The Chemistry of Boryllithium: Synthesis, Structure, and Reactivity

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Experimental Section

General

All manipulations were carried out in the argon-filled glove box (Miwa MFG) unless otherwise noted. The ^1H , $^1\text{H}\{^{11}\text{B}\}$, ^2H , $^7\text{Li}\{^1\text{H}\}$, ^{11}B , $^{11}\text{B}\{^1\text{H}\}$, $^{13}\text{C}\{^1\text{H}\}$, and ^{19}F NMR spectra were recorded on 500 MHz spectrometers with residual protiated solvent for ^1H and $^1\text{H}\{^{11}\text{B}\}$, deuterated solvent for ^2H and $^{13}\text{C}\{^1\text{H}\}$, an external LiBr in D_2O for $^7\text{Li}\{^1\text{H}\}$, an external $\text{BF}_3\cdot\text{OEt}_2$ for ^{11}B and $^{11}\text{B}\{^1\text{H}\}$, and an external CFCl_3 for $^{19}\text{F}\{^1\text{H}\}$ used as reference. **38a-d**, **55**, **56**, and **59** were purified by using a recycling preparative HPLC (LC-928, Japan Analytical Industries, 60 cm $\times$ 20 ϕ Jaigel-1H and 2H, CHCl_3 eluent). Mass spectra were recorded on a JEOL JMS-SX 102 spectrometer using PEG calibration and NBA matrix solvent. Melting points were measured on a Yanagimoto micro melting point apparatus MP-500D and MPA100 Optimelt Automated Melting Point System and are uncorrected. Ether, THF and hexane were purified by passing through a solvent purification system (Grass Contour). Dimethoxyethane (DME) was distilled from sodium/benzophenone. All these solvents were further dried by stirring with Na/K alloy at room temperature in the glovebox prior to use unless otherwise noted. Lithium dispersion (purchased from Kanto Chemical Co., Inc., containing 1% sodium) was washed with hexane before the use to make a lithium powder. Carbon dioxide (>99.990 vol%, containing <0.005 vol% water) was obtained from Showa Tansan Co., Ltd. PhCH_2K ,¹ **34f**,² **34g**,³ **36**,⁴ **39**,⁴ **40**,⁵ **41**,⁴ **42**,⁴ and **48**⁶ were synthesized according to literature procedures.

Synthesis of **34a-Br** (Method A)

A suspension of **36** (7.20 g, 19.0 mmol) and Mg (2.00 g, 82.0 mmol) in ether (100 mL) was heated to reflux until the color of the solution became red under argon atmosphere. After cooling the solution to 0 $^\circ\text{C}$, a solution of BBr_3 in hexane (1.00 M; 20.0 mL, 20.0 mmol) was added to the mixture at 0 $^\circ\text{C}$. The resulting solution was stirred for 12 h at 0 $^\circ\text{C}$ to afford a cream-green suspension. After solvents were evaporated under reduced pressure, hexane (50 mL) was added to a residue. The resulting suspension was filtered through Celite pad to remove magnesium salt under argon, and the insoluble salts were washed with hexane. Volatiles were removed from the filtrate to give a white solid (5.00 g, 56.0%). An analytically pure sample was obtained from the recrystallization from hexane. ^1H NMR

(C₆D₆, 500 MHz) δ 1.20 (d, J = 7 Hz, 12H), 1.31 (d, J = 7 Hz, 12H), 3.16 (sep, J = 7 Hz, 4H), 6.12 (s, 2H), 7.14 (d, J = 9 Hz, 4H), 7.22 (dd, J = 8 Hz, 9 Hz, 2H); ¹³C NMR (C₆D₆, 125 MHz) δ 24.2 (CH₃), 24.5 (CH₃), 28.9 (CH), 120.2 (CH), 123.9 (CH), 128.5 (CH), 137.5 (4°), 146.4 (4°); ¹¹B NMR (C₆D₆, 160 MHz) δ 20.2 (brs, $h_{1/2}$ = 152 Hz); mp: 182.0–187.0 °C (dec.); HRMS–FAB (m/z): [M]⁺ calcd for C₂₆H₃₆BBrN₂, 466.2155, 468.2135; found, 466.2156, 468.2156.

Synthesis of 34a-Br (Method B)

A suspension of **36** (34.6 g, 91.9 mmol) and lithium granule (1.89 g, 272 mmol) in ether (400 mL) was stirred at room temperature for 2 days under argon atmosphere to afford a dark yellow suspension. After removing excess lithium by filtration, NEt₃HCl (26.2 g, 190 mmol) was added to the filtrate, and the resulting white suspension was stirred at room temperature for 1 h. The suspension was filtered through Celite pad to remove excess NEt₃HCl, the solvent and NEt₃ were evaporated and the resulting residue was dissolved in CH₂Cl₂ (100 mL). BBr₃ solution (1 M CH₂Cl₂, 100 mL, 100 mmol) was added dropwise to the resulting solution at 0 °C and stirred at room temperature for 12 h. Reaction was quenched with ⁱPr₂EtN (28.2 g, 218 mmol), and the solvents and excess ⁱPr₂EtN were removed at reduced pressure. Hexane (400 mL) was added to the resulting residue, the suspension was filtered through Celite pad and the insoluble solids were washed with hexane. After volatiles were removed from the filtrate, recrystallization from hexane at –45 °C yielded a colorless crystal (32.9 g, 77%).

Synthesis of 34a-Cl⁷

A suspension of **36** (891 mg, 2.37 mmol) and lithium granule (49.2 mg, 7.09 mmol) in ether (30 mL) was stirred at room temperature for 1 day under argon atmosphere to afford a dark yellow suspension. After removing excess lithium by filtration, NEt₃HCl (814 mg, 5.91 mmol) was added to the filtrate, and the resulting white suspension was stirred at room temperature for 1 h. The suspension was filtered through Celite pad to remove excess NEt₃HCl, the solvent and NEt₃ were evaporated and the resulting residue was dissolved in CH₂Cl₂ (50 mL). BCl₃ solution (1 M heptane, 2.48 mL, 2.48 mmol) was added dropwise to the resulting solution at 0 °C and stirred at room temperature for 12 h. Reaction was quenched with ⁱPr₂EtN (764 mg, 5.92 mmol), and the solvents and excess ⁱPr₂EtN were removed at reduced pressure. Hexane (100 mL) was added to the resulting residue, the suspension was filtered through Celite pad and the insoluble solids were washed with hexane. After reducing volatiles, the resulting solution was charged on the top of a silica gel column (hexane) and the product was separated to give a white solid. (324 g, 32%) ¹H NMR (C₆D₆) δ : 1.20 (d, J = 7 Hz, 12H), 1.30 (d, J = 7 Hz, 12H), 3.18 (sep, J = 7 Hz, 4H), 6.05 (s, 2H), 7.14 (d, J = 8 Hz, 4H), 7.22 (dd, J = 8, 7 Hz, 2H); ¹³C NMR (C₆D₆, 125 MHz) δ 24.2 (CH₃), 24.3 (CH₃), 28.9 (CH), 119.2 (CH), 123.8 (CH), 128.4 (CH), 137.1 (4°), 146.5 (4°); ¹¹B NMR (C₆D₆, 160 MHz) δ 22.5 (brs) mp: 174.9–175.2 °C; Anal. calcd. for C₂₆H₃₆BClN₂: C, 73.85; H, 8.58; N, 6.63. Found: C, 73.56; H, 8.43; N, 6.36.

Synthesis of **34a-I**

A solid of **BI**₃ (2.13 g, 5.44 mmol) was added to a suspension of **36** (2.00 g, 5.44 mmol) in hexane/ether (1:1, 300 mL) at -10 °C. The resulting solution was stirred for 2 h at room temperature to afford a red suspension. After solvents were evaporated under reduced pressure, hexane (200 mL) was added to a residue. The resulting suspension was filtered through Celite pad under argon, and the insoluble salts were washed with hexane. After removing volatiles Et₂O (100 ml) and Mg (1.00 g) were added to the residue. The resulting suspension was stirred for 1h at room temperature to remove I₂. After solvents were evaporated under reduced pressure, hexane (200 mL) was added to a residue. The resulting suspension was filtered through Celite pad under argon, and the insoluble salts were washed with hexane. Volatiles were removed from the suspension to give a cream-yellow solid (290 mg, 10%). An analytically pure sample was obtained from the recrystallization from hexane. ¹H NMR (C₆D₆, 500 MHz) δ 1.19 (d, *J* = 7 Hz, 12H), 1.34 (d, *J* = 7 Hz, 12H), 3.14 (sep, *J* = 7 Hz, 4H), 6.24 (s, 2H), 7.14 (d, *J* = 8 Hz, 4H), 7.22 (dd, *J* = 7 Hz, 8 Hz, 2H); ¹³C NMR (C₆D₆, 125 MHz) δ 24.0 (CH₃), 24.7 (CH₃), 29.0 (CH), 121.6 (CH), 123.9 (CH), 128.5 (CH), 138.0 (4°), 146.3 (4°); ¹¹B NMR (C₆D₆, 160 MHz) δ 13.1 (brs); mp: 166.8–169.4 °C (dec.); Anal. calcd. for C₂₆H₃₆BiN₂: C, 60.72; H, 7.06; N, 5.45. Found: C, 60.72; H, 7.13; N, 5.24.

Synthesis of (**35a**·DME)₂

In a glovebox, **34a-Br** (200 mg, 428 μmol) and naphthalene (11.0 mg, 85.8 μmol) was dissolved in DME (4 mL). Lithium powder (30.0 mg, 4.32 mmol) was added to the solution at -45 °C and the resulting suspension was stirred for 35 h at -45 °C to afford a dark red suspension. After solvents were evaporated at room temperature under reduced pressure, hexane (distilled from *n*-buthyllithium solution, 5 mL) was added to the residue. The resulting suspension was filtered through Celite pad to remove an excess of lithium, a lithium salt, and lithium naphthalenide. Volatiles were removed from the filtrate to give a pale yellow solid. Thermally unstable colorless crystals were obtained by cooling its hexane solution at -45 °C (58.7 mg, 28.3%). Crystals were washed with hexane (distilled from neopentyllithium solution) at -45 °C and were quickly dried under vacuum at room temperature. The isolated crystals were placed into a pre-cooled 4 mL vial at -45 °C and were dissolved in THF-*d*₈ distilled from Na-K alloy to make a NMR sample. In the THF-*d*₈ solution, **35a** was stable at room temperature. All the following NMR data contains a decomposed product **38a** (**35a** : **38a** = 93 : 7) and an equimolar amount of free DME to **35a**. ¹H NMR (THF-*d*₈, 500 MHz) δ 1.12 (d, *J* = 7 Hz, 12H), 1.18 (d, *J* = 7 Hz, 12H), 3.60 (sep, *J* = 7 Hz, 4H), 6.22 (s, 2H), 7.06 (brs, 6H); ¹³C NMR (THF-*d*₈, 125 MHz) δ 24.6 (CH₃), 25.3 (CH₃), 28.9 (CH), 119.3 (CH), 123.1 (CH), 125.4 (CH), 147.7 (4°), 148.6 (4°); ¹¹B NMR (THF-*d*₈, 160 MHz) δ 45.4 (brs, *h*_{1/2} = 535 Hz); ⁷Li NMR (THF-*d*₈, 194 MHz) 0.46 (brs, *h*_{1/2} = 36 Hz).

Synthesis of **35a**·(THF)₂

In a glove box, a 20 mL vial equipped with a magnetic stir bar was charged with **34a-Br** (500 mg, 1.07 mmol), lithium powder (74.2 mg, 10.7 mmol) and naphthalene (68.6 mg,

0.535 mmol) in THF (10 mL). The mixture was stirred vigorously at $-45\text{ }^{\circ}\text{C}$ for 12 h. After the solution was filtered through a pad of Celite® to remove an excess of lithium, a lithium salt, and lithium naphthalenide, solvents were evaporated from the filtrate under reduced pressure. The residue was extracted with pentane and the resulting suspension was filtered through a pad of Celite® to remove inorganic salts. The crude product was recrystallized from pentane at $-45\text{ }^{\circ}\text{C}$ to give dark crystals (281 mg, 66%) of **35a**·(THF)₂. The ^1H , ^{11}B , and ^{13}C NMR data were identical to the values obtained by dissolution of (**35a**·DME)₂ into THF-*d*₈.

Independent synthesis of **38a**

In a glovebox, LiAlH₄ (13.0 mg, 342 μmol) was added to a solution of **34a-Br** (200 mg, 428 μmol) in THF (3 mL) at room temperature and the resulting mixture was stirred for 1 h. After solvents were evaporated under reduced pressure and the vial was brought out from the glovebox, hexane (25 mL) and water (25 mL) was added to a residue. The aqueous phase was extracted twice with 25 mL portions of hexane. The combined organic phase was dried over Na₂SO₄ and the solvent was removed under reduced pressure to give a white solid (101 mg, 61.0%). An analytically pure crystals were obtained from a hexane solution. $^1\text{H}\{^{11}\text{B}\}$ NMR (C₆D₆, 500 MHz) δ 1.220 (d, $J = 7\text{ Hz}$, 12H), 1.224 (d, $J = 7\text{ Hz}$, 12H), 3.22 (sep, $J = 7\text{ Hz}$, 4H), 4.71 (s, 1H), 6.18 (s, 2H), 7.17 (d, $J = 8\text{ Hz}$, 4H), 7.23 (dd, $J = 8\text{ Hz}$, 7 Hz, 2H); ^{13}C NMR (C₆D₆, 125 MHz) δ 23.9 (CH₃), 24.0 (CH₃), 28.7 (CH), 119.8 (CH), 123.6 (CH), 127.8 (CH), 139.5 (4°), 146.2 (4°); ^{11}B NMR (C₆D₆, 160 MHz) δ 22.9 (brs, $h_{1/2} = 379\text{ Hz}$); mp: 122.0–123.7 $^{\circ}\text{C}$; HRMS–FAB (m/z): [M]⁺ calcd for C₂₆H₃₇BN₂, 388.3050; found, 388.3045.

Independent synthesis of **38a-d₁**

In a glovebox, LiAlD₄ (16.5 mg, 393 μmol) was added to a solution of **34a-Br** (200 mg, 428 μmol) in THF (3 mL) at room temperature and the resulting mixture was stirred for 1 h. After solvents were evaporated under reduced pressure and the vial was brought out from the glovebox, hexane (25 mL) and water (25 mL) was added to a residue. The aqueous phase was extracted twice with 25 mL portions of hexane. The combined organic phase was dried over Na₂SO₄ and the solvent was removed under reduced pressure. The obtained crude product was purified by recycling HPLC to give a white solid (113 mg, 67.8%). Analytically pure crystals were obtained from a hexane solution. ^1H NMR (C₆D₆, 500 MHz) δ 1.220 (d, $J = 7\text{ Hz}$, 12H), 1.224 (d, $J = 7\text{ Hz}$, 12H), 3.22 (sep, $J = 7\text{ Hz}$, 4H), 6.18 (s, 2H), 7.16 (d, $J = 8\text{ Hz}$, 4H), 7.23 (dd, $J = 8\text{ Hz}$, 7 Hz, 2H); ^2H NMR (C₆H₆, 76.8 MHz) δ 4.69 (brs, $h_{1/2} = 14\text{ Hz}$); ^{11}B NMR (C₆D₆, 160 MHz) δ 22.7 (brs, $h_{1/2} = 268\text{ Hz}$); mp: 125.6–126.6 $^{\circ}\text{C}$; HRMS–FAB (m/z): [M]⁺ calcd for C₂₆H₃₆DBN₂, 389.3113; found, 389.3106.

Synthesis of **34b**

A CH₂Cl₂ solution of BBr₃ (1.0 M, 7.00 mL, 7.00 mmol) was added to a hexane solution of **39** (1.90 g, 5.00 mmol, 25 mL) at room temperature under argon atmosphere. After stirred for 5 min the solvents were evaporated. After dissolution of the residue to CH₂Cl₂ (30 mL),

NEt₃ (4.55 g, 45.0 mmol) was added to the solution. The resulting suspension was stirred for 1 h at 50 °C. After solvents were evaporated under reduced pressure, hexane (200 mL) was added to a residue. The resulting suspension was filtered through a pad of Celite® and silica-gel. Volatiles were removed from the filtrate to give a white solid of **34b** (1.60 g, 68%). An analytically pure sample was obtained by recrystallization from hexane. ¹H NMR (C₆D₆, 500 MHz) δ 1.28 (d, *J* = 7 Hz, 12H), 1.27 (d, *J* = 7 Hz, 12H), 3.41 (s, 4H), 3.46 (sep, *J* = 7 Hz, 4H), 7.13 (d, *J* = 8 Hz, 4H), 7.19 (dd, *J* = 7 Hz, 8 Hz, 2H); ¹³C NMR (C₆D₆, 125 MHz) δ 24.7 (CH₃), 24.9 (CH₃), 28.8 (CH), 52.8 (CH₂), 124.1 (CH), 127.8 (CH), 138.2 (4°), 147.6 (4°); ¹¹B NMR (C₆D₆, 160 MHz) δ 26.8 (brs); mp: 193.0–196.0 °C (dec.); Anal. calcd. for C₂₆H₃₉BN₂: C, 66.54; H, 8.16; N, 5.97. Found: C, 66.37; H, 8.25; N, 5.94.

Synthesis of **34c**

To a suspension of **40** (1.71 g, 3.99 mmol) and CaH₂ (263 mg, 6.25 mmol) in toluene (25 mL), BBr₃ (1 M in CH₂Cl₂, 4.80 mL, 4.80 mmol) was added dropwise at 0 °C and stirred at room temperature for 24 h. Reaction was quenched with ⁱPr₂EtN (1.39 mL, 7.98 mmol), and the solvents and excess ⁱPr₂EtN were removed at reduced pressure. Hexane (200 mL) was added to the resulting residue, the suspension was filtered through Celite pad and the insoluble salts were washed with hexane. After reducing volatiles, the resulting solution was charged on the top of a silica gel column (hexane) and the product was separated to give a white solid. (975 mg, 47%) ¹H NMR (C₆D₆, 500 MHz) δ: 1.04 (d, *J* = 7 Hz, 12H), 1.30 (d, *J* = 7 Hz, 12H), 2.99 (sep, *J* = 7 Hz, 4H), 6.57 (dd, *J* = 6, 3 Hz, 2H), 6.83 (dd, *J* = 6, 3 Hz, 2H), 7.215 (d, *J* = 8 Hz, 4H), 7.216 (d, *J* = 7 Hz, 4H), 7.29 (dd, *J* = 8, 7 Hz, 2H); ¹³C NMR (C₆D₆, 125 MHz) δ 24.3 (CH₃), 24.4 (CH₃), 29.1 (CH), 110.9 (CH), 121.2 (CH), 124.4 (CH), 129.0 (CH), 133.9 (4°), 138.2 (4°), 147.1 (4°); ¹¹B NMR (C₆D₆, 160 MHz) δ 24.5 (brs) mp: 147.3–149.0 °C; Anal. calcd. for C₃₀H₃₈BBrN₂: C, 69.65; H, 7.40; N, 5.41. Found: C, 69.52; H, 7.50; N, 5.21.

Synthesis of **34d**

A suspension of **41** (2.00 g, 6.84 mmol) and Mg (555 mg, 22.8 mmol) in ether (50 mL) was heated to reflux until the color of the solution became red under argon atmosphere. After cooling the solution to 0 °C, a solution of BBr₃ in hexane (1.00 M; 7.50 mL, 7.5 mmol) was added to the mixture at 0 °C. The resulting solution was stirred for 40 h at 0 °C to afford a red suspension. After solvents were evaporated under reduced pressure, hexane (50 mL) was added to a residue. The resulting suspension was filtered through Celite pad to remove magnesium salt under argon, and the insoluble salts were washed with hexane. Volatiles were removed from the filtrate to give a white solid. An analytically pure sample was obtained from the recrystallization from hexane (2.32 g, 89%). ¹H NMR (C₆D₆) δ: 2.13 (s, 6H), 2.19 (s, 12H), 5.98 (s, 2H), 6.79 (s, 4H); ¹¹B NMR (C₆D₆, 160 MHz) δ: 19.0 (brs), ¹³C NMR (C₆D₆) δ: 18.2 (CH₃), 21.0 (CH₃), 118.9 (CH₂), 129.2 (CH), 135.4 (4°), 136.6 (4°), 137.7 (4°). ¹¹B NMR (C₆D₆, 160 MHz) δ 19.0 (brs); mp: 153.3–156.4 °C (dec.); Anal. calcd. for C₂₀H₂₄BBrN₂: C, 62.70; H, 6.31; N, 7.31. Found: C, 62.69; H, 6.46; N, 7.19.

Synthesis of **34e**

A CH₂Cl₂ solution of BBr₃ (1M, 30.0 mL, 30.0 mmol) was added dropwise to a solution of **42** (8.09 g, 27.3 mmol) in CH₂Cl₂ (200 mL) under argon atmosphere at 0 °C and stirred at room temperature for 1 h. ⁱPr₂EtN (8.81 g, 68.2 mmol) was added to the resulting solution and stirred for 1 h. After solvents were evaporated under reduced pressure, pentane (500 mL) was added to a residue. The resulting suspension was filtered through Celite pad under argon, and the insoluble salts were washed with hexane. Volatiles were removed from the filtrate to give a white solid (6.76 g, 64%). ¹H NMR (C₆D₆) δ: 2.13 (s, 6H), 2.32 (s, 12H), 3.30 (s, 4H), 6.82 (s, 4H); ¹¹B NMR (C₆D₆, 160 MHz) δ: 25.7 (brs); ¹³C NMR (C₆D₆) δ: 18.2 (CH₃), 21.0 (CH₃), 49.8 (CH₂), 129.5 (CH), 135.8 (4°), 136.5 (4°), 138.5 (4°). ¹¹B NMR (C₆D₆, 160 MHz) δ 25.7 (brs); mp: 174.3–178.0 °C (dec.); Anal. calcd. for C₂₀H₂₆BBrN₂: C, 62.37; H, 6.80; N, 7.27. Found: C, 62.20; H, 6.86; N, 7.06.

Generation of **35b** in THF-*d*₈

In a glovebox, **34b** (50 mg, 106 μmol) and naphthalene (2.7 mg, 21 μmol) was dissolved in THF-*d*₈ (1 mL). Lithium powder (7.4 mg, 1.07 mmol) was added to the solution at –45 °C and the resulting suspension was stirred for 35 h at –45 °C to afford a dark red suspension. An aliquot of the resulting suspension was pipetted into a screw-capped NMR tube to take the NMR spectra. ¹H NMR (THF-*d*₈, 500 MHz) δ 1.21 (d, *J* = 7 Hz, 12H), 1.22 (d, *J* = 7 Hz, 12H), 3.44 (s, 4H), 3.84 (sep, *J* = 7 Hz, 4H), 6.97 (dd, *J* = 9 Hz, 6 Hz, 2H), 7.02 (d, *J* = 7 Hz, 4H); ¹³C NMR (THF-*d*₈, 125 MHz) δ 25.46 (CH₃), 25.55 (CH₃), 28.9 (CH), 55.1 (CH₂), 123.5 (CH), 124.7 (CH), 149.3 (4°), 149.7 (4°); ¹¹B NMR (THF-*d*₈, 160 MHz) δ 51.9 (brs).

Synthesis of **35b**·(THF)₂

In a glovebox, **34b** (586 mg, 1.25 mmol) and naphthalene (80.0 mg, 624 μmol) was dissolved in THF (5 mL). Lithium powder (43.3 mg, 6.24 mmol) was added to the solution at –45 °C and the resulting suspension was stirred for 24 h at –45 °C to afford a dark red suspension. After solvents were evaporated at room temperature under reduced pressure, hexane (distilled from *n*-butyllithium solution, 20 mL) was added to the residue. The resulting suspension was filtered through Celite pad to remove an excess of lithium, a lithium salt, and lithium naphthalenide. Volatiles were removed from the filtrate to give a pale yellow solid. Thermally unstable colorless crystals were obtained by cooling its hexane solution at –45 °C (142 mg, 21%). ⁷Li NMR (THF-*d*₈, 194 MHz) 0.68 (brs, *h*_{1/2} = 35 Hz). The ¹H, ¹¹B, and ¹³C NMR data were identical to the values of **35b** generating in THF-*d*₈.

Generation of **35c** in THF-*d*₈

In a glovebox, **34c** (51.9 mg, 107 μmol) and naphthalene (7.4 mg, 58 μmol) was dissolved in THF-*d*₈ (1 mL). Lithium powder (2.7 mg, 389 μmol) was added to the solution at –45 °C and the resulting suspension was stirred for 48 h at –45 °C to afford a dark red suspension. An aliquot of the resulting suspension was pipetted into a screw-capped NMR tube to take the NMR spectra. ¹H NMR (THF-*d*₈, 500 MHz) δ: 1.00 (d, *J* = 7 Hz, 12H),

1.17 (d, $J = 7$ Hz, 12H), 3.26 (sep, $J = 7$ Hz, 4H), 6.18 (dd, $J = 5, 3$ Hz, 2H), 6.44 (dd, $J = 5, 3$ Hz, 2H), 7.19 (s, 6H); ^{13}C NMR (THF- d_8 , 125 MHz) δ 24.7 (CH₃), 25.2 (CH₃), 29.1 (CH), 108.0 (CH), 116.5 (CH), 123.7 (CH), 126.3 (CH), 141.8 (4°), 144.6 (4°), 148.3 (4°); ^{11}B NMR (THF- d_8 , 160 MHz) δ 52.1 (brs).

Synthesis of **35c**·(THF)₂

In a glovebox, **34c** (300 mg, 580 μmol) and naphthalene (37.2 mg, 290 μmol) was dissolved in THF (3.0 mL). Lithium powder (20.1 mg, 2.90 mmol) was added to the solution at -45°C and the resulting suspension was stirred for 24 h at -45°C to afford a dark red suspension. After solvents were evaporated at room temperature under reduced pressure, hexane (distilled from *n*-butyllithium solution, 20 mL) was added to the residue. The resulting suspension was filtered through Celite pad to remove an excess of lithium, a lithium salt, and lithium naphthalenide. Volatiles were removed from the filtrate to give a pale yellow solid. Thermally unstable colorless crystals were obtained by cooling its hexane solution at -45°C (28.3 mg, 8.3%). ^7Li NMR (THF- d_8 , 194 MHz) 0.44 (brs, $h_{1/2} = 50$ Hz). The ^1H , ^{11}B , and ^{13}C NMR data were identical to the values of **35c** generating in THF- d_8 .

Generation of **35d** in THF- d_8

In a glovebox, **34d** (41.0 mg, 107 μmol) and naphthalene (7.4 mg, 58 μmol) was dissolved in THF- d_8 (1 mL). Lithium powder (2.7 mg, 389 μmol) was added to the solution at -45°C and the resulting suspension was stirred for 24 h at -45°C to afford a dark red suspension. An aliquot of the resulting suspension was pipetted into a screw-capped NMR tube to take the NMR spectra. ^1H NMR (THF- d_8 , 500 MHz) δ 2.18 (s, 6H), 2.21 (s, 12H), 6.07 (s, 2H), 6.77 (s, 4H); ^{13}C NMR (THF- d_8 , 125 MHz) δ 19.5 (CH₃), 21.3 (CH₃), 117.2 (CH), 128.4 (CH), 133.0 (4°), 137.1 (4°), 148.5 (4°); ^{11}B NMR (THF- d_8 , 160 MHz) δ 42.9 (brs).

Generation of **35e**

In a glovebox, **34e** (212 mg, 550 μmol) and 4,4'-di-*tert*-butylbiphenyl (29.3 mg, 110 μmol) was dissolved in THF- d_8 (5 mL). Lithium powder (19.1 mg, 2.75 mmol) was added to the solution at -45°C and the resulting suspension was stirred for 15 h at -45°C to afford a dark green suspension. An aliquot of the resulting suspension was pipetted into a pre-cooled (-45°C) screw-capped NMR tube, then the NMR tube was quickly brought out from glovebox. The NMR sample was set to pre-cooled (-40°C) NMR spectrometry. **35e**: ^1H NMR (THF- d_8 , 500 MHz, -40°C) δ 2.20 (s, 6H), 2.36 (s, 12H), 3.34 (s, 4H), 6.77 (s, 4H); ^{13}C NMR (THF- d_8 , 125 MHz, -40°C) δ 17.8 (CH₃), 20.3 (CH₃), 48.9 (CH₂), 129.6 (CH), 134.9 (4°), 135.9 (4°), 147.3 (4°); ^{11}B NMR (THF- d_8 , 160 MHz, -40°C) δ 52.4 (brs).

In a glovebox, **34e** (41.2 mg, 107 μmol) and naphthalene (2.7 mg, 21 μmol) was dissolved in THF- d_8 (1 mL). Lithium powder (7.4 mg, 1.06 mmol) was added to the solution at -45°C and the resulting suspension was stirred for 15 h at -45°C to afford a dark green suspension. After stirring for 1 h at 20°C , An aliquot of the resulting suspension was pipetted into a screw-capped NMR tube to take the NMR spectra. In the ^1H NMR

spectrum, **35e** signals were fully disappeared and the new signals which correspond to **43e** increased. **43e**: ^{11}B NMR (THF- d_8 , 160 MHz) δ 0.7 (d, $^1J_{\text{BH}} = 64$ Hz).

The resulting solution was evaporated and pentane (not dried over Na-K, 50 mL) was added. The resulting suspension was filtered through Celite and washed with pentane (50 mL). Volatiles were removed to give colorless oil containing **44e** with 7% impurity (25.4 mg, 78%). **44e**: ^1H -NMR (C_6D_6) δ 1.89 (s, 2H), 2.14 (s, 3H), 2.19 (s, 6H), 2.26 (s, 3H), 2.30 (s, 3H), 3.47 (dd, $J = 9$, 2 Hz, 1H), 3.49 (d, $J = 8$ Hz, 1H), 3.55 (d, $J = 8$ Hz, 1H), 3.56 (dd, $J = 9$, 2 Hz, 1H), 6.74 (s, 1H), 6.81 (s, 3H); ^{13}C NMR (C_6D_6 , 125 MHz) δ 18.3 (CH_3), 21.0 (CH_3), 21.1 (CH_3), 46.2 (CH_2), 56.0 (CH_2), 118.6 (4°), 126.9 (CH), 129.4 (CH), 129.7 (CH), 135.1 (4°), 135.9 (4°), 136.1 (4°), 139.4 (4°), 146.8 (4°); ^{11}B NMR (C_6D_6 , 160 MHz) δ 39.6 (brs).

Independent Synthesis of **38b**

In a glovebox, **34b** (601 mg, 1.28 mmol) and naphthalene (93.7 mg, 731 μmol) were dissolved in THF (10 mL). Lithium powder (72.4 mg, 10.4 mmol) was added to the solution at -45°C and the resulting suspension was stirred for 24 h at -45°C to afford a dark red suspension. The suspension was filtered through Celite pad to remove an excess of lithium and lithium naphthalenide. To the THF solution of Et_3NHCl (882 mg, 6.41 mmol, 10 mL), the filtrate was added dropwise at -45°C and the resulting suspension was stirred for 1 h at room temperature. After solvents were evaporated under reduced pressure, hexane (20 mL) was added to a residue. The resulting suspension was filtered through a pad of Celite®, and the residue was washed with hexane. Volatiles were removed from the filtrate and recrystallization from hexane to give a colorless crystal of **38b** (438 mg, 88%). $^1\text{H}\{^{11}\text{B}\}$ NMR (C_6D_6 , 500 MHz) δ 1.25 (d, $J = 7$ Hz, 12H), 1.30 (d, $J = 7$ Hz, 12H), 3.45 (s, 4H), 3.50 (sep, $J = 7$ Hz, 4H), 4.26 (s, 1H), 7.13-7.14 (m, 4H), 7.20 (dd, $J = 7$ Hz, 9 Hz, 2H); ^{13}C NMR (C_6D_6 , 125 MHz) δ 24.0 (CH_3), 25.6 (CH_3), 28.7 (CH), 53.8 (CH_2), 123.9 (CH), 127.1 (CH), 140.44 (4°), 147.5 (4°); ^{11}B NMR (C_6D_6 , 160 MHz) δ 29.1 (brs); mp: 130.4–131.0 $^\circ\text{C}$ (dec.); Anal. calcd. for $\text{C}_{26}\text{H}_{39}\text{BN}_2$: C, 79.99; H, 10.07; N, 7.18. Found: C, 79.73; H, 10.23; N, 6.99.

Independent Synthesis of **38c**

In a glovebox, LiAlH_4 (15.6 mg, 411 μmol) was added to a solution of **34c** (98.2 mg, 202 μmol) in THF (3 mL) at room temperature and the resulting mixture was stirred for 1 h. After solvent was evaporated under reduced pressure, hexane (10 mL) was added to a residue. The resulting suspension was filtered through a Celite pad, and the residue was washed with hexane. Volatiles were removed from the filtrate and recrystallization from hexane gave colorless crystal (42.1 mg, 47%). $^1\text{H}\{^{11}\text{B}\}$ NMR (C_6D_6 , 500 MHz) δ : 1.08 (d, $J = 7$ Hz, 12H), 1.20 (d, $J = 7$ Hz, 12H), 3.01 (sep, $J = 7$ Hz, 4H), 4.97 (s, 1H), 6.67 (dd, $J = 6$, 3 Hz, 2H), 6.90 (dd, $J = 6$, 3 Hz, 2H), 7.23 (d, $J = 7$ Hz, 4H), 7.31 (dd, $J = 8$, 7 Hz, 2H); ^{13}C NMR (C_6D_6 , 125 MHz) δ 23.5 (CH_3), 25.3 (CH_3), 28.9 (CH), 110.6 (CH), 120.6 (CH), 124.1 (CH), 128.4 (CH), 136.0 (4°), 138.4 (4°), 146.9 (4°); ^{11}B NMR (C_6D_6 , 160 MHz) δ 26.1 (brs, $^1J_{\text{B-H}}$ was not observed.) mp: 126.2-130.0 $^\circ\text{C}$ (dec); Anal. calcd. for $\text{C}_{30}\text{H}_{39}\text{BN}_2$: C, 82.18; H, 8.97; N, 6.39. Found: C, 81.94; H, 9.20; N, 6.41.

Preparation of Stock Solution A of Boryllithium 35a

In a glove box, **34a-Br** (4.67 g, 10.0 mmol) and naphthalene (256 mg, 2.00 mmol) was dissolved in THF (40 mL). Lithium powder (347 mg, 50 mmol) was added to the solution at $-45\text{ }^{\circ}\text{C}$ and the resulting suspension was stirred for 24 h at $-45\text{ }^{\circ}\text{C}$ to afford a dark red suspension. The suspension was filtered through a Celite® pad to remove an excess of lithium and lithium naphthalenide. THF was added to the filtrate to make boryllithium **35a** stock solution **A** (100 mM, 100 mL, 10.0 mmol), which can be stocked for a few months at $-45\text{ }^{\circ}\text{C}$.

Preparation of Stock Solution B of Boryllithium 35b

In a glove box, **34b** (1.76 mg, 3.75 mmol) and naphthalene (96.0 mg, 750 μmol) was dissolved in THF (15 mL). Lithium powder (130 mg, 18.7 mmol) was added to the solution at $-45\text{ }^{\circ}\text{C}$ and the resulting suspension was stirred for 24 h at $-45\text{ }^{\circ}\text{C}$ to afford a dark red suspension. The suspension was filtered through a Celite® pad to remove an excess of lithium and lithium naphthalenide. THF was added to the filtrate to make boryllithium **35b** stock solution **B** (75.0 mM, 50 mL, 3.75 mmol), which can be stocked for a few months at $-45\text{ }^{\circ}\text{C}$.

General procedure for the reaction of 35a and 35b with electrophiles (H_2O , D_2O , MeOTf, *n*-BuCl, BnCl, *n*-BuBr, BnBr, PhCHO, PhCOCl, PhCO₂Ph, (PhCO)₂O, (PhO)₂CO, Boc₂O, CO₂, PhF, and C₆F₆)

In a glovebox, **34a-Br** (500 mg, 1.07 mmol) and naphthalene (27.5 mg, 214 μmol) was dissolved in THF (10 mL). Lithium powder (75.0 mg, 10.8 mmol) was added to the solution at $-45\text{ }^{\circ}\text{C}$ and the resulting suspension was stirred for 35 h at $-45\text{ }^{\circ}\text{C}$ to afford a dark red suspension. The resulting suspension was filtered through Celite pad to remove an excess of lithium and lithium naphthalenide. The filtrate was diluted with THF to 25.0 mL. To a 0.50 mL aliquot (21.4 mmol) of the resulting boryllithium solution, excess of H_2O , D_2O , or a THF solution of *n*-BuCl (910 μL , 47.1 mM, 42.8 mmol) was added at $-45\text{ }^{\circ}\text{C}$ and the resulting suspension was stirred for 10 min at room temperature. [For the reaction of MeOTf, solvents were removed from the boryllithium solution and ether (500 μL) was added to the residue to make an ether solution of boryllithium. To the resulting ether solution, an ether solution of MeOTf (500 μL , 47.1 mM, 1.1 eq) was added at $-45\text{ }^{\circ}\text{C}$ and the resulting suspension was stirred for 10 min at room temperature.]

To the stock solution **A** (100 mM, 0.5 mL, 50 μmol), BnCl (9.5 mg, 75 μmol), *n*-BuBr (103 mg, 75 μmol), BnBr (12.8 mg, 75 μmol), 1 eq. or 3 eq. of PhCHO (1 eq.; 5.3 mg, 50 μmol , 3 eq.; 15.9 mg, 150 μmol), PhCOCl (10.5 mg, 75 μmol), PhCO₂Ph (9.9 mg, 75 μmol), (PhCO)₂O (11.3 mg, 75 μmol), (PhO)₂CO (10.7 mg, 75 μmol), Boc₂O (10.0 mg, 75 μmol), excess CO₂ [at 1 atm after removal of argon with freeze thaw], PhF (4.8 mg, 75 μmol), or C₆F₆ (14.0 mg, 75 μmol) was added at $-45\text{ }^{\circ}\text{C}$ [in the case of CO₂: $-78\text{ }^{\circ}\text{C}$] and the resulting suspension was stirred for 10 min [in the case of C₆F₆: 24 h] at room temperature.

To the stock solution **B** (75.0 mM, 10.0 mL, 750 μmol), PhCOCl (158 mg, 1.13 mmol), or excess CO₂ [at 1 atm after removal of argon with freeze thaw], was added at $-45\text{ }^{\circ}\text{C}$ [in

the case of CO₂: −78 °C] and the resulting suspension was stirred for 10 min at room temperature.

After solvents were evaporated under reduced pressure, C₆D₆ (600 μL, including phenanthrene as an internal standard, 71.4 mM) was added to a residue to make NMR samples. The characterizations of the products were carried out by comparison with independently synthesized compounds. The product yields were estimated from the integral ratio of the products over the internal standard in their ¹H NMR spectra.

Reexamination of 35a with D₂O

In a glovebox, **34a-Br** (100 mg, 214 μmol) and naphthalene (5.5 mg, 43 μmol) was dissolved in THF (2 mL). Lithium powder (7.5 mg, 1.07 mmol) was added to the solution at −45 °C and the resulting suspension was stirred for 35 h at −45 °C to afford a dark red suspension. The resulting suspension was filtered through Celite pad to remove an excess of lithium and lithium naphthalenide. D₂O was added at −45 °C and the resulting suspension was stirred for 10 min at room temperature. After phenanthrene (38.1 mg, 214 μmol) was added to the suspension, solvents were evaporated under reduced pressure. Then C₆D₆ (600 μL) was added to a residue to make NMR samples. The characterizations of the products were carried out by comparison with independently synthesized compounds. The product yields were estimated from the integral ratio of the products over the internal standard in its ¹H NMR spectrum (97% **38a-d₁** with 2.6% **38a**).

Independent synthesis of 55

In a glovebox, a solution of MeLi in hexane (1.04 M; 1.41 mL, 1.47 mmol) was added to a solution of **34a-Br** (200 mg, 428 μmol) in THF (3 mL) at room temperature and the resulting mixture was stirred for 4 h. After solvents were evaporated under reduced pressure and the vial was brought out from the glovebox, hexane (20 mL) and water (25 mL) was added to a residue. The aqueous phase was extracted twice with 20 mL portions of hexane. The combined organic phase was dried over Na₂SO₄ and the solvent was removed under reduced pressure. Purified by recycling HPLC to give a white solid (102 mg, 59.2%). Analytically pure crystals were obtained from a hexane solution. ¹H NMR (C₆D₆, 500 MHz) δ 0.31 (s, 3H), 1.21 (d, *J* = 7 Hz, 12H), 1.22 (d, *J* = 7 Hz, 12H), 3.19 (sep, *J* = 7 Hz, 4H), 6.15 (s, 2H), 7.16 (d, *J* = 7 Hz, 4H), 7.23 (dd, *J* = 9 Hz, 7 Hz, 2H), ¹¹B NMR (C₆D₆, 160 MHz) 27.9 (brs, *h*_{1/2} = 307 Hz); ¹³C NMR (C₆D₆, 126 MHz) −6.0 (br, B−CH₃), 24.1 (CH₃), 24.6 (CH₃), 29.0 (CH), 119.0 (CH), 123.7 (CH), 127.7 (CH), 139.3 (4°), 146.5 (4°). mp: 103.7–104.7 °C; HRMS–FAB (*m/z*): [*M*]⁺ calcd for C₂₇H₃₉BN₂, 402.3206; found, 402.3205.

Isolation of 56

In a glovebox, lithium granular (75.0 mg, 5.30 mmol) was added to a solution of **34a-Br** (500 mg, 1.06 mmol) and naphthalene (26.0 mg, 203 μmol) in THF (10 mL) at −45 °C under argon atmosphere and stirred for 12 h at −45 °C. After the resulting suspension was filtered through Celite pad to remove an excess of lithium and lithium naphthalenide, 1-chlorobutane (149 mg, 1.60 mmol) was added to the solution at −45 °C and the resulting

mixture was stirred for 10 min at room temperature. After removal of solvent, hexane (25 mL) was added to a residue. The resulting suspension was filtered through Celite pad to remove a lithium salt under argon, and the solids were washed with hexane. Volatiles were removed from the filtrate. Purified by recycling HPLC to give a white solid (132 mg, 69.4%). Analytically pure crystals were obtained from a methanol solution. ^1H NMR (C_6D_6 , 500 MHz) δ 0.66 (t, J = 7 Hz, 3H), 0.98-1.07 (m, 4H), 1.18 (t, J = 7 Hz, 2H), 1.20 (d, J = 7 Hz, 6H), 1.28 (d, J = 7 Hz, 6H), 3.26 (sep, J = 8 Hz, 4H), 6.18 (s, 2H), 7.16 (d, J = 8 Hz, 2H), 7.23 (dd, J = 8 Hz, 7 Hz, 2H); ^{11}B NMR (C_6D_6 , 160 MHz) 27.9 (brs, $h_{1/2}$ = 286 Hz); ^{13}C NMR (C_6D_6 , 126 MHz) 12.1 (br, B- CH_2), 14.0 (CH_3), 23.7 (CH_3), 25.4 (CH_3), 26.4 (CH_2), 28.2 (CH_2), 28.6 (CH), 119.3 (CH), 120.1 (CH), 123.7 (CH), 139.4 (4°), 146.4 (4°). mp: 81.6-82.4 $^\circ\text{C}$; HRMS-FAB (m/z): $[\text{M}]^+$ calcd for $\text{C}_{30}\text{H}_{45}\text{BN}_2$, 444.3676; found, 444.3674.

Independent Synthesis of 57

To the THF solution of **34a-Br** (488 mg, 1.04 mmol, 20 mL), PhCH_2K (204 mg, 1.57 mmol) was added under argon atmosphere at room temperature and the resulting solution was stirred at room temperature for 3 h. After quenched by $^i\text{Pr}_2\text{EtNHCl}$ (344 mg, 2.08 mmol), solvent was evaporated under reduced pressure and hexane (50 mL) was added to a residue. The resulting suspension was filtered through a Celite pad, and the residue was washed with hexane. Volatiles were removed from the filtrate and recrystallization from hexane gave colorless crystal (263 mg, 53%) ^1H NMR (C_6D_6) δ : 1.13 (d, J = 7 Hz, 12H), 1.16 (d, J = 7 Hz, 12H), 2.42 (s, 2H), 3.12 (sep, J = 7 Hz, 4H), 6.18 (s, 2H), 6.62 (d, J = 7 Hz, 2H), 6.84 (t, J = 7 Hz, 1H), 6.91 (t, J = 7 Hz, 2H), 7.14 (d, J = 7 Hz, 4H), 7.24 (dd, J = 8, 7 Hz, 2H); ^{13}C NMR (C_6D_6 , 125 MHz) δ 20.9 (br, CH_2), 23.2 (CH_3), 25.9 (CH_3), 28.7 (CH), 119.6 (CH), 123.7 (CH), 124.5 (CH), 127.9 (CH), 128.2 (CH), 129.1 (CH), 139.0 (4°), 140.6 (4°), 146.4 (4°); ^{11}B NMR (C_6D_6 , 160 MHz) δ 26.6 (brs) mp: 124.1-125.5 $^\circ\text{C}$; Anal. calcd. for $\text{C}_{33}\text{H}_{43}\text{BN}_2$: C, 82.83; H, 9.06; N, 5.85. Found: C, 82.92; H, 9.01; N, 5.83.

Large Scale Synthesis of 58

In a glovebox, lithium granular (70.0 mg, 10.1 mmol) was added to a solution of **34a-Br** (500 mg, 1.07 mmol) and naphthalene (52.0 mg, 406 μmol) in THF (10 mL) at -45°C under argon atmosphere and stirred for 12 h at -45°C . After the resulting suspension was filtered through Celite pad to remove an excess of lithium and lithium naphthalenide,, solvents were evaporated under reduced pressure and the residue was dissolved in diethyl ether (20 mL). Benzaldehyde (1.05 g, 9.85 mmol) was added to the solution at -45°C and the resulting mixture was stirred for 10 min at room temperature. After removal of solvent, the residue was dissolved in a mixture of hexane and dichloromethane (1 : 2). The resulting solution was charged on the top of a silica gel column (hexane : dichloromethane = 1 : 2) and the product was separated to give a white solid (240 mg, 485 μmol , 45.4%). Analytically pure crystals were obtained from a hexane solution. ^1H NMR (C_6D_6 , 500 MHz) 0.85 (d, J = 4 Hz, 1H), 1.10 (d, J = 7 Hz, 6H), 1.15 (d, J = 7 Hz, 6H), 1.18 (d, J = 7 Hz, 6H), 1.28 (d, J = 7 Hz, 6H), 3.11 (sep, J = 7 Hz, 2H), 3.27 (sep, J = 7 Hz, 2H), 4.64 (d, J = 4 Hz, 1H), 6.15 (s, 2H), 6.81 (d, J = 7 Hz, 2H), 6.90 (d, J = 7 Hz, 1H), 6.96 (t, J = 7 Hz,

2H), 7.11 (dd, $J = 6$ Hz, 8 Hz, 2H), 7.1 (dd, $J = 6$ Hz, 8 Hz, 2H), 7.24 (t, $J = 8$ Hz, 2H); ^{11}B NMR (C_6D_6 , 160 MHz) 25.3 (brs, $h_{1/2} = 314$ Hz); ^{13}C NMR (C_6D_6 , 126 MHz, two ipso 4° carbons connected to nitrogen atoms are magnetically equivalent) δ 23.0 (CH_3), 23.1 (CH_3), 26.1 (CH_3), 26.2 (CH_3), 28.65 (CH), 28.71 (CH), 65.3 (br, B-CH(OH)), 120.1 (CH), 123.6 (CH), 126.0 (CH), 126.2 (CH), 127.9 (CH), 128.1 (CH), 128.4 (CH), 139.0 (4° , N-C), 145.6 (4°), 146.5 (4°), 146.8 (4°). mp: 139.6-140.4 $^\circ\text{C}$; HRMS-FAB (m/z): $[\text{M}]^+$ calcd for $\text{C}_{33}\text{H}_{43}\text{BN}_2\text{O}$, 494.3468; found, 494.3465.

Preparation of stock solution C of boryllithium 35a

In a glovebox, a 80 mL vial equipped with a glass magnetic stir bar was charged with **1** (3.59 g, 7.69 mmol), Li powder (267 mg, 38.5 mmol), and naphthalene (493 mg, 3.85 mmol). After cooling the vial to -45°C , THF (15 mL) was added to the vial. The resulting mixture was stirred for 12 h at -45°C . After a portion of the reaction mixture was monitored by ^{11}B NMR to confirm the reaction was complete, the resulting mixture was filtered through a pad of Celite® and the residue was washed with THF. The filtrate was diluted to 25 mL with volumetric flask to give **stock solution C** (boryllithium **35a**, 0.308 M).

Independent synthesis of 59 by the reaction of 35a with 5 eq of PhCHO

In a glovebox, a 4 mL vial equipped with a glass stir bar was charged with PhCHO (204 μL , 2.00 mmol). To the vial, an aliquot of **stock solution C** of boryllithium **35a** (0.308 M, 1.30 mL, 0.400 mmol) was added dropwise at room temperature. After the reaction mixture was stirred at room temperature for 1 h, solvents were evaporated under reduced pressure. CHCl_3 was added to the residue and the resulting solution was subjected to recycle GPC with CHCl_3 eluent to give a gummy yellow solids of borylester **59** ($R_T = 51$ min, 105 mg, 44%). ^1H NMR (C_6D_6 , 500 MHz) δ : 0.84 (d, $J = 7$ Hz, 6H), 1.10 (d, $J = 7$ Hz, 6H), 1.18 (d, $J = 7$ Hz, 6H), 1.45 (d, $J = 7$ Hz, 6H), 2.97 (sep, $J = 7$ Hz, 2H), 3.45 (sep, $J = 7$ Hz, 2H), 6.17 (s, 2H), 6.61 (s, 1H), 6.82-6.86 (m, 1H), 6.89-6.94 (m, 4H), 6.97-7.08 (m, 5H), 7.20-7.24 (m, 4H), 7.33-7.36 (m, 2H). ^{11}B NMR (C_6D_6 , 160 MHz) δ 25.3 (brs). ^{13}C NMR (C_6D_6 , 126 MHz) δ 22.6 (CH_3), 23.2 (CH_3), 26.0 (CH_3), 26.2 (CH_3), 28.7 (CH), 28.9 (CH), 68.9 (br, CH), 120.5 (NCH), 123.7 (CH), 124.0 (CH), 126.9 (CH), 127.8 (CH), 127.9 (CH), 128.0 (CH), 128.3 (CH), 128.4 (CH), 130.1 (CH), 131.0 (4°), 132.3 (CH), 139.3 (CH), 141.3 (4°), 145.9 (4°), 146.4 (4°), 165.9 (C=O); IR (KBr): $\nu_{\text{CO}} = 1719\text{ cm}^{-1}$; Anal. Calcd for $\text{C}_{40}\text{H}_{47}\text{BN}_2\text{O}_2$: C, 80.26; H, 7.91; N, 4.68. Found: C, 80.00; H, 8.19; N, 4.49.

Synthesis of 60a

In a glovebox, a 20 mL vial equipped with a glass magnetic stir bar was charged with an aliquot of **stock solution C** of boryllithium **35a**, (10.0 mL, 3.08 mmol). To the vial, benzoyl chloride (649 mg, 4.61 mmol) was added dropwise at room temperature, and then the reaction mixture was stirred for 12 h at room temperature. After removing all volatiles, the crude product was purified by silica gel chromatography with hexane : $\text{CH}_2\text{Cl}_2 = 3 : 1$ eluent to give yellow solids (856 mg, 57%). ^1H NMR (C_6D_6 , 500 MHz) δ 1.20 (d, $J = 7$ Hz, 12H), 1.27 (d, $J = 7$ Hz, 12H), 3.41 (sept, $J = 7$ Hz, 4H), 6.24 (s, 2H), 6.90-6.92 (m, 3H),

7.01-7.09 (m, 6H), 7.79-7.80 (m, 2H). ^{11}B NMR (C_6D_6 , 160 MHz) δ 21.8 (brs). ^{13}C NMR (C_6D_6 , 126 MHz) δ 23.5 (CH_3), 25.9 (CH_3), 28.8 (CH), 120.2 (NCH), 123.8 (CH), 128.1 (CH), 128.3 (CH), 128.5 (CH), 132.4 (CH), 137.9 (4°), 141.8 (4°), 145.9 (4°), 218.7 (br, C=O); IR (KBr): ν_{CO} = 1618 cm^{-1} ; mp: 126.7-128.5 $^\circ\text{C}$ (dec.); Anal. Calcd for $\text{C}_{33}\text{H}_{41}\text{BN}_2\text{O}$: C, 80.48; H, 8.39; N, 5.69. Found: C, 80.51; H, 8.61; N, 5.50.

Large Scale Synthesis of 61

In a glovebox, to Boc_2O (327 mg, 1.50 mmol), an aliquot of stock solution **A** of boryllithium **35a** (100 mM, 10.0 mL, 1.00 mmol) was added at room temperature and the resulting suspension was stirred for 1 h. After solvent was evaporated under reduced pressure, hexane (100 mL) was add to a residue. The resulting suspension was filtered through a Celite pad, and the residue was washed with hexane. Volatiles were removed from the filtrate and recrystallization from hexane gave pale yellow crystal (42.4 mg, 8.7%). ^1H NMR (C_6D_6 , 500 MHz) δ 1.06 (s, 9H), 1.21 (d, J = 7 Hz, 12H), 1.32 (d, J = 7 Hz, 12H), 3.13 (sep, J = 7 Hz, 4H), 6.11 (s, 2H), 7.15 (d, J = 8 Hz, 4H), 7.22 (dd, J = 7 Hz, 8 Hz, 2H); ^{13}C NMR (C_6D_6 , 125 MHz) δ 24.1 (CH_3), 24.6 (CH_3), 28.2 (CH), 28.8 (CH_3), 78.2 (4°), 120.2 (CH), 123.4 (CH), 127.8 (CH), 139.0 (4°), 145.6 (4°), 174.4 (br, 4°); ^{11}B NMR (C_6D_6 , 160 MHz) δ 19.1 (brs); IR (KBr): 1690, (CHCl_3): 1680 cm^{-1} ; mp: 81.9–83.7 $^\circ\text{C}$; Anal. calcd. for $\text{C}_{31}\text{H}_{45}\text{BN}_2\text{O}_2$: C, 76.22; H, 9.28; N, 5.73. Found: C, 76.07; H, 9.30; N, 5.64.

Large Scale Synthesis of 62

In a glovebox, to $(\text{PhO})_2\text{CO}$ (321 mg, 1.50 μmol), an aliquot of stock solution **A** of boryllithium **35a** (100 mM, 10.0 mL, 1.00 mmol) was added at room temperature and the resulting suspension was stirred for 1 h. After solvent was evaporated under reduced pressure, hexane (300 mL) was add to a residue. The resulting suspension was filtered through a Celite pad, and the residue was washed with hexane. Volatiles were removed from the filtrate and recrystallization from hexane gave colorless crystal (84.6 mg, 17%). ^1H NMR (C_6D_6) δ : 1.22 (d, J = 7 Hz, 12H), 1.30 (d, J = 7 Hz, 12H), 3.18 (sep, J = 7 Hz, 4H), 6.17 (s, 2H), 6.72 (d, J = 8 Hz, 2H), 6.87 (t, J = 7 Hz, 2H), 6.98 (t, J = 8 Hz, 1H), 7.11 (d, J = 8 Hz, 2H), 7.17 (d, J = 7 Hz, 2H), 7.25 (t, J = 8 Hz, 2H); ^{13}C NMR (C_6D_6 , 125 MHz) δ 24.2 (CH_3), 24.6 (CH_3), 28.9 (CH), 120.7 (CH), 121.9 (CH), 123.6 (CH), 125.1 (CH), 128.2 (CH), 129.2 (CH), 138.3 (4°), 145.9 (4°), 151.0 (4°), 172.5 (br, 4°); ^{11}B NMR (C_6D_6 , 160 MHz) δ 19.3 (brs) IR (KBr): 1719, (CHCl_3): 1713 cm^{-1} ; mp: 98.9–100.7 $^\circ\text{C}$; Anal. calcd. for $\text{C}_{33}\text{H}_{41}\text{BN}_2\text{O}_2$: C, 77.95; H, 8.13; N, 5.51. Found: C, 77.84; H, 8.31; N, 5.42.

Large Scale Synthesis of 63a

In a glovebox, a 25 mL J-Young tube equipped with a glass stir bar was charged with an aliquot of stock solution **A** of boryllithium **35a** (100 mM, 20.0 mL, 2.00 mmol). After the J-Young tube was brought out from the glovebox, the solution was freezed in liquid N_2 bath and vacuumed. CO_2 gas was filled in the J-Young tube at -78°C and the solution was stirred at -78°C for 1 h. After removal of solvent, the J-Young tube was brought into the glovebox. The residue was dissolved in a mixture of hexane and Et_2O (9 : 1). The resulting

solution was charged on the top of a silica gel column (hexane : Et₂O = 9 : 1) and the product was separated to give a white solid. Analytically pure crystals were obtained from a hexane solution. (692 mg, 80%). ¹H NMR (C₆D₆, 500 MHz) δ 1.18 (d, *J* = 7 Hz, 12H), 1.23 (d, *J* = 7 Hz, 12H), 3.07 (sep, *J* = 7 Hz, 4H), 6.06 (s, 2H), 7.11 (d, *J* = 8 Hz, 4H), 7.19 (t, *J* = 8 Hz, 2H), 8.36 (br s, 1H); ¹³C NMR (C₆D₆) δ: 24.1 (CH₃), 24.6 (CH₃), 28.7 (CH), 120.7 (CH), 123.5 (CH), 128.1 (CH), 138.1 (4°), 145.5 (4°), 181.6 (4°); ¹¹B NMR (C₆D₆, 160 MHz) δ 19.0 (brs); IR (KBr): 1666, (CHCl₃): 1672, 1709 cm⁻¹; mp: 206.2-207.8 °C; Anal. calcd. for C₂₆H₃₇BN₂O: C, 75.00; H, 8.62; N, 6.48. Found: C, 74.85; H, 8.62; N, 6.43.

Large Scale Synthesis of 64a

In a glovebox, a 25 mL J-Young tube equipped with a glass stir bar was charged with an aliquot of stock solution **A** of boryllithium **35a** (100 mM, 10.0 mL, 1.00 mmol). After the J-Young tube was brought out from the glovebox, the solution was freeze-dried in liquid N₂ bath and vacuumed. CO₂ gas was filled in the J-Young tube at -78 °C and the solution was stirred at -78 °C for 1 h. After removal of solvent, the J-Young tube was brought into the glovebox and hexane (50 mL) was added to a residue. The resulting suspension was filtered through a pad of Celite, and the residue was washed with hexane. Volatiles were removed from the filtrate and recrystallization from hexane solution to give a colorless crystal. (20.0 mg, 4.9%). ¹H NMR (C₆D₆, 500 MHz) δ 1.23 (d, *J* = 7 Hz, 12H), 1.25 (d, *J* = 7 Hz, 12H), 2.41 (s, 1H), 3.31 (sep, *J* = 7 Hz, 4H), 5.89 (s, 2H), 7.15 (d, *J* = 7 Hz, 4H), 7.22 (dd, *J* = 7 Hz, 8 Hz, 2H); ¹³C NMR (C₆D₆, 125 MHz) δ 24.1 (CH₃), 24.4 (CH₃), 28.8 (CH), 116.5 (CH), 123.8 (CH), 128.3 (CH), 137.7 (4°), 147.2 (4°); ¹¹B NMR (C₆D₆, 160 MHz) δ 21.9 (brs); mp: 186.2-188.8 °C; Anal. calcd. for C₂₆H₃₇BN₂O: C, 77.22; H, 9.22; N, 6.93. Found: C, 77.02; H, 9.45; N, 6.67.

Independent Synthesis of 65

A solution of phenyllithium (in cyclohexane-Et₂O, 1.08 M, 12.0 mL, 12.1 mmol) was added to a hexane solution of **34a-Br** (599 mg, 1.28 mmol, 50 mL) under argon atmosphere at room temperature and the resulting solution was stirred at reflux for 12 h. After quenched by ⁱPr₂EtNHCl (2.07 g, 12.5 mmol), solvent was evaporated under reduced pressure and hexane (100 mL) was added to a residue. The resulting suspension was filtered through a Celite pad, and the residue was washed with hexane. Volatiles were removed from the filtrate and recrystallization from hexane gave colorless crystal (476 mg, 80%). ¹H NMR (C₆D₆) δ: 1.08 (d, *J* = 7 Hz, 12H), 1.21 (d, *J* = 7 Hz, 12H), 3.30 (sep, *J* = 7 Hz, 4H), 6.25 (s, 2H), 6.79-6.87 (m, 3H), 7.13 (d, *J* = 7 Hz, 2H), 7.20 (d, *J* = 7 Hz, 4H), 7.27 (dd, *J* = 8, 7 Hz, 2H); ¹³C NMR (C₆D₆, 125 MHz) δ 23.7 (CH₃), 25.0 (CH₃), 28.7 (CH), 120.3 (CH), 124.2 (CH), 127.7 (CH), 128.1 (CH), 128.6 (CH), 132.7 (br, 4°), 133.6 (CH), 140.2 (4°), 146.1 (4°); ¹¹B NMR (C₆D₆, 160 MHz) δ 25.0 (brs) mp: 141.9-144.0 °C; Anal. calcd. for C₃₂H₄₁BN₂: C, 82.74; H, 8.90; N, 6.03. Found: C, 82.85; H, 9.16; N, 5.82.

Large Scale Synthesis of 66

In a glovebox, to C₆F₆ (279 mg, 1.50 μmol), an aliquot of stock solution **A** of boryllithium **35a** (100 mM, 10.0 mL, 1.00 mmol) was added at room temperature and the

resulting suspension was stirred for 1 h. After solvent was evaporated under reduced pressure, hexane (100 mL) was added to a residue. The resulting suspension was filtered through a Celite pad, and the residue was washed with hexane. Volatiles were removed from the filtrate and recrystallization from hexane gave colorless crystal (115 mg, 21%). ^1H NMR (C_6D_6) δ : 1.18 (d, J = 7 Hz, 12H), 1.24 (d, J = 7 Hz, 12H), 3.17 (sep, J = 7 Hz, 4H), 6.32 (s, 2H), 7.059 (d, J = 8 Hz, 2H), 7.061 (d, J = 7 Hz, 2H), 7.12 (dd, J = 8, 7 Hz, 2H); ^{13}C NMR (C_6D_6 , 125 MHz) δ 23.2 (CH_3), 26.4 (CH_3), 28.6 (CH), 105.8 (br, 4°), 121.2 (CH), 123.9 (CH), 128.4 (CH), 137.4 (d, J = 250 Hz, 4°), 137.5 (4°), 141.7 (d, J = 253 Hz, 4°), 146.4 (4°), 147.7 (d, J = 242 Hz, 4°); ^{11}B NMR (C_6D_6 , 160 MHz) δ 22.5 (brs); ^{19}F NMR (C_6D_6 , 470 MHz) δ : -130.5 (d, J = 12 Hz, 2F), -151.4 (t, J = 23 Hz, 1F), -162.2 (dt, J = 12 Hz, 23 Hz, 2F); mp: 156.0–157.0 $^\circ\text{C}$; Anal. calcd. for $\text{C}_{32}\text{H}_{36}\text{BN}_2\text{F}_5$: C, 69.32; H, 6.54; N, 5.05. Found: C, 69.60; H, 6.67; N, 4.96.

Large Scale Synthesis of 60b

In a glovebox, the THF solution of benzoyl chloride (141 mg, 1.35 mmol, 1 mL THF) was added to the stock solution **B** of boryllithium **35b** (75.0 mM, 16.4 mL, 1.23 mmol), the filtrate was added at -45°C and the resulting suspension was stirred for 1 h at room temperature. After solvents were evaporated under reduced pressure, the residue was purified by silica gel column chromatography (hexane : dichloromethane = 3 : 1) to give a white solid (173 mg, 28%). ^1H NMR (C_6D_6) δ : 1.28 (d, J = 7 Hz, 12H), 1.30 (d, J = 7 Hz, 12H), 3.62 (s, 4H), 3.81 (sep, J = 7 Hz, 4H), 6.90–7.05 (m, 9H), 7.89 (dt, J = 8 Hz, 1 Hz, 2H); ^{13}C NMR (C_6D_6 , 125 MHz) δ 26.3 (CH_3), 26.3 (CH_3), 28.7 (CH), 54.1 (CH), 124.2 (CH), 127.4 (CH), 128.3 (CH), 128.5 (CH), 132.7 (CH), 138.5 (4°), 140.1 (4°), 147.3 (4°), 221.0 (br, 4°); ^{11}B NMR (C_6D_6 , 160 MHz) δ 27.4 (brs), IR (KBr): 1638, (CHCl_3): 1638 cm^{-1} ; mp: 120.0–123.8 $^\circ\text{C}$ (dec); Anal. calcd. for $\text{C}_{33}\text{H}_{43}\text{BN}_2\text{O}$: C, 80.15; H, 8.76; N, 5.66. Found: C, 79.90; H, 9.00; N, 5.66.

Independent Synthesis of 64b

CsOH (277 mg, 1.85 mmol) was added to the hexane solution of **34b** (488 mg, 1.04 mmol) under argon atmosphere at room temperature and the resulting solution was stirred at room temperature for 3 h. After solvent was evaporated under reduced pressure, hexane (50 mL) was added to a residue. The resulting suspension was filtered through a Celite pad, and the residue was washed with hexane. Volatiles were removed from the filtrate and recrystallization from hexane gave colorless crystal (339 mg, 68%). ^1H NMR (C_6D_6) δ : 1.28 (d, J = 7 Hz, 12H), 1.29 (d, J = 7 Hz, 12H), 2.31 (s, 1H), 3.39 (s, 4H), 3.53 (sep, J = 7 Hz, 4H), 7.111 (d, J = 8 Hz, 2H), 7.112 (d, J = 7 Hz, 2H), 7.17 (dd, J = 8, 6 Hz, 2H); ^{13}C NMR (C_6D_6 , 125 MHz) δ 24.4 (CH_3), 25.2 (CH_3), 28.7 (CH), 50.9 (CH_2), 124.1 (CH), 127.1 (CH), 139.2 (4°), 148.5 (4°); ^{11}B NMR (C_6D_6 , 160 MHz) δ 24.2 (brs) mp: 189.8–190.7 $^\circ\text{C}$; Anal. calcd. for $\text{C}_{26}\text{H}_{39}\text{BN}_2\text{O}$: C, 76.84; H, 9.67; N, 6.89. Found: C, 76.73; H, 9.82; N, 6.70.

X-ray Crystallography

Details of the crystal data and a summary of the intensity data collection parameters for **34a-Br**, **34a-I**, **34b**, **(35a-DME)₂**, **35a·(THF)₂**, **35b·(THF)₂**, **35c·(THF)₂**, **38a**, **38b**, **38c**, **55**, **57**, **58**, **60a**, **60b**, **61**, **62**, **64a**, and **65** are listed in Table S1. In each case a suitable crystal was mounted with a mineral oil to the glass fiber and transferred to the goniometer of a Rigaku Mercury CCD diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71069$ Å). The structures were solved by direct methods with (SIR-97)⁸ and refined by full-matrix least-squares techniques against F^2 (SHELXL-97).⁹ The intensities were corrected for Lorentz and polarization effects. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically in the difference Fourier maps or placed using AFIX instructions.

Table S1. Crystallographic data and structure refinement details for **34a-Br**, **34a-I**, **34b**, **(35a-DME)₂**, **35a·(THF)₂**, **35b·(THF)₂**, **35c·(THF)₂**, **38a**, **38b**, **38c**, **55**, **57**, **58**, **60a**, **60b**, **61**, **62**, **64a**, and **65**

	34a-Br	34a-I	34b	(35a-DME)₂	35a·(THF)₂
formula	C ₂₆ H ₃₆ BBrN ₂	C ₂₆ H ₃₆ BrIN ₂	C ₂₆ H ₃₈ BBrN ₂	C ₃₀ H ₄₆ BLiN ₂ O ₂	C ₃₄ H ₅₂ BLiN ₂ O ₂
fw	467.29	514.28	455.29	484.44	538.53
T (K)	120(2)	120(2)	103(2)	103(2)	103(2)
λ (Å)	0.71070	0.71070	0.71070 Å	0.71070	0.71070
cryst syst	Monoclinic	Triclinic	Monoclinic	Orthorhombic	Orthorhombic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> -1	<i>P</i> 2 ₁ / <i>n</i>	<i>Pbca</i>	<i>Pbca</i>
<i>a</i> , (Å)	19.153(12)	7.4883(2)	19.222(14)	17.0118(11)	11.5625(10)
<i>b</i> , (Å)	6.945(4)	9.48350(10)	6.924(5)	19.5103(11)	19.603(2)
<i>c</i> , (Å)	19.384(13)	18.5512(4)	19.362(14)	18.3570(11)	28.941(2)
α, (deg)	90	77.6015(8)	90	90	90
β, (deg)	105.996(9)	86.8095(12)	105.271(3)	90	90
γ, (deg)	90	80.4265(12)	90	90	90
<i>V</i> , (Å ³)	2478(3)	1268.50(5)	2486(3)	6092.8(6)	6559.9(10)
<i>Z</i>	4	2	4	8	8
D _{calc} , (g / cm ³)	1.252	1.346	1.217	1.056	1.091
μ (mm ⁻¹)	1.673	1.277	1.665	0.064	0.065
F(000)	984	528	964	2112	2352
cryst size (mm)	0.50 x 0.50 x 0.10	0.60 x 0.50 x 0.20	0.60 x 0.50 x 0.20	0.60 × 0.50 × 0.25	0.60 × 0.60 × 0.50
2θ range, (deg)	3.13-25.00	2.23-25.00	3.14–25.00	1.94–25.00	3.07–25.00
reflns collected	22348	12253	20953	36996	47794
indep reflns/ <i>R</i> _{int}	4353/0.0785	4350/0.0128	4369/0.0710	5355/0.0460	5758/0.0823
params	279	279	279	155	369
GOF on <i>F</i> ²	1.099	1.106	1.111	1.071	1.223
<i>R</i> ₁ , w <i>R</i> ₂ [<i>I</i> >2σ(<i>I</i>)]	0.0912, 0.2386	0.0165, 0.0421	0.0647, 0.1569	0.0814, 0.2329	0.0874, 0.1634
<i>R</i> ₁ , w <i>R</i> ₂ (all data)	0.1086, 0.2570	0.0168, 0.0423	0.0688, 0.1599	0.1036, 0.2575	0.0892, 0.1642

	35b·(THF)₂	35c·(THF)₂	38a	38b	38c
formula	C ₃₄ H ₅₄ BN ₂ O ₂	C ₃₈ H ₅₄ BLiN ₂ O ₂	C ₂₆ H ₃₇ BN ₂	C ₂₆ H ₃₉ BN ₂	C ₃₀ H ₃₉ BN ₂
fw	540.54	588.58	388.39	390.40	438.44
T (K)	103(2)	103(2)	120(2)	103(2)	103(2)
λ (Å)	0.71070	0.71070	0.71070	0.71070	0.71070
cryst syst	Orthorhombic	Monoclinic	Orthorhombic	Orthorhombic	Triclinic
space group	<i>Pbcn</i>	<i>C2/c</i>	<i>Pccn</i>	<i>Pccn</i>	<i>P-1</i>
<i>a</i> , (Å)	12.580(3)	11.190(11)	18.891(5)	19.035(9)	10.450(6)
<i>b</i> , (Å)	16.395(4)	17.754(17)	15.567(4)	15.165(7)	12.028(9)
<i>c</i> , (Å)	16.766(4)	18.410(18)	16.711(5)	16.723(7)	12.684(7)
α, (deg)	90	90	90	90	69.23(5)
β, (deg)	90	99.290(6)	90	90	67.00(5)
γ, (deg)	90	90	90	90	75.57(6)
<i>V</i> , (Å ³)	34579(15)	3610(6)	4914(2)	4970(4)	1360.6(15)
<i>Z</i>	4	4	8	8	2
D _{calc} , (g / cm ³)	1.038	1.083	1.050	1.043	1.070
μ (mm ⁻¹)	0.062	0.065	0.060	0.059	0.061
F(000)	1184	1280	1696	1712	476
cryst size (mm)	0.50 × 0.50 × 0.40	0.30 × 0.20 × 0.10	0.50 × 0.45 × 0.30	0.70 × 0.25 × 0.15	0.55 × 0.50 × 0.40
2θ range, (deg)	3.17–25.00	3.21–25.00	3.08–25.00	3.07–25.00	3.24–25.00
reflns collected	21152	11712	30228	29906	8742
indep reflns/ <i>R</i> _{int}	3036/0.0291	3170/0.0521	4302/0.0284	4144/0.0395	4669/0.0350
params	186	205	278	335	310
GOF on <i>F</i> ²	1.139	1.155	1.067	1.276	1.038
<i>R</i> ₁ , w <i>R</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0481, 0.1140	0.0829, 0.1853	0.0638, 0.1550	0.0690, 0.1372	0.0629, 0.1622
<i>R</i> ₁ , w <i>R</i> ₂ (all data)	0.0530, 0.1169	0.1072, 0.1993	0.0717, 0.1633	0.0780, 0.1411	0.0834, 0.1813

	55	57	58	60a	60b
formula	C ₂₇ H ₃₉ BN ₂	C ₃₃ H ₄₃ BN ₂	C ₃₃ H ₄₃ BN ₂ O	C ₃₃ H ₄₁ BN ₂ O	C ₃₃ H ₄₃ BN ₂ O
fw	402.41	478.50	494.50	492.49	494.50
T (K)	120(2)	103(2)	103(2)	103(2)	103(2)
λ (Å)	0.71070	0.71070	0.71070	0.71070	0.71070
cryst syst	Triclinic	Orthorhombic	Orthorhombic	Monoclinic	Triclinic
space group	<i>P</i> -1	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ / <i>a</i>	<i>P</i> -1
<i>a</i> , (Å)	7.413(5)	12.099(4)	12.205(3)	12.660(6)	9.294(4)
<i>b</i> , (Å)	9.362(7)	13.535(4)	13.677(3)	15.480(8)	11.154(4)
<i>c</i> , (Å)	18.458(14)	18.125(6)	17.907(4)	14.755(7)	14.663(6)
α , (deg)	77.366(18)	90	90	90	81.830(11)
β , (deg)	86.92(2)	90	90	90.479(2)	82.698(11)
γ , (deg)	77.526(19)	90	90	90	85.549(11)
<i>V</i> , (Å ³)	1220.5(15)	2968.1(17)	2989.3(12)	2892(2)	1489.8(10)
<i>Z</i>	2	4	4	4	2
D _{calc} , (g / cm ³)	1.095	1.071	1.099	1.131	1.102
μ (mm ⁻¹)	0.062	0.061	0.065	0.067	0.065
F(000)	440	1040	1072	1064	536
cryst size (mm)	0.35 × 0.25 × 0.05	0.60 × 0.50 × 0.30	0.60 × 0.45 × 0.30	0.60 × 0.45 × 0.25	0.55 × 0.40 × 0.20
2 θ range, (deg)	3.03–24.95	3.01–26.49	3.19–27.00	3.06–25.00	3.16–25.00
reflns collected	7891	21720	22778	18257	9800
indep reflns/ <i>R</i> _{int}	4168/0.0454	3427/0.0236	3653/0.0314	4990/0.0414	5115/0.0300
params	280	333	354	342	342
GOF on <i>F</i> ²	1.107	1.081	1.086	1.122	1.074
<i>R</i> ₁ , w <i>R</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0925, 0.2483	0.0351, 0.0841	0.0402, 0.1034	0.0572, 0.1295	0.0554, 0.1337
<i>R</i> ₁ , w <i>R</i> ₂ (all data)	0.1329, 0.2771	0.0363, 0.0849	0.0419, 0.1051	0.0782, 0.1415	0.0825, 0.1498

	61	62	64a	65
formula	C ₃₁ H ₄₅ BN ₂ O ₂	C ₃₃ H ₄₁ BN ₂ O ₂	C ₂₆ H ₃₇ BN ₂ O	C ₃₂ H ₄₁ BN ₂
fw	488.50	508.49	404.39	464.48
T (K)	103(2)	103(2)	103(2)	103(2)
λ (Å)	0.71070	0.71070	0.71070	0.71070
cryst syst	Monoclinic	Triclinic	Orthorhombic	Monoclinic
space group	<i>P2₁/n</i>	<i>P</i> -1	<i>Pccn</i>	<i>P2₁/c</i>
<i>a</i> , (Å)	9.300(3)	9.474(4)	18.522(4)	13.378(10)
<i>b</i> , (Å)	12.312(4)	10.358(5)	15.505(4)	12.642(9)
<i>c</i> , (Å)	25.655(8)	16.620(9)	16.871(4)	16.528(11)
α , (deg)	90	81.12(3)	90	90
β , (deg)	94.2715(14)	74.61(3)	90	95.338(5)
γ , (deg)	90	71.70(2)	90	90
<i>V</i> , (Å ³)	2929.3(16)	1488.5(13)	4845(2)	2783(3)
<i>Z</i>	4	2	8	4
<i>D</i> _{calc} , (g / cm ³)	1.108	1.135	1.109	1.108
μ (mm ⁻¹)	0.068	0.069	0.066	0.063
<i>F</i> (000)	1064	548	1760	1008
cryst size (mm)	0.60 x 0.30 x 0.25	0.40 × 0.30 × 0.15	0.50 × 0.50 × 0.35	0.50 × 0.30 × 0.25
2 θ range, (deg)	3.09–25.00	3.03–25.00	3.09–25.00	3.03–25.00
reflns collected	18381	9725	28956	17819
indep reflns/ <i>R</i> _{int}	5201/0.0348	5105/0.0318	4024/0.0509	4879/0.0370
params	336	351	301	324
GOF on <i>F</i> ²	1.189	1.154	1.287	1.108
<i>R</i> ₁ , w <i>R</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0559, 0.1134	0.0653, 0.1472	0.0725, 0.1389	0.0498, 0.1071
<i>R</i> ₁ , w <i>R</i> ₂ (all data)	0.0641, 0.1173	0.0949, 0.1659	0.0796, 0.1420	0.0633, 0.1137

Figure S1. ORTEP drawing of **34a-Br** with 50% thermal ellipsoid (All hydrogen atoms were omitted for clarity.)

Figure S2. ORTEP drawing of **34a-I** with 50% thermal ellipsoid (All hydrogen atoms were omitted for clarity.)

Figure S3. ORTEP drawing of **34b** with 50% thermal ellipsoid (All hydrogen atoms were omitted for clarity.)

Figure S4. ORTEP drawing of **38a** with 50% thermal ellipsoid (All hydrogen atoms except the hydrogen atom on the boron atom and minor parts of disordered isopropyl groups were omitted for clarity.)

Figure S5. ORTEP drawing of **38b** with 50% thermal ellipsoid (All hydrogen atoms except the hydrogen atom on the boron atom and minor parts of disordered isopropyl groups were omitted for clarity.)

Figure S6. ORTEP drawing of **38c** with 50% thermal ellipsoid (All hydrogen atoms except the hydrogen atom on the boron atom were omitted for clarity.)

Figure S7. ORTEP drawing of **55** with 50% thermal ellipsoid (All hydrogen atoms were omitted for clarity.)

Figure S8. ORTEP drawing of **57** with 50% thermal ellipsoid (All hydrogen atoms were omitted for clarity.)

Figure S9. ORTEP drawing of **60b** with 50% thermal ellipsoid (All hydrogen atoms were omitted for clarity.)

Figure S10. ORTEP drawing of **61** with 50% thermal ellipsoid (All hydrogen atoms were omitted for clarity.)

Figure S11. ORTEP drawing of **62** with 50% thermal ellipsoid (All hydrogen atoms were omitted for clarity.)

Figure S12. ORTEP drawing of **64a** with 50% thermal ellipsoid (All hydrogen atoms except the hydrogen atom on the oxygen atom and minor parts of disordered isopropyl groups were omitted for clarity.)

Figure S13. ORTEP drawing of **65** with 50% thermal ellipsoid (All hydrogen atoms were omitted for clarity.)

Computational Details. Gaussian 03 program¹⁰ equipped onto SGI Altix4700 system was used for all optimization (B3LYP/6-31+G(d)), frequency analysis (B3LYP/6-31+G(d)), population analysis (B3LYP/6-31+G(d)), GIAO calculation (B3LYP/6-311++G(d,p)), and generating wavefunctions for AIM analyses (B3LYP/6-311++G(d,p)). Visualization of the results was performed by use of GaussView 3.0 software. AIM-2000 ver. 2.0 software was used for AIM analyses and generating molecular graphs.^{11,12}

Optimized Cartesian coordinates for opt-46a

B 0.,0.,0.5293459601
N 0.000001522,1.126398325,-0.4543131768
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C -0.0000006438,-0.6795382315,-1.7856235687
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Optimized Cartesian coordinates for opt-35a

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Optimized Cartesian coordinates for opt-35a·(THF)₂

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Optimized Cartesian coordinates for opt-35a·(THF)₃

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C	0.42213	3.18347	1.84588
O	-1.09851	2.16141	-1.93048
C	-1.60294	1.3592	-3.02784
C	-3.12534	1.54131	-3.03138
C	-3.29566	2.92131	-2.37544
C	-2.18499	2.90077	-1.32652
O	1.94917	1.53988	-1.8965
C	3.28755	1.2225	-1.43866
C	4.15874	1.19261	-2.69596
C	3.45447	2.21416	-3.6041
C	1.97946	1.96836	-3.27386
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H	4.49484	-3.07553	-1.42506
H	6.04369	-2.06388	0.21717
H	5.14837	-0.90592	2.20845
H	0.7535	-2.97184	-1.07063
H	3.01384	-4.90668	-1.84258
H	1.28679	-5.1192	-2.17616
H	1.87582	-5.13213	-0.50266
H	1.69233	-1.41898	-2.74708
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H	2.92574	-2.61514	-3.20756
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H	2.18319	-2.41817	4.04518
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 H -3.54631 1.48679 -4.04082
 H -3.12481 3.7248 -3.10344
 H -4.28537 3.06439 -1.93023
 H -1.80462 3.89135 -1.05969
 H -2.50514 2.37983 -0.41576
 H 3.2471 0.27362 -0.90209
 H 3.60988 2.01041 -0.74328
 H 4.13675 0.19514 -3.15018
 H 5.2025 1.44633 -2.48489
 H 3.74558 3.23645 -3.33113
 H 3.67195 2.07334 -4.66802
 H 1.3476 2.85683 -3.36836
 H 1.55745 1.16961 -3.89935

Optimized Cartesian coordinates for opt-38a

B 0.0000041717,-0.0000024742,-0.5126842412
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 H -1.3632161568,-0.0000775087,2.5212822632
 C 0.6793680542,0.0000533547,1.6837412888
 H 1.3632313554,0.0001026874,2.5212791857
 N 1.1414159872,0.0000773253,0.3587009193

C -2.5403228958,-0.0001686206,0.0356817714
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 C -4.5762270182,1.2051227217,-0.4478410878
 H -5.1138824608,2.1409991883,-0.5779671608
 C -5.2550033971,-0.0003532284,-0.6125685729
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 C -4.5760694069,-1.2057367372,-0.4478147786
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 H -1.4739904363,2.3697089383,0.3508299591
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 C -3.1463329105,3.4335790873,1.1526835883
 H -4.1761914818,3.7162236792,0.9022491788
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 C 4.5762358312,-1.2051271021,-0.4478380267
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 H 6.3118566919,0.0004164825,-0.868531007
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H 4.1762043628,-3.716213481,0.9022806497
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C 2.5039852185,2.5740884862,0.0456364171
H 1.4736877566,2.3699038596,0.3508432263
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C 3.1458892651,3.4339795866,1.1527194234
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H 2.5734946767,4.3591062232,1.2949934712

Optimized Cartesian coordinates for opt-46b

B 0.,0.,-0.678152544
N -0.1380304438,1.1274553956,-1.6161552709
C -0.2374347939,0.7305610468,-3.0394973874
H 0.3807313975,1.3669153366,-3.69271467
H -1.2777968591,0.8142790428,-3.4066734383
C -0.4237916756,2.482846582,-1.3078628727
C -1.7492113151,2.9002314441,-1.0209703581
C -1.9948540757,4.2499250967,-0.7310373636
H -3.008117625,4.5711179643,-0.4952705501
C -0.9651749105,5.1892634973,-0.7283910097
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C 0.3368616696,4.7783128893,-1.0132756198
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C 0.6258752742,3.4392753251,-1.3075766261
C -2.9004166935,1.9012934346,-0.9793008002
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H 3.8356590832,2.4880896819,-0.3647052451
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 H 4.8356741905,-1.5182375185,-1.9084659939
 H 3.7288854597,-2.4593195785,-2.9319001076
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 H 2.5538226979,-1.2990727834,1.0781319108
 H 4.1909105302,-0.9302885135,0.4914116498
 H 3.7621940491,-2.6036063492,0.9140525296
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 H -2.3080723642,-4.0530256609,-3.4563105131
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Optimized Cartesian coordinates for opt-46c

B 0.,0.,0.9576409548
 N 1.137371695,0.0082582593,-0.0248444095
 C 0.7103478409,0.0051565746,-1.3520642249

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 H 3.3816824654,3.1590494335,-1.5829537494
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 C -5.2578503007,-0.0381748327,0.9408200553

H -6.3154257197,-0.0458530964,1.1992798804
 C -4.5843391777,1.1711876902,0.7770681073
 H -5.1257044121,2.1048167963,0.9148229869
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 C -3.1905481233,-3.587028393,-0.5914409153
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 H -1.6898618934,4.0974512755,1.6260999297
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 H -3.4271985411,3.1096148436,-1.5829552496
 H -2.6388623984,4.448218608,-0.7234937545
 H -4.2090409733,3.8489335529,-0.1715393752

Optimized Cartesian coordinates for Ph⁻

C 0.8837857098,-0.8394127292,0.0006191083
 C 2.2902870298,-0.8628241541,0.0011750558
 C 3.0101731837,0.339773848,0.0006771077
 C 2.2904018282,1.5424455426,-0.0003630697
 C 0.8839035262,1.5191719558,-0.000878267
 C 0.0890535023,0.3399153839,-0.0004347899
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 H 2.8295107778,-1.8164338675,0.0019916157
 H 4.1012820366,0.339725187,0.0010901465
 H 2.8297255183,2.4959992061,-0.0007720464
 H 0.3837875194,2.4968055657,-0.001709083

Figure S14. Molecular graph of opt-**35a**·(THF)₂ (purple: boron, blue: nitrogen, black: carbon, red: oxygen, dark gray: lithium, gray: hydrogen, small red: bond critical point)

Figure S15. Molecular graph of opt-PhLi·(THF)₃ (blue: nitrogen, black: carbon, red: oxygen, dark gray: lithium, gray: hydrogen, small red: bond critical point)

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¹H NMR (THF-d₈)

THF-d₈

* hexane

+ THF-d₇

‡ decomposed product

^{13}C NMR (THF- d_8)

S45

^{11}B NMR ($\text{THF}-d_8$)

^7Li NMR (THF- d_8)

¹H NMR (THF-*d*₈)

+ THF-*d*₇

¹³C NMR (THF-*d*₈)

+ THF-*d*₈

^{11}B NMR ($\text{THF}-d_8$)

¹H NMR (methylocyclohexane-d₁₄)

^1H NMR (THF- d_8)

reaction solution
without any purification

* hexane

+ THF- d_7

^{13}C NMR (THF- d_8)

reaction solution
without any purification

+ THF- d_8

^1H NMR (THF- d_8)

reaction solution
without any purification

+ THF- d_7

^{13}C NMR ($\text{THF-}d_8$)

reaction solution
without any purification

+ THF- d_8

^{11}B NMR ($\text{THF-}d_8$)

reaction solution
without any purification

S57

^{13}C NMR (THF- d_8)

+ THF- d_8

^{11}B NMR ($\text{THF-}d_8$)

^7Li NMR ($\text{THF-}d_8$)

¹H NMR (THF-d₈)

35c

reaction solution
without any purification

+ THF-d₇

^{13}C NMR (THF- d_8)

35c

reaction solution
without any purification

+ THF- d_8

^{11}B NMR (THF-d_8)

35c

reaction solution
without any purification

¹H NMR (THF-d₈)

* hexane
+ THF-d₇

^{13}C NMR (THF- d_8)

+ THF- d_8

^{11}B NMR ($\text{THF-}d_8$)

^7Li NMR (THF- d_8)

^1H NMR (THF- d_8)

reaction solution
without any purification

+ THF- d_7

¹³C NMR (THF-*d*₈)

reaction solution
without any purification

+ THF-*d*₈

^{11}B NMR ($\text{THF-}d_8$)

reaction solution
without any purification

^1H NMR (THF- d_8 , $-40\text{ }^\circ\text{C}$)

35e

reaction solution
without any purification

+ THF- d_7

^{13}C NMR (THF- d_8 , -40°C)

35e

reaction solution
without any purification

+ THF- d_8

^{11}B NMR ($\text{THF-}d_8$, -40°C)

35e

reaction solution
without any purification

¹H NMR (THF-d₈)

S74

+ THF-d₇

^{13}C NMR (THF- d_8)

S75

+ THF- d_8

^{11}B NMR ($\text{THF-}d_8$)

¹H NMR (C₆D₆)

C₆D₅H

^{13}C NMR (C_6D_6)

44e

C_6D_6

^{11}B NMR (C_6D_6)

44a