Supporting Information

Visible-light-induced radical-cascade alkylation/cyclization of acrylamides: Access to 3,3-dialkylated oxindoles

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1 Experimental section

1.1 General information

All chemicals were commercially available and used as received without further. Column chromatography was performed using 300-400 mesh silica. Nuclear magnetic resonance spectra were recorded on Bruker Avance 400 MHz and 500 MHz spectrometer. ^{1}H NMR spectra are recorded in parts per million from tetramethylsilane. ^{13}C NMR spectra were recorded in parts per million from tetramethylsilane. ^{19}F NMR spectra were recorded in parts per million with fluorobenzene as external standard. High resolution mass spectra (HR MS) were performed using an Agilent 6546 LC/Q-TOF mass spectrometer. IR spectra were recorded on WQF-510 Fourier transform infrared spectrophotometer. Melting points were measured on an XT4A microscopic apparatus uncorrected. Photochemical reaction was carried out under visible light irradiation by a blue LED at 25 °C. RLH-18 8-position Photo Reaction System manufactured by Beijing Roger Tech Ltd. was used in this system.

1.2 The spectrum of our lamp and the visible-light irradiation instrument

Photochemical reaction was carried out under visible light irradiation by a blue LED at 25 °C. RLH-18 8-position Photo Reaction System manufactured by Beijing Roger Tech Ltd. was used in this system. Eight 10 W blue LEDs were equipped in this Photo reactor. The blue LED's energy peak wavelength is 460 nm, peak width at half-height is 25.0 nm, irradiance@10 W is 307.51 mW/cm^2. The reaction vessel is a borosilicate glass test tube and the distance between it and the lamp is 15 mm, no filter applied.

1.3 Optimization of reaction conditions

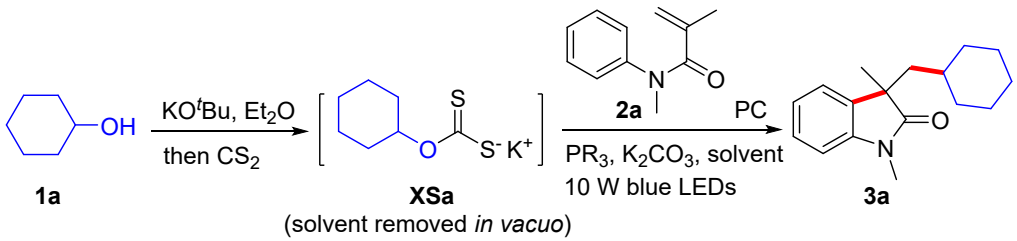


Table S1 The molar ratio of substrates

Entry	The molar ratio of **1a**:**2a**	Yield (%)
1	1 : 1	73
2	1.5 : 1	79
3	2 : 1	83
4	2.5:1	83
5	3:1	82

[a] Reaction conditions: cyclohexanol **1a** (0.3 mmol, 30 mg), *t*-BuOK (0.32 mmol, 35.3 mg), Et_2O (3.0 mL), CS_2 (1.5 mmol, 114 mg), 3.0 h. After removing the solvent in vacuo, then *N*-methyl-*N*-phenylmethacrylamide **2a** (0.15 mmol, 26.3 mg), PCy_3 (0.3 mmol, 84 mg), K_2CO_3 (0.3 mmol, 41.4 mg), *fac*-Ir(ppy)$_3$ (0.003 mmol, 2.3 mg), DMF (3.0 mL) 10 W blue LEDs irradiation for 36 h under air. [b] Isolated yield.

Table S2 The screen of various bases

Entry	Base	Yield (%)
1	K_2CO_3	83
2	K_3PO_4	69
3	Na_2CO_3	80
4	Cs_2CO_3	73
5	DBU	39
6	KO^tBu	0

[a] Reaction conditions: cyclohexanol **1a** (0.3 mmol, 30 mg), *t*-BuOK (0.32 mmol, 35.3 mg), Et_2O (3.0 mL), CS_2 (1.5 mmol, 114 mg), 3.0 h. After removing the solvent in vacuo, then *N*-methyl-*N*-phenylmethacrylamide **2a** (0.15 mmol, 26.3 mg), PCy_3 (0.3 mmol, 84 mg), base (0.3 mmol), *fac*-Ir(ppy)$_3$ (0.003 mmol, 2.3 mg), DMF (3.0 mL) 10 W blue LEDs irradiation for 36 h under air. [b] Isolated yield.

Table S3 The amount of base

Entry	K_2CO_3 (equiv.)	Yield (%)
1	1.0	77
2	1.5	88
3	2.0	83
4	2.5	82

[a] Reaction conditions: cyclohexanol **1a** (0.3 mmol, 30 mg), *t*-BuOK (0.32 mmol, 35.3 mg), Et_2O (3.0 mL), CS_2 (1.5 mmol, 114 mg), 3.0 h. After removing the solvent in vacuo, then *N*-methyl-*N*-phenylmethacrylamide **2a** (0.15 mmol, 26.3 mg), PCy_3 (0.3 mmol, 84 mg), K_2CO_3, *fac*-Ir(ppy)$_3$ (0.003 mmol, 2.3 mg), DMF (3.0 mL) 10 W blue LEDs irradiation for 36 h under air. [b] Isolated yield.

Table S4 The amount of PCy_3

Entry	PCy_3 (equiv.)	Yield (%)
1	1 eq	63
2	1.5 eq	76
3	2 eq	88
4	3 eq	71

[a] Reaction conditions: cyclohexanol **1a** (0.3 mmol, 30 mg), *t*-BuOK (0.32 mmol, 35.3 mg), Et_2O (3.0 mL), CS_2 (1.5 mmol, 114 mg), 3.0 h. After removing the solvent in vacuo, then *N*-methyl-*N*-phenylmethacrylamide **2a** (0.15 mmol, 26.3 mg), PCy_3 (0.3 mmol, 84 mg), K_2CO_3 (0.225 mmol, 31 mg), *fac*-Ir(ppy)$_3$ (0.003 mmol, 2.3 mg), DMF (3.0 mL) 10 W blue LEDs irradiation for 36 h under air. [b] Isolated yield.

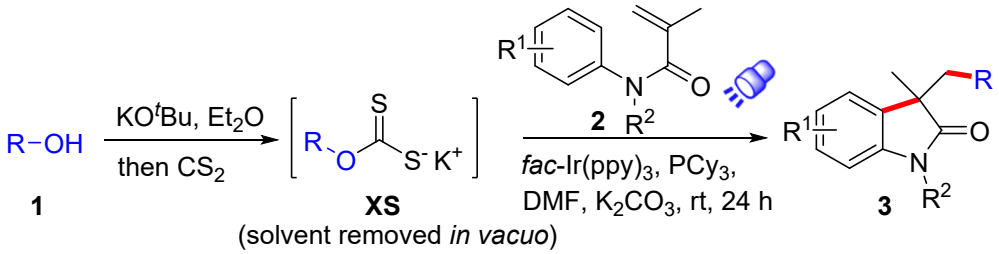
1.4 General procedure for the synthesis of 3-alkyl-1,3-dimethylindolin-2-ones 3

In a N_2-filled glovebox, an oven-dried 10 mL glass vial was charged sequentially with alcohol **1** (0.30 mmol), KO^{t}Bu (0.32 mmol, 35.3 mg), and dry Et_2O (3.0 mL). After being sealed with a septum cap and transferred out of the glovebox, the reaction mixture was stirred at room temperature for 30 minutes, followed by the addition of CS_2 (1.5 mmol, 114 mg) *via* microsyringe at 0 ^oC and continued to be stirred for 3 hours at 0 ^oC before removing the solvent in vacuo.

Then substituted *N*-phenylmethacrylamides **2** (0.15 mmol), PCy_3 (0.3 mmol, 84 mg), *fac*-Ir(ppy)$_3$ (0.003 mmol, 2.3 mg), K_2CO_3 (0.225 mmol, 31 mg), and DMF (3.0 mL) were added the above

reaction system. The reaction mixture was irradiated with a 10 W blue LEDs lamp, maintained at ambient temperature, and stirred for 24 hours under air atmosphere. The solvent was removed in vacuo and the residue was purified by column chromatography to afford the product **3** using ethyl acetate/petroleum ether as eluant.

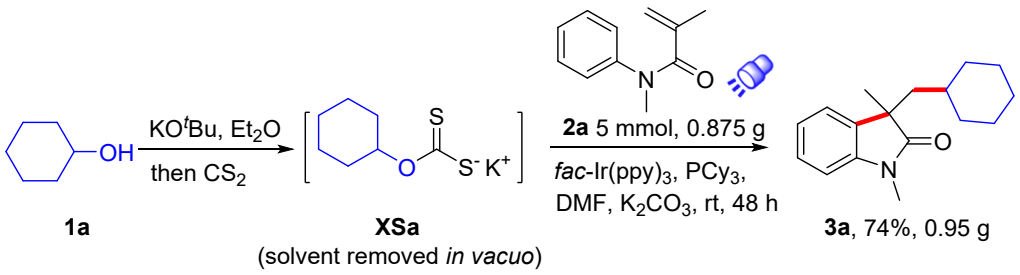
However, this synthetic method has still some limitations under the present conditions. When alcohols containing esters, acids or alkyl halides functional group, such as $Ph(CH_2)_3OH$, $CH_3CH_2OOC(CH_2)_2OH$, $I(CH_2)_3OH$, $Br(CH_2)_3OH$ were used, no reaction occurred. Moreover, four distinct classes of alkyl radical addition and cyclization reactions have also been verified, and the result shows that various alcohols including 3°, 2° and 1° alcohols are tolerated to this reaction, whereas methanol does not.



2 Procedure for gram-scale reaction

In a N_2-filled glovebox, an oven-dried 50 mL glass vial equipped with a magnetic stir bar was charged sequentially with cyclohexanol **1a** (10 mmol, 1 g), KO^{t}Bu (10.7 mmol, 1.2 g), and dry Et_2O (30 mL). After being sealed with a septum cap and transferred out of the glovebox, the reaction mixture was stirred at room temperature for 6.0 hours, followed by the addition of CS_2 (50 mmol, 3.8 g) *via* microsyringe at 0 °C and continued to be stirred for 10 hours at 0 °C before removing the solvent in vacuo.

Then *N*-methyl phenylmethacrylamide **2a** (5 mmol, 875 mg), PCy_3 (10 mmol, 2.8 g), *fac*-Ir(ppy)$_3$ (0.1 mmol, 65.5 mg), K_2CO_3 (7.5 mmol, 1.0 g) and DMF (30 mL) were added the above reaction system. The reaction mixture was irradiated with a 10 W blue LEDs lamp, maintained at ambient temperature, and stirred for 48 hours under air atmosphere. The solvent was removed in vacuo and the residue was purified by column chromatography to afford the product **3a** (0.95 g).

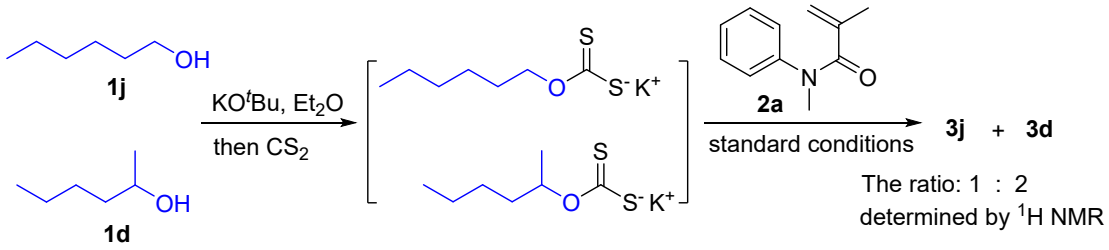


3 Procedure for competitive reaction of 1°, 2° and 3° alcohols

In a N_2-filled glovebox, an oven-dried 10 mL glass vial equipped with a magnetic stir bar was charged sequentially with hexan-1-ol **1j** (0.15 mmol, 15.3 mg) and hexan-2-ol **1d** (0.15 mmol, 15.3 mg), KO^{t}Bu (0.32 mmol, 35.3 mg), and dry Et_2O (3.0 mL). After being sealed with a septum cap and transferred out of the glovebox, the reaction mixture was stirred at room temperature for 30 minutes, followed by the addition of CS_2 (1.5 mmol, 114 mg) *via* microsyringe at 0 ℃ and continued to be stirred for 3 hours at 0 °C before removing the solvent in vacuo.

Then *N*-methyl-*N*-phenylmethacrylamide **2a** (0.15 mmol, 26.3 mg), PCy_3 (0.3 mmol, 84 mg), *fac*-Ir(ppy)$_3$ (0.003 mmol, 2.3 mg), K_2CO_3 (0.225 mmol, 31 mg), and DMF (3.0 mL) were added the above reaction system. The reaction mixture was irradiated with a 10 W blue LEDs lamp, maintained at ambient temperature, and stirred for 24 hours under air atmosphere. The solvent was removed in vacuo and the residue was purified by column chromatography to afford the products **3j** and **3d** using ethyl acetate/ petroleum ether as eluant.

The molar ratio of **3j** and **3d** was obtained by ^{1}H NMR.



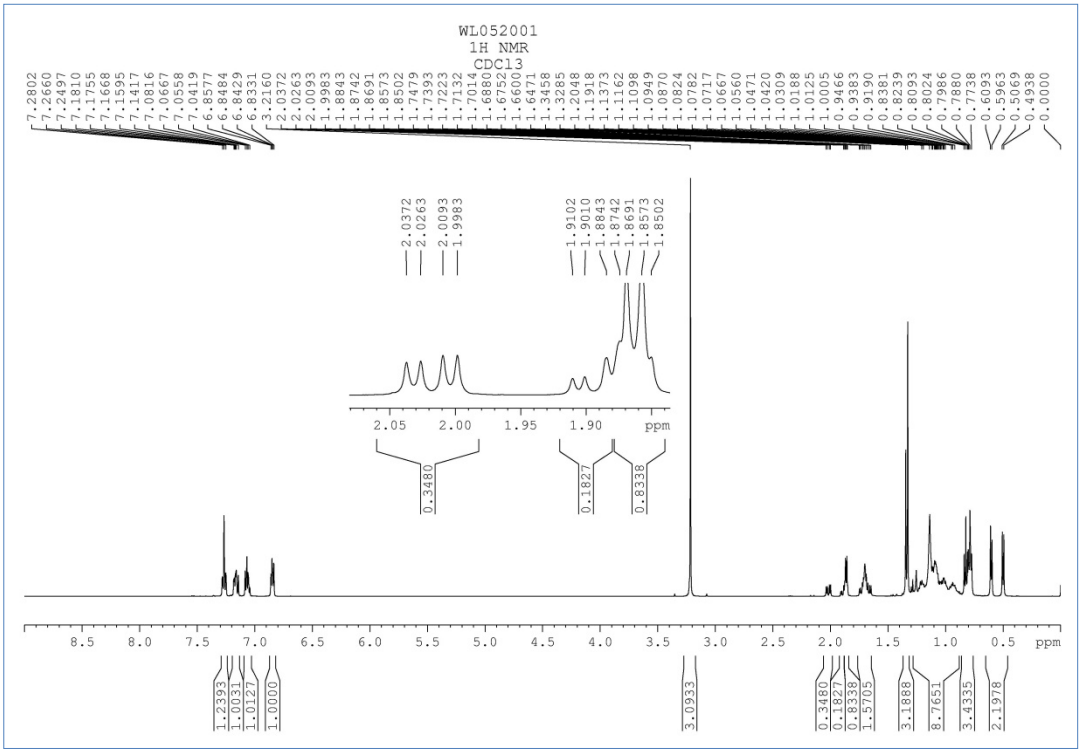


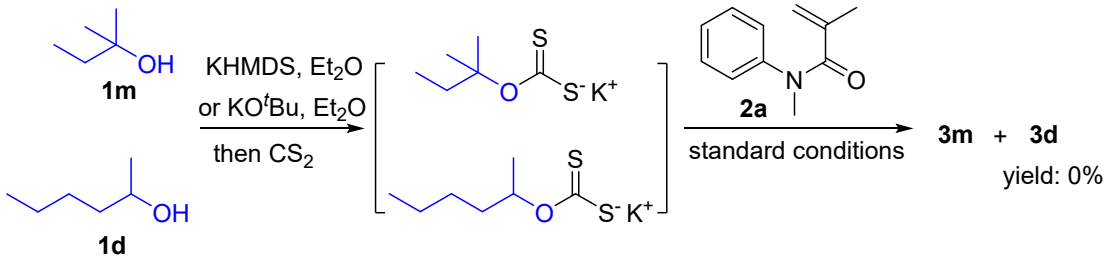
Figure S1 ^{1}H NMR spectrum of mixed products **3j** and **3d**

In a N_2-filled glovebox, an oven-dried 10 mL glass vial equipped with a magnetic stir bar was charged sequentially with 2-methylbutan-2-ol **1m** (0.15 mmol, 13.2 mg), KHMDS (0.16 mmol, 32 mg), and dry Et_2O (3.0 mL). After being sealed with a septum cap and transferred out of the glovebox, the reaction mixture was stirred at room temperature for 30 minutes, followed by the addition of CS_2 (0.75 mmol, 57 mg) *via* microsyringe at 0 ^{o}C and continued to be stirred for 3 hours at 0 ^{o}C before removing the solvent in vacuo.

In a N_2-filled glovebox, an oven-dried 10 mL glass vial equipped with a magnetic stir bar was charged sequentially with hexan-2-ol **1d** (0.15 mmol, 15.3 mg), KO^{t}Bu (0.16 mmol, 18 mg), and dry Et_2O (3.0 mL). After being sealed with a septum cap and transferred out of the glovebox, the reaction mixture was stirred at room temperature for 30 minutes, followed by the addition of CS_2 (0.75 mmol, 57 mg) *via* microsyringe at 0 ^{o}C and continued to be stirred for 3 hours at 0 ^{o}C before removing the solvent in vacuo.

The aforementioned two residues were combined. Then *N*-methyl-*N*-phenylmethacrylamide **2a** (0.15 mmol, 26.3 mg), PCy_3 (0.3 mmol, 84 mg), *fac*-Ir(ppy)$_3$ (0.003 mmol, 2.3 mg), K_2CO_3 (0.225 mmol, 31 mg), and DMF (3.0 mL) were added the above reaction system. The reaction mixture was irradiated with a 10 W blue LEDs lamp, maintained at ambient temperature, and stirred for

24 hours under air atmosphere. The solvent was removed in vacuo and the residue was purified by column chromatography to afford the products **3j** and **3d** using ethyl acetate/ petroleum ether as eluant.



4 Luminescence quenching study

Emission intensities were recorded using a RF-6000 Spectrophotometer. First, the emission intensity of *fac*-Ir(ppy)$_3$ solutions was observed at 520 nm. The solutions were irradiated at 510 nm (Maximum absorption wavelength of *fac*-Ir(ppy)$_3$) and fluorescence was measured from 450 nm to 700 nm. In a typical experiment, the emission spectrum of a 2.5 × 10^{-4} M solution of *fac*-Ir(ppy)$_3$ with different concentration of **2a** (**XSa)** in degassed anhydrous DMF and the linear relationship between I_0/I and the increasing concentration of **2a** (**XSa)** from 0 M to 2.5 × 10^{-2} M**.**

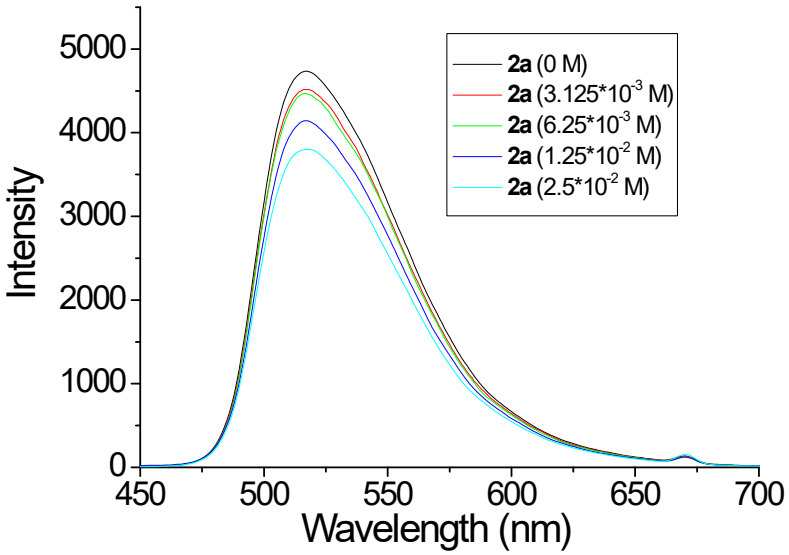


Figure S2 Luminescence quenching spectrum of *fac*-Ir(ppy)$_3$ by **2a**

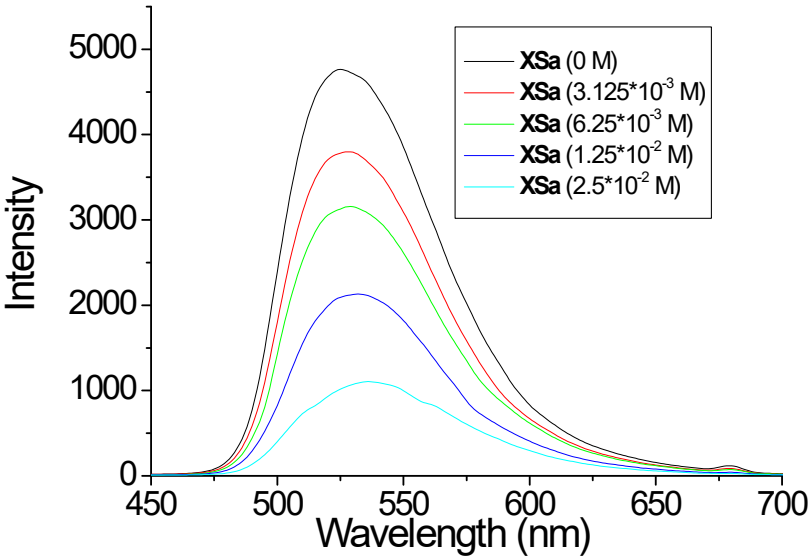


Figure S3 Luminescence quenching spectrum of *fac*-Ir(ppy)$_3$ by **XSa**

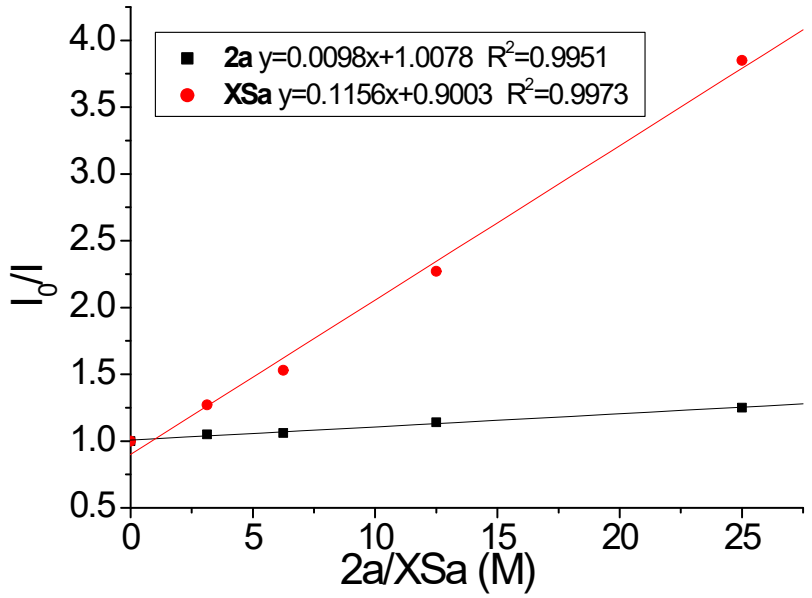


Figure S4 The Stern-Volmer plots

5 HR MS spectrum of the adduct

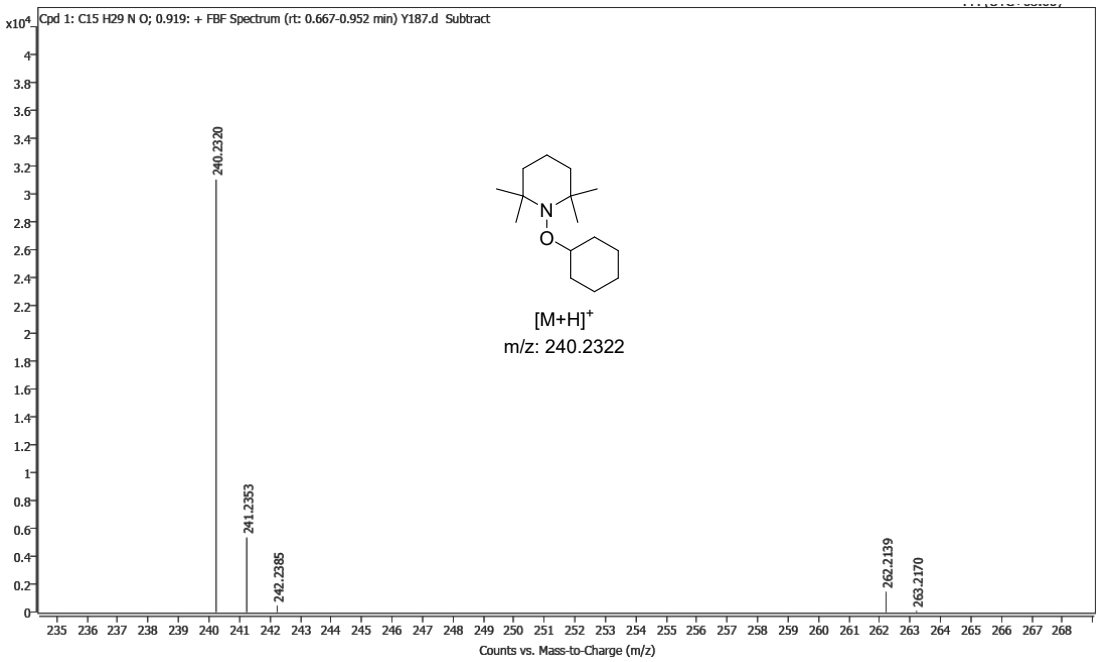


Figure S5 HR MS spectrum of the adduct TEMPO-cyclohexyl

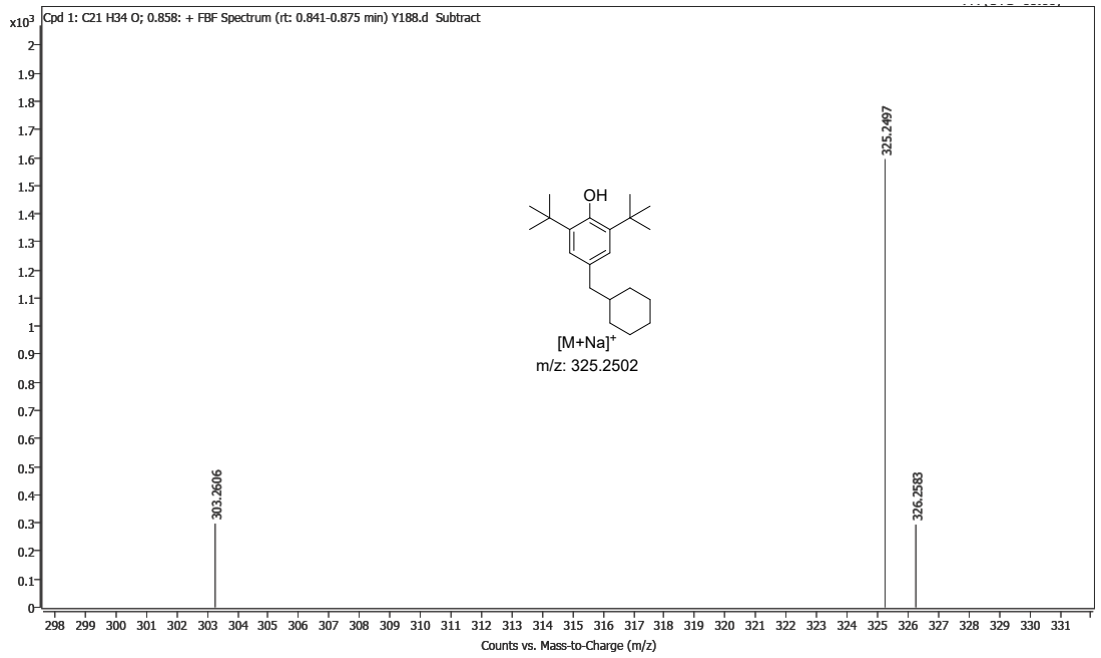


Figure S6 HR MS spectrum of the adduct BHT-cyclohexyl

6 Copies of spectra of products

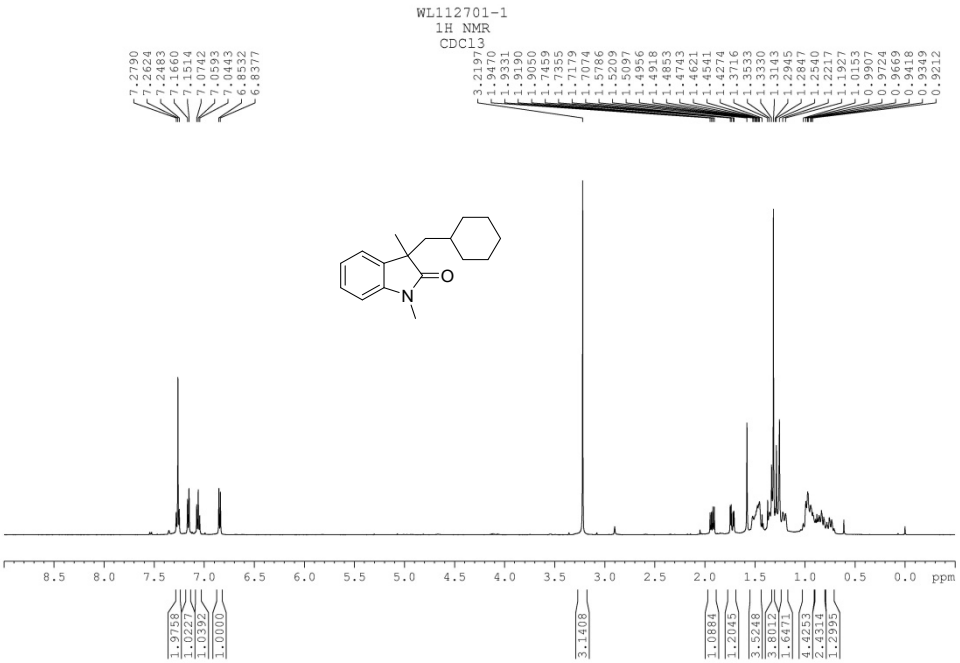


Fig. S7 ^{1}H NMR (500 MHz) spectrum of compound **3a**

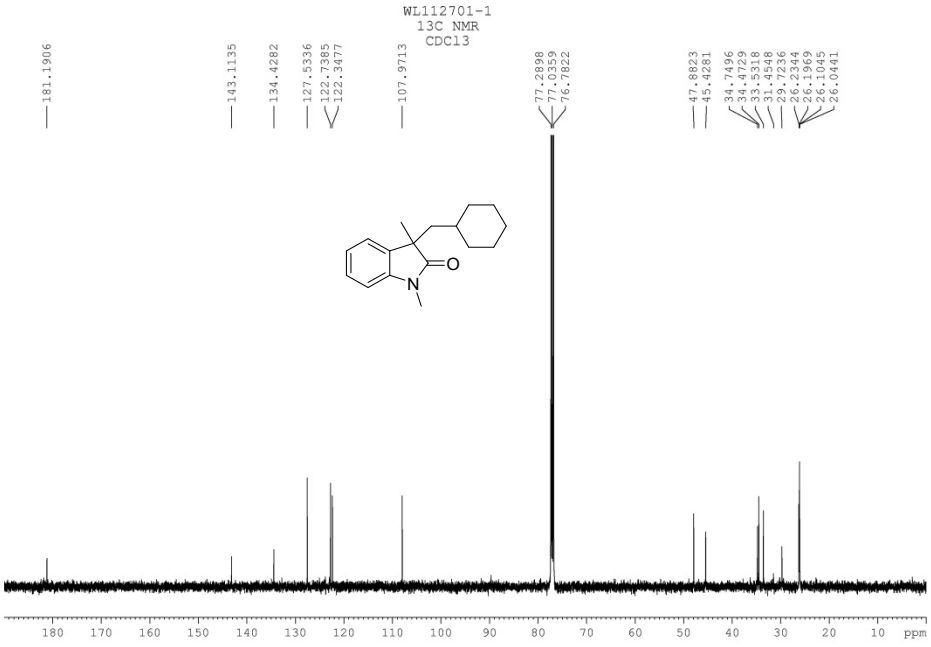


Fig. S8 ^{13}C{^{1}H} NMR (126 MHz) spectrum of compound **3a**

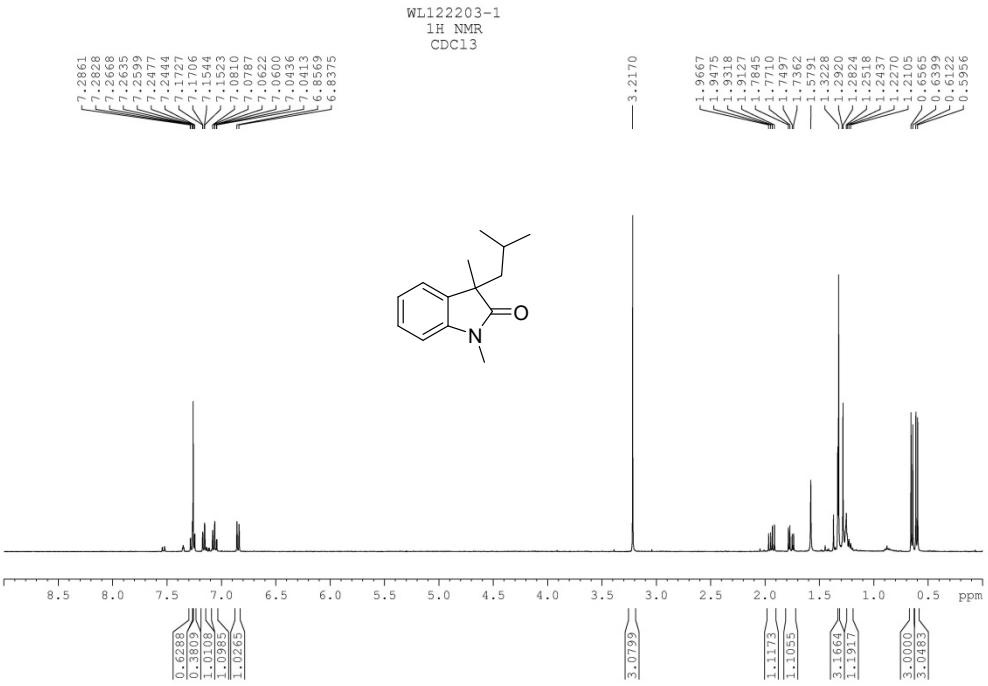


Fig. S9 ^{1}H NMR (400 MHz) spectrum of compound **3b**

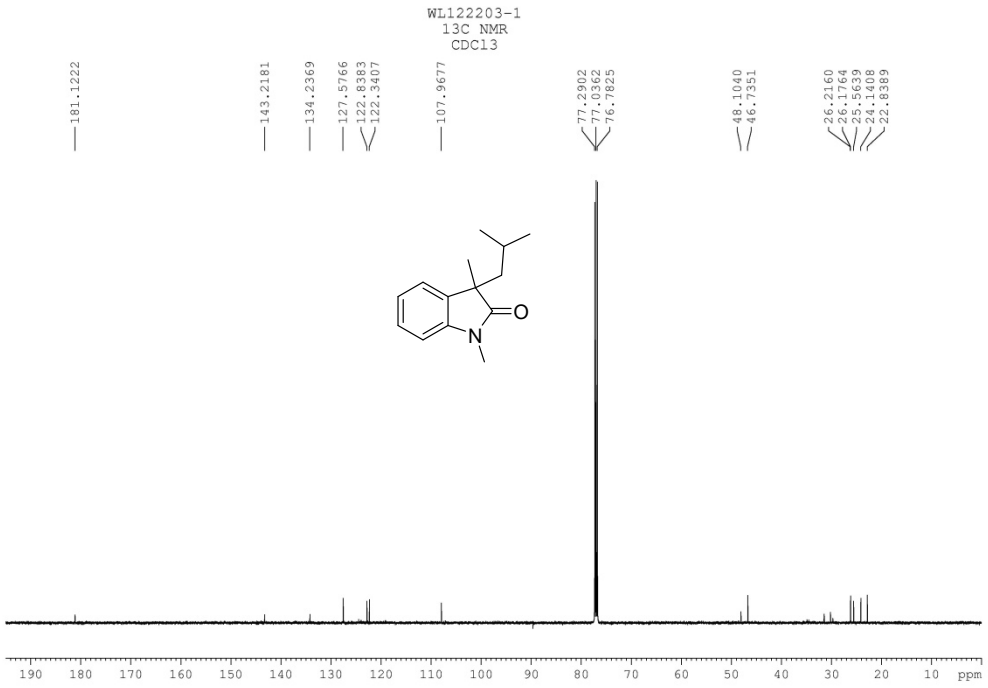


Fig. S10 ^{13}C{^{1}H} NMR (126 MHz) spectrum of compound **3b**

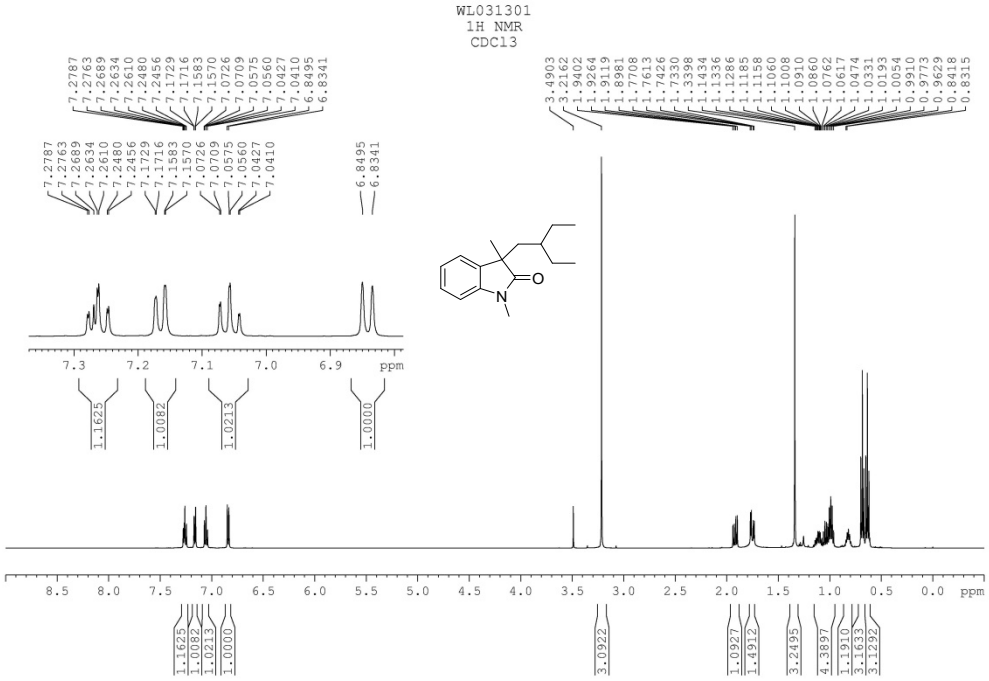


Fig. S11 ^{1}H NMR (500 MHz) spectrum of compound **3c**

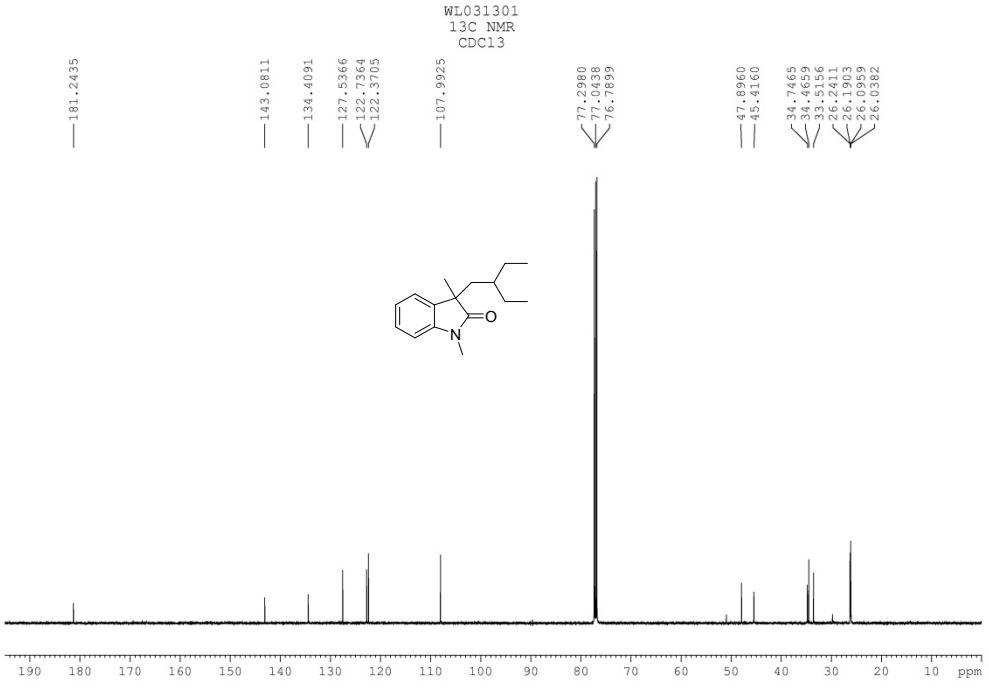


Fig. S12 ^{13}C{^{1}H} NMR (126 MHz) spectrum of compound **3c**

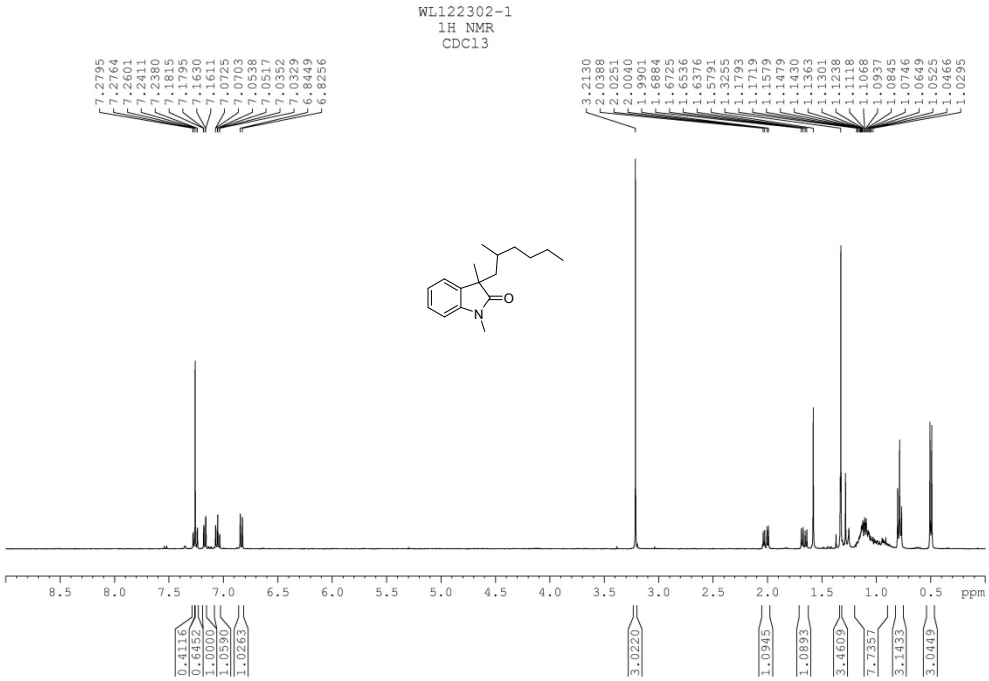


Fig. S13 ^{1}H NMR (400 MHz) spectrum of compound **3d**

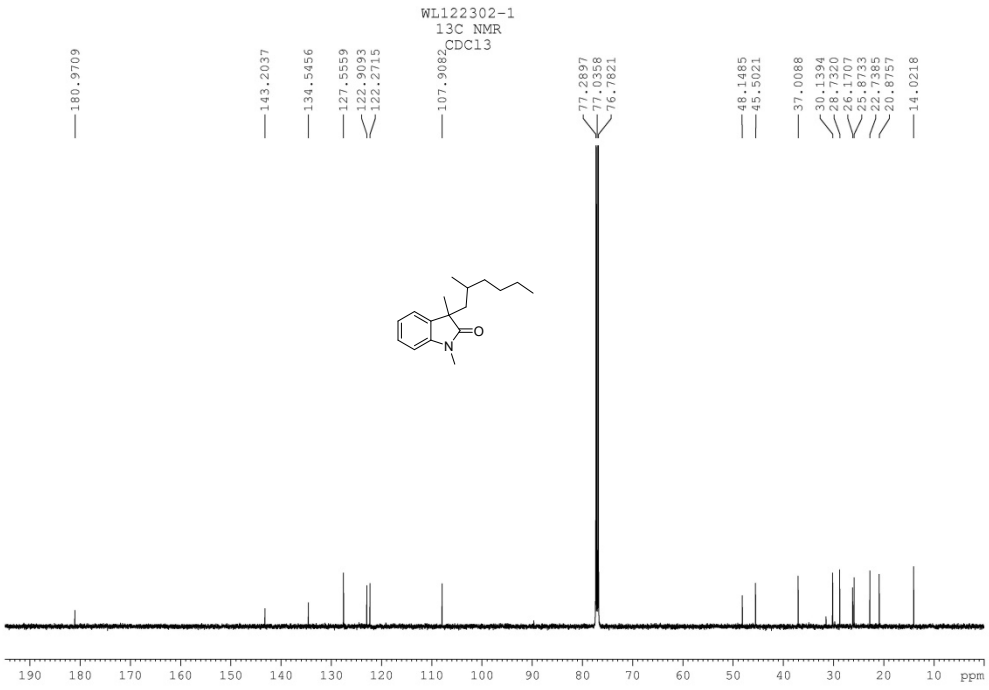


Fig. S14 ^{13}C{^{1}H} NMR (126 MHz) spectrum of compound **3d**

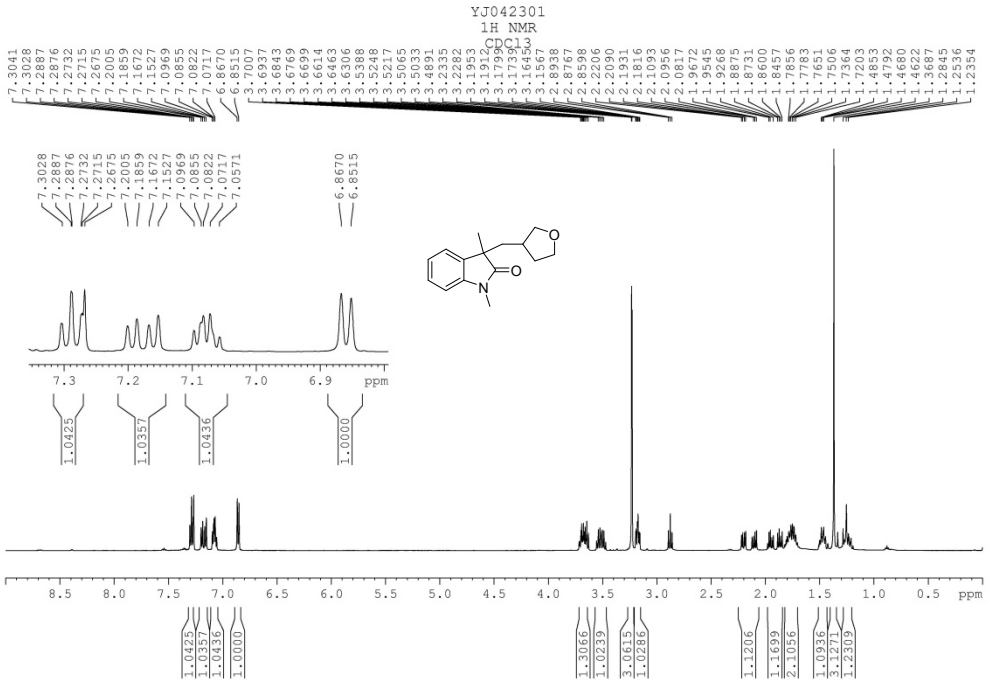


Fig. S15 ^{1}H NMR (500 MHz) spectrum of compound **3e**

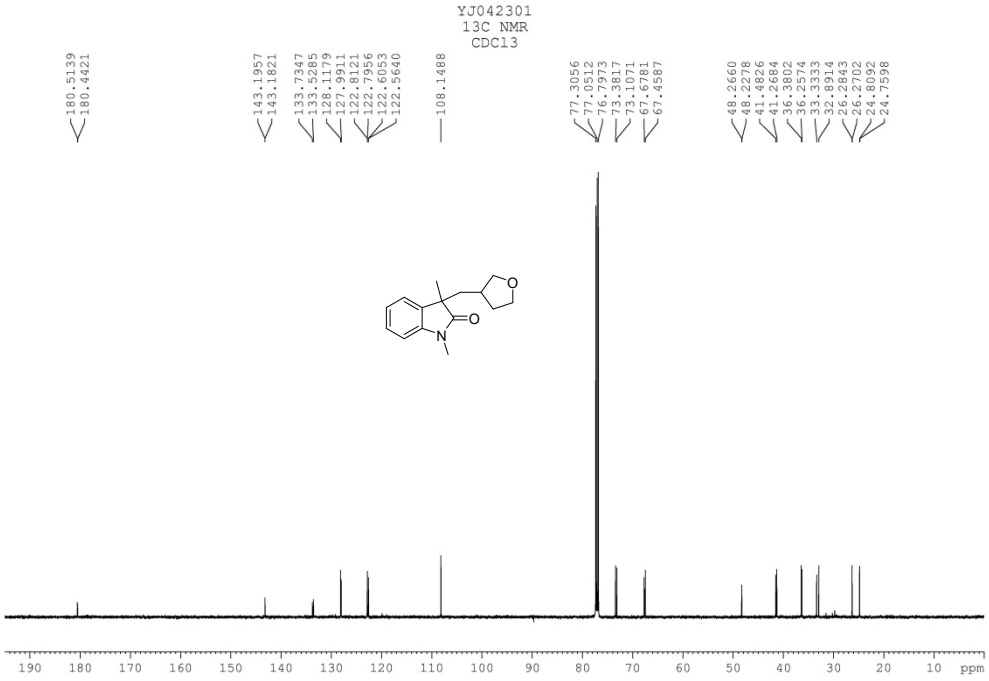


Fig. S16 ^{13}C{^{1}H} NMR (126 MHz) spectrum of compound **3e**

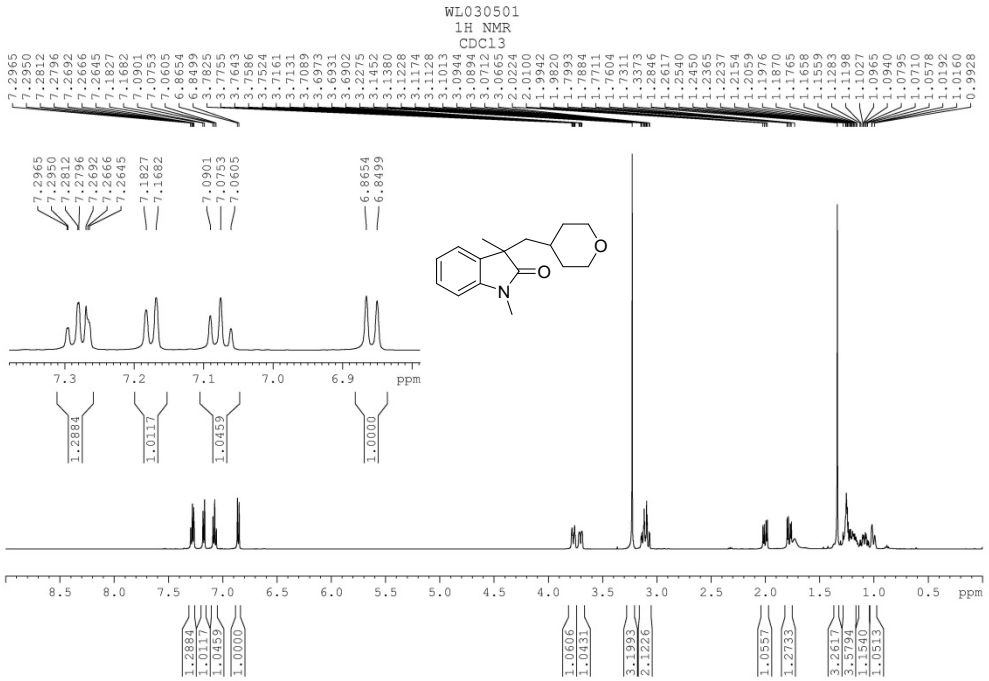


Fig. S17 ^{1}H NMR (500 MHz) spectrum of compound **3f**

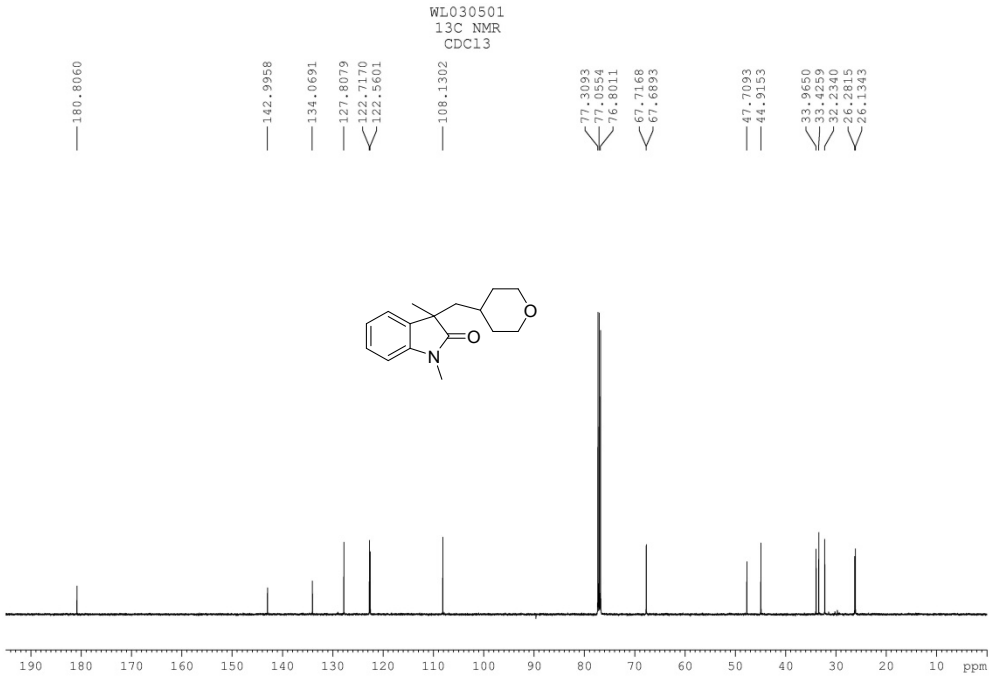


Fig. S18 ^{13}C{^{1}H} NMR (126 MHz) spectrum of compound **3f**

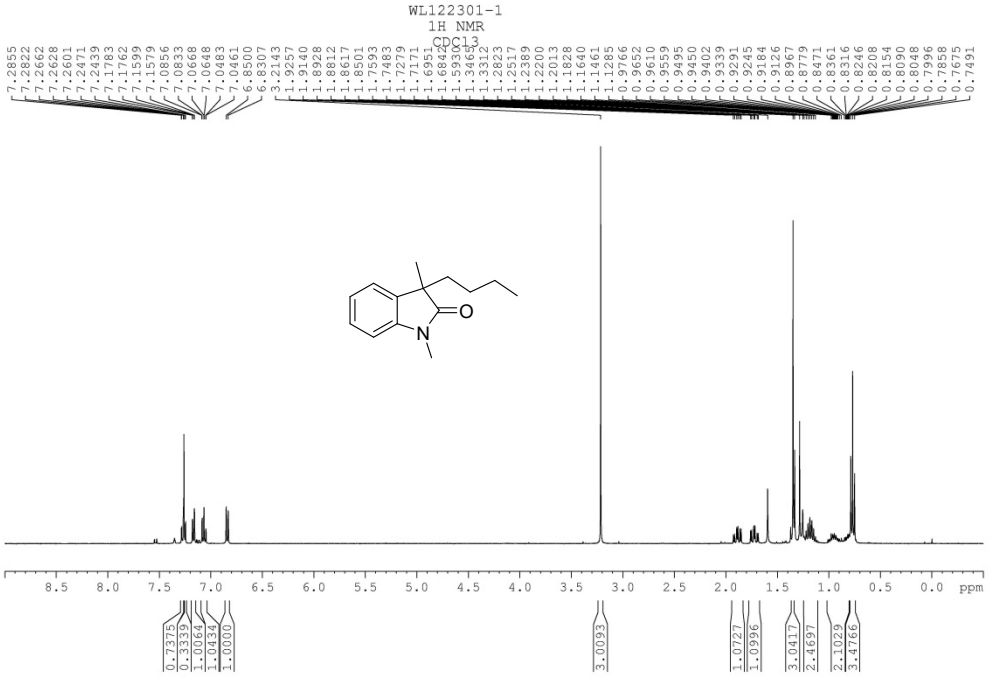


Fig. S19 ^{1}H NMR (400 MHz) spectrum of compound **3g**

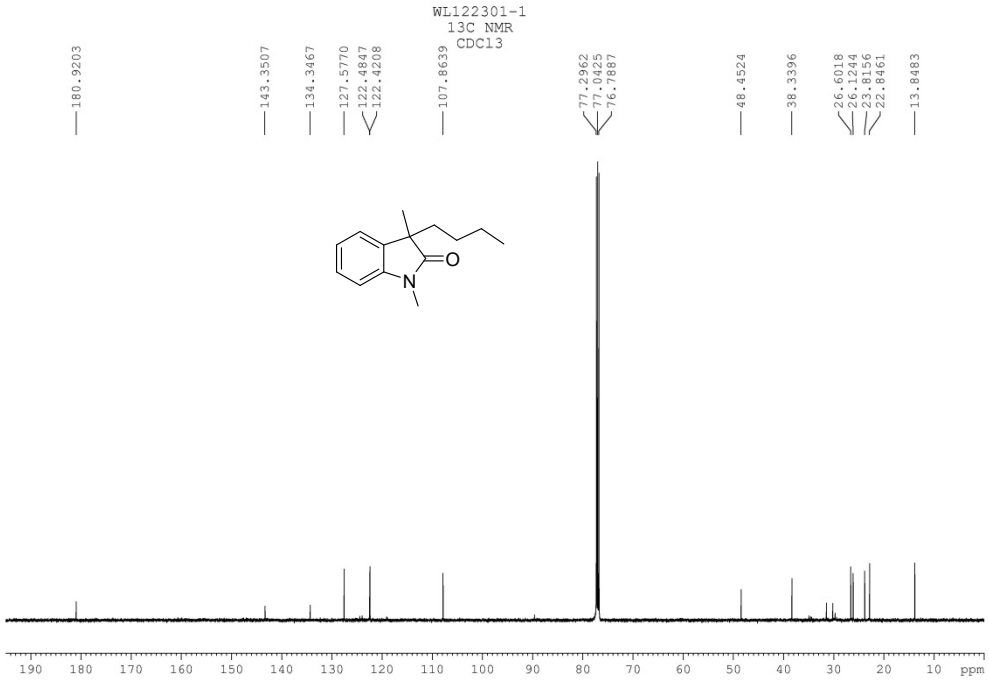


Fig. S20 ^{13}C{^{1}H} NMR (126 MHz) spectrum of compound **3g**

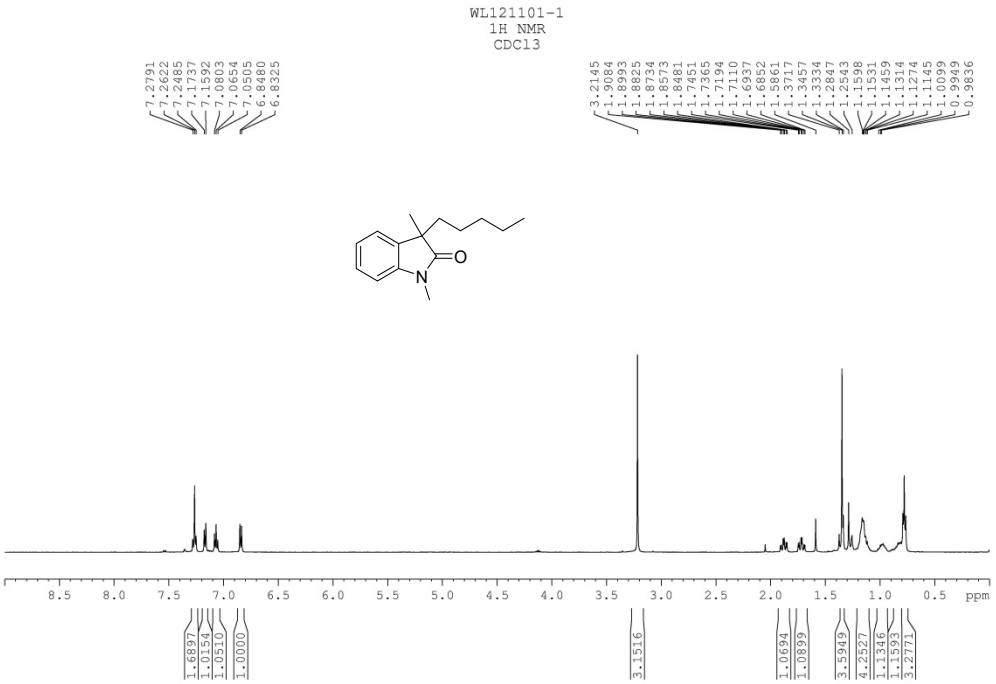


Fig. S21 ^{1}H NMR (500 MHz) spectrum of compound **3h**

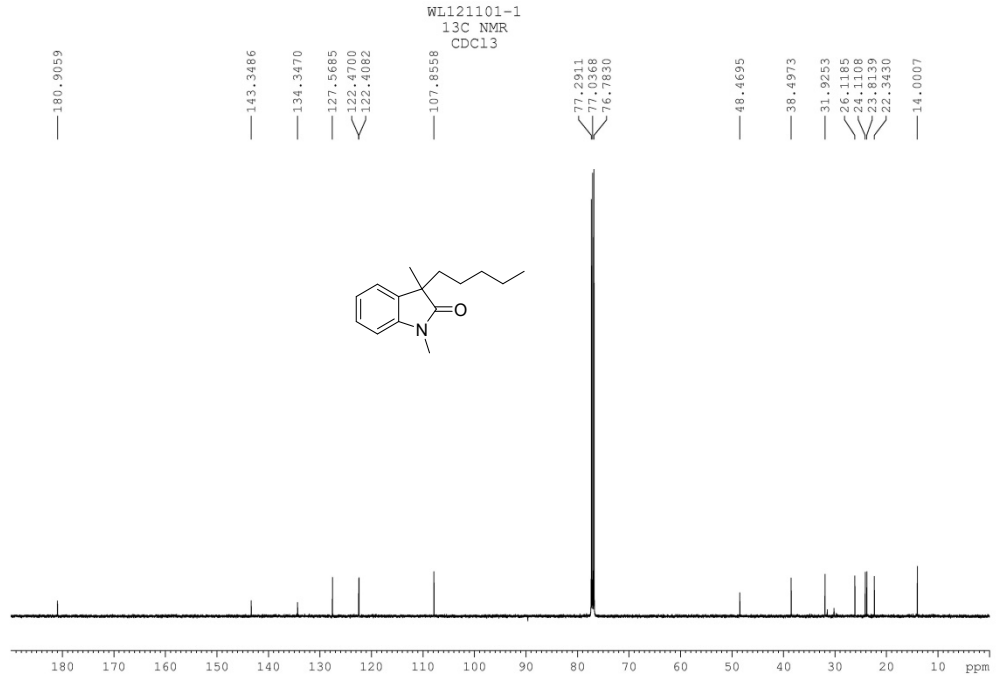


Fig. S22 ^{13}C{^{1}H} NMR (126 MHz) spectrum of compound **3h**

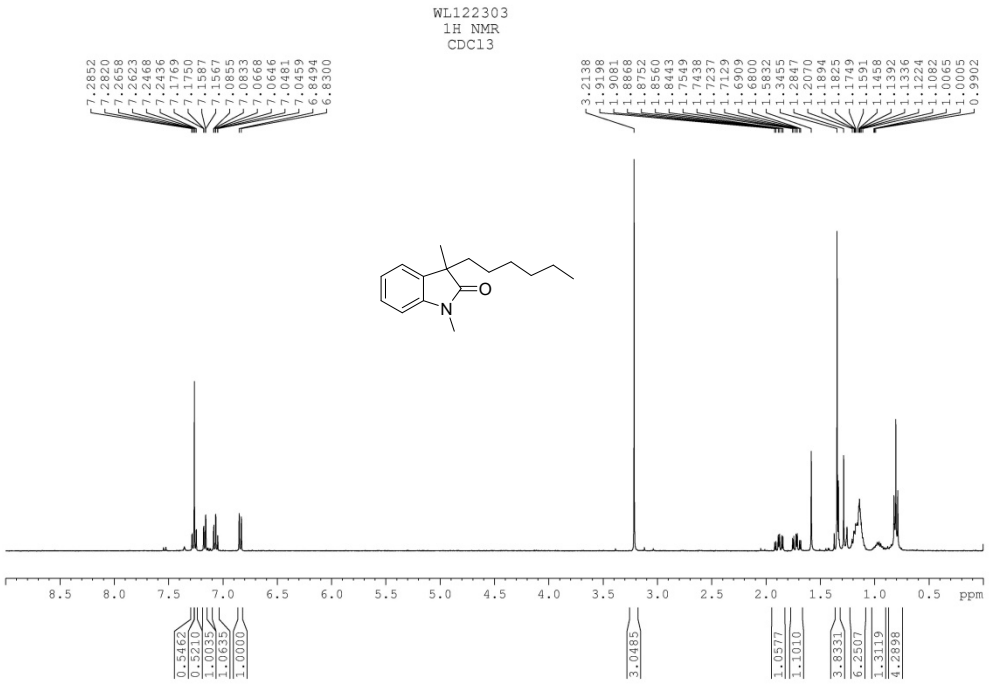


Fig. S23 ^{1}H NMR (400 MHz) spectrum of compound **3i**

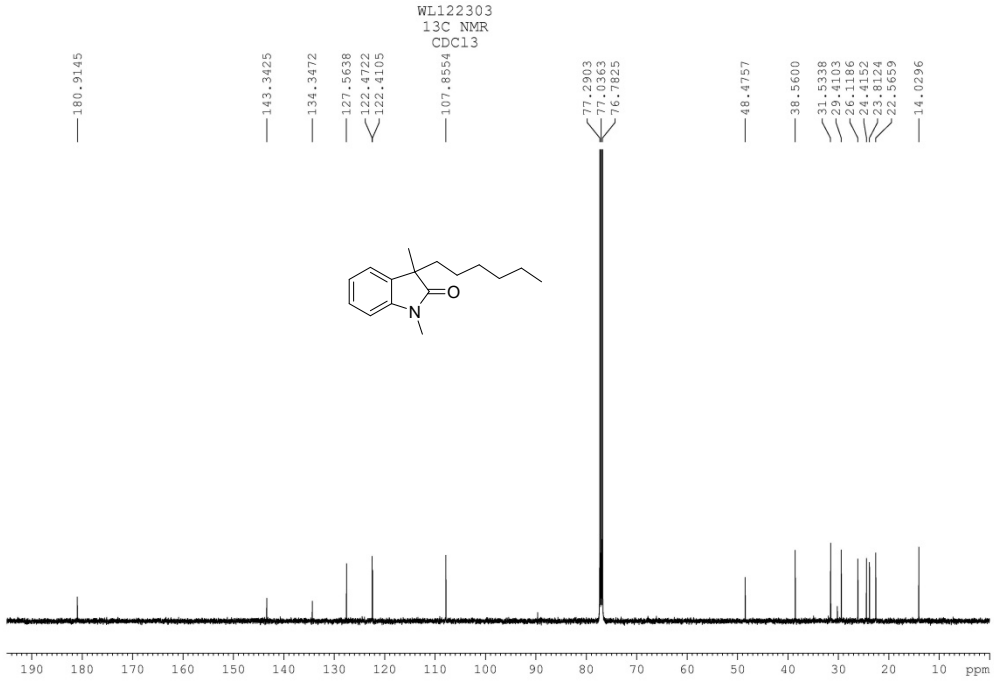


Fig. S24 ^{13}C{^{1}H} NMR (126 MHz) spectrum of compound **3i**

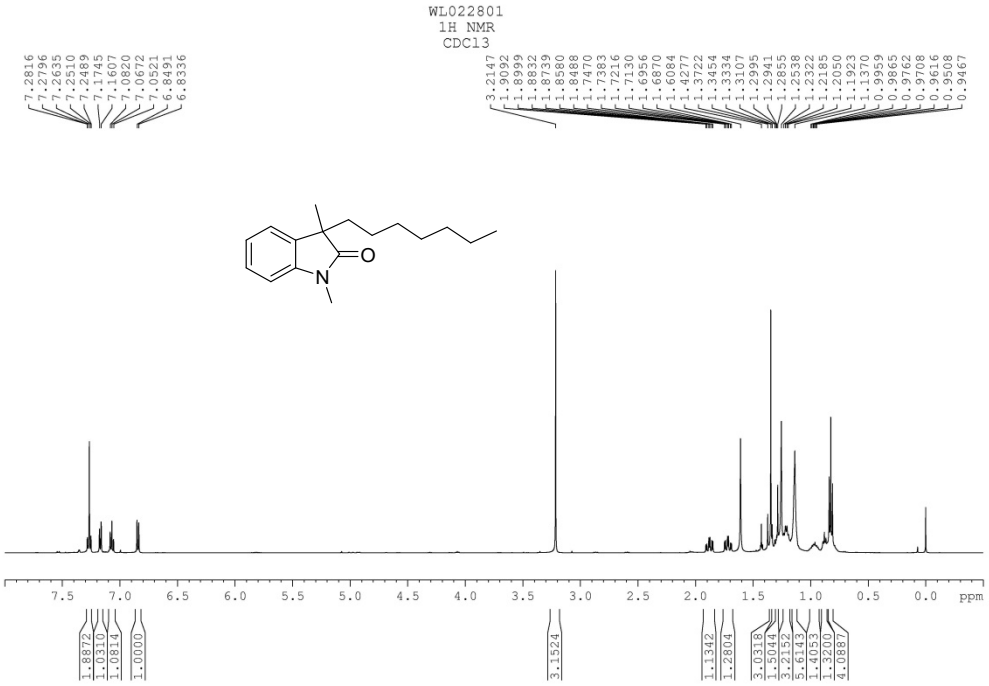


Fig. S25 ^{1}H NMR (500 MHz) spectrum of compound **3j**

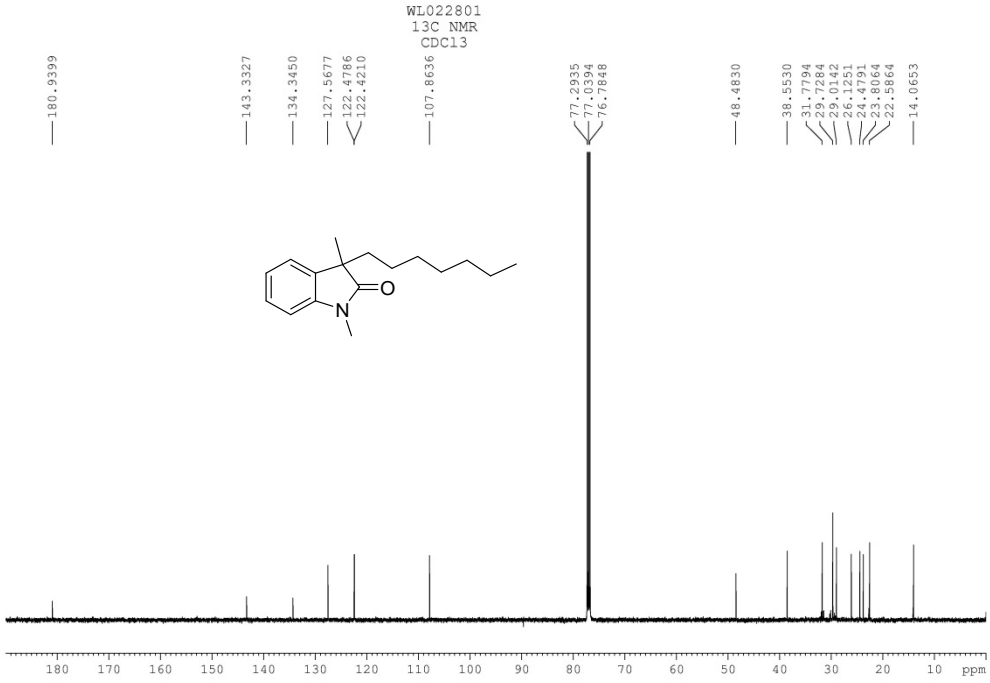


Fig. S26 ^{13}C{^{1}H} NMR (126 MHz) spectrum of compound **3j**

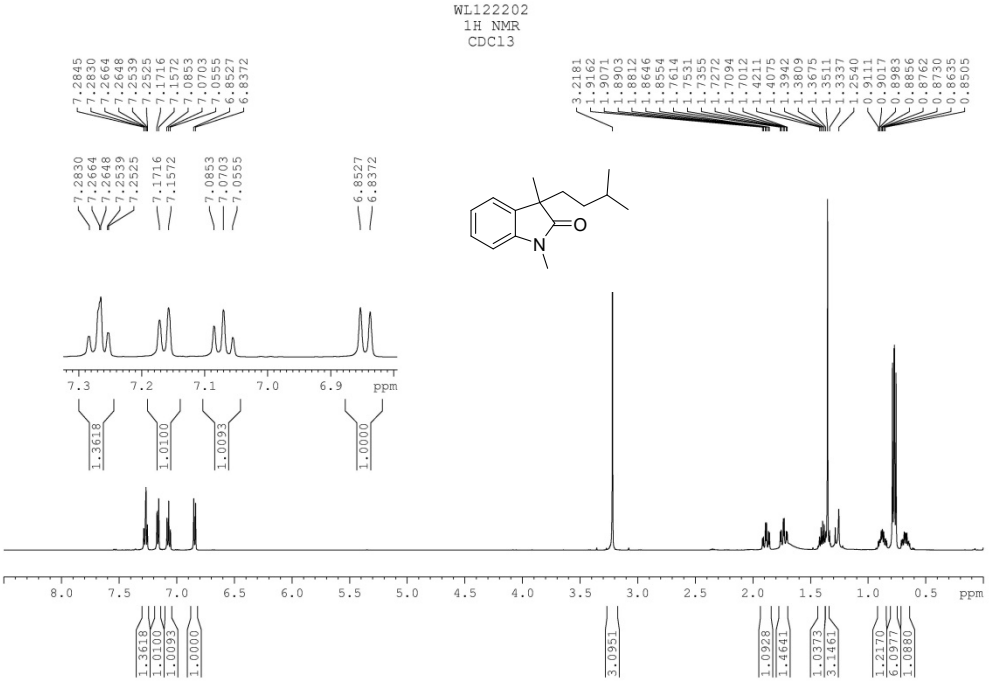


Fig. S27 ^{1}H NMR (500 MHz) spectrum of compound **3k**

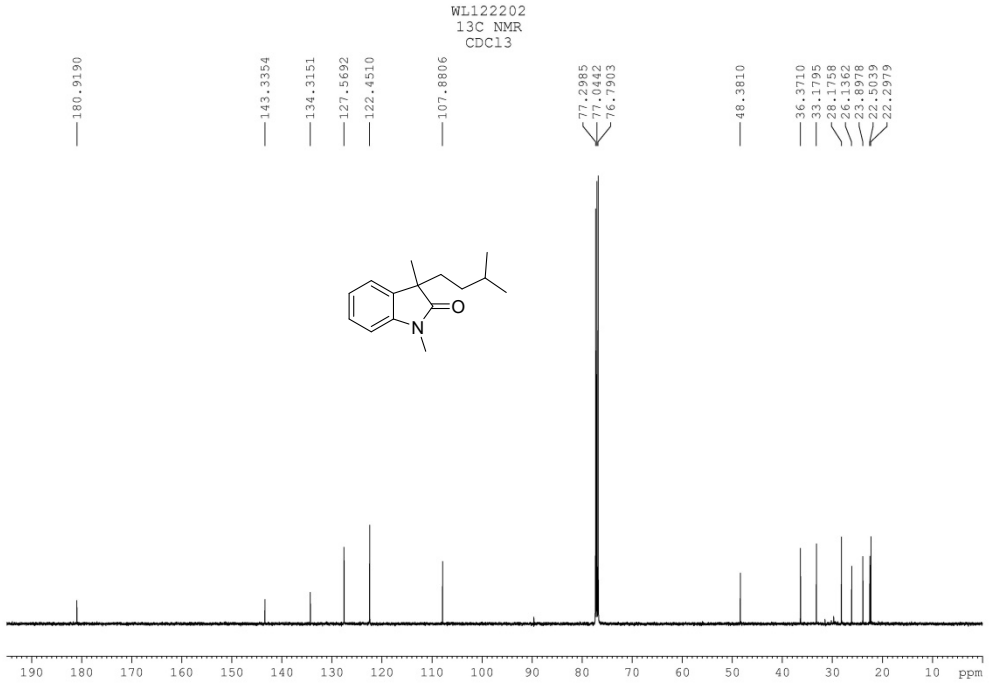


Fig. S28 ^{13}C{^{1}H} NMR (126 MHz) spectrum of compound **3k**

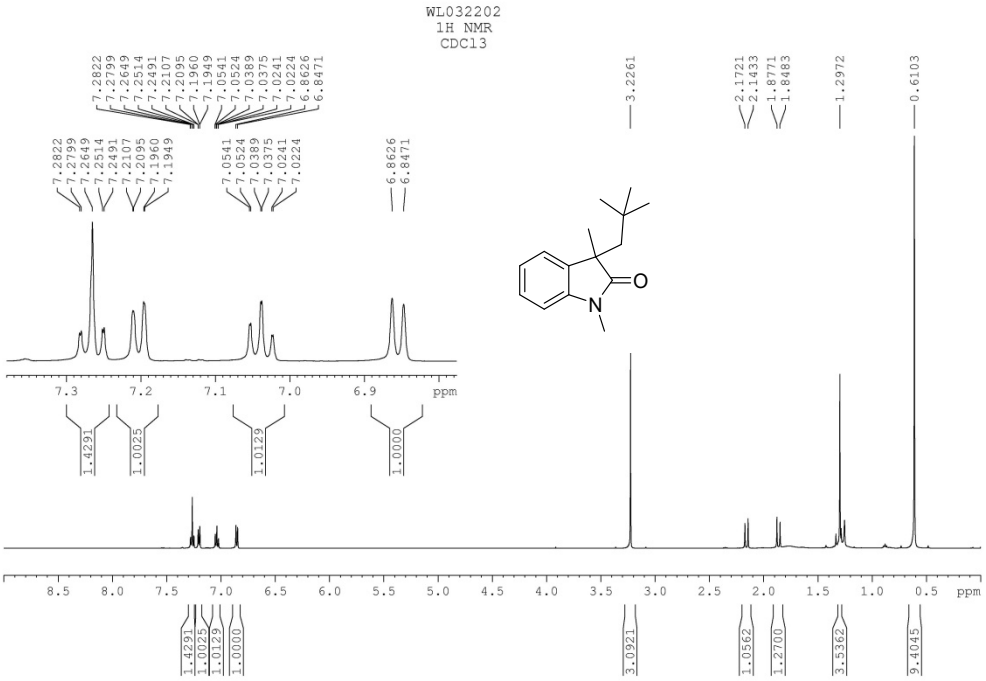


Fig. S29 ^{1}H NMR (500 MHz) spectrum of compound **3l**

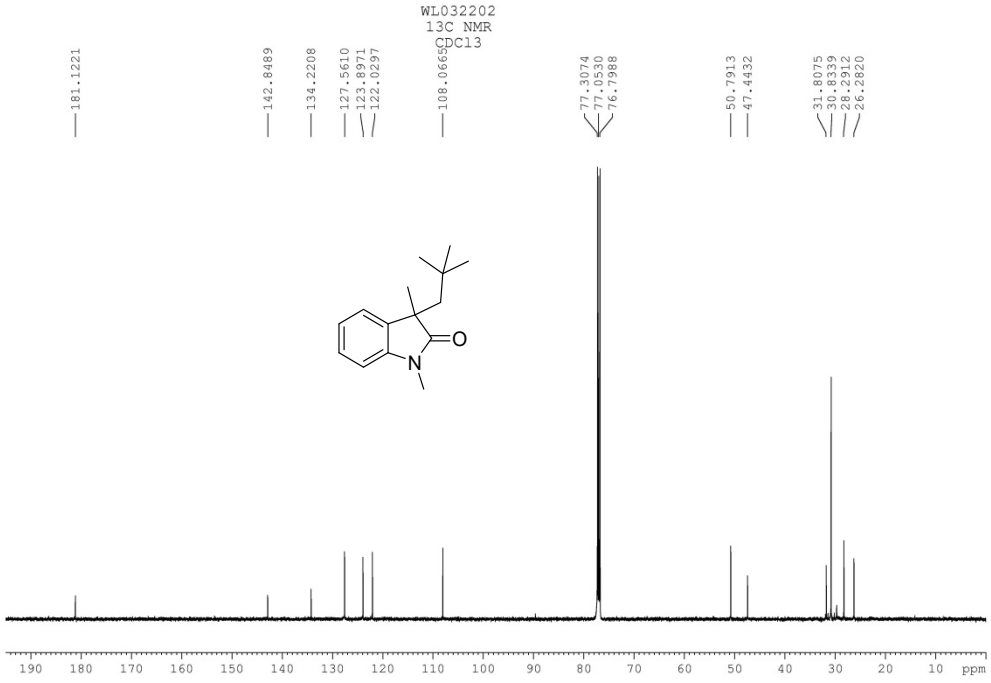


Fig. S30 ^{13}C{^{1}H} NMR (126 MHz) spectrum of compound **3l**

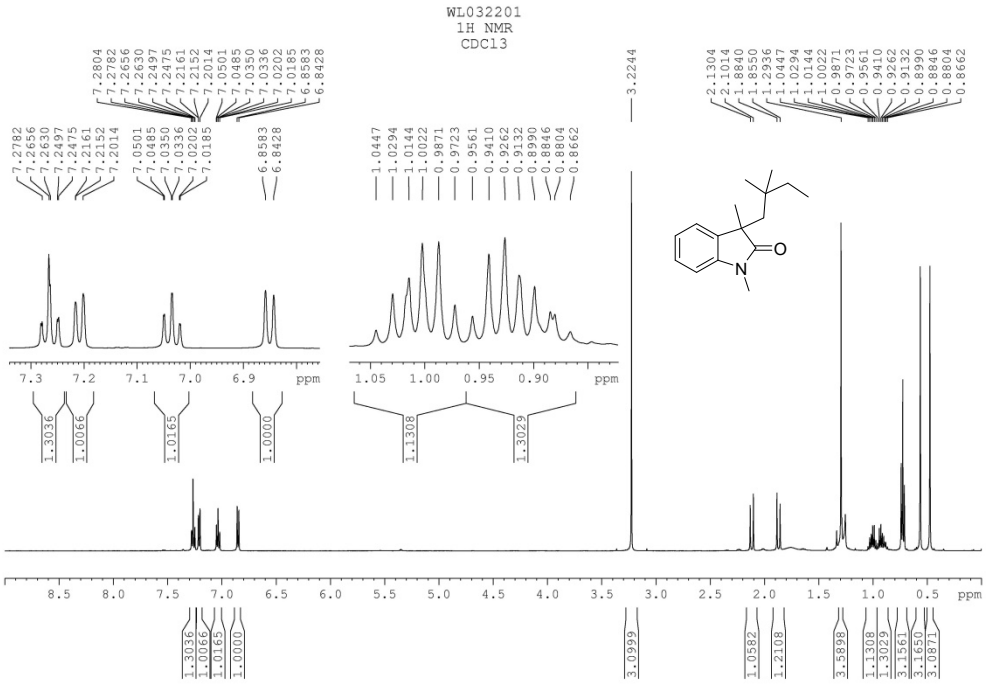


Fig. S31 ^{1}H NMR spectrum of compound **3m**

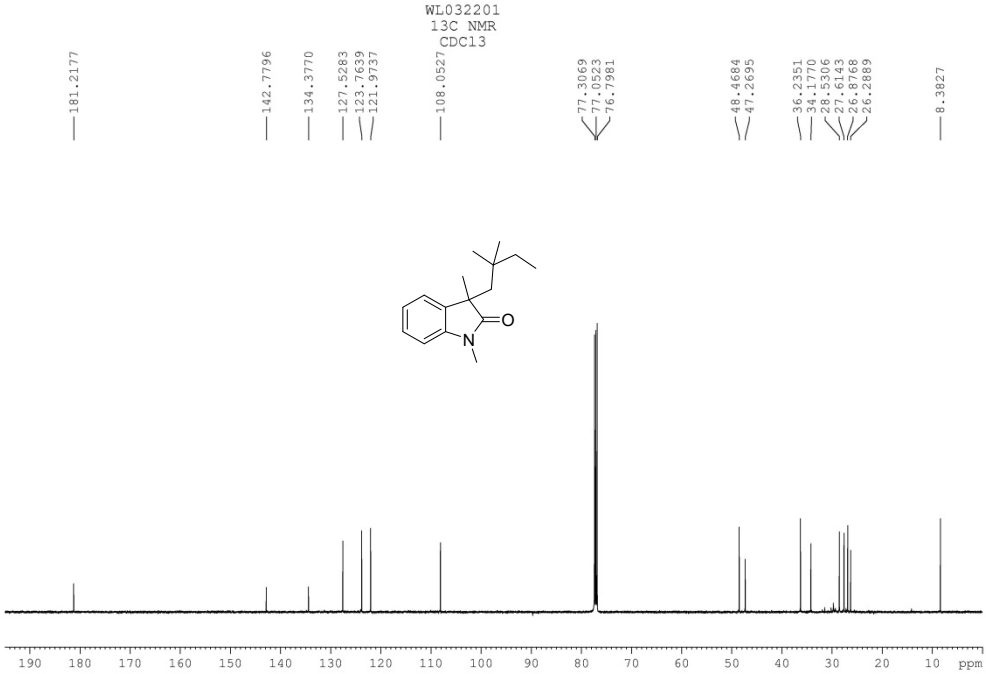


Fig. S32 ^{13}C{^{1}H} NMR spectrum of compound **3m**

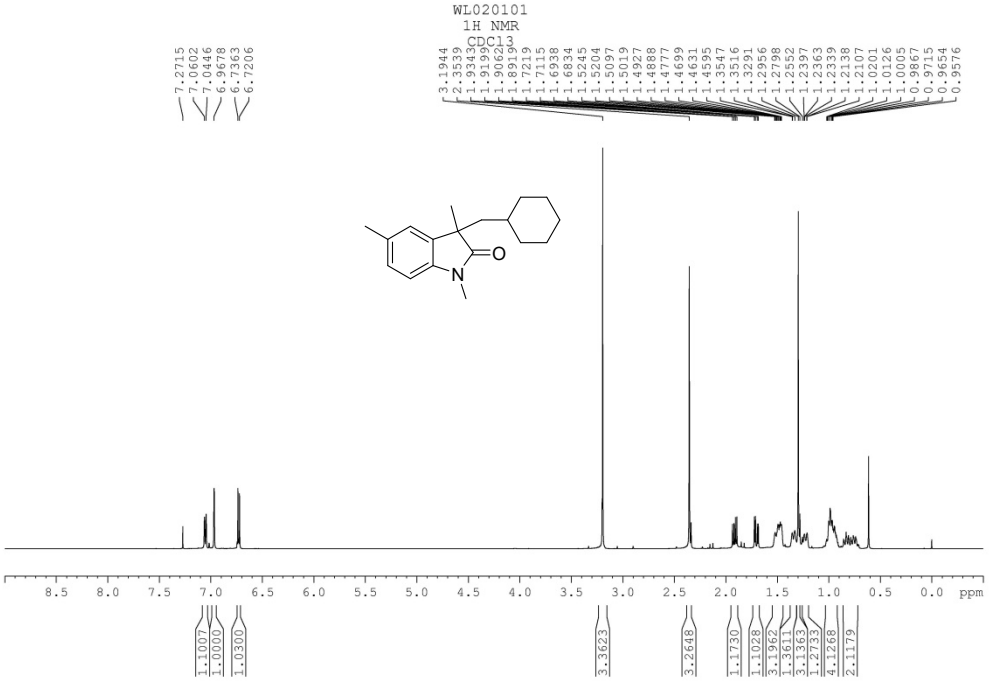


Fig. S33 ^{1}H NMR (500 MHz) spectrum of compound **3ba**

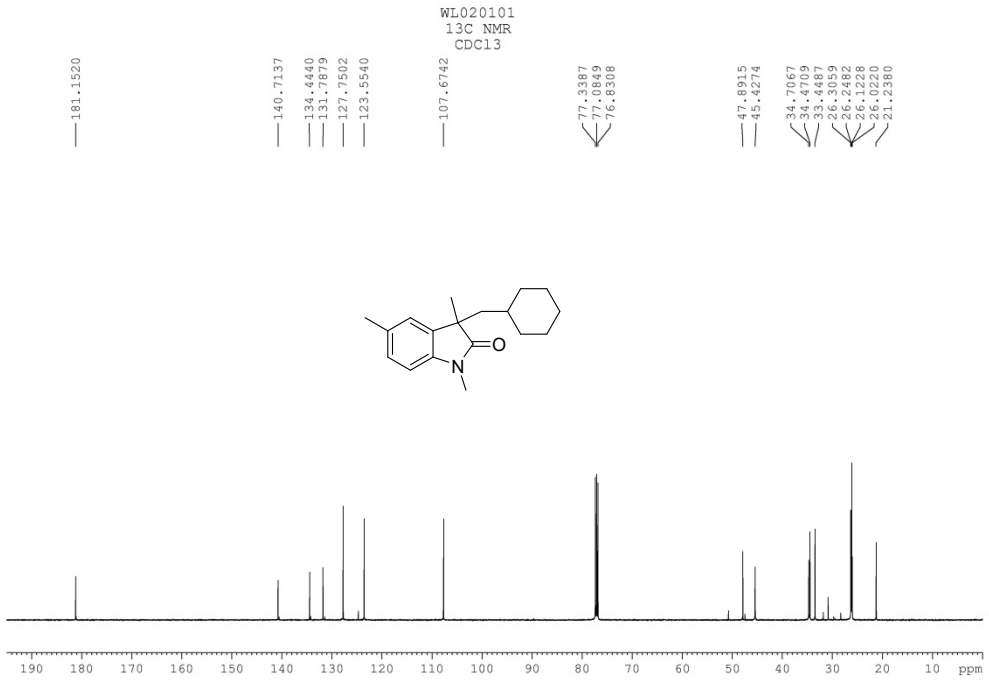


Fig. S34 ^{13}C{^{1}H} NMR (126 MHz) spectrum of compound **3ba**

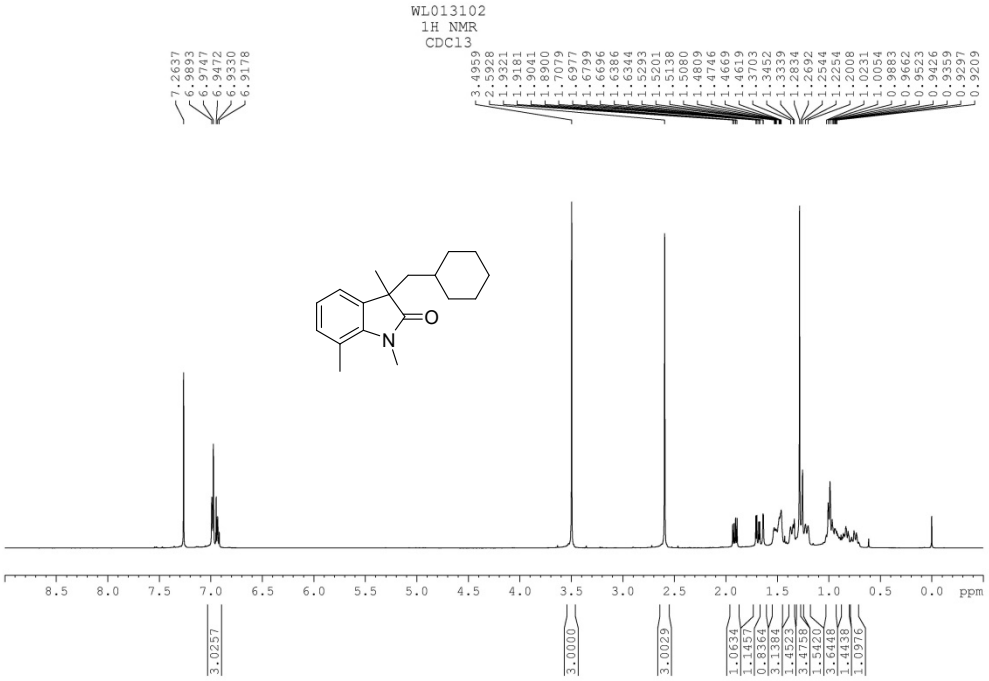


Fig. S35 ^{1}H NMR (500 MHz) spectrum of compound **3ca**

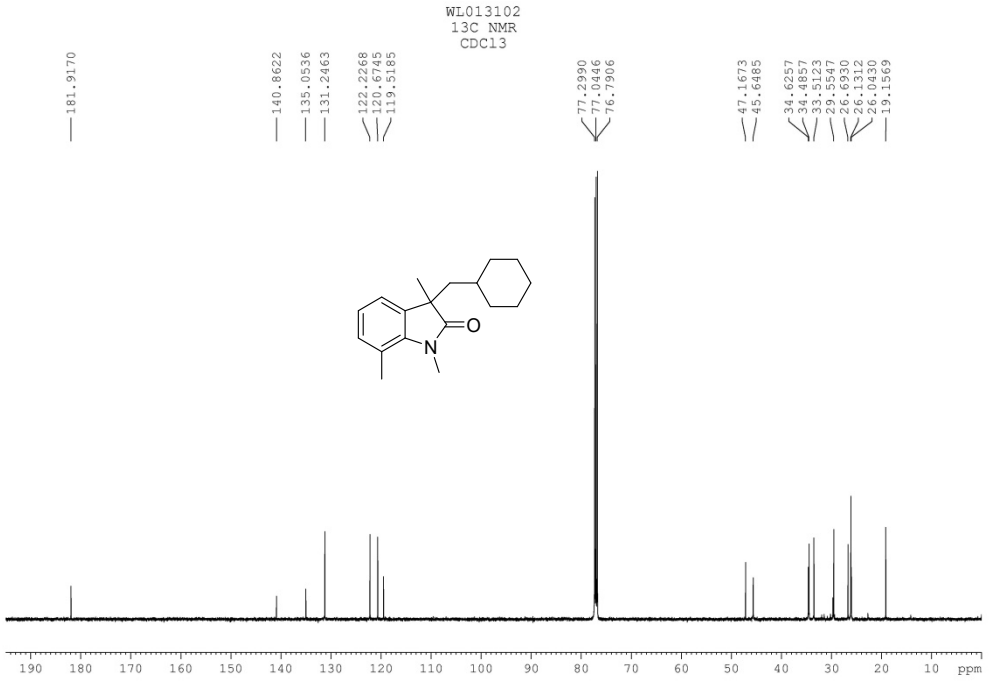


Fig. S36 ^{13}C{^{1}H} NMR (126 MHz) spectrum of compound **3ca**

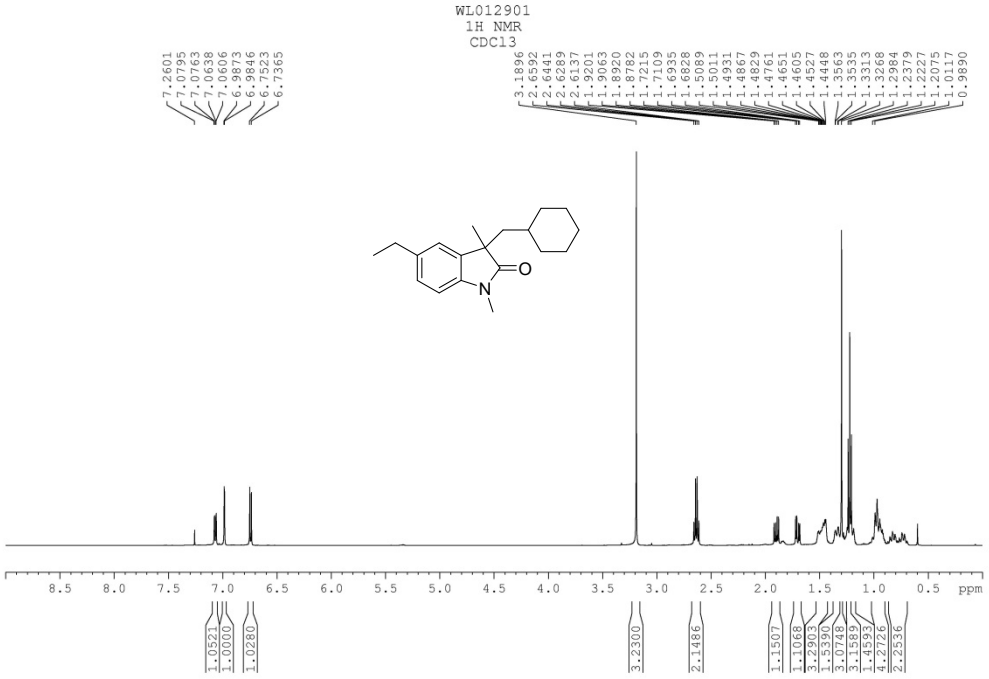


Fig. S37 ^{1}H NMR (500 MHz) spectrum of compound **3da**

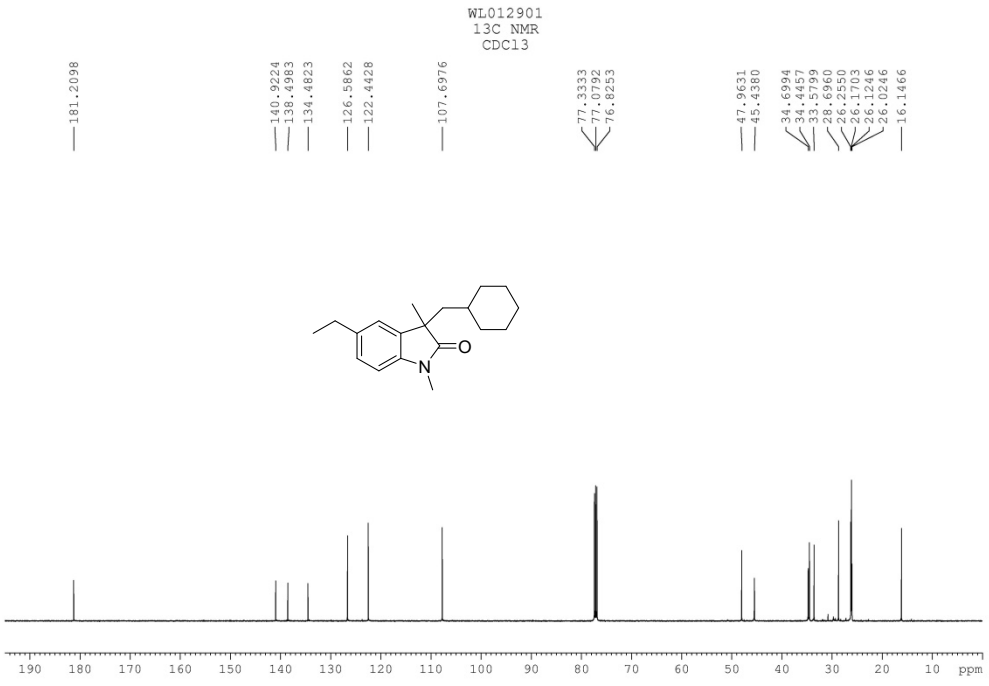


Fig. S38 ^{13}C{^{1}H} NMR (126 MHz) spectrum of compound **3da**

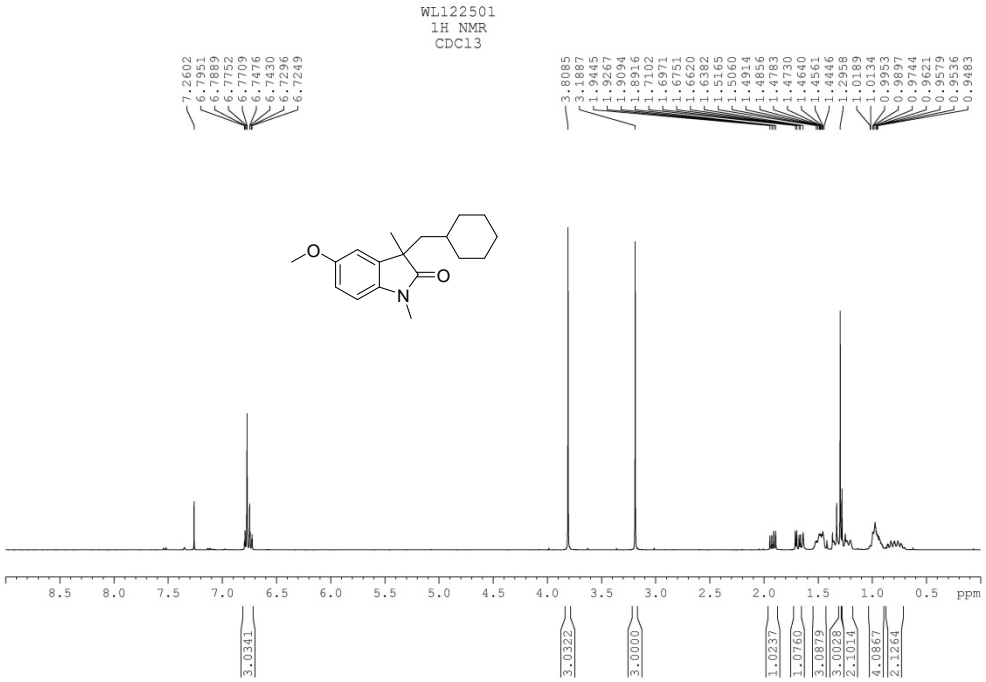


Fig. S39 ^{1}H NMR (400 MHz) spectrum of compound **3ea**

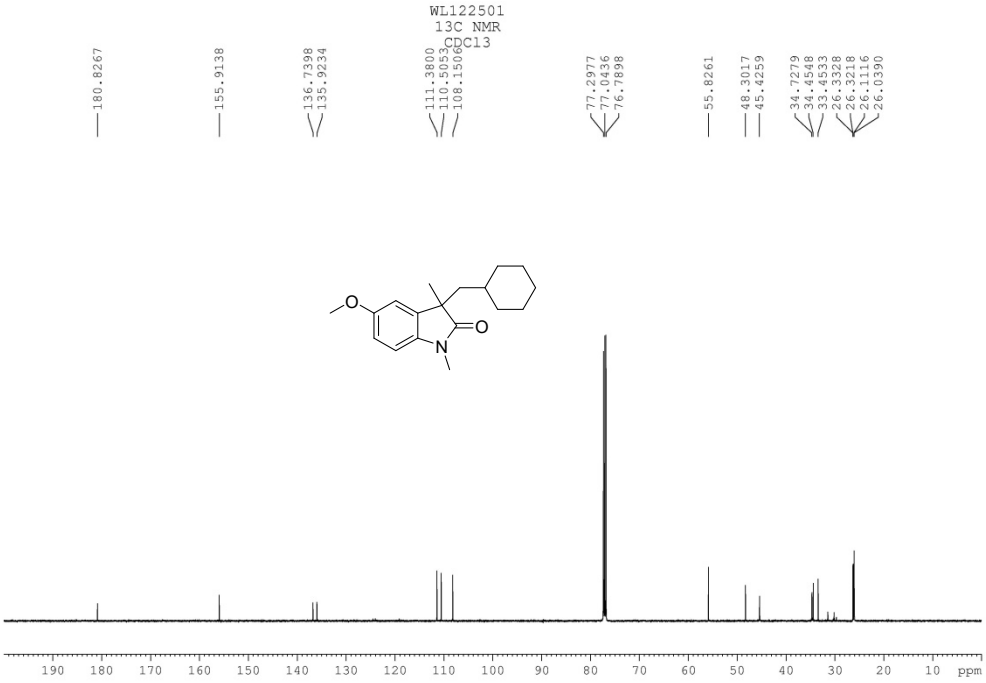


Fig. S40 ^{13}C{^{1}H} NMR (126 MHz) spectrum of compound **3ea**

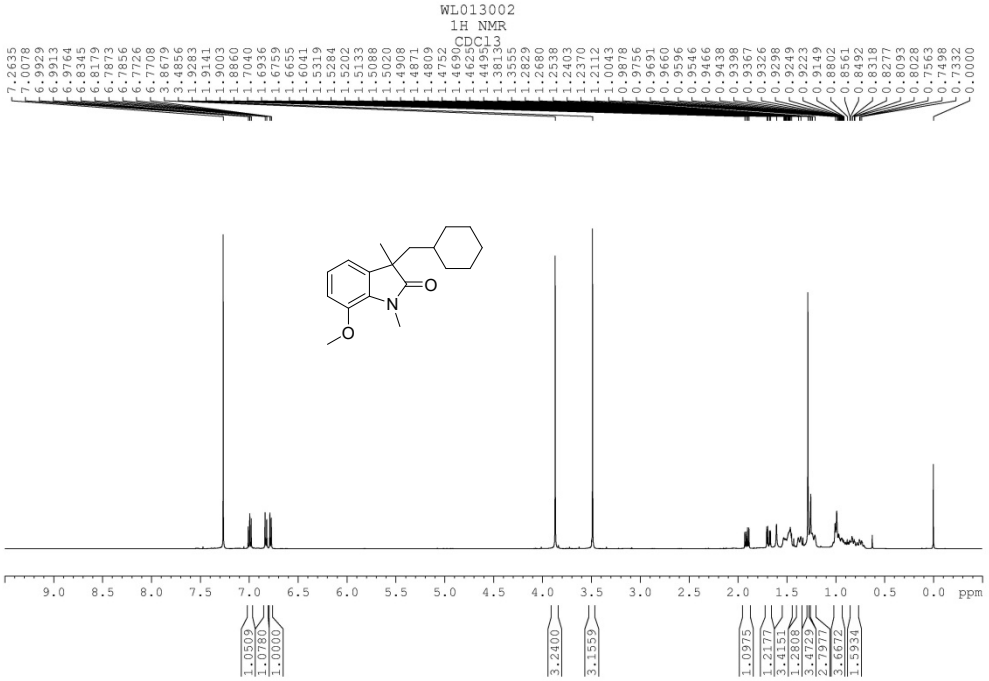


Fig. S41 ^{1}H NMR (500 MHz) spectrum of compound **3fa**

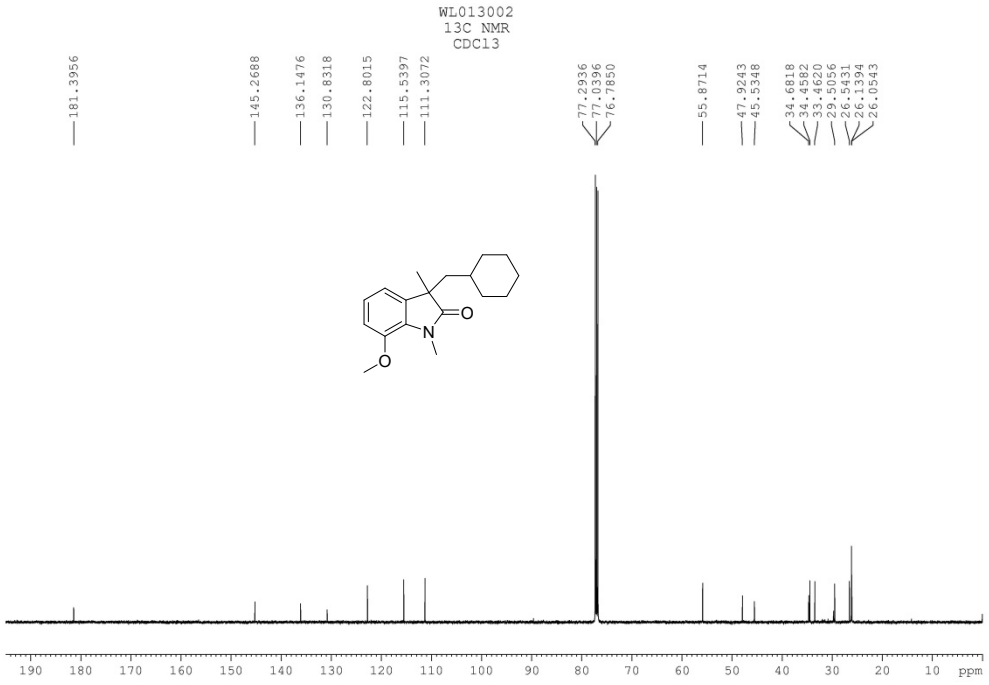


Fig. S42 ^{13}C{^{1}H} NMR (126 MHz) spectrum of compound **3fa**

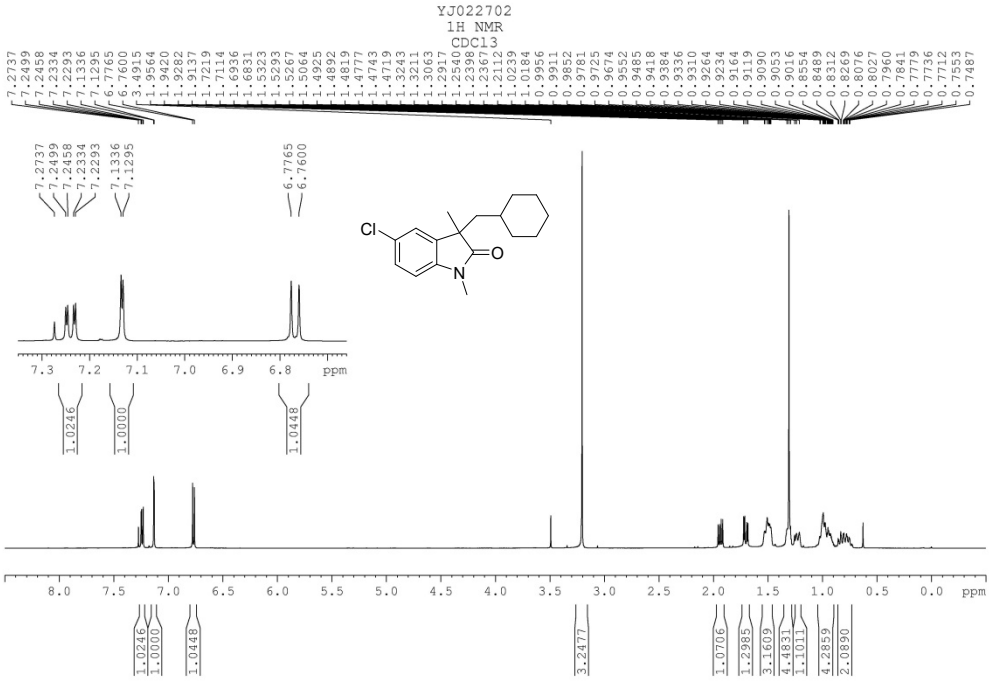


Fig. S43 ^{1}H NMR spectrum of compound **3ga**

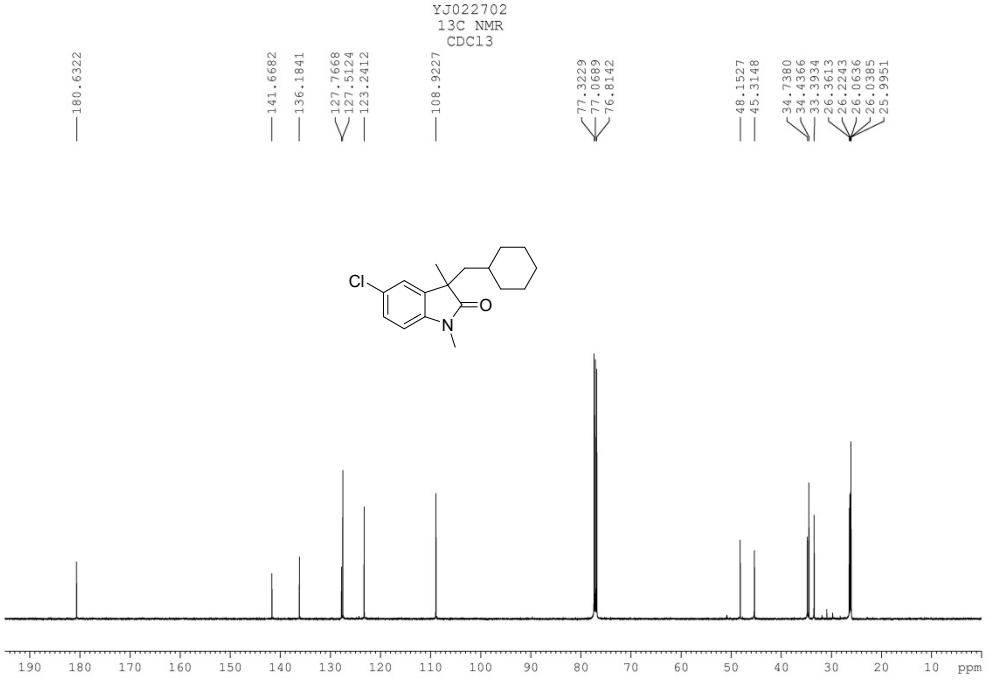


Fig. S44 ^{13}C{^{1}H} NMR spectrum of compound **3ga**

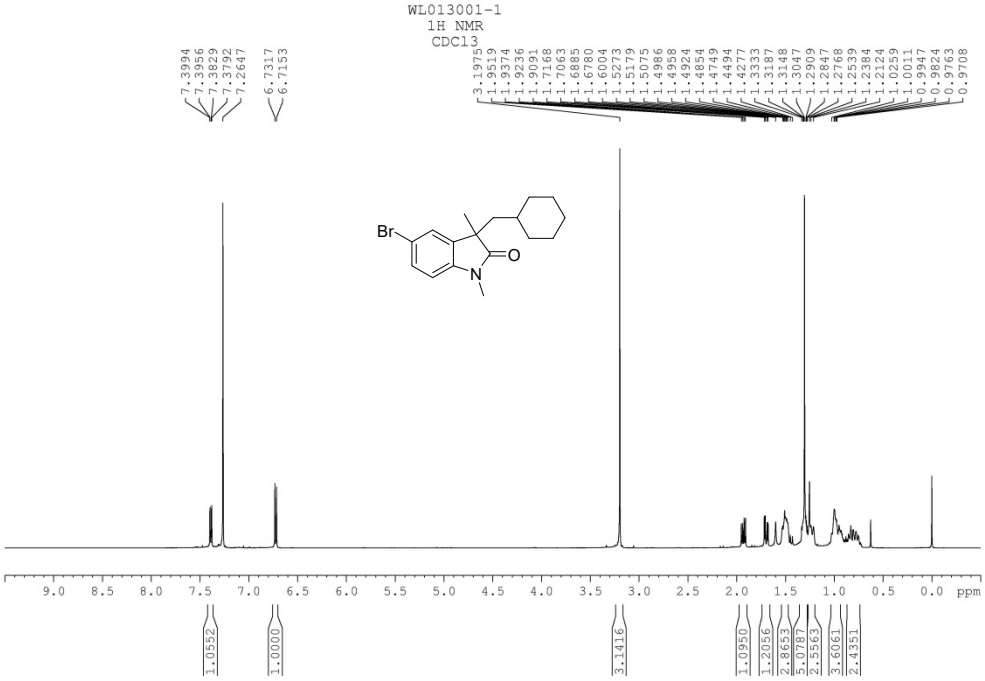


Fig. S45 ^{1}H NMR (500 MHz) spectrum of compound **3ha**

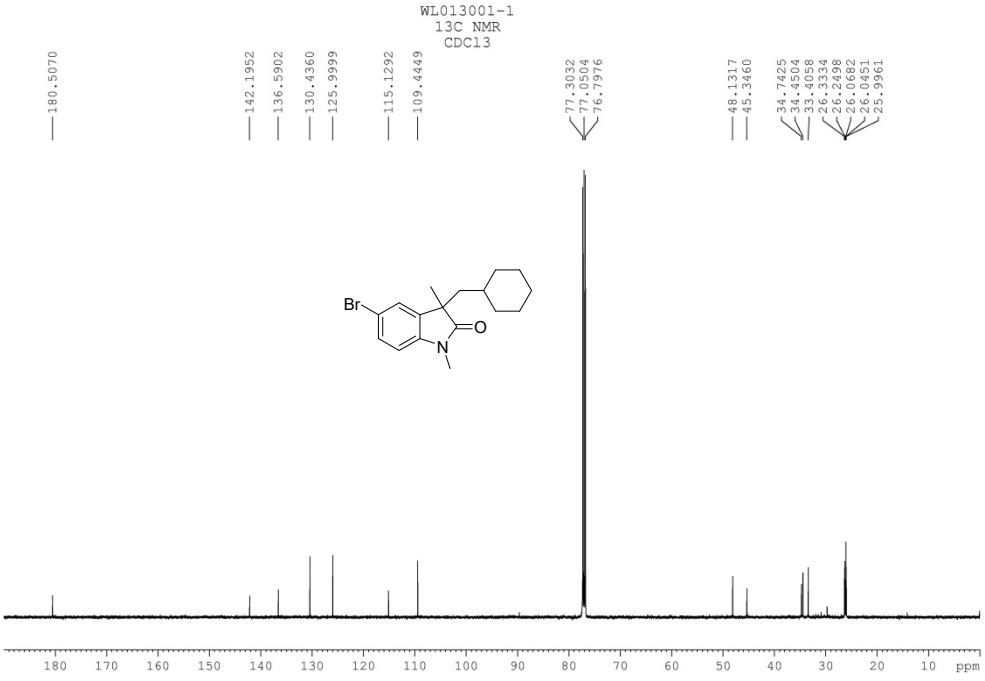


Fig. S46 ^{13}C{^{1}H} NMR (126 MHz) spectrum of compound **3ha**

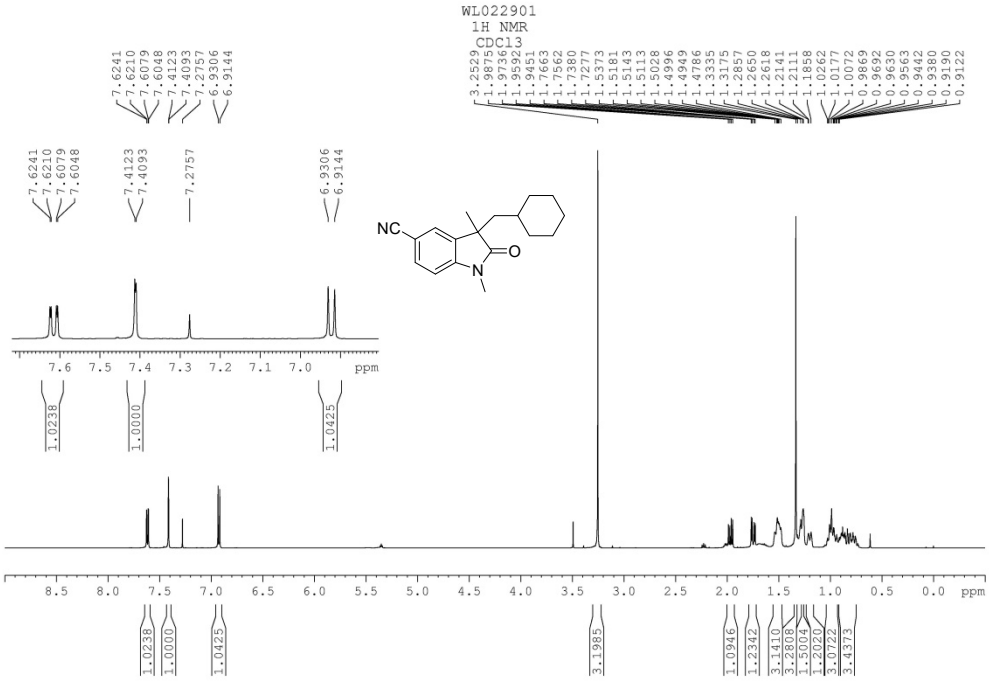


Fig. S47 ^{1}H NMR (500 MHz) spectrum of compound **3ia**

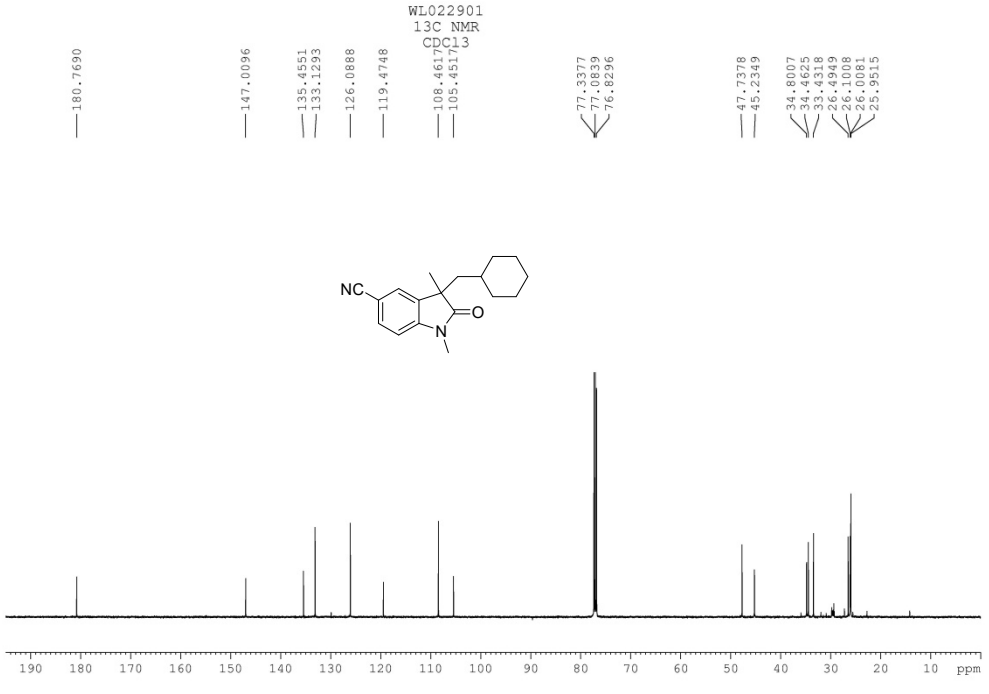


Fig. S48 ^{13}C{^{1}H} NMR (126 MHz) spectrum of compound **3ia**

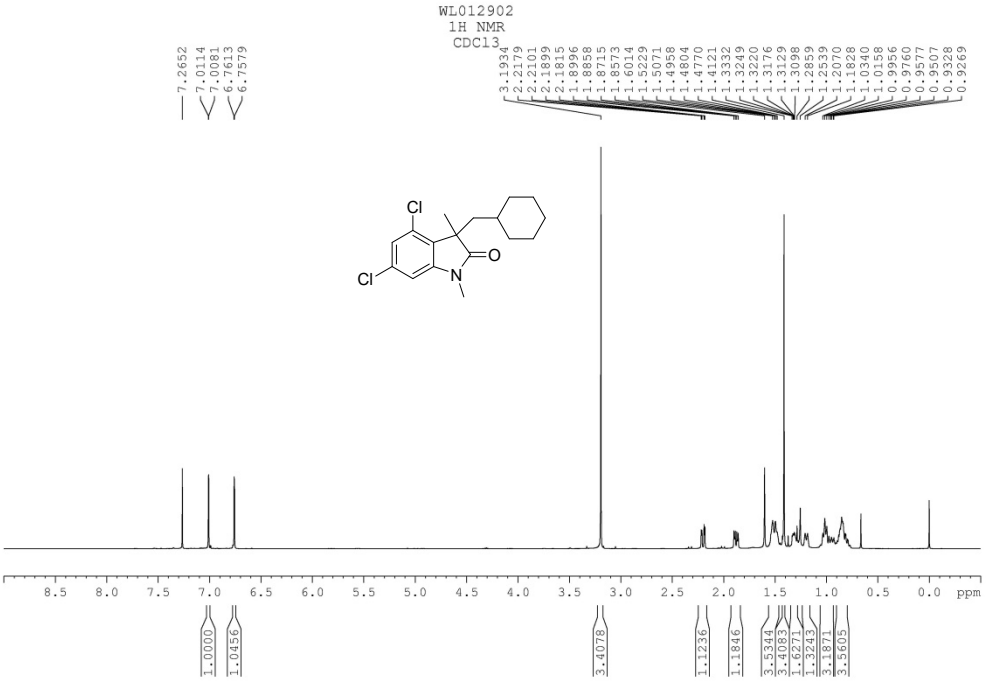


Fig. S49 ^{1}H NMR (500 MHz) spectrum of compound **3ka**

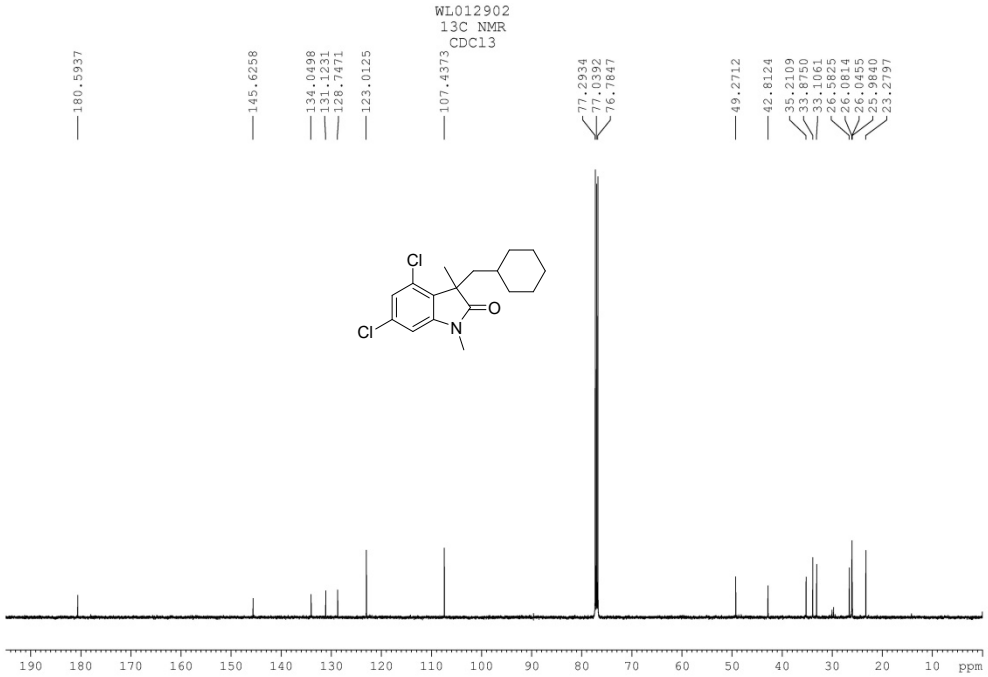


Fig. S50 ^{13}C{^{1}H} NMR (126 MHz) spectrum of compound **3ka**

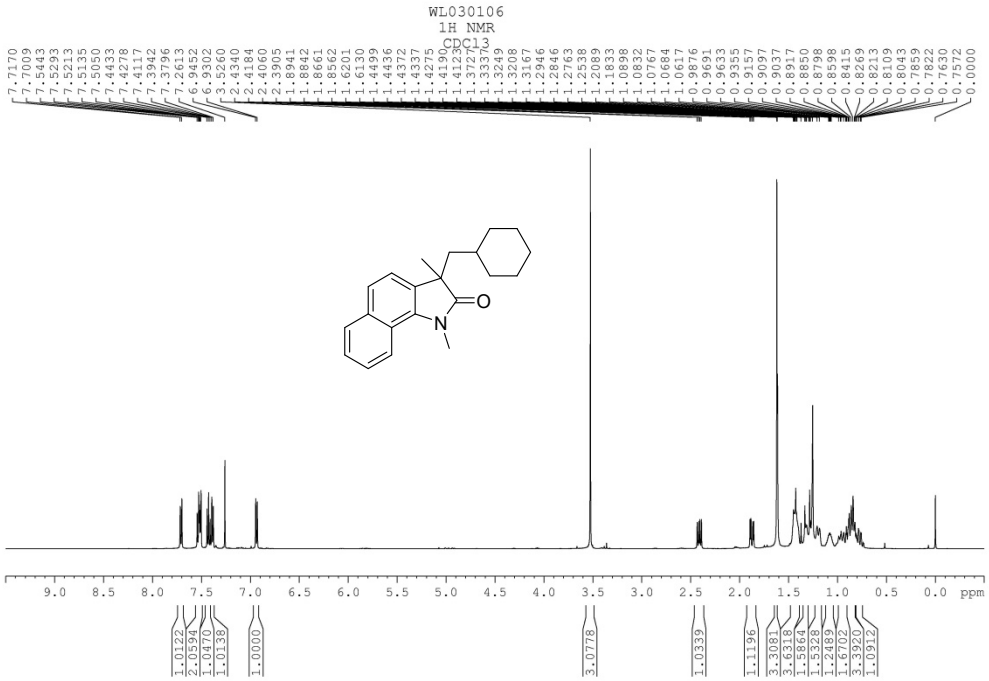


Fig. S51 ^{1}H NMR (500 MHz) spectrum of compound **3la**

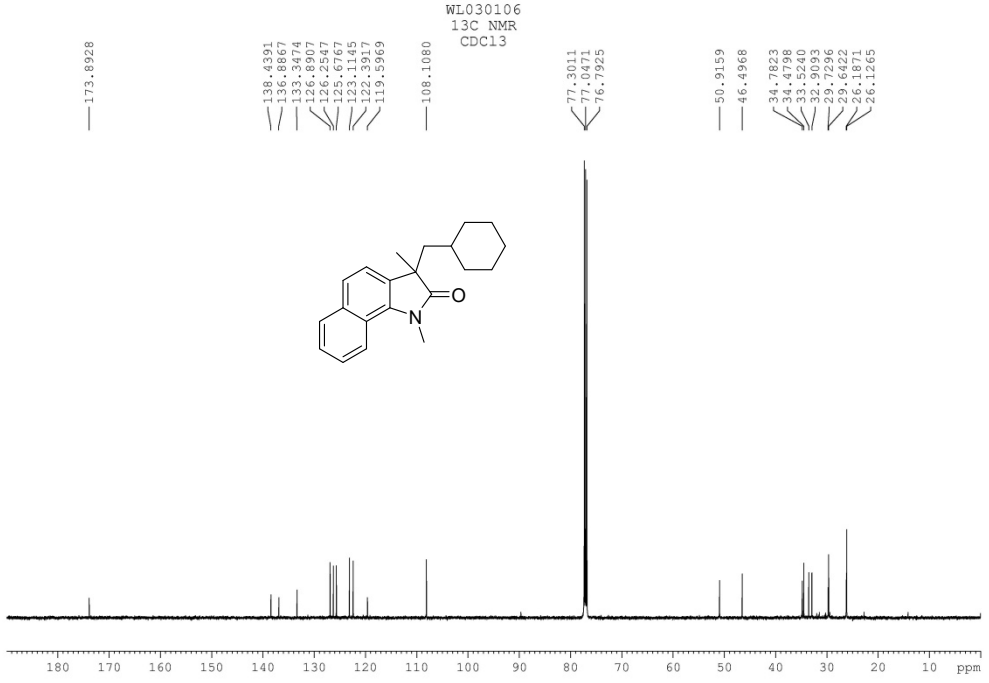


Fig. S52 ^{13}C{^{1}H} NMR (126 MHz) spectrum of compound **3la**

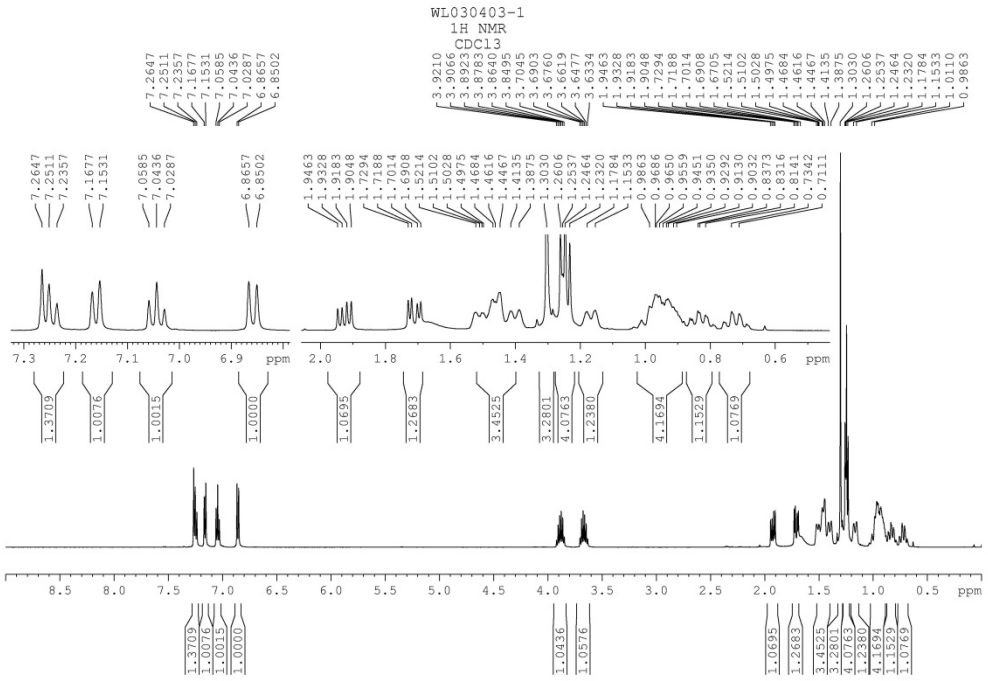


Fig. S53 ^{1}H NMR (500 MHz) spectrum of compound **3ma**

Fig. S54 ^{13}C{^{1}H} NMR (126 MHz) spectrum of compound **3ma**

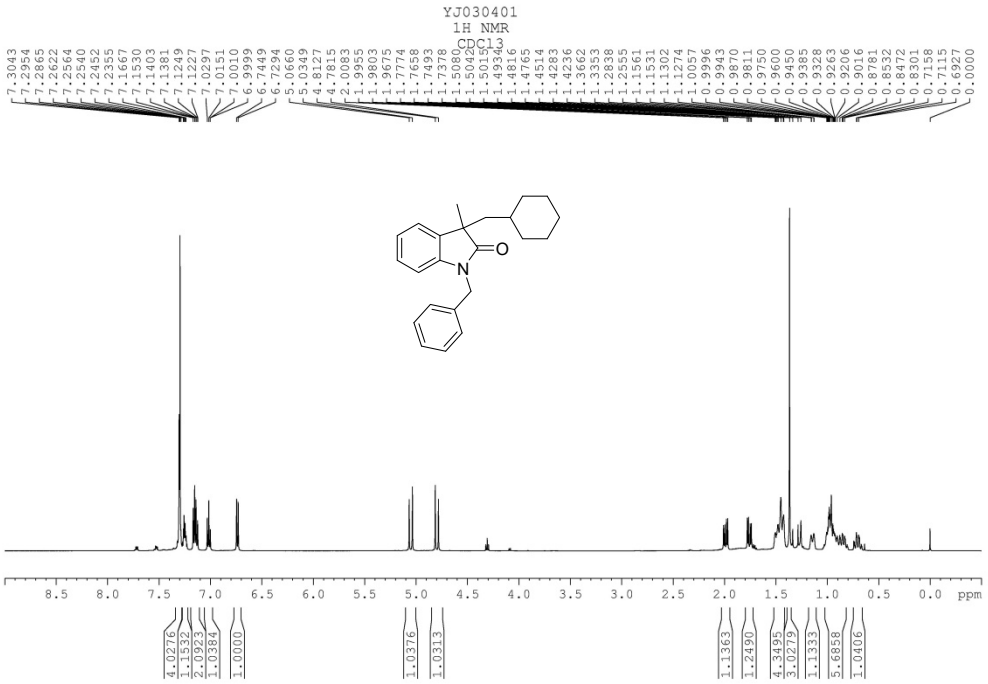


Fig. S55 ^{1}H NMR (500 MHz) spectrum of compound **3na**

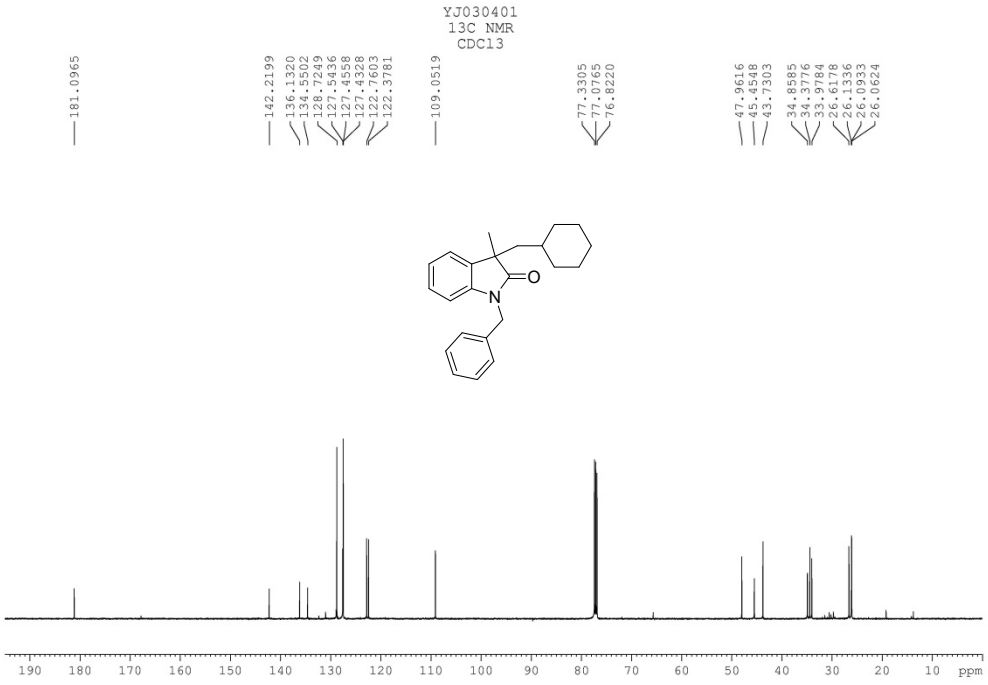


Fig. S56 ^{13}C{^{1}H} NMR (126 MHz) spectrum of compound **3na**

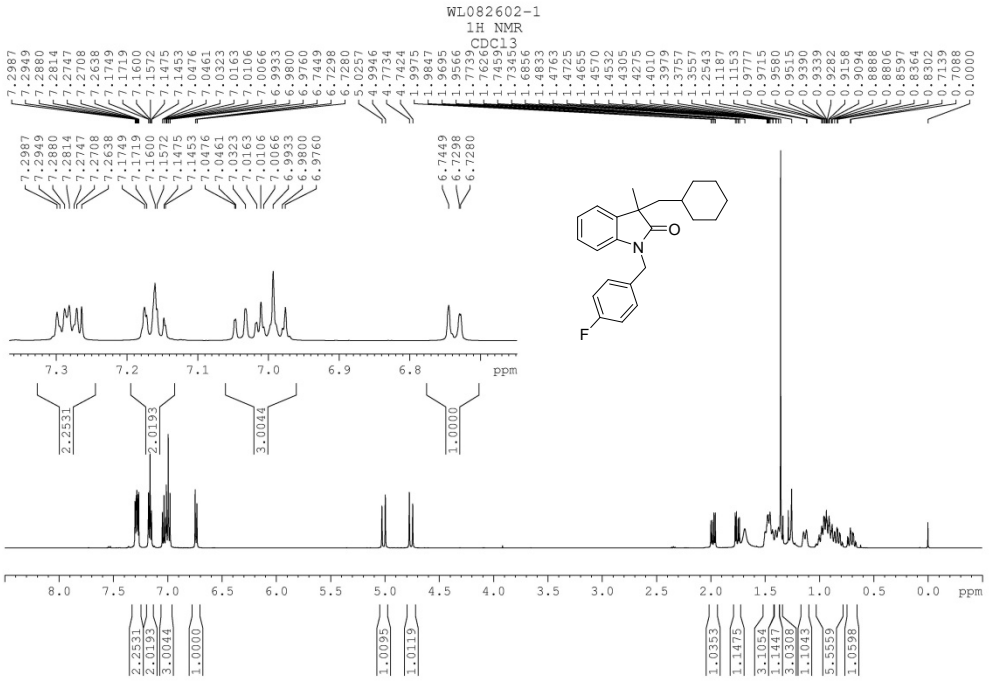


Fig. S57 ^{1}H NMR (500 MHz) spectrum of compound **3oa**

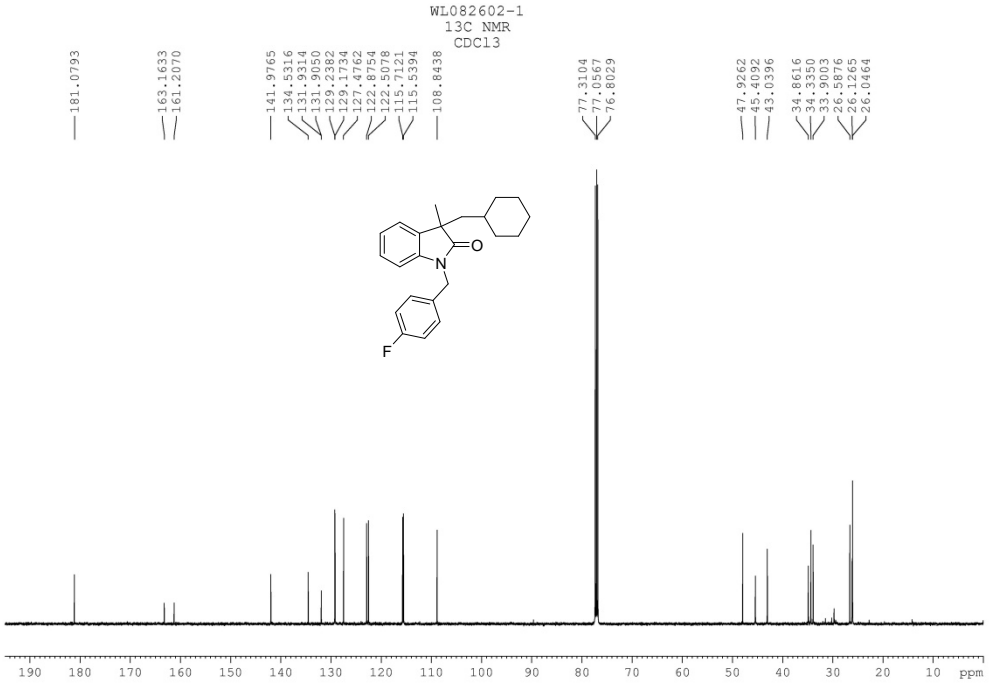


Fig. S58 ^{13}C{^{1}H} NMR (126 MHz) spectrum of compound **3oa**

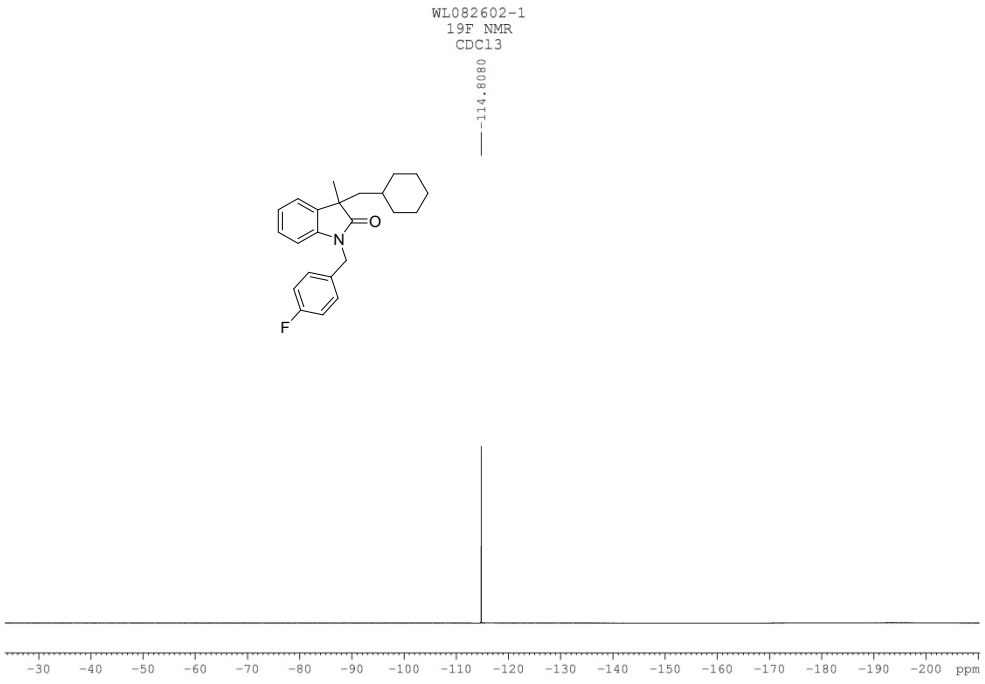


Fig. S59 $^{19}F\{^{1}H\}$ NMR (471 MHz) spectrum of compound **3oa**