

9-Hetero-10-boraanthracene-derived borinic acid catalysts for regioselective activation of polyols

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Electronic Supplementary Information

General: Reactions were carried out without effort to exclude air or moisture, unless otherwise indicated. Stainless steel syringes were used to transfer air- and moisture-sensitive liquids. Flash chromatography was carried out using neutral silica gel from Silicycle.

Materials: All reagents and solvents were purchased from Sigma Aldrich, Caledon, Carbosynth or Alfa Aesar and used without further purification. Acetonitrile and THF were purified by passing through two columns of activated alumina under argon (Innovative Technology, Inc.). Nuclear magnetic resonance (NMR) solvents were purchased from Cambridge Isotope Laboratories. Diphenylborinic acid was prepared from 2-aminoethyl diphenylborinate according to a reported procedure.¹

Instrumentation: ¹H and ¹³C NMR spectra were recorded in CDCl₃ or DMSO-*d*₆ using either a Bruker Avance III 400 MHz, Varian Mercury 300 or 400 MHz, or Agilent 500 or 600 MHz spectrometer. ¹H NMR are reported in parts per million (ppm) relative to tetramethylsilane and referenced to residual protium in the solvent. Spectral features are tabulated in the following order: chemical shift (δ , ppm); multiplicity (s-singlet, d-doublet, t-triplet, q-quartet, m-complex multiplet); number of protons; coupling constants (*J*, Hz). High-resolution mass spectra (HRMS) were obtained on a VS 70- 250S (double focusing) mass spectrometer at 70 eV. Infrared (IR) spectra were obtained on a Perkin-Elmer Spectrum 100 instrument equipped with a single-bounce diamond / ZnSe ATR accessory, either in the solid state or as neat liquids, as indicated. Spectral features are tabulated as follows: wavenumber (cm⁻¹); intensity (s-strong, m-medium, w-weak, br-broad). Optical absorption spectra were collected at room temperature on a Perkin-Elmer Lambda 35 spectrometer using 10 mm quartz cuvettes and corrected for background signal with a solvent-filled quartz cuvette. pH measurements were performed on a EcoMet P25 pH meter with a glass electrode. All solutions were prepared in 10 mM HEPES buffer in distilled water:methanol (1:3) and adjusted to pH 7.4.

¹ Lee, D.; Newman, S. G.; Taylor, M. S. *Org. Lett.* **2009**, *11*, 5486–5489.

I. Experimental and Characterization Data

Catalyst Synthesis

General procedure A. Procedure adapted from Letsinger and Nazy.² To an oven-dried Schlenk flask, equipped with a magnetic stirring bar, the corresponding organolithium or organomagnesium reagent (1 equiv.) was dropwise added over 1 h to a 0.6 M solution of phenylboronic acid 1,3-propanediol ester in anhydrous diethyl ether under argon, at -78 °C. After stirring the resulting suspension for 1 h at that temperature, it was allowed to warm to room temperature overnight. 4 N HCl was added and the solution stirred under argon for 20 minutes. The aqueous layer was then removed *via* syringe, maintaining the remaining solution under argon. The ethereal layer was washed with water. A 0.007 M solution containing 2.5 equivs. of 2-aminoethanol in methanol was added *via* syringe, and the resulting suspension was stirred overnight. Following this (the reaction could be exposed to air at this point), water was added and the ethereal layer was removed using a rotary evaporator to crash out the product as a white solid, which could then be filtered and dried.

2-Methyl-2-phenyl-1,3,2-oxazaborolidin-3-ium-2-uide. Synthesized according to general procedure A using MeMgBr in 43% yield as a white solid, in agreement with previous reports.² **¹H NMR (400 MHz; CD₃OD):** δ 7.39 (d, *J* = 7.0 Hz, 1H), 7.30 (d, *J* = 7.3 Hz, 1H), 7.14-7.11 (m, 2H), 7.02-6.99 (m, 1H), 3.72 (t, *J* = 5.1 Hz, 2H), 3.35 (s, 3H), 2.97 (t, *J* = 5.0 Hz, 2H).

2-Butyl-2-phenyl-1,3,2-oxazaborolidin-3-ium-2-uide. Synthesized according to general procedure A using *n*-butyllithium in 50% yield, white solid. **¹H NMR (400 MHz; CDCl₃):** δ 7.42 (d, *J* = 6.7 Hz, 2H), 7.30-7.25 (m, 2H), 7.19 (dd, *J* = 9.4, 5.1 Hz, 1H), 3.98 (t, *J* = 6.2 Hz, 2H), 3.73 (br, 2H), 2.98 (br, 2H), 1.28 (tt, *J* = 7.2, 7.2 Hz, 2H), 1.18-1.10 (m, 2H), 0.83 (t, *J* = 7.2 Hz, 3H), 0.60-0.56 (m, 2H). **¹³C NMR (75 MHz; CDCl₃):** δ 131.15, 127.73, 126.22, 63.37, 42.35, 28.42, 26.66, 14.31, 12.85. **IR (powder, cm⁻¹):** 3330 (w), 2960 (m), 2915 (m), 2867 (m), 1612 (m), 1430 (w), 1210 (m), 1172 (m), 1069 (s), 946 (m), 737 (s), 700 (s). **HRMS (DART, m/z):** Calculated for C₁₂H₂₁BNO [(M+H)⁺]: 206.17162. Found: 206.17197.

2-(*sec*-Butyl)-2-phenyl-1,3,2-oxazaborolidin-3-ium-2-uide. Synthesized according to general procedure A using *sec*-butyllithium. Isolated as a diastereomeric mixture in 18% yield, white solid. Major diastereoisomer: **¹H NMR (400 MHz; CDCl₃):** δ 7.41-7.36 (m, 2H), 7.30-7.26 (m, 2H), 7.18 (tt, *J* = 7.2, 1.8 Hz, 1H), 3.93 (t, *J* = 6 Hz, 2H), 3.79-3.77 (br, 2H), 2.98 (t, *J* = 6.0 Hz, 2H), 1.40-1.34 (m, 1H), 0.90-0.97 (m, 1H), 0.86 (t, *J* = 7.1 Hz, 3H), 0.79 (d, *J* = 7.1 Hz, 3H), 0.58-0.52 (m, 1H). **¹³C NMR (125 MHz; CDCl₃):** δ 131.24, 127.75, 127.57, 126.00, 63.31, 42.62, 26.23, 15.23, 13.91, 10.12. **IR (powder, cm⁻¹):** 3288 (w), 2957 (m), 2868 (m), 1606 (m), 1452 (w), 1168 (m), 1075 (s), 1057 (s), 896 (m), 740 (s), 700 (s). **HRMS (ESI+, m/z):** Calculated for C₁₂H₂₁BNO [(M+H)⁺]: 206.1713. Found: 206.1713.

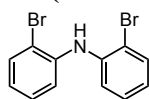
² Letsinger, R. L.; Nazy, J. R. *J. Org. Chem.* **1958**, *23*, 914–915.

General procedure B. Procedure adapted from previous reports.³ To an oven-dried Schlenk flask, equipped with a magnetic stirring bar, *n*-butyllithium (2 M in hexanes, 2.11 equiv.) was dropwise added to a 1.26 M solution of diphenyl ether (1 equiv) in anhydrous THF under argon, at -30 °C. After stirring the resulting suspension overnight (-30 °C - 23 °C), tributyl borate (1.5 equiv) was added. The resulting solution was heated to reflux for 2 h. Upon cooling to room temperature, 4 N HCl was added, and the mixture was stirred for 30 minutes at 23 °C. The two phases were separated and the organic phase was washed with water, dried over MgSO₄ and concentrated *in vacuo*. The resulting crude material was recrystallized using the given conditions.

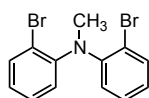
10H-Dibenzo[*b,e*][1,4]thiaborinin-10-ol (2a). Synthesized according to general procedure B from diphenyl sulfide. Recrystallization from hot toluene yielded the title compound as a fine, white powder, 20% yield. ¹H NMR (300 MHz; DMSO-*d*₆): δ 9.88 (s, 1H, BOH), 8.36 (ddd, *J* = 7.8, 1.5, 0.9 Hz, 2H), 7.60-7.57 (m, 4H), 7.39 (ddd, *J* = 7.8, 5.7, 2.6 Hz, 2H). ¹³C NMR (75 MHz; DMSO-*d*₆): δ 142.98, 133.80, 131.19, 125.11, 124.51, 45.77. IR (powder, cm⁻¹): 1590 (m), 1422 (s), 1301 (s), 1113 (m), 1069 (m), 1032 (m), 895 (m). HRMS (DART, *m/z*): Calculated for C₁₂H₁₀BOS [(M+H)⁺]: 213.05454. Found: 213.05437. mp >300 °C (toluene).

10H-Dibenzo[*b,e*][1,4]oxaborinin-10-ol (2b). Synthesized according to general procedure B from diphenyl ether. Recrystallization from hot toluene yielded the title compound as a white, fluffy solid, 61% yield (combined yield of 3 consecutive recrystallizations of the mother liquor). ¹H NMR (300 MHz; DMSO-*d*₆): δ 9.85 (s, 1H, BOH), 8.14 (ddd, 2H, *J* = 7.5, 1.8, 0.3 Hz, 2H), 7.67 (ddd, *J* = 8.4, 7.2, 1.8 Hz, 2H), 7.42 (ddd, *J* = 8.4, 0.9, 0.3 Hz, 2H), 7.28 (ddd, *J* = 7.5, 7.2, 0.9 Hz, 2H). ¹³C NMR (75 MHz; DMSO-*d*₆): δ 160.74, 133.26, 131.92, 122.19, 117.11, 45.77. IR (powder, cm⁻¹): 3292 (br), 1607 (m), 1470 (s), 1334 (s), 1221 (m), 1136 (m), 907 (m). HRMS (DART, *m/z*): Calculated for C₁₂H₁₀BO₂ [(M+H)⁺]: 197.07738. Found: 197.07721. mp = 290–295 °C (toluene).

Bis(2-bromophenyl)amine. Synthesized according to a previous report from 2-bromiodobenzene and 2-bromoaniline, 96% yield. Spectral data were in agreement with previous reports.⁴



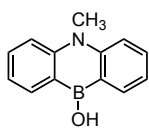
2-Bromo-*N*-(2-bromophenyl)-*N*-methylaniline. Synthesized according to a previous report from bis(2-bromophenyl)amine, 89% yield. Spectral data were in agreement with previous reports.⁴



³ Maitlis, P. M. *J. Chem. Soc.* **1961**, 425–429. Davidson, J. M.; French, C. M. *J. Chem. Soc.* **1960**, 191–195.

⁴ Uchiyama, M.; Matsumoto, Y.; Nakamura, S.; Ohwada, T.; Kobayashi, N.; Yamashita, N.; Matsumiya, A.; Sakamoto, T. *J. Am. Chem. Soc.* **2004**, *126*, 8755–8759.

5-Methyldibenzo[*b,e*][1,4]azaborinin-10(5*H*)-ol (2c). Synthesized according to general procedure B from 2-bromo-*N*-(2-bromophenyl)-*N*-methylaniline. Recrystallization from 2:1 pentane:dichloromethane yielded the title compound as a white solid, 55% yield (combined yield of 2 consecutive recrystallizations). ¹H NMR (300 MHz; DMSO-*d*₆): δ 9.00 (s, 1H, BOH), 8.22 (ddd, *J* = 7.5, 1.8, 0.6 Hz, 2H), 7.64 (ddd, *J* = 8.7, 6.8, 1.8 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.12 (ddd, *J* = 7.5, 6.8, 0.9 Hz, 2H), 3.79 (s, 3H, NCH₃). ¹³C NMR (75 MHz; DMSO-*d*₆): δ 148.32, 132.10, 131.96, 118.62, 114.83, 34.97. IR (powder, cm⁻¹): 3337 (br), 1600 (s), 1470 (s), 1354(s), 1232 (m), 1122 (s), 1042 (m), 903 (m). HRMS (DART, *m/z*): Calculated for C₁₃H₁₃BNO [(M+H)⁺]: 210.10902. Found: 210.10925. mp = 297–300 °C (pentane / dichloromethane).

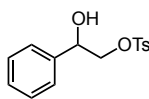


Sulfonylation

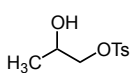
General procedure C. Diol (1 equiv) and 4-toluenesulfonyl chloride (1.5 equiv) were transferred to a 5-dram vial equipped with a magnetic stirring bar. Anhydrous acetonitrile, *N,N*-diisopropylethylamine (1.5 equiv) and a solution of catalyst **2b** (0.1 mol %) were added (final reaction concentration was 0.2 M). The resulting mixture was capped and stirred under ambient atmosphere and temperature for 24 hours. The reaction was quenched with methanol, concentrated *in vacuo* and purified by silica gel chromatography.

Reaction monitoring (Fig. 5). General procedure C was used with 1-phenyl-1,2-ethanediol (138.2 mg, 1.0 mmol), 4-toluenesulfonyl chloride (190.7 mg, 1.0 mmol), 1,3,5-trimethoxybenzene (56.1 mg, 0.33 mmol) and *N,N*-diisopropylethylamine (174.2 μL, 1.0 mmol). This was performed for each of the four catalysts (**1a**, **2a-c**, 0.1 mol %). 100 μL aliquots, taken at the given time intervals, were quenched with methanol and concentrated *in vacuo*. ¹H NMR data were collected for each aliquot and the conversions obtained using 1,3,5-trimethoxybenzene were tabulated.

2-Hydroxy-2-phenylethyl 4-toluenesulfonate (3a). Synthesized according to general procedure C from 1-phenyl-1,2-ethanediol. The resulting crude material was purified by silica gel chromatography (30% EtOAc/pentane), 90% yield, colorless oil. The spectral data were in agreement with previous reports.⁵



2-hydroxypropyl 4-methylbenzenesulfonate (3b). Synthesized according to general procedure C from propylene glycol. The resulting crude material was purified by silica gel chromatography (30% EtOAc/pentane), 95% yield, white solid. The spectral data were in agreement with previous reports.⁶



⁵ Uccello-Barretta, G.; Cuzzola, A.; Balzano, F.; Menicagli, R.; Iuliano, A.; Salvadori, P. *J. Org. Chem.* **1997**, *62*, 827–835.

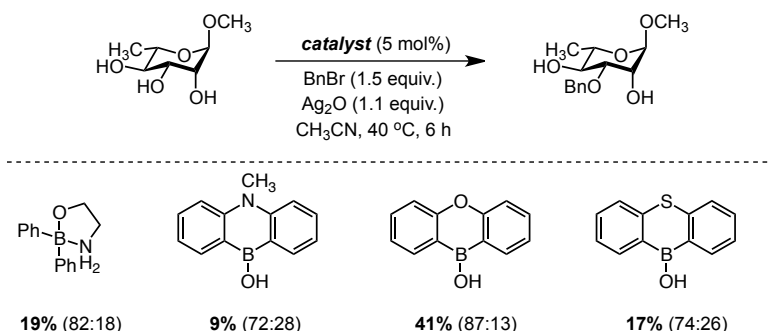
⁶ Huszthy, P.; Oue, M.; Bradshaw, J. S.; Zhu, C. Y.; Wang, T.; Dalley, N. K.; Curtis, J. C.; Izatt, R. M. *J. Org. Chem.* **1992**, *57*, 5383–5394.

Alkylation

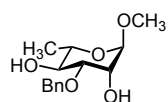
General procedure D (Table 1). Pyranoside (1 equiv), silver (I) oxide (1.5 equiv) and catalyst (**2b**, 5 mol %) were transferred to a 5-dram vial, equipped with a magnetic stirring bar. The vial was sealed with a septum and purged with a balloon of argon. Anhydrous acetonitrile (0.1 M) and benzyl bromide (1.5 equiv) were added and the reaction stirred at 40 °C for 24 h. The reaction was quenched with methanol, filtered over a plug of Celite and concentrated *in vacuo*. The resulting crude material was purified by silica gel chromatography.

Reaction monitoring. General procedure D was used with methyl- α -L-rhamnopyranoside and each of the catalysts (**1a**, **2a-c**). The reactions were stopped after stirring at 40 °C for 6 h. Following work-up, the resulting crude material was purified by silica gel chromatography (40% EtOAc/pentane). Isolated yields obtained with each catalyst are shown in Table S1. Regiomeric ratio of *O3*:*O2* alkylated products is indicated in parentheses.

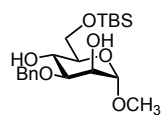
Table S1. Methyl- α -L-rhamnopyranoside benzylation catalyzed by **1a**, **2a-c**.



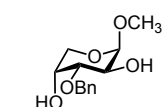
Methyl-3-O-benzyl- α -L-rhamnopyranoside (4a). Synthesized according to general procedure D from methyl- α -L-rhamnopyranoside. Purified using 40% EtOAc/pentane, 92% yield (isolated as an 8:1 mixture of regioisomers), white solid. Spectral data are in agreement with previous reports.⁷



Methyl-6-(*tert*-butyldimethylsilyloxy)-3-O-benzyl- α -D-mannopyranoside (4b). Synthesized according to general procedure D from methyl-6-(*tert*-butyldimethylsilyloxy)- α -D-mannopyranoside. Purified using 25% EtOAc/pentane, 82% yield (+12% yield of regioisomer), pale yellow solid. Spectral data are in agreement with previous reports.⁷

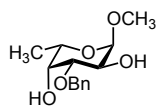


Methyl-3-O-benzyl- β -D-arabinopyranoside (4c). Synthesized according to general procedure D from methyl- β -D-arabinopyranoside. Purified using 60% EtOAc/pentane, 63% yield, white solid. Spectral data are in agreement with previous reports.⁷



⁷ Chan, L.; Taylor, M. S. *Org. Lett.* **2011**, *13*, 3090–3093.

Methyl-3-*O*-benzyl- α -L-fucopyranoside (4d). Synthesized according to general procedure D from methyl- α -L-fucopyranoside. Purified using 40% EtOAc/pentane, 81% yield, pale yellow solid. Spectral data are in agreement with previous reports.⁷



Glycosylation

General procedure E (Table 2). Glycosyl donor (1 equiv.), acceptor (1.1 equiv.), silver (I) oxide (1 equiv.) and catalyst (**2c**, 10 mol %) were added to a 5-dram vial, equipped with a magnetic stirring bar. The vial was capped and purged with argon. Anhydrous acetonitrile (0.13 M) was added and the resulting mixture was stirred at room temperature for 16 hours. The reaction was quenched with a few drops of methanol, diluted with dichloromethane and filtered through a plug of Celite. The resulting crude material was purified by silica gel chromatography.

Reaction monitoring. 2,3,4,6-Tetra-*O*-acetyl- α -D-glucopyranosyl bromide (329.0 mg, 0.8 mmol), methyl-6-*O*-*tert*-butyldimethylsilyl- α -D-mannopyranoside (259.1 mg, 0.88 mmol), silver (I) oxide (185.4 mg, 0.8 mmol), 1,3,5-trimethoxybenzene (44.9 mg, 0.267 mmol) and catalyst (0.032 mmol, 4 mol %) were added to an oven-dried round bottom flask, equipped with a magnetic stirring bar, under argon. Anhydrous acetonitrile (6.2 mL) was added and the reaction stirred at 750 rpm for 24 hours. This was performed for each of the three catalysts (**2a-c**). Aliquots (100 μ L) were taken at the given time points, quenched with methanol, diluted with dichloromethane and filtered over a Celite plug. Conversion to product was determined by ¹H NMR using the added 1,3,5-trimethoxybenzene as an internal standard (Figure S1).

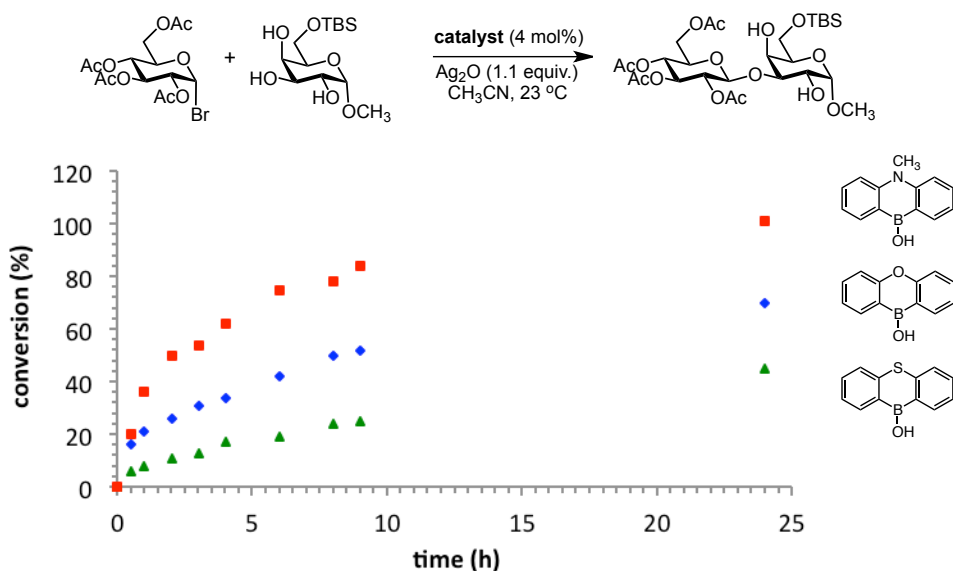
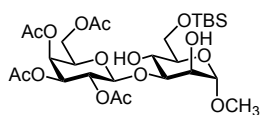


Figure S1. Glycosylation using catalysts **2a-c**.

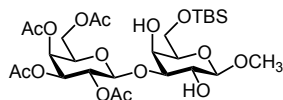
Methyl-6-*O*-*tert*-butyldimethylsilyl-3-*O*-(2',3',4',6'-tetra-*O*-acetyl-β-D-



galactopyranosyl)-α-D-mannopyranoside (5a). Synthesized according to general procedure E, from 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide and methyl-6-*O*-*tert*-butyldimethylsilyl-α-D-mannopyranoside. Purified using gradient 10-45%

EtOAc/pentane (40% EtOAc/pentane: R_f (catalyst) = 0.7, R_f (product) = 0.16), 81% yield, white solid (catalyst isolated in >95% yield). Spectral data are in agreement with previous reports.⁸

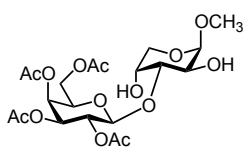
Methyl-6-*O*-*tert*-butyldimethylsilyl-3-*O*-(2',3',4',6'-tetra-*O*-acetyl-β-D-



galactopyranosyl)-β-D-galactopyranoside (5b). Synthesized according to general procedure E, from 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide and methyl-6-*O*-*tert*-

butyldimethylsilyl-β-D-galactopyranoside. Purified using gradient 10-60% EtOAc/pentane (40% EtOAc/pentane: R_f (catalyst) = 0.7, R_f (product) = 0.11), 82% yield, white solid (catalyst isolated in 48% yield). ¹H NMR (500 MHz; CDCl₃): δ 5.39 (dd, J = 3.5, 1.0 Hz, 1H, H -4'), 5.23 (dd, J = 10.5, 7.9 Hz, 1H, H -2'), 5.05 (dd, J = 10.5, 3.5 Hz, 1H, H -3'), 4.80 (d, J = 8.0 Hz, 1H, H -1'), 4.15-4.11 (m, 3H, H -1, H -6'), 4.03 (dd, J = 3.3, 1.1 Hz, 1H, H -4), 3.93-3.89 (m, 2H, H -5', H -6_A), 3.82 (dd, J = 10.0, 5.5 Hz, 1H, H -6_B), 3.75 (dd, J = 9.5, 7.5 Hz, 1H, H -2), 3.58 (dd, J = 9.5, 3.3 Hz, 1H, H -3), 3.53 (s, 3H, OCH₃), 3.50-3.47 (m, 1H, H -5), 2.16 (s, 3H, COCH₃), 2.05 (s, 3H, COCH₃), 2.04 (s, 3H, COCH₃), 1.99 (s, 3H, COCH₃), 0.89 (s, 9H, Si(C(CH₃)₃)(CH₃)₂), 0.07 (s, 6H, Si(C(CH₃)₃)(CH₃)₂). ¹³C NMR (126 MHz; CDCl₃): δ 170.45, 170.34, 170.24, 170.09, 103.82, 102.03, 82.86, 74.81, 70.95, 70.86, 70.63, 69.08, 67.81, 66.90, 62.07, 61.14, 57.00, 25.98, 20.92, 20.81, 20.77, 20.72, 18.45, -5.26, -5.21. IR (powder, cm⁻¹): 3473 (br), 2931 (br), 1741 (s), 1368 (m), 1216 (s), 1042 (s), 835 (m). HRMS (ESI, m/z): Calculated for C₂₇H₅₀NO₁₅Si [(M+NH₄)⁺]: 656.2944. Found: 656.2946.

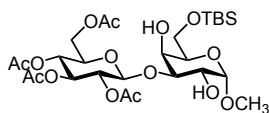
Methyl-3-*O*-(2',3',4',6'-tetra-*O*-acetyl-β-D-galactopyranosyl)-β-D-arabinopyranoside



(5c). Synthesized according to general procedure E, from 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide and methyl-β-D-arabinopyranoside. Purified using gradient 10-80% EtOAc/pentane (40% EtOAc/pentane: R_f (catalyst) = 0.7, R_f (product) = 0.03), 86% yield, white solid (catalyst isolated in 70% yield).

Spectral data are in agreement with previous reports.⁸

Methyl-6-*O*-*tert*-butyldimethylsilyl-3-*O*-(2',3',4',6'-tetra-*O*-acetyl-β-D-

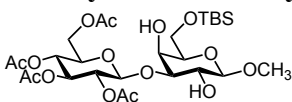


glucopyranosyl)-α-D-galactopyranoside (5d). Synthesized according to general procedure E, from 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide and methyl-6-*O*-*tert*-butyldimethylsilyl-α-D-galactopyranoside. Purified using 50-70%

EtOAc/pentane (40% EtOAc/pentane: R_f = 0.15), 69% yield, white solid. Spectral data are in agreement with previous reports.⁸

⁸ Gouliaras, C.; Lee, D.; Chan, L.; Taylor, M. S. *J. Am. Chem. Soc.* **2011**, *133*, 13926–13929.

Methyl-6-*O*-*tert*-butyldimethylsilyl-3-*O*-(2',3',4',6'-tetra-*O*-acetyl- β -D-glucofuranosyl)- β -D-galactopyranoside (5e). Synthesized according to general procedure E, from 2,3,4,6-tetra-*O*-acetyl- α -D-glucofuranosyl bromide and methyl-6-*O*-*tert*-butyldimethylsilyl- β -D-galactopyranoside. Purified using 50-70% EtOAc/pentane (40% EtOAc/pentane: R_f = 0.14), 84% yield, white solid. Spectral data are in agreement with previous reports.⁸



Control experiments of catalyst stability. Catalyst (0.02 mmol) and silver (I) oxide (0.2 mmol) were added to a 2-dram vial containing a magnetic stirring bar under argon. 2 mL of anhydrous acetonitrile were added and the resulting solution was stirred vigorously at room temperature. After 4 hours, the reactions were quenched by the addition of methanol, diluted with dichloromethane, filtered through a Celite plug and concentrated *in vacuo*. The resultant NMRs (red) were compared to those of the authentic product (green) (Figure S2).

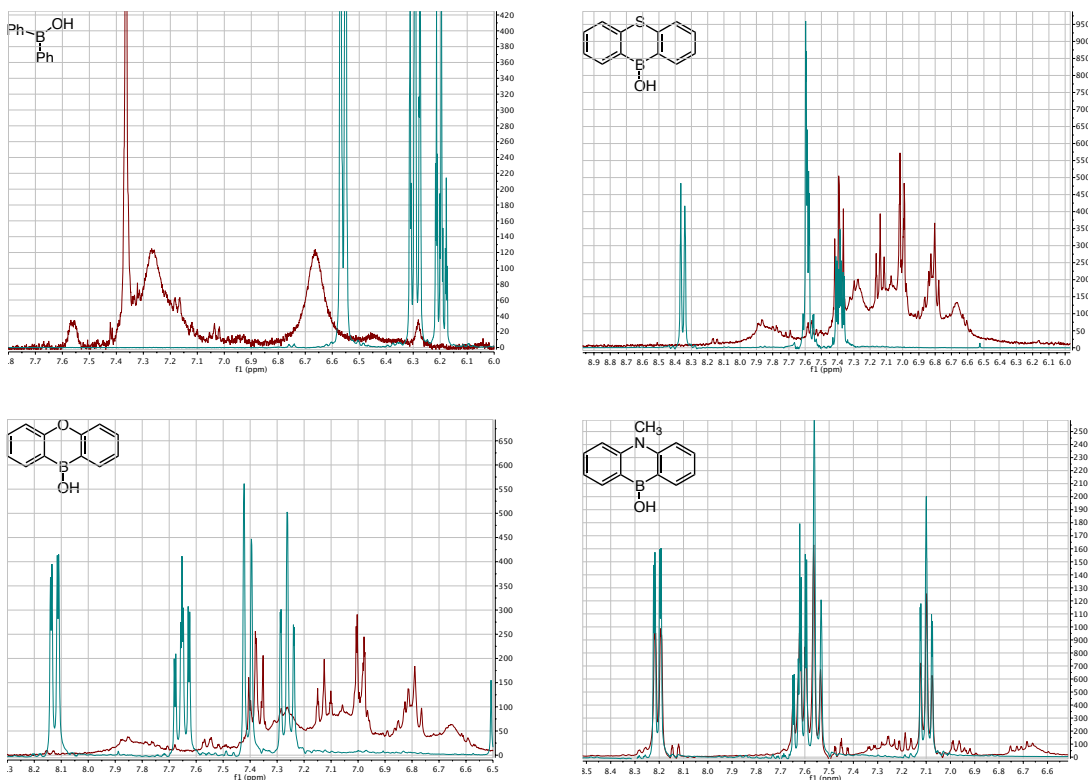


Figure S2. Catalyst stability under glycosylation conditions.

II. UV-Vis Titration Data

Optical absorption spectra were collected at room temperature on a Perkin-Elmer Lambda 35 spectrometer using 10 mm quartz cuvettes and corrected for background signal with a solvent-filled quartz cuvette. All solutions were prepared in 10 mM HEPES buffer in distilled water:methanol (1:3) and adjusted to pH 7.4. Binding constants were determined by measuring the change in absorbance of solutions containing various concentrations of analyte.

A solution of the catalyst (host) was prepared (solution **A**). This solution was then used as the parent solution to prepare a guest (catechol) solution (solution **B**). Titration experiments were carried out by sequentially adding aliquots of solution **B** by syringe to 2.5 mL of solution **A**. The solution was stirred for 30 seconds prior to obtaining absorption spectra. Concentrations of host were chosen to yield data such that the occupancy ratio $\beta = [\text{complex}]/[\text{guest}]_{\text{total}}$ would fall in the range $0.2 < \beta < 0.8$ as described by Hirose.⁹ Graphs of ΔA (change in absorbance at 350 nm for **2a**, 320 nm for **2b** and 372 nm for **2c**) against $[\text{catechol}]$ were curve-fitted to a 1:1 binding isotherm (eq. 1), using Igor Pro 5.0 (WaveMetrics, Inc.):

$$A_{\text{obs}} = A_{\text{H}} + \Delta\epsilon \left[\frac{\kappa[\text{H}]_{\text{t}}[\text{G}]}{1 + \kappa[\text{G}]} \right] \quad (1)$$

A_{obs} is the observed absorbance, A_{H} is the absorbance of the unbound catalyst, $\Delta\epsilon = \epsilon_{\text{HG}} - \epsilon_{\text{H}}$ (ϵ_{HG} and ϵ_{H} are the molar absorption coefficients of the host-guest (catalyst-catechol) complex and the catalyst, respectively), $[\text{H}]_{\text{t}}$ is the total concentration of catalyst and $[\text{G}]$ is defined by the quadratic:

$$K[\text{G}]^2 + (K[\text{H}]_{\text{t}} - K[\text{G}]_{\text{t}} + 1)[\text{G}] - [\text{G}]_{\text{t}} = 0 \quad (2)$$

where $[\text{H}]_{\text{t}}$ is the total host concentration. Initially estimated values for the parameters A_{H} , $\Delta\epsilon$ and K allowed for the determination of the value of $[\text{H}]$ from the positive quadratic root of equation (2). Subsequent iterative nonlinear curve-fitting of the experimental ΔA vs. $[\text{H}]_{\text{t}}$ to equation (1) at a known $[\text{G}]_{\text{t}}$ was then applied resulting in refinement of the parameters and yielding values for A_{H} , $\Delta\epsilon$ and K .

Equations were derived as follows:

The equilibrium between the host and guest is described by equation (3):

$$K = \frac{[\text{HG}]}{[\text{H}][\text{G}]} \quad (3)$$

where $[\text{HG}]$, $[\text{H}]$ and $[\text{G}]$ are the concentrations of host-guest complex, unbound host and unbound guest, respectively, and K is the host-guest equilibrium constant. The mass

⁹ Hirose, K. J. *Inclusion Phenom. Macrocyclic Chem.* **2001**, *39*, 193–209.

balance equations for the host and guest are described by equations (4) and (5):

$$[H]_t = [H] + [HG] \quad (4)$$

$$[G]_t = [G] + [HG] \quad (5)$$

where $[H]_t$ and $[G]_t$ are the total concentrations of host and guest, respectively.

Solving equation (4) for $[H]$ and equation (5) for $[HG]$, substituting into equation (3), expanding, rearranging and collecting like terms yields the quadratic equation (2).

By applying the Beer-Lambert Law to the complexed system, and substituting a cell length of 1 cm, equation (6) can be obtained, which describes the observed absorbance with respect to the host and host-guest concentrations.

$$A_{\text{obs}} = \epsilon_H[H] + \epsilon_{HG}[HG] \quad (6)$$

A_{obs} is the observed absorbance at a given wavelength and ϵ_H and ϵ_{HG} are the molar absorption coefficients of the host and host-guest complex, respectively.

Solving equation (4) for $[H]$, substituting into equation (6), expanding and collecting like terms yields equation (7).

$$A_{\text{obs}} = \epsilon_H[H]_t + (\epsilon_{HG} - \epsilon_H)[HG] \quad (7)$$

Substituting for the absorbance of the unbound host, A_H , and defining $\Delta\epsilon = \epsilon_{HG} - \epsilon_H$ yields equation (8).

$$A_{\text{obs}} = A_H + \Delta\epsilon[HG] \quad (8)$$

Solving equation (4) for $[H]$, substituting into equation (3), expanding and rearranging in terms of $[HG]$ yields equation (9),

$$[HG] = \left| \frac{\kappa[G]_t[H]_t}{1 + \kappa[G]} \right| \quad (9)$$

which upon substitution into equation (8) yields equation (1).

Changes in absorbance ΔA are plotted against substrate concentration (M). The curves obtained by fitting to a 1:1 or competitive binding isotherm are shown.

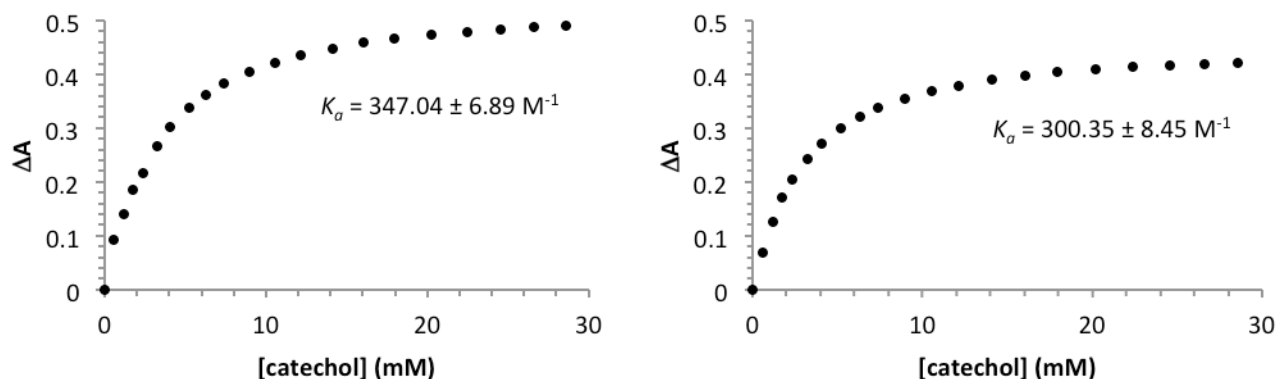


Figure S3. UV-vis titration of **2a** (0.15 mM) with catechol and the corresponding 1:1 binding isotherms (10 mM HEPES buffered MeOH:H₂O (3:1) solution, pH 7.4, 295 K). Two trials shown.

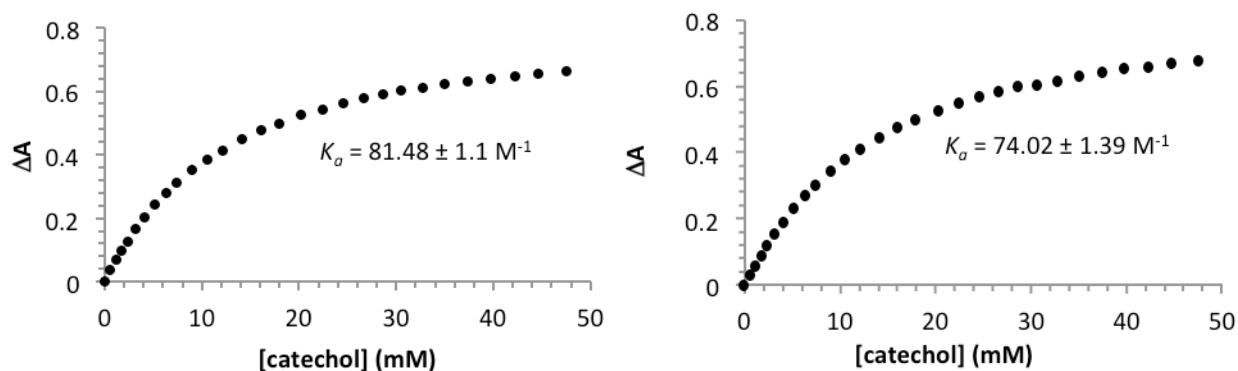


Figure S4. UV-vis titration of **2b** (0.15 mM) with catechol and the corresponding 1:1 binding isotherms (10 mM HEPES buffered MeOH:H₂O (3:1) solution, pH 7.4, 295 K). Two trials shown.

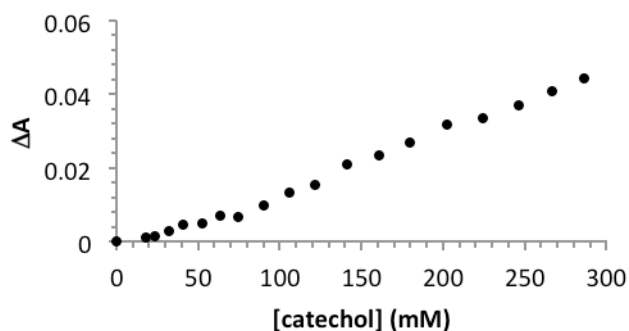


Figure S5. UV-vis titration of **2c** (0.05 mM) with catechol and the corresponding 1:1 binding isotherms (10 mM HEPES buffered MeOH:H₂O (3:1) solution, pH 7.4, 295 K).

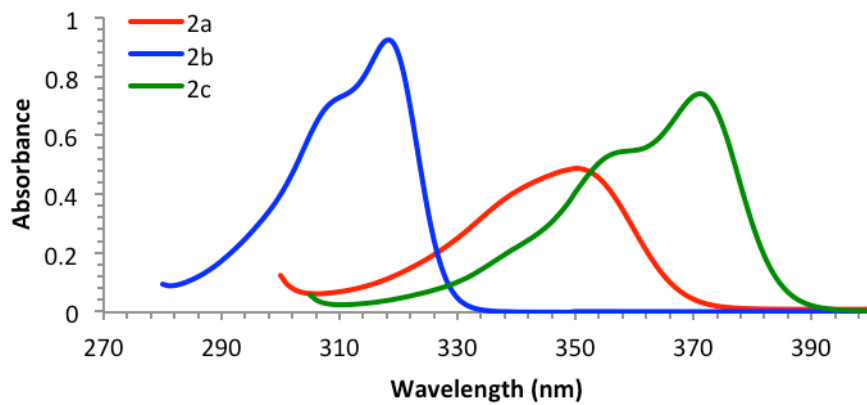


Figure S6. Absorption spectra of catalysts **2a-c** in 10 mM HEPES buffered MeOH:H₂O (3:1) solution, pH 7.4, 295 K.

III. Kinetic Data

Using **2b** as catalyst, the reaction progression was monitored by ^1H NMR at room temperature. The conversion of 1,2-*cis*-cyclohexanediol (0.2 mmol) to product was monitored using 5.0 equivalents (1 mmol) each of 4-toluenesulfonyl chloride and *N,N*-diisopropylethylamine, and 3 mol % **2b** in 0.02 M (10 mL) CD_3CN . Using 1,3,5-trimethoxybenzene as the internal standard, product formation and starting material consumption were monitored over time (Figure S7). The reaction was set up in two separate vials (one containing diol TsCl, and internal standard and the other containing solvent, catalyst and base). Immediately following mixing, the solution was transferred to an NMR tube. The presented graphs have been corrected for the time between mixing and the first spectrum acquisition.

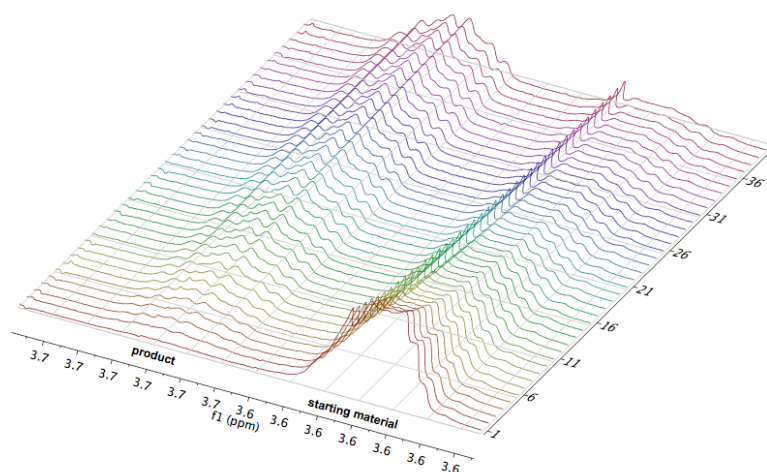


Figure S7. Overlay of ^1H NMR spectra obtained during reaction monitoring for the tosylation of 1-phenyl-1,2-ethanediol. Integrated data is plotted in Fig. 7.

IV. Details of Computational Studies

Calculations were carried out with the Gaussian '09 software package,¹⁰ on a Linux workstation equipped with two quad-core AMD Shanghai processors built by HardData, Inc. Edmonton, Alberta, Canada).

Geometry optimizations of the complexes were performed using density functional theory (B3LYP functional), with the 6-31+G(d,p) basis set for all atoms. Frequency calculations at the same level of theory demonstrated that the optimum structures had no imaginary vibrational frequencies. The calculated energies (Hartrees), zero-point energy corrections, and geometries (Cartesian coordinates, Å) of all complexes are provided on the pages that follow.

Optimized geometries of 2b and 2c dimers

Geometry optimizations were performed using the above specifications.

Table S2. Computed bond distances (Å).

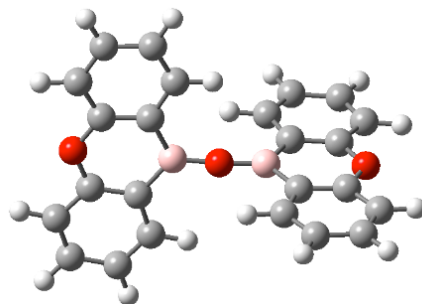
	2b	2c
<i>B-C₁</i>	1.54669	1.54276
<i>B-C₂</i>	1.54674	1.54084
<i>B-O</i>	1.35367	1.36009

¹⁰ Gaussian 09, Revision B.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

2b:

Imaginary frequencies: none

$E = -1199.8023381$



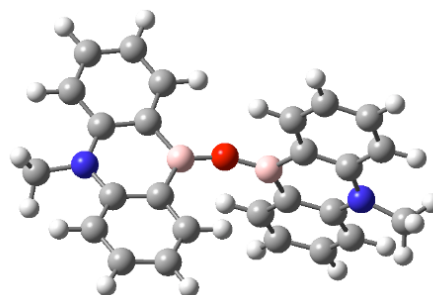
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4	6	0	-3.625427	-0.793031	-0.825136
5	6	0	-4.496827	-1.536067	-1.634947
6	6	0	-3.964417	-2.413473	-2.571009
7	6	0	-3.538344	0.846020	0.933027
8	6	0	-2.131387	0.872973	0.981769
9	6	0	-1.538413	1.743047	1.923919
10	1	0	-0.453939	1.781814	1.982265
11	6	0	-2.302282	2.539593	2.766785
12	6	0	-3.704810	2.484656	2.687037
13	6	0	-4.328214	1.642475	1.775186
14	1	0	-2.164907	-3.244824	-3.440708
15	1	0	-0.649930	-1.917885	-1.994148
16	1	0	-5.568073	-1.411404	-1.515362
17	1	0	-4.633707	-2.991911	-3.201503
18	1	0	-1.823287	3.200583	3.482620
19	1	0	-4.310635	3.104138	3.342234
20	1	0	-5.409072	1.585465	1.698519
21	5	0	-1.352945	-0.043568	0.008859
22	8	0	-0.000475	-0.092034	-0.019226
23	6	0	2.212038	-0.982992	0.855408
24	6	0	2.145216	0.932406	-0.923232
25	6	0	1.698711	-1.955924	1.742060
26	6	0	3.612708	-0.865510	0.775577
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28	6	0	1.565969	1.869524	-1.807853
29	6	0	2.532354	-2.763702	2.504260
30	1	0	0.620420	-2.066053	1.820138
31	6	0	4.472273	-1.670789	1.537121
32	6	0	4.353526	1.746430	-1.636090
33	1	0	0.482342	1.916979	-1.874774
34	6	0	2.342106	2.719977	-2.584224
35	6	0	3.926313	-2.615365	2.396891
36	1	0	2.114243	-3.504813	3.178589
37	1	0	5.545215	-1.541451	1.439780
38	6	0	3.743457	2.653362	-2.493229
39	1	0	5.433250	1.679451	-1.551804
40	1	0	1.873553	3.431574	-3.257166
41	1	0	4.586429	-3.242666	2.989174
42	1	0	4.358875	3.314581	-3.096639
43	5	0	1.352445	-0.047815	-0.027087

44	8	0	4.241989	0.035699	-0.045403
45	8	0	-4.241639	0.047127	0.067372

2c:

Imaginary frequencies: none

$E = -1238.6970067$

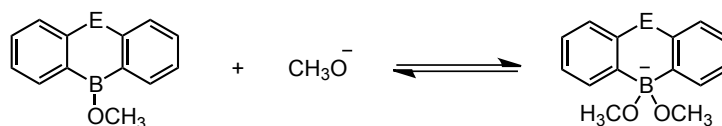


Center Number	Atomic Number	Forces (Hartrees/Bohr)		
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4	6	-0.000012734	0.000027905	-0.000009499
5	6	0.000002143	-0.000010295	0.000001146
6	6	0.000000550	0.000006012	0.000008034
7	6	-0.000026376	0.000007927	-0.000025777
8	6	-0.000016928	-0.000017313	0.000003889
9	6	0.000009107	-0.000001266	0.000009883
10	1	-0.000001904	0.000001882	-0.000001485
11	6	0.000005987	0.000004818	-0.000004401
12	6	0.000000927	0.000004385	0.000004954
13	6	-0.000002047	-0.000000611	0.000001854
14	1	-0.000000138	-0.000002041	0.000003402
15	1	0.000000878	-0.000001066	0.000002643
16	1	-0.000005196	0.000012736	0.000002029
17	1	0.000000121	-0.000001164	0.000002609
18	1	-0.000001354	-0.000001538	-0.000001730
19	1	-0.000001314	-0.000002259	-0.000000556
20	1	0.000002873	0.000001008	0.000006961
21	5	0.000021348	0.000012269	-0.000042957
22	8	0.000014060	0.000016810	0.000093518
23	6	0.000017868	0.000023316	-0.000013865
24	6	0.000002506	0.000026427	0.000015191
25	6	-0.000009460	-0.000007745	0.000005279
26	6	-0.000001272	0.000019518	0.000024274
27	6	0.000005635	0.000014312	-0.000024100
28	6	-0.000003735	-0.000002697	-0.000010010
29	6	0.000002596	0.000002107	0.000000890
30	1	-0.000005201	-0.000008436	0.000004051
31	6	-0.000004806	-0.000015864	0.000004928
32	6	-0.000003301	-0.000013994	-0.000008699
33	1	-0.000002494	-0.000006905	-0.000003122
34	6	0.000006043	0.000005708	-0.000004722
35	6	-0.000004675	-0.000012336	0.000004944
36	1	-0.000005607	-0.000001474	-0.000007503
37	1	0.000004306	0.000009819	-0.000012974
38	6	-0.000004869	-0.000008094	-0.000006738
39	1	0.000004092	0.000010560	0.000008269

40	1	-0.000000703	0.000001842	0.000005770
41	1	0.000002150	0.000005826	-0.000008040
42	1	0.000006978	0.000009039	0.000003145
43	5	-0.000029920	-0.000047095	-0.000048117
44	7	0.000031887	-0.000023576	0.000027632
45	7	0.000014609	-0.000013285	-0.000008405
46	6	-0.000020546	0.000012143	-0.000006118
47	1	-0.000000285	-0.000003102	0.000005659
48	1	0.000001495	-0.000020217	-0.000002460
49	1	0.000002592	-0.000002350	-0.000013454
50	6	0.000010630	-0.000001966	-0.000006662
51	1	-0.000014553	0.000003928	0.000009165
52	1	0.000001633	0.000008330	-0.000008454
53	1	0.000013396	-0.000004333	0.000015313

Tetracoordinate boron stabilities (Fig. 3)

The relative stabilities of tetracoordinate boron adducts of **1b**, **2a-c** were assessed using the reaction shown in equation 10. Computed complexes corresponding to the methyl esters of the catalysts are reported as **1b'**, **2a'**, **2b'** and **2c'** respectively. The binding energies, ΔE , were estimated by equation 11.



$$\Delta E = E_{\text{complex}} - (E_{\text{donor}} + E_{\text{acceptor}}) \quad (11)$$

where E_{complex} , E_{donor} and E_{acceptor} are the calculated energies of the complex, donor and acceptor, respectively.

Methoxide (CH_3O^-):

Imaginary frequencies: none

$E = -115.1155202$

ZPE = 0.0349809



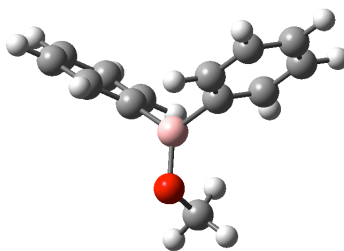
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4	1	0	1.037945	-0.372126	0.958668
5	1	0	1.040186	-0.643272	-0.801229

1b':

Imaginary frequencies: none

$E = -603.3894322$

ZPE = 0.2289224



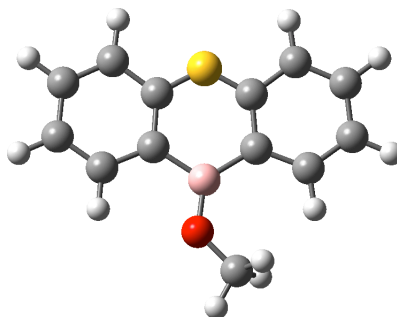
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4	6	0	-2.751840	-1.671820	0.983446
5	6	0	-3.738857	-1.394083	0.034108
6	6	0	-3.516840	-0.398732	-0.922136
7	1	0	-2.169107	1.093433	-1.666890
8	1	0	-0.783677	-1.205029	1.703042
9	1	0	-2.916312	-2.444102	1.729985
10	1	0	-4.672412	-1.949859	0.037348
11	1	0	-4.276685	-0.180910	-1.667799
12	5	0	0.062640	0.850193	0.023160
13	6	0	1.459604	0.132201	-0.036606
14	6	0	1.584855	-1.233201	-0.361828
15	6	0	2.646031	0.851352	0.220730
16	6	0	2.834389	-1.855369	-0.427013
17	1	0	0.693013	-1.815372	-0.576181
18	6	0	3.896591	0.235989	0.165617
19	1	0	2.574933	1.906867	0.466461
20	6	0	3.993120	-1.121766	-0.159610
21	1	0	2.904144	-2.908367	-0.686091
22	1	0	4.795644	0.810149	0.373142
23	1	0	4.966219	-1.603401	-0.206114
24	8	0	0.113509	2.214191	0.076268
25	6	0	-0.992982	3.096145	0.245532
26	1	0	-0.672440	3.906105	0.906524
27	1	0	-1.272625	3.524599	-0.722755
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2a':

Imaginary frequencies: none

$E = -1000.3783212$

ZPE = 0.2091963



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
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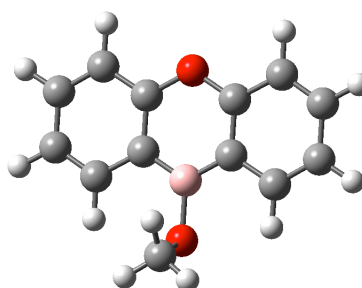
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6	6	0	-3.947634	-0.745290	0.000020
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8	6	0	1.337795	0.313558	-0.000021
9	6	0	2.636756	0.884955	-0.000005
10	1	0	2.741467	1.960744	-0.000007
11	6	0	3.800854	0.126986	0.000012
12	6	0	3.712968	-1.270907	0.000017
13	6	0	2.467426	-1.880994	0.000007
14	1	0	-4.713579	1.278027	0.000018
15	1	0	-2.459401	2.308462	-0.000015
16	1	0	-2.904462	-2.625265	0.000020
17	1	0	-4.929378	-1.210598	0.000033
18	1	0	4.770056	0.616590	0.000022
19	1	0	4.612022	-1.880548	0.000031
20	1	0	2.395654	-2.965389	0.000016
21	5	0	0.019447	1.159802	-0.000045
22	8	0	-0.079957	2.528624	-0.000010
23	6	0	0.898852	3.551967	0.000014
24	1	0	1.529412	3.506286	-0.895285
25	1	0	0.365301	4.506292	0.000023
26	1	0	1.529396	3.506261	0.895323
27	16	0	-0.182404	-2.084403	-0.000008

2b':

Imaginary frequencies: none

$E = -677.4180169$

ZPE = 0.21246



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-3.787678	0.332766	-0.000001
2	6	0	-2.597754	1.049470	-0.000015
3	6	0	-1.341235	0.403002	-0.000029
4	6	0	-1.349617	-1.000302	-0.000022
5	6	0	-2.536818	-1.746440	0.000011
6	6	0	-3.751678	-1.072758	0.000023
7	6	0	1.048582	-1.171569	0.000004
8	6	0	1.276173	0.225181	-0.000052
9	6	0	2.636696	0.625666	-0.000038
10	1	0	2.877698	1.681304	-0.000076
11	6	0	3.685425	-0.284934	-0.000011
12	6	0	3.409364	-1.661316	0.000024
13	6	0	2.095828	-2.106139	0.000035
14	1	0	-4.741745	0.851417	-0.000003

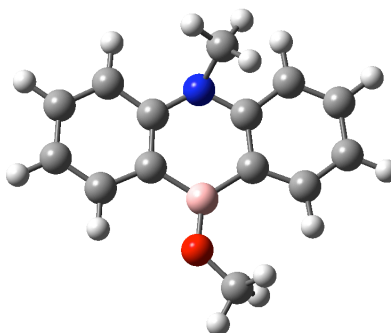
15	1	0	-2.613171	2.135321	-0.000016
16	1	0	-2.484565	-2.830278	0.000027
17	1	0	-4.677825	-1.640610	0.000051
18	1	0	4.712832	0.066189	-0.000004
19	1	0	4.221604	-2.382522	0.000062
20	1	0	1.851891	-3.163398	0.000071
21	8	0	-0.195790	-1.742571	-0.000014
22	5	0	0.019589	1.146244	-0.000040
23	8	0	-0.047728	2.513702	0.000033
24	6	0	1.019623	3.448750	0.000041
25	1	0	1.643510	3.343503	-0.894979
26	1	0	0.574976	4.447137	0.000073
27	1	0	1.643535	3.343410	0.895027

2c':

Imaginary frequencies: none

$E = -696.8642857$

ZPE = 0.253723



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	3.734204	0.751162	-0.298520
2	6	0	2.495705	1.369417	-0.185987
3	6	0	1.301509	0.636863	-0.028151
4	6	0	1.379689	-0.777643	0.032968
5	6	0	2.639945	-1.408340	-0.098876
6	6	0	3.792738	-0.648776	-0.261785
7	6	0	-1.067795	-1.024533	0.039217
8	6	0	-1.303266	0.384614	-0.027736
9	6	0	-2.636399	0.810999	-0.228496
10	1	0	-2.840020	1.871725	-0.304582
11	6	0	-3.703594	-0.069020	-0.351535
12	6	0	-3.450946	-1.443929	-0.283701
13	6	0	-2.159624	-1.917246	-0.095975
14	1	0	4.639979	1.337160	-0.421988
15	1	0	2.421306	2.452405	-0.218706
16	1	0	2.727905	-2.487473	-0.110079
17	1	0	4.746478	-1.157955	-0.372154
18	1	0	-4.711677	0.302096	-0.508407
19	1	0	-4.263402	-2.156724	-0.396094
20	1	0	-2.002269	-2.988024	-0.096311
21	5	0	-0.076720	1.329440	0.068083
22	8	0	-0.050153	2.696611	0.205475
23	6	0	-1.131689	3.590005	0.406341
24	1	0	-1.816156	3.231964	1.183883
25	1	0	-0.708113	4.546679	0.724537
26	1	0	-1.691148	3.752106	-0.523091
27	7	0	0.219719	-1.544944	0.222517

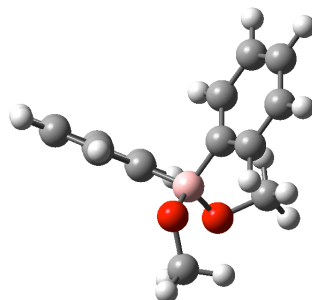
28	6	0	0.364815	-2.948699	0.604230
29	1	0	-0.473406	-3.244882	1.235326
30	1	0	0.413285	-3.623117	-0.261401
31	1	0	1.272289	-3.070684	1.195265

1b'---CH₃O⁻:

Imaginary frequencies: none

$E = -718.6008297$

ZPE = 0.2679565



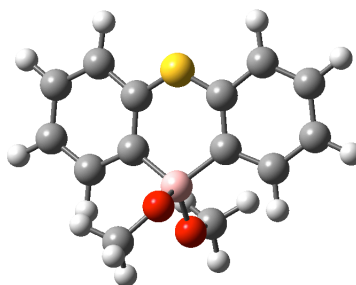
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.350963	-0.094205	-0.025607
2	6	0	2.223128	-0.150534	-1.128927
3	6	0	1.687530	-0.904483	1.077028
4	6	0	3.361711	-0.966991	-1.138775
5	1	0	1.995133	0.471286	-1.991157
6	6	0	2.821874	-1.722683	1.086076
7	1	0	1.038812	-0.888411	1.951486
8	6	0	3.668782	-1.760271	-0.028448
9	1	0	4.011981	-0.983571	-2.012964
10	1	0	3.046599	-2.333848	1.959390
11	1	0	4.551743	-2.396932	-0.030065
12	6	0	-1.351201	-0.093749	0.025419
13	6	0	-1.688782	-0.902090	-1.078345
14	6	0	-2.222431	-0.151924	1.129375
15	6	0	-2.823167	-1.720214	-1.087822
16	1	0	-1.040821	-0.884485	-1.953333
17	6	0	-3.361050	-0.968345	1.138796
18	1	0	-1.993698	0.468423	1.992473
19	6	0	-3.669104	-1.759709	0.027379
20	1	0	-3.048698	-2.329847	-1.961999
21	1	0	-4.010570	-0.986389	2.013512
22	1	0	-4.552080	-2.396349	0.028664
23	8	0	-0.055883	1.684907	1.236164
24	8	0	0.056245	1.685743	-1.235142
25	6	0	0.990122	2.590228	1.452556
26	1	0	1.107141	3.305404	0.620101
27	1	0	0.777745	3.163592	2.367999
28	1	0	1.963499	2.085941	1.585622
29	6	0	-0.989162	2.591967	-1.450651
30	1	0	-1.963000	2.088493	-1.583426
31	1	0	-1.105190	3.306888	-0.617845
32	1	0	-0.776794	3.165517	-2.365979
33	5	0	0.000004	0.851422	0.000203

2a'---CH₃O⁻:

Imaginary frequencies: none

$E = -1115.5873391$

ZPE = 0.2483841



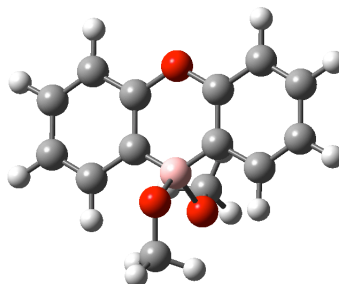
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			X	Y	Z
1	6	0	-3.836878	0.396803	-0.374449
2	6	0	-2.585165	1.001816	-0.240814
3	6	0	-1.405265	0.276808	0.014470
4	6	0	-1.550193	-1.118002	0.114623
5	6	0	-2.797853	-1.753023	-0.028009
6	6	0	-3.943444	-0.995151	-0.265955
7	6	0	1.287163	-1.289369	0.038505
8	6	0	1.306188	0.114360	-0.078910
9	6	0	2.549975	0.677810	-0.429873
10	1	0	2.595290	1.758923	-0.544559
11	6	0	3.708799	-0.079491	-0.622093
12	6	0	3.651022	-1.470906	-0.485087
13	6	0	2.435976	-2.075377	-0.165145
14	1	0	-4.723395	1.000832	-0.559091
15	1	0	-2.497803	2.083643	-0.316619
16	1	0	-2.865924	-2.836937	0.041291
17	1	0	-4.906992	-1.488924	-0.374945
18	1	0	4.647873	0.407650	-0.878303
19	1	0	4.537528	-2.082667	-0.639335
20	1	0	2.372218	-3.158701	-0.082796
21	5	0	0.005414	1.082586	0.241608
22	8	0	0.067873	2.325394	-0.586132
23	8	0	-0.010584	1.496227	1.662295
24	6	0	0.032492	2.232421	-1.981071
25	1	0	0.102986	3.246049	-2.404655
26	1	0	0.866057	1.636682	-2.393429
27	1	0	-0.902453	1.777048	-2.353319
28	6	0	1.023777	2.308577	2.145385
29	1	0	2.003665	1.797712	2.137818
30	1	0	1.127007	3.240246	1.565445
31	1	0	0.796575	2.576172	3.188087
32	16	0	-0.181099	-2.206706	0.496725

2b'---CH₃O⁻:

Imaginary frequencies: none

$E = -792.6222168$

ZPE = 0.2512311



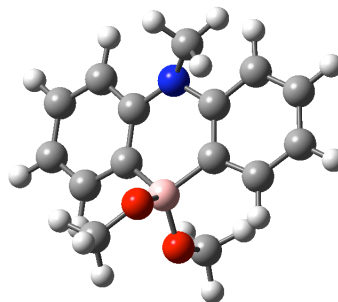
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	3.820628	0.069102	0.103592
2	6	0	2.631145	0.802987	0.092521
3	6	0	1.366701	0.204284	-0.047851
4	6	0	1.361046	-1.191459	-0.169027
5	6	0	2.535301	-1.960234	-0.166466
6	6	0	3.768879	-1.325173	-0.031290
7	6	0	-1.049396	-1.369251	-0.123598
8	6	0	-1.257070	0.012207	0.022134
9	6	0	-2.590259	0.400269	0.257306
10	1	0	-2.789492	1.458853	0.413041
11	6	0	-3.654281	-0.506249	0.305931
12	6	0	-3.401011	-1.871769	0.125317
13	6	0	-2.092817	-2.306643	-0.082980
14	1	0	4.779366	0.573144	0.209805
15	1	0	2.665319	1.886679	0.186586
16	1	0	2.461259	-3.039929	-0.267922
17	1	0	4.683029	-1.915457	-0.027845
18	1	0	-4.669279	-0.155643	0.482751
19	1	0	-4.213168	-2.595143	0.157579
20	1	0	-1.859088	-3.361057	-0.206065
21	8	0	0.200268	-1.932458	-0.312160
22	5	0	-0.010716	1.076041	-0.129983
23	8	0	-0.082551	2.156114	0.896467
24	8	0	0.005263	1.732594	-1.457778
25	6	0	-0.061378	1.810381	2.250198
26	1	0	-0.138431	2.728836	2.852184
27	1	0	-0.899177	1.149043	2.535590
28	1	0	0.872148	1.295444	2.541765
29	6	0	-1.025830	2.619299	-1.791554
30	1	0	-1.997232	2.108526	-1.925677
31	1	0	-1.161640	3.406571	-1.032233
32	1	0	-0.773816	3.103428	-2.747274

2c'---CH₃O⁻:

Imaginary frequencies: none

$E = -812.0620120$

ZPE = 0.2921256



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	3.770659	-0.470993	-0.382295
2	6	0	2.539604	-1.118376	-0.218754
3	6	0	1.341246	-0.432643	0.012877
4	6	0	1.401698	0.980250	0.074259
5	6	0	2.632879	1.648714	-0.109051
6	6	0	3.807607	0.923534	-0.328742
7	6	0	-1.056524	1.227901	-0.006651
8	6	0	-1.272026	-0.171847	-0.093555
9	6	0	-2.563451	-0.596060	-0.435069
10	1	0	-2.734544	-1.668384	-0.514164
11	6	0	-3.628127	0.285900	-0.664331
12	6	0	-3.392850	1.657931	-0.572180
13	6	0	-2.115269	2.129658	-0.255688
14	1	0	4.682359	-1.041874	-0.547876
15	1	0	2.493316	-2.205398	-0.253072
16	1	0	2.686283	2.732690	-0.107989
17	1	0	4.745111	1.458913	-0.468209
18	1	0	-4.618559	-0.090505	-0.913005
19	1	0	-4.192588	2.372042	-0.760145
20	1	0	-1.951736	3.202250	-0.235585
21	5	0	-0.061772	-1.220746	0.265036
22	8	0	-0.172969	-2.485131	-0.524197
23	8	0	-0.071906	-1.597241	1.700711
24	6	0	-0.133053	-2.433965	-1.920062
25	1	0	-0.248004	-3.455503	-2.315150
26	1	0	-0.939441	-1.813912	-2.350949
27	1	0	0.821397	-2.031007	-2.304157
28	6	0	-1.155944	-2.336416	2.190235
29	1	0	-2.108558	-1.777489	2.140473
30	1	0	-1.295822	-3.283453	1.643262
31	1	0	-0.966290	-2.575802	3.247838
32	7	0	0.225174	1.727453	0.321087
33	6	0	0.351112	3.108730	0.735603
34	1	0	0.442367	3.821571	-0.103746
35	1	0	-0.522938	3.393412	1.327407
36	1	0	1.233916	3.219069	1.370591

Mulliken atomic charge (Fig. 6)

Geometry optimizations of the ethylene glycol adduct of each borinic acid was performed and the Mulliken charges for the *B*-bound oxygens calculated, with the averages reported. Computed complexes corresponding to the ethylene glycol adducts are reported as **1b''**, **2a''**, **2b''** and **2c''** respectively (Table S3).

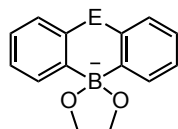
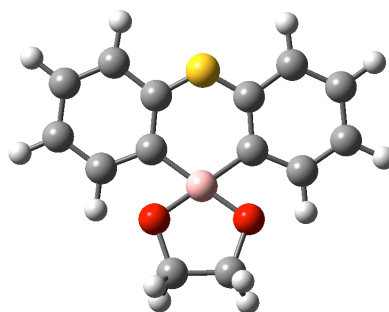


Table S3. Computed Mulliken charges

	1b'' ¹¹	2a''	2b''	2c''
<i>O</i> -1	-0.388	-0.440	-0.492	-0.479
<i>O</i> -2	-0.388	-0.601	-0.537	-0.577
Avg.	-0.388	-0.521	-0.515	-0.528

2a'':

$E = -1114.3876503$



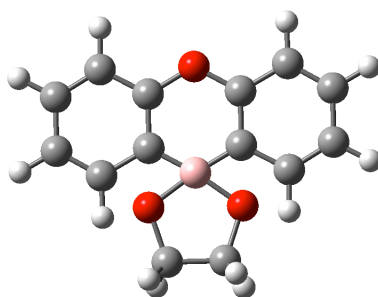
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-3.709945	0.058634	-0.907111
2	6	0	-2.498144	0.742860	-0.778040
3	6	0	-1.357694	0.163640	-0.193697
4	6	0	-1.479545	-1.178774	0.212329
5	6	0	-2.685342	-1.889184	0.087282
6	6	0	-3.806846	-1.264871	-0.460643
7	6	0	1.330554	-1.294435	0.184246
8	6	0	1.310834	0.051545	-0.232775
9	6	0	2.488376	0.528040	-0.838237
10	1	0	2.482231	1.551911	-1.204988
11	6	0	3.639547	-0.254208	-0.974196
12	6	0	3.634297	-1.576785	-0.516826
13	6	0	2.471558	-2.102304	0.049634
14	1	0	-4.573721	0.549248	-1.352412
15	1	0	-2.414343	1.768804	-1.130167
16	1	0	-2.737877	-2.929577	0.401220

¹¹ Data obtained from: Lee, D.; Williamson, C. L.; Chan, L.; Taylor, M. S. *J. Am. Chem. Soc.*, 2012, **134**, 8260–8267.

17	1	0	-4.740233	-1.815786	-0.557563
18	1	0	4.534247	0.160580	-1.435467
19	1	0	4.517935	-2.203386	-0.620152
20	1	0	2.442070	-3.141515	0.370648
21	16	0	-0.101833	-2.067395	0.942109
22	6	0	0.537013	2.861064	1.374032
23	6	0	0.062281	3.380798	0.007234
24	1	0	1.644289	2.868834	1.418986
25	1	0	0.160248	3.460334	2.217381
26	1	0	-0.960698	3.796695	0.091315
27	1	0	0.713360	4.170709	-0.401714
28	5	0	0.013578	1.018390	0.030663
29	8	0	0.083208	2.244816	-0.826901
30	8	0	0.025826	1.554359	1.438960

2b'':

$E = -791.4204941$

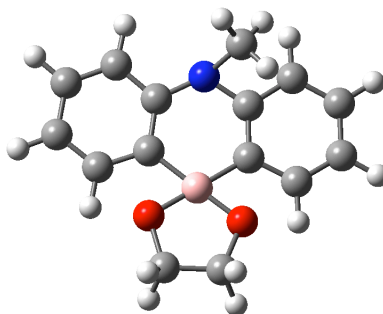


Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-3.708275	-0.468757	-0.366589
2	6	0	-2.604021	0.387759	-0.373906
3	6	0	-1.292217	-0.049467	-0.112496
4	6	0	-1.148208	-1.425629	0.121889
5	6	0	-2.234189	-2.314261	0.140302
6	6	0	-3.519625	-1.831500	-0.098601
7	6	0	1.264272	-1.352496	0.130140
8	6	0	1.327956	0.031847	-0.083991
9	6	0	2.612599	0.554673	-0.317547
10	1	0	2.699224	1.623790	-0.500977
11	6	0	3.765758	-0.233701	-0.319569
12	6	0	3.657025	-1.610865	-0.079306
13	6	0	2.402303	-2.174468	0.142883
14	1	0	-4.705971	-0.083741	-0.568779
15	1	0	-2.749805	1.442355	-0.597489
16	1	0	-2.050562	-3.368270	0.332292
17	1	0	-4.365454	-2.515918	-0.087514
18	1	0	4.740483	0.214784	-0.501710
19	1	0	4.542815	-2.242789	-0.072537
20	1	0	2.282147	-3.240066	0.320316
21	8	0	0.076796	-2.027802	0.350759
22	6	0	0.026820	3.281538	-0.454072
23	6	0	-0.430987	3.041552	0.994666
24	1	0	-0.597438	4.019924	-0.983883
25	1	0	1.069805	3.655846	-0.468028

26	1	0	0.013580	3.753645	1.708089
27	1	0	-1.532910	3.136945	1.067767
28	5	0	-0.010091	0.955163	-0.013942
29	8	0	-0.004041	1.733909	1.279041
30	8	0	-0.074097	2.020183	-1.069882

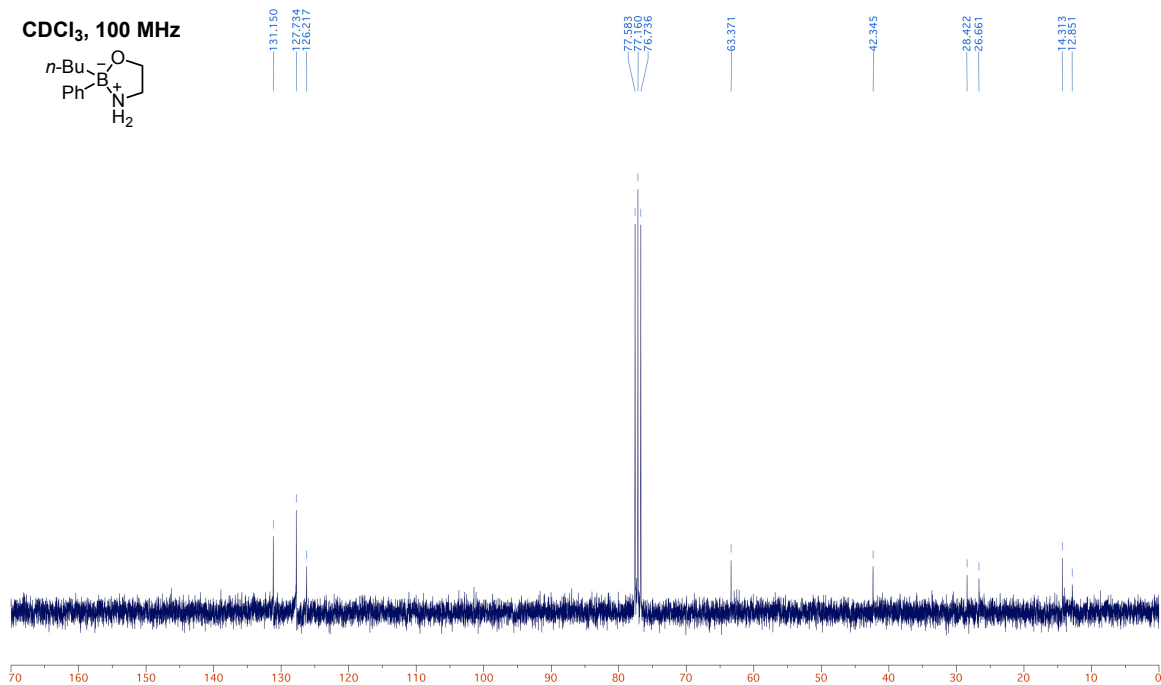
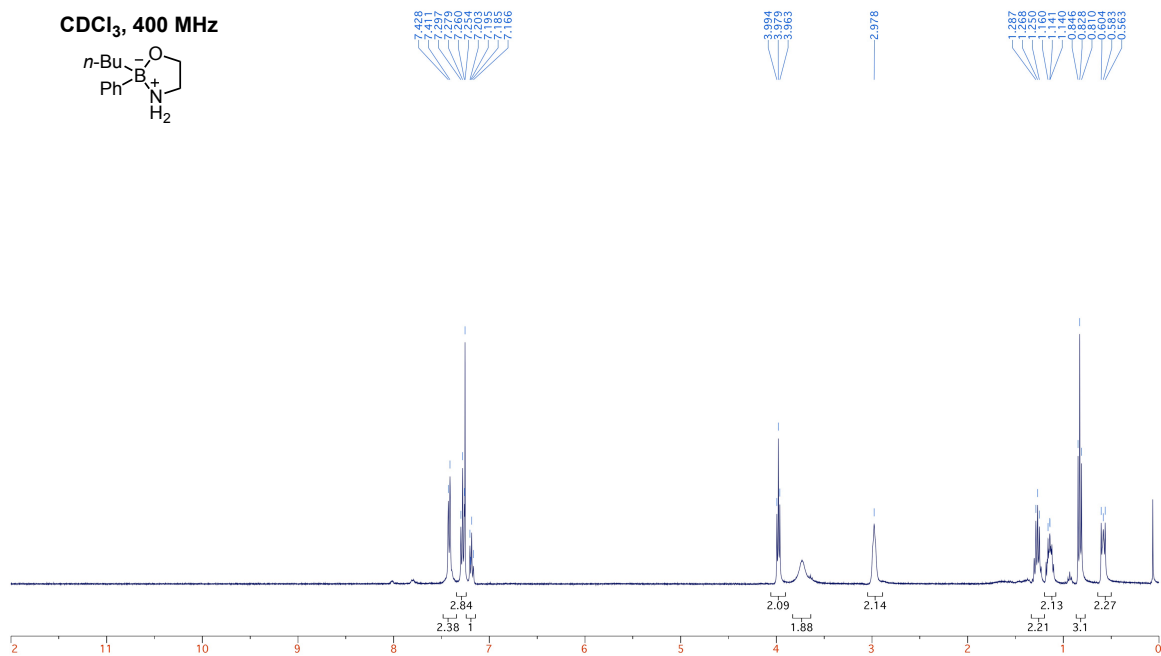
2c'':

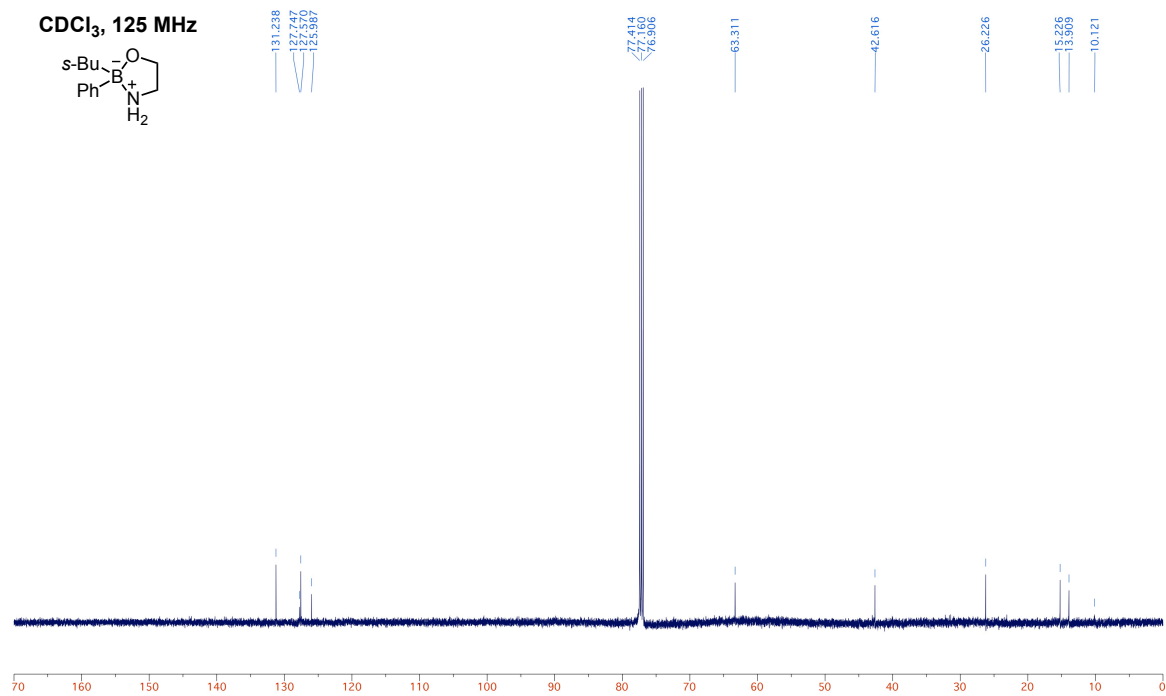
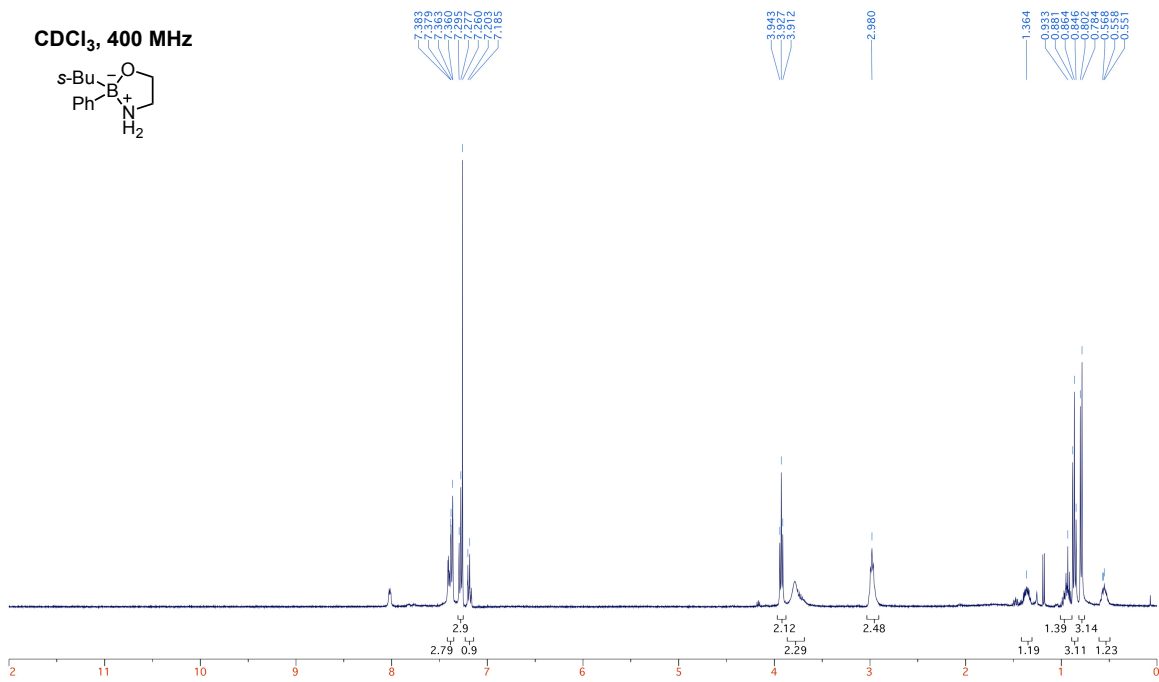
$E = -810.8614371$

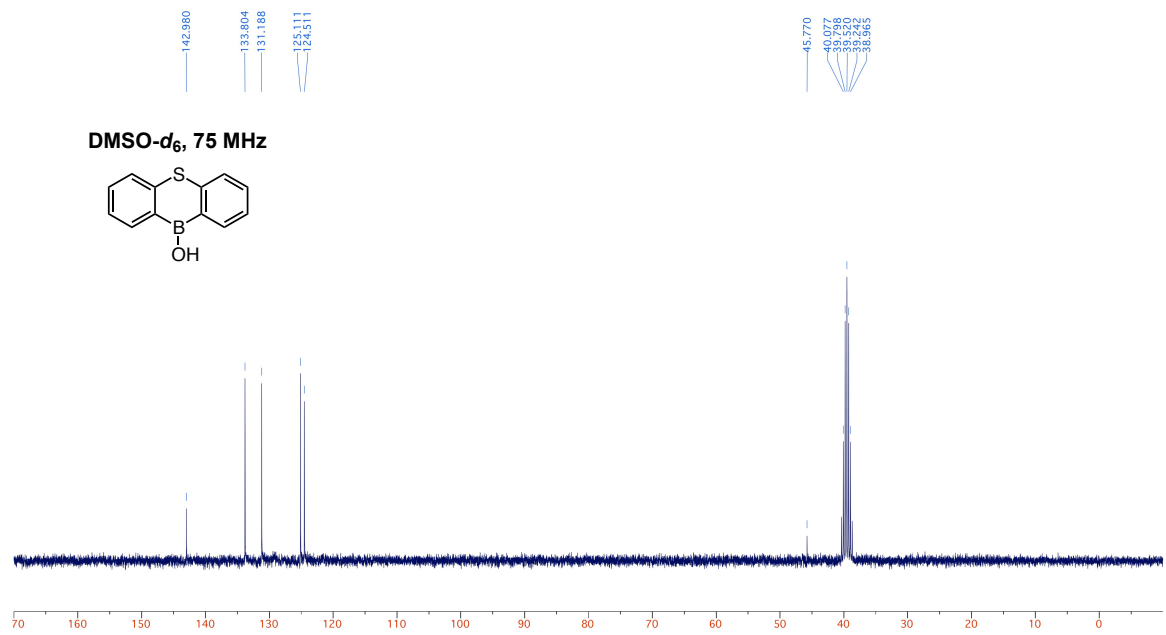
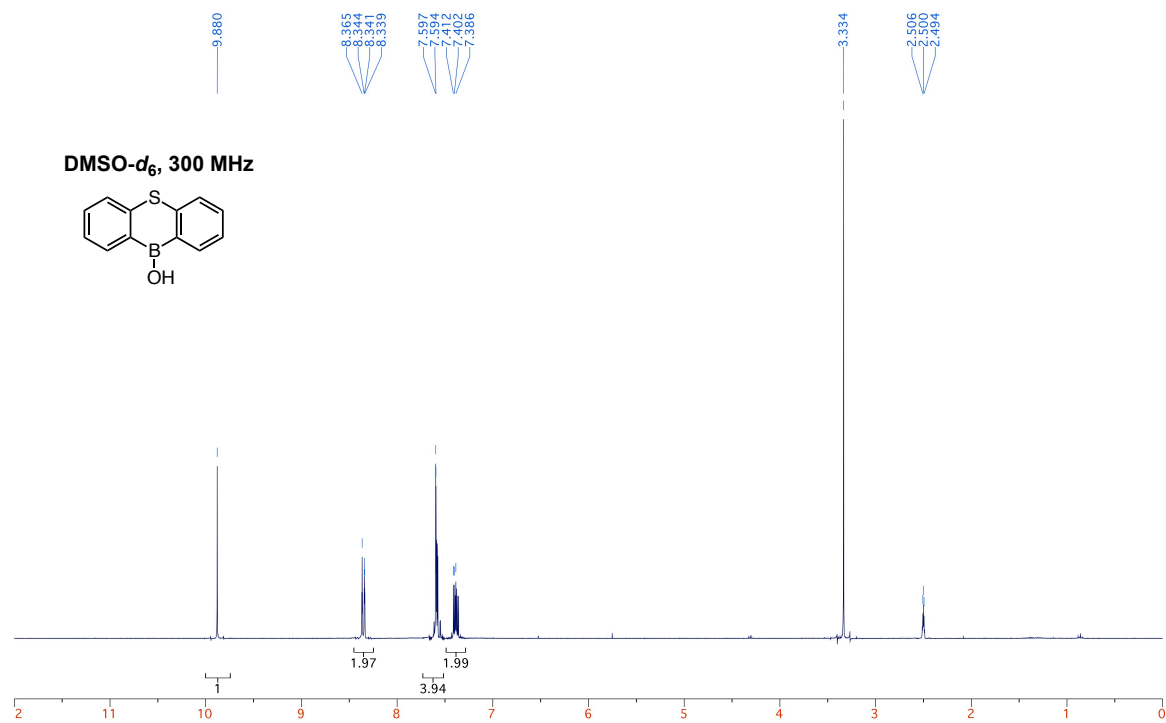


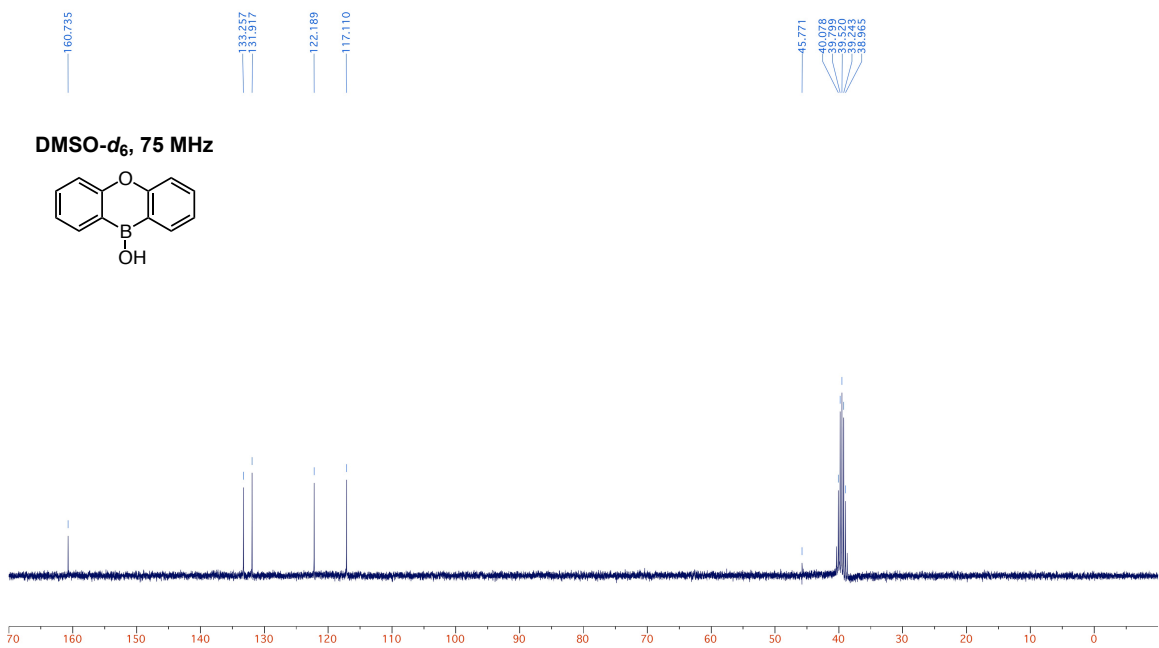
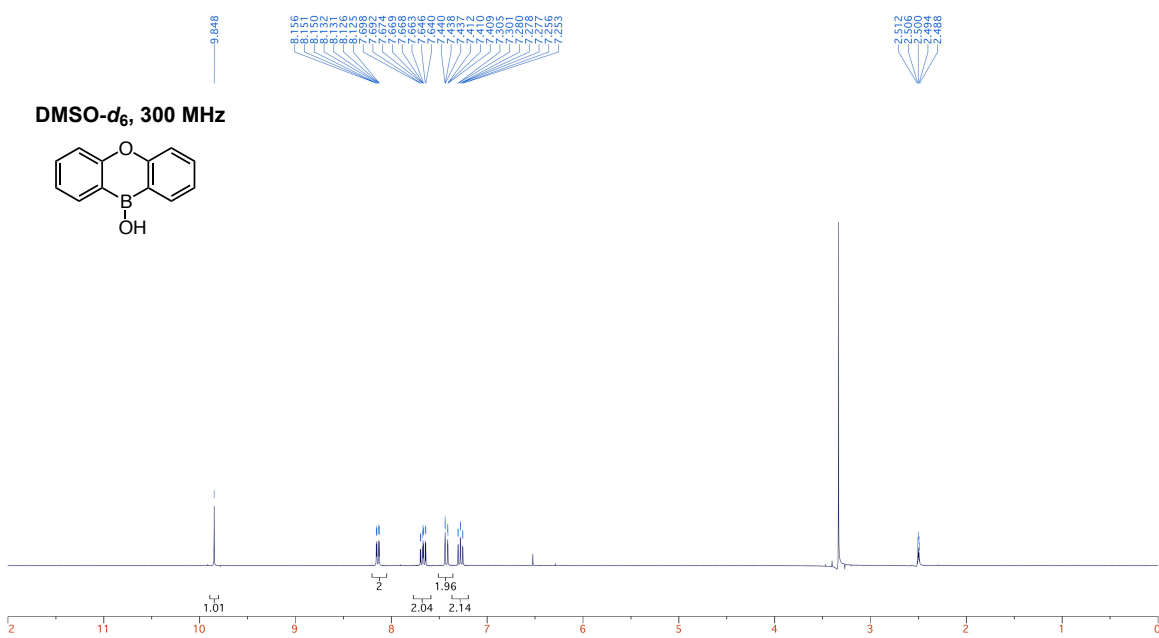
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-3.697771	0.236843	-0.779342
2	6	0	-2.487481	0.931569	-0.659024
3	6	0	-1.308549	0.329130	-0.206855
4	6	0	-1.356770	-1.053187	0.099391
5	6	0	-2.568112	-1.767862	-0.021924
6	6	0	-3.731084	-1.119731	-0.449435
7	6	0	1.094671	-1.275075	0.075186
8	6	0	1.285692	0.093241	-0.247375
9	6	0	2.546066	0.469253	-0.726754
10	1	0	2.684075	1.511401	-1.007519
11	6	0	3.613087	-0.430714	-0.852526
12	6	0	3.410791	-1.767668	-0.506329
13	6	0	2.157071	-2.194410	-0.055973
14	1	0	-4.598130	0.743310	-1.122063
15	1	0	-2.444481	1.988333	-0.916078
16	1	0	-2.612164	-2.832692	0.183366
17	1	0	-4.654765	-1.688623	-0.539516
18	1	0	4.582989	-0.095648	-1.215613
19	1	0	4.216836	-2.492878	-0.602981
20	1	0	2.014200	-3.248739	0.158490
21	7	0	-0.176799	-1.716838	0.514178
22	6	0	-0.290238	-3.018068	1.136170
23	1	0	-0.372606	-3.853546	0.417140
24	1	0	0.585550	-3.198541	1.765384
25	1	0	-1.174052	-3.036986	1.779491
26	6	0	0.699045	2.950419	1.378088
27	6	0	0.256466	3.506123	0.013953
28	1	0	1.805297	2.892323	1.422977
29	1	0	0.359725	3.568313	2.224645
30	1	0	-0.738156	3.986164	0.102534
31	1	0	0.955605	4.257623	-0.389432
32	5	0	0.072713	1.146994	0.018333
33	8	0	0.205460	2.378159	-0.827500
34	8	0	0.110389	1.677331	1.435594

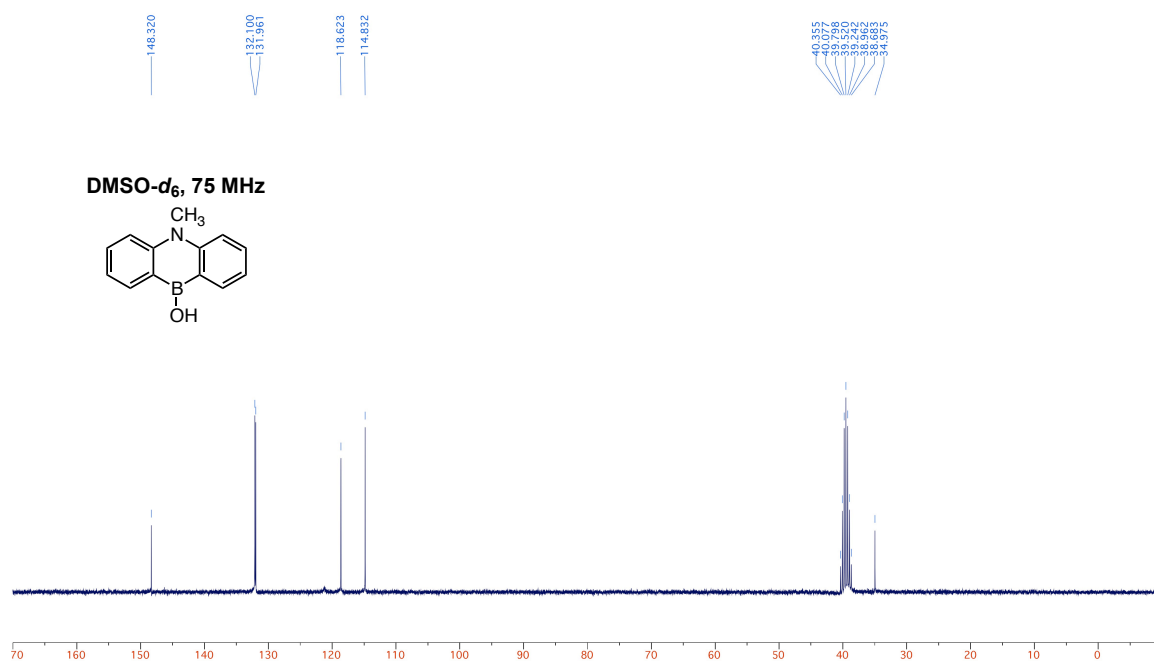
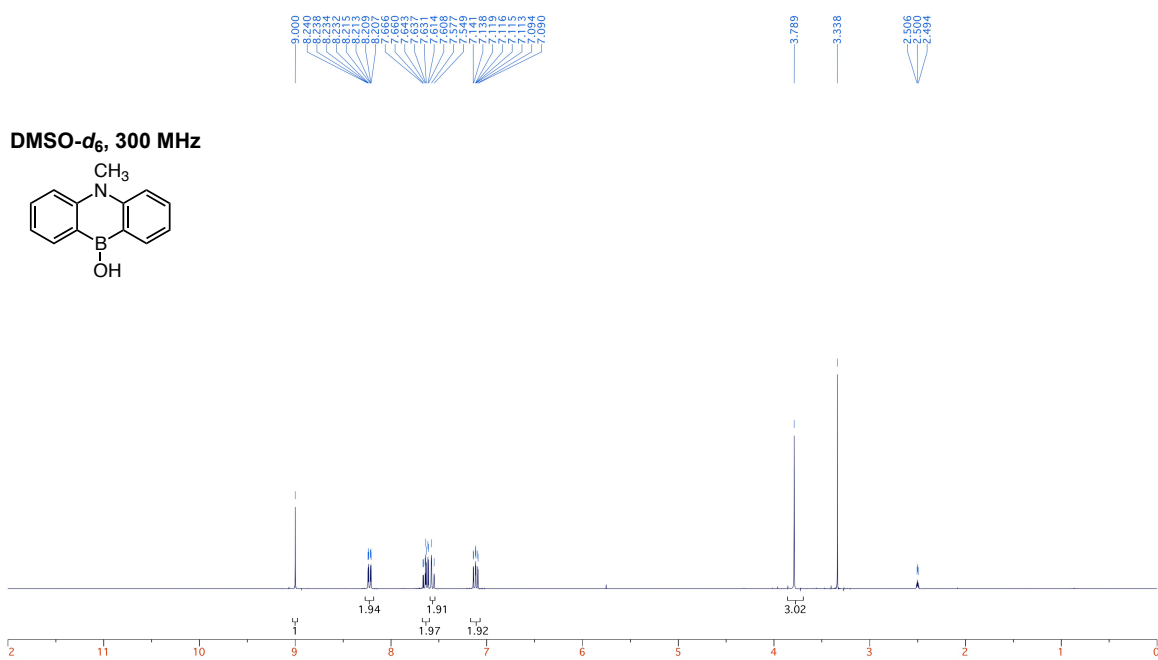
V. ^1H and ^{13}C NMR Spectra



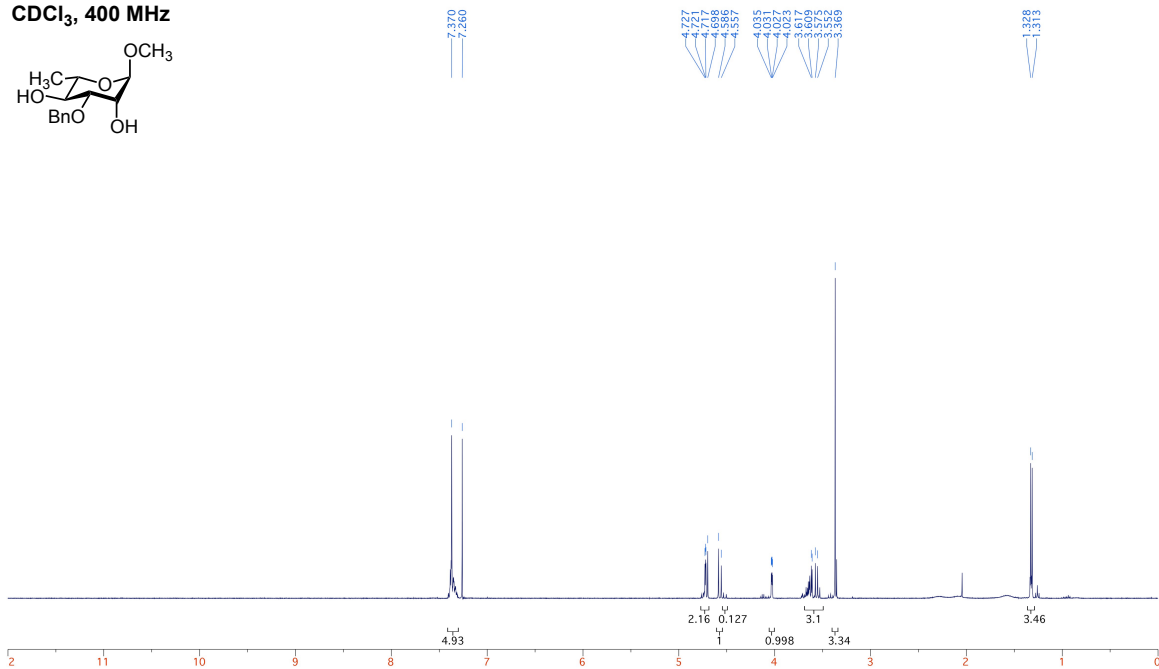
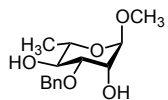








CDCl₃, 400 MHz



CDCl₃, 400 MHz

