Supporting Information

Base Promoter Direct Difunctionalization/Cascade Cyclization of 1,6-Enynes
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General Remarks

For column chromatography, silica gel (200-300 mesh) was employed. $^1$H NMR (400 MHz), $^{13}$C NMR (100 MHz) and $^{19}$F NMR (376 MHz) spectra were recorded in CDCl$_3$ and chemical shifts (ppm) were recorded with TMS as the internal reference standard. All newly synthesized products were further characterized by HR-MS, copies of their $^1$H NMR, $^{13}$C NMR and $^{19}$F NMR spectra are provided in the Supporting Information. Unless otherwise noted, reactions were carried out under an argon atmosphere. Toluene was distilled from CaH$_2$ under standard method. Other commercially available reagents and solvents were used without further purification.
General Procedure

The starting Materials were obtained by the Liang’s work.\(^1\)

For the synthesis of new product 3a

\[
\text{TsN} = \text{ICF}_2\text{COOEt} + \text{K}_2\text{CO}_3 (\text{2.5 equiv}) \xrightarrow{\text{toluene} 110^\circ\text{C}, \text{Ar}} \text{product 3a}\]

In an oven-dried tube, 1,6-enynes (1a; 67.8 mg, 0.2 mmol), borophenylic acid (2a; 48.8 mg, 0.4 mmol) and K\(_2\)CO\(_3\) (69 mg, 0.5 mmol) were added. The tube was charged with argon (repeated three times). Then, toluene (2 mL) was injected after ICF\(_2\)COOEt (75 mg, 0.3 mmol) were added. The reaction mixture was stirring at 110 \(^\circ\)C for 24 h. After the reaction was completed, the residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate, 8:1) to obtain product 3a.

For the synthesis of product 5a

\[
\text{TsN} = \text{ICF}_2\text{COOEt} + N\text{-methylpiperidine (1.0 equiv)} \xrightarrow{\text{toluene 110}^\circ\text{C}, \text{Ar}} \text{product 5a}\]

An oven-dried tube charged with 1,6-enynes (1a; 67.8 mg, 0.2 mmol) was evacuated and backfilled with argon. Then N-methylpiperidine (19.8 mg, 0.2 mmol), ICF\(_2\)COOEt (75 mg, 0.3 mmol) and toluene were added respectively. The reaction system was then stirring at 110 \(^\circ\)C for 48 h. After the reaction was completed, the residue
was purified by chromatography on silica gel (petroleum ether/ethyl acetate, 8:1) to obtain product 5a.

Reference
X-ray Single Crystal Diffraction Data of 3a, 4b and 5a

Bond precision: C-C = 0.0053 Å

Wavelength = 0.71073 Å

Cell:
\[a = 13.8373(7) \quad b = 14.6324(8) \quad c = 16.7936(8)\]
\[\alpha = 65.506(5) \quad \beta = 85.068(4) \quad \gamma = 61.827(5)\]

Temperature: 173 K

Volume: 2702.0(3) Å³

Space group: P -1

Hall group: -P 1

Moiety formula: C30 H31 F2 N O4 S

Sum formula: C30 H31 F2 N O4 S

Mr: 539.62

Dx, g cm⁻³: 1.327

Z: 4

Mu (mm⁻¹): 0.170

F000: 1136.0

F000': 1137.09

h,k,lmax: 17,18,20

Nref: 10642

Tmin,Tmax: 0.975,0.990

Correction method = # Reported T Limits: Tmin = 0.754, Tmax = 1.000

AbsCorr = MULTI-SCAN

Data completeness = 0.998

Theta(max) = 26.020

R(reflections) = 0.0594 (7033)

wR2(reflections) = 0.1599 (10621)

S = 1.034

Npar = 744

Thermal ellipsoids are shown at 50% probability
For 3a there are two molecules in the asymmetric unit, in fact there are same molecules, which just are rotamers due to rotation of ester group
ond precision:  C-C = 0.0036 Å  
Wavelength=1.54184

Cell:  
a=12.5836(4)  
b=13.0599(5)  
c=17.6689(7)  
alpha=90  
beta=91.349(3)  
gamma=90  
Temperature:  293 K

Volume  
2902.91(18)  
2902.91(19)

Space group  
P 21/n  
P 1 21/n 1

Hall group  
-P 2yn  
-P 2yn

Moiety formula  
C31 H33 F2 N O5 S  
C31 H33 F2 N O5 S

Sum formula  
C31 H33 F2 N O5 S  
C31 H33 F2 N O5 S

Mr  
569.64  
569.64

Dx, g cm-3  
1.303  
1.303

Z  
4  
4

Mu (mm-1)  
1.442  
1.442

F000  
1200.0  
1200.0

F000'  
1205.13

h,k,lmax  
14,15,21  
14,15,21

Nref  
5125  
4980

Tmin, Tmax  
0.805, 0.841  
0.922, 1.000

Tmin'  
0.805

Correction method= # Reported T Limits: Tmin=0.922 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.972  
Theta(max)= 66.593

R(reflections)= 0.0473(4041)  
wR2(reflections)= 0.1381(4980)

S = 1.037  
Npar= 365

Thermal ellipsoids are shown at 30% probability
Bond precision: C-C = 0.0123 Å

Wavelength=1.54178

Cell:
- a=12.1269(6)
- b=15.7054(7)
- c=25.7543(12)
- alpha=90
- beta=91.456(2)
- gamma=90

Temperature: 150 K

Volume
- Calculated: 4903.5(4)
- Reported: 4903.5(4)

Space group
- Calculated: P 21/n
- Reported: P 1 21/n 1

Hall group
- Calculated: -P 2yn
- Reported: -P 2yn

Moietry formula
- Calculated: C24 H26 F2 I N O4 S
- Reported: C24 H26 F2 I N O4 S

Sum formula
- Calculated: C24 H26 F2 I N O4 S
- Reported: C24 H26 F2 I N O4 S

Mr
- Calculated: 589.42
- Reported: 589.42

Dx,g cm-3
- Calculated: 1.597
- Reported: 1.597

Z
- Calculated: 8
- Reported: 8

Mu (mm-1)
- Calculated: 11.458
- Reported: 11.458

F000
- Calculated: 2368.0
- Reported: 2368.0

F000’
- Calculated: 2375.12

h,k,lmax
- Calculated: 14, 18, 30
- Reported: 14, 18, 30

Nref
- Calculated: 8722
- Reported: 8282

Tmin,Tmax
- Calculated: 0.136, 0.201
- Reported: 0.120, 0.753

Tmin’
- Calculated: 0.038

Correction method= # Reported T Limits: Tmin=0.120 Tmax=0.753
AbsCorr = MULTI-SCAN

Data completeness= 0.950
Theta(max)= 66.827

R(reflections)= 0.1176( 7190)

wR2(reflections)= 0.3344( 8282)

S = 1.189
Npar= 601

Thermal ellipsoids are shown at 50% probability
Characterization Data

**ethyl**

**3-(4-(diphenylmethylene)-3-methyl-1-tosylpyrrolidin-3-yl)-2,2-difluoropropanoate**

White solid; melting point 40–42 °C; 75.5 mg; 70% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ ppm 7.62 (d, $J$ = 8.4 Hz, 2H), 7.34 (d, $J$ = 8 Hz, 2H), 7.29–7.26 (m, 4H), 7.23–7.20 (m, 2H), 7.16 (d, $J$ = 8 Hz, 2H), 7.07 (d, $J$ = 8 Hz, 2H), 4.27–4.19 (m, 1H), 3.77 (d, $J$ = 14.8 Hz, 1H), 3.68 (d, $J$ = 14.8 Hz, 1H), 3.22 (d, $J$ = 9.6 Hz, 1H), 3.15 (d, $J$ = 9.6 Hz, 1H), 2.46 (s, 3H), 2.10 (t, $J$ = 18.4 Hz, 2H), 1.27 (t, $J$ = 7.2 Hz, 3H), 1.20 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ ppm 163.8 (t, $J$ = 32.2 Hz), 143.8 (s), 142.5 (s), 140.2 (s), 140.2 (s), 137.7 (s), 131.6 (s), 129.6 (s), 128.8 (s), 128.7 (s), 128.7 (s), 128.2 (s), 128.0 (s), 127.2 (s), 127.1 (s), 115.7 (t, $J$ = 252.0 Hz), 63.0 (s), 59.9 (s), 52.1 (s), 43.6 (d, $J$ = 3.3 Hz), 41.2 (t, $J$ = 21.0 Hz), 25.7 (s), 25.5 (s), 13.8 (s).

$^{19}$F NMR (376 MHz, CDCl$_3$) δ ppm -100.3 (d, $J$ = 263.2 Hz, 1F), -103.6 (d, $J$ = 263.7 Hz, 1F).

HRMS (ESI) Calcd for C$_{30}$H$_{31}$F$_2$NO$_4$S: [M]+Na = 562.1834. Found: 562.1834.
(E)-ethyl

2,2-difluoro-3-(4-((4-methoxyphenyl)(phenyl)methylene)-3-methyl-1-tosylpyrrolidin-3-yl)propanoate

White solid; melting point 50–52 °C; 60.3 mg; 53% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm 7.62 (d, $J = 8.4$ Hz, 2H), 7.35 (d, $J = 8.0$ Hz, 2H), 7.29–7.26 (m 2H), 7.21–7.20 (m 1H), 7.07–7.02 (m, 4H), 6.82–6.80 (m, 2H), 4.28–4.22 (m, 2H), 3.78 (d, $J = 14.8$ Hz, 1H), 3.76 (s, 3H), 3.68 (d, $J = 14.8$ Hz, 1H), 3.19 (d, $J = 9.2$ Hz, 1H), 3.13 (d, $J = 9.2$ Hz, 1H), 2.48 (s, 3H), 2.18–2.08 (m, 2H), 1.29 (t, $J = 7.2$ Hz, 3H), 1.22 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ ppm 164.2 (t, $J = 32.0$ Hz), 158.6 (s), 143.8 (s), 142.8 (s), 140.2 (s), 137.3 (s), 132.5 (s), 131.4 (s), 129.8 (s), 129.6 (s), 128.7 (s), 128.0 (s), 127.1 (s), 127.0 (s), 115.8 (t, $J = 252.0$ Hz), 113.6 (s), 63.0 (s), 59.9 (s), 55.1 (s), 52.2 (s), 43.6 (d, $J = 2.0$ Hz), 41.2 (t, $J = 22.0$ Hz), 25.8 (s), 21.6 (s), 13.7 (s).

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ ppm -100.3 (d, $J = 263.2$Hz), -103.6 (d, $J = 263.2$ Hz).

HRMS (ESI) Calcd for C$_{31}$H$_{33}$F$_2$NO$_5$S: [M]+Na = 592.1940. Found: 592.1940.
(E)-ethyl

3-(4-[[1,1'-biphenyl]-4-yl(phenyl)methylene]-3-methyl-1-tosylpyrrolidin-3-yl)-2,2-difluoropropanoate

White solid; melting point 62–64 °C; 76.3 mg; 62% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm 7.63 (d, $J = 8.0$ Hz, 2H), 7.54–7.50 (m, 4H), 7.42–7.38 (m 2H), 7.35–7.33 (m 2H), 7.31–7.27 (m, 3H), 7.24–7.21 (m, 3H), 7.12–7.10 (m, 2H), 4.23–4.17 (m, 2H), 3.78 (d, $J = 14.4$ Hz, 1H), 3.72 (d, $J = 14.4$ Hz, 1H), 3.26 (d, $J = 9.6$ Hz, 1H), 3.14 (d, $J = 9.6$ Hz, 1H), 2.45 (s, 3H), 2.23–2.14 (m, 2H), 1.24 (s, 3H), 1.21 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ ppm 163.8 (t, $J = 32.0$ Hz), 143.8 (s), 142.5 (s), 140.4 (s), 140.2 (s), 140.0 (s), 139.2 (s), 137.3 (s), 131.6 (s), 129.7 (s), 129.1 (s), 128.8 (s), 128.7 (s), 128.0(s), 127.4(s), 127.2(s), 126.9(s),126.8 (s),115.7 (t, $J = 253.0$ Hz), 63.0 (s), 59.9 (s), 52.2 (s), 43.7 (d, $J = 2.0$ Hz), 41.3 (t, $J = 21.0$ Hz), 25.8 (s), 21.5 (s), 13.7 (s).

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ ppm -100.1 (d, $J = 263.2$Hz), -103.6 (d, $J = 263.2$ Hz).

HRMS (ESI) Calcd for C$_{36}$H$_{35}$F$_2$NO$_4$S: [M]+Na = 620.1889. Found: 620.1890.
(E)-ethyl
3-(4-((3,5-dimethylphenyl)(phenyl)methylene)-3-methyl-1-tosylpyrrolidin-3-yl)-2,2-difluoropropanoate

White solid; melting point 46–48 °C; 72.6 mg; 64% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm 7.62 (d, $J = 8.0$ Hz, 2H), 7.35 (d, $J = 8.0$ Hz, 2H), 7.29–7.25 (m, 2H), 7.21–7.20 (m, 1H), 7.09–7.06 (m, 2H), 6.84 (s, 1H), 6.76 (s, 2H), 4.27–4.21 (m, 2H), 3.74 (d, $J = 14.4$ Hz, 1H), 3.63 (d, $J = 14.4$ Hz, 1H), 3.19 (d, $J = 9.6$ Hz, 1H), 3.14 (d, $J = 9.6$ Hz, 1H), 2.46 (s, 3H), 2.24 (s, 6H), 2.17–2.07 (m, 2H), 1.28 (t, $J = 7.2$ Hz, 3H), 1.21 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ ppm 163.9 (t, $J = 32.2$ Hz), 143.8 (s), 142.6 (s), 140.0 (s), 139.6 (s), 137.8 (s), 131.3 (s), 129.6 (s), 128.8 (s), 128.7 (s), 128.0 (s), 127.1 (s), 127.0 (s), 126.3 (s), 115.8 (t, $J = 253.0$ Hz), 63.0 (s), 59.9 (s), 52.1 (s), 43.6 (d, $J = 2.0$ Hz), 41.1 (t, $J = 21.0$ Hz), 25.8 (s), 21.6 (s), 21.2 (s), 13.7 (s).

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ ppm -100.7 (d, $J = 263.2$ Hz, 1F), -103.7 (d, $J = 263.7$ Hz, 1F).

HRMS (ESI) Calcd for C$_{32}$H$_{35}$F$_2$NO$_4$S: [M]+Na = 590.2147. Found: 590.2147.
(E)-ethyl 2,2-difluoro-3-(4-((4-fluorophenyl)(phenyl)methylene)-3-methyl-1-tosylpyrrolidin-3-yl)propanoate

White solid; melting point 42–44 °C; 40.1 mg; 36% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ ppm 7.62 (d, $J = 8.$ Hz, 2H), 7.36–7.34 (m, 2H), 7.31–7.26 (m, 2H), 7.23–7.20 (m, 1H), 7.15–7.12 (m, 2H), 7.06–7.04 (m, 2H), 7.00–6.96 (m, 2H), 4.30–4.21 (m, 2H), 3.75 (d, $J = 14.8$ Hz, 1H), 3.68 (d, $J = 14.8$ Hz, 1H), 3.23 (d, $J = 9.6$ Hz, 1H), 3.13 (d, $J = 9.6$ Hz, 1H), 2.46 (s, 3H), 2.15–2.04 (m, 2H), 1.29 (t, $J = 7.2$ Hz, 2H), 1.19 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ ppm 163.8 (t, $J = 30$ Hz), 161.9 (d, $J = 245,6$ Hz), 143.9 (s), 142.3 (s), 140.9 (s), 136.6 (s), 136.2 (d, $J = 3,6$ Hz), 131.6 (s), 130.3 (d, $J = 7.8$ Hz), 129.7 (s), 128.9 (s), 128.1 (s), 127.3 (s), 127.1 (s), 115.7 (d, $J = 249,4$ Hz), 115.3 (d, $J = 21,4$ Hz), 63.1 (s), 60.0 (s), 52.2 (s), 43.7 (d, J=2.6 Hz), 41.2 (t, J=21.8 Hz) 25.8 (s), 21.6 (s), 13.8 (s).

$^{19}$F NMR (376 MHz, CDCl3) δ ppm -100.3 (d, $J = 263.2$ Hz, 1F), -103.5 (d, $J = 263.2$ Hz, 1F), -114.5 (1F)

HRMS (ESI) Calcd for C$_{30}$H$_{30}$F$_3$NO$_4$S: [M]+Na = 580.1740. Found: 580.1740.
(E)-ethyl

3-(4-((4-chlorophenyl)(phenyl)methylene)-3-methyl-1-tosylpyrrolidin-3-yl)-2,2-difluoropropanoate

White solid; melting point 56–58 °C; 75.7 mg; 66% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm 7.62 (d, $J = 8.0$ Hz, 2H), 7.34 (d, $J = 8.0$ Hz, 2H), 7.30–7.20 (m, 5H), 7.11 (d, $J = 8.0$ Hz, 2H), 7.05–7.03 (m, 2H), 4.29–4.31 (m, 2H), 3.75 (d, $J = 14.8$ Hz, 1H), 3.68 (d, $J = 11.2$ Hz, 1H), 3.24 (d, $J = 9.2$ Hz, 1H), 3.12 (d, $J = 9.6$ Hz, 1H), 2.46 (s, 3H), 2.16–2.07 (m, 2H), 1.30 (t, $J = 7.2$ Hz, 3H), 1.19 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ ppm 163.8 (t, $J = 32.3$ Hz), 143.9 (s), 142.1 (s), 140.1 (s), 138.7 (s), 136.4 (s), 133.3 (s), 131.5 (s), 130.1 (s), 129.7 (s), 128.9 (s), 128.5 (s), 128.1 (s), 127.4 (s), 127.1 (s), 115.6 (t, $J = 253.0$ Hz), 63.1 (s), 59.9 (s), 52.2 (s), 43.7 (d, $J = 3.0$ Hz), 41.3 (t, $J = 22.0$ Hz), 25.9 (s), 21.6 (s), 13.8 (s).

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ ppm -100.3 (d, $J = 263.2$ Hz, 1F), -103.5 (d, $J = 263.2$ Hz, 1F).

HRMS (ESI) Calcd for C$_{30}$H$_{30}$ClF$_2$NO$_4$S: [M]+H = 574.1625. Found: 574.1625
(E)-ethyl

3-(4-((4-bromophenyl)(phenyl)methylene)-3-methyl-1-tosylpyrrolidin-3-yl)-2,2-difluoropropanoate

White solid; melting point 58–60 °C; 76.5 mg; 62% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm 7.62 (d, $J = 8.0$ Hz, 2H), 7.41 (d, $J = 8.4$ Hz, 2H), 7.34 (d, $J = 8.0$ Hz, 2H), 7.30–7.26 (m 2H), 7.22 (d, $J = 8$ Hz, 1H), 7.06–7.02 (m, 4H), 4.30–4.21 (m, 2H), 3.74 (d, $J = 16.0$ Hz, 1H), 3.68 (d, $J = 16.0$ Hz, 1H), 3.24 (d, $J = 9.2$ Hz, 1H), 3.12 (d, $J = 9.6$ Hz, 1H), 2.45 (s, 3H), 2.17–2.08 (m, 2H), 1.30 (t, $J = 7.2$ Hz, 3H), 1.18 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ ppm 163.7 (t, $J = 32.0$ Hz), 143.9 (s), 141.9 (s), 140.9 (s), 139.2 (s), 136.4 (s), 131.5 (s), 130.4 (s), 129.7 (s), 128.9 (s), 128.0 (s), 127.4 (s), 127.1 (s), 121.4 (s), 115.6 (t, $J = 253.0$ Hz), 63.1 (s), 59.9 (s), 52.2 (s), 43.7 (d, $J = 3.0$ Hz), 41.3 (t, $J = 22.0$ Hz), 25.8 (s), 21.5 (s), 13.8 (s).

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ ppm -100.1 (d, $J = 263.2$ Hz), -103.55 (d, $J = 263.2$ Hz).

HRMS (ESI) Calcd for C$_{30}$H$_{30}$BrF$_2$NO$_4$S: [M]+H = 618.1120. Found: 618.1126.
(E)-ethyl
2,2-difluoro-3-(3-methyl-4-((4-nitrophenyl)(phenyl)methylene)-1-tosylpyrrolidin-3-yl)propanoate

Yellow solid; melting point 66–68 °C; 39.7 mg; 34% yield.

$^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm 8.16 (d, $J = 8.4$ Hz, 2H), 7.62 (d, $J = 8.0$ Hz, 2H), 7.39–7.35 (m, 4H), 7.32–7.30 (m 2H), 7.27–7.25 (m, 1H), 7.07–7.05 (m, 2H), 4.30–4.24 (m, 2H), 3.74 (s, 2H), 3.30 (d, $J = 9.6$ Hz, 1H), 3.08 (d, $J = 9.6$ Hz, 1H), 2.47 (s, 3H), 2.17–2.08 (m, 2H), 1.29 (t, $J = 7.2$ Hz, 3H), 1.15 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ ppm 163.6 (t, $J = 32.2$ Hz), 147.2 (s), 147.0 (s), 144.0 (s), 141.7 (s), 141.1 (s), 135.6 (s), 131.5 (s), 129.8 (s), 129.7 (s), 129.2 (s), 128.1 (s), 127.8 (s), 127.2 (s), 123.6 (s), 115.5 (t, $J = 250.7$ Hz), 63.3 (s), 59.9 (s), 52.3 (s), 43.7 (d, $J = 2.0$ Hz), 41.4 (t, $J = 22.0$ Hz), 25.8 (s), 21.6 (s), 13.8 (s).

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ ppm -100.2 (d, $J = 267.0$ Hz, 1F), -103.3 (d, $J = 267.0$ Hz, 1F).

HRMS (ESI) Calcd for C$_{30}$H$_{30}$F$_{2}$N$_{2}$O$_{6}$S: [M]+Na = 607.1685. Found: 607.1686.
\[ \text{White solid; melting point 52–54 °C; 76.5 mg; 63\% yield.} \]

\[ \text{\textsuperscript{1}H NMR (400 MHz, CDCl}_3\text{) \delta ppm 7.62 (d, } J = 8.4 \text{ Hz, 2H), 7.56 (d, } J = 8.0 \text{ Hz, 2H), 7.36 (d, } J = 8.0 \text{ Hz, 2H), 7.33–7.29 (m 4H), 7.26–7.24 (m, 1H), 7.08–7.06 (m, 2H), 4.28–4.21 (m, 2H), 3.76–3.68 (m, 4H), 3.10 (d, } J = 9.6 \text{ Hz, 1H), 2.47 (s, 3H), 2.14–2.05 (m, 2H), 1.27 (t, } J = 7.2 \text{ Hz, 3H), 1.17 (s, 3H).} \]

\[ \text{\textsuperscript{13}C NMR (100 MHz, CDCl}_3\text{) \delta ppm 163.7 (t, } J = 32.1 \text{ Hz), 144.0 (s), 144.0 (s), 141.6 (s), 141.1 (s), 136.2 (s), 131.2 (s), 129.7 (s), 129.4 (q, } J = 32.8 \text{ Hz), 129.1 (s), 129.0 (s), 128.0 (s), 127.5 (s), 127.1 (s), 125.3–125.2 (m), 123.9 (q, } J = 270.4 \text{ Hz), 115.6 (t, } J = 249.4 \text{ Hz), 63.1 (s), 59.8 (s), 52.2 (s), 43.6 (d, } J = 2.8 \text{ Hz), 41.3 (t, } J = 21.0 \text{ Hz), 25.8 (s), 21.6 (s), 13.7 (s).} \]

\[ \text{\textsuperscript{19}F NMR (376 MHz, CDCl}_3\text{) \delta ppm -62.6 (s, 3F), -99.9 (d, } J = 263.2 \text{ Hz, 1F), -103.9 (d, } J = 263.2 \text{Hz, 1F).} \]

\[ \text{HRMS (ESI) Calcd for C}_{31}\text{H}_{30}\text{F}_{5}\text{NO}_{4}\text{S: [M]+Na = 630.1708. Found: 630.1704.} \]
(E)-ethyl 2,2-difluoro-3-(3-methyl-4-((3-nitrophenyl)(phenyl)methylene)-1-tosylpyrrolidin-3-yl)propanoate

Yellow solid; melting point 54–56 °C; 58.4 mg; 50% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ ppm 8.12–8.10 (m, 1H), 8.03 (s, 1H) 7.62 (d, J = 8.0 Hz, 2H), 7.57–7.49 (m, 2H), 7.37–7.30 (m 4H), 7.27–7.23 (m, 1H), 7.09–7.07 (m, 2H), 4.28–4.22 (m, 2H), 3.75 (s, 2H), 3.30 (d, J = 9.6 Hz, 1H), 3.09 (d, J = 9.6 Hz, 1H), 2.47 (s, 3H), 2.17–2.08 (m, 2H), 1.28 (t, J = 7.2 Hz, 3H), 1.15 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ ppm 163.9 (t, J = 32.0 Hz), 148.0 (s), 144.0 (s), 142.1 (s), 141.9 (s), 141.2 (s), 135.3 (s), 134.8 (s), 131.4 (s), 129.7 (s), 129.4 (s), 129.1 (s), 128.0 (s), 127.8 (s), 127.2 (s), 123.6 (s), 122.3 (s), 115.5 (t, J = 253.0 Hz), 63.2 (s), 59.8 (s), 52.3 (s), 43.7 (d, J = 2.0 Hz), 41.4(t, J = 22..0 Hz), 25.8 (s), 21.5 (s), 13.7 (s).

$^{19}$F NMR (376 MHz, CDCl$_3$) δ ppm -100.5 (d, J = 267.0 Hz, 1F), -103.4 (d, J = 267.0 Hz, 1F).

(E)-methyl

4-((4-(3-ethoxy-2,2-difluoro-3-oxopropyl)-4-methyl-1-tosylpyrrolidin-3-ylidene)(phenyl)methyl)benzoate

White solid; melting point 192–194 °C; 46.6 mg; 39% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ ppm 7.96 (d, $J = 8.4$ Hz, 2H), 7.62 (d, $J = 8.0$ Hz, 2H), 7.36–7.34 (m 2H), 7.31–7.22 (m 5H), 7.08–7.06 (m, 2H), 4.28–4.20 (m, 2H), 3.88 (s, 3H), 3.76 (d, $J = 14.4$ Hz, 1H), 3.73 (d, $J = 14.4$ Hz, 1H), 3.25 (d, $J = 9.6$ Hz, 1H), 3.11 (d, $J = 9.6$ Hz, 1H), 2.46 (s, 3H), 2.16–2.06 (m, 2H), 1.27 (t, $J = 7.2$ Hz, 3H), 1.17 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ ppm 166.5 (s), 163.7 (t, $J = 32.0$ Hz), 145.1 (s), 143.9 (s), 141.7 (s), 140.9 (s), 136.7 (s), 131.5 (s), 129.7 (s), 129.6 (s), 129.1 (s), 128.9 (s), 128.0 (s), 127.4 (s), 127.2 (s), 115.6 (t, $J = 249.0$ Hz), 63.1 (s), 59.9 (s), 52.2 (s), 52.1 (s), 43.7 (d, $J = 3.0$ Hz), 41.3 (t, $J = 22.0$ Hz), 25.7 (s), 21.5 (s), 13.7 (s).

$^{19}$F NMR (376 MHz, CDCl$_3$) δ ppm -100.3 (d, $J = 263.2$ Hz), -103.4 (d, $J = 263.2$ Hz).

HRMS (ESI) Calcd for C$_{32}$H$_{33}$F$_2$NO$_6$S: [M]+Na = 620.1889. Found: 620.1890.
(E)-ethyl

3-((3,4-dichlorophenyl)(phenyl)methylene)-3-methyl-1-tosylpyrrolidin
n-3-yl)-2,2-difluoropropanoate

White solid; melting point 54–56 °C; 43.7 mg; 36% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ ppm 7.61 (d, $J$ = 8.4 Hz, 2H), 7.39–7.33 (m, 3H), 7.30–7.28 (m, 2H), 7.26–7.24 (m, 2H), 7.06–7.02 (m, 3H), 4.31–4.24 (m, 2H), 3.74 (d, $J$ = 14.8 Hz, 1H), 3.68 (d, $J$ = 14.8 Hz, 1H), 3.26 (d, $J$ = 9.6 Hz, 1H), 3.11 (d, $J$ = 9.6 Hz, 1H), 2.46 (s, 3H), 2.18–2.09 (m, 2H), 1.30 (t, $J$ = 7.2 Hz, 3H), 1.19 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ ppm 163.7 (t, $J$ = 32.2 Hz), 143.9 (s), 141.6 (s), 141.5 (s), 140.2 (s), 135.2 (s), 132.4 (s), 131.6 (s), 131.4 (s), 130.6 (s), 130.3 (s), 129.7 (s), 129.0 (s), 128.2 (s), 128.0 (s), 115.5 (t, $J$ = 253.0 Hz), 63.2 (s), 59.9 (s), 52.3 (s), 43.7 (d, $J$ = 2 Hz), 41.3 (t, $J$ = 21.0 Hz), 25.9 (s), 21.5 (s), 13.8 (s).

$^{19}$F NMR (376 MHz, CDCl$_3$) δ ppm -100.4 (d, $J$ = 263.2 Hz, 1F), -103.5 (d, $J$ = 263.7 Hz, 1F).

HRMS (ESI) Calcd for C$_{30}$H$_{29}$Cl$_2$F$_2$NO$_4$S: [M]+Na = 638.2147. Found: 638.2147.
ethyl

3-((4-(diphenylmethylene)-3-phenyl-1-tosylpyrroolidin-3-yl)-2,2-difluoropropyl)acetate

White solid; melting point 54–56 °C; 80.6 mg; 67% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm 7.62 (d, $J = 8.0$ Hz, 2H), 7.33 (d, $J = 8.0$ Hz, 2H), 7.28–7.24 (m, 2H), 7.21–7.18 (m, 6H), 7.06–7.00 (m, 5H), 6.75–6.73 (m, 2H), 4.11 (q, $J = 7.2$ Hz, 2H), 3.88 (s, 2H), 3.68 (d, $J = 10.0$ Hz, 1H), 3.56 (d, $J = 10.0$ Hz, 1H), 2.73–2.60 (m, 1H), 2.53–2.41 (m, 1H), 2.46 (s, 3H), 1.24 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ ppm 163.5 (t, $J = 32.0$ Hz), 144.3 (s), 143.8 (s), 142.4 (s), 139.6 (s), 139.5 (s), 137.7 (s), 131.5 (s), 129.6 (s), 128.6 (s), 128.5 (s), 128.0 (s), 127.7 (s), 127.2 (s), 126.9 (s), 126.7 (s), 126.3 (s), 115.6 (t, $J = 254.0$ Hz), 63.0 (s), 59.7 (s), 52.7 (s), 50.0 (d, $J = 4.2$ Hz), 39.7 (t, $J = 22.4$ Hz), 21.6 (s), 13.7 (s).

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ ppm -96.8 (d, $J = 263.2$ Hz, 1F), -102.0 (d, $J = 267.0$ Hz, 1F).

2,2-difluoro-3-(3-methyl-4-(phenyl(thiophen-2-yl)methylene)-1-tosylpyrroloidin-3-yl)propanoate

White solid; melting point 44–46 °C; 38.2 mg; 35% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ ppm 7.61 (d, $J = 8.0$ Hz, 2H), 7.34 (d, $J = 8.0$ Hz, 2H), 7.29 (d, $J = 8.0$ Hz, 2H), 7.25–7.22 (m, 2H), 7.08–7.06 (m, 2H), 6.93–6.91 (m, 1H), 6.88–6.87 (m, 1H), 4.30–4.24 (m, 2H), 3.74 (d, $J = 15.2$ Hz, 1H), 3.63 (d, $J = 15.2$ Hz, 1H), 3.21 (d, $J = 9.6$ Hz, 1H), 3.18 (d, $J = 9.6$ Hz, 1H), 2.45 (s, 3H), 2.39–2.17 (m, 1H), 1.34 (s, 3H), 1.30 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ ppm 163.8 (t, $J = 32.2$ Hz), 144.5(s), 143.9(s), 142.2 (s), 141.0 (s), 131.4 (s), 130.3 (s), 129.7 (s), 128.8 (s), 128.0 (s), 127.4 (s), 127.1 (s), 126.8 (s), 126.6 (s), 126.1 (s), 115.8 (t, $J = 252.8$ Hz), 63.0 (s), 60.0 (s), 52.4 (s), 43.9 (d, $J = 3.0$ Hz), 40.5 (t, $J = 21.0$ Hz), 25.3 (d, $J = 2.0$ Hz), 21.5 (s), 13.8 (s).

$^{19}$F NMR (376 MHz, CDCl$_3$) δ ppm -100.5 (d, $J = 263.2$ Hz, 1F), -103.4 (d, $J = 263.2$ Hz, 1F).

HRMS (ESI) Calcd for C$_{28}$H$_{29}$F$_2$NO$_4$S$_2$: [M]+Na = 568.1398. Found: 568.1399.
(Z)-ethyl

2,2-difluoro-3-(3-methyl-4-(phenyl(p-tolyl)methylene)-1-tosylpyrrolidin-3-yl)propanoate

White solid; melting point 43–45 °C; 75.2 mg; 68% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ ppm 7.63 (d, $J$ = 8.4 Hz, 2H), 7.35 (d, $J$ = 8.0 Hz, 2H), 7.29–7.25 (m, 2H), 7.21 (d, $J$ = 8.0 Hz, 1H), 7.09–7.07 (m, 2H), 6.95 (d, $J$ = 8.0 Hz 2H), 4.27–4.18 (m, 2H), 3.78 (d, $J$ = 14.4 Hz, 1H), 3.68 (d, $J$ = 14.4 Hz, 1H), 3.19 (d, $J$ = 9.6 Hz, 1H), 3.14 (d, $J$ = 9.6 Hz, 1H), 2.47 (s, 3H), 2.30 (s, 3H), 2.13–2.04 (m, 2H), 1.27 (t, $J$ = 7.2 Hz, 3H), 1.19 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ ppm 163.8 (t, $J$ = 32.4 Hz), 143.8 (s), 140.4 (s), 139.8 (s), 139.6 (s), 137.5 (s), 136.8 (s), 131.3 (s), 129.6 (s), 129.4 (s), 128.6 (s), 128.2 (s), 128.0 (s), 127.1 (s), 127.0 (s), 115.7 (t, $J$ = 253.0 Hz), 62.9 (s), 59.9 (s), 52.1 (s), 43.5 (d, $J$ = 3.0 Hz), 41.1 (t, $J$ = 22.0 Hz), 25.7 (s), 21.5(S), 21.0 (s), 13.8 (s).

$^{19}$F NMR (376 MHz, CDCl$_3$) δ ppm -100.3 (d, $J$ = 263.2 Hz, 1F), -103.8 (d, $J$ = 263.2 Hz, 1F).

(Z)-ethyl

2,2-difluoro-3-(4-((4-methoxyphenyl)(phenyl)methylene)-3-methyl-1-tosylpyrrolidin-3-yl)propanoate

White solid; melting point 42–44 °C; 75.1 mg; 66% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm 7.64 (d, $J = 8.0$ Hz, 2H), 7.34 (d, $J = 8.0$ Hz, 2H), 7.29–7.25 (m, 2H), 7.22–7.21 (m, 1H), 7.14–7.12 (m, 2H), 6.99 (d, $J = 8.4$ Hz 2H), 6.79 (d, $J = 8.4$ Hz 2H), 4.26–4.19 (m, 2H), 3.81–3.69 (m, 5H), 3.21 (d, $J = 9.6$ Hz, 1H), 3.14 (d, $J = 9.6$ Hz, 1H), 2.45 (s, 3H), 2.14–2.03 (m, 2H), 1.27 (t, $J = 7.2$ Hz, 3H), 1.18 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ ppm 163.8 (t, $J = 32.8$ Hz), 158.5 (s), 143.8 (s), 140.1 (s), 139.9 (s), 137.2 (s), 134.9 (s), 131.6 (s), 129.6 (s), 128.6 (s), 128.4 (s), 128.2 (s), 128.0 (s), 127.1 (s), 115.8 (t, $J = 251.0$ Hz), 114.0 (s), 62.9 (s), 59.9 (s), 55.2 (s), 52.2 (s), 43.6 (d, $J = 2.0$ Hz), 41.2 (t, $J = 22.0$ Hz), 25.8 (s), 21.5 (s), 13.8 (s).

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ ppm -100.3 (d, $J = 263.2$ Hz, 1F), -103.7 (d, $J = 263.2$ Hz, 1F).

HRMS (ESI) Calcd for C$_{31}$H$_{33}$F$_2$NO$_5$S: [M]+Na = 592.1940. Found: 592.1939.
(Z)-ethyl

3-((4-((4-(tert-butyl)phenyl)(phenyl)methylene)-3-methyl-1-tosylpyrrolidin-3-yl)-2,2-difluoropropanoate

White solid; melting point 42–44 °C; 75.0 mg; 63% yield.

{
^1^H } NMR (400 MHz, CDCl₃) δ ppm 7.65 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.28–7.26 (m, 4H), 7.23–7.21 (m, 1H), 7.16–7.14 (m, 2H), 6.98 (d, J = 8.0 Hz, 2H), 4.26–4.19 (m, 2H), 3.83 (d, J = 14.4 Hz, 1H) 3.73 (d, J = 14.4 Hz, 1H), 3.20 (d, J = 9.6 Hz, 1H), 3.14 (d, J = 9.6 Hz, 1H), 2.46 (s, 3H), 2.13–2.04 (m, 2H), 1.29 (s, 9H), 1.27–1.26 (m, 3H), 1.18 (s, 3H).

{
^{13^C } } NMR (100 MHz, CDCl₃) δ ppm 163.9 (t, J = 32.0 Hz), 149.9 (s), 143.8 (s), 140.5 (s), 139.9 (s), 139.4 (s), 137.6 (s), 131.7 (s), 129.7 (s), 128.8 (s), 128.2 (s), 128.1 (s), 127.1 (s), 126.8 (s), 125.6 (s), 115.8 (t, J = 253.0 Hz), 62.9 (s), 60.0 (s), 52.2 (s), 43.6 (d, J = 3.0 Hz), 41.2 (t, J = 22.0 Hz), 34.4 (s), 31.3 (s), 25.8 (s), 21.6 (s), 13.8 (s).

{
^{19^F } } NMR (376 MHz, CDCl₃) δ ppm -100.4 (d, J = 263.2 Hz, 1F), -103.7 (d, J = 263.2 Hz, 1F).

(Z)-ethyl

2,2-difluoro-3-(4-((4-fluorophenyl)(phenyl)methylene)-3-methyl-1-tosylpyrrolidin-3-yl)propanoate

White solid; melting point 42–44 °C; 73.6 mg; 66% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ ppm 7.63 (d, $J = 8.4$ Hz, 2H), 7.35 (d, $J = 8.0$ Hz, 2H), 7.31–7.23 (m, 3H), 7.15–7.13 (m, 2H), 7.07–7.03 (m, 2H), 6.97 (t, $J = 8.8$ Hz 2H), 4.27–4.20 (m, 2H), 3.74 (d, $J = 14.8$ Hz, 1H), 3.66 (d, $J = 14.4$ Hz, 1H), 3.22 (d, $J = 9.6$ Hz, 1H), 3.14 (d, $J = 9.6$ Hz, 1H), 2.46 (s, 3H), 2.14–2.05 (m, 2H), 1.28 (t, $J = 7.2$ Hz 3H), 1.19 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ ppm 163.9 (t, $J = 32.2$ Hz), 160.5 (s), 143.9 (s), 140.8 (s), 140.2 (s), 138.5 (d, $J = 3.0$ Hz), 136.7 (s), 131.6 (s), 129.7 (s), 129.0 (s), 129.0 (s), 128.7 (s), 128.4 (s), 128.1 (s), 127.5 (s), 115.8 (t, $J = 21.2$ Hz), 115.7 (t, $J = 253.0$ Hz), 63.1 (s), 60.0 (s), 52.2 (s), 43.7 (d, $J = 3.0$ Hz), 41.2 (t, $J = 21.6$ Hz), 25.9 (s), 21.6 (s), 13.8 (s).

$^{19}$F NMR (376 MHz, CDCl$_3$) δ ppm -100.3 (d, $J = 263.2$ Hz, 1F), -103.6 (d, $J = 263.2$ Hz, 1F), -114.8 (s, 1F).

(Z)-ethyl

3-(4-((4-chlorophenyl)(phenyl)methylene)-3-methyl-1-tosylpyrrolidin-3-yl)-2,2-difluoropropanoate

White solid; melting point 42–44 °C; 74.5 mg; 65% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm 7.63 (d, $J = 8.4$ Hz, 2H), 7.35 (d, $J = 8.0$ Hz, 2H), 7.29–7.25 (m, 5H), 7.15–7.13 (m, 5H), 7.03–7.01 (m, 2H), 4.27–4.21 (m, 2H), 3.72 (d, $J = 14.4$ Hz, 1H), 3.64 (d, $J = 14.4$ Hz, 1H), 3.21 (d, $J = 9.6$ Hz, 1H), 3.13 (d, $J = 9.6$ Hz, 1H), 2.46 (s, 3H), 2.14–2.04 (m, 2H), 1.28 (t, $J = 7.2$ Hz 3H), 1.19 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ ppm 163.8 (t, $J = 32.4$ Hz), 143.9 (s), 140.8 (s), 140.8 (s), 139.7 (s), 136.4 (s), 133.0 (s), 131.3 (s), 129.7 (s), 129.0 (s), 128.6 (s), 128.6 (s), 128.4 (s), 128.0 (s), 127.5 (s), 115.7 (t, $J = 249.1$ Hz), 63.0 (s), 59.8 (s), 52.1 (s), 43.7 (d, $J = 2.8$ Hz), 41.1 (t, $J = 21.4$ Hz), 25.8 (s), 21.6 (s), 13.8 (s).

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ ppm -100.2 (d, $J = 263.2$ Hz, 1F), -103.7 (d, $J = 263.2$ Hz, 1F).

HRMS (ESI) Calcd for C$_{30}$H$_{30}$ClF$_2$NO$_4$S: [M]+H = 574.1625. Found: 574.1620.
(Z)-ethyl

3-(4-((4-bromophenyl)(phenyl)methylene)-3-methyl-1-tosylpyrrolidin-3-yl)-2,2-difluoropropanoate

White solid; melting point 46–48 °C; 58.0 mg; 47% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ ppm 7.63 (d, $J = 8.4$ Hz, 2H), 7.41 (d, $J = 8.4$ Hz, 2H), 7.36 (d, $J = 8.4$ Hz, 2H), 7.31–7.25 (m, 3H), 7.14–7.12 (m, 2H), 6.96 (d, $J = 8.4$ Hz, 2H), 4.26–4.21 (m, 2H), 3.72 (d, $J = 14.4$ Hz, 1H), 3.64 (d, $J = 14.4$ Hz, 1H), 3.21 (d, $J = 9.6$ Hz, 1H), 3.13 (d, $J = 9.6$ Hz, 1H), 2.46 (s, 3H), 2.14–2.05 (m, 2H), 1.28 (t, $J = 7.2$ Hz 3H), 1.19 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ ppm 163.8 (t, $J = 32.4$ Hz), 143.9 (s), 141.3 (s), 140.7 (s), 139.6 (s), 136.4 (s), 131.9 (s), 131.2 (s), 129.7 (s), 128.9 (s), 128.6 (s), 128.4 (s), 128.0 (s), 127.5 (s), 121.2 (s), 115.6 (t, $J = 253.0$ Hz), 63.0 (s), 59.8 (s), 52.1 (s), 43.7 (d, $J = 2.6$ Hz), 41.1 (t, $J = 21.4$ Hz), 25.8 (s), 21.6 (s), 13.8 (s).

$^{19}$F NMR (376 MHz, CDCl$_3$) δ ppm -100.1 (d, $J = 263.2$ Hz, 1F), -103.7 (d, $J = 263.2$ Hz, 1F).

HRMS (ESI) Calcd for C$_{30}$H$_{30}$BrF$_2$NO$_4$S: [M]+H = 618.1120. Found: 618.1123.
(Z)-ethyl

2,2-difluoro-3-(3-methyl-4-(phenyl(4-(trifluoromethyl)phenyl)methylen)-1-tosylpyrroloidin-3-yl)propanoate

White solid; melting point 44–46 °C; 48.6 mg; 40% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm 7.63 (d, $J = 8.0$ Hz, 2H), 7.55 (d, $J = 8.0$ Hz, 2H), 7.36 (d, $J = 8.0$ Hz, 2H), 7.33–7.29 (m, 2H), 7.27–7.25 (m, 1H), 7.22 (d, $J = 8.0$ Hz, 2H), 7.18–7.16 (m, 2H), 4.28–4.22 (m, 2H), 3.71 (d, $J = 14.4$ Hz, 1H), 3.64 (d, $J = 14.4$ Hz, 1H), 3.23 (d, $J = 9.6$ Hz, 1H), 3.14 (d, $J = 9.6$ Hz, 1H), 2.46 (s, 3H), 2.17–2.07 (m, 2H), 1.29 (t, $J = 7.2$ Hz 3H), 1.21 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ ppm 163.7 (t, $J = 32.0$ Hz), 145.9 (s), 144.0 (s), 141.2 (s), 139.3 (s), 136.3 (s), 131.1 (s), 129.7 (s), 129.2 (q, $J = 32.2$ Hz), 128.6, 128.5 (s), 128.0 (s), 127.7 (s), 127.6 (s), 125.9–125.8 (m) 123.9 (q, $J = 269.2$ Hz), 115.7 (t, $J = 248.2$ Hz), 63.1 (s), 59.8 (s), 52.0 (s), 43.8 (d, $J = 2.6$ Hz), 41.1 (t, $J = 21.0$ Hz), 25.8 (s), 21.6 (s), 13.8 (s).

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ ppm -62.509 (s, 3F), -100.0 (d, $J = 263.2$ Hz, 1F), -103.7 (d, $J = 263.2$ Hz, 1F).

HRMS (ESI) Calcd for C$_{31}$H$_{30}$F$_{5}$NO$_{4}$S: [M]+H = 608.1888. Found: 608.1899.
(Z)-ethyl 2,2-difluoro-3-(3-methyl-4-(phenyl(m-tolyl)methylene)-1-tosylpyrrolidin-3-yl)propanoate

White solid; melting point 42−44 °C; 74.1 mg; 67% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ ppm 7.62 (d, $J$ = 8.0 Hz, 2H), 7.35 (d, $J$ = 8.0 Hz, 2H), 7.29–7.26 (m, 2H), 7.22 (d, $J$ = 7.2 Hz, 1H), 7.16–7.15 (m, 2H), 7.01 (d, $J$ = 7.6 Hz 1H), 6.88–6.85 (m, 2H), 4.27–4.20 (m, 2H), 3.76 (d, $J$ = 14.4 Hz, 1H), 3.66 (d, $J$ = 14.4 Hz, 1H), 3.19 (d, $J$ = 9.6 Hz, 1H), 3.14 (d, $J$ = 9.6 Hz, 1H), 2.46 (s, 3H), 2.29 (s, 3H), 2.13–2.04 (m, 2H), 1.28 (t, $J$ = 7.2 Hz, 3H), 1.20 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ ppm 163.8 (t, $J$ = 32.2 Hz), 143.8 (s), 142.4 (s), 140.3, (s), 139.8 (s), 138.4 (s), 137.7 (s), 131.3 (s), 129.6 (s), 128.5 (s), 128.2 (s), 128.0 (s), 127.9 (s), 127.7 (s),127.1 (s), 115.7 (t, $J$ = 249.0 Hz), 62.9 (s), 59.9 (s), 52.1 (s), 43.5 (d, $J$ = 2.0 Hz), 41.1 (t, $J$ = 21.4 Hz), 25.7 (s), 21.5 (s), 21.4 (s), 13.8 (s).

$^{19}$F NMR (376 MHz, CDCl$_3$) δ ppm -100.3 (d, $J$ = 263.2 Hz, 1F), -103.8 (d, $J$ = 263.2 Hz, 1F).

HRMS (ESI) Calcd for C$_{31}$H$_{33}$F$_2$NO$_4$S: [M]+Na = 576.1991. Found:

(Z)-ethyl

3-(4-((3-chlorophenyl)(phenyl)methylene)-3-methyl-1-tosylpyrrolidin-3-yl)-2,2-difluoropropanoate

White solid; melting point 42–44 °C; 86.0 mg; 75% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ ppm 7.63 (d, $J = 8.0$ Hz, 2H), 7.35 (d, $J = 8.0$ Hz, 2H), 7.29–7.27 (m, 2H), 7.26–7.24 (m, 1H), 7.22–7.19 (m, 2H), 7.16–7.14 (m, 2H), 7.06 (s, 1H), 6.98–6.97 (m, 1H), 4.28–4.20 (m, 2H), 3.74 (d, $J = 14.8$ Hz, 1H), 3.66 (d, $J = 14.4$ Hz, 1H), 3.22 (d, $J = 9.6$ Hz, 1H), 3.14 (d, $J = 9.6$ Hz, 1H), 2.46 (s, 3H), 2.14–2.03 (m, 2H), 1.28 (t, $J = 7.2$ Hz 3H), 1.18 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ ppm 163.7 (t, $J = 32.4$ Hz), 144.1 (s), 143.9 (s), 141.1 (s), 139.5 (s), 136.3 (s), 134.5 (s), 131.4 (s), 130.2 (s), 129.7 (s), 128.6 (s), 128.0 (s), 127.5 (s), 127.3 (s), 127.3 (s), 125.4 (s), 115.8 (t, $J = 252.8$ Hz), 63.0 (s), 59.8 (s), 52.1 (s), 43.7 (d, $J = 2.0$ Hz), 41.1 (t, $J = 21.6$ Hz), 25.7 (s), 21.5 (s), 13.8 (s).

$^{19}$F NMR (376 MHz, CDCl$_3$) δ ppm -100.3 (d, $J = 263.2$ Hz, 1F), -103.5 (d, $J = 263.2$ Hz, 1F).

HRMS (ESI) Calcd for C$_{30}$H$_{30}$ClF$_2$NO$_4$S: [M]+H = 574.1625. Found:
(Z)-ethyl

3-(4-((3,5-bis(trifluoromethyl)phenyl)(phenyl)methylene)-3-methyl-1-tosylpyrrolidin-3-yl)-2,2-difluoropropanoate

White solid; melting point 46–48 °C; 52.7 mg; 39% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm 7.77 (s, 1H), 7.61 (d, $J = 8.4$ Hz, 2H), 7.51 (s, 2H) 7.39–7.31 (m, 5H), 7.18–7.16 (m, 2H), 4.29–4.23 (m, 2H), 3.66 (d, $J = 14.4$ Hz, 1H), 3.58 (d, $J = 14.4$ Hz, 1H), 3.21 (d, $J = 9.6$ Hz, 1H), 3.14 (d, $J = 9.6$ Hz, 1H), 2.49 (s, 3H), 2.16–2.07 (m, 2H), 1.30 (t, $J = 7.2$ Hz 3H), 1.23 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ ppm 163.7 (t, $J = 32.4$ Hz), 144.3 (s), 144.2 (s), 143.0 (s), 138.3 (s), 134.9 (s), 132.2 (q, $J = 33.2$ Hz), 130.4 (s), 129.8 (s), 128.8 (s), 128.7 (s), 128.2 (s), 128.1 (s), 127.7 (s), 123.0 (q, $J = 271.2$ Hz),121.3–121.2 (m) 115.6 (t, $J = 252.8$ Hz), 63.1 (s), 59.9 (s), 52.3 (s), 44.0 (d, $J = 2.6$ Hz), 41.0 (t, $J = 21.6$ Hz), 25.8 (s), 21.6 (s), 13.8 (s).

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ ppm -62.78(s, 6F), -100.3 (d, $J = 265.3$ Hz, 1F), -103.5 (d, $J = 265.3$ Hz, 1F).

HRMS (ESI) Calcd for C$_{32}$H$_{29}$F$_8$NO$_4$S: [M]+H = 676.1762 Found: 676.1770.
(Z)-ethyl

3-(4-((3,5-dichlorophenyl)(phenyl)methylene)-3-methyl-1-tosylpyrrolidin-3-yl)-2,2-difluoropropanoate

White solid; melting point 54–56 °C; 70.4 mg; 58% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm 7.65 (d, $J$ = 8.4 Hz, 2H), 7.38 (d, $J$ = 8.0 Hz, 2H), 7.33–7.27 (m, 3H), 7.23–7.22 (s, 1H), 7.14–7.13 (m, 2H), 6.97–6.96 (m, 2H), 4.28–4.22 (m, 2H), 3.72 (d, $J$ = 14.4 Hz, 1H), 3.65 (d, $J$ = 14.4 Hz, 1H), 3.22 (d, $J$ = 9.6 Hz, 1H), 3.12 (d, $J$ = 9.6 Hz, 1H), 2.48 (s, 3H), 2.12–2.03 (m, 2H), 1.29 (t, $J$ = 7.2 Hz 3H), 1.18 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ ppm 163.7 (t, $J$ = 32.2 Hz), 145.0 (s), 144.1 (s), 141.8 (s), 138.8 (s), 135.3 (s), 135.1 (s), 131.0 (s), 129.8 (s), 128.6(s), 128.6(s), 128.0(s), 127.8 (s), 127.4 (s), 125.7 (s), 115.6 (t, $J$ = 253.0 Hz), 63.1 (s), 59.8 (s), 52.0 (s), 43.8 (d, $J$ = 2.6 Hz), 41.0 (t, $J$ = 21.4 Hz), 25.7 (s), 21.6 (s), 13.8 (s).

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ ppm -100.3 (d, $J$ = 267.0 Hz, 1F), -103.7 (d, $J$ = 267.0 Hz, 1F).

HRMS (ESI) Calcd for C$_{30}$H$_{29}$Cl$_2$F$_2$NO$_4$S: [M]+H = 608.1235. Found: 608.1238.
(Z)-ethyl

2,2-difluoro-3-(4-iodo(phenyl)methylene)-3-methyl-1-tosylpyrrolidin-3-yl]propanoate

White solid; melting point 36–38 °C; 90.7 mg; 77% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ ppm 7.75 (d, $J$ = 8.0 Hz, 2H), 7.41 (d, $J$ = 8.0 Hz, 2H), 7.33–7.29 (m, 2H), 7.18–7.16 (m, 2H), 4.28–4.194 (m, 2H), 3.95 (d, $J$ = 15.2 Hz, 1H), 3.79 (d, $J$ = 15.2 Hz, 1H), 3.34 (d, $J$ = 9.6 Hz, 1H), 3.25 (d, $J$ = 9.6 Hz, 1H), 2.48 (s, 3H), 2.07–1.92 (m, 2H), 1.28 (t, $J$ = 7.2 Hz, 3H), 1.10 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ ppm 163.6 (t, $J$ = 32.2 Hz), 148.6 (s), 144.1 (s), 142.7 (s), 131.3 (s), 129.9 (s), 128.5 (s), 128.4 (s), 128.1 (s), 127.8 (s), 115.3 (t, $J$ = 253.1 Hz), 93.5 (s), 63.1 (s), 61.0 (s), 60.7 (s), 45.3 (d, $J$ = 2.0 Hz), 40.8 (t, $J$ = 21.0 Hz), 24.8 (d, $J$ = 2.0 Hz), 21.6 (s), 13.8 (s).

$^{19}$F NMR (376 MHz, CDCl$_3$) δ ppm -100.4 (d, $J$ = 263.2 Hz, 1F), -103.9 (d, $J$ = 263.2Hz, 1F).

HRMS (ESI) Calcd for C$_{24}$H$_{26}$F$_2$INO$_4$S: [M]+Na = 612.0487. Found: 612.0482.
(Z)-ethyl

2,2-difluoro-3-(4-ido(4-methoxyphenyl)methylene)-3-methyl-1-tosylpyrrolidin-3-yl)propanoate

White solid; melting point 40–42 °C; 99.0 mg; 80% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ ppm 8.21 (d, $J = 9.2$ Hz, 2H), 7.75 (d, $J = 8.4$ Hz, 2H), 7.42 (d, $J = 8.0$ Hz, 2H), 7.37 (d, $J = 8.4$ Hz, 2H), 4.30–4.24 (m, 2H), 3.90 (s, 2H), 3.45 (d, $J = 9.6$ Hz, 1H), 3.16 (d, $J = 9.6$ Hz, 1H), 2.49 (s, 3H), 2.13–1.97 (m, 2H), 1.29 (t, $J = 7.2$ Hz, 3H), 1.05 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ ppm 163.4 (t, $J = 32.2$ Hz), 150.3 (s), 148.9 (s), 147.3 (s), 144.3 (s), 131.0 (s), 129.9 (s), 129.1 (s), 128.1 (s), 123.7 (s), 115.0 (t, $J = 253.0$ Hz), 89.4 (s), 63.4 (s), 61.2 (s), 60.6 (s), 45.3 (d, $J = 3.0$ Hz), 41.1 (t, $J = 21.9$ Hz), 24.9 (s), 21.6 (s), 13.8 (s).

$^{19}$F NMR (376 MHz, CDCl$_3$) δ ppm -99.9(d, $J = 267.0$ Hz, 1F),-103.6 (d, $J = 267.0$ Hz, 1F).

HRMS (ESI) Calcd for C$_{25}$H$_{28}$F$_2$INO$_5$S: [M]+Na = 657.0338. Found: 657.0328.
(Z)-ethyl

2,2-difluoro-3-(4-iodo(p-tolyl)methylene)-3-methyl-1-tosylpyrrolidin-3-yl)propanoate

White solid; melting point 40–42 °C; 85.6 mg; 71% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ ppm 7.74 (d, $J = 8.0$ Hz, 2H), 7.40 (d, $J = 8.0$ Hz, 2H), 7.11 (d, $J = 8.0$ Hz, 2H), 7.05 (d, $J = 8.2$ Hz, 2H), 4.27–4.21 (m, 2H), 3.92 (d, $J = 15.2$ Hz, 1H), 3.79 (d, $J = 15.2$ Hz, 1H), 3.34 (d, $J = 9.6$ Hz, 1H), 3.23 (d, $J = 9.6$ Hz, 1H), 2.48 (s, 3H), 2.33 (s, 3H), 2.09–1.95 (m, 2H), 1.27 (t, $J = 7.2$ Hz, 3H), 1.10 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ ppm 163.6 (t, $J = 32.2$ Hz), 148.3 (s), 144.0 (s), 139.8 (s), 138.5 (s), 131.2 (s), 129.8 (s), 129.0 (s), 128.1 (s), 127.7 (s), 115.3 (t, $J = 254.0$ Hz), 94.0 (s), 63.0 (s), 61.0 (s), 60.6 (s), 45.2 (d, $J = 2.0$ Hz), 40.8 (t, $J = 21.8$ Hz), 24.8 (s), 21.6 (s), 21.2 (s), 13.7 (s).

$^{19}$F NMR (376 MHz, CDCl$_3$) δ ppm -100.4 (d, $J = 263.2$ Hz, 1F), -103.8 (d, $J = 263.2$ Hz, 1F).

HRMS (ESI) Calcd for C$_{25}$H$_{28}$F$_2$INO$_4$S: [M]+Na = 626.0644. Found: 626.0645.
(Z)-ethyl

2,2-difluoro-3-(4-((4-fluorophenyl)iodomethylene)-3-methyl-1-tosylpyrrolidin-3-yl)propanoate

White solid; melting point 42–44 °C; 85.0 mg; 70% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm 7.74 (d, $J = 8.0$ Hz, 2H), 7.40 (d, $J = 8.0$ Hz, 2H), 7.18–7.15 (m, 2H), 7.04–7.00 (m, 2H), 4.29–4.22 (m, 2H), 3.92 (d, $J = 15.2$ Hz, 1H), 3.79 (d, $J = 15.2$ Hz, 1H), 3.36 (d, $J = 9.6$ Hz, 1H), 3.22 (d, $J = 9.6$ Hz, 1H), 2.48 (s, 3H), 2.08–1.94 (m, 2H), 1.29 (t, $J = 7.2$ Hz, 3H), 1.09 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ ppm 163.5 (t, $J = 32.3$ Hz), 162.1 (d, $J = 248.5$ Hz), 149.3 (s), 144.1 (s), 138.7 (d, $J = 3.6$ Hz), 131.0 (s), 129.8 (s), 129.7 (s), 128.1 (s), 115.5 (t, $J = 21.7$ Hz), 115.2 (t, $J = 253.4$ Hz), 112.7 (s), 92.1 (s), 63.2 (s), 61.1 (s), 60.6 (s), 45.3 (d, $J = 2.6$ Hz), 40.9 (t, $J = 21.7$ Hz), 24.8 (d, $J = 2.6$ Hz), 21.6 (s), 13.7 (s).

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ ppm -100.3 (d, $J = 263.2$ Hz, 1F), -103.8 (d, $J = 263.2$ Hz, 1F), -111.6 (s, 1F).

HRMS (ESI) Calcd for C$_{24}$H$_{25}$F$_3$INO$_4$S: [M]+Na = 630.0393. Found: 630.0391.
(Z)-ethyl

3-[(4-((4-chlorophenyl)iodomethylene)-3-methyl-1-tosylpyrrolidin-3-yl)]-2,2-difluoropropanoate

White solid; melting point 42–44 °C; 99.7 mg; 80% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm 7.74 (d, $J = 8.0$ Hz, 2H), 7.41 (d, $J = 8.0$ Hz, 2H), 7.30 (d, $J = 8.6$ Hz, 2H), 7.12 (d, $J = 8.4$ Hz, 2H), 4.30–4.22 (m, 2H), 3.91 (d, $J = 15.2$ Hz, 1H), 3.80 (d, $J = 15.2$ Hz, 1H), 3.37 (d, $J = 9.6$ Hz, 1H), 3.21 (d, $J = 9.5$ Hz, 1H), 2.48 (s, 3H), 2.09–1.96 (m, 2H), 1.30 (t, $J = 7.2$ Hz, 3H), 1.08 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ ppm 163.5 (t, $J = 32.2$ Hz), 149.4 (s), 144.1 (s), 141.1 (s), 134.4 (s), 131.1 (s), 129.9 (s), 129.3 (s), 128.7 (s), 128.1 (s), 115.1 (t, $J = 254.0$ Hz), 91.7 (s), 63.2 (s), 61.1 (s), 60.6 (s), 45.3 (d, $J = 3.0$ Hz), 40.9 (t, $J = 21.9$ Hz), 24.9 (s), 21.6 (s), 13.7 (s).

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ ppm -100.2 (d, $J = 267.0$ Hz, 1F), -103.8 (d, $J = 267.0$ Hz, 1F).

HRMS (ESI) Calcd for C$_{24}$H$_{25}$ClF$_2$INO$_4$S: [M]+Na = 646.0095. Found: 646.0098.
(Z)-ethyl

3-({4-{(4-bromophenyl)iodomethylene}-3-methyl-1-tosylpyrrolidin-3-yl}-2,2-difluoropropanoate

White solid; melting point 44–46 °C; 98.7 mg; 74% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm 7.74 (d, $J = 8.4$ Hz, 2H), 7.46 (d, $J = 8.4$ Hz, 2H), 7.40 (d, $J = 8.0$ Hz, 2H), 7.06 (d, $J = 8.4$ Hz, 2H), 4.31–4.22 (m, 2H), 3.91 (d, $J = 15.2$ Hz, 1H), 3.80 (d, $J = 15.2$ Hz, 1H), 3.37 (d, $J = 9.6$ Hz, 1H), 3.21 (d, $J = 9.6$ Hz, 1H), 2.48 (s, 3H), 2.09–1.96 (m, 2H), 1.30 (t, $J = 7.2$ Hz, 3H), 1.08 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ ppm 163.5 (t, $J = 32.2$ Hz), 149.4 (s), 144.2 (s), 141.6 (s), 131.6 (s), 131.1 (s), 129.9 (s), 129.5 (s), 128.1 (s), 122.6 (s), 115.1 (t, $J = 253.6$ Hz), 91.6 (s), 63.3 (s), 61.1 (s), 60.6 (s), 45.4 (d, $J = 3.0$ Hz), 40.9 (t, $J = 21.6$ Hz), 24.9 (s), 21.6 (s), 13.8 (s).

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ ppm -100.1 (d, $J = 266.0$ Hz, 1F), -103.8 (d, $J = 266.0$ Hz, 1F).

(Z)-ethyl 2,2-difluoro-3-(4-iodo(4-nitrophenyl)methylene)-3-methyl-1-tosylpyrroloidin-3-yl)propanoate

Yellow solid; melting point 44–46 °C; 67.2 mg; 53% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm 7.74 (d, $J$ = 8.4 Hz, 2H), 7.40 (d, $J$ = 8.0 Hz, 2H), 7.10 (d, $J$ = 8.8 Hz, 2H), 6.82 (d, $J$ = 8.8 Hz, 2H), 4.28–4.22 (m, 2H), 3.91 (d, $J$ = 15.2 Hz, 1H), 3.80 (s, 3H), 3.77 (d, $J$ = 15.2 Hz, 1H), 3.33 (d, $J$ = 9.6 Hz, 1H), 3.23 (d, $J$ = 9.6 Hz, 1H), 2.48 (s, 3H), 2.09–1.96 (m, 2H), 1.28 (t, $J$ = 7.2 Hz, 3H), 1.11 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ ppm 163.6 (t, $J$ = 32.4 Hz), 159.4 (s), 148.6 (s), 144.1 (s), 135.1 (s), 131.2 (s), 129.8 (s), 129.2 (s), 128.1 (s), 115.3 (t, $J$ = 253.0 Hz), 112.8 (s), 94.2 (s), 63.1 (s), 61.1 (s), 60.6 (s), 55.2 (s), 45.2 (d, $J$ = 2.6 Hz), 40.8 (t, $J$ = 22.0 Hz), 24.9 (s), 21.6 (s), 13.7 (s).

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ ppm -100.3 (d, $J$ = 263.2 Hz, 1F), -103.7 (d, $J$ = 263.2 Hz, 1F).

HRMS (ESI) Calcd for C$_{24}$H$_{25}$F$_2$IN$_2$O$_6$S: [M]+Na = 642.0593. Found: 642.0593
(Z)-ethyl 2,2-difluoro-3-(4-iodo(m-tolyl)methylene)-3-methyl-1-tosylpyrrolidin-3-yl)propanoate

White solid; melting point 39–41 °C; 91.7 mg; 76% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm 7.74 (d, $J = 8.4$ Hz, 2H), 7.40 (d, $J = 8.0$ Hz, 2H), 7.21–7.17 (m, 1H), 7.07 (d, $J = 7.6$ Hz, 1H), 6.99–6.96 (m, 2H), 4.27–4.20 (m, 2H), 3.93 (d, $J = 15.2$ Hz, 1H), 3.78 (d, $J = 15.2$ Hz, 1H), 3.33 (d, $J = 9.6$ Hz, 1H), 3.25 (d, $J = 9.6$ Hz, 1H), 2.48 (s, 3H), 2.31 (s, 3H), 2.09–1.90 (m, 2H), 1.27 (t, $J = 7.2$ Hz, 3H), 1.10 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ ppm 163.6 (t, $J = 32.4$ Hz), 148.2 (s), 144.1 (s), 142.5 (s), 138.1 (s), 131.2 (s), 129.8 (s), 129.3 (s), 128.4 (s), 128.2 (s), 128.1 (s), 124.8 (s), 115.3 (t, $J = 253.0$ Hz), 93.8 (s), 63.0 (s), 61.0 (s), 60.6 (s), 45.3 (d, $J = 2.6$ Hz), 40.8 (t, $J = 21.7$ Hz), 24.8 (d, $J = 2.0$ Hz), 21.6 (s), 21.3 (s), 13.7 (s).

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ ppm -100.4 (d, $J = 263.2$ Hz, 1F), -103.9 (d, $J = 263.2$ Hz, 1F).

(Z)-ethyl

3-((4-((3,5-dimethylphenyl)iodomethylene)-3-methyl-1-tosylpyrrolidin-3-yl)-2,2-difluoropropanoate

White solid; melting point 42–44 °C; 96.3 mg; 78% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ ppm 7.74 (d, $J = 8.0$ Hz, 2H), 7.40 (d, $J = 8.0$ Hz, 2H), 6.89 (s, 1H), 6.78 (s, 2H), 4.27–4.21 (m, 2H), 3.94 (d, $J = 14.8$ Hz, 1H), 3.76 (d, $J = 14.8$ Hz, 1H), 3.32 (d, $J = 9.6$ Hz, 1H), 3.25 (d, $J = 9.6$ Hz, 1H), 2.48 (s, 3H), 2.26 (s, 6H), 2.08–1.95 (m, 2H), 1.28 (t, $J = 7.2$ Hz, 3H), 1.11 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ ppm 163.6 (t, $J = 32.2$ Hz), 147.9 (s), 144.0 (s), 142.4 (s), 137.9 (s), 131.1 (s), 130.2 (s), 128.1 (s), 125.5 (s), 115.3 (t, $J = 253.0$ Hz), 94.1 (s), 63.0 (s), 61.0 (s), 60.6 (s), 45.2 (d, $J = 2.0$ Hz), 40.7 (t, $J = 21.0$ Hz), 24.9 (s), 21.6 (s), 21.2 (s), 13.7 (s).

$^{19}$F NMR (376 MHz, CDCl$_3$) δ ppm -100.7 (d, $J = 263.2$ Hz, 1F), -103.8 (d, $J = 263.2$ Hz, 1F).

HRMS (ESI) Calcd for C$_{26}$H$_{30}$F$_2$INO$_4$S: [M]+Na = 640.0800. Found: 640.0801
(E)-dimethyl

4-((4-bromophenyl)iodomethylene)-3-(3-ethoxy-2,2-difluoro-3-oxopropyl)-3-methylcyclopentane-1,1-dicarboxylate

White solid; melting point 43–45 °C; 89.2 mg; 71% yield.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) ppm 7.46 (d, \(J = 8.8\) Hz, 2H), 7.00 (d, \(J = 8.0\) Hz, 2H), 4.24–4.20 (m, 2H), 3.80 (s, 3H), 3.77 (s, 3H), 3.48–3.43 (m, 1H), 3.17 (d, \(J = 18.0\) Hz, 1H), 2.86 (d, \(J = 14.0\) Hz, 1H), 2.65 (d, \(J = 14.0\) Hz, 1H), 2.06–1.92 (m, 2H), 1.29 (t, \(J = 7.2\) Hz, 3H), 1.02 (s, 3H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) ppm 171.9 (s), 171.7 (s), 163.9 (t, \(J = 32.0\) Hz), 153.7 (s), 142.6 (s), 131.4 (s), 130.0 (s), 122.2 (s), 115.5 (t, \(J = 252.0\) Hz), 92.4 (s), 63.0 (s), 56.6 (s), 53.2 (s), 53.1 (s), 50.5 (s), 48.1 (s), 44.9 (d, \(J = 1.4\) Hz), 42.9 (t, \(J = 21.2\) Hz), 27.3 (s), 13.8 (s).

\(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) ppm -101.4 (d, \(J = 263.2\) Hz, 1F), -103.3 (d, \(J = 263.2\) Hz, 1F).

(Z)-ethyl

2,2-difluoro-3-(4-iodo(thiophen-2-yl)methylene)-3-methyl-1-tosylpyrroli

din-3-yl)propanoate

White solid; melting point 38–40 °C; 71.4 mg; 60% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ ppm 7.74 (d, $J = 8.0$ Hz, 2H), 7.40 (d, $J = 8.0$ Hz, 2H), 7.36–7.34 (m, 1H), 6.98–6.97 (m, 1H), 6.93–6.90 (m, 1H), 4.29–4.25 (m, 2H), 3.93 (d, $J = 15.2$ Hz, 1H), 3.76 (d, $J = 15.2$ Hz, 1H), 3.34 (d, $J = 9.6$ Hz, 1H), 3.28 (d, $J = 9.6$ Hz, 1H), 2.48 (s, 3H), 2.21–2.05 (m, 2H), 1.31 (t, $J = 7.2$ Hz, 3H), 1.21 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ ppm 163.6 (t, $J = 32.0$ Hz), 153.2 (s), 144.2 (s), 144.1 (s), 131.1 (s), 129.9 (s), 128.1 (s), 127.6 (s), 126.9 (s), 126.7 (s), 115.4 (t, $J = 252.0$ Hz), 83.7 (s), 63.2 (s), 61.3 (s), 60.7 (s), 45.8 (d, $J = 3.0$ Hz), 40.2 (t, $J = 22.0$ Hz), 24.4 (s), 21.6 (s), 13.8 (s).

$^{19}$F NMR (376 MHz, CDCl$_3$) δ ppm -100.7 (d, $J = 263.2$ Hz, 1F), -103.7 (d, $J = 263.2$ Hz, 1F).

HRMS (ESI) Calcd for C$_{22}$H$_{24}$F$_2$INO$_4$S$_2$: [M]+Na = 618.0052. Found: 618.0049.
(Z)-ethyl

2,2-difluoro-3-(4-(1-iodoethylidene)-3-methyl-1-tosylpyrrolidin-3-yl)propanoate

White liquid; 81.2 mg; 77% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm 7.70 (d, $J = 8.4$ Hz, 2H), 7.38 (d, $J = 8.0$ Hz, 2H), 4.37–4.31 (m, 2H), 3.79–3.74 (m, 1H), 3.63–3.62 (m, 1H), 3.54 (d, $J = 15.2$ Hz, 1H), 2.98 (d, $J = 9.6$ Hz, 1H), 2.59 (s, 3H), 2.53–2.32 (m, 2H), 2.46 (s, 3H), 1.42–1.35 (m, 2H), 1.37 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ ppm 163.8 (t, $J = 32.0$ Hz), 145.4 (s), 144.1 (s), 131.3 (s), 129.8 (s), 128.1 (s), 115.6 (t, $J = 249.0$ Hz), 94.0 (s), 63.4 (s), 61.5 (s), 44.1 (d, $J = 3.0$ Hz), 40.3 (t, $J = 22.0$ Hz), 30.5 (s), 23.0 (s), 21.6 (s), 13.9 (s).

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ ppm -100.3 (d, $J = 267.7$ Hz, 1F), -103.2 (d, $J = 267.3$ Hz, 1F).

HRMS (ESI) Calcd for C$_{19}$H$_{24}$F$_2$INO$_4$S: [M]+H = 528.0512. Found: 528.0513.
(Z)-ethyl

2,2-difluoro-3-(4-iodo(phenyl)methylene)-3-methyltetrahydrofuran-3-y

lpropanoate

White liquid; 26.4 mg; 30% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm 7.37–7.34 (m, 2H), 7.31–7.26 (m, 3H), 4.43 (d, $J$ = 14.8 Hz, 1H), 4.39 (d, $J$ = 14.8 Hz, 1H), 4.26–4.20 (m, 2H), 4.05 (d, $J$ = 8.8 Hz, 1H), 3.83–3.81 (m, 1H), 2.18–1.95 (m, 2H), 1.29 (t, $J$ = 8.0 Hz, 3H), 1.05 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ ppm 163.7 (t, $J$ = 32.0 Hz), 151.8 (s), 142.7 (s), 128.4 (s), 128.3 (s), 128.1 (s), 115.5 (t, $J$ = 253.0 Hz), 89.5 (s), 81.0 (s), 80.1 (s), 62.9 (s), 46.6 (d, $J$ = 3.0 Hz), 40.8 (t, $J$ = 22.0 Hz), 23.4 (t, $J$ = 2.0 Hz), 13.8 (s).

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ ppm -99.2 (d, $J$ = 265.1 Hz, 1F), -104.3 (d, $J$ = 264.7Hz, 1F).

(E)-ethyl

2,2-difluoro-3-(2-iodo(phenyl)methylene)-1-methylcyclopentyl)propanoate

White liquid; 60.2 mg; 69% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm 7.32–7.28 (m, 2H), 7.25–7.23 (m, 3H), 4.22–4.17 (m, 2H), 2.71–2.54 (m, 2H), 2.01–1.99 (m, 2H), 1.91–1.81 (m, 2H), 1.79–1.72 (m, 2H), 1.26 (t, $J = 7.2$ Hz, 3H), 1.05 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ ppm 164.7 (t, $J = 32.0$ Hz), 156.4 (s), 144.4 (s), 128.6 (s), 128.1 (s), 127.8 (s), 116.0 (t, $J = 250.0$ Hz), 93.3 (s), 62.7 (s), 45.4 (s), 44.3 (s), 42.4 (d, $J = 7.2$ Hz), 26.5 (s), 21.9 (s), 13.8 (s).

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ ppm -101.9 (s, 1F), -101.9 (s, 1F).

HRMS (ESI) Calcd for C$_{18}$H$_{21}$F$_2$I$_2$O$_2$: [M]+Na = 457.0447. Found: 457.0449.
(6-methylhept-6-en-1-yn-1-yl)benzene

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm 7.41–7.38 (m, 2H), 7.29–7.24 (m, 3H), 4.75–4.73 (m, 2H), 2.40 (t, $J = 7.2$ Hz, 2H), 2.18 (t, $J = 2.0$ Hz, 2H), 1.79–1.71 (m, 2H), 1.74 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ ppm 145.0 (s), 131.5 (s), 128.2 (s), 127.5 (s), 124.0 (s), 110.4 (s), 90.0 (s), 80.8 (s), 36.9 (s), 26.7 (s), 22.4 (s), 18.9 (s).
**ethyl 2,2-difluoro-4,4-diphenylbutanoate**

**ethyl 2,2-difluoro-4,4-diphenylbut-3-enoate**

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm 7.37–7.18 (m, 20H), 6.27 (d, J = 12.0 Hz, 1H), 4.27 (d, J = 7.2Hz, 1H), 3.89 (dd, J = 7.2Hz, J = 14.4Hz, 2H), 3.82 (dd, J = 7.2Hz, J = 14.4Hz, 2H), 2.98–2.89 (m, 2H), 1.16 (t, J = 7.2Hz, 3H), 1.16 (t, J = 7.2Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ ppm 163.8 (t, J = 33.0 Hz), 163.8 (t, J = 33.0 Hz), 150.1 (t, J = 9.0 Hz), 142.8 (s), 140.4 (s), 137.0 (s), 129.8 (s), 129.1 (s), 128.6 (s), 128.4 (s), 128.0 (s), 127.9 (s), 127.7 (s), 126.7 (s), 119.5 (t, J = 28.0 Hz), 115.6 (t, J = 249.0Hz), 112.5 (t, J = 243.0Hz), 62.7 (s), 62.7 (s), 44.8 (t, J = 5.0Hz), 40.2 (t, J = 23.0Hz), 13.6 (s).

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ ppm -90.9 (s, 2F), -103.5 (s, 2F).
NMR Spectroscopic Data

\[
\begin{align*}
\text{TsN} & \quad \text{CF}_2\text{COOEt} \\
3a & \\
\end{align*}
\]

- \[
\text{Diagram of NMR Spectroscopic Data}
\]
$E/Z = 7:1$
TsN
CF₂COOEt
3d
Br
TsN
CF$_2$COOEt

4f

$Z/E = 13:1$
4h
Z/E = 18:1
Cl-\text{-}\text{Cl} \\
\text{TsN} \\
\text{CF}_2\text{COOEt} \\
4k \\
Z/E = 17:1
5f

Z/E = 12:1
TsN

CF₂COOEt

5g

Z/E = 9:1
TSN
CF₂COOEt
5i
Z/E = 14:1
H-H Cosy and NOE spectra for 3d

![Chemical structure and spectra](image-url)