Supplementary Information

Iodine Promoted Cascade Cycloisomerization of

1-En-6,11-diynes

Yi-Feng Qiu,[†]^a Yue-Jie Niu,[†]^a Xian-Rong Song,^b Xi Wei,^a Hui Chen,^a Shun-Xi Li,^a Xi-Cun Wang,^a Congde Huo,^{*a} Zheng-Jun Quan,^{*a} and Yong-Min Liang^c

^a College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou, People's Republic of China

^b Jiangxi Key Laboratory of Organic Chemistry, Jiangxi Science Technology Normal University, Nanchang, People's Republic of China

^c State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou, People's Republic of China

† These authors contributed equally.

Table of Contents

General Remarks1
General Procedures2
X-ray Single Crystal Diffraction Data8
Characterization Data 10
¹ H NMR, ¹³ C NMR, and ¹⁹ F NMR Spectra

General Remarks

Column chromatography was carried out on silica gel (200-300 mesh). ¹H NMR spectra were recorded on 400 or 600 MHz in CDCl₃ and chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard. ¹³C NMR spectra were recorded on 100 or 150 MHz in CDCl₃, ¹⁹F NMR spectra were recorded on 376 MHz in CDCl₃. Multiplicities are given as: s (singlet), d (doublet), t (triplet), dd (doublet of doublets), dq (doublet of quartets), q (quartet) or m (multiplet). HR-MS was obtained using a Q-TOF or Q-Orbitrap instrument equipped with ESI source. The copies of ¹H NMR, ¹³C NMR, and ¹⁹F NMR spectra of all compounds are provided in the Supporting Information. Room temperature is 23–25 °C. THF was distilled immediately before use from Na/benzophenone. 3-Ethoxypropanenitrile was purchased from Shanghai Bide Pharmaceutical Technology Co., Ltd without further purification. Other commercially available reagents and solvents were used without further purification.

General Procedures

For the Preparation of Starting Materials

For the synthesis of **1a** (This procedure was also used for the synthesis of substrate **1b–1j**, **1m–1n**, **1p–1y**):

Pd(PPh₃)₂Cl₂ (71.9 mg, 0.1 mmol, 1 mol %) and CuI (38.1 mg, 0.2 mmol, 2 mol %) were sequentially added to a stirred solution of 2iodobenzaldehyde **A** (2.32 g, 10 mmol) in triethylamine (40 mL) under argon at room temperature. The mixture was allowed to stir for 10 min. Then *N*-allyl-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (2.74 g, 11 mmol, 1.1 equiv) was added. The mixture was allowed to stir overnight. An aqueous saturated solution of NH₄Cl (40 mL) was poured into the resulting mixture, and the mixture was extracted with ethyl acetate (2 × 50 mL). The organic layers were combined to be washed with brine and dried over Na₂SO₄ for 20 min. Then the solution would be concentrated under reduced pressure. The obtained residue would be further purified by flash column chromatography (silica gel, petroleum ether/ethyl acetate, 5:1) to give *N*-allyl-*N*-(3-(2-formylphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide **B** (98%, 3.46 g, 9.8 mmol).



n-BuLi (2.5 M, 2.9 mL, 1.4 equiv) was added dropwise via a syringe to a stirred solution of phenylacetylene (0.61 g, 6 mmol, 1.2 equiv) in dry THF (30 mL) under argon at -78 °C. The reaction mixture was allowed to stir for 10 min. Then, the solution of N-allyl-N-(3-(2-formylphenyl) prop-2-yn-1-yl)-4-methylbenzenesulfonamide **B** (1.77 g, 5 mmol) in THF was added at -78 °C. The reaction mixture was allowed to stir for 10 min at room temperature. After the completion of the reaction determined by TLC, the reaction mixture was quenched by an aqueous saturated solution of NH₄Cl (30 mL) and extracted with ethyl acetate (2×50 mL). The organic layers were combined to be washed with brine and dried over Na₂SO₄ for 20 min. Then the solution would be concentrated under reduced pressure. The obtained residue would be further purified by flash column chromatography (silica gel, petroleum ether/ethyl acetate, 3:1) to give N-allyl-N-(3-(2-(1-hydroxy-3-phenylprop-2-yn-1-yl)phenyl)prop-2yn-1-yl)-4-methylbenzenesulfonamide 1a (95%, 2.16 g, 4.75 mmol).

For the synthesis of **10** (This procedure was also used for the synthesis of substrate **1k** and **1l**):

Ethynylmagnesium bromide (0.5 mol/L in THF, 24 mL, 1.2 equiv) was added dropwise into a stirred solution of *N*-allyl-*N*-(3-(2-formylphenyl) prop-2-yn-1-yl)-4-methylbenzenesulfonamide **B** (3.53 g, 10 mmol) in THF (35 mL) under argon. The mixture was allowed to stir for 4 h at room temperature. After the completion of the reaction determined by TLC, the reaction mixture was quenched by addition of an aqueous saturated solution of NH₄Cl (35 mL) and extracted with ethyl acetate (2×50 mL). The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The resulting material *N*-allyl-*N*-(3-(2-(1-hydroxyprop-2-yn-1-yl)phenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide **C** (90%, 3.42 g, 9 mmol) was directly used for the next step without further purification.



Pd(PPh₃)₂Cl₂ (56.2 mg, 0.08 mmol, 1 mol %) and CuI (30.5 mg, 0.16 mmol, 2 mol %) were sequentially added to a stirred solution of 2-iodo-1-methoxy-4-nitrobenzene (2.68 g, 9.6 mmol, 1.2 equiv) in triethylamine (40 mL) under argon at room temperature. The mixture was allowed to stir for 10 min. Then *N*-allyl-*N*-(3-(2-(1-hydroxyprop-2-yn-1-yl)phenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide **C** (3.04 g, 8 mmol) was added. The mixture was allowed to stir overnight. An aqueous saturated solution of NH₄Cl (40 mL) was poured into the resulting mixture, and the mixture was extracted with ethyl acetate (2 × 40 mL). The organic layers were combined to be washed with brine and dried over Na₂SO₄ for 20 min. Then the solution would be concentrated under

reduced pressure. The obtained residue would be further purified by flash column chromatography (silica gel, petroleum ether/ethyl acetate, 2:1) to give *N*-allyl-*N*-(3-(2-(1-hydroxy-3-(2-methoxy-5-nitrophenyl)prop-2-yn-1-yl)phenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide **10** (96%, 4.08 g, 7.7 mmol).

For the synthesis of **1z**:

Compound 3-(3-chloro-4-methylphenyl)-1-(2-iodophenyl)prop-2-yn-1ol **D** (98%) was synthesized via a similar preparation procedure as substrate **1a**.



Substrate dimethyl 2-allyl-2-(3-(2-(3-(3-chloro-4-methylphenyl)-1hydroxyprop-2-yn-1-yl)phenyl)prop-2-yn-1-yl)malonate 1z (86%) was synthesized via a similar preparation procedure as compound **B**.

For the Synthesis of Intermediate Int-C

Acetophenone (1.2 g, 10 equiv, 10 mmol) and NaOH (0.6 g, 1.5 equiv, 15 mmol) were sequentially added to a stirred solution of 2-iodobenzaldehyde **A** (2.32 g, 10 mmol) in EtOH (40 mL) at room temperature. The mixture was allowed to stir for 3 h. An aqueous saturated solution of NH₄Cl (40 mL) was poured into the resulting mixture, and the mixture was extracted with ethyl acetate (2 × 40 mL). The organic layers were combined to be washed with brine and dried over Na₂SO₄ for 20 min. Then the solution would be concentrated under reduced pressure. The obtained residue would be further purified by flash column chromatography (silica gel, petroleum ether/ethyl acetate, 20:1) to give 3-(2-iodophenyl)-1-phenylprop-2-en-1-one **E** (82%, 2.74 g, 8.2 mmol).



Compound *N*-allyl-4-methyl-*N*-(3-(2-(3-oxo-3-phenylprop-1-en-1-yl) phenyl)prop-2- yn-1-yl)benzenesulfonamide **Int-C** (95%) was synthesized via a similar preparation procedure as substrate **1a**.

For the Synthesis of Products

For the synthesis of **2a**:



Water (7.2 µL, 0.40 mmol, 2.0 equiv) and iodine (50.8 mg, 0.2 mmol, 1.0 equiv) were sequentially added to an oven-dried tube charged with of N-allyl-N-(3-(2-(1-hydroxy-3-phenylprop-2-yn-1-yl)phenyl)prop-2-yn-1yl)-4-methylbenzenesulfonamide (**1a**: 91.0 mg, 0.2 mmol) in 3-ethoxypropanenitrile. The resulting mixture was allowed to stir at 80 °C for 0.5 h. And the reaction mixture was quenched with a saturated aqueous solution of $Na_2S_2O_3$ (3–5 mL) and then extracted with ethyl ether (2×15 mL), washed with saturated brine, dried over Na₂SO₄, and evaporated under reduced pressure. The residue was further purified by chromatography on silica gel (petroleum ether/ethyl acetate, 10:1) to afford the product (1-(iodomethyl)-3-tosyl-1,2,3,4-tetrahydrobenzo[f])isoquinolin-5-yl)(phenyl)methanone 2a in 82% yield.

X-ray Single Crystal Diffraction Data

C19	C13 C12 C14 C15 C10 C16 C19 C17 C17 C19 C19 C19 C19 C19 C19 C19 C19 C19 C19	ĺ	Br	
C27 C26 C25 C24 C23 C24	C1B C1B C1 C1 C2 C1 C2 C2 C2 C2 C2 C2 C2 C2 C2 C2 C2 C2 C2	Brl The proba	2j ellipsoid contour percent ability level is 50% in the on of the thermal ellipsoid CCDC 1913985	
Bond precision:	C-C = 0.0085 A	W	Vavelength=0.71073	
Cell:	a=14.8474(5) alpha=90 l	b=30.0430(2 beta=90	15) c=26.3798(6) gamma=90	
Temperature:	173 K			
Volume	Calculated		Reported	
Space group	Phcn		Ph c n	
Hall group	-P 2n 2ab		-P 2n 2ab	
Moiety formula	-r 2ll 2a0 C28 H23 Br I N O3 S [solvent]		⁺ C28 H23 Br I N O3 S	
Sum formula	C28 H23 Br I N O3 S [+ solvent]		C28 H23 Br I N O3 S	
Mr	660.33		660.34	
Dx,g cm-3	1.491		1.491	
Z	16		16	
Mu (mm-1)	2.545		2.545	
F000	5216.0		5216.0	
F000'	5207.75			
h,k,lmax	18, 37, 32		18, 37, 32	
Nref	11606		11570	
Tmin,Tmax	0.565,0.683		0.703,1.000	

Data completeness= 0.997	Theta(max)= 26.022
R(reflections)= 0.0609(6211)	wR2(reflections)= 0.1049(11570)
S = 0.978	Npar= 633





21

The ellipsoid contour percent probability level is 50% in the caption of the thermal ellipsoid plot. CCDC 1935327

Bond precision:	C-C = 0.0146 A	Wavelength=0.71073					
Cell:	a=25.670(2)	b=10.5220(7)	c=9.8072(12)				
	alpha=90	beta=90	gamma=90				
Temperature:	293 K		-				
	Calculated		Reported				
Volume	2648.9(4)		2648.9(4)				
Space group	P n a 21		P n a 21				
Hall group	P 2c -2n		P 2c -2n				
Moiety formula	C29 H23 I N2	2 O3 S	C29 H23 I N2 O3 S				
Sum formula	C29 H23 I N2	2 O3 S	C29 H23 I N2 O3 S				
Mr	606.45		606.45				
Dx,g cm-3	1.521		1.521				
Ζ	4		4				
Mu (mm-1)	1.321		1.321				
F000	1216.0		1216.0				
F000'	1215.04						
h,k,lmax	31, 12, 12		31, 12, 12				
Nref	5206 [2763]		4113				
Tmin,Tmax	0.788,0.853		0.483,1.000				
Tmin'	0.788						
Correction method= # Reported T Limits: Tmin=0.483 Tmax=1.000 AbsCorr = MULTI-SCAN							
Data completeness= 1.49/0.79		1 heta(max) = 26.020					
R(reflections)= 0.0	0515(3092)	wR2(reflections)= 0.1061(4113)					
S = 1.067		Npar= 326					

Characterization Data

Characterization Data of 2a-2v

(1-(iodomethyl)-3-tosyl-1,2,3,4-tetrahydrobenzo[f]isoquinolin-5-yl)(phenyl)methanone

(2*a*): white solid; 95.4 mg; 82% yield; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.92 (d, J = 8.4 Hz, 1H), 7.84–7.77 (m, 6H), 7.73–7.69 (m, 1H), 7.65 (t, J = 7.6 Hz, 1H), 7.57–7.48 (m, 3H), 7.37 (d, J = 8.0 Hz, 2H), 4.77 (d, J = 16.8 Hz, 1H), 4.44 (d, J = 12.0 Hz, 1H), 4.12 (d, J = 16.4 Hz, 1H), 3.84 (d, J = 10.8 Hz, 1H), 3.70 (t, J = 10.8 Hz, 1H), 3.53 (d, J = 10.0 Hz, 1H), 2.75 (d, J = 11.6 Hz, 1H), 2.43 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ ppm 196.8, 143.9, 137.4, 133.4, 132.4, 132.1, 131.9, 131.0, 131.0, 130.4, 129.9, 129.8, 129.3, 128.5, 128.2, 127.8, 126.7, 122.4, 47.5, 45.9, 40.1, 21.5, 7.7; HRMS (ESI/Q-TOF) m/z [M+H]⁺ calcd for C₂₈H₂₅INO₃S 582.0594, found 582.0593 (0.2 ppm).

(1-(iodomethyl)-3-tosyl-1,2,3,4-tetrahydrobenzo[f]isoquinolin-5-yl)(p-tolyl)methanone (2b): light yellow solid; 89.3 mg; 75% yield; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.91 (d, J = 8.4 Hz, 1H), 7.81–7.68 (m, 7H), 7.54 (t, J = 7.6 Hz, 1H), 7.36 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 4.75 (d, J = 16.4 Hz, 1H), 4.43 (d, J = 12.0 Hz, 1H), 4.10 (d, J = 16.4 Hz, 1H), 3.83 (d, J = 11.2 Hz, 1H), 3.69 (t, J = 10.8 Hz, 1H), 3.53 (d, J = 10.4 Hz, 1H), 2.74 (d, J = 11.6 Hz, 1H), 2.46 (s, 3H), 2.43 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ ppm 196.5, 144.5, 143.8, 134.7, 133.8, 132.4, 132.0, 131.8, 131.0, 130.6, 130.5, 129.8, 129.8, 129.2, 129.1, 128.0, 127.8, 126.7, 122.4, 47.4, 45.9, 40.1, 21.7, 21.5, 7.8; HRMS (ESI/Q-TOF) m/z [M+Na]⁺ calcd for C₂₉H₂₆INNaO₃S 618.0570, found 618.0570 (0 ppm).

(4-ethylphenyl)(1-(iodomethyl)-3-tosyl-1,2,3,4-tetrahydrobenzo[f]isoquinolin-5-yl)methano ne (2c): yellow solid; 86.5 mg; 71% yield; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.91 (d, J = 8.4 Hz, 1H), 7.81–7.76 (m, 6H), 7.70 (t, J = 7.6 Hz, 1H), 7.54 (t, J = 7.6 Hz, 1H), 7.37–7.31 (m, 4H), 4.75 (d, J = 16.4 Hz, 1H), 4.43 (d, J = 11.6 Hz, 1H), 4.10 (d, J = 16.4 Hz, 1H), 3.83 (d, J = 10.8 Hz, 1H), 3.69 (t, J = 10.8 Hz, 1H), 3.53 (d, J = 10.0 Hz, 1H), 2.79–2.73 (m, 3H), 2.43 (s, 3H), 1.30 (t, J = 7.6 Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ ppm 196.5, 150.6, 143.8, 134.9, 133.8, 132.4, 132.0, 131.8, 131.0, 130.6, 130.5, 129.8, 129.8, 129.1, 128.0, 127.8, 126.7, 122.4, 47.4, 45.9, 40.1, 29.0, 21.5, 15.2, 7.8; HRMS (ESI/Q-TOF) m/z [M+H]⁺ calcd for C₃₀H₂₉INO₃S 610.0907, found 610.0907 (0 ppm).



(4-(tert-butyl)phenyl)(1-(iodomethyl)-3-tosyl-1,2,3,4-tetrahydrobenzo[f]isoquinolin-5-yl) methanone (2d): light yellow solid; 98.2 mg; 77% yield; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.93 (d, J = 8.4 Hz, 1H), 7.83–7.78 (m, 6H), 7.71 (t, J = 7.6 Hz, 1H), 7.54 (dd, J = 18.0 Hz 7.6 Hz, 3H), 7.37 (d, J = 8.0 Hz, 2H), 4.74 (d, J = 16.8 Hz, 1H), 4.43 (d, J = 12.0 Hz, 1H), 4.11 (d, J = 16.4 Hz, 1H), 3.84 (t, J = 10.8 Hz, 1H), 3.70 (t, J = 10.8 Hz, 1H), 3.54 (d, J =10.0 Hz, 1H), 2.77 (d, J = 12.0 Hz, 1H), 2.43 (s, 3H), 1.38 (s, 9H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ ppm 196.5, 157.5, 143.9, 134.7, 133.9, 132.7, 132.1, 131.9, 131.1, 130.5, 130.5, 129.9, 129.8, 129.1, 128.2, 127.9, 126.7, 125.6, 122.5, 47.5, 45.9, 40.2, 35.2, 31.1, 21.5, 7.8; HRMS (ESI/Q-TOF) m/z [M+Na]⁺ calcd for C₃₂H₃₂INNaO₃S 660.1040, found 660.1041 (0.2 ppm).



(1-(iodomethyl)-3-tosyl-1,2,3,4-tetrahydrobenzo[f]isoquinolin-5-yl)(4-pentylphenyl)metha none (2e): light yellow solid; 75.6 mg; 58% yield; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.92 (d, J = 8.4 Hz, 1H), 7.83–7.74 (m, 6H), 7.75–7.69 (m, 1H), 7.55 (t, J = 7.6 Hz, 1H), 7.37 (d, J =7.6 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 4.74 (d, J = 16.4 Hz, 1H), 4.43 (d, J = 11.6 Hz, 1H), 4.11 (d, J = 16.4 Hz, 1H), 3.84 (d, J = 10.8 Hz, 1H), 3.70 (t, J = 10.8 Hz, 1H), 3.54 (d, J =10.0 Hz, 1H), 2.77–2.67 (m, 3H), 2.43 (s, 3H), 1.68 (t, J = 6.8 Hz, 2H), 1.36 (d, J = 6.8 Hz, 4H), 0.93–0.90 (m, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ ppm 196.6, 149.6, 143.9, 134.9, 133.9, 132.5, 132.1, 131.9, 131.0, 130.7, 130.5, 129.9, 129.8, 129.1, 128.6, 128.2, 127.9, 126.7, 122.5, 47.5, 45.9, 40.2, 36.0, 31.4, 30.8, 22.5, 21.5, 14.0, 7.8; HRMS (ESI/Q-TOF) *m*/*z* [M+H]⁺ calcd for C₃₃H₃₅INO₃S 652.1377, found 652.1376 (0.2 ppm).

O I NTs

(1-(iodomethyl)-3-tosyl-1,2,3,4-tetrahydrobenzo[f]isoquinolin-5-yl)(4-methoxyphenyl)met hanone (2f): light yellow solid; 75.8 mg; 62% yield; ¹H NMR (600 MHz, CDCl₃) δ ppm 7.92 (d, J = 8.4 Hz, 1H), 7.84–7.81 (m, 3H), 7.78–7.76 (m, 3H), 7.72–7.69 (m, 1H), 7.55 (t, J = 7.8 Hz, 1H), 7.36 (d, J = 7.8 Hz, 2H), 6.97 (d, J = 9.0 Hz, 2H), 4.70 (d, J = 16.2 Hz, 1H), 4.43 (d, J = 12.0 Hz, 1H), 4.08 (d, J = 16.2 Hz, 1H), 3.91 (s, 3H), 3.84–3.82 (m, 1H), 3.71–3.67 (m, 1H), 3.54 (d, J = 10.2 Hz, 1H), 2.76 (d, J = 11.4 Hz, 1H), 2.43 (s, 3H); ¹³C{¹H} NMR (150 MHz, CDCl₃) δ ppm 195.4, 164.1, 143.9, 134.3, 132.8, 132.6, 132.0, 131.7, 131.2, 130.1, 129.9, 129.7, 129.6, 129.0, 128.0, 127.9, 126.7, 122.5, 113.9, 55.6, 47.4, 46.0, 40.2, 21.5, 7.7; HRMS (ESI/Q-TOF) m/z [M+H]⁺ calcd for C₂₉H₂₇INO₄S 612.0700, found 612.0700 (0 ppm).



[1,1'-biphenyl]-4-yl(1-(iodomethyl)-3-tosyl-1,2,3,4-tetrahydrobenzo[f]isoquinolin-5-yl)me thanone (2g): yellow solid; 93.4 mg; 71% yield; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.92 (t, J = 8.4 Hz, 3H), 7.87–7.83 (m, 2H), 7.78 (d, J = 7.6 Hz, 2H), 7.72 (d, J = 8.0 Hz, 3H), 7.67 (d, J = 7.2 Hz, 2H), 7.56 (t, J = 7.6 Hz, 1H), 7.50 (t, J = 7.2 Hz, 2H), 7.44–7.40 (m, 1H), 7.35 (d, J = 7.6 Hz, 2H), 4.78 (d, J = 16.4 Hz, 1H), 4.44 (d, J = 12.0 Hz, 1H), 4.12 (d, J = 16.8 Hz, 1H), 3.85 (d, J = 10.8 Hz, 1H), 3.71 (t, J = 10.4 Hz, 1H), 3.54 (d, J = 10.0 Hz, 1H), 2.75 (d, J = 11.6 Hz, 1H), 2.41 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ ppm 196.4, 146.2, 143.9, 139.6, 136.1, 133.7, 132.5, 132.2, 131.9, 131.1, 131.0, 130.8, 130.5, 129.9, 129.3, 129.0, 128.4, 128.1, 127.8, 127.3, 127.2, 126.8, 122.5, 47.6, 45.9, 40.2, 21.5, 7.8; HRMS (ESI/Q-TOF) m/z [M+H]⁺ calcd for C₃₄H₂₉INO₃S 658.0907, found 658.0907 (0 ppm).

(4-fluorophenyl)(1-(iodomethyl)-3-tosyl-1,2,3,4-tetrahydrobenzo[f]isoquinolin-5-yl)meth anone (2h): yellow solid; 95.9 mg; 80% yield; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.92 (d, J = 8.4 Hz, 1H), 7.89–7.59 (m, 2H), 7.80 (dd, J = 16.0 Hz 8.4 Hz, 4H), 7.73 (t, J = 8.0 Hz, 1H), 7.56 (t, J = 7.6 Hz, 1H), 7.37 (d, J = 8.0 Hz, 2H), 7.18 (t, J = 8.4 Hz, 2H), 4.73 (d, J = 16.8 Hz, 1H), 4.43 (d, J = 11.6 Hz, 1H), 4.09 (d, J = 16.4 Hz, 1H), 3.84 (d, J = 10.8 Hz, 1H), 3.69 (t, J = 10.8 Hz, 1H), 3.52 (d, J = 10.0 Hz, 1H), 2.75 (d, J = 11.6 Hz, 1H), 2.44 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ ppm 195.2, 166.0 (d, ¹J = 254 Hz, 1C), 144.0, 133.7 (d, ³J = 3 Hz, 1C), 133.3, 133.1, 133.0, 132.4, 132.3, 132.0, 131.0, 130.7, 129.9, 129.4, 128.0, 127.8, 126.9, 122.5, 115.8 (d, ²J = 22 Hz, 1C), 47.5, 45.9, 40.1, 21.5, 7.6; ¹⁹F NMR (376 MHz, CDCl₃) δ ppm -104.27—-104.34 (m, 1F); HRMS (ESI/Q-TOF) m/z [M+Na]⁺ calcd for C₂₈H₂₃FINNaO₃S 622.0320, found 622.0320 (0 ppm).

(4-chlorophenyl)(1-(iodomethyl)-3-tosyl-1,2,3,4-tetrahydrobenzo[f]isoquinolin-5-yl)meth

anone (2*i*): yellow solid; 97.3 mg; 79% yield; ¹H NMR (600 MHz, CDCl₃) δ ppm 7.93 (d, J = 8.4 Hz, 1H), 7.82 (d, J = 7.8 Hz, 1H), 7.79–7.77 (m, 5H), 7.73 (t, J = 7.8 Hz, 1H), 7.57 (t, J = 7.8 Hz, 1H), 7.48 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 4.74 (d, J = 16.8 Hz, 1H), 4.43 (d, J = 12.0 Hz, 1H), 4.09 (d, J = 16.8 Hz, 1H), 3.84 (d, J = 10.8 Hz, 1H), 3.70–3.67 (m, 1H), 3.52 (d, J = 10.2 Hz, 1H), 2.76 (d, J = 11.4 Hz, 1H), 2.44 (s, 3H); ¹³C{¹H} NMR (150 MHz, CDCl₃) δ ppm 195.6, 144.0, 140.0, 135.8, 133.2, 132.5, 132.4, 132.1, 131.7, 131.1, 131.0, 129.9, 129.9, 129.5, 128.9, 128.1, 127.9, 126.9, 122.5, 47.6, 45.9, 40.2, 21.5, 7.6; HRMS (ESI/Q-TOF) m/z [M+H]⁺ calcd for C₂₈H₂₄ClINO₃S 616.0205, found 616.0205 (0 ppm).

(4-bromophenyl)(1-(iodomethyl)-3-tosyl-1,2,3,4-tetrahydrobenzo[f]isoquinolin-5-yl)meth anone (2j): yellow solid; 110.9 mg; 84% yield; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.98 (s, 1H), 7.83–7.76 (m, 6H), 7.71 (s, 1H), 7.66 (t, J = 7.6 Hz, 1H), 7.53–7.49 (m, 2H), 7.37 (d, J =8.0 Hz, 2H), 4.72 (d, J = 16.8 Hz, 1H), 4.42 (d, J = 12.0 Hz, 1H), 4.07 (d, J = 16.4 Hz, 1H), 3.79 (d, J = 10.8 Hz, 1H), 3.71–3.66 (m, 1H), 3.46 (d, J = 10.0 Hz, 1H), 2.76 (d, J = 12.0 Hz, 1H), 2.44 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ ppm 195.7, 144.0, 136.2, 133.0, 132.4, 132.4, 132.1, 131.9, 131.8, 131.1, 131.0, 129.9, 129.9, 129.5, 128.7, 128.1, 127.8, 126.9, 122.5, 47.6, 45.9, 40.1, 21.5, 7.6; HRMS (ESI/Q-TOF) m/z [M+Na]⁺ calcd for C₂₈H₂₃BrINNaO₃S 681.9519, found 681.9520 (0.1 ppm).



I-(*4*-(*1*-(*iodomethyl*)-*3*-*tosyl*-*1*,*2*,*3*,*4*-*tetrahydrobenzo[f]isoquinoline*-*5*-*carbonyl*)*phenyl*)*et han*-*1*-*one* (*2k*): yellow solid; 77.3 mg; 62% yield; ¹H NMR (400 MHz, CDCl₃) δ ppm 8.06 (d, *J* = 8.0 Hz, 2H), 7.94–7.89 (m, 3H), 7.82–7.78 (m, 4H), 7.74 (t, *J* = 7.6 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.38 (d, *J* = 7.6 Hz, 2H), 4.82 (d, *J* = 16.4 Hz, 1H), 4.44 (d, *J* = 12.0 Hz, 1H), 4.14 (d, *J* = 16.8 Hz, 1H), 3.84 (d, *J* = 10.8 Hz, 1H), 3.69 (t, *J* = 10.8 Hz, 1H), 3.52 (d, *J* = 10.0 Hz, 1H), 2.76 (d, *J* = 12.0 Hz, 1H), 2.68 (s, 3H), 2.44 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ ppm 197.3, 196.1, 143.9, 141.0, 140.2, 132.7, 132.5, 132.5, 132.2, 131.8, 130.9, 130.4, 130.0, 129.9, 129.7, 128.3, 128.3, 127.8, 126.9, 122.5, 47.6, 45.8, 40.2, 26.9, 21.5, 7.6; HRMS (ESI/Q-Orbitrap) *m*/*z* [M+H]⁺ calcd for C₃₀H₂₇INO₄S 624.0700, found 624.0703 (0.5 ppm).



4-(1-(iodomethyl)-3-tosyl-1,2,3,4-tetrahydrobenzo[f]isoquinoline-5-carbonyl)benzonitrile (2l): white solid; 66.7 mg; 55% yield; ¹H NMR (600 MHz, CDCl₃) δ ppm 7.95–7.92 (m, 3H), 7.83–7.79 (m, 6H), 7.76 (t, J = 7.8 Hz, 1H), 7.59 (t, J = 7.8 Hz, 1H), 7.39 (d, J = 8.4 Hz, 2H), 4.80 (d, J = 16.8 Hz, 1H), 4.44 (d, J = 12.0 Hz, 1H), 4.13 (d, J = 16.8 Hz, 1H), 3.85 (d, J =10.8 Hz, 1H), 3.69 (t, J = 10.8 Hz, 1H), 3.51 (d, J = 10.2 Hz, 1H), 2.77 (d, J = 11.4 Hz, 1H), 2.45 (s, 3H); ¹³C{¹H} NMR (150 MHz, CDCl₃) δ ppm 195.2, 144.1, 141.1, 132.8, 132.6, 132.4, 132.3, 132.2, 132.0, 130.9, 130.6, 130.1, 130.0, 129.9, 128.4, 127.9, 127.1, 122.6, 117.8, 116.5, 47.7, 45.9, 40.3, 21.5, 7.4; HRMS (ESI/Q-Orbitrap) m/z [M+Na]⁺ calcd for C₂₉H₂₃IN₂NaO₃S 629.0366, found 629.0365 (0.2 ppm).

(1-(iodomethyl)-3-tosyl-1,2,3,4-tetrahydrobenzo[f]isoquinolin-5-yl)(m-tolyl)methanone (2m): light yellow solid; 81.0 mg; 68% yield; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.91 (d, J =8.4 Hz, 1H), 7.80–7.76 (m, 4H), 7.69 (dd, J = 15.2 Hz 7.6 Hz, 2H), 7.59 (d, J = 7.6 Hz, 1H), 7.54 (t, J = 7.6 Hz, 1H), 7.45 (d, J = 7.6 Hz, 1H), 7.37 (t, J = 7.6 Hz, 3H), 4.77 (d, J = 8.4 Hz, 1H), 4.43 (d, J = 11.6 Hz, 1H), 4.11 (d, J = 16.8 Hz, 1H), 3.82 (d, J = 10.8 Hz, 1H), 3.69 (t, J =10.8 Hz, 1H), 3.52 (d, J = 10.0 Hz, 1H), 2.74 (d, J = 12.0 Hz, 1H), 2.42 (s, 3H), 2.41 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ ppm 197.0, 143.8, 138.4, 137.4, 134.2, 133.6, 132.4, 132.0, 131.8, 130.9, 130.8, 130.6, 129.8, 129.8, 129.2, 128.3, 128.1, 127.7, 127.7, 126.7, 122.3, 47.5, 45.8, 40.0, 21.5, 21.2, 7.7; HRMS (ESI/Q-TOF) m/z [M+Na]⁺ calcd for C₂₉H₂₆INNaO₃S 618.0570, found 618.0570 (0 ppm).

(3-chlorophenyl)(1-(iodomethyl)-3-tosyl-1,2,3,4-tetrahydrobenzo[f]isoquinolin-5-yl)meth anone (2n): light yellow solid; 91.2 mg; 74% yield; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.93 (d, J = 8.4 Hz, 1H), 7.84–7.80 (m, 5H), 7.78–7.68 (m, 2H), 7.63–7.55 (m, 2H), 7.45 (t, J =8.0 Hz, 1H), 7.38 (d, J = 8.0 Hz, 2H), 4.76 (d, J = 16.4 Hz, 1H), 4.44 (d, J = 10.4 Hz, 1H), 4.10 (d, J = 16.4 Hz, 1H), 3.84 (d, J = 10.8 Hz, 1H), 3.70 (t, J = 10.8 Hz, 1H), 3.53 (d, J =10.4 Hz, 1H), 2.76 (d, J = 11.6 Hz, 1H), 2.44 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ ppm 195.4, 144.0, 139.1, 134.9, 133.3, 132.7, 132.4, 132.1, 131.3, 130.9, 130.1, 130.0, 129.9, 129.8, 129.6, 128.5, 128.2, 127.8, 126.9, 122.5, 47.5, 45.9, 40.2, 21.5, 7.6 (One of the peak of aryl group is overlapped in ¹³C NMR spectrum); HRMS (ESI/Q-TOF) m/z [M+H]⁺ calcd for C₂₈H₂₄ClINO₃S 616.0205, found 616.0205 (0 ppm).



(1-(iodomethyl)-3-tosyl-1,2,3,4-tetrahydrobenzo[f]isoquinolin-5-yl)(2-methoxy-5-nitrophe nyl)methanone (2o): light yellow solid; 61.7 mg; 47% yield; ¹H NMR (600 MHz, CDCl₃) δ ppm 8.42 (dd, J = 9.6 Hz 3.0 Hz, 1H), 8.32 (d, J = 2.4 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H), 7.86–7.82 (m, 3H), 7.78–7.73 (m, 2H), 7.54 (t, J = 7.8 Hz, 1H), 7.40 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 9.0 Hz, 1H), 5.07 (d, J = 17.4 Hz, 1H), 4.46 (d, J = 11.4 Hz, 1H), 4.22 (d, J = 16.8 Hz, 1H), 3.85–3.83 (m, 4H), 3.72 (t, J = 10.8 Hz, 1H), 3.53 (d, J = 10.2 Hz, 1H), 2.78 (d, J = 12.0Hz, 1H), 2.45 (s, 3H); ¹³C{¹H} NMR (150 MHz, CDCl₃) δ ppm 194.6, 162.2, 143.9, 141.1, 133.5, 132.9, 132.7, 132.6, 132.4, 131.1, 130.3, 130.1, 129.9, 129.6, 128.8, 128.2, 127.8, 126.8, 125.8, 122.5, 111.7, 56.7, 48.1, 45.7, 40.2, 21.5, 7.7; HRMS (ESI/Q-Orbitrap) m/z[M+H]⁺ calcd for C₂₉H₂₆IN₂O₆S 657.0551, found 657.0551 (0 ppm).

(3,5-dimethylphenyl)(1-(iodomethyl)-3-tosyl-1,2,3,4-tetrahydrobenzo[f]isoquinolin-5-yl) methanone (2p): light yellow solid; 80.5 mg; 66% yield; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.92 (d, J = 8.4 Hz, 1H), 7.82–7.77 (m, 4H), 7.70 (t, J = 7.6 Hz, 1H), 7.54 (t, J = 7.6 Hz, 1H), 7.42 (s, 2H), 7.36 (d, J = 7.6 Hz, 2H), 7.28 (s, 1H), 4.75 (d, J = 16.4 Hz, 1H), 4.44 (d, J =12.0 Hz, 1H), 4.10 (d, J = 16.8 Hz, 1H), 3.83 (d, J = 11.2 Hz, 1H), 3.70 (t, J = 10.8 Hz, 1H), 3.53 (d, J = 10.0 Hz, 1H), 2.75 (d, J = 11.6 Hz, 1H), 2.42 (s, 3H), 2.36 (s, 6H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ ppm 197.2, 143.8, 138.2, 137.5, 135.2, 133.9, 132.4, 131.9, 131.8, 131.0, 130.6, 129.8, 129.8, 129.1, 128.1, 127.8, 127.6, 126.6, 122.4, 47.5, 45.9, 40.0, 21.5, 21.1, 7.7; HRMS (ESI/Q-TOF) m/z [M+H]⁺ calcd for C₃₀H₂₉INO₃S 610.0907, found 610.0906 (0.2 ppm).

(3,5-dichlorophenyl)(1-(iodomethyl)-3-tosyl-1,2,3,4-tetrahydrobenzo[f]isoquinolin-5-yl)m ethanone (2q): yellow solid; 97.6 mg; 75% yield; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.93 (d, J = 8.4 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.81–7.74 (m, 4H), 7.67 (d, J = 0.8 Hz, 2H), 7.60–7.57 (m, 2H), 7.39 (d, J = 7.6 Hz, 2H), 4.76 (d, J = 16.4 Hz, 1H), 4.44 (d, J = 11.6 Hz, 1H), 4.09 (d, J = 16.8 Hz, 1H), 3.84 (d, J = 10.8 Hz, 1H), 3.69 (t, J = 10.8 Hz, 1H), 3.52 (d, J = 10.4 Hz, 1H), 2.75 (d, J = 11.6 Hz, 1H), 2.44 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ ppm 194.0, 144.0, 140.2, 135.5, 132.9, 132.7, 132.4, 132.3, 132.0, 131.6, 130.8, 130.1, 129.9, 128.5, 128.2, 127.8, 127.0, 122.5, 47.5, 45.8, 40.1, 21.5, 7.5; HRMS (ESI/Q-TOF) m/z [M+H]⁺ calcd for C₂₈H₂₃Cl₂INO₃S 649.9815, found 649.9815 (0 ppm).



(3,4-dimethylphenyl)(1-(iodomethyl)-3-tosyl-1,2,3,4-tetrahydrobenzo[f]isoquinolin-5-yl) methanone (2r): yellow solid; 95.1 mg; 78% yield; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.93 (d, *J* = 8.8 Hz, 1H), 7.82–7.77 (m, 4H), 7.73–7.68 (m, 1H), 7.64 (s, 1H), 7.57–7.52 (m, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.26–7.23 (m, 2H), 4.73 (d, *J* = 16.4 Hz, 1H), 4.44 (d, *J* = 11.6 Hz, 1H), 4.11 (d, *J* = 16.4 Hz, 1H), 3.84 (d, *J* = 10.8 Hz, 1H), 3.71 (t, *J* = 10.8 Hz, 1H), 3.54 (d, *J* = 10.0 Hz, 1H), 2.76 (d, *J* = 11.6 Hz, 1H), 2.43 (s, 3H), 2.37 (s, 3H), 2.32 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ ppm 196.9, 143.9, 143.4, 137.1, 135.2, 134.1, 132.5, 132.0, 131.8, 131.3, 131.1, 130.5, 129.9, 129.8, 129.8, 129.1, 128.4, 128.2, 127.9, 126.7, 122.5, 47.5, 46.0, 40.2, 21.5, 20.2, 19.8, 7.8; HRMS (ESI/Q-TOF) *m*/*z* [M+Na]⁺ calcd for C₃₀H₂₈INNaO₃S 632.0727, found 632.0727 (0 ppm).



(3-chloro-4-methylphenyl)(1-(iodomethyl)-3-tosyl-1,2,3,4-tetrahydrobenzo[f]isoquinolin-5-yl)methanone (2s): yellow solid; 107.1 mg; 85% yield; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.91 (d, J = 8.4 Hz, 1H), 7.82–7.77 (m, 5H), 7.73–7.69 (m, 1H), 7.61–7.53 (m, 2H), 7.38–7.34 (m, 3H), 7.56 (d, J = 16.4 Hz, 1H), 4.43 (d, J = 12.0 Hz, 1H), 4.09 (d, J = 16.4 Hz, 1H), 3.82 (d, J = 10.8 Hz, 1H), 3.68 (t, J = 10.8 Hz, 1H), 3.51 (d, J = 10.8 Hz, 1H), 2.74 (d, J = 12.0 Hz, 1H), 2.47 (s, 3H), 2.43 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ ppm 195.1, 143.9, 142.2, 136.6, 134.8, 132.9, 132.3, 132.2, 131.9, 130.9, 130.9, 130.9, 130.6, 129.9, 129.8, 129.3, 128.6, 128.0, 127.7, 126.8, 122.4, 47.4, 45.8, 40.0, 21.5, 20.4, 7.6; HRMS (ESI/Q-TOF) m/z [M+Na]⁺ calcd for C₂₉H₂₅ClINNaO₃S 652.0181, found 652.0181 (0 ppm).



(1-(iodomethyl)-8-methyl-3-tosyl-1,2,3,4-tetrahydrobenzo[f]isoquinolin-5-yl)(phenyl)met hanone (2t): light yellow solid; 104.8 mg; 88% yield; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.84–7.78 (m, 5H), 7.74 (s, 1H), 7.65 (t, J = 7.6 Hz, 1H), 7.58–7.48 (m, 4H), 7.37 (d, J = 8.0Hz, 2H), 4.75 (d, J = 16.4 Hz, 1H), 4.42 (d, J = 12.0 Hz, 1H), 4.10 (d, J = 16.4 Hz, 1H), 3.81 (d, J = 10.8 Hz, 1H), 3.70 (t, J = 10.8 Hz, 1H), 3.52 (d, J = 9.6 Hz, 1H), 2.75 (d, J = 12.0 Hz, 1H), 2.51 (s, 3H), 2.43 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ ppm 197.0, 143.9, 137.6, 136.7, 133.5, 133.4, 132.5, 132.0, 131.5, 131.3, 130.6, 130.4, 130.2, 129.9, 128.9, 128.5, 127.9, 127.3, 122.3, 47.6, 45.9, 40.2, 21.5, 21.3, 7.9; HRMS (ESI/Q-TOF) *m*/*z* [M+Na]⁺ calcd for C₂₉H₂₆INNaO₃S 618.0570, found 618.0569 (0.2 ppm).



(8-chloro-1-(iodomethyl)-3-tosyl-1,2,3,4-tetrahydrobenzo[f]isoquinolin-5-yl)(phenyl)meth anone (2u): deep yellow solid; 76.4 mg; 62% yield; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.86–7.81 (m, 3H), 7.76 (d, J = 8.0 Hz, 3H), 7.70–7.60 (m, 3H), 7.50 (t, J = 7.6 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 4.73 (d, J = 16.4 Hz, 1H), 4.42 (d, J = 12.0 Hz, 1H), 4.07 (d, J = 12.4 Hz, 1H), 3.78 (d, J = 10.8 Hz, 1H), 3.68 (t, J = 10.8 Hz, 1H), 3.45 (d, J = 9.6 Hz, 1H), 2.75 (d, J =11.6 Hz, 1H), 2.43 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ ppm 196.4, 143.9, 137.0, 134.7, 133.7, 132.6, 132.4, 132.3, 131.8, 130.3, 130.1, 129.8, 129.8, 129.5, 128.6, 128.4, 128.3, 127.7, 124.2, 47.4, 45.7, 40.1, 21.5, 7.3; HRMS (ESI/Q-TOF) m/z [M+Na]⁺ calcd for C₂₈H₂₃ClINNaO₃S 638.0024, found 638.0023 (0.2 ppm).



(1-(iodomethyl)-10-methyl-3-tosyl-1,2,3,4-tetrahydrobenzo[f]isoquinolin-5-yl)(phenyl)me thanone (2v): light yellow solid; 91.7 mg; 77% yield; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.80 (dd, J = 16.8 Hz 8.0 Hz, 5H), 7.73 (s, 1H), 7.64 (t, J = 7.6 Hz, 1H), 7.56–7.47 (m, 4H), 7.36 (d, J = 8.0 Hz, 2H), 4.76 (d, J = 16.4 Hz, 1H), 4.42 (d, J = 11.6 Hz, 1H), 4.09 (d, J = 16.8Hz, 1H), 3.79 (d, J = 11.6 Hz, 1H), 3.69 (t, J = 10.4 Hz, 1H), 3.51 (d, J = 10.0 Hz, 1H), 2.73 (d, J = 11.6 Hz, 1H), 2.49 (s, 3H), 2.42 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ ppm 196.9, 143.8, 137.5, 136.6, 133.4, 133.3, 132.4, 131.9, 131.4, 131.2, 130.6, 130.3, 130.1, 129.8, 128.8, 128.4, 127.8, 127.2, 122.2, 47.5, 45.8, 40.1, 21.5, 21.3, 7.88; HRMS (ESI/Q-TOF) m/z [M+Na]⁺ calcd for C₂₉H₂₆INNaO₃S 618.0570, found 618.0571 (0.2 ppm).

Characterization Data of 2y and 2z



phenyl(*1-(prop-1-en-2-yl)-3-tosyl-1,2,3,4-tetrahydrobenzo[f]isoquinolin-5-yl)methanone* (*2y*): yellow solid; 67.4 mg; 70% yield; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.89–7.83 (m, 3H), 7.79–7.71 (m, 4H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.59–7.55 (m, 1H), 7.51–7.46 (m, 3H), 7.32 (d, J = 8.0 Hz, 2H), 5.01 (m, 1H), 4.78 (d, J = 16.4 Hz, 1H), 4.48 (s, 1H), 4.23 (d, J = 16.4 Hz, 1H), 4.10–4.04 (m, 2H), 2.93 (dd, J = 11.6 Hz 3.6 Hz, 1H), 2.41 (s, 3H), 1.96 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ ppm 197.2, 145.1, 143.5, 137.7, 133.5, 133.3, 133.1, 132.9, 132.4, 130.8, 130.5, 130.4, 129.7, 129.3, 128.6, 128.5, 128.3, 127.7, 126.4, 123.9, 115.9, 47.1, 47.0, 43.6, 21.8, 21.5; HRMS (ESI/Q-TOF) m/z [M+H]⁺ calcd for C₃₀H₂₈NO₃S 482.1784, found 482.1784 (0 ppm).



dimethyl 10-(3-chloro-4-methylbenzoyl)-4-(iodomethyl)-3,4-dihydrophenanthrene-2, 2(1H)-dicarboxylate (2z): yellow solid; 89.8 mg; 76% yield; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.92 (d, J = 8.8 Hz, 1H), 7.83 (d, J = 7.6 Hz, 2H), 7.71 (s, 1H), 7.68–7.63 (m, 2H), 7.53 (t, J = 7.6 Hz, 1H), 7.35 (d, J = 7.6 Hz, 1H), 4.15 (d, J = 7.2 Hz, 1H), 3.74 (s, 3H), 3.65 (d, J = 12.0 Hz, 1H), 3.46 (s, 3H), 3.34 (s, 2H), 3.29 (t, J = 10.0 Hz, 1H), 3.07–3.02 (m, 1H), 2.46 (s, 3H), 2.36–2.27 (m, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ ppm 196.2, 171.8, 170.6, 142.3, 136.9, 136.7, 134.8, 133.9, 131.7, 131.5, 131.1, 130.8, 130.3, 129.7, 128.5, 128.3, 128.2, 126.3, 122.8, 54.1, 52.9, 52.6, 35.7, 35.2, 33.8, 20.5, 14.8; HRMS (ESI/Q-TOF) m/z[M+H]⁺ calcd for C₂₇H₂₅CIIO₅ 591.0430, found 591.0430 (0 ppm).

Characterization Data of 3a, 4a-4c, 4i, 4j and Int-C



N-allyl-N-(3-(2-(2,3-diiodo-1H-inden-1-yl)phenyl)prop-2-yn-1-yl)-4-methylbenzenesulfo namide (3a): yellow solid; 88.4 mg; 64% yield; ¹H NMR (600 MHz, CDCl₃) δ ppm 7.76 (d, *J* = 8.4 Hz, 2H), 7.34–7.30 (m, 2H), 7.22–7.21 (m, 1H), 7.18–7.15 (m, 3H), 7.13–7.09 (m, 2H), 7.01 (d, *J* = 7.2 Hz, 1H), 6.44 (d, *J* = 7.8 Hz, 1H), 5.82–5.76 (m, 1H), 5.30–5.21 (m, 2H), 4.93 (s, 1H), 4.43 (d, *J* = 5.4 Hz, 2H), 3.97–3.94 (m, 2H), 2.23 (m, 3H); ¹³C{¹H} NMR (150 MHz, CDCl₃) δ ppm 147.2, 145.0, 143.5, 139.7, 136.2, 132.7, 132.1, 129.5, 129.3, 127.8, 127.6, 127.2, 126.7, 126.6, 123.3, 123.1, 122.9, 119.9, 116.4, 110.1, 87.1, 84.0, 62.2, 49.3, 36.8, 21.5; HRMS (ESI/Q-Orbitrap) *m/z* [M+H]⁺ calcd for C₂₈H₂₄I₂NO₂S 691.9612, found 691.9607 (0.7 ppm).



(*1-methylbenzo[f]isoquinolin-5-yl*)(*phenyl*)*methanone* (4a): white solid; 95% yield; ¹H NMR (600 MHz, CDCl₃) δ ppm 9.25 (s, 1H), 8.95 (d, J = 8.4 Hz, 1H), 8.62 (s, 1H), 7.94–7.91 (m, 3H), 7.88 (s, 1H), 7.79–7.72 (m, 2H), 7.46 (t, J = 7.8 Hz, 2H), 3.10 (s, 3H); ¹³C{¹H} NMR (150 MHz, CDCl₃) δ ppm 196.9, 148.9, 148.4, 137.7, 134.9, 134.7, 133.7, 132.7, 130.7, 130.3, 130.2, 129.9, 128.7, 128.6, 128.3, 128.0, 127.9, 125.3, 23.8; HRMS (ESI/Q-Orbitrap) m/z [M+H]⁺ calcd for C₂₁H₁₆NO 298.1226, found 298.1226 (0 ppm).



(*1-methylbenzo[f]isoquinolin-5-yl*)(*p-tolyl*)*methanone* (4b): yellow solid; 88% yield; ¹H NMR (400 MHz, CDCl₃) δ ppm 9.24 (s, 1H), 8.93 (d, J = 8.0 Hz, 1H), 8.60 (s, 1H), 7.92–7.69 (m, 6H), 7.25 (d, J = 7.6 Hz, 2H), 3.08 (s, 3H), 2.41 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ ppm 196.5, 148.7, 148.3, 144.7, 135.1, 134.6, 132.6, 130.5, 130.4, 129.8, 129.8, 129.3, 128.6, 128.3, 127.8, 127.8, 125.2, 23.8, 21.6; HRMS (ESI/Q-Orbitrap) m/z [M+H]⁺ calcd for C₂₂H₁₈NO 312.1383, found 312.1381 (0.6 ppm).



(4-ethylphenyl)(1-methylbenzo[f]isoquinolin-5-yl)methanone (4c): yellow solid; 90% yield; ¹H NMR (400 MHz, CDCl₃) δ ppm 9.25 (s, 1H), 8.89 (d, J = 8.4 Hz, 1H), 8.58 (s, 1H), 7.90–7.82 (m, 4H), 7.74–7.66 (m, 2H), 7.26 (d, J = 8.0 Hz, 2H), 3.05 (s, 3H), 2.69 (q, J = 7.6 Hz, 2H), 1.24 (t, J = 7.6 Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ ppm 196.4, 150.7, 148.7, 148.3, 135.2, 135.0, 134.5, 132.6, 130.4, 129.8, 129.7, 128.5, 128.2, 128.0, 127.8, 127.7, 125.2, 28.8, 23.7, 15.0; HRMS (ESI/Q-Orbitrap) m/z [M+H]⁺ calcd for C₂₃H₂₀NO 326.1539, found 326.1538 (0.3 ppm).



(4-chlorophenyl)(1-methylbenzo[f]isoquinolin-5-yl)methanone (4i): yellow solid; 99% yield; ¹H NMR (400 MHz, CDCl₃) δ ppm 9.22 (s, 1H), 8.95 (d, J = 8.0 Hz, 1H), 8.62 (s, 1H), 7.94 (dd, J = 7.6 Hz 1.6 Hz, 1H), 7.86 (t, J = 8.0 Hz, 3H), 7.81–7.73 (m, 2H), 7.44 (dd, J = 6.8 Hz 2.0 Hz, 2H), 3.10 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ ppm 195.6, 149.0, 148.2, 140.2, 136.0, 134.7, 134.3, 132.5, 131.6, 130.8, 130.4, 130.0, 129.0, 128.7, 128.4, 128.2, 127.9, 125.0, 23.8; HRMS (ESI/Q-Orbitrap) m/z [M+H]⁺ calcd for C₂₁H₁₅ClNO

332.0837, found 332.0836 (0.3 ppm).



(4-bromophenyl)(1-methylbenzo[f]isoquinolin-5-yl)methanone (4j): yellow solid; 97% yield; ¹H NMR (400 MHz, CDCl₃) δ ppm 9.22 (s, 1H), 8.93 (d, J = 8.0 Hz, 1H), 8.61 (s, 1H), 7.93 (d, J = 7.6 Hz, 1H), 7.86 (s, 1H), 7.80–7.71 (m, 4H), 7.60–7.58 (m, 2H), 3.09 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ ppm 195.7, 149.0, 148.2, 136.4, 134.7, 134.2, 132.5, 131.9, 131.6, 130.7, 130.4, 129.9, 129.0, 128.7, 128.4, 128.2, 127.8, 125.0, 23.8; HRMS (ESI/Q-Orbitrap) m/z [M+H]⁺ calcd for C₂₁H₁₅BrNO 376.0332, found 376.0329 (0.8 ppm).



N-allyl-4-methyl-N-(3-(2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)prop-2-yn-1-yl)benzenes ulfonamide (Int-C): light yellow solid; ¹H NMR (400 MHz, CDCl₃) δ ppm 8.02–8.00 (m, 2H), 7.88 (d, *J* = 15.6 Hz, 1H), 7.74–7.71 (m, 3H), 7.62–7.58 (m, 1H), 7.53–7.47 (m, 3H), 7.36–7.27 (m, 2H), 7.11 (d, *J* = 8.0 Hz, 3H), 5.85–5.75 (m, 1H), 5.38 (d, *J* = 16.8 Hz, 1H), 5.29–5.26 (m, 1H), 4.36 (s, 2H), 3.92 (d, *J* = 6.4 Hz, 2H), 2.18 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ ppm 190.1, 143.4, 141.9, 137.9, 135.9, 135.5, 132.9, 132.9, 131.8, 129.6, 129.4, 128.6, 128.6, 128.4, 127.6, 125.7, 123.5, 123.4, 120.2, 88.0, 83.2, 49.4, 36.7, 21.2; HRMS (ESI/Q-Orbitrap) *m/z* [M+H]⁺ calcd for C₂₈H₂₆NO₃S 456.1628, found 456.1628 (0 ppm).

¹H NMR, ¹³C NMR, and ¹⁹F NMR Spectra



¹H NMR spectrum was recorded on 400 MHz in CDCl₃.

1a





¹H NMR spectrum was recorded on 600 MHz in CDCl₃.

1b





¹H NMR spectrum was recorded on 600 MHz in CDCl₃.

1c





^{NTs} 1d ¹H NMR spectrum was recorded on 600 MHz in CDCl₃.





¹H NMR spectrum was recorded on 600 MHz in CDCl₃.

1e



200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



^{NTs} 1f ¹H NMR spectrum was recorded on 600 MHz in CDCl₃.





¹H NMR spectrum was recorded on 600 MHz in CDCl₃.

1g







S29



¹H NMR spectrum was recorded on 600 MHz in CDCl₃.

1i







^{NTs} 1k ¹H NMR spectrum was recorded on 600 MHz in CDCl₃.





S33



¹H NMR spectrum was recorded on 600 MHz in CDCl₃.

1m





^{NTs} 1n ¹H NMR spectrum was recorded on 600 MHz in CDCl₃.




10







1q





1r





1s





1t







1v





^{NTs} 1w ¹H NMR spectrum was recorded on 600 MHz in CDCl₃.





1x

0
の の の 4 の ん の ん <br< th=""></br<>
WW/4W/444W/4004W/4WW/6W/W/4WW/4/4444W/FW/94W/0000/0/00
- 900mmmnnnnnnnnnnnnnnnnnnnnnnnnnnnnnnnnn
LLLLLLLLLLLLLLLL0000000000000000000000





1y





1z











2b





2c







2d ¹H NMR spectrum was recorded on 400 MHz in CDCl₃. -1.383 000.000 130 553 752431 321 M 12 11 9 2 -6 5 1 3 10 7 0 8 4 0.97 3.00 9.04 1.03 ¹³C{H} NMR spectrum was recorded on 100 MHz in CDCl₃. 134.66 133.93.93 132.15 132.15 132.15 133.93 133.93 133.93 133.93 133.15 133.93 133.95 133.55 133.55 135.55 155.55 155.55 155.55 135.55 155.55 -196.49 52 77.32 77.00 76.68 -21.53 47.46 45.94 40.22 35.24 31.07 -7.78

ppm





2e











60 50 40 30 20 10

0 ppm

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70



¹ ^{NTs} 2h ¹H NMR spectrum was recorded on 400 MHz in CDCl₃.



¹⁹F NMR spectrum was recorded on 376 MHz in CDCl₃.





2i





¹ ¹ ^{NTs} 2j ¹H NMR spectrum was recorded on 400 MHz in CDCl₃.





0072 9911 9911 9911 9012 9012 9012 9012 901	8004411880080200 490301128000000046 488440000044000 901044000040000000000000000
0.0111111111000	4 4 4 4 4 4 M M M M M M M M M M M M M M

000.000





¹ ^{NTs} 2l ¹H NMR spectrum was recorded on 600 MHz in CDCl₃.











¹H NMR spectrum was recorded on 400 MHz in CDCl₃.

2p









¹H NMR spectrum was recorded on 400 MHz in CDCl₃.

2r





2s











2v

000000000000000000000000000000000000000	HOHN4N0HN0000000004	0
01100000000000000000000	04001000000004000	0
000000000000000000000000000000000000000	トレムない00011000140044	0
	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	0





2y




¹H NMR spectrum was recorded on 400 MHz in CDCl₃.

 $2\mathbf{z}$ 





3a

¹H NMR spectrum was recorded on 600 MHz in CDCl₃. (This by-product could not be isolated from a complex thoroughly)

	000000000000000000000000000000000000000	000777000770007000700070000700000700
04400H0H0000000	- 400000000000000000	240110000000000000000000110000004400
PPB00000000000000000000000000000000000	199900000000000000000000000000000000000	)44000000000000000000000000000000000000
	r r r r r r r r r r r r r r r v	~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~
hand have been been been been been been been be		ا امرا <del>ب او </del>



¹³C{H} NMR spectrum was recorded on 150 MHz in CDCl₃. (This by-product could not be isolated from a complex thoroughly)

-	œ	(C)	୍ଦ୍ର	-	- (° )	യ	(C)	5	S.	5	$\langle N \rangle$	ന	- 05	$\langle N \rangle$	ാ	- (° )	$\sim$	10.5	ন্দ									
N	5	£	6	N	~	0	ŝ	N	00	S	(V)	6	S	3	C	5	5	(1)	-	N	N	5-1	0	S)	00	on a	9	0
																				- H	0	N	0	5		01	[~-	LO LO
-1	4	00	ON	0	N	N	0	0	-	-	-	v	Q	C	(m)	N	0	0	0									
4	4	$\nabla$	3	3	3	3	N	N	N	N	N	N	N	N	N	N	-	-	-	5	d'	1	-	6	N	S	9	-
i 1	1 1	51	11	+ 1	+ 1	1.1	1.1	11	51	+ 1	+ 1	51	51	+ 1	. 1	+ 1	11	11	× 1	00	00	r~	F**	-	6	1	3	CV.
5	-	1	- 4	-	-	- 4	. 4		1	1	1	1	1	1	1	_	_	_	~	1	1	L.	1	1	1		T	
	-	and the second division of the second divisio	225		2	-	-		2		1				-			-		- 1	1	1	1	/				
					-	17	- L	~~~	<b>~</b> n~	n Wr	- r	-	_	-						- 1	- 1		۱r		8	2		









¹H NMR spectrum was recorded on 400 MHz in CDCl₃.

4b





4c ¹H NMR spectrum was recorded on 400 MHz in CDCl₃.









4i ¹H NMR spectrum was recorded on 400 MHz in CDCl₃.





4j ¹H NMR spectrum was recorded on 400 MHz in CDCl₃.







