Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

A Lutidine-Promoted Photoredox Catalytic Atom-Transfer Radical Cyclization Reaction for the Synthesis of 4-Bromo-3,3-dialkyl-octahydro-indol-2-ones

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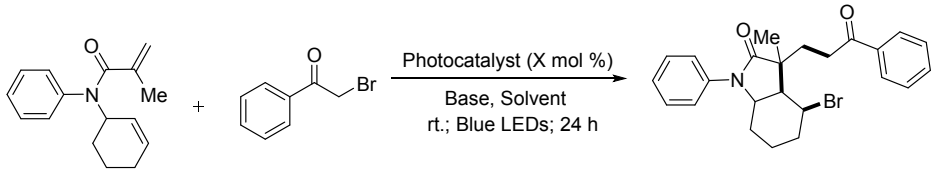
1. General information

All glassware was thoroughly oven-dried. Chemicals and solvents were either purchased from commercial suppliers or purified by standard techniques. Thin-layer chromatography (TLC) plates were visualized by exposure to ultraviolet light and/or staining with phosphomolybdic acid followed by heating on a hot plate. Flash chromatography was carried out using silica gel (200-300 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-400 (400 MHz). The spectra were recorded in deuterochloroform ($CDCl_3$) as solvent at room temperature, ^{1}H and ^{13}C NMR chemical shifts are reported in ppm relative to the residual solvent peak. The residual solvent signals were used as references and the chemical shifts were converted to the TMS scale ($CDCl_3$: δ_H = 0 ppm, δ_C = 77.00 ppm). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), mul-tiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet), integration, coupling constant (Hz) and assignment. Data for ^{13}C NMR are reported as chemical shift. HRMS were performed on a Bruker Apex II mass instrument (ESI).

2. Optimization of the reaction conditions

Table S1. Screening of Photocatalysts, Bases, and Solvents[a]



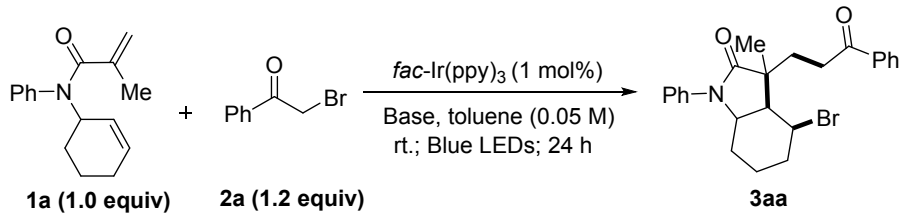
1a (0.1 mmol) **2a** (1 equiv) **3aa**

Entry	1a:2a	Photocatalyst (X mol%)	Base (Y equiv)	Solvent	Yield (%)[b]
1	1:1	*fac*-Ir(ppy)$_3$	2,6-lutidine	MeCN	57
2	1:1	Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$	2,6-lutidine	MeCN	55
3	1:1	Ir(ppy)$_2$(dtbbpy)PF$_6$	2,6-lutidine	MeCN	50
4	1:1	Ru(bpy)$_3$Cl$_2$	2,6-lutidine	MeCN	36
5[c]	1:1	Eosin Y	2,6-lutidine	MeCN	NR[d]
6	1:1	AcrMesClO$_4$	2,6-lutidine	MeCN	NR
7	1:1	-	2,6-lutidine	MeCN	NR
8[e]	1:1	*fac*-Ir(ppy)$_3$	2,6-lutidine	MeCN	NR
9	1:1	*fac*-Ir(ppy)$_3$	-	MeCN	24
10	1:1	*fac*-Ir(ppy)$_3$(Open air)	2,6-lutidine	MeCN	trace
11	1:1	*fac*-Ir(ppy)$_3$	Na$_2$HPO$_4$	MeCN	50
12	1:1	*fac*-Ir(ppy)$_3$	K$_2$CO$_3$	MeCN	36
13	1:1	*fac*-Ir(ppy)$_3$	DIPEA	MeCN	33
14	1:1	*fac*-Ir(ppy)$_3$	Et$_3$N	MeCN	37
15	1:1	*fac*-Ir(ppy)$_3$	2,6-lutidine	toluene	68
16	1:1	*fac*-Ir(ppy)$_3$	2,6-lutidine	DCM	60
17	1:1	*fac*-Ir(ppy)$_3$	2,6-lutidine	THF	70
18	1:1	*fac*-Ir(ppy)$_3$	2,6-lutidine	1,4-dioxane	56
19	1:1	*fac*-Ir(ppy)$_3$	2,6-lutidine	DMSO	trace
20	1:1	*fac*-Ir(ppy)$_3$	2,6-lutidine	Mesitylene	67
21	1:1	*fac*-Ir(ppy)$_3$	2,6-lutidine	Et$_2$O	41

22[f]	1:1	*fac*-Ir(ppy)$_3$	2,6-lutidine(0.5)	toluene	75
23[fg]	1:1.2	*fac*-Ir(ppy)$_3$	2,6-lutidine(0.5)	toluene	81
24	1:1.5	*fac*-Ir(ppy)$_3$	2,6-lutidine(0.5)	toluene	81
25	1:1.2	*fac*-Ir(ppy)$_3$/ 0.5	2,6-lutidine(0.5)	toluene	64
26[fgh]	1:1.2	*fac*-Ir(ppy)$_3$/ 2	2,6-lutidine(0.5)	toluene	82
27	1:1.2	*fac*-Ir(ppy)$_3$/ 2	2,6-lutidine(0.5)	toluene(0.5 mL)	70
28[fhi]	1:1.2	*fac*-Ir(ppy)$_3$	2,6-lutidine(0.5)	toluene (2 mL)	85

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (1.0 equiv), photocatalyst (1 mol%), base (1.0 equiv), solvent (1 mL), and blue LEDs under N_2 at room temperature for 24 h. [b]Isolated yield. [c]Green LEDs. [d]NR (No Reaction). [e]No light. [f]Base (0.5 equiv). [g]2a (1.2 equiv). [h]photocatalyst (2 mol%). [i]solvent (2 mL).

Table S2. Screening of Amounts of Pyridine

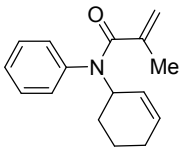


1a (1.0 equiv) **2a (1.2 equiv)** **3aa**

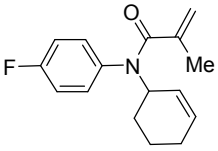
Entry	Base (0.5 equiv)	Yield
1	2,6-lutidine	85
2	pyridine	29
3	2,6-di*t*Bu-Py	68
4	2,6-di*t*Bu-4-Me-Py	65
5	2,4,6-Collidine	80
6	2,6-diCl-Py	41
7	Pentafluoropyridine	30
8	4-Dimethylaminopyridine (DMAP)	trace
9	4-Pyrrolidinopyridine	trace
10	2-NH_2-Py	NR
11	2,6-lutidine (0.5 equiv) + PyHBr (0.5 equiv)	78
12	2,6-lutidine (0.25 equiv)	56
13	2,6-lutidine (0.10 equiv)	35

3. Preparation of substrates

3.1 List of substrates



1a



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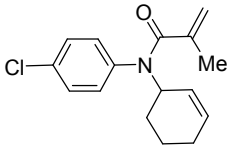

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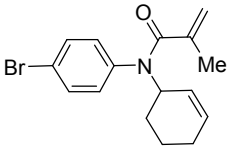

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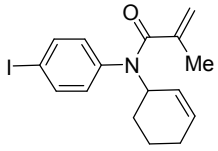

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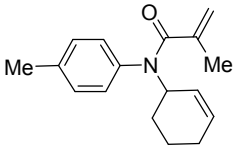

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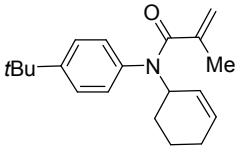

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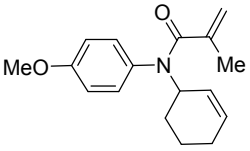

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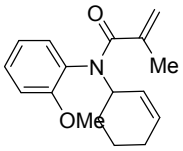

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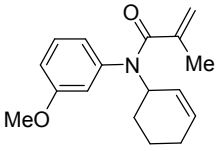

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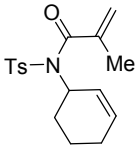

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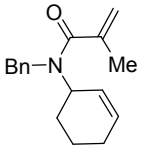

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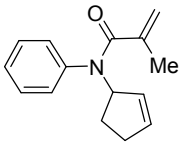

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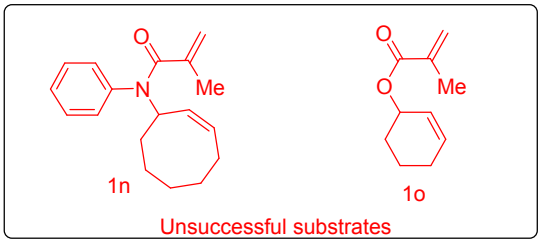

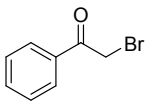

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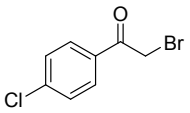

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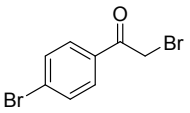

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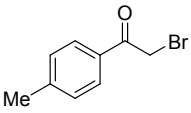

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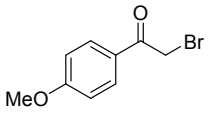

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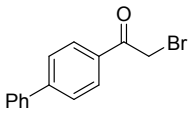

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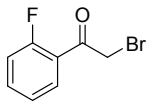

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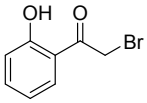

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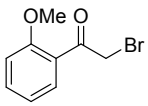

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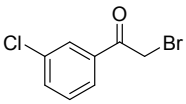

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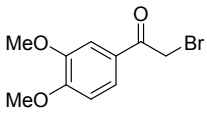

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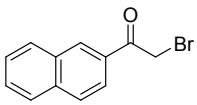

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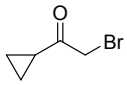

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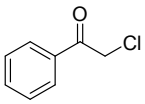

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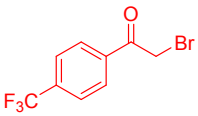

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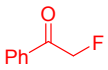

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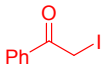
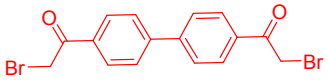


2q

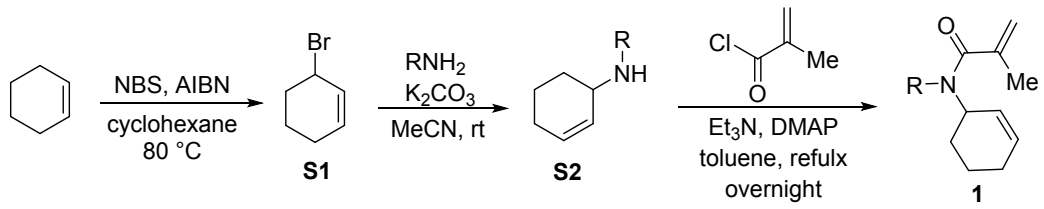
2r



2s

Unsuccessful examples

3.2 General procedure for the synthesis of substrates



Preparation of S1

According to a modified literature procedure,[1] under an air atmosphere, cyclohexene (10.1 mL, 100 mmol, 1.0 equiv) was added to a 150 mL round bottom flask containing a suspension of AIBN (12.5 mg, cat.) and NBS (11.572 g, 65 mmol, 0.65 equiv) in cyclohexane (50 mL); the round bottom was fitted with a condenser, and refluxed at 80 ℃ for 3 hours. The reaction was cooled to room temperature, filtered through a glass frit, and carefully concentrated *in vacuo* to yield a crude oil. Vacuum distillation yielded **S1** (8.35 g, 80% with respect to NBS) as a colorless oil. The material was used within one day of preparation, or stored at –20 ℃ indefinitely.

Preparation of S2-a

According to a modified literature procedure,[2] a solution of aniline (3.2 mL, 35 mmol, 2.7 equiv) in MeCN (40 mL) was treated with 3-bromocyclohexene **S1** (1.50 mL, 13.0 mmol, 1.0 equiv) and K_2CO_3 (1.97 g, 14.3 mmol, 1.1 equiv). After 2 h at rt, the reaction mixture was quenched with H_2O (20 mL) and extracted with EtOAc (2 x 30 mL). The combined organic extracts were washed with brine (30 mL), dried over Na_2SO_4, filtered, evaporated under reduced pressure and purified by column chromatography (PE/EA = 50:1–30:1) to give amine **S2-a** (2.137 g, 95 %) as a colourless oil.

Preparation of 1

According to a modified literature procedure,[3] methacryloyl chloride (2 equiv) in toluene (0.13 M) was added on a mixture of amine **S2** (1 equiv), triethylamine (2 equiv) and DMAP (0.1 equiv) in toluene (0.13 M). The mixture was stirred overnight at reflux. The reaction was quenched with saturated aqueous Na_2CO_3 (15 mL), then the mixture was extracted with dichloromethane (3 x 15 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (PE/EA = 6:1–4:1) affording the corresponding substrate **1.**

References

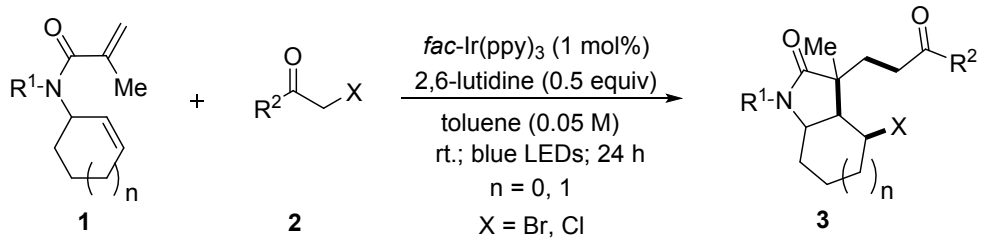
(1) Shuler, S. A.; Yin, G.; Krause, S. B.; Vesper, C. M.; Watson, D. A. Synthesis of Secondary Unsaturated Lactams via an Aza-Heck Reaction. *J. Am. Chem. Soc.* **2016**, *138*, 13830−13833.

(2) Grainger, R. S.; Betou, M.; Male, L.; Pitak, M. B.; Coles, S. J. Semipinacol Rearrangement of Cis-Fused *β*-Lactam Diols into Keto-Bridged Bicyclic Lactams. *Org. Lett.* **2012**, *14*, 2243−2237.

(3) Kong, W.; Casimiro, M.; Fuentes, N.; Merino, E.; Nevado,C. Metal-Free Aryltrifluoromethylation of Activated Alkenes. *Angew. Chem., Int. Ed.* **2013**, *52*, 13086–13090.

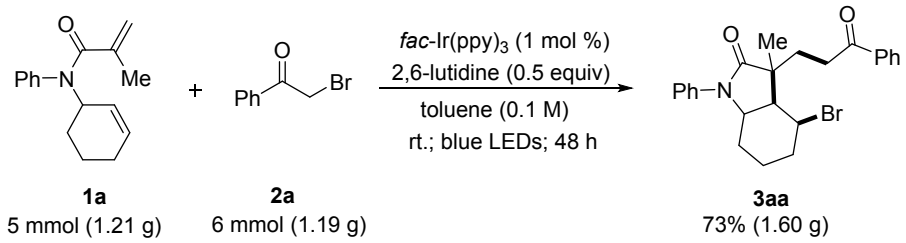
4. General procedure for the photocatalytic ATRC reactions

4.1 General procedure for the synthesis of compounds 3



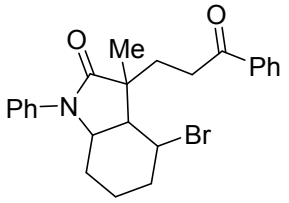
2-Bromo(Chloro)acetophenone **2** (0.12 mmol, 1.2 equiv) and 2,6-lutidine (0.05 mmol, 0.5 equiv) were added to a solution of substrate **1** (0.1 mmol, 1 equiv) and photocatalyst *fac*-Ir(ppy)$_3$ (1 mol%) in dry toluene (2 mL) at room temperature. The mixture was degassed by three cycles of freeze-pump-thaw and then placed in the irradiation apparatus equipped with a 3 W blue light-emitting diodes (LEDs) strip. The resulting mixture was stirred at room temperature for 24 h. After completion of the reaction, the reaction mixture was concentrated under reduced pressure, and the resulting crude mixture was purified by flash column chromatography on silica gel (PE/EA = 6:1–2:1) to afford the desired product **3**.

4.2 Procedure for scale-up preparation of 3aa



2-Bromoacetophenone **2a** (6 mmol, 1.19 g, 1.2 equiv) and 2,6-lutidine (2.5 mmol, 0.6 mL, 0.5 equiv) were added to a solution of substrate **1a** (5 mmol, 1.21 g, 1 equiv) and photocatalyst *fac*-Ir(ppy)$_3$ (32.5 mg, 1 mol%) in dry toluene (50 mL) at room temperature. The mixture was degassed by three cycles of freeze-pump-thaw and then placed in the irradiation apparatus equipped with a 3 W blue LEDs strip. The resulting mixture was stirred at room temperature for 48 h. After completion of the reaction, the reaction mixture was concentrated under reduced pressure, and the resulting crude mixture was purified by flash column chromatography on silica gel (PE/EA = 4:1) to afford the desired product **3aa** (yield 73%, 1.60 g).

5. Characterization of products



4-Bromo-3-methyl-3-(3-oxo-3-phenylpropyl)-1-phenyloctahydro-2H-indol-2-one (3aa)

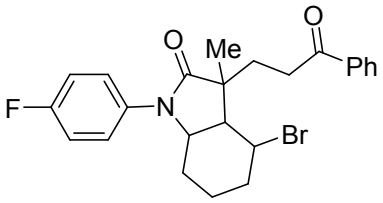
Purification by flash column chromatography (SiO_2, PE/EA = 4:1) afforded **3aa**.

White solid, 37.3 mg, 85% yield, mp = 156–158 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.4 Hz, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.49–7.35 (m, 6H), 7.24–7.21 (m, 1H), 4.63–4.38 (m, 2H), 3.18–3.07 (m, 2H), 2.87 (dd, *J* = 7.1, 5.0 Hz, 1H), 2.24–2.02 (m, 4H), 1.96–1.92 (m, 1H), 1.79–1.68 (m, 1H), 1.64–1.52 (m, 2H), 1.43 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.60, 176.84 137.20, 136.69, 133.05, 129.11, 128.55, 128.15, 126.11, 124.03, 55.70, 50.22, 48.38, 47.90, 34.23, 33.68, 31.69, 27.16, 20.72, 18.88.

HRMS (ESI) for $C_{24}H_{27}BrNO_2$ $[M+H]^+$ calcd. 440.1220, found 440.1221.



4-Bromo-1-(4-fluorophenyl)-3-methyl-3-(3-oxo-3-phenylpropyl)octahydro-2H-indol-2-one (3ba)

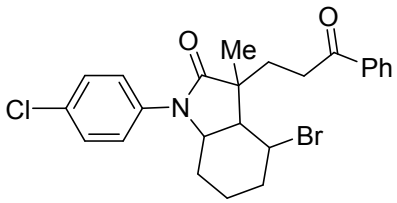
Purification by flash column chromatography (SiO_2, PE/EA = 3:1) afforded **3ba**.

Yellow solid, 29.2 mg, 64% yield, mp = 120–122 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.3 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.39–7.33 (m, 2H), 7.08 (t, *J* = 8.6 Hz, 2H), 4.49 (dd, *J* = 11.3, 4.7 Hz, 1H), 4.43 (dd, *J* = 12.8, 7.6 Hz, 1H), 3.22–3.01 (m, 2H), 2.86 (dd, *J* = 7.0, 5.2 Hz, 1H), 2.19–2.03 (m, 4H), 1.94–1.87 (m, 1H), 1.73–1.70 (m, 1H), 1.60–1.49 (m, 2H), 1.42 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.41, 176.91, 160.48 (d, *J* = 247.5 Hz), 136.59, 133.01, 128.49, 128.04, 126.02, 125.93, 115.99, 115.77, 55.91, 50.04, 48.46, 47.68, 34.23, 33.51, 31.50, 26.98, 20.50, 18.81.

HRMS (ESI) for $C_{24}H_{26}BrFNO_2$ $[M+H]^+$ calcd. 458.1125, found 458.1124.



4-Bromo-1-(4-chlorophenyl)-3-methyl-3-(3-oxo-3-phenylpropyl)octahydro-2H-indol-2-one (3ca)

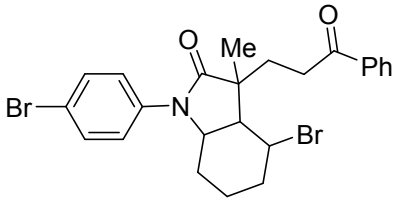
Purification by flash column chromatography (SiO_2, PE/EA = 4:1) afforded **3ca**.

Yellow solid, 33.1 mg, 70% yield, mp = 154–156 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.5 Hz, 2H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.45–7.35 (m, 6H), 4.49 (d, *J* = 9.6 Hz, 2H), 3.27–2.96 (m, 2H), 2.86 (d, *J* = 5.2 Hz, 1H), 2.22–2.03 (m, 4H), 1.96–1.91 (m, 1H), 1.75–1.70 (m, 1H), 1.55–1.50 (m, 2H), 1.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.32, 176.83, 136.55, 135.67, 133.01, 131.19, 129.13, 128.48, 128.03, 124.97, 55.46, 49.97, 48.19, 47.79, 34.03, 33.53, 31.57, 26.96, 20.71, 18.74.

HRMS (ESI) for $C_{24}H_{26}BrClNO_2$ $[M+H]^+$ calcd. 474.0830, found 474.0833.



4-Bromo-1-(4-bromophenyl)-3-methyl-3-(3-oxo-3-phenylpropyl)octahydro-2H-indol-2-one (3da)

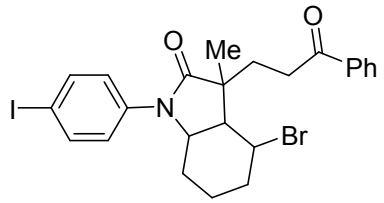
Purification by flash column chromatography (SiO_2, PE/EA = 4:1) afforded **3da**.

White solid, 37.7 mg, 73% yield, mp = 162–164 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99–7.92 (m, 2H), 7.57–7.49 (m, 3H), 7.46–7.41 (m, 2H), 7.37–7.32 (m, 2H), 4.60–4.39 (m, 2H), 3.14–3.07 (m, 2H), 2.85 (dd, *J* = 7.2, 4.8 Hz, 1H), 2.15–2.07 (m, 4H), 2.01–1.91 (m, 1H), 1.76–1.72 (m, 1H), 1.61–1.49 (m, 2H), 1.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.37, 176.84, 136.62, 136.27, 133.06, 132.11, 128.52, 128.07, 125.22, 119.06, 55.40, 49.94, 48.21, 47.87, 34.05, 33.54, 31.62, 26.99, 20.70, 18.76.

HRMS (ESI) for $C_{24}H_{26}Br_2NO_2$ $[M+H]^+$ calcd. 518.0325, found 518.0324.



4-Bromo-1-(4-iodophenyl)-3-methyl-3-(3-oxo-3-phenylpropyl)octahydro-2H-indol-2-one (3ea)

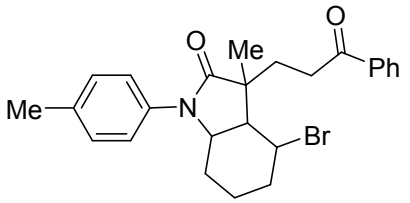
Purification by flash column chromatography (SiO_2, PE/EA = 3:1) afforded **3ea**.

White solid, 36.7 mg, 65% yield, mp = 136–138 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99–7.91 (m, 2H), 7.75–7.66 (m, 2H), 7.53 (dd, *J* = 10.5, 4.3 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.26–7.19 (m, 2H), 4.53–4.51 (m, 2H), 3.25–2.96 (m, 2H), 2.85 (dd, *J* = 7.2, 4.8 Hz, 1H), 2.21–2.03 (m, 4H), 2.00–1.89 (m, 1H), 1.78–1.67 (m, 1H), 1.59–1.48 (m, 2H), 1.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.31, 176.77, 138.03, 136.98, 136.59, 133.02, 128.49, 128.04, 125.35, 90.05, 55.24, 49.94, 48.12, 47.87, 34.00, 33.52, 31.61, 26.95, 20.70, 18.73.

HRMS (ESI) for $C_{24}H_{26}BrINO_2$ $[M+H]^+$ calcd. 566.0186, found 566.0185.



4-Bromo-3-methyl-3-(3-oxo-3-phenylpropyl)-1-(p-tolyl)octahydro-2H-indol-2-one (3fa)

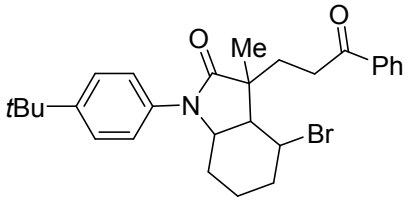
Purification by flash column chromatography (SiO_2, PE/EA = 5:1) afforded **3fa**.

Yellow oil, 35.3 mg, 78% yield.

^{1}H NMR (400 MHz , $CDCl_3$) δ7.99–7.92 (m, 2H), 7.54–7.50 (m, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.27 (d, *J* = 8.3 Hz, 2H), 7.19 (d, *J* = 8.2 Hz, 2H), 4.51–4.47 (m, 1H), 4.45–4.40 (m, 1H), 3.20–3.03 (m, 2H), 2.85 (dd, *J* = 7.1, 5.2 Hz, 1H), 2.33 (s, 3H), 2.18–2.00 (m, 4H), 1.94–1.85 (m, 1H), 1.72–1.66 (m, 1H), 1.61–1.48 (m, 2H), 1.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ199.46, 176.65, 136.55, 135.83, 134.41, 132.90, 129.56, 128.41, 128.00, 123.98, 55.68, 50.25, 48.36, 47.67, 34.22, 33.56, 31.53, 26.94, 20.86, 20.47, 18.81.

HRMS (ESI) for $C_{25}H_{29}BrNO_2$ $[M+H]^+$ calcd. 454.1376, found 454.1374.



4-Bromo-1-(4-(tert-butyl)phenyl)-3-methyl-3-(3-oxo-3-phenylpropyl)octahydro-2H-indol-2-one (3ga)

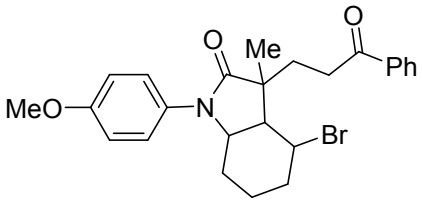
Purification by flash column chromatography (SiO_2, PE/EA = 5:1) afforded **3ga**.

White solid, 37.1 mg, 75% yield, mp = 140–142 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.4 Hz, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.45–7.39 (m, 4H), 7.32 (d, *J* = 8.6 Hz, 2H), 4.52 (dd, *J* = 10.8, 4.8 Hz, 1H), 4.45 (dd, *J* = 13.0, 7.7 Hz, 1H), 3.14–3.09 (m, 2H), 2.86 (dd, *J* = 7.1, 5.1 Hz, 1H), 2.20–2.03 (m, 4H), 1.97–1.92 (m, 1H), 1.75–1.72 (m, 1H), 1.61–1.54 (m, 2H), 1.42 (s, 3H), 1.31 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ199.51, 176.68, 148.93, 136.63, 134.40, 132.93, 128.45, 128.07, 125.91, 123.50, 55.67, 50.25, 48.28, 47.75, 34.39, 34.15, 33.63, 31.69, 31.22, 27.13, 20.68, 18.83.

HRMS (ESI) for $C_{28}H_{35}BrNO_2$ $[M+H]^+$ calcd. 496.1846, found 496.1845.



4-Bromo-1-(4-methoxyphenyl)-3-methyl-3-(3-oxo-3-phenylpropyl)octahydro-2H-indol-2-one (3ha)

Purification by flash column chromatography (SiO_2, PE/EA = 2:1) afforded **3ha**.

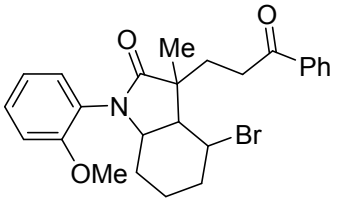
Yellow solid, 37.1 mg, 79% yield, mp = 132–134 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.6 Hz, 2H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.27 (t, *J* = 3.9 Hz, 2H), 6.92 (d, *J* = 7.8 Hz, 2H), 4.57–4.31 (m, 2H), 3.79 (s, 3H), 3.24–

3.02 (m, 2H), 2.85 (t, *J* = 5.3 Hz, 1H), 2.12–2.03 (m, 4H), 1.87–1.83 (m, 1H), 1.70–1.67 (m, 1H), 1.60–1.49 (m, 2H), 1.42 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.51, 176.81, 157.70, 136.56, 132.93, 129.79, 128.43, 128.02, 125.87, 114.28, 56.09, 55.36, 50.27, 48.55, 47.56, 34.35, 33.57, 31.47, 26.99, 20.41, 18.87.

HRMS (ESI) for $C_{25}H_{29}BrNO_3$ $[M+H]^+$ calcd. 470.1325, found 470.1326.



4-Bromo-1-(2-methoxyphenyl)-3-methyl-3-(3-oxo-3-phenylpropyl)octahydro-2H-indol-2-one (3ia)

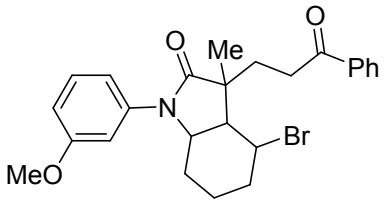
Purification by flash column chromatography (SiO_2, PE/EA = 3:1) afforded **3ia**.

White solid, 32.8 mg, 70% yield, mp = 116–118 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01–7.97 (m, 2H), 7.56–7.52 (m, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.31–7.26 (m, 1H), 7.14 (dd, *J* = 7.7, 1.6 Hz, 1H), 6.99–6.92 (m, 2H), 4.39–4.26 (m, 2H), 3.74 (s, 3H), 3.19–3.13 (m, 2H), 2.78 (t, *J* = 7.0 Hz, 1H), 2.31–2.19 (m, 2H), 2.15–2.05 (m, 1H), 2.03–1.92 (m, 1H), 1.63–1.49 (m, 4H), 1.47 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ199.92, 178.02, 155.19, 136.75, 132.90, 129.89, 129.11, 128.45, 128.02, 125.32, 120.68, 111.86, 56.25, 55.47, 50.61, 50.23, 47.59, 35.78, 33.64, 31.18, 26.50, 19.68, 19.33.

HRMS (ESI) for $C_{25}H_{29}BrNO_3$ $[M+H]^+$ calcd. 470.1325, found 470.1322.



4-Bromo-1-(3-methoxyphenyl)-3-methyl-3-(3-oxo-3-phenylpropyl)octahydro-2H-indol-2-one (3ja)

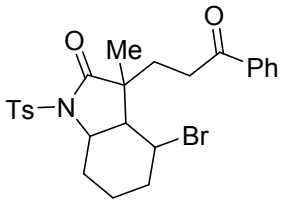
Purification by flash column chromatography (SiO_2, PE/EA = 3:1) afforded **3ja**.

White solid, 34.7 mg, 74% yield, mp = 114–116 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.5 Hz, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.45 – 7.41 (m, 2H), 7.31–7.27 (m, 1H), 7.09 (s, 1H), 6.97 (d, *J* = 7.9 Hz, 1H), 6.79–6.76 (m, 1H), 4.54–4.44 (m, 2H), 3.81 (s, 3H), 3.20–3.03 (m, 2H), 2.86 (dd, *J* = 7.0, 5.0 Hz, 1H), 2.21–2.03 (m, 4H), 1.99–1.94 (m 1H), 1.76–1.73 (m, 1H), 1.62–1.50 (m, 2H), 1.42 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.30, 176.62, 159.95, 138.21, 136.45, 132.86, 129.54, 128.35, 127.92, 115.61, 111.50, 109.65, 55.52, 55.16, 50.14, 47.97, 47.76, 33.93, 33.47, 31.54, 26.89, 20.58, 18.70.

HRMS (ESI) for $C_{25}H_{29}BrNO_3$ $[M+H]^+$ calcd. 470.1325, found 470.1326.



4-Bromo-3-methyl-3-(3-oxo-3-phenylpropyl)-1-tosyloctahydro-2H-indol-2-one (3ka)

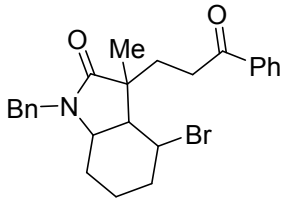
Purification by flash column chromatography (SiO_2, PE/EA = 3:1) afforded **3ka**.

White solid, 27.4 mg, 53% yield, mp = 102–104 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.2 Hz, 2H), 7.83 (d, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 4.68–4.56 (m, 2H), 2.91–2.71 (m, 3H), 2.58–2.50 (m, 1H), 2.40 (s, 3H), 2.13–2.05 (m, 1H), 2.03–1.87 (m, 4H), 1.76–1.73 (m, 1H), 1.54–1.43 (m, 1H), 1.23 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.59, 176.35, 145.18, 136.42, 135.79, 133.18, 129.56, 128.54, 128.32, 128.02, 55.54, 48.83, 47.91, 47.28, 33.14, 32.24, 32.02, 29.85, 21.65, 21.58, 18.21.

HRMS (ESI) for $C_{25}H_{29}BrNO_4S$ $[M+H]^+$ calcd. 518.0995, found 518.0997.



1-Benzyl-4-bromo-3-methyl-3-(3-oxo-3-phenylpropyl)octahydro-2H-indol-2-one (3la)

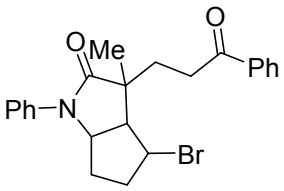
Purification by flash column chromatography (SiO_2, PE/EA = 4:1) afforded **3la**.

White solid, 26.7 mg, 59% yield, mp = 96–98 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01–7.95 (m, 2H), 7.60–7.53 (m, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.37–7.27 (m, 3H), 7.25–7.19 (m, 2H), 4.96 (d, *J* = 15.0 Hz, 1H), 4.44–4.39 (m, 1H), 4.01 (d, *J* = 15.0 Hz, 1H), 3.71–3.66 (m, 1H), 3.17–3.01 (m, 2H), 2.63 (dd, *J* = 7.4, 5.1 Hz, 1H), 2.11–1.97 (m, 4H), 1.96–1.88 (m, 1H), 1.74–1.67 (m, 1H), 1.56–1.44 (m, 2H), 1.35 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ199.53, 177.52, 136.82, 136.65, 133.03, 128.78, 128.58, 128.13, 127.87, 127.64, 53.24, 50.04, 48.58, 46.90, 44.32, 34.11, 33.74, 31.78, 26.92, 20.41, 18.84.

HRMS (ESI) for $C_{25}H_{29}BrNO_2$ $[M+H]^+$ calcd. 454.1376, found 454.1375.



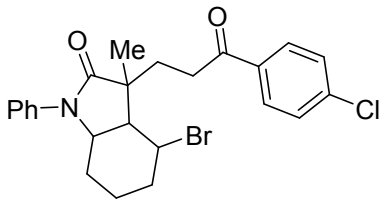
4-Bromo-3-methyl-3-(3-oxo-3-phenylpropyl)-1-phenylhexahydrocyclopenta[b]pyrrol-2(1H)-one (3ma)

Purification by flash column chromatography (SiO_2, PE/EA = 5:1) afforded **3ma**.

White solid, 31.0 mg, 73% yield, mp = 134–136 °C.

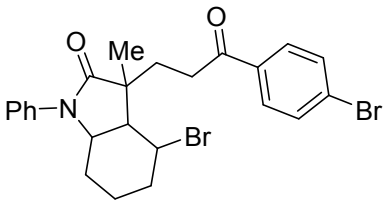
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95–7.91 (m, 2H), 7.56–7.51 (m, 1H), 7.49–7.36 (m, 6H), 7.22–7.17 (m, 1H), 4.84–4.75 (m, 1H), 4.34 (q, *J* = 5.9 Hz, 1H), 3.15–3.08 (m, 2H), 2.99 (dd, *J* = 7.8, 5.9 Hz, 1H), 2.31–2.14 (m, 2H), 2.09–2.04 (m, 3H), 1.69–1.64 (m, 1H), 1.42 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.30, 176.11, 137.35, 136.63, 133.03, 128.93, 128.51, 127.98, 125.43, 122.45, 60.79, 56.89, 50.24, 46.54, 36.36, 34.86, 33.44, 29.93, 17.93.
.**HRMS (ESI)** for $C_{23}H_{25}BrNO_2$ $[M+H]^+$ calcd. 426.1063, found 426.1074.



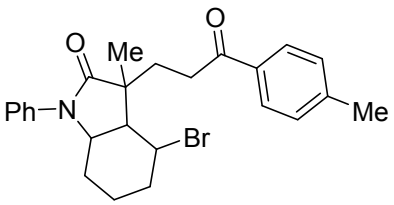
4-Bromo-3-(3-(4-chlorophenyl)-3-oxopropyl)-3-methyl-1-phenyloctahydro-2H-indol-2-one (3ab)

Purification by flash column chromatography (SiO_2, PE/EA = 6:1) afforded **3ab**.
White solid, 33.6 mg, 71% yield, mp = 132–134 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.5 Hz, 2H), 7.41–7.38 (m, 6H), 7.25–7.20 (m, 1H), 4.54–4.45 (m, 2H), 3.16–3.01 (m, 2H), 2.86 (dd, *J* = 7.2, 5.0 Hz, 1H), 2.18–2.04 (m, 4H), 2.00–1.91 (m, 1H), 1.78–1.70 (m, 1H), 1.61–1.51 (m, 2H), 1.42 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 198.35, 176.72, 139.45, 137.12, 134.96, 129.58, 129.11, 128.84, 126.13, 123.98, 55.68, 50.09, 48.40, 47.80, 34.13, 33.65, 31.66, 27.11, 20.75, 18.84.
HRMS (ESI) for $C_{24}H_{26}BrClNO_2$ $[M+H]^+$ calcd. 474.0830, found 474.0844.



4-Bromo-3-(3-(4-bromophenyl)-3-oxopropyl)-3-methyl-1-phenyloctahydro-2H-indol-2-one (3ac)

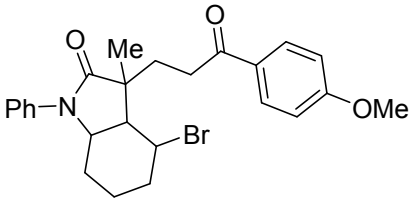
Purification by flash column chromatography (SiO_2, PE/EA = 3:1) afforded **3ac**.
Yellow solid, 34.6 mg, 67% yield, mp = 116–118 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.46–7.35 (m, 4H), 7.29–7.23 (m, 1H), 4.52–4.48 (m, 2H), 3.22–2.98 (m, 2H), 2.95–2.78 (m, 1H), 2.14–2.08 (m, 4H), 1.95–1.91 (m, 1H), 1.76–1.72 (m, 1H), 1.62–1.53 (m, 2H), 1.42 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 198.54, 176.71, 137.10, 135.35, 131.83, 129.69, 129.12, 128.20, 126.14, 123.99, 55.69, 50.08, 48.40, 47.79, 34.13, 33.65 31.64, 27.11, 20.77, 18.84.
HRMS (ESI) for $C_{24}H_{26}Br_2NO_2$ $[M+H]^+$ calcd. 518.0325, found 518.0340.



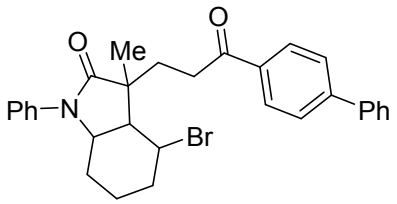
4-Bromo-3-methyl-3-(3-oxo-3-(p-tolyl)propyl)-1-phenyloctahydro-2H-indol-2-one (3ad)

Purification by flash column chromatography (SiO_2, PE/EA = 4:1) afforded **3ad**.
Yellow solid, 35.8 mg, 79% yield, mp = 114–116 °C.

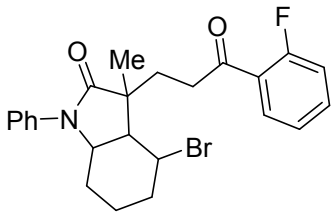
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.2 Hz, 2H), 7.44–7.35 (m, 4H), 7.24–7.18 (m, 3H), 4.59–4.40 (m, 2H), 3.17–3.01 (m, 2H), 2.86 (dd, *J* = 7.2, 5.0 Hz, 1H), 2.37 (s, 3H), 2.18–2.03 (m, 4H), 1.97–1.89 (m, 1H), 1.77–1.67 (m, 1H), 1.59–1.49 (m, 2H), 1.41 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 199.11, 176.78, 143.71, 137.17, 134.15, 129.14, 129.01, 128.19, 125.98, 123.92, 55.60, 50.22, 48.24, 47.84, 34.14, 33.47, 31.72, 27.07, 21.52, 20.62, 18.81.
HRMS (ESI) for $C_{25}H_{29}BrNO_2$ $[M+H]^+$ calcd. 454.1376, found 454.1386.



4-Bromo-3-(3-(4-methoxyphenyl)-3-oxopropyl)-3-methyl-1-phenyloctahydro-2H-indol-2-one (3ae)
Purification by flash column chromatography (SiO_2, PE/EA = 2:1) afforded **3ae**.
White solid, 40.8 mg, 87% yield, mp = 136–138 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.9 Hz, 2H), 7.43–7.36 (m, 4H), 7.24–7.20 (m, 1H), 6.90 (d, *J* = 8.9 Hz, 2H), 4.54–4.45 (m, 2H), 3.84 (s, 3H), 3.11–2.99 (m, 2H), 2.87 (dd, *J* = 7.2, 4.9 Hz, 1H), 2.17–2.05 (m, 4H), 1.97–1.89 (m, 1H), 1.75–1.69 (m, 1H), 1.59–1.52 (m, 2H), 1.42 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 198.12, 176.86, 163.42, 137.23, 130.42, 129.77, 129.07, 126.05, 124.00, 113.65, 55.67, 55.38, 50.24, 48.27, 47.95, 34.19, 33.32, 31.94, 27.14, 20.69, 18.85.
HRMS (ESI) for $C_{25}H_{29}BrNO_3$ $[M+H]^+$ calcd. 470.1325, found 470.1338.



3-(3-([1,1'-Biphenyl]-4-yl)-3-oxopropyl)-4-bromo-3-methyl-1-phenyloctahydro-2H-indol-2-one (3af)
Purification by flash column chromatography (SiO_2, PE/EA = 3:1) afforded **3af**.
Yellow solid, 39.7 mg, 77% yield, mp = 78–80°C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 8.5 Hz, 2H), 7.62–7.60 (m, 2H), 7.47–7.44 (m, 3H), 7.42–7.38 (m, 4H), 7.28–7.21 (m, 1H), 4.58–4.45 (m, 2H), 3.18–3.11 (m, 2H), 2.89 (dd, *J* = 7.2, 4.9 Hz, 1H), 2.19–2.07 (m, 4H), 1.98–1.91 (m, 1H), 1.77–1.70 (m, 1H), 1.62–1.53 (m, 2H), 1.44 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.18, 176.85, 145.70, 139.89, 137.25, 135.42, 129.11, 128.89, 128.76, 128.14, 127.23, 127.19, 126.10, 124.04, 55.73, 50.20, 48.41, 47.94, 34.22, 33.75, 31.83, 27.17, 20.74, 18.89.
HRMS (ESI) for $C_{30}H_{31}BrNO_2$ $[M+H]^+$ calcd. 516.1533, found 516.1548.



4-Bromo-3-(3-(2-fluorophenyl)-3-oxopropyl)-3-methyl-1-phenyloctahydro-2H-indol-2-one (3ag)

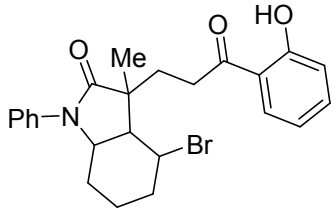
Purification by flash column chromatography (SiO_2, PE/EA = 3:1) afforded **3ag**.

White solid, 32.0 mg, 70% yield, mp = 144–146 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (t, *J* = 7.1 Hz, 1H), 7.50–7.46 (m, 1H), 7.42–7.36 (m, 4H), 7.23–7.17 (m, 2H), 7.12–7.07 (m, 1H), 4.50–4.45 (m, 2H), 3.24–3.14 (m, 1H), 3.11–3.01 (m, 1H), 2.90–2.82 (m, 1H), 2.20–2.03 (m, 4H), 1.95–1.91 (m, 1H), 1.73–1.69 (m, 1H), 1.61–1.50 (m, 2H), 1.42 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.72 (d, *J* = 4.0 Hz), 176.74, 161.68 (d, *J* = 256.5 Hz), 137.16, 134.35 (d, *J* = 9.0 Hz), 130.52, 128.95, 125.94, 125.54 (d, *J* = 12.9 Hz), 124.31, 123.99, 116.66, 116.43, 55.61, 50.32, 48.33, 47.63, 38.45, 34.21, 31.34, 27.04, 20.44, 18.82.

HRMS (ESI) for $C_{24}H_{26}BrFNO_2$ $[M+H]^+$ calcd. 458.1125, found 458.1137.



4-Bromo-3-(3-(2-hydroxyphenyl)-3-oxopropyl)-3-methyl-1-phenyloctahydro-2H-indol-2-one (3ah)

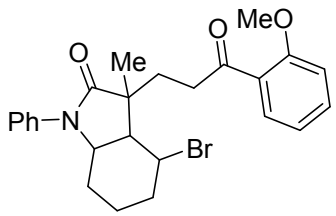
Purification by flash column chromatography (SiO_2, PE/EA = 2:1) afforded **3ah**.

Yellow solid, 25.9 mg, 57% yield, mp = 128–130 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.22 (s, 1H), 7.79 (d, *J* = 7.7 Hz, 1H), 7.46–7.38 (m, 5H), 7.24–7.21 (m, 1H), 6.96 (d, *J* = 8.3 Hz, 1H), 6.87 (t, *J* = 7.5 Hz, 1H), 4.57–4.45 (m, 2H), 3.23–3.08 (m, 2H), 2.87 (dd, *J* = 7.1, 4.8 Hz, 1H), 2.17–2.06 (m, 4H), 1.98–1.94 (m, 1H), 1.76–1.70 (m, 1H), 1.61–1.53 (m, 2H), 1.43 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 205.73, 176.58, 162.34, 137.10, 136.34, 130.12, 129.12, 126.14, 123.93, 119.11, 118.98, 118.38, 55.68, 49.94, 48.27, 47.80, 34.02, 33.44, 31.65, 27.11, 20.80, 18.80.

HRMS (ESI) for $C_{24}H_{27}BrNO_3$ $[M+H]^+$ calcd. 456.1169, found 456.1179.



4-Bromo-3-(3-(2-methoxyphenyl)-3-oxopropyl)-3-methyl-1-phenyloctahydro-2H-indol-2-one (3ai)

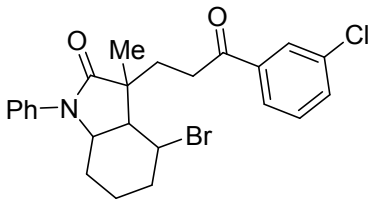
Purification by flash column chromatography (SiO_2, PE/EA = 3:1) afforded **3ai**.

Yellow oil, 38.9 mg, 83% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.45–7.35 (m, 5H), 7.23–7.20 (m, 1H), 7.00–6.92 (m, 2H), 4.53–4.43 (m, 2H), 3.87 (s, 3H), 3.15–3.08 (m, 2H), 2.85 (dd, *J* = 7.0, 5.2 Hz, 1H), 2.16–2.02 (m, 4H), 1.93–1.89 (m, 1H), 1.75–1.67 (m, 1H), 1.61–1.55 (m, 2H), 1.40 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.86, 177.08, 158.40, 137.35, 133.32, 130.27, 129.01, 128.25, 125.94, 124.01, 120.58, 111.48, 55.66, 55.53, 50.73, 48.30, 47.96, 38.79, 34.44, 31.84, 27.19, 20.34, 18.94.

HRMS (ESI) for $C_{25}H_{29}BrNO_3$ $[M+H]^+$ calcd. 470.1325, found 470.1339.



4-Bromo-3-(3-(3-chlorophenyl)-3-oxopropyl)-3-methyl-1-phenyloctahydro-2H-indol-2-one (3aj)

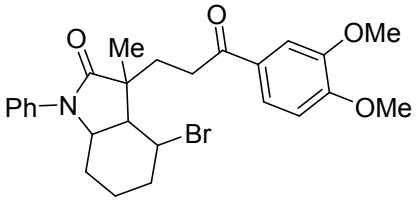
Purification by flash column chromatography (SiO_2, PE/EA = 4:1) afforded **3aj**.

Yellow solid, 35.5 mg, 75% yield, mp = 116–118 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (t, *J* = 1.8 Hz, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.53–7.49 (m, 1H), 7.43–7.35 (m, 5H), 7.25–7.21 (m, 1H), 4.55–4.46 (m, 2H), 3.18–3.02 (m, 2H), 2.85 (dd, *J* = 7.2, 5.0 Hz, 1H), 2.16–2.08 (m, 4H), 1.97–1.90 (m, 1H), 1.78–1.70 (m, 1H), 1.62–1.53 (m, 2H), 1.43 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.18, 176.69, 138.19, 137.08, 134.83, 132.92, 129.86, 129.07, 128.08, 126.24, 124.09, 123.96, 55.66, 50.07, 48.46, 47.71, 34.14, 33.72, 31.46, 27.03, 20.67, 18.83.

HRMS (ESI) for $C_{24}H_{26}BrClNO_2$ $[M+H]^+$ calcd. 474.0830, found 474.0842.



4-Bromo-3-(3-(3,4-dimethoxyphenyl)-3-oxopropyl)-3-methyl-1-phenyloctahydro-2H-indol-2-one (3ak)

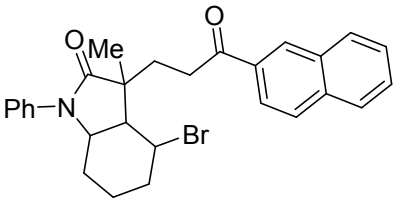
Purification by flash column chromatography (SiO_2, PE/EA = 2:1) afforded **3ak**.

White solid, 39.9 mg, 80% yield, mp = 144–146 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.52 (d, *J* = 1.9 Hz, 1H), 7.44–7.37 (m, 4H), 7.25–7.20 (m, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 4.55–4.45 (m, 2H), 3.92 (s, 3H), 3.91 (s, 3H), 3.13–3.00 (m, 2H), 2.88 (dd, *J* = 7.2, 4.9 Hz, 1H), 2.14–2.08 (m, 4H), 1.99–1.92 (m, 1H), 1.75–1.71 (m, 1H), 1.61–1.52 (m, 2H), 1.42 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.28, 176.83, 153.20, 148.92, 137.21, 129.85, 129.07, 126.05, 123.94, 122.94, 110.19, 109.97, 55.99, 55.95, 55.64, 50.24, 48.18, 47.98, 34.12, 33.27, 32.17, 27.16, 20.74, 18.82.

HRMS (ESI) for $C_{26}H_{31}BrNO_4$ $[M+H]^+$ calcd. 500.1431, found 500.1446.



4-Bromo-3-methyl-3-(3-(naphthalen-2-yl)-3-oxopropyl)-1-phenyloctahydro-2H-indol-2-one (3al)

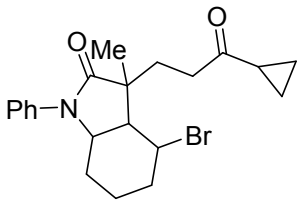
Purification by flash column chromatography (SiO_2, PE/EA = 6:1) afforded **3al**.

White solid, 38.1 mg, 78% yield, mp = 140–142 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.03 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.89–7.83 (m, 2H), 7.60–7.51 (m, 2H), 7.45–7.38 (m, 4H), 7.25–7.19 (m, 1H), 4.57–4.48 (m, 2H), 3.32–3.19 (m, 2H), 2.90 (dd, *J* = 7.2, 4.9 Hz, 1H), 2.22–2.17 (m, 2H), 2.14–2.07 (m, 2H), 1.98–1.90 (m, 1H), 1.77–1.70 (m, 1H), 1.63–1.52 (m, 2H), 1.46 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.48, 176.86, 137.18, 135.53, 133.97, 132.46, 129.83, 129.60, 129.10, 128.35, 127.66, 126.65, 126.08, 123.98, 123.86, 55.66, 50.24, 48.40, 47.93, 34.20, 33.69, 31.78, 27.13, 20.74, 18.86.

HRMS (ESI) for $C_{28}H_{29}BrNO_2$ $[M+H]^+$ calcd. 490.1376, found 490.1386.



4-Bromo-3-(3-cyclopropyl-3-oxopropyl)-3-methyl-1-phenyloctahydro-2H-indol-2-one (3am)

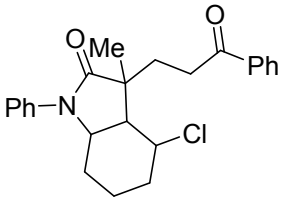
Purification by flash column chromatography (SiO_2, PE/EA = 8:1) afforded **3am**.

White solid, 28.2 mg, 70% yield, mp = 70–72 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.36 (m, 4H), 7.24–7.20 (m, 1H), 4.50–4.42 (m, 2H), 2.81–2.63 (m, 3H), 2.15–2.02 (m, 2H), 2.00–1.89 (m, 4H), 1.76–1.68 (m, 1H), 1.61–1.50 (m, 2H), 1.37 (s, 3H), 1.02–0.97 (m, 2H), 0.86–0.83 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 209.95, 176.80, 137.21, 129.02, 126.01, 123.95, 55.63, 50.28, 48.21, 47.76, 38.35, 34.24, 31.13, 27.07, 20.57, 20.53, 18.88, 10.78, 10.74.

HRMS (ESI) for $C_{21}H_{27}BrNO_2$ $[M+H]^+$ calcd. 404.1220, found 404.1229.



4-Chloro-3-methyl-3-(3-oxo-3-phenylpropyl)-1-phenyloctahydro-2H-indol-2-one (3an)

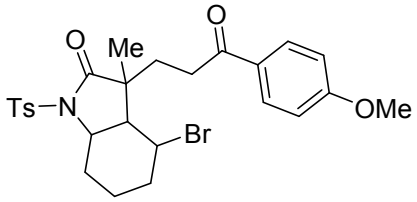
Purification by flash column chromatography (SiO_2, PE/EA = 6:1) afforded **3an**.

White solid, 26.1 mg, 66% yield, mp = 140–142 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98–7.94 (m, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.46–7.40 (m, 3H), 7.39–7.34 (m, 3H), 7.26–7.21 (m, 1H), 4.49 (dd, *J* = 12.4, 6.8 Hz, 1H), 4.31–4.26 (m, 1H), 3.21–3.06 (m, 2H), 2.63 (t, *J* = 6.5 Hz, 1H), 2.16–2.08 (m, 3H), 1.92–1.80 (m, 2H), 1.70–1.63 (m, 2H), 1.49–1.44 (m, 1H), 1.43 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.57, 177.06, 137.06, 136.66, 132.99, 129.02, 128.49, 128.05, 126.14, 124.32, 57.67, 55.61, 48.61, 47.51, 33.86, 33.57, 31.27, 26.54, 20.10, 18.11.

HRMS (ESI) for $C_{24}H_{27}ClNO_2$ $[M+H]^+$ calcd. 396.1725, found 396.1735.



4-Bromo-3-(3-(4-methoxyphenyl)-3-oxopropyl)-3-methyl-1-tosyloctahydro-2H-indol-2-one (3ke)

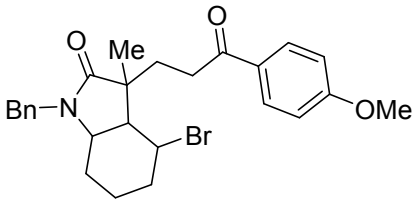
Purification by flash column chromatography (SiO_2, PE/EA = 3:1) afforded **3ke**.

White solid, 34.5 mg, 63% yield, mp = 134–136 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.82 (d, *J* = 8.9 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 4.67–4.58 (m, 2H), 3.88 (s, 3H), 2.84–2.69 (m, 3H), 2.58–2.52 (m, 1H), 2.42 (s, 3H), 2.11–2.06 (m, 1H), 2.01–1.87 (m, 4H), 1.79–1.71 (m, 1H), 1.53–1.44 (m, 1H), 1.22 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.18, 176.42, 163.46, 145.20, 135.64, 130.31, 129.57, 129.37, 128.27, 113.61, 55.46, 48.97, 47.95, 47.05, 32.75, 32.32, 31.92, 29.88, 21.71, 21.65, 18.14.

HRMS (ESI) for $C_{26}H_{31}BrNO_5S$ $[M+H]^+$ calcd. 548.1101, found 548.1095.



1-Benzyl-4-bromo-3-(3-(4-methoxyphenyl)-3-oxopropyl)-3-methyloctahydro-2H-indol-2-one (3le)

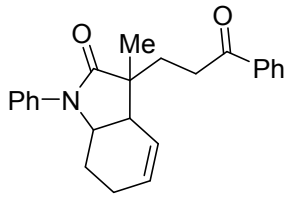
Purification by flash column chromatography (SiO_2, PE/EA = 2:1) afforded **3le**.

White solid, 26.6 mg, 55% yield, mp = 86–88 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.8 Hz, 2H), 7.34–7.29 (m, 3H), 7.22 (d, *J* = 6.6 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 4.97 (d, *J* = 15.0 Hz, 1H), 4.43–4.41 (m, 1H), 4.00 (d, *J* = 15.0 Hz, 1H), 3.88 (s, 3H), 3.71–3.66 (m, 1H), 3.15–2.93 (m, 2H), 2.67–2.59 (m, 1H), 2.06–2.02 (m, 4H), 1.93–1.86 (m, 1H), 1.72–1.61 (m, 1H), 1.54–1.45 (m, 2H), 1.35 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.14, 177.52, 163.39, 136.55, 130.41, 129.75, 128.76, 127.82, 127.61, 113.66, 55.44, 53.07, 50.17, 48.31, 46.95, 44.21, 34.05, 33.37, 31.86, 26.93, 20.44, 18.78.

HRMS (ESI) for $C_{26}H_{31}BrNO_3$ $[M+H]^+$ calcd. 484.1482, found 484.1479.



3-Methyl-3-(3-oxo-3-phenylpropyl)-1-phenyl-1,3,3a,6,7,7a-hexahydro-2H-indol-2-one (4aa)

Purification by flash column chromatography (SiO_2, PE/EA = 4:1) afforded **4aa**.

White solid, 33.4 mg, 93% yield, mp = 103–105 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01–7.92 (m, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.49–7.35 (m, 6H), 7.21 (t, *J* = 7.2 Hz, 1H), 6.03–5.89 (m, 1H), 5.74–5.60 (m, 1H), 4.43 (td, *J* = 8.5, 3.8 Hz, 1H), 3.20–3.13 (m, 2H), 2.90–2.79 (m, 1H), 2.21–2.03 (m, 2H), 1.99–1.85 (m, 3H), 1.71–1.64 (m, 1H), 1.26 (s, 3H).

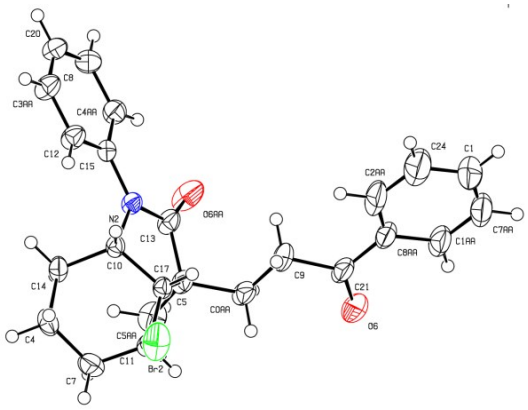
^{13}C NMR (101 MHz, $CDCl_3$) δ 200.11, 177.56, 137.47, 136.68, 133.01, 128.96, 128.52, 128.14, 125.71, 124.22, 123.77, 55.60, 47.07, 40.47, 33.83, 32.34, 24.76, 21.28, 20.91.

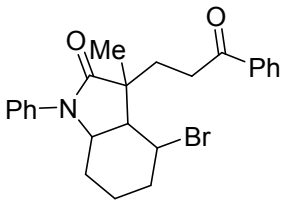
HRMS (ESI) for $C_{24}H_{26}NO_2$ $[M+H]^+$ calcd. 360.1958, found 360.1955.

6. X-Ray crystallographic data

6.1 X-Ray Crystallographic Data of Product 3aa

The crystal structure **3aa** has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: **CCDC 1950969**.





Bond precision:	C-C = 0.0044 A	Wavelength=1.54184	
Cell:	a=8.8862(4)	b=9.2731(5)	c=14.1317(6)
	alpha=90.728(4)	beta=101.126(4)	gamma=116.691(5)
Temperature:	291 K		
	Calculated	Reported	
Volume	1014.27(10)	1014.26(9)	
Space group	P -1	P -1	
Hall group	-P 1	-P 1	
Moiety formula	C24 H26 Br N O2	C24 H26 Br N O2	
Sum formula	C24 H26 Br N O2	C24 H26 Br N O2	
Mr	440.36	440.37	
Dx,g cm-3	1.442	1.442	
Z	2	2	
Mu (mm-1)	2.910	2.910	
F000	456.0	456.0	
F000’	455.72		
h,k,lmax	10,11,16	10,11,16	
Nref	3587	3573	
Tmin,Tmax	0.622,0.705	0.528,1.000	
Tmin’	0.564		

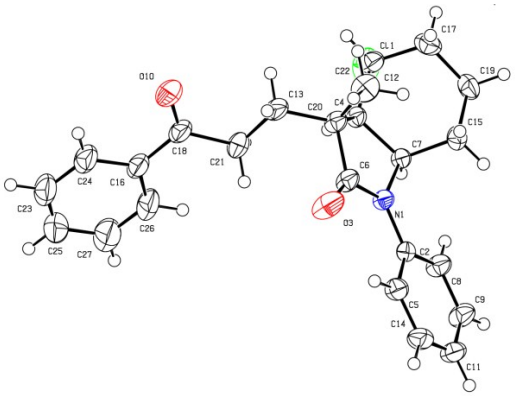
Correction method= # Reported T Limits: Tmin=0.528 Tmax=1.000

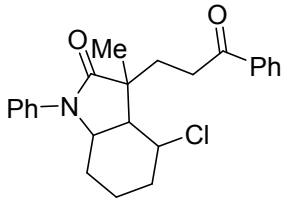
AbsCorr = MULTI-SCAN

Data completeness= 0.996	Theta(max)= 66.596
R(reflections)= 0.0412(3380)	wR2(reflections)= 0.1082(3573)
S = 1.068	Npar= 254

6.2 X-Ray Crystallographic Data of product 3an

The crystal structure **3an** has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: **CCDC 1950971**.

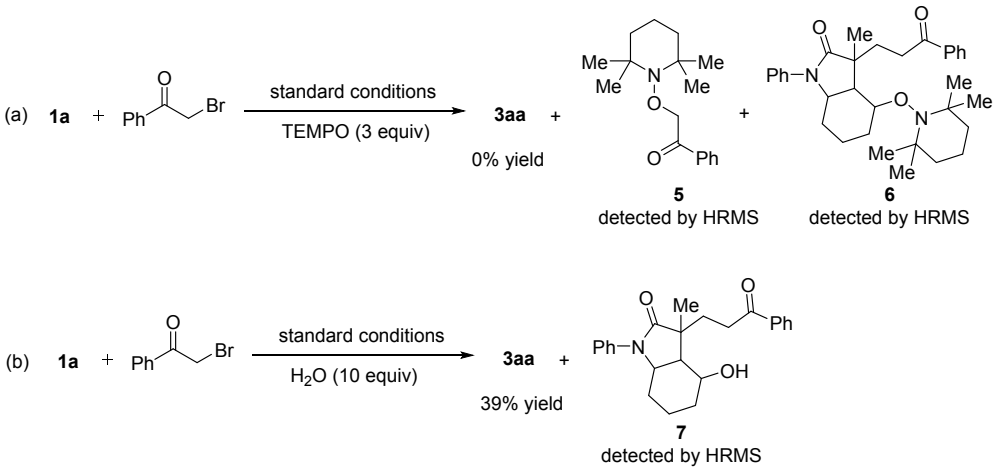




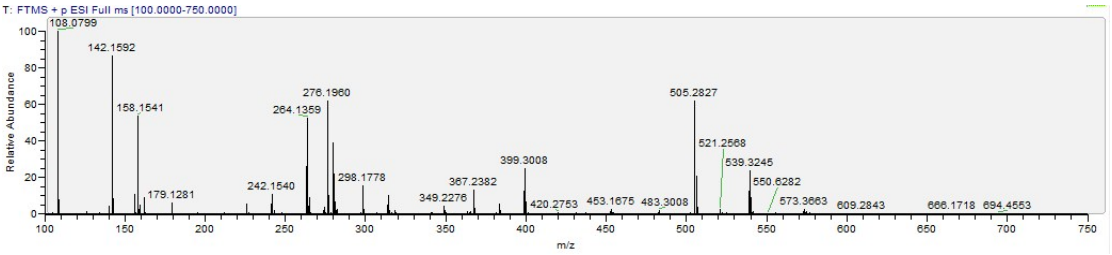
Bond precision:	C-C =0.0028 A	Wavelength=1.54184	
Cell:	a=8.7322(5)	b=9.3453(4)	c=13.9189(7)
	alpha=90.640(4)	beta=99.884(4)	gamma=116.102(5)
Temperature:	292 K		
	Calculated	Reported	
Volume	1000.03(10)	1000.04(9)	
Space group	P -1	P -1	
Hall group	-P 1	-P 1	
Moiety formula	C24 H26 Cl N O2	C24 H26 Cl N O2	
Sum formula	C24 H26 Cl N O2	C24 H26 Cl N O2	
Mr	395.91	395.91	
Dx,g cm-3	1.315	1.315	
Z	2	2	
Mu (mm-1)	1.839	1.839	
F000	420.0	420.0	
F000’	421.81		
h,k,lmax	10,11,16	10,11,16	
Nref	3537	3537	
Tmin,Tmax	0.740,0.802	0.740,0.802	
Tmin’	0.672		
Correction method= # Reported T Limits: Tmin=0.248 Tmax=1.000			
AbsCorr = MULTI-SCAN			
Data completeness=0.999		Theta(max)= 66.595	
R(reflections)= 0.0473(3266)		wR2(reflections)= 0.1248(3532)	
S =1.078		Npar=261	

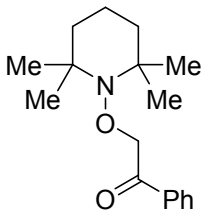
7. Mechanistic studies

7.1 Radical trapping experiments



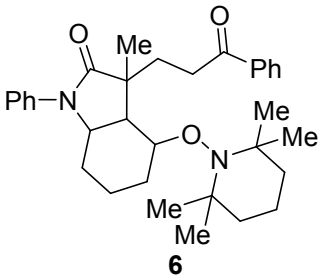
The radical trapping experiments were conducted with different scavengers to capture the radical intermediates in the system, and the products were detected by HRMS. Under the standard conditions, TEMPO-trapped product **5** and **6** were observed when TEMPO was used as the scavenger with no product **3aa** detected (Scheme 4a). This observation indicated the existence of radical intermediates **Ⅱ** and **Ⅳ**. Moreover, both product **3aa** and **7** were observed when H_2O was added to the reaction (Scheme 4b). This observation indicated the existence of carbon cation intermediate **Ⅴ**.





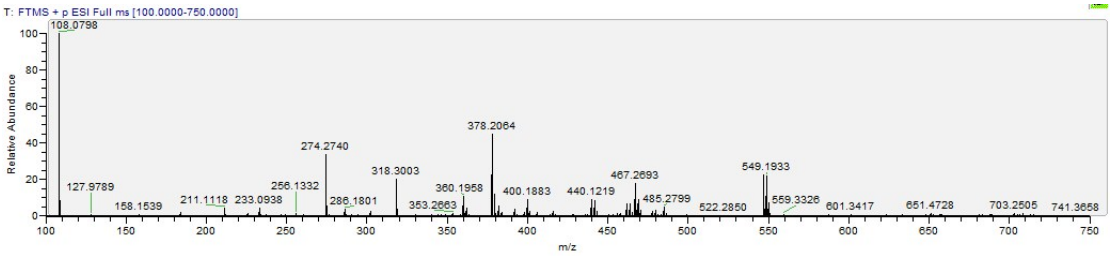
5

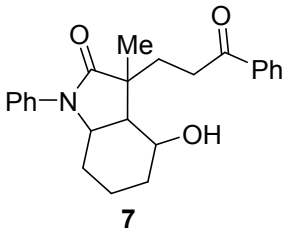
HRMS (ESI) for $C_{17}H_{26}NO_2$ $[M+H]^+$ calcd. 276.1958, found 276.1960.



6

HRMS (ESI) for $C_{33}H_{44}N_2NaO_3$ $[M+H]^+$ calcd. 539.3244, found 539.3245.





7

HRMS (ESI) for $C_{24}H_{28}NO_3$ $[M+H]^+$ calcd. 378.2064, found 378.2064.

7.2 Stern-Volmer fluorescence quenching experiments

According to the procedure of related literature, Stern-Volmer fluorescence quenching experiments were run with freshly prepared solutions of 0.1 mM *fac*-Ir(ppy)$_3$ in toluene at room temperature. The solutions were irradiated at 375 nm and fluorescence was measured from 450 nm to 650 nm. Control experiments show that excited state of *fac*-Ir(ppy)$_3$ was primarily quenched by 2-bromoacetophenone **2a** while 1,6-dienes **1a** and 2,6-lutidine showed a much less effect.

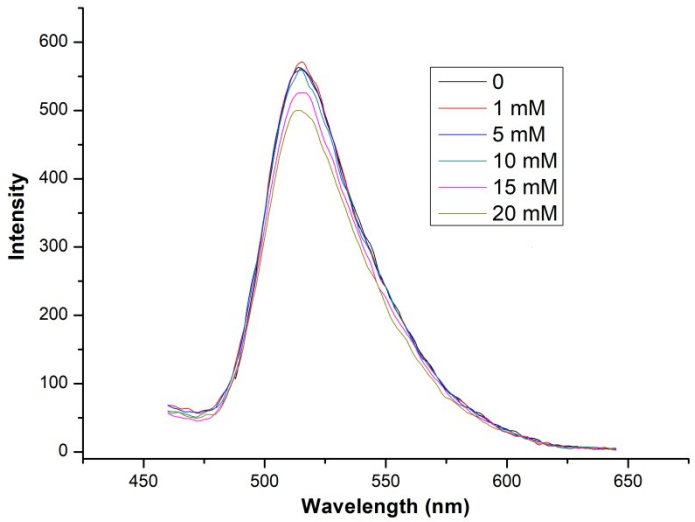


Fig. S1. Fluorescence quenching date with *fac*-Ir(ppy)$_3$ and variable 1,6-dienes **1a**.

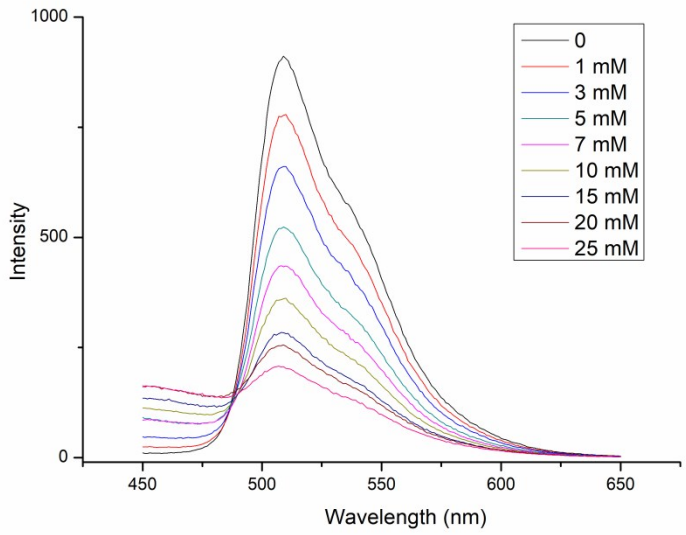


Fig. S2. Fluorescence quenching date with *fac*-Ir(ppy)$_3$ and variable 2-bromoacetophenone **2a**.

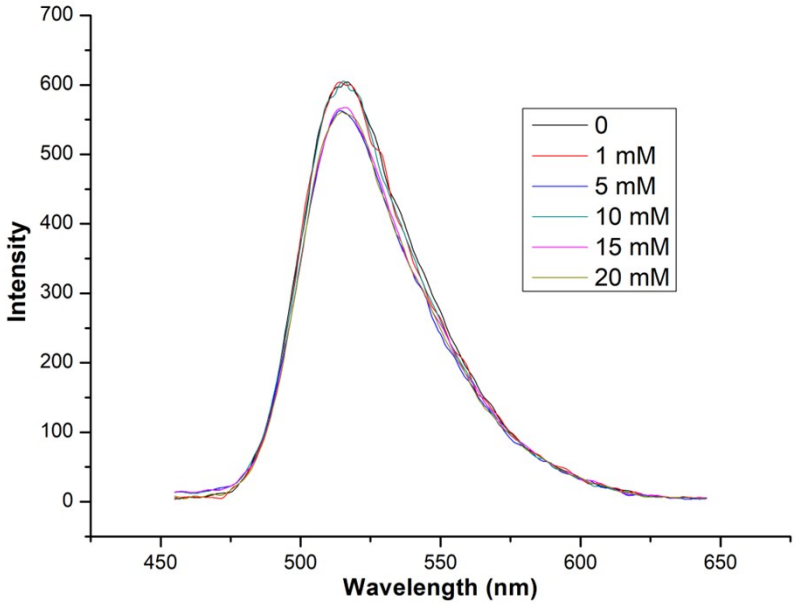


Figure S3. Fluorescence quenching experiments date with *fac*-Ir(ppy)$_3$ and variable 2, 6-lutidine.

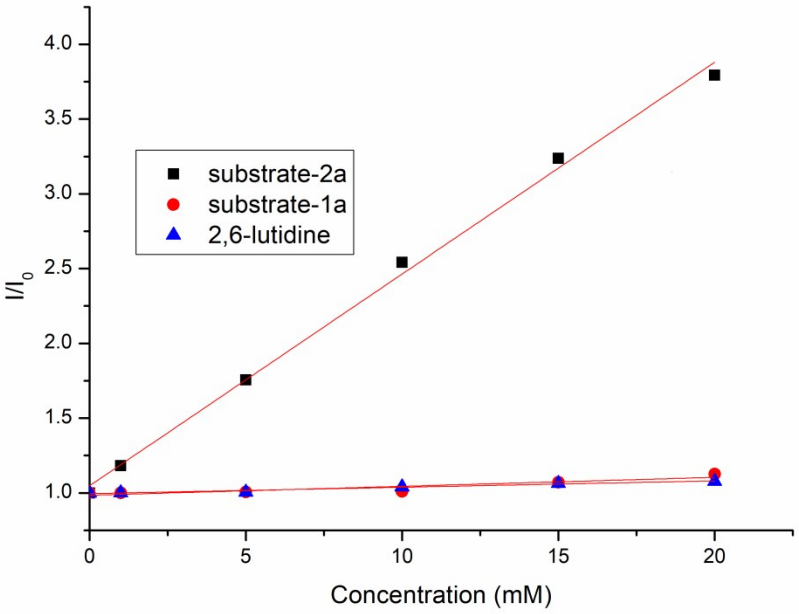
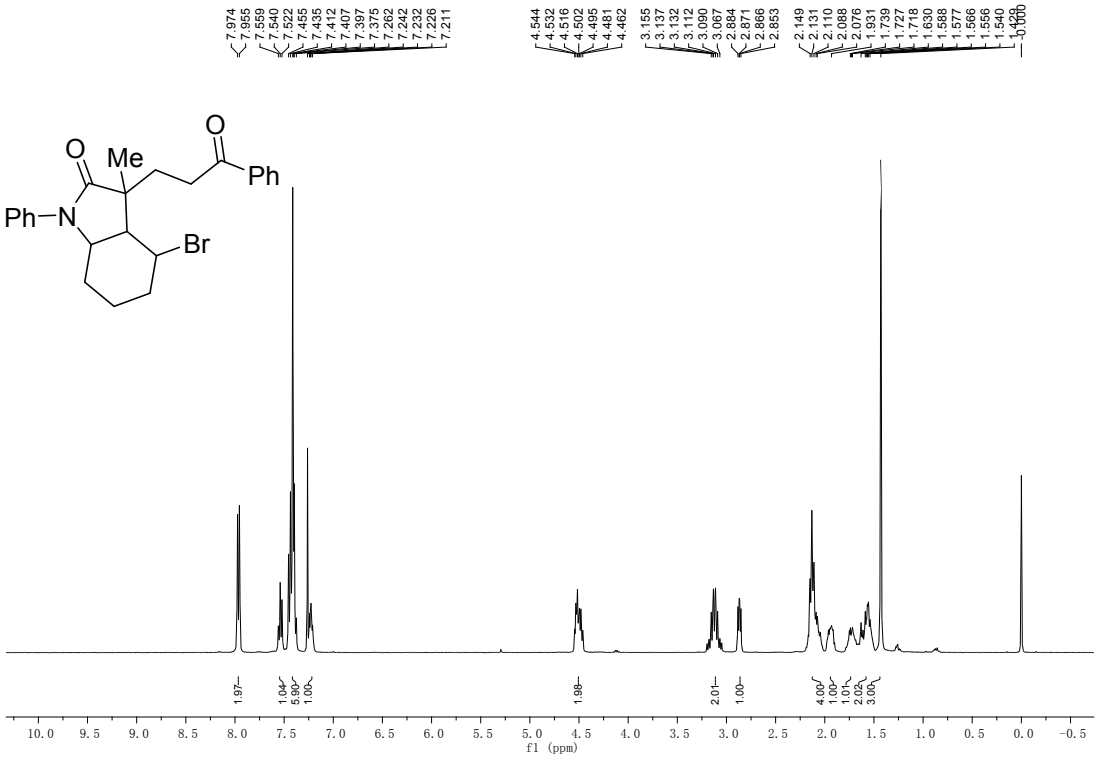


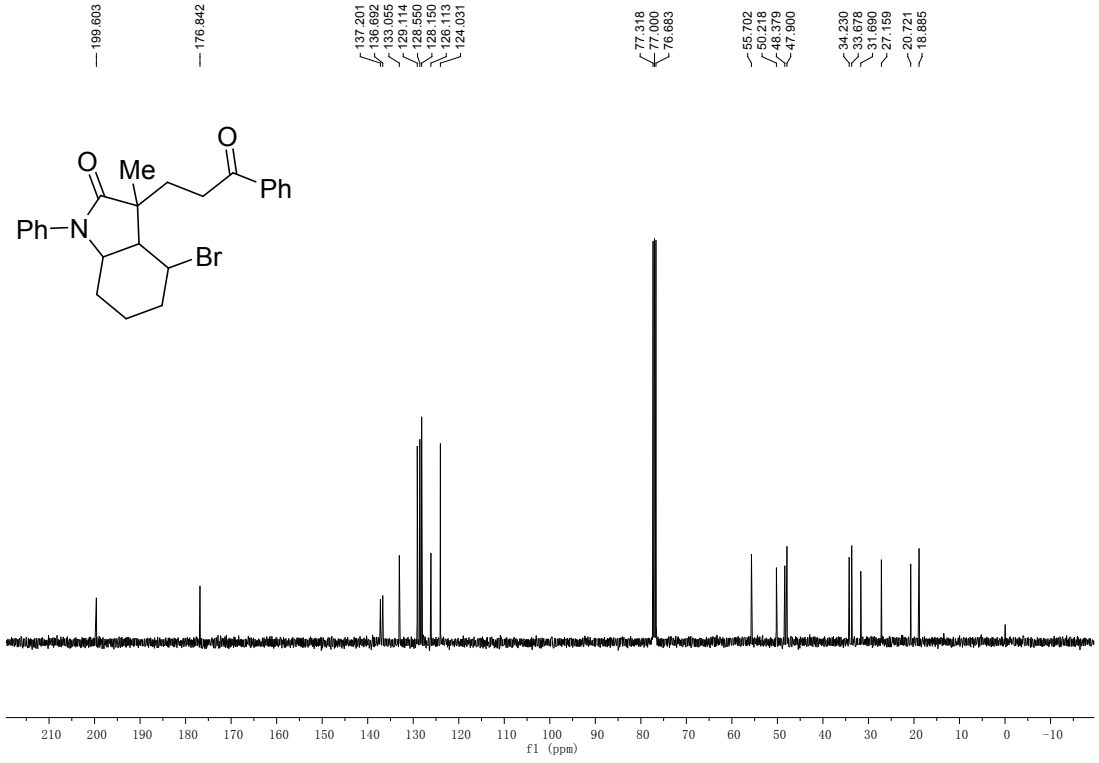
Figure S4. Stern-Volmer plots of *fac*-Ir(ppy)$_3$ with different quenchers.

8. NMR spectra of products

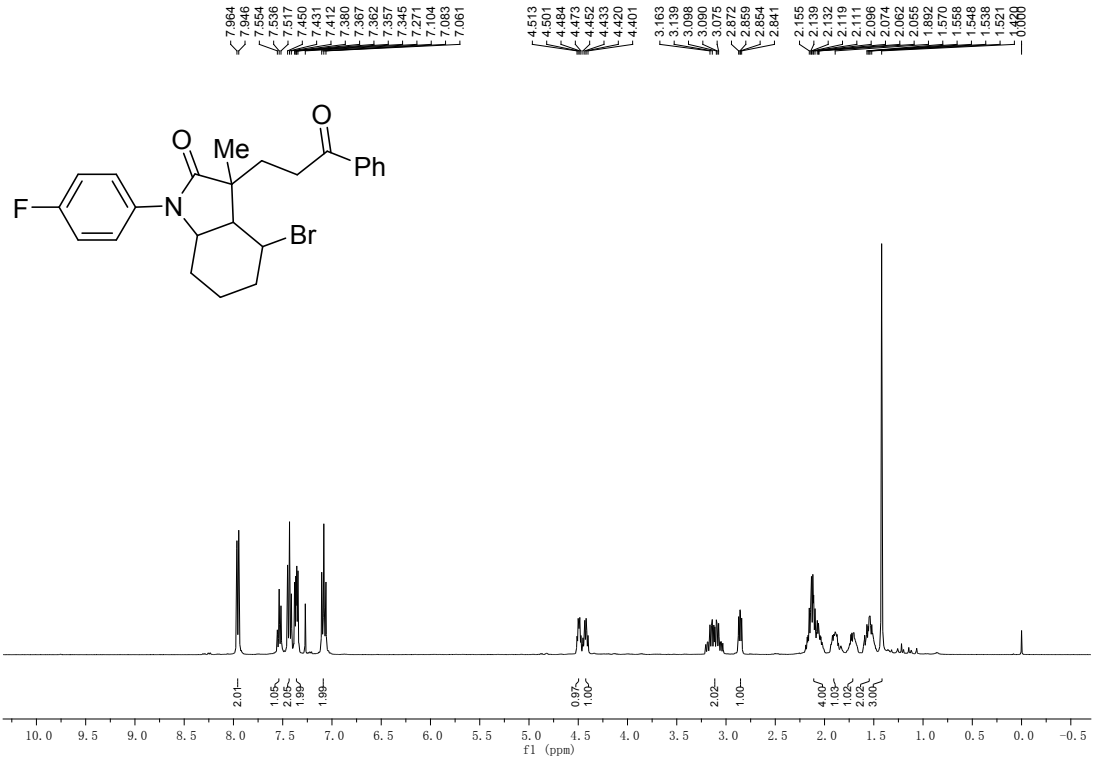
^{1}H NMR of **3aa** in $CDCl_3$



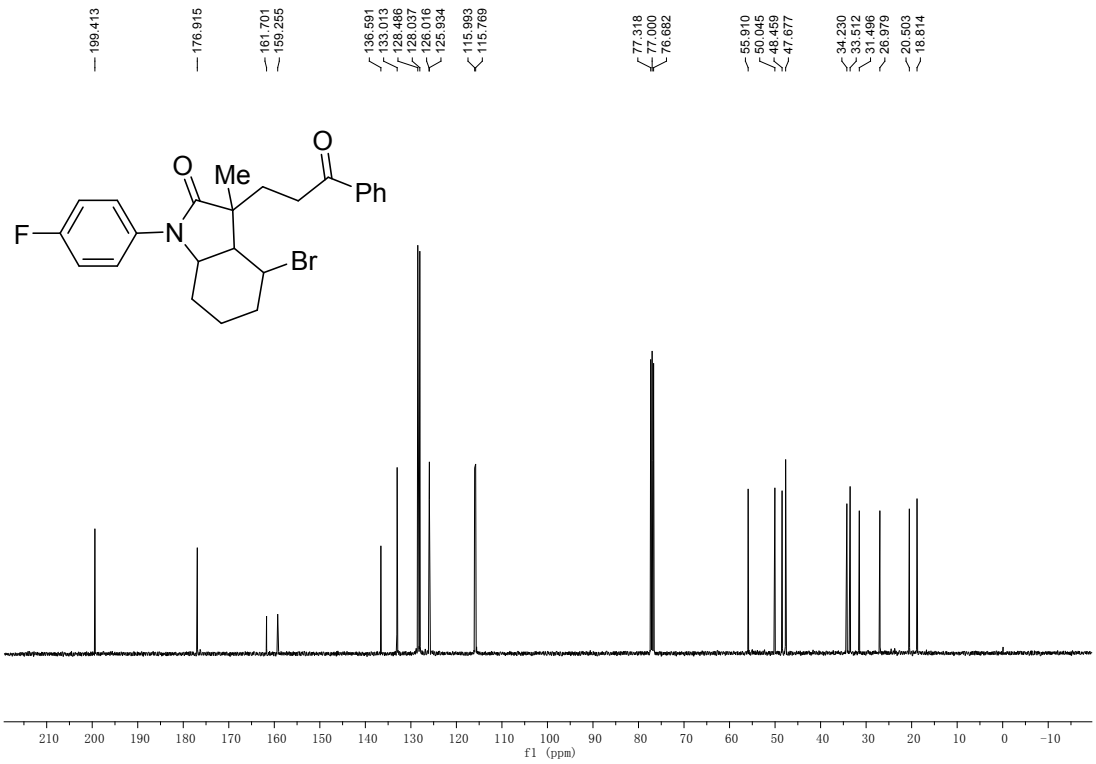
^{13}C NMR of **3aa** in $CDCl_3$



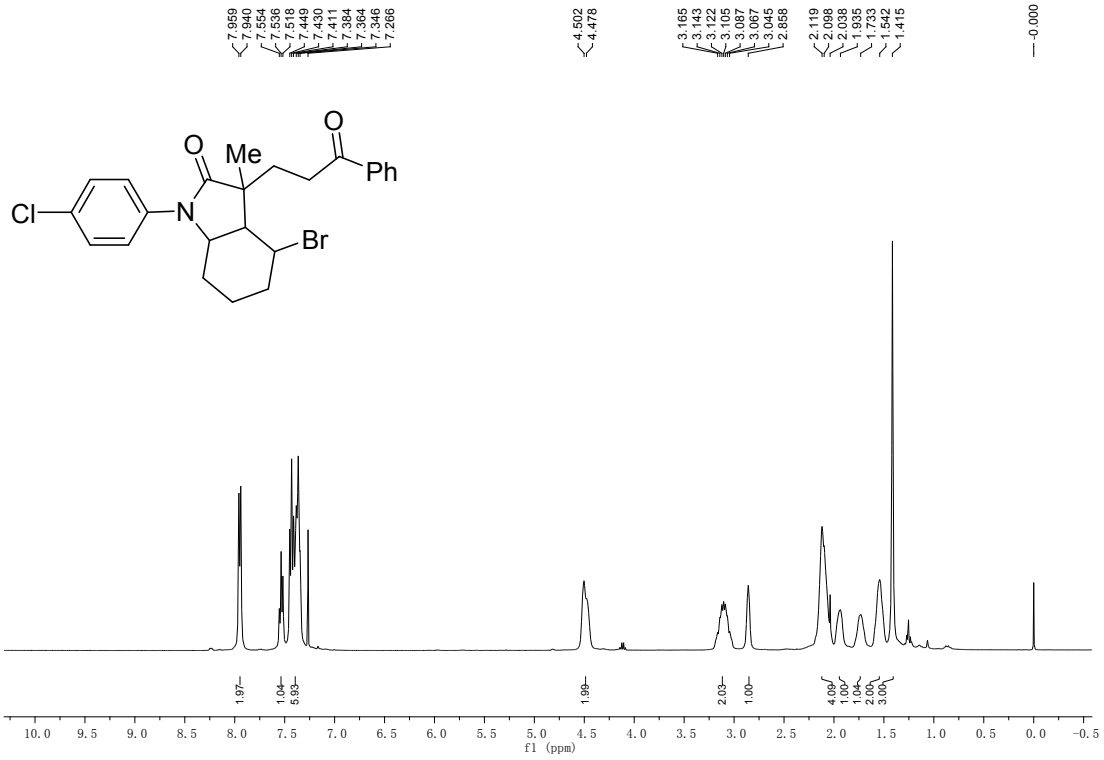
^{1}H NMR of **3ba** in $CDCl_3$



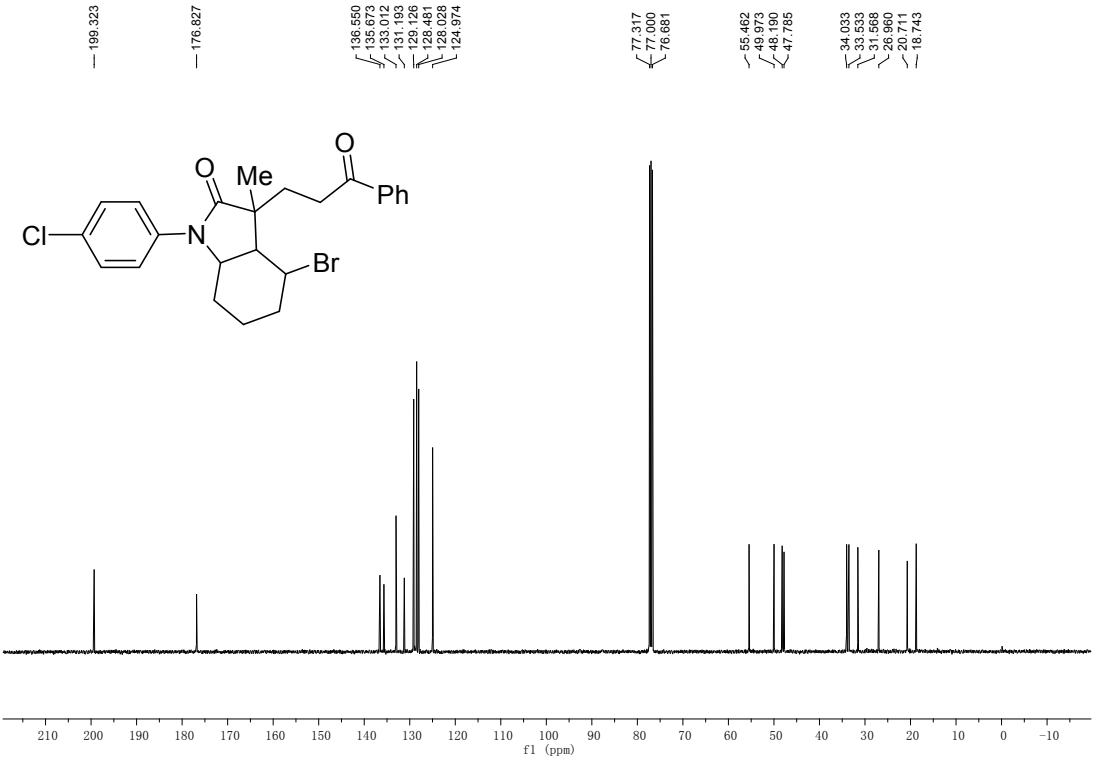
^{13}C NMR of **3ba** in $CDCl_3$



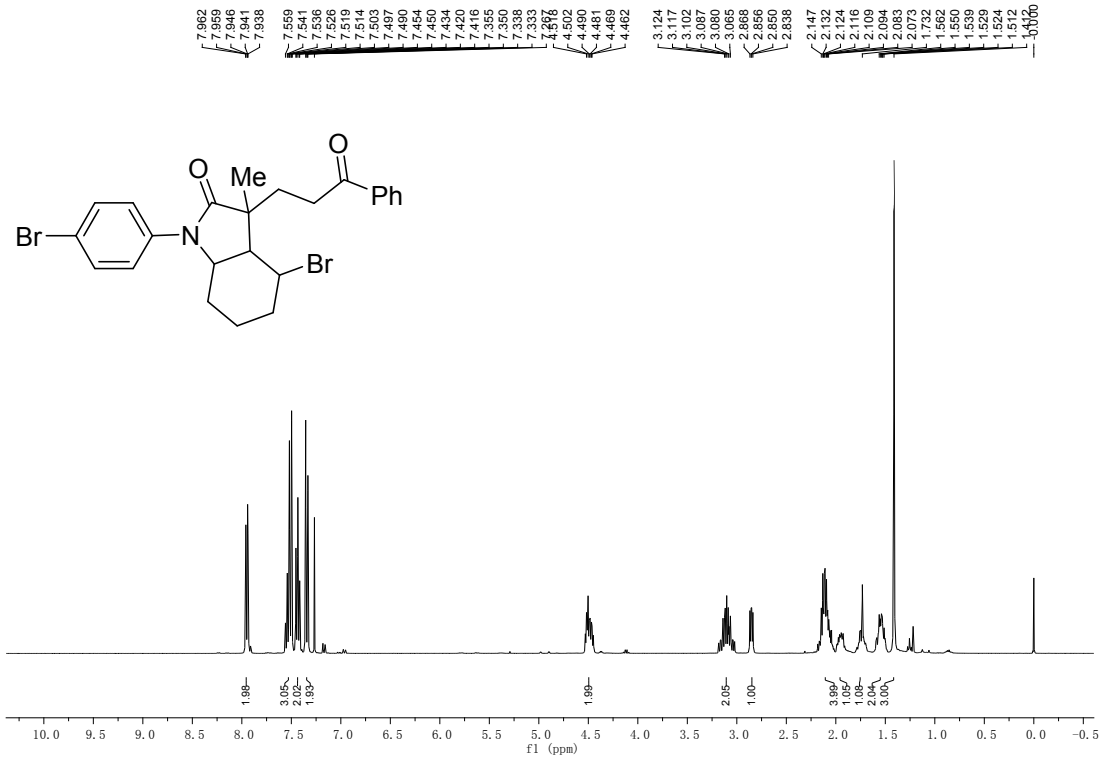
^{1}H NMR of **3ca** in $CDCl_3$



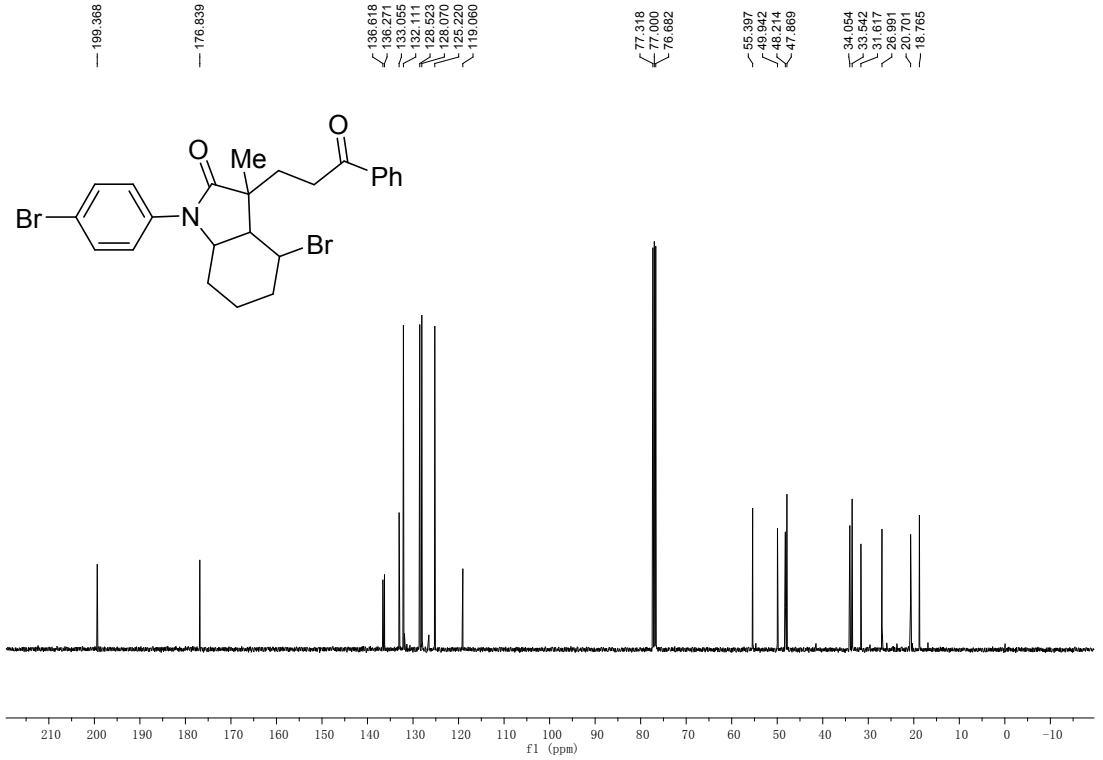
^{13}C NMR of **3ca** in $CDCl_3$



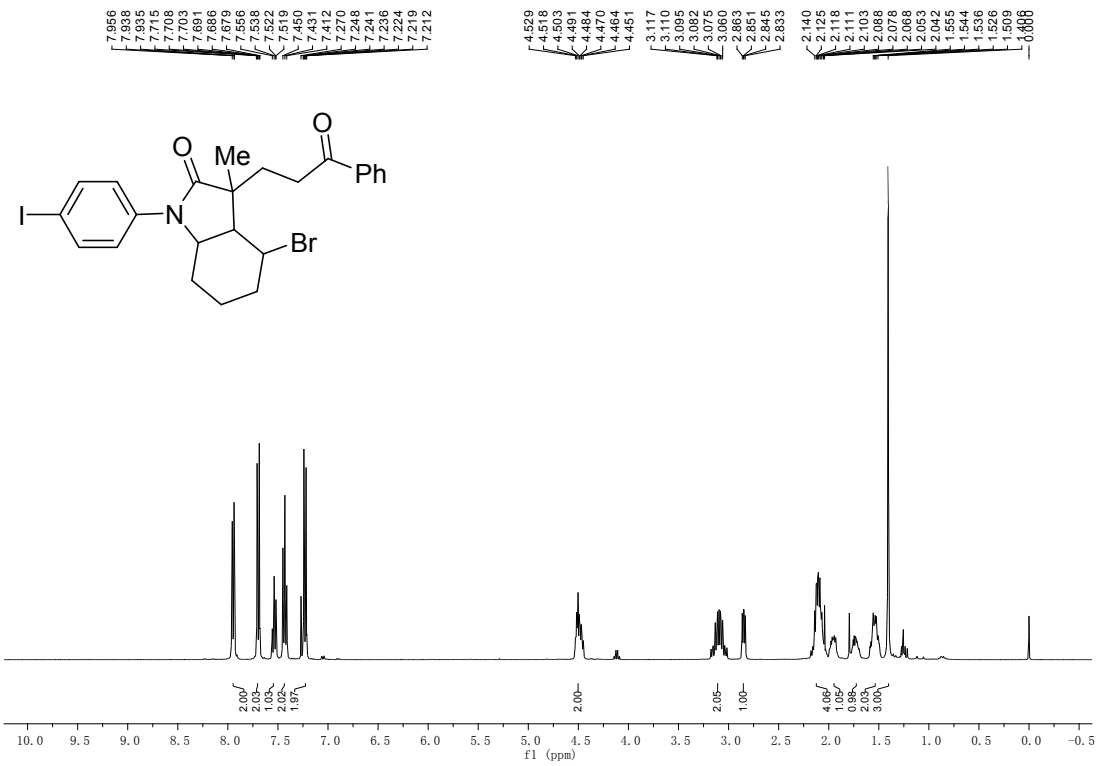
^{1}H NMR of **3da** in $CDCl_3$



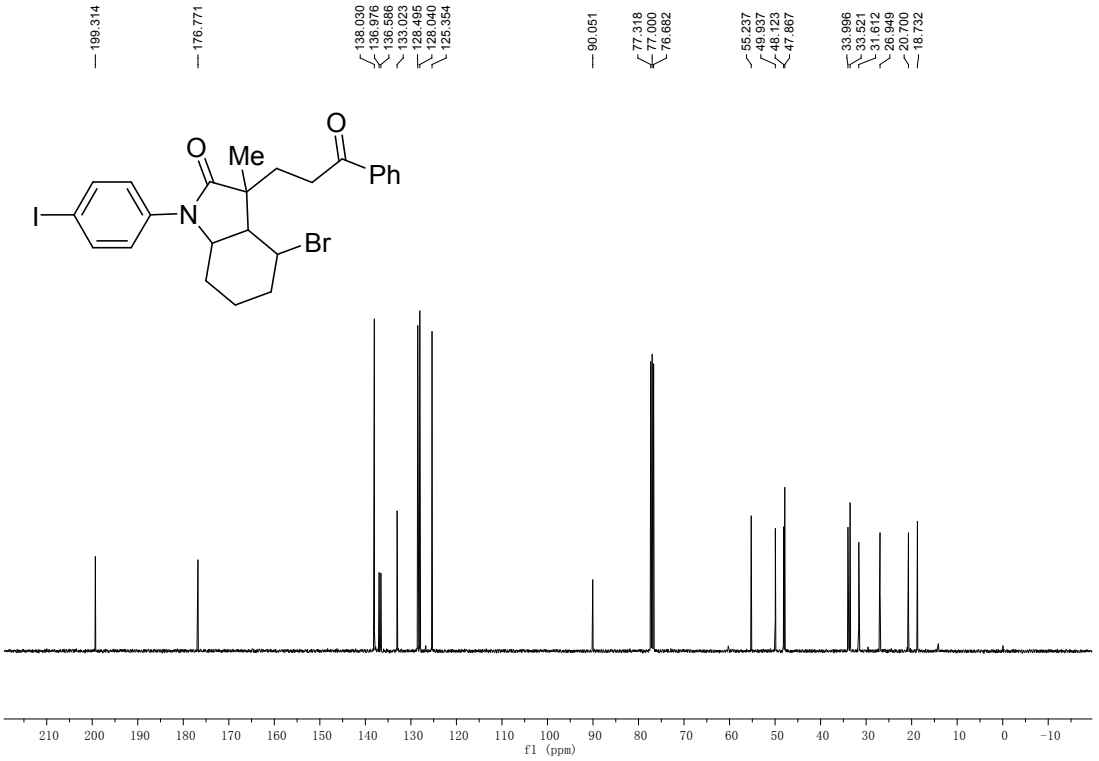
^{13}C NMR of **3da** in $CDCl_3$



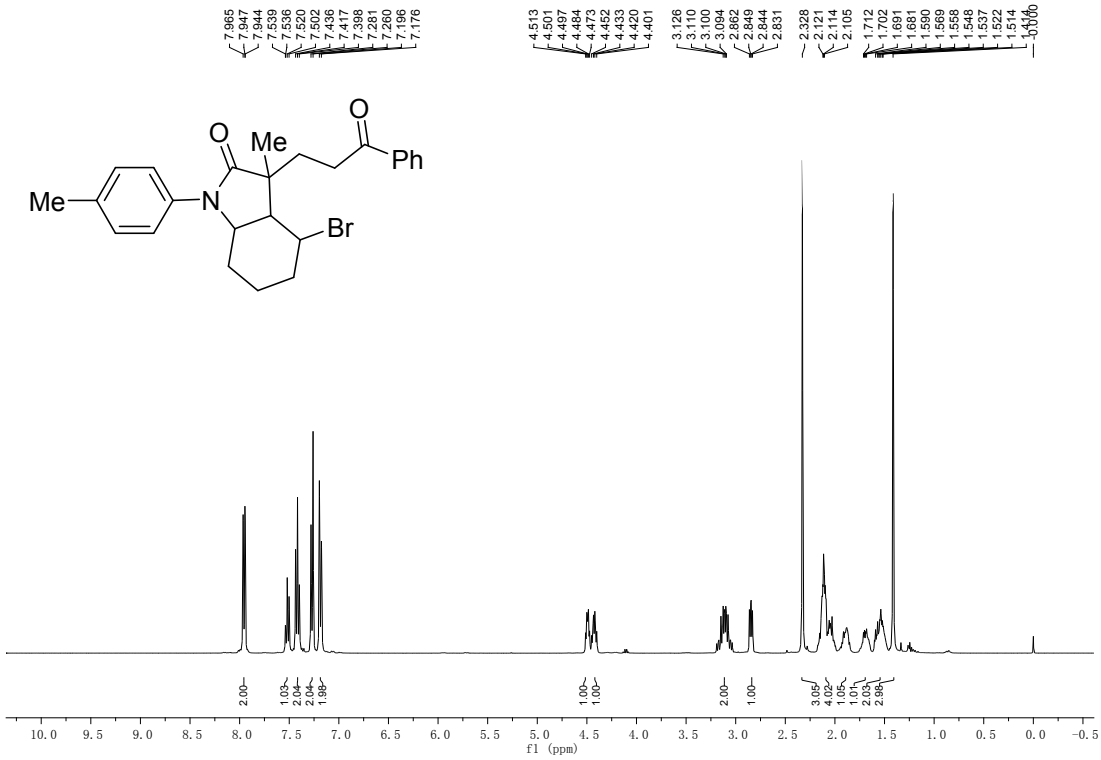
^{1}H NMR of **3ea** in $CDCl_3$



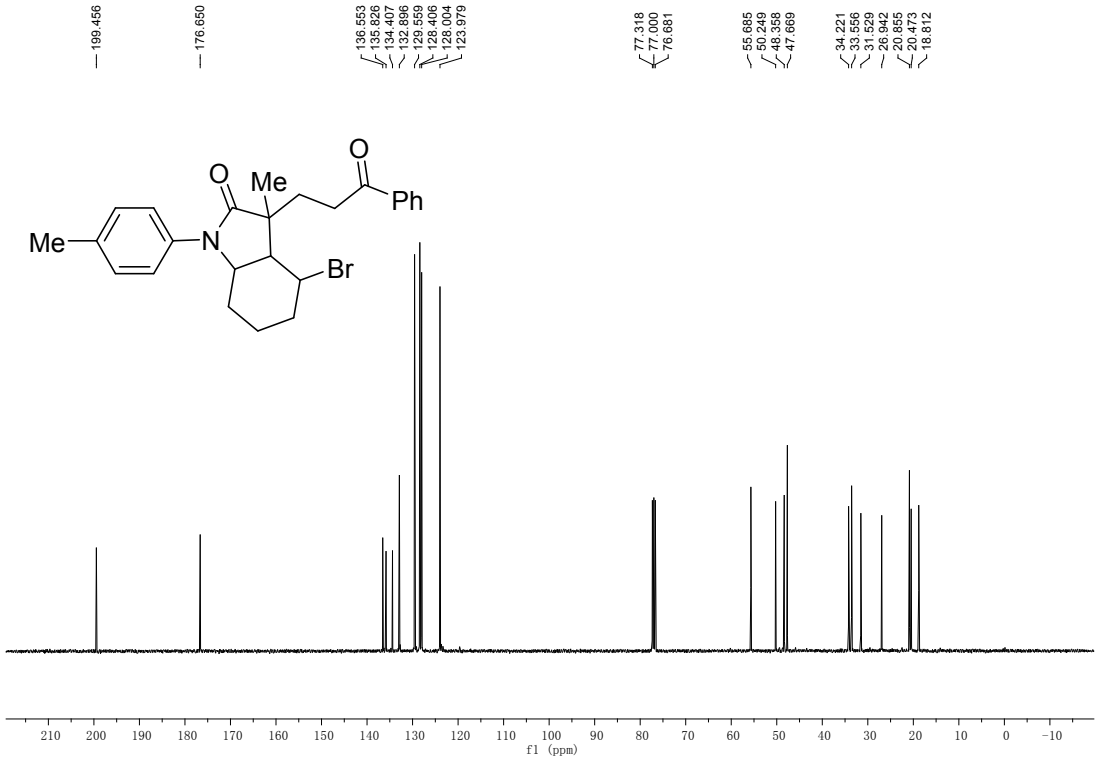
^{13}C NMR of **3ea** in $CDCl_3$



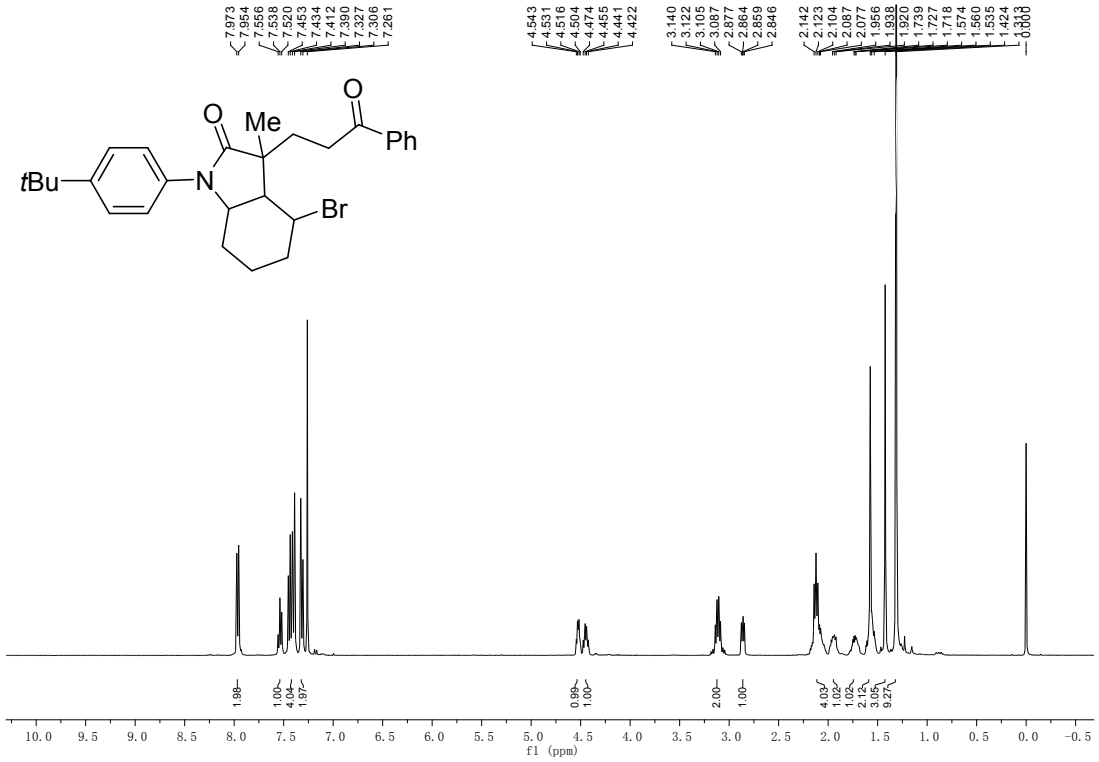
^{1}H NMR of **3fa** in $CDCl_3$



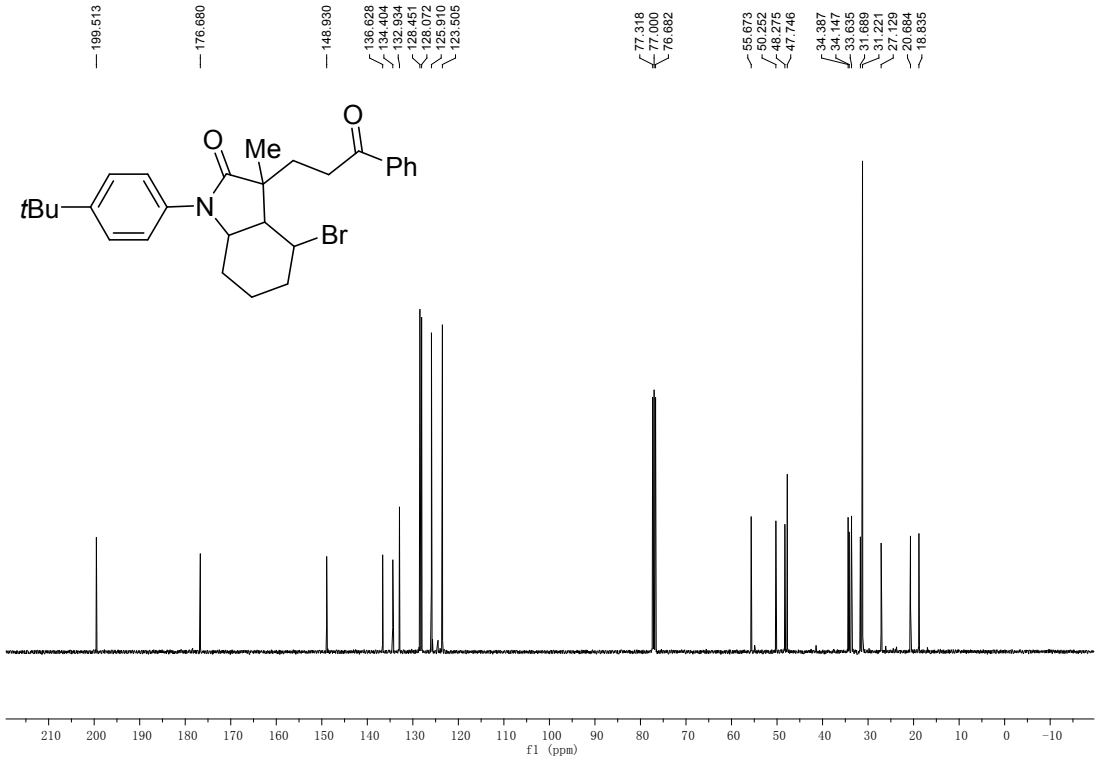
^{13}C NMR of **3fa** in $CDCl_3$



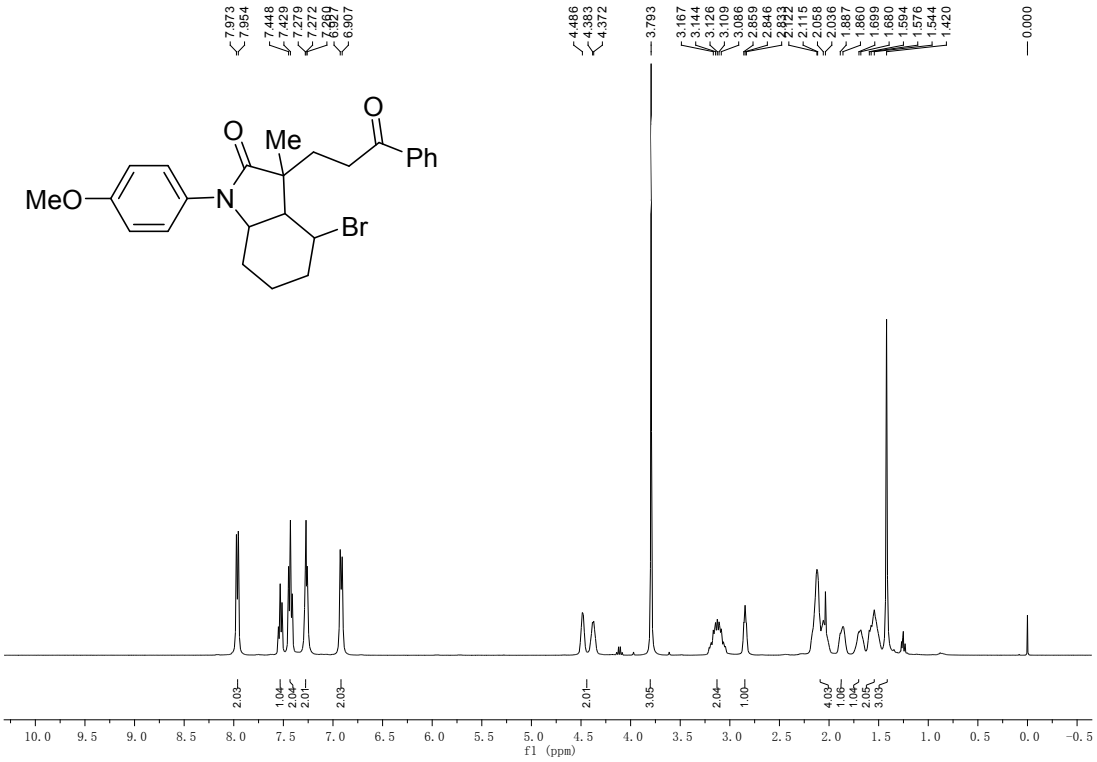
^{1}H NMR of **3ga** in $CDCl_3$



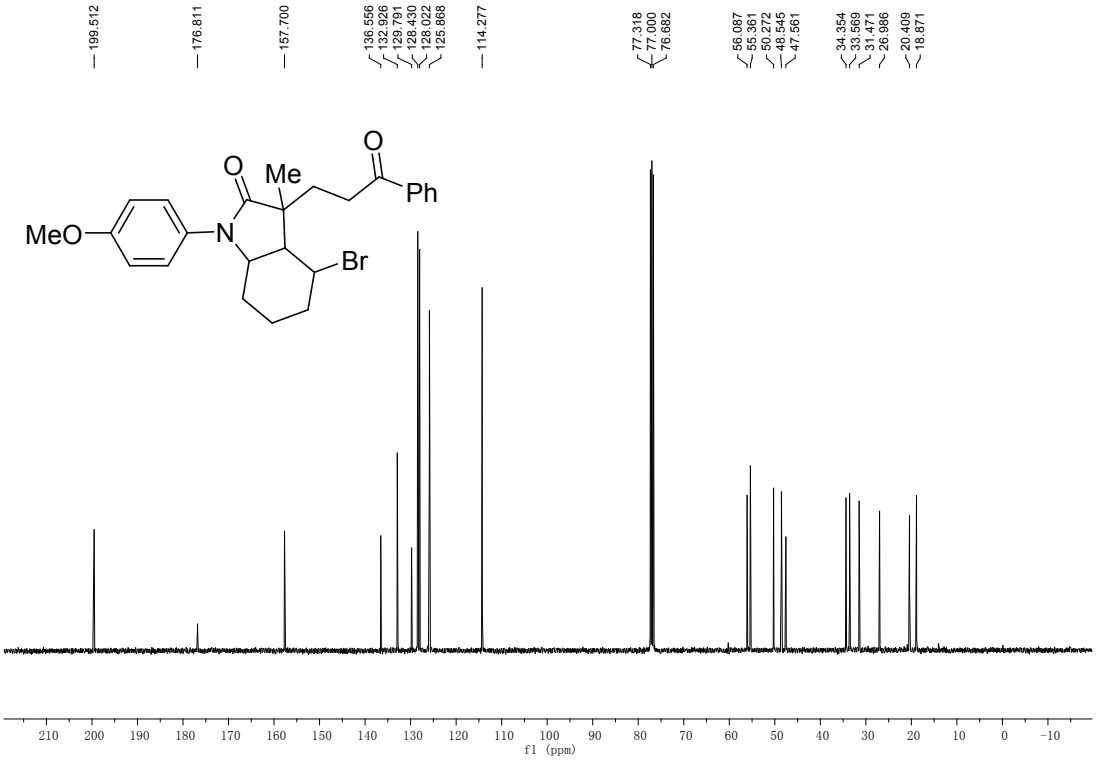
^{13}C NMR of **3ga** in $CDCl_3$



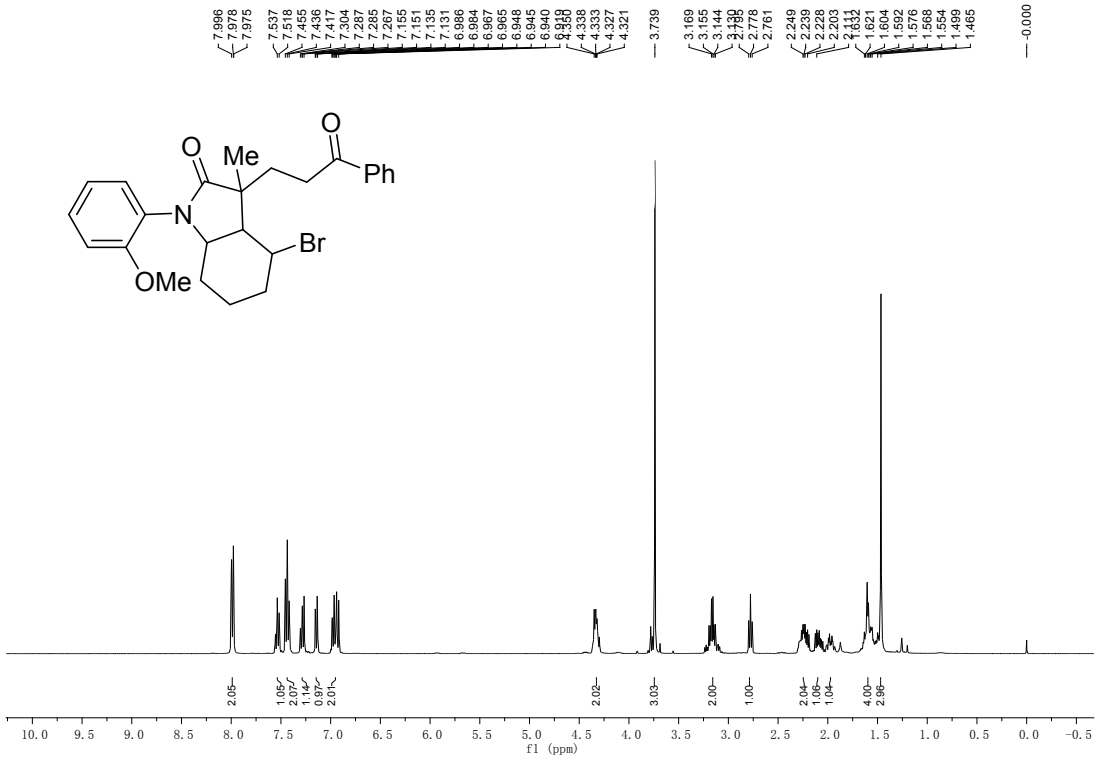
^{1}H NMR of **3ha** in $CDCl_3$



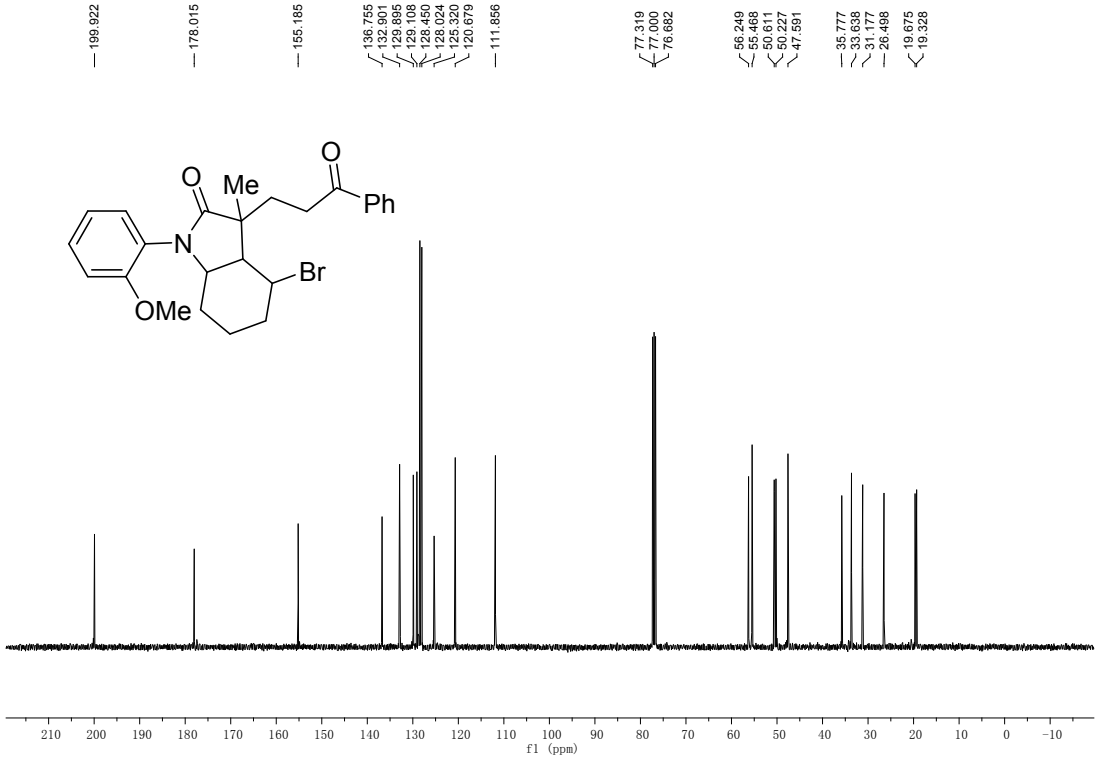
^{13}C NMR of **3ha** in $CDCl_3$



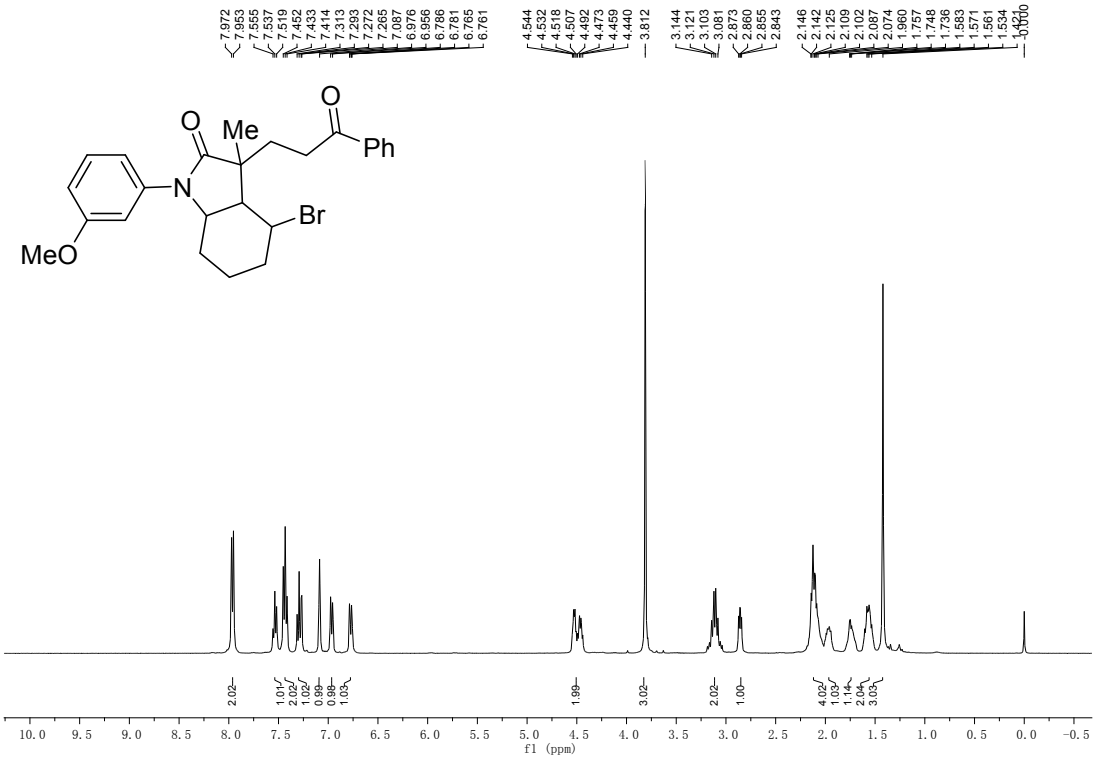
^{1}H NMR of **3ia** in $CDCl_3$



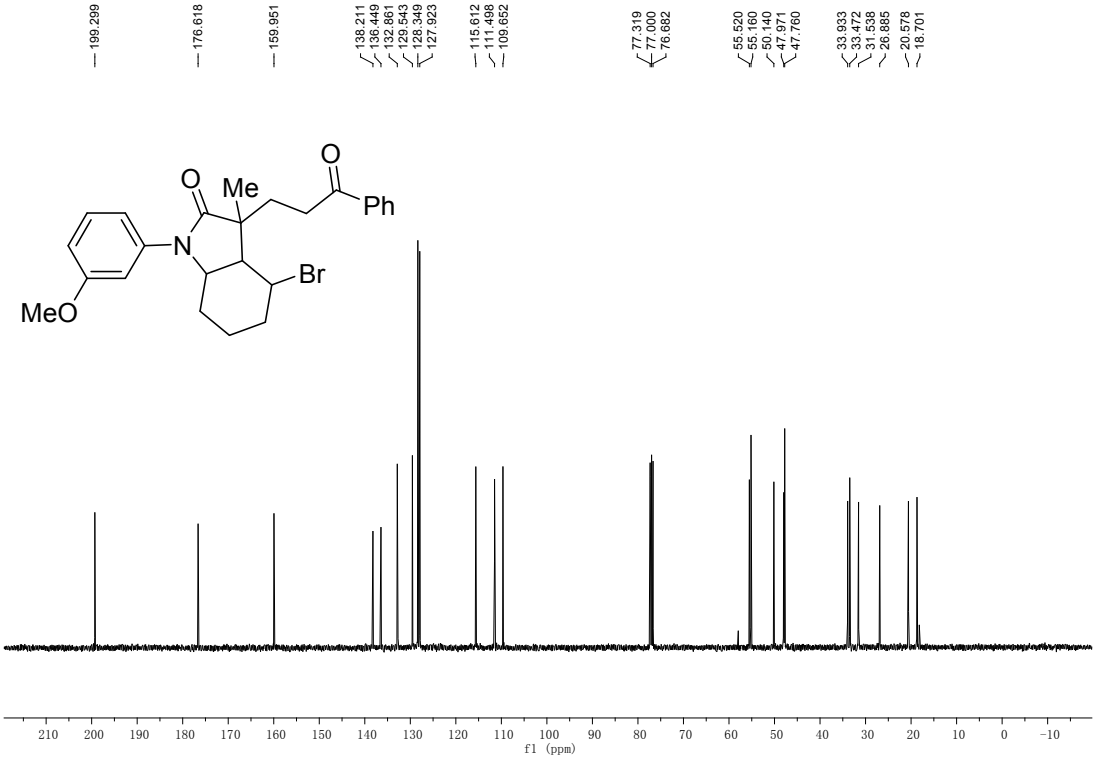
^{13}C NMR of **3ia** in $CDCl_3$



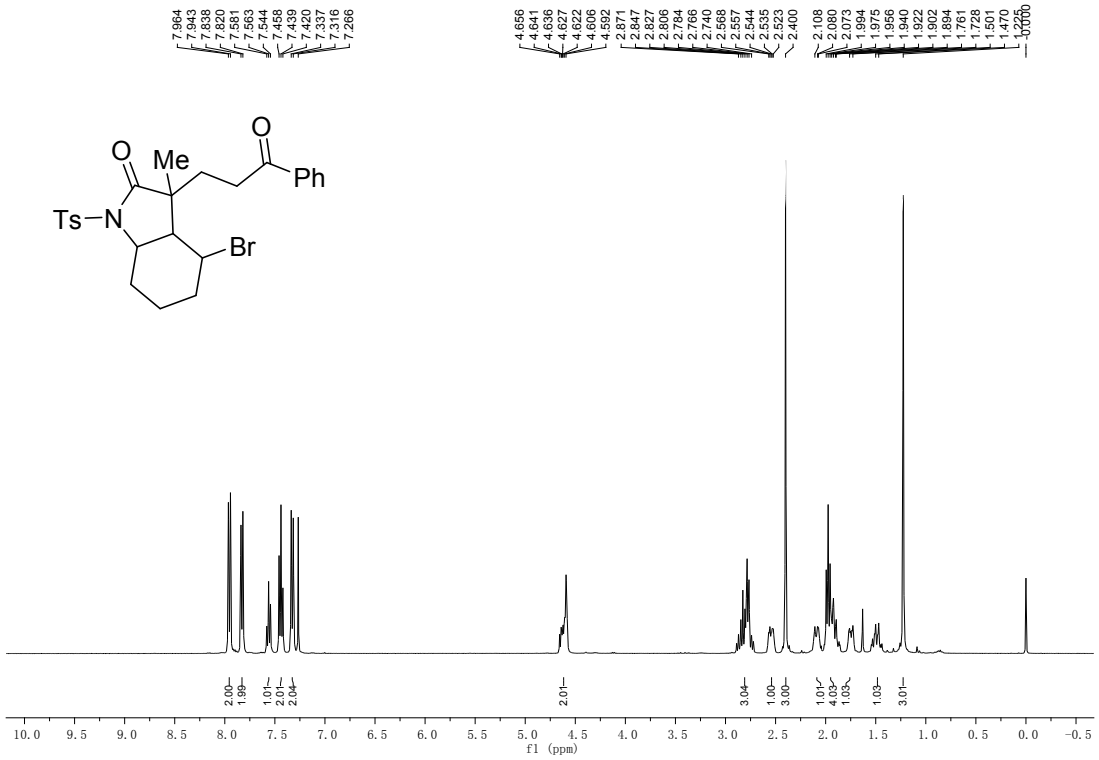
^{1}H NMR of **3ja** in $CDCl_3$



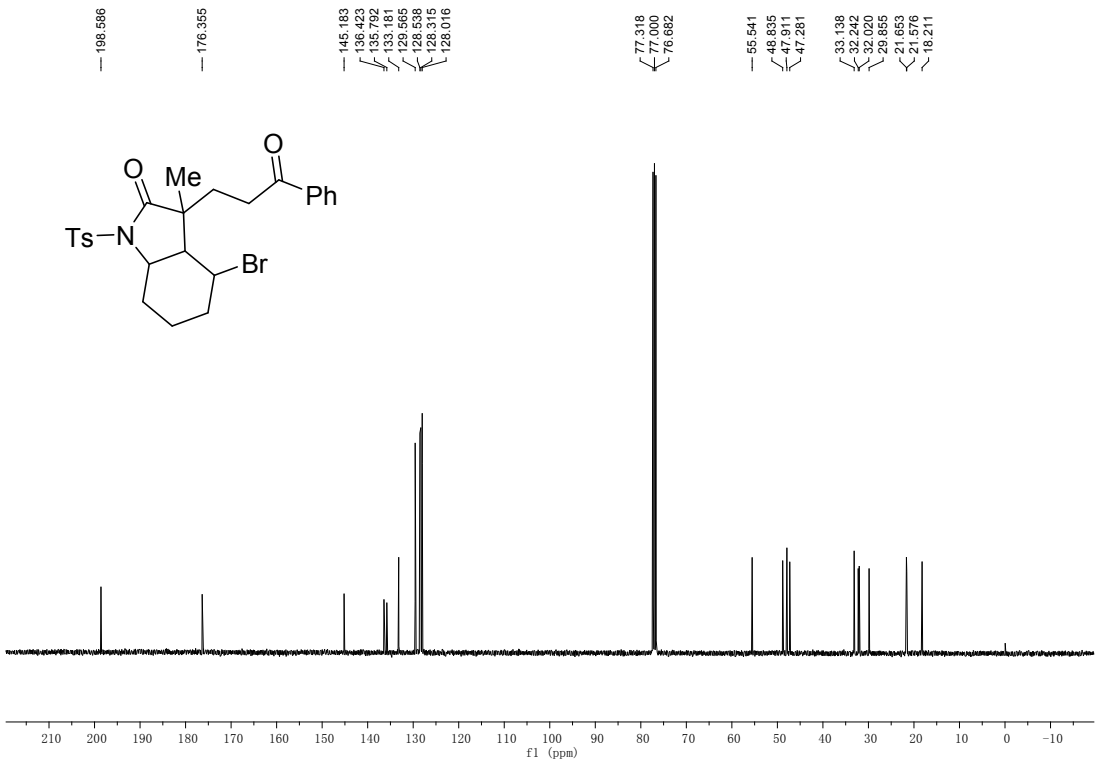
^{13}C NMR of **3ja** in $CDCl_3$



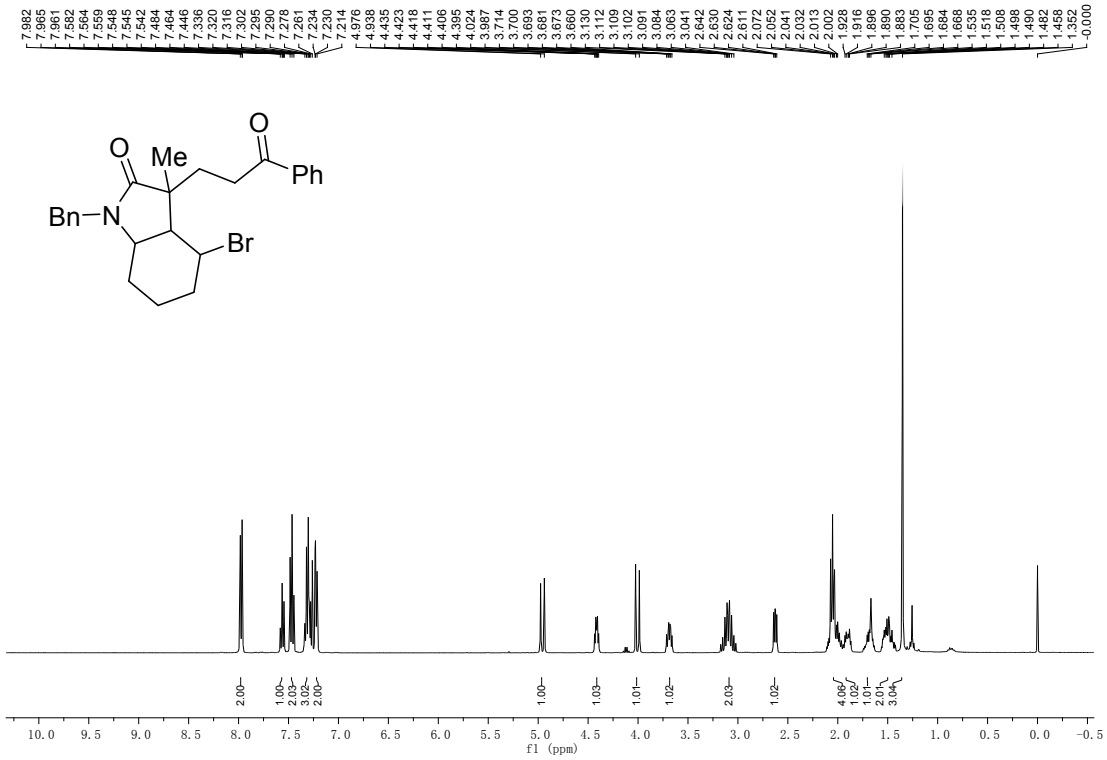
^{1}H NMR of **3ka** in $CDCl_3$



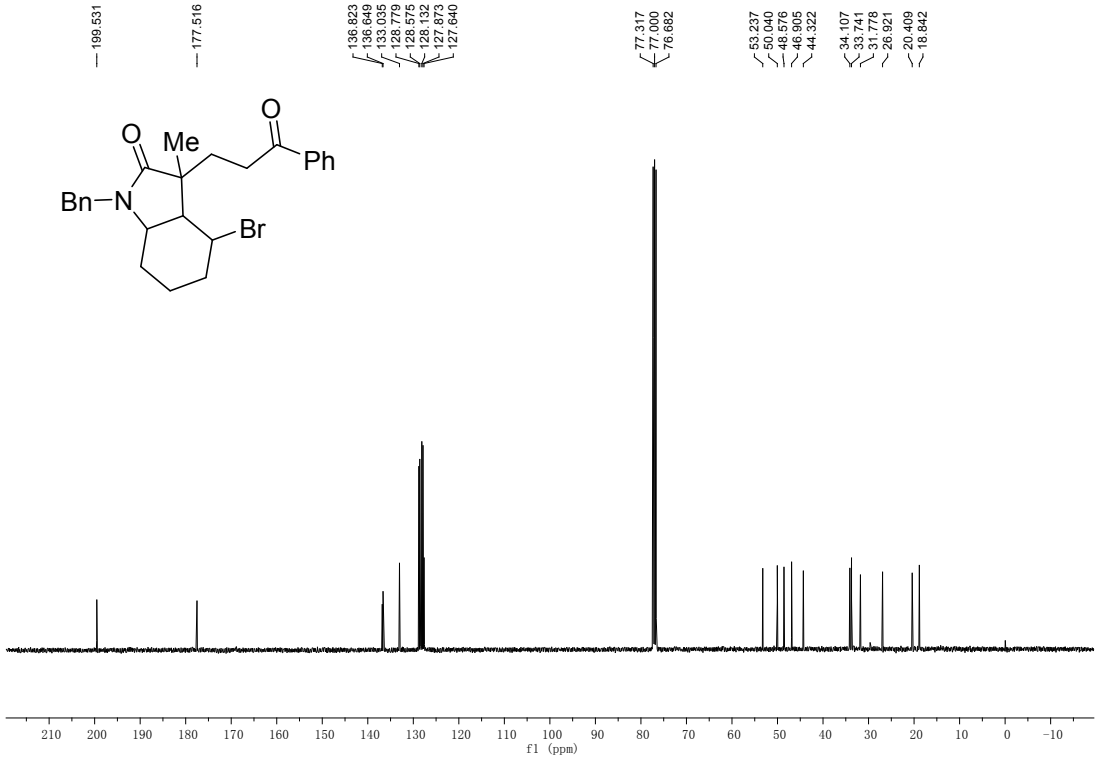
^{13}C NMR of **3ka** in $CDCl_3$



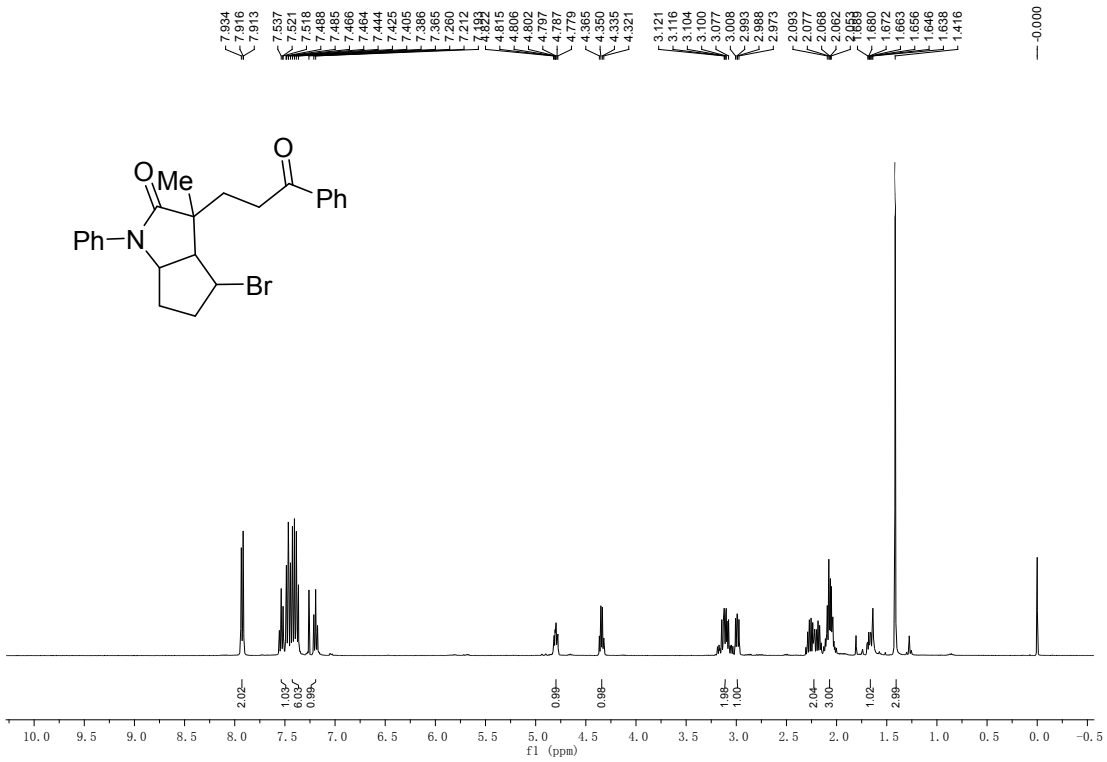
^{1}H NMR of **3la** in $CDCl_3$



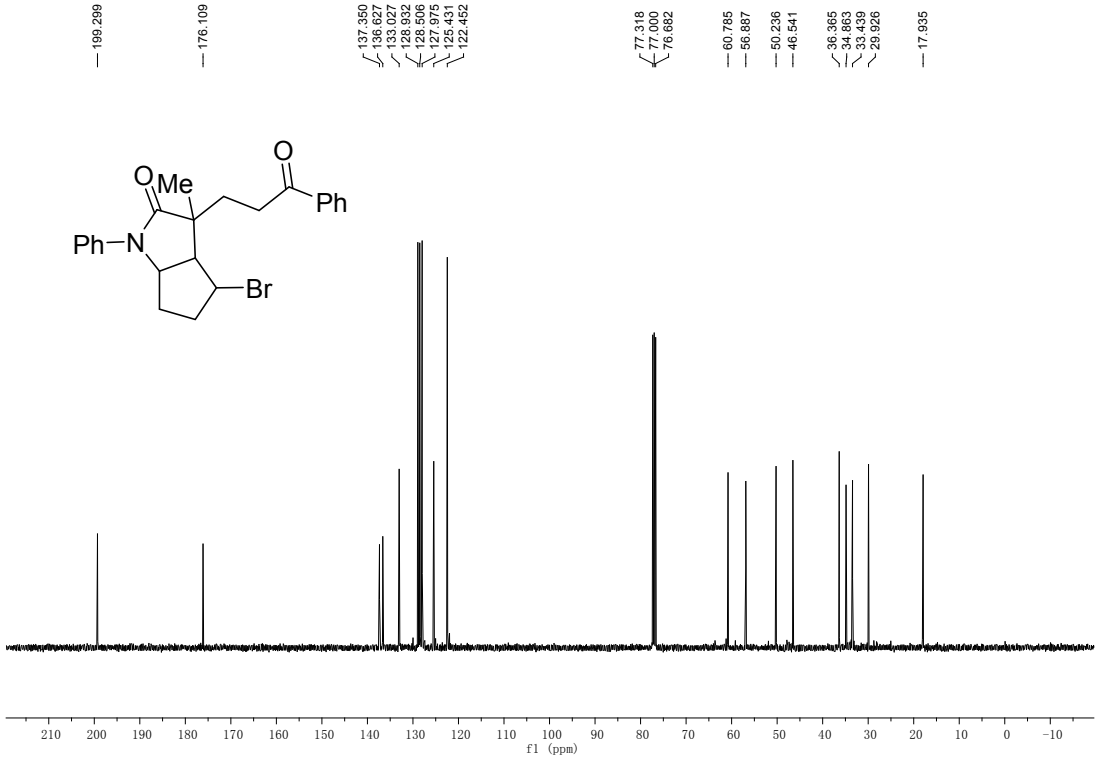
^{13}C NMR of **3la** in $CDCl_3$



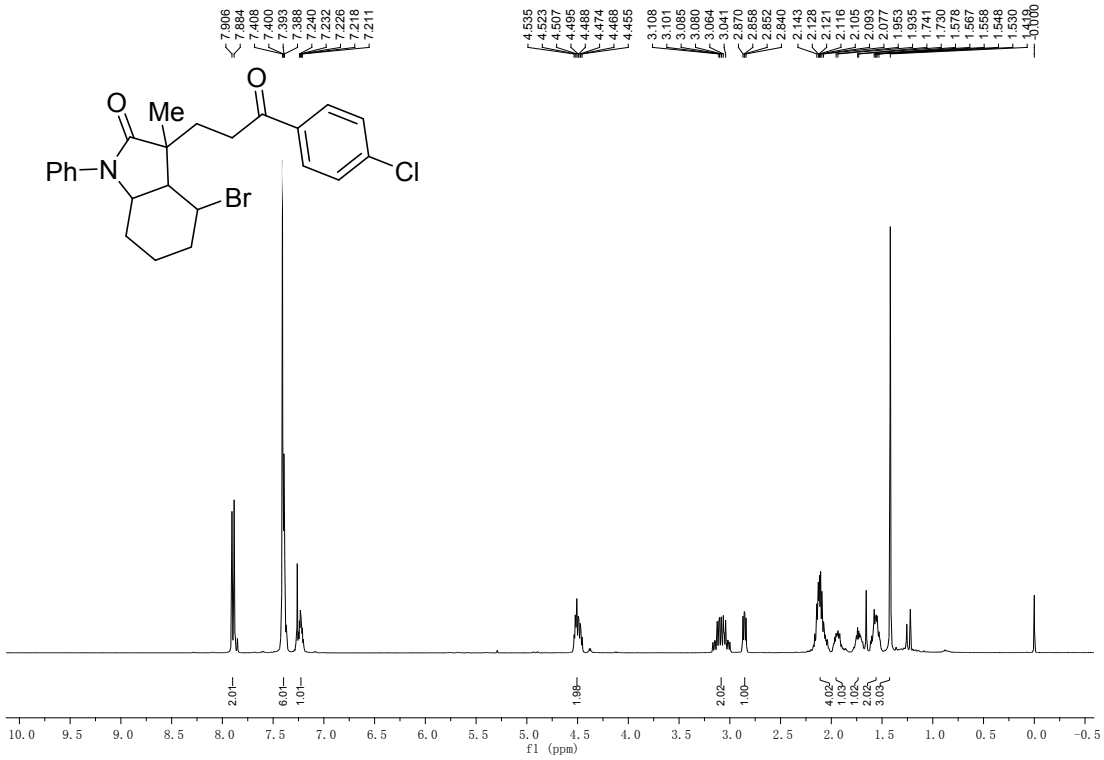
^{1}H NMR of **3ma** in $CDCl_3$



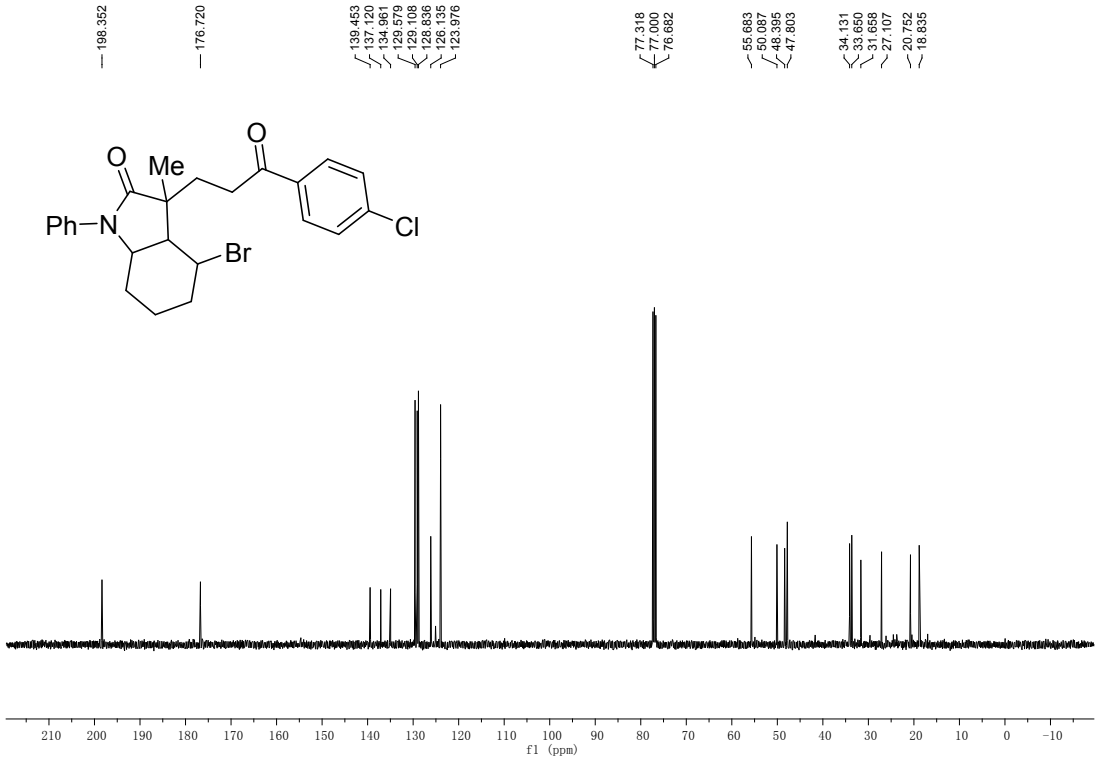
^{13}C NMR of **3ma** in $CDCl_3$



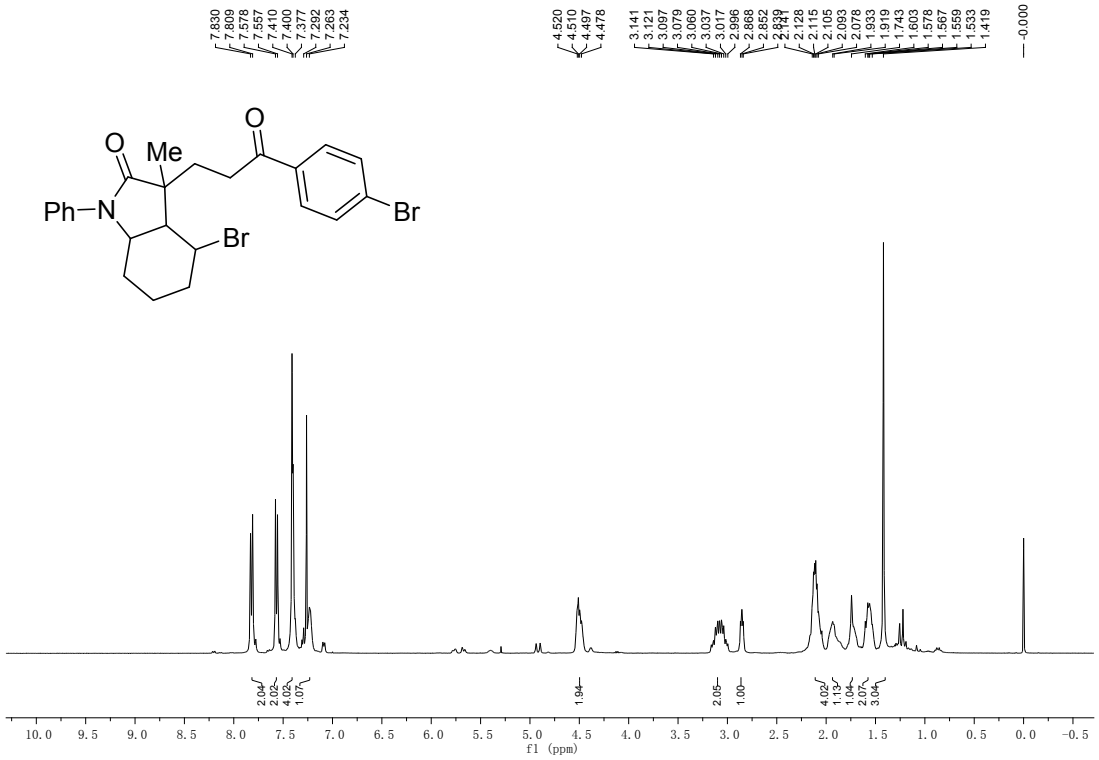
^{1}H NMR of **3ab** in $CDCl_3$



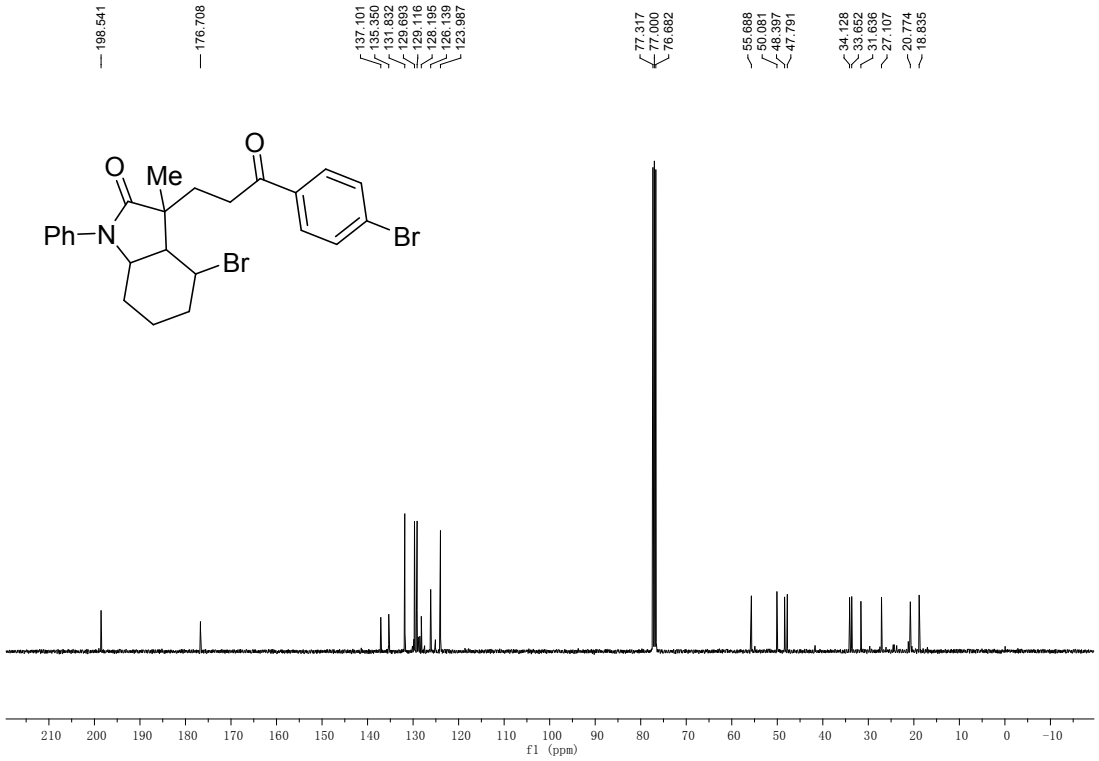
^{13}C NMR of **3ab** in $CDCl_3$



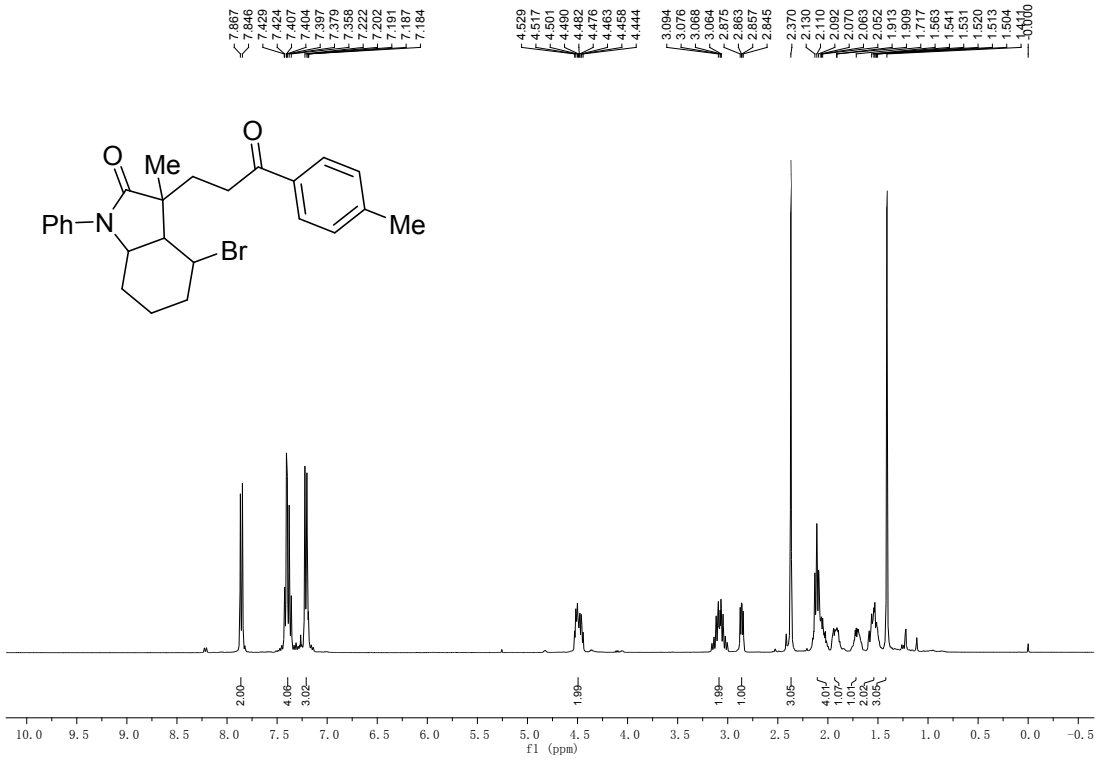
^{1}H NMR of **3ac** in $CDCl_3$



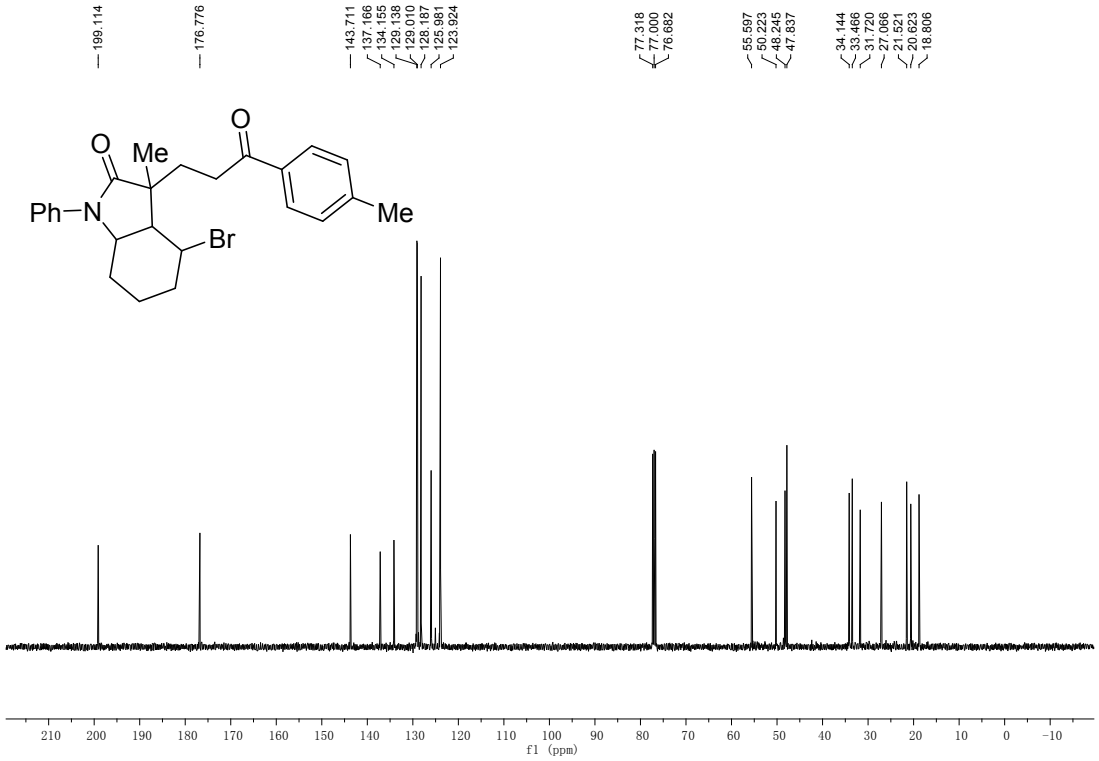
^{13}C NMR of **3ac** in $CDCl_3$



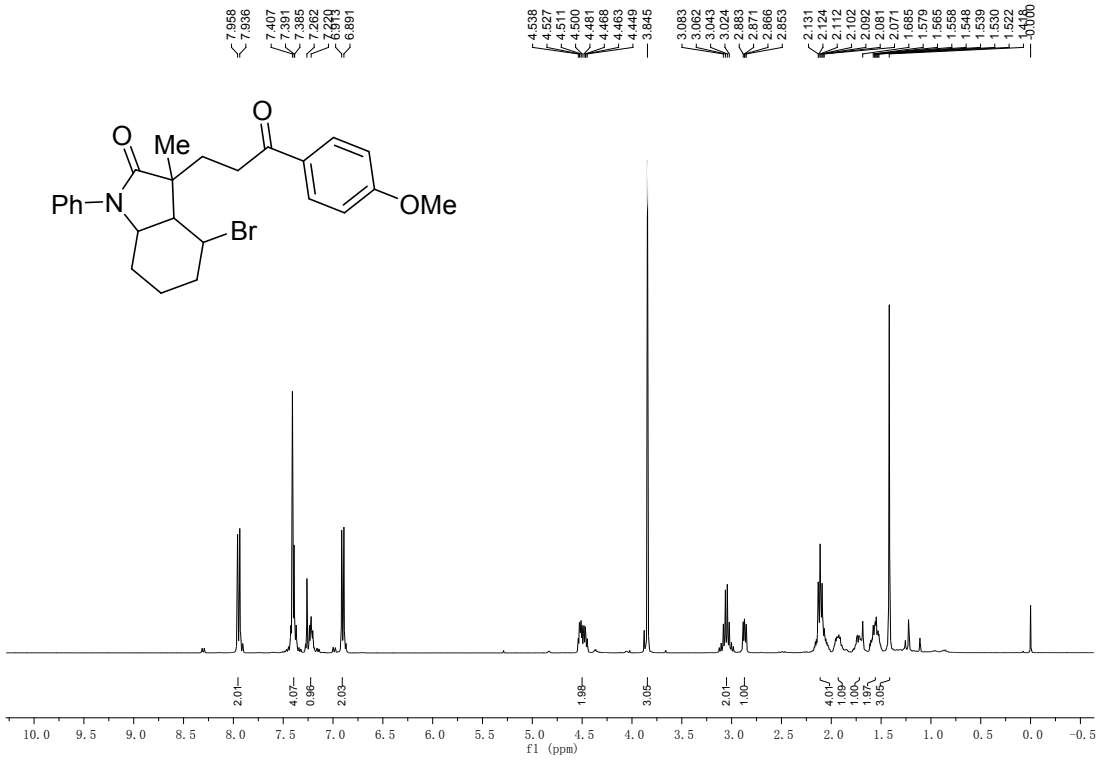
^{1}H NMR of **3ad** in $CDCl_3$



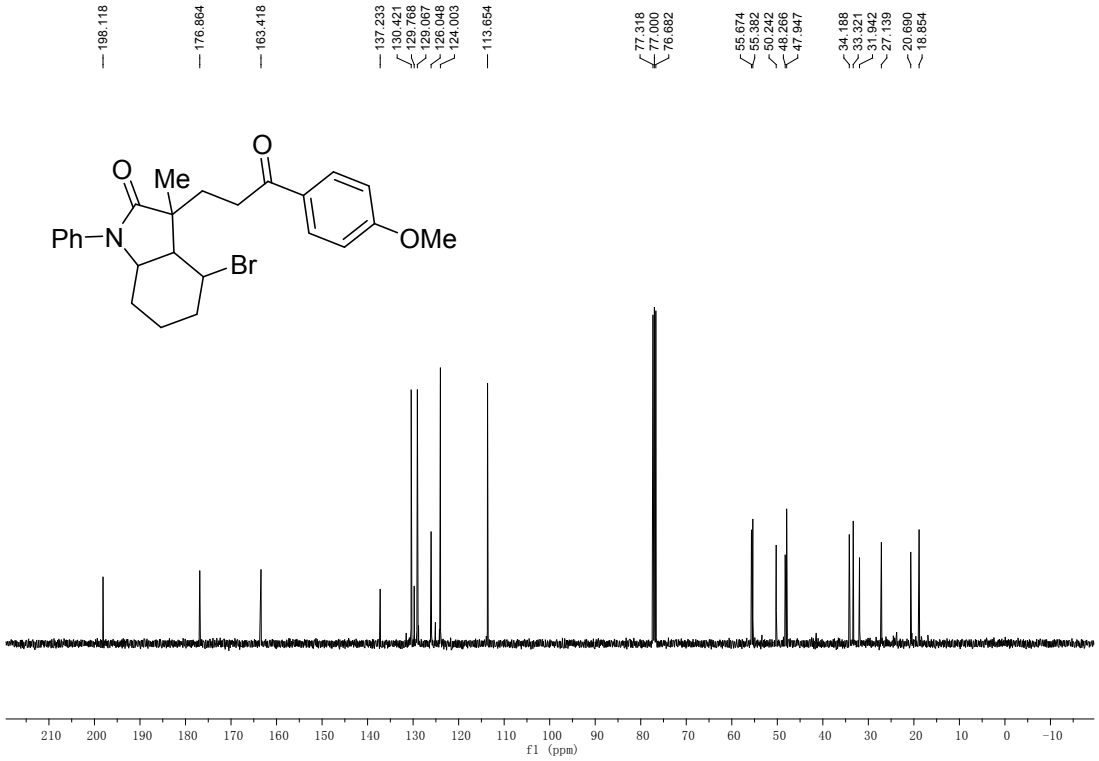
^{13}C NMR of **3ad** in $CDCl_3$



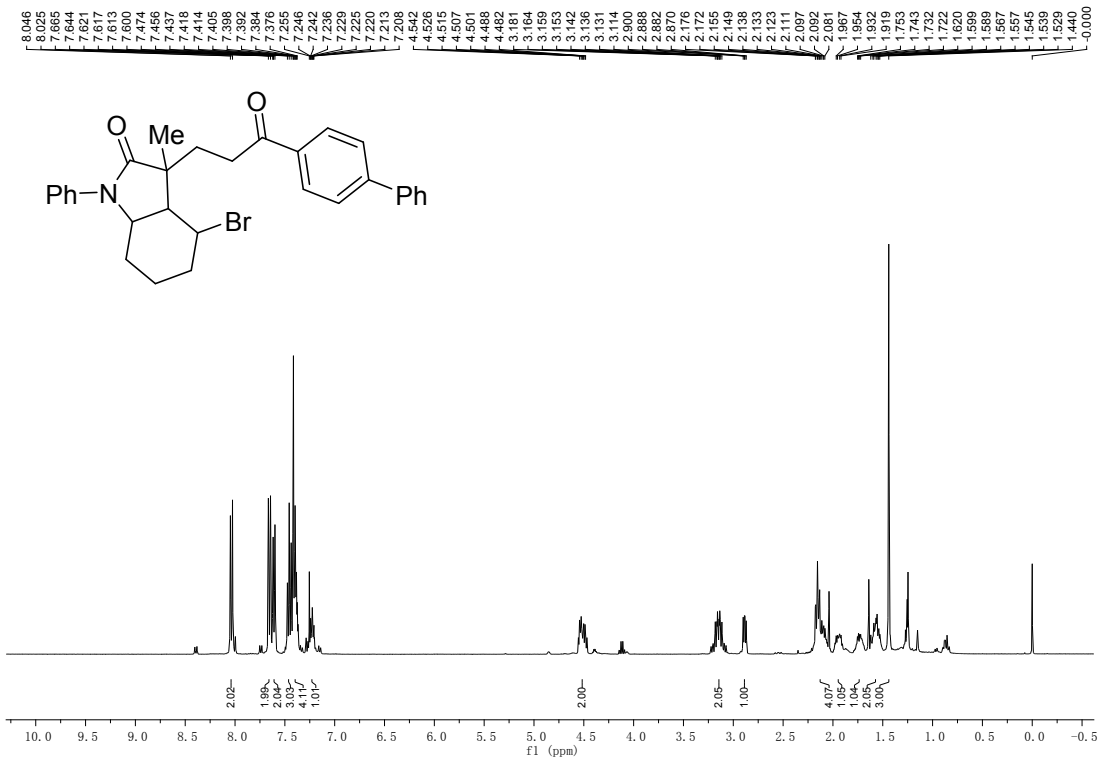
^{1}H NMR of **3ae** in $CDCl_3$



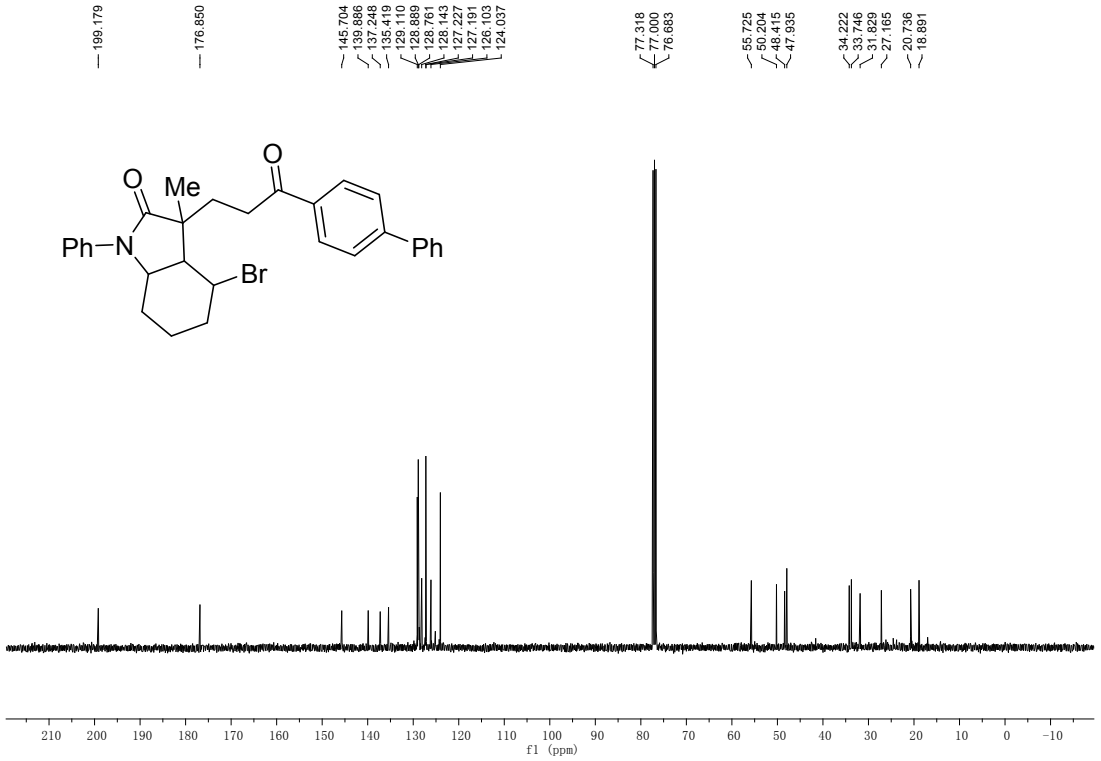
^{13}C NMR of **3ae** in $CDCl_3$



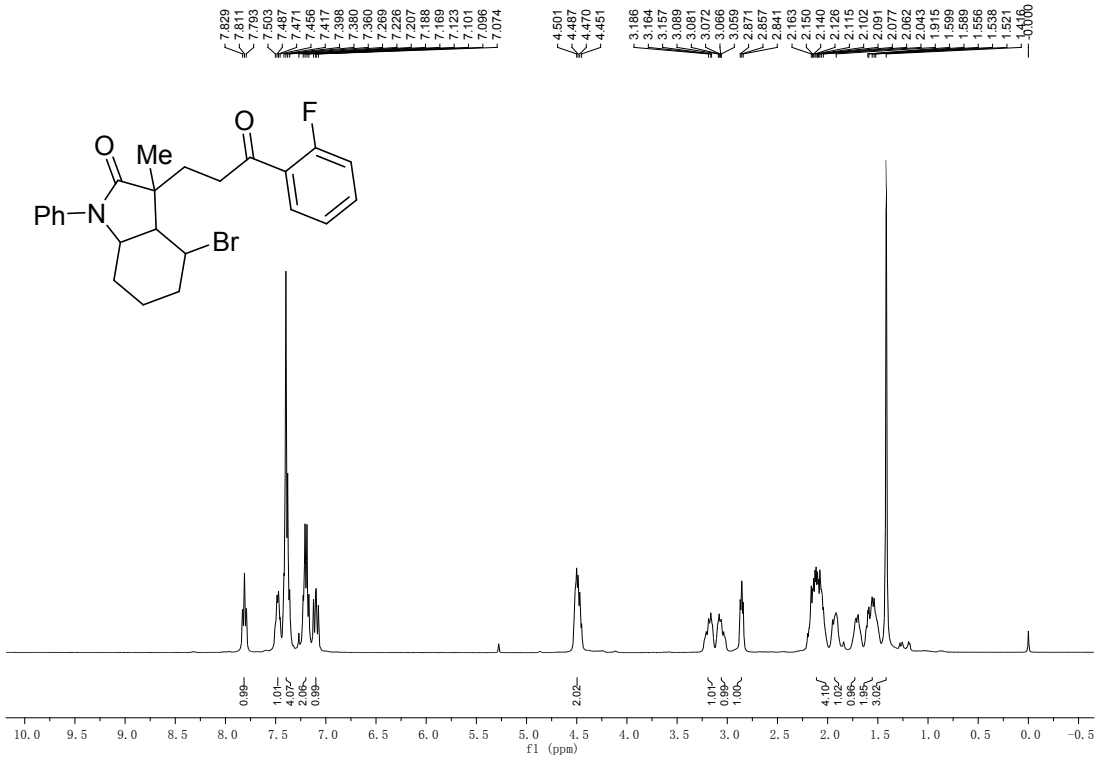
^{1}H NMR of **3af** in $CDCl_3$



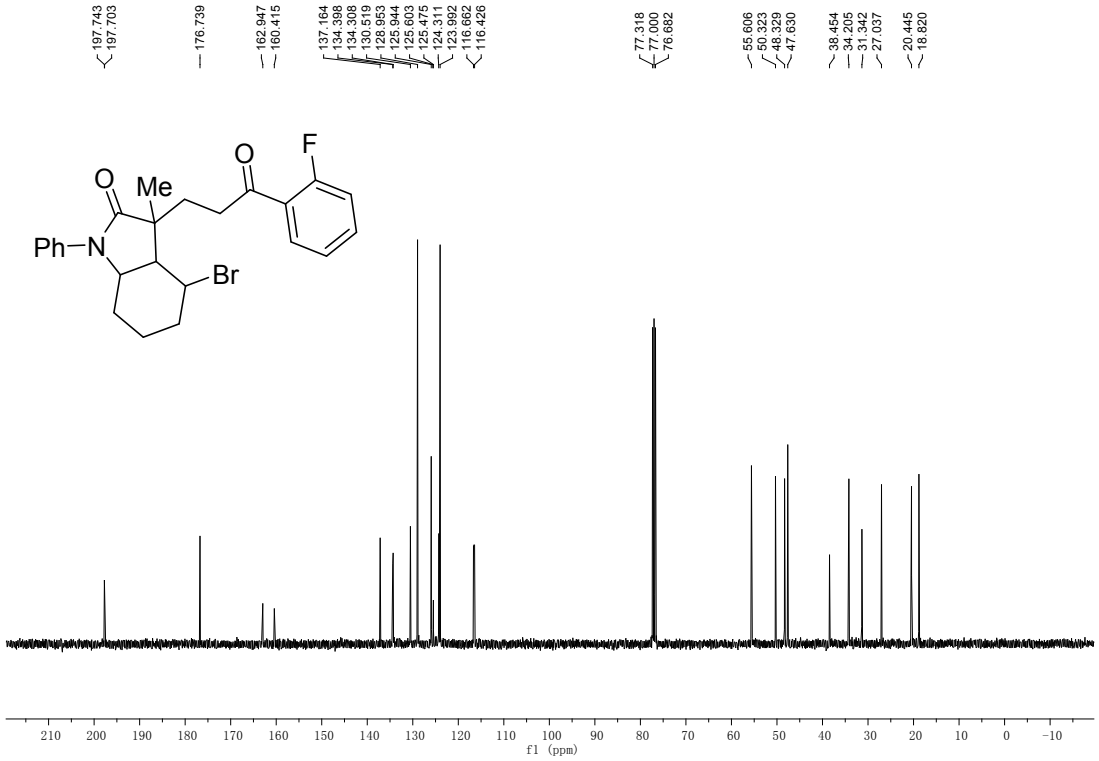
^{13}C NMR of **3af** in $CDCl_3$



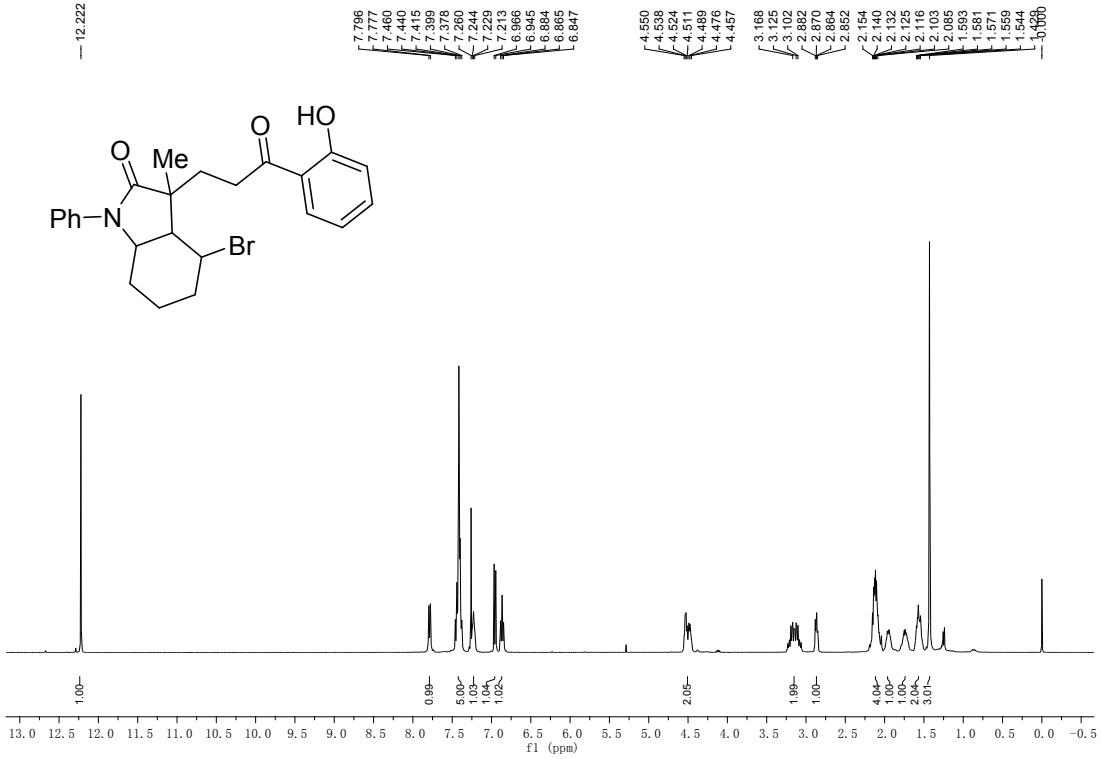
^{1}H NMR of **3ag** in $CDCl_3$



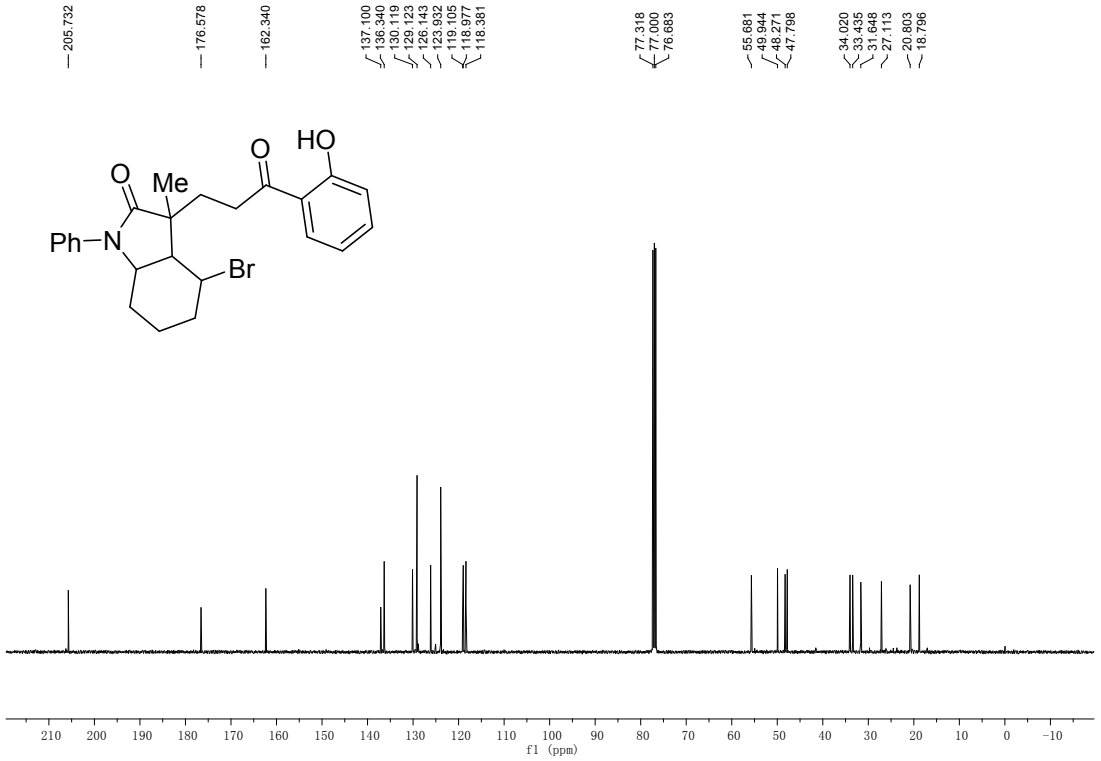
^{13}C NMR of **3ag** in $CDCl_3$



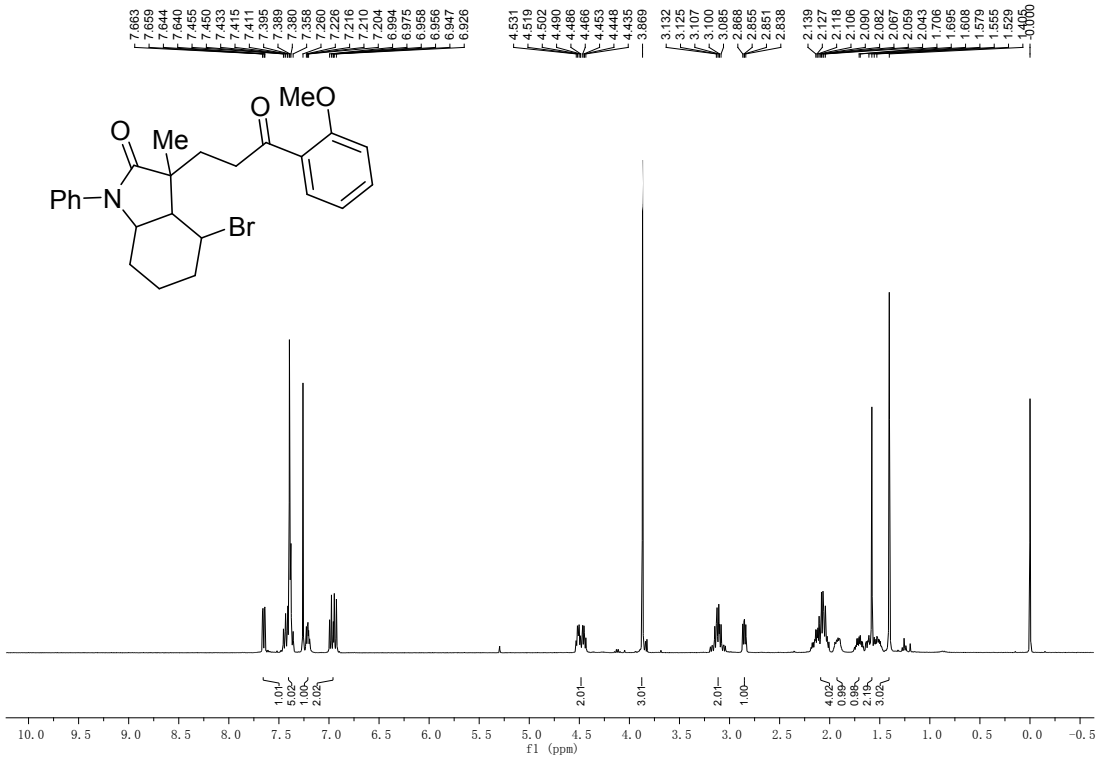
^{1}H NMR of **3ah** in $CDCl_3$



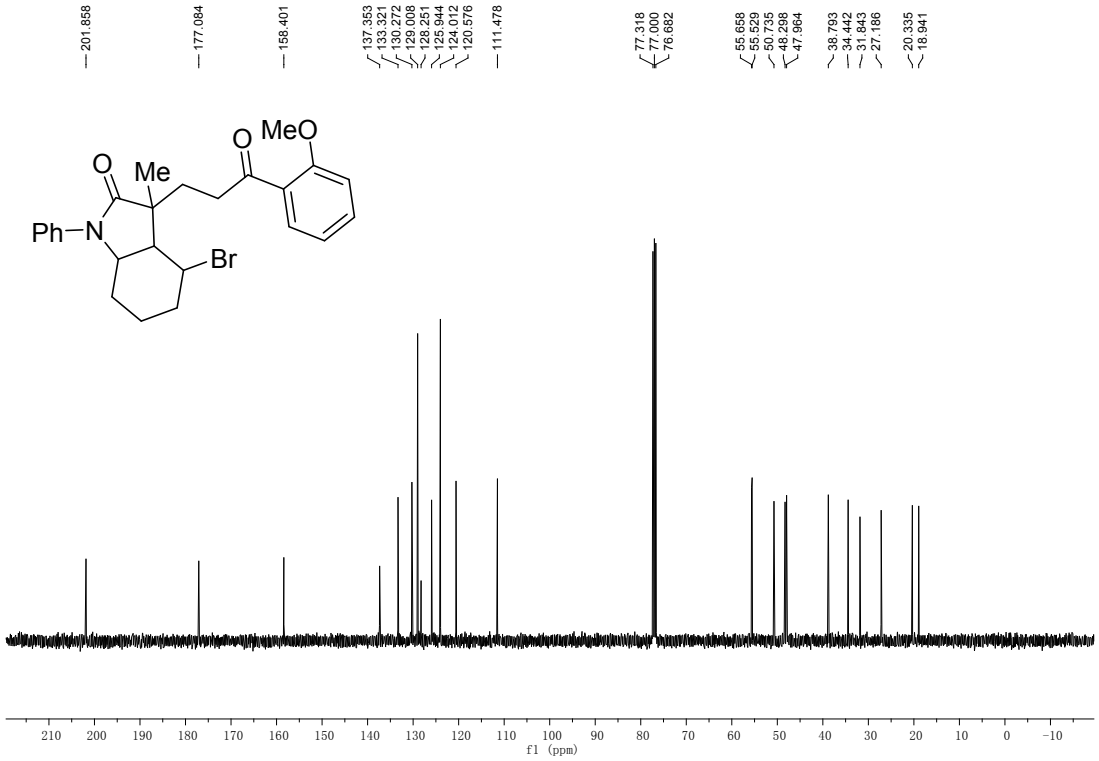
^{13}C NMR of **3ah** in $CDCl_3$



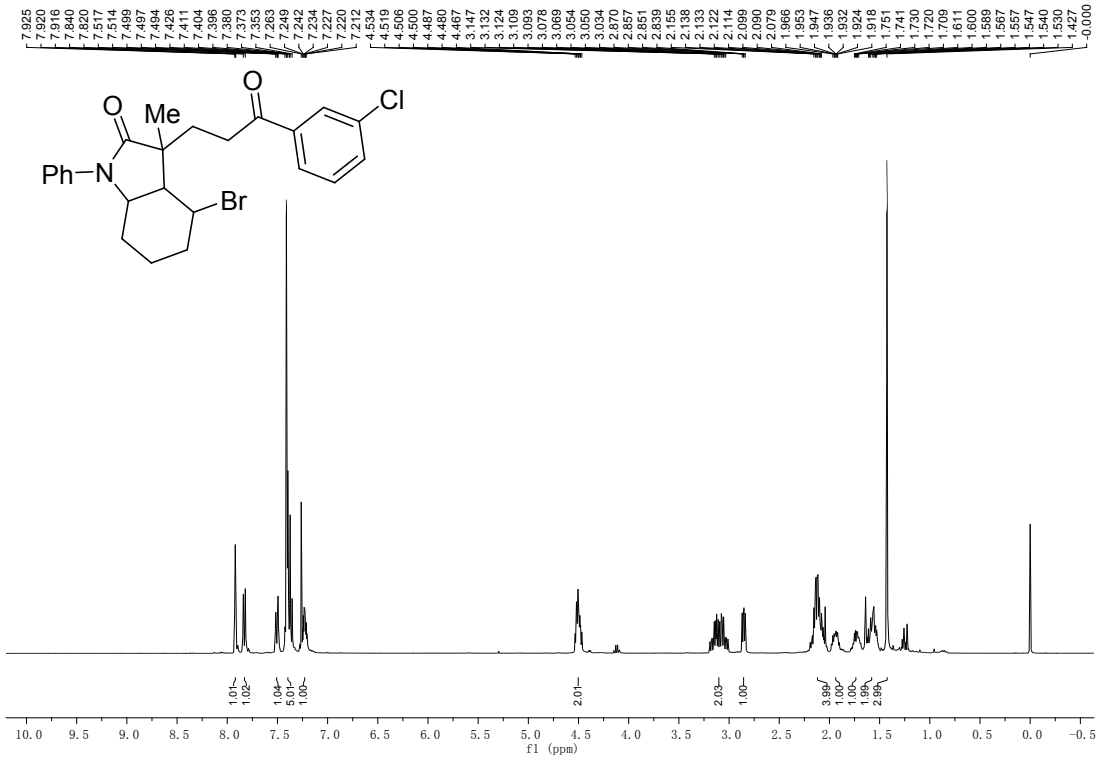
^{1}H NMR of **3ai** in $CDCl_3$



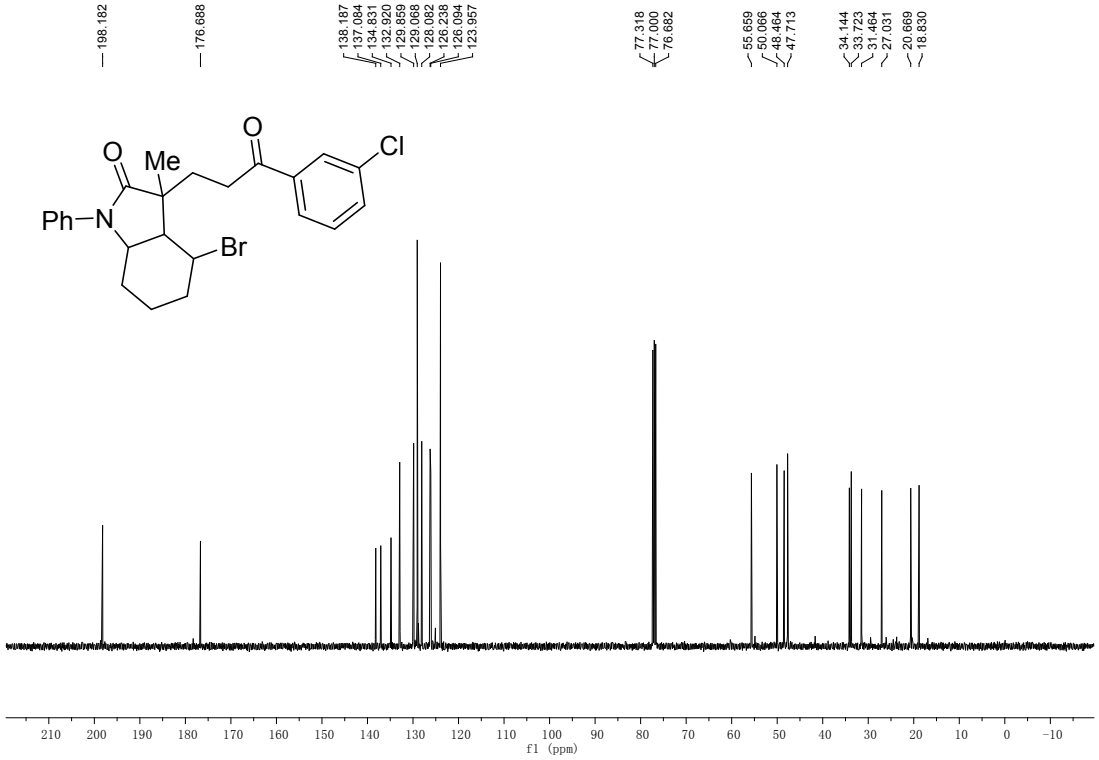
^{13}C NMR of **3ai** in $CDCl_3$



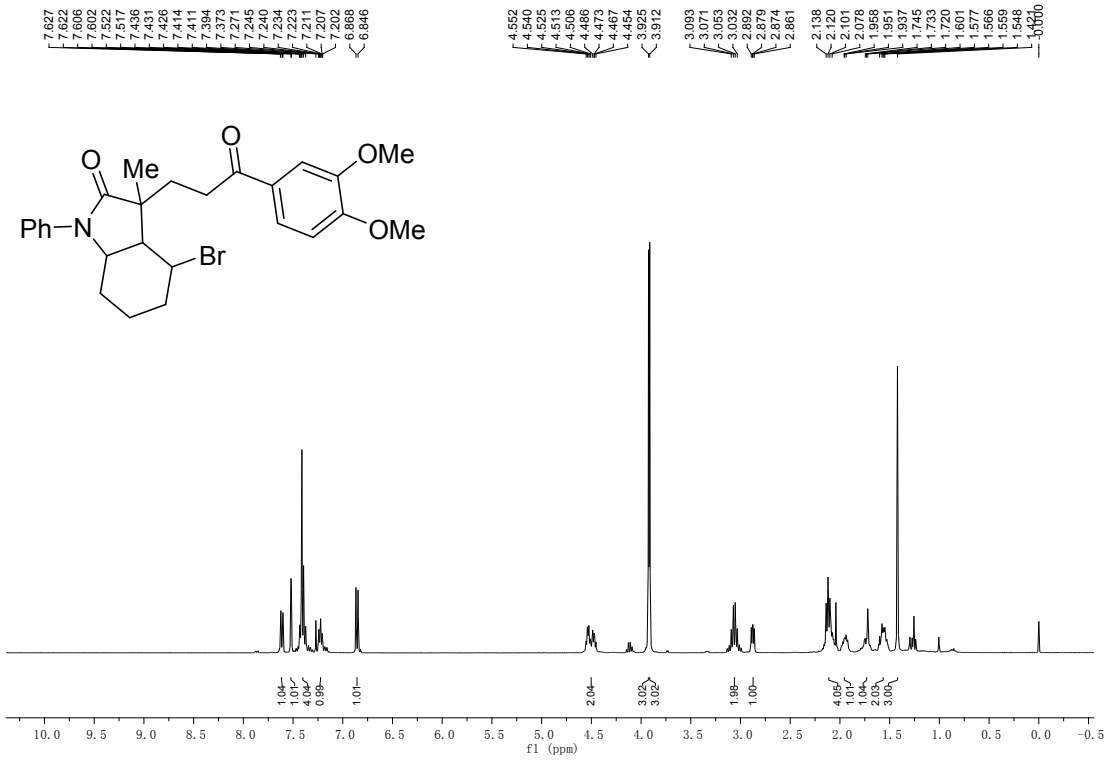
^{1}H NMR of **3aj** in $CDCl_3$



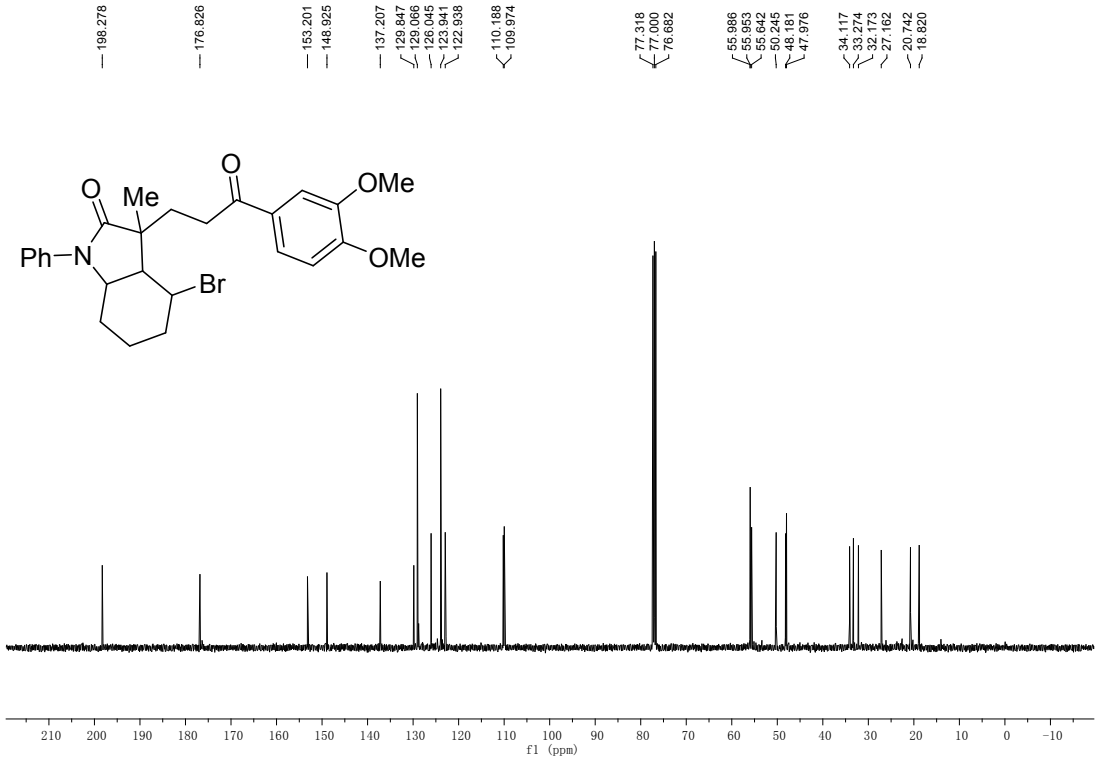
^{13}C NMR of **3aj** in $CDCl_3$



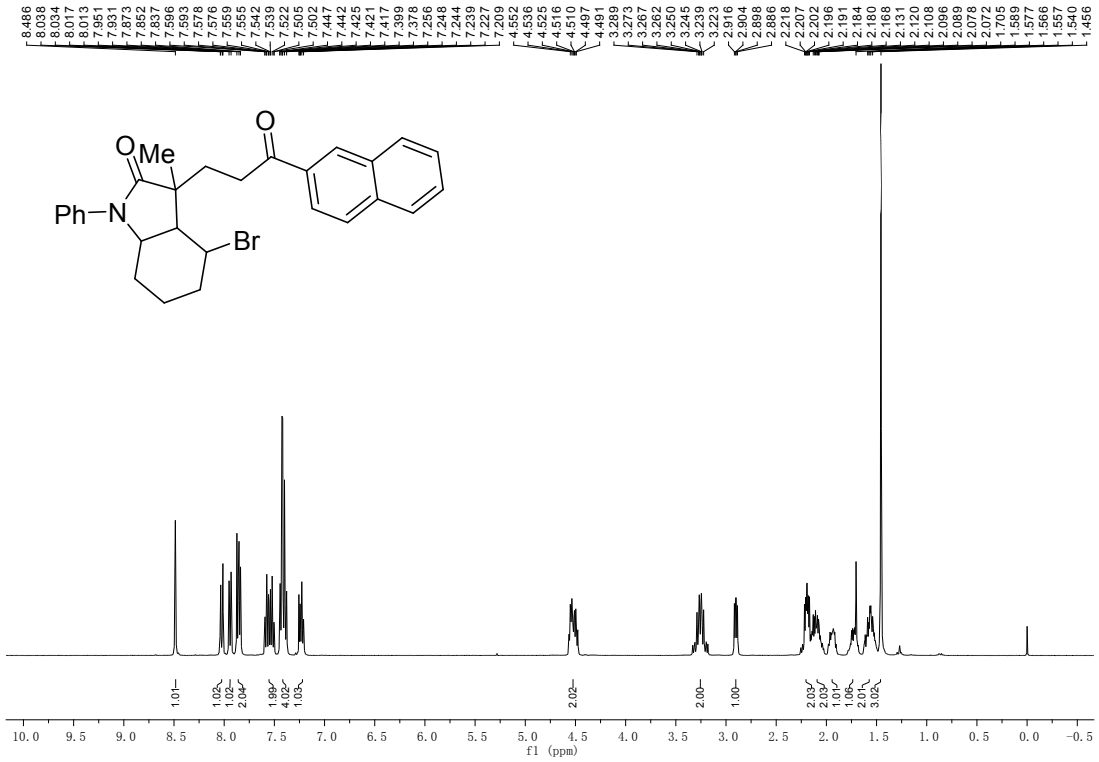
^{1}H NMR of **3ak** in $CDCl_3$



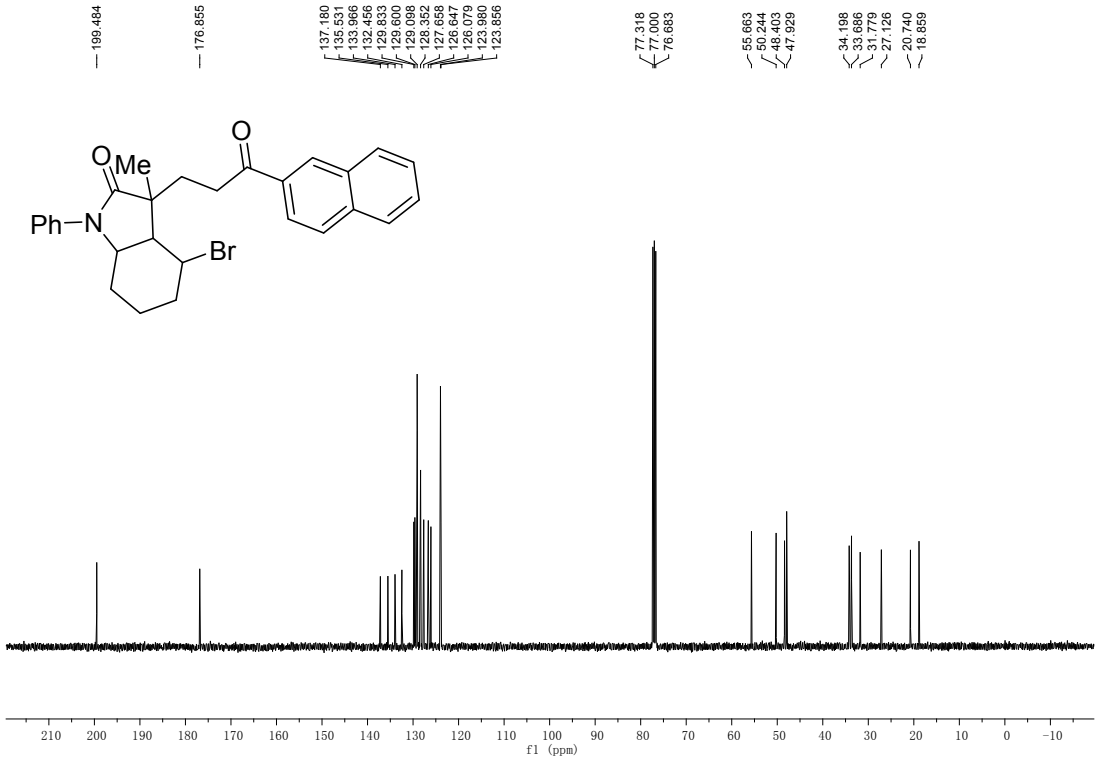
^{13}C NMR of **3ak** in $CDCl_3$



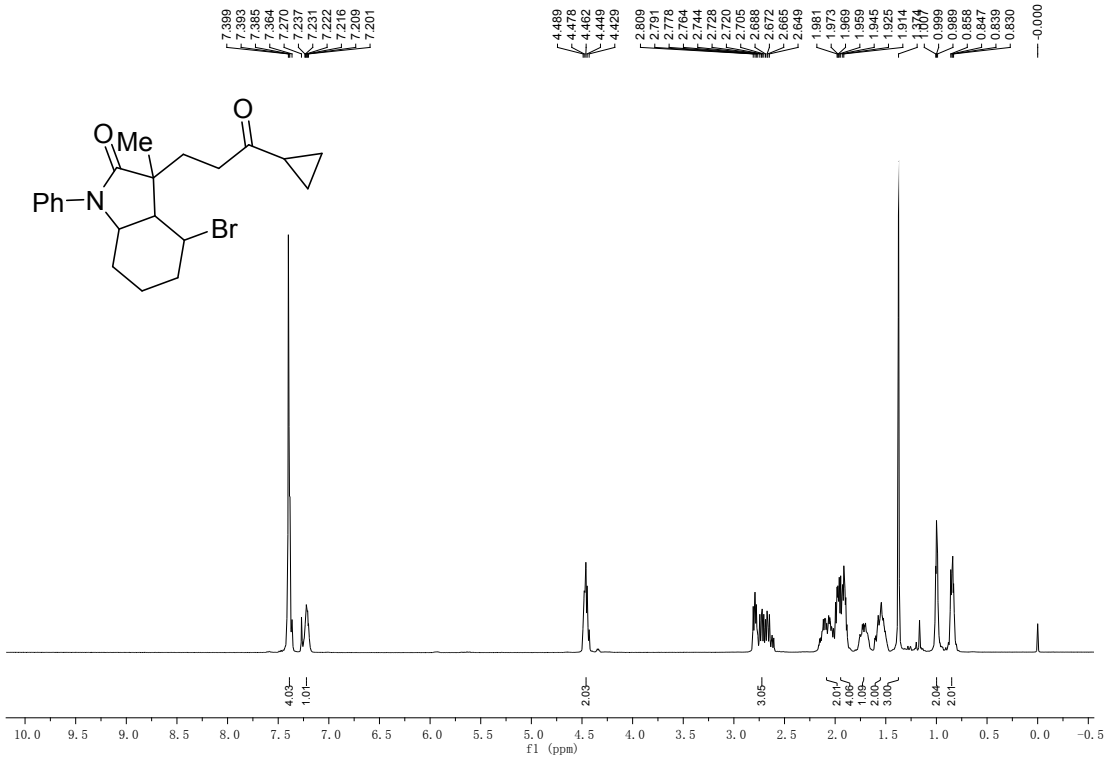
^{1}H NMR of **3al** in $CDCl_3$



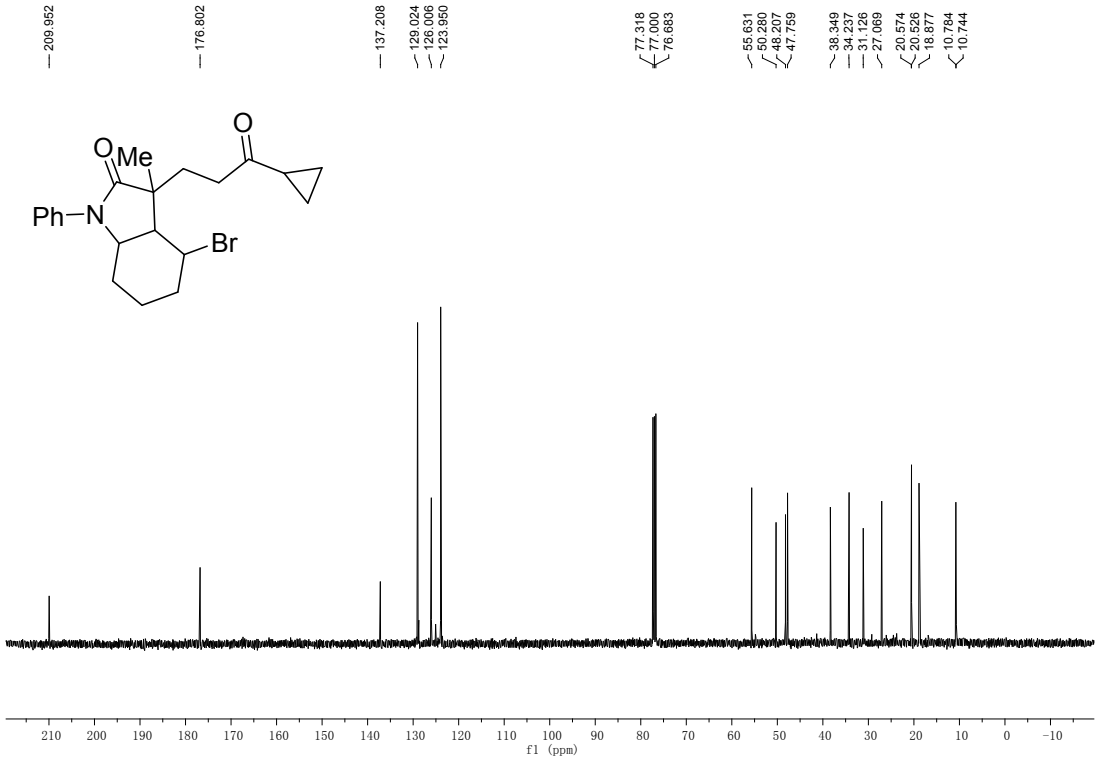
^{13}C NMR of **3al** in $CDCl_3$



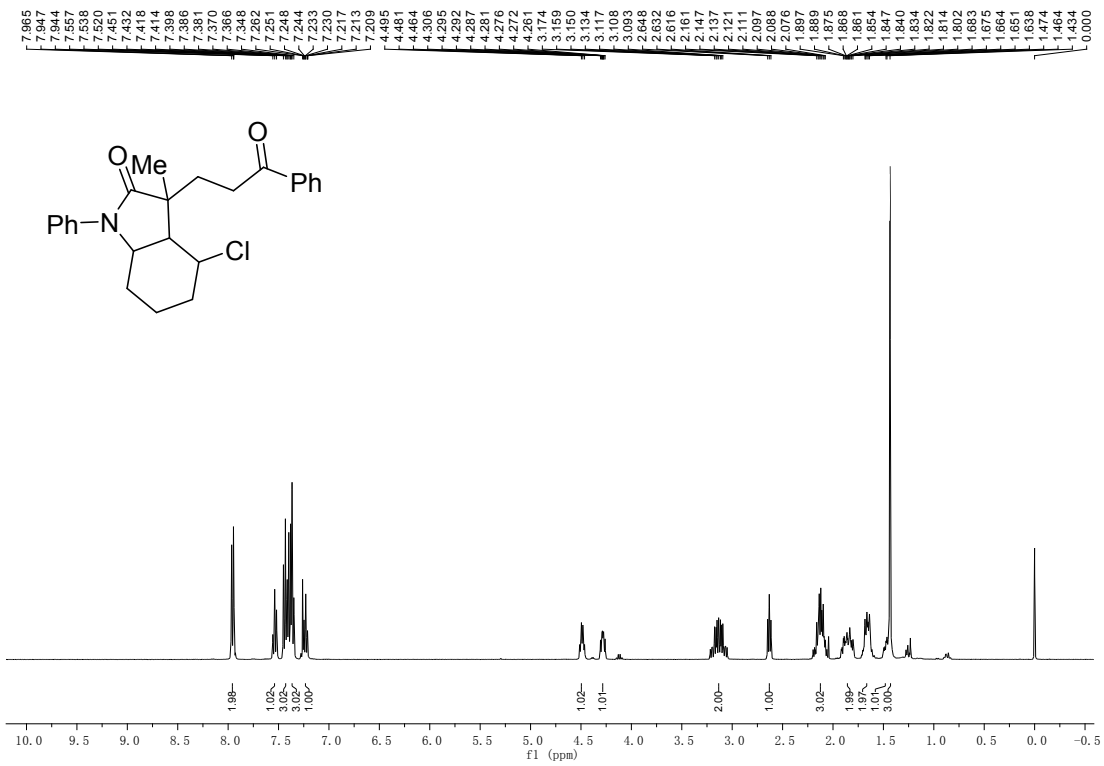
^{1}H NMR of **3am** in $CDCl_3$



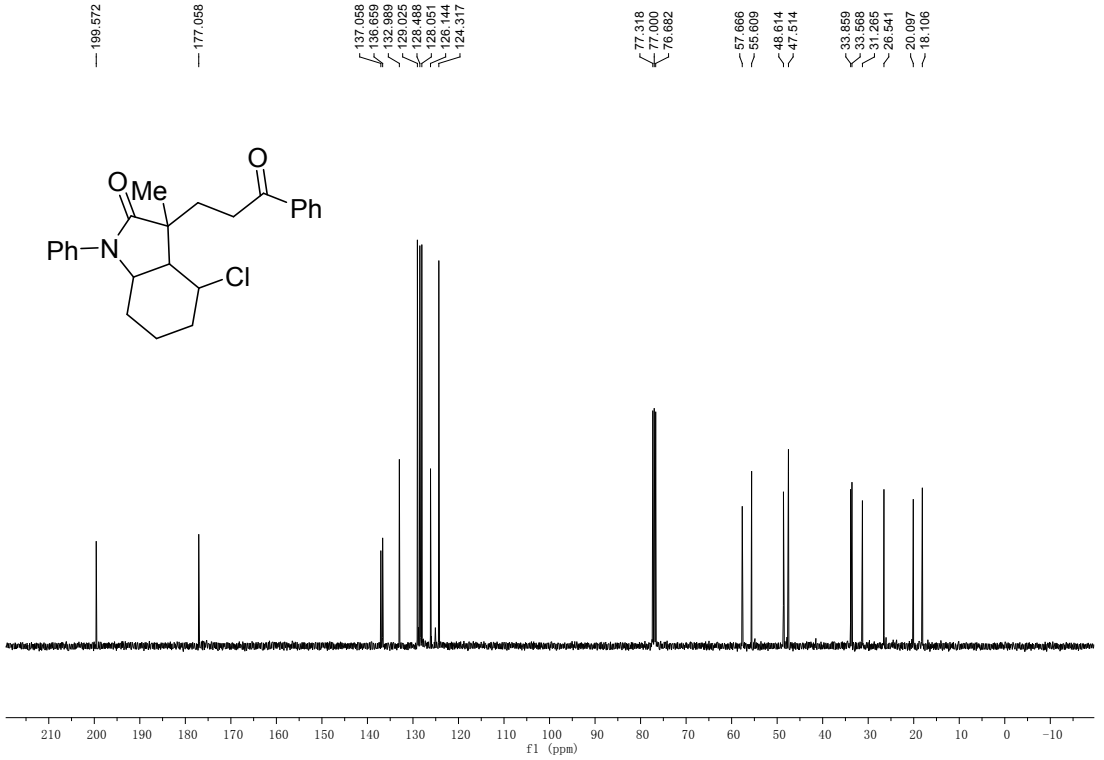
^{13}C NMR of **3am** in $CDCl_3$



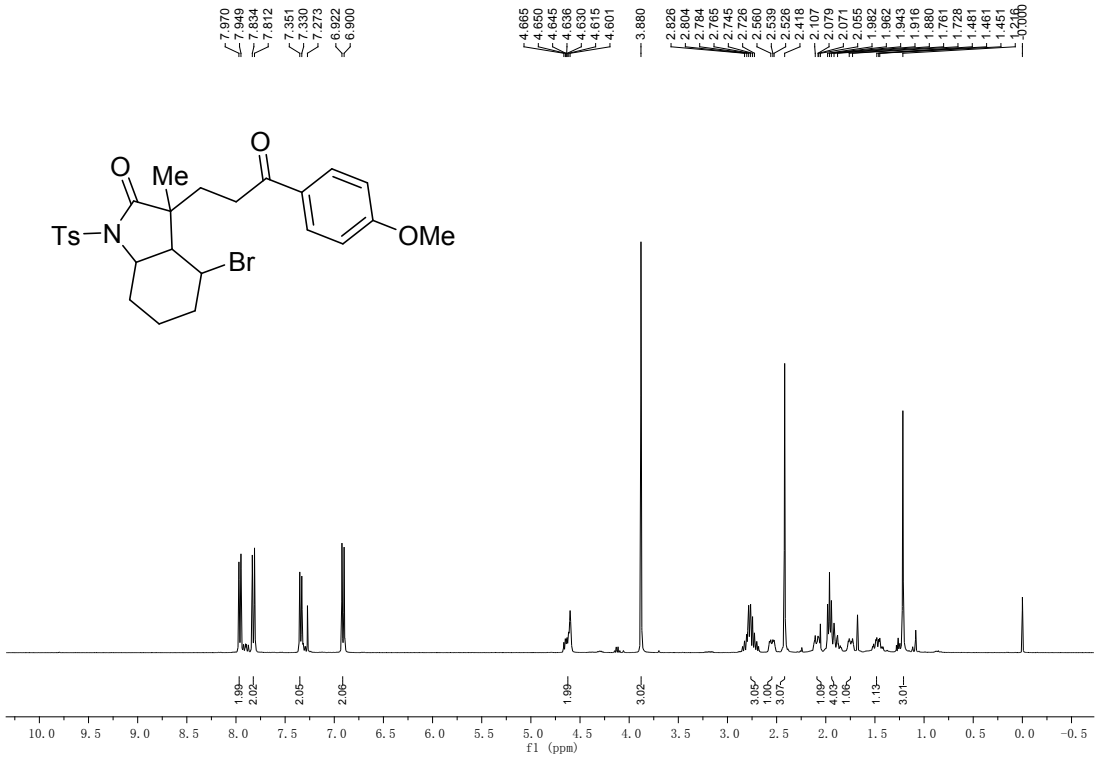
^{1}H NMR of **3an** in $CDCl_3$



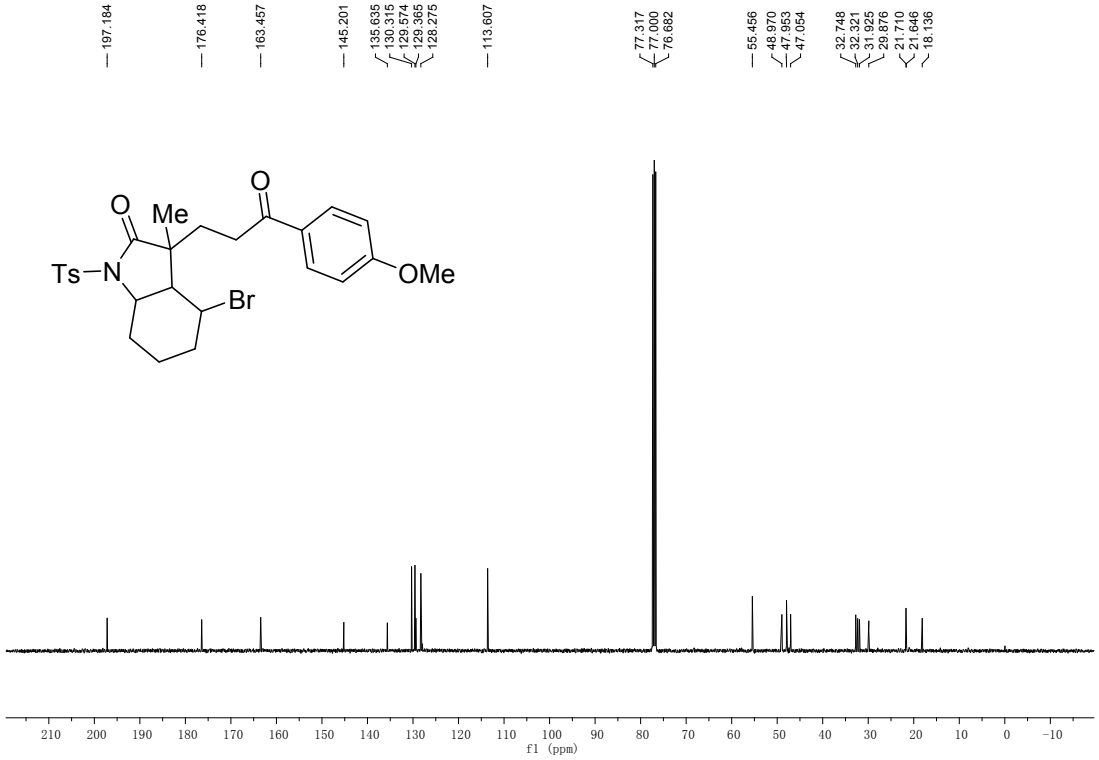
^{13}C NMR of **3an** in $CDCl_3$



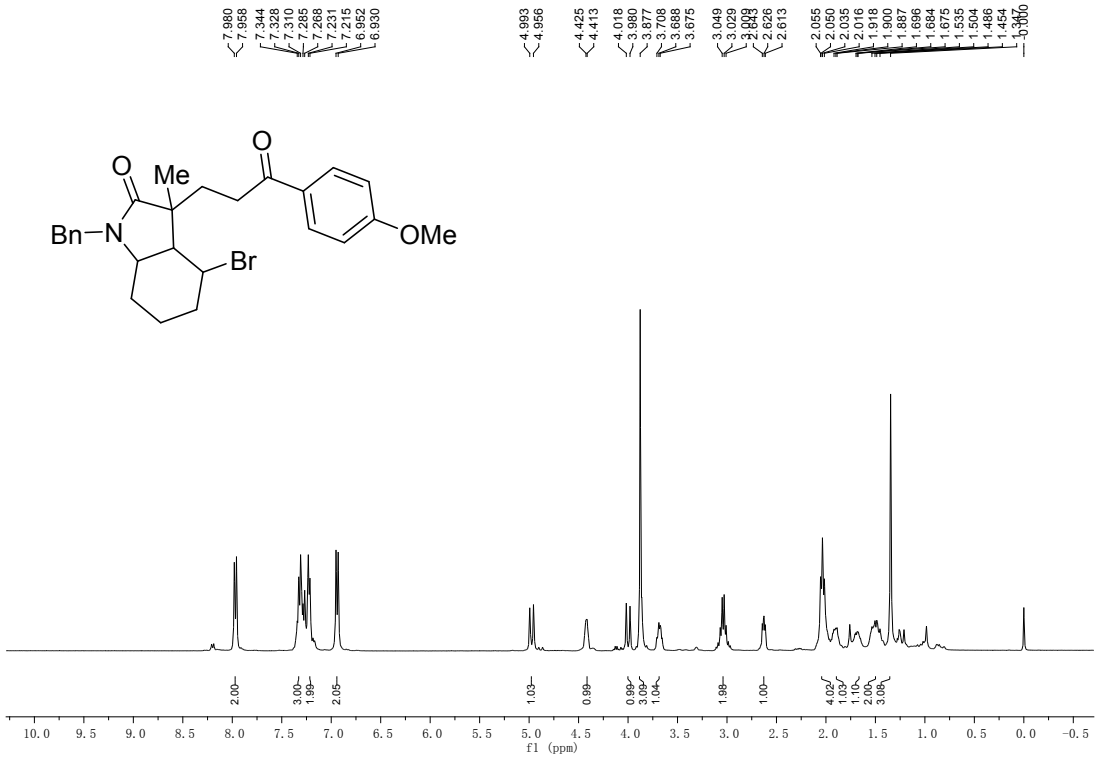
^{1}H NMR of **3ke** in $CDCl_3$



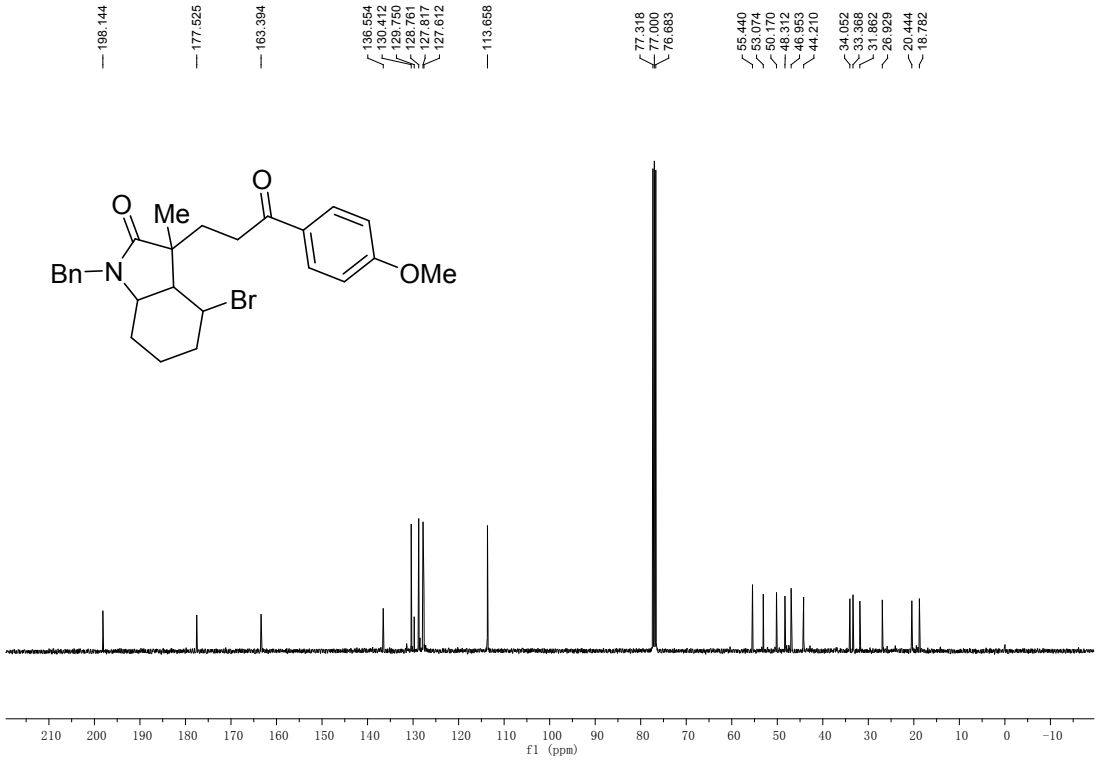
^{13}C NMR of **3ke** in $CDCl_3$



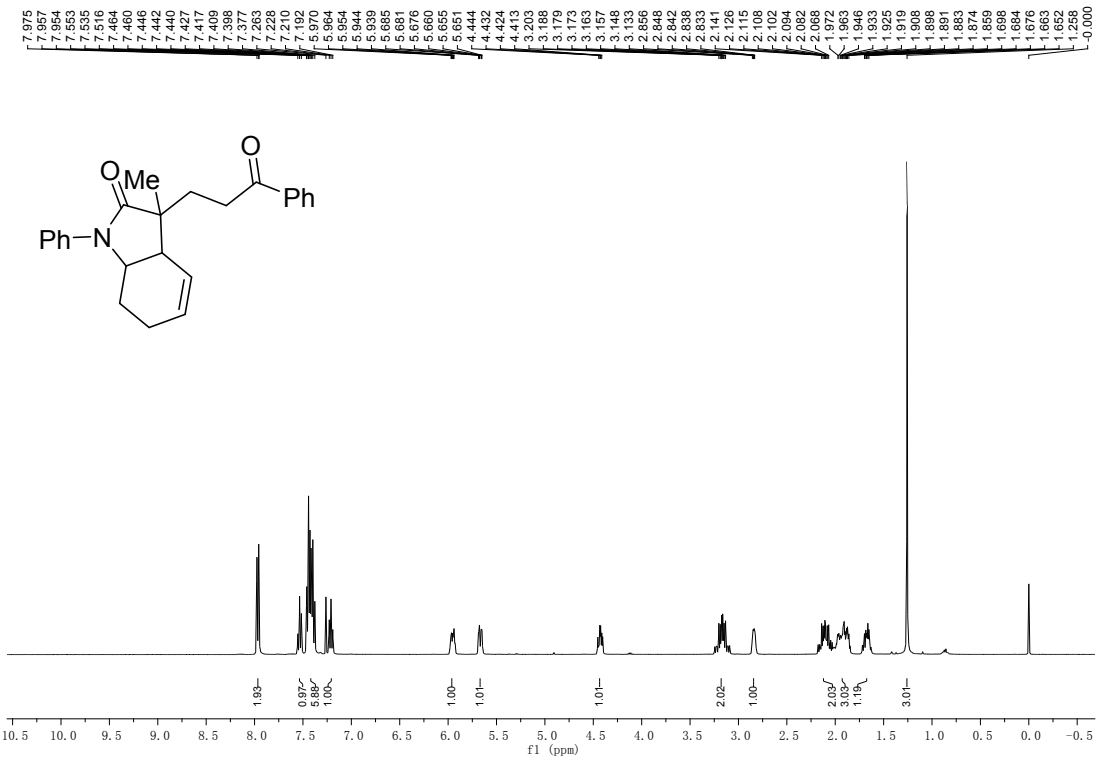
^{1}H NMR of **3le** in $CDCl_3$



^{13}C NMR of **3le** in $CDCl_3$



^{1}H NMR of **4aa** in $CDCl_3$



^{13}C NMR of **4aa** in $CDCl_3$