Supporting Information

Preparation and Wittig Reactions of Organotrifluoroborato Phosphonium Ylides

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General Considerations: ^1H , ^{13}C , and ^{19}F NMR spectra were recorded at 500.39, 125.75, and 470.55 MHz, respectively. ^{19}F NMR chemical shifts were referenced to external CFCl_3 (0.0 ppm). ^{11}B NMR spectra at 128.4 MHz were obtained on a spectrometer equipped with the appropriate decoupling accessories. All ^{11}B NMR chemical shifts were referenced to external $\text{BF}_3\cdot\text{OEt}_2$ (0.0 ppm) with a negative sign indicating an upfield shift. Mass spectra of potassium organotrifluoroborates were performed using negative ion electrospray at the mass spectrometry facilities at the University of Pennsylvania.

Preparation of Potassium 2-, 3-, and 4-(Chloromethyl)phenyltrifluoroborates 1–3.¹

Potassium 4-(Chloromethyl)phenyltrifluoroborate (1). To a soln of 4-bromobenzyl chloride (2.06 g, 10 mmol) and $\text{B}(\text{O}-i\text{Pr})_3$ (1.77 g, 9.4 mmol) in THF (80 mL) was slowly added $n\text{-BuLi}$ (2.5 M soln in hexanes, 3.6 mL, 9.0 mmol) at -78°C for 1 h under N_2 . The soln was vigorously stirred for 1 h. KHF_2 (1.95 g, 25 mmol) was subsequently added in one portion followed by the dropwise addition of H_2O (20 mL). The reaction mixture was warmed to rt. After stirring at rt for 30 min, the suspension was concentrated on a rotary evaporator and dried under high vacuum for 3 h. The residual white solid was dissolved in dry acetone (70 mL), and the insoluble salts were filtered off. The resulting organic soln was concentrated on a rotary evaporator. The crude product was purified by dissolution in acetone and precipitation with Et_2O to obtain the desired compound **1** as a white solid (2.05 g, 98% yield). mp = $233\text{--}235^\circ\text{C}$. ^1H NMR (500 MHz, Acetone- d_6) δ 7.48 (d, 2H, $J = 7.7$ Hz), 7.17 (d, 2H, $J = 7.7$ Hz), 4.62 (s, 2H). ^{13}C NMR (125.8 MHz, Acetone- d_6) δ 134.3, 131.9, 126.8, 47.1. ^{19}F (470.8 MHz, Acetone- d_6) δ -143.1. ^{11}B NMR (128.4 MHz, Acetone- d_6) δ 3.67. FT-IR (neat): 3650, 3041, 2959, 1701, 1669, 1398, 1259, 1229, 967, 919, 830, 744 cm^{-1} . HRMS (m/z): $[\text{M}-\text{K}^+]$ calcd. for $\text{C}_7\text{H}_6\text{BClF}_3$, 193.0203; found, 193.0203.

Potassium 3-(Chloromethyl)phenyltrifluoroborate (2). The desired compound was prepared using 3-bromobenzyl chloride (2.00 g, 9.7 mmol), $\text{B}(\text{O}-i\text{Pr})_3$ (1.73 g, 9.2 mmol), $n\text{-BuLi}$ (2.5 M soln in hexanes, 3.50 mL, 8.75 mmol), and KHF_2 (1.89 g, 24.3 mmol) by the procedure used for compound **1** (1.65 g, 81% yield). mp = 227°C (dec.). ^1H NMR (500 MHz, Acetone- d_6) δ 7.52 (s, 1H), 7.44 (t, 1H, $J = 4.4$ Hz), 7.12 (m, 2H), 4.61 (s, 2H). ^{13}C NMR (125.8 MHz, Acetone- d_6) δ 135.2, 132.2, 131.8, 126.5, 125.6, 47.5. ^{19}F (470.8 MHz, Acetone- d_6) δ -143.7. ^{11}B NMR (128.4 MHz, Acetone- d_6) δ 3.55. FT-IR (neat): 3611, 3553, 3062, 3014, 1699, 1631, 1450, 1440, 1262, 1212, 1196, 937, 747 cm^{-1} . HRMS (m/z): $[\text{M}-\text{K}^+]$ calcd. for $\text{C}_7\text{H}_6\text{BClF}_3$, 193.0203; found, 193.0200.

Potassium 2-(Chloromethyl)phenyltrifluoroborate (3).

The desired compound was prepared using 2-iodobenzyl chloride (1.62 g, 6.24 mmol), B(O^{*i*}Pr)₃ (1.13 g, 6.0 mmol), *n*-BuLi (2.5 M soln in hexanes, 2.3 mL, 5.6 mmol), and KHF₂ (1.22 g, 15.6 mmol) by the procedure used for compound **1** as a white solid (755 mg, 58% yield). mp = 153 °C (dec.). ¹H NMR (500 MHz, Acetone-*d*₆) δ 7.52 (d, 1H, *J* = 7.2 Hz), 7.31 (d, 1H, *J* = 7.5 Hz), 7.08 (m, 1H), 7.03 (m, 1H), 4.95 (s, 2H). ¹³C NMR (125.8 MHz, Acetone-*d*₆) δ 132.2, 127.8, 125.8, 125.6, 47.0. ¹⁹F (470.8 MHz, Acetone-*d*₆) δ -139.8. ¹¹B NMR (128.4 MHz, Acetone-*d*₆) δ 3.60 (q, *J* = 50.1 Hz). FT-IR (neat): 3611, 3553, 3062, 3014, 1699, 1631, 1450, 1440, 1212, 937, 747 cm⁻¹. HRMS (*m/z*): [M-K⁺] calcd. for C₇H₆BClF₃, 193.0203; found, 193.0205.

Preparation of potassium [(2-, 3-, 4-trifluoroboratophenyl)methyl]triphenylphosphonium chlorides 4–6 (Scheme 1).

Potassium [(4-trifluoroboratophenyl)methyl]triphenylphosphonium

chloride (4). A mixture of potassium 4-(chloromethyl)phenyltrifluoroborate (**1**) (233 mg, 1.0 mmol) and triphenylphosphine (393 mg, 1.5 mmol) in 3-pentanone (2.0 mL) was heated in an oil bath at 100 °C. After 4 h, the reaction mixture was cooled to rt and then acetone (3 mL) was added for the precipitation of the product. The white solid was collected by sintered glass, washed with acetone (3×2 mL), and dried under high vacuum to obtain the desired pure compound **4** as a white solid (458 mg, 93% yield). mp > 260 °C. ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.85 (t, 3H, *J* = 7.5 Hz), 7.70 (m, 6H), 7.62 (m, 6H), 7.12 (d, 2H, *J* = 7.0 Hz), 6.68 (d, 2H, *J* = 7.9 Hz), 4.98 (d, 2H, *J* = 15.4 Hz). ¹³C NMR (125.8 MHz, DMSO-*d*₆) δ 135.4 (2C), 134.5, 134.4, 132.1, 130.5, 130.4, 129.5, 129.4, 124.0, 123.9, 119.9, 118.3, 29.0, 28.7. ¹⁹F (470.8 MHz, DMSO-*d*₆) δ -139.7. ¹¹B NMR (128.4 MHz, DMSO-*d*₆) δ 3.24. FT-IR (KBr) ν 3436, 3067, 3029, 2951, 2908, 1607, 1588, 1484, 1438, 1413, 1209, 1183, 1111, 995, 970, 954, 835, 747, 723, 690, 591, 518, 506, 492 cm⁻¹. HRMS (ESI): *m/z* calcd. for C₂₅H₂₀BF₃P [M-KCl-H⁺]⁺ 419.1348, found 419.1346.

Potassium [(3-trifluoroboratophenyl)methyl]triphenylphosphonium

chloride (5). The desired compound was prepared using potassium 3-(chloromethyl)phenyltrifluoroborate (**2**) (233 mg, 1.0 mmol) by the procedure used for compound **4** (a white solid, 463 mg, 94% yield). mp > 260 °C. ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.85 (t, 3H, *J* = 7.5 Hz), 7.69 (m, 6H), 7.59 (m, 6H), 7.21 (d, 1H, *J* = 7.0 Hz), 7.12 (s, 1H), 6.88 (t, 1H, *J* = 7.4 Hz), 6.55 (d, 1H, *J* = 7.4 Hz), 4.98 (d, 2H, *J* = 15.4 Hz). ¹³C NMR (125.8 MHz, DMSO-*d*₆) δ 135.4 (2C), 135.0 (2C), 134.5, 134.4, 131.8, 130.4, 130.3, 128.1, 128.0, 127.0 (2C), 125.4, 125.3, 119.0, 118.4, 29.3, 29.0. ¹⁹F (470.8 MHz, DMSO-*d*₆) δ -140.0. ¹¹B NMR (128.4 MHz, DMSO-*d*₆) δ 3.01. FT-IR (KBr) ν 3436, 3058, 2952, 2892, 1587, 1482, 1438, 1397, 1245, 1217, 1149, 1111, 1014, 978, 908, 851, 837, 804, 746, 716, 691, 513, 505 cm⁻¹. HRMS (ESI): *m/z* calcd. for C₂₅H₂₀BF₃P [M-KCl-H⁺]⁻ 419.1348, found 419.1340.

Potassium [(2-trifluoroboratophenyl)methyl]triphenylphosphonium chloride

(6). The desired compound was prepared using potassium 2-(chloromethyl)phenyltrifluoroborate (**3**) (233 mg, 1.0 mmol) by the procedure used for compound **4** (a white solid, 427 mg, 86% yield). mp > 260 °C. ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.82 (t, 3H, *J* = 7.5 Hz), 7.66 (m, 6H), 7.42 (m, 6H), 7.36 (d, 1H, *J* = 6.9 Hz), 7.09 (t, 1H, *J* = 7.1 Hz), 6.68 (d, 1H, *J* = 8.1 Hz), 5.02 (d, 2H, *J* = 14.7 Hz). ¹³C NMR (125.8 MHz, DMSO-*d*₆) δ 135.1 (2C), 134.4, 134.3, 133.4, 130.9, 130.8, 130.3, 130.2, 128.4, 128.3, 127.2, 127.1, 126.5, 126.4, 119.9, 119.2, 30.2, 29.9. ¹⁹F (470.8 MHz, DMSO-*d*₆) δ -135.6. ¹¹B NMR (128.4 MHz, DMSO-*d*₆) δ 3.07. FT-IR (KBr) ν 3435, 3060, 3011, 1617, 1438, 1201, 1175, 1111, 1018, 1003, 965, 947, 834, 785, 748, 720, 690, 523, 501 cm⁻¹. HRMS (ESI): *m/z* calcd. for C₂₅H₂₀BF₃P [M-KCl-H⁺]⁻ 419.1348, found 419.1336.

Stereoelectronic Effects of Substituted Potassium Organotrifluoroborates of Wittig Reaction of Potassium 2-, 3-, and 4-(Chloromethyl)phenyltrifluoroborates with *o* -, *m* -, and *p*-Substituted Aryl Aldehydes (Table 2, entries 7–13).

Potassium 4-[2-(4-methoxyphenyl)vinyl]phenyltrifluoroborate (7).

Potassium [(4-trifluoroboratophenyl)methyl]triphenylphosphonium chloride (**4**) (49.5 mg, 0.10 mmol), *p*-anisaldehyde (16.3 mg, 0.12 mmol), and K₂CO₃ (16.6 mg, 0.12 mmol) were dissolved in DMSO-*d*₆ (800 μL) in an NMR tube at rt under atmospheric conditions. The mixture was sonicated for 20 min at rt and heated to 80 °C using an oil bath. After the reaction was complete (the reaction was directly monitored by ¹H NMR

every 1 h), the resulting soln in the NMR tube was moved into a 10 mL pear flask and then the solvent was completely removed under high vacuum at 60–70 °C. The residual product was dissolved in dry acetone (3 mL), and the insoluble salts were removed by filtration through Celite. The resulting organic soln was concentrated on a rotary evaporator. The crude solid was precipitated with Et₂O (2.5 mL), filtrated by sintered glass, washed with ether (2×2 mL), and dried under high vacuum to obtain the desired pure compound **7** as a white solid (26.6 mg, 84% yield). mp (*E+Z*) = 148–154 °C. **E isomer**: ¹H NMR (500 MHz, Acetone-*d*₆+DMSO-*d*₆) δ 7.50 (d, 2H, *J* = 8.8 Hz), 7.47 (d, 2H, *J* = 7.9 Hz), 7.29 (d, 2H, *J* = 7.5 Hz), 7.06 (d, 1H, *J* = 16.4 Hz), 7.01 (d, 1H, *J* = 16.4 Hz), 6.91 (d, 2H, *J* = 8.8 Hz), 3.80 (s, 3H). **Z isomer**: ¹H NMR (500 MHz, Acetone-*d*₆+DMSO-*d*₆) δ 7.37 (d, 2H, *J* = 7.5 Hz), 7.22 (d, 2H, *J* = 8.5 Hz), 7.03 (d, 2H, *J* = 7.5 Hz), 6.78 (d, 2H, *J* = 8.8 Hz), 6.46 (d, 1H, *J* = 12.4 Hz), 6.38 (d, 1H, *J* = 12.3 Hz), 3.75 (s, 3H). **E+Z mixture** ¹³C NMR (125.8 MHz, Acetone-*d*₆+DMSO-*d*₆) δ 159.0, 134.0, 132.1, 131.7, 130.9, 130.2, 130.1, 130.0, 128.1, 127.5, 127.3, 126.5, 125.2, 124.4, 114.0, 113.4, 54.7, 54.6. **E+Z mixture** ¹⁹F (470.8 MHz, Acetone-*d*₆+DMSO-*d*₆) δ -142.2. ¹¹B NMR (128.4 MHz, Acetone-*d*₆+DMSO-*d*₆) δ 3.58. FT-IR (neat): 3582, 3009, 2837, 1605, 1510, 1249, 1177, 969, 830 cm⁻¹. HRMS (ESI): *m/z* calcd. for C₁₅H₁₃BF₃O [M-K⁺]⁻ 277.1012, found 277.1005. The *E:Z* ratio was 2.5:1 based on the integration of peaks at 6.91 (*E*) and 6.78 (*Z*) ppm, respectively.

Potassium 3-[2-(4-methoxyphenyl)vinyl]phenyltrifluoroborate (8**).**

The desired compound was prepared using potassium [(3-trifluoroboratophenyl)methyl]triphenylphosphonium chloride (**5**) (49.5 mg, 0.10 mmol), *p*-anisaldehyde (16.3 mg, 0.12 mmol), and K₂CO₃ (16.6 mg, 0.12 mmol) by the procedure used for compound **7** (a white solid, 26.8 mg, 85% yield). mp (*E+Z*) = 236–243 °C. **E isomer**: ¹H NMR (500 MHz, Acetone-*d*₆) δ 7.68 (s, 1H), 7.51 (d, 2H, *J* = 8.7 Hz), 7.38 (d, 1H, *J* = 7.2 Hz), 7.24 (dt, 1H, *J* = 7.6, 1.5 Hz), 7.09 (t, 1H, *J* = 7.3 Hz), 7.07 (d, 1H, *J* = 16.3 Hz), 7.03 (d, 1H, *J* = 16.4 Hz), 6.92 (d, 2H, *J* = 8.8 Hz), 3.80 (s, 3H). **Z isomer**: ¹H NMR (500 MHz, Acetone-*d*₆) δ 7.46 (s, 1H), 7.35 (d, 1H, *J* = 7.2 Hz), 7.21 (d, 2H, *J* = 8.8 Hz), 6.97 (dt, 1H, *J* = 7.7, 1.9 Hz), 6.95 (t, 1H, *J* = 7.1 Hz), 6.74 (d, 2H, *J* = 8.8 Hz), 6.49 (d, 1H, *J* = 12.3 Hz), 6.39 (d, 1H, *J* = 12.3 Hz), 3.75 (s, 3H). **E+Z mixture** ¹³C NMR (125.8 MHz, Acetone-*d*₆) δ 159.1, 135.1, 131.2, 130.9, 130.6, 130.0 (2C), 128.5, 127.6, 127.3, 126.4, 125.8, 125.6, 125.0, 123.2, 114.0, 113.3, 54.6, 54.5. **E+Z mixture** ¹⁹F (470.8 MHz, Acetone-*d*₆) δ -143.1. **E+Z mixture** ¹¹B NMR (128.4 MHz, Acetone-*d*₆) δ 3.75. **E+Z mixture** FT-IR (neat): 3618, 3523, 3007, 1602, 1510, 1462, 1440, 1287, 1253, 1177, 1028, 967, 949, 898, 822, 792 cm⁻¹. HRMS (ESI): *m/z* calcd. for C₁₅H₁₃BF₃O [M-K⁺]⁻ 277.1012, found 277.1015. The *E:Z* ratio was 4.1:1 based on the integration of peaks at 7.68 (*E*) and 7.46 (*Z*) ppm, respectively.

Potassium 2-[2-(4-methoxyphenyl)vinyl]phenyltrifluoroborate (9). The desired compound was prepared using potassium [(2-trifluoroboratophenyl)methyl]triphenylphosphonium chloride (**6**) (49.5 mg, 0.10 mmol), *p*-anisaldehyde (16.3 mg, 0.12 mmol), and K₂CO₃ (16.6 mg, 0.12 mmol) by the procedure used for compound **7** (an amorphous solid, 26.1 mg, 82% yield). **E isomer:** ¹H NMR (500 MHz, Acetone-*d*₆) δ 7.93 (d, 1H, *J* = 16.6 Hz), 7.57 (d, 2H, *J* = 7.6 Hz), 7.44 (d, 2H, *J* = 8.8 Hz), 7.04 (td, 1H, *J* = 7.4, 1.3 Hz), 6.97 (t, 1H, *J* = 7.2 Hz), 6.89 (d, 1H, *J* = 16.1 Hz), 6.88 (d, 2H, *J* = 8.8 Hz), 3.79 (s, 3H). **E, Z, and compound 6 mixture** ¹³C NMR (125.8 MHz, Acetone-*d*₆) δ 158.6, 140.5, 134.4, 134.3, 134.0, 132.6, 132.0, 131.8, 131.7, 131.3, 130.2, 129.8, 129.7, 128.6, 128.5, 127.6, 127.2, 125.4, 125.2, 124.9, 124.7, 124.3, 122.6, 113.8, 113.0, 54.6, 54.4. **E, Z, and compound 6 mixture** ¹⁹F (470.8 MHz, Acetone-*d*₆) δ -138.4, -140.6. **E, Z, and compound 6 mixture** ¹¹B NMR (128.4 MHz, Acetone-*d*₆) δ 3.61. **E, Z, and compound 6 mixture** FT-IR (neat): 3621, 3051, 2836, 1605, 1510, 1438, 1292, 1248, 1199, 1184, 1119, 1092, 1029, 953, 822, 746 cm⁻¹. HRMS (ESI): *m/z* calcd. for C₁₅H₁₃BF₃O [M-K⁺]⁻ 277.1012, found 277.0999. The *E*:*Z* ratio was 4.7:1 based on the integration of peaks at 3.79 (*E*) and 3.72 (*Z*) ppm, respectively.

Potassium 4-[2-(3-methoxyphenyl)vinyl]phenyltrifluoroborate (10).

The desired compound was prepared using potassium [(4-trifluoroboratophenyl)methyl]triphenylphosphonium chloride (**4**) (49.5 mg, 0.10 mmol), *m*-anisaldehyde (16.3 mg, 0.12 mmol), and K₂CO₃ (16.6 mg, 0.12 mmol) by the procedure used for compound **7** (a white solid, 31.4 mg, 99% yield). mp (*E*+*Z*) = 253–262 °C. **E isomer:** ¹H NMR (500 MHz, Acetone-*d*₆) δ 7.49 (d, 2H, *J* = 7.9 Hz), 7.34 (d, 2H, *J* = 8.0 Hz), 7.24 (t, 1H, *J* = 8.1 Hz), 7.18 (d, 1H, *J* = 16.4 Hz), 7.13 (m, 2H), 7.00 (d, 1H, *J* = 16.4 Hz), 6.79 (ddd, 1H, *J* = 8.2, 2.4, 1.0 Hz), 3.82 (s, 3H). **Z isomer:** ¹H NMR (500 MHz, Acetone-*d*₆) δ 7.38 (d, 2H, *J* = 7.9 Hz), 7.13 (m, 1H), 7.05 (d, 2H, *J* = 8.0 Hz), 6.86 (m, 2H), 6.74 (ddd, 1H, *J* = 8.2, 2.6, 1.0 Hz), 6.57 (d, 1H, *J* = 12.3 Hz), 6.44 (d, 1H, *J* = 12.3 Hz), 3.63 (s, 3H). **E+Z mixture** ¹³C NMR (125.8 MHz, Acetone-*d*₆) δ 160.1, 159.5, 139.6, 139.3, 134.0, 133.7, 132.0, 131.8, 131.5 (2C), 130.0, 129.4, 128.9, 127.9, 126.7, 125.7, 124.7, 121.8, 121.2, 118.7, 114.5, 113.9, 112.7, 112.5, 111.2, 54.5, 54.3. **E+Z mixture** ¹⁹F (470.8 MHz, Acetone-*d*₆) δ -143.1. **E+Z mixture** ¹¹B NMR (128.4 MHz, Acetone-*d*₆) δ 3.85. **E+Z mixture** FT-IR (neat): 3583, 3012, 1703, 1596, 1578, 1486, 1464, 1433, 1245, 1165, 1040, 968, 849, 813 cm⁻¹. HRMS (ESI): *m/z* calcd. for C₁₅H₁₃BF₃O [M-K⁺]⁻ 277.1012 found 277.1003. The *E*:*Z* ratio was 1.7:1 based on the integration of peaks at 6.79 (*E*) and 6.74 (*Z*) ppm, respectively.

Potassium 4-[2-(2-methoxyphenyl)vinyl]phenyltrifluoroborate (11). The desired compound was prepared using potassium [(4-trifluoroboratophenyl)methyl]triphenylphosphonium chloride (**4**) (49.5 mg, 0.10 mmol), *o*-anisaldehyde (16.3 mg, 0.12 mmol), and K₂CO₃ (16.6 mg, 0.12 mmol) by the procedure used for compound **7** (a white solid, 30.4 mg, 96% yield). mp (*E*+*Z*) = 168–176 °C. ***E* isomer:** ¹H NMR (500 MHz, Acetone-*d*₆) δ 7.64 (dd, 1H, *J* = 7.7, 1.6 Hz), 7.49 (d, 2H, *J* = 7.9 Hz), 7.42 (d, 1H, *J* = 16.6 Hz), 7.32 (d, 2H, *J* = 7.9 Hz), 7.21 (m, 1H), 7.16 (d, 1H, *J* = 16.6 Hz), 6.98 (d, 1H, *J* = 7.9 Hz), 6.93 (t, 1H, *J* = 7.6 Hz), 3.88 (s, 3H). ***Z* isomer:** ¹H NMR (500 MHz, Acetone-*d*₆) δ 7.32 (d, 2H, *J* = 7.9 Hz), 7.23 (m, 2H), 7.01 (d, 2H, *J* = 8.0 Hz), 6.99 (d, 1H, *J* = 6.4 Hz), 6.71 (td, 1H, *J* = 7.4, 0.8 Hz), 6.54 (d, 1H, *J* = 12.4 Hz), 6.51 (d, 1H, *J* = 12.4 Hz), 3.82 (s, 3H). ***E*+*Z* mixture** ¹³C NMR (125.8 MHz, Acetone-*d*₆) δ 157.4, 156.8, 134.6, 133.8, 132.0, 131.8, 131.7, 131.4, 131.0, 130.3, 129.8, 128.2, 128.0, 126.8, 125.8, 124.6, 123.6, 120.5, 120.4, 119.8, 111.0, 110.8, 54.9, 54.8. ***E*+*Z* mixture** ¹⁹F (470.8 MHz, Acetone-*d*₆) δ -143.1. ***E*+*Z* mixture** ¹¹B NMR (128.4 MHz, Acetone-*d*₆) δ 3.78. ***E*+*Z* mixture** FT-IR (neat): 3621, 3013, 2835, 1691, 1596, 1486, 1462, 1435, 1289, 1244, 1105, 1025, 969, 814, 751 cm⁻¹. HRMS (ESI): *m/z* calcd. for C₁₅H₁₃BF₃O [M-K⁺]⁻ 277.1012, found 277.1021. The *E*:*Z* ratio was 1:1.2 based on the integration of peaks at 7.49 (*E*) and 7.01 (*Z*) ppm, respectively.

Potassium 4-[2-(4-nitrophenyl)vinyl]phenyltrifluoroborate (12). The desired compound was prepared using potassium [(4-trifluoroboratophenyl)methyl]triphenylphosphonium chloride (**4**) (49.5 mg, 0.10 mmol), *p*-nitrobenzaldehyde (18.1 mg, 0.12 mmol), and K₂CO₃ (16.6 mg, 0.12 mmol) by the procedure used for compound **7** (a yellow solid, 28.8 mg, 87% yield). mp (*E*+*Z*) = 134–138 °C (dec.). ***E* isomer:** ¹H NMR (500 MHz, Acetone-*d*₆+DMSO-*d*₆) δ 8.22 (d, 2H, *J* = 8.9 Hz), 7.85 (d, 2H, *J* = 8.8 Hz), 7.48 (d, 2H, *J* = 8.1 Hz), 7.47 (d, 1H, *J* = 16.2 Hz), 7.42 (d, 2H, *J* = 7.8 Hz), 7.29 (d, 1H, *J* = 16.4 Hz). ***Z* isomer:** ¹H NMR (500 MHz, Acetone-*d*₆+DMSO-*d*₆) δ 8.12 (d, 2H, *J* = 8.9 Hz), 7.53 (d, 2H, *J* = 8.5 Hz), 7.34 (d, 2H, *J* = 7.9 Hz), 7.01 (d, 2H, *J* = 8.0 Hz), 6.80 (d, 1H, *J* = 12.2 Hz), 6.57 (d, 1H, *J* = 12.3 Hz). ***E*+*Z* mixture** ¹³C NMR (125.8 MHz, Acetone-*d*₆+DMSO-*d*₆) δ 145.3, 145.2, 135.5, 135.3, 132.3, 131.9, 129.8, 127.0, 126.8, 125.9, 125.5, 124.1, 123.7, 123.5. ***E*+*Z* mixture** ¹⁹F (470.8 MHz, Acetone-*d*₆+DMSO-*d*₆) δ -141.6. ***E*+*Z* mixture** ¹¹B NMR (128.4 MHz, Acetone-*d*₆+DMSO-*d*₆) δ 3.10. ***E*+*Z* mixture** FT-IR (KBr): 3447, 1600, 1515, 1345, 1219, 1110, 958, 887, 855 cm⁻¹. HRMS (ESI): *m/z* calcd. for C₁₄H₁₀BF₃NO₂ [M-K⁺]⁻ 292.0757 found 292.0754. The *E*:*Z* ratio was 1:2.1 based on the integration of peaks at 8.21 (*E*) and 8.12 (*Z*) ppm, respectively.

Potassium 4-[2-(2-cyanophenyl)vinyl]phenyltrifluoroborate (13). The desired compound was prepared using potassium [(4-trifluoroboratophenyl)methyl]triphenylphosphonium chloride (**4**) (49.5 mg, 0.10 mmol), 2-cyanobenzaldehyde (15.7 mg, 0.12 mmol), and K_2CO_3 (16.6 mg, 0.12 mmol) by the procedure used for compound **7** (a yellow solid, 30.2 mg, 97% yield). mp (*E*+*Z*) = 114–122 °C. ***E* isomer:** 1H NMR (500 MHz, Acetone- d_6) δ 7.98 (d, 1H, J = 8.1 Hz), 7.74 (dd, 1H, J = 7.4, 0.9 Hz), 7.67 (td, 1H, J = 7.5, 0.8 Hz), 7.55 (d, 2H, J = 7.9 Hz), 7.47–7.37 (m, 5H). ***Z* isomer:** 1H NMR (500 MHz, Acetone- d_6) δ 7.75 (dd, 1H, J = 7.1, 0.8 Hz), 7.48 (m, 1H), 7.42–7.40 (m, 2H), 7.36 (d, 2H, J = 7.9 Hz), 6.95 (d, 2H, J = 7.9 Hz), 6.84 (d, 1H, J = 12.2 Hz), 6.63 (d, 1H, J = 12.2 Hz). ***E*+*Z* mixture** ^{13}C NMR (125.8 MHz, Acetone- d_6) δ 142.0, 141.0, 135.6, 135.2, 133.1, 133.0, 132.9, 132.8, 132.3, 132.2, 131.8, 131.7, 129.7, 127.5, 127.3, 126.9, 125.2 (2C), 123.6, 121.0, 117.7, 110.5. ***E*+*Z* mixture** ^{19}F (470.8 MHz, Acetone- d_6) δ -143.3. ***E*+*Z* mixture** ^{11}B NMR (128.4 MHz, Acetone- d_6) δ 3.63. ***E*+*Z* mixture** FT-IR (neat): 3622, 3392, 3067, 2221, 1701, 1630, 1475, 1396, 1219, 965, 814, 755 cm^{-1} . HRMS (ESI): m/z calcd. for $C_{15}H_{10}BF_3N [M-K]^+$ 272.0858, found 272.0870. The *E*:*Z* ratio was 2:1 based on the integration of peaks at 7.55 (*E*) and 6.95 (*Z*) ppm, respectively.

Wittig Reaction of Various Aldehydes with **4** (Table 4, entries 14–21).

Potassium 4-(non-1-enyl)phenyltrifluoroborate (14). The desired compound was prepared using potassium [(4-trifluoroboratophenyl)methyl]triphenylphosphonium chloride (**4**) (49.5 mg, 0.10 mmol), octanal (15.4 mg, 0.12 mmol), and K_2CO_3 (16.6 mg, 0.12 mmol) by the procedure used for compound **7** (a white solid, 25.2 mg, 82% yield). mp (*E*+*Z*) = 242–246 °C. ***E* isomer:** 1H NMR (500 MHz, Acetone- d_6) δ 7.41 (d, 2H, J = 7.9 Hz), 7.12 (d, 2H, J = 8.0 Hz), 6.33 (d, 1H, d = 15.8 Hz), 6.14 (dt, 1H, J = 15.8, 6.9 Hz), 2.17 (qd, 2H, J = 7.1, 1.4 Hz), 1.44 (m, 2H), 1.36–1.27 (m, 8H), 0.88 (t, 3H, J = 6.9 Hz). ***Z* isomer:** 1H NMR (500 MHz, Acetone- d_6) δ 7.45 (d, 2H, J = 7.9), 7.06 (d, 2H, J = 7.9 Hz), 6.34 (d, 1H, J = 11.6 Hz), 5.51 (dt, 1H, J = 11.6, 7.2 Hz), 2.34 (qd, 2H, J = 7.3, 1.8 Hz), 1.44 (m, 2H), 1.36–1.27 (m, 8H), 0.87 (t, 3H, J = 7.1 Hz). ***E*+*Z* mixture** ^{13}C NMR (125.8 MHz, Acetone- d_6) δ 134.6, 131.8, 131.4, 131.1, 130.4, 130.0, 127.6, 126.8, 124.0, 32.8, 31.7, 30.0, 29.5, 29.0, 22.4, 13.4. ***E*+*Z* mixture** ^{19}F (470.8 MHz, Acetone- d_6) δ -143.0. ***E*+*Z* mixture** ^{11}B NMR (128.4 MHz, Acetone- d_6) δ 3.92. ***E*+*Z* mixture** FT-IR (neat): 3568, 2926, 2855, 1702, 1458, 1248, 1029, 967, 843, 799 cm^{-1} . HRMS (ESI): m/z calcd. for $C_{15}H_{21}BF_3 [M-K]^+$ 269.1688, found 269.1692. The *E*:*Z* ratio was 1.7:1 based on the integration of peaks at 7.12 (*E*) and 7.06 (*Z*) ppm, respectively.

Potassium 4-(2-cyclohexylvinyl)phenyltrifluoroborate (15). The desired compound was prepared using potassium [(4-trifluoroborato-phenyl)methyl]triphenylphosphonium chloride (**4**) (49.5 mg, 0.10 mmol), cyclohexane carboxaldehyde (13.5 mg, 0.12 mmol), and K_2CO_3 (16.6 mg, 0.12 mmol) by the procedure used for compound **7** (a white solid, 25.4 mg, 82% yield). mp (*E*+*Z*) > 260 °C. ***E* isomer:** 1H NMR (500 MHz, Acetone- d_6) δ 7.40 (d, 2H, J = 7.8 Hz), 7.12 (d, 2H, J = 8.0 Hz), 6.31 (d, 1H, J = 15.9 Hz), 6.09 (dd, 1H, J = 16.0, 7.1 Hz), 2.08 (m, 1H), 1.80–1.65 (m, 5H), 1.32 (m, 2H), 1.24–1.12 (m, 3H). ***Z* isomer:** 1H NMR (500 MHz, Acetone- d_6) δ 7.45 (d, 2H, J = 7.8 Hz), 7.04 (d, 2H, J = 7.4 Hz), 6.26 (d, 1H, J = 11.5 Hz), 5.33 (dd, 1H, J = 11.6, 9.8 Hz), 2.66 (m, 1H), 1.80–1.65 (m, 5H), 1.32 (m, 2H), 1.24–1.12 (m, 3H). ***E*+*Z* mixture** ^{13}C NMR (125.8 MHz, Acetone- d_6) δ 136.3, 134.6, 133.3, 131.8, 131.5, 128.7, 128.3, 126.5, 124.0, 41.1, 33.2, 33.0, 26.0, 25.9, 25.6. ***E*+*Z* mixture** ^{19}F (470.8 MHz, Acetone- d_6) δ -142.9. ***E*+*Z* mixture** ^{11}B NMR (128.4 MHz, Acetone- d_6) δ 3.77. ***E*+*Z* mixture** FT-IR (neat): 3652, 2921, 2849, 1446, 1393, 1228, 968, 849, 805 cm^{-1} . HRMS (ESI): m/z calcd. for $C_{14}H_{17}BF_3$ [$M-K^+$] $^-$ 253.1375; found 253.1382. The *E*:*Z* ratio was 4.6:1 based on the integration of peaks at 6.09 (*E*) and 5.33 (*Z*) ppm, respectively.

Potassium 4-(3,7-dimethylocta-1,6-dienyl)phenyltrifluoroborate (16). The desired compound was prepared using potassium [(4-trifluoroborato-phenyl)methyl]triphenylphosphonium chloride (**4**) (49.5 mg, 0.10 mmol), 2,6-dimethyl-5-heptenal (16.8 mg, 0.12 mmol), and K_2CO_3 (16.6 mg, 0.12 mmol) by the procedure used for compound **7** (a white solid, 20.2 mg, 63% yield). mp (*E*+*Z*) = 226–233 °C. ***E* isomer:** 1H NMR (500 MHz, Acetone- d_6) δ 7.41 (d, 2H, J = 7.9 Hz), 7.13 (d, 2H, J = 8.0 Hz), 6.31 (d, 1H, J = 15.8 Hz), 6.01 (dd, 1H, J = 15.9, 8.1 Hz), 5.14 (m, 1H), 2.25 (m, 1H), 2.02 (m, 2H), 1.66 (d, 3H, J = 1.1 Hz), 1.58 (s, 3H), 1.40 (q, 2H, J = 5.2 Hz), 1.06 (d, 3H, J = 6.7 Hz). ***Z* isomer:** 1H NMR (500 MHz, Acetone- d_6) δ 7.45 (d, 2H, J = 7.8 Hz), 7.05 (d, 2H, J = 8.0 Hz), 6.32 (d, 1H, J = 11.4 Hz), 5.29 (dd, 1H, J = 11.7 Hz), 5.08 (m, 1H), 2.88 (m, 1H), 1.95 (m, 2H), 1.62 (d, 3H, J = 1.1 Hz), 1.53 (s, 3H), 1.35 (m, 2H), 1.02 (d, 3H, J = 6.6 Hz). ***E*+*Z* mixture** ^{13}C NMR (125.8 MHz, Acetone- d_6) δ 136.8, 134.4, 133.2, 131.8 (2C), 131.5, 130.7, 129.7, 128.9, 126.6, 124.7, 124.6, 124.1, 37.7, 37.2, 36.7, 31.7, 35.8, 25.7, 24.9, 20.4, 20.3, 16.9. ***E*+*Z* mixture** ^{19}F (470.8 MHz, Acetone- d_6) δ -142.9. ***E*+*Z* mixture** ^{11}B NMR (128.4 MHz, Acetone- d_6) δ 3.72. ***E*+*Z* mixture** FT-IR (neat): 3582, 2963, 2914, 1606, 1451, 1376, 1225, 969, 857, 807 cm^{-1} . HRMS (ESI): m/z calcd. for $C_{16}H_{21}BF_3$ [$M-K^+$] $^-$ 281.1688, found 281.1663. The *E*:*Z* ratio was 7.6:1 based on the integration of peaks at 6.01 (*E*) and 5.29 (*Z*) ppm, respectively.

Potassium 4-((1E,3E)-4-phenylbuta-1,3-dienyl)phenyltrifluoroborate (17). The desired compound was prepared using potassium [(4-trifluoroboratophenyl)methyl]triphenylphosphonium chloride (**4**) (49.5 mg, 0.10 mmol), *trans*-cinnamaldehyde (16.8 mg, 0.12 mmol), and K₂CO₃ (16.6 mg, 0.12 mmol) by the procedure used for compound **7** (a pale yellow solid, 22.5 mg, 72% yield). mp (*E*+*Z*) > 260 °C. **E isomer:** ¹H NMR (500 MHz, Acetone-*d*₆) δ 7.48–7.44 (m, 5H), 7.32 (d, 2H, *J* = 7.6 Hz), 7.24 (d, 2H, *J* = 7.7 Hz), 7.06 (dd, 1H, *J* = 10.5, 15.4 Hz), 6.96 (dd, 1H, *J* = 10.5, 15.3 Hz), 6.69 (d, 1H, *J* = 12.4 Hz), 6.66 (d, 1H, *J* = 12.5 Hz). **Z isomer:** ¹H NMR (500 MHz, Acetone-*d*₆) δ 7.51 (d, 2H, *J* = 8.0 Hz), 7.30 (d, 2H, *J* = 7.7 Hz), 7.21–7.16 (m, 6H), 6.70 (d, 1H, *J* = 15.3 Hz), 6.49 (d, 1H, *J* = 11.5 Hz), 6.32 (t, 1H, *J* = 13.1 Hz). **E+Z mixture** ¹³C NMR (125.8 MHz, Acetone-*d*₆+DMSO-*d*₆) δ 137.9, 134.9, 133.8, 132.3, 132.1, 131.9, 130.9, 130.1, 128.7, 128.6, 127.4, 127.1, 126.6, 126.4, 126.2, 124.6. **E+Z mixture** ¹⁹F (470.8 MHz, Acetone-*d*₆+DMSO-*d*₆) δ -142.2. **E+Z mixture** ¹¹B NMR (128.4 MHz, Acetone-*d*₆+DMSO-*d*₆) δ 3.57. **E+Z mixture** FT-IR (KBr): 3435, 3017, 1624, 1395, 1234, 1213, 986, 921, 845, 810, 750, 692 cm⁻¹. HRMS (ESI): *m/z* calcd. for C₁₆H₁₃BF₃ [M-K⁺]⁻ 273.1062, found 273.1066. The *E*:*Z* ratio was 2.9:1 based on the integration of peaks at 7.06 (*E*) and 6.49 (*Z*) ppm, respectively.

Potassium 4-((1E,3Z)-3-bromo-4-phenylbuta-1,3-dienyl)phenyltrifluoroborate (18). The desired compound was prepared using potassium [(4-trifluoroboratophenyl)methyl]triphenylphosphonium chloride (**4**) (49.5 mg, 0.10 mmol), α-bromocinnamaldehyde (25.3 mg, 0.12 mmol), and K₂CO₃ (16.6 mg, 0.12 mmol) by the procedure used for compound **7** (a yellow solid, 29.8 mg, 76% yield). mp (*E*+*Z*) = 211–215 °C (dec.). **E isomer:** ¹H NMR (500 MHz, Acetone-*d*₆) δ 7.76 (d, 2H, *J* = 7.3 Hz), 7.50 (d, 2H, *J* = 7.9 Hz), 7.40 (m, 3H), 7.30 (m, 3H, *J* = 7.8 Hz), 7.12 (d, 1H, *J* = 15.1 Hz), 7.04 (d, 1H, *J* = 15.2 Hz). ¹³C NMR (125.8 MHz, Acetone-*d*₆) δ 136.2, 135.4, 132.2 (2C), 130.9, 129.4, 128.1, 127.9, 126.6, 125.2, 123.7. ¹⁹F (470.8 MHz, Acetone-*d*₆) δ -143.3. ¹¹B NMR (128.4 MHz, Acetone-*d*₆) δ 3.62. FT-IR (KBr): 3437, 3025, 1618, 1384, 1222, 1025, 968, 840, 810, 749, 690, 560 cm⁻¹. HRMS (ESI): *m/z* calcd. for C₁₆H₁₂BF₃Br [M-K⁺]⁻ 351.0168, found 351.0150. The *E*:*Z* ratio was 6.2:1 based on the integration of peaks at 7.04 (*E*) and 6.19 (*Z*) ppm, respectively.

Potassium 4-[2-(furan-2-yl)vinyl]phenyltrifluoroborate (19). The desired

compound was prepared using potassium [(4-trifluoroboratophenyl)methyl]triphenylphosphonium chloride (**4**) (49.5 mg, 0.10 mmol), 2-furaldehyde (11.5 mg, 0.12 mmol), and K₂CO₃ (16.6 mg, 0.12 mmol) by the procedure used for compound **7** (a yellow solid, 27.1 mg, 98% yield). mp (*E*+*Z*) = 176–182 °C (dec.). ***E* isomer:** ¹H NMR (500 MHz, Acetone-*d*₆) δ 7.50 (d, 1H, *J* = 1.7 Hz), 7.48 (d, 2H, *J* = 7.9 Hz), 7.28 (d, 2H, *J* = 8.0 Hz), 6.99 (d, 1H, *J* = 16.4 Hz), 6.94 (d, 1H, *J* = 16.4 Hz), 6.45 (dd, 1H, *J* = 3.27, 1.9 Hz), 6.38 (d, 1H, *J* = 3.2 Hz). ***Z* isomer:** ¹H NMR (500 MHz, Acetone-*d*₆) δ 7.47 (d, 2H, *J* = 7.7 Hz), 7.42 (d, 1H, *J* = 1.8 Hz), 7.21 (d, 2H, *J* = 8.0 Hz), 6.46 (d, 1H, *J* = 13 Hz), 6.36 (ddd, 1H, *J* = 3.4, 1.8, 0.4 Hz), 6.33 (d, 1H, *J* = 3.3 Hz), 6.27 (d, 1H, *J* = 12.7 Hz). ***E*+*Z* mixture** ¹³C NMR (125.8 MHz, Acetone-*d*₆) δ 153.9, 152.6, 141.8, 141.2, 133.7, 133.5, 132.1, 131.4, 129.9, 128.6, 126.4, 124.4, 116.0, 114.0, 111.5, 111.1, 108.9, 107.3. ***E*+*Z* mixture** ¹⁹F (470.8 MHz, Acetone-*d*₆) δ -143.2. ***E*+*Z* mixture** ¹¹B NMR (128.4 MHz, Acetone-*d*₆) δ 3.84. ***E*+*Z* mixture** FT-IR (neat): 3622, 3067, 1691, 1658, 1605, 1483, 1392, 1223, 966, 861, 726 cm⁻¹. HRMS (ESI): *m/z* calcd. for C₁₂H₉BF₃O [M-K⁺]⁻ 237.0698, found 237.0695. The *E*:*Z* ratio was 1.5:1 based on the integration of peaks at 6.38 (*E*) and 6.33 (*Z*) ppm, respectively.

Potassium 4-[2-(thiophen-2-yl)vinyl]phenyltrifluoroborate (20**).**

Method A: (Two-Steps) The desired compound was prepared using potassium [(4-trifluoroboratophenyl)methyl]triphenylphosphonium chloride (**4**) (49.5 mg, 0.10 mmol), 2-thiophenecarboxaldehyde (13.6 mg, 0.12 mmol), and K₂CO₃ (16.6 mg, 0.12 mmol) by the procedure used for compound **7** (a white solid, 26.8 mg, 92% yield).

Method B: (One-Pot) A mixture of potassium 4-(chloromethyl)phenyltrifluoroborate (**1**) (233 mg, 1.0 mmol) and triphenylphosphine (268 mg, 1.02 mmol) in DMSO (2.0 mL) was heated in an oil bath at 100 °C. After the reaction was complete (the reaction mixture was monitored by ¹H NMR every 2 h), 2-thiophenecarboxaldehyde (268 mg, 1.02 mmol) and K₂CO₃ (141 mg, 1.02 mmol) were added to the resulting mixture. The mixture was sonicated for 20 min at rt and heated to 80 °C using an oil bath. After the reaction was complete (the reaction was directly monitored by ¹H NMR every 2 h), the resulting soln was moved into a 20 mL pear flask and then the solvent was completely removed under high vacuum at 60–70 °C. The residual product was dissolved in dry acetone (10 mL), and the insoluble salts were removed by filtration through Celite. The resulting organic soln was concentrated on a rotary evaporator. The crude solid was precipitated with Et₂O (3×6 mL) (due to the low solubility of triphenylphosphine oxide in Et₂O, sonication was used to increase the solubility), filtered by sintered glass, washed with Et₂O (2×6 mL), and dried under high vacuum to obtain the desired pure compound **20** (a white solid 254 mg, 87% yield). mp (*E*+*Z*) > 260 °C. ***E* isomer:** ¹H NMR (500 MHz, Acetone-*d*₆) δ 7.48 (d, 2H, *J* = 7.8 Hz), 7.30 (d, 2H, *J* = 8.0 Hz), 7.29 (d, 1H, *J* = 16.2 Hz), 7.13 (m, 1H), 7.11 (m, 1H), 7.01 (dd, 1H, *J* = 3.5, 1.9 Hz), 6.93 (d, 1H, *J* = 16.2 Hz). ***Z* isomer:** ¹H NMR (500 MHz, Acetone-*d*₆) δ 7.47 (d, 2H, *J* = 7.8 Hz), 7.31–7.28 (m, 3H), 7.20 (dd, 1H, *J* = 5.1, 1.2

Hz), 6.89 (d, 1H, $J = 5.1, 3.6$ Hz), 6.62 (d, 1H, $J = 12$ Hz), 6.54 (d, 1H, $J = 12$ Hz). ***E+Z* mixture** ^{13}C NMR (125.8 MHz, Acetone- d_6) δ 143.5, 133.6, 132.0, 131.7, 130.4, 129.7, 127.7, 127.5, 126.5, 126.2, 125.4, 125.0, 124.5, 123.6, 121.4, 119.2. ***E+Z* mixture** ^{19}F (470.8 MHz, Acetone- d_6) δ -143.2. ***E+Z* mixture** ^{11}B NMR (128.4 MHz, Acetone- d_6) δ 3.56. ***E+Z* mixture** FT-IR (neat): 3583, 3068, 3014, 1692, 1603, 1431, 1394, 1265, 1226, 1199, 988, 968, 949, 920, 826 cm^{-1} . HRMS (ESI): m/z calcd. for $\text{C}_{12}\text{H}_9\text{BF}_3\text{S}$ $[\text{M}-\text{K}^+]^-$ 253.0470, found 253.0477. The *E:Z* ratio was 2.8:1 for method A and 3.2:1 for method B based on the integration of peaks at 6.93 (*E*) and 6.54 (*Z*) ppm, respectively.

Potassium 4-[2-(pyridin-2-yl)vinyl]phenyltrifluoroborate (21). The desired compound was prepared using potassium [(4-trifluoroboratophenyl)methyl]triphenylphosphonium chloride (**4**) (49.5 mg, 0.10 mmol), 2-pyridinecarboxaldehyde (13.6 mg, 0.12 mmol), and K_2CO_3 (16.6 mg, 0.12 mmol) by the procedure used for compound **7** (a brown solid, 23.8 mg, 83% yield). mp (*E+Z*) = 98–104 °C. ***E* isomer:** ^1H NMR (500 MHz, Acetone- d_6) δ 8.52 (m, 1H), 7.70 (td, 1H, $J = 7.7, 1.9$ Hz), 7.69 (d, 1H, $J = 16.2$ Hz), 7.52 (d, 2H, $J = 7.2$ Hz), 7.46 (d, 1H, $J = 7.9$ Hz), 7.40 (d, 2H, $J = 7.4$ Hz), 7.17 (d, 1H, $J = 16.1$ Hz), 7.15 (ddd, 1H, $J = 7.4, 4.8, 1.1$ Hz). ***Z* isomer:** ^1H NMR (500 MHz, Acetone- d_6) δ 8.53 (m, 1H), 7.49 (td, 1H, $J = 7.6, 1.8$ Hz), 7.40 (d, 2H, $J = 7.4$ Hz), 7.26 (d, 1H, $J = 8.0$ Hz), 7.11 (ddd, 1H, $J = 7.4, 4.9, 1.0$ Hz), 7.07 (d, 2H, $J = 7.9$ Hz), 7.77 (d, 1H, $J = 12.5$ Hz), 6.52 (d, 1H, $J = 12.5$ Hz). ***E+Z* mixture** ^{13}C NMR (125.8 MHz, Acetone- d_6) δ 157.0, 156.3, 149.4, 149.3, 136.2, 135.2, 134.1, 133.9, 133.4, 133.2, 132.1, 131.6, 128.9, 126.7, 125.5, 125.2, 123.4, 121.6, 121.5, 121.4. ***E+Z* mixture** ^{19}F (470.8 MHz, Acetone- d_6) δ -143.3. ***E+Z* mixture** ^{11}B NMR (128.4 MHz, Acetone- d_6) δ 3.63. ***E+Z* mixture** FT-IR (neat): 3621, 3014, 1691, 1930, 1588, 1561, 1469, 1433, 1408, 1221, 1152, 965, 820 cm^{-1} . HRMS (ESI): m/z calcd. for $\text{C}_{13}\text{H}_{10}\text{BF}_3\text{N}$ $[\text{M}-\text{K}^+]^-$ 248.0858, found 248.0870. The *E:Z* ratio was 1:1.7 based on the integration of peaks at 7.46 (*E*) and 7.26 (*Z*) ppm, respectively.

Potassium 4-[2-(3-methoxyphenyl)ethyl]phenyltrifluoroborate (22). To a solution of potassium 4-[2-(3-methoxyphenyl)vinyl]phenyltrifluoroborate (**10**) (60.0 mg, 0.19 mmol) in CH_3CN (3 mL) was quickly added Pd/C (12 mg, 20 wt %). The reaction flask was evacuated and purged with N_2 ($\times 3$). The reaction mixture was stirred at rt under a balloon of H_2 for 2 d (the reaction was monitored by ^1H NMR). The residual product was dissolved in dry acetone (3 mL), and the insoluble impurities were removed by filtration through Celite. The resulting organic soln was concentrated on a rotary evaporator. The crude solid was precipitated with Et_2O (2.5 mL), filtered by sintered glass, washed with Et_2O (2×2 mL), and

dried under high vacuum to obtain the desired pure compound **22** (a white solid 51.6 mg 86% yield). mp >200. ^1H NMR (500 MHz, Acetone- d_6) δ 7.39 (d, 2H, J = 7.6 Hz), 7.15 (t, 1H, J = 8.0 Hz), 6.97 (d, 2H, J = 7.4 Hz), 6.80 (d, 2H, J = 7.6 Hz), 6.71 (m 1H, J = 8.5, 2.0, and 1.7 Hz), 3.74 (s, 3H), 2.81 (m, 4H). ^{13}C NMR (125.8 MHz, Acetone- d_6) δ 159.8, 144.0, 138.1, 131.7, 129.1, 126.4, 120.7, 114.0, 111.1, 54.4, 38.3, 37.9. ^{19}F (470.8 MHz, Acetone- d_6) δ -143.1. ^{11}B NMR (128.4 MHz, Acetone- d_6) δ 3.87. FT-IR (neat): 2918, 1594, 1493, 1455, 1434, 1261, 1164, 1041, 925, 837, 810 cm^{-1} . HRMS (ESI): m/z calcd. for $\text{C}_{15}\text{H}_{15}\text{BF}_3\text{O}$ $[\text{M}-\text{K}^+]^-$ 279.1168, found 279.1169.

References

1. Molander, G. A.; Ham, J. *Org. Lett.* **2006**, 8, 2767–2770.

500 MHz ^1H NMR of Compound (4) in $\text{DMSO-}d_6$

126 MHz ^{13}C NMR of Compound (4) in $\text{DMSO-}d_6$

471 MHz ^{19}F NMR of Compound **(4)** in $\text{DMSO-}d_6$

128 MHz ^{11}B NMR of Compound **(4)** in $\text{DMSO-}d_6$

471 MHz ^{19}F NMR of Compound **(6)** in $\text{DMSO-}d_6$

128 MHz ^{11}B NMR of Compound **(6)** in $\text{DMSO-}d_6$

471 MHz ^{19}F NMR of Compound (7) in Acetone- d_6 +DMSO- d_6

128 MHz ^{11}B NMR of Compound (7) in Acetone- d_6 +DMSO- d_6

500 MHz ^1H NMR of Compound **(8)** in Acetone- d_6

126 MHz ^{13}C NMR of Compound **(8)** in Acetone- d_6

471 MHz ^{19}F NMR of Compound (8) in $\text{Acetone-}d_6$

128 MHz ^{11}B NMR of Compound (8) in $\text{Acetone-}d_6$

471 MHz ^{19}F NMR of Compound (9) in Acetone- d_6

128 MHz ^{11}B NMR of Compound (9) in Acetone- d_6

500 MHz ^1H NMR of Compound **(10)** in Acetone- d_6

126 MHz ^{13}C NMR of Compound **(10)** in Acetone- d_6

471 MHz ^{19}F NMR of Compound (10) in Acetone- d_6

128 MHz ^{11}B NMR of Compound (10) in Acetone- d_6

500 MHz ^1H NMR of Compound (**11**) in Acetone- d_6

126 MHz ^{13}C NMR of Compound (**11**) in Acetone- d_6

471 MHz ^{19}F NMR of Compound **(11)** in Acetone- d_6

128 MHz ^{11}B NMR of Compound **(11)** in Acetone- d_6

500 MHz ^1H NMR of Compound **(13)** in Acetone- d_6

126 MHz ^{13}C NMR of Compound **(13)** in Acetone- d_6

471 MHz ^{19}F NMR of Compound **(13)** in Acetone- d_6

128 MHz ^{11}B NMR of Compound **(13)** in Acetone- d_6

471 MHz ^{19}F NMR of Compound **(14)** in Acetone- d_6

128 MHz ^{11}B NMR of Compound **(14)** in Acetone- d_6

500 MHz ¹H NMR of Compound **(15)** in Acetone-*d*₆

126 MHz ¹³C NMR of Compound **(15)** in Acetone-*d*₆

500 MHz ^1H NMR of Compound **(16)** in Acetone- d_6

126 MHz ^{13}C NMR of Compound **(16)** in Acetone- d_6

471 MHz ^{19}F NMR of Compound **(16)** in Acetone- d_6

128 MHz ^{11}B NMR of Compound **(16)** in Acetone- d_6

471 MHz ^{19}F NMR of Compound (17) in Acetone- d_6 +DMSO- d_6

128 MHz ^{11}B NMR of Compound (17) in Acetone- d_6 +DMSO- d_6

471 MHz ^{19}F NMR of Compound **(18)** in Acetone- d_6

128 MHz ^{11}B NMR of Compound **(18)** in Acetone- d_6

471 MHz ^{19}F NMR of Compound **(19)** in Acetone- d_6

128 MHz ^{11}B NMR of Compound **(19)** in Acetone- d_6

471 MHz ^{19}F NMR of Compound (20) in Acetone- d_6

128 MHz ^{11}B NMR of Compound (20) in Acetone- d_6

500 MHz ^1H NMR of Compound (21) in Acetone- d_6

126 MHz ^{13}C NMR of Compound (21) in Acetone- d_6

(21)

471 MHz ^{19}F NMR of Compound (21) in Acetone- d_6

128 MHz ^{11}B NMR of Compound (21) in Acetone- d_6

471 MHz ^{19}F NMR of Compound **(22)** in $\text{Acetone-}d_6$

128 MHz ^{11}B NMR of Compound **(22)** in $\text{Acetone-}d_6$