Supporting Information

Double Strain-Release Enables Formal C–O/C–F and C–N/C–F Ring-Opening Metathesis

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1. **General Information**

Unless otherwise stated, all reactions were set up in vials under a nitrogen atmosphere. Anhydrous solvents were purchased from Energy Chemical or Adamas in AcroSeal glass bottle (extra dry over molecular sieve) and used directly. All NMR spectra were recorded on a JEOL JNM-ECZ400S (400 MHz for $^1$H, 100 MHz for $^{13}$C, 376 MHz for $^{19}$F) with CDCl$_3$ as the solvent. Unless otherwise noted, chemical shifts for $^1$H NMR are reported in ppm using tetramethylsilane (TMS, $\delta = 0$ ppm) or CHCl$_3$ ($\delta = 7.26$ ppm) as the internal standard when using CDCl$_3$ as the solvent; Chemical shifts for $^{13}$C NMR spectra are reported in ppm with the center line of the triplet for CDCl$_3$ set at 77.0 ppm. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad. Gas chromatography mass spectrometry (GC-MS) analysis was performed on Agilent Technologies 5975C and SHIMADZU GC-2030. High-resolution mass spectrometry (HRMS) was recorded on a Q-TOF (AB SCIEX X500R with ESI source, and Agilent 7250 with EI source), which combines quadrupole precursor ion selection and a high-resolution accurate-mass (HR/AM) Time of Flight mass analyzer to deliver mass accuracy. Flash column chromatography was performed with silica gel (200-300 mesh, Haiyang, Qingdao). Melting points were determined using a digital melting point apparatus (JHX-4).
2. Synthesis of Substrates

![Figure S1. Substrates used in this work.](image)

2.1 General Procedure A: Synthesis of gem-Difluorinated Cyclopropanes

Substrates 1a-1w were synthesized according to the previous work. To a flame-dried 100 mL three-necked flask equipped with a magnetic stir bar was added anhydrous NaI (0.3 g, 3.0 mmol, 0.2 equiv.), dry THF (20 mL), TMSCF₃ (3.7 mL, 3.55 g, 25 mmol, 2.5 equiv.) and corresponding alkenes (10.0 mmol, 1 equiv.) under nitrogen atmosphere. The flask was sealed and stirred at 65 °C for 12 h. The reaction mixture was then cooled to room temperature, which was evaporated to dryness under
reduce pressure and directly filtered through a pad of celite. The crude mixture was extracted with ethyl acetate (20 mL) and washed with saturated Na₂SO₃ solution (20 mL), brine (20 mL). The organic layer was dried over MgSO₄, filtered and concentrated, which was purified by silica gel column chromatography with PE (petroleum ether) to afford corresponding gem-difluorinated cyclopropanes. All these gem-difluorinated cyclopropanes 1a-1g, 1h-1s, 1t-1u, 1v, 1w are literature reported compounds.

2.2 General Procedure B: Synthesis of Cyclic Ethers

Substrates 2b-2d, 2f-2j were synthesized according to the previous work. To a solution of KOtBu (561 mg, 5.0 mmol, 1.0 equiv.) in DMSO (5 mL), trimethylsulfoxonium iodide (1.22 g, 5.5 mmol, 1.1 equiv.) was added and the mixture was stirred at room temperature for 30 minutes. A solution of ketone (5 mmol) in DMSO (1 mL) was then added and stirred for 12 hours. The reaction mixture was diluted with EA (ethyl acetate, 5 mL) and water (5 mL), and the layers were separated. The aqueous layer was back-extracted with EA (2 × 15 mL). The combined organic extracts were washed with brine and dried over Na₂SO₄. The solvent was removed under reduced pressure and purified by chromatography on silica gel column (PE:EA = 20:1) to provide the oxiranes. Oxiranes 2b, 2c-2d, 2f, 2g, 2h-2i are literature reported compounds.

2-(3,5-bis(trifluoromethyl)phenyl)-2-ethyloxirane (2e)

Substrate 2e was synthesized from the general procedure, and was obtained as colorless oil in 65% isolated yield (923 mg). Rf = 0.3 (PE:EA = 50:1). ¹H NMR (400 MHz, CDCl₃) δ 7.83 (s, 2H), 7.80 (s, 1H), 3.07 (d, J = 5.1 Hz, 1H), 2.73 (d, J = 5.1 Hz, 1H), 2.30 (dq, J = 15.0, 7.5 Hz, 1H), 1.85 (dq, J = 14.7, 7.4 Hz, 1H), 0.96 (t, J = 7.5 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 143.0, 131.8 (q, J = 18.8 Hz), 126.2 (d, J = 5.6 Hz), 124.6, 121.9, 121.5 – 121.4 (m), 60.1, 55.5, 27.5, 8.7. ¹⁹F NMR (376 MHz, Chloroform-d) δ -62.77.

Substrate 2k was synthesized from the previous work. In a 250 mL oven-dried round bottom
flask, trimethylsulfoxonium iodide (5.15 g, 25 mmol, 5.0 equiv.) was weighed and dissolved in 'BuOH (40 mL). KO'Bu (2.81 g, 25 mmol, 5.0 equiv.) was added to the reaction mixture in 4 portions and stirred at 50 °C for 30 min. Afterwards, a solution of 1-(4-methoxyphenyl)ethan-1-one (631 mg, 5.0 mmol, 1.0 equiv.) in 'BuOH (10 mL) was added dropwise. The reaction mixture was heated gradually to 70 °C and stirred for 8 h. Once the reaction was completed, water (30 mL) was added to the reaction mixture and the two resulting layers were separated and the aqueous phase was extracted with hexanes (3 × 20 mL). The organic layers were combined, dried over anhydrous MgSO₄ and then concentrated to under vacuum. The crude product was purified by chromatography on silica gel column (PE:EA = 20:1) to give 2-(4-methoxyphenyl)-2-methyloxetane 2k as colorless oil in 65% yield (578 mg).

2-(4-methoxyphenyl)-2-methyloxetane (2k)

\[
\begin{align*}
    \text{HNMR} & (400 \text{ MHz, CDCl}_3) \delta 7.14 \text{ (d, } J = 7.8 \text{ Hz, 2H), } 6.84 \text{ (d, } J = 7.2 \text{ Hz, 2H), } \ 3.80 \text{ (s, 3H), } 2.80 \text{ (q, } J = 14.2 \text{ Hz, 2H), } 2.64 \text{ – 2.59 (m, 2H), } 1.27 \text{ (s, 3H).} \\
    \text{C NMR} & (101 \text{ MHz, CDCl}_3) \delta 158.3, 130.5, 129.2, 113.7, 57.4, 55.2, 53.2, 42.1, 20.8.
\end{align*}
\]

2.3 General Procedure C: Synthesis of Azetidines

To a solution of methyl triphenylphosphoniumbromide (16169 mg, 40.0 mmol, 1.0 equiv.) in DMSO (30 mL) was added 'BuOK (4.49 g, 40.0 mmol, 2.0 equiv.). The mixture was stirred at 25 °C for 60 minutes and 1-(diphenylmethyl)azetidin-3-one (4.72 g, 11.63 mmol, 2.0 equiv.) in DMSO (30 mL) was then added. The reaction mixture was heated at 60°C for 18 hours before being quenched with H₂O (30 mL). The combined organic layer was washed with brine (30 mL), dried over MgSO₄, filtered and concentrated in vacuo, which was then purified by silica gel column chromatography (PE/EA = 20:1) to afford 1-benzhydryl-3-methyleneazetidine 4a as white solid in 65% yield (3.06 g).

1-benzhydryl-3-methyleneazetidine (4a)

\[
\begin{align*}
    \text{HNMR} & (400 \text{ MHz, CDCl}_3) \delta 7.46 \text{ – 7.40 (m, 4H), } 7.30 \text{ – 7.24 (m, 4H), } 7.21 \text{ – 7.15 (m, 2H), } 4.84 \text{ (p, } J = 2.3 \text{ Hz, 2H), } 4.47 \text{ (s, 1H), } 3.77 \text{ (t, } J = 2.4 \text{ Hz, 4H).} \\
    \text{C NMR} & (101 \text{ MHz, CDCl}_3) \delta 142.5, 140.9, 128.5, 127.4, 127.1, 105.0, 77.8, 61.9.
\end{align*}
\]
3. C–O/C–F Bond Metathesis Reaction

General Procedure D: C–O/C–F Cross Metathesis Reaction

In a nitrogen filled glove box, a 4 mL vial equipped with stir bar was charged with [Rh(CO)_2Cl]_2 (0.8 mg, 0.002 mmol, 2 mol%), IPr (2.4 mg, 0.006 mmol, 6 mol%) and nPr_2CHCN (3.1 μL) and PhCF_3 (0.3 mL). The mixture was stirred for about 3 min, which afforded a brown homogeneous catalyst solution, and then transferred the catalyst solution into another vial with stir bar, gem-difluorinated cyclopropane (0.1 mmol, 1 equiv.), cyclic ether (0.3 mmol, 3 equiv.) and AgBF_4 (1.0 mg, 0.005 mmol, 5 mol%). Generally, several such type of reactions were carried out parallelly, thus the catalyst solution can be prepared in one vial together. The 4 mL vial was sealed and removed from the glove box and stirred at 80 °C for 24 hours. The reaction mixture was purified by chromatography on silica gel column to give the allyl ether product.
Figure S2. Allyl ethers synthesized in this work.

(Z)-4-(2-fluoro-3-(2-fluoro-2-methylpropoxy)prop-1-en-1-yl)-1,1'-biphenyl (3a)

Product 3a were synthesized from the general procedure D, and was obtained as colorless oil in 76% isolated yield (23.1 mg). Rf = 0.3 (PE:EA = 50:1). 1H NMR (400 MHz, CDCl3) δ 7.61 (d, J = 1.4 Hz, 1H), 7.59 − 7.55 (m, 5H), 7.44 (t, J = 7.6 Hz, 2H), 7.34 (t, J = 7.3 Hz, 1H), 5.81 (d, J = 38.4 Hz, 1H), 4.24 (d, J = 15.5 Hz, 2H), 3.55 (d, J = 19.3 Hz, 2H), 1.40 (d, J = 21.4 Hz, 6H). 13C NMR (101 MHz,
CDCl₃ δ 156.2 (d, J = 268.7 Hz), 140.6, 140.2 (d, J = 2.5 Hz), 131.7 (d, J = 2.9 Hz), 129.2 (d, J = 7.3 Hz), 128.8, 127.4, 127.2, 127.00, 108.8 (d, J = 6.6 Hz), 95.0 (d, J = 167.6 Hz), 76.0 (d, J = 24.5 Hz), 70.1 (d, J = 30.8 Hz), 23.8 (d, J = 24.1 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -110.53 (dt, J = 38.8, 15.8 Hz), -144.78 (dd, J = 41.7, 20.9, 20.4 Hz). HRMS (ESI, m/z) for C₁₉H₂₀F₂NaO⁺ [M+Na]⁺: calcd for 325.1374, found 325.1376.

(Z)-(2-fluoro-3-(2-fluoro-2-methylpropoxy)prop-1-en-1-yl)benzene (3b)

Product 3b were synthesized from the general procedure D, and was obtained as colorless oil in 73% isolated yield (16.5 mg). Rᵣ = 0.3 (PE:EA = 50:1). ¹H NMR (400 MHz, CDCl₃) δ 7.52 (d, J = 7.1 Hz, 1H), 7.34 (t, J = 7.5 Hz, 2H), 7.27 – 7.24 (m, 1H), 5.77 (d, J = 38.4 Hz, 1H), 4.22 (d, J = 15.4 Hz, 2H), 3.54 (d, J = 19.2 Hz, 2H), 1.40 (d, J = 21.5 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 156.0 (d, J = 266.8 Hz), 132.7, 128.8 (d, J = 7.6 Hz), 128.5, 127.6, 109.2 (d, J = 6.4 Hz), 95.0 (d, J = 167.6 Hz), 76.0 (d, J = 24.7 Hz), 70.1 (d, J = 31.0 Hz), 23.8 (d, J = 24.1 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -111.02 (dt, J = 37.9, 15.4 Hz), -144.85 (dd, J = 42.1, 21.5, 21.1 Hz). HRMS (ESI, m/z) for C₁₃H₁₈F₂NaO⁺ [M+Na]⁺: calcd for 249.1061, found 249.1072.

(Z)-1-(2-fluoro-3-(2-fluoro-2-methylpropoxy)prop-1-en-1-yl)-4-methylbenzene (3c)

Product 3c were synthesized from the general procedure D, and was obtained as colorless oil in 71% isolated yield (17.0 mg). Rᵣ = 0.3 (PE:EA = 50:1). ¹H NMR (400 MHz, CDCl₃) δ 7.42 (d, J = 8.3 Hz, 2H), 7.15 (d, J = 7.9 Hz, 2H), 5.74 (d, J = 38.6 Hz, 1H), 4.21 (d, J = 16.1 Hz, 2H), 3.53 (d, J = 19.2 Hz, 2H), 2.34 (s, 3H), 1.39 (d, J = 21.4 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 155.3 (d, J = 267.2 Hz), 137.5 (d, J = 2.5 Hz), 129.8 (d, J = 2.9 Hz), 129.2, 128.7, 128.6, 109.2 (d, J = 6.5 Hz), 95.0 (d, J = 167.5 Hz), 75.9 (d, J = 24.5 Hz), 70.1 (d, J = 30.7 Hz), 23.8 (d, J = 24.2 Hz), 21.2. ¹⁹F NMR (376 MHz, CDCl₃) δ -111.93 (dt, J = 37.6, 16.9 Hz), -144.81 (dd, J = 41.7, 21.2 Hz). HRMS (ESI, m/z) for C₁₄H₁₈F₂NaO⁺ [M+Na]⁺: calcd for 263.1218, found 263.1218.

(Z)-1-(2-fluoro-3-(2-fluoro-2-methylpropoxy)prop-1-en-1-yl)-2-methylbenzene (3d)

Product 3d were synthesized from the general procedure D, and was obtained as colorless oil in 76% isolated yield (18.3 mg). Rᵣ = 0.3 (PE:EA = 50:1). ¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, J = 5.9 Hz, 1H), 7.20 – 7.16 (m, 3H), 5.92 (d, J = 37.6 Hz, 1H), 4.25 (d, J = 14.8 Hz, 2H), 3.56 (d, J = 19.1 Hz, 2H),
2.32 (s, 3H), 1.41 (d, J = 21.5 Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 155.7 (d, J = 267.3 Hz), 135.8, 131.1, 130.1, 129.3 (d, J = 9.9 Hz), 127.6, 125.9, 106.4 (d, J = 7.1 Hz), 95.00 (d, J = 167.5 Hz), 76.0 (d, J = 24.6 Hz), 70.0 (d, J = 31.4 Hz), 23.8 (d, J = 24.2 Hz), 20.1. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -113.1 (dt, J = 37.6, 14.5 Hz), -144.8 (qd, J = 41.8, 20.7 Hz). HRMS (ESI, m/z) for C$_{14}$H$_{18}$F$_2$NaO$^+$ [M+Na]$^+$: calcd for 263.1218, found 263.1218.

(Z)-1-(2-fluoro-3-(2-fluoro-2-methylpropoxy)prop-1-en-1-yl)-4-methoxybenzene (3e)

Product 3e were synthesized from the general procedure, and was obtained as yellow oil in 43% isolated yield (11.0 mg). R$_f$ = 0.32 (PE:EA = 20:1). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.48 – 7.46 (m, 2H), 6.89 – 6.86 (m, 2H), 5.71 (d, J = 38.6 Hz, 1H), 4.20 (d, J = 16.6 Hz, 2H), 3.81 (s, 3H), 3.53 (d, J = 19.3 Hz, 2H), 1.39 (d, J = 21.4 Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 158.9 (d, J = 3.0 Hz), 154.6 (d, J = 265.7 Hz), 130.1 (d, J = 7.4 Hz), 125.3 (d, J = 3.0 Hz), 113.9, 109.0 (d, J = 6.8 Hz), 95.0 (d, J = 167.3 Hz), 75.9 (d, J = 24.6 Hz), 70.2 (d, J = 30.5 Hz), 55.2, 23.8 (d, J = 24.2 Hz). $^{19}$F NMR (376 MHz, CDCl$_3$) -113.75 (dt, J = 37.6, 16.9 Hz), -144.85 (dh, J = 42.2, 21.4, 21.0 Hz). HRMS (ESI, m/z) for C$_{14}$H$_{22}$F$_2$NO$_2$$^+$ [M+NH$_4$]$^+$: calcd for 274.1613, found 274.1610.

(Z)-1-(2-fluoro-3-(2-fluoro-2-methylpropoxy)prop-1-en-1-yl)-2-methoxybenzene (3f)

Product 3f were synthesized from the general procedure D, and was obtained as yellow oil in 60% isolated yield (15.3 mg). R$_f$ = 0.2 (PE:EA = 20:1). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.81 (dd, J = 7.8, 1.7 Hz, 1H), 7.26 – 7.22 (m, 1H), 6.96 (t, J = 7.6 Hz, 1H), 6.88 (d, J = 8.3 Hz, 1H), 6.21 (d, J = 39.4 Hz, 1H), 4.23 (d, J = 16.6 Hz, 2H), 3.84 (s, 3H), 3.54 (d, J = 18.9 Hz, 2H), 1.40 (d, J = 21.5 Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 156.2, 155.8 (d, J = 268.2 Hz), 130.0 (d, J = 12.7 Hz), 128.8, 121.3, 120.6, 110.4, 103.0 (d, J = 5.0 Hz), 95.0 (d, J = 167.5 Hz), 75.8 (d, J = 24.8 Hz), 70.4 (d, J = 30.2 Hz), 55.5, 23.8 (d, J = 24.1 Hz). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -112.6 (dt, J = 39.5, 16.7 Hz), -144.9 (hept, J = 21.4, 20.9 Hz). HRMS (ESI, m/z) for C$_{14}$H$_{22}$F$_2$NO$_2$$^+$ [M+NH$_4$]$^+$: calcd for 274.1613, found 274.1610.

(Z)-1-(tert-butyl)-4-(2-fluoro-3-(2-fluoro-2-methylpropoxy)prop-1-en-1-yl)benzene (3g)

Product 3g were synthesized from the general procedure D, and was obtained as colorless oil in 64% isolated yield (18.0 mg). R$_f$ = 0.3 (PE:EA = 50:1). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.47 (d, J = 8.5 Hz, 2H), 7.37 (d, J = 8.5 Hz, 2H), 5.75 (d, J = 38.5 Hz, 2H), 4.21 (d, J = 16.1 Hz, 2H), 3.52 (d, J = 19.2 Hz, 3H), 1.36 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 154.6, 131.1, 130.1, 129.3 (d, J = 9.9 Hz), 127.6, 125.9, 106.4 (d, J = 7.1 Hz), 95.00 (d, J = 167.5 Hz), 76.0 (d, J = 24.6 Hz), 70.0 (d, J = 31.4 Hz), 23.8 (d, J = 24.2 Hz), 20.1. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -113.1 (dt, J = 37.6, 14.5 Hz), -144.8 (qd, J = 41.8, 20.7 Hz). HRMS (ESI, m/z) for C$_{14}$H$_{22}$F$_2$NO$_2$$^+$ [M+Na]$^+$: calcd for 263.1218, found 263.1218.
[Z]-1-fluoro-4-(2-fluoro-3-(2-fluoro-2-methylpropoxy)prop-1-en-1-yl)benzene (3h)

Product 3h were synthesized from the general procedure D, and was obtained as colorless oil in 73% isolated yield (17.8 mg). \( R_t = 0.3 \) (PE:EA = 50:1). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.30 – 7.23 (m, 2H), 7.03 (t, \( J = 8.8 \) Hz, 2H), 5.74 (d, \( J = 38.0 \) Hz, 1H), 4.21 (d, \( J = 15.4 \) Hz, 2H), 3.53 (d, \( J = 19.4 \) Hz, 2H), 1.40 (d, \( J = 21.4 \) Hz, 6H). \(^13\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 161.9 (dd, \( J = 247.7 \), 3.4 Hz), 155.7 (d, \( J = 267.3 \) Hz), 130.4 (t, \( J = 7.8 \) Hz), 128.8 (t, \( J = 3.1 \) Hz), 115.4 (d, \( J = 21.6 \) Hz), 108.0 (d, \( J = 6.5 \) Hz), 95.0 (d, \( J = 167.6 \) Hz), 76.1 (d, \( J = 24.5 \) Hz), 69.9 (d, \( J = 30.9 \) Hz), 23.7 (d, \( J = 24.1 \) Hz). \(^19\)F NMR (376 MHz, CDCl\(_3\)) -112.23 (dt, \( J = 37.8 \), 15.1 Hz), -113.47 – -113.55 (m), -144.82 (dh, \( J = 41.9 \), 20.9 Hz). HRMS (ESI, \( m/z \)) for C\(_{17}\)H\(_{28}\)F\(_2\)NO\(^+\) [M+NH\(_4\)]\(^+\): calcd for 262.1413, found 262.1411.

(Z)-1-fluoro-3-(2-fluoro-3-(2-fluoro-2-methylpropoxy)prop-1-en-1-yl)benzene (3i)

Product 3i were synthesized from the general procedure D, and was obtained as colorless oil in 76% isolated yield (18.5 mg). \( R_t = 0.3 \) (PE:EA = 50:1). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.30 – 7.23 (m, 2H), 6.98 – 6.94 (m, 0H), 5.77 (d, \( J = 37.7 \) Hz, 1H), 4.22 (d, \( J = 14.6 \) Hz, 2H), 3.54 (d, \( J = 19.5 \) Hz, 2H), 1.40 (d, \( J = 21.5 \) Hz, 6H). \(^13\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 162.8 (d, \( J = 244.8 \) Hz), 156.9 (d, \( J = 269.9 \) Hz), 134.7 (dd, \( J = 8.4 \), 2.5 Hz), 129.8 (d, \( J = 8.3 \) Hz), 124.5 (dd, \( J = 6.6 \), 2.9 Hz), 115.4 (dd, \( J = 22.6 \), 8.6 Hz), 114.4 (dd, \( J = 21.2 \), 2.1 Hz), 108.0 (dd, \( J = 5.8 \), 2.7 Hz), 95.0 (d, \( J = 167.9 \) Hz), 76.2 (d, \( J = 24.4 \) Hz), 69.8 (d, \( J = 31.3 \) Hz), 23.7 (d, \( J = 24.1 \) Hz). \(^19\)F NMR (376 MHz, CDCl\(_3\)) \( \delta \) -109.15 (dt, \( J = 37.7 \), 14.8 Hz), -113.06 (dd, \( J = 15.5 \), 9.8 Hz), -144.87 (dh, \( J = 41.7 \), 20.7 Hz). HRMS (ESI, \( m/z \)) for C\(_{17}\)H\(_{19}\)F\(_3\)NO\(^+\) [M+NH\(_4\)]\(^+\): calcd for 262.1413, found 262.1411.

(Z)-1-chloro-4-(2-fluoro-3-(2-fluoro-2-methylpropoxy)prop-1-en-1-yl)benzene (3j)

Product 3j were synthesized from the general procedure D, and was obtained as colorless oil in 71% isolated yield (18.4 mg). \( R_t = 0.3 \) (PE:EA = 50:1). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.46 – 7.44 (m, 2H),
Product 3k were synthesized from the general procedure D, and was obtained as colorless oil in 65% isolated yield (16.9 mg). \( R_t = 0.3 \) (PE:EA = 50:1). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.53 (s, 1H), 7.38 (dt, \( J = 7.4, 1.6 \) Hz, 1H), 7.27 – 7.21 (m, 2H), 5.74 (d, \( J = 37.8 \) Hz, 1H), 4.22 (d, \( J = 14.4 \) Hz, 2H), 3.54 (d, \( J = 19.4 \) Hz, 2H), 1.40 (d, \( J = 21.4 \) Hz, 6H). \(^1^3\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 156.97 (d, \( J = 270.0 \) Hz), 134.4, 134.3, 129.7, 128.6 (d, \( J = 8.1 \) Hz), 127.6 (d, \( J = 2.2 \) Hz), 126.8 (d, \( J = 7.2 \) Hz), 107.7 (d, \( J = 6.0 \) Hz), 95.0 (d, \( J = 167.7 \) Hz), 76.2 (d, \( J = 24.4 \) Hz), 69.7 (d, \( J = 31.4 \) Hz), 23.7 (d, \( J = 24.1 \) Hz). \(^1^9\)F NMR (376 MHz, CDCl\(_3\)) \( \delta \) -109.01 (dt, \( J = 37.8, 14.2 \) Hz), -144.81 (dd, \( J = 41.8, 21.1 \) Hz). HRMS (ESI, \( m/z \)) for C\(_{13}\)H\(_9\)Cl\(_2\)NO\(^{+}\) [M+NH\(_4\)]\(^{+}\): calcd for 278.1117, found 278.1114.

Product 3l were synthesized from the general procedure D, and was obtained as yellow oil in 42% isolated yield (12.8 mg). \( R_t = 0.3 \) (PE:EA = 50:1). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.47 – 7.37 (m, 4H), 5.73 (d, \( J = 38.0 \) Hz, 1H), 4.21 (d, \( J = 14.8 \) Hz, 2H), 3.54 (d, \( J = 19.5 \) Hz, 5H), 1.40 (d, \( J = 21.5 \) Hz, 6H). \(^1^3\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 156.57 (d, \( J = 269.3 \) Hz), 131.62, 131.57, 130.25 (d, \( J = 7.4 \) Hz), 121.35 (d, \( J = 3.4 \) Hz), 107.93 (d, \( J = 6.2 \) Hz), 95.00 (d, \( J = 167.6 \) Hz), 76.21 (d, \( J = 24.4 \) Hz), 69.86 (d, \( J = 31.1 \) Hz), 23.72 (d, \( J = 24.3 \) Hz). \(^1^9\)F NMR (376 MHz, CDCl\(_3\)) \( \delta \) -109.87 (dt, \( J = 38.0, 14.8 \) Hz), -144.80 (dd, \( J = 41.9, 20.7 \) Hz). HRMS (ESI, \( m/z \)) for C\(_{21}\)H\(_{23}\)BrF\(_2\)ONa\(^{+}\) [M+Na\(^{+}\)]: calcd for 431.0792, found 431.0793.

Product 3m were synthesized from the general procedure D, and was obtained as colorless oil in 66% isolated yield (16.7 mg). \( R_t = 0.3 \) (PE:EA = 50:1). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.15 (s, 2H), 6.91 (s, 1H), 5.70 (d, \( J = 38.6 \) Hz, 1H), 4.20 (d, \( J = 15.8 \) Hz, 2H), 3.52 (d, \( J = 19.2 \) Hz, 2H), 2.31 (s, 6H),
1.39 (d, J = 21.5 Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 155.6 (d, J = 268.0 Hz), 137.9, 132.4 (d, J = 3.0 Hz), 129.3, 126.6 (d, J = 7.2 Hz), 109.4 (d, J = 6.3 Hz), 95.0 (d, J = 167.5 Hz), 75.9 (d, J = 24.6 Hz), 70.1 (d, J = 30.9 Hz), 23.8 (d, J = 24.2 Hz), 21.3. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -111.09 (dt, J = 38.0, 15.9 Hz), -144.91 (dh, J = 42.5, 20.8 Hz). HRMS (ESI, m/z) for C$_{15}$H$_{25}$F$_{2}$NO$_{2}^+$ [M+NH$_4$]$^+$: calcd for 272.1820, found 272.1819.

(Z)-1-(2-fluoro-3-(2-fluoro-2-methylpropoxy)prop-1-en-1-yl)-3,5-dimethoxybenzene (3n)

Product 3n were synthesized from the general procedure D, and was obtained as colorless oil in 33% isolated yield (9.4 mg). R$_f$ = 0.2 (PE:EA = 20:1). $^1$H NMR (400 MHz, CDCl$_3$) δ 6.68 (d, J = 2.3 Hz, 2H), 6.38 (t, J = 2.3 Hz, 1H), 5.70 (d, J = 37.8 Hz, 1H), 4.20 (d, J = 15.3 Hz, 2H), 3.78 (s, 6H), 3.52 (d, J = 19.4 Hz, 2H), 1.38 (d, J = 21.4 Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 160.7, 156.3 (d, J = 269.0 Hz), 134.3 (d, J = 2.6 Hz), 109.2 (d, J = 5.7 Hz), 106.8 (d, J = 7.6 Hz), 100.1, 95.0 (d, J = 167.6 Hz), 76.0 (d, J = 24.4 Hz), 70.0 (d, J = 30.9 Hz), 55.3, 23.7 (d, J = 24.3 Hz). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -109.72 (dt, J = 37.7, 15.2 Hz), -144.82 (d, J = 41.1, 21.0, 20.4 Hz). HRMS (ESI, m/z) for C$_{15}$H$_{20}$F$_{2}$NaO$_3^+$ [M+Na]$^+$: calcd for 309.1273, found 309.1274.

(Z)-4-(2-fluoro-3-(2-fluoro-2-methylpropoxy)prop-1-en-1-yl)phenyl acetate (3o)

Product 3o were synthesized from the general procedure, and was obtained as colorless oil in 75% isolated yield (21.3 mg). R$_f$ = 0.2 (PE:EA = 50:1). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.53 (d, J = 8.7 Hz, 2H), 7.07 (d, J = 8.7 Hz, 2H), 5.76 (d, J = 38.1 Hz, 1H), 4.21 (d, J = 15.4 Hz, 2H), 3.55 (d, J = 19.4 Hz, 2H), 2.30 (s, 3H), 1.39 (d, J = 21.4 Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 169.4, 156.0 (d, J = 268.5 Hz), 149.8, 130.4, 129.8 (d, J = 7.6 Hz), 121.6, 108.2 (d, J = 6.3 Hz), 95.0 (d, J = 167.7 Hz), 76.0 (d, J = 24.5 Hz), 69.9 (d, J = 31.0 Hz), 23.7 (d, J = 24.3 Hz), 21.1. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -111.35 (dt, J = 38.1, 15.7 Hz), -144.86 (d, J = 41.9, 20.7 Hz). HRMS (ESI, m/z) for C$_{15}$H$_{22}$F$_{2}$NO$_3^+$ [M+NH$_4$]$^+$: calcd for 302.1562, found 302.1565.

ethyl (Z)-4-(2-fluoro-3-(2-fluoro-2-methylpropoxy)prop-1-en-1-yl)benzoate (3p)

Product 3p were synthesized from the general procedure D, and was obtained as colorless oil in 65% isolated yield (19.4 mg). R$_f$ = 0.2 (PE:EA = 50:1). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.01 (d, J = 8.5 Hz, 2H), 7.57 (d, J = 8.5 Hz, 2H), 5.84 (d, J = 38.1 Hz, 1H), 4.38 (q, J = 7.1 Hz, 2H), 4.24 (d, J = 14.0 Hz, 2H), 3.86 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 155.6 (d, J = 268.0 Hz), 137.9, 132.4 (d, J = 3.0 Hz), 129.3, 126.6 (d, J = 7.2 Hz), 109.4 (d, J = 6.3 Hz), 95.0 (d, J = 167.5 Hz), 75.9 (d, J = 24.6 Hz), 70.1 (d, J = 30.9 Hz), 23.8 (d, J = 24.2 Hz), 21.3. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -111.09 (dt, J = 38.0, 15.9 Hz), -144.91 (dh, J = 42.5, 20.8 Hz). HRMS (ESI, m/z) for C$_{15}$H$_{25}$F$_{2}$NO$_2^+$ [M+NH$_4$]$^+$: calcd for 272.1820, found 272.1819.
Hz, 2H), 3.55 (d, J = 19.5 Hz, 2H), 1.43 – 1.38 (m, 9H). 13C NMR (101 MHz, CDCl3) δ 166.3, 157.6 (d, J = 271.5 Hz), 137.1, 129.7, 129.2, 128.5 (d, J = 7.4 Hz), 108.1 (d, J = 5.8 Hz), 95.0 (d, J = 167.9 Hz), 76.3 (d, J = 24.4 Hz), 69.9, 61.0, 23.7 (d, J = 24.2 Hz), 14.3. 19F NMR (376 MHz, CDCl3) δ -107.68 (dt, J = 38.4, 14.2 Hz), -144.78 (dh, J = 41.8, 20.9 Hz). HRMS (ESI, m/z) for C17H18F2NaO+ [M+Na]+: calcd for 299.1218, found 299.1216.

(Z)-2-(2-fluoro-3-(2-fluoro-2-methylpropoxy)prop-1-en-1-yl)naphthalene (3q)

Product 3q were synthesized from the general procedure D, and was obtained as colorless oil in 57% isolated yield (15.7 mg). Rf = 0.3 (PE:EA = 50:1). 1H NMR (400 MHz, CDCl3) δ 7.95 (s, 1H), 7.83 – 7.79 (m, 4H), 7.70 – 7.68 (m, 2H), 7.48 – 7.45 (m, 2H), 5.94 (d, J = 38.4 Hz, 2H), 4.27 (d, J = 15.3 Hz, 4H), 3.57 (d, J = 19.3 Hz, 4H), 1.42 (d, J = 21.5 Hz, 13H). 13C NMR (101 MHz, CDCl3) δ 156.27 (d, J = 268.7 Hz), 133.35, 132.60, 130.20 (d, J = 2.6 Hz), 128.09, 128.04, 128.00, 127.93, 127.55, 126.53 (d, J = 7.5 Hz), 126.17 (d, J = 6.4 Hz), 109.26 (d, J = 6.2 Hz), 95.04 (d, J = 167.7 Hz), 76.10 (d, J = 24.3 Hz), 70.12 (d, J = 31.0 Hz), 23.77 (d, J = 24.3 Hz). HRMS (ESI, m/z) for C17H22F2NO+ [M+NH4]+: calcd for 294.1664, found 294.1664.

(Z)-2-(2-fluoro-3-(2-fluoro-2-methylpropoxy)prop-1-en-1-yl)benzofuran (3r)

Product 3r were synthesized from the general procedure D, and was obtained as colorless oil in 58% isolated yield (15.4 mg). Rf = 0.3 (PE:EA = 50:1). 1H NMR (400 MHz, CDCl3) δ 7.68 (s, 1H), 7.43 (d, J = 7.8 Hz, 1H), 7.40 – 7.37 (m, 1H), 7.21 (t, J = 7.9 Hz, 1H), 5.73 (d, J = 37.8 Hz, 1H), 4.22 (d, J = 14.4 Hz, 2H), 3.54 (d, J = 19.4 Hz, 2H), 1.40 (d, J = 21.5 Hz, 6H). 13C NMR (101 MHz, CDCl3) δ 157.0 (d, J = 270.3 Hz), 135.4 – 133.6 (m), 131.5 (d, J = 8.0 Hz), 130.5 (d, J = 2.1 Hz), 130.0, 127.3 (d, J = 7.3 Hz), 124.1, 123.5, 122.5, 107.6 (d, J = 6.0 Hz), 95.0 (d, J = 167.7 Hz), 76.2 (d, J = 24.3 Hz), 69.7 (d, J = 31.2 Hz), 23.7 (d, J = 24.2 Hz). 19F NMR (376 MHz, CDCl3) δ -110.62 (dt, J = 38.7, 15.6 Hz), -144.81 (dh, J = 42.3, 21.3 Hz). HRMS (ESI, m/z) for C15H17F2NO2+ [M+NH4]+: calcd for 284.1457, found 284.1458.
(Z)-1-chloro-4-(2-fluoro-3-((2-fluoro-2-methylnonyl)oxy)prop-1-en-1-yl)benzene (3s)

Product 3s were synthesized from the general procedure D, and was obtained as colorless oil in 74% isolated yield (25.5 mg). Rr = 0.3 (PE:EA = 50:1). 1H NMR (400 MHz, CDCl₃) δ 7.45 – 7.43 (m, 2H), 7.31 – 7.29 (m, 2H), 5.73 (d, J = 37.9 Hz, 1H), 4.19 (d, J = 15.0 Hz, 2H), 3.54 (d, J = 19.5 Hz, 2H), 1.71 – 1.60 (m, 2H), 1.37 (s, 3H), 1.32 – 1.26 (m, 10H), 0.91 – 0.85 (m, 3H). 13C NMR (101 MHz, CDCl₃) δ 156.5 (d, J = 269.1 Hz), 133.1 (d, J = 3.4 Hz), 131.1 (d, J = 2.8 Hz), 129.9 (d, J = 7.6 Hz), 128.6, 107.9 (d, J = 6.2 Hz), 96.9 (d, J = 169.5 Hz), 75.0 (d, J = 25.0 Hz), 69.8 (d, J = 31.0 Hz), 53.9, 36.7 (d, J = 22.5 Hz), 31.7, 29.9, 29.2, 23.3 (d, J = 5.8 Hz), 22.6, 21.5 (d, J = 24.4 Hz), 14.1. 19F NMR (376 MHz, CDCl₃) δ -110.12 (dt, J = 38.7, 15.1 Hz), -150.52 (dq, J = 41.2, 20.3 Hz). HRMS (ESI, m/z) for C₁₉H₁₆ClF₂NO₂⁺ [M+NH₄]⁺: calcd for 362.2056, found 362.2060.

(Z)-1-chloro-4-(2-fluoro-3-(2-fluoro-2-methyl-4-phenylbutoxy)prop-1-en-1-yl)benzene (3t)

Product 3t were synthesized from the general procedure D, and was obtained as colorless oil in 68% isolated yield (23.8 mg). Rr = 0.3 (PE:EA = 50:1). 1H NMR (400 MHz, CDCl₃) δ 7.45 – 7.43 (m, 2H), 7.32 – 7.27 (m, 4H), 7.21 – 7.17 (m, 3H), 5.74 (d, J = 37.9 Hz, 1H), 4.19 (d, J = 15.3 Hz, 2H), 3.59 (d, J = 18.4 Hz, 2H), 2.75 – 2.69 (m, 2H), 2.08 – 1.91 (m, 2H), 1.43 (d, J = 21.9 Hz, 3H). 13C NMR (101 MHz, CDCl₃) δ 156.35 (d, J = 269.0 Hz), 141.69, 133.21 (d, J = 3.4 Hz), 131.07 (d, J = 2.7 Hz), 129.94, 128.68, 128.39, 128.38 (d, J = 15.5 Hz), 125.96, 108.10 (d, J = 6.3 Hz), 96.35 (d, J = 170.4 Hz), 74.96 (d, J = 25.7 Hz), 69.91 (d, J = 31.1 Hz), 38.58 (d, J = 22.5 Hz), 29.58 (d, J = 5.8 Hz), 21.69 (d, J = 24.3 Hz). 19F NMR (376 MHz, CDCl₃) δ -110.11 (dt, J = 37.9, 14.7 Hz), -151.68 – -152.06 (m). HRMS (ESI, m/z) for C₂₀H₂₅ClF₂NO⁺ [M+H⁺]: calcd for 368.1587, found 368.1586.

(Z)-1-chloro-4-(2-fluoro-3-(2-fluoro-2-methyl-3-phenoxypropoxy)prop-1-en-1-yl)benzene (3u)

Product 3u were synthesized from the general procedure D, and was obtained as colorless oil in 63% isolated yield (22.1 mg). Rr = 0.3 (PE:EA = 50:1). 1H NMR (400 MHz, CDCl₃) δ 7.40 – 7.38 (m, 2H), 7.31 – 7.27 (m, 4H), 6.99 – 6.96 (m, 1H), 6.93 – 6.91 (m, 2H), 5.70 (d, J = 37.9 Hz, 1H), 5.20 (dd, J = 14.9, 1.7 Hz, 2H), 4.15 – 4.01 (m, 2H), 3.83 – 3.71 (m, 2H), 1.51 (d, J = 22.1 Hz, 3H). 13C NMR (101 MHz, CDCl₃) δ 158.44, 156.17 (d, J = 268.9 Hz), 133.19 (d, J = 3.4 Hz), 131.02 (d, J
= 2.8 Hz), 129.97 (d, J = 7.6 Hz), 129.49, 128.64, 121.24, 114.61, 108.07 (d, J = 6.2 Hz), 95.06 (d, J = 172.4 Hz), 72.43 (d, J = 25.4 Hz), 69.95 (d, J = 31.3 Hz), 69.56 (d, J = 28.7 Hz), 19.69 (d, J = 23.0 Hz). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -109.77 (dt, 37.6, 15.0 Hz), -150.57 (dh, J = 41.5, 20.5 Hz).

HRMS (ESI, m/z) for C$_{19}$H$_{23}$ClF$_2$NO$_2$ $^+$ [M+H]$^+$: calcd for 370.1380, found 370.1388.

$^{(Z)}$-1-chloro-4-(3-(3-chloro-2-fluoro-2-methylpropoxy)-2-fluoroprop-1-en-1-yl)benzene (3v)

Product 3v were synthesized from the general procedure D, and was obtained as colorless oil in 36% isolated yield (12.3 mg). $R_f$ = 0.3 (PE:EA = 50:1). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.46 – 7.44 (m, 2H), 7.32 – 7.30 (m, 2H), 5.74 (d, J = 37.9 Hz, 1H), 4.26 – 4.14 (m, 2H), 3.77 – 3.63 (m, 4H), 1.47 (d, J = 21.7 Hz), 1.35 – 1.24 (m, 6H), 0.92 – 0.86 (m, 6H).

$^1$C NMR (101 MHz, CDCl$_3$) $\delta$ 155.9 (d, J = 268.9 Hz), 133.1 (d, J = 3.4 Hz), 130.9 (d, J = 2.7 Hz), 128.7, 108.3 (d, J = 6.3 Hz), 94.9 (d, J = 175.2 Hz), 72.2 (d, J = 25.5 Hz), 70.0 (d, J = 31.0 Hz), 46.6 (d, J = 30.1 Hz), 20.4 (d, J = 22.9 Hz).

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -110.24 – -110.43 (m), -155.00 – -155.34 (m).

HRMS (ESI, m/z) for C$_{13}$H$_{18}$ClF$_2$NO$_2$ $^+$ [M+NH$_4$]$^+$: calcd for 312.0728, found 312.0733.

$^{(Z)}$-1-chloro-4-(3-(2-ethyl-2-fluoroheptyloxy)-2-fluoroprop-1-en-1-yl)benzene (3w)

Product 3w were synthesized from the general procedure D, and was obtained as colorless oil in 68% isolated yield (21.9 mg). $R_f$ = 0.3 (PE:EA = 50:1). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.44 – 7.42 (m, 2H), 7.31 – 7.28 (m, 2H), 5.72 (d, J = 38.0 Hz, 1H), 4.17 (d, J = 15.1 Hz, 2H), 3.55 (d, J = 19.4 Hz, 2H), 1.74 – 1.60 (m, 4H), 1.35 – 1.24 (m, 6H), 0.92 – 0.86 (m, 6H). $^1$C NMR (101 MHz, CDCl$_3$) $\delta$ 156.5 (d, J = 269.1 Hz), 133.1 (d, J = 3.4 Hz), 131.1 (d, J = 2.7 Hz), 130.0 (d, J = 7.7 Hz), 128.7, 107.9 (d, J = 6.2 Hz), 98.8 (d, J = 171.1 Hz), 72.9 (d, J = 25.8 Hz), 69.8 (d, J = 30.9 Hz), 33.8 (d, J = 22.4 Hz), 32.2, 27.1 (d, J = 23.4 Hz), 22.7 (d, J = 6.0 Hz), 22.5, 14.0, 7.5 (d, J = 7.2 Hz).

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$-110.08 (dt, J = 37.7, 15.2 Hz), -157.97 (hept, J = 19.0 Hz).

HRMS (ESI, m/z) for C$_{18}$H$_{29}$ClF$_2$NO$_2$ $^+$ [M+NH$_4$]$^+$: calcd for 348.1900, found 348.1896.

$^{(Z)}$-1-chloro-4-(2-fluoro-3-((2-fluoro-2-phenethylpentyl)oxy)prop-1-en-1-yl)benzene (3x)

Product 3x were synthesized from the general procedure D, and was obtained as colorless oil in 35%
isolated yield (13.2 mg). Rr = 0.3 (PE:EA = 50:1). 1H NMR (400 MHz, CDCl3) δ 7.45 – 7.43 (m, 2H), 7.31 – 7.26 (m, 4H), 7.21 – 7.17 (m, 3H), 5.73 (d, J = 37.9 Hz, 1H), 4.18 (d, J = 15.4 Hz, 2H), 3.61 (dd, J = 18.4, 0.9 Hz, 2H), 2.71 – 2.66 (m, 2H), 2.04 – 1.95 (m, 2H), 1.77 – 1.68 (m, 2H), 1.44 – 1.38 (m, 2H), 0.96 (t, J = 7.3 Hz, 3H). 13C NMR (101 MHz, CDCl3) δ 156.3 (d, J = 269.1 Hz), 141.8, 133.2, 131.1 (d, J = 2.6 Hz), 130.0 (d, J = 7.6 Hz), 128.7, 128.4 (d, J = 14.8 Hz), 125.9, 108.1 (d, J = 6.4 Hz), 98.0 (d, J = 171.8 Hz), 73.0 (d, J = 26.7 Hz), 69.9 (d, J = 30.9 Hz), 36.9 (d, J = 22.1 Hz), 36.5 (d, J = 22.6 Hz), 29.4 (d, J = 6.4 Hz), 16.5 (d, J = 6.3 Hz), 14.5. 19F NMR (376 MHz, CDCl3) -110.04 (dt, J = 38.1, 15.9 Hz), -157.01 (hept, J = 19.2 Hz). HRMS (ESI, m/z) for C22H29ClF2NO+ [M+NH4]+: calcd for 396.1900, found 396.1904.

(Z)-(2-(((3-(4-chlorophenyl)-2-fluoroallyloxy)methyl)-2-fluoropropane-1,3-diyl)dibenzene (3y)

Product 3y were synthesized from the general procedure D, and was obtained as colorless oil in 70% isolated yield (28.8 mg). Rr = 0.3 (PE:EA = 50:1). 1H NMR (400 MHz, CDCl3) δ 7.45 – 7.43 (m, 2H), 7.33 – 7.31 (m, 2H), 7.28 – 7.24 (m, 10H), 5.67 (d, J = 37.7 Hz, 1H), 4.07 (d, J = 16.6 Hz, 2H), 3.25 (d, J = 11.8 Hz, 2H), 3.11 – 2.99 (m, 4H). 13C NMR (101 MHz, CDCl3) δ 156.1 (d, J = 269.0 Hz), 135.8, 133.3 (d, J = 3.4 Hz), 131.0 (d, J = 2.6 Hz), 130.6, 130.0 (d, J = 7.6 Hz), 128.7, 128.2, 126.7, 108.5 (d, J = 6.5 Hz), 96.7 (d, J = 176.6 Hz), 70.7 (d, J = 31.3 Hz), 69.8 (d, J = 30.5 Hz), 41.9 (d, J = 21.0 Hz). 19F NMR (376 MHz, CDCl3) δ -109.33 (dt, 33.8, 18.8 Hz), -160.34 – -160.72 (m). HRMS (ESI, m/z) for C25H27ClF2NO+ [M+NH4]+: calcd for 430.1743, found 430.1749.

(Z)-1-chloro-4-(2-fluoro-3-((1-fluoro-4,4-dimethylcyclohexyl)methoxy)prop-1-en-1-yl)benzene (3z)

Product 3z were synthesized from the general procedure D, and was obtained as colorless oil in 62% isolated yields (20.4 mg). Rr = 0.3 (PE:EA = 50:1). 1H NMR (400 MHz, CDCl3) δ 7.46 – 7.44 (m, 2H), 7.31 – 7.29 (m, 2H), 5.74 (d, J = 38.0 Hz, 1H), 4.20 (d, J = 14.8 Hz, 2H), 3.55 (d, J = 19.9 Hz, 2H), 1.80 (dt, J = 6.2, 3.0 Hz, 2H), 1.69 – 1.60 (m, 1H), 1.56 – 1.50 (m, 4H), 1.27 – 1.22 (m, 4H), 0.93 (d, J = 26.4 Hz, 6H). 13C NMR (101 MHz, CDCl3) δ 156.49 (d, J = 269.0 Hz), 132.12 (d, J = 200.3 Hz), 129.96 (d, J = 7.6 Hz), 128.66, 107.87 (d, J = 6.1 Hz), 95.30 (d, J = 172.2 Hz), 75.63 (d, J = 24.5 Hz), 69.89 (d, J = 31.3 Hz), 34.02 (d, J = 2.6 Hz), 31.24, 29.56, 28.22 (d, J = 22.2 Hz), 24.63. 19F NMR (376 MHz, CDCl3) δ -110.11 – -110.32 (m), -162.07 (w). HRMS (ESI, m/z) for
C_{18}H_{27}ClF_{2}NO^{+} [M+NH_{4}]^{+}: calcd for 346.1743, found 346.1748.

(Z)-1-(1-((3-(4-chlorophenyl)-2-fluorallyloxy)-2-florobutan-2-yl)-3,5-bis(trifluoromethyl)benzene (3aa)

Product 3v were synthesized from the general procedure D, and was obtained as colorless oil in 73% isolated yield (22.6 mg). R_{f} = 0.3 (PE:EA = 50:1). \textsuperscript{1}H NMR (400 MHz, CDCl_{3}) δ 7.84 (s, 3H), 7.40 (d, J = 8.6 Hz, 2H), 7.30 (d, J = 8.7 Hz, 2H), 5.65 (d, J = 37.6 Hz, 1H), 4.15 (d, J = 15.4 Hz, 2H), 3.92 – 3.76 (m, 2H), 2.23 – 2.17 (m, 2H), 2.04 – 1.92 (m, 2H), 0.86 (t, J = 7.4 Hz, 7H). \textsuperscript{13}C NMR (101 MHz, CDCl_{3}) δ 155.7 (d, J = 268.8 Hz), 143.4 (d, J = 23.1 Hz), 133.4 (d, J = 3.4 Hz), 131.6 (q, J = 33.2 Hz), 130.8 (d, J = 2.4 Hz), 130.0 (d, J = 7.7 Hz), 128.7, 125.3 (d, J = 9.6 Hz), 121.9, 121.7, 108.5 (d, J = 6.2 Hz), 98.4 (d, J = 179.8 Hz), 74.6 (d, J = 27.6 Hz), 70.0 (d, J = 30.8 Hz), 29.6 (d, J = 22.8 Hz), 6.9 (d, J = 4.6 Hz). \textsuperscript{19}F NMR (376 MHz, CDCl_{3}) δ -62.69, -110.29 (dt, J = 37.4, 15.4 Hz), -166.16 – -166.45 (m). HRMS (EI, m/z) for C_{21}H_{17}ClF_{8}O^{+}[M]^{+}: calcd for 472.0840, found 472.0839.

(Z)-1-chloro-4-(2-fluoro-3-(3-fluoro-4-methoxyphenyl)butoxy)prop-1-en-1-yl)benzene (3ab)

Product 3ab were synthesized from the general procedure D, and was obtained as colorless oil in 51% isolated yields (18.6 mg). R_{f} = 0.3 (PE:EA = 50:1). \textsuperscript{1}H NMR (400 MHz, CDCl_{3}) δ 7.46 – 7.44 (m, 2H), 7.32 – 7.30 (m, 2H), 7.17 – 7.15 (m, 2H), 6.83 – 6.81 (m, 2H), 5.74 (d, J = 37.8 Hz, 1H), 4.19 (dd, J = 15.7, 2.5 Hz, 2H), 3.78 (s, 3H), 3.53 – 3.41 (m, 2H), 3.03 – 2.90 (m, 2H), 1.31 (d, J = 21.9 Hz, 3H). \textsuperscript{13}C NMR (101 MHz, CDCl_{3}) δ 158.4, 156.3 (d, J = 269.0 Hz), 133.2, 131.4, 131.1 (d, J = 2.6 Hz), 130.0 (d, J = 7.6 Hz), 128.7, 128.0 (d, J = 5.2 Hz), 113.6, 108.2 (d, J = 6.5 Hz), 96.4 (d, J = 172.0 Hz), 74.1 (d, J = 25.8 Hz), 69.9 (d, J = 30.8 Hz), 55.2, 41.8 (d, J = 22.8 Hz), 21.8 (d, J = 23.7 Hz). \textsuperscript{19}F NMR (376 MHz, CDCl_{3}) δ -109.76 (dt, J = 37.6, 15.0 Hz), -150.59 (dh, J = 41.4, 20.6 Hz). HRMS (ESI, m/z) for C_{20}H_{23}ClIF_{2}NO_{2}^{+}[M+NH_{4}]^{+}: calcd for 384.1536, found 384.1533.

4. C–N/C–F Bond Metathesis Reaction

Table S1. Optimization of the reaction conditions for ring-opening C–N/C–F cross metathesis.
General Procedure E: C–N/C–F Cross Metathesis Reaction

General procedure for the ring-opening C–N/C–F cross metathesis of azetidine with gem-DFCP, catalyzed by dimeric rhodium(I) chloride carbonyl ([Rh(CO)\(_2\)Cl\(_2\)]\(_2\)) to prepare compound 5:

In a nitrogen filled glove box, to a 20 mL screw-cap vial equipped with a stirring bar was charged with [Rh(CO)\(_2\)Cl\(_2\)]\(_2\) (0.38 mg, 0.001 mmol, 0.5 mol%), IPr (0.77 mg, 0.002 mmol, 1 mol%) and DCM (2 mL). Generally, several such type of reactions were carried out parallelly, thus the catalyst solution can be prepared in one vial together. After the mixture stirred for 5 min, the brown homogeneous
catalyst solution was transferred into another 8 mL vial with a stirring bar which containing gem-difluorinated cyclopropane (0.3 mmol, 1.5 equiv), 1-benzhydryl-3-methyleneazetidine (0.2 mmol, 1.0 equiv) and AgBF$_4$ (1.9 mg, 0.01 mmol, 5 mol%). The vial was sealed with screw-cap and removed from glove box to be stirred at 80 °C for 12 hours. The product was purified by column chromatography on silica gel to afford the corresponding product.

Figure S3. Allyl amines synthesized in this work.

(Z)-N-benzhydryl-2-fluoro-N-(2-(fluoromethyl)allyl)-3-phenylprop-2-en-1-amine (5a)
Product 5a were synthesized from the general procedure E, and was obtained as colorless oil in 93% isolated yields (72.3 mg). \( R_f = 0.3 \) (PE:DCM = 10:1). \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.49 - 7.44 (m, 2H), 7.37 - 7.39 (m, 4H), 7.29 - 7.33 (m, 6H), 7.19 - 7.26 (m, 3H), 5.50 (d, \( J = 39.2 \) Hz, 1H), 5.32 (s, 2H), 5.05 (s, 1H), 4.97 (d, \( J = 47.2 \) Hz, 2H), 3.32 (d, \( J = 17.5 \) Hz, 2H), 3.26 (s, 2H). \( ^{13}C \) NMR (101 MHz, CDCl\(_3\)) \( \delta \) 157.75 (d, \( J = 271.2 \) Hz), 142.32 (d, \( J = 14.2 \) Hz), 140.80, 133.11 (d, \( J = 2.3 \) Hz), 128.65, 128.55, 128.48, 128.44, 128.37, 127.21, 115.39 (d, \( J = 10.4 \) Hz), 109.41 (d, \( J = 7.0 \) Hz), 83.94 (d, \( J = 167.7 \) Hz), 69.00, 52.55 (d, \( J = 2.7 \) Hz), 50.80 (d, \( J = 26.0 \) Hz). \( ^{19}F \) NMR (376 MHz, CDCl\(_3\)) \( \delta \) -104.20 (dt, \( J = 37.3, 17.5 \) Hz), -218.95 (t, \( J = 47.2 \) Hz). HRMS (ESI, m/z) for C\(_{26}\)H\(_{26}\)F\(_2\)N\(_2\)\([M+H]^+\): calcd for 390.2028, found 390.2024.

\((Z)-N\)-benzhydryl-2-fluoro-N-(2-(fluoromethyl)allyl)-3-(p-tolyl)prop-2-en-1-amine (5b)

Product 5b were synthesized from the general procedure E, and was obtained as colorless oil in 90% isolated yields (72.6 mg). \( R_f = 0.3 \) (PE:DCM = 10:1). \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.37 (t, \( J = 6.7 \) Hz, 6H), 7.31 (t, \( J = 7.5 \) Hz, 4H), 7.23 (t, \( J = 7.2 \) Hz, 2H), 7.13 (d, \( J = 8.0 \) Hz, 2H), 5.45 (d, \( J = 39.4 \) Hz, 1H), 5.31 (s, 2H), 5.04 (s, 1H), 4.96 (d, \( J = 47.2 \) Hz, 2H), 3.30 (d, \( J = 17.8 \) Hz, 2H), 3.25 (s, 2H), 2.32 (s, 3H). \( ^{13}C \) NMR (101 MHz, CDCl\(_3\)) \( \delta \) 157.1 (d, \( J = 270.1 \) Hz), 142.4 (d, \( J = 14.2 \) Hz), 140.9, 137.0 (d, \( J = 2.3 \) Hz), 130.3 (d, \( J = 2.4 \) Hz), 129.1, 128.6, 128.5, 128.4, 127.2, 115.3 (d, \( J = 10.5 \) Hz), 109.4 (d, \( J = 7.1 \) Hz), 83.9 (d, \( J = 167.9 \) Hz), 69.0, 52.5 (d, \( J = 2.7 \) Hz), 50.8 (d, \( J = 25.8 \) Hz), 21.2. \( ^{19}F \) NMR (376 MHz, CDCl\(_3\)) \( \delta \) -104.20 (dt, \( J = 37.3, 17.5 \) Hz), -218.95 (t, \( J = 47.2 \) Hz). HRMS (ESI, m/z) for C\(_{27}\)H\(_{28}\)F\(_2\)N\(_2\)\([M+H]^+\): calcd for 404.2184, found 404.2179.

\((Z)-N\)-benzhydryl-2-fluoro-N-(2-(fluoromethyl)allyl)-3-(4-methoxyphenyl)prop-2-en-1-amine (5c)

Product 5c were synthesized from the general procedure E, and was obtained as colorless oil in 85% isolated yields (71.3 mg). \( R_f = 0.3 \) (PE:DCM = 4:1). \( ^1H \) NMR (400 MHz, ) \( \delta \) 7.46 - 7.34 (m, 6H), 7.35 - 7.29 (m, 4H), 7.27 - 7.21 (m, 2H), 6.86 (d, \( J = 8.5 \) Hz, 2H), 5.43 (d, \( J = 39.4 \) Hz, 1H), 5.31 (s, 2H), 5.04 (s, 1H), 4.97 (d, \( J = 47.2 \) Hz, 2H), 3.80 (s, 3H), 3.30 (d, \( J = 17.9 \) Hz, 2H), 3.25 (s, 2H). \( ^{13}C \) NMR (101 MHz, ) \( \delta \) 158.6 (d, \( J = 2.5 \) Hz), 156.3 (d, \( J = 268.6 \) Hz), 142.4 (d, \( J = 13.9 \) Hz), 140.9, 129.8 (d, \( J = 7.4 \) Hz), 128.7, 128.4, 127.2, 125.9, 115.3 (d, \( J = 10.5 \) Hz), 113.9, 109.0 (d, \( J = 26019.0 \) Hz).
7.4 Hz), 84.0 (d, J = 167.8 Hz), 69.0, 55.2, 52.5 (d, J = 2.4 Hz), 50.8 (d, J = 25.9 Hz). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -107.06 (dt, J = 36.5, 17.4 Hz), -219.05 (t, J = 47.6 Hz). HRMS (ESI, m/z) for C$_{27}$H$_{28}$F$_2$NO$^+$ [M+H]$^+$: calc for C$_{27}$H$_{28}$F$_2$NO$^+$ 420.2133, found 420.2126.

(Z)-N-benzhydryl-2-fluoro-N-(2-(fluoromethyl)allyl)-3-(4-phenoxyphenyl)prop-2-en-1-amine (5d)

Product 5d were synthesized from the general procedure E, and was obtained as colorless oil in 85\% isolated yields (81.8 mg). $R_f = 0.2$ (PE:DCM = 10:1). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.49 – 7.35 (m, 6H), 7.38 – 7.20 (m, 8H), 7.10 (t, J = 7.4 Hz, 1H), 7.06 – 6.91 (m, 4H), 5.48 (d, J = 39.1 Hz, 1H), 5.32 (s, 2H), 5.05 (s, 1H), 4.97 (d, J = 47.2 Hz, 2H), 3.32 (d, J = 17.5 Hz, 2H), 3.26 (s, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 157.1 (d, J = 270.0 Hz), 157.1, 156.3, 142.4 (d, J = 14.2 Hz), 140.8, 130.0, 129.9, 129.8, 128.7, 128.4, 127.2, 123.4, 119.0, 118.8, 115.4 (d, J = 10.5 Hz), 108.7 (d, J = 7.2 Hz), 84.0 (d, J = 167.9 Hz), 69.1, 52.6, 50.9 (d, J = 25.9 Hz). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -105.65 (dt, J = 37.3, 17.5 Hz), -218.75 (t, J = 47.5 Hz). HRMS (ESI, m/z) for C$_{32}$H$_{30}$F$_2$NO$^+$ [M+H]$^+$: calc for 482.2290, found 482.2281.

(Z)-N-benzhydryl-3-(4-cyclopropylphenyl)-2-fluoro-N-(2-(fluoromethyl)allyl)prop-2-en-1-amine (5e)

Product 5e were synthesized from the general procedure E, and was obtained as colorless oil in 71\% isolated yields (61.0 mg). $R_f = 0.3$ (PE:DCM = 10:1). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.44 – 7.26 (m, 10H), 7.27 – 7.20 (m, 2H), 7.02 (d, J = 8.2 Hz, 2H), 5.44 (d, J = 39.4 Hz, 1H), 5.31 (s, 2H), 5.04 (s, 1H), 4.96 (d, J = 47.2 Hz, 2H), 3.30 (d, J = 17.8 Hz, 2H), 3.25 (s, 2H), 1.93 – 1.81 (m, 1H), 1.05 – 0.90 (m, 2H), 0.69 (d, J = 6.8 Hz, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 157.1 (d, J = 270.3 Hz), 143.2, 142.4 (d, J = 14.1 Hz), 140.9, 130.3, 128.7, 128.5 (d, J = 7.2 Hz), 128.4, 127.2, 125.7, 115.3 (d, J = 10.5 Hz), 109.3 (d, J = 7.2 Hz), 84.0 (d, J = 167.8 Hz), 69.0, 52.5 (d, J = 2.4 Hz), 50.8 (d, J = 26.0 Hz), 15.2, 9.3. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -105.65 (dt, J = 37.2, 17.5 Hz), -219.06 (t, J = 47.6 Hz). HRMS (ESI, m/z) for C$_{29}$H$_{30}$F$_2$N$^+$ [M+H]$^+$ : calc for 430.2341, found 432.2336.

(Z)-3-((1,1'-biphenyl)-4-yl)-N-benzhydryl-2-fluoro-N-(2-(fluoromethyl)allyl)prop-2-en-1-amine (5f)

Product 5f were synthesized from the general procedure E, and was obtained as colorless oil in 72\% isolated yields (67.0 mg). $R_f = 0.3$ (PE:DCM = 10:1). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.65
- 7.52 (m, 6H), 7.47 – 7.37 (m, 6H), 7.33 (t, J = 7.6 Hz, 5H), 7.28 – 7.22 (m, 2H), 5.55 (d, J = 39.2 Hz, 1H), 5.34 (s, 2H), 5.06 (s, 1H), 4.98 (d, J = 47.2 Hz, 2H), 3.35 (d, J = 17.5 Hz, 2H), 3.28 (s, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 158.0 (d, J = 272.0 Hz), 142.3 (d, J = 14.4 Hz), 140.8, 140.7, 139.9, 132.2, 128.9 (d, J = 7.3 Hz), 128.8, 128.7, 128.4, 127.3, 127.2, 127.1, 127.0, 115.5 (d, J = 10.5 Hz), 109.1 (d, J = 6.7 Hz), 84.0 (d, J = 167.7 Hz), 69.1, 52.6, 50.9 (d, J = 25.9 Hz).

$^{19}$F NMR (376 MHz, CDCl$_3$) δ -103.59 (dt, J = 36.2, 17.3 Hz), -218.88 (t, J = 47.7 Hz).

HRMS (ESI, m/z) for C$_{32}$H$_{30}$F$_{2}$N$^+$ [M+H$^+$]: calcd for 466.2341, found 466.2332.

(Z)-N-benzhydryl-2-fluoro-N-(2-(fluoromethyl)allyl)-3-(4-fluorophenyl)prop-2-en-1-amine (5g)

Product 5g were synthesized from the general procedure E, and was obtained as colorless oil in 85% isolated yields (69.3 mg). $R_t$ = 0.3 (PE:DCM = 10:1).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.47 – 7.36 (m, 6H), 7.35 – 7.20 (m, 6H), 7.00 (t, J = 8.6 Hz, 2H), 5.47 (d, J = 38.8 Hz, 1H), 5.31 (s, 2H), 5.04 (s, 1H), 4.97 (d, J = 47.3 Hz, 2H), 3.31 (d, J = 17.4 Hz, 2H), 3.26 (s, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 161.7 (d, J = 248.3 Hz), 157.4 (d, J = 271.2 Hz), 142.3 (d, J = 14.1 Hz), 140.8, 130.1 (t, J = 7.7 Hz), 129.2, 128.6, 128.4, 127.2, 115.5 (d, J = 11.4 Hz), 115.3 (d, J = 21.7 Hz), 108.3 (d, J = 7.1 Hz), 83.9 (d, J = 167.7 Hz), 69.0, 52.6 (d, J = 2.7 Hz), 50.8 (d, J = 26.0 Hz).

$^{19}$F NMR (376 MHz, CDCl$_3$) δ -105.59 (dt, J = 37.1, 17.5 Hz), -114.52, -218.82 (t, J = 47.4 Hz).

HRMS (ESI, m/z) for C$_{26}$H$_{25}$F$_{3}$N$^+$ [M+H$^+$]: calcd for 408.1934, found 408.1937.

(Z)-N-benzhydryl-3-(4-chlorophenyl)-2-fluoro-N-(2-(fluoromethyl)allyl)prop-2-en-1-amine (5h)

Product 5h were synthesized from the general procedure E, and was obtained as colorless oil in 90% isolated yields (76.3 mg).

$R_t$ = 0.3 (PE:DCM = 10:1).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.41 – 7.35 (m, 6H), 7.34 – 7.28 (m, 5H), 7.28 – 7.21 (m, 3H), 5.46 (d, J = 38.7 Hz, 1H), 5.31 (s, 2H), 5.02 (s, 1H), 4.96 (d, J = 48.2 Hz, 2H), 3.31 (d, J = 17.3 Hz, 2H), 3.25 (s, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 158.30 (d, J = 272.1 Hz), 142.25 (d, J = 14.1 Hz), 140.71, 132.73 (d, J = 3.3 Hz), 131.57 (d, J = 2.4 Hz), 129.74 (d, J = 7.4 Hz), 128.62, 128.59, 128.40, 127.27, 115.60 (d, J = 10.4 Hz), 108.24 (d, J = 6.8 Hz), 83.92 (d, J = 167.7 Hz), 69.11, 52.66 (d, J = 2.6 Hz), 50.84 (d, J = 25.9 Hz).

$^{19}$F NMR (376 MHz, CDCl$_3$) δ -103.45 (dt, J = 36.6, 17.3 Hz), -218.73 (t, J = 46.7 Hz).

HRMS (ESI, m/z) for C$_{26}$H$_{25}$ClF$_2$N$^+$ [M+H$^+$]: calcd for 442.1638, found 442.1637.

(Z)-N-benzhydryl-3-(4-bromophenyl)-2-fluoro-N-(2-(fluoromethyl)allyl)prop-2-en-1-amine (5i)

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Product 5i were synthesized from the general procedure E (except that the reaction was performed with 2 mol % [Rh(CO)₂Cl]₂ and 4 mol % IPr.), and was obtained as colorless oil in 85% isolated yields (79.6 mg). R_t = 0.3 (PE:DCM = 10:1). ¹H NMR (400 MHz, CDCl₃) δ 7.40 (dd, J = 21.9, 8.0 Hz, 6H), 7.33 – 7.29 (m, 6H), 7.25 – 7.21 (m, 2H), 5.44 (d, J = 38.7 Hz, 1H), 5.31 (s, 2H), 5.02 (s, 1H), 4.96 (d, J = 48.1 Hz, 2H), 3.30 (d, J = 17.2 Hz, 2H), 3.25 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 158.4 (d, J = 272.3 Hz), 142.2 (d, J = 14.1 Hz), 140.7, 132.0 (d, J = 2.3 Hz), 131.5, 130.0 (d, J = 7.4 Hz), 128.6, 128.4, 127.3, 120.9 (d, J = 3.3 Hz), 115.6 (d, J = 10.4 Hz), 128.3, 128.4, 127.3, 120.9 (d, J = 3.3 Hz), 115.6 (d, J = 10.4 Hz), 108.3 (d, J = 6.9 Hz), 83.9 (d, J = 167.6 Hz), 69.1, 52.7 (d, J = 6.9 Hz), 50.9 (d, J = 26.0 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -103.03 (dt, J = 37.6, 18.8 Hz), -218.67 (t, J = 46.7 Hz). HRMS (ESI, m/z) for C_{26}H_{25}BrF_{2}N⁺ [M+H]⁺: calcd for 468.1133, found 468.1136.

(Z)-N-benzhydryl-2-fluoro-N-(2-(fluoromethyl)allyl)-3-(3-fluorophenyl)prop-2-en-1-amine (5j)

Product 5j were synthesized from the general procedure E, and was obtained as colorless oil in 95% isolated yields (77.4 mg). R_t = 0.3 (PE:DCM = 10:1). ¹H NMR (400 MHz, CDCl₃) δ 7.40 – 7.36 (m, 4H), 7.32 (t, J = 7.6 Hz, 4H), 7.28 – 7.21 (m, 4H), 7.17 (d, J = 7.8 Hz, 1H), 5.49 (d, J = 38.3 Hz, 1H), 5.32 (s, 2H), 5.03 (s, 1H), 4.96 (d, J = 47.2 Hz, 2H), 3.32 (d, J = 17.1 Hz, 2H), 3.26 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 162.8 (d, J = 244.6 Hz), 158.8 (d, J = 272.9 Hz), 142.2 (d, J = 14.2 Hz), 140.7, 135.2 (d, J = 8.6 Hz), 129.8 (d, J = 8.5 Hz), 128.6, 128.4, 127.3, 124.2 (dd, J = 6.5, 2.6 Hz), 115.7 (d, J = 10.3 Hz), 115.2 (dd, J = 22.6, 8.8 Hz), 114.1 (d, J = 21.2 Hz), 108.4 (d, J = 6.3 Hz), 83.9 (d, J = 167.7 Hz), 69.2, 52.7 (d, J = 2.8 Hz), 50.8 (d, J = 26.0 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -102.17 (dt, J = 36.5, 17.2 Hz), -113.56 (q, J = 8.5 Hz), -218.67 (t, J = 47.3 Hz). HRMS (ESI, m/z) for C_{26}H_{25}F_{3}N⁺ [M+H]⁺: calcd for 408.1934, found 408.1930.

(Z)-N-benzhydryl-3-(3-chlorophenyl)-2-fluoro-N-(2-(fluoromethyl)allyl)prop-2-en-1-amine (5k)

Product 5k were synthesized from the general procedure E, and was obtained as colorless oil in 74% isolated yields (72.6 mg). R_t = 0.3 (PE:DCM = 10:1). ¹H NMR (400 MHz, CDCl₃) δ 7.48 (s, 1H), 7.38 (d, J = 7.6 Hz, 4H), 7.32 (t, J = 7.5 Hz, 5H), 7.29 – 7.15 (m, 4H), 5.46 (d, J = 38.3 Hz, 1H), 5.32 (s, 2H), 5.02 (s, 1H), 4.96 (d, J = 47.7 Hz, 2H), 3.32 (d, J = 17.2 Hz, 2H), 3.25 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 158.9 (d, J = 273.1 Hz), 142.2 (d, J = 14.2 Hz), 140.7, 134.8 (d, J = 2.2
Hz), 134.3, 129.6, 128.6, 128.4, 128.3, 127.3, 127.2, 126.6 (d, J = 7.0 Hz), 115.7 (d, J = 10.5 Hz), 108.2 (d, J = 6.7 Hz), 83.9 (d, J = 167.7 Hz), 69.2, 52.7 (d, J = 2.6 Hz), 50.8 (d, J = 26.0 Hz). 19F NMR (376 MHz, CDCl3) δ -101.99 (dt, J = 35.3, 17.2 Hz), -218.63 (t, J = 46.9 Hz). HRMS (ESI, m/z) for C26H25ClF2N⁺ [M+H]⁺: calcd for 424.1638, found 424.1635.

(Z)-N-benzhydryl-3-(2-chlorophenyl)-2-fluoro-N-(2-(fluoromethyl)allyl)prop-2-en-1-amine (5l)

Product 5h were synthesized from the general procedure E (except that the reaction was performed with 24 h), and was obtained as colorless oil in 35% isolated yields (29.7 mg). Rf = 0.3 (PE:DCM = 10:1). 1H NMR (400 MHz, CDCl3) δ 7.80 (d, J = 7.8 Hz, 1H), 7.44 – 7.30 (m, 9H), 7.25 (t, J = 7.9 Hz, 3H), 7.17 (t, J = 8.4 Hz, 1H), 5.99 (d, J = 38.2 Hz, 1H), 5.34 (d, J = 11.3 Hz, 2H), 5.07 (s, 1H), 4.99 (d, J = 47.2 Hz, 2H), 3.36 (d, J = 16.9 Hz, 2H), 3.27 (s, 2H). 13C NMR (101 MHz, CDCl3) δ 158.9 (d, J = 273.4 Hz), 142.1 (d, J = 14.1 Hz), 140.7, 132.6, 131.0, 130.4 (d, J = 11.9 Hz), 129.4, 128.7, 128.4, 128.3, 127.3, 126.7, 115.5 (d, J = 10.5 Hz), 105.4 (d, J = 5.7 Hz), 84.0 (d, J = 167.9 Hz), 69.0, 52.5, 50.8 (d, J = 26.1 Hz). 19F NMR (376 MHz, CDCl3) δ -103.45 (dt, J = 36.8, 17.1 Hz), -218.94 (t, J = 47.4 Hz). HRMS (ESI, m/z) for C26H25ClF2N⁺ [M+H]⁺: calcd for 424.1638, found 424.1635.

(Z)-N-benzhydryl-2-fluoro-N-(2-(fluoromethyl)allyl)-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-amine (5m)

Product 5m were synthesized from the general procedure E, and was obtained as colorless oil in 92% isolated yields (84.2 mg). Rf = 0.3 (PE:DCM = 10:1). 1H NMR (400 MHz, CDCl3) δ 7.58 – 7.53 (m, 4H), 7.38 (d, J = 8.2 Hz, 4H), 7.33 (t, J = 7.4 Hz, 4H), 7.29 – 7.21 (m, 2H), 5.56 (d, J = 38.4 Hz, 1H), 5.33 (s, 2H), 5.03 (s, 1H), 4.97 (d, J = 48.0 Hz, 2H), 3.35 (d, J = 16.9 Hz, 2H), 3.27 (s, 2H). 13C NMR (101 MHz, CDCl3) δ 159.7 (d, J = 274.4 Hz), 142.2 (d, J = 14.1 Hz), 140.7, 136.6, 128.7, 128.6, 128.4, 127.3, 125.3 (d, J = 4.0 Hz), 124.1 (q, J = 271.7 Hz), 115.8 (d, J = 10.3 Hz), 108.1 (d, J = 6.5 Hz), 83.9 (d, J = 167.6 Hz), 69.3, 52.8, 50.9 (d, J = 26.0 Hz). 19F NMR (376 MHz, CDCl3) δ -62.89, -101.12 (dt, J = 37.3, 16.9 Hz), -218.52 (t, J = 47.6 Hz). HRMS (ESI, m/z) for C27H25F5N⁺ [M+H]⁺: calcd for 458.1902, found 458.1905.

methyl (Z)-4-(3-(benzhydryl(2-(fluoromethyl)allyl)amino)-2-fluoroprop-1-en-1-yl)benzoate (5n)

S23
Product 5n were synthesized from the general procedure E, and was obtained as colorless oil in 87% isolated yields (77.8 mg). \( R_t = 0.3 \) (PE:DCM = 5:1). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.99 (d, \( J = 8.4 \) Hz, 2H), 7.52 (d, \( J = 8.4 \) Hz, 2H), 7.42 – 7.28 (m, 8H), 7.25 (t, \( J = 7.1 \) Hz, 2H), 5.57 (d, \( J = 38.7 \) Hz, 1H), 5.33 (s, 2H), 5.04 (s, 1H), 4.97 (d, \( J = 47.3 \) Hz, 2H), 3.91 (s, 3H), 3.35 (d, \( J = 16.7 \) Hz, 2H), 3.27 (s, 2H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 166.8, 159.7 (d, \( J = 274.8 \) Hz), 142.2 (d, \( J = 14.4 \) Hz), 140.7, 137.7 (d, \( J = 2.6 \) Hz), 129.7, 128.6, 128.4, 128.3, 127.3, 115.8 (d, \( J = 10.5 \) Hz), 108.6 (d, \( J = 6.5 \) Hz), 83.9 (d, \( J = 167.7 \) Hz), 69.2, 52.8, 52.1, 50.9 (d, \( J = 26.0 \) Hz). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \( \delta \) -100.41 (dt, \( J = 38.4, 16.6 \) Hz), -218.56 (t, \( J = 47.3 \) Hz). HRMS (ESI, m/z) for C\(_{28}\)H\(_{28}\)F\(_2\)NO\(_2\)\([\text{M+H}]^+\): calcd for 448.2083, found 448.2086.

(Z)-N-benzhydryl-3-(3,5-dimethylphenyl)-2-fluoro-N-(2-(fluoromethyl)allyl)prop-2-en-1-amine (5o)

Product 5o were synthesized from the general procedure E, and was obtained as colorless oil in 87% isolated yields (72.6 mg). \( R_t = 0.3 \) (PE:DCM = 10:1). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.38 (d, \( J = 7.8 \) Hz, 1H), 7.32 (t, \( J = 7.6 \) Hz, 1H), 7.27 – 7.21 (m, 0H), 7.10 (s, 0H), 6.88 (s, 0H), 5.43 (d, \( J = 39.4 \) Hz, 0H), 5.32 (s, 1H), 5.05 (s, 0H), 4.97 (d, \( J = 47.2 \) Hz, 0H), 3.30 (d, \( J = 17.7 \) Hz, 0H), 3.25 (s, 0H), 2.31 (s, 1H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 157.4 (d, \( J = 271.1 \) Hz), 142.4 (d, \( J = 14.1 \) Hz), 140.9, 137.9, 132.9, 128.9, 128.7, 128.4, 127.2, 126.4 (d, \( J = 7.1 \) Hz), 115.3 (d, \( J = 10.5 \) Hz), 109.6 (d, \( J = 6.8 \) Hz), 84.0 (d, \( J = 167.8 \) Hz), 69.0, 52.5 (d, \( J = 2.5 \) Hz), 50.8 (d, \( J = 26.0 \) Hz), 21.3. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \( \delta \) -104.10 (dt, \( J = 37.1, 17.5 \) Hz), -219.05 (t, \( J = 46.7 \) Hz). HRMS (ESI, m/z) for C\(_{28}\)H\(_{30}\)F\(_2\)N\(_2\)\([\text{M+H}]^+\): calcd for 418.2341, found 418.2333.

(Z)-N-benzhydryl-3-(3,5-dimethoxyphenyl)-2-fluoro-N-(2-(fluoromethyl)allyl)prop-2-en-1-amine (5p)

Product 5m were synthesized from the general procedure E, and was obtained as colorless oil in 82% isolated yields (73.7 mg). \( R_t = 0.3 \) (PE:DCM = 5:1). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.38 (d, \( J = 7.3 \) Hz, 4H), 7.32 (t, \( J = 7.3 \) Hz, 4H), 7.25 (t, \( J = 7.2 \) Hz, 2H), 6.64 (d, \( J = 2.2 \) Hz, 2H), 6.38 (t, \( J = 2.2 \) Hz, 1H), 5.43 (d, \( J = 38.6 \) Hz, 1H), 5.32 (s, 2H), 5.04 (s, 1H), 4.97 (d, \( J = 47.2 \) Hz, 2H), 3.80 (s, 6H), 3.31 (d, \( J = 17.6 \) Hz, 2H), 3.26 (s, 2H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 160.7, 158.1 (d, \( J = 272.2 \) Hz), 142.3 (d, \( J = 14.3 \) Hz), 140.8, 134.8, 128.7, 128.4,
127.2, 115.5 (d, J = 10.5 Hz), 109.5 (d, J = 6.3 Hz), 106.6 (d, J = 7.4 Hz), 99.6, 84.0 (d, J = 167.7 Hz), 69.1, 55.3, 52.6, 50.9 (d, J = 26.2 Hz). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -102.85 (dt, J = 36.5, 17.4 Hz), -218.85 (d, J = 45.9 Hz). HRMS (ESI, m/z) for C$_{28}$H$_{30}$F$_2$NO$_2$+ [M+H]$^+$: calcd for 450.2239, found 450.2235.

(Z)-N-benzhydryl-3-(benzo[d][1,3]dioxol-5-yl)-2-fluoro-N-(2-(fluoromethyl)allyl)prop-2-en-1-amine (5q)

Product 5q were synthesized from the general procedure E, and was obtained as colorless oil in 74% isolated yields (64.1 mg). $R_f = 0.3$ (PE:DCM = 5:1). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.38 (d, J = 7.4 Hz, 4H), 7.32 (t, J = 7.4 Hz, 4H), 7.28 – 7.21 (m, 2H), 7.11 (s, 1H), 6.84 (d, J = 8.1 Hz, 1H), 6.76 (d, J = 8.1 Hz, 1H), 5.95 (d, J = 1.1 Hz, 2H), 5.40 (d, J = 38.8 Hz, 1H), 5.31 (s, 2H), 5.03 (s, 1H), 4.96 (d, J = 47.5 Hz, 2H), 3.29 (d, J = 17.8 Hz, 2H), 3.25 (s, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 156.6 (d, J = 269.7 Hz), 147.7, 146.6, 142.4, 142.3, 140.9, 128.6, 128.4, 127.2, 122.5 (d, J = 5.8 Hz), 115.4 (d, J = 10.3 Hz), 109.2 (d, J = 6.8 Hz), 108.7 (d, J = 9.6 Hz), 108.2, 101.0, 84.0 (d, J = 167.9 Hz), 69.1, 52.6, 50.8 (d, J = 25.9 Hz). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -106.13 (dt, J = 37.0, 17.7 Hz), -218.93 (t, J = 47.1 Hz). HRMS (ESI, m/z) for C$_{27}$H$_{26}$F$_2$NO$_2$+ [M+H]$^+$: calcd for 434.1926, found 434.1923.

(Z)-N-benzhydryl-2-fluoro-N-(2-(fluoromethyl)allyl)-3-(naphthalen-2-yl)prop-2-en-1-amine (5r)

Product 5r were synthesized from the general procedure E, and was obtained as white solid in 80% isolated yields (79.3 mg). $R_f = 0.3$ (PE:DCM = 10:1). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.88 (s, 1H), 7.78 (d, J = 8.2 Hz, 3H), 7.64 (d, J = 8.6 Hz, 1H), 7.46 – 7.38 (m, 6H), 7.33 (t, J = 6.9 Hz, 4H), 7.28 – 7.19 (m, 2H), 5.65 (d, J = 39.1 Hz, 1H), 5.33 (d, J = 7.4 Hz, 2H), 5.08 (s, 1H), 4.99 (d, J = 47.2 Hz, 2H), 3.37 (d, J = 17.5 Hz, 2H), 3.29 (s, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 158.13 (d, J = 271.8 Hz), 142.35 (d, J = 14.1 Hz), 140.85, 133.42, 132.44, 130.67, 128.67, 128.41, 128.01, 127.96, 127.53, 127.45, 127.24, 126.54 (d, J = 7.3 Hz), 126.15, 125.95, 115.47 (d, J = 10.3 Hz), 109.53 (d, J = 6.7 Hz), 83.97 (d, J = 167.8 Hz), 69.15, 52.66 (d, J = 2.8 Hz), 50.97 (d, J = 25.9 Hz). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -103.68 (dt, J = 36.0, 17.4 Hz), -218.93 (t, J = 46.9 Hz). HRMS (ESI, m/z) for C$_{30}$H$_{28}$F$_2$N$^+$ [M+H]$^+$: calcd for 440.2184, found 440.2183.

(Z)-N-benzhydryl-3-(benzofuran-2-yl)-2-fluoro-N-(2-(fluoromethyl)allyl)prop-2-en-1-amine (5s)
Product 5s were synthesized from the general procedure E, and was obtained as colorless oil in 72% isolated yields (61.8 mg). $R_f = 0.3 \ (PE:DCM = 5:1)$. $^1H$ NMR (400 MHz, CDCl$_3$) $\delta$ 7.56 – 7.51 (m, 1H), 7.47 – 7.36 (m, 5H), 7.35 – 7.31 (m, 4H), 7.28 – 7.17 (m, 4H), 6.90 (s, 1H), 5.76 (d, $J = 37.3$ Hz, 1H), 5.33 (s, 2H), 5.05 (s, 1H), 4.97 (d, $J = 47.2$ Hz, 2H), 3.37 (d, $J = 16.5$ Hz, 2H), 3.26 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 159.7 (d, $J = 275.5$ Hz), 153.9, 150.1, 142.1 (d, $J = 14.2$ Hz), 140.6, 129.0, 128.6, 128.5, 127.3, 124.3, 122.9, 120.8, 115.8 (d, $J = 10.3$ Hz), 110.9, 105.9 (d, $J = 10.0$ Hz), 100.2 (d, $J = 9.2$ Hz), 83.9 (d, $J = 167.7$ Hz), 69.3, 52.8, 50.4 (d, $J = 24.9$ Hz). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -95.03 (dt, $J = 35.2$, 16.7 Hz), -218.24 (t, $J = 47.6$ Hz). HRMS (ESI, m/z) for C$_{28}$H$_{26}$F$_2$NO$^+$ [M+H$^+$]: calcd for 430.1977, found 430.1978.

(Z)-N-benzhydryl-4-(Ferrocene)-2-fluoro-N-(2-(fluoromethyl)allyl)prop-2-en-1-amine (5t)

(Product 5t were synthesized from the general procedure E, and was obtained as colorless oil in 87% isolated yields (86.5 mg). $R_f = 0.3 \ (PE:DCM = 5:1)$. $^1H$ NMR (400 MHz, CDCl$_3$) $\delta$ 7.42 – 7.28 (m, 8H), 7.30 – 7.21 (m, 2H), 5.30 (d, $J = 40.0$ Hz, 1H), 5.33 (s, 2H), 5.05 (s, 1H), 4.97 (d, $J = 47.2$ Hz, 2H), 4.43 (s, 2H), 4.20 (t, $J = 1.9$ Hz, 2H), 4.09 (d, $J = 2.4$ Hz, 5H), 3.24 (s, 2H), 3.21 (d, $J = 17.8$ Hz, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 155.74 (d, $J = 265.2$ Hz), 142.43 (d, $J = 14.1$ Hz), 140.77, 128.71, 128.35, 127.18, 115.32 (d, $J = 10.5$ Hz), 107.27 (d, $J = 10.7$ Hz), 84.00 (d, $J = 167.8$ Hz), 69.07, 68.72, 68.67, 68.49, 52.23, 50.51 (d, $J = 25.9$ Hz). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -106.92 (dt, $J = 37.6$, 17.9 Hz), -218.87 (t, $J = 47.6$ Hz). HRMS (ESI, m/z) for C$_{30}$H$_{30}$F$_2$FeN$^+$ [M+H$^+$]: calcd for 498.1690, found 498.1665.

(Z)-N-benzhydryl-2-fluoro-N-(2-(fluoromethyl)allyl)-5-phenylpent-2-en-1-amine (5u)

(Product 5u were synthesized from the general procedure E, and was obtained as colorless oil in 72% isolated yields (60.1 mg). $R_f = 0.3 \ (PE:DCM = 10:1)$. $^1H$ NMR (400 MHz, CDCl$_3$) $\delta$ 7.33 – 7.23 (m, 9H), 7.27 – 7.11 (m, 6H), 5.25 (s, 1H), 5.22 (s, 1H), 4.94 (s, 1H), 4.87 (d, $J = 33.2$ Hz, 2H), 4.57 (dt, $J = 37.2$, 7.4 Hz, 1H), 3.14 – 3.04 (m, 4H), 2.68 (t, $J = 7.5$ Hz, 2H), 2.43 (q, $J = 7.5$ Hz, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 156.67 (d, $J = 258.8$ Hz), 142.44 (d, $J = 14.0$ Hz), 141.39, 140.78, 128.69, 128.40, 128.32, 128.25, 127.07, 125.95, 114.88 (d, $J = 10.5$ Hz), 108.65 (d, $J = 13.9$ Hz), 83.94 (d, $J = 167.9$ Hz), 68.51, 52.16 (d, $J = 2.8$ Hz), 49.86 (d, $J = 26.9$ Hz), 35.37, 24.98 (d, $J = 4.8$ Hz).
5. Synthetic Applications

5.1 Post-Functionalization of Allyl Ethers

Hydrogenation of 3a

In a nitrogen filled glove box, a round bottom flask equipped with a stirring bar, was charged with Pd/C (42.4 mg, 40 wt%, 10 mol%). After the flask was evacuated and filled with H₂ (three cycles), 3a (60.4 mg, 0.2 mmol, 1.0 equiv.) and EA (5 mL) was added and the reaction mixture was stirred at room temperature for 2 hours under a H₂ atmosphere (H₂ balloon). The reaction mixture was filtered through a pad of celite and concentrated. Purification by column chromatography on silica gel with PE afforded the desired product 4-(2-fluoro-3-(2-fluoro-2-methylpropoxy)propyl)-1,1'-biphenyl (6) as colorless oil in 96% yield (58.4 mg).

**4-(2-fluoro-3-(2-fluoro-2-methylpropoxy)propyl)-1,1'-biphenyl (6)**

Colorless oil. Rf = 0.4 (PE:EA = 50:1). ¹H NMR (400 MHz, CDCl₃) δ 7.60 – 7.53 (m, 4H), 7.45 – 7.41 (m, 2H), 7.36 – 7.30 (m, 3H), 4.94 – 4.79 (m, 1H), 3.76 – 3.61 (m, 2H), 3.52 (d, J = 18.6 Hz, 2H), 3.07 (d, J = 6.4 Hz, 1H), 3.02 (dd, J = 6.4, 3.1 Hz, 1H), 1.39 (dd, J = 21.4, 2.9 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 140.8, 139.6, 135.6 (d, J = 5.3 Hz), 129.8, 128.7, 127.2, 127.1, 95.1 (d, J = 167.6 Hz), 94.0 (d, J = 5.6 Hz), 92.3 (d, J = 11.2 Hz), 77.6, 72.5 (d, J = 22.6 Hz), 37.5 (d, J = 21.5 Hz), 23.7 (d, J = 24.4 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -144.65 (dh, J = 41.8, 20.8 Hz), -183.81 – -184.18 (m). HRMS (ESI, m/z) for C₁₉H₂₆F₂NO⁺ [M+NH₄]⁺: calcd for 322.1977, found 322.1973.

Alkylation of 3a
According to the previous C–F bond alkylation method,[11] the alkyl migration product (7) was synthesized. To a DCM solution (1.6 mL) of 3a (30.2 mg, 0.1 mmol, 1.0 equiv.), Et₃Al (0.1 mL, 1.4 M in hexane, 0.14 mmol, 1.4 equiv.) was added, and the mixture was stirred at room temperature under N₂ atmosphere for 12 h. Then, water (2 mL) was added to the mixture and extracted with DCM. The combined organic layer was dried over MgSO₄ and concentrated under reduced pressure. Purification by column chromatography on silica gel (PE:EA = 50:1) gave (Z)-4-(2-fluoro-3-((2-methylpentan-3-yl)oxy)prop-1-en-1-yl)-1,1'-biphenyl (7) as colorless oil in 88% yield (27.5 mg).

(Z)-4-(2-fluoro-3-((2-methylpentan-3-yl)oxy)prop-1-en-1-yl)-1,1'-biphenyl (7)

Colorless oil. Rₜ = 0.4 (PE:EA = 50:1). ¹H NMR (400 MHz, CDCl₃) δ 7.61 – 7.56 (m, 6H), 7.46 – 7.42 (m, 2H), 7.36 – 7.32 (m, 1H), 5.81 (d, J = 38.5 Hz, 1H), 4.16 (d, J = 15.2 Hz, 2H), 3.11 (dt, J = 6.8, 5.0 Hz, 1H), 1.92 – 1.84 (m, 1H), 1.56 – 1.51 (m, 2H), 0.98 – 0.94 (m, 6H), 0.92 (d, J = 6.8 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 157.5 (d, J = 268.2 Hz), 140.8, 140.1 (d, J = 2.4 Hz), 132.2 (d, J = 2.8 Hz), 129.2 (d, J = 7.2 Hz), 128.9, 127.4, 127.2, 127.1, 108.0 (d, J = 6.4 Hz), 86.4, 68.6 (d, J = 31.0 Hz), 30.5, 23.2, 18.3 (d, J = 2.7 Hz), 10.0. ¹⁹F NMR (376 MHz, CDCl₃) δ 109.71 (dt, J = 38.8, 15.6 Hz). HRMS (ESI, m/z) for C₂₁H₂₉FN₂O⁺ [M+NH₄]⁺: calcd for 330.2227, found 330.2232.

Allylation of 3a

According to the previous C–F bond alkylation method,[12] the allyl migration product (8) was synthesized. B(C₆F₅)₃ (1.0 mg, 0.002 mmol, 2 mol%) was added to a solution of 3a (30.2 mg, 0.1 mmol, 1.0 equiv.) and Allyl-TMS (47 μL, 34.3 mg, 3 equiv) in DCM (0.5 mL) under N₂ atmosphere. After being stirred at 25 °C for 4 h, the reaction mixture was concentrated, and purified by chromatography on silica gel column (PE:EA = 50:1) to afford corresponding product (Z)-4-(2-fluoro-3-((2-methylhex-5-en-3-yl)oxy)prop-1-en-1-yl)-1,1'-biphenyl (8) as colorless oil in 76% yield (24.6 mg).

(Z)-4-(2-fluoro-3-((2-methylhex-5-en-3-yl)oxy)prop-1-en-1-yl)-1,1'-biphenyl (8)
Colorless oil. $R_t = 0.4$ (PE:EA = 50:1). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.62 – 7.58 (m, 6H), 7.44 (t, $J = 7.6$ Hz, 2H), 7.36 – 7.32 (m, 1H), 5.93 – 5.85 (m, 1H), 5.81 (d, $J = 38.5$ Hz, 1H), 5.15 – 5.06 (m, 1H), 4.18 (dq, $J = 15.3, 13.4$ Hz, 2H), 3.23 (q, $J = 5.7$ Hz, 1H), 2.33 – 2.29 (m, 2H), 1.89 – 1.85 (m, 1H), 0.96 (dd, $J = 8.4, 6.8$ Hz, 6H). $^{13}$C NMR 157.1 (d, $J = 268.4$ Hz), 140.6, 140.0, 135.3, 132.0, 129.1 (d, $J = 7.3$ Hz), 128.8, 127.3, 127.1, 127.9, 116.8, 108.0 (d, $J = 6.2$ Hz), 84.48, 68.6 (d, $J = 31.3$ Hz), 35.4, 31.0, 18.2 (d, $J = 39.1$ Hz). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ 109.82 (dt, $J = 37.6, 15.0$ Hz). HRMS (ESI, m/z) for C$_{22}$H$_{29}$FNO$^+$ [M+NH$_4$]$^+$: calcd for 342.2228, found 342.2226.

5.2 Synthetic Application of Allyl Amine

**Removal of The Protecting Group**

(Z)-N-benzhydryl-2-fluoro-N-(2-(fluoromethyl)allyl)-3-phenylprop-2-en-1-amine (5a) (778 mg, 2.0 mmol, 1.0 equiv.) was treated with TFA (1140 mg, 10 mmol, 5.0 equiv.) in DCM (10 mL) at 60 °C in a 40 mL screw-cape vial for 12 h. The reaction mixture was diluted with dichloromethane and washed with water. The layers were separated and the aqueous layer was extracted with dichloromethane two times. The combined organic layers were dried over magnesium sulfate, filtered and concentrated under reduced pressure, which was then purified by silica gel column chromatography (PE/EA = 5:1) to afford corresponding product (Z)-2-fluoro-N-(2-(fluoromethyl)allyl)-3-phenylprop-2-en-1-amine (9) as colorless oil in 85% yield (379 mg).

(Z)-2-fluoro-N-(2-(fluoromethyl)allyl)-3-phenylprop-2-en-1-amine (9)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.50 (d, $J = 7.3$ Hz, 2H), 7.33 (t, $J = 7.3$ Hz, 2H), 7.29 – 7.18 (m, 1H), 5.66 (d, $J = 39.2$ Hz, 1H), 5.24 (d, $J = 8.0$ Hz, 2H), 4.91 (d, $J = 47.2$ Hz, 2H), 3.45 (d, $J = 16.0$ Hz, 2H), 3.38 (s, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 157.9 (d, $J = 267.0$ Hz), 142.6 (d, $J = 14.7$ Hz), 133.1, 128.6, 128.5, 127.2, 114.8 (d, $J = 10.0$ Hz), 107.6, 84.3 (d, $J = 165.8$ Hz), 49.9, 49.6. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -109.58 (dt, $J = 39.0, 15.9$ Hz), -217.84 (t, $J = 47.2$ Hz). HRMS (ESI, m/z) for C$_{13}$H$_{16}$F$_2$N$^+$ [M+H]$^+$: calcd for 224.1245, found 224.1243.

**Electrophilic Substitution**
To a solution of (Z)-2-fluoro-N-(2-(fluoromethyl)allyl)-3-phenylprop-2-en-1-amine (22.3 mg, 0.1 mmol) in acetone (0.5 mL), K₂CO₃ (27.6 mg, 0.2 mmol, 2 equiv.) and BnBr (benzyl bromide) (25.7 mg, 0.15 mmol, 1.5 equiv) were added. The mixture was stirred at 60°C for 12 hours. After concentration, the mixture yielded a crude product, which was purified by silica gel column chromatography ((PE/EA = 30:1) to afford (Z)-N-benzyl-2-fluoro-N-(2-(fluoromethyl)allyl)-3-phenylprop-2-en-1-amine (10) as colorless oil in 96% yield (30.0 mg).

(Z)-N-benzyl-2-fluoro-N-(2-(fluoromethyl)allyl)-3-phenylprop-2-en-1-amine (10)

**[Relevant NMR data]**

1H NMR (400 MHz, CDCl₃) δ 7.49 (d, J = 8.0 Hz, 2H), 7.38 – 7.28 (m, 6H), 7.30 – 7.18 (m, 2H), 5.64 (d, J = 39.0 Hz, 1H), 5.27 (d, J = 5.3 Hz, 2H), 4.93 (d, J = 47.3 Hz, 2H), 3.70 (s, 2H), 3.27 (d, J = 17.3 Hz, 2H), 3.24 (s, 2H). 13C NMR (101 MHz, CDCl₃) δ 157.58 (d, J = 270.3 Hz), 142.28 (d, J = 14.4 Hz), 138.77, 133.11, 128.60, 128.56, 128.49, 128.46, 128.36, 127.14, 115.27 (d, J = 10.5 Hz), 108.98 (d, J = 6.7 Hz), 83.86 (d, J = 167.5 Hz), 57.65, 55.10, 54.09 (d, J = 26.7 Hz). 19F NMR (376 MHz, CDCl₃) δ -104.25 (dt, J = 39.0, 17.1 Hz), -220.05 (t, J = 47.6 Hz). HRMS (ESI, m/z) for C₂₀H₂₂F₂N⁺ [M+H]⁺: calcd for 314.1715, found 314.1707.

6. Deuterium-labeling Experiment

**Synthesis of Deuterated Substrates**

(a) In a 100 mL Schlenk tube, PPh₃ (2620 mg, 10.0 mmol, 1.0 equiv.) was placed, evacuated, and backfilled with nitrogen three times. THF (30 mL) was then added. CD₃I (1739 mg, 12.0 mmol, 1.2 equiv.) was added to the solution, and the reaction mixture was refluxed for 1 hour. After cooling to room temperature, the resulting white solid was separated, washed with diethyl ether (Et₂O), and dried under reduced pressure to yield [PPh₃(CD₃)]I (3.27 mg, 80% yield).
(b) To a solution of \([\text{PPh}_3(\text{CD}_3)]\text{I}\) (610.5 mg, 1.5 mmol, 1.0 equiv.) in THF (5 mL), \(^7\text{BuOK}\) (168.3 mg, 1.5 mmol, 1.0 equiv.) was added. The mixture was stirred at 25°C for 60 minutes. Then, 1-(diphenylmethyl)azetidin-3-one (356 mg, 1.5 mmol, 1.0 equiv.) in THF (5 mL) was added. The reaction mixture was heated at 50 °C for 12 hours. The organic mixture was washed with brine, dried over MgSO\(_4\), filtered, and concentrated under reduced pressure. It was then purified by silica gel column chromatography (PE/EA = 20:1) to afford the corresponding product 1-benzhydryl-3-(methylene-d2) azetidine (70% D) as white solid in 60% yield (213 mg).

To elucidate the reaction mechanism, we carried out a deuterium labeling experiment. Beginning with compound 1a and deuterated 4, under our standard reaction conditions. The resulting product mixture was then analyzed by \(^1\text{H}\) NMR spectroscopy, using 1,1,2,2-tetrachloroethane as an internal standard for calibration. The \(^1\text{H}\) NMR results indicated a high yield of 92% for our target product. Notably, the deuterium incorporation was observed exclusively at the alkene position, as evidenced by a signal at 5.32 ppm in the NMR spectrum. This observation suggests that the Rh-F intermediate more likely participated in a nucleophilic attack on the methylene group within the azetidine structure (path a), rather than attacking the deuterated alkene present in the starting material d-4 (path b).
1H NMR spectroscopy of deuterium-labeling experiment

1,1,2,2-Tetrachloroethane

Ph\(\text{F}\)\(\text{N}\)\(\text{PC}\)\(\text{D}\)\(\text{CH}_2\text{F}\)

found 1.4 D + 0.6 H
5.32 ppm

1H NMR (400 MHz, CDCl\(_3\)) spectrum of deuterated 4

70% D

Ph\(\text{N}\)\(\text{Ph}\)
7. X-ray Crystallographic Data

Table S2. Crystal data and structure refinement for 5r.

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<td>γ/°</td>
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<tr>
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<td>Largest diff. peak/hole / e Å(^{-3})</td>
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8. References


9. NMR Spectra

$^1$H NMR (400 MHz, CDCl$_3$) spectrum of 2f
$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 2f

$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 2f
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of 2k

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 2k
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of 3a

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 3a
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 3a
\(^1\)H NMR (400 MHz, CDCl\(_3\)) spectrum of 3b

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) spectrum of 3b
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 3b
$^1$H NMR (376 MHz, CDCl$_3$) spectrum of 3c

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 3c
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 3c
$^1$H NMR (376 MHz, CDCl$_3$) spectrum of 3d

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 3d
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 3d
$^1$H NMR (376 MHz, CDCl$_3$) spectrum of 3e

$^13$C NMR (101 MHz, CDCl$_3$) spectrum of 3e
"$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 3e"
$^{1} H$ NMR (376 MHz, CDCl$_3$) spectrum of 3f

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 3f
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 3f
$^1$H NMR (376 MHz, CDCl₃) spectrum of 3g

$^{13}$C NMR (101 MHz, CDCl₃) spectrum of 3g
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 3g
$^1$H NMR (376 MHz, CDCl$_3$) spectrum of 3h

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 3h
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 3h
$^1$H NMR (376 MHz, CDCl$_3$) spectrum of 3i

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 3i
$^{19}\text{F NMR (376 MHz, CDCl}_3\text{) spectrum of 3i}$

![Diagram of $^{19}\text{F NMR (376 MHz, CDCl}_3\text{) spectrum of 3i}$]
$^1$H NMR (376 MHz, CDCl$_3$) spectrum of 3j

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 3j
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 3j
$^1$H NMR (376 MHz, CDCl$_3$) spectrum of 3k

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 3k
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 3k
$^1$H NMR (376 MHz, CDCl$_3$) spectrum of 3l

$^1$C NMR (101 MHz, CDCl$_3$) spectrum of 3l
$^{19}$F NMR (376 MHz, CDCl₃) spectrum of 3l
$^1$H NMR (376 MHz, CDCl$_3$) spectrum of 3m

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 3m
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 3m
$^{1}H$ NMR (376 MHz, CDCl$_3$) spectrum of 3n

$^{13}C$ NMR (101 MHz, CDCl$_3$) spectrum of 3n
$^{19}\text{F NMR (376 MHz, CDCl}_3\text{)}$ spectrum of 3n
$^1$H NMR (376 MHz, CDCl$_3$) spectrum of 3

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 3
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 3o
$^1$H NMR (376 MHz, CDCl$_3$) spectrum of 3p

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 3p
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 3p
$^1$H NMR (376 MHz, CDCl$_3$) spectrum of 3q

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 3q
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 3q
$^1$H NMR (376 MHz, CDCl$_3$) spectrum of 3r

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 3r
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 3r
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of 3s

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 3s
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 3s
$^1$H NMR (376 MHz, CDCl$_3$) spectrum of 3t

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 3t
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of $3t$
$^1$H NMR (376 MHz, CDCl$_3$) spectrum of 3u

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 3u
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 3u
$^1$H NMR (376 MHz, CDCl$_3$) spectrum of 3v

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 3v
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 3v
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of 3w

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 3w
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 3w

-109.9 -110.0 -110.1 -110.2 -110.3
f1 (ppm)

-157.82 -157.87 -158.02 -158.12
f1 (ppm)
$^1$H NMR (376 MHz, CDCl$_3$) spectrum of 3x

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 3x
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 3x
$^1$H NMR (376 MHz, CDCl$_3$) spectrum of 3y

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 3y
$^{19}\text{F NMR (376 MHz, CDCl}_3\text{)}$ spectrum of 3y
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of 3z

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 3z
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 3z
$^{1}H$ NMR (376 MHz, CDCl$_3$) spectrum of 3aa

$^{13}C$ NMR (101 MHz, CDCl$_3$) spectrum of 3aa
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 3aa
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of 3ab

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 3ab
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 3ab
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of 4a

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 4a
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5a

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 5a
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 5a
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5b

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 5b
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 5b
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5c

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 5c
$^{19}\text{F NMR (376 MHz, CDCl}_3$} spectrum of $5c$
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5d

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 5d
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 5d
$^{1}H$ NMR (400 MHz, CDCl$_3$) spectrum of 5e

$^{13}C$ NMR (101 MHz, CDCl$_3$) spectrum of 5e
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 5e
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5f

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 5f
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 5f
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5g

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 5g
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 5g
$\text{H NMR (400 MHz, CDCl}_3\text{) spectrum of 5h}$

$\text{C NMR (101 MHz, CDCl}_3\text{) spectrum of 5h}$
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 5h
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5i

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 5i
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 5i
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5j

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 5j
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 5j
$^{1}H$ NMR (400 MHz, CDCl$_3$) spectrum of 5k

$^{13}C$ NMR (101 MHz, CDCl$_3$) spectrum of 5k
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 5k
$^{1}H$ NMR (400 MHz, CDCl$_3$) spectrum of 5l

$^{13}C$ NMR (101 MHz, CDCl$_3$) spectrum of 5l
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 5l
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5m

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 5m
$^{19}\text{F NMR (376 MHz, CDCl}_3\text{)}$ spectrum of 5m
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5n

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 5n
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 5n
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5o

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 5o
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 5o
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5p

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 5p
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 5p
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5q

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 5q
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 5q
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5r

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 5r
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 5r
$^{1}H$ NMR (400 MHz, CDCl$_3$) spectrum of 5s

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 5s
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 5s
$^{1}H$ NMR (400 MHz, CDCl$_3$) spectrum of 5t

$^{13}C$ NMR (101 MHz, CDCl$_3$) spectrum of 5t
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 5t
$^{1}H$ NMR (400 MHz, CDCl$_3$) spectrum of 5u

$^{13}C$ NMR (101 MHz, CDCl$_3$) spectrum of 5u
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 5u

![NMR Spectrum Diagram]
$^{1}H$ NMR (400 MHz, CDCl$_3$) spectrum of 5x

$^{13}C$ NMR (101 MHz, CDCl$_3$) spectrum of 5x
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 5x
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5y

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 5y
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 5y
$^1$H NMR (376 MHz, CDCl$_3$) spectrum of 6

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 6
$^{19}\text{F NMR (376 MHz, CDCl}_3\text{) spectrum of 6}$
$^1$H NMR (376 MHz, CDCl$_3$) spectrum of 7

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 7
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 7
$^1$H NMR (376 MHz, CDCl$_3$) spectrum of 8

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 8
$^{19}$F NMR (376 MHz, CDCl₃) spectrum of 8