Supporting Information

Synthesis, Structure, and Reaction of 1-Alkynyl(aryl)- $\text{B}(\text{F}_4)^-$ -bromanes

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Preparation of Difluoro[4-(trifluoromethyl)phenyl]- $\text{B}(\text{F}_4)^-$ -bromane 1. Bromine trifluoride (952 mg, 6.95 mmol) was frozen in a PFA tube at -78°C under argon. Under intensive magnetic stirring, cold dichloromethane (5.8 mL, -78°C) was added slowly. After dropwise addition of cold MeCN (571 mg, 13.9 mmol, -40°C), a slightly yellow solution resulted. Dry NaF (58 mg, 1.4 mmol) was added followed by the dropwise transfer of a cold solution (-78°C) of [4-(trifluoromethyl)phenyl]-trimethylsilane (1.8 g, 8.3 mmol) in dichloromethane (2.9 mL) at -78°C . The mixture was gradually warmed to -25°C and a white precipitate was removed. The solvent was evaporated under reduced pressure to give a yellow solid, which was washed with pentane (each 3 mL, three times). The yellow solid was recrystallized from dichloromethane-pentane (1:2) at -78°C to give difluoro[4-(trifluoromethyl)phenyl]- $\text{B}(\text{F}_4)^-$ -bromane **1** (1.3 g, 72%).¹ ^1H NMR (400 MHz, CD_3CN) δ 8.21 (d, $J = 8.7$ Hz, 2H), 7.97 (d, $J = 8.7$ Hz, 2H).

General Procedure for the Synthesis of 1-Alkynyl(aryl)- $\text{B}(\text{F}_4)^-$ -bromanes 2. A Typical Example (Table 1, Entry 6): (3, 3-Dimethyl-1-butynyl)[4-(trifluoromethyl)phenyl](tetrafluoroborato)- $\text{B}(\text{F}_4)^-$ -bromane **2f.** To a stirred solution of trimethyl(3, 3-dimethyl-1-butynyl)tin (63 mg, 0.26 mmol) in dichloromethane (1.1 mL) in a PFA tube was added dropwise a solution of difluoro[4-(trifluoromethyl)phenyl]- $\text{B}(\text{F}_4)^-$ -bromane **1** (101 mg, 0.39 mmol) in dichloromethane (0.4 mL) and then $\text{BF}_3\cdot\text{Et}_2\text{O}$ (110 mg, 0.78 mmol) at -78°C under argon and the solution was stirred for 3 h. After addition of a saturated aqueous solution of NaBF_4 (0.72 mL, 5.1 mmol), the mixture was gradually warmed to -5°C and then cooled to -50°C . After separation and filtration of the organic phase, dichloromethane was evaporated under an aspirator vacuum to give an oil, which was washed several times with hexane by decantation at room temperature to give the $\text{B}(\text{F}_4)^-$ -bromane **2f** (89.7 mg, 89%) as an oil (93% purity). IR (neat) 3105, 2979, 2208, 1590, 1480, 1407, 1324, 1180-990, 838, 770 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.26 (d, $J = 8.8$ Hz, 2H), 7.94 (d, $J = 8.8$ Hz, 2H), 1.32 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ 138.6, 135.2 (q, $^2J_{\text{CF}} = 33.6$ Hz), 130.0 (q, $^3J_{\text{CF}} = 3.8$ Hz), 129.2, 122.4 (q, $^1J_{\text{CF}} = 273.4$ Hz), 109.6, 38.5, 29.7, 29.1; FAB MS m/z 305 $[(\text{M}-\text{BF}_4)^+]$; HRMS (FAB) calcd for $\text{C}_{13}\text{H}_{13}\text{BrF}_3$ $[(\text{M}-\text{BF}_4)^+]$ 305.0153, found 305.0178.

(1-Hexynyl)[4-(trifluoromethyl)phenyl](tetrafluoroborato)- $\text{B}(\text{F}_4)^-$ -bromane 2a: oil (96% purity); IR (neat) 3105, 2963, 2875, 2207, 1591, 1406, 1324, 1200-950, 838 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.21 (d, $J = 8.7$ Hz, 2H), 7.91 (d, $J = 8.7$ Hz, 2H), 2.56 (t, $J = 7.1$ Hz, 2H), 1.61 (quint, $J = 7.1$ Hz, 2H), 1.39 (sext, $J = 7.1$ Hz, 2H), 0.90 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 138.7, 135.4 (q, $^2J_{\text{CF}} = 33.6$ Hz), 130.1 (q, $^3J_{\text{CF}} = 3.7$ Hz), 129.4, 122.5 (q, $^1J_{\text{CF}} = 272.8$ Hz), 103.5, 38.8, 28.9, 21.9, 19.8, 13.3; FAB MS m/z 305 $[(\text{M}-\text{BF}_4)^+]$; HRMS (FAB) calcd for $\text{C}_{13}\text{H}_{13}\text{BrF}_3$ $[(\text{M}-\text{BF}_4)^+]$ 305.0153, found 305.0154.

(1-Decynyl)[4-(trifluoromethyl)phenyl](tetrafluoroborato)- $\text{B}(\text{F}_4)^-$ -bromane 2b: oil (91% purity); IR (neat) 3199, 2927, 2856, 1739, 1594, 1465, 1324, 1180-1010, 839 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.21 (d, $J = 9.0$ Hz, 2H), 7.94 (d, $J = 9.0$ Hz, 2H), 2.59 (t, $J = 7.5$ Hz, 2H), 1.65 (quint, $J = 7.5$ Hz, 2H), 1.37 (quint, $J = 7.5$ Hz, 2H), 1.32-1.21 (m, 8H), 0.88 (t, $J = 6.5$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 138.8, 135.4 (q, $^2J_{\text{CF}} = 33.7$ Hz), 130.2 (q, $^3J_{\text{CF}} = 3.5$ Hz), 129.5, 122.6 (q, $^1J_{\text{CF}} = 273.2$ Hz), 103.7, 38.5, 31.8, 29.1, 28.9, 28.9, 27.0, 22.6, 20.1, 14.1; FAB MS m/z 361 $[(\text{M}-\text{BF}_4)^+]$; HRMS (FAB) calcd for $\text{C}_{17}\text{H}_{21}\text{BrF}_3$ $[(\text{M}-\text{BF}_4)^+]$ 361.0779, found 361.0790.

(4-Methyl-1-pentynyl)[4-(trifluoromethyl)phenyl](tetrafluoroborato)- $\text{B}(\text{F}_4)^-$ -bromane 2c: oil (90% purity); IR (neat) 3104, 2963, 2205, 1591, 1467, 1406, 1324, 1140-1000, 837, 771 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.23 (d, $J = 8.9$ Hz, 2H), 7.91 (d, $J = 8.9$ Hz, 2H), 2.46 (d, $J = 6.7$ Hz, 2H), 1.98 (nonet, $J = 6.7$ Hz, 1H), 1.00 (d, $J = 6.7$ Hz, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 138.8, 135.4 (q, $^2J_{\text{CF}} = 33.8$

Hz), 130.1 (q, $^3J_{\text{CF}} = 3.7$ Hz), 129.4, 122.6 (q, $^1J_{\text{CF}} = 273.4$ Hz), 102.6, 39.5, 28.9, 27.4, 21.8; FAB MS m/z 305 [(M-BF₄)⁺]; HRMS (FAB) calcd for C₁₃H₁₃BrF₃ [(M-BF₄)⁺] 305.0153, found 305.1028.

(5-Methyl-1-hexynyl)[4-(trifluoromethyl)phenyl](tetrafluoroborato)- Γ^3 -bromane 2d: oil (90% purity); IR (neat) 2958, 2214, 1645, 1469, 1402, 1325, 1210-990, 833, 774 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.22 (d, $J = 8.9$ Hz, 2H), 7.92 (d, $J = 8.9$ Hz, 2H), 2.57 (t, $J = 7.8$ Hz, 2H), 1.63 (nonet, $J = 6.7$ Hz, 1H), 1.53 (m, 2H), 0.90 (d, $J = 6.7$ Hz, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 138.6, 135.4 (q, $^2J_{\text{CF}} = 33.8$ Hz), 130.1 (q, $^3J_{\text{CF}} = 3.7$ Hz), 129.4, 122.5 (q, $^1J_{\text{CF}} = 273.4$ Hz), 103.7, 38.5, 35.6, 27.4, 21.8, 18.1; FAB MS m/z 319 [(M-BF₄)⁺]; HRMS (FAB) calcd for C₁₄H₁₅BrF₃ [(M-BF₄)⁺] 319.0309, found 319.0309.

(Cyclohexylethynyl)[4-(trifluoromethyl)phenyl](tetrafluoroborato)- Γ^3 -bromane 2e: oil (90% purity); IR (neat) 3205, 2932, 2198, 1602, 1450, 1325, 1190-1000, 835, 771 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.22 (d, $J = 8.9$ Hz, 2H), 7.92 (d, $J = 8.9$ Hz, 2H), 2.75 (tt, $J = 9.2, 3.7$ Hz, 1H), 1.94-1.84 (m, 2H), 1.74-1.64 (m, 2H), 1.62-1.47 (m, 2H), 1.41-1.27 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 138.7, 135.3 (q, $^2J_{\text{CF}} = 34.9$ Hz), 130.1 (q, $^3J_{\text{CF}} = 3.7$ Hz), 129.3, 122.5 (q, $^1J_{\text{CF}} = 274.0$ Hz), 106.6, 39.0, 30.8, 30.4, 25.2, 24.5; FAB MS m/z 331 [(M-BF₄)⁺]; HRMS (FAB) calcd for C₁₅H₁₅BrF₃ [(M-BF₄)⁺] 331.0309, found 331.0313.

(Trimethylsilylethynyl)[4-(trifluoromethyl)phenyl](tetrafluoroborato)- Γ^3 -bromane 2g: yellow oil (94% purity); IR (neat) 3105, 2966, 2144, 1591, 1482, 1407, 1323, 1240-930, 986, 855, 770 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.23 (d, $J = 8.8$ Hz, 2H), 7.93 (d, $J = 8.8$ Hz, 2H), 0.30 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 138.9, 135.5 (q, $^2J_{\text{CF}} = 33.8$ Hz), 130.3 (q, $^3J_{\text{CF}} = 3.7$ Hz), 129.6, 122.5 (q, $^1J_{\text{CF}} = 273.8$ Hz), 109.9, 56.9, -1.3; FAB MS m/z 321 [(M-BF₄)⁺]; HRMS (FAB) calcd for C₁₂H₁₃BrF₃Si [(M-BF₄)⁺] 320.9922, found 320.9924.

Preparation of [t-BuCCBr(*p*-CF₃C₆H₄)BF₄]₂·18-Crown-6 Complex 4. The Γ^3 -bromane **2f** (124 mg, 0.32 mmol) and 18-crown-6 (42 mg, 0.16 mmol) were dissolved in dichloromethane (1.5 mL) and the solution was stirred for 1 h at room temperature under argon. After addition of diethyl ether (1.5 mL), slow evaporation of the solvent at 4 °C yielded the complex **4** (64 mg, 31%) as colorless prisms: mp 128-130 °C (decomp); IR (KBr) 3453, 3100, 2898, 2208, 1587, 1475, 1403, 1354, 1322, 1288, 1180-1010, 839, 769 cm⁻¹; ¹H NMR (CDCl₃) δ 8.25 (d, $J = 8.8$ Hz, 4H), 7.94 (d, $J = 8.8$ Hz, 4H), 3.66 (s, 24H), 1.34 (s, 18H); ¹³C NMR (75 MHz, CDCl₃) δ 139.2, 135.4 (q, $^2J_{\text{CF}} = 34.3$ Hz), 130.2 (q, $^3J_{\text{CF}} = 3.7$ Hz), 129.3, 122.5 (q, $^1J_{\text{CF}} = 272.9$ Hz), 109.7, 70.0, 39.1, 29.8, 29.4. Anal. Calcd for C₃₈H₅₀B₂Br₂F₁₄O₆: C, 43.46; H, 4.80. Found: C, 43.40; H, 4.79.

Michael Addition of Sulfonate Anion to Γ^3 -Bromane 2. A Representative Example. Reaction of 2b with Tetrabutylammonium *p*-Toluenesulfonate. To a solution of 1-decynyl- Γ^3 -bromane **2b** (63 mg, 0.13 mmol, 90% purity) in dichloromethane (1 mL) was added a solution of tetrabutylammonium *p*-toluenesulfonate (105 mg, 0.25 mmol) in dichloromethane (2 mL) at room temperature under argon and the solution was stirred for 2 h. The reaction mixture was quenched with water and extracted with dichloromethane. The organic layer was dried over anhydrous sodium sulfate and concentrated under aspirator vacuum to give a purple oil, which was purified by preparative TLC (hexane-ethyl acetate 4:1) to give a 92:8 mixture of 1-decynyl tosylate **5a** (55%) and 3-pentyl-1-cyclopentenyl tosylate **6a** (5%). **5a**: colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, $J = 8.0$ Hz, 2H), 7.41 (d, $J = 8.0$ Hz, 2H), 2.50 (s, 3H), 2.10 (t, $J = 7.0$ Hz, 2H), 1.40 (quint, $J = 7.0$ Hz, 2H), 1.33-1.19 (m, 10H), 0.89 (t, $J = 6.9$ Hz, 3H). **6a**: colorless oil; IR (CHCl₃) 2928, 1602, 1457, 1379, 1178, 1009, 815 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, $J = 8.0$ Hz, 2H), 7.34 (d, $J = 8.0$ Hz, 2H), 5.25-5.23 (m, 1H), 2.61-2.52 (m, 1H), 2.46 (s, 3H), 2.30 (tt, $J = 7.6, 2.2$ Hz, 2H), 2.06-1.96 (m, 1H), 1.46-1.36 (m, 1H), 1.32-1.15 (m, 8H), 0.87 (t, $J = 6.9$ Hz, 3H); MS m/z (relative intensity) 308 (M⁺, 6), 237 (74), 155 (100), 91 (72); HRMS calcd for C₁₇H₂₄O₃S (M⁺) 308.1446, found 308.1442.

1-Decynyl Mesylate 5b: pale yellow oil; IR (CHCl₃) 2929, 2278, 1419, 1392, 1188 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.28 (s, 3H), 2.20 (t, $J = 7.1$ Hz, 2H), 1.51 (quint, $J = 7.1$ Hz, 2H), 1.41-1.33 (m, 2H), 1.32-1.23 (m, 8H), 0.89 (t, $J = 6.6$ Hz, 3H); FAB MS m/z 232 (M⁺); HRMS (FAB) calcd for

C₁₁H₂₀O₃S (M⁺) 232.1133, found 232.1184.

3-Pentyl-1-cyclopentenyl Mesylate 6b: ¹H NMR (400 MHz, CDCl₃) δ 5.49 (q, *J* = 1.7 Hz, 1H), 3.11 (s, 3H), 2.74-2.67 (m, 1H), 2.52 (tt, *J* = 7.7, 2.1 Hz, 2H), 2.18-2.09 (m, 1H), 1.55-1.2 (9H), 0.88 (3H). These chemical shifts were obtained from NMR spectrum of a 3:1 mixture of **5b** and **6b**.

3, 3-Dimethyl-1-butynyl Tosylate 5c:³ colorless oil; IR (neat) 2970, 2280, 1597, 1476, 1401, 1199, 1121, 1090, 814, 707, 693 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, *J* = 8.3 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 2H), 2.50 (s, 3H), 1.12 (s, 9H).

3, 3-Dimethyl-1-butynyl Mesylate 5d:³ colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 3.27 (s, 3H), 1.24 (s, 9H); MS *m/z* (relative intensity) 176 (M⁺, 13), 161 (55), 97 (24), 79 (73), 67 (100), 57 (59); HRMS calcd for C₇H₁₂O₃S (M⁺) 176.0507, found 176.0506.

References

- 1) Frohn, H. J.; Giesen, M. *J. Fluorine Chem.* **1998**, 89, 59.
- 2) Grubbs, R. H.; Wagaman, M. W. *PCT Int. Appl.* **1998**, 81 pp. PIXXD2 WO 9846652.
- 3) Stang, P. J.; Surber, B. W.; Chen, Z. C.; Roberts, K. A.; Anderson, A. G. *J. Am. Chem. Soc.* **1987**, 109, 228