Supporting Information

Palladium-catalyzed decarboxylation of vinyloxazolidine-2,4-

diones used in the divergent reaction with 2-alkynylphenols and

2-alkynylanilines

Zhong-Lie Yang,^{a,c} Zhen-Hua Wang,^{b,} Yan-Ping Zhang,^b Yong You,^b Jian-Qiang Zhao,^b Ming-Qiang Zhou,^{a,c,*} Wei-Cheng Yuan^{a,b,c,*}

^aChina National Engineering Research Center of Chiral Drugs, Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu 610041, China

^bInnovation Research Center of Chiral Drugs, Institute for Advanced Study, Chengdu University, Chengdu 610106, China

°University of Chinese Academy of Sciences, Beijing, 100049, China

screenfilm@foxmail.com yuanwc@cioc.ac.cn

Table of Contents

1. General information
2. Optimization of the reaction conditions
3. General procedures for the synthesis of compounds 1 2
4. General procedure for the synthesis of the product 3
5. General procedure for the synthesis of the product 6
6. General procedure for the synthesis of the product 4 and 7
7. Further transformation of the products
7.1 The procedure for the synthesis of compound 8
7.2 The procedure for the synthesis of compound 9
7.3 The procedure for the synthesis of compound 10
8. Scale-up experiment
9. Reference
10. X-ray crystallographic data of 3e and 4a
11. NMR spectra of substrates and products

1. General information

Reagents were purchased from commercial sources and were used as received unless mentioned otherwise. Reactions were monitored by TLC. ¹H NMR and ¹³C NMR spectra were recorded in CDCl₃ and DMSO-d₆. ¹H NMR chemical shifts are reported in ppm relative to tetramethylsilane (TMS) with the solvent resonance employed as internal standard (CDCl₃ at 7.26 ppm, DMSO- d_6 at 2.50 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. ¹³C NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as internal standard (CDCl₃ at 77.16 ppm, DMSO-d₆ at 39.51 ppm). HRMS was recorded on Bruker Q TOF. Melting points were recorded on Büchi Melting Point B-545.

2. Optimization of the reaction conditions^a

		DH 2a	2(dba) ₂ •CHCl ₃ (5 m L (10 mol%) Cu(OTf) ₂ (2.5 mol%) solvent (1.0 mL) rt, argon, 17 h		NHPMP -Me +	O NHPN Ph 4a	P
	PPh ₂ L1			PPh ₂ PPh ₂ Ph ₂ P	PPh ₂ Ph ₂ P	PPh ₂	
	PPh ₂ PPh ₂ L6	C N N Ph L7	O N Ph	Ph CN L9			
Entry	[Pd]	Solvent	Ligand	Additive	3a Yield (%) ^b	Z/E ^c	4a Yield (%) ^b
1	Pd ₂ (dba) ₃ ·CHCl ₃	CH ₃ CN	L1		18	1.5:1	21
2	Pd ₂ (dba) ₃ ·CHCl ₃	CH ₃ CN	L2		51	4.8:1	23
3	Pd ₂ (dba) ₃ ·CHCl ₃	CH ₃ CN	L3		28	1.2:1	24
4	Pd ₂ (dba) ₃ ·CHCl ₃	CH ₃ CN	L4		16	2.0:1	51
5	Pd ₂ (dba) ₃ ·CHCl ₃	CH ₃ CN	L5		10	2.8:1	58
6	Pd ₂ (dba) ₃ ·CHCl ₃	CH ₃ CN	L6		31	2.0:1	31
7	Pd ₂ (dba) ₃ ·CHCl ₃	CH ₃ CN	L7		17	2.1:1	21
8	Pd ₂ (dba) ₃ ·CHCl ₃	CH ₃ CN	L8		26	1.9:1	16
9	Pd ₂ (dba) ₃ ·CHCl ₃	CH ₃ CN	L9		37	1.4:1	28
10	Pd ₂ (dba) ₃ ·CHCl ₃	CH ₃ CN	L10		41	1.5:1	30
11	Pd ₂ (dba) ₃ ·CHCl ₃	EtOH	L2		13	1.7:1	20
12	Pd ₂ (dba) ₃ ·CHCl ₃	MeOH	L2		40	3.6:1	40
13	Pd ₂ (dba) ₃ ·CHCl ₃	ⁱ PrOH	L2		38	2.8:1	21
14	Pd ₂ (dba) ₃ ·CHCl ₃	^t BuOH	L2		15	2.2:1	14
15	Pd ₂ (dba) ₃ ·CHCl ₃	CH ₃ CN	L2		51	4.8:1	23
16	Pd ₂ (dba) ₃ ·CHCl ₃	DMF	L2		12	4.3:1	20
17	Pd ₂ (dba) ₃ ·CHCl ₃	CH ₃ CN	L2	Cu(OTf) ₂	53	1:1.1	n.p.
18	Pd ₂ (dba) ₃ ·CHCl ₃	CH ₃ CN	L2	CuI	21	1:1.4	n.p.
19	Pd ₂ (dba) ₃ ·CHCl ₃	CH ₃ CN	L2	Cu(OAc) ₂	27	1:1.1	n.p.
20		CH ₃ CN	L2	Cu(OTf) ₂	n.p.		n.p.
21 ^{d,}	Pd ₂ (dba) ₃ ·CHCl ₃	CH ₃ CN		Cu(OTf) ₂	93	1:1.2	n.p.
22 ^{d,e}	Pd ₂ (dba) ₃ ·CHCl ₃	CH ₃ CN	PPh ₃		0		94

^aThe reactions were carried out with **1a** (0.055 mmol), **2a** (0.050 mmol), and palladium catalyst (5 mol%) in a sealed tube with the specified solvent at room temperature under an argon atmosphere for 17 h. ^bYields of two isomers were determined by ¹H NMR with CH₂Br₂ as internal standard. n.p. = no product. ^cThe ratio of Z/E isomers was determined by ¹H NMR. ^dEntries 21 and 22 are the optimal reaction conditions used in our manuscript. ^e50 mol% PPh₃ was used, and run for 3 h.

3. General procedures for the synthesis of compounds 1



To a solution of **S1** (1.0 equiv.) in methanol (100 mL) and water (40 mL) was added NaOH (1.2 equiv.) under ice-bath. The mixture was stirred at room temperature for 1 h. After the completion of the reaction, methanol was removed in vacuo and the residue was acidified by conc. HCl to pH = 1 under ice bath. The mixture was extracted with ethyl acetate and washed with water, the combined organic extracts were dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was used in the next step without further purification.



Oxalyl chloride (1.1 equiv.) and two drops of DMF were added to a solution of S2 (1.0 equiv.) in dichloromethane under ice bath conditions and stirred at room temperature for 6 h. After the completion of the reaction, the suspension of 2-oxo-2-phenylacetyl chloride in DCM, was added amine (1.1 equiv.) and TEA (3.3 equiv.) at 0 °C. The reaction was stirred at room temperature for 12 h. The reaction was quenched with water, and extracted with DCM. The combined organic extracts were dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by flash chromatography to provide S4.



S4 (1.0 equiv.) was suspended in anhydrous THF under argon atmosphere and then cooled to 0 °C. Then 1 M solution of vinylmagnesiumbromide (2.5 equiv.) was added slowly via cannulating needle and the solution was stirred for 2 h at room temperature. The mixture was quenched with saturated aqueous NH_4Cl and extracted with DCM. The extracts were successively washed with water and brine, dried over anhydrous sodium sulfate and concentrated in vacuo. The residue was purified by chromatography.



 Et_3N (2.0 equiv.) and CDI (3.0 equiv.) were added to a solution of S5 (1.0 equiv.) in DCM. The resulting solution was stirred at room temperature for 6 h. The residue was cooled to room

temperature and then purified by flash column chromatography to afford product **1**. If necessary, the crude product can be recrystallized in ethyl acetate and hexane.

1a-1s were prepared according to the above method for the preparation of **1**. The data **1a-1h**, **1m-1p** were in accordance with previous work¹. The data **1l** was in accordance with previous work².

3-(4-methoxyphenyl)-5-phenyl-5-vinyloxazolidine-2,4-dione (1a)



¹**H NMR (400 MHz, Chloroform-***d***)** δ 7.67 – 7.60 (m, 2H), 7.50 – 7.39 (m, 3H), 7.35 – 7.27 (m, 2H), 7.02 – 6.94 (m, 2H), 6.28 (dd, *J* = 17.2, 10.7 Hz, 1H), 5.72 (d, *J* = 17.1 Hz, 1H), 5.51 (d, *J* = 10.8 Hz, 1H), 3.83 (s, 3H).

3,5-diphenyl-5-vinyloxazolidine-2,4-dione (1b)



¹**H NMR (400 MHz, Chloroform-***d*) δ 7.68 – 7.60 (m, 2H), 7.53 – 7.36 (m, 8H), 6.29 (dd, *J* = 17.1, 10.7 Hz, 1H), 5.72 (d, *J* = 17.1 Hz, 1H), 5.51 (d, *J* = 10.7 Hz, 1H).

5-phenyl-3-(p-tolyl)-5-vinyloxazolidine-2,4-dione (1c)



¹H NMR (400 MHz, Chloroform-*d*) δ 7.68 – 7.60 (m, 2H), 7.50 – 7.37 (m, 3H), 7.28 (s, 4H), 6.28 (dd, *J* = 17.1, 10.6 Hz, 1H), 5.72 (d, *J* = 17.1 Hz, 1H), 5.51 (d, *J* = 10.6 Hz, 1H), 2.39 (s, 3H). 3-(4-fluorophenyl)-5-phenyl-5-vinyloxazolidine-2,4-dione (1d)



¹**H NMR (400 MHz, Chloroform-***d***)** δ 7.67 – 7.58 (m, 2H), 7.51 – 7.35 (m, 5H), 7.23 – 7.12 (m, 2H), 6.28 (dd, J = 17.1, 10.7 Hz, 1H), 5.72 (d, J = 17.1 Hz, 1H), 5.52 (d, J = 10.7 Hz, 1H).

3-(4-chlorophenyl)-5-phenyl-5-vinyloxazolidine-2,4-dione (1e)

¹**H NMR (400 MHz, Chloroform-***d***)** δ 7.62 (d, J = 7.1 Hz, 2H), 7.50 – 7.37 (m, 7H), 6.27 (dd, J = 17.2, 10.6 Hz, 1H), 5.71 (d, J = 17.1 Hz, 1H), 5.52 (d, J = 10.7 Hz, 1H).

3-(4-bromophenyl)-5-phenyl-5-vinyloxazolidine-2,4-dione (1f)



¹H NMR (400 MHz, Chloroform-*d*) δ 7.66 – 7.57 (m, 4H), 7.48 – 7.40 (m, 3H), 7.37 – 7.30 (m, 2H), 6.27 (dd, *J* = 17.2, 10.7 Hz, 1H), 5.71 (d, *J* = 17.1 Hz, 1H), 5.52 (d, *J* = 10.7 Hz, 1H). 5-phenyl-3-(*m*-tolyl)-5-vinyloxazolidine-2,4-dione (1g)



¹**H NMR (400 MHz, Chloroform**-*d*) δ 7.67 – 7.60 (m, 2H), 7.48 – 7.39 (m, 3H), 7.36 (m, 1H), 7.25 – 7.15 (m, 3H), 6.28 (dd, *J* = 17.1, 10.7 Hz, 1H), 5.72 (d, *J* = 17.1 Hz, 1H), 5.51 (d, *J* = 10.7 Hz, 1H), 2.39 (s, 3H).

3-(3-chlorophenyl)-5-phenyl-5-vinyloxazolidine-2,4-dione (1h)



¹**H NMR (400 MHz, Chloroform-***d*) δ 7.66 – 7.58 (m, 2H), 7.52 – 7.33 (m, 7H), 6.28 (dd, *J* = 17.1, 10.7 Hz, 1H), 5.72 (d, *J* = 17.1 Hz, 1H), 5.53 (d, *J* = 10.6 Hz, 1H).

5-phenyl-3-(o-tolyl)-5-vinyloxazolidine-2,4-dione (1i)



White solid, m.p.70.3 – 71.0 °C.

Mixture of **major** and **minor** isomers, ¹**H NMR** (**400 MHz**, **Chloroform-***d*) δ 7.65 (m, 3.7H), 7.50 – 7.27 (m, 11.1H), 7.24 – 7.17 (m, 0.9H), 7.12 (dd, *J* = 7.9, 1.3 Hz, 1H), 6.31 (m, 1.8H), 5.78 (d, *J* = 6.8 Hz, 1H), 5.74 (d, *J* = 6.8 Hz, 0.9H), 5.55 (d, *J* = 4.9 Hz, 1H), 5.53 (d, *J* = 4.9 Hz, 0.9H), 2.23 (s, 3H), 2.06 (s, 2.6H).

Mixture of **major** and **minor** isomers, ¹³C **NMR** (**101 MHz, Chloroform-***d*) δ 170.96, 153.23, 153.19, 136.17, 136.06, 135.02, 134.79, 133.78, 133.26, 131.57, 131.53, 130.39, 130.32, 129.61, 129.42, 129.37, 129.19, 129.15, 128.22, 128.11, 127.34, 125.58, 125.41, 118.62, 118.10, 88.04, 87.99, 17.58, 17.56.

HRMS (ESI) m/z: [M + H]⁺ Calc. for C₁₈H₁₆NO₃ 294.1131; found: 294.1125. 3-(naphthalen-2-yl)-5-phenyl-5-vinyloxazolidine-2,4-dione (1j)



White solid, m.p.103.3 – 104.5 °C.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, J = 8.7 Hz, 2H), 7.91 – 7.82 (m, 2H), 7.71 – 7.64 (m, 2H), 7.59 – 7.38 (m, 6H), 6.32 (m, 1H), 5.76 (d, J = 17.3 Hz, 1H), 5.54 (d, J = 10.7 Hz, 1H).
¹³C NMR (101 MHz, Chloroform-*d*) δ 171.0, 153.3, 134.9, 133.5, 133.2, 133.1, 129.6, 129.5, 129.2, 128.4, 128.2, 127.9, 127.4, 127.1, 125.5, 125.1, 123.0, 118.5, 87.5.

HRMS (ESI) m/z: [M + Na]⁺ Calc. for C₂₁H₁₅NO₃Na 352.0950; found: 352.0944.

3-(naphthalen-1-yl)-5-phenyl-5-vinyloxazolidine-2,4-dione (1k)



White solid, m.p. 120.2 – 120.8 °C.

Mixture of **major** and **minor** isomers, ¹**H NMR** (400 MHz, Chloroform-*d*) δ 8.02 – 7.89 (m, 3.6H), 7.77 – 7.67 (m, 3.6H), 7.61 – 7.55 (m, 4H), 7.54 – 7.41 (m, 8.6H), 7.39 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.34 (dd, *J* = 8.6, 1.2 Hz, 0.8H), 6.43 (dd, *J* = 17.0, 10.6 Hz, 1H), 6.39 – 6.31 (m, 0.8H), 5.90 (d, *J* = 17.1 Hz, 1H), 5.80 (d, *J* = 17.1 Hz, 0.8H), 5.64 (d, *J* = 10.7 Hz, 1H), 5.57 (d, *J* = 10.7 Hz, 0.8H). Mixture of **major** and **minor** isomers, ¹³C **NMR** (101 MHz, Chloroform-*d*) δ 171.40, 171.38, 153.52, 135.09, 134.82, 134.60, 134.54, 133.96, 133.41, 130.97, 130.92, 129.73, 129.67, 129.47, 129.34, 129.21, 128.95, 128.87, 127.89, 127.83, 127.03, 126.96, 126.79, 126.70, 126.66, 125.61, 125.49, 125.45, 121.33, 118.63, 118.30, 88.28, 88.23.

HRMS (ESI) m/z: [M + Na]⁺ Calc. for C₂₁H₁₅NO₃Na 352.0950; found: 352.0943.

3-(4-methoxybenzyl)-5-phenyl-5-vinyloxazolidine-2,4-dione (11)



¹**H NMR (400 MHz, Chloroform-***d***)** δ 7.44 – 7.37 (m, 2H), 7.33 – 7.25 (m, 3H), 7.23 – 7.17 (m, 2H), 6.78 – 6.70 (m, 2H), 6.06 (dd, *J* = 17.1, 10.7 Hz, 1H), 5.47 (d, *J* = 17.1 Hz, 1H), 5.31 (d, *J* = 10.7 Hz, 1H), 4.53 (s, 2H), 3.67 (s, 3H).

3-(4-methoxyphenyl)-5-(p-tolyl)-5-vinyloxazolidine-2,4-dione (1m)



¹**H NMR (400 MHz, Chloroform-***d***)** δ 7.54 – 7.46 (m, 2H), 7.35 – 7.28 (m, 2H), 7.27 – 7.25 (m, 1H), 7.24 (s, 1H), 7.04 – 6.93 (m, 2H), 6.27 (dd, *J* = 17.1, 10.7 Hz, 1H), 5.70 (d, *J* = 17.1 Hz, 1H), 5.49 (d, *J* = 10.7 Hz, 1H), 3.82 (s, 3H), 2.37 (s, 3H).

5-(4-fluorophenyl)-3-(4-methoxyphenyl)-5-vinyloxazolidine-2,4-dione (1n)



¹**H NMR (400 MHz, Chloroform-***d***)** δ 7.67 – 7.57 (m, 2H), 7.35 – 7.27 (m, 2H), 7.19 – 7.08 (m, 2H), 7.03 – 6.94 (m, 2H), 6.24 (dd, *J* = 17.1, 10.7 Hz, 1H), 5.70 (d, *J* = 17.1 Hz, 1H), 5.52 (d, *J* = 10.7 Hz, 1H), 3.83 (s, 3H).

5-(4-chlorophenyl)-3-(4-methoxyphenyl)-5-vinyloxazolidine-2,4-dione (10)



¹**H NMR (400 MHz, Chloroform-***d***)** δ 7.62 – 7.54 (m, 2H), 7.46 – 7.38 (m, 2H), 7.34 – 7.27 (m, 2H), 7.02 – 6.94 (m, 2H), 6.23 (dd, *J* = 17.1, 10.7 Hz, 1H), 5.70 (d, *J* = 17.1 Hz, 1H), 5.52 (d, *J* = 10.7 Hz, 1H), 3.83 (s, 3H).

5-(4-bromophenyl)-3-(4-methoxyphenyl)-5-vinyloxazolidine-2,4-dione (1p)



¹**H NMR (400 MHz, Chloroform-***d***)** δ 7.62 – 7.55 (m, 2H), 7.55 – 7.48 (m, 2H), 7.34 – 7.27 (m, 2H), 7.02 – 6.94 (m, 2H), 6.23 (dd, *J* = 17.1, 10.7 Hz, 1H), 5.70 (d, *J* = 17.1 Hz, 1H), 5.51 (d, *J* = 10.7 Hz, 1H), 3.83 (s, 3H).

3-(4-methoxyphenyl)-5-(naphthalen-1-yl)-5-vinyloxazolidine-2,4-dione (1q)



White solid, m.p. 111.1 – 112.5 °C.

¹**H NMR (400 MHz, Chloroform-***d***)** δ 8.36 – 8.27 (m, 1H), 7.97 – 7.83 (m, 3H), 7.60 – 7.50 (m, 2H), 7.46 (dd, J = 8.2, 7.4 Hz, 1H), 7.41 – 7.32 (m, 2H), 7.06 – 6.97 (m, 2H), 6.43 (dd, J = 17.2, 10.7 Hz, 1H), 5.69 – 5.56 (m, 2H), 3.84 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 170.9, 160.1, 153.5, 135.0, 134.4, 131.4, 130.5, 129.7, 129.1, 127.4, 126.7, 126.4, 126.3, 125.1, 124.7, 123.5, 120.1, 114.8, 89.5, 55.7.

HRMS (ESI) m/z: $[M + H]^+$ Calc. for C₂₂H₁₈NO₄ 360.1237; found: 360.1226.

3-(4-methoxyphenyl)-5-(thiophen-2-yl)-5-vinyloxazolidine-2,4-dione (1r)



White solid, m.p. 59.3 – 60.5 °C.

¹**H NMR (400 MHz, Chloroform-***d***)** δ 7.43 (dd, J = 5.1, 1.3 Hz, 1H), 7.36 – 7.31 (m, 2H), 7.26 (dd, J = 2.5, 1.2 Hz, 1H), 7.07 (dd, J = 5.1, 3.7 Hz, 1H), 7.02 – 6.96 (m, 2H), 6.32 (dd, J = 17.1, 10.7 Hz, 1H), 5.78 (d, J = 17.1 Hz, 1H), 5.56 (d, J = 10.6 Hz, 1H), 3.84 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 170.2, 160.1, 137.4, 132.6, 127.9, 127.5, 127.3, 127.0, 123.3, 119.0, 114.8, 114.4, 85.6, 55.7.

HRMS (ESI) m/z: $[M + H]^+$ Calc. for C₁₆H₁₄NO₄S 316.0644; found: 316.0639.

(E)-3-(4-methoxyphenyl)-5-phenyl-5-(prop-1-en-1-yl)oxazolidine-2,4-dione (1s)



Blue gray solid, m.p. 126.4 – 128.1 °C.

¹**H NMR (400 MHz, Chloroform-***d*) δ 7.63 – 7.56 (m, 2H), 7.47 – 7.37 (m, 3H), 7.34 – 7.28 (m, 2H), 7.02 – 6.93 (m, 2H), 6.10 – 5.95 (m, 2H), 3.83 (s, 3H), 1.76 – 1.70 (m, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 172.5, 159.9, 154.0, 136.7, 134.7, 129.3, 129.1, 127.2, 125.6, 125.5, 123.6, 114.7, 87.1, 55.7, 15.0.

HRMS (ESI) m/z: [M + Na]⁺ Calc. for C₁₉H₁₇NO₄Na 346.1056; found: 346.1050.

4. General procedure for the synthesis of the product 3



To an oven-dried 25 mL of Schlenk tube equipped with a stir bar, $Pd_2(dba)_3CHCl_3$ (5 mol%) and $Cu(OTf)_2$ (2.5 mol%) was added along with **1** (0.11 mmol), **2** (0.1 mmol) and acetonitrile (2.0 mL). The reaction was stirred at 25 °C under argon atmosphere for 17 h. The reaction mixture was directly purified by silica gel column chromatography to afford the desired product **3**.

(E)-N-(4-methoxyphenyl)-2-phenyl-4-(2-(p-tolyl)benzofuran-3-yl)but-2-enamide (3a)



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1). Colorless oil; 40.7 mg, 86% yield; Z/E = 1:1.2.

¹**H NMR (400 MHz, Chloroform-***d***)** δ 7.41 (m, 6H), 7.37 – 7.33 (m, 1H), 7.32 – 7.27 (m, 2H), 7.25 – 7.17 (m, 4H), 7.16 – 7.09 (m, 3H), 6.94 (s, 1H), 6.76 – 6.68 (m, 2H), 3.68 (d, *J* = 1.0 Hz, 3H), 3.57 (d, *J* = 7.3 Hz, 2H), 2.32 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 164.3, 156.6, 154.0, 151.8, 138.6, 138.5, 137.0, 135.0, 131.0, 130.1, 129.5, 128.9, 128.0, 127.2, 124.4, 122.6, 121.8, 119.6, 114.2, 112.2, 111.2, 55.6, 25.0, 21.5.

HRMS (ESI) m/z: [M + Na]⁺ Calc. for C₃₂H₂₇NO₃Na 496.1889; found: 496.1883. *N*,2-diphenyl-4-(2-(*p*-tolyl)benzofuran-3-yl)but-2-enamide (3b)



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1). Colorless oil; 37.3 mg, 84% yield; Z/E = 1:1.5.

Mixture of **Z** and E(Z/E = 1:2.5), ¹H NMR (400 MHz, Chloroform-*d*) δ 7.59 (m, 1.2H) (*Z*), 7.50 – 7.37 (m, 7.3H) (*Z*+*E*), 7.36 – 7.10 (m, 17.1H) (*Z*+*E*), 7.03 (s, 1H) (*E*), 6.98 (t, *J* = 7.4 Hz, 1H) (*E*), 6.19 (t, *J* = 7.1 Hz, 0.4H) (*Z*), 4.14 (d, *J* = 7.1 Hz, 0.8H) (*Z*), 3.58 (d, *J* = 7.3 Hz, 2H) (*E*), 2.32 (s, 3H) (*E*), 2.28 (s, 1.2H) (*Z*).

Mixture of **Z** and **E**, ¹³**C NMR** (101 MHz, Chloroform-*d*) δ 164.38, 154.03, 153.99, 151.88, 151.85, 139.02, 138.57, 138.48, 137.86, 137.73, 137.19, 137.05, 134.86, 130.32, 130.09, 129.59, 129.51, 129.47, 129.21, 129.04, 129.02, 129.00, 128.00, 127.45, 127.15, 124.80, 124.56, 124.46, 122.77, 122.66, 120.05, 119.99, 119.75, 119.54, 113.04, 112.11, 111.18, 25.16, 25.01, 21.51, 21.49.

HRMS (ESI) m/z: $[M + Na]^+$ Calc. for $C_{31}H_{25}NO_2Na$ 466.1783; found: 466.1775.

2-phenyl-*N*-(*p*-tolyl)-4-(2-(*p*-tolyl)benzofuran-3-yl)but-2-enamide (3c)



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1). Colorless oil; 36.1 mg, 79% yield; Z/E = 1:1.3.

Mixture of **Z** and **E** (Z/E = 1:1.3), ¹**H NMR** (400 MHz, Chloroform-*d*) δ 7.59 (m, 2.4H) (Z+E), 7.46 – 7.32 (m, 9.5H) (Z+E), 7.31 – 7.20 (m, 8.9H) (Z+E), 7.17 – 7.05 (m, 8H) (Z+E), 7.00 – 6.94 (m, 3H) (*E*), 6.17 (t, J = 7.1 Hz, 0.8H) (*Z*), 4.12 (d, J = 7.1 Hz, 1.6H) (*Z*), 3.56 (d, J = 7.3 Hz, 2H) (*E*), 2.31 (s, 3H) (*E*), 2.28 (s, 2.3H) (*Z*), 2.26 (s, 2.3H) (*Z*), 2.19 (s, 3H) (*E*).

Mixture of **Z** and **E**, ¹³**C NMR** (101 MHz, Chloroform-*d*) δ 166.46, 164.29, 154.02, 153.98, 151.85, 151.81, 138.74, 138.58, 138.52, 138.44, 137.26, 137.09, 135.31, 135.17, 134.95, 134.54, 134.46, 134.19, 130.33, 130.08, 129.66, 129.57, 129.51, 129.46, 129.45, 128.97, 128.92, 128.44, 128.11, 128.00, 127.41, 127.14, 124.44, 122.76, 122.64, 120.13, 120.02, 119.77, 119.55, 113.09, 112.15, 111.15, 25.15, 24.97, 21.49, 21.47, 21.03, 20.96.

HRMS (ESI) m/z: [M + Na]⁺ Calc. for C₃₂H₂₇NO₂Na 480.1940; found: 480.1932.

N-(4-fluorophenyl)-2-phenyl-4-(2-(p-tolyl)benzofuran-3-yl)but-2-enamide (3d)



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1). Colorless oil; 39.7 mg, 86% yield; Z/E = 1:1.8.

Mixture of **Z** and E(Z/E = 1:1.8), ¹**H NMR (400 MHz, Chloroform-***d*) δ 7.62 – 7.54 (m, 1.7H) (Z), 7.47 – 7.36 (m, 7.7H) (Z+E), 7.35 – 7.20 (m, 10H) (Z+E), 7.18 – 7.08 (m, 5.3H) (Z+E), 7.00 (s, 1H) (E), 6.94 (t, J = 8.6 Hz, 1.2H) (Z), 6.86 (t, J = 8.7 Hz, 2H) (E), 6.19 (t, J = 7.1 Hz, 0.6H) (Z), 4.11 (d, J = 7.1 Hz, 1.1H) (Z), 3.56 (d, J = 7.3 Hz, 2H) (E), 2.31 (s, 3H) (E), 2.28 (s, 1.6H) (Z).

Mixture of **Z** and **E**, ¹³**C NMR** (101 MHz, Chloroform-*d*) δ 166.50, 164.39, 154.03, 153.98, 151.87, 151.84, 139.16, 138.58, 138.49, 138.31, 137.15, 136.82, 134.90, 134.75, 133.88, 133.85, 133.74, 133.71, 130.27, 130.05, 130.04, 129.57, 129.53, 129.46, 129.03, 129.02, 128.53, 128.07, 127.97, 127.40, 127.17, 127.13, 124.47, 122.76, 122.66, 121.90, 121.86, 121.82, 121.78, 119.71, 119.49, 115.91, 115.76, 115.69, 115.54, 112.97, 112.03, 111.21, 111.19, 25.16, 24.98, 21.49, 21.47. HRMS (ESI) m/z: [M + H]⁺ Calc. for C₃₁H₂₅FNO₂ 462.1870; found: 462.1866.

 $15 (ESI) 112. [11 + 11] Calc. 101 C_3(11251 110) + 02.1070, 10414. +02.1000.$

N-(4-chlorophenyl)-2-phenyl-4-(2-(p-tolyl)benzofuran-3-yl)but-2-enamide~(3e)



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1). Colorless oil; 40.6 mg, 85% yield; Z/E = 1:2.

Mixture of **Z** and **E** (Z/E = 1:1.6), ¹**H NMR (400 MHz, Chloroform-***d*) δ 7.61 – 7.53 (m, 1.9H) (Z), 7.46 – 7.36 (m, 7.8H) (Z+E), 7.34 – 7.19 (m, 12H) (Z+E), 7.18 – 7.08 (m, 7.5H) (Z+E), 7.02 (s, 1H) (E), 6.19 (t, J = 7.1 Hz, 0.6H) (Z), 4.10 (d, J = 7.1 Hz, 1.2H) (Z), 3.56 (d, J = 7.3 Hz, 2H) (E), 2.31 (s, 3H) (E), 2.27 (s, 1.8H) (Z).

Mixture of **Z** and **E**, ¹³**C NMR** (101 MHz, Chloroform-*d*) δ 166.51, 164.37, 154.02, 153.97, 151.88, 151.86, 139.44, 138.61, 138.51, 138.23, 137.04, 136.76, 136.43, 136.30, 135.16, 134.62, 130.24, 130.05, 130.01, 129.69, 129.57, 129.49, 129.46, 129.14, 129.09, 129.05, 129.02, 128.58, 128.53, 128.04, 127.95, 127.41, 127.15, 127.12, 124.49, 122.77, 122.67, 121.22, 121.20, 119.68, 119.47, 112.91, 111.97, 111.22, 111.20, 25.16, 25.00, 21.50, 21.48.

HRMS (ESI) m/z: [M + Na]⁺ Calc. for C₃₁H₂₄ClNO₂Na 500.1394; found: 500.1392.

N-(4-bromophenyl)-2-phenyl-4-(2-(p-tolyl)benzofuran-3-yl)but-2-enamide (3f)



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1). Colorless oil; 44.9 mg, 86% yield; Z/E = 1:2.1.

Mixture of **Z** and **E** (Z/E = 1:1.2), ¹**H NMR (400 MHz, Chloroform-***d*) δ 7.62 – 7.52 (m, 2.6H) (Z), 7.47 – 7.30 (m, 11.4H) (Z+E), 7.29 – 7.19 (m, 13.4H) (Z+E), 7.12 (m, 5.5H) (Z+E), 7.01 (s, 1H) (E), 6.21 (t, J = 7.1 Hz, 0.9H) (Z), 4.11 (d, J = 7.1 Hz, 1.7H) (Z), 3.56 (d, J = 7.3 Hz, 2H) (E), 2.31 (s, 3H) (E), 2.28 (s, 2.5H) (Z).

Mixture of **Z** and **E**, ¹³**C NMR** (101 MHz, Chloroform-*d*) δ 166.49, 164.36, 154.03, 153.98, 151.89, 151.86, 139.51, 138.63, 138.52, 138.22, 137.04, 136.94, 136.81, 136.78, 135.29, 134.61, 132.11, 131.97, 130.24, 130.05, 130.02, 129.58, 129.47, 129.11, 129.06, 128.60, 128.04, 127.96, 127.44,

127.16, 127.13, 124.50, 122.78, 122.68, 121.52, 119.68, 119.47, 117.32, 117.13, 112.91, 111.96, 111.23, 111.20, 25.16, 25.02, 21.50, 21.49.

HRMS (ESI) m/z: $[M + Na]^+$ Calc. for $C_{31}H_{24}BrNO_2Na$ 544.0888, 546.0868; found: 544.0881, 546.0866.

2-phenyl-N-(m-tolyl)-4-(2-(p-tolyl)benzofuran-3-yl)but-2-enamide (3g)



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1). Colorless oil; 30.2 mg, 66% yield; Z/E = 1:1.4.

Mixture of **Z** and *E* (Z/E = 1:1.4), ¹**H** NMR (400 MHz, Chloroform-*d*) δ 7.59 (m, 2.2H) (*Z*), 7.47 – 7.32 (m, 8.6H) (*Z*+*E*), 7.31 – 7.20 (m, 8.2H) (*Z*+*E*), 7.18 – 7.09 (m, 9.1H) (*Z*+*E*), 7.05 (t, *J* = 7.7 Hz, 1H) (*E*), 6.98 (s, 1H) (*E*), 6.89 (d, *J* = 7.6 Hz, 0.8H) (*Z*), 6.80 (d, *J* = 7.4 Hz, 1H) (*E*), 6.18 (t, *J* = 7.1 Hz, 0.7H) (*Z*), 4.13 (d, *J* = 7.1 Hz, 1.4H) (*Z*), 3.57 (d, *J* = 7.3 Hz, 2H) (*E*), 2.31 (s, 3H) (*E*), 2.28 (s, 4.2H) (*Z*), 2.20 (s, 3H) (*E*).

Mixture of **Z** and **E**, ¹³**C NMR** (101 MHz, Chloroform-*d*) δ 166.52, 164.36, 154.03, 153.99, 151.87, 151.83, 139.16, 138.95, 138.87, 138.57, 138.54, 138.46, 137.76, 137.65, 137.21, 137.11, 134.90, 134.72, 130.33, 130.08, 129.58, 129.49, 129.46, 129.02, 129.00, 128.96, 128.85, 128.48, 128.11, 128.00, 127.42, 127.17, 127.15, 125.61, 125.37, 124.45, 122.76, 122.65, 120.66, 120.61, 119.76, 119.55, 117.13, 117.08, 113.07, 112.12, 111.17, 25.16, 24.99, 21.63, 21.53, 21.50, 21.47.

HRMS (ESI) m/z: $[M + Na]^+$ Calc. for $C_{32}H_{27}NO_2Na$ 480.1940; found: 480.1932.

N-(3-chlorophenyl)-2-phenyl-4-(2-(*p*-tolyl)benzofuran-3-yl)but-2-enamide (3h)



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1). Colorless oil; 40.2 mg, 84% yield; Z/E = 1:2.1.

Mixture of **Z** and E(Z/E = 1:2.2), ¹**H NMR (400 MHz, Chloroform-***d*) δ 7.62 – 7.55 (m, 1.8H) (Z), 7.41 (m, 7.6H) (Z+E), 7.36 – 7.21 (m, 7.8H) (Z+E), 7.19 – 7.04 (m, 7.9H) (Z+E), 7.02 (s, 1H) (E), 6.95 (m, 1H) (E), 6.21 (t, J = 7.1 Hz, 0.5H) (Z), 4.12 (d, J = 7.1 Hz, 0.9H) (Z), 3.57 (d, J = 7.3 Hz, 2H) (E), 2.32 (s, 3H) (E), 2.28 (s, 1.3H) (Z).

Mixture of **Z** and **E**, ¹³**C NMR** (101 MHz, Chloroform-*d*) δ 166.54, 164.41, 154.04, 153.99, 151.93, 151.88, 139.61, 138.99, 138.86, 138.64, 138.53, 138.16, 136.98, 136.75, 135.41, 134.84, 134.65, 134.55, 130.24, 130.13, 130.04, 130.02, 129.60, 129.59, 129.48, 129.14, 129.08, 128.62, 128.04, 127.96, 127.43, 127.17, 127.15, 124.76, 124.55, 124.50, 122.79, 122.69, 120.05, 120.01, 119.69, 119.48, 117.97, 117.92, 112.90, 111.96, 111.23, 111.21, 25.16, 25.02, 21.51, 21.48.

HRMS (ESI) m/z: $[M + Na]^+$ Calc. for C₃₁H₂₄ClNO₂Na 500.1394, 502.1364; found: 500.1389, 502.1377.

2-phenyl-N-(o-tolyl)-4-(2-(p-tolyl)benzofuran-3-yl)but-2-enamide (3i)



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1). Colorless oil; 36.6 mg, 80% yield; Z/E = 1:1.9.

Mixture of **Z** and **E** (Z/E = 1:1.9), ¹**H NMR** (400 MHz, Chloroform-*d*) δ 7.97 (d, J = 8.1 Hz, 1.5H) (Z), 7.61 (t, J = 7.9 Hz, 1.5H) (Z), 7.48 – 7.35 (m, 7.7H) (Z+E), 7.34 – 7.21 (m, 6.1H) (Z+E), 7.18 – 7.06 (m, 7H) (Z+E), 7.06 – 6.87 (m, 4.2H) (Z+E), 6.18 (t, J = 7.0 Hz, 0.5H) (Z), 4.22 (d, J = 7.0 Hz, 1H) (E), 3.58 (d, J = 7.3 Hz, 2H) (E), 2.32 (s, 3H) (E), 2.28 (s, 1.5H) (Z), 1.95 (s, 1.5H) (Z), 1.73 (s, 3H) (E).

Mixture of **Z** and **E**, ¹³**C NMR** (101 MHz, Chloroform-*d*) δ 166.28, 164.09, 154.03, 153.98, 151.86, 151.83, 138.89, 138.53, 138.45, 138.26, 137.69, 137.13, 136.18, 136.08, 135.65, 135.15, 130.63, 130.37, 130.34, 130.09, 130.06, 129.56, 129.47, 129.45, 128.98, 128.69, 128.53, 128.13, 128.02, 127.83, 127.64, 127.17, 127.15, 127.01, 126.99, 125.36, 124.76, 124.44, 122.74, 122.63, 121.59, 119.76, 119.57, 113.19, 112.10, 111.16, 25.12, 25.01, 21.49, 21.47, 17.69, 17.19.

HRMS (ESI) m/z: [M + H]⁺ Calc. for C₃₂H₂₈NO₂ 458.2121; found: 458.2118.

N-(naphthalen-2-yl)-2-phenyl-4-(2-(p-tolyl)benzofuran-3-yl)but-2-enamide (3j)



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1). Colorless oil; 42.0 mg, 85% yield; Z/E = 1:1.7.

Mixture of **Z** and E(Z/E = 1:1.6), ¹**H NMR (400 MHz, Chloroform-***d***)** δ 8.21 (s, 0.6H) (*Z*), 8.07 (s, 1H) (*E*), 7.78 – 7.67 (m, 2H) (*Z*+*E*), 7.62 (m, 5H) (*Z*+*E*), 7.49 – 7.36 (m, 8.6H) (*Z*+*E*), 7.35 – 7.20 (m, 11.6H) (*Z*+*E*), 7.19 – 7.05 (m, 6.4H) (*Z*+*E*), 6.22 (t, *J* = 7.1 Hz, 0.6H) (*Z*), 4.17 (d, *J* = 7.1 Hz, 1.2H) (*Z*), 3.59 (d, *J* = 7.3 Hz, 2H) (*E*), 2.31 (s, 3H) (*E*), 2.20 (s, 1.9H) (*Z*).

Mixture of **Z** and **E**, ¹³**C NMR** (101 MHz, Chloroform-*d*) δ 166.71, 164.55, 154.03, 153.99, 151.89, 151.84, 139.14, 138.55, 138.48, 137.20, 137.05, 135.28, 135.16, 134.94, 134.82, 133.94, 133.88, 130.93, 130.79, 130.30, 130.11, 130.06, 129.55, 129.46, 129.04, 128.90, 128.72, 128.53, 128.06, 127.99, 127.85, 127.80, 127.70, 127.62, 127.46, 127.14, 126.73, 126.60, 125.30, 125.16, 124.46, 122.78, 122.67, 119.93, 119.89, 119.75, 119.53, 116.86, 116.79, 113.02, 112.08, 111.18, 25.20, 25.03, 21.49, 21.40.

HRMS (ESI) m/z: [M + Na]⁺ Calc. for C₃₅H₂₇NO₂Na 516.1940; found: 516.1934.

N-(naphthalen-1-yl)-2-phenyl-4-(2-(*p*-tolyl)benzofuran-3-yl)but-2-enamide (3k)



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1). Colorless oil; 36.0 mg, 73% yield; Z/E = 1:2.6.

Mixture of **Z** and **E** (Z/E = 1:2.5), ¹**H NMR** (**400 MHz, Chloroform-***d*) δ 8.10 (d, J = 7.5 Hz, 0.4H) (Z), 8.04 (d, J = 7.6 Hz, 1H) (E), 7.78 (d, J = 8.2 Hz, 0.4H) (Z), 7.72 (d, J = 8.1 Hz, 1H) (E), 7.66 – 7.59 (m, 2H) (E), 7.56 – 7.22 (m, 19.5H) (Z+E), 7.19 – 7.05 (m, 6H) (Z+E), 6.25 (t, J = 7.0 Hz, 0.4H) (Z), 4.27 (d, J = 7.0 Hz, 0.8H) (Z), 3.62 (d, J = 7.4 Hz, 2H) (E), 2.32 (s, 3H) (E), 2.24 (s, 1.2H) (Z).

Mixture of **Z** and **E**, ¹³**C** NMR (101 MHz, Chloroform-*d*) δ 166.77, 164.61, 154.05, 154.00, 151.92, 151.87, 139.29, 138.53, 138.48, 138.25, 137.71, 137.05, 136.44, 135.18, 134.24, 134.07, 132.42, 132.08, 130.37, 130.18, 130.11, 129.66, 129.56, 129.47, 129.15, 129.12, 128.98, 128.95, 128.66, 128.11, 128.03, 127.90, 127.17, 127.16, 126.54, 126.48, 126.34, 126.11, 125.97, 125.93, 125.91, 125.50, 124.46, 122.78, 122.66, 120.44, 120.28, 119.85, 119.78, 119.62, 119.58, 113.18, 112.09, 111.18, 25.21, 25.05, 21.51, 21.43.

HRMS (ESI) m/z: [M + Na]⁺ Calc. for C₃₅H₂₇NO₂Na 516.1940; found: 516.1934.

(E)-N-(4-methoxybenzyl)-2-phenyl-4-(2-(p-tolyl)benzofuran-3-yl)but-2-enamide (3l)



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1). White solid, m.p. 143.5 - 144.0 °C; 23.4 mg, 48% yield; *Z/E* = 1:1.2.

¹**H NMR (400 MHz, Chloroform-***d*) δ 7.46 – 7.27 (m, 7H), 7.22 – 7.08 (m, 7H), 7.06 – 6.99 (m, 2H), 6.76 – 6.69 (m, 2H), 5.61 (t, *J* = 5.8 Hz, 1H), 4.31 (d, *J* = 5.8 Hz, 2H), 3.68 (s, 3H), 3.53 (d, *J* = 7.3 Hz, 2H), 2.31 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 166.4, 159.0, 154.0, 151.8, 138.4, 138.0, 136.5, 135.2, 130.4, 130.1, 130.0, 129.4, 129.2, 128.9, 128.6, 128.0, 127.1, 124.4, 122.6, 119.6, 114.1, 112.3, 111.1, 55.4, 43.5, 24.8, 21.5.

HRMS (ESI) m/z: [M + Na]⁺ Calc. for C₃₃H₂₉NO₃Na 510.2045; found: 510.2040.

(E)-N-(4-methoxyphenyl)-2-(p-tolyl)-4-(2-(p-tolyl)benzofuran-3-yl)but-2-enamide (3m)



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1). White solid, m.p. 162.3 - 163.0 °C; 41.4 mg, 85% yield; *Z/E* = 1:1.3.

¹**H NMR (400 MHz, Chloroform-***d*) δ 7.43 – 7.34 (m, 4H), 7.27 – 7.23 (m, 2H), 7.22 – 7.14 (m, 6H), 7.14 – 7.09 (m, 3H), 6.99 (s, 1H), 6.76 – 6.68 (m, 2H), 3.68 (s, 3H), 3.56 (d, *J* = 7.3 Hz, 2H), 2.37 (s, 3H), 2.32 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 164.4, 156.5, 154.0, 151.8, 138.8, 138.5, 138.4, 137.0, 131.9, 131.1, 130.1, 130.0, 129.4, 128.1, 127.2, 124.4, 122.6, 121.7, 119.6, 114.1, 112.3, 111.1, 55.6, 25.0, 21.5, 21.5.

HRMS (ESI) m/z: [M + Na]⁺ Calc. for C₃₃H₂₉NO₃Na 510.2045; found: 510.2038.

(E) - 2 - (4 - fluorophenyl) - N - (4 - methoxyphenyl) - 4 - (2 - (p - tolyl) benzofuran - 3 - yl) but - 2 - enamide



Following the general procedure, the crude product was purified by flash chromatography

(petroleum ether/ethyl acetate = 5:1). White solid, m.p. 125.3 - 125.9 °C; 40.8 mg, 83% yield; Z/E = 1:1.3.

¹**H** NMR (400 MHz, Chloroform-*d*) δ 7.40 (dd, J = 8.2, 3.7 Hz, 3H), 7.35 (dd, J = 7.7, 1.4 Hz, 1H), 7.27 – 7.18 (m, 6H), 7.17 – 7.10 (m, 3H), 7.07 (m, 2H), 6.87 (s, 1H), 6.76 – 6.68 (m, 2H), 3.68 (s, 3H), 3.56 (d, J = 7.4 Hz, 2H), 2.33 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 164.2, 162.9 (d, *J* = 247.1 Hz), 156.7, 154.0, 151.8, 138.9, 138.6, 136.2, 131.9 (d, *J* = 8.1 Hz), 130.9, 130.8 (d, *J* = 3.6 Hz), 130.0, 129.5, 128.0, 127.2, 124.5, 122.7, 121.8, 119.5, 116.5 (d, *J* = 21.6 Hz), 114.2, 112.0, 111.2, 55.6, 24.9, 21.5.

HRMS (ESI) m/z: [M + Na]⁺ Calc. for C₃₂H₂₆FNO₃Na 514.1795; found: 514.1792.

(E)-2-(4-chlorophenyl)-N-(4-methoxyphenyl)-4-(2-(p-tolyl)benzofuran-3-yl)but-2-enamide



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1). White solid, m.p. 135.0 - 135.8 °C; 41.7 mg, 82% yield; *Z/E* = 1:1.3.

¹**H NMR (400 MHz, Chloroform-***d*) δ 7.41 – 7.31 (m, 6H), 7.23 – 7.19 (m, 3H), 7.19 – 7.09 (m, 6H), 6.84 (s, 1H), 6.75 – 6.68 (m, 2H), 3.67 (s, 3H), 3.55 (d, *J* = 7.4 Hz, 2H), 2.34 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 164.0, 156.7, 154.0, 151.8, 138.9, 138.7, 136.2, 135.0, 133.3, 131.4, 130.8, 129.9, 129.6, 129.5, 127.9, 127.2, 124.5, 122.7, 121.8, 119.5, 114.2, 111.9, 111.2, 55.6, 24.9, 21.5.

HRMS (ESI) m/z: $[M + Na]^+$ Calc. for C₃₂H₂₆ClNO₃Na 530.1499, 532.1469; found: 530.1498, 532.1482.

(E)-2-(4-bromophenyl)-N-(4-methoxyphenyl)-4-(2-(p-tolyl)benzofuran-3-yl)but-2-enamide



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1). White solid, m.p. 129.5 - 130.2 °C; 44.2 mg, 80% yield; *Z/E* = 1:1.4.

¹**H NMR (400 MHz, Chloroform-***d*) δ 7.50 – 7.45 (m, 2H), 7.38 (m, 4H), 7.23 (m, 3H), 7.19 – 7.06 (m, 6H), 6.84 (s, 1H), 6.76 – 6.69 (m, 2H), 3.68 (s, 3H), 3.56 (d, *J* = 7.4 Hz, 2H), 2.35 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 163.9, 156.7, 154.0, 151.9, 138.9, 138.7, 136.2, 133.7, 132.6, 131.6, 130.8, 129.9, 129.5, 127.9, 127.2, 124.5, 123.2, 122.7, 121.9, 119.5, 114.2, 111.9, 111.3, 55.6, 24.9, 21.6.

HRMS (ESI) m/z: $[M + Na]^+$ Calc. for C₃₂H₂₆BrNO₃Na 574.0994, 576.0974; found: 574.0992, 576.0978.

(E)-N-(4-methoxyphenyl)-2-(naphthalen-1-yl)-4-(2-(p-tolyl)benzofuran-3-yl)but-2-enamide (3q)



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1). White solid, m.p. 162.5 - 163.3 °C; 39.8 mg, 76% yield; *Z/E* = 1:1.3.

¹**H NMR (400 MHz, Chloroform-***d*) δ 7.89 (m, 2H), 7.85 – 7.79 (m, 1H), 7.59 – 7.36 (m, 6H), 7.36 – 7.27 (m, 3H), 7.17 (m, 1H), 7.12 – 7.05 (m, 3H), 6.96 (d, *J* = 7.9 Hz, 2H), 6.82 (s, 1H), 6.68 – 6.61 (m, 2H), 3.64 (s, 3H), 3.43 (d, *J* = 7.2 Hz, 2H), 2.27 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 164.2, 156.6, 153.9, 151.8, 140.8, 138.3, 135.3, 134.1, 132.1, 132.0, 130.9, 130.1, 129.6, 129.3, 128.8, 128.5, 127.9, 127.4, 127.0, 126.9, 125.8, 125.3, 124.4, 122.6, 122.0, 119.6, 114.1, 112.0, 111.1, 55.5, 25.1, 21.5.

HRMS (ESI) m/z: [M + Na]⁺ Calc. for C₃₆H₂₉NO₃Na 546.2045; found: 546.2042.

N-(4-methoxyphenyl)-2-(thiophen-2-yl)-4-(2-(*p*-tolyl)benzofuran-3-yl)but-2-enamide (3r)



Following the general procedure. the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1). Colorless oil; 42.2 mg, 88% yield; Z/E = 1:2.

Mixture of **Z** and **E** (Z/E = 1:1.7), ¹**H NMR (400 MHz, Chloroform-***d*) δ 7.63 – 7.53 (m, 1.8H) (Z), 7.50 – 7.34 (m, 7.3H) (Z+E), 7.32 – 7.19 (m, 5.3H) (Z+E), 7.19 – 7.09 (m, 7H) (Z+E), 7.06 (dd, J = 3.5, 1.1 Hz, 1H) (E), 6.98 (d, J = 3.6 Hz, 0.6H) (Z), 6.89 (dd, J = 5.1, 3.7 Hz, 0.6H) (Z), 6.85 – 6.79 (m, 1.2H) (Z), 6.76 – 6.70 (m, 2H) (E), 6.21 (t, J = 7.2 Hz, 0.6H) (Z), 4.04 (d, J = 7.2 Hz, 1.2H) (Z), 3.74 (s, 1.8H) (Z), 3.71 (d, J = 7.2 Hz, 2H) (E), 3.68 (s, 3H) (E), 2.32 (s, 3H) (E), 2.29 (s, 1.8H) (Z). Mixture of **Z** and **E**, ¹³**C NMR (101 MHz, Chloroform-***d*) δ 165.26, 163.76, 156.92, 156.70, 154.02, 153.99, 152.01, 151.90, 141.82, 140.56, 138.60, 138.56, 135.03, 132.87, 132.13, 130.88, 130.62, 130.22, 130.15, 130.07, 129.60, 129.50, 129.49, 128.20, 128.02, 127.95, 127.81, 127.20, 126.05, 125.62, 124.50, 124.48, 122.81, 122.71, 121.95, 121.89, 119.80, 119.50, 114.37, 114.20, 112.64, 111.89, 111.19, 55.66, 55.57, 25.35, 25.09, 21.50, 21.49.

HRMS (ESI) m/z: [M + Na]⁺ Calc. for C₃₀H₂₅NO₃SNa 502.1453; found: 502.1448.

(E)-N-(4-methoxyphenyl)-2-phenyl-4-(2-(p-tolyl)benzofuran-3-yl)pent-2-enamide (3s)



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1). Colorless oil; 23.4 mg, 48% yield; Z/E = 1:2.3. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.78 (dd, J = 6.8, 2.0 Hz, 1H), 7.62 (d, J = 10.3 Hz, 1H), 7.43 – 7.36 (m, 1H), 7.23 – 7.10 (m, 9H), 7.01 (dd, J = 7.8, 2.9 Hz, 4H), 6.82 (s, 1H), 6.74 – 6.67 (m, 2H), 3.94 (dq, J = 10.3, 7.0 Hz, 1H), 3.67 (s, 3H), 2.32 (s, 3H), 1.49 (d, J = 7.0 Hz, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 164.5, 156.6, 154.5, 150.8, 143.5, 138.4, 135.5, 134.7, 131.0, 129.8, 129.2, 129.1, 128.5, 128.3, 128.0, 127.7, 124.2, 122.6, 121.7, 121.3, 117.7, 114.1, 111.4, 55.6, 31.2, 21.5, 21.1.

HRMS (ESI) m/z: [M + Na]⁺ Calc. for C₃₃H₂₉NO₃Na 510.2045; found: 510.2039.

(E)-N-(4-methoxyphenyl)-2-phenyl-4-(2-phenylbenzofuran-3-yl)but-2-enamide (3t)



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1). Colorless oil; 38.6 mg, 84% yield; Z/E = 1:1.5.

¹**H NMR (400 MHz, Chloroform-***d*) δ 7.56 – 7.49 (m, 2H), 7.46 – 7.35 (m, 5H), 7.31 (m, 4H), 7.27 – 7.21 (m, 4H), 7.20 – 7.12 (m, 2H), 6.94 (s, 1H), 6.76 – 6.68 (m, 2H), 3.68 (s, 3H), 3.59 (d, *J* = 7.3 Hz, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 164.2, 156.6, 154.1, 151.6, 138.5, 137.1, 134.9, 131.0, 130.8, 130.1, 130.0, 129.5, 129.0, 128.7, 128.4, 127.2, 124.7, 122.7, 121.8, 119.7, 114.2, 112.8, 111.2, 55.6, 25.0.

HRMS (ESI) m/z: [M + Na]⁺ Calc. for C₃₁H₂₅NO₃Na 482.1732; found: 482.1726.

(*E*)-*N*-(4-methoxyphenyl)-4-(2-(4-methoxyphenyl)benzofuran-3-yl)-2-phenylbut-2-enamide (3u)



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1). Colorless oil; 33.3 mg, 68% yield; Z/E = 1:1.1.

¹**H NMR (400 MHz, Chloroform-***d*) δ 7.47 – 7.39 (m, 5H), 7.38 – 7.27 (m, 4H), 7.23 (dd, *J* = 8.1, 6.1 Hz, 3H), 7.19 – 7.11 (m, 2H), 6.94 (s, 1H), 6.87 – 6.81 (m, 2H), 6.77 – 6.68 (m, 2H), 3.78 (s, 3H), 3.68 (s, 3H), 3.55 (d, *J* = 7.3 Hz, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 164.3, 159.8, 156.6, 153.9, 151.7, 138.7, 137.0, 135.0, 131.0, 130.2, 130.1, 129.5, 128.9, 128.7, 124.3, 123.5, 122.6, 121.8, 119.5, 114.2, 114.2, 111.4, 111.1, 55.6, 55.5, 25.0.

HRMS (ESI) m/z: [M + Na]⁺ Calc. for C₃₂H₂₇NO₄Na 512.1838; found: 512.1832.

(E)-4-(2-(4-fluorophenyl)benzofuran-3-yl)-N-(4-methoxyphenyl)-2-phenylbut-2-enamide (3v)



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1). Colorless oil; 37.2 mg, 78% yield; Z/E = 1:1.5.

¹**H NMR (400 MHz, Chloroform-***d*) δ 7.49 – 7.35 (m, 7H), 7.28 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.25 – 7.18 (m, 4H), 7.18 – 7.12 (m, 1H), 6.99 (t, *J* = 8.7 Hz, 2H), 6.94 (s, 1H), 6.76 – 6.69 (m, 2H), 3.68 (s, 3H), 3.55 (d, *J* = 7.4 Hz, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 164.1, 162.7 (d, *J* = 250.0 Hz), 156.7, 154.0, 150.7, 138.2, 137.1, 134.9, 131.0, 130.1, 129.9, 129.5, 129.1 (d, *J* = 8.3 Hz), 129.0, 127.1 (d, *J* = 3.3 Hz), 124.8, 122.8, 121.8, 119.7, 115.8 (d, *J* = 21.8 Hz), 114.2, 112.6, 111.2, 55.6, 24.9.

HRMS (ESI) m/z: $[M + H]^+$ Calc. for $C_{31}H_{25}FNO_3$ 478.1819; found: 478.1813.

(E)-4-(2-(4-chlorophenyl)benzofuran-3-yl)-N-(4-methoxyphenyl)-2-phenylbut-2-enamide

(**3**w)



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1). White solid, m.p. 147.6 - 148.8 °C; 37.5 mg, 76% yield; *Z/E* = 1:1.6.

¹**H NMR (400 MHz, Chloroform-***d*) δ 7.46 – 7.37 (m, 7H), 7.31 – 7.25 (m, 4H), 7.25 – 7.13 (m, 5H), 6.94 (s, 1H), 6.77 – 6.68 (m, 2H), 3.68 (s, 3H), 3.57 (d, *J* = 7.4 Hz, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 164.1, 156.7, 154.1, 150.4, 138.1, 137.2, 134.8, 134.3, 130.9, 130.0, 129.8, 129.5, 129.3, 129.1, 129.0, 128.3, 125.0, 122.9, 121.8, 119.8, 114.2, 113.3, 111.3, 55.6, 24.9.

HRMS (ESI) m/z: $[M + Na]^+$ Calc. for C₃₁H₂₄ClNO₃Na 516.1343, 518.1313; found: 516.1339, 518.1326.

(*E*)-4-(2-(4-bromophenyl)benzofuran-3-yl)-*N*-(4-methoxyphenyl)-2-phenylbut-2-enamide (3x)



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1). White solid, m.p. 167.2 - 167.6 °C; 40.4 mg, 75% yield; *Z/E* = 1:1.5.

¹**H NMR (400 MHz, Chloroform-***d*) δ 7.46 – 7.33 (m, 9H), 7.28 (d, *J* = 2.0 Hz, 1H), 7.27 – 7.12 (m, 6H), 6.94 (s, 1H), 6.76 – 6.68 (m, 2H), 3.68 (s, 3H), 3.56 (d, *J* = 7.4 Hz, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 164.1, 156.7, 154.1, 150.4, 138.0, 137.2, 134.8, 131.9, 130.9, 130.0, 129.8, 129.7, 129.5, 129.1, 128.6, 125.0, 122.9, 122.5, 121.8, 119.8, 114.2, 113.5, 111.3, 55.6, 24.9.

HRMS (ESI) m/z: $[M + Na]^+$ Calc. for C₃₁H₂₄BrNO₃Na 560.0838, 562.0817; found: 560.0832, 562.0818.

(E)-N-(4-methoxyphenyl)-2-phenyl-4-(2-(*m*-tolyl)benzofuran-3-yl)but-2-enamide (3y)



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1). Colorless oil; 31.3 mg, 66% yield; Z/E = 1:1.2.

¹**H NMR (400 MHz, Chloroform-***d*) δ 7.43 – 7.35 (m, 6H), 7.29 (m, 3H), 7.25 – 7.11 (m, 6H), 7.09 (d, *J* = 7.6 Hz, 1H), 6.93 (s, 1H), 6.75 – 6.69 (m, 2H), 3.68 (s, 3H), 3.58 (d, *J* = 7.3 Hz, 2H), 2.31 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 164.3, 156.6, 154.1, 151.8, 138.6, 138.5, 137.1, 135.0, 131.0, 130.8, 130.1, 130.0, 129.5, 129.3, 128.9, 128.6, 127.9, 124.6, 124.5, 122.7, 121.8, 119.7, 112.7, 111.2, 55.6, 25.0, 21.7.

HRMS (ESI) m/z: [M + Na]⁺ Calc. for C₃₂H₂₇NO₃Na 496.1889; found: 496.1888.

N-(4-methoxyphenyl)-2-phenyl-4-(2-(*o*-tolyl)benzofuran-3-yl)but-2-enamide (3z)



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1). Colorless oil; 17.0 mg, 36% yield; Z/E = 1:1.6.

Mixture of **Z** and *E* (Z/E = 1:1.6), ¹**H NMR (400 MHz, Chloroform-***d*) δ 7.65 (dd, J = 7.4, 1.6 Hz, 0.6H) (Z), 7.47 – 7.37 (m, 3H) (E), 7.37 – 7.28 (m, 5.4H) (Z+E), 7.25 – 7.12 (m, 16.4H) (Z+E), 6.96 (s, 0.7H) (Z), 6.86 (s, 1H) (E), 6.82 – 6.76 (m, 1.3H) (Z), 6.74 – 6.69 (m, 2H) (E), 6.09 (t, J = 7.2 Hz, 0.6H) (Z), 3.88 (d, J = 7.2 Hz, 1.3H) (Z), 3.72 (s, 1.9H) (Z), 3.68 (s, 3H) (E), 3.32 (d, J = 7.5 Hz, 2H) (E), 2.27 (s, 1.9H) (Z), 2.22 (s, 3H) (E).

Mixture of **Z** and **E**, ¹³**C NMR** (101 MHz, Chloroform-*d*) δ 166.34, 164.24, 156.82, 156.60, 154.50, 154.45, 152.91, 152.88, 138.85, 138.53, 138.51, 138.31, 137.33, 136.75, 134.89, 134.45, 131.02, 130.84, 130.80, 130.74, 130.72, 130.70, 130.08, 129.90, 129.54, 129.46, 129.38, 129.14, 128.94, 128.72, 128.38, 127.32, 125.79, 125.74, 124.36, 122.75, 122.65, 122.00, 121.77, 120.03, 119.79, 114.80, 114.29, 114.16, 113.94, 111.31, 55.65, 55.58, 25.00, 24.68, 20.40, 20.37.

HRMS (ESI) m/z: [M + Na]⁺ Calc. for C₃₂H₂₇NO₃Na 496.1889; found: 496.1882.

(E) - N - (4 - methoxy phenyl) - 4 - (2 - (naphthalen - 2 - yl) benzofuran - 3 - yl) - 2 - phenyl but - 2 - enamide



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1). White solid, m.p. 163.5 - 164.1 °C; 40.8 mg, 80% yield; *Z/E* = 1:1.2.

¹**H NMR (400 MHz, Chloroform-***d***)** δ 8.01 (s, 1H), 7.81 – 7.73 (m, 3H), 7.63 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.42 (m, 4H), 7.38 – 7.31 (m, 3H), 7.31 – 7.26 (m, 3H), 7.24 – 7.14 (m, 4H), 6.92 (s, 1H), 6.75 – 6.66 (m, 2H), 3.68 (s, 2H), 3.67 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 164.2, 156.6, 154.2, 151.6, 138.5, 137.2, 134.9, 133.4, 133.1, 131.0, 130.1, 130.0, 129.4, 128.9, 128.6, 128.4, 128.3, 127.8, 126.7, 126.6, 126.6, 124.8, 124.8, 122.8, 121.8, 119.8, 114.2, 113.3, 111.3, 55.6, 25.0.

HRMS (ESI) m/z: [M + Na]⁺ Calc. for C₃₅H₂₇NO₃Na 532.1889; found: 532.1885.

(E)-N-(4-methoxyphenyl)-2-phenyl-4-(2-(thiophen-2-yl)benzofuran-3-yl)but-2-enamide (3b')



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1). White solid, m.p. 109.3 - 110.1 °C; 26.1 mg, 56% yield; *Z/E* = 1:1.1.

¹**H NMR (400 MHz, Chloroform-***d*) δ 7.48 – 7.40 (m, 3H), 7.37 (d, *J* = 8.3 Hz, 1H), 7.30 (m, 4H), 7.25 – 7.09 (m, 6H), 7.00 (dd, *J* = 5.0, 3.7 Hz, 1H), 6.94 (s, 1H), 6.76 – 6.68 (m, 2H), 3.68 (s, 3H), 3.60 (d, *J* = 7.3 Hz, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 164.2, 156.6, 153.9, 147.1, 138.0, 137.4, 135.0, 132.7, 131.0, 130.1, 129.8, 129.5, 129.0, 127.7, 126.2, 125.7, 124.8, 122.9, 121.8, 119.6, 114.2, 112.3, 111.1, 55.6, 24.9.

HRMS (ESI) m/z: $[M + H]^+$ Calc. for C₂₉H₂₄NO₃S 466.1478; found: 466.1476.

4-(2-butylbenzofuran-3-yl)-N-(4-methoxyphenyl)-2-phenylbut-2-enamide (3c')



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1). Colorless oil; 22.4 mg, 51% yield; Z/E = 1:1.4.

Mixture of **Z** and *E* (*Z*/*E* = 1:1.5), ¹**H NMR** (**400 MHz, Chloroform-***d*) δ 7.49 – 7.37 (m, 5H) (*Z*+*E*), 7.35 – 7.12 (m, 13.1H) (*Z*+*E*), 7.10 – 7.05 (m, 1.9H) (*Z*+*E*), 6.92 (s, 1H) (*E*), 6.84 – 6.78 (m, 1.4H) (*Z*), 6.74 – 6.69 (m, 2H) (*E*), 6.13 (t, *J* = 7.3 Hz, 0.7H) (*Z*), 3.82 (d, *J* = 7.3 Hz, 1.4H) (*Z*), 3.72 (s, 2H) (*E*), 3.67 (s, 3H) (*E*), 3.26 (d, *J* = 7.6 Hz, 2H) (*E*), 2.69 (t, *J* = 7.5 Hz, 1.4H) (*Z*), 2.49 (t, *J* = 7.6 Hz, 2H) (*E*), 1.60 – 1.54 (m, 3.4H) (*Z*+*E*), 1.28 – 1.20 (m, 3.4H) (*Z*+*E*), 0.82 (t, *J* = 7.3 Hz, 5H) (*Z*+*E*).

Mixture of **Z** and **E**, ¹³**C NMR** (101 MHz, Chloroform-*d*) δ 166.43, 164.22, 156.81, 156.61, 155.48, 155.21, 154.11, 154.01, 139.21, 138.08, 137.42, 136.56, 135.17, 134.91, 131.01, 130.84, 130.08, 129.52, 129.48, 129.27, 128.98, 128.91, 128.38, 127.36, 123.36, 122.36, 122.27, 121.85, 121.81, 119.13, 118.97, 114.36, 114.16, 112.13, 111.21, 110.85, 110.78, 55.65, 55.57, 30.66, 30.49, 26.27, 24.40, 24.12, 22.52, 22.49, 13.96, 13.93.

HRMS (ESI) m/z: [M + Na]⁺ Calc. for C₂₉H₂₉NO₃Na 462.2045; found: 462.2039.

4-(2-(tert-butyl)benzofuran-3-yl)-N-(4-methoxyphenyl)-2-phenylbut-2-enamide (3d')



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1). Colorless oil; 18.8 mg, 43% yield; Z/E = 1:1.3.

Mixture of **Z** and **E** (Z/E = 1:1.3), ¹**H NMR** (400 MHz, Chloroform-*d*) δ 7.53 – 7.38 (m, 5.6H) (Z+E), 7.37 – 7.22 (m, 9.8H) (Z+E), 7.17 – 7.02 (m, 6.5H) (Z+E), 6.94 (s, 1H) (E), 6.86 – 6.79 (m,

1.6H) (*Z*), 6.75 – 6.69 (m, 2H) (*E*), 6.09 (t, *J* = 6.9 Hz, 1H) (*Z*), 4.03 (d, *J* = 6.9 Hz, 1.6H) (*Z*), 3.73 (s, 2.4H) (*Z*), 3.68 (s, 3H) (*E*), 3.45 (d, *J* = 7.1 Hz, 2H) (*E*), 1.38 (s, 7.2H) (*Z*), 1.28 (s, 9H) (*E*). Mixture of **Z** and **E**, ¹³**C NMR (101 MHz, Chloroform-***d*) δ 166.35, 164.22, 160.81, 160.61, 156.81, 156.56, 153.08, 153.01, 140.13, 137.57, 137.48, 136.81, 136.13, 135.19, 131.05, 130.79, 130.65, 130.43, 130.14, 129.51, 129.00, 128.95, 128.39, 127.60, 123.51, 123.48, 122.21, 122.03, 121.95, 121.76, 119.11, 118.90, 114.35, 114.14, 110.71, 110.65, 110.58, 109.58, 55.65, 55.57, 34.57, 34.51, 29.93, 29.81, 24.86, 24.65.

HRMS (ESI) m/z: [M + Na]⁺ Calc. for C₂₉H₂₉NO₃Na 462.2045; found: 462.2045.

(E)-4-(5-fluoro-2-phenylbenzofuran-3-yl)-N-(4-methoxyphenyl)-2-phenylbut-2-enamide (3e')



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1). Colorless oil; 28.2 mg, 59% yield; Z/E = 1:1.4.

¹**H NMR (400 MHz, Chloroform-***d*) δ 7.53 (m, 2H), 7.48 – 7.38 (m, 3H), 7.36 – 7.28 (m, 6H), 7.25 – 7.16 (m, 3H), 7.00 – 6.86 (m, 3H), 6.77 – 6.69 (m, 2H), 3.68 (s, 3H), 3.54 (d, *J* = 7.3 Hz, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 164.1, 159.3 (d, *J* = 239.3 Hz), 156.7, 153.4, 150.3, 138.0, 137.3, 134.8, 130.9, 130.8 (d, *J* = 10.3 Hz), 130.5, 130.1, 129.6, 129.1, 128.8 (d, *J* = 4.1 Hz), 127.3, 121.8, 114.2, 113.0 (d, *J* = 4.1 Hz), 112.3 (d, *J* = 26.3 Hz), 111.9 (d, *J* = 9.6 Hz), 105.3 (d, *J* = 25.1 Hz), 55.6, 24.9.

HRMS (ESI) m/z: [M + Na]⁺ Calc. for C₃₁H₂₄FNO₃Na 500.1638; found: 500.1642.

methyl (E)-3-(4-((4-methoxyphenyl)amino)-4-oxo-3-phenylbut-2-en-1-yl)-2-

phenylbenzofuran-5-carboxylate (3f')



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1). White solid, m.p. 155.6 - 156.6 °C; 16.6 mg, 32% yield; Z/E = 1:1.3.

¹**H NMR (400 MHz, Chloroform**-*d*) δ 8.10 (d, *J* = 1.7 Hz, 1H), 7.95 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.59 – 7.52 (m, 2H), 7.48 (dd, *J* = 8.0, 6.3 Hz, 2H), 7.44 – 7.39 (m, 2H), 7.37 – 7.30 (m, 5H), 7.24 – 7.16 (m, 3H), 6.95 (s, 1H), 6.77 – 6.69 (m, 2H), 3.90 (s, 3H), 3.69 (s, 3H), 3.61 (d, *J* = 7.3 Hz, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 167.4, 164.1, 156.7, 156.7, 153.1, 137.9, 137.4, 134.8, 131.0, 130.3, 130.1, 129.6, 129.1, 128.9, 128.9, 127.3, 126.5, 125.1, 122.1, 121.8, 114.2, 113.2, 111.1, 55.6, 52.3, 24.8.

HRMS (ESI) m/z: [M + H]⁺ Calc. for C₃₃H₂₈NO₅ 518.1968; found: 518.1964.

5. General procedure for the synthesis of the product 6



To an oven-dried 25 mL of Schlenk tube equipped with a stir bar, $Pd_2(dba)_3CHCl_3$ (5 mol%) and $Cu(OTf)_2$ (2.5 mol%) was added along with **1** (0.11 mmol), **5** (0.1 mmol) and acetonitrile (2.0 mL). The reaction was stirred at 85 °C under argon atmosphere for 17 h. The reaction mixture was directly purified by silica gel column chromatography to afford the desired product **6**.

tert-butyl-3-(4-oxo-3-phenyl-4-(phenylamino)but-2-en-1-yl)-2-(*p*-tolyl)-1*H*-indole-1carboxylate (6a)



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1). Colorless oil; 41.2 mg, 76% yield; Z/E = 1:1.5.

Mixture of **Z** and **E** (Z/E = 1:1.4), ¹**H NMR** (400 MHz, Chloroform-*d*) δ 8.14 (dd, J = 11.6, 8.2 Hz, 1.7H) (Z+E), 7.58 (d, J = 7.8 Hz, 0.7H) (Z), 7.42 – 7.32 (m, 4.5H) (Z+E), 7.31 – 7.13 (m, 14.5H) (Z+E), 7.12 – 6.95 (m, 11.2H) (Z+E), 6.94 (s, 1H) (E), 6.02 (t, J = 7.1 Hz, 0.7H) (Z), 3.73 (d, J = 7.1 Hz, 1.4H) (Z), 3.22 (d, J = 7.3 Hz, 2H) (E), 2.34 (s, 3H) (E), 2.22 (s, 2.1H) (Z), 1.17 (s, 6.3H) (Z), 1.16 (s, 9H) (E).

Mixture of **Z** and **E**, ¹³**C NMR** (101 MHz, Chloroform-*d*) δ 166.63, 164.46, 150.30, 150.27, 140.09, 137.90, 137.70, 137.65, 137.59, 137.41, 137.17, 136.67, 136.60, 136.56, 136.02, 134.93, 134.76, 134.74, 131.11, 131.03, 129.99, 129.77, 129.51, 129.36, 129.33, 129.07, 128.97, 128.87, 128.76, 128.74, 128.63, 128.24, 127.13, 124.67, 124.63, 124.60, 124.42, 122.96, 122.77, 120.14, 119.91, 119.07, 118.83, 118.10, 117.28, 115.38, 83.13, 83.10, 27.64, 25.22, 24.99, 21.46, 21.36.

HRMS (ESI) m/z: $[M + Na]^+$ Calc. for C₃₆H₃₄N₂O₃Na 565.2467; found: 565.2461.

tert-butyl-3-(4-((4-methoxyphenyl)amino)-4-oxo-3-phenylbut-2-en-1-yl)-2-(*p*-tolyl)-1*H*indole-1-carboxylate (6b)



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1). Colorless oil; 38.9 mg, 68% yield; Z/E = 1:1.1.

Mixture of **Z** and **E** (Z/E = 1:1.3), ¹**H NMR (400 MHz, Chloroform-d**) δ 8.22 (dd, J = 13.1, 8.3 Hz, 1.8H) (Z+E), 7.66 (d, J = 7.7 Hz, 0.8H) (Z), 7.42 (dd, J = 5.2, 1.9 Hz, 3H) (Z+E), 7.37 – 7.26 (m, 10.2H) (Z+E), 7.24 – 7.08 (m, 11.7H) (Z+E), 6.97 (s, 0.8H) (Z), 6.92 (s, 1H) (E), 6.89 – 6.83 (m, 1.6H) (Z), 6.80 – 6.75 (m, 2H) (E), 6.08 (t, J = 7.1 Hz, 0.8H) (Z), 3.80 (d, J = 6.1 Hz, 3.8H) (Z), 3.74 (s, 3H) (E), 3.28 (d, J = 7.3 Hz, 2H) (E), 2.41 (s, 3H) (E), 2.31 (s, 2.3H) (Z), 1.25 (s, 6.9H) (Z), 1.24 (s, 9H) (E).

Mixture of **Z** and **E**, ¹³**C NMR** (101 MHz, Chloroform-*d*) δ 166.53, 164.37, 156.78, 156.53, 150.32, 150.29, 139.73, 137.66, 137.60, 137.40, 137.32, 136.66, 136.58, 136.02, 135.09, 134.48, 134.47, 131.18, 131.09, 131.05, 130.73, 130.01, 129.82, 129.79, 129.54, 129.40, 129.29, 128.86, 128.78, 128.74, 128.56, 128.20, 127.13, 124.64, 124.59, 122.97, 122.77, 122.09, 121.73, 119.09, 118.87, 118.19, 117.37, 115.40, 115.37, 114.24, 114.12, 83.15, 83.10, 55.65, 55.56, 27.67, 27.65, 25.21, 24.97, 21.47, 21.39.

HRMS (ESI) m/z: [M + H]⁺ Calc. for C₃₇H₃₇N₂O₄ 573.2754; found: 573.2754.

1-carboxylate (6c)



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1). Colorless oil; 40.4 mg, 70% yield; Z/E = 1:1.2.

Mixture of **Z** and **E** (Z/E = 1:1.2), ¹**H NMR (400 MHz, Chloroform-d**) δ 8.14 (dd, J = 11.3, 8.3 Hz, 1.8H) (Z+E), 7.56 (d, J = 7.7 Hz, 1H) (E), 7.38 – 7.30 (m, 4.8H) (Z+E), 7.29 – 7.11 (m, 16.5H) (Z+E), 7.10 – 7.02 (m, 8.1H) (Z+E), 6.97 (s, 0.8H) (Z), 6.93 (s, 1H) (E), 6.03 (t, J = 7.1 Hz, 0.8H) (Z), 3.72 (d, J = 7.2 Hz, 1.6H) (Z), 3.21 (d, J = 7.3 Hz, 2H) (E), 2.34 (s, 3H) (E), 2.23 (s, 2.4H) (Z), 1.17 (s, 7.3H) (Z), 1.17 (s, 9H) (E).

Mixture of **Z** and **E**, ¹³**C NMR** (101 MHz, Chloroform-*d*) δ 166.57, 164.46, 150.28, 150.26, 140.58, 137.62, 137.46, 137.34, 137.09, 136.72, 136.65, 136.58, 136.56, 136.51, 136.27, 135.75, 135.39, 134.73, 131.12, 131.01, 129.98, 129.80, 129.78, 129.63, 129.46, 129.42, 129.36, 129.32, 129.07, 128.98, 128.96, 128.77, 128.75, 128.37, 127.19, 124.68, 124.64, 122.98, 122.80, 121.35, 121.15, 118.99, 118.78, 117.98, 117.16, 115.45, 115.42, 83.21, 83.16, 27.65, 25.22, 25.03, 21.47, 21.38. **HRMS (ESI)** m/z: [M + Na]⁺ Calc. for C₃₆H₃₃ClN₂O₃Na 599.2078; found: 599.2075.

tert-butyl-3-(4-(naphthalen-2-ylamino)-4-oxo-3-phenylbut-2-en-1-yl)-2-(*p*-tolyl)-1*H*-indole-1carboxylate (6d)



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1). Colorless oil; 42.1 mg, 71% yield; Z/E = 1:1.2.

Mixture of **Z** and **E** (Z/E = 1:1.2), ¹**H NMR** (400 MHz, Chloroform-*d*) δ 8.19 – 8.10 (m, 2.7H) (Z+E), 8.05 (s, 1H) (E), 7.76 – 7.56 (m, 6.8H) (Z+E), 7.42 – 7.20 (m, 15.5H) (Z+E), 7.20 – 7.12 (m, 8.4H) (Z+E), 7.10 – 7.00 (m, 5H) (Z+E), 6.06 (t, J = 7.1 Hz, 0.9H) (Z), 3.78 (d, J = 7.1 Hz, 1.7H) (Z), 3.24 (d, J = 7.4 Hz, 2H) (E), 2.34 (s, 3H) (E), 2.16 (s, 2.5H) (Z), 1.17 (s, 9H) (E), 1.16 (s, 7.6H) (Z).

Mixture of **Z** and **E**, ¹³**C NMR** (101 MHz, Chloroform-*d*) δ 166.77, 164.64, 150.31, 150.29, 140.28, 137.62, 137.44, 137.25, 136.73, 136.63, 136.59, 136.03, 135.35, 135.22, 135.12, 134.92, 133.92, 133.89, 131.12, 131.04, 130.90, 130.74, 130.05, 129.79, 129.52, 129.41, 129.37, 128.95, 128.80, 128.77, 128.70, 128.67, 128.32, 127.82, 127.80, 127.68, 127.61, 127.24, 126.69, 126.57, 125.26, 125.11, 124.65, 124.63, 122.99, 122.81, 120.03, 119.94, 119.07, 118.85, 118.12, 117.27, 116.95, 116.70, 115.41, 83.16, 83.13, 27.65, 25.27, 25.05, 21.47, 21.33.

HRMS (ESI) m/z: $[M + Na]^+$ Calc. for C₄₀H₃₆N₂O₃Na 615.2624; found: 615.2633.

tert-butyl-3-(4-((4-methoxyphenyl)amino)-4-oxo-3-(*p*-tolyl)but-2-en-1-yl)-2-(*p*-tolyl)-1*H*indole-1-carboxylate (6e)



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1). Colorless oil; 29.3 mg, 50% yield; Z/E = 1:1.

Mixture of **Z** and *E* (Z/E = 1:1), ¹**H** NMR (400 MHz, Chloroform-*d*) δ 8.14 (m, 2H) (Z+E), 7.58 (d, J = 7.7 Hz, 1H) (Z), 7.32 – 7.10 (m, 17H) (Z+E), 7.08 – 6.98 (m, 9H) (Z+E), 6.90 (s, 1H) (Z), 6.86 (s, 1H) (E), 6.81 – 6.76 (m, 2H) (Z), 6.71 (m, 2H) (E), 5.96 (t, J = 7.1 Hz, 1H) (Z), 3.72 (s, 3H) (Z), 3.71 (s, 2H) (Z), 3.67 (s, 3H) (E), 3.21 (d, J = 7.3 Hz, 2H) (E), 2.34 (s, 6H) (Z+E), 2.25 (s, 3H) (Z), 2.23 (s, 3H) (E), 1.18 (s, 9H) (Z), 1.17 (s, 9H) (E).

Mixture of **Z** and **E**, ¹³**C NMR** (101 MHz, Chloroform-*d*) δ 166.68, 164.55, 156.73, 156.47, 150.33, 150.31, 139.60, 138.40, 138.12, 137.56, 137.47, 137.36, 136.63, 136.57, 136.52, 135.94, 134.49, 133.87, 131.98, 131.18, 131.07, 130.80, 129.99, 129.90, 129.82, 129.80, 129.58, 129.54, 129.45, 128.76, 128.70, 127.07, 124.60, 124.56, 122.95, 122.74, 122.05, 121.69, 119.13, 118.94, 118.34, 117.50, 115.38, 115.34, 114.23, 114.11, 83.13, 83.08, 55.65, 55.57, 27.67, 27.65, 25.16, 25.01, 21.47, 21.45, 21.39, 21.25.

HRMS (ESI) m/z: [M + Na]⁺ Calc. for C₃₈H₃₈N₂O₄Na 609.2730; found: 609.2727.

tert-butyl-3-(3-(4-bromophenyl)-4-((4-methoxyphenyl)amino)-4-oxobut-2-en-1-yl)-2-(*p*-tolyl)-1*H*-indole-1-carboxylate (6f)



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1). Colorless oil; 31.3 mg, 48% yield; Z/E = 1:1.1.

Mixture of **Z** and **E** (Z/E = 1.1:1), ¹**H** NMR (400 MHz, Chloroform-*d*) δ 8.15 (m, 1.8H) (Z+E), 7.55 (d, J = 7.7 Hz, 1H) (Z), 7.44 (d, J = 8.2 Hz, 1.8H) (E), 7.37 – 7.13 (m, 12.3H) (Z+E), 7.12 – 6.99 (m, 9.3H) (Z+E), 6.92 (d, J = 8.3 Hz, 2H) (Z), 6.79 (m, 4H) (Z+E), 6.71 (d, J = 8.8 Hz, 2H) (Z), 5.98 (t, J = 7.1 Hz, 1H) (Z), 3.73 (s, 3H) (Z), 3.69 (d, J = 7.1 Hz, 4.7H) (Z+E), 3.21 (d, J = 7.4 Hz, 1.8H) (E), 2.36 (s, 2.7H) (E), 2.24 (s, 3H) (Z), 1.18 (s, 9H) (Z), 1.17 (s, 8.1H) (E).

Mixture of **Z** and **E**, ¹³**C** NMR (101 MHz, Chloroform-*d*) δ 166.12, 164.00, 156.91, 156.65, 150.27, 150.24, 139.87, 137.72, 137.57, 136.80, 136.71, 136.62, 136.57, 136.54, 136.10, 135.08, 134.25, 133.87, 132.42, 131.97, 131.63, 131.16, 130.97, 130.88, 130.49, 129.82, 129.77, 129.41, 129.21, 128.82, 128.77, 128.56, 124.73, 124.70, 123.03, 122.86, 122.83, 122.31, 122.17, 121.81, 118.95, 118.77, 117.80, 116.99, 115.46, 114.29, 114.17, 83.24, 83.20, 55.66, 55.58, 27.67, 27.65, 25.23, 24.97, 21.51, 21.41.

HRMS (ESI) m/z: $[M + Na]^+$ Calc. for $C_{37}H_{35}BrN_2O_4Na$ 673.1678, 675.1658; found: 673.1677, 675.1664.

tert-butyl (*E*)-3-(4-((4-methoxyphenyl)amino)-3-(naphthalen-1-yl)-4-oxobut-2-en-1-yl)-2-(*p*-tolyl)-1*H*-indole-1-carboxylate (6g)



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1). Colorless oil; 36.1 mg, 58% yield; Z/E = 1:3.3.

¹**H NMR (400 MHz, Chloroform-***d***)** δ 8.10 (d, J = 8.3 Hz, 1H), 7.85 (dd, J = 8.3, 4.0 Hz, 2H), 7.75 (d, J = 8.3 Hz, 1H), 7.48 (m, 1H), 7.45 – 7.38 (m, 2H), 7.35 (t, J = 7.2 Hz, 1H), 7.25 – 7.18 (m, 3H), 7.10 – 7.04 (m, 3H), 6.99 (s, 4H), 6.73 (s, 1H), 6.68 – 6.60 (m, 2H), 3.64 (s, 3H), 3.08 (d, J = 7.2 Hz, 2H), 2.31 (s, 3H), 1.15 (s, 9H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 164.3, 156.5, 150.3, 141.9, 137.3, 136.6, 136.5, 134.2, 134.1, 132.2, 132.0, 130.9, 130.9, 129.7, 129.4, 129.3, 128.7, 128.6, 128.4, 127.2, 126.7, 125.8, 125.4, 124.5, 122.7, 121.9, 118.9, 117.2, 115.3, 114.0, 83.1, 55.5, 27.6, 25.1, 21.5.

HRMS (ESI) m/z: $[M + H]^+$ Calc. for C₄₁H₃₉N₂O₄ 623.2911; found: 623.2915.

tert-butyl-3-(4-(naphthalen-2-ylamino)-4-oxo-3-phenylbut-2-en-1-yl)-2-(*p*-tolyl)-1*H*-indole-1carboxylate (6h)



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1). Colorless oil; 39.6 mg, 75% yield; Z/E = 1:1.2.

Mixture of **Z** and **E** (Z/E = 1:1.2), ¹**H NMR** (400 MHz, Chloroform-*d*) δ 8.17 (m, 1.8H) (Z+E), 7.59 (d, J = 7.7 Hz, 0.8H) (Z), 7.43 – 7.32 (m, 4.9H) (Z+E), 7.31 – 7.12 (m, 24.5H) (Z+E), 7.10 – 7.02 (m, 3.6H) (Z+E), 6.99 (s, 0.8H) (Z), 6.97 (m, 1H) (E), 6.94 (s, 1H) (E), 6.00 (t, J = 7.1 Hz, 0.8H) (Z), 3.74 (d, J = 7.1 Hz, 1.7H) (Z), 3.21 (d, J = 7.3 Hz, 2H) (E), 1.14 (s, 8H) (Z), 1.13 (s, 9H) (E).

Mixture of **Z** and **E**, ¹³**C NMR** (101 MHz, Chloroform-*d*) δ 166.60, 164.42, 150.25, 150.22, 140.00, 137.89, 137.73, 137.68, 137.17, 136.65, 136.47, 136.40, 136.10, 134.89, 134.21, 134.11, 129.96, 129.94, 129.48, 129.39, 129.30, 129.09, 128.98, 128.90, 128.69, 128.29, 128.09, 127.84, 127.74, 127.17, 124.78, 124.77, 124.70, 124.45, 123.04, 122.86, 120.13, 119.93, 119.17, 118.91, 118.33, 117.48, 115.41, 83.16, 83.12, 27.61, 27.59, 25.19, 24.97.

HRMS (ESI) m/z: [M + Na]⁺ Calc. for C₃₅H₃₂N₂O₃Na 551.2311; found: 551.2304.

tert-butyl-2-(4-methoxyphenyl)-3-(4-oxo-3-phenyl-4-(phenylamino)but-2-en-1-yl)-1*H*-indole-1-carboxylate (6i)



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1). Colorless oil; 50.3 mg, 90% yield; Z/E = 1:1.1.

Mixture of **Z** and **E** (Z/E = 1:1.1), ¹**H** NMR (400 MHz, Chloroform-*d*) δ 8.14 (dd, J = 11.4, 8.3 Hz, 1.9H) (Z+E), 7.57 (d, J = 7.7 Hz, 0.9H) (Z), 7.43 – 7.33 (m, 4.8H) (Z+E), 7.32 – 7.11 (m, 18.8H) (Z+E), 7.09 – 6.95 (m, 5.3H) (Z+E), 6.94 (s, 1H) (E), 6.85 – 6.76 (m, 3.9H) (Z+E), 6.02 (t, J = 7.1

Hz, 0.9H) (*Z*), 3.78 (s, 3H) (*E*), 3.74 (d, *J* = 7.1 Hz, 1.8H) (*Z*), 3.64 (s, 2.7H) (*Z*), 3.21 (d, *J* = 7.3 Hz, 2H) (*E*), 1.20 (s, 8H) (*Z*), 1.19 (s, 9H) (*E*).

Mixture of **Z** and **E**, ¹³**C NMR** (101 MHz, Chloroform-*d*) δ 166.62, 164.46, 159.33, 150.35, 150.32, 140.07, 137.89, 137.70, 137.63, 137.19, 136.54, 136.45, 136.33, 136.01, 134.94, 134.87, 131.10, 131.07, 130.00, 129.47, 129.35, 129.32, 129.10, 128.98, 128.90, 128.66, 128.28, 127.17, 126.37, 126.35, 124.68, 124.62, 124.59, 124.44, 122.97, 122.79, 120.11, 119.93, 119.01, 118.79, 118.19, 117.38, 115.43, 115.41, 113.55, 83.10, 83.06, 55.48, 55.34, 27.74, 25.24, 25.02.

HRMS (ESI) m/z: $[M + Na]^+$ Calc. for $C_{36}H_{34}N_2O_4Na$ 581.2417; found: 581.2411.

tert-butyl-2-(4-fluorophenyl)-3-(4-oxo-3-phenyl-4-(phenylamino)but-2-en-1-yl)-1*H*-indole-1carboxylate (6j)



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1). Colorless oil; 44.3 mg, 81% yield; Z/E = 1:1.3.

Mixture of **Z** and **E** (Z/E = 1:1.6), ¹**H NMR** (400 MHz, Chloroform-*d*) δ 8.16 (m, 1.6H) (Z+E), 7.60 (d, J = 7.8 Hz, 0.6H) (Z), 7.43 – 7.32 (m, 4.9H) (Z+E), 7.31 – 7.13 (m, 15.6H) (Z+E), 7.09 – 6.95 (m, 8.2H) (Z+E), 6.94 (s, 1H) (E), 6.01 (t, J = 7.1 Hz, 0.6H) (Z), 3.73 (d, J = 7.1 Hz, 1.2H) (Z), 3.19 (d, J = 7.3 Hz, 2H) (E), 1.19 (s, 5.6H) (Z), 1.18 (s, 9H) (E).

Mixture of **Z** and **E**, ¹³**C** NMR (101 MHz, Chloroform-*d*) δ 166.45, 164.33, 163.76, 161.30, 150.17, 150.12, 139.66, 137.87, 137.84, 137.63, 137.17, 136.62, 136.59, 136.15, 135.31, 135.24, 134.94, 134.80, 131.68, 131.65, 131.60, 131.57, 130.18, 130.14, 130.11, 130.07, 129.91, 129.42, 129.36, 129.16, 129.14, 129.01, 128.96, 128.78, 128.40, 127.26, 124.95, 124.76, 124.51, 123.14, 122.99, 120.01, 119.96, 119.23, 118.95, 118.77, 117.92, 115.55, 115.27, 115.21, 115.06, 115.00, 83.39, 83.36, 27.72, 25.19, 24.92.

HRMS (ESI) m/z: [M + H]⁺ Calc. for C₃₅H₃₂FN₂O₃ 547.2398; found: 547.2392.

tert-butyl-2-(4-chlorophenyl)-3-(4-oxo-3-phenyl-4-(phenylamino)but-2-en-1-yl)-1*H*-indole-1carboxylate (6k)



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1). Colorless oil; 43.4 mg, 77% yield; Z/E = 1:1.6. Mixture of **Z** and **E** (Z/E = 1:1.6), ¹**H NMR (400 MHz, Chloroform-d**) δ 8.15 (m, 1.6H) (Z+E), 7.60 (d, J = 7.8 Hz, 0.6H) (Z), 7.44 – 7.32 (m, 5.5H) (Z+E), 7.31 – 7.13 (m, 17.1H) (Z+E), 7.10 – 7.02 (m, 5.2H) (Z+E), 6.97 (t, J = 7.4 Hz, 1H) (E), 6.93 (s, 1H) (E), 6.00 (t, J = 7.1 Hz, 0.6H) (Z), 3.74 (d, J = 7.1 Hz, 1.3H) (Z), 3.20 (d, J = 7.3 Hz, 2H) (E), 1.20 (s, 5.8H) (Z), 1.19 (s, 9H) (E). Mixture of **Z** and **E**, ¹³**C NMR (101 MHz, Chloroform-d**) δ 166.42, 164.31, 150.10, 150.05, 139.46, 137.92, 137.83, 137.61, 137.15, 136.68, 136.63, 136.18, 135.09, 135.03, 134.88, 134.72, 133.92, 133.80, 132.64, 132.57, 131.26, 131.22, 129.88, 129.43, 129.37, 129.19, 129.13, 129.01, 128.97, 128.77, 128.42, 128.35, 128.32, 127.27, 125.06, 124.78, 124.52, 123.18, 123.04, 120.04, 119.96, 119.30, 119.01, 118.90, 118.03, 115.57, 115.55, 83.56, 83.54, 27.72, 25.17, 24.88. **HRMS (ESI)** m/z: $[M + H]^+$ Calc. for $C_{35}H_{32}ClN_2O_3$ 563.2102, 565.2082; found: 563.2098, 565.2090.

tert-butyl 2-butyl-3-(4-oxo-3-phenyl-4-(phenylamino)but-2-en-1-yl)-1H-indole-1-carboxylate



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1). Colorless oil; 27.7 mg, 54% yield; Z/E = 1:1.3.

Mixture of **Z** and *E* (Z/E = 1:1.3), ¹**H NMR** (400 MHz, Chloroform-*d*) δ 8.11 (d, J = 8.2 Hz, 0.7H) (*Z*), 8.07 (d, J = 8.2 Hz, 1H) (*E*), 7.60 – 7.50 (m, 5H) (*Z*+*E*), 7.44 – 7.26 (m, 12.5H) (*Z*+*E*), 7.24 – 7.02 (m, 7.9H) (*Z*+*E*), 6.17 (t, J = 7.1 Hz, 0.8H) (*Z*), 3.95 (d, J = 7.2 Hz, 1.5H) (*Z*), 3.39 (d, J = 7.3 Hz, 2H) (*E*), 3.08 – 2.99 (m, 1.5H) (*Z*), 2.86 – 2.78 (m, 2H) (*E*), 1.67 (s, 6.7H) (*Z*), 1.67 (s, 9H) (*E*), 1.59 – 1.47 (m, 3.5H) (*Z*+*E*), 1.35 – 1.25 (m, 3.5H) (*Z*+*E*), 0.87 (m, 5.3H) (*Z*+*E*).

Mixture of **Z** and **E**, ¹³**C** NMR (101 MHz, Chloroform-*d*) δ 166.64, 164.39, 150.58, 150.52, 143.49, 140.10, 138.50, 138.37, 137.90, 137.80, 137.59, 137.36, 136.20, 136.12, 135.15, 130.15, 129.55, 129.53, 129.20, 129.10, 129.01, 128.98, 128.94, 128.53, 128.37, 127.39, 125.52, 124.73, 124.47, 123.64, 123.62, 122.65, 122.52, 119.97, 118.24, 118.06, 116.15, 115.72, 115.66, 115.19, 83.64, 83.62, 32.81, 32.56, 28.34, 26.78, 24.93, 24.69, 22.84, 22.82, 14.23, 14.15.

HRMS (ESI) m/z: $[M + Na]^+$ Calc. for $C_{33}H_{36}N_2O_3Na$ 531.2624; found: 531.2630.

4-(1-methyl-2-(p-tolyl)-1H-indol-3-yl)-N,2-diphenylbut-2-enamide (6m)



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1). Colorless oil; 14.2 mg, 31% yield; Z/E = 1:1.

Mixture of **Z** and *E* (Z/E = 1.4:1), ¹**H** NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, J = 7.9 Hz, 1H) (*Z*), 7.42 – 7.30 (m, 6.1H) (*Z*+*E*), 7.29 – 7.15 (m, 17.6H) (*Z*+*E*), 7.13 – 7.04 (m, 6H) (*Z*+*E*), 6.99 – 6.93 (m, 2.6H) (*Z*+*E*), 6.16 (t, J = 7.2 Hz, 1H) (*Z*), 3.87 (d, J = 7.2 Hz, 2H) (*Z*), 3.50 (s, 3H) (*Z*), 3.49 (s, 2.1H) (*E*), 3.37 (d, J = 7.4 Hz, 1.4H) (*E*), 2.37 (s, 2.1H) (*E*), 2.26 (s, 3H) (*Z*).

Mixture of **Z** and **E**, ¹³**C** NMR (101 MHz, Chloroform-*d*) δ 166.89, 164.80, 141.57, 138.57, 138.43, 138.26, 138.08, 138.03, 137.80, 137.39, 137.21, 136.89, 136.08, 135.26, 135.12, 130.68, 130.66, 130.13, 129.36, 129.33, 129.24, 129.07, 128.98, 128.83, 128.81, 128.46, 128.08, 127.67, 127.61, 127.09, 124.58, 124.33, 121.91, 121.86, 120.09, 119.93, 119.65, 119.49, 119.07, 118.97, 110.56, 109.64, 109.53, 109.46, 30.90, 25.66, 25.40, 21.50, 21.42.

HRMS (ESI) m/z: [M + Na]⁺ Calc. for C₃₂H₂₈N₂ONa 479.2100; found: 479.2095.

(E)-4-(1-acetyl-2-(p-tolyl)-1H-indol-3-yl)-N,2-diphenylbut-2-enamide (6n)



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1). Colorless oil; 24.7 mg, 51% yield; Z/E = 1:1.3.

¹**H NMR (400 MHz, Chloroform-***d*) δ 8.34 – 8.29 (m, 1H), 7.37 (m, 3H), 7.31 – 7.24 (m, 5H), 7.20 – 7.11 (m, 9H), 7.07 (t, *J* = 7.2 Hz, 1H), 6.98 – 6.95 (m, 1H), 3.22 (d, *J* = 7.3 Hz, 2H), 2.37 (s, 3H), 1.86 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 171.3, 164.4, 139.7, 138.9, 137.9, 136.9, 136.3, 135.9, 134.9, 130.3, 130.0, 129.7, 129.4, 129.0, 128.7, 127.2, 125.5, 124.5, 123.7, 120.0, 120.0, 119.0, 118.8, 116.6, 27.8, 25.1, 21.5.

HRMS (ESI) m/z: [M + Na]⁺ Calc. for C₃₃H₂₈N₂O₂Na 507.2049; found: 507.2046.

6. General procedure for the synthesis of the product 4 and 7



An oven-dried 25 mL of Schlenk tube was added $Pd_2(dba)_3CHCl_3$ (5 mol%) and PPh₃ (50 mol%), acetonitrile (1.0 mL) under argon atmosphere and stirred for 0.5 h. **1** (0.11 mmol), **2** or **5** (0.1 mmol) and acetonitrile (1.0 mL) were added under argon atmosphere. The mixture was stirred at 25 °C for 3 h. The reaction mixture was directly purified by silica gel column chromatography to afford the desired product **4** and **7**.



(Z)-N-(4-methoxyphenyl)-2-phenyl-4-(2-(p-tolylethynyl)phenoxy)but-2-enamide (4a)



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1). White solid, m.p. 132.4 - 133.2 °C; 41.7 mg, 88% yield.

¹**H NMR (400 MHz, Chloroform-***d***)** δ 7.45 – 7.36 (m, 4H), 7.35 – 7.28 (m, 7H), 7.19 – 7.15 (m, 1H), 7.03 (d, J = 7.9 Hz, 2H), 6.94 – 6.82 (m, 2H), 6.76 – 6.69 (m, 2H), 6.38 (t, J = 5.7 Hz, 1H), 5.09 (d, J = 5.8 Hz, 2H), 3.68 (s, 3H), 2.26 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 165.4, 158.8, 156.8, 139.6, 138.4, 136.9, 134.4, 133.6, 131.6, 130.5, 129.8, 129.2, 129.1, 128.9, 128.1, 122.0, 121.2, 120.5, 114.3, 113.4, 112.9, 94.0, 85.3, 67.1, 55.6, 21.6.

HRMS (ESI) m/z: $[M + H]^+$ Calc. for $C_{32}H_{28}NO_3$ 474.2070; found: 474.2067.

(Z)-N,2-diphenyl-4-(2-(p-tolylethynyl)phenoxy)but-2-enamide (4b)



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1). White solid, m.p. 139.1 - 139.8 °C; 30.2 mg, 68% yield.

¹**H NMR (400 MHz, Chloroform-***d*) δ 7.47 (s, 1H), 7.44 – 7.37 (m, 5H), 7.36 – 7.30 (m, 5H), 7.23 – 7.16 (m, 3H), 7.04 (d, *J* = 7.7 Hz, 3H), 6.95 – 6.84 (m, 2H), 6.42 (t, *J* = 5.7 Hz, 1H), 5.11 (d, *J* = 5.7 Hz, 2H), 2.27 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 165.5, 158.8, 139.4, 138.4, 137.5, 136.9, 135.1, 133.7, 131.6, 129.8, 129.2, 129.2, 129.0, 128.2, 124.9, 121.2, 120.6, 120.2, 113.4, 112.9, 94.0, 85.3, 67.2, 21.6.

HRMS (ESI) m/z: $[M + H]^+$ Calc. for $C_{31}H_{26}NO_2$ 444.1964; found: 444.1960.

(Z)-N-(4-chlorophenyl)-2-phenyl-4-(2-(*p*-tolylethynyl)phenoxy)but-2-enamide (4c)



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1). White solid, m.p. 143.7 - 144.6 °C; 36.8 mg, 77% yield.

¹**H NMR (400 MHz, Chloroform-***d***)** δ 7.56 (s, 1H), 7.42 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.37 (m, 4H), 7.33 – 7.30 (m, 4H), 7.28 – 7.12 (m, 4H), 7.03 (d, *J* = 7.9 Hz, 2H), 6.94 – 6.83 (m, 2H), 6.42 (t, *J* = 5.8 Hz, 1H), 5.07 (d, *J* = 5.9 Hz, 2H), 2.27 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 165.5, 158.7, 139.6, 138.5, 136.7, 136.1, 134.8, 133.7, 131.6, 129.9, 129.8, 129.2, 129.2, 129.1, 129.1, 128.1, 121.4, 121.4, 120.5, 113.4, 113.0, 94.1, 85.2, 67.0, 21.6.

HRMS (ESI) m/z: $[M + Na]^+$ Calc. for C₃₁H₂₄ClNO₂Na 500.1394, 502.1364; found: 500.1386, 502.1381.

(Z)-N-(4-methoxyphenyl)-2-(p-tolyl)-4-(2-(p-tolylethynyl)phenoxy)but-2-enamide (4d)



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1). White solid, m.p. 150.3 - 151.2 °C; 26.3 mg, 54% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.42 (dd, *J* = 7.7, 1.7 Hz, 2H), 7.33 (dd, *J* = 8.4, 4.7 Hz, 4H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.23 - 7.18 (m, 1H), 7.12 (d, *J* = 7.9 Hz, 2H), 7.04 (d, *J* = 7.9 Hz, 2H), 6.93 - 6.84 (m, 2H), 6.76 - 6.70 (m, 2H), 6.36 (t, *J* = 5.7 Hz, 1H), 5.09 (d, *J* = 5.8 Hz, 2H), 3.69 (s, 3H), 2.20 (s, 3H), 2.27 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 165.5, 158.9, 156.8, 139.4, 138.9, 138.4, 134.1, 133.9, 133.6, 131.6, 130.6, 129.8, 129.2, 128.1, 122.0, 121.1, 120.6, 114.3, 113.3, 112.9, 94.0, 85.3, 67.2, 55.6, 21.6, 21.3.

HRMS (ESI) m/z: [M + H]⁺ Calc. for C₃₃H₃₀NO₃ 488.2226; found: 488.2224.

(Z)-2-(4-bromophenyl)-N-(4-methoxyphenyl)-4-(2-(p-tolylethynyl)phenoxy)but-2-enamide



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1). White solid, m.p. 162.4 - 163.5 °C; 27.6 mg, 50% yield.

¹**H NMR (400 MHz, Chloroform-***d***)** δ 7.49 (s, 1H), 7.43 (td, *J* = 5.9, 3.0 Hz, 3H), 7.36 – 7.29 (m, 4H), 7.26 (d, *J* = 8.3 Hz, 2H), 7.18 (d, *J* = 7.8 Hz, 1H), 7.04 (d, *J* = 7.9 Hz, 2H), 6.89 (d, *J* = 7.8 Hz, 2H), 6.77 – 6.69 (m, 2H), 6.39 (t, *J* = 6.0 Hz, 1H), 5.01 (d, *J* = 5.6 Hz, 2H), 3.69 (s, 3H), 2.27 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 165.0, 158.7, 156.9, 139.3, 138.5, 135.7, 133.7, 133.5, 132.2, 131.6, 130.4, 129.8, 129.6, 129.2, 123.2, 122.0, 121.4, 120.4, 114.3, 113.5, 113.0, 94.1, 85.2, 66.9, 55.6, 21.6.

HRMS (ESI) m/z: $[M + H]^+$ Calc. for C₃₂H₂₇BrNO₃ 552.1175, 554.1155; found: 552.1172, 554.1158.

(Z)-4-(4-fluoro-2-(phenylethynyl)phenoxy)-N-(4-methoxyphenyl)-2-phenylbut-2-enamide (4f)



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1). White solid, m.p. 159.5 - 160.6 °C; 39.2 mg, 82% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.47 - 7.42 (m, 2H), 7.41 - 7.37 (m, 2H), 7.37 - 7.30 (m,

6H), 7.30 - 7.21 (m, 4H), 7.13 (dd, J = 8.6, 2.8 Hz, 1H), 6.95 - 6.85 (m, 2H), 6.79 - 6.72 (m, 2H), 6.38 (t, J = 5.6 Hz, 1H), 5.11 (d, J = 5.7 Hz, 2H), 3.71 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 165.3, 156.9, 156.9 (d, *J* = 241.0 Hz), 155.4 (d, *J* = 2.1 Hz), 139.3, 137.0, 135.1, 131.8, 130.5, 129.2, 129.0, 128.6, 128.5, 128.2, 123.2, 122.0, 119.8 (d, *J* = 24.4 Hz), 116.4 (d, *J* = 23.0 Hz), 114.5 (d, *J* = 9.9 Hz), 114.4, 114.3 (d, *J* = 8.8 Hz), 114.3, 94.6, 84.9 (d, *J* = 2.9 Hz), 68.1, 55.6.

HRMS (ESI) m/z: [M + Na]⁺ Calc. for C₃₁H₂₄FNO₃Na 500.1638; found: 500.1632.

(Z)-N-(4-methoxyphenyl)-2-phenyl-4-(2-(phenylethynyl)phenoxy)but-2-enamide (4g)



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1). White solid, m.p. 141.2 - 142.5 °C; 31.7 mg, 69% yield.

¹**H NMR (400 MHz, Chloroform-***d***)** δ 7.47 – 7.36 (m, 6H), 7.35 – 7.28 (m, 5H), 7.23 – 7.15 (m, 4H), 6.95 – 6.84 (m, 2H), 6.76 – 6.70 (m, 2H), 6.39 (t, *J* = 5.7 Hz, 1H), 5.10 (d, *J* = 5.7 Hz, 2H), 3.68 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 165.3, 158.9, 156.9, 139.5, 137.0, 134.6, 133.7, 131.7, 130.5, 130.0, 129.1, 128.9, 128.4, 128.3, 128.1, 123.6, 122.0, 121.2, 114.3, 113.2, 112.9, 93.8, 86.0, 67.1, 55.6.

HRMS (ESI) m/z: [M + Na]⁺ Calc. for C₃₁H₂₅NO₃Na 482.1732; found: 482.1725.

(Z) - 4 - (2 - ((4 - chlorophenyl) ethynyl) phenoxy) - N - (4 - methoxyphenyl) - 2 - phenylbut - 2 - enamide



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1). White solid, m.p. 114.3 - 114.9 °C; 45.9 mg, 93% yield.

¹**H NMR (400 MHz, Chloroform-***d*) δ 7.44 – 7.29 (m, 11H), 7.23 – 7.16 (m, 3H), 6.96 – 6.84 (m, 2H), 6.79 – 6.70 (m, 2H), 6.37 (t, *J* = 5.6 Hz, 1H), 5.12 (d, *J* = 5.6 Hz, 2H), 3.69 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 165.3, 158.9, 156.9, 139.3, 137.0, 135.0, 134.2, 133.7, 132.9, 130.5, 130.2, 129.2, 129.0, 128.7, 128.2, 122.2, 122.0, 121.2, 114.3, 112.9, 112.8, 92.6, 87.0, 67.2, 55.6.

HRMS (ESI) m/z: $[M + Na]^+$ Calc. for C₃₁H₂₄ClNO₃Na 516.1343, 518.1313; found: 516.1340, 518.1326.

(Z)-4-(2-(hex-1-yn-1-yl)phenoxy)-N-(4-methoxyphenyl)-2-phenylbut-2-enamide (4i)



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1). White solid, m.p. 111.2 - 112.1 °C; 31.2 mg, 71% yield; Z/E = 5.9:1.

¹**H NMR (400 MHz, Chloroform-***d*) δ 7.41 (m, 3H), 7.37 – 7.29 (m, 6H), 7.15 (m, 1H), 6.90 – 6.80 (m, 2H), 6.80 – 6.75 (m, 2H), 6.38 (t, *J* = 5.8 Hz, 1H), 5.06 (d, *J* = 5.8 Hz, 2H), 3.71 (s, 3H), 2.37 (t, *J* = 6.9 Hz, 2H), 1.51 – 1.29 (m, 4H), 0.82 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 165.4, 158.8, 156.9, 139.5, 137.0, 134.7, 133.8, 130.6, 129.1, 129.1, 128.9, 128.2, 122.0, 121.1, 114.3, 113.9, 112.7, 95.0, 67.0, 55.6, 31.0, 22.1, 19.6, 13.8.
HRMS (ESI) m/z: [M + Na]⁺ Calc. for C₂₉H₂₉NO₃Na 462.2045; found: 462.2040.

(Z)-N,2-diphenyl-4-(p-tolyloxy)but-2-enamide (4j)



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1). White solid, m.p. 113.5 - 114.2 °C; 30.2 mg, 88% yield; Z/E = 8:1.

¹**H NMR (400 MHz, Chloroform-***d*) δ 7.43 – 7.30 (m, 8H), 7.23 (m, 2H), 7.02 (m, 3H), 6.78 (d, J = 8.2 Hz, 2H), 6.31 (t, J = 5.6 Hz, 1H), 4.99 (d, J = 5.5 Hz, 2H), 2.20 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 165.5, 156.3, 138.8, 137.5, 136.9, 135.9, 130.4, 130.1, 129.2, 129.1, 128.9, 128.1, 124.9, 120.1, 114.7, 66.4, 20.6.

HRMS (ESI) m/z: [M + Na]⁺ Calc. for C₂₃H₂₁NO₂Na 366.1470; found: 366.1463.

(Z)-N-(4-methoxyphenyl)-4-((4-methyl-N-(2-(*p*-tolylethynyl)phenyl)phenyl)sulfonamido)-2phenylbut-2-enamide (7a)



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 3:1). Yellow solid, m.p. 99.1 - 100.0 °C; 39.5 mg, 63% yield.

¹**H NMR (400 MHz, Chloroform-***d***)** δ 7.53 (s, 1H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.41 – 7.35 (m, 3H), 7.30 – 7.27 (m, 3H), 7.23 (m, 2H), 7.21 – 7.17 (m, 3H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.97 (dd, *J* = 8.1, 6.4 Hz, 4H), 6.78 – 6.73 (m, 2H), 6.21 (t, *J* = 7.0 Hz, 1H), 4.65 (d, *J* = 7.0 Hz, 2H), 3.72 (s, 3H), 2.28 (s, 3H), 2.14 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 165.8, 156.7, 143.6, 140.6, 139.8, 138.9, 136.9, 136.5, 133.6, 131.9, 131.6, 130.9, 129.7, 129.5, 129.0, 129.0, 128.8, 128.6, 128.5, 127.7, 127.2, 124.4, 121.8, 119.6, 114.2, 95.2, 85.6, 55.6, 51.0, 21.7, 21.5.

HRMS (ESI) m/z: [M + H]⁺ Calc. for C₃₉H₃₅N₂O₄S 627.2318; found: 627.2315.

(Z)-N-(4-methoxyphenyl)-4-((4-methyl-N-phenylphenyl)sulfonamido)-2-phenylbut-2-

enamide (7b)



Following the general procedure, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 3:1). Colorless oil; 43.5 mg, 85% yield; Z/E = 7:1.

¹**H NMR (400 MHz, Chloroform-***d***)** δ 7.39 – 7.29 (m, 5H), 7.26 (m, 5H), 7.20 (m, 3H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.06 – 7.01 (m, 2H), 6.80 – 6.75 (m, 2H), 6.07 (t, *J* = 6.6 Hz, 1H), 4.56 (d, *J* = 6.6 Hz, 2H), 3.71 (s, 3H), 2.31 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 165.5, 156.7, 143.8, 140.0, 139.4, 136.6, 135.2, 131.6, 130.6, 129.6, 129.3, 129.0, 128.8, 128.8, 128.1, 127.7, 127.5, 121.8, 114.2, 55.6, 51.0, 21.6.

HRMS (ESI) m/z: $[M + Na]^+$ Calc. for $C_{30}H_{28}N_2O_4SNa$ 535.1668; found: 535.1666.

7. Further transformation of the products

7.1 The procedure for the synthesis of compound 8



3ba (22.2 mg, 0.05 mmol) and palladium on activated carbon (10.0 mg, 10% wet) were stirred in EA (2.0 mL). The mixture was degassed, and charged with hydrogen balloon and stirred at 40 °C for 12 h. Then the mixture was filtered through a short pad of Celite, which was rinsed with EA concentrated and purified by flash chromatography on silica gel (ethyl acetate/petroleum ether = 1:10) to afford product **8**.

N,2-diphenyl-4-(2-(p-tolyl)benzofuran-3-yl)butanamide (8)



White solid, m.p. 167.2 - 168.0 °C; 18.7 mg, 84% yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 8.2 Hz, 2H), 7.47 – 7.43 (m, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.34 – 7.26 (m, 3H), 7.25 – 7.16 (m, 7H), 7.16 – 7.08 (m, 3H), 6.99 (t, *J* = 7.4 Hz, 1H), 6.90 (s, 1H), 3.44 (t, *J* = 7.3 Hz, 1H), 2.89 (m, 2H), 2.74 – 2.60 (m, 1H), 2.28 (s, 3H), 2.14 (m 1H).
¹³C NMR (101 MHz, Chloroform-*d*) δ 171.2, 154.0, 151.4, 139.5, 138.3, 137.9, 130.5, 129.5, 129.2, 129.0, 128.4, 128.1, 127.8, 126.9, 124.4, 124.3, 122.5, 119.9, 119.7, 114.6, 111.1, 53.7, 33.1, 22.4, 21.5.

HRMS (ESI) m/z: $[M + H]^+$ Calc. for C₃₁H₂₈NO₂ 446.2121; found: 446.2116.

7.2 The procedure for the synthesis of compound 9



TFA (0.5 mL) was added cautiously to a stirred solution of **6a** (27.1 mg, 0.05 mmol) in DCM (2 mL) at 0 °C. The solution was stirred at room temperature for 12h. The reaction mixture was quenched with NaHCO₃, diluted with DCM and washed with water and brine. The organic layer was dried over MgSO₄ and concentrated in vacuo. Purification by silica gel column chromatography (ethyl acetate/petroleum ether = 1:5) gave **9**.

N,2-diphenyl-4-(2-(p-tolyl)-1H-indol-3-yl)but-2-enamide (9)



Colorless oil; 20.1 mg, 91 % yield; Z/E = 1:1.4.

Mixture of **Z** and E(Z/E = 1:1.4), ¹**H NMR (400 MHz, Chloroform-***d***)** δ 8.16 (s, 1H) (*E*), 8.10 (s, 0.7H) (*Z*), 7.61 (d, *J* = 7.9 Hz, 1H) (*E*), 7.44 – 7.28 (m, 10.5H) (*Z*+*E*), 7.28 – 7.14 (m, 15.6H) (*Z*+*E*),

7.08 - 7.00 (m, 6.5H) (Z+E), 6.22 (t, J = 7.1 Hz, 0.7H) (Z), 4.05 (d, J = 7.1 Hz, 1.5H) (Z), 3.52 (d, J = 7.3 Hz, 2H) (E), 2.29 (s, 3H) (E), 2.24 (s, 2.2H) (Z).

Mixture of **Z** and **E**, ¹³**C** NMR (101 MHz, Chloroform-*d*) δ 166.91, 164.89, 141.30, 137.96, 137.82, 137.60, 137.35, 137.31, 136.09, 135.91, 135.89, 135.66, 135.23, 135.16, 135.12, 130.17, 129.98, 129.92, 129.70, 129.57, 129.33, 129.17, 129.10, 129.04, 128.99, 128.86, 128.66, 128.16, 128.11, 128.06, 127.20, 124.62, 124.42, 122.37, 122.31, 120.05, 119.96, 119.77, 119.19, 119.02, 110.98, 110.94, 110.32, 109.34, 25.60, 25.35, 21.38, 21.35.

HRMS (ESI) m/z: $[M + H]^+$ Calc. for C₃₁H₂₇N₂O 443.2124; found: 443.2118.

7.3 The procedure for the synthesis of compound 10



To a Schlenk tube, **4b** (0.05 mmol, 22.2 mg) was dissolved in anhydrous THF (2.0 mL) under an atmosphere of nitrogen and cooled to 0 °C. NaH (60 % in mineral oil, 0.06 mmol, 2.4 mg) was added portion wise and the resulting suspension was stirred for 15 mins before the addition of iodomethane (0.06 mmol, 3.4 μ L). The reaction mixture was warmed and stirred at rt for 2 hours, after which time it was quenched with H₂O and extracted with DCM. The combined organic layers were washed H₂O, brine, dried over MgSO₄ and concentrated in vacuo. Purification by silica gel column chromatography (ethyl acetate/petroleum ether = 1:5) gave **10**.

(Z)-N-methyl-N,2-diphenyl-4-(2-(p-tolylethynyl)phenoxy)but-2-enamide (10)



Colorless oil; 22.4 mg, 98 % yield; Z/E = 5.5:1.

¹**H NMR (400 MHz, Chloroform-***d***)** δ 7.43 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.35 (m, 3H), 7.25 – 7.16 (m, 2H), 7.11 – 7.04 (m, 4H), 7.02 – 6.97 (m, 4H), 6.95 – 6.88 (m, 2H), 6.81 – 6.74 (m, 2H), 5.95 (t, *J* = 6.3 Hz, 1H), 4.81 (d, *J* = 6.3 Hz, 2H), 3.32 (s, 3H), 2.29 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 169.0, 159.0, 142.6, 141.2, 138.3, 136.9, 133.6, 131.7, 129.8, 129.2, 128.9, 128.5, 128.0, 127.4, 127.0, 126.8, 126.1, 121.1, 120.7, 113.4, 112.9, 93.9, 85.4, 66.9, 37.0, 21.7.

HRMS (ESI) m/z: $[M + Na]^+$ Calc. for $C_{32}H_{27}NO_2Na$ 480.1940; found: 480.1937.

8. Scale-up experiment



A round-bottom flask (50 mL) containing a stirring bar was charged with **1b** (558 mg, 2.0 mmol, 1.0 equiv.), **2a** (416 mg, 2.0 mmol, 1.0 equiv.), $Pd_2(dba)_3CHCl_3$ (2.5 mol%) and $Cu(OTf)_2$ (1.25 mol%), and acetonitrile (10.0 mL). The resulting mixture was stirred at 25 °C for 17 h. After completion of the reaction (monitored by TLC), the reaction mixture was concentrated. The reaction

mixture was directly purified by silica gel column chromatography (petroleum ether/ethyl acetate as eluent) to afford the desired product **3b** in 75% yield.



A 25 mL of Schlenk tube containing a stirring bar was charged with **1b** (558 mg, 2.0 mmol, 1.0 equiv.), **5a** (614 mg, 2.0 mmol, 1.0 equiv.), $Pd_2(dba)_3CHCl_3$ (2.5 mol%) and $Cu(OTf)_2$ (1.25 mol%), and acetonitrile (10.0 mL). The resulting mixture was stirred at 85 °C for 24 h. After completion of the reaction (monitored by TLC), the reaction mixture was concentrated. The reaction mixture was directly purified by silica gel column chromatography (petroleum ether/ethyl acetate as eluent) to afford the desired product **6a** in 66% yield.



A round-bottom flask (50 mL) containing a stirring bar was added $Pd_2(dba)_3CHCl_3$ (2.5 mol%) and PPh₃ (25 mol%), acetonitrile (10.0 mL) under argon atmosphere and stirred for 0.5 h. **1b** (558 mg, 2.0 mmol, 1.0 equiv.), **2a** (416 mg, 2.0 mmol, 1.0 equiv.) and acetonitrile (5.0 mL) were added under argon atmosphere. The resulting mixture was stirred at 25 °C for 3 h. After completion of the reaction (monitored by TLC), the reaction mixture was concentrated. The reaction mixture was directly purified by silica gel column chromatography (petroleum ether/ethyl acetate as eluent) to afford the desired product **4b** in 82% yield.

9. Reference

1. Li, K.; Zhen, S.; Wang, W.; Du, J.; Yu, S.; Wu, Y.; Guo, H. Fungicide-inspired precursors of π allylpalladium intermediates for palladium-catalyzed decarboxylative cycloadditions. *Chemical Science* **2023**, *14*, 3024-3029.

2. Scuiller, A.; Casaretto, N.; Archambeau, A. Diastereo- and Enantioselective (3 + 2) Cycloaddition of a New Aza- π -Allylpalladium Zwitterionic Intermediate. *The Journal of Organic Chemistry* **2023**, 88, 9941-9945.

10. X-ray crystallographic data of 3e and 4a.

Single crystals of compound **3e** was prepared through dissolving the sample in mixture solvent of EtOH/EA (1:1) at room temperature and crystalizing by slow evaporation of solvent.

	and a second sec						
3e	CCDC 2410445						
Table 1 Crystal data and structure refinement for 3e.							
Identification code	3e						
Empirical formula	$C_{31}H_{24}CINO_2$						
Formula weight	477.96						
Temperature/K	149.99(10)						
Crystal system	orthorhombic						
Space group	Pbca						
a/Å	19.1841(4)						
b/Å	10.0695(2)						
c/Å	26.0275(5)						
α/°	90						
β/°	90						
$\gamma/^{\circ}$	90						
Volume/Å ³	5027.84(17)						
Z	8						
$\rho_{calc}g/cm^3$	1.263						
µ/mm ⁻¹	1.563						
F(000)	2000.0						
Crystal size/mm ³	$0.14 \times 0.11 \times 0.09$						
Radiation	Cu Ka ($\lambda = 1.54184$)						
2Θ range for data collection/°	6.792 to 147.134						
Index ranges	$-16 \le h \le 23, -12 \le k \le 8, -25 \le l \le 32$						
Reflections collected	12648						
Independent reflections	4957 [R_{int} = 0.0390, R_{sigma} = 0.0418]						
Data/restraints/parameters	4957/0/321						
Goodness-of-fit on F ²	1.016						
Final R indexes [I>= 2σ (I)]	$R_1 = 0.0577, wR_2 = 0.1574$						
Final R indexes [all data]	$R_1 = 0.0684, wR_2 = 0.1700$						
Largest diff. peak/hole / e Å ⁻³	0.36/-0.30						

Single crystals of compound **4a** was prepared through dissolving the sample in mixture solvent of EtOH/EA (1:1) at room temperature and crystalizing by slow evaporation of solvent.

Ì

	Jos -					
ŃH	the for					
	CCDC 2410441					
Table 2 Crystal data and structure refinement for 4a.						
Identification code	4a					
Empirical formula	C ₃₂ H ₂₇ NO ₃					
Formula weight	473.54					
Temperature/K	169.98(10)					
Crystal system	tetragonal					
Space group	I-4					
a/Å	32.4772(4)					
b/Å	32.4772(4)					
c/Å	5.00380(10)					
$\alpha/^{\circ}$	90					
β/°	90					
$\gamma/^{\circ}$	90					
Volume/Å ³	5277.85(17)					
Z	8					
$\rho_{calc}g/cm^3$	1.192					
µ/mm⁻¹	0.603					
F(000)	2000.0					
Crystal size/mm ³	$0.14 \times 0.12 \times 0.1$					
Radiation	Cu Ka ($\lambda = 1.54184$)					
2Θ range for data collection/°	5.442 to 146.832					
Index ranges	$-39 \le h \le 27, -39 \le k \le 23, -5 \le l \le 5$					
Reflections collected	9975					
Independent reflections	4583 [R_{int} = 0.0181, R_{sigma} = 0.0224]					
Data/restraints/parameters	4583/0/331					
Goodness-of-fit on F ²	1.062					
Final R indexes [I>= 2σ (I)]	$R_1 = 0.0323$, $wR_2 = 0.0827$					
Final R indexes [all data]	$R_1 = 0.0334$, $wR_2 = 0.0836$					
Largest diff. peak/hole / e Å ⁻³	0.17/-0.16					
Flack/Hooft parameter	0.02(7)/0.03(8)					

11. NMR spectra of substrates and products





35


¹H NMR (400 MHz, Chloroform-*d*) of 1d





¹H NMR (400 MHz, Chloroform-d) of 1e



¹H NMR (400 MHz, Chloroform-*d*) of 1f

7,6340 7,6291 7,6291 7,6180 7,6180 7,6180 7,6180 7,56956 7,56956 7,4673 7,4673 7,4673 7,4673 7,4673 7,4673 7,4673 7,4673 7,4673 7,47480 7,44800 7,44800 7,44800 7,44800 7,44800 7,44800 7,44800 7,44800 7,44800 7,46









¹H NMR (400 MHz, Chloroform-*d*) of 1h









¹³C NMR (101 MHz, Chloroform-*d*) of 1k









¹H NMR (400 MHz, Chloroform-d) of 10





























90 80 f1 (ppm)







90 80 fl (ppm)




90 80 f1 (ppm)




90 80 f1 (ppm)







































166.35 166.155 166.155 166.155 166.155 166.155 155.061 155.061 155.061 157.051 157.051 157.051 157.052 157.056 157.056 157.056 157.056 157.056 157.056 157.056 157.056 110.557 1110.57 1110.57 1110.55



































90 80 f1 (ppm)
























¹H NMR (400 MHz, Chloroform-d) and ¹³C NMR (101 MHz, Chloroform-d) of 4h












