Metal-Free Visible-Light-Driven Cascade Cyclization Reaction to Synthesize 2-Oxindoles via Benzoyl and Phenylsulfinyl Radicals with Acrylamide Derivatives

Xin Sun,^{*,a} Jing-Ping Zhu,^{a,f} Qing-Chuang Qiu,^{a,f} Ya-Li He,^a Da-Rong Hu,^a Xin-Ling Li,^a Gui-Ping Lu,^a Ying-Hui Yuan,^a Xiang-Fei Zhang,^a Miao Yu,^{*,a} and Bin Wu^{*,b}

^aSchool of Chemistry and Pharmaceutical Engineering, Huanghuai University, Zhumadian 463000, China ^bSchool of Pharmaceutical Sciences, South-Central Minzu University, Wuhan 430074, China

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Experiment Section.

1. NMR spectra were recorded on Bruker DPX-400, DRX-600 and Bruker Ascend IIITM 600 MHz NMR spectrometer instruments and calibrated using residual solvent peaks as internal reference, such as CDCl₃ solutions. High resolution mass spectra were performed on API STAR Pulsar and Thermo Q Exactive. Fluorescence data were obtained with Hitachi F-2700 spectrofluorometer. TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel 60F₂₅₄. Silica gel (Wakogel 200 - 300 mesh) was used for column chromatography.

2.Reagent: Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Unsaturated ketenes were purchased from Accela ChemBio Co., Ltd and Shanghai Titan Scientific Co., Ltd.. Cinnamic acids were purchased from Energy-Chemical Co., Ltd.. Other reagents were purchased from Thermo Fisher Scientific Co., Ltd. and Shanghai Aladdin Biochemical Technology Co., Ltd.. Solvents were purchased from Shanghai Titan Scientific Co., Ltd. and Thermo Fisher Scientific Co., Ltd..

The preparation of 2-oxindole reactions were carried out under N₂ atmosphere.



Figure S1. Photos of photochemical reaction devices

Table S1. Screening of Reaction Conditions.^a

ć	Me	0	CFL PC-1, 0.2 equiv, K ₂ CO ₃ , 2.0 equiv,	Ph	O	CI
Į	N O + Ph		$K_2S_2O_8$, 2.0 equiv	Me	s l	
	Ме 5а	O solv	N_2 , rt, 24 h	, N 6a Me	PC-1	
Entry	solvent /H ₂	0 (v/v)	РС	Base	Oxidant	Yield (%) ^a
1	DMF	neat	PC-1	K ₂ CO ₃	$K_2S_2O_8$	29
2	DMF/H ₂ O	1/1	PC-1	K ₂ CO ₃	$K_2S_2O_8$	57
3	DMF/H ₂ O	1/1	PC-1	K_2CO_3	$K_2S_2O_8$	37
4	CH₃CN/H₂O	1/1	PC-1	K_2CO_3	$K_2S_2O_8$	90
5	CH₃CN	neat	PC-1	K_2CO_3	$K_2S_2O_8$	16
6	CH_3CN/H_2O	9/1	PC-1	K_2CO_3	$K_2S_2O_8$	54
7	CH_3CN/H_2O	18eq	PC-1	K_2CO_3	$K_2S_2O_8$	41
8	CH₃CN/H₂O	4/1	PC-1	K ₂ CO ₃	$K_2S_2O_8$	96
9	CH_3CN/H_2O	4/1	PC-1	None	$K_2S_2O_8$	33
10	CH₃CN/H₂O	4/1	PC-1	K_2CO_3	None	14
11	CH_3CN/H_2O	4/1	None	K_2CO_3	$K_2S_2O_8$	0
12 ^b	CH_3CN/H_2O	4/1	PC-1	K_2CO_3	$K_2S_2O_8$	0
13	THF/H₂O	4/1	PC-1	K_2CO_3	$K_2S_2O_8$	85
14	dioxane/H $_2O$	4/1	PC-1	K_2CO_3	$K_2S_2O_8$	66
15	DMSO/H ₂ O	4/1	PC-1	K_2CO_3	$K_2S_2O_8$	94
16	PhMe/H₂O	4/1	PC-1	K_2CO_3	$K_2S_2O_8$	19
17	CH₃CN/H₂O	4/1	Ru(bpy) ₃ Cl ₂ •6H ₂ O	K_2CO_3	$K_2S_2O_8$	trace
18	CH₃CN/H₂O	4/1	lr(ppy)₃	K ₂ CO ₃	$K_2S_2O_8$	0
19	CH_3CN/H_2O	4/1	4CzIPN	K_2CO_3	$K_2S_2O_8$	0
20	CH₃CN/H₂O	4/1	xanthen-9-one	K_2CO_3	$K_2S_2O_8$	0
21	CH_3CN/H_2O	4/1	Ru(bpy)₃ Cl₂	K_2CO_3	$K_2S_2O_8$	trace
22	CH_3CN/H_2O	4/1	PC-1	Na_2CO_3	$K_2S_2O_8$	95
23	CH₃CN/H₂O	4/1	PC-1	Cs_2CO_3	$K_2S_2O_8$	84
24	CH_3CN/H_2O	4/1	PC-1	NaOAc	$K_2S_2O_8$	90
25	CH_3CN/H_2O	4/1	PC-1	LiOHH ₂ O	$K_2S_2O_8$	78
26	CH_3CN/H_2O	4/1	PC-1	K_2CO_3	$Na_2S_2O_8$	93
27	CH_3CN/H_2O	4/1	PC-1	K_2CO_3	(NH ₄) ₂ S ₂ O ₈	92
28	CH_3CN/H_2O	4/1	PC-1	K_2CO_3	CAN	0
29	CH_3CN/H_2O	4/1	PC-1	K_2CO_3	Cu(OAc) ₂	0
30	CH_3CN/H_2O	1/1	PC-1	K_2CO_3	$K_2S_2O_8$	54
31	CH_3CN/H_2O	3/2	PC-1	K_2CO_3	$K_2S_2O_8$	39
32	CH_3CN/H_2O	7/3	PC-1	K_2CO_3	$K_2S_2O_8$	50
33	CH_3CN/H_2O	9/1	PC-1	K_2CO_3	$K_2S_2O_8$	48
34	CH_3CN/H_2O	4/1	PC-1	K_2CO_3	$K_2S_2O_8$	79
35 ^c	CH_3CN/H_2O	4/1	PC-1	K_2CO_3	$K_2S_2O_8$	59
36 ^{<i>d</i>}	CH₃CN/H₂O	4/1	PC-1	K ₂ CO ₃	$K_2S_2O_8$	46

37 ^e	CH ₃ CN/H ₂ O	4/1	PC-1	K ₂ CO ₃	$K_2S_2O_8$	46
38 ^f	CH₃CN/H₂O	4/1	PC-1	K ₂ CO ₃	$K_2S_2O_8$	44
39	CH₃CN/H₂O	4/1	PC-1	K ₂ CO ₃	$K_2S_2O_8$	30
40 ^{<i>h</i>}	CH₃CN/H₂O	4/1	PC-1	K ₂ CO ₃	$K_2S_2O_8$	34

^{*a*}Isolated yield. ^{*b*}The reaction was run in dark. ^{*c*}K₂CO₃ (1.2 equiv) was used. ^{*d*}K₂S₂O₈ (1.2 equiv) was used. ^{*e*}ketonic acid (1.2 equiv) was used. ^{*f*}PC-1 (0.1 equiv) was used. ^{*g*}PC-1 (0.05 equiv) was used. ^{*h*}The reaction was run in air.







Entry	Solvent/H ₂ O (v/v)		РС	Oxidant	Yield ^a
1	MeCN/H ₂ O	4/1	PC-1	$K_2S_2O_8$	22
2	MeCN	neat	PC-2	$K_2S_2O_8$	40
3	MeOH /H ₂ O	4/1	PC-1	K ₂ S ₂ O ₈	90
4	MeOH/H ₂ O	9/1	PC-2	$K_2S_2O_8$	63
5	MeOH/H ₂ O	4/1	PC-2	K ₂ S ₂ O ₈	92
5	DMSO/H ₂ O	4/1	PC-2	$K_2S_2O_8$	86
6	DMF/H ₂ O	4/1	PC-2	$K_2S_2O_8$	47
7	MeOH/H ₂ O	4/1	PC-3	$K_2S_2O_8$	0
8	MeOH/H ₂ O	4/1	PC-4	$K_2S_2O_8$	63
9	MeOH/H ₂ O	4/1	PC-5	$K_2S_2O_8$	81
10	MeOH/H ₂ O	4/1	PC-6	$K_2S_2O_8$	40
11	MeOH/H ₂ O	4/1	PC-7	$K_2S_2O_8$	49
12	MeOH/H ₂ O	4/1	PC-2	$Na_2S_2O_8$	89
13	MeOH/H ₂ O	4/1	PC-2	(NH ₄) ₂ S ₂ O ₈	86
14	MeOH/H ₂ O	4/1	none	$K_2S_2O_8$	12
15	MeOH/H ₂ O	4/1	PC-2	none	34
16 ^{<i>b</i>}	MeOH/H ₂ O	4/1	PC-2	$K_2S_2O_8$	0
17 ^c	MeOH/H ₂ O	4/1	PC-2	$K_2S_2O_8$	26
18 ^{<i>d</i>}	MeOH/H ₂ O	4/1	PC-2	$K_2S_2O_8$	68
19 ^e	MeOH/H ₂ O	4/1	PC-2	$K_2S_2O_8$	56
20 ^{<i>f</i>}	MeOH/H ₂ O	4/1	PC-2	$K_2S_2O_8$	66

^{*a*}Isolated yield. ^{*b*}The reaction was run in dark. ^{*c*}The reaction was run in air. ^{*d*}Sodium benzenesulfinate (1.2 equiv) was used. ^{*e*}PC-2 (0.02 equiv) was used. ^{*f*}K₂S₂O₈ (1.2 equiv) was used.



General procedure for synthesis of starting materials.



To the mixture of aniline derivatives (10 mmol, 1.0 equiv) and Et₃N (20.0 mmol, 2.0 equiv) in dichloromethane (DCM, 30.0 mL) was added 2-methacryloyl chloride (12.0 mmol, 1.2 equiv) in portions at 0 °C, the resulting mixture was stirred at room temperature until the aniline derivatives totally consumed. The reaction mixture was quenched with water (3.0 mL) and saturated NaHCO₃ (3.0 mL), and then extracted with dichloromethane (DCM, 10.0 mL \times 3), the combined organic phase was dried over anhydrous Na₂SO₄. The solvent was removed by rotary evaporation, the residual was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford N-phenylmethacrylamide products. The above mentioned N-phenylmethacrylamide (5.0 mmol, 1.0 equiv) was dissolved in anhydrous THF (20.0 mL), then NaH (7.5 mmol, 1.5 equiv) was added into the solvent in portions under N₂ atmosphere at 0 °C. After 30 min, CH₃I (6.0 mmol, 1.2 equiv) was added dropwise into the solution, the resulting mixture was stirred at room temperature until N-phenylmethacrylamide totally consumed. The reaction mixture was quenched with water (3.0 mL) and saturated NH₄Cl (3.0 mL) and extracted with dichloromethane (DCM, 10.0 mL \times 3), the combined organic phase was dried over anhydrous Na₂SO₄. The solvent was removed by rotary evaporation, the residual was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford desired *N*-methyl-*N*-phenylmethacrylamide product.

N-methyl-*N*-phenylmethacrylamide (5a): 543 mg, 62% yield. Light yellow crystal; ¹H NMR (400 MHz, CDCl₃) δ 7.31 (t, *J* = 7.9 Hz, 2H), 7.23 (t, *J* = 7.9 Hz, 1H), 7.13 – 7.11 (m, 2H), 4.99 (d, *J* = 17.6 Hz, 2H), 3.33 (s, 3H), 1.74 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 171.9, 144.6, 140.6, 129.1, 126.8, 126.4, 119.2, 37.6, 20.2. The NMR spectra data are consistent with previously reported^[S1].



N-methyl-*N*-(*p*-tolyl)methacrylamide (5b): 587 mg, 62% yield. Light yellow oil;¹H NMR (400 MHz, CDCl₃) δ 7.11 (d, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 8.3 Hz, 2H), 4.98(t, *J* = 1.4 Hz, 1H), 4.96 (t, *J* = 10 Hz, 1H), 3.28 (s, 3H), 2.31 (s, 3H), 1.72 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 171.9, 141.9, 140.7, 136.6, 129.7, 126.2, 118.9, 115.1, 37.5, 20.8, 20.2. The NMR spectra data are consistent with previously reported^[S2].



N-methyl-*N*-(*o*-tolyl)methacrylamide (5c): 748 mg, 79% yield. Light yellow oil;¹H NMR (400 MHz, CDCl₃) δ 7.20 – 7.12 (m, 3H), 7.01 (d, *J* = 7.2 Hz, 1H), 4.91 (s, 2H), 3.19 (s, 3H), 2.22 (s, 3H), 1.70 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 171.9, 143.0,

140.4, 134.7, 131.1, 128.0, 127.7, 126.8, 118.3, 36.5, 20.1, 17.5. The NMR spectra data are consistent with previously reported^[S3].



N-methyl-*N*-(*m*-tolyl)methacrylamide (5d): 776 mg, 82% yield. Light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.19 (t, *J* = 7.7 Hz, 1H), 7.04 (d, *J* = 8.8 Hz, 1H), 6.98 – 6.78 (m, 2H), 5.01 (s, 1H), 4.97 (s, 1H), 3.31 (s, 3H), 2.32 (s, 3H), 1.75 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 171.9, 144.5, 140.7, 139.1, 128.9, 127.6, 127.0, 123.5, 119.0, 37.6, 21.2, 20.2. The NMR spectra data are consistent with previously reported^[S4].



N-(4-isopropylphenyl)-*N*-methylmethacrylamide (5e): 369 mg, 34% yield. Light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.18 (d, *J* = 8.2 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 5.01 (d, *J* = 10.0 Hz, 2H), 3.32 (s, 3H), 2.93-2.87 (m, 1H), 1.74 (s, 3H), 1.25 (s, 3H), 1.22 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 172.0, 147.7, 142.2, 140.8, 127.1, 126.3, 119.1, 37.7, 33.6, 23.9, 20.3. The NMR spectra data are consistent with previously reported^[S5].



N-(4-(*tert*-butyl)phenyl)-*N*-methylmethacrylamide (5f): 821mg, 71% yield. Light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.33 (d, *J* = 8.5 Hz, 2H), 7.04 (d, *J* = 8.5 Hz,

2H), 5.02 (d, J = 7.2 Hz, 2H), 3.32 (s, 3H), 1.74 (s, 3H), 1.31 (s, 9H). ¹³C NMR (100 MHz, cdcl₃) δ 172.0, 149.9, 141.8, 140.8, 126.0, 125.9, 119.2, 37.7, 34.5, 31.3, 20.3. The NMR spectra data are consistent with previously reported^[S6].



N-(4-methoxyphenyl)-*N*-methylmethacrylamide (5g): 688 mg, 67% yield. Yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.03 (d, J = 8.9 Hz, 2H), 6.84 (d, J = 8.9 Hz, 2H), 4.99 (d, J = 12.3 Hz, 2H), 3.79 (s, 3H), 3.28 (s, 3H), 1.72 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 172.1, 158.3, 140.9, 137.4, 127.7, 118.8, 114.3, 55.4, 37.8, 20.3. The NMR spectra data are consistent with previously reported^[S7].



N-(3,5-dimethoxyphenyl)-*N*-methylmethacrylamide (5h): 529 mg, 45% yield. Yellow solid;¹H NMR (400 MHz, CDCl₃) δ 6.35 (s, 1H), 6.28 (s, 2H), 5.06 (d, *J* = 4.9 Hz, 2H), 3.77 (s, 3H), 3.31 (s, 3H), 1.80 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 171.9, 161.0, 146.3, 140.8, 119.0, 105.1, 98.7, 55.4, 37.6, 20.3. The NMR spectra data are consistent with previously reported^[S8].



N-(4-fluorophenyl)-*N*-methylmethacrylamide (5i): 918 mg, 95% yield. Light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.12-7.08 (m, 2H), 7.02 (t, *J* = 8.6 Hz, 2H),

5.04 (s, 1H), 4.96 (s, 1H), 3.30 (s, 3H), 1.75 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 171.9, 161.1 (d, $J_{C-F} = 245.7$ Hz), 140.6 (d, $J_{C-F} = 3.3$ Hz), 128.2 (d, $J_{C-F} = 8.5$ Hz), 119.3, 116.1 (d, $J_{C-F} = 22.5$ Hz), 37.8, 20.3. ¹⁹F NMR (376 MHz, CDCl₃) δ -114.67. The NMR spectra data are consistent with previously reported^[S9].



N-(2-fluorophenyl)-*N*-methylmethacrylamide (5j): 869 mg, 90% yield. Light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.30 – 7.24 (m, 1H), 7.19 – 7.08 (m, 3H), 5.01 (s, 1H), 4.94 (s, 1H), 3.30 (s, 3H), 1.82 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 172.19, 157.6 (d, J_{C-F} = 247.6 Hz), 140.1, 132.4-132.2 (m), 128.9 (t, J_{C-F} = 4.3 Hz), 124.6 (d, J_{C-F} = 3.9 Hz), 118.3, 116.4 (d, J_{C-F} = 20.1 Hz), 36.8, 19.8. ¹⁹F NMR (376 MHz, CDCl₃) δ -121.60. The NMR spectra data are consistent with previously reported^[S10].



N-(4-chlorophenyl)-*N*-methylmethacrylamide (5k): 828 mg, 79% yield. Light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.30 (d, *J* = 8.8 Hz, 2H), 7.06 (d, *J* = 8.8 Hz, 2H), 5.13 – 5.01 (t, *J* = 1.4 Hz, 1H), 5.01 – 4.88 (t, *J* = 1.0 Hz, 1H), 3.31 (s, 3H), 1.76 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 171.8, 143.1, 140.4, 132.5, 129.3, 129.0, 127.7, 119.6, 116.3, 37.6, 20.2. The NMR spectra data are consistent with previously reported^[S10].



N-(4-bromophenyl)-*N*-methylmethacrylamide (5l): 813mg, 64% yield. White solid; ¹H NMR (400 MHz, CDCl₃) δ 7.45 (d, *J* = 8.3 Hz, 2H), 7.01 (d, *J* = 8.7 Hz, 2H), 5.07 (s, 1H), 4.97 (s, 1H), 3.31 (s, 3H), 1.77 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 171.7, 143.7, 140.3, 132.3, 128.0, 120.3, 119.7, 37.5, 20.2. The NMR spectra data are consistent with previously reported^[S11].



N-(4-iodophenyl)-*N*-methylmethacrylamide (5m): 858 mg, 57% yield. Light yellow crystal solid; ¹H NMR (400 MHz, CDCl₃) δ 7.66 (d, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 8.6 Hz, 2H), 5.07 (s, 1H), 4.98 (s, 1H), 3.32 (s, 3H), 1.78 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 171.7, 144.4, 140.4, 138.4, 128.3, 119.8, 91.5, 37.5, 20.3. The NMR spectra data are consistent with previously reported^[S12].



N-methyl-*N*-(2-(trifluoromethoxy)phenyl)methacrylamide (5n): 804 mg, 62% yield. Light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.24-7.21 (m, 4H), 4.95 (s, 1H), 4.79 (s, 1H), 3.22 (s, 3H), 1.78 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 171.9, 144.6, 140.0, 136.9, 129.2, 128.5, 127.3, 120.9, 120.3 (q, *J* = 257.6 Hz), 118.8, 37.0, 19.8. ¹⁹F NMR (376 MHz, CDCl₃) δ -57.31. The NMR spectra data are consistent with previously reported^[S13].



N-methyl-*N*-(4-(trifluoromethoxy)phenyl)methacrylamide (50): 959 mg, 74% yield. Light yellow crystal; ¹H NMR (400 MHz, CDCl₃) δ 7.20 (s, 4H), 5.09 (s, 1H), 5.00 (s, 1H), 3.36 (s, 3H), 1.80 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 171.8, 147.4 (q, $J_{C-F} = 7.5$ Hz), 143.1, 140.3, 127.7, 124.1, 121.6, 120.3 (q, $J_{C-F} = 256.1$ Hz), 119.6, 37.6, 20.1. ¹⁹F NMR (376 MHz, CDCl₃) δ -58.15. The NMR spectra data are consistent with previously reported^[S5].



N-methyl-*N*-(4-(trifluoromethyl)phenyl)methacrylamide (5p): 1.08 g, 89% yield. Light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.59 (d, J = 8.7 Hz, 2H), 7.25 (d, J = 8.8 Hz, 2H), 5.09 (s, 2H), 4.98 (s, 2H), 3.36 (s, 3H), 1.80 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 171.7, 147.8 (d, $J_{C-F} = 1.2$ Hz), 140.2, 128.7 (q, $J_{C-F} = 32.7$ Hz), 126.4, 126.3 (q, $J_{C-F} = 3.8$ Hz), 123.7 (q, $J_{C-F} = 270.5$ Hz), 120.1, 37.5, 20.1. ¹⁹F NMR (376 MHz, CDCl₃) δ -62.55. The NMR spectra data are consistent with previously reported ^[S7].



N-(3,5-bis(trifluoromethyl)phenyl)-N-methylmethacrylamide (5q): 763mg, 49%

yield. Yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.74 (s, 1H), 7.62 (s, 2H), 5.18 (s, 1H), 4.99 (s, 1H), 3.42 (s, 3H), 1.86 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 171.7, 146.0, 139.9, 132.7 (q, *J*_{C-F} =33.7 Hz), 126.16-126.07 (m), 122.8 (q, *J*_{C-F} =271.3 Hz), 120.3, 120.18-120.03 (m), 37.6, 20.0. ¹⁹F NMR (376 MHz, CDCl₃) δ -63.16. HRMS(EI) Calcd for C₁₃H₁₁F₆NO [M + H]⁺:312.0823, Found 312.0817; IR (KBr) v(cm⁻¹): 3054, 2925, 1665, 1633, 1615, 1471, 1424, 1356, 1110, 1055, 847.



N-methyl-*N*-(3,4,5-trifluorophenyl)methacrylamide (5r): 367mg, 32% yield. Light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 6.82 (dd, J = 8.2 and 6.1 Hz, 2H), 5.16 (s, 1H), 5.03 (s, 1H), 3.31 (s, 3H), 1.84 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 171.6, 161.3 (dd, $J_{C-F} = 25.0$ and 14.2 Hz), 152.4 (dd, $J_{C-F} = 10.5$ and 5.2 Hz), 150.2 (dd, $J_{C-F} = 7.5$ and 5.2 Hz), 149.9 (dd, $J_{C-F} = 10.5$ and 5.5Hz), 140.0, 139.9 (dd, $J_{C-F} = 4.6$ and 2.1 Hz), 131.0 (dd, $J_{C-F} = 15.8$ and 6.6 Hz), 119.9, 111.1 (dd, $J_{C-F} = 16.2$ and 6.4 Hz) 110.0, 37.7, 20.2. ¹⁹F NMR (376 MHz, CDCl₃) δ -132.6 (dd, J = 20.7 and 8.1 Hz), -161.6 (tt, J = 20.8 and 6.0 Hz). HRMS(EI) Calcd for C₁₁H₁₀F₃NO [M + H]⁺: 230.0793, Found 230.0784; IR (KBr) v(cm⁻¹): 2924, 2852, 1662, 1623, 1527, 1350, 1239, 1105, 1048.



N-phenyl-*N*-(p-tolyl)methacrylamide (5s): 452 mg, 36% yield. Light yellow solid; ¹H NMR (400 MHz, CDCl₃) δ 7.32 (t, *J* = 7.9 Hz, 2H), 7.22 – 7.12 (m, 4H), 7.05 (d, *J* = 8.3 Hz, 2H), 5.23 (s, 1H), 5.16 (s, 1H), 2.34 (s, 3H), 1.83 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 171.9, 143.6, 141.3, 140.9, 136.4, 129.7, 129.0, 127.04, 126.95, 126.3, 120.7, 21.0, 19.9. The NMR spectra data are consistent with previously reported^[S11].



N-benzyl-*N*-phenylmethacrylamide (5t): 666 mg, 53% yield. Light green oil; ¹H NMR (400 MHz, CDCl₃) δ 7.35 – 7.29 (m, 7H), 7.03 (d, *J* = 7.8 Hz, 2H), 5.08 (d, *J* = 7.2 Hz, 2H), 5.03 (s, 2H), 1.84 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 171.8, 143.1, 140.7, 137.4, 129.0, 128.3, 127.4, 127.2, 127.0, 119.3, 53.1, 20.3. The NMR spectra data are consistent with previously reported^[S12].



N, *N*-diphenylmethacrylamide (5u): 759 mg, 64% yield. Light green crystal solid; ¹H NMR (400 MHz, CDCl₃) δ 7.33 (t, *J* = 7.7 Hz, 3H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.17 (m, 3H), 5.23 (s, 1H), 5.17 (s, 1H), 1.84 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 171.9, 143.5, 141.2, 129.1, 127.1, 126.5, 120.9, 19.9. The NMR spectra data are consistent with previously reported^[S7].



N-(2-fluoro-5-(trifluoromethyl)phenyl)-*N*-methylmethacrylamide (7la): 1.21 g, 93% yield. Light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.56 – 7.53 (m, 1H), 7.47 (dd, *J* = 7.0 and 1.9 Hz, 1H), 7.23 (t, *J* = 9.1 Hz, 1H), 5.07 (s, 1H), 4.93 (s, 1H), 3.32 (s, 3H), 1.85 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 172.0, 159.5 (d, *J*_{C-F} = 254.9 Hz), 139.8,

133.1(ddd, $J_{C-F} = 12.3$, 1.9 and 0.9 Hz), 127.6 (dd, $J_{C-F} = 33.7$ and 4.1 Hz), 126.6-126.4 (m), 126.2-126.0 (m), 123.1 (d, $J_{C-F} = 270.6$ Hz), 118.9, 117.4 (d, $J_{C-F} = 21.7$ Hz), 36.9, 19.8. ¹⁹F NMR (376 MHz, CDCl₃) δ -62.26, -115.57. The NMR spectra data are consistent with previously reported^[S14].



N-(4-cyanophenyl)-*N*-methylmethacrylamide (70a): 451 mg, 45% yield. Light yellow crystal; ¹H NMR (400 MHz, CDCl₃) δ 7.64 (d, *J* = 8.7 Hz, 2H), 7.25 (d, *J* = 8.7 Hz, 2H), 5.14 (s, 1H), 4.99 (s, 1H), 3.38 (s, 3H), 1.83 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 171.6, 148.6, 140.0, 133.1, 126.5, 120., 118.1, 110.1, 37.4, 20.1. The NMR spectra data are consistent with previously reported^[S6].



N-methyl-*N*-(naphthalen-1-yl)methacrylamide (7pa): 878 mg, 78% yield. Light yellow powder solid; ¹H NMR (400 MHz, CDCl₃) δ 7.88 (t, *J* = 8.8 Hz, 2H), 7.82 (d, *J* = 8.3 Hz, 1H), 7.60 – 7.52 (m, 2H), 7.43 (t, *J* = 7.7 Hz, 1H), 7.25 (d, *J* = 5.9 Hz, 1H), 4.90 (s, 1H), 4.76 (s, 1H), 3.41 (s, 3H), 1.70 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 172.9, 141.0, 140.5, 134.6, 130.1, 128.6, 128.2, 127.2, 126.5, 125.6, 125.4, 122.8, 117.8, 110.0, 37.6, 20.3. The NMR spectra data are consistent with previously reported^[S15].



N-methyl-*N*-(naphthalen-2-yl)methacrylamide (7qa): 451 mg, 40% yield. Light yellow crystal solid; ¹H NMR (400 MHz, CDCl₃) δ 7.85-7.78 (m, 3H), 7.57 (d, *J* = 1.8 Hz, 1H), 7.53 – 7.48 (m, 2H), 7.29 – 7.26 (m, 1H), 5.04 (s, 1H), 5.01 (s, 1H), 3.43 (s, 3H), 1.78 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 172.1, 142.0, 140.7, 133.4, 131.9, 129.2, 127.7, 126.7, 126.3, 125.0, 124.4, 119.5, 37.7, 20.3. The NMR spectra data are consistent with previously reported^[S16].



N-ethyl-*N*-(*o*-tolyl)methacrylamide (7ra): 579 mg, 57% yield. Dark yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.22-7.15 (m, 3H), 7.01 (d, *J* = 7.5 Hz, 1H), 4.91 (s, 2H), 4.14-4.06 (m, 1H), 3.37-3.28 (m, 1H), 2.24 (s, 3H), 1.71 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 171.4, 141.3, 140.9, 135.4, 131.2, 129.5, 127.7, 126.5, 118.0, 43.6, 20.2, 17.8, 12.4. HRMS(EI) Calcd for C₁₃H₁₇NO [M + H]⁺: 204.1388, Found 204.1385; IR (KBr) v(cm⁻¹): 2975, 2933, 1651, 1626, 1492, 1411, 1320, 1228, 1110, 915.



N-methyl-*N*-(phenyl-d₅)methacrylamide (7ra): 243 mg, 27% yield. Light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 5.03 (s, 1H), 4.98 (s, 1H), 3.35 (s, 3H), 1.76 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 172.0, 140.7, 128.7 (t), 126.1 (t), 119.3, 37.7, 20.3. The NMR spectra data are consistent with previously reported^[S17].

General procedure for preparation of 2-oxindoles.



1). General procedure for benzoyl radical cyclization reactions

N-methyl-*N*-phenylmethacrylamide **5a** (0.1 mmol, 1.0 equiv), ketonic acid (0.2 mmol, 2.0 equiv), K₂CO₃ (0.2 mmol, 2.0 equiv), K₂S₂O₈ (0.2 mmol, 2.0 equiv) and 2-chlorothioxanthone (0.02 mmol, 0.2 equiv) were added into schlenk tubes, followed by the addition of CH₃CN/H₂O (2.0 mL, 4/1, v/v), the resulting mixture were then exposed to a 23 W white fluorescent lamp (LEDs) under nitrogen atmosphere for corresponding hours until the starting materials *N*-methyl-*N*-phenylmethacrylamide totally consumed or left maintain without change (A fan is used to cool down the reaction temperature). The reaction mixture was filtrated and the filtrate was extracted with dichloromethane (DCM, 5.0 mL×3), the combined organic phase was dried over anhydrous Na₂SO₄. The solvent was removed by rotary evaporation, the residual was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford desired 3-methyl-3-acetophenone-2-oxindoles **6**.



1,3-dimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (6a): 26.8 mg, 96% yield. Colorless viscous oil; ¹H NMR (400 MHz, CDCl₃) δ 7.84 – 7.82 (m, 2H), 7.51 (t, J = 7.4 Hz, 1H), 7.39 (t, J = 7.7 Hz, 2H), 7.25 (td, J = 7.7 and 1.2 Hz,1H), 7.14 (d, J = 7.3 Hz, 1H), 6.97 (td, J = 7.6 and 0.9 Hz, 1H), 6.90 (d, J = 7.7 Hz, 1H), 3.68 (q, J = 17.9//11.3 Hz, 2H), 3.31 (s, 3H), 1.44 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 196.1, 180.5, 143.8, 136.4, 133.7, 133.1, 128.4, 127.9, 127.8, 122.1, 121.7, 108.1, 46.00, 45.3, 26.4, 24.9. The NMR spectra data are consistent with previously reported^[S17].



1,3,5-trimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (6b): 15.4 mg, 53% yield. Colorless viscous oil; ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, J = 7.2 Hz, 2H), 7.51 (d, J = 7.4 Hz, 1H), 7.40 (t, J = 7.9 Hz, 2H), 7.05 (d, J = 7.9 Hz, 1H), 6.95 (s, 1H), 6.78 (d, J = 7.9 Hz, 1H), 3.92 – 3.55 (m, 1H), 3.29 (s, 3H), 2.27 (s, 3H), 1.43 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 196.1, 180.5, 141.5, 136.4, 133.8, 133.1, 131.6, 128.4, 128.1, 128.0, 122.7, 107.8, 46.0, 45.3, 26.5, 25.0, 21.1. The NMR spectra data are consistent with previously reported^[S18-S20].



1,3,7-trimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (6c): 25.6 mg, 87% yield. Colorless viscous oil; ¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, J = 7.2 Hz, 2H), 7.51 (t, J = 7.4 Hz, 1H), 7.39 (t, J = 7.7 Hz, 2H), 6.95 (t, J = 6.9 Hz, 2H), 6.85 (t, J = 7.5 Hz, 1H), 3.67 (d, J = 2.8 Hz, 2H), 3.58 (s, 3H), 2.62 (s, 3H), 1.41 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 196.1, 181.3, 141.6, 136.4, 134.3, 133.1, 131.5, 128.4, 127.9, 122.0, 119.7, 119.5, 46.3, 44.6, 29.8, 25.5, 19.1. The NMR spectra data are consistent with previously reported^[S18-S20].



Mixture of 1,3,5-trimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one

and **1,3,4-trimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (6d)**: 15.7 mg, 54% yield. Colorless viscous oil; ¹H NMR (400 MHz, CDCl₃) δ 7.84-7.80 (m, 3.07 H), 7.51 (t, *J* = 7.4 Hz, 1.55 H), 7.39 (t, *J* = 7.7 Hz, 3.02 H), 7.15 (t, *J* = 7.8 Hz, 1.11 H), 7.02 (d, *J* = 7.5 Hz, 0.63 H), 6.78 (d, *J* = 7.5 Hz, 0.59 H), 6.73 (d, *J* = 7.9 Hz, 2.44 H), 3.94 (d, *J* = 17.7 Hz, 1.24 H), 3.72 – 3.59 (m, 2.35H), 3.29 (s, 1.51 H), 3.26 (s, 2.95 H), 2.37 (s, 1.54 H), 2.30 (s, 3.00 H), 1.49 (s, 3.15 H), 1.43 (s, 1.70 H). ¹³C NMR (100 MHz, CDCl₃) δ 196.23, 196.15, 180.8, 180.4, 144.0, 143.8, 137.8, 136.4, 136.2, 133.1, 133.0, 132.7, 130.7, 130.3, 128.4, 127.91, 127.87, 127.6, 124.7, 122.6, 121.5, 109.1, 105.9, 46.1, 46.0, 45.04, 44.98, 26.5, 26.4, 24.9, 22.9, 21.8, 18.2. The NMR spectra data are consistent with previously reported^[S20-S21].



5-isopropyl-1,3-dimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (6e): 29.6 mg, 92% yield. Colorless viscous oil; ¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, *J* = 7.3 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.10 (dd, *J* = 8.0 and 1.6 Hz, 1H), 7.00 (d, *J* = 1.2 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 3.97 – 3.48 (m, 1H), 3.28 (s, 3H), 1.45 (s, 3H), 1.17 (dd, *J* = 6.8, 4.9 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 196.3, 180.6, 143.0, 141.6, 136.6, 133.5, 133.0, 128.4, 127.9, 125.4, 120.3, 107.8, 45.9, 45.5, 33.8, 26.4, 24.8, 24.2, 24.1. HRMS(EI) Calcd for C₂₁H₂₃NO₂ [M + H]⁺: 322.1802, Found 322.1802; IR (KBr) v(cm⁻¹): 2961, 2869, 1712, 1691, 1599, 1498, 1351, 1217, 1119, 815.



5-(*tert*-butyl)-1,3-dimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (6f): 20.8 mg, 62% yield. Colorless viscous oil; ¹H NMR (400 MHz, CDCl₃) δ 7.83 – 7.81 (m, 2H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.26 (dd, *J* = 8.1 and 1.9 Hz, 1H), 7.17 (d, *J* = 1.7 Hz, 1H), 6.81 (d, *J* = 8.1 Hz, 1H), 3.65 (q, *J* = 17.5 Hz, 2H), 3.28 (s, 3H), 1.46 (s, 3H), 1.24 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 196.4, 180.6, 145.3, 141.3, 136.7, 133.2, 133.0, 128.4, 128.0, 124.4, 119.2, 107.5, 45.9, 45.7, 34.5, 31.5, 26.4, 24.8. HRMS(EI) Calcd for C₂₂H₂₅NO₂ [M + H]⁺ : 336.1964, Found 336.1954; IR (KBr) v(cm⁻¹): 2963, 2869, 1712, 1693, 1500, 1351, 1256, 1215, 1057, 815.



5-methoxy-1,3-dimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (6g): 22.3 mg, 72% yield. Colorless viscous oil; 1H NMR (400 MHz, CDCl3) δ 7.84 – 7.82 (m, 2H), 7.53 – 7.49 (m, 1H), 7.39 (t, *J* = 7.5 Hz, 2H), 6.81-6.75 (m, 3H), 3.73 (d, *J* = 1.3 Hz, 3H), 3.66 (d, *J* = 1.6 Hz, 2H), 3.28 (d, *J* = 1.3 Hz, 3H), 1.43 (d, *J* = 1.4 Hz, 3H). 13C NMR (100 MHz, CDCl3) δ 196.0, 180.2, 155.7, 137.4, 136.3, 135.2, 133.1, 128.4, 127.9, 111.4, 109.9, 108.3, 55.7, 46.0, 45.7, 26.5, 24.9. The NMR spectra data are consistent with previously reported^[S19].



4,6-dimethoxy-1,3-dimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (6h): 6.6 mg, 19%

yield. Colorless viscous oil; ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, *J* = 8.5 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 6.15 (d, *J* = 2.0 Hz, 1H), 6.06 (d, *J* = 1.9 Hz, 1H), 4.08 (d, *J* = 17.5 Hz, 1H), 3.80 (s, 3H), 3.71 (s, 3H), 3.46 (d, *J* = 17.5 Hz, 1H), 3.27 (s, 3H), 1.45 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 197.1, 181.4, 161.2, 155.9, 145.7, 136.7, 132.8, 128.3, 128.0, 110.9, 92.1, 55.5, 55.2, 45.1, 44.6, 26.6, 23.0. HRMS(EI) Calcd for C₂₀H₂₁NO₄ [M + H]⁺: 340.1549, Found 340.1533; IR (KBr) v(cm⁻¹): 2965, 2933, 1714, 1690, 1450, 1380, 1256, 1211, 1146, 1071, 813.



5-fluoro-1,3-dimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (**6i**): 22.8 mg, 77% yield. Colorless viscous oil; ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, J = 7.2 Hz, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.40 (t, J = 7.7 Hz, 2H), 6.97 – 6.89 (m, 2H), 6.81 (dd, J = 8.4 and 4.2 Hz, 1H), 3.67 (s, 2H), 3.29 (s, 3H), 1.43 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 195.9, 180.2, 159.1 (d, $J_{C-F} = 238.6$ Hz), 139.8 (d, $J_{C-F} = 1.9$ Hz), 136.2, 135.4 (d, $J_{C-F} = 7.8$ Hz), 133.3, 128.5, 127.9, 113.8 (d, $J_{C-F} = 23.2$ Hz), 110.1 (d, $J_{C-F} = 24.7$ Hz), 108.5 (d, $J_{C-F} = 8.1$ Hz), 45.9, 45.7, 26.6, 24.8. ¹⁹F NMR (376 MHz, CDCl₃) δ -121.24. The NMR spectra data are consistent with previously reported^[S19-S20].



7-fluoro-1,3-dimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (6j): 22.0 mg, 74% yield. Colorless viscous oil; ¹H NMR (400 MHz, CDCl₃) δ 7.83 (dd, J = 8.2 and 1.1 Hz, 2H), 7.52 (tt, J = 6.9 and 1.2 Hz, 1H), 7.40 (t, J = 7.7 Hz, 2H), 7.00 – 6.94 (m,

1H), 6.90 – 6.87 (m, 2H), 3.69 (d, J = 0.9 Hz, 2H), 3.52 (d, J = 2.7 Hz, 3H), 1.43 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 195.9, 180.2, 148.2 (d, $J_{C-F} = 241.9$ Hz), 136.8 (d, $J_{C-F} = 3.5$ Hz), 136.2, 133.3, 130.5 (d, $J_{C-F} = 8.1$ Hz), 128.5, 127.9, 122.6 (d, $J_{C-F} = 6.4$ Hz), 117.4 (d, $J_{C-F} = 3.1$ Hz), 115.9 (d, $J_{C-F} = 19.3$ Hz), 46.3, 45.5, 28.9 (d, $J_{C-F} = 5.7$ Hz), 25.1. ¹⁹F NMR (376 MHz, CDCl₃) δ -136.62. The NMR spectra data are consistent with previously reported^[S19, S23].



5-chloro-1,3-dimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (6k)[5a]: 25.9 mg, 83% yield. Colorless viscous oil; 1H NMR (400 MHz, CDCl3) δ 7.84 (d, *J* = 7.9 Hz, 2H), 7.53 (t, *J* = 6.8 Hz, 1H), 7.41 (t, *J* = 7.0 Hz, 2H), 7.22 (dd, *J* = 8.3 and 2.0 Hz, 1H), 7.10 (s, 1H), 6.82 (dd, *J* = 8.3 and 1.7 Hz, 1H), 3.69 (s, 2H), 3.30 (d, *J* = 1.8 Hz, 3H), 1.43 (d, *J* = 1.7 Hz, 3H). 13C NMR (100 MHz, CDCl3) δ 195.8, 180.1, 142.5, 136.0, 135.5, 133.3, 128.5, 127.9, 127.7, 127.4, 122.3, 109.0, 46.0, 45.4, 26.6, 24.8. The NMR spectra data are consistent with previously reported^[S19].



5-bromo-1,3-dimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (6l): 18.6 mg, 52% yield. Colorless viscous oil; ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, *J* = 7.2 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.42 – 7.46 (m, 3H), 7.24 (d, *J* = 1.9 Hz, 1H), 6.78 (d, *J* = 8.3 Hz, 1H), 3.68 (s, 2H), 3.29 (s, 3H), 1.42 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 195.7, 180.0, 143.0, 136.0, 135.9, 133.3, 130.6, 128.5, 127.9, 125.0, 114.8, 109.6, 46.1, 45.4, 26.5, 24.8. The NMR spectra data are consistent with previously reported^[S18, S22, S24].



5-iodo-1,3-dimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (6m): 25.8 mg, 64% yield. Colorless viscous oil; ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, *J* = 7.2 Hz, 2H), 7.57 (dd, *J* = 8.2 and 1.7 Hz, 1H), 7.52 (d, *J* = 7.4 Hz, 1H), 7.43 – 7.39 (m, 3H), 6.69 (d, *J* = 8.2 Hz, 1H), 3.67 (s, 2H), 3.29 (s, 3H), 1.42 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 195.8, 179.8, 143.7, 136.6, 136.3, 136.1, 133.3, 130.5, 128.5, 128.0, 110.2, 84.6, 46.1, 45.2, 26.5, 24.9. The NMR spectra data are consistent with previously reported^[S19-S20, S22].



1,3-dimethyl-3-(2-oxo-2-phenylethyl)-7-(trifluoromethoxy)indolin-2-one (6n): 16.3 mg, 45% yield. Colorless viscous oil; ¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, J =7.4 Hz, 2H), 7.52 (t, J = 7.3 Hz, 1H), 7.40 (t, J = 7.7 Hz, 2H), 7.13 (d, J = 8.4 Hz, 1H), 7.05 (d, J = 7.3 Hz, 1H), 6.94 (t, J = 7.3 Hz, 1H), 3.70 (s, 2H), 3.52 (s, 3H), 1.43 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 195.8, 180.5, 136.9, 136.1, 135.5, 133.3, 133.2 (q, $J_{C-F} =$ 2.0 Hz), 128.5, 127.9, 122.5, 121.3, 120.7 (q, $J_{C-F} =$ 256.6 Hz), 120.2, 46.4, 45.1, 28.9, 25.1. ¹⁹F NMR (376 MHz, CDCl₃) δ -57.41. HRMS(EI) Calcd for C₁₉H₁₆F₃NO₃ [M + H]⁺: 364.1161, Found 364.1156; IR (KBr) ν (cm⁻¹): 2934, 2898, 1714, 1625, 1483, 1361, 1126, 1058, 798.



1,3-dimethyl-3-(2-oxo-2-phenylethyl)-5-(trifluoromethoxy)indolin-2-one (60): 33.5 mg, 92% yield. Colorless viscous oil; ¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, J =7.3 Hz, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.40 (t, J = 7.7 Hz, 2H), 7.19 – 7.07 (m, 1H), 7.03 (s, 1H), 6.87 (d, J = 8.5 Hz, 1H), 3.69 (d, J = 1.6 Hz, 2H), 3.31 (s, 3H), 1.44 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 195.9, 180.2, 144. 5 (q, $J_{C-F} =$ 2.0 Hz), 142.5, 136.1, 135.3, 133.3, 128.5, 127.9, 120.8, 120.5 (q, $J_{C-F} =$ 254.9 Hz), 115.9, 108.4, 46.0, 45.6, 26.6, 24.7. ¹⁹F NMR (376 MHz, CDCl₃) δ -58.34. HRMS(EI) Calcd for C₁₉H₁₆F₃NO₃ [M + H]⁺: 364.1161, Found 364.1156; IR (KBr) v (cm⁻¹): 2970, 2931, 1719, 1690, 1622, 1499, 1450, 1353, 1258, 690.



1,3-dimethyl-3-(2-oxo-2-phenylethyl)-5-(trifluoromethyl)indolin-2-one (6p): 26.1 mg, 75% yield. Colorless viscous oil; ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, *J* = 7.2 Hz, 2H), 7.53 (t, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.35 (s, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 3.74 (d, *J* = 2.2 Hz, 2H), 3.35 (s, 3H), 1.45 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 195.8, 180.5, 146.9, 136.0, 134.4, 133.4, 128.6, 127.9, 125.7 (q, *J*_{C-F}= 4.1 Hz), 124.5 (q, *J*_{C-F}= 270 Hz), 124.3 (q, *J*_{C-F}= 32.2 Hz), 118.6 (q, *J*_{C-F}= 3.6 Hz), 118.6 (q, *J*=14.7 Hz), 107.8, 46.1, 45.1, 26.6, 24.8. ¹⁹F NMR (376 MHz, CDCl₃) δ -61.30. The NMR spectra data are consistent with previously reported^[S19, S21].



1,3-dimethyl-3-(2-oxo-2-phenylethyl)-4,6-bis(trifluoromethyl)indolin-2-one (6q): 18.6 mg, 45% yield. Colorless viscous oil; ¹H NMR (400 MHz, CDCl₃) δ 7.84 – 7.81 (m, 2H), 7.56 – 7.51 (m, 2H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.32 (s, 1H), 4.13 (d, *J* = 18.8 Hz, 1H), 3.79 (d, *J* = 20.0 Hz, 1H), 3.40 (s, 3H), 1.51 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 196.5, 179.8, 146.5, 135.7, 135.61-135.56 (m), 130.8 (d, *J*_{C-F} = 33.4 Hz), 128.6, 127.9, 125.93, 125.6 (q, *J*_{C-F} = 33.4 Hz), 124.7 (d, *J*_{C-F} = 7.0 Hz), 122.0 (d, *J*_{C-F} = 6.3 Hz), 116.6-116.4 (m), 108.2 (q, *J*_{C-F} = 3.6 Hz), 46.9, 45.7 (q, *J*_{C-F} = 3.0 Hz), 27.1, 24.5 (q, *J*_{C-F} = 2.3 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -58.56, -62.88. HRMS(EI) Calcd for C₂₀H₁₅F₆NO₂ [M + H]⁺: 416.1085, Found 416.1068; IR (KBr) v (cm⁻¹): 2978, 1737, 1687, 1470, 1319, 1211, 1135, 874.



4,5,6-trifluoro-1,3-dimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (6r): 19.5 mg, 59% yield. Colorless viscous oil; ¹H NMR (400 MHz, CDCl₃) δ 7.85 (d, *J* = 8.5 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 6.55 (ddd, *J* = 9.5, 5.3 and 1.6 Hz, 1H), 3.95 (d, *J* = 18.2 Hz, 1H), 3.70 (d, *J* = 18.2 Hz, 1H), 3.27 (s, 3H), 1.51 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 196.2, 179.6, 152.4 (dd, *J*_{C-F} = 11.2 and 4.2 Hz), 139.8(td, *J*_{C-F} = 11.7 and 3.0 Hz), 137.2 (dd, *J*_{C-F} = 16.8 and 4.2 Hz), 93.9 (dq, *J*_{C-F} = 23.2 and 1.5 Hz), 70.3, 45.3, 26.9, 23.4. ¹⁹F NMR (376 MHz, CDCl₃) δ -134.60, -143.68, -169.82. HRMS(EI) Calcd for C₁₈H₁₄F₃NO₂ [M + H]⁺: 334.1055, Found 334.1046; IR (KBr) v (cm⁻¹): 2986, 1748, 1689, 1468, 1326, 1208, 1146, 868.

The NMR spectra data are consistent with previously reported^[S19-S20, S22].



3-(2-oxo-2-phenylethyl)-1-(p-tolyl)indolin-2-one and

3-methyl-3-(2-oxo-2-(*p***-tolyl)ethyl)-1-phenylindolin-2-one (6s+6s')**: 26.4 mg, 74% yield. Colorless viscous oil; ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, *J* = 7.2 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 2H), 6.96 (t, *J* = 8.4 Hz, 2H), 6.85 (t, *J* = 7.5 Hz, 1H), 4.07-3.97 (m, 2H), 3.67 (s, 2H), 2.58 (s, 3H), 1.39 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 195.9, 181.1, 140.8, 136.5, 134.8, 133.0, 131.7, 128.4, 127.9, 121.8, 119.5, 119.2, 46.2, 44.5, 36.5, 25.7, 19.0, 14.5. HRMS(EI) Calcd for C₂₄H₂₁NO₂ [M + H]⁺: 356.1651, Found 356.1642; IR (KBr) v (cm⁻¹): 2961, 2928, 1712, 1691, 1498, 1351, 1217, 1119, 815, 760, 691. The NMR spectra data are consistent with previously reported^[S8].



1-benzyl-3-methyl-3-(2-oxo-2-phenylethyl)indolin-2-one (6t): 10.3 mg, 29% yield. Colorless viscous oil; ¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, J = 7.2 Hz, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.44-7.40 (m, 4H), 7.35 (t, J = 7.5 Hz, 2H), 7.28 (d, J = 7.3 Hz, 1H), 7.16 – 7.10 (m, 2H), 6.94 (td, J = 7.7 and 0.9 Hz, 1H), 6.74 (d, J = 7.7 Hz, 1H), 5.10 (d, J = 15.8 Hz, 1H), 4.97 (d, J = 15.8 Hz, 1H), 3.76 (d, J = 5.5 Hz, 2H), 1.51 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 195.9, 180.6, 142.9, 136.4, 136.2, 133.7, 133.1, 128.7, 128.5, 128.0, 127.7, 127.3, 127.2, 122.2, 121.7, 109.3, 45.8, 45.4, 44.0, 25.5. The NMR spectra data are consistent with previously reported^[S18-S19, S24].



3-methyl-3-(2-oxo-2-phenylethyl)-1-phenylindolin-2-one (6u): 15.4 mg, 45% yield. Colorless viscous oil; ¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, J = 7.3 Hz, 2H), 7.58 – 7.51 (m, 5H), 7.41 (t, J = 7.6 Hz, 3H), 7.17 (t, J = 7.4 Hz, 2H), 7.00 (t, J = 7.5 Hz, 1H), 6.85 (d, J = 7.9 Hz, 1H), 3.98 – 3.65 (m, 2H), 1.57 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 196.0, 180.1, 144.1, 136.4, 135.2, 133.5, 133.2, 129.5, 128.5, 128.0, 127.9, 127.7, 127.0, 122.5, 121.8, 109.4, 46.7, 45.4, 25.3. The NMR spectra data are consistent with previously reported^[S18].



1,3-dimethyl-3-(2-oxopropyl)indolin-2-one (6v): 18.8 mg, 87% yield. Colorless viscous oil; ¹H NMR (400 MHz, CDCl₃) δ 7.29 – 7.21 (td, J = 7.7 and 1.2 Hz, 1H), 7.14 (dd, J = 7.3 and 1.1 Hz, 1H), 7.00 (td, J = 7.7 and 0.9 Hz, 1H), 6.86 (d, J = 7.8 Hz, 1H), 3.26 (s, 3H), 3.09 (d, J = 2.5 Hz, 2H), 1.97 (s, 3H), 1.33 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 204.5, 180.3, 143.7, 133.4, 127.9, 122.2, 121.8, 108.1, 50.5, 45.2, 30.0, 26.4, 24.3. The NMR spectra data are consistent with previously reported^[S22].



1,3-dimethyl-3-(2-oxobutyl)indolin-2-one (6w): 19.6 mg, 85% yield. Colorless

viscous oil; ¹H NMR (400 MHz, CDCl₃) δ 7.55-7.50 (m, 3H), 7.38 (t, J = 7.7 Hz, 2H), 7.28 (d, J = 7.7 Hz, 1H), 7.06 (d, J = 7.4 Hz, 1H), 6.90 (t, J = 7.5 Hz, 1H), 6.85 (d, J =7.8 Hz, 1H), 3.87 (d, J = 14.5 Hz, 1H), 3.68 (d, J = 14.5 Hz, 1H), 3.16 (s, 3H), 1.39 (s, 3H). ¹³C NMR (100MHz, CDCl₃) δ 177.6, 143.3, 140.0, 133.3, 129.5, 128.9, 128.6, 127.8, 124.1, 122.5, 108.4, 61.9, 45.6, 26.5, 25.4. The NMR spectra data are consistent with previously reported^[S2].



1,3-dimethyl-3-(2-oxo-4-phenylbutyl)indolin-2-one (6x): 12.9 mg, 42% yield. Colorless viscous oil; ¹H NMR (400 MHz, CDCl₃) δ 7.29 – 7.21 (m, 3 H), 7.18 – 7.15 (m, 1 H), 7.09 (d, *J* = 6.1 Hz, 1H), 7.04-6.99 (m, 3 H), 6.87 (d, *J* = 7.8 Hz, 1H), 3.27 (s, 3H), 3.17 – 2.94 (m, 2H), 2.72 (t, *J* = 7.6 Hz, 2H), 2.65 – 2.50 (m, 2H), 1.33 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 205.9, 180.2, 143.7, 140.7, 133.4, 128.4, 128.1, 127.9, 126.0, 122.2, 121.8, 108.2, 49.9, 45.2, 44.3, 29.4, 26.4, 24.4. The NMR spectra data are consistent with previously reported^[S25].



1,3-dimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one-4,5,6,7-d4 (*D5-6a*) and **1,3-dimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one** (6a): 14.3 mg, 51% yield. Colorless viscous oil; ¹H NMR (400 MHz, CDCl₃) δ 7.84 – 7.82 (m, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.25 (td, *J* = 7.7 and 1.2 Hz, 0.68 H), 7.14 (dd, *J* = 7.3 and 0.6 Hz, 0.51 H), 6.97 (td, *J* = 8.2 and 0.8 Hz, 0.54 H), 6.89 (d, *J* = 7.8 Hz, 0.52 H), 3.68 (q, *J* = 17.9 Hz, 2.2 H), 3.31 (s, 3H), 1.44 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 196.1, 180.5, 143.8, 143.77, 136.4, 133.7, 133.6, 133.1, 128.4, 127.9, 127.8, 122.1, 121.8, 108.1, 46.01, 45.28, 45.27, 26.44, 26.43, 24.9. The NMR spectra data are consistent with previously reported^[S17].



3,3,5,5-tetramethylpiperidin-1-yl benzoate (8): 32.9 mg, 63% yield. Light yellow solid; ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, J = 8.3 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 1.82 – 1.68 (m, 4H), 1.60-1.57 (m, 2H), 1.49-1.45 (m, 1H), 1.28 (s, 6H), 1.12 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 166.3, 132.8, 129.8, 129.5, 128.4, 60.4, 39.1, 32.0, 20.8, 17.0. The NMR spectra data are consistent with previously reported^[S25].

2). General procedure for phenylsulfinyl radical cyclization reactions Condition A:

N-methyl-*N*-phenylmethacrylamide 5a (0.1 mmol, 1.0 Sodium equiv), benzenesulfinate (0.2 mmol, 2.0 equiv), K₂S₂O₈ (0.2 mmol, 2.0 equiv) and Eosin Y disodium salt (0.005 mmol, 0.05 equiv) were added into schlenk tubes, followed by the addition of MeOH/H₂O (2.0 mL, 4/1, v/v), the resulting mixture were then exposed to a 23 W white fluorescent lamp (LEDs) under nitrogen atmosphere for corresponding hours until the starting materials N-methyl-N-phenylmethacrylamide totally consumed or left maintain without change (A fan is used to cool down the reaction temperature). The reaction mixture was filtrated and the filtrate was extracted with dichloromethane (5.0 mL×3), the combined organic phase was dried over anhydrous Na₂SO₄. The solvent was removed by rotary evaporation, the residual was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford desired 3-methyl-3-(methylsulfonyl)benzene-2-oxindoles 7.

Condition B:

N-methyl-*N*-phenylmethacrylamide 5a (0.1)mmol. 1.0 equiv), Sodium benzenesulfinate (0.2 mmol, 2.0 equiv), K₂S₂O₈ (0.2 mmol, 2.0 equiv) and 2-chlorothioxanthone (0.02 mmol, 0.2 equiv) were added into schlenk tubes, followed by the addition of MeOH/H₂O (2.0 mL, 4/1, v/v), the resulting mixture were then exposed to a 23 W purple fluorescent lamp (LEDs) under nitrogen atmosphere for corresponding hours until the starting materials N-methyl-N-phenylmethacrylamide totally consumed or left maintain without change (A fan is used to cool down the reaction temperature). The reaction mixture was filtrated and the filtrate was extracted with dichloromethane (5.0 mL×3), the combined organic phase was dried over anhydrous Na₂SO₄. The solvent was removed by rotary evaporation, the residual was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford desired 3-methyl-3-(methylsulfonyl)benzene-2-oxindoles 7.



1,3-dimethyl-3-((phenylsulfonyl)methyl)indolin-2-one (7a): 28.4 mg, 90% yield, condition A; 29.0 mg, 92% yield, condition B. Colorless viscous oil; ¹H NMR (400 MHz, CDCl₃) δ 7.56 – 7.50 (m, 3H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.31 – 7.27 (m, 1H), 7.07 (d, *J* = 8.4 Hz, 1H), 6.91 (td, *J* = 7.6 and 0.8 Hz, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 3.88 (d, *J* = 14.5 Hz, 1H), 3.68 (d, *J* = 14.5 Hz, 1H), 3.17 (s, 3H), 1.40 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 177.6, 143.3, 140.0, 133.3, 129.5, 128.9, 128.6, 127.8, 124.1, 122.5, 108.4, 61.9, 45.6, 26.6, 25.5. The NMR spectra data are consistent with previously reported ^[S9].



1,3,5-trimethyl-3-((phenylsulfonyl)methyl)indolin-2-one (7b): 31.6 mg, 96% yield, condition A; 30.3 mg, 92% yield, condition B. Colorless viscous oil; ¹H NMR (400 MHz, CDCl₃) δ 7.51 (t, J = 7.4 Hz, 1H), 7.42 (d, J = 7.3 Hz, 2H), 7.33 (t, J = 7.7 Hz, 2H), 7.03 (d, J = 7.9 Hz, 1H), 6.72 (d, J = 7.9 Hz, 1H), 6.64 (s, 1H), 3.88 (dd, J = 14.7 Hz, 1H), 3.67 (d, J = 14.7 Hz, 1H), 3.17 (s, 3H), 2.13 (s, 3H), 1.34 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 177.5, 141.0, 140.0, 133.0, 131.8, 129.3, 128.9, 128.6, 127.7, 124.7, 108.1, 61.9, 45.5, 26.5, 25.4, 20.8. The NMR spectra data are consistent with previously reported ^[S9].



1,3,4-trimethyl-3-((phenylsulfonyl)methyl)indolin-2-one and

1,3,5-trimethyl-3-((phenylsulfonyl)methyl)indolin-2-one (7c+7c'): 32.6 mg, 99% yield, condition A; 30. 6 mg, 93% yield, condition B. Colorless viscous oil; ¹H NMR (400 MHz, CDCl₃) δ 7.56 – 7.52 (m, 4.04 H), 7.44 (d, *J* = 8.5 Hz, 2.72 H), 7.40-7.34 (q, *J* = 8.4 Hz, 4.66 H), 7.20 (t, *J* = 7.8 Hz, 1.55 H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.72 – 6.66 (m, 4.65 H), 3.98 (d, *J* = 14.7 Hz, 1.91 H), 3.86 – 3.81 (m, 2.87 H), 3.66 (d, *J* = 14.5 Hz, 1.41 H), 3.15 (s, 2.8 H), 3.13 (s, 4.32 H), 2.38 (s, 2.96 H), 2.08 (s, 4.55 H), 1.40 (s, 4.39 H), 1.37 (s, 3.07 H). ¹³C NMR (100 MHz, CDCl₃) δ 177.9, 177.6, 143.7, 143.3, 140.1, 139.5, 138.8, 135.4, 133.4, 133.3, 128.8, 128.7, 128.6, 128.1, 127.8, 126.60, 126.59, 125.0, 123.8, 123.1, 109.3, 106.1, 62.0, 60.9, 45.9, 45.4, 26.6, 26.5, 25.4, 23.2, 21.8, 18.2. The NMR spectra data are consistent with previously reported [⁵⁹].



5-methoxy-1,3-dimethyl-3-((phenylsulfonyl)methyl)indolin-2-one (7d): 28.7 mg, 83% yield, condition A; 21.8 mg, 63% yield, condition B. Colorless viscous oil; ¹H NMR (400 MHz, CDCl₃) δ 7.52 (t, J = 2.3 Hz, 1H), 7.48 – 7.46 (m, 2H), 7.36 (t, J = 7.7 Hz, 2H), 6.80 – 6.73 (m, 2H), 6.56 (d, J = 2.3 Hz, 1H), 3.86 (d, J = 14.6 Hz, 1H), 3.66 (d, J = 14.6 Hz, 1H), 3.65 (s, 3H), 3.15 (s, 3H), 1.37 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 177.2, 155.8, 140.0, 136.8, 133.2, 130.6, 128.7, 127.8, 113.3, 111.1, 108.7, 61.8, 55.5, 46.0, 26.6, 25.3. The NMR spectra data are consistent with previously reported ^[S9].



4,6-dimethoxy-1,3-dimethyl-3-((phenylsulfonyl)methyl)indolin-2-one (7e): 24.8 mg, 66%yield, condition A; 15.8 mg, 42 % yield, condition B. Colorless viscous oil; ¹H NMR (400 MHz, CDCl₃) δ 7.51 – 7.46 (m, 1H), 7.40 – 7.38 (m, 2H), 7.34 – 7.39 (m, 2H), 6.10 (d, *J* = 2.0 Hz, 1H), 5.75 (d, *J* = 1.8 Hz, 1H), 4.01 (d, *J* = 14.5 Hz, 1H), 3.82 (s, 3H), 3.81(d, *J* = 14.5 Hz, 1H), 3.41 (s, 3H), 3.17 (s, 3H), 1.34 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 178.5, 162.2, 156.6, 145.3, 139.9, 132.7, 128.3, 127.9, 107.3, 92.0, 88.4, 60.6, 55.6, 54.8, 44.8, 26.8, 23.0. HRMS(EI) Calcd for C₁₉H₂₁NO₅S [M + H]⁺: 376.1219, Found 376.1211; IR (KBr) v (cm⁻¹): 2930, 2850, 1719, 1690, 1622, 1499, 1450, 1353, 1258, 690.



5-fluoro-1,3-dimethyl-3-((phenylsulfonyl)methyl)indolin-2-one (7f): 32.1 mg, 96% yield, condition A; 20.7 mg, 62% yield, condition B. Colorless viscous oil; 1H NMR (400 MHz, CDCl₃) δ 7.58 – 7.52 (m, 3H), 7.41 (t, J = 8.1 Hz, 2 H), 6.97 (td, J = 14.7 Hz, 1H), 6.79 – 6.74 (m, 2H), 3.86 (d, J = 14.6 Hz, 1H), 3.65 (d, J = 14.7 Hz, 1H), 3.18 (s, 3H), 1.38 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 177.3, 159.0 (d, $J_{C-F} = 239.8$ Hz), 139.9, 139. (d, $J_{C-F} = 2.0$ Hz), 133.5, 131.1 (d, $J_{C-F} = 8.2$ Hz), 128.9, 127.7, 115.0 (d, $J_{C-F} = 23.4$ Hz), 112.3 (d, $J_{C-F} = 24.9$ Hz), 108.8 (d, $J_{C-F} = 8.1$ Hz), 61.6, 46.0, 26.7, 25.2. ¹⁹F NMR (376 MHz, CDCl₃) δ -120.63. The NMR spectra data are consistent with previously reported ^[S9].



5-chloro-1,3-dimethyl-3-((phenylsulfonyl)methyl)indolin-2-one (7g): 27.7 mg, 79% yield, condition A; 16.5 mg, 47% yield, condition B. Colorless viscous oil; ¹H NMR (400 MHz, CDCl₃) δ 7.57 (t, *J* = 7.4 Hz, 1H), 7.48 – 7.46(m, 2H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.22 (dd, *J* = 8.3 and 2.1 Hz, 1H), 6.82 (d, *J* = 1.9 Hz, 1H), 6.78 (d, *J* = 8.3 Hz, 1H), 3.88 (d, *J* = 14.7 Hz, 1H), 3.66 (d, *J* = 14.7 Hz, 1H), 3.20 (s, 3H), 1.36 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 177.1, 142.0, 139.7, 133.6, 131.0, 128.9, 128.6, 127.8, 127.6, 124.5, 109.3, 61.7, 45.7, 26.7, 25.2. The NMR spectra data are consistent with previously reported ^[S9].



5-bromo-1,3-dimethyl-3-((phenylsulfonyl)methyl)indolin-2-one (7h): 21.0 mg, 53% yield, condition A; 34.4 mg, 87% yield, condition B. Colorless viscous oil; ¹H NMR (400 MHz, CDCl₃) δ 7.58 (t, *J* = 7.3 Hz, 1H), 7.45 (dd, *J* = 8.5 and 1.3 Hz, 2H), 7.43 – 7.32 (m, 3H), 6.92 (d, *J* = 1.9 Hz, 1H), 6.73 (d, *J* = 8.3 Hz, 1H), 3.88 (d, *J* = 14.7 Hz, 1H), 3.66 (d, *J* = 14.7 Hz, 1H), 3.20 (s, 3H), 1.35 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 177.0, 142.5, 139.7, 133.7, 131.5, 131.4, 128.9, 127.5, 127.1, 115.1, 109.8, 61.7, 45.7, 26.7, 25.2. The NMR spectra data are consistent with previously reported ^[S9].



5-iodo-1,3-dimethyl-3-((phenylsulfonyl)methyl)indolin-2-one (7i): 14.1 mg, 32% yield, condition A; 26.5 mg, 60% yield, condition B. Colorless viscous oil; ¹H NMR (400 MHz, CDCl₃) δ 7.60 (t, J = 7.2 Hz, 1H), 7.54 (dd, J = 8.1 and 1.5 Hz, 1H), 7.44-7.37 (m, 4H), 7.04 (s, 1H), 6.64 (d, J = 8.2 Hz, 1H), 3.87 (d, J = 14.8 Hz, 1H), 3.65 (d, J = 14.8 Hz, 1H), 3.20 (s, 3H), 1.34 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 176.9, 143.3, 139.7, 137.4, 133.8, 132.6, 128.9, 127.5, 110.4, 85.1, 61.7, 45.5, 26.6, 25.2. The NMR spectra data are consistent with previously reported ^[S24].



1,3-dimethyl-3-((phenylsulfonyl)methyl)-7-(trifluoromethoxy)indolin-2-one (7j): 20.0 mg, 50% yield, condition A; 32 mg, 80% yield, condition B. Colorless viscous oil; ¹H NMR (400 MHz, CDCl₃) δ 7.57 – 7.53 (m, 3H), 7.40 (td, *J* = 7.2 and 2.1 Hz,

2H), 7.15 (dt, J = 8.4 and 1.4 Hz, 1H), 6.97 (dd, J = 7.4 and 0.9 Hz, 1H), 6.86 (dd, J = 8.3 and 7.5 Hz, 1H), 3.89 (d, J = 14.6 Hz, 1H), 3.68 (d, J = 14.6 Hz, 1H), 3.38 (s, 3H), 1.39 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 177.5, 139.8, 135.0, 133.5, 133.2 (q, $J_{C-F} = 2.1$ Hz), 132.5, 129.0, 127.7, 122.8, 122.6, 122.1 (d, $J_{C-F} = 0.9$ Hz), 120.6 (q, $J_{C-F} = 257.1$ Hz), 61.8, 45.5, 29.1, 25.7. ¹⁹F NMR (376 MHz, CDCl₃) δ -57.41. HRMS(EI) Calcd for C₁₈H₁₆F₃NO₄S [M + H]⁺: 400.0830, Found 400.0820; IR (KBr) v(cm⁻¹): 2985, 2970, 1729, 1624, 1484, 1371, 1182, 874.



1,3-dimethyl-3-((phenylsulfonyl)methyl)-5-(trifluoromethyl)indolin-2-one (7k): 34.9 mg, 91% yield, condition A; 25.3 mg, 66% yield, condition B. Colorless viscous oil; ¹H NMR (400 MHz, CDCl₃) δ 7.53 (t, *J* = 7.9 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.12 (s, 1H), 6.94 (d, *J* = 8.2 Hz, 1H), 3.93 (d, *J* = 14.7 Hz, 1H), 3.74 (d, *J* = 14.8 Hz, 1H), 3.26 (s, 3H), 1.40 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 177.6, 146.4 (d, *J*_{C-F} = 1.2 Hz), 139.8, 133.7, 129.9, 129.34, 129.00, 127.86, 127.41, 125.15, 124.83, 124.50, 124.18, 122.67, 120.94, 120.91, 120.87, 120.83, 119.51, 108.3, 61.8, 45.5, 26.8, 25.2. ¹⁹F NMR (376 MHz, CDCl₃) δ -61.28. The NMR spectra data are consistent with previously reported ^[S9].



7-fluoro-1,3-dimethyl-3-((phenylsulfonyl)methyl)-4-(trifluoromethyl)indolin-2-on e (71): 11.7 mg, 29% yield, condition A; 22.1 mg, 55% yield, condition B. Colorless viscous oil; ¹H NMR (400 MHz, CDCl₃) δ 7.61 – 7.56 (m, 3H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.19 (d, *J* = 7.3 Hz, 2H), 3.88 (d, *J* = 2.0 Hz, 2H), 3.49 (d, *J* = 3.6 Hz, 3H), 1.47 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 177.1, 151.08-151.05 (m), 148.60-148.56 (m), 139.6, 133.7, 132.4-132.2 (m), 130.05-130.00 (m), 129.1, 127.8, 124.5 (d, *J*_{C-F} = 20.3 Hz), 121.6-121.3 (m), 117.3 (d, *J*_{C-F} = 20.3 Hz), 62.1, 46.8, 29.5, 23.8. ¹⁹F NMR (376 MHz, CDCl₃) δ -57.45, -129.69. HRMS(EI) Calcd for C₁₈H₁₅F₄NO₃S [M + H]⁺: 402.0787, Found 402.0781; IR (KBr) (cm⁻¹): 3054, 2944, 1731, 1624, 1467, 1353, 1101, 1086, 907, 831.



1,3-dimethyl-3-((phenylsulfonyl)methyl)-4,6-bis(trifluoromethyl)indolin-2-one(7 m): 40.7 mg, 90% yield, condition A; 35.7 mg, 79% yield, condition B. Colorless viscous oil; ¹H NMR (400 MHz, CDCl₃) δ 7.60 – 7.53 (m, 3H), 7.44 – 7.40 (m, 3H), 7.30 (s, 1H), 3.91 (s, 2H), 3.34 (s, 3H), 1.49 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 177.0, 146.2, 139.4, 133.8, 132.2 (q, *J*_{C-F} = 33.5 Hz), 130.57-130.45 (m), 129.1, 128.3 (q, *J*_{C-F} = 33.9 Hz), 127.7, 123.1 (q, *J*_{C-F} = 271.9 Hz), 117.4- 117.2 (m), 108.4 (q, *J*_{C-F} = 3.1 Hz), 61.9, 46.5, 27.3, 23.5. ¹⁹F NMR (376 MHz, CDCl₃) δ -58.37, -63.04. The NMR spectra data are consistent with previously reported ^[S26].



4,5,6-trifluoro-1,3-dimethyl-3-((phenylsulfonyl)methyl)indolin-2-one (7n): trace, condition A; 14.4 mg, 39% yield, condition B. Colorless viscous oil; ¹H NMR (400 MHz, CDCl₃) δ 7.63 – 7.57 (m, 3H), 7.45 (t, *J* = 7.8 Hz, 2H), 6.53 (ddd, *J* = 9.4, 5.2 and 1.6 Hz, 1H), 3.85 (q, *J* = 3.6 Hz, 1H), 3.20 (s, 3H), 1.43 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 176.7, 139.3, 133.8, 129.0, 127.6, 111.8 (dd, *J*_{C-F} = 15 and 5.1 Hz), 94.2 (ddd, *J*_{C-F} = 234.5, 3.4 and 1.4 Hz), 44.9, 29.7, 27.1, 23.6. ¹⁹F NMR (376 MHz, CDCl₃) δ -132.40, -139.23, -169.22. HRMS(EI) Calcd for C₁₇H₁₄F₃NO₃S [M + H]⁺:

370.0725, Found 370.0701; IR (KBr) v(cm⁻¹): 2974, 1727, 1627, 1499, 1320, 1155, 1062, 876, 745.



1,3-dimethyl-2-oxo-3-((phenylsulfonyl)methyl)indoline-5-carbonitrile (70): 19.7 mg, 58% yield, condition A; 13.6 mg, 40% yield, condition B. Colorless viscous oil; ¹H NMR (400 MHz, CDCl₃) δ 7.65-7.58 (m, 2H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.43 (t, *J* = 7.2 Hz, 2H), 7.13 (s, 1H), 6.94 (d, *J* = 8.1 Hz, 1H), 3.90 (d, *J* = 15.7 Hz, 1H), 3.71 (d, *J* = 14.7 Hz, 1H), 3.27 (s, 3H), 1.39 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 177.5, 147.3, 139.7, 133.9, 133.8, 130.5, 129.2, 127.4, 127.3, 118.7, 108.9, 105.7, 61.5, 45.3, 26.9, 25.1. The NMR spectra data are consistent with previously reported ^[S9].



1,3-dimethyl-3-((phenylsulfonyl)methyl)-1,3-dihydro-2H-benzo[g]indol-2-one(7p): 24.5 mg, 67% yield, condition A; 21.2 mg, 58% yield, condition B. Colorless viscous oil; ¹H NMR (400 MHz, CDCl₃) δ 7.67 (dd, J = 8.1 and 0.9 Hz, 1H), 7.52 (dd, J = 8.3 and 0.8 Hz, 1H), 7.48-7.43 (m, 2H), 7.39-7.37 (dd, J = 8.4 and 1.2 Hz, 2H), 7.31 – 7.27 (m, 2H), 7.24 – 7.20 (m, 1H), 6.98 (dd, J = 7.5 and 0.8 Hz, 1H), 4.64 (d, J = 14.5 Hz, 1H), 3.91 (d, J = 14.5 Hz, 1H), 3.52 (s, 3H), 1.65 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 170.8, 140.6, 136.4, 133.5, 133.4, 133.0, 128.6, 127.7, 126.8, 126.6, 126.5, 123.7, 122.7, 119.2, 65.9, 45.7, 33.7, 30.0. The NMR spectra data are consistent with previously reported ^[S9].


1,3-dimethyl-3-((phenylsulfonyl)methyl)-1,3-dihydro-2H-benzo[f]indol-2-one and **1,3-dimethyl-1-((phenylsulfonyl)methyl)-1,3-dihydro-2H-benzo[e]indol-2-one(7q +7q')**: 7.7 mg, 21% yield, condition A; 22.3 mg, 61% yield, condition B. Colorless viscous oil; 1H NMR (400 MHz, CDCl₃) δ 7.83 (d, *J* = 8.6 Hz, 1.02H), 7.78 (d, *J* = 8.2 Hz, 0.49 H), 7.72 – 7.65 (m, 1.07 H), 7.53 (d, *J* = 8.1 Hz, 0.47 H), 7.47 (td, *J* = 7.1 and 1.1Hz, 0.49 H), 7.40 (dd, *J* = 8.2 and 0.7 Hz, 1H), 7.34-7.31 (m, 1.94 H), 7.23 – 7.19 (m, 2.69H), 7.17-7.16 (m, 0.32 H), 7.14 – 7.10 (m, 3.43H), 6.92 (t, *J* = 7.9 Hz, 2.01H), 4.14 (d, *J* = 1.0 Hz, 2.13 H), 3.97 (d, *J* = 14.7 Hz, 0.51H), 3.78 (d, *J* = 14.7 Hz, 0.49 H), 3.36 (s, 3.00 H), 3.31 (s, 0.96 H), 1.57 (s, 3.23H), 1.47 (s, 1.13H). ¹³C NMR (100 MHz, CDCl₃) δ 178.8, **177.2** // **176.1**, 141.6, 140.1, 138.7, 133.9, 133.2, 132.6, 130.3, 130.2, 129.7, 129.4, 128.6, 128.2, 128.1, 127.6, 127.4, 127.2, 127.0, 126.8, 124.2, 123.8, 123.3, 121.1, 120.9, 109.7, 104.1, 62.3, 62.1, 46.6, 45.2, 26.9, 26.8, 25.8, 24.5. The NMR spectra data are consistent with previously reported ^[S9].



1-ethyl-3,7-dimethyl-3-((phenylsulfonyl)methyl)indolin-2-one (7r): trace, condition A; 24.7 mg, 72% yield, condition B. Colorless viscous oil; ¹H NMR (400 MHz, CDCl₃) δ 7.54 – 7.52 (m, 3H), 7.38 (t, *J* = 7.6 Hz, 2H), 6.99 (d, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 7.3 Hz, 1H), 6.75 (t, *J* = 7.5 Hz, 1H), 4.05 – 3.95 (m, 1H), 3.94 – 3.88 (m, 1H), 3.88 (d, *J* = 14.4 Hz, 1H), 3.65 (d, *J* = 14.5 Hz, 1H), 2.55 (s, 3H), 1.34 – 1.31 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 178.3, 140.4, 140.2, 133.2, 132.4, 130.5, 128.9, 127.7, 122.2, 121.8, 119.5, 62.0, 44.9, 36.8, 26.1, 18.9, 14.5. HRMS(EI) Calcd for C₁₉H₂₁NO₃S [M + H]⁺: 344.1320, Found 344.1311; IR (KBr) v(cm⁻¹): 2925, 1706, 1603, 1447, 1352, 1216, 1141, 1084, 745.



1-benzyl-3-methyl-3-((phenylsulfonyl)methyl)indolin-2-one (7s): 30.2 mg, 77% yield, condition A; 18.8 mg, 48% yield, condition B. Colorless viscous oil; ¹H NMR (400 MHz, CDCl₃) δ 7.56-7.52 (m, 3H), 7.40-7.36 (dd, J = 8.5 and 7.1 Hz, 3H), 7.33 (t, J = 7.3 Hz, 2H), 7.28-7.24 (m, 1H), 7.13 (td, J = 7.8 and 1.2 Hz, 1H), 7.03 (dd, J = 7.4 and 0.6 Hz, 1H), 6.83 (td, J = 7.6 and 0.9 Hz, 1H), 6.71 (d, J = 7.8 Hz, 1H), 5.00 (d, J = 15.8 Hz, 1H), 4.79 (d, J = 15.8 Hz, 1H), 3.93 (d, J = 14.5 Hz, 1H), 3.74 (d, J = 14.5 Hz, 1H), 1.46 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 177.8, 142.4, 140.2, 135.8, 133.3, 129.6, 128.9, 128.8, 128.5, 127.8, 127.6, 127.3, 124.0, 122.5, 109.6, 61.7, 45.8, 44.3, 26.0. The NMR spectra data are consistent with previously reported ^[S27].



1,3-dimethyl-3-(tosylmethyl)indolin-2-one (7t): 13.8 mg, 42% yield, condition A; 30.6 mg, 93% yield, condition B. Colorless viscous oil; ¹H NMR (400 MHz, CDCl₃) δ 7.38 (d, *J* = 8.3 Hz, 1H), 7.30 – 7.26 (m, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 7.09 (d, *J* = 6.8 Hz, 1H), 6.92 (td, *J* = 7.6 and 0.9 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 3.84 (d, *J* = 14.5 Hz, 1H), 3.65 (d, *J* = 14.5 Hz, 1H), 3.15 (s, 3H), 2.39 (s, 3H), 1.38 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 177.6, 144.3, 143.2, 137.1, 129.5, 128.5, 127.8, 124.1, 122.4, 108.3, 61.9, 45.6, 26.5, 25.5, 21.5. The NMR spectra data are consistent with previously reported ^[S28].



3-(((4-fluorophenyl)sulfonyl)methyl)-1,3-dimethylindolin-2-one (7u): 25.0 mg, 75% yield, condition A; 29.3 mg, 88% yield, condition B. Colorless viscous oil; ¹H NMR (400 MHz, CDCl₃) δ 7.49 – 7.46 (m, 2 H), 7.29 (td, J = 7.7 and 1.3 Hz, 1H), 7.03 (t, J = 8.6 Hz, 3H), 6.92 (td, J = 7.6 and 0.9 Hz, 1H), 6.85 (d, J = 7.8 Hz, 1H), 3.89 (d, J = 14.6 Hz, 1H), 3.67 (d, J = 14.6 Hz, 1H), 3.17 (s, 3H), 1.38 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 177.5, 165.5 (d, J_{C-F} = 254.8 Hz), 143.3, 136.0 (d, J_{C-F} = 3.1 Hz), 130.7 (d, J_{C-F} = 9.6 Hz), 129.4, 128.7, 124.0, 122.5, 116.1 (d, J_{C-F} = 22.6 Hz), 108.4, 62.0, 45.6, 26.5, 25.5. ¹⁹F NMR (376 MHz, CDCl₃) δ -103.88. The NMR spectra data are consistent with previously reported ^[S26].



3-(((4-chlorophenyl)sulfonyl)methyl)-1,3-dimethylindolin-2-one (7v): 7.4 mg, 21% yield, condition A; 34.3 mg, 98% yield, condition B. Colorless viscous oil; ¹H NMR (400 MHz, CDCl₃) δ 7.38 (d, J = 8.8 Hz, 2H), 7.37-7.27 (m, 3H), 7.00 (d, J = 7.9 Hz, 1H), 6.91 (t, J = 7.5 Hz, 1H), 6.84 (d, J = 7.8 Hz, 1H), 3.89 (d, J = 14.6 Hz, 1H), 3.67 (d, J = 14.6 Hz, 1H), 3.16 (s, 3H), 1.38 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 177.4, 143.3, 140.1, 138.3, 129.29, 129.26, 129.1, 128.7, 123.9, 122.5, 108.4, 62.0, 45.5, 26.5, 25.5. The NMR spectra data are consistent with previously reported ^[S9].



3-(((4-bromophenyl)sulfonyl)methyl)-1,3-dimethylindolin-2-one (7w): 30.8 mg, 78% yield, condition A; 37.5 mg, 95% yield, condition B. Colorless viscous oil; ¹H NMR (400 MHz, CDCl₃) δ 7.49 (d, J = 8.7 Hz, 2 H), 7.31 – 7.27 (m, 3H), 7.00 (d, J = 7.4 Hz, 1H), 6.91 (t, J = 7.5 Hz, 1H), 6.84 (d, J = 7.8 Hz, 1H), 3.89 (d, J = 14.6 Hz, 1H), 3.67 (d, J = 14.6 Hz, 1H), 3.16 (s, 3H), 1.37 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 177.4, 143.3, 138.7, 132.1, 129.3, 129.2, 128.7, 128.7, 123.9, 122.5, 108.4, 61.9, 45.5, 26.5, 25.5. The NMR spectra data are consistent with previously reported ^[S26].



1,3-dimethyl-3-((phenylsulfonyl)methyl)indolin-2-one-4,5,6,7-d4 (D-7a) and 1,3-dimethyl-3-((phenylsulfonyl)methyl)indolin-2-one (7a): 16.5 mg, 52% yield. Colorless viscous oil; ¹H NMR (400 MHz, CDCl₃) δ 7.55 – 7.49 (m, 3H), 7.37 (td, J = 7.6 and 1.8 Hz, 2H), 7.27 (td, J = 7.8 and 1.2 Hz, 1 H), 7.05 (dd, 7.4 and 0.55 H), 6.90 (td, J = 7.6 and 0.9 Hz, 0.58 H), 6.84 (d, J = 7.8 Hz, 0.57 H), 3.87 (d, J = 14.6 Hz, 1.33 H), 3.68 (d, J = 14.6 Hz, 1.25 H), 3.16 (s, 3H), 1.39 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 177.6, 143.3, 140.0, 133.3, 129.5, 129.1, 128.9, 128.6, 127.7, 108.4, 61.8, 45.60, 45.59, 26.53, 26.52, 25.4. The NMR spectra data are consistent with previously reported ^[S17].

3) Synthesis of indole alkaloid derivatives



To a solution of **6a** (72 mg, 0.256 mmol) in pyridine (3 mL) and EtOH (2.5 mL) (a) was added NH₂OH·HCl (104 mg, 1.50 mmol) and the reaction mixture was stirred at 10 °C for 24 hours. After the completion of **6a**, the reaction was quenched with water (10 mL) in room temperature and extracted with ethyl acetate for three times. The combined extracts were washed with 1 N HCl and dried over Na₂SO₄. After concentration under reduced pressure, the residue the residue was purified by column chromatography on silica gel with ethyl acetate/petroleum ether (1:5) to afford 8aa (24.9 mg, 33%) and **8ab** (30.8 mg, 41%). A solution of **8aa** (17 mg, 0.058 mmol) in THF (0.72 mL) was added to the stirred solution of LiAlH₄ (6.6 mg, 0.174 mmol) at 10 °C in air. The reaction mixture was stirred at 10 °C for 2.0 h. Then quenched with water (10 mL) in the same temperature and extracted with ethyl acetate for three times. The combined organic layer was washed with brine, dried over Na₂SO₄ and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel with ethyl acetate/petroleum ether (1:100) to afford the 8 42 product (6.8 %). mg, (4aS,9aS)-4a,9-dimethyl-3-phenyl-4,4a,9,9a-tetrahydro-[1,2]oxazino[6,5-b]indole (8): 6.8 mg, 42% yield. Colorless viscous oil. ¹H NMR (400 MHz, CDCl₃) δ 7.46 (d, *J* = 7.4 Hz, 2H), 7.37-7.28 (m, 3H), 7.04 – 6.99 (m, 2H), 6.59 (t, *J* = 7.4 Hz, 1H), 6.32 (d, J = 7.8 Hz, 1H), 5.24 (s, 1H), 3.06 (m, 4H), 2.65 (d, J = 14.2 Hz, 1H), 1.54 (s, 3H).¹³C NMR (100 MHz, CDCl₃) & 170.5, 150.2, 134.6, 132.9, 130.1, 128.5, 128.4, 126.1, 121.7, 117.3, 104.7, 100.9, 47.3, 33.6, 30.3, 26.8. **(b)**



To a stirred solution of **6a** (56 mg, 0.2 mmol) in 2.0 mL of anhydrous THF was added LiAlH₄ (15.2 mg, 2.0 equiv) at 10 °C in one portion in air. The resulting mixture was stirred at 10 °C for 15 min. Then the reaction was quenched by the addition of 1.0 mL of ethyl acetate, and the resulting mixture was stirred at room temperature until the generation of gas ceased. The reaction mixture was filtered through a plug of Celite with ethyl acetate. Then the filtrate was extracted with ethyl acetate (5.0 mL×3), the combined organic layer was dried over anhydrous Na₂SO₄, and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel with ethyl acetate/petroleum ether (1:100) to afford the product **9a** (10.1 mg, 19%) and **9b** (36.6 mg, 69%).

(2S,3aS,8aS)-3a,8-dimethyl-2-phenyl-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]indole

(**9a**): colorless oil; 10.1 mg, 19% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.27 – 7.26 (m, 4H), 7.22-7.20 (m, 1H), 7.10 (t, J = 7.6 Hz, 1H), 7.03 (d, J = 7.2 Hz, 1H), 6.67 (t, J = 7.4 Hz, 1H), 6.37 (d, J = 7.8 Hz, 1H), 5.24 (s, 1H), 4.69 – 4.56 (ddd, 11.2, 4.5 and 1.2Hz, 1H), 2.92 (d, J = 1.5 Hz, 3H), 2.44 (dd, J = 12.1 and 3.5 Hz, 1H), 1.99 – 1.92 (m, 1H), 1.46 (d, J = 1.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 150.7, 141.0, 134.5, 128.3, 128.2, 127.6, 126.1, 122.5, 117.3, 104.9, 104.8, 80.4, 53.1, 50.5, 30.9, 25.0.

(2R,3aS,8aS)-3a,8-dimethyl-2-phenyl-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]indole (9b): colorless oil; 36.6 mg, 69% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.29 – 7.21 (m, 5H), 7.14 (t, *J* = 7.7 Hz, 1H), 7.04 (d, *J* = 7.2 Hz, 1H), 6.70 (t, *J* = 7.4 Hz, 1H), 6.47 (d, *J* = 7.7 Hz, 1H), 5.17 – 5.13 (m, 2H), 3.04 (d, *J* = 1.9 Hz, 3H), 2.50 (ddd, *J* = 12.5, 6.4 and 1.9 Hz, 1H), 2.18 (ddd, *J* = 12.2, 9.1 and 1.7 Hz, 10H), 1.51 (d, *J* = 1.9 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 148.8, 141.9, 135.6, 128.1, 128.0, 127.3, 126.0, 122.2, 117.6, 107.2, 106.0, 79.7, 52.5, 49.1, 31.8, 23.3.

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¹H NMR of **5b** (400 M, CDCl₃)









































230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 f1 (ppm)









230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 f1 (ppm)



¹³C NMR of **5s** (100 M, CDCl₃)





¹³C NMR of **5u** (100 M, CDCl₃)




















¹H NMR of **6a** (400 M, CDCl₃)







¹H NMR of **6d** (400 M, CDCl₃)











¹H NMR of **6i** (400 M, CDCl₃)



230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 f1 (ppm)





¹H NMR of **6k** (400 M, CDCl₃)





230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 f1 (ppm)













¹³C NMR of **6q** (100 M, CDCl₃)



¹H NMR of **6r** (400 M, CDCl₃)



230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 f1 (ppm)







¹³C NMR of **6t** (100 M, CDCl₃)

















¹³C NMR of **9b** (100 M, CDCl₃)








¹³C NMR of **7b** (100 M, CDCl₃)

















210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 f1 (ppm)











0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 f1 (ppm)



121



















¹³C NMR of **7s** (100 M, CDCl₃)













