Stereoselective synthesis of (*Z*)-2-fluoroalk-1- enyl(phenyl)iodonium tetrafluoroborate

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Supporting Information

Materials. Commercial grade reagents and solvents were used without further purification.

General Procedures.

(*Z*)-2-Fluoro-1-dodecenyl(phenyl)iodonium tetrafluoroborate (2a). White solid: mp 27 – 28 °C, ¹H NMR (400MHz, CDCl₃) δ 0.88 (3H, t, *J* = 7.3 Hz), 1.19 – 1.31 (14H, m), 1.52 – 1.60 (2H, m), 2.57 (2H, dt, ³*J*_{H-F} = 17.3, *J* = 7.6 Hz), 6.52 (1H, d, ³*J*_{H-F(olefin)} = 33.2 Hz), 7.45 – 8.02 (5H, m); ¹⁹F NMR (376 MHz, CDCl₃) δ -63.90 (1F, dt, ³*J*_{H-F} = 17.3, ³*J*_{H-F(olefin)} = 33.2 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 14.11, 22.67, 25.48, 28.69, 29.03, 29.26, 29.35, 29.47, 31.86, 32.26 (d, ²*J*_{C-F} = 23.2 Hz), 74.20 (d, ²*J*_{C-F} = 21.5 Hz), 111.4, 132.28 (2C), 132.64, 135.27 (2C), 174.19 (d, ¹*J*_{C-F} 280.0 Hz); IR (KBr) 3061, 3048, 2956, 2923, 2852, 1653, 1564, 1470, 1440, 1301, 1115, 1055, 989, 880, 738, 680 cm⁻¹; LRMS (FAB): *m/z* 389 (M⁺ - BF₄ 100 %), 307 (9), 289 (4), 154 (28), 136 (17), 107 (5), 89 (5), 77 (6), 69 (5), 55 (8), 43 (6); HRMS (FAB): Calc. for C₁₈H₂₇FI (*M* - BF₄): 389.1142. Found: 389.1127; Anal. Calcd for C₁₈H₂₇BF₅I: C, 45.41; H, 5.72%. Found: C, 45.48; H, 5.85%.

(*Z*)-3,3-Dimethyl-2-fluoro-1-butenyl(phenyl)iodonium tetrafluoroborate (2b). White solid: mp 160.7 – 161.5 °C, ¹H NMR (400MHz, CDCl₃) δ 1.24 (9H, s), 6.55 (1H, d, ³*J*_{H-F(olefin)} = 33.9 Hz), 7.52 – 8.01 (5H, m); ¹⁹F NMR (376 MHz, CDCl₃) δ -70.65 (1F, d, ³*J*_{H-F(olefin)} = 33.9 Hz); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 26.39 (3C), 36.39 (d, ²*J*_{C-F} = 22.3 Hz), 79.39 (d, ²*J*_{C-F} = 21.5 Hz), 115.05, 131.76 (2C), 131.88, 134.68 (2C), 176.45 (d, ¹*J*_{C-F} = 275.9 Hz); IR (KBr) 3120, 3094, 2976, 2941, 2908, 2876, 1633, 1471, 1444, 1284, 1073, 1034, 988, 867, 764, 744, 679 cm⁻¹; LRMS (FAB): *m/z* 305 (M⁺ - BF₄ 100 %), 282 (5), 154 (23), 136 (17), 107 (3), 89 (3), 77 (5); HRMS (FAB): Calc. for C₁₂H₁₅FI (*M* - BF₄): 305.0203. Found: 305.0223; Anal. Calcd for C₁₂H₁₅BF₅I: C, 36.77; H, 3.86%. Found: C, 36.63; H, 3.76%.

(*Z*)-3-Cyclohexyl-2-fluoro-1-propenyl(phenyl)iodonium tetrafluoroborate (2c). White solid: mp 84.0 – 84.5 °C, ¹H NMR (400MHz, CDCl₃) δ 0.86 – 1.25 (5H, m), 1.60 – 1.69 (6H, m), 2.47 (2H, dd, ³*J*_{H-F} = 21.2, *J* = 6.8 Hz), 6.49 (1H, d, ³*J*_{H-F(olefin)} = 32.7 Hz), 7.46 – 8.03 (5H, m); ¹⁹F NMR (376 MHz, CDCl₃) δ -63.00 (1F, dt, ³*J*_{H-F} = 21.2, ³*J*_{H-F(olefin)} = 32.7 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 25.80 (2C), 25.87, 32.54 (2C), 35.25, 39.70 (d, ²*J*_{C-F} = 23.1 Hz), 74.78 (d, ²*J*_{C-F} = 21.4 Hz), 111.60, 132.25 (2C), 132.63, 135.30 (2C), 173.07 (d, ¹*J*_{C-F} = 280.0 Hz); IR (KBr) 3122, 3097, 3066, 2929, 2852, 1652, 1564, 1472, 1444, 1115, 1049, 873, 738, 678 cm⁻¹; LRMS (FAB): *m/z* 345 (M⁺ - BF₄ 100 %), 154 (11), 136 (8), 77 (3); HRMS (FAB): Calc. for C₁₅H₁₉FI (*M* - BF₄): 345.0516. Found: 345.0505; Anal. Calcd for C₁₅H₁₉BF₅I: C, 41.70; H, 4.43%. Found: C, 41.74; H, 4.45%.

(*Z*)-11-Chloro-2-fluoro-1-undecenyl(phenyl)iodonium tetrafluoroborate (2d). White solid: mp 34.5 - 35.0 °C, ¹H NMR (400MHz, CDCl₃) δ 1.21 – 1.44 (10H, m), 1.53 – 1.61 (2H, m), 1.72 – 1.79 (2H, m), 2.58 (2H, dt, ³*J*_{H-F} = 17.3, *J* = 7.3 Hz), 3.53 (2H, t, *J* = 6.6 Hz), 6.52 (1H, d, ³*J*_{H-F(olefin)} = 33.2 Hz), 7.46 – 8.03 (5H, m); ¹⁹F NMR (376 MHz, CDCl₃) δ -63.99 (1F, dt, ³*J*_{H-F} = 17.7, ³*J*_{H-F(olefin)} = 33.1 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 25.32, 26.66, 28.46, 28.59, 28.78, 29.02, 32.04 (d, ²*J*_{C-F} = 23.1 Hz), 32.45, 45.11, 74.22 (d, ²*J*_{C-F} = 21.5 Hz), 111.42, 132.16 (2C), 132.50, 135.13 (2C), 173.90 (d, ¹*J*_{C-F} = 279.1 Hz); IR (KBr) 3060, 2930, 2853, 1650, 1564, 1469, 1441, 1306, 1106, 1056, 989, 881, 740, 681, 654 cm⁻¹; LRMS (FAB): *m/z* 409 (M⁺ - BF₄ 100 %), 307 (6), 282 (6), 154 (29), 136 (19), 107 (5), 89 (5), 77 (7); HRMS (FAB): Calc. for C₁₇H₂₄ClFI (*M* - BF₄): 409.0595. Found: 409.0609; Anal. Calcd for C₁₇H₂₄BClF₅I: C, 41.12; H, 4.87%. Found: C, 40.94; H, 4.85%.

(*Z*)-12,12-Dimethyl-2-fluoro-11-oxo-1-tridecenyl(phenyl)iodonium tetrafluoroborate (2e). Colorless oil, ¹H

NMR (400MHz, CDCl₃) δ 1.26 (9H, s), 1.17 – 1.34 (8H, m), 1.50 – 1.57 (4H, m), 2.46 (2H, t, J = 6.8 Hz), 2.59 (2H, dt, $^3J_{\text{H-F}}$ = 17.1, J = 7.8 Hz), 6.50 (1H, d, $^3J_{\text{H-F(olefin)}}$ = 32.9 Hz), 7.47 – 8.03 (5H, m); ¹⁹F NMR (376 MHz, CDCl₃) δ - 63.77 (1F, dt, $^3J_{\text{H-F}}$ = 17.1, $^3J_{\text{H-F(olefin)}}$ = 32.9 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 23.80, 25.41, 26.41 (3C), 28.52, 28.80, 29.09, 29.17, 32.21 (d, $^2J_{\text{C-F}}$ 23.1 Hz), 36.37, 44.11, 74.30 (d, $^2J_{\text{C-F}}$ 21.5 Hz), 111.42, 132.31 (2C), 132.68, 135.28 (2C), 174.11 (d, $^1J_{\text{C-F}}$ 280.0 Hz), 216.29; IR (neat) 3104, 2932, 2858, 1702, 1646, 1565, 1472, 1444, 1366, 1065, 988, 741, 679, 651 cm⁻¹; LRMS (FAB): m/z 445 (M⁺ - BF₄ 100 %), 154 (11), 136 (9), 77 (4), 57 (8); HRMS (FAB): Calc. for C₂₁H₃₁FIO (M - BF₄): 445.1404. Found: 445.1415; Anal. Calcd for C₂₁H₃₁BF₅IO: C, 47.39; H, 5.87%. Found: C, 47.62; H, 5.91%.

(Z)-10-(2-Propoxy)carbonyl-2-fluoro-1-decenyl(phenyl)iodonium tetrafluoroborate (2f). Colorless oil, ¹H NMR (400MHz, CDCl₃) δ 1.20 – 1.32 (14H, m), 1.53 – 1.62 (4H, m), 2.24 (2H, t, J = 7.3 Hz), 2.58 (2H, dt, $^3J_{\text{H-F}}$ = 17.3, J = 7.6 Hz), 4.96 – 5.03 (1H, m), 6.51 (1H, d, $^3J_{\text{H-F(olefin)}}$ = 32.9 Hz), 7.47 – 8.03 (5H, m); ¹⁹F NMR (376 MHz, CDCl₃) δ - 63.89 (1F, dt, $^3J_{\text{H-F}}$ = 16.9, $^3J_{\text{H-F(olefin)}}$ = 33.1 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 21.67 (2C), 24.74, 25.25, 28.36, 28.63, 28.73, 28.7, 31.93 (d, $^2J_{\text{C-F}}$ = 23.1 Hz), 34.46, 67.26, 74.21 (d, $^2J_{\text{C-F}}$ = 21.5 Hz), 111.46, 132.09 (2C), 132.43, 135.03 (2C), 173.27, 173.78 (d, $^1J_{\text{C-F}}$ = 279.2 Hz); IR (neat) 3104, 2980, 2933, 2857, 1727, 1646, 1565, 1470, 1445, 1374, 1109, 1064, 988, 741, 679, 651 cm⁻¹; LRMS (FAB): m/z 447 (M⁺ - BF₄ 100 %), 154 (10), 136 (8), 77 (4); HRMS (FAB): Calc. for C₂₀H₂₉FIO₂ (M - BF₄): 447.1196. Found: 447.1225; Anal. Calcd for C₂₀H₂₉BF₅IO₂: C, 44.97; H, 5.47%. Found: C, 44.89; H, 5.57%.

(Z)-2-Fluoro-1-iodo-1-dodecene (3). To a DMF solution (2 ml) of CuI (4.8 mg, 0.025 mmol) and KI (83 mg, 0.5 mmol) was added at room temperature, a DMF solution (1 ml) of **2a** (238 mg, 0.5 mmol) and the reaction mixture was stirred at the temperature for 36 h. The reaction mixture was poured into a 15 % aqueous solution of NH₄Cl and the aqueous layer was extracted with ether (10 ml x 4). The combined organic phases were dried over MgSO₄ and concentrated under reduced pressure. The purification by column chromatography (hexane) gave **3** in 89 % yield as a colorless liquid, ¹H NMR (400MHz, CDCl₃) δ 0.88 (3H, t, J = 7.1 Hz), 1.20 – 1.37 (14H, m), 1.48 – 1.55 (2H, m), 2.33 (2H, dt, $^3J_{\text{H-F}}$ = 16.6, J = 7.6 Hz), 5.17 (1H, d, $^3J_{\text{H-F(olefin)}}$ = 34.6 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ - 79.84 (1F, dt, $^3J_{\text{H-F}}$ = 16.6, $^3J_{\text{H-F(olefin)}}$ = 34.6 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 14.13, 22.69, 25.91, 28.76, 29.22, 29.31, 29.46, 29.56, 31.89, 32.80 (d, $^2J_{\text{C-F}}$ = 26.4 Hz), 50.65 (d, $^2J_{\text{C-F}}$ = 27.3 Hz), 166.67 (d, $^1J_{\text{C-F}}$ = 261.3 Hz); IR (neat) 2955, 2925, 2854, 1656, 1466, 1117, 876, 746 cm⁻¹; LRMS (EI): m/z 312 (M⁺ 100 %), 185 (27), 123 (11), 109 (35), 95 (47), 69 (35), 43 (38), 41 (20); HRMS (EI): Calc. for C₁₂H₂₂FI (M): 312.0750. Found: 312.0732; Anal. Calcd for C₁₂H₂₂FI: C, 46.16; H, 7.10%. Found: C, 45.99; H, 6.88%.

Methyl (Z)-3-fluoro-2-tridecenoate (4). To a 10 ml round flask equipped with septum inlet, was introduced PdCl₂ (0.9 mg, 0.005 mmol) and then the atmosphere was substituted with CO. A MeOH solution (5 ml) of **2a** (238 mg, 0.5 mmol) and Et₃N (50 mg, 0.5 mmol) was introduced through the septum inlet to the flask. The mixture was stirred at room temperature for 2 h and then poured into a 30 % aqueous solution of NH₄Cl. The aqueous layer was extracted with ether (10 ml x 4), and the combined organic layers were dried over MgSO₄ and concentrated under the reduced pressure. The purification by column chromatography (silicage/hexane-ether) gave **4** in 60% yield as colorless liquid, ¹H NMR (400MHz, CDCl₃) δ 0.88 (3H, t, J = 7.1 Hz), 1.21 – 1.37 (14H, m), 1.52 – 1.59 (2H, m), 2.26 (2H, dt, $^3J_{\text{H-F}}$ = 17.3, J = 7.6 Hz), 3.72 (3H, s), 5.18 (1H, d, $^3J_{\text{H-F(olefin)}}$ = 33.1 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ - 79.53 (1F, dt, $^3J_{\text{H-F}}$ = 17.3, $^3J_{\text{H-F(olefin)}}$ = 33.1 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 14.11, 22.68, 25.54, 28.80, 29.21, 29.29, 29.42, 29.53, 31.88, 32.98 (d, $^2J_{\text{C-F}}$ 24.1 Hz), 51.33, 98.38 (d, $^2J_{\text{C-F}}$ = 6.0 Hz), 164.30, 172.40 (d, $^1J_{\text{C-F}}$ = 281.1 Hz); IR (neat) 2951, 2926, 2855, 1736, 1685, 1466, 1436, 1349, 1278, 1217, 1137, 1033, 889, 833, 722 cm⁻¹; LRMS (EI): m/z 213 (M⁺ - OMe 100 %), 192 (14), 164 (27), 150 (94), 131 (87), 119 (65), 118 (58), 94 (57), 77 (60), 55 (53), 43 (61), 41 (40); HRMS (EI): Calc. for C₁₃H₂₂FO (M - OMe): 213.1655. Found: 213.1648; Anal. Calcd for C₁₄H₂₅FO₂: C, 68.82; H, 10.31%. Found: C, 68.78; H, 10.42%.

(Z)-8-Fluoro-7-octadecen-5-yne (5). To a DMF solution (4 ml) of Ph₃P (13 mg, 0.05 mmol), Pd(OAc)₂ (5.6 mg, 0.025 mmol) were added under the nitrogen atmosphere 1-hexyne (49 mg, 0.6 mmol), **2a** (238 mg, 0.5 mmol), Et₃N (75 mg, 0.75 mmol), and CuI (7.6 mg, 0.04 mmol) in DMF (1 ml). The mixture was stirred at room temperature for 15 min and then poured into a 30 % aqueous solution of NH₄Cl. The aqueous layer was extracted with ether (10 ml x 4), and the combined organic layers were dried over MgSO₄ and concentrated under reduced pressure. The purification by column chromatography (silica gel/hexane-ether) gave **5** (86 mg, 0.325 mmol) in 65 % yield as a light yellow liquid, ¹H NMR (400MHz, CDCl₃) δ 0.86 – 0.93 (6H, m), 1.22 – 1.55 (20H, m), 2.20 (2H, dt, $^3J_{\text{H-F}}$ 17.1, J = 7.6 Hz), 2.33 (2H, t, J = 7.1 Hz), 4.75 (1H, d, $^3J_{\text{H-F(olefin)}}$ = 34.1 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ - 92.08 (1F, dt, $^3J_{\text{H-F}}$ = 17.1, $^3J_{\text{H-F(olefin)}}$ = 34.1 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 13.59, 14.10, 19.23, 21.94, 22.66, 25.91, 28.84, 29.25, 29.28, 29.46, 29.55, 30.81, 31.87, 31.93 (d, $^2J_{\text{C-F}}$ = 24.8 Hz), 72.40 (d, $^4J_{\text{C-F}}$ = 3.2 Hz), 87.51 (d, $^2J_{\text{C-F}}$ = 14.9 Hz), 94.00 (d, $^3J_{\text{C-F}}$ = 5.7 Hz), 168.75 (d, $^1J_{\text{C-F}}$ = 268.5 Hz); IR (neat) 2957, 2927, 2856, 1674, 1466, 1332, 1261, 1165, 1103, 873, 801 cm⁻¹; LRMS (EI): m/z 266 (M⁺ 87 %), 251 (18), 153 (27), 140 (22), 125 (100), 97 (48), 93 (59), 79 (30), 55 (27), 43 (30), 41 (22); HRMS (EI): Calc. for C₁₈H₃₁F (M):

266.2410. Found: 266.2406; Anal. Calcd for $C_{18}H_{31}F$: C, 81.14; H, 11.73%. Found: C, 80.99; H, 11.45%.