Supporting Information

Transition-metal free oxidative carbo-carboxylation of alkenes with formate in air

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1. General Information

^{1}H NMR (400 MHz) spectra, ^{13}C NMR (100 MHz) spectra, and ^{19}F NMR (376 MHz) spectra were recorded on a JEOL ECZ400 (400 MHz) spectrometers in $CDCl_3$, CD_3OD or DMSO-d_6. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, td = triplet of doublet, ddd = doublet of doublet of doublet, sep = septet, m = multiplet, br = broad. Flash column chromatography was performed using Nuo Tai silica gel (Size: 200-300) with distilled solvents. High Resolution Mass Spectra were obtained from the Xuzhou Medical University Mass Spectral facility.

All reactions were set up on the bench top and conducted under air or nitrogen atmosphere while subject to irradiation from blue LEDs (25 W, λ_{max} = 450 nm). Reagents and solvents and photocatalysts were purchased from various vendors and used as received, unless stated otherwise. Thin-layer chromatography (TLC) was performed on 0.2-0.3 mm SiliCycle silica gel F-254 plates.

2. Optimization of Reaction Conditions

General Procedure:

An oven-dried Schlenk tube (10 mL) containing a stirring bar was charged with the substrate (0.2 mmol), HCOONa (60.8 mg, 1.0 mmol, 5.0 equiv), DABCO (11.2 mg, 0.1 mmol, 50 mol%), K_3PO_4 (42.5 mg, 0.2 mmol, 1.0 equiv) and 4CzIPN (3.2 mg, 0.004 mmol, 2 mol%). Then anhydrous DMSO (2 mL) was added. Finally, the Schlenk tube was placed in an oil bath at the distance of 3 cm from a 25 W blue LED (wavelength: 450 nm) and stirred at 60 °C for 12 - 48 hours. After completion of the reaction, the reaction mixture was quenched with 2 mL of HCl (2 N), diluted with water (20 mL) and extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with water and brine before dried over sodium sulfate and concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (5% AcOH in petroleum ether/ EtOAc 1/5 ~ 1/2) to give the pure desired product.

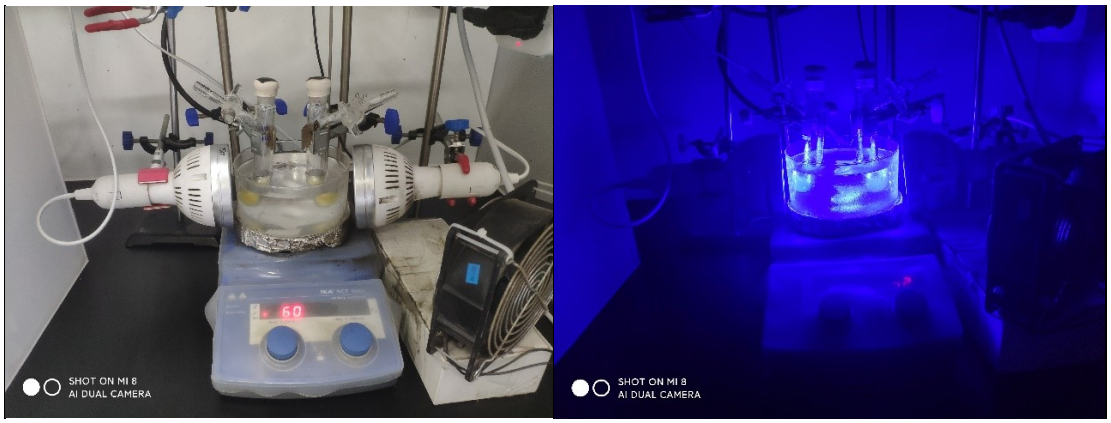
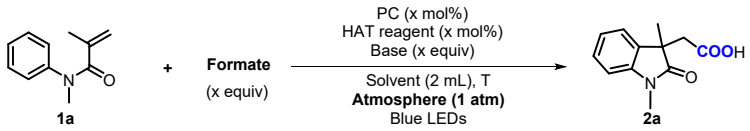


Figure S1. Standard setup for reactions

Table S1. Screening table of the reaction of *N*-methyl-*N*-phenylmethacrylamide with formate.



Entry	PC (x mol%)	Formate (x euqiv)	Base (x equiv)	HAT reagent (x mol%)	Solvent (2 mL)	Atmosphere	T (°C)	Yield of **2a**[a] (%)	RSM
1	4CzIPN (2)	HCOONa (5)	Cs_2CO_3 (3)	DABCO(50)	DMSO	**Air**	rt	20	0
2	4CzIPN (2)	HCOONa (5)	Cs_2CO_3 (3)	DABCO(50)	DMSO	**Air**	50	43	0
3	4CzIPN (2)	HCOONa (5)	Cs_2CO_3 (3)	DABCO(50)	DMSO	**N_2**	50	10(0)[b]	0
4	4CzIPN (2)	HCOONa (5)	Cs_2CO_3 (3)	DABCO(50)	DMSO	**O_2**	50	ND	25
5	4CzIPN (2)	HCOONa (5)	**KH_2PO_4 (3)**	DABCO(50)	DMSO	Air	50	35	0
6	4CzIPN (2)	HCOONa (5)	**Na_3PO_4 (3)**	DABCO(50)	DMSO	Air	50	42	0
7	4CzIPN (2)	HCOONa (5)	**Na_2HPO_4 (3)**	DABCO(50)	DMSO	Air	50	40	0
8	4CzIPN (2)	HCOONa (5)	**Na_2CO_3 (3)**	DABCO(50)	DMSO	Air	50	36	0
9	4CzIPN (2)	HCOONa (5)	**k_3PO_4 (3)**	DABCO(50)	DMSO	Air	50	47	0
10	4CzIPN (2)	HCOONa (5)	**k_3PO_4 (0.5)**	DABCO(50)	DMSO	Air	50	36	0
11	4CzIPN (2)	HCOONa (5)	**k_3PO_4 (1)**	DABCO(50)	DMSO	Air	50	51	0
12	4CzIPN (2)	HCOONa (5)	**k_3PO_4 (2)**	DABCO(50)	DMSO	Air	50	49	0
13	4CzIPN (2)	HCOONa (5)	**k_3PO_4 (4)**	DABCO(50)	DMSO	Air	50	51	0
14	4CzIPN (2)	HCOONa (5)	k_3PO_4 (3)	–	DMSO	Air	50	12	68
15	4CzIPN (2)	HCOONa (5)	k_3PO_4 (3)	**DIPEA(50)**	DMSO	Air	50	17	41
16	4CzIPN (2)	HCOONa (5)	k_3PO_4 (3)	**Quinuclidine(50)**	DMSO	Air	50	23	8
17	4CzIPN (2)	HCOONa (5)	k_3PO_4 (1)	**DABCO(20)**	DMSO	Air	50	26	23
18	4CzIPN (2)	HCOONa (5)	k_3PO_4 (1)	**DABCO(80)**	DMSO	Air	50	46	13
19	4CzIPN (2)	HCOONa (5)	K_3PO_4 (1)	DABCO(50)	DMSO	Air	**25**	39	0
20	***4CzIPN (2)***	***HCOONa (5)***	***K_3PO_4 (1)***	***DABCO(50)***	***DMSO***	***Air***	***60***	***62***[c]	**0**
21	4CzIPN (2)	HCOONa (5)	K_3PO_4 (1)	DABCO(50)	DMSO	Air	**70**	56	0
22	4CzIPN (2)	HCOONa (5)	K_3PO_4 (1)	DABCO(50)	DMSO	Air	**80**	52	0
23	4CzIPN (2)	**HCOOLi (5)**	K_3PO_4 (1)	DABCO(50)	DMSO	Air	60	46	0
24	4CzIPN (2)	**HCOOK (5)**	K_3PO_4 (1)	DABCO(50)	DMSO	Air	60	52	0
25	4CzIPN (2)	**HCOOCs (5)**	K_3PO_4 (1)	DABCO(50)	DMSO	Air	60	60	0
26	4CzIPN (2)	**$HCOONH_4$ (5)**	K_3PO_4 (1)	DABCO(50)	DMSO	Air	60	29	0
27	4CzIPN (2)	**HCOONa (1)**	K_3PO_4 (1)	DABCO(50)	DMSO	Air	60	20	5
28	4CzIPN (2)	**HCOONa (3)**	K_3PO_4 (1)	DABCO(50)	DMSO	Air	60	55	0
29	4CzIPN (2)	**HCOONa (7)**	K_3PO_4 (1)	DABCO(50)	DMSO	Air	60	42	0
30	**-**	HCOONa (5)	K_3PO_4 (1)	DABCO(50)	DMSO	Air	60	0	100
31	**4DPAIPN (2)**	HCOONa (5)	K_3PO_4 (1)	DABCO(50)	DMSO	Air	60	42	0
32	***fac*-Ir(ppy)$_3$(2)**	HCOONa (5)	K_3PO_4 (1)	DABCO(50)	DMSO	Air	60	55	0
33	**Ir[(dttpy)(ppy)$_2$]PF_6(2)**	HCOONa (5)	K_3PO_4 (1)	DABCO(50)	DMSO	Air	60	55	0
34	**Eosin B (2)**	HCOONa (5)	K_3PO_4 (1)	DABCO(50)	DMSO	Air	60	55	14
35	**Eosin Y(2)**	HCOONa (5)	K_3PO_4 (1)	DABCO(50)	DMSO	Air	60	43	0
36	**4CzIPN (1)**	HCOONa (5)	K_3PO_4 (1)	DABCO(50)	DMSO	Air	60	47	0
37	**4CzIPN (3)**	HCOONa (5)	K_3PO_4 (1)	DABCO(50)	DMSO	Air	60	48	0
38	4CzIPN (2)	HCOONa (5)	K_3PO_4 (1)	DABCO(50)	**DMF**	Air	60	42	0
39	4CzIPN (2)	HCOONa (5)	K_3PO_4 (1)	DABCO(50)	**DMA**	Air	60	10	0

[a]Yields were determined by ^{1}H NMR analysis with 1,2-dicloroethane as an internal standard.
[b]solvent was degased by three vacuum-purge/nitrogen-flush cycles or freeze-pump-thaw (in parentheses) .
[c]Isolated yields.

Large Scale Reaction Procedure:

An oven-dried Schlenk tube (50 mL) containing a stirring bar was charged with the *N*-(4-(*tert*-butyl)phenyl)-*N*-methylmethacrylamide (0.4627 g, 2.0 mmol), HCOONa (0.6801 g, 10.0 mmol, 5.0 equiv), DABCO (0.1122 g, 0.1 mmol, 50 mol%), K_3PO_4 (0.4245 g, 0.2 mmol, 1.0 equiv) and 4CzIPN (31.6 mg, 0.004 mmol, 2 mol%). The anhydrous DMSO (20 mL) were added. Finally, the Schlenk tube was placed in an oil bath at the distance of 3 cm from a 45 W blue LED (wavelength: 450 nm) and stirred at 60 °C for 12 hours. After completion of the reaction, the reaction mixture was quenched with 10 mL of HCl (2 N), diluted with water (60 mL) and extracted with EtOAc (3 x 60 mL). The combined organic layers were washed with water and brine before dried over sodium sulfate and concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (5% AcOH in petroleum ether/ EtOAc 1/5 ~ 1/2) to give the pure desired product.

3. Synthesis of Substrates

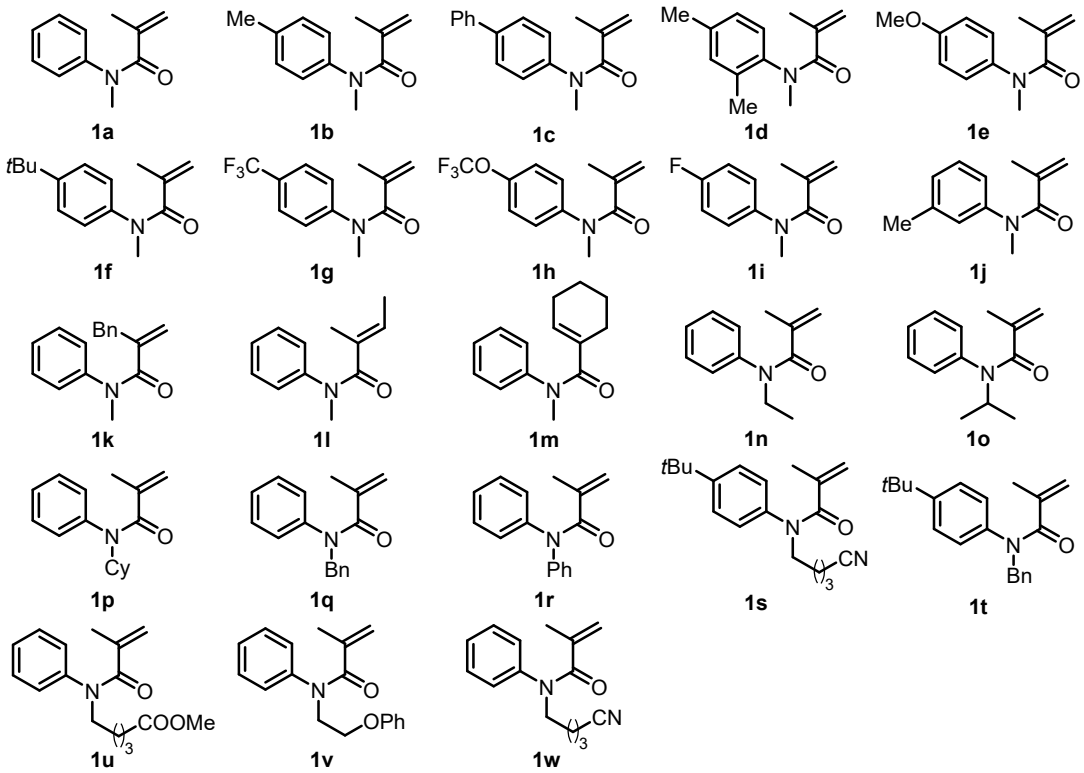
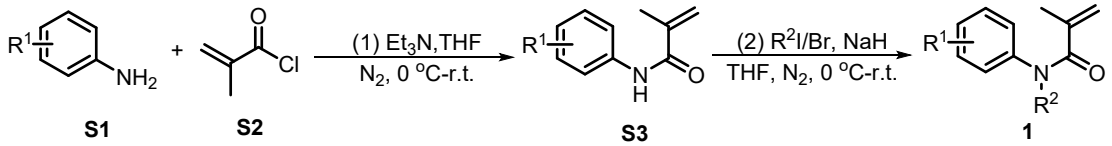


Figure S3. The scope of various alkenes.

General Procedure A: substrates **1a-1j, 1n-1o, 1q, 1s-1w** were synthesized following the reported procedures in the literature. [1]

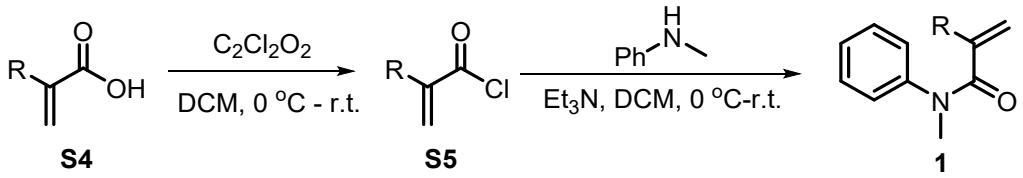
General Procedure A for Preparation of Substrates



To a 50 mL round-bottom flask was added the solution of corresponding aniline **S1** (10.0 mmol) in THF (15 mL) and triethylamine (2.1 mL, 15.0 mmol, 1.5 equiv). The mixture was stirred at 0 ℃, and methacryloyl chloride **S2** (1.2 mL, 12 mmol, 1.2 equiv) was added slowly under nitrogen atmosphere. The resulting solution was stirred at room temperature for 6 hours, quenched with H_2O (15 mL), and extracted with EtOAc (20 mL x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on a silica gel using petroleum ether and EtOAc (5:1, v/v) as the eluent to give corresponding intermediates **S3**.

To a 50 mL round-bottom flask was added the solution of corresponding intermediates **S3** (2.0 mmol) in THF (10 mL). The mixture was stirred at 0 ℃, and NaH (0.07 g, 3.0 mmol, 1.5 equiv) was added slowly. Then the reaction mixture was stirred at 0 ℃ for 15 min followed by addition of halohydrocarbon (3.0 mmol, 1.5 equiv). The resulting solution was stirred at room temperature for 8 hours, quenched with H_2O (15 mL), and extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on a silica gel using petroleum ether and EtOAc (5:1, v/v) as the eluent to give corresponding compounds **1a-1j, 1n-1o, 1q, 1s-1w**.

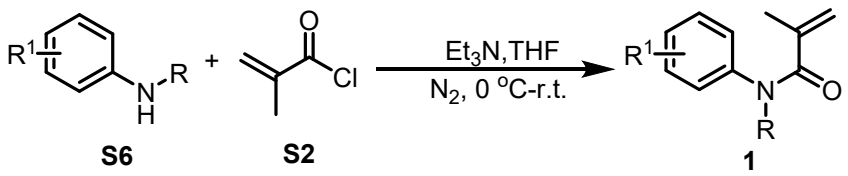
General Procedure B: substrates **1k-1m** were synthesized following the reported procedures in the literature. [2]



The acid **S4** (2.0 mmol) and DCM (10 mL) were added to a 50 mL round-bottom flask. The mixture was stirred at 0 ℃, and oxalyl chloride (3.0 mmol, 2 equiv) was added slowly. The resulting solution was then stirred at room temperature for 8 hours. The solvent was removed under reduced pressure to get product **S5**, which was used directly to the next step.

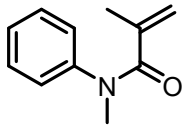
To a 50 mL round-bottom flask was added the solution of *N*-methylaniline (2.0 mmol) in DCM (15 mL) and triethylamine (4.0 mmol, 2.0 equiv). The mixture was stirred at 0 ℃, and added slowly the solution of **S5** (0.31 g, 3.0 mmol, 1.5 equiv) in DCM (5 mL) under argon atmosphere. The resulting solution was stirred at room temperature for 8 hours, followed by the addition of H_2O (10 mL) to quench excess acyl chloride, and extracted with DCM (3 x 20 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on a silica gel using petroleum ether and EtOAc (5:1, v/v) as the eluent to give product **1k-1m**.

General Procedure C: substrates **1p, 1r** were synthesized following the reported procedures in the literature. [1]

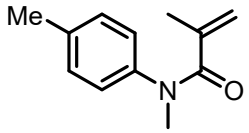


To a 50 mL round-bottom flask was added the solution of corresponding aniline **S1** (10.0 mmol) in THF (15 mL) and triethylamine (2.1 mL, 15.0 mmol, 1.5 equiv). The mixture was stirred at 0 ℃, and added slowly methacryloyl chloride **S2** (1.2 mL, 12

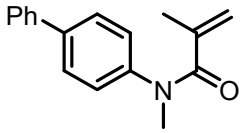
mmol, 1.2 equiv) under nitrogen atmosphere. The resulting solution was stirred at room temperature for 6 hours, quenched with H_2O (15 mL), and extracted with EtOAc (20 mL x 3). The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on a silica gel using petroleum ether and EtOAc (5:1, v/v) as the eluent to give product **1p, 1r**.



***N*-methyl-*N*-phenylmethacrylamide (1a)**: Prepared according to general procedure A using aniline and iodomethane. The spectra matched with reported literature.[1]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (td, J = 6.8, 1.6 Hz, 2H), 7.27 (dd, J = 2.8, 1.6 Hz, 1H), 7.16 – 7.12 (m, 2H), 5.05 – 5.02 (m, 1H), 5.00 – 4.98 (m, 1H), 3.35 (s, 3H), 1.76 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 144.7, 140.8, 129.3, 127.0, 126.6, 119.4, 37.7, 20.4.

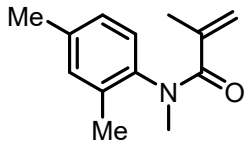


***N*-methyl-*N*-(*p*-tolyl)methacrylamide (1b)**: Prepared according to general procedure A using *p*-toluidine and iodomethane. The spectra matched with reported literature.[1]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (d, J = 7.6 Hz, 2H), 6.94 (d, J = 7.6 Hz, 2H), 5.01 – 4.86 (m, 2H), 3.24 (s, 3H), 2.26 (s, 3H), 1.68 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 141.9, 140.7, 136.7, 129.7, 126.2, 119.0, 37.6, 20.9, 20.3.

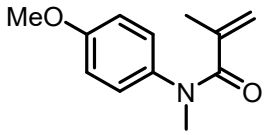


***N*-([1,1'-biphenyl]-4-yl)-*N*-methylmethacrylamide (1c)**: Prepared according to general procedure A [1,1'-biphenyl]-4-amine and iodomethane. The spectra matched with reported literature.[3]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (t, J = 7.2 Hz, 4H), 7.44 (t, J = 7.2 Hz, 2H), 7.35 (t, J = 8.0 Hz, 1H), 7.20 (d, J = 8.0 Hz, 2H), 5.06 (d, J = 10.8 Hz, 2H), 3.38 (s, 3H), 1.81 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 143.8, 140.7, 140.0, 139.8, 128.9, 127.9, 127.6,

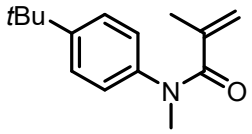
127.0, 126.8, 119.6, 37.7, 20.4.



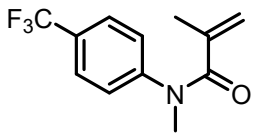
***N*-(2,4-dimethylphenyl)-*N*-methylmethacrylamide (1d)**: Prepared according to general procedure A using 3,5-dimethylaniline and iodomethane.[4]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (s, 1H), 6.97 (d, J = 9.2 Hz, 1H), 6.92 (d, J = 8.0 Hz, 1H), 4.95 (d, J = 1.2 Hz, 2H), 3.20 (s, 3H), 2.32 (s, 3H), 2.21 (s, 3H), 1.73 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 140.6, 140.5, 137.6, 134.4, 131.8, 127.8, 127.5, 118.1, 36.6, 20.9, 20.2, 17.5.



***N*-(4-methoxyphenyl)-*N*-methylmethacrylamide (1e)**: Prepared according to general procedure A using 4-methoxyaniline and iodomethane. The spectra matched with reported literature.[1]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 – 7.02 (m, 2H), 6.89 – 6.81 (m, 2H), 5.01 (d, J = 13.6 Hz, 2H), 3.81 (s, 3H), 3.31 (s, 3H), 1.74 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 157.9, 140.5, 136.9, 127.3, 118.4, 114.0, 54.9, 37.3, 20.0.

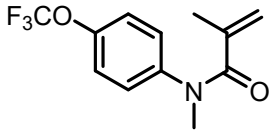


***N*-(4-(*tert*-butyl)phenyl)-*N*-methylmethacrylamide (1f)**: Prepared according to general procedure A using 4-(*tert*-butyl)aniline and iodomethane. The spectra matched with reported literature.[5]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 8.4 Hz, 2H), 7.05 (d, J = 8.4 Hz, 2H), 5.02 (d, J = 8.0 Hz, 2H), 3.33 (s, 3H), 1.75 (s, 3H), 1.32 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 149.8, 141.8, 140.7, 126.0, 125.9, 119.2, 37.6, 34.5, 31.3, 20.3.

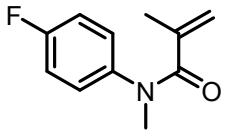


***N*-methyl-*N*-(4-(trifluoromethyl)phenyl)methacrylamide (1g)**: Prepared according to general procedure A using 4-(trifluoromethyl)aniline and iodomethane. The spectra matched with reported literature.[1]

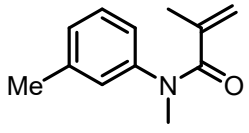
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 4.97 (d, J = 44.6 Hz, 2H), 3.31 (s, 3H), 1.74 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 147.8, 140.2, 128.6 (d, J_{FC} = 32.6 Hz), 126.4, 126.3 (d, J_{FC} = 3.7 Hz), 126.2(6), 123.8 (q, J_{FC}= 270.6 Hz), 37.4, 20.0.
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.4.



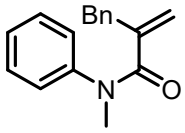
***N*-methyl-*N*-(4-(trifluoromethoxy)phenyl)methacrylamide (1h)**: Prepared according to general procedure A using 4-(trifluoromethoxy)aniline and iodomethane The spectra matched with reported literature.[5]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.15 (m, 4H), 5.09 (dt, J = 2.8, 1.2 Hz, 1H), 5.00 (p, J = 1.0 Hz, 1H), 3.35 (s, 3H), 1.79 (dd, J = 1.6, 1.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 147.5 (d, J_{FC} = 1.9 Hz), 143.1, 140.4, 127.8, 120.4 (q, J_{FC} = 260.2 Hz), 119.7, 37.7, 20.2.
^{19}F NMR (376 MHz, $CDCl_3$) δ -58.1.



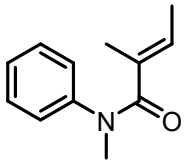
***N*-(4-fluorophenyl)-*N*-methylmethacrylamide (1i)**: Prepared according to general procedure A using 4-fluoroaniline and iodomethane. The spectra matched with reported literature.[1]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (dd, J = 8.8, 4.8 Hz, 2H), 7.04 (t, J = 8.4 Hz, 2H), 5.02 (d, J = 31.2 Hz, 2H), 3.33 (s, 3H), 1.77 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 161.2 (d, J_{FC}= 245.8 Hz), 140.6, 128.4, 128.3, 119.5, 116.2 (d, J_{FC}= 22.6 Hz), 37.9, 20.4.
^{19}F NMR (376 MHz, $CDCl_3$) δ -114.5.



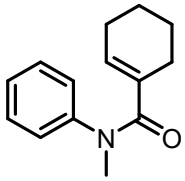
***N*-methyl-*N*-(*m*-tolyl)methacrylamide (1j)**: Prepared according to general procedure A using *m*-toluidine and iodomethane. The spectra matched with reported literature.[1]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.14 (m, 3H), 7.04 (d, J = 7.2 Hz, 1H), 4.95 (d, J = 5.6 Hz, 2H), 3.23 (s, 3H), 2.26 (s, 3H), 1.74 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 144.7, 140.9, 139.3, 129.1, 127.8, 127.2, 123.7, 119.3, 37.8, 21.4, 20.5.



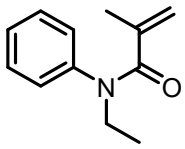
2-benzyl-*N*-methyl-*N*-phenylacrylamide (1k): Prepared according to general procedure B using 2-benzylacrylic acid. The spectra matched with reported literature.[1]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.22 (m, 6H), 7.07 (d, J = 6.8 Hz, 2H), 6.82 (d, J = 6.8 Hz, 2H), 4.96 (d, J = 15.6 Hz, 2H), 3.46 (s, 2H), 3.29 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 144.5, 144.4, 137.8, 129.6, 129.2, 128.5, 127.0, 126.9, 126.6, 119.6, 40.4, 38.0.



(*E*)-*N*,2-dimethyl-*N*-phenylbut-2-enamide (1l): Prepared according to general procedure B using (*E*)-2-methylbut-2-enoic acid. The spectra matched with reported literature.[2]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 2H), 7.24 – 7.19 (m, 1H), 7.10 (dt, J = 8.8, 2.0 Hz, 2H), 5.74 (qq, J = 6.8, 1.2 Hz, 1H), 3.34 (s, 3H), 1.58 – 1.52 (m, 3H), 1.48 (dd, J = 6.8, 1.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 145.1, 132.7, 130.6, 129.2, 126.5, 126.5, 37.9, 14.2, 13.4.

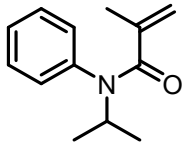


***N*-methyl-*N*-phenylcyclohex-1-ene-1-carboxamide (1m)**: Prepared according to general procedure B using cyclohex-1-ene-1-carboxylic acid. The spectra matched with reported literature.[2]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 2H), 7.25 – 7.18 (m, 1H), 7.14 – 7.09 (m, 2H), 5.83 (dt, J = 3.6, 2.0 Hz, 1H), 3.34 (s, 3H), 1.99 – 1.81 (m, 4H), 1.42 (m, 4H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 144.8, 134.4, 132.5, 128.9, 126.4, 126.3, 37.6, 25.8, 24.8, 21.9, 21.3.

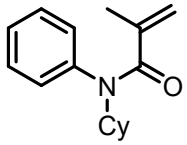


***N*-ethyl-*N*-phenylmethacrylamide (1n)**: Prepared according to general procedure A using aniline and bromoethane. The spectra matched with reported literature.[6]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (dd, J = 8.8, 6.8 Hz, 2H), 7.28 (d, J = 7.6 Hz, 1H),

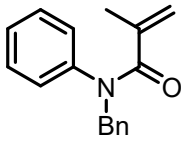
7.11 (dd, J = 7.6, 2.0 Hz, 2H), 5.00 (d, J = 12.4 Hz, 2H), 3.84 (q, J = 7.2 Hz, 2H), 1.75 (s, 3H), 1.15 (t, J = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 142.7, 140.8, 129.1, 127.5, 127.1, 119.1, 44.6, 20.3, 12.8.



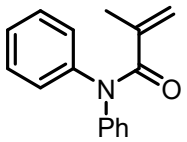
***N*-isopropyl-*N*-phenylmethacrylamide (1o)**: Prepared according to general procedure A using aniline and 2-bromopropane. The spectra matched with reported literature.[7]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 3H), 7.09 – 7.02 (m, 2H), 4.97 (dt, J = 13.2, 6.4 Hz, 1H), 4.90 (s, 1H), 4.85 (s, 1H), 1.73 (s, 3H), 1.12 (d, J = 6.8 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 141.7, 139.2, 130.4, 128.8, 127.8, 117.8, 46.8, 21.1, 20.8.



***N*-cyclohexyl-*N*-phenylmethacrylamide (1p)**: Prepared according to general procedure C using *N*-cyclohexylaniline.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.30 (m, 3H), 7.09 – 7.03 (m, 2H), 4.86 (d, J = 24.4 Hz, 2H), 4.56 (t, J = 11.6 Hz, 1H), 1.92 – 1.82 (m, 2H), 1.73 (s, 3H), 1.64 – 1.54 (m, 3H), 1.41 (qt, J = 13.2, 3.6 Hz, 2H), 1.13 (qd, J = 12.4, 3.6 Hz, 2H), 0.93 (qt, J = 13.2, 3.6 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 141.7, 139.7, 130.6, 128.7, 127.8, 117.6, 54.8, 31.7, 25.9, 25.5, 20.9.
ESIHRMS: *m/z* Calcd. For $C_{16}H_{21}NO$: $(M+H)^+$ 244.1696. Found: 244.1696.



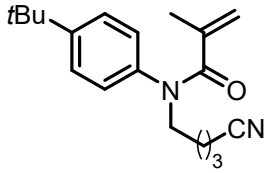
***N*-benzyl-*N*-phenylmethacrylamide (1q)**: Prepared according to general procedure A using aniline and benzyl bromide. The spectra matched with reported literature.[1]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.08 (m, 8H), 6.93 (d, J = 7.6 Hz, 2H), 4.96 (d, J = 6.8 Hz, 2H), 4.92 (s, 2H), 1.73 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 142.8, 140.4, 137.2, 128.8, 128.1(3), 128.0(9), 127.1, 127.0, 126.8, 119.2, 52.8, 20.1.



***N*,*N*-diphenylmethacrylamide (1r)**: Prepared according to general procedure C using diphenylamine. The spectra matched with reported literature.[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 4H), 7.25 – 7.20 (m, 2H), 7.19 – 7.15 (m, 4H), 5.25 – 5.23 (p, J = 1.2 Hz, 1H), 5.17 (p, J = 1.2 Hz, 1H), 1.84 (t, J = 1.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 143.6, 141.3, 129.2, 127.3, 126.6, 121.1, 20.1.

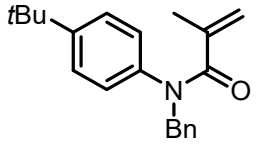


***N*-(4-(*tert*-butyl)phenyl)-*N*-(4-cyanobutyl)methacrylamide (1s)**: Prepared according to general procedure A using 4-(*tert*-butyl)aniline and 5-bromopentanenitrile.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 2H), 7.03 – 6.98 (m, 2H), 5.03 – 4.96 (m, 2H), 3.82 – 3.76 (m, 2H), 2.44 – 2.36 (m, 2H), 1.71 – 1.70 (m, 4H), 1.69 (s, 3H), 1.32 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 150.5, 140.9, 139.9, 126.9, 126.3, 119.6, 119.4, 48.3, 34.7, 31.4, 26.8, 22.8, 20.4, 16.9.

ESIHRMS: *m/z* Calcd. For $C_{19}H_{26}N_2O$: $(M+Na)^+$ 321.1937. Found: 321.1930.

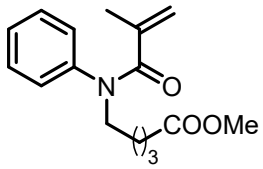


***N*-benzyl-*N*-(4-(*tert*-butyl)phenyl)methacrylamide (1t)**: Prepared according to general procedure A using 4-(*tert*-butyl)aniline and benzyl bromide.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 1H), 7.27 – 7.21 (m, 6H), 6.92 – 6.87 (m, 2H), 5.04 (dq, J = 2.8, 1.2 Hz, 2H), 4.95 (s, 2H), 1.78 – 1.73 (m, 3H), 1.28 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 150.1, 140.8, 140.6, 137.8, 128.5, 128.3, 127.3, 126.8, 126.0, 119.5, 53.3, 34.6, 31.4, 20.5.

ESIHRMS: *m/z* Calcd. For $C_{21}H_{25}NO$: $(M+H)^+$ 308.2009. Found: 308.2014.

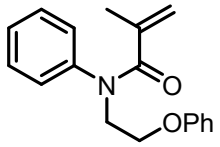


methyl 5-(*N*-phenylmethacrylamido)pentanoate (1u): Prepared according to general procedure A using aniline and 5-bromopentanoic acid.

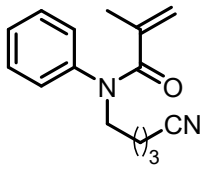
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 2H), 7.28 (d, J = 6.4 Hz, 1H), 7.11 (d, J = 7.6 Hz, 2H), 4.98 (d, J = 18.4 Hz, 2H), 3.79 (t, J = 6.8 Hz, 2H), 3.64 (s, 3H), 2.32 (t, J = 6.8 Hz, 2H), 1.74 (s, 3H), 1.63 (dq, J = 13.6, 7.6 Hz, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 171.9, 143.1, 141.1, 129.3, 127.6, 127.2, 119.2,

51.6, 49.2, 33.8, 27.2, 22.3, 20.5.
ESIHRMS: *m/z* Calcd. For $C_{16}H_{21}NO_3$: $(M+Na)^+$ 298.1414. Found: 298.1407.



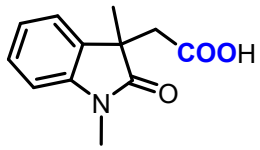
***N*-(2-phenoxyethyl)-*N*-phenylmethacrylamide (1v)**: Prepared according to general procedure A using aniline and (2-bromoethoxy)benzene.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (ddd, J = 7.6, 6.4, 1.2 Hz, 2H), 7.28 – 7.24 (m, 3H), 7.23 – 7.20 (m, 2H), 6.94 (tt, J = 7.6, 1.2 Hz, 1H), 6.87 – 6.82 (m, 2H), 5.06 – 5.03 (m, 1H), 5.01 (s, 1H), 4.22 (t, J = 5.2 Hz, 2H), 4.15 (td, J = 5.2, 1.2 Hz, 2H), 1.75 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 158.6, 143.9, 140.7, 129.5, 129.2, 127.5, 127.2, 121.0, 119.9, 114.5, 65.1, 49.8, 20.3.
ESIHRMS: *m/z* Calcd. For $C_{18}H_{19}NO_2$: $(M+H)^+$ 282.1489. Found: 282.1482.



***N*-(4-cyanobutyl)-*N*-phenylmethacrylamide (1w)**: Prepared according to general procedure A using aniline and 5-bromopentanenitrile.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (ddd, J = 7.6, 6.4, 1.2 Hz, 2H), 7.32 – 7.27 (m, 1H), 7.13 – 7.08 (m, 2H), 5.03 – 5.00 (m, 1H), 4.99 – 4.93 (m, 1H), 3.87 – 3.77 (m, 2H), 2.45 – 2.36 (m, 2H), 1.73 (t, J = 2.4 Hz, 3H), 1.70 (p, J = 3.6 Hz, 4H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 142.6, 140.6, 129.3, 127.3, 127.2, 119.4, 119.3, 48.0, 26.6, 22.6, 20.2, 16.7.
ESIHRMS: *m/z* Calcd. For $C_{15}H_{18}N_2O$: $(M+Na)^+$ 265.1311. Found: 265.1311.

4. Succinic Acid Derivatives

All reactions were conducted according to the general procedure with 0.2 mmol alkenes unless otherwise stated.

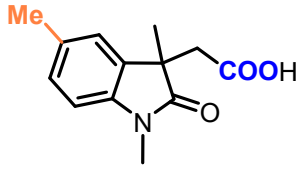


2-(1,3-dimethyl-2-oxoindolin-3-yl)acetic acid (2a): Prepared according to general procedure using *N*-methyl-*N*-phenylmethacrylamide (0.2 mmol, 35.0 mg, 1.0 equiv). After 12 hours, the product was purified by flash column chromatography (5% AcOH in petroleum ether/ EtOAc 1/5 ~ 1/2 as the eluent) and obtained as white solid (27.2 mg, 62% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 7.6 Hz, 1H), 7.19 (d, J = 7.2 Hz, 1H), 7.06 (t, J = 7.6 Hz, 1H), 6.85 (d, J = 8.0 Hz, 1H), 3.21 (s, 3H), 2.98 (d, J = 16.8 Hz, 1H), 2.80 (d, J = 16.8 Hz, 1H), 1.38 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 180.5, 174.1, 143.3, 132.8, 128.5, 123.0, 122.5, 108.6, 45.4, 41.5, 26.6, 24.1.

ESIHRMS: *m/z* Calcd. For $C_{12}H_{13}NO_3$: $(M+Na)^+$ 242.0788. Found: 242.0780.

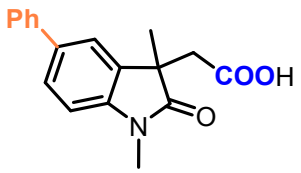


2-(1,3,5-trimethyl-2-oxoindolin-3-yl)acetic acid (2b): Prepared according to general procedure using *N*-methyl-*N*-(*p*-tolyl)methacrylamide (0.2 mmol, 37.9 mg, 1.0 equiv). After 12 hours, the product was purified by flash column chromatography (5% AcOH in petroleum ether/ EtOAc 1/5 ~ 1/2 as the eluent) and obtained as white solid (28.0 mg, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, J = 8.0 Hz, 1H), 7.01 (s, 1H), 6.74 (d, J = 8.0 Hz, 1H), 3.20 (s, 3H), 2.97 (d, J = 16.4 Hz, 1H), 2.78 (d, J = 16.4 Hz, 1H), 2.33 (s, 3H), 1.37 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 180.6, 173.8, 140.8, 132.9, 132.6, 128.7, 123.3, 108.3, 45.5, 41.5, 26.7, 24.1, 21.3.

ESIHRMS: *m/z* Calcd. For $C_{13}H_{15}NO_3$: $(M+Na)^+$ 256.0944. Found: 256.0934.



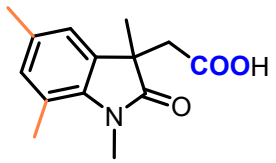
2-(1,3-dimethyl-2-oxo-5-phenylindolin-3-yl)acetic acid (2c): Prepared according to

general procedure using *N*-([1,1'-biphenyl]-4-yl)-*N*-methylmethacrylamide (0.2 mmol, 50.3 mg, 1.0 equiv). After 12 hours, the product was purified by flash column chromatography (5% AcOH in petroleum ether/ EtOAc 1/5 ~ 1/2 as the eluent) and obtained as white solid (40.8 mg, 69% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 2H), 7.48 (dd, J = 8.0, 2.0 Hz, 1H), 7.45 – 7.39 (m, 3H), 7.35 – 7.29 (m, 1H), 6.89 (d, J = 8.0 Hz, 1H), 3.22 (s, 3H), 3.02 (d, J = 16.8 Hz, 1H), 2.85 (d, J = 16.8 Hz, 1H), 1.40 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 180.5, 174.1, 142.7, 140.9, 136.3, 133.5, 128.9, 127.3, 127.2, 127.0, 121.4, 108.8, 45.6, 41.4, 26.7, 24.3.

ESIHRMS: *m/z* Calcd. For $C_{18}H_{17}NO_3$: $(M+H)^+$ 296.1281. Found: 296.1268.

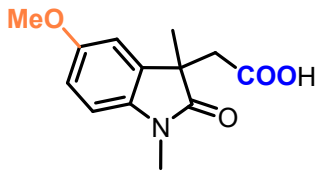


2-(1,3,5,7-tetramethyl-2-oxoindolin-3-yl)acetic acid (2d): Prepared according to general procedure using *N*-(2,4-dimethylphenyl)-*N*-methylmethacrylamide (0.2 mmol, 40.7 mg, 1.0 equiv). After 12 hours, the product was purified by flash column chromatography (5% AcOH in petroleum ether/ EtOAc 1/5 ~ 1/2 as the eluent) and obtained as yellow solid (24.2 mg, 49% yield).

^{1}H NMR (400 MHz, DMSO-d_6) δ 6.93 (s, 1H), 6.74 (s, 1H), 3.31 (s, 3H), 2.80 (d, J = 16.4 Hz, 1H), 2.71 (d, J = 16.4 Hz, 1H), 2.45 (s, 3H), 2.17 (s, 3H), 1.13 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 180.4, 171.4, 139.3, 134.6, 132.1, 131.0, 121.2, 119.4, 44.8, 41.8, 29.6, 25.4, 20.9, 18.9.

ESIHRMS: *m/z* Calcd. For $C_{14}H_{17}NO_3$: $(M+Na)^+$ 270.1101. Found: 270.1099.

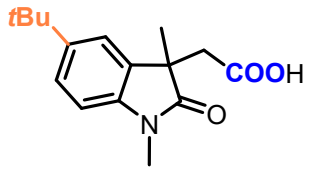


2-(5-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)acetic acid (2e): Prepared according to general procedure using *N*-(4-methoxyphenyl)-*N*-methylmethacrylamide (0.2 mmol, 41.1 mg, 1.0 equiv). After 12 hours, the product was purified by flash column chromatography (5% AcOH in petroleum ether/ EtOAc 1/5 ~ 1/2 as the eluent) and obtained as brown solid (20.9 mg, 42% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 – 6.78 (m, 2H), 6.76 (dd, J = 8.4, 0.8 Hz, 1H), 3.79 (s, 3H), 3.20 (s, 3H), 2.97 (d, J = 16.4 Hz, 1H), 2.78 (d, J = 16.4 Hz, 1H), 1.38 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 180.3, 173.7, 156.3, 136.7, 134.3, 112.4, 110.2, 108.9, 55.9, 45.8, 41.4, 26.7, 24.1.

ESIHRMS: *m/z* Calcd. For $C_{13}H_{15}NO_4$: $(M+Na)^+$ 272.0893. Found: 272.0900.

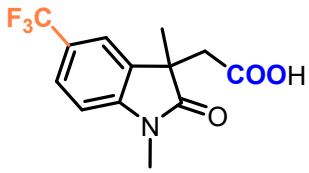


2-(5-(*tert*-butyl)-1,3-dimethyl-2-oxoindolin-3-yl)acetic acid (2f): Prepared according to general procedure using *N*-(4-(*tert*-butyl)phenyl)-*N*-methylmethacrylamide (0.2 mmol, 46.3 mg, 1.0 equiv). After 19 hours, the product was purified by flash column chromatography (5% AcOH in petroleum ether/ EtOAc 1/5 ~ 1/2 as the eluent) and obtained as white solid (43.5 mg, 79% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (s, 1H), 7.30 (dd, J = 8.0, 2.0 Hz, 1H), 7.25 (d, J = 2.0 Hz, 1H), 6.78 (d, J = 8.0 Hz, 1H), 3.20 (s, 3H), 2.98 (d, J = 16.4 Hz, 1H), 2.83 (d, J = 16.4 Hz, 1H), 2.05 (s, 2H), 1.39 (s, 3H), 1.30 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 180.8, 173.9, 146.3, 140.7, 132.5, 125.0, 119.7, 108.0, 45.7, 41.6, 34.7, 31.7, 26.6, 24.0.

ESIHRMS: *m/z* Calcd. For $C_{16}H_{21}NO_3$: $(M+Na)^+$ 298.1414. Found: 298.1414.



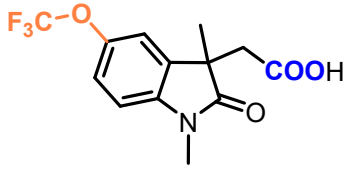
2-(1,3-dimethyl-2-oxo-5-(trifluoromethyl)indolin-3-yl)acetic acid (2g): Prepared according to general procedure using *N*-methyl-*N*-(4-(trifluoromethyl)phenyl)methacrylamide (0.2 mmol, 48.6 mg, 1.0 equiv). After 12 hours, the product was purified by flash column chromatography (5% AcOH in petroleum ether/ EtOAc 1/5 ~ 1/2 as the eluent) and obtained as white solid (23.0 mg, 40% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, J = 8.4, 0.8 Hz, 1H), 7.43 – 7.39 (d, J = 1.2 Hz, 1H), 6.91 (d, J = 8.0 Hz, 1H), 3.24 (s, 3H), 3.04 (d, J = 17.2 Hz, 1H), 2.87 (d, J = 17.2 Hz, 1H), 1.38 (s, 3H).

^{13}C NMR (100 MHz, CD_3OD) δ 182.6, 173.2, 148.3, 135.8, 126.1 (q, J = 269.1 Hz), 126.9 (q, J = 3.7 Hz), 125.7 (q, J = 32.2 Hz), 120.3 (q, J = 3.3 Hz), 109.6, 46.9, 41.9, 26.9, 24.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -61.2.

ESIHRMS: *m/z* Calcd. For $C_{13}H_{12}F_3NO_3$: $(M+Na)^+$ 310.0661. Found: 310.0658.



2-(1,3-dimethyl-2-oxo-5-(trifluoromethoxy)indolin-3-yl)acetic acid (2h): Prepared according to general procedure using *N*-methyl-*N*-(4-

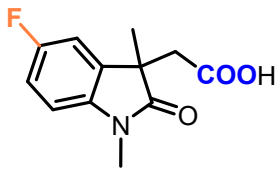
(trifluoromethoxy)phenyl)methacrylamide (0.2 mmol, 51.8 mg, 1.0 equiv). After 12 hours, the product was purified by flash column chromatography (5% AcOH in petroleum ether/ EtOAc 1/5 ~ 1/2 as the eluent) and obtained as white solid (32.1 mg, 53% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (ddd, J = 8.4, 2.4, 0.8 Hz, 1H), 7.10 (d, J =1.2 Hz, 1H), 6.82 (d, J = 8.4 Hz, 1H), 3.21 (s, 3H), 3.00 (d, J = 16.8 Hz, 1H), 2.82 (d, J = 16.8 Hz, 1H), 1.37 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 180.0, 174.2, 144.9, 142.1, 134.4, 120.6 (q, J = 255.2 Hz), 121.4, 116.6, 108.8, 45.8, 41.1, 26.7, 24.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -58.2.

ESIHRMS: *m/z* Calcd. For $C_{13}H_{12}F_3NO_4$: $(M+Na)^+$ 326.0611. Found: 326.0605.



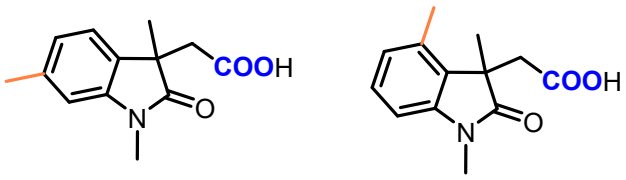
2-(5-fluoro-1,3-dimethyl-2-oxoindolin-3-yl)acetic acid (2i): Prepared according to general procedure using *N*-(4-fluorophenyl)-*N*-methylmethacrylamide (0.2 mmol, 51.8 mg, 1.0 equiv). After 12 hours, the product was purified by flash column chromatography (5% AcOH in petroleum ether/ EtOAc 1/5 ~ 1/2 as the eluent) and obtained as deep brown oil (28.0 mg, 59% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (t, J = 9.6 Hz, 2H), 6.79 – 6.76 (m, 1H), 3.21 (s, 3H), 2.99 (d, J = 16.8 Hz, 1H), 2.80 (d, J = 16.8 Hz, 1H), 1.37 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 180.1, 173.8, 159.5 (d, J = 239.8 Hz), 139.3, 134.5 (d, J = 7.8 Hz), 114.6 (d, J = 23.4 Hz), 110.8 (d, J = 24.8 Hz), 109.0 (d, J = 8.1 Hz), 45.9, 41.2, 26.8, 24.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -120.0.

ESIHRMS: *m/z* Calcd. For $C_{12}H_{12}FNO_3$: $(M+Na)^+$ 260.0693. Found: 260.0693.



0.6:1

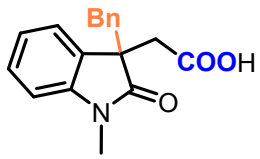
2-(1,3,6-trimethyl-2-oxoindolin-3-yl)acetic acid (2j) and 2-(1,3,4-trimethyl-2-oxoindolin-3-yl)acetic acid (2j') (0.6:1): Prepared according to general procedure using *N*-methyl-*N*-(*m*-tolyl)methacrylamide (0.2 mmol, 37.9 mg, 1.0 equiv). After 12 hours, the product was purified by flash column chromatography (5% AcOH in petroleum ether/ EtOAc 1/5 ~ 1/2 as the eluent) and obtained as white solid (28.0 mg, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.04 (m, 1H), 6.84 (m, 1H), 6.70 – 6.66 (m, 1H), 3.19 (d, J = 3.2 Hz, 3H), 3.14 – 2.73 (m, 2H), 2.37 (d, J = 10.4 Hz, 3H), 1.38 (d, J =

22.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 180.8, 180.3, 174.4, 174.2, 143.7, 143.3, 138.6, 133.9, 129.9, 129.4, 128.2, 125.4, 123.5, 122.2, 109.6, 106.3, 46.4, 45.2, 41.6, 40.4, 26.7, 26.6, 24.1, 22.2, 21.9, 18.2.

ESIHRMS: *m/z* Calcd. For $C_{13}H_{15}NO_3$: $(M+Na)^+$ 256.0944. Found: 256.0939.

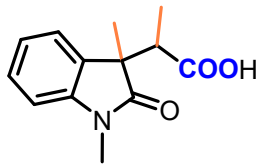


2-(3-benzyl-1-methyl-2-oxoindolin-3-yl)acetic acid (2k): Prepared according to general procedure using 2-benzyl-*N*-methyl-*N*-phenylacrylamide (0.2 mmol, 50.3 mg, 1.0 equiv). After 18 hours, the product was purified by flash column chromatography (5% AcOH in petroleum ether/ EtOAc 1/5 ~ 1/2 as the eluent) and obtained as white solid (35.4 mg, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (td, J = 7.6, 1.6 Hz, 1H), 7.11 – 7.05 (m, 2H), 7.05 – 6.99 (m, 3H), 6.77 – 6.72 (m, 2H), 6.57 (d, J = 7.6 Hz, 1H), 3.13 (d, J = 16.8 Hz, 1H), 3.07 – 3.02 (m, 2H), 2.95 (s, 3H), 2.89 (d, J = 16.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 179.1, 173.7, 143.8, 143.4, 134.6, 130.0, 128.6, 127.7, 126.9, 123.3, 122.5, 108.2, 51.2, 43.8, 40.3, 26.2.

ESIHRMS: *m/z* Calcd. For $C_{18}H_{17}NO_3$: $(M+Na)^+$ 318.1101. Found: 318.1097.



2-(1,3-dimethyl-2-oxoindolin-3-yl)propanoic acid (2l): Prepared according to general procedure using (*E*)-*N*,2-dimethyl-*N*-phenylbut-2-enamide (0.2 mmol, 37.9 mg, 1.0 equiv). After 48 hours, the product was purified by flash column chromatography (5% AcOH in petroleum ether/ EtOAc 1/5 ~ 1/2 as the eluent) and obtained as white solid (15.5 + 9.4 = 24.9 mg, 53% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.40 (m, 1H), 7.30 (td, J = 7.6, 1.2 Hz, 1H), 7.08 (td, J = 7.6, 1.2 Hz, 1H), 6.86 (d, J = 7.6 Hz, 1H), 3.23 (s, 3H), 3.10 (q, J = 7.2 Hz, 1H), 1.47 (s, 3H), 1.01 (d, J = 7.2 Hz, 3H).

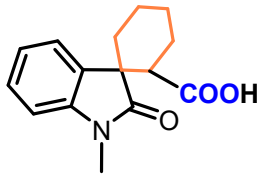
^{13}C NMR (100 MHz, $CDCl_3$) δ 179.6, 179.5, 143.5, 131.4, 128.4, 124.7, 122.8, 108.2, 49.5, 45.8, 26.5, 22.3, 13.1.

ESIHRMS: *m/z* Calcd. For $C_{13}H_{15}NO_3$: $(M+Na)^+$ 256.0944. Found: 256.0945.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (ddd, J = 8.0, 6.8, 2.0 Hz, 1H), 7.23 – 7.16 (m, 2H), 6.95 (d, J = 8.0 Hz, 1H), 3.32 (s, 3H), 3.12 (q, J = 7.2 Hz, 1H), 1.55 (s, 3H), 0.97 (d, J = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 182.0, 174.7, 142.6, 132.4, 128.9, 124.4, 122.4, 109.2, 49.8, 48.6, 26.8, 22.8, 13.6.

ESIHRMS: *m/z* Calcd. For $C_{13}H_{15}NO_3$: $(M+Na)^+$ 234.1125. Found: 234.1126.



1'-methyl-2'-oxospiro[cyclohexane-1,3'-indoline]-2-carboxylic acid (2m): Prepared according to general procedure using *N*-methyl-*N*-phenylcyclohex-1-ene-1-carboxamide (0.2 mmol, 43.1 mg, 1.0 equiv). After 48 hours, the product was purified by flash column chromatography (5% AcOH in petroleum ether/ EtOAc 1/5 ~ 1/2 as the eluent) and obtained as pale yellow solid (19.4 + 12.0 =31.4 mg, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, J = 7.6, 0.8 Hz, 1H), 7.27 (td, J = 7.6, 1.2 Hz, 1H), 6.98 (td, J = 7.6, 1.2 Hz, 1H), 6.82 (dd, J = 7.6, 0.8 Hz, 1H), 3.15 (s, 3H), 3.00 (dd, J = 13.2, 4.4 Hz, 1H), 2.15 – 2.10 (m, 1H), 2.03 – 1.89 (m, 2H), 1.88 – 1.78 (m, 1H), 1.74 – 1.59 (m, 2H), 1.53 – 1.40 (m, 2H).

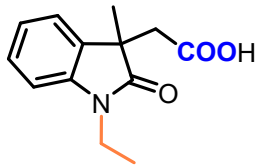
^{13}C NMR (100 MHz, $CDCl_3$) δ 180.3, 177.2, 143.7, 131.7, 128.0, 124.7, 121.9, 108.4, 49.7, 46.3, 35.0, 26.6, 24.6, 24.0, 20.7.

ESIHRMS: *m/z* Calcd. For $C_{15}H_{17}NO_3$: $(M+Na)^+$ 282.1101. Found: 282.1098.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (td, J = 7.6, 1.4 Hz, 1H), 7.07 – 6.97 (m, 2H), 6.76 (d, J = 7.6 Hz, 1H), 3.13 (s, 3H), 2.84 (dd, J = 12.8, 3.6 Hz, 1H), 2.48 (qd, J = 13.6, 13.2, 4.2 Hz, 1H), 2.23 – 2.12 (m, 1H), 2.02 – 1.91 (m, 2H), 1.70 – 1.60 (m, 2H), 1.55 (dt, J = 13.2, 3.2 Hz, 1H), 1.43 (qt, J = 14.4, 4.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 178.9, 178.3, 143.5, 133.8, 128.0, 122.3, 121.4, 108.0, 50.0, 46.9, 35.7, 26.2, 25.6, 24.9, 19.9.

ESIHRMS: *m/z* Calcd. For $C_{15}H_{17}NO_3$: $(M+H)^+$ 260.1281. Found: 260.1288.

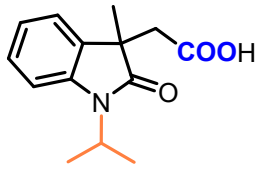


2-(1-ethyl-3-methyl-2-oxoindolin-3-yl)acetic acid (2n): Prepared according to general procedure using *N*-ethyl-*N*-phenylmethacrylamide (0.2 mmol, 37.9 mg, 1.0 equiv). After 18 hours, the product was purified by flash column chromatography (5% AcOH in petroleum ether/ EtOAc 1/5 ~ 1/2 as the eluent) and obtained as white solid (23.3 mg, 50% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.24 (m, 1H), 7.20 – 7.16 (m, 1H), 7.07 – 7.01 (m, 1H), 6.87 – 6.83 (m, 1H), 3.84 (dq, J = 14.4, 7.2 Hz, 1H), 3.67 (dq, J = 14.4, 7.2 Hz, 1H), 2.99 (d, J = 16.4 Hz, 1H), 2.79 (d, J = 16.4 Hz, 1H), 1.35 (s, 3H), 1.21 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 180.0, 174.4, 142.4, 133.1, 128.3, 122.6, 122.5, 108.7, 45.3, 41.4, 34.9, 24.2, 12.2.

ESIHRMS: *m/z* Calcd. For $C_{13}H_{15}NO_3$: $(M+Na)^+$ 256.0944. Found: 256.0934.

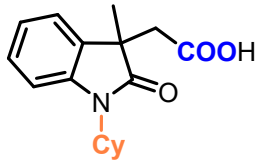


2-(1-isopropyl-3-methyl-2-oxoindolin-3-yl)acetic acid (2o): Prepared according to general procedure using *N*-isopropyl-*N*-phenylmethacrylamide (0.2 mmol, 40.7 mg, 1.0 equiv). After 12 hours, the product was purified by flash column chromatography (5% AcOH in petroleum ether/ EtOAc 1/5 ~ 1/2 as the eluent) and obtained as white solid (27.7 mg, 56% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (t, J = 8.0 Hz, 1H), 7.16 (d, J = 7.2 Hz, 1H), 7.05 – 6.98 (m, 2H), 4.61 (p, J = 6.8 Hz, 1H), 2.99 (d, J = 16.4 Hz, 1H), 2.77 (d, J = 16.4 Hz, 1H), 1.44 (dd, J = 10.8, 7.2 Hz, 6H), 1.33 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 180.1, 174.5, 142.0, 133.4, 128.1, 122.5, 122.3, 110.3, 45.1, 44.0, 41.6, 24.4, 19.4, 19.0.

ESIHRMS: *m/z* Calcd. For $C_{14}H_{17}NO_3$: $(M+Na)^+$ 270.1101. Found: 270.1096.

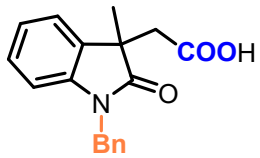


2-(1-cyclohexyl-3-methyl-2-oxoindolin-3-yl)acetic acid (2p): Prepared according to general procedure using *N*-cyclohexyl-*N*-phenylmethacrylamide (0.2 mmol, 48.7 mg, 1.0 equiv). After 24 hours, the product was purified by flash column chromatography (5% AcOH in petroleum ether/ EtOAc 1/5 ~ 1/2 as the eluent) and obtained as brown solid (35.1 mg, 61% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (td, J = 7.6, 1.2 Hz, 1H), 7.17 – 7.13 (m, 1H), 7.07 – 6.98 (m, 2H), 4.14 (t, J = 12.4 Hz, 1H), 2.98 (d, J = 16.8 Hz, 1H), 2.76 (d, J = 16.8 Hz, 1H), 2.18 – 2.01 (m, 2H), 1.88 (d, J = 13.2 Hz, 2H), 1.72 (d, J = 10.4 Hz, 2H), 1.45 – 1.37 (m, 2H), 1.33 (s, 3H), 1.30 – 1.20 (m, 2H).

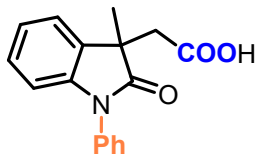
^{13}C NMR (100 MHz, $CDCl_3$) δ 180.3, 174.6, 142.4, 133.3, 128.0, 122.5, 122.2, 110.4, 52.4, 45.0, 41.6, 29.1, 28.7, 26.3, 26.1, 25.5, 24.5.

ESIHRMS: *m/z* Calcd. For $C_{17}H_{15}NO_3$: $(M+Na)^+$ 310.1414. Found: 310.1409.

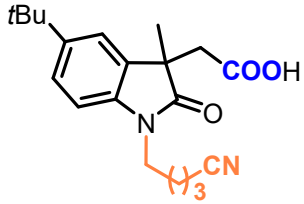


2-(1-benzyl-3-methyl-2-oxoindolin-3-yl)acetic acid (2q): Prepared according to general procedure using *N*-benzyl-*N*-phenylmethacrylamide (0.2 mmol, 50.3 mg, 1.0 equiv). After 18 hours, the product was purified by flash column chromatography (5% AcOH in petroleum ether/ EtOAc 1/5 ~ 1/2 as the eluent) and obtained as white solid (25.4 mg, 43% yield).

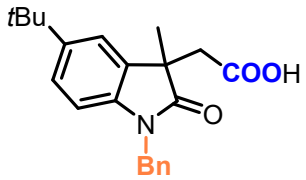
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 4H), 7.26 – 7.23 (m, 1H), 7.21 – 7.18 (m, 1H), 7.14 (td, J = 7.6, 1.2 Hz, 1H), 7.01 (td, J = 7.6, 1.2 Hz, 1H), 6.69 (d, J = 7.6 Hz, 1H), 5.00 (d, J = 15.6 Hz, 1H), 4.86 (d, J = 15.6 Hz, 1H), 3.11 (d, J = 16.8 Hz, 1H), 2.90 (d, J = 16.8 Hz, 1H), 1.44 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 180.4, 174.6, 142.4, 135.8, 132.8, 128.9, 128.3, 127.7, 127.3, 122.9, 122.3, 109.7, 45.5, 44.1, 41.2, 25.0.
ESIHRMS: *m/z* Calcd. For $C_{18}H_{17}NO_3$: $(M+Na)^+$ 318.1101. Found: 318.1102.



2-(3-methyl-2-oxo-1-phenylindolin-3-yl)acetic acid (2r): Prepared according to general procedure using *N*,*N*-diphenylmethacrylamide (0.2 mmol, 47.5 mg, 1.0 equiv). After 48 hours, the product was purified by flash column chromatography (5% AcOH in petroleum ether/ EtOAc 1/5 ~ 1/2 as the eluent) and obtained as white solid (29.3 mg, 52% yield).
^{1}H NMR (400 MHz, CD_3OD) δ 7.56 (t, J = 8.0 Hz, 2H), 7.46 (t, J = 8.0 Hz, 3H), 7.36 (d, J = 7.6 Hz, 1H), 7.20 (t, J = 7.6 Hz, 1H), 7.09 (t, J = 7.6 Hz, 1H), 6.71 (d, J = 7.6 Hz, 1H), 3.06 (d, J = 3.2 Hz, 2H), 1.44 (s, 3H).
^{13}C NMR (100 MHz, CD_3OD) δ 182.4, 173.3, 145.2, 136.3, 134.5, 130.7, 129.4, 129.1, 128.2, 124.2, 123.6, 110.5, 47.0, 42.6, 25.1.
ESIHRMS: *m/z* Calcd. For $C_{17}H_{15}NO_3$: $(M+Na)^+$ 304.0944. Found: 304.0940.



2-(5-(*tert*-butyl)-1-(4-cyanobutyl)-3-methyl-2-oxoindolin-3-yl)acetic acid (2s): Prepared according to general procedure using *N*-(4-(*tert*-butyl)phenyl)-*N*-(4-cyanobutyl)methacrylamide (0.2 mmol, 59.7 mg, 1.0 equiv). After 48 hours, the product was purified by flash column chromatography (5% AcOH in petroleum ether/ EtOAc 1/5 ~ 1/2 as the eluent) and obtained as white solid (47.9 mg, 70% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, J = 7.6 Hz, 1H), 7.21 (s, 1H), 6.77 (d, J = 8.0 Hz, 1H), 3.83 (dt, J = 13.6, 6.8 Hz, 1H), 3.65 (dt, J = 13.6, 6.4 Hz, 1H), 3.00 (d, J = 16.8 Hz, 1H), 2.84 (d, J = 16.8 Hz, 1H), 2.38 (q, J = 7.2 Hz, 2H), 1.84 (p, J = 6.8 Hz, 2H), 1.69 (p, J = 6.8 Hz, 2H), 1.34 (s, 3H), 1.30 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 180.6, 174.6, 146.2, 139.8, 132.6, 125.0, 119.7, 119.6, 107.9, 45.5, 41.2, 38.9, 34.7, 31.7, 26.4, 24.8, 22.5, 16.7.
ESIHRMS: *m/z* Calcd. For $C_{20}H_{26}N_2O_3$: $(M+Na)^+$ 365.1836. Found: 365.1826.

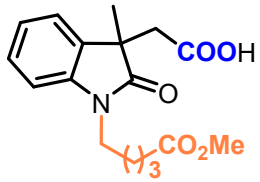


2-(1-benzyl-5-(*tert*-butyl)-3-methyl-2-oxoindolin-3-yl)acetic acid (2t): Prepared according to general procedure using *N*-benzyl-*N*-(4-(*tert*-butyl)phenyl)methacrylamide (0.2 mmol, 61.5 mg, 1.0 equiv). After 12 hours, the product was purified by flash column chromatography (5% AcOH in petroleum ether/ EtOAc 1/5 ~ 1/2 as the eluent) and obtained as white solid (44.8 mg, 64% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 4.7 Hz, 4H), 7.27 – 7.25 (m, 1H), 7.23 (d, J = 2.0 Hz, 1H), 7.18 (dd, J = 8.2, 2.0 Hz, 1H), 6.66 (d, J = 8.0 Hz, 1H), 4.92 (q, J = 15.6 Hz, 2H), 3.07 (d, J = 16.4 Hz, 1H), 2.87 (d, J = 16.4 Hz, 1H), 1.49 (s, 3H), 1.26 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 181.1, 173.2, 146.5, 139.6, 135.8, 132.5, 128.9, 127.8, 127.5, 125.1, 119.6, 109.2, 45.6, 44.2, 41.6, 34.7, 31.7, 24.5.

ESIHRMS: *m/z* Calcd. For $C_{22}H_{25}NO_3$: $(M+Na)^+$ 374.1727. Found: 374.1736.

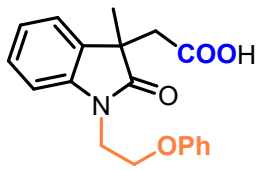


2-(1-(5-methoxy-5-oxopentyl)-3-methyl-2-oxoindolin-3-yl)acetic acid (2u): Prepared according to general procedure using methyl 5-(*N*-phenylmethacrylamido)pentanoate (0.2 mmol, 55.1 mg, 1.0 equiv). After 48 hours, the product was purified by flash column chromatography (5% AcOH in petroleum ether/ EtOAc 1/5 ~ 1/2 as the eluent) and obtained as white solid (29.4 mg, 46% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (td, J = 7.6, 0.8 Hz, 1H), 7.18 (d, J = 7.2 Hz, 1H), 7.04 (t, J = 7.6 Hz, 1H), 6.85 (d, J = 7.6 Hz, 1H), 3.83 – 3.75 (m, 1H), 3.70 – 3.67 (m, 1H), 3.65 (s, 3H), 2.99 (d, J = 16.4 Hz, 1H), 2.80 (d, J = 16.4 Hz, 1H), 2.34 (t, J = 6.8 Hz, 2H), 1.68 (t, J = 3.2 Hz, 4H), 1.36 (s, 3H).

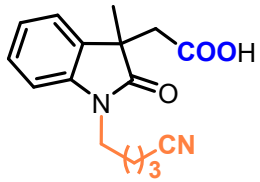
^{13}C NMR (100 MHz, $CDCl_3$) δ 180.3, 174.1, 173.9, 142.6, 133.0, 128.4, 122.7, 122.6, 108.7, 51.8, 45.4, 41.4, 39.7, 33.6, 26.7, 24.4, 22.2.

ESIHRMS: *m/z* Calcd. For $C_{17}H_{21}NO_5$: $(M+Na)^+$ 342.1312. Found: 342.1303.



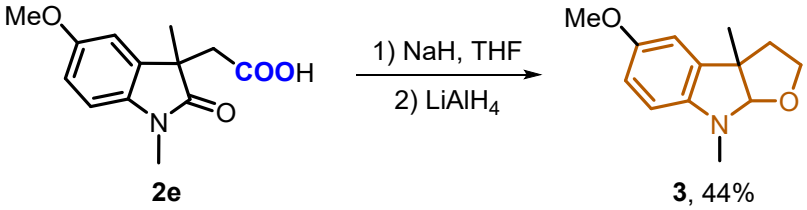
2-(3-methyl-2-oxo-1-(2-phenoxybutyl)indolin-3-yl)acetic acid (2v): Prepared according to general procedure using methyl *N*-(2-phenoxyethyl)-*N*-phenylmethacrylamide (0.2 mmol, 56.3 mg, 1.0 equiv). After 12 hours, the product was

purified by flash column chromatography (5% AcOH in petroleum ether/ EtOAc 1/5 ~ 1/2 as the eluent) and obtained as orange oil (31.8 mg, 49% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.22 (m, 3H), 7.15 (d, J = 7.2 Hz, 1H), 7.03 (dt, J = 7.2, 3.6 Hz, 2H), 6.93 (t, J = 7.2 Hz, 1H), 6.83 (d, J = 8.4 Hz, 2H), 4.19 – 4.05 (m, 4H), 2.98 (d, J = 16.8 Hz, 1H), 2.78 (d, J = 16.8 Hz, 1H), 1.34 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 180.7, 174.2, 158.4, 142.8, 132.7, 129.6, 128.4, 122.9, 122.4, 121.2, 114.6, 109.4, 64.9, 45.2, 41.5, 39.8, 24.2.
ESIHRMS: *m/z* Calcd. For $C_{19}H_{19}NO_4$: $(M+Na)^+$ 348.1206. Found: 348.1192.



2-(1-(4-cyanobutyl)-3-methyl-2-oxoindolin-3-yl)acetic acid (2w): Prepared according to general procedure using methyl *N*-(4-cyanobutyl)-*N*-phenylmethacrylamide (0.2 mmol, 48.5 mg, 1.0 equiv). After 18 hours, the product was purified by flash column chromatography (5% AcOH in petroleum ether/ EtOAc 1/5 ~ 1/2 as the eluent) and obtained as white solid (35.5 mg, 62% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (t, J = 7.6 Hz, 1H), 7.17 (d, J = 7.2 Hz, 1H), 7.05 (t, J = 7.6 Hz, 1H), 6.85 (d, J = 8.0 Hz, 1H), 3.86 (dt, J = 14.0, 7.2 Hz, 1H), 3.65 (dt, J = 14.0, 7.2 Hz, 1H), 3.02 (d, J = 16.8 Hz, 1H), 2.83 (d, J = 16.8 Hz, 1H), 2.44 – 2.30 (m, 2H), 1.83 (dt, J = 14.0, 6.8 Hz, 2H), 1.68 (dt, J = 14.0, 6.8 Hz, 2H), 1.33 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 180.3, 174.5, 142.4, 132.9, 128.4, 122.9, 122.5, 119.6, 108.6, 45.3, 41.1, 38.9, 26.3, 24.8, 22.5, 16.8.
ESIHRMS: *m/z* Calcd. For $C_{16}H_{18}N_2O_3$: $(M+Na)^+$ 309.1210. Found: 309.1209.

5. The Application of the Reaction

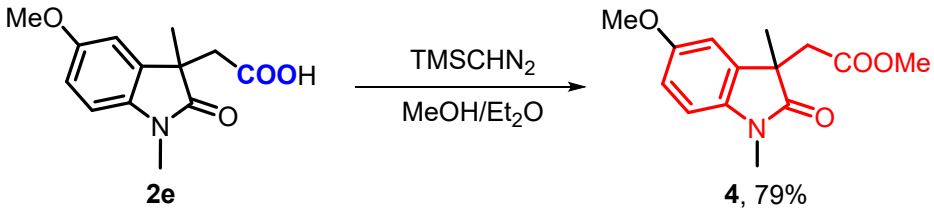


5-methoxy-3a,8-dimethyl-3,3a,8,8a-tetrahydro-2*H*-furo[2,3-*b*]indole (3): To a solution of **2e** (49.9 mg, 0.2 mmol) in THF (5 mL) was added NaH (20.0 mg, 0.5 mmol) at 0 °C under N_2 atmosphere. The reaction mixture was stirred at room temperature for 30 min, then $LiAlH_4$ (30.4 mg, 0.8 mmol) was added under N_2 atmosphere. The mixture was stirred at room temperature for 12 hours. After full conversion, the reaction was cooled to 0 °C and quenched with EtOAc. After filtration, the filtrate was concentrated in vacuo. The residue was purified by silica gel flash column chromatography (PE/EA = 10:1) to afford the product **3** as brown oil (19.1 mg, 44% yield).[8]

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.69 (d, J = 2.4 Hz, 1H), 6.66 (dd, J = 8.4, 2.4 Hz, 1H), 6.29 (d, J = 8.4 Hz, 1H), 5.03 (s, 1H), 3.94 (td, J = 8.0, 7.2, 1.6 Hz, 1H), 3.75 (s, 3H), 3.47 (ddd, J = 10.8, 8.8, 5.2 Hz, 1H), 2.88 (s, 3H), 2.13 (ddd, J = 12.0, 5.2, 1.6 Hz, 1H), 2.04 (td, J = 11.2, 7.2 Hz, 1H), 1.45 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 145.1, 136.1, 112.2, 110.6, 105.7, 105.4, 67.5, 56.2, 52.6, 41.6, 31.8, 24.6.

ESIHRMS: *m/z* Calcd. For $C_{13}H_{17}NO_2$: $(M+H)^+$ 220.1332. Found: 220.1332.

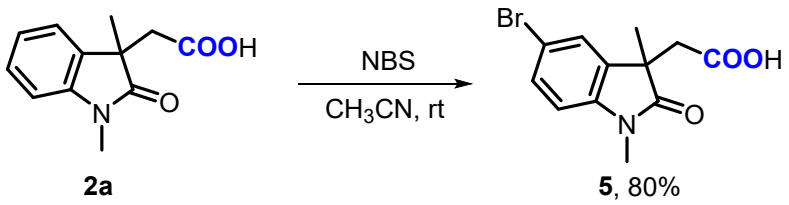


methyl 2-(5-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)acetate (4): To a solution of **2e** (49.9 mg, 0.2 mmol,) in 10 mL $MeOH/Et_2O$ (1:1, v:v) was added $TMSCHN_2$ solution in hexane (0.4 mL, 0.8 mmol, 2M hexane solution) at 0 °C. The reaction mixture was stirred for 4 hours at room temperature. The solvent was removed in vacuo and the residue was purified by flash column chromatography (PE/EA=10:1) to afford the ester product as a colorous oil (41.7 mg, 79% yield).[8]

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (dd, J = 2.4, 0.8 Hz, 1H), 6.81 – 6.75 (m, 2H), 3.79 (s, 3H), 3.48 (s, 3H), 3.24 (s, 3H), 3.00 (d, J = 16.4 Hz, 1H), 2.83 (d, J = 16.4 Hz, 1H), 1.37 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 179.6, 170.4, 155.9, 137.2, 134.4, 111.9, 110.2, 108.4, 55.8, 51.7, 45.9, 41.3, 26.6, 24.4.

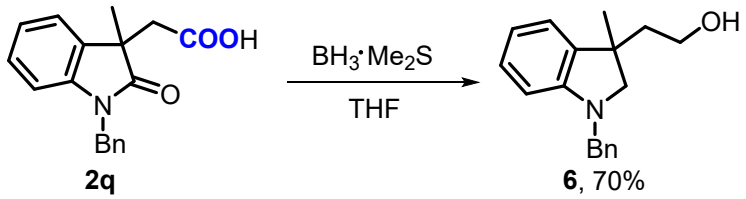
ESIHRMS: *m/z* Calcd. For $C_{14}H_{17}NO_4$: $(M+H)^+$ 264.1230. Found: 264.1236.



2-(5-bromo-1,3-dimethyl-2-oxoindolin-3-yl)acetic acid (5): To a solution of **2a** (43.8 mg, 0.2 mmol) in 4 mL CH_3CN was added NBS (0.26 mmol, 46.3 mg). The reaction was stirred at room temperature for 22 hours. The solvent was removed in vacuo and the residue was purified by flash column chromatography using petroleum/ethyl acetate (5:1) to afford the 5 as a white solid (47.7 mg, 80% yield).[8]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (dd, J = 8.4, 2.0 Hz, 1H), 7.30 (d, J = 2.0 Hz, 1H), 6.72 (d, J = 8.4 Hz, 1H), 3.18 (s, 3H), 3.00 (d, J = 16.8 Hz, 1H), 2.80 (d, J = 16.8 Hz, 1H), 1.34 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 179.7, 174.3, 142.6, 135.0, 131.2, 125.7, 115.4, 109.9, 45.6, 41.2, 26.7, 24.2.



2-(1-benzyl-3-methylindolin-3-yl)ethan-1-ol (6): To a solution of **2q** (59.1 mg, 0.2 mmol) in 2 mL anhydrous THF was added BH_3·Me_2S solution in THF (l mL, 2 mmol, 2M THF solution) under nitrogen atmosphere at 0 °C. The reaction was stirred at room temperature for 24 hours and quenched with 3 mL MeOH. The solvent was removed in vacuo and the residue was purified by flash column chromatography using petroleum/EtOAc (5:1, v:v) to afford indoline **6** as a colorous oil (39.4 mg, 70% yield).[8]

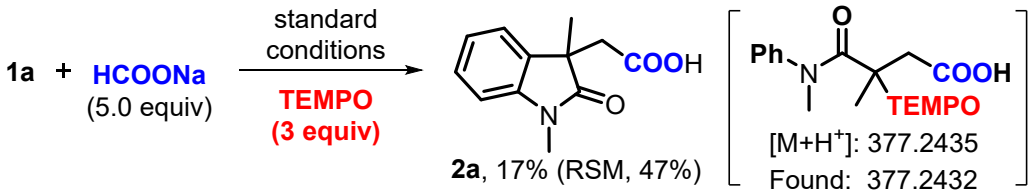
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 4H), 7.28 (ddd, J = 8.4, 3.2, 2.0 Hz, 1H), 7.11 (td, J = 7.4, 1.2 Hz, 1H), 7.01 (dd, J = 7.4, 1.2 Hz, 1H), 6.78 (td, J = 7.4, 1.2 Hz, 1H), 6.63 (d, J = 8.0 Hz, 1H), 4.43 (d, J = 14.4 Hz, 1H), 4.00 (d, J = 14.4 Hz, 1H), 3.53 (dt, J = 11.2, 5.6 Hz, 1H), 3.37 (ddd, J = 11.2, 8.4, 5.6 Hz, 1H), 3.30 (d, J = 8.8 Hz, 1H), 2.94 (d, J = 8.8 Hz, 1H), 1.92 (ddd, J = 14.4, 8.4, 6.0 Hz, 1H), 1.78 – 1.68 (m, 1H), 1.35 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.8, 137.9, 137.1, 128.8, 128.3, 128.0, 127.6, 122.6, 119.3, 108.6, 66.6, 60.5, 54.3, 44.6, 42.9, 26.9.

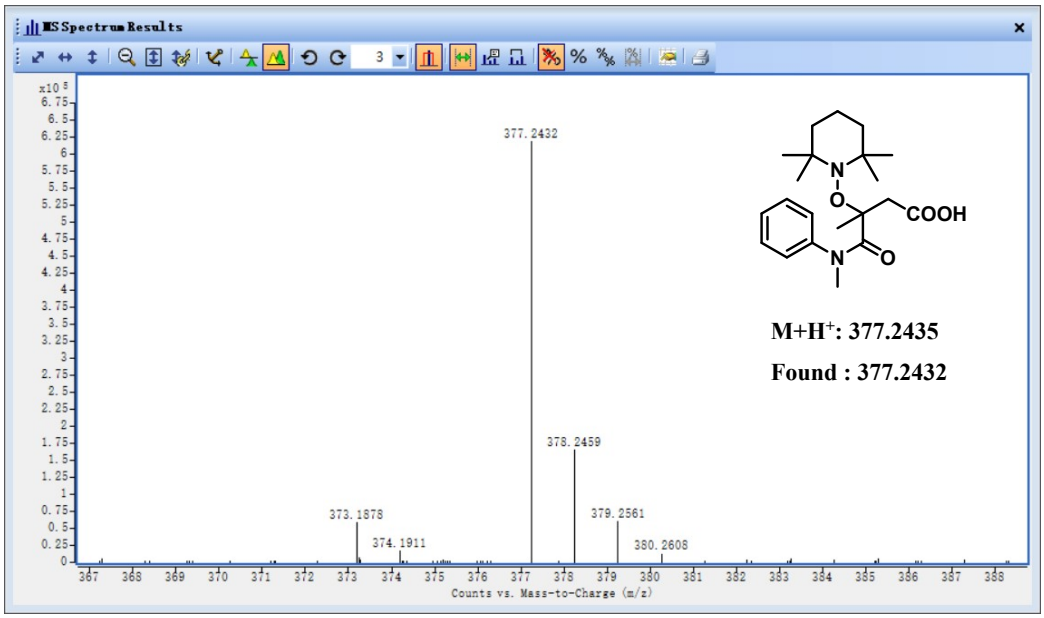
ESIHRMS: *m/z* Calcd. For $C_{18}H_{21}NO$: $(M+H)^+$ 268.1696. Found: 268.1697.

6. Control Experiments

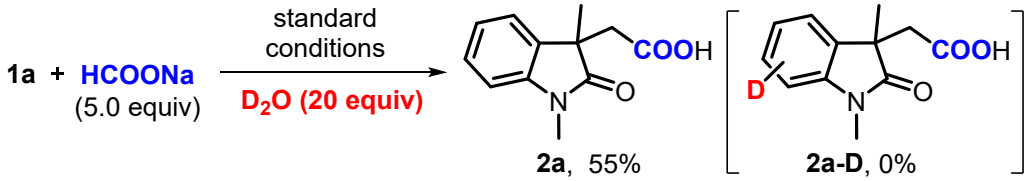
6.1 TEMPO Trapping Experiment



An oven-dried Schlenk tube (10 mL) containing a stirring bar was charged with *N*-methyl-*N*-phenylmethacrylamide (35.0 mg, 0.2 mmol, 1.0 equiv), HCOONa (60.8 mg, 1.0 mmol, 5.0 equiv), DABCO (11.2 mg, 0.1 mmol, 50 mol%), K_3PO_4 (42.5 mg, 0.2 mmol, 1.0 equiv) TEMPO (31.3 mg, 0.2 mmol, 1 equiv) and 4CzIPN (3.2 mg, 0.004 mmol, 2 mol%). Then anhydrous DMSO (2 mL) were added. Finally, the Schlenk tube was placed in an oil bath at the distance of 3 cm from a 45 W blue LED (wavelength: 450 nm) and stirred at 60 °C for 12 hours. After completion of the reaction, the reaction mixture was quenched with 2 mL of HCl (2 N), diluted with water (20 mL) and extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with water and brine before dried over sodium sulfate and concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (5% AcOH in petroleum ether/ EtOAc 1/5 ~ 1/2) to give the desired product 2a (7.5 mg, 17% yield) and 47% of starting material was recovered. **HRMS showed trapping of the reactive radical intermediate by TEMPO.**

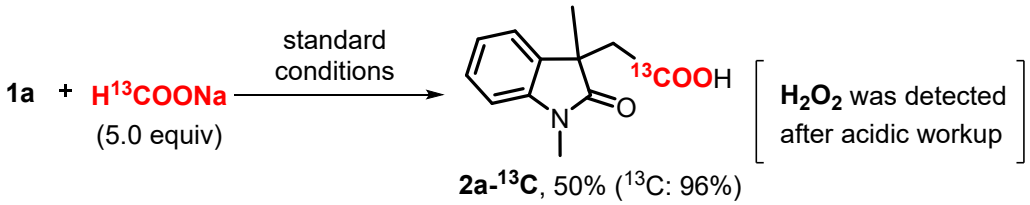


6.2 D-Labeling Experiment

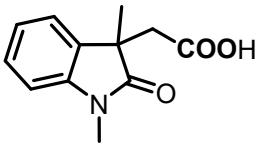


An oven-dried Schlenk tube (10 mL) containing a stirring bar was charged with *N*-methyl-*N*-phenylmethacrylamide (35.0 mg, 0.2 mmol, 1.0 equiv), HCOONa (60.8 mg, 1.0 mmol, 5.0 equiv), DABCO (11.2 mg, 0.1 mmol, 50 mol%), K_3PO_4 (42.5 mg, 0.2 mmol, 1.0 equiv) and 4CzIPN (3.2 mg, 0.004 mmol, 2 mol%). Then D_2O (4.0 mol, 20 equiv) and anhydrous DMSO (2 mL) were added. Finally, the Schlenk tube was placed in an oil bath at the distance of 3 cm from a 25 W blue LED (λ_{max}: 450 nm) and stirred at 60 °C for 12 hours. After completion of the reaction, the reaction mixture was quenched with 2 mL of HCl (2 N), diluted with water (30 mL) and extracted with EtOAc (3 x 30 mL). The combined organic layers were washed with water and brine before dried over sodium sulfate and concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (5% AcOH in petroleum ether/ EtOAc 1/5 ~ 1/2) to give the desired product **2a** (24.1 mg, 55% yield).

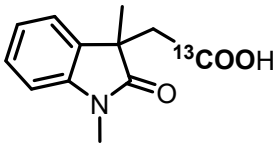
6.3 ^{13}C Isotope Labeling Experiment and Detection of H_2O_2



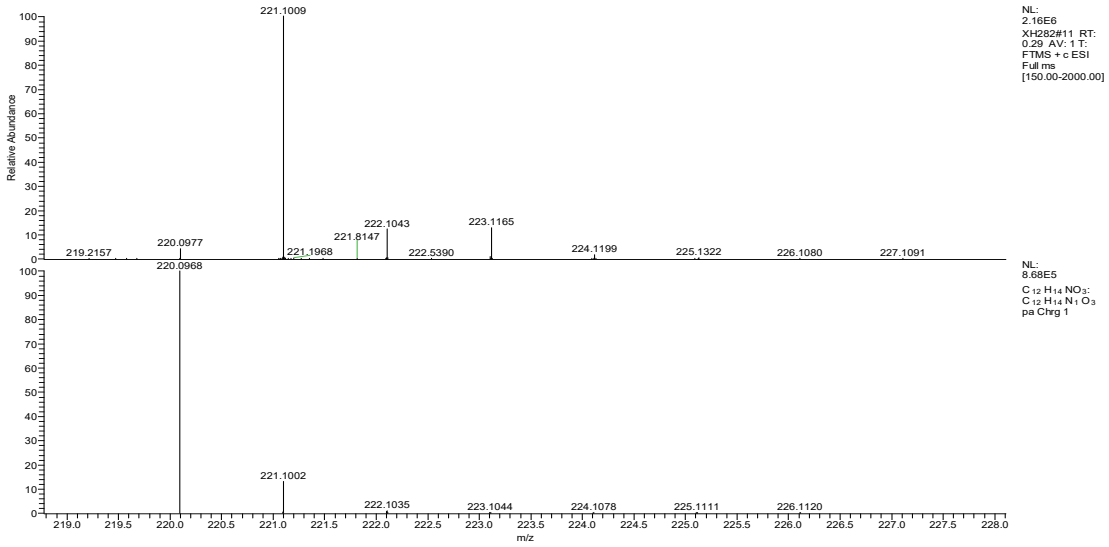
The experiment was conducted following the standard reaction condition but using **H^{13}COONa** instead of HCOONa. The products obtained in the reaction were detected by HRMS. The result showed **2a-^{13}C** in a ratio of 96%.



Chemical Formula: $C_{12}H_{13}NO_3$
calculated m/z:
219.0895 (100.0%),
220.0929 (13.0%)

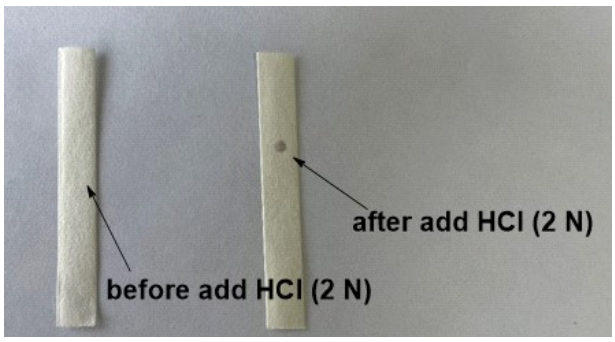


Chemical Formula: $C_{11}{}^{13}CH_{13}NO_3$
calculated m/z:
220.0929 (100.0%),
221.0963 (11.9%)



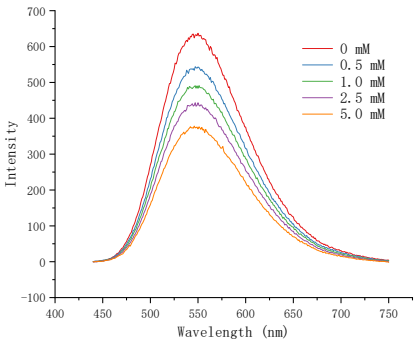
up: experimental data

When the reaction was completed, dipping the solution of the reaction mixture on the repotassium iodide-starch test paper showed no color change. After addition of HCl (2 N), dipping the solution of this reaction on the repotassium iodide-starch test paper showed the color changed to blue.

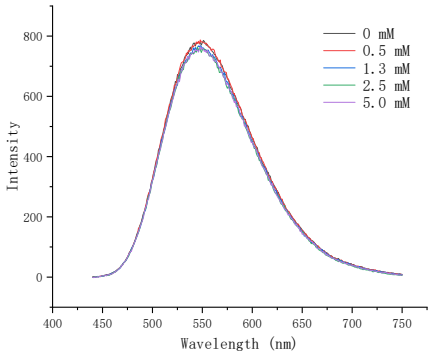


6.4 Stern-Volmer Fluorescence Quenching Analysis

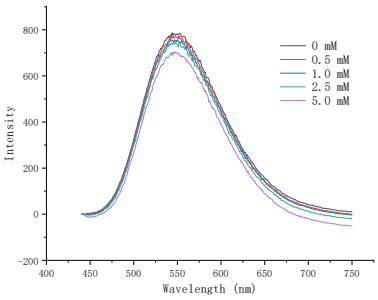
Stern-Volmer fluorescence quenching experiments were run with freshly prepared solution of 5×10^{-5} M 4CzIPN in degassed anhydrous DMSO at room temperature. The solution was irradiated at 440 nm and the fluorescence was measured from 440 nm to 750 nm. Data was collected on an Agilent Technologices F-4600 spectrofluorometer at 25 °C. Parameters: data interval = 1 nm, scan rate = 645 nm/min, Averaging time = 0.1 sec. The samples were measured in Jingke ES quartz cuvettes (chamber volume = 2.5 mL, H × W × D = 56 nm × 12.5 nm × 12.5 nm).



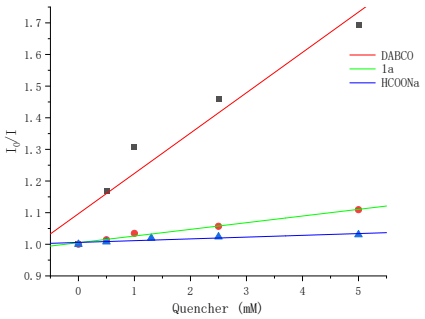
DABCO



HCOONa



Substrate 1a



Stern-Volmer Quenching

7. References

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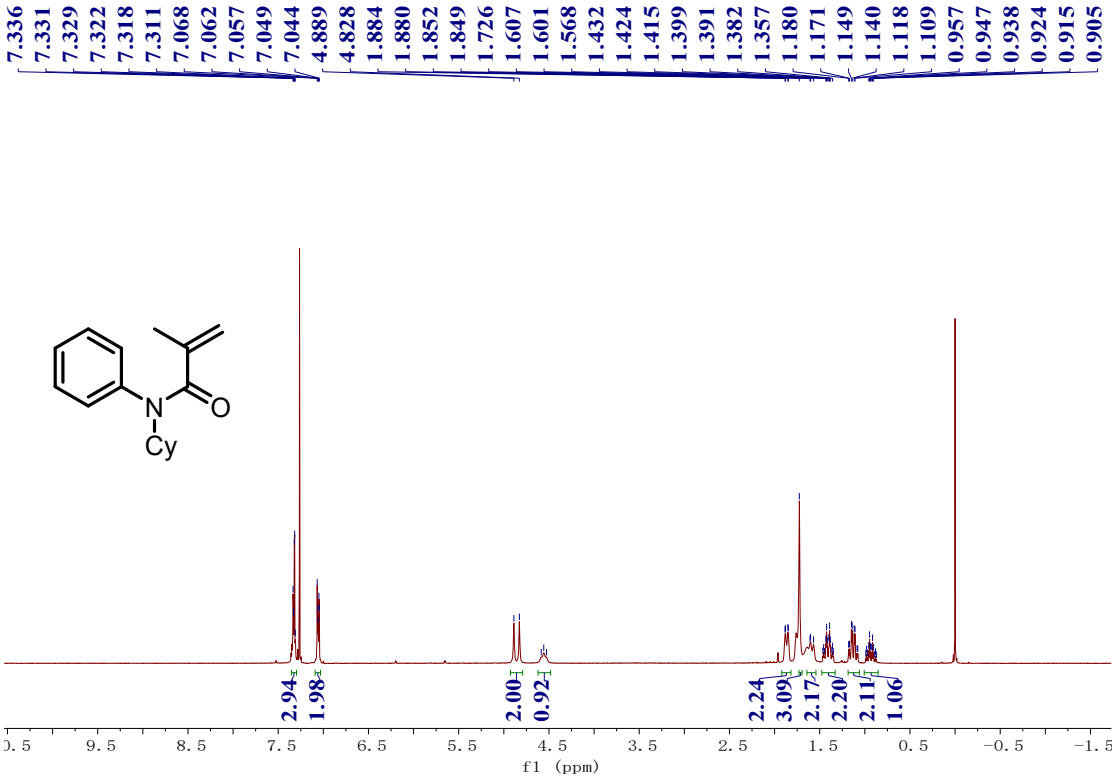
8. NMR Spectra

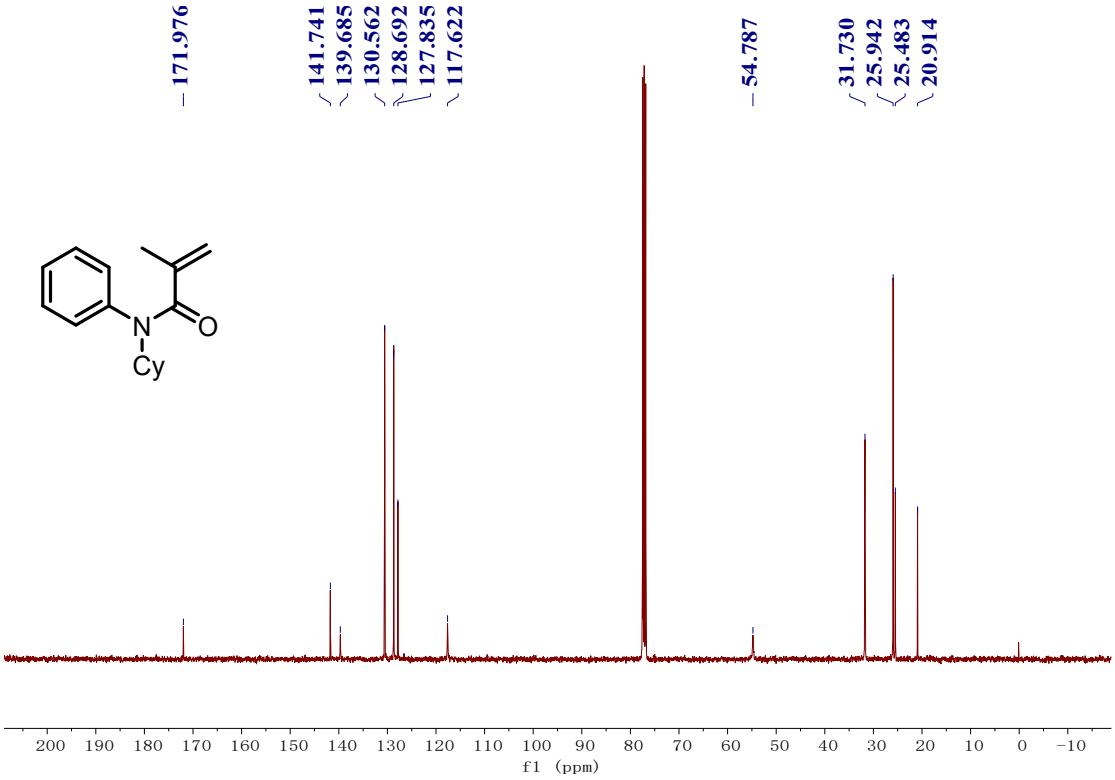
***N*-cyclohexyl-*N*-phenylmethacrylamide (1p)**

^{1}H NMR (400 MHz, $CDCl_3$)



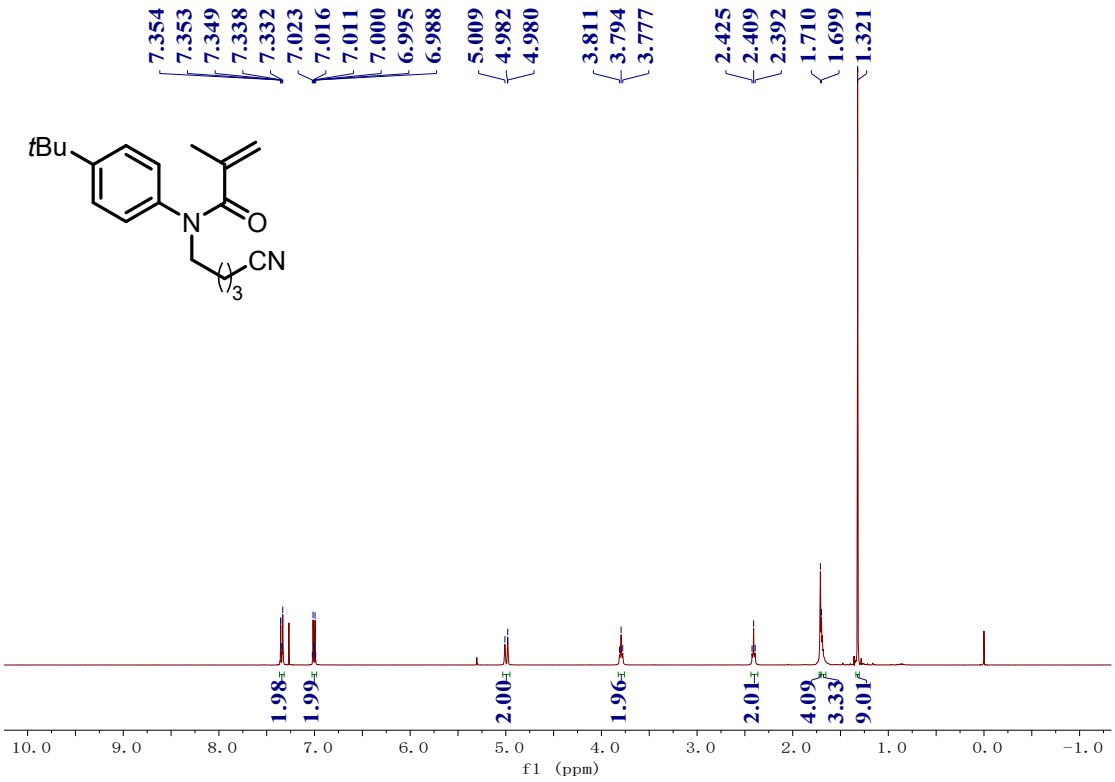
***N*-cyclohexyl-*N*-phenylmethacrylamide (1p)**

^{13}C NMR (100 MHz, $CDCl_3$)



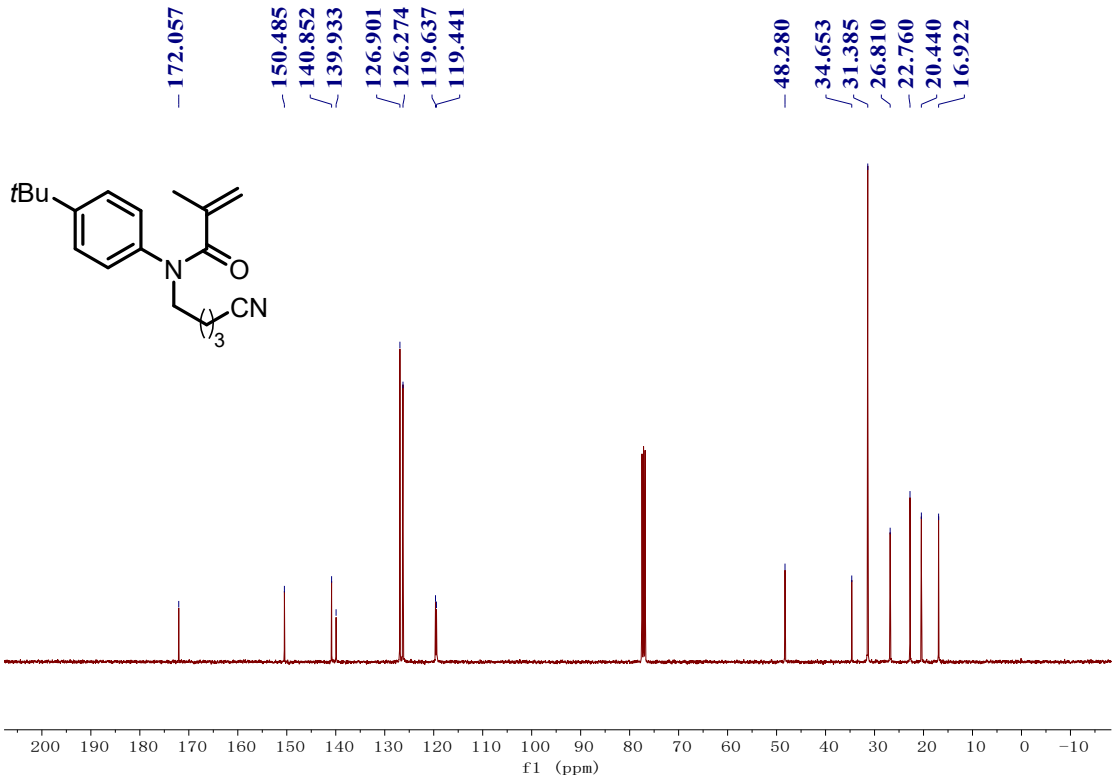
***N*-(4-(*tert*-butyl)phenyl)-*N*-(4-cyanobutyl)methacrylamide (1s)**

^{1}H NMR (400 MHz, $CDCl_3$)



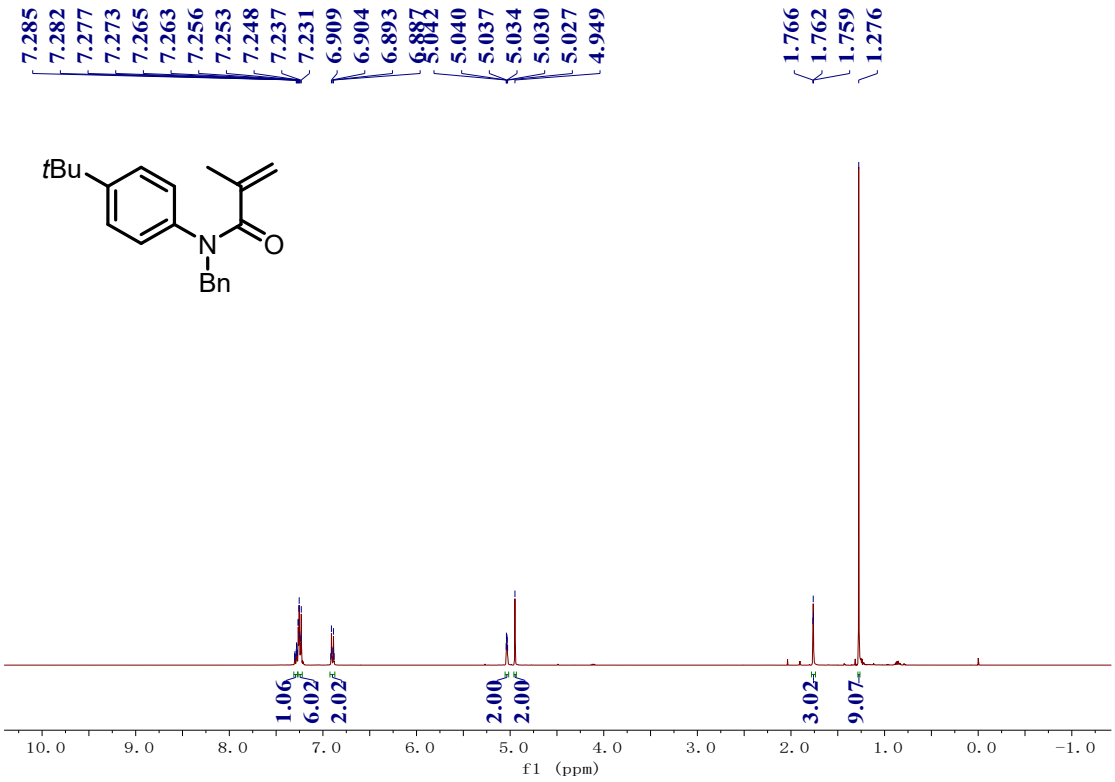
***N*-(4-(*tert*-butyl)phenyl)-*N*-(4-cyanobutyl)methacrylamide (1s)**

^{13}C NMR (100 MHz, $CDCl_3$)



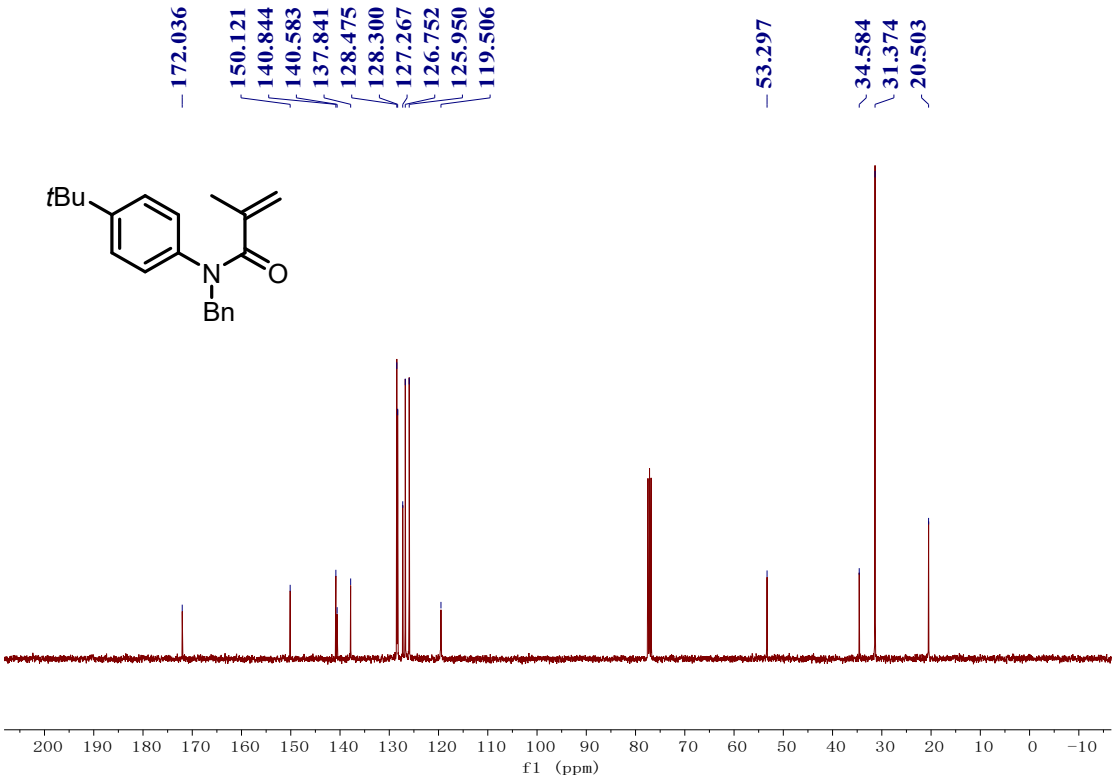
***N*-benzyl-*N*-(4-(*tert*-butyl)phenyl)methacrylamide (1t)**

^{1}H NMR (400 MHz, $CDCl_3$)



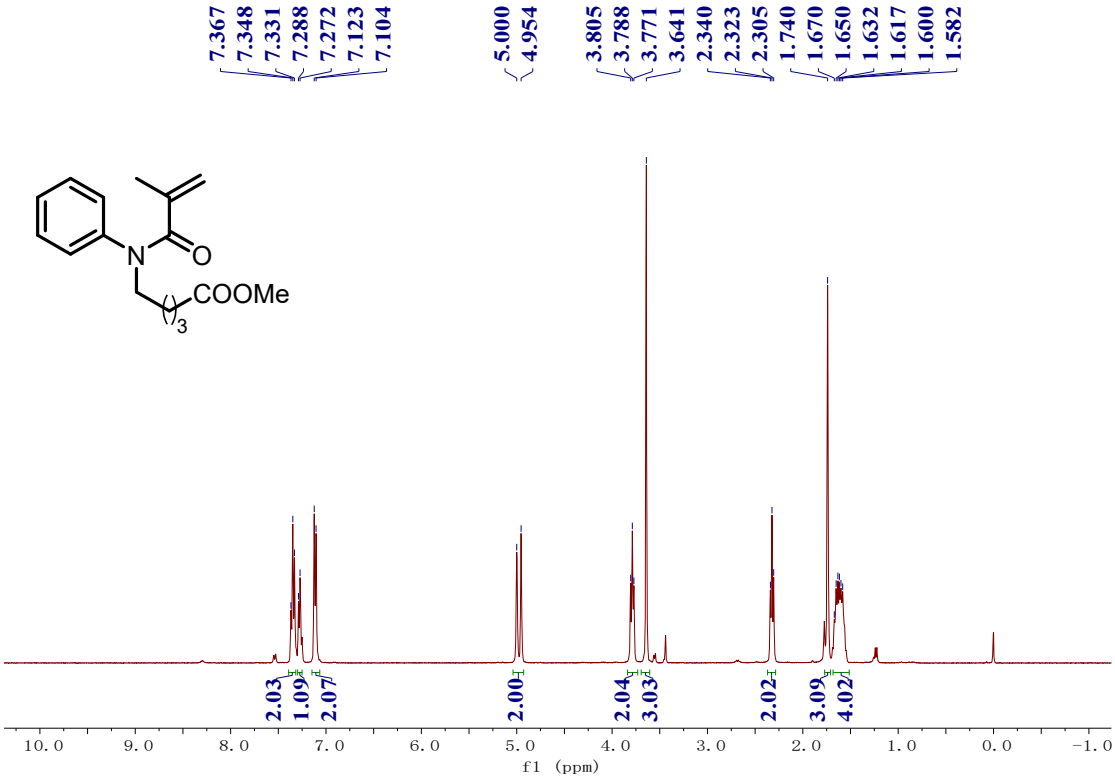
***N*-benzyl-*N*-(4-(*tert*-butyl)phenyl)methacrylamide (1t)**

^{13}C NMR (100 MHz, $CDCl_3$)



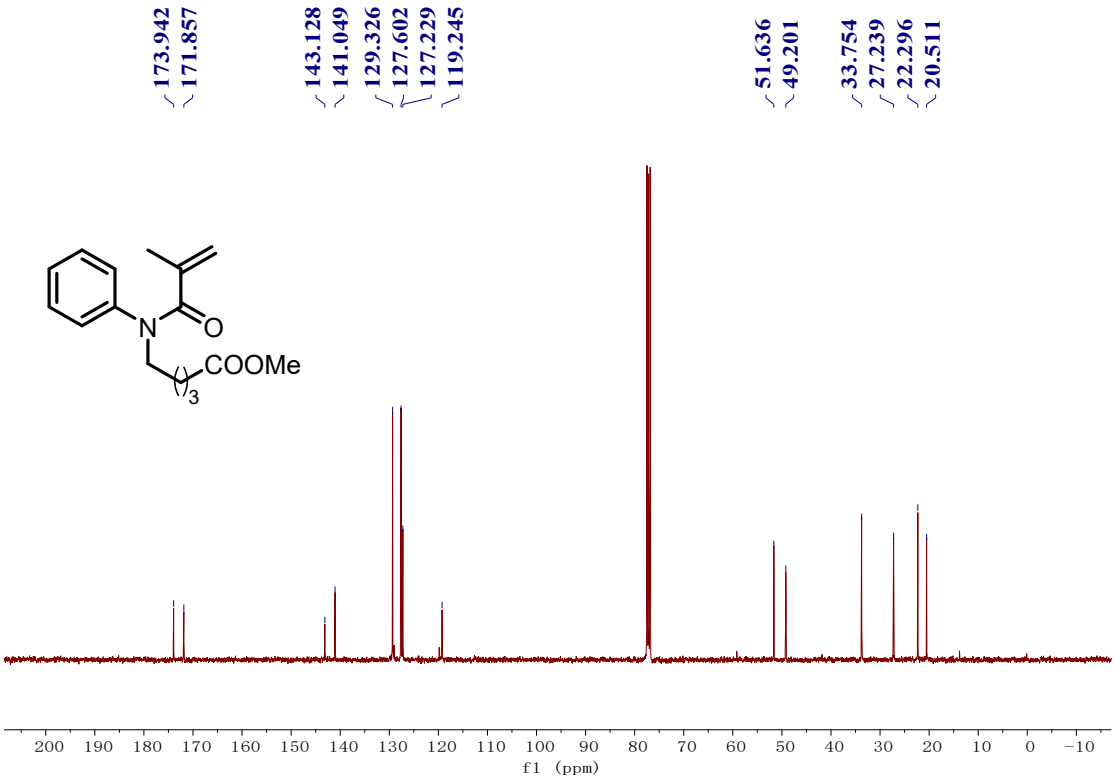
methyl 5-(*N*-phenylmethacrylamido)pentanoate (1u)

^{1}H NMR (400 MHz, $CDCl_3$)



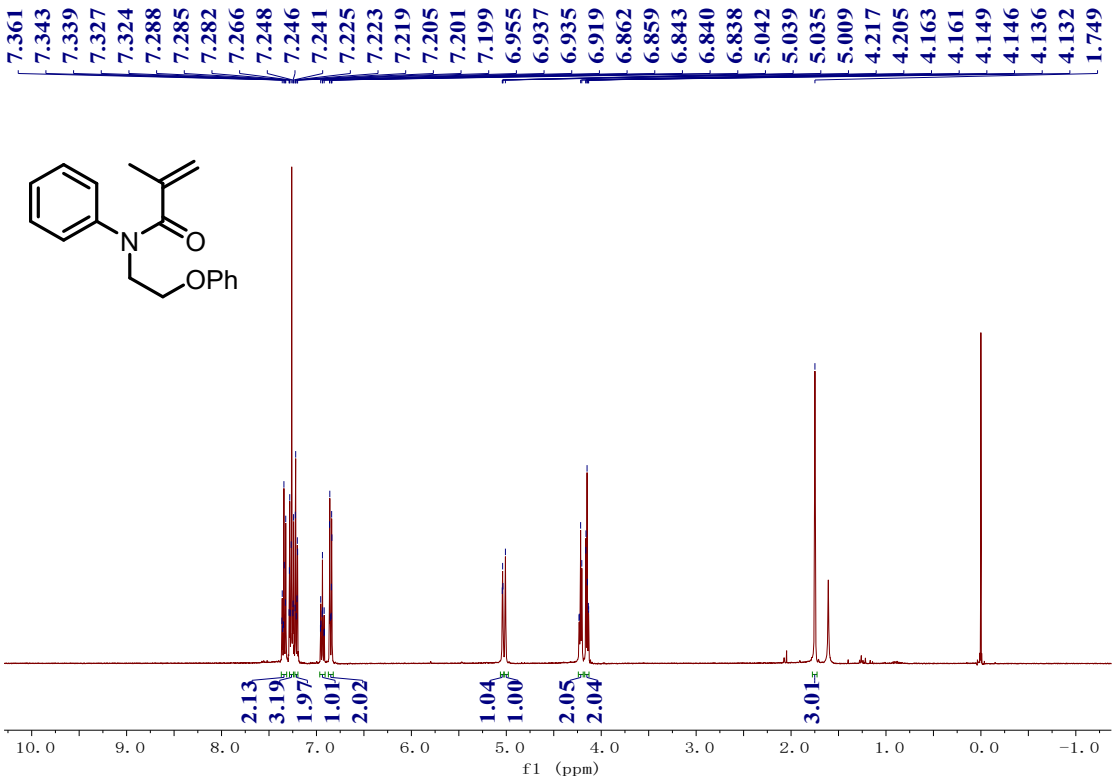
methyl 5-(*N*-phenylmethacrylamido)pentanoate (1u)

^{13}C NMR (100 MHz, $CDCl_3$)



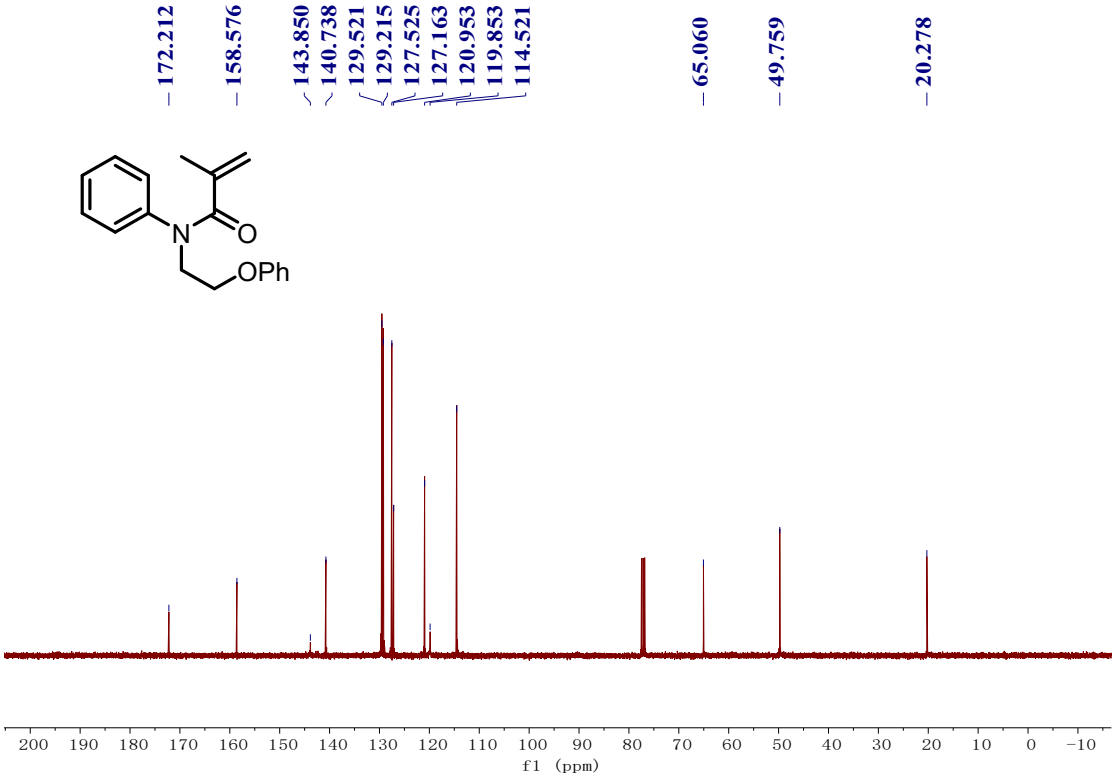
***N*-(2-phenoxyethyl)-*N*-phenylmethacrylamide (1v)**

^{1}H NMR (400 MHz, $CDCl_3$)



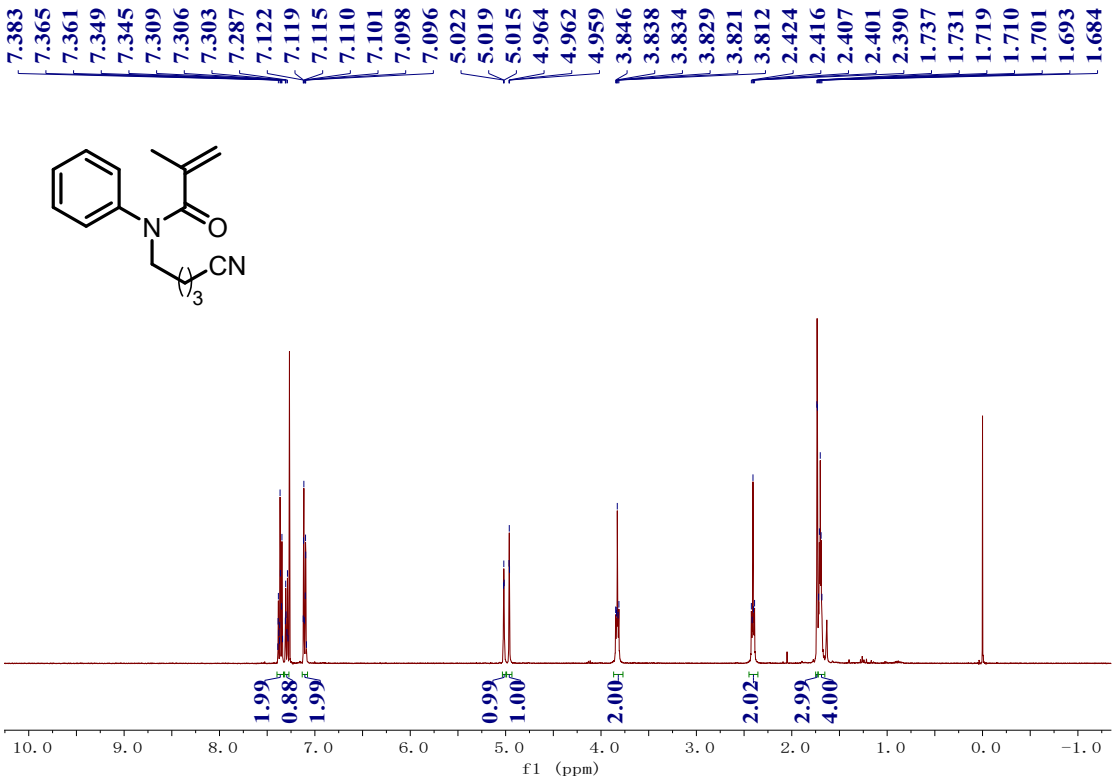
***N*-(2-phenoxyethyl)-*N*-phenylmethacrylamide (1v)**

^{13}C NMR (100 MHz, $CDCl_3$)



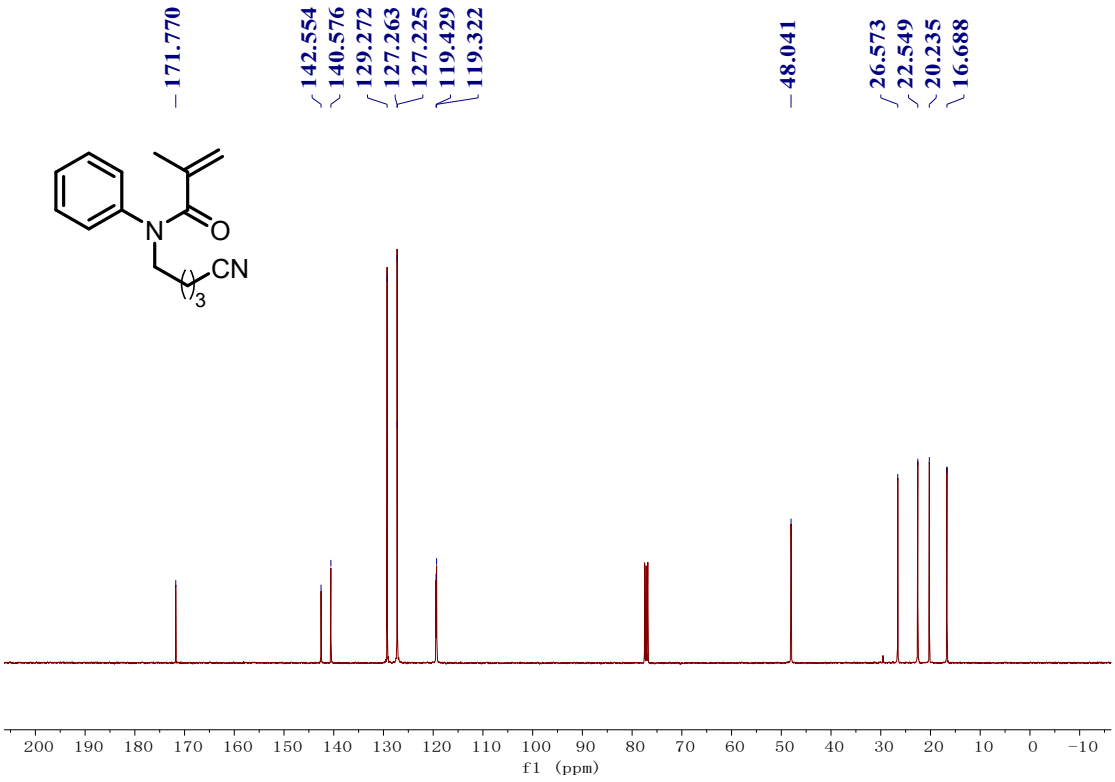
***N*-(4-cyanobutyl)-*N*-phenylmethacrylamide (1w)**

^{1}H NMR (400 MHz, $CDCl_3$)



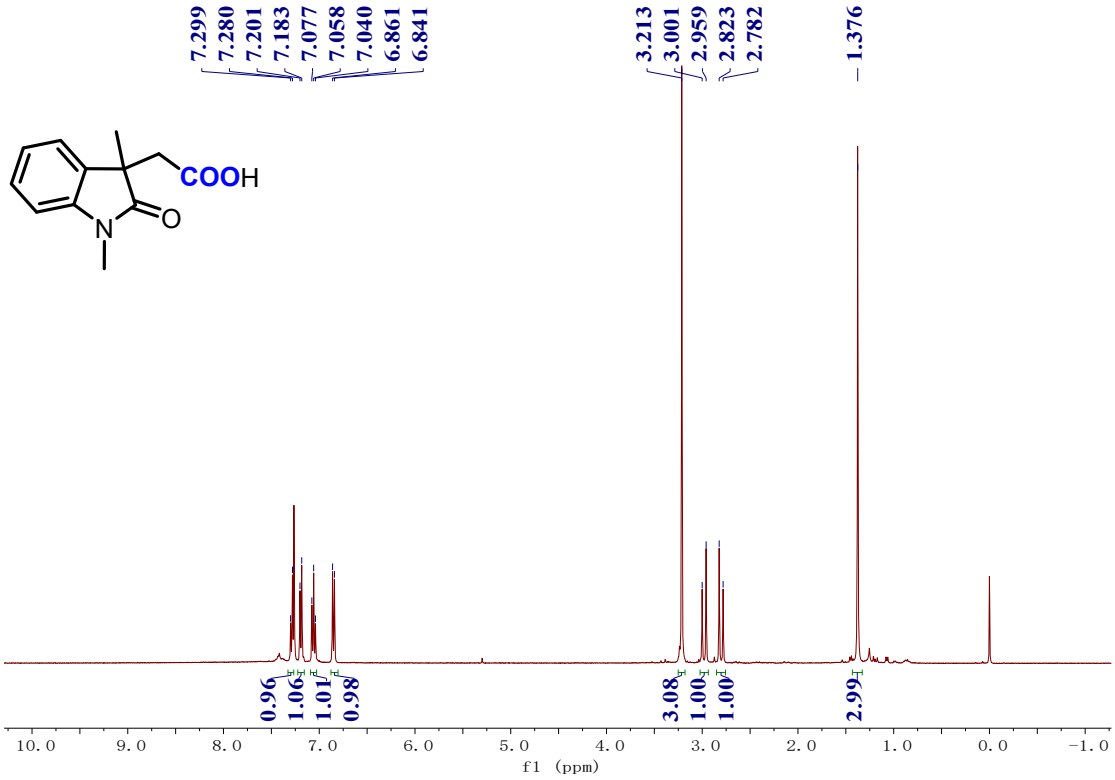
***N*-(4-cyanobutyl)-*N*-phenylmethacrylamide (1w)**

^{13}C NMR (100 MHz, $CDCl_3$)



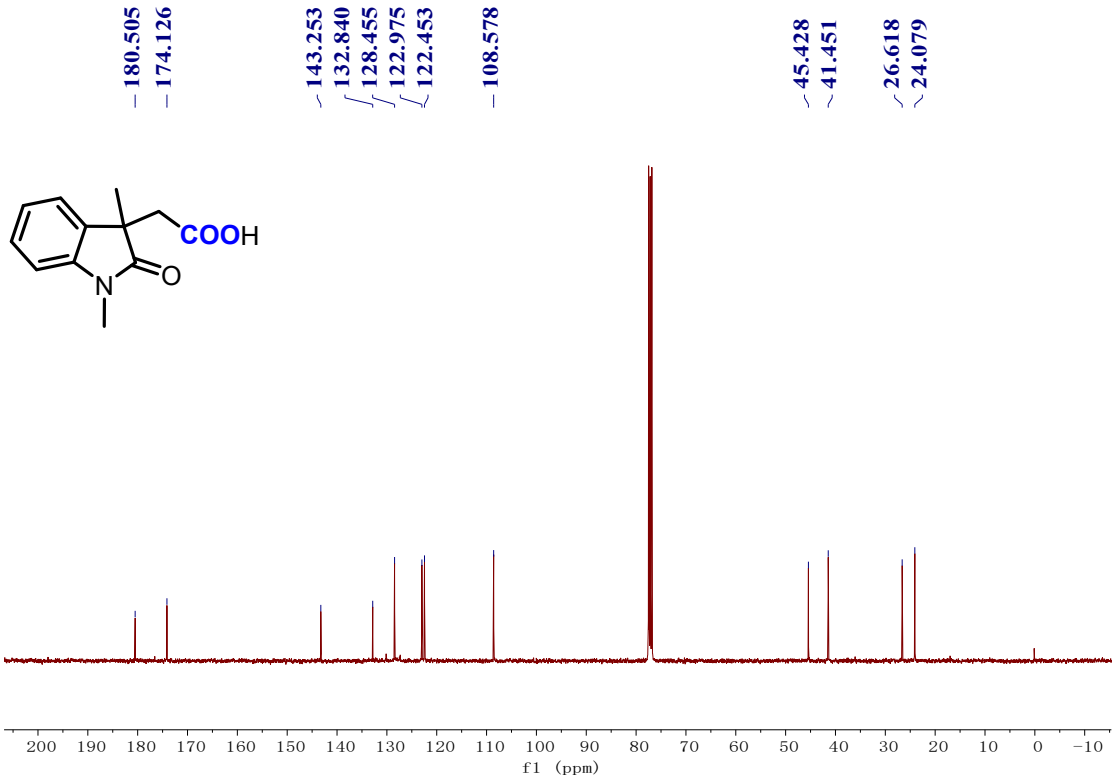
2-(1,3-dimethyl-2-oxoindolin-3-yl)acetic acid (2a)

^{1}H NMR (400 MHz, $CDCl_3$)



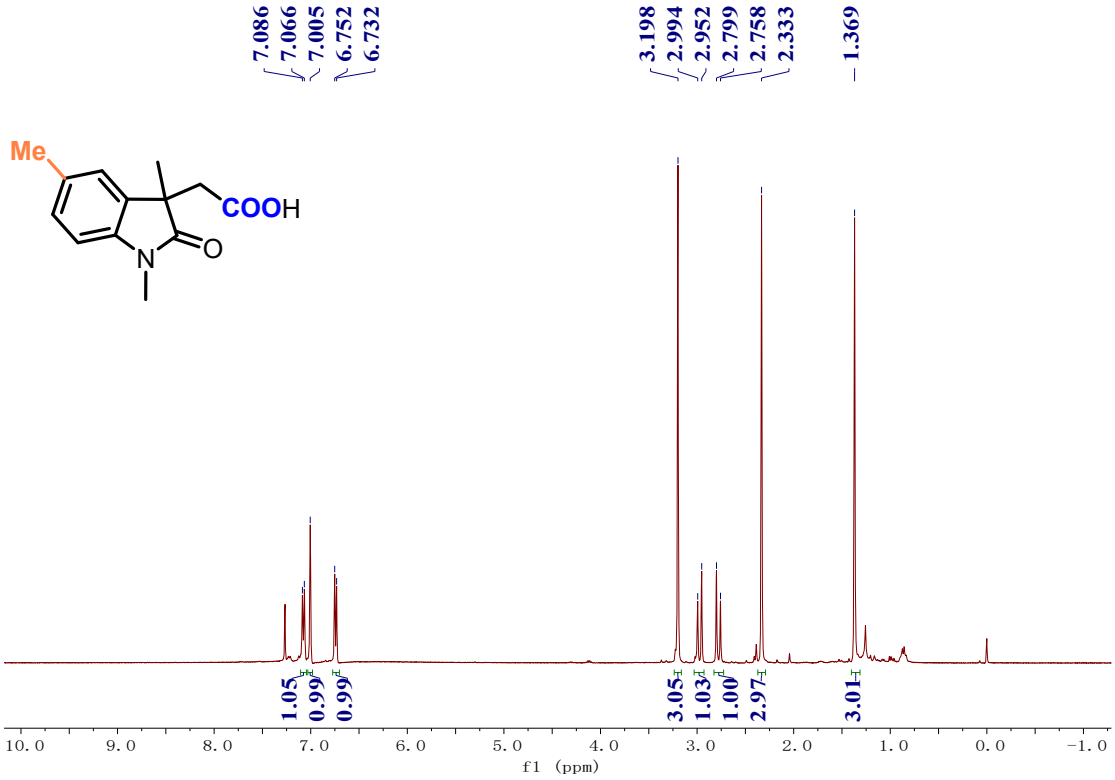
2-(1,3-dimethyl-2-oxoindolin-3-yl)acetic acid (2a)

^{13}C NMR (100 MHz, $CDCl_3$)



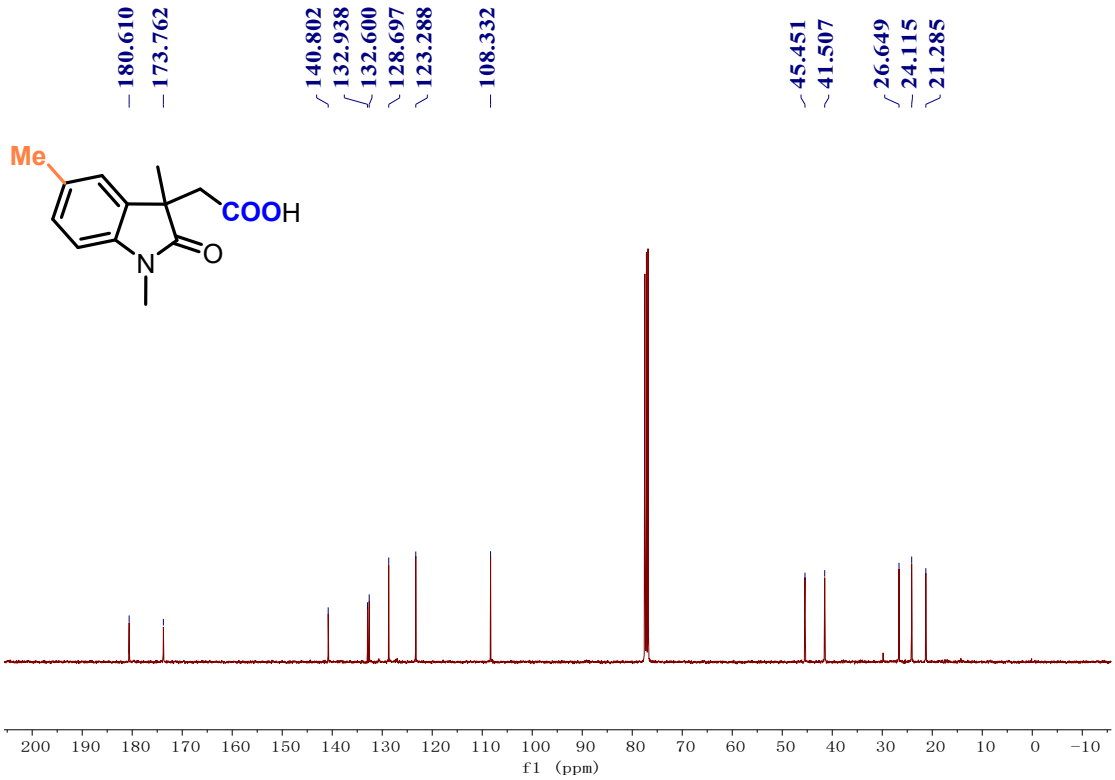
2-(1,3,5-trimethyl-2-oxoindolin-3-yl)acetic acid (2b)

^{1}H NMR (400 MHz, $CDCl_3$)



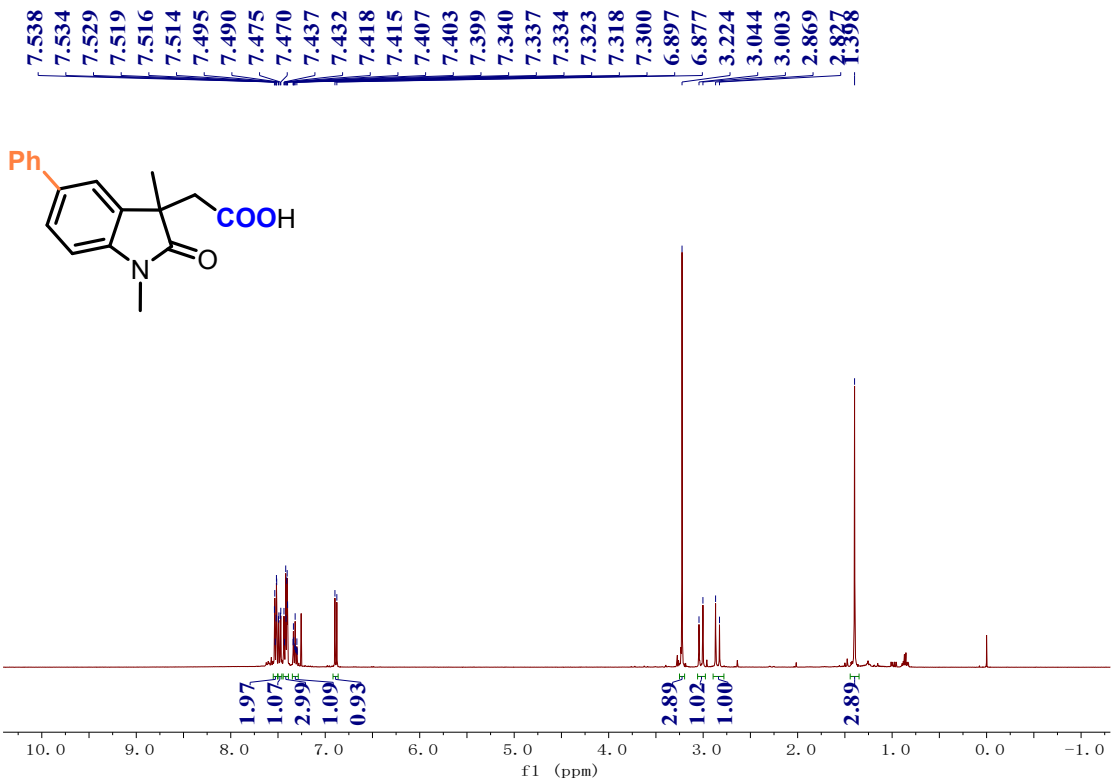
2-(1,3,5-trimethyl-2-oxoindolin-3-yl)acetic acid (2b)

^{13}C NMR (100 MHz, $CDCl_3$)



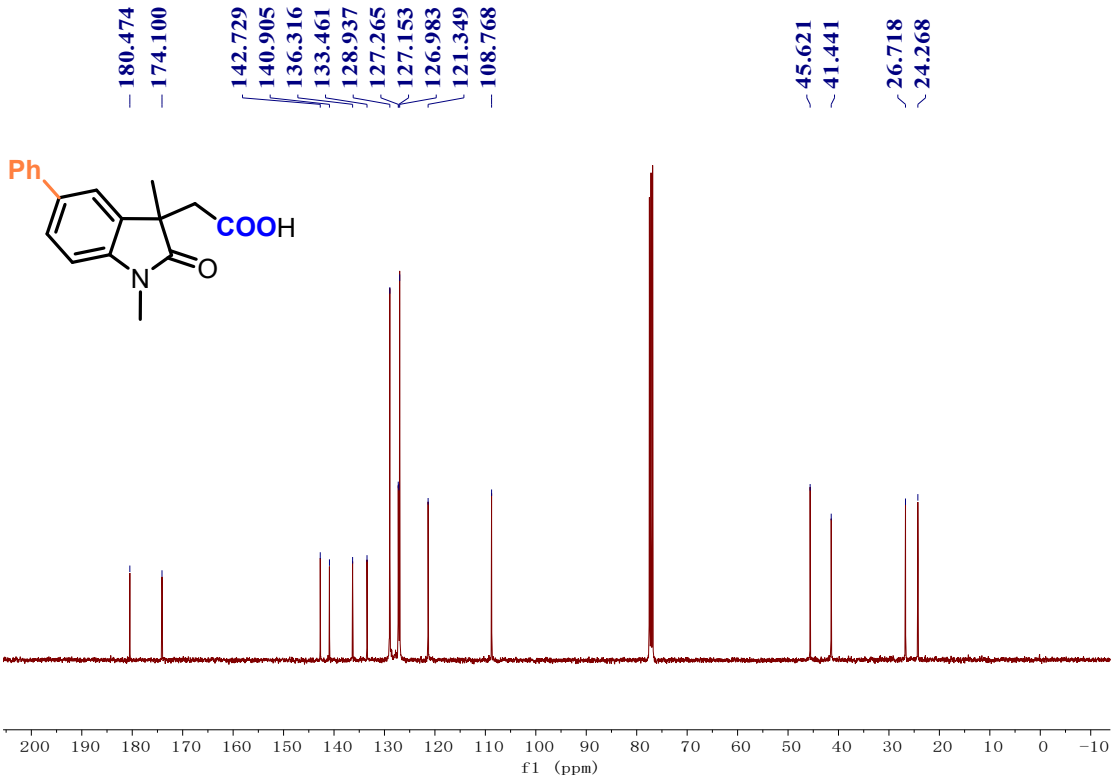
2-(1,3-dimethyl-2-oxo-5-phenylindolin-3-yl)acetic acid (2c)

^{1}H NMR (400 MHz, $CDCl_3$)



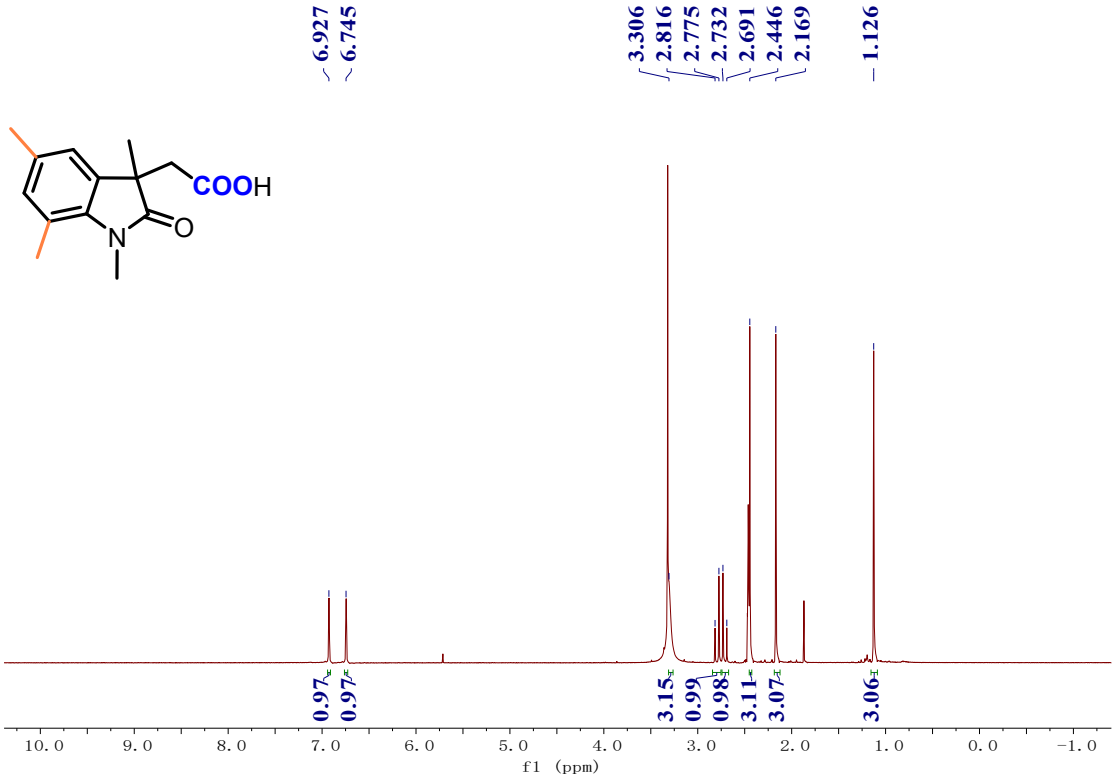
2-(1,3-dimethyl-2-oxo-5-phenylindolin-3-yl)acetic acid (2c)

^{13}C NMR (100 MHz, $CDCl_3$)



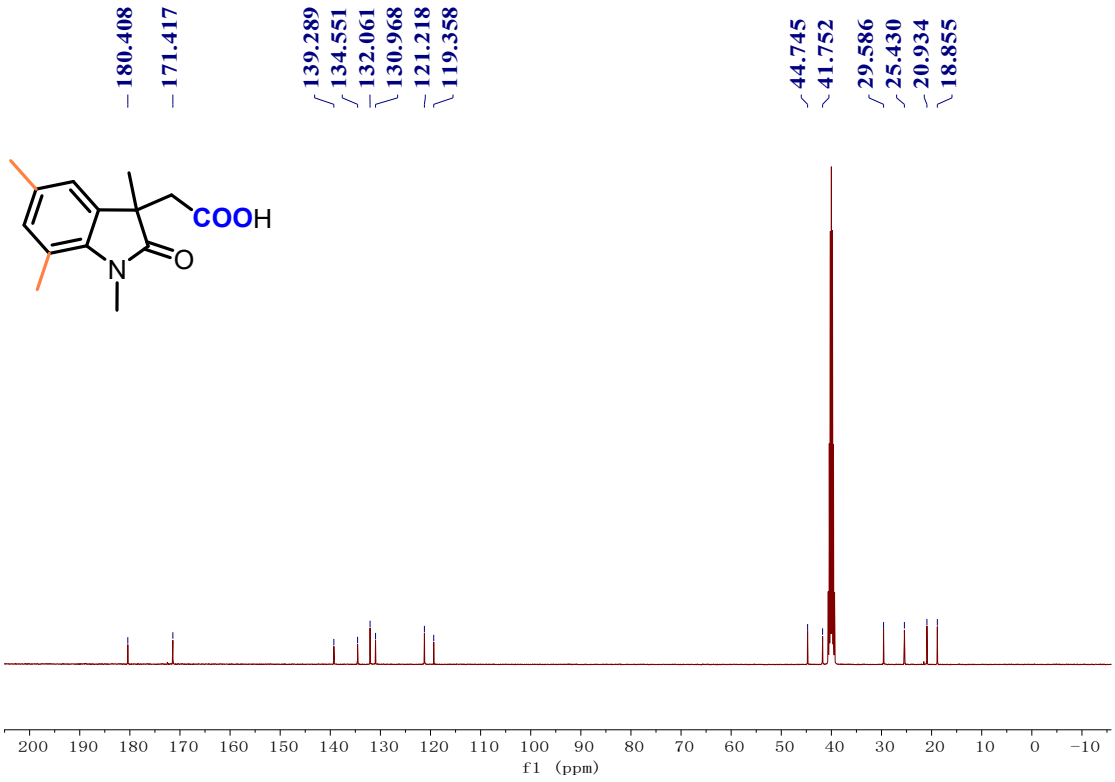
2-(1,3,5,7-tetramethyl-2-oxoindolin-3-yl)acetic acid (2d)

^{1}H NMR (400 MHz, DMSO-d_6)



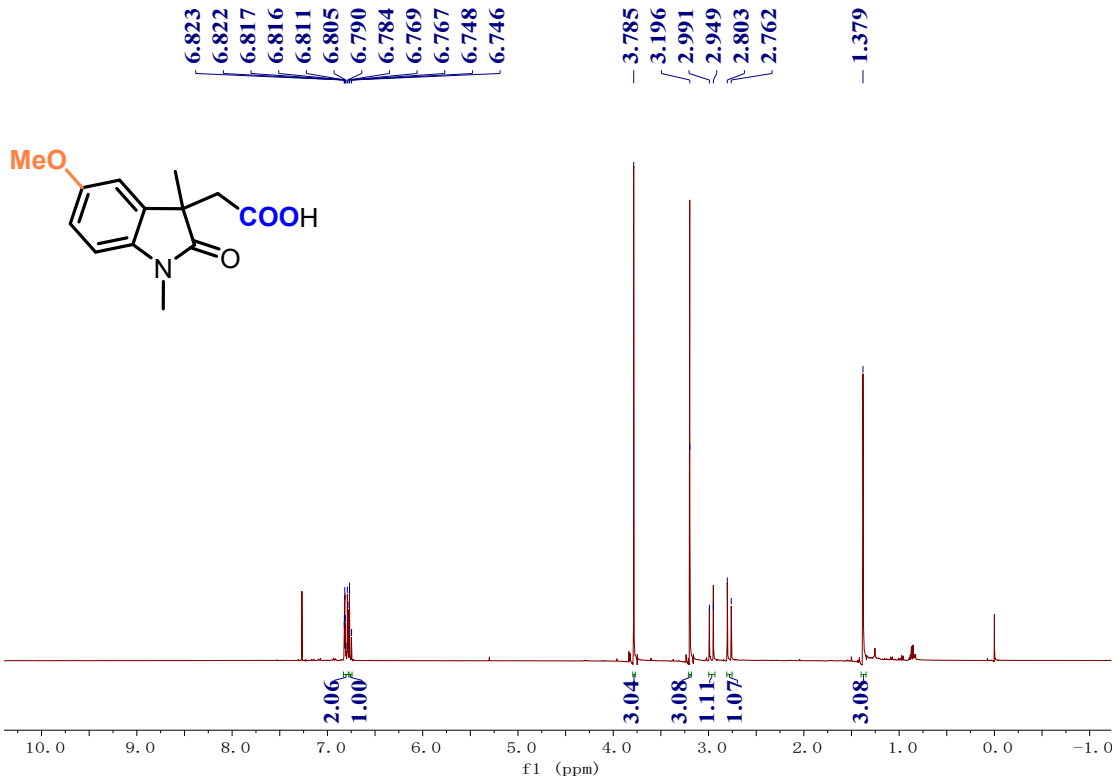
2-(1,3,5,7-tetramethyl-2-oxoindolin-3-yl)acetic acid (2d)

^{13}C NMR (100 MHz, DMSO-d_6)



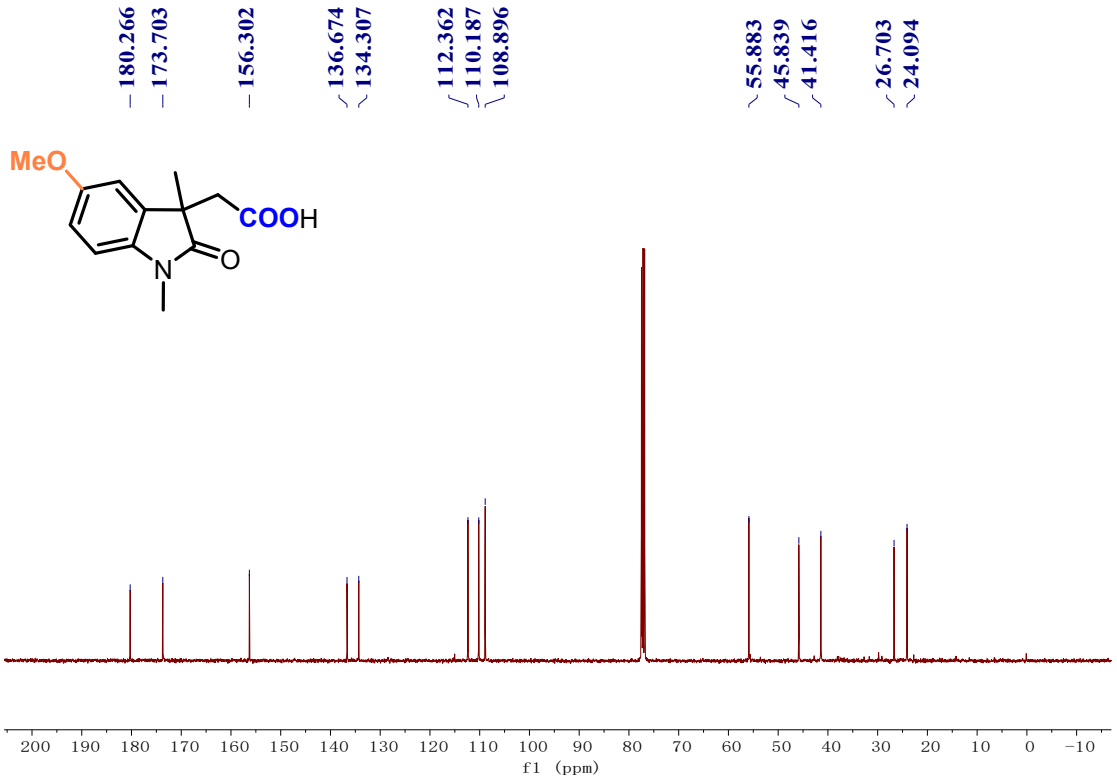
2-(5-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)acetic acid (2e)

^{1}H NMR (400 MHz, $CDCl_3$)



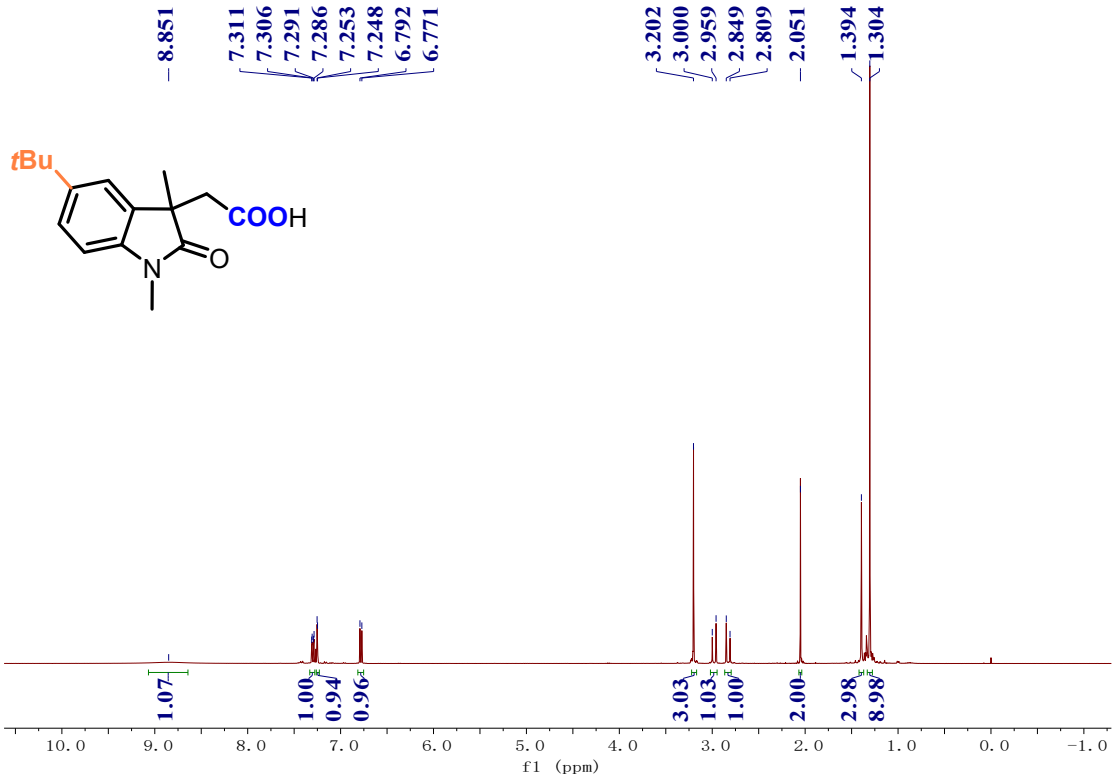
2-(5-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)acetic acid (2e)

^{13}C NMR (100 MHz, $CDCl_3$)



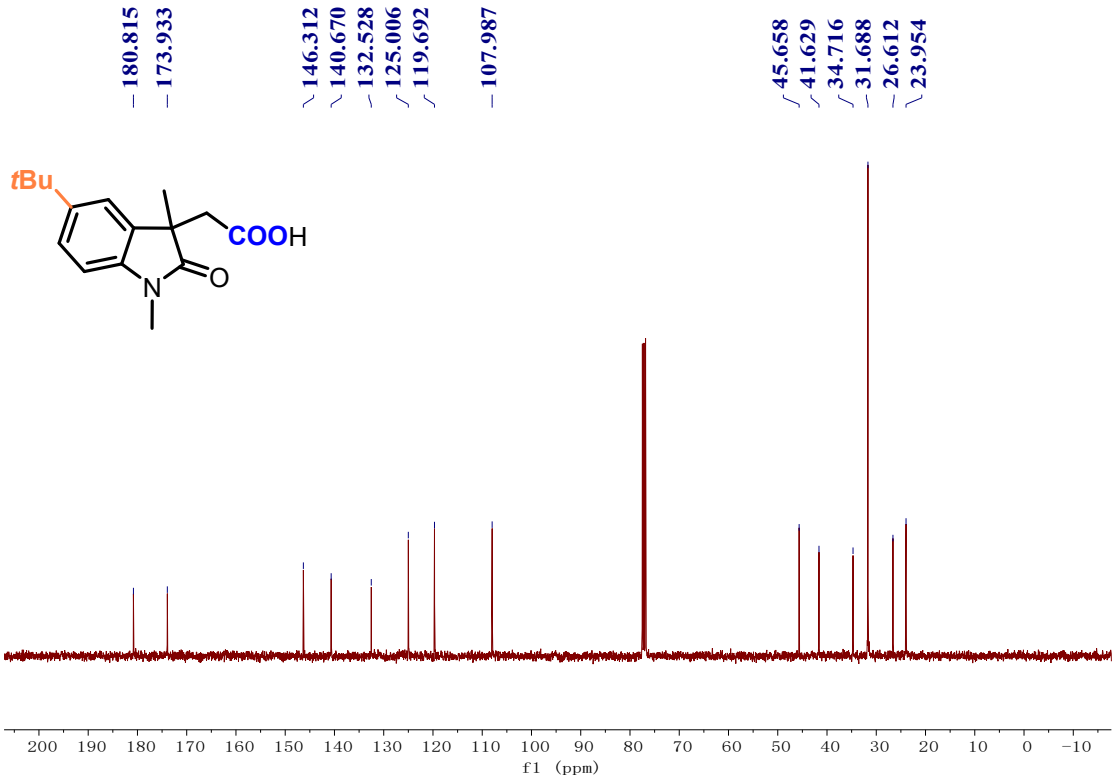
2-(5-(*tert*-butyl)-1,3-dimethyl-2-oxoindolin-3-yl)acetic acid (2f)

^{1}H NMR (400 MHz, $CDCl_3$)



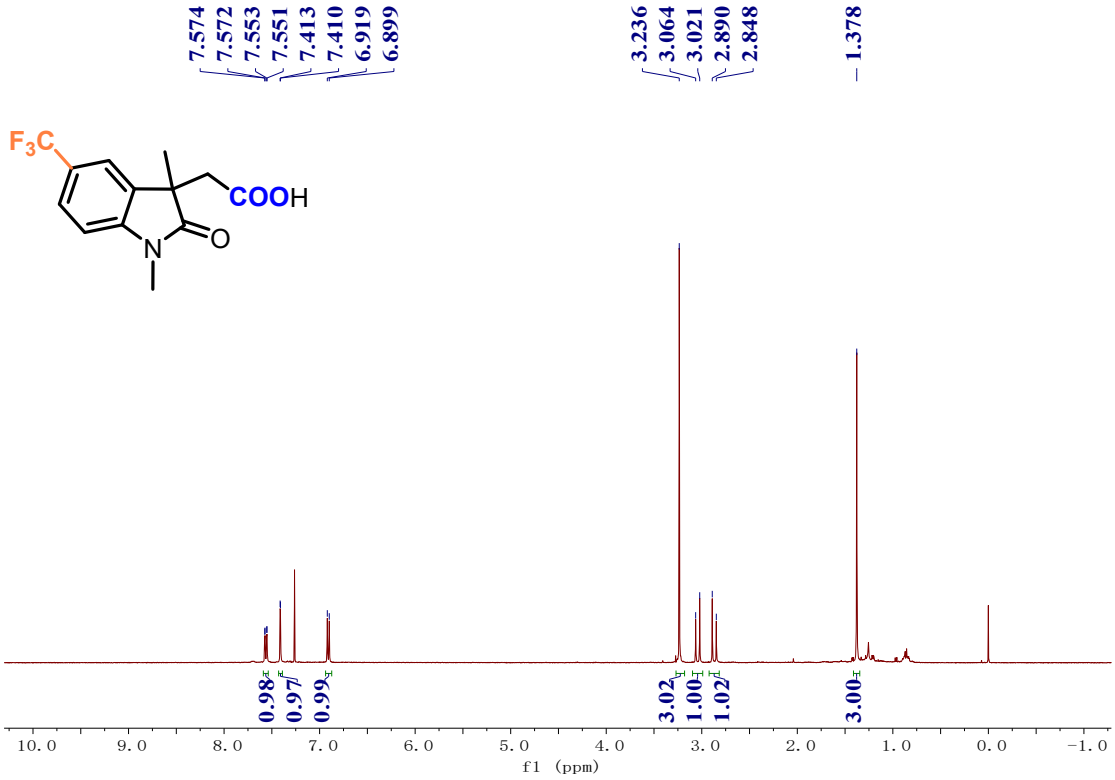
2-(5-(*tert*-butyl)-1,3-dimethyl-2-oxoindolin-3-yl)acetic acid (2f)

^{13}C NMR (100 MHz, $CDCl_3$)



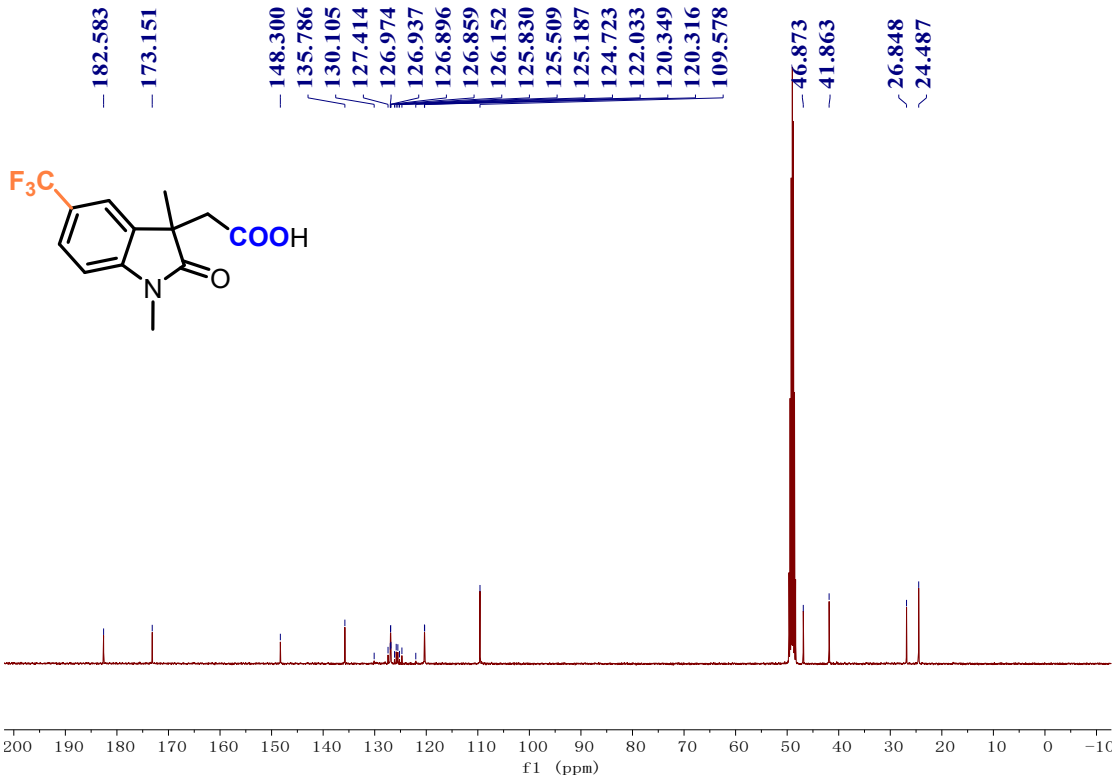
2-(1,3-dimethyl-2-oxo-5-(trifluoromethyl)indolin-3-yl)acetic acid (2g)

^{1}H NMR (400 MHz, $CDCl_3$)



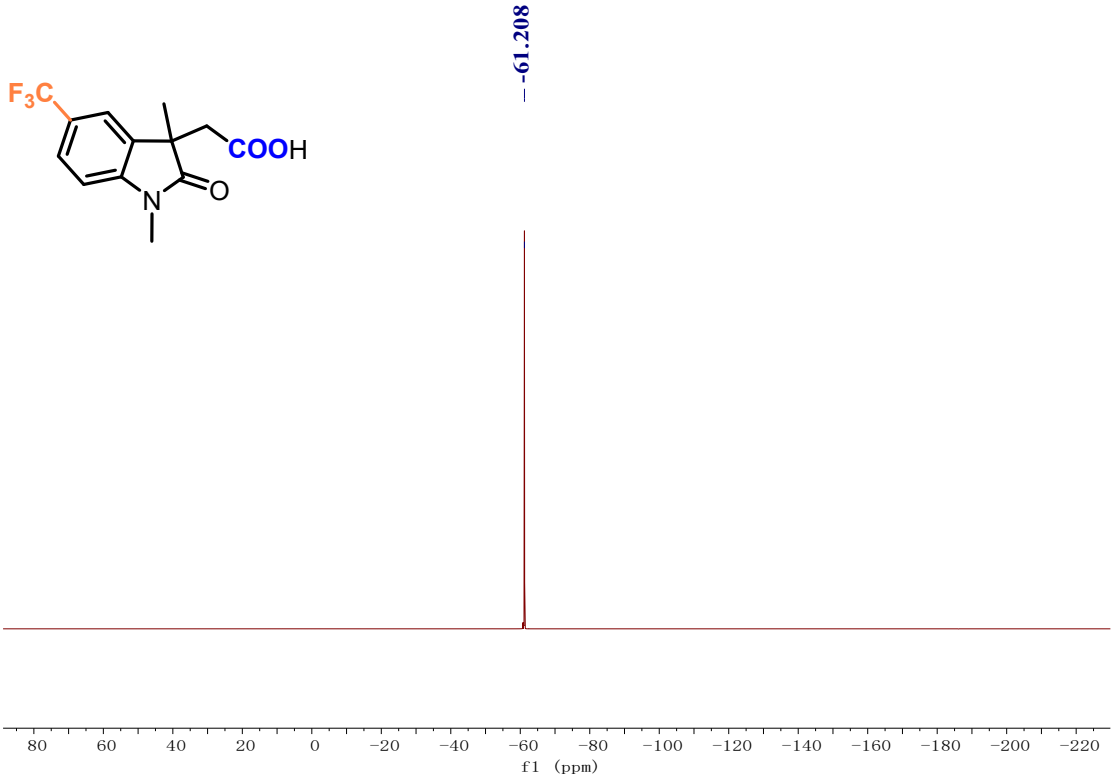
2-(1,3-dimethyl-2-oxo-5-(trifluoromethyl)indolin-3-yl)acetic acid (2g)

^{13}C NMR (100 MHz, CD_3OD)



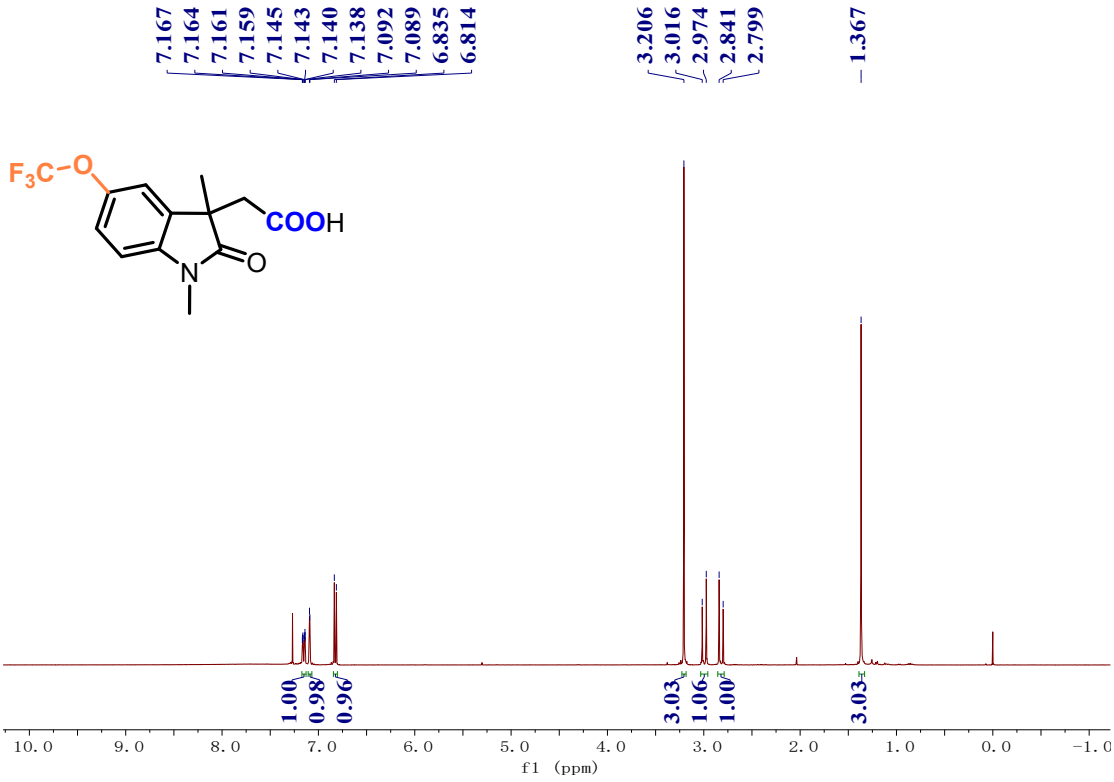
2-(1,3-dimethyl-2-oxo-5-(trifluoromethyl)indolin-3-yl)acetic acid (2g)

^{19}F NMR (376 MHz, $CDCl_3$)



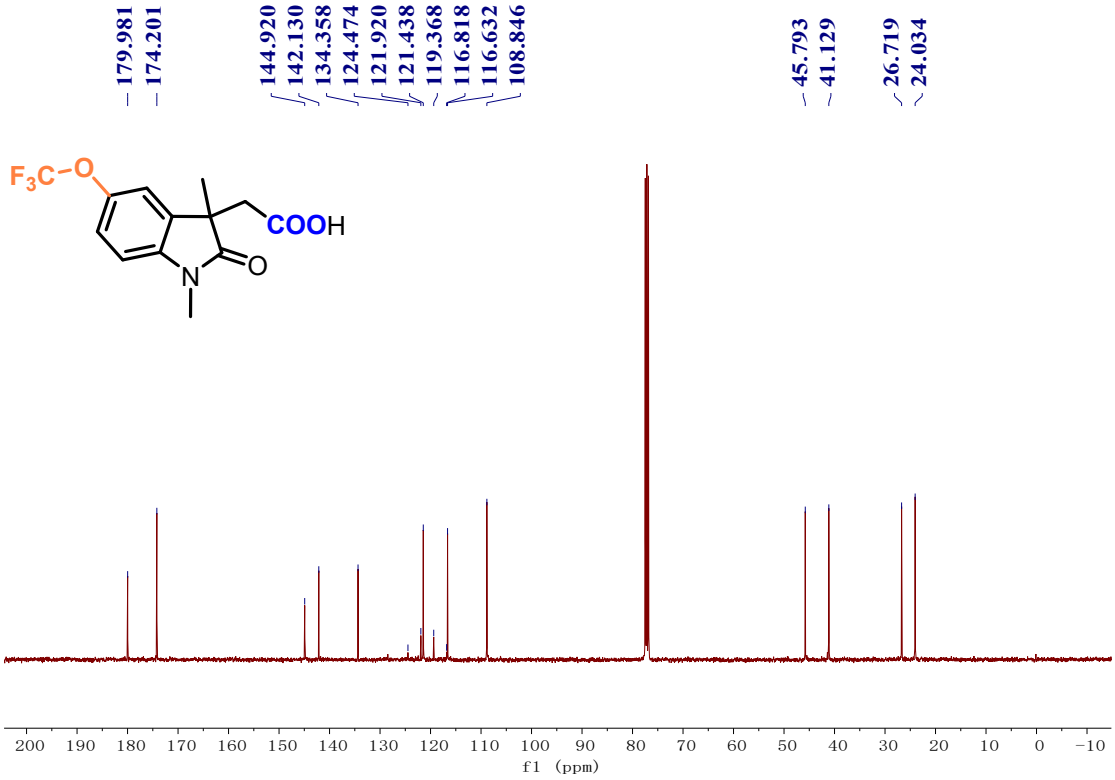
2-(1,3-dimethyl-2-oxo-5-(trifluoromethoxy)indolin-3-yl)acetic acid (2h)

^{1}H NMR (400 MHz, $CDCl_3$)



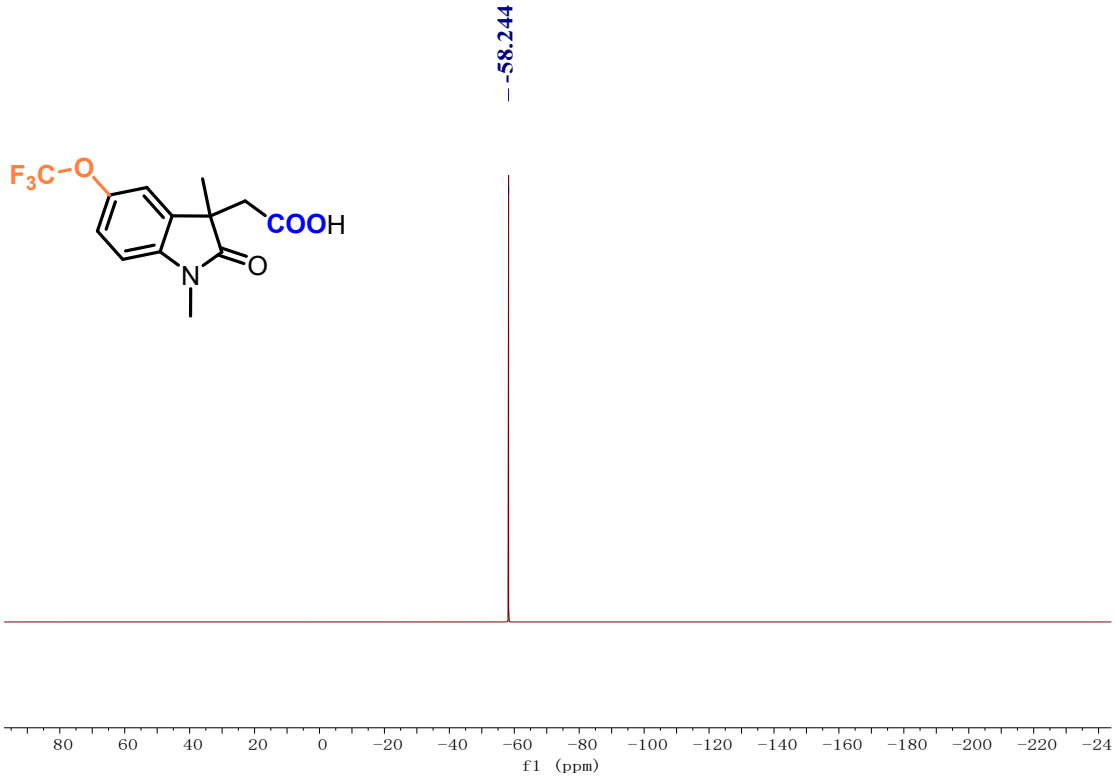
2-(1,3-dimethyl-2-oxo-5-(trifluoromethoxy)indolin-3-yl)acetic acid (2h)

^{13}C NMR (100 MHz, $CDCl_3$)



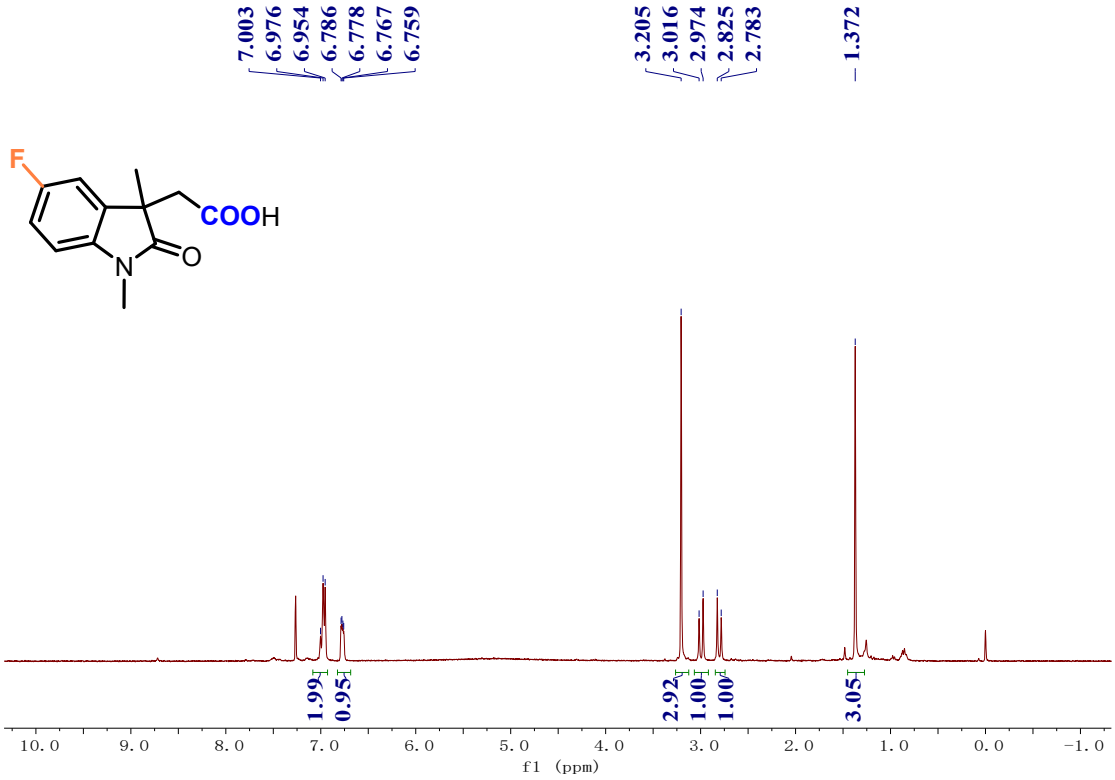
2-(1,3-dimethyl-2-oxo-5-(trifluoromethoxy)indolin-3-yl)acetic acid (2h)

^{19}F NMR (376 MHz, $CDCl_3$)



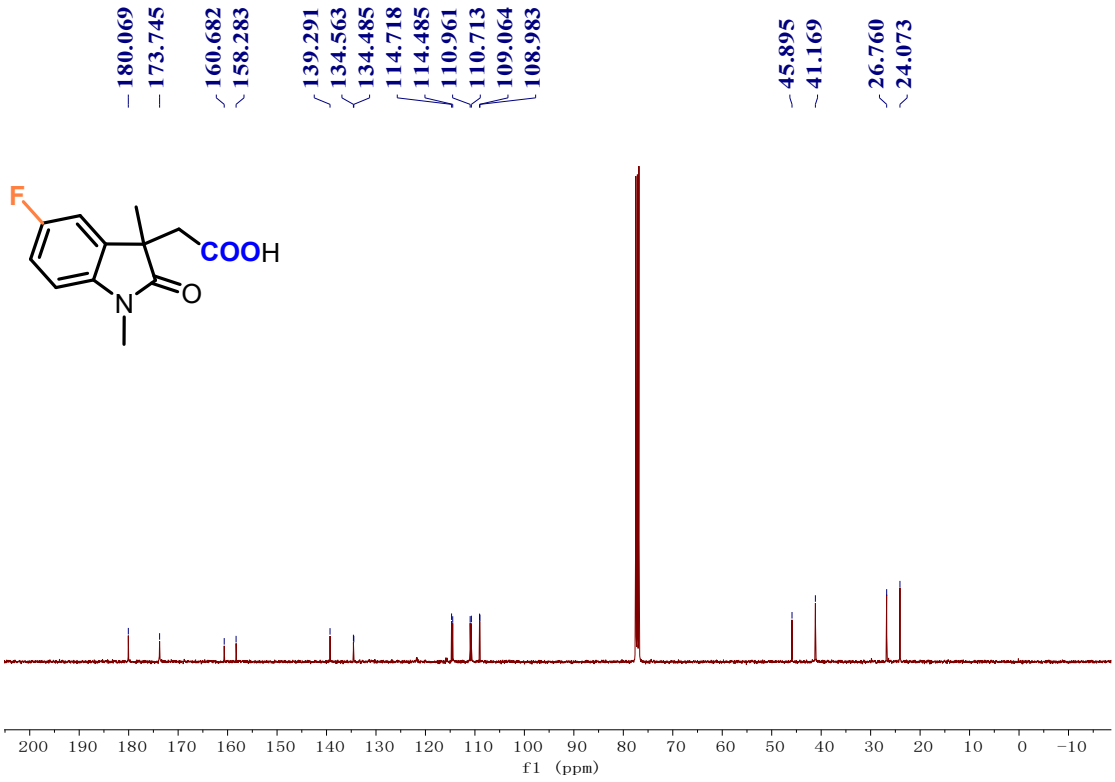
2-(5-fluoro-1,3-dimethyl-2-oxoindolin-3-yl)acetic acid (2i)

^{1}H NMR (400 MHz, $CDCl_3$)



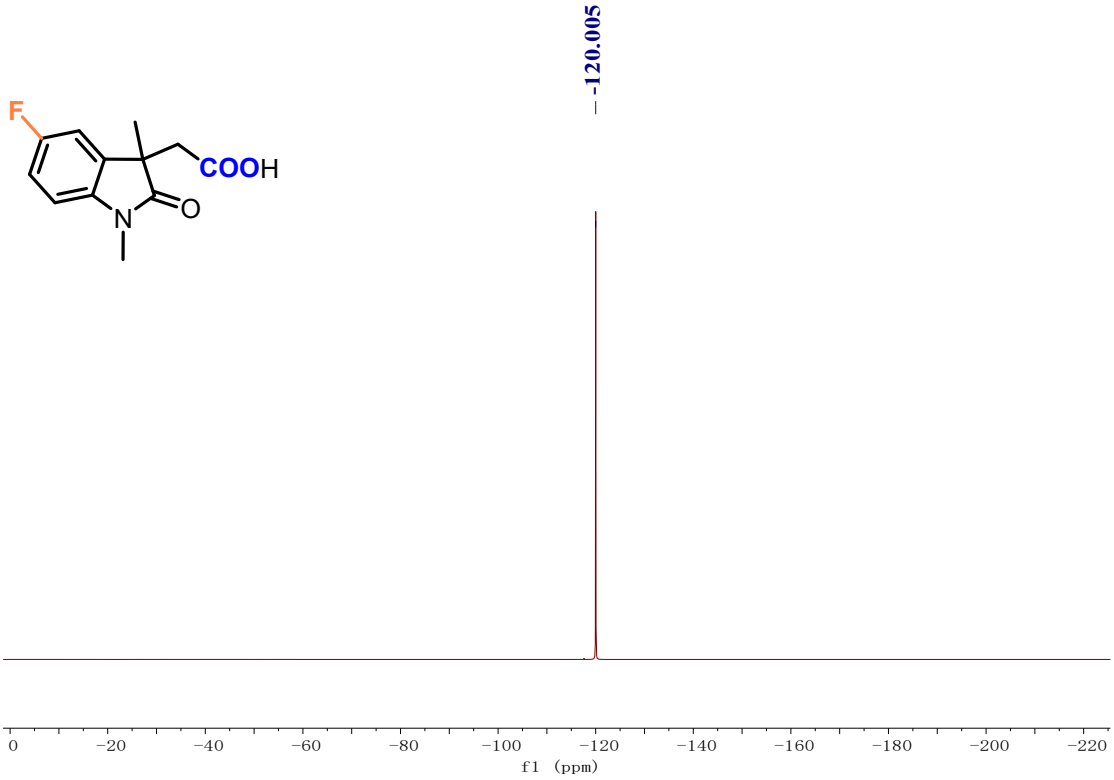
2-(5-fluoro-1,3-dimethyl-2-oxoindolin-3-yl)acetic acid (2i)

^{13}C NMR (100 MHz, $CDCl_3$)



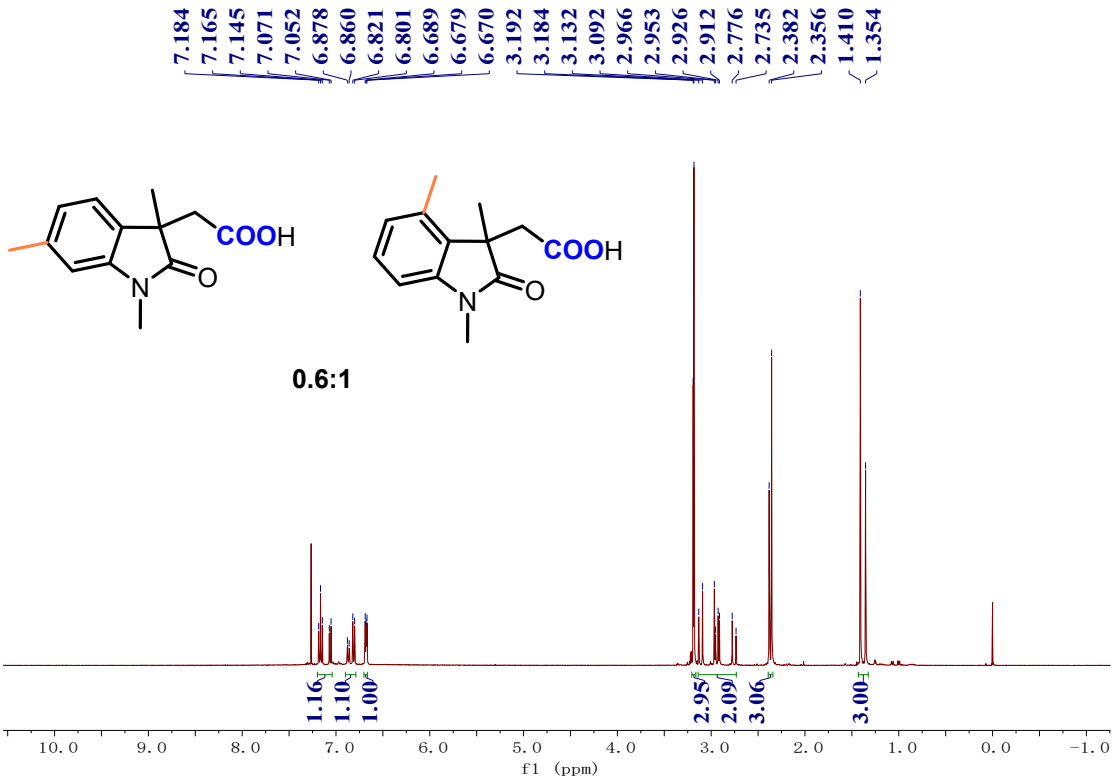
2-(5-fluoro-1,3-dimethyl-2-oxoindolin-3-yl)acetic acid (2i)

^{19}F NMR (376 MHz, $CDCl_3$)



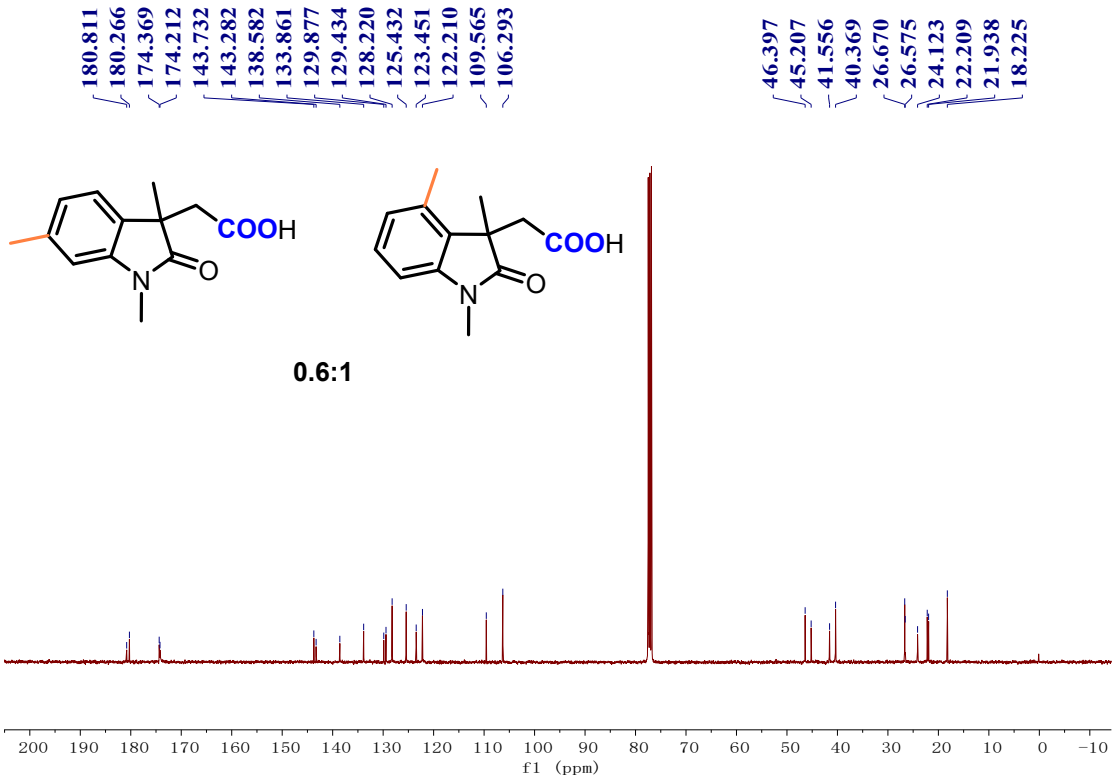
2-(1,3,6-trimethyl-2-oxoindolin-3-yl)acetic acid (2j) and 2-(1,3,4-trimethyl-2-oxoindolin-3-yl)acetic acid (2j') (0.6:1)

^{1}H NMR (400 MHz, $CDCl_3$)



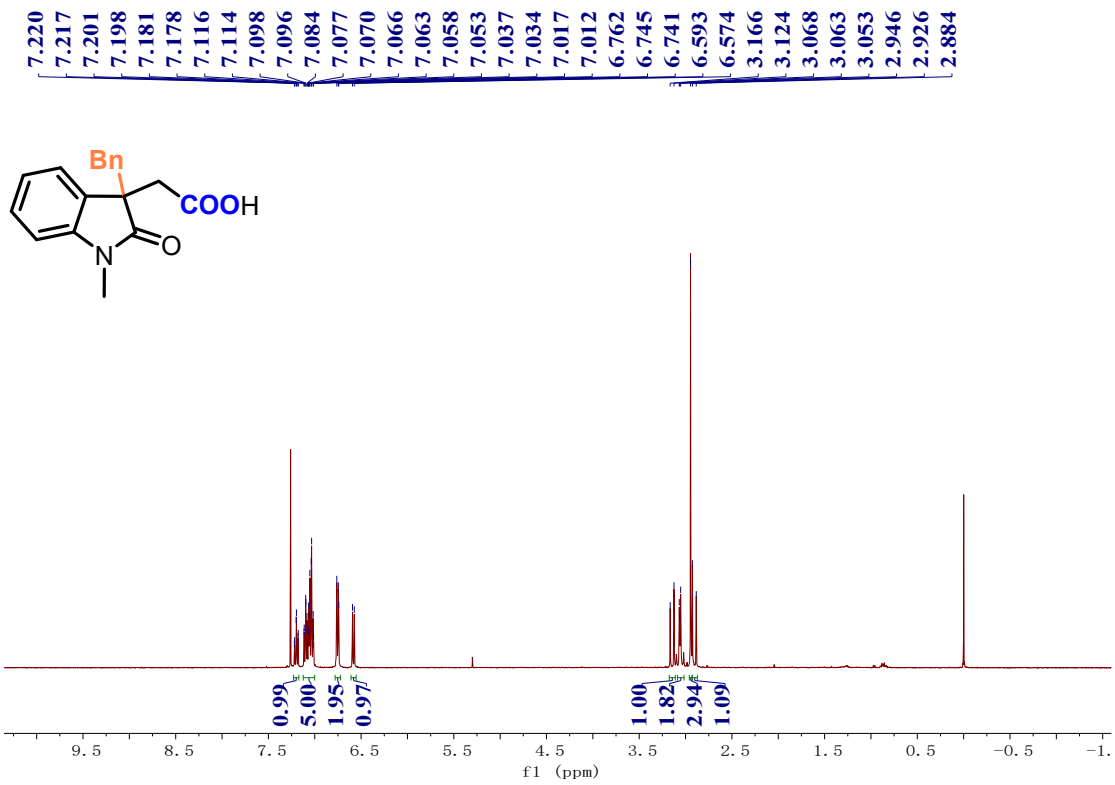
2-(1,3,6-trimethyl-2-oxoindolin-3-yl)acetic acid (2j) and 2-(1,3,4-trimethyl-2-oxoindolin-3-yl)acetic acid (2j') (0.6:1)

^{13}C NMR (100 MHz, $CDCl_3$)



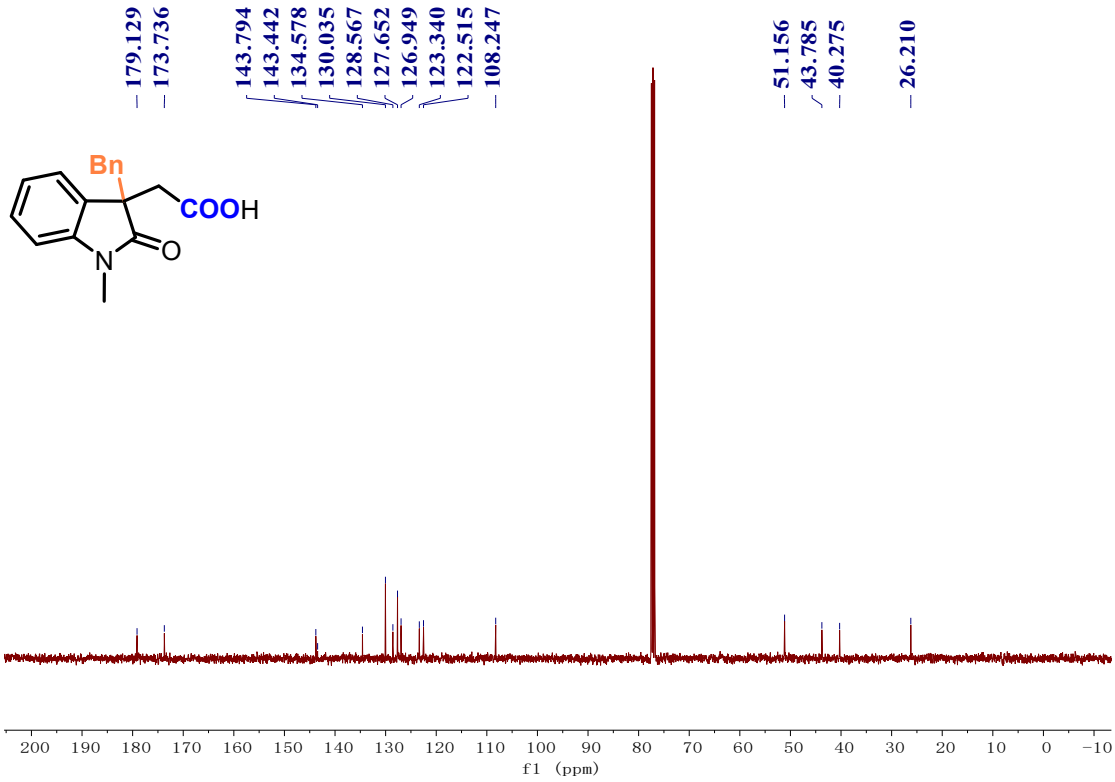
2-(3-benzyl-1-methyl-2-oxoindolin-3-yl)acetic acid (2k)

^{1}H NMR (400 MHz, $CDCl_3$)



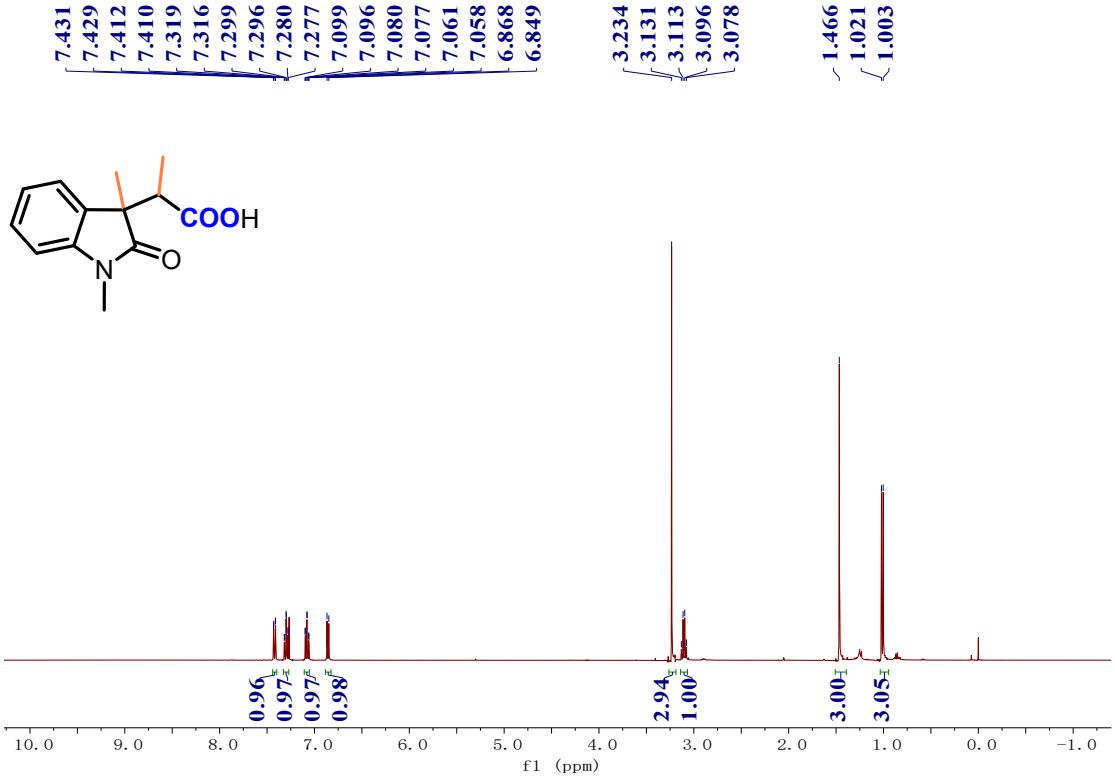
2-(3-benzyl-1-methyl-2-oxoindolin-3-yl)acetic acid (2k)

^{13}C NMR (100 MHz, $CDCl_3$)



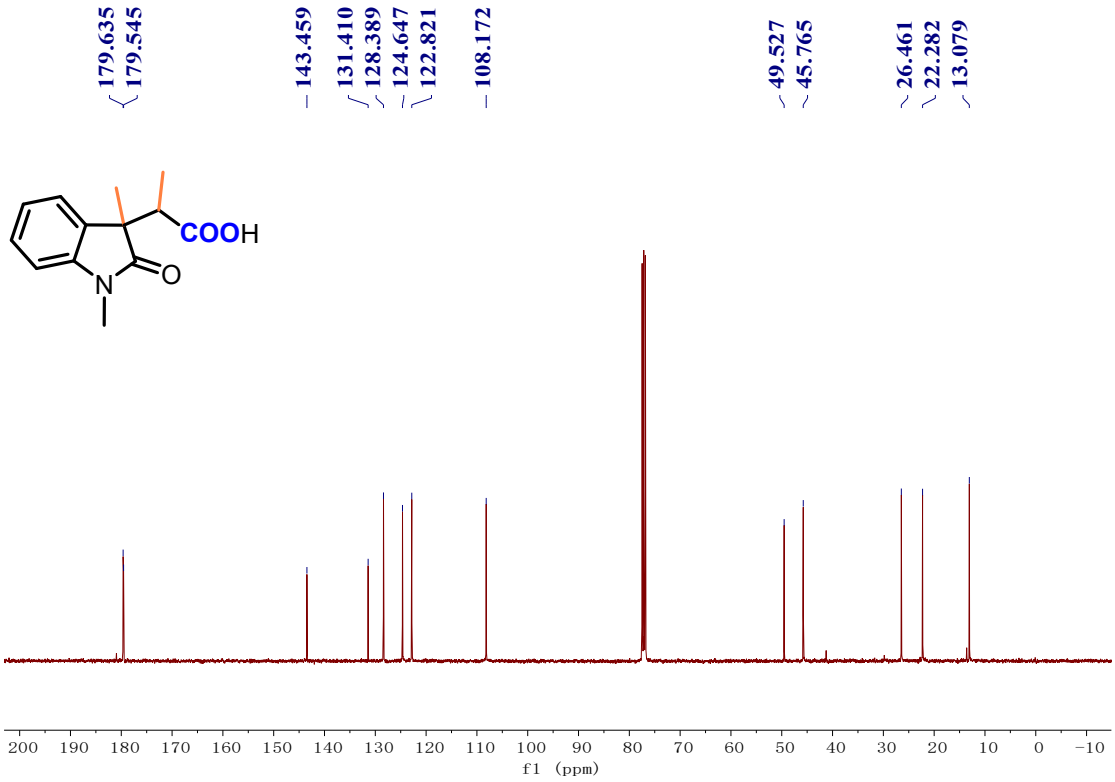
2-(1,3-dimethyl-2-oxoindolin-3-yl)propanoic acid (2l)

^{1}H NMR (400 MHz, $CDCl_3$)



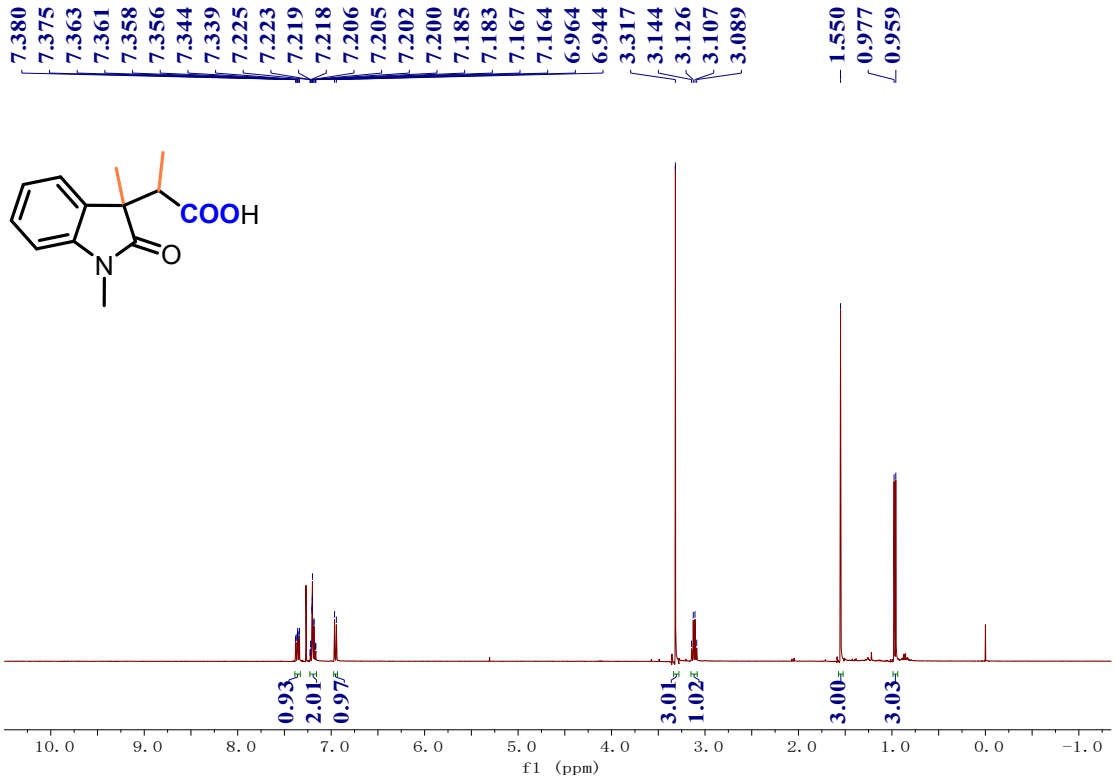
2-(1,3-dimethyl-2-oxoindolin-3-yl)propanoic acid (2l)

^{13}C NMR (100 MHz, $CDCl_3$)



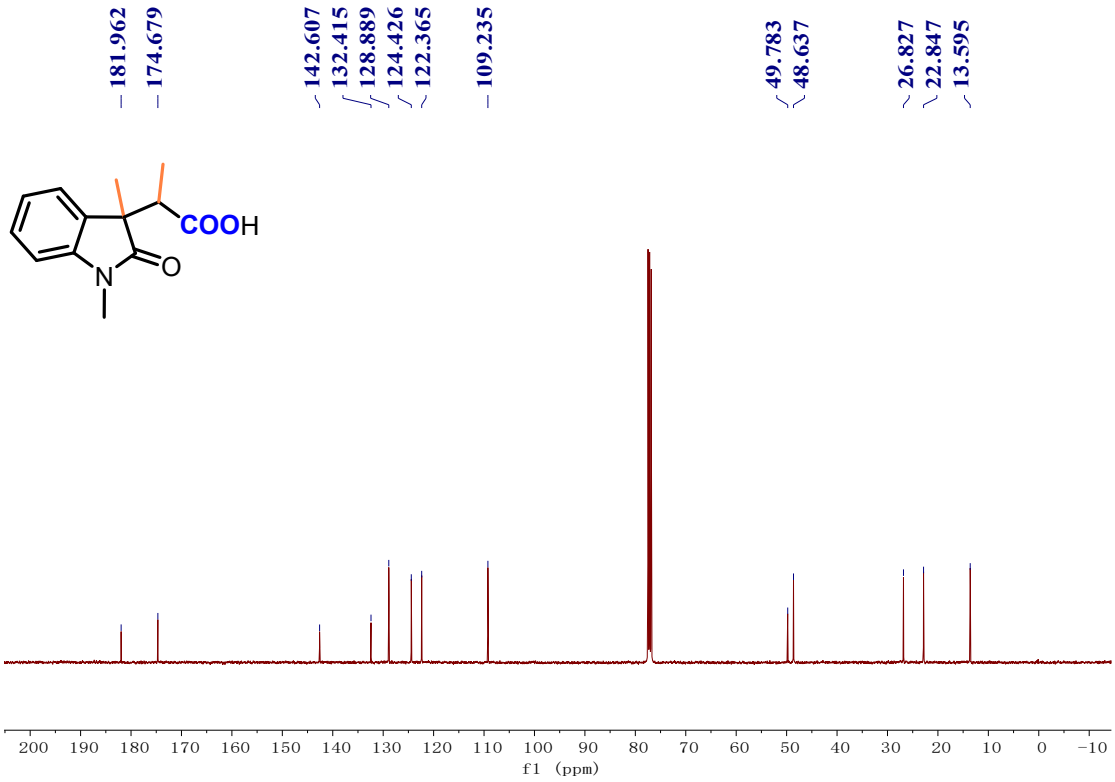
2-(1,3-dimethyl-2-oxoindolin-3-yl)propanoic acid (2l')

^{1}H NMR (400 MHz, $CDCl_3$)



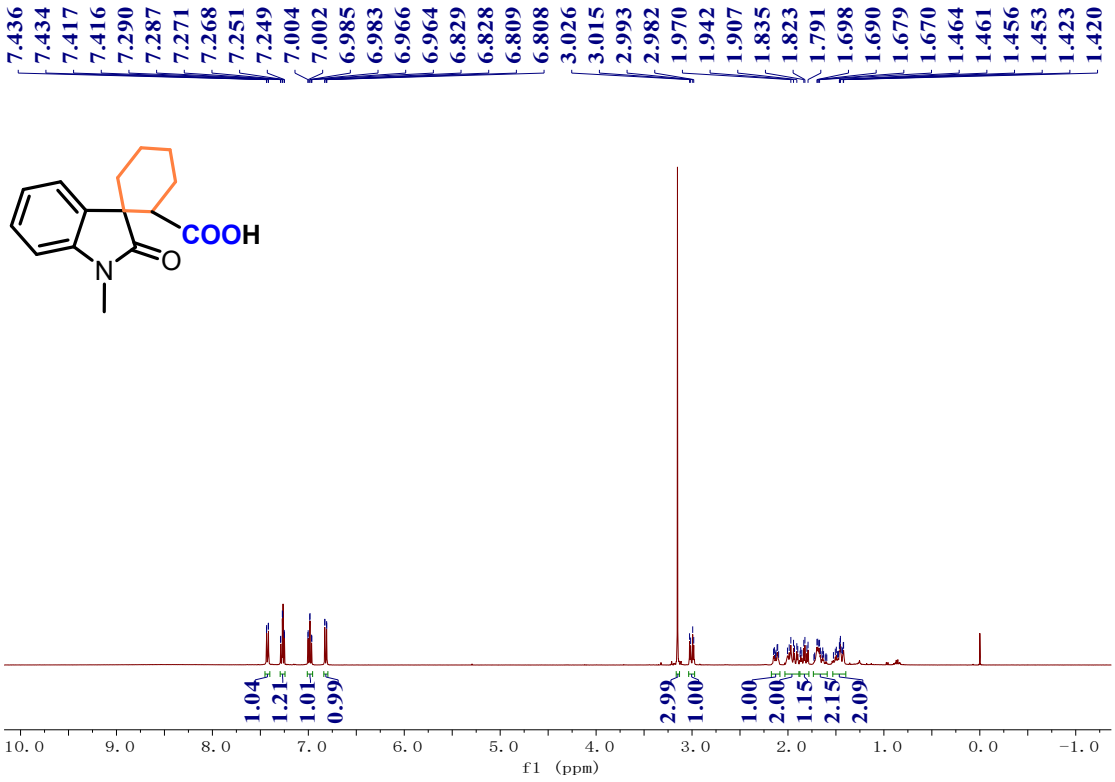
2-(1,3-dimethyl-2-oxoindolin-3-yl)propanoic acid (2l')

^{13}C NMR (100 MHz, $CDCl_3$)



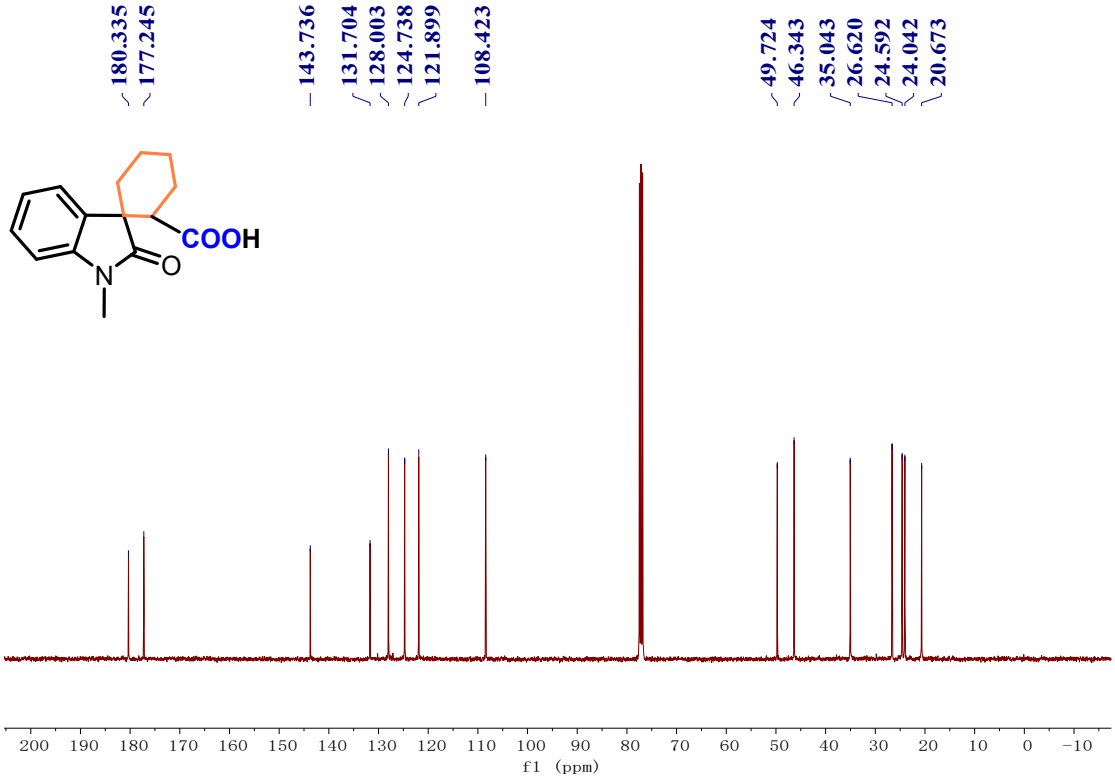
1'-methyl-2'-oxospiro[cyclohexane-1,3'-indoline]-2-carboxylic acid (2m)

^{1}H NMR (400 MHz, $CDCl_3$)



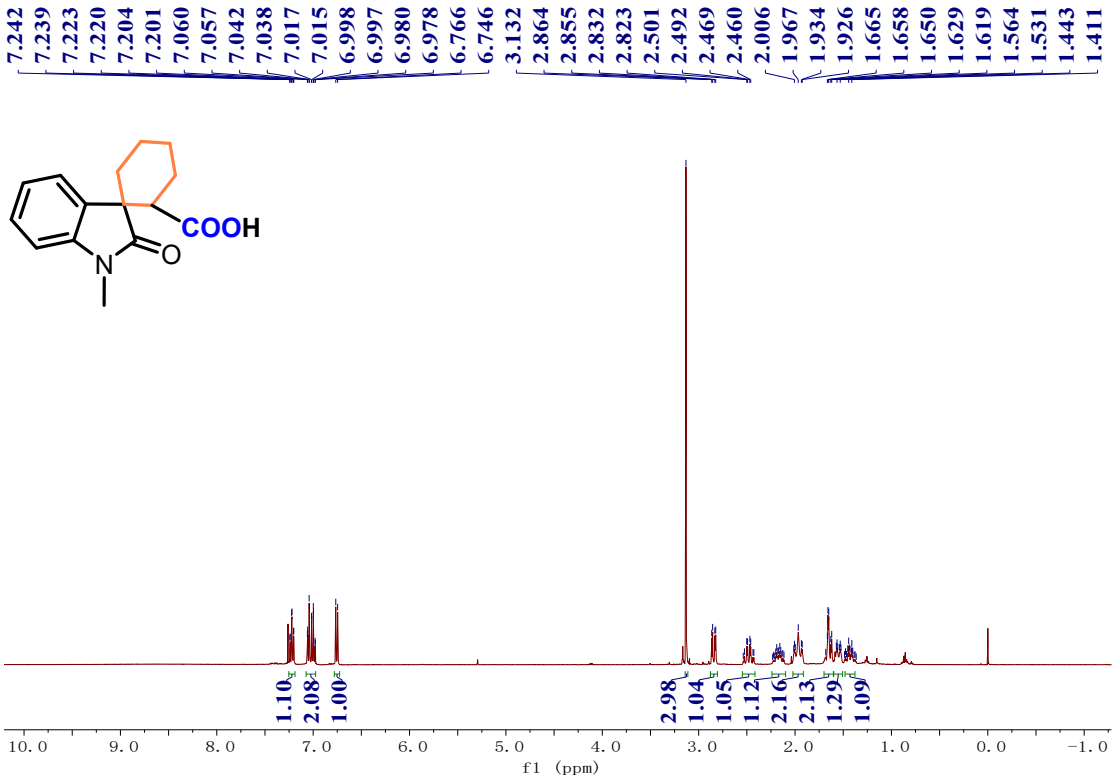
1'-methyl-2'-oxospiro[cyclohexane-1,3'-indoline]-2-carboxylic acid (2m)

^{13}C NMR (100 MHz, $CDCl_3$)



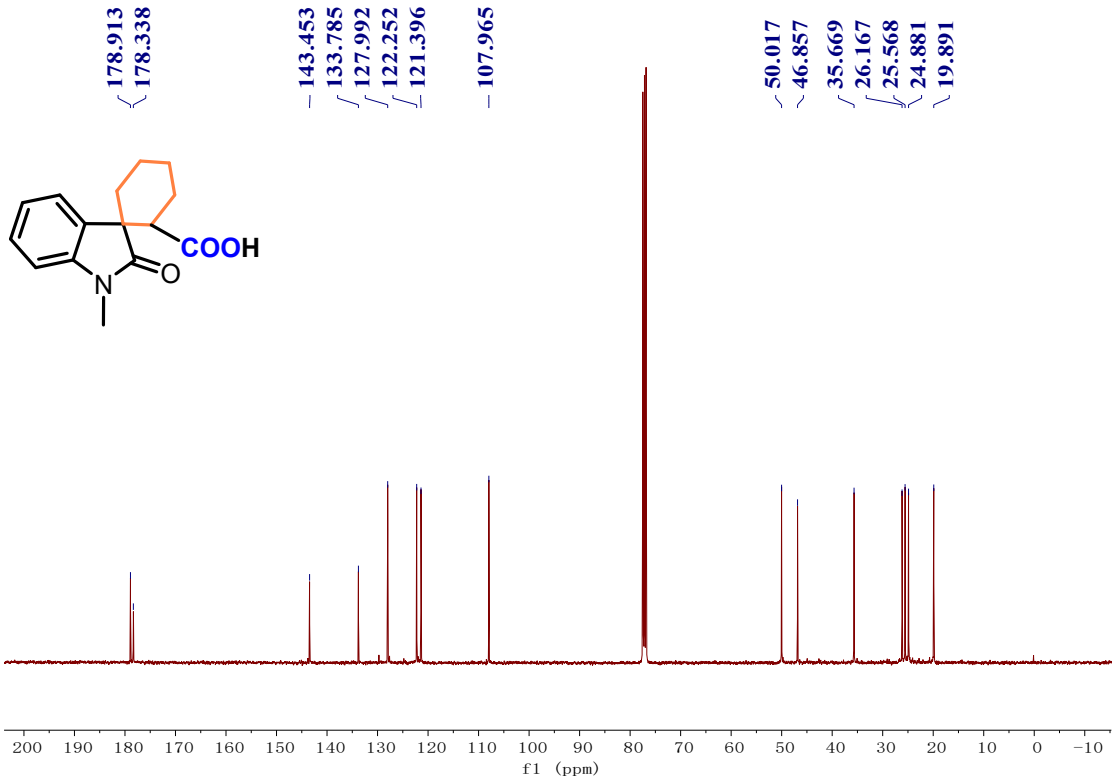
1'-methyl-2'-oxospiro[cyclohexane-1,3'-indoline]-2-carboxylic acid (2m')

^{1}H NMR (400 MHz, $CDCl_3$)



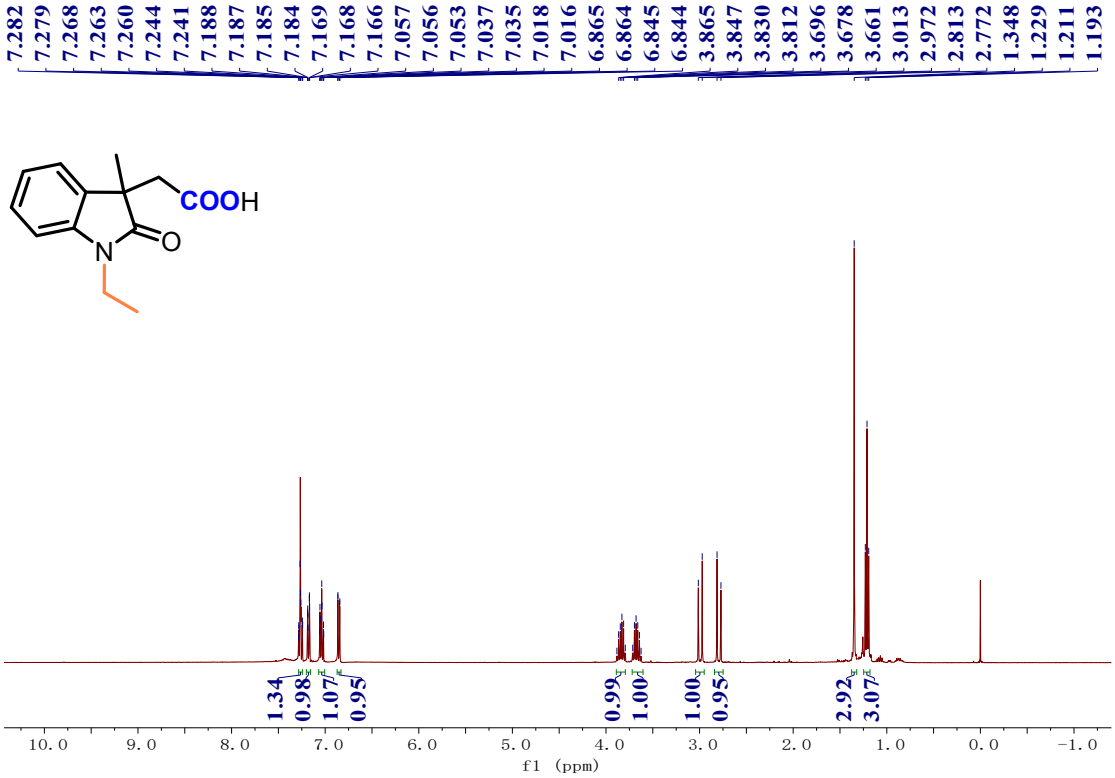
1'-methyl-2'-oxospiro[cyclohexane-1,3'-indoline]-2-carboxylic acid (2m')

^{13}C NMR (100 MHz, $CDCl_3$)



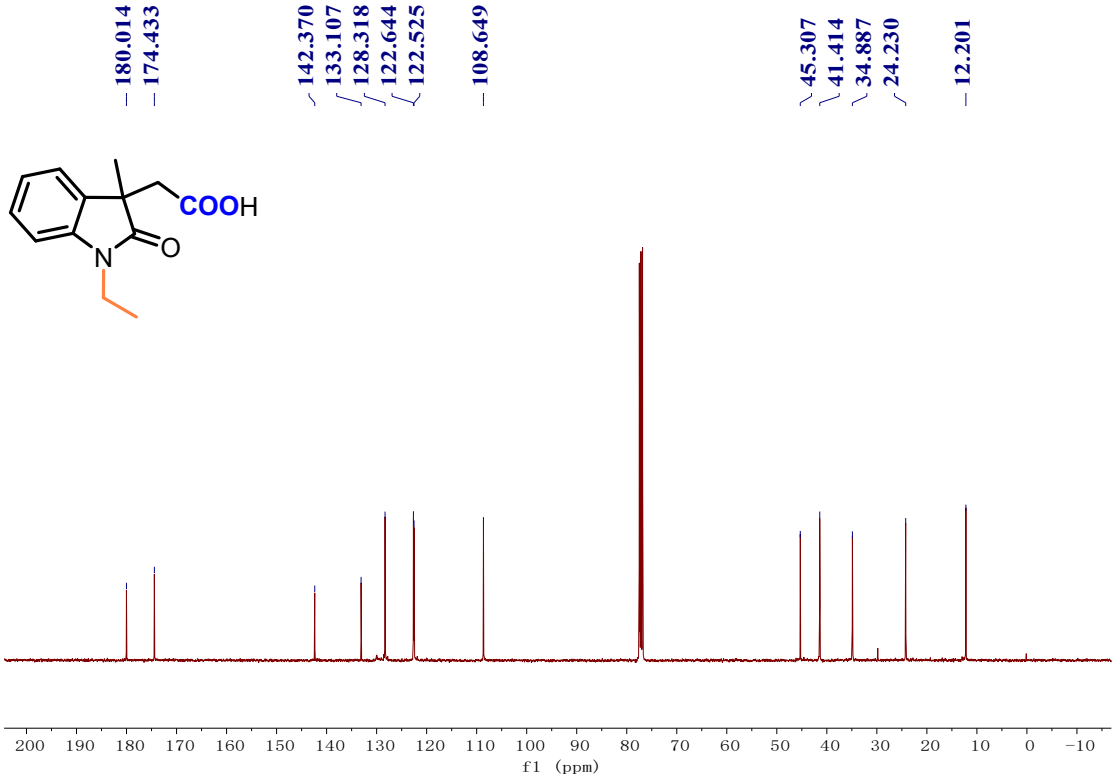
2-(1-ethyl-3-methyl-2-oxoindolin-3-yl)acetic acid (2n)

^{1}H NMR (400 MHz, $CDCl_3$)



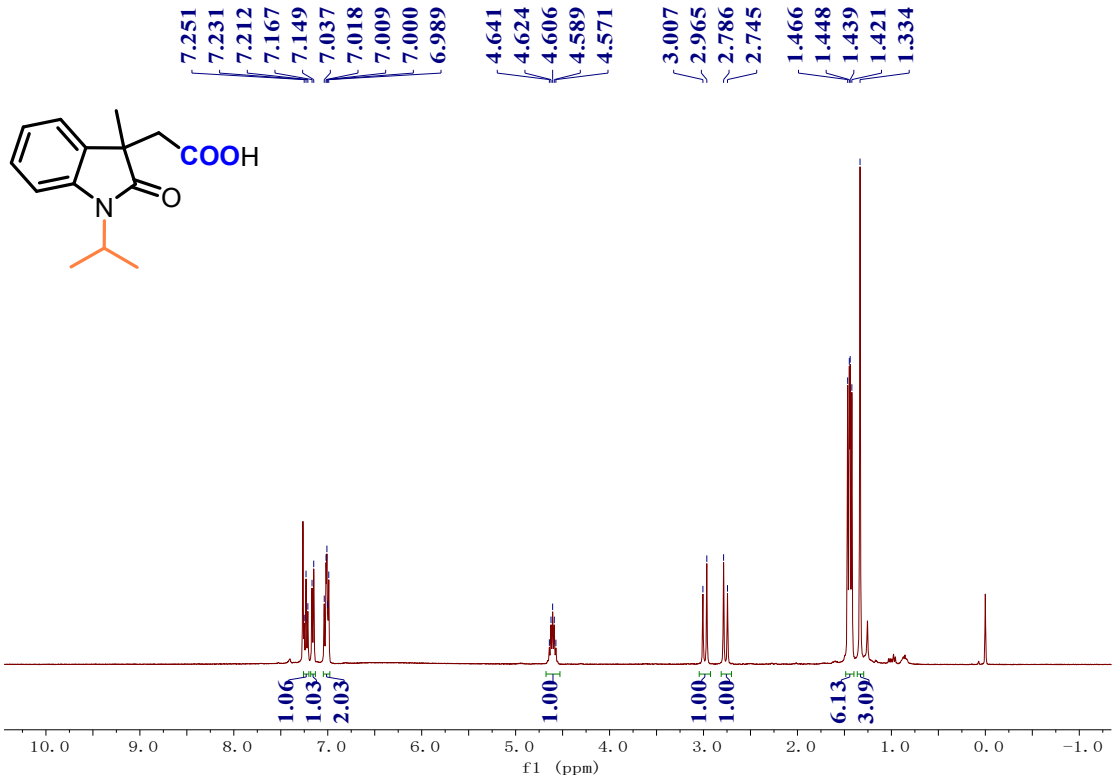
2-(1-ethyl-3-methyl-2-oxoindolin-3-yl)acetic acid (2n)

^{13}C NMR (100 MHz, $CDCl_3$)



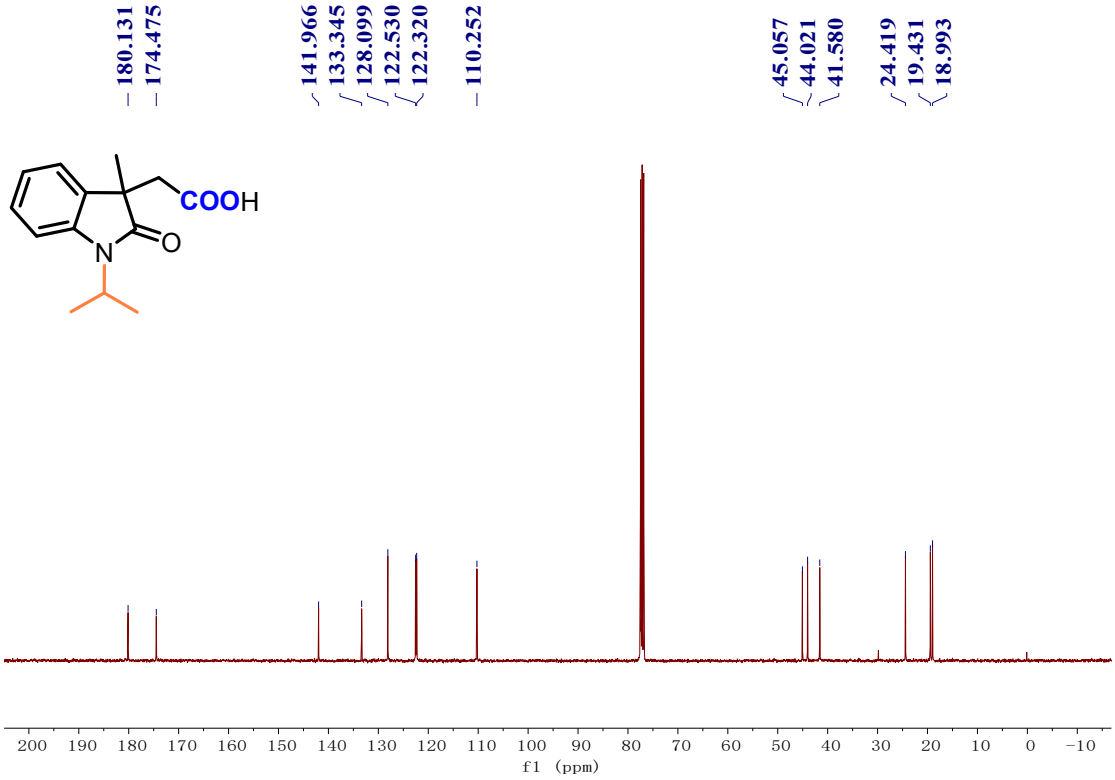
2-(1-isopropyl-3-methyl-2-oxoindolin-3-yl)acetic acid (2o)

^{1}H NMR (400 MHz, $CDCl_3$)



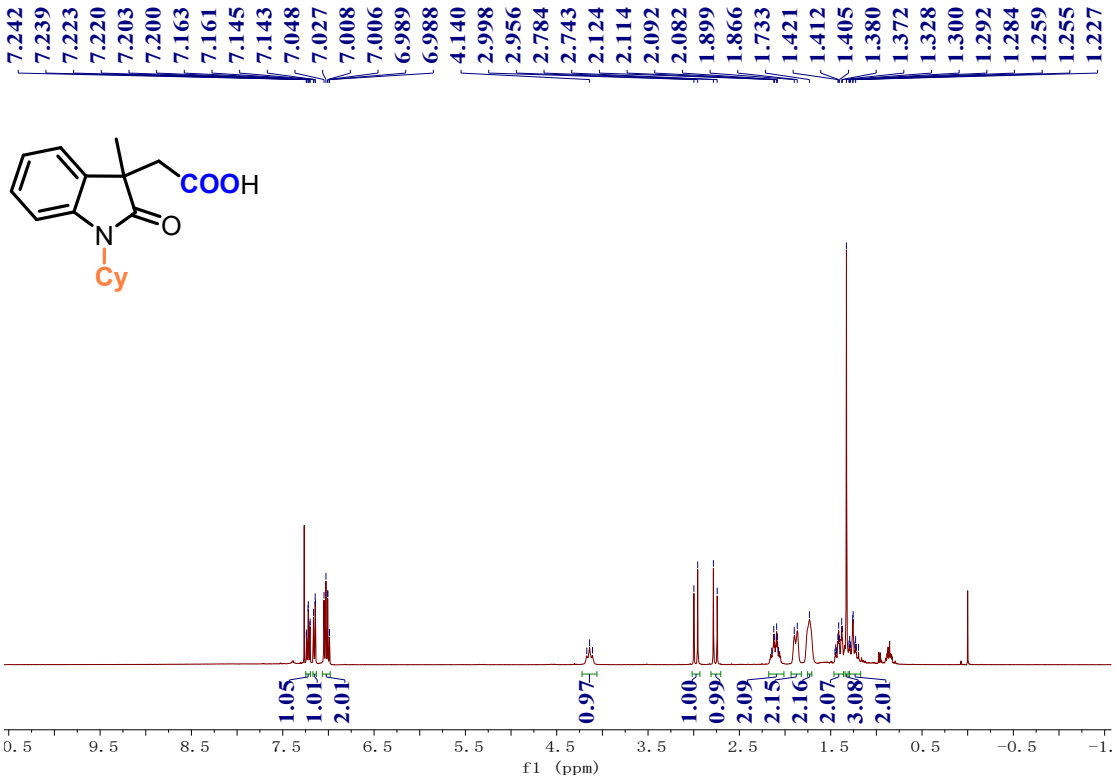
2-(1-isopropyl-3-methyl-2-oxoindolin-3-yl)acetic acid (2o)

^{13}C NMR (100 MHz, $CDCl_3$)



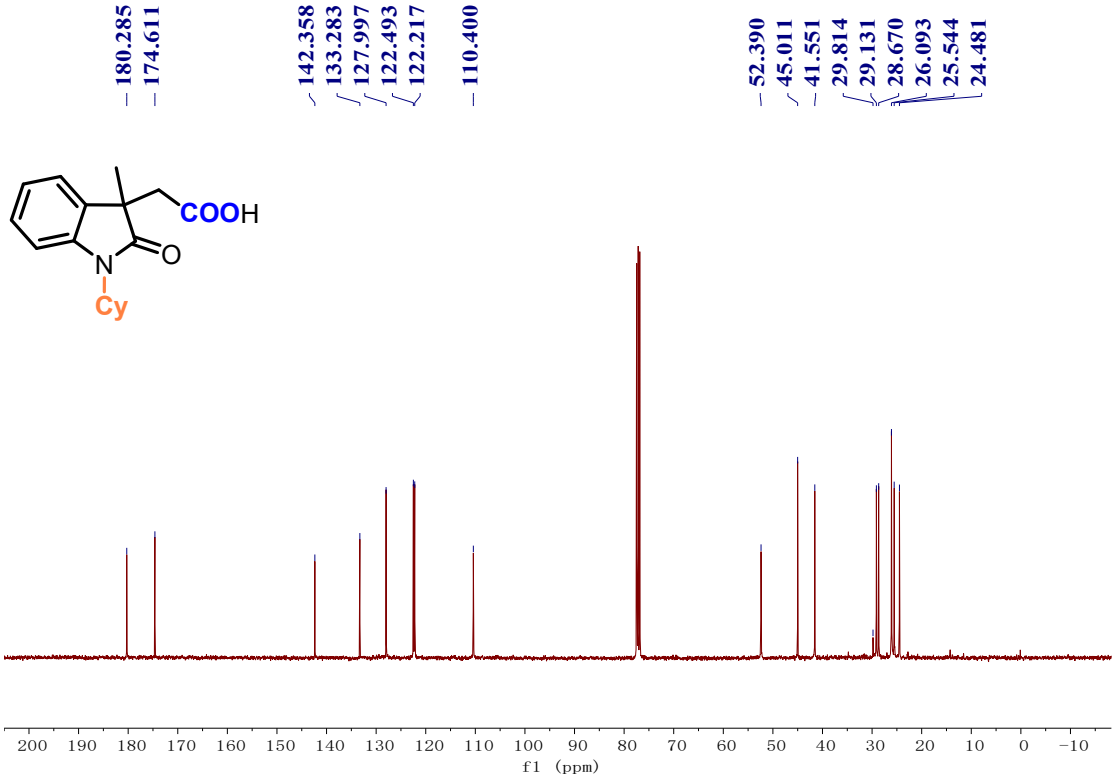
2-(1-cyclohexyl-3-methyl-2-oxoindolin-3-yl)acetic acid (2p)

^{1}H NMR (400 MHz, $CDCl_3$)



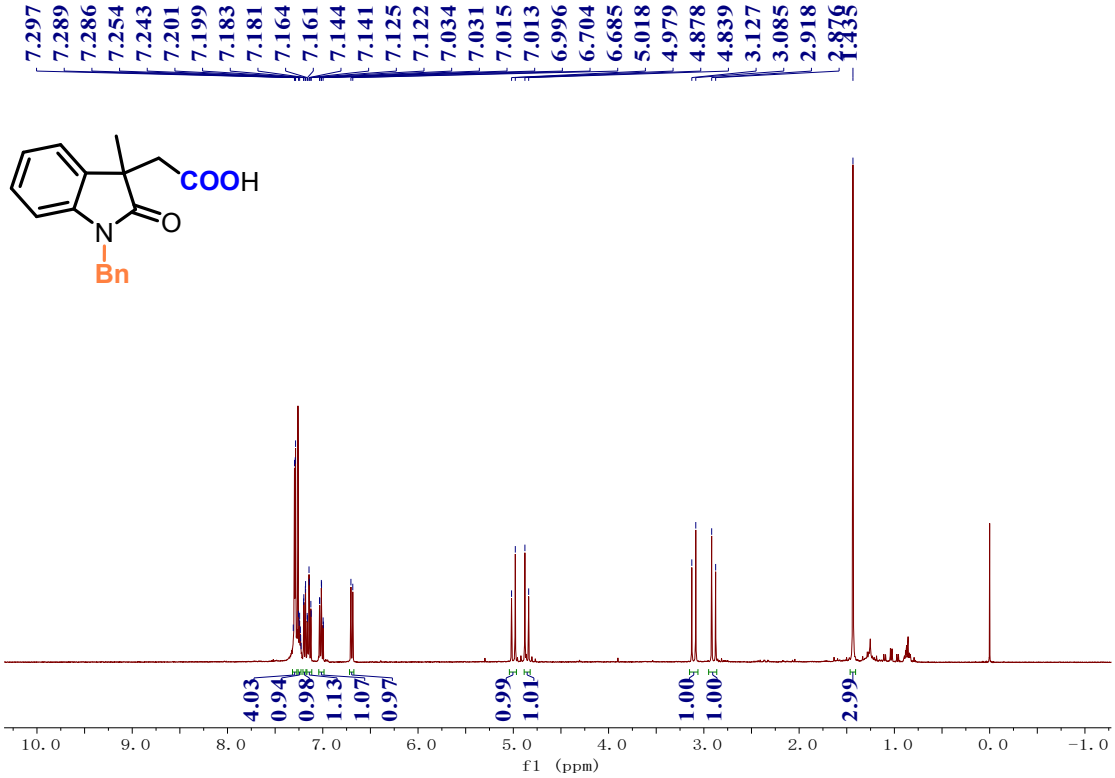
2-(1-cyclohexyl-3-methyl-2-oxoindolin-3-yl)acetic acid (2p)

^{13}C NMR (100 MHz, $CDCl_3$)



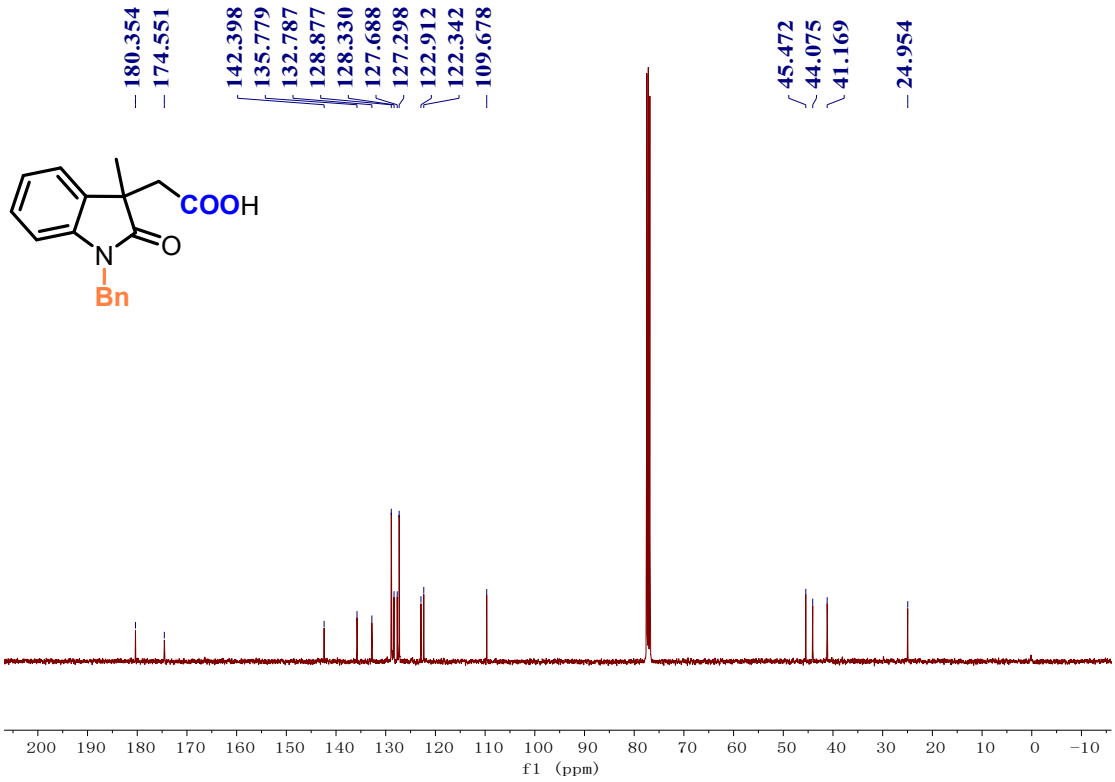
2-(1-benzyl-3-methyl-2-oxoindolin-3-yl)acetic acid (2q)

^{1}H NMR (400 MHz, $CDCl_3$)



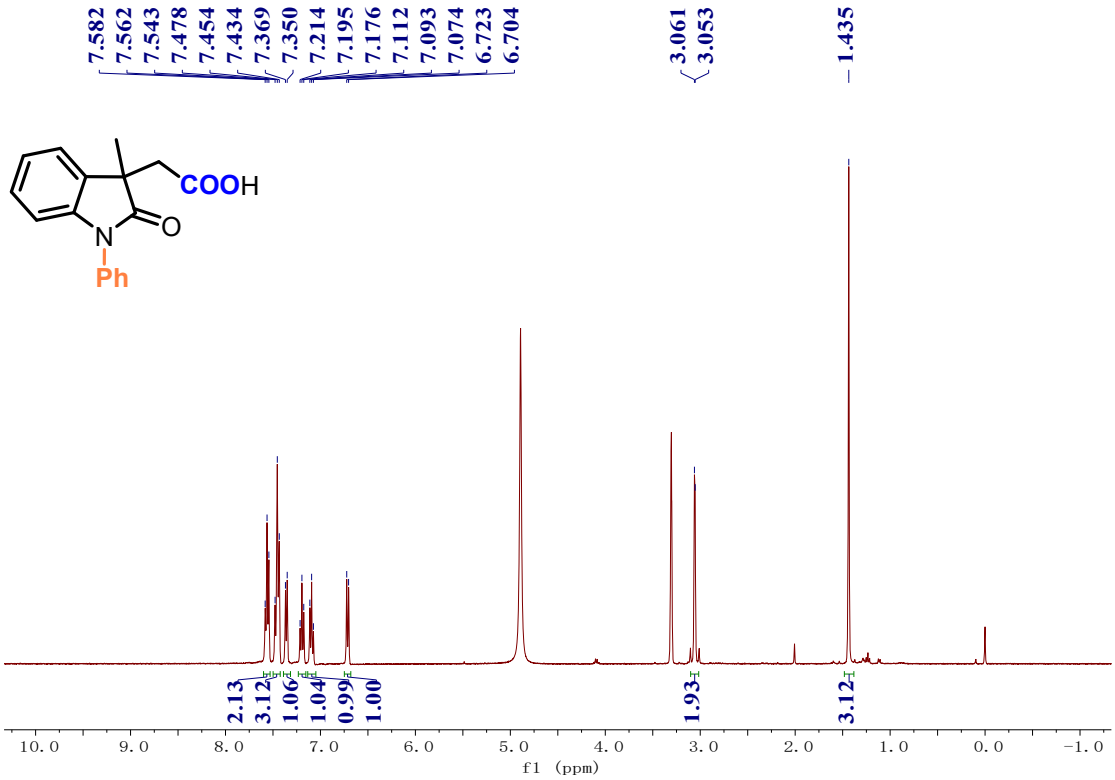
2-(1-benzyl-3-methyl-2-oxoindolin-3-yl)acetic acid (2q)

^{13}C NMR (100 MHz, $CDCl_3$)



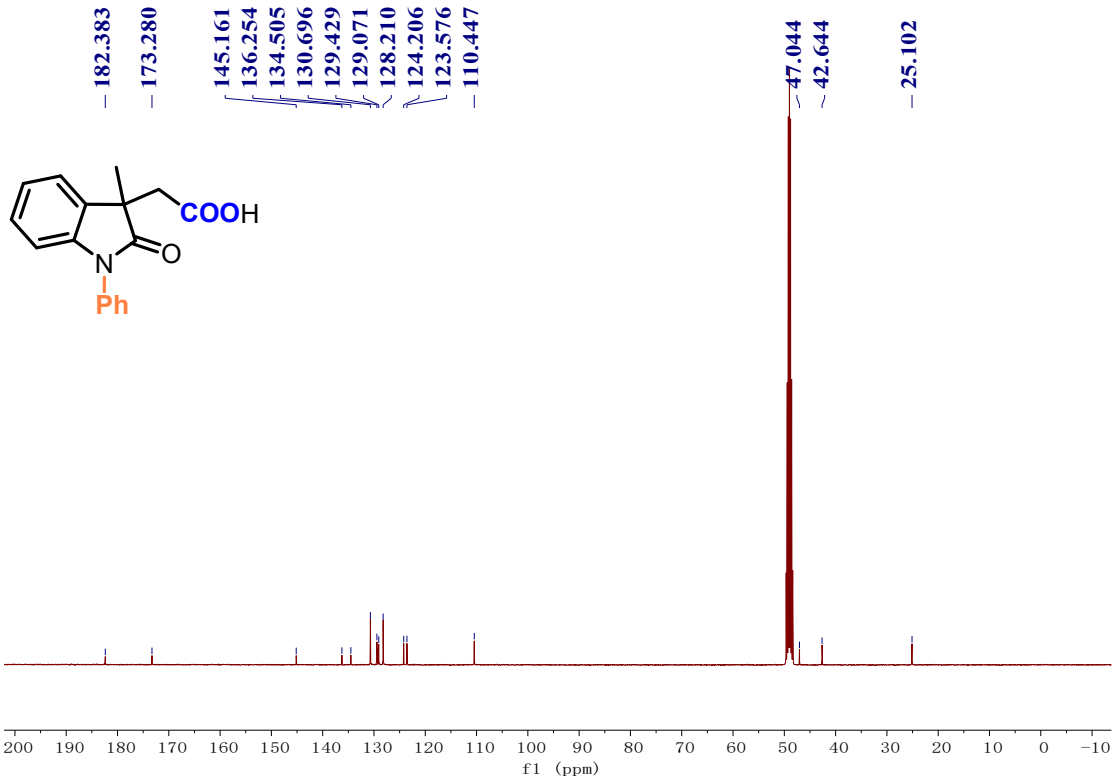
2-(3-methyl-2-oxo-1-phenylindolin-3-yl)acetic acid (2r)

^{1}H NMR (400 MHz, CD_3OD)



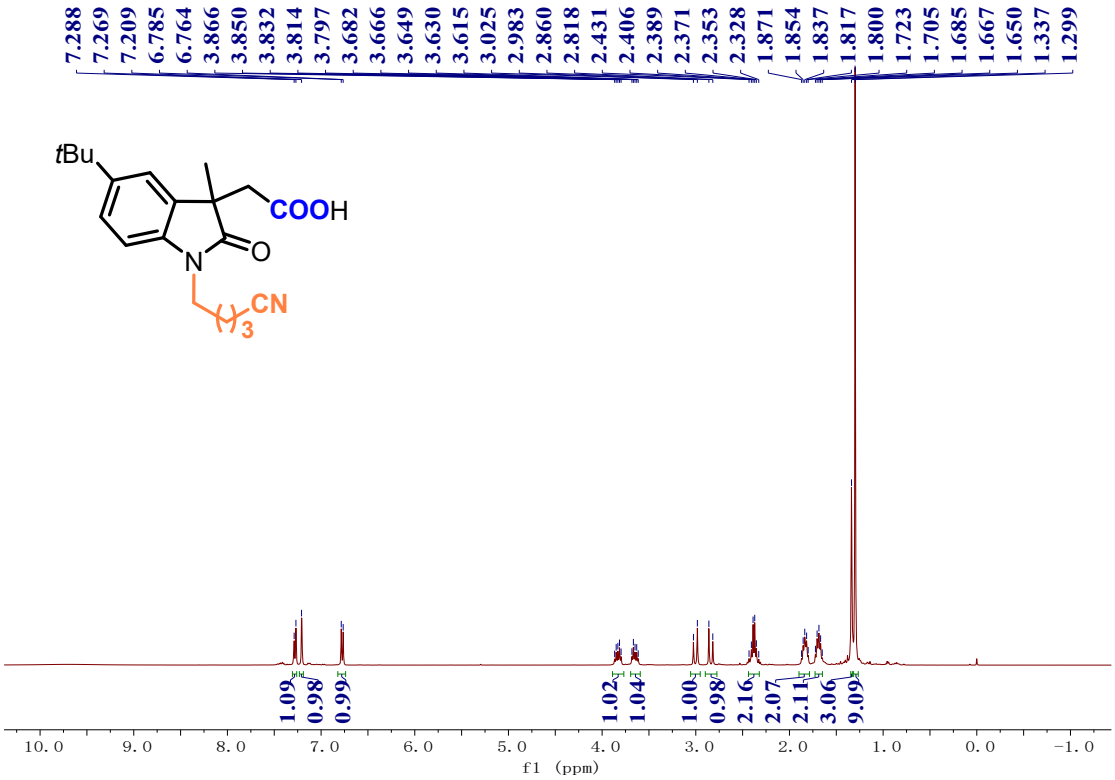
2-(3-methyl-2-oxo-1-phenylindolin-3-yl)acetic acid (2r)

^{13}C NMR (100 MHz, CD_3OD)



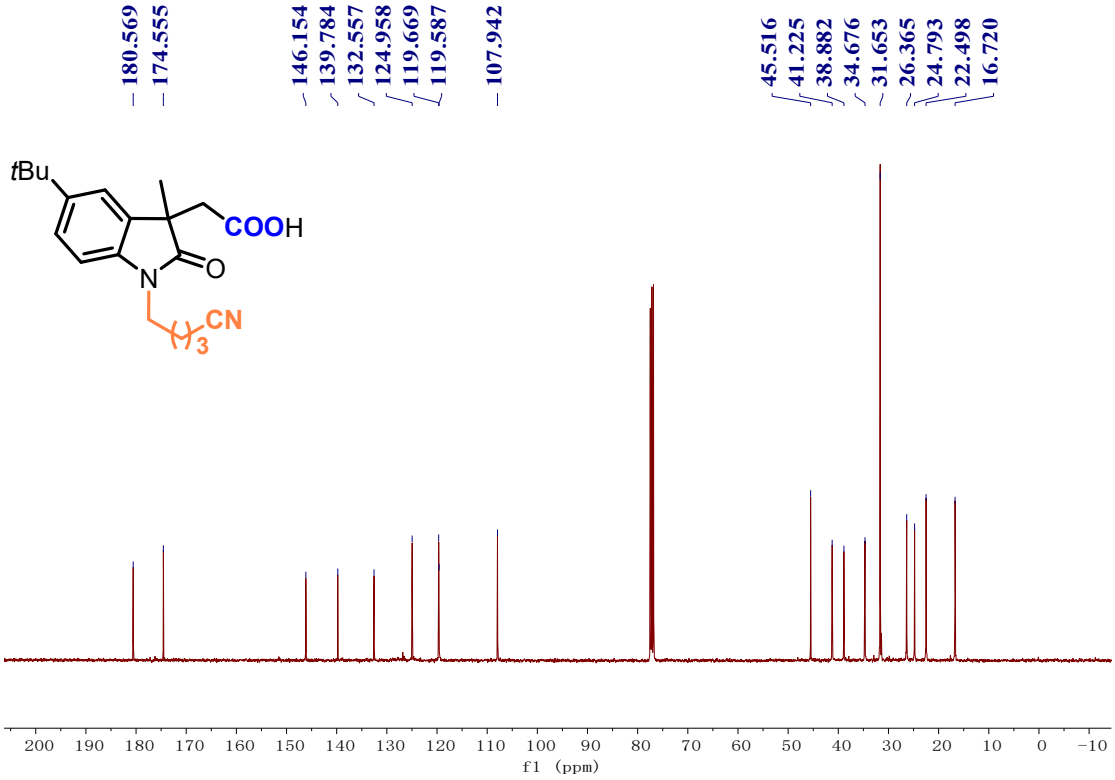
2-(5-(*tert*-butyl)-1-(4-cyanobutyl)-3-methyl-2-oxoindolin-3-yl)acetic acid (2s)

^{1}H NMR (400 MHz, $CDCl_3$)



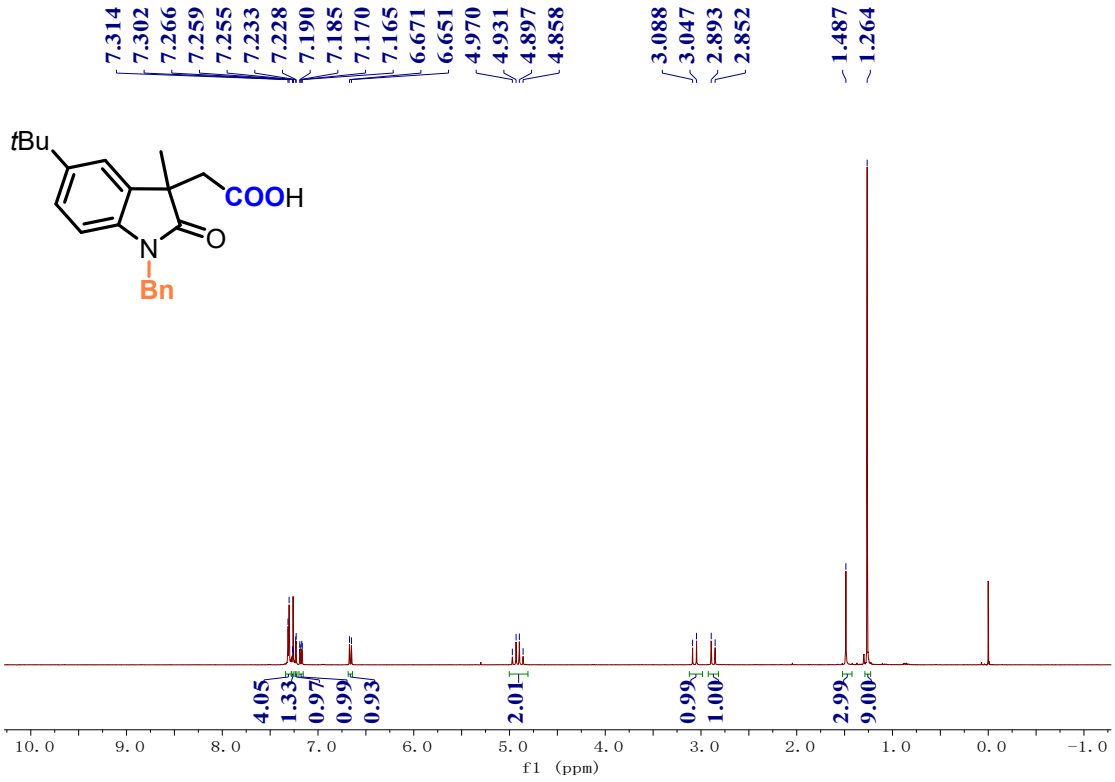
2-(5-(*tert*-butyl)-1-(4-cyanobutyl)-3-methyl-2-oxoindolin-3-yl)acetic acid (2s)

^{13}C NMR (100 MHz, $CDCl_3$)



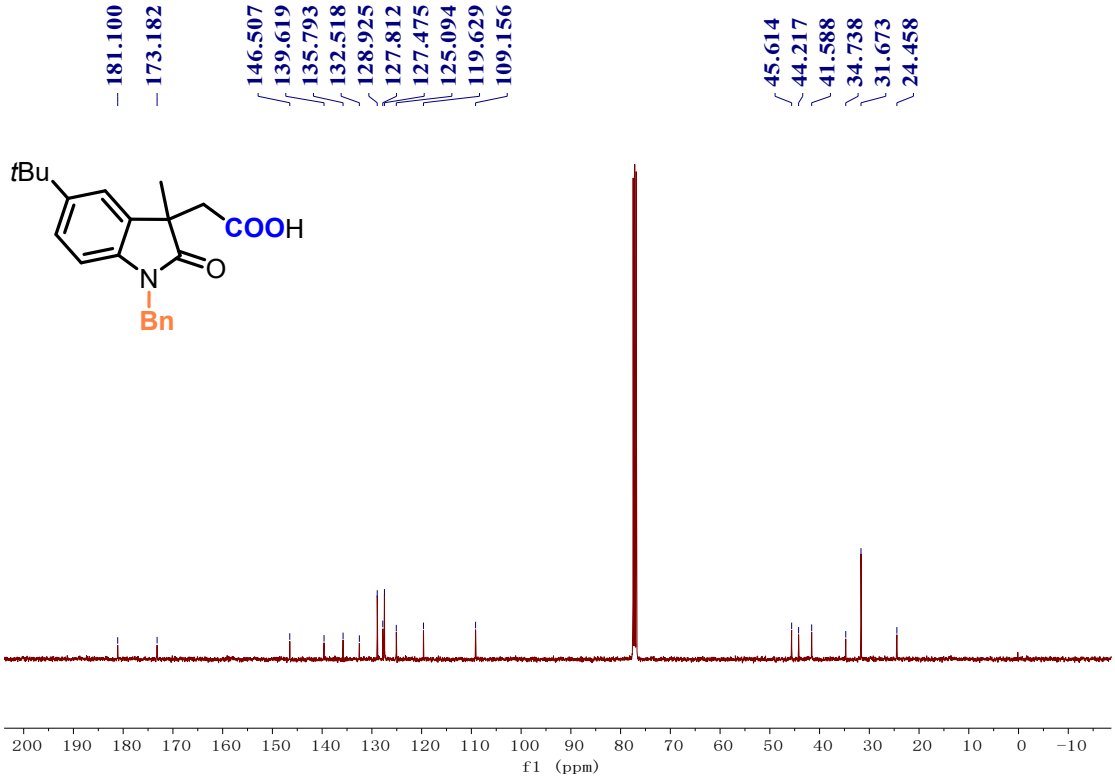
2-(1-benzyl-5-(*tert*-butyl)-3-methyl-2-oxoindolin-3-yl)acetic acid (2t)

^{1}H NMR (400 MHz, $CDCl_3$)



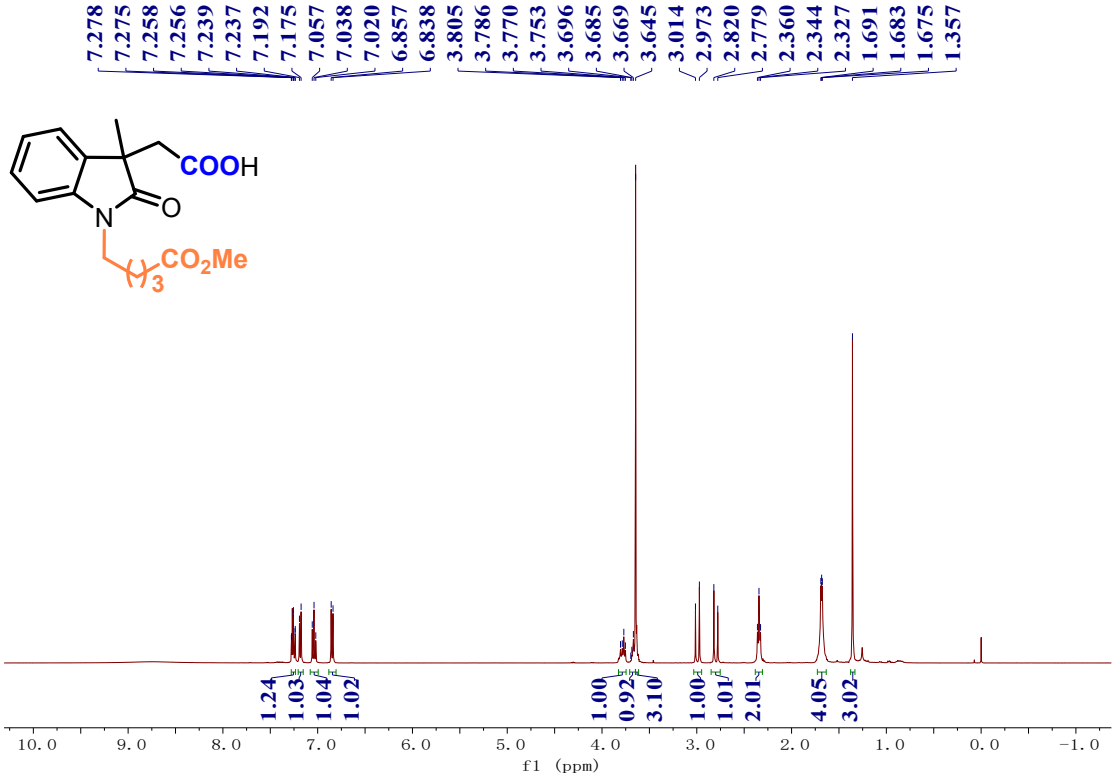
2-(1-benzyl-5-(*tert*-butyl)-3-methyl-2-oxoindolin-3-yl)acetic acid (2t)

^{13}C NMR (100 MHz, $CDCl_3$)



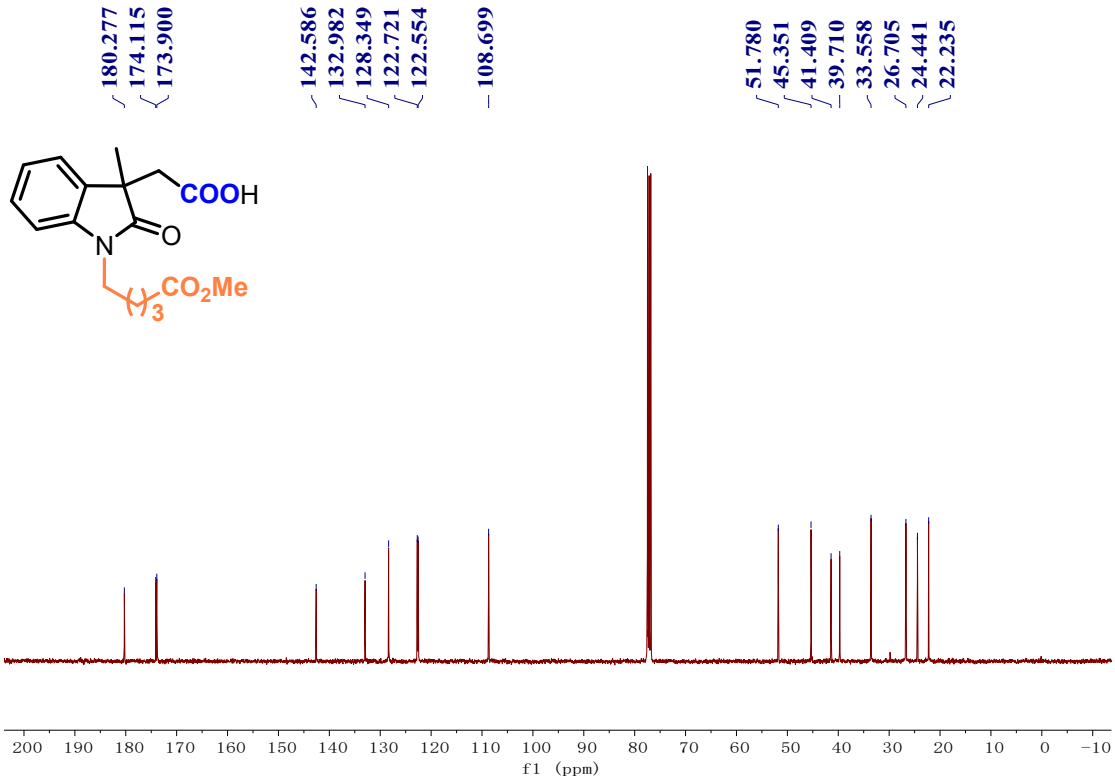
2-(1-(5-methoxy-5-oxopentyl)-3-methyl-2-oxoindolin-3-yl)acetic acid (2u)

^{1}H NMR (400 MHz, $CDCl_3$)



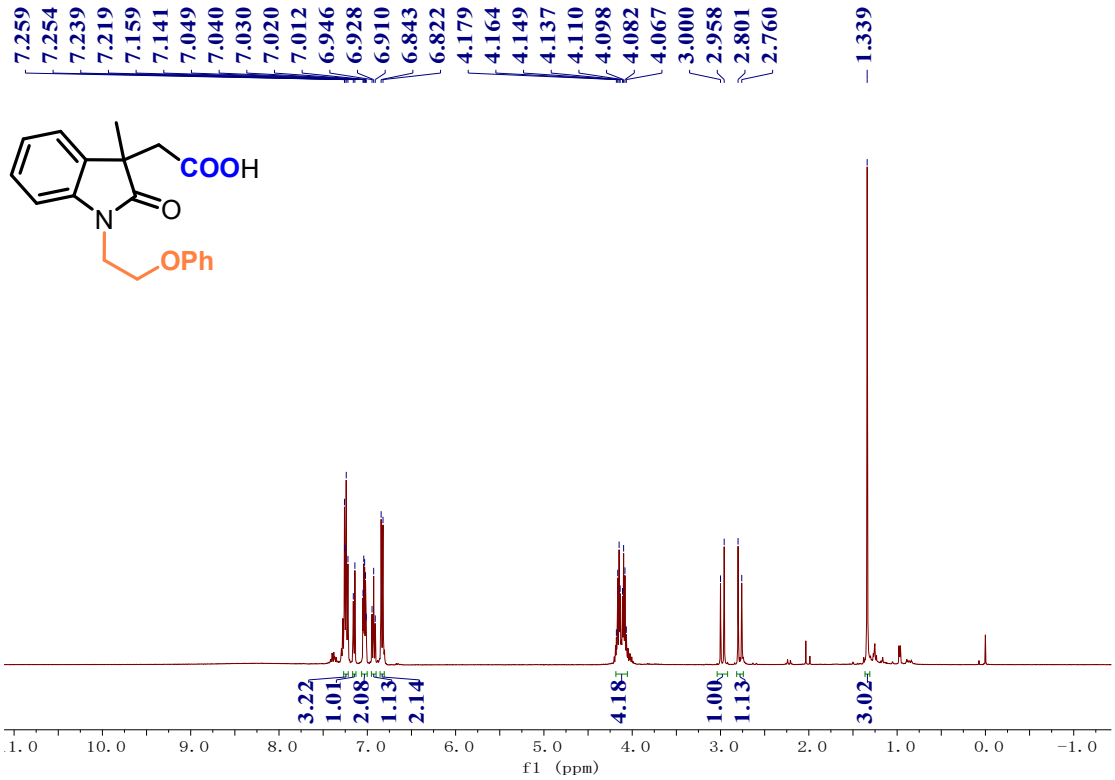
2-(1-(5-methoxy-5-oxopentyl)-3-methyl-2-oxoindolin-3-yl)acetic acid (2u)

^{13}C NMR (100 MHz, $CDCl_3$)



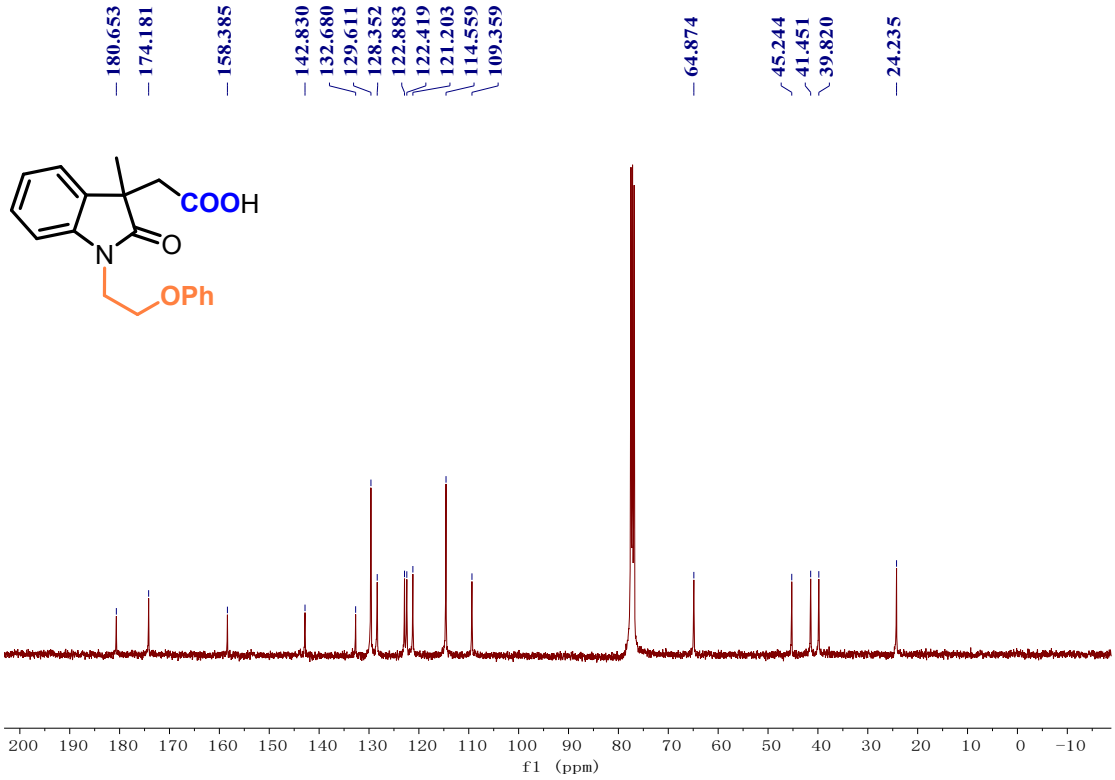
2-(3-methyl-2-oxo-1-(2-phenoxybutyl)indolin-3-yl)acetic acid (2v)

^{1}H NMR (400 MHz, $CDCl_3$)



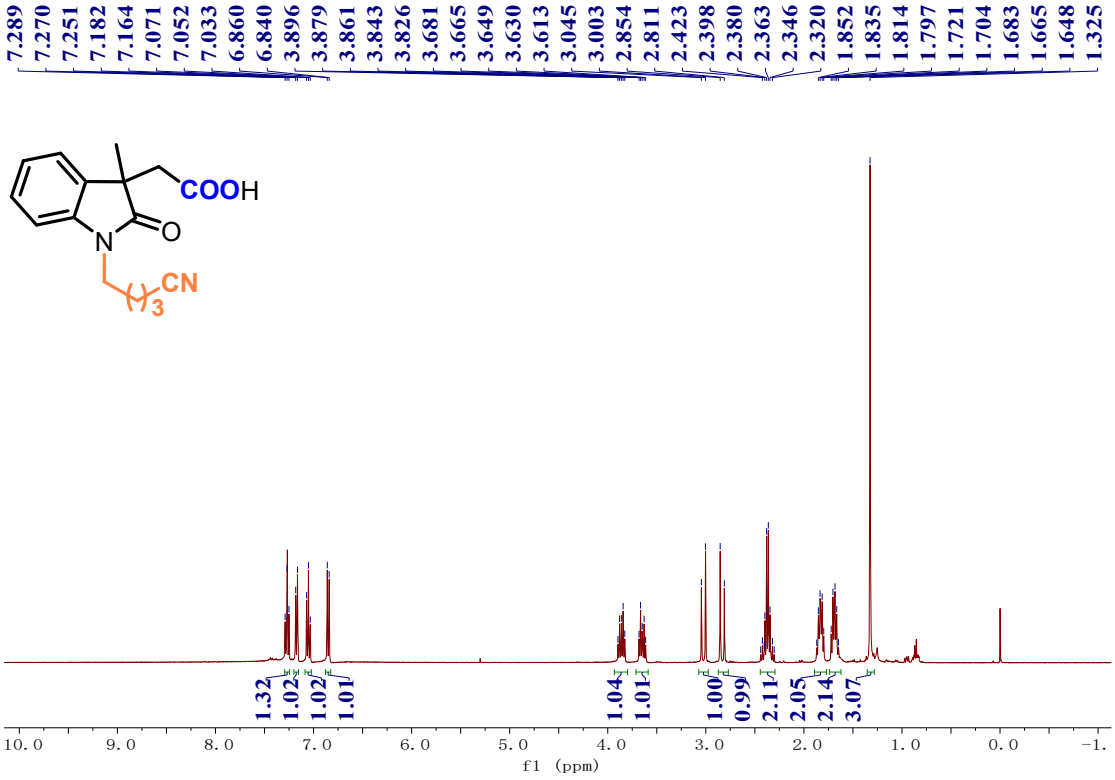
2-(3-methyl-2-oxo-1-(2-phenoxybutyl)indolin-3-yl)acetic acid (2v)

^{13}C NMR (100 MHz, $CDCl_3$)



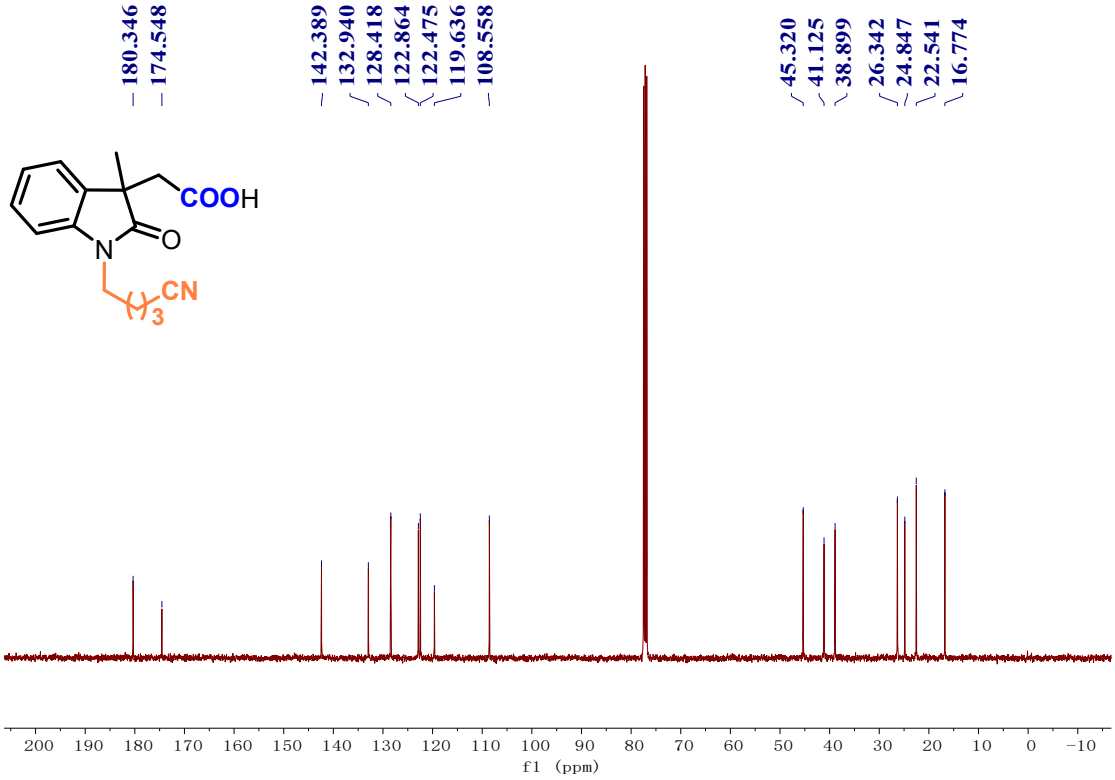
2-(1-(4-cyanobutyl)-3-methyl-2-oxoindolin-3-yl)acetic acid (2w)

^{1}H NMR (400 MHz, $CDCl_3$)



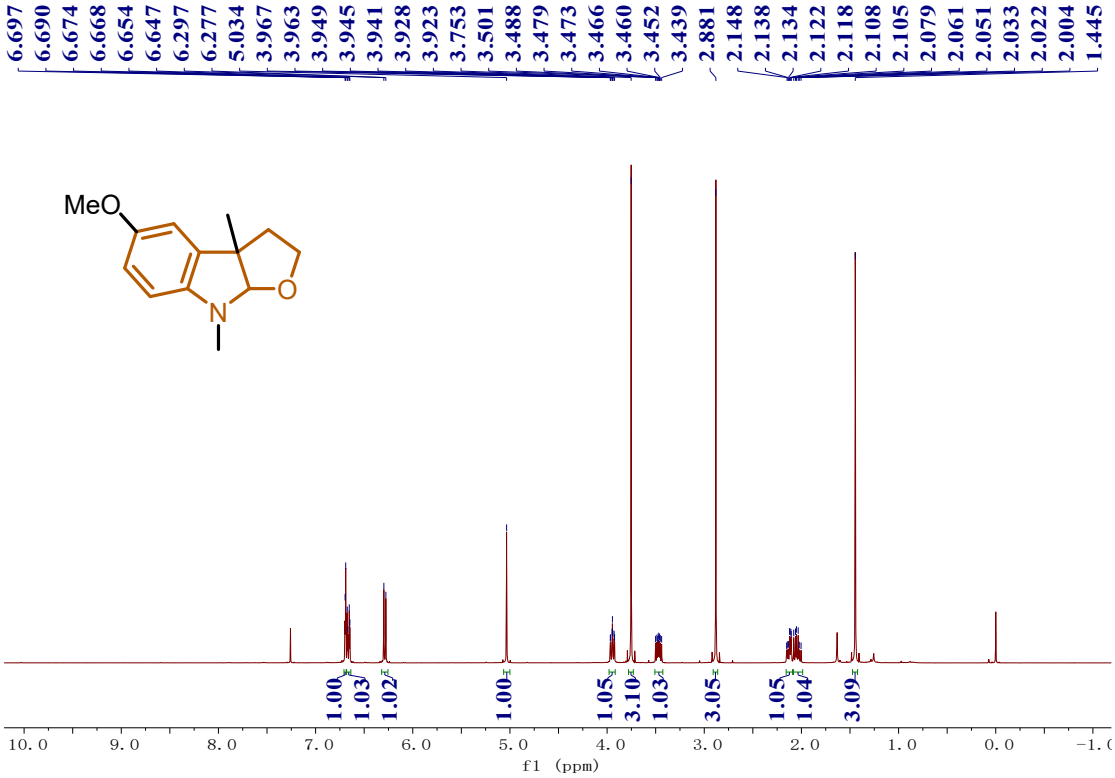
2-(1-(4-cyanobutyl)-3-methyl-2-oxoindolin-3-yl)acetic acid (2w)

^{13}C NMR (100 MHz, $CDCl_3$)



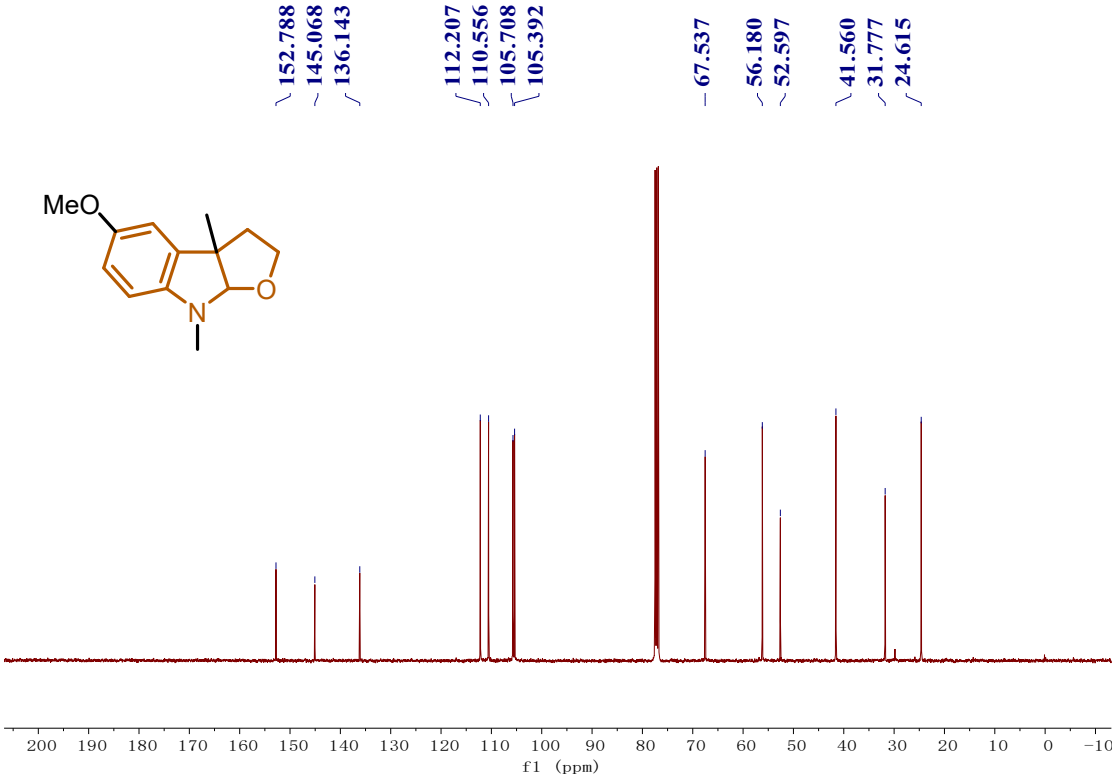
5-methoxy-3a,8-dimethyl-3,3a,8,8a-tetrahydro-2*H*-furo[2,3-*b*]indole (3)

^{1}H NMR (400 MHz, $CDCl_3$)



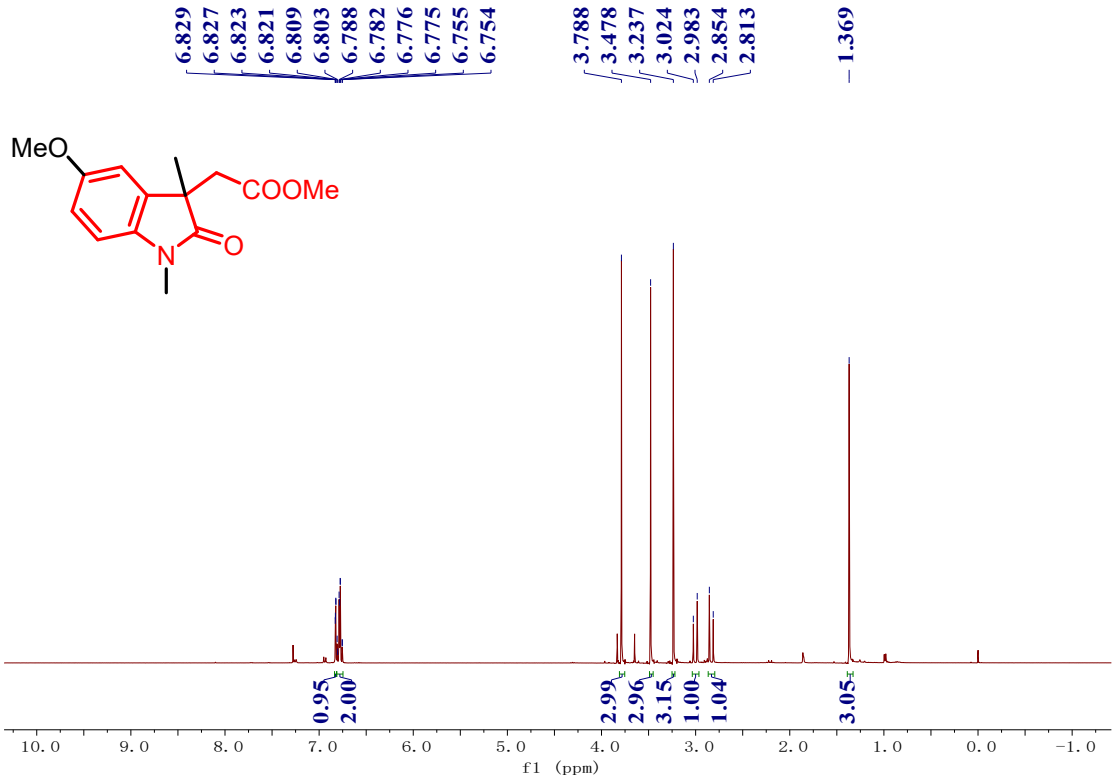
5-methoxy-3a,8-dimethyl-3,3a,8,8a-tetrahydro-2*H*-furo[2,3-*b*]indole (3)

^{13}C NMR (100 MHz, $CDCl_3$)



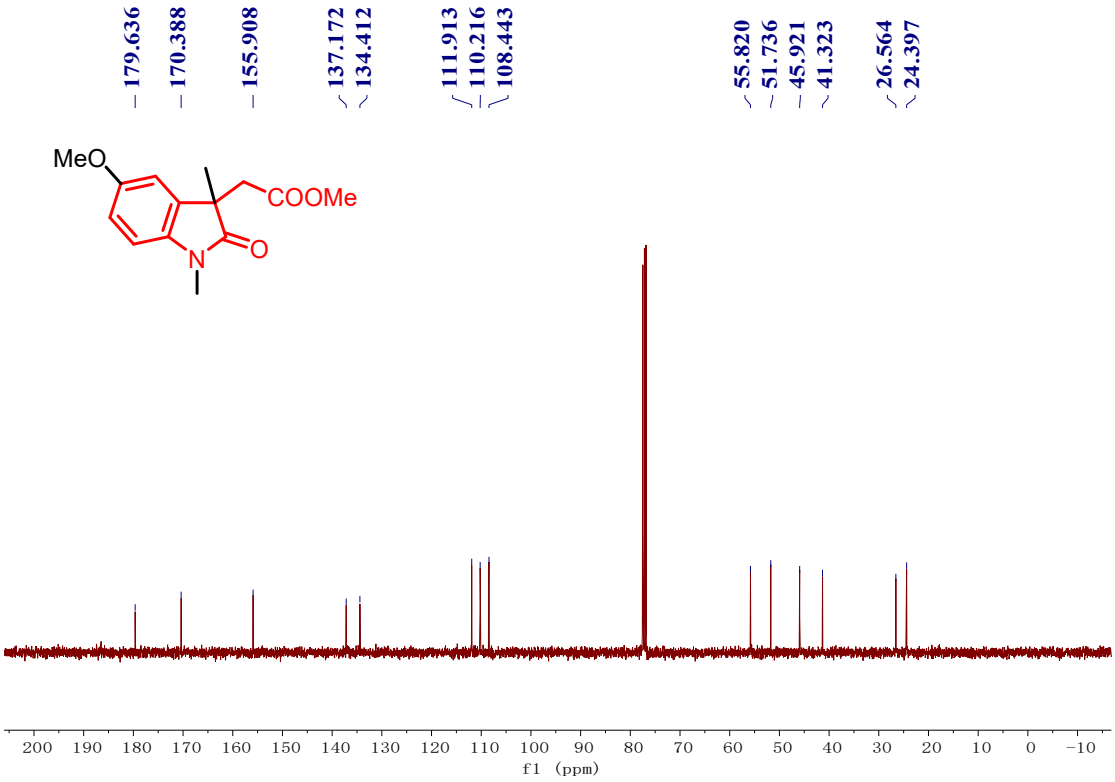
methyl 2-(5-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)acetate (4)

^{1}H NMR (400 MHz, $CDCl_3$)



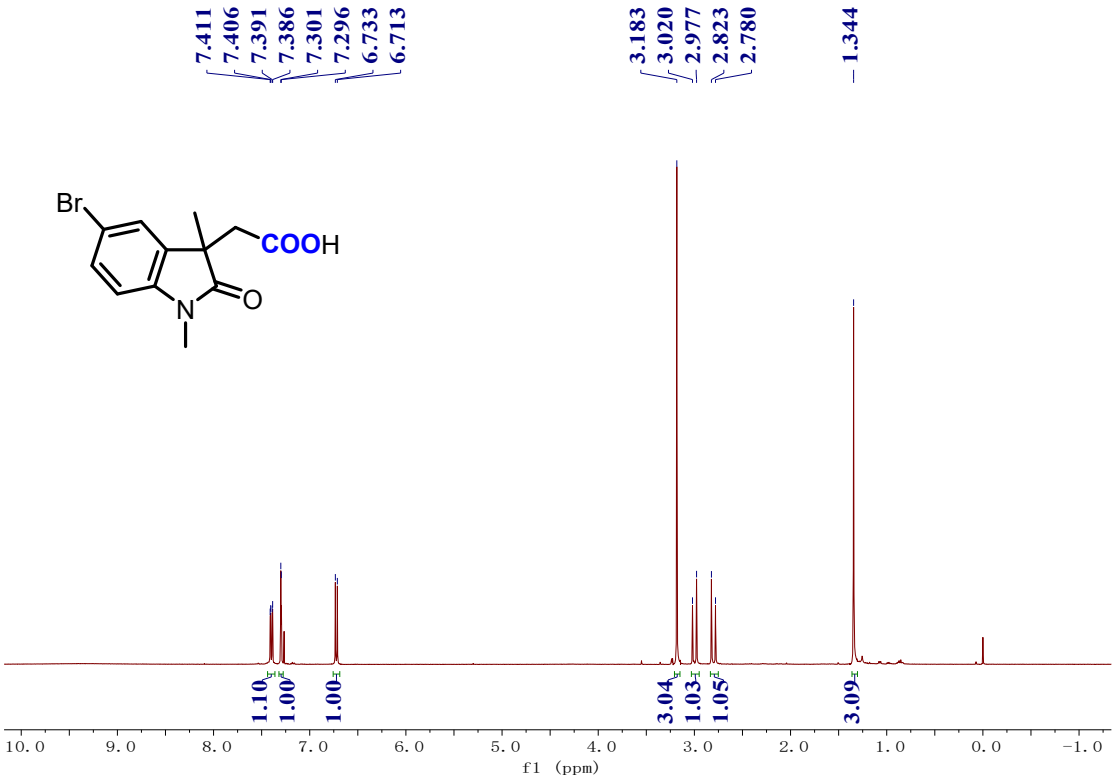
methyl 2-(5-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)acetate (4)

^{13}C NMR (100 MHz, $CDCl_3$)



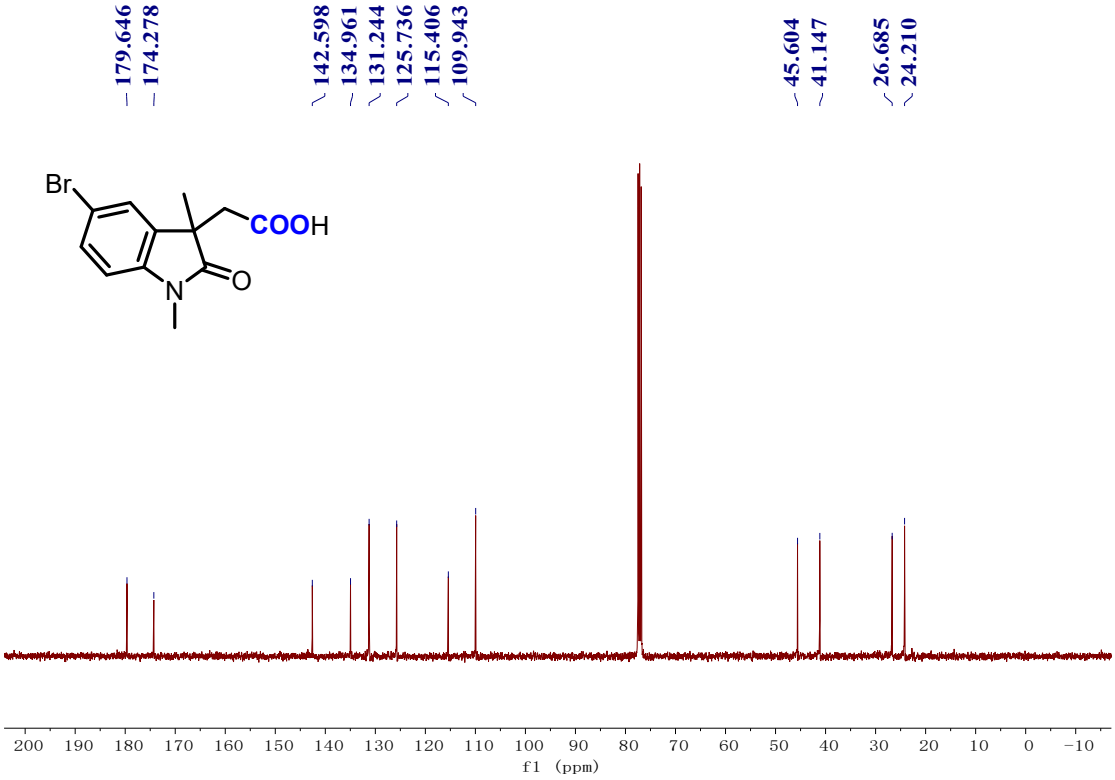
2-(5-bromo-1,3-dimethyl-2-oxoindolin-3-yl)acetic acid (5)

^{1}H NMR (400 MHz, $CDCl_3$)



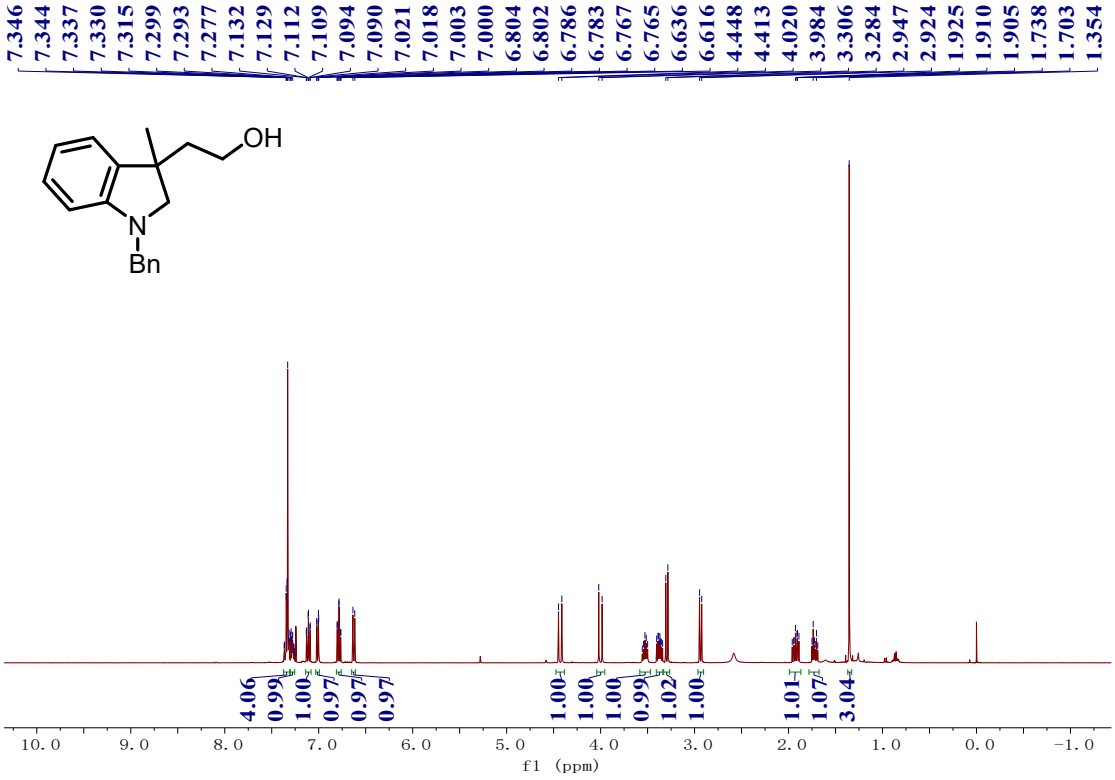
2-(5-bromo-1,3-dimethyl-2-oxoindolin-3-yl)acetic acid (5)

^{13}C NMR (100 MHz, $CDCl_3$)



2-(1-benzyl-3-methylindolin-3-yl)ethan-1-ol (6)

^{1}H NMR (400 MHz, $CDCl_3$)



2-(1-benzyl-3-methylindolin-3-yl)ethan-1-ol (6)

^{13}C NMR (100 MHz, $CDCl_3$)