Supporting Information

Visible light photocatalytic decarboxylative monofluoroalkenylation of α-amino acids with gem-difluoroalkenes

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1. **General procedures**

All reactions were carried out in dry solvents under an atmosphere of argon unless otherwise indicated. Reagents including carbonyl compounds and N-protected amino acids (N-Boc-proline, N-Cbz-proline, N-Boc-glycine, N-Boc-alanine, N-Boc-phenylalanine, N-Boc-serine) were purchased from commercial sources. 1,1-Difluoroalkenes were prepared according to the previous procedures. N-Boc-pipericolinic acid and N-Boc-methionine were prepared according to the reported procedures. The reactions were monitored by thin layer chromatography (TLC) and the products were isolated by column chromatography on silica gel. High resolution mass spectra (HRMS) were recorded on a Shimadzu LCMS-IT/TOF quadrupole-time of flight mass spectrometer. $^1$H NMR (400 MHz) and $^{13}$C NMR (100 MHz) spectra were recorded on JNM-ECS 400 using tetramethylsilane (TMS) in the solvent of CDCl$_3$ as the internal standard ($^1$H NMR: TMS at 0.00 ppm, CHCl$_3$ at 7.26 ppm; $^{13}$C NMR: CDCl$_3$ at 77.16 ppm).

2. **General procedures for synthesis of 1,1-difluoroalkenes**

**Method A**

\[
\begin{align*}
& \text{Ph} \quad \text{O} \quad \text{Ph} \\
& \text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{O} \quad \text{EtOH, reflux, 12 h} \quad \text{NNH}_2 \\
& \text{Ph} \quad \text{Ph} \\
& \text{MnO}_2, \text{ MgSO}_4 \quad \text{CH}_2\text{Cl}_2, \text{ rt, 12 h} \quad \text{Ph} \quad \text{Ph}
\end{align*}
\]

To a mixture of benzophenone (10 mmol, 1.82 g) and hydrazine monohydrate (80%, 6 mL, 100 mmol) in ethanol (20 mL) was added HOAc (0.2 mL), and the mixture was heated at reflux for 12 h. After cooling to room temperature, ethanol in the resulting solution was removed, and the residue was dissolved in ethyl acetate (50 mL). The separated organic phase was dried over anhydrous Na$_2$SO$_4$ and concentrated to give benzophenone hydrazone as a white solid.

Mixed solution of benzophenone hydrazone (10 mmol, 1.96 g), anhydrous MgSO$_4$ (1.0 g) and CH$_2$Cl$_2$ (30 mL) was cooled to 0 °C. To this rapidly stirring mixture was added activated MnO$_2$ (21.5 mmol, 3.5 g) in one portion. The reaction mixture was
warmed to room temperature and kept stirring for 12 h, then the solid was filtered off and washed with CH₂Cl₂. After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography (pretreated with petroleum ether (PE) and Et₃N (PE/Et₃N = 10:1), final purification with PE/Et₃N = 20:1) to afford diphenyldiazomethane as a purple solid, which was kept at -20 °C.

To a mixture of diphenyldiazomethane (5 mmol, 0.97 g) and NaI (2 mmol, 0.3 g) in THF (50 mL) under Ar was added TMSCF₂Cl (12 mmol, 1.77 mL) at room temperature, and the reaction mixture was stirred for 18 h until color of the reaction mixture was changed from purple to light yellow. Then ethyl acetate (50 mL) was added, and the mixture was washed with H₂O (20 mL), brine (20 mL) and dried over anhydrous Na₂SO₄. The organic phase was concentrated, and the residue was purified by silica gel column chromatography.

1,1-Difluoroalkenes ²a, ²i, ²j, ²m and ²n were prepared according to Method A.

**Method B²**

\[
\text{Ph₃P}^+\text{CF}_2\text{CO}_2^- + \text{R} \text{CH} = \text{O} \xrightarrow{80 \degree \text{C}, \text{4 h}} \text{R} \text{CF} = \text{O}
\]

To a 50 mL flask, (triphenylphosphonio)difluoroacetate (6 mmol, 2.14 g) and acetophenone (3 mmol) were mixed with NMP (6 mL). The mixture was degassed and filled with N₂. Then the reaction mixture was stirred at 80 °C for 4 h. After cooling to room temperature, the reaction mixture was treated with 30% H₂O₂ (10 mL), and extracted with ethyl acetate (3 × 10 mL). The combined organic phase was washed with brine and dried over anhydrous Na₂SO₄. The solution was concentrated, and the residue was purified by silica gel column chromatography.

1,1-Difluoroalkenes ²o, ²p and ²ab were prepared according to Method B.

**Method C³**

\[
\text{ClCF}_2\text{CO}_2\text{Na} \xrightarrow{\text{PPh}_3, 100 \degree \text{C}, \text{NMP, N}_2} \text{R} \text{CH} = \text{CF} = \text{H}
\]

To a mixture of benzaldehyde (3 mmol) and triphenylphosphine (3.6 mmol, 0.94 mg) in N-methylpyrrolidone (6 mL) was added solid ClCF₂CO₂Na (4.5 mmol, 0.68 mg)
slowly at 100 °C under an argon atmosphere, and the reaction mixture was stirred at the same temperature for about 3 h. After completion of the reaction, the reaction mixture was treated with 30% H₂O₂ (10 mL), and extracted with ethyl acetate (3 × 10 mL). The combined organic phase was washed with brine and dried over anhydrous Na₂SO₄. The solution was concentrated, and the residue was purified by silica gel column chromatography.

1,1-Difluoroalkenes 2q-2aa were prepared according to Method C.

Preparation of 1-(tert-butoxycarbonyl)piperidine-2-carboxylic acid (2c) and 2-(tert-butoxycarbonyl)amino-4-(methylthio)butanoic acid (2h)⁴

To a mixture of α-amino acid (5 mmol) in dioxane (4 mL) and aqueous 1.25 M NaOH (4 mL) was added Boc₂O (5.25 mmol, 1.14 g) in dioxane (3 mL) at 0 °C in an ice bath under N₂. The mixture was stirred at room temperature for 18 h, and then the organic phase was evaporated in vacuo. The remaining aqueous layer was diluted with aqueous 1 M KHSO₄ (10 mL), and the solution was extracted with EtOAc (3 × 10 mL). The combined organic layer was washed with brine, dried over anhydrous Na₂SO₄, and the solvent was removed in vacuo to get product 2c or 2h.

3. Optimization of conditions for photocatalytic decarboxylative monofluoroalkenylation

Table S1 Optimization of conditions for photocatalytic decarboxylative monofluoroalkenylation of N-Boc-proline (1a) with 1-(2,2-difluoro-1-phenylethenyl)benzene (2a)⁷

<table>
<thead>
<tr>
<th>Entry</th>
<th>PC</th>
<th>Base</th>
<th>Solvent</th>
<th>Yield (%)</th>
<th>&lt;sup&gt;8&lt;/sup&gt;</th>
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S4
We started our investigation of the proposed reaction starting with N-tertbutoxycarbonyl proline (N-Boc-Pro) (1a) and 1-(2,2-difluoro-1-phenylethenyl)benzene (2a) under irradiation of visible light with photocatalyst Ir[dF(CF3)ppy]2(dtbbpy) (A) and Cs₂CO₃ as base (Table 1). To our delight, we found that the decarboxylative monofluoroalkenylation of 1a with gem-difluoroalkenes was feasible under this catalytic system, generating the target product 3a in 33% yield (entry 1). To optimize the reaction conditions, a series of factors including bases,
photocatalysts and solvents were tested. Among various bases examined (entries 1-11), Li$_2$CO$_3$ provided a prominent increase in yield of the decarboxylative monofluoroalkenylation (entry 4, 83% yield). Indeed, literature suggests that the lithium ion is beneficial for the departure of the fluorine atom in related transformations.\textsuperscript{5} No reaction occurred in the absence of base (entry 12). Next, the effect of solvents on the reaction was investigated (entries 13-17), showing that dimethylsulfoxide and dimethyl formamide (entries 4 and 10) were favourable to the progress of the reaction. However, the reaction did not work in dichloromethane, MeCN or toluene (entries 15-17). Other photocatalysts, Ir(ppy)$_2$(dtbbpy)PF$_6$ (B), Ir(ppy)$_3$ and Ru(ppy)$_3$Cl$_2$, were screened and gave poor results (entries 18-20). No reaction was observed in the absence of photocatalyst (entry 21). Yields decreased when the amount of photocatalyst A (entry 22) or base Li$_2$CO$_3$ (entry 23) was reduced. Shortening the reaction time led to a lower yield (entry 24). A poor result was obtained when the reaction was performed in air (entry 25) or in the absence of light (entry 26).

4. General procedures for synthesis of compounds 3a-ac

$N$-Protected $\alpha$-amino acid (1) (0.4 mmol), substituted gem-difluoroalkene (2) (0.2 mmol), Ir[dF(CF$_3$)ppy]$_2$(dtbbpy) (A) (4 μmol, 4.5 mg), Li$_2$CO$_3$ (0.6 mmol, 44 mg), DMSO (2.0 mL) were added to a 25-mL Schlenk tube. The tube was filled with argon and then sealed, and irradiated with a 23 W fluorescent lamp (approximately 2 cm away from the light source). After the complete conversion of the substrates (monitored by TLC), the reaction mixture was concentrated, and the residue was purified by silica gel column chromatography to give the desired product (3a-ac).

5. Characterization data of compounds 3a-ac and 7
**tert-Butyl 2-(1-fluoro-2,2-diphenylvinyl)pyrrolidine-1-carboxylate (3a):** Eluent: petroleum ether (PE)/ethyl acetate (EA) (20:1). Yield (61 mg, 83%). White solid, mp 125 - 126 °C. \(^1\)H NMR (CDCl\(_3\), 400 MHz): rotameric mixture, \(\delta 7.36 - 7.21\) (m, 10H), 4.46 - 4.39 (m, 1H), 3.53 - 3.46 (m, 2H), 2.22 - 2.16 (m, 2H), 2.05 - 1.95 (m, 1H), 1.81 - 1.73 (m, 1H), 1.43 (s, 9H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): rotameric mixture, \(\delta 156.67\) (d, \(J = 264.54\) Hz), 154.22, 137.90, 137.50, 130.65 (d, \(J = 1.92\) Hz), 129.72 (d, \(J = 4.79\) Hz), 128.37, 128.10, 127.60, 127.20, 119.99 (d, \(J = 14.38\) Hz), 79.84 (79.20), 55.56 (d, \(J = 24.92\) Hz), 47.37, 33.23 (31.78), 28.72, 23.80; \(^{19}\)F NMR (CDCl\(_3\), 564 MHz) rotameric mixture: \(\delta -122.07\) (d, \(J = 26.31\) Hz) (major), -122.75 (d, \(J = 23.02\) Hz) (minor); HRMS (ESI): Calculated for C\(_{23}\)H\(_{26}\)NNaO\(_2\)F, [M+Na]^+ m/z 390.1840. Found 390.1843.

![Image of tert-Butyl 2-(1-fluoro-2,2-diphenylvinyl)pyrrolidine-1-carboxylate (3a)](image.png)

**Benzyl 2-(1-fluoro-2,2-diphenylvinyl)pyrrolidine-1-carboxylate (3b):** Eluent: PE/EA (20:1). Yield (60 mg, 75%). White solid, mp 87 – 88 °C. \(^1\)H NMR (CDCl\(_3\), 400 MHz): rotameric mixture. \(\delta 7.41 - 7.17\) (m, 14H), 6.92 (d, \(J = 6.87\) Hz, 1H), 5.21 – 4.99 (m, 2H), 4.61 – 4.39 (m, 1H), 3.65 – 3.51 (m, 2H), 2.17 – 2.01 (m, 3H), 1.84 – 1.72 (m, 1H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): rotameric mixture, \(\delta 156.00\) (d, \(J = 261.66\) Hz) (major), 155.71 (d, \(J = 261.66\) Hz) (minor), 154.70, 137.84 (major), 137.76 (minor), 137.01, 136.71, 130.55 (major), 130.32 (minor), 129.62 (major), 129.57 (minor), 128.60 (minor), 128.52 (major), 128.35, 128.10, 127.99, 127.73, 127.46, 127.19, 121.16 (d, \(J = 13.42\) Hz) (minor), 120.58 (d, \(J = 12.46\) Hz) (major), 67.14 (major), 66.78 (minor), 56.24 (d, \(J = 24.92\) Hz) (minor), 55.54 (d, \(J = 24.92\) Hz) (major), 47.73 (major), 47.24 (minor), 32.20 (major), 31.20 (minor), 24.60 (minor), 23.97 (major); \(^{19}\)F NMR (CDCl\(_3\), 564 MHz): rotameric mixture, \(\delta -124.13\) (d, \(J = 26.31\) Hz) (major), -124.25 (d, \(J = 29.60\) Hz) (minor); HRMS (ESI): Calculated for C\(_{26}\)H\(_{25}\)FNO\(_2\), [M+H]^+ m/z 402.1864. Found 402.1864.
**tert-Butyl 2-(1-fluoro-2,2-diphenylvinyl)piperidine-1-carboxylate (3c):** Eluent: PE/EA (20:1). Yield (54 mg, 71%). White solid, mp 86 - 87 °C. $^1$H NMR (CDCl$_3$, 400 MHz): δ 7.37 – 7.20 (m, 10H), 5.10 – 5.02 (m, 1H), 4.02 (dd, $J$ = 9.62 Hz, $J$ = 3.21 Hz, 1H), 3.21 (tt, $J$ = 12.82 Hz, $J$ = 3.21 Hz, 1H), 1.97 – 1.92 (m, 1H), 1.78 – 1.66 (m, 4H), 1.47 – 1.41 (m, 1H), 1.32 (s, 9H); $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 159.14 (d, $J$ = 270.29 Hz), 155.06, 137.92 (d, $J$ = 7.67 Hz), 137.63, 130.27 (d, $J$ = 1.92 Hz), 129.80 (d, $J$ = 4.79 Hz), 128.49, 128.04, 127.54, 127.17, 120.96 (d, $J$ = 15.34 Hz), 79.77, 49.22 (d, $J$ = 22.04 Hz), 41.78 (d, $J$ = 4.79 Hz), 29.69, 28.38, 24.91, 20.43; $^{19}$F NMR (CDCl$_3$, 564 MHz) δ -108.65; HRMS (ESI): Calculated for C$_{24}$H$_{28}$FNNaO$_2$, [M+Na]$^+$ m/z 404.1995. Found 404.1995.

**tert-Butyl (2-fluoro-3,3-diphenylallyl)carbamate (3d):** Eluent: PE/EA (20:1). Yield (39 mg, 60%). White solid, mp 76 - 77 °C. $^1$H NMR (CDCl$_3$, 400 MHz) 7.38 – 7.31 (m, 3H), 7.29 – 7.23 (m, 5H), 7.20 – 7.18 (m, 2H), 4.75 (brs, 1H), 4.00 (dd, $J$ = 19.23 Hz, $J$ = 5.50 Hz, 2H), 1.44 (s, 9H); $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 155.54, 153.30 (d, $J$ = 261.66 Hz), 137.64 (d, $J$ = 6.71 Hz), 136.84, 130.25 (d, $J$ = 2.88 Hz), 129.72 (d, $J$ = 4.79 Hz), 128.68, 128.14, 127.91, 127.52, 122.94 (d, $J$ = 13.42 Hz), 79.85, 40.14 (d, $J$ = 27.80 Hz), 28.46; $^{19}$F NMR (CDCl$_3$, 564 MHz): δ -113.47 (t, $J$ = 19.51 Hz); HRMS (ESI): Calculated for C$_{20}$H$_{22}$NNaO$_2$F, [M+Na]$^+$ m/z 350.1527. Found 350.1529.

**tert-Butyl (3-fluoro-4,4-diphenylbut-3-en-2-yl)carbamate (3e):** Eluent: PE/EA
(20:1). Yield (51 mg, 75%). White solid, mp 89 - 90 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.37 – 7.23 (m, 10H), 4.84 (brs, 1H), 4.61 – 4.50 (m, 1H), 1.44 (s, 9H), 1.35 (d, $J$ = 6.87 Hz, 6H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 156.17 (d, $J$ = 262.62 Hz), 154.51, 137.46, 137.05, 130.25 (d, $J$ = 2.88 Hz), 129.72 (d, $J$ = 4.79 Hz), 128.66, 128.11, 127.82, 127.37, 120.45 (d, $J$ = 14.38 Hz), 79.59, 45.84 (d, $J$ = 27.80 Hz), 28.47, 19.64; $^{19}$F NMR (CDCl$_3$, 564 MHz): $\delta$ -125.42 (d, $J$ = 26.31 Hz); HRMS (ESI): Calculated for C$_{21}$H$_{24}$NNaO$_2$F, [M+Na]$^+$ m/z 364.1683. Found 364.1682.

tert-Butyl (3-fluoro-1,4,4-triphenylbut-3-en-2-yl)carbamate (3f): Eluent: PE/EA (20:1). Yield (70 mg, 84%). White solid, mp 85 - 86 °C. $^1$H NMR (CDCl$_3$, 400 MHz) rotameric mixture: $\delta$ 7.30 – 7.18 (m, 11H), 7.11 – 7.10 (m, 2H), 6.77 (m, 2H), 5.00 (brs, 1H), 4.70 – 4.61 (m, 1H), 2.97 – 2.94 (m, 2H), 1.46 (s, 9H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 154.46, 153.82 (d, $J$ = 263.58 Hz), 137.02, 130.06 (d, $J$ = 1.92 Hz), 129.64, 129.45 (d, $J$ = 4.79 Hz), 128.46, 128.29, 128.06, 127.58, 127.37, 126.76, 122.60 (d, $J$ = 12.46 Hz), 79.75, 51.73 (d, $J$ = 25.88 Hz), 39.75, 28.44; $^{19}$F NMR (CDCl$_3$, 564 MHz): $\delta$ -125.06 (d, $J$ = 28.18 Hz); ESI: Calculated for C$_{27}$H$_{28}$FNNaO$_2$, [M+Na]$^+$ m/z 440.21. Found 440.25.

tert-Butyl (3-fluoro-1-hydroxy-4,4-diphenylbut-3-en-2-yl)carbamate (3g): Eluent: PE/EA (2:1). Yield (53 mg, 82%). White solid, mp 129 - 130 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.38 – 7.23 (m, 10H), 5.08 (brs, 1H), 4.62 – 4.54 (m, 1H), 3.76 – 3.68 (m, 2H), 2.40 (m, 1H), 1.43 (s, 9H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 155.43, 153.47 (d, $J$ = 261.66 Hz), 137.21, 136.72, 130.28 (d, $J$ = 2.88 Hz), 129.70 (d, $J$ = 4.79 Hz), 128.74, 128.15, 128.00, 127.62, 123.37 (d, $J$ = 13.42 Hz), 80.25, 63.96, 52.11 (d, $J$ = 23 Hz), 28.41; $^{19}$F NMR (CDCl$_3$, 564 MHz): $\delta$ -122.29 (d, $J$ = 23.84 Hz); ESI:
Calculated for C$_{21}$H$_{24}$FNNaO$_{3}$, [M+Na]$^{+}$ m/z 380.17. Found 380.15.

tert-Butyl (3-fluoro-1-(methylthio)-4,4-diphenylbut-3-en-2-yl)carbamate (3h):
Eluent: PE/EA (20:1). Yield (60 mg, 75%). Colorless oil. $^1$H NMR (CDCl$_3$, 400 MHz):
$\delta$ 7.39 – 7.21 (m, 10H), 4.92 – 4.90 (m, 1H), 4.66 – 4.53 (m, 1H), 2.50 – 2.43 (m, 2H), 2.02 (s, 3H), 2.00 – 1.91 (m, 2H), 1.45 (s, 9H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$
154.78 (d, $J$ = 264.54 Hz), 154.64, 137.19, 136.89, 130.30 (d, $J$ = 1.92 Hz), 129.65 (d, $J$ = 5.75 Hz), 128.68, 128.14, 127.92, 127.51, 122.05 (d, $J$ = 16.29 Hz), 79.79, 49.53 (d, $J$ = 24.92 Hz), 33.43, 30.38, 28.43, 15.54; $^{19}$F NMR (CDCl$_3$, 564 MHz): $\delta$
123.96 (d, $J$ = 30.34 Hz). ESI: Calculated for C$_{23}$H$_{28}$FNNaO$_{2}$S, [M+Na]$^{+}$ m/z 424.18. Found 424.15.

$$
\text{tert-Butyl 2-(1-fluoro-2,2-bis(4-fluorophenyl)vinyl)pyrrolidine-1-carboxylate (3i):}
$$
Eluent: PE/EA (20:1). Yield (73 mg, 91%). White solid, mp 134 -135 °C. $^1$H NMR (CDCl$_3$, 400 MHz): rotameric mixture, $\delta$ 7.34 – 7.16 (m, 4H), 7.05 (t, $J$ = 8.70 Hz, 2H), 7.00 – 6.96 (m, 2H), 4.41 – 4.35 (m, 1H), 3.54 – 3.44 (m, 2H), 2.21 – 2.13 (m, 2H), 2.04 – 1.95 (m, 1H), 1.81 – 1.75 (m, 1H), 1.42 (s, 9H); $^{13}$C NMR (CDCl$_3$, 100 MHz): rotameric mixture, $\delta$
162.33 (d, $J$ = 247.03 Hz), 161.85 (d, $J$ = 247.03 Hz), 156.84 (d, $J$ = 266.20 Hz), 154.06, 133.67, 133.28, 132.27, 131.32 (dd, $J$ = 7.67 Hz, $J$
= 5.37 Hz), 118.17 (d, $J$ = 15.34 Hz), 115.54 (d, $J$ = 21.48 Hz), 115.15 (d, $J$ = 20.71 Hz), 79.89 (79.34), 55.49 (d, $J$ = 24.55 Hz), 47.40, 33.13 (31.55), 28.71, (24.46) 23.80; $^{19}$F NMR (CDCl$_3$, 564 MHz): rotameric mixture, $\delta$
-113.83 (s) (major), -114.62 (s) (minor), -114.28 (s) (major), -114.80 (s) (minor), -121.58 (d, $J$ = 24.66 Hz) (major), -122.62 (d, $J$ = 24.66 Hz) (minor); ESI: Calculated for C$_{23}$H$_{25}$F$_{3}$NO$_{2}$, [M+H]$^{+}$ m/z
404.18. Found 404.10.

**tert-Butyl 2-(2,2-bis(4-chlorophenyl)-1-fluorovinyl)pyrrolidin-1-carboxylate (3j):**
Eluent: PE/EA (20:1). Yield (84 mg, 96%). White solid, mp 99 – 100 °C. $^1$H NMR (CDCl$_3$, 400 MHz): rotameric mixture, $\delta$ 7.34 - 7.22 (m, 5H), 7.16 – 7.12 (m, 3H), 4.39 – 4.33 (m, 1H), 3.53 – 3.43 (m, 2H), 2.20 – 1.94 (m, 3H), 1.80 – 1.73 (m, 1H), 1.40 (s, 9H); $^{13}$C NMR (CDCl$_3$, 100 MHz): rotameric mixture, $\delta$ 157.30 (d, $J = 269.33$ Hz), 153.99, 135.83, 135.46, 133.92, 133.25, 131.90, 130.95 (d, $J = 5.75$ Hz), 128.81, 128.43, 118.04 (d, $J = 15.34$ Hz), 79.98 (79.42), 55.50 (d, $J = 23.96$ Hz), 47.40, 33.12 (31.46), 28.69, (24.52) 23.79; $^{19}$F NMR (CDCl$_3$, 282 MHz): rotameric mixture, $\delta$ -119.98 (d, $J = 26.01$ Hz) (major), -121.09 (d, $J = 26.01$ Hz) (minor); ESI: Calculated for C$_{23}$H$_{25}$Cl$_2$FNO$_2$, [M+H]$^+$ m/z 436.12. Found 436.10.

1-Benzyl-2-(2,2-bis(4-chlorophenyl)-1-fluorovinyl)pyrrolidine (3k): Eluent: PE/EA (20:1). Yield (38 mg, 45%). Colorless oil. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.33 (d, $J = 8.70$ Hz, 2H), 7.30 – 7.21 (m, 7H), 7.08 (d, $J = 8.70$ Hz, 2H), 7.00 (d, $J = 8.24$ Hz, 2H), 3.84 (d, $J = 13.28$ Hz, 1H), 3.36 (d, $J = 13.28$ Hz, 1H), 3.28 (dt, $J = 28.39$ Hz, $J = 8.24$ Hz, 1H), 3.04 – 3.00 (m, 1H), 2.28 – 2.22 (m, 1H), 2.12 – 2.08 (m, 1H), 2.03 – 1.90 (m, 2H), 1.77 – 1.72 (m, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 157.17 (d, $J = 267.41$ Hz), 139.11, 136.35 (d, $J = 7.67$ Hz), 135.47, 133.82, 133.18, 131.87 (d, $J = 2.88$ Hz), 131.00 (d, $J = 4.79$ Hz), 128.87 (d, $J = 3.83$ Hz), 128.29 (d, $J = 1.92$ Hz), 127.12, 120.89 (d, $J = 15.34$ Hz), 62.04 (d, $J = 23.00$ Hz), 58.26, 54.02, 29.14, 23.19; $^{19}$F NMR (CDCl$_3$, 282 MHz): $\delta$ -119.76 (d, $J = 26.01$ Hz); HRMS (ESI): Calculated for C$_{25}$H$_{23}$Cl$_2$FN, [M+H]$^+$ m/z 426.1186. Found 426.1188.
4-(4,4-Bis(4-chlorophenyl)-3-florobut-3-en-2-yl)morpholine (3l): Eluent: PE/EA (10:1). Yield (36.6 mg, 48%). Colorless oil. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.33 (d, $J$ = 8.24 Hz, 2H), 7.27 – 7.24 (m, 2H), 7.18 – 7.16 (m, 2H), 7.10 (d, $J$ = 8.24 Hz, 2H), 3.72 – 3.62 (m, 4H), 3.30 (dq, $J$ = 31.60 Hz, $J$ = 6.87 Hz, 1H), 2.62 – 2.59 (m, 2H), 2.42 – 2.39 (m, 2H), 1.32 (d, $J$ = 6.87 Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 157.89 (d, $J$ = 273.16 Hz), 136.41 (d, $J$ = 8.63 Hz), 135.13, 133.98, 133.38, 131.70 (d, $J$ = 2.88 Hz), 130.96 (d, $J$ = 5.75 Hz), 129.05, 128.42, 67.39, 58.22 (d, $J$ = 23.00 Hz), 50.50, 14.87; $^{19}$F NMR (CDCl$_3$, 282 MHz): $\delta$ -114.82 (d, $J$ = 26.00 Hz); HRMS (ESI): Calculated for C$_{20}$H$_{21}$Cl$_2$FNO, [M+H]$^+$ m/z 380.0979. Found 380.0981.

**tert-Butyl 2-(1-fluoro-2-(4-fluorophenyl)-2-phenylvinyl)pyrrolidine-1-carboxylate (3m):** Z/E = 2:3. Eluent: PE/EA (20:1). Yield (66 mg, 86%). White solid, mp 107 – 108 °C. $^1$H NMR (CDCl$_3$, 400 MHz): rotameric mixture, $\delta$ 7.37 – 7.29 (m, 3H), 7.28 – 7.20 (m, 4H), 7.04 (t, $J$ = 8.70 Hz, 1H), 6.99 – 6.95 (m, 1H), 4.44 – 4.37 (m, 1H), 3.53 – 3.45 (m, 2H), 2.21 – 2.14 (m, 2H), 2.03 – 1.94 (m, 1H), 1.79 – 1.73 (m, 1H), 1.42 (s, 9H); $^{13}$C NMR (CDCl$_3$, 100 MHz): rotameric mixture, $\delta$ 162.26 (d, $J$ = 247.28 Hz), 161.78 (d, $J$ = 247.28 Hz), 156.82 (d, $J$ = 265.50 Hz), 156.70 (d, $J$ = 269.33 Hz), 154.12, 137.60, 137.30, 133.87, 133.47, 132.30, 131.45 – 131.32 (m), 130.58 (d, $J$ = 2.88 Hz), 129.64 (d, $J$ = 4.79 Hz), 128.48, 128.18, 127.75, 127.34, 119.12, 115.41 (d, $J$ = 21.09 Hz), 115.04 (d, $J$ = 21.09 Hz), 79.85, 55.54 (d, $J$ = 23.96 Hz), 47.38, 33.20, 28.72, 23.80; $^{19}$F NMR (CDCl$_3$, 282 MHz): rotameric mixture, $\delta$ -114.11 (major), -114.56 (major), -114.89 (minor), -115.07 (minor), -121.42 (d, $J$ = 26.31 Hz) (major), -122.26 (d, $J$ = 26.31 Hz, 1H), -123.06 (d, $J$ = 26.31 Hz) (minor); ESI: Calculated for C$_{23}$H$_{26}$F$_2$NO$_2$, [M+H]$^+$ m/z 386.19. Found 386.10.
**cis-**-** tert**-Butyl 2-(2-(2-chlorophenyl)-1-fluoro-2-phenylvinyl)pyrrolidin-1-carboxylate ((**Z**)-3n): Eluent: PE/EA (20:1). Yield (18 mg, 22%). White solid, mp 117 – 118 °C. $^1$H NMR (CDCl$_3$, 400 MHz): rotameric mixture, δ 7.77 – 7.21 (m, 9H), 4.40 – 4.12 (m, 1H), 3.54 – 3.27 (m, 2H), 2.08 – 1.96 (m, 3H), 1.72 – 1.62 (m, 1H), 1.46 – 1.43 (m, 9H); $^{19}$F NMR (CDCl$_3$, 282 MHz): rotameric mixture, δ – 120.90 (d, $J$ = 19.73 Hz) (minor), – 123.25 (d, $J$ = 24.66 Hz) (major); HRMS (ESI): Calculated for C$_{23}$H$_{25}$ClFNNaO$_2$, [M+Na]$^+$ m/z 424.1450. Found 424.1455.

**trans-**-** tert**-Butyl 2-(2-(2-chlorophenyl)-1-fluoro-2-phenylvinyl)pyrrolidin-1-carboxylate ((**E**)-3n): Eluent: PE/EA (20:1). Yield (57 mg, 71%). White solid, mp 96 – 97 °C. $^1$H NMR (CDCl$_3$, 400 MHz): rotameric mixture, δ 7.44 – 7.38 (m, 2H), 7.32 – 7.23 (m, 7H), 4.74 (dt, $J$ = 27.02 Hz, $J$ = 6.41 Hz, 1H), 3.53 – 3.44 (m, 2H), 2.27 – 2.14 (m, 2H), 2.05 – 2.00 (m, 1H), 1.83 – 1.81 (m, 1H), 1.51 – 1.39 (m, 9H); $^{13}$C NMR (CDCl$_3$, 100 MHz): rotameric mixture, δ 157.58 (d, $J$ = 256.87 Hz), 154.20, 136.66, 136.49, 134.12, 131.65, 129.90, 129.76, 128.92, 128.28, 127.46, 126.68, 118.04 (d, $J$ = 26.84 Hz), 79.94 (79.23), 54.74 (d, $J$ = 23.96 Hz), 47.27, 32.75 (major), 31.26 (minor), 28.69, (24.43) 23.81; $^{19}$F NMR (CDCl$_3$, 282 MHz): rotameric mixture, δ -114.52 (major), -115.10 (minor); HRMS (ESI): Calculated for C$_{23}$H$_{25}$ClFNNaO$_2$, [M+Na]$^+$ m/z 424.1450. Found 424.1455.

**(E/Z)-**tert-Butyl 2-(1-fluoro-2-(4-(methylsulfonyl)phenyl)prop-1-en-1-yl)piperidin-1-carboxylate (3o): $Z/E$ = 1:1. Eluent: PE/EA (20:1). Yield (72 mg, 91%). Colorless oil. $^1$H NMR (CDCl$_3$, 400 MHz): δ 7.83 (t, $J$ = 8.24 Hz, 2H), 7.46 (d, $J$ =
8.24 Hz, 1H), 7.39 (d, J = 8.24 Hz, 1H), 5.13 (dd, J = 29.31 Hz, J = 5.04 Hz, 0.5H),
4.81 (d, J = 28.39 Hz, 0.5H), 3.95 (dd, J = 13.17 Hz, J = 2.99 Hz, 0.5H), 3.84 (d, J =
10.53 Hz, 0.5H), 3.04 – 2.94 (m, 4H), 1.98 (d, J = 2.75 Hz, 1.5H), 1.90 (d, J = 3.66
Hz, 1.5H), 1.81 – 1.69 (m, 1H), 1.60 – 1.56 (m, 4H), 1.45 – 1.36 (m, 5.5H), 1.24 –
1.17 (m, 4.5H); 13C NMR (CDCl3, 100 MHz): δ 158.99 (d, J = 263.58 Hz), 158.50 (d,
J = 265.50 Hz), 154.82, 154.48, 145.08 (d, J = 9.58 Hz), 144.03, 139.01, 138.55,
129.27 (d, J = 2.88 Hz), 129.08 (d, J = 4.79 Hz), 127.43, 127.03, 114.06 (d,
J = 21.09 Hz), 111.89 (d, J = 11.50 Hz), 79.85, 79.55, 48.16 (d, J = 23.00 Hz), 44.37 (d, J =
5.75 Hz), 41.54, 29.17, 28.35, 28.13, 28.04, 24.65, 20.20, 20.15, 16.36, 16.25; 19F
NMR (CDCl3, 282 MHz): δ -107.03 – -108.19 (m), -109.80 (d, J = 26.01 Hz); HRMS

cis-tert-Butyl 2-(1-fluoro-2-(4-(trifluoromethyl)phenyl)prop-1-en-1-yl)piperi-
dine-1-carboxylate ((Z)-3p): Eluent: PE/EA (20:1). Yield (15.4 mg, 20%). Colorless
oil. 1H NMR (CDCl3, 400 MHz): δ 7.58 – 7.56 (m, 2H), 7.44 – 7.42 (m, 2H), 5.24 –
5.16 (m, 1H), 4.04 – 4.01 (m, 1H), 3.09 – 3.02 (m, 1H), 2.05 – 2.02 (m, 3H), 1.90 –
1.67 (m, 6H), 1.48 – 1.47 (m, 9H); 13C NMR (CDCl3, 100 MHz): δ 158.18 (d, J =
263.58 Hz), 155.12, 142.18, 129.03 (q, J = 32.59 Hz), 128.69 (d, J = 3.83 Hz), 125.10
(d, J = 2.88 Hz), 124.31 (q, J = 271.25 Hz), 112.44 (d, J = 12.46 Hz), 80.07, 48.39 (d,
J = 23.00 Hz), 41.80, 28.61, 28.37, 24.95, 20.44, 16.70 (d, J = 3.83 Hz); 19F NMR
(CDCl3, 282 MHz): δ -62.44 (s, 3H), -110.79 (d, J = 34.68 Hz, 1H); ESI: Calculated
for C20H26F4NO2, [M+H]+ m/z 388.18. Found 388.10.

trans-tert-Butyl 2-(1-fluoro-2-(4-(trifluoromethyl)phenyl)prop-1-en-1-yl)piperi-
dine-1-carboxylate ((E)-3p): Eluent: PE/EA (20:1). Yield (41.5 mg, 54%). White
solid, mp 68 – 69 °C 1H NMR (CDCl3, 400 MHz): δ 7.57 (d, J = 7.33 Hz, 2H), 7.34 (d,
J = 7.33 Hz, 2H), 4.89 (d, J = 31.14 Hz, 1H), 3.92 (d, J = 12.82 Hz, 1H), 3.11 – 3.05 (m, 1H), 1.96 – 1.94 (m, 3H), 1.80 – 1.62 (m, 5H), 1.38 – 1.35 (m, 1H), 1.24 (s, 9H); 
13C NMR (CDCl3, 100 MHz): δ 158.90 (d, J = 262.62 Hz), 154.76, 143.25 (d, J = 8.63 Hz), 129.35 (q, J = 32.59 Hz), 128.83 (d, J = 2.88 Hz), 125.47 (d, J = 2.88 Hz), 124.26 (q, J = 272.20 Hz), 114.57 (d, J = 21.09 Hz), 79.72, 48.40 (d, J = 23 Hz), 41.68 (d, J = 3.83 Hz), 29.44, 28.27, 24.96, 20.52, 16.5 (d, J = 8.63 Hz); 19F NMR (CDCl3, 282 MHz): δ -62.54 (s, 3H), -108.68 – -109.75 (m, 1H); ESI: Calculated for C20H26F4NO2, [M+H]+ m/z 388.18. Found 388.10.

cis-tert-Butyl 2-(1-fluoro-2-(p-tolyl)vinyl)pyrrolidine-1-carboxylate (Z)-3q:
Eluent: PE/EA (20:1). Yield (24 mg, 39%). White solid, mp 78 – 79 °C. 1H NMR (CDCl3, 400 MHz): rotameric mixture, δ 7.36 (d, J = 7.79 Hz, 2H), 7.13 (d, J = 6.87 Hz, 2H), 5.52 (d, J = 38.93 Hz, 1H), 4.52 – 4.34 (m, 1H), 3.50 – 3.49 (m, 2H), 2.33 (s, 3H), 2.09 – 1.98 (m, 3H), 1.90 – 1.84 (m, 1H), 1.47 – 1.37 (m, 9H); 13C NMR (CDCl3, 100 MHz): rotameric mixture, δ 159.09 (d, J = 267.41 Hz), 154.43, 136.94, 130.46, 129.30, 128.47, 105.60, 79.92, 58.30 (d, J = 32.59 Hz), 46.82 46.48, 30.61 (29.85), 28.52, (24.06) 23.24, 21.32; 19F NMR (CDCl3, 282 MHz): rotameric mixture, δ -116.85 (dd, J = 39.01 Hz, J = 17.34 Hz); ESI: Calculated for C18H24FNNaO2, [M+Na]+ m/z 328.18. Found 328.15.

trans-tert-Butyl 2-(1-fluoro-2-(p-tolyl)vinyl)pyrrolidine-1-carboxylate (E)-3q:
Eluent: PE/EA (20:1). Yield (19 mg, 31%). Colorless oil. 1H NMR (CDCl3, 400 MHz): rotameric mixture, δ 7.29 – 7.11 (m, 4H), 6.18 (d, J = 21.52 Hz, 1H), 4.78 – 4.71 (m, 1H), 3.52 – 3.43 (m, 2H), 2.33 (s, 3H), 2.25 – 1.96 (m, 3H), 1.85 – 1.79 (m, 1H), 1.46 – 1.25 (m, 9H); 13C NMR (CDCl3, 100 MHz): rotameric mixture, δ 160.70 (d, J = 261.66 Hz), 154.21, 136.72, 130.50 (d, J = 12.46 Hz), 129.21, 128.70, 108.13 (d, J =
28.75 Hz), 79.92 (79.47), 54.24 (d, $J = 24.92$ Hz), 47.46 (minor), 47.10 (major), 32.26 (major), 31.51 (minor), 28.50, 24.45 (minor), 23.95 (major), 21.26; $^{19}$F NMR (CDCl$_3$, 282 MHz): rotameric mixture, $\delta$ -116.70 – -116.87 (m) (minor), -117.47 – -117.64 (m) (major); ESI: Calculated for C$_{18}$H$_{24}$FNNaO$_2$, [M+Na]$^+$ m/z 328.18. Found 328.15.

cis-tert-Butyl 2-(1-fluoro-2-(naphthalen-2-yl)vinyl)piperidine-1-carboxylate ((Z)-3r): Eluent: PE/EA (20:1). Yield (38 mg, 54%). White solid, mp 82 – 83 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.93 (s, 1H), 7.83 – 7.80 (m, 3H), 7.69 – 7.67 (m, 1H), 7.49 – 7.45 (m, 2H), 5.73 (d, $J = 39.84$ Hz, 1H), 5.15 – 5.07 (m, 1H), 4.12 (d, $J = 12.36$ Hz, 1H), 3.03 (t, $J = 12.82$ Hz, 1H), 2.16 (d, $J = 13.28$ Hz, 1H), 1.75 – 1.61 (m, 4H), 1.52 – 1.49 (m, 10H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 158.75 (d, $J = 273.16$ Hz), 155.30, 133.54, 132.49, 130.81, 128.06 (d, $J = 3.83$ Hz), 127.61, 127.53, 126.65 (d, $J = 7.67$ Hz), 126.22, 126.00, 107.03 (d, $J = 7.67$ Hz), 80.18, 51.80 (d, $J = 24.92$ Hz), 40.63, 28.50, 26.26, 25.27, 19.96; $^{19}$F NMR (CDCl$_3$, 282 MHz): $\delta$ -109.37 (d, $J = 43.35$ Hz); ESI : Calculated for C$_{22}$H$_{26}$FNNaO$_2$, [M+Na]$^+$ m/z 378.19. Found 378.20.

trans-tert-Butyl 2-(1-fluoro-2-(naphthalen-2-yl)vinyl)piperidine-1-carboxylate ((E)-3r): Eluent: PE/EA (20:1). Yield (25 mg, 35%). White solid, mp 99 – 100 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.82 – 7.79 (m, 3H), 7.68 (s, 1H), 7.50 – 7.43 (m, 2H), 7.37 (d, $J = 8.24$ Hz, 1H), 6.36 (d, $J = 23.81$ Hz, 1H), 5.36 (dd, $J = 30.22$ Hz, $J = 4.58$ Hz, 1H), 4.00 (dd, $J = 13.05$ Hz, $J = 2.75$ Hz, 1H), 3.15 (tt, $J = 13.28$ Hz, $J = 3.21$ Hz, 1H), 2.04 – 2.00 (m, 1H), 1.88 – 1.81 (m, 1H), 1.79 – 1.71 (m, 3H), 1.51 – 1.42 (m, 1H), 1.17 (s, 9H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 163.52 (d, $J = 263.58$ Hz), 155.12, 133.49, 132.40, 131.00, 128.18, 127.92, 127.66, 127.36 (d, $J = 2.88$ Hz), 126.82 (d, $J = 1.92$ Hz), 126.34, 126.00, 108.77 (d, $J = 27.80$ Hz), 79.85, 48.30 (d, $J = 23.00$ Hz), 41.87, 29.12, 28.16, 24.88, 20.43; $^{19}$F NMR (CDCl$_3$, 282 MHz): $\delta$ -102.24 (t, $J =$
cis-tert-Butyl 2-(2-(1,1'-biphenyl)-4-yl)-1-fluorovinyl)piperidine-1-carboxylate

\((Z)\text{-3s}\): Eluent: PE/EA (20:1). Yield (40 mg, 52%). White solid, mp 119 – 120 °C. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.63 – 7.57 (m, 6H), 7.46 (t, \(J = 7.23\) Hz, 2H), 7.36 (t, \(J = 7.33\) Hz, 1H), 5.62 (dd, \(J = 40.30\) Hz, \(J = 0.92\) Hz, 1H), 5.11 – 5.06 (m, 1H), 4.11 (d, \(J = 12.82\) Hz, 1H), 3.00 (t, \(J = 12.82\) Hz, 1H), 2.14 (d, \(J = 13.28\) Hz, 1H), 1.74 – 1.59 (m, 4H), 1.54 – 1.48 (m, 10H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 158.64 (d, \(J = 273.11\) Hz), 155.27, 140.74, 139.87, 132.33, 129.02 (d, \(J = 7.67\) Hz), 128.87, 127.40, 127.19, 127.02, 106.56 (d, \(J = 7.67\) Hz), 80.16, 51.75 (d, \(J = 33.75\) Hz), 40.59, 28.49, 26.23, 25.26, 19.95; \(^{19}\)F NMR (CDCl\(_3\), 282 MHz): \(\delta\) -109.30 (d, \(J = 34.68\) Hz); ESI: Calculated for C\(_{22}\)H\(_{26}\)FNNaO\(_2\), [M+Na]\(^+\) m/z 378.19. Found 378.20.

trans-tert-Butyl 2-(2-(1,1'-biphenyl)-4-yl)-1-fluorovinyl)piperidine-1-carboxylate

\((E)\text{-3s}\): Eluent: PE/EA (20:1). Yield (31 mg, 41%). White solid, mp 99 – 100 °C. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.59 – 7.56 (m, 4H), 7.44 (t, \(J = 7.33\) Hz, 2H), 7.37 – 7.29 (m, 3H), 6.24 (d, \(J = 23.36\) Hz, 1H), 5.32 (dd, \(J = 31.14\) Hz, \(J = 4.58\) Hz, 1H), 4.02 (dd, \(J = 11.22\) Hz, \(J = 3.21\) Hz, 1H), 3.14 (tt, \(J = 12.82\) Hz, \(J = 2.75\) Hz, 1H), 2.01 – 1.98 (m, 1H), 1.89 – 1.72 (m, 4H), 1.50 – 1.42 (m, 1H), 1.23 (s, 9H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 163.49 (d, \(J = 263.58\) Hz), 155.09, 140.75, 139.92, 132.50 (d, \(J = 13.42\) Hz), 129.01 (d, \(J = 2.88\) Hz), 128.90, 127.44, 127.30, 127.02, 108.33 (d, \(J = 27.80\) Hz), 79.88, 48.09 (d, \(J = 22.04\) Hz), 41.78, 29.12, 28.17, 24.87, 20.41; \(^{19}\)F NMR (CDCl\(_3\), 282 MHz): \(\delta\) -102.27 (t, \(J = 26.01\) Hz); ESI: Calculated for C\(_{24}\)H\(_{29}\)FNO\(_2\), [M+H]\(^+\) m/z 382.21. Found 382.10.
**cis-**tert-Butyl 2-(1-fluoro-2-(3-methoxyphenyl)vinyl)pyrrolidine-1-carboxylate

((Z)-3t): Eluent: PE/EA (20:1). Yield (28 mg, 43.5%). Colorless oil. $^1$H NMR (CDCl$_3$, 400 MHz): rotameric mixture, δ 7.25 – 7.20 (m, 1H), 7.03 – 7.01 (m, 2H), 6.78 – 6.77 (m, 1H), 5.51 (d, $J$ = 38.47 Hz, 1H), 4.47 – 4.37 (m, 1H), 3.79 (s, 3H), 3.49 – 3.48 (m, 2H), 2.20 – 1.99 (m, 3H), 1.88 – 1.85 (m, 1H), 1.46 – 1.41 (m, 9H); $^{13}$C NMR (CDCl$_3$, 100 MHz): rotameric mixture, δ 159.83 (d, $J$ = 279.87 Hz), 159.69, 154.39, 134.56, 129.50, 121.18, 113.86 (d, $J$ = 7.67 Hz), 112.98, 105.65, 79.98, 58.28 (d, $J$ = 31.63 Hz), 55.28, 46.79 (minor), 46.48 (major), 30.60 (major), 29.65 (minor), 28.52, 24.00 (minor), 23.22 (major); $^{19}$F NMR (CDCl$_3$, 282 MHz): rotameric mixture, δ -114.99 (dd, $J$ = 39.01 Hz, $J$ = 13.00 Hz); ESI: Calculated for C$_{18}$H$_{24}$FNNaO$_3$, [M+Na]$^+$ m/z 344.17. Found 344.20.

![cis-tert-Butyl 2-(1-fluoro-2-(3-methoxyphenyl)vinyl)pyrrolidine-1-carboxylate ((Z)-3t)](image)

**trans-**tert-Butyl 2-(1-fluoro-2-(3-methoxyphenyl)vinyl)pyrrolidine-1-carboxylate

((E)-3t): Eluent: PE/EA (20:1). Yield (28 mg, 43.5%). Colorless oil. $^1$H NMR (CDCl$_3$, 400 MHz) rotameric mixture: δ 7.26 – 7.22 (m, 1H), 7.14 – 6.97 (m, 1H), 6.80 – 6.75 (m, 2H), 6.19 (d, $J$ = 21.52 Hz, 1H), 4.81 – 4.74 (m, 1H), 3.80 (s, 3H), 3.53 – 3.44 (m, 2H), 2.26 – 1.98 (m, 3H), 1.86 – 1.82 (m, 1H), 1.46 – 1.31 (m, 9H); $^{13}$C NMR (CDCl$_3$, 100 MHz): rotameric mixture, δ 161.36 (d, $J$ = 264.54 Hz), 159.62, 154.18, 134.85 (d, $J$ = 12.46 Hz), 129.47, 121.35, 114.78, 112.19, 108.15 (d, $J$ = 26.84 Hz), 79.96 (79.52), 55.32, 54.23 (d, $J$ = 23.00 Hz), 47.39 (minor), 47.09 (major), 32.24 (major), 31.28 (minor), 28.49, 24.54 (minor), 23.94 (major); $^{19}$F NMR (CDCl$_3$, 282 MHz) rotameric mixture: δ -116.83 (m) (minor), -116.38 (m) (major); ESI: Calculated for C$_{18}$H$_{24}$FNNaO$_3$, [M+Na]$^+$ m/z 344.17. Found 344.20.

![trans-tert-Butyl 2-(1-fluoro-2-(3-methoxyphenyl)vinyl)pyrrolidine-1-carboxylate ((E)-3t)](image)

**tert-Butyl** 2-(1-fluoro-2-(4-methoxyphenyl)vinyl)pyrrolidine-1-carboxylate (3u):

Z/E = 3:2. Eluent: PE/EA (20:1). Yield (43 mg, 67%). Colorless oil. $^1$H NMR (CDCl$_3$, 

![tert-Butyl 2-(1-fluoro-2-(4-methoxyphenyl)vinyl)pyrrolidine-1-carboxylate (3u)](image)
400 MHz): rotameric mixture, δ 7.40 – 7.38 (d, J = 8.7 Hz, 2H), 7.13 – 7.11 (m, 0.67H), 6.85 (d, J = 8.7 Hz, 3.5H), 6.15 (d, J = 21.52 Hz, 0.66Hz), 5.47 (d, J = 38.75 Hz, 1H), 4.76 – 4.69 (m, 0.68H), 4.49 – 4.32 (m, 1H), 3.79 (s, 5H), 3.48 – 3.44 (m, 3.33H), 2.23 – 1.97 (m, 5H), 1.88 – 1.80 (m, 1.69H), 1.47 – 1.29 (m, 15H); 13C NMR (CDCl3, 100 MHz): rotameric mixture, δ 158.63, 158.28 (d, J = 272.20 Hz), 154.45, 154.21, 129.94, 129.81, 126.02, 125.90, 113.98, 107.74 (d, J = 35.46 Hz), 105.23, 79.88, 58.29 (d, J = 27.80 Hz), 55.35, 54.15 (d, J = 14.38 Hz), 47.09, 46.48, 32.21, 30.61, 28.53, 23.96, 23.25; 19F NMR (CDCl3, 282 MHz): rotameric mixture, δ -117.62 – -117.81 (m) (minor), -118.42 – -118.59 (m) (major), -118.84 (dd, J = 39.01 Hz, J = 13.00 Hz); ESI: Calculated for C18H24FNNaO3, [M+Na]+ m/z 344.17. Found 344.20.

*cis-tert*-Butyl 2-(1-fluoro-2-(4-(methylthio)phenyl)vinyl)piperidine-1-carboxylate ((Z)-3v): Eluent: PE/EA (20:1). Yield (29 mg, 41%). White solid, mp 79 – 80 °C. 1H NMR (CDCl3, 400 MHz): δ 7.40 (d, J = 8.24 Hz, 2H), 7.20 (d, J = 8.24 Hz, 2H), 5.49 (d, J = 39.84 Hz, 1H), 5.05 – 4.97 (m, 1H), 4.05 (d, J = 12.82 Hz, 1H), 2.94 (t, J = 12.82 Hz, 1H), 2.47 (s, 3H), 2.10 – 2.07 (m, 1H), 1.72 – 1.65 (m, 4H), 1.57 – 1.50 (m, 1H), 1.47 (s, 9H); 13C NMR (CDCl3, 100 MHz): δ 158.29 (d, J = 272.20 Hz), 155.27, 137.36, 130.14, 128.98 (d, J = 7.67 Hz), 126.60, 106.38 (d, J = 7.67 Hz), 80.15, 40.58 (d, J = 29.71 Hz), 40.58, 28.49, 26.21, 25.25, 19.93, 15.86; 19F NMR (CDCl3, 282 MHz): δ -109.86 (d, J = 43.35 Hz); ESI: Calculated for C19H27FNO2S, [M+H]+ m/z 352.17. Found 352.10.

*trans-tert*-Butyl 2-(1-fluoro-2-(4-(methylthio)phenyl)vinyl)piperidine-1-carboxylate ((E)-3v): Eluent: PE/EA (20:1). Yield (23 mg, 33%). White solid, mp 83 – 84 °C. 1H NMR (CDCl3, 400 MHz): δ 7.21 (d, J = 8.24 Hz, 2H), 7.14 (d, J = 8.24 Hz, 2H), 6.14 (d, J
= 23.81 Hz, 1H), 5.21 (dd, J = 30.68 Hz, J = 4.12 Hz, 1H), 3.97 (dd, J = 13.28 Hz, J = 3.66 Hz, 1H), 3.08 (tt, J = 12.82 Hz, J = 2.75 Hz, 1H), 2.46 (s, 3H), 1.94 – 1.91 (m, 1H), 1.82 – 1.75 (m, 1H), 1.71 – 1.68 (m, 3H), 1.48 – 1.40 (m, 1H), 1.24 (s, 9H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): 163.14 (d, J = 258.79 Hz), 155.08, 137.30, 130.30 (d, J = 13.42 Hz), 129.01 (d, J = 1.92 Hz), 126.87, 108.17 (d, J = 27.80 Hz), 79.89, 48.14 (d, J = 2.75 Hz), 41.80, 29.04, 28.22, 24.85, 20.39, 16.03; \(^{19}\)F NMR (CDCl\(_3\), 282 MHz): \(\delta\) -102.91 (t, J = 26.01 Hz); ESI: Calculated for C\(_{19}\)H\(_{27}\)FNO\(_2\)S, [M+H]\(^+\) m/z 352.17. Found 352.10.

tert-Butyl 2-(2-(2-chlorophenyl)-1-fluorovinyl)pyrrolidine-1-carboxylate (3w): Z/E = 2:3. Eluent: PE/EA (20:1). Yield (38 mg, 58%). Colorless oil. \(^1\)H NMR (CDCl\(_3\), 400 MHz): rotameric mixture, \(\delta\) 7.89 – 7.74 (m, 1H), 7.37 – 7.33 (m, 1.68H), 7.25 – 7.14 (m, 4H), 6.32 (d, J = 20.61 Hz, 1H), 5.98 (d, J = 38.01 Hz, 1H), 4.73 – 4.63 (m, 1H), 4.54 – 4.41 (m, 0.66H), 3.51 – 3.42 (m, 3.41H), 2.23 – 1.82 (m, 6.79H), 1.50 – 1.43 (m, 9H), 1.30 (s, 6H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): rotameric mixture, \(\delta\) 161.93 (d, J = 258.79 Hz), 160.85 (d, J = 273.16 Hz), 154.28, 154.08, 134.13, 132.71, 131.83 (d, J = 14.38 Hz), 131.14, 130.34, 130.12, 129.64, 129.47, 128.51, 128.24, 126.76, 126.64, 105.81 (d, J = 30.67 Hz), 101.49 (d, J = 29.71 Hz), 80.05 (major), 79.53 (minor), 58.29 (d, J = 32.59 Hz), 53.94 (d, J = 24.92 Hz), 47.29 (minor), 47.04 (major), 46.70 (minor), 46.46 (major), 32.11 (major), 31.18 (minor), 30.67 (major), 29.74 (minor), 28.46, 28.30, 24.42 (minor), 23.78 (major), 23.18; \(^{19}\)F NMR (CDCl\(_3\), 282 MHz) rotameric mixture: -113.21 – -113.40 (m), -113.98 – -114.29 (m), -115.12 – -115.27 (m); ESI: Calculated for C\(_{17}\)H\(_{22}\)ClFNO\(_2\), [M+H]\(^+\) m/z 326.12. Found 326.10.

cis-tert-Butyl 2-(2-(4-chlorophenyl)-1-fluorovinyl)pyrrolidine-1-carboxylate
**(Z)-3x**: Eluent: PE/EA (20:1). Yield (27 mg, 42%). Colorless oil. $^1$H NMR (CDCl$_3$, 400 MHz): rotameric mixture, $\delta$ 7.38 (d, $J = 8.24$ Hz, 2H), 7.28 – 7.25 (m, 2H), 5.61 – 5.45 (m, 1H), 4.49 – 4.35 (m, 1H), 3.48 – 3.38 (m, 2H), 2.08 – 1.88 (m, 3H), 1.87 – 1.86 (m, 1H), 1.46 – 1.40 (m, 9H); $^{13}$C NMR (CDCl$_3$, 100 MHz): rotameric mixture, $\delta$ 160.18 (d, $J = 278.91$ Hz, 1H), 154.35, 132.75, 131.76, 129.74, 128.77, 104.72, 79.99, 58.24 (d, $J = 31.63$ Hz), 46.95 (minor), 46.50 (major), 30.61 (major), 29.80 (minor), 28.52, 24.05 (minor), 23.25 (major); $^{19}$F NMR (CDCl$_3$, 282 MHz): rotameric mixture, $\delta$ -114.72 – -114.81 (m); ESI: Calculated for C$_{17}$H$_{22}$ClFNO$_2$, [M+H]$^+$ m/z 326.12. Found 326.10.

![Image](Z-3x)

**trans-tert-Butyl 2-(2-(4-chlorophenyl)-1-fluorovinyl)pyrrolidine-1-carboxylate**

**(E)-3x**: Eluent: PE/EA (20:1). Yield (25 mg, 38%). Colorless oil. $^1$H NMR (CDCl$_3$, 400 MHz): rotameric mixture, $\delta$ 7.36 – 7.25 (m, 3H), 7.13 (m, 1H), 6.15 (d, $J = 21.07$ Hz, 1H), 4.72 – 4.65 (m, 1H), 3.52 – 3.42 (m, 2H), 2.24 – 1.99 (m, 3H), 1.83 – 1.82 (m, 1H), 1.44 – 1.24 (m, 9H); $^{13}$C NMR (CDCl$_3$, 100 MHz): rotameric mixture, $\delta$ 161.53 (d, $J = 254.95$ Hz), 154.08, 132.84, 131.97 (d, $J = 13.42$ Hz), 130.03, 128.69, 107.26 (d, $J = 28.75$ Hz), 80.02 (major), 79.63 (minor), 54.09 (d, $J = 23.00$ Hz), 47.37 (minor), 47.08 (major), 32.17 (major), 31.30 (minor), 28.48, 24.54 (minor), 23.92 (major); $^{19}$F NMR (CDCl$_3$, 282 MHz): rotameric mixture, $\delta$ -115.05 – -115.24 (m); ESI: Calculated for C$_{17}$H$_{22}$ClFNO$_2$, [M+H]$^+$ m/z 326.12. Found 326.10.

![Image](E-3x)

**cis-tert-Butyl 2-(2-(3-bromophenyl)-1-fluorovinyl)pyrrolidine-1-carboxylate**

**(Z)-3y**: Eluent: PE/EA (20:1). Yield (32 mg, 43%). White solid, mp 84 – 85 °C. $^1$H NMR (CDCl$_3$, 400 MHz): rotameric mixture, $\delta$ 7.63 (s, 1H), 7.36 – 7.34 (m, 2H), 7.19 – 7.17 (m, 1H), 5.60 – 5.44 (m, 1H), 4.47 – 4.36 (m, 1H), 3.48 – 3.40 (m, 2H), 2.07 – 1.88 (m, 3H), 1.85 – 1.80 (m, 9H); $^{13}$C NMR (CDCl$_3$, 100 MHz): rotameric mixture, $\delta$ 160.18 (d, $J = 254.95$ Hz), 154.08, 132.84, 131.97 (d, $J = 13.42$ Hz), 130.03, 128.69, 107.26 (d, $J = 28.75$ Hz), 80.02 (major), 79.63 (minor), 54.09 (d, $J = 23.00$ Hz), 47.37 (minor), 47.08 (major), 32.17 (major), 31.30 (minor), 28.48, 24.54 (minor), 23.92 (major); $^{19}$F NMR (CDCl$_3$, 282 MHz): rotameric mixture, $\delta$ -115.05 – -115.24 (m); ESI: Calculated for C$_{17}$H$_{22}$BrFNO$_2$, [M+H]$^+$ m/z 344.95. Found 344.96.
1.96 (m, 3H), 1.90 – 1.86 (m, 1H), 1.46 – 1.41 (m, 9H); 13C NMR (CDCl₃, 100 MHz)
rotameric mixture:  δ 160.79 (d, J = 273.16 Hz), 154.30, 135.28, 131.27, 130.07,
127.05, 122.68, 104.49, 80.04, 58.18 (d, J = 31.63 Hz), 46.92 (minor), 46.48 (major),
30.61 (major), 29.78 (minor), 28.50, 24.03 (minor), 23.20 (major); 19F NMR (CDCl₃,
282 MHz): rotameric mixture, δ -113.09 – -113.41 (m); ESI: Calculated for C₁₇H₂₂BrFNO₂,
[M+H]⁺ m/z 370.07. Found 370.00.

trans-tert-Butyl 2-(2-(3-bromophenyl)-1-fluorovinyl)pyrrolidine-1-carboxylate
((E)-3y): Eluent: PE/EA (20:1). Yield (30 mg, 41%). Colorless oil. 1H NMR (CDCl₃,
400 MHz): rotameric mixture, δ 7.53 – 7.35 (m, 2H), 7.21 – 7.13 (m, 2H), 6.14 (d, J =
20.61 Hz, 1H), 4.73 – 4.66 (m, 1H), 3.53 – 3.42 (m, 2H), 2.24 – 1.99 (m, 3H), 1.86 –
1.82 (m, 1H), 1.45 – 1.31 (m, 9H); 13C NMR (CDCl₃, 100 MHz): rotameric mixture, δ
162.03 (d, J = 260.70 Hz), 154.03, 135.61 (d, J = 12.46 Hz), (131.90) 131.63, 130.00,
(127.68) 127.40, 122.48, 107.06 (d, J = 28.75 Hz), 80.12 (79.62), 54.02 (d, J = 23.96
Hz), 47.35 (minor) 47.10 (major), 32.14 (major), 31.33 (minor), 28.45, 24.52 (minor)
23.88 (major); 19F NMR (CDCl₃, 282 MHz): rotameric mixture, δ -113.93 – -114.40
(m); ESI: Calculated for C₁₇H₂₂BrFNO₂, [M+H]⁺ m/z 370.07. Found 370.00.

cis-tert-Butyl (3-fluoro-4-(4-iodophenyl)-1-phenylbut-3-en-2-yl)carbamate
((Z)-3z): Eluent: PE/EA (20:1). Yield (27 mg, 29%). White solid, mp 137 – 138 °C.
1H NMR (CDCl₃, 400 MHz): δ 7.61 (d, J = 8.24 Hz, 2H), 7.29 – 7.25 (m, 2H), 7.23 –
7.17 (m, 3H), 7.13 (d, J = 8.24 Hz, 2H), 5.44 (d, J = 38.93 Hz, 1H), 5.00 – 4.55 (m,
2H), 3.02 – 3.00 (m, 2H), 1.43 – 1.40 (m, 9H); 13C NMR (CDCl₃, 100 MHz): δ
158.32 (d, J = 264.67 Hz), 154.85, 137.63, 136.46, 132.37, 130.47 (d, J = 6.90 Hz),
129.46, 128.92, 128.64, 126.99, 106.64, 92.75, 80.23, 53.85 (d, J = 32.22 Hz), 38.78,
28.42; 19F NMR (CDCl₃, 282 MHz): rotameric mixture, δ -114.08 – -115.43 (m); ESI:
Calculated for C$_{21}$H$_{23}$FINNaO$_2$, [M+Na]$^+$ m/z 490.08. Found 490.40.

**trans-tert-Butyl** (3-fluoro-4-(4-iodophenyl)-1-phenylbut-3-en-2-yl)carbamate (**(E)-3z**): Eluent: PE/EA (20:1). Yield (32 mg, 34%). White solid, mp 70 – 71 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.53 (d, $J$ = 7.79 Hz, 2H), 7.26 – 7.21 (m, 3H), 7.12 – 7.10 (m, 2H), 6.61 (d, $J$ = 7.79 Hz, 2H), 6.10 (d, $J$ = 21.07 Hz, 1H), 4.93 – 4.80 (m, 2H), 3.00 – 2.87 (m, 2H), 1.42 (s, 9H); $\delta$; $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 158.45 (d, $J$ = 253.99 Hz), 154.60, 137.52, 136.50, 131.99 (d, $J$ = 13.42 Hz), 130.40, 129.48, 129.26, 128.90, 128.51, 126.92, 109.47 (d, $J$ = 26.84 Hz), 92.81, 80.02, 50.26 (d, $J$ = 23.96 Hz), 39.24, 28.40; $^{19}$F NMR (CDCl$_3$, 282 MHz): $\delta$ -117.36 (t, $J$ = 26.01 Hz); ESI: Calculated for C$_{21}$H$_{23}$FINNaO$_2$, [M+Na]$^+$ m/z 490.08. Found 490.40.

**cis-tert-Butyl** 2-(2-(4-(ethoxycarbonyl)phenyl)-1-fluorovinyl)pyrrolidine-1-carboxylate ((Z)-3aa): Eluent: PE/EA (20:1). Yield (25.7mg, 36%). White solid, mp 72 – 73 °C. $^1$H NMR (CDCl$_3$, 400 MHz): rotameric mixture, $\delta$ 7.99 – 7.98 (m, 2H), 7.51 (d, $J$ = 8.24 Hz, 2H), 5.65 – 5.55 (m, 1H), 4.52 – 4.33 (m, 3H), 3.49 – 3.40 (m, 2H), 2.10 – 1.98 (m, 3H), 1.93 – 1.86 (m, 1H), 1.47 – 1.36 (m, 12H); $^{13}$C NMR (CDCl$_3$, 100 MHz): rotameric mixture, $\delta$ 166.45, 161.45 (d, $J$ = 275.00 Hz) (major), 161.03 (d, $J$ = 277.00 Hz) (minor), 154.30, 137.74, 129.85, 128.90, 128.30, 105.15, 80.06, 60.98, 58.30 (d, $J$ = 31.63 Hz), 46.94 (minor), 46.52 (major), 30.66 (major), 29.78 (minor), 28.49, 24.07 (minor), 23.27 (major), 14.42; $^{19}$F NMR (CDCl$_3$, 282 MHz) rotameric mixture: $\delta$ -111.78 (dd, $J$ = 39.01 Hz, $J$ = 13.00 Hz); ESI: Calculated for C$_{20}$H$_{27}$FNO$_4$, [M+H]$^+$ m/z 364.18. Found 364.10.
**trans-tert-Butyl** 2-(2-(4-(ethoxycarbonyl)phenyl)-1-fluorovinyl)pyrroolidine-1-carboxylate ((E)-3aa): Eluent: PE/EA (20:1). Yield (32.8 mg, 45%). Colorless oil. $^1$H NMR (CDCl$_3$, 400 MHz): rotameric mixture, $\delta$ 7.98 (d, $J = 8.24$ Hz, 2H), 7.53 – 7.48 (m, 1H), 7.26 – 7.25 (m, 1H), 6.22 (d, $J = 21.07$ Hz, 1H), 4.76 – 4.69 (m, 1H), 4.35 (q, $J = 7.28$ Hz, 2H), 3.52 – 3.42 (m, 2H), 2.26 – 2.00 (m, 3H), 1.99 – 1.82 (m, 1H), 1.43 – 1.35 (m, 6H), 1.26 (s, 6H); $^{13}$C NMR (CDCl$_3$, 100 MHz): rotameric mixture, $\delta$ 166.38, 162.40 (d, $J = 260.70$ Hz), 154.05, 138.23 (d, $J = 12.46$ Hz), 129.77, 128.98, 128.64, 107.83 (d, $J = 260.70$ Hz), 80.07 (79.58), 61.04 (d, $J = 10.54$ Hz), 54.20 (d, $J = 23.96$ Hz), 47.39 (minor), 47.10 (major), 32.18 (major), 31.32 (minor), 28.45, 24.57 (minor), 23.95 (major), 14.43; $^{19}$F NMR (CDCl$_3$, 282 MHz) rotameric mixture: $\delta$ [-111.69 – -111.87 (m)] -112.82 – -112.99 (m); ESI: Calculated for C$_{20}$H$_{27}$FNO$_4$, [M+H]$^+$ m/z 364.18. Found 364.10.

![Image of trans-tert-Butyl structure](image)

**cis-tert-Butyl** 2-(1-fluoro-2-(1-tosyl-1H-indol-3-yl)vinyl)piperidine-1-carboxylate ((Z)-3ab): Eluent: PE/EA (20:1). Yield (26 mg, 26%). Colorless oil. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.98 (d, $J = 8.24$ Hz, 1H), 7.87 (s, 1H), 7.77 (d, $J = 8.24$ Hz, 2H), 7.49 (d, $J = 7.79$ Hz, 1H), 7.31 (t, $J = 7.79$ Hz, 1H), 7.26 – 7.19 (m, 3H), 5.71 (d, $J = 39.38$ Hz, 1H), 5.12 – 5.04 (m, 1H), 4.06 (d, $J = 12.82$ Hz, 1H), 2.98 – 2.95 (m, 1H), 2.31 (s, 3H), 2.13 – 2.10 (m, 1H), 1.76 – 1.59 (m, 4H), 1.55 – 1.44 (m, 10H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$; $^{19}$F NMR (CDCl$_3$, 282 MHz): rotameric mixture, $\delta$ 159.54 (d, $J = 273.16$ Hz), 155.24, 145.05, 135.28, 134.48, 129.99, 129.66, 126.95, 125.07, 124.93, 123.33, 119.06, 114.30, 113.70, 96.75 (d, $J = 11.50$ Hz), 80.24, 51.53 (d, $J = 21.09$ Hz), 40.68, 28.49, 26.18, 25.23, 21.64, 19.98; $^{19}$F NMR (CDCl$_3$, 282 MHz): $\delta$ -101.98 (d, $J = 43.35$ Hz); HRMS (ESI): Calculated for C$_{27}$H$_{31}$FN$_2$NaO$_4$S, [M+Na]$^+$ m/z 521.1881. Found 521.1884.

![Image of cis-tert-Butyl structure](image)
trans-tert-Butyl 2-(1-fluoro-2-(1-tosyl-1H-indol-3-yl)vinyl)piperidine-1-carboxylate ((E)-3ab): Eluent: PE/EA (20:1). Yield (30 mg, 30%). Yellow solid, mp 154 – 155 °C. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 8.00 – 7.96 (m, 1H), 7.80 (d, \(J = 8.24\) Hz, 2H), 7.59 – 7.54 (m, 1H), 7.44 (d, \(J = 7.79\) Hz, 1H), 7.32 (t, \(J = 11.50\) Hz, 1H), 7.25 – 7.19 (m, 3H), 6.09 (d, \(J = 21.07\) Hz, 1H), 5.18 (dd, \(J = 30.68\) Hz, \(J = 4.12\) Hz, 1H), 4.00 (dd, \(J = 13.51\) Hz, \(J = 4.12\) Hz, 1H), 3.16 – 3.08 (m, 1H), 2.31 (s, 3H), 1.92 – 1.81 (m, 2H), 1.72 – 1.70 (m, 3H), 1.50 – 1.45 (m, 1H), 1.13 (s, 9H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 164.49 (d, \(J = 265.50\) Hz), 155.10, 145.09, 135.27, 134.85, 130.74, 130.00, 127.05, 125.20, 123.50, 123.22, 119.46, 115.14 (d, \(J = 13.42\) Hz), 113.76, 98.01 (d, \(J = 29.71\) Hz), 79.92, 48.45 (d, \(J = 21.09\) Hz), 41.97, 28.96, 28.06, 24.83, 21.65, 20.46; \(^{19}\)F NMR (CDCl\(_3\), 282 MHz): \(\delta\) -100.83 (t, \(J = 26.01\) Hz); HRMS (ESI): Calculated for C\(_{27}\)H\(_{31}\)FN\(_2\)NaO\(_4\)S, [M+Na]\(^+\) m/z 521.1881. Found 521.1880.

2-(1-Fluoro-2,2-diphenylvinyl)tetrahydrofuran (3ac): Eluent: PE/EA (20:1). Yield (42 mg, 78%). White solid, mp 91 – 92 °C. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.38 – 7.22 (m, 10H), 4.56 (dt, \(J = 29.31\) Hz, \(J = 7.33\) Hz, 1H), 4.01 – 3.96 (m, 1H), 2.19 – 2.02 (m, 3H), 2.01 – 1.87 (m, 1H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 155.93 (d, \(J = 265.50\) Hz), 137.94 (d, \(J = 7.67\) Hz), 137.16, 130.57 (d, \(J = 2.88\) Hz), 129.88 (d, \(J = 4.79\) Hz), 128.45, 128.06, 127.70, 127.44, 123.30 (d, \(J = 14.38\) Hz), 75.02 (d, \(J = 25.88\) Hz), 69.33, 28.97, 26.95; \(^{19}\)F NMR (CDCl\(_3\), 282 MHz): \(\delta\) -100.83 (t, \(J = 26.01\) Hz); ESI: Calculated for C\(_{18}\)H\(_{18}\)FO, [M+H]\(^+\) m/z 269.13. Found 269.10.

tert-Butyl ((2S)-1-((2S)-1-(2-(1-fluoro-2,2-diphenylvinyl)pyrrolidin-1-yl)-1-oxo-3-phenylpropan-2-yl)amino)-1-oxopropan-2-yl)carbamate (7) Eluent: PE/EA (2:1). Yield (84 mg, 72%). Waxy solid. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.39 - 7.33 (m, 5H), 7.24 - 7.04 (m, 10H), 6.82 (brs, 1H), 4.99 - 4.91 (m, 2H), 4.68 - 4.46 (m, 1H), 4.14 -
4.08 (m, 1H), 3.54 - 3.39 (m, 1H), 3.03 - 2.92 (m, 2H), 2.82 - 2.76 (m, 1H), 1.93 - 1.86 (m, 4H), 1.44 - 1.30 (m, 12H); $^{13}$C NMR (CDCl$_3$, 100 MHz): 172.00, 169.34, 155.27 (d, $J = 264.54$ Hz), 155.18, 138.05 (d, $J = 7.67$ Hz), 137.20, 136.37, 130.57, 129.62, 129.54, 128.52 (d, $J = 5.75$ Hz), 128.36, 128.23, 127.94, 127.52, 127.06 (d, $J = 6.71$ Hz), 120.43 (d, $J = 11.50$ Hz), 80.02, 56.27 (d, $J = 24.92$ Hz), 52.49, 50.35, 47.46, 39.69, 30.63, 28.37, 24.49, 18.78; $^{19}$F NMR (CDCl$_3$, 282 MHz) : $\delta$ -119.92 (d, $J = 26.01$Hz) (minor), -123.26 (d, $J = 26.01$Hz) (major); ESI: Calculated for C$_{35}$H$_{41}$FN$_3$O$_4$, [M+H]$^+$ m/z 586.30. Found 586.00.

6. References

7. $^1$H, $^{13}$C and $^{19}$F NMR spectra of compounds 3a-ac and 7
SMe

(E)-3v

Boc F

X: parts per Million : 19F