

Supporting Information

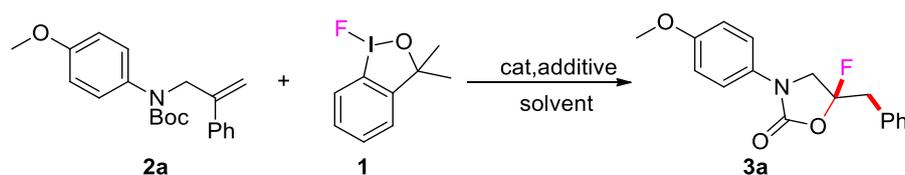
Silver-Promoted (Radio)fluorination of Unsaturated Carbamates via a Radical Process

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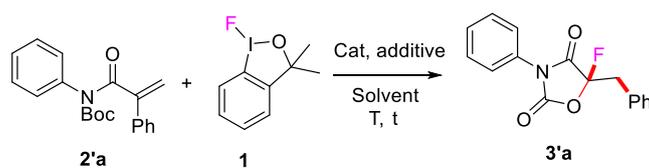
Table S1. Conditions optimizations for the fluorocyclization of **2a with **1****^[a]



Entry	Catalyst (mol %)	Additive	Solvent (1 mL)	Temp. (°C)	Time (h)	Yield ^[b] (%)
1	AgBF ₄ (10)	none	DCM	35	12	42
2	AgBF ₄ (10)	none	THF	35	12	<10
3	AgBF ₄ (10)	none	MeCN	35	12	trace
4	AgBF ₄ (10)	none	Dioxane	35	12	trace
5	AgBF ₄ (10)	none	DCM	45	12	48
6	AgBF ₄ (10)	none	DCM	55	12	84
7	AgBF ₄ (10)	none	DCE	55	12	60
8	AgBF ₄ (10)	none	DCE	65	12	59
9	AgNTf ₂ (10)	none	DCM	55	12	66
10	AgOTFA (10)	none	DCM	55	12	ND ^[c]
11	AgOTf (10)	none	DCM	55	12	42
12	AgNO ₃ (20)	none	DCM	55	12	<5%
13	AgSbF ₆ (10)	none	DCM	55	12	89 (74 ^[d])
14	AgF ₂ (20)	none	DCM	55	12	<5
15	Cu(OTf) ₂ (10)	none	DCM	55	12	27
16	Cu(OAc) ₂ (20)	none	DCM	55	12	19
17	CuI (10)	none	DCM	55	12	trace
18	Fe(OAc) ₂ (20)	none	DCM	55	12	trace
19	AgSbF ₆ (10)	none	DMSO	55	12	ND
20	AgSbF ₆ (10)	none	NMP	55	12	ND
21	AgSbF ₆ (10)	none	TFE	55	12	ND
22	AgSbF ₆ (10)	4Å Ms (34 mg)	DCM	55	12	ND
23	AgSbF ₆ (10)	MgSO ₄ (34 mg)	DCM	55	12	42
24	AgSbF ₆ (10)	Na ₂ CO ₃ (2.0 equiv)	DCM	55	12	ND
25	AgSbF ₆ (10)	DABCO (0.4 equiv)	DCM	55	12	ND
26	AgSbF ₆ (10)	H ₂ O (10 µL)	DCM	55	12	<10
27	AgSbF₆ (10)	none	DCM	55	3.5	90 (79^[d])
28	AgSbF ₆ (10)	none	DCM	55	1	79
29	AgSbF ₆ (100)	none	DCM	55	3.5	18
30	none	none	DCM	55	3.5	ND

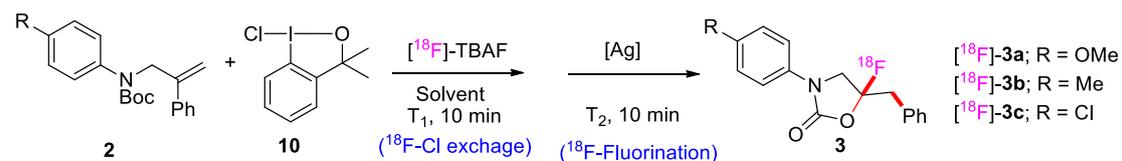
[a] Reaction conditions: substrate **2a** (0.1 mmol), **1** (1.5 equiv), catalyst, solvent, additive, temperature, time. [b] ¹H NMR yield with dibromomethane as internal standard. [c] ND = Not detected. [d] Isolated yield of compound **3a**.

Table S2. Conditions Optimizations for the fluorocyclization of 2'a with 1^[a]



Entry	Catalyst (mol %)	Additive	Solvent (mL)	Temp. (°C)	Time (h)	Yield ^[b] (%)
1	AgSbF ₆ (10)	none	DCM (1)	60	12	21
2	AgNO ₃ (10)	none	DCM (1)	60	12	ND ^[c]
3	AgOTf (10)	none	DCM (1)	60	12	ND
4	CH ₃ COOAg (10)	none	DCM (1)	60	12	ND
5	AgNTf ₂ (10)	none	DCM (1)	60	12	37
6	AgPF ₆ (10)	none	DCM (1)	60	12	27
7	AgBF ₄ (10)	none	DCM (1)	60	12	45
8	AgBF ₄ (10)	none	DCE (1)	60	12	43
9	AgBF ₄ (10)	none	DCE (1)	70	12	41
10	AgBF ₄ (20)	none	DCM (1)	60	12	45
11	AgBF ₄ (100)	none	DCM (1)	60	12	31
12	AgBF ₄ (10)	4Å Ms (20 mg)	DCM (1)	60	12	trace
13	AgBF ₄ (10)	Na ₂ SO ₄ (20 mg)	DCM (1)	60	12	28
14	AgBF ₄ (10)	MgSO ₄ (20 mg)	DCM (1)	60	12	43
15	AgBF ₄ (10)	none	DCM (0.7)	60	7	45
16	AgBF ₄ (10)	none	THF (1)	60	7	trace
17	AgBF ₄ (10)	none	Dioxane (1)	60	7	trace
18	AgBF ₄ (10)	none	DCM (0.5)	60	6	45
19	AgBF ₄ (10)	none	DCM (0.3)	60	6	47
20	AgBF ₄ (10)	none	DCM (0.1)	60	6	47
21	AgBF₄ (10)	none	DCM (0.1)	60	4	49 (48^[d])
22	AgBF ₄ (10)	none	DCM (0.1)	60	2	35
23	AgBF ₄ (10)	none	DCM (0.1)	55	4	47
24	AgBF ₄ (10)	none	DCM (0.1)	50	4	43
25	AgBF ₄ (10)	none	DCM (0.1)	45	4	30

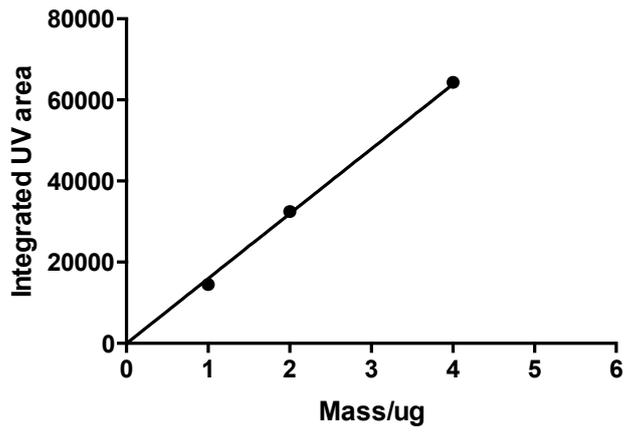
[a] Reaction conditions: substrate **2'a** (0.1 mmol), **1** (1.5 equiv), catalyst, solvent, additive, temperature, time. [b] ¹H NMR yield with dibromomethane as internal standard. [c] ND = Not detected. [d] Isolated yield of compound **3'a**.

Table S3. Radiosynthesis of [¹⁸F]-3a, [¹⁸F]-3b, and [¹⁸F]-3c (Two steps)

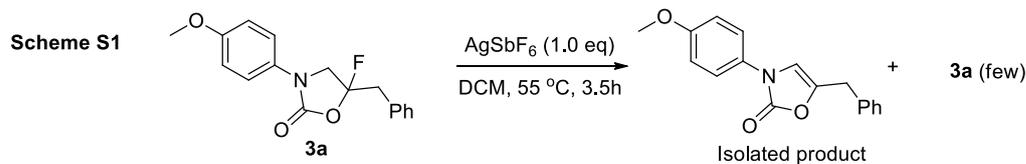
Entry	2 (μM)	10 (equiv)	solvent	T ₁ (°C)	[Ag] (equiv)	T ₂ (°C)	RCY ^[a] (%)
1	2a (0.24)	1.0	MeCN	60	AgOTf (1.0)	60	3
2	2a (0.24)	1.0	MeCN	60	AgOTf (1.0)	80	6±1^[c]
3	2a (0.24)	1.0	MeCN	80	AgOTf (1.0)	80	6
4	2a (0.24)	1.0	MeCN	60	AgSbF ₆ (1.0)	80	6 ^[d]
5	2a (0.03)	1.0	MeCN	60	AgOTf (1.0)	80	ND ^[b]
6	2a (0.24)	1.0	DMSO	60	AgOTf (1.0)	80	ND
7	2a (0.24)	1.0	DMF	60	AgOTf (1.0)	80	ND
8	2a (0.24)	1.0	MeCN	60	-	80	ND
9	2b (0.24)	1.0	MeCN	60	AgOTf (1.0)	80	6±2
10	2b (0.03)	1.0	MeCN	60	AgOTf (1.0)	80	ND
11	2b (0.24)	1.0	MeCN	60	AgBF ₄ (1.0)	80	4
12	2b (0.24)	1.0	MeCN	60	AgSbF ₆ (1.0)	80	7
13	2b (0.24)	1.0	MeCN	60	AgSbF ₆ (0.5)	80	ND
14	2b (0.24)	1.0	MeCN	60	AgSbF ₆ (0.05)	80	ND
15	2b (0.24)	1.0	MeCN	60	-	80	ND
16	2c (0.24)	1.0	MeCN	60	AgOTf (1.0)	80	4±1
17	2c (0.03)	1.0	MeCN	60	AgOTf (1.0)	80	ND

[a] Decay corrected radiochemical yield (RCY) is calculated by dividing the ¹⁸F-activity of the isolated product by the decay corrected starting ¹⁸F-activity. [b] ND = Not detected. [c] For 3 runs, SA = 34.2±2.1GBq/μmol. [d] SA = 29.8 GBq/μmol.

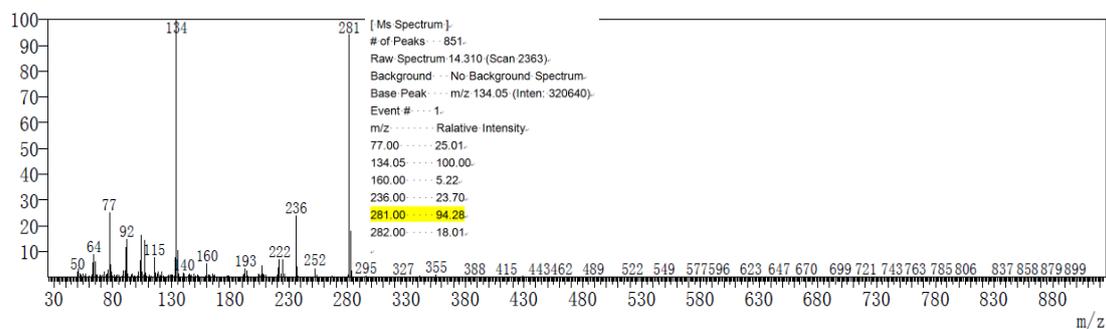
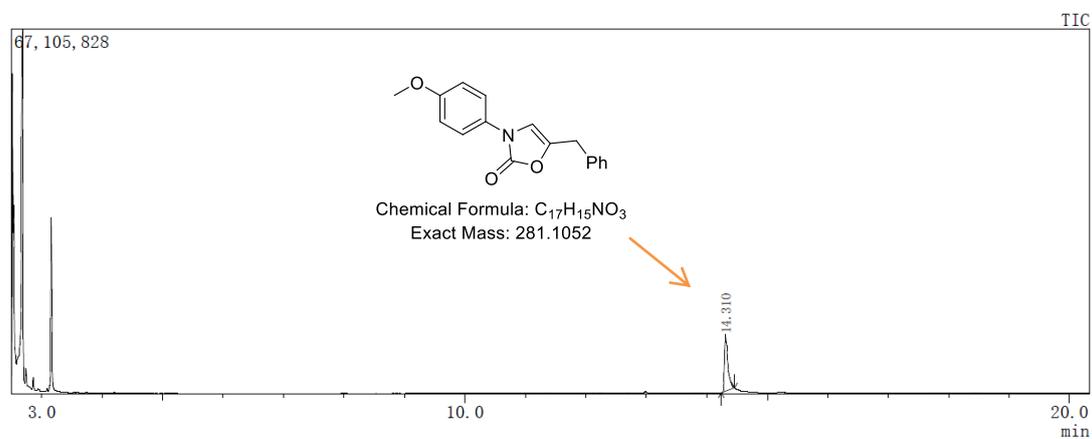
Specific activity: In order to determine the specific activity of the product after labeling, a standard solution of **3a** was used to establish a UV-HPLC mass curve. Reference compound **3a** was dissolved in MeCN at concentration of 1mg/mL. 1μL, 2μL and 4μL of this solution was then analyzed by HPLC (monitored at 212 nm). The corresponding peak area in the HPLC profile was integrated and a mass curve was acquired based on the relationship between the UV peak area and the analyzed mass of **3a** (as shown below). For example, to determine the specific activity of radiolabeled product ([¹⁸F]-**3a**), 1 MBq of [¹⁸F]-**3a** was reinjected to the HPLC (monitored at 212 nm). The resulting UV peak had an area of 138.3 integrated area. Using the mass curve below, the mass of [¹⁸F]-**3a** was calculated to be 8.62 ng (0.0286 nmol). Based on the activity measured at dose-calibrator (1MBq), the specific activity was calculated to be 1MBq/0.0286nmol =34.9 GBq/μmol. The experiment was repeated two more times and the specific activity was determined to be 31.8 and 35.9GBq/μmol, respectively at the end of synthesis. The average specific activity was determined to be 34.2±2.1GBq/μmol at the end of synthesis.



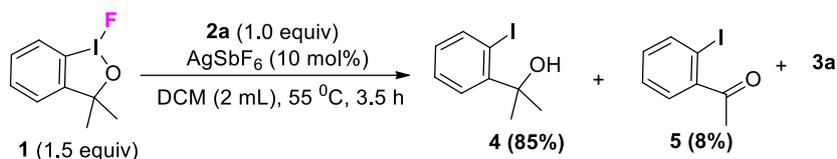
Schemes S1-3



Isolated product: Mp: 45-48 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.43 – 7.28 (m, 7H), 6.92 (d, J = 8.9 Hz, 2H), 6.38 (s, 1H), 3.80 (s, 1H), 3.78 (s, 1H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 158.06, 153.65, 140.57, 135.30, 129.08, 128.92, 128.80, 127.38, 122.90, 114.65, 110.88, 55.68, 32.70 ppm. IR (KBr) ν 3141, 2919, 2849, 1750, 1673, 1515, 1496, 1400, 1252, 1118, 1031, 978, 830, 734, 702.



Scheme S2. The side products **4** and **5** in the template reaction

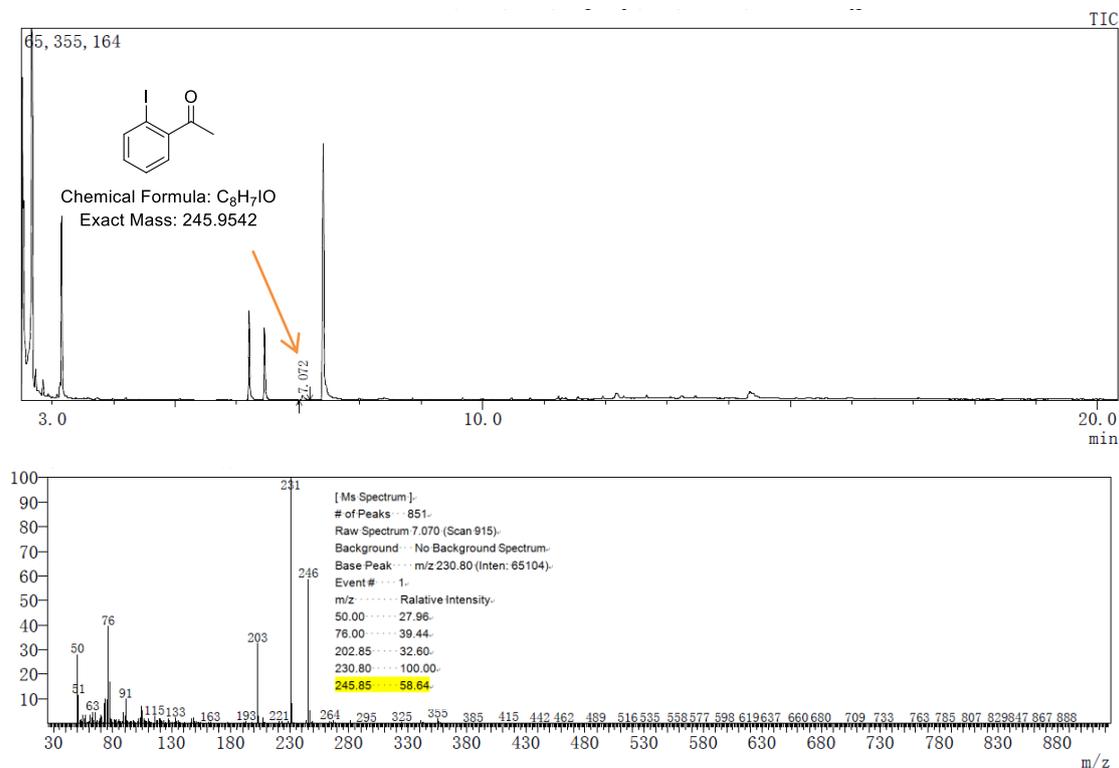


The substrate **2a** (67.8 mg, 0.20 mmol, 1.0 equiv), **1** (84 mg, 0.30 mmol, 1.5 equiv), AgSbF_6 (6.8 mg, 0.02 mmol, 0.1 equiv) and DCM (2 mL) were introduced to a glass vial. The vial was then sealed and the mixture was allowed to stir at 55 °C for 3.5 hours. After which, the reaction mixture was concentrated to dryness and CH_2Br_2 was added. 8% NMR yield of compound **5** was calculated by ^1H NMR spectroscopy using CH_2Br_2 as the internal standard. The mixture was purified by column chromatography (EtOAc/PE = 1/15) to afford compound **4** as a yellow oil (66.6 mg, 85% yield on the basis of the molality of compound **1**), and compound **5** with a few impurities (6 mg). The analytical data corresponds to those reported in the literature.

Compound 4^[1] ^1H NMR (400 MHz, CDCl_3) δ 7.96 (dd, J = 7.8, 1.2 Hz, 1H), 7.62 (dd, J = 8.0, 1.6 Hz, 1H), 7.32 (td, J = 8.0, 1.3 Hz, 1H), 6.89 (td, J = 7.7, 1.6 Hz, 1H), 2.62 (brs, 1H), 1.76 (s, 6H) ppm.

Compound 5^[2] ^1H NMR (400 MHz, CDCl_3) δ 7.94 (dd, J = 8.0, 0.8 Hz, 1H), 7.47 (dd, J = 7.7, 1.8 Hz, 1H), 7.41 (td, J = 7.5, 1.0 Hz, 1H), 7.16 – 7.10 (m, 1H), 2.62 (s, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 201.95, 144.12, 141.01, 131.96, 128.46, 128.20, 91.10, 29.64 ppm.

GCMS of reaction mixture



Scheme S3. One-pot radiosynthesis of [^{18}F]-**3a**, [^{18}F]-**3b**, and [^{18}F]-**3c**

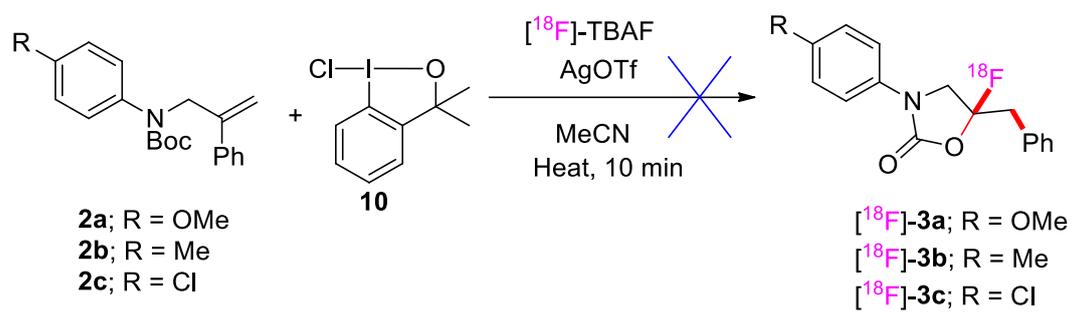
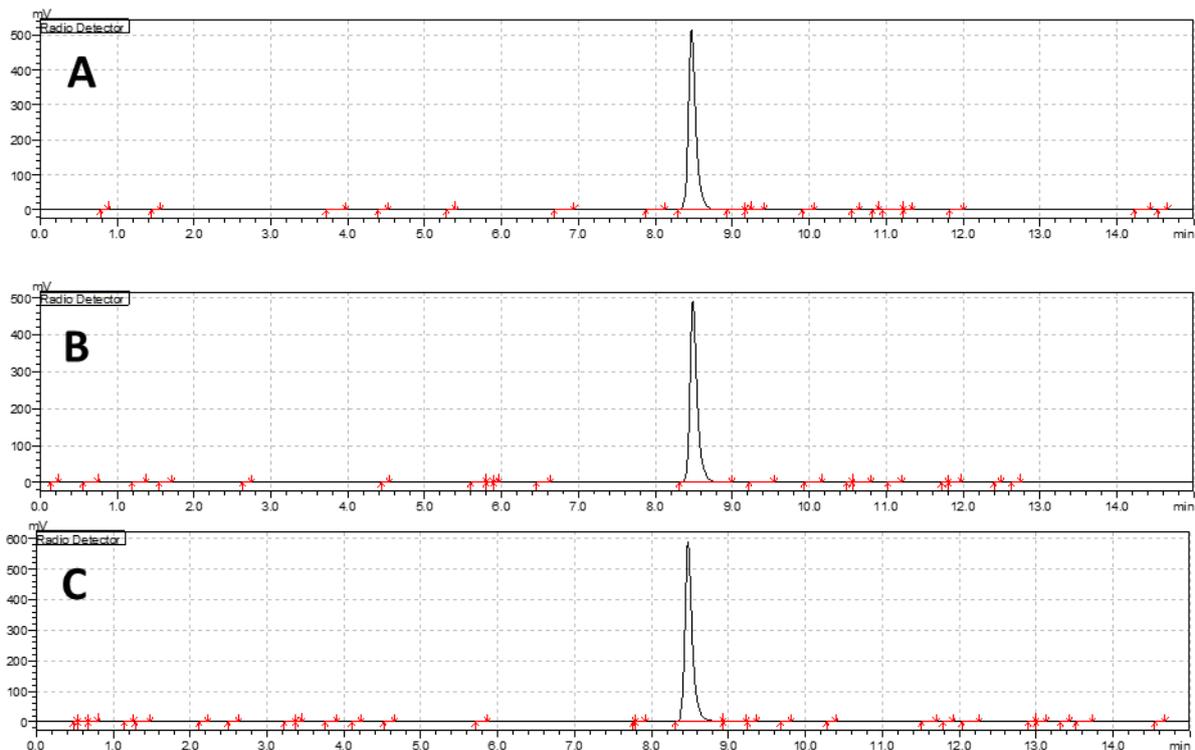


Figure S1. *In vitro* stability test

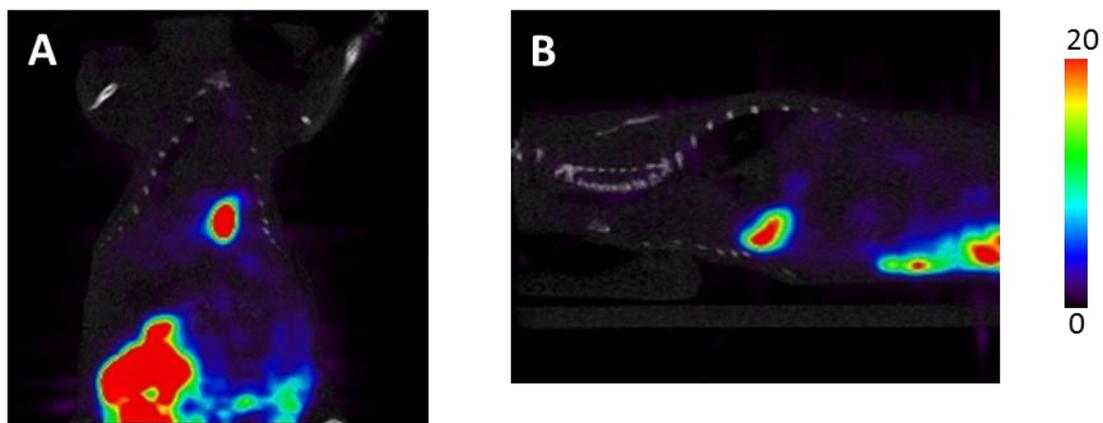
After HPLC purification, a fraction of purified [^{18}F]-**3a** was re-injected into the HPLC to confirm that only single radio peak was obtained at the starting point. Then, the probes were adjusted to pH 7 with 0.1 N NaOH. Then, 10X PBS was added to each solution to reconstruct the solution to 1X PBS. After 1 hour, 2 hours and 3 hours incubation at room temperature, a fraction of each probe (50 μCi) was injected into the HPLC.



Radio-HPLC profiles of [^{18}F]-3a** after incubation in phosphate buffer solution (PBS) pH=7.5 for 1 hour (A), 2 hours (B) and 3 hours (C)**

Figure S2. *In vivo* PET/CT Imaging

For PET image acquiring, nude mice was injected with 0.1 mCi of [¹⁸F]-**3a** in 1X PBS pH 7.5 (300 μ L) via the tail vein. At post-injection time point, the mice were anesthetized using isoflurane (2% in oxygen), then placed on the imaging cradle with body temperature maintained. The static PET/CT acquisition were then achieved and reconstructed for analysis.



Decay corrected microPET/CT images of nude mice from a static scan at 1 hour post-injection (A: Coronal image, B: Sagittal image) after the injection of [¹⁸F]-**3a**

1 General Information

Chemistry experiments:

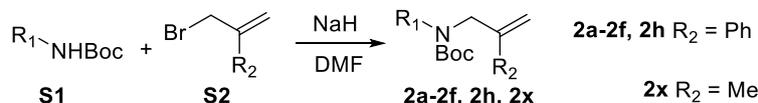
All reagents and solvents were used as received from commercial suppliers unless otherwise noted. All reactions were monitored by thin layer chromatography (TLC) with pre-coated silica gel GF254 plates and visualized by UV (wavelength 254 nm). Column chromatography was performed on silica gel (300-400 mesh). ^1H NMR spectra was recorded on FT AM 400 (400 MHz). Chemical shifts are given in parts per million (ppm) referenced to ^1H solvent peaks (δ 7.26 ppm for CDCl_3 , δ 2.50 ppm for DMSO-d_6). The fully decoupled ^{13}C NMR was recorded on FT AM 400 (101 MHz). Chemical shifts were reported in ppm referenced to residue ^{13}C solvent peaks (77.16 ppm for CDCl_3 , δ 39.52 ppm for DMSO-d_6). The following abbreviations were used to describe peak splitting patterns: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, td = triplet of doublet, ddd = doublet of doublet of doublet, m = multiplet. Coupling constants, J , were reported in hertz (Hz). Infrared (IR) spectra were recorded neat in KBr cell. Frequencies are given in centimeter inverse (cm^{-1}) and only selected absorbance is reported. High resolution mass spectra (ESI) were obtained by using the UHD Accurate-Mass Q-TOF. High resolution mass spectra (EI) were obtained from National Center for Organic Mass Spectrometry, Shanghai Institute of Organic Chemistry. Melting points were measured with SGW X-4 micro melting point apparatus.

Radiochemistry experiments:

All chemicals are analytical grade and used without further purification. Analytical reversed-phase high-performance liquid chromatography (HPLC) was accomplished on a SHIMADZU chromatography system (Model CBM-20A). The λ absorbance detector and the model 2200 scaler ratemeter radiation detector were added to the HPLC system. HPLC was performed on a Phenomenex, Kinetex[®] 5 μm EVO C18 100 Å, 250 x 4.6 mm LC Column with a flow of 1 mL/min.

2 Preparation and characterization of Substrates

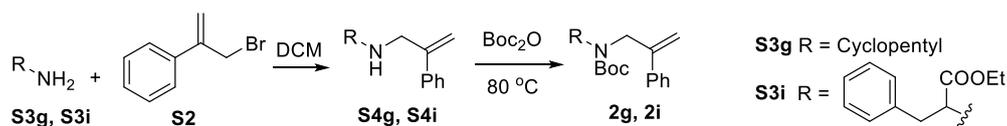
2.1 Synthesis of substrates 2a-2f, 2h, 2x^[3]



The typical procedure of preparing **2a** ($\text{R}_1 = 4\text{-OMeC}_6\text{H}_4$; $\text{R}_2 = \text{C}_6\text{H}_5$)

To a sealing tube was added NaH (60%, 264 mg, 6.6 mmol, 1.5 equiv) and 5 mL DMF, which was filled with N_2 gas. The solution of **S1** (1 g, 4.4 mmol, 1.0 equiv) in DMF (5 mL) was charged to the system dropwise at 0°C . The reaction mixture was allowed to stir at 0°C for 1.5 hours. After which, **S2** (1.14 g, 5.8 mmol, 1.3 equiv) was added. The reaction mixture was allowed to stir at room temperature overnight. EtOAc (30 mL) and water (30 mL) were added to the mixture. Then, the aqueous solution was extracted by EtOAc (30 mL \times 2). The combined organic phases were washed by brine (30 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (eluted with EtOAc/PE = 1/15) to afford **2a** as a colorless oil (1.35 g, 91% yield).

2.2 Synthesis of substrates 2g, 2i

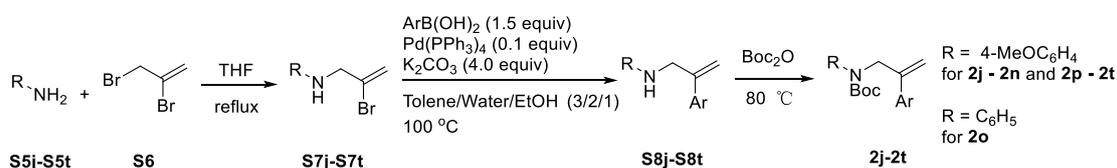


The typical procedures of preparing **2i**

The solution of **S3i** (1.1 g, 5.7 mmol, 2.0 equiv) in DCM (10 mL) was cooled to 0°C . The mixture of **S2** (561 mg, 2.85 mmol, 1.0 equiv) and DCM (5 mL) was dropwise added to the system. The reaction was stirred at room temperature overnight. DCM (30 mL) and water (30 mL) were added to the mixture. Then, the aqueous solution was extracted by DCM (30 mL \times 2). The combined organic phases were washed by brine, dried with Na_2SO_4 , concentrated and purified by column chromatography (eluted with EtOAc/PE = 1/10) to afford **S4i** as a colorless oil (500 mg, 57% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.37 (d, $J = 7.1$ Hz, 2H), 7.33 – 7.17 (m, 6H), 7.14 (d, $J = 7.2$ Hz, 2H), 5.38 (s, 1H), 5.18 (s, 1H), 4.12 (q, $J = 7.1$ Hz, 2H), 3.71 (d, $J = 14.2$ Hz, 1H), 3.57 (t, $J = 7.0$ Hz, 1H), 3.47 (d, $J = 14.2$ Hz, 1H), 3.03 – 2.85 (m, 2H), 1.18 (t, $J = 7.1$ Hz, 3H) ppm.

To a sealing tube was added **S4i** (500 mg, 1.62 mmol, 1.0 equiv) and Boc_2O (706 mg, 3.24 mmol, 2.0 equiv). The mixture was allowed to stir at 80°C overnight. The mixture was purified by silica gel column directly and eluted with EtOAc/PE = 1/10 to afford product **2i** as a colorless oil (616 mg, 93% yield).

2.3 Synthesis of substrates 2j-2t



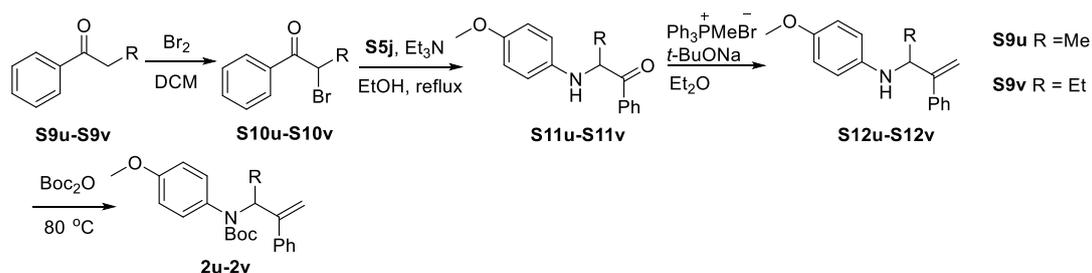
The typical procedures of preparing **2p** (R = 4-MeOC₆H₄; Ar = 3,5-diMeC₆H₃)

S6 (8 g, 40 mmol, 1.0 equiv) was added to a solution of **S5p** (24.6 g, 200 mmol, 5.0 equiv) in THF (100 mL). The reaction mixture was allowed to stir at 70 °C overnight. The mixture was cooled to room temperature, and then most of the solvent was evaporated. EtOAc (100 mL) and water (100 mL) were added to the mixture. Then, the aqueous solution was extracted by EtOAc (50 mL × 2). The combined organic phases was dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography (eluted with EtOAc/PE = 1/15) to afford **S7p** as a dark red oil (7.88 g, 81% yield). ¹H NMR (400 MHz, CDCl₃) δ 6.84 – 6.69 (m, 2H), 6.70 – 6.51 (m, 2H), 5.85 (s, 1H), 5.55 (s, 1H), 3.95 (s, 2H), 3.75 (s, 3H) ppm.

(3,5-Dimethylphenyl)boronic acid (900 mg, 6 mmol, 1.5 equiv), Pd(PPh₃)₄ (462 mg, 0.4 mmol, 0.1 equiv), and K₂CO₃ (2.2 g, 16 mmol, 4.0 equiv) were added to a Schlenk tube, which was protected with N₂ gas. **S7p** (968 mg, 4 mmol, 1.0 equiv), dissolved in solvent (tolene/water/ethanol = 3/2/1, 18 mL), was added to the tube. The mixture was allowed to stir at 100 °C overnight. TLC monitoring showed the complete consumption of starting material **S7p**. EtOAc (30 mL) and water (30 mL) were added to the mixture. Then, the aqueous solution was extracted by EtOAc (30 mL × 2). The combined organic phases were washed by brine, dried with Na₂SO₄, concentrated and purified by column chromatography (eluted with EtOAc/PE = 1/20) to afford **S8p** as a colorless oil (506 mg, 47% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.06 (s, 2H), 6.96 (s, 1H), 6.82 – 6.75 (m, 2H), 6.64 – 6.56 (m, 2H), 5.42 (s, 1H), 5.28 (d, *J* = 0.8 Hz, 1H), 4.09 (s, 2H), 3.75 (s, 3H), 3.64 (brs, 1H), 2.33 (s, 6H) ppm.

S8p (500 mg, 1.87 mmol, 1.0 equiv) and Boc₂O (2 g, 9.35 mmol, 5.0 equiv) was added to a sealing tube. The mixture was allowed to stir at 80 °C overnight. The mixture was purified by silica gel column directly and eluted with DCM/PE (2/1) to afford product **2p** as a colorless oil (365 mg, 53% yield).

2.4 Synthesis of substrate 2u-2v



The typical procedures of preparing **2u**

To a solution of **S9u** (2 g, 15 mmol, 1.0 equiv) in DCM (25 mL) was added bromine (2.4 g, 15 mmol, 1.0 equiv) dropwise at 0 °C. The reaction was stirred at room temperature for 30 min. Saturated NaHCO₃ solution was added to the reaction mixture. After being added Na₂S₂O₃ (1 mol/L, 2 mL), the organic phase was separated, washed by water (30 mL), brine (30 mL) respectively and dried over anhydrous Na₂SO₄. The organic phase was concentrated to afford **S10u** as a colorless oil (3 g, 94% yield). ¹H NMR (400 MHz, CDCl₃) δ 8.05 – 8.00 (m, 2H), 7.63 – 7.55 (m, 1H), 7.51 – 7.46 (m, 2H), 5.30 (q, *J* = 6.6 Hz, 1H), 1.91 (d, *J* = 6.6 Hz, 3H) ppm.

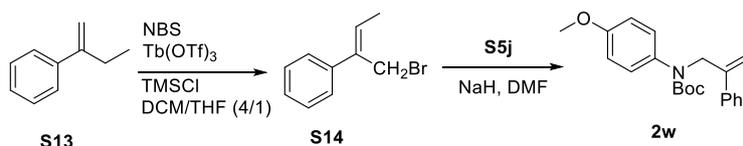
S10u (1.5 g, 7 mmol, 1.0 equiv), **S5j** (1.03 g, 8.4 mmol, 1.2 equiv) and triethylamine (1.4 g, 14 mmol, 2.0 equiv) in a round bottom flask were dissolved in ethanol (20 mL). The reaction

mixture was allowed to reflux for 4 hours, until the complete consumption of **S10u**, which was monitored by TLC. The mixture was cooled to room temperature, and then most of the solvent was removed. EtOAc (30 mL) and water (30 mL) were added to the mixture. The aqueous phase was extracted by EtOAc (30 mL × 2). The combined organic phases were washed by brine (30 mL), dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography (eluted with EtOAc/PE = 1/10) to afford **S11u** as a colorless oil (1.69 g, 95% yield). ¹H NMR (400 MHz, CDCl₃) δ 8.06 – 7.95 (m, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 6.80 – 6.72 (m, 2H), 6.71 – 6.61 (m, 2H), 5.06 (q, *J* = 6.9 Hz, 1H), 3.73 (s, 3H), 1.46 (d, *J* = 6.9 Hz, 3H) ppm.

Methyltriphenylphosphonium bromide (2.14 g, 6 mmol, 1.5 equiv) and *t*-BuONa (500 mg, 5.2 mmol, 1.3 equiv) were added to a Schlenk tube, which was protected with N₂ gas and cooled to 0 °C. Then, Et₂O (15 mL) was charged to the tube. The reaction was stirred at the same temperature for 15 min, after which the color of reaction mixture turned into yellow. The solution of **S11u** (1.02 g, 4 mmol, 1.0 equiv) in Et₂O (5 mL) was added to the system. The reaction was allowed to stir at room temperature overnight. Et₂O (30 mL) and water (30 mL) were added to the mixture. The aqueous phase was extracted by Et₂O (20 mL × 2). The combined organic phases were washed by brine, dried with Na₂SO₄, concentrated and purified by column chromatography (eluted with EtOAc/PE = 1/30) to afford **S12u** as a colorless oil (385 mg, 38% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.42 – 7.38 (m, 2H), 7.37 – 7.27 (m, 3H), 6.81 – 6.73 (m, 2H), 6.63 – 6.54 (m, 2H), 5.30 (d, *J* = 1.0 Hz, 1H), 5.26 (d, *J* = 0.8 Hz, 1H), 4.35 (q, *J* = 6.6 Hz, 1H), 3.74 (s, 3H), 3.63 (brs, 1H), 1.33 (d, *J* = 6.6 Hz, 3H) ppm.

To a sealing tube was added **S12u** (380 mg, 1.5 mmol, 1.0 equiv) and Boc₂O (1.64 g, 7.5 mmol, 5.0 equiv). The mixture was allowed to stir at 80 °C overnight. The mixture was purified by silica gel column directly and eluted with EtOAc/PE (1/20) to afford product **2u** as a colorless oil (513 mg, 97% yield).

2.5 Synthesis of substrate 2w

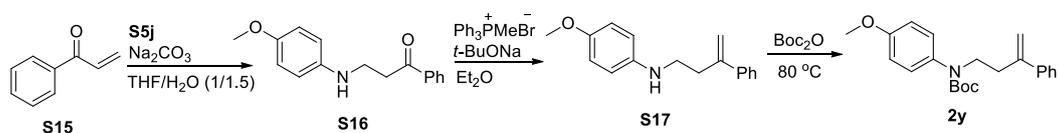


Compound **S14** was prepared according to literature procedures.^[4]

To a round bottom flask was added **S13** (700 mg, 5.3 mmol, 1.0 equiv), NBS (1.13 g, 6.4 mmol, 1.2 equiv), Yb(OTf)₃ (81 mg, 0.13 mmol, 0.025 equiv) and solvent (DCM/THF = 4/1, 15 mL). The reaction was stirred at room temperature for 30 min. TMSCl (15 mg, 0.13 mmol, 0.025 equiv) was added and the reaction mixture was stirred for 1 hour. After water (30 mL) were added to the mixture, the aqueous solution was extracted by DCM (20 mL × 3). The organic phases were combined, washed by brine (30 mL), dried over Na₂SO₄ and concentrated under reduced pressure successively. The residue was purified by column chromatography (eluted with PE) to afford **S14** (760 mg, 90% purity, 61% yield), which participated in the next step without further purification. The analytical data corresponds to those reported in the literature.^[4] ¹H NMR (400 MHz, CDCl₃) δ 7.44 (d, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 7.2 Hz, 1H), 6.10 (q, *J* = 7.1 Hz, 1H), 4.40 (s, 2H), 1.92 (d, *J* = 7.1 Hz, 3H) ppm.

NaH (60%, 180 mg, 4.5 mmol, 1.5 equiv) and 5 mL DMF was added to a sealing tube which was filled with N₂ gas. The solution of **S5j** (669 mg, 3 mmol, 1.0 equiv) in DMF (5 mL) was added to the system dropwise at 0 °C. The mixture was allowed to stir at the same temperature for 1.5 hours. After which, **S14** (696 mg, 90% purity, 2.96 mmol, 1.0 equiv) was added. The mixture was allowed to stir at room temperature for 4 hours. EtOAc (30 mL) and water (30 mL) were added to the mixture. The aqueous phase was extracted by EtOAc (15 mL × 2) again. The combined organic phases were washed by brine (20 mL), dried over Na₂SO₄ and concentrated under reduced pressure successively. The residue was purified by column chromatography (eluted with EtOAc/PE = 1/15) to afford **2w** as a white solid (654 mg, 62% yield).

2.6 Synthesis of substrate 2y

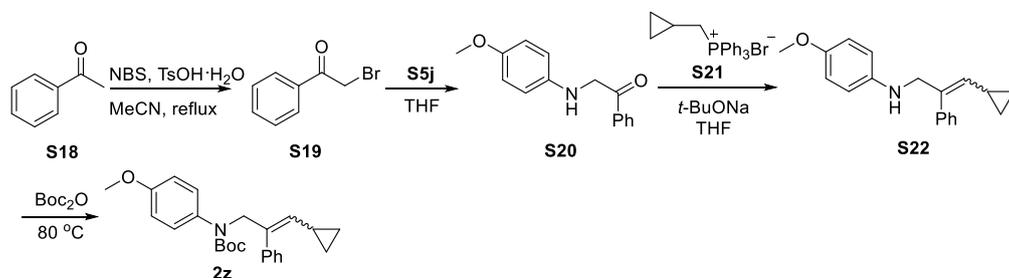


To a round bottom flask was added **S5j** (1.02 g, 8.3 mmol, 1.1 equiv), **S15** (1 g, 7.6 mmol, 1.0 equiv), Na₂CO₃ (1.6 g, 15.2 mmol, 2.0 equiv), H₂O (15 mL) and THF (10 mL). The reaction mixture was stirred at room temperature for 4 hours. Modulating the PH value to neutral by diluted hydrochloric acid (1 mol/L), EtOAc (50 mL) and water (50 mL) were added to the mixture. The aqueous phase was extracted by EtOAc (30 mL × 2). The combined organic phases were washed by brine (30 mL), dried over Na₂SO₄ and concentrated under reduced pressure successively. The residue was purified by column chromatography (eluted with EtOAc/PE = 1/10) to afford **S16** as a white solid (920 mg, 47% yield). ¹H NMR (400 MHz, CDCl₃) δ 8.03 – 7.88 (m, 2H), 7.61 – 7.54 (m, 1H), 7.49 – 7.42 (m, 2H), 6.85 – 6.72 (m, 2H), 6.67 – 6.56 (m, 2H), 3.85 (brs, 1H), 3.75 (s, 3H), 3.56 (t, *J* = 6.1 Hz, 2H), 3.27 (t, *J* = 6.1 Hz, 2H) ppm.

Methyltriphenylphosphonium bromide (3.86 g, 10.8 mmol, 3.0 equiv) and *t*-BuONa (1.04 g, 10.8 mmol, 3.0 equiv) were added to a Schlenk tube, which was protected with N₂ gas and cooled to 0 °C. Then, Et₂O (25 mL) was introduced to the tube. The reaction was stirred at the same temperature for 30 min, after which the color of the reaction mixture turned into yellow. The solution of **S16** (0.92 g, 3.6 mmol, 1.0 equiv) in Et₂O (5 mL) was added to the system. The reaction mixture was allowed to stir at room temperature for 24 hours, until the complete consumption of **S16**, which was monitored by TLC. EtOAc (30 mL) and water (30 mL) were added to the mixture. The aqueous phase was extracted by EtOAc (30 mL × 2) again. The combined organic phases were washed by brine (30 mL), dried over Na₂SO₄ and concentrated under reduced pressure successively. The residue was purified by column chromatography (eluted with EtOAc/PE = 1/15) to afford **S17** as a colorless oil (800 mg, 88% yield), which participated in the next step directly.

To a sealing tube was added **S17** (800 mg, 3.16 mmol, 1.0 equiv) and Boc₂O (2.07 g, 9.48 mmol, 3.0 equiv). The mixture was allowed to stir at 80 °C for 24 hours. The mixture was purified by silica gel column directly and eluted with EtOAc/PE (1/10) to afford product **2y** as a colorless oil (990 mg, 89% yield).

2.7 Synthesis of substrate **2z**



Compound **S19** was prepared according to literature procedures.^[5]

To a sealing tube was added **S18** (2.4 g, 20 mmol, 1.0 equiv), NBS (4.63 g, 26 mmol, 1.3 equiv), TsOH·H₂O (380 mg, 2 mmol, 0.1 equiv) and MeCN (30 mL). The reaction mixture was heated to reflux overnight. EtOAc (50 mL) and water (50 mL) were added to the mixture. The aqueous phase was extracted by EtOAc (30 mL × 2) again. The combined organic phases were washed by brine (30 mL), dried over Na₂SO₄ and concentrated under reduced pressure. The crude product (3.64 g) was used without purification.

To a solution of **S5j** (4.5 g, 36.6 mmol, 2.0 equiv) in THF (80 mL) was dropwise added **S19** (3.64 g, 18.3 mmol, 1.0 equiv), which was dissolved in 20 mL THF. The reaction was stirred at room temperature until **S19** consumption completed, which was monitored by TLC. Then, after most of the solvent was removed, EtOAc (100 mL) and water (100 mL) was added to the mixture. The aqueous phase was extracted by EtOAc (50 mL × 2). The combined organic phases were washed by brine (20 mL), dried over Na₂SO₄ and concentrated under reduced pressure successively. The residue was purified by column chromatography (eluted with EtOAc/PE = 1/15) to afford **S20** as a yellow solid (1.14 g, 26% yield), which was used directly.

(bromomethyl)cyclopropane (2.7 g, 20 mmol, 1.0 equiv) and triphenylphosphane (5.24 g, 20 mmol, 1.0 equiv) was added to a sealing tube. The mixture was allowed to stir at 110 °C for 30 min. The reaction system was cooled to room temperature, and then EtOAc (30 mL) was introduced. The mixture was filtered, and the white solid was washed by EtOAc three times to afford **S21** (6.2 g, 78% yield). ¹H NMR (400 MHz, CD₃CN) δ 8.00 – 7.59 (m, 15H), 3.44 (dd, *J* = 12.0, 6.8 Hz, 2H), 1.03 – 0.88 (m, 1H), 0.62 – 0.42 (m, 2H), 0.31 – 0.15 (m, 2H) ppm.

S21 (4.3 g, 10.8 mmol, 2.3 equiv) and *t*-BuONa (0.93 g, 9.4 mmol, 2.0 equiv) were added to a Schlenk tube, which was protected with N₂ gas and cooled to 0 °C. Then, THF (15 mL) was added to the tube. The reaction was stirred at the same temperature for 30 min, after which the color of the reaction mixture turned into red. **S20** (1.14 g, 4.7 mmol, 1.0 equiv) dissolved in THF (10 mL) was added to the system. The reaction mixture was allowed to stir at room temperature for 24 hours. The mixture was filtered and got rid of most of the solvent. EtOAc (50 mL) and water (50 mL) were added to the mixture. The aqueous phase was extracted by EtOAc (30 mL × 2) again. The combined organic phases were washed by brine (30 mL), dried over Na₂SO₄ and concentrated under reduced pressure successively. The residue was purified by column chromatography (eluted with EtOAc/PE = 1/20) to afford **S22** as a colorless

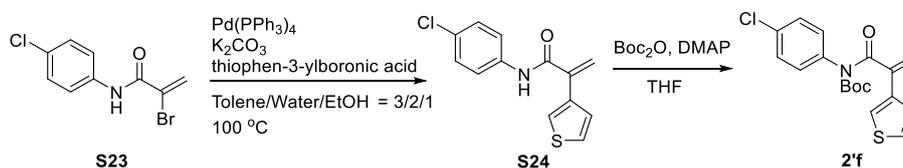
oil (945 mg, 72% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.40 – 7.18 (m, 5H), 6.84 – 6.72 (m, 2H), 6.68 – 6.51 (m, 2H), [5.30 (d, $J = 9.8$ Hz), 5.08 (d, $J = 10.0$ Hz), (1H)], [4.20 (s), 3.93 (s), (2H)], [3.76 (s), 3.74 (s), (3H)], 1.51 – 1.39 (m, 1H), [0.92 – 0.85 (m), 0.72 – 0.62 (m), (2H)], [0.56 – 0.48 (m), 0.44 – 0.34 (m), (2H)] ppm.

To a sealing tube was added **S22** (945 mg, 3.4 mmol, 1.0 equiv) and Boc_2O (2.23 g, 10.2 mmol, 3.0 equiv). The mixture was allowed to stir at 80 °C for 24 hours. The mixture was purified by silica gel column directly and eluted with DCM/PE (1/1) to afford product **2z** as a colorless oil (1.27 g, 98% yield).

2.8 Synthesis of substrate 2'a-2'e

Compound **2'a-2'e** were synthesized according to literature procedures.^[3]

2.9 Synthesis of substrate 2'f

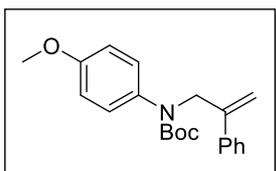


S23 (782 mg, 3 mmol, 1.0 equiv) which was prepared according to literature procedures,^[3] thiophen-3-ylboronic acid (684 mg, 4.5 mmol, 1.5 equiv), $\text{Pd}(\text{PPh}_3)_4$ (347 mg, 0.3 mmol, 0.1 equiv), and K_2CO_3 (2.2 g, 16 mmol, 4.0 equiv) were added to a Schlenk tube, which was protected with N_2 gas. The solvent (toluene/water/ethanol = 3/2/1, 18 mL) was added to the tube and the mixture was allowed to stir at 100 °C overnight. After TLC analysis showed the complete consumption of starting material **S23**, EtOAc (30 mL) and water (30 mL) were added to the mixture. The aqueous phase was extracted by EtOAc (30 mL \times 2). The combined organic phases were washed by brine, dried over Na_2SO_4 , concentrated and purified by column chromatography (eluted with EtOAc/ CH_2Cl_2 /PE = 1/1/10) to afford **S24** as a white solid (430 mg, 54% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.56 – 7.46 (m, 4H), 7.41 (dd, $J = 5.0, 3.0$ Hz, 1H), 7.34 – 7.28 (m, 2H), 7.22 (dd, $J = 5.0, 1.3$ Hz, 1H), 6.14 (s, 1H), 5.79 (d, $J = 0.5$ Hz, 1H) ppm.

To a round bottom flask was added **S24** (150 mg, 0.57 mmol, 1.0 equiv), Boc_2O (186 mg, 0.85 mmol, 1.5 equiv), DMAP (7.3 mg, 0.06 mmol, 0.1 equiv) and THF (5 mL). The mixture was stirred at room temperature. TLC analysis showed the complete consumption of starting material **S24**. EtOAc (20 mL) and water (20 mL) were added to the mixture. The aqueous phase was extracted by EtOAc (15 mL \times 2). The combined organic phases were washed by brine, dried over Na_2SO_4 , concentrated and purified by column chromatography (eluted with EtOAc/PE = 1/10) to afford **2'f** as a white solid (200 mg, 96% yield).

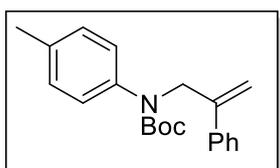
2.10 characterization of Substrates

tert-Butyl (4-methoxyphenyl)(2-phenylallyl)carbamate (2a)



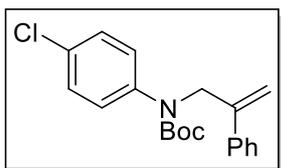
1.35 g, 91% yield. Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.40 (d, $J = 7.1$ Hz, 2H), 7.36 – 7.28 (m, 3H), 6.96 (brs, 2H), 6.78 (d, $J = 8.2$ Hz, 2H), 5.34 (s, 1H), 5.11 (s, 1H), 4.68 (s, 2H), 3.77 (s, 3H), 1.41 (s, 9H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 157.44, 155.00, 144.84, 139.30, 135.17, 128.32, 127.96, 127.82, 126.63, 114.27, 113.74, 80.28, 55.42, 53.80, 28.36 ppm. IR (KBr) ν 3005, 2919, 2849, 1697, 1513, 1470, 1384, 1275, 1260, 764, 750. HRMS (ESI) m/z calcd. for $\text{C}_{21}\text{H}_{25}\text{NNaO}_3^+$ ($M + \text{Na}^+$): 362.1727, Found: 362.1716.

tert-Butyl (2-phenylallyl)(*p*-tolyl)carbamate (2b)



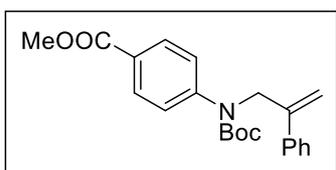
532 mg, 66% yield. Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.40 (dd, $J = 8.0, 1.3$ Hz, 2H), 7.36 – 7.27 (m, 3H), 7.07 (d, $J = 8.0$ Hz, 2H), 6.99 (brs, 2H), 5.36 (s, 1H), 5.14 (s, 1H), 4.69 (s, 2H), 2.31 (s, 3H), 1.43 (s, 9H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 154.83, 144.84, 139.78, 139.39, 135.45, 129.15, 128.35, 127.84, 126.62, 126.32, 113.81, 80.40, 53.74, 28.39, 21.08 ppm. IR (KBr) ν 2976, 2921, 2851, 1670, 1515, 1496, 1420, 1380, 1366, 1277, 1169, 823, 780, 705. HRMS (ESI) m/z calcd. for $\text{C}_{21}\text{H}_{25}\text{NNaO}_3^+$ ($M + \text{Na}^+$): 346.1778, Found: 346.1769.

tert-Butyl (4-chlorophenyl)(2-phenylallyl)carbamate (2c)



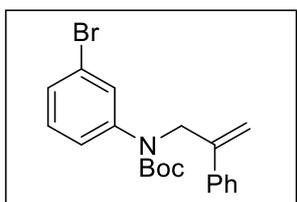
503 mg, 59% yield. Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.41 – 7.36 (m, 2H), 7.36 – 7.29 (m, 3H), 7.22 (d, $J = 8.7$ Hz, 2H), 7.02 (brs, 2H), 5.36 (d, $J = 0.6$ Hz, 1H), 5.10 (s, 1H), 4.70 (s, 2H), 1.43 (s, 9H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 154.38, 144.54, 140.76, 139.01, 131.20, 128.60, 128.42, 128.00, 127.78, 126.57, 114.21, 80.91, 53.52, 28.32 ppm. IR (KBr) ν 2979, 2920, 1701, 1493, 1367, 1275, 1261, 1164, 764, 750. HRMS (ESI) m/z calcd. for $\text{C}_{20}\text{H}_{22}\text{ClNNaO}_2^+$ ($M + \text{Na}^+$): 366.1231, Found: 366.1235.

Methyl 4-((tert-butoxycarbonyl)(2-phenylallyl)amino)benzoate (2d)



1.12 g, 59% yield. Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.94 (d, $J = 8.6$ Hz, 2H), 7.36 (dd, $J = 7.8, 1.5$ Hz, 2H), 7.34 – 7.26 (m, 3H), 7.21 (d, $J = 8.4$ Hz, 2H), 5.36 (s, 1H), 5.11 (s, 1H), 4.74 (s, 2H), 3.88 (s, 3H), 1.44 (s, 9H). ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 166.67, 153.99, 146.61, 144.40, 139.00, 129.96, 128.42, 128.02, 126.83, 126.46, 125.31, 113.69, 81.25, 53.27, 52.08, 28.26 ppm. IR (KBr) ν 3005, 2988, 1717, 1606, 1435, 1368, 1276, 1261, 1163, 764, 750. HRMS (ESI) m/z calcd. for $\text{C}_{22}\text{H}_{25}\text{NNaO}_4^+$ ($M + \text{Na}^+$): 390.1676, Found: 390.1671.

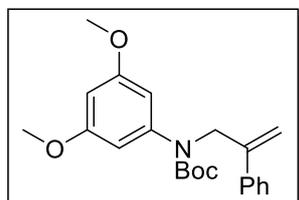
tert-Butyl (3-bromophenyl)(2-phenylallyl)carbamate (2e)



700 mg, 60% yield. Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.39 – 7.25 (m, 7H), 7.12 (t, $J = 8.1$ Hz, 1H), 7.08 – 6.98 (m, 1H), 5.37 (d, $J = 0.7$ Hz, 1H), 5.11 (s, 1H), 4.68 (s, 2H), 1.42 (s, 9H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 154.11, 144.42, 143.57, 138.99, 129.62, 129.44, 128.69, 128.37, 127.97, 126.49, 124.88,

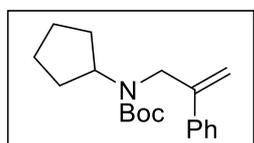
121.71, 113.95, 81.00, 53.49, 28.25 ppm. IR (KBr) ν 3005, 2988, 1701, 1590, 1478, 1368, 1275, 1261, 1159, 764, 750. HRMS (ESI) m/z calcd. for $C_{20}H_{22}BrNNaO_2^+$ ($M + Na^+$): 410.0726, Found: 410.0725.

***tert*-Butyl (3,5-dimethoxyphenyl)(2-phenylallyl)carbamate (2f)**



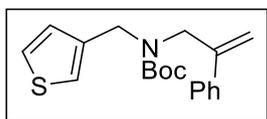
773 mg, 70% yield. White solid, Mp 67-69 °C. 1H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, $J = 6.9$ Hz, 2H), 7.35 – 7.27 (m, 3H), 6.27 (s, 3H), 5.36 (s, 1H), 5.14 (s, 1H), 4.67 (s, 2H), 3.70 (s, 6H), 1.43 (s, 9H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.47, 154.44, 144.82, 144.12, 139.37, 128.32, 127.84, 126.63, 113.83, 104.98, 98.23, 80.58, 55.37, 53.81, 28.38 ppm. IR (KBr) ν 3005, 1698, 1594, 1457, 1367, 1275, 1260, 1155, 764, 750. HRMS (ESI) m/z calcd. for $C_{22}H_{27}NNaO_4^+$ ($M + Na^+$): 392.1832, Found: 392.1828.

***tert*-Butyl cyclopentyl(2-phenylallyl)carbamate (2g)**



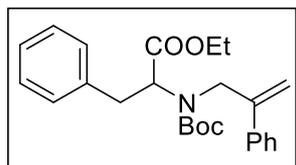
184 mg, 87% yield. Colorless oil. 1H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, $J = 7.2$ Hz, 2H), 7.36 – 7.27 (m, 3H), 5.35 (s, 1H), 5.08 (s, 1H), 4.43 (brs, 1H), 4.11 (brs, 2H), 1.81 (brs, 2H), 1.64 (brs, 2H), 1.51 (brs, 4H), 1.45 (s, 9H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.81, 145.67, 140.19, 128.41, 127.76, 126.33, 111.74, 79.57, 57.70, 47.68, 29.55, 28.57, 23.97 ppm. IR (KBr) ν 2975, 1693, 1456, 1365, 1275, 1261, 1169, 764, 750, 704. HRMS (ESI) m/z calcd. for $C_{20}H_{29}NNaO_2^+$ ($M + Na^+$): 324.1934, Found: 324.1939.

***tert*-Butyl (2-phenylallyl)(thiophen-3-ylmethyl)carbamate (2h)**



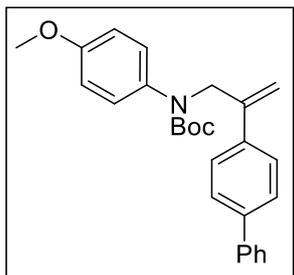
370 mg, 48% yield. Colorless oil. 1H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.38 (m, 2H), 7.37 – 7.26 (m, 3H), 7.22 (d, $J = 6.1$ Hz, 1H), 7.01 – 6.83 (m, 2H), [5.53 (s), 5.43 (s), (1H)] , [5.20 (s), 5.15 (s), (1H)], 4.58 – 4.22 (m, 4H), 1.51 (s, 9H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.40, 155.18, 144.19, 144.11, 140.81, 139.37, 138.66, 128.42, 128.00, 126.52, 126.36, 125.29, 114.58, 113.98, 80.52, 80.32, 49.54, 48.67, 43.69, 28.51 ppm. IR (KBr) ν 2977, 2922, 2851, 1694, 1632, 1455, 1410, 1366, 1275, 1261, 1167, 764, 750, 701. HRMS (ESI) m/z calcd. for $C_{19}H_{23}NNaO_2S^+$ ($M + Na^+$): 352.1342, Found: 352.1339.

Ethyl *N*-(*tert*-butoxycarbonyl)-*N*-(2-phenylallyl)phenylalaninate (2i)



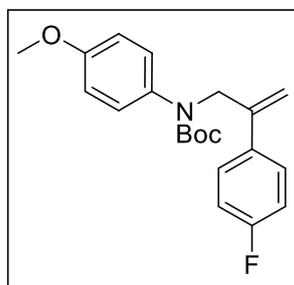
616 mg, 93% yield. Colorless oil. 1H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, $J = 6.5$ Hz, 1H), 7.38 - 7.14 (m, 9H), [5.46 (s), 5.34 (s), (1H)], 5.06 (s, 1H), [4.58 (d, $J = 15.7$ Hz), 4.34 (d, $J = 16.3$ Hz), (1H)], 4.29 - 3.86 (m, 3H), 3.54 - 3.28 (m, 2H), [3.21 - 3.09 (m), 3.04 - 2.91 (m), (1H)], 1.46 (s, 9H), 1.11 - 0.97 (m, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.92, 154.62, 144.17, 143.75, 139.40, 138.49, 129.69, 129.42, 128.52, 128.46, 128.14, 127.71, 126.59, 126.32, 115.68, 114.55, 80.83, 80.37, 60.85, 60.39, 51.41, 36.66, 35.70, 28.32, 28.22, 13.82 ppm. IR (KBr) ν 3005, 2983, 1739, 1680, 1496, 1455, 1367, 1275, 1260, 1164, 764, 750, 701. HRMS (ESI) m/z calcd. for $C_{25}H_{31}NNaO_4^+$ ($M + Na^+$): 432.2145, Found: 432.2144.

tert-Butyl (2-([1,1'-biphenyl]-4-yl)allyl)(4-methoxyphenyl)carbamate (2j)



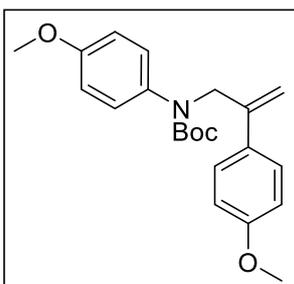
306 mg, 36% yield. Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.61 (d, $J = 7.5$ Hz, 2H), 7.57 (d, $J = 7.5$ Hz, 2H), 7.50 – 7.42 (m, 4H), 7.35 (t, $J = 7.2$ Hz, 1H), 6.97 (brs, 2H), 6.78 (d, $J = 7.6$ Hz, 2H), 5.40 (s, 1H), 5.13 (s, 1H), 4.71 (s, 2H), 3.78 (s, 3H), 1.41 (s, 9H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 157.53, 154.96, 144.27, 140.67, 140.54, 138.08, 135.02, 128.83, 127.96, 127.38, 126.99, 126.96, 126.93, 114.26, 113.71, 80.25, 55.33, 53.72, 28.34 ppm. IR (KBr) ν 2975, 2921, 2851, 1696, 1512, 1455, 1387, 1366, 1275, 1259, 1166, 1027, 834, 764, 750, 698. HRMS (ESI) m/z calcd. for $\text{C}_{27}\text{H}_{29}\text{NNaO}_3^+$ ($M + \text{Na}^+$): 438.2040, Found: 438.2035.

tert-Butyl (2-(4-fluorophenyl)allyl)(4-methoxyphenyl)carbamate (2k)



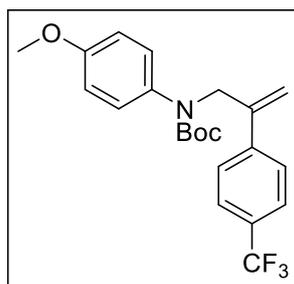
600 mg, 66% yield. White solid, Mp 58-61 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.40 – 7.32 (m, 2H), 7.03 – 6.82 (m, 4H), 6.77 (d, $J = 8.4$ Hz, 2H), 5.27 (s, 1H), 5.08 (s, 1H), 4.66 (s, 2H), 3.75 (s, 3H), 1.40 (s, 9H) ppm. ^{19}F NMR (376 MHz, CDCl_3) δ -114.60 ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 162.49 (d, $J = 246.7$ Hz), 157.52, 154.88, 143.82, 135.13 (d, $J = 2.7$ Hz), 134.79, 128.25 (d, $J = 7.9$ Hz), 127.92, 115.04 (d, $J = 21.3$ Hz), 114.37, 113.64, 80.25, 55.31, 53.63, 28.25 ppm. IR (KBr) ν 2976, 2931, 2837, 1698, 1603, 1512, 1455, 1385, 1367, 1294, 1248, 1162, 1046, 1027, 863, 835. HRMS (ESI) m/z calcd. for $\text{C}_{21}\text{H}_{24}\text{FNNaO}_3^+$ ($M + \text{Na}^+$): 380.1632, Found: 380.1631.

tert-Butyl (4-methoxyphenyl)(2-(4-methoxyphenyl)allyl)carbamate (2l)



620 mg, 96% yield. White solid, 92-93 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.34 (d, $J = 8.5$ Hz, 2H), 7.19 – 6.83 (m, 4H), 6.77 (d, $J = 8.3$ Hz, 2H), 5.26 (s, 1H), 5.01 (s, 1H), 4.65 (s, 2H), 3.81 (s, 3H), 3.77 (s, 3H), 1.41 (s, 9H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 159.45, 157.57, 155.06, 144.13, 135.13, 131.74, 128.05, 128.02, 127.77, 113.74, 112.82, 80.27, 55.45, 55.39, 53.85, 28.41 ppm. IR (KBr) ν 3005, 1696, 1512, 1457, 1275, 1260, 1167, 834, 764, 750. HRMS (ESI) m/z calcd. for $\text{C}_{22}\text{H}_{27}\text{NNaO}_4^+$ ($M + \text{Na}^+$): 392.1832, Found: 392.1831.

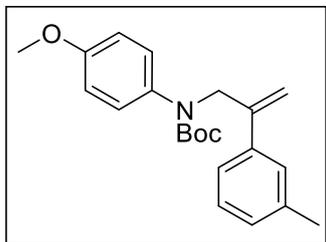
tert-Butyl (4-methoxyphenyl)(2-(4-(trifluoromethyl)phenyl)allyl)carbamate (2m)



296 mg, 48% yield. White solid, Mp 51-54 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.57 (d, $J = 8.3$ Hz, 2H), 7.49 (d, $J = 8.1$ Hz, 2H), 6.88 (brs, 2H), 6.77 (d, $J = 8.4$ Hz, 2H), 5.39 (s, 1H), 5.19 (s, 1H), 4.69 (s, 2H), 3.77 (s, 3H), 1.38 (s, 9H) ppm. ^{19}F NMR (376 MHz, CDCl_3) δ -62.54 ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 157.71, 154.97, 143.94, 142.81, 134.76, 129.86 (q, $J = 32.4$ Hz), 128.03, 127.03, 125.27 (q, $J = 14.6$ Hz), 124.30 (q, $J = 271.9$ Hz), 116.52, 113.83,

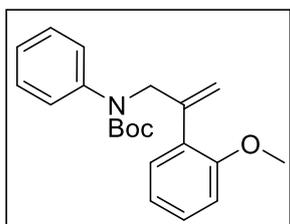
80.51, 55.43, 53.56, 28.34 ppm. IR (KBr) ν 3005, 2989, 2916, 1775, 1512, 1465, 1324, 1275, 1261, 765, 750. HRMS (ESI) m/z calcd. for $C_{22}H_{24}F_3NNaO_3^+$ ($M + Na^+$): 430.1600, Found: 430.1603.

tert-Butyl (4-methoxyphenyl)(2-(*m*-tolyl)allyl)carbamate (2n)



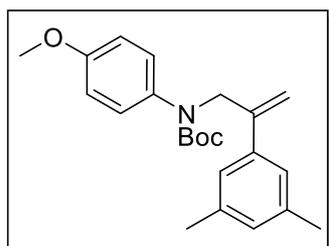
216 mg, 42% yield. Colorless oil. 1H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.18 (m, 3H), 7.15 – 6.85 (m, 3H), 6.79 (d, $J = 8.2$ Hz, 2H), 5.35 (d, $J = 0.7$ Hz, 1H), 5.11 (s, 1H), 4.67 (s, 2H), 3.78 (s, 3H), 2.36 (s, 3H), 1.43 (s, 9H) ppm. ^{13}C NMR (101 MHz, DMSO) δ 156.87, 153.85, 144.01, 138.35, 137.21, 134.40, 128.38, 128.09, 127.71, 126.61, 123.17, 113.55, 113.40, 79.28, 55.05, 52.68, 27.81, 20.98 ppm. IR (KBr) ν 2975, 2928, 1698, 1604, 1584, 1513, 1455, 1384, 1366, 1282, 1248, 1166, 1046, 1027, 834, 793, 765. HRMS (ESI) m/z calcd. for $C_{22}H_{27}NNaO_3^+$ ($M + Na^+$): 376.1883, Found: 376.1882.

tert-Butyl (2-(2-methoxyphenyl)allyl)(phenyl)carbamate (2o)



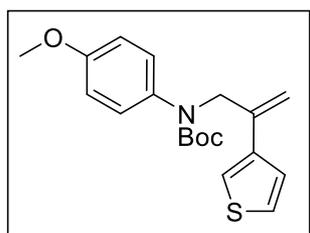
227 mg, 80% yield. Colorless oil. 1H NMR (400 MHz, $CDCl_3$) δ 7.29 -7.21 (m, 3H), 7.21 – 7.07 (m, 4H), 6.91 (t, $J = 7.4$ Hz, 1H), 6.78 (d, $J = 8.2$ Hz, 1H), 5.25 (s, 1H), 5.14 (s, 1H), 4.64 (s, 2H), 3.63 (s, 3H), 1.42 (s, 9H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.86, 154.67, 145.31, 143.32, 130.65, 129.89, 129.02, 128.33, 125.99, 125.20, 120.63, 114.65, 110.44, 80.31, 55.20, 54.59, 28.37 ppm. IR (KBr) ν 3002, 2977, 2931, 1702, 1598, 1491, 1456, 1379, 1275, 1260, 1170, 1021, 764, 750, 697. HRMS (ESI) m/z calcd. for $C_{21}H_{25}NaO_3^+$ ($M + Na^+$): 362.1727, Found: 362.1727.

tert-Butyl (2-(3,5-dimethylphenyl)allyl)(4-methoxyphenyl)carbamate (2p)



365 mg, 53% yield. Colorless oil. 1H NMR (400 MHz, $CDCl_3$) δ 7.20 – 6.86 (m, 5H), 6.80 (d, $J = 8.1$ Hz, 2H), 5.35 (s, 1H), 5.10 (s, 1H), 4.66 (s, 2H), 3.78 (s, 3H), 2.33 (s, 6H), 1.44 (s, 9H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.52, 155.01, 144.98, 139.29, 137.74, 135.40, 129.47, 127.94, 124.47, 113.73, 113.54, 80.23, 55.46, 54.04, 28.39, 21.43 ppm. IR (KBr) ν 2975, 2927, 1698, 1600, 1513, 1455, 1386, 1366, 1294, 1247, 1165, 1046, 1027, 851, 833. HRMS (ESI) m/z calcd. for $C_{23}H_{29}NNaO_3^+$ ($M + Na^+$): 390.2040, Found: 390.2036.

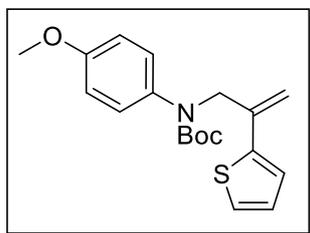
tert-Butyl (4-methoxyphenyl)(2-(thiophen-3-yl)allyl)carbamate (2q)



1.23 g, 98% yield. White solid, Mp 78-81 $^{\circ}C$. 1H NMR (400 MHz, $CDCl_3$) δ 7.39 (brs, 1H), 7.29 – 7.22 (m, 2H), 7.00 (brs, 2H), 6.81 (d, $J = 8.7$ Hz, 2H), 5.42 (s, 1H), 5.05 (s, 1H), 4.65 (s, 2H), 3.77 (s, 3H), 1.45 (s, 9H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.60, 155.09, 140.22, 139.11, 135.02, 128.00, 126.07, 125.46, 121.15, 113.75, 113.27, 80.35, 55.40, 53.82, 28.39 ppm. IR (KBr) ν 3096,

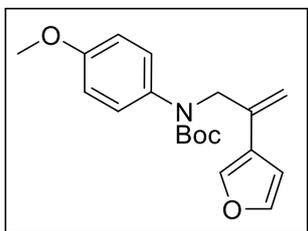
2976, 2931, 2836, 1694, 1512, 1455, 1388, 1366, 1277, 1248, 1164, 1026, 834, 764, 750. HRMS (ESI) m/z calcd. for $C_{19}H_{23}NNaO_3S^+$ ($M + Na^+$): 368.1291, Found: 368.1287.

***tert*-Butyl (4-methoxyphenyl)(2-(thiophen-2-yl)allyl)carbamate (2r)**



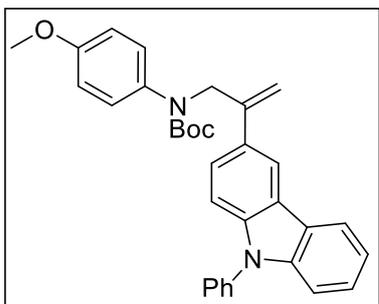
625 mg, 49% yield. White solid, Mp 50-54 °C. 1H NMR (400 MHz, $CDCl_3$) δ 7.22 – 6.94 (m, 5H), 6.79 (d, J = 8.2 Hz, 2H), 5.44 (s, 1H), 4.99 (s, 1H), 4.62 (s, 2H), 3.78 (s, 3H), 1.42 (s, 9H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.56, 154.90, 142.60, 137.87, 135.01, 127.79, 127.40, 124.51, 123.99, 113.75, 112.84, 80.33, 55.31, 53.64, 28.31 ppm. IR (KBr) ν 3004, 2979, 2929, 1697, 1512, 1456, 1386, 1276, 1260, 1163, 1027, 833, 764, 750. HRMS (ESI) m/z calcd. for $C_{19}H_{23}NNaO_3S^+$ ($M + Na^+$): 368.1291, Found: 368.1289.

***tert*-Butyl (2-(furan-3-yl)allyl)(4-methoxyphenyl)carbamate (2s)**



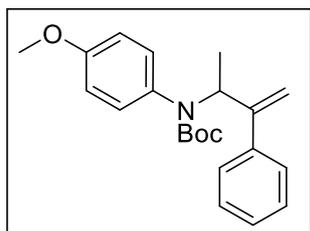
1.07 g, 94% yield. White solid, Mp 82-84 °C. 1H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.37 (t, J = 1.6 Hz, 1H), 7.02 (brs, 2H), 6.79 (d, J = 8.8 Hz, 2H), 6.51 (d, J = 1.0 Hz, 1H), 5.28 (s, 1H), 4.94 (s, 1H), 4.49 (s, 2H), 3.77 (s, 3H), 1.41 (s, 9H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.62, 155.04, 143.18, 139.44, 135.79, 135.04, 127.97, 124.55, 113.75, 112.51, 108.34, 80.34, 55.36, 53.45, 28.35 ppm. IR (KBr) ν 2976, 2932, 2837, 1694, 1642, 1513, 1456, 1390, 1367, 1283, 1248, 1163, 1025, 873, 835, 793, 765, 596. HRMS (ESI) m/z calcd. for $C_{19}H_{23}NNaO_4^+$ ($M + Na^+$): 352.1519, Found: 352.1518.

***tert*-Butyl (4-methoxyphenyl)(2-(9-phenyl-9H-carbazol-3-yl)allyl)carbamate (2t)**



720 mg, 94% yield. Foam. 1H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 8.20 (d, J = 7.7 Hz, 1H), 7.66 – 7.58 (m, 4H), 7.57 – 7.38 (m, 5H), 7.36 – 7.30 (m, 1H), 7.02 (brs, 2H), 6.83 (d, J = 7.1 Hz, 2H), 5.49 (s, 1H), 5.20 (s, 1H), 4.89 (s, 2H), 3.79 (s, 3H), 1.48 (s, 9H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.51, 155.11, 145.08, 141.31, 140.63, 137.71, 135.22, 131.21, 129.95, 128.06, 127.53, 127.04, 126.09, 124.92, 123.57, 123.39, 120.43, 120.12, 118.34, 113.69, 113.02, 109.92, 109.56, 80.19, 55.36, 54.17, 28.41 ppm. IR (KBr) ν 3006, 2988, 2927, 1696, 1598, 1511, 1457, 1365, 1275, 1260, 1165, 1026, 834, 764, 750. HRMS (ESI) m/z calcd. for $C_{33}H_{32}N_2NaO_3^+$ ($M + Na^+$): 527.2305, Found: 527.2302.

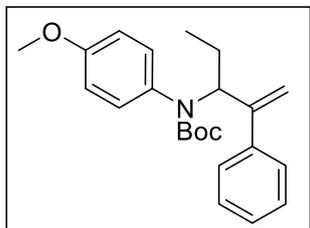
***tert*-Butyl (4-methoxyphenyl)(3-phenylbut-3-en-2-yl)carbamate (2u)**



513 mg, 97% yield. Colorless oil. 1H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 7.3 Hz, 2H), 7.39 – 7.27 (m, 3H), 6.70 (brs, 4H), 5.68 (brs, 1H), 5.31 (s, 1H), 4.97 (d, J = 1.1 Hz, 1H), 3.77 (s, 3H), 1.42 (d, J = 6.9 Hz, 3H), 1.32 (brs, 9H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.15, 155.32, 149.02, 140.67, 131.82, 130.56, 128.29, 127.67, 126.92, 114.74, 113.24, 79.86, 55.32, 53.04,

28.36, 18.01 ppm. IR (KBr) ν 3051, 3002, 2977, 2934, 2836, 1689, 1512, 1456, 1386, 1367, 1322, 1247, 1167, 1076, 1048, 1032, 837, 764, 750, 697. HRMS (ESI) m/z calcd. for $C_{22}H_{27}NNaO_3^+$ ($M + Na^+$): 376.1883, Found: 376.1883.

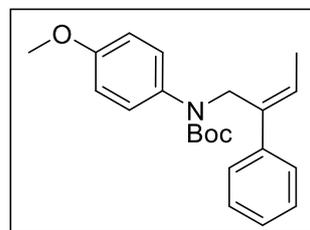
tert-Butyl (4-methoxyphenyl)(2-phenylpent-1-en-3-yl)carbamate (2v)



544 mg, 86% yield. Colorless oil. 1H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, $J = 7.3$ Hz, 2H), 7.39 – 7.27 (m, 3H), 6.72 (brs, 4H), 5.46 (brs, 1H), 5.34 (s, 1H), 4.86 (s, 1H), 3.77 (s, 3H), 1.90 - 1.75 (m, 2H), 1.31 (brs, 9H), 1.14 (t, $J = 7.3$ Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.21, 155.82, 147.44, 141.01, 131.76, 130.65, 128.37, 127.71, 126.89, 115.39, 113.33, 79.84, 58.76, 55.39,

28.41, 24.84, 11.48 ppm. IR (KBr) ν 3005, 2986, 1689, 1512, 1456, 1387, 1275, 1260, 1167, 764, 750. HRMS (ESI) m/z calcd. for $C_{23}H_{29}NNaO_3^+$ ($M + Na^+$): 390.2040, Found: 390.2040.

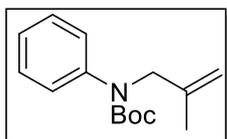
tert-Butyl (Z)-(4-methoxyphenyl)(2-phenylbut-2-en-1-yl)carbamate (2w)



654 mg, 62% yield. White solid, Mp 76-79 °C. 1H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.18 (m, 5H), 6.73 (brs, 4H), 5.74 (d, $J = 6.7$ Hz, 1H), 4.79 (s, 2H), 3.76 (s, 3H), 1.58 (d, $J = 6.9$ Hz, 3H), 1.34 (s, 9H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.80, 155.24, 141.33, 137.31, 134.25, 128.91, 128.04, 127.07, 126.84, 113.55, 79.98, 55.41, 46.47, 28.36, 13.85 ppm. IR (KBr) ν 3005, 2987, 2929,

1691, 1512, 1456, 1388, 1275, 1260, 1166, 1027, 834, 764, 750, 699. HRMS (ESI) m/z calcd. for $C_{22}H_{27}NNaO_3^+$ ($M + Na^+$): 376.1883, Found: 376.1883.

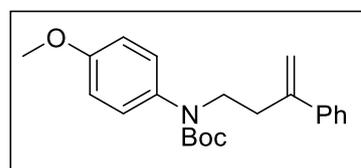
tert-Butyl (2-methylallyl)(phenyl)carbamate (2x)^[3]



593 mg, 92% yield. Colorless oil. 1H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, $J = 7.7$ Hz, 2H), 7.24 (d, $J = 7.7$ Hz, 2H), 7.15 (t, $J = 7.2$ Hz, 1H), 4.85 (s, 1H), 4.82 (s, 1H), 4.17 (s, 2H), 1.76 (s, 3H), 1.45 (s, 9H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.71, 142.96, 141.73, 128.54, 126.03, 125.58,

111.37, 80.39, 55.89, 28.34, 20.22 ppm.

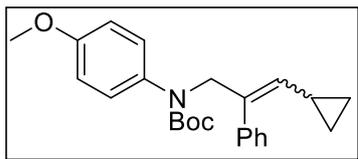
tert-Butyl (4-methoxyphenyl)(3-phenylbut-3-en-1-yl)carbamate (2y)



990 mg, 89% yield. Colorless oil. 1H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, $J = 7.1$ Hz, 2H), 7.32 – 7.22 (m, 3H), 7.08 (brs, 2H), 6.85 (d, $J = 8.8$ Hz, 2H), 5.33 (s, 1H), 5.07 (d, $J = 0.7$ Hz, 1H), 3.81 (s, 3H), 3.74 – 3.68 (m, 2H), 2.81 – 2.71 (m, 2H), 1.42 (s, 9H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.70, 154.97,

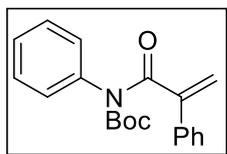
145.43, 140.58, 135.37, 128.46, 128.38, 127.54, 125.99, 114.01, 113.91, 80.01, 55.48, 49.67, 34.18, 28.43 ppm. IR (KBr) ν 2976, 2933, 2837, 1695, 1513, 1455, 1392, 1365, 1293, 1247, 1166, 1146, 1033, 835, 778, 707, 604, 575, 542. HRMS (ESI) m/z calcd. for $C_{22}H_{27}NNaO_3^+$ ($M + Na^+$): 376.1883, Found: 376.1881.

tert-butyl (3-cyclopropyl-2-phenylallyl)(4-methoxyphenyl)carbamate (2z)



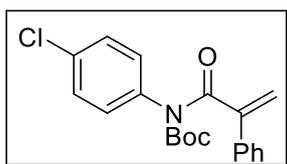
1.27 g, 98% yield. Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.39 – 7.22 (m, 5H), 6.97 (brs, 2H), [6.79 (d, $J = 8.1$ Hz), 6.74 (d, $J = 8.1$ Hz), (2H)], [5.05 (d, $J = 9.6$ Hz), 4.83 (d, $J = 9.9$ Hz), (1H)], [4.93 (s), 4.49 (s), (2H)], [3.77 (s), 3.76 (s), (3H)], 1.49 – 1.24 (m, 10H), 0.71 – 0.59 (m, 2H), 0.35 – 0.25 (m, 2H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 157.79, 157.40, 154.93, 139.03, 137.38, 135.53, 134.91, 133.84, 129.26, 129.07, 128.08, 127.99, 126.91, 126.68, 113.69, 113.55, 80.03, 56.57, 55.49, 55.45, 28.39, 28.34, 11.07, 10.76, 7.55, 7.51 ppm. IR (KBr) ν 3002, 2975, 2929, 2833, 1697, 1512, 1379, 1366, 1247, 1159, 1027, 833, 765, 702. HRMS (ESI) m/z calcd. for $\text{C}_{24}\text{H}_{29}\text{NNaO}_3^+$ ($M + \text{Na}^+$): 402.2040, Found: 402.2041.

tert-Butyl phenyl(2-phenylacryloyl)carbamate (2'a)^[3]



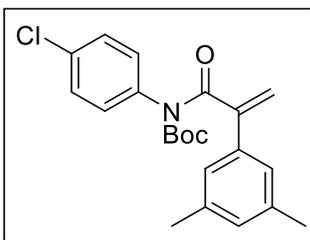
760 mg, 60% yield. White solid. ^1H NMR (400 MHz, CDCl_3) δ 7.49 – 7.44 (m, 2H), 7.42 – 7.28 (m, 6H), 7.21 – 7.15 (m, 2H), 5.78 (s, 2H), 1.22 (s, 9H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 171.97, 152.53, 146.93, 138.39, 136.23, 129.09, 128.50, 128.38, 127.99, 127.94, 126.74, 118.14, 83.78, 27.53 ppm.

tert-Butyl (4-chlorophenyl)(2-phenylacryloyl)carbamate (2'b)



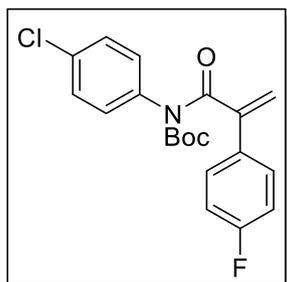
680mg, 98% yield. White solid, Mp 92-93 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.46 – 7.41 (m, 2H), 7.40 – 7.29 (m, 5H), 7.15 – 7.10 (m, 2H), 5.79 (s, 1H), 5.78 (s, 1H), 1.22 (s, 9H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 171.85, 152.20, 146.78, 136.91, 136.16, 133.85, 129.45, 129.35, 128.61, 128.54, 126.76, 118.54, 84.23, 27.59 ppm. IR (KBr) ν 3002, 2981, 2929, 1741, 1688, 1492, 1369, 1275, 1260, 1152, 1091, 1015, 843, 764, 750, 702. HRMS (ESI) m/z calcd. for $\text{C}_{20}\text{H}_{20}\text{ClNNaO}_3^+$ ($M + \text{Na}^+$): 380.1204, Found: 380.1201.

tert-Butyl (4-chlorophenyl)(2-(3,5-dimethylphenyl)acryloyl)carbamate (2'c)^[3]



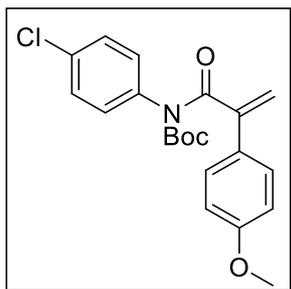
110 mg. 36% yield. White solid. ^1H NMR (400 MHz, CDCl_3) δ 7.37 (d, $J = 8.6$ Hz, 2H), 7.12 (d, $J = 8.6$ Hz, 2H), 7.04 (s, 2H), 6.96 (s, 1H), 5.76 (s, 1H), 5.72 (s, 1H), 2.33 (s, 6H), 1.26 (s, 9H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 172.00, 152.27, 146.91, 138.00, 136.97, 135.91, 133.75, 130.15, 129.44, 129.29, 124.66, 117.96, 84.15, 27.59, 21.41 ppm.

tert-Butyl (4-chlorophenyl)(2-(4-fluorophenyl)acryloyl)carbamate (2'd)^[3]



340 mg. 45% yield. White solid. ^1H NMR (400 MHz, CDCl_3) δ 7.46 – 7.34 (m, 4H), 7.13 – 7.03 (m, 4H), 5.74 (s, 1H), 5.73 (s, 1H), 1.25 (s, 9H) ppm. ^{19}F NMR (376 MHz, CDCl_3) δ -113.07 ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 171.70, 162.89 (d, $J = 248.3$ Hz), 152.20, 145.74, 136.77, 133.91, 132.33 (d, $J = 3.4$ Hz), 129.38, 129.35, 128.66 (d, $J = 8.2$ Hz), 118.17, 115.56 (d, $J = 21.7$ Hz), 84.31, 27.61 ppm.

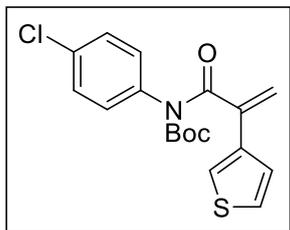
***tert*-Butyl (4-chlorophenyl)(2-(4-methoxyphenyl)acryloyl)carbamate (2'e)**^[3]



300 mg, 70% yield. White solid. ¹H NMR (400 MHz, CDCl₃) δ 7.41 – 7.32 (m, 4H), 7.15 – 7.04 (m, 2H), 6.94 – 6.82 (m, 2H), 5.69 (s, 1H), 5.64 (s, 1H), 3.82 (s, 3H), 1.25 (s, 9H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 172.18, 159.97, 152.35, 146.26, 137.00, 133.84, 129.44, 129.35, 128.73, 128.11, 116.37, 114.04, 84.25, 55.48, 27.67 ppm.

***tert*-Butyl (4-chlorophenyl)(2-(thiophen-3-yl)acryloyl)carbamate (2'f)**

200 mg, 97% yield. White solid, Mp 102-105 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.42 – 7.36 (m,

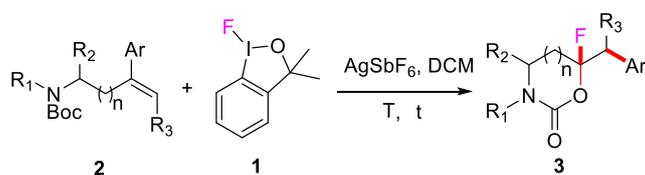


3H), 7.32 (dd, *J* = 5.1, 2.9 Hz, 1H), 7.26 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.18 – 7.11 (m, 2H), 5.76 (s, 1H), 5.68 (s, 1H), 1.27 (s, 9H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 171.56, 152.44, 141.60, 137.16, 136.92, 133.90, 129.45, 129.32, 126.22, 125.85, 122.86, 116.74, 84.47, 27.59 ppm. IR (KBr) ν 3005, 2988, 1741, 1687, 1491, 1345, 1275, 1260, 1152, 1091, 1016, 765, 750, 704. HRMS (ESI) *m/z*

calcd. for C₁₈H₁₈ClNNaO₃S⁺ (*M* + Na⁺): 386.0588, Found: 386.0587.

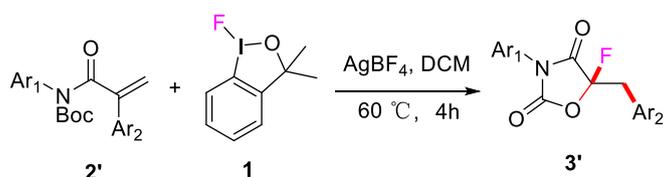
3 General Procedures for the fluorocyclizations

3.1 Procedures for the fluorocyclizations of 2a-2y



Compound 3. The substrate **2** (0.2 mmol, 1.0 equiv), the required amount of compound **1**, AgSbF₆ (6.8 mg, 0.02 mmol, 0.1 equiv) and DCM (2 mL) were introduced to a glass vial. The vial was then sealed and the mixture was allowed to stir at the matched temperature for the required time. After which, the reaction mixture was concentrated to dryness and CH₂Br₂ was added. The NMR yield was calculated by ¹H NMR spectroscopy using CH₂Br₂ as the internal standard and the dr value was determined from ¹⁹F NMR spectrum analysis. The mixture was purified by column chromatography to afford product **3**.

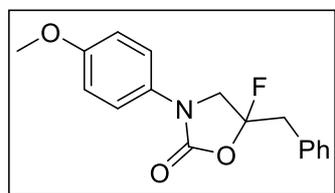
3.2 Procedures for the fluorocyclizations of 2'a-2'f



Compound 3'. The substrate **2'** (0.2 mmol, 1.0 equiv), compound **1** (0.3 mmol, 1.5 equiv), AgBF₄ (3.8 mg, 0.02 mmol, 0.1 equiv) and DCM (0.2 mL) were introduced to a glass vial. The vial was then sealed and the mixture was allowed to stir at 60 °C for 4 hours. After which, the reaction mixture was concentrated to dryness and CH₂Br₂ was added. The NMR yield was calculated by ¹H NMR spectroscopy using CH₂Br₂ as the internal standard. The mixture was purified by column chromatography to afford product **3'**.

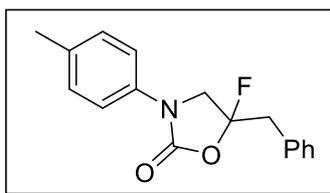
3.3 Characterization of Products

5-Benzyl-5-fluoro-3-(4-methoxyphenyl)oxazolidin-2-one (**3a**)



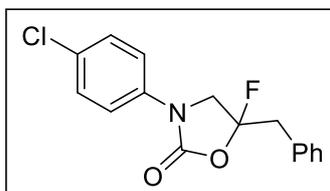
47.6 mg, 79% yield. White solid, Mp 123-129 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.40 – 7.29 (m, 7H), 6.90 – 6.84 (m, 2H), 4.04, 3.89 (ABq, *J* = 10.9 Hz, 1H), 3.96, 3.84 (ABq, *J* = 10.9 Hz, 1H), 3.78 (s, 3H), 3.46 – 3.27 (m, 2H) ppm. ¹⁹F NMR (376 MHz, CDCl₃) δ -92.52 ppm. ¹³C NMR (101 MHz, CDCl₃) δ 156.96, 152.32 (d, *J* = 1.7 Hz), 132.23 (d, *J* = 4.2 Hz), 130.37, 130.20, 128.95, 128.03, 120.68, 114.49, 112.31 (d, *J* = 233.1 Hz), 55.58, 54.10 (d, *J* = 30.6 Hz), 42.03 (d, *J* = 29.1 Hz) ppm. IR (KBr) ν 3005, 2990, 1771, 1515, 1456, 1339, 1275, 1360, 1080, 828, 764, 750, 704. HRMS (ESI) *m/z* calcd. for C₁₇H₁₆FNNaO₃⁺ (*M* + Na⁺): 324.1006, Found: 324.1002.

5-Benzyl-5-fluoro-3-(*p*-tolyl)oxazolidin-2-one (**3b**)



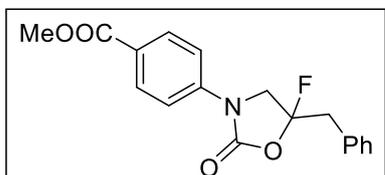
41.4 mg, 73% yield. White solid, Mp 115-117 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.40 - 7.28 (m, 7H), 7.15 (d, J = 8.6 Hz, 2H), 4.04, 3.92 (ABq, J = 10.9 Hz, 1H), 3.96, 3.86 (ABq, J = 10.9 Hz, 1H), 3.46 - 3.28 (m, 2H), 2.31 (s, 3H) ppm. ^{19}F NMR (376 MHz, CDCl_3) δ -92.40 ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 152.13, 134.70, 132.25 (d, J = 4.3 Hz), 130.42, 129.86, 129.04, 128.11, 118.69, 112.31 (d, J = 233.1 Hz), 53.77 (d, J = 30.7 Hz), 42.15 (d, J = 29.1 Hz), 20.90 ppm. IR (KBr) ν 3033, 3006, 2986, 2921, 2851, 1774, 1517, 1468, 1404, 1335, 1275, 1261, 1080, 976, 810, 764, 750, 702. HRMS (ESI) m/z calcd. for $\text{C}_{17}\text{H}_{16}\text{FNNaO}_2^+$ ($M + \text{Na}^+$): 308.1057, Found: 308.1045.

5-Benzyl-3-(4-chlorophenyl)-5-fluorooxazolidin-2-one (3c)



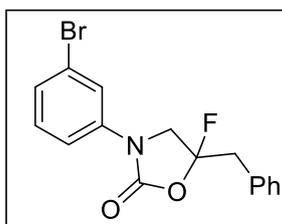
46.4 mg, 76% yield. White solid, Mp 123-125 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.44 - 7.27 (m, 9H), 4.04, 3.91 (ABq, J = 10.8 Hz, 1H), 3.96, 3.86 (ABq, J = 10.8 Hz, 1H), 3.47 - 3.29 (m, 2H) ppm. ^{19}F NMR (376 MHz, CDCl_3) δ -92.42 ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 151.90, 135.81, 132.00 (d, J = 4.2 Hz), 130.39, 130.18, 129.36, 129.08, 128.20, 119.66, 112.24 (d, J = 233.9 Hz), 53.51 (d, J = 30.8 Hz), 42.03 (d, J = 28.9 Hz) ppm. IR (KBr) ν 3005, 2986, 1771, 1496, 1338, 1275, 1261, 1094, 1080, 978, 826, 764, 750, 704. HRMS (ESI) m/z calcd. for $\text{C}_{16}\text{H}_{14}\text{ClFNO}_2^+$ ($M + \text{H}^+$): 306.0692, Found: 306.0688.

Methyl 4-(5-benzyl-5-fluoro-2-oxooxazolidin-3-yl)benzoate (3d)



27.7 mg, 42% yield. White solid, Mp 136-140 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.02 (d, J = 8.7 Hz, 2H), 7.53 (d, J = 8.7 Hz, 2H), 7.40 - 7.29 (m, 5H), 4.09, 3.98 (ABq, J = 10.9 Hz, 1H), 4.01, 3.93 (ABq, J = 10.9 Hz, 1H), 3.90 (s, 3H), 3.49 - 3.30 (m, 2H) ppm. ^{19}F NMR (376 MHz, CDCl_3) δ -92.28 ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 166.44, 151.72, 141.16, 131.93 (d, J = 4.2 Hz), 131.01, 130.41, 129.14, 128.27, 126.24, 117.51, 112.27 (d, J = 234.1 Hz), 53.36 (d, J = 30.8 Hz), 52.27, 42.06 (d, J = 28.9 Hz) ppm. IR (KBr) ν 3033, 3004, 2951, 2920, 2849, 1778, 1717, 1608, 1517, 1497, 1281, 1187, 1112, 980, 853, 767, 748, 703. HRMS (ESI) m/z calcd. for $\text{C}_{18}\text{H}_{16}\text{FNNaO}_4^+$ ($M + \text{Na}^+$): 352.0956, Found: 352.0956.

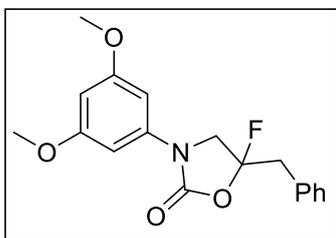
5-Benzyl-3-(3-bromophenyl)-5-fluorooxazolidin-2-one (3e)



41.4 mg, 59% yield. White solid, Mp 114-118 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.59 (t, J = 1.9 Hz, 1H), 7.48 - 7.31 (m, 6H), 7.30 - 7.25 (m, 1H), 7.21 (t, J = 8.1 Hz, 1H), 4.03, 3.92 (ABq, J = 10.8 Hz, 1H), 3.96, 3.87 (ABq, J = 10.8 Hz, 1H), 3.48 - 3.28 (m, 2H) ppm. ^{19}F NMR (376 MHz, CDCl_3) δ -92.30 ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 151.73, 138.48, 131.95 (d, J = 4.3 Hz), 130.62, 130.39, 129.11, 128.23, 127.83, 123.08, 121.27, 116.89, 112.26 (d, J = 234.0 Hz), 53.39 (d, J = 30.8 Hz), 42.00 (d, J = 28.8 Hz) ppm. IR (KBr) ν 3004, 2990, 2920, 2849, 1779, 1593, 1482, 1339,

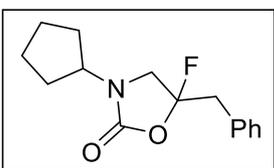
1275, 1261, 1080, 992, 938, 764, 750, 700. HRMS (ESI) m/z calcd. for $C_{16}H_{14}BrFNO_2^+$ ($M + H^+$): 350.0186, Found: 350.0184.

5-Benzyl-3-(3,5-dimethoxyphenyl)-5-fluorooxazolidin-2-one (3f)



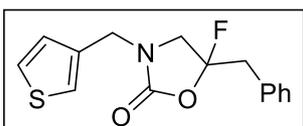
27.1 mg, 41% yield. Colorless oil. 1H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.30 (m, 5H), 6.64 (d, $J = 2.1$ Hz, 2H), 6.25 (t, $J = 2.1$ Hz, 1H), 4.01, 3.89 (ABq, $J = 10.9$ Hz, 1H), 3.93, 3.84 (ABq, $J = 10.9$ Hz, 1H), 3.77 (s, 6H), 3.45 – 3.27 (m, 2H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -92.27 ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.37, 151.87, 139.05, 132.15 (d, $J = 4.3$ Hz), 130.40, 129.05, 128.14, 112.18 (d, $J = 233.2$ Hz), 97.21, 96.67, 55.63, 53.77 (d, $J = 30.7$ Hz), 42.08 (d, $J = 29.1$ Hz) ppm. IR (KBr) ν 3005, 2984, 1771, 1596, 1456, 1275, 1261, 1205, 1156, 1012, 764, 750, 704. HRMS (ESI) m/z calcd. for $C_{18}H_{18}FNNaO_4^+$ ($M + Na^+$): 354.1112 Found: 354.1112

5-Benzyl-3-cyclopentyl-5-fluorooxazolidin-2-one (3g)



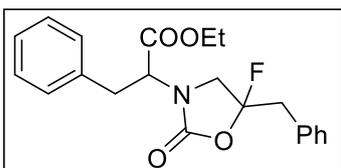
41.0 mg, 78% yield. White solid, Mp 79-82 °C. 1H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 5H), 4.16 (p, $J = 8.1$ Hz, 1H), 3.57 – 3.18 (m, 4H), 1.95 – 1.82 (m, 1H), 1.81 – 1.69 (m, 1H), 1.67 – 1.50 (m, 4H), 1.50 – 1.39 (m, 1H), 1.36 – 1.24 (m, 1H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -93.00 ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.64, 132.54 (d, $J = 4.3$ Hz), 130.29, 128.83, 127.85, 113.11 (d, $J = 232.5$ Hz), 54.47, 49.57 (d, $J = 30.4$ Hz), 42.20 (d, $J = 29.6$ Hz), 29.37, 28.68, 23.89, 23.81 ppm. IR (KBr) ν 3005, 2989, 1771, 1456, 1275, 1260, 1040, 908, 765, 704. HRMS (ESI) m/z calcd. for $C_{15}H_{18}FNNaO_2^+$ ($M + Na^+$): 286.1214, Found: 286.1214.

5-Benzyl-5-fluoro-3-(thiophen-3-ylmethyl)oxazolidin-2-one (3h)



43.8 mg, 75% yield. White solid, Mp 68-72 °C. 1H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 3H), 7.28 – 7.19 (m, 3H), 6.95 – 6.90 (m, 1H), 6.84 (d, $J = 3.3$ Hz, 1H), 4.57 (s, 2H), 3.54, 3.43 (ABq, $J = 10.8$ Hz, 1H), 3.46, 3.37 (ABq, $J = 10.8$ Hz, 1H), 3.32 – 3.17 (m, 2H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -93.09 ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.74, 137.07, 132.29 (d, $J = 4.7$ Hz), 130.33, 128.86, 127.88, 127.20, 127.12, 126.22, 113.10 (d, $J = 233.9$ Hz), 52.03 (d, $J = 30.3$ Hz), 42.38, 42.07 (d, $J = 29.4$ Hz) ppm. IR (KBr) ν 3005, 2989, 1776, 1473, 1275, 1261, 1029, 897, 765, 750, 703. HRMS (ESI) m/z calcd. for $C_{15}H_{15}FNO_2S^+$ ($M + H^+$): 292.0802, Found: 292.0807.

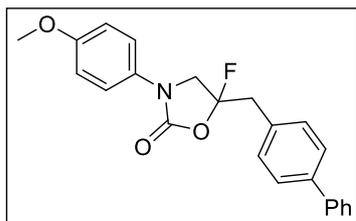
Ethyl 2-(5-benzyl-5-fluoro-2-oxooxazolidin-3-yl)-3-phenylpropanoate (3i)



48.9 mg, 66% yield, dr = 1.3:1. Colorless oil. 1H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.14 (m, 9H), 7.06 – 7.00 (m, 1H), [4.77 (dd, $J = 10.4, 5.6$ Hz), 4.74 (dd, $J = 10.6, 5.5$ Hz), (1H)], 4.23 – 4.07 (m, 2H), 3.91 – 3.36 (m, 2H), 3.35 – 3.04 (m, 3H), 2.95 – 2.81 (m, 1H), [1.23 (t, $J = 7.1$ Hz), 1.18 (t, $J = 7.1$ Hz), (3H)] ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -92.12, -94.35 ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.95,

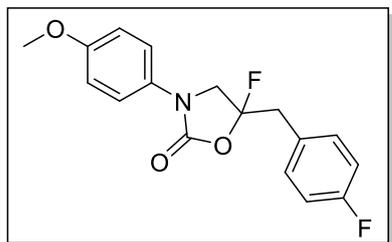
169.81, 155.15 (d, $J = 1.5$ Hz), 154.92 (d, $J = 1.4$ Hz), 135.71, 135.63, 132.33 (d, $J = 3.2$ Hz), 132.31 (d, $J = 4.7$ Hz), 130.38, 130.30, 128.92, 128.89, 128.85, 128.81, 128.69, 128.54, 127.89, 127.85, 127.36, 127.29, 113.42 (d, $J = 234.4$ Hz), 113.38 (d, $J = 234.5$ Hz), 61.92, 61.83, 56.63, 56.54, 50.60 (d, $J = 29.6$ Hz), 50.48 (d, $J = 30.7$ Hz), 42.18 (d, $J = 28.9$ Hz), 42.06 (d, $J = 29.5$ Hz), 35.48, 35.18, 14.14 ppm. IR (KBr) ν 3005, 2989, 1779, 1738, 1456, 1275, 1261, 1031, 897, 765, 750, 703. HRMS (ESI) m/z calcd. for $C_{21}H_{22}FNNaO_4^+$ ($M + Na^+$): 394.1425, Found: 394.1425.

5-([1,1'-Biphenyl]-4-ylmethyl)-5-fluoro-3-(4-methoxyphenyl)oxazolidin-2-one (3j)



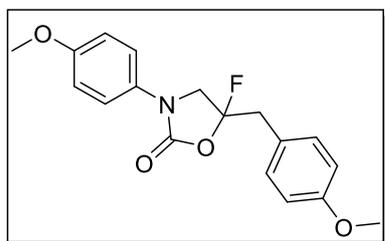
59.6 mg, 79% yield. White solid, Mp 197-201 °C. 1H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, $J = 7.9$ Hz, 4H), 7.49 – 7.39(m, 4H), 7.39 – 7.31 (m, 3H), 6.88 (d, $J = 9.1$ Hz, 2H), 4.08, 3.95 (ABq, $J = 10.9$ Hz, 1H), 4.00, 3.89 (ABq, $J = 10.9$ Hz, 1H), 3.78 (s, 3H), 3.55 – 3.29 (m, 2H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -92.48 ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.01, 152.33, 140.99, 140.53, 131.20 (d, $J = 4.1$ Hz), 130.81, 130.24, 128.95, 127.67, 127.63, 127.17, 120.70, 114.54, 112.32 (d, $J = 233.2$ Hz), 55.62, 54.20 (d, $J = 30.6$ Hz), 41.75 (d, $J = 29.2$ Hz) ppm. IR (KBr) ν 3006, 2919, 2849, 1765, 1748, 1520, 1470, 1275, 1259, 1158, 824, 764, 750, 692. HRMS (ESI) m/z calcd. for $C_{23}H_{21}FNO_3^+$ ($M + H^+$): 378.1500, Found: 378.1495.

5-Fluoro-5-(4-fluorobenzyl)-3-(4-methoxyphenyl)oxazolidin-2-one (3k)



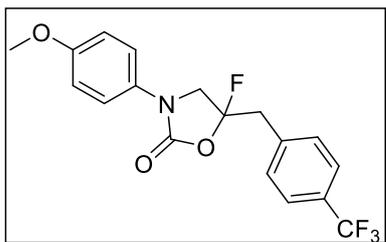
41.5 mg, 65% yield. White solid, Mp 124-126 °C. 1H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 4H), 7.05 (t, $J = 8.5$ Hz, 2H), 6.88 (d, $J = 8.9$ Hz, 2H), 4.04 – 3.83 (m, 2H), 3.78 (s, 3H), 3.43 – 3.23 (m, 2H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -93.10, -114.22 ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.64 (d, $J = 246.9$ Hz), 157.06, 152.23, 132.03 (d, $J = 8.1$ Hz), 130.13, 127.96 (t, $J = 3.7$ Hz), 120.72, 115.93 (d, $J = 21.4$ Hz), 114.56, 112.07 (dd, $J = 233.0, 1.2$ Hz), 55.63, 54.19 (d, $J = 30.6$ Hz), 41.32 (d, $J = 29.6$ Hz) ppm. IR (KBr) ν 3008, 2992, 2920, 2845, 1771, 1760, 1512, 1275, 1258, 1080, 826, 764, 750. HRMS (ESI) m/z calcd. for $C_{17}H_{16}F_2NO_3^+$ ($M + H^+$): 320.1093, Found: 320.1091.

5-Fluoro-5-(4-methoxybenzyl)-3-(4-methoxyphenyl)oxazolidin-2-one (3l)



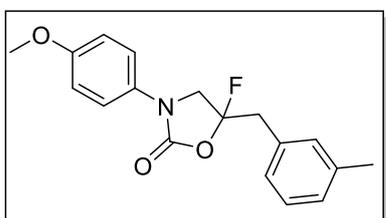
44.2 mg, 66% yield. White solid, Mp 135-137 °C. 1H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, $J = 9.1$ Hz, 2H), 7.25 (d, $J = 9.1$ Hz, 2H), 6.93 – 6.84 (m, 4H), 4.01, 3.88 (ABq, $J = 10.8$ Hz, 1H), 3.94, 3.83 (ABq, $J = 10.8$ Hz, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 3.38 – 3.21 (m, 2H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -92.77 ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.46, 157.00, 152.40, 131.46, 130.31, 124.19 (d, $J = 4.6$ Hz), 120.69, 114.55, 114.43, 112.49 (d, $J = 232.9$ Hz), 55.64, 55.41, 54.04 (d, $J = 30.6$ Hz), 41.23 (d, $J = 29.4$ Hz) ppm. IR (KBr) ν 3005, 2984, 1771, 1515, 1456, 1339, 1275, 1260, 764, 750. HRMS (ESI) m/z calcd. for $C_{18}H_{18}FNNaO_4^+$ ($M + Na^+$): 354.1112, Found: 354.1104.

5-Fluoro-3-(4-methoxyphenyl)-5-(4-(trifluoromethyl)benzyl)oxazolidin-2-one (3m)



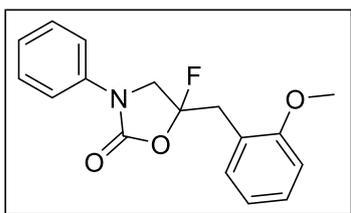
42.8 mg, 58% yield. White solid, Mp 151-155 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.63 (d, *J* = 8.1 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.36 – 7.29 (m, 2H), 6.92 – 6.85 (m, 2H), 4.02, 3.95 (ABq, *J* = 10.9 Hz, 1H), 3.95, 3.90 (ABq, *J* = 10.9 Hz, 1H), 3.79 (s, 3H), 3.51 – 3.34 (m, 2H) ppm. ¹⁹F NMR (376 MHz, CDCl₃) δ -62.69, -92.86 ppm. ¹³C NMR (101 MHz, CDCl₃) δ 157.18, 152.07 (d, *J* = 1.7 Hz), 136.22 (dd, *J* = 3.2, 1.3 Hz), 130.84 (d, *J* = 0.8 Hz), 130.52 (q, *J* = 32.6 Hz), 130.03, 125.93 (q, *J* = 3.7 Hz), 124.10 (q, *J* = 272.1 Hz), 120.80, 114.63, 111.72 (d, *J* = 233.4 Hz), 55.66, 54.46 (d, *J* = 30.6 Hz), 42.02 (d, *J* = 29.5 Hz) ppm. IR (KBr) ν 3005, 2990, 1759, 1275, 1261, 1159, 1123, 825, 764, 750. HRMS (ESI) *m/z* calcd. for C₁₈H₁₆F₄NO₃⁺ (*M* + H⁺): 370.1061, Found: 370.1065.

5-Fluoro-3-(4-methoxyphenyl)-5-(3-methylbenzyl)oxazolidin-2-one (3n)



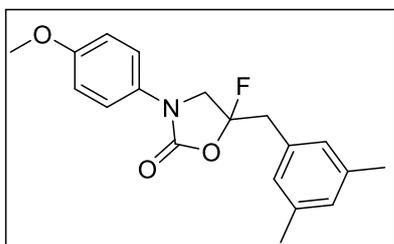
52.3 mg, 83% yield. White solid, Mp 63-68 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.31 (m, 2H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.17 – 7.11 (m, 3H), 6.91 – 6.84 (m, 2H), 4.04, 3.89 (ABq, *J* = 10.9 Hz, 1H), 3.96, 3.84 (ABq, *J* = 10.9 Hz, 1H), 3.78 (s, 3H), 3.42 – 3.22 (m, 2H), 2.36 (s, 3H) ppm. ¹⁹F NMR (376 MHz, CDCl₃) δ -92.42 ppm. ¹³C NMR (101 MHz, CDCl₃) δ 156.92, 152.36, 138.66, 132.12 (d, *J* = 4.1 Hz), 131.13, 130.24, 128.81, 128.78, 127.35, 120.64, 114.48, 112.38 (d, *J* = 233.1 Hz), 55.60, 54.06 (d, *J* = 30.6 Hz), 41.95 (d, *J* = 29.0 Hz), 21.49 ppm. IR (KBr) ν 3005, 2989, 1771, 1515, 1457, 1339, 1275, 1260, 1086, 764, 750, 706. HRMS (ESI) *m/z* calcd. for C₁₈H₁₈FNNaO₃⁺ (*M* + Na⁺): 338.1163, Found: 338.1162.

5-Fluoro-5-(2-methoxybenzyl)-3-phenyloxazolidin-2-one (3o)



42.1 mg, 70% yield. White solid, Mp 88-90 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.45 (dd, *J* = 8.7, 0.9 Hz, 2H), 7.39 – 7.27 (m, 4H), 7.14 (t, *J* = 7.4 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 8.3 Hz, 1H), 4.14, 3.94 (ABq, *J* = 11.0 Hz, 1H), 4.06, 3.89 (ABq, *J* = 11.0 Hz, 1H), 3.88 (s, 3H), 3.54 – 3.37 (m, 2H) ppm. ¹⁹F NMR (376 MHz, CDCl₃) δ -91.60 ppm. ¹³C NMR (101 MHz, CDCl₃) δ 157.56, 152.26 (d, *J* = 2.0 Hz), 137.48, 132.80, 129.48, 129.31, 124.70, 121.27, 120.72 (d, *J* = 5.1 Hz), 118.49, 112.77 (d, *J* = 233.2 Hz), 111.00, 55.70, 53.53 (d, *J* = 30.4 Hz), 34.98 (d, *J* = 30.1 Hz) ppm. IR (KBr) ν 3391, 3004, 2920, 2849, 1778, 1646, 1601, 1503, 1496, 1468, 1406, 1336, 1248, 752, 696, 669. HRMS (ESI) *m/z* calcd. for C₁₇H₁₆FNNaO₃⁺ (*M* + Na⁺): 324.1006, Found: 324.0998.

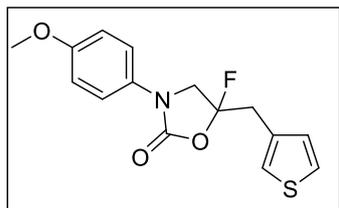
5-(3,5-Dimethylbenzyl)-5-fluoro-3-(4-methoxyphenyl)oxazolidin-2-one (3p)



54.0 mg, 82% yield. Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.31 (m, 2H), 6.96 (s, 1H), 6.94 (s, 2H), 6.91 – 6.85 (m, 2H), 4.03, 3.89 (ABq, *J* = 10.9 Hz, 1H), 3.96, 3.84 (ABq, *J* = 10.9 Hz, 1H), 3.78 (s, 3H), 3.39 – 3.18 (m, 2H), 2.32 (s, 6H) ppm. ¹⁹F NMR (376 MHz,

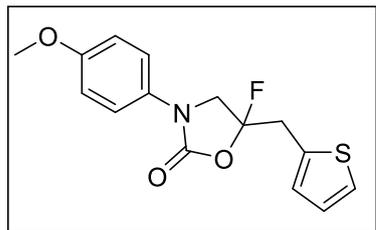
CDCl₃) δ -92.25 ppm. ¹³C NMR (101 MHz, CDCl₃) δ 156.97, 152.44, 138.53, 132.08 (d, *J* = 4.2 Hz), 130.34, 129.69, 128.16, 120.70, 114.53, 112.48 (d, *J* = 233.0 Hz), 55.64, 54.10 (d, *J* = 30.6 Hz), 41.93 (d, *J* = 28.9 Hz), 21.38 ppm. IR (KBr) ν 3005, 2988, 1771, 1515, 1457, 1339, 1275, 1260, 1086, 1067, 764, 750. HRMS (ESI) *m/z* calcd. for C₁₉H₂₀FNNaO₃⁺ (*M* + Na⁺): 352.1319, Found: 352.1314.

5-Fluoro-3-(4-methoxyphenyl)-5-(thiophen-3-ylmethyl)oxazolidin-2-one (3q)



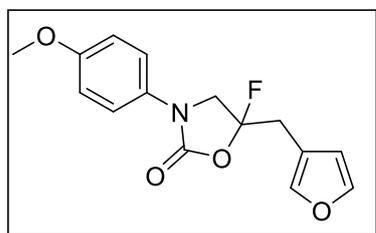
47.3 mg, 77% yield. White solid, Mp 95-98 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.29 (m, 3H), 7.23 (d, *J* = 1.8 Hz, 1H), 7.08 (d, *J* = 4.9 Hz, 1H), 6.91 – 6.83 (m, 2H), 4.01, 3.92 (ABq, *J* = 10.9 Hz, 1H), 3.93, 3.87 (ABq, *J* = 10.9 Hz, 1H), 3.78 (s, 3H), 3.49 – 3.32 (m, 2H) ppm. ¹⁹F NMR (376 MHz, CDCl₃) δ -92.91 ppm. ¹³C NMR (101 MHz, CDCl₃) δ 157.00, 152.27, 132.24 (d, *J* = 4.4 Hz), 130.18, 128.99, 126.64, 124.68, 120.72, 114.53, 112.05 (d, *J* = 232.9 Hz), 55.62, 54.19 (d, *J* = 30.5 Hz), 36.79 (d, *J* = 30.7 Hz) ppm. IR (KBr) ν 2920, 2849, 1771, 1646, 1515, 1469, 1338, 1276, 1255, 1090, 1060, 830, 764, 750. HRMS (ESI) *m/z* calcd. for C₁₅H₁₅FNO₃S⁺ (*M* + H⁺): 308.0751, Found: 308.0742.

5-Fluoro-3-(4-methoxyphenyl)-5-(thiophen-2-ylmethyl)oxazolidin-2-one (3r)



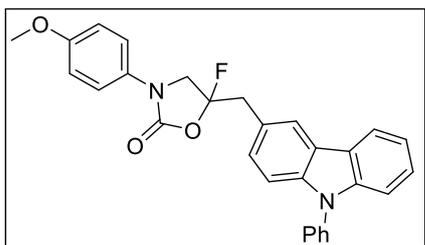
36.8 mg, 60% yield. White solid, Mp 82-85 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.31 (m, 2H), 7.28 – 7.25 (m, 1H), 7.06 – 6.96 (m, 2H), 6.93 – 6.84 (m, 2H), 4.09, 3.96 (ABq, *J* = 10.9 Hz, 1H), 4.02, 3.91 (ABq, *J* = 10.9 Hz, 1H), 3.79 (s, 3H), 3.67 – 3.51 (m, 2H) ppm. ¹⁹F NMR (376 MHz, CDCl₃) δ -93.23 ppm. ¹³C NMR (101 MHz, CDCl₃) δ 157.10, 152.14, 133.14 (d, *J* = 5.2 Hz), 130.17, 128.56, 127.47, 126.20, 120.82, 114.59, 111.68 (d, *J* = 233.3 Hz), 55.65, 54.00 (d, *J* = 30.4 Hz), 36.57 (d, *J* = 32.4 Hz) ppm. IR (KBr) ν 3006, 2920, 2849, 1775, 1646, 1515, 1469, 1338, 1275, 1257, 975, 829, 764, 750. HRMS (ESI) *m/z* calcd. for C₁₅H₁₅FNO₃S⁺ (*M* + H⁺): 308.0751, Found: 308.0747.

5-Fluoro-5-(furan-3-ylmethyl)-3-(4-methoxyphenyl)oxazolidin-2-one (3s)



37.8 mg, 65% yield. White solid, Mp 104-108 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.45 – 7.39 (m, 2H), 7.38– 7.32 (m, 2H), 6.93 – 6.84 (m, 2H), 6.43 (s, 1H), 4.02, 3.95 (ABq, *J* = 10.9 Hz, 1H), 3.94, 3.90 (ABq, *J* = 10.9 Hz, 1H), 3.79 (s, 3H), 3.29 – 3.11 (m, 2H) ppm. ¹⁹F NMR (376 MHz, CDCl₃) δ -93.33 ppm. ¹³C NMR (101 MHz, CDCl₃) δ 157.13, 152.28, 143.81, 141.47, 130.28, 120.79, 116.06 (d, *J* = 4.9 Hz), 114.63, 112.10 (d, *J* = 232.6 Hz), 111.69, 55.66, 54.28 (d, *J* = 30.6 Hz), 32.20 (d, *J* = 31.7 Hz) ppm. IR (KBr) ν 3392, 3006, 2920, 2849, 1771, 1646, 1515, 1469, 1338, 1251, 1092, 1024, 874, 749. HRMS (ESI) *m/z* calcd. for C₁₅H₁₅FNO₄⁺ (*M* + H⁺): 292.0980, Found: 292.0967.

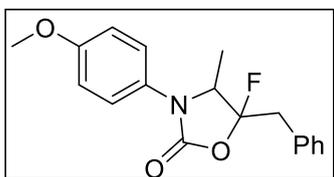
5-Fluoro-3-(4-methoxyphenyl)-5-((9-phenyl-9H-carbazol-3-yl)methyl)oxazolidin-2-one (3t)



26.1 mg, 28% yield. Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.15 (d, $J = 7.8$ Hz, 1H), 8.09 (s, 1H), 7.61 (t, $J = 7.7$ Hz, 2H), 7.55 (d, $J = 7.6$ Hz, 2H), 7.51 – 7.27 (m, 8H), 6.84 (d, $J = 9.0$ Hz, 2H), 4.12, 3.90 (ABq, $J = 10.9$ Hz, 1H), 4.04, 3.85 (ABq, $J = 10.9$ Hz, 1H), 3.76 (s, 3H), 3.65 – 3.46 (m, 2H) ppm. ^{19}F NMR (376 MHz, CDCl_3) δ -92.29 ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 156.91

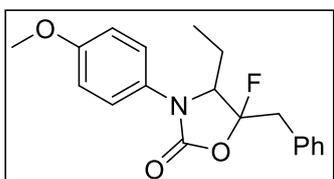
152.48, 141.39, 140.63, 137.60, 130.36, 130.08, 128.11, 127.79, 127.20, 126.48, 123.87, 123.58 (d, $J = 4.4$ Hz), 122.99, 122.12, 120.59, 120.54, 120.29, 114.50, 112.82 (d, $J = 232.9$ Hz), 110.31, 110.09, 55.63, 54.03 (d, $J = 30.7$ Hz), 42.10 (d, $J = 29.1$ Hz) ppm. IR (KBr) ν 3055, 3006, 2955, 2930, 2835, 1774, 1597, 1514, 1503, 1458, 1333, 1251, 1234, 1151, 977, 937, 828, 763, 749, 698. HRMS (ESI) m/z calcd. for $\text{C}_{29}\text{H}_{23}\text{FN}_2\text{NaO}_3^+$ ($\text{M} + \text{Na}^+$): 489.1585, Found: 489.1583.

5-Benzyl-5-fluoro-3-(4-methoxyphenyl)-4-methyloxazolidin-2-one (3u)



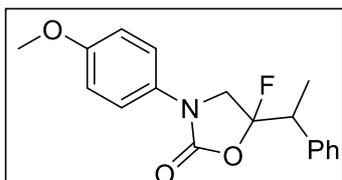
50.0 mg, 79% yield, dr = 2.3:1. White solid, Mp 102-105 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.43 – 7.28 (m, 5.6H), 7.12 – 7.05 (m, 1.4H), 6.94 – 6.85 (m, 2H), [4.36 (dq, $J = 19.3, 6.7$ Hz), 4.22 (dq, $J = 21.0, 6.5$ Hz), (1H)], [3.80 (s), 3.78 (s), (3H)], 3.49 – 3.16 (m, 2H), [1.27 (d, $J = 6.7$ Hz), 1.03 (dd, $J = 6.5, 2.4$ Hz), (3H)] ppm. ^{19}F NMR (376 MHz, CDCl_3) δ -93.67, -111.55 ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 158.37, 157.89, 153.47 (d, $J = 1.4$ Hz), 152.40 (d, $J = 1.6$ Hz), 132.32, 132.27, 130.58 (d, $J = 1.2$ Hz), 130.51, 128.87, 128.58, 128.41, 127.95, 127.87, 127.61, 126.06, 124.52, 114.74, 114.65, 114.52 (d, $J = 232.8$ Hz), 113.64 (d, $J = 238.9$ Hz), 62.40 (d, $J = 31.4$ Hz), 59.18 (d, $J = 25.7$ Hz), 55.60, 55.58, 41.87 (d, $J = 29.6$ Hz), 38.78 (d, $J = 26.4$ Hz), 14.78 (d, $J = 9.1$ Hz), 12.41 (d, $J = 12.0$ Hz) ppm. IR (KBr) ν 3000, 2920, 2849, 1775, 1646, 1515, 1456, 1396, 1297, 1250, 1151, 1038, 989, 962, 831, 750, 702. HRMS (ESI) m/z calcd. for $\text{C}_{18}\text{H}_{18}\text{FNNaO}_3^+$ ($\text{M} + \text{Na}^+$): 338.1163 Found: 338.1163.

5-Benzyl-4-ethyl-5-fluoro-3-(4-methoxyphenyl)oxazolidin-2-one (3v)



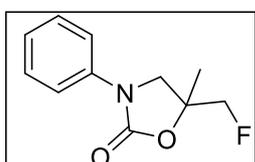
49.4 mg, 75% yield, dr = 1.5:1. White solid, Mp 100-104 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.44 – 7.29 (m, 6H), 7.06 – 6.97 (m, 1H), 6.94 – 6.89 (m, 1H), 6.89 – 6.84 (m, 1H), [4.35 (ddd, $J = 18.8, 5.6, 4.2$ Hz), 4.03 (ddd, $J = 20.4, 9.2, 3.9$ Hz), (1H)], [3.80 (s), 3.77 (s), (3H)], 3.55 – 3.09 (m, 2H), 1.90 – 1.56 (m, 2H), 0.95 – 0.85 (m, 3H) ppm. ^{19}F NMR (376 MHz, CDCl_3) δ -90.21, -111.31 ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 158.47, 157.69, 153.38, 152.81, 132.47 (d, $J = 7.4$ Hz), 132.28, 130.71, 130.59 (d, $J = 0.9$ Hz), 129.06, 128.89, 128.56, 128.22, 127.93, 127.61, 126.32, 124.19, 114.68, 114.66, 114.26 (d, $J = 232.6$ Hz), 113.92 (d, $J = 239.1$ Hz), 66.52 (d, $J = 29.5$ Hz), 63.72 (d, $J = 24.9$ Hz), 55.59, 55.56, 43.27 (d, $J = 30.9$ Hz), 38.67 (d, $J = 26.4$ Hz), 21.56 (d, $J = 8.9$ Hz), 20.85 (d, $J = 10.7$ Hz), 9.95 (d, $J = 2.4$ Hz), 8.61 ppm. IR (KBr) ν 3006, 2986, 2921, 2851, 1776, 1515, 1456, 1403, 1275, 1259, 1125, 1032, 978, 829, 764, 750, 701. HRMS (ESI) m/z calcd. for $\text{C}_{19}\text{H}_{21}\text{FNO}_3^+$ ($\text{M} + \text{H}^+$): 330.1500, Found: 330.1500.

5-Fluoro-3-(4-methoxyphenyl)-5-(1-phenylethyl)oxazolidin-2-one (3w)



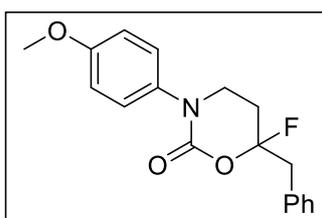
25.8 mg, 41% yield, dr = 1.1:1. Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.44 – 7.24 (m, 7H), 6.91 – 6.82 (m, 2H), 4.01 – 3.64 (m, 5H), [3.40 (dq, J = 10.3, 7.2 Hz), 3.27 (dq, J = 21.2, 7.0 Hz), (1H)], 1.55 (t, J = 6.9 Hz, 3H) ppm. ^{19}F NMR (376 MHz, CDCl_3) δ -97.07, -106.34 ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 157.00, 156.95, 152.54 (d, J = 1.7 Hz), 152.43, 138.48 (d, J = 4.7 Hz), 138.33, 130.27, 130.22, 129.00, 128.97, 128.79, 128.74 (d, J = 2.0 Hz), 128.12, 128.08, 120.79, 120.69, 114.51, 114.49, 113.87 (d, J = 234.9 Hz), 113.65 (d, J = 237.8 Hz), 55.63, 54.49 (d, J = 30.9 Hz), 53.46 (d, J = 31.1 Hz), 46.50 (d, J = 26.2 Hz), 45.21 (d, J = 27.6 Hz), 14.98 (d, J = 5.0 Hz), 14.87 (d, J = 3.9 Hz) ppm. IR (KBr) ν 3005, 2989, 2918, 2849, 1773, 1514, 1463, 1406, 1337, 1275, 1260, 897, 765, 750. HRMS (ESI) m/z calcd. for $\text{C}_{18}\text{H}_{18}\text{FNNaO}_3^+$ ($M + \text{Na}^+$): 338.1163, Found: 338.1165.

5-(Fluoromethyl)-5-methyl-3-phenyloxazolidin-2-one (3x)



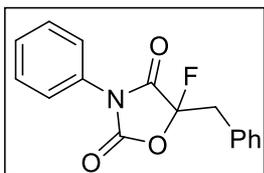
18.4 mg, 44% yield. Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.54 (d, J = 8.1 Hz, 2H), 7.38 (t, J = 7.9 Hz, 2H), 7.15 (t, J = 7.4 Hz, 1H), 4.57, 4.43 (ABq, J = 9.9 Hz, 1H), 4.45, 4.32 (ABq, J = 9.9 Hz, 1H), 4.09 (d, J = 8.9 Hz, 1H), 3.76 (dd, J = 9.0, 1.4 Hz, 1H), 1.56 (d, J = 2.1 Hz, 3H) ppm. ^{19}F NMR (376 MHz, CDCl_3) δ -227.85 ppm. ^{13}C NMR (101 MHz, DMSO) δ 153.44, 138.29, 128.92, 123.57, 117.98, 85.80 (d, J = 174.2 Hz), 77.19 (d, J = 17.5 Hz), 51.19 (d, J = 5.2 Hz), 21.00 (d, J = 4.8 Hz) ppm. IR (KBr) ν 3005, 2989, 2920, 2851, 1749, 1460, 1414, 1322, 1275, 1261, 1119, 897, 763, 750, 706. HRMS (ESI) m/z calcd. for $\text{C}_{11}\text{H}_{12}\text{FNNaO}_2^+$ ($M + \text{Na}^+$): 232.0744, Found: 232.0737.

6-Benzyl-6-fluoro-3-(4-methoxyphenyl)-1,3-oxazinan-2-one (3y)



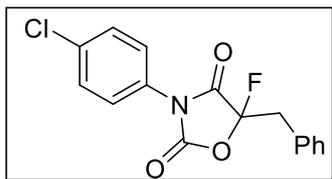
35.0 mg, 56% yield. White solid, Mp 142-146 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.38 – 7.29 (m, 5H), 7.23 – 7.18 (m, 2H), 6.93 – 6.86 (m, 2H), 3.93 – 3.83 (m, 1H), 3.80 (s, 3H), 3.46 – 3.40 (m, 1H), 3.38 – 3.21 (m, 2H), 2.15 – 1.98 (m, 2H) ppm. ^{19}F NMR (376 MHz, CDCl_3) δ -101.73 ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 158.66, 150.16, 135.14, 133.39 (d, J = 4.9 Hz), 130.60, 128.74, 127.69, 127.23, 114.75, 113.29 (d, J = 226.8 Hz), 55.63, 44.73 (d, J = 26.2 Hz), 44.52 (d, J = 4.5 Hz), 28.43 (d, J = 26.0 Hz) ppm. IR (KBr) ν 3005, 2989, 2916, 1719, 1512, 1478, 1426, 1275, 1260, 1164, 832, 763, 750, 705. HRMS (ESI) m/z calcd. for $\text{C}_{18}\text{H}_{18}\text{FNNaO}_3^+$ ($M + \text{Na}^+$): 338.1163, Found: 338.1157.

5-Benzyl-5-fluoro-3-phenyloxazolidine-2,4-dione (3'a)^[3]



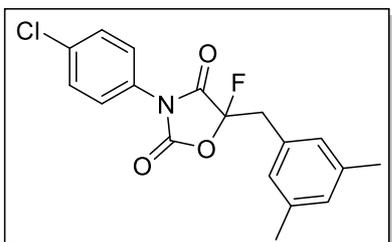
27.4 mg, 48% yield. White solid. ^1H NMR (400 MHz, CDCl_3) δ 7.45 – 7.38 (m, 3H), 7.38 – 7.30 (m, 5H), 7.06 – 6.97 (m, 2H), 3.63 – 3.52 (m, 2H) ppm. ^{19}F NMR (376 MHz, CDCl_3) δ -110.11 ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 165.52 (d, J = 24.3 Hz), 150.78, 130.62, 129.79, 129.68, 129.59, 129.18, 128.65, 125.58, 110.06 (d, J = 244.5 Hz), 38.91 (d, J = 28.2 Hz) ppm.

5-Benzyl-3-(4-chlorophenyl)-5-fluorooxazolidine-2,4-dione (3'b)



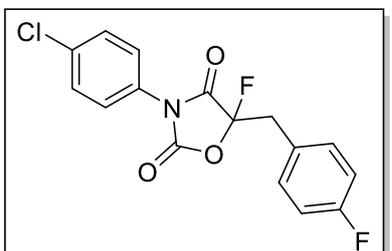
34.6 mg, 54% yield. White solid, Mp 136-139 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.41 – 7.33 (m, 5H), 7.32 – 7.28 (m, 2H), 7.02 – 6.94 (m, 2H), 3.62 – 3.51 (m, 2H) ppm. ¹⁹F NMR (376 MHz, CDCl₃) δ -110.11 ppm. ¹³C NMR (101 MHz, CDCl₃) δ 165.23 (d, *J* = 24.4 Hz), 150.40, 135.56, 130.58, 129.82, 129.60 (d, *J* = 10.4 Hz), 129.21, 128.71, 128.21, 126.70, 110.09 (d, *J* = 245.1 Hz), 38.91 (d, *J* = 28.1 Hz) ppm. IR (KBr) ν 3005, 2987, 2922, 2847, 1842, 1765, 1500, 1426, 1275, 1260, 825, 764, 750, 699. HRMS (EI) *m/z* calcd. for C₁₆H₁₁ClFNO₃⁺: 319.0406, Found: 319.0406

3-(4-Chlorophenyl)-5-(3,5-dimethylbenzyl)-5-fluorooxazolidine-2,4-dione (3'c)^[3]



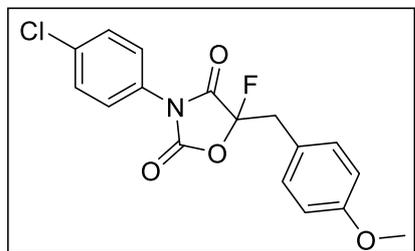
30.1 mg, 43% yield. White solid. ¹H NMR (400 MHz, CDCl₃) δ 7.40 (d, *J* = 8.6 Hz, 2H), 7.01 (d, *J* = 8.6 Hz, 2H), 6.95 (s, 1H), 6.90 (s, 2H), 3.61 – 3.35 (m, 2H), 2.28 (s, 6H) ppm. ¹⁹F NMR (376 MHz, CDCl₃) δ -110.37 ppm. ¹³C NMR (101 MHz, CDCl₃) δ 165.43 (d, *J* = 24.6 Hz), 150.50, 138.83, 135.55, 130.25, 129.83, 129.39 (d, *J* = 10.2 Hz), 128.35, 128.25, 126.72, 110.19 (d, *J* = 245.0 Hz), 38.79 (d, *J* = 27.7 Hz), 21.31 ppm.

3-(4-Chlorophenyl)-5-fluoro-5-(4-fluorobenzyl)oxazolidine-2,4-dione (3'd)^[3]



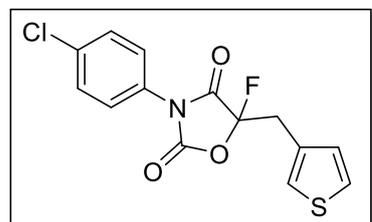
33.1 mg, 49% yield. White solid. ¹H NMR (400 MHz, CDCl₃) δ 7.41 (d, *J* = 8.5 Hz, 2H), 7.33 – 7.24 (m, 2H), 7.10 – 7.01 (m, 4H), 3.61 – 3.46 (m, 2H). ¹⁹F NMR (376 MHz, CDCl₃) δ -109.62, -112.81 ppm. ¹³C NMR (101 MHz, CDCl₃) δ 165.11 (d, *J* = 24.5 Hz), 162.93 (d, *J* = 248.4 Hz), 150.33, 135.65, 132.35 (d, *J* = 8.2 Hz), 129.91, 128.17, 126.56, 125.37 (dd, *J* = 10.3, 3.4 Hz), 116.25 (d, *J* = 21.6 Hz), 109.72 (dd, *J* = 244.7, 1.7 Hz), 37.99 (d, *J* = 28.6 Hz) ppm.

3-(4-Chlorophenyl)-5-fluoro-5-(4-methoxybenzyl)oxazolidine-2,4-dione (3'e)^[3]



39.2 mg, 56% yield. White solid. ¹H NMR (400 MHz, CDCl₃) δ 7.39 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 2H), 7.03 (d, *J* = 8.2 Hz, 2H), 6.86 (d, *J* = 8.1 Hz, 2H), 3.79 (s, 3H), 3.58 – 3.43 (m, 2H) ppm. ¹⁹F NMR (376 MHz, CDCl₃) δ -110.15 ppm. ¹³C NMR (101 MHz, CDCl₃) δ 165.35 (d, *J* = 24.5 Hz), 159.83, 150.50, 135.51, 131.71, 129.81, 128.26, 126.69, 121.28 (d, *J* = 10.8 Hz), 114.57, 110.15 (d, *J* = 245.3 Hz), 55.43, 37.98 (d, *J* = 28.1 Hz) ppm.

3-(4-Chlorophenyl)-5-fluoro-5-(thiophen-3-ylmethyl)oxazolidine-2,4-dione (3'f)

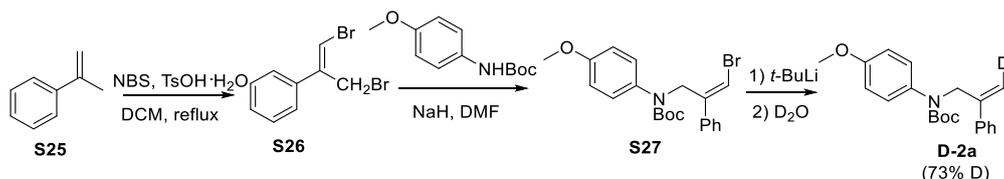


28.0mg, 43% yield. White solid, Mp 140-142 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.41 (d, *J* = 8.2 Hz, 2H), 7.37 – 7.32 (m,

1H), 7.25 (s, 1H), 7.07 – 7.01 (m, 3H), 3.71 – 3.54 (m, 2H) ppm. ^{19}F NMR (376 MHz, CDCl_3) δ -111.01 ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 165.29 (d, $J = 24.5$ Hz), 150.47, 135.64, 129.89, 129.59 (d, $J = 10.9$ Hz), 128.91, 128.23, 127.17, 126.76, 126.01, 109.69 (d, $J = 245.4$ Hz), 33.52 (d, $J = 29.6$ Hz) ppm. IR (KBr) ν 3005, 2989, 1765, 1501, 1457, 1427, 1275, 1261, 763, 750, 706. HRMS (EI) m/z calcd. for $\text{C}_{14}\text{H}_9\text{ClFNO}_3\text{S}^+$: 324.9970, Found: 324.9969

4. Studies on the Mechanism

4.1 Deuterium experiments



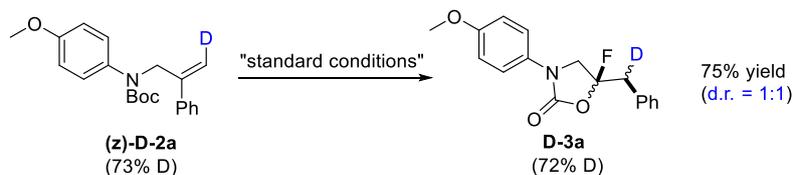
Compound **S26** was prepared according to literature procedures.^[6]

Compound D-2a. To a sealing tube was added **S25** (1 g, 8.5 mmol, 1.0 equiv), NBS (3.8 g, 21.2 mmol, 2.5 equiv), TsOH·H₂O (155 mg, 0.9 mmol, 0.1 equiv) and DCM (30 mL). The reaction was refluxed overnight. DCM (30 mL) and water (30 mL) were added to the mixture. The aqueous phase was extracted by DCM (20 mL × 2) again. The combined organic phases were washed by brine (30 mL), dried over Na₂SO₄ and concentrated under reduced pressure successively. The residue was purified by column chromatography (eluted with PE) to afford **S26** as a colorless oil (1.04 g, 44% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.45 – 7.35 (m, 5H), 6.67 (s, 1H), 4.49 (s, 2H) ppm.

NaH (60%, 135 mg, 3.36 mmol, 1.5 equiv) and 3 mL DMF was added to a sealing tube, which was filled with N₂ gas. The solution of *tert*-butyl (4-methoxyphenyl)carbamate (500 mg, 2.24 mmol, 1.0 equiv) in DMF (3 mL) was charged to the system dropwise at 0 °C. The mixture was allowed to stir at 0 °C for 1.5 hours. After which, **S26** (870 mg, 3.13 mmol, 1.4 equiv) was added. The mixture was allowed to stir at room temperature overnight. EtOAc (20 mL) and water (20 mL) were added to the mixture. The aqueous phase was extracted by EtOAc (20 mL × 2). The combined organic phases were washed by brine (20 mL), dried over Na₂SO₄ and concentrated under reduced pressure successively. The residue was purified by column chromatography (eluted with EtOAc/PE = 1/15) to afford **S27** as a white solid (870 mg, 93% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.34 – 7.28 (m, 3H), 7.22 (brs, 2H), 6.70 (brs, 4H), 6.31 (s, 1H), 5.00 (s, 2H), 3.77 (s, 3H), 1.30 (brs, 9H) ppm.

To a dried flask was added **S27** (418 mg, 1 mmol, 1.0 equiv) and anhydrous Et₂O (40 mL). The mixture was cooled to -78 °C. *t*-BuLi (1.6 M, 1 mL, 1.5 mmol, 1.5 equiv) was introduced cautiously at this temperature. The mixture was stirred at this temperature for 30 min before the D₂O (0.1 g) was added. Then, the reaction mixture was allowed to stir at room temperature overnight, after which, it was quenched by water (15 mL). The mixture was extracted by Et₂O (20 mL × 2). The combined organic phases were washed by brine (20 mL), dried over Na₂SO₄ and concentrated under reduced pressure successively. The residue was purified by column chromatography (eluted with EtOAc/PE = 1/30) to afford **(z)-D-2a** as a white solid (193 mg, 57% yield, 73% D). ^1H NMR (400 MHz, CDCl_3) δ 7.39 (d, $J = 6.8$ Hz, 2H), 7.35 – 7.27 (m, 3H),

7.10 – 6.66 (m, 4H), 5.34 (s, 0.27H), 5.32 (s, 0.73H), 5.10 (s, 0.27H), 4.66 (s, 2H), 3.77 (s, 3H), 1.40 (s, 9H) ppm.



Compound D-3a. 1-Fluoro-3,3-dimethyl-1,3-dihydro- λ^3 -benzo[d][1,2]iodoxole **1** (42 mg, 0.15 mmol, 1.5 equiv), the substrate (*z*)-**D-2a** (34 mg, 0.1 mmol, 1.0 equiv), AgSbF₆ (3.4 mg, 0.01 mmol, 0.1 equiv) and DCM (1 mL) were introduced to a glass vial. The vial was then sealed and the mixture was allowed to stir at 55 °C for 3.5 hours. After that, the reaction mixture was concentrated on a rotary evaporator. The dr value was determined by ¹⁹F NMR analysis of the crude product, which was purified by column chromatography (eluted with EtOAc/PE = 1/15) to afford product **D-3a** as a white solid (22.7 mg, 75% yield, dr = 1:1, 72% D). ¹H NMR (400 MHz, CDCl₃) δ 7.41 – 7.30 (m, 7H), 6.87 (d, *J* = 9.0 Hz, 2H), 4.03, 3.90 (ABq, *J* = 10.9 Hz, 1H), 3.95, 3.89 (ABq, *J* = 10.9 Hz, 1H), 3.78 (s, 3H), 3.47 – 3.27 (m, 1.28H) ppm. ¹⁹F NMR (376 MHz, CDCl₃) δ -92.51, -92.65, -92.69 ppm. HRMS (ESI) *m/z* calcd. for C₁₇H₁₅DFNNaO₃⁺ (*M* + Na⁺): 325.1069 Found: 325.1067. The dr value was determined by ¹⁹F NMR analysis, which was illustrated as below:

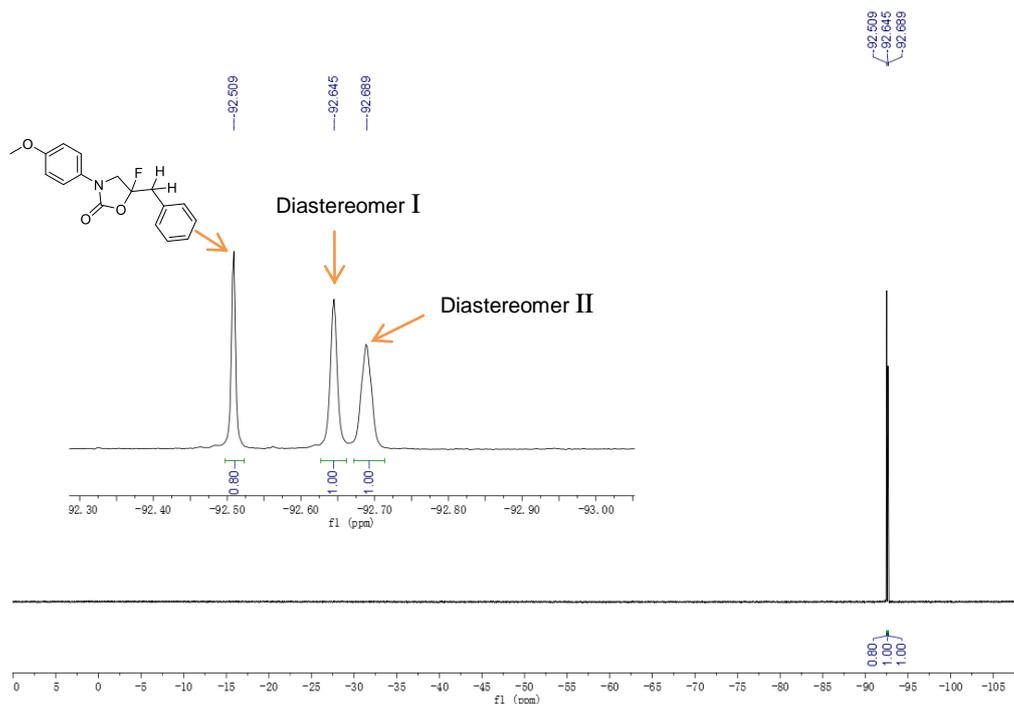
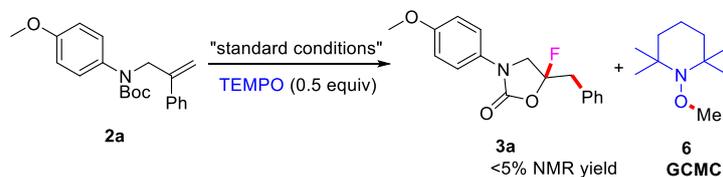


Figure S3. ¹⁹F NMR (376 MHz) of compound **D-3a**

4.2 Radical trapping experiments

4.2.1 Tempo as a radical trapping reagent



1-Fluoro-3,3-dimethyl-1,3-dihydro- λ^3 -benzo[d][1,2]iodoxole **1** (42 mg, 0.15 mmol, 1.5 equiv), the substrate **2a** (33.9 mg, 0.1 mmol, 1.0 equiv), Tempo (7.8 mg, 0.05 mmol, 0.5 equiv), AgSbF₆ (3.4 mg, 0.01 mmol, 0.1 equiv) and DCM (1 mL) were introduced to a glass vial. The vial was then sealed and the mixture was allowed to stir at 55 °C for 3.5 hours. After which, the reaction mixture was concentrated to dryness and CH₂Br₂ was added. The NMR yield was calculated by ¹H NMR spectroscopy using CH₂Br₂ as the internal standard. Compound **6** was detected by GCMS analysis.

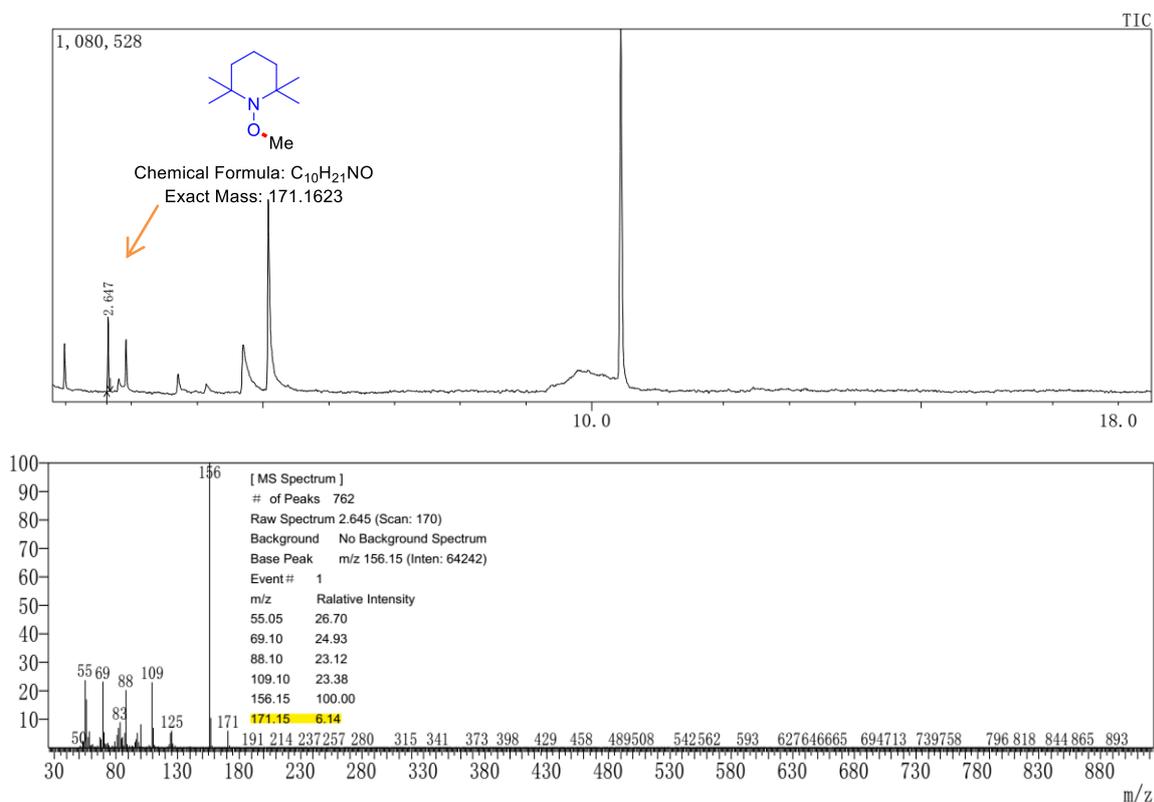
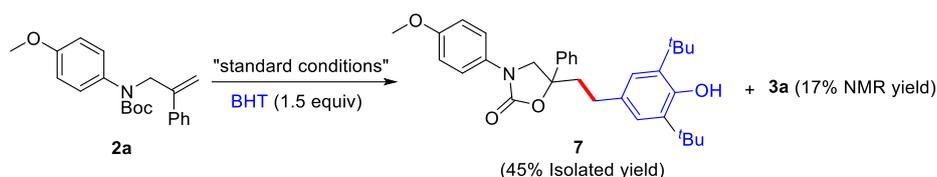


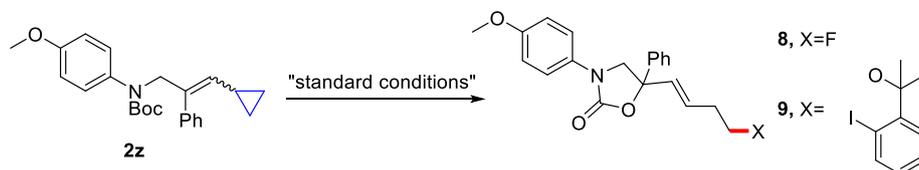
Figure S4. GCMS analysis of compound **6**

4.2.2 BHT as a radical trapping reagent



1-Fluoro-3,3-dimethyl-1,3-dihydro- λ^3 -benzo[d][1,2]iodoxole **1** (42 mg, 0.15 mmol, 1.5 equiv), the substrate **2a** (33.9 mg, 0.1 mmol, 1.0 equiv), BHT (33 mg, 0.15 mmol, 1.5 equiv), AgSbF₆ (3.4 mg, 0.01 mmol, 0.1 equiv) and DCM (1 mL) were introduced to a glass vial. The vial was then sealed and the mixture was allowed to stir at 55 °C for 3.5 hours. After which, the reaction mixture was concentrated to dryness and CH₂Br₂ was added. The NMR yield was calculated by ¹H NMR spectroscopy using CH₂Br₂ as the internal standard. The NMR yield of **7** and **3a** were 47% and 17% respectively. The mixture was purified by column chromatography (eluted with EtOAc/PE = 1/30 \rightarrow 1/15) to afford compound **7** as a thick oil (22.4 mg, 45% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.52 – 7.38 (m, 6H), 7.35 (t, *J* = 7.0 Hz, 1H), 6.92 – 6.86 (m, 4H), 5.04 (s, 1H), 4.13 (dd, *J* = 22.7, 8.6 Hz, 2H), 3.79 (s, 3H), 2.81 – 2.65 (m, 1H), 2.45 – 2.31 (m, 3H), 1.40 (s, 18H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 156.62, 154.76, 152.19, 142.71, 136.13, 131.49, 131.47, 128.99, 128.15, 124.88, 124.51, 120.61, 114.46, 81.64, 58.18, 55.68, 44.30, 34.45, 30.46, 29.74 ppm. IR (KBr) ν 3642, 3627, 3004, 2986, 2955, 2920, 1747, 1514, 1434, 1403, 1275, 1260, 1148, 828, 764, 750, 702. HRMS (ESI) *m/z* calcd. for C₃₂H₃₉NNaO₄⁺ (*M* + Na⁺): 524.2771 Found: 524.2773.

4.3 Radical clock experiments



Compound 8, 9. 1-Fluoro-3,3-dimethyl-1,3-dihydro- λ^3 -benzo[d][1,2]iodoxole **1** (126 mg, 0.45 mmol, 1.5 equiv), the substrate **2z** (114 mg, 0.3 mmol, 1.0 equiv), AgSbF₆ (10.3 mg, 0.03 mmol, 0.1 equiv) and DCM (3 mL) were introduced to a glass vial. The vial was then sealed and the mixture was allowed to stir at 55 °C for 3.5 hours. After that, the reaction mixture was concentrated on a rotary evaporator. The residue was purified by column chromatography (eluted with EtOAc/PE = 1/15) to afford compound **8** (9.6 mg, 9% yield, thick oil) and compound **9** (14.1 mg, 8% yield, thick oil).

compound 8. ¹H NMR (400 MHz, CDCl₃) δ 7.48 – 7.38 (m, 6H), 7.38 – 7.31 (m, 1H), 6.94 – 6.83 (m, 2H), 5.99 (d, *J* = 15.6 Hz, 1H), 5.84 (dt, *J* = 15.5, 6.7 Hz, 1H), 4.47 (dt, *J* = 47.1, 6.1 Hz, 2H), 4.24 (d, *J* = 8.8 Hz, 1H), 4.19 (d, *J* = 8.8 Hz, 1H), 3.79 (s, 3H), 2.49 (ddd, *J* = 24.8, 12.8, 6.4 Hz, 2H) ppm. ¹⁹F NMR (376 MHz, CDCl₃) δ -218.12 ppm. ¹³C NMR (101 MHz, CDCl₃) δ 156.66, 154.48, 141.26, 133.94, 131.39, 128.94, 128.46, 127.53 (d, *J* = 5.9 Hz), 125.10, 120.68, 114.45, 82.54 (d, *J* = 168.0 Hz), 80.82, 57.84, 55.67, 33.29 (d, *J* = 20.6 Hz) ppm. IR (KBr) ν 3005, 2989, 1750, 1514, 1400, 1275, 1260, 1153, 829, 765, 750, 704. HRMS (ESI) *m/z* calcd. for C₂₀H₂₀FNNaO₃⁺ (*M* + Na⁺): 364.1319 Found: 364.1320.

compound 9. ^1H NMR (400 MHz, CDCl_3) δ 7.99 (d, $J = 7.8$ Hz, 1H), 7.47 – 7.37 (m, 6H), 7.35 – 7.27 (m, 3H), 6.93 – 6.83 (m, 3H), 5.91 (d, $J = 15.7$ Hz, 1H), 5.83 (dt, $J = 15.5, 6.2$ Hz, 1H), 4.24 (d, $J = 8.7$ Hz, 1H), 4.15 (d, $J = 8.7$ Hz, 1H), 3.79 (s, 3H), 3.12 (t, $J = 7.0$ Hz, 2H), 2.44 (dd, $J = 13.2, 6.8$ Hz, 2H), 1.64 (s, 3H), 1.63 (s, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 156.59, 154.55, 145.40, 143.41, 141.58, 132.42, 131.54, 130.13, 128.86, 128.82, 128.30, 128.25, 128.02, 125.21, 120.60, 114.43, 93.71, 81.05, 61.87, 57.80, 55.67, 33.29, 27.29 ppm. IR (KBr) ν 3004, 2985, 2927, 2853, 1748, 1514, 1399, 1275, 1260, 1155, 1073, 1006, 827, 764, 750, 699. HRMS (ESI) m/z calcd. for $\text{C}_{29}\text{H}_{30}\text{INNaO}_4^+$ ($\text{M} + \text{Na}^+$): 606.1112 Found: 606.1112.

5 Radiosynthesis of [¹⁸F]-3:

No-carrier-added ¹⁸F-fluoride was produced via the ¹⁸O(p,n)¹⁸F reaction using GE PETTrace 880 (GE Health, IL, USA) under 55 μA irradiation for 20min. The cyclotron-produced aqueous ¹⁸F-fluoride was trapped on a pre-conditioned QMA anion-exchange cartridge followed by releasing with phase transfer reagent (477μL acetonitrile and 70μL 20% tetrabutylammonium bicarbonate aqueous solution). The ¹⁸F-fluoride was azeotropically dried at 70°C under a stream of nitrogen with vacuum on for 4 min, the reactor was then heated to 100°C under vacuum for 2 min. The ¹⁸F-fluoride was then dissolved in 1 mL anhydrous acetonitrile for following procedures.

The radiolabeling reactions were performed using the following protocol. The alkene precursor **2a**, **2b**, or **2c** (6 μmol) was mixed with 1.0 equivalent of chloriodane (**10**) in 20 μL of anhydrous MeCN. The resulting solution was then combined with [¹⁸F]-TBAF in 20 μL MeCN. The reaction mixture was incubated at elevated temperature (60/80 °C) to allow ¹⁸F-Cl exchange reaction to proceed. Then, the Ag salt (1.0 equiv.) in acetonitrile was added to the reaction mixture. After addition of Ag salt, the reaction was incubated at elevated temperature (60/80 °C) for another 10 min to allow ¹⁸F-radiofluorination to process, quenched with 1 mL of 1:1 (v/v) water: MeCN, and passed through Sep-Pak light alumina N cartridge, respectively. An aliquot of aqueous fraction was analyzed by HPLC using method A. The identity of [¹⁸F]-fluorinated heterocycles ([¹⁸F]-**3a**, [¹⁸F]-**3b**, and [¹⁸F]-**3c**) was confirmed by the comparison of their retention times with those of non-radiolabeled analogues (**3a**, **3b**, and **3c**).

HPLC Method A : Phenomenex, Kinetex® 5μm EVO C18 100 Å, 250 x 4.6 mm LC Column. Solvent A: 0.1% TFA water; Solvent B: 0.1% TFA acetonitrile; 0 to 2 min: isocratic elution at 50% solvent B, 2 to 12 min, 50% to 95% solvent B. Flow rate: 1 mL/min, column temperature: 19 to 21 °C.

6 References

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- [5] K. Venkata Rao, M. Raghu Prasad, A. Raghuram Rao, *J. Heterocyclic Chem.*, 2014, **51**, E380.
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7 Data Analysis for radiochemistry experiments

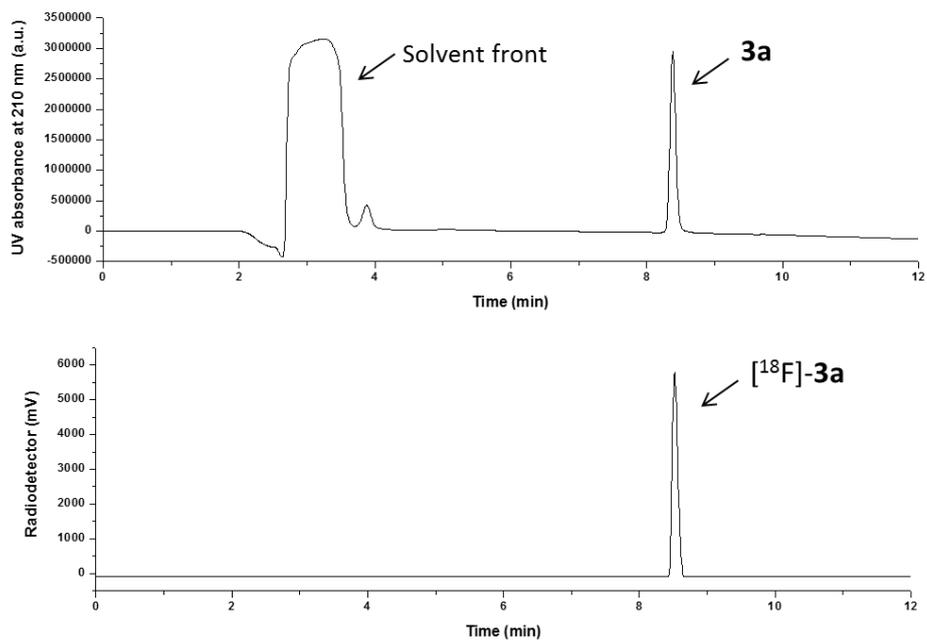


Figure S5. HPLC UV-Chromatogram (above) and radio-chromatogram (below) of the HPLC purified [¹⁸F]-3a solution co-injected with the standard (3a)

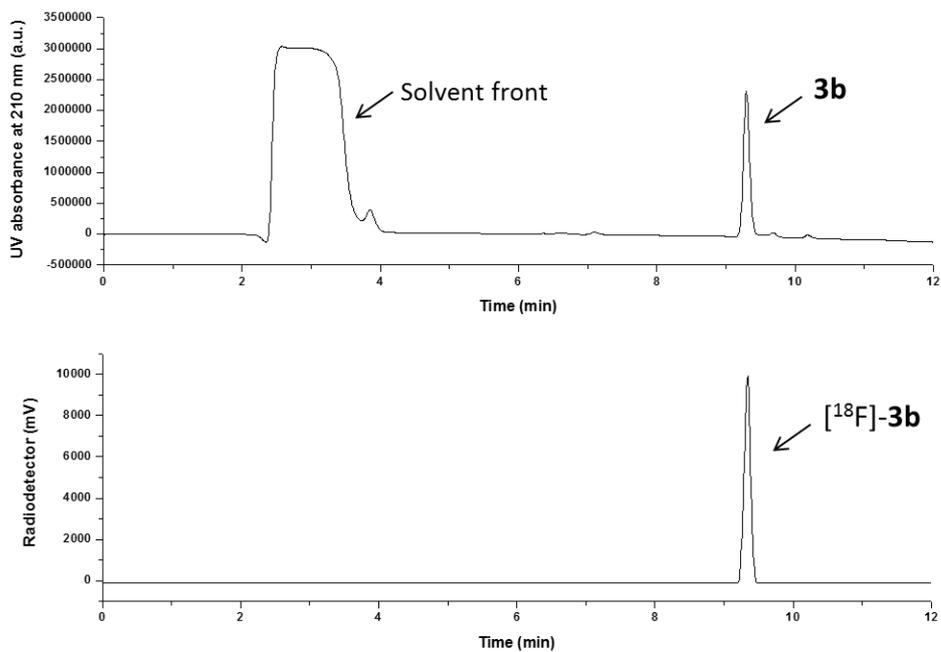


Figure S6. HPLC UV-Chromatogram (above) and radio-chromatogram (below) of the HPLC purified [¹⁸F]-3b solution co-injected with the standard (3b)

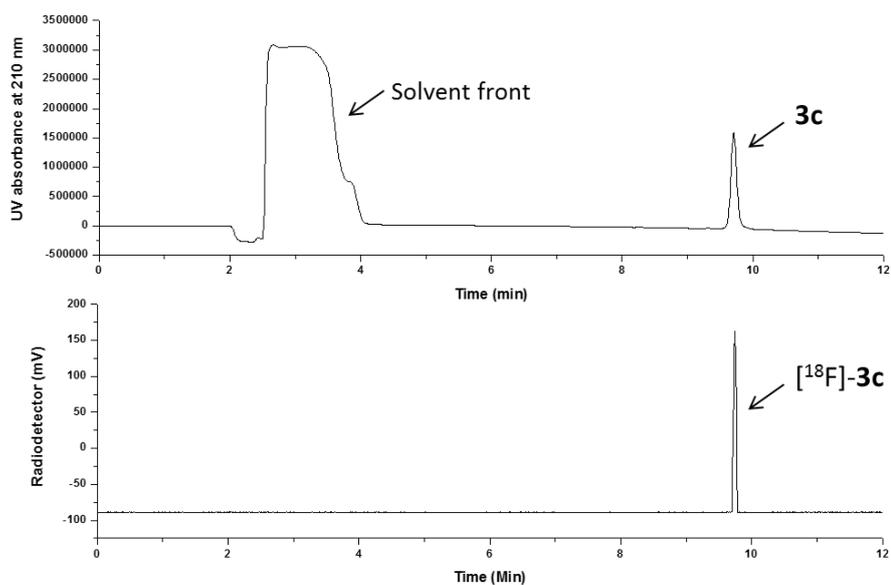


Figure S7. HPLC UV-Chromatogram (above) and radio-chromatogram (below) of the HPLC purified [¹⁸F]-3c solution co-injected with the standard (3c)

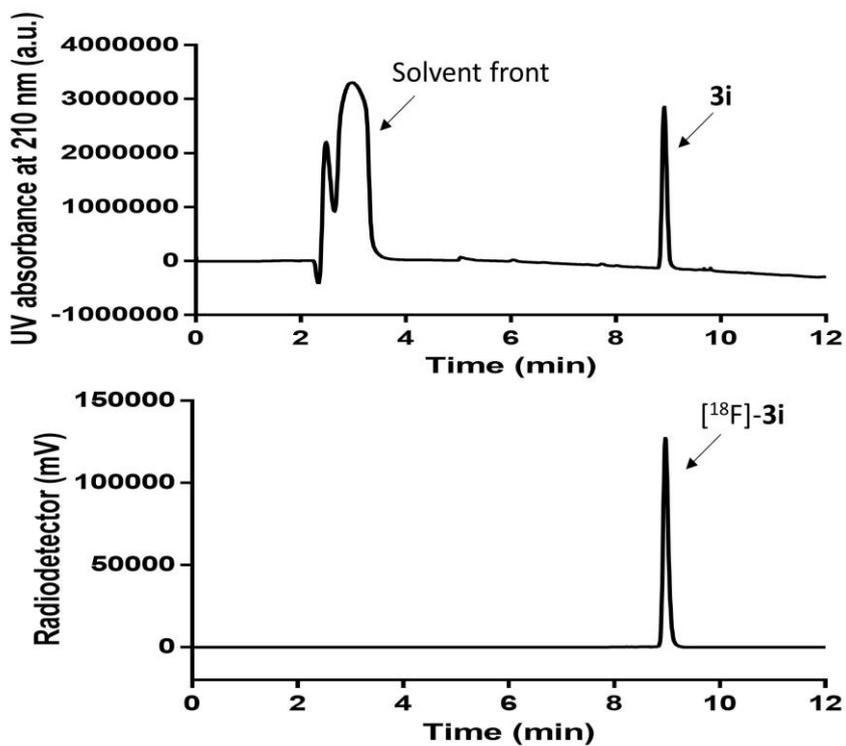


Figure S8. HPLC UV-Chromatogram (above) and radio-chromatogram (below) of the HPLC purified [¹⁸F]-3i solution co-injected with the standard (3i)

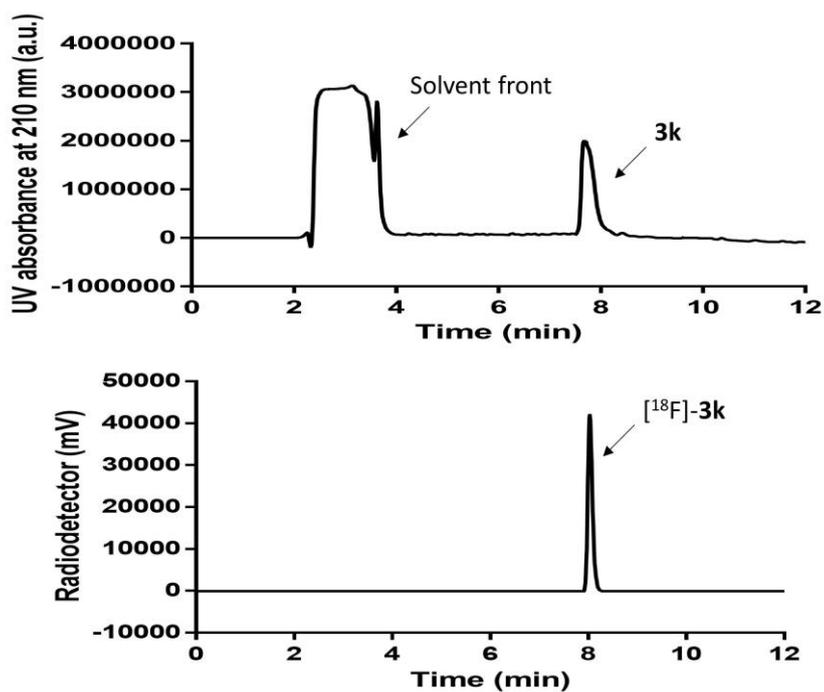


Figure S9. HPLC UV-Chromatogram (above) and radio-chromatogram (below) of the HPLC purified [¹⁸F]-3k solution co-injected with the standard (3k)

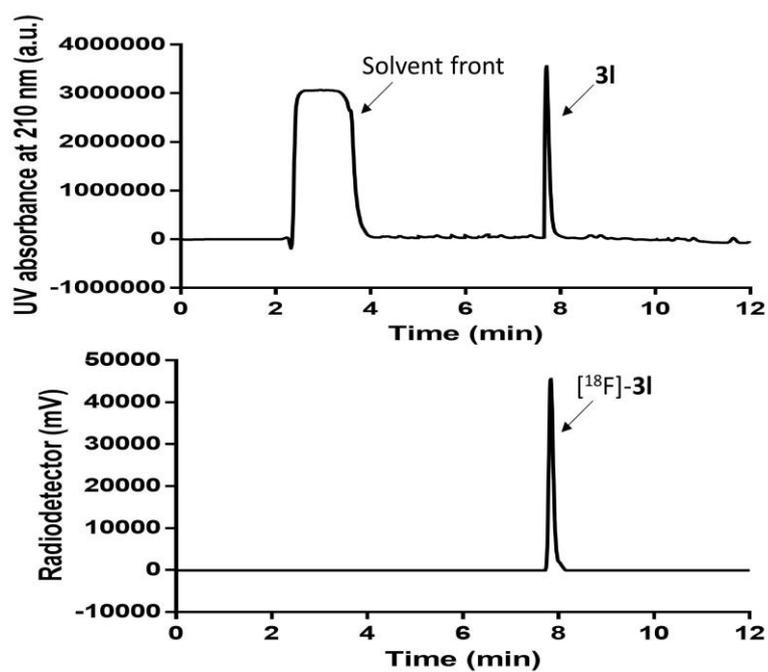


Figure S10. HPLC UV-Chromatogram (above) and radio-chromatogram (below) of the HPLC purified [¹⁸F]-3l solution co-injected with the standard (3l)

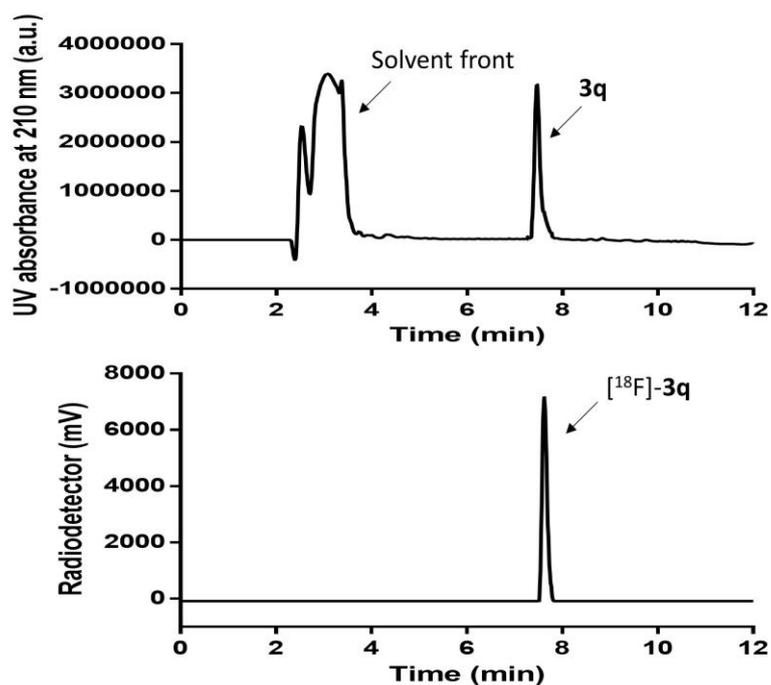


Figure S11. HPLC UV-Chromatogram (above) and radio-chromatogram (below) of the HPLC purified [¹⁸F]-3q solution co-injected with the standard (3q)

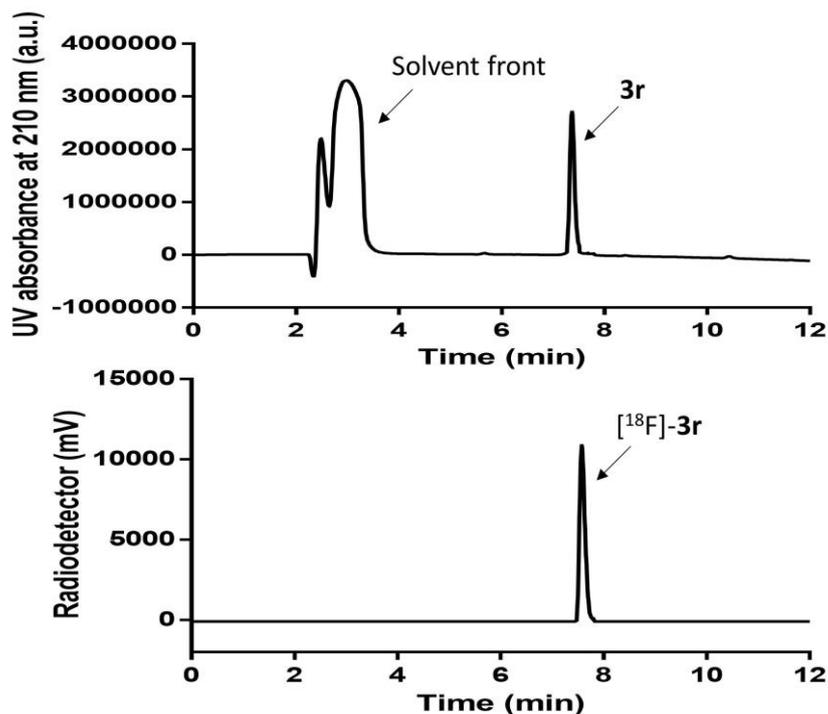


Figure S12. HPLC UV-Chromatogram (above) and radio-chromatogram (below) of the HPLC purified [¹⁸F]-3r solution co-injected with the standard (3r)

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