Supplementary Information

Synthesis of fluorovinyl aryl ethers by a three-component reaction of gem-difluoroalkenes with arylboronic acids and oxygen

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General experimental procedures

All reagents were of analytical grade, and obtained from commercial suppliers and used without further purification. NMP and other solvents were dried by standard method prior to use. Melting points were measured in an open capillary using Büchi melting point B-540 apparatus and are uncorrected. $^1$H NMR and $^{13}$C NMR spectra were recorded on a 400 spectrometer (400 MHz for $^1$H and 100 MHz for $^{13}$C NMR, respectively) using TMS as internal standard. The $^{19}$F NMR spectra were obtained using a 400 spectrometer (376 MHz). CDCl$_3$ was used as the NMR solvent in all cases. High resolution mass spectra (HRMS) were recorded under electron impact conditions using a MicroMass GCT CA 055 instrument and recorded on a MicroMass LCTTM spectrometer. Silica gel (300–400 mesh size) was used for column chromatography. TLC analysis of reaction mixtures was performed using silica gel plates.

Preparation of 1,1-difluoroalkenes 1a–g and 1-aryl-2,2-difluoroethenes 1h–k

The 1,1-difluoroalkenes (1a–g) were prepared according to the Hu’s reported procedure.$^1$ The 1-aryl-2,2-difluoroethenes (1h–k) was prepared according to the reported procedure.$^2$

General procedure for the synthesis of 3aa–df and 3ha–kl

To a solution of gem-difluoroalkenes (1a–d, 1h–k, 1.0 mmol) in NMP (2 mL) was added arylboronic acids (2.0 mmol) and K$_3$PO$_4$ (2.0 mmol, 424 mg) at room temperature. The mixture was stirred at 100 °C for 24 h under air atmosphere (monitored by TLC). After the completion of reaction, the reaction mixture was quenched with water (5 mL) and extracted with CH$_2$Cl$_2$ (3 × 10 mL). The combined organic layer was washed with water and brine, then dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated under vacuum. The crude residue was then purified by column chromatography on silica gel using n-hexane/EtOAc (100/1) as eluent to afford the pure target compounds 3aa–df and 3ha–kl.

General procedure for the synthesis of 3ea–ga

To a solution of gem-difluoroalkenes (1e–g, 1.0 mmol) in toluene (2 mL) was added phenylboronic acid 2a (2.0 mmol), Cs$_2$CO$_3$ (2.0 mmol, 652 mg), and Ni(acac)$_2$ (0.05 mmol, 13 mg) at room temperature. The mixture was stirred at 100 °C for 24 h under an oxygen atmosphere (balloon). After the completion of reaction, the reaction mixture was quenched with water (5 mL) and extracted with CH$_2$Cl$_2$ (3 × 10 mL). The combined organic layer was washed with water and brine, then dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated under vacuum. The crude residue was then purified by column chromatography on silica gel using n-hexane/EtOAc (100/1) as eluent to afford the pure target compounds 3ea–ga.

References

Spectral and analytical data of compounds 3

(2-Fluoro-2-phenoxyethene-1,1-diyl)dibenzene (3aa): White solid. Yield: 81%, mp 77.9–79.0 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.35–7.19 (m, 12H), 7.11–7.08 (m, 3H) ppm; \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 154.9 (d, \(J_{\text{CF}} = 2.7\) Hz), 151.0 (d, \(J_{\text{CF}} = 286.8\) Hz), 136.3 (d, \(J_{\text{CF}} = 4.1\) Hz), 136.2 (d, \(J_{\text{CF}} = 3.7\) Hz), 129.9 (d, \(J_{\text{CF}} = 4.0\) Hz), 129.8, 129.6 (d, \(J_{\text{CF}} = 3.2\) Hz), 128.3, 128.2, 127.3, 127.2, 124.1, 116.5, 106.1 (d, \(J_{\text{CF}} = 25.0\) Hz) ppm; \(^19\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) −87.1 (s, 1F) ppm; HRMS (EI): calcd for C\(_{20}\)H\(_{15}\)FO [M]+: 290.1107, found: 290.1108.

(2-Fluoro-2-(p-tolyloxy)ethene-1,1-diyl)dibenzene (3ab): White solid. Yield: 69%, mp 70.8–72.4 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.34–7.21 (m, 10H), 7.11 (d, \(J = 8.4\) Hz, 2H), 6.99 (d, \(J = 7.6\) Hz, 2H), 2.29 (s, 3H) ppm; \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 152.8 (d, \(J_{\text{CF}} = 2.5\) Hz), 151.2 (d, \(J_{\text{CF}} = 286.9\) Hz), 136.4 (d, \(J_{\text{CF}} = 4.0\) Hz), 136.3 (d, \(J_{\text{CF}} = 3.8\) Hz), 133.6, 130.3, 130.0 (d, \(J_{\text{CF}} = 4.0\) Hz), 129.6 (d, \(J_{\text{CF}} = 3.2\) Hz), 128.3, 128.2, 127.3, 127.2, 116.4, 105.7 (d, \(J_{\text{CF}} = 25.3\) Hz), 20.7 ppm; \(^19\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) −87.0 (s, 1F) ppm; HRMS (EI): calcd for C\(_{21}\)H\(_{17}\)FO [M]+: 304.1263, found: 304.1262.

(2-Fluoro-2-(o-tolyloxy)ethene-1,1-diyl)dibenzene (3ac): White solid. Yield: 73%, mp 68.8–70.5 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.35–7.17 (m, 10H), 7.15–7.10 (m, 3H), 7.01–6.97 (m, 1H), 2.20 (s, 3H) ppm; \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 153.2 (d, \(J_{\text{CF}} = 2.3\) Hz), 151.3 (d, \(J_{\text{CF}} = 286.4\) Hz), 136.4 (d, \(J_{\text{CF}} = 4.1\) Hz), 136.3 (d, \(J_{\text{CF}} = 3.6\) Hz), 131.5, 130.0 (d, \(J_{\text{CF}} = 4.0\) Hz), 129.6 (d, \(J_{\text{CF}} = 3.1\) Hz), 128.3, 128.2, 127.5, 127.3, 127.1, 127.0, 124.0, 115.0, 105.5 (d, \(J_{\text{CF}} = 25.3\) Hz), 16.0 ppm; \(^19\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) −85.9 (s, 1F) ppm; HRMS (EI): calcd for C\(_{21}\)H\(_{17}\)FO [M]+: 304.1263, found: 304.1262.

(2-Fluoro-2-(4-methoxyphenoxy)ethene-1,1-diyl)dibenzene (3ad): White solid. Yield: 65%, mp 67.6–69.1 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.34–7.21 (m, 10H), 7.03–7.01 (m, 2H), 6.85–6.81 (m, 2H), 3.73 (s, 3H) ppm; \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 156.2, 151.5 (d, \(J_{\text{CF}} = 286.9\) Hz), 148.6 (d, \(J_{\text{CF}} = 2.3\) Hz), 136.4 (d, \(J_{\text{CF}} = 4.1\) Hz), 136.3 (d, \(J_{\text{CF}} = 3.7\) Hz), 130.0 (d, \(J_{\text{CF}} = 4.0\) Hz), 129.7 (d, \(J_{\text{CF}} = 3.2\) Hz), 128.3, 128.2, 127.2, 127.1, 117.7, 114.9, 105.3 (d, \(J_{\text{CF}} = 25.5\) Hz), 55.7 ppm; \(^19\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) −87.0 ppm; HRMS (EI): calcd for C\(_{21}\)H\(_{17}\)FO\(_2\) [M]+: 320.1213, found: 320.1214.
(2-(4-Chlorophenoxy)-2-fluoroethene-1,1-diyl)dibenzene (3ae): White solid. Yield: 76%, mp 67.4–68.2 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.34–7.33 (m, 4H), 7.27–7.19 (m, 8H), 7.03–7.00 (m, 2H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 153.5 (d, $^3J_{CF} = 2.8$ Hz), 150.7 (d, $^1J_{CF} = 287.2$ Hz), 136.0 (d, $^3J_{CF} = 4.0$ Hz), 135.8 (d, $^3J_{CF} = 3.9$ Hz), 129.9, 129.8, 129.6 (d, $^4J_{CF} = 3.1$ Hz), 129.3, 128.4, 128.3, 127.5, 127.4, 117.8, 106.5 (d, $^2J_{CF} = 24.4$ Hz) ppm; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ –88.0 (s, 1F) ppm; HRMS (EI): calcd for C$_{20}$H$_{14}$ClFO [M]$^+$: 324.0717, found: 324.0722.

(2-Fluoro-2-(4-fluorophenoxy)ethene-1,1-diyl)dibenzene (3af): White solid. Yield: 78%, mp 93.8–94.7 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.37–7.32 (m, 4H), 7.30–7.23 (m, 6H), 7.07–6.98 (m, 4H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 159.2 (d, $^1J_{CF} = 240.8$ Hz), 151.0 (d, $^1J_{CF} = 286.9$ Hz), 150.8–150.7 (m), 136.1 (d, $^3J_{CF} = 4.0$ Hz), 135.9 (d, $^4J_{CF} = 3.8$ Hz), 129.8 (d, $^3J_{CF} = 4.1$ Hz), 129.6 (d, $^4J_{CF} = 3.2$ Hz), 128.3, 128.2, 127.4, 127.3, 117.9 (d, $^3J_{CF} = 8.0$ Hz), 116.3 (d, $^3J_{CF} = 23.5$ Hz), 106.0 (d, $^3J_{CF} = 24.7$ Hz) ppm; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ –87.8 (s, 1F), –119.2 to –119.3 (m, 1F) ppm; HRMS (EI): calcd for C$_{20}$H$_{14}$F$_2$O [M]$^+$: 308.1013, found: 308.1014.

(2-Fluoro-2-(4-(trifluoromethyl)phenoxy)ethene-1,1-diyl)dibenzene (3ag): Colorless liquid. Yield: 83%. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.60 (d, $^1J = 8.8$ Hz, 2H), 7.37–7.34 (m, 4H), 7.33–7.17 (m, 8H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.3, 150.2 (d, $^1J_{CF} = 287.3$ Hz), 135.7 (d, $^3J_{CF} = 3.9$ Hz), 135.6 (d, $^4J_{CF} = 3.8$ Hz), 129.8 (d, $^3J_{CF} = 4.2$ Hz), 129.5 (d, $^4J_{CF} = 3.1$ Hz), 128.4, 128.3, 127.6, 127.5, 127.3 (q, $^3J_{CF} = 3.7$ Hz), 126.3 (q, $^2J_{CF} = 32.8$ Hz), 124.0 (q, $^1J_{CF} = 269.9$ Hz), 116.5, 107.2 (d, $^3J_{CF} = 23.7$ Hz) ppm; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ –88.6 (s, 1F) ppm; HRMS (EI): calcd for C$_{21}$H$_{14}$F$_4$O [M]$^+$: 358.0981, found: 358.0986.

4-((1-Fluoro-2,2-diphenylvinyl)oxy)benzaldehyde (3ah): Colorless oil. Yield: 88%. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.89 (s, 1H), 7.84 (d, $^1J = 8.8$ Hz, 2H), 7.36–7.20 (m, 12H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 190.6, 159.5 (d, $^3J_{CF} = 3.3$ Hz), 150.1 (d, $^1J_{CF} = 287.3$ Hz), 135.7 (d, $^4J_{CF} = 3.8$ Hz), 135.6 (d, $^3J_{CF} = 3.9$ Hz), 132.7, 132.0, 129.8 (d, $^3J_{CF} = 4.4$ Hz), 129.5 (d, $^4J_{CF} = 3.2$ Hz), 128.4, 128.3, 127.7, 127.6, 116.7, 107.5 (d, $^2J_{CF} = 23.4$ Hz) ppm; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ –88.2 (s, 1F) ppm; HRMS (EI): calcd for C$_{21}$H$_{15}$FO$_2$ [M]$^+$: 318.1056, found: 318.1055.
3-((1-Fluoro-2,2-diphenylvinyl)oxy)pyridine (3ai): Yellow oil. Yield: 85%. 1H NMR (400 MHz, CDCl$_3$) δ 8.47 (d, $J=2.4$ Hz, 1H), 8.37–8.36 (m, 1H), 7.41–7.21 (m, 12H) ppm; 13C NMR (100 MHz, CDCl$_3$) δ 151.5 (d, $J_{CF}=2.8$ Hz), 150.6 (d, $J_{CF}=287.6$ Hz), 145.4, 139.4 (d, $J_{CF}=0.9$ Hz), 135.7 (d, $J_{CF}=3.9$ Hz), 135.6 (d, $J_{CF}=3.9$ Hz), 129.8, 129.7, 129.6 (d, $J_{CF}=3.2$ Hz), 128.4, 128.3, 127.6, 124.2, 123.6, 106.8 (d, $J_{CF}=23.6$ Hz) ppm; 19F NMR (376 MHz, CDCl$_3$) δ −88.6 ppm; HRMS (EI): calcd for C$_{19}$H$_{14}$FNO [M$^+$]: 291.1059, found: 291.1058.

![3ai](image)

4-((1-Fluoro-2,2-diphenylvinyl)oxy)pyridine (3aj): White solid. Yield: 91%, mp 144.6–146.2 °C. 1H NMR (400 MHz, CDCl$_3$) δ 7.41–7.27 (m, 10H), 7.05–7.03 (m, 2H), 6.27–6.23 (m, 2H) ppm; 13C NMR (100 MHz, CDCl$_3$) δ 179.0, 146.3 (d, $J_{CF}=269.3$ Hz), 138.5 (d, $J_{CF}=1.7$ Hz), 134.9 (d, $J_{CF}=3.8$ Hz), 134.8 (d, $J_{CF}=3.2$ Hz), 129.7 (d, $J_{CF}=4.5$ Hz), 129.5 (d, $J_{CF}=3.7$ Hz), 129.1, 128.7, 128.6, 128.5, 118.8, 117.4 (d, $J_{CF}=20.5$ Hz) ppm; 19F NMR (376 MHz, CDCl$_3$) δ −95.0 (s, 1F) ppm; HRMS (EI): calcd for C$_{19}$H$_{14}$FNO [M$^+$]: 291.1059, found: 291.1060.

![3aj](image)

3-((1-Fluoro-2,2-diphenylvinyl)oxy)thiophene (3ak): Colorless oil. Yield: 71%. 1H NMR (400 MHz, CDCl$_3$) δ 7.34–7.23 (m, 10H), 7.18 (dd, $J=5.2$, 3.2 Hz, 1H), 6.85–6.83 (m, 1H), 6.74–6.72 (m, 1H) ppm; 13C NMR (100 MHz, CDCl$_3$) δ 152.0 (d, $J_{CF}=287.9$ Hz), 151.7 (d, $J_{CF}=2.3$ Hz), 136.2 (d, $J_{CF}=4.0$ Hz), 136.0 (d, $J_{CF}=3.8$ Hz), 129.9 (d, $J_{CF}=4.1$ Hz), 129.7 (d, $J_{CF}=3.2$ Hz), 128.3, 128.2, 127.3, 127.2, 125.4, 119.0 (d, $J_{CF}=0.5$ Hz), 105.4 (d, $J_{CF}=1.5$ Hz), 104.7 (d, $J_{CF}=24.7$ Hz) ppm; 19F NMR (376 MHz, CDCl$_3$) δ −88.3 ppm; HRMS (EI): calcd for C$_{18}$H$_{13}$FOS [M$^+$]: 296.0671, found: 296.0674.

![3ak](image)

3,3'-(2-Fluoro-2-(p-tolyloxy)ethene-1,1-diyl)bis(fluorobenzene) (3bb): Yellow solid. Yield: 75%, mp 80.4–81.5 °C. 1H NMR (400 MHz, CDCl$_3$) δ 7.33–7.27 (m, 10H), 7.18 (dd, $J=5.2$, 3.2 Hz, 1H), 6.85–6.83 (m, 1H), 6.74–6.72 (m, 1H) ppm; 13C NMR (100 MHz, CDCl$_3$) δ 152.0 (d, $J_{CF}=287.9$ Hz), 151.7 (d, $J_{CF}=2.3$ Hz), 136.2 (d, $J_{CF}=4.0$ Hz), 136.0 (d, $J_{CF}=3.8$ Hz), 129.9 (d, $J_{CF}=4.1$ Hz), 129.7 (d, $J_{CF}=3.2$ Hz), 128.3, 128.2, 127.3, 127.2, 125.4, 119.0 (d, $J_{CF}=0.5$ Hz), 105.4 (d, $J_{CF}=1.5$ Hz), 104.7 (d, $J_{CF}=24.7$ Hz) ppm; 19F NMR (376 MHz, CDCl$_3$) δ −84.1 (s, 1F), −113.0 to −113.1 (m, 2F) ppm; HRMS(EI): calcd for C$_{21}$H$_{15}$F$_3$O [M$^+$]: 340.1075, found: 340.1076.
4,4’-(2-Fluoro-2-(4-methoxyphenoxy)ethene-1,1-diyl)bis(fluorobenzene) (3cd): Yellow solid. Yield: 76%, mp 79.6–81.4 °C. \( ^1 \text{H} \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.29–7.21 (m, 4H), 7.05–6.94 (m, 6H), 6.87–6.82 (m, 2H), 3.76 (s, 3H) ppm; \( ^{13} \text{C} \) NMR (100 MHz, CDCl\(_3\)) \( \delta \) 161.9 (d, \( ^1 J_{CF} = 245.5 \) Hz), 156.3, 151.5 (d, \( ^1 J_{CF} = 286.7 \) Hz), 148.4 (d, \( ^3 J_{CF} = 2.3 \) Hz), 132.2–132.1 (m), 132.0–131.9 (m), 131.5 (dd, \( ^3 J_{CF} = 8.0 \) Hz, \( ^4 J_{CF} = 3.9 \) Hz), 131.2 (dd, \( ^3 J_{CF} = 7.9 \) Hz, \( ^4 J_{CF} = 3.2 \) Hz), 117.7, 115.3 (d, \( ^2 J_{CF} = 21.4 \) Hz), 115.2 (d, \( ^2 J_{CF} = 21.3 \) Hz), 114.9, 103.4 (d, \( ^2 J_{CF} = 26.3 \) Hz), 55.7 ppm; \( ^{19} \text{F} \) NMR (376 MHz, CDCl\(_3\)) \( \delta \) –87.0 (s, 1F), –114.4 to –114.5 (m, 1F), –114.6 to –114.7 (m, 1F) ppm; HRMS (EI): calcd for C\(_{21}\)H\(_{15}\)F\(_3\)O\(_2\) [M]+: 356.1024, found: 356.1025.

4,4’-(2-Fluoro-2-(4-fluorophenoxy)ethene-1,1-diyl)bis(methylbenzene) (3df): Colorless liquid. Yield: 85%. \( ^1 \text{H} \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.23–7.22 (m, 2H), 7.14 (d, \( J = 8.4 \) Hz, 4H), 7.06–7.00 (m, 4H), 6.98–6.94 (m, 2H), 2.34 (s, 3H), 2.28 (m, 3H) ppm; \( ^{13} \text{C} \) NMR (100 MHz, CDCl\(_3\)) \( \delta \) 159.2 (d, \( ^1 J_{CF} = 240.7 \) Hz), 150.8 (d, \( ^1 J_{CF} = 285.9 \) Hz), 151.0–150.9 (m), 137.1, 137.0, 133.4 (d, \( ^3 J_{CF} = 4.0 \) Hz), 133.2 (d, \( ^4 J_{CF} = 3.8 \) Hz), 129.8 (d, \( ^3 J_{CF} = 4.1 \) Hz), 129.5 (d, \( ^4 J_{CF} = 3.2 \) Hz), 129.0, 128.9, 117.9 (d, \( ^3 J_{CF} = 8.1 \) Hz), 116.4 (d, \( ^2 J_{CF} = 23.5 \) Hz), 105.9 (d, \( ^2 J_{CF} = 24.7 \) Hz), 21.3, 21.2 ppm; \( ^{19} \text{F} \) NMR (376 MHz, CDCl\(_3\)) \( \delta \) –88.7 (s, 1F), –119.3 to –119.4 (m, 1F), –114.4 to –114.5 (m, 1F), –114.6 to –114.7 (m, 1F) ppm; HRMS (EI): calcd for C\(_{22}\)H\(_{18}\)F\(_2\)O [M]+: 336.1326, found: 336.1327.

4,4’-(2-Fluoro-2-phenoxyethene-1,1-diyl)bis(chlorobenzene) (3ea): Colorless liquid. Yield: 57%. \( ^1 \text{H} \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.34–7.30 (m, 4H), 7.26–7.16 (m, 6H), 7.14–7.06 (m, 3H) ppm; \( ^{13} \text{C} \) NMR (100 MHz, CDCl\(_3\)) \( \delta \) 154.5 (d, \( ^3 J_{CF} = 2.5 \) Hz), 151.2 (d, \( ^1 J_{CF} = 288.4 \) Hz), 134.3 (d, \( ^3 J_{CF} = 4.1 \) Hz), 134.2 (d, \( ^4 J_{CF} = 4.0 \) Hz), 133.4, 133.3, 131.2 (d, \( ^3 J_{CF} = 4.2 \) Hz), 130.9 (d, \( ^4 J_{CF} = 3.2 \) Hz), 130.0, 128.6, 128.5, 124.4, 116.5, 104.1 (d, \( ^2 J_{CF} = 25.7 \) Hz) ppm; \( ^{19} \text{F} \) NMR (376 MHz, CDCl\(_3\)) \( \delta \) –85.5 (s, 1F) ppm; HRMS (EI): calcd for C\(_{20}\)H\(_{13}\)Cl\(_2\)FO [M]+: 358.0327, found: 358.0326.
4,4’-(2-Fluoro-2-phenoxyethene-1,1-diyl)bis(bromobenzene) (3fa): White solid. Yield: 47%, mp 96.8–98.1 °C. 

\[ ^1H \text{NMR (400 MHz, CDCl}_3) \delta 7.49–7.46 (m, 2H), 7.40–7.31 (m, 4H), 7.23–7.06 (m, 7H) ppm; ^13C \text{NMR (100 MHz, CDCl}_3) \delta 154.4 (d, \_J_{CF} = 2.4 Hz), 151.1 (d, \_J_{CF} = 288.7 Hz), 134.7 (d, \_J_{CF} = 4.2 Hz), 134.5 (d, \_J_{CF} = 3.8 Hz), 131.6 (d, \_J_{CF} = 6.3 Hz), 131.5 (d, \_J_{CF} = 4.1 Hz), 131.2, 131.1, 130.0, 124.4, 121.6, 121.5, 116.5, 104.2 (d, \_J_{CF} = 25.8 Hz) ppm; ^19F \text{NMR (376 MHz, CDCl}_3) \delta –85.3 (s, 1F) ppm; HRMS (EI): calcd for C\(_{20}\)H\(_{13}\)Br\(_2\)FO [M]+: 447.9297, found: 447.9304. \]

9-(Fluoro(phenoxy)methylene)-9H-fluorene (3ga): Yellow solid. Yield: 73%, mp 76.9–78.4 °C. 

\[ ^1H \text{NMR (400 MHz, CDCl}_3) \delta 7.87–7.85 (m, 1H), 7.80–7.76 (m, 3H), 7.40–7.31 (m, 5H), 7.23–7.17 (m, 4H) ppm; ^13C \text{NMR (100 MHz, CDCl}_3) \delta 153.7 (d, \_J_{CF} = 2.0 Hz), 152.4 (d, \_J_{CF} = 299.6 Hz), 139.1, 138.8, 135.3 (d, \_J_{CF} = 7.6 Hz), 135.2 (d, \_J_{CF} = 6.5 Hz), 130.1, 127.4, 127.3, 127.2, 125.1, 124.3, 124.2, 123.6, 120.0, 117.4, 103.1 (d, \_J_{CF} = 25.9 Hz) ppm; ^19F \text{NMR (376 MHz, CDCl}_3) \delta –72.9 (s, 1F) ppm; HRMS (EI): calcd for C\(_{20}\)H\(_{13}\)FO [M]+: 288.0950, found: 288.0949. \]

\((E/Z)-(4-(2-Fluoro-2-phenoxyvinyl)phenyl)(methyl)sulfane (3ha): Colorless liquid. Yield: 86%. A mixture of E- and Z-isomers (47:53, the E/Z ratio was determined by \(^{19}\text{F NMR spectroscopy).} \)

\[ ^1H \text{NMR (400 MHz, CDCl}_3) \delta 7.37–7.31 (m, 4H, both E- and Z-isomer), 7.21–7.12 (m, 5H, both E- and Z-isomer), 5.64 (d, \_J = 5.6 Hz, 1H, E-isomer), 5.26 (d, \_J = 28.8 Hz, 1H, Z-isomer), 2.45 (s, 3H, Z-isomer), 2.41 (s, 3H, E-isomer) ppm; ^13C \text{NMR (100 MHz, CDCl}_3) \delta 155.0 (d, \_J_{CF} = 286.0 Hz), 154.8 (d, \_J_{CF} = 0.9 Hz), 153.7 (d, \_J_{CF} = 2.6 Hz), 153.5 (d, \_J_{CF} = 282.1 Hz), 136.9, 136.8, 130.0, 129.9, 129.2 (d, \_J_{CF} = 6.5 Hz), 128.9 (d, \_J_{CF} = 8.1 Hz), 128.2, 128.1, 128.0 (d, \_J_{CF} = 3.6 Hz), 126.8 (d, \_J_{CF} = 4.6 Hz), 124.6, 124.5, 117.4, 116.6, 91.9 (d, \_J_{CF} = 37.9 Hz), 90.0 (d, \_J_{CF} = 19.4 Hz), 15.9, 15.8 ppm; ^19\text{F NMR (376 MHz, CDCl}_3) \delta –82.1 (d, \_J = 28.6 Hz, 1F, Z-isomer), –82.5 (d, \_J = 5.6 Hz, 1F, E-isomer) ppm; HRMS (EI): calcd for C\(_{15}\)H\(_{13}\)FOS [M]+: 260.0671, found: 260.0673. \]

\((E/Z)-1-(2-Fluoro-2-(4-methoxyphenoxy)vinyl)naphthalene (3id): Yellow solid. Yield: 81%. A mixture of E- and Z-isomers (65:35, the E/Z ratio was determined by \(^{19}\text{F NMR spectroscopy).} \)

\[ ^1H \text{NMR (400 MHz, CDCl}_3) \delta 8.21 (d, \_J = 8.4 Hz, 1H, E-isomer), 8.10–8.08 (m, 1H, Z-isomer), 7.98–7.85 (m, 3H, both E- and Z-isomer), 7.68–7.53 (m, 3H, both E- and Z-isomer), 7.34 (d, \_J = 8.8 Hz, 2H, Z-isomer), 7.20 (d, \_J = 8.8 Hz, 2H, E-isomer), 7.05 (d, \_J = 9.2 Hz, 2H, Z-isomer), 6.94 (d, \_J = 8.8 Hz, 2H, E-isomer), 6.42 (d, \_J = 5.6 Hz, 1H, E-isomer), 5.95 (d, \_J = 27.2 Hz, 1H, Z-isomer), 3.88 (s, 3H, Z-isomer), 3.82 (s, 3H, E-isomer) ppm; ^13C \text{NMR (100 MHz, CDCl}_3) \delta 157.4 \]
(E/Z)-1-(tert-Butyl)-4-(2-fluoro-2-(4-fluorophenoxy)vinyl)benzene (3jf): Colorless liquid. Yield: 88%. A mixture of E- and Z-isomers (74:26, the E/Z ratio was determined by $^{19}$F NMR spectroscopy). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.35–7.30 (m, 4H, both E- and Z-isomer), 7.11–7.08 (m, 2H, both E- and Z-isomer), 5.66 (d, $J = 5.6$ Hz, 1H, E-isomer), 5.27 (d, $J = 28.8$ Hz, 1H, Z-isomer), 1.31 (s, 9H, tert-butyl-E-isomer), 1.28 (s, 9H, E-isomer) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 159.4 (d, $^1$J$_{CF} = 241.5$ Hz), 159.3 (d, $^1$J$_{CF} = 241.1$ Hz), 155.0 (d, $^1$J$_{CF} = 285.7$ Hz), 153.4 (d, $^1$J$_{CF} = 281.6$ Hz), 150.8, 150.7, 149.9 (d, $^3$J$_{CF} = 2.0$ Hz), 149.8 (d, $^3$J$_{CF} = 2.1$ Hz), 149.7–149.6 (m), 129.2 (d, $^3$J$_{CF} = 6.4$ Hz), 128.9 (d, $^3$J$_{CF} = 7.9$ Hz), 127.5 (d, $^4$J$_{CF} = 6.9$ Hz), 127.3 (d, $^4$J$_{CF} = 3.6$ Hz), 125.6, 118.8 (d, $^3$J$_{CF} = 8.4$ Hz), 118.0 (d, $^3$J$_{CF} = 8.2$ Hz), 116.5 (d, $^2$J$_{CF} = 23.5$ Hz), 116.4 (d, $^2$J$_{CF} = 23.5$ Hz), 92.0 (d, $^2$J$_{CF} = 37.0$ Hz), 90.0 (d, $^2$J$_{CF} = 19.4$ Hz), 34.6, 34.5, 31.3, 31.2 ppm; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ –83.6 (d, $^1$J$_{CF} = 28.2$ Hz), –81.1 (d, $^1$J$_{CF} = 28.9$ Hz), 55.7, 55.6 ppm; HRMS (EI): calcd for C$_{19}$H$_{15}$F$_2$O $[M]^+$: 294.1056, found: 294.1058.

(E/Z)-1-Bromo-3-(2-fluoro-2-(3-methoxyphenoxy)vinyl)benzene (3kl): Yellow oil. Yield: 80%. A mixture of E- and Z-isomers (44:56, the E/Z ratio was determined by $^{19}$F NMR spectroscopy). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.46 (s, 1H, both E- and Z-isomer), 7.25–7.14 (m, 3H, both E- and Z-isomer), 6.65–6.60 (m, 3H, both E- and Z-isomer), 5.50 (d, $J = 5.6$ Hz, 1H, E-isomer), 5.12 (d, $J = 28.4$ Hz, 1H, Z-isomer), 3.70 (s, 3H, both E- and Z-isomer) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 160.0, 159.9, 154.7 (d, $^1$J$_{CF} = 286.2$ Hz), 154.3, 153.3 (d, $^3$J$_{CF} = 2.1$ Hz), 153.1 (d, $^1$J$_{CF} = 284.1$ Hz), 133.4 (d, $^3$J$_{CF} = 6.5$ Hz), 133.2 (d, $^3$J$_{CF} = 8.6$ Hz), 129.5, 129.4, 129.3, 129.0, 128.6 (d, $^4$J$_{CF} = 1.9$ Hz), 128.4 (d, $^4$J$_{CF} = 2.0$ Hz), 125.2 (d, $^4$J$_{CF} = 7.1$ Hz), 125.0 (d, $^4$J$_{CF} = 3.5$ Hz), 121.6, 121.5, 109.4, 109.3, 108.6, 107.7, 102.9, 102.1, 90.0 (d, $^2$J$_{CF} = 38.4$ Hz), 87.7 (d, $^2$J$_{CF} = 28.9$ Hz), 54.4 ppm; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ –80.1 (d, $J = 5.6$ Hz, 1F, E-isomer), –80.3 (d, $J = 28.2$ Hz, 1F, Z-isomer) ppm; HRMS (EI): calcd for C$_{18}$H$_{13}$BrFO$_2$ [M]$^+$: 322.0005, found: 322.0007.
$^1$H, $^{13}$C, $^{19}$F NMR and HRMS (EI) spectra of compounds 3

$^1$H NMR Spectrum of 3aa

$^{13}$C NMR Spectrum of 3aa
$^{19}$F NMR Spectrum of 3aa

HRMS (EI) of 3aa
$^1$H NMR Spectrum of 3ab

$^{13}$C NMR Spectrum of 3ab
$^{19}$F NMR Spectrum of 3ab

HRMS (EI) of 3ab
$^1$H NMR Spectrum of 3ac

$^{13}$C NMR Spectrum of 3ac
$^{19}$F NMR Spectrum of 3ac

[Image of 19F NMR spectrum]

HRMS (EI) of 3ac

[Image of HRMS (EI) spectrum]
$^1$H NMR Spectrum of 3ad

$^{13}$C NMR Spectrum of 3ad
$^{19}$F NMR Spectrum of 3ad

HRMS (EI) of 3ad
$^1$H NMR Spectrum of 3ae

$^{13}$C NMR Spectrum of 3ae
$^{19}$F NMR Spectrum of 3ae
HRMS (EI) of 3ae

20142345 188 (3.133) Cm (188-(4+253))

1H NMR Spectrum of 3af
$^{13}$C NMR Spectrum of 3af
$^{19}$F NMR Spectrum of 3af

HRMS (EI) of 3af
$^1$H NMR Spectrum of 3ag

$^{13}$C NMR Spectrum of 3ag
$^{19}$F NMR Spectrum of 3ag

HRMS (EI) of 3ag
\[1^1\text{H} \text{ NMR Spectrum of 3ah}\]

\[1^{13}\text{C} \text{ NMR Spectrum of 3ah}\]
$^{19}$F NMR Spectrum of 3ah
$^1$H NMR Spectrum of 3ai

$^{13}$C NMR Spectrum of 3ai
$^{19}$F NMR Spectrum of 3ai

HRMS (EI) of 3ai
$^1$H NMR Spectrum of 3aj

$^{13}$C NMR Spectrum of 3aj
$^{19}$F NMR Spectrum of 3aj

HRMS (EI) of 3aj
$^1$H NMR Spectrum of 3ak

$^{13}$C NMR Spectrum of 3ak
$^{19}$F NMR Spectrum of 3ak

HRMS (EI) of 3ak

20142349 137 (2.283) Cm (137-48+11)

TOF MS EI+
296.0974 1.69e4
\(^1\)H NMR Spectrum of 3bb

\(^{13}\)C NMR Spectrum of 3bb
$^{19}\text{F NMR Spectrum of 3bb}$

HRMS (EI) of 3bb
$^1$H NMR Spectrum of 3cd

$^{13}$C NMR Spectrum of 3cd
$^{19}$F NMR Spectrum of 3cd
HRMS (EI) of 3cd

\[
20142360\ 206\ (3.433)\ Cm\ (206-(9+11))
\]

1H NMR Spectrum of 3df

![1H NMR Spectrum of 3df](image)

![Chemical Structure of 3df](image)
$^{13}$C NMR Spectrum of 3df

$^{19}$F NMR Spectrum of 3df
HRMS (EI) of 3df
$^1$H NMR Spectrum of 3ea

$^{13}$C NMR Spectrum of 3ea
$^{19}$F NMR Spectrum of 3ea

HRMS (EI) of 3ea
$^1$H NMR Spectrum of 3fa

$^{13}$C NMR Spectrum of 3fa
$^{19}$F NMR Spectrum of 3fa

HRMS (EI) of 3fa
$^1$H NMR Spectrum of 3ga

$^{13}$C NMR Spectrum of 3ga
$^{19}$F NMR Spectrum of 3ga
HRMS (EI) of 3ga

1H NMR Spectrum of 3ha
$^{13}$C NMR Spectrum of 3ha

$^{19}$F NMR Spectrum of 3ha
HRMS (EI) of 3ha

1H NMR Spectrum of 3id
13C NMR Spectrum of 3id

19F NMR Spectrum of 3id
HRMS (EI) of 3id

20142816 151 (2.527) Cm (151+(3+200))

159.0604
247.1117
249.1162
251.0983
254.1126
274.0985
295.1103
294.1058 2.68e4
$^1$H NMR Spectrum of 3kl

$^{13}$C NMR Spectrum of 3kl
$^{19}$F NMR Spectrum of 3kl

HRMS (EI) of 3kl