

A New Route to Organoboron Polymers via Highly Selective Polymer Modification Reactions

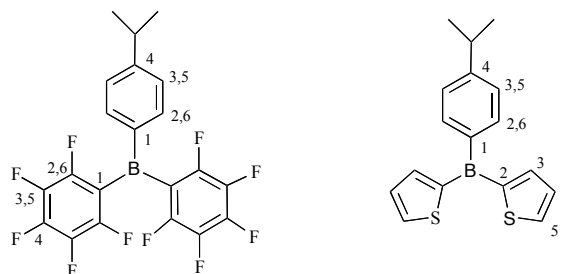
Yang Qin, Guanglou Cheng, Obianuju Achara, Kshitij Parab, and Frieder Jäkle*

Department of Chemistry, Rutgers University-Newark, 73 Warren Street, Newark, NJ 07102

Supplementary Material

The labeling schemes on the right are used for ^1H and ^{13}C NMR assignments.

The abbreviations Ph, Th, and Pf are used for phenyl, 2-thienyl, and pentafluorophenyl, respectively.



Synthesis and Spectroscopic Data of Cumene Model Compounds

Synthesis of 4-Trimethylsilylcumene¹. 4-Bromocumene (10.44 g, 52.4 mmol) was dissolved in 200 ml diethyl ether at 0 °C and *n*-BuLi (36 ml, 1.6M in hexanes, 58 mmol) was added dropwise. The mixture was allowed to warm to room temperature, stirred for 2 h and then cooled down to -78 °C. Neat Me₃SiCl (8.6 ml, 68 mmol) was added dropwise, and the mixture was warmed to room temperature, stirred overnight, and then poured into ice water containing 1% NaOH. After standard workup and removal of all volatile components under vacuum at room temperature, the product was distilled at 43 °C under high vacuum. 4-Trimethylsilylcumene was obtained as a colorless liquid (7.7 g, 76%). ^1H NMR (399.952 MHz, C₆D₆): δ = 7.47 (d, $^3J_{\text{HH}}$ = 8.0 Hz, 2H, Ph-H2,6), 7.16 (d, $^3J_{\text{HH}}$ = 8.0 Hz, 2H, Ph-H3,5), 2.73 (septet, $^3J_{\text{HH}}$ = 7.2 Hz, 1H, CH[CH₃]₂), 1.16 (d, $^3J_{\text{HH}}$ = 7.2 Hz, 6H, CH[CH₃]₂), 0.24 (s, 9H, Si[CH₃]₃); ^{13}C NMR (100.564 MHz, C₆D₆): δ = 149.6 (Ph-C4), 137.3 (Ph-C1), 133.8 (Ph-C2,6), 126.3 (Ph-C3,5), 34.4 (CH[CH₃]₂), 24.1 (CH[CH₃]₂), -0.9 (Si[CH₃]₃); ^{29}Si NMR (79.4 MHz, C₆D₆): δ = -4.3; GC-MS (*t* = 5.7 min): *m/z*: 192 [*M*⁺], 177 [*M*⁺-CH₃].

Synthesis of 4-Dibromoborylcumene. A solution of BBr₃ (4.85 g, 19.4 mmol) in 5 ml CH₂Cl₂ was added dropwise to a solution of 4-trimethylsilylcumene (3.38 g, 17.6 mmol) in 10 ml CH₂Cl₂. The reaction mixture was stirred for 2 h, and all volatile material was subsequently

removed under reduced pressure (10^{-3} torr). The crude product was distilled at 56 °C under high vacuum to give 4-dibromoborylcumene as a colorless liquid with a yield of 4.88 g (96%). ^1H NMR (399.952 MHz, C_6D_6): δ = 8.08 (d, $^3J_{\text{HH}}$ = 8.0 Hz, 2H, Ph-H2,6), 6.92 (d, $^3J_{\text{HH}}$ = 8.0 Hz, 2H, Ph-H3,5), 2.53 (heptet, $^3J_{\text{HH}}$ = 7.2 Hz, 1H, $\text{CH}[\text{CH}_3]_2$), 0.99 (d, $^3J_{\text{HH}}$ = 7.2 Hz, 6H, $\text{CH}[\text{CH}_3]_2$); ^1H NMR (399.952 MHz, CDCl_3): δ = 8.07 (d, $^3J_{\text{HH}}$ = 8.0 Hz, 2H, Ph-H2,6), 7.23 (d, $^3J_{\text{HH}}$ = 8.0 Hz, 2H, Ph-H3,5), 2.87 (heptet, $^3J_{\text{HH}}$ = 7.2 Hz, 1H, $\text{CH}[\text{CH}_3]_2$), 1.19 (d, $^3J_{\text{HH}}$ = 7.2 Hz, 6H, $\text{CH}[\text{CH}_3]_2$); ^{13}C NMR (100.564 MHz, C_6D_6): δ = 157.2 (Ph-C4), 138.5 (Ph-C2,6), 126.6 (Ph-C3,5), 34.6 ($\text{CH}[\text{CH}_3]_2$), 23.3 ($\text{CH}[\text{CH}_3]_2$), Ph-C1 not observed; ^{11}B NMR (160.370 MHz, C_6D_6): δ = 56 ($w_{1/2}$ = 300 Hz); EI-MS (%): m/z : 290 [M^+] (40), 275 [$\text{M}^+ - \text{CH}_3$] (100); elemental analysis: calcd. C 37.30 H 3.83; found C 38.06 H 3.85.

Synthesis of 4-Diethoxyborylcumene. Neat Me_3SiOEt (0.65 ml, 4.2 mmol) was added dropwise to a solution of 4-dibromoborylcumene (0.50 g, 1.73 mmol) in CH_2Cl_2 (10 ml) at room temperature. The mixture was stirred for 1 d, and all volatile material was subsequently removed under reduced pressure (10^{-3} torr). 4-Diethoxyborylcumene was obtained as a colorless liquid in a yield of 0.37 g (98%) with >95% spectroscopic purity as confirmed by ^1H NMR analysis. ^1H NMR (399.952 MHz, C_6D_6): δ = 7.75 (d, $^3J_{\text{HH}}$ = 8.0 Hz, 2H, Ph-H2,6), 7.17 (d, $^3J_{\text{HH}}$ = 8.0 Hz, 2H, Ph-H3,5), 4.02 (quartet, $^3J_{\text{HH}}$ = 7.2 Hz, 4H, OCH_2CH_3), 2.73 (heptet, $^3J_{\text{HH}}$ = 7.2 Hz, 1H, $\text{CH}[\text{CH}_3]_2$), 1.16 (d, $^3J_{\text{HH}}$ = 7.2 Hz, 6H, $\text{CH}[\text{CH}_3]_2$), 1.14 (t, $^3J_{\text{HH}}$ = 7.2 Hz, 6H, OCH_2CH_3); ^{13}C NMR (100.564 MHz, C_6D_6): δ = 150.4 (Ph-C4), 134.3 (Ph-C2,6), 131.0 (br, Ph-C1), 126.0 (Ph-C3,5), 60.2 (OCH_2CH_3), 34.5 ($\text{CH}[\text{CH}_3]_2$), 24.0 ($\text{CH}[\text{CH}_3]_2$), 17.7 (OCH_2CH_3); ^{11}B NMR (160.370 MHz, C_6D_6): δ = 28 ($w_{1/2}$ = 450 Hz); GC-MS (t = 7.21 min): m/z : 220 [M^+], 205 [$\text{M}^+ - \text{CH}_3$], 175, 135; (due to partial hydrolysis on the GC-MS column an additional band for the boroxin ($i\text{PrPhBO}$)₃ is observed at a higher retention time of 14.8 min); elemental analysis: calcd. C 70.94 H 9.62; found C 69.98 H 9.50.

Synthesis of 4-Bis(4'-bromobutoxy)borylcumene. A solution of THF (1.6 ml, 20 mmol) in 5 ml CH_2Cl_2 was added dropwise to a solution of 4-dibromoborylcumene (0.25 g, 0.86 mmol) in CH_2Cl_2 (10 ml) at room temperature and the mixture was kept stirring for 2 h. All volatile material was removed under reduced pressure (10^{-3} torr). Distillation of the crude product at 90 °C under high vacuum gave 0.32 g (86%) 4-bis(4'-bromobutoxy)borylcumene as a colorless liquid. ^1H NMR (399.952 MHz, C_6D_6): δ = 7.70 (d, $^3J_{\text{HH}}$ = 8.0 Hz, 2H, Ph-H2,6), 7.20 (d, $^3J_{\text{HH}}$ = 8.0 Hz, 2H, Ph-H3,5), 3.84 (t, $^3J_{\text{HH}}$ = 6.4 Hz, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$), 2.96 (t, $^3J_{\text{HH}}$ = 6.4 Hz, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$), 2.73 (septet, $^3J_{\text{HH}}$ = 7.2 Hz, 1H, $\text{CH}[\text{CH}_3]_2$), 1.62, 1.47 (m, 8H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$), 1.16 (d, $^3J_{\text{HH}}$ = 7.2 Hz, 6H, $\text{CH}[\text{CH}_3]_2$); ^{13}C NMR (100.564 MHz, C_6D_6): δ = 150.7 (Ph-C4), 134.3 (Ph-C2,6), 131.0 (br, Ph-C1), 126.1 (Ph-C3,5), 63.6 ($\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$), 34.5 ($\text{CH}[\text{CH}_3]_2$), 33.5 ($\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$), 30.4, 29.6 ($\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$), 24.0 ($\text{CH}[\text{CH}_3]_2$); ^{11}B NMR (160.370 MHz, C_6D_6): δ = 28 ($w_{1/2}$ = 550 Hz); GC-MS (t = 12.2 min): m/z : 434 [M^+], 419 [$\text{M}^+ - \text{CH}_3$], 233, 205, 135, 55 (due to partial hydrolysis on the GC-MS column an additional band for the boroxin ($i\text{PrPhBO}$)₃ is observed at a higher retention time of 14.8 min); elemental analysis: calcd. C 47.05 H 6.27; found C 46.65 H 6.46.

Synthesis of 4-(Pinacolatoboryl)cumene. A solution of pinacol (0.16 g, 1.36 mmol) in 10 ml CH_2Cl_2 was added dropwise to a solution of 4-diethoxyborylcumene (0.30 g, 1.36 mmol) in 10 ml CH_2Cl_2 and the mixture was stirred at room temperature for 48 h. All volatile material was removed under vacuum and the remaining solid was sublimed under high vacuum at 50-60 °C to give pinacolatoborylcumene as a white solid (0.20 g, 59% yield). ^1H NMR (499.893 MHz, CDCl_3) δ = 7.76 (d, $^3J_{\text{HH}}$ = 8.5 Hz, 2H, Ph-H2,6), 7.25 (d, $^3J_{\text{HH}}$ = 8.5 Hz, 2H, Ph-H3,5), 2.92

(septet, $^3J_{\text{HH}} = 6.5$ Hz, 1H, $\text{CH}[\text{CH}_3]_2$), 1.34 (s, 12H, $\text{O}[\text{CH}_3]_2\text{CC}[\text{CH}_3]_2\text{O}$), 1.26 (d, $^3J_{\text{HH}} = 6.5$ Hz, 6H, $\text{CH}[\text{CH}_3]_2$); ^{13}C NMR (125.698 MHz, CDCl_3): $\delta = 152.5$ (Ph-C4), 135.2 (Ph-C2,6), 126.1 (Ph-C3,5), 83.8 ($\text{O}[\text{CH}_3]_2\text{CC}[\text{CH}_3]_2\text{O}$), 34.6 ($\text{CH}[\text{CH}_3]_2$), 25.1 ($\text{O}[\text{CH}_3]_2\text{CC}[\text{CH}_3]_2\text{O}$), 24.1 ($\text{CH}[\text{CH}_3]_2$), Ph-C1 was not resolved; ^{11}B NMR (160.386 MHz, CDCl_3): $\delta = 31$ ($w_{1/2} = 320$ Hz); GC-MS ($t = 8.1$ min): m/z : 246 [M^+], 231 [$\text{M}^+ - \text{CH}_3$], 203, 160, 147, 131, 105; elemental analysis: calcd. C 73.19 H 9.42; found C 73.28 H 9.75.

Synthesis of 4-Bis(2-thienyl)borylcumene. To a solution of 4-dibromoborylcumene (1.00 g, 3.45 mmol) in CH_2Cl_2 (10 ml) was added dropwise a solution of 2-trimethylstannylthiophene (1.70 g, 6.90 mmol) in CH_2Cl_2 (10 ml). The mixture was stirred at room temperature for 2 h, and all volatile material was subsequently removed under vacuum. High vacuum distillation (145 °C, 10^{-3} torr) gave compound **M-BTh** as colorless viscous oil (0.88 g, 86%). ^1H NMR (499.893 MHz, CDCl_3): $\delta = 8.05$ (d, $^3J_{\text{HH}} = 4.8$ Hz, 2H, Th-H3), 7.97 (d, $^3J_{\text{HH}} = 3.5$ Hz, 2H, Th-H5), 7.90 (d, $^3J_{\text{HH}} = 8.0$ Hz, 2H, Ph-H2,6), 7.48 (m, 4H, Th-H4 & Ph-H3,5), 3.15 (septet, $^3J_{\text{HH}} = 7.0$ Hz, 1H, $\text{CH}[\text{CH}_3]_2$), 1.49 (d, $^3J_{\text{HH}} = 7.0$ Hz, 6H, $\text{CH}[\text{CH}_3]_2$); ^{13}C NMR (125.698 MHz, CDCl_3): $\delta = 151.8$ (Ph-C4), 145.2 (br., Th-C2), 142.5 (Th-C3), 140.8 (br., Ph-C1), 137.4 (Ph-C2,6), 137.1 (Th-C5), 129.1 (Th-C4), 125.7 (Ph-C3,5), 34.4 ($\text{CH}[\text{CH}_3]_2$), 24.1 ($\text{CH}[\text{CH}_3]_2$); ^{11}B NMR (128.286 MHz, CDCl_3): $\delta = 55$ ($w_{1/2} = 1000$ Hz); GC-MS ($t = 11.5$ min): m/z : 296 [M^+], 281 [$\text{M}^+ - \text{CH}_3$], 253, 177.

Synthesis of 4-Bis(pentafluorophenyl)borylcumene.^{2,3} A solution of $[\text{CuC}_6\text{F}_5]_4(\text{toluene})_2$ (1.00 g, 0.90 mmol) in CH_2Cl_2 (10 ml) was added dropwise to a solution of 4-dibromoborylcumene (0.50 g, 1.73 mmol) in 10 ml CH_2Cl_2 at -78 °C. The mixture was kept stirring for 1 h at -78 °C and then allowed to slowly warm to room temperature. A solid precipitate (CuBr) formed and was removed by filtration through a fritted glass disk. All volatile material was removed under reduced pressure (10^{-3} torr) to give a sticky white solid. The spectroscopic purity of the crude product was estimated to ca. 95% by ^1H and ^{19}F NMR analysis. Distillation of the crude product at 100 °C under high vacuum gave a colorless viscous liquid that gradually solidified at low temperature (0.60 g, 75%). ^1H NMR (399.952 MHz, C_6D_6): $\delta = 7.61$ (d, $^3J_{\text{HH}} = 8.0$ Hz, 2H, Ph-H2,6), 7.13 (d, $^3J_{\text{HH}} = 8.0$ Hz, 2H, Ph-H3,5), 2.63 (heptet, $^3J_{\text{HH}} = 7.2$ Hz, 1H, $\text{CH}[\text{CH}_3]_2$), 1.05 (d, $^3J_{\text{HH}} = 7.2$ Hz, 6H, $\text{CH}[\text{CH}_3]_2$); ^{13}C NMR (100.564 MHz, C_6D_6): $\delta = 159.4$ (Ph-C4), 146.5 (dm, $^1J_{\text{CF}} = 250$ Hz, Ph-C2,6), 142.9 (dm, $^1J_{\text{CF}} = 250$ Hz, Ph-C4), 140.6 (Ph-C2,6), 137.7 (dm, $^1J_{\text{CF}} = 250$ Hz, Ph-C3,5), 127.0 (Ph-C3,5), 114.1 (m, Ph-C1), 34.9 ($\text{CH}[\text{CH}_3]_2$), 23.3 ($\text{CH}[\text{CH}_3]_2$), Ph-C1 not observed; ^{19}F NMR (376.263 MHz, C_6D_6): $\delta = -130.4$ (dd, $^3J_{\text{FF}} = 23.0$ Hz, $^4J_{\text{FF}} = 9.2$ Hz, 4F, Ph-F2,6), -149.3 (t, $^3J_{\text{FF}} = 23.0$ Hz, 2F, Ph-F4), -161.3 (dt, $^3J_{\text{FF}} = 23.0$ Hz, $^4J_{\text{FF}} = 9.2$ Hz, 4F, Ph-F3,5); ^{11}B NMR (160.370 MHz, C_6D_6): $\delta = 62$ ($w_{1/2} = 1,100$ Hz); GC-MS ($t = 10.1$ min): m/z : 464 [M^+], 449 [$\text{M}^+ - \text{CH}_3$], 326 [$\text{M}^+ - \text{cumene-F}$], 277; elemental analysis: calcd. F 40.93; found F 40.46.

Additional References

- (1) Eaborn, C. *J. Chem. Soc.* **1956**, 4858.
- (2) For the related phenylbis(pentafluorophenyl)borane see: Deck, P. A.; Beswick, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 1772.
- (3) For the reactivity of $[\text{CuC}_6\text{F}_5]_4(\text{toluene})_2$ toward boron halides see: Sundararaman, A.; Jäkle, F. *J. Organomet. Chem.* **2003**, *681*, 134.