**Supplementary Information**

*ortho*-Selective nucleophilic addition of amines to 3-borylbenzynes: Synthesis of multisubstituted anilines by triple role of boryl group

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The graphics of Figure 1 was prepared with CYLview, 1.0b: C. Y. Legault, Université de Sherbrooke, 2009 (http://www.cylview.org).
General considerations

Reagents: All reactions were carried out under an argon or nitrogen atmosphere. A round-bottomed flask, a pear-shaped flask, or a test tube, each of which contained a stir-bar and was equipped with a three-way stopcock, was used as a reactor. 1.7 M t-BuLi in n-pentane was purchased from Kanto Chemical Co. Anhydrous THF, CH₂Cl₂ and diethyl ether (Et₂O) were purchased from Wako Pure Chemical Industries and used without further purification. HMPA was purchased from Tokyo Chemical Industry Co. and used after distillation from CaH₂. 2-[(Pin)boryl]-6-(trimethylsilyl)phenyl triflate 2A was synthesized according to the literature.¹ Freshly prepared 3-[(dan)boryl]benzyne precursors 2B, 2D, 2E were used for all reactions. All other reagents were purchased from Wako Pure Chemical Industries, Tokyo Chemical Industry Co., Aldrich Chemical Co., and Kishida Chemical Co. and used without further purification. Flash chromatography² was performed with Silica gel 60N, spherical neutral (40–50 μm) purchased from Kanto Chemical Co.

Analytical methods: IR spectra were obtained on a JASCO WS/IR-8000 or a SHIMAZU FTIR-8400S. ¹H NMR and ¹³C NMR spectra were recorded on a JEOL JMN-ECA-500 (¹H: 500 MHz, ¹³C: 125 MHz), JEOL JMN-AL-300 (¹H: 300 MHz, ¹³C: 75 MHz) or a JEOL JMN-ECS-400 (¹H: 400 MHz, ¹³C: 100 MHz) instrument with chemical shifts reported in ppm relative to the residual deuterated solvent. The mass spectra were recorded on a Bruker microTOF-Q (ESI) or a JEOL JMS-S3000 (MALDI) spectrometer. Yield refers to isolated yields of compounds greater than 95% purity as determined by ¹H NMR analysis. ¹H NMR and melting points (where applicable) of all known compounds were taken. All new products were further characterized by high resolution mass spectrum (HRMS). All carbons bearing the boron substituents could not be observed in ¹³C NMR of ortho-6Ba, ortho-6Bb, ortho-6Da, meta-6Da, ortho-6Dc, ortho-6Dd, ortho-6De, ortho-6Df, ortho-6Dg, ortho-6Dh, ortho-6Di, ortho-6Dj, ortho-6Dk, ortho-6Dl, ortho-6Dm, ortho-6Dn, ortho-6Do, ortho-6Ea, ortho-6Em, ortho-6Ep, 9, 2B, 2C, 2D and 2E due to quadrupolar relaxation.³
Nucleophilic addition of amines to 3-borylbenzenes (Table 2)

General procedure: An oven-dried round-bottomed flask was evacuated and back-filled with argon after cooling to room temperature. The flask was charged with a borylbenzyne precursor 2 [freshly purified by SiO$_2$ flash chromatography prior to use] (1.0 equiv) and 18-crown-6 (2.0 equiv), and then capped with a rubber septum. Anhydrous THF/HMPA (THF/HMPA = 1:1, 0.10 M) and amine 3 (3.0 equiv) were successively added to the flask via syringes. After the mixture was stirred at 0 °C for 5 min, CsF (2.0 equiv) was added. The reaction mixture was stirred at 0 °C for 2 h, quenched by a saturated aqueous NH$_4$Cl solution and extracted with EtOAc. The aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over anhydrous Na$_2$SO$_4$ and then filtrated. The filtrate was evaporated under reduced pressure. The resultant residue, containing a significant amount of HMPA, was filtered through a short pad of silica gel to afford a mixture of ortho-6 and meta-6, and the ratio of these two regioisomers was determined by the $^1$H NMR analyses. Further purification of the mixture by flash column chromatography on silica gel provided pure ortho-6. Pure meta-6Da was obtained under different conditions (vide infra) and characterized by its $^1$H NMR, $^{13}$C NMR, IR and HRMS. Other meta-6 were identified based on similarities of their $^1$H NMR data to those of meta-6Da.

The abbreviations shown below are used in this supplementary information.

B(pin) = ![B(pin)](image)

B(dan) = ![B(dan)](image)

B(MIDA) = ![B(MIDA)](image)
**N-Butyl-4-methyl-2-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)aniline (ortho-6Ba)** (Table 1, entry 12). Following the general procedure, a mixture of 2B (32 mg, 67 µmol), n-butylamine 3a (20 µL, 0.20 mmol), 18-crown-6 (35 mg, 0.13 mmol) and CsF (20 mg, 0.13 mmol) in THF (0.34 mL) and HMPA (0.34 mL) was stirred for 2 h at 0 °C. The crude product was filtered through flash column chromatography (hexane/EtOAc = 3:1) to provide a mixture of ortho-6Ba and meta-6Ba (22 mg, 99% total yield, ortho-6Ba/meta-6Ba = 9.2:1). The mixture was purified by flash column chromatography (hexane/EtOAc = 5:1) to provide ortho-6Ba. Rf: 0.4 (hexane/EtOAc = 6:1). A colorless oil. 1H NMR (500 MHz, CDCl3) δ: 0.98 (3 H, t, J = 7.5 Hz), 1.46 (2 H, sext, J = 7.5 Hz), 1.63 (2 H, quint, J = 7.5 Hz), 2.29 (3 H, s), 3.11 (2 H, t, J = 7.5 Hz), 6.17 (2 H, d, J = 7.5 Hz), 6.62 (1 H, d, J = 8.0 Hz), 7.07 (2 H, d, J = 7.5 Hz), 7.13 (1 H, dd, J = 1.5, 8.0 Hz), 7.15 (2 H, t, J = 7.5 Hz), 7.19 (1 H, d, J = 1.5 Hz); 13C NMR (125 MHz, CDCl3) δ: 13.9, 20.38, 20.44, 31.6, 44.4, 106.0, 111.2, 117.7, 119.8, 126.6, 127.6, 131.6, 133.7, 136.3, 141.0, 149.5; IR (cm⁻¹) 3433; HRMS m/z (ESI) Calcd for C32H32BN3 [(M + H)+]: 330.2142, found: 330.2131.

**N-Decyl-4-methyl-2-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)aniline (ortho-6Bb)** (Table 2, entry 1). Following the general procedure, a mixture of 2B (32 mg, 67 µmol), n-decylamine 3b (40 µL, 0.20 mmol), 18-crown-6 (35 mg, 0.13 mmol) and CsF (20 mg, 0.13 mmol) in THF (0.34 mL) and HMPA (0.34 mL) was stirred for 2 h at 0 °C. The crude product was filtered through flash column chromatography (hexane/EtOAc = 5:1) to provide a mixture of ortho-6Bb and meta-6Bb (22 mg, 99% total yield, ortho-6Bb/meta-6Bb = 9:2:1). The mixture was purified by flash column chromatography (hexane/EtOAc = 10:1) to provide ortho-6Bb. Rf: 0.55 (hexane/EtOAc = 10:1). A colorless oil. 1H NMR (500 MHz, CDCl3) δ: 0.90 (3 H, t, J = 7.0 Hz), 1.20–1.38 (12 H, m), 1.39–1.45 (2 H, m), 1.64 (2 H, quint, J = 7.0 Hz), 2.29 (3 H, s), 3.10 (2 H, t, J = 7.0 Hz), 3.82 (1 H, brs), 6.16 (2 NH, brs), 6.38 (2 H, d, J = 7.5 Hz), 6.62 (1 H, d, J = 8.0 Hz), 7.07 (2 H, d, J = 7.5 Hz), 7.13 (1 H, dd, J = 2.0, 8.0 Hz), 7.15 (2 H, t, J = 7.5 Hz), 7.19 (1 H, brs); 13C NMR (125 MHz, CDCl3) δ: 14.1, 20.4, 22.7, 27.3, 29.3, 29.4, 29.5, 29.6, 31.9, 44.8, 105.9, 111.2, 117.7, 119.8, 126.6, 127.6, 131.6, 133.7, 136.6, 141.0, 149.6; IR (cm⁻¹) 3434; HRMS m/z (ESI) Calcd for C29H37BN3 [(M + H)+]: 414.3081, found: 414.3091.

**N-Butyl-2-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)aniline (ortho-6Da)** (Table 2, entry 2). Following the general procedure, a mixture of 2D (31 mg, 66 µmol), n-butylamine 3a (20 µL, 0.20 mmol), 18-crown-6 (35 mg, 0.13 mmol) and CsF (20 mg, 0.13 mmol) in THF...
(0.34 mL) and HMPA (0.34 mL) was stirred for 2 h at 0 °C. The crude product was filtered through flash column chromatography (hexane/EtOAc = 5:1) to provide a mixture of ortho-6Da and meta-6Da (21 mg, 99% total yield, ortho-6Da/meta-6Da = 14:1). The mixture was purified by flash column chromatography (hexane/EtOAc = 10:1) to provide ortho-6Da. Rf: 0.55 (hexane/EtOAc = 5:1). A colorless oil. 1H NMR (500 MHz, CDCl3) δ: 0.98 (3 H, t, J = 7.5 Hz), 1.46 (2 H, sext, J = 7.5 Hz), 1.64 (2 H, quint, J = 7.5 Hz), 3.17 (2 H, t, J = 7.5 Hz), 3.71 (1 H, dt, J = 1.5, 7.5 Hz), 3.76 (1 H, dd, J = 1.5, 7.5 Hz); 13C NMR (125 MHz, CDCl3) δ: 13.9, 20.4, 31.6, 43.9, 106.0, 110.6, 117.4, 117.8, 119.8, 127.6, 131.2, 133.1, 136.3, 141.0, 151.6; IR (cm−1) 3433; HRMS m/z (ESI) Calcd for C20H22BN3 [(M + H)+]: 316.1985, found: 316.1989.

N-Butyl-3-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)aniline (meta-6Da) (Table 2, entry 2). Pure meta-6Da was obtained under different conditions: An oven-dried round-bottomed flask was evacuated and back-filled with argon after cooling to room temperature. The flask was charged with a borylbenzyne precursor 2D (100 mg, 0.22 mmol) and 18-crown-6 (114 mg, 0.43 mmol), and then capped with a rubber septum. Anhydrous DMF (2.2 mL, 0.10 M) and n-butylamine 3a (89 µL, 0.90 mmol) were successively added to the flask via syringes. After the mixture was stirred at 0 °C for 5 min, KF (25 mg, 0.43 mmol) was added. The reaction mixture was stirred for 2 h at 40 °C, quenched by a saturated aqueous NH4Cl solution and extracted with EtOAc. The aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over anhydrous Na2SO4 and then filtrated. The filtrate was evaporated under reduced pressure. The crude product (ortho-6Da/meta-6Da = 1:9) was purified by flash column chromatography (hexane/EtOAc = 9:1) to provide meta-6Da (12 mg, 18%). Rf: 0.55 (hexane/EtOAc = 5:1). A colorless oil. 1H NMR (400 MHz, CDCl3) δ: 0.98 (3 H, t, J = 7.5 Hz), 1.48 (2 H, sext, J = 7.5 Hz), 1.61 (2 H, quint, J = 7.5 Hz), 3.17 (2 H, t, J = 7.5 Hz), 3.68 (NH, brs), 6.00 (2NH, brs), 6.40 (2 H, d, J = 8.0 Hz), 6.71 (1 H, dd, J = 2.0, 7.5 Hz), 6.85 (1 H, d, J = 2.0 Hz), 6.96 (1 H, d, J = 7.5 Hz), 7.05 (2 H, d, J = 8.0 Hz), 7.13 (2 H, t, J = 8.0 Hz), 7.26 (1 H, t, J = 7.5 Hz); 13C NMR (100 MHz, CDCl3) δ: 13.9, 20.3, 31.7, 43.7, 105.9, 114.4, 115.5, 117.7, 119.8, 120.1, 127.6, 129.2, 136.4 141.2, 148.3; IR (cm−1) 3416; HRMS m/z (MALDI) Calcd for C20H22BN3 [M+]: 315.1907, found: 315.1905.

N-Allyl-2-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)aniline (ortho-6Dc) (Table 2, entry 3). Following the general procedure, a mixture of 2D (32 mg, 67 µmol), allylamine 3c (15 µL, 0.20 mmol), 18-crown-6 (35 mg, 0.13 mmol) and CsF (20 mg, 0.13 mmol) in THF (0.34 mL) and HMPA (0.34 mL) was stirred for 2 h at 0 °C. The crude product was purified by flash column chromatography (hexane/EtOAc = 10:1) to provide ortho-6Dc (18 mg, 87%). Rf: 0.45 (hexane/EtOAc = 5:1). A colorless oil. 1H NMR (500 MHz, CDCl3) δ: 3.80 (2 H, d, J = 5.0 Hz), 4.18 (NH, brs), 5.19 (1 H, dd, J = 1.5, 10.0 Hz), 5.30 (1 H, dd, J = 1.5, 17.0 Hz), 5.95–6.03 (1 H,
Following the general procedure, a mixture of 2D (31 mg, 67 \( \mu \)mol), c-hexylamine 3d (23 \( \mu \)L, 0.20 mmol), 18-crown-6 (35 mg, 0.13 mmol) and CsF (20 mg, 0.13 mmol) in THF (0.34 mL) and HMPA (0.34 mL) was stirred for 2 h at 0 °C. The crude product was filtered through flash column chromatography (hexane/EtOAc = 4:1) to provide a mixture of ortho-6Dd and meta-6Dd (23 mg, 99% total yield, ortho-6Dd/meta-6Dd = 10:1). The mixture was purified by flash column chromatography (hexane/EtOAc = 10:1) to provide ortho-6Dd. RF: 0.4 (hexane/EtOAc = 10:1). A colorless oil. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\): 1.22–1.28 (3 H, m), 1.35–1.43 (2 H, m), 1.59–1.62 (1 H, m), 1.61–1.69 (1 H, m), 1.73–1.80 (2 H, m), 2.03–2.09 (2 H, m), 3.30 (1 H, t, \(J = 4.0, 10.0\) Hz), 3.92 (NH, brs), 6.12 (2 NH, brs), 6.37 (2 H, d, \(J = 7.5\) Hz), 6.68 (1 H, d, \(J = 7.5\) Hz), 6.76 (1 H, t, \(J = 7.5\) Hz), 7.01 (2 H, d, \(J = 7.5\) Hz), 7.11 (2 H, t, \(J = 7.5\) Hz), 7.27 (1 H, dt, \(J = 1.5, 7.5\) Hz), 7.35 (1 H, dd, \(J = 1.5, 7.5\) Hz); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\): 24.9, 25.9, 33.4, 52.1, 106.1, 111.2, 116.3, 117.9, 119.7, 127.6, 131.0, 133.3, 136.8, 141.0, 150.5; IR (cm\(^{-1}\)) 3434; HRMS m/z (ESI) Calcd for C\(_{23}H\_22BN\(_3\) [(M + H)+]: 342.2142, found: 342.2143.

Following the general procedure, a mixture of 2D (32 mg, 68 \( \mu \)mol), t-butylamine 3e (21 \( \mu \)L, 0.20 mmol), 18-crown-6 (35 mg, 0.13 mmol) and CsF (20 mg, 0.13 mmol) in THF (0.34 mL) and HMPA (0.34 mL) was stirred for 2 h at 0 °C. The crude product was filtered through flash column chromatography (hexane/EtOAc = 5:1) to provide a mixture of ortho-6De and meta-6De (20 mg, 94% total yield, ortho-6De/meta-6De = 2.5:1). The mixture was purified by flash column chromatography (hexane/EtOAc = 10:1) to provide ortho-6De. RF: 0.45 (hexane/EtOAc = 5:1). A colorless oil. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\): 1.34 (9 H, s), 6.34–6.40 (4 H, m), 6.90 (1 H, t, \(J = 7.5\) Hz), 6.94 (1 H, d, \(J = 7.5\) Hz), 7.05 (2 H, d, \(J = 7.5\) Hz), 7.14 (2 H, t, \(J = 7.5\) Hz), 7.28 (1 H, dt, \(J = 1.5, 7.5\) Hz), 7.40 (1 H, dd, \(J = 1.5, 7.5\) Hz); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\): 29.9, 52.1, 105.9, 117.6, 118.3, 119.4, 119.8, 127.6, 130.3, 133.3, 136.3, 141.1, 149.9; IR (cm\(^{-1}\)) 3433; HRMS m/z (ESI) Calcd for C\(_{20}H\_22BN\(_3\) [(M + H)+]: 316.1985, found: 316.1987.
\[ \text{ortho-6Df} \]

\emph{N-Benzyl-2-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)aniline (ortho-6Df) (Table 2, entry 6).} Following the general procedure, a mixture of 2D (31 mg, 67 \text{\( \mu \)}mol), benzylamine 3f (22 \text{\( \mu \)}L, 0.20 mmol), 18-crown-6 (35 mg, 0.13 mmol) and CsF (20 mg, 0.13 mmol) in THF (0.34 mL) and HMPA (0.34 mL) was stirred for 2 h at 0 °C. The crude product was filtered through flash column chromatography (hexane/EtOAc = 5:1) to provide a mixture of \emph{ortho-6Df} and \emph{meta-6Df} (23 mg, 97% total yield, \emph{ortho-6Df/meta-6Df} = 12:1). The mixture was purified by flash column chromatography (hexane/EtOAc = 9:1) to provide \emph{ortho-6Df}. Rf: 0.5 (hexane/EtOAc = 5:1). A colorless solid. Mp: 107–109 °C; \( ^1 \text{H} \) NMR (500 MHz, CDCl\(_3\)) \( \delta \): 4.37 (2 H, s), 4.47 (NH, brs), 6.10 (2 NH, brs), 6.34 (2 H, d, \( J = 7.5 \) Hz), 6.68 (1 H, d, \( J = 7.5 \) Hz), 6.82 (1 H, t, \( J = 7.5 \) Hz), 7.05 (2 H, d, \( J = 7.5 \) Hz), 7.13 (2 H, d, \( J = 7.5 \) Hz), 7.27–7.31 (2 H, m), 7.35–7.40 (5 H, m); \( ^{13} \text{C} \) NMR (125 MHz, CDCl\(_3\)) \( \delta \): 48.7, 106.1, 111.3, 117.9, 118.0, 119.8, 127.3, 127.6, 128.7, 131.2, 133.2, 136.2, 139.2, 140.9, 131.2; IR (cm\(^{-1}\)) 3435; HRMS m/z (ESI) Calcd for C\(_{23}\)H\(_{26}\)BN\(_3\) [(M + H)]\(^+\): 350.1829, found: 350.1827.

\[ \text{ortho-6Dg} \]

\emph{N-(3-Iodobenzyl)-2-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)aniline (ortho-6Dg) (Table 2, entry 7).} Following the general procedure, a mixture of 2D (31 mg, 67 \text{\( \mu \)}mol), \( m \)-iodobenzylamine 3g (48 mg, 0.21 mmol), 18-crown-6 (35 mg, 0.13 mmol) and CsF (20 mg, 0.13 mmol) in THF (0.34 mL) and HMPA (0.34 mL) was stirred for 2 h at 0 °C. The crude product was filtered through flash column chromatography (hexane/EtOAc = 2:1) to provide a mixture of \emph{ortho-6Dg} and \emph{meta-6Dg} (85% total NMR yield, \emph{ortho-6Dg/meta-6Dg} = 10:1). The mixture was purified by trituration with hexane to provide \emph{ortho-6Dg} (20 mg, 64%). Rf: 0.3 (hexane/EtOAc = 5:1). A colorless solid. Mp: 109–111 °C; \( ^1 \text{H} \) NMR (400 MHz, CDCl\(_3\)) \( \delta \): 4.32 (2 H, s), 6.11 (2 NH, brs), 6.38 (2 H, d, \( J = 7.5 \) Hz), 6.64 (1 H, d, \( J = 7.5 \) Hz), 6.84 (1 H, t, \( J = 7.5 \) Hz), 7.07 (2 H, d, \( J = 7.5 \) Hz), 7.08 (1 H, t, \( J = 7.5 \) Hz), 7.14 (2 H, t, \( J = 7.5 \) Hz), 7.27 (1 H, dt, \( J = 1.5, 7.5 \) Hz), 7.33 (1 H, d, \( J = 7.5 \) Hz), 7.39 (1 H, dd, \( J = 1.5, 7.5 \) Hz), 7.60 (1 H, d, \( J = 7.5 \) Hz), 7.75 (1 H, brs); \( ^{13} \text{C} \) NMR (75 MHz, CDCl\(_3\)) \( \delta \): 48.1, 94.7, 106.2, 111.3, 118.0, 118.3, 119.8, 126.4, 127.6, 130.4, 131.2, 133.2, 136.2, 136.3, 136.4, 140.8, 141.8, 150.8; IR (cm\(^{-1}\)) 3431; HRMS m/z (ESI) Calcd for C\(_{23}\)H\(_{26}\)BN\(_3\) [(M + H)]\(^+\): 476.0795, found: 476.0783.

\[ \text{ortho-6Dh} \]

\emph{N-(Furan-2-ylmethyl)-2-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)aniline (ortho-6Dh) (Table 2, entry 8).} Following the general procedure, a mixture of 2D (32 mg, 67 \text{\( \mu \)}mol), furfurylamine 3h (18 \text{\( \mu \)}L, 0.20 mmol), 18-crown-6 (35 mg, 0.13 mmol) and CsF (20 mg, 0.13 mmol) in THF (0.34 mL) and HMPA (0.34 mL) was stirred for 2 h at 0 °C. The crude
product was filtered through flash column chromatography (hexane/EtOAc = 3:1) to provide a mixture of ortho-6Di and meta-6Di (21 mg, 93% total yield, ortho-6Di/meta-6Di = 15:1). The mixture was purified by flash column chromatography (hexane/EtOAc = 5:1) to provide ortho-6Di. Rf: 0.45 (hexane/EtOAc = 5:1). A colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) δ: 4.36 (2 H, s), 6.14 (2 NH, brs), 6.25 (1 H, d, $J = 3.0$ Hz), 6.34 (1 H, d, $J = 7.5$ Hz), 6.49 (1 H, d, $J = 7.5$ Hz), 6.63 (1 H, d, $J = 7.5$ Hz), 6.85 (1 H, t, $J = 7.5$ Hz), 7.07 (2 H, d, $J = 7.5$ Hz), 7.14 (2 H, t, $J = 7.5$ Hz), 7.32 (1 H, dt, $J = 1.5$, 7.5 Hz), 7.39 (1 H, dd, $J = 1.5$, 7.5 Hz), 7.40 (1 H, brs); $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 42.1, 106.1, 107.1, 110.4, 111.8, 117.9, 118.6, 119.8, 127.6, 131.1, 133.2, 136.3, 140.9, 142.0, 150.7, 152.6. IR (cm$^{-1}$) 3433; HRMS m/z (ESI) Calcd for [(M + H)$^+$]: 340.1621, found: 340.1633.

3-(2-(2-(1H-Naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)phenyl)amino)ethyl)-1H-indol-5-ol (ortho-6Di) (Table 2, entry 9). Following the general procedure, a mixture of 2D (32 mg, 68 µmol), 5-hydroxytryptamine 3i (36 mg, 0.20 mmol), 18-crown-6 (35 mg, 0.13 mmol) and CsF (20 mg, 0.13 mmol) in THF (0.34 mL) and HMPA (0.34 mL) was stirred for 2 h at 0 °C. The crude product was filtered through flash column chromatography (hexane/EtOAc = 1:2) to provide a mixture of ortho-6Di and meta-6Di (28 mg, 98% total yield, ortho-6Di/meta-6Di = 13:1). The mixture was purified by flash column chromatography (hexane/EtOAc = 2:1) to provide ortho-6Di. Rf: 0.15 (hexane/EtOAc = 3:1). A colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) δ: 3.04 (2 H, t, $J = 6.5$ Hz), 3.44 (2 H, t, $J = 6.5$ Hz), 5.82 (2 NH, brs), 6.15 (2 H, d, $J = 7.5$ Hz), 6.71-6.75 (2 H, m), 6.78 (1 H, t, $J = 7.5$ Hz), 6.79-6.85 (1 H, m), 6.92-6.98 (1 H, m), 7.04 (2 H, d, $J = 7.5$ Hz), 7.10 (2 H, t, $J = 7.5$ Hz), 7.14 (1 H, d, $J = 8.5$ Hz), 7.29-7.33 (2 H, m), 7.70 (OH, brs); $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 24.5, 44.2, 103.4, 105.9, 106.0, 111.1, 112.0, 112.1, 112.7, 117.7, 119.7, 123.5, 127.6, 128.0, 131.1, 131.6, 133.1, 136.2, 141.0, 149.3, 151.0; IR (cm$^{-1}$) 3601, 3478, 3433; HRMS m/z (ESI) Calcd for C$_{23}$H$_{22}$BN$_2$O [(M + H)$^+$]: 419.3060, found: 419.3072.

2-(1H-Naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)-N-(p-tolyl)aniline (ortho-6Dj) (Table 2, entry 10). Following the general procedure, a mixture of 2D (31 mg, 67 µmol), p-toluvaline 3j (22 mg, 0.20 mmol), 18-crown-6 (35 mg, 0.13 mmol) and CsF (20 mg, 0.13 mmol) in THF (0.34 mL) and HMPA (0.34 mL) was stirred for 2 h at 0 °C. The crude product was filtered through flash column chromatography (hexane/EtOAc = 3:1) to provide a mixture of ortho-6Dj and meta-6Dj (20 mg, 86% total yield, ortho-6Dj/meta-6Dj = 2.9:1). The mixture was purified by flash column chromatography (hexane/EtOAc = 7:1) to provide ortho-6Dj. Rf: 0.55 (hexane/EtOAc = 5:1). A colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) δ: 2.32 (3 H, s), 5.73 (NH, brs), 6.18 (2 NH, brs), 6.34 (2 H, d, $J = 7.5$ Hz), 6.96 (2 H, d, $J = 8.0$ Hz), 7.02 (1 H, t, $J = 8.0$ Hz), 7.04 (2 H, d, $J = 7.5$ Hz), 7.11 (2 H, d, $J = 8.0$ Hz), 7.12 (2 H, t, $J = 7.5$ Hz), 7.23 (1 H, d, $J = 8.0$ Hz), 7.32 (1 H, dt, $J = 1.5$, 8.0 Hz), 7.51 (1 H, dd, $J = 1.5$, 8.0 Hz); $^{13}$C NMR (125 MHz,
N,N-Diethyl-2-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)aniline (ortho-6Dk) (Table 2, entry 11). Following the general procedure, a mixture of 2D (31 mg, 67 μmol), N,N-diethylamine 3k (21 μL, 0.20 mmol), 18-crown-6 (35 mg, 0.13 mmol) and CsF (20 mg, 0.13 mmol) in THF (0.34 mL) and HMPA (0.34 mL) was stirred for 2 h at 0 °C. The crude product was filtered through flash column chromatography (hexane/EtOAc = 4:1) to provide a mixture of ortho-6Dk and meta-6Dk (21 mg, >99% total yield, ortho-6Dk/meta-6Dk = 1.6:1). The mixture was purified by flash column chromatography (hexane/EtOAc = 10:1) to provide ortho-6Dk. Ref: 0.6 (hexane/EtOAc = 5:1). A colorless oil. 1H NMR (500 MHz, CDCl3) δ: 1.08 (6 H, t, J = 7.0 Hz), 3.14 (4 H, q, J = 7.0 Hz), 6.37 (2 H, d, J = 7.5 Hz), 7.02 (2 H, d, J = 7.5 Hz), 7.13 (2 H, t, J = 7.5 Hz), 7.14–7.18 (4 H, m), 7.39 (1 H, dt, J = 1.5, 7.5 Hz), 7.57 (1 H, dd, J = 1.5, 7.5 Hz); 13C NMR (125 MHz, CDCl3) δ: 12.3, 48.4, 105.5, 117.1, 120.0, 121.8, 123.2, 127.6, 130.6, 133.0, 136.5, 141.7, 156.8; IR (cm−1) 3434; HRMS m/z (ESI) Calcd for C20H23BN3 [(M + H)+]: 316.1985, found: 316.1979.

2-(2-(Pyrrrolidin-1-yl)phenyl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine (ortho-6Dl) (Table 2, entry 12). Following the general procedure, a mixture of 2D (32 mg, 68 μmol), pyrrolidine 3l (17 μL, 0.20 mmol), 18-crown-6 (35 mg, 0.13 mmol) and CsF (20 mg, 0.13 mmol) in THF (0.34 mL) and HMPA (0.34 mL) was stirred for 2 h at 0 °C. The crude product was filtered through flash column chromatography (hexane/EtOAc = 3:1) to provide a mixture of ortho-6Dl and meta-6Dl (22 mg, >99% total yield, ortho-6Dl/meta-6Dl = 6:7:1). The mixture was purified by flash column chromatography (hexane/EtOAc = 7:1) to provide ortho-6Dl. Ref: 0.5 (hexane/EtOAc = 5:1). A colorless oil. 1H NMR (500 MHz, CDCl3) δ: 1.89–1.95 (4 H, m), 3.30–3.37 (4 H, m), 6.06 (2 NH, brs), 6.34 (2 H, d, J = 7.5 Hz), 6.77 (1 H, d, J = 8.0 Hz), 6.82 (1 H, t, J = 8.0 Hz), 7.04 (2 H, d, J = 7.5 Hz), 7.13 (2 H, t, J = 7.5 Hz), 7.30 (1 H, dt, J = 1.5, 8.0 Hz), 7.40 (1 H, dd, J = 1.5, 8.0 Hz); 13C NMR (125 MHz, CDCl3) δ: 25.5, 51.2, 105.7, 113.2, 117.5, 119.6, 127.6, 130.2, 133.6, 136.3, 141.3, 152.6; IR (cm−1) 3433; HRMS m/z (ESI) Calcd for C20H23BN3 [(M + H)+]: 314.1829, found: 314.1840.

4-(2-(1H-Naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)phenyl)morpholine (ortho-6Dm)
Following the general procedure, a mixture of 2D (32 mg, 67 μmol), morpholine 3m (18 μL, 0.21 mmol), 18-crown-6 (35 mg, 0.13 mmol) and CsF (20 mg, 0.13 mmol) in THF (0.34 mL) and HMPA (0.34 mL) was stirred for 2 h at 0 °C. The crude product was filtered through flash column chromatography (hexane/EtOAc = 1:1) to provide a mixture of ortho-6Dm and meta-6Dm (22 mg, 99% total yield, ortho-6Dm/meta-6Dm = 5.7:1). The mixture was purified by flash column chromatography (hexane/EtOAc = 3:1) to provide ortho-6Dm. Rf: 0.45 (hexane/EtOAc = 3:1). A colorless oil. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\): 3.09 (4 H, t, \(J = 4.5 \text{ Hz}\)), 3.89 (4 H, d, \(J = 4.5 \text{ Hz}\)), 6.41 (2 H, d, \(J = 7.5 \text{ Hz}\)), 6.88 (2 NH, brs), 7.04 (2 H, d, \(J = 7.5 \text{ Hz}\)), 7.09 (1 H, d, \(J = 8.0 \text{ Hz}\)), 7.14 (1 H, t, \(J = 8.0 \text{ Hz}\)), 7.15 (2 H, t, \(J = 7.5 \text{ Hz}\)), 7.42 (1 H, dt, \(J = 1.5, 8.0 \text{ Hz}\)), 7.57 (1 H, dd, \(J = 1.5, 8.0 \text{ Hz}\)); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\): 53.9, 67.5, 105.7, 117.5, 117.9, 119.9, 123.2, 127.7, 131.2, 133.6, 136.4, 141.3, 157.5; IR (cm\(^{-1}\)) 3433; HRMS m/z (ESI) Calcd for C\(_{20}\)H\(_{23}\)BN\(_4\)O [(M + H)\(^+\)]: 330.1778, found: 330.1768.

**tert-Butyl 2-(2-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)phenyl)hydrazine-carboxylate (ortho-6Do)** (Table 2, entry 14). Following the general procedure, a mixture of 2D (31 mg, 66 μmol), t-butylcarbazate 3n (28 mg, 0.20 mmol), 18-crown-6 (35 mg, 0.13 mmol) and CsF (20 mg, 0.13 mmol) in THF (0.34 mL) and HMPA (0.34 mL) was stirred for 2 h at 0 °C. The crude product was purified by flash column chromatography (hexane/EtOAc = 5:1) to provide ortho-6Do (21 mg, 81%). Rf: 0.3 (hexane/EtOAc = 5:1). A colorless oil. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\): 1.48 (9 H, s), 6.39 (2 H, d, \(J = 7.5 \text{ Hz}\)), 6.61 (1 NH, brs), 6.69 (2 NH, brs), 6.97 (1 H, t, \(J = 7.5 \text{ Hz}\)), 7.02 (1 H, d, \(J = 7.5 \text{ Hz}\)), 7.05 (2 H, d, \(J = 7.5 \text{ Hz}\)), 7.13 (2 H, t, \(J = 7.5 \text{ Hz}\)), 7.34 (1 H, dt, \(J = 1.5, 7.5 \text{ Hz}\)), 7.40 (1 H, dd, \(J = 1.5, 7.5 \text{ Hz}\)); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\): 28.3, 81.6, 106.1, 114.5, 117.8, 119.9, 121.4, 127.6, 130.8, 132.9, 136.3, 141.1, 152.1, 157.0; IR (cm\(^{-1}\)) 3435, 3339, 1717; HRMS m/z (ESI) Calcd for C\(_{21}\)H\(_{25}\)BN\(_2\)O \([(M + H)\(^+\)]: 375.1992, found: 375.1978.

**N1-(2-(1H-Naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)phenyl)ethane-1,2-diamine (ortho-6Do)** (Table 2, entry 15). An oven-dried test tube was evacuated and back-filled with argon after cooling to room temperature. The tube was charged with a borylbenzyne precursor 2D (31 mg, 67 μmol) and 18-crown-6 (35 mg, 0.13 mmol), and then capped with a rubber septa. Anhydrous THF, HMPA (THF/HMPA = 1:1, 0.10 M) and ethylenediamine 3o (12 μL, 0.20 mmol) were added to the reaction tube via syringes respectively. After the mixture was cooled at 0 °C for 5 min, CsF (20 mg, 0.13 mmol) was added. The reaction mixture was stirred for 2 h at 0 °C and quenched by a saturated aqueous NH\(_4\)Cl solution. The mixture was extracted with EtOAc. The aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over anhydrous Na\(_2\)SO\(_4\) and then filtrated. The filtrate was evaporated under reduced pressure. The residue was filtered by flash column chromatography (CH\(_2\)Cl\(_2\)/MeOH = 10:1) to provide a mixture of ortho-6Do (76% NMR yield), HMPA and a small amount of impurity, that did not contain meta-6Do. This mixture was purified by washing with a saturated LiCl solution.
and then by column chromatography (CH$_2$Cl$_2$/MeOH = 10:1) to provide ortho-6Do (9.0 mg, 46%). Rf: 0.3 (hexane/EtOAc = 10:1). A colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ: 2.93 (2 H, brt, $J = 5.0$ Hz), 3.28 (2 H, brt, $J = 5.0$ Hz), 6.34 (2 NH, brs), 6.37 (2 H, d, $J = 7.0$ Hz), 6.57 (1 H, d, $J = 8.0$ Hz), 6.79 (1 H, t, $J = 8.0$ Hz), 6.99 (2 H, d, $J = 8.5$ Hz), 7.07 (2 H, t, $J = 8.0$ Hz), 7.25 (1 H, t, $J = 8.0$ Hz), 7.31 (1 H, d, $J = 8.0$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 39.8, 43.0, 106.2, 110.8, 117.7, 118.5, 119.8, 127.6, 131.1, 133.6, 136.2, 141.1, 150.2; IR (cm$^{-1}$) 3433, 3149; HRMS m/z (ESI) Calcd for C$_{18}$H$_{20}$BN$_4$ [(M + H)$^+$]: 303.1781, found: 303.1784.

**4-Bromo-N-butyl-2-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)aniline (ortho-6Ea)** (Table 2, entry 16). Following the general procedure, a mixture of 2E (37 mg, 68 µmol), n-butylamine 3a (20 µL, 0.20 mmol), 18-crown-6 (35 mg, 0.13 mmol) and CsF (20 mg, 0.13 mmol) in THF (0.34 mL) and HMPA (0.34 mL) was stirred for 2 h at 0 °C. The crude product was purified by flash column chromatography (hexane/EtOAc = 5:1) to provide ortho-6Ea (24 mg, 89%). Rf: 0.55 (hexane/EtOAc = 3:1). A colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) δ: 0.97 (3 H, t, $J = 7.5$ Hz), 1.44 (2 H, sext, $J = 7.5$ Hz), 1.62 (2 H, quint, $J = 7.5$ Hz), 3.09 (2 H, t, $J = 7.5$ Hz), 4.01 (1 NH, brs), 4.03 (2 NH, brs), 6.37 (2 H, d, $J = 8.0$ Hz), 6.52 (1 H, d, $J = 8.5$ Hz), 7.07 (2 H, d, $J = 8.0$ Hz), 7.14 (2 H, t, $J = 7.5$ Hz), 7.35 (1 H, dd, $J = 2.0$, 8.5 Hz), 7.40 (1 H, d, $J = 2.0$ Hz); $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 13.9, 20.4, 31.4, 44.0, 106.2, 109.5, 112.3, 118.2, 119.9, 127.6, 133.5, 135.3, 136.3, 140.6, 150.4; IR (cm$^{-1}$) 3436; HRMS m/z (ESI) Calcd for C$_{20}$H$_{22}$B$_{3}$BrN$_4$ [(M + H)$^+$]: 396.1070, found: 396.1068.

**4-(4-Bromo-2-(1H-Naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)phenyl)morpholine (ortho-6Em)** (Table 2, entry 17). Following the general procedure, a mixture of 2E (0.27 g, 0.50 mmol), morpholine 3m (0.13 mL, 1.49 mmol), 18-crown-6 (0.26 g, 1.00 mmol) and CsF (0.15 g, 0.99 mmol) in THF (1.0 mL) and HMPA (4.0 mL) was stirred for 2 h at 0 °C. The crude product was filtered through flash column chromatography (hexane/EtOAc = 2:1) to provide a mixture of ortho-6Em and meta-6Em (0.17 g, 86% total yield, ortho-6Em/meta-6Em = 2.2:1). The mixture was purified by flash column chromatography (hexane/EtOAc = 5:1) to provide ortho-6Em. Rf: 0.5 (hexane/EtOAc = 3:1). A colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) δ: 3.04 (4 H, t, $J = 4.0$ Hz), 3.87 (4 H, t, $J = 4.0$ Hz) 6.40 (2 H, d, $J = 8.0$ Hz), 6.76 (2 NH, brs), 6.93 (1 H, d, $J = 8.5$ Hz), 7.05 (2 H, d, $J = 8.0$ Hz), 7.14 (2 H, t, $J = 8.0$ Hz), 7.49 (1 H, dd, $J = 2.5$, 8.5 Hz), 7.63 (1 H, d, $J = 2.5$ Hz); $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 53.7, 67.3, 105.9, 116.6, 117.8, 119.7, 120.0, 127.7, 133.7, 136.2, 136.4, 140.9, 156.3; IR (cm$^{-1}$) 3435; HRMS m/z (ESI) Calcd for C$_{20}$H$_{20}$B$_{3}$BrN$_4$O [(M + H)$^+$]: 408.0883, found: 408.0876.
4-Bromo-N-(3,4-dimethoxyphenethyl)-2-(1H-naphth[1,8-de][1,3,2]diazaborin-2(3H)-yl) aniline (ortho-6Ep) (Table 2, entry 18). Following the general procedure, a mixture of 2E (37 mg, 67 µmol), 2-(3,4-dimethoxyphenyl)ethylamine 3p (34 µL, 0.20 mmol), 18-crown-6 (35 mg, 0.13 mmol) and CsF (20 mg, 0.13 mmol) in THF (0.34 mL) and HMPA (0.34 mL) was stirred for 2 h at 0 °C. The crude product was filtered through flash column chromatography (hexane/EtOAc = 1:2) to provide a mixture of ortho-6Ep and meta-6Ep (34 mg, 85% total yield, ortho-6Ep/meta-6Ep = 8.0:1). The mixture was purified by flash column chromatography (hexane/EtOAc = 2:1) to provide ortho-6Ep. Rf: 0.2 (hexane/EtOAc = 3:1). A colorless oil. 1H NMR (500 MHz, CDCl3) δ: 2.89 (2 H, t, J = 6.5 Hz), 3.38 (2 H, t, J = 6.5 Hz), 3.76 (3 H, s), 3.77 (3 H, s), 5.80 (2 NH, brs), 6.24 (2 H, d, J = 7.5 Hz), 6.56 (1 H, d, J = 8.0 Hz), 6.67–6.72 (3 H, m), 7.05 (2 H, d, J = 7.5 Hz), 7.12 (2 H, t, J = 7.5 Hz), 7.36 (1 H, d, J = 7.5 Hz), 7.38 (1 H, brs); 13C NMR (125 MHz, CDCl3) δ: 34.3, 44.9, 55.76, 55.81, 106.3, 109.7, 111.3, 111.8, 112.3, 118.1, 119.8, 120.8, 127.6, 131.3, 133.5, 135.4, 136.2, 140.5, 147.8, 149.2, 149.8; IR (cm⁻¹) 3431, 3387; HRMS m/z (ESI) Calcd for C26H26B79BrN3O2 [(M + H)⁺]: 502.1301, found: 502.1308.
Stepwise Suzuki–Miyaura cross coupling reactions of nucleophilic adduct 6Em (Scheme 2)

![Chemical Structure](image)

4-(4′-Methoxy-3-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)-[1,1′-biphenyl]-4-yl)morpholine (9) (Scheme 2). An oven dried test tube was charged with 6Em (0.10 g, 0.25 mmol), p-methoxyphenylboronic acid (77 mg, 0.50 mmol), PdCl₂(dppf)-CH₂Cl₂ (21 mg, 25 μmol), and K₃PO₄ (0.16 g, 0.76 mmol). The reaction tube was evacuated and back-filled with argon, and 1,4-dioxane (1.3 mL) was added via a syringe. The reaction mixture was stirred for 5 h at 80 °C. The reaction mixture was diluted with Et₂O (3.0 mL) and filtered through a pad of Celite, and the filtrate was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (hexane/EtOAc = 4:1) to provide the product 9 (0.10 g, 92%). Rf: 0.35 (hexane/EtOAc = 2:1). A colorless oil. ¹H NMR (500 MHz, CDCl₃) δ: 3.13 (4 H, brs), 3.86 (3 H, s), 3.91 (4 H, t, J = 4.5 Hz), 6.42 (2 H, d, J = 7.5 Hz), 6.91 (2 NH, brs), 7.00 (2 H, td, J = 2.0, 8.5 Hz), 7.05 (2 H, d, J = 7.5 Hz), 7.14 (1 H, d, J = 8.0 Hz), 7.15 (2 H, t, J = 7.5 Hz), 7.53 (2 H, td, J = 2.0, 8.5 Hz), 7.58 (1 H, dd, J = 2.5, 8.0 Hz), 7.71 (1 H, d, J = 2.5 Hz); ¹³C NMR (125 MHz, CDCl₃) δ: 53.9, 55.4, 67.5, 105.7, 114.3, 117.6, 118.2, 120.0, 127.7, 128.0, 129.4, 132.0, 133.3, 135.8, 136.5, 141.3, 156.3, 159.0; IR (cm⁻¹) 3434; HRMS m/z (ESI) Caled for C₂₇H₂₇BN₃O₂ [(M + H)⁺]: 436.2196, found: 436.2186.

![Chemical Structure](image)

(4′-Methoxy-4-morpholino-[1,1′-biphenyl]-3-yl)boronic acid (10) (Scheme 2). A round-bottomed flask was charged with 9 (97 mg, 0.22 mmol) and THF (2.3 mL), and the reaction mixture was stirred for 5 min at room temperature. Then 1N HCl (2.3 mL, 2.3 mmol) was added. The mixture was stirred for another 12 h at room temperature and washed with Et₂O. The aqueous layer was washed twice with Et₂O. The aqueous layer was adjusted to pH 12 by aqueous NaOH and washed by Et₂O to remove 1,8-diaminonaphthalene. The aqueous layer was neutralized with HCl and extracted with EtOAc three times. The combined EtOAc layers were dried over anhydrous Na₂SO₄, and the solvent was removed under reduced pressure to give 10 (61 mg), which was used for the next reaction without further purification.
4-(4-Methoxy-[1,1’;3’,1”-terphenyl]-4’-yl)morpholine (11) (Scheme 2). An oven dried test tube was filled with the crude product 10 (61 mg), bromobenzene (47 µL, 0.45 mmol), PdCl₂(dppf)-CH₂Cl₂ (18 mg, 22 µmol), and K₃PO₄ (0.14 g, 0.67 mmol), then evacuated and backfilled with argon. 1,4-Dioxane (1.1 mL) was added. The reaction mixture was stirred at 80 °C for 5 h, diluted with Et₂O (3.0 mL) and filtered through a pad of Celite. The filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/EtOAc = 5:1) to provide the product 11 (34 mg, 44%, over 2 steps). RF: 0.5 (hexane/EtOAc = 3:1). A colorless solid. Mp: 151–153 °C; ¹H NMR (500 MHz, CDCl₃) δ: 2.85 (4 H, t, J = 4.5 Hz), 3.62 (4 H, t, J = 4.5 Hz), 3.85 (3 H, s), 6.96 (2 H, td, J = 2.5, 9.0 Hz), 7.08 (1 H, d, J = 8.0 Hz), 7.32 (1 H, t, J = 7.5 Hz), 7.42 (2 H, t, J = 7.5 Hz), 7.46 (1 H, d, J = 2.5 Hz), 7.49 (1 H, dd, J = 2.5, 8.0 Hz), 7.52 (2 H, td, J = 2.5, 9.0 Hz), 7.69 (2 H, dd, J = 1.5, 8.0 Hz); ¹³C NMR (125 MHz, CDCl₃) δ: 51.5, 55.3, 66.9, 114.2, 118.3, 126.4, 127.0, 127.8, 128.3, 128.9, 130.0, 133.2, 135.2, 135.4, 141.0, 148.8, 158.8; IR (cm⁻¹) 2822; HRMS m/z (ESI) Calcd for C₂₃H₂₄NO₂ [(M + H)⁺]: 346.1807, found: 346.1817.
Procedures for the synthesis of borylbenzyne precursors 2B–2E

Scheme S1 Synthesis of 2B and 2C.

(5-Methyl-2-((trifluoromethyl)sulfonyl)oxy)-3-(trimethylsilyl)phenyl)boronic acid (S1). A round-bottomed flask was charged with 2A\(^1\) (2.6 g, 6.0 mmol), NaIO\(_4\) (3.9 g, 14 mmol), and THF/H\(_2\)O (4:1, 30 mL). The reaction mixture was stirred for 5 min at room temperature, to which 1N HCl (6.1 mL, 6.1 mmol) was added. The reaction mixture was stirred for 9.5 h at 60 °C, cooled to room temperature, quenched with H\(_2\)O and extracted with EtOAc. The aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na\(_2\)SO\(_4\) and concentrated under reduced pressure. Because some amount of 2A remained in the crude product, the hydrolysis was repeated using NaIO\(_4\) (3.9 g, 14 mmol) and 1N HCl (6.1 mL, 6.1 mmol) in THF/H\(_2\)O (4:1, 30 mL) for 17 h at 60 °C. The same workup provided S1 (2.5 g), which was used for the next reaction without further purification.

4-Methyl-2-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)-6-(trimethylsilyl)phenyl trifluoromethanesulfonate (2B). A round-bottomed flask was charged with the crude S1 (2.5 g), 1,8-diaminonaphthalene (1.0 g, 6.3 mmol) and CH\(_2\)Cl\(_2\) (60 mL). The reaction mixture was stirred for 8.0 h at room temperature, and H\(_2\)O was added. The mixture was extracted with CH\(_2\)Cl\(_2\). The aqueous layer was extracted twice with CH\(_2\)Cl\(_2\). The combined organic layers were washed with saturated aqueous NaCl, dried over anhydrous Na\(_2\)SO\(_4\), and concentrated under reduced pressure. The crude product was purified by flash column chromatography.
(hexane/EtOAc = 12:1) to provide 2B (2.2 g, 76% over 2 steps). Rf: 0.3 (hexane/EtOAc = 10:1). A brown solid. Mp: 128–130 °C; 1H NMR (500 MHz, CDCl3) δ: 0.42 (9 H, s), 2.41 (3 H, s), 5.92 (2 NH, brs), 6.38 (2 H, d, J = 7.5 Hz), 7.07 (2 H, d, J = 7.5 Hz), 7.14 (2 H, t, J = 7.5 Hz), 7.42 (2 H, brs); 13C NMR (125 MHz, CDCl3) δ: 0.08, 20.8, 106.1, 118.0, 118.4 (q, J = 320 Hz), 119.8, 127.6, 134.6, 136.1, 136.3, 137.5, 138.9, 140.6, 152.8; IR (cm⁻¹) 3433; HRMS m/z (ESI) Calcd for C21H23BF3N2O3SSi [(M + H)+]: 479.1244, found: 479.1248.

Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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4-Methyl-2-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocotan-2-yl)-6-(trimethylsilyl)phenyl trifluoromethanesulfonate (2C). A round-bottomed flask was charged with S1 (0.50 g) and N-methyliminodiacetic acid (0.18 g, 1.2 mmol). Toluene (6.0 mL) and DMSO (0.60 ml) were added. The reaction flask was attached with a Dean-Stark apparatus, and the reaction mixture was refluxed for 14 h, cooled to room temperature, filtered through a short pad of silica gel using EtOAc, and evaporated under reduced pressure. The crude mixture was triturated with EtOAc to provide 2C (57 mg). The mother liquid was concentrated under reduced pressure, and the residue was recrystallized from a mixture of cyclohexane and EtOAc (10:1) to provide 2C (0.15 g). Thus, the total yield of 2C was 0.21 g (37% for 2 steps). Rf: 0.5 (EtOAc). A colorless solid. Mp: 203–207 °C; 1H NMR (500 MHz, acetone-d₆) δ: 0.36 (9 H, s), 2.36 (3 H, s), 2.85 (3 H, s), 4.21 (2 H, d, J = 21 Hz), 4.37 (2 H, d, J = 21 Hz), 7.42 (1 H, d, J = 2.0 Hz), 7.54 (1 H, d, J = 2.0 Hz); 13C NMR (125 MHz, acetone-d₆) δ: 0.68, 20.6, 48.8, 64.0, 119.5 (q, J = 318 Hz), 135.8, 138.2, 138.5, 139.9, 153.9, 168.7; IR (cm⁻¹) 1775; HRMS m/z (ESI) Calcd for C16H23BF3N1O3SSi [(M + Na)+]: 490.0760, found: 490.0779.
**Scheme S2** Synthesis of 2D and 2E.

**S2** (2,6-Dibromophenoxy)trimethylsilane. An oven-dried round-bottomed flask was charged with 2,6-dibromophenol (10 g, 40 mmol), capped with an inlet adapter with a three-way stopcock, evacuated and back-filled with nitrogen. Anhydrous CH$_2$Cl$_2$ (100 mL) was added. Then the mixture was cooled to 0 °C. Triethylamine (6.7 mL, 48 mmol) and chlorotrimethylsilane (5.6 mL, 44 mmol) were added. The reaction mixture was stirred for 7.5 h at room temperature, and CH$_2$Cl$_2$ was evaporated. The residue was diluted with hexane, and the mixture was filtered with a pad of Celite and concentrated under reduced pressure to give S2 (13 g), which was used for the next reaction without further purification.

**S3** (2-Hydroxy-3-(trimethylsilyl)phenyl)boronic acid. An oven-dried round-bottomed flask was charged with S2 (13 g), capped with an inlet adapter with a three-way stopcock, evacuated and back-filled with argon. Anhydrous THF (130 mL) was added. Then the mixture was cooled to −78 °C. 1.7 M solution of t-BuLi (0.10 L, 0.17 mol) in pentane was added. After 1.0 h at the same temperature, trimethoxyborane (20 mL, 0.18 mol) was added. The mixture was warmed up to room temperature and stirred for 20 h. A saturated aqueous NH$_4$Cl solution was added to the reaction mixture. After evaporation of the organic solvents under reduced pressure, the residue was extracted with EtOAc. The aqueous layer was extracted twice with EtOAc. The combined organic layers were washed with saturated aqueous NaCl, dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure to give S3 (12 g), which was used for the next reaction without further purification.
2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(trimethylsilyl)phenol (S4). A round-bottomed flask was charged with S3 (11 g), pinacol (4.3 g, 36 mmol) and CH₂Cl₂ (50 mL). The reaction mixture was stirred overnight and H₂O was added. The reaction mixture was extracted with CH₂Cl₂. The aqueous layer was extracted twice with CH₂Cl₂. The combined organic layers were washed with saturated aqueous NaCl, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure to give S4 (10 g), which was used for the next reaction without further purification.

2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(trimethylsilyl)phenyl trifluoromethanesulfonate (S5). An oven-dried round-bottomed flask was charged with S4 (9.5 g), capped with an inlet adapter with a three-way stopcock, evacuated and back-filled with nitrogen. Anhydrous Et₂O (100 mL) was added. Then the mixture was cooled to –78 °C. 1.7 M t-BuLi (20 mL, 33 mmol) was added. After 10 min at the same temperature, trifluoromethanesulfonic anhydride (8.0 mL, 48 mmol) was added. The reaction mixture was warmed up to room temperature and stirred for 2.0 h at room temperature. Aqueous NH₄Cl was added, and the reaction mixture was extracted with EtOAc. The aqueous layer was extracted twice with EtOAc. The combined organic layers were washed with saturated aqueous NaCl, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude product was filtered through a pad of silica gel (hexane/EtOAc = 10:1) to give S5 (9.1 g), which was used for the next reaction without further purification. Rf: 0.5 (hexane/EtOAc = 10:1).

(2-(((Trifluoromethyl)sulfonyl)oxy)-3-(trimethylsilyl)phenyl)boronic acid (S6). A round-bottomed flask was filled with S5 (8.0 g), NaIO₄ (12 g, 57 mmol) and THF/H₂O (4:1, 94 mL). The reaction mixture was stirred for 5 min at room temperature, and 1N HCl (19 mL, 19 mmol) was added. The reaction mixture was stirred for 10 h at 60 °C, cooled to room temperature, quenched with H₂O and extracted with EtOAc. The aqueous layer was washed twice with EtOAc. The combined organic layers were dried over NaSO₄ and concentrated under reduced pressure. The residue was added to a solution of NaIO₄ (12 g, 57 mmol) in THF/H₂O (4:1, 94 mL), and the reaction mixture was stirred for 5 min at room temperature. 1N HCl (19 mL, 19 mmol) was added. The reaction mixture was stirred for 6.0 h at 60 °C, cooled to room temperature, quenched with H₂O and extracted with EtOAc. The aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over NaSO₄ and concentrated under
reduced pressure to give S6 (7.7 g), which was used for the next reaction without further purification.

2-(1H-Naphtho[1,8-de][1,3,2]diazaborin-2(3H)-yl)-6-(trimethylsilyl)phenyl trifluoromethanesulfonate (2D). A round-bottomed flask was charged with S6 (7.7 g) and 1,8-diaminonaphthalene (3.0 g, 19 mmol) and CH₂Cl₂ (100 mL). The reaction mixture was stirred for 13 h at room temperature, and H₂O was added. The reaction mixture was extracted with CH₂Cl₂. The aqueous layer was extracted twice with CH₂Cl₂. The combined organic layers were washed with a saturated aqueous NaCl solution, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was purified by flash column chromatography (hexane/EtOAc = 12:1) to provide 2D (6.9 g, 37% over 6 steps). Rf: 0.4 (hexane/EtOAc = 10:1). A brown solid. Mp: 104–105 °C; ¹H NMR (500 MHz, CDCl₃) δ: 0.43 (9 H, s), 5.94 (2 NH, brs), 6.38 (2 H, d, J = 7.5 Hz), 7.08 (2 H, d, J = 7.5 Hz), 7.14 (2 H, t, J = 7.5 Hz), 7.44 (1 H, t, J = 7.0 Hz), 7.63 (1 H, dd, J = 2.0, 7.0 Hz), 7.67 (1 H, dd, J = 2.0, 7.0 Hz); ¹³C NMR (125 MHz, CDCl₃) δ: 0.07, 106.1, 118.1, 118.4 (q, J = 320 Hz), 119.8, 127.6, 127.9, 135.0, 135.5, 136.3, 138.5, 140.6, 154.7; IR (cm⁻¹) 3344; HRMS m/z (ESI) Calcd for C₂₀H₂₁BF₃N₂O₃SSi [(M + H)⁺]: 465.1087, found: 465.1093.

(4-Bromo-2,6-diiodophenoxy)trimethylsilane (S7). An oven-dried round-bottomed flask was charged with 4-bromo-2,6-diiodophenol (1.0 g, 2.4 mmol), capped with an inlet adapter with a three-way stopcock, evacuated and back-filled with nitrogen. Anhydrous CH₂Cl₂ (8.0 mL), triethylamine (0.40 mL, 2.9 mmol) and chlorotrimethylsilane (0.33 mL, 2.6 mmol) were added in this order. The reaction mixture was stirred for 1.0 h at room temperature and concentrated under reduced pressure. The residue was diluted with hexane, and the mixture was filtered with a pad of Celite. The filtrate was concentrated under reduced pressure to give S7 (1.2 g), which was used for the next reaction without further purification.

(5-Bromo-2-hydroxy-3-(trimethylsilyl)phenyl)boronic acid (S8). An oven-dried round-bottomed flask was charged with S7 (1.2 g), capped with an inlet adapter with a three-way stopcock, evacuated and back-filled with argon. Anhydrous THF (7.9 mL) was added. Then the mixture was cooled to −78 °C. 1.7 M solution of t-BuLi (5.7 mL, 9.4 mmol) in pentane was added, and the reaction mixture was stirred for 1.0 h at the same temperature.
Trimethoxyborane (1.2 mL, 11 mmol) was added. The mixture was warmed up to room temperature and stirred for 1.5 h. A saturated aqueous NH₄Cl solution was added to the reaction mixture. After evaporation of the organic solvents, the reaction mixture was extracted with EtOAc. The aqueous layer was extracted twice with EtOAc. The combined organic layers were washed with saturated aqueous NaCl, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure to give S₈ (0.91 g), which was used for the next reaction without further purification.

4-Bromo-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(trimethylsilyl)phenol (S₉). A round-bottomed flask was charged with S₈ (0.91 g), pinacol (0.28 g, 2.4 mmol) and CH₂Cl₂ (8.0 mL). The reaction mixture was stirred for 8.0 h at room temperature, and H₂O was added. The reaction mixture was extracted with CH₂Cl₂. The aqueous layer was extracted twice with CH₂Cl₂. The combined organic layers were washed with saturated aqueous NaCl, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure to give S₉ (0.87 g), which was used for the next reaction without further purification.

4-Bromo-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(trimethylsilyl)phenyl trifluoromethanesulfonate (S₁₀). An oven-dried round-bottomed flask was charged with S₉ (0.87 g), capped with an inlet adapter with a three-way stopcock, evacuated and back-filled with nitrogen. Anhydrous Et₂O (8.0 mL) was added. Then the mixture was cooled to ~78 °C. 1.7 M t-BuLi (1.5 mL, 2.5 mmol) was added, and the mixture was stirred for 10 min at the same temperature. Trifluoromethanesulfonic anhydride (0.60 mL, 3.6 mmol) was added. The reaction mixture was warmed up to room temperature and stirred for 2.0 h at room temperature. An aqueous NH₄Cl solution was added, and the reaction mixture was extracted with EtOAc. The aqueous layer was extracted twice with EtOAc. The combined organic layers were washed with saturated aqueous NaCl, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was filtered through a pad of silica gel (hexane/EtOAc = 50:1) to give S₅ (0.50 g), which was used for the next reaction without further purification. Rf: 0.5 (hexane/EtOAc = 20:1).

5-Bromo-2-(((trifluoromethyl)sulfonyl)oxy)-3-(trimethylsilyl)phenylboronic acid (S₁₁). A round-bottomed flask was filled with S₁₀ (0.49 g, 6.0 mmol), NaIO₄ (0.63 g, 2.9 mmol) and
THF/H$_2$O (4:1, 4.5 mL). The reaction mixture was stirred for 5 min at room temperature, and 1M HCl (1.0 mL, 1.0 mmol) was added. The reaction mixture was stirred for 21 h at 60 °C, cooled to room temperature, quenched with H$_2$O and extracted with EtOAc. The aqueous layer was washed twice with EtOAc. The combined organic layers were dried over Na$_2$SO$_4$ and concentrated under reduced pressure to give S11 (0.41 g), which was used for the next reaction without further purification.

4-Bromo-2-(1H-naphthro[1,8-de][1,3,2]diazaborinin-2(3H)-yl)-6-(trimethylsilyl)phenyl trifluoromethanesulfonate (2E). A round-bottomed flask was charged with S11 (0.41 g), 1,8-diaminonaphthalene (0.15 g, 0.97 mmol) and CH$_2$Cl$_2$ (12 mL). The reaction mixture was stirred for 11 h at room temperature, and H$_2$O was added. The reaction mixture was extracted with CH$_2$Cl$_2$. The aqueous layer was extracted twice with CH$_2$Cl$_2$. The combined organic layers were washed with saturated aqueous NaCl, dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography (hexane/EtOAc = 10:1) to provide 2E (0.47 g, 37% over 6 steps). Rf: 0.5 (hexane/EtOAc = 10:1). A brown solid. Mp: 67–70 °C; $^1$H NMR (500 MHz, CDCl$_3$) δ: 0.43 (9 H, s), 5.89 (2 N H, brs), 6.38 (2 H, d, $J = 7.5$ Hz), 7.08 (2 H, d, $J = 7.5$ Hz), 7.14 (2 H, d, $J = 7.5$ Hz), 7.71 (1 H, d, $J = 2.0$ Hz), 7.73 (1 H, d, $J = 2.0$ Hz); $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 0.04, 106.4, 118.47 (q, $J = 320$ Hz), 118.48, 120.0, 123.0, 127.7, 136.4, 138.1, 138.4, 140.4, 140.8, 153.4; IR (cm$^{-1}$) 3435; HRMS m/z (ESI) Calcd for C$_{20}$H$_{20}$B$_7$BrF$_5$N$_2$O$_3$Si [(M + H)$^+$]: 543.0192, found: 543.0198.

**Experimental references**


Cartesian coordinates of 3-[(dan)boryl]benzyne 1D

\[\text{Image of 3-[(dan)boryl]benzyne 1D}\\
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ortho-6De
Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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S39

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X_sweep = 7.5030032[XHz]
Irr_domain = 1H
Irr_freq = 399.78219838[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 399.78219838[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 10.7[us]
X_acq_time = 2.19365952[s]
X_angle = 45[deg]
X_att = 2.4[db]
X_pulse = 5.35[us]
Irr_mode = OFF
Tri_mode = OFF
Datal_preset = FALSE
Initial_wait = 1[s]
Recvr_gain = 44
Relaxation_delay = 1.5[s]
Repetition_time = 3.68365952[s]
Temp_gain = 22.8[dc]
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--- PROCESSING PARAMETERS ---

dc_balance = 0.2 [Hz] : 0.0 [s]
trapezoid3 = 0 [s] : 80 [%] : 100 [%]
recenter = TRUE
machinphase = ppm

Filename = 60_1H-6.5df
Author = delta
Experiment = single_pulse.ox2
Sample_id = 8462464
Solvent = CDCl3/DMSO-D6
Creation_time = 10-APR-2013 17:22:30
Revision_time = 10-APR-2013 17:25:30
Current_time = 1-JUN-2013 20:44:33

Comment = single_pulse
Data_format = 1D_CHEMICAL
Dim_0size = 15107
Dim_1size = 18
Dim_2size = 18
Dimensions = 3
Site = ECA590
Spectrometer = DELTA2_500 MHz

Field_strength = 11.74735797 [T] (500 MHz)
X_acq_duration = 1.74587904 [s]
X_observable = 18
X_freq = 500.15991521 [MHz]
X_offset = 5.0 [ppm]
X_points = 16284
X_resolution = 0.57277737 [Hz]
X_sweep = 9.38438438 [kHz]

Irr_domain = 18
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Trl_domain = 18
Trl_freq = 500.15991521 [MHz]
Trl_offset = 5.0 [ppm]

Scans = 1
Total_scans = 16

X_90_width = 11.2 [us]
X_acq_time = 1.74587904 [s]
X_angle = 45 [deg]
X_att = 3.5 [dB]
X_pulse = 5.0 [us]
Irr_mode = Off
Trl_mode = Off
Dante_preset = FALSE
Initial_wait = 1 [s]
Recvr_gain = 48
Relaxation_delay = 3.5 [s]

Repetition_time = 3.24587904 [s]
Temp_qed = 24.9 [C]

X : parts per Million : 1H
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--- PROCESSING PARAMETERS ---
do_balance : 0 : FALSE
seqp : 2 (0) : 0.0 (s)
trapezoid3 : 0 (%) : 80 (%) : 100 (%
zero_fill : 1
rzt : 1 : TRUE : TRUE
machine_phase
ppm
Derived from: ethylenediamine-finalC-1-j

Filename = ethylenediamine-final
Author = delta
Experiment = single_pulse_dec
Sample_id = 1
Solvent = CHLOROFORM-D
Creation_time = 7-SEP-2013 07:43:23
Revision_time = 22-SEP-2013 23:32:50
Current_time = 22-SEP-2013 23:32:07
Comment = single_pulse decouple
Data_format = ID: COMPLEX
Dim_Little = 13C
Dim_Large = 1 ppm
Dimensions = X
Site = ECS 400
Spectrometer = JWN-ECS400
Field_strength = 9.38976637 [T] (400 [MHz])
X_acq_duration = 1.0433312 [s]
X_domain = 13C
X_freq = 100 (ppm)
X_points = 32768
X_prescans = 4
X_resolution = 0.95846665 [Hz]
X_sweep = 31.45703518 [kHz]
Irr_domain = 18
Irr_freq = 399.78219838 [MHz]
Irr_offset = 6.0 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8775
Total_scans = 8775
X_90_width = 9.5 [us]
X_acq_time = 1.0433312 [s]
X_angle = 30 [deg]
X_ata = 4 [deg]
Irr_ata_dec = 23 [deg]
Irr_ata_none = 23 [deg]
Irr_noise = WALTZ
Decoupling = TRUS
Initial_wait
None
None_time = 2 [s]
Recovery = 60
Relaxation_delay = 2 [s]
Repetition_time = 3.0433312 [s]
Temp_set = 22.2 [°C]
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