**Supporting Information for
Stereoselective Generation of (*E*)- and (*Z*)-2-Fluoroalkylidene-type Carbenoids from (2-Fluoro-1-alkenyl)iodonium Salts and their Application for Stereoselective Synthesis of Fluoroalkenes.**

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Synthesis of (*E*)-4-fluoro-3-tetradecene ((*E*)-**5a**): To a THF solution (7 ml) of (*Z*)-(2-fluoro-1-dodecenyl)(4-methylphenyl)iodonium tetrafluoroborate ((*Z*)-**1a**) (238 mg, 0.5 mmol) and Et₃B (58 mg, 0.6 mmol) was slowly added at -78 °C through a cannula, a THF solution of LDA, prepared by the addition of a hexane solution of BuLi (0.47 ml of a 1.6 M solution, 0.75 mmol) to diisopropyl amine (76 mg, 0.75 mmol) in THF (5 ml) at 0 °C. After stirring at the temperature for 2h, a THF solution (10 ml) of acetic acid (3 ml) was added. The mixture was stirred at -78 °C for 1h and at room temperature for 2h, and aqueous NaOH (15 ml of 3M solution) and 30% H₂O₂ (10 ml) were added at 0 °C. The mixture was stirred at room temperature for 2 h and extracted with ether three times. The combined organic layer was dried over MgSO₄ and concentrated under reduced pressure. Purification by column chromatography (silica gel/hexane) gave (*E*)-**5a** (77mg, 0.36 mmol) in 72% yield. IR (NaCl, neat) 2926, 2855, 1700, 1465 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz) δ 0.88 (t, *J* = 7.1 Hz, 3H), 0.97 (t, *J* = 7.4 Hz, 3H), 1.26-1.51 (m, 16 H), 1.93 (q, *J* = 7.6 Hz, 2H), 2.20 (dt, *J* = 23.4, 7.3 Hz, 2H), 4.99 (dt, *J* = 21.9, 8.0 Hz, 1H). ¹⁹F NMR (CDCl₃, 376 MHz) δ -106.66 (dt, *J* = 22.6, 22.9 Hz, 1F). ¹³C NMR (CDCl₃, 100 MHz) δ 14.10, 14.87, 18.91, 22.68, 26.45, 27.83 (d, *J* = 29.0 Hz), 28.99, 29.32, 29.38, 29.56, 29.60, 31.90, 107.11 (d, *J* = 21.3 Hz), 159.87 (d, *J* = 245.7 Hz). HRMS (EI) calc. for C₁₄H₂₇F: 214.2097; found 214.2073.

Synthesis of (*Z*)-4-fluoro-3-iodo-3-tetradecene ((*Z*)-**6a**): To a THF solution (7 ml) of (*Z*)-**1a** (238 mg, 0.5 mmol) and Et₃B (58 mg, 0.6 mmol) was slowly added at -78 °C through a cannula, a THF solution of LDA, prepared by the addition of a hexane solution of BuLi (0.47 ml of a 1.6 M solution, 0.75 mmol) to diisopropyl amine (76 mg, 0.75 mmol) in THF (5 ml) at 0 °C. After stirring at the temperature for 2 h, a THF solution (5 ml) of I₂ (191 mg, 0.75 mmol) was slowly added. The mixture was stirred at -78 °C for 1h and at room temperature for 2 h, and aqueous NaOH (15 ml of 3M solution) and 30% H₂O₂ (10 ml) were added at 0 °C. The mixture was stirred at room temperature for 2 h and extracted with ether three times. The combined organic layer was dried over MgSO₄ and concentrated under reduced pressure. Purification by column chromatography (silica gel/hexane) gave (*Z*)-**6a** (111 mg, 0.33 mmol) in 65% yield. IR (NaCl, neat) 2925, 2854, 1671, 1459 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz) δ 0.88 (t, *J* = 7.0 Hz, 3H), 1.07 (t, *J* = 7.3 Hz, 3H), 1.26-1.53 (m, 16H), 2.31-2.40 (m, 4H). ¹⁹F NMR (CDCl₃, 376 MHz) δ -74.55 (t, *J* = 22.0 Hz, 1F). ¹³C NMR (CDCl₃, 100 MHz) δ 14.09, 14.76, 22.66, 26.53, 28.74 (d, *J* = 31.5 Hz), 28.89, 29.27, 29.28, 29.47, 29.55, 30.52, 31.86, 81.66 (d, *J* = 25.8 Hz), 159.28 (d, *J* = 252.2 Hz). HRMS (EI) calc. for C₁₄H₂₆FI: 340.1064; found 340.1063.

Synthesis of 4-fluoro-3-tetradecanone (**7a**): To a THF solution (7 ml) of (*Z*)-**1a** (238 mg, 0.5 mmol) and Et₃B (58 mg, 0.6 mmol) was slowly added at -78 °C through a cannula, a THF solution of LDA, prepared by the addition of a hexane solution of BuLi (0.47 ml of a 1.6 M solution, 0.75 mmol) to diisopropyl amine (76 mg, 0.75 mmol) in THF (5 ml) at 0 °C. After stirring at the temperature for 2 h, 30% H₂O₂ (10 ml) in MeOH (15 ml) was added. The mixture was stirred at -78 °C for 1 h and at room temperature for 2 h, and extracted with ether three times. The combined organic layer was dried over MgSO₄ and concentrated under reduced pressure. Purification by column chromatography (silica gel/hexane-ether) gave **7a** (86 mg, 0.37 mmol) in 75% yield. IR (NaCl, neat) 2925, 2855, 1725, 1461 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz) δ 0.88 (t, *J* = 7.0 Hz, 3H), 1.07 (t, *J* = 7.2 Hz, 3H), 1.26-1.39 (m, 14H), 1.41-1.45 (m, 2H), 1.71-1.85 (m, 2H), 2.56-2.66 (m, 2H), 4.72 (ddd, *J* = 50.4, 8.1, 4.2 Hz, 1H). ¹⁹F NMR (CDCl₃, 376 MHz) δ -193.06 - -192.77 (m, 1F). ¹³C NMR (CDCl₃, 100 MHz) δ 6.69, 14.07, 22.66, 24.52, 29.17, 29.30, 29.34, 29.50, 29.55, 31.32, 31.89, 32.15 (d, *J* = 20.4 Hz), 96.07 (d, *J* = 183.6 Hz), 210.85 (d, *J* = 24.0 Hz). HRMS (EI) calc. for C₁₄H₂₇OF: 230.2046; found 230.2053.

(*Z*)-4-Fluoro-3-tetradecene ((*Z*)-**5a**): The reaction was carried out as the synthesis of (*E*)-**5a**, except (*E*)-**1a** was used in stead of (*Z*)-**1a** and the reaction was carried out at -90 °C. (*Z*)-**5a** was obtained in 61% yield. IR (NaCl, neat) 2926, 2855, 1708, 1464 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz) δ 0.88 (t, *J* = 6.6 Hz, 3H), 0.95 (t, *J* = 7.4 Hz, 3H), 1.26-1.48 (m, 16H), 2.02-2.15 (m, 4H), 4.46 (dt, *J* = 38.2, 7.3 Hz, 1H). ¹⁹F NMR (CDCl₃, 376 MHz) δ -111.01 (dt, *J* = 37.8, 17.7 Hz, 1F). ¹³C NMR (CDCl₃, 100 MHz) δ 14.10, 14.33, 16.96, 22.68, 26.86, 28.93, 29.32, 29.36, 29.55, 29.59, 31.91, 31.95 (d, *J* = 27.9 Hz), 106.52 (d, *J* = 16.3 Hz), 159.24 (d, *J* = 252.2 Hz). HRMS (EI) calc. for C₁₄H₂₇F: 214.2097; found 214.2083.

(*E*)-4-Fluoro-3-iodo-3-tetradecene ((*E*)-**6a**): The reaction was carried out as the synthesis of (*Z*)-**6a**, except (*E*)-**1a** was used in stead of (*Z*)-**1a** and the reaction was carried out at -90 °C. (*E*)-**6a** was obtained in 52% yield. IR (NaCl, neat) 2925, 2854, 1671, 1459 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz) δ 0.88 (t, *J* = 7.1 Hz, 3H), 1.07 (t, *J* = 7.3 Hz, 3H), 1.26-1.55 (m, 16H), 2.44-2.57 (m, 4H). ¹⁹F NMR (CDCl₃, 376 MHz) δ -95.32 (t, *J* = 23.1 Hz, 1F). ¹³C NMR (CDCl₃, 100 MHz) δ 14.11, 14.28, 22.69, 26.16, 28.76, 28.81, 28.84, 29.33, 29.51, 29.59, 31.90, 33.40 (d, *J* = 28.1 Hz), 85.36 (d, *J* = 33.0 Hz), 157.58 (d, *J* = 260.0 Hz). HRMS (EI) calc. for C₁₄H₂₆FI: 340.1064; found: 340.1051.

(*E*)-8-Fluoro-7-octadecene ((*E*)-**5b**): The reaction was carried out as the synthesis of (*E*)-**5a**, except for the use of Hex₃B in stead of Et₃B, and (*E*)-**5b** was obtained in 72% yield. IR (NaCl, neat) 2925, 2855, 1700, 1466 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz) δ 0.88 (t, *J* = 7.1 Hz, 6H), 1.26-1.51 (m, 24H), 1.90 (dt, *J* = 7.3, 6.8 Hz, 2H), 2.19 (dt, *J* = 23.7, 7.1 Hz, 2H), 4.98 (dt, *J* = 22.4, 8.1 Hz, 1H). ¹⁹F NMR (CDCl₃, 376 MHz) δ -105.99 (dt, *J* = 23.3, 22.9 Hz, 1F). ¹³C NMR (CDCl₃, 100 MHz) δ 14.08, 14.11, 22.66, 22.71, 25.48, 26.45, 27.88 (d, *J* = 29.0 Hz), 28.80, 29.03, 29.36, 29.41, 29.59, 29.63, 30.10, 31.71, 31.92, 105.52 (d, *J* = 21.5 Hz), 160.12 (d, *J* = 245.6 Hz). HRMS (EI) calc. for C₁₈H₃₅F: 270.2723; found 270.2740.

(*Z*)-8-Fluoro-7-iodo-7-octadecene ((*Z*)-**6b**): The reaction was carried out as the synthesis of (*Z*)-**6a**, except for the use of Hex₃B in stead of Et₃B, and ICl (490 mg, 3 mmol) and AcONa (250 mg, 3 mmol) in MeOH (5 ml) instead of I₂. (*Z*)-**6b** was obtained in 65% yield. IR (NaCl, neat) 2925, 2854, 1672, 1465 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz) δ 0.86-0.91 (m, 6H), 1.26-1.32 (m, 22H), 1.48-1.53 (m, 2H), 2.30-2.40 (m, 4H). ¹⁹F NMR (CDCl₃, 376 MHz) δ -73.68 (t, *J* = 22.0 Hz, 1F). ¹³C NMR (CDCl₃, 4100 MHz) δ 14.04, 14.10, 22.59, 22.67, 26.51, 28.07, 28.87 (d, *J* = 29.8 Hz), 28.93, 29.28, 29.30, 29.46, 29.49, 29.56, 31.62, 31.87, 36.64, 80.25 (d, *J* = 25.8 Hz), 159.58 (d, *J* = 252.2 Hz). HRMS (EI) calc. for C₁₈H₃₄FI: 396.1689; found 396.1688.

8-Fluoro-7-octadecanone (**7b**): The reaction was carried out as the synthesis of **7a**, except for the use of Hex₃B in stead of Et₃B, and **7b** was obtained in 82% yield. IR (NaCl, neat) 2926, 2855, 1725, 1466 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz) δ 0.86-0.90 (m, 6H), 1.26-1.60 (m, 24H), 1.69-1.86 (m, 2H), 2.50-2.66 (m, 2H), 4.72 (ddd, *J* = 50.4, 7.9, 4.2 Hz, 1H). ¹⁹F NMR (CDCl₃, 100 MHz) δ -192.60 - -192.31 (m, 1F). ¹³C NMR (CDCl₃, 376 MHz) δ 14.00, 14.09, 22.47, 22.62, 22.67, 24.52, 28.82, 29.17, 29.29, 29.33, 29.49, 29.54, 31.55, 31.88, 32.06 (d, *J* = 20.7 Hz), 38.02, 96.07 (d, *J* = 183.6 Hz), 210.49 (d, *J* = 24.6 Hz). HRMS (EI) calc. for C₁₈H₃₅OF: 286.2672; found 286.2671.

(*Z*)-8-Fluoro-7-octadecene ((*Z*)-**5b**): The reaction was carried out as the synthesis of (*Z*)-**5a**, except for the use of Hex₃B in stead of Et₃B, and (*Z*)-**5b** was obtained in 70% yield. IR (NaCl, neat) 2925, 2855, 1707, 1466 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz) δ 0.88 (t, *J* = 6.9 Hz, 6H), 1.26-1.48 (m, 24H), 2.04 (dt, *J* = 6.8, 6.8 Hz, 2H), 2.12 (dt, *J* = 17.5, 7.4 Hz, 2H), 4.45 (dt, *J* = 38.3, 7.5 Hz, 1H). ¹⁹F NMR (CDCl₃, 376 MHz) δ -110.90 (dt, *J* = 38.4, 17.7 Hz, 1F). ¹³C NMR (CDCl₃, 100 MHz) δ 14.26, 14.29, 22.80, 22.85, 23.61, 23.66, 26.44, 29.00, 29.07, 29.50, 29.51, 29.73, 29.75, 31.83, 32.06, 32.15 (d, *J* = 27.0 Hz), 105.07 (d, *J* = 15.7 Hz), 159.74 (d, *J* = 252.2 Hz). HRMS (EI) calc. for C₁₈H₃₅F: 270.2723; found 270.2732.

(*E*)-Methyl 10-fluoro-10-heptadecenoate ((*E*)-**5c**): The reaction was carried out as the synthesis of (*E*)-**5b**, except for the use of (*E*)-**1b** in stead of (*E*)-**1a**, and (*E*)-**5c** was obtained in 71% yield. IR (NaCl, neat) 2929, 2856, 1742, 1700, 1437 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz) δ 0.88 (t, *J* = 6.8 Hz, 3H), 1.28-1.64 (m, 20H), 1.90 (dt, *J* = 7.3, 7.3 Hz, 2H), 2.19 (dt, *J* = 23.4, 7.3 Hz, 2H), 2.30 (t, *J* = 7.4 Hz, 2H), 3.67 (s, 3H), 4.98 (dt, *J* = 22.5, 7.9 Hz, 1H). ¹⁹F NMR (CDCl₃, 376 MHz) δ -105.92 (dt, *J* = 23.2, 23.2 Hz, 1F). ¹³C NMR (CDCl₃, 100 MHz) δ 14.06,

22.63, 24.93, 25.45, 26.39, 27.85 (d, $J = 28.5$ Hz), 28.77, 28.92, 29.10, 29.15, 29.17, 30.07, 31.68, 34.07, 51.41, 105.56 (d, $J = 21.3$ Hz), 160.05 (d, $J = 245.7$ Hz), 174.25. HRMS (EI) calc. for $C_{18}H_{33}O_2F$: 300.2464; found 300.2456.

Synthesis of (Z)-4-fluoro-3-phenyl-3-tetradecene ((Z)-**8**): To a benzene solution (7ml) of $Pd(PPh_3)_4$ (29mg, 0.025mmol) and phenylboronic acid (74mg, 0.6mmol) was added a EtOH solution (0.5ml) of KOH (1mmol) and (Z)-**6a** (0.5mmol, 170mg) at room temperature. The mixture was stirring at 80 °C for 1 h, poured into 3M aqueous solution of NH_4Cl (40ml), and extracted with ether 3 times. The combined organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. Purification by column chromatography (silica gel/hexane) gave (Z)-**8** (126mg, 0.43 mmol) in 87% yield. IR (NaCl, neat) 2926, 2854, 1685, 1465 cm^{-1} . 1H NMR ($CDCl_3$, 400 MHz) δ 0.88 (t, $J = 7.0$ Hz, 3H), 0.93 (t, $J = 7.7$ Hz, 3H), 1.28-1.62 (m, 16H), 2.31-2.42 (m, 4H), 7.21-7.36 (m, 5H). ^{19}F NMR ($CDCl_3$, 376 MHz) δ -109.07 (t, $J = 23.8$ Hz, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.56, 14.11, 22.68, 24.60, 26.88, 28.92, 29.14, 29.27 (d, $J = 12.4$ Hz), 29.45, 29.57, 29.60, 31.91, 118.80 (d, $J = 12.4$ Hz), 126.53, 127.96 (2C), 128.76 (2C), 137.40 (d, $J = 3.1$ Hz), 155.54 (d, $J = 250.6$ Hz). HRMS (EI) calc. for $C_{20}H_{31}F$: 290.2410; found 290.2402.

(E)-4-Fluoro-3-phenyl-3-tetradecene ((E)-**8**): The reaction was carried out as the synthesis of (Z)-**8**, except for the use of (E)-**6a** instead of (Z)-**6a**, and (E)-**8** was obtained in 78% yield. IR (NaCl, neat) 2926, 2855, 1689, 1463 cm^{-1} . 1H NMR ($CDCl_3$, 400 MHz) δ 0.86-0.93 (m, 6H), 1.21-1.49 (m, 16H), 2.10 (dt, $J = 23.3, 7.4$ Hz, 2H), 2.42 (dq, $J = 2.8, 7.6$ Hz, 2H), 7.13-7.34 (m, 5H). ^{19}F NMR ($CDCl_3$, 376 MHz) δ -112.64 (tt, $J = 23.2, 2.4$ Hz, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 12.80, 14.11, 22.67, 23.28, 26.73, 28.95, 29.27 (d, $J = 28.2$ Hz), 29.27, 29.31, 29.50, 29.57, 31.89, 120.76 (d, $J = 19.0$ Hz), 126.65, 128.12 (2C), 129.08 (d, $J = 3.3$ Hz, 2C), 139.14 (d, $J = 9.1$ Hz), 156.70 (d, $J = 250.7$ Hz). HRMS (EI) calc. for $C_{20}H_{31}F$: 290.2410; found 290.2409.

NOE data