Supplementary Material

Stereoselective Preparation of (*E*)- and (*Z*)- α -fluorostilbenes via Palladium-Catalyzed Cross-Coupling Reaction of High *E/Z* ratio and (*Z*)-1-Bromo-1-fluoroalkenes

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Supporting Information Available: Experimental procedures for the synthesis of **3a**, **3b**, **3c**, **3d**, **3e**, **3f**, **3g**, **3h**, and their characterization by ¹⁹F, ¹H, ¹³C NMR, GC-MS, and HRMS; copies of ¹H and ¹³C NMR spectra of compounds **3a-3i**, **6a-6g**. Photolytic isomerization example of **1** to **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Supplemental Experimental Section

General Methods. The ^1H , ^{19}F , ^{13}C spectra of the final products were obtained on a 300 MHz NMR spectrometer (TMS, CFCl_3 or CDCl_3 as internal references, respectively). GC-MS analyses were performed at 70 eV in the electron-impact mode. Melting points are uncorrected.

Materials. DMF was dried by stirring overnight over CaH_2 , then distilled at reduced pressure. NBu_3 was dried over NaH before distillation. $\text{Pd}(\text{PPh}_3)_4$ was prepared by Coulson's procedure;¹ $\text{Cl}_2\text{Pd}(\text{PPh}_3)_2$ was prepared by Negishi's procedure.² 1-Bromo-1-fluoroalkenes ($E/Z \approx 1:1$) **1** were prepared from the corresponding aldehydes, CFBr_3 , and PPh_3 as described in the literature³ except that THF was used as the solvent.

(Z)-1-Fluoro-1,2-diphenylethene (3a). Following the general method to prepare **3**, a mixture of 1-bromo-1-fluorostyrene (0.40 g, 2.0 mmol, $E/Z = 88:12$), $\text{Pd}(\text{PPh}_3)_4$ (0.08 g, 0.07 mmol), PhSnBu_3 (0.77 g, 2.11 mmol), CuI (0.17 g, 0.88 mmol) in DMF (4 ml) was reacted at room temperature for 20 hours. ^{19}F NMR analysis of the reaction mixture showed that the Z/E ratio of the crude product is 98:2. Silica gel column chromatography (hexanes, $R_f = 0.22$) followed by recrystallization from hexanes gave white crystals, 0.29 g; yield 73 % (the conversion is 83 % based on the consumed E 1-bromo-1-fluoroalkene). (Z) 100 %. ^{19}F NMR (CDCl_3) δ -114.7 (d, $^3J_{\text{FH}(\text{trans})} = 39.2$ Hz) ppm; ^1H NMR (CDCl_3) δ 7.64 (dm, $J = 8.2$ Hz, 4 H), 7.32-7.43 (m, 5 H), 7.22 (m, 1 H), 6.31 (d, $^3J_{\text{HF}(\text{trans})} = 39.5$ Hz, 1 H) ppm. ^{13}C NMR (CDCl_3) δ 157.3 (d, $^1J_{\text{CF}} = 259.5$ Hz), 133.8 (d, $J = 2.3$ Hz), 133.0 (d, $J = 27.7$ Hz), 129.2, 129.1, 128.7 (broad), 127.5 (d, $J = 2.8$ Hz), 124.4 (d, $J = 6.9$ Hz), 106.0 (d, $J = 10.7$ Hz) ppm; mp: 88-90 °C; GC-MS, m/z (relative intensity):

199 ($M^+ + 1$, 13), 198 (M^+ , 100), 197 (84), 196 (61), 183 (39), 178 (20), 177 (18), 176 (12), 170 (11), 98 (16), 89 (9), 85 (13). This compound has been previously reported.⁴

(Z)-1-Fluoro-1-(4-fluorophenyl)-2-phenylethene (3b). Similarly, a mixture of 1-bromo-1-fluoro-2-phenylethene (0.40 g, 2.0 mmol, *E/Z* = 88: 12), $\text{Pd(PPh}_3)_4$ (0.08 g, 0.07 mmol), *p*- $\text{FC}_6\text{H}_4\text{SnBu}_3$ (0.947 g, 2.46 mmol), CuI (0.17 g, 0.88 mmol) in DMF (4 ml) was reacted at room temperature for 16 hours. ^{19}F NMR analysis of the reaction mixture showed that the *Z/E* ratio of the crude product was 98: 2. Silica gel column chromatography (hexanes, R_f = 0.57) followed by recrystallization from hexanes gave white crystals, 0.29 g; yield 67 % (the conversion is 76 % based on the consumed (*E*) 1-bromo-1-fluoroalkene). (*Z*) 100 %. ^{19}F NMR (CDCl_3) δ -112.2 (m, 1 F), -114.0 (d, $^3J_{\text{FH(trans)}} = 39.6$ Hz, 1 F) ppm; ^1H NMR (CDCl_3) δ 7.62 (dt, $J = 8.9$ Hz, $J = 2.2$ Hz, 4 H), 7.38 (tm, $J = 7.6$ Hz, 2 H), 7.24- 7.29 (m, 1 H), 7.10 (tm, $J = 8.7$ Hz, 2 H), 6.24 (d, $^3J_{\text{HF(trans)}} = 39.3$ Hz, 1 H) ppm; ^{13}C NMR (CDCl_3) δ 163.1 (d, $^1J_{\text{CF}} = 248.5$ Hz), 156.3 (d, $^1J_{\text{CF}} = 258.4$ Hz), 133.4 (d, $J = 2.5$ Hz), 129.2 (d, $J = 1.3$ Hz), 128.8 (d, $J = 7.2$ Hz), 128.5, 127.3, 126.2 (t, $J = 8.1$ Hz), 115.6 (d, $J = 22.0$ Hz), 105.6 (d, $J = 12.4$ Hz) ppm; mp 104-106 °C; GC-MS *m/z* (relative intensity) 218 ($M^+ + 2$, 1), 217 ($M^+ + 1$, 17), 216 (M^+ , 100), 215 (72), 214 (55), 201 (37), 196 (45), 195 (45), 194 (19), 183 (16), 175 (17), 170 (8), 151 (8), 120 (12), 107 (16), 98 (17), 94 (14), 85 (12), 81 (7), 75 (10); HRMS calculated 216.0751 for $\text{C}_{14}\text{H}_{10}\text{F}_2$, observed 216.0760.

(Z)-2-(2-Chlorophenyl)-1-fluoro-1-phenylethene (3c). Similarly, a mixture of 1-bromo-1-fluoro-2-(2-chlorophenyl)-ethene (0.47 g, 2.0 mmol, *E/Z* = 82: 18), $\text{Pd(PPh}_3)_4$ (0.08 g, 0.07 mmol), PhSnBu_3 (0.97 g, 2.38 mmol), CuI (0.16 g, 0.82 mmol) in DMF (4 ml) was reacted at room temperature for 15 hours. ^{19}F NMR analysis of the reaction

mixture showed that the *Z/E* ratio of the crude product is 94: 6. Silica gel column chromatography (hexanes, R_f = 0.39) gave a colorless liquid 0.33 g; yield 71 % (the conversion is 87 % based on the consumed (*E*) 1-bromo-1-fluoroalkene). (*Z*) 100 %. ^{19}F NMR (CDCl_3) δ -114.2 ppm (d, $^3J_{\text{FH}(\text{trans})}$ = 39.0 Hz, 1 F) ppm; ^1H NMR (CDCl_3) δ 7.97 (dd, J = 8.0 Hz, J = 1.4 Hz, 1 H), 7.68 (dm, J = 8.2 Hz, 2 H), 7.35 - 7.45 (m, 4 H), 7.28 (t, J = 7.3 Hz, 1 H), 7.18 (td, J = 7.6 Hz, J = 1.6 Hz, 1 H), 6.75 (d, $^3J_{\text{HF}(\text{trans})}$ = 38.6 Hz) ppm; ^{13}C NMR (CDCl_3) δ 158.4 (d, $^1J_{\text{CF}}$ = 261.5 Hz), 133.3, 132.7 (d, J = 27.6 Hz), 131.7 (d, J = 3.5 Hz), 130.6 (d, J = 13.3 Hz), 129.7, 129.6, 128.8 (d, J = 2.4 Hz), 128.4, 127.0, 124.7 (d, J = 7.2 Hz), 101.8 (d, J = 8.9 Hz) ppm; GC-MS, product isomerized on the GC column. m/s (relative intensity) of one isomer: 235 ($\text{M}^+ + 3$, 10), 234 ($\text{M}^+ + 2$, 53), 233 ($\text{M}^+ + 1$, 29), 232 (M^+ , 91), 212 (8), 198 (32), 197 (81), 196 (100), 194 (35), 178 (17), 177 (54), 176 (38), 175 (23), 170 (31), 165 (4), 151 (11), 98 (68), 97 (28), 85 (64), 75 (22); the other isomer: 235 ($\text{M}^+ + 3$, 3), 234 ($\text{M}^+ + 2$, 21), 233 (9), 232 (M^+ , 65), 197 (93), 196 (100), 177 (22), 176 (14), 170 (11), 98 (24), 88 (11), 85 (23); HRMS calculated 232.0455 for $\text{C}_{14}\text{H}_{10}\text{F}^{35}\text{Cl}$, found 232.0454.

(*Z*)-2-(2-Chlorophenyl)-1-fluoro-1-(4-fluorophenyl)ethene (3d). Similarly, a mixture of 1-bromo-1-fluoro-2-(2-chlorophenyl)-ethene (0.471 g, 2.0 mmol, *E/Z* = 82: 18), $\text{Pd}(\text{PPh}_3)_4$ (0.076 g, 0.0656 mmol), $p\text{-FC}_6\text{H}_4\text{SnBu}_3$ (0.884 g, 2.296 mmol), CuI (0.076 g, 0.0656 mmol) in DMF (4 ml) was reacted at room temperature for 16 hours. ^{19}F NMR analysis of the reaction mixture showed that the *Z/E* ratio of the crude product was 94: 6. Silica gel column chromatography (hexanes only, R_f = 0.33) followed by recrystallization from hexanes gave white crystals, 0.26 g; yield 52 % (the conversion is 63 % based on the amount of the consumed (*E*)-1-bromo-1-fluoroalkenes). (*Z*) 100 %. ^{19}F NMR (CDCl_3)

δ -111.4 (m, 1 F), -113.6 (d, $^3J_{\text{FH(trans)}} = 40.2$ Hz, 1 F) ppm; ^1H NMR (CDCl_3) δ 7.79 (dd, $J = 7.9$ Hz, $J = 1.5$ Hz, 1 H), 7.66 (ddm, $J = 8.8$ Hz, $J = 5.1$ Hz, 2 H), 7.41 (d, $J = 8.1$ Hz, 1 H), 7.29 (t, $J = 7.3$ Hz, 1 H), 7.21 (ddd, $J = 7.7$ Hz, $J = 7.5$ Hz, $J = 1.4$ Hz, 1 H), 7.12 (t, $J = 8.8$ Hz, 2 H), 6.67 (d, $^3J_{\text{HF(trans)}} = 38.5$ Hz, 1 H) ppm; ^{13}C NMR (CDCl_3) δ 163.3 (d, $^1J_{\text{CF}} = 250.6$ Hz), 157.3 (d, $^1J_{\text{CF}} = 259.6$ Hz), 133.0, 131.3 (d, $J = 2.8$ Hz), 130.3 (d, $J = 13.4$ Hz), 129.4, 128.7 (dd, $J = 28.4$ Hz, $J = 3.5$ Hz), 128.3, 126.8, 126.5 (t, $J = 8.0$ Hz), 115.6 (d, $J = 21.8$ Hz), 101.3 (dm, $J = 11.2$ Hz) ppm; mp: 53-55 °C; GC-MS m/z (relative intensity) 253 (4), 252 ($\text{M}^+ + 2$, 30), 251 (12), 250 (M^+ , 85), 232 (2), 230 (5), 216 (11), 215 (76), 214 (100), 212 (12), 196 (14), 195 (74), 194 (29), 188 (13), 175 (21), 168 (8), 125 (8), 107 (41), 97 (9), 94 (33), 75 (12); HRMS calculated 250.0361 for $\text{C}_{14}\text{H}_9\text{F}_2^{35}\text{Cl}$, observed 250.0354.

(Z)-1-Fluoro-2-(4-methoxyphenyl)-1-phenylethene (3e). Similarly, a mixture of 1-bromo-1-fluoro-2-(4-methoxyphenyl)ethene (0.46 g, 2.0 mmol, $E/Z = 83:17$), $\text{Pd}(\text{PPh}_3)_4$ (0.08 g, 0.07 mmol), PhSnBu_3 (0.85 g, 2.32 mmol), CuI (0.16 g, 0.83 mmol) in DMF (4 ml) was reacted at room temperature for 22 hours. ^{19}F NMR analysis of the reaction mixture showed that the Z/E ratio of the crude product was 93:7. Silica gel column chromatography (ethyl acetate: hexanes = 5:95, $R_f = 0.33$) followed by recrystallization from hexanes gave white crystals, 0.28 g; yield 61 % (the conversion is 74 % based on the consumed (E)-1-bromo-1-fluoroalkene). (Z) 100 %. ^{19}F NMR (CDCl_3) δ -117.7 (d, $^3J_{\text{FH(trans)}} = 39.9$ Hz) ppm; ^1H NMR (CDCl_3) δ 7.61 (tm, $J = 8.2$ Hz, 4 H), 7.30 - 7.42 (m, 3 H), 6.91 (dm, $J = 8.8$ Hz, 2 H), 6.26 (d, $^3J_{\text{HF(trans)}} = 39.9$ Hz, 1 H), 3.83 (s, 3 H) ppm; ^{13}C NMR (CDCl_3) δ 158.7 (d, $J = 1.7$ Hz), 155.9 (d, $^1J_{\text{CF}} = 255.3$ Hz), 133.1 (d, $J = 28.2$ Hz), 130.2 (d, $J = 8.2$ Hz), 128.51, 128.47, 126.3 (d, $J = 4.3$ Hz), 123.9 ($J = 7.2$ Hz), 114.0,

105.4 (d, $J = 10.9$ Hz), 55.2 ppm; mp: 97- 99 °C; GC-MS, product isomerized on GC column. m/z (relative intensity) of one isomer: 230 ($M^+ + 2$, 3), 229 ($M^+ + 1$, 4), 228 (M^+ , 100), 213 (69), 196 (13), 185 (25), 183 (51), 170 (35), 165 (75), 157 (12), 146 (11), 133 (19), 114 (15); the other isomer: 230 ($M^+ + 2$, 8), 229 ($M^+ + 1$, 8), 228 (M^+ , 100), 213 (50), 196 (7), 185 (16), 183 (41), 170 (21), 165 (93), 157 (9), 146 (8), 133 (15), 107 (8); HRMS calculated 228.0950 for $C_{15}H_{13}OF$, found 228.0945.

(Z)-1-Fluoro-2-(4-fluorophenyl)-1-phenylethene (3f). Similarly, a mixture of 1-bromo-1-fluoro-2-(4-fluorophenyl)-ethene (0.219 g, 1.0 mmol, $E/Z = 87: 13$), $Pd(PPh_3)_4$ (0.040g, 0.0348 mmol), $PhSnBu_3$ (0.447 g, 1.218 mmol), CuI (0.083 g, 0.435 mmol) in DMF (3 ml) was reacted at room temperature for 16 hours. ^{19}F NMR analysis of the reaction mixture showed that the Z/E ratio of the crude product was 96: 4. Silica gel column chromatography (hexanes only, $R_f = 0.35$) followed by recrystallization from hexanes gave white crystals, 0.15 g; yield 69 % (the conversion is 80 % based on the amount of the consumed (E)-1-bromo-1-fluoroalkenes). (Z) 100 %. ^{19}F NMR ($CDCl_3$) δ -114.3 (m, 1 F), -115.9 (d, $^3J_{FH(trans)} = 39.7$ Hz, 1 F) ppm; 1H NMR ($CDCl_3$) δ 7.59- 7.64 (m, 4 H), 7.33- 7.44 (m, 3 H), 7.06 (tm, $J = 8.8$ Hz, 2 H), 6.27 (d, $^3J_{HF(trans)} = 39.2$ Hz, 1 H) ppm; ^{13}C NMR ($CDCl_3$) δ 161.8 (dd, $^1J_{CF} = 247.3$ Hz, $J = 3.4$ Hz), 156.9 (dd, $^1J_{CF} = 257.7$ Hz, $J = 2.6$ Hz), 132.6 (d, $J = 27.4$ Hz), 130.5 (t, $J = 8.1$ Hz), 129.8 (m), 129.0, 128.6 (d, $J = 2.4$ Hz), 124.2 (d, $J = 8.2$ Hz), 115.5 (d, $J = 20.2$ Hz), 104.7 (d, $J = 10.3$ Hz) ppm; mp: 76- 77°C; GC-MS m/z (relative intensity) 217 ($M^+ + 1$, 14), 216 (M^+ , 100), 215 (52), 214 (39), 201 (27), 196 (42), 195 (35), 194 (16), 183 (15), 175 (12), 170 (7), 138 (4), 120(4), 107 (12), 98 (13), 85 (9), 75 (8); HRMS calculated 216.0751 for $C_{14}H_{10}F_2$, observed 216.0756.

(Z)-1-Fluoro-2-(3-nitrophenyl)-1-phenylethene (3g). Similarly, a mixture of 1-bromo-1-fluoro-2-(3-nitrophenyl)-ethene (0.246 g, 1.0 mmol, *E/Z* = 76: 24), Pd(PPh₃)₄ (0.035 g, 0.030 mmol), PhSnBu₃ (0.39 g, 1.064 mmol), CuI (0.072 g, 0.38 mmol) in DMF (3 ml) was reacted at room temperature for 16 hours. ¹⁹F NMR analysis of the reaction mixture showed that the *Z/E* ratio of the crude product was 87: 13. Silica gel column chromatography (ethyl acetate: hexanes = 5: 95, *R_f* = 0.33) followed by recrystallization from hexanes gave white crystals, 0.13 g; yield 53 % (the conversion is 70 % based on the amount of the consumed (*E*)-1-bromo-1-fluoroalkenes). (*Z*) 100 %. ¹⁹F NMR (CDCl₃) δ -110.9 (d, ³J_{FH(trans)} = 38.0 Hz, 1 F) ppm; ¹H NMR (CDCl₃) δ 8.49 (s, 1 H), 8.10 (dm, *J* = 8.3 Hz, 1 H), 7.94 (dm, *J* = 7.6 Hz, 1 H), 7.66- 7.69 (m, 2 H), 7.54 (t, *J* = 7.9 Hz, 1 H), 7.43- 7.48 (m, 3 H), 6.37 (d, ³J_{HF(trans)} = 38.0 Hz, 1 H) ppm; ¹³C NMR (CDCl₃) δ 158.9 (d, ¹J_{CF} = 260.0 Hz), 148.3, 135.2 (d, *J* = 2.8 Hz), 134.3 (d, *J* = 8.7 Hz), 131.7 (d, *J* = 27.4 Hz), 129.7, 129.3, 128.6 (d, *J* = 2.1 Hz), 124.4 (d, *J* = 6.6 Hz), 123.2 (d, *J* = 7.8 Hz), 121.6 (d, *J* = 2.4 Hz), 103.6 (d, *J* = 10.0 Hz) ppm; mp: 90- 91 °C; GC-MS *m/z* (relative intensity) 244 (M⁺ + 1, 7), 243 (M⁺, 51), 226 (4), 224 (4), 198 (14), 197 (24), 196 (100), 183 (11), 177 (14), 176 (25), 170 (26), 165 (12), 98 (11), 75 (10); HRMS calculated 243.0696 for C₁₄H₁₀FNO₂, observed 243.0694.

(Z)-2-(4-Chlorophenyl)-1-fluoro-1-(4-fluorophenyl)ethene (3h). Similarly, a mixture of 1-bromo-1-fluoro-2-(4-chlorophenyl)-ethene (0.236 g, 1.0 mmol, *E/Z* = 88: 12), Pd(PPh₃)₄ (0.041 g, 0.035 mmol), *p*-FC₆H₄SnBu₃ (0.474 g, 1.23 mmol), CuI (0.041 g, 0.035 mmol) in DMF (3 mL) was reacted at room temperature for 12 hours. ¹⁹F NMR analysis of the reaction mixture showed that the *Z/E* ratio of the crude product is 98: 2. Silica gel column chromatography (hexanes 100 %, *R_f* = 0.33) followed by

recrystallization from hexanes gave white crystals, 0.18 g; yield 72 % (the conversion is 82 % based on the amount of the consumed (*E*)-1-bromo-1-fluoroalkenes). (*Z*) 100 %. ^{19}F NMR (CDCl_3) δ -111.7 (m, 1 F), -113.3 (d, $^3J_{\text{FH}(\text{trans})} = 38.1$ Hz, 1 F) ppm; ^1H NMR (CDCl_3) δ 7.61 (ddm, $J = 8.7$ Hz, $J = 5.3$ Hz, 2 H), 7.54 (dm, $J = 8.5$ Hz, 2 H), 7.33 (dm, $J = 8.4$ Hz, 2 H), 7.10 (tm, $J = 8.7$ Hz, 2 H), 6.18 (d, $^3J_{\text{HF}(\text{trans})} = 39.0$ Hz, 1 H) ppm; ^{13}C NMR (CDCl_3) δ 163.2 (d, $^1J_{\text{CF}} = 250.9$ Hz), 156.7 (d, $^1J_{\text{CF}} = 258.7$ Hz), 132.9 (d, $J = 4.1$ Hz), 131.9 (d, $J = 2.5$ Hz), 130.90 (d, $J = 8.4$ Hz), 128.7, 128.66 (dd, $J = 28.3$ Hz, $J = 3.0$ Hz), 126.2 (t, $J = 7.8$ Hz), 115.6 (d, $J = 22.0$ Hz), 104.5 (dm, $J = 10.8$ Hz) ppm; mp: 90-91 °C; GC-MS m/z (relative intensity) 253 (5), 252 ($\text{M}^+ + 2$, 32), 251 (14), 250 (M^+ , 100), 232 (3), 230 (9), 215 (51), 214 (100), 196 (11), 195 (46), 194 (24), 188 (11), 175 (16), 107 (26), 97 (14), 94 (21); HRMS calculated 250.0361 for $\text{C}_{14}\text{H}_9\text{F}_2^{35}\text{Cl}$, observed 250.0360.

^1H and ^{13}C NMR spectra of 3a-3i and 6a-6g:

3a:

3b:

3c:

3d:

3e:

3f:

3g:

3h:

3i:

6a:

6b:

6c:

6d:

6e:

6f:

6g:

Photolytic isomerization example of 1 to 2. 1-Bromo-1-fluoro-2-(2-chlorophenyl)-ethene (neat, E/Z = 63: 37) was kept in a quartz NMR tube. The E/Z ratio was confirmed by ^{19}F NMR spectroscopy before experiment. The tube was UV irradiated at 254 nm at room temperature for 1 hr. ^{19}F NMR spectroscopy showed that the E/Z ratio has changed to 78:22; and no obvious impurity peak was observed.

Reference:

1. Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121-124.
2. King, A. O.; Negishi, E. *J. Org. Chem.* **1978**, *43*, 358-360.
3. (a) Vanderhaar, R. W.; Burton, D. J.; Nae, D. G. *J. Fluorine Chem.* **1971/72**, *1*, 381-383. (b) Burton, D. J.; Yang, Z-Y.; Qiu, W. *Chem. Rev.* **1996**, *96*, 1641-1715. (c) Burton, D. J. *J. Fluorine Chem.* **1983**, *23*, 339-357.
4. Chen, C.; Wilcoxen, K.; Zhu, Y-F.; Kim, K-i.; McCarthy, J. R. *J. Org. Chem.* **1999**, *64*, 3476-3482.