Supporting Information

Boronic, Diboronic and Boric Acid Esters of 1,8-Naphthalenediol – Synthesis, Structure and Formation of Boronium Salts

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1. General Remarks

All air- and moisture-sensitive manipulations were carried out using standard vacuum line, Schlenk or cannula techniques or in a Vacuum Atmospheres OMNI inert atmosphere dry box containing an atmosphere of purified nitrogen. Toluene, hexanes and benzene were distilled under nitrogen from alkali metals and stored over 4 Å molecular sieves prior to use. All deuterated solvents were purchased from Cambridge Isotope Labs. C₆D₆ and CDCl₃ were dried and stored over 4 Å molecular sieves prior to use. All the non-sensitive reactions were carried out using the undried solvents. Catechol (Alfa Aesar), 2,2-bipyridine (Strem), 1,8-dihydroxynaphthalene (Accela), PhB(OH)₂ (Chem-Impex), 3,4,5-F₃-C₆H₂BCat (Frontier Scientific), 2,4,6-F₃-C₆H₂BCat (Combi-Blocks), 2,6-F₂-C₆H₃BCat (Oakwood Chemicals), C₆F₅BCat (BTC chemicals) and 2,6-Cl₂-C₆H₃BCat (Combi Blocks) were purchased from commercial sources and used without further purification. 4-dimethylaminopyridine was purchased from Acros Organics and sublimed prior to use. The boronic catechol esters PhBCat (1b) [1], 3,4,5-F₃-C₆H₂BCat (3b) [2], 2,4,6-F₃-C₆H₂BCat (4b) [2], 2,6-F₂-C₆H₃BCat (5b) [2], C₆F₅BCat (2b) [2], 2, 4, 6-Me₃-C₆H₂BCat (7b) [3] and Ph-BDan [4] were prepared according to the literature. The ¹H-, ¹³C-, ¹¹B- ¹⁹F-NMR spectra were obtained from a JOEL ECS 400. All measurements, unless noted otherwise, were carried out at 298 K and NMR chemical shifts were given in ppm. The ¹¹B NMR spectra referenced to H₃BO₃ in D₂O (δ = 36 ppm), ¹⁹F NMR spectrum was referenced to C₆H₅CF₃ in C₆D₆ (δ = 62.3 ppm), The ¹H-NMR spectra were referenced to the residual protonated solvent for ¹H and the ¹³C NMR spectra were referenced to the deuterated solvent peaks. The following abbreviations were used to describe peak multiplicities in the reported NMR spectroscopic data: “s” for singlet, “d” for doublet, “t” for triplet, “q” for quartet, “sept” for septet, “m” for multiplet and “br” for broadened resonances. Elemental analyses were performed using a Perkin Elmer 2400 Series II CHNS/O Analyzer.
2. Experimental

2.1. Acid-ester equilibrium of phenyl boronic acid and 1,8-naphthalenediol

\[
\text{PhB(OH)}_2 + \text{HO-Ph} \rightleftharpoons \text{PhBO(OH)-Ph} + 2 \text{H}_2\text{O}
\]

A standard NMR tube was charged with 1,8-naphthalenediol (3.3 mg, 0.02 mmol), phenyl boronic acid (2.5 mg, 0.02 mmol) and 0.5 mL of CDCl₃. After 10 minutes, the resulting solution was analyzed by $^1$H-NMR (400 MHz, CDCl₃): 6.99 (d, $^3J_{HH} = 8$ Hz, CH-naphthyl, 2 H), 7.41 (m, CH-phenyl, 4 H), 7.49 (t, $^3J_{HH} = 8$ Hz, CH-naphthyl, 2 H), 7.58 (t, $^3J_{HH} = 8$ Hz, CH-phenyl, 1 H), 8.13 (d, $^3J_{HH} = 8$ Hz, CH-naphthyl, 2 H) ppm.

Figure S1. $^1$H NMR spectrum of the reaction of phenyl boronic acid with 1,8-naphthalenediol (room temperature, CDCl₃).
2.2. Ligand exchange experiments

2.2.1 1b and 1,8-naphthalenediol

A standard NMR tube was charged with 1,8-naphthalenediol (6.5 mg, 0.04 mmol), 1b (7.8 mg, 0.04 mmol) and 0.5 mL of CDCl₃. The progress of the reaction was monitored by ¹H-NMR spectroscopy. Figure S2 shows the ¹H NMR spectrum of the reaction mixture after reaching equilibrium.

![reaction diagram](image)

**Figure S2.** ¹H NMR spectrum of the reaction mixture of 1b and 1,8-naphthalenediol after 1 hour at room temperature.
2.2.2 1c and 1,8-naphthalenediol

A standard NMR tube was charged with 1,8-naphthalenediol (6.5 mg, 0.04 mmol), 1c (8.2 mg, 0.04 mmol) and 0.5 mL of CDCl₃. The progress of the reaction was monitored periodically by ¹H-NMR spectroscopy. Figure S3 shows the ¹H NMR spectrum of the reaction mixture after reaching equilibrium.

![Diagram of chemical reactions]

Figure S3. ¹H NMR spectrum of 1c and 1,8-naphthalenediol after heating for 24 hours at 50 °C (CDCl₃).
2.2.3 1a and pinacol

A standard NMR tube was charged with pinacol (4.7 mg, 0.04 mmol), 1a (9.8 mg, 0.04 mmol) and 0.5 mL of CDCl3. The progress of the reaction was monitored periodically by \(^1\)H-NMR spectroscopy. **Figure S4** shows the \(^1\)H NMR spectrum of the reaction mixture after reaching equilibrium.

**Figure S4.** \(^1\)H NMR spectrum of 1a and pinacol after heating for 48 hours at 50 °C (CDCl3).
2.2.4 1d and 1,8-naphthalenediol

A standard NMR tube was charged with 1,8-naphthalenediol (6.5 mg, 0.04 mmol), 1d (9.8 mg, 0.04 mmol) and 0.5 mL of CDCl₃. The progress of the reaction was monitored periodically by ¹H-NMR spectroscopy. Figure S4 shows the ¹H NMR spectrum of the reaction mixture after reaching equilibrium.

Figure S5. ¹H NMR spectrum of the reaction mixture of 1d and 1,8-naphthalenediol after heating for 4 days at 50 °C (CDCl₃).
2.2.5 1a and 1,8-diaminonaphthalene

A standard NMR tube was charged with 1,8-diaminonaphthalene (6.4 mg, 0.04 mmol), 1d (9.8 mg, 0.04 mmol) and 0.5 mL of CDCl₃. The progress of the reaction was monitored periodically by ¹H-NMR spectroscopy. Figure S6 shows the ¹H NMR spectrum of the reaction mixture after reaching equilibrium.

![Reaction Scheme](image)

**Figure S6.** ¹H NMR spectrum of the reaction mixture of 1a and 1,8-diaminonaphthalene after heating for 4 days at 50 °C (CDCl₃).
2.3 Hydrolytic stability of 1a-d.

2.3.1 Hydrolysis of 1a

A standard NMR tube was charged with 1a (7.38 mg, 0.03 mmol) and 0.6 mL of a DMSO-D$_6$/water mixture (10 vol% H$_2$O). The progress of the hydrolysis was monitored periodically by $^1$H NMR spectroscopy. The hydrolytic conversion was calculated from integrating distinguishable peaks of 1a and 1,8-naphthalenediol.

![Chemical Structure](image)

**Figure S7.** $^1$H NMR spectrum of 1a in 0.6 mL of DMSO-D$_6$/water mixture (10 vol% H$_2$O). after 2 weeks at room temperature.
2.3.2 Hydrolysis of 1b

A standard NMR tube was charged with 1b (5.88 mg, 0.03 mmol) and 0.6 mL of a DMSO-D_6/water mixture (10 vol% H_2O). The progress of the hydrolysis was monitored periodically by ¹H NMR spectroscopy. The hydrolytic conversion was calculated from integrating distinguishable peaks of 1b and 1,8-naphthalenediol.

![Diagram of reaction](image)

**Figure S8.** ¹H NMR spectrum of 1b in DMSO-D_6/water mixture (10 vol% H_2O) after 30 min at room temperature.
2.3.3 Hydrolysis of 1c

A standard NMR tube was charged with 1c (6.12 mg, 0.03 mmol) and 0.6 mL of a DMSO-D$_6$/water mixture (10 vol% H$_2$O). The progress of the hydrolysis was monitored periodically by $^1$H NMR spectroscopy. The hydrolytic conversion was calculated from integrating distinguishable peaks of 1c and 1,8-naphthalenediol.

![chemical structure]

Figure S9. $^1$H NMR spectrum of 1c in DMSO/water mixture (10 vol% H$_2$O) after one week at room temperature.
2.3.4 Hydrolysis of 1d

A standard NMR tube was charged with 1d (7.32 mg, 0.03 mmol) and 0.6 mL of a DMSO-D$_6$/water mixture (10 vol% H$_2$O). The progress of the hydrolysis was monitored periodically by $^1$H NMR spectroscopy. The hydrolytic conversion was calculated from integrating distinguishable peaks of 1d and 1,8-naphthalenediol.

Figure S10. $^1$H NMR spectrum of 1d in DMSO/water mixture (10 vol% H$_2$O) after 12 days at room temperature.
Table S1. Hydrolysis of the phenyl boronic acid esters 1a-c and amino borate 1d.

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2.4 Synthetic procedures

2.4.1 Synthesis of 1a, 3a-5a and 8a

The aryl boronic acid esters 1a, 3a-5a and 8a were synthesized in acetonitrile by mixing one equivalent of the aryl boronic acid with one equivalent of 1,8-naphthalenediol in a 20 mL scintillation vial with screw cap. The mixture was heated until all materials dissolved and subsequently cooled to room temperature. After the solutions were allowed to stand overnight (if not stated otherwise), crystalline precipitates formed, which were collected, washed once with cold acetonitrile and dried under vacuum to give the analytically pure products.

1a. 1,8-naphthalenediol (85 mg, 0.7 mmol), phenyl boronic acid (112 mg, 0.7 mmol) and acetonitrile (5 mL). Colorless crystals. Yield 145 mg (84%). M.p. 152-153 °C. \(^1\)H NMR [400 MHz, CDCl\(_3\)]: 6.99 (d, \(^3\)J\(_{H-H} = 8\) Hz, CH-naphthyl, 2 H), 7.41 (m, CH-phenyl, 4 H), 7.49 (t, \(^3\)J\(_{H-H} = 8\) Hz, CH-naphthyl, 2 H), 7.58 (t, \(^3\)J\(_{H-H} = 8\) Hz, CH-phenyl, 1 H), 8.13 (d, \(^3\)J\(_{H-H} = 8\) Hz, CH-naphthyl, 2 H) ppm. \(^{13}\)C[H] NMR [100.4 MHz, CDCl\(_3\)]: 109.6 (CH-naphthyl), 117.8 (C-quart), 121.2 (CH-naphthyl), 128.0 (CH-phenyl), 128.1 (CH-naphthyl), 132.4 (CH-phenyl), 134.8 (C-quart), 135.3 (CH-naphthyl), 148.0 (C-quart) ppm. Note: The ipso carbon bound to boron could not be detected in the \(^{13}\)C NMR. \(^{11}\)B NMR [128.4 MHz, CDCl\(_3\)]: 28.0 ppm. Anal. Calc. for C\(_{16}\)H\(_{11}\)BO\(_2\) (246.07): C, 78.10; H, 4.51; Found: C, 77.67; H, 4.17.
Figure S11. $^1$H NMR spectrum of 1a in CDCl$_3$ at room temperature.

Figure S12. $^{13}$C NMR spectrum of 1a in CDCl$_3$ at room temperature.
Figure S13. $^{11}$B NMR spectrum of 1a in CDCl₃ at room temperature.

3a. 1,8-naphthalenediol (0.36 g, 2.05 mmol), 3,4,5-trifluorophenyl boronic acid (0.33 g, 2.05 mmol) and acetonitrile (12 mL). Colorless crystals. Yield 0.59 g (95%). M.p. 153-154 °C. $^1$H NMR [400 MHz, CDCl₃]: 6.93 (d, $^3$Jₕ-ₕ = 8 Hz, CH-naphthyl, 2 H), 7.36 (t, $^3$Jₕ-ₕ = 8 Hz, CH-naphthyl, 2 H), 7.42 (d, $^3$Jₕ-ₕ = 8 Hz, CH-naphthyl, 2 H), 7.65 (d, $^3$Jₕ-ₕ = 8 Hz, CH-phenyl, 2 H) ppm. $^{13}$C{H} NMR [100.4 MHz, CDCl₃]: 109.7 (CH-naphthyl), 117.4 (C-quart), 118.3 (dd, $^2$JC-F = 14 Hz, $^3$JC-F = 5 Hz, (CH-phenyl), 121.6, 127.9 (CH-naphthyl), 135.1 (C-quart.), 142.6 (dt, $^1$JC-F = 257 Hz, $^2$JC-F = 15.0 Hz, p-CF), 147.2, (C-quart), 151.1 (dd, $^1$JC-F = 251 Hz, $^2$JC-F = 12 Hz, m-CF) ppm. Note: The ipso carbon bound to boron could not be detected in the $^{13}$C NMR. $^{11}$B NMR [128.4 MHz, CDCl₃]: 27.0 ppm. $^{19}$F NMR (376.3 MHz, CDCl₃): -134.3, -154.2 ppm. Anal. Calc. for C₁₆H₈F₃BO₂ (300.04): C, 64.05; H, 2.69; Found: C, 63.64; H, 2.29.
Figure S14. $^1$H NMR spectrum of 3a in CDCl$_3$ at room temperature.

Figure S15. $^{13}$C NMR spectrum of 3a in CDCl$_3$ at room temperature.
**Figure S16.** $^{11}$B NMR spectrum of 3a in CDCl$_3$ at room temperature.

**Figure S17.** $^{19}$F NMR spectrum of 3a in CDCl$_3$ at room temperature.
4a. 1,8-naphthalenediol (0.27 g, 1.7 mmol), 2,6-difluorophenyl boronic acid (0.3 g, 1.7 mmol) and acetonitrile (10 mL). Colorless crystals. Yield 0.47 g (92%). M.p. 140-141 °C. $^1$H NMR [400 MHz, CDCl$_3$]: 6.70 (t, $^3$J$_{HH}$ = 8 Hz, CH-naphthyl, 2 H), 6.95 (d, $^3$J$_{HH}$ = 8 Hz, CH-naphthyl, 2 H), 7.37 (t, $^3$J$_{HH}$ = 8 Hz, CH-phenyl, 2 H), 7.45 (d, $^3$J$_{HH}$ = 8 Hz, CH-naphthyl, 2 H) ppm. $^{13}$C{H} NMR [100.4 MHz, CDCl$_3$]: 100.7 (t, $^2$J$_{C-F}$ = 26 Hz, CH-phenyl), 109.9 (CH-naphthyl), 117.08 (C-quart.), 121.6, 128.0 (CH-naphthyl), 135.1, 147.5 (C-quart.), 167.8 (dt, $^1$J$_{C-F}$ = 256 Hz, $^2$J$_{C-F}$ = 16.0 Hz, para-CF), 165.7 (dt, $^1$J$_{C-F}$ = 240 Hz, $^2$J$_{C-F}$ = 15 Hz, ortho-CF) ppm. Note: The ipso carbon bound to boron could not be detected in the $^{13}$C NMR. $^{11}$B NMR [128.4 MHz, CDCl$_3$]: 27.1 ppm. $^{19}$F NMR [376.3 MHz, CDCl$_3$]: -96.8, -102.3 ppm. Anal. Calc. for C$_{16}$H$_8$F$_3$BO$_2$ (300.06): C, 64.05; H, 2.69; Found: C, 63.47; H, 2.52.

![Figure S18. $^1$H NMR spectrum of 4a in CDCl$_3$ at room temperature.](image-url)
Figure S19. $^{13}$C NMR spectrum of 4a in CDCl$_3$ at room temperature.

Figure S20. $^{11}$B NMR spectrum of 4a in CDCl$_3$ at room temperature.
Figure S21. $^{19}$F NMR spectrum of 4a in CDCl$_3$ at room temperature.

5a. 1,8-naphthalenediol (0.25 g, 1.5 mmol), 2,6-difluorophenyl boronic acid (0.24 g, 1.5 mmol), acetonitrile (10 mL). Colorless crystals. Yield 0.36 g (85%). M.p. 142-143 °C. $^1$H NMR [400 MHz, CDCl$_3$]: 6.92-6.97 (m, 4H), 7.35-7.50 (m, 5 H) ppm. $^{13}$C{H} NMR [100.4 MHz, CDCl$_3$]: 109.9 (d, $^3$J$_{C-F}$ = 11 Hz, CH), 111.6 (CH), 117.8 (C-quart.), 121.6, 128.0, 133.9 (CH), 135.2, 147.6 (C-quart.), 167.0 (dd, $^1$J$_{C-F}$ = 253 Hz, $^2$J$_{C-F}$ = 12.1 Hz ortho-CF) ppm. Note: The ipso carbon bound to boron could not be detected in the $^{13}$C NMR. $^{11}$B NMR [128.4 MHz, CDCl$_3$]: 27.0 ppm. $^{19}$F NMR [376.3 MHz, CDCl$_3$]: -100.4 ppm. Anal. Calc. for C$_{16}$H$_9$F$_2$BO$_2$ (282.05): C, 68.13; H, 3.22; Found: C, 67.55; H, 3.05.
Figure S22. $^1$H NMR spectrum of 5a in CDCl$_3$ at room temperature.

Figure S23. $^{13}$C NMR spectrum of 5a in CDCl$_3$ at room temperature.
**Figure S24.** $^{11}$B NMR spectrum of 5a in CDCl$_3$ at room temperature.

**Figure S25.** $^{19}$F NMR spectrum of 5a in CDCl$_3$ at room temperature.
8a. 1,8-naphthalenediol (0.14 g, 0.76 mmol), phenyl boronic acid (0.12 g, 0.76 mmol), acetonitrile (10 mL). Stored for 2 days in a fridge. Colorless crystals. Yield 0.23 g (75%). M.p. 202-203°C. 

$^1$H NMR [400 MHz, CDCl$_3$]: 3.80 (s, CH$_3$, 6 H), 6.57 (d, $^3$J$_{H-H}$ = 12 Hz, CH-naphthyl, 2 H), 6.94 (d, $^3$J$_{H-H}$ = 8 Hz, CH-naphthyl, 2 H), 7.32-7.44 (m, CH-naphthyl, CH-phenyl, 5 H) ppm; $^{13}$C{H} NMR [100.4 MHz, CDCl$_3$]: 55.9 (OCH$_3$), 103.7 (CH-phenyl), 109.7 (CH-naphthyl), 117.9 (C-quart), 121.1, 127.9 (CH-naphthyl), 132.1 (CH-phenyl), 135.2, 148.3, 163.4 (C-quart) ppm. Note: The ipso carbon bound to boron could not be detected in the $^{13}$C NMR. $^{11}$B NMR [128.4 MHz, CDCl$_3$]: 28.3 ppm. Anal. Calc. for C$_{16}$H$_{11}$BO$_2$ (306.12): C, 70.62; H, 4.94; Found: C, 70.43; H, 4.78.

![Figure S26. $^1$H NMR spectrum of 8a in CDCl$_3$ at room temperature.](image)
Figure S27. $^{13}$C NMR spectrum of 8a in CDCl$_3$ at room temperature.

Figure S28. $^{11}$B NMR spectrum of 8a in CDCl$_3$ at room temperature.
2.4.2 Synthesis of 2a

1,8-naphthalenediol (0.26 g, 1.6 mmol), C_6F_5B(OH)_2 (0.35 g, 1.6 mmol) and 15 mL of dry DCM were added to a 60 mL Schlenk flask with a magnetic stir bar under nitrogen. After stirring the mixture for about 20 hours at room temperature, all volatiles were removed under vacuum and the solid residue was recrystallized from acetonitrile to give 2a as colorless crystals. Yield 0.34 g (60%). M.p. 167-168 °C. ^1H NMR [400 MHz, CDCl_3]: 6.97 (d, ^3J_H-H = 8 Hz, CH-naphtyl, 2 H), 7.39 (t, ^3J_H-H = 8 Hz, CH-naphtyl, 2 H), 7.47 (d, ^3J_H-H = 8 Hz, CH-naphtyl, 2 H) ppm. ^13C{H} NMR [100.4 MHz, CDCl_3]: 110.2 (CH-naphtyl), 117.6 (C-quart.), 122.0, 128.0 (CH-naphtyl), 135.2 (C-quart.), 137.6 (d, ^1J_C-F = 253 Hz, C-F), 143.6 (d, ^1J_C-F = 258 Hz, C-F), 147.0 (C-quart.), 149.9 (d, ^1J_C-F = 252 Hz, C-F) ppm. Note: The ipso carbon bound to boron could not be detected in the ^13C NMR. ^11B NMR [128.4 MHz, CDCl_3]: 27.9 ppm. ^19F NMR [376 MHz, CDCl_3]: -129.3, -148.1, -161.2 ppm. Anal. Calc. for C_16H_6BF_5O_2 (336.02): C, 57.19; H, 1.8. Found: C, 56.92; H, 1.26.
Figure S29. $^1$H NMR spectrum of 2a in CDCl$_3$ at room temperature.

Figure S30. $^{13}$C NMR spectrum of 2a in CDCl$_3$ at room temperature.
Figure S31. $^{11}$B NMR spectrum of 2a in CDCl$_3$ at room temperature.

Figure S32. $^{19}$F NMR spectrum of 2a in CDCl$_3$ at room temperature.
2.4.3 Synthesis of 7a

1,8-naphthalenediol (0.24 g, 1.5 mmol), 2,4,6-trimethylphenyl boronic acid (0.246 g, 1.5 mmol) and 15 mL of toluene were added to a 20 mL scintillation vial with magnetic stir bar. After stirring the mixture for one day at room temperature, all volatiles were removed under vacuum and the residue was recrystallized from acetonitrile to give 0.26 g (63%) of 7a as a colorless crystalline solid. M.p. 98-100 °C. $^1$H NMR [400 MHz, CDCl$_3$]: 2.31 (s, para-CH$_3$, 3 H), 2.49 (s, ortho-CH$_3$, 6 H), 6.89 (s, CH-phenyl, 2 H), 6.92 (d, $^3$J$_{HH}$ = 8 Hz, CH-naphthyl, 2 H), 7.37 (t, $^3$J$_{HH}$ = 8 Hz, CH-naphthyl, 2 H), 7.45 (d, $^3$J$_{HH}$ = 8 Hz, CH-naphthyl, 2 H) ppm; $^{13}$C{H} NMR [100.4 MHz, CDCl$_3$]: 21.5 (p-CH$_3$), 22.6 (m-CH$_3$), 109.6 (CH-naphthyl), 117.7 (C-quart.), 121.3 (CH-naphthyl), 127.9, 128.0 (CH-phenyl), 135.2, 139.9, 142.0, 147.9 (C-quart.) ppm. Note: The ipso carbon bound to boron could not be detected in the $^{13}$C NMR. $^{11}$B NMR [128.4 MHz, CDCl$_3$]: 29.9 ppm. Anal. Calc. for C$_{19}$H$_{17}$BO$_2$ (288.15): C, 79.20; H, 5.95. Found: C, 78.74; H, 5.87.
**Figure S33.** $^1$H NMR spectrum of 7a in CDCl$_3$ at room temperature.

**Figure S34.** $^{13}$C NMR spectrum of 7a in CDCl$_3$ at room temperature.
**2.4.4 Synthesis of 6a**

1,8-naphthalenediol (0.29 g, 1.5 mmol), 2,6-dichlorophenyl boronic acid (0.242 g, 1.5 mmol), Na₂SO₄ (2 g) and 15 mL of CHCl₃ were added to a 100 mL round bottom flask equipped with a magnetic stir bar. The mixture was stirred for ca. 20 hours at room temperature and filtered to separate Na₂SO₄. Then all volatiles were evaporated under vacuum (rotavap) and the solid residue was extracted with circa 100 mL of hexanes. After removal of hexanes under vacuum (rotavap) the raw product was distilled under vacuum using a Kugelrohr ofen (180°C, 10⁻¹ mbar) to give 6a as a colorless crystalline solid. Yield 0.4 g (84%). M.p. 158-159 °C. ¹H NMR [400 MHz, CDCl₃]: 6.96 (d, 3J_H-H = 8 Hz, CH-naphthyl, 2 H), 7.32 (s, CH-naphthyl, 3 H), 7.39 (t, 3J_H-H = 8 Hz, CH-naphthyl), 2 H, 7.48...
(d, $^3J_{HH} = 8$ Hz, CH-naphthyl, 2 H) ppm. $^{13}$C{H} NMR [100.4 MHz, CDCl$_3$] 110.0 (CH-naphthyl), 117.8 (C-quart), 121.8, 127.2 (CH-naphthyl), 128.0 (m-CH-phenyl), 131.8 (p-CH-phenyl), 135.2, 137.9, 147.7 (C-quart.) ppm. Note: The ipso carbon bound to boron could not be detected in the $^{13}$C NMR. $^{11}$B NMR [128.4 MHz, CDCl$_3$]: 27.6 ppm. Anal. Calc. for $C_{16}H_9BCl_2O_2$ (314.96): C, 61.02; H, 2.88. Found: C, 60.76; H, 2.61.

Figure S36. $^1$H NMR spectrum of 6a in CDCl$_3$ at room temperature.

Figure S37. $^{13}$C NMR spectrum of 6a in CDCl$_3$ at room temperature.
Figure S38. $^{11}$B NMR spectrum of 6a in CDCl$_3$ at room temperature.

2.4.5 Synthesis of 6b

Catechol (0.12 g, 1.05 mmol), 2,6-dichlorophenyl boronic acid (0.2 g, 1.05 mmol) and acetonitrile (10 mL) were added to a 20 mL scintillation vial. The mixture was heated overnight at 80°C. After cooling to room temperature, all the volatiles were removed under vacuum. The residue was sublimed under vacuum using a Kugelrohrofen (180°C, 10$^{-1}$ mbar) to give 6b as a colorless crystalline solid. Yield 0.15 g (65%). M.p: 85-86°C. $^1$H NMR [400 MHz, C$_6$D$_6$]: 6.45 (t, $^3$$J_{H,H} = 8$ Hz, CH-phenyl, 1 H), 6.78 (d, $^3$$J_{H,H} = 8.0$ Hz, CH-catechol, 4 H), 7.09 (d, $^3$$J_{H,H} = 4$ Hz, CH-phenyl, 2 H) ppm. $^{13}$C{H} NMR [100.4 MHz, C$_6$D$_6$]: 113.0, 123.2, 126.9, 132.2 (CH), 139.0, 148.3 (C-quart) ppm. Note: The ipso carbon bound to boron could not be detected in the $^{13}$C NMR. $^{11}$B NMR (128.4 MHz,

Figure S39. ¹H NMR spectrum of 6b in CDCl₃ at room temperature.

Figure S40. ¹³C NMR spectrum of 6b in CDCl₃ at room temperature.

Figure S41. ¹¹B NMR spectrum of 6b in CDCl₃ at room temperature.
2.4.6 Synthesis of 9a

1,8-naphthalenediol (0.16 g, 0.1 mmol), n-butyl-boronic acid (0.1 g, 0.1 mmol) and acetonitrile (10 mL) were added to a 20 mL scintillation vial with screw cap. After heating the reaction mixture at 80°C overnight, all volatiles were removed under vacuum. The residue was distilled under vacuum using a Kugelrohrofen (130°C, 10⁻¹ mbar) to give 210 mg (93%) of 9a as colorless oil. ¹H NMR [400 MHz, CDCl₃]: 0.96 (t, J_H-H = 8.0 Hz, CH₃, 3 H), 1.10 (t, J_H-H = 8 Hz, BCH₂, 2 H), 1.42 (m, CH₂, 2 H), 1.58 (m, CH₂, 2 H), 6.84 (d, J_H-H = 8 Hz, CH-naphthyl, 2 H), 7.35 (m, CH-naphthyl, 4 H). ¹³C{H} NMR [100.4 MHz, CDCl₃] 14.1 (CH₃), 14.9, 25.5, 25.7 (CH₂), 109.3 (CH-naphthyl), 117.6 (C-quart), 121.0, 127.9 (CH-naphthyl), 135.8, 147.9 (C-quart) ppm. ¹¹B NMR [128.4 MHz, CDCl₃]: 31.9 ppm. Anal. Calc. for C₁₆H₁₁BO₂ (MW. 226.08) C, 74.38; H, 6.69; Found: C, 74.52; H, 7.11.

![Figure S42. ¹H NMR spectrum of 9a in CDCl₃ at room temperature.](image-url)
Figure S43. $^{13}$C NMR spectrum of $9a$ in CDCl$_3$ at room temperature.

Figure S44. $^{11}$B NMR spectrum of $9a$ in CDCl$_3$ at room temperature.
2.4.7 Synthesis of 10a

1,8-naphthalenediol (1 g, 6.2 mmol) was added portion-wise to a stirred solution of B(OMe)$_3$ (1.9 g, 18.6 mmol) in anhydrous CH$_2$Cl$_2$ (10 mL). After stirring the reaction mixture overnight at room temperature, all volatiles were removed under vacuum. The residue was distilled under vacuum using a Kugelrohr ofen (140°C, 10$^{-2}$ mbar) to give 10a as a colorless crystalline solid. Yield 1.22 g (98%). $^1$H NMR [400 MHz, CDCl$_3$]: 3.86 (s, CH$_3$, 3 H), 6.88 (d, $^3$$J_{H-H}$ = 8 Hz, CH-naphthyl, 2 H), 7.34 (t, $^3$$J_{H-H}$ = 8 Hz, CH-naphthyl, 2 H), 7.40 (d, $^3$$J_{H-H}$ = 8 Hz, CH-naphthyl, 2 H) ppm. $^{13}$C{H} NMR [100.4 MHz, CDCl$_3$] 52.1 (OCH$_3$), 109.6 (CH-naphthyl), 116.3 (C-quart), 121.0, 127.9 (CH-naphthyl), 135.3, 148.9 (C-quart) ppm. $^{11}$B NMR [128.4 MHz, CDCl$_3$]: 17.8 ppm. Anal. Calc. for C$_{11}$H$_9$BO$_3$ (200.0): C, 66.06; H, 4.54; Found: 65.50; H, 4.25.

Figure S45. $^1$H NMR spectrum of 10a in CDCl$_3$ at room temperature.
Figure S46. $^{13}$C NMR spectrum of 10a in CDCl$_3$ at room temperature.

Figure S47. $^{11}$B NMR spectrum of 10a in CDCl$_3$ at room temperature.
2.4.8 Synthesis of 11a

Powdered boric acid (0.73, 1.25 mmol) and 1,8-naphthalenediol (0.2 g, 1.25 mmol) were dissolved in acetonitrile (10 mL) in a 20 mL scintillation vial. The solution was gently heated until all the starting material dissolved and then heated 80°C for one hour. After cooling to room temperature, all volatiles were removed under vacuum. After the residue was extracted twice with toluene, the solvent of the combine extracts was removed under vacuum to give 11a as a colorless solid. Yield 0.21 g (93%). ¹H NMR [400 MHz, CD₃CN]: 6.42 (br, OH, 1 H), 6.85 (d, ³J_H-H = 8 Hz, CH-naphthyl, 2 H), 7.38 (t, ³J_H-H = 8 Hz, CH-naphthyl, 2 H), 7.44 (d, ³J_H-H = 8 Hz, CH-naphthyl, 2 H) ppm. ¹³C{H} NMR [125 MHz, CD₃CN]: 110.4 (CH), 117.4 (C-quart), 121.7, 129.2 (CH), 136.5, 150.4 (C-quart) ppm. ¹¹B NMR (128.4 MHz, CD₃CN): 18.0 ppm. ¹¹B NMR (128.4 MHz, CDCl₃): 18.4 ppm Anal. Calc. for C₁₂H₉BO₃ (185.97): C, 64.58, H, 3.79 Found: C, 64.90; H, 4.00.

Figure S48. ¹H NMR spectrum of 11a in CDCl₃ at room temperature.
Figure S49. $^{13}$C NMR spectrum of 11a in CDCl$_3$ at room temperature.

Figure S50. $^{11}$B NMR spectrum of 11a in CDCl$_3$ at room temperature.
2.4.9 Synthesis of 12a

1,8-naphthalenediol (134 mg, 0.84 mmol) was added to a solution of B(NMe₂)₃ (60 mg, 0.42 mmol) in THF (5 mL) and resulting suspension was stirred for an hour. The precipitate was filtered, washed with THF and dried under vacuum to give 12a as a white powder. Yield 0.15 g (96 %). ¹H NMR [400 MHz, DMSO-D₆]: 2.57 (s, CH₃, 6 H), 6.41 (d, ³J_H-H = 4 Hz, CH-naphthyl, 4 H), 7.10 (d, ³J_H-H = 8 Hz, CH-naphthyl, 4 H), 7.21 (t, ³J_H-H = 8 Hz, CH-naphthyl, 4 H), 8.16 (br, NH, 2 H); ¹³C{H} NMR [100.4 MHz, DMSO-D₆]: 34.5 (CH₃), 106.7, 115.4 (CH), 116.5 (C-quart), 127.4 (CH), 135.5, 154.9 (C-quart) ppm. ¹¹B NMR [128.4 MHz, DMSO-D₆]: 0.5 ppm. Anal. Calc. for C₂₂H₂₀BNO₄ (373.15): C, 70.80; H, 5.40; N, 3.75 Found: C, 69.87; H, 5.10; N, 3.84.

Figure S51. ¹H NMR spectrum of 12a in CDCl₃ at room temperature.
Figure S52. $^{13}$C NMR spectrum of 12a in CDCl$_3$ at room temperature.

Figure S53. $^{11}$B NMR spectrum of 12a in CDCl$_3$ at room temperature.
2.4.10 Synthesis of 13a

1,8-naphthalenediol (0.7 g, 4.4 mmol) was added portion-wise to a 1 M hexanes solution of BCl₃ (13.2 ml, 13.2 mmol) in CH₂Cl₂ (10 mL) at -78°C. After the reaction mixture was allowed to warm to room temperature, all volatiles were quickly removed under vacuum to give 13a as colorless solid, slightly contaminated with CH₂Cl₂. Yield 0.85 g (95%). ¹H NMR [400 MHz, CDCl₃]: 6.94 (d, 3J_H-H = 8 Hz, CH-naphthyl, 2 H), 7.37 (t, 3J_H-H = 8.0 Hz, CH-naphthyl, 2 H), 7.47 (d, 3J_H-H = 8 Hz, CH-naphthyl, 2 H) ppm. ¹³C{H} NMR [125 MHz, CDCl₃]: 110.4 (CH), 117.1 (C-quart), 122.2, 128.2 (CH), 135.5, 148.1 (C-quart) ppm. ¹¹B NMR [128.4 MHz, CDCl₃]: 24.8 ppm. Attempts to obtain accurate microanalysis have failed due to the extreme water sensitivity of this molecule.

Figure S54. ¹H NMR spectrum of 13a in CDCl₃ at room temperature.
Figure S55. $^{13}$C NMR spectrum of 13a in CDCl$_3$ at room temperature.

Figure S56. $^{13}$C DEPT NMR spectrum of 13a in CDCl$_3$ at room temperature.
2.4.11 Hydrolysis of 13a in CDCl₃

In the Glove box, a standard NMR tube was charged with ca. 20 mg of 13a and dry CDCl₃ (0.5 mL), removed from the glove box and stored on the bench. After ca. 10 days, a crystalline precipitate formed. Analysis of the isolated crystals by multi-nuclear NMR spectroscopy revealed the formation of 11a and 14a (see also Figures S56 and S57). Single crystals of 14a suitable for X-ray analysis were grown from benzene. The NMR spectroscopic data of 14a are shown in Figures S58-S61. ¹H NMR [400 MHz, C₆D₆]: 6.74 (d, ³J_H-H = 8 Hz, CH-naphthyl, 2 H), 7.01 (t, ³J_H-H = 8.0 Hz, CH-naphthyl, 2 H), 7.15 (d, ³J_H-
$\nu = 8 \text{ Hz, CH-naphthyl, 2 H ppm.} \text{ } ^{13}\text{C(H)} \text{ NMR [100.4 MHz, C}_{6}\text{D}_{6}]: 110.0 (\text{CH}), 116.8 (\text{C-quart}), 121.2, 127.9 (\text{CH}), 135.5, 149.1 (\text{C-quart}) \text{ ppm. } ^{11}\text{B NMR [128.4 MHz, C}_{6}\text{D}_{6}]: 16.9 \text{ ppm.}$

**Figure S58.** $^1\text{H NMR}$ spectrum of the mixture of $11\text{a}/14\text{a}$ in CDCl$_3$ at room temperature.

**Figure S59.** $^{11}\text{B NMR}$ spectrum of the mixture of $11\text{a}/14\text{a}$ in CDCl$_3$ at room temperature.
**Figure S60.** $^{1}$H NMR spectrum of the mixture of 14a in C$_6$D$_6$ at room temperature.

**Figure S61.** $^{13}$C NMR spectrum of the mixture of 14a in C$_6$D$_6$ at room temperature.
**Figure S62.** $^{13}$C DEPT NMR spectrum of the mixture of 14a in C$_6$D$_6$ at room temperature.

**Figure S63.** $^{11}$B NMR spectrum of the mixture of 14a in C$_6$D$_6$ at room temperature.
2.4.12 Attempted synthesis of diboronic acid ester 16a

A standard NMR tube was charged with 1,8-naphthalenediol (51 mg, 0.32 mmol), (HO)$_2$B-B(OH)$_2$ (14 mg, 0.16 mmol) and 0.6 mL of DMSO-D$_6$. The reaction mixture was heated at 80°C for 1 hour and subsequently analyzed by NMR spectroscopy. $^1$H NMR [400 MHz, DMSO-D$_6$]: 6.42 (d, $^3$J$_{HH} = 8$ Hz, CH-naphthyl, 4 H), 6.09 (d, $^3$J$_{HH} = 8$ Hz, CH-naphthyl, 4 H), 7.20 (t, $^3$J$_{HH} = 8$ Hz, CH-naphthyl, 4 H) ppm. $^{13}$C{H} NMR [100.4 MHz, DMSO-D$_6$] 106.9, 115.6 (CH-naphthyl), 116.7 (C-quart), 127.6 (CH-naphthyl), 135.6, 155.1 (C-quart) ppm. $^{11}$B NMR [128.4 MHz, DMSO-D$_6$]: 0.46 (15a), 18.9 (boric acid) ppm.

![NMR spectrum](image)

**Figure S64.** $^1$H NMR spectrum of 15a in CDCl$_3$ at room temperature.
Figure S65. $^{13}$C NMR spectrum of 15a in CDCl$_3$ at room temperature.

Figure S66. $^{11}$B NMR spectrum of 15a in CDCl$_3$ at room temperature.
In the glove box, a 30 mL Schlenk flask was charged with a magnetic stir bar, 1,8-naphthalenediol (0.1 g, 0.62 mmol) and diethyl ether (7 mL). In addition, a 20 mL scintillation vial was charged with B$_2$(NMe$_2$)$_4$ (0.063 g, 0.31 mmol) and diethyl ether (3 mL). Upon adding B$_2$(NMe$_2$)$_4$ solution to 1,8-naphthalenediol, a precipitate formed, which was identified by NMR spectroscopy as 17a: $^1$H NMR [400 MHz, C$_6$D$_6$]: 1.8 (s, 12 H), 2.8 (br, NH, 2 H) 6.99 (d, $^3$J$_{H,H}$ = 8 Hz, CH-napthyl, 4 H), 7.31-7.39 (m,CH-napthyl, 8 H), ppm. $^{13}$C{H} NMR [125 MHz, C$_6$D$_6$]: 36.3 (CH$_3$, N-Me), 108.3 (CH-naphthyl), 115.9 (C-quart), 117.5 (CH-naphthyl), 127.8 (CH-naphthyl), 136.6 (C-quart), 153.0 (C-quart) ppm. $^{11}$B NMR [128.4 MHz, C$_6$D$_6$]: 4.4 ppm. After stirring the ethereal suspension of 17a for one hour, an ether solution of HCl (2 N, 0.7 mL, 1.4 mmol) was added at 0 ºC. The reaction mixture was stirred for another hour at room temperature and 5 mL of deionized water were added. The obtained precipitate was immediately filtered over a frit, washed with acetone to remove all water and dried under vacuum to give 16a as a colorless solid (Note! 16a contains ca. 5-10% diethyl ether. Attempts to remove residual diethyl ether under dynamic vacuum (50°C, 10$^{-2}$ mbar, 24 hours) failed. Yield 71 mg (70%). $^1$H NMR [400 MHz, DMSO-D$_6$]: 6.79 (d, $^3$J$_{H,H}$ = 8 Hz, CH-naphthyl, 4 H), 7.31-7.38 (m, CH-naphthyl, 8 H) ppm. $^{13}$C{H} NMR [100.4 MHz, DMSO-D$_6$]: 108.1 (CH-naphthyl), 117.6 (C-quart), 118.4 (CH-naphthyl), 127.8 (CH-naphthyl), 134.9 (C-quart), 159.6 (C-quart) ppm. $^{11}$B NMR [128.4 MHz, DMSO-D$_6$]: 4.8 ppm. Anal. Calc. for C$_{20}$H$_{12}$B$_2$O$_4$ (337.93): C, 71.09; H, 3.58; Found: C, 70.50; H, 3.45.
Figure S67. $^1$H NMR spectrum of 16a in CDCl$_3$ at room temperature.

Figure S68. $^{13}$C NMR spectrum of 16a in CDCl$_3$ at room temperature.
Figure S69. $^{11}$B NMR spectrum of 16a in CDCl$_3$ at room temperature.

Figure S70. $^1$H NMR spectrum of 17a in CDCl$_3$ at room temperature.
**Figure S71.** $^{13}$C NMR spectrum of 17a in CDCl$_3$ at room temperature.

**Figure S72.** $^{13}$C DEPT NMR spectrum of 17a in CDCl$_3$ at room temperature.
Figure S73. $^{11}$B NMR spectrum of 17a in CDCl$_3$ at room temperature.

2.4.13 Synthesis of 18a

In the glove box, 13a (102 mg, 0.5 mmol), O=PEt$_3$ (134 mg, 1 mmol) and anhydrous benzene (10 mL) were added to a 30 mL Schlenk flask under nitrogen. After stirring the mixture for one hour, crystalline precipitate was washed two times with benzene and dried under vacuum to give 18a as a colorless solid. Yield 0.2 g (85 %) $^1$H NMR [400 MHz, CD$_2$Cl$_2$]: 6.66 (d, $^3$J$_{H-H} = 8$ Hz, CH-naphthyl, 2 H), 7.26-7.32 (m, CH-naphthyl, 4 H), 2.24 (m, CH$_2$, 12 H), 1.17 (m, CH$_3$, 18 H) ppm. $^{13}$C{H} NMR [125 MHz, CD$_2$Cl$_2$]: 5.5 (CH$_3$), 17.7 (d, $^1$J$_{P-C} = 204$ Hz, P-CH$_2$), 108.6 (CH-naphthyl), 115.7 (CH-phenyl), 119.0 (CH-naphthyl), 128.2 (CH-phenyl), 136.1, 151.1 (C-quart) ppm. $^{11}$B NMR [128.4 MHz, CD$_2$Cl$_2$]: 0.1 ppm.
$^{31}$P NMR [161.9 MHz, CD$_2$Cl$_2$]: 84.0 ppm. Attempts to obtain accurate microanalysis have failed due to the extreme water sensitivity of this compound.

**Figure S74.** $^1$H NMR spectrum of 18a in CDCl$_3$ at room temperature.

**Figure S75.** $^{13}$C NMR spectrum of 18a in CDCl$_3$ at room temperature.
Figure S76. $^{11}$B NMR spectrum of 18a in CDCl$_3$ at room temperature.

Figure S77. $^{31}$P NMR spectrum of 17a in CDCl$_3$ at room temperature.
2.4.14 Synthesis of 19a

In the glove box, 13a (51 mg, 0.25 mmol), pyridine (19.8 mg, 0.25 mol) and dry CH₂Cl₂ (5 mL) were added to a 30 mL Schlenk flask. After the mixture was stirred for one hour, all volatiles were removed under vacuum. The solid residue was washed once with benzene and dried under vacuum to give 19a as a colorless solid. Yield 50 mg (70%). ¹H NMR [400 MHz, C₆D₆]: 6.15 (t, ³J₃-H = 8 Hz, CH-py, 4 H), 6.47 (t, ³J₃-H = 8 Hz, CH-py, 1 H), 7.11 (d, ³J₃-H, CH-naphthyl, 2 H), 7.27-7.34 (m, CH-naphthyl, 4 H), 8.62 (d, ³J₃-H = 4 Hz, CH-py, 2 H) ppm. ¹³C{H} NMR [100.4 MHz, C₆D₆] 109.2 (CH-py), 117.1 (C-quart), 119.3, 125.0, 127.9 (CH-naphthyl) 136.2 (C-quart), 142.7, 143.2 (CH-py), 151.3 (C-quart) ppm. ¹¹B NMR [128.4 MHz, C₆D₆]: 5.2 ppm. Attempts to obtain accurate microanalysis have failed due to the extreme water sensitivity of this compound.

Figure S78. ¹H NMR spectrum of 19a in CDCl₃ at room temperature.
Figure S79. $^{13}$C NMR spectrum of 19a in CDCl$_3$ at room temperature.

Figure S80. $^{13}$C DEPT NMR spectrum of 19a in CDCl$_3$ at room temperature.
2.4.15 Reaction of 19 with pyridine - attempted synthesis of 20a

In the glove box, a J-Young NMR tube was charged with 19a (6 mg, 0.02 mmol), one equivalent of anhydrous pyridine (1.5 mg, 0.02 mmol) and CDCl₃ (0.5 mL) and a ¹H NMR spectrum of the resulting solution was taken. Then another equivalent of anhydrous pyridine (1.5 mg, 0.02 mmol) was added and again a ¹H NMR spectrum of the solution was taken.
2.4.16 Synthesis of 22a

In the glove box, 13a (0.51 mg, 0.25 mmol), DMAP (60 mg, 0.5 mmol) and dry CH₂Cl₂ (5 mL) were added to a 30 mL Schlenk flask. The mixture was stirred one hour, and all volatiles were removed under vacuum. The resulting precipitate was washed once with benzene and dried under vacuum to give 22a as a white solid. Yield 95 mg (85%). ¹H
NMR [400 MHz, CDCl₃]: 3.10 (s, CH₃, 12 H), 6.75 (d, J_H-H = 8 Hz, CH-DMAP, 4 H), 6.84 (d, J_H-H = 8 Hz, CH-naphthyl, 2 H), 7.22-7.27 (m, CH-naphthyl, 4 H), 8.18 (d, J_H-H = 8 Hz, CH-DMAP, 4 H) ppm. \(^{13}\)C{NMR} [100.4 MHz, CDCl₃]: 40.2 (CH₃), 107.8 (CH-DMAP), 109.3 (CH-naphthyl), 116.1 (CH-naphthyl), 119.2 (C-quart), 127.7 (CH-naphthyl), 135.3 (C-quart), 141.5 (CH-DMAP), 149.6, 156.7 (C-quart) ppm. \(^{11}\)B NMR [128.4 MHz, CDCl₃]: 1.1 ppm. Attempts to obtain accurate microanalysis have failed due to the extreme water sensitivity of this compound.

**Figure S83.** \(^1\)H NMR spectrum of 22a in CDCl₃ at room temperature.
Figure S84. $^{13}$C NMR spectrum of 22a in CDCl$_3$ at room temperature.

Figure S85. $^{11}$B NMR spectrum of 22a in CDCl$_3$ at room temperature.
In a glove box, 13a (86 mg, 0.42 mmol) was dissolved in toluene (10 mL) in a 30 mL Schlenk flask. Separately, anhydrous 2,2'-bipyridine (62 mg, 0.4 mmol) was dissolved in toluene (5 mL) in a shell vial. The resulting solution was slowly transferred to the solution of 13a, upon which an orange colored solid precipitated immediately. The orange suspension was stirred overnight, and the precipitate washed twice with toluene and dried under vacuum to give 23a·½toluene as an orange solid. Note! Attempts to fully remove toluene by heating the solid under dynamic vacuum for one day failed as partial degradation of 23a occurred. Yield 140 mg (86 % toluene included). $^1$H NMR [400 MHz, CDCl₃]: 6.80 (d, $^3$J$_{H-H}$ = 8 Hz, CH-naphthyl, 2 H), 7.40 (t, $^3$J$_{H-H}$ = 8.0 Hz, CH-naphthyl, 2 H), 7.48 (d, $^3$J$_{H-H}$ = 8.0 Hz, CH-naphthyl, 2 H), 8.01 (t, $^3$J$_{H-H}$ = 8 Hz, CH-bipy, 2 H), 8.53 (d, $^3$J$_{H-H}$ = 8 Hz, CH-bipy, 2 H), 8.79 (t, $^3$J$_{H-H}$ = 8 Hz, CH-bipy, 2 H), 10.57 (d, $^3$J$_{H-H}$ = 8 Hz, CH-bipy, 2 H) ppm. $^{13}$C{H} NMR [100.4 MHz, CDCl₃]: 110.1 (CH), 114.6 (C-quart), 120.5, 127.4, 128.2 (CH), 129.3 (C-quart), 135.5, 142.2 (CH), 145.2, 148.2 (C-quart), 148.3 (CH) ppm. $^{11}$B NMR [128.4 MHz, CDCl₃]: 5.9 ppm. Attempts to obtain accurate microanalysis have failed due to the extreme water sensitivity of this compound.
Figure S86. $^1$H NMR spectrum of 23a in CDCl$_3$ at room temperature (toluene signals labelled with asterisks).

Figure S87. $^{13}$C NMR spectrum of 23a in CDCl$_3$ at room temperature (toluene signals labelled with asterisks).
Figure S88. $^{11}$B NMR spectrum of 23a in CDCl$_3$ at room temperature.

2.4.17 Synthesis of 24a

![Diagram showing the synthesis of 24a from 13a with 1,10-phenanthroline](image)

In a glove box, 13a (53 mg, 0.26 mmol) was dissolved in toluene (5 mL) in 30 mL Schlenk flask. Separately, anhydrous 1,10-phenanthroline (43 mg, 0.24 mmol) was dissolved in dry toluene (5 mL) in a shell vial. The resulting solution was slowly transferred to the solution of 13a, upon which an orange colored solid precipitated immediately. The orange suspension was stirred overnight, and the precipitate washed twice with toluene and dried under vacuum to give 24a·0.4toluene as an orange solid. Note! Attempts to fully remove
toluene by heating the solid under dynamic vacuum for one day failed as partial of degradation of 24a occurred. Yield 91 mg (90 % toluene included). ¹H NMR [400 MHz, CDCl₃]: 6.94 (d, 3Jₗ-ₗ = 8 Hz, CH-naphthyl, 2 H), 7.37 (t, 3Jₗ-ₗ = 8 Hz, CH-naphthyl, 2 H), 7.44 (d, 3Jₗ-ₗ = 8 Hz, CH-naphthyl, 2 H), 8.05 (t, 3Jₗ-ₗ = 8 Hz, CH-phen, 2 H), 8.11 (s, CH-phen, 2 H), 8.74 (t, 3Jₗ-ₗ = 8 Hz, CH-phen, 2 H), 9.64 (d, 3Jₗ-ₗ = 8 Hz, CH-phen, 2 H) ppm. ¹³C{H} NMR [100.4 MHz, CDCl₃]: 110.0 (CH), 116.5 (C-quart.), 121.4, 125.3, 127.6, 127.9 (CH), 129.8, 135.3, 138.3 (C-quart.), 140.9, 148.7 (CH) ppm. ¹¹B NMR [128.4 MHz, CDCl₃]: 16.7 ppm. Attempts to obtain accurate microanalysis have failed due to the extreme water sensitivity of this compound.

Figure S89. ¹H NMR spectrum of 24a in CDCl₃ at room temperature (toluene signals labelled with asterisks).
Figure S90. $^{13}$C NMR spectrum of 24a in CDCl$_3$ at room temperature (toluene signals labelled with asterisks).

Figure S91. $^{13}$C DEPT NMR spectrum of 24a in CDCl$_3$ at room temperature (toluene signals labelled with asterisks).
Figure S92. $^{11}$B NMR spectrum of 24a in CDCl$_3$ at room temperature.
2.5 Estimation of the Lewis acid strength of 1a-7a and 1b-7b via the Gutmann-Beckett method

All samples for $^{31}$P NMR chemical shift measurements with different Lewis acids to O=PEt$_3$ ratios were prepared in the Glove box using dry C$_6$D$_6$. To a solution of ca. $\approx$ 3 mg of OPEt$_3$ in 0.5 mL of C$_6$D$_6$, variable amounts of Lewis acids were added and $^{31}$P NMR spectra were taken. For all the measured Lewis acids (LAs), the equilibrium between LA←O=PEt$_3$ complex and free LA and O=PEt$_3$ is fast within the NMR time scale. Consequently, the observed signal is a weighted average of the LA←O=PEt$_3$ complex and free acid and O=PEt$_3$. To determine accurate $^{31}$P NMR chemical shifts for these LA←O=PEt$_3$ complexes, additional equivalents of Lewis acid were added until the $^{31}$P NMR chemical shift did not change significantly.

**Table S2.** $^{31}$P NMR chemical shift measured for different Lewis acids to O=PEt$_3$ ratios in C$_6$D$_6$ [$\delta$ O=PEt$_3$ = 46.2 ppm].

<table>
<thead>
<tr>
<th>Lewis Acid: OPEt$_3$</th>
<th>(1:1) $\delta_{31P}$</th>
<th>(2:1) $\delta_{31P}$</th>
<th>(3:1) $\delta_{31P}$</th>
<th>(4:1) $\delta_{31P}$</th>
<th>(5:1) $\delta_{31P}$</th>
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<tr>
<td>C$_6$H$_5$-BNad (1a)</td>
<td>58.9</td>
<td>65.3</td>
<td>66.8</td>
<td>67.3</td>
<td>67.9$^a$</td>
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<tr>
<td>C$_6$F$_5$-BNad (2a)</td>
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<td>77.5</td>
<td><strong>77.5</strong></td>
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<td>-</td>
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<td>3,4,5-F$_3$-C$_6$H$_2$-BNad (3a)</td>
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<td>73.4</td>
<td>73.7</td>
<td><strong>73.8</strong></td>
<td>-</td>
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<tr>
<td>2,4,6-F$_3$-C$_6$H$_2$-BNad (4a)</td>
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<td>74.6</td>
<td>74.2</td>
<td><strong>74.3</strong></td>
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<tr>
<td>2,6-F$_2$-C$_6$H$_3$-BNad (5a)</td>
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<td>73.7</td>
<td>73.5</td>
<td><strong>73.6</strong></td>
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<tr>
<td>2,6-Cl$_2$-C$_6$H$_3$-BNad (6a)</td>
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<td>64.4</td>
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<tr>
<td>2,4,6-Me$_3$-C$_6$H$_2$-BNad (7a)</td>
<td>46.2</td>
<td><strong>46.3</strong></td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Values marked in red were used for the calculation of the acceptor number (AN); a ….
**Table S3.** $^{31}$P NMR chemical shift measured for different Lewis acids to O-PEt$_3$ ratios in C$_6$D$_6$ [$\delta$ O-PEt$_3$ = 46.2 ppm].

<table>
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<tr>
<td>$\delta_{31P}$</td>
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<td>$\delta_{31P}$</td>
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<td>$\delta_{31P}$</td>
<td>$\delta_{31P}$</td>
<td>$\delta_{31P}$</td>
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<td>C$_6$H$_5$-BCat (1b)</td>
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<td>66.7</td>
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<td>-</td>
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<td><strong>69.2</strong></td>
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<td>C$_6$F$_5$-BCat (2b)</td>
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<td>74.7</td>
<td>-</td>
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<td><strong>74.9</strong></td>
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<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2,4,6-F$_3$C$_6$H$_2$-BCat (4b)</td>
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<td>-</td>
<td>74.1</td>
<td>-</td>
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<td>-</td>
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</tr>
<tr>
<td>2,6-F$_2$C$_6$H$_3$-BCat (5b)</td>
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<td>-</td>
<td>73.7</td>
<td>73.7</td>
<td>-</td>
<td>73.8</td>
<td>-</td>
<td><strong>73.9</strong></td>
<td>-</td>
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<tr>
<td>2,6-Cl$_2$C$_6$H$_3$-BCat (6b)</td>
<td>55.4</td>
<td>61.9</td>
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<td>68.1</td>
<td>68.9</td>
<td>-</td>
<td>69.8</td>
<td><strong>70.2</strong></td>
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<tr>
<td>2,4,6-Me$_3$C$_6$H$_2$-BCat (7b)</td>
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<td>-</td>
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</table>

Values marked in red were used for the calculation of the acceptor number (AN).
3. X-ray crystallography

CCDC1962509 (1a), CCDC1962510 (2a), CCDC1962511 (3a), CCDC1962512 (4a),
CCDC1962513 (5a), CCDC1962514 (8a), CCDC1962515 (10a), CCDC1962516 (14a),
CCDC1965596 (16a), CCDC1962517 (17a), CCDC1962518 (18a), and CCDC1962519
(23a) contain the supplementary crystallographic data for this paper.

These data can be obtained from the Cambridge Crystallographic Data Centre via
http://www.ccdc.cam.ac.uk/data_request/cif, or from the Cambridge Crystallographic
Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; e-mail:
deposit@ccdc.cam.ac.uk.

3.1 General Data Collection

Data for complexes 3a and 8a were collected on a Bruker PLATFORM three circle
diffractometer equipped with an APEX II CCD detector and operated at 1500 W (50kV,
30 mA) to generate (graphite monochromated) Mo Kα radiation (λ = 0.71073 Å). For
structures 2a, 4a, 5a, 10a, 14a, 16a, 17a, 18a, and 23a data were collected on collected
on a Rigaku XtaLAB Synergy-i Kappa diffractometer equipped with a PhotonJet-i X-ray
source operated at 50 W (50kV, 1 mA) to generate Cu Kα radiation (λ = 1.54178 Å) and
a HyPix-6000HE HPC detector. In all cases, crystals were transferred from the mother
liquor and placed on a glass slide in polyisobutylene. A Zeiss Stemi 305 microscope was
used to identify a suitable specimen for X-ray diffraction from a representative sample of
the material. The crystal and a small amount of the oil were collected on either a MiTiGen
cryoloop or a Hampton nylon loop and transferred to the instrument where it was placed
under a cold nitrogen stream (Oxford) maintained at 100K throughout the duration of the
experiment. The samples were optically centered with the aid of a video camera to insures
that no translations were observed as the crystal was rotated through all positions.

A unit cell collection was then carried out. After it was determined that the unit cell was
not present in the CCDC database a sphere of data was collected. For 3a, and 8a, omega
scans were carried out with a 10 sec/frame exposure time and a rotation of 0.50° per frame. For structures 2a, 4a, 5a, 10a, 14a, 16a, 17a, 18a, and 23a a data collection strategy was calculated by CrysAlisPro [5] using omega, phi, and kappa scans. After data collection, the crystal was measured for size, morphology, and color. These values are reported in Tables S4-S6.

3.2 Refinement Details

After data collection, the unit cell was re-determined using a subset of the full data collection. Intensity data for 3a and 8a were corrected for Lorentz, polarization, and background effects using the Bruker program APEX 3. A semi-empirical correction for adsorption was applied using the program SADABS[6]. Intensity data for 2a, 4a, 5a, 10a, 14a, 16a, 17a, 18a, and 23a were corrected for Lorentz, polarization, and background effects using the CrysAlisPro[5]. A numerical absorption correction was applied based on a Gaussian integration over a multifaceted crystal and followed by a semi-empirical correction for adsorption applied using the program SCALE3 ABSPACK [7]. The SHELXL-2014 [8], series of programs was used for the solution and refinement of the crystal structures.

For 1a, hydrogen atoms bound to carbon atoms were located in the difference Fourier map and were geometrically constrained using the appropriate AFIX commands. Inconsistent reflections -7 3 4 and -7 3 6 were omitted during the final refinements.

For 2a, hydrogen atoms bound to carbon atoms were located in the difference Fourier map and were geometrically constrained using the appropriate AFIX commands. Inconsistent reflection 4 0 0 was omitted during the final refinements.

For 3a, hydrogen atoms bound to carbon atoms were located in the difference Fourier map and were geometrically constrained using the appropriate AFIX commands. Inconsistent reflections 1 3 4, -4 2 4, and -6 0 4 were omitted during the final refinements.
For structures 4a, 5a, 8a, and 14a, hydrogen atoms bound to carbon atoms were located in the difference Fourier map and were geometrically constrained using the appropriate AFIX commands.

For 10a, hydrogen atoms bound to carbon atoms were located in the difference Fourier map and were geometrically constrained using the appropriate AFIX commands. The Z’ value for the structure is 3.

For 16a, every atom position was disordered over two sites. The site occupancies were 0.92 and 0.08 for PART 1 and PART 2, respectively. To help maintain reasonable ADP values for the minor component, RIGU and SIMU restraints were applied. Inconsistent reflections 1 0 8 and 3 3 8 were omitted during the final refinements. Hydrogen atoms bound to carbon atoms were located in the difference Fourier map and were geometrically constrained using the appropriate AFIX commands.

For 17a, once the atom positions of the main molecule and an interstitial acetonitrile molecule were determined, it was suspected that a highly disordered acetonitrile molecule existed about an inversion center on a three-fold axis. This disordered electron density was treated as diffuse scattering using the SQUEEZE [9] routine within PLATON [10], which resulted in a total of three void spaces each containing electron count of 24. Based on the electron density of acetonitrile, this is approximately one molecule of acetonitrile per void space. However, due to the lack of any other empirical evidence, this information was not added to the CIF. Hydrogen atoms bound to carbon atoms were geometrically constrained using the appropriate AFIX commands.

For 18a, the ethyl groups bound to P2 (C17 < C22) were positionally disordered over two sites (A and B). The sites occupancies for the A and B sites were 0.93 and 0.07, respectively. To help maintain reasonable ADP values and atom positions for the minor components, SIMU, DELU, DFIX and EADP restraints and constraints were applied where needed. Hydrogen atoms bound to carbon atoms were located in the difference Fourier map and were geometrically constrained using the appropriate AFIX commands.

For 23a, the interstitial benzene ring (C47 < C52) was disordered and was modeled as split sites A and B. To help maintain reasonable ADP values and C-C bond lengths,
SIMU, RIGU, and AFIX 66 restraints and constraints were applied. There was also a 1,8-naphthalenediol complexed to a B-OH group disordered about an inversion center, resulting in the SOF values of the atoms being set to 0.5. Hydrogen atoms bound to carbon atoms were located in the difference Fourier map and were geometrically constrained using the appropriate AFIX commands, while the hydrogen atom bound to oxygen (O5) was restrained with a DFIX command. The Z’ value for the structure was 2.
Table S4. Crystallographic data for compounds 1a-4a.

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<tr>
<th></th>
<th>1a</th>
<th>2a</th>
<th>3a</th>
<th>4a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C_{16}H_{11}BO_{2}</td>
<td>C_{16}H_{6}BF_{5}O_{2}</td>
<td>C_{16}H_{6}BF_{3}O_{2}</td>
<td>C_{16}H_{8}BF_{3}O_{2}</td>
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<tr>
<td>Molecular weight</td>
<td>246.06</td>
<td>336.02</td>
<td>300.03</td>
<td>300.03</td>
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<td>Space group</td>
<td>P2_1/c</td>
<td>P2_1/c</td>
<td>P2_1/c</td>
<td>P2_1/c</td>
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<td>a (Å)</td>
<td>13.8170(2)</td>
<td>9.30604(7)</td>
<td>9.000(2)</td>
<td>14.68950(10)</td>
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<tr>
<td>b (Å)</td>
<td>4.72630(10)</td>
<td>9.01092(6)</td>
<td>9.222(2)</td>
<td>4.72070(10)</td>
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<tr>
<td>c (Å)</td>
<td>18.1904(3)</td>
<td>15.64505(12)</td>
<td>15.177(3)</td>
<td>18.1961(2)</td>
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<tr>
<td>β (°)</td>
<td>102.366(2)</td>
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<td>102.4210(10)</td>
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<td>1229.1(5)</td>
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<td>ρ_{calc} (g cm⁻³)</td>
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<td>Unique reflections</td>
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<td>2676</td>
<td>2270</td>
<td>2579</td>
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<tr>
<td>(R_{int})</td>
<td>(0.0352)</td>
<td>(0.0366)</td>
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<td>(0.0426)</td>
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<tr>
<td>R_1 [I &gt; 2σ(I)]</td>
<td>0.0394</td>
<td>0.0329</td>
<td>0.0419</td>
<td>0.0348</td>
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<tr>
<td>wR_2 (all data)</td>
<td>0.1135</td>
<td>0.0955</td>
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<td>0.1033</td>
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<tr>
<td>Goodness-of-fit on F^2</td>
<td>1.098</td>
<td>1.055</td>
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Table S5. Crystallographic data for compounds 5a, 8a, 10a and 14a.

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<th>8a</th>
<th>10a</th>
<th>14a</th>
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<tr>
<td>Formula</td>
<td>(\text{C}<em>{16}\text{H}</em>{9}\text{BF}<em>{2}\text{O}</em>{2})</td>
<td>(\text{C}<em>{18}\text{H}</em>{15}\text{BO}_{4})</td>
<td>(\text{C}<em>{11}\text{H}</em>{9}\text{BO}_{3})</td>
<td>(\text{C}<em>{20}\text{H}</em>{12}\text{B}<em>{2}\text{O}</em>{5})</td>
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<td>Molecular weight</td>
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<td>Space group</td>
<td>(P2_1/c)</td>
<td>(P2_1/n)</td>
<td>(P2_1/c)</td>
<td>(P\overline{1})</td>
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<td>a (Å)</td>
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<td>b (Å)</td>
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<td>8.76840(10)</td>
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<td>c (Å)</td>
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<td>(\beta) (°)</td>
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<td>4</td>
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<td>2</td>
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<td>(\rho_{\text{calc}}) (g cm(^{-3}))</td>
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<td>(\mu) (mm(^{-1}))</td>
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<td>((R_{\text{int}}))</td>
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<td>(R_1) [(I&gt;2\sigma(I))]</td>
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<td>(wR_2) (all data)</td>
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<td>1.054</td>
<td>1.059</td>
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Table S6. Crystallographic data for compounds 16a, 17a, 18a and 23a.

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<td>P1</td>
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<td>b (Å)</td>
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<tr>
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<td>β (°)</td>
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<td>90</td>
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<td>3</td>
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<td>1</td>
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<td>10099</td>
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<tr>
<td>(R_{int})</td>
<td>(0.0290)</td>
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<td>(0.0410)</td>
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<tr>
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<td>1.045</td>
<td>1.039</td>
<td>1.045</td>
</tr>
</tbody>
</table>
4. References


