Supplementary information

Visible-Light Excited Copper Activating Unactivated Alkyl Iodides for Radical Cascade Addition/Cyclization to Access Oxindole Derivatives

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Copper photocatalysis, Alkyl radical, Unactivated iodides, Radical cyclization.

Content

1. General Information

1.1 Materials and methods

Unless otherwise noted, all the materials were commercially available and used without further purification. All solvents were dried before use according to the standard methods. All reactions were performed in an N_2-filled glovebox using standard Schlenk techniques unless otherwise noted. All reactions were monitored by thin-layer chromatography (TLC), visualized by UV and $KMnO_4$ staining. Chromatographic purification of products was accomplished by silica gel chromatography. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Bruker Avance II 400. NMR data is reported relative to internal $CHCl_3$ (^{1}H, $\delta = 7.26$), $CDCl_3$ (^{13}C, $\delta = 77.0$). Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ) in ppm; multiplicities are indicated s (singlet), brs (broad singlet), d (doublet), t (triplet), m (multiplet); coupling constants (J) are in Hertz (Hz) ^{13}C NMR spectra were reported as chemical shifts in ppm. The HRMS were obtained by using a Q Exactive high resolution liquid chromatography mass spectrometer (Q Exactive Plus) in ESI^{+} mode or ESI^{-} mode. The eight-position parallel light reaction system (RLH-18) and the large volume light reaction system (RLH-054) with 410 nm blue LEDs were purchased from Beijing Roger Technologies.

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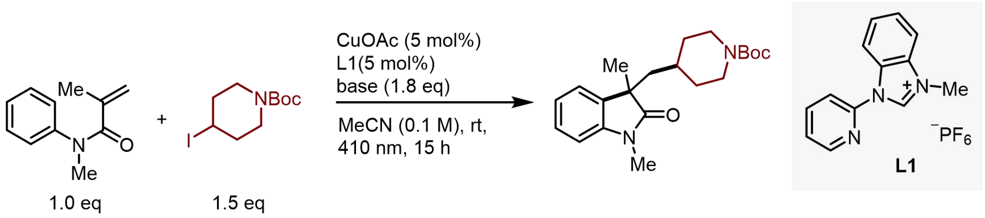
2. Experimental details for radical cascade cyclization

2.1 Reaction optimization

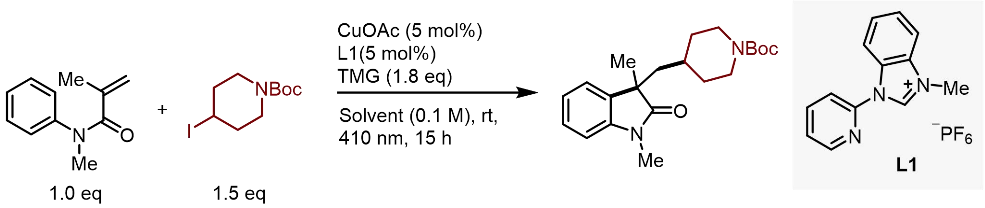
Procedure for optimization : To an oven-dried 10 mL reaction vial were added Cu salt (5 mol%), L1 (5 mol%), and 1 mL solvent in a nitrogen-filled glove box. The resulting mixture was stirred for 5 min, followed by adding base, *N*-Arylacrylamides (1.0 equiv) and *tert*-butyl 4-iodopiperidine-1-carboxylate (1.5 equiv) in sequence, and sealed with a screwed cap. The sealed vial was placed on a photo-reactor under irradiation of 6W LEDs. The mixture was stirred at 25 °C for 15 h, quenched with H_2O, and extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4, concentrated in vacuo. The crude product was analyzed by ^1H NMR with 1,3,5-Trimethoxybenzene as the internal standard.

Table S1 base effect



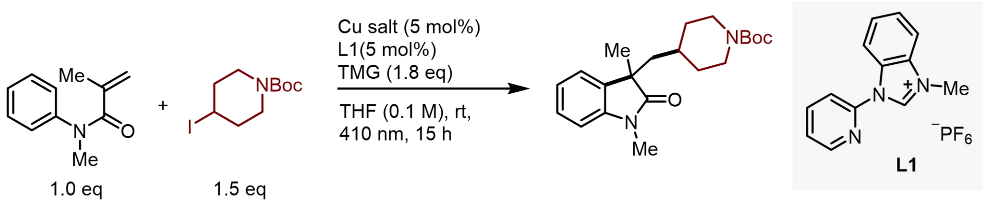
entry	base	Yield(%)
1	MTBD	38
2	Et_3N	15
3	DIPEA	18
4	DBU	trace
5	TMG	47
6	Cs_2CO_3	trace
7	K_3PO_4	18
8	BTMG	15
9	DBACO	15

Table S2 solvent effect



entry	solvent	Yield(%)
1	THF	72
2	DMF	54
3	DME	42
4	DMSO	27

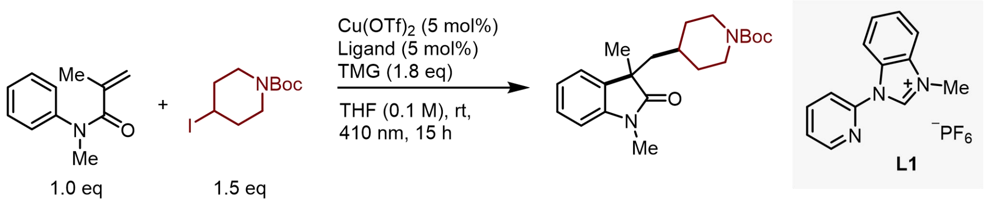
Table S3 copper salt effect



entry	Cu salt	Yield(%)
1	CuBr	75
2	CuI	63
3	$Cu(OAc)_2$	69
4	$Cu(OTf)_2$	90 (88)

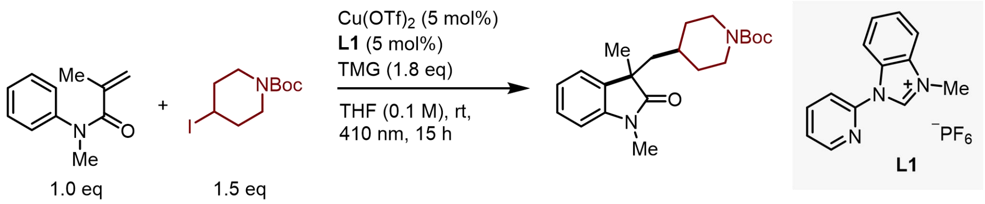
Isolated yield in parentheses.

Table S4 ligand effect



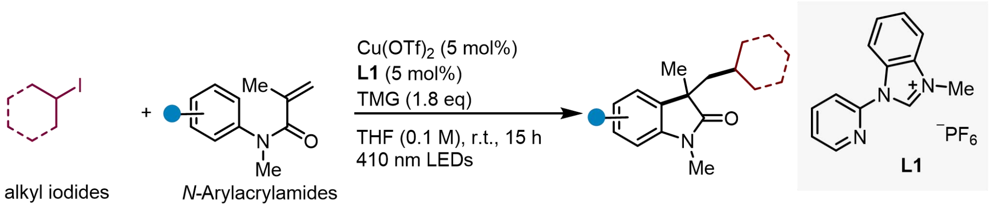
entry	Ligand	Yield(%)
1	BINAP	16
2	1,10-Phenanthroline	trace
3	dtbbpy	trace
4	terpyridine	trace
5	IMes NHC	5

Table S5 Control experiments



entry	variants from standard conditions	Yield(%)
1	w/o light	n.d.
2	w/o $Cu(OTf)_2$	8%
3	w/o L1	trace
4	open in air	n.d.

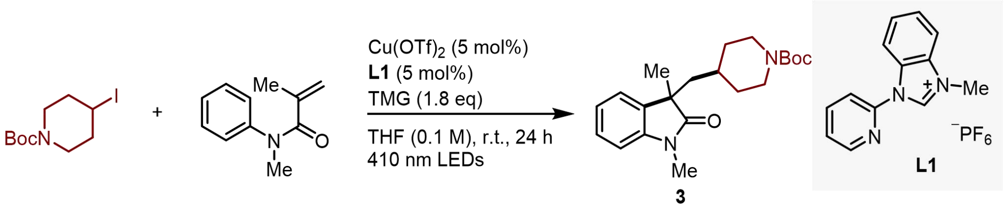
2.2 General procedure of C(sp3)-C formation (general procedure)



To an oven-dried 10 mL reaction vial were added $Cu(OTf)_2$ (1.81 mg, 0.005 mmol, 5 mol%), **L1** (1.77 mg, 0.005 mmol, 5 mol%), and 1 mL THF in a nitrogen-filled glove box. The resulting mixture was stirred for 5 min, followed by adding 1,1,3,3-Tetramethylguanidine (TMG) (23 μL, 0.18 mmol, 1.8 equiv), *N*-Arylacrylamides (0.1 mmol, 1.0 equiv) and alkyl iodides (0.15 mmol, 1.5 equiv) in sequence, and sealed with a screwed cap. The sealed vial was placed on a photo-reactor under irradiation of LEDs (410 nm, 6 W). The mixture was stirred at 25 °C for 15 h, quenched with H_2O, and extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4, concentrated in vacuo. The crude product was purified by silica gel column chromatography to afford the coupling product.

Figure S1. The eight-position parallel light reaction system (RLH-18)

2.3 scale up reaction



6 mmol scale for synthesis of 3:

To an oven-dried 250 mL round-bottomed flask were added Cu(OTf)$_2$ (108.6 mg, 0.30 mmol, 5 mol%), **L1** (106.2 mg, 0.30 mmol, 5 mol%), and 60 mL THF in a nitrogen-filled glove box. The resulting mixture was stirred for 10 min, followed by adding 1,1,3,3-Tetramethylguanidine (TMG) (1.38 mL, 10.8 mmol, 1.8 equiv), *N*-Arylacrylamides (1.05 g, 6.0 mmol, 1.0 equiv) and *tert*-butyl 4-iodopiperidine-1-carboxylate (2.80 g, 9.0 mmol, 1.5 equiv) in sequence, and sealed with a screwed cap. The sealed flask was placed on a large volume photo-reactor under irradiation of LEDs (410 nm, 50 W × 2). The mixture was stirred at 25 °C for 24 h, quenched with H$_2$O, and extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na$_2$SO$_4$, concentrated in vacuo. The crude product was purified by silica gel column chromatography to afford the coupling product **3** (1.72 g, 80% yield).

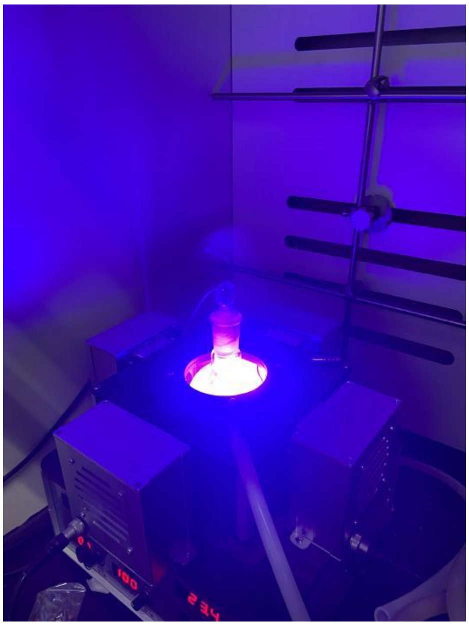
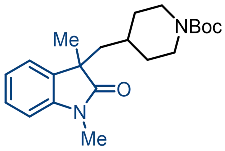


Figure S2. The large volume light reaction system (RLH-054)

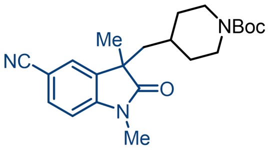
3. Characterization data of cyclization products

tert-butyl 4-((1,3-dimethyl-2-oxoindolin-3-yl)methyl)piperidine-1-carboxylate (3)



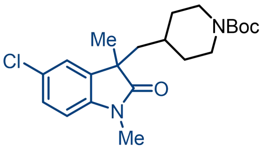
Prepared according to the ***general procedure*** from *N*-methyl-*N*-phenylmethacrylamide (17.5 mg, 0.1 mmol) and *tert*-butyl 4-iodopiperidine-1-carboxylate (46.7 mg, 0.15 mmol), The crude residue was purified by column chromatography to yield **3** (28.9 mg, 88% yield) as a colorless oil.
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.29 – 7.24 (m, 1H), 7.15 (d, *J* = 7.2 Hz, 1H), 7.09 – 7.03 (m, 1H), 6.85 (d, *J* = 7.7 Hz, 1H), 3.84 (brs, 2H), 3.22 (s, 3H), 2.41 (q, *J* = 13.3, 12.7 Hz, 2H), 1.97 (dd, *J* = 14.1, 6.1 Hz, 1H), 1.76 (dd, *J* = 14.1, 5.2 Hz, 1H), 1.39 (s, 9H), 1.33 – 1.24 (m, 4H), 1.12 – 0.99 (m, 3H), 0.96 – 0.84 (m, 1H). **^{13}C NMR (101 MHz, CDCl$_3$):** δ 180.7, 154.6, 142.9, 134.0, 127.8, 122.6, 122.5, 108.1, 79.1, 47.7, 44.4, 33.1, 33.0, 32.4, 28.4, 26.2, 26.1.
All other spectroscopic analyses were in agreement with the literature[1].

***N*-(4-cyanophenyl)-N-methylmethacrylamide (4)**



Prepared according to the ***general procedure*** from *N*-(4-cyanophenyl)-*N*-methyl methacrylamide (20.2 mg, 0.1 mmol) and *tert*-butyl 4-iodopiperidine-1-carboxylate (46.7 mg, 0.15 mmol), The crude residue was purified by column chromatography to yield **4** (35.1 mg, 92% yield) as a colorless oil.
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.61 (d, *J* = 8.1 Hz, 1H), 7.40 (s, 1H), 6.92 (d, *J* = 8.1 Hz, 1H), 3.86 (brs, 2H), 3.24 (s, 3H), 2.49 – 2.34 (m, 2H), 2.05 – 1.96 (m, 1H), 1.81 – 1.73 (m, 1H), 1.39 (s, 9H), 1.33 (s, 3H), 1.26 – 1.19 (m, 1H), 1.11 – 0.89 (m, 4H). **^{13}C NMR (101 MHz, CDCl$_3$):** δ 180.3, 154.5, 146.8, 135.0, 133.3, 126.0, 119.2, 108.6, 105.7, 79.3, 47.5, 44.1, 33.1, 33.0, 32.2, 28.3, 26.5, 26.0. **HRMS (ESI):** Calcd for $C_{22}H_{29}N_3O_3Na$ $[M+Na]^+$:406.2101, found 406.2099

tert-butyl 4-((5-chloro-1,3-dimethyl-2-oxoindolin-3-yl)methyl)piperidine-1-carboxylate (5)

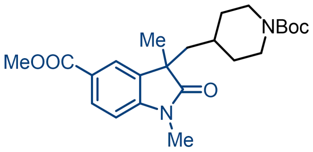


Prepared according to the ***general procedure*** from *N*-(4-chlorophenyl)-*N*-methyl methacrylamide (21.0 mg, 0.1 mmol) and *tert*-butyl 4-iodopiperidine-1-carboxyla te (46.7 mg, 0.15 mmol), The crude residue was purified by column chromatography to yield **5** (34.6 mg, 88% yield) as a colorless oil.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.24 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.12 (d, *J* = 1.9 Hz, 1H), 6.77 (d, *J* = 8.3 Hz, 1H), 3.86 (brs, 2H), 3.20 (s, 3H), 2.43 (t, *J* = 11.5 Hz, 2H), 1.97 (dd, *J* = 14.2, 6.4 Hz, 1H), 1.73 (dd, *J* = 14.2, 5.1 Hz, 1H), 1.39 (s, 9H), 1.31 (s, 3H), 1.28 – 1.22 (m, 1H), 1.15 – 0.90 (m, 4H). **^{13}C NMR (101 MHz, CDCl$_3$):** δ 180.1, 154.6, 141.5, 135.7, 128.0, 127.8, 123.2, 109.0, 79.2, 47.9, 44.3, 33.1, 33.0, 32.3, 28.4, 26.3, 26.2.

All other spectroscopic analyses were in agreement with the literature[2].

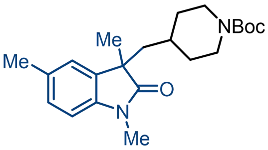
methyl 3-((1-(tert-butoxycarbonyl)piperidin-4-yl)methyl)-1,3-dimethyl-2-oxoindoline-5-carboxylate (6)



Prepared according to the ***general procedure*** from methyl 4-(*N*-methylmethacrylamido)benzoate (23.3 mg, 0.1 mmol) and *tert*-butyl 4-iodopiperidine-1-carboxylate (46.7 mg, 0.15 mmol), The crude residue was purified by column chromatography to yield **71** (27.0 mg, 65% yield) as a colorless oil.

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.03 (d, *J* = 8.2 Hz, 1H), 7.83 (s, 1H), 6.89 (d, *J* = 8.2 Hz, 1H), 3.91 (s, 3H), 3.84 (brs, 2H), 3.25 (s, 3H), 2.46 – 2.34 (m, 2H), 2.00 (dd, *J* = 14.2, 6.2 Hz, 1H), 1.81 (dd, *J* = 14.1, 4.9 Hz, 1H), 1.39 (s, 9H), 1.34 (s, 3H), 1.29 – 1.20 (m, 1H), 1.12 – 0.98 (m, 3H), 1.12 – 0.98 (m, 1H). **^{13}C NMR (101 MHz, CDCl$_3$):** δ 181.0, 166.9, 154.6, 147.1, 133.9, 130.6, 124.5, 123.9, 107.7, 79.2, 52.1, 47.5, 44.2, 33.1, 33.0, 32.3, 28.4, 26.4, 26.1. **HRMS (ESI):** Calcd for $C_{23}H_{32}N_2O_5Na$ $[M+Na]^+$:439.2203, found 439.2198

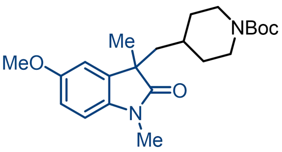
***tert*-butyl 4-((1,3,5-trimethyl-2-oxoindolin-3-yl)methyl)piperidine-1-carboxylate (7)**



Prepared according to the ***general procedure*** from *N*-methyl-*N*-(*p*-tolyl)methacrylamide (18.9 mg, 0.1 mmol) and *tert*-butyl 4-iodopiperidine-1-carboxylate (46.7 mg, 0.15 mmol), The crude residue was purified by column chromatography to yield **7** (32.4 mg, 87% yield) as a colorless oil.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.05 (d, *J* = 7.8 Hz, 1H), 6.95 (s, 1H), 6.73 (d, *J* = 7.9 Hz, 1H), 3.83 (brs, 2H), 3.19 (s, 3H), 2.50 – 2.29 (m, 5H), 1.95 (dd, *J* = 14.1, 6.3 Hz, 1H), 1.72 (dd, *J* = 14.1, 5.3 Hz, 1H), 1.39 (s, 9H), 1.31 – 1.28 (m, 4H), 1.15 – 0.85 (m, 4H). **^{13}C NMR (101 MHz, CDCl$_3$):** δ 180.6, 154.6, 140.5, 134.0, 132.0, 128.0, 123.4, 107.8, 79.1, 47.7, 44.4, 33.1, 33.0, 32.4, 28.4, 26.2, 26.2, 21.2. **HRMS (ESI):** Calcd for $C_{22}H_{32}N_2O_3Na$ $[M+Na]^+$:395.2305, found 395.2303

***tert*-butyl 4-((5-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)methyl)piperidine-1-carboxylate (8)**

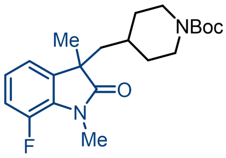


Prepared according to the ***general procedure*** from *N*-(4-methoxyphenyl)-*N*-methylmethacrylamide (20.5 mg, 0.1 mmol) and *tert*-butyl 4-iodopiperidine-1-carboxylate (46.7 mg, 0.15 mmol), The crude residue was purified by column chromatography to yield **70** (23.1 mg, 59% yield) as a colorless oil.

^{1}H NMR (400 MHz, CDCl$_3$): δ 6.81 – 6.73 (m, 3H), 3.92 – 3.78 (m, 5H), 3.20 (s, 3H), 2.49 – 2.36 (m, 1H), 1.97 (dd, *J* = 14.1, 6.4 Hz, 1H), 1.72 (dd, *J* = 14.1, 5.4 Hz, 1H), 1.39 (s, 9H), 1.31 (s, 3H), 1.27 – 1.21 (m, 1H), 1.15 – 0.99 (m, 3H), 0.95 – 0.84 (m, 1H). **^{13}C NMR (101 MHz, CDCl$_3$):** δ 180.4, 156.0, 154.6, 136.5, 135.5, 111.5, 110.5, 108.3, 79.1, 55.8, 48.1, 44.4, 33.1, 33.0, 32.4, 28.4, 26.3, 26.3.

All other spectroscopic analyses were in agreement with the literature[3].

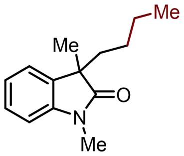
***tert*-butyl 4-((7-fluoro-1,3-dimethyl-2-oxoindolin-3-yl)methyl)piperidine-1-carboxylate (9)**



Prepared according to the ***general procedure*** from *N*-(2-fluorophenyl)-*N*-methylmethacrylamide (19.3 mg, 0.1 mmol) and *tert*-butyl 4-iodopiperidine-1-carboxylate (46.7 mg, 0.15 mmol), The crude residue was purified by column chromatography to yield **9** (15.7 mg, 41% yield) as a colorless oil.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.02 – 6.92 (m, 3H), 3.87 (brs, 2H), 3.44 (d, *J* = 2.6 Hz, 3H), 2.45 (q, *J* = 11.8, 10.2 Hz, 2H), 1.98 (dd, *J* = 14.1, 6.0 Hz, 1H), 1.74 (dd, *J* = 14.2, 5.1 Hz, 1H), 1.40 (s, 9H), 1.32 (s, 3H), 1.28 – 1.24 (m, 1H), 1.13 – 1.01 (m, 3H), 0.94 – 0.83 (m, 1H). **^{13}C NMR (101 MHz, CDCl$_3$):** δ 180.3, 154.7, 147.8 (d, *J* = 243.9 Hz), 137.0 (d, *J* = 3.2 Hz), 129.5 (d, *J* = 7.4 Hz), 123.1 (d, *J* = 6.3 Hz), 118.5 (d, *J* = 3.0 Hz), 115.8 (d, *J* = 19.3 Hz), 79.2, 48.1 (d, *J* = 1.7 Hz), 44.5, 33.1, 33.0, 32.4, 28.7 (d, *J* = 5.7 Hz), 28.4, 26.4.**^{19}F NMR (377 MHz, CDCl$_3$):** δ -136.3. **HRMS (ESI):** Calcd for $C_{21}H_{29}FN_2O_3Na$ $[M+Na]^+$:399.2054, found 399.2049

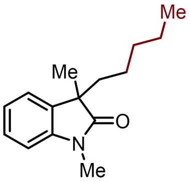
3-butyl-1,3-dimethylindolin-2-one (10)



Prepared according to the ***general procedure*** from *N*-methyl-*N*-phenylmethacrylamide (17.5 mg, 0.1 mmol) and 1-iodopropane (25.5 mg, 0.15 mmol), The crude residue was purified by column chromatography to yield **10** (8.8 mg, 40% yield) as a colorless oil

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.29 – 7.23 (m, 1H), 7.18 – 7.14 (m, 1H), 7.09 – 7.03 (m, 1H), 6.86 – 6.81 (m, 1H), 3.21 (s, 3H), 1.93 – 1.84 (m, 1H), 1.77 – 1.68 (m, 1H), 1.34 (s, 3H), 1.23 – 1.12 (m, 2H), 1.01 – 0.89 (m, 1H), 0.86 – 0.80 (m, 1H), 0.79 – 0.74 (m, 3H).**^{13}C NMR (101 MHz, CDCl$_3$):** δ 180.9, 143.3, 134.3, 127.5, 122.4, 122.4, 107.8, 48.4, 38.3, 26.6, 26.1, 23.8, 22.8, 13.8. **HRMS (ESI):** Calcd for $C_{14}H_{19}NONa$ $[M+Na]^+$:240.1359, found 240.1353

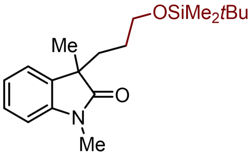
1,3-dimethyl-3-pentylindolin-2-one (11)



Prepared according to the ***general procedure*** from *N*-methyl-*N*-phenylmethacrylamide (17.5 mg, 0.1 mmol) and 1-iodobutane (27.6 mg, 0.15 mmol), The crude residue was purified by column chromatography to yield **11** (10.4 mg, 45% yield) as a colorless oil

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.29 – 7.23 (m, 1H), 7.18 – 7.14 (m, 1H), 7.09 – 7.04 (m, 1H), 6.85 – 6.82 (m, 1H), 3.21 (s, 3H), 1.92 – 1.83 (m, 1H), 1.75 – 1.68 (m, 1H), 1.34 (s, 3H), 1.20 – 1.10 (m, 4H), 1.03 – 0.92 (m, 1H), 0.87 – 0.80 (m, 1H), 0.79 – 0.75 (m, 3H).**^{13}C NMR (126 MHz, CDCl$_3$):** δ 180.9, 143.3, 134.3, 127.5, 122.4, 122.4, 107.8, 48.4, 38.4, 31.9, 26.1, 24.1, 23.8, 22.3, 13.9. **HRMS (ESI):** Calcd for $C_{15}H_{21}NONa$ $[M+Na]^+$:254.1515, found 254.1518

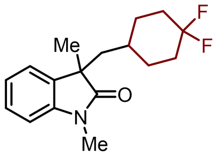
3-(3-((tert-butyldimethylsilyl)oxy)propyl)-1,3-dimethylindolin-2-one (12)



Prepared according to the ***general procedure*** from *N*-methyl-*N*-phenylmethacrylamide (17.5 mg, 0.1 mmol) and *tert*-butyl(2-iodoethoxy)dimethylsilane (42.9 mg, 0.15 mmol), The crude residue was purified by column chromatography to yield **12** (17.3 mg, 52% yield) as a colorless oil.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.29 – 7.21 (m, 1H), 7.18 – 7.14 (m, 1H), 7.08 – 7.03 (m, 1H), 6.86 – 6.79 (m, 1H), 3.50 – 3.39 (m, 2H), 3.20 (s, 3H), 1.93 – 1.76 (m, 2H), 1.35 (s, 3H), 1.28 – 1.15 (m, 1H), 1.11 – 1.01 (m, 1H), 0.84 (s, 9H), -0.02 – -0.05 (m, 6H).**^{13}C NMR (101 MHz, CDCl$_3$):** δ 180.6, 143.3, 134.0, 127.6, 122.5, 122.4, 107.8, 62.9, 48.1, 34.7, 27.8, 26.1, 25.9, 23.8, 18.3, -5.4, -5.4.**HRMS (ESI):** Calcd for $C_{19}H_{31}NO_2Na$ [M+Na]$^+$:356.2016, found 356.2021

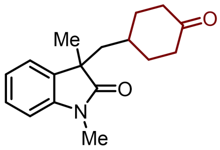
3-((4,4-difluorocyclohexyl)methyl)-1,3-dimethylindolin-2-one (13)



Prepared according to the ***general procedure*** from *N*-methyl-*N*-phenylmethacrylamide (17.5 mg, 0.1 mmol) and 1,1-difluoro-4-iodocyclohexane (36.9 mg, 0.15 mmol), The crude residue was purified by column chromatography to yield **13** (19.7 mg, 67% yield) as a colorless oil.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.32 – 7.25 (m, 1H), 7.16 (d, J = 7.3 Hz, 1H), 7.10 – 7.04 (m, 1H), 6.86 (d, J = 7.8 Hz, 1H), 3.23 (s, 3H), 2.01 (dd, J = 14.1, 5.8 Hz, 1H), 1.95 – 1.81 (m, 2H), 1.77 (dd, J = 14.1, 5.1 Hz, 1H), 1.51 – 1.39 (m, 3H), 1.33 (s, 3H), 1.28 – 1.19 (m, 2H), 1.13 – 1.01 (m, 2H). **^{13}C NMR (101 MHz, CDCl$_3$):** δ 180.6, 143.0, 133.9, 132.2 (t, J = 242.4 Hz), 127.9, 122.6, 122.6, 108.2, 47.8, 43.4 (d, J = 2.1 Hz), 33.1 (m, 2C), 32.8, 29.61 (dd, J = 54.6, 9.0 Hz, 2C), 26.2, 26.1. **^{19}F NMR (377 MHz, CDCl$_3$):** δ -92.4 (d, J = 234.6 Hz), -101.8 (d, J = 234.2 Hz). **HRMS (ESI):** Calcd for $C_{17}H_{21}F_2NONa$ [M+Na]$^+$:316.1483, found 316.1484

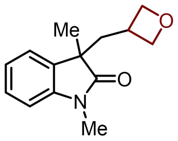
1,3-dimethyl-3-((4-oxocyclohexyl)methyl)indolin-2-one (14)



Prepared according to the ***general procedure*** from *N*-methyl-*N*-phenylmethacrylamide (17.5 mg, 0.1 mmol) and 4-iodocyclohexan-1-one (33.6 mg, 0.15 mmol), The crude residue was purified by column chromatography to yield **14** (23.0 mg, 85% yield) as a colorless oil.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.31 – 7.27 (m, 1H), 7.18 (d, J = 7.3 Hz, 1H), 7.11 – 7.06 (m, 1H), 6.88 (d, J = 7.8 Hz, 1H), 3.24 (s, 3H), 2.27 – 2.20 (m, 1H), 2.18 – 2.12 (m, 1H), 2.11 – 2.00 (m, 3H), 1.83 (dd, J = 14.1, 5.2 Hz, 1H), 1.77 – 1.70 (m, 1H), 1.56 – 1.48 (m, 1H), 1.44 – 1.31 (m, 5H), 1.31 – 1.16 (m, 2H). **^{13}C NMR (101 MHz, CDCl$_3$):** δ 211.6, 180.6, 143.0, 133.7, 127.9, 122.6, 122.6, 108.2, 47.8, 43.1, 40.4, 40.3, 33.6, 33.0, 33.0, 26.3, 26.1. **HRMS (ESI):** Calcd for $C_{17}H_{21}NO_2Na$ [M+Na]$^+$:294.1464, found 294.1465

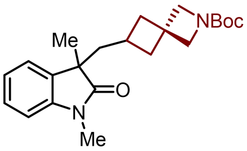
1,3-dimethyl-3-(oxetan-3-ylmethyl)indolin-2-one (15)



Prepared according to the ***general procedure*** from *N*-methyl-*N*-phenylmethacrylamide (17.5 mg, 0.1 mmol) and 3-iodooxetane (27.6 mg, 0.15 mmol), The crude residue was purified by column chromatography to yield **15** (22.2 mg, 96% yield) as a colorless oil.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.29 – 7.24 (m, 1H), 7.16 (d, *J* = 7.2 Hz, 1H), 7.08 – 7.03 (m, 1H), 6.85 – 6.81 (m, 1H), 4.50 (dd, *J* = 8.0, 6.0 Hz, 1H), 4.40 – 4.32 (m, 1H), 4.15 – 4.06 (m, 2H), 3.20 (s, 3H), 2.75 (dt, *J* = 14.9, 7.4 Hz, 1H), 2.26 (dd, *J* = 13.7, 6.2 Hz, 1H), 2.12 (dd, *J* = 13.7, 8.2 Hz, 1H), 1.35 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$):** δ 180.0, 143.0, 132.9, 128.1, 122.7, 122.5, 108.0, 77.6, 77.4, 47.4, 42.0, 32.1, 26.1, 23.3. **HRMS (ESI):** Calcd for $C_{14}H_{17}NO_2Na$ [M+Na]$^+$:254.1152, found 254.1149

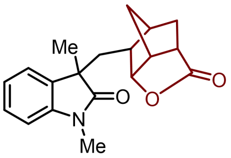
***tert*-butyl 6-((1,3-dimethyl-2-oxoindolin-3-yl)methyl)-2-azaspiro[3.3]heptane-2-carboxylate (16)**



Prepared according to the ***general procedure*** from *N*-methyl-*N*-phenylmethacrylamide (17.5 mg, 0.1 mmol) and *tert*-butyl 6-iodo-2-azaspiro[3.3]heptane-2-carboxylate (48.5 mg, 0.15 mmol), The crude residue was purified by column chromatography to yield **16** (25.0 mg, 67% yield) as a colorless oil.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.29 – 7.23 (m, 1H), 7.13 (d, *J* = 7.2 Hz, 1H), 7.08 – 7.02 (m, 1H), 6.83 (d, *J* = 7.7 Hz, 1H), 3.75 – 3.67 (m, 2H), 3.67 – 3.59 (m, 2H), 3.19 (s, 3H), 2.02 (dd, *J* = 13.5, 6.3 Hz, 1H), 1.92 (dd, *J* = 9.9, 5.6 Hz, 1H), 1.83 (dd, *J* = 13.5, 5.8 Hz, 1H), 1.78 – 1.70 (m, 3H), 1.54 – 1.48 (m, 1H), 1.45 – 1.41 (m, 1H), 1.37 (s, 4H), 1.31 (s, 3H).**^{13}C NMR (101 MHz, CDCl$_3$):** δ 180.4, 156.1, 143.1, 133.6, 127.8, 122.7, 122.3, 107.9, 79.0, 47.8, 45.0, 39.7, 39.1, 34.4, 28.3, 26.6, 26.1, 24.0. **HRMS (ESI):** Calcd for $C_{22}H_{30}N_2O_3Na$ [M+Na]$^+$:393.2149, found 393.2144

1,3-dimethyl-3-((2-oxohexahydro-2H-3,5-methanocyclopenta[b]furan-6-yl)methyl)indolin-2-one (17)

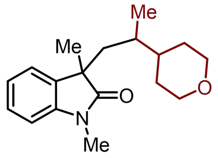


Prepared according to the ***general procedure*** from *N*-methyl-*N*-phenylmethacrylamide (17.5 mg, 0.1 mmol) and 6-iodohexahydro-2H-3,5-methanocyclopenta[b]furan-2-one (39.6 mg, 0.15 mmol), The crude residue was purified by column chromatography to yield **17** (29.7 mg, 95% yield, d.r. = 1:1) as a colorless oil.

^{1}H NMR (400 MHz, CDCl$_3$, diastereomers): δ 7.32 – 7.27 (m, 1H), 7.20 – 7.13 (m, 1H), 7.11 – 7.05 (m, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 4.51 – 3.99 (m, 1H), 3.24 – 3.23 (m, 3H), 3.04 – 2.95 (m, 1H), 2.41 – 2.34 (m, 1H), 2.01 – 1.88 (m, 2H), 1.84 – 1.60

(m, 3H), 1.47 – 1.38 (m, 2H), 1.37 – 1.34 (m, 3H), 1.22 – 0.94 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$, diastereomers):** δ 181.1, 180.9, 180.3, 180.2, 143.4, 143.0, 133.0, 132.8, 128.3, 128.2, 122.8, 122.7, 122.6, 122.3, 108.5, 108.5, 86.5, 85.5, 47.8, 47.3, 46.3, 46.1, 45.9, 45.4, 43.4, 41.6, 41.1, 40.6, 38.6, 35.2, 35.0, 34.9, 34.8, 26.3, 26.2, 24.9, 24.0. **HRMS (ESI):** Calcd for $C_{19}H_{21}NO_3Na$ $[M+Na]^+$:334.1414, found 334.1409

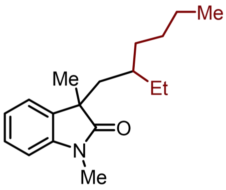
1,3-dimethyl-3-(2-(tetrahydro-2H-pyran-4-yl)propyl)indolin-2-one (18)



Prepared according to the ***general procedure*** from *N*-methyl-*N*-phenylmethacrylamide (17.5 mg, 0.1 mmol) and (4-(1-iodoethyl)tetrahydro-2H-pyran (36.0 mg, 0.15 mmol), The crude residue was purified by column chromatography to yield **18** (20.7 mg, 72% yield, d.r. = 1:1) as a colorless oil.

^1H NMR (400 MHz, $CDCl_3$, diastereomers): δ 7.30 – 7.24 (m, 1H), 7.20 – 7.11 (m, 1H), 7.09 – 7.03 (m, 1H), 6.87 – 6.82 (m, 1H), 3.93 (dd, *J* = 20.8, 7.6 Hz, 2H), 3.30 – 3.15 (m, 5H), 1.94 – 1.82 (m, 1H), 1.66 – 1.58 (m, 1H), 1.34 (s, 3H), 1.30 – 1.19 (m, 4H), 1.17 – 1.07 (m, 1H), 1.05 – 0.91 (m, 1H), 0.63 – 0.42 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$, diastereomers)**: δ 181.1, 180.6, 143.3, 143.1, 134.3, 133.8, 127.7, 123.0, 122.7, 122.4, 122.3, 108.0, 108.0, 68.5, 68.4, 68.3, 48.2, 47.8, 42.6, 41.7, 41.1, 40.8, 34.6, 34.4, 30.4, 29.9, 28.8, 27.8, 26.2, 26.1, 26.0, 25.5, 17.0, 16.3. **HRMS (ESI):** Calcd for $C_{18}H_{25}NO_2Na$ $[M+Na]^+$:310.1778, found 310.1770

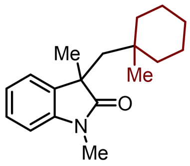
3-(2-ethylhexyl)-1,3-dimethylindolin-2-one (19)



Prepared according to the ***general procedure*** from *N*-methyl-*N*-phenylmethacrylamide (17.5 mg, 0.1 mmol) and 3-iodoheptane (33.9 mg, 0.15 mmol), The crude residue was purified by column chromatography to yield **19** (20.2 mg, 74% yield, d.r. = 1:1) as a colorless oil.

^1H NMR (400 MHz, $CDCl_3$, diastereomers): δ 7.29 – 7.23 (m, 1H), 7.16 (d, *J* = 7.3 Hz, 1H), 7.08 – 7.02 (m, 1H), 6.83 (d, *J* = 7.7 Hz, 1H), 3.24 – 3.17 (m, 3H), 1.97 – 1.86 (m, 1H), 1.80 – 1.70 (m, 1H), 1.33 (s, 3H), 1.15 – 1.06 (m, 3H), 1.05 – 0.95 (m, 5H), 0.93 – 0.84 (m, 2H), 0.81 – 0.74 (m, 3H), 0.71 – 0.62 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$, diastereomers):** δ 181.1, 143.3, 134.3, 127.5, 122.9, 122.8, 122.2, 122.2, 107.8, 76.7, 48.1, 48.0, 42.0, 41.9, 35.7, 35.6, 33.2, 32.7, 28.2, 28.2, 26.4, 26.1, 26.1, 25.6, 25.5, 22.8, 22.7, 14.0, 10.3, 10.3. **HRMS (ESI):** Calcd for $C_{18}H_{27}NONa$ $[M+Na]^+$:296.1985, found 296.1982

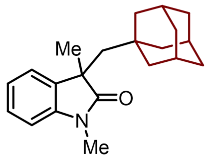
1,3-dimethyl-3-((1-methylcyclohexyl)methyl)indolin-2-one (20)



Prepared according to the ***general procedure*** from *N*-methyl-*N*-phenylmethacrylamide (17.5 mg, 0.1 mmol) and 1-iodo-1-methylcyclohexane (33.6 mg, 0.15 mmol), The crude residue was purified by column chromatography to yield **20** (17.0 mg, 63% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 – 7.23 (m, 1H), 7.21 (d, J = 7.3 Hz, 1H), 7.05 – 7.00 (m, 1H), 6.84 (d, J = 7.7 Hz, 1H), 3.22 (s, 3H), 2.10 (d, J = 14.5 Hz, 1H), 1.92 (d, J = 14.5 Hz, 1H), 1.39 – 1.32 (m, 2H), 1.29 (s, 3H), 1.26 – 1.22 (m, 1H), 1.20 – 1.11 (m, 2H), 1.05 – 0.97 (m, 1H), 0.92 – 0.84 (m, 2H), 0.49 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 181.2, 142.7, 134.5, 127.4, 123.8, 121.9, 108.0, 47.0, 39.1, 38.9, 34.2, 28.6, 26.2, 26.2, 21.9, 21.8. **HRMS (ESI):** Calcd for $C_{18}H_{25}NONa$ $[M+Na]^+$:294.1828, found 294.1825

3-(adamantan-1-yl)methyl)-1,3-dimethylindolin-2-one (21)

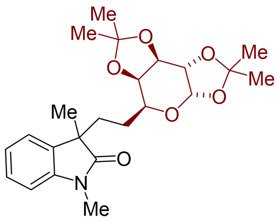


Prepared according to the ***general procedure*** from *N*-methyl-*N*-phenylmethacrylamide (17.5 mg, 0.1 mmol) and 1-iodoadamantane (39.3 mg, 0.15 mmol), The crude residue was purified by column chromatography to yield **21** (30.9 mg, 99% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 – 7.22 (m, 1H), 7.18 (d, J = 7.2 Hz, 1H), 7.05 – 7.00 (m, 1H), 6.84 (d, J = 7.8 Hz, 1H), 3.23 (s, 3H), 1.99 (d, J = 14.5 Hz, 1H), 1.76 – 1.69 (m, 4H), 1.50 (d, J = 12.0 Hz, 3H), 1.37 (d, J = 11.6 Hz, 3H), 1.26 (s, 3H), 1.21 – 1.10 (m, 6H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 181.2, 142.6, 134.7, 127.5, 123.6, 122.0, 107.9, 52.0, 46.6, 43.3, 36.7, 33.9, 28.6, 28.5, 26.2. **HRMS (ESI):** Calcd for $C_{21}H_{27}NONa$ $[M+Na]^+$:332.1985, found 332.1980

All other spectroscopic analyses were in agreement with the literature[1].

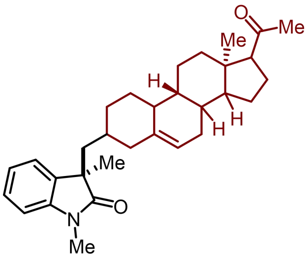
1,3-dimethyl-3-(2-(2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)ethyl)indolin-2-one (22)



Prepared according to the ***general procedure*** from N-methyl-N-phenylmethacrylamide (17.5 mg, 0.1 mmol) and 5-iodo-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]d ioxolo)[4,5-b:4', 5'-d]pyran (53.4 mg, 0.15 mmol), The crude residue was purified by column chromatography to yield **22** (32.5 mg, 78% yield, d.r. = 1:1) as a white solid.

^{1}H NMR (400 MHz, CDCl$_3$, diastereomers): δ 7.26 – 7.15 (m, 2H), 7.07 – 7.02 (m, 1H), 6.81 (d, J = 7.7 Hz, 1H), 5.50 – 5.42 (m, 1H), 4.55 – 4.47 (m, 1H), 4.26 – 4.21 (m, 1H), 4.06 – 3.94 (m, 1H), 3.62 – 3.53 (m, 1H), 3.20 (d, J = 3.4 Hz, 3H), 2.14 – 2.02 (m, 1H), 1.90 – 1.67 (m, 1H), 1.77 – 1.67 (m, 1H), 1.50 (d, J = 12.9 Hz, 3H), 1.36 (d, J = 4.3 Hz, 5H), 1.32 – 1.28 (m, 6H), 1.26 – 1.24 (m, 2H). **^{13}C NMR (101 MHz, CDCl$_3$, diastereomers):** δ 180.64, 180.50, 143.24, 143.15, 133.96, 133.66, 127.64, 127.59, 122.74, 122.69, 122.59, 122.33, 108.97, 108.93, 108.33, 108.24, 107.96, 107.93, 96.46, 96.39, 72.75, 72.23, 70.83, 70.80, 70.45, 70.35, 67.95, 67.69, 48.24, 47.89, 34.71, 34.18, 26.15, 26.14, 26.08, 26.04, 25.91, 25.80, 25.14, 24.99, 24.89, 24.85, 24.50, 24.41, 24.30, 23.32. **HRMS (ESI):** Calcd for $C_{23}H_{31}NO_6Na$ $[M+Na]^+$:440.2044, found 440.2045

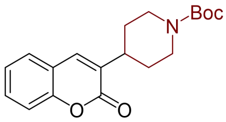
(3S)-3-(((8R,9S,13S,14S)-17-acetyl-13-methyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl)methyl)-1,3-dimethylindolin-2-one (23)



Prepared according to the ***general procedure*** from N-methyl-N-phenylmethacrylamide (17.5 mg, 0.1 mmol) and 3-iodo-13-methyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17 -tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl)ethan-1-one (61.8 mg, 0.15 mmol), The crude residue was purified by column chromatography to yield **23** (31.9 mg, 69% yield, d.r. = 1:1.3:1:1) as a white solid.

^{1}H NMR (400 MHz, CDCl$_3$, diastereomers): δ 7.39 – 6.82 (m, 4H), 5.31 – 4.97 (m, 1H), 3.42 – 3.15 (m, 3H), 2.61 – 2.46 (m, 1H), 2.30 – 0.57 (m, 32H). **^{13}C NMR (101 MHz, CDCl$_3$, diastereomers):** δ 209.7, 181.1, 180.9, 180.7, 143.3, 143.2, 143.1, 142.9, 142.6, 140.3, 139.8, 134.4, 134.3, 134.0, 129.2, 127.6, 127.6, 127.6, 126.9, 126.5, 122.9, 122.8, 122.7, 122.5, 122.4, 122.3, 122.2, 121.5, 121.0, 119.3, 119.1, 119.0, 107.9, 107.9, 107.8, 63.7, 63.7, 57.0, 56.9, 50.2, 50.0, 48.2, 48.2, 47.7, 45.3, 45.1, 44.0, 44.0, 43.9, 40.4, 39.8, 39.4, 39.2, 39.1, 38.9, 38.8, 38.0, 37.8, 37.1, 37.1, 36.7, 36.6, 36.6, 36.5, 34.1, 34.0, 31.7, 31.7, 31.6, 31.6, 31.5, 31.5, 31.4, 31.1, 30.1, 29.1, 27.2, 26.9, 26.2, 26.2, 26.1, 26.1, 25.9, 25.6, 25.0, 24.4, 24.4, 22.8, 22.7, 20.8, 20.7, 20.3, 19.3, 19.2, 19.2, 13.2, 13.2, 13.1. **HRMS (ESI):** Calcd for $C_{32}H_{43}NO_2Na$ $[M+Na]^+$:496.3186, found 496.3195

tert-butyl 4-(2-oxo-2H-chromen-4-yl)piperidine-1-carboxylate (24)



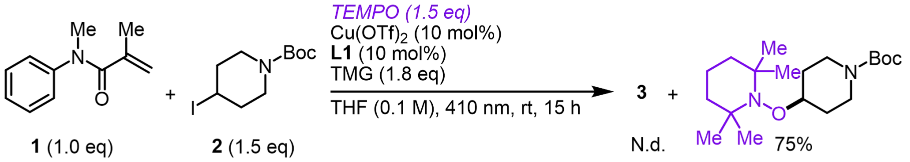
Prepared according to the ***general procedure*** from 2H-chromen-2-one (14.6 mg, 0.1 mmol) and and *tert*-butyl 4-iodopiperidine-1-carboxylate (46.7 mg, 0.15 mmol), The crude residue was purified by column chromatography to yield **24** (15.5 mg, 47% yield) as a white solid.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.51 – 7.41 (m, 3H), 7.34 – 7.23 (m, 2H), 4.31 (s, 2H), 2.97 – 2.73 (m, 3H), 1.94 (m, 2H), 1.55 – 1.41 (m, 11H). **^{13}C NMR (101 MHz, CDCl$_3$):** δ 161.3, 154.7, 152.8, 136.9, 132.8, 130.9, 127.5, 124.4, 119.3, 116.4, 79.6, 43.9, 36.5, 30.8, 28.4. **HRMS (ESI):** Calcd for $C_{19}H_{23}NO_4Na$ $[M+Na]^+$:352.1519, found 352.1528

All other spectroscopic analyses were in agreement with the literature[4].

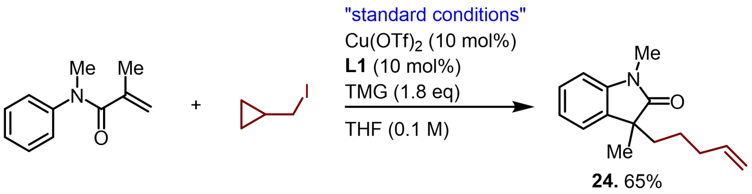
3. Mechanistic study

3.1 TEMPO trapping experiments



Experimental Procedure: To an oven-dried 10ml reaction vial were added Cu(OTf)$_2$ (3.72 mg.0 01 mmol, 10 mol), **L1** (3.55mg, 0.01 mmol, 10 mol%), and 1 mL THF in a nitrogen-filled glove box. The resulting mixture was stirred for 5 min, followed by adding 1,1,3,3-Tetramethylguanidine (22.6 uL, 0.18 mmol, 1.8 equiv), with tert-butyl 4-iodopiperidine-1-carboxylate (46.7 mg, 0.15 mmol, 1.5 equiv), N-methyl-N-phenylmethacrylamide (17.5 mg, 0.1 mmol, 1.5 equiv), TEMPO (23.4 mg, 0.15 mmol, 1.5 equiv) in sequence, and sealed with a screwed cap. The sealed vial was placed on a photo-reactor under irradiation of LEDs (410 nm, 6W). The mixture was stirred at 25 °C for 15 h, quenched with H$_2$0, and extracted with ethyl acetate. The combined organic layers were died over anhydrous Na$_2$SO$_4$, concentrated in vacuum. The crude product was analyzed by ^{1}H NMR, with 13.5-Timethoxybenzene as an internal standard.

3.2 Radical clock experiments: involvement of alkyl radicals



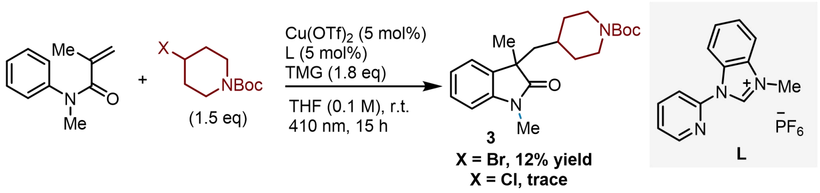
Experimental Procedure: To an oven-dried 10ml reaction vial were added Cu(OTf)$_2$ (3.72 mg.0 01 mmol, 10 mol), **L1** (3.55mg, 0.01 mmol, 10 mol%), and 1 mL THF in a nitrogen-filled glove box. The resulting mixture was stirred for 5 min, followed by adding 1,1,3,3-Tetramethylguanidine (22.6 uL, 0.18 mmol, 1.8 equiv), with N-methyl-N-phenylmethacrylamide (17.5 mg, 0.1 mmol, 1.0 equiv), (iodomethyl)cyclopropane (27.3 mg, 0.15 mol, 1.5 equiv) in sequence and sealed with a screwed cap, The sealed vial was placed on a photo reactor under irradiation of LEDs (410 nm, 6 W). The mixture was stirred at 25 °C for 15 h, quenched with H$_2$O, and extracted with ethyl acetate. The crude product was purified by silica gel column chromatography to afford the product **25** (14.9 mg, 65% yield).

1,3-dimethyl-3-(pent-4-en-1-yl)indolin-2-one (25)

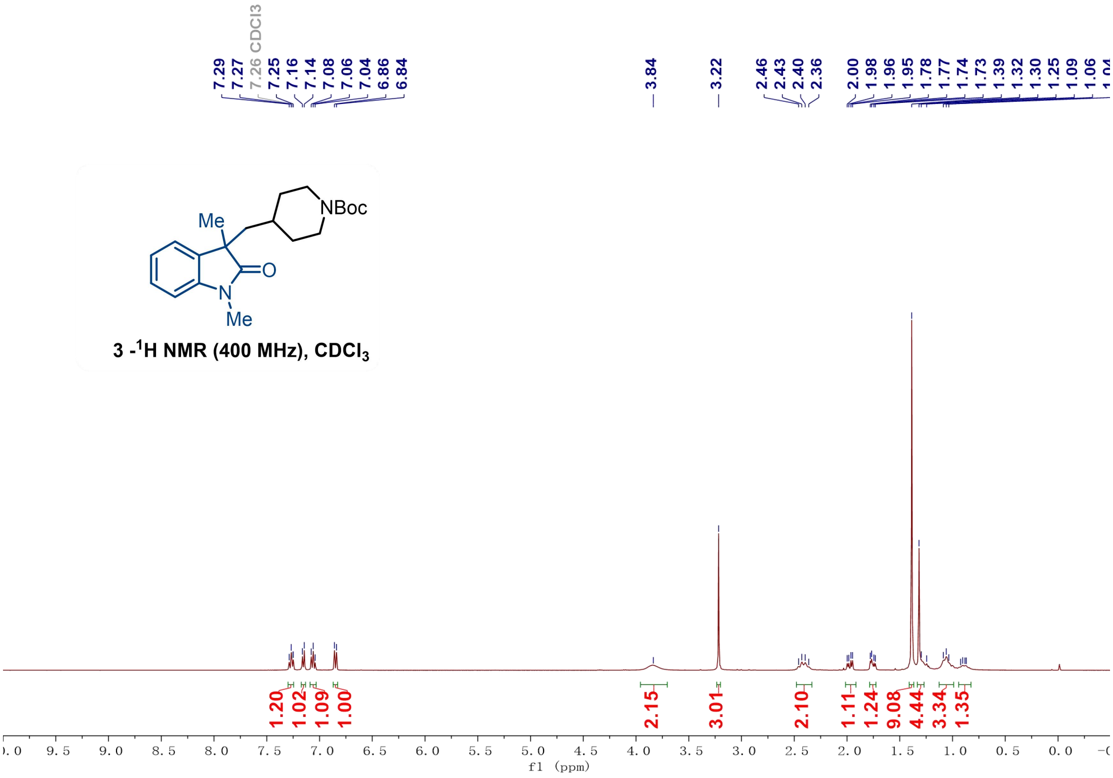
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.30 – 7.23 (m, 1H), 7.17 (d, J = 7.5 Hz, 1H), 7.09 – 7.04 (m, 1H), 6.84 (d, J = 8.5 Hz, 1H), 5.69 – 5.60 (m, 1H), 4.94 – 4.85 (m, 2H), 3.21 (s, 3H), 1.97 – 1.86 (m, 3H), 1.77 – 1.70 (m, 1H), 1.35 (s, 3H), 1.14 – 1.04 (m, 1H), 0.97 – 0.89 (m, 1H). **^{13}C NMR (101 MHz, CDCl$_3$):** δ 181.3, 144.4, 138.2, 134.1, 127.6, 122.4, 115.4, 108.7, 49.6, 37.9, 34.4, 27.6, 23.7. **HRMS (ESI):** Calcd for $C_{15}H_{19}NONa$ $[M+Na]^+$:252.1359, found 252.1362

3.3 Attempted reaction

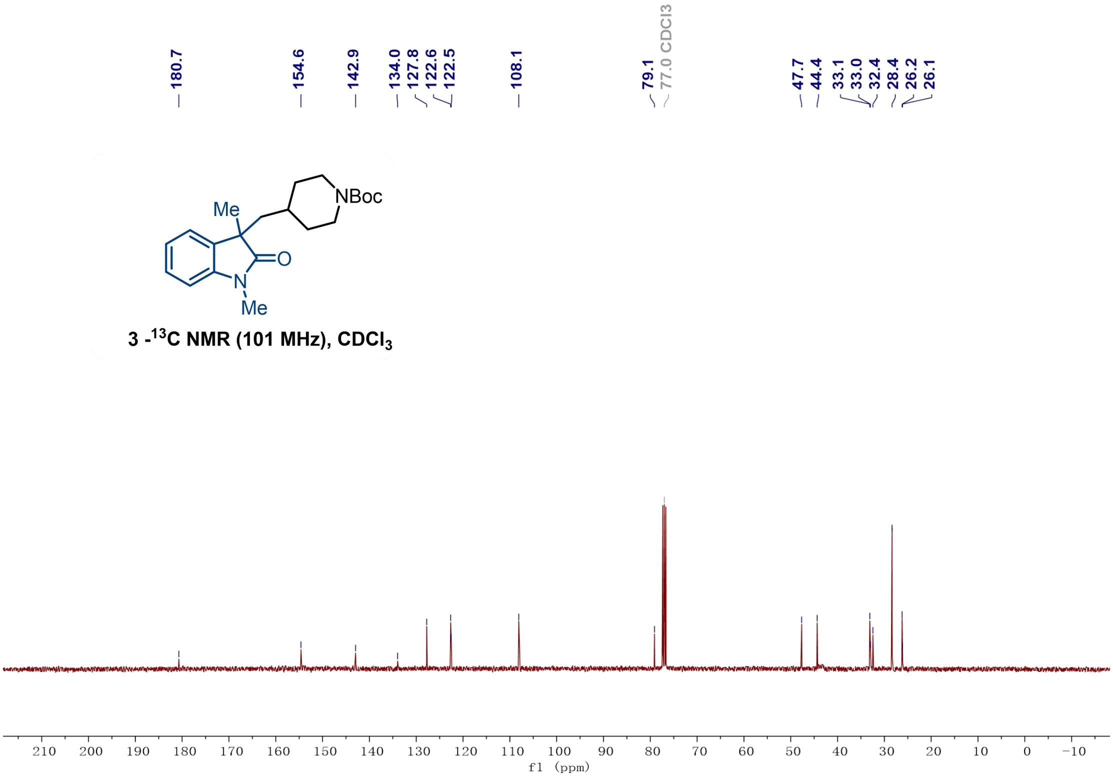
Using unactivated bromides and chlorides as electrophiles.



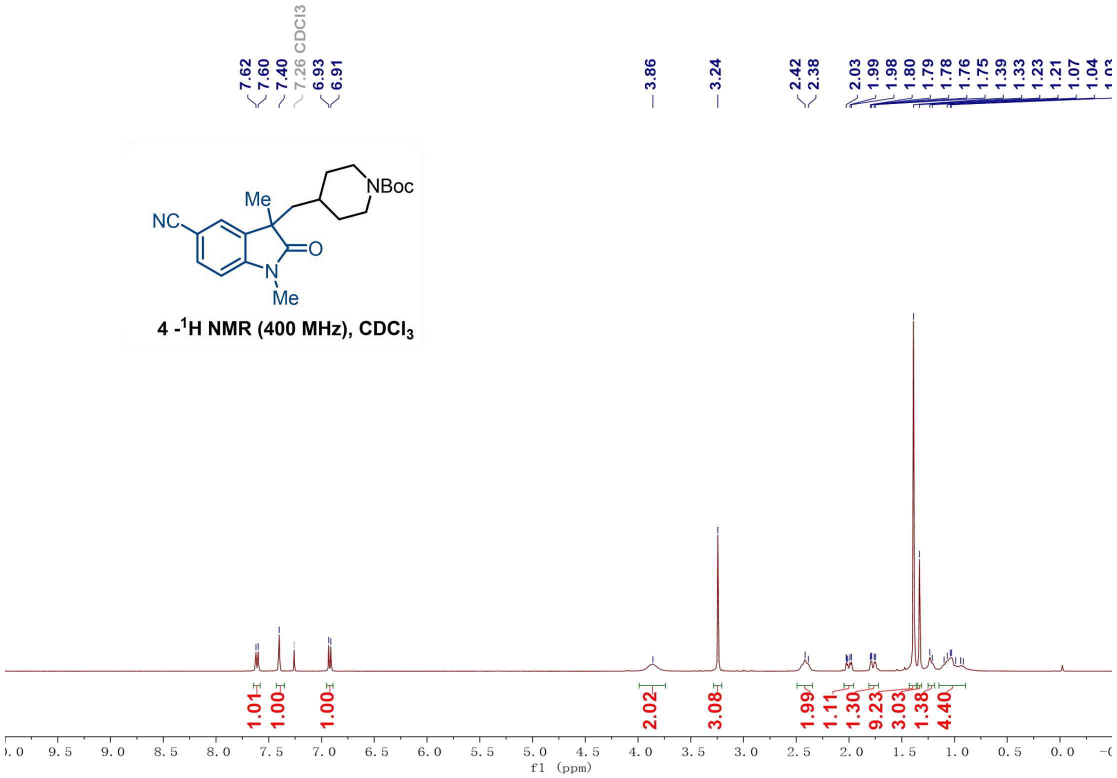
4. NMR Spectra

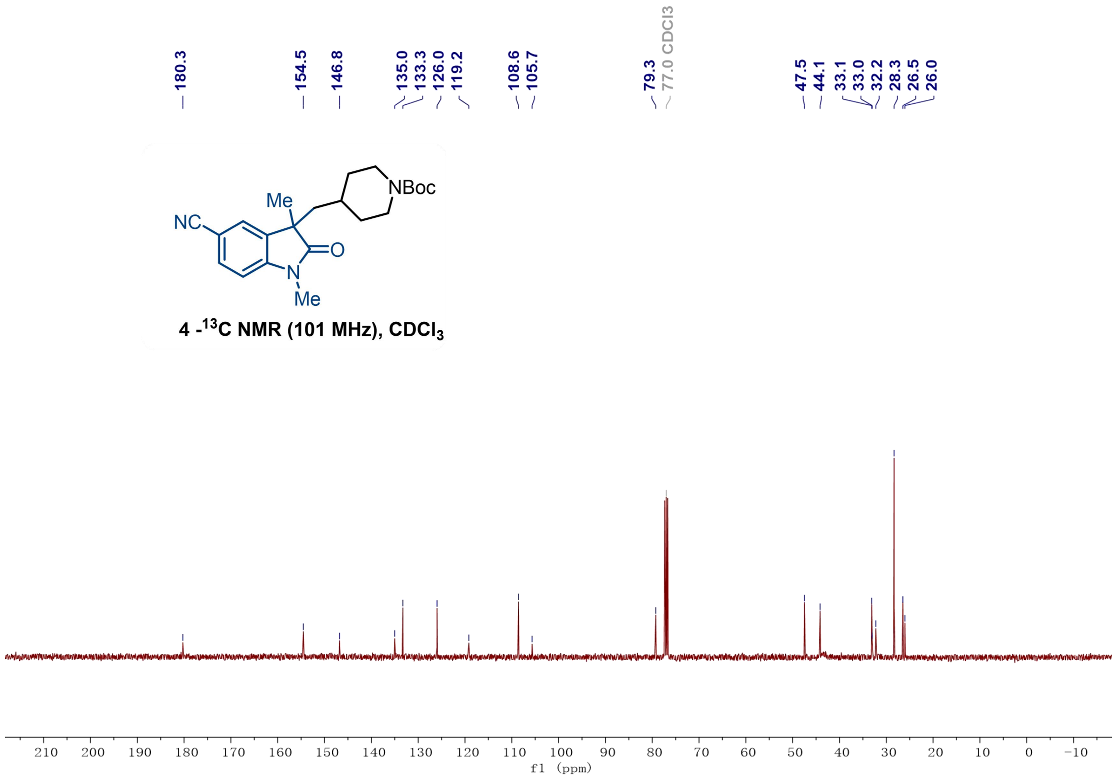


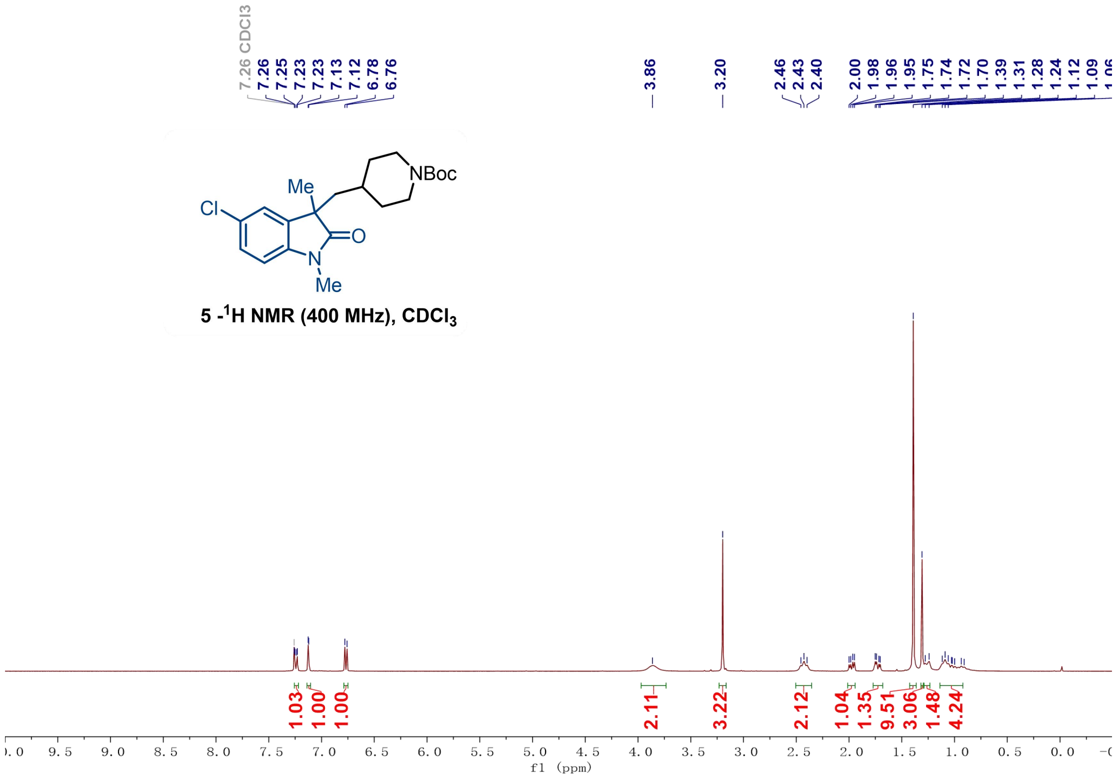
3 -^{1}H NMR (400 MHz), CDCl$_3$



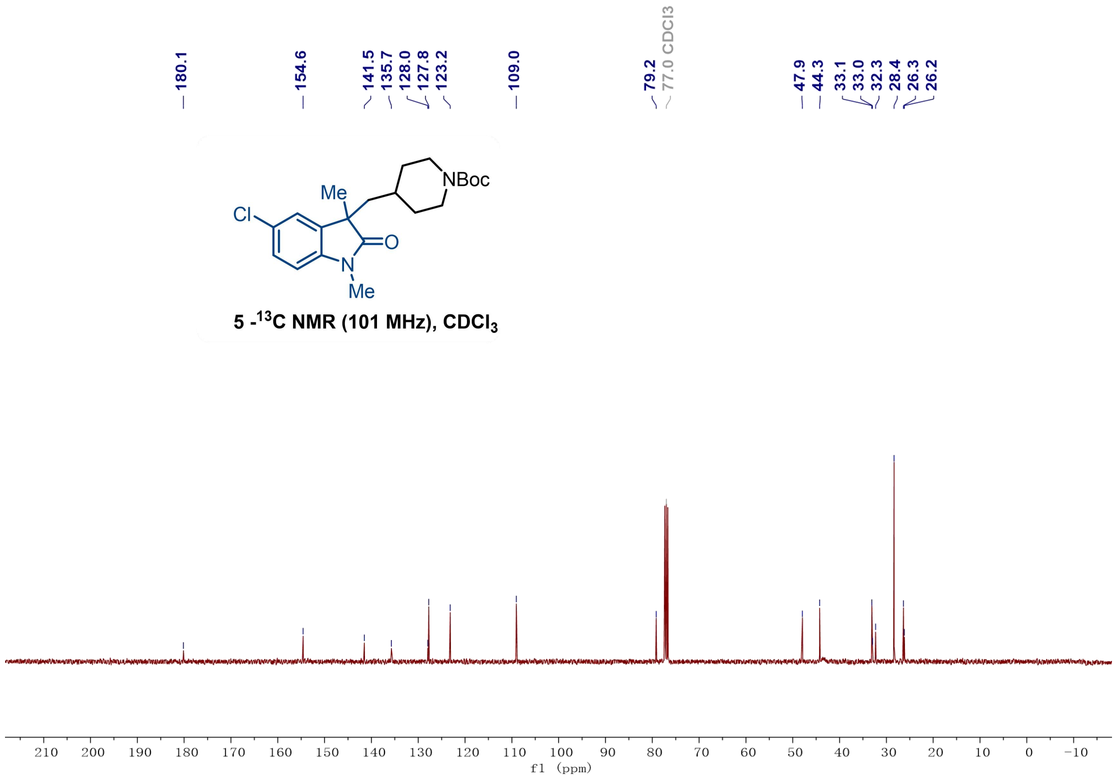
3 -^{13}C NMR (101 MHz), CDCl$_3$


4 -^{1}H NMR (400 MHz), CDCl$_3$

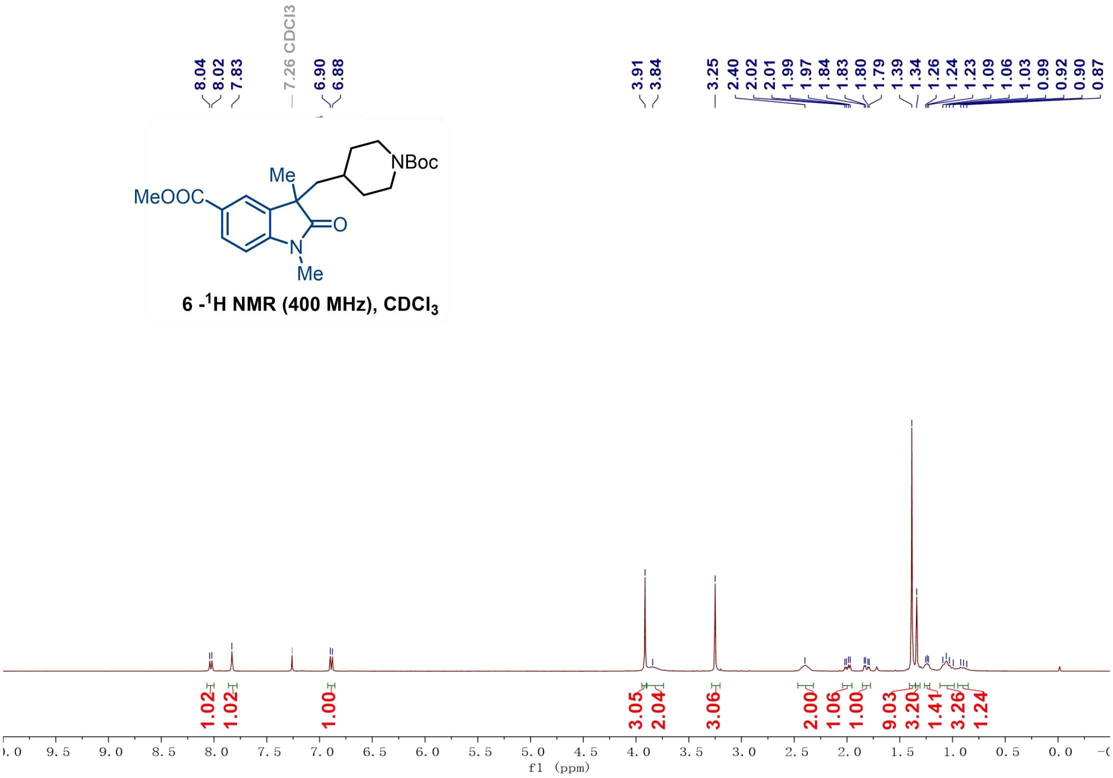

4 -^{13}C NMR (101 MHz), CDCl$_3$

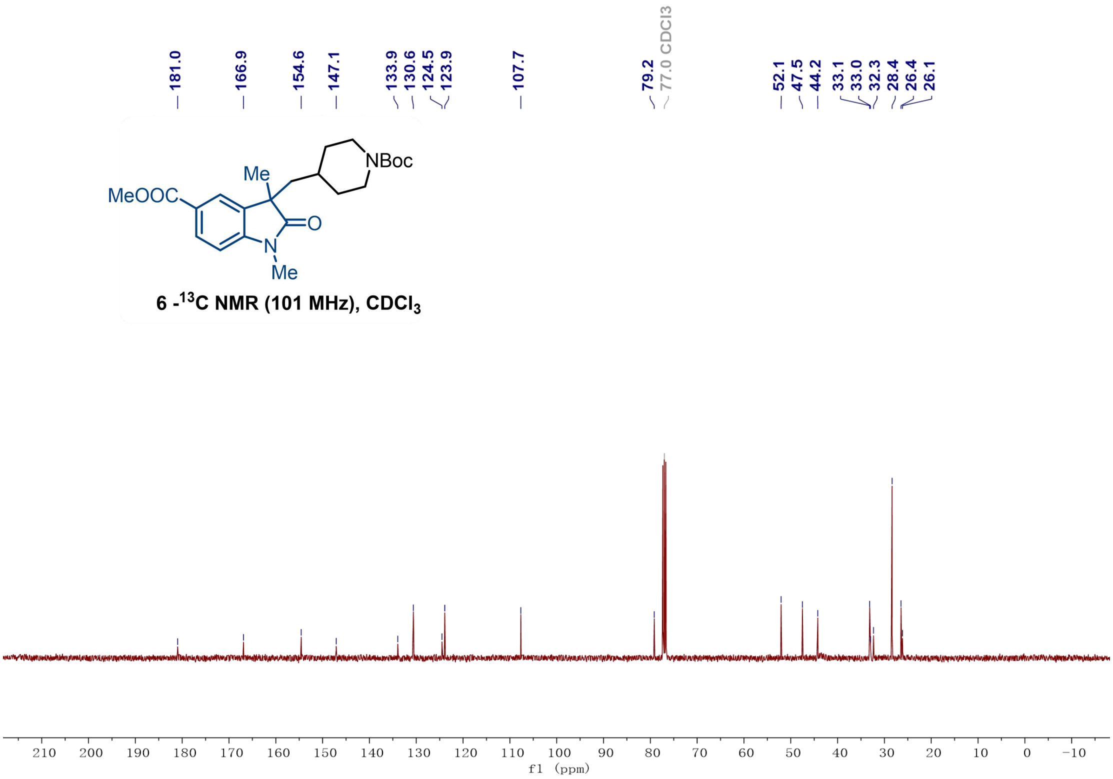


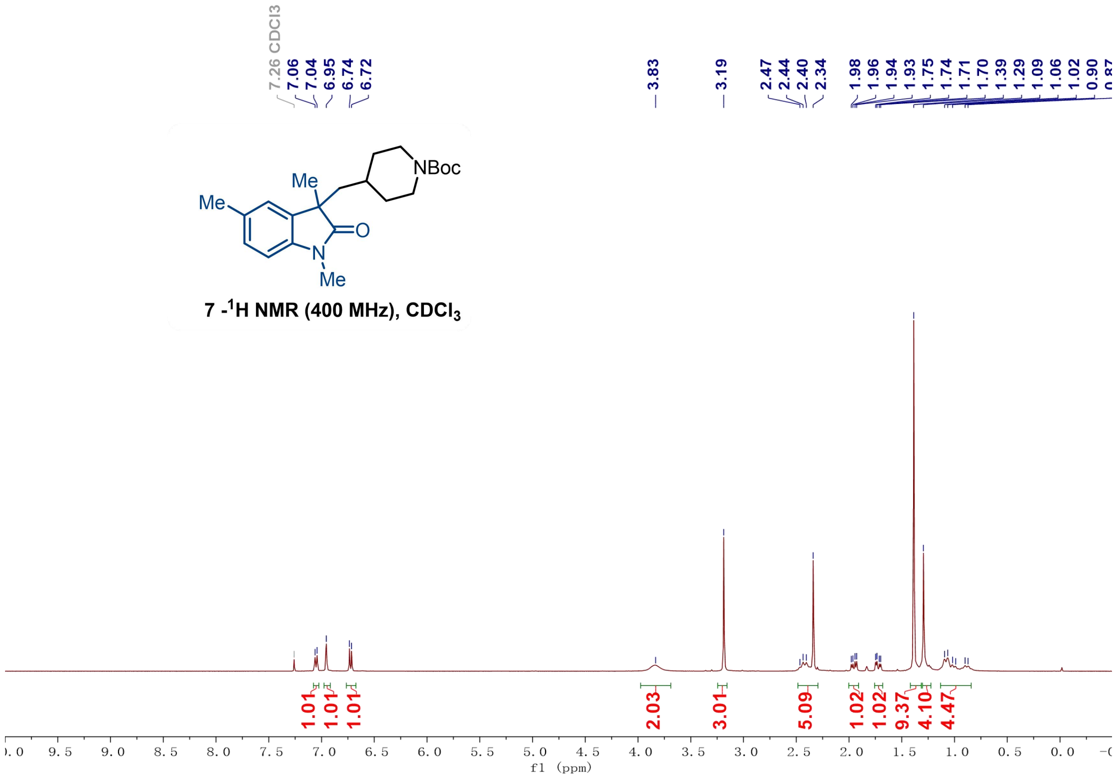
5 -^{1}H NMR (400 MHz), CDCl$_3$



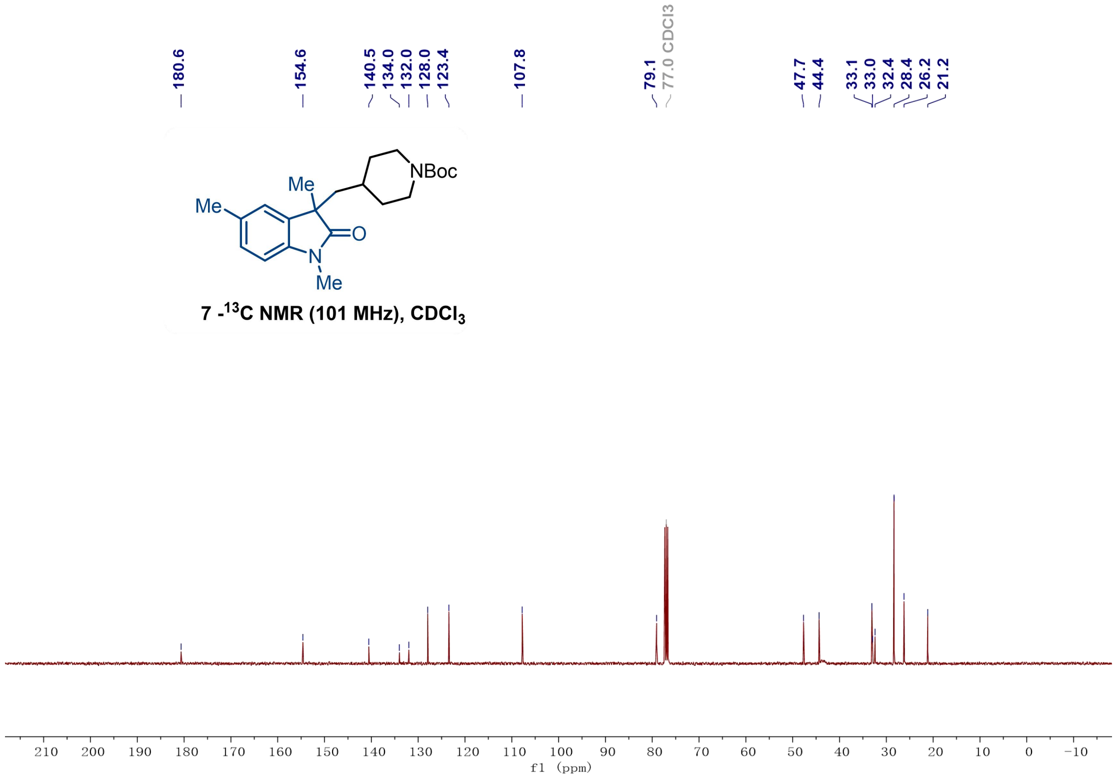
5 -^{13}C NMR (101 MHz), CDCl$_3$


6 -^{1}H NMR (400 MHz), CDCl$_3$

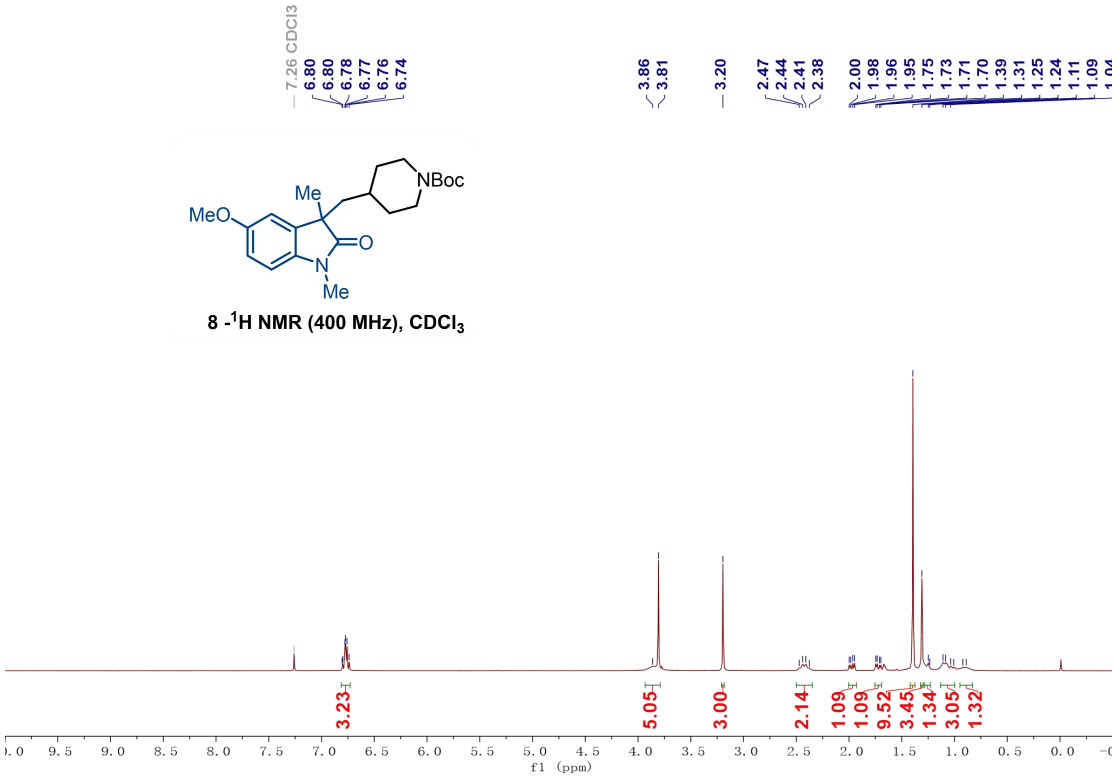

6 -^{13}C NMR (101 MHz), CDCl$_3$



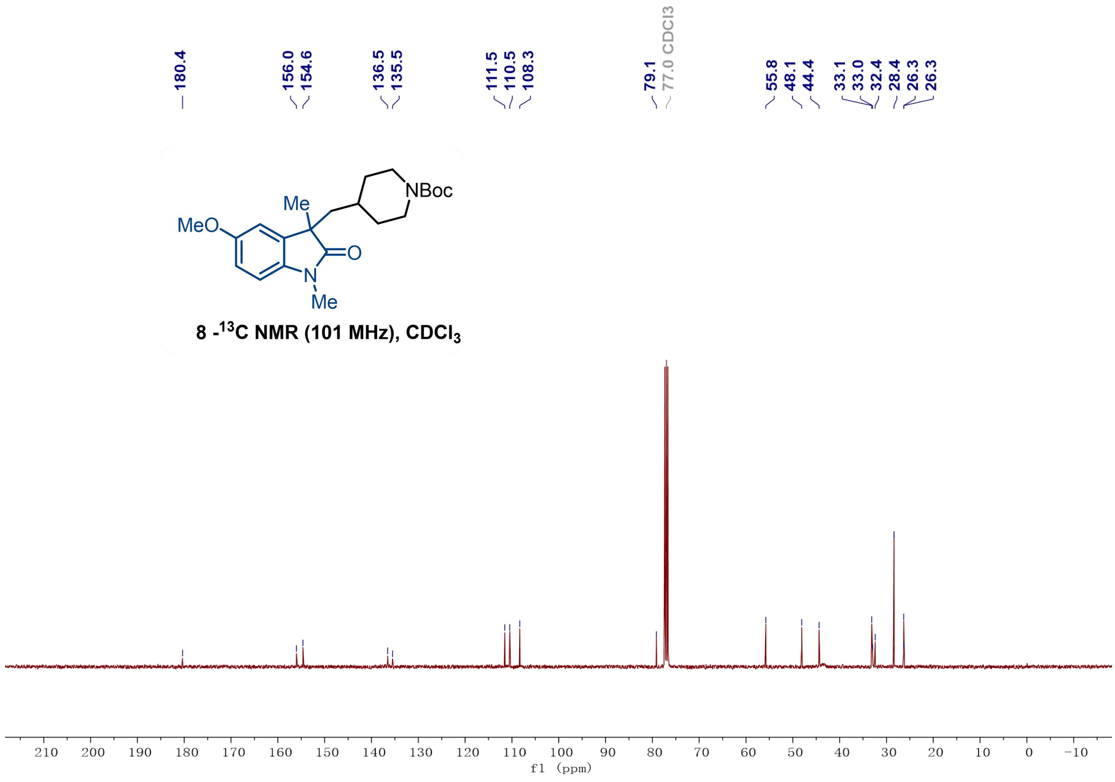
7 -^{1}H NMR (400 MHz), CDCl$_3$



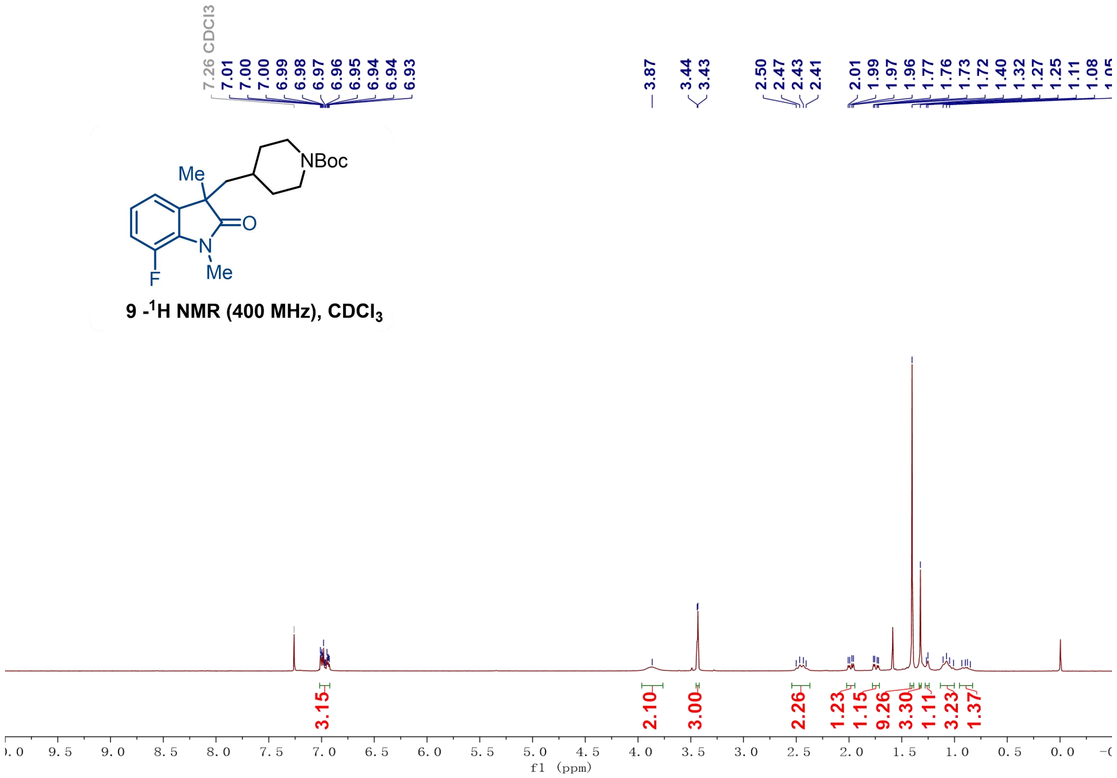
7 -^{13}C NMR (101 MHz), CDCl$_3$

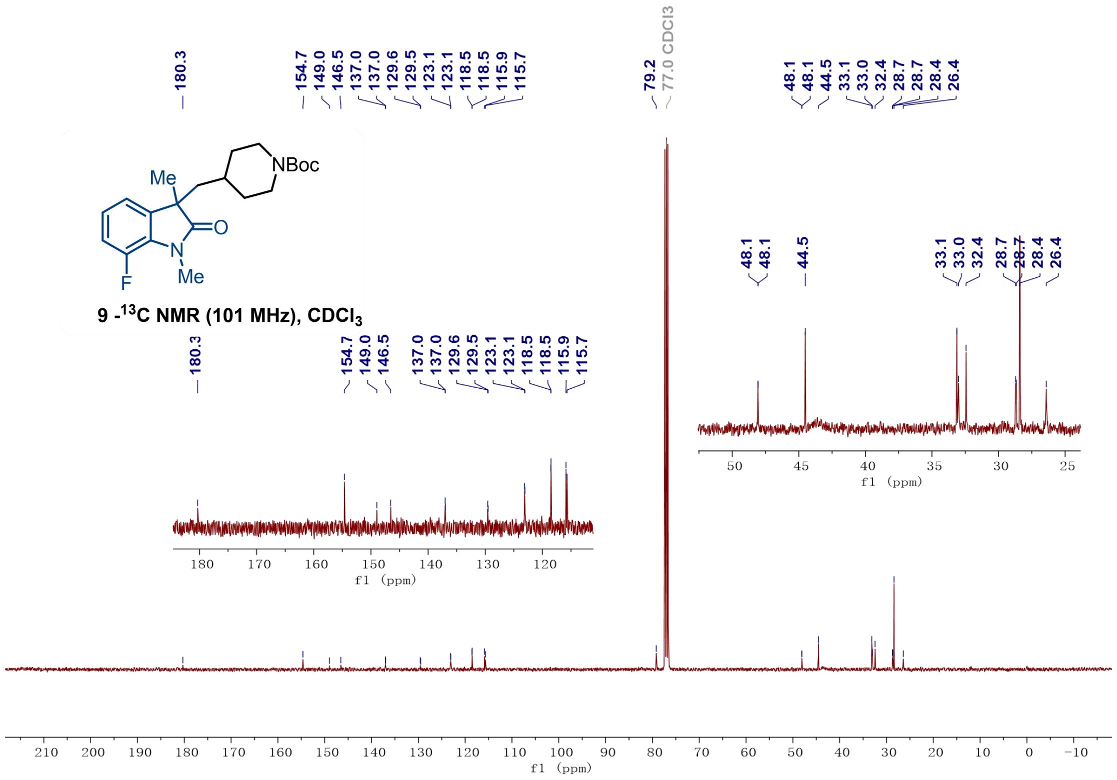


8 -^{1}H NMR (400 MHz), CDCl$_3$

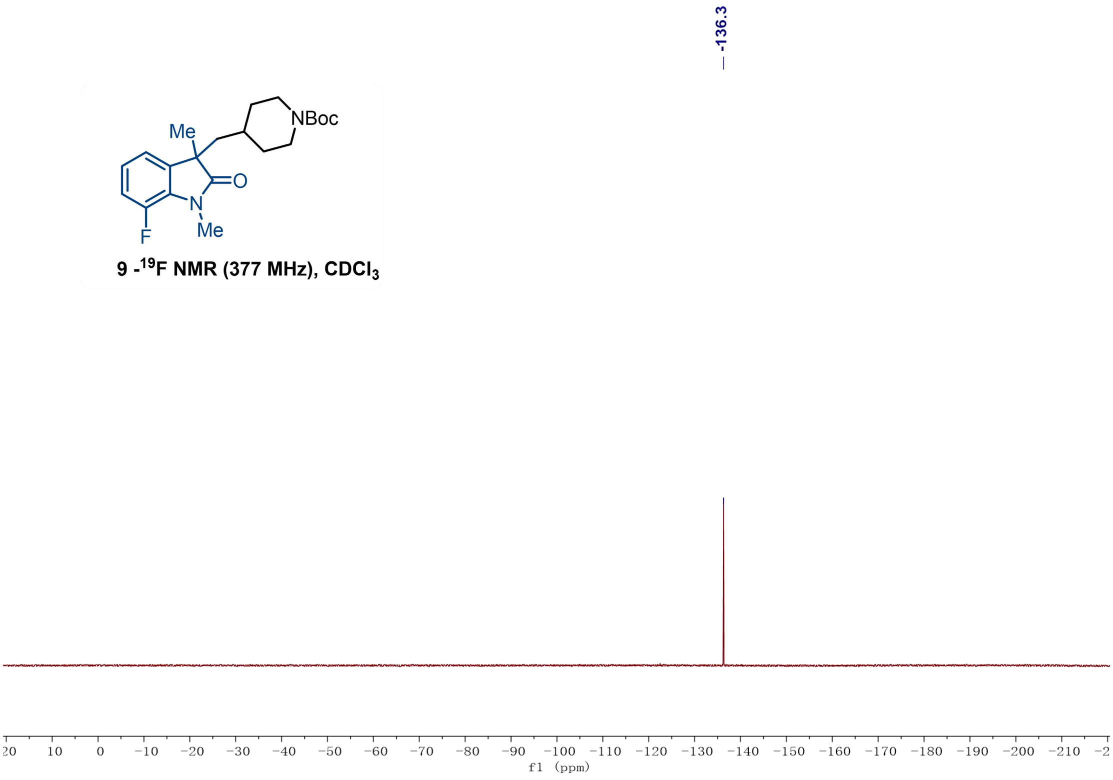


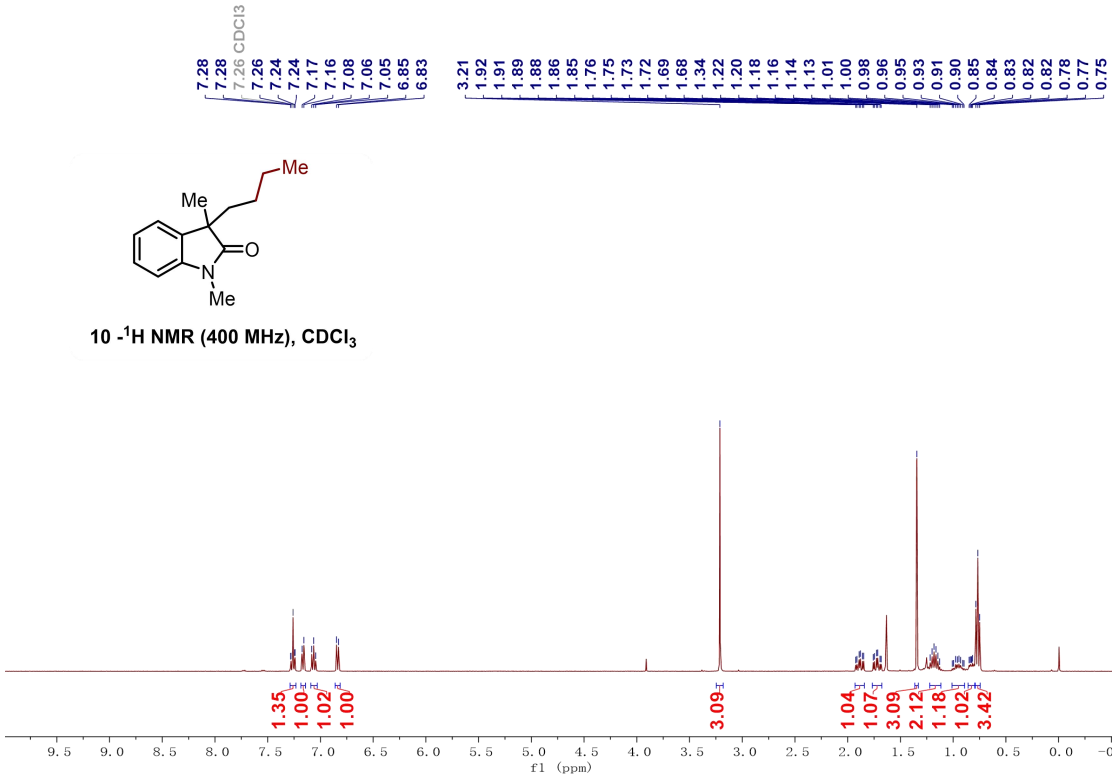
8 -^{13}C NMR (101 MHz), CDCl$_3$


9 -^{1}H NMR (400 MHz), CDCl$_3$

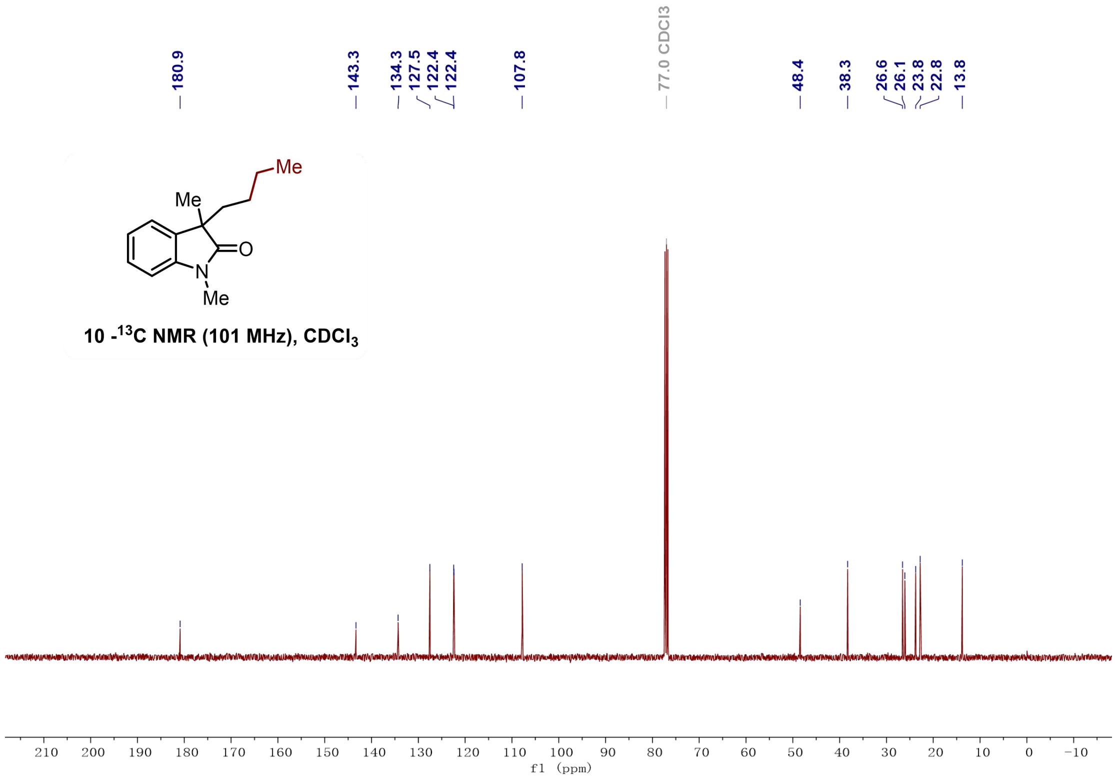

9 -^{13}C NMR (101 MHz), CDCl$_3$

9 -^{19}F NMR (377 MHz), CDCl$_3$

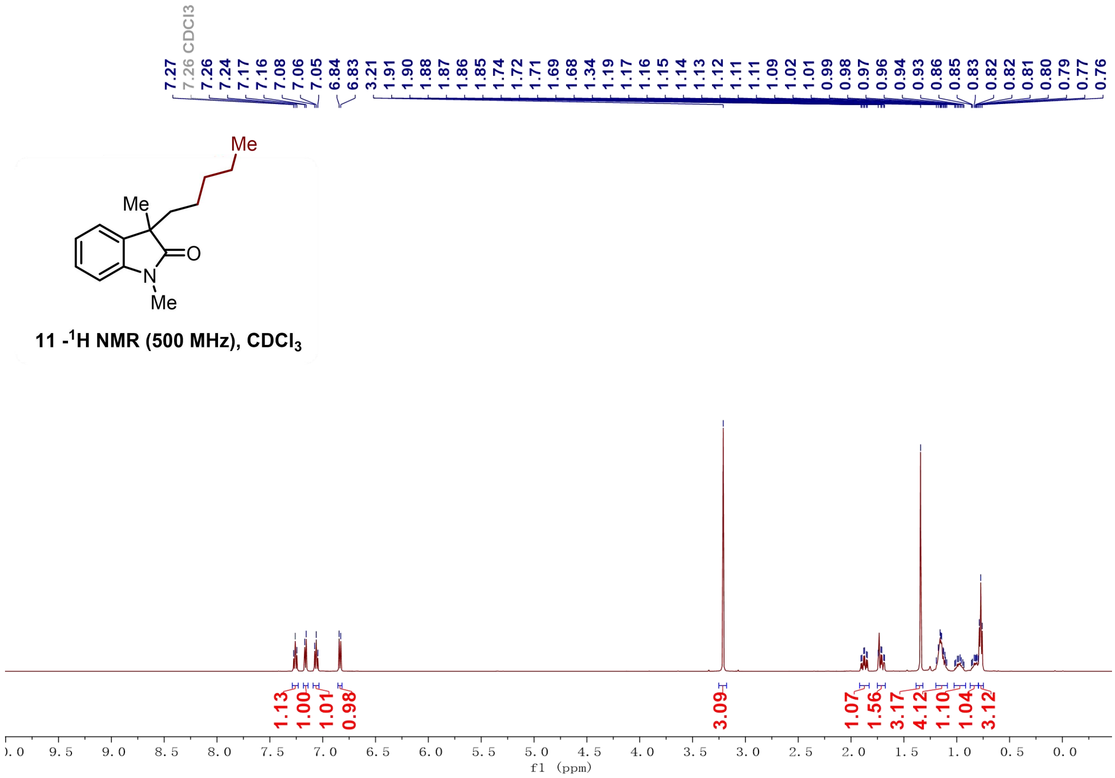




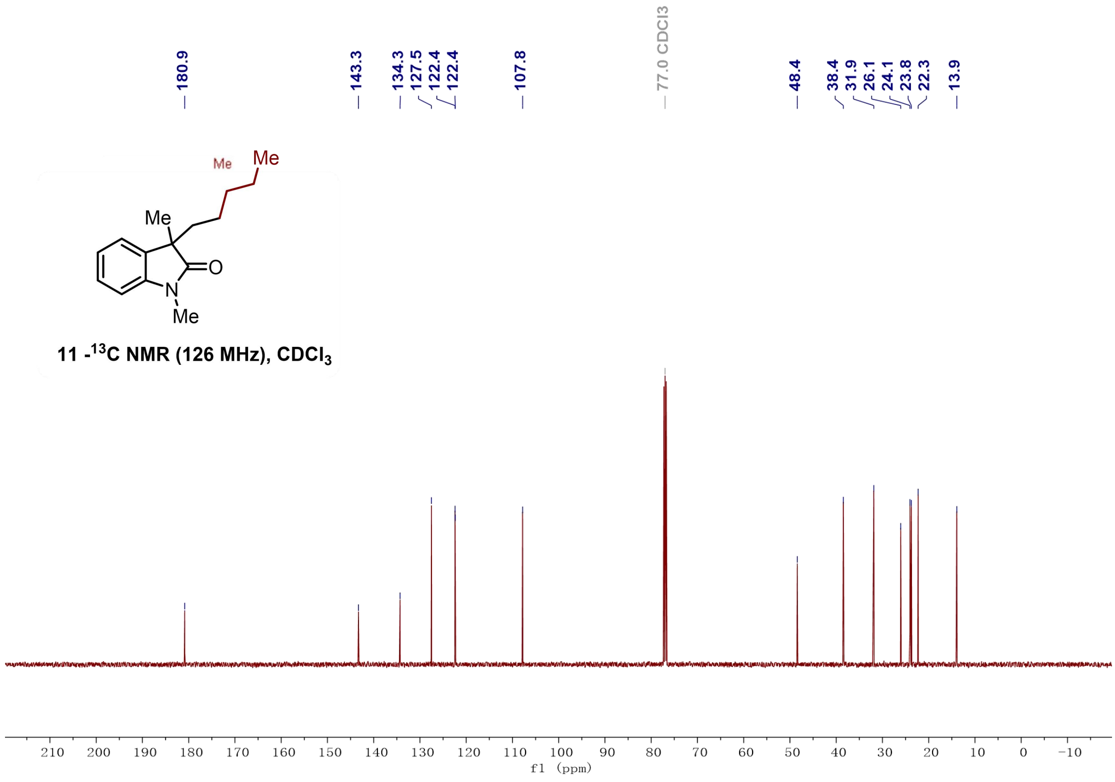
10 -^{1}H NMR (400 MHz), CDCl$_3$



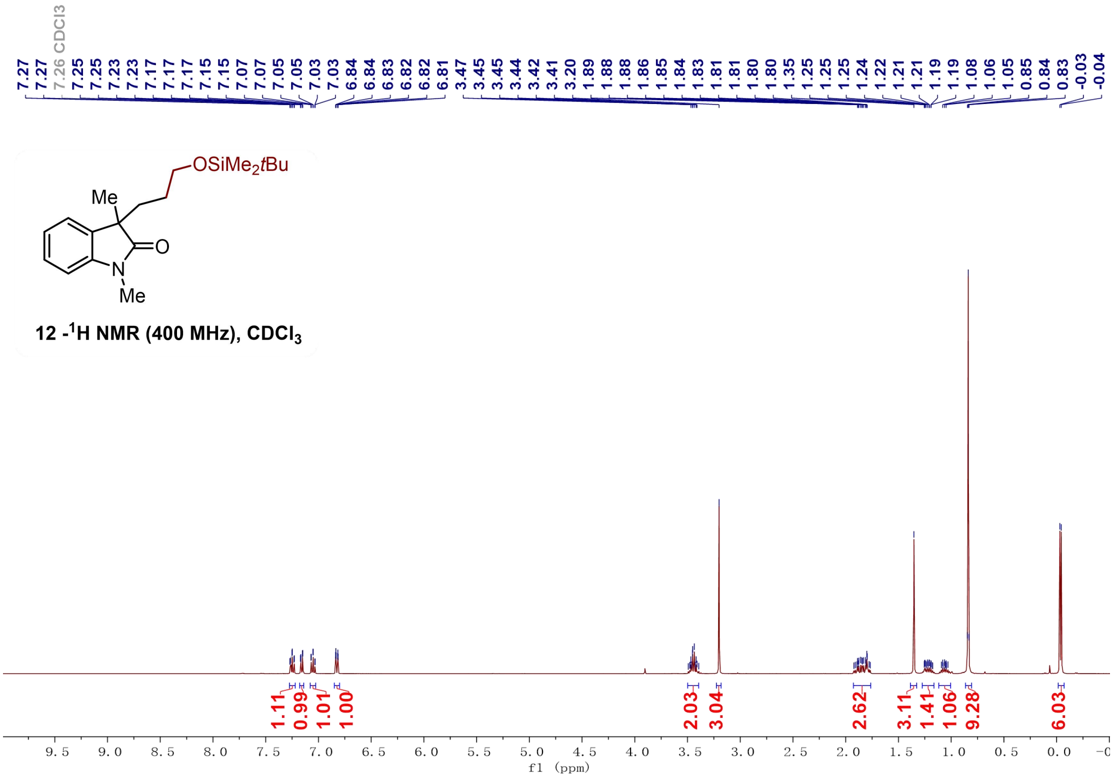
10 -^{13}C NMR (101 MHz), CDCl$_3$



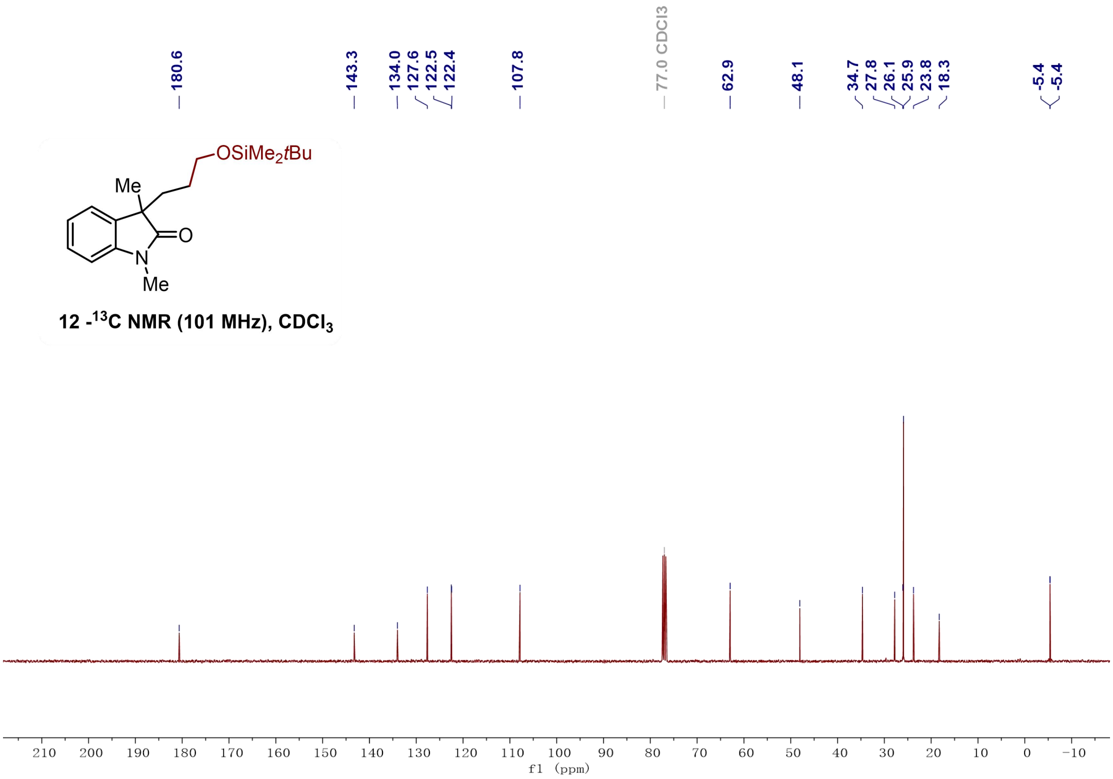
11 -^{1}H NMR (500 MHz), CDCl$_3$



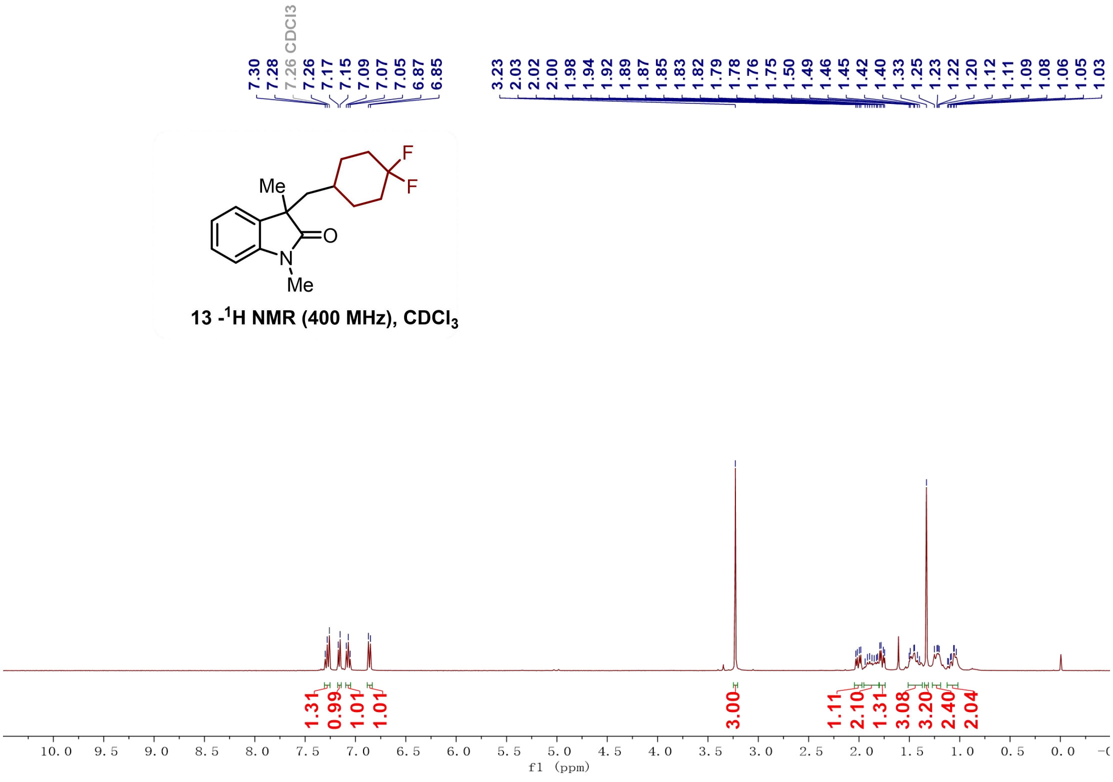
11 -^{13}C NMR (126 MHz), CDCl$_3$



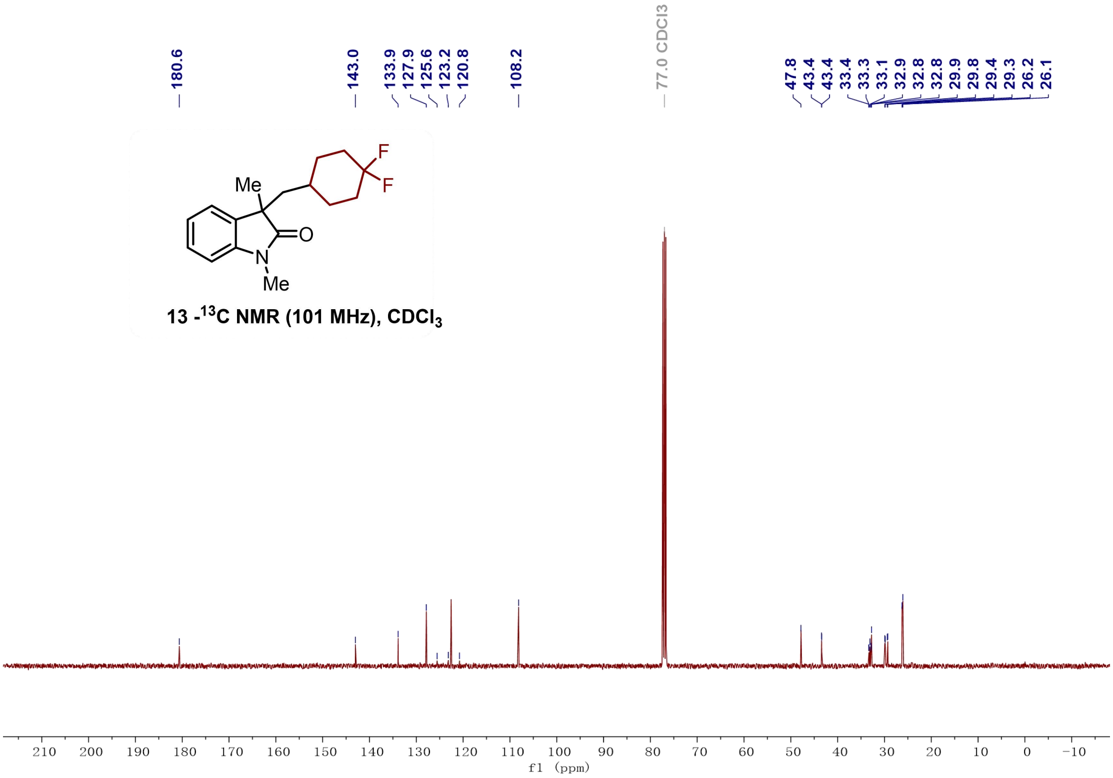
12 -^{1}H NMR (400 MHz), CDCl$_3$



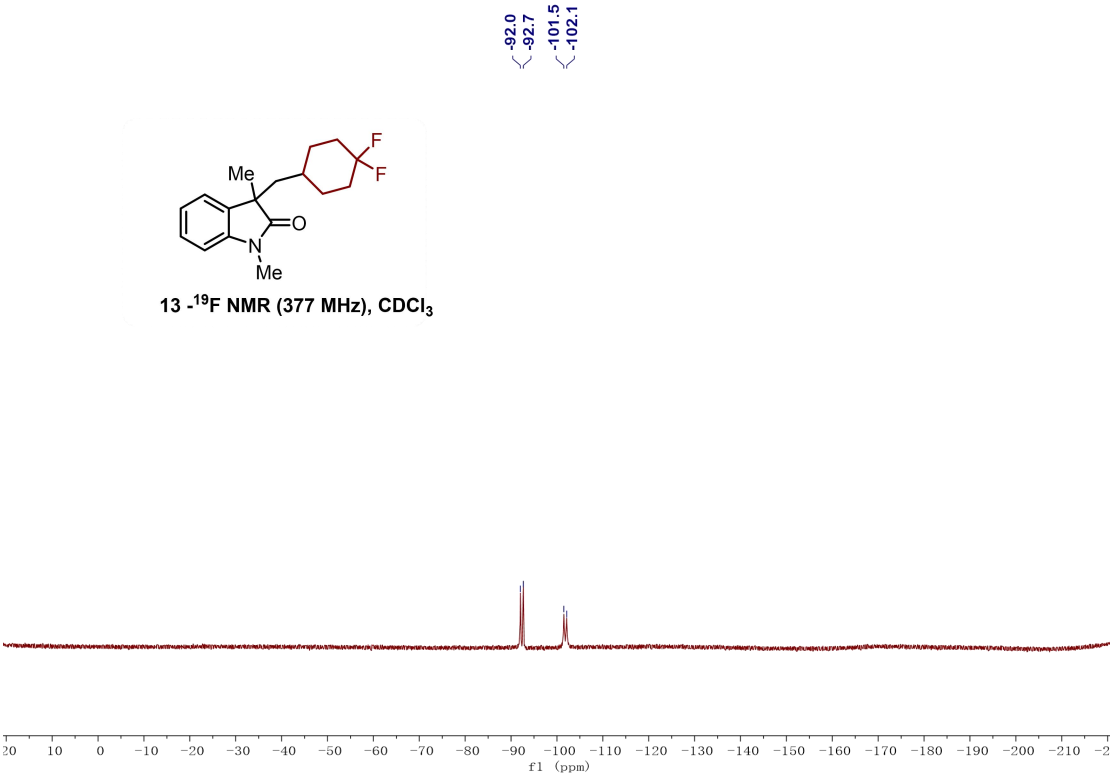
12 -^{13}C NMR (101 MHz), CDCl$_3$



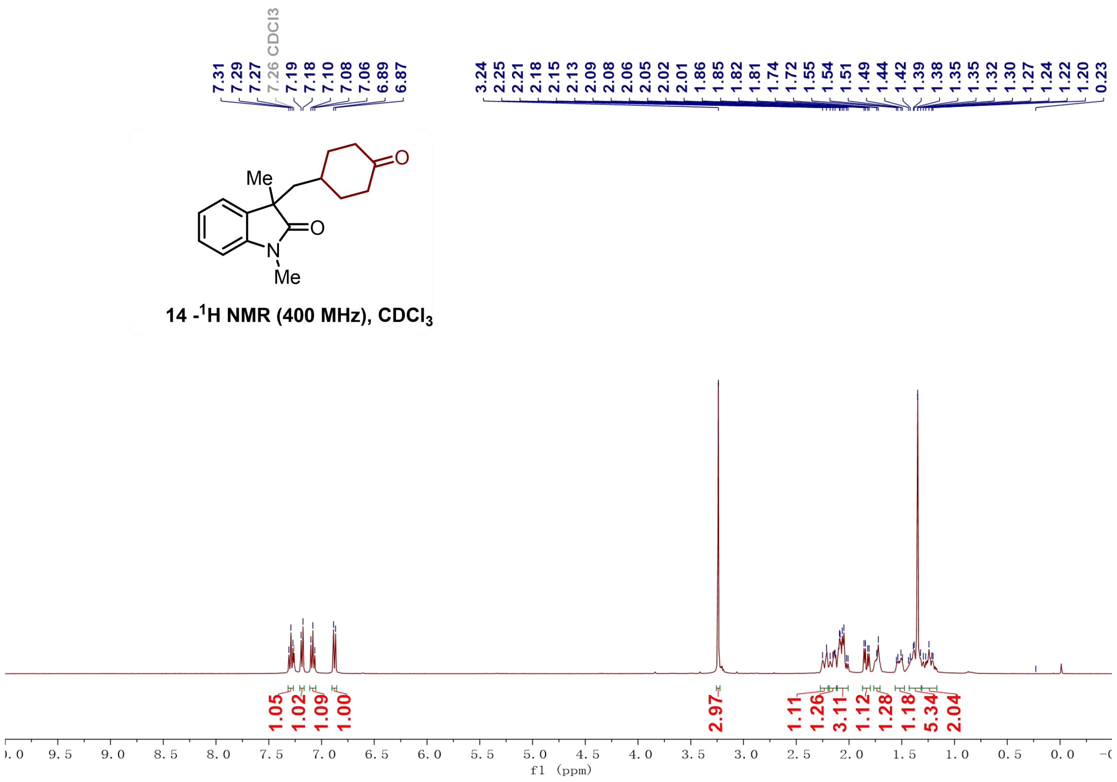
13 -^{1}H NMR (400 MHz), $CDCl_3$



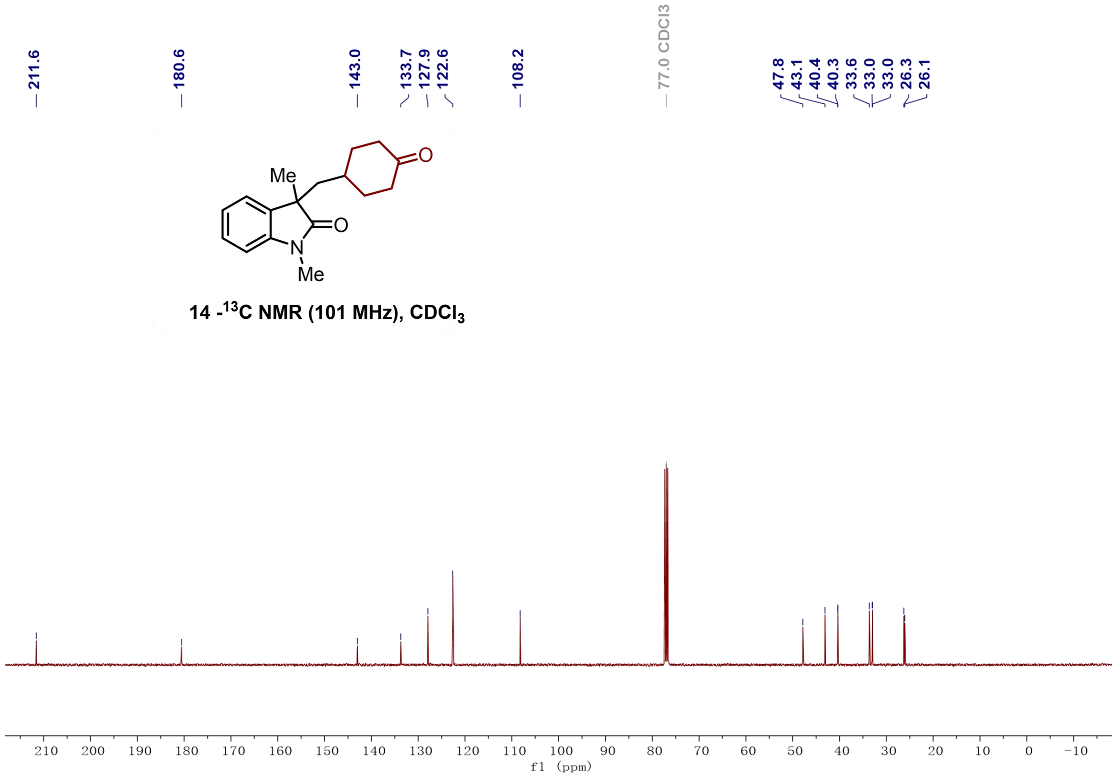
13 -^{13}C NMR (101 MHz), $CDCl_3$



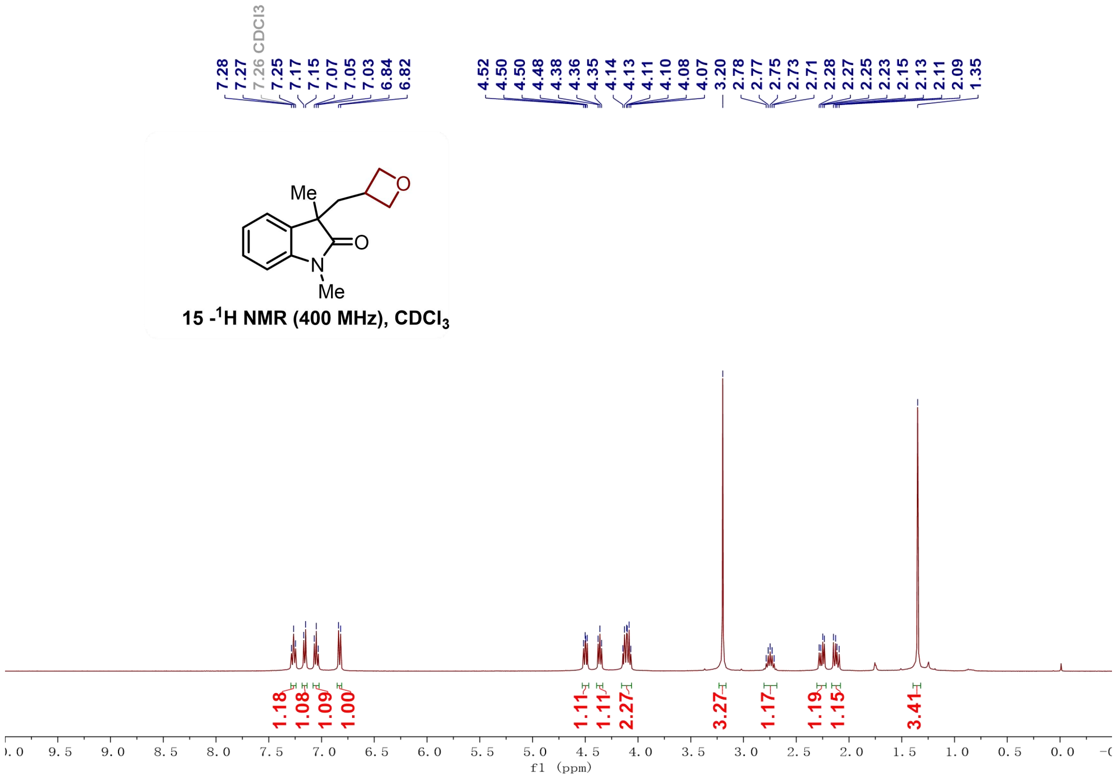
13 -^{19}F NMR (377 MHz), CDCl$_3$



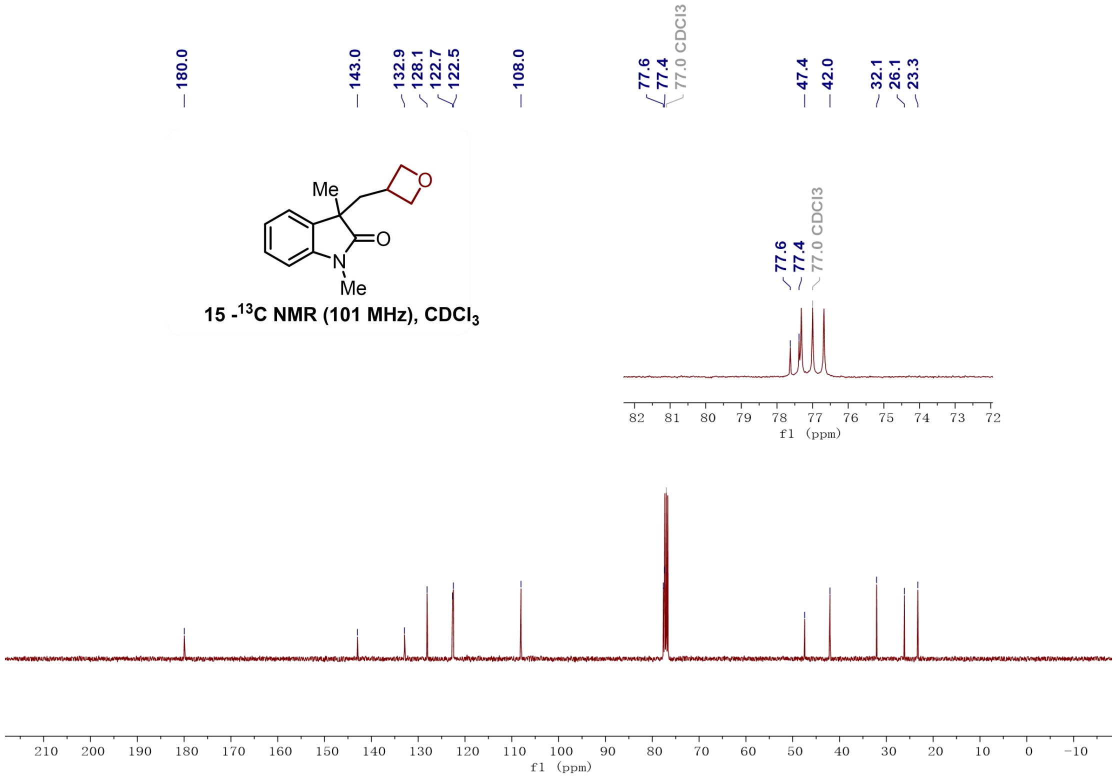
14 -^{1}H NMR (400 MHz), CDCl$_3$



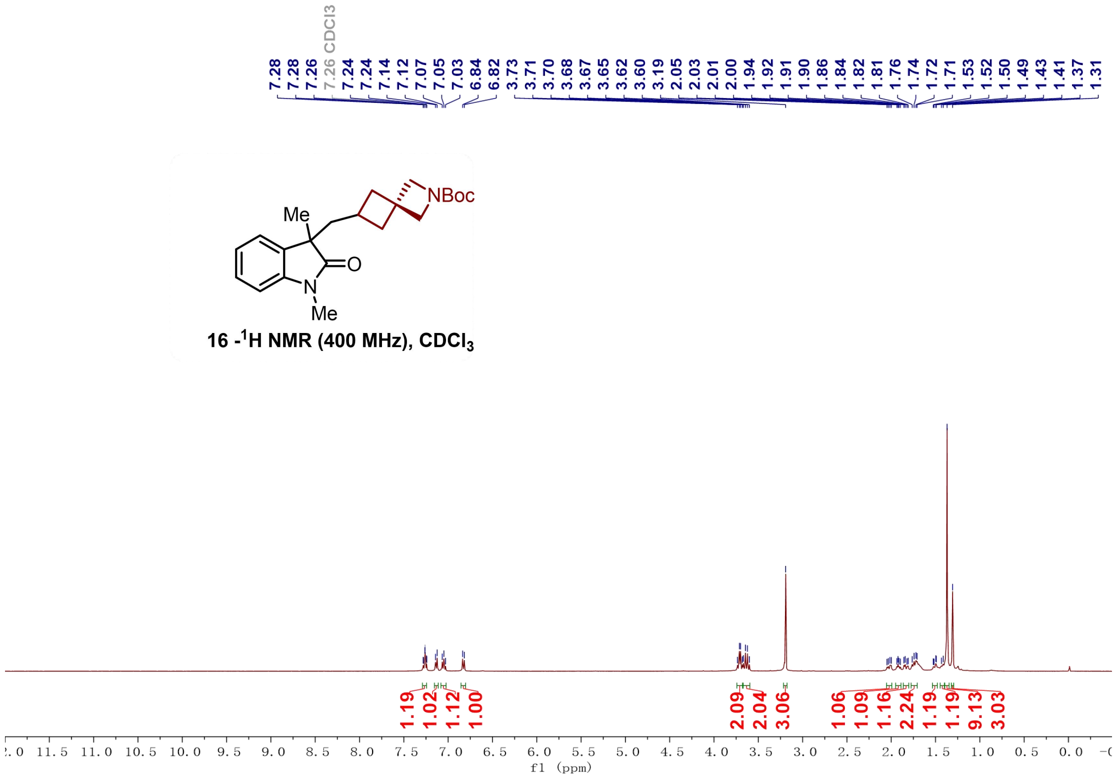
14 -^{13}C NMR (101 MHz), CDCl$_3$



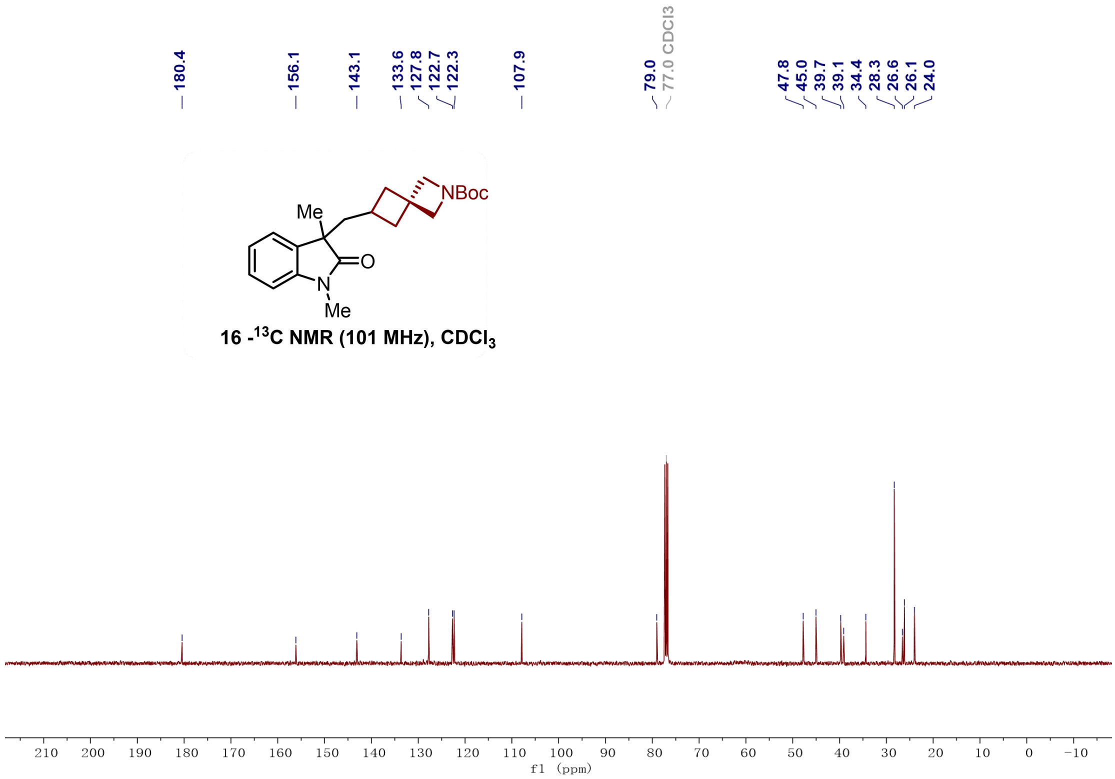
15 -^{1}H NMR (400 MHz), CDCl$_3$



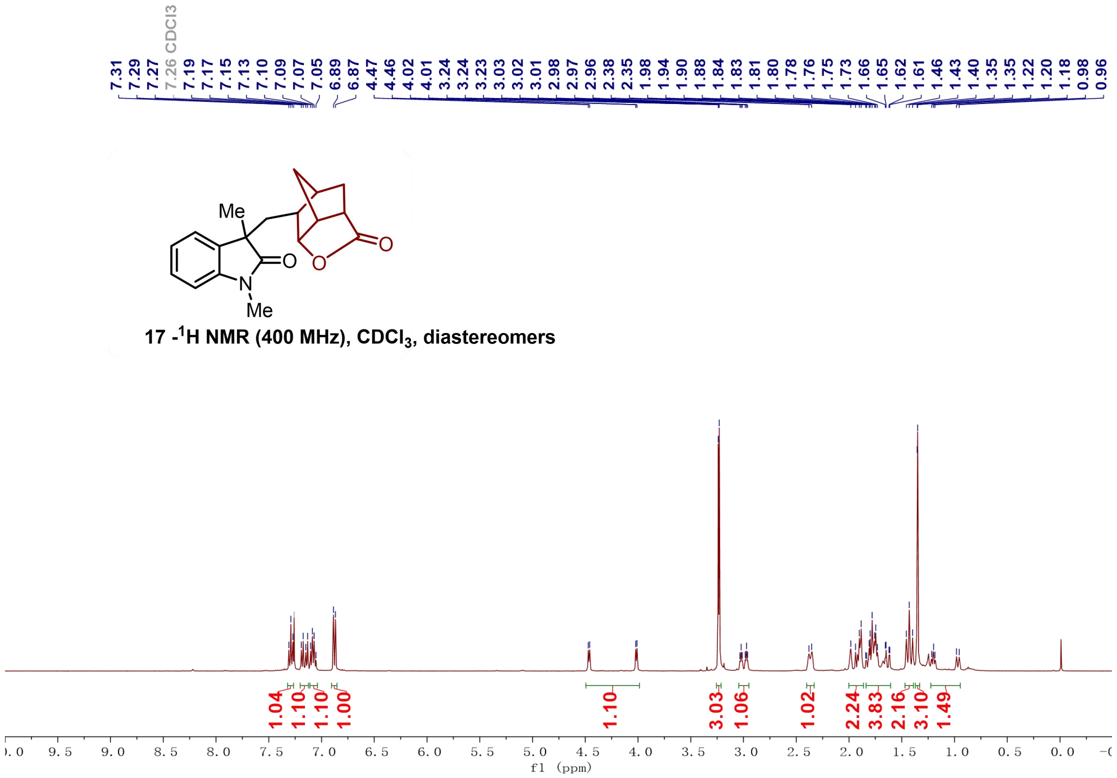
15 -^{13}C NMR (101 MHz), CDCl$_3$



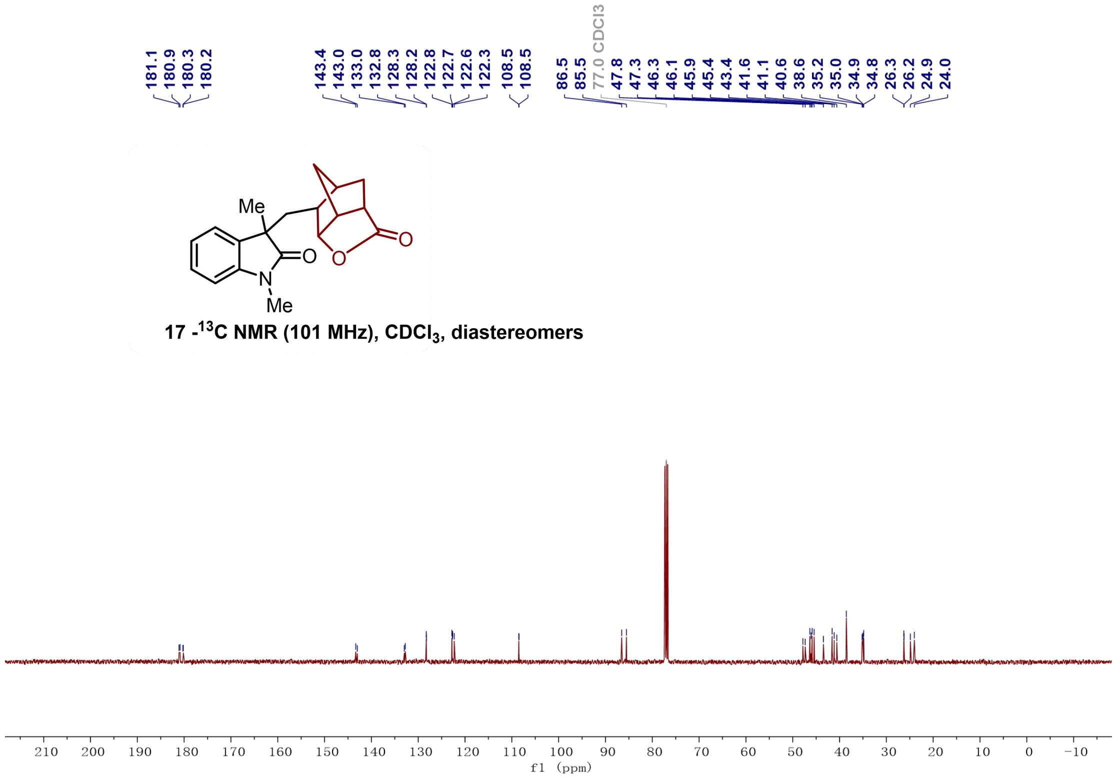
16 -^{1}H NMR (400 MHz), $CDCl_3$



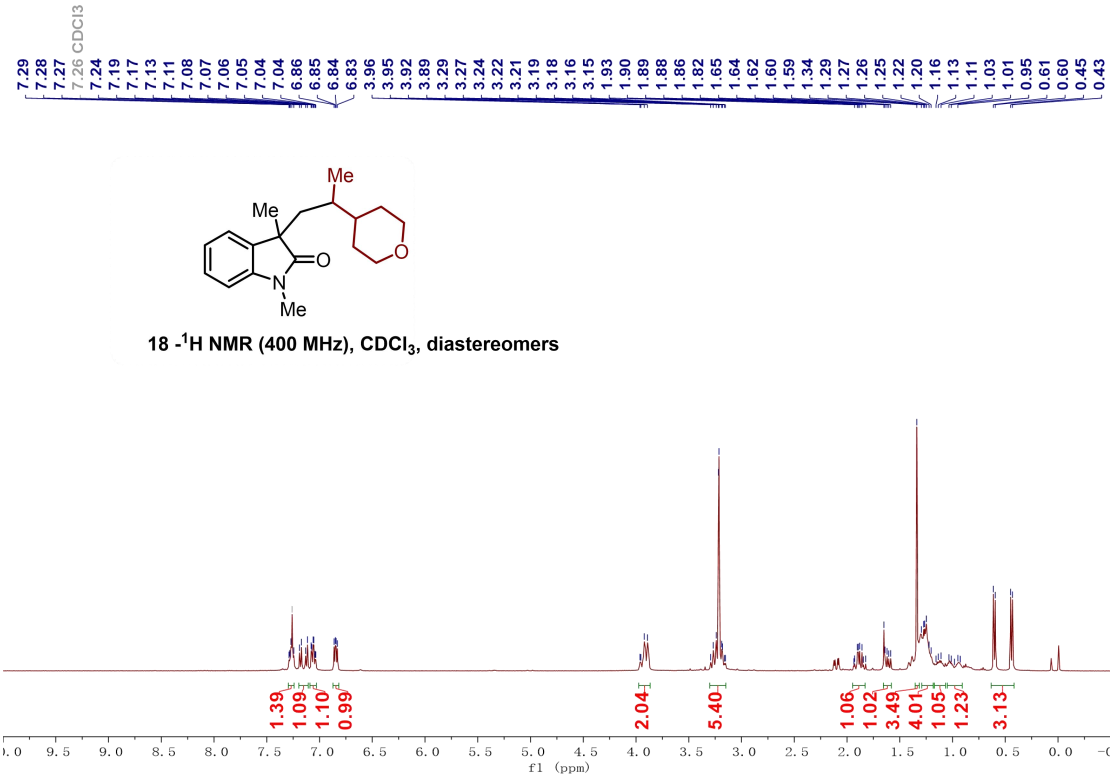
16 -^{13}C NMR (101 MHz), $CDCl_3$



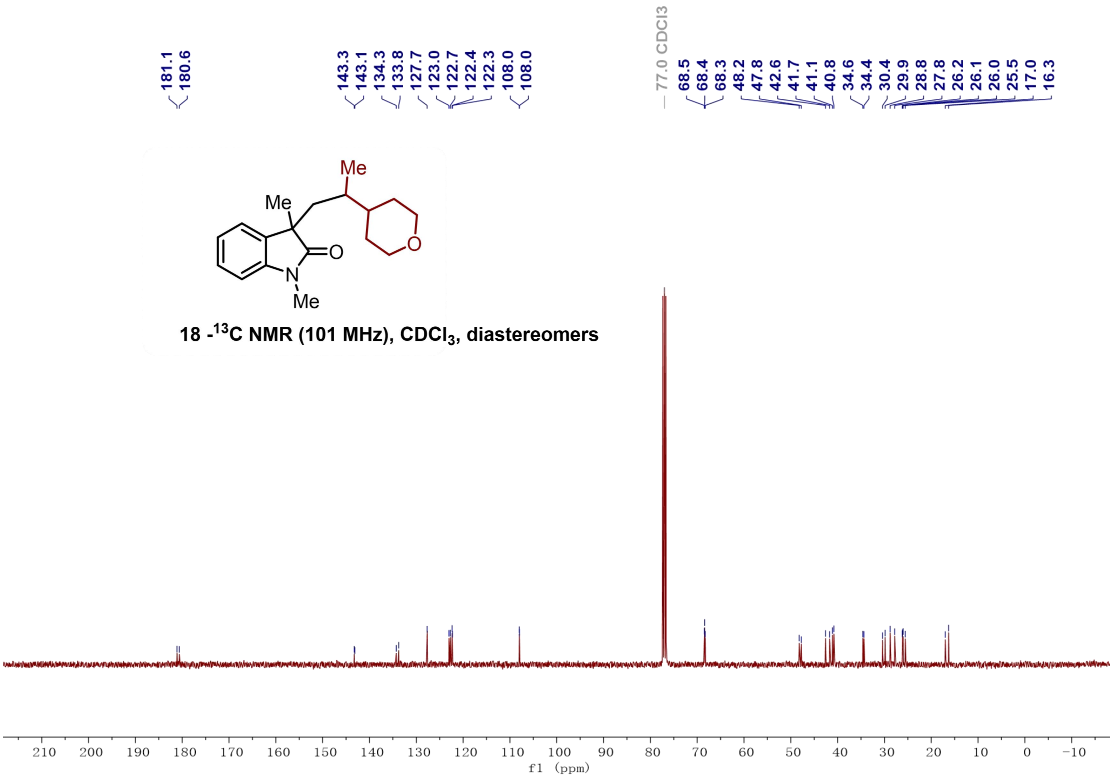
17 -^{1}H NMR (400 MHz), $CDCl_3$, diastereomers



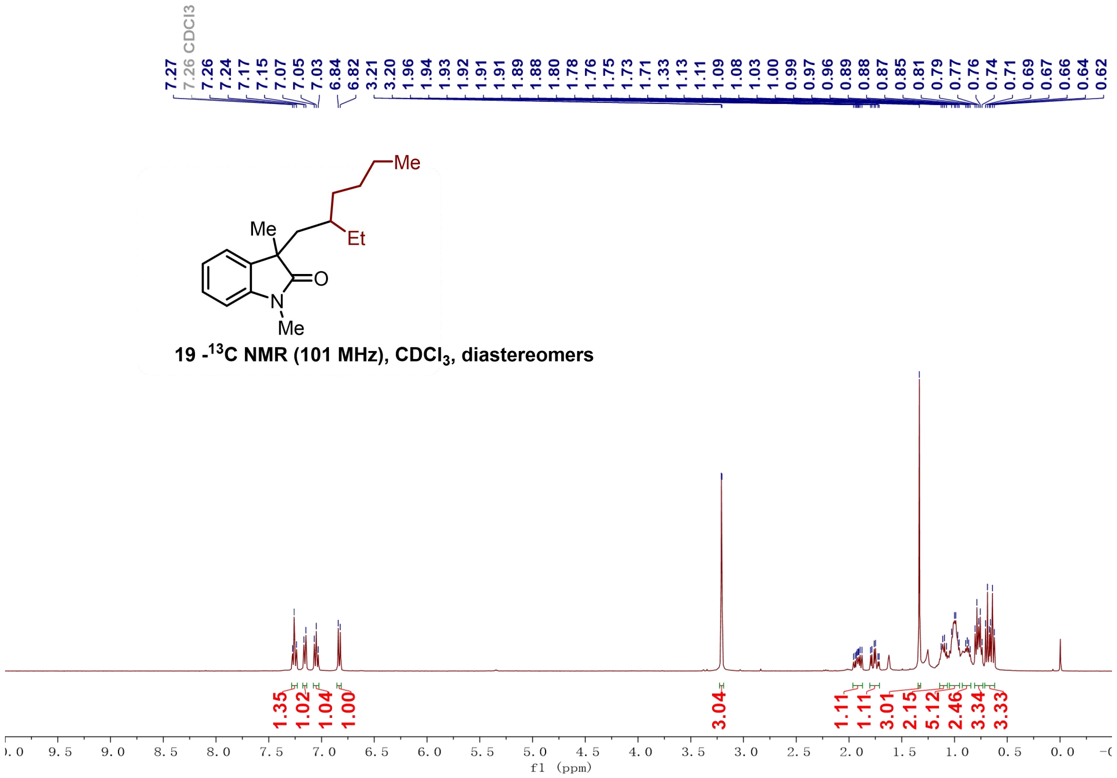
17 -^{13}C NMR (101 MHz), $CDCl_3$, diastereomers



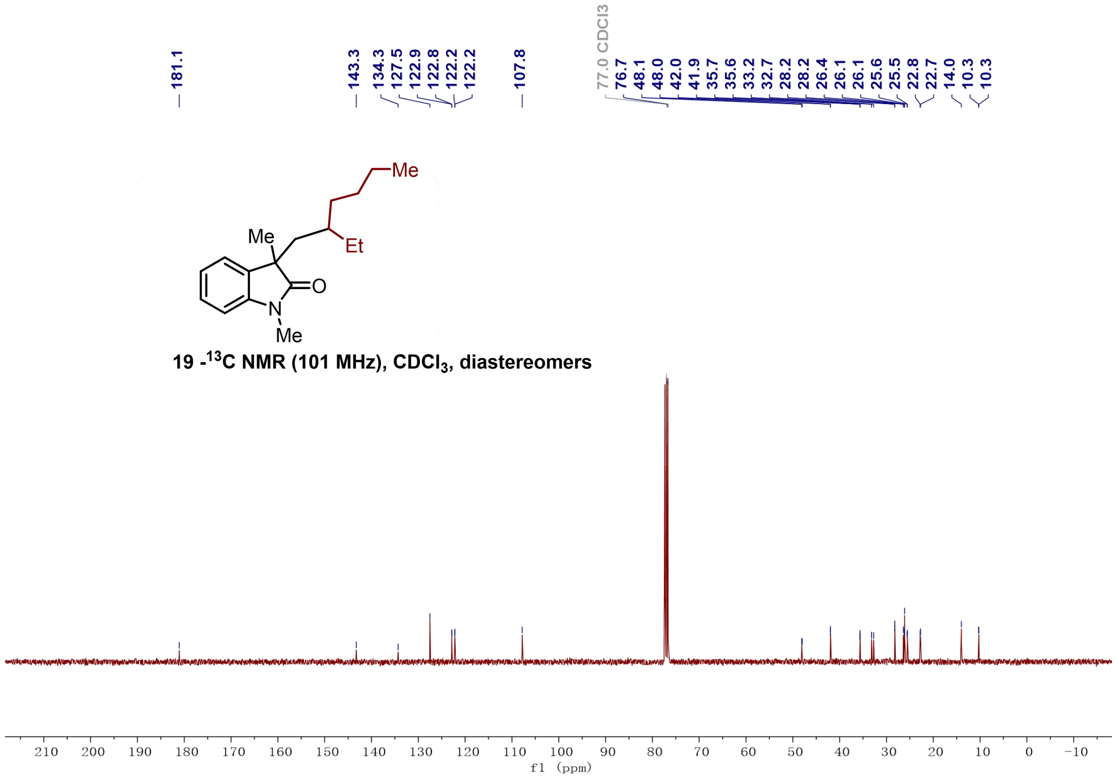
18 -^{1}H NMR (400 MHz), CDCl$_3$, diastereomers



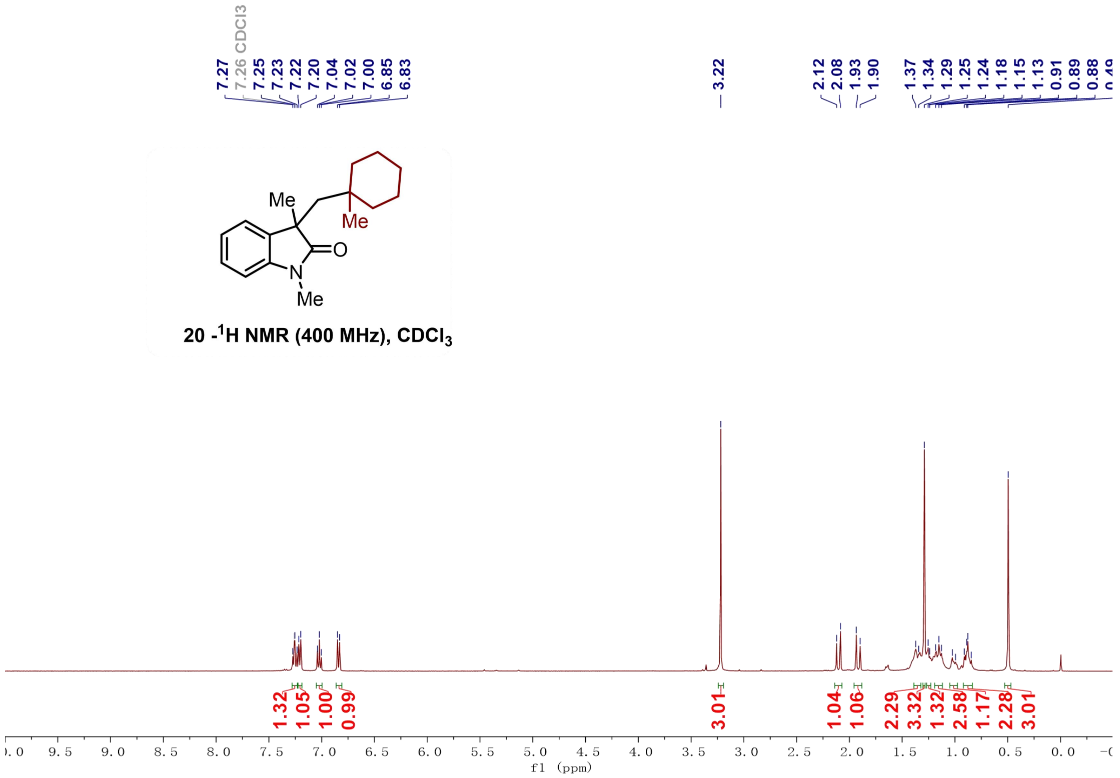
18 -^{13}C NMR (101 MHz), CDCl$_3$, diastereomers

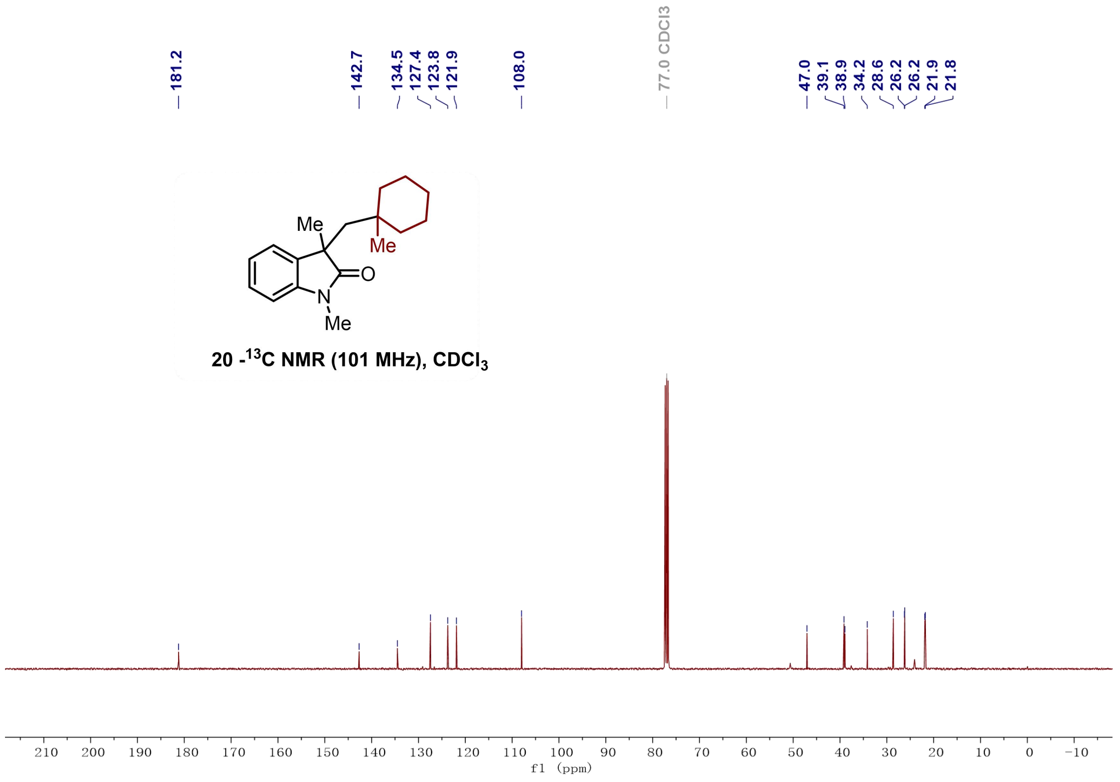


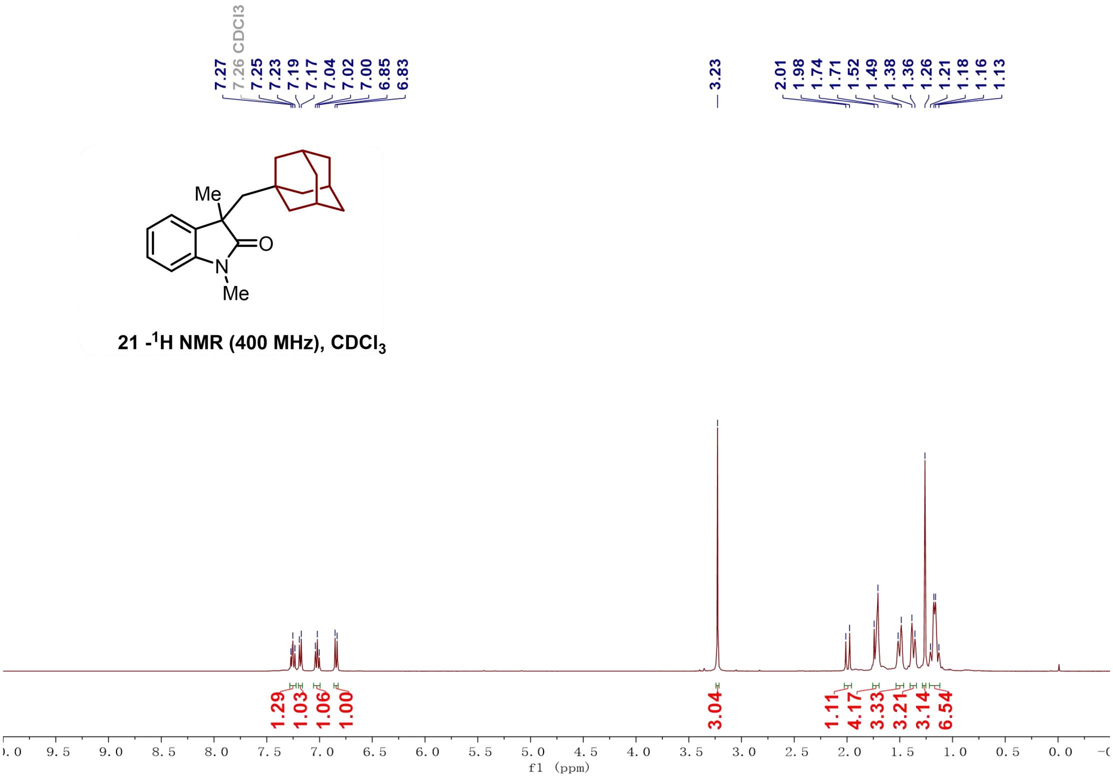
19 -^{13}C NMR (101 MHz), CDCl$_3$, diastereomers



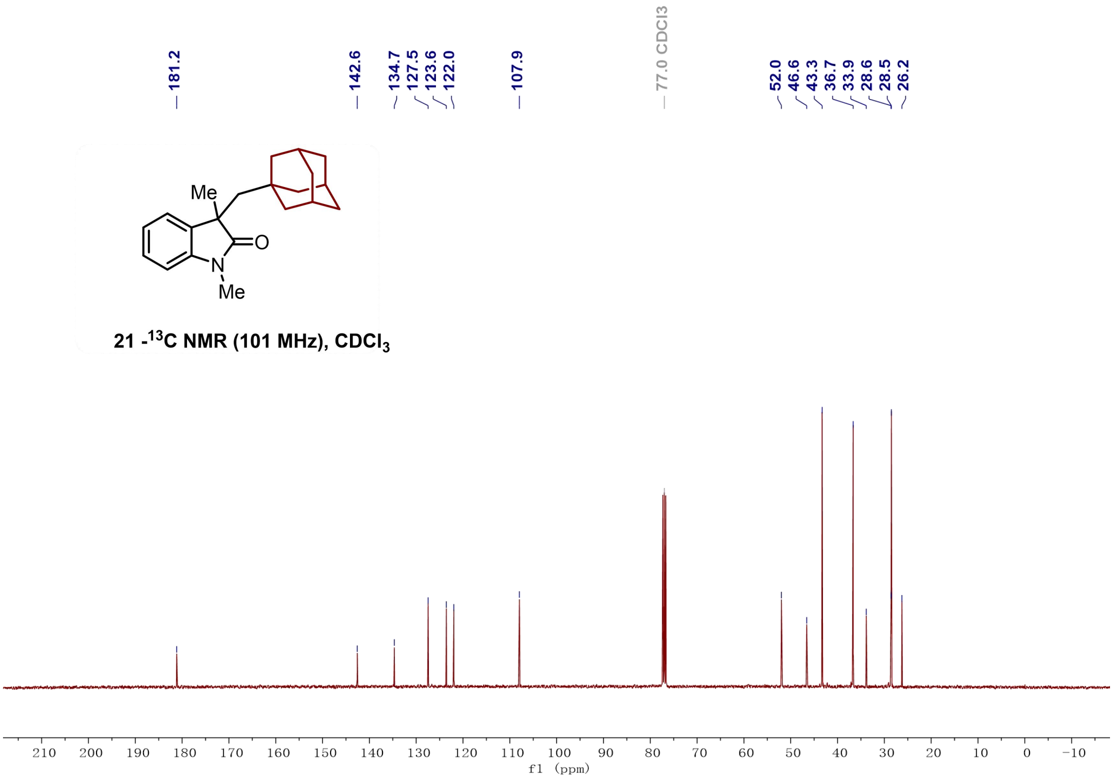
19 -^{13}C NMR (101 MHz), CDCl$_3$, diastereomers


20 -^{1}H NMR (400 MHz), CDCl$_3$

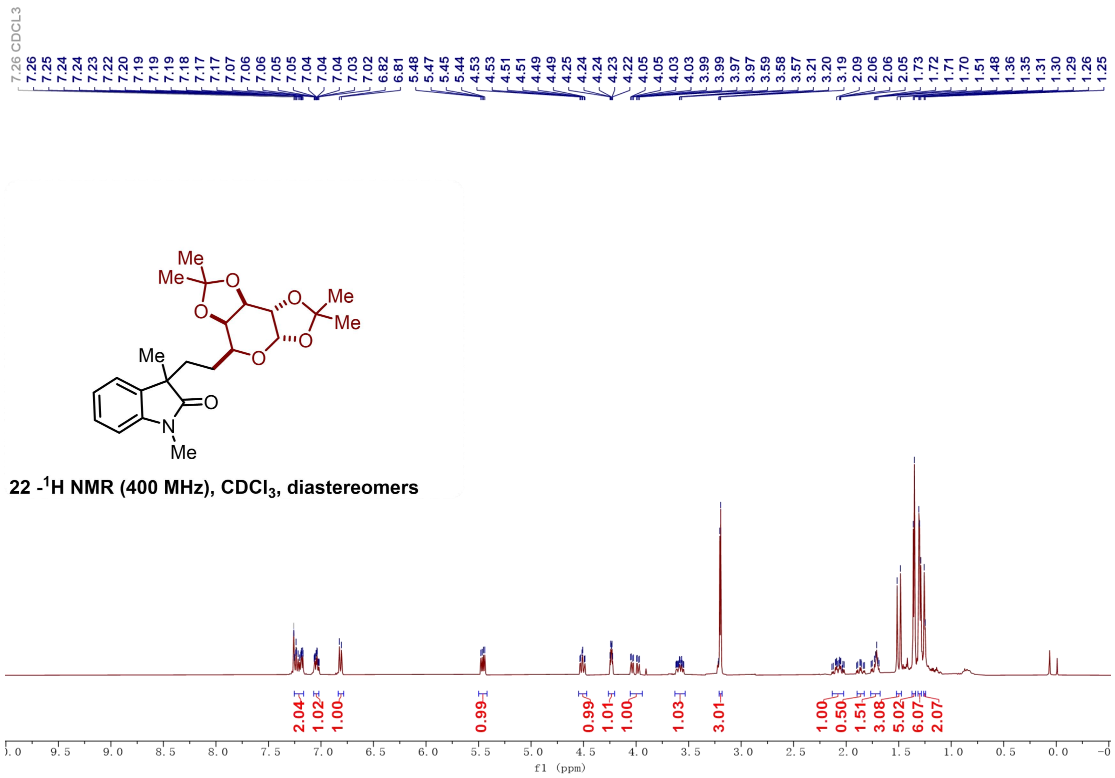

20 -^{13}C NMR (101 MHz), CDCl$_3$



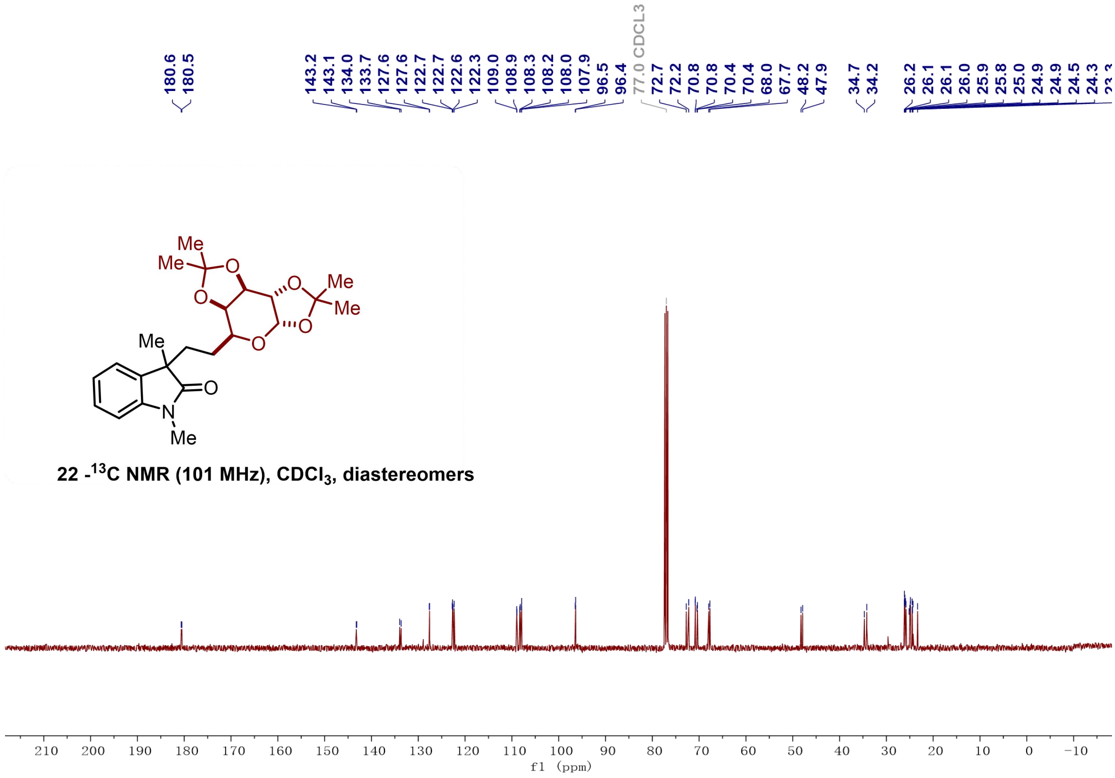
21 -^{1}H NMR (400 MHz), CDCl$_3$



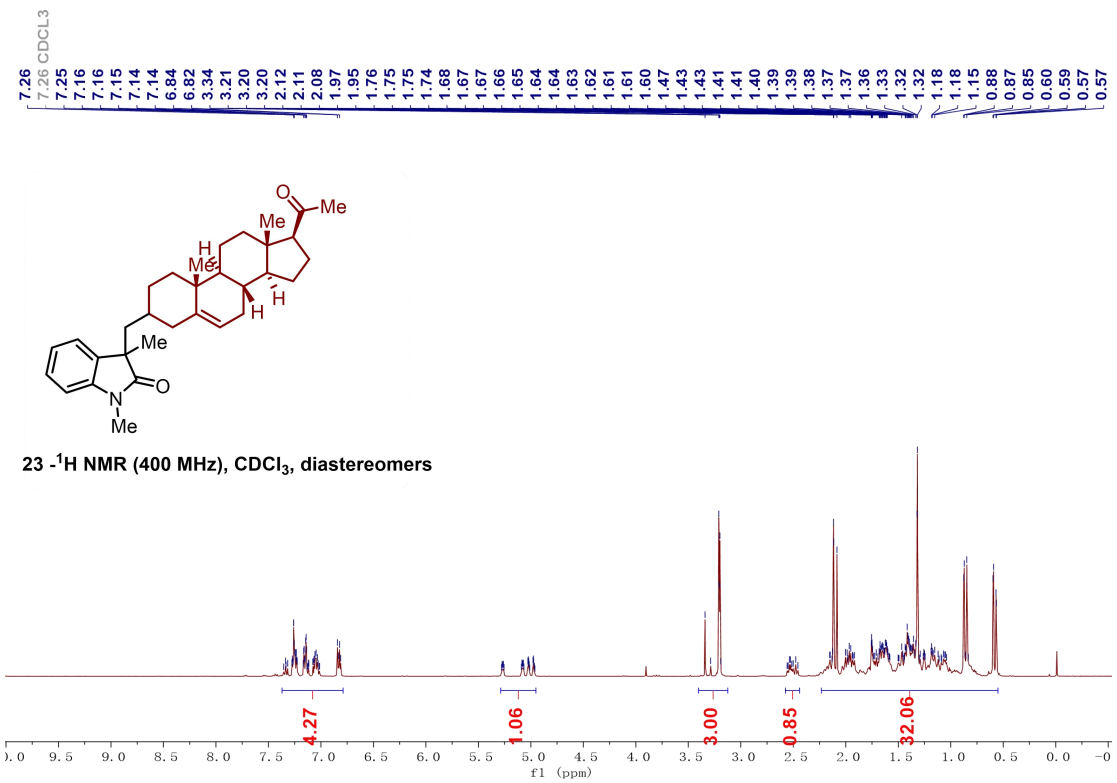
21 -^{13}C NMR (101 MHz), CDCl$_3$



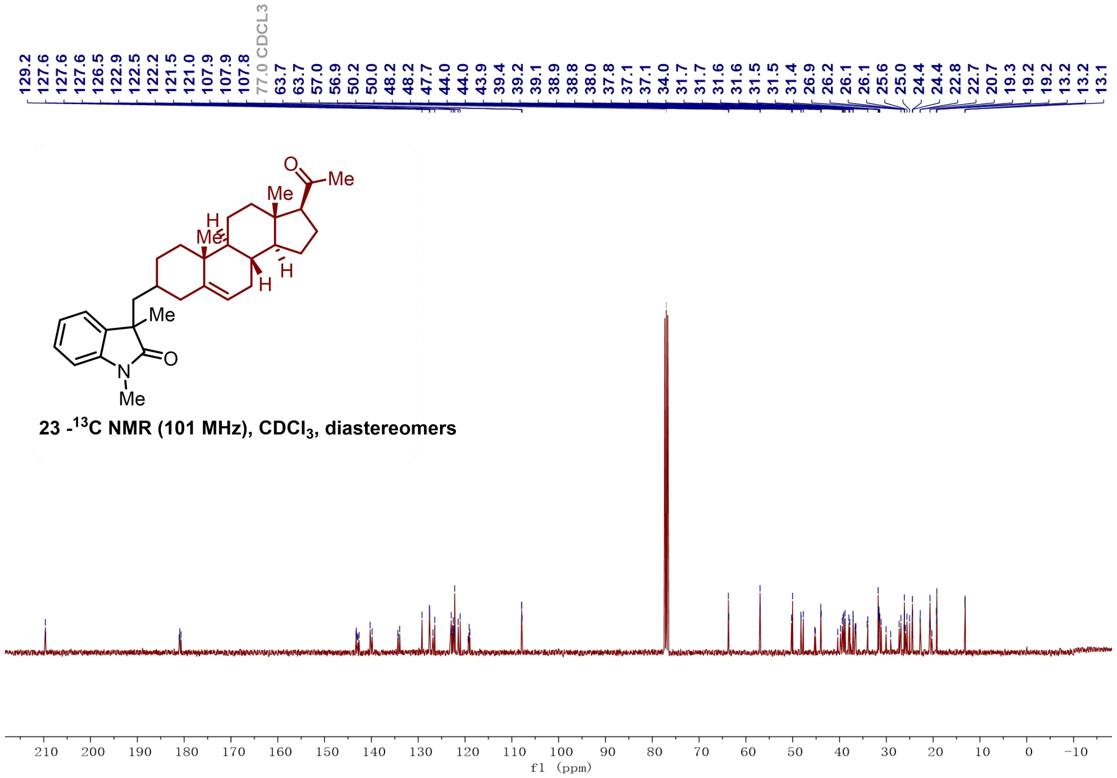
22 -^{1}H NMR (400 MHz), CDCl$_3$, diastereomers



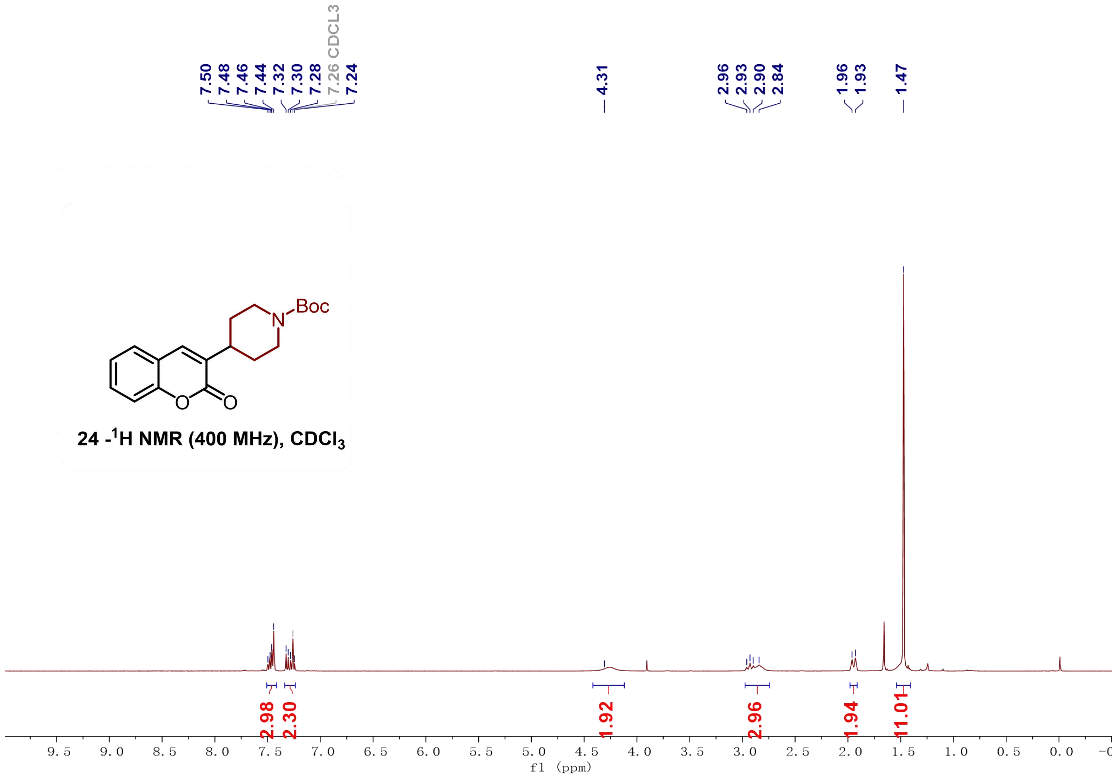
22 -^{13}C NMR (101 MHz), CDCl$_3$, diastereomers

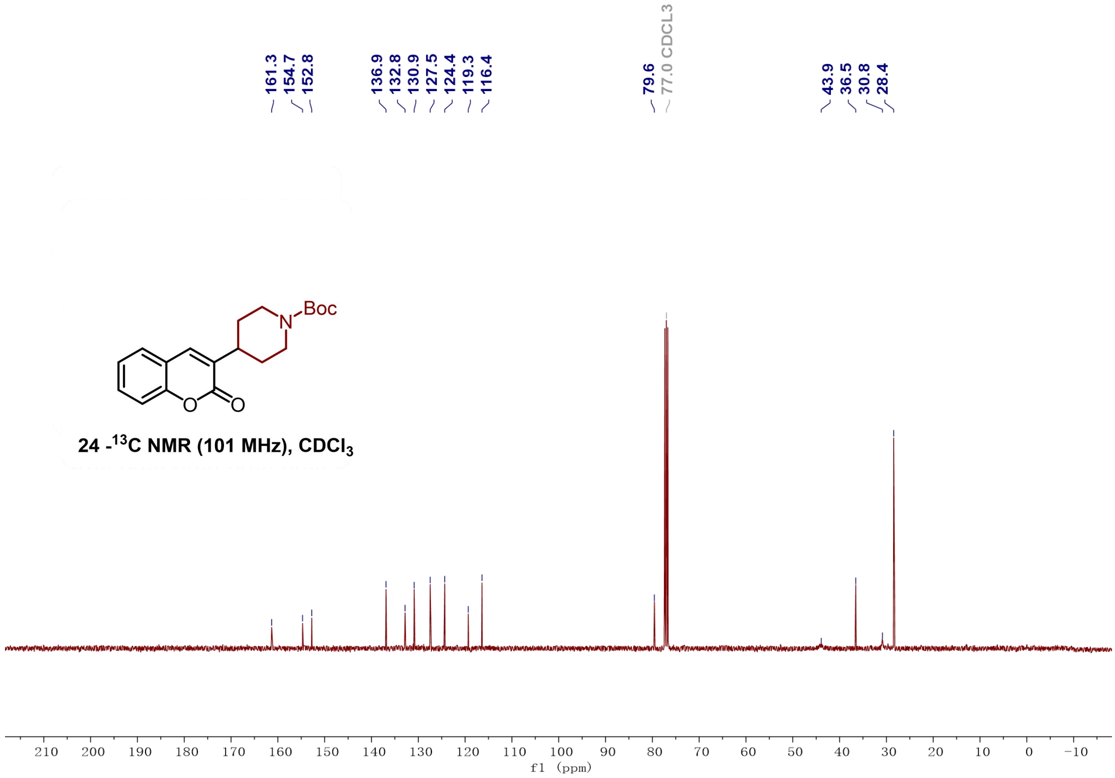


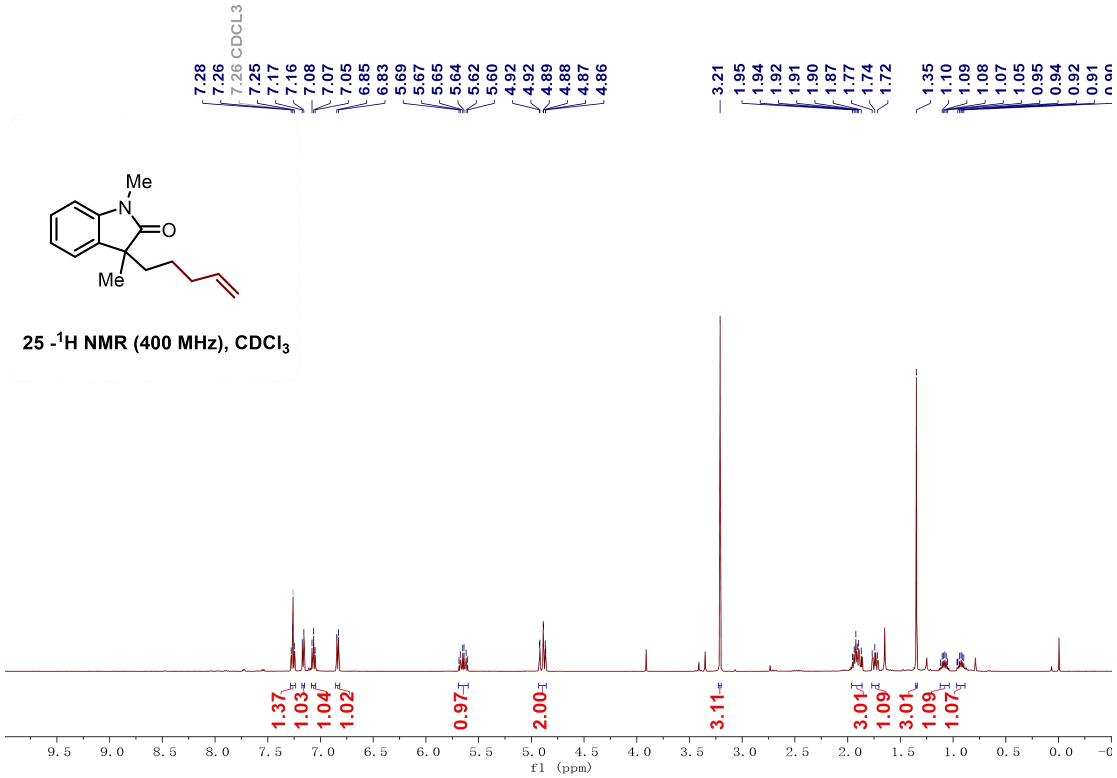
23 -^{1}H NMR (400 MHz), CDCl$_3$, diastereomers

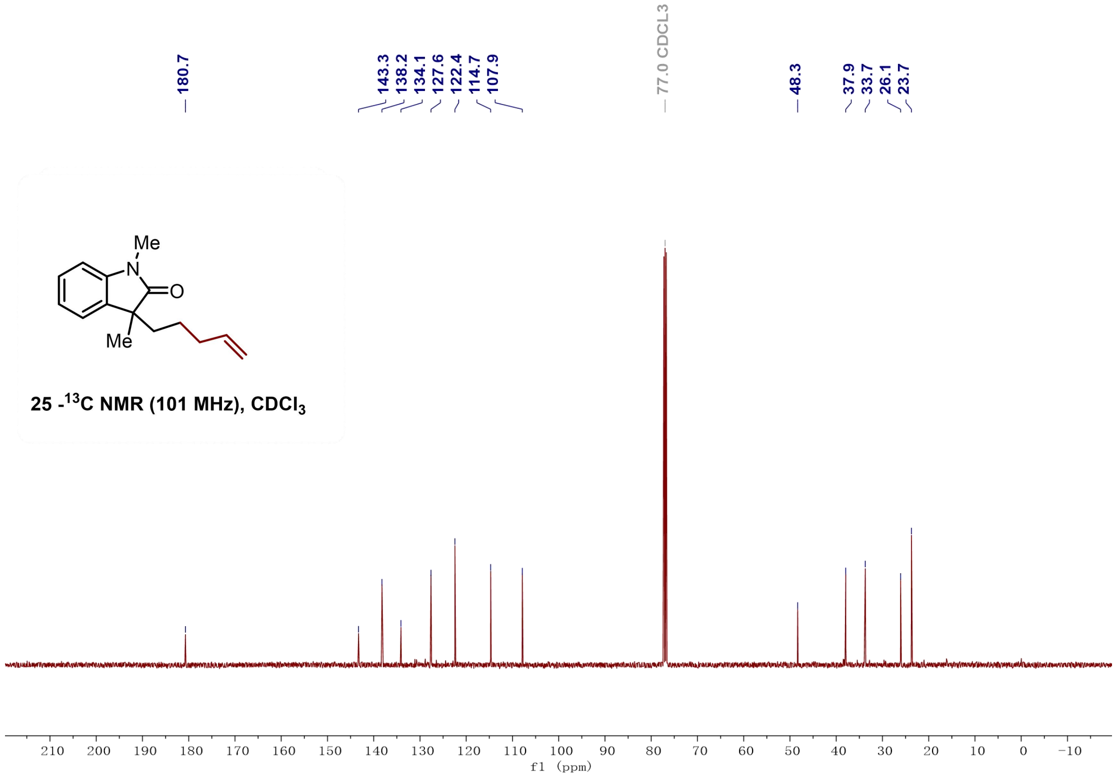


23 -^{13}C NMR (101 MHz), CDCl$_3$, diastereomers


7.50
7.48
7.46
7.44
7.32
7.30
7.28
7.26 CDCL3
7.24
4.31
2.96
2.93
2.90
2.84
1.96
1.93
1.47
N
Boc
O
O
24 -^{1}H NMR (400 MHz), CDCl$_3$
2.98
2.30
1.92
2.96
1.94
11.01
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−
f1 (ppm)


161.3
154.7
152.8
136.9
132.8
130.9
127.5
124.4
119.3
116.4
79.6
77.0 CDCL3
43.9
36.5
30.8
28.4
N
Boc
O
O
24 -^{13}C NMR (101 MHz), CDCl$_3$
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


7.28
7.26
7.26 CDCL3
7.25
7.17
7.16
7.08
7.07
7.05
6.85
6.83
5.69
5.67
5.65
5.64
5.62
5.60
4.92
4.92
4.89
4.88
4.87
4.86
3.21
1.95
1.94
1.92
1.91
1.90
1.87
1.77
1.74
1.72
1.35
1.10
1.09
1.08
1.07
1.05
0.95
0.94
0.92
0.91
Me
N
O
Me
25 -^{1}H NMR (400 MHz), CDCl$_3$
1.37
1.03
1.04
1.02
0.97
2.00
3.11
3.01
1.09
3.01
1.09
1.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


180.7
143.3
138.2
134.1
127.6
122.4
114.7
107.9
77.0 CDCL3
48.3
37.9
33.7
26.1
23.7
Me
N
O
Me
25 -^{13}C NMR (101 MHz), CDCl$_3$
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

5. Reference

1. Muralirajan, K.; Kancherla, R.; Gimnkhan, A.; Rueping, M., *Org. Lett.* **2021**, *23,* 6905-6910.
2. Chen, H.; Sun, Z.; Yang, H.; Mao, F.; Yan, X.; Li, X.; Xu, X., *Synlett* **2022**, *34,* 63-66.
3. Yu, W.-Q.; Fan, J.-H.; Chen, P.; Xiong, B.-Q.; Xie, J.; Tang, K.-W.; Liu, Y., *Org. Biomol. Chem.* **2022**, *20,* 1958-1968.
4. Jin, C.; Yan, Z.; Sun, B.; Yang, J., *Org. Lett.* **2019**, 21, 2064-2068.