dried over Na_2SO_4, and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (50 g of silica-gel, *n*-hexane/ethyl acetate = 10/1) to give **18** (1.19 g, 4.51 mmol, 90.1%) as a colorless solid.
TLC R_f = 0–0.20, a broad spot (*n*-hexane/ethyl acetate = 5/1);
mp 100–102 ºC;
^{1}H NMR ($CDCl_3$) δ 7.60 (s, 1H, ArO*H*), 7.01 (s, 1H, aromatic), 6.80 (s, 1H, aromatic), 3.86 (s, 3H, ArOCH_3), 2.27 (s, 3H, ArCH_3), 1.37 (s, 12H, $ArBO_2C_2(CH_3)_4$);
^{13}C NMR ($CDCl_3$) δ 150.9, 147.2, 129.2, 126.7, 116.8, 84.5 (2C), 56.1, 24.9 (4C), 20.9 (the signal for the carbon which is attached to the boron atom was not observed);
^{11}B NMR ($CDCl_3$) δ 30.6;
IR (KBr, cm^{-1}) 3416, 1478, 1389, 1374, 1262, 1226, 1146, 1059, 967, 849;
HRMS (ESI^+) *m*/*z* 287.1428 (287.1425 calcd for $C_{14}H_{21}BNaO_4^+$, $[M+Na]^+$).

2-Methoxy-4-methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl trifluoromethanesulfonate (19)



To a solution of **18** (1.06 g, 4.00 mmol) in dichloromethane (7 mL) was added diisopropylethylamine (827 μL, 4.80 mmol) at room temperature. After stirring for 20 min at the same temperature, to the mixture was slowly added trifluoromethanesulfonic anhydride (737 μL, 4.38 mmol) at –78 ºC and the mixture was warmed to room temperature. After stirring for 20 min, to the reaction mixture was added saturated aqueous $NaHCO_3$ and extracted with diethyl ether (×3). The combined organic extracts was washed with water (×1) and brine (×1), dried over Na_2SO_4, and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (50 g of silica-gel, *n*-hexane/ethyl acetate = 10/1) to give **19** (1.58 g, 3.99 mmol, 99.7%) as a colorless solid.

TLC R_f = 0.29 (*n*-hexane/ethyl acetate = 5/1);

mp 89–90 ºC;

^{1}H NMR ($CDCl_3$) δ 7.17 (d, *J* = 2.0 Hz, 1H, aromatic), 6.90 (d, *J* = 2.0 Hz, 1H, aromatic), 3.85 (s, 3H, ArOC*H*$_3$), 2.36 (s, 3H, ArC*H*$_3$), 1.36 (s, 12H, $ArBO_2C_2(CH_3)_4$);

^{13}C NMR ($CDCl_3$) δ 150.2, 141.0, 138.6, 127.8, 118.8 (q, *J* = 320.7 Hz), 116.6, 84.5 (2C), 55.9, 24.8 (4C), 21.2 (the signal for the carbon which is attached to the boron atom was not observed);

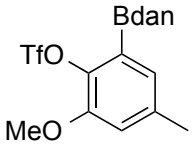
^{19}F NMR ($CDCl_3$) δ –74.1;

^{11}B NMR ($CDCl_3$) δ 29.9;

IR (KBr, cm^{-1}) 2981, 2940, 2360, 1420, 1366, 1212, 1200, 1142, 1057, 883;

HRMS (EI$^+$) *m*/*z* 396.1022 (396.1026 calcd for $C_{15}H_{20}BF_3O_6S$, $[M]^+$).

2-Methoxy-4-methyl-6-(1*H*-naphtho[1,8-*de*]-1,3,2-diazaborin-2(3*H*)-yl)phenyl trifluoromethanesulfonate (4i)



Under air, to a solution of **19** (792 mg, 2.00 mmol) in THF (8 mL) and distilled water (1.6 mL) was added sodium periodate (1.71 g, 7.99 mmol) at room temperature. After stirring for 30 min, to the mixture was added aqueous HCl (1 M, 1.2 mL). After stirring overnight at room temperature, the mixture was diluted with water and extracted with ethyl acetate (×3). The combined organic extracts was washed with brine (×1), dried over Na_2SO_4, and after filtration, the filtrate was concentrated under reduced pressure.

The residue was dissolved in dichloromethane (dehydrated, 10 mL) and to the solution was added 1,8-diaminonaphthalene (316 mg, 2.00 mmol) and molecular sieves 4A (ca. 500 mg) at room temperature. After stirring for 20 min, the mixture was filtered and the filtrate was concentrated under reduced pressure. The residue was purified by silica-gel flash column chromatography (25 g of silica-gel, *n*-hexane/ethyl acetate = 5/1) to give **4i** (765 mg, 1.75 mmol, 87.7% from **19**) as a colorless solid.

TLC R_f = 0.29 (*n*-hexane/ethyl acetate = 5/1);

mp 166–168 ºC;

^{1}H NMR ($CDCl_3$) δ 7.12 (dd, *J* = 7.5, 8.0 Hz, 2H, aromatic), 7.06 (d, *J* = 8.0 Hz, 2H, aromatic), 6.93 (d, *J* = 2.0 Hz, 1H, aromatic), 6.88 (d, *J* = 2.0 Hz, 1H, aromatic), 6.37 (d, *J* = 7.5 Hz, 2H, aromatic), 6.00 (br s, 2H, N*H*×2), 3.89 (s, 3H, ArOC*H*$_3$), 2.38 (s, 3H, ArC*H*$_3$);

^{13}C NMR ($CDCl_3$) δ 150.9, 140.7 (2C), 139.8, 139.6, 136.4, 128.8 127.7 (2C), 125.3, 120.1, 118.8 (q, *J* = 320.7 Hz), 118.3 (2C), 115.5, 106.4 (2C), 56.2, 21.6;

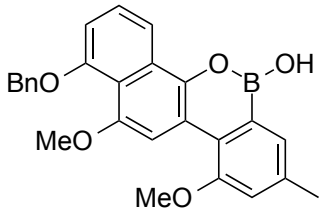
^{19}F NMR ($CDCl_3$) δ –74.0;

^{11}B NMR ($CDCl_3$) δ 28.3;

IR (KBr, cm^{-1}) 3422, 1601, 1587, 1509, 1411, 1328, 1206, 1139, 1066, 875, 821;

HRMS (EI^+) *m*/*z* 436.0883 (436.0876 calcd for $C_{19}H_{16}BF_3N_2O_4S$, $[M]^+$).

1-Benzyloxy-10,12-dimethoxy-6-hydroxy-8-methyl-6*H*-benzo[*c*]naphth[2,1-*e*][1,2]oxaborin (2q)



A suspension of **3i** (610 mg, 1.50 mmol), **4i** (436 mg, 1.00 mmol), and $Pd(PPh_3)_4$ (57.8 mg, 50.0 μmol) in 1,2-dimethoxyethane (7.5 mL) and aqueous Na_2CO_3 (2 M, 0.75 mL, 1.5 mmol) was stirred for 3 h at 90 ºC (oil bath temperature). After cooling to room temperature, to the mixture was added aqueous NH_4Cl (saturated, ca. 10 mL) and extracted with ethyl acetate (×3). The combined organic extracts was washed with water (×1) and brine (×2), dried over Na_2SO_4, and after filtration, the filtrate was concentrated under reduced pressure. The residue was dissolved in ethyl acetate (1 mL) and to the solution was added MeOH (1 mL) to form a pale yellow precipitate, which was collected by filtration. The filtrate was concentrated under reduced pressure and the same operation was repeated three times and the combined solid was washed with MeOH on a funnel to give **2q** (368 mg, 0.863 mmol, 86.3%) as a colorless solid.

TLC R_f = 0–0.16, a broad spot (*n*-hexane/ethyl acetate = 5/1);

mp 192−194 ºC;

^{1}H NMR (acetone-d_6) δ 8.75 (s, 1H, aromatic), 8.21–8.16 (m, 2H, BO*H*, aromatic), 7.73–7.68 (m, 2H, aromatic), 7.65 (s, 1H, aromatic), 7.49–7.41 (m, 3H, aromatic), 7.34 (t, *J* = 7.5 Hz, 1H, aromatic), 7.28 (d, *J* = 1.0 Hz, 1H, aromatic), 7.11 (d, *J* = 7.5 Hz, 1H, aromatic), 5.26 (s, 2H, C*H*$_2$Ph), 4.11 (s, 3H, ArOC*H*$_3$), 4.00 (s, 3H, ArOC*H*$_3$), 2.47 (s, 3H, ArC*H*$_3$);

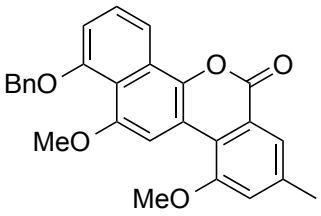
^{13}C NMR (acetone-d_6) δ 158.7, 156.7, 152.0, 141.5, 139.2, 139.1, 130.1, 129.2 (2C), 128.2, 127.8 (2C), 127.6, 127.01, 126.95, 118.7, 118.6, 117.8, 116.5, 109.9, 108.0, 71.7, 57.0, 56.5, 21.5 (the signal for the carbon which is attached to the boron atom was not observed);

^{11}B NMR (acetone-d_6) δ 28.3;

IR (KBr, cm^{-1}) 3396, 2360, 2341, 2333, 1601, 1376, 1342, 1270, 1053, 847;

Anal. calcd for $C_{26}H_{23}BO_5$: C, 73.26; H, 5.44%. Found: C, 73.22; H, 5.38%.

1-Benzyloxy-10,12-dimethoxy-8-methyl-6*H*-benzo[*d*]naphtho[1,2-*b*]pyran-6-one (20)



A suspension of **2q** (212 mg, 0.500 mmol) and $Pd(OAc)_2$ (112 mg, 0.499 mmol) in DMSO (12.5 mL) and MeOH (6.3 mL), placed in a two-necked round-bottomed flask equipped with a balloon filled with a CO gas, was stirred for 3 h at room temperature. After replacement with air followed by filtration of the mixture through a pad of Celite, to the filtrate was added water and extracted with ethyl acetate (ca. 5 mL×3). The combined organic extracts was washed with water (×1) and brine (×2), dried over Na_2SO_4, and after filtration, the filtrate was concentrated under reduced pressure. The residual yellow solid was washed with dichloromethane/ethyl acetate (1/2) on a funnel to give **20** (173 mg, 0.406 mmol, 81.1%) as a yellow solid.

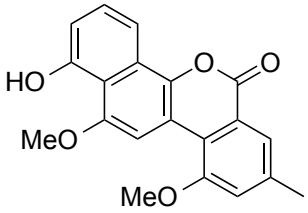
TLC R_f = 0.45 (*n*-hexane/ethyl acetate = 1/1);

^{1}H NMR ($CDCl_3$) δ 8.42 (s, 1H, aromatic), 8.25 (dd, *J* = 8.5, 0.5 Hz, 1H, aromatic), 7.96 (d, *J* = 0.5 Hz, 1H, aromatic), 7.62 (d, *J* = 7.5 Hz, 2H, aromatic), 7.49 (dd, *J* = 8.5, 7.5 Hz, 1H, aromatic), 7.43 (dd, *J* = 7.5, 7.5 Hz, 2H, aromatic), 7.35 (t, *J* = 7.5 Hz, 1H, aromatic), 7.15 (s, 1H, aromatic), 7.06 (d, *J* = 7.5 Hz, 1H, aromatic), 5.24 (s, 2H, C*H*$_2$Ph), 4.08 (s, 3H, ArOC*H*$_3$), 4.01 (s, 3H, ArOC*H*$_3$), 2.50 (s, 3H, ArC*H*$_3$);

^{13}C NMR ($CDCl_3$) δ 161.7, 157.4, 155.8, 153.1, 140.7, 140.0, 137.6, 128.6 (2C), 127.8, 127.4, 127.2 (2C), 127.0, 123.4, 123.0, 122.2, 118.3, 118.2, 115.5, 114.0, 110.4, 104.5, 71.7, 56.7, 56.5, 21.9;

The chemical shifts were consistent with those reported in the literature.[S12]

Defucogilvocarcin M (12)



A suspension of **20** (42.4 mg, 99.9 μmol) and Pd/C (10 wt%, 11 mg, 10 μmol) in THF (dehydrated, 1.0 mL) and DMF (dehydrated, 100 μL), placed in a two-necked round-bottomed flask equipped with a balloon filled with a hydrogen gas, was stirred for 1 h at room temperature. After replacement with air followed by filtration through a pad of Celite, the filtrate was concentrated

(S12) Takemura, I.; Imura, K.; Matsumoto, T.; Suzuki, K. *Org. Lett.* **2004**, *6*, 2503–2505.

under reduced pressure to give defucogilvocarcin M (**12**) (32.7 mg, 97.2 μmol, 97.2%) as a colorless solid;

TLC R_f = 0.35 (*n*-hexane/ethyl acetate/dichloromethane = 3/1/1);

^{1}H NMR ($CDCl_3$) δ 9.34 (s, 1H, ArO*H*), 8.24 (s, 1H, aromatic), 8.04 (dd, *J* = 8.0, 1.0 Hz, 1H, aromatic), 7.89 (s, 1H, aromatic), 7.48 (dd, *J* = 8.0, 8.0 Hz, 1H, aromatic), 7.07 (s, 1H, aromatic), 6.99 (dd, *J* = 8.0, 1.0 Hz, 1H, aromatic), 4.08 (s, 3H, ArOCH_3), 4.04 (s, 3H, ArOCH_3), 2.48 (s, 3H, ArCH_3).

^{13}C NMR ($CDCl_3$) δ 161.5, 157.1, 154.4, 151.9, 141.4, 140.1, 128.6, 126.3, 123.2, 122.9, 121.9, 118.2, 114.8, 113.6, 113.1, 112.6, 101.9, 56.4, 56.2, 21.9;

The chemical shifts were consistent with those reported in the literature.[S12]

Crystallographic Analyses

Compound 2n

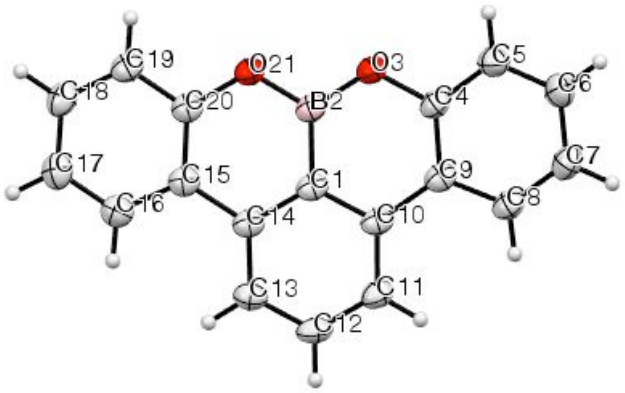


Figure S1. ORTEP diagram of the X-ray structure of **2n**. Ellipsoids are drawn at 50% probability.

Table S5. Crystal data and structure refinement for **2n**.

Identification code	compound **2n**
Empirical formula	$C_{18}H_{11}BO_2$
Formula weight	270.08
Temperature	173(2) K
Wavelength	1.54186 Å
Crystal system	Monoclinic
Space group	$P\,2_1/c$
Unit cell dimensions	a = 5.1612(1) Å.
	b = 15.5151(3) Å β = 91.214(1)°.
	c = 15.9033(3) Å.
Volume	1273.20(4) Å^3
Z	4
Density (calculated)	1.409 Mg/m^3
Absorption coefficient	0.715 mm^{-1}
F(000)	560
Crystal size	0.22 × 0.07 × 0.05 mm^3
Theta range for data collection	3.98 to 68.21°.
Index ranges	–6 <= h <= 5, –18 <= k <= 18, –19 <= l <= 19
Reflections collected	14557
Independent reflections	2293 [R(int) = 0.0685]
Completeness to theta = 68.21°	98.4%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9651 and 0.5936
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2293 / 0 / 190
Goodness-of-fit on F^2	1.081
Final R indices [I>2sigma(I)]	R_1 = 0.0438, wR_2 = 0.1218
R indices (all data)	R_1 = 0.0540, wR_2 = 0.1385
Largest diff. peak and hole	0.262 and –0.176 e.Å^{-3}

Table S6. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **2n**. U (eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	6414(3)	-1010(1)	2434(1)	31(1)
B(2)	6891(3)	-375(1)	3142(1)	32(1)
O(3)	5428(2)	-389(1)	3852(1)	37(1)
C(4)	3527(3)	-1009(1)	3934(1)	33(1)
C(5)	2170(3)	-989(1)	4675(1)	40(1)
C(6)	208(3)	-1574(1)	4811(1)	43(1)
C(7)	-408(3)	-2181(1)	4196(1)	41(1)
C(8)	944(3)	-2201(1)	3460(1)	36(1)
C(9)	2963(3)	-1618(1)	3296(1)	32(1)
C(10)	4435(3)	-1625(1)	2512(1)	32(1)
C(11)	3994(3)	-2198(1)	1841(1)	36(1)
C(12)	5510(3)	-2147(1)	1135(1)	39(1)
C(13)	7479(3)	-1544(1)	1066(1)	37(1)
C(14)	7949(3)	-956(1)	1717(1)	31(1)
C(15)	9942(3)	-276(1)	1707(1)	32(1)
C(16)	11595(3)	-152(1)	1027(1)	37(1)
C(17)	13486(3)	478(1)	1037(1)	41(1)
C(18)	13822(3)	1005(1)	1737(1)	40(1)
C(19)	12226(3)	905(1)	2417(1)	36(1)
C(20)	10302(3)	280(1)	2401(1)	33(1)
O(21)	8779(2)	241(1)	3105(1)	35(1)

Table S7. Bond lengths [Å] and angles [°] for **2n**.

C(1)-C(14)	1.4046(19)
C(1)-C(10)	1.406(2)
C(1)-B(2)	1.512(2)
B(2)-O(21)	1.3676(18)
B(2)-O(3)	1.3729(18)
O(3)-C(4)	1.3823(16)
C(4)-C(5)	1.3846(19)
C(4)-C(9)	1.4117(19)
C(5)-C(6)	1.380(2)
C(5)-H(5)	0.9500
C(6)-C(7)	1.390(2)
C(6)-H(6)	0.9500
C(7)-C(8)	1.375(2)
C(7)-H(7)	0.9500
C(8)-C(9)	1.4076(19)
C(8)-H(8)	0.9500
C(9)-C(10)	1.474(2)
C(10)-C(11)	1.4024(19)
C(11)-C(12)	1.385(2)
C(11)-H(11)	0.9500
C(12)-C(13)	1.387(2)
C(12)-H(12)	0.9500
C(13)-C(14)	1.3977(19)
C(13)-H(13)	0.9500
C(14)-C(15)	1.473(2)
C(15)-C(16)	1.404(2)
C(15)-C(20)	1.411(2)
C(16)-C(17)	1.381(2)
C(16)-H(16)	0.9500
C(17)-C(18)	1.389(2)
C(17)-H(17)	0.9500
C(18)-C(19)	1.382(2)
C(18)-H(18)	0.9500
C(19)-C(20)	1.388(2)
C(19)-H(19)	0.9500
C(20)-O(21)	1.3828(16)
C(14)-C(1)-C(10)	122.39(12)
C(14)-C(1)-B(2)	118.69(13)
C(10)-C(1)-B(2)	118.92(14)
O(21)-B(2)-O(3)	116.76(13)
O(21)-B(2)-C(1)	121.95(15)
O(3)-B(2)-C(1)	121.30(14)
B(2)-O(3)-C(4)	119.43(11)
O(3)-C(4)-C(5)	115.88(12)
O(3)-C(4)-C(9)	122.35(13)
C(5)-C(4)-C(9)	121.76(14)
C(6)-C(5)-C(4)	120.27(14)

C(6)-C(5)-H(5)	119.9
C(4)-C(5)-H(5)	119.9
C(5)-C(6)-C(7)	119.58(15)
C(5)-C(6)-H(6)	120.2
C(7)-C(6)-H(6)	120.2
C(8)-C(7)-C(6)	120.05(14)
C(8)-C(7)-H(7)	120.0
C(6)-C(7)-H(7)	120.0
C(7)-C(8)-C(9)	122.29(13)
C(7)-C(8)-H(8)	118.9
C(9)-C(8)-H(8)	118.9
C(8)-C(9)-C(4)	116.04(14)
C(8)-C(9)-C(10)	123.26(13)
C(4)-C(9)-C(10)	120.70(13)
C(11)-C(10)-C(1)	117.98(14)
C(11)-C(10)-C(9)	124.75(13)
C(1)-C(10)-C(9)	117.26(12)
C(12)-C(11)-C(10)	119.73(14)
C(12)-C(11)-H(11)	120.1
C(10)-C(11)-H(11)	120.1
C(11)-C(12)-C(13)	121.98(13)
C(11)-C(12)-H(12)	119.0
C(13)-C(12)-H(12)	119.0
C(12)-C(13)-C(14)	119.85(14)
C(12)-C(13)-H(13)	120.1
C(14)-C(13)-H(13)	120.1
C(13)-C(14)-C(1)	118.07(14)
C(13)-C(14)-C(15)	124.73(14)
C(1)-C(14)-C(15)	117.20(12)
C(16)-C(15)-C(20)	116.50(14)
C(16)-C(15)-C(14)	122.85(13)
C(20)-C(15)-C(14)	120.64(13)
C(17)-C(16)-C(15)	121.98(14)
C(17)-C(16)-H(16)	119.0
C(15)-C(16)-H(16)	119.0
C(16)-C(17)-C(18)	120.09(15)
C(16)-C(17)-H(17)	120.0
C(18)-C(17)-H(17)	120.0
C(19)-C(18)-C(17)	119.68(15)
C(19)-C(18)-H(18)	120.2
C(17)-C(18)-H(18)	120.2
C(18)-C(19)-C(20)	120.14(14)
C(18)-C(19)-H(19)	119.9
C(20)-C(19)-H(19)	119.9
O(21)-C(20)-C(19)	115.73(12)
O(21)-C(20)-C(15)	122.68(13)
C(19)-C(20)-C(15)	121.59(14)
B(2)-O(21)-C(20)	118.81(12)

Symmetry transformations used to generate equivalent atoms:

Table S8. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **2n**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U11	U22	U33	U23	U13	U12
C(1)	33(1)	23(1)	36(1)	0(1)	-4(1)	5(1)
B(2)	35(1)	25(1)	34(1)	1(1)	-3(1)	2(1)
O(3)	42(1)	30(1)	38(1)	-5(1)	2(1)	-6(1)
C(4)	36(1)	26(1)	38(1)	2(1)	-2(1)	-2(1)
C(5)	47(1)	35(1)	36(1)	-2(1)	1(1)	-2(1)
C(6)	47(1)	43(1)	38(1)	5(1)	3(1)	-4(1)
C(7)	42(1)	35(1)	46(1)	7(1)	-1(1)	-6(1)
C(8)	40(1)	27(1)	41(1)	2(1)	-4(1)	-1(1)
C(9)	34(1)	25(1)	38(1)	1(1)	-3(1)	3(1)
C(10)	36(1)	23(1)	37(1)	-1(1)	-5(1)	5(1)
C(11)	36(1)	27(1)	43(1)	-5(1)	-3(1)	0(1)
C(12)	44(1)	32(1)	41(1)	-11(1)	-4(1)	4(1)
C(13)	42(1)	34(1)	36(1)	-5(1)	0(1)	4(1)
C(14)	34(1)	25(1)	35(1)	0(1)	-3(1)	5(1)
C(15)	35(1)	27(1)	34(1)	2(1)	-3(1)	5(1)
C(16)	41(1)	33(1)	36(1)	3(1)	-1(1)	5(1)
C(17)	43(1)	35(1)	45(1)	10(1)	3(1)	4(1)
C(18)	38(1)	30(1)	51(1)	6(1)	0(1)	0(1)
C(19)	41(1)	26(1)	42(1)	0(1)	-2(1)	2(1)
C(20)	34(1)	27(1)	36(1)	1(1)	-1(1)	4(1)
O(21)	39(1)	29(1)	37(1)	-4(1)	2(1)	-2(1)

Table S9. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **2n**.

	x	y	z	U(eq)
H(5)	2591	-570	5092	47
H(6)	-715	-1561	5321	51
H(7)	-1764	-2583	4284	49
H(8)	501	-2622	3048	43
H(11)	2661	-2618	1872	43
H(12)	5193	-2538	684	47
H(13)	8504	-1531	577	45
H(16)	11407	-511	546	44
H(17)	14558	552	564	49
H(18)	15143	1431	1748	48
H(19)	12447	1265	2897	44

Table S10. Torsion angles [°] for **2n**.

C(14)-C(1)-B(2)-O(21)	-0.5(2)
C(10)-C(1)-B(2)-O(21)	-179.85(12)
C(14)-C(1)-B(2)-O(3)	179.09(12)
C(10)-C(1)-B(2)-O(3)	-0.2(2)
O(21)-B(2)-O(3)-C(4)	-178.58(11)
C(1)-B(2)-O(3)-C(4)	1.8(2)
B(2)-O(3)-C(4)-C(5)	178.87(12)
B(2)-O(3)-C(4)-C(9)	-2.2(2)
O(3)-C(4)-C(5)-C(6)	179.06(13)
C(9)-C(4)-C(5)-C(6)	0.1(2)
C(4)-C(5)-C(6)-C(7)	-0.4(2)
C(5)-C(6)-C(7)-C(8)	0.4(2)
C(6)-C(7)-C(8)-C(9)	-0.3(2)
C(7)-C(8)-C(9)-C(4)	0.1(2)
C(7)-C(8)-C(9)-C(10)	-179.85(13)
O(3)-C(4)-C(9)-C(8)	-178.84(12)
C(5)-C(4)-C(9)-C(8)	0.0(2)
O(3)-C(4)-C(9)-C(10)	1.1(2)
C(5)-C(4)-C(9)-C(10)	179.92(13)
C(14)-C(1)-C(10)-C(11)	-0.5(2)
B(2)-C(1)-C(10)-C(11)	178.85(13)
C(14)-C(1)-C(10)-C(9)	179.83(12)
B(2)-C(1)-C(10)-C(9)	-0.87(19)
C(8)-C(9)-C(10)-C(11)	0.7(2)
C(4)-C(9)-C(10)-C(11)	-179.20(14)
C(8)-C(9)-C(10)-C(1)	-179.60(13)
C(4)-C(9)-C(10)-C(1)	0.5(2)
C(1)-C(10)-C(11)-C(12)	0.6(2)
C(9)-C(10)-C(11)-C(12)	-179.69(13)
C(10)-C(11)-C(12)-C(13)	0.1(2)
C(11)-C(12)-C(13)-C(14)	-1.0(2)
C(12)-C(13)-C(14)-C(1)	1.1(2)
C(12)-C(13)-C(14)-C(15)	-178.64(13)
C(10)-C(1)-C(14)-C(13)	-0.4(2)
B(2)-C(1)-C(14)-C(13)	-179.70(13)
C(10)-C(1)-C(14)-C(15)	179.35(12)
B(2)-C(1)-C(14)-C(15)	0.05(19)
C(13)-C(14)-C(15)-C(16)	0.0(2)
C(1)-C(14)-C(15)-C(16)	-179.71(12)
C(13)-C(14)-C(15)-C(20)	-178.99(13)
C(1)-C(14)-C(15)-C(20)	1.3(2)
C(20)-C(15)-C(16)-C(17)	0.4(2)
C(14)-C(15)-C(16)-C(17)	-178.69(13)
C(15)-C(16)-C(17)-C(18)	0.9(2)
C(16)-C(17)-C(18)-C(19)	-1.1(2)
C(17)-C(18)-C(19)-C(20)	0.2(2)
C(18)-C(19)-C(20)-O(21)	-178.90(12)
C(18)-C(19)-C(20)-C(15)	1.1(2)

C(16)-C(15)-C(20)-O(21)	178.64(11)
C(14)-C(15)-C(20)-O(21)	-2.3(2)
C(16)-C(15)-C(20)-C(19)	-1.3(2)
C(14)-C(15)-C(20)-C(19)	177.75(12)
O(3)-B(2)-O(21)-C(20)	-179.99(11)
C(1)-B(2)-O(21)-C(20)	-0.4(2)
C(19)-C(20)-O(21)-B(2)	-178.25(12)
C(15)-C(20)-O(21)-B(2)	1.8(2)

Symmetry transformations used to generate equivalent atoms:

Compound 11

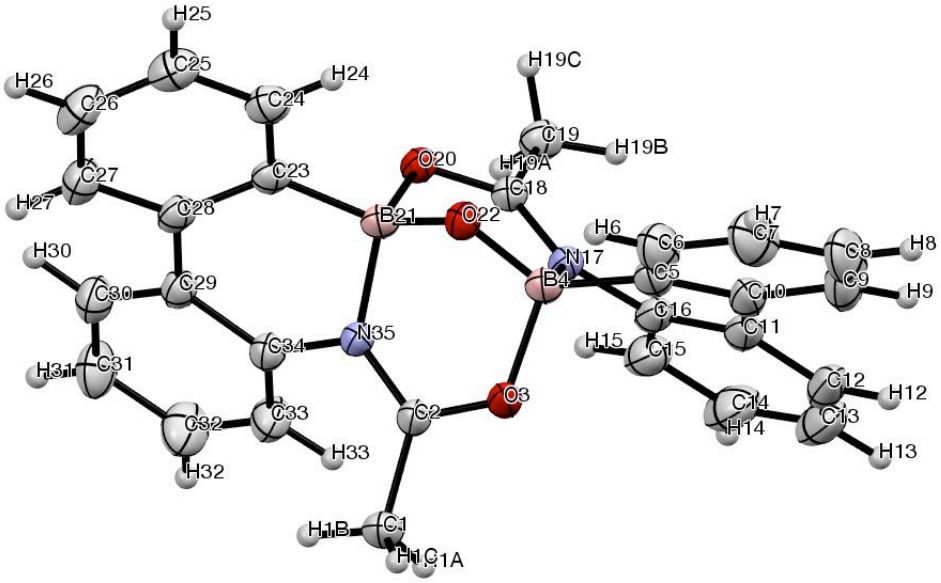


Figure S2. ORTEP diagram of the X-ray structure of **11**. Ellipsoids are drawn at 50% probability; only one unit is shown.

Table S11. Crystal data and structure refinement for **11**.

Identification code	compound **11**
Empirical formula	$C_{32}H_{30}B_2N_2O_5$
Formula weight	1632.60
Temperature	173(2) K
Wavelength	1.54186 Å
Crystal system	Monoclinic
Space group	$P\ 2_1/n$
Unit cell dimensions	a = 17.2259(3) Å.
	b = 19.4533(4) Å β = 103.161(1)°.
	c = 25.7366(5) Å.
Volume	8397.8(3) Å^3
Z	12
Density (calculated)	1.291 Mg/m^3
Absorption coefficient	0.692 mm^{-1}
F(000)	3432
Crystal size	0.23 × 0.11 × 0.07 mm^3
Theta range for data collection	3.48 to 68.22°.
Index ranges	–20 <= h <= 20, –22 <= k <= 23, –30 <= l <= 30
Reflections collected	97584
Independent reflections	15297 [R(int) = 0.0453]
Completeness to theta = 68.22°	99.6%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9531 and 0.7171
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	15297 / 1 / 1147
Goodness-of-fit on F^2	1.079
Final R indices [I>2sigma(I)]	R_1 = 0.0445, wR_2 = 0.1143
R indices (all data)	R_1 = 0.0532, wR_2 = 0.1211
Largest diff. peak and hole	0.676 and –0.302 e.Å^{-3}

Table S12. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **11**. U (eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	8280(1)	2400(1)	4237(1)	40(1)
C(2)	7729(1)	2627(1)	3734(1)	28(1)
O(3)	8080(1)	2905(1)	3391(1)	31(1)
B(4)	7541(1)	3111(1)	2845(1)	28(1)
C(5)	8063(1)	3471(1)	2486(1)	33(1)
C(6)	8116(1)	4186(1)	2464(1)	42(1)
C(7)	8554(1)	4505(1)	2141(1)	54(1)
C(8)	8931(1)	4109(1)	1826(1)	58(1)
C(9)	8881(1)	3403(1)	1836(1)	50(1)
C(10)	8456(1)	3074(1)	2168(1)	38(1)
C(11)	8423(1)	2314(1)	2199(1)	37(1)
C(12)	8995(1)	1891(1)	2047(1)	49(1)
C(13)	8985(1)	1186(1)	2096(1)	57(1)
C(14)	8409(1)	872(1)	2310(1)	53(1)
C(15)	7837(1)	1273(1)	2464(1)	41(1)
C(16)	7824(1)	1981(1)	2397(1)	33(1)
N(17)	7242(1)	2391(1)	2573(1)	27(1)
C(18)	6482(1)	2219(1)	2480(1)	26(1)
C(19)	6084(1)	1696(1)	2085(1)	32(1)
O(20)	6013(1)	2524(1)	2736(1)	27(1)
B(21)	6406(1)	3052(1)	3168(1)	26(1)
O(22)	6891(1)	3491(1)	2941(1)	28(1)
C(23)	5771(1)	3425(1)	3434(1)	26(1)
C(24)	5492(1)	4084(1)	3274(1)	32(1)
C(25)	4981(1)	4433(1)	3526(1)	37(1)
C(26)	4759(1)	4136(1)	3962(1)	40(1)
C(27)	5033(1)	3489(1)	4135(1)	35(1)
C(28)	5531(1)	3124(1)	3869(1)	27(1)
C(29)	5814(1)	2423(1)	4039(1)	27(1)
C(30)	5389(1)	1994(1)	4311(1)	34(1)
C(31)	5655(1)	1343(1)	4473(1)	42(1)
C(32)	6344(1)	1092(1)	4352(1)	46(1)
C(33)	6768(1)	1498(1)	4072(1)	36(1)
C(34)	6521(1)	2165(1)	3928(1)	27(1)
N(35)	6946(1)	2582(1)	3626(1)	25(1)
C(36)	2144(1)	3064(1)	5855(1)	34(1)
C(37)	2314(1)	2658(1)	5404(1)	26(1)
O(38)	1701(1)	2354(1)	5104(1)	28(1)
B(39)	1857(1)	1937(1)	4625(1)	26(1)
C(40)	1055(1)	1577(1)	4308(1)	28(1)
C(41)	896(1)	890(1)	4397(1)	33(1)
C(42)	220(1)	557(1)	4105(1)	40(1)
C(43)	-304(1)	915(1)	3708(1)	43(1)
C(44)	-162(1)	1595(1)	3608(1)	38(1)
C(45)	511(1)	1937(1)	3907(1)	31(1)

C(46)	660(1)	2670(1)	3814(1)	31(1)
C(47)	46(1)	3126(1)	3584(1)	42(1)
C(48)	190(1)	3812(1)	3509(1)	50(1)
C(49)	955(1)	4072(1)	3671(1)	51(1)
C(50)	1573(1)	3638(1)	3906(1)	40(1)
C(51)	1434(1)	2946(1)	3967(1)	31(1)
N(52)	2073(1)	2508(1)	4229(1)	26(1)
C(53)	2789(1)	2539(1)	4129(1)	26(1)
C(54)	2978(1)	2853(1)	3645(1)	34(1)
O(55)	3390(1)	2253(1)	4454(1)	26(1)
B(56)	3214(1)	1925(1)	4965(1)	24(1)
O(57)	2526(1)	1508(1)	4813(1)	26(1)
C(58)	4006(1)	1574(1)	5306(1)	25(1)
C(59)	4140(1)	868(1)	5286(1)	30(1)
C(60)	4817(1)	560(1)	5598(1)	34(1)
C(61)	5372(1)	963(1)	5943(1)	34(1)
C(62)	5256(1)	1660(1)	5973(1)	30(1)
C(63)	4580(1)	1976(1)	5654(1)	25(1)
C(64)	4450(1)	2726(1)	5685(1)	26(1)
C(65)	5083(1)	3180(1)	5873(1)	34(1)
C(66)	4968(1)	3881(1)	5884(1)	41(1)
C(67)	4215(1)	4155(1)	5703(1)	40(1)
C(68)	3574(1)	3721(1)	5515(1)	33(1)
C(69)	3687(1)	3013(1)	5519(1)	26(1)
N(70)	3027(1)	2568(1)	5306(1)	24(1)
C(71)	979(1)	7923(1)	2484(1)	33(1)
C(72)	1344(1)	7433(1)	2915(1)	27(1)
O(73)	864(1)	7191(1)	3192(1)	28(1)
B(74)	1250(1)	6727(1)	3670(1)	30(1)
C(75)	617(1)	6463(1)	3993(1)	34(1)
C(76)	307(1)	5800(1)	3921(1)	48(1)
C(77)	-155(1)	5530(1)	4251(1)	62(1)
C(78)	-316(1)	5926(1)	4660(1)	61(1)
C(79)	-37(1)	6594(1)	4734(1)	48(1)
C(80)	428(1)	6867(1)	4401(1)	36(1)
C(81)	741(1)	7580(1)	4474(1)	33(1)
C(82)	348(1)	8099(1)	4690(1)	40(1)
C(83)	648(1)	8758(1)	4760(1)	46(1)
C(84)	1346(1)	8923(1)	4604(1)	45(1)
C(85)	1735(1)	8422(1)	4378(1)	38(1)
C(86)	1447(1)	7754(1)	4323(1)	31(1)
N(87)	1832(1)	7242(1)	4070(1)	30(1)
C(88)	2612(1)	7158(1)	4179(1)	32(1)
C(89)	3182(1)	7440(1)	4655(1)	51(1)
O(90)	2935(1)	6790(1)	3865(1)	33(1)
B(91)	2364(1)	6536(1)	3343(1)	32(1)
O(92)	1703(1)	6216(1)	3483(1)	34(1)
C(93)	2854(1)	6101(1)	3000(1)	39(1)
C(94)	2843(1)	5384(1)	2996(1)	50(1)
C(95)	3261(1)	5010(1)	2688(1)	66(1)

C(96)	3692(1)	5350(2)	2377(1)	69(1)
C(97)	3701(1)	6057(1)	2364(1)	59(1)
C(98)	3289(1)	6442(1)	2677(1)	42(1)
C(99)	3302(1)	7203(1)	2674(1)	39(1)
C(100)	3913(1)	7579(1)	2529(1)	52(1)
C(101)	3943(1)	8287(1)	2546(1)	57(1)
C(102)	3360(1)	8653(1)	2720(1)	50(1)
C(103)	2749(1)	8298(1)	2872(1)	38(1)
C(104)	2706(1)	7586(1)	2838(1)	32(1)
N(105)	2096(1)	7227(1)	3022(1)	28(1)
C(201)	2754(1)	141(1)	3934(1)	58(1)
C(202)	3112(1)	740(1)	3708(1)	47(1)
O(203)	3637(1)	474(1)	3389(1)	51(1)
C(204)	3951(1)	941(1)	3116(1)	52(1)
O(205)	3810(1)	1544(1)	3124(1)	63(1)
C(206)	4469(2)	618(2)	2786(1)	94(1)
C(207)	7094(1)	4765(1)	818(1)	61(1)
C(208)	6836(1)	4082(1)	984(1)	44(1)
O(209)	6212(1)	4205(1)	1267(1)	40(1)
C(210)	5955(1)	3648(1)	1485(1)	37(1)
O(211)	6228(1)	3085(1)	1467(1)	49(1)
C(212)	5292(1)	3817(1)	1749(1)	55(1)
C(213)	3176(4)	5310(4)	4594(3)	94(2)
C(214)	2303(3)	5312(2)	4687(2)	74(1)
O(215)	2271(2)	5105(2)	5207(1)	63(1)
C(216)	2358(3)	5597(2)	5591(2)	63(1)
O(217)	2431(2)	6187(2)	5489(2)	93(1)
C(218)	2378(3)	5310(3)	6111(2)	84(2)
O(301)	2557(3)	6309(3)	5078(3)	96(2)
O(302)	2537(4)	5258(4)	5380(3)	84(2)
C(301)	2628(4)	5729(3)	5040(3)	60(2)
C(302)	2864(7)	5314(7)	4575(5)	85(4)
C(304)	2175(7)	4983(6)	6182(4)	105(3)
C(303)	2138(8)	5546(6)	5833(6)	105(4)

Table S13. Bond lengths [Å] and angles [°] for **11**.

C(1)-C(2)	1.487(2)	C(26)-C(27)	1.383(2)
C(1)-H(1A)	0.9800	C(26)-H(26)	0.9500
C(1)-H(1B)	0.9800	C(27)-C(28)	1.405(2)
C(1)-H(1C)	0.9800	C(27)-H(27)	0.9500
C(2)-O(3)	1.2982(18)	C(28)-C(29)	1.481(2)
C(2)-N(35)	1.3164(19)	C(29)-C(30)	1.398(2)
O(3)-B(4)	1.5499(19)	C(29)-C(34)	1.407(2)
B(4)-O(22)	1.409(2)	C(30)-C(31)	1.378(2)
B(4)-C(5)	1.592(2)	C(30)-H(30)	0.9500
B(4)-N(17)	1.599(2)	C(31)-C(32)	1.383(3)
C(5)-C(6)	1.395(3)	C(31)-H(31)	0.9500
C(5)-C(10)	1.405(2)	C(32)-C(33)	1.384(2)
C(6)-C(7)	1.391(2)	C(32)-H(32)	0.9500
C(6)-H(6)	0.9500	C(33)-C(34)	1.389(2)
C(7)-C(8)	1.383(3)	C(33)-H(33)	0.9500
C(7)-H(7)	0.9500	C(34)-N(35)	1.4329(19)
C(8)-C(9)	1.378(3)	C(36)-C(37)	1.487(2)
C(8)-H(8)	0.9500	C(36)-H(36A)	0.9800
C(9)-C(10)	1.400(2)	C(36)-H(36B)	0.9800
C(9)-H(9)	0.9500	C(36)-H(36C)	0.9800
C(10)-C(11)	1.484(3)	C(37)-O(38)	1.3005(17)
C(11)-C(12)	1.405(2)	C(37)-N(70)	1.3207(19)
C(11)-C(16)	1.409(2)	O(38)-B(39)	1.5495(19)
C(12)-C(13)	1.378(3)	B(39)-O(57)	1.4155(19)
C(12)-H(12)	0.9500	B(39)-C(40)	1.597(2)
C(13)-C(14)	1.380(3)	B(39)-N(52)	1.605(2)
C(13)-H(13)	0.9500	C(40)-C(41)	1.394(2)
C(14)-C(15)	1.384(2)	C(40)-C(45)	1.411(2)
C(14)-H(14)	0.9500	C(41)-C(42)	1.393(2)
C(15)-C(16)	1.389(3)	C(41)-H(41)	0.9500
C(15)-H(15)	0.9500	C(42)-C(43)	1.387(3)
C(16)-N(17)	1.4328(19)	C(42)-H(42)	0.9500
N(17)-C(18)	1.3196(19)	C(43)-C(44)	1.379(3)
C(18)-O(20)	1.2977(18)	C(43)-H(43)	0.9500
C(18)-C(19)	1.490(2)	C(44)-C(45)	1.405(2)
C(19)-H(19A)	0.9800	C(44)-H(44)	0.9500
C(19)-H(19B)	0.9800	C(45)-C(46)	1.479(2)
C(19)-H(19C)	0.9800	C(46)-C(47)	1.404(2)
O(20)-B(21)	1.5498(19)	C(46)-C(51)	1.407(2)
B(21)-O(22)	1.411(2)	C(47)-C(48)	1.380(3)
B(21)-C(23)	1.593(2)	C(47)-H(47)	0.9500
B(21)-N(35)	1.609(2)	C(48)-C(49)	1.383(3)
C(23)-C(24)	1.398(2)	C(48)-H(48)	0.9500
C(23)-C(28)	1.404(2)	C(49)-C(50)	1.384(2)
C(24)-C(25)	1.384(2)	C(49)-H(49)	0.9500
C(24)-H(24)	0.9500	C(50)-C(51)	1.384(2)
C(25)-C(26)	1.390(3)	C(50)-H(50)	0.9500
C(25)-H(25)	0.9500	C(51)-N(52)	1.4326(19)

N(52)-C(53)	1.3188(19)
C(53)-O(55)	1.2988(17)
C(53)-C(54)	1.489(2)
C(54)-H(54A)	0.9800
C(54)-H(54B)	0.9800
C(54)-H(54C)	0.9800
O(55)-B(56)	1.5519(19)
B(56)-O(57)	1.4151(19)
B(56)-C(58)	1.598(2)
B(56)-N(70)	1.603(2)
C(58)-C(59)	1.396(2)
C(58)-C(63)	1.409(2)
C(59)-C(60)	1.391(2)
C(59)-H(59)	0.9500
C(60)-C(61)	1.389(2)
C(60)-H(60)	0.9500
C(61)-C(62)	1.377(2)
C(61)-H(61)	0.9500
C(62)-C(63)	1.405(2)
C(62)-H(62)	0.9500
C(63)-C(64)	1.481(2)
C(64)-C(65)	1.401(2)
C(64)-C(69)	1.404(2)
C(65)-C(66)	1.380(2)
C(65)-H(65)	0.9500
C(66)-C(67)	1.382(2)
C(66)-H(66)	0.9500
C(67)-C(68)	1.385(2)
C(67)-H(67)	0.9500
C(68)-C(69)	1.391(2)
C(68)-H(68)	0.9500
C(69)-N(70)	1.4341(18)
C(71)-C(72)	1.488(2)
C(71)-H(71A)	0.9800
C(71)-H(71B)	0.9800
C(71)-H(71C)	0.9800
C(72)-O(73)	1.2981(18)
C(72)-N(105)	1.3236(18)
O(73)-B(74)	1.548(2)
B(74)-O(92)	1.415(2)
B(74)-C(75)	1.598(3)
B(74)-N(87)	1.612(2)
C(75)-C(76)	1.393(3)
C(75)-C(80)	1.405(2)
C(76)-C(77)	1.392(3)
C(76)-H(76)	0.9500
C(77)-C(78)	1.382(3)
C(77)-H(77)	0.9500
C(78)-C(79)	1.383(3)
C(78)-H(78)	0.9500
C(79)-C(80)	1.405(2)
C(79)-H(79)	0.9500
C(80)-C(81)	1.485(3)
C(81)-C(82)	1.399(2)
C(81)-C(86)	1.402(2)
C(82)-C(83)	1.378(3)
C(82)-H(82)	0.9500
C(83)-C(84)	1.388(3)
C(83)-H(83)	0.9500
C(84)-C(85)	1.385(2)
C(84)-H(84)	0.9500
C(85)-C(86)	1.385(2)
C(85)-H(85)	0.9500
C(86)-N(87)	1.433(2)
N(87)-C(88)	1.3182(19)
C(88)-O(90)	1.2975(19)
C(88)-C(89)	1.489(2)
C(89)-H(89A)	0.9800
C(89)-H(89B)	0.9800
C(89)-H(89C)	0.9800
O(90)-B(91)	1.555(2)
B(91)-O(92)	1.415(2)
B(91)-N(105)	1.590(2)
B(91)-C(93)	1.595(2)
C(93)-C(94)	1.396(3)
C(93)-C(98)	1.406(3)
C(94)-C(95)	1.392(3)
C(94)-H(94)	0.9500
C(95)-C(96)	1.379(4)
C(95)-H(95)	0.9500
C(96)-C(97)	1.375(4)
C(96)-H(96)	0.9500
C(97)-C(98)	1.405(2)
C(97)-H(97)	0.9500
C(98)-C(99)	1.480(3)
C(99)-C(100)	1.400(3)
C(99)-C(104)	1.410(2)
C(100)-C(101)	1.377(3)
C(100)-H(100)	0.9500
C(101)-C(102)	1.385(3)
C(101)-H(101)	0.9500
C(102)-C(103)	1.388(2)
C(102)-H(102)	0.9500
C(103)-C(104)	1.387(2)
C(103)-H(103)	0.9500
C(104)-N(105)	1.428(2)
C(201)-C(202)	1.496(3)
C(201)-H(20A)	0.9800
C(201)-H(20B)	0.9800
C(201)-H(20C)	0.9800

C(202)-O(203)	1.449(2)
C(202)-H(20D)	0.9900
C(202)-H(20E)	0.9900
O(203)-C(204)	1.337(2)
C(204)-O(205)	1.200(2)
C(204)-C(206)	1.501(3)
C(206)-H(20F)	0.9800
C(206)-H(20G)	0.9800
C(206)-H(20H)	0.9800
C(207)-C(208)	1.494(3)
C(207)-H(20J)	0.9800
C(207)-H(20I)	0.9800
C(207)-H(20K)	0.9800
C(208)-O(209)	1.450(2)
C(208)-H(20L)	0.9900
C(208)-H(20M)	0.9900
O(209)-C(210)	1.341(2)
C(210)-O(211)	1.197(2)
C(210)-C(212)	1.492(3)
C(212)-H(21A)	0.9800
C(212)-H(21B)	0.9800
C(212)-H(21C)	0.9800
C(213)-C(214)	1.574(8)
C(213)-H(21D)	0.9800
C(213)-H(21E)	0.9800
C(213)-H(21F)	0.9800
C(214)-O(215)	1.410(5)
C(214)-H(21G)	0.9900
C(214)-H(21H)	0.9900
O(215)-C(216)	1.360(5)
C(216)-O(217)	1.190(5)
C(216)-C(218)	1.444(7)
C(218)-H(21I)	0.9800
C(218)-H(21J)	0.9800
C(218)-H(21K)	0.9800
O(301)-C(301)	1.140(8)
O(302)-C(301)	1.302(9)
O(302)-C(303)	1.585(15)
C(301)-C(302)	1.573(14)
C(302)-H(30A)	0.9800
C(302)-H(30B)	0.9800
C(302)-H(30C)	0.9800
C(304)-C(303)	1.408(15)
C(304)-H(30D)	0.9800
C(304)-H(30E)	0.9800
C(304)-H(30F)	0.9800
C(303)-H(30G)	0.9900
C(303)-H(30H)	0.9900
C(2)-C(1)-H(1A)	109.5
C(2)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
C(2)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
O(3)-C(2)-N(35)	119.84(13)
O(3)-C(2)-C(1)	114.30(13)
N(35)-C(2)-C(1)	125.84(14)
C(2)-O(3)-B(4)	116.65(11)
O(22)-B(4)-O(3)	108.28(13)
O(22)-B(4)-C(5)	116.59(15)
O(3)-B(4)-C(5)	109.82(12)
O(22)-B(4)-N(17)	110.30(12)
O(3)-B(4)-N(17)	103.74(12)
C(5)-B(4)-N(17)	107.36(13)
C(6)-C(5)-C(10)	118.61(16)
C(6)-C(5)-B(4)	120.82(16)
C(10)-C(5)-B(4)	120.53(16)
C(7)-C(6)-C(5)	121.26(19)
C(7)-C(6)-H(6)	119.4
C(5)-C(6)-H(6)	119.4
C(8)-C(7)-C(6)	119.5(2)
C(8)-C(7)-H(7)	120.2
C(6)-C(7)-H(7)	120.2
C(9)-C(8)-C(7)	120.32(18)
C(9)-C(8)-H(8)	119.8
C(7)-C(8)-H(8)	119.8
C(8)-C(9)-C(10)	120.7(2)
C(8)-C(9)-H(9)	119.7
C(10)-C(9)-H(9)	119.7
C(9)-C(10)-C(5)	119.56(19)
C(9)-C(10)-C(11)	121.23(17)
C(5)-C(10)-C(11)	119.20(15)
C(12)-C(11)-C(16)	116.76(18)
C(12)-C(11)-C(10)	122.14(17)
C(16)-C(11)-C(10)	121.08(15)
C(13)-C(12)-C(11)	122.17(19)
C(13)-C(12)-H(12)	118.9
C(11)-C(12)-H(12)	118.9
C(12)-C(13)-C(14)	120.15(18)
C(12)-C(13)-H(13)	119.9
C(14)-C(13)-H(13)	119.9
C(13)-C(14)-C(15)	119.2(2)
C(13)-C(14)-H(14)	120.4
C(15)-C(14)-H(14)	120.4
C(14)-C(15)-C(16)	121.07(19)
C(14)-C(15)-H(15)	119.5
C(16)-C(15)-H(15)	119.5
C(15)-C(16)-C(11)	120.51(16)
C(15)-C(16)-N(17)	120.38(15)

C(11)-C(16)-N(17)	118.88(16)
C(18)-N(17)-C(16)	122.59(13)
C(18)-N(17)-B(4)	120.63(13)
C(16)-N(17)-B(4)	116.55(12)
O(20)-C(18)-N(17)	119.85(13)
O(20)-C(18)-C(19)	114.71(13)
N(17)-C(18)-C(19)	125.43(14)
C(18)-C(19)-H(19A)	109.5
C(18)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(18)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(18)-O(20)-B(21)	116.54(11)
O(22)-B(21)-O(20)	107.93(12)
O(22)-B(21)-C(23)	115.50(14)
O(20)-B(21)-C(23)	112.30(12)
O(22)-B(21)-N(35)	110.48(12)
O(20)-B(21)-N(35)	103.62(12)
C(23)-B(21)-N(35)	106.36(12)
B(4)-O(22)-B(21)	108.83(13)
C(24)-C(23)-C(28)	118.22(14)
C(24)-C(23)-B(21)	120.99(14)
C(28)-C(23)-B(21)	120.55(14)
C(25)-C(24)-C(23)	121.61(16)
C(25)-C(24)-H(24)	119.2
C(23)-C(24)-H(24)	119.2
C(24)-C(25)-C(26)	119.72(16)
C(24)-C(25)-H(25)	120.1
C(26)-C(25)-H(25)	120.1
C(27)-C(26)-C(25)	120.09(16)
C(27)-C(26)-H(26)	120.0
C(25)-C(26)-H(26)	120.0
C(26)-C(27)-C(28)	120.25(16)
C(26)-C(27)-H(27)	119.9
C(28)-C(27)-H(27)	119.9
C(23)-C(28)-C(27)	120.05(15)
C(23)-C(28)-C(29)	118.87(13)
C(27)-C(28)-C(29)	121.08(14)
C(30)-C(29)-C(34)	117.69(15)
C(30)-C(29)-C(28)	121.61(14)
C(34)-C(29)-C(28)	120.70(14)
C(31)-C(30)-C(29)	121.65(16)
C(31)-C(30)-H(30)	119.2
C(29)-C(30)-H(30)	119.2
C(30)-C(31)-C(32)	119.99(16)
C(30)-C(31)-H(31)	120.0
C(32)-C(31)-H(31)	120.0
C(31)-C(32)-C(33)	119.76(17)
C(31)-C(32)-H(32)	120.1
C(33)-C(32)-H(32)	120.1
C(32)-C(33)-C(34)	120.45(16)
C(32)-C(33)-H(33)	119.8
C(34)-C(33)-H(33)	119.8
C(33)-C(34)-C(29)	120.38(14)
C(33)-C(34)-N(35)	120.72(14)
C(29)-C(34)-N(35)	118.72(13)
C(2)-N(35)-C(34)	123.17(13)
C(2)-N(35)-B(21)	120.70(12)
C(34)-N(35)-B(21)	115.95(11)
C(37)-C(36)-H(36A)	109.5
C(37)-C(36)-H(36B)	109.5
H(36A)-C(36)-H(36B)	109.5
C(37)-C(36)-H(36C)	109.5
H(36A)-C(36)-H(36C)	109.5
H(36B)-C(36)-H(36C)	109.5
O(38)-C(37)-N(70)	119.45(13)
O(38)-C(37)-C(36)	115.33(13)
N(70)-C(37)-C(36)	125.17(13)
C(37)-O(38)-B(39)	116.48(11)
O(57)-B(39)-O(38)	108.12(12)
O(57)-B(39)-C(40)	117.32(14)
O(38)-B(39)-C(40)	110.35(12)
O(57)-B(39)-N(52)	109.71(12)
O(38)-B(39)-N(52)	104.46(12)
C(40)-B(39)-N(52)	106.14(12)
C(41)-C(40)-C(45)	118.27(14)
C(41)-C(40)-B(39)	121.06(14)
C(45)-C(40)-B(39)	120.56(14)
C(42)-C(41)-C(40)	121.88(16)
C(42)-C(41)-H(41)	119.1
C(40)-C(41)-H(41)	119.1
C(43)-C(42)-C(41)	119.20(17)
C(43)-C(42)-H(42)	120.4
C(41)-C(42)-H(42)	120.4
C(44)-C(43)-C(42)	120.35(15)
C(44)-C(43)-H(43)	119.8
C(42)-C(43)-H(43)	119.8
C(43)-C(44)-C(45)	120.75(16)
C(43)-C(44)-H(44)	119.6
C(45)-C(44)-H(44)	119.6
C(44)-C(45)-C(40)	119.55(16)
C(44)-C(45)-C(46)	121.36(15)
C(40)-C(45)-C(46)	119.09(13)
C(47)-C(46)-C(51)	116.91(16)
C(47)-C(46)-C(45)	122.39(15)
C(51)-C(46)-C(45)	120.69(14)
C(48)-C(47)-C(46)	121.91(17)
C(48)-C(47)-H(47)	119.0
C(46)-C(47)-H(47)	119.0

C(47)-C(48)-C(49)	119.96(17)
C(47)-C(48)-H(48)	120.0
C(49)-C(48)-H(48)	120.0
C(48)-C(49)-C(50)	119.63(19)
C(48)-C(49)-H(49)	120.2
C(50)-C(49)-H(49)	120.2
C(49)-C(50)-C(51)	120.51(17)
C(49)-C(50)-H(50)	119.7
C(51)-C(50)-H(50)	119.7
C(50)-C(51)-C(46)	121.03(15)
C(50)-C(51)-N(52)	119.96(14)
C(46)-C(51)-N(52)	118.82(14)
C(53)-N(52)-C(51)	122.19(13)
C(53)-N(52)-B(39)	121.18(12)
C(51)-N(52)-B(39)	116.50(12)
O(55)-C(53)-N(52)	119.85(14)
O(55)-C(53)-C(54)	114.95(13)
N(52)-C(53)-C(54)	125.12(13)
C(53)-C(54)-H(54A)	109.5
C(53)-C(54)-H(54B)	109.5
H(54A)-C(54)-H(54B)	109.5
C(53)-C(54)-H(54C)	109.5
H(54A)-C(54)-H(54C)	109.5
H(54B)-C(54)-H(54C)	109.5
C(53)-O(55)-B(56)	116.22(11)
O(57)-B(56)-O(55)	108.31(12)
O(57)-B(56)-C(58)	117.69(13)
O(55)-B(56)-C(58)	109.44(12)
O(57)-B(56)-N(70)	109.83(12)
O(55)-B(56)-N(70)	104.11(12)
C(58)-B(56)-N(70)	106.61(12)
B(56)-O(57)-B(39)	108.79(12)
C(59)-C(58)-C(63)	118.13(13)
C(59)-C(58)-B(56)	121.81(13)
C(63)-C(58)-B(56)	120.01(13)
C(60)-C(59)-C(58)	121.76(15)
C(60)-C(59)-H(59)	119.1
C(58)-C(59)-H(59)	119.1
C(61)-C(60)-C(59)	119.38(15)
C(61)-C(60)-H(60)	120.3
C(59)-C(60)-H(60)	120.3
C(62)-C(61)-C(60)	120.25(15)
C(62)-C(61)-H(61)	119.9
C(60)-C(61)-H(61)	119.9
C(61)-C(62)-C(63)	120.65(15)
C(61)-C(62)-H(62)	119.7
C(63)-C(62)-H(62)	119.7
C(62)-C(63)-C(58)	119.83(14)
C(62)-C(63)-C(64)	120.89(14)
C(58)-C(63)-C(64)	119.27(13)
C(65)-C(64)-C(69)	117.13(14)
C(65)-C(64)-C(63)	121.69(13)
C(69)-C(64)-C(63)	121.17(13)
C(66)-C(65)-C(64)	121.76(15)
C(66)-C(65)-H(65)	119.1
C(64)-C(65)-H(65)	119.1
C(65)-C(66)-C(67)	120.12(16)
C(65)-C(66)-H(66)	119.9
C(67)-C(66)-H(66)	119.9
C(66)-C(67)-C(68)	119.72(16)
C(66)-C(67)-H(67)	120.1
C(68)-C(67)-H(67)	120.1
C(67)-C(68)-C(69)	120.13(15)
C(67)-C(68)-H(68)	119.9
C(69)-C(68)-H(68)	119.9
C(68)-C(69)-C(64)	121.05(14)
C(68)-C(69)-N(70)	119.87(13)
C(64)-C(69)-N(70)	118.84(13)
C(37)-N(70)-C(69)	122.52(12)
C(37)-N(70)-B(56)	121.23(12)
C(69)-N(70)-B(56)	116.16(11)
C(72)-C(71)-H(71A)	109.5
C(72)-C(71)-H(71B)	109.5
H(71A)-C(71)-H(71B)	109.5
C(72)-C(71)-H(71C)	109.5
H(71A)-C(71)-H(71C)	109.5
H(71B)-C(71)-H(71C)	109.5
O(73)-C(72)-N(105)	119.48(14)
O(73)-C(72)-C(71)	115.29(13)
N(105)-C(72)-C(71)	125.22(14)
C(72)-O(73)-B(74)	115.90(12)
O(92)-B(74)-O(73)	108.09(13)
O(92)-B(74)-C(75)	116.47(14)
O(73)-B(74)-C(75)	112.38(12)
O(92)-B(74)-N(87)	110.01(13)
O(73)-B(74)-N(87)	103.66(12)
C(75)-B(74)-N(87)	105.44(13)
C(76)-C(75)-C(80)	118.04(17)
C(76)-C(75)-B(74)	120.92(16)
C(80)-C(75)-B(74)	120.66(15)
C(77)-C(76)-C(75)	121.5(2)
C(77)-C(76)-H(76)	119.3
C(75)-C(76)-H(76)	119.3
C(78)-C(77)-C(76)	119.8(2)
C(78)-C(77)-H(77)	120.1
C(76)-C(77)-H(77)	120.1
C(77)-C(78)-C(79)	120.30(19)
C(77)-C(78)-H(78)	119.8
C(79)-C(78)-H(78)	119.8
C(78)-C(79)-C(80)	120.0(2)

C(78)-C(79)-H(79)	120.0
C(80)-C(79)-H(79)	120.0
C(79)-C(80)-C(75)	120.37(18)
C(79)-C(80)-C(81)	121.01(17)
C(75)-C(80)-C(81)	118.62(15)
C(82)-C(81)-C(86)	117.69(17)
C(82)-C(81)-C(80)	122.15(15)
C(86)-C(81)-C(80)	120.16(15)
C(83)-C(82)-C(81)	121.51(17)
C(83)-C(82)-H(82)	119.2
C(81)-C(82)-H(82)	119.2
C(82)-C(83)-C(84)	120.00(17)
C(82)-C(83)-H(83)	120.0
C(84)-C(83)-H(83)	120.0
C(85)-C(84)-C(83)	119.59(19)
C(85)-C(84)-H(84)	120.2
C(83)-C(84)-H(84)	120.2
C(84)-C(85)-C(86)	120.41(17)
C(84)-C(85)-H(85)	119.8
C(86)-C(85)-H(85)	119.8
C(85)-C(86)-C(81)	120.75(15)
C(85)-C(86)-N(87)	120.46(15)
C(81)-C(86)-N(87)	118.60(15)
C(88)-N(87)-C(86)	122.86(14)
C(88)-N(87)-B(74)	121.02(13)
C(86)-N(87)-B(74)	115.96(12)
O(90)-C(88)-N(87)	119.77(14)
O(90)-C(88)-C(89)	114.79(14)
N(87)-C(88)-C(89)	125.42(15)
C(88)-C(89)-H(89A)	109.5
C(88)-C(89)-H(89B)	109.5
H(89A)-C(89)-H(89B)	109.5
C(88)-C(89)-H(89C)	109.5
H(89A)-C(89)-H(89C)	109.5
H(89B)-C(89)-H(89C)	109.5
C(88)-O(90)-B(91)	115.91(12)
O(92)-B(91)-O(90)	107.84(14)
O(92)-B(91)-N(105)	110.53(12)
O(90)-B(91)-N(105)	103.42(13)
O(92)-B(91)-C(93)	117.73(15)
O(90)-B(91)-C(93)	109.65(12)
N(105)-B(91)-C(93)	106.74(14)
B(74)-O(92)-B(91)	108.40(13)
C(94)-C(93)-C(98)	118.44(17)
C(94)-C(93)-B(91)	121.73(18)
C(98)-C(93)-B(91)	119.80(16)
C(95)-C(94)-C(93)	121.2(2)
C(95)-C(94)-H(94)	119.4
C(93)-C(94)-H(94)	119.4
C(96)-C(95)-C(94)	119.8(2)
C(96)-C(95)-H(95)	120.1
C(94)-C(95)-H(95)	120.1
C(97)-C(96)-C(95)	120.3(2)
C(97)-C(96)-H(96)	119.9
C(95)-C(96)-H(96)	119.9
C(96)-C(97)-C(98)	120.7(2)
C(96)-C(97)-H(97)	119.7
C(98)-C(97)-H(97)	119.7
C(97)-C(98)-C(93)	119.6(2)
C(97)-C(98)-C(99)	121.3(2)
C(93)-C(98)-C(99)	119.10(15)
C(100)-C(99)-C(104)	116.48(19)
C(100)-C(99)-C(98)	122.56(17)
C(104)-C(99)-C(98)	120.92(16)
C(101)-C(100)-C(99)	122.60(19)
C(101)-C(100)-H(100)	118.7
C(99)-C(100)-H(100)	118.7
C(100)-C(101)-C(102)	119.97(19)
C(100)-C(101)-H(101)	120.0
C(102)-C(101)-H(101)	120.0
C(101)-C(102)-C(103)	119.1(2)
C(101)-C(102)-H(102)	120.4
C(103)-C(102)-H(102)	120.4
C(104)-C(103)-C(102)	120.82(18)
C(104)-C(103)-H(103)	119.6
C(102)-C(103)-H(103)	119.6
C(103)-C(104)-C(99)	120.93(16)
C(103)-C(104)-N(105)	120.04(15)
C(99)-C(104)-N(105)	118.74(16)
C(72)-N(105)-C(104)	122.80(14)
C(72)-N(105)-B(91)	121.18(13)
C(104)-N(105)-B(91)	115.96(12)
C(202)-C(201)-H(20A)	109.5
C(202)-C(201)-H(20B)	109.5
H(20A)-C(201)-H(20B)	109.5
C(202)-C(201)-H(20C)	109.5
H(20A)-C(201)-H(20C)	109.5
H(20B)-C(201)-H(20C)	109.5
O(203)-C(202)-C(201)	107.86(15)
O(203)-C(202)-H(20D)	110.1
C(201)-C(202)-H(20D)	110.1
O(203)-C(202)-H(20E)	110.1
C(201)-C(202)-H(20E)	110.1
H(20D)-C(202)-H(20E)	108.4
C(204)-O(203)-C(202)	115.70(15)
O(205)-C(204)-O(203)	123.2(2)
O(205)-C(204)-C(206)	124.7(2)
O(203)-C(204)-C(206)	112.01(19)
C(204)-C(206)-H(20F)	109.5
C(204)-C(206)-H(20G)	109.5

H(20F)-C(206)-H(20G)	109.5	O(215)-C(214)-H(21H)	109.0
C(204)-C(206)-H(20H)	109.5	C(213)-C(214)-H(21H)	109.0
H(20F)-C(206)-H(20H)	109.5	H(21G)-C(214)-H(21H)	107.8
H(20G)-C(206)-H(20H)	109.5	C(216)-O(215)-C(214)	117.9(4)
C(208)-C(207)-H(20J)	109.5	O(217)-C(216)-O(215)	121.2(5)
C(208)-C(207)-H(20I)	109.5	O(217)-C(216)-C(218)	126.6(5)
H(20J)-C(207)-H(20I)	109.5	O(215)-C(216)-C(218)	112.2(4)
C(208)-C(207)-H(20K)	109.5	C(216)-C(218)-H(21I)	109.5
H(20J)-C(207)-H(20K)	109.5	C(216)-C(218)-H(21J)	109.5
H(20I)-C(207)-H(20K)	109.5	H(21I)-C(218)-H(21J)	109.5
O(209)-C(208)-C(207)	107.44(16)	C(216)-C(218)-H(21K)	109.5
O(209)-C(208)-H(20L)	110.2	H(21I)-C(218)-H(21K)	109.5
C(207)-C(208)-H(20L)	110.2	H(21J)-C(218)-H(21K)	109.5
O(209)-C(208)-H(20M)	110.2	C(301)-O(302)-C(303)	112.6(8)
C(207)-C(208)-H(20M)	110.2	O(301)-C(301)-O(302)	127.4(8)
H(20L)-C(208)-H(20M)	108.5	O(301)-C(301)-C(302)	128.7(8)
C(210)-O(209)-C(208)	115.50(14)	O(302)-C(301)-C(302)	103.9(8)
O(211)-C(210)-O(209)	123.64(17)	C(301)-C(302)-H(30A)	109.5
O(211)-C(210)-C(212)	124.52(17)	C(301)-C(302)-H(30B)	109.5
O(209)-C(210)-C(212)	111.84(16)	H(30A)-C(302)-H(30B)	109.5
C(210)-C(212)-H(21A)	109.5	C(301)-C(302)-H(30C)	109.5
C(210)-C(212)-H(21B)	109.5	H(30A)-C(302)-H(30C)	109.5
H(21A)-C(212)-H(21B)	109.5	H(30B)-C(302)-H(30C)	109.5
C(210)-C(212)-H(21C)	109.5	C(303)-C(304)-H(30D)	109.5
H(21A)-C(212)-H(21C)	109.5	C(303)-C(304)-H(30E)	109.5
H(21B)-C(212)-H(21C)	109.5	H(30D)-C(304)-H(30E)	109.5
C(214)-C(213)-H(21D)	109.5	C(303)-C(304)-H(30F)	109.5
C(214)-C(213)-H(21E)	109.5	H(30D)-C(304)-H(30F)	109.5
H(21D)-C(213)-H(21E)	109.5	H(30E)-C(304)-H(30F)	109.5
C(214)-C(213)-H(21F)	109.5	C(304)-C(303)-O(302)	103.3(9)
H(21D)-C(213)-H(21F)	109.5	C(304)-C(303)-H(30G)	111.1
H(21E)-C(213)-H(21F)	109.5	O(302)-C(303)-H(30G)	111.1
O(215)-C(214)-C(213)	112.8(4)	C(304)-C(303)-H(30H)	111.1
O(215)-C(214)-H(21G)	109.0	O(302)-C(303)-H(30H)	111.1
C(213)-C(214)-H(21G)	109.0	H(30G)-C(303)-H(30H)	109.1

Symmetry transformations used to generate equivalent atoms:

Table S14. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **11**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U11	U22	U33	U23	U13	U12
C(1)	25(1)	67(1)	27(1)	9(1)	3(1)	3(1)
C(2)	20(1)	43(1)	21(1)	-2(1)	6(1)	0(1)
O(3)	18(1)	53(1)	21(1)	0(1)	4(1)	-3(1)
B(4)	21(1)	42(1)	22(1)	0(1)	3(1)	-2(1)
C(5)	21(1)	55(1)	23(1)	2(1)	2(1)	-7(1)
C(6)	34(1)	57(1)	37(1)	4(1)	10(1)	-10(1)
C(7)	45(1)	68(1)	50(1)	13(1)	14(1)	-17(1)
C(8)	40(1)	96(2)	42(1)	13(1)	18(1)	-18(1)
C(9)	31(1)	90(2)	33(1)	0(1)	14(1)	-11(1)
C(10)	21(1)	68(1)	23(1)	-1(1)	5(1)	-6(1)
C(11)	20(1)	67(1)	22(1)	-6(1)	2(1)	1(1)
C(12)	22(1)	91(2)	33(1)	-14(1)	5(1)	4(1)
C(13)	32(1)	86(2)	48(1)	-24(1)	2(1)	20(1)
C(14)	37(1)	64(1)	54(1)	-15(1)	2(1)	17(1)
C(15)	31(1)	51(1)	39(1)	-6(1)	3(1)	9(1)
C(16)	20(1)	53(1)	24(1)	-6(1)	2(1)	5(1)
N(17)	18(1)	41(1)	21(1)	-1(1)	4(1)	1(1)
C(18)	21(1)	36(1)	21(1)	1(1)	4(1)	0(1)
C(19)	26(1)	39(1)	31(1)	-6(1)	4(1)	-3(1)
O(20)	18(1)	37(1)	24(1)	-2(1)	4(1)	-1(1)
B(21)	19(1)	34(1)	23(1)	0(1)	1(1)	-2(1)
O(22)	22(1)	37(1)	25(1)	1(1)	7(1)	-4(1)
C(23)	18(1)	34(1)	26(1)	-4(1)	1(1)	-3(1)
C(24)	27(1)	35(1)	32(1)	-2(1)	1(1)	-1(1)
C(25)	30(1)	33(1)	46(1)	-7(1)	2(1)	3(1)
C(26)	29(1)	41(1)	53(1)	-14(1)	14(1)	2(1)
C(27)	26(1)	42(1)	38(1)	-8(1)	13(1)	-3(1)
C(28)	17(1)	35(1)	28(1)	-5(1)	4(1)	-3(1)
C(29)	21(1)	37(1)	24(1)	-4(1)	6(1)	-4(1)
C(30)	29(1)	40(1)	36(1)	-4(1)	14(1)	-4(1)
C(31)	45(1)	42(1)	48(1)	3(1)	25(1)	-6(1)
C(32)	51(1)	37(1)	54(1)	9(1)	23(1)	4(1)
C(33)	35(1)	38(1)	39(1)	3(1)	15(1)	6(1)
C(34)	22(1)	35(1)	23(1)	0(1)	6(1)	-2(1)
N(35)	18(1)	36(1)	21(1)	0(1)	5(1)	1(1)
C(36)	24(1)	47(1)	31(1)	-12(1)	6(1)	3(1)
C(37)	17(1)	34(1)	25(1)	-2(1)	3(1)	2(1)
O(38)	17(1)	41(1)	25(1)	-6(1)	3(1)	1(1)
B(39)	20(1)	35(1)	23(1)	-3(1)	5(1)	0(1)
C(40)	19(1)	41(1)	24(1)	-6(1)	7(1)	-1(1)
C(41)	25(1)	43(1)	32(1)	-6(1)	7(1)	-3(1)
C(42)	31(1)	46(1)	43(1)	-10(1)	7(1)	-10(1)
C(43)	25(1)	62(1)	38(1)	-14(1)	2(1)	-13(1)
C(44)	22(1)	60(1)	31(1)	-6(1)	1(1)	-2(1)
C(45)	18(1)	47(1)	27(1)	-4(1)	6(1)	0(1)

C(46)	20(1)	47(1)	26(1)	-2(1)	4(1)	4(1)
C(47)	23(1)	63(1)	39(1)	2(1)	4(1)	9(1)
C(48)	35(1)	56(1)	56(1)	6(1)	5(1)	20(1)
C(49)	43(1)	41(1)	64(1)	1(1)	2(1)	12(1)
C(50)	30(1)	39(1)	49(1)	-3(1)	1(1)	4(1)
C(51)	23(1)	40(1)	28(1)	-1(1)	4(1)	6(1)
N(52)	18(1)	33(1)	25(1)	-2(1)	3(1)	1(1)
C(53)	20(1)	31(1)	26(1)	-3(1)	3(1)	0(1)
C(54)	27(1)	45(1)	29(1)	8(1)	5(1)	0(1)
O(55)	18(1)	36(1)	23(1)	0(1)	4(1)	1(1)
B(56)	20(1)	31(1)	23(1)	-3(1)	7(1)	-1(1)
O(57)	18(1)	32(1)	26(1)	-3(1)	4(1)	-1(1)
C(58)	19(1)	32(1)	24(1)	0(1)	7(1)	1(1)
C(59)	24(1)	33(1)	32(1)	-1(1)	8(1)	1(1)
C(60)	32(1)	33(1)	40(1)	4(1)	12(1)	7(1)
C(61)	25(1)	43(1)	33(1)	7(1)	7(1)	9(1)
C(62)	19(1)	42(1)	28(1)	1(1)	4(1)	2(1)
C(63)	17(1)	35(1)	24(1)	1(1)	6(1)	1(1)
C(64)	20(1)	35(1)	24(1)	-3(1)	6(1)	0(1)
C(65)	21(1)	40(1)	39(1)	-8(1)	6(1)	-2(1)
C(66)	28(1)	40(1)	54(1)	-12(1)	8(1)	-9(1)
C(67)	36(1)	32(1)	52(1)	-6(1)	9(1)	-2(1)
C(68)	26(1)	33(1)	37(1)	-2(1)	4(1)	2(1)
C(69)	20(1)	33(1)	25(1)	-3(1)	5(1)	-1(1)
N(70)	18(1)	30(1)	23(1)	-3(1)	3(1)	1(1)
C(71)	25(1)	45(1)	29(1)	3(1)	5(1)	7(1)
C(72)	21(1)	35(1)	24(1)	-5(1)	4(1)	3(1)
O(73)	19(1)	38(1)	28(1)	1(1)	4(1)	5(1)
B(74)	23(1)	34(1)	32(1)	2(1)	2(1)	6(1)
C(75)	22(1)	40(1)	40(1)	12(1)	4(1)	10(1)
C(76)	35(1)	40(1)	68(1)	15(1)	12(1)	7(1)
C(77)	43(1)	47(1)	98(2)	29(1)	21(1)	6(1)
C(78)	37(1)	70(2)	79(2)	41(1)	21(1)	9(1)
C(79)	28(1)	72(1)	46(1)	22(1)	13(1)	11(1)
C(80)	20(1)	54(1)	34(1)	15(1)	4(1)	10(1)
C(81)	23(1)	52(1)	24(1)	6(1)	4(1)	9(1)
C(82)	29(1)	64(1)	27(1)	4(1)	8(1)	15(1)
C(83)	43(1)	62(1)	33(1)	-6(1)	10(1)	19(1)
C(84)	47(1)	50(1)	39(1)	-10(1)	9(1)	6(1)
C(85)	32(1)	52(1)	29(1)	-5(1)	7(1)	3(1)
C(86)	25(1)	46(1)	21(1)	0(1)	3(1)	8(1)
N(87)	20(1)	44(1)	25(1)	0(1)	5(1)	6(1)
C(88)	22(1)	50(1)	25(1)	-2(1)	4(1)	5(1)
C(89)	26(1)	92(2)	31(1)	-17(1)	0(1)	10(1)
O(90)	20(1)	51(1)	27(1)	-4(1)	3(1)	8(1)
B(91)	22(1)	41(1)	30(1)	-4(1)	0(1)	8(1)
O(92)	24(1)	37(1)	39(1)	0(1)	4(1)	7(1)
C(93)	23(1)	53(1)	34(1)	-10(1)	-5(1)	14(1)
C(94)	33(1)	54(1)	56(1)	-16(1)	-4(1)	16(1)
C(95)	44(1)	68(2)	74(2)	-32(1)	-11(1)	26(1)

C(96)	45(1)	100(2)	57(1)	-34(1)	-2(1)	36(1)
C(97)	37(1)	99(2)	38(1)	-15(1)	4(1)	27(1)
C(98)	23(1)	72(1)	29(1)	-9(1)	0(1)	17(1)
C(99)	22(1)	71(1)	24(1)	0(1)	3(1)	10(1)
C(100)	22(1)	102(2)	34(1)	10(1)	7(1)	10(1)
C(101)	26(1)	100(2)	44(1)	18(1)	5(1)	-7(1)
C(102)	33(1)	71(1)	41(1)	12(1)	1(1)	-10(1)
C(103)	27(1)	55(1)	31(1)	1(1)	4(1)	-2(1)
C(104)	19(1)	54(1)	23(1)	-1(1)	2(1)	2(1)
N(105)	19(1)	40(1)	25(1)	-4(1)	4(1)	5(1)
C(201)	56(1)	60(1)	63(1)	-4(1)	25(1)	4(1)
C(202)	47(1)	44(1)	51(1)	-7(1)	14(1)	10(1)
O(203)	57(1)	44(1)	55(1)	8(1)	23(1)	14(1)
C(204)	47(1)	54(1)	54(1)	15(1)	9(1)	9(1)
O(205)	78(1)	46(1)	64(1)	7(1)	12(1)	2(1)
C(206)	96(2)	91(2)	114(2)	44(2)	68(2)	37(2)
C(207)	64(1)	58(1)	66(1)	12(1)	24(1)	-13(1)
C(208)	39(1)	47(1)	50(1)	5(1)	19(1)	-2(1)
O(209)	40(1)	39(1)	43(1)	7(1)	16(1)	2(1)
C(210)	34(1)	44(1)	30(1)	7(1)	3(1)	-2(1)
O(211)	56(1)	41(1)	51(1)	8(1)	14(1)	0(1)
C(212)	51(1)	74(2)	44(1)	14(1)	20(1)	4(1)
C(213)	101(5)	117(5)	80(4)	59(3)	56(4)	47(4)
C(214)	101(4)	59(2)	55(2)	-4(2)	4(2)	24(2)
O(215)	62(2)	54(2)	64(2)	-1(1)	-5(2)	10(1)
C(216)	57(2)	48(2)	85(3)	-28(2)	16(2)	-8(2)
O(217)	131(3)	62(2)	85(3)	-22(2)	25(2)	-3(2)
C(218)	90(4)	99(4)	72(3)	-51(3)	36(3)	-44(3)

Table S15. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **11**.

	x	y	z	U(eq)
H(1A)	8557	1981	4170	60
H(1B)	7975	2308	4508	60
H(1C)	8672	2763	4365	60
H(6)	7847	4459	2673	51
H(7)	8595	4992	2137	64
H(8)	9226	4325	1601	69
H(9)	9137	3136	1615	60
H(12)	9403	2098	1906	58
H(13)	9375	915	1983	68
H(14)	8406	387	2350	64
H(15)	7447	1059	2618	49
H(19A)	5968	1284	2273	49
H(19B)	6438	1573	1850	49
H(19C)	5586	1885	1871	49
H(24)	5657	4298	2985	38
H(25)	4784	4873	3402	45
H(26)	4418	4379	4141	48
H(27)	4883	3289	4435	42
H(30)	4906	2155	4386	41
H(31)	5365	1067	4667	51
H(32)	6525	641	4460	55
H(33)	7231	1320	3978	43
H(36A)	1852	3482	5716	51
H(36B)	2647	3189	6100	51
H(36C)	1821	2788	6045	51
H(41)	1259	642	4665	40
H(42)	120	90	4176	48
H(43)	-763	691	3504	51
H(44)	-524	1835	3335	46
H(47)	-484	2957	3478	50
H(48)	-236	4107	3346	60
H(49)	1056	4544	3621	61
H(50)	2096	3818	4026	48
H(54A)	3283	3277	3744	51
H(54B)	2481	2959	3385	51
H(54C)	3294	2529	3486	51
H(59)	3760	591	5053	36
H(60)	4899	79	5575	41
H(61)	5833	755	6160	41
H(62)	5638	1931	6211	36
H(65)	5606	3000	5996	40
H(66)	5408	4177	6017	50
H(67)	4136	4638	5707	49
H(68)	3057	3908	5383	39
H(71A)	892	8366	2642	49
H(71B)	467	7739	2286	49

H(71C)	1336	7985	2241	49
H(76)	413	5525	3640	57
H(77)	-358	5076	4196	74
H(78)	-619	5738	4891	73
H(79)	-161	6868	5010	58
H(82)	-136	7996	4791	48
H(83)	377	9100	4915	55
H(84)	1554	9376	4653	54
H(85)	2203	8536	4260	45
H(89A)	3478	7823	4546	76
H(89B)	3555	7079	4817	76
H(89C)	2887	7603	4915	76
H(94)	2545	5146	3208	60
H(95)	3250	4522	2692	79
H(96)	3984	5096	2171	83
H(97)	3988	6287	2141	70
H(100)	4323	7337	2415	63
H(101)	4363	8523	2439	69
H(102)	3379	9141	2735	60
H(103)	2356	8545	3000	46
H(20A)	3179	-130	4161	86
H(20B)	2461	-146	3642	86
H(20C)	2388	308	4147	86
H(20D)	2687	1024	3485	70
H(20E)	3417	1031	4000	70
H(20F)	5011	802	2897	140
H(20G)	4253	721	2409	140
H(20H)	4481	119	2839	140
H(20J)	6632	5009	605	91
H(20I)	7492	4698	604	91
H(20K)	7327	5037	1136	91
H(20L)	6633	3791	666	66
H(20M)	7292	3843	1218	66
H(21A)	4785	3664	1522	82
H(21B)	5275	4315	1802	82
H(21C)	5382	3584	2095	82
H(21D)	3502	5642	4836	141
H(21E)	3161	5438	4224	141
H(21F)	3406	4850	4666	141
H(21G)	2078	5780	4621	88
H(21H)	1968	4998	4426	88
H(21I)	2712	5599	6386	127
H(21J)	2601	4845	6132	127
H(21K)	1836	5291	6170	127
H(30A)	2530	5463	4232	127
H(30B)	2783	4822	4624	127
H(30C)	3426	5399	4578	127
H(30D)	1883	4594	5989	157
H(30E)	1935	5112	6479	157
H(30F)	2733	4853	6321	157

H(30G)	2439	5944	6017	126
H(30H)	1579	5686	5685	126

Table S16. Torsion angles [°] for **11**.

N(35)-C(2)-O(3)-B(4)	-5.3(2)	O(22)-B(4)-N(17)-C(16)	173.22(12)
C(1)-C(2)-O(3)-B(4)	176.40(14)	O(3)-B(4)-N(17)-C(16)	-71.01(15)
C(2)-O(3)-B(4)-O(22)	49.29(18)	C(5)-B(4)-N(17)-C(16)	45.23(17)
C(2)-O(3)-B(4)-C(5)	177.61(14)	C(16)-N(17)-C(18)-O(20)	165.92(14)
C(2)-O(3)-B(4)-N(17)	-67.90(16)	B(4)-N(17)-C(18)-O(20)	-19.7(2)
O(22)-B(4)-C(5)-C(6)	27.2(2)	C(16)-N(17)-C(18)-C(19)	-15.4(2)
O(3)-B(4)-C(5)-C(6)	-96.37(18)	B(4)-N(17)-C(18)-C(19)	159.01(15)
N(17)-B(4)-C(5)-C(6)	151.47(14)	N(17)-C(18)-O(20)-B(21)	-3.6(2)
O(22)-B(4)-C(5)-C(10)	-150.38(14)	C(19)-C(18)-O(20)-B(21)	177.56(13)
O(3)-B(4)-C(5)-C(10)	86.03(17)	C(18)-O(20)-B(21)-O(22)	48.38(16)
N(17)-B(4)-C(5)-C(10)	-26.13(19)	C(18)-O(20)-B(21)-C(23)	176.83(13)
C(10)-C(5)-C(6)-C(7)	-0.8(3)	C(18)-O(20)-B(21)-N(35)	-68.81(15)
B(4)-C(5)-C(6)-C(7)	-178.42(16)	O(3)-B(4)-O(22)-B(21)	-67.52(15)
C(5)-C(6)-C(7)-C(8)	1.5(3)	C(5)-B(4)-O(22)-B(21)	168.11(13)
C(6)-C(7)-C(8)-C(9)	-0.8(3)	N(17)-B(4)-O(22)-B(21)	45.37(16)
C(7)-C(8)-C(9)-C(10)	-0.6(3)	O(20)-B(21)-O(22)-B(4)	-68.05(14)
C(8)-C(9)-C(10)-C(5)	1.4(3)	C(23)-B(21)-O(22)-B(4)	165.34(12)
C(8)-C(9)-C(10)-C(11)	-177.56(17)	N(35)-B(21)-O(22)-B(4)	44.60(16)
C(6)-C(5)-C(10)-C(9)	-0.6(2)	O(22)-B(21)-C(23)-C(24)	24.6(2)
B(4)-C(5)-C(10)-C(9)	177.00(15)	O(20)-B(21)-C(23)-C(24)	-99.77(16)
C(6)-C(5)-C(10)-C(11)	178.30(15)	N(35)-B(21)-C(23)-C(24)	147.55(13)
B(4)-C(5)-C(10)-C(11)	-4.0(2)	O(22)-B(21)-C(23)-C(28)	-149.83(13)
C(9)-C(10)-C(11)-C(12)	21.1(2)	O(20)-B(21)-C(23)-C(28)	85.81(16)
C(5)-C(10)-C(11)-C(12)	-157.86(15)	N(35)-B(21)-C(23)-C(28)	-26.87(18)
C(9)-C(10)-C(11)-C(16)	-160.74(16)	C(28)-C(23)-C(24)-C(25)	-1.1(2)
C(5)-C(10)-C(11)-C(16)	20.3(2)	B(21)-C(23)-C(24)-C(25)	-175.63(14)
C(16)-C(11)-C(12)-C(13)	-1.0(2)	C(23)-C(24)-C(25)-C(26)	2.3(2)
C(10)-C(11)-C(12)-C(13)	177.24(16)	C(24)-C(25)-C(26)-C(27)	-1.5(2)
C(11)-C(12)-C(13)-C(14)	-1.3(3)	C(25)-C(26)-C(27)-C(28)	-0.6(2)
C(12)-C(13)-C(14)-C(15)	1.1(3)	C(24)-C(23)-C(28)-C(27)	-1.0(2)
C(13)-C(14)-C(15)-C(16)	1.4(3)	B(21)-C(23)-C(28)-C(27)	173.60(13)
C(14)-C(15)-C(16)-C(11)	-3.8(3)	C(24)-C(23)-C(28)-C(29)	179.30(13)
C(14)-C(15)-C(16)-N(17)	-178.23(15)	B(21)-C(23)-C(28)-C(29)	-6.1(2)
C(12)-C(11)-C(16)-C(15)	3.5(2)	C(26)-C(27)-C(28)-C(23)	1.8(2)
C(10)-C(11)-C(16)-C(15)	-174.77(15)	C(26)-C(27)-C(28)-C(29)	-178.48(15)
C(12)-C(11)-C(16)-N(17)	178.04(13)	C(23)-C(28)-C(29)-C(30)	-155.05(14)
C(10)-C(11)-C(16)-N(17)	-0.2(2)	C(27)-C(28)-C(29)-C(30)	25.2(2)
C(15)-C(16)-N(17)-C(18)	-45.0(2)	C(23)-C(28)-C(29)-C(34)	24.4(2)
C(11)-C(16)-N(17)-C(18)	140.49(15)	C(27)-C(28)-C(29)-C(34)	-155.36(15)
C(15)-C(16)-N(17)-B(4)	140.42(15)	C(34)-C(29)-C(30)-C(31)	0.9(2)
C(11)-C(16)-N(17)-B(4)	-34.12(19)	C(28)-C(29)-C(30)-C(31)	-179.62(16)
O(22)-B(4)-N(17)-C(18)	-1.50(19)	C(29)-C(30)-C(31)-C(32)	-2.1(3)
O(3)-B(4)-N(17)-C(18)	114.27(14)	C(30)-C(31)-C(32)-C(33)	0.6(3)
C(5)-B(4)-N(17)-C(18)	-129.49(14)	C(31)-C(32)-C(33)-C(34)	2.1(3)

C(32)-C(33)-C(34)-C(29)	-3.3(3)
C(32)-C(33)-C(34)-N(35)	-178.33(16)
C(30)-C(29)-C(34)-C(33)	1.8(2)
C(28)-C(29)-C(34)-C(33)	-177.68(14)
C(30)-C(29)-C(34)-N(35)	176.89(13)
C(28)-C(29)-C(34)-N(35)	-2.6(2)
O(3)-C(2)-N(35)-C(34)	166.94(14)
C(1)-C(2)-N(35)-C(34)	-14.9(2)
O(3)-C(2)-N(35)-B(21)	-18.1(2)
C(1)-C(2)-N(35)-B(21)	160.00(16)
C(33)-C(34)-N(35)-C(2)	-44.8(2)
C(29)-C(34)-N(35)-C(2)	140.13(15)
C(33)-C(34)-N(35)-B(21)	140.09(15)
C(29)-C(34)-N(35)-B(21)	-35.02(19)
O(22)-B(21)-N(35)-C(2)	-1.75(19)
O(20)-B(21)-N(35)-C(2)	113.63(14)
C(23)-B(21)-N(35)-C(2)	-127.81(14)
O(22)-B(21)-N(35)-C(34)	173.52(12)
O(20)-B(21)-N(35)-C(34)	-71.09(15)
C(23)-B(21)-N(35)-C(34)	47.46(16)
N(70)-C(37)-O(38)-B(39)	-3.6(2)
C(36)-C(37)-O(38)-B(39)	178.96(13)
C(37)-O(38)-B(39)-O(57)	48.71(17)
C(37)-O(38)-B(39)-C(40)	178.22(13)
C(37)-O(38)-B(39)-N(52)	-68.09(15)
O(57)-B(39)-C(40)-C(41)	26.1(2)
O(38)-B(39)-C(40)-C(41)	-98.25(17)
N(52)-B(39)-C(40)-C(41)	149.13(14)
O(57)-B(39)-C(40)-C(45)	-149.95(14)
O(38)-B(39)-C(40)-C(45)	85.67(17)
N(52)-B(39)-C(40)-C(45)	-26.95(18)
C(45)-C(40)-C(41)-C(42)	-0.3(2)
B(39)-C(40)-C(41)-C(42)	-176.46(15)
C(40)-C(41)-C(42)-C(43)	1.0(3)
C(41)-C(42)-C(43)-C(44)	-0.7(3)
C(42)-C(43)-C(44)-C(45)	-0.2(3)
C(43)-C(44)-C(45)-C(40)	0.9(2)
C(43)-C(44)-C(45)-C(46)	-178.45(16)
C(41)-C(40)-C(45)-C(44)	-0.7(2)
B(39)-C(40)-C(45)-C(44)	175.53(14)
C(41)-C(40)-C(45)-C(46)	178.74(14)
B(39)-C(40)-C(45)-C(46)	-5.1(2)
C(44)-C(45)-C(46)-C(47)	23.8(2)
C(40)-C(45)-C(46)-C(47)	-155.60(16)
C(44)-C(45)-C(46)-C(51)	-157.74(16)
C(40)-C(45)-C(46)-C(51)	22.9(2)
C(51)-C(46)-C(47)-C(48)	0.2(3)
C(45)-C(46)-C(47)-C(48)	178.73(17)
C(46)-C(47)-C(48)-C(49)	-1.2(3)
C(47)-C(48)-C(49)-C(50)	0.3(3)
C(48)-C(49)-C(50)-C(51)	1.7(3)
C(49)-C(50)-C(51)-C(46)	-2.8(3)
C(49)-C(50)-C(51)-N(52)	-177.67(17)
C(47)-C(46)-C(51)-C(50)	1.8(2)
C(45)-C(46)-C(51)-C(50)	-176.78(16)
C(47)-C(46)-C(51)-N(52)	176.74(14)
C(45)-C(46)-C(51)-N(52)	-1.8(2)
C(50)-C(51)-N(52)-C(53)	-44.1(2)
C(46)-C(51)-N(52)-C(53)	140.93(15)
C(50)-C(51)-N(52)-B(39)	139.97(16)
C(46)-C(51)-N(52)-B(39)	-35.04(19)
O(57)-B(39)-N(52)-C(53)	-1.31(19)
O(38)-B(39)-N(52)-C(53)	114.38(14)
C(40)-B(39)-N(52)-C(53)	-128.98(14)
O(57)-B(39)-N(52)-C(51)	174.71(12)
O(38)-B(39)-N(52)-C(51)	-69.61(15)
C(40)-B(39)-N(52)-C(51)	47.04(16)
C(51)-N(52)-C(53)-O(55)	164.31(13)
B(39)-N(52)-C(53)-O(55)	-19.9(2)
C(51)-N(52)-C(53)-C(54)	-19.2(2)
B(39)-N(52)-C(53)-C(54)	156.60(14)
N(52)-C(53)-O(55)-B(56)	-3.48(19)
C(54)-C(53)-O(55)-B(56)	179.66(13)
C(53)-O(55)-B(56)-O(57)	48.41(16)
C(53)-O(55)-B(56)-C(58)	177.90(12)
C(53)-O(55)-B(56)-N(70)	-68.44(14)
O(55)-B(56)-O(57)-B(39)	-68.24(14)
C(58)-B(56)-O(57)-B(39)	167.03(13)
N(70)-B(56)-O(57)-B(39)	44.86(15)
O(38)-B(39)-O(57)-B(56)	-68.25(15)
C(40)-B(39)-O(57)-B(56)	166.25(13)
N(52)-B(39)-O(57)-B(56)	45.10(15)
O(57)-B(56)-C(58)-C(59)	24.7(2)
O(55)-B(56)-C(58)-C(59)	-99.50(16)
N(70)-B(56)-C(58)-C(59)	148.47(14)
O(57)-B(56)-C(58)-C(63)	-152.86(13)
O(55)-B(56)-C(58)-C(63)	82.98(16)
N(70)-B(56)-C(58)-C(63)	-29.05(18)
C(63)-C(58)-C(59)-C(60)	0.0(2)
B(56)-C(58)-C(59)-C(60)	-177.55(14)
C(58)-C(59)-C(60)-C(61)	0.7(2)
C(59)-C(60)-C(61)-C(62)	-0.6(2)
C(60)-C(61)-C(62)-C(63)	-0.2(2)
C(61)-C(62)-C(63)-C(58)	0.9(2)
C(61)-C(62)-C(63)-C(64)	179.78(14)
C(59)-C(58)-C(63)-C(62)	-0.8(2)
B(56)-C(58)-C(63)-C(62)	176.79(14)
C(59)-C(58)-C(63)-C(64)	-179.68(14)
B(56)-C(58)-C(63)-C(64)	-2.1(2)
C(62)-C(63)-C(64)-C(65)	22.8(2)

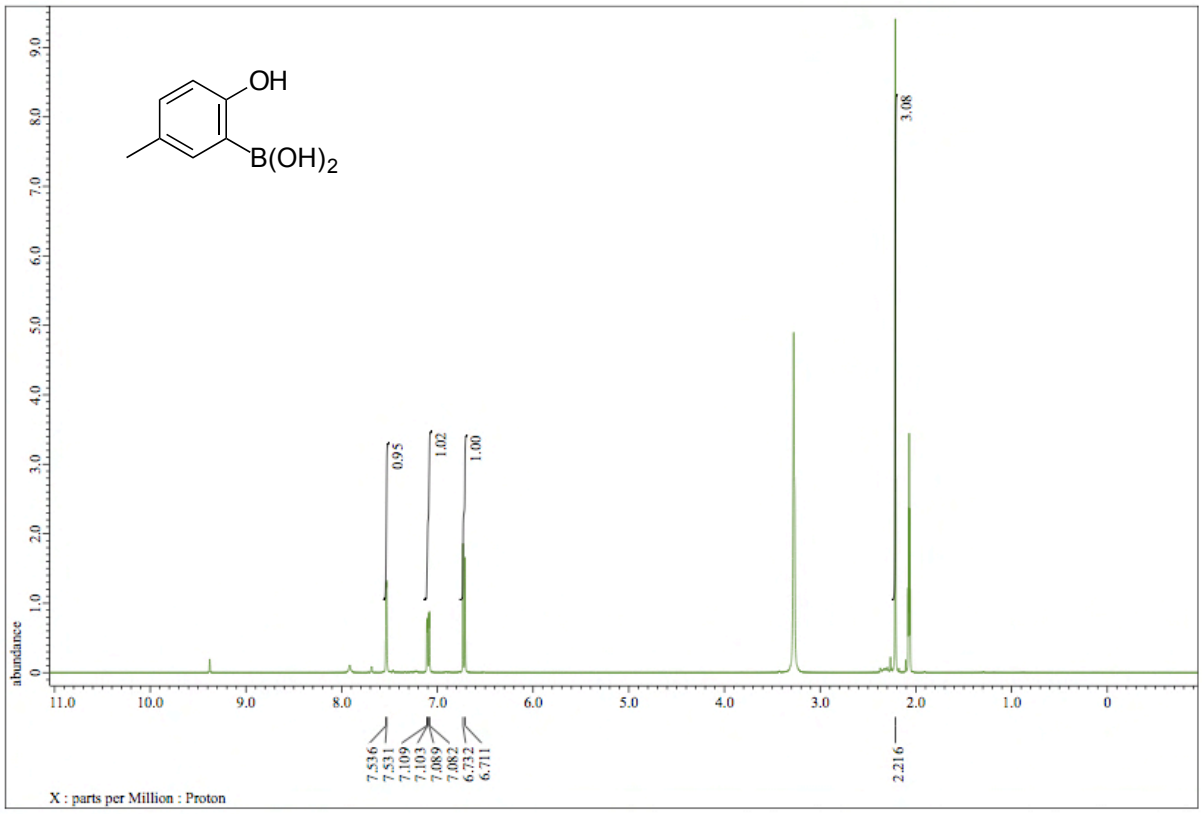
C(58)-C(63)-C(64)-C(65)	-158.31(15)
C(62)-C(63)-C(64)-C(69)	-158.22(14)
C(58)-C(63)-C(64)-C(69)	20.6(2)
C(69)-C(64)-C(65)-C(66)	-1.4(2)
C(63)-C(64)-C(65)-C(66)	177.58(16)
C(64)-C(65)-C(66)-C(67)	-0.6(3)
C(65)-C(66)-C(67)-C(68)	0.7(3)
C(66)-C(67)-C(68)-C(69)	1.3(3)
C(67)-C(68)-C(69)-C(64)	-3.4(2)
C(67)-C(68)-C(69)-N(70)	-177.65(15)
C(65)-C(64)-C(69)-C(68)	3.4(2)
C(63)-C(64)-C(69)-C(68)	-175.59(14)
C(65)-C(64)-C(69)-N(70)	177.68(14)
C(63)-C(64)-C(69)-N(70)	-1.3(2)
O(38)-C(37)-N(70)-C(69)	163.30(13)
C(36)-C(37)-N(70)-C(69)	-19.5(2)
O(38)-C(37)-N(70)-B(56)	-20.3(2)
C(36)-C(37)-N(70)-B(56)	156.90(15)
C(68)-C(69)-N(70)-C(37)	-43.5(2)
C(64)-C(69)-N(70)-C(37)	142.12(15)
C(68)-C(69)-N(70)-B(56)	139.88(15)
C(64)-C(69)-N(70)-B(56)	-34.49(19)
O(57)-B(56)-N(70)-C(37)	-0.75(19)
O(55)-B(56)-N(70)-C(37)	115.03(14)
C(58)-B(56)-N(70)-C(37)	-129.30(14)
O(57)-B(56)-N(70)-C(69)	175.91(12)
O(55)-B(56)-N(70)-C(69)	-68.31(14)
C(58)-B(56)-N(70)-C(69)	47.36(16)
N(105)-C(72)-O(73)-B(74)	5.9(2)
C(71)-C(72)-O(73)-B(74)	-175.27(13)
C(72)-O(73)-B(74)-O(92)	-50.98(17)
C(72)-O(73)-B(74)-C(75)	179.11(13)
C(72)-O(73)-B(74)-N(87)	65.76(15)
O(92)-B(74)-C(75)-C(76)	-24.1(2)
O(73)-B(74)-C(75)-C(76)	101.37(18)
N(87)-B(74)-C(75)-C(76)	-146.38(15)
O(92)-B(74)-C(75)-C(80)	148.71(15)
O(73)-B(74)-C(75)-C(80)	-85.82(18)
N(87)-B(74)-C(75)-C(80)	26.43(18)
C(80)-C(75)-C(76)-C(77)	-2.2(3)
B(74)-C(75)-C(76)-C(77)	170.82(16)
C(75)-C(76)-C(77)-C(78)	0.3(3)
C(76)-C(77)-C(78)-C(79)	1.6(3)
C(77)-C(78)-C(79)-C(80)	-1.6(3)
C(78)-C(79)-C(80)-C(75)	-0.3(2)
C(78)-C(79)-C(80)-C(81)	-179.45(16)
C(76)-C(75)-C(80)-C(79)	2.2(2)
B(74)-C(75)-C(80)-C(79)	-170.83(14)
C(76)-C(75)-C(80)-C(81)	-178.69(14)
B(74)-C(75)-C(80)-C(81)	8.3(2)
C(79)-C(80)-C(81)-C(82)	-28.4(2)
C(75)-C(80)-C(81)-C(82)	152.50(15)
C(79)-C(80)-C(81)-C(86)	152.15(15)
C(75)-C(80)-C(81)-C(86)	-27.0(2)
C(86)-C(81)-C(82)-C(83)	-1.0(2)
C(80)-C(81)-C(82)-C(83)	179.52(15)
C(81)-C(82)-C(83)-C(84)	1.5(3)
C(82)-C(83)-C(84)-C(85)	0.1(3)
C(83)-C(84)-C(85)-C(86)	-2.1(3)
C(84)-C(85)-C(86)-C(81)	2.6(2)
C(84)-C(85)-C(86)-N(87)	177.55(15)
C(82)-C(81)-C(86)-C(85)	-1.0(2)
C(80)-C(81)-C(86)-C(85)	178.48(15)
C(82)-C(81)-C(86)-N(87)	-176.08(13)
C(80)-C(81)-C(86)-N(87)	3.4(2)
C(85)-C(86)-N(87)-C(88)	45.8(2)
C(81)-C(86)-N(87)-C(88)	-139.13(16)
C(85)-C(86)-N(87)-B(74)	-138.71(15)
C(81)-C(86)-N(87)-B(74)	36.36(19)
O(92)-B(74)-N(87)-C(88)	0.4(2)
O(73)-B(74)-N(87)-C(88)	-115.01(15)
C(75)-B(74)-N(87)-C(88)	126.72(15)
O(92)-B(74)-N(87)-C(86)	-175.22(13)
O(73)-B(74)-N(87)-C(86)	69.40(16)
C(75)-B(74)-N(87)-C(86)	-48.87(17)
C(86)-N(87)-C(88)-O(90)	-165.73(15)
B(74)-N(87)-C(88)-O(90)	19.0(2)
C(86)-N(87)-C(88)-C(89)	16.0(3)
B(74)-N(87)-C(88)-C(89)	-159.24(18)
N(87)-C(88)-O(90)-B(91)	6.1(2)
C(89)-C(88)-O(90)-B(91)	-175.47(16)
C(88)-O(90)-B(91)-O(92)	-51.30(18)
C(88)-O(90)-B(91)-N(105)	65.81(17)
C(88)-O(90)-B(91)-C(93)	179.35(15)
O(73)-B(74)-O(92)-B(91)	68.27(15)
C(75)-B(74)-O(92)-B(91)	-164.13(14)
N(87)-B(74)-O(92)-B(91)	-44.28(17)
O(90)-B(91)-O(92)-B(74)	68.99(15)
N(105)-B(91)-O(92)-B(74)	-43.40(17)
C(93)-B(91)-O(92)-B(74)	-166.38(14)
O(92)-B(91)-C(93)-C(94)	-22.8(2)
O(90)-B(91)-C(93)-C(94)	100.89(18)
N(105)-B(91)-C(93)-C(94)	-147.72(15)
O(92)-B(91)-C(93)-C(98)	154.98(15)
O(90)-B(91)-C(93)-C(98)	-81.29(18)
N(105)-B(91)-C(93)-C(98)	30.09(19)
C(98)-C(93)-C(94)-C(95)	1.0(3)
B(91)-C(93)-C(94)-C(95)	178.84(16)
C(93)-C(94)-C(95)-C(96)	-0.4(3)
C(94)-C(95)-C(96)-C(97)	-0.9(3)

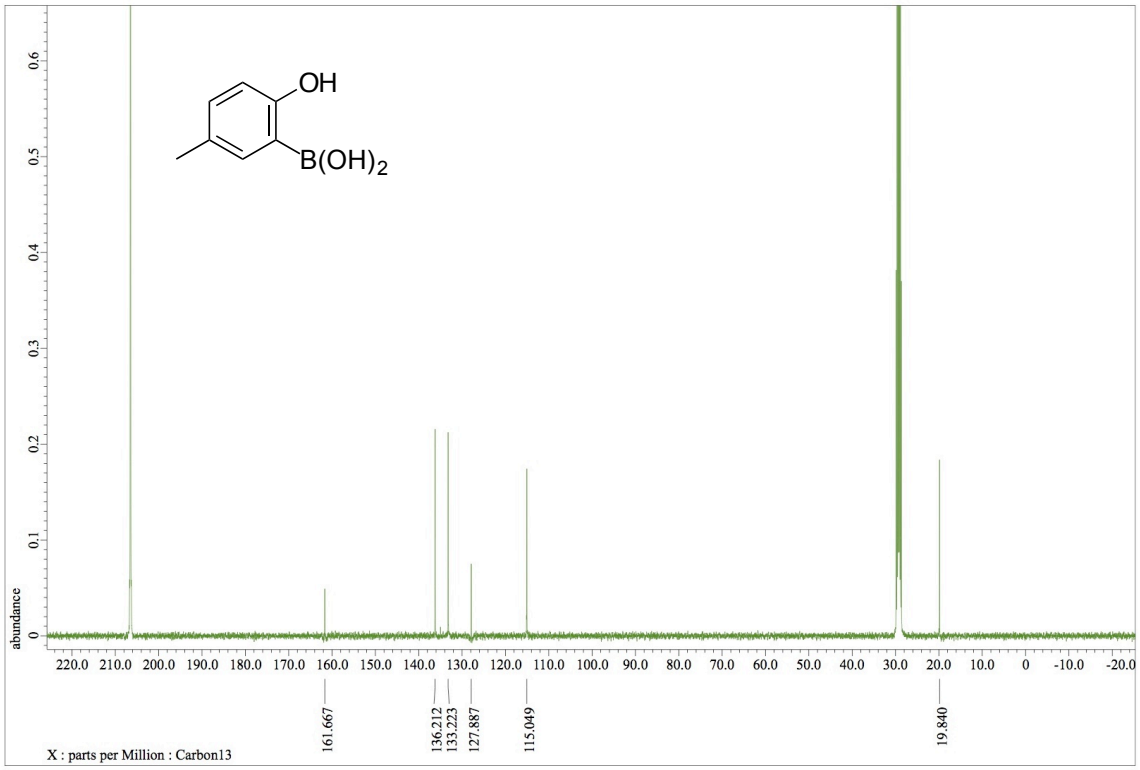
C(95)-C(96)-C(97)-C(98)	1.6(3)	O(73)-C(72)-N(105)-B(91)	19.6(2)
C(96)-C(97)-C(98)-C(93)	-1.0(3)	C(71)-C(72)-N(105)-B(91)	-159.14(15)
C(96)-C(97)-C(98)-C(99)	179.03(17)	C(103)-C(104)-N(105)-C(72)	44.0(2)
C(94)-C(93)-C(98)-C(97)	-0.3(2)	C(99)-C(104)-N(105)-C(72)	-142.24(15)
B(91)-C(93)-C(98)-C(97)	-178.20(15)	C(103)-C(104)-N(105)-B(91)	-138.87(15)
C(94)-C(93)-C(98)-C(99)	179.67(15)	C(99)-C(104)-N(105)-B(91)	34.88(19)
B(91)-C(93)-C(98)-C(99)	1.8(2)	O(92)-B(91)-N(105)-C(72)	-0.5(2)
C(97)-C(98)-C(99)-C(100)	-23.3(3)	O(90)-B(91)-N(105)-C(72)	-115.67(14)
C(93)-C(98)-C(99)-C(100)	156.68(16)	C(93)-B(91)-N(105)-C(72)	128.69(15)
C(97)-C(98)-C(99)-C(104)	159.05(16)	O(92)-B(91)-N(105)-C(104)	-177.65(13)
C(93)-C(98)-C(99)-C(104)	-20.9(2)	O(90)-B(91)-N(105)-C(104)	67.15(16)
C(104)-C(99)-C(100)-C(101)	0.4(3)	C(93)-B(91)-N(105)-C(104)	-48.49(17)
C(98)-C(99)-C(100)-C(101)	-177.36(17)	C(201)-C(202)-O(203)-C(204)	173.96(17)
C(99)-C(100)-C(101)-C(102)	1.0(3)	C(202)-O(203)-C(204)-O(205)	-0.7(3)
C(100)-C(101)-C(102)-C(103)	-0.3(3)	C(202)-O(203)-C(204)-C(206)	-178.6(2)
C(101)-C(102)-C(103)-C(104)	-1.7(3)	C(207)-C(208)-O(209)-C(210)	-174.67(16)
C(102)-C(103)-C(104)-C(99)	3.2(2)	C(208)-O(209)-C(210)-O(211)	2.3(2)
C(102)-C(103)-C(104)-N(105)	176.78(15)	C(208)-O(209)-C(210)-C(212)	-177.72(15)
C(100)-C(99)-C(104)-C(103)	-2.4(2)	C(213)-C(214)-O(215)-C(216)	88.5(5)
C(98)-C(99)-C(104)-C(103)	175.33(15)	C(214)-O(215)-C(216)-O(217)	2.5(7)
C(100)-C(99)-C(104)-N(105)	-176.13(14)	C(214)-O(215)-C(216)-C(218)	-175.2(4)
C(98)-C(99)-C(104)-N(105)	1.6(2)	C(303)-O(302)-C(301)-O(301)	11.4(12)
O(73)-C(72)-N(105)-C(104)	-163.41(14)	C(303)-O(302)-C(301)-C(302)	-169.1(8)
C(71)-C(72)-N(105)-C(104)	17.8(2)	C(301)-O(302)-C(303)-C(304)	-173.8(8)

Symmetry transformations used to generate equivalent atoms:

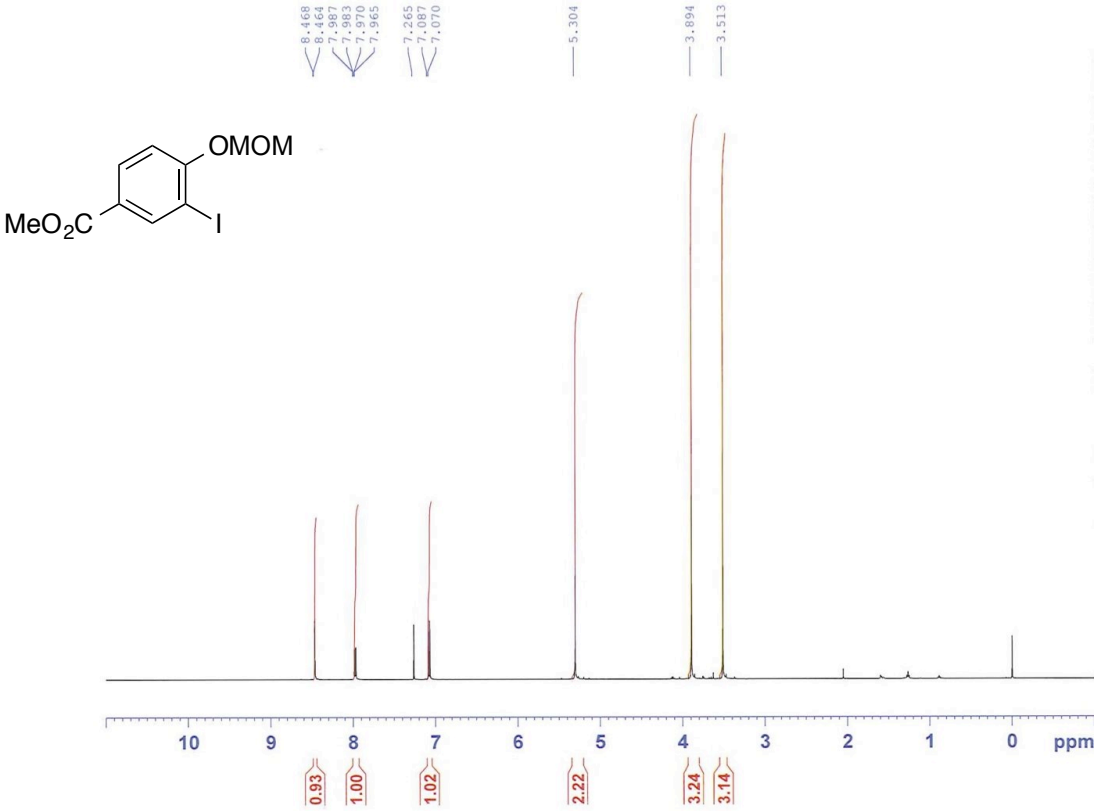
NMR spectra

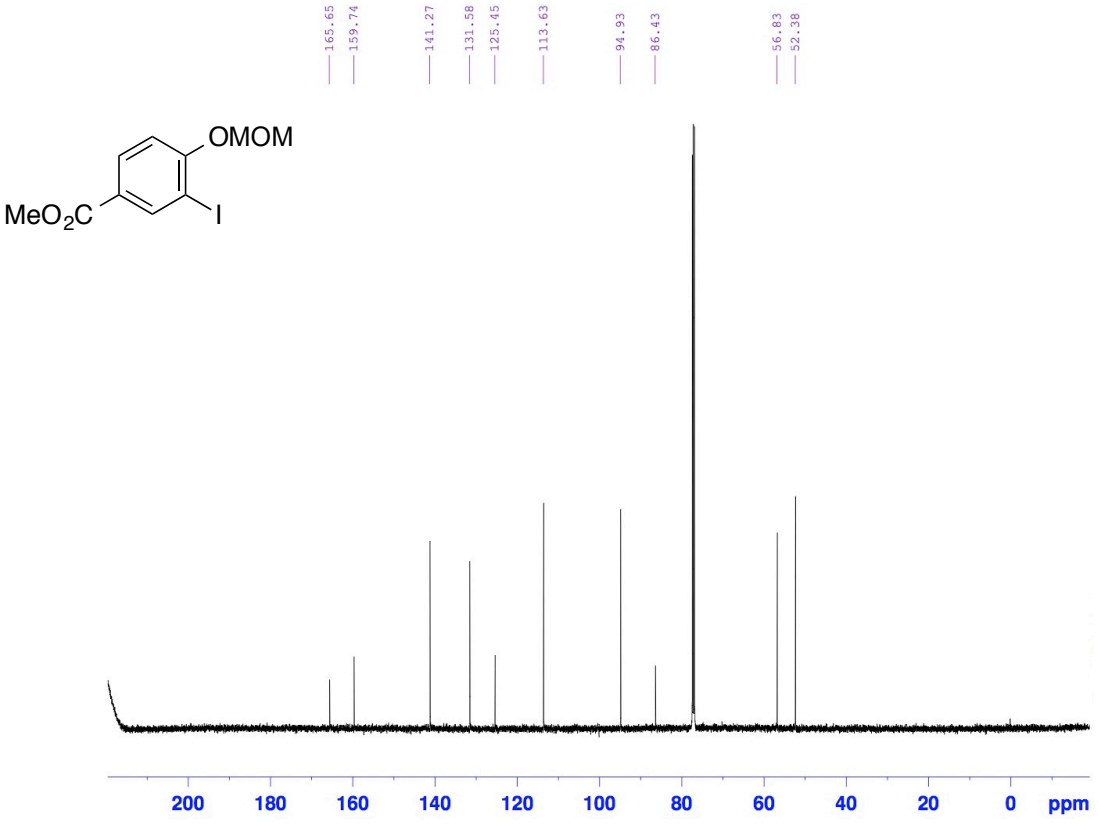
^{1}H and ^{13}C NMR spectra of **3c** (1 M D_2O in acetone-d_6)



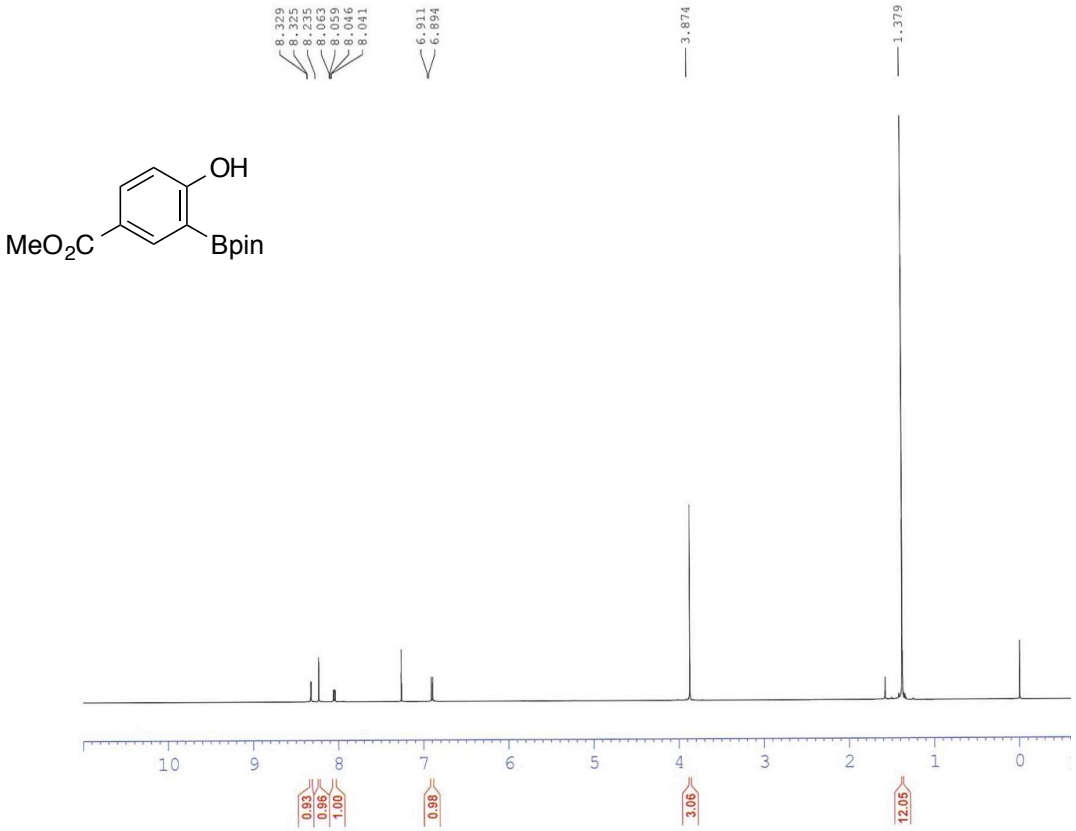


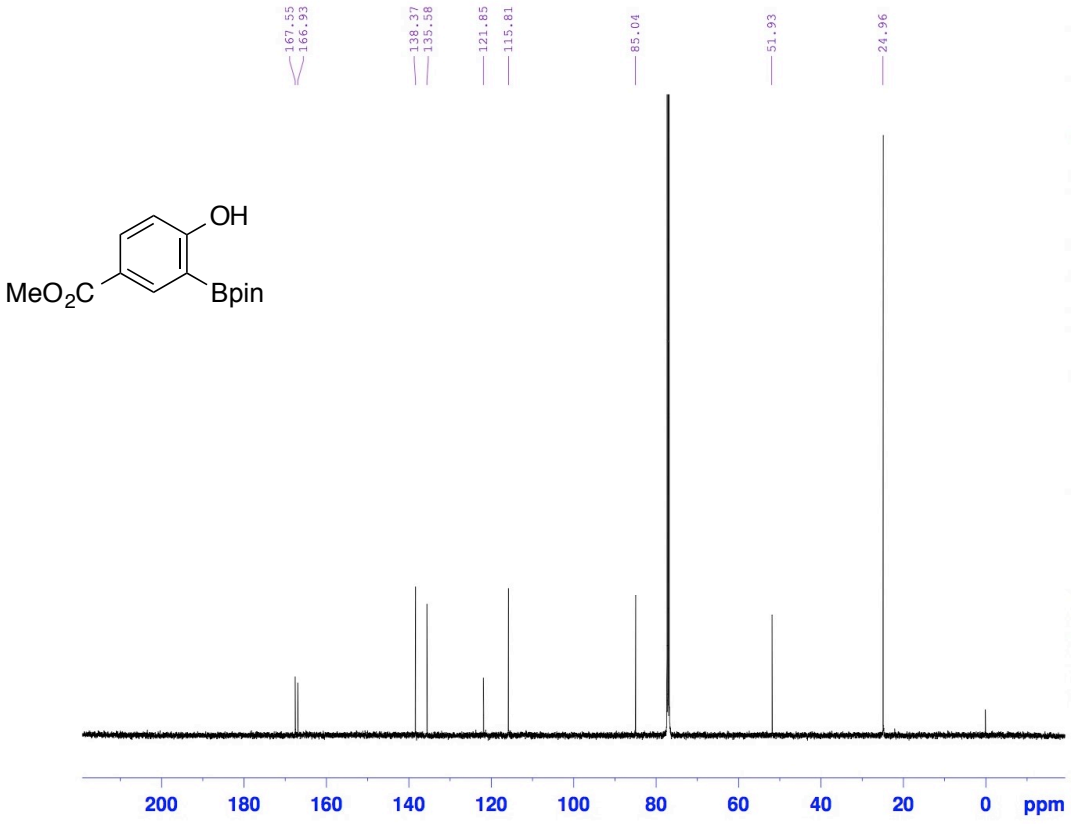
^{1}H and ^{13}C NMR spectra of methyl 3-iodo-4-(methoxymethoxy)benzoate ($CDCl_3$)

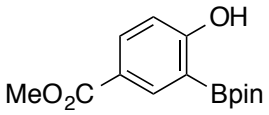


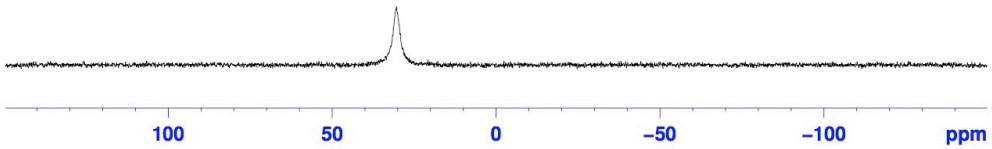


^{1}H, ^{13}C and ^{11}B NMR spectra of **3e** ($CDCl_3$)

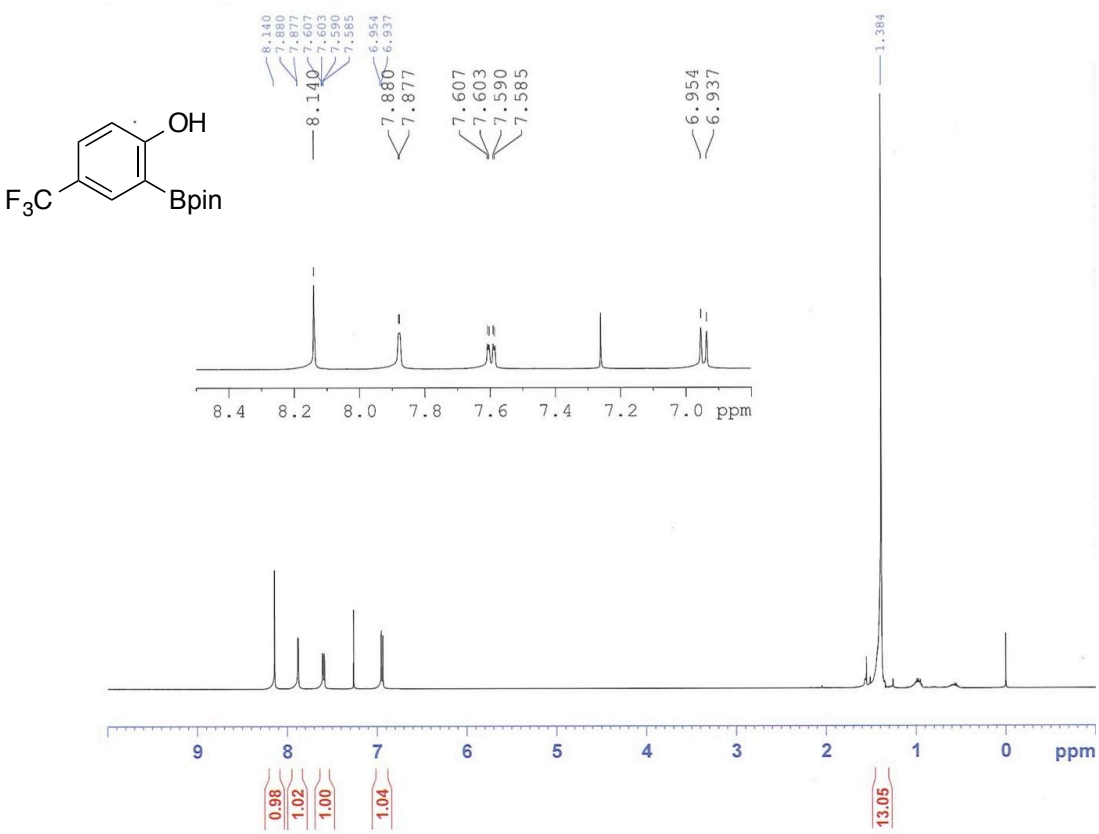


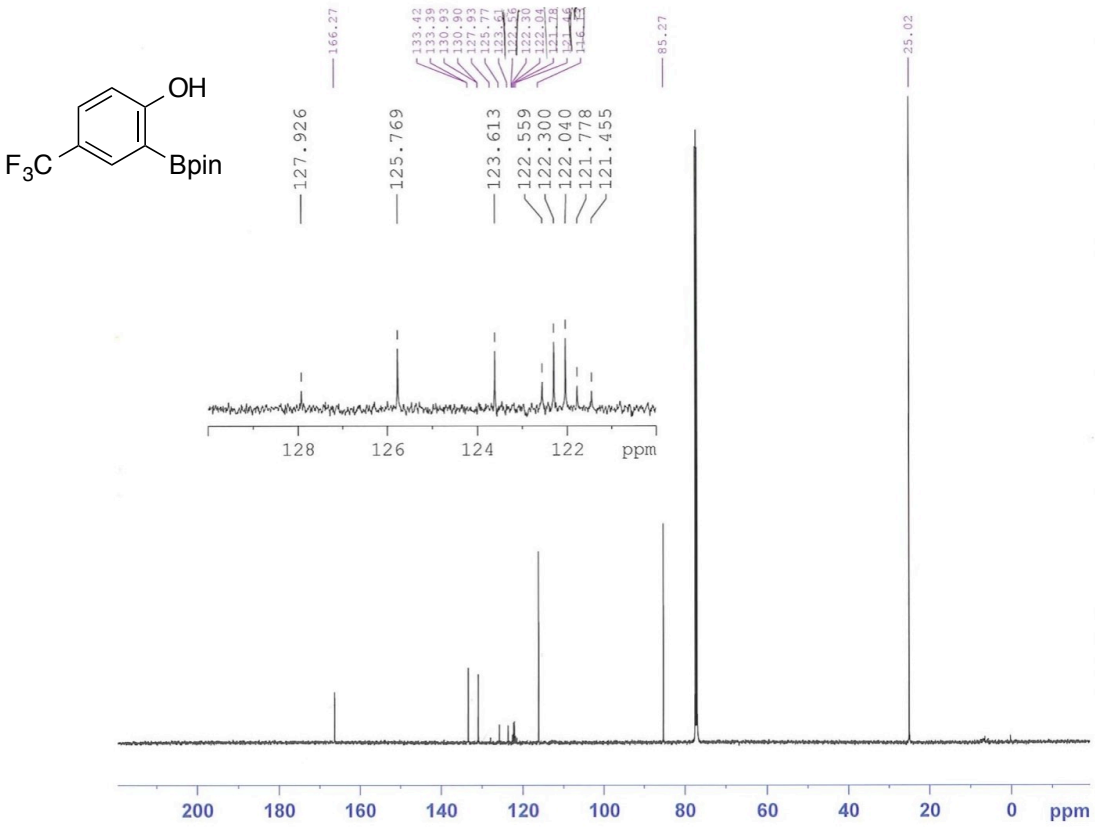


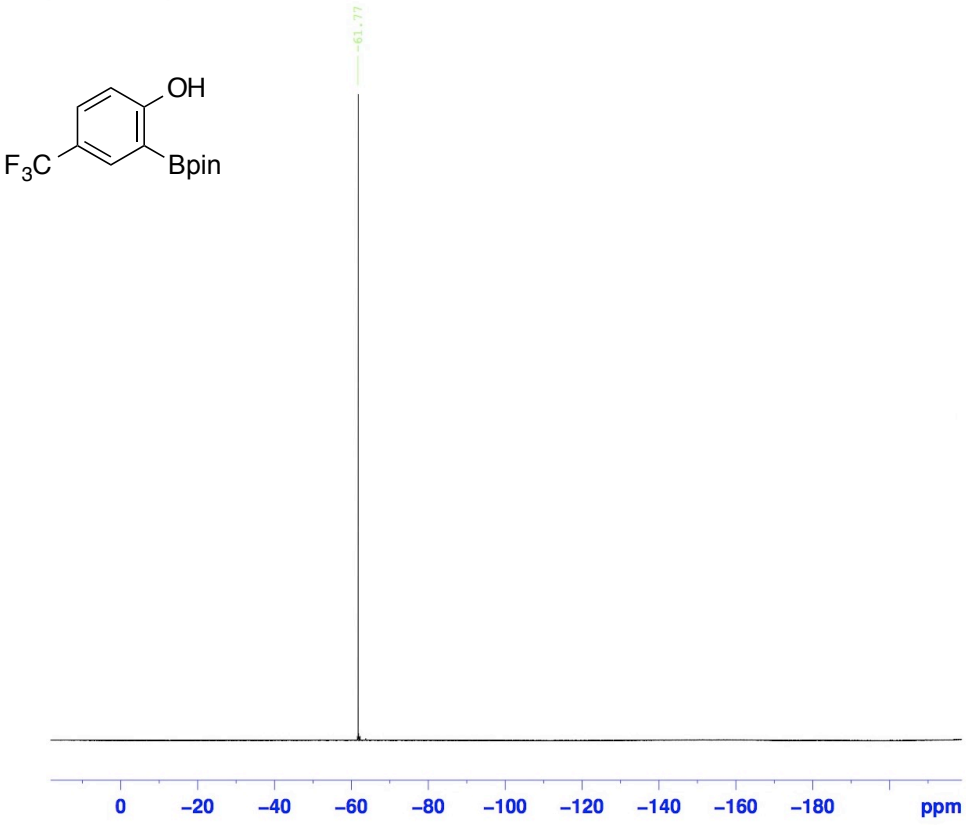


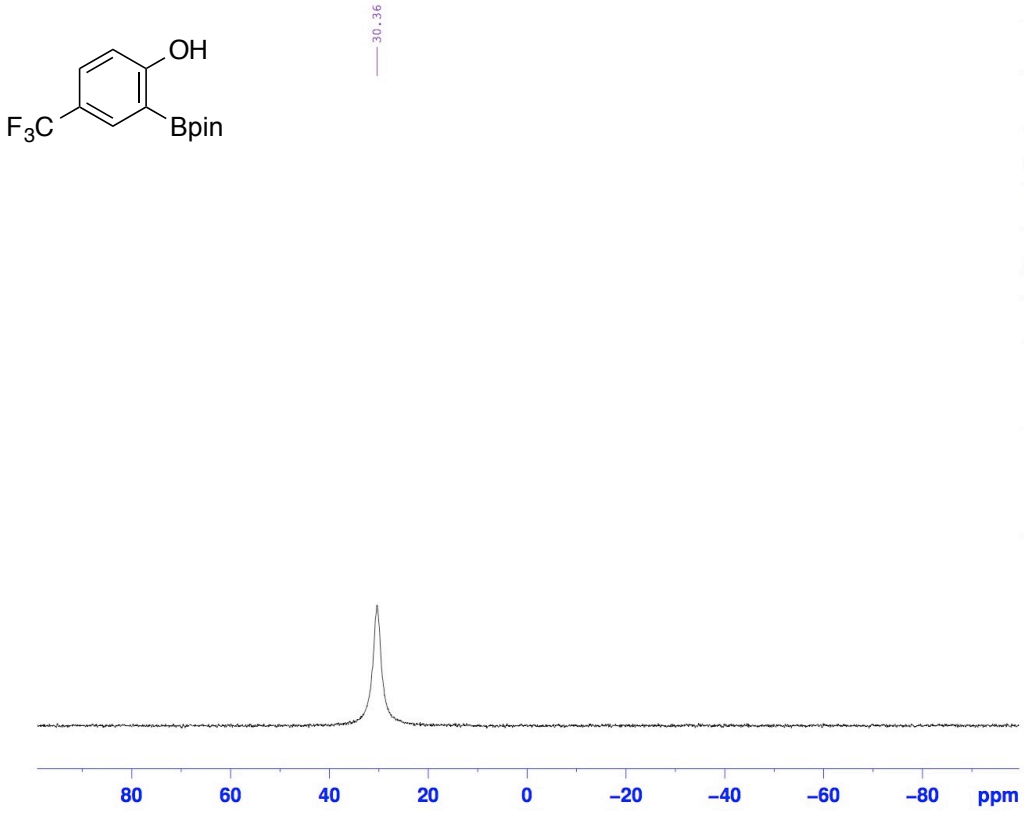


^{1}H, ^{13}C, ^{19}F, and ^{11}B NMR spectra of **3f** ($CDCl_3$)

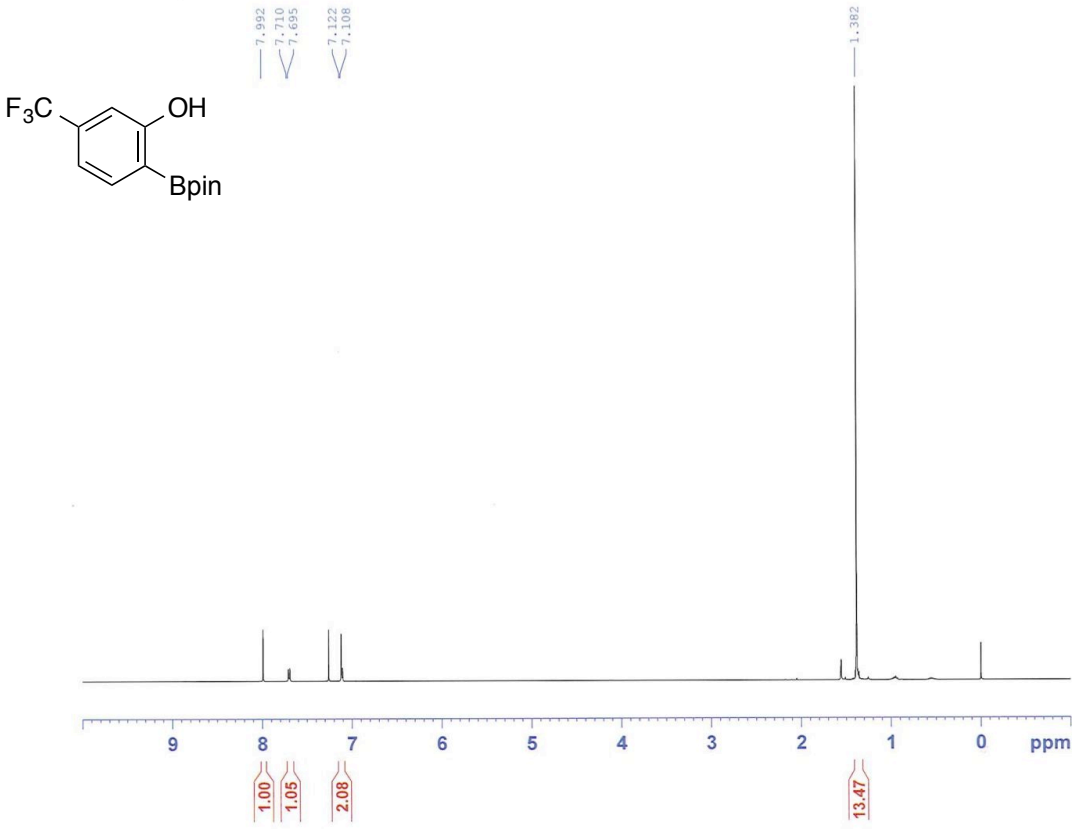


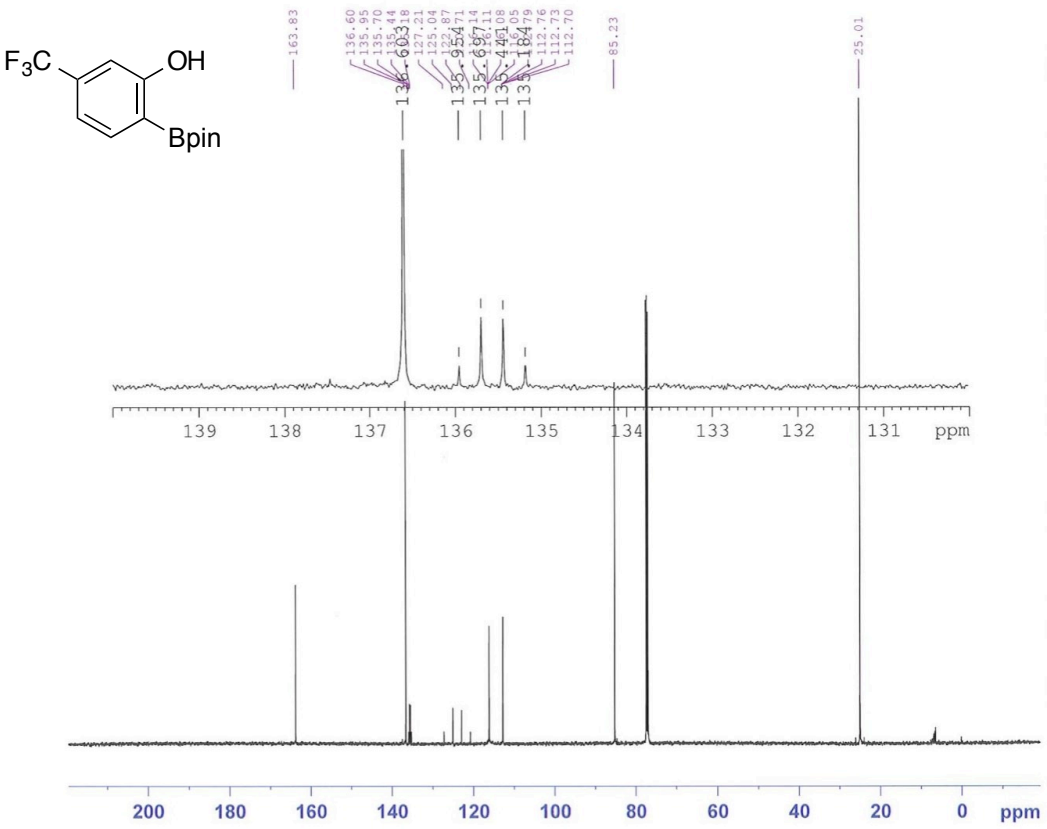

OH
F3C
Bpin
166.27
133.42
133.39
130.93
130.90
127.93
125.77
123.61
122.56
122.30
122.04
121.78
121.46
116.18
85.27
25.02
127.926
125.769
123.613
122.559
122.300
122.040
121.778
121.455
128
126
124
122
ppm
200
180
160
140
120
100
80
60
40
20
0
ppm

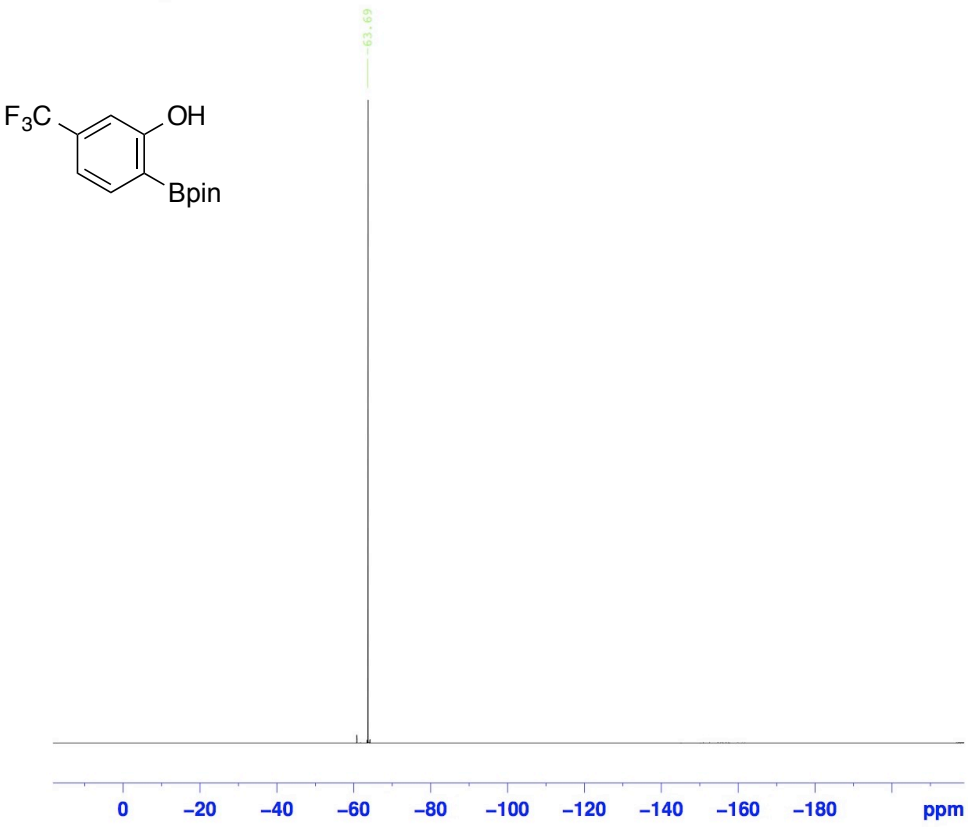

OH
F3C
Bpin
-61.77
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

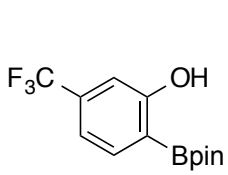


^{1}H, ^{13}C, ^{19}F, and ^{11}B NMR spectra of **3g** ($CDCl_3$)

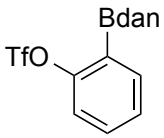


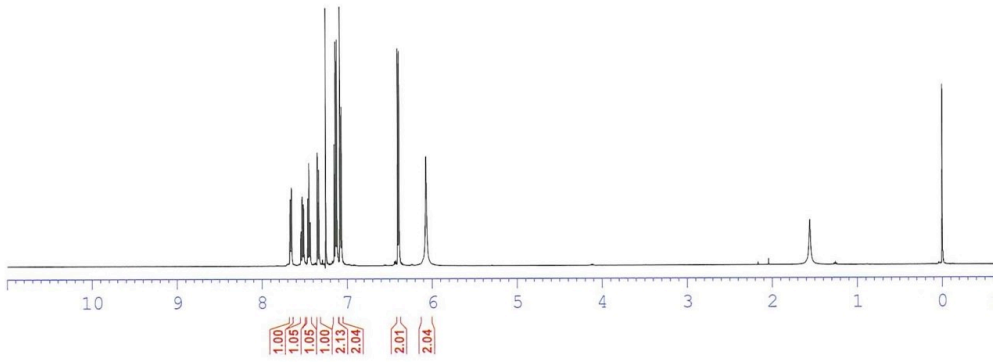

F3C
OH
Bpin
163.83
136.60
135.95
135.70
135.44
136.6033
127.21
125.04
122.87
135.9547
135.6967
135.6114
135.4108
135.1805
135.1779
112.76
112.73
112.70
85.23
25.01
139
138
137
136
135
134
133
132
131
ppm
200
180
160
140
120
100
80
60
40
20
0
ppm

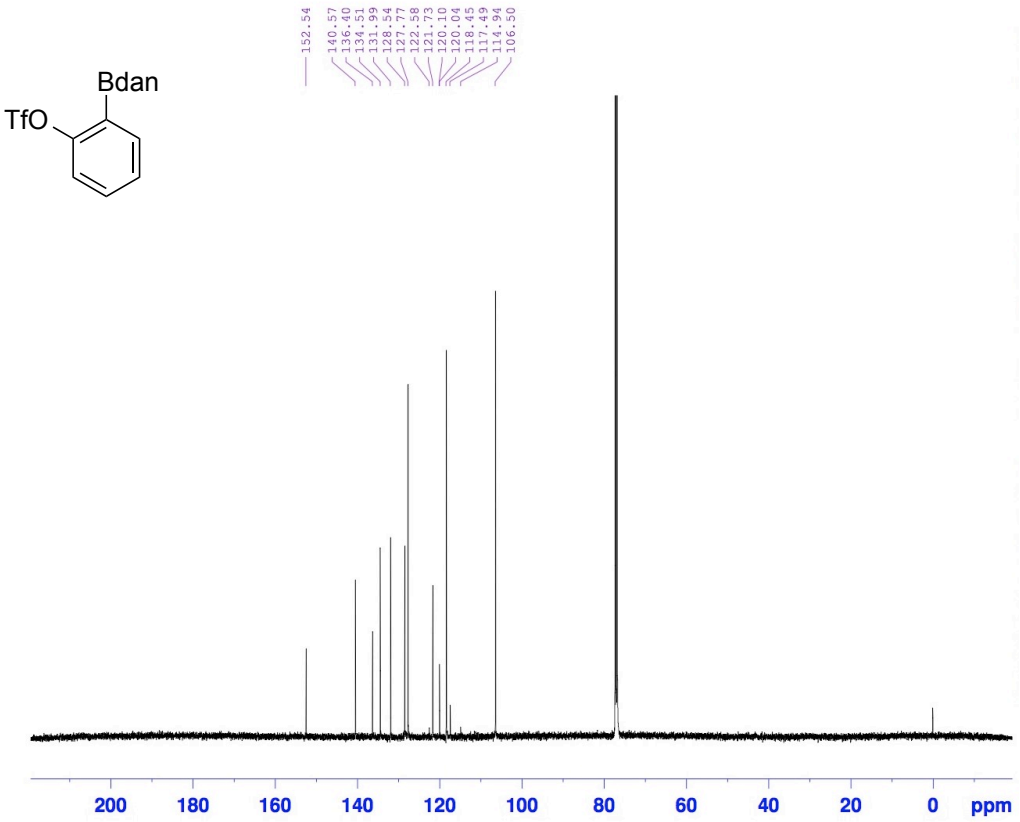

F3C
OH
Bpin
63.69
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

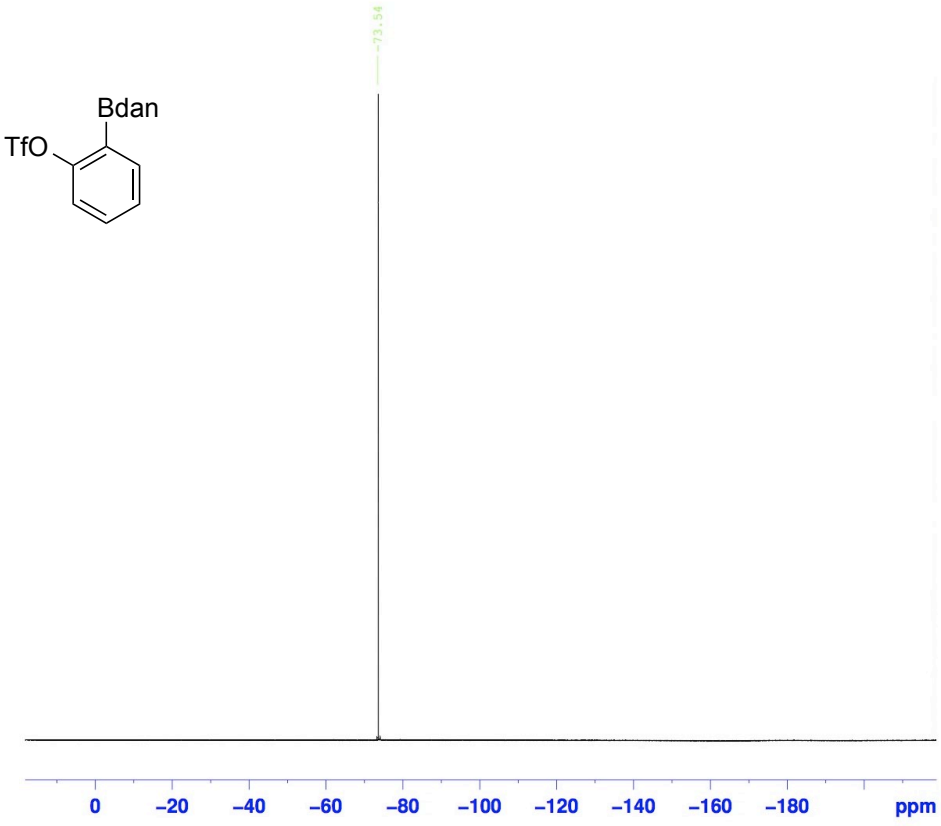


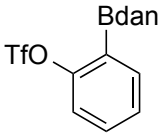
^{1}H, ^{13}C, ^{19}F, and ^{11}B NMR spectra of **4a** ($CDCl_3$)



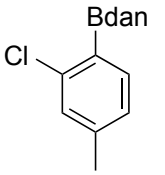


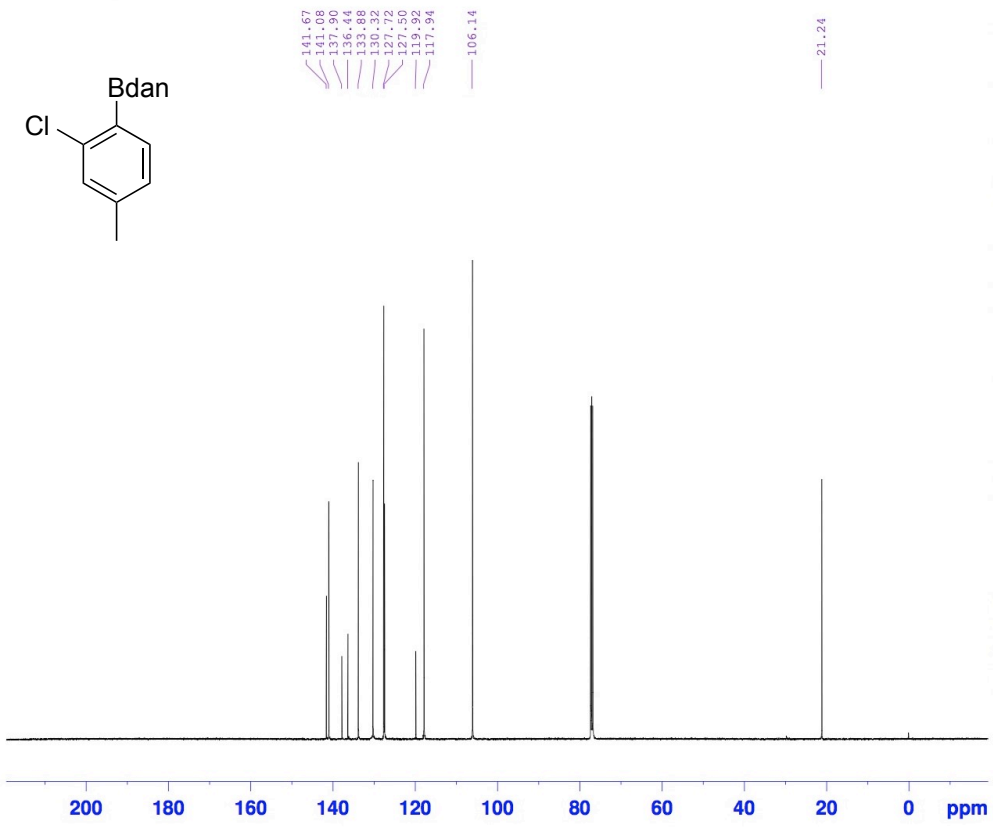

Bdan
TfO
152.54
140.57
136.40
134.51
131.99
128.54
127.77
122.58
121.73
120.10
120.04
118.45
117.49
114.94
106.50
200
180
160
140
120
100
80
60
40
20
0
ppm

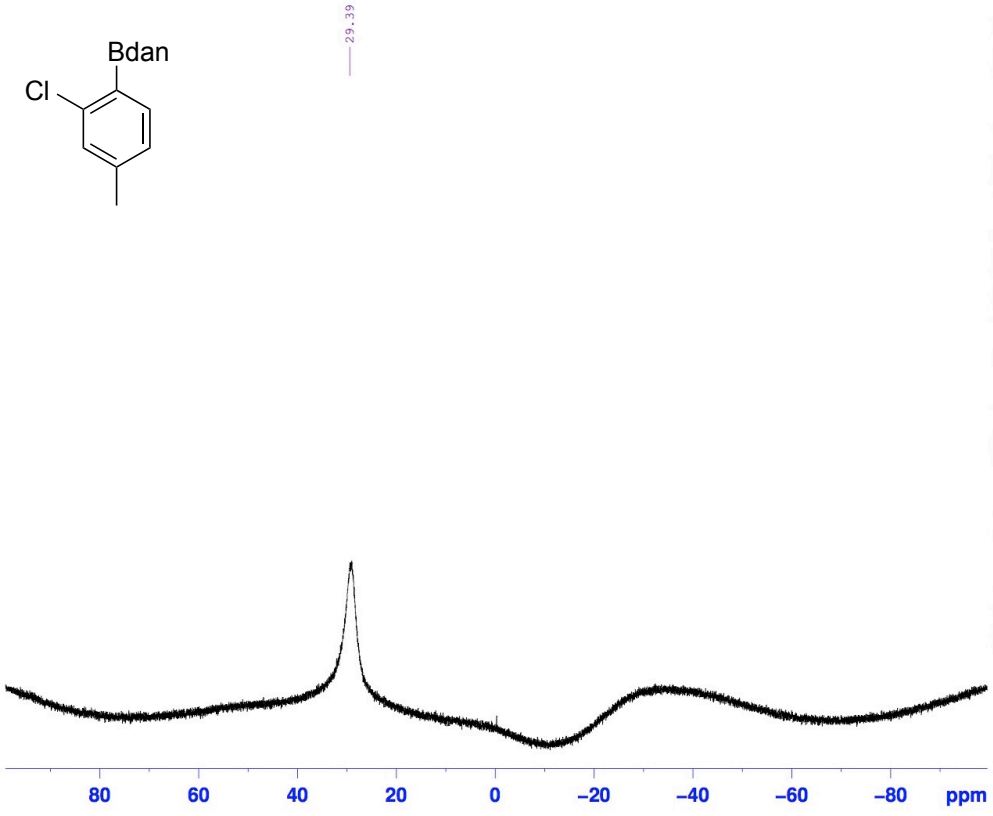

Bdan
TfO
-73.54
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm



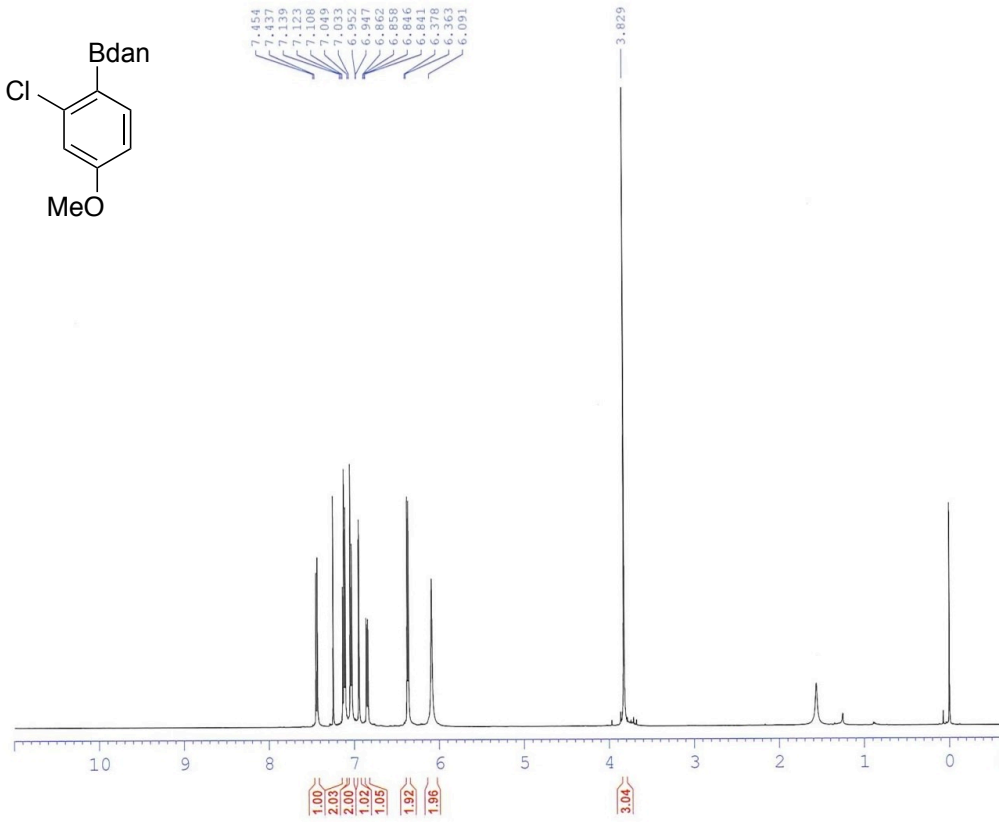
^{1}H, ^{13}C, and ^{11}B NMR spectra of **4b** ($CDCl_3$)

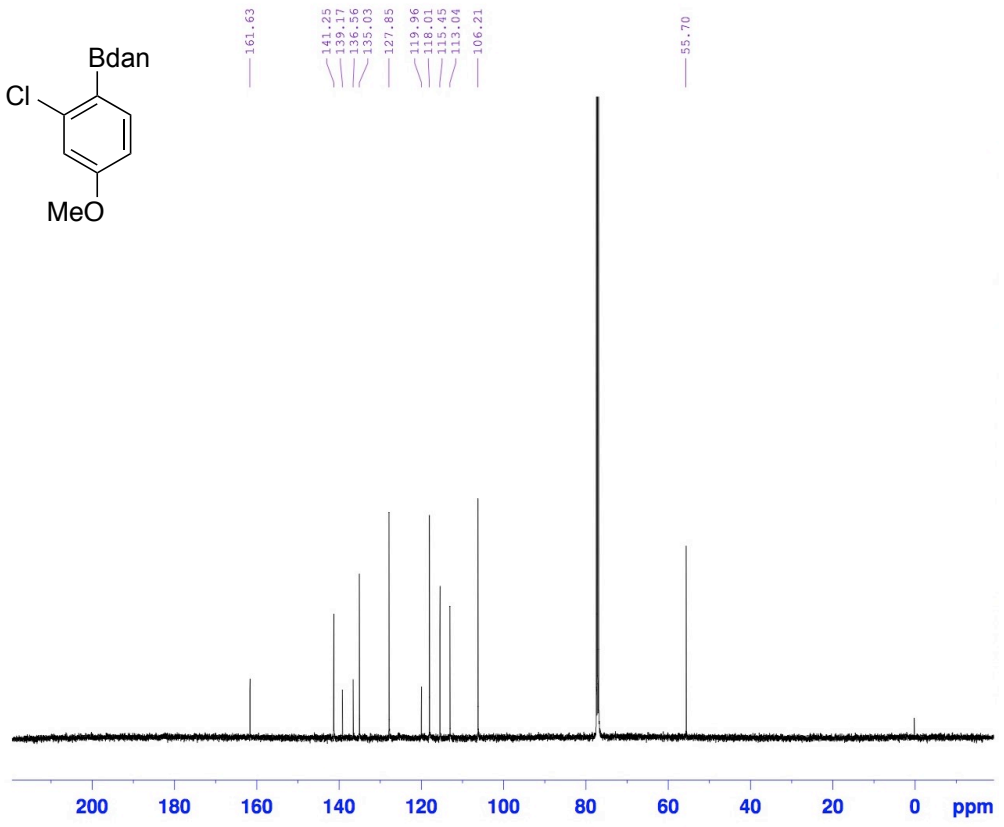


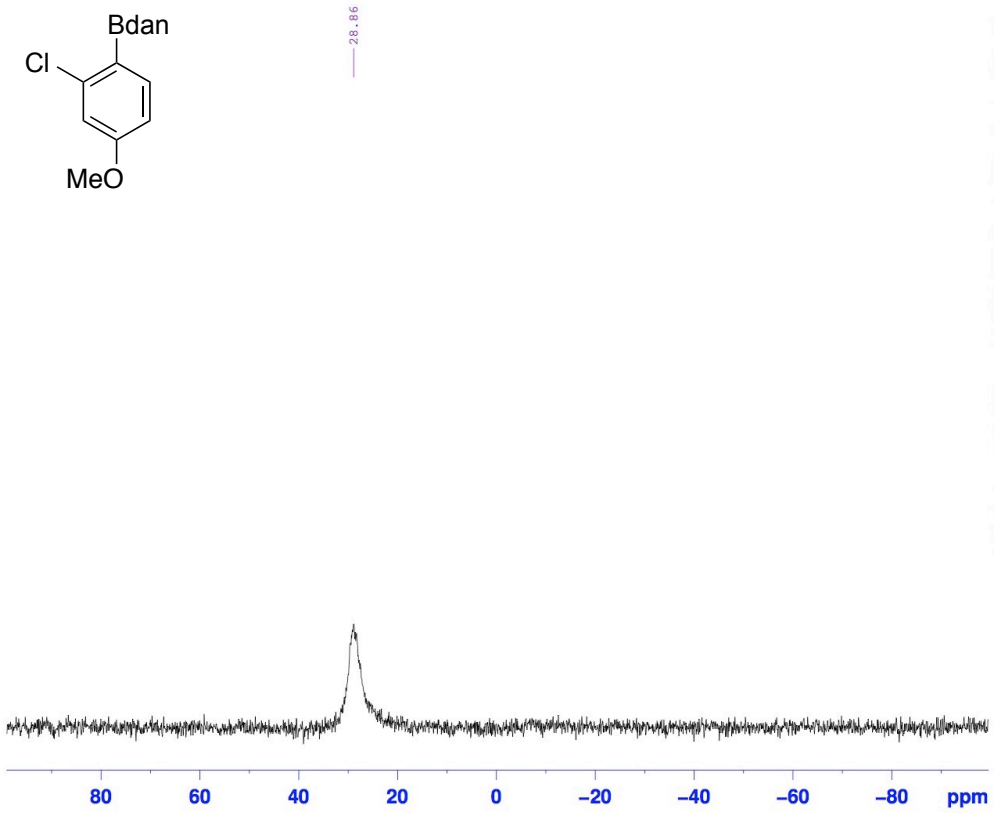

Bdan
Cl
141.67
141.08
137.90
136.44
133.88
130.32
127.72
127.50
119.92
117.94
106.14
21.24
200
180
160
140
120
100
80
60
40
20
0
ppm


Bdan
Cl
29.39
80
60
40
20
0
−20
−40
−60
−80
ppm

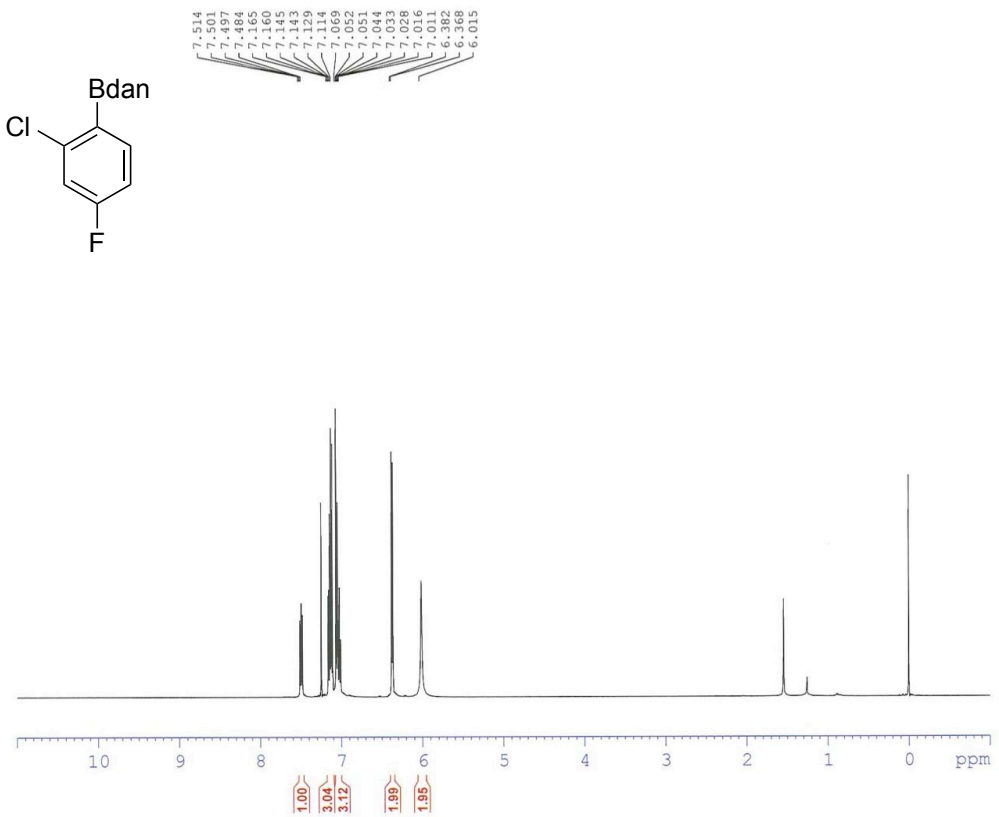
^{1}H, ^{13}C, and ^{11}B NMR spectra of **4c** ($CDCl_3$)

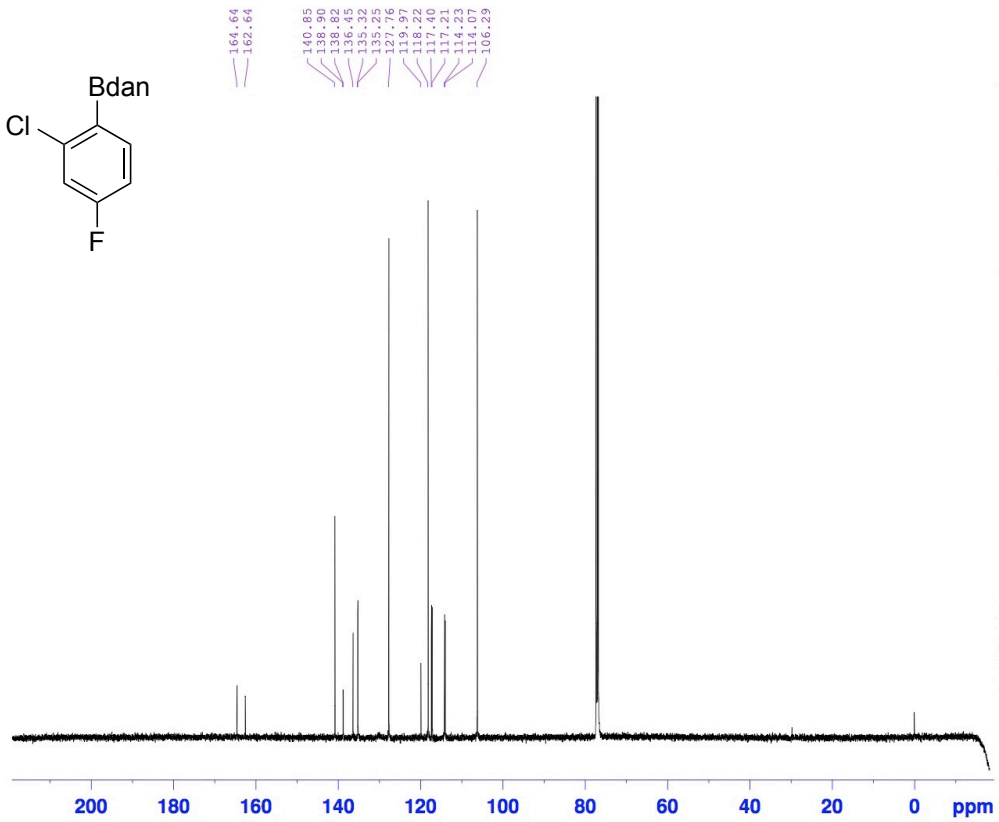


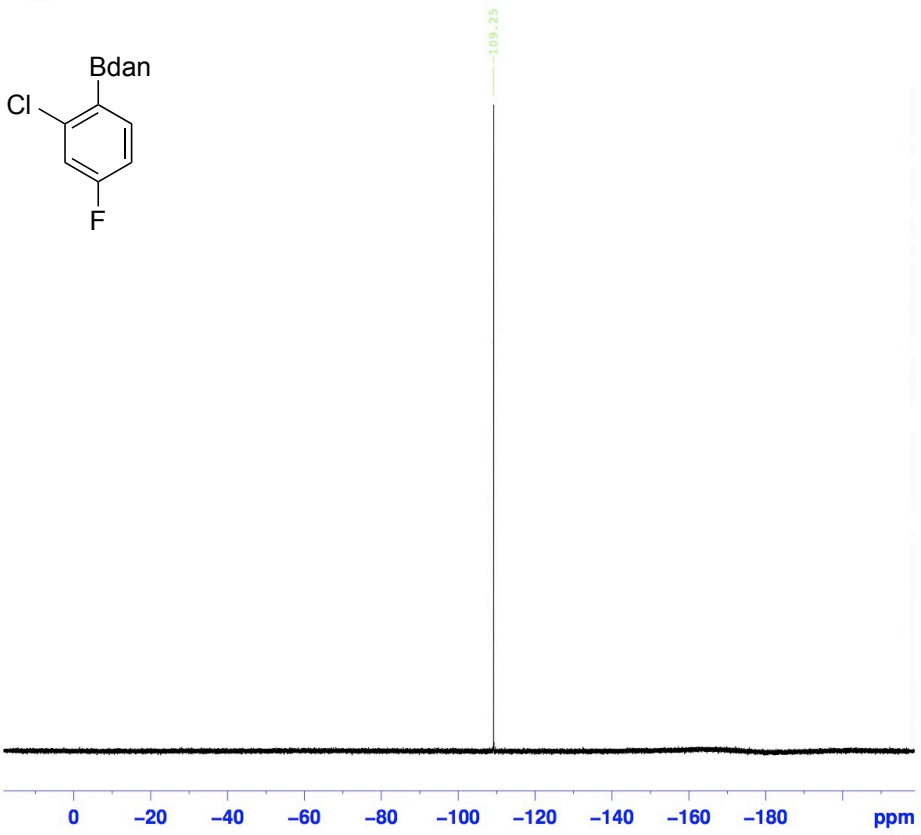


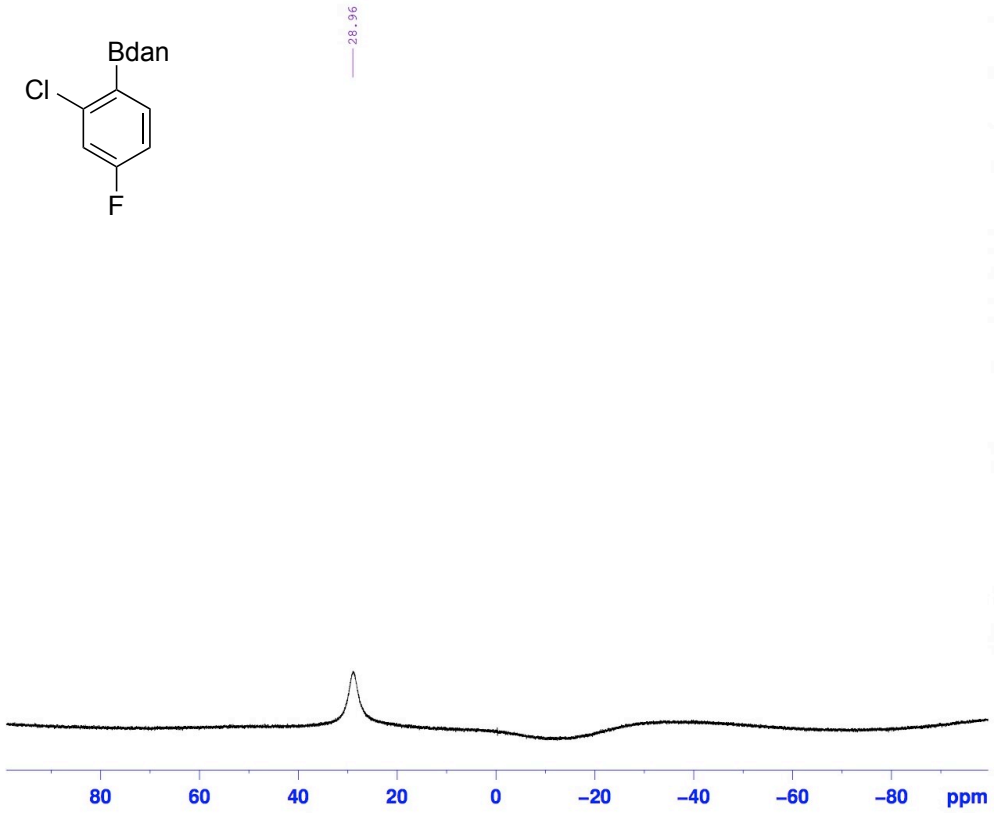


^{1}H, ^{13}C, ^{19}F, and ^{11}B NMR spectra of **4d** ($CDCl_3$)

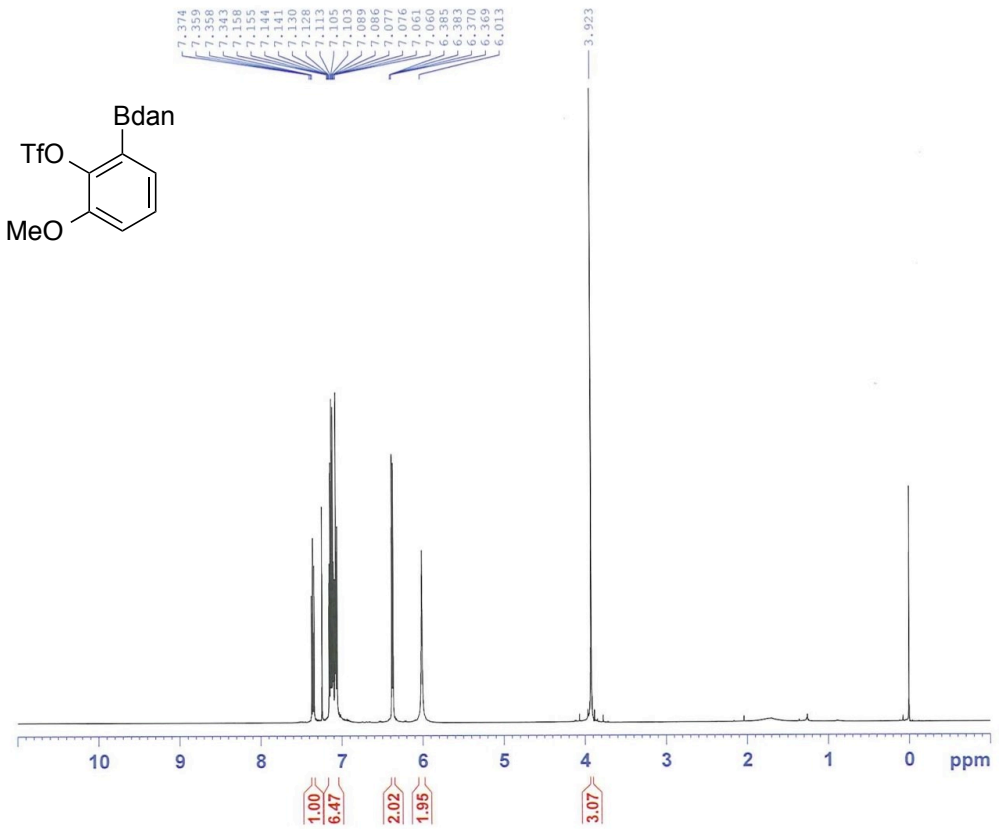


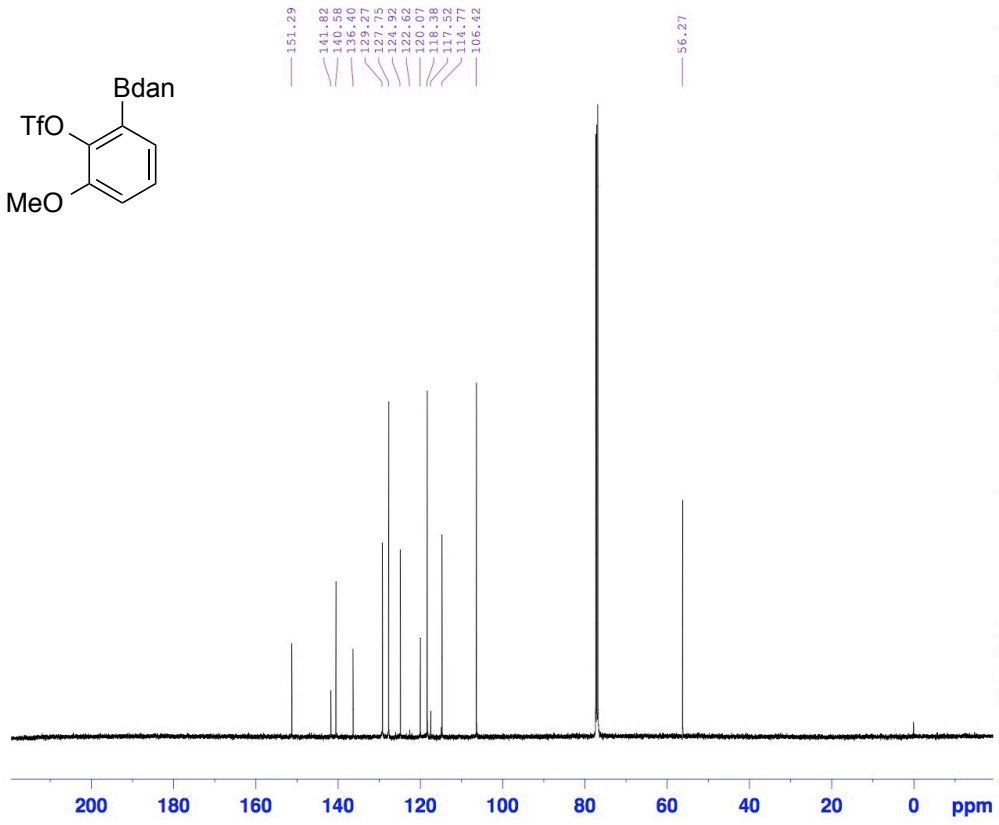

Bdan
Cl
F
164.64
162.64
140.85
138.90
138.82
136.45
136.32
135.25
127.76
119.97
118.22
117.40
117.21
114.23
114.07
106.29
200
180
160
140
120
100
80
60
40
20
0
ppm


Bdan
Cl
F
-109.25
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

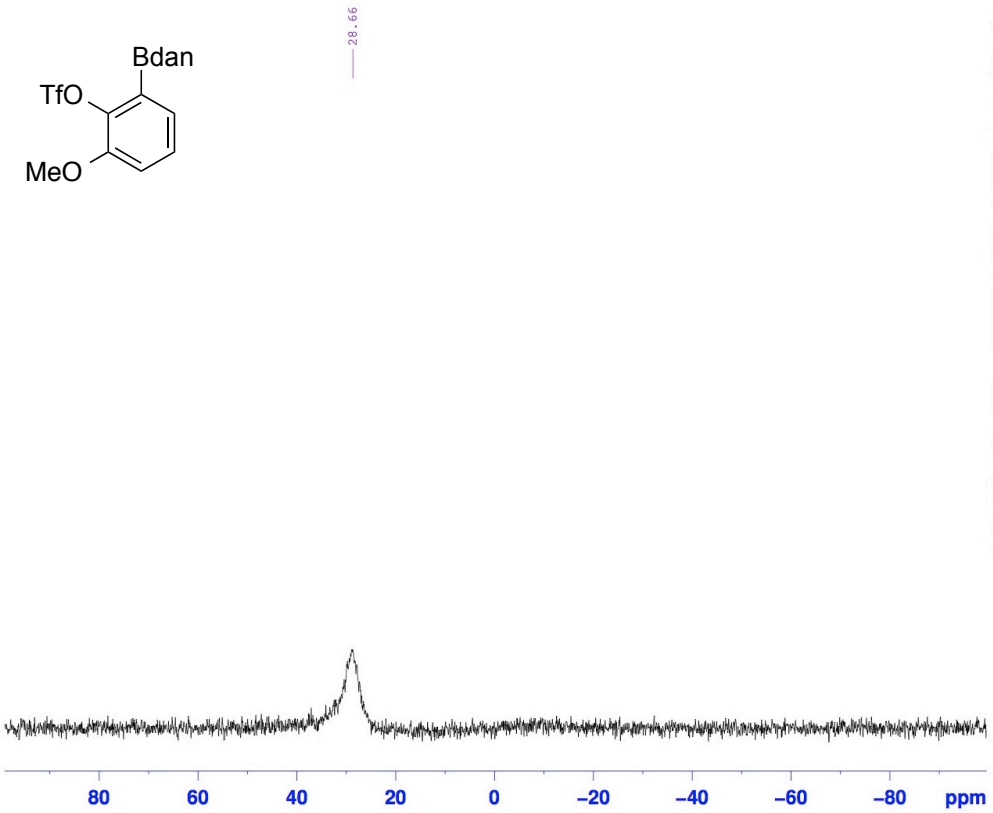


^{1}H, ^{13}C, ^{19}F, and ^{11}B NMR spectra of **4e** ($CDCl_3$)

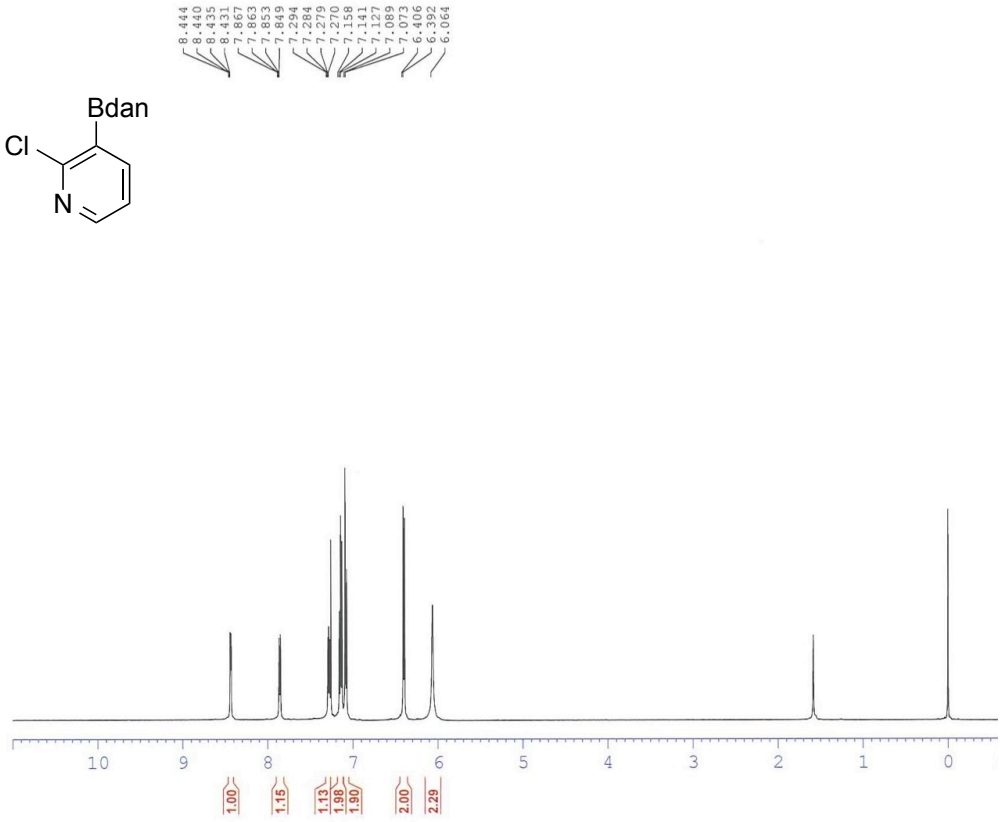


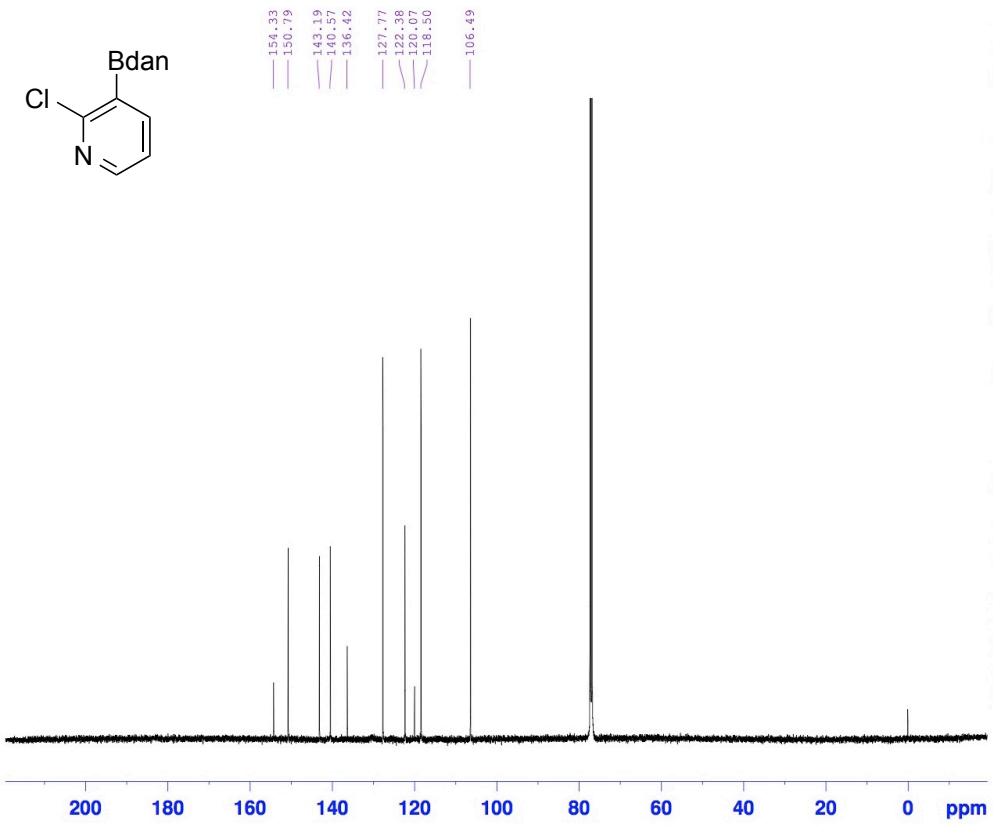

151.29
141.82
140.58
136.40
129.27
127.75
124.92
122.62
120.07
118.38
117.52
114.77
106.42
56.27
Bdan
TfO
MeO
200
180
160
140
120
100
80
60
40
20
0
ppm

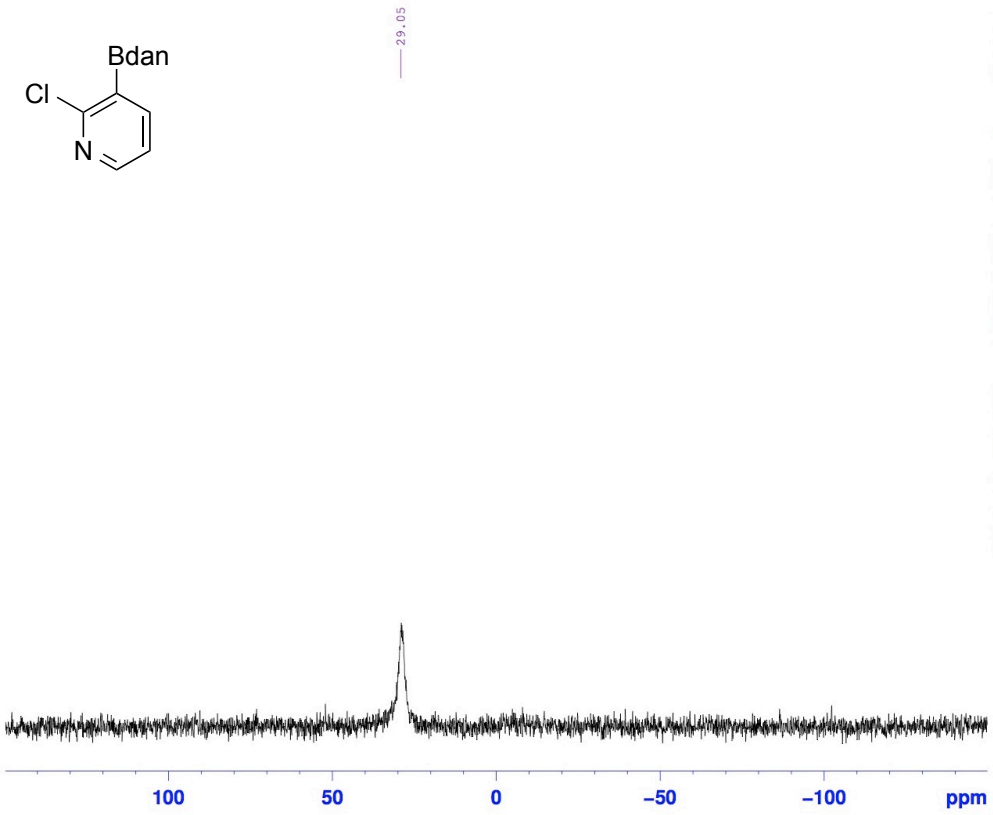

-73.97
Bdan
TfO
MeO
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm



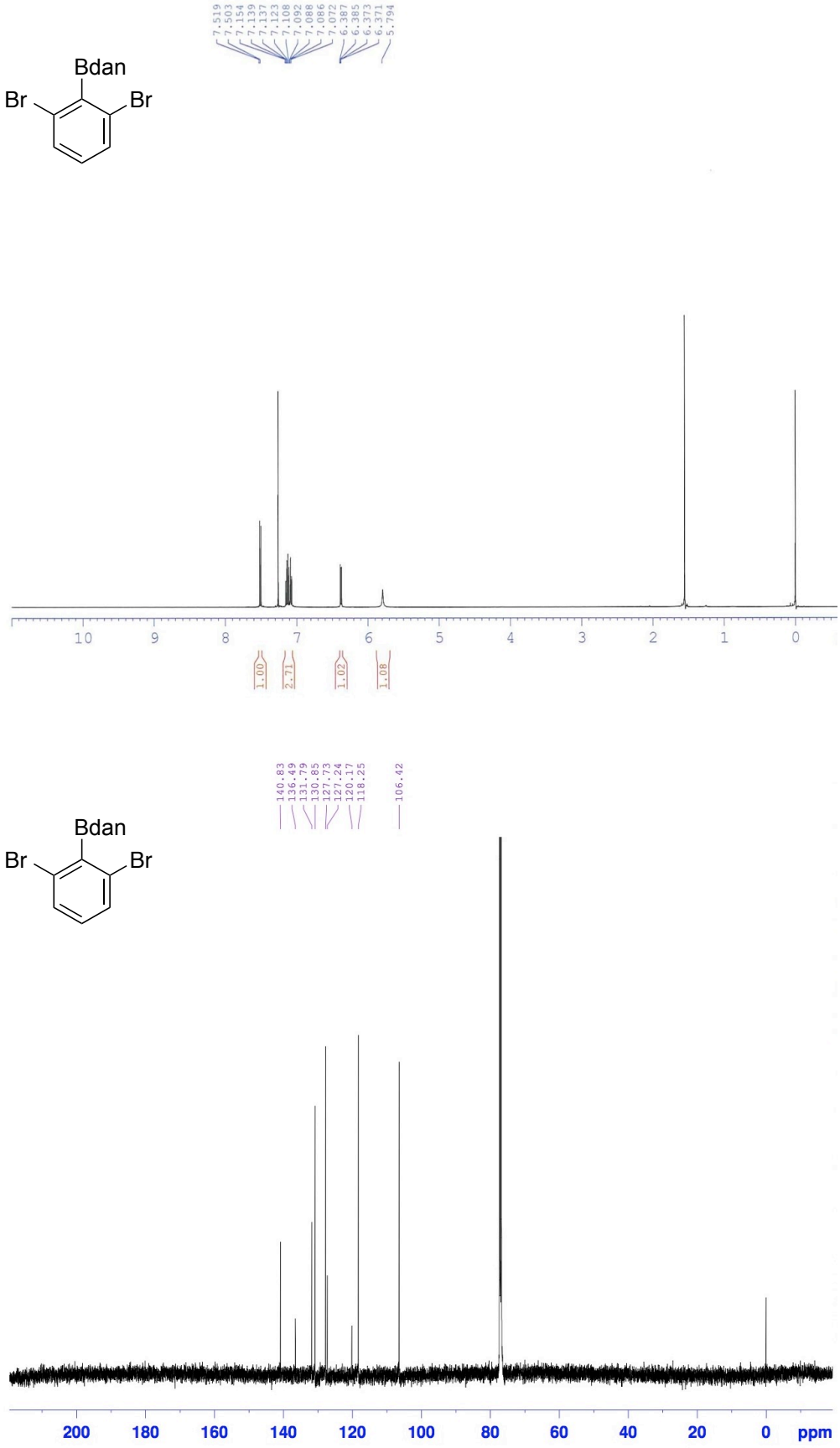
^{1}H, ^{13}C, and ^{11}B NMR spectra of **4f** ($CDCl_3$)

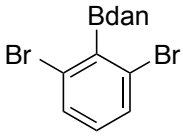



Bdan
Cl
N
154.33
150.79
143.19
140.57
136.42
127.77
122.38
120.07
118.50
106.49
200
180
160
140
120
100
80
60
40
20
0
ppm

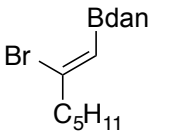

Bdan
Cl
N
29.05
100
50
0
−50
−100
ppm

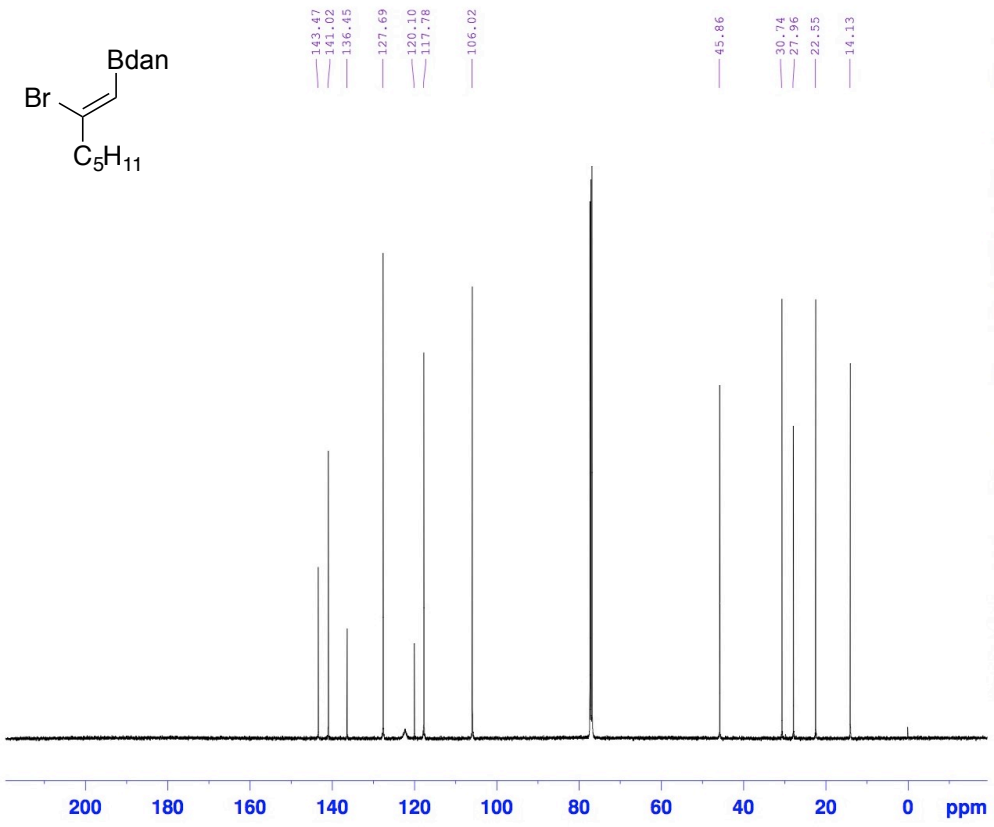
^{1}H, ^{13}C, and ^{11}B NMR spectra of **4g** ($CDCl_3$)

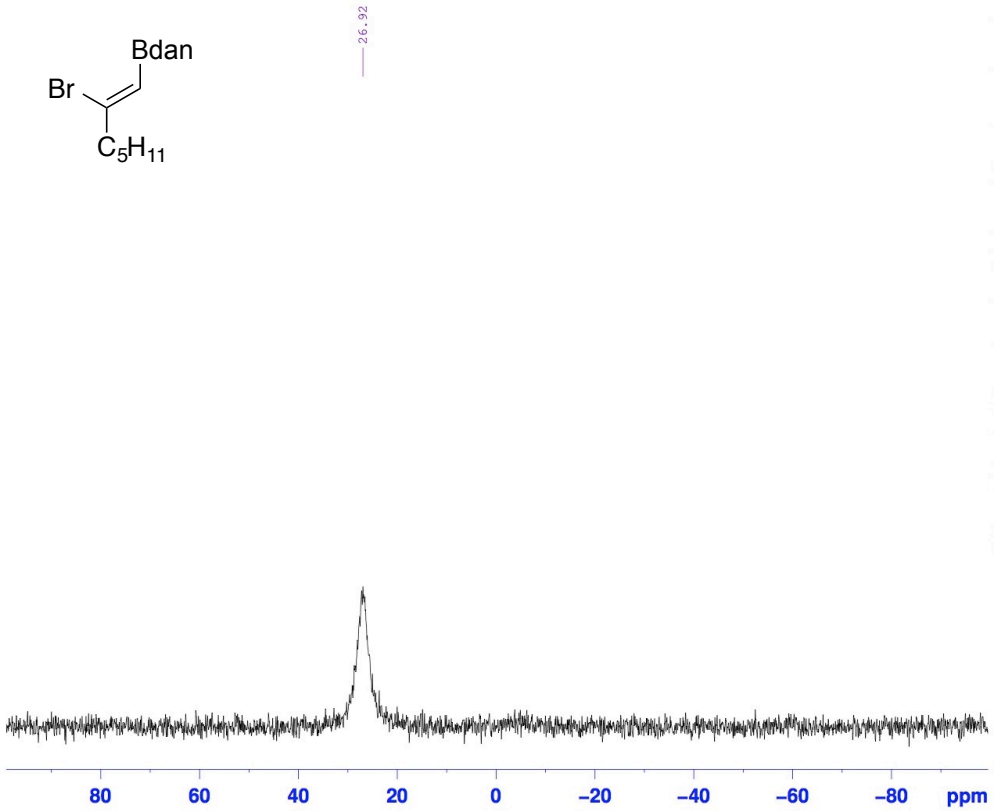




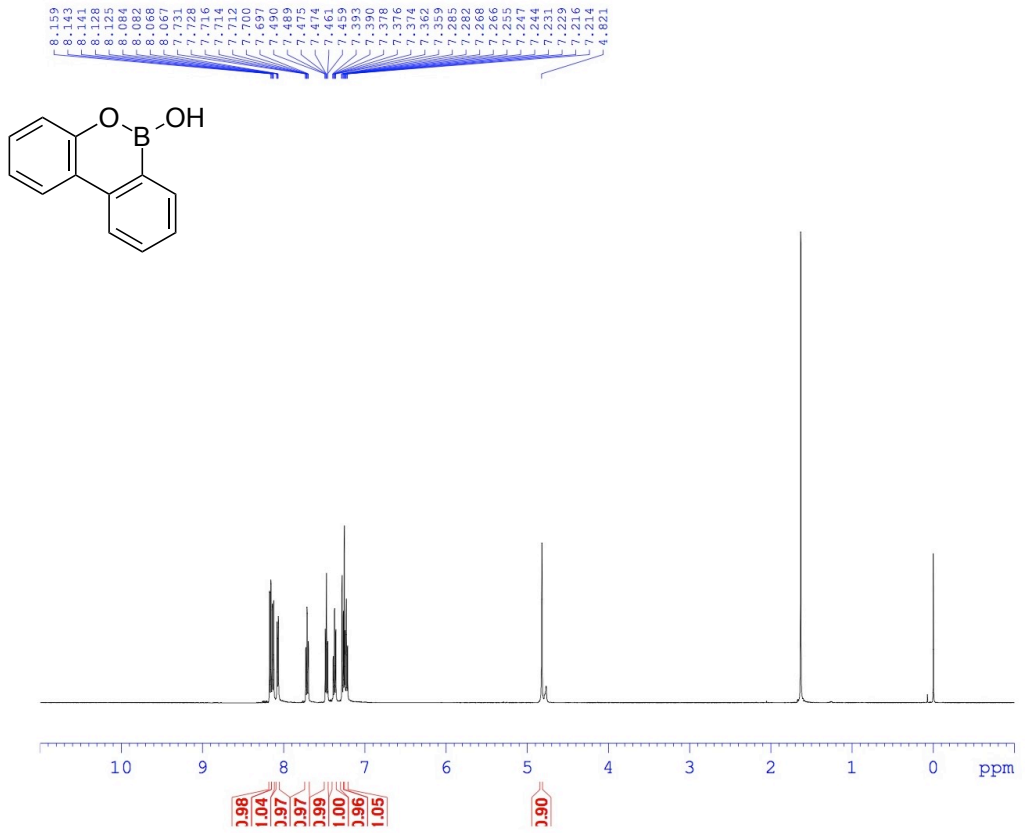
^{1}H, ^{13}C, and ^{11}B NMR spectra of **4h** ($CDCl_3$)

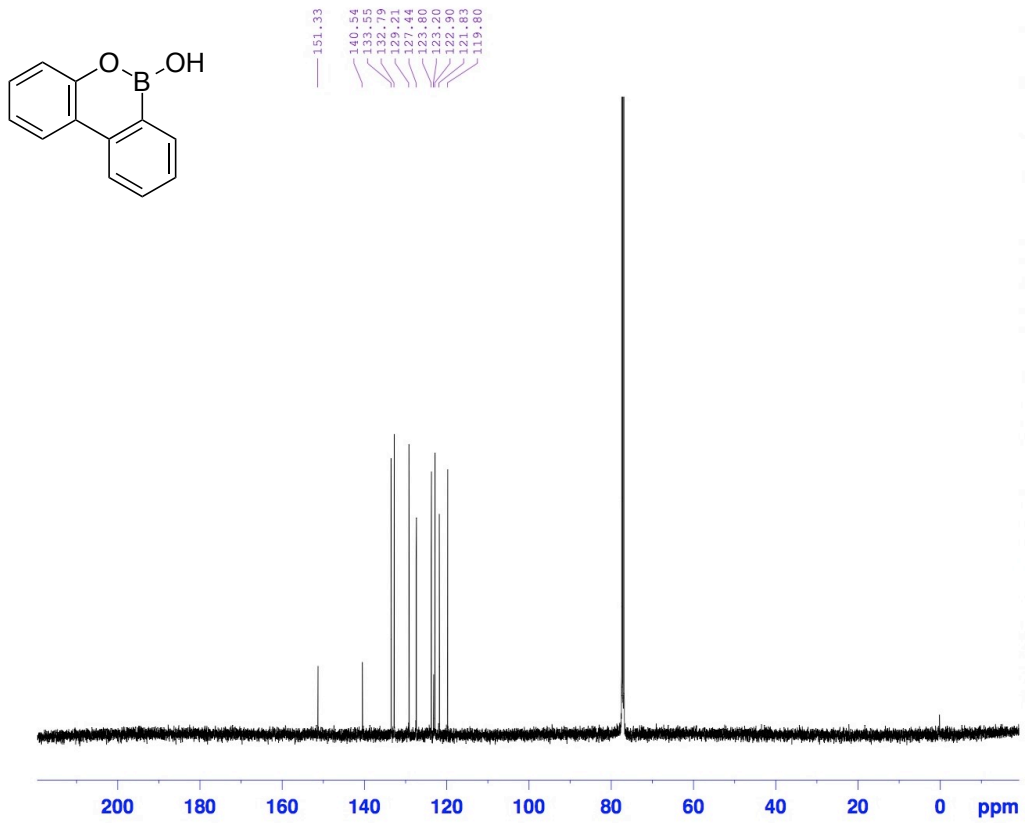



Bdan
Br
C_5H_{11}
143.47
141.02
136.45
127.69
120.10
117.78
106.02
45.86
30.74
27.96
22.55
14.13
200
180
160
140
120
100
80
60
40
20
0
ppm

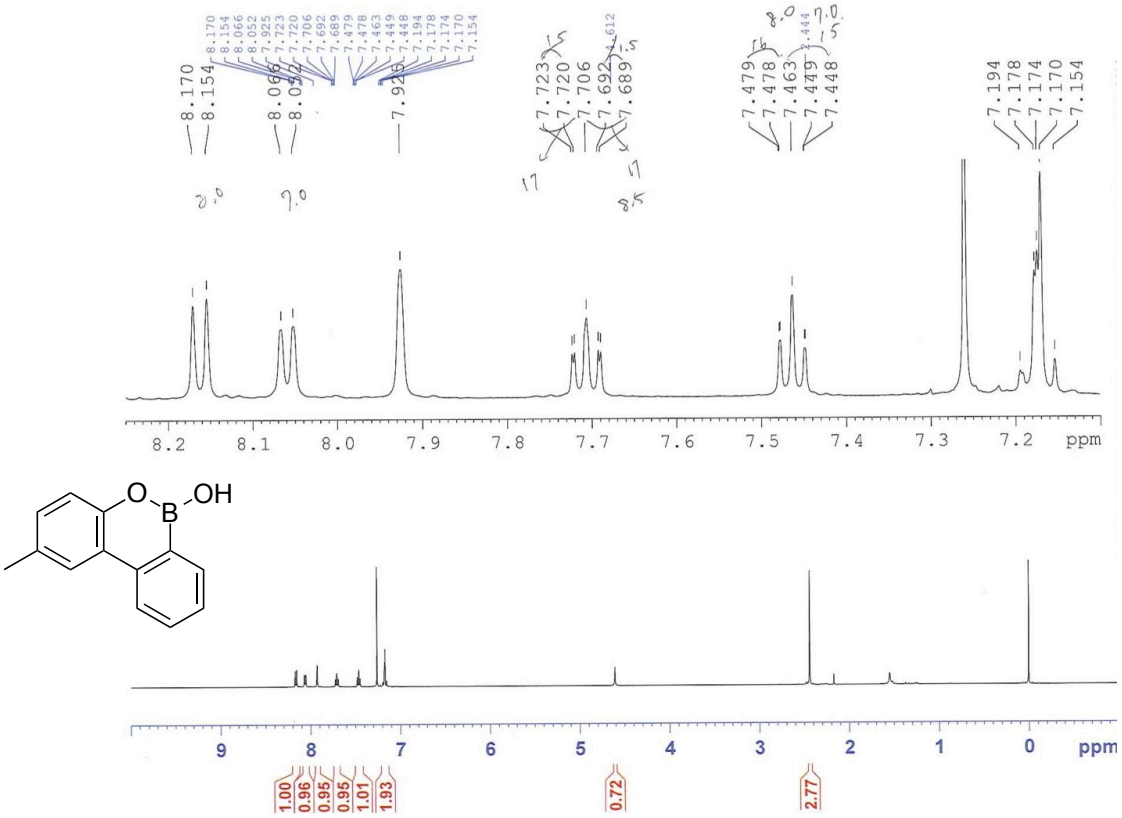

Bdan
Br
C_5H_{11}
26.92
80
60
40
20
0
−20
−40
−60
−80
ppm

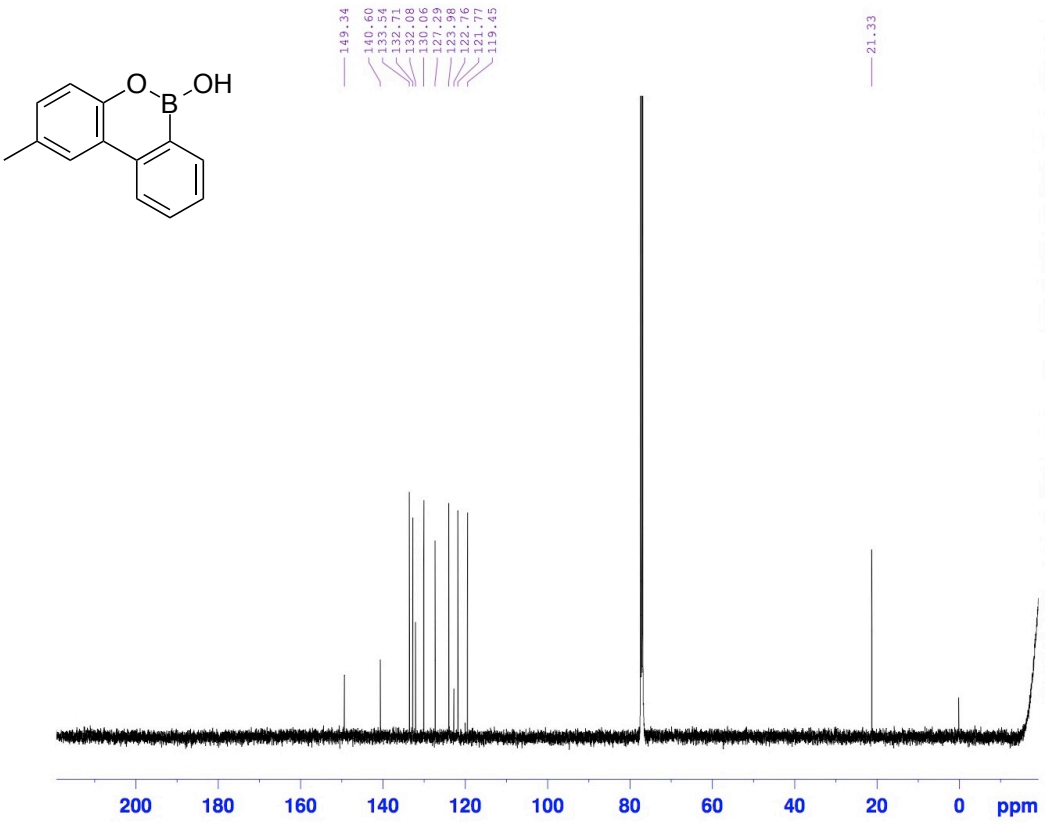
^{1}H and ^{13}C NMR spectra of **2a** ($CDCl_3$)



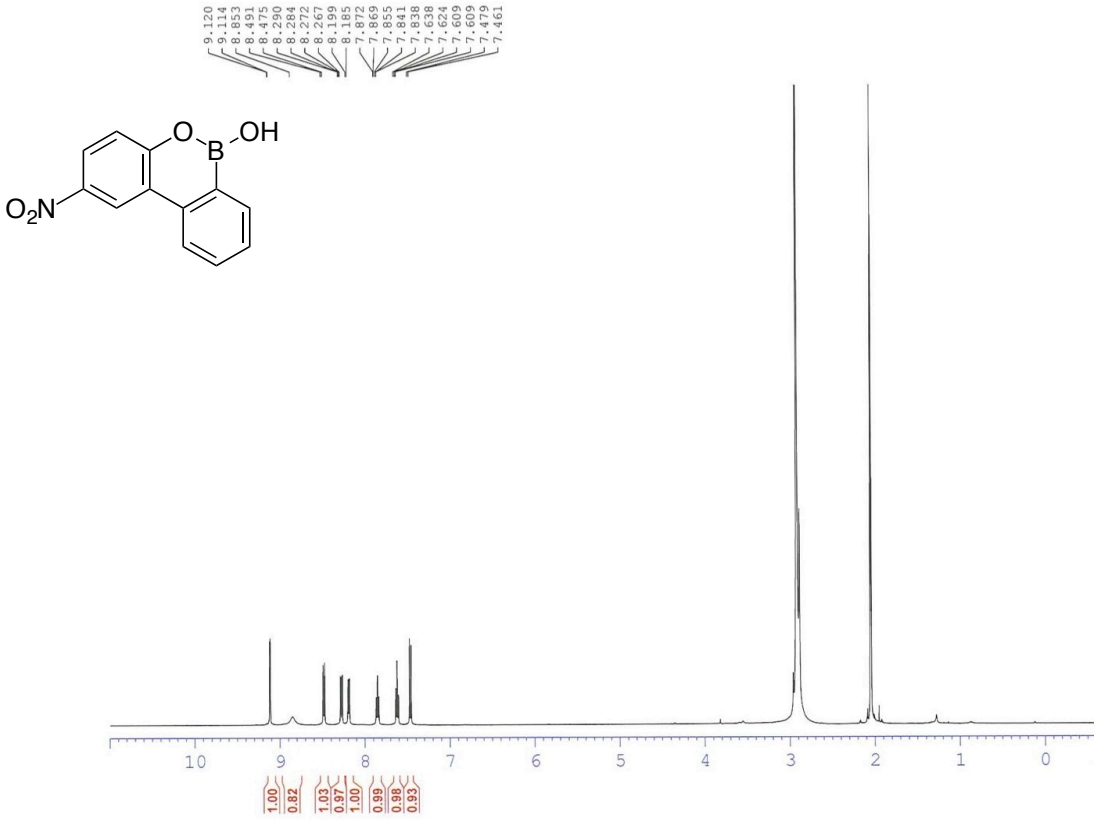


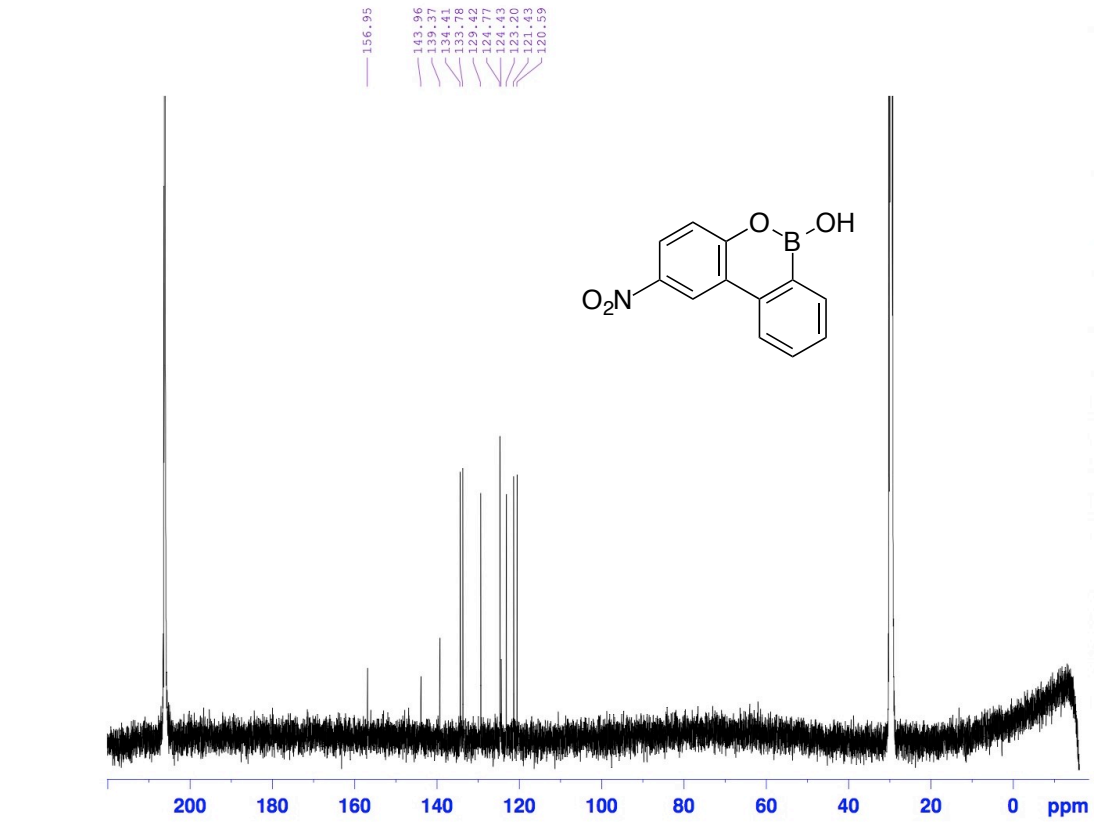
^{1}H and ^{13}C NMR spectra of **2b** ($CDCl_3$)

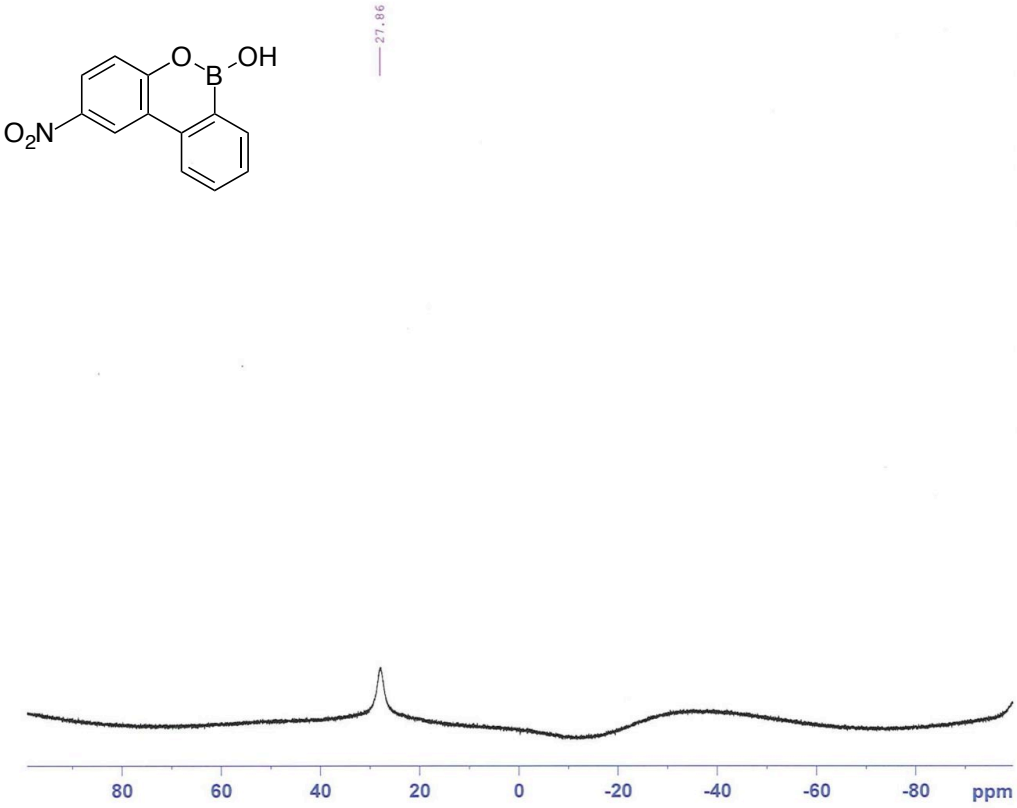




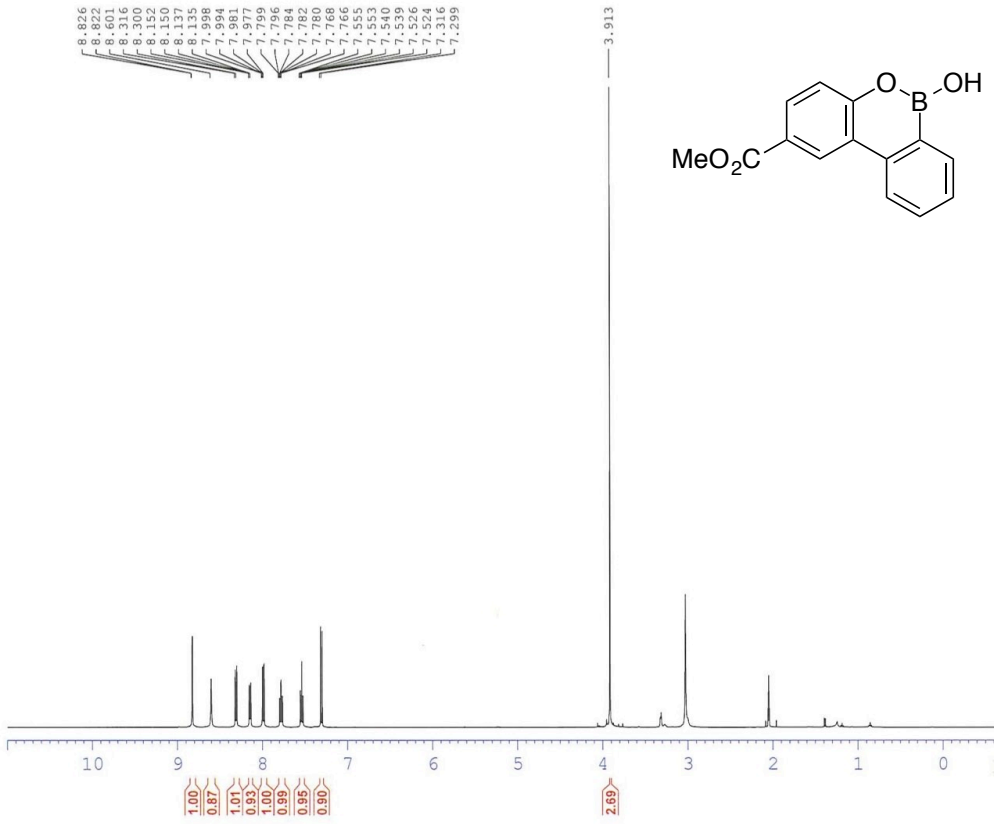
^{1}H, ^{13}C, and ^{11}B NMR spectra of **2c** (acetone-d_6)

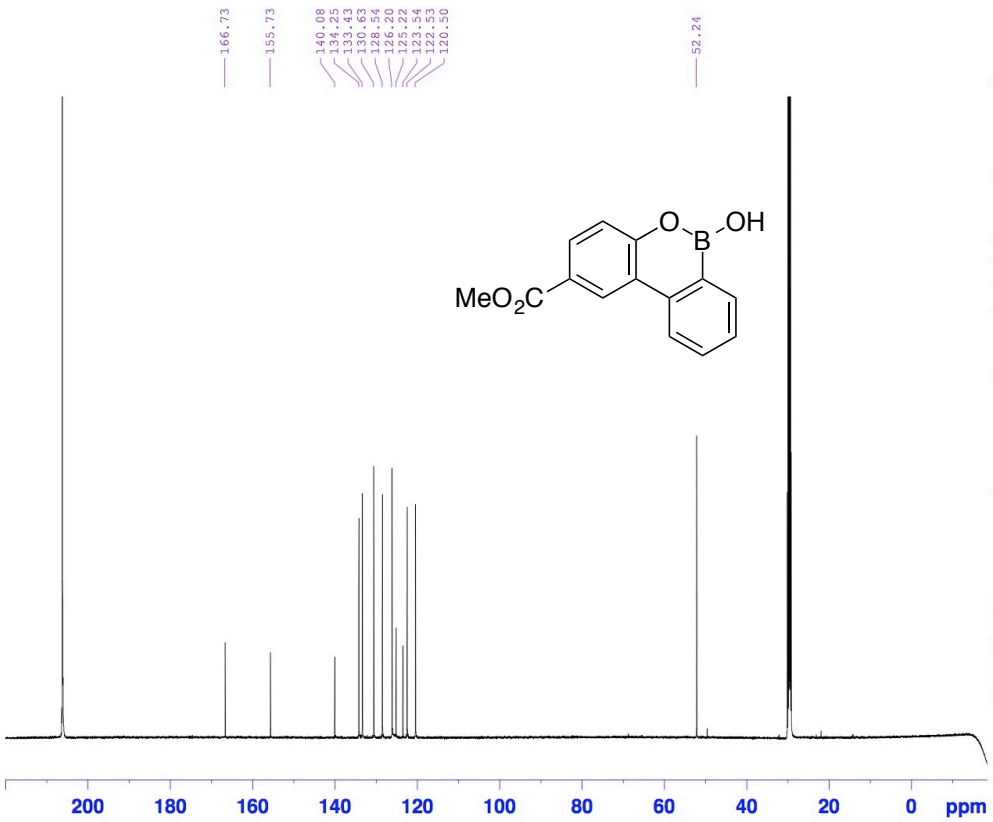


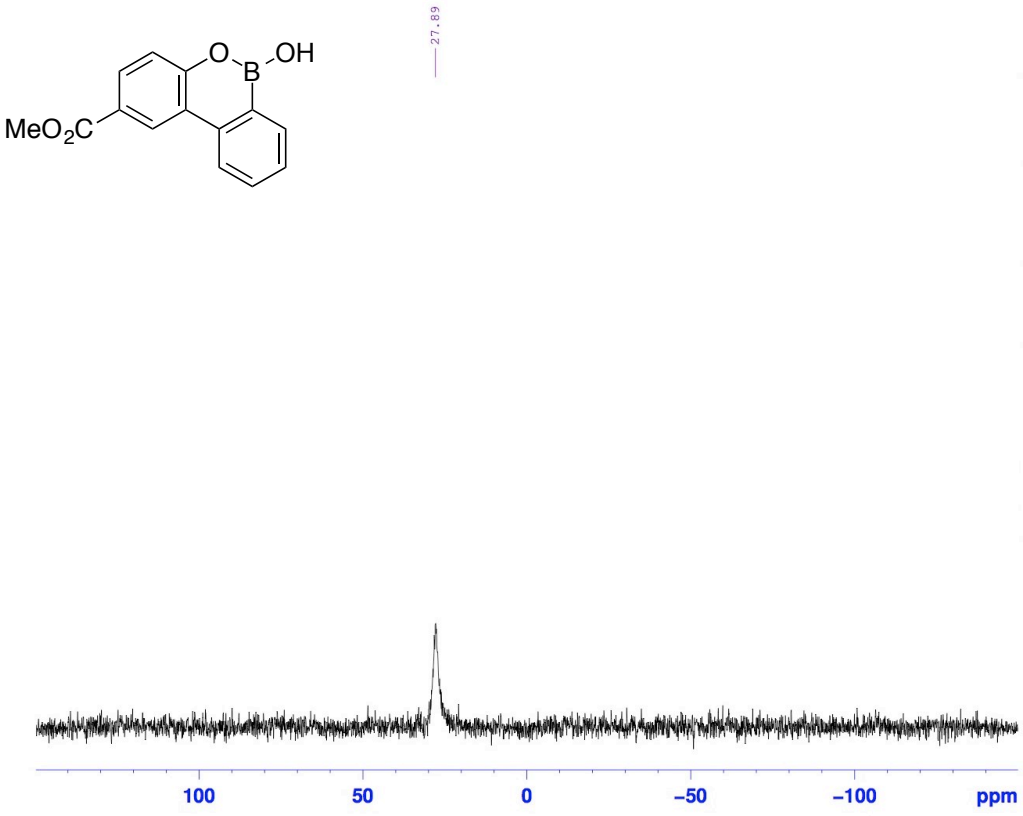




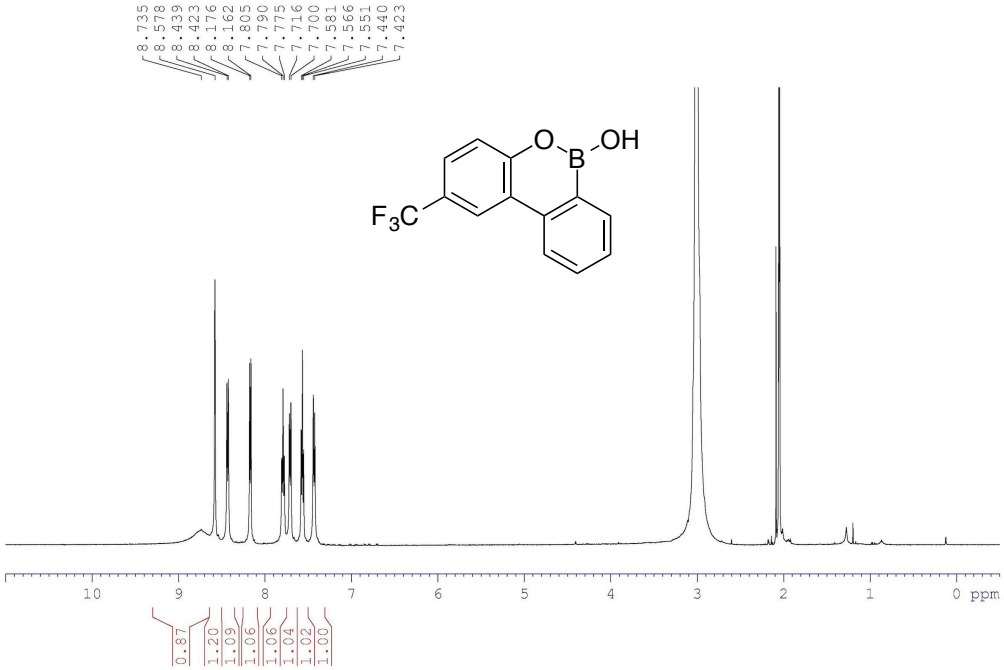
^{1}H, ^{13}C, and ^{11}B NMR spectra of **2d** (acetone-d_6)

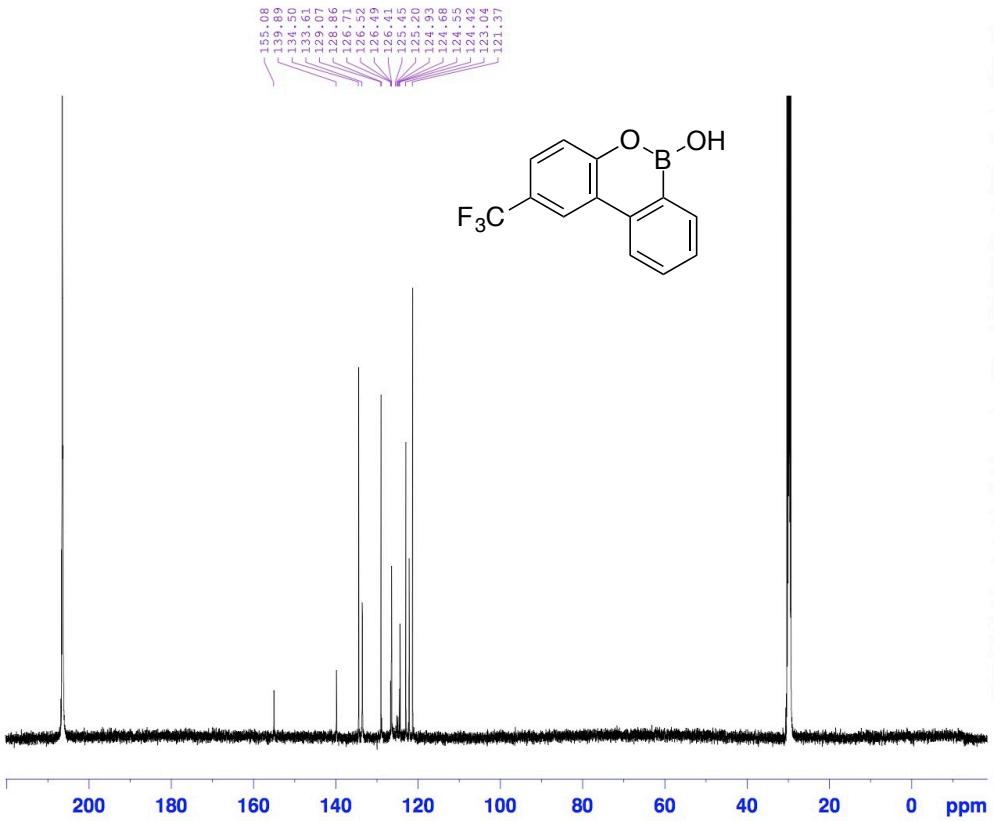


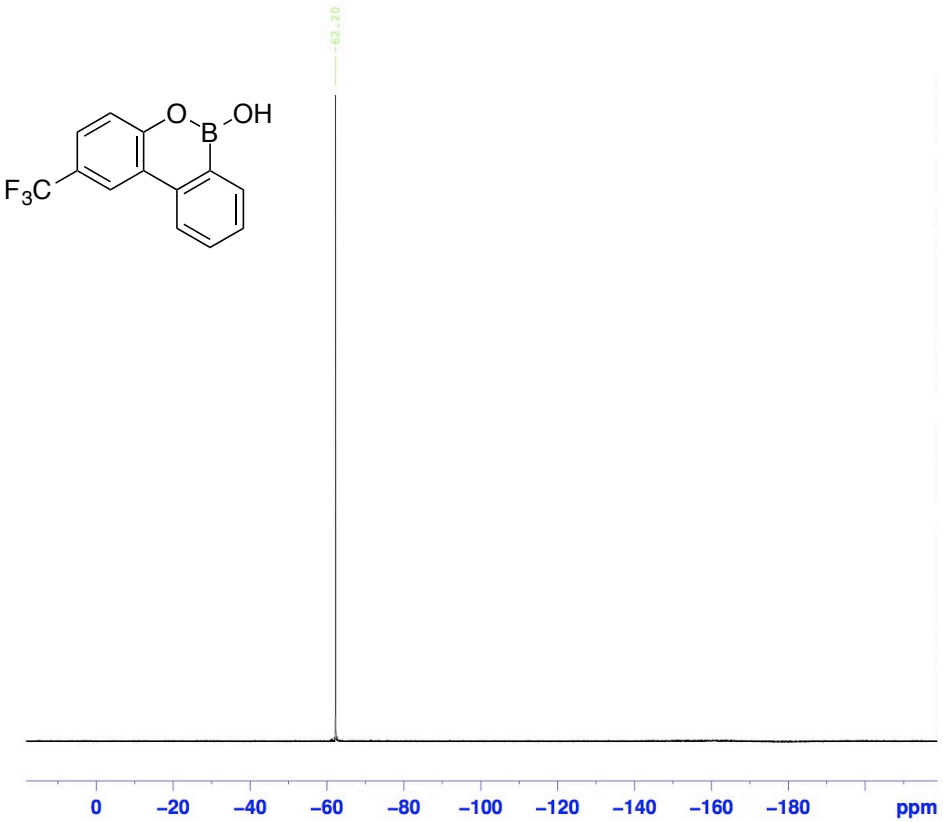

166.73
155.73
140.08
134.25
133.43
130.63
128.54
126.20
125.22
123.54
122.53
120.50
52.24
O
B
OH
MeO2C
200
180
160
140
120
100
80
60
40
20
0
ppm

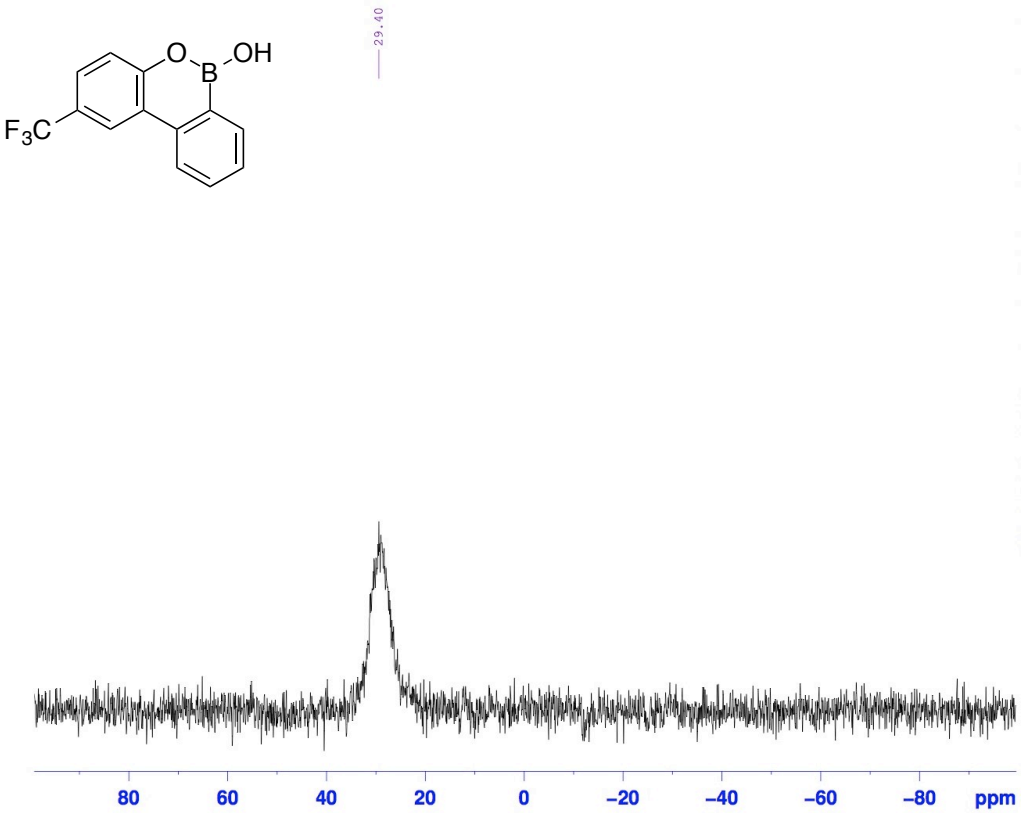

27.89
O
B
OH
MeO2C
100
50
0
−50
−100
ppm

^{1}H, ^{13}C, and ^{19}F spectra (1 M D_2O in acetone-d_6) and ^{11}B NMR spectra (acetone-d_6) of **2e**

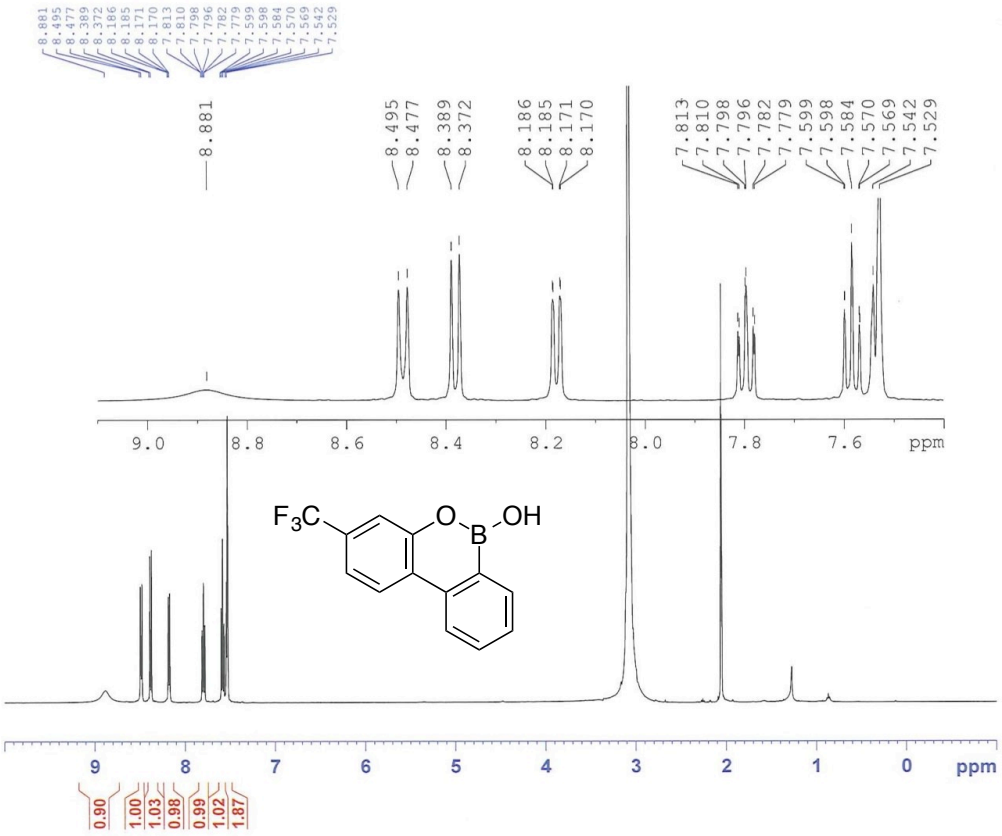


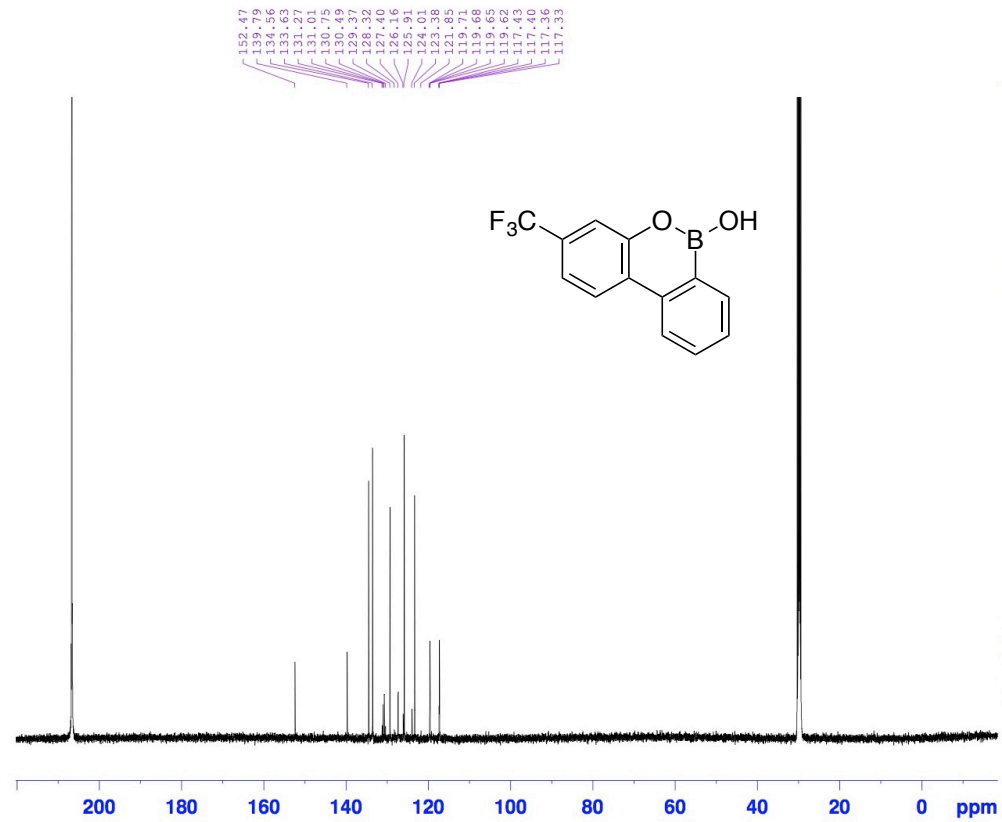


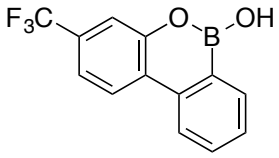

62.20
O
B
OH
F3C
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
ppm


29.40
O
B
OH
F3C
80
60
40
20
0
−20
−40
−60
−80
ppm

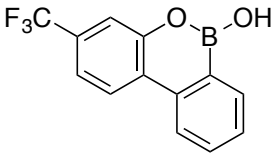
^{1}H, ^{13}C, and ^{19}F spectra (1 M D_2O in acetone-d_6) and ^{11}B NMR spectra (acetone-d_6) of **2f**





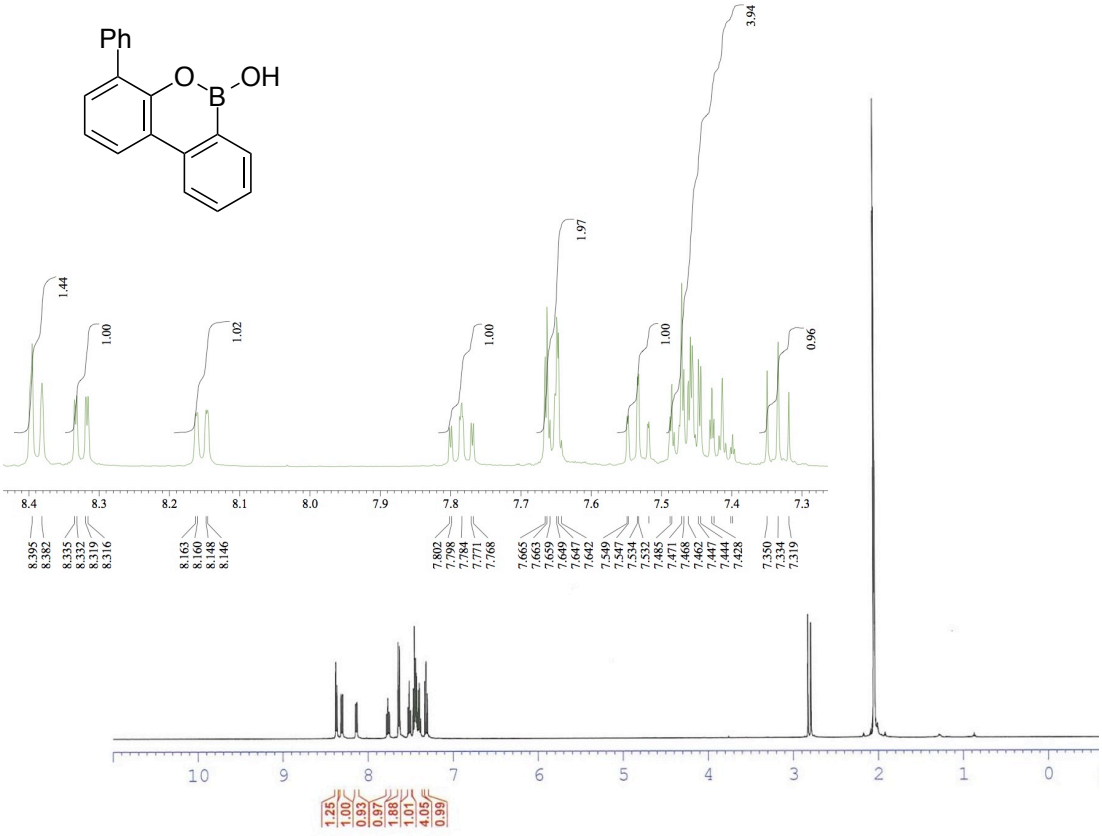

F3C
O
B
OH

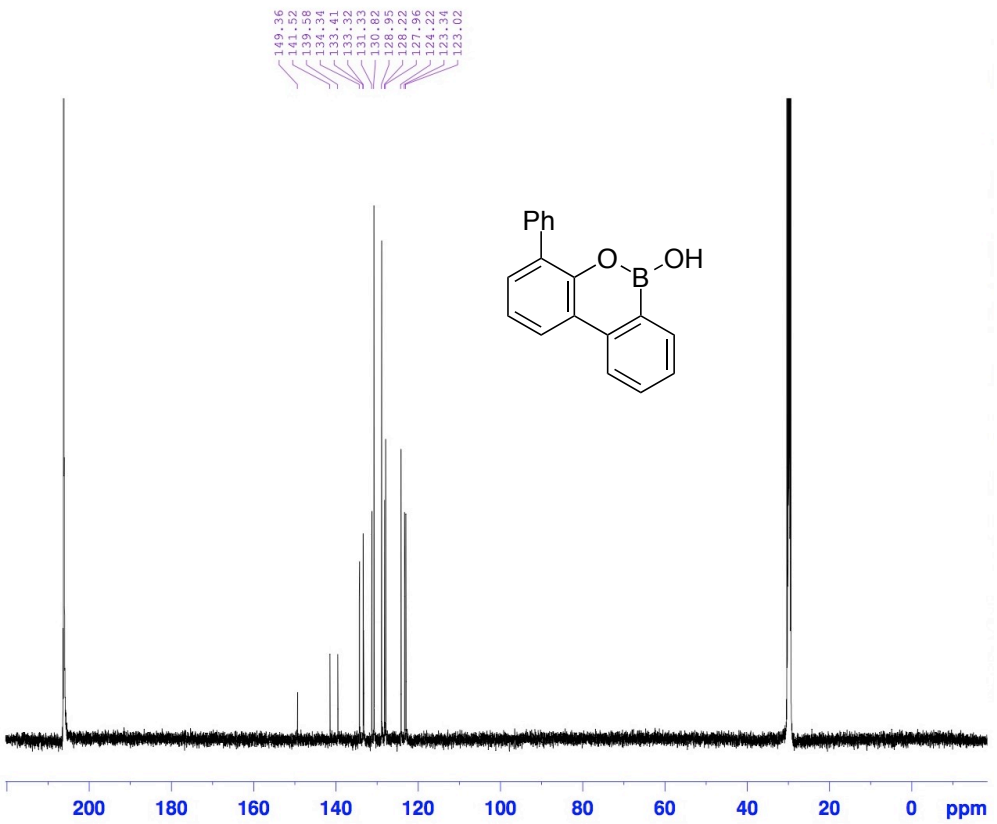
-63.24
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

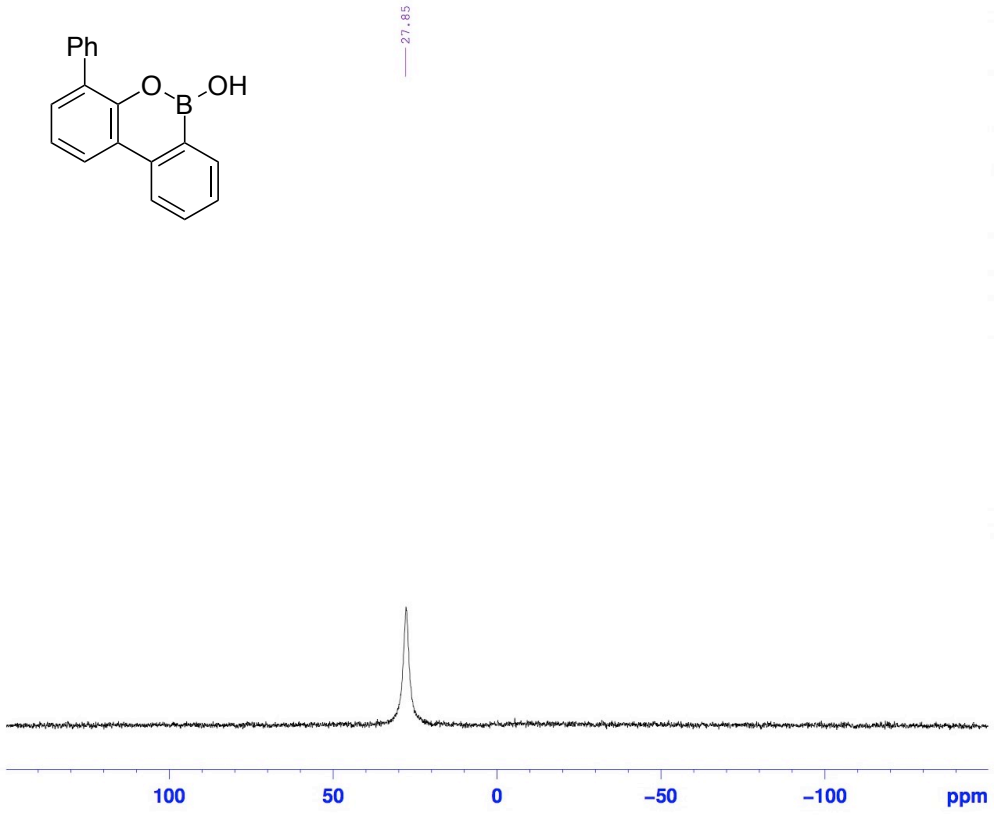

F3C
O
B
OH

27.87
100
50
0
-50
-100
ppm

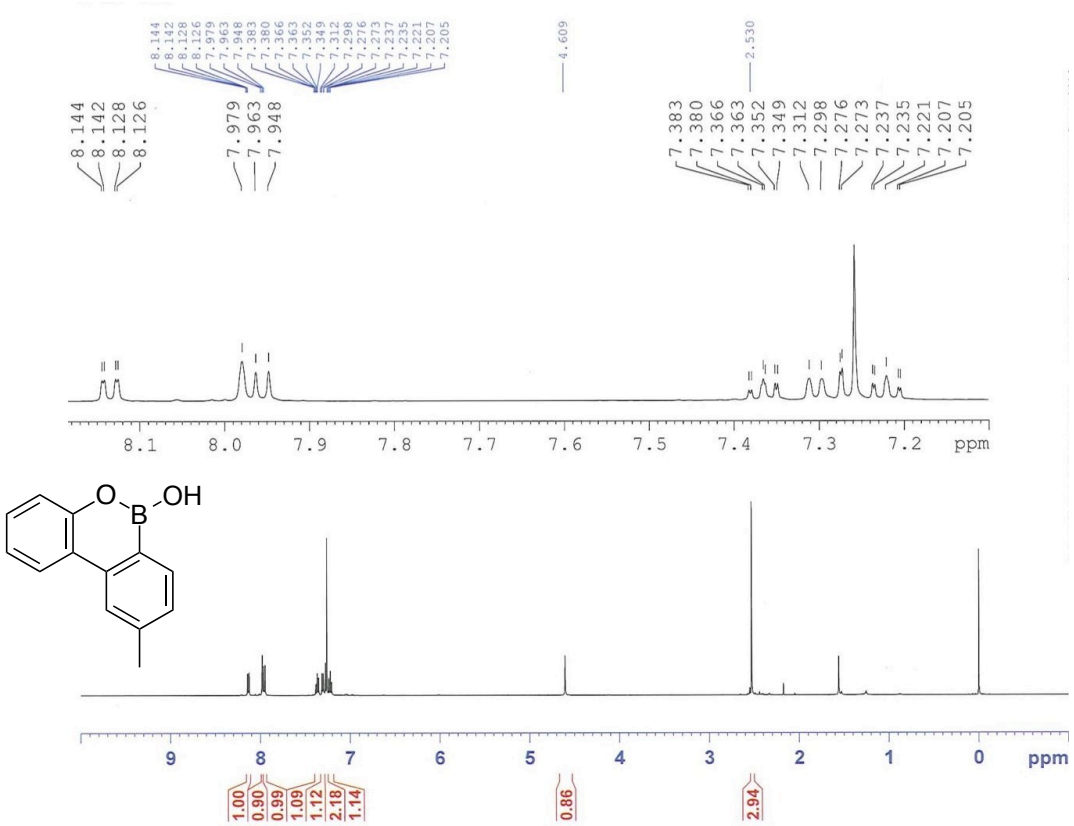
^{1}H, ^{13}C, and ^{11}B NMR spectra of **2g** (acetone-d_6)

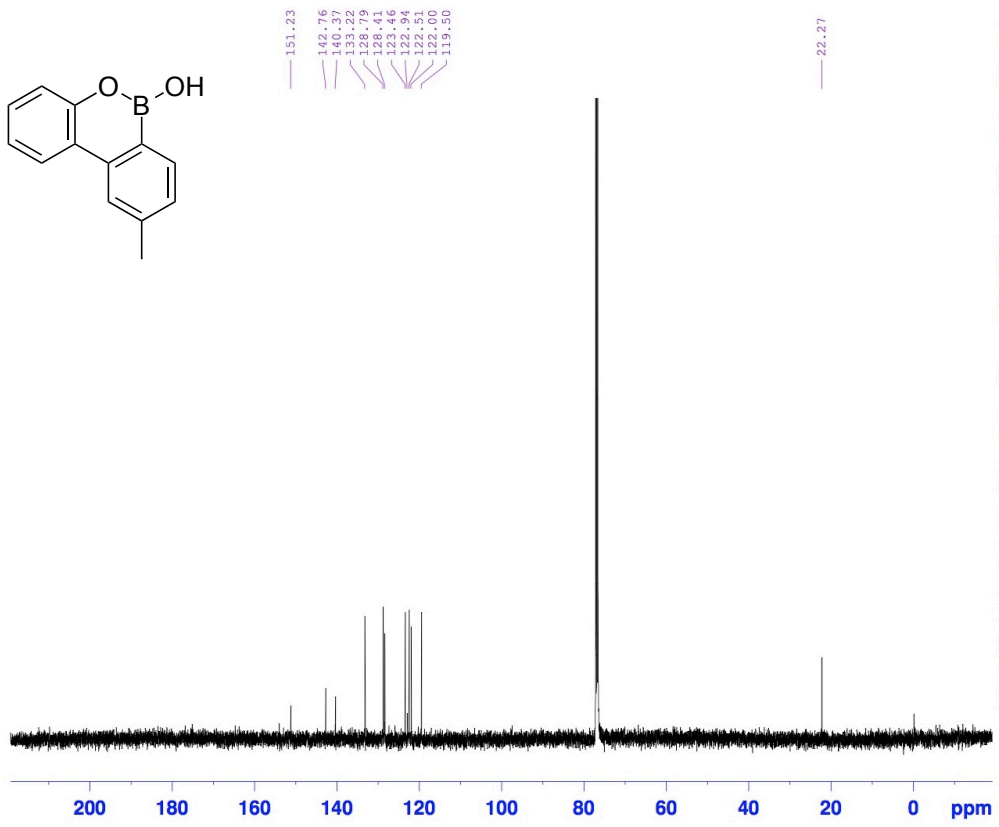




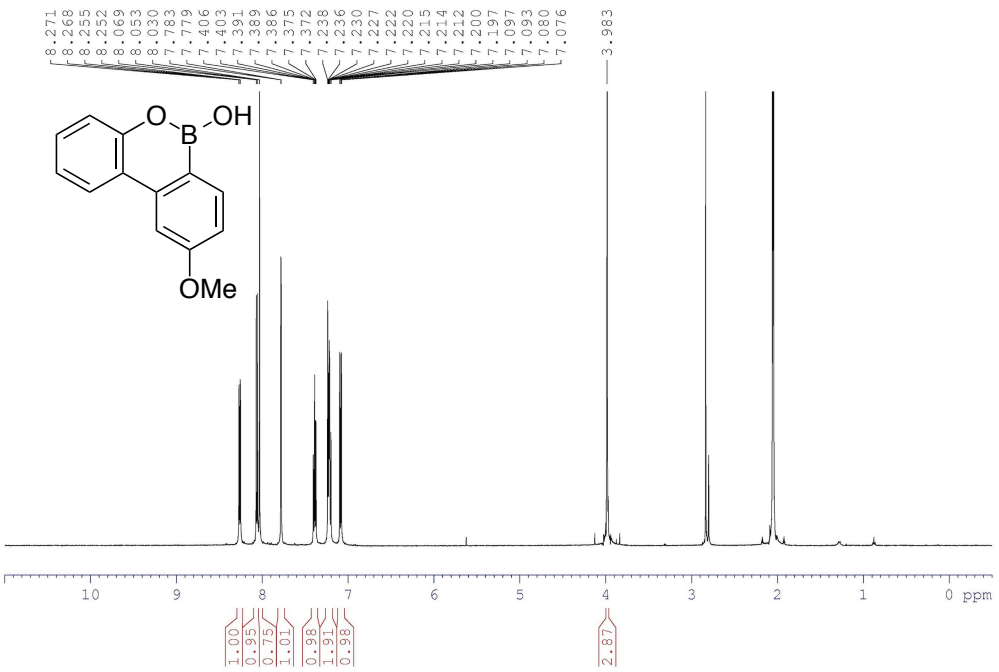


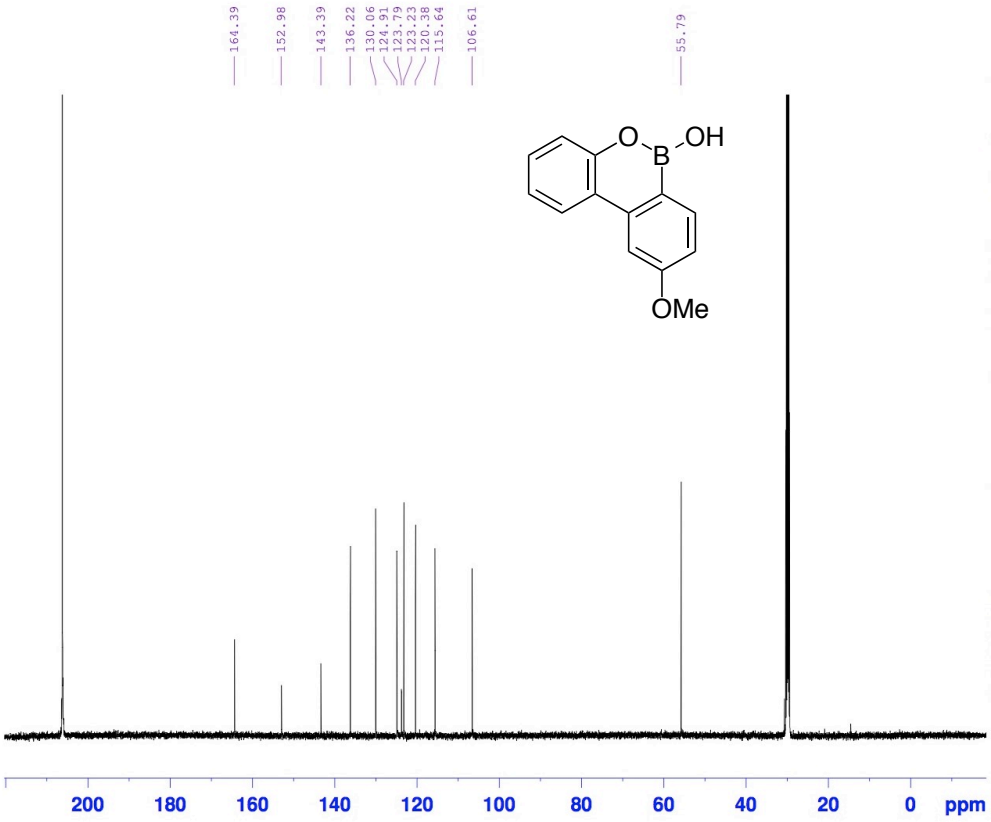
^{1}H and ^{13}C NMR spectra of **2h** ($CDCl_3$)

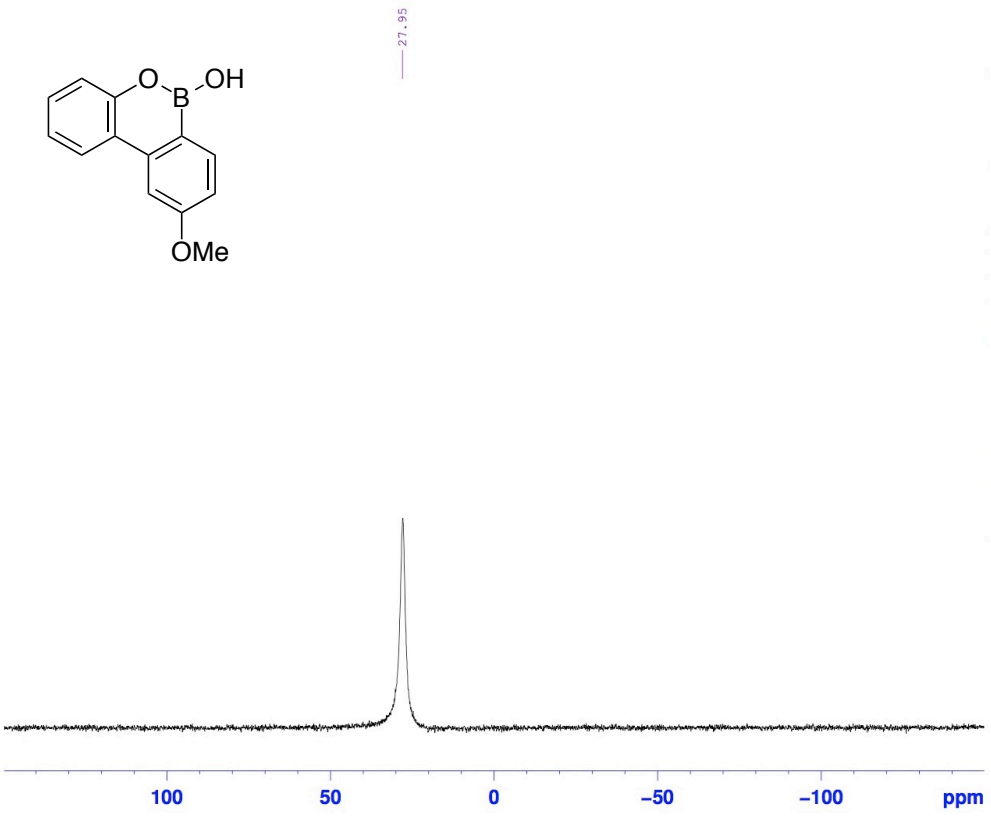




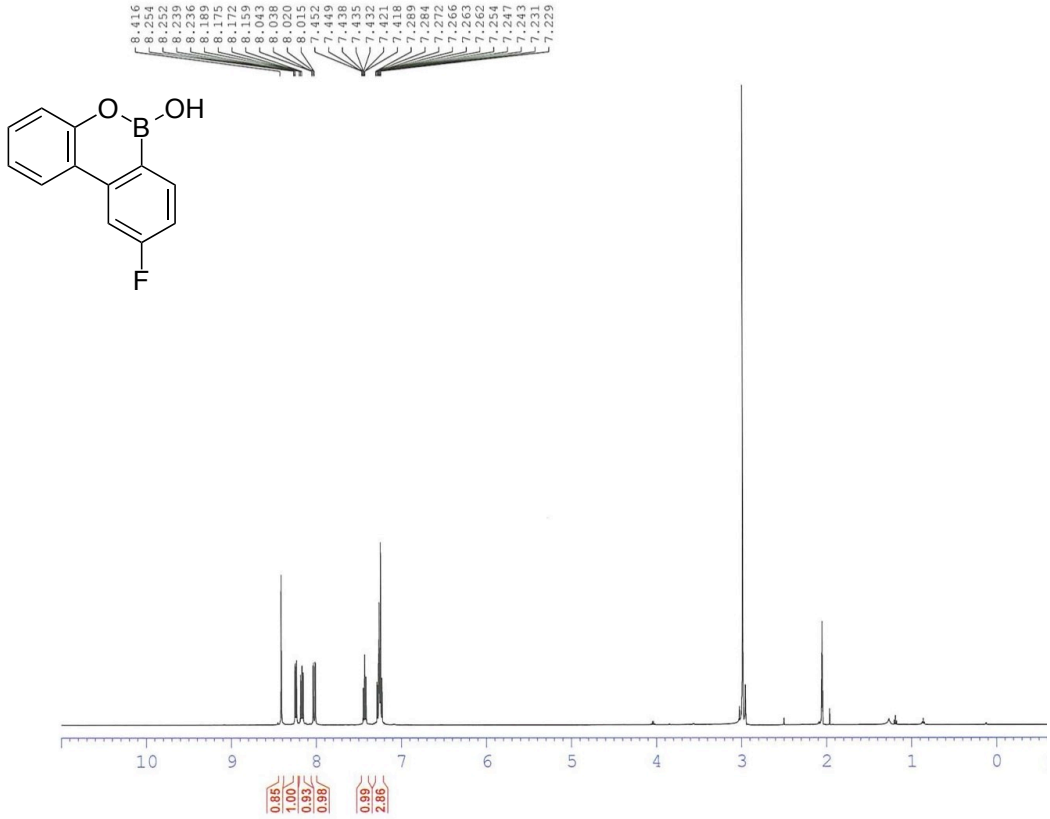
^{1}H, ^{13}C, and ^{11}B NMR spectra of **2i** (acetone-d_6)

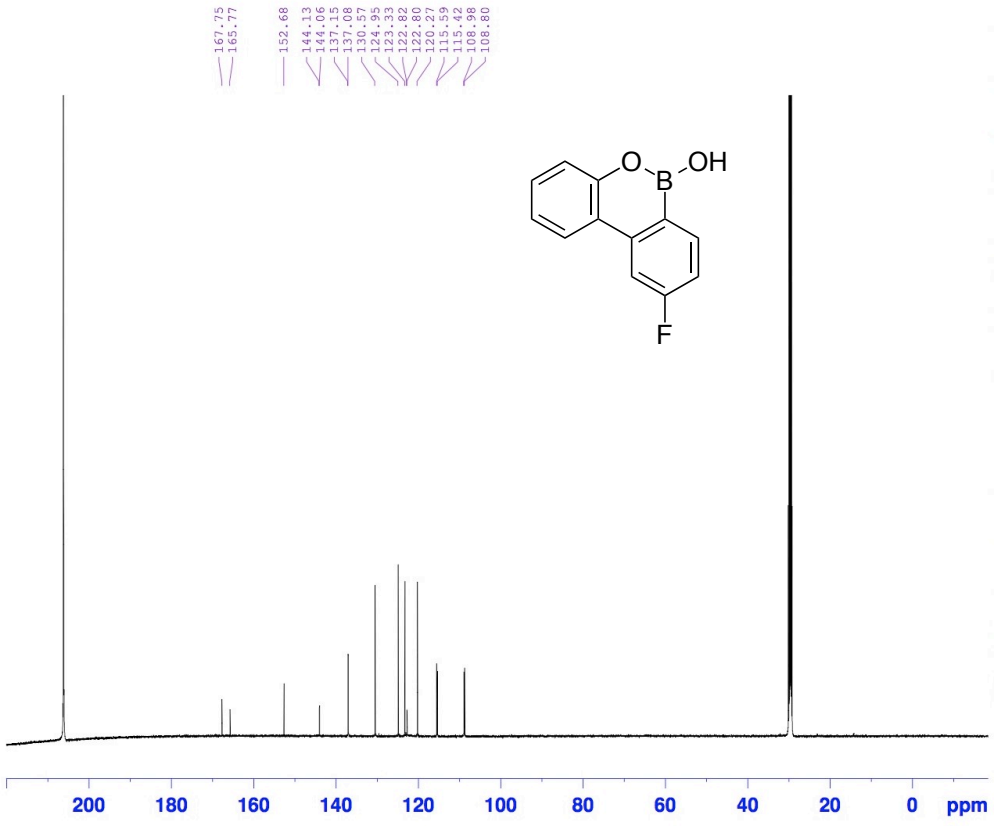


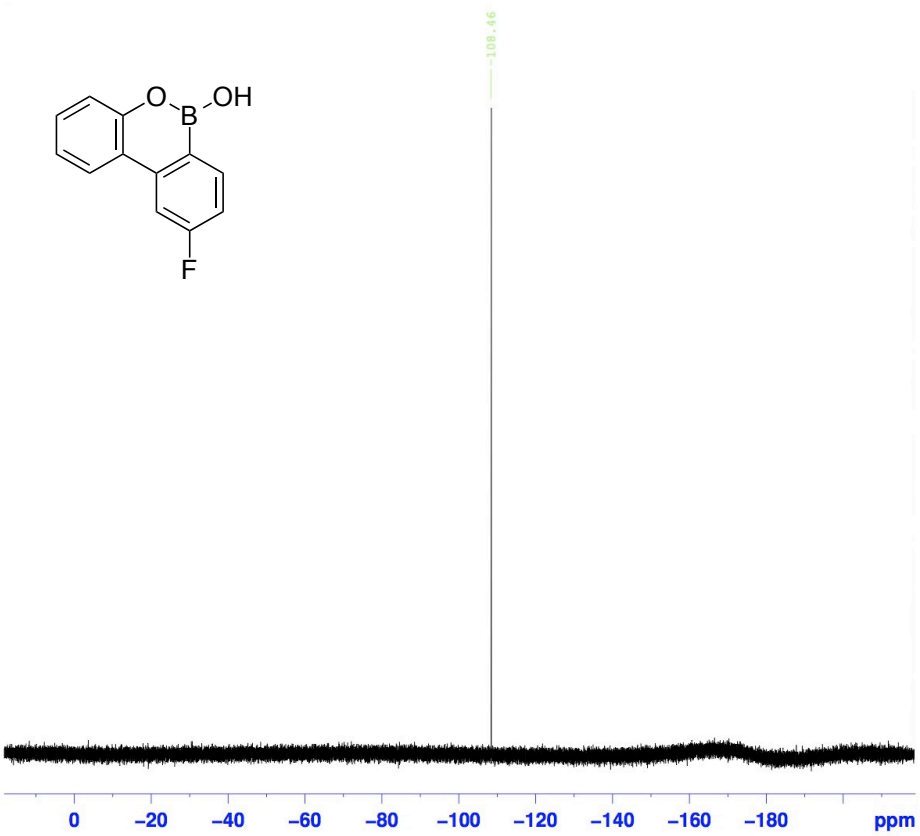

164.39
152.98
143.39
136.22
130.06
124.91
123.79
123.23
120.38
115.64
106.61
55.79
O
B
OH
OMe
200
180
160
140
120
100
80
60
40
20
0
ppm

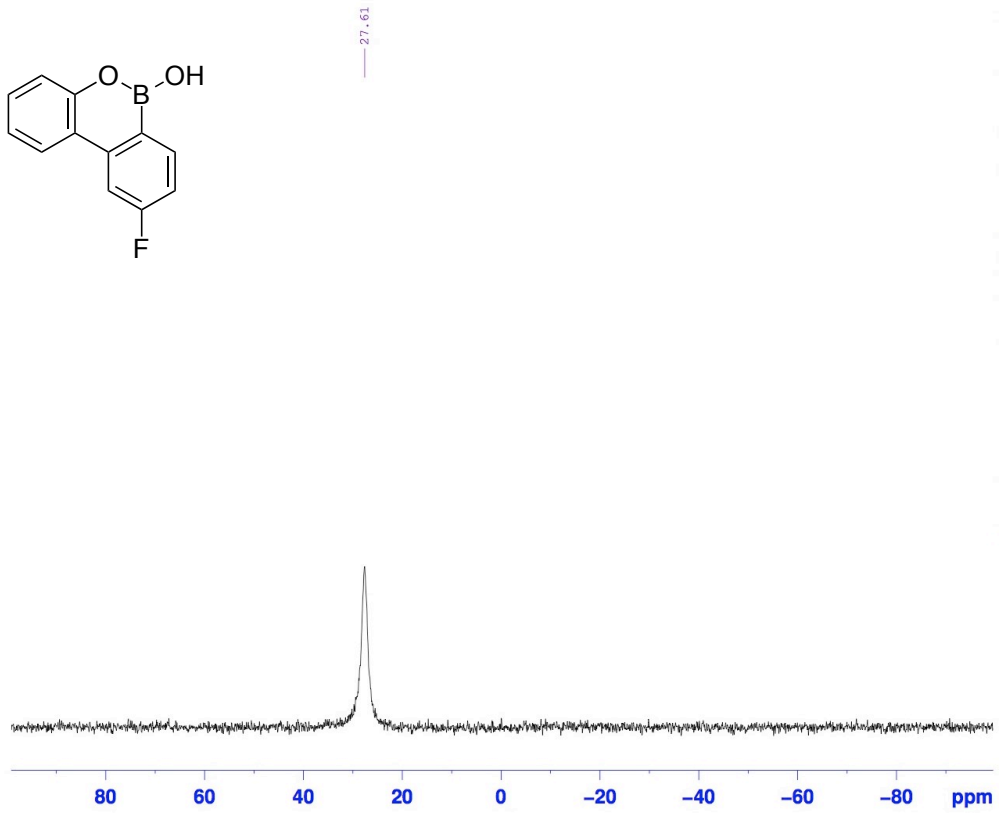

27.95
O
B
OH
OMe
100
50
0
−50
−100
ppm

^{1}H and ^{13}C spectra (acetone-d_6), ^{19}F spectra (1 M D_2O in acetone-d_6), and ^{11}B NMR spectra (acetone-d_6) of **2j**

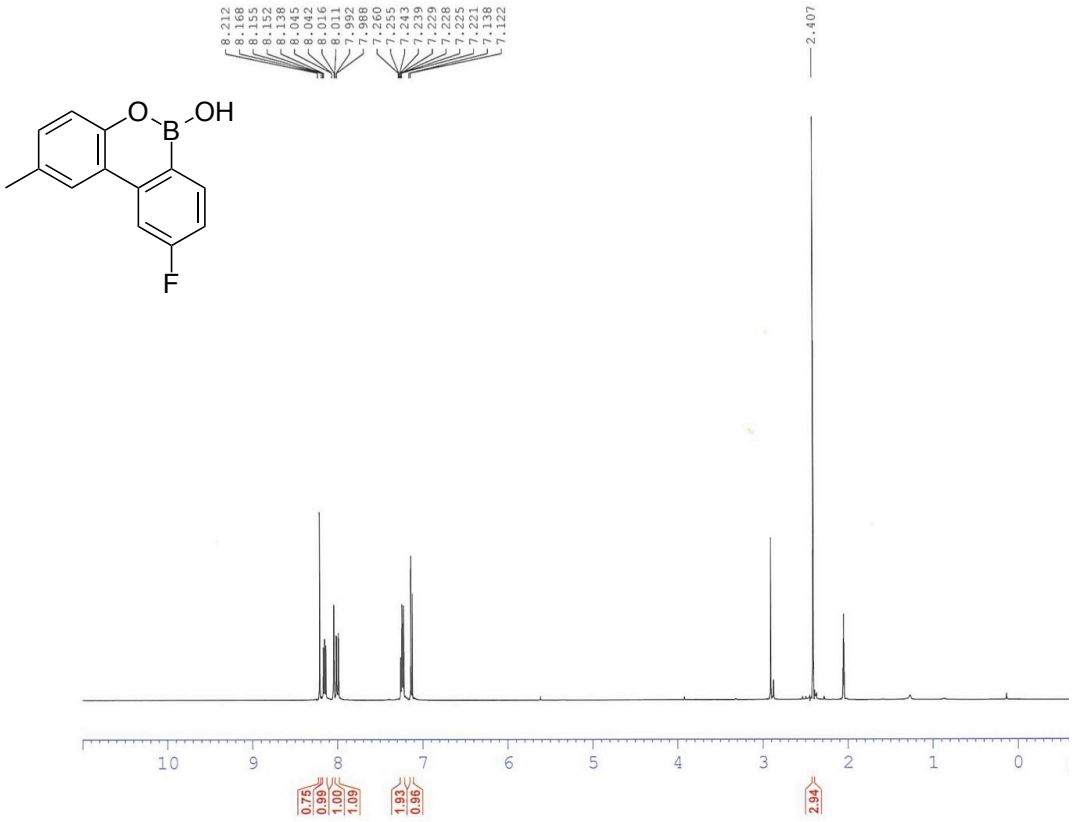


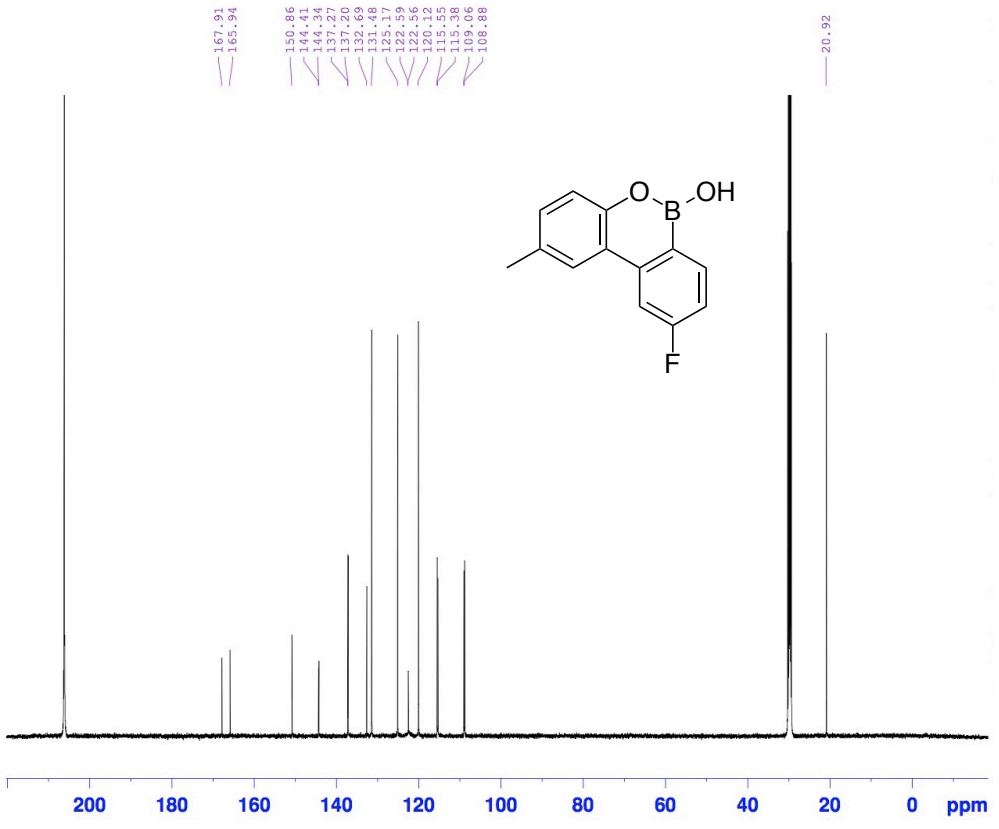


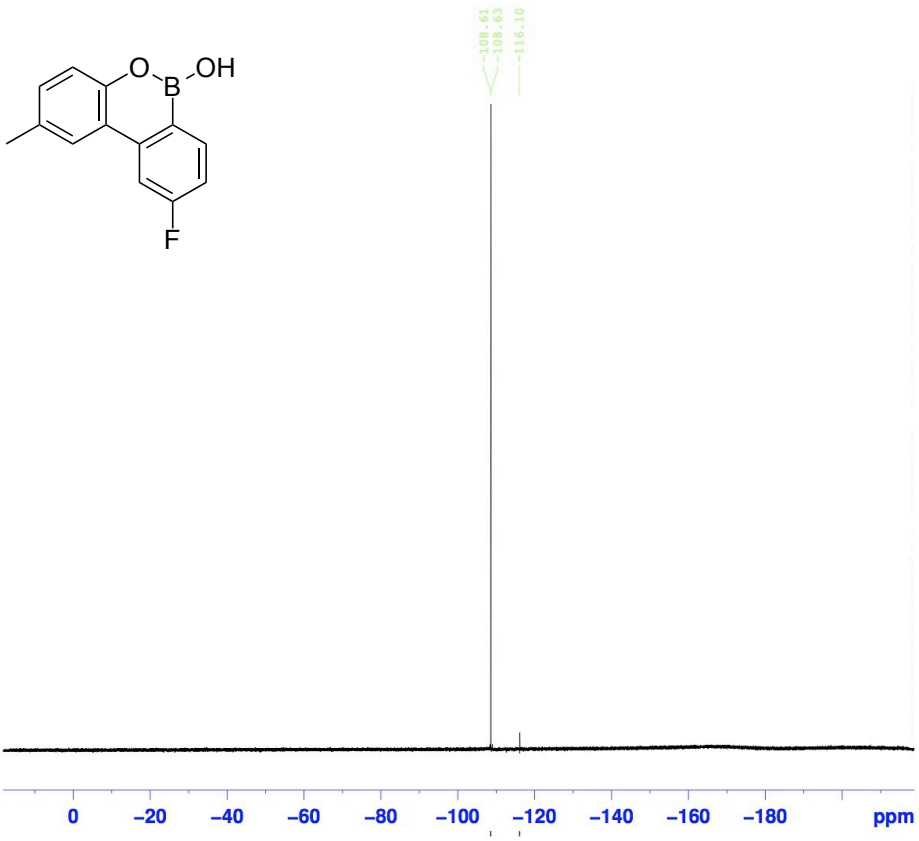

O
B
OH
F
-108.46
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

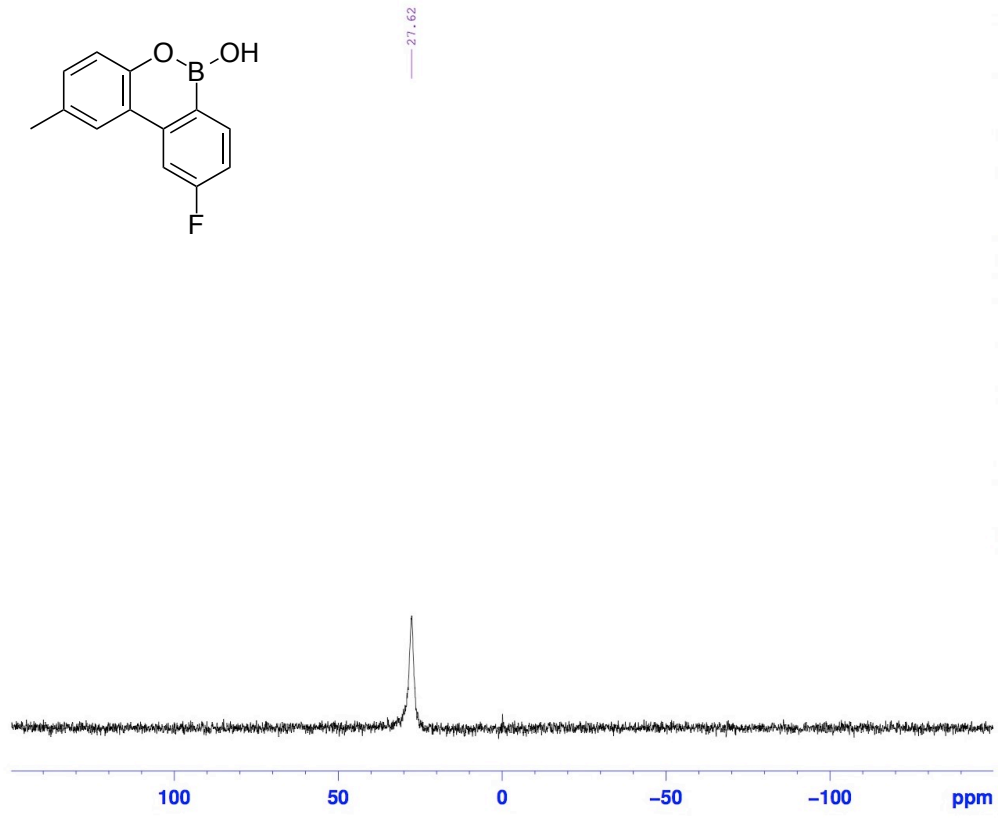

O
B
OH
F
27.61
80
60
40
20
0
-20
-40
-60
-80
ppm

^{1}H and ^{13}C spectra (acetone-d_6), ^{19}F spectra (1 M D_2O in acetone-d_6), and ^{11}B NMR spectra (acetone-d_6) of **2k**

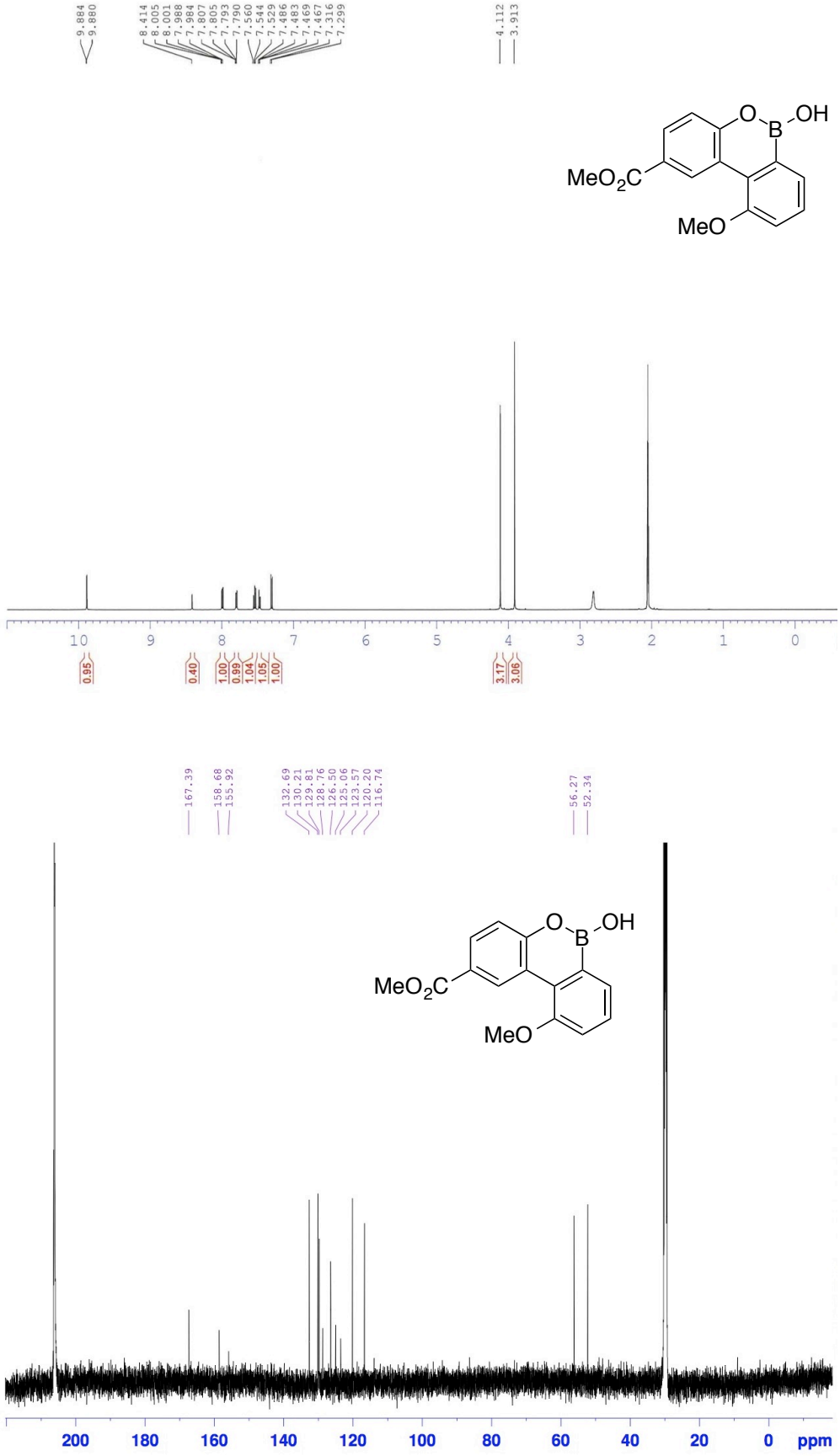


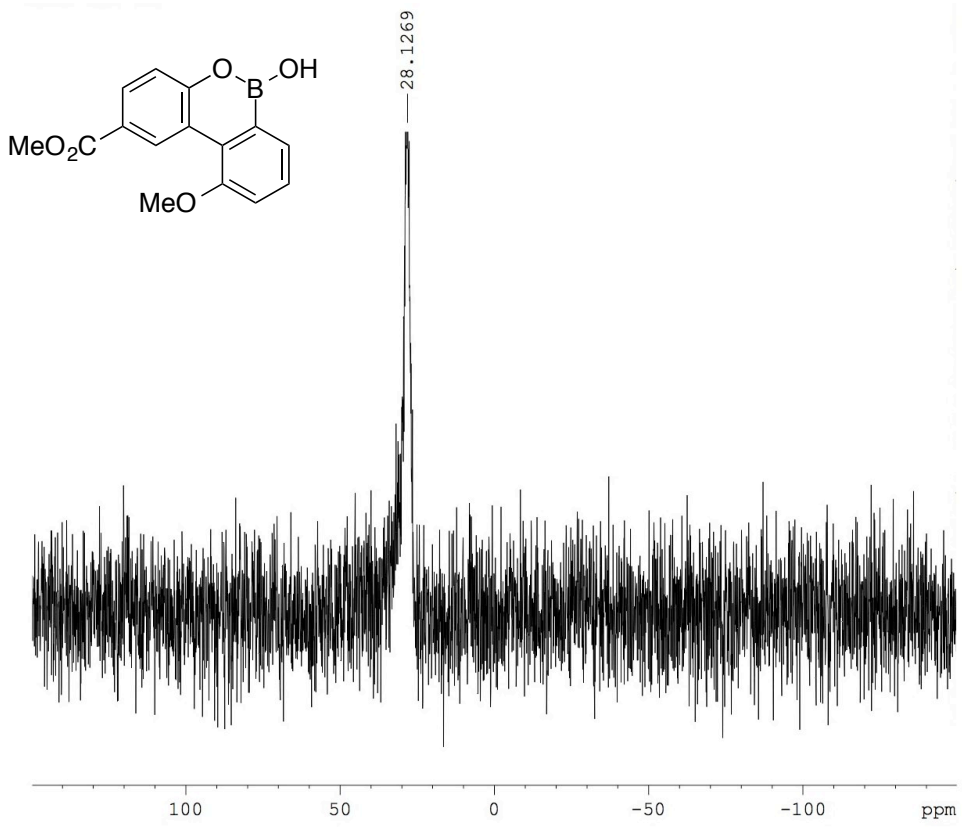



O
B
OH
F
-108.61
-108.63
-116.10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

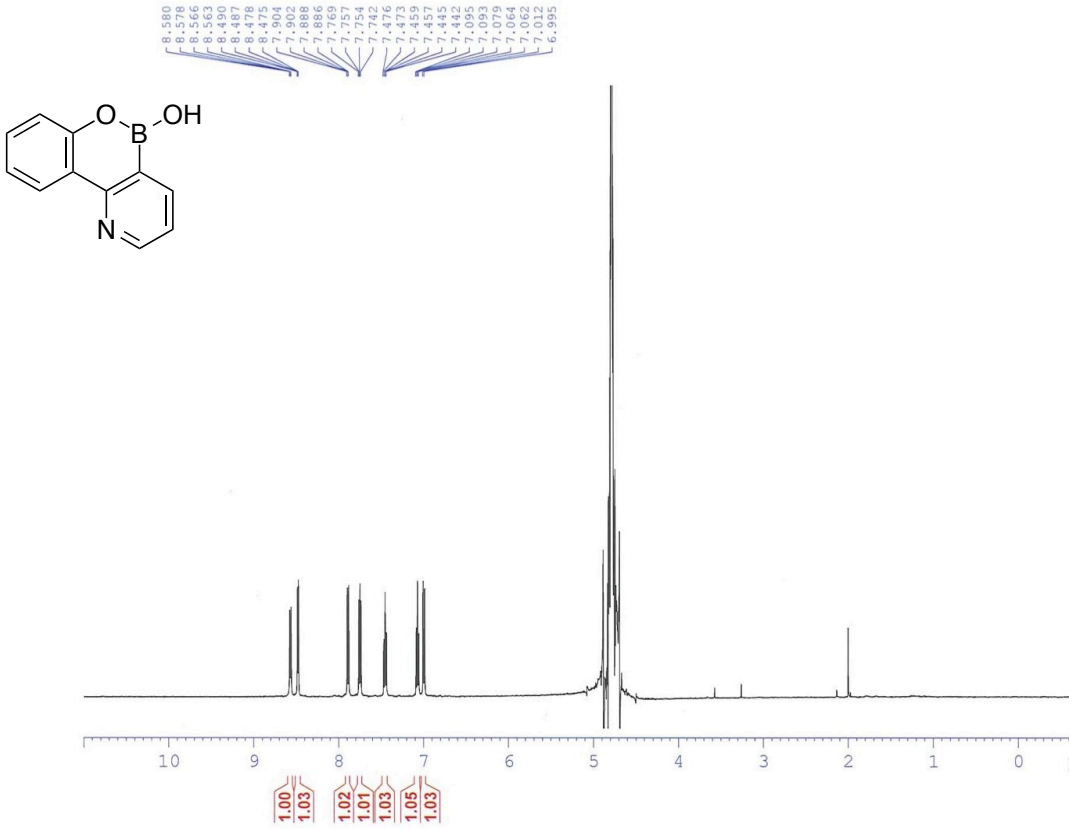

O
B
OH
F
27.62
100
50
0
-50
-100
ppm

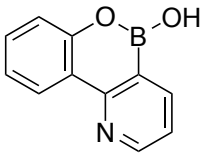
^{1}H, ^{13}C, and ^{11}B NMR spectra of **2l** (acetone-d_6)



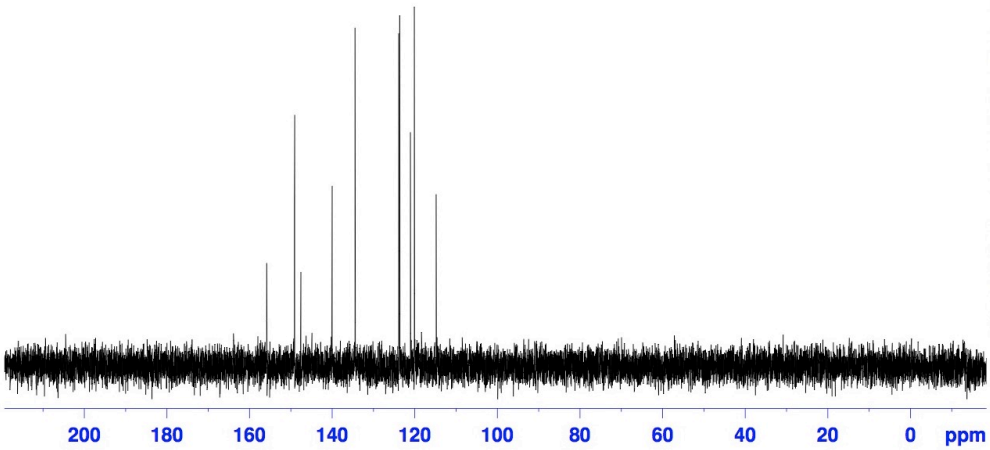


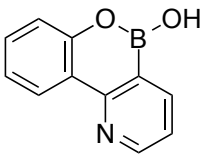
^{1}H and ^{13}C spectra (0.2 mM DCl in D_2O) and ^{11}B NMR spectra (acetone-d_6) of **2m**



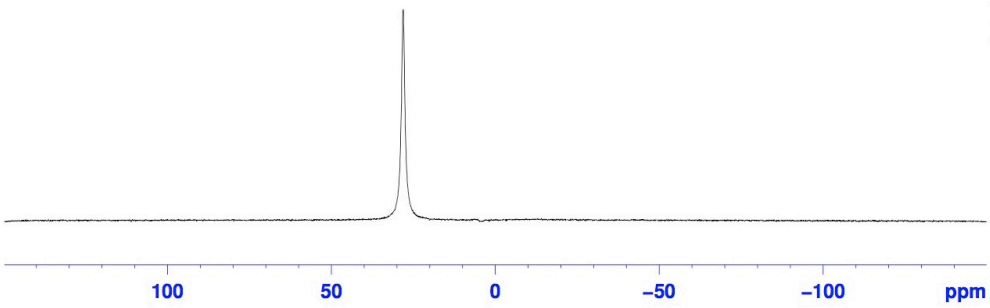

O
B
OH
N


155.87
149.15
147.63
140.04
134.50
123.92
123.71
121.12
120.14
114.89

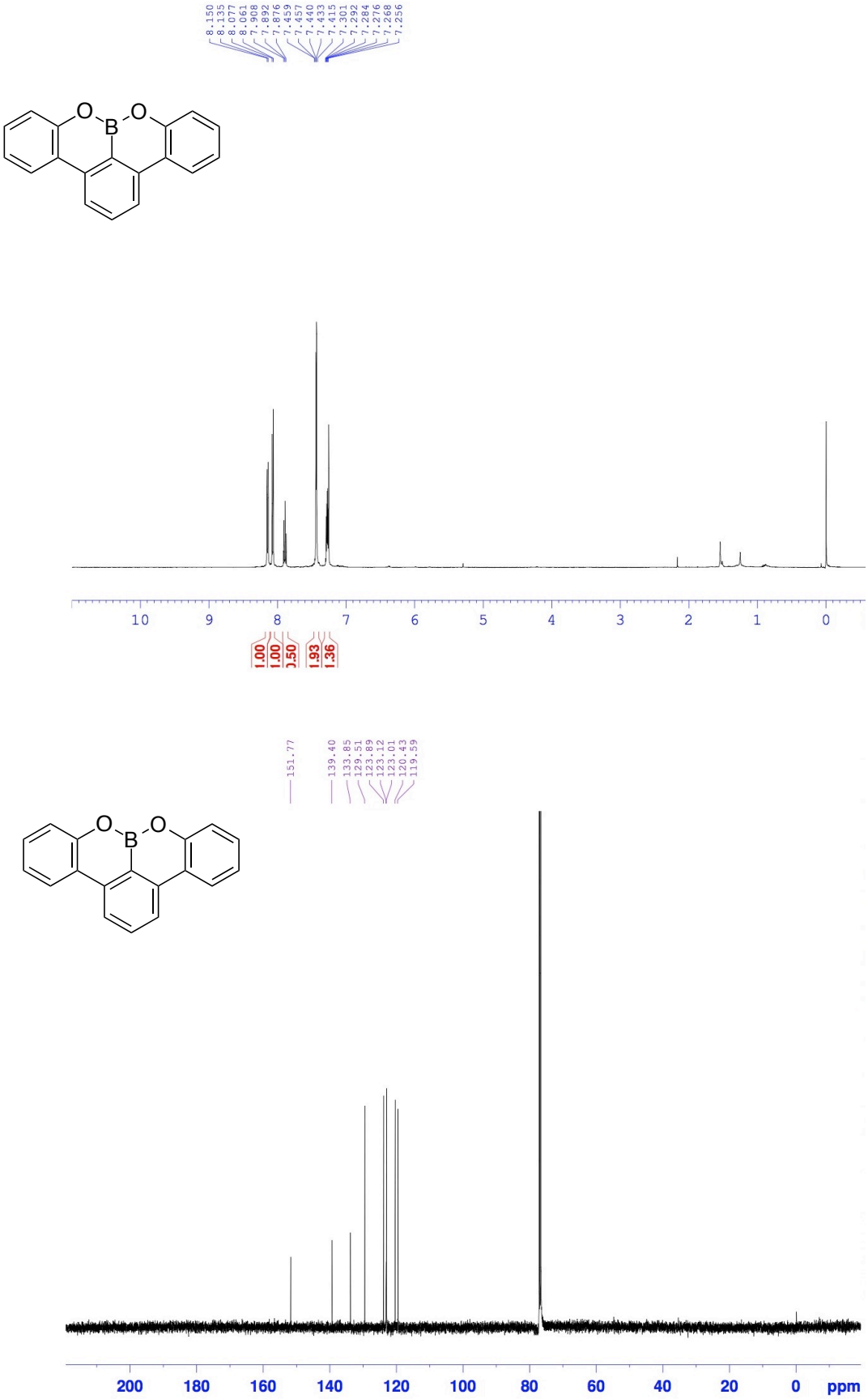

200
180
160
140
120
100
80
60
40
20
0
ppm

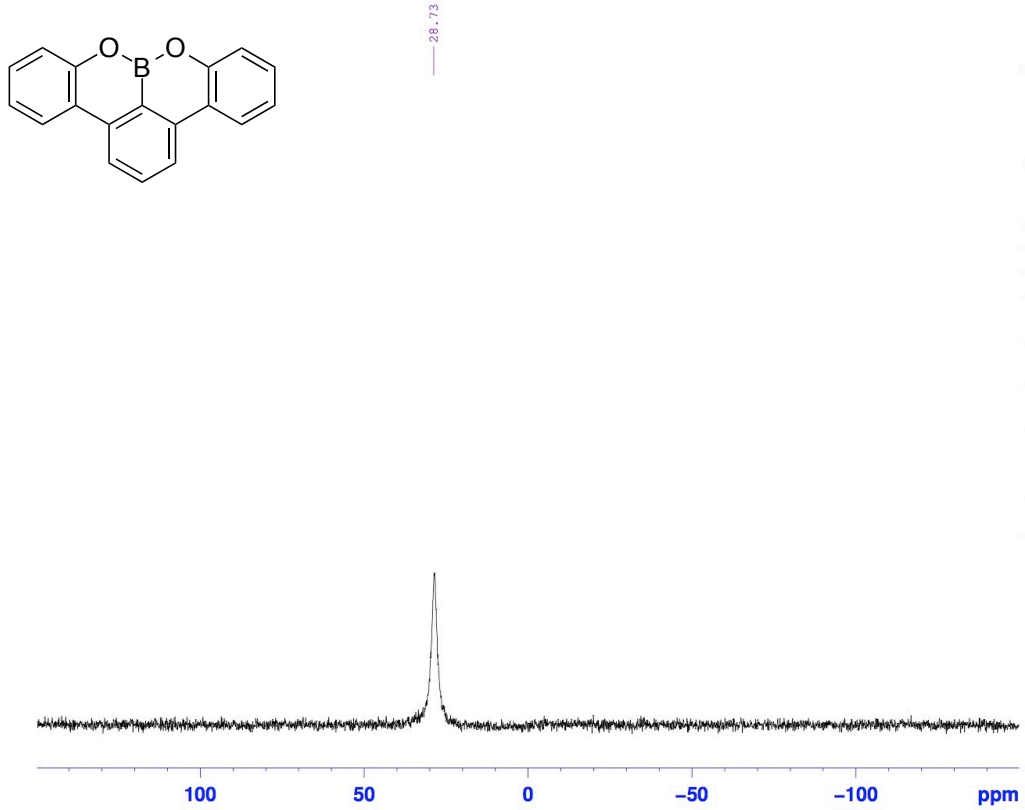

O
B
OH
N

28.17

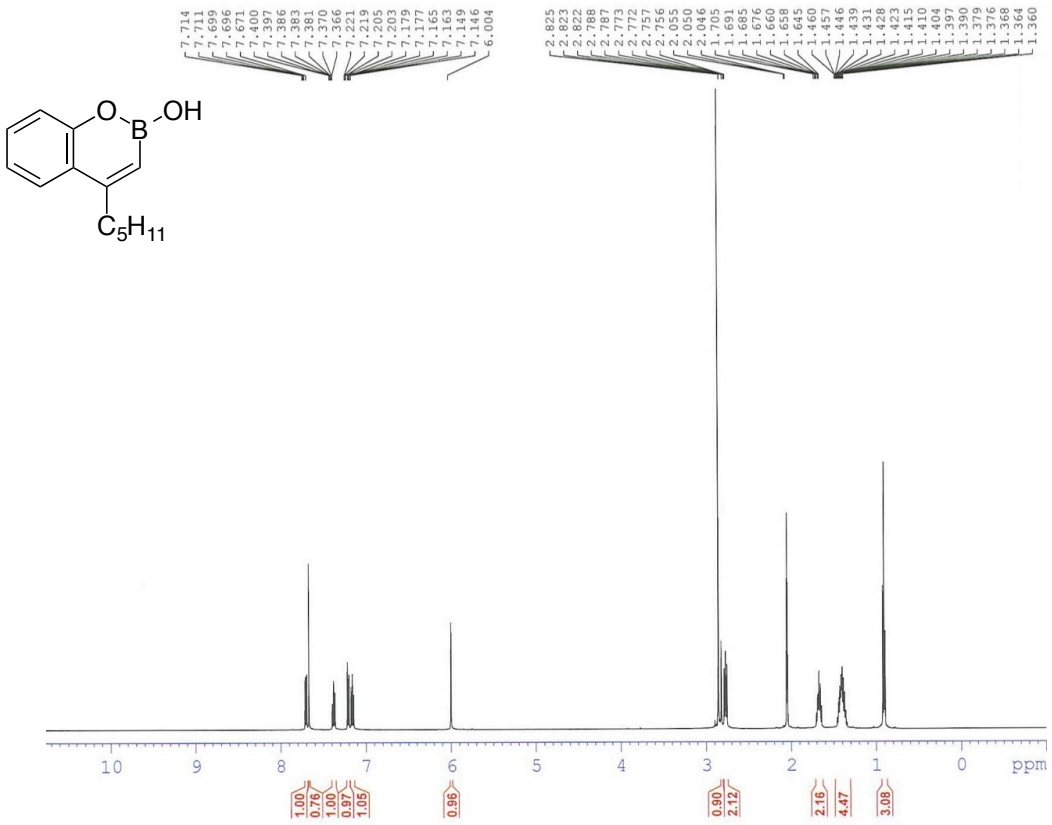

100
50
0
−50
−100
ppm

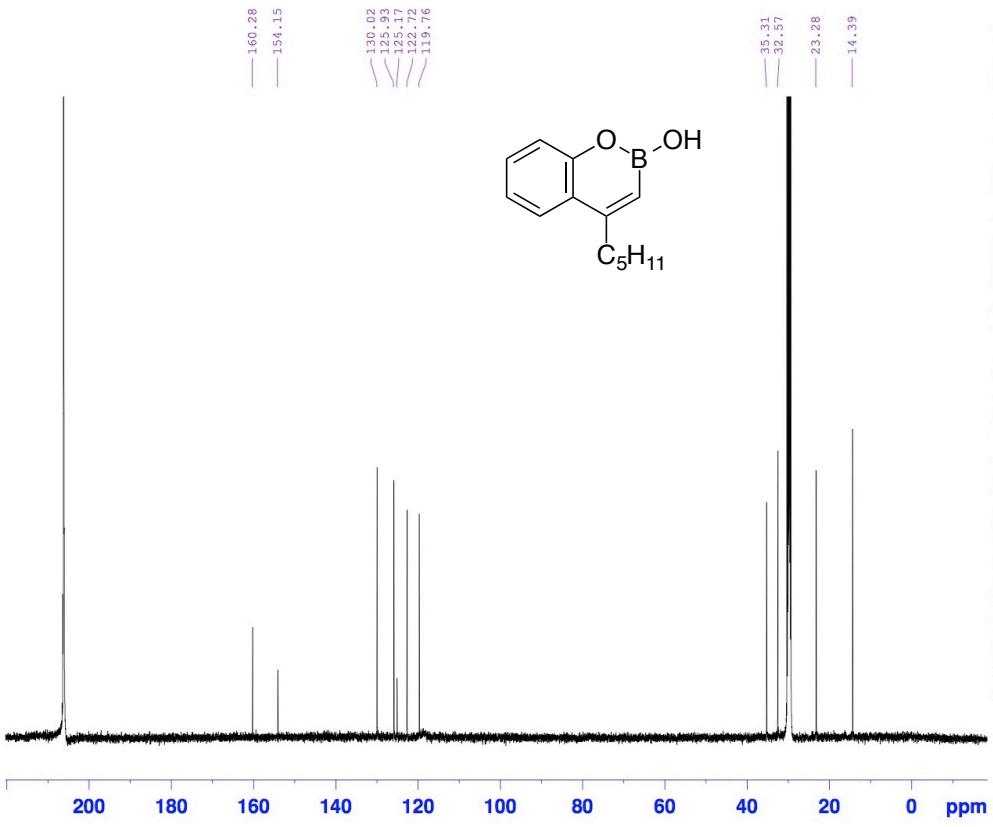
^{1}H, ^{13}C, and ^{11}B NMR spectra of **2n** ($CDCl_3$)

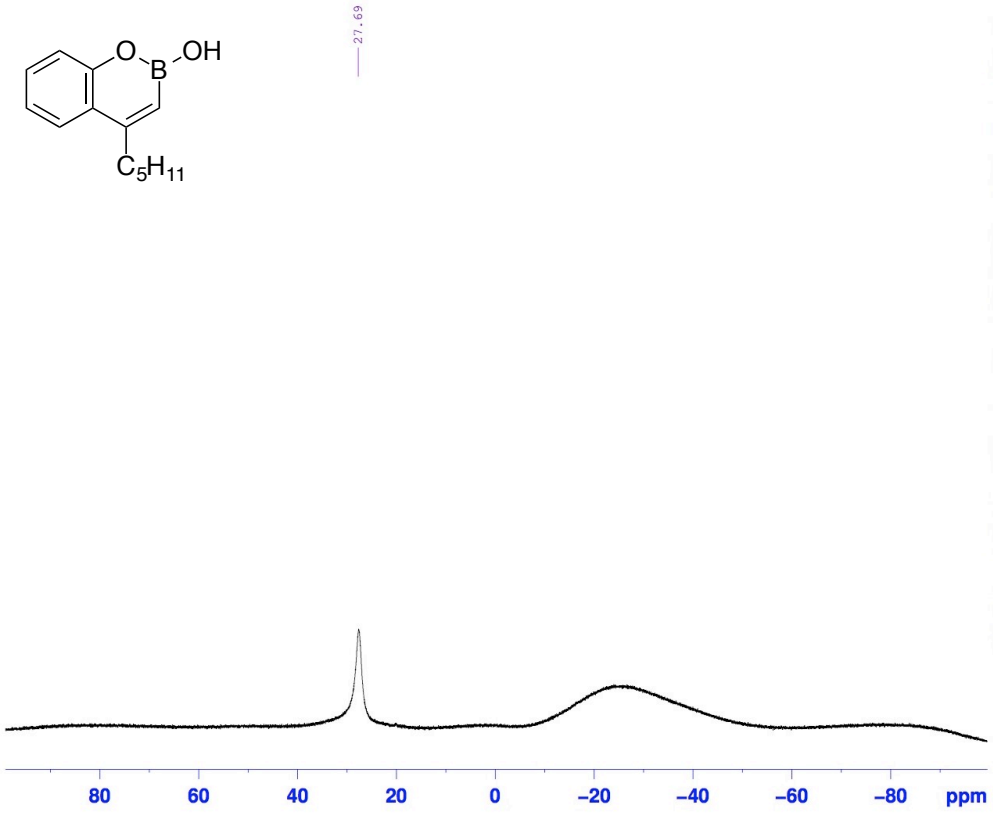




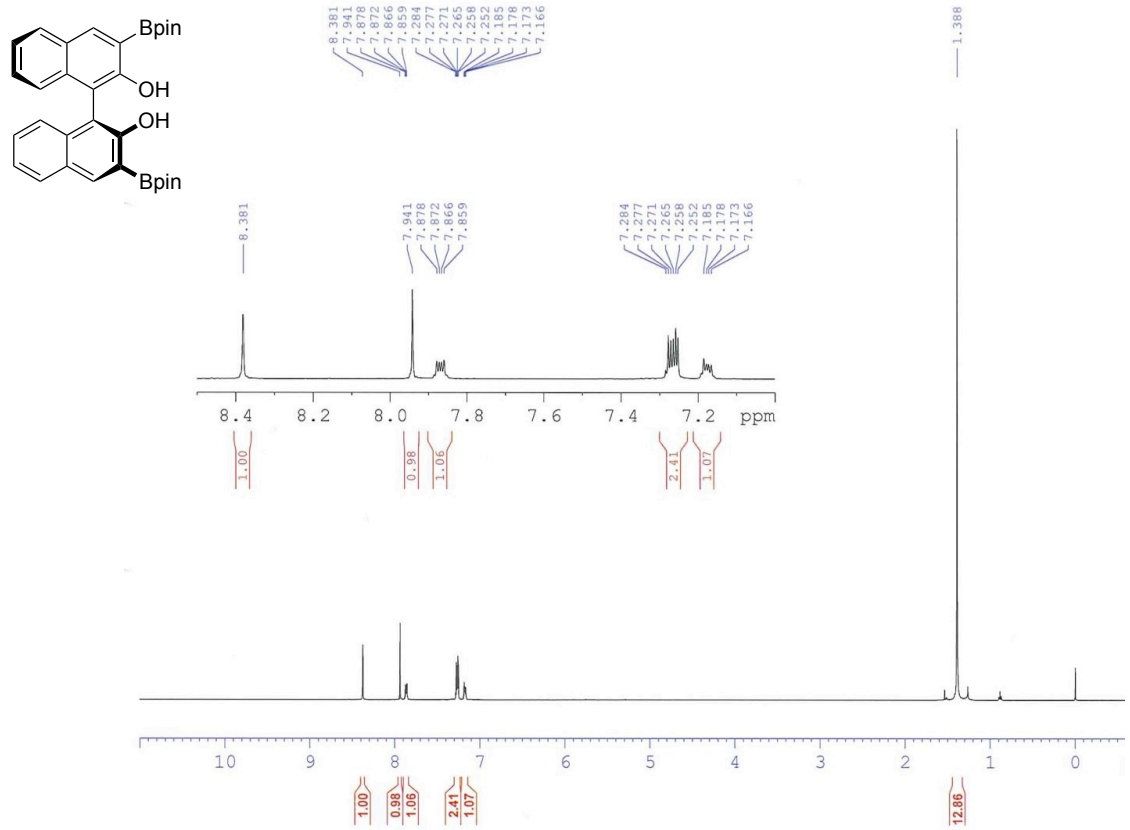
^{1}H, ^{13}C, and ^{11}B NMR spectra of **2o** (acetone-d_6)

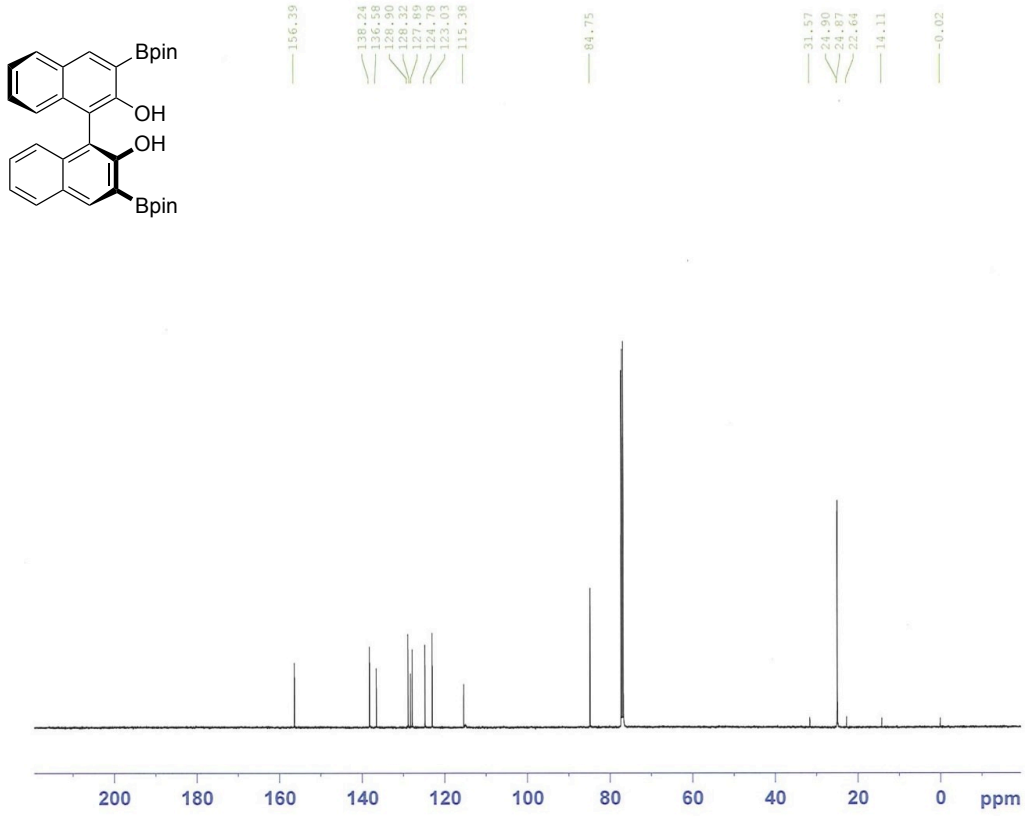


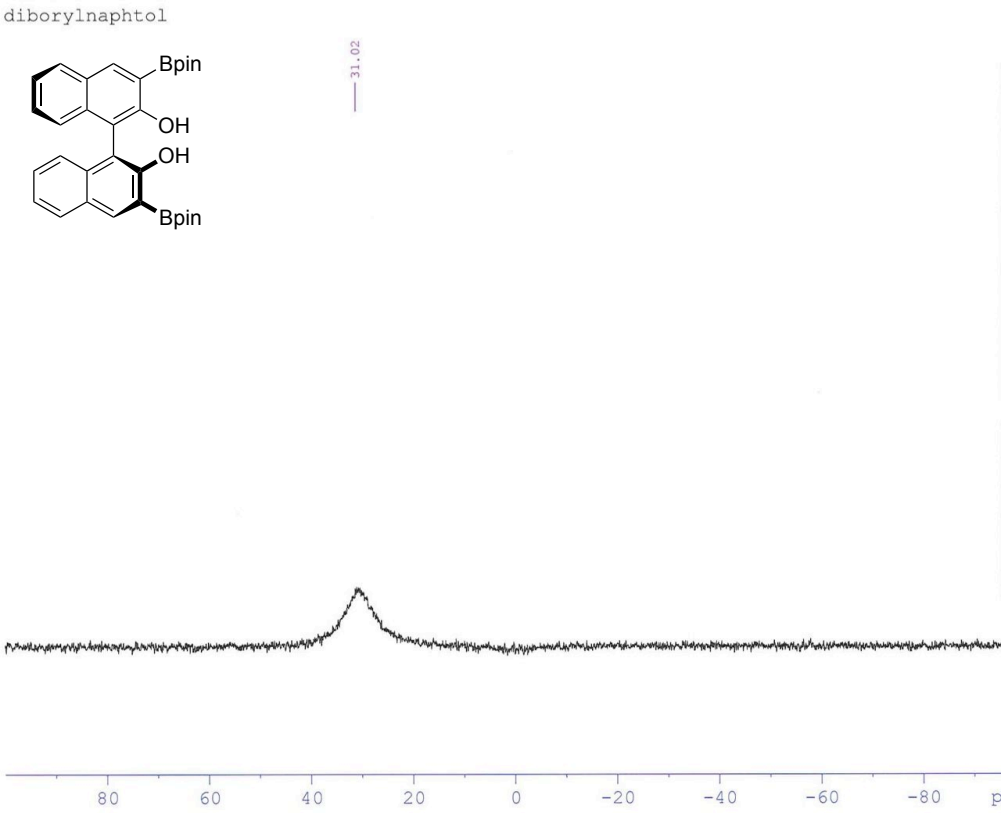

160.28
154.15
130.02
125.93
125.17
122.72
119.76
35.31
32.57
23.28
14.39
O
B
OH
C5H11
200
180
160
140
120
100
80
60
40
20
0
ppm


27.69
O
B
OH
C5H11
80
60
40
20
0
−20
−40
−60
−80
ppm

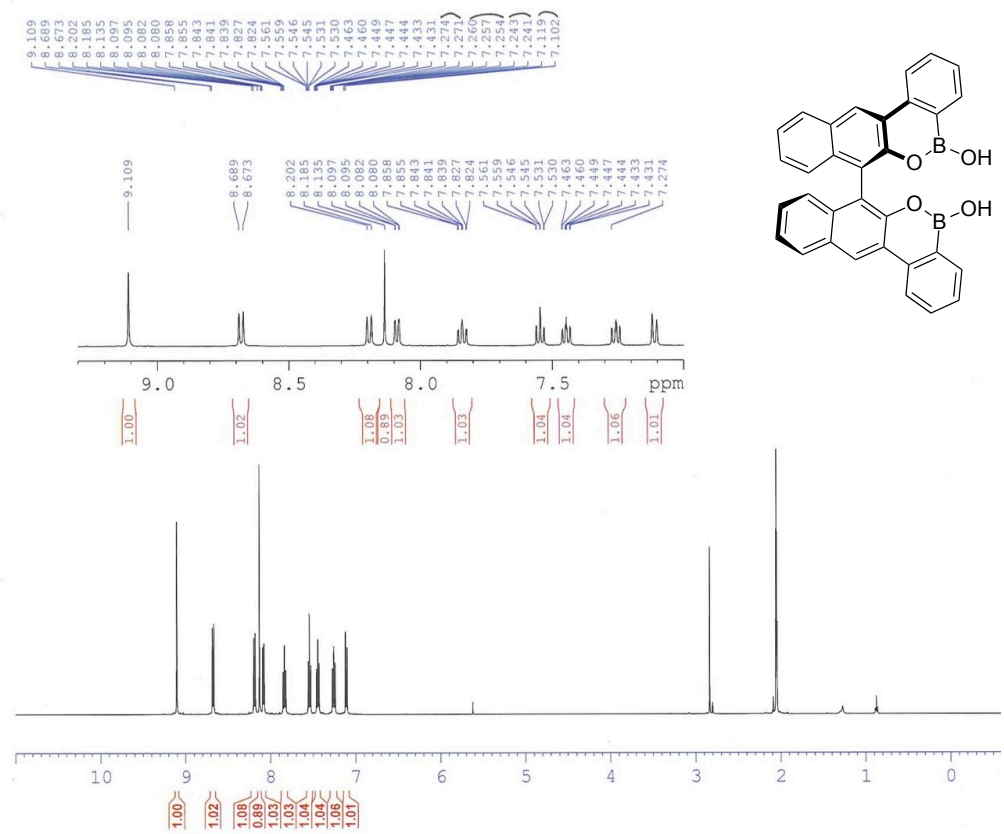
^{1}H, ^{13}C, and ^{11}B NMR spectra of **21** ($CDCl_3$)

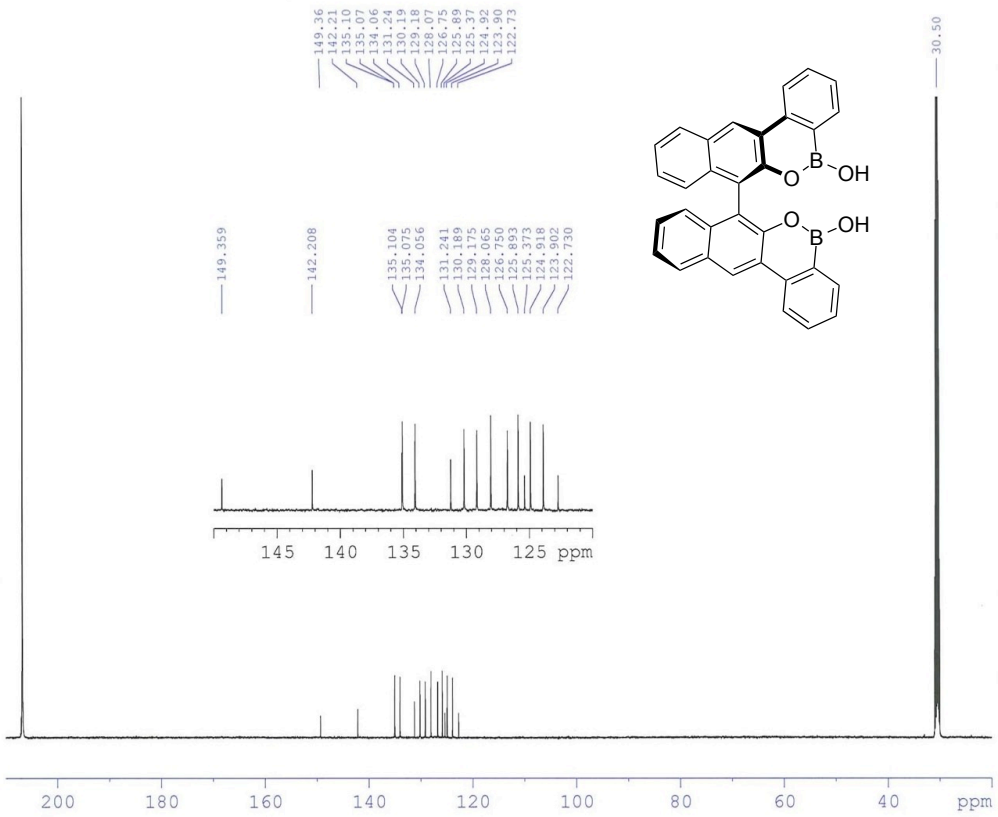


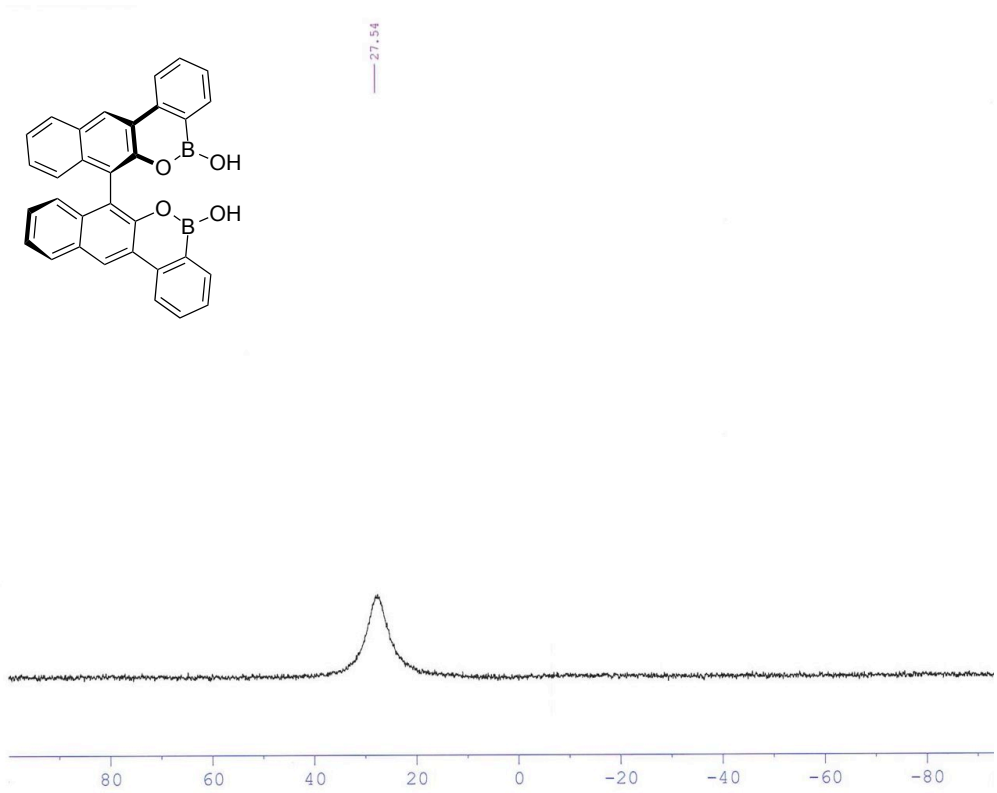




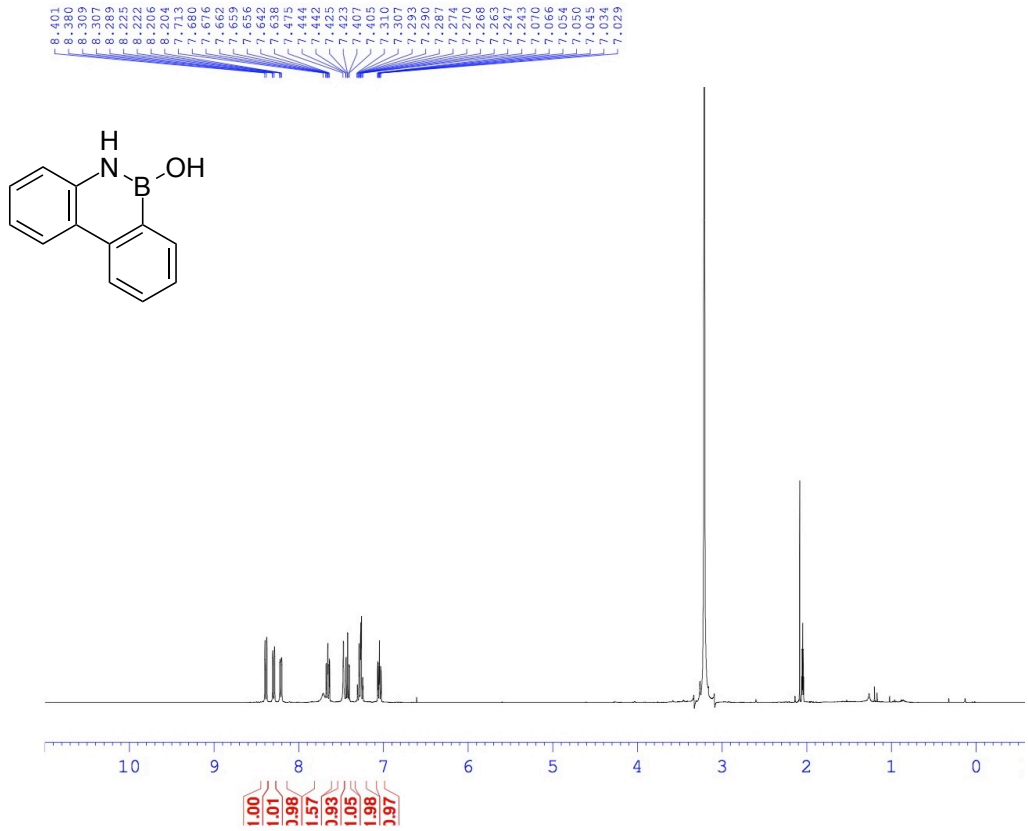
^{1}H, ^{13}C, and ^{11}B NMR spectra of **2p** (acetone-d_6)

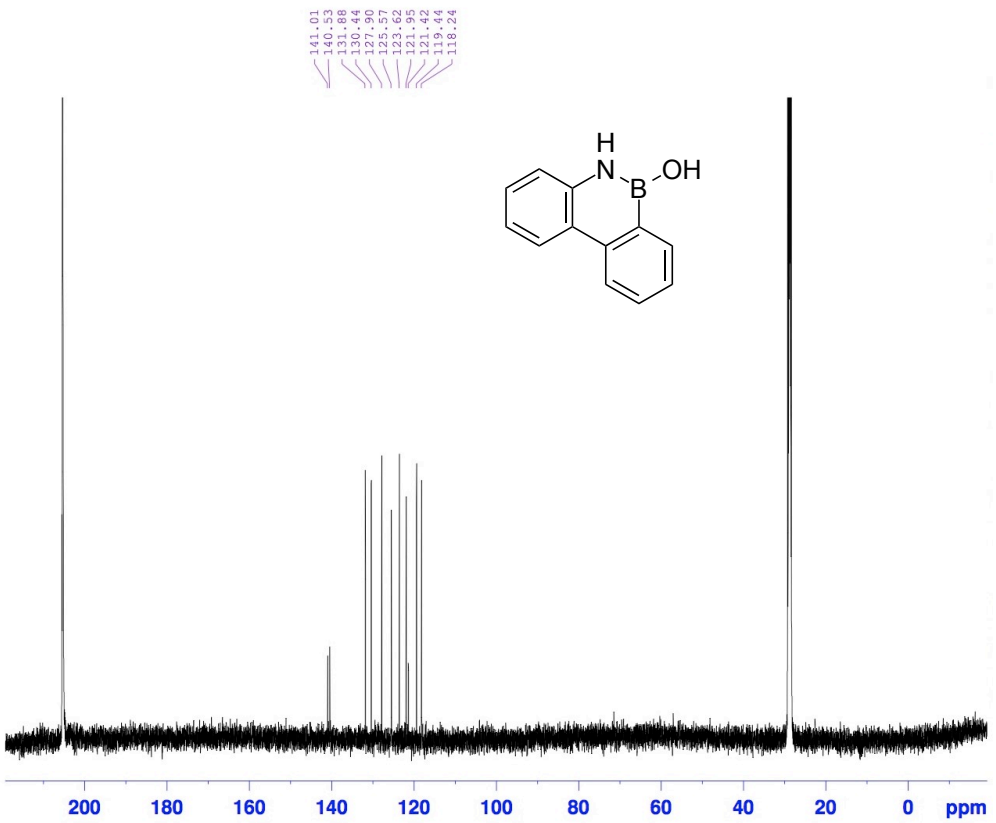



149.36
142.21
135.10
135.07
134.06
131.24
130.19
129.18
128.07
126.75
125.89
125.37
124.92
123.90
122.73
30.50
149.359
142.208
135.104
135.075
134.056
131.241
130.189
129.175
128.065
126.750
125.893
125.373
124.918
123.902
122.730
B
OH
O
145 140 135 130 125 ppm
200 180 160 140 120 100 80 60 40 ppm

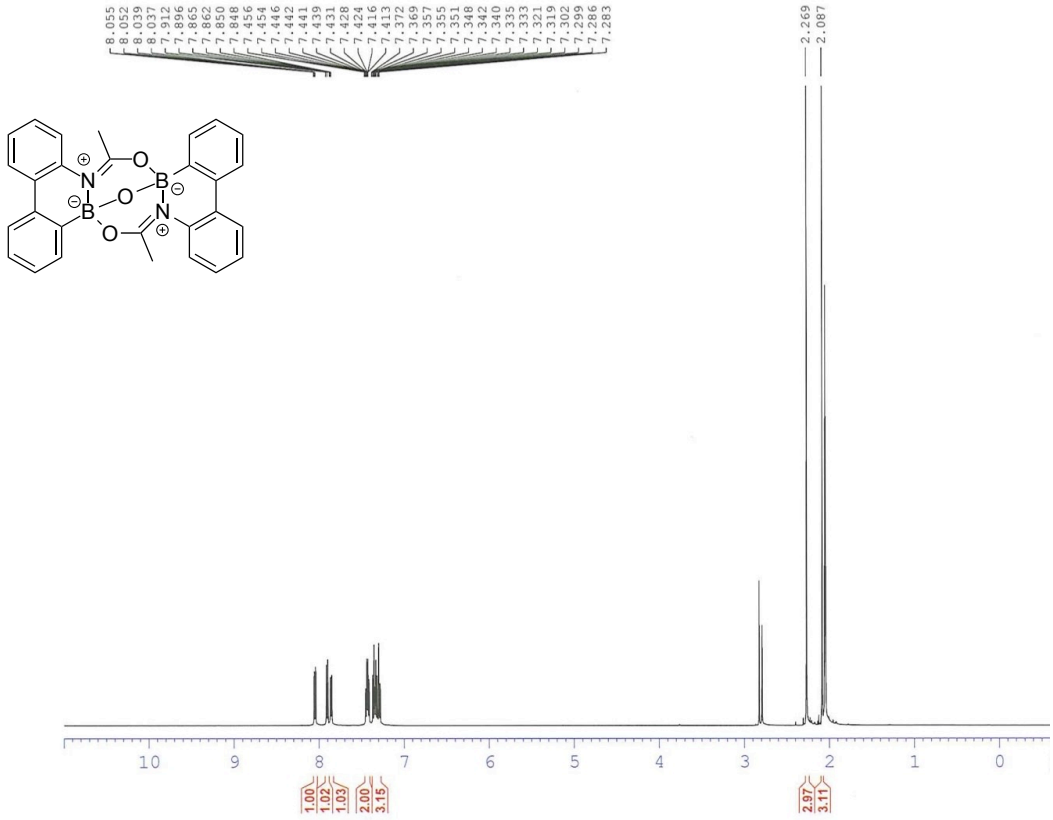

27.54
B
OH
O
80 60 40 20 0 -20 -40 -60 -80

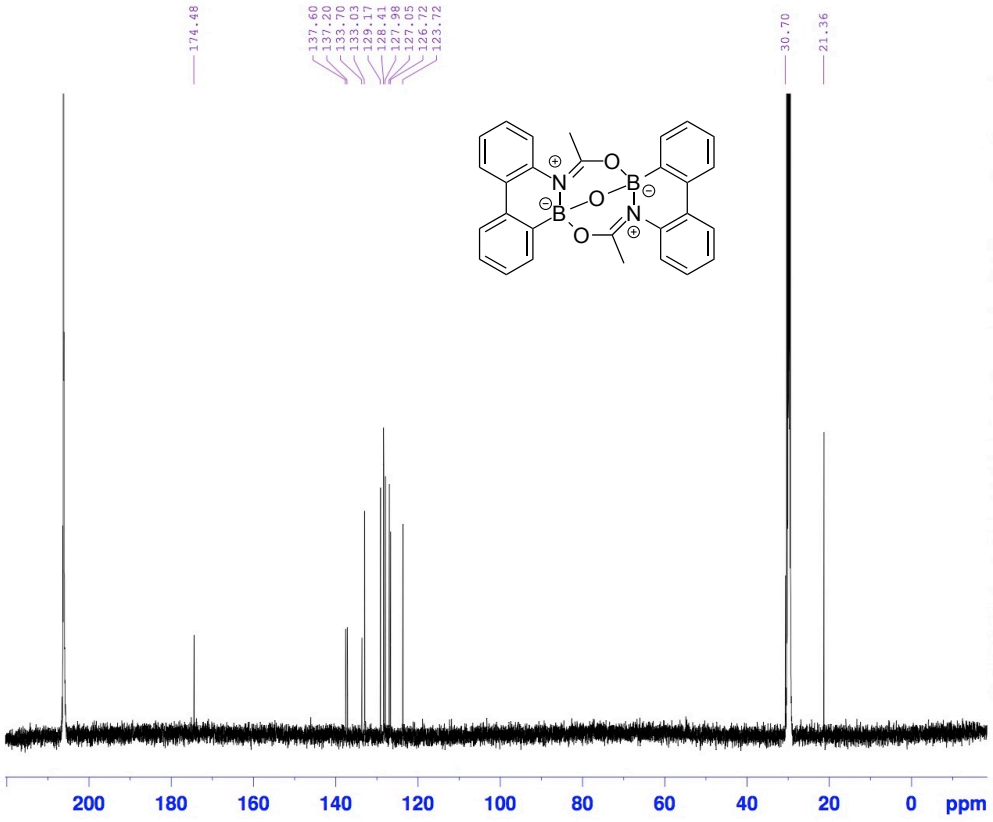
^{1}H and ^{13}C NMR spectra of **9** (acetone-d_6)

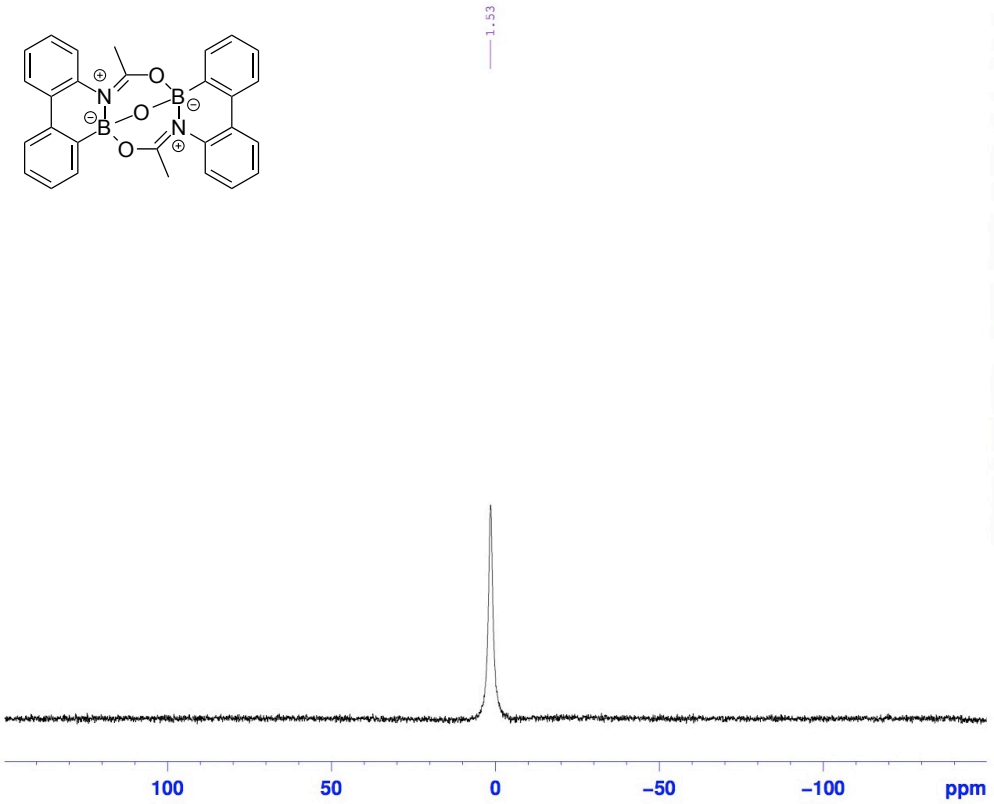




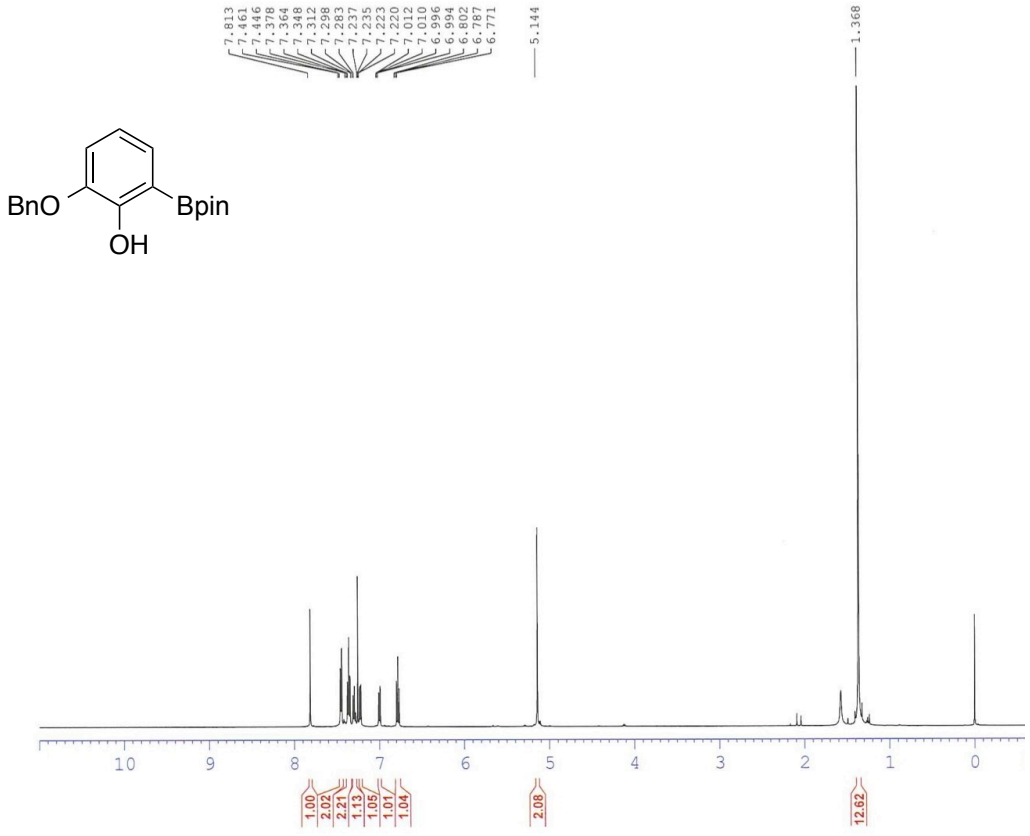
^{1}H, ^{13}C, and ^{11}B NMR spectra of **11** (acetone-d_6)

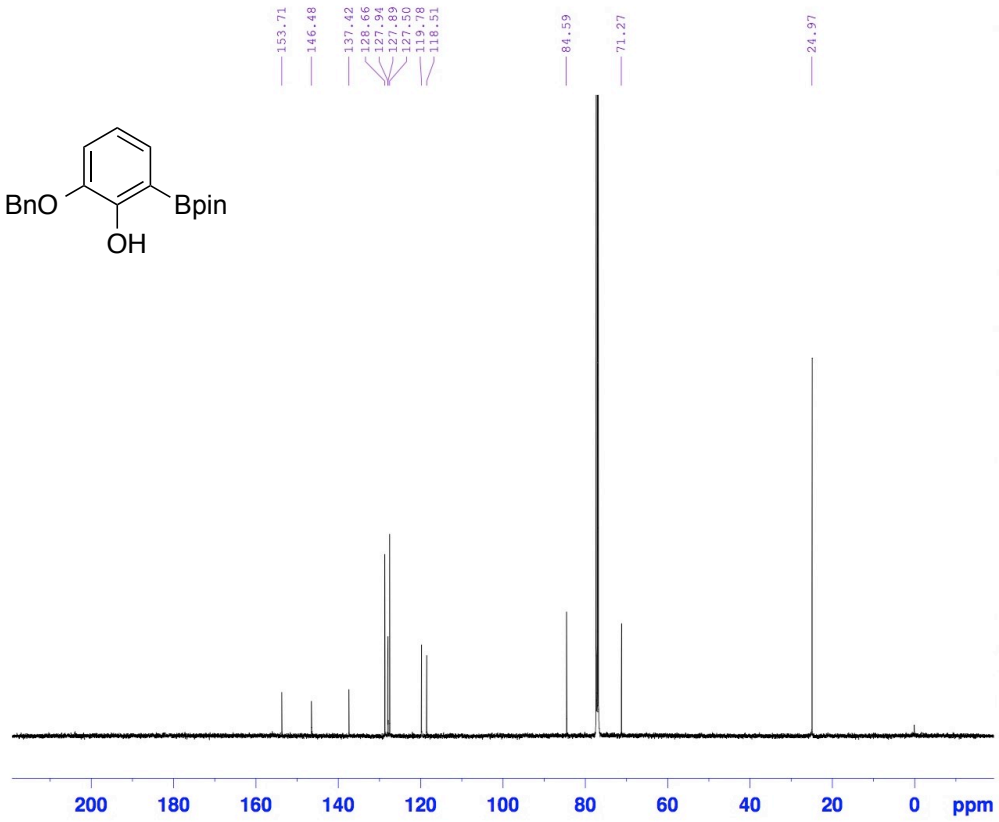


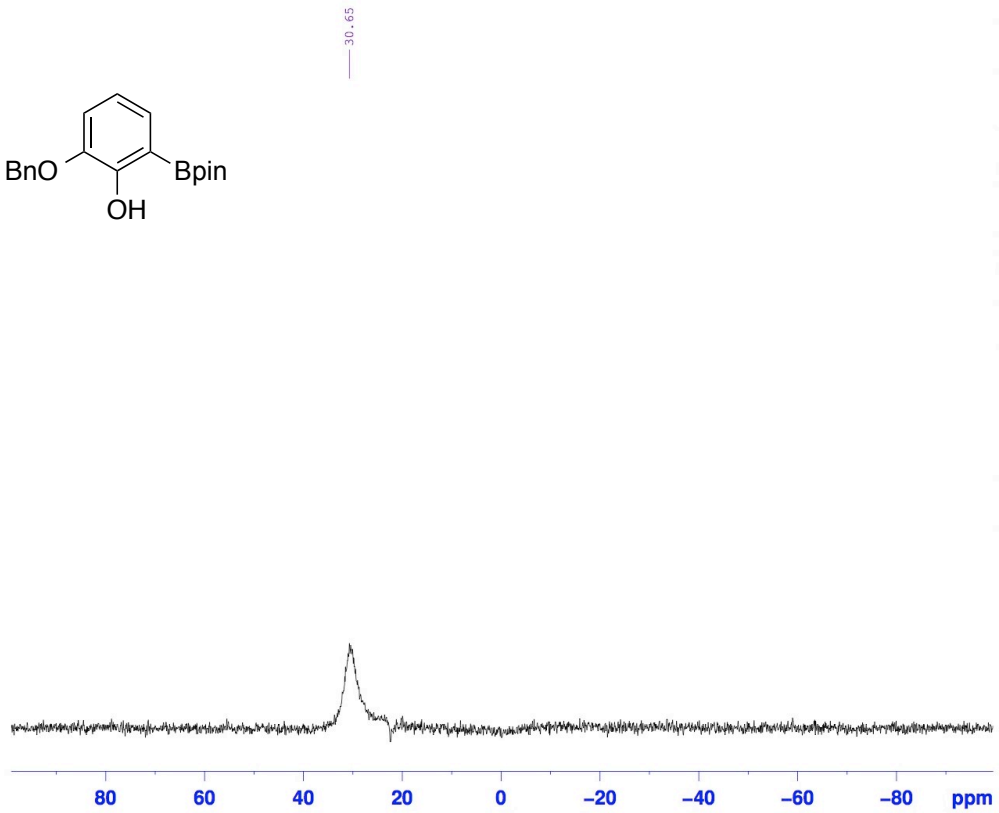




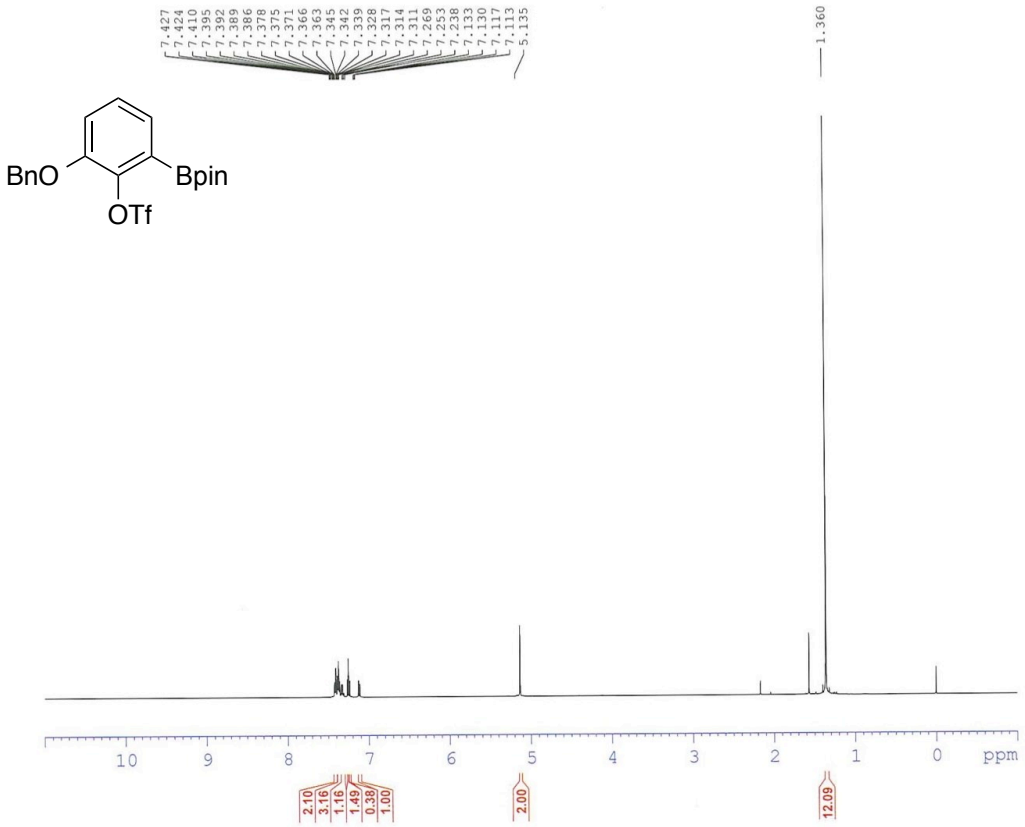
^{1}H, ^{13}C, and ^{11}B NMR spectra of **14** ($CDCl_3$)

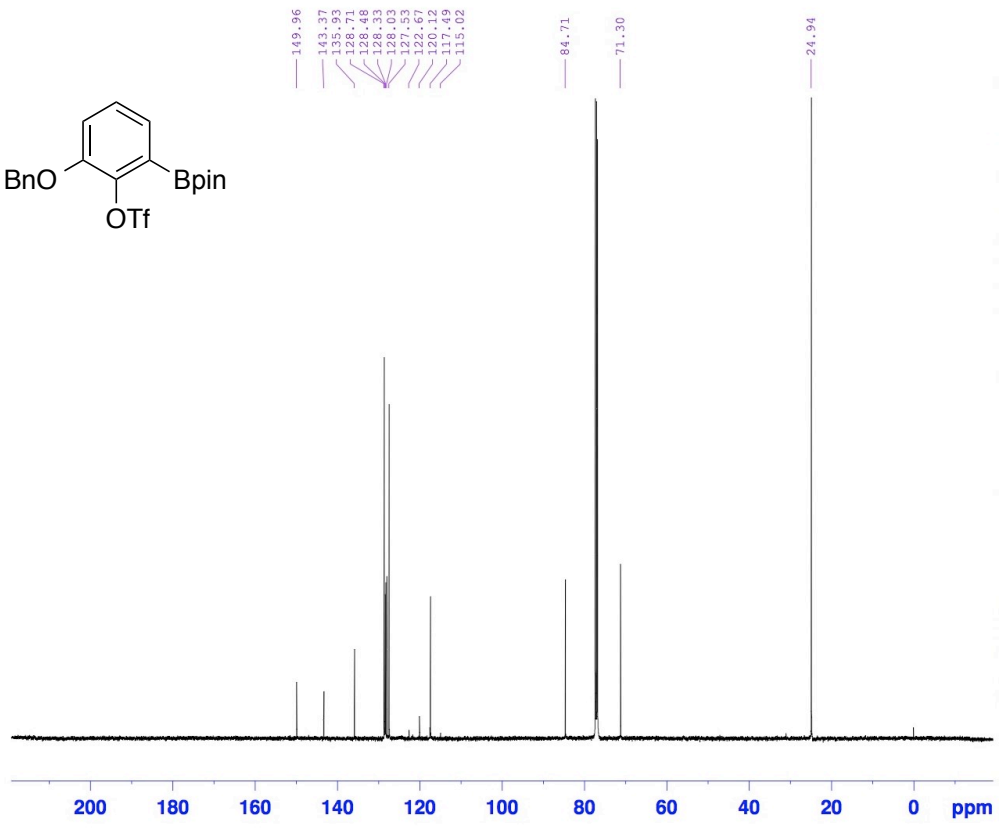


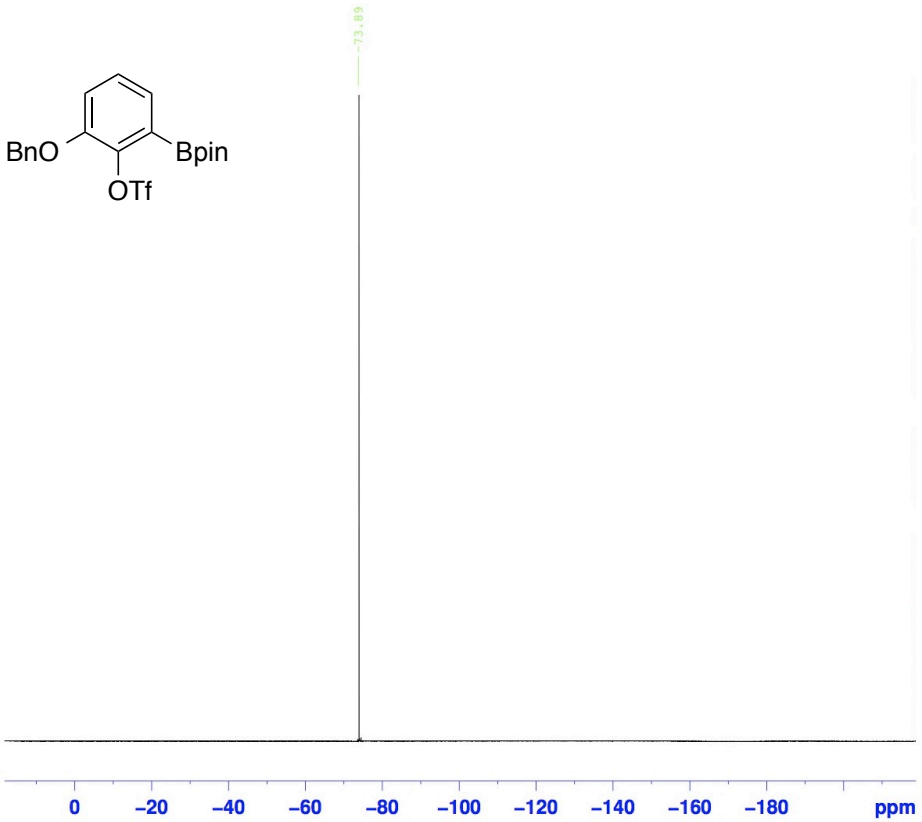

153.71
146.48
137.42
128.66
127.94
127.89
127.50
119.78
118.51
84.59
71.27
24.97
BnO
Bpin
OH
200
180
160
140
120
100
80
60
40
20
0
ppm

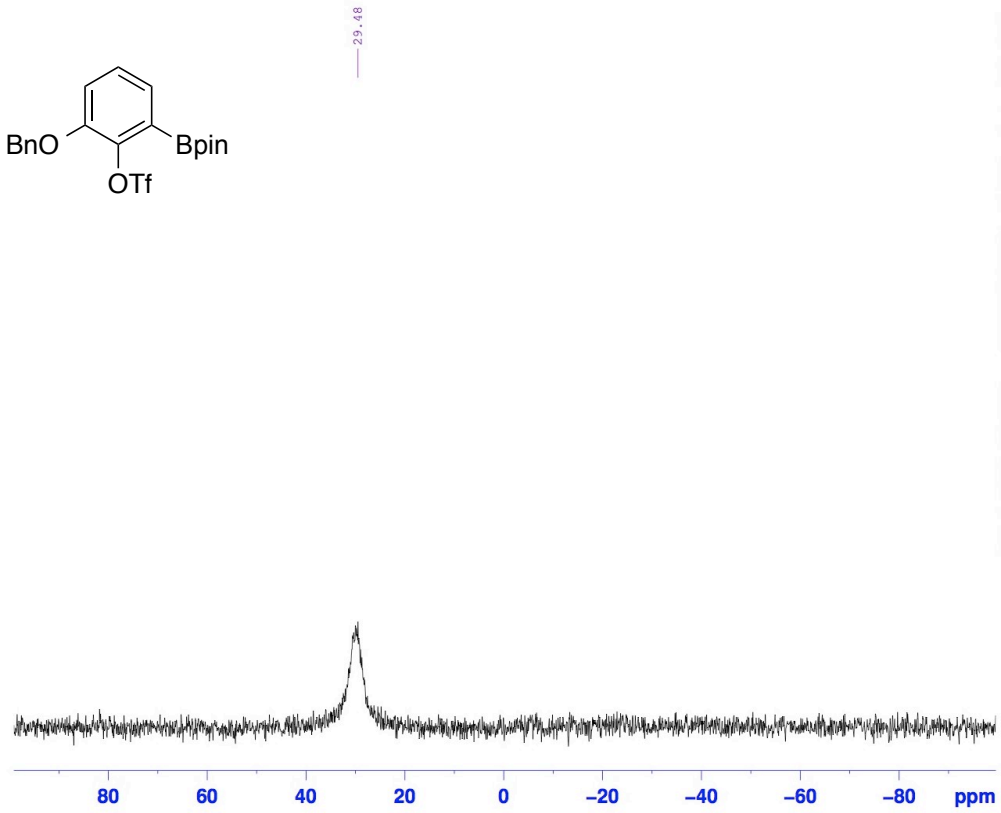

30.65
BnO
Bpin
OH
80
60
40
20
0
−20
−40
−60
−80
ppm

^{1}H, ^{13}C, ^{19}F, and ^{11}B NMR spectra of **15** ($CDCl_3$)

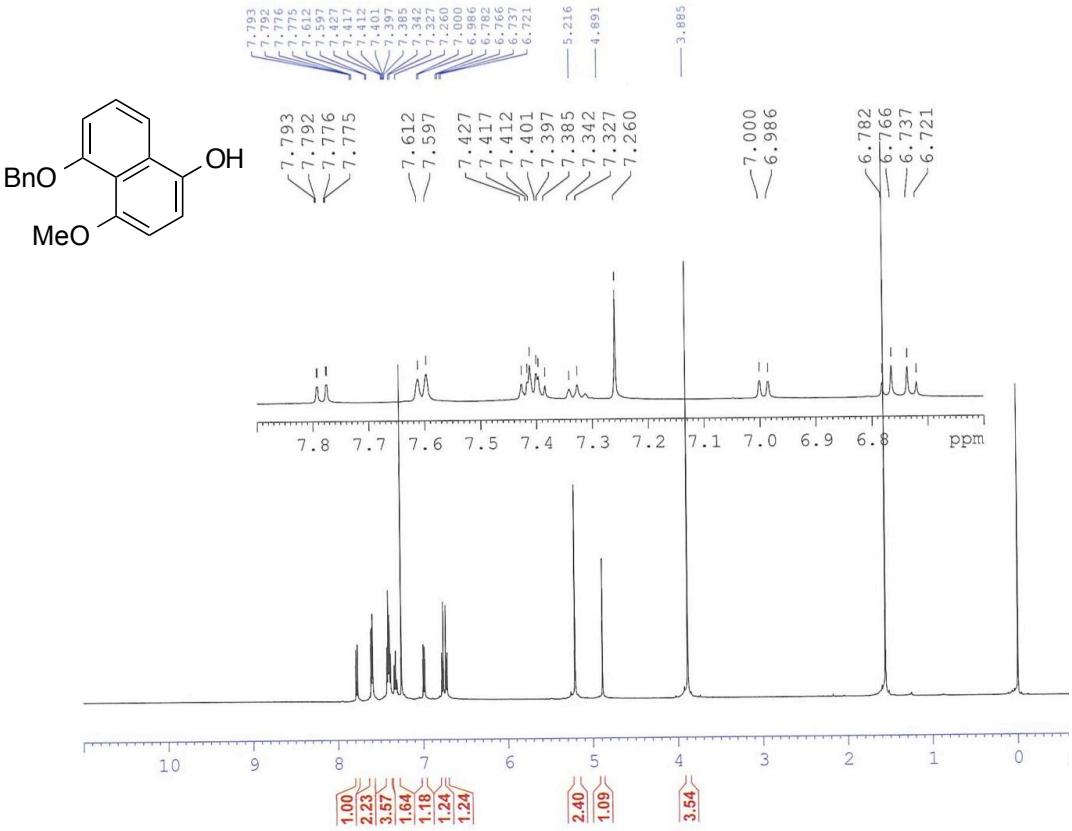


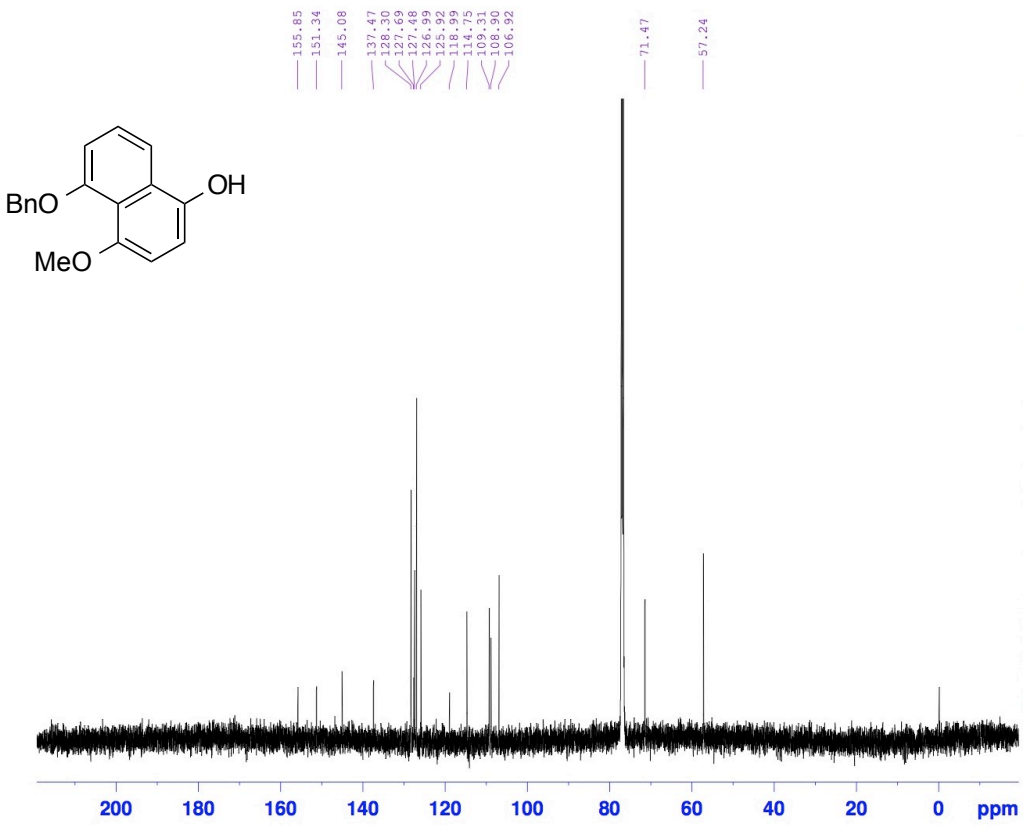



BnO
Bpin
OTf
-73.89
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

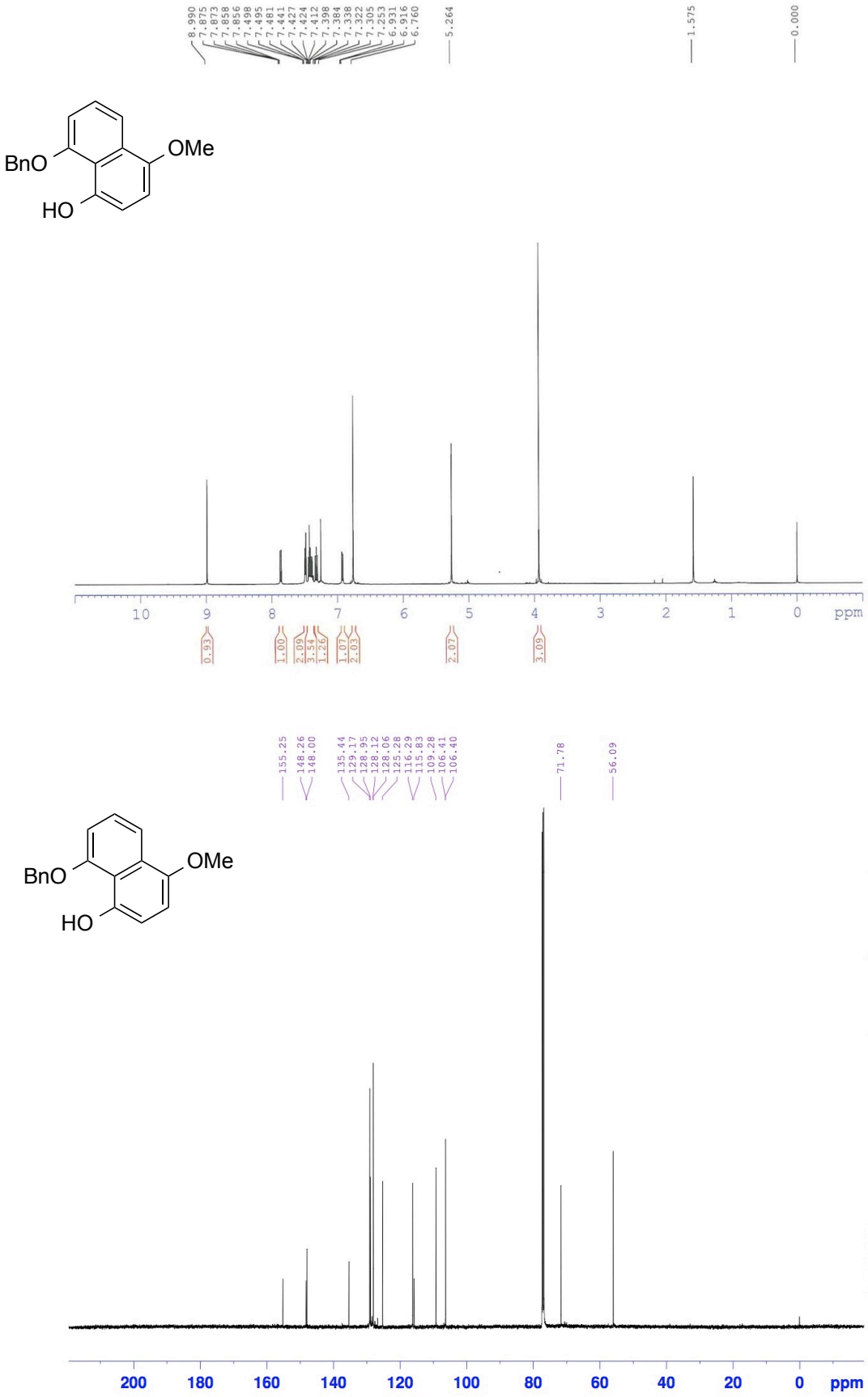

BnO
Bpin
OTf
29.48
80
60
40
20
0
-20
-40
-60
-80
ppm

^{1}H and ^{13}C NMR spectra of **16** ($CDCl_3$)

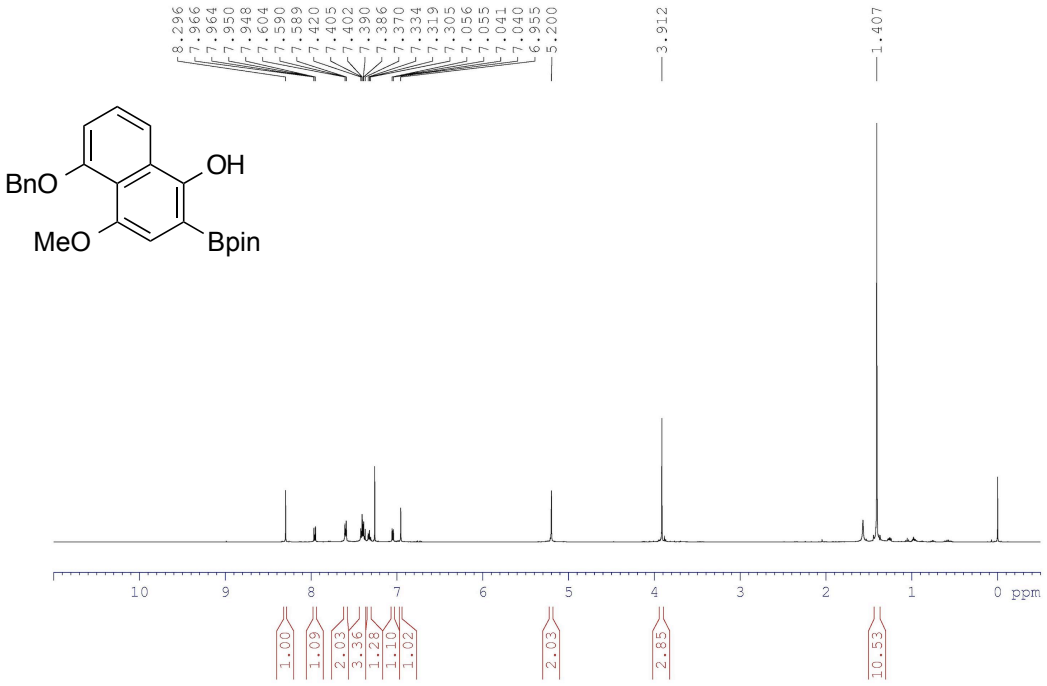


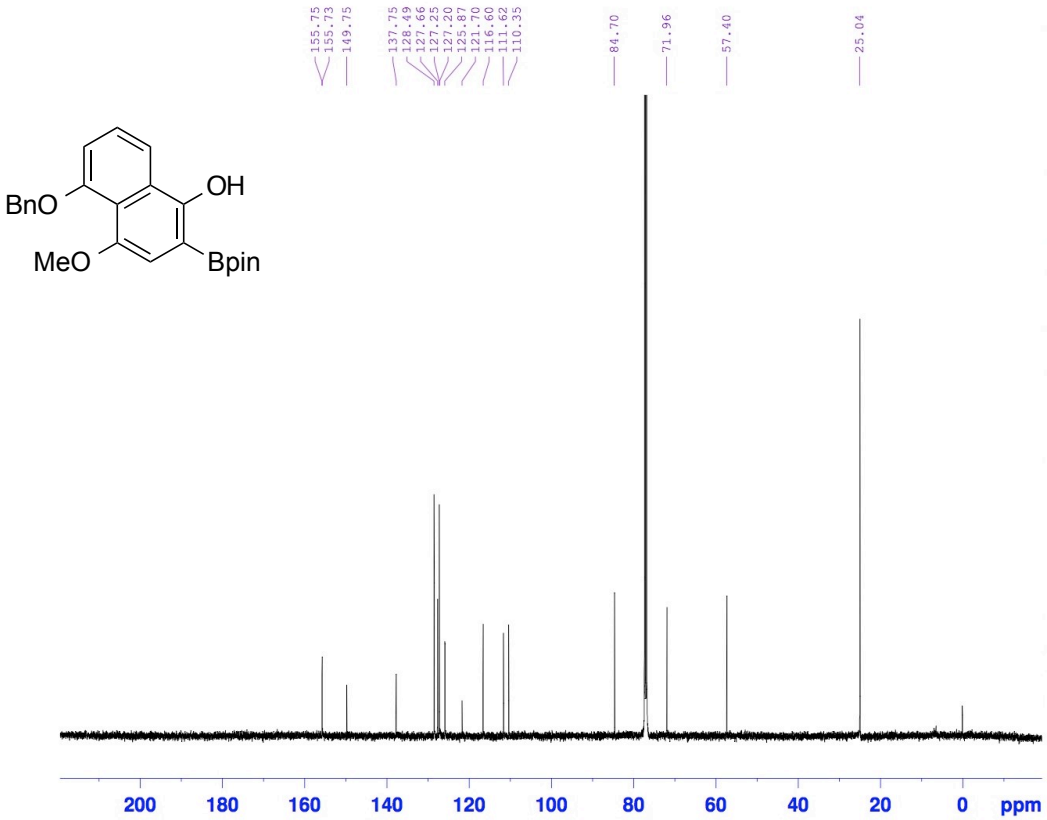


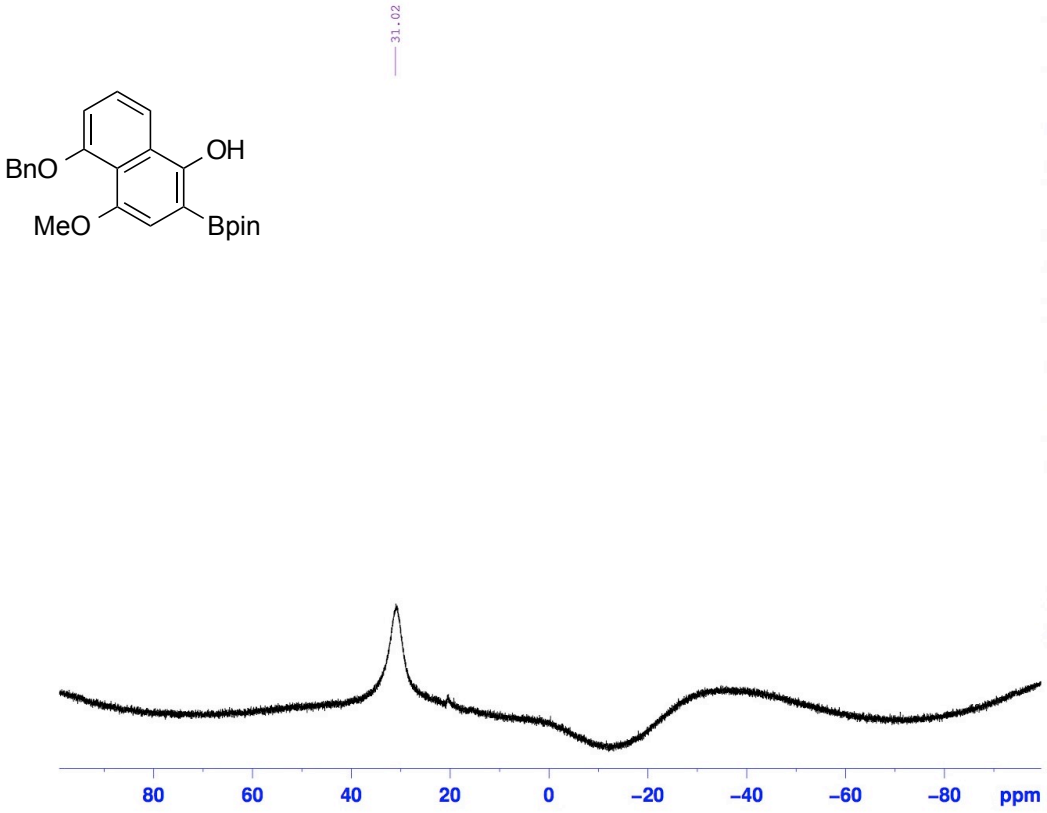
^{1}H and ^{13}C NMR spectra of **16′** ($CDCl_3$)



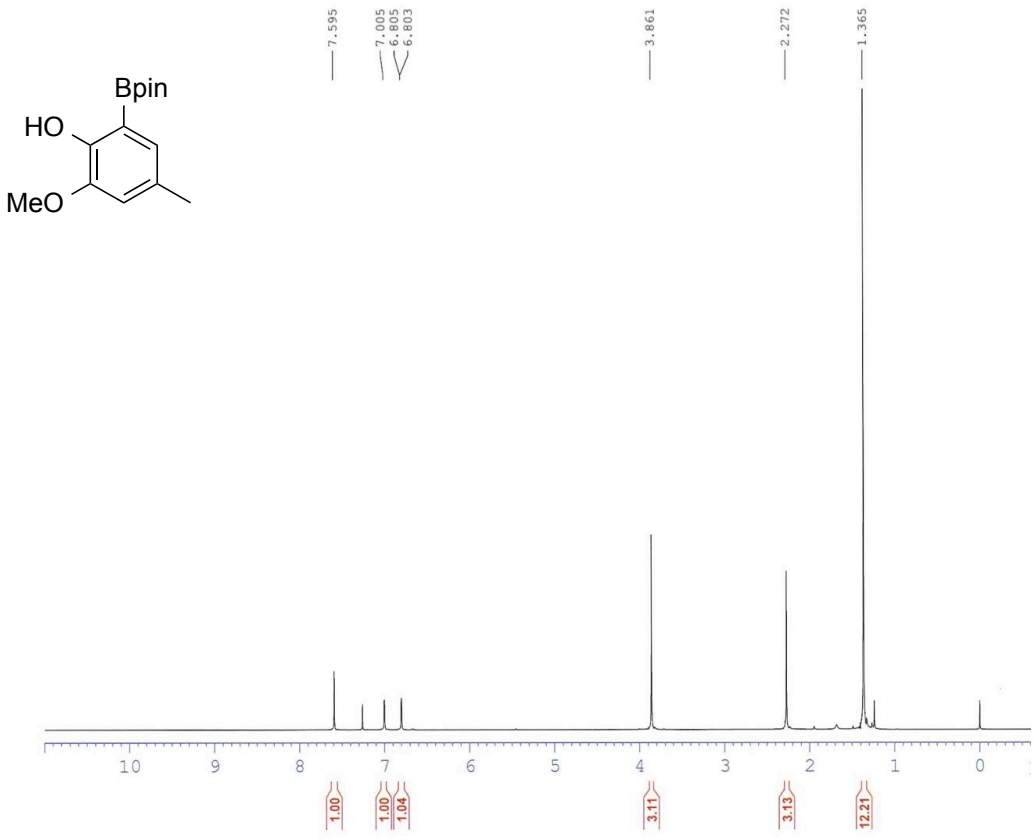
^{1}H and ^{13}C spectra ($CDCl_3$) and ^{11}B NMR spectra (acetone-d_6) of **3i**

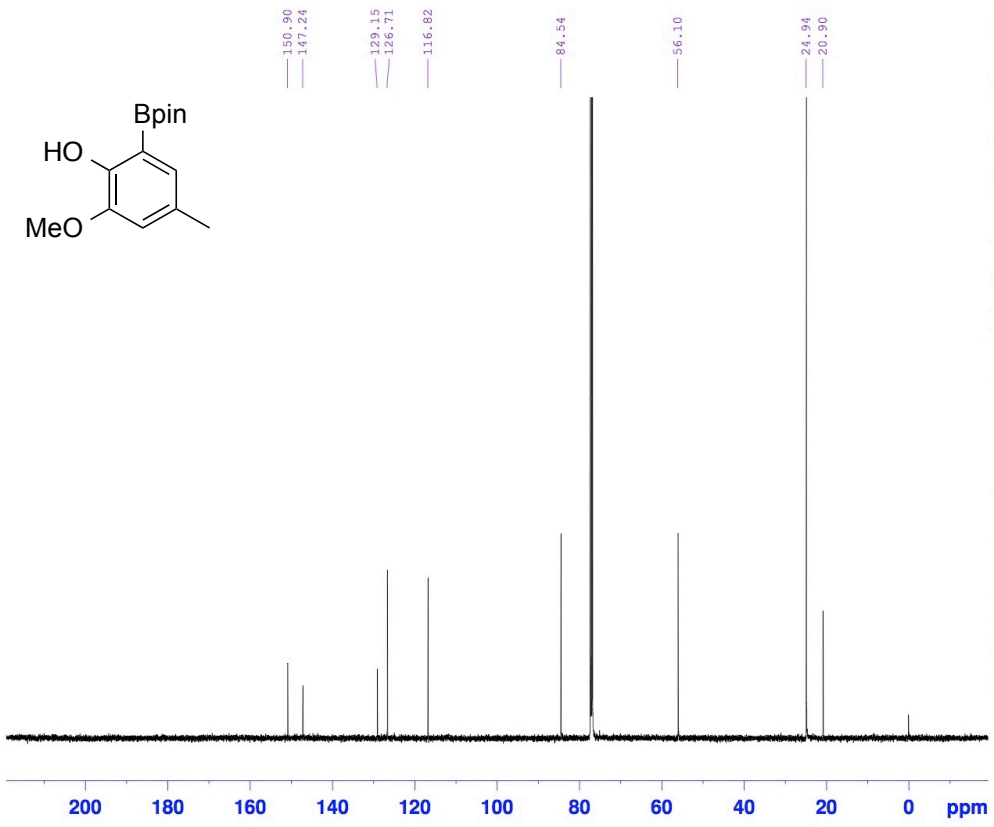


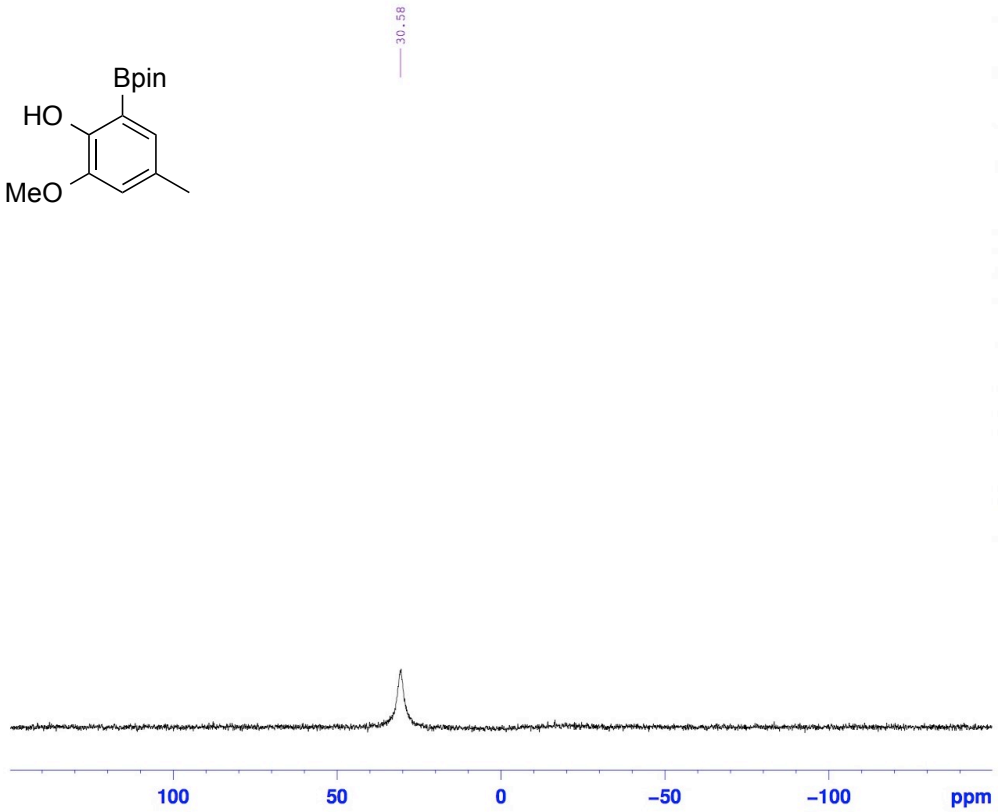




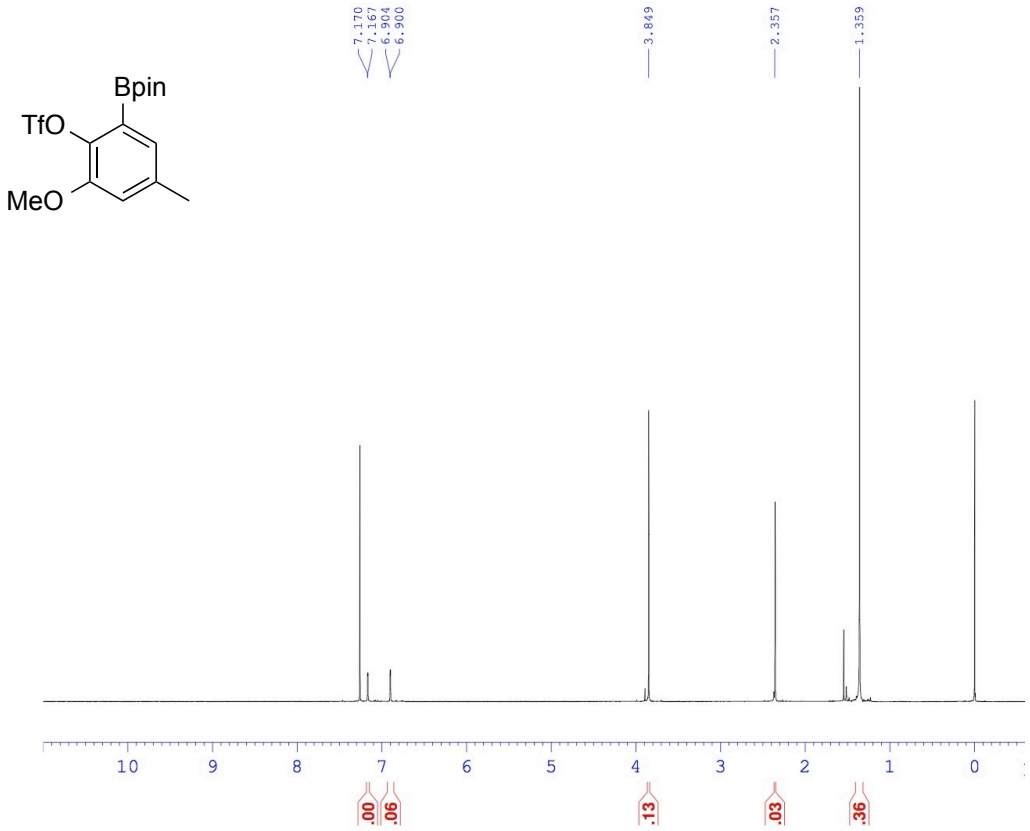
^{1}H, ^{13}C, and ^{11}B NMR spectra of **18** ($CDCl_3$)

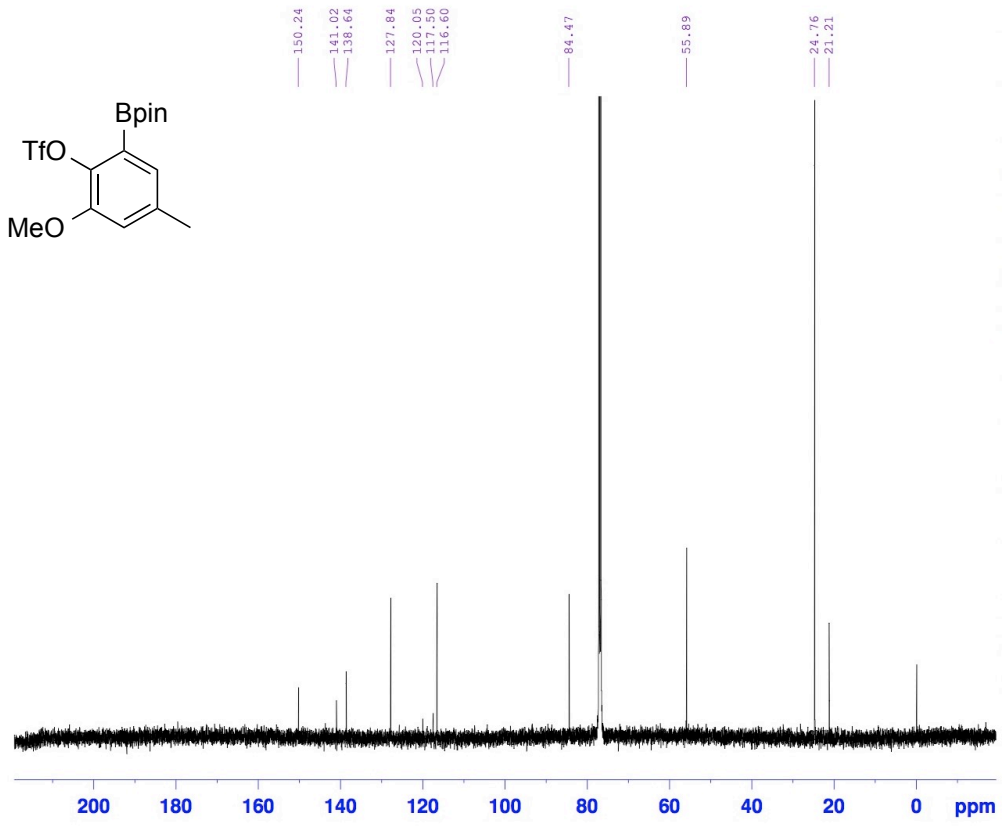


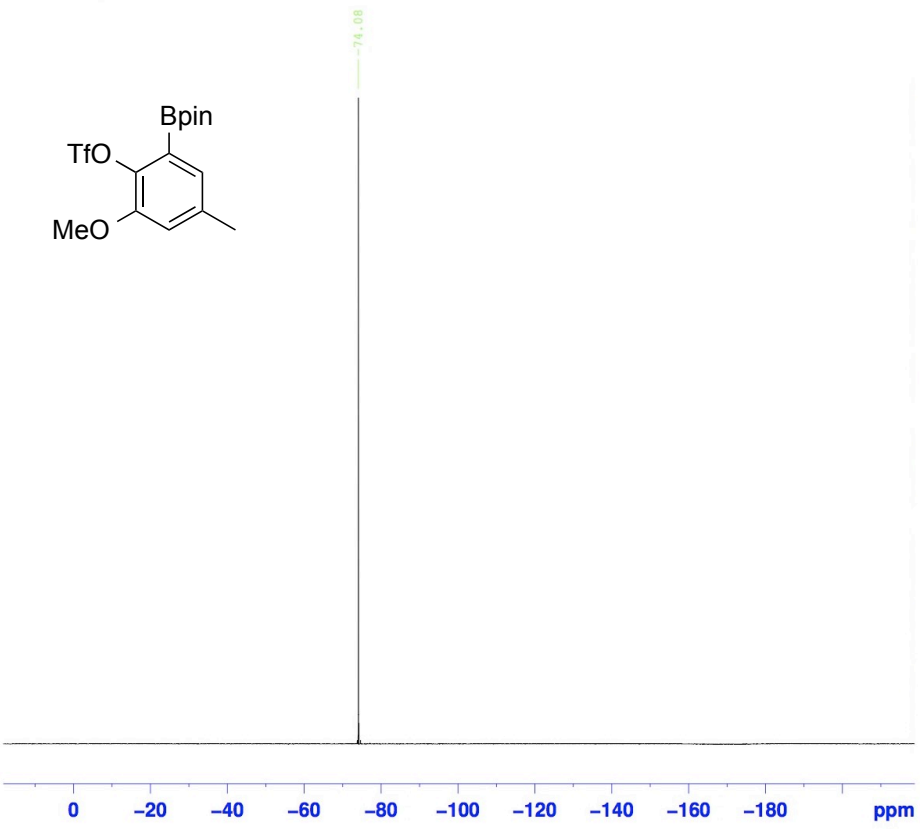

150.90
147.24
129.15
126.71
116.82
84.54
56.10
24.94
20.90
Bpin
HO
MeO
200
180
160
140
120
100
80
60
40
20
0
ppm

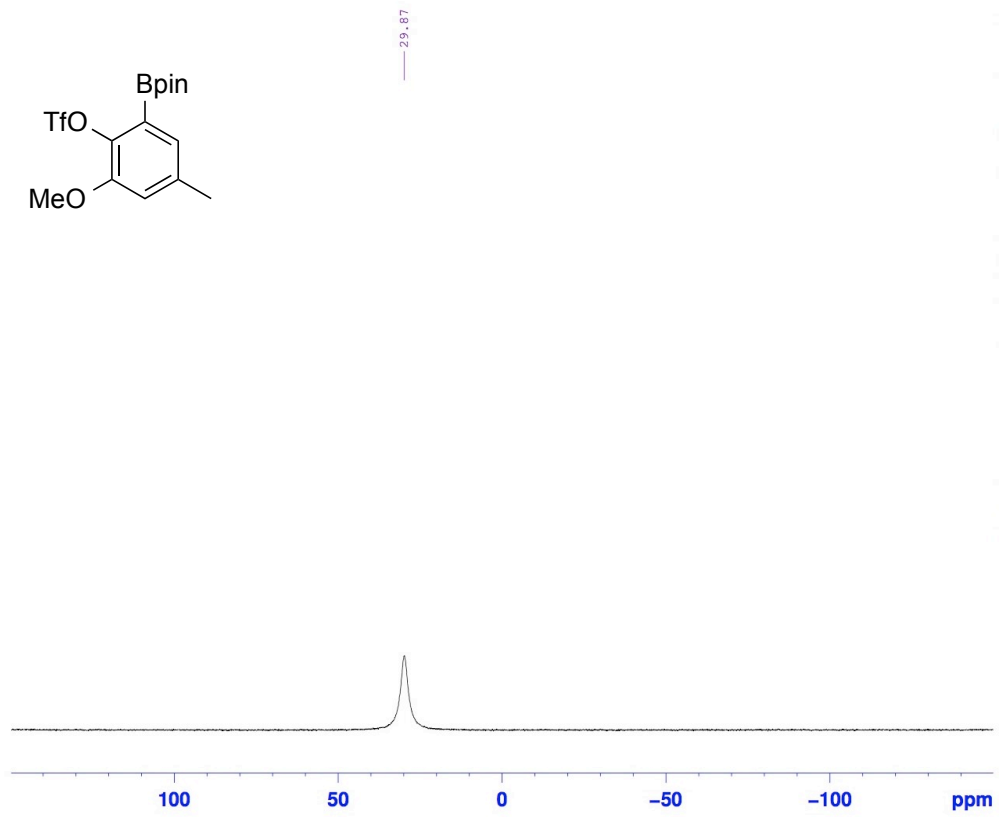

30.58
Bpin
HO
MeO
100
50
0
−50
−100
ppm

^{1}H, ^{13}C, ^{19}F, and ^{11}B NMR spectra of **19** ($CDCl_3$)

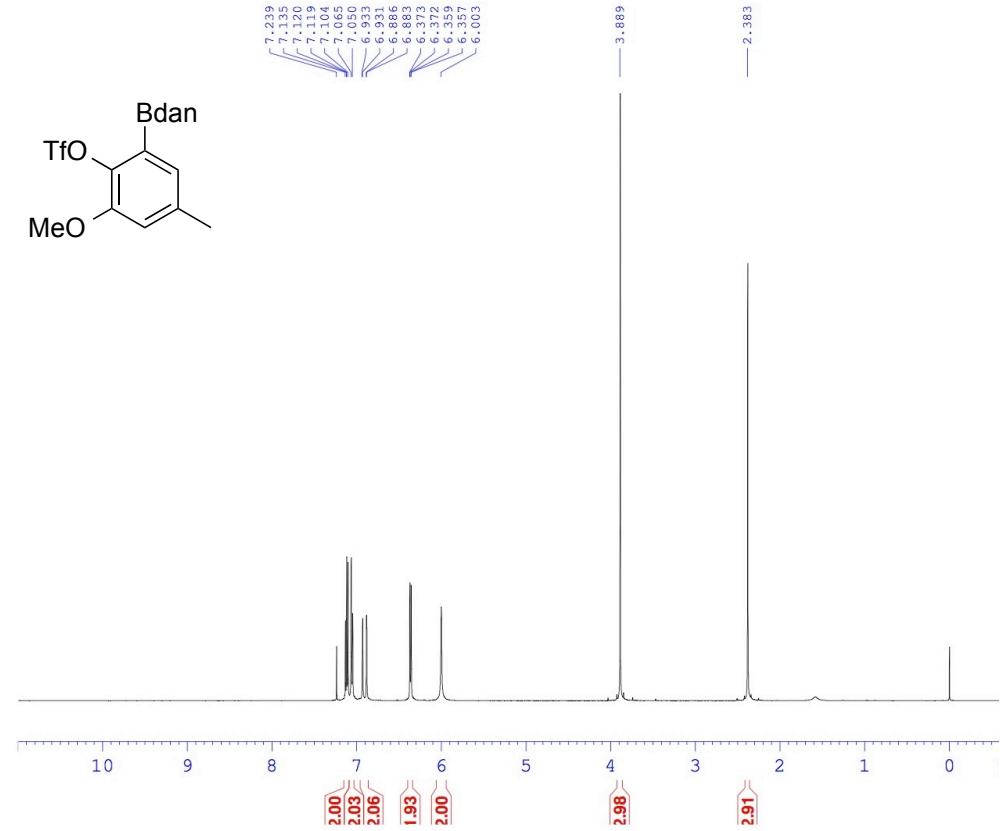


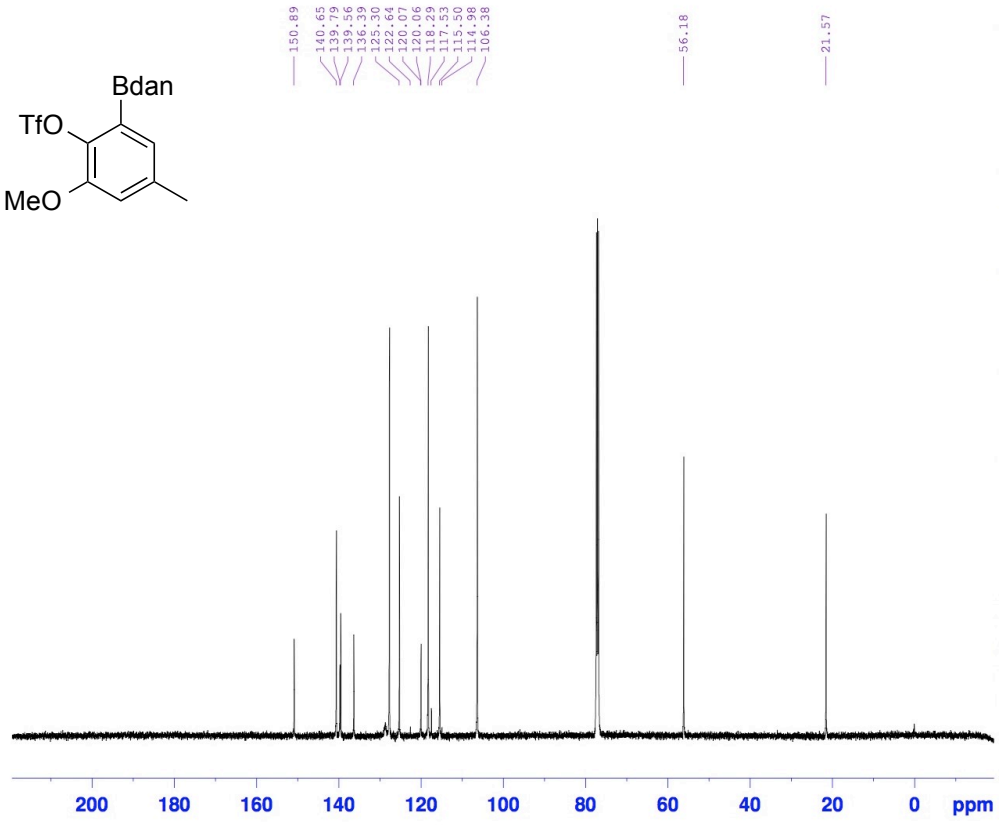


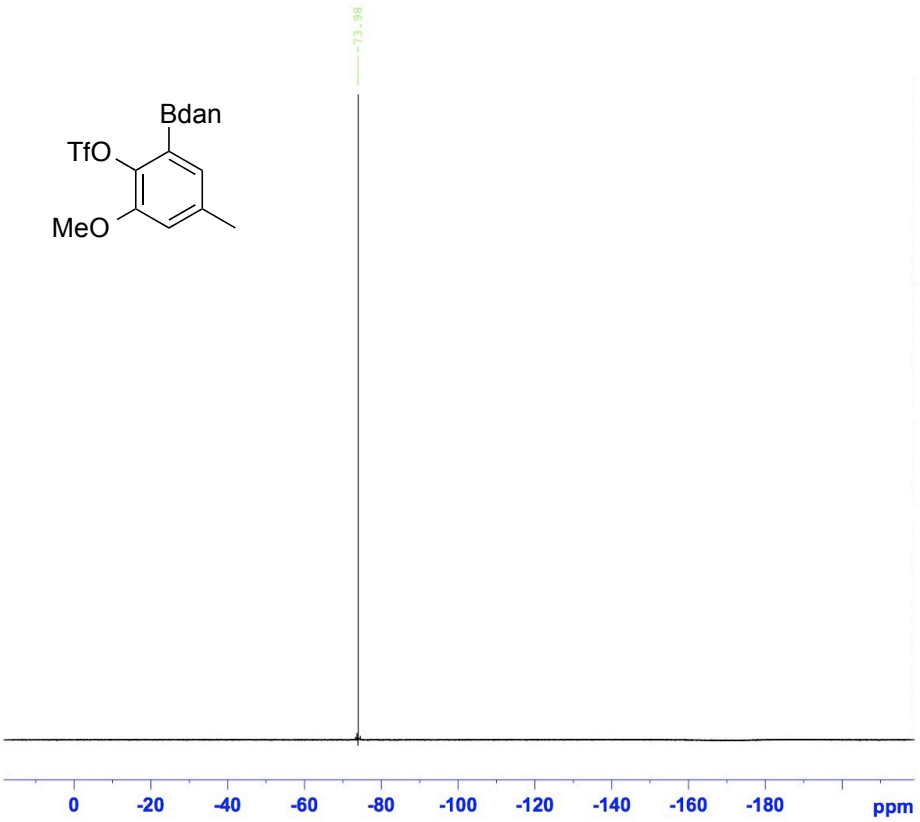

Bpin
TfO
MeO
-74.08
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

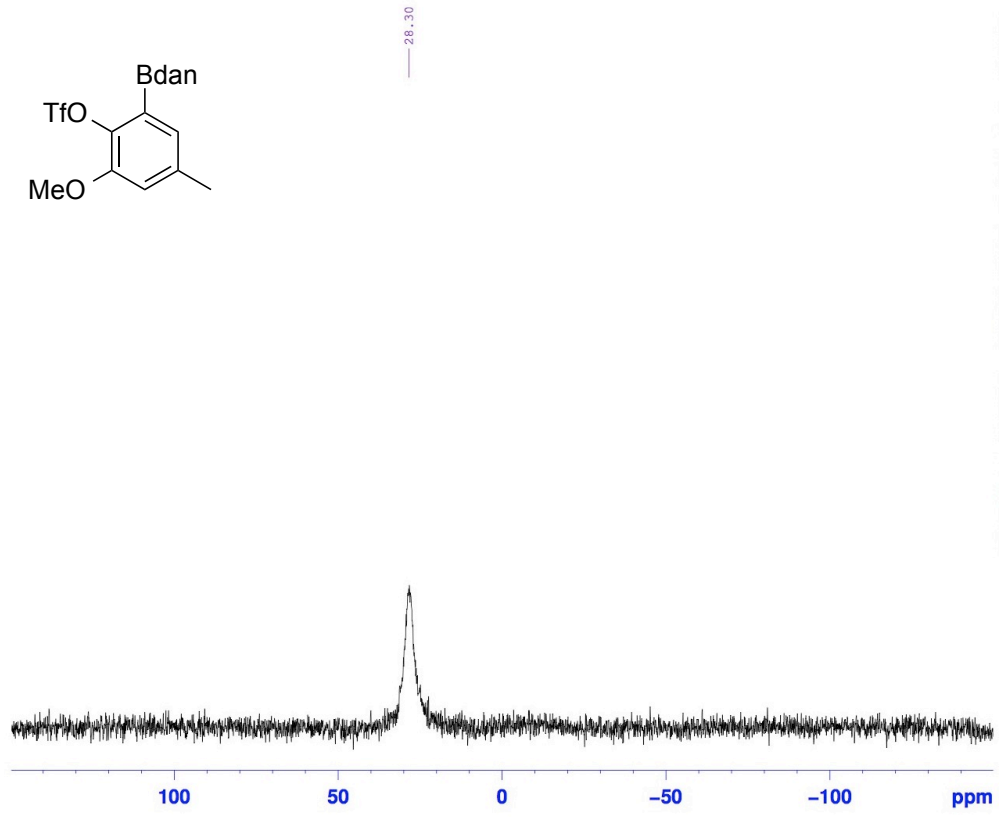

Bpin
TfO
MeO
29.87
100
50
0
-50
-100
ppm

^{1}H, ^{13}C, ^{19}F and ^{11}B NMR spectra of **4i** ($CDCl_3$)

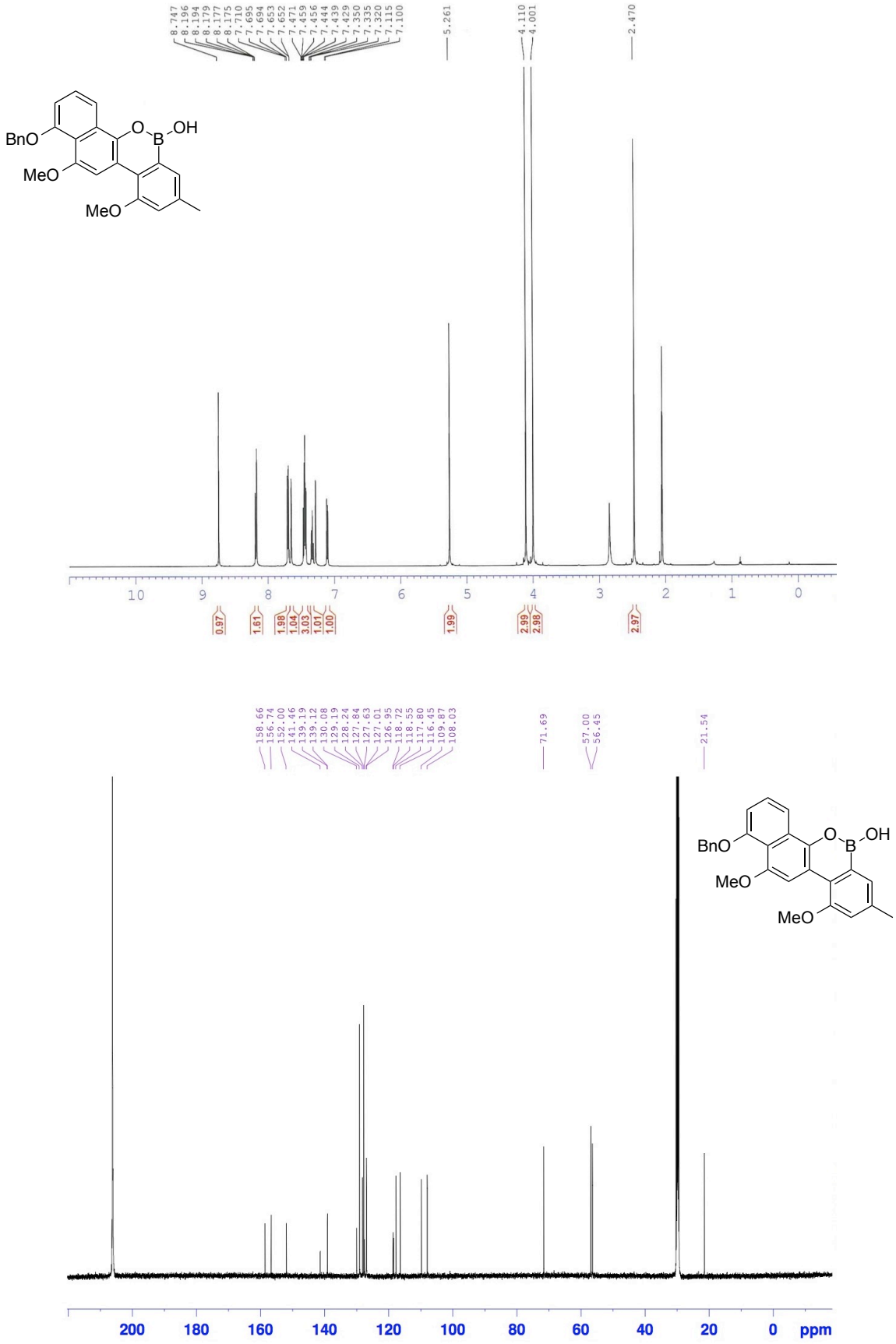


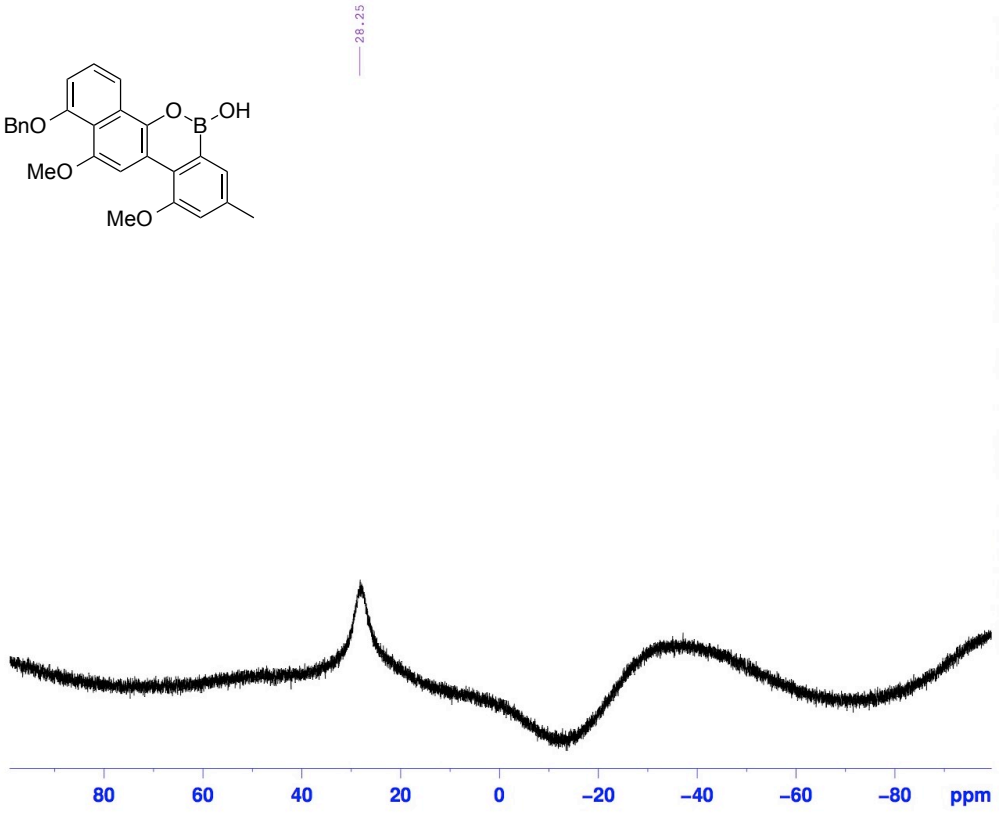



Bdan
TfO
MeO
-73.98
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

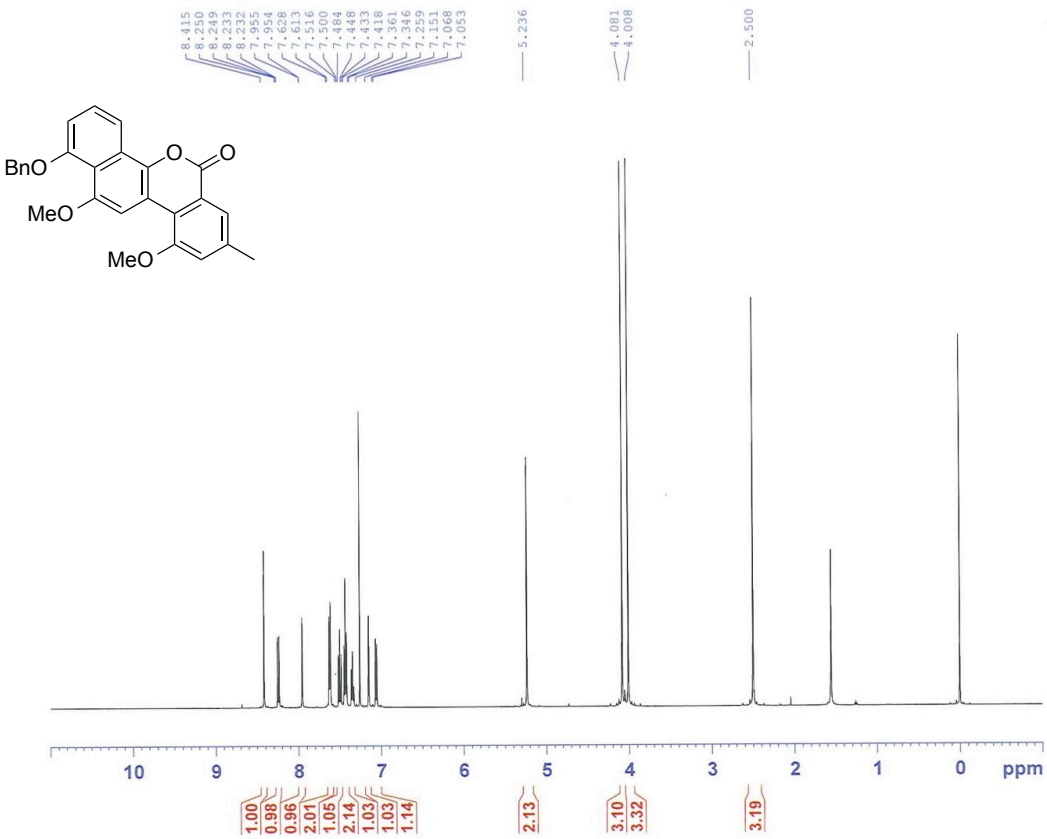

Bdan
TfO
MeO
28.30
100
50
0
-50
-100
ppm

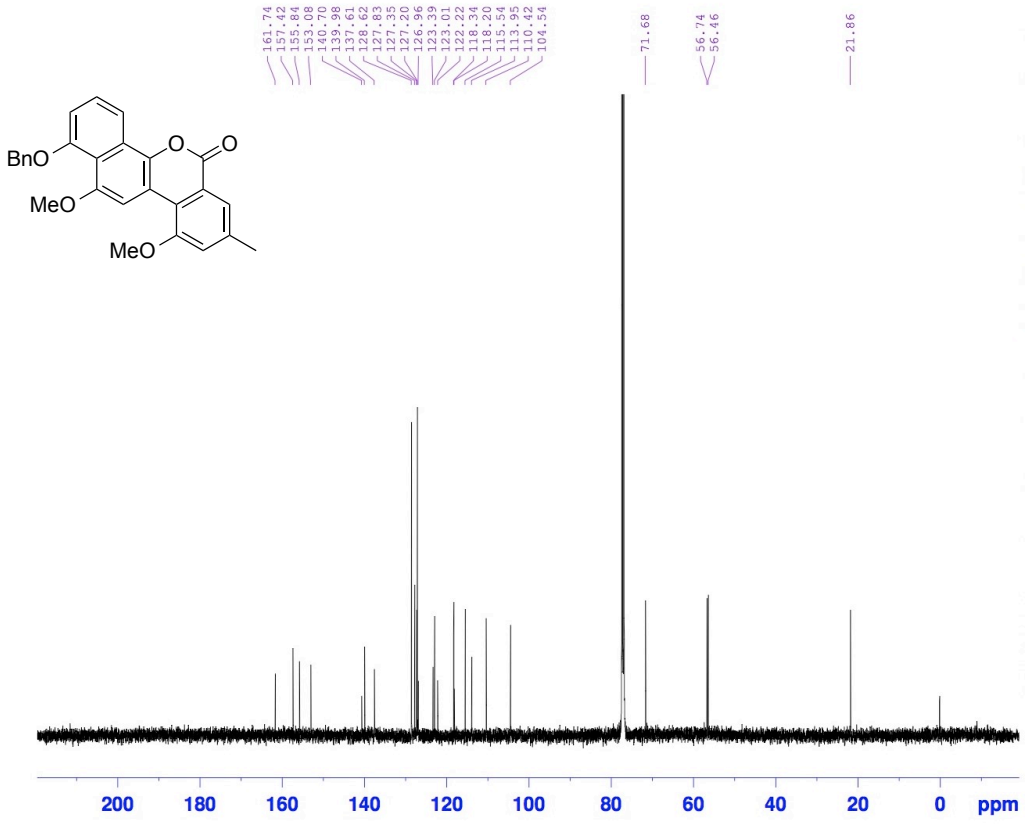
^{1}H, ^{13}C, and ^{11}B NMR spectra of **2q** (acetone-d_6)



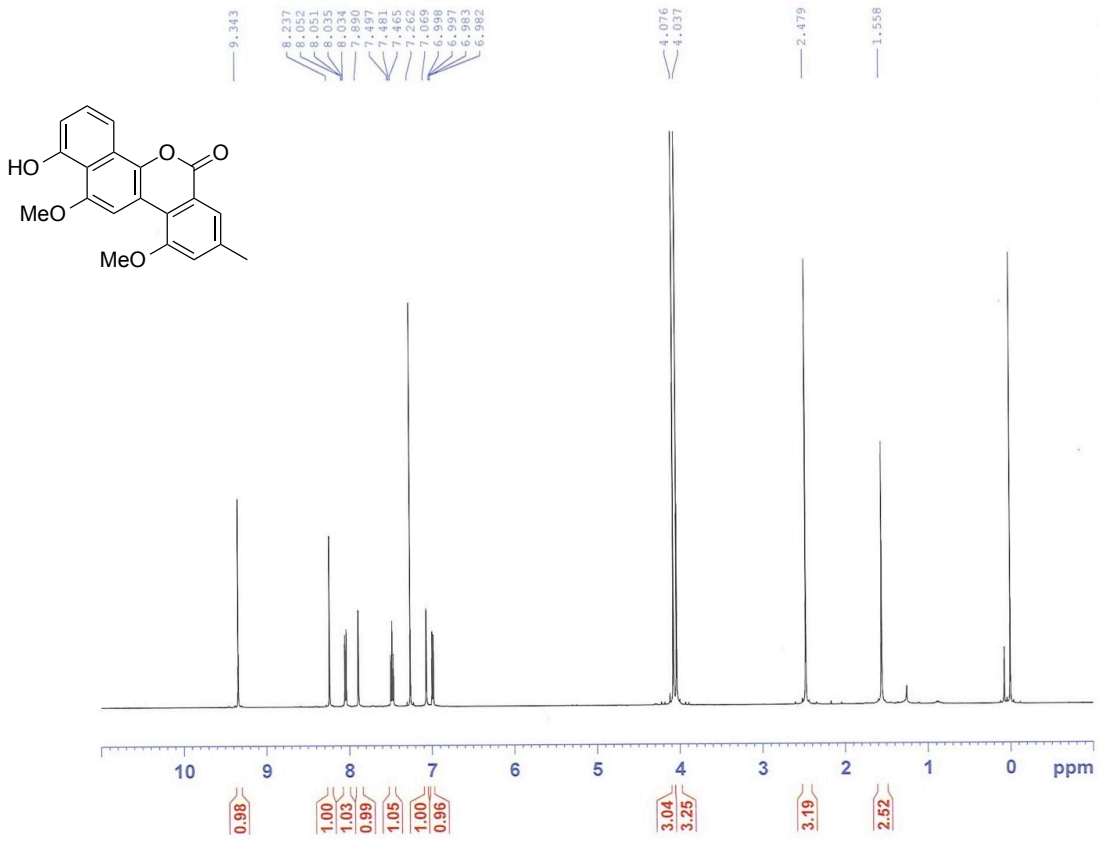


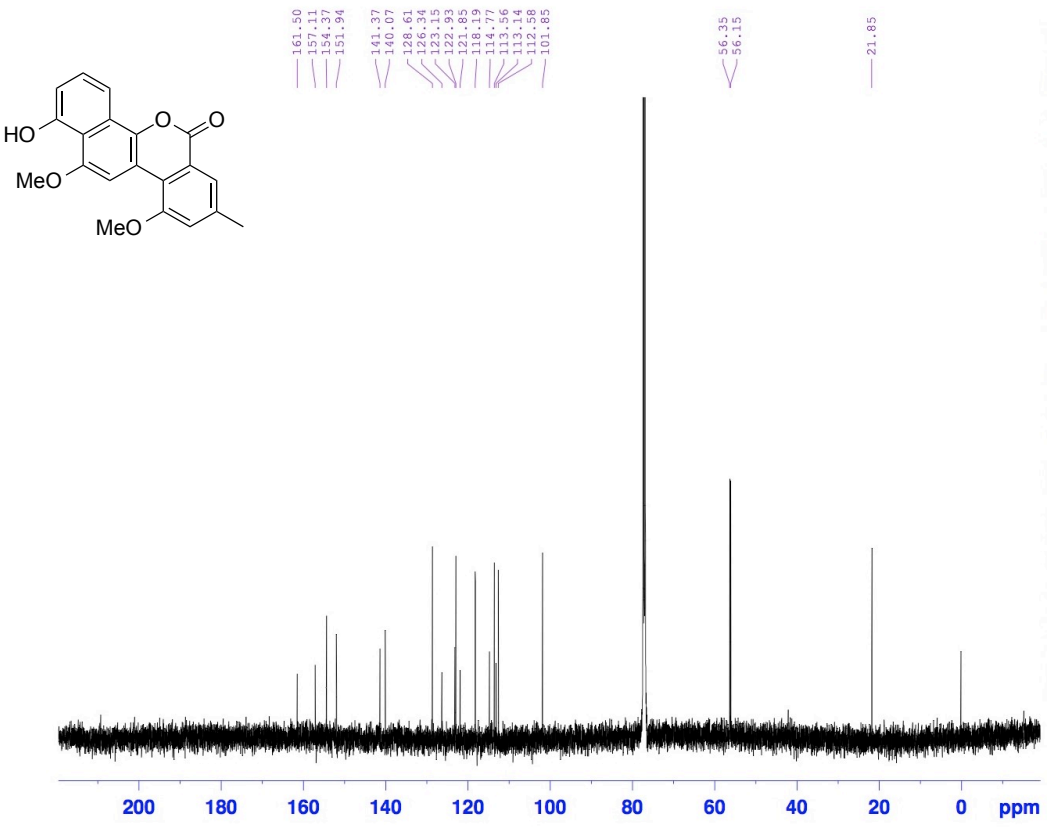
^{1}H and ^{13}C NMR spectra of **20** ($CDCl_3$)





^{1}H and ^{13}C NMR spectra of defucogirvocarcin M (**12**) ($CDCl_3$)




HO
MeO
MeO
O
O
161.50
157.11
154.37
151.94
141.37
140.07
128.61
126.34
123.15
122.93
121.85
118.19
114.77
113.56
113.14
112.58
101.85
56.35
56.15
21.85
200
180
160
140
120
100
80
60
40
20
0
ppm