# Stereodivergent Hydrodefluorination of *gem*-Difluoroalkenes: Selective Synthesis of (*Z*)- and (*E*)-Monofluoroalkenes

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#### 1. Instrumentation and Chemicals

Materials were obtained from commercial suppliers and purified by standards procedures unless otherwise noted. Solvents (Tetrahydrofuran, dehydrated –super–, 41001-05, Kanto Chemical Co., Inc.) for reactions were purchased from commercial suppliers, degassed via three freeze-pump-thaw cycles, and further dried over molecular sieve (MS 4Å). NMR spectra were recorded on JEOL JNM-ECX400P and JNM-ECS400 spectrometers (<sup>1</sup>H: 392 or 396 MHz, <sup>13</sup>C: 99 or 100 MHz and <sup>19</sup>F: 373 MHz). Tetramethylsilane (<sup>1</sup>H), CDCl<sub>3</sub> (<sup>13</sup>C) and Fluorobenzene (<sup>19</sup>F,  $\delta$  –113.60) were employed as external standards, respectively. Multiplicity was recorded as follows: s = singlet, brs = broad singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sept = septet, o = octet, m = multiplet. CuCl (ReagentPlus® grade, 224332-25G, ≥99%) was purchased from Sigma-Aldrich Co., and CuOAc was purchased from Wako Pure Chemical Industries Ltd, and used as received.

Dimethyl terephthalate and 1,1,2,2-tetrachloroethane were used as an internal standard to determine NMR yields. GLC analyses were conducted with a Shimadzu GC-2014 or GC-2025 equipped with ULBON HR-1 glass capillary column (Shinwa Chemical Industries) and a FID detector. Medium-pressure column chromatography was carried out on a Biotage Flash Purification System Isolera, which is equipped with a UV detector. Recycle preparative gel permeation chromatography (GPC) was conducted with a JAI LC-9101 using CHCl<sub>3</sub> as the eluent. High-resolution mass spectra were recorded at the Global Facility Center, Hokkaido University.

## 2. Substrate Preparation

All *gem*-difluoroalkenes were known compounds and synthesized according to the procedure in the literatures. The *gem*-difluoroalkenes **1a**, **1f**, **1j**, **1k** and **1l** were synthesized through direct difluoromethylenation from corresponding aldehydes using TMSCF<sub>3</sub>.<sup>1</sup> The *gem*-difluoroalkenes **1b**–**1e**, **1g** and **1i** were synthesized through difluoromethylation of corresponding aldehydes using 2,2-difluoro-2-(fluorosulfonyl)acetate.<sup>2</sup> The *gem*-difluoroalkenes **1h** was synthesized through decarboxylative Wittig reaction of difluoromethylene phosphobetaine with aldehydes.<sup>3</sup> The synthesized *gem*-difluoroalkenes were subjected to purification by Kugelrohr distillation prior to use.

#### 3. General Defluorination Procedures

# Procedure for the copper(I)-catalyzed Z-selective defluorination of *gem*-difluoroalkenes 1a (Table 1).

Copper chloride (2.7 mg, 0.027 mmol), Xantphos (14.4 mg, 0.025 mmol), bis(pinacolato)diboron (154.0 mg, 0.61 mmol) and **1a** (107.1 mg, 0.50 mmol) were placed in an oven-dried reaction vial. And then, the vial was transferred to the glove box and Na(O-*t*-Bu) (48.0 mg, 0.50 mmol) was added to the vial under argon atmosphere. After the vial was sealed with a screw cap containing a Teflon-coated rubber septum, the vial was removed from the glove box and connected to a vacuum/nitrogen manifold through a needle. After dry THF (1 mL) was added to the reaction mixture, MeOH (22  $\mu$ L, 0.54 mmol) was added dropwise to the reaction mixture at 30 °C. After the reaction was complete, the mixture was passed through a short silica gel eluting with Et<sub>2</sub>O. The crude material was purified by medium-pressure column chromatography (SiO<sub>2</sub>, hexane) to give the corresponding defluorination product (*Z*)-**2a** (81.1 mg, 0.41 mmol, 83%) as a white solid.

# Procedure for the copper(I)-catalyzed *E*-selective defluorination of *gem*-difluoroalkenes 1a (Table 3).

Dppp (10.4 mg, 0.025 mmol) and **1a** (106.9 mg, 0.5 mmol) were placed in an oven-dried reaction vial. And then, the vial was transferred to the glove box and copper acetate (3.1 mg, 0.025 mmol) and NaOTMS (123.2 mg, 1.0 mmol) were added to the vial under argon atmosphere. After the vial was sealed with a screw cap containing a Teflon-coated rubber septum, the vial was removed from the glove box and connected to a vacuum/nitrogen manifold through a needle. After dry THF (500  $\mu$ L) was added to the mixture, dimethylphenylsilane (155  $\mu$ L, 1.0 mmol) was added dropwise to the reaction mixture at –20 °C. After the reaction was complete, the mixture was passed through a short silica gel eluting with Et<sub>2</sub>O. The crude material was purified by medium-pressure column chromatography (SiO<sub>2</sub>, hexane) to give the corresponding defluorination product (*E*)-**2a** (71.5 mg, 0.36 mmol, 73%) as a white solid.

#### 4. Characterization of Defluorination Product



The reaction was conducted with 107.1 mg (0.495 mmol) of **1a**. The product (*Z*)-**2a** was obtained in 83% yield (81.1 mg, 0.409 mmol) as a white solid (m.p. = 83–85°C). The stereoselectivity of (*Z*)-**2a** was determined by <sup>1</sup>H NMR analysis (*E/Z* 1:>99).

<sup>1</sup>H NMR (396 MHz, CDCl<sub>3</sub>, δ): 5.66 (dd, J = 5.2, 44.7 Hz, 1H), 6.69 (dd, J = 5.2, 82.7 Hz, 1H), 7.32–7.38 (m, 1H), 7.41–7.48 (m, 2H), 7.57–7.63 (m, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): 110.4 (CH), 126.9 (CH), 127.1 (CH), 127.4 (CH), 128.8 (CH), 129.2 (d,  $J_{C-F} = 6.7$  Hz, CH), 131.6 (C), 140.2 (d,  $J_{C-F} = 1.9$  Hz, CH), 140.6 (C), 148.3 (d,  $J_{C-F} = 270.9$  Hz, CH). <sup>19</sup>F NMR (373 MHz, CDCl<sub>3</sub>, δ): –122.3 (dd, J = 45.8, 79.7 Hz, 1F). HRMS-EI (m/z): [M]<sup>+</sup> calcd for C<sub>14</sub>H<sub>11</sub>F, 198.08448; found, 198.08478. (Z)-1-(2-Fluorovinyl)-4-methylbenzene [(Z)-2b].



The reaction was conducted with 77.5 mg (0.503 mmol) of **1b**. The product (*Z*)-**2b** was obtained in 69% yield (47.3 mg, 0.347 mmol) as an oil. The stereoselectivity of (*Z*)-**2b** was determined by <sup>1</sup>H NMR analysis (*E*/*Z* 1:>99).

<sup>1</sup>H NMR (392 MHz, CDCl<sub>3</sub>,  $\delta$ ): 2.34 (s, 3H), 5.58 (dd, J = 5.5, 45.4 Hz, 1H), 6.62 (dd, J = 5.5, 83.1 Hz, 1H), 7.15 (d, J = 7.8 Hz, 2H), 7.41 (d, J = 8.2 Hz, 2H). <sup>13</sup>C NMR (99 MHz, CDCl<sub>3</sub>,  $\delta$ ): 21.2 (CH<sub>3</sub>), 110.6 (CH), 128.7 (d,  $J_{C-F} = 6.6$  Hz, CH), 129.2 (CH), 129.7 (C), 137.3 (C), 147.7 (d,  $J_{C-F} = 268.6$  Hz, CH). <sup>19</sup>F NMR (373 MHz, CDCl<sub>3</sub>,  $\delta$ ): -123.8 (dd, J = 45.4, 79.7 Hz, 1F). HRMS-EI (*m/z*): [M]<sup>+</sup> calcd for C<sub>9</sub>H<sub>9</sub>F, 136.06883; found, 136.06847.

#### (Z)-1-(2-Fluorovinyl)-4-methoxybenzene [(Z)-2c].



The reaction was conducted with 86.0 mg (0.505 mmol) of **1c**. The product (*Z*)-**2c** was obtained in 51% yield (39.3 mg, 0.258 mmol) as an oil. The stereoselectivity of (*Z*)-**2c** was determined by <sup>1</sup>H NMR analysis (*E*/*Z* 1:>99).

<sup>1</sup>H NMR (392 MHz, CDCl<sub>3</sub>,  $\delta$ ): 3.81 (s, 3H), 5.55 (dd, J = 5.5, 45.5 Hz, 1H), 6.59 (dd, J = 5.3, 82.9 Hz, 1H), 6.87 (d, J = 8.6 Hz, 2H), 7.45 (d, J = 9.0 Hz, 2H). <sup>13</sup>C NMR (99 MHz, CDCl<sub>3</sub>,  $\delta$ ): 55.2 (CH<sub>3</sub>), 110.2 (CH), 113.8 (CH), 125.3 (C), 130.1 (d,  $J_{C-F} = 6.6$  Hz, CH), 147.0 (d,  $J_{C-F} = 267.8$  Hz, CH), 158.8 (d,  $J_{C-F} = 2.9$  Hz, C). <sup>19</sup>F NMR (373 MHz, CDCl<sub>3</sub>,  $\delta$ ): -125.8 (dd, J = 45.4, 79.7 Hz, 1F). HRMS-EI (m/z): [M]<sup>+</sup> calcd for C<sub>9</sub>H<sub>9</sub>FO, 152.06374; found, 152.06410.

#### (Z)-1-Chloro-4-(2-fluorovinyl)benzene [(Z)-2d].



The reaction was conducted with 87.7 mg (0.502 mmol) of **1d**. The product (*Z*)-**2d** was obtained in 52% yield (40.7 mg, 0.260 mmol) as an oil. The stereoselectivity of (*Z*)-**2d** was determined by <sup>1</sup>H NMR analysis (*E*/*Z* 1:>99). <sup>1</sup>H NMR (392 MHz, CDCl<sub>3</sub>, δ): 5.58 (dd, J = 5.5, 44.7 Hz, 1H), 6.66 (dd, J = 5.5, 82.7 Hz, 1H), 7.28–7.37 (m, 2H), 7.40–7.48 (m, 2H). <sup>13</sup>C NMR (99 MHz, CDCl<sub>3</sub>, δ): 109.8 (CH), 128.6 (CH), 130.0 (d,  $J_{C-F} = 7.5$  Hz, CH), 131.0 (C), 133.1 (d,  $J_{C-F} = 2.8$  Hz, C), 148.6 (d,  $J_{C-F} = 270.6$  Hz, CH). <sup>19</sup>F NMR (373 MHz, CDCl<sub>3</sub>, δ): –121.9 (dd, J = 45.4, 79.7 Hz, 1F). HRMS-EI (m/z): [M]<sup>+</sup> calcd for C<sub>8</sub>H<sub>6</sub>ClF, 156.01421; found, 156.01457.

#### (Z)-1-Bromo-4-(2-fluorovinyl)benzene [(Z)-2e].



The reaction was conducted with 108.7 mg (0.496 mmol) of **1e**. The product (*Z*)-**2e** was obtained in 82% yield (81.8 mg, 0.407 mmol) as an oil. The stereoselectivity of (*Z*)-**2e** was determined by <sup>1</sup>H NMR analysis (*E*/*Z* 1:>99).

<sup>1</sup>H NMR (392 MHz, CDCl<sub>3</sub>, δ): 5.57 (dd, J = 5.3, 43.7 Hz, 1H), 6.67 (dd, J = 5.5, 81.5 Hz, 1H), 7.34–7.41 (m, 2H), 7.43–7.49 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): 109.8 (CH), 121.3 (d,  $J_{C-F} = 3.9$  Hz, C), 130.3 (d,  $J_{C-F} = 7.6$  Hz, CH), 131.4 (C), 131.6 (CH), 148.6 (d,  $J_{C-F} = 272.8$  Hz, CH). <sup>19</sup>F NMR (373 MHz, CDCl<sub>3</sub>, δ): –121.5 (dd, J = 45.8, 79.7 Hz, 1F). HRMS-EI (m/z): [M]<sup>+</sup> calcd for C<sub>8</sub>H<sub>6</sub>BrF, 199.96369; found, 199.96354.

(Z)-4-(2-Fluorovinyl)benzonitrile [(Z)-2f].



The reaction was conducted with 81.7 mg (0.495 mmol) of **1f**. The product (*Z*)-**2f** was obtained in 28% yield (20.7 mg, 0.141 mmol) as an oil. The stereoselectivity of (*Z*)-**2f** was determined by <sup>1</sup>H NMR analysis (*E*/*Z* 1:>99).

<sup>1</sup>H NMR (392 MHz, CDCl<sub>3</sub>, δ): 5.67 (dd, J = 5.1, 43.1 Hz, 1H), 6.76 (dd, J = 5.3, 81.7 Hz, 1H), 7.57–7.66 (m, 4H). <sup>13</sup>C NMR (99 MHz, CDCl<sub>3</sub>, δ): 109.7 (CH), 110.8 (C), 118.8 (C), 129.2 (d,  $J_{C-F} = 7.6$  Hz, CH), 132.2 (CH), 137.0 (C), 150.4 (d,  $J_{C-F} = 275.3$  Hz, CH). <sup>19</sup>F NMR (373 MHz, CDCl<sub>3</sub>, δ): -117.1 (dd, J = 45.4, 79.7 Hz, 1F). HRMS-EI (m/z): [M]<sup>+</sup> calcd for C<sub>9</sub>H<sub>6</sub>FN, 147.04843; found, 147.04830. (*Z*)-4-(1-Fluoroprop-1-en-2-yl)-1,1'-biphenyl [(*Z*)-2h].



The reaction was conducted with 115.8 mg (0.503 mmol) of **1h**. The product (*Z*)-**2h** was obtained in 16% yield (16.8 mg, 0.0791 mmol) as a white solid (m.p. =  $52-54^{\circ}$ C). The stereoselectivity of (*Z*)-**2h** was determined by <sup>1</sup>H NMR analysis (*E*/*Z* 1:>99). Borylated product **3h** was obtained in moderate yield (45% NMR yield) and unreacted substrate **1h** was recovered in low yield (20% NMR yield) except for (*Z*)-**2h**.

<sup>1</sup>H NMR (392 MHz, CDCl<sub>3</sub>,  $\delta$ ): 1.95 (dd, J = 1.4, 4.9 Hz, 3H), 6.70 (dd, J = 1.2, 84.2 Hz, 1H), 7.31–7.39 (m, 1H), 7.40–7.49 (m, 2H), 7.55–7.65 (m, 6H). <sup>13</sup>C NMR (99 MHz, CDCl<sub>3</sub>,  $\delta$ ): 15.9 (d,  $J_{C-F} = 7.6$  Hz, CH<sub>3</sub>), 116.5 (C), 126.9 (CH), 127.0 (CH), 127.3 (CH), 128.1 (d,  $J_{C-F} = 6.6$  Hz, CH), 128.8 (CH), 134.7 (C), 140.1 (C), 140.7 (C), 144.4 (d,  $J_{C-F} = 264.0$  Hz, CH). <sup>19</sup>F NMR (373 MHz, CDCl<sub>3</sub>,  $\delta$ ): –128.8 (d, J = 79.7 Hz, 1F). HRMS-EI (m/z): [M]<sup>+</sup> calcd for C<sub>15</sub>H<sub>13</sub>F, 212.10013; found, 212.09999.

### (Z)-2-(2-Fluorovinyl)benzofuran [(Z)-2i].



The reaction was conducted with 90.1 mg (0.500 mmol) of **1i**. The product (*Z*)-**2i** was obtained in 55% yield (44.4 mg, 0.274 mmol) as an oil. The stereoselectivity of (*Z*)-**2i** was determined by <sup>1</sup>H NMR analysis (*E*/*Z* 1:>99).

<sup>1</sup>H NMR (396 MHz, CDCl<sub>3</sub>,  $\delta$ ): 5.88 (dd, *J* = 5.1, 41.6 Hz, 1H), 6.76 (dd, *J* = 4.9, 80.2 Hz, 1H), 6.94 (s, 1H), 7.19–7.31 (m, 2H), 7.42–7.48 (m, 1H), 7.53–7.59 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 101.8 (*C*H), 106.8 (d, *J*<sub>C-F</sub> = 10.5 Hz, *C*H), 111.0 (*C*H), 121.0 (*C*H), 122.9 (*C*H), 124.5 (*C*H), 128.8 (*C*), 149.32 (*C*), 149.34 (d, *J*<sub>C-F</sub> = 274.7 Hz, *C*H), 154.0 (*C*). <sup>19</sup>F NMR (373 MHz, CDCl<sub>3</sub>,  $\delta$ ): –115.6 (dd, *J* = 45.4, 79.7 Hz, 1F). HRMS-EI (*m/z*): [M]<sup>+</sup> calcd for C<sub>10</sub>H<sub>7</sub>FO, 162.04809; found, 162.04808. (Z)-2-(2-Fluorovinyl)naphthalene [(Z)-2j].



The reaction was conducted with 95.9 mg (0.504 mmol) of **1j**. The product (*Z*)-**2j** was obtained in 73% yield (63.5 mg, 0.369 mmol) as a white solid (m.p. = 60–62°C). The stereoselectivity of (*Z*)-**2j** was determined by <sup>1</sup>H NMR analysis (*E*/*Z* 1:>99).

<sup>1</sup>H NMR (392 MHz, CDCl<sub>3</sub>, δ): 5.78 (dd, J =5.3, 44.9 Hz, 1H), 6.74 (dd, J = 5.5, 83.1 Hz, 1H), 7.43–7.51 (m, 2H), 7.69 (dd, J = 1.6, 8.6 Hz, 1H), 7.77–7.85 (m, 3H), 7.93 (s, 1H). <sup>13</sup>C NMR (99 MHz, CDCl<sub>3</sub>, δ): 110.9 (CH), 126.1 (CH), 126.2 (CH), 126.6 (d,  $J_{C-F}$  = 7.6 Hz, CH), 127.5 (CH), 127.9 (d,  $J_{C-F}$  = 6.6 Hz, CH), 128.02 (CH), 128.04 (CH), 130.1 (C), 132.5 (C), 133.3 (C), 148.4 (d,  $J_{C-F}$  = 270.5 Hz, CH). <sup>19</sup>F NMR (373 MHz, CDCl<sub>3</sub>, δ): –122.2 (dd, J = 45.4, 79.7 Hz, 1F). HRMS-EI (m/z): [M]<sup>+</sup> calcd for C<sub>12</sub>H<sub>9</sub>F, 172.06883; found, 172.06893.

#### (Z)-1-(2-Fluorovinyl)pyrene [(Z)-2k].



The reaction was conducted with 133.4 mg (0.505 mmol) of **1k**. The product (*Z*)-**2k** was obtained in 63% yield (77.9 mg, 0.316 mmol) as a white solid (m.p. =  $125-126^{\circ}$ C). The stereoselectivity of (*Z*)-**2k** was determined by <sup>1</sup>H NMR analysis (*E*/*Z* 1:>99).

<sup>1</sup>H NMR (392 MHz, CDCl<sub>3</sub>,  $\delta$ ): 6.60 (dd, *J* = 5.1, 43.1 Hz, 1H), 7.00 (dd, *J* = 5.7, 83.3 Hz, 1H), 7.98–8.23 (m, 7H), 8.26 (d, *J* = 9.4 Hz, 1H), 8.35 (d, *J* = 8.2 Hz, 1H). <sup>13</sup>C NMR (99 MHz, CDCl<sub>3</sub>,  $\delta$ ): 107.9 (*C*H), 123.1 (*C*H), 124.57 (*C*), 124.65 (*C*H), 125.0 (*C*H), 125.3 (*C*H), 125.8 (*C*H), 126.0 (*C*), 127.26 (*C*H), 127.36 (*C*H), 127.44 (*C*H), 127.6 (*C*H), 128.2 (*C*), 130.6 (*C*), 131.2 (*C*), 148.7 (d, *J*<sub>C-F</sub> = 270.6 Hz, *C*H). <sup>19</sup>F NMR (373 MHz, CDCl<sub>3</sub>,  $\delta$ ): –123.9 (dd, *J* = 45.4, 79.7 Hz, 1F). HRMS-EI (*m*/*z*): [M]<sup>+</sup> calcd for C<sub>18</sub>H<sub>11</sub>F, 246.08448; found, 246.08360. (*E*)-4-(2-Fluorovinyl)-1,1'-biphenyl [(*E*)-2a].



The reaction was conducted with 106.9 mg (0.494 mmol) of **1a**. The stereoselectivity of the crude material was determined by GLC analysis (E/Z 95:5) as a white solid (m.p. = 108–116°C). The product (E)-**2a** was obtained in 73% yield (71.5 mg, 0.361 mmol, E/Z 90:10) determined by <sup>1</sup>H NMR analysis.

<sup>1</sup>H NMR (392 MHz, CDCl<sub>3</sub>,  $\delta$ ): 6.43 (dd, J = 11.2, 19.4 Hz, 1H), 7.09–7.38 (m, 4H), 7.41–7.47 (m, 2H), 7.52–7.63 (m, 4H). <sup>13</sup>C NMR (99 MHz, CDCl<sub>3</sub>,  $\delta$ ): 113.5 (d,  $J_{C-F} = 16.0$  Hz, CH), 126.5 (d,  $J_{C-F} = 2.8$  Hz, CH), 126.9 (CH), 127.38 (CH), 127.42 (CH), 128.8 (CH), 131.6 (d,  $J_{C-F} = 11.3$  Hz, C), 140.3 (d,  $J_{C-F} = 1.9$  Hz, C), 140.5 (C), 150.2 (d,  $J_{C-F} = 259.4$  Hz, CH). <sup>19</sup>F NMR (373 MHz, CDCl<sub>3</sub>,  $\delta$ ): –130.1 (dd, J = 22.7, 79.7 Hz, 1F). HRMS-EI (m/z): [M]<sup>+</sup> calcd for C<sub>14</sub>H<sub>11</sub>F, 198.08448; found, 198.08445.

#### (E)-1-(2-Fluorovinyl)-4-methylbenzene [(E)-2b].



The reaction was conducted with 77.0 mg (0.499 mmol) of **1b**. After the reaction was complete, the crude material was dissolved in THF (1.0 mL) and TBAF (1.0 M, 800  $\mu$ L) was added to the mixture at 0 °C to remove byproducts. The resultant solution was stirred for 3 h at 0 °C. After that, the mixture was added to the H<sub>2</sub>O, then extracted with Et<sub>2</sub>O. The organic layer was washed with water two times. The combined organic layer was then dried over MgSO<sub>4</sub> followed by evaporation. The crude material was purified by medium-pressure column chromatography (SiO<sub>2</sub>, pentane) to give the product (*E*)-**2b** in 27% yield (18.2 mg, 0.134 mmol) as an oil. The stereoselectivity of (*E*)-**2b** was determined by <sup>1</sup>H NMR analysis of the crude material (*E*/*Z* 95:5).

<sup>1</sup>H NMR (396 MHz, CDCl<sub>3</sub>, δ): 2.33 (s, 3H), 6.36 (dd, J = 11.5, 19.4 Hz, 1H), 7.08–7.18 (m, 4H), 7.14 (dd, J = 11.5, 72.4 Hz, 1H). <sup>13</sup>C NMR (99 MHz, CDCl<sub>3</sub>, δ): 21.1 (*C*H<sub>3</sub>), 113.6 (d,  $J_{C-F} = 16.0$  Hz, *C*H), 126.0 (d,  $J_{C-F} = 2.8$  Hz, *C*H), 129.4 (*C*H), 129.6 (d,  $J_{C-F} = 12.2$  Hz, *C*), 137.3 (*C*), 149.6 (d,  $J_{C-F} = 257.4$  Hz, *C*H). <sup>19</sup>F NMR (373 MHz, CDCl<sub>3</sub>, δ): –131.9 (dd, J = 22.7, 79.7 Hz, 1F). HRMS-EI (m/z): [M]<sup>+</sup> calcd for C<sub>9</sub>H<sub>9</sub>F, 136.06883; found, 136.06893.

(*E*)-1-(2-Fluorovinyl)-4-methoxybenzene [(*E*)-2c].



The reaction was conducted with 83.6 mg (0.491 mmol) of 1c. The product (*E*)-2c was obtained in 94% yield (70 mg, 0.460 mmol) as an oil. The stereoselectivity of (*E*)-2c was determined by <sup>1</sup>H NMR analysis of the crude material (*E*/*Z* 95:5).

<sup>1</sup>H NMR (396 MHz, CDCl<sub>3</sub>, δ): 3.80 (s, 3H), 6.35 (dd, J = 11.3, 19.6 Hz, 1H), 6.82–6.89 (m, 2H), 7.09 (dd, J = 11.5, 83.9 Hz, 1H), 7.15–7.20 (m, 2H). <sup>13</sup>C NMR (99 MHz, CDCl<sub>3</sub>, δ): 55.2 (CH<sub>3</sub>), 113.2 (d,  $J_{C-F} = 16.0$  Hz, CH), 114.2 (CH), 125.0 (d,  $J_{C-F} = 12.2$  Hz, C), 127.2 (d,  $J_{C-F} = 2.8$  Hz, CH), 148.9 (d,  $J_{C-F} = 256.5$  Hz, CH), 159.0 (C). <sup>19</sup>F NMR (373 MHz, CDCl<sub>3</sub>, δ): –131.9 (dd, J = 28.3, 74.1 Hz, 1F). HRMS-EI (m/z): [M]<sup>+</sup> calcd for C<sub>9</sub>H<sub>9</sub>FO, 152.06374; found, 152.06433.

#### (E)-1-Chloro-4-(2-fluorovinyl)benzene [(E)-2d].



The reaction was conducted with 87.1 mg (0.499 mmol) of **1d**. The product (*E*)-**2d** was obtained in 13% yield (10.0 mg, 0.0639 mmol) as an oil. The stereoselectivity of (*E*)-**2d** was determined by <sup>1</sup>H NMR analysis of the crude material (*E*/*Z* 90:10).

<sup>1</sup>H NMR (392 MHz, CDCl<sub>3</sub>,  $\delta$ ): 6.35 (dd, J = 11.4, 19.2 Hz, 1H), 7.15 (dd, J = 11.0, 82.3 Hz, 1H), 7.18 (d, J = 8.6 Hz, 2H), 7.23–7.32 (m, 2H). <sup>13</sup>C NMR (99 MHz, CDCl<sub>3</sub>,  $\delta$ ): 112.9 (d,  $J_{C-F} = 16.9$  Hz, CH), 127.3 (d,  $J_{C-F} = 2.8$  Hz, CH), 128.9 (CH), 131.1 (d,  $J_{C-F} = 12.2$  Hz, C), 133.1 (d,  $J_{C-F} = 1.9$  Hz, C), 150.4 (d,  $J_{C-F} = 260.3$  Hz, CH). <sup>19</sup>F NMR (373 MHz, CDCl<sub>3</sub>,  $\delta$ ): –129.2 (dd, J = 23.1, 79.7 Hz, 1F). HRMS-EI (*m*/*z*): [M]<sup>+</sup> calcd for C<sub>8</sub>H<sub>6</sub>ClF, 156.01421; found, 156.01484.

(E)-1-Bromo-4-(2-fluorovinyl)benzene [(E)-2e].



The reaction was conducted with 107.9 mg (0.493 mmol) of **1e**. The product (*E*)-**2e** was obtained in 14% yield (14.3 mg, 0.071 mmol) as an oil. The stereoselectivity of (*E*)-**2e** was determined by <sup>1</sup>H NMR analysis (E/Z > 99:1).

<sup>1</sup>H NMR (396 MHz, CDCl<sub>3</sub>,  $\delta$ ): 6.34 (dd, *J* = 11.1, 19.0 Hz, 1H), 7.09–7.15 (m, 2H), 7.17 (dd, *J* = 11.5, 82.3 Hz, 1H), 7.41–7.47 (m, 2H). <sup>13</sup>C NMR (99 MHz, CDCl<sub>3</sub>,  $\delta$ ): 113.0 (d, *J*<sub>C-F</sub> = 16.9 Hz, *C*H), 121.2 (d, *J*<sub>C-F</sub> = 1.9 Hz, *C*), 127.6 (d, *J*<sub>C-F</sub> = 2.8 Hz, *C*H), 131.6 (d, *J*<sub>C-F</sub> = 12.2 Hz, *C*), 131.9 (CH), 150.4 (d, *J*<sub>C-F</sub> = 260.3 Hz, CH). <sup>19</sup>F NMR (373 MHz, CDCl<sub>3</sub>,  $\delta$ ): –128.9 (dd, *J* = 22.7, 79.7 Hz, 1F). HRMS-EI (*m*/*z*): [M]<sup>+</sup> calcd for C<sub>8</sub>H<sub>6</sub>BrF, 199.96369; found, 199.96403.

#### (E)-2-(2-Fluorovinyl)-1,3,5-trimethylbenzene [(E)-2g].



The reaction was conducted with 90.8 mg (0.498 mmol) of **1g**. The product (*E*)-**2g** was obtained in 20% NMR yield. The stereoselectivity of (*E*)-**2g** was determined by <sup>1</sup>H NMR analysis (*E*/*Z* >99:1). (*E*)-**2g** contains inseparable impurities.

<sup>1</sup>H NMR (396 MHz, CDCl<sub>3</sub>, δ): 2.27 (s, 9H), 6.29 (dd, J = 11.7, 20.4 Hz, 1H), 6.66 (dd, J = 11.5, 85.9 Hz, 1H), 6.88 (s, 2H). <sup>13</sup>C NMR (99 MHz, CDCl<sub>3</sub>, δ): 20.9 (CH<sub>3</sub>), 21.0 (CH<sub>3</sub>), 110.0 (d,  $J_{C-F} = 14.1$  Hz, CH), 127.4 (d,  $J_{C-F} = 12.2$  Hz, C), 128.5 (CH), 136.8 (d,  $J_{C-F} = 2.9$  Hz, C), 140.1 (C), 151.3 (d,  $J_{C-F} = 259.3$  Hz, CH). <sup>19</sup>F NMR (373 MHz, CDCl<sub>3</sub>, δ): -123.7 (dd, J = 22.9, 91.1 Hz, 1F). HRMS-EI (m/z): [M]<sup>+</sup> calcd for C<sub>11</sub>H<sub>13</sub>F, 164.10013; found, 164.10026.

(*E*)-4-(1-Fluoroprop-1-en-2-yl)-1,1'-biphenyl [(*E*)-2h].



The reaction was conducted with 114.4 mg (0.497 mmol) of **1h**. The product (*E*)-**2h** was obtained in 77% yield (81.2 mg, 0.383 mmol) as a white solid (m.p. =  $102-109^{\circ}$ C). The stereoselectivity of (*E*)-**2h** was determined by <sup>1</sup>H NMR analysis (*E*/*Z* >99:1). No byproducts could be observed.

<sup>1</sup>H NMR (392 MHz, CDCl<sub>3</sub>,  $\delta$ ): 2.08 (dd, *J* = 1.6, 3.9 Hz, 3H), 6.98 (dq, *J* = 1.5, 84.9 Hz, 1H), 7.32–7.41 (m, 3H), 7.41–7.48 (m, 2H), 7.54–7.63 (m, 4H). <sup>13</sup>C NMR (99 MHz, CDCl<sub>3</sub>,  $\delta$ ): 12.1 (d, *J*<sub>C-F</sub> = 5.7 Hz, CH<sub>3</sub>), 119.6 (d, *J*<sub>C-F</sub> = 10.3 Hz, *C*), 126.1 (d, *J*<sub>C-F</sub> = 2.9 Hz, *C*H), 127.1 (*C*H), 127.4 (*C*H), 127.5 (*C*H), 129.0 (*C*H), 136.4 (d, *J*<sub>C-F</sub> = 9.4 Hz, *C*), 140.4 (*C*), 140.7 (*C*), 146.0 (d, *J*<sub>C-F</sub> = 258.4 Hz, *C*H). <sup>19</sup>F NMR (373 MHz, CDCl<sub>3</sub>,  $\delta$ ): –131.5 (d, *J* = 79.7 Hz, 1F). HRMS-EI (*m*/*z*): [M]<sup>+</sup> calcd for C<sub>15</sub>H<sub>13</sub>F, 212.10013; found, 212.09996.

#### (E)-4-(2-Fluorovinyl)-N,N-dimethylaniline [(E)-21].



The reaction was conducted with 92.4 mg (0.504 mmol) of **11**. The product (*E*)-**21** was obtained in 80% yield (66.6 mg, 0.403 mmol) as a white solid (m.p. =  $62-64^{\circ}$ C). The stereoselectivity of (*E*)-**21** was determined by <sup>1</sup>H NMR analysis of the crude material (*E*/*Z* 94:6).

<sup>1</sup>H NMR (392 MHz, CDCl<sub>3</sub>,  $\delta$ ): 2.94 (s, 6H), 6.32 (dd, J = 11.4, 20.0 Hz, 1H), 6.67 (d, J = 8.6 Hz, 2H), 7.08 (dd, J = 11.2, 84.4 Hz, 1H), 7.13 (d, J = 8.6 Hz, 2H). <sup>13</sup>C NMR (99 MHz, CDCl<sub>3</sub>,  $\delta$ ): 40.5 (*C*H<sub>3</sub>), 112.6 (*C*H), 113.5 (d,  $J_{C-F} = 16.0$  Hz, *C*H), 120.4 (d,  $J_{C-F} = 11.2$  Hz, *C*), 127.0 (d,  $J_{C-F} = 2.9$  Hz, *C*H), 148.0 (d,  $J_{C-F} = 253.7$  Hz, *C*H), 149.9 (*C*). <sup>19</sup>F NMR (373 MHz, CDCl<sub>3</sub>,  $\delta$ ): -136.0 (dd, J = 22.9, 91.1 Hz, 1F). HRMS-ESI (*m*/*z*): [M+H]<sup>+</sup> calcd for C<sub>10</sub>H<sub>13</sub>NF, 166.10265; found, 166.10280.

#### 5. Deuterium Labelling Experiment about Z-selective Synthesis



The defluorination of **1a** under optimized conditions using NaH/MeOD instead Na(O-*t*-Bu)/MeOH gave (*Z*)-**2a'** bearing a deuterium label at its  $\beta$ -position (D 91%), with perfect *Z* selectivity (*E*/*Z* 1:>99) determined by <sup>1</sup>H NMR analysis. (*Z*)-**2a'** was obtained as a white solid (m.p. = 82–83°C).

<sup>1</sup>H NMR (392 MHz, CDCl<sub>3</sub>,  $\delta$ ): 5.66 (d, *J* = 44.7 Hz, 1H), 6.69 (dd, *J* = 5.5, 83.1 Hz, 0.09H), 7.32–7.38 (m, 1H), 7.42–7.48 (m, 2H), 7.56–7.64 (m, 6H). <sup>13</sup>C NMR (99 MHz, CDCl<sub>3</sub>,  $\delta$ ): 110.2 (CH), 126.9 (CH), 127.1 (CH), 127.3 (CH), 128.8 (CH), 129.2 (d, *J*<sub>C-F</sub> = 7.5 Hz, CH), 131.6 (C), 140.1 (d, *J*<sub>C-F</sub> = 1.9 Hz, C), 140.5 (C), 148.0 (dt, *J* = 29.6, 269.7 Hz, C). <sup>19</sup>F NMR (373 MHz, CDCl<sub>3</sub>,  $\delta$ ): –122.6– –123.1 (m, 1F). HRMS-EI (*m*/*z*): [M]<sup>+</sup> calcd for C<sub>14</sub>H<sub>10</sub>DF, 199.09076; found, 199.09029.

#### 6. Synthesis of Monofluoroalkenyl Boronate Ester (Z)-3a



The product (*Z*)-**3a** was synthesized through the borylation with a copper(I)/PPh<sub>3</sub> complex catalyst system. The crude mixture was purified by flash column chromatography (SiO<sub>2</sub>, ethyl acetate/hexane, 0:100–3:97) followed by GPC to give the corresponding borylation product (*Z*)-**3a** (58.1 mg, 0.18 mmol, 18%) as a white solid (m.p. = 90–93°C). The stereoselectivity of (*Z*)-**3a** was determined by <sup>1</sup>H NMR analysis (*E/Z* 1:>99).

<sup>1</sup>H NMR (392 MHz, CDCl<sub>3</sub>,  $\delta$ ): 1.35 (s, 12H), 6.43 (d, J = 47.4 Hz, 1H), 7.32–7.39 (m, 1H), 7.41–7.48 (m, 2H), 7.57–7.64 (m, 4H), 7.70 (d, J = 8.2 Hz, 2H). <sup>13</sup>C NMR (99 MHz, CDCl<sub>3</sub>,  $\delta$ ): 24.7 (CH<sub>3</sub>), 84.8 (C), 123.4 (CH), 127.0 (CH), 127.1 (CH), 127.5 (CH), 128.8 (CH), 130.3 (d,  $J_{C-F} = 8.5$  Hz, CH), 131.9 (C), 140.5 (C), 141.0 (C). The carbon directly attached to the boron atom was not detected, likely due to quadrupolar relaxation. <sup>4,5 19</sup>F NMR (373 MHz, CDCl<sub>3</sub>,  $\delta$ ): –123.8 (d, J = 45.4 Hz, 1F). HRMS-EI (m/z): [M]<sup>+</sup> calcd for C<sub>20</sub>H<sub>22</sub><sup>10</sup>BFO<sub>2</sub>, 323.17332; found, 323.17306.

#### 7. Deuterium Labelling Experiment about E-Selective Synthesis



PhMe<sub>2</sub>Si–D was synthesized according to the literature procedure.<sup>6</sup> The defluorination of **1a** at 30°C using PhMe<sub>2</sub>Si–D instead of PhMe<sub>2</sub>Si–H gave (*E*)-**2a**' bearing a deuterium label at its  $\beta$ -position (D 94%), with high *E* selectivity (*E*/*Z* 90:10) determined by <sup>1</sup>H NMR analysis. (*E*)-**2a**' was obtained as a white solid (m.p. = 117°C).

<sup>1</sup>H NMR (392 MHz, CDCl<sub>3</sub>, δ): 5.66 (d, J = 45.1 Hz, 0.06H), 6.43 (d, J = 19.2 Hz, 1H), 7.29– 7.39 (m, 3H), 7.41–7.48 (m, 2H), 7.52–7.63 (m, 4H). <sup>13</sup>C NMR (99 MHz, CDCl<sub>3</sub>, δ): 113.3 (d,  $J_{C-F} = 16.0$  Hz, CH), 126.5 (d,  $J_{C-F} = 2.8$  Hz, CH), 126.9 (CH), 127.38 (CH), 127.43 (CH), 128.8 (CH), 131.6 (d,  $J_{C-F} = 11.3$  Hz, C), 140.3 (d,  $J_{C-F} = 1.9$  Hz, C), 140.5 (C), 149.9 (dt, J = 30.3, 258.1 Hz, C). <sup>19</sup>F NMR (373 MHz, CDCl<sub>3</sub>, δ): –130.5– –130.8 (m, 1F). HRMS-EI (m/z): [M]<sup>+</sup> calcd for C<sub>14</sub>H<sub>10</sub>DF, 199.09076; found, 199.09049.

#### 8. Details of the DFT Calculations

All calculations were performed with the Gaussian 09W (revision C.01) program package.<sup>7</sup> Geometry optimizations were performed with  $\omega$ B97XD/cc-PVDZ in the gas-phase. The frequency calculations were conducted on gas-phase optimized geometries to check the all the stationary points as either minima or transition states. The intrinsic reaction coordinate (IRC) was calculated for the transition states to confirm that the structures were indeed connected by two relevant minimas.

#### TS1

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С	-3.124700	2.528000	0.547600
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Sum of electronic and thermal Energies=

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TS3

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Н	-1.349100	-2.153700	-2.340500
Н	0.353100	-2.104200	-2.869500
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С	-3.907300	-0.418100	1.659700
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Zero-point correction=

Thermal correction to Energy=

Thermal correction to Enthalpy=

Thermal correction to Gibbs Free Energy=

Sum of electronic and zero-point Energies=

Sum of electronic and thermal Energies=

Sum of electronic and thermal Enthalpies=

Sum of electronic and thermal Free Energies=

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## TS4

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Cu	0.650600	0.634700	-0.086700
Р	2.779100	0.139300	0.552100
Р	0.280800	-1.548900	-0.717400
С	3.395700	0.059100	2.288900
Н	4.387200	-0.414900	2.355200
Н	3.456900	1.081200	2.690600
Н	2.678500	-0.509400	2.897800
С	4.193500	0.935700	-0.319600
Н	4.281100	1.974900	0.029500
Н	5.143500	0.409100	-0.140500
Н	3.977000	0.955700	-1.396900
С	-0.761400	-2.663200	0.310800

Н	-1.816800	-2.396400	0.151300	
Н	-0.602000	-3.723100	0.059500	
Н	-0.526100	-2.493700	1.370700	
С	-0.169200	-2.061400	-2.426500	
Н	-0.049500	-3.144000	-2.585500	
Н	-1.220300	-1.782000	-2.591700	
Н	0.451800	-1.507100	-3.144000	
С	-1.120000	1.699200	0.762900	
Н	-0.705900	1.897900	1.755600	
С	-0.887800	2.716200	-0.161000	
С	-2.205100	0.711500	0.679700	
С	-2.630000	0.050300	1.847000	
С	-2.831800	0.347500	-0.530500	
С	-3.636800	-0.910300	1.816700	
Н	-2.157100	0.303800	2.799500	
С	-3.841700	-0.610300	-0.556600	
Н	-2.519000	0.825400	-1.458500	
С	-4.255500	-1.250000	0.613500	
Н	-3.942500	-1.398200	2.745100	
Н	-4.314200	-0.860000	-1.509800	
Н	-5.048500	-1.999200	0.587900	
F	-1.802600	3.016700	-1.086100	
Н	-0.284200	3.581100	0.121100	
F	0.362700	2.181300	-1.382200	
Zero-po	int correction	_		
Therma	l correction to	Energy=		
Therma	l correction to	Enthalpy=		
Therma	l correction to	Gibbs Free E	nergy=	
Sum of electronic and zero-point Energies=				

Sum of electronic and thermal Energies= Sum of electronic and thermal Enthalpies=

Sum of electronic and thermal Free Energies=

0.316763 (Hartree/Particle)	
0.340319	
0.341263	
0.263042	
-3068.651299	
-3068.627743	
-3068.626798	
-3068.705020	

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**S80** 







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