Supporting Information

NHC induced Radical Formation *via* Homolytic Cleavage of B–B Bonds and its Role in Organic Reactions

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Table of Contents

1 Experimental Section	S2
1.1 General Considerations	S2
1.2 Synthesis	S4
1.3 General Procedures for the Reaction of 3 with Aryl Halides	S5
2 Mechanistic Investigations	S10
3 Crystallographic Details	S19
4 Computational Details	S20
5 NMR Spectra	S25
6 References	S36

1 Experimental Section

1.1 General Considerations

All reactions and subsequent manipulations were performed in oven-dried glassware under an argon atmosphere using standard Schlenk techniques or in a glovebox (Innovative Technology Inc. and Braun Uni Lab). Reagent grade solvents (Fisher Scientific and J.T. Baker) were nitrogen saturated and were dried and deoxygenated using an Innovative Technology Inc. Pure-Solv 400 Solvent Purification System, and further deoxygenated using the freeze-pump-thaw method. C_6D_6 , CD_2Cl_2 and $CDCl_3$ were purchased from Sigma-Aldrich. Me₂Im^{Me} was prepared according to published procedures.^[1-3] The diborane(4) reagents B₂pin₂, and B₂neop₂ were a generous gift from AllyChem Co. Ltd. All other reagents were purchased from Sigma-Aldrich.

NMR spectra were recorded at 298 K using Bruker Avance 300 (¹H, 300 MHz; ¹³C, 75 MHz, ¹¹B, 96 MHz), Bruker DPX-400 (¹H, 400 MHz; ¹³C, 100 MHz, ¹¹B, 128 MHz; ¹⁹F, 376 MHz), or Bruker Avance 500 (¹H, 500 MHz; ¹³C, 125 MHz, ¹¹B, 160 MHz; ¹⁹F, 470 MHz) spectrometers. ¹H NMR chemical shifts are reported relative to TMS and were referenced *via* residual proton resonances of the corresponding deuterated solvent (CDHCl₂: 5.32 ppm; CHCl₃: 7.26 ppm; C_6D_5H : 7.16 ppm) whereas ¹³C{¹H} NMR spectra are reported relative to TMS using the natural-abundance carbon resonances (CD₂Cl₂: 53.84 ppm; CDCl₃: 77.16 ppm; C₆D₆: 128.0 ppm). ¹¹B and ¹⁹F NMR chemical shifts are reported relative to external BF₃·OEt₃ or CFCl₃, respectively. Coupling constants are given in Hertz. Elemental analyses were performed in the microanalytical laboratory of the Institute of Inorganic Chemistry, Universität Würzburg, using an Elementar vario micro cube instrument. Automated flash chromatography was performed using a Biotage® Isolera Four system, on silica gel (Biotage SNAP cartridge KP-Sil 10 g and KP-Sil 25 g). Precoated TLC plates (Polygram® Sil G/UV254) were purchased from Machery-Nagel. The removal of solvent was performed on a rotary evaporator in vacuo at a maximum temperature of 30 °C. GC/MS analyses were performed using a Thermo Fisher Scientific Trace 1310 gas chromatograph (column: TG-SQC 5% phenyl methyl siloxane, 15 m, Ø 0.25 mm, film 0.25 µm; injector: 250 °C; oven: 40 °C (2 min), 40 °C to 280 °C; carrier gas: He (1.2 mL min⁻¹). High-resolution mass spectra were obtained using a Thermo Scientific Exactive Plus spectrometer equipped with an Orbitrap Mass Analyzer. Measurements were accomplished using an ASAP/APCI source with a corona needle, and a carrier-gas (N_2) temperature of 250 °C. ESI mass spectrometry was performed using HESI source with an auxiliary gas temperature of 50 °C. Gel permeation chromatography was conducted on a Viscotek SECmax system with a refractive index (RI) detector (Viscotek VE3580), both from Malvern. The column was a 30 cm long, linear (2) Phenogel 5 µm with a width of 7.8 mm, heated to 35 °C in a column oven. The column material was porous polystyrene (PS) with a pore diameter of 13 µm. CHCl₃, including 0.5-1.0% EtOH, was used as the solvent with a flow rate of 1.0 mL/min. For calibration, PS standards were utilized. EPR measurements at X-band (9.4 GHz) were carried out using a Bruker ELEXSYS E580 CW EPR spectrometer equipped with an Oxford Instruments helium cryostat (ESR900) and a MercuryiTC temperature controller. The spectral simulations were performed using MATLAB 9.6 (R2019a) and the EasySpin 5.2.25 toolbox.^[4]

Cyclic Voltammetry (CV)

CV experiments were performed under an argon atmosphere with a Metrohm PGSTAT30 potentiostat (Metrohm Autolab B.V., Netherlands) and a three-electrode set-up at room temperature with a scan rate of 50 mV·s⁻¹. Evaluation of the CV experiments was performed using the software Nova 2.0 (Metrohm Autolab B.V., Netherlands). An ESA EE047 glassy carbon electrode (surface area: 7.1 mm²) was used as working electrode. As a reference electrode a RE-7 non aqueous reference electrode, filled with 0.1 mol·L⁻¹ [nBu_4N][PF₆]/0.01 mol·L⁻¹ AgNO₃ THF solution and a silver wire was used. As a counter electrode a platinum wire (surface area: 78.7 mm²) was used. The samples were prepared in a 0.1 mol·L⁻¹ [nBu_4N][PF₆] THF solution with a concentration of 1·10⁻³ mol·L⁻¹.

1.2 Synthesis

Me₂Im^{Me}·B₂pin₂ 3

 B_2pin_2 (2.54 g, 10.0 mmol, 1.0 equiv.) and Me_2Im^{Me} (1.24 g, 10.0 mmol, 1.0 equiv.) were dissolved in toluene (50 mL). After stirring the reaction mixture overnight at room temperature, the solvent was removed under reduced pressure. The residue was suspended in *n*-pentane (20 mL), collected by filtration and dried *in vacuo*.

Yield: 2.75 g (7.27 mmol, 73%) of a colorless solid.

Elemental analysis for C₁₉H₃₆B₂N₂O₄ [378.13 g/mol]: calculated (found) C 60.35 (60.34), H 9.60 (9.78), N 7.41 (7.60).

¹**H NMR** (400 MHz, 25 °C, C₆D₆): δ = 1.19 (s, 6H, NC(CH₃)), 1.29 (s, 24H, pin-CH₃), 3.67 (s, 6H, NCH₃) ppm.

¹³C{¹H} NMR (100 MHz, 25 °C, C_6D_6): δ = 7.6 (NC(CH₃)), 25.6 (pin-CH₃), 32.4 (NCH₃), 79.9 (pin-C_q), 123.1 (NCCN), 168.1 (NCN) ppm.

¹¹B{¹H} NMR (128 MHz, 25 °C, C₆D₆): δ = 1.91 (sp³-B atom), 29.5 (sp²-B atom) ppm.

HRMS-ASAP (m/z): calculated (found) for $C_{19}H_{37}B_2N_2O_4$ [M+H]⁺ 379.2934 (379.2930).

1.3 General Procedures for the Reaction of 3 with Aryl Halides

Method A

In a Young's tap NMR tube $Me_2Im^{Me}\cdot B_2pin_2$ **3** (70.8 mg, 187 µmol, 2.5 equiv.; 3.0 equiv. when using **5I/5Br** as the aryl halide) was dissolved in C_6D_6 (0.7 mL) and the aryl halide (62.4 µmol, 1.0 equiv.) was added at room temperature. The reaction mixture was stirred for 16 h at 50 °C or 80 °C. Afterwards, the products and yields were determined by ¹H NMR spectroscopy and GC/MS with biphenyl as an internal standard.

Method B

This method was performed on a preparative scale: $Me_2Im^{Me}\cdot B_2pin_2$ **3** (531 mg, 1.40 mmol, 2.5 equiv.; 3.0 equiv. when using **5I** as the aryl iodide) was dissolved in benzene (7 mL) and the aryl iodide (467 µmol, 1.0 equiv.) was added at room temperature. The reaction mixture was stirred for 16 h at 50 °C and was then filtered, and the remaining solid was washed with diethyl ether (10 mL). The filtrate was concentrated *in vacuo*, purified by silica-gel column chromatography with *n*-hexane and then an *n*-hexane and ethyl acetate mixture (*n*-hexane/EtOAc =100/1) as eluent. The solvent of the product-containing fraction of the eluent was evaporated *in vacuo*.

2-(4-Methyl-phenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane 4a



The reaction was performed on a preparative scale using method B with 4-iodotoluene **4I** (102 mg, 467 μ mol), which afforded 86.6 mg (397 μ mol, 85%) of **4a** as a colorless solid after workup.

¹**H NMR** (400 MHz, 25 °C, C₆D₆): 1.13 (s, 12H, pin-CH₃), 2.07 (s, 3H, tolyl-CH₃), 7.05 (d, 2H, ${}^{3}J_{H-H} = 7.7$ Hz, aryl-CH_m), 8.11 (d, 2H, ${}^{3}J_{H-H} = 7.7$ Hz, aryl-CH_o) ppm.

¹³C{¹H} NMR (100 MHz, 25 °C, C₆D₆): 21.7 (tolyl-CH₃), 25.0 (pin-CH₃), 83.6 (pin-C_q), 129.0 (aryl-C_m), 135.6 (aryl-C_o) 141.5 (aryl-C_qtolyl) ppm.

¹¹B{¹H} NMR (128 MHz, 25 °C, C₆D₆): 31.2 ppm.

HRMS-ASAP (m/z): Calculated (found) for C₁₃H₂₀BO₂ [M+H]⁺ 219.1551 (219.1548).

The spectroscopic data for 4a match those reported in the literature.^[5, 6]

4-Methyl-1,1'-bipehnyl 4b-H



¹**H NMR** (400 MHz, 25 °C, CDCl₃): δ = 2.40 (s, 3H, C*H*₃), 7.26 (m, 2H, aryl-C*H*), 7.33 (m, 1H, aryl-C*H*), 7.43 (m, 2H, aryl-C*H*), 7.50 (m, 2H, aryl-C*H*), 7.59 (m, 2H, aryl-C*H*) ppm.

¹³C{¹H} NMR (100 MHz, 25 °C, C₆D₆): δ = 21.2 (CH₃), 127.1 (aryl-CH), 127.1 (aryl-CH), 128.8 (aryl-CH), 129.6 (aryl-CH), 137.2 (aryl-C_q), 138.5 (aryl-C_q), 141.3 (aryl-C_q) ppm.

HRMS-ASAP (m/z): calculated (found) for $C_{13}H_{13}$ [M+H]⁺ 169.1012 (169.1008).

The spectroscopic data for 4b-H match those reported in the literature.^[7]



¹**H NMR** (500 MHz, 25 °C, CD₂Cl₂): δ = 2.39 (s, 3H, CH₃), 7.26 (m, 2H, aryl-C*H*), 7.51 (m, 2H, aryl-C*H*) ppm.

¹³C{¹H} NMR (100 MHz, 25 °C, C_6D_6): δ = 21.2 (CH₃), 126.6 (¹J_{C-D} = 24 Hz, aryl-CD), 126.9 (¹J_{C-D} = 24 Hz, aryl-CD), 127.2 (aryl-CH), 128.6 (¹J_{C-D} = 24 Hz, aryl-CD), 129.9 (aryl-CH), 137.6 (aryl-C_q), 138.5 (aryl-C_q), 141.2 (aryl-C_q) ppm.

HRMS-ASAP (m/z): calculated (found) for C₁₃H₈D₅ [M+H]⁺ 174.1326 (174.1320).

The spectroscopic data for 4b match those reported in the literature.^[8]

2-(4-Trifluoromethyl-phenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane 5a



The reaction was performed on a preparative scale using method B with 4-iodobenzotrifluoride **5I** (127 mg, 467 μ mol), which afforded 55.9 mg (205 μ mol, 44%) of **5a** as a pale yellow solid after workup.

¹**H NMR** (400 MHz, 25 °C, C₆D₆): 1.08 (s, 12H, CH₃), 7.37 (d, 2H, ${}^{3}J_{H-H} = 7.6$ Hz, aryl-CH_m), 7.95 (d, 2H, ${}^{3}J_{H-H} = 7.6$ Hz, aryl-CH_o) ppm.

¹³C{¹H} NMR (100 MHz, 25 °C, C_6D_6): 24.9 (CH₃), 84.2 (pin- C_q), 124.7 (¹ J_{C-F} = 272 Hz, CF₃), 124.7 (³ J_{C-F} = 4 Hz, aryl- C_m), 133.2 (² J_{C-F} = 32 Hz, aryl- C_qCF_3), 135.6 (aryl- C_o) ppm.

¹¹B{¹H} NMR (128 MHz, 25 °C, C₆D₆): 30.7 ppm.

¹⁹F{¹H} NMR (376 MHz, 25 °C, C₆D₆): -62.7(s) ppm.

GC/MS: Ret.: 7.27 min; m/z: 272 [M]⁺, 257 [M-CH₃]⁺, 186 [M-C₅H₁₀O]⁺, 173 [M-C₆H₁₁O]⁺.

HRMS-ASAP (m/z): Calculated (found) for C₁₃H₁₇BF₃O₂ [M+H]⁺ 273.1268 (273.1255).

The spectroscopic data for 5a match those reported in the literature.^[9, 10]



4-CF₃-C₆H₄Bpin (219 mg, 805 μ mol, 1.0 equiv.) and Me₂Im^{Me} (100 mg, 805 μ mol, 1.0 equiv.) were dissolved in toluene (5 mL). After stirring the reaction mixture overnight at room temperature, the solvent was removed under reduced pressure. The residue was suspended in *n*-hexane (8 mL), collected by filtration and dried *in vacuo*.

Yield: 218 mg (550 µmol, 68%) of a colorless solid.

Elemental analysis for C₂₀H₂₈BF₃N₂O₂ [396.22 g/mol]: calculated (found) C 60.62 (60.87), H 7.12 (7.23), N 7.07 (7.04).

¹**H NMR** (400 MHz, 25 °C, C₆D₆): δ = 1.12 (s, 6H, NC(C*H*)₃), 1.25 (s, 6H, pin-C*H*₃), 1.39 (s, 6H, pin-C*H*₃), 3.50 (s, 6H, NC*H*₃), 7.68 (m, 2H, aryl-C*H*), 7.96 (s, 2H, aryl-C*H*) ppm.

¹³C{¹H} NMR (125 MHz, 25 °C, C₆D₆): δ = 7.6 (NC(CH₃)), 25.5 (pin-CH₃), 26.5 (pin-CH₃), 32.3 (NCH₃), 79.4 (pin-C_q), 123.7 (NCCN), 123.9 (³J_{CF} = 3Hz, aryl-CH), 126.2 (¹J_{CF} = 271 Hz, CF₃), 127.6 (²J_{CF} = 31 Hz, C_qCF₃), 132.1 (aryl-CH), 160.8 (br, C_qB), 165.7 (NCN) ppm.

¹¹B{¹H} NMR (128 MHz, 25 °C, C₆D₆): δ = 4.13 ppm.

¹⁹F{¹H} NMR (376 MHz, 25 °C, C₆D₆): δ = -61.4 ppm.

HRMS-ASAP (m/z): calculated (found) for C₂₀H₂₈BF₃N₂O₂ [M]⁺ 396.2190 (396.2189).

2-(4-Methoxy-phenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane 6a



The reaction was performed on a preparative scale using method B with 4-iodoanisole **6I** (109 mg, 467 μ mol), which afforded 89.6 mg (383 μ mol, 82%) of **6a** as a pale yellow solid after workup.

¹**H NMR** (400 MHz, 25 °C, C₆D₆): 1.14 (s, 12H, pin-CH₃), 3,24 (s, 3H, OCH₃), 6.83 (m, 2H, ${}^{3}J_{H-H}$ = 8.7 Hz, aryl-CH_m), 8.12 (m, 2H, ${}^{3}J_{H-H}$ = 8.7 Hz, aryl-CH_o) ppm.

¹³C{¹H} NMR (100 MHz, 25 °C, C₆D₆): 25.0 (pin-CH₃), 54.6 (OCH₃), 83.5 (C_q-pin), 113.8 (aryl-C), 137.2 (aryl-C) 162.9 (aryl-C_qOMe) ppm.

¹¹B{¹H} NMR (128 MHz, 25 °C, C₆D₆): 31.1 ppm.

GC/MS: Ret.: 9.01 min; m/z: 234 [M]⁺, 219 [M-CH₃]⁺, 148 [M-C₅H₁₀O]⁺, 134 [M-C₆H₁₁O]⁺.

HRMS-ASAP (m/z): Calculated (found) for $C_{13}H_{20}BO_3$ [M+H]⁺ 235.1500 (235.1489).

The spectroscopic data for **6a** match those reported in the literature.^[5]

2 Mechanistic Investigations

a) Monitoring the RER by EPR spectroscopy

B₂neop₂ (115 μg, 1.00 μmol, 1.0 equiv.) and Me₂Im^{Me} (125 μg, 0.50 μmol, 2.0 equiv.) were dissolved in THF (160 μL) and immediately cooled to -196 °C (liquid N₂). The EPR monitoring was started at -80 °C, and the temperature was slowly raised. A signal was detected at 16.9 °C (see Figure 2, main text).

b) RER in styrene to initiate radical polymerization reaction



In a Schlenk tube, B_2neop_2 (62.5 mg, 277 µmol, 5.0 wt%, based on styrene) and Me_2Im^{Me} (62.5 mg, 554 µmol, 2.0 equiv., based on B_2neop_2) were combined in precooled (0 °C) styrene (1.25 g, 1.40mL, 12.0 mmol). The reaction mixture was allowed to warm slowly to room temperature and was stirred for 16 h. All volatiles were removed under reduced pressure, the residue was dissolved in THF and poured into 50 mL of methanol. The colorless precipitate was analyzed by GPC (see Figure 6, main text).

c) Analyzing the precipitate formed during the boryl transfer reaction

Me₂Im^{Me}·B₂pin₂ **3** (150 mg, 397 µmol, 3.0 equiv.) was dissolved in C₆D₆ (2 mL) and 4iodobenzotrifluoride **5I** (36.0 mg, 132 µmol, 1.0 equiv.) was added at room temperature and the reaction mixture was stirred for 16 h at 50 °C. The precipitate which formed during the reaction was collected by filtration and dried *in vacuo* (45.9 mg). It was dissolved in chloroform/CDCl₃ and analyzed by GC/MS and NMR spectroscopy. While the GC/MS only showed traces of the aryl boronate **5a** and B₂pin₂, the ¹H NMR spectrum additionally revealed the formation of two other species (Figure S1). In the corresponding ¹¹B NMR spectrum, only one significant signal was observed with a chemical shift of 1.77 ppm (Figure S2) which, together with HRMS and X-ray analysis, was assigned to the boronium cation [(Me₂Im^{Me})₂·Bpin]⁺ **7** (see Figure 8, main text).

[(Me₂Im^{Me})₂·Bpin]⁺ I⁻ 7

¹**H NMR** (400 MHz, 25 °C, CDCl₃): 0.99 (s, 12H, pin-C*H*₃), 2,16 (s, 12H, NC(C*H*)₃), 3.83 (s, 12H, NC*H*₃) ppm.

¹¹B{¹H} NMR (128 MHz, 25 °C, CDCl₃): 1.77 ppm.

HRMS-ESI pos (m/z): Calculated (found) for $C_{20}H_{36}BN_4O_2$ [M]⁺ 375.2926 (375.2919). **HRMS-ESI neg** (m/z): Calculated (found) for I [M]⁻ 126.9050 (126.9038).



Figure S1. ¹H NMR spectrum of **7** recorded in CDCl₃ (400 MHz). Peaks marked with squares result from an as yet unidentified species.



Figure S2. ¹¹B{¹H} NMR spectrum of 7 recorded in CDCl₃ (128 MHz).

d) Stoichiometric reaction of Me2Im^{Me} with 4-iodotoluene 4I



 Me_2Im^{Me} (41.7 mg, 33.6 µmol, 1.0 equiv.) and 4-iodobenzotrifluoride **4I** (73.2 mg, 33.6 µmol, 1.0 equiv.) were dissolved in benzene (2 mL) and stirred for 16 h at 80 °C. The precipitate that formed during the reaction was collected by filtration, and the filtrate was concentrated *in vacuo* and purified by silica-gel column chromatography with *n*-hexane as eluent. The solvent of the product-containing fraction of the eluent was evaporated *in vacuo*. The product was identified as the C–C coupling product with the solvent **4b-H** with an isolated yield of 26%.

The precipitate that was formed during the reaction was washed with benzene (5 mL) and dried *in vacuo*. NMR analysis revealed the formation of the imidazolium salt [4-CH₃-C₆H₄- Me_2Im^{Me}]⁺I⁻**8** (Figure S3), which was confirmed by HRMS.

[4-CH₃-Ph-Me₂Im^{Me}]⁺I⁻ 8

¹**H NMR** (400 MHz, 25 °C, CDCl₃): δ = 2.24 (s, 6H, NC(CH₃)), 2.44 (s, 24H, tolyl-CH₃), 3.61 (s, 6H, NCH₃), 7.40 (d, 2H, ³J_{H-H} = 7.9 Hz, aryl-CH_m), 7.59 (d, 2H, ³J_{H-H} = 7.9 Hz, aryl-CH_o) ppm.

¹³C{¹H} NMR (100 MHz, 25 °C, CDCl₃): δ = 9.7 (NC(CH₃)), 21.7 (tolyl-CH₃), 33.9 (NCH₃), 118.7 (aryl-C_{ipso}), 127.1 (NCCN), 130.6 (aryl-C), 130.9 (aryl-C), 143.3. (aryl-C_qtolyl), 143.6 (NCN) ppm.

HRMS-ESI pos (m/z): Calculated (found) for $C_{14}H_{19}N_2$ [M]⁺ 215.1543 (215.1537). **HRMS-ESI neg** (m/z): Calculated (found) for I [M]⁻ 126.9050 (126.9038).



Figure S3. ¹H NMR spectrum recorded in $CDCl_3$ (400 MHz) of the formed residue of the reaction of stoichiometric amounts of the free NHC with 4-iodotoluene **4I** showing the imidazolium salt [4-CH₃-C₆H₄-Me₂Im^{Me}]⁺I⁻ **8**, and an unknown compound (marked with open squares).



Figure S4. Cyclic voltammograms of (a) 4-iodotoluene 4I, (b) Me₂Im^{Me}, and (c) Me₂Im^{Me}·B₂pin₂ 3.

f) Stoichiometric reaction of Me₂Im^{Me} with 4-iodobenzotrifluoride 5I in the presence of TEMPO



In a Schlenk tube, Me_2Im^{Me} (108 mg, 873 µmol, 0.05 equiv., based on styrene) and 4iodotoluene (190 mg, 873 µmol, 113 µl, 0.05 equiv., based on styrene) or 4-bromotoluene (149 mg, 873 µmol, 106 µl, 0.05 equiv., based on styrene), respectively, were combined in styrene (1.82 g, 2.00 mL, 17.5 mmol). The reaction mixture was heated to 80°C and was stirred for 16 h. All volatiles were removed under reduced pressure, and the residue was dissolved in THF and poured into 50 mL of methanol, whereupon a white solid precipitated which was identified as polystyrene.

Control experiment:

In a Schlenk tube, Me₂Im^{Me} (108 mg, 873 µmol, 0.05 equiv., based on styrene) was dissolved in styrene (1.82 g, 2.00 mL, 17.5 mmol). The reaction mixture was heated to 80°C and was stirred for 16 h. All volatiles were removed under reduced pressure, and the residue was dissolved in THF and poured into 50 mL of methanol without any precipitation.

g) Stoichiometric reaction of Me₂Im^{Me} with 4-iodobenzotrifluoride **5I** in the presence of TEMPO



In a Young's tap NMR tube Me_2Im^{Me} (6 mg, 51 µmol, 1.0 equiv.) and TEMPO (8 mg, 51 µmol, 1.0 equiv.) were dissolved in C_6D_6 (0.7 mL) and 4-iodobenzotrifluoride **5I** (14 mg, 7.5 µL, 51 µmol, 1.0 equiv.) was added at room temperature. The reaction mixture was stirred for 16 h at 80 °C. Besides the imidazolium salt [4-CF₃-Ph-Me₂Im^{Me}]⁺I⁻, and traces of amount of the C-C coupling product **5b**, GC/MS analysis indicated the formation of trace of amounts of the coupling product aryl–TEMPO.

h) Boryl transfer reaction in the presence of TEMPO



In a Young's tap NMR tube $Me_2Im^{Me}\cdot B_2pin_2$ **3** (50 mg, 130 µmol, 3.0 equiv.) and TEMPO (7 mg, 44 µmol, 1.0 equiv.) were dissolved in C_6D_6 (0.7 mL) and 4-iodobenzotrifluoride **5I** (12 mg, 6.5 µL, 44 µmol, 1.0 equiv.) was added at room temperature. The reaction mixture was stirred for 16 h at 80 °C. Besides residual starting material **5I**, aryl boronate **5a**, and the C-C coupling product **5b**, GC/MS analysis indicated the formation of the coupling product aryl–TEMPO (Figure S5).



Figure S5. Left: GC/MS TIC of the reaction mixture of **3** and 4-iodobenzotrifluoride **5**I, in the presence of TEMPO in C_6D_6 after 16 h at 80 °C. Right: Mass spectrum of the coupling product aryl–TEMPO.

i) Boryl transfer reaction in styrene to initiate radical polymerization reaction



In a Schlenk tube, $Me_2Im^{Me}\cdot B_2pin_2$ **3** (261 mg, 690 µmol, 3.0 equiv., based on **4-I**) was dissolved in styrene (1.25 g, 1.40 mL, 12.0 mmol) and 4-iodobenzotrifluoride **5I** (63 mg, 34 µL, 230 µmol, 5.0 wt%, based on styrene) was added at room temperature. The reaction mixture was stirred for 16 h at 50 °C. All volatiles were removed under reduced pressure, the residue was dissolved in THF and poured into 50 mL of methanol. The white precipitate was analyzed by GPC (Figure S6).



Figure S6. Size exclusion chromatography (SEC) analysis of polystyrene formed during the boryl transfer reaction using $Me_2Im^{Me} \cdot B_2pin_2 \mathbf{3}$ and 4-iodobenzotrifluoride **5I** (detection of the polymer chains by refractive index detection).

j) Monitoring the boryl transfer reaction by EPR spectroscopy



Via a standard solution, $Me_2Im^{Me}\cdot B_2pin_2$ **3** (1.70 mg, 4.50 µmol, 3.0 equiv.) and 4iodobenzotrifluoride **5I** (408 µg, 1.50 µmol, 1.0 equiv.) were dissolved in benzene (160 µL) at room temperature. The reaction mixture was immediately monitored by EPR spectroscopy at room temperature (Figure S7).



Figure S7. In situ EPR spectrum of the reaction of $Me_2Im^{Me}B_2pin_2$ **3** with 4-iodobenzotrifluoride **5I** in benzene at room temperature.

3 Crystallographic Details

Table S1. Crystal data and structure refinement for $(Me_2Im^{Me})_2 \cdot B_2neop_2 \mathbf{1}$ and $[(Me_2Im^{Me})_2 \cdot Bpin]^+I^- \mathbf{7}$.

Identification code	CCDC 2162556	CCDC 2162556
Empirical formula	$C_{24}H_{44}B_2N_4O_4\cdot 2(C_7H_8)$	$C_{20}H_{36}BIN_4O_2$
Formula weight [g/mol]	658.52	502.24
Temperature [K]	100	100
Wavelength [Å]	0.71073 Mo-K $_{\alpha}$	1.54184 Cu-K _α
Crystal system	Monoclinic	Monoclinic
Space group	P2 ₁ /n	P2/c
Unit cell dimensions	<i>a</i> = 8.4650(4) Å	<i>a</i> = 13.3858(2) Å
	<i>b</i> = 16.1068(8) Å	<i>b</i> = 14.2988(2) Å
	<i>c</i> = 13.6527(6) Å	<i>c</i> = 13.1709(2) Å
	α = 90 °	α = 90°
	$\beta = 95.327(2)^{\circ}$	$\beta = 109.650(2)^{\circ}$
	γ = 90 °	γ = 90°
Volume [A ³]	1853.43(15)	2374.11(7)
Z	4	4
Density (calculated) [g/cm ³]	1.180	1.405
Absorption coefficient [mm ⁻¹]	0.075	10.760
F(000)	716	1032
Θ range [°]	1.960 – 26.093	3.136 – 76.469
No. of reflections collected	24084	26822
No. of unique reflections	3681 [R _{int} = 0.0199]	5002 [R _{int} = 0.0845]
Observed reflections [I>2σ(I)]	3325	4539
Data / restraints / parameters	3681 / 0 / 224	5002 / 78 / 297
GooF	1.060	1.090
Final R indices [I>2σ (I)]	R ₁ = 0.0359, wR ₂ = 0.0929	R ₁ = 0.0367, wR ₂ = 0.0946
R indices (all data)	R ₁ = 0.0401, wR ₂ = 0.0963	R ₁ = 0.0422, wR ₂ = 0.1018
Largest diff. peak and hole [e A ³]	0.458 and -0.181	0.889 and -1.368
Diffractometer	Bruker Smart Apex 2	XtaLAB Synergy

4 Computational Details

Calculations were carried out using the TURBOMOLE V7.2 2017 program suite, a development of the University of Karlsruhe and the Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from http://www.turbomole.com.^[11, 12] Geometry optimizations were performed using (RI-)DFT calculations^[13-16] on an m4 grid employing the M06-2x^[17] functional and the def2-TZVP basis set for boron and def2-SVP basis set for C, H and O atoms.^[18-24] Vibrational frequencies were calculated at the same level with the AOFORCE^[25] module and all structures represented true minima without imaginary frequencies. Energies were calculated on single point calculations of the def2-TZVP/def2-SVP optimized structures using the M06-2X functional and a def2-TZVPP basis set for boron and def2-SVP basis set for C, H and O. Wiberg bond indices^[26] have been evaluated from the DFT ground state electron density.



Figure S8. a) DFT computed (M06-2x//def2-TZVPP(B)/def2-TZVP) B-B dissociation energies and Wiberg bond indices (red) for B_2neop_2 , (Me₂Im)·B₂neop₂ and (Me₂Im)₂·B₂neop₂. b) Calculated SOMO (top) and spin density (bottom) for (Me₂Im)·Bneop.

Cartesian Coordinates for the optimized geometries

Bneop

Energy = -371.858200 h; ZPE = 0.1541425 h; NIMAG = 0

В	-4.1028118	-0.1632682	0.3576554
0	-4.7986817	-1.2106320	-0.1220183
0	-4.6550271	0.9170493	0.9394494
С	-6.2201651	-1.2043028	-0.0316189
Н	-6.6340079	-0.7859705	-0.9647649
Н	-6.5527500	-2.2500471	0.0474338
С	-6.0709494	0.9926836	1.0736460
Н	-6.2882362	1.5797220	1.9785472
Н	-6.4806125	1.5390493	0.2074110
С	-6.7098969	-0.3951609	1.1719140
С	-6.2893207	-1.0800206	2.4761631
Н	-6.7337068	-2.0840119	2.5440368
Н	-5.1975543	-1.1880750	2.5471778
Н	-6.6285019	-0.4954296	3.3438873
С	-8.2295456	-0.2596085	1.1084286
Н	-8.7092408	-1.2488118	1.1541705
Н	-8.6009607	0.3334969	1.9572874
Н	-8.5513074	0.2341655	0.1790061

B₂neop₂

Energy = -743.875771 h; ZPE = 0.3119072 h; NIMAG = 0

в	-4 1486159	0 2247828	0 2074351
0	-4 8436106	-0 7752013	-0 4084934
õ	-4 7796137	1 1468408	0.9910551
č	-6 2398395	-0.8989848	-0 2388341
н	-6 7551597	-0 3675518	-1 0585102
н	-6 4969195	-1 9668478	-0.3225362
C	-6 1745659	1.0000470	1 1996480
н	-6 3862645	1 5100729	2 1937997
н	-6 6824607	1 7197899	0 4519130
Ċ	-6 7090311	-0.3456252	1 1085590
č	-6 1498348	-1 1949003	2 2537063
н	-6 5201654	-2 2284422	2 1821389
Н	-5.0513814	-1.2282411	2.2366538
Н	-6.4613914	-0.7841958	3.2257404
С	-8.2343392	-0.3299086	1.1554305
H	-8.6366301	-1.3498442	1.0607487
Н	-8.5901681	0.0845135	2.1108111
Н	-8.6545796	0.2796479	0.3410290
В	-2.4550999	0.3168350	0.0042943
0	-1.7713018	-0.7774900	-0.4404254
0	-1.8138236	1.4914815	0.2704387
С	-0.3778895	-0.7200245	-0.6623333
Н	-0.1359367	-1.4282608	-1.4705430
Н	0.1505640	-1.0581302	0.2464572
С	-0.4221565	1.6181560	0.0700831
Н	-0.2115190	2.6681421	-0.1880257
Н	0.1030690	1.3956850	1.0158529
С	0.0888297	0.6890997	-1.0334834
С	-0.4948152	1.1019693	-2.3879143
Н	-1.5933554	1.0701753	-2.3843618

Н	-0.1859342	2.1263342	-2.6443591
Н	-0.1402541	0.4276752	-3.1817247
С	1.6136370	0.7334957	-1.0775805
Н	2.0007808	0.0513390	-1.8494598
Н	1.9660188	1.7477077	-1.3187354
Н	2.0523637	0.4406475	-0.1116085

(Me₂lm)⋅Bneop

Energy = -676.727368 h; ZPE = 0.2844116 h; NIMAG = 0

В	-4.3060910	-0.7234789	0.8273420
0	-5.1346127	-1.3043431	-0.1247276
0	-4.7949664	0.2282358	1.7133667
С	-6.4669426	-0.8826142	-0.2476435
Н	-6.5344983	-0.0486815	-0.9731030
Н	-7.0565271	-1.7209642	-0.6551806
С	-6.1261428	0.6618727	1.6209368
Н	-6.4539812	0.9817356	2.6245186
Н	-6.1911730	1.5455038	0.9567677
С	-7.0583987	-0.4298378	1.0891280
С	-7.1077032	-1.6056109	2.0682817
Н	-7.5156633	-1.2828999	3.0380734
Н	-7.7501460	-2.4082665	1.6754749
Н	-6.1065864	-2.0258524	2.2421956
С	-8.4539510	0.1447134	0.8673597
Н	-9.1273122	-0.6182320	0.4482322
Н	-8.8884369	0.4911982	1.8173311
Н	-8.4309275	0.9972859	0.1714480
С	-2.8638136	-1.1587229	0.9221091
Ν	-2.2113673	-2.1324710	0.1590345
Ν	-1.8803045	-0.6830748	1.7954497
С	-0.8928325	-2.2297998	0.5564875
Н	-0.2055958	-2.9314762	0.0943809
С	-0.6890595	-1.3389524	1.5573699
Н	0.2100866	-1.1173978	2.1239862
С	-2.8358975	-2.9142728	-0.8744884
Н	-3.2296856	-2.2674212	-1.6719763
Н	-2.0905919	-3.6001452	-1.2958521
Н	-3.6794619	-3.4941804	-0.4712919
С	-2.0740793	0.3872778	2.7370906
Н	-1.1294850	0.5669784	3.2652752
Н	-2.8581739	0.1335458	3.4647181
Н	-2.3849788	1.3090487	2.2224056

(Me₂Im)·B₂neop₂

Energy = -1048.686477 h; ZPE = 0.4424407 h;NIMAG = 0

В	-4.1846318	0.0121296	0.3932282
0	-4.7741034	-1.3126379	0.3137011
0	-4.7223890	0.8444620	1.4543062
С	-6.1636430	-1.3326892	0.3921774
Н	-6.6188151	-0.8602574	-0.5126294
Н	-6.5078929	-2.3824777	0.4184599
С	-6.1115671	0.8398301	1.5431506
Н	-6.4176455	1.4187461	2.4330520
Н	-6.5672331	1.3392496	0.6531076
С	-6.6915682	-0.5805031	1.6230624
С	-6.2032418	-1.2678360	2.8980456
Н	-6.5914850	-2.2967767	2.9584291
Н	-5.1064893	-1.3073644	2.9102052

Н	-6.5433430	-0.7188636	3.7900460
С	-8.2144945	-0.5225483	1.5869074
Н	-8.6465117	-1.5351360	1.6180719
Н	-8.6047595	0.0355123	2.4522902
Н	-8.5759015	-0.0268218	0.6717012
В	-2.4619464	0.0064042	0.3233449
0	-1.8079377	-1.0023864	-0.3492097
0	-1.7572425	1.1120347	0.7463163
С	-0.4292145	-0.9236516	-0.6328091
Н	-0.2391438	-1.4871210	-1.5614572
Н	0.1444469	-1.4127398	0.1743941
С	-0.3771626	1.2464694	0.4917684
Н	-0.1478178	2.3221486	0.4133914
Н	0.1989975	0.8475966	1.3453825
С	0.0405294	0.5235693	-0.7902343
С	-0.6323324	1.1702800	-2.0051664
Н	-1.7296940	1.1558421	-1.9202877
Н	-0.3156596	2.2193198	-2.1085994
Н	-0.3580847	0.6378101	-2.9287150
С	1.5583440	0.5639022	-0.9398992
Н	1.8758538	0.0185845	-1.8416940
Н	1.9142501	1.6013612	-1.0315323
Н	2.0580774	0.1076131	-0.0719316
С	-4.4499798	0.7984600	-1.0828894
Ν	-4.4295647	0.2288227	-2.3067003
Ν	-4.3892256	2.1287676	-1.3049975
С	-4.3762949	1.1924767	-3.2909313
Н	-4.3559199	0.9431998	-4.3468788
С	-4.3506710	2.3948613	-2.6571562
Н	-4.3032645	3.4057291	-3.0492450
С	-4.3914116	-1.2091424	-2.5466938
Н	-3.6468381	-1.6610803	-1.8815398
Н	-5.3703169	-1.6571247	-2.3364480
Н	-4.1250330	-1.3704243	-3.5976442
С	-4.3009595	3.1370500	-0.2550318
Н	-5.2632991	3.2335895	0.2620831
Н	-4.0316075	4.0909481	-0.7229474
Н	-3.5396983	2.8292522	0.4711656

(Me₂lm)₂·B₂neop₂ Energy = -1353.506390 h; ZPE = 0.5724607 h; NIMAG = 0

В	-4.1884250	0.1830642	0.0416949
0	-4.7286097	-1.1819222	0.0331777
0	-4.7201388	0.9684830	1.1614423
С	-6.1140926	-1.2615981	0.1597741
Н	-6.6184813	-0.8193297	-0.7307053
Н	-6.4140120	-2.3250402	0.2088648
С	-6.1053351	0.9171640	1.3059039
Н	-6.3970633	1.4794710	2.2123642
Н	-6.6115751	1.4042845	0.4401049
С	-6.6184491	-0.5270356	1.4109849
С	-6.0340556	-1.1863604	2.6602500
Н	-6.3620396	-2.2353620	2.7386958
Н	-4.9359579	-1.1662605	2.6186418
Н	-6.3594567	-0.6573340	3.5703535
С	-8.1422488	-0.5411068	1.4505030
Н	-8.5239658	-1.5722039	1.5158944
Н	-8.5165448	0.0116847	2.3264277
Н	-8.5701974	-0.0773354	0.5476288

В	-2.4305585	0.1765978	0.0443769
0	-1.8989092	-0.6087813	-1.0754277
0	-1.8904683	1.5416198	0.0528389
С	-0.5137347	-0.5573582	-1.2200547
Н	-0.2220684	-1.1196473	-2.1265458
H	-0.0073523	-1.0444290	-0.3543110
С	-0.5050082	1.6214052	-0.0739259
Ĥ	-0 2051752	2 6848703	-0 1230479
н	-0.0004745	1 1791672	0 8164867
c	-0.0007589	0 8868870	-1 3252083
c	-0 5854209	1 5461538	-2 5743804
й	-0 2575350	2 5951810	-2 6528933
н	-0.2601361	1 0171//8	-2.0020000
ц	1 6835121	1.5250650	2 5325800
\hat{c}	1 5230333	0.0011058	1 36/0670
ц	1.0200000	0.3011030	2 2400365
ц Ц	1.0972407	1 022220	-2.2409505
	1.9040391	1.9322303	-1.4304302
	1.9511712	0.4374020	-0.4021400
N	-4.4379710	0.9430924	-1.4000339
IN N	-4.4107240	0.3733731	1 620/006
	-4.4000030	2.2777030	-1.0304000
	-4.3393077	1.0046004	-3.0200306
	-4.200/301	1.0010334	-4.0/30/22
	-4.3307 147	2.5391500	-2.9900000
	-4.2017302	3.5510404	-3.3790901
	-4.3479039	-1.0400204	-2.9241923
	-4.3293033	-1.3003347	-1.9722040
	-0.2210704	-1.3400031	-3.5212090
П	-3.4230159	-1.2005094	-3.4749598
	-4.3506340	3.3249141	-0.0312340
п	-5.2529099	3.9499440	-0.0924114
н	-3.456/846	3.9368987	-0.8043563
Н	-4.2778982	2.8491131	0.3506148
	-2.1608539	-0.5840292	1.4929018
N	-2.2120533	-1.9181053	1.7245528
N	-2.2079531	-0.015/134	2.7221639
C	-2.2817654	-2.1794891	3.0766633
C	-2.2681992	-2.9652617	0.7173140
C	-2.2789458	-0.9787805	3.7061066
C	-2.2708343	1.4082865	3.0102472
н	-2.3366209	-3.1913805	3.4651882
н	-2.3411480	-2.4894701	-0.2645235
н	-2.3315368	-0.7219684	4.7591508
н	-2.2897420	1.9459802	2.0583176
Н	-3.1955947	1.6200830	3.5612618
Н	-1.3970383	1.7057570	3.6070886
Н	-1.3658683	-3.5902293	0.7783256
Н	-3.1619738	-3.5773074	0.8906051

5 NMR Spectra



Figure S9. ¹H NMR spectrum of 3 recorded in C₆D₆ (400 MHz).



Figure S10 ¹¹B NMR spectrum (160 MHz) of $Me_2Im^{Me} \cdot B_2pin_2$ **20** recorded in d_8 -toluene at 25 °C (top) and 0 °C (bottom).



Figure S11. ${}^{13}C{}^{1}H$ NMR spectrum of 3 recorded in C_6D_6 (100 MHz).





Figure S13. ¹H NMR spectrum of 4a recorded in C₆D₆ (400 MHz).



Figure S14. ¹³C{¹H} NMR spectrum of 4a recorded in C₆D₆ (100 MHz).



Figure S16. ¹H NMR spectrum of 4b recorded in CD₂Cl₂ (400 MHz).



Figure S17. ¹³C{¹H} NMR spectrum of 4b recorded in CD₂Cl₂ (100 MHz).



Figure S18. ¹H NMR spectrum of 4b-H recorded in C₆D₆ (400 MHz).



Figure S19. $^{13}C\{^{1}H\}$ NMR spectrum of 4b-H recorded in CDCl3 (100 MHz).



Figure S20. ¹H NMR spectrum of **5a** recorded in C_6D_6 (400 MHz).



Figure S21. ¹³C{¹H} NMR spectrum of **5a** recorded in C_6D_6 (100 MHz).



Figure S22. ¹¹B{¹H} NMR spectrum of **5a** recorded in C_6D_6 (128 MHz).



Figure S23. $^{19}F\{^{1}H\}$ NMR spectrum of 5a recorded in $C_6D_6\,(376$ MHz).



Figure S24. ¹H NMR spectrum of **5a-ADD** recorded in C₆D₆ (400 MHz).



Figure S25. ¹³C{¹H} NMR spectrum of **5a-ADD** recorded in C_6D_6 (100 MHz).



Figure S26.¹¹B{¹H} NMR spectrum of **5a-ADD** recorded in C_6D_6 (128 MHz).



Figure S27. $^{19}F{^1H}$ NMR spectrum of **5a-ADD** recorded in C₆D₆ (376 MHz).



Figure S28. ¹H NMR spectrum of 6a recorded in C₆D₆ (400 MHz).



Figure S29. ¹³C{¹H} NMR spectrum of **6a** recorded in C_6D_6 (100 MHz).



Figure S30. ¹¹B{¹H} NMR spectrum of **6a** recorded in C_6D_6 (128 MHz).

6 References

- [1] F. Graf, L. Hupfer, **1981**, *DE2940709A1*.
- [2] A. J. Arduengo III, **1991**, US5077414.
- [3] A. J. Arduengo III, H. V. R. Dias, R. L. Harlow, M. Kline, J. Am. Chem. Soc. 1992, 114, 5530-5534.
- [4] S. Stoll, A. Schweiger, J. Magn. Reson. 2006, 178, 42-55.
- [5] M. Murata, T. Oyama, S. Watanabe, Y. Masuda, J. Org. Chem. 2000, 65, 164-168.
- [6] A. Wolan, M. Zaidlewicz, Org. Biomol. Chem. 2003, 1, 3274-3276.
- [7] T. Kawamoto, A. Sato, I. Ryu, *Org. Lett.* **2014**, *16*, 2111-2113.
- [8] Y. Wu, P. Y. Choy, F. Y. Kwong, Org. Biomol. Chem. 2014, 12, 6820-6823.
- [9] J.-Y. Cho, C. N. Iverson, M. R. Smith, J. Am. Chem. Soc. 2000, 122, 12868-12869.
- [10] T. Ishiyama, J. Takagi, K. Ishida, N. Miyaura, N. R. Anastasi, J. F. Hartwig, J. Am. Chem. Soc. 2002, 124, 390-391.
- [11] F. Furche, R. Ahlrichs, C. Hättig, W. Klopper, M. Sierka, F. Weigend, *WIREs Comput. Mol. Sci.* **2014**, *4*, 91-100.
- [12] R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.* **1989**, *162*, 165-169.
- [13] M. Häser, R. Ahlrichs, J. Comput. Chem. **1989**, *10*, 104-111.
- [14] O. Treutler, R. Ahlrichs, J. Chem. Phys. 1995, 102, 346-354.
- [15] M. Von Arnim, R. Ahlrichs, J. Comput. Chem. 1998, 19, 1746-1757.
- [16] F. Weigend, *Phys. Chem. Chem. Phys.* **2002**, *4*, 4285-4291.
- [17] M. Sierka, A. Hogekamp, R. Ahlrichs, *J. Chem. Phys.* **2003**, *118*, 9136-9148.
- [18] Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215-241.
- [19] A. Schäfer, H. Horn, R. Ahlrichs, J. Chem. Phys. 1992, 97, 2571-2577.
- [20] A. Schäfer, C. Huber, R. Ahlrichs, J. Chem. Phys. 1994, 100, 5829-5835.
- [21] K. Eichkorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett.* **1995**, *242*, 652-660.
- [22] K. Eichkorn, F. Weigend, O. Treutler, R. Ahlrichs, *Theor. Chem. Acc.* **1997**, *97*, 119-124.
- [23] F. Weigend, *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057-1065.
- [24] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297-3305.
- [25] P. Deglmann, K. May, F. Furche, R. Ahlrichs, *Chem. Phys. Lett.* **2004**, 384, 103-107.
- [26] K. B. Wiberg, *Tetrahedron* **1968**, *24*, 1083-1096.