Supporting Information

Palladium-Catalyzed Intramolecular Asymmetric Hydrocyclopropanylation of Alkynes: Synthesis of Cyclopropane-Fused γ -Lactams

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1. General Information

Reagents, solvents and analytical methods:

Unless otherwise noted, all reactions were carried out under a nitrogen atmosphere. All reagents were from commercial sources and used as received without further purification. All solvents were dried by standard techniques and distilled prior to use. Column chromatography was performed on silica gel (200-300 meshes) using petroleum ether (bp. 60~90 °C) and ethyl acetate as eluent. ¹NMR spectra were recorded on a Bruker Avance operating at for ¹H NMR at 500 MHz, ¹³C NMR at 126 MHz and ¹⁹F NMR at 471 MHz and spectral data were reported in ppm relative to tetramethylsilane (TMS) as internal standard and CDCl₃ (¹H NMR δ 7.27, ¹³C NMR δ 77.0) as solvent. High-resolution mass spectra (HRMS) is produced by Thermo Fisher Scientific. Its main body is composed of two parts: Thermo Scientific's UltiMate 3000 Series liquid system and Thermo Scientific Q-Exactive combined quadrupole Orbitrap mass spectrometer. All coupling constants (*J*) are reported in Hz. The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, dd = double doublet, ddd = double doublet of doublets, t = triplet, dt = double triplet, q = quatriplet, m = multiplet, br = broad. Compounds **1a-1r** were prepared according to the previous literatures.^[1, 2, 3, 4]

2 Preparation of the Compounds 1a-1r

Compounds 1a-1r were prepared according to the previous literature.

$$\begin{array}{ccc} \mathsf{NH}_2 & + & \mathsf{TsCI} & \underbrace{\mathsf{Et}_3\mathsf{N}, \mathsf{DCM},}_{\mathsf{0}\ ^\circ\mathsf{C}\ \mathsf{to}\ \mathsf{rt}} & & \mathsf{N}_{\mathsf{H}}^{\mathsf{Ts}} \end{array}$$

Following a modified version of a reported procedure,^[1] to a solution of acyl chloride (12 mmol, 1.2 equiv.) in dichloromethane (10 mL). Then, triethylamine (1.40 mL, 10.0 mmol, 1.1 equiv.) was added slowly. Then a solution of cyclopropylamine (0.70 mL, 10 mmol, 1.0 equiv.) in dichloromethane (10 mL) was added slowly at 0 °C. The reaction mixture was stirred at room temperature usually for 16 hours. Upon completion, the aqueous layer was then extracted with dichloromethane. The organic extract was dried over Na₂SO₄, filtered and concentrated in vacuo. the residue was purified by a flash column chromatograph on silica gel using petroleum ether / ethyl acetate as the eluent to yield the products **II**.



Following a modified version of a reported procedure,^[2] A small round bottomed flask was charged with aryl iodide (5.0 mmol), DBU (1.67 g, 2.2 equiv., 12 mmol), Pd(PPh₃)₄ (173 mg, 3 mol%) and DMSO (6 mL). The solution of propiolic acid (420 mg, 1.2 equiv., 6.0 mmol) in DMSO (6 mL) was poured to the flask. The mixture was stirred at ambient temperature for 12 h. Upon completion of the reaction, the reaction mixture was diluted with ethyl acetate (20 mL), then extracted with NaHCO₃ (sat. aq). The aqueous layer was separated, acidified to pH 1.0 by adding HCl (1 N), and extracted with ethyl acetate. The combined organic layers were dried with Na₂SO₄, and the solvent was removed under reduced pressure. The resulting crude product was purified by flash chromatography (on silica, ethyl acetate: petroleum ether = 4:1) gave the corresponding aryl alkynyl carboxylic acids **IV**.



Following a modified version of a reported procedure,^[3] dichloromethane (20 mL) and phenylpropynoic acid (11 mmol) were added into a 50 mL round bottom glass flask, and then *N*-alkylaniline (10 mmol) was added at 0 °C. Thereafter, a solution of DCC (15 mmol), DMAP (0.5 mmol) and dichloromethane (20 mL) was slowly added dropwise with stirring. The mixture was washed with 5 mL saturated Na₂CO₃ solution, 5 mL saturated NaCl solution, and 5 mL water. The organic phase was dried over Na₂SO₄, filtered and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate as the eluent) affording the corresponding *N*-cyclopropyl-3-phenyl-*N*-tosylpropiolamide **1a**.

$$\begin{array}{ccc} H_2N & \text{COOH} \\ & \swarrow & & \\ \mathbf{V} & & \\ \mathbf{V} & & \\ \end{array} \xrightarrow{\begin{array}{c} 1) \text{ SOCI}_2, 0 \ ^\circ\text{C},} \\ & \underline{15 \text{ min}} \\ 2) \text{ ref., 2 h} & & \\ \mathbf{VI} \end{array} \xrightarrow{\begin{array}{c} H_2N & \text{COOMe} \\ & \swarrow & \\ \mathbf{VI} \end{array}}$$

Following a modified version of a reported procedure,^[4] Add ethanol (2 mL) to a round-bottom flask. Cool the reaction mixture to 0 °C. Add thionyl chloride (706 mg, 430 μ L) dropwise to the reaction mixture. Stir the reaction mixture for 15 minutes. Add 1-aminocyclopropanecarboxylic acid (300 mg) to the reaction mixture. Reflux the reaction mixture for 2 hours. Remove the solvent and affording the corresponding product VI.



Figure S1 Substrates of N-cyclopropyl-3-phenyl-N-tosylpropiolamide derivatives

3 Optimization of Reaction Conditions

Table S1. Optimization of the Catalyst.

	o N,∽Ts ∆ 1a	Cat., DPPF, Tol., 24 h, N ₂ ,100 °C 2a
Entry	Catalyst	Yield (%) ^[b]
1	PdCl ₂	NR
2	$Pd(acac)_2$	17
3	$Pd(OAc)_2$	52
4	$Pd_2(dba)_3$	23
5	$Pd(PPh_3)_4$	trace
6	Pd/C	NR

[a] Reaction conditions: 1a (0.2 mmol), Catalyst (5 mol%), DPPF (5 mol%), toluene (2 mL), N_2 atmosphere. [b] Isolated yield.

Table S2. Optimization of the Ligand.^[a]

	N Ts	Pd(OAc) ₂ , L., Tol., 24 h, N ₂ ,100 °C 2a
Entry	Ligand	Yield (%) ^[b]
1	PPh ₃	35
2	PCy ₃	90
3	BuPAd ₂	96
4	dppp	95
5	DPEphos	27
6	Xantphos	trace

[a] Reaction conditions: **1a** (0.2 mmol), Pd(OAc)₂ (5 mol%), Ligand (10 mol% for monodentate ligand, 5 mol% for bidentate ligand), toluene (2 mL), N₂ atmosphere. [b] Isolated yield.

Table S3. Optimization of the Solvent.^[a]



Entry	Solvent	Yield (%) ^[b]
1	toluene	96
2	THF	85
3	Dioxane	88
4	DCM	27

5	MeCN	trace	
6	DMSO	36	
7	DMF	44	
[a] Reaction conditions: 1a (0.2 mmol), Pd(OAc) ₂ (5 mol%), Ligand (10 mol%), solvent (2 mL),			
N ₂ atmosphere. [b] Isolated yield.			

Table S4. Optimization of the Ligand.^[a]

	O N Ia	$\begin{array}{c} \underline{Pd(OAc)_2, L_{\cdot, \cdot}} \\ \hline Tol., 24 h, \\ N_2, 100 \ ^{\circ}C \end{array} \qquad $
Entry	Ligand	Yield (%) ^[b]
1	PPh ₃	35
2	PCy ₃	90
3	BuPAd ₂	96
4	dppp	95
5	DPEphos	27
6	Xantphos	trace

[a] Reaction conditions: **1a** (0.2 mmol), Pd(OAc)₂ (5 mol%), Ligand (10 mol% for monodentate ligand, 5 mol% for bidentate ligand), toluene (2 mL), N₂ atmosphere. [b] Isolated yield.

Table S5. Optimization of the ratio of chiral Ligand and Catalyst.^[a]

	0 N Ts Tol., 24 h, N ₂ , 100 °C	$ \begin{array}{c} $	
Entry	Cat. and L.	Yield (%) ^[b]	<i>ee</i> (%) ^[c]
1	2%+4%	56	67
2	2%+5%	NR	-
3	3%+6%	43	69
4	5%+10%	59	67
5	5%+12%	60	65

[a] Reaction conditions: 1a (0.2 mmol), Pd(OAc)₂ (5 mol%), Ligand (10 mol%), toluene (2 mL),
N₂ atmosphere. [b] Isolated yield. [c] Determined by HPLC analysis on a chiral stationary phase.

Table S6. Optimization of the Catalyst.^[a]

	0 N [−] Ts Tol., 24 h, N ₂ , 100 °C	O N 2a	
Entry	Catalyst	Yield (%) ^[b]	<i>ee</i> (%) ^[c]
1	Pd(OAc) ₂	35	67

2	PdCl ₂	NR	-
3	$Pd(acac)_2$	50	67
4	$Pd_2(dba)_3$	23	57
5	$Pd(PPh_3)_4$	NR	-
6	Pd/C	NR	-
7	PdBr ₂	NR	-
8	$Pd(TFA)_2$	NR	-
9	Pd(MeCN) ₂ Cl ₂	NR	-

[a] Reaction conditions: **1a** (0.2 mmol), Pd(OAc)₂ (5 mol%), Ligand (10 mol%), toluene (2 mL), N₂ atmosphere. [b] Isolated yield. [c] Determined by HPLC analysis on a chiral stationary phase.

Table S7. Optimization of Temperature.^[a]

		Pd(OAc) ₂ , L*, Tol., 24 h, N ₂ , T.	O N 2a	
Entry	Temp.		Yield (%) ^[b]	<i>ee</i> (%) ^[c]
1	30		NR	-
2	60		17	60
3	80		35	59
4	100		47	63
5	120		49	68

[a] Reaction conditions: 1a (0.2 mmol), Pd(OAc)₂ (5 mol%), Ligand (10 mol%), toluene (2 mL),
N₂ atmosphere. [b] Isolated yield. [c] Determined by HPLC analysis on a chiral stationary phase.

Table S8. Optimization of the Solvent.^[a]

	0 N ^{-Ts} Sol., 24 h, N ₂ , 100 °C	O N Za	
Entry	Solvent	Yield (%) ^[b]	<i>ee</i> (%) ^[c]
1	toluene	45	63
2	THF	NR	-
3	MeCN	NR	-
4	dioxane	NR	-
5	DCM	NR	-
6	DMF	NR	-
7	DMSO	NR	-
8	o-xylene	NR	-
9	m-Xylene	55	63
10	p-Xylene	33	63

11	Chlorobenzene	35	70
12	Bromobenzene	trace	-
13	fluorobenzene	73	70
14	(trifluoromethyl)benzene	67	66

[a] Reaction conditions: 1a (0.2 mmol), Pd(OAc)₂ (5 mol%), Ligand (10 mol%), Solvent (2 mL), N₂ atmosphere. [b] Isolated yield. [c] Determined by HPLC analysis on a chiral stationary phase.

Table S9. Optimization of additive.

	$\begin{array}{c} & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & $	2a Ts Za	Coppensition of the second sec
Entry	Additive	Yield (%) ^[b]	<i>ee</i> (%) ^[c]
1	(R)-(+)-alpha	45	63
2	L(-)-Proline	55	70
3	N-Boc-L-Tert-Leucine	35	57
4	N-Boc-L-valine	37	60
5	N-Ac-Phe-OH	35	63
6	L-Phenylalanine	NR	-
7	Ag ₂ O	51	67
8	AgOTf	trace	-
9	4Å MS	59	67
10	K ₂ CO ₃	NR	63
11	'BuOK	53	69
12	4-Chlorobenzenesulfonic acid	NR	-
14	PTSA	NR	-
[] D			

[a] Reaction conditions: 1a (0.2 mmol), Pd(OAc)₂ (5 mol%), Ligand (10 mol%), Solvent (2 mL), additive (20 mol%) N₂ atmosphere. [b] Isolated yield. [c] Determined by HPLC analysis on a chiral stationary phase.



Table S10. Optimization of the chiral Ligand.^[a]

Reaction conditions: **1a** (0.2 mmol), Pd(OAc)₂ (5 mol%), Ligand (10 mol% for monodentate ligand, 5 mol% for bidentate ligand), fluorobenzene (2 mL), N₂ atmosphere.



Table S11. Optimization of the chiral Ligand.^[a]

[a] Reaction conditions: 1a (0.2 mmol), Pd(OAc)2 (5 mol%), Ligand (20 mol% for monodentate ligand, 10 mol% for bidentate ligand), Solvent (2 mL), N₂ atmosphere. [b] Isolated yield. [c] Determined by HPLC analysis on a chiral stationary phase.

4 General Procedure



1a (67.8 mg, 0.2 mmol, 1 eq.), $Pd(OAc)_2$ (2.2 mg, 5 mol%), $BuPAd_2$ (71.8 mg, 10 mol%), were transferred into a 15 mL tube. A 2.0 mL vial was placed in the tube and the tube was sealed with a septum. The tube was connected to an nitrogen-vacuum line, evacuated and backfilled with $N_2(x3)$. Then, a solution of toluene (2 mL) was added to the reaction tube. Then, the reaction tube was sealed with a screw-top septum cap quickly and placed in a heating block that was preheated to 100 °C. After a time period of 24 h, the reaction tube was allowed cooled to room temperature. The mixture was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel eluting with petroleum ether / EtOAc to afford the products **2a**.

^aFor preparation of the asymmetric products, chiral ligand L12 (or L7) was used with fluorobenzene as solvent.



5 Experimental Characterization Data for the Starting

Materials

N-cyclopropyl-3-phenyl-*N*-tosylpropiolamide (1a). The compound was prepared according to the general procedure to give a yellow solid.

¹**H NMR (500 MHz, CDCl₃)** δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.53 (dd, *J* = 5.1, 3.3 Hz, 2H), 7.48 – 7.43 (m, 1H), 7.37 (dd, *J* = 10.5, 4.6 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 2.96 – 2.88 (m, 1H), 2.42 (s, 3H), 1.23 – 1.19 (m, 2H), 1.15 – 1.11 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 154.7, 145.0, 136.0, 132.7, 130.9, 129.4, 128.6, 119.6, 93.6, 82.3, 28.6, 21.6, 10.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{18}NO_3S^+$ 340.1002; Found 340.0997.

N-cyclopropyl-3-(p-tolyl)-*N*-tosylpropiolamide (1b). The compound was prepared according to the general procedure to give a yellow solid.

¹**H NMR (500 MHz, CDCl₃)** δ 7.93 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 2.96 – 2.90 (m, 1H), 2.43 (s, 3H), 2.38 (s, 3H), 1.24 – 1.19 (m, 2H), 1.16 – 1.10 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 154.9, 145.1, 141.8, 136.2, 132.9, 129.6, 128.6, 116.6, 94.4, 82.2, 28.7, 21.8, 10.4. HPMS (FSI) m/z; [M+H][±] Calad for C. H. NO S[±] 354 1158; Found 354 1154

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{20}NO_3S^+$ 354.1158; Found 354.1154.

N-cyclopropyl-3-(m-tolyl)-*N*-tosylpropiolamide (1c). The compound was prepared according to the general procedure to give a yellow solid.

¹H NMR (500 MHz, CDCl₃) δ 7.93 (d, J = 8.3 Hz, 2H), 7.35 – 7.33 (m, 4H), 7.32 – 7.27 (m, 2H), 2.95 – 2.91 (m, 1H), 2.44 (s, 3H), 2.35 (s, 3H), 1.25 – 1.21 (m, 2H), 1.16 – 1.12 (m, 2H).
¹³C NMR (126 MHz, CDCl₃) δ 154.9, 145.1, 138.7, 136.2, 133.3, 132.0, 130.0, 129.6, 128.7, 119.5, 94.1, 82.2, 28.7, 21.8, 21.3, 10.5.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₀H₂₀NO₃S⁺ 354.1158; Found 354.1154.



N-cyclopropyl-3-(o-tolyl)-*N*-tosylpropiolamide (1d). The compound was prepared according to the general procedure to give a yellow solid.

¹**H NMR (500 MHz, CDCl₃)** δ 7.94 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.38 – 7.31 (m, 3H), 7.25 (d, *J* = 7.7 Hz, 1H), 7.20 (t, *J* = 7.6 Hz, 1H), 2.98 – 2.92 (m, 1H), 2.47 (s, 3H), 2.44 (s, 3H), 1.25 – 1.19 (m, 2H), 1.16 – 1.10 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 156.0, 145.0, 140.7, 137.3, 136.2, 133.8, 130.5, 130.1, 129.5, 128.6, 116.8, 94.7, 82.1, 28.7, 21.7, 20.1, 19.6, 10.5.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₀H₂₀NO₃S⁺ 354.1158; Found 354.1153.



N-cyclopropyl-3-(4-ethylphenyl)-*N*-tosylpropiolamide (1e). The compound was prepared according to the general procedure to give a yellow solid.

¹**H NMR (500 MHz, CDCl₃)** δ 7.93 (d, *J* = 8.3 Hz, 2H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 2.98 – 2.89 (m, 1H), 2.67 (q, *J* = 7.6 Hz, 2H), 2.42 (s, 3H), 1.27 – 1.19 (m, 5H), 1.16 – 1.08 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 154.8, 147.9, 144.9, 136.1, 132.9, 129.4, 128.6, 128.2, 116.7, 94.3, 82.1, 29.0, 28.6, 21.6, 15., 10.3.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₁H₂₂NO₃S⁺ 368.1315; Found 368.1310.



3-(4-(tert-butyl)phenyl)-*N*-cyclopropyl-*N*-tosylpropiolamide (1h). The compound was prepared according to the general procedure to give a yellow oil.

¹**H NMR (500 MHz, CDCl₃)** δ 7.97 (d, J = 8.3 Hz, 2H), 7.73 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.5 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 6.95 (s, 1H), 4.00 (ddd, J = 7.3, 5.1, 2.4 Hz, 1H), 2.42 (s, 3H), 2.35 (td, J = 7.6, 4.7 Hz, 1H), 1.30 (s, 9H), 1.13 – 1.08 (m, 1H), 0.53 – 0.48 (m, 1H). ¹³**C NMR (126 MHz, CDCl₃)** δ 163.9, 152.9, 145.0, 140.2, 135.2, 130.6, 129.6, 128.8, 128.3, 125.0, 34.8, 33.5, 31.1, 21.6, 17.5, 16.3.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₃H₂₆NO₃S⁺ 396.1628; Found 396.1623.



3-([1,1'-biphenyl]-4-yl)-*N***-cyclopropyl-***N***-tosylpropiolamide (1i)**. The compound was prepared according to the general procedure to give a white solid.

¹**H NMR (500 MHz, CDCl₃)** δ 7.95 (d, *J* = 8.3 Hz, 2H), 7.65 – 7.58 (m, 6H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 2H), 2.95 (ddd, *J* = 10.5, 7.0, 3.7 Hz, 1H), 2.45 (s, 3H), 1.24 (dd, *J* = 10.8, 4.1 Hz, 2H), 1.16 (dd, *J* = 10.1, 7.4 Hz, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 154.7, 145.0, 143.9, 139.8, 136.2, 133.4, 129.6, 129.1, 128.7, 128.4, 127.5, 127.2, 118.4, 93.7, 83.3, 28.6, 21.6, 10.3.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₅H₂₂NO₃S⁺ 416.1315; Found 416.1311.



N-cyclopropyl-3-(4-fluorophenyl)-*N*-tosylpropiolamide (1f). The compound was prepared according to the general procedure to give a white solid.

¹**H NMR (500 MHz, CDCl₃)** δ 8.12 – 8.04 (m, 2H), 7.59 – 7.51 (m, 2H), 7.47 (dd, *J* = 10.7, 4.3 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 8.6 Hz, 2H), 3.00 – 2.88 (m, 1H), 1.29 – 1.21 (m, 5H), 1.18 – 1.12 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 165.1, 163.1, 154.7, 145.2, 136.0, 135.2, 129.6, 128.6, 116.4, 116.3, 92.7, 82.3, 28.7, 21.7, 10.7.

¹⁹F NMR (471 MHz, CDCl₃) δ -105.60 (s).

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₉H₁₇FNO₂S⁺ 358.0908; Found 358.0902.



3-(4-chlorophenyl)-*N*-cyclopropyl-*N*-tosylpropiolamide (1g). The compound was prepared according to the general procedure to give a yellow solid.

¹**H NMR (500 MHz, CDCl₃)** δ 7.92 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 2.94 – 2.86 (m, 1H), 2.44 (s, 3H), 1.24 – 1.18 (m, 2H), 1.15 – 1.10 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 154.6, 145.3, 137.5, 136.1, 134.1, 129.7, 129.3, 128.7, 118.6, 92.4, 83.2, 28.7, 21.8, 10.4.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₉H₁₇ClNO₃S⁺ 374.0612; Found 374.0606.



N-cyclopropyl-3-(3,4-difluorophenyl)-*N*-tosylpropiolamide (1j). The compound was prepared according to the general procedure to give a brown solid.

¹**H NMR (500 MHz, CDCl₃)** δ 7.95 (d, *J* = 8.3 Hz, 2H), 7.65 – 7.58 (m, 6H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 2H), 2.95 (ddd, *J* = 10.5, 7.0, 3.7 Hz, 1H), 2.45 (s, 3H), 1.24 (dd, *J* = 10.8, 4.1 Hz, 2H), 1.16 (dd, *J* = 10.1, 7.4 Hz, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 154., 153.2, 151.1, 149.1, 145.3, 135.9, 129.9, 129.6, 128.5, 121.7, 118.2, 116.5, 91.0, 82.5, 28.6, 21.7, 10.3.

¹⁹F NMR (471 MHz, CDCl3) δ -130.69 (s), -135.47 (s).

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₉H₁₆NO₃S⁺ 376.0813; Found 376.0811.



N-cyclopropyl-3-phenyl-*N*-(phenylsulfonyl)propiolamide (11). The compound was prepared according to the general procedure to give a white solid.

¹**H NMR (500 MHz, CDCl₃)** δ 8.05 (d, *J* = 7.7 Hz, 2H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.53 (s, 4H), 7.46 (t, *J* = 7.3 Hz, 1H), 7.37 (t, *J* = 7.3 Hz, 2H), 2.95 (s, 1H), 1.23 (d, *J* = 6.0 Hz, 2H), 1.14 (s, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 154.8, 139.1, 134.0, 132.9, 131.1, 129.0, 128.8, 128.6, 119.7, 94.0, 82.4, 28.8, 10.5.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₈H₁₆NO₃S⁺ 326.0845; Found 326.0842.



N-cyclopropyl-*N*-((4-fluorophenyl)sulfonyl)-3-phenylpropiolamide (1m). The compound was prepared according to the general procedure to give a white solid.

¹**H NMR (500 MHz, CDCl₃)** δ 8.12 – 8.06 (m, 2H), 7.57 – 7.52 (m, 2H), 7.48 (dd, *J* = 10.7, 4.3 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.24 – 7.18 (m, 2H), 2.99 – 2.93 (m, 1H), 1.24 (d, *J* = 6.3 Hz, 2H), 1.19 – 1.13 (m, 2H), 0.86 (ddd, *J* = 18.7, 11.5, 6.7 Hz, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 167.0, 164.9, 154.8, 135.0, 132.9, 131.8, 131.2, 128.9, 119.6, 116.4, 116.2, 94.2, 82.3, 28.8, 10.6.

¹⁹F NMR (471 MHz, CDCl3) δ -102.75 (s).

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₈H₁₅FNO₂S⁺ 344.0751; Found 344.0746.



N-cyclopropyl-*N*-((4-nitrophenyl)sulfonyl)-3-phenylpropiolamide (1n). The compound was prepared according to the general procedure to give a white solid.

¹**H NMR (500 MHz, CDCl₃)** δ 8.43 – 8.35 (m, 2H), 8.28 – 8.22 (m, 2H), 7.58 – 7.53 (m, 2H), 7.52 – 7.47 (m, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 3.05 – 2.98 (m, 1H), 1.32 – 1.28 (m, 2H), 1.22 – 1.16 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 154.7, 150.6, 144.4, 132.9, 131.3, 130.1, 128.8, 124.0, 119.1, 95.0, 81.8, 28.8, 10.6.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₈H1₅N₂O₅S⁺ 371.0696; Found 371.0691.



N-cyclopropyl-*N*-(3-phenylpropioloyl)benzamide (10). The compound was prepared according to the general procedure to give a yellow oil.

¹**H NMR (500 MHz, CDCl₃)** δ 7.90 – 7.65 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.42 – 7.37 (m, 1H), 7.36 – 7.27 (m, 4H), 3.16 – 2.90 (m, 1H), 1.08 (q, *J* = 6.8 Hz, 2H), 0.83 – 0.72 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 173.9, 155.5, 135.3, 133.1, 132.7, 130.6, 129.20, 128.5, 119.7, 93.8, 82.6, 28.6, 9.4.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₉H₁₆NO₂⁺ 290.1176; Found 290.1171.

N-cyclopropyl-*N*-methyl-3-phenylpropiolamide (1k). The compound was prepared according to the general procedure to give a white solid.

¹**H NMR (500 MHz, CDCl₃)** δ 7.55 – 7.50 (m, 2H), 7.39 – 7.32 (m, 3H), 2.96 (s, 3H), 2.84 (ddd, *J* = 10.7, 7.0, 4.0 Hz, 1H), 0.96 – 0.90 (m, 2H), 0.90 – 0.86 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 132.2, 132.2, 129.8, 128.4, 120.8, 90.5, 82.9, 33.7, 31.7, 8.7. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₃H₁₄NO⁺ 200.1070; Found 200.1068.



methyl 1-(3-phenyl-*N***-tosylpropiolamido)cyclopropane-1-carboxylate (1p)**. The compound was prepared according to the general procedure to give a white solid.

¹**H NMR (500 MHz, CDCl₃)** δ 8.03 (d, *J* = 8.1 Hz, 2H), 7.47 – 7.39 (m, 3H), 7.38 – 7.28 (m, 4H), 3.81 – 3.71 (m, 3H), 2.46 – 2.33 (m, 3H), 2.12 (ddd, *J* = 7.1, 4.1, 2.4 Hz, 1H), 2.05 – 1.91 (m, 2H), 1.65 – 1.54 (m, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 171.7, 154.0, 145.3, 135.2, 132.8, 131.1, 129.9, 129.2, 128.7, 119.2, 93.5, 81.7, 53.0, 39.6, 22.9, 21.7, 21.3.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₃H₂₅N₂O₂⁺ 361.1911; Found 361.1907.

ethyl 1-(3-phenyl-*N***-tosylpropiolamido)cyclopropane-1-carboxylate (1q)**. The compound was prepared according to the general procedure to give a yellow solid.

¹**H NMR (500 MHz, CDCl₃)** δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.42 – 7.33 (m, 3H), 7.27 (dd, *J* = 19.5, 7.9 Hz, 4H), 4.26 – 4.10 (m, 2H), 2.35 (s, 3H), 2.11 – 2.03 (m, 1H), 2.00 – 1.85 (m, 2H), 1.58 – 1.45 (m, 1H), 1.16 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 171.0, 154.0, 145.2 (s), 135.3 (s), 132.6, 131.1, 129.7, 129.0, 128.7, 119.0, 93.2, 81.7, 62.0, 39.6, 22.8, 21.5, 20.9, 14.1.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₁H₂₀NO₅S⁺ 398.1057; Found 398.1055.

isopropyl 1-(3-phenyl-*N***-tosylpropiolamido)cyclopropane-1-carboxylate (1r)**. The compound was prepared according to the general procedure to give a yellow solid.

¹H NMR (500 MHz, CDCl₃) δ 8.05 (d, J = 8.4 Hz, 2H), 7.48 – 7.42 (m, 3H), 7.39 – 7.29 (m, 4H), 5.10 (hept, J = 6.3 Hz, 1H), 2.43 (s, 3H), 2.15 – 2.08 (m, 1H), 2.01 – 1.92 (m, 2H), 1.60 – 1.54 (m, 1H), 1.29 (d, J = 6.3 Hz, 3H), 1.19 (d, J = 6.3 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 168.0, 164.7, 145.2, 141.6, 135.6, 133.1, 131.0, 130.1, 129.5, 129.2, 128.2, 127.7, 70.3, 44.4, 28.4, 24.1, 21.9, 21.8, 21.8, 1.1.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₃H₂₄NO₅S⁺ 426.1370; Found 426.1364.

methyl 1-(3-(p-tolyl)-N-tosylpropiolamido)cyclopropane-1-carboxylate (1s). The compound was prepared according to the general procedure to give a foam yellow solid.

¹**H NMR (500 MHz, CDCl₃)** δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.33 (dd, *J* = 8.0, 5.1 Hz, 4H), 7.16 (d, *J* = 7.9 Hz, 2H), 3.76 (s, 3H), 2.43 (s, 3H), 2.37 (s, 3H), 2.16 – 2.09 (m, 1H), 1.98 (ddt, *J* = 13.3, 8.6, 4.5 Hz, 2H), 1.64 – 1.57 (m, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 171.8, 154.2, 145.3, 142.0, 135.3, 132.8, 129.9, 129.5, 129.0, 116.1, 94.2, 81.6, 53.0, 39.6, 22.9, 21.7, 21.7, 21.3.

CI

methyl 1-(3-(4-chlorophenyl)-N-tosylpropiolamido)cyclopropane-1-carboxylate (1t). The compound was prepared according to the general procedure to give a foam yellow solid. ¹H NMR (500 MHz, CDCl₃) δ 8.02 (d, *J* = 8.4 Hz, 2H), 7.39 – 7.30 (m, 6H), 3.76 (s, 3H), 2.43 (s, 3H), 2.16 – 2.09 (m, 1H), 2.02 – 1.93 (m, 2H), 1.59 (dt, *J* = 8.2, 6.1 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 171.6, 153.8, 145.3, 137.5, 135.1, 133.9, 129.9, 129.2, 129.0, 117.6, 92.1, 82.4, 52.9, 39.5, 22.7, 21.6, 21.2.



Methyl 1-(N-((4-fluorophenyl)sulfonyl)-3-phenylpropiolamido)cyclopropane-1-carboxylate (1u). The compound was prepared according to the general procedure to give a foam yellow solid. ¹H NMR (500 MHz, CDCl₃) δ 8.25 – 8.14 (m, 2H), 7.49 – 7.43 (m, 3H), 7.37 (dd, *J* = 10.5, 4.8 Hz, 2H), 7.21 (t, *J* = 8.6 Hz, 2H), 3.77 (s, 3H), 2.15 (ddd, *J* = 9.4, 5.4, 2.2 Hz, 1H), 2.01 (tdd, *J* = 13.8, 8.6, 5.0 Hz, 2H), 1.68 – 1.61 (m, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 171.6, 154.0, 133.16, 133.1, 132.8, 131.2, 128.7, 119.0, 115.7, 115.5, 93.9, 81.5, 53.0, 39.6, 22.7, 21.3.

¹⁹F NMR (471 MHz, CDCl₃) δ -102.48.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₀H_{16F}NO₅S⁺402.0806; Found 402.0816.



(Z)-4-benzylidene-2-tosyl-2-azabicyclo[3.1.0]hexan-3-one (2a). The compound was prepared according to the general procedure to give a yellow solid.

¹**H NMR (500 MHz, CDCl₃)** δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.76 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.32 (dd, *J* = 7.5, 5.2 Hz, 5H), 6.96 (s, 1H), 4.00 (ddd, *J* = 7.2, 5.1, 2.4 Hz, 1H), 2.41 (s, 3H), 2.35 (td, *J* = 7.8, 4.8 Hz, 1H), 1.15 – 1.08 (m, 1H), 0.55 – 0.49 (m, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 163.9, 145.3, 140.3, 135.3, 133.4, 130.8, 129.8, 128.4, 128.2, 33.7, 21.8, 17.7, 16.4.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₉H₁₈NO₂S⁺ 340.1002; Found 340.0997.

 $[\alpha]_{D}^{20}$ -20 (*c* 1.0, CHCl₃, 85% ee sample).

(*Z*)-4-(4-methylbenzylidene)-2-tosyl-2-azabicyclo[3.1.0]hexan-3-one (2b). The compound was prepared according to the general procedure to give a yellow solid.

¹**H NMR (500 MHz, CDCl₃)** δ 7.96 (d, J = 8.3 Hz, 2H), 7.68 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 6.92 (s, 1H), 3.98 (ddd, J = 7.3, 5.0, 2.5 Hz, 1H), 2.41 (s, 3H), 2.37 – 2.26 (m, 4H), 1.09 (ddd, J = 8.5, 6.1, 5.3 Hz, 1H), 0.54 – 0.43 (m, 1H). ¹³**C NMR (126 MHz, CDCl₃)** δ 164.1, 145.2, 140.5, 140.1, 135.4, 130.9, 129.7, 128.9, 128.4, 33.6, 21.8, 21.6, 17.5, 16.5.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₀H₂₀NO₃S⁺ 354.1158; Found 354.1156.

 $[\alpha]_{D}^{20}$ -270 (*c* 1.0, CHCl₃, 80% ee sample).

O N N

(*Z*)-4-(3-methylbenzylidene)-2-tosyl-2-azabicyclo[3.1.0]hexan-3-one (2c). The compound was prepared according to the general procedure to give a yellow solid.

¹**H NMR (500 MHz, CDCl₃)** δ 7.97 (d, J = 8.3 Hz, 2H), 7.63 (d, J = 7.7 Hz, 1H), 7.51 (s, 1H), 7.32 (d, J = 8.1 Hz, 2H), 7.23 (t, J = 7.7 Hz, 1H), 7.13 (d, J = 7.6 Hz, 1H), 6.94 (s, 1H), 4.00 (ddd, J = 7.2, 5.0, 2.5 Hz, 1H), 2.42 (s, 3H), 2.38 – 2.32 (m, 4H), 1.11 (ddd, J = 8.5, 6.1, 5.3 Hz, 1H), 0.54 – 0.49 (m, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 163.8, 145.2, 140.5, 137.8, 135.4, 133.4, 131.4, 130.5, 129.7, 128.4, 128.1, 127.9, 33.7, 21.8, 21.5, 17.7, 16.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{20}NO_3S^+$ 354.1158; Found 354.1154.

 $[\alpha]_{D}^{20}$ -150 (*c* 1.0, CHCl₃, 79% ee sample).

(*Z*)-4-(2-methylbenzylidene)-2-tosyl-2-azabicyclo[3.1.0]hexan-3-one (2d). The compound was prepared according to the general procedure to give a yellow solid.

¹**H NMR (500 MHz, CDCl₃)** δ 7.94 (d, *J* = 8.3 Hz, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 8.1 Hz, 1H), 7.21 (t, *J* = 7.3 Hz, 1H), 7.14 (d, *J* = 7.4 Hz, 2H), 2.42 (s, 1H), 2.38 (td, *J* = 7.8, 4.9 Hz, 1H), 2.26 (s, 2H), 1.18 – 1.11 (m, 1H), 0.93 – 0.86 (m, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 163.8, 145.3, 140.5, 137.8, 135.4, 133.4, 131.4, 130.5, 129.7, 128.4, 128.1, 127.9, 33.7, 21.8, 21.5, 17.7, 16.5.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₀H₂₀NO₃S⁺ 354.1158; Found 354.1155.



(*Z*)-4-(4-ethylbenzylidene)-2-tosyl-2-azabicyclo[3.1.0]hexan-3-one (2e). The compound was prepared according to the general procedure to give a yellow solid.

¹**H NMR (500 MHz, CDCl₃)** δ 7.97 (d, *J* = 8.2 Hz, 2H), 7.71 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 6.94 (s, 1H), 4.04 – 3.96 (m, 1H), 2.64 (q, *J* = 7.6 Hz, 2H), 2.42 (s, 3H), 2.38 – 2.29 (m, 1H), 1.22 (t, *J* = 7.6 Hz, 3H), 1.10 (dt, *J* = 8.5, 5.7 Hz, 1H), 0.56 – 0.48 (m, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 163.9, 146.2, 145.0, 140.4, 135.3, 130.9, 129.6, 128.7, 128.3, 127.6, 33.5, 28.8, 21.7, 17.5, 16.4, 15.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{22}NO_3S^+$ 368.1315; Found 368.1311.

 $[\alpha]_{D}^{20}$ -10 (*c* 1.0, CHCl₃, 71% ee sample).

(*Z*)-4-(4-(tert-butyl)benzylidene)-2-tosyl-2-azabicyclo[3.1.0]hexan-3-one (2h). The compound was prepared according to the general procedure to give a yellow solid.

¹**H NMR (500 MHz, CDCl₃)** δ 7.89 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.38 (d, *J* = 7.4 Hz, 2H), 7.34 (m, 1H), 7.28 (dd, *J* = 10.5, 4.8 Hz, 2H), 7.24 – 7.17 (m, 2H), 6.99 (m, 1H), 1.60 (dd, *J* = 8.9, 6.8 Hz, 2H), 1.10 (dd, *J* = 8.9, 6.8 Hz, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 164.1, 153.1, 145.2, 140.3, 135.4, 130.8, 129.8, 129.0, 128.4, 125.2, 34.9, 33.6, 31.2, 21.8, 17.6, 16.5.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₃H₂₆NO₃S⁺ 396.1628; Found 396.1625.



(*Z*)-4-([1,1'-biphenyl]-4-ylmethylene)-2-tosyl-2-azabicyclo[3.1.0]hexan-3-one (2i). The compound was prepared according to the general procedure to give a yellow solid.

¹**H NMR (500 MHz, CDCl₃)** δ 7.99 (d, J = 8.3 Hz, 2H), 7.87 (d, J = 8.3 Hz, 2H), 7.64 – 7.53 (m, 4H), 7.45 (t, J = 7.6 Hz, 2H), 7.37 (d, J = 7.3 Hz, 1H), 7.34 (t, J = 7.1 Hz, 2H), 7.00 (s, 1H), 4.03 (ddd, J = 7.2, 5.1, 2.4 Hz, 1H), 2.43 (s, 3H), 2.38 (td, J = 7.7, 4.9 Hz, 1H), 1.17 – 1.10 (m, 1H), 0.60 – 0.50 (m, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 164.0, 145.3, 142.3, 140.5, 139.9, 135.3, 132.5, 131.4, 129.8, 128.9, 128.4, 127.8, 127.2, 126.8, 33.8, 21.8, 17.8, 16.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{22}NO_3S^+$ 416.1315; Found 416.1310.

F O N

(Z)-4-(4-fluorobenzylidene)-2-tosyl-2-azabicyclo[3.1.0]hexan-3-one (2f). The compound was prepared according to the general procedure to give a yellow solid.

¹**H NMR (500 MHz, CDCl₃)** δ 7.96 (d, *J* = 7.6 Hz, 2H), 7.83 – 7.74 (m, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 6.99 (t, *J* = 8.1 Hz, 2H), 6.91 (s, 1H), 4.00 (s, 1H), 2.42 (s, 3H), 2.38 – 2.31 (m, 1H), 1.12 (dd, *J* = 12.5, 6.4 Hz, 1H), 0.52 (s, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 163.8, 145.2, 138.8, 135.0, 132.9, 132.9, 129.6, 129.4, 128.2, 115.1, 114.9, 33.6, 21.6, 17.5, 16.2.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₉H₁₇FNO₂S⁺ 358.0908; Found 358.0901.

 $[\alpha]_{D}^{20}$ -340 (*c* 1.0, CHCl₃, 84% ee sample).

(*Z*)-4-(4-chlorobenzylidene)-2-tosyl-2-azabicyclo[3.1.0]hexan-3-one (2g). The compound was prepared according to the general procedure to give a yellow solid.

¹**H NMR (500 MHz, CDCl₃)** δ 7.97 (d, *J* = 8.3 Hz, 2H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.6 Hz, 2H), 6.91 (s, 1H), 4.03 (ddd, *J* = 7.2, 5.0, 2.4 Hz, 1H), 2.44 (s, 3H), 2.36 (td, *J* = 7.7, 4.9 Hz, 1H), 1.19 – 1.12 (m, 1H), 0.56 (ddd, *J* = 6.7, 4.6, 2.5 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 163.9, 145.4, 138.7, 135.4, 135.2, 132.2, 131.9, 130.6, 129.8, 128.4, 33.9, 21.8, 17.9, 16.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{17}CINO_3S^+ 374.0612$; Found 374.0606.

 $[\alpha]_{D}^{20}$ -70 (*c* 1.0, CHCl₃, 85% ee sample).

F O N F

(*Z*)-4-(3,4-difluorobenzylidene)-2-tosyl-2-azabicyclo[3.1.0]hexan-3-one (2j). The compound was prepared according to the general procedure to give a yellow solid.

¹**H NMR (500 MHz, CDCl₃)** δ 7.95 (d, J = 8.3 Hz, 2H), 7.65 – 7.58 (m, 6H), 7.47 (t, J = 7.6 Hz, 2H), 7.40 (t, J = 7.3 Hz, 1H), 7.34 (d, J = 8.2 Hz, 2H), 2.95 (ddd, J = 10.5, 7.0, 3.7 Hz, 1H), 2.45 (s, 3H), 1.24 (dd, J = 10.8, 4.1 Hz, 2H), 1.16 (dd, J = 10.1, 7.4 Hz, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 163.8 (s), 151.9, 150.7, 149.9, 148.8, 145.5, 137.7, 135.1, 131.1, 130.5, 129.9, 128.4, 127.8, 119.7, 116.9, 34.0, 21.8, 18.0, 16.5.

¹⁹F NMR (471 MHz, CDCl₃) δ -255.60 (s), -258.05 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{16}NO_3S^+$ 376.0813; Found 376.0810.

 $[\alpha]_{D}^{20}$ -340 (*c* 1.0, CHCl₃, 85% ee sample).

(*Z*)-4-benzylidene-2-(phenylsulfonyl)-2-azabicyclo[3.1.0]hexan-3-one (2l). The compound was prepared according to the general procedure to give a yellow solid.

¹**H** NMR (500 MHz, CDCl₃) δ 8.10 – 8.06 (m, 2H), 7.75 (dd, J = 7.5, 1.6 Hz, 2H), 7.62 (d, J = 7.5 Hz, 1H), 7.52 (t, J = 7.8 Hz, 2H), 7.32 (d, J = 7.1 Hz, 3H), 6.97 (s, 1H), 4.01 (ddd, J = 7.3, 5.0, 2.5 Hz, 1H), 2.36 (td, J = 7.7, 4.9 Hz, 1H), 1.12 (ddd, J = 8.5, 6.1, 5.2 Hz, 1H), 0.55 – 0.46 (m, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 163.8, 140.6, 133.2, 131.2, 131.2, 130.6, 129.6, 129.4, 128.1, 116.4, 116.3, 33.5, 17.6, 16.3.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₈H₁₆NO₃S⁺ 326.0845; Found 326.0841.

 $[\alpha]_{D}^{20}$ -230 (*c* 1.0, CHCl₃, 83% ee sample).

(*Z*)-4-benzylidene-2-((4-fluorophenyl)sulfonyl)-2-azabicyclo[3.1.0]hexan-3-one (2m). The compound was prepared according to the general procedure to give a yellow solid.

¹**H NMR (500 MHz, CDCl₃)** δ 8.14 – 8.09 (m, 2H), 7.75 (dd, *J* = 7.5, 2.0 Hz, 2H), 7.36 – 7.32 (m, 3H), 7.20 (t, *J* = 8.5 Hz, 2H), 7.00 (s, 1H), 4.01 (ddd, *J* = 7.2, 5.0, 2.4 Hz, 1H), 2.39 (td, *J* = 7.7, 4.7 Hz, 1H), 1.17 – 1.11 (m, 1H), 0.57 – 0.49 (m, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 163.7, 140.3, 138.7, 134.0, 133.2, 130.6, 129.6, 129.5, 129.0, 128.2, 128.0, 33.6, 17.6, 16.3.

¹⁹F NMR (471 MHz, CDCl₃) δ -102.66 (s).

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₈H₁₅FNO₂S⁺ 344.0751; Found 344.0748.

 $[\alpha]_{D}^{20}$ -30 (*c* 1.0, CHCl₃, 80% ee sample).

$$\overset{\mathsf{Ph}}{\underset{\mathsf{V}}{\overset{\mathsf{O}}}} \overset{\mathsf{O}}{\underset{\mathsf{O}}{\overset{\mathsf{V}}{\overset{\mathsf{V}}}}} \overset{\mathsf{O}}{\underset{\mathsf{O}}{\overset{\mathsf{NO}_2}}} \overset{\mathsf{NO}_2}{\overset{\mathsf{O}}{\overset{\mathsf{O}}{\overset{\mathsf{O}}}}}$$

(Z)-4-benzylidene-2-((4-nitrophenyl)sulfonyl)-2-azabicyclo[3.1.0]hexan-3-one (2n). The compound was prepared according to the general procedure to give a yellow solid.

¹**H NMR (500 MHz, CDCl₃)** δ 8.35 (dd, *J* = 8.8, 1.5 Hz, 2H), 8.30 – 8.25 (m, 2H), 7.75 – 7.67 (m, 2H), 7.34 (dd, *J* = 4.3, 1.5 Hz, 3H), 7.04 (s, 1H), 4.05 (ddd, *J* = 7.3, 5.1, 2.5 Hz, 1H), 2.46 – 2.40 (m, 1H), 1.20 (ddd, *J* = 8.6, 6.4, 5.1 Hz, 1H), 0.60 – 0.56 (m, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 163.8, 150.8, 143.4, 141.5, 133.0, 130.6, 129.8, 129.8, 129.7, 129.6, 128.9, 128.7, 128.1, 124.2, 124.2, 33.6, 17.6, 16.5, 1.0.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₈H1₅N₂O₅S⁺ 371.0696; Found 371.0692.

 $[\alpha]_{D}^{20}$ -50 (*c* 1.0, CHCl₃, 76% ee sample).

(*Z*)-2-benzoyl-4-benzylidene-2-azabicyclo[3.1.0]hexan-3-one (20). The compound was prepared according to the general procedure to give a yellow oil.

¹**H NMR (500 MHz, CDCl₃)** δ 8.11 – 8.06 (m, 1H), 7.76 (dd, J = 7.5, 1.6 Hz, 1H), 7.63 (t, J = 7.5 Hz, 1H), 7.53 (t, J = 7.8 Hz, 1H), 7.33 (d, J = 7.1 Hz, 1H), 6.98 (s, 1H), 4.02 (ddd, J = 7.3, 5.0, 2.5 Hz, 1H), 2.37 (td, J = 7.7, 4.9 Hz, 1H), 1.13 (ddd, J = 8.5, 6.1, 5.2 Hz, 1H), 0.55 – 0.48 (m, 1H). ¹³**C NMR (126 MHz, CDCl₃)** δ 166.9, 165.3, 143.6, 135.5, 132.0, 129.4, 128.9, 128.8, 128.8, 128.6, 128.0, 126.9, 24.7, 8.4, 1.0.

Ph O N

(Z)-4-benzylidene-2-methyl-2-azabicyclo[3.1.0]hexan-3-one (2k). The compound was prepared according to the general procedure to give a yellow solid.

¹**H NMR (500 MHz, CDCl₃)** δ 7.89 (d, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.29 (d, *J* = 7.1 Hz, 1H), 6.91 (s, 1H), 3.26 (ddd, *J* = 6.8, 4.8, 2.3 Hz, 1H), 2.97 (s, 3H), 2.27 (td, *J* = 7.4, 4.7 Hz, 1H), 1.03 (dt, *J* = 8.4, 5.1 Hz, 1H), 0.69 (td, *J* = 5.5, 2.3 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 166.1, 135.0, 134.6, 133.0, 130.5, 128.3, 127.9, 36.1, 30.0, 19.4, 16.7.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₃H₁₄NO⁺ 200.1070; Found 200.1068.

methyl (*Z*)-4-benzylidene-3-oxo-2-tosyl-2-azabicyclo[3.1.0]hexane-1-carboxylate (2p). The compound was prepared according to the general procedure to give a yellow solid.

¹**H NMR (500 MHz, CDCl₃)** δ 8.09 (d, *J* = 8.4 Hz, 2H), 7.77 (dd, *J* = 6.8, 2.8 Hz, 2H), 7.35 – 7.30 (m, 5H), 7.01 (s, 1H), 3.85 (s, 3H), 2.73 – 2.66 (m, 1H), 2.41 (s, 3H), 2.26 (dd, *J* = 8.9, 6.0 Hz, 1H), 1.48 (t, *J* = 5.8 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 168.8, 164.4, 145.2, 141.7, 135.3, 132.8, 130.8), 129.9, 129.3, 129.0, 128.0, 127.2, 52.8, 43.9, 28.3, 24.1, 21.6.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₁H₂₀NO₅S⁺ 398.1053; Found 398.1057.

 $[\alpha]_{D}^{20}$ 110 (*c* 1.0, CHCl₃, 91% ee sample).

ethyl (*Z*)-4-benzylidene-3-oxo-2-tosyl-2-azabicyclo[3.1.0]hexane-1-carboxylate (2q). The compound was prepared according to the general procedure at 120 °C to give a yellow solid. ¹H NMR (500 MHz, CDCl₃) δ 8.10 (d, *J* = 8.3 Hz, 2H), 7.77 (dd, *J* = 6.5, 2.9 Hz, 2H), 7.37 – 7.30 (m, 5H), 7.02 (s, 1H), 4.39 – 4.26 (m, 2H), 2.69 (dd, *J* = 8.8, 5.6 Hz, 1H), 2.43 (s, 3H), 2.27

(dd, *J* = 8.9, 6.0 Hz, 1H), 1.48 (t, *J* = 5.8 Hz, 1H), 1.35 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 168.4, 164.5, 145.1, 141.6, 135.4, 132.9, 130.87, 130.0 (s), 129.4, 129.1, 128.1, 127.4, 62.2, 44.1, 28.4, 24.1, 21.7, 14.1, 1.0.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₂H₂₂NO₅S⁺ 412.1213; Found 412.1209.

isopropyl (*Z*)-4-benzylidene-3-oxo-2-tosyl-2-azabicyclo[3.1.0]hexane-1-carboxylate (2r). The compound was prepared according to the general procedure at 120 °C to give a yellow solid. ¹H NMR (500 MHz, CDCl₃) δ 8.11 (d, *J* = 8.2 Hz, 2H), 7.78 (dd, *J* = 6.4, 2.7 Hz, 2H), 7.37 – 7.30 (m, 5H), 7.01 (s, 1H), 5.17 (dt, *J* = 12.5, 6.2 Hz, 1H), 2.67 (dd, *J* = 8.8, 5.6 Hz, 1H), 2.43 (s, 3H), 2.26 (s, 1H), 1.46 (t, *J* = 5.7 Hz, 1H), 1.34 (t, *J* = 6.4 Hz, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 168.0, 164.7, 145.2, 141.6, 135.6, 133.1), 131.0, 130.0, 129.5, 129.2, 128.2, 127.7, 70.2, 44.4, 28.4, 24.2, 21.9, 21.8, 21.8, 1.1. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₃H₂₄NO₅S⁺ 426.1370; Found 426.1366.



methyl (Z)-4-(4-methylbenzylidene)-3-oxo-2-tosyl-2-azabicyclo[3.1.0]hexane-1-carboxylate (2s). The compound was prepared according to the general procedure to give a yellow solid. ¹H NMR (500 MHz, CDCl₃) δ 8.08 (d, J = 8.3 Hz, 2H), 7.69 (d, J = 8.1 Hz, 2H), 7.32 (t, J = 12.6 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 6.97 (s, 1H), 3.84 (s, 3H), 2.68 (dd, J = 8.7, 5.7 Hz, 1H), 2.43 (s, 3H), 2.36 (d, J = 22.4 Hz, 3H), 2.24 (dt, J = 14.3, 7.2 Hz, 1H), 1.45 (dd, J = 15.2, 9.4 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 168.9, 164.5, 145.1, 141.8, 140.5, 135.4, 131.0, 130.2, 129.3, 129.0, 128.8, 126.1, 52.8, 43.8, 28.5, 24.0, 21.6, 21.5

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{20}NO_5S^+$ 398.1053; Found 98.1057.

 $[\alpha]_{D}^{20}$ -30 (*c* 1.0, CHCl₃, 91% ee sample).



methyl (Z)-4-(4-chlorobenzylidene)-3-oxo-2-tosyl-2-azabicyclo[3.1.0]hexane-1-carboxylate (2t). The compound was prepared according to the general procedure to give a yellow solid. ¹H NMR (500 MHz, CDCl₃) δ 8.07 (d, J = 8.3 Hz, 2H), 7.71 (d, J = 8.5 Hz, 2H), 7.32 (dd, J = 26.7, 8.3 Hz, 4H), 6.94 (s, 1H), 3.84 (s, 3H), 2.69 (dd, J = 8.5, 5.8 Hz, 1H), 2.43 (s, 3H), 2.27 (dd, J = 8.9, 6.1 Hz, 1H), 1.50 (t, J = 5.8 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 168.7, 164.4, 145.3, 140.1, 135.8, 135.2, 132.2, 131.3, 129.4, 129.0, 128.3, 127.9, 52.9, 44.1, 28.3, 24.3, 21.7.

 $[\alpha]_{D}^{20}$ -280 (*c* 1.0, CHCl₃, 91% ee sample).



Methyl(Z)-4-benzylidene-2-((4-fluorophenyl)sulfonyl)-3-oxo-2-azabicyclo[3.1.0]hexane-1carboxylate (2u). The compound was prepared according to the general procedure to give a yellow solid.

¹**H NMR (500 MHz, CDCl₃)** δ 8.29 – 8.22 (m, 2H), 7.79 – 7.72 (m, 2H), 7.38 – 7.32 (m, 3H), 7.22 (t, *J* = 8.6 Hz, 2H), 7.05 (s, 1H), 3.84 (s, 3H), 2.73 (dd, *J* = 8.8, 5.7 Hz, 1H), 2.29 (dd, *J* = 8.9, 6.1 Hz, 1H), 1.54 (t, *J* = 5.9 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 168.8, 164.5, 142.2, 132.8, 132.2, 132.1, 130.9, 130.1, 128.1, 127.0, 116.2, 116.0, 52.9, 44.0, 28.5, 24.5.

¹⁹F NMR (471 MHz, CDCl₃) δ -102.71 (s).

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₀H_{16F}NO₅S⁺ 402.0806; Found 402.0813.

 $[\alpha]_{D}^{20}$ -10 (*c* 1.0, CHCl₃, 90% ee sample).

7 X-ray Crystal Structure Determination of the Products

To grow the crystals used to collect the X-ray data for 2f, the following method was used: the sample was dissolved with 3 mL petroleum ether and 1 mL CH₂Cl₂ in a small vial, which was kept aside at room temperature to obtain crystals.

A suitable crystal was selected a ROD, Synergy Custom system, HyPix diffractometer. The crystal was kept at 296.6 K during data collection. Using Olex2, the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimisation. The data have been deposited at the Cambridge Crystallographic Data Center (CCDC 2257065).



Figure S2. The X-ray Diffraction Configuration of 2f.

Identification code	2f
Empirical formula	C ₂₃ H ₂₅ NO ₃ S
Formula weight	395.50
Temperature/K	298
Crystal system	Orthorhombic
Space group	Pna2 ₁
a/Å	15.4097(9)
b/Å	10.4118(4)
c/Å	12.7879(7)
$\alpha/^{\circ}$	90°
$\beta/^{\circ}$	90°
γ/°	90°
Volume/Å ³	2051.73(18)
Ζ	4
ρcalcg/cm ³	1.280
µ/mm ⁻¹	1.587
F(000)	840.0

Table S8. Crystallographic data for compounds 2f

Crystal size/mm ³	$? \times ? \times ?$
Radiation	Cu Ka (λ = 1.54184)
2Θ range for data collection/°	10.254 to 154.352
Index ranges	$-18 \le h \le 18, -12 \le k \le 12, -15 \le I \le 6$
Reflections collected	7909
Independent reflections	2859 [$R_{int} = 0.0459, R_{sigma} = 0.0493$]
Data/restraints/parameters	2859/1/258
Goodness-of-fit on F ²	1.031
Final R indexes [I>=2σ (I)]	$R_1 = 0.0492, wR_2 = 0.1326$
Final R indexes [all data]	$R_1 = 0.0536, wR_2 = 0.1383$
Largest diff. peak/hole / e Å ⁻³	0.34/-0.33

To grow the crystals used to collect the X-ray data for 2i, the following method was used: the sample was dissolved with 3 mL petroleum ether and 1 mL CH₂Cl₂ in a small vial, which was kept aside at room temperature to obtain crystals.

A suitable crystal was selected a ROD, Synergy Custom system, HyPix diffractometer. The crystal was kept at 296.6 K during data collection. Using Olex2, the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimisation. The data have been deposited at the Cambridge Crystallographic Data Center (CCDC 2257688).



Figure S3. The X-ray Diffraction Configuration of (*R*,*R*)-2i.

Identification code	2i
Empirical formula	C ₁₉ H ₁₆ ClNO ₃ S
Formula weight	373.85
Temperature/K	296.6
Crystal system	triclinic
Space group	P1
a/Å	6.7397(2)
b/Å	8.1678(2)
c/Å	16.0806(3)
$\alpha/^{\circ}$	93.714(2)
β°	95.548(2)
γ/°	96.111(2)
Volume/Å ³	873.54(4)
Ζ	1

Table S8. Crystallographic data for compounds 2i

ρcalcg/cm ³	1.416
μ/mm ⁻¹	3.208
F(000)	385.0
Crystal size/mm ³	$? \times ? \times ?$
Radiation	Cu Ka ($\lambda = 1.54184$)
20 range for data collection/°	10.926 to 155.292
Index ranges	$-8 \le h \le 8, -10 \le k \le 10, -20 \le I \le 19$
Reflections collected	23126
Independent reflections	6332 [$R_{int} = 0.0338, R_{sigma} = 0.0341$]
Data/restraints/parameters	6332/3/453
Goodness-of-fit on F ²	1.028
Final R indexes [I>=2σ (I)]	$R_1 = 0.0592, wR_2 = 0.1586$
Final R indexes [all data]	$R_1 = 0.0731, wR_2 = 0.1723$
Largest diff. peak/hole / e Å ⁻³	0.32/-0.32

8 References

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9 Copies of NMR Spectra for Compounds



Figure S4. ¹H NMR (500 MHz, CDCl₃) spectrum of 1a



Figure S5. ¹³C NMR (126 MHz, CDCl₃) spectrum of 1a



Figure S6. ¹H NMR (500 MHz, CDCl₃) spectrum of 1b



Figure S7. ¹³C NMR (126 MHz, CDCl₃) spectrum of 1b



Figure S8. ¹H NMR (500 MHz, CDCl₃) spectrum of 1c



Figure S9. ¹³C NMR (126 MHz, CDCl₃) spectrum of 1c



Figure S10. ¹H NMR (500 MHz, CDCl₃) spectrum of 1d



Figure S11. ¹³C NMR (126 MHz, CDCl₃) spectrum of 1d



Figure S12. ¹H NMR (500 MHz, CDCl₃) spectrum of 1e



Figure S13. ¹³C NMR (126 MHz, CDCl₃) spectrum of 1e



Figure S14. ¹H NMR (500 MHz, CDCl₃) spectrum of 1f



Figure S15. ¹³C NMR (126 MHz, CDCl₃) spectrum of 1f



Figure S16. ¹H NMR (500 MHz, CDCl₃) spectrum of 1g



Figure S17. ¹³C NMR (126 MHz, CDCl₃) spectrum of 1g



Figure S18. ¹H NMR (500 MHz, CDCl₃) spectrum of 1h



Figure S19. ¹³C NMR (126 MHz, CDCl₃) spectrum of 1h



Figure S20. ¹⁹F NMR (471 MHz, CDCl₃) spectrum of 1h



Figure S21. ¹H NMR (500 MHz, CDCl₃) spectrum of 1i


Figure S22. ¹³C NMR (126 MHz, CDCl₃) spectrum of 1i



Figure S23. ¹H NMR (500 MHz, CDCl₃) spectrum of 1j



Figure S24. ¹³C NMR (126 MHz, CDCl₃) spectrum of 1j



Figure S25. ¹⁹F NMR (471 MHz, CDCl₃) spectrum of 1j



Figure S26. ¹H NMR (500 MHz, CDCl₃) spectrum of 1k



Figure S27. ¹³C NMR (126 MHz, CDCl₃) spectrum of 11



Figure S28. ¹H NMR (500 MHz, CDCl₃) spectrum of 11



Figure S29. ¹³C NMR (126 MHz, CDCl₃) spectrum of 11



102.75

-5. 0E+08

-4. 5E+08

2.41 ± 2.04 ±

1.0

0.5

1.5

-1.00E+08

0.0

0.93 I

3.0

2.5

2.0

3.5

4.0

Figure S31. ¹H NMR (500 MHz, CDCl₃) spectrum of 1m

6.0

5.5

5.0

4.5 fl (ppm)

1.85 <u>1</u>

8.0

0 8.5

182 87 月

7.5

7.0

6.5



Figure S32. ¹³C NMR (126 MHz, CDCl₃) spectrum of 1m



Figure S33. ¹H NMR (500 MHz, CDCl₃) spectrum of 1n



Figure S34. ¹³C NMR (126 MHz, CDCl₃) spectrum of 1n



Figure S35. ¹H NMR (500 MHz, CDCl₃) spectrum of 10



Figure S36. ¹³C NMR (126 MHz, CDCl₃) spectrum of 10



Figure S37. ¹H NMR (500 MHz, CDCl₃) spectrum of 1p



Figure S38. ¹³C NMR (126 MHz, CDCl₃) spectrum of 1p



Figure S39. ¹H NMR (500 MHz, CDCl₃) spectrum of 1q



Figure S40. ¹³C NMR (126 MHz, CDCl₃) spectrum of 1q



Figure S41. ¹H NMR (500 MHz, CDCl₃) spectrum of 1r



Figure S42. ¹³C NMR (126 MHz, CDCl₃) spectrum of 1r



Figure S43. ¹H NMR (500 MHz, CDCl₃) spectrum of 1s



Figure S44. ¹³C NMR (126 MHz, CDCl₃) spectrum of 1s



Figure S45. ¹H NMR (500 MHz, CDCl₃) spectrum of 1t



Figure S46. ¹³C NMR (126 MHz, CDCl₃) spectrum of 2a



Figure S47. ¹H NMR (500 MHz, CDCl₃) spectrum of 1u



Figure S48. ¹³C NMR (126 MHz, CDCl₃) spectrum of 2a



Figure S49. ¹⁹F NMR (471 MHz, CDCl₃) spectrum of 1u5



Figure S50. ¹H NMR (500 MHz, CDCl₃) spectrum of 2a



Figure S51. ¹³C NMR (126 MHz, CDCl₃) spectrum of 2a



Figure S52. ¹H NMR (500 MHz, CDCl₃) spectrum of 2b



Figure S53. ¹³C NMR (126 MHz, CDCl₃) spectrum of 2b



Figure S54. ¹H NMR (500 MHz, CDCl₃) spectrum of 2c



Figure S55. ¹³C NMR (126 MHz, CDCl₃) spectrum of 2c



Figure S56. ¹H NMR (500 MHz, CDCl₃) spectrum of 2d



Figure S57. ¹³C NMR (126 MHz, CDCl₃) spectrum of 2d



Figure S58. ¹H NMR (500 MHz, CDCl₃) spectrum of 2e



Figure S59. ¹³C NMR (126 MHz, CDCl₃) spectrum of 2e



Figure S60. ¹H NMR (500 MHz, CDCl₃) spectrum of 2f



Figure S61. ¹³C NMR (126 MHz, CDCl₃) spectrum of 2f



Figure S62. ¹H NMR (500 MHz, CDCl₃) spectrum of 2g



Figure S63. ¹³C NMR (126 MHz, CDCl₃) spectrum of 2g



Figure S64. ¹H NMR (500 MHz, CDCl₃) spectrum of 2h



Figure S65. ¹³C NMR (126 MHz, CDCl₃) spectrum of 2i



Figure S66. ¹⁹F NMR (471 MHz, CDCl₃) spectrum of 2h



Figure S67. ¹H NMR (500 MHz, CDCl₃) spectrum of 2i



Figure S68. ¹³C NMR (126 MHz, CDCl₃) spectrum of 2i



Figure S69. ¹H NMR (500 MHz, CDCl₃) spectrum of 2j



Figure S70. ¹³C NMR (126 MHz, CDCl₃) spectrum of 2j



Figure S71. ¹⁹F NMR (471 MHz, CDCl₃) spectrum of 2j



Figure S70. ¹H NMR (500 MHz, CDCl₃) spectrum of 2k



Figure S73.¹³C NMR (126 MHz, CDCl₃) spectrum of 2k



Figure S74. ¹H NMR (500 MHz, CDCl₃) spectrum of 21



Figure S75. ¹³C NMR (126 MHz, CDCl₃) spectrum of 21



Figure S76. ¹⁹F NMR (471 MHz, CDCl₃) spectrum of 2l



Figure S77. ¹H NMR (500 MHz, CDCl₃) spectrum of 2m



Figure S78. ¹³C NMR (126 MHz, CDCl₃) spectrum of 2m



Figure S79. ¹H NMR (500 MHz, CDCl₃) spectrum of 2n



Figure S80. ¹³C NMR (126 MHz, CDCl₃) spectrum of 2n



Figure S81. ¹H NMR (500 MHz, CDCl₃) spectrum of 20



Figure S82. ¹³C NMR (126 MHz, CDCl₃) spectrum of 20



Figure S83. ¹H NMR (500 MHz, CDCl₃) spectrum of 2r



Figure S84. ¹³C NMR (126 MHz, CDCl₃) spectrum of 2p



Figure S85. ¹H NMR (500 MHz, CDCl₃) spectrum of 2q



Figure S86. ¹³C NMR (126 MHz, CDCl₃) spectrum of 2q



Figure S87. ¹H NMR (500 MHz, CDCl₃) spectrum of 2r



Figure S88. ¹³C NMR (126 MHz, CDCl₃) spectrum of 2r



Figure S89. ¹H NMR (500 MHz, CDCl₃) spectrum of 2s



Figure S91. ¹H NMR (500 MHz, CDCl₃) spectrum of 2s



Figure S92. ¹³C NMR (126 MHz, CDCl₃) spectrum of 2s



Figure S93. ¹H NMR (500 MHz, CDCl₃) spectrum of 2u


Figure S95. ¹⁹F NMR (471 MHz, CDCl₃) spectrum of 2u











 $C_{\rm L} \sim 0$



2 55.571 1377977 7.43 14423 4.53















