

SUPPORTING INFORMATION

Photoredox Nickel-Catalyzed Radical Cyclization of *N*- Arylacrylamides with Alkyl Bromides

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1. General Information

Unless otherwise noted, all the reagents were purchased from commercial suppliers and used without further purification. The light source used for illuminating the reaction vessel consists of 30 W blue LEDs ($\lambda_{\text{max}} = 450 \text{ nm}$) were purchased from Taobao (<https://gpiled.taobao.com/>, manufacture: Shenzhen Star Sources Lighting Technology Co., Ltd.). A clip fan was placed over the reaction vials to cool down the system during the whole reaction process. ^1H NMR spectra were recorded with a Bruker AVANCE III 400 MHz spectrometer. The chemical shifts were recorded in ppm with reference to tetramethylsilane and with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, dd = double doublet, td = triple doublet), coupling constants (in Hz), integration. $^{13}\text{C}\{^1\text{H}\}$ NMR at 100 MHz, and ^{19}F NMR at 376 MHz were collected with complete proton decoupling. Infrared spectra (IR) were measured by FT-IR apparatus. High resolution mass spectroscopy (HRMS) was recorded on TOF MS ES⁺ mass spectrometer and acetonitrile were used to dissolve the sample. Column chromatography was carried out on silica gel (200-300 mesh). All fluorescence measurements were recorded using a Hitachi FL-7000 Fluorometer. Melting points (m.p.) were measured by Büchi 510 melting point apparatus and uncorrected.

2. Experimental Procedures

2.1 Procedure A: preparation of compound 1

Compound **1a**¹, **1b**¹, **1c**¹, **1d**¹, **1e**², **1f**¹, **1g**², **1h**³, **1i**², **1j**¹, **1k**², **1l**¹, **1m**⁴, **1n**², **1o**⁶ are known compounds, and their NMR data are consistent with these reported literature.

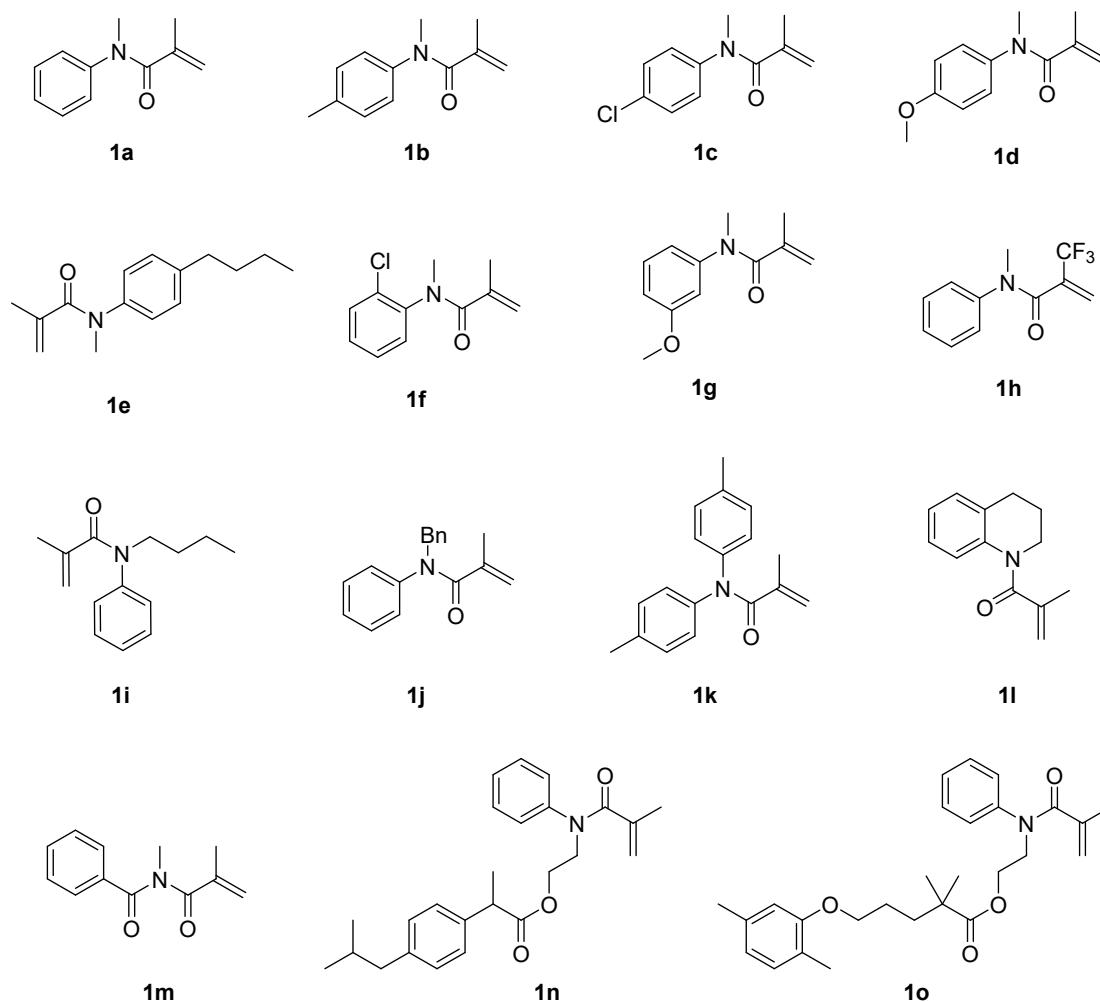


Figure S1. The scope of acrylamides **1**.

2.2 Procedure B: preparation of compound 2

Compounds **2a**, **2b**, **2c**, **2d**, **2e**, **2f**, **2g**, **2h**, **2i**, **2j**, **2k**, **2l**, **2m**, **2o**, **2p**, **2q**, **2r**, **2s** are commercially available and were used without further purification.

Compound **2n**⁷, **2t**⁸, **2u**⁸ are known compounds, and their NMR data are consistent with these reported literature.

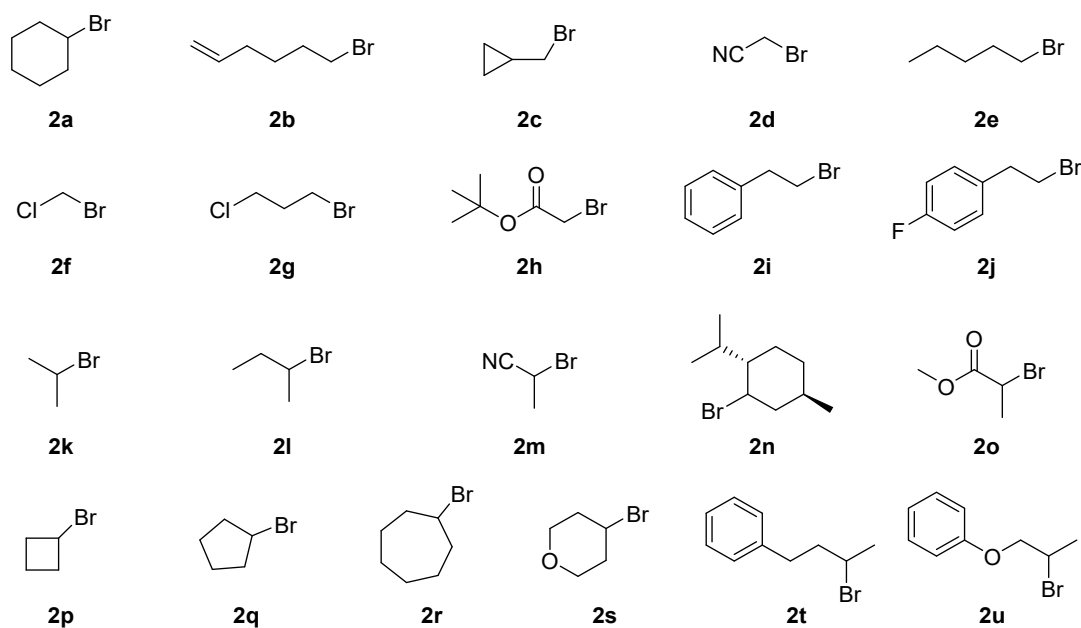
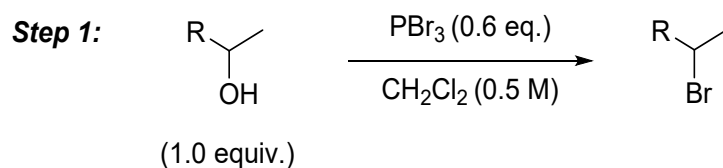


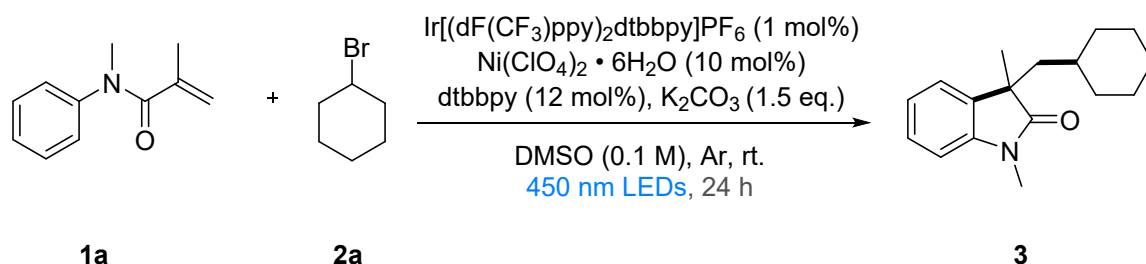
Figure S2. The scope of alkyl bromides **2**.

Compound **2n**, **2t**, **2u** was prepared following the literature by step **1**.



Step 1⁹: To a 50 mL round bottomed flask, alcohol (1.0 eq.) in CH₂Cl₂ (0.5 M) was added. The reaction mixture was cooled to 0 °C and stirred for further 10 minutes. Add PBr₃ (0.6 eq.) dropwise to the flask. After 10 minutes, the reaction mixture was warmed slowly to room temperature and stirred overnight. Cool the reaction to room temperature. Water was added to the reaction mixture, and the aqueous solution was extracted with ethyl acetate. The combined organic extracts were washed with brine, and dried over Na₂SO₄. The extracts were concentrated on a rotary evaporator to give the crude product. Purify the crude product by flash chromatography to obtain the product.

2.3 Procedure C: preparation of compound 3



(Using the synthesis of 3 as an example) To an oven-dried 15 mL reaction tube equipped with a magnetic stir bar, **1a** (0.2 mmol, 1.0 eq.), Ir[(dF(CF₃)ppy)₂dtbbpy]PF₆ (1 mol%) (2mg, 1 mol%), K₂CO₃ (0.3mmol, 1.5 eq.), Ni(ClO₄)₂·6H₂O (7.4 mg, 10 mol%) and dtbbpy (6.4 mg, 12 mol%) were added. The reaction tube was evacuated and backfilled with argon for three times, then DMSO (2.0 mL) was added *via* a 2.5 mL syringe and the mixture was stirred for 15 min. Subsequently, **2a** (0.6 mmol, 3.0 eq., 66 μL) was added to the reaction mixture *via* a 100 μL microsyringe. Then the reaction mixture was stirred at 24 h under irradiation of 30 W blue LEDs (distance app. 3 cm). Thereafter, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (PE/EA = 9:1 to 4:1) to afford the desired pure product **3**.

2.4 Procedure D: scale-up synthesis of 3

To an oven-dried 120 mL reaction tube equipped with a magnetic stir bar, **1a** (2.0 mmol, 1.0 eq.), Ir[(dF(CF₃)ppy)₂dtbbpy]PF₆ (1 mol%) (20 mg, 1 mol%), K₂CO₃ (3.0mmol, 1.5 eq.), Ni(ClO₄)₂·6H₂O (74 mg, 10 mol%) and dtbbpy (64 mg, 12 mol%) were added. The reaction vessel was evacuated and backfilled with argon for three times, then DMSO (20 mL) was added *via* a 20 mL syringe and the mixture was stirred for 15 min. Subsequently, **2a** (6.0 mmol, 3.0 eq., 0.74 mL) was added to the reaction mixture *via* a 1 mL syringe. Then, the reaction mixture was stirred at room temperature for 24 h under irradiation of a 30 W 450 nm blue LEDs (distance app. 5 cm). Then, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (PE/EA = 9:1 to 4:1) to afford the desired pure product **3** (365 mg, 71% yield).

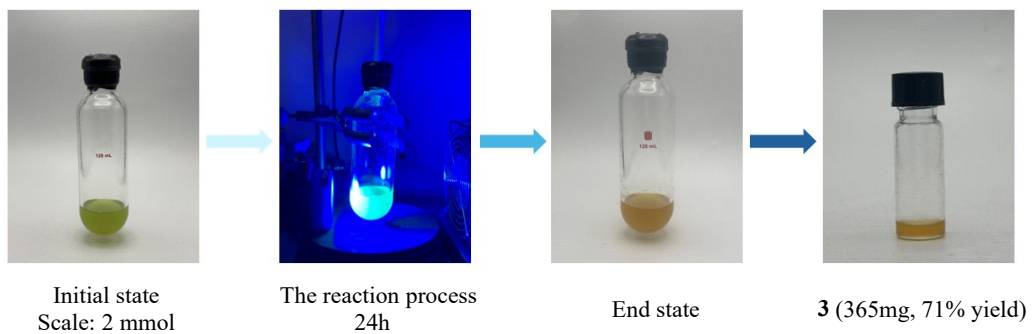
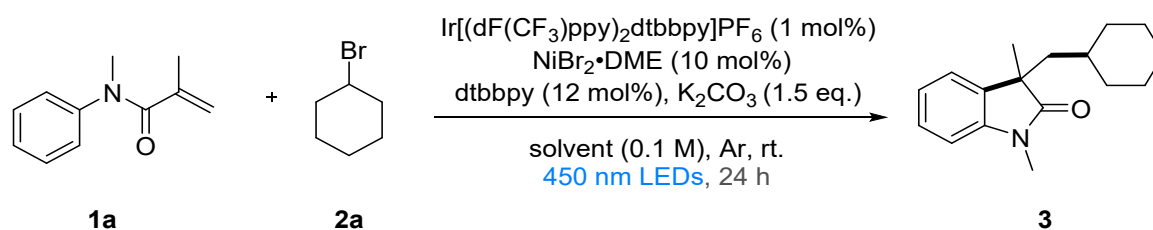


Figure S3. Scale-up reaction

3. Detailed Optimization of Reaction Conditions

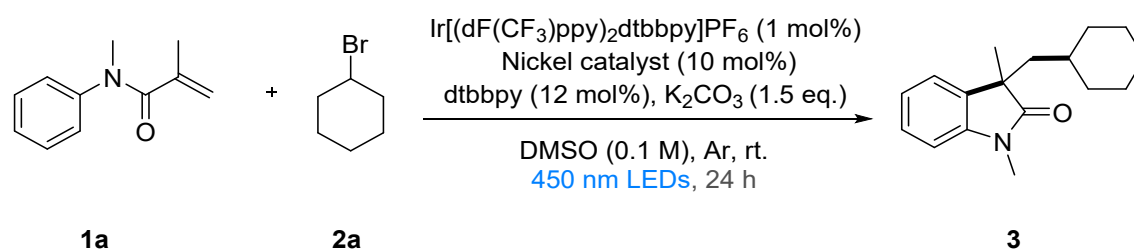
3.1 Solvent screening



Entry	Solvent	Yield 3 (%) ^b
1	MeOH	11
2	DMF	trace
3	MeCN	12
4	EtOH	15
5	DMSO	23
6	DEGME	13

^aReaction conditions: **1a** (0.6 mmol, 3.0 eq.), **2a** (0.2 mmol, 1.0 eq.), NiBr₂·DME (10 mol%), dtbbpy (12 mol%), Ir[(dF(CF₃)ppy)₂dtbbpy]PF₆ (1 mol%), solvent (0.1 M), K₂CO₃ (1.5 eq.), 30 W blue LEDs (450 nm), Ar, rt, 24 h. ^bYields were determined by ¹H NMR analysis of the crude reaction mixture with 1,3,5-trimethoxybenzene as an internal standard.

3.2 Nickel catalyst screening

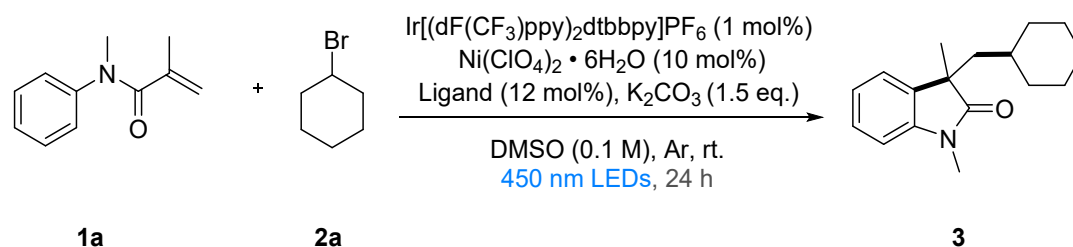


Entry	Nickel catalyst	Yield 3 (%) ^b
1	NiBr ₂ ·DME	23
2	NiI ₂	n.d.
3	NiBr ₂ (PPh ₃) ₂	trace

4	NiCl ₂ ·glyme	24
5	Ni(acac) ₂	11
6	Ni(ClO ₄) ₂ ·6H ₂ O	39
7	Ni(BF ₄)·H ₂ O	24

^aReaction conditions: **1a** (0.6 mmol, 3.0 eq.), **2a** (0.2 mmol, 1.0 eq.), Nickel catalyst (10 mol%), dtbbpy (12 mol%), Ir[(dF(CF₃)ppy)₂dtbbpy]PF₆ (1 mol%), DMSO (0.1 M), K₂CO₃ (1.5 eq.), 30 W blue LEDs (450 nm), Ar, rt, 24 h. ^bYields were determined by ¹H NMR analysis of the crude reaction mixture with 1,3,5-trimethoxybenzene as an internal standard.

3.3 Ligand screening



Entry	Ligand	Yield 3 (%) ^b
1	L1	39
2	L2	15
3	L3	30
4	L4	trace
5	L5	n.d.

^aReaction conditions: **1a** (0.6 mmol, 3.0 eq.), **2a** (0.2 mmol, 1.0 eq.), Ni(ClO₄)₂·6H₂O (10 mol%), ligand (12 mol%), Ir[(dF(CF₃)ppy)₂dtbbpy]PF₆ (1 mol%), DMSO (0.1 M), K₂CO₃ (1.5 eq.), 30 W blue LEDs (450 nm), Ar, rt, 24 h. ^bYields were determined by ¹H NMR analysis of the crude reaction mixture with 1,3,5-trimethoxybenzene as an internal standard.

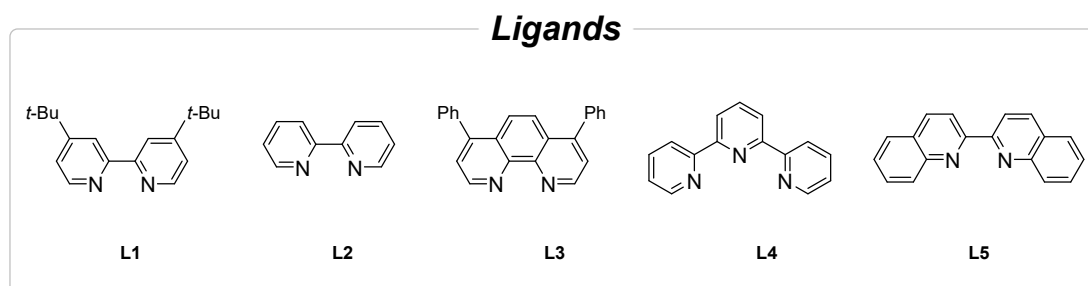
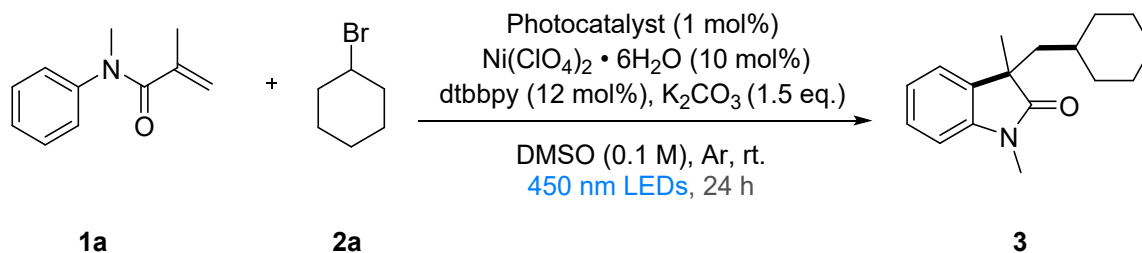


Figure S4. the scope of ligands.

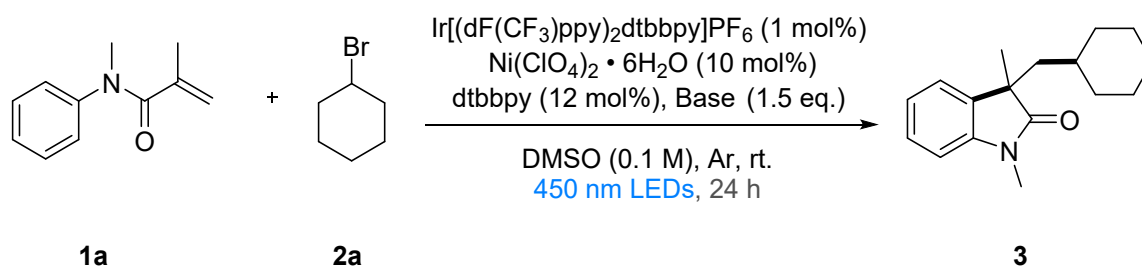
3.4 Photocatalyst screening



Entry	Photocatalyst	Yield 3 (%) ^b
1	Ir[(dF(CF ₃)ppy) ₂ dtbbpy]PF ₆	39
2	Ir[(ppy) ₂ dtbbpy]PF ₆	24
3	Ru(bpy) ₃ (PF ₆) ₂	n.d.
4	4-CzIPN	25

^aReaction conditions: **1a** (0.6 mmol, 3.0 eq.), **2a** (0.2 mmol, 1.0 eq.), Ni(ClO₄)₂ · 6H₂O (10 mol%), dtbbpy (12 mol%), photocatalyst (1 mol%), DMSO (0.1 M), K₂CO₃ (1.5 eq.), 30 W blue LEDs (450 nm), Ar, rt, 24 h. ^bYields were determined by ¹H NMR analysis of the crude reaction mixture with 1,3,5-trimethoxybenzene as an internal standard.

3.5 Base screening

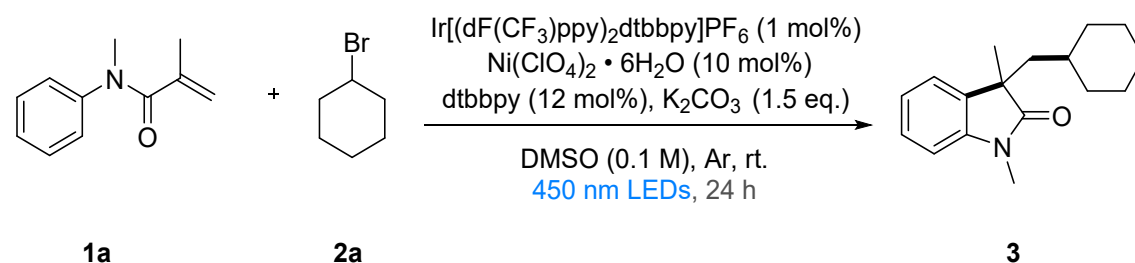


Entry	Base	Yield 3 (%) ^b
1	K ₂ CO ₃	39
2	Na ₂ CO ₃	36
3	K ₃ PO ₄	25
4	CH ₃ COONa	32
5	NaOH	trace

6	DBU	38
7	Et ₃ N	trace
8	NaHCO ₃	25
9	DABCO	31
10	NaF	trace

^aReaction conditions: **1a** (0.6 mmol, 3.0 eq.), **2a** (0.2 mmol, 1.0 eq.), Ni(ClO₄)₂·6H₂O (10 mol%), dtbbpy (12 mol%), Ir[(dF(CF₃)ppy)₂dtbbpy]PF₆ (1 mol%), DMSO (0.1 M), base (1.5 eq.), 30 W blue LEDs (450 nm), Ar, rt, 24 h. ^bYields were determined by ¹H NMR analysis of the crude reaction mixture with 1,3,5-trimethoxybenzene as an internal standard.

3.6 Detailed Optimization of Reaction Conditions



Entry	1a : 2a	Yield ^b 3 (%)
1 ^a	3:1	39
2	1:2	58
3	1:3	73
4	1:4	56

^aReaction conditions: **1a** (0.6 mmol, 3 eq.), **2a** (0.2 mmol, 1.0 eq.), Ni(ClO₄)₂·6H₂O (10 mol%), dtbbpy (12 mol%), Ir[(dF(CF₃)ppy)₂dtbbpy]PF₆ (1 mol%), DMSO (0.1 M), K₂CO₃ (1.5 eq.), 30 W blue LEDs (450 nm), Ar, rt, 24 h. ^bYields were determined by ¹H NMR analysis of the crude reaction mixture with 1,3,5-trimethoxybenzene as an internal standard.

4. Limitation of the Substrate Scope

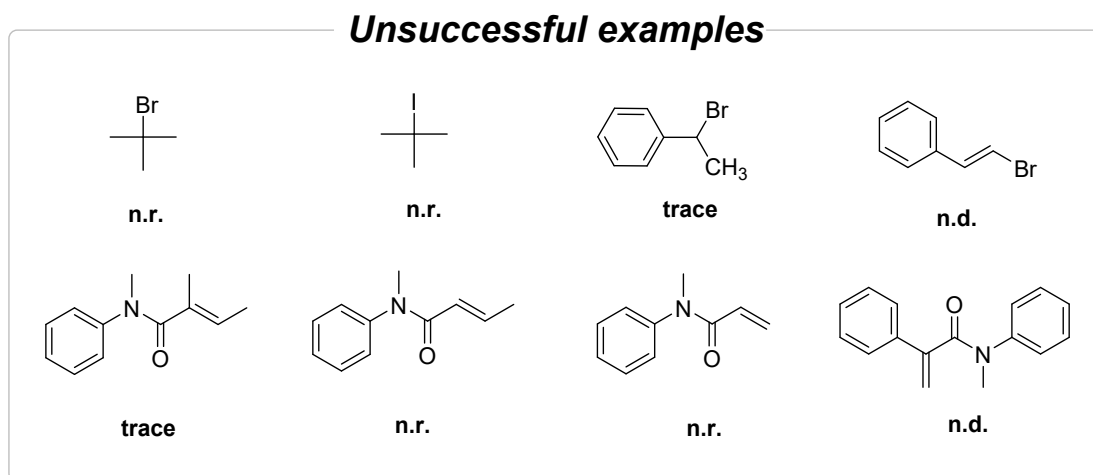
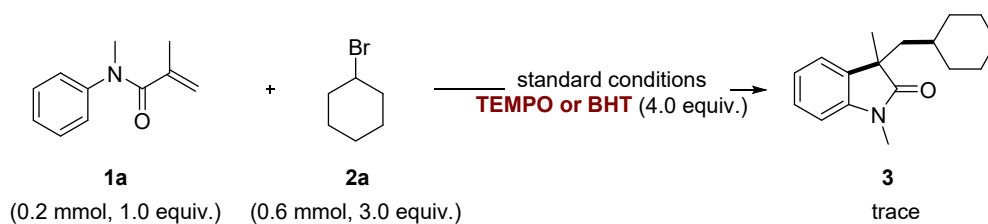


Figure S5. Limitation of the substrate scope.

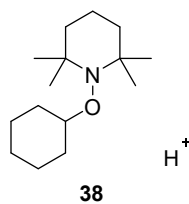
5. Mechanistic Studies

5.1 Trapping experiment

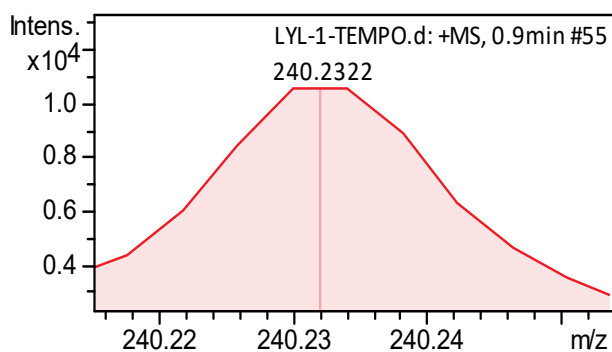
Radical trapping experiments between **1a** and **2a** were conducted under standard conditions with trapping agents (TEMPO or BHT) to capture the putative radicals. The expected product **3** was obtained in trace. ESI-MS analysis of the crude reaction mixture was performed, and the corresponding radical adducts were successfully detected by HRMS (**Figure S6**).



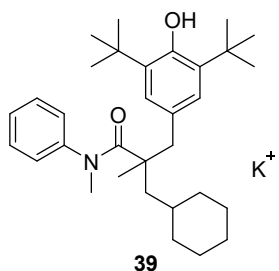
detected by HRMS



38
Chemical Formula: C₁₅H₃₀NO⁺
[M+H]⁺ Calcd: 240.2322
Found: 240.2322



detected by HRMS



39
Chemical Formula: C₃₂H₄₇KNO₂⁺
[M+K]⁺ Calcd: 516.3238
Found: 516.3262

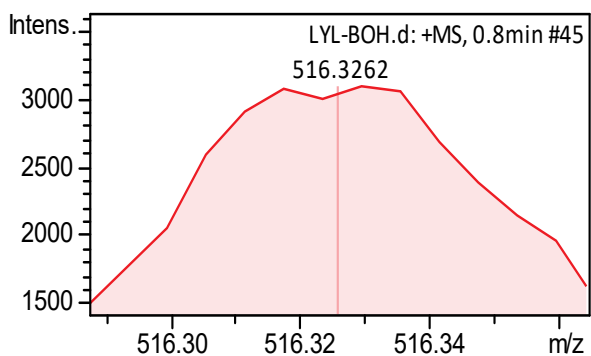
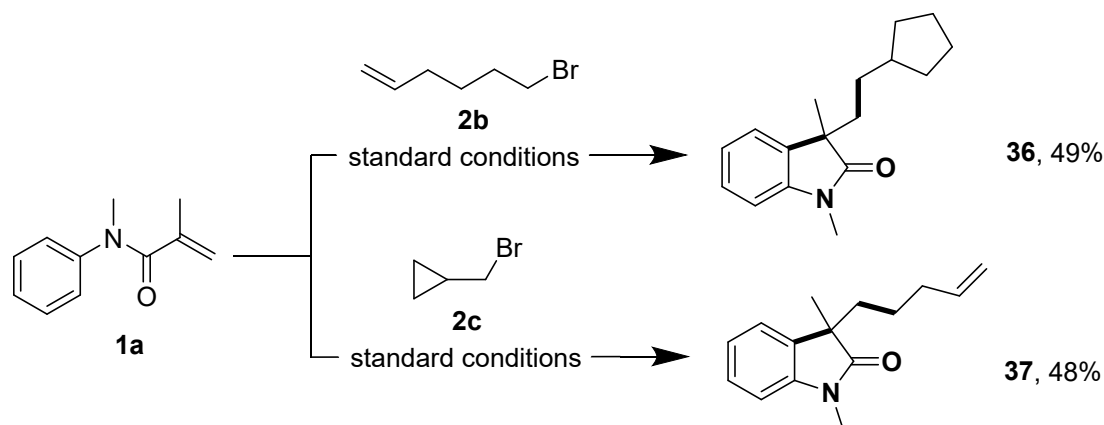


Figure S6. Crude ESI-MS of the radical trapping experiments.

5.2 Radical clock experiments



To an oven-dried 12 mL reaction tube equipped with a magnetic stir bar, **1a** (0.2 mmol, 1.0 eq.), Ir[(dF(CF₃)ppy)₂dtbbpy]PF₆ (2mg, 1 mol%), K₂CO₃ (0.3mmol, 1.5 eq.), Ni(ClO₄)₂·6H₂O (7.4 mg, 10 mol%) and dtbbpy (6.4 mg, 12 mol%) were added. The reaction tube was evacuated and backfilled with argon for three times, then DMSO (2.0 mL) was added *via* a 2.5 mL syringe and the mixture was stirred for 15 min. Subsequently, **2b/2c** was added to the reaction mixture *via* a 100 μL microsyringe. Then the reaction mixture was stirred for 24 h under irradiation of 30 W blue LEDs (distance app. 3 cm). Thereafter, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (PE/EA = 9:1 to 4:1) to afford the desired pure product.

5.3 Time profile of the transformation with the light ON-OFF over time

Standard reaction was set up with **1a** (1.0 eq.) and **2j** (3.0 eq.) in a 0.4 mmol scale according to the experiment procedure for the preparation of **20**, and extra 3.0 eq. of benzotrifluoride was added as internal standard to determine the NMR yield. The reaction was placed in light or dark in every alternative 1 hour. After every time interval of 1 hours, the reaction aliquot (100 μL) from the reaction mixture was transferred into a nuclear magnetic tube charged with 400 μL of CDCl₃. The yield of product was determined by ¹⁹F NMR using benzotrifluoride as internal standard.

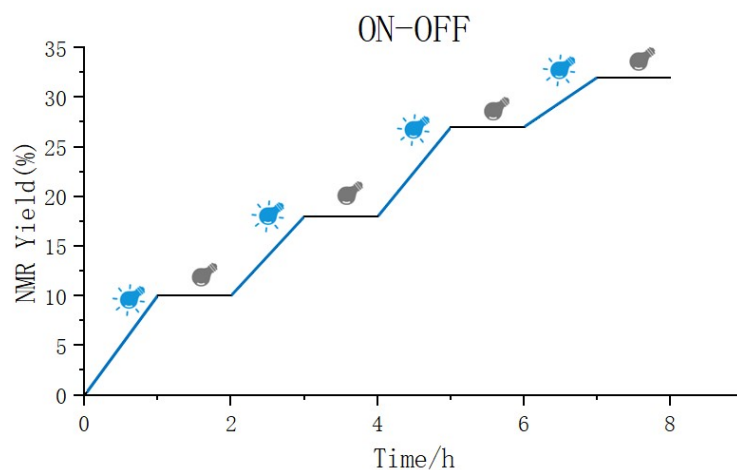
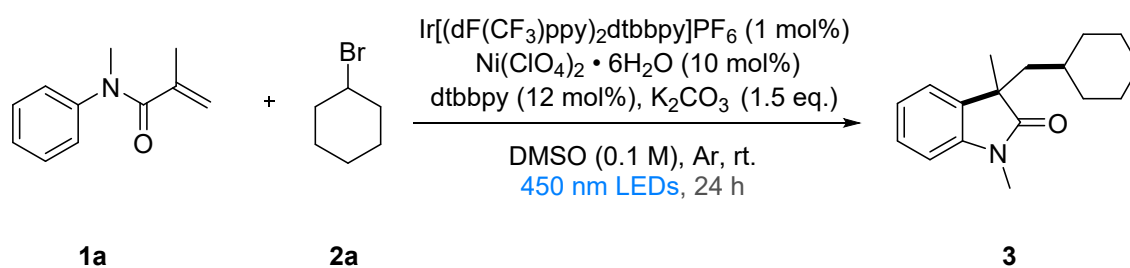


Figure S7 Time profile of the NMR yield with the light on/off over time.

5.4 Control experiments



Entry	PC	[Ni]	Ligand	Base	$h\nu$	Ar	Yield ^b 3 (%)
1	-	+	+	+	+	+	trace
2	+	-	+	+	+	+	trace
3	+	+	-	+	+	+	trace
4	+	+	+	-	+	+	trace
5	+	+	+	+	-	+	n.r.
6	+	+	+	+	+	-	n.d.

^aReaction conditions: **1a** (0.2 mmol, 1.0 eq.), **2a** (0.6 mmol, 3.0 eq.), Ni(ClO₄)₂·6H₂O (10 mol%), dtbbpy (12 mol%), Ir[(dF(CF₃)ppy)₂dtbbpy]PF₆ (1 mol%), DMSO (0.1 M), K₂CO₃ (1.5 eq.), 30 W blue LEDs (450 nm), Ar, rt, 24 h. ^bYields were determined by ¹H NMR analysis of the crude reaction mixture with 1,3,5-trimethoxybenzene as an internal standard.

5.5 Emission quenching experiments (Stern-Volmer Studies)

All fluorescence measurements were recorded using a Hitachi FL-7000 Fluorometer. Quenching studies were conducted in MeCN. Measurements using corresponding quenchers were taken in triplicate at different concentrations.

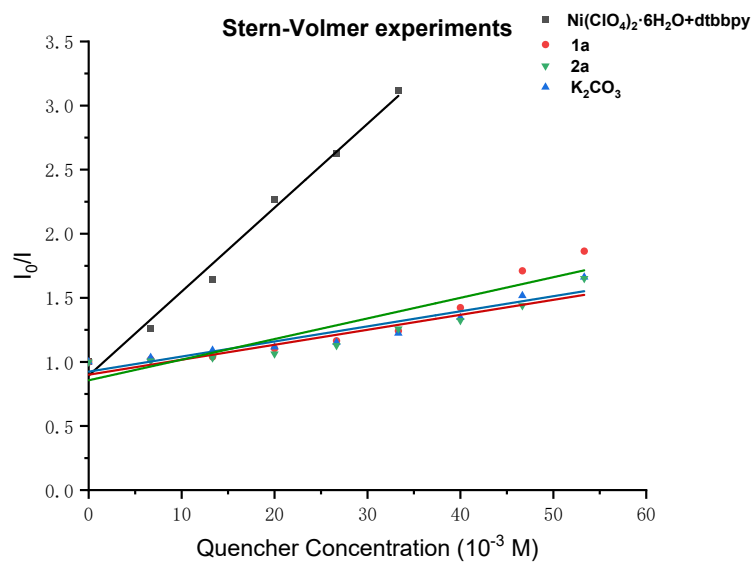
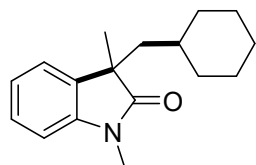


Figure S8 Stern-Volmer experiments in MeCN.

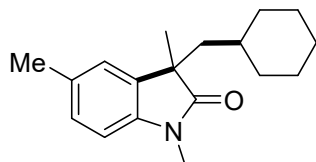
6. Characterization Data of Compounds



3¹⁰: Colorless oil (38 mg, yield 73%) using the general procedure C;

$R_f = 0.7$ (PE/EA: 4/1);

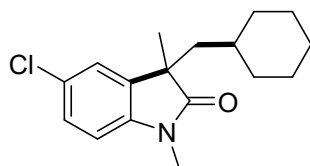
¹H NMR (400 MHz, CDCl₃) δ 7.27 (td, $J = 7.7, 1.1$ Hz, 1H), 7.18 – 7.14 (m, 1H), 7.06 (td, $J = 7.5, 0.7$ Hz, 1H), 6.85 (d, $J = 7.7$ Hz, 1H), 3.22 (s, 3H), 1.93 (dd, $J = 14.0, 7.0$ Hz, 1H), 1.73 (dd, $J = 14.0, 5.2$ Hz, 1H), 1.55 – 1.43 (m, 3H), 1.38 – 1.29 (m, 4H), 1.21 (d, $J = 12.7$ Hz, 1H), 1.03 – 0.68 (m, 6H).



4¹¹: Colorless oil (45 mg, yield 82%) using the general procedure C;

$R_f = 0.7$ (PE/EA: 4/1);

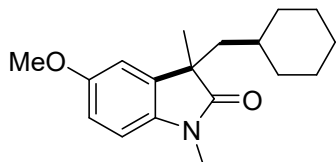
¹H NMR (400 MHz, CDCl₃) δ 7.05 (d, $J = 7.8$ Hz, 1H), 6.96 (s, 1H), 6.72 (d, $J = 7.8$ Hz, 1H), 3.19 (s, 3H), 2.35 (s, 3H), 1.91 (dd, $J = 14.0, 7.1$ Hz, 1H), 1.69 (dd, $J = 14.0, 5.2$ Hz, 1H), 1.54 – 1.40 (m, 3H), 1.35 (d, $J = 12.9$ Hz, 1H), 1.29 (s, 3H), 1.25 – 1.20 (m, 1H), 1.04 – 0.91 (m, 4H), 0.88 – 0.70 (m, 2H).



5¹²: Colorless oil (33 mg, yield 57%) using the general procedure C;

$R_f = 0.7$ (PE/EA: 4/1);

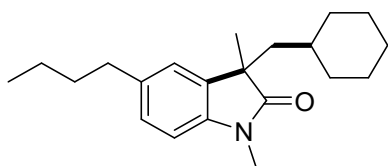
¹H NMR (400 MHz, CDCl₃) δ 7.23 (dd, $J = 8.2, 2.1$ Hz, 1H), 7.12 (d, $J = 2.0$ Hz, 1H), 6.75 (d, $J = 8.3$ Hz, 1H), 3.19 (s, 3H), 1.92 (dd, $J = 14.1, 7.1$ Hz, 1H), 1.69 (dd, $J = 14.1, 5.2$ Hz, 1H), 1.54 – 1.44 (m, 3H), 1.33 (s, 1H), 1.30 (s, 3H), 1.26 – 1.19 (m, 1H), 1.03 – 0.89 (m, 4H), 0.87 – 0.70 (m, 2H).



6¹²: Pale yellow oil (51 mg, yield 88%) using the general procedure **C**;

$R_f = 0.7$ (PE/EA: 4/1);

¹H NMR (400 MHz, CDCl₃) δ 6.81 – 6.69 (m, 3H), 3.79 (s, 3H), 3.17 (s, 3H), 1.91 (dd, $J = 14.0, 7.0$ Hz, 1H), 1.68 (dd, $J = 14.0, 5.2$ Hz, 1H), 1.53 – 1.42 (m, 3H), 1.38 – 1.30 (m, 1H), 1.29 (s, 3H), 1.26 – 1.18 (m, 1H), 1.03 – 0.89 (m, 4H), 0.86 – 0.67 (m, 2H).



7: Colorless liquid (37 mg, yield 59%) using the general procedure **C**;

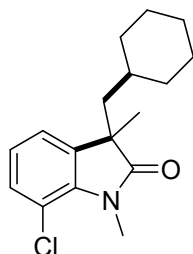
$R_f = 0.7$ (PE/EA: 4/1);

IR (neat) ν 2919, 1708, 1599, 1494, 1242, 1054, 809, 701 cm⁻¹;

¹H NMR (400 MHz, CDCl₃) δ 7.06 (dd, $J = 7.9, 1.7$ Hz, 1H), 6.98 (d, $J = 1.7$ Hz, 1H), 6.75 (d, $J = 7.9$ Hz, 1H), 3.20 (s, 3H), 2.61 (t, $J = 7.6$ Hz, 2H), 1.91 (dd, $J = 14.0, 6.7$ Hz, 1H), 1.71 (dd, $J = 14.0, 5.3$ Hz, 1H), 1.64 – 1.55 (m, 2H), 1.53 – 1.42 (m, 3H), 1.35 (t, $J = 7.4$ Hz, 3H), 1.31 (s, 3H), 1.24 – 1.16 (m, 1H), 1.01 – 0.89 (m, 7H), 0.88 – 0.67 (m, 2H);

¹³C{¹H} NMR (100 MHz, CDCl₃) δ 181.2, 140.9, 137.0, 134.4, 127.2, 123.0, 107.6, 48.0, 45.4, 35.4, 34.7, 34.5, 34.1, 33.6, 26.3, 26.1, 26.1, 22.2, 14.0;

HRMS (ESI) m/z : [M+H]⁺+MeCN Calcd for C₂₃H₃₅N₂O⁺ 355.2744; Found 354.2745.

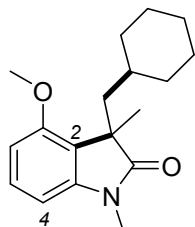


8¹¹: Pale yellow oil (20 mg, yield 35%) using the general procedure **C**;

$R_f = 0.7$ (PE/EA: 4/1);

¹H NMR (400 MHz, CDCl₃) δ 7.18 (dd, $J = 8.0, 1.3$ Hz, 1H), 7.05 – 7.01 (m, 1H), 6.95

(t, $J = 7.7$ Hz, 1H), 3.58 (s, 3H), 1.93 (dd, $J = 14.1, 6.9$ Hz, 1H), 1.69 (dd, $J = 14.1, 5.1$ Hz, 1H), 1.57 – 1.45 (m, 3H), 1.39 – 1.33 (m, 1H), 1.30 (s, 3H), 1.21 (d, $J = 12.4$ Hz, 1H), 1.04 – 0.86 (m, 4H), 0.85 – 0.70 (m, 2H).



9-C2¹³: Yellow oil (34 mg, yield 59%) using the general procedure C;

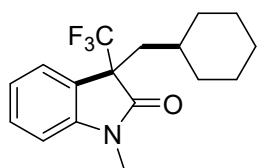
$R_f = 0.7$ (PE/EA: 4/1);

¹H NMR (400 MHz, CDCl₃) δ 7.22 (t, $J = 8.1$ Hz, 1H), 6.60 (d, $J = 8.4$ Hz, 1H), 6.50 (d, $J = 7.7$ Hz, 1H), 3.83 (s, 3H), 3.18 (s, 3H), 2.07 (dd, $J = 13.7, 4.6$ Hz, 1H), 1.81 (dd, $J = 13.7, 6.3$ Hz, 1H), 1.53 – 1.42 (m, 3H), 1.35 (s, 3H), 1.32 – 1.21 (m, 2H), 1.03 – 0.90 (m, 3H), 0.87 – 0.71 (m, 3H).

9-C4¹³: Yellow oil (16 mg, yield 27%) using the general procedure C;

$R_f = 0.7$ (PE/EA: 4/1);

¹H NMR (400 MHz, CDCl₃) δ 7.03 (d, $J = 8.1$ Hz, 1H), 6.56 (dd, $J = 8.1, 2.3$ Hz, 1H), 6.43 (d, $J = 2.2$ Hz, 1H), 3.84 (s, 3H), 3.19 (s, 3H), 1.89 (dd, $J = 14.0, 6.9$ Hz, 1H), 1.68 (dd, $J = 14.0, 5.2$ Hz, 1H), 1.55 – 1.45 (m, 3H), 1.34 (d, $J = 14.9$ Hz, 1H), 1.28 (s, 3H), 1.24 (d, $J = 13.9$ Hz, 1H), 1.05 – 0.95 (m, 3H), 0.93 – 0.69 (m, 3H).

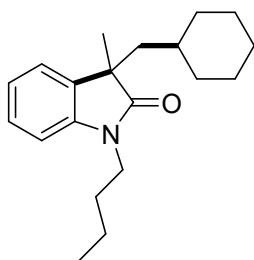


10³: Colorless liquid (21 mg, yield 34%) using the general procedure C;

$R_f = 0.7$ (PE/EA: 4/1);

¹H NMR (500 MHz, CDCl₃) δ 7.39 (td, $J = 7.8, 1.2$ Hz, 1H), 7.33 (d, $J = 7.5$ Hz, 1H), 7.13 (td, $J = 7.6, 1.0$ Hz, 1H), 6.89 (d, $J = 7.8$ Hz, 1H), 3.25 (s, 3H), 2.27 (dd, $J = 13.9, 7.2$ Hz, 1H), 2.05 (dd, $J = 13.9, 5.0$ Hz, 1H), 1.56 – 1.43 (m, 3H), 1.31 (d, $J = 12.5$ Hz, 1H), 1.22 (d, $J = 12.7$ Hz, 1H), 1.04 – 0.76 (m, 6H);

¹⁹F NMR (471 MHz, CDCl₃) δ -73.38.



11: Colorless liquid (40 mg, yield 67%) using the general procedure C;

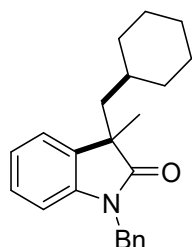
$R_f = 0.7$ (PE/EA: 4/1);

IR (neat) ν 2920, 1705, 1610, 1487, 1190, 1022, 752, 698 cm^{-1} ;

^1H NMR (400 MHz, CDCl_3) δ 7.24 (td, $J = 7.7, 1.3$ Hz, 1H), 7.16 (dd, $J = 7.3, 1.3$ Hz, 1H), 7.04 (td, $J = 7.4, 1.0$ Hz, 1H), 6.85 (d, $J = 7.7$ Hz, 1H), 3.85 – 3.75 (m, 1H), 3.62 (dt, $J = 14.2, 7.1$ Hz, 1H), 1.93 (dd, $J = 14.0, 6.5$ Hz, 1H), 1.71 (dd, $J = 14.0, 5.5$ Hz, 1H), 1.64 (tdd, $J = 7.9, 4.9, 1.5$ Hz, 2H), 1.55 – 1.35 (m, 6H), 1.30 (s, 3H), 1.20 – 1.12 (m, 1H), 1.03 – 0.89 (m, 7H), 0.86 – 0.66 (m, 2H);

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 180.9, 142.6, 134.7, 127.4, 122.8, 122.0, 108.2, 47.8, 45.4, 39.6, 34.8, 34.4, 33.8, 29.5, 26.3, 26.2, 26.1, 26.0, 20.3, 13.8;

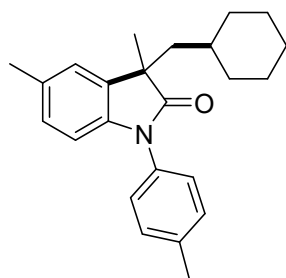
HRMS (ESI) m/z : $[\text{M}+\text{Na}]^{++}\text{MeCN}$ Calcd for $\text{C}_{22}\text{H}_{32}\text{N}_2\text{NaO}^+$ 363.2407; Found 363.2392.



12¹¹: A white solid (42 mg, yield 63%) using the general procedure C;

$R_f = 0.7$ (PE/EA: 4/1);

^1H NMR (400 MHz, CDCl_3) δ 7.31 - 7.28 (m, 4H), 7.27 – 7.22 (m, 1H), 7.18 – 7.11 (m, 2H), 7.01 (t, $J = 7.4$ Hz, 1H), 6.73 (d, $J = 7.7$ Hz, 1H), 5.04 (d, $J = 15.6$ Hz, 1H), 4.80 (d, $J = 15.6$ Hz, 1H), 1.99 (dd, $J = 14.0, 6.3$ Hz, 1H), 1.75 (dd, $J = 14.0, 5.7$ Hz, 1H), 1.53 – 1.40 (m, 4H), 1.36 (s, 3H), 1.15 (d, $J = 11.6$ Hz, 1H), 1.05 – 0.80 (m, 5H), 0.77 – 0.62 (m, 1H).



13: A white solid (14 mg, yield 20%) using the general procedure C;

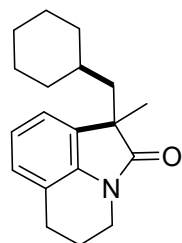
$R_f = 0.7$ (PE/EA: 4/1);

IR (neat) ν 2919, 1716, 1599, 1488, 1207, 1019, 806, 633 cm^{-1} ;

^1H NMR (400 MHz, CDCl_3) δ 7.31 (d, $J = 8.2$ Hz, 2H), 7.27 – 7.23 (m, 2H), 7.03 – 6.95 (m, 2H), 6.70 (d, $J = 7.9$ Hz, 1H), 2.41 (s, 3H), 2.36 (s, 3H), 2.01 (dd, $J = 14.0, 7.4$ Hz, 1H), 1.77 (dd, $J = 14.0, 5.2$ Hz, 1H), 1.58 – 1.47 (m, 4H), 1.41 (s, 3H), 1.34 – 1.24 (m, 2H), 1.06 – 0.97 (m, 3H), 0.91 – 0.76 (m, 2H);

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 180.5, 140.9, 137.6, 134.3, 132.3, 132.2, 130.2, 127.7, 126.2, 123.7, 109.0, 47.9, 45.9, 34.9, 34.5, 33.5, 26.6, 26.2, 26.14, 26.07, 21.3, 21.2;

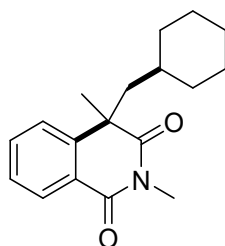
HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{30}\text{NO}^+$ 348.2322; Found 348.2314.



14¹⁴: Orange oil (36 mg, yield 63%) using the general procedure C;

$R_f = 0.7$ (PE/EA: 4/1);

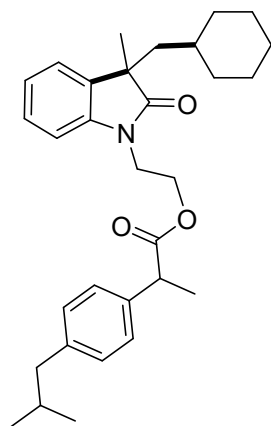
^1H NMR (400 MHz, CDCl_3) δ 7.03 – 6.86 (m, 3H), 3.70 (t, $J = 5.8$ Hz, 2H), 2.79 (t, $J = 5.0$ Hz, 2H), 2.07 – 1.86 (m, 3H), 1.71 (dd, $J = 14.0, 5.2$ Hz, 1H), 1.56 – 1.44 (m, 3H), 1.43 – 1.31 (m, 4H), 1.29 – 1.21 (m, 2H), 1.05 – 0.93 (m, 3H), 0.90 – 0.71 (m, 2H);



15¹⁰: A white solid (41 mg, yield 72%) using the general procedure C;

$R_f = 0.7$ (PE/EA: 4/1);

¹H NMR (400 MHz, CDCl₃) δ 8.24 (d, $J = 7.9$ Hz, 1H), 7.61 (t, $J = 7.1$ Hz, 1H), 7.45 – 7.37 (m, 2H), 3.37 (s, 3H), 2.31 (dd, $J = 14.0, 7.3$ Hz, 1H), 1.88 (dd, $J = 14.0, 4.6$ Hz, 1H), 1.55 (s, 3H), 1.46 (t, $J = 13.7$ Hz, 3H), 1.27 – 1.22 (m, 1H), 1.13 (d, $J = 12.4$ Hz, 1H), 0.99 – 0.73 (m, 6H).



16: Pale yellow oil (54 mg, yield 57%) using the general procedure C;

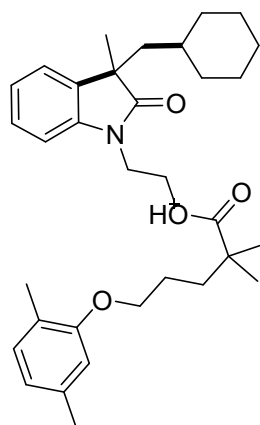
$R_f = 0.7$ (PE/EA: 4/1);

IR (neat) ν 2921, 2849, 1713, 1612, 1466, 1352, 1156, 752 cm⁻¹;

¹H NMR (400 MHz, CDCl₃, a complex of diastereoisomers, d.r. = 1:1) δ 7.23 – 7.18 (m, 1H), 7.17 – 7.09 (m, 3H), 7.08 – 7.02 (m, 3H), 6.87 – 6.81 (m, 1H), 4.41 – 4.18 (m, 2H), 4.07 – 3.81 (m, 2H), 3.64 – 3.55 (m, 1H), 2.48 – 2.39 (m, 2H), 1.97 – 1.89 (m, 1H), 1.89 – 1.79 (m, 1H), 1.77 – 1.68 (m, 1H), 1.56 – 1.45 (m, 2H), 1.45 – 1.40 (m, 4H), 1.38 – 1.33 (m, 1H), 1.31 – 1.25 (m, 3H), 1.24 – 1.16 (m, 1H), 1.06 – 0.92 (m, 4H), 0.91 – 0.87 (m, 6H), 0.86 – 0.67 (m, 2H);

¹³C{¹H} NMR (100 MHz, CDCl₃, a complex of diastereoisomers) δ 181.21 (181.19), 174.65 (174.62), 142.53 (142.47), 140.7, 137.5 (137.4), 134.41 (134.39), 129.4, 127.6, 127.3 (127.2), 122.94 (122.90), 122.43 (122.41), 108.5 (108.4), 62.1 (62.0), 47.79 (47.77), 45.45 (45.43), 45.2 (45.1), 38.90 (38.86), 34.89 (34.85), 34.51 (34.47), 33.69 (33.66), 30.2, 26.33 (26.21), 26.18, 26.10 (26.05), 22.5, 18.52 (18.46);

HRMS (ESI) m/z : [M+H]⁺ Calcd for C₃₁H₄₂NO₃⁺ 476.3159; Found 476.3175.



+

17: Pale yellow oil (84 mg, yield 81%) using the general procedure C;

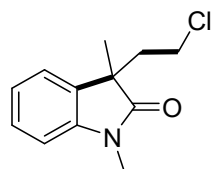
$R_f = 0.7$ (PE/Ea: 4/1);

IR (neat) ν 2920, 2851, 1714, 1612, 1449, 1263, 1129, 752 cm^{-1} ;

^1H NMR (400 MHz, CDCl_3) δ 7.19 – 7.13 (m, 1H), 7.07 (d, $J = 6.2$ Hz, 1H), 6.96 (t, $J = 7.5$ Hz, 1H), 6.91 (d, $J = 7.5$ Hz, 1H), 6.86 (d, $J = 7.7$ Hz, 1H), 6.57 (d, $J = 7.5$ Hz, 1H), 6.50 (s, 1H), 4.28 – 4.15 (m, 2H), 3.92 – 3.86 (m, 2H), 3.75 (t, $J = 5.4$ Hz, 2H), 2.23 (s, 3H), 2.08 (s, 3H), 1.85 (dd, $J = 14.0, 6.8$ Hz, 1H), 1.64 (dd, $J = 14.1, 5.3$ Hz, 2H), 1.59 (d, $J = 6.5$ Hz, 3H), 1.46 – 1.36 (m, 3H), 1.29 (d, $J = 11.2$ Hz, 1H), 1.22 (s, 3H), 1.13 (d, $J = 13.6$ Hz, 1H), 1.06 (d, $J = 1.7$ Hz, 6H), 0.95 – 0.85 (m, 3H), 0.82 – 0.63 (m, 3H);

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 181.2, 177.8, 157.0, 142.5, 136.5, 134.4, 130.4, 127.6, 123.7, 123.0, 122.5, 120.8, 112.1, 108.5, 67.9, 61.8, 47.8, 45.4, 42.2, 38.9, 37.1, 34.8, 34.5, 33.7, 29.8, 26.4, 26.19, 26.17, 26.11, 25.2, 25.1, 21.5, 15.9;

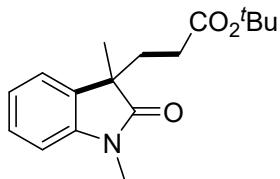
HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{33}\text{H}_{46}\text{NO}_4^+$ 520.3421; Found 520.3421.



18¹⁰: Purplish oil (32 mg, yield 71%) using the general procedure C;

$R_f = 0.7$ (Petroleum ether/EtOAc: 4/1);

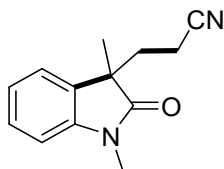
^1H NMR (400 MHz, CDCl_3) δ 7.29 (td, $J = 7.7, 1.2$ Hz, 1H), 7.19 (dd, $J = 7.3, 1.3$ Hz, 1H), 7.08 (td, $J = 7.6, 0.7$ Hz, 1H), 6.86 (d, $J = 7.8$ Hz, 1H), 3.26 – 3.10 (m, 5H), 2.49 – 2.39 (m, 1H), 2.25 – 2.17 (m, 1H), 1.39 (s, 3H).



19¹⁰: Colorless oil (31 mg, yield 54%) using the general procedure C;

$R_f = 0.5$ (PE/EA: 7/3);

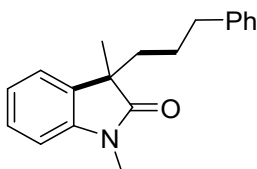
¹H NMR (400 MHz, CDCl₃) δ 7.27 (td, $J = 7.6, 1.3$ Hz, 1H), 7.19 (dd, $J = 7.4, 1.2$ Hz, 1H), 7.07 (td, $J = 7.5, 1.0$ Hz, 1H), 6.84 (d, $J = 7.7$ Hz, 1H), 3.21 (s, 3H), 2.25 – 2.12 (m, 1H), 2.10 – 2.02 (m, 1H), 2.02 – 1.93 (m, 1H), 1.82 – 1.71 (m, 1H), 1.38 (s, 3H), 1.36 (s, 9H).



20¹⁵: A pale yellow solid (30 mg, yield 70%) using the general procedure C;

$R_f = 0.7$ (PE/EA: 4/1);

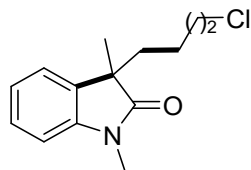
¹H NMR (400 MHz, CDCl₃) δ 7.32 (td, $J = 7.7, 1.3$ Hz, 1H), 7.19 (dd, $J = 7.5, 1.3$ Hz, 1H), 7.12 (t, $J = 7.5$ Hz, 1H), 6.88 (d, $J = 7.8$ Hz, 1H), 3.22 (s, 3H), 2.38 – 2.28 (m, 1H), 2.14 – 1.97 (m, 3H), 1.40 (s, 3H).



21¹¹: Colorless liquid (43 mg, yield 77%) using the general procedure C;

$R_f = 0.7$ (PE/EA: 4/1);

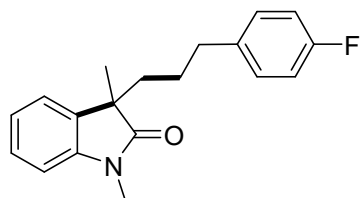
¹H NMR (400 MHz, CDCl₃) δ 7.27 – 7.18 (m, 3H), 7.15 – 7.10 (m, 2H), 7.07 – 7.01 (m, 3H), 6.81 (d, $J = 7.8$ Hz, 1H), 3.18 (s, 3H), 2.58 – 2.39 (m, 2H), 1.96 (td, $J = 12.9, 4.8$ Hz, 1H), 1.77 (td, $J = 12.9, 4.3$ Hz, 1H), 1.34 (s, 3H), 1.32 – 1.25 (m, 1H), 1.21 – 1.09 (m, 1H).



22¹⁶: Pale yellow oil (29 mg, yield 57%) using the general procedure C;

$R_f = 0.7$ (PE/EA: 4/1);

¹H NMR (400 MHz, CDCl₃) δ 7.27 (td, $J = 7.7, 1.2$ Hz, 1H), 7.17 (dd, $J = 7.4, 1.3$ Hz, 1H), 7.07 (td, $J = 7.5, 0.9$ Hz, 1H), 6.85 (d, $J = 7.8$ Hz, 1H), 3.39 (td, $J = 6.8, 1.3$ Hz, 2H), 3.22 (s, 3H), 1.91 (td, $J = 12.7, 4.9$ Hz, 1H), 1.76 (td, $J = 12.7, 4.7$ Hz, 1H), 1.70 – 1.58 (m, 2H), 1.36 (s, 3H), 1.17 – 0.95 (m, 2H).

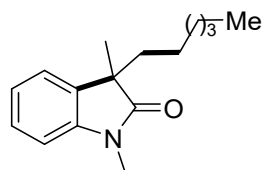


23¹⁷: A white solid (41 mg, yield 69%) using the general procedure C;

$R_f = 0.7$ (PE/EA: 4/1);

¹H NMR (400 MHz, CDCl₃) δ 7.22 (t, $J = 7.7$ Hz, 1H), 7.08 (d, $J = 7.0$ Hz, 1H), 7.02 (t, $J = 7.4$ Hz, 1H), 6.98 – 6.92 (m, 2H), 6.86 (t, $J = 8.6$ Hz, 2H), 6.79 (d, $J = 7.7$ Hz, 1H), 3.17 (s, 3H), 2.51 – 2.33 (m, 2H), 1.91 (td, $J = 12.8, 4.7$ Hz, 1H), 1.72 (td, $J = 12.8, 4.2$ Hz, 1H), 1.31 (s, 3H), 1.29 – 1.21 (m, 1H), 1.16 – 1.05 (m, 1H);

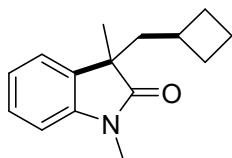
¹⁹F NMR (376 MHz, CDCl₃) δ -117.80.



24¹¹: Colorless oil (27 mg, yield 54%) using the general procedure C;

$R_f = 0.7$ (PE/EA: 4/1);

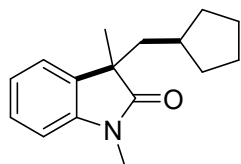
¹H NMR (400 MHz, CDCl₃) δ 7.26 (td, $J = 7.7, 1.1$ Hz, 1H), 7.16 (dd, $J = 7.4, 1.3$ Hz, 1H), 7.06 (td, $J = 7.5, 1.0$ Hz, 1H), 6.83 (d, $J = 7.7$ Hz, 1H), 3.21 (s, 3H), 1.88 (td, $J = 12.8, 4.7$ Hz, 1H), 1.72 (td, $J = 12.8, 4.4$ Hz, 1H), 1.34 (s, 3H), 1.22 – 1.09 (m, 6H), 1.03 – 0.91 (m, 1H), 0.80 (t, $J = 7.0$ Hz, 4H).



25¹⁰: Colorless oil (14 mg, yield 30%) using the general procedure **C**;

$R_f = 0.7$ (PE/EA: 4/1);

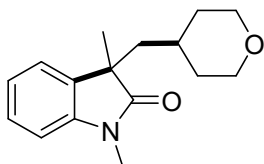
¹H NMR (400 MHz, CDCl₃) δ 7.26 (td, $J = 7.7, 1.0$ Hz, 1H), 7.16 (dd, $J = 7.3, 1.3$ Hz, 1H), 7.05 (td, $J = 7.5, 1.0$ Hz, 1H), 6.82 (d, $J = 7.7$ Hz, 1H), 3.20 (s, 3H), 2.09 – 2.01 (m, 1H), 1.95 – 1.82 (m, 2H), 1.76 – 1.68 (m, 1H), 1.64 – 1.54 (m, 3H), 1.51 – 1.38 (m, 2H), 1.32 (s, 3H).



26¹⁰: Yellow oil (29 mg, yield 59%) using the general procedure **C**;

$R_f = 0.7$ (PE/EA: 4/1);

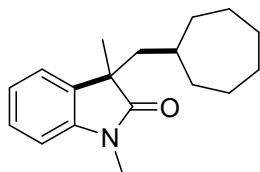
¹H NMR (400 MHz, CDCl₃) δ 7.26 (td, $J = 7.7, 1.2$ Hz, 1H), 7.16 (dd, $J = 7.4, 1.3$ Hz, 1H), 7.05 (td, $J = 7.5, 1.0$ Hz, 1H), 6.83 (d, $J = 7.7$ Hz, 1H), 3.21 (s, 3H), 2.06 (dd, $J = 13.7, 7.2$ Hz, 1H), 1.89 (dd, $J = 13.7, 5.9$ Hz, 1H), 1.52 – 1.37 (m, 3H), 1.34 (s, 3H), 1.31 – 1.17 (m, 4H), 1.07 – 0.96 (m, 1H), 0.90 – 0.76 (m, 1H).



27¹⁰: Yellow oil (35 mg, yield 68%) using the general procedure **C**;

$R_f = 0.4$ (PE/EA: 4/1);

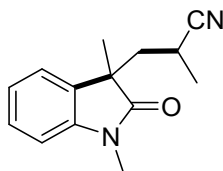
¹H NMR (400 MHz, CDCl₃) δ 7.26 (td, $J = 7.7, 1.2$ Hz, 1H), 7.15 (dd, $J = 7.4, 1.2$ Hz, 1H), 7.05 (td, $J = 7.5, 1.0$ Hz, 1H), 6.84 (d, $J = 7.7$ Hz, 1H), 3.78 – 3.65 (m, 2H), 3.21 (s, 3H), 3.14 – 3.04 (m, 2H), 1.98 (dd, $J = 14.0, 5.8$ Hz, 1H), 1.76 (dd, $J = 14.0, 5.0$ Hz, 1H), 1.32 (s, 3H), 1.27 – 0.99 (m, 5H).



28¹⁰: Pale yellow oil (39 mg, yield 72%) using the general procedure C;

R_f = 0.7 (PE/EA: 4/1);

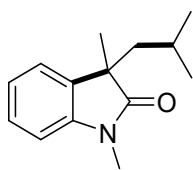
¹H NMR (400 MHz, CDCl₃) δ 7.26 (td, J = 7.7, 1.3 Hz, 1H), 7.16 (dd, J = 7.4, 1.3 Hz, 1H), 7.06 (td, J = 7.5, 1.1 Hz, 1H), 6.84 (d, J = 7.7 Hz, 1H), 3.21 (s, 3H), 1.98 (dd, J = 14.0, 6.9 Hz, 1H), 1.75 (dd, J = 14.0, 4.7 Hz, 1H), 1.50 – 1.30 (m, 11H), 1.19 – 0.97 (m, 5H).



29¹⁰: Colorless oil (36 mg, yield 79%) using the general procedure C;

R_f = 0.7 (PE/EA: 4/1);

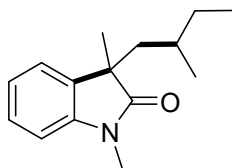
¹H NMR (400 MHz, CDCl₃, a complex of diastereoisomers, d.r. = 1:1) δ 7.37 – 7.26 (m, 1H), 7.18 – 7.06 (m, 2H), 6.90 (d, J = 7.8 Hz, 1H), 3.24 (s, 1.5 H), 3.24 (s, 1.5H), 2.45 – 2.33 (m, 1H), 2.30 – 2.11 (m, 1H), 1.90 – 1.80 (m, 1H), 1.43 (s, 1.5 H), 1.40 (s, 1.5 H), 1.19 – 1.17 (m, 3H).



30¹⁰: Pale yellow oil (27 mg, yield 62%) using the general procedure C;

R_f = 0.7 (PE/EA: 4/1);

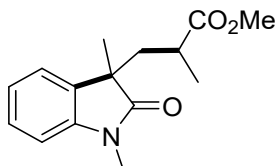
¹H NMR (400 MHz, CDCl₃) δ 7.26 (td, J = 7.7, 1.1 Hz, 1H), 7.16 (dd, J = 7.3, 1.3 Hz, 1H), 7.05 (td, J = 7.4, 1.0 Hz, 1H), 6.84 (d, J = 7.8 Hz, 1H), 3.21 (s, 3H), 1.94 (dd, J = 13.9, 7.6 Hz, 1H), 1.75 (dd, J = 13.9, 5.4 Hz, 1H), 1.32 (s, 3H), 1.30 – 1.15 (m, 1H), 0.62 (dd, J = 19.1, 6.7 Hz, 6H).



31¹⁰: Pale yellow oil (26 mg, yield 56%) using the general procedure **C**;

$R_f = 0.7$ (PE/EA: 4/1);

¹H NMR (400 MHz, CDCl₃, a complex of diastereoisomers, d.r. = 1:1) δ 7.29 – 7.21 (m, 1H), 7.19 – 7.14 (m, 1H), 7.08 – 7.04 (m, 1H), 6.84 – 6.83 (m, 1H), 3.24 – 3.20 (m, 3H), 2.03 (dd, $J = 14.0, 5.1$ Hz, 0.5H), 1.90 – 1.83 (m, 1H), 1.65 (dd, $J = 13.9, 6.5$ Hz, 0.5H), 1.33 (s, 3H), 1.19 – 0.91 (m, 3H), 0.74 – 0.69 (m, 3H), 0.60 (d, $J = 6.2$ Hz, 1.5H), 0.49 (d, $J = 6.4$ Hz, 1.5H).

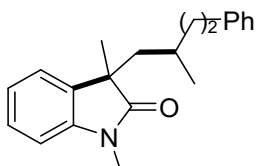


32(1-2)¹⁰: Yellow oil (40 mg, yield 76%, d.r.=1:1) using the general procedure **C**;

$R_f = 0.7$ (PE/EA: 4/1); a complex of diastereoisomers, d.r. = 1:1.

32-1: **¹H NMR** (400 MHz, CDCl₃) δ 7.27 (td, $J = 7.7, 1.3$ Hz, 1H), 7.15 (dd, $J = 7.3, 1.3$ Hz, 1H), 7.06 (td, $J = 7.6, 1.0$ Hz, 1H), 6.84 (d, $J = 7.8$ Hz, 1H), 3.57 (s, 3H), 3.18 (s, 3H), 2.47 (dd, $J = 14.2, 8.6$ Hz, 1H), 2.25 – 2.15 (m, 1H), 1.78 (dd, $J = 14.2, 4.1$ Hz, 1H), 1.34 (s, 3H), 0.93 (d, $J = 7.1$ Hz, 3H).

32-2: **¹H NMR** (400 MHz, CDCl₃) δ 7.25 (td, $J = 7.7, 2.0$ Hz, 1H), 7.14 (dd, $J = 7.4, 1.4$ Hz, 1H), 7.04 (td, $J = 7.6, 1.1$ Hz, 1H), 6.84 (d, $J = 7.8$ Hz, 1H), 3.24 (s, 3H), 3.17 (s, 3H), 2.36 (dd, $J = 13.6, 9.3$ Hz, 1H), 2.11 – 1.97 (m, 2H), 1.34 (s, 3H), 1.03 (d, $J = 6.9$ Hz, 3H).

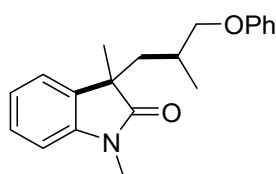


33¹⁸: Colorless oil (42 mg, yield 69%) using the general procedure **C**;

$R_f = 0.7$ (PE/EA: 4/1);

¹H NMR (400 MHz, CDCl₃, a complex of diastereoisomers, d.r. = 1:1) δ 7.29 – 7.24

(m, 1H), 7.23 – 7.17 (m, 2H), 7.16 – 7.09 (m, 2H), 7.08 – 7.00 (m, 2H), 6.97 (d, $J = 7.3$ Hz, 1H), 6.81 (t, $J = 8.2$ Hz, 1H), 3.16 (s, 1.5H), 3.15 (s, 1.5H), 2.57 – 2.31 (m, 2H), 2.09 (dd, $J = 14.0, 5.9$ Hz, 0.5H), 1.98 – 1.86 (m, 1H), 1.71 (dd, $J = 14.0, 5.9$ Hz, 0.5H), 1.46 – 1.36 (m, 1H), 1.33 (s, 3H), 1.30 – 1.22 (m, 1H), 1.19 – 1.04 (m, 1H), 0.70 (d, $J = 6.6$ Hz, 1.5H), 0.61 (d, $J = 6.4$ Hz, 1.5 H).



34: Pale yellow oil (45 mg, yield 73%) using the general procedure C;

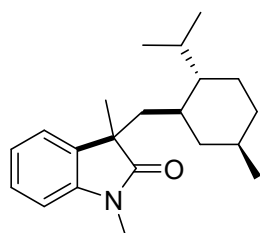
$R_f = 0.7$ (PE/EA: 4/1);

IR (neat) ν 2925, 1706, 1611, 1492, 1241, 1036, 751, 691 cm^{-1} ;

^1H NMR (400 MHz, CDCl_3 , a complex of diastereoisomers, d.r. = 1:1) δ 7.30 – 7.14 (m, 4H), 7.10 – 6.98 (m, 1H), 6.91 – 6.82 (m, 2H), 6.74 (d, $J = 7.9$ Hz, 1H), 6.69 (d, $J = 7.9$ Hz, 1H), 3.67 (dd, $J = 9.2, 4.7$ Hz, 0.5H), 3.52 – 3.45 (m, 1H), 3.22 (s, $J = 1.5$ H), 3.18 (s, 1.5 H), 2.21 – 2.08 (m, 1H), 1.97 (dd, $J = 14.0, 7.8$ Hz, 0.5H), 1.80 (dd, $J = 14.2, 6.0$ Hz, 0.5H), 1.66 – 1.49 (m, 1H), 1.36 (s, 3H), 0.82 (d, $J = 6.8$ Hz, 1.5 H), 0.73 (d, $J = 6.7$ Hz, 1.5H);

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , a complex of diastereoisomers, d.r. = 1:1) δ 181.0 (180.7), 158.95 (158.89), 143.22 (143.21), 134.0 (133.7), 129.39 (129.38), 127.94 (127.89), 123.00 (122.97), 122.69 (122.63), 120.51 (120.49), 114.53 (114.45), 108.3 (108.2), 72.71 (72.68), 48.1 (47.9), 41.7 (41.1), 30.52 (30.47), 26.4 (26.3), 26.0 (25.8), 19.0 (17.7);

HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{23}\text{NNaO}_2^+$ 332.1621; Found 332.1629.



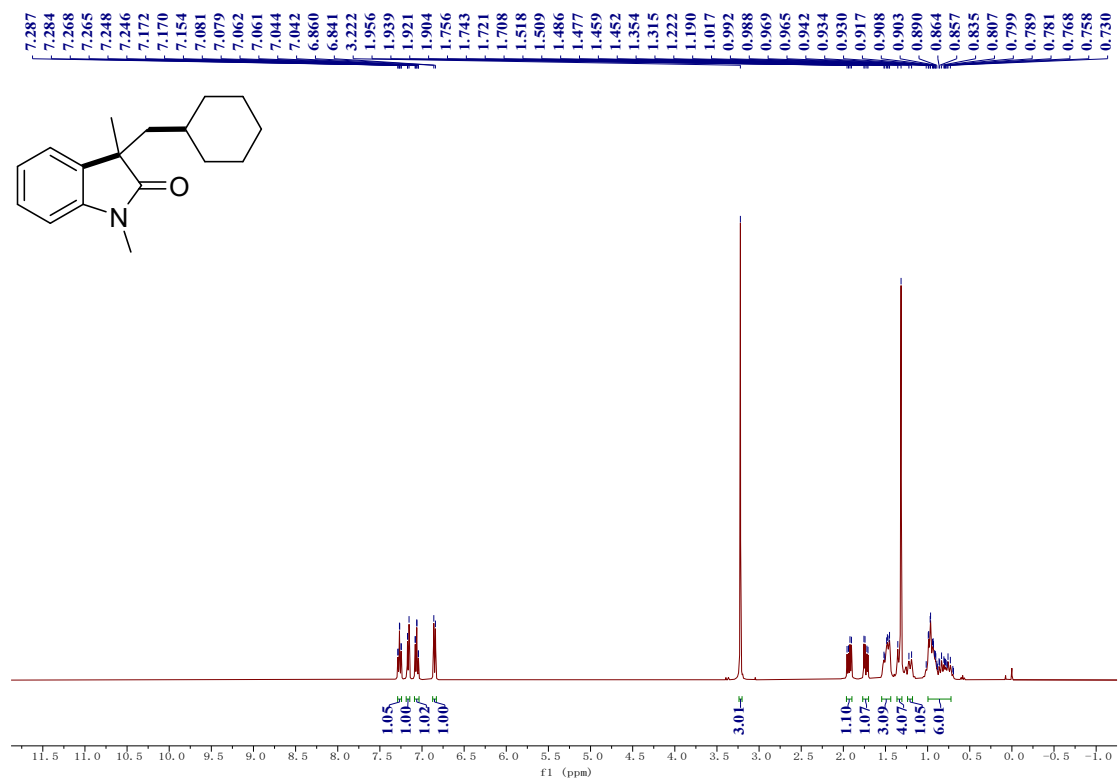
35¹⁸: Pale yellow oil (19 mg, yield 31%) using the general procedure C;

$R_f = 0.7$ (PE/EA: 4/1);

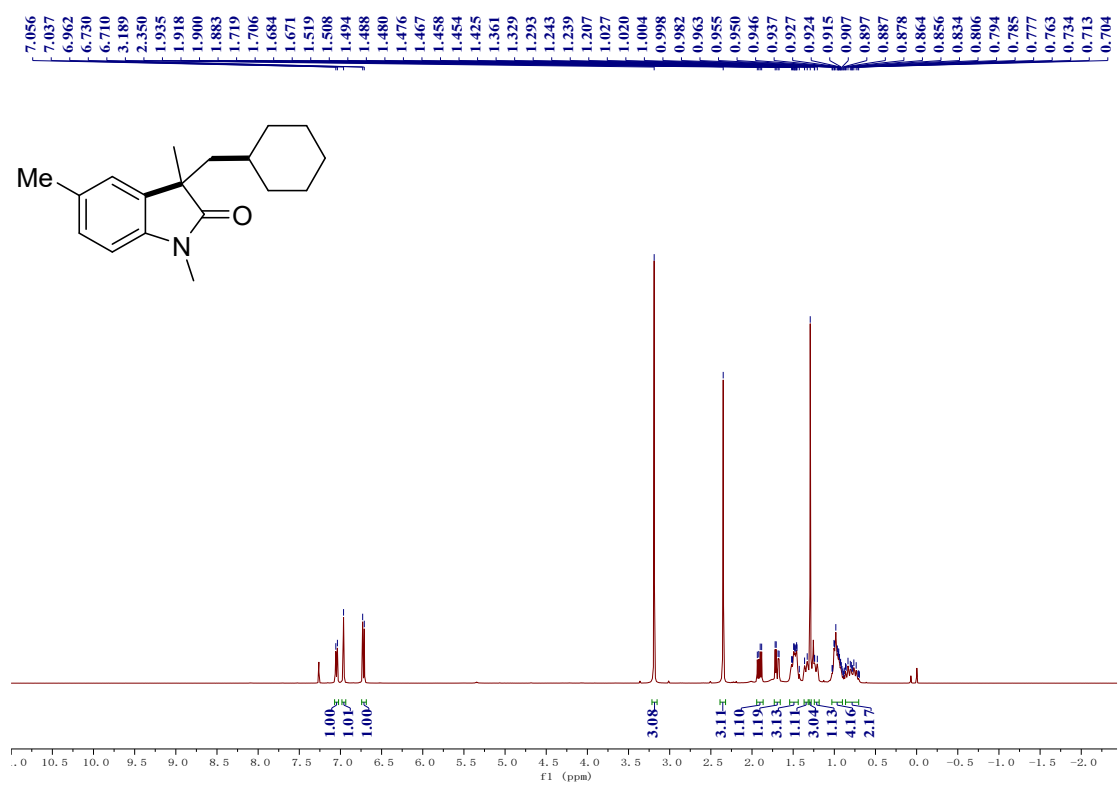
¹H NMR (400 MHz, CDCl₃, a complex of 4 diastereoisomers) δ 7.31 – 7.10 (m, 2H), 7.10 – 6.98 (m, 1H), 6.87 – 6.79 (m, 1H), 3.24 – 3.18 (m, 3H), 2.32 – 2.14 (m, 1H), 2.14 – 1.93 (m, 1H), 1.88 – 1.40 (m, 5H), 1.36 – 1.31 (m, 3H), 1.14 – 0.99 (m, 1H), 0.93 – 0.79 (m, 5H), 0.76 – 0.62 (m, 5H), 0.59 – 0.51 (m, 2H), 0.49 – 0.35 (m, 1H).

7. Copies of NMR Spectra

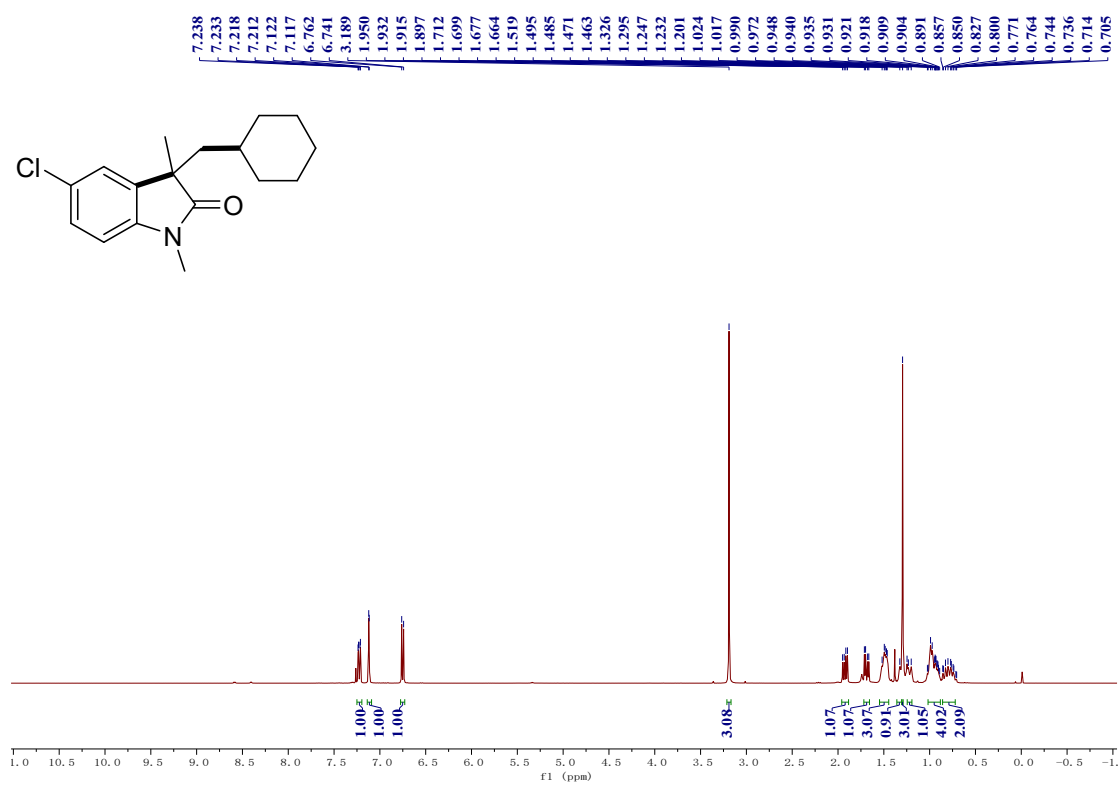
Substrate 3: ^1H NMR (CDCl_3 , 400 MHz)



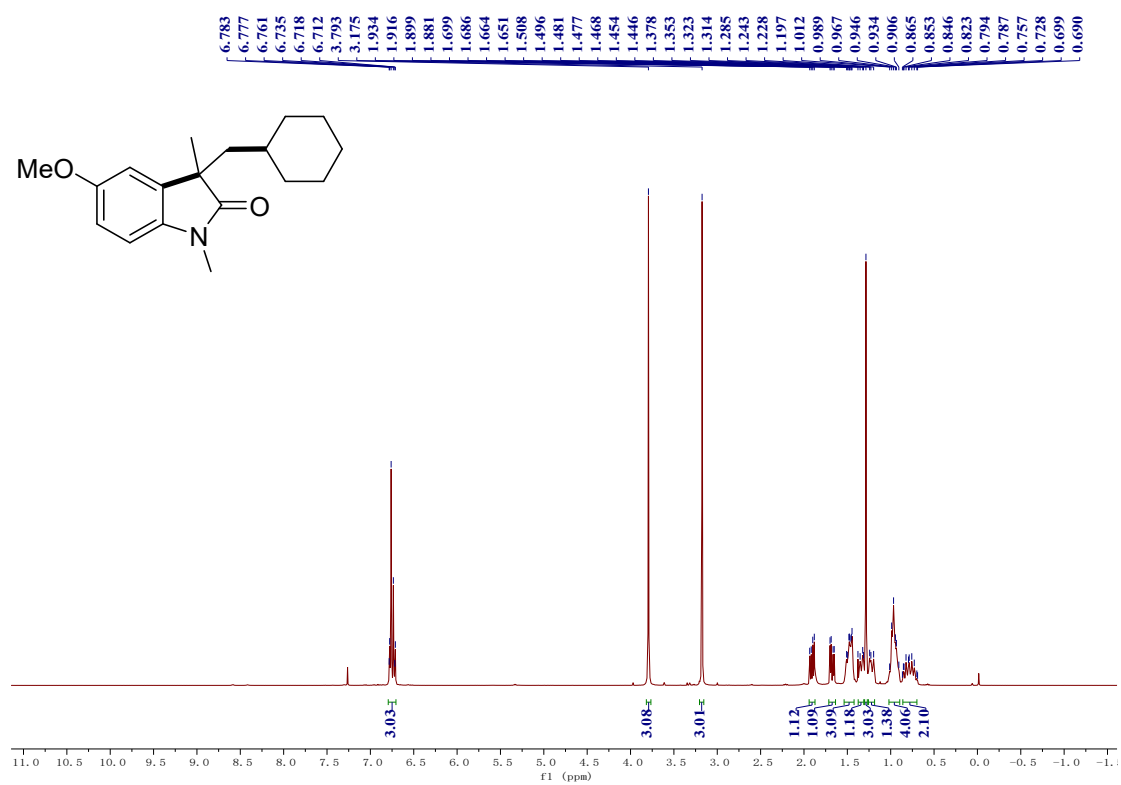
Substrate 4: ^1H NMR (CDCl_3 , 400 MHz)



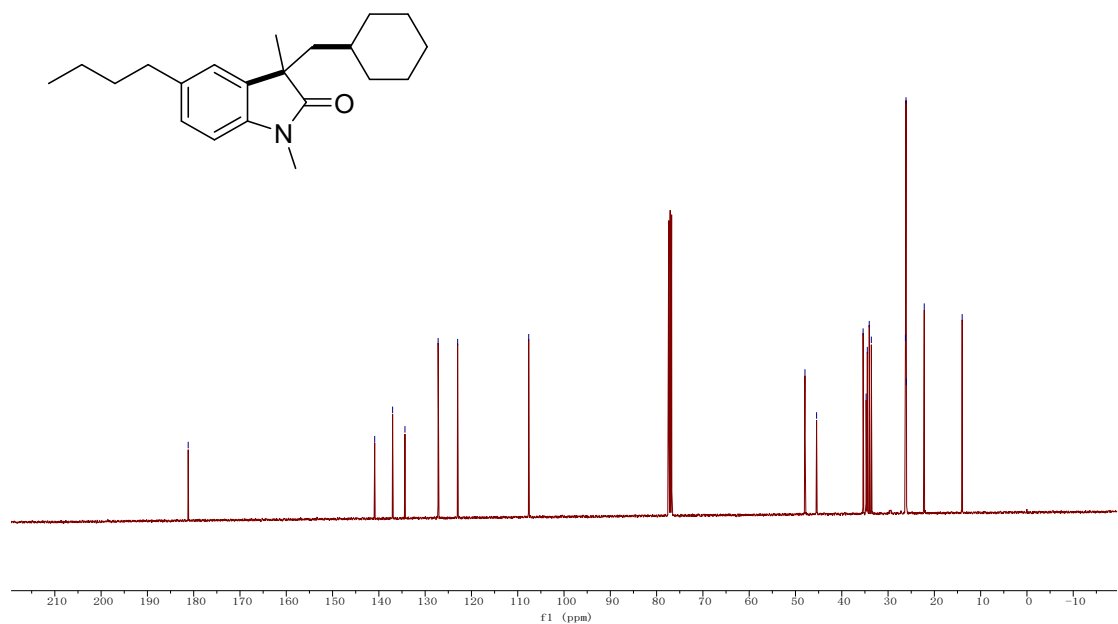
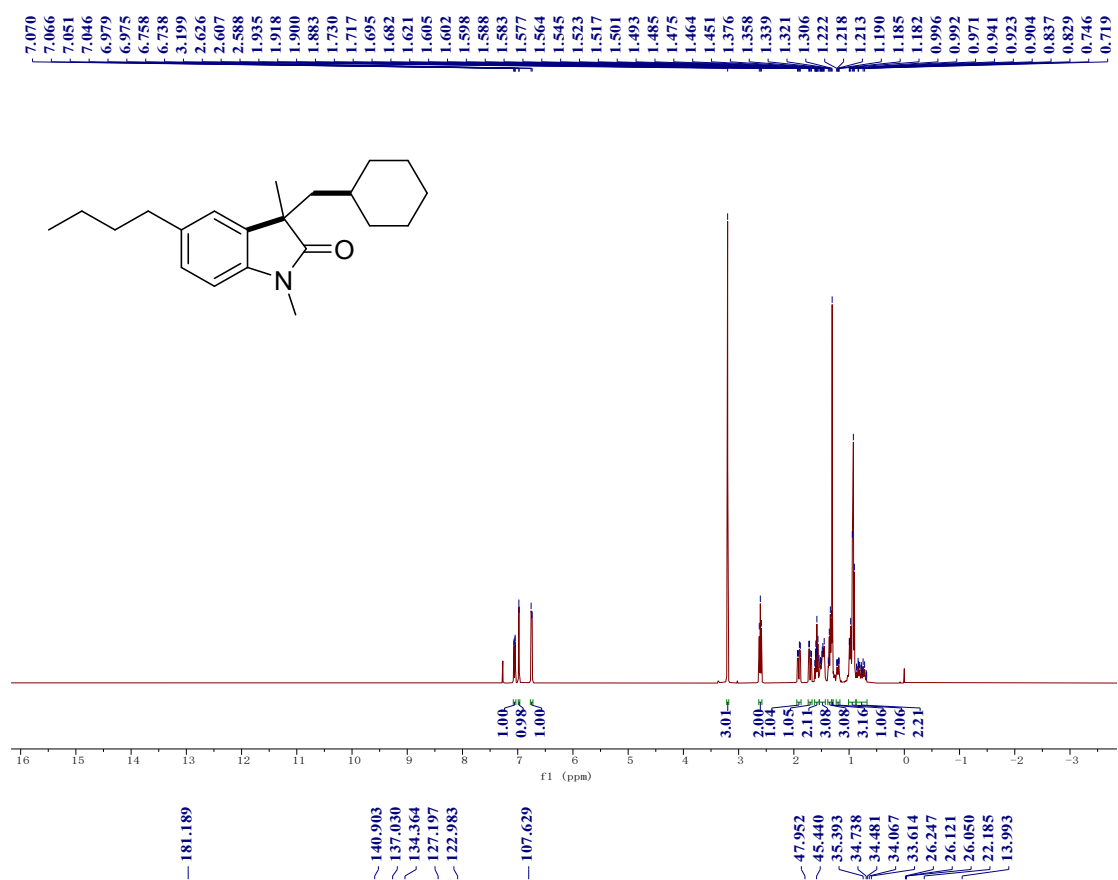
Substrate 5: ^1H NMR (CDCl_3 , 400 MHz)



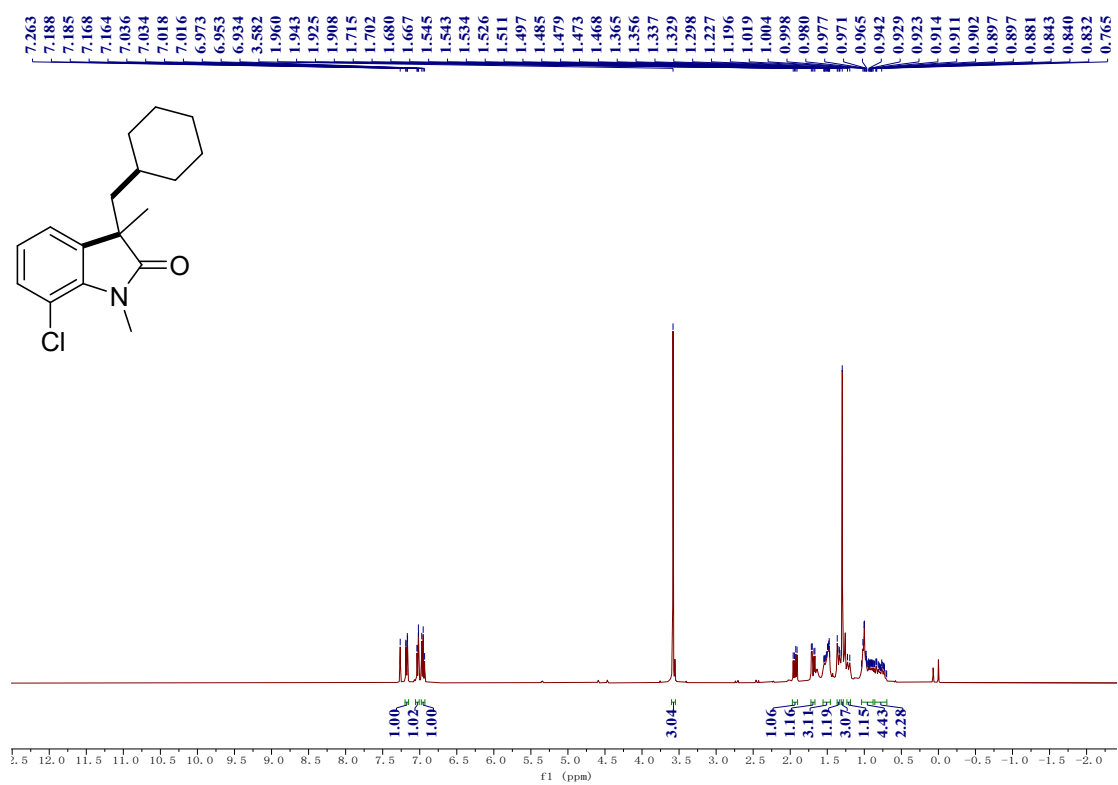
Substrate **6**: ^1H NMR (CDCl_3 , 400 MHz)



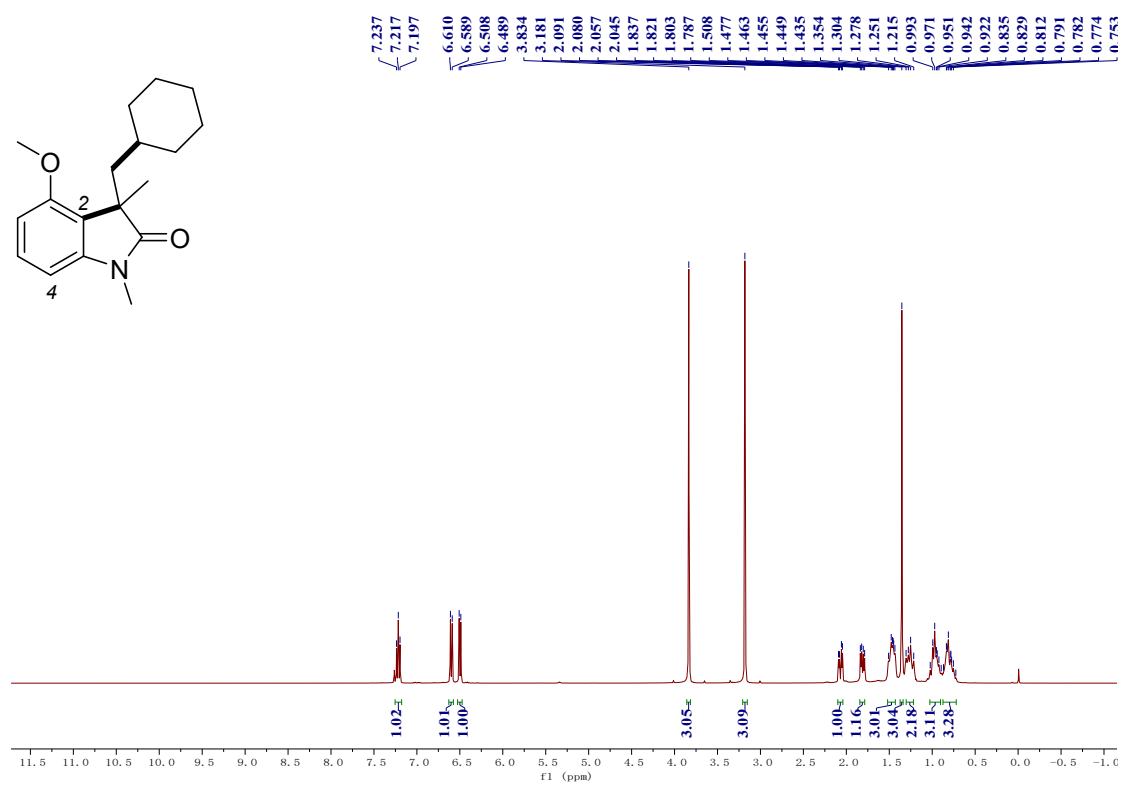
Substrate 7: ^1H NMR (CDCl_3 , 400 MHz), $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz)



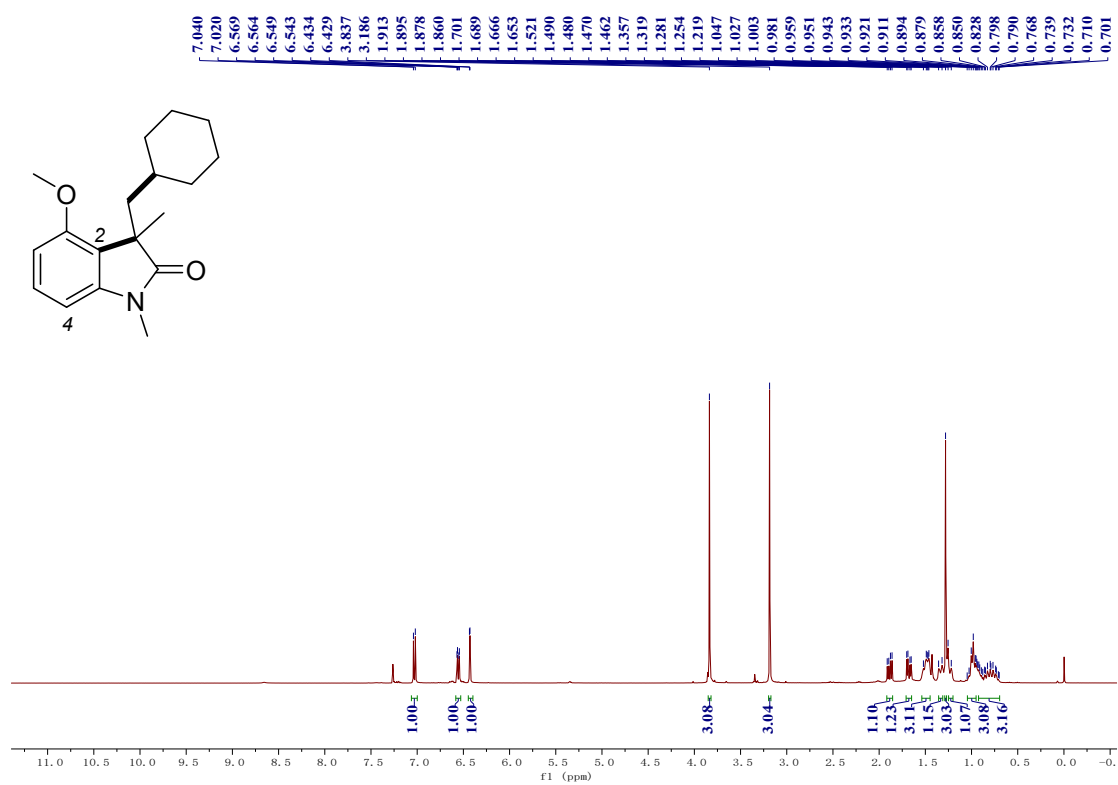
Substrate **8**: ^1H NMR (CDCl_3 , 400 MHz)



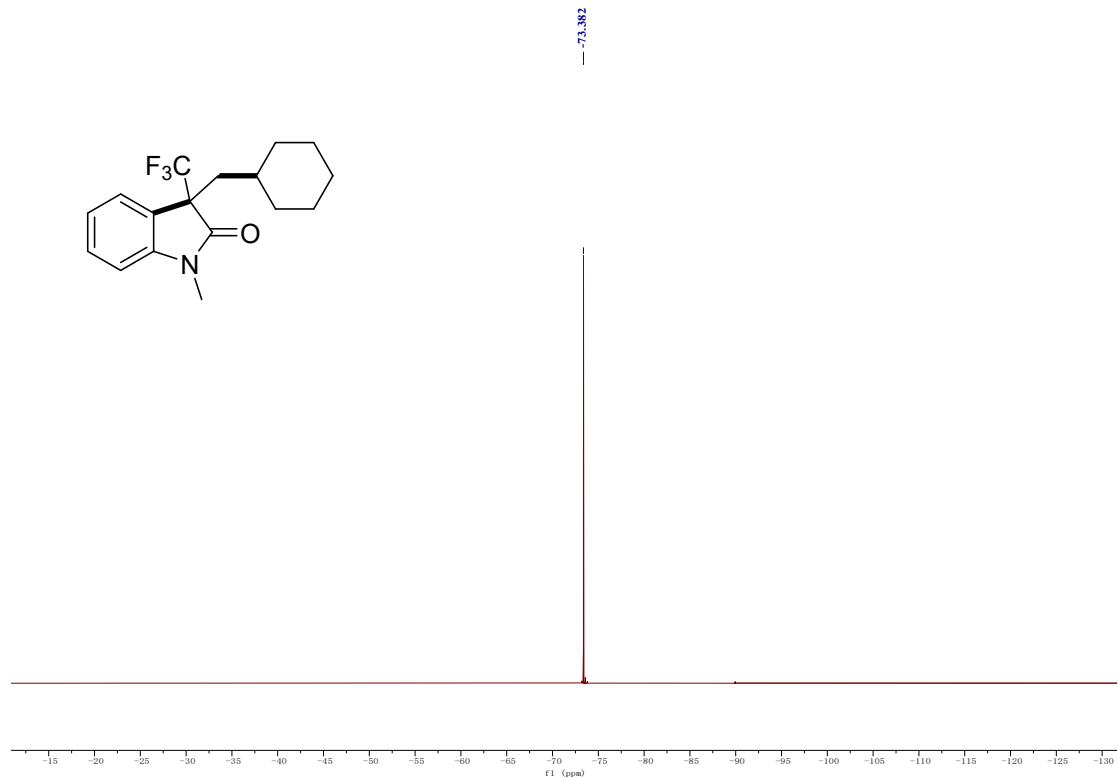
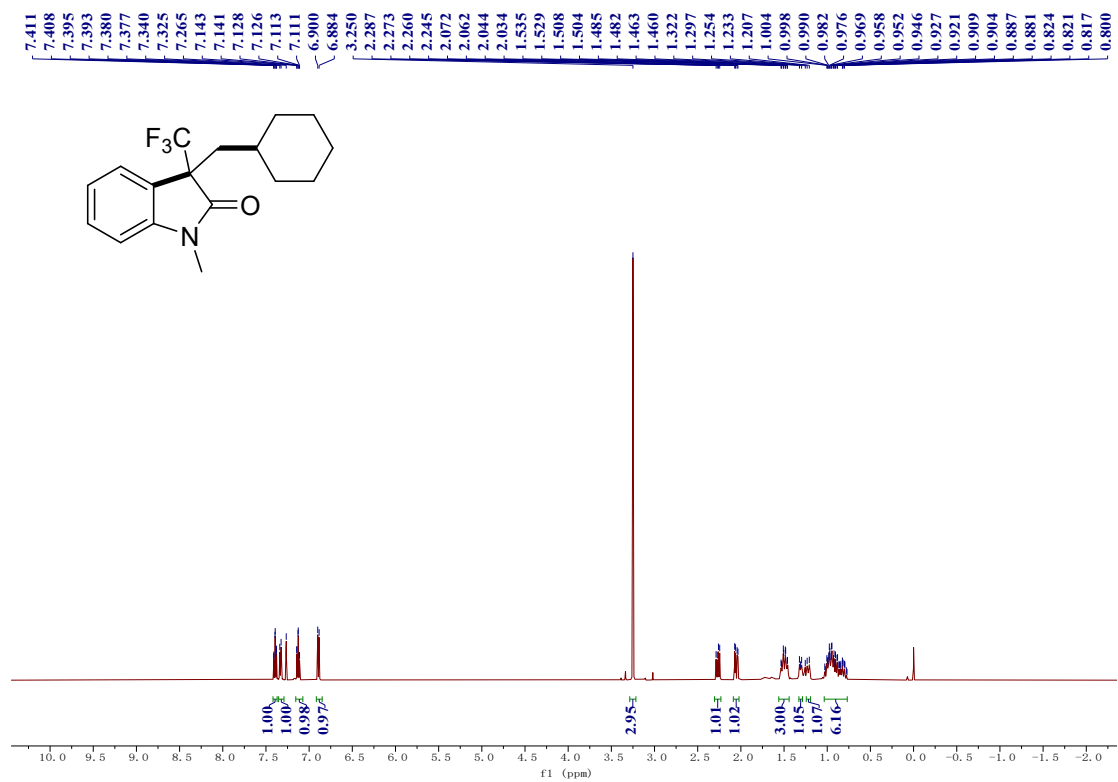
Substrate **9-C2**: ^1H NMR (CDCl_3 , 400 MHz)



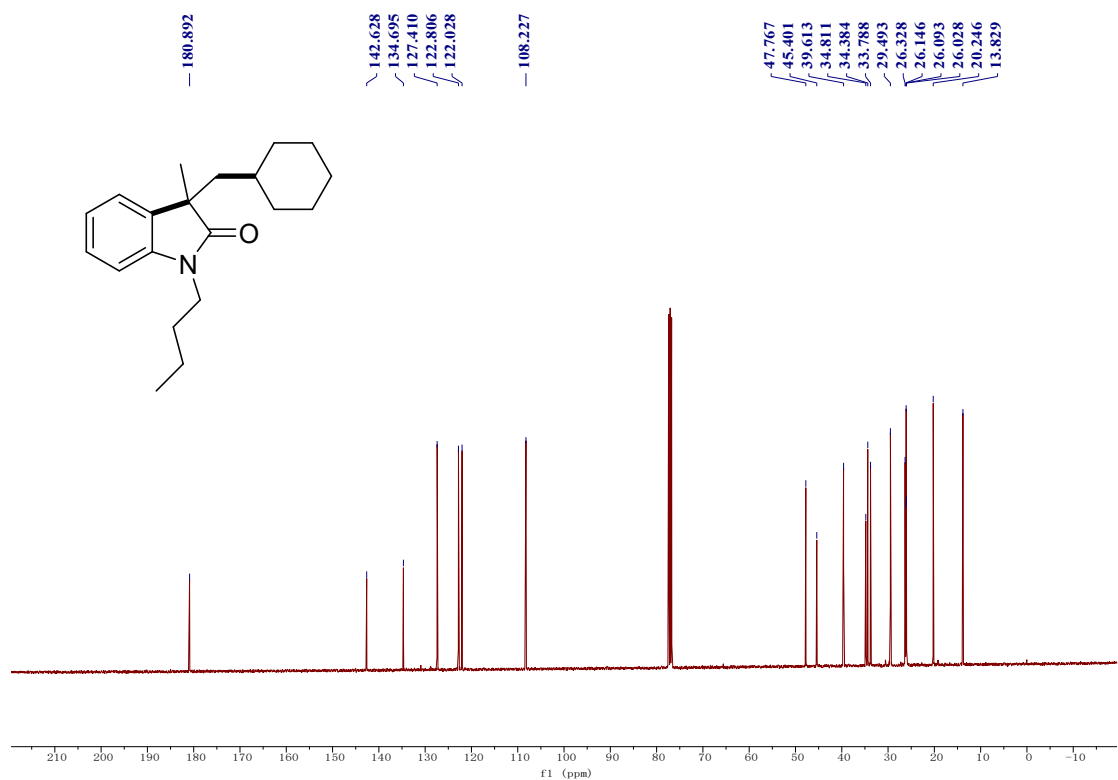
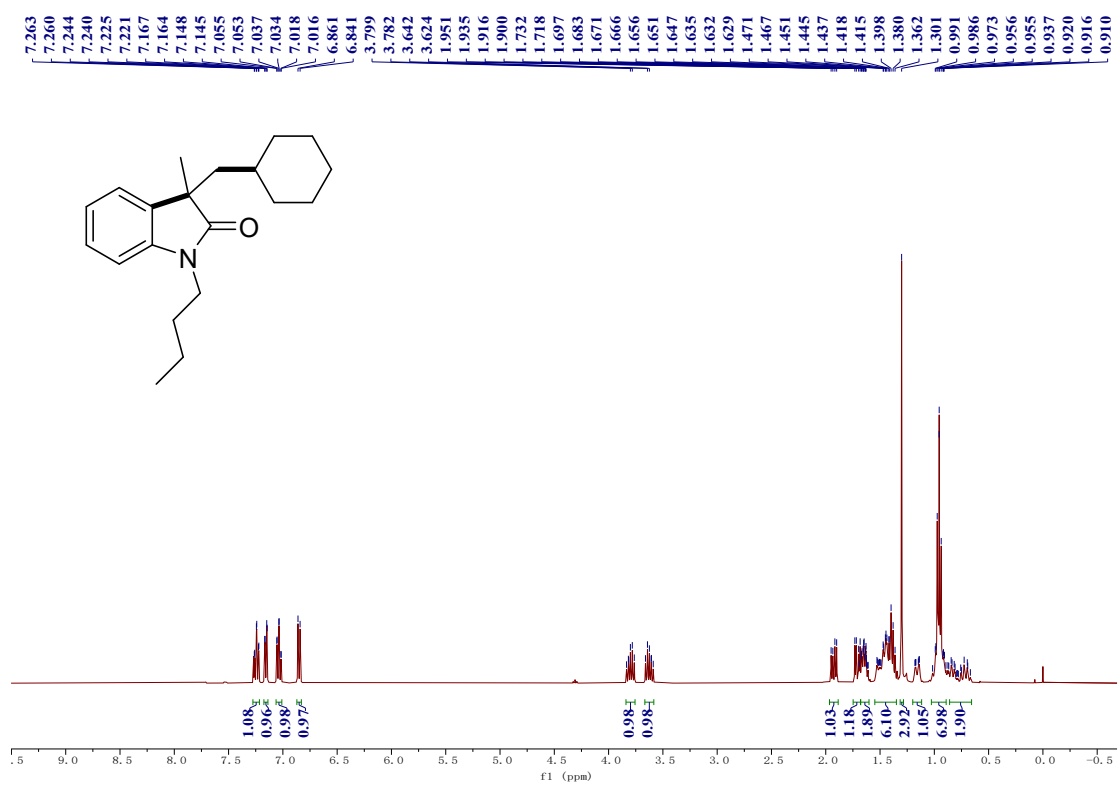
Substrate **9-C4**: ^1H NMR (CDCl_3 , 400 MHz)



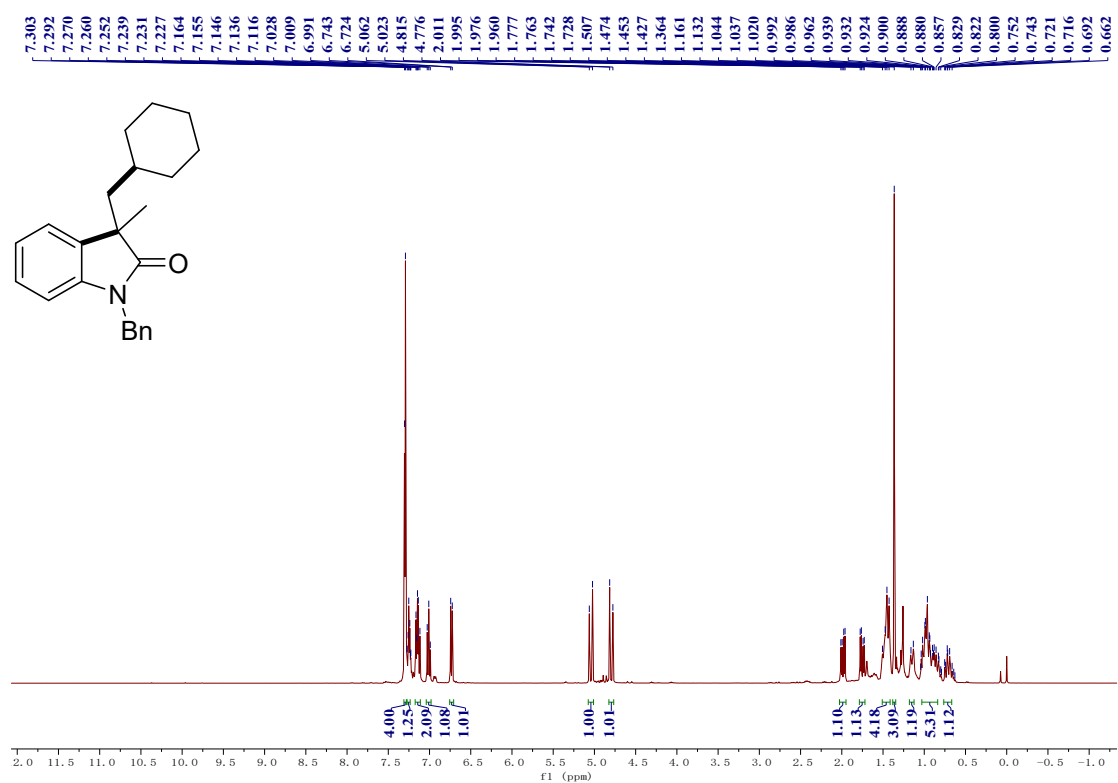
Substrate **10**: ^1H NMR (CDCl_3 , 500 MHz), ^{19}F NMR (471 MHz, CDCl_3)



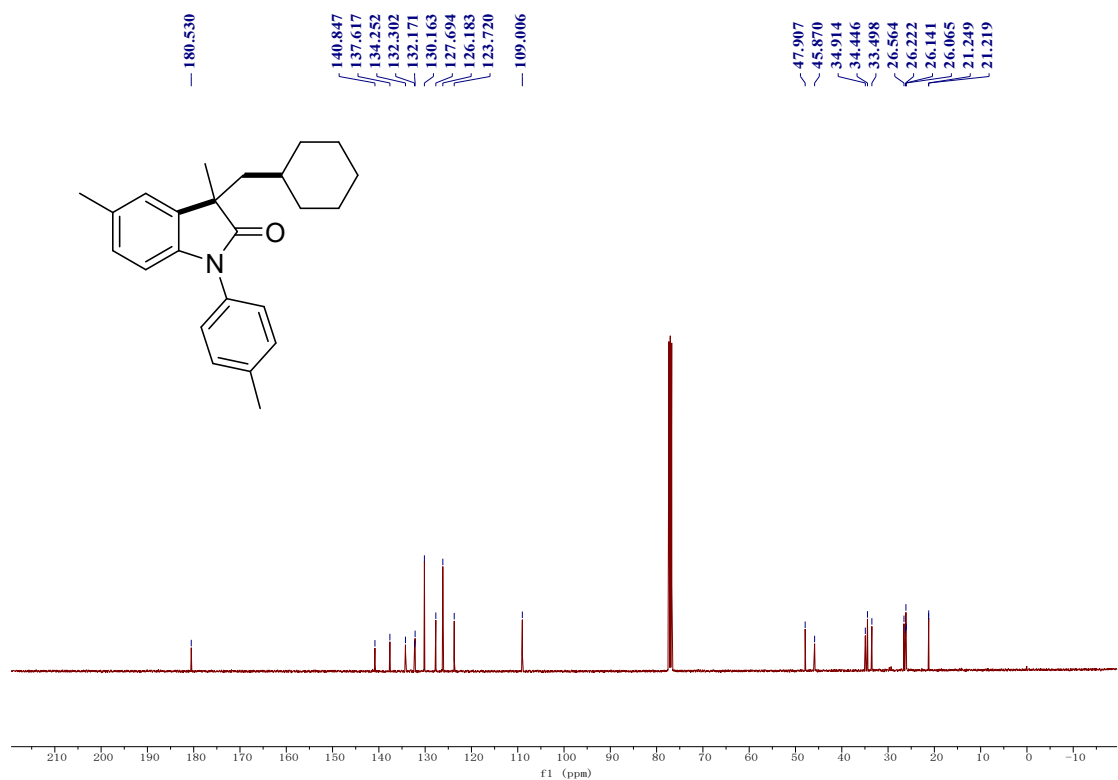
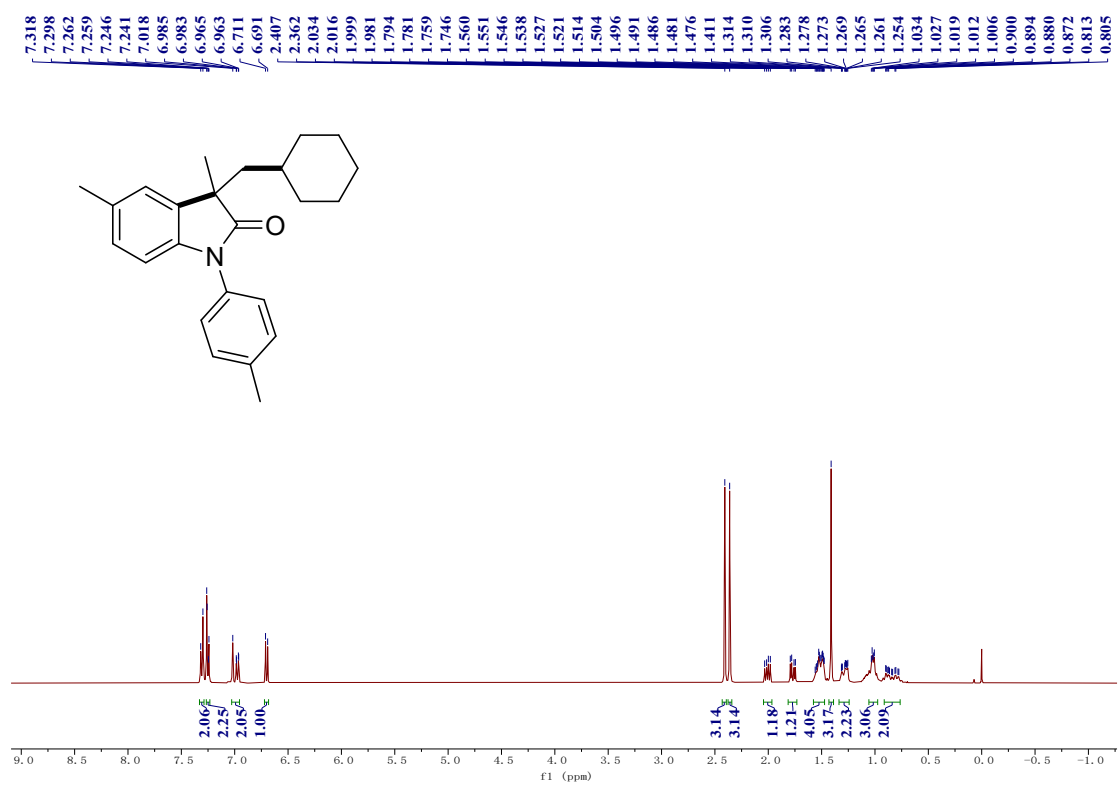
Substrate 11: ^1H NMR (CDCl_3 , 400 MHz), ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz)



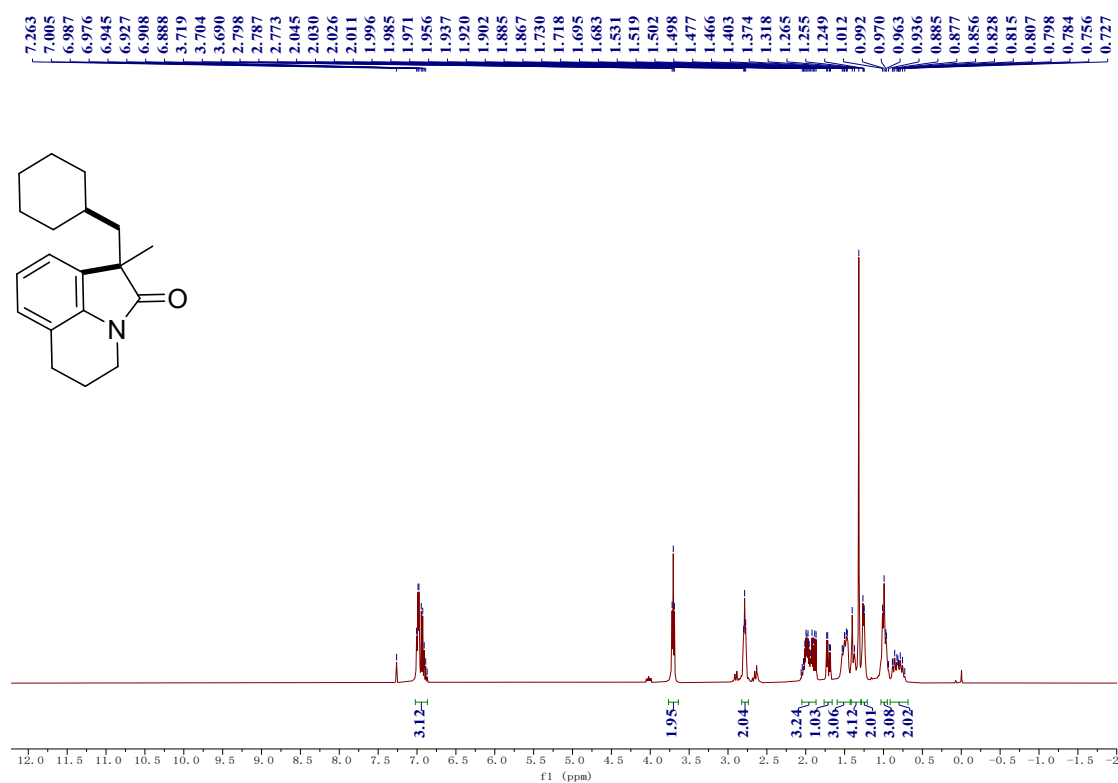
Substrate 12: ^1H NMR (CDCl_3 , 400 MHz)



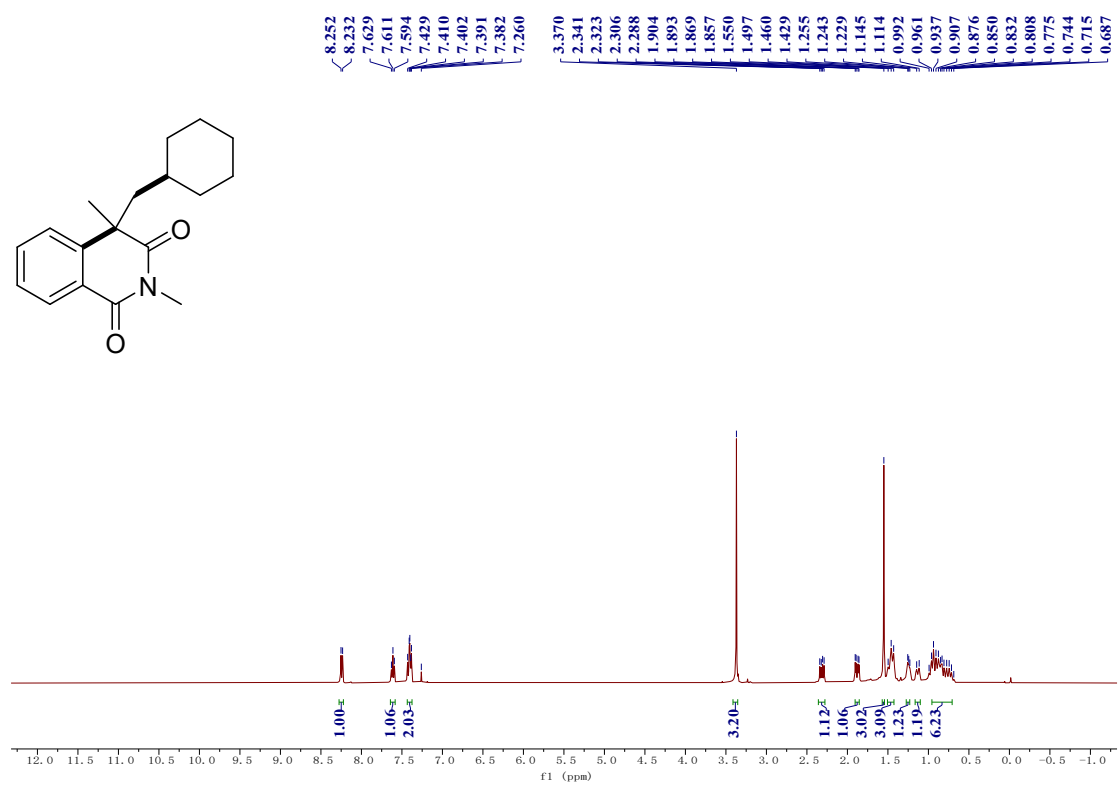
Substrate **13**: ^1H NMR (CDCl_3 , 400 MHz), ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz)



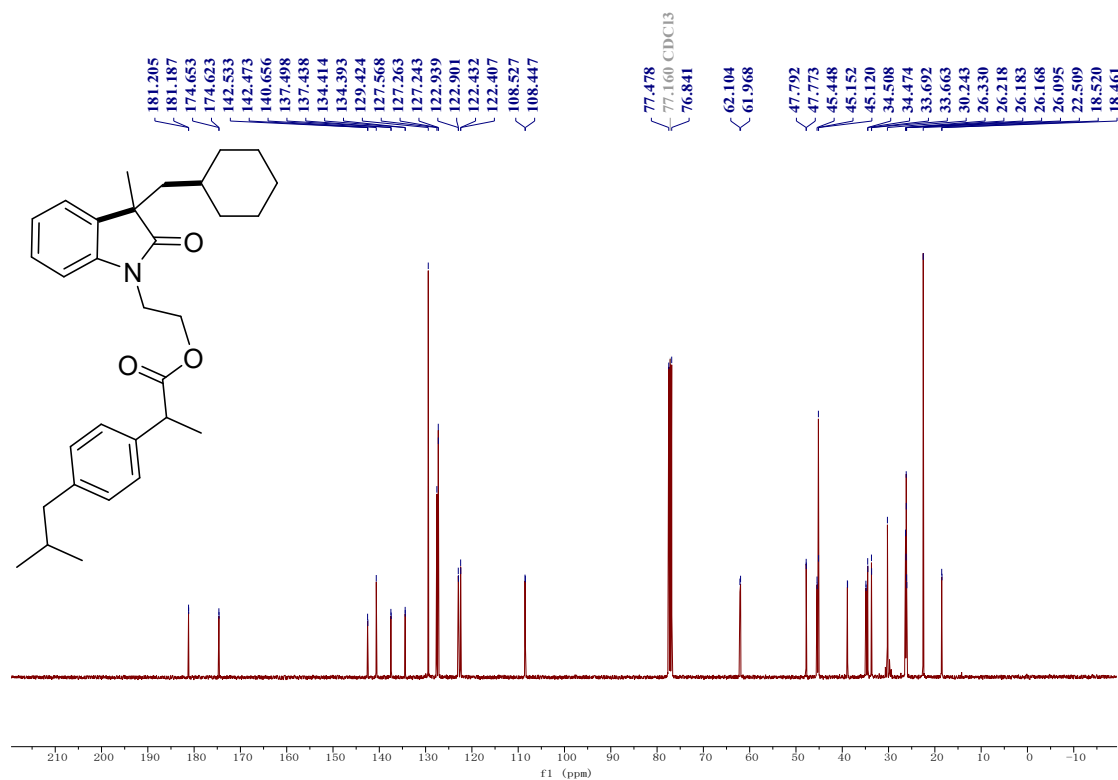
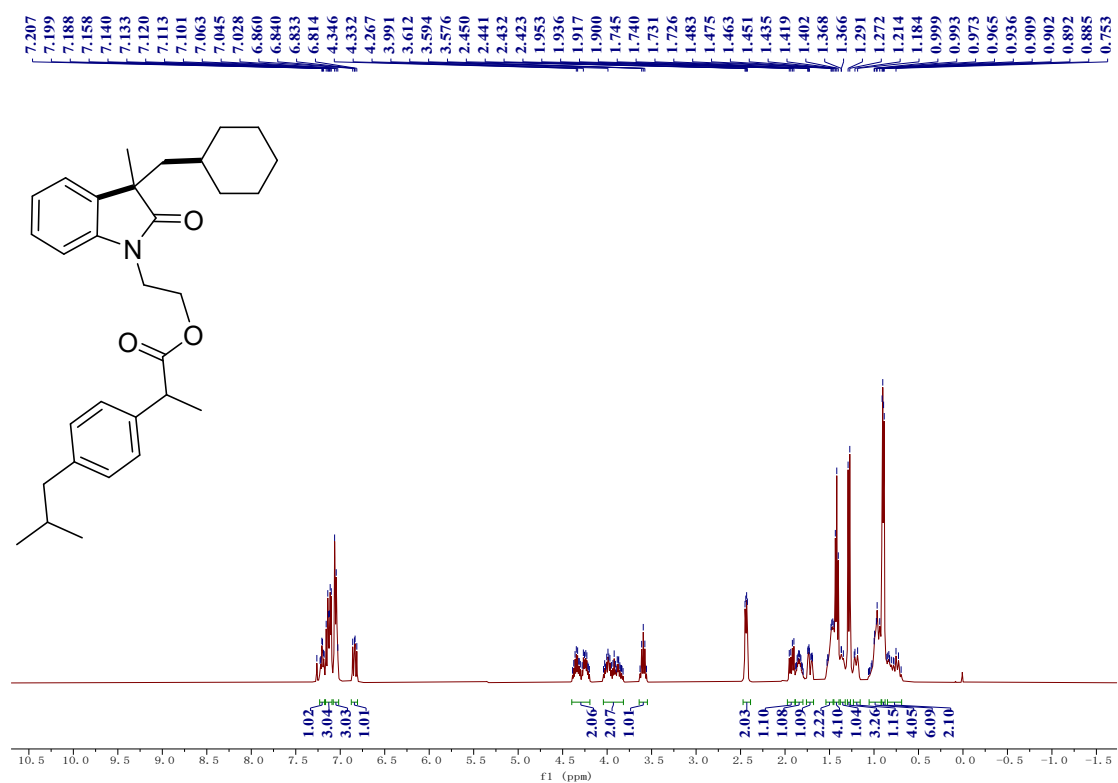
Substrate 14: ^1H NMR (CDCl_3 , 400 MHz)



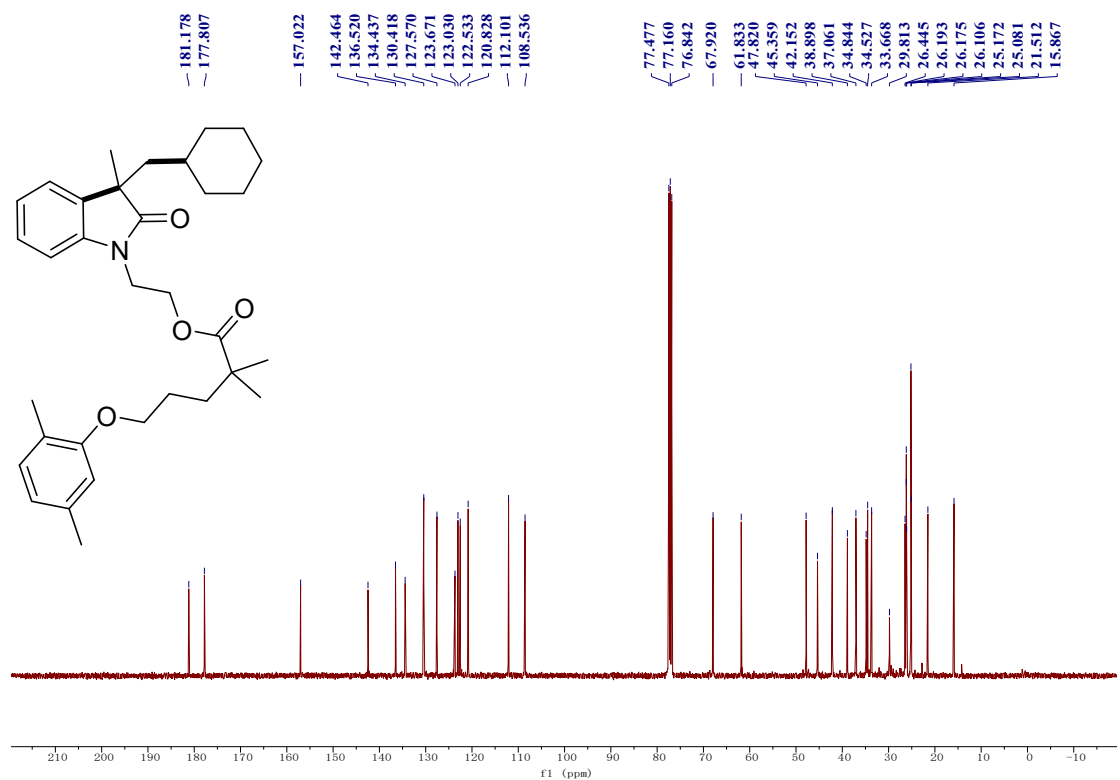
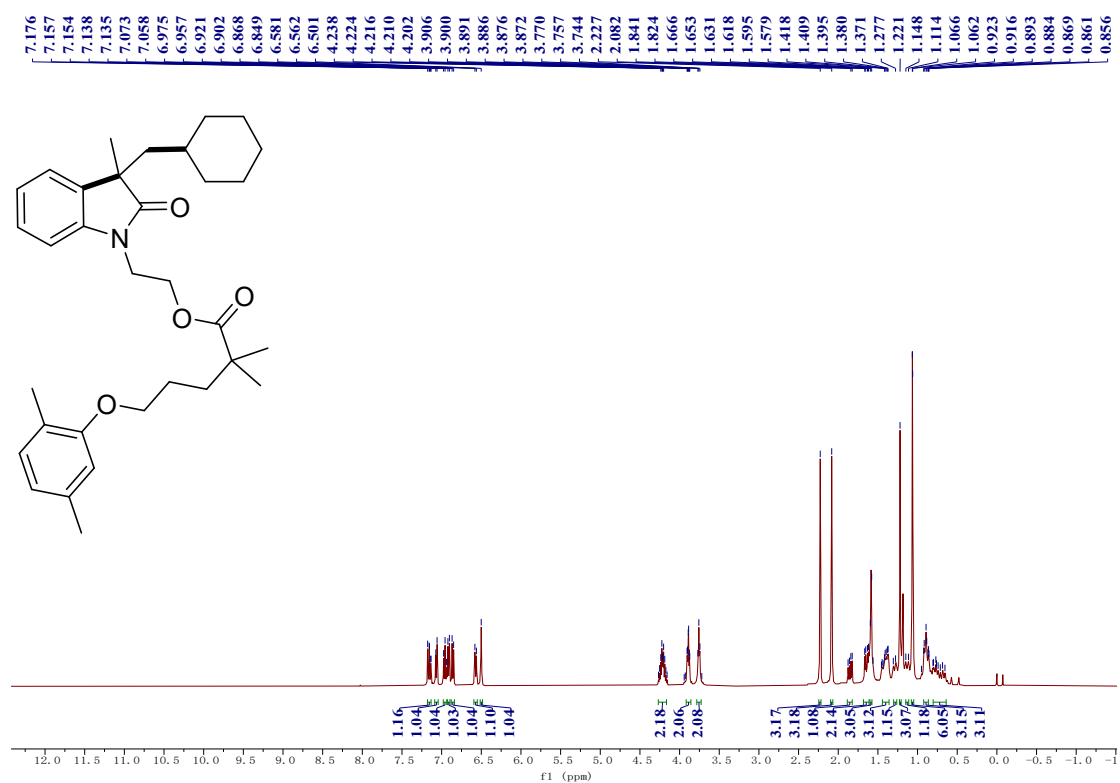
Substrate 15: ^1H NMR (CDCl_3 , 400 MHz)



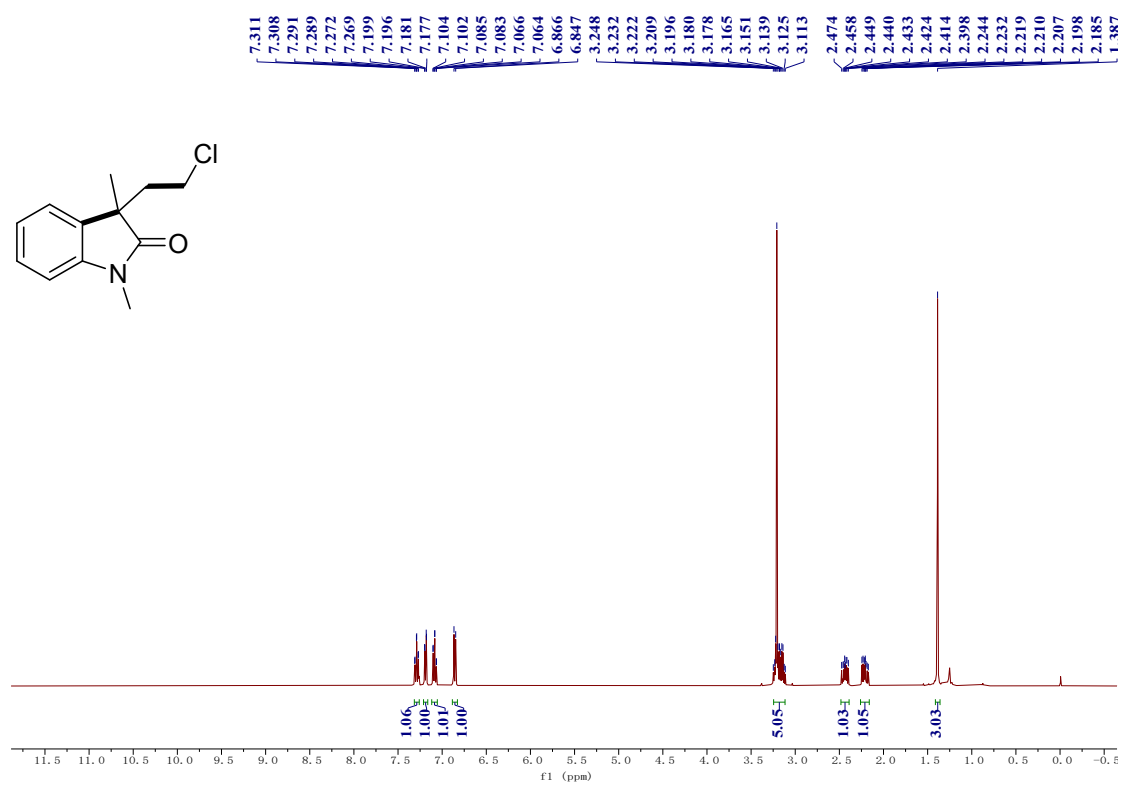
Substrate 16: ^1H NMR (CDCl_3 , 400 MHz), ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz)



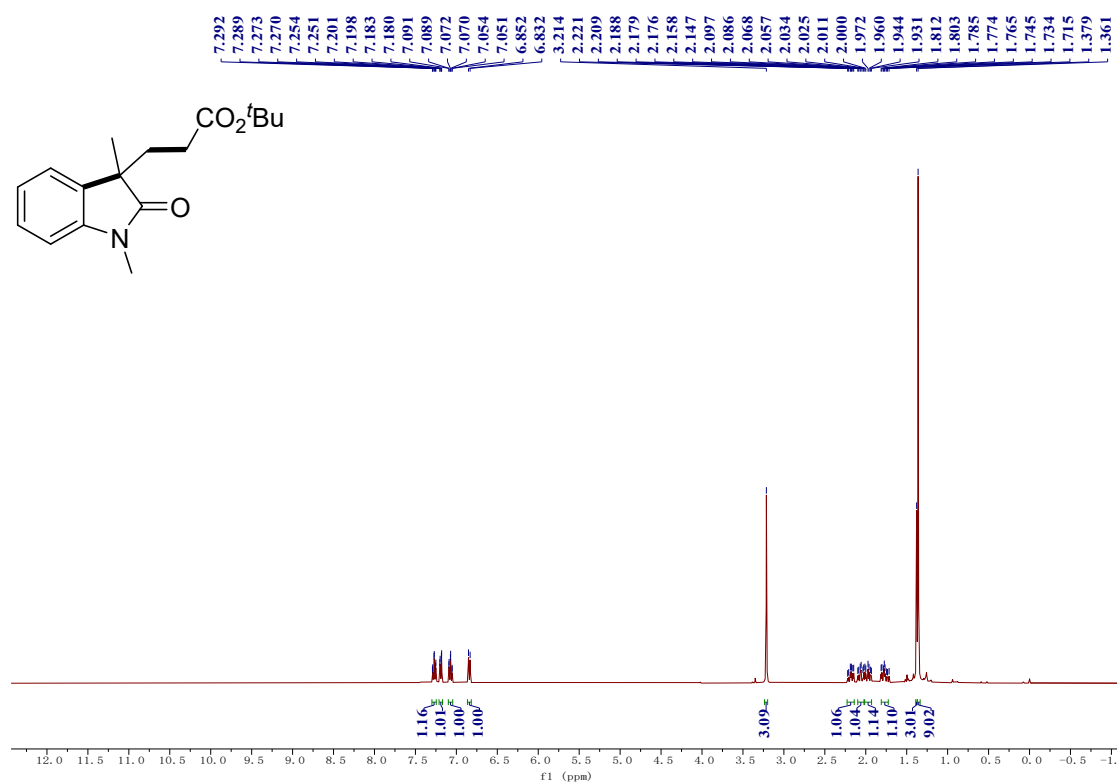
Substrate 17: ^1H NMR (CDCl_3 , 400 MHz), ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz)



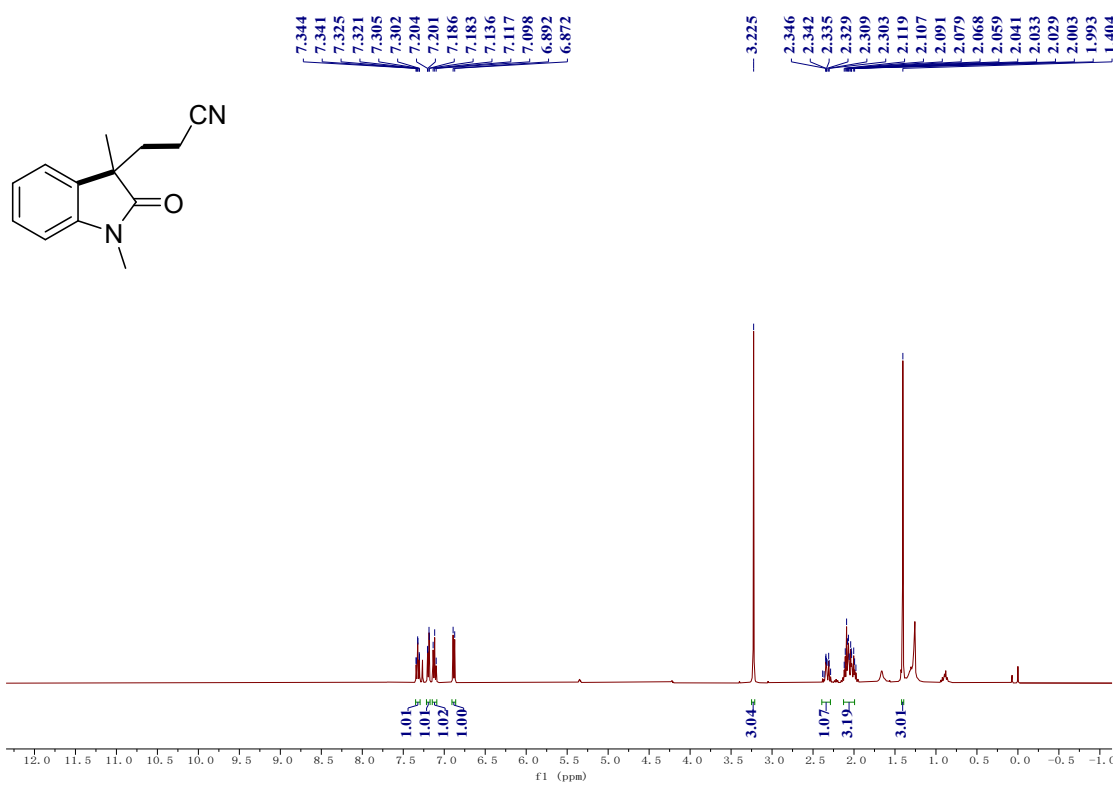
Substrate **18**: ^1H NMR (CDCl_3 , 400 MHz)



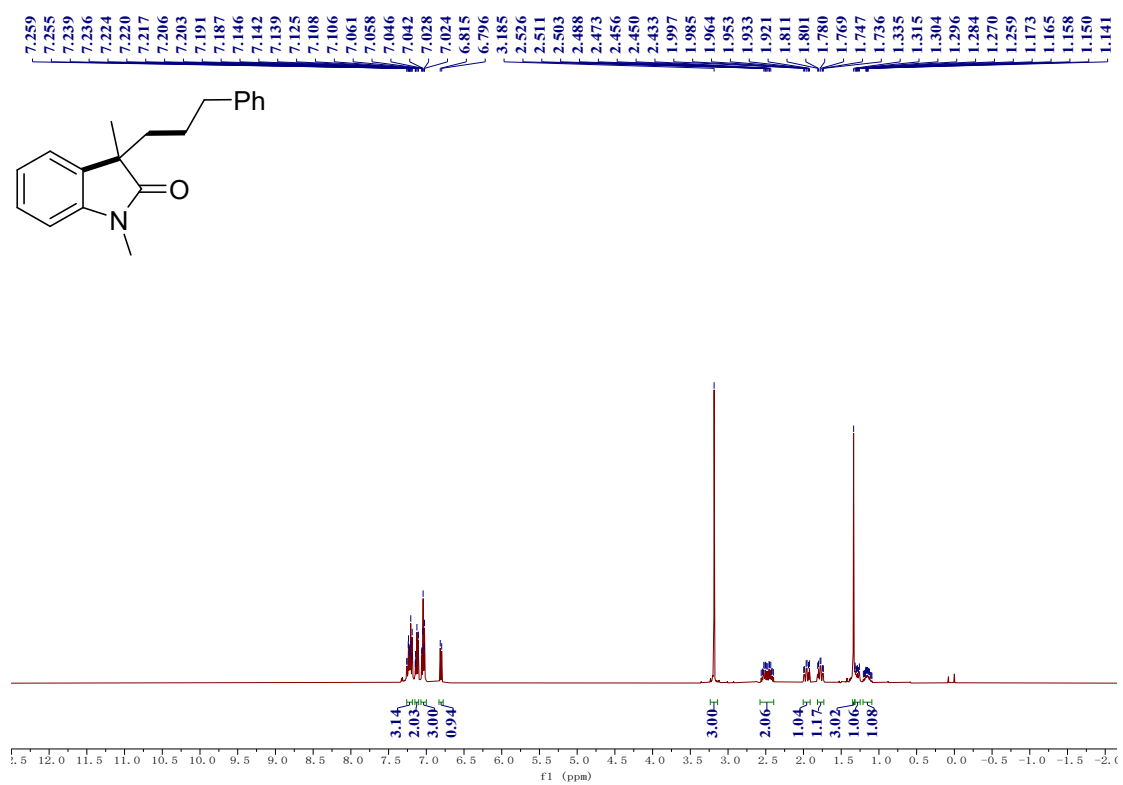
Substrate 19: ^1H NMR (CDCl_3 , 400 MHz)



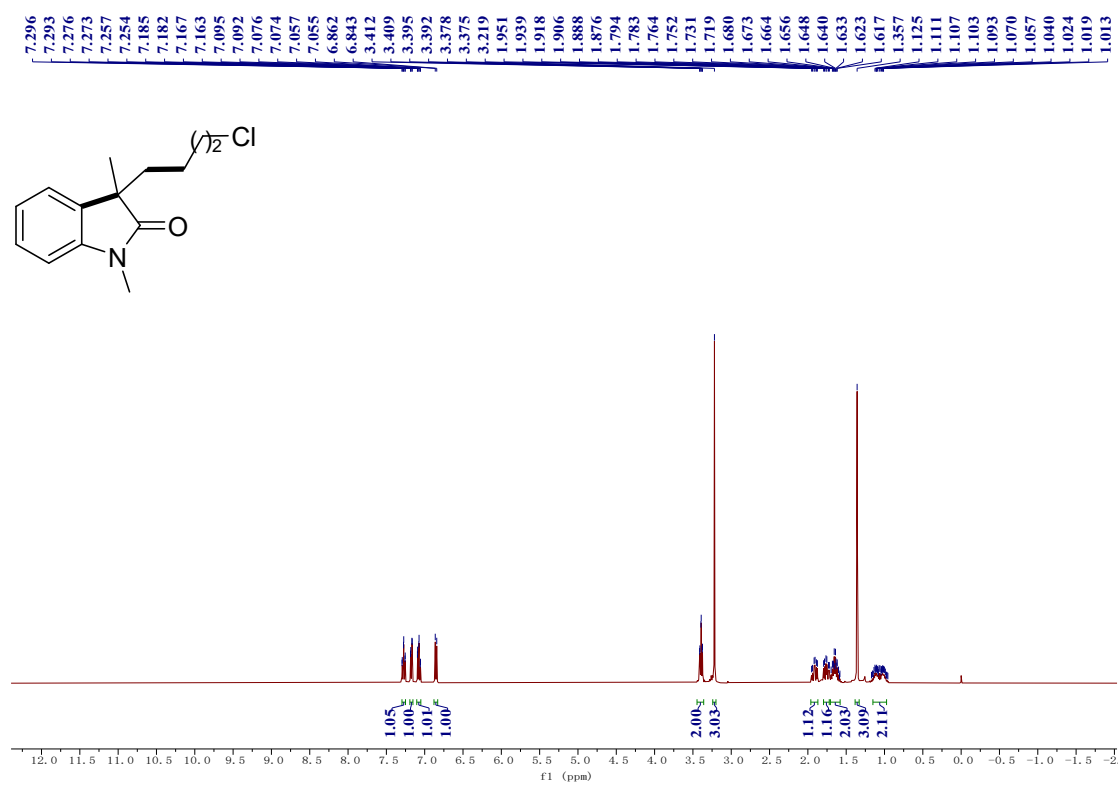
Substrate **20**: ^1H NMR (CDCl_3 , 400 MHz)



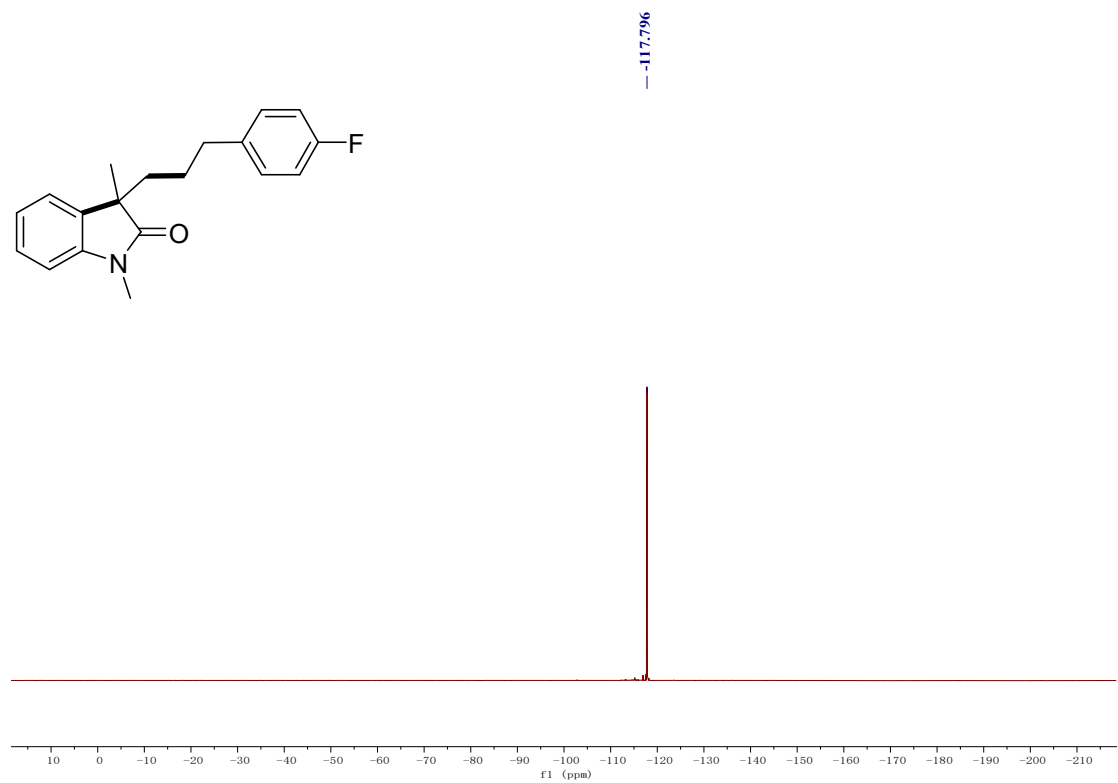
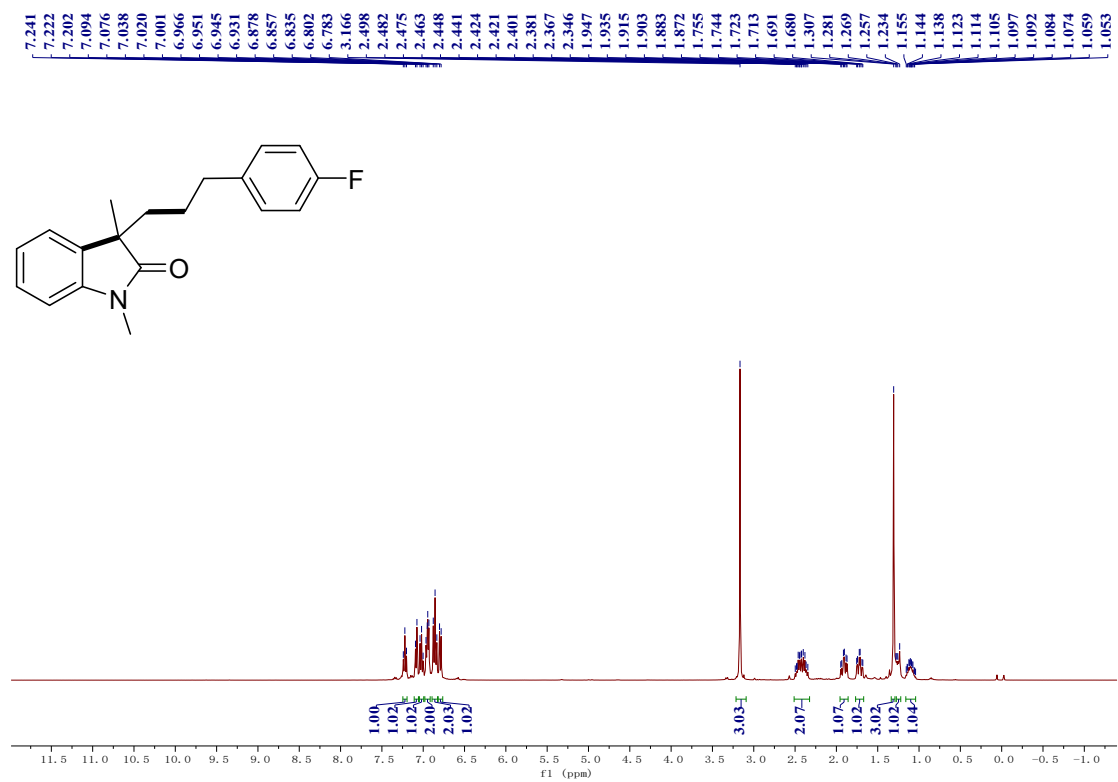
Substrate 21: ^1H NMR (CDCl_3 , 400 MHz)



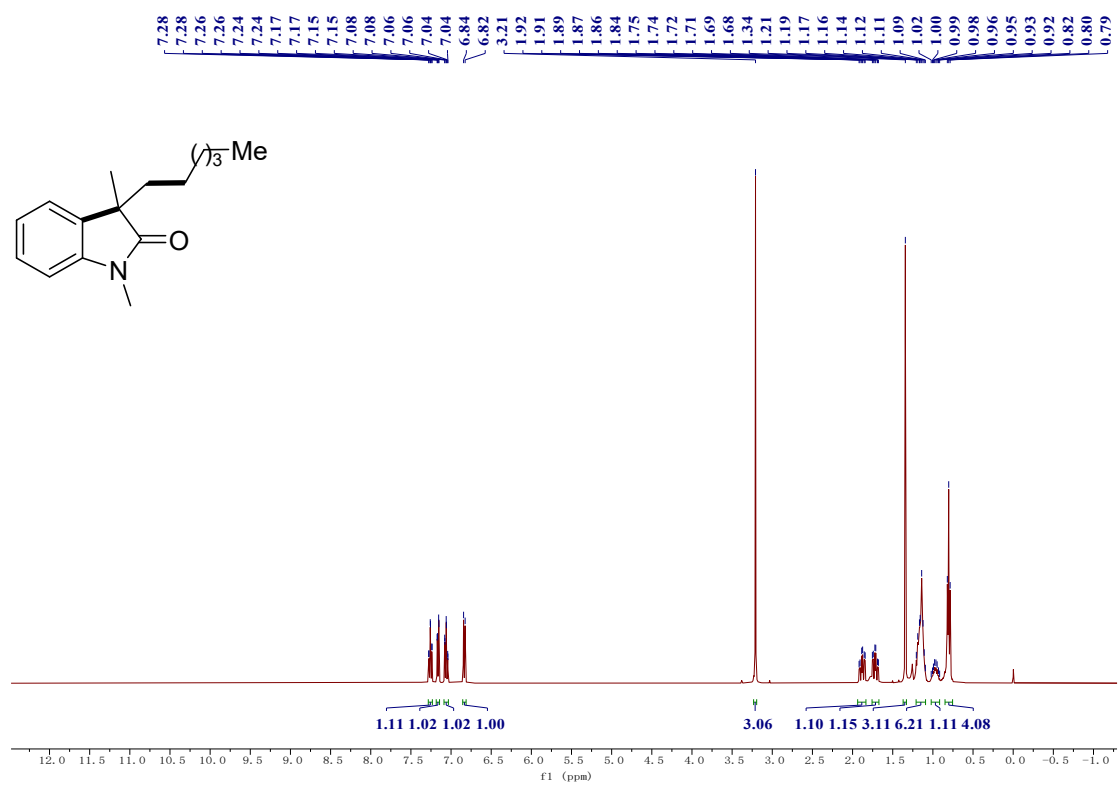
Substrate **22**: ^1H NMR (CDCl_3 , 400 MHz)



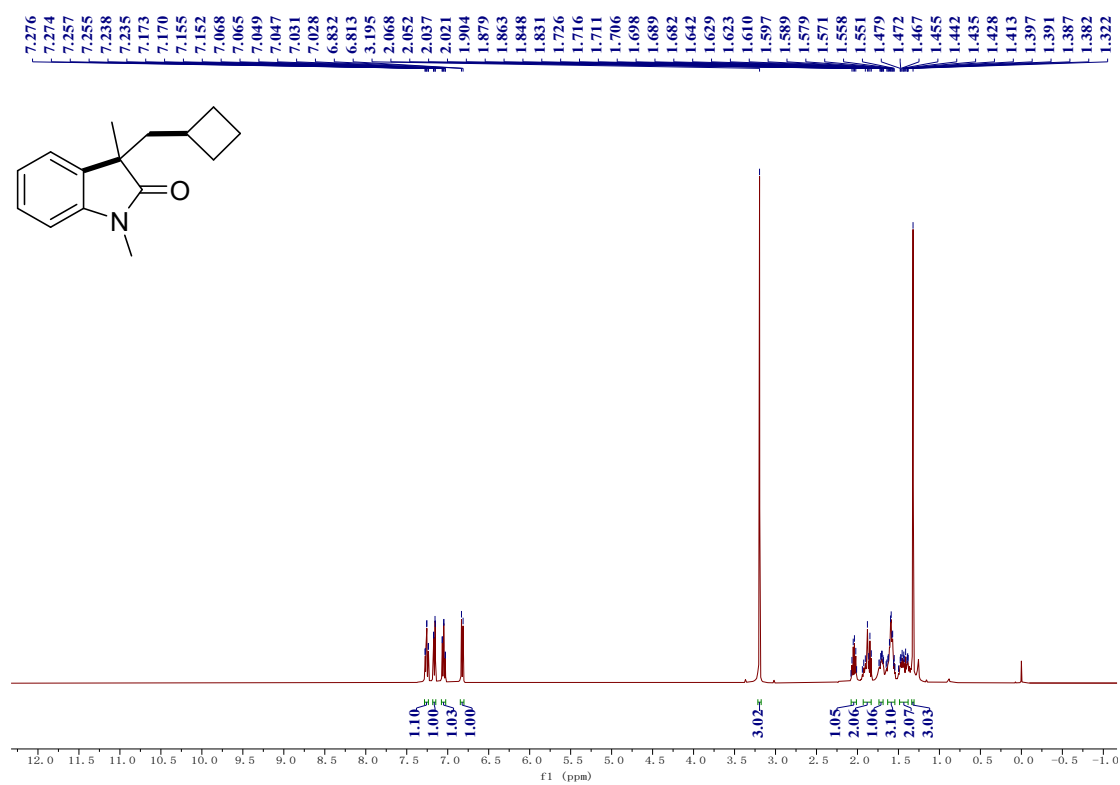
Substrate **23**: ^1H NMR (CDCl_3 , 400 MHz), ^{19}F NMR (376 MHz, CDCl_3)



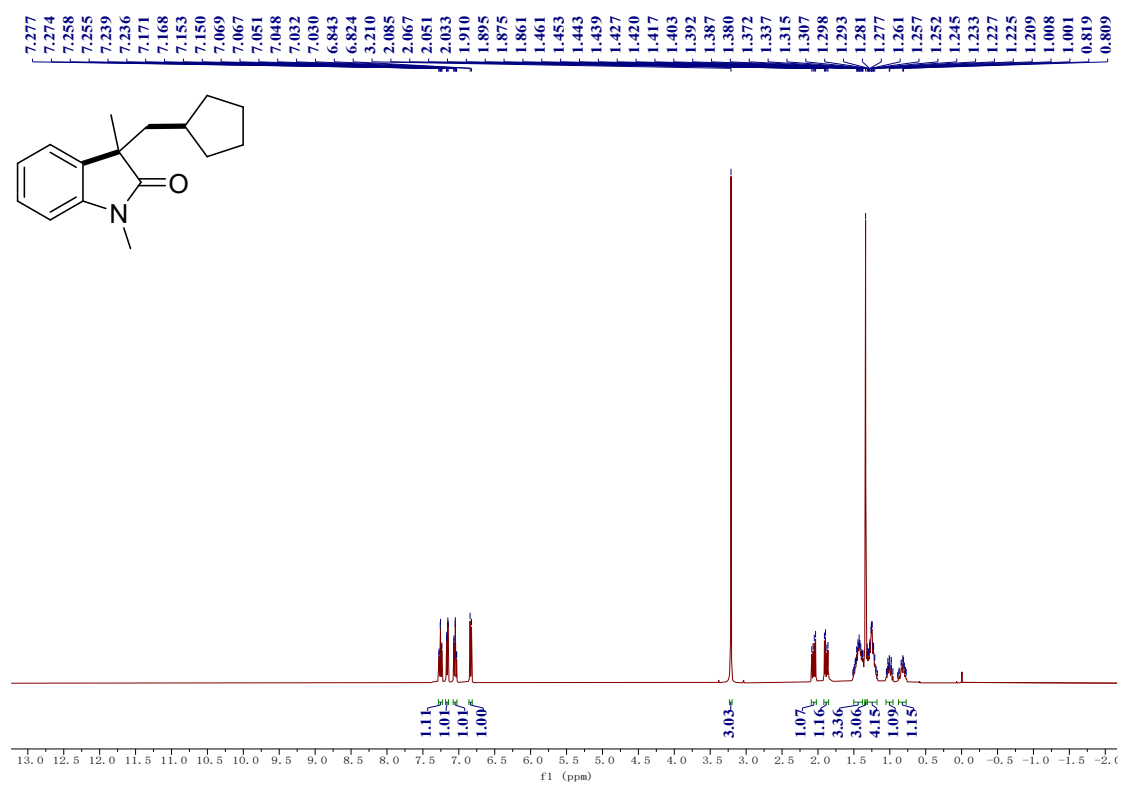
Substrate **24**: ^1H NMR (CDCl_3 , 400 MHz)



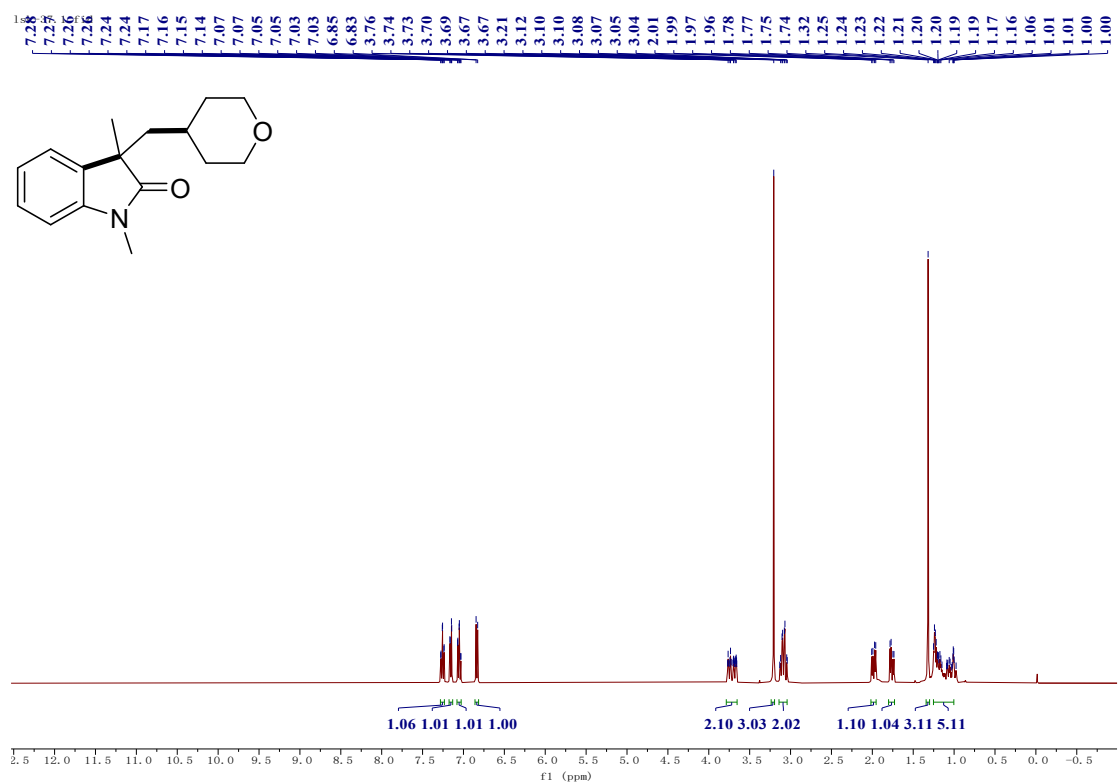
Substrate **25**: ^1H NMR (CDCl_3 , 400 MHz)



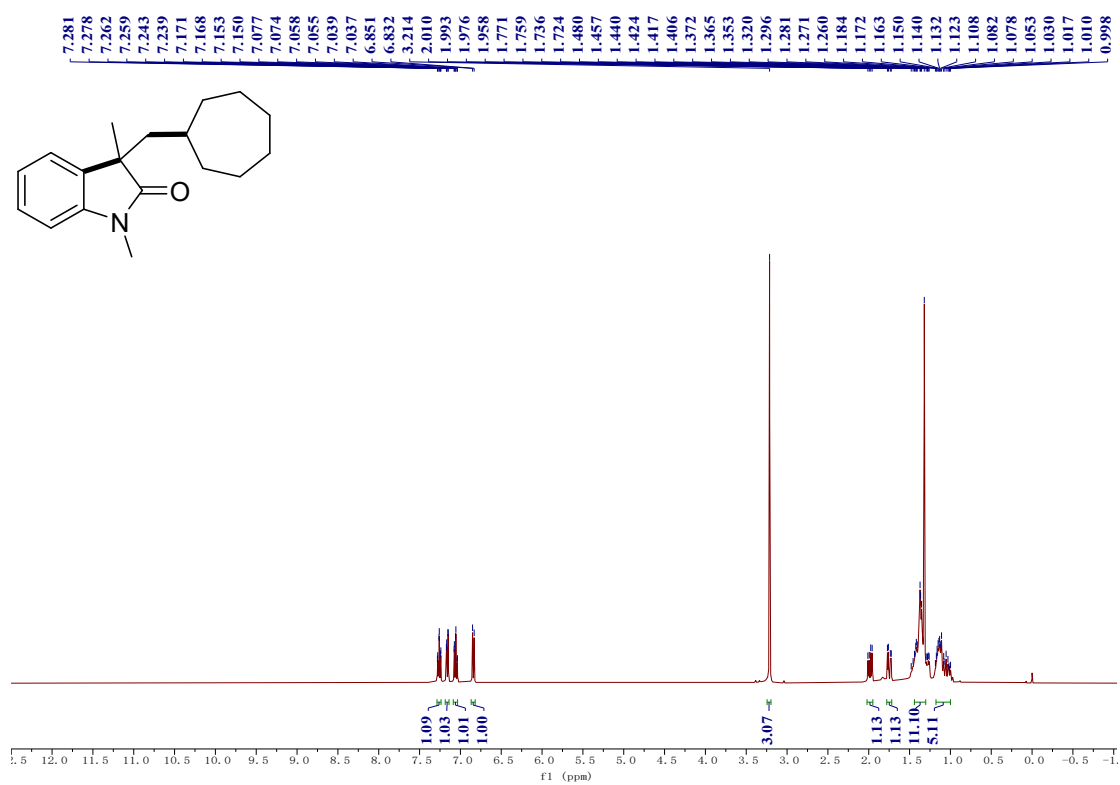
Substrate **26**: ^1H NMR (CDCl_3 , 400 MHz)



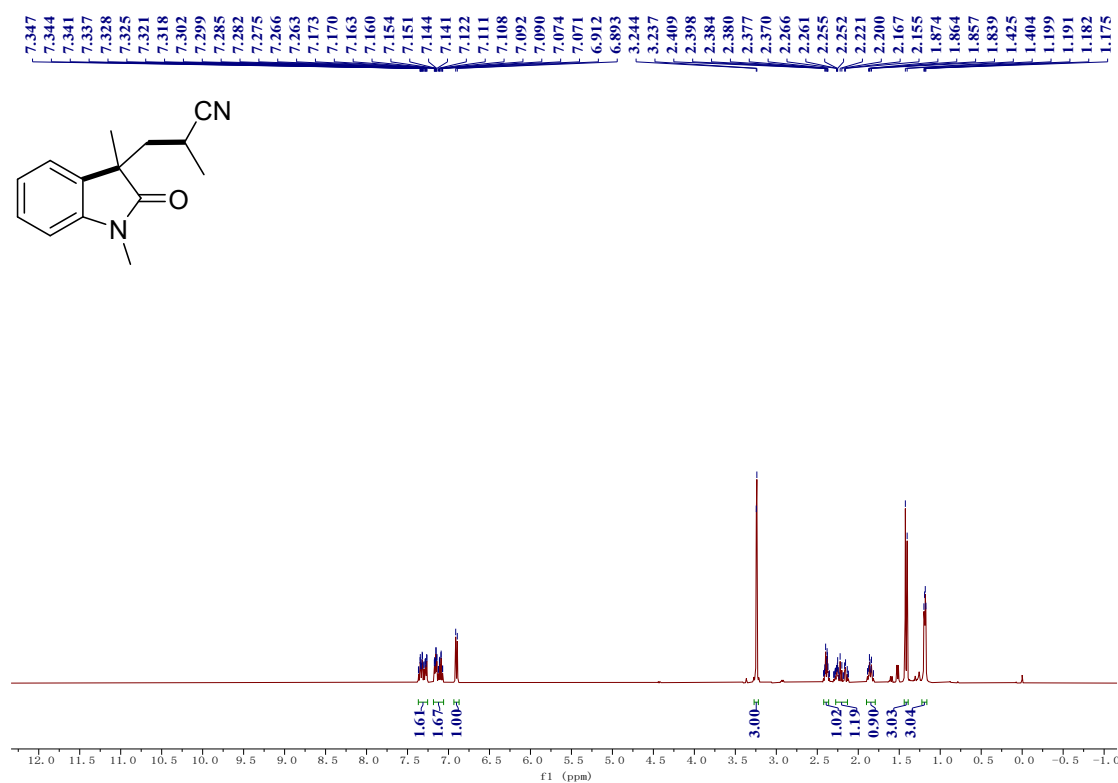
Substrate 27: ^1H NMR (CDCl_3 , 400 MHz)



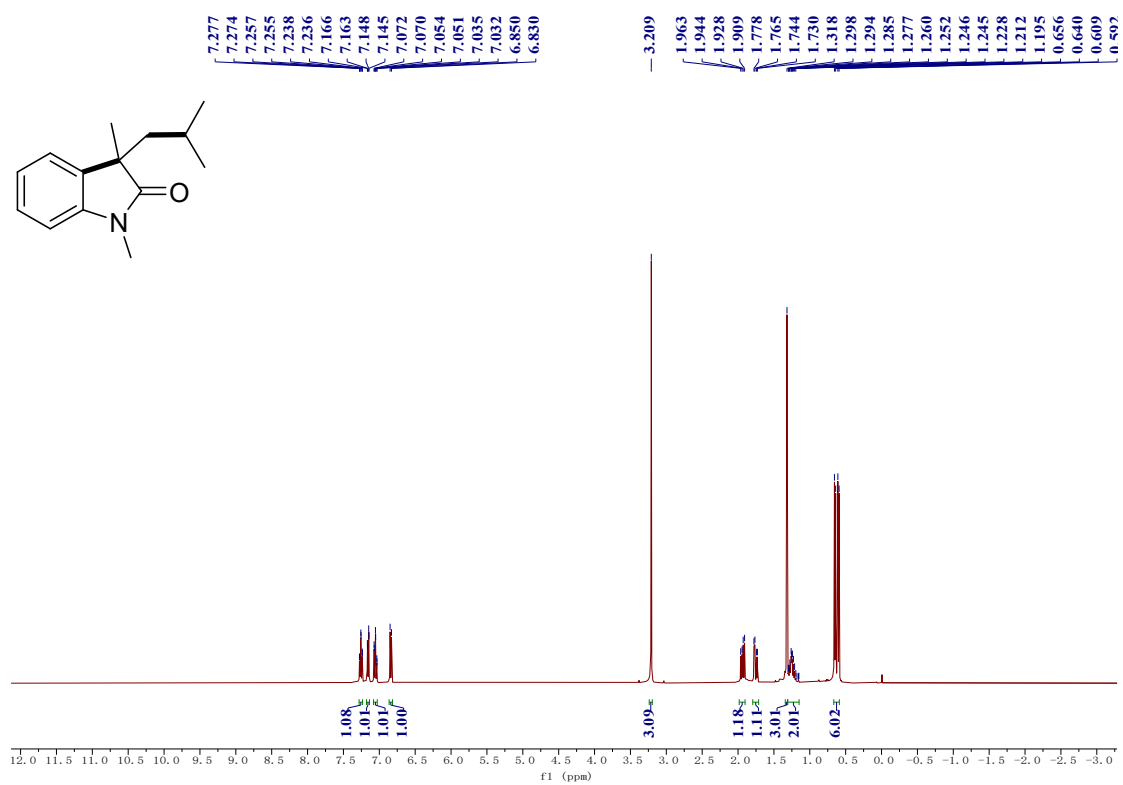
Substrate **28**: ^1H NMR (CDCl_3 , 400 MHz)



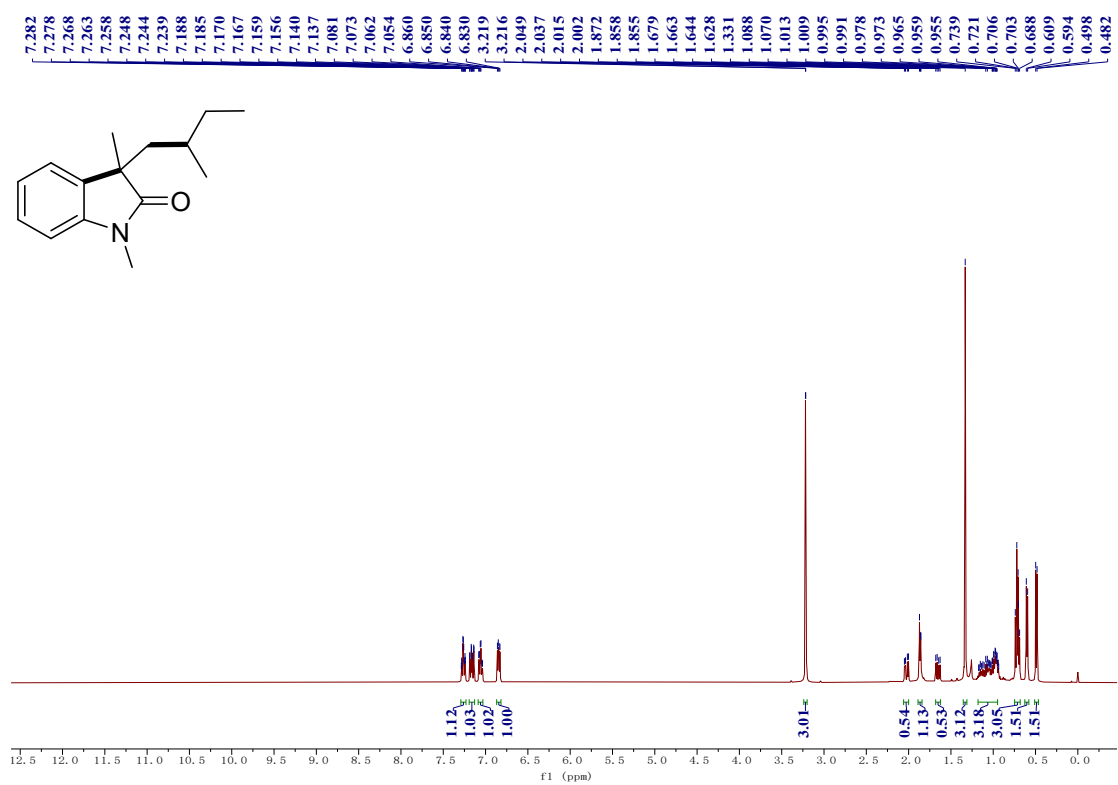
Substrate **29**: ^1H NMR (CDCl_3 , 400 MHz)



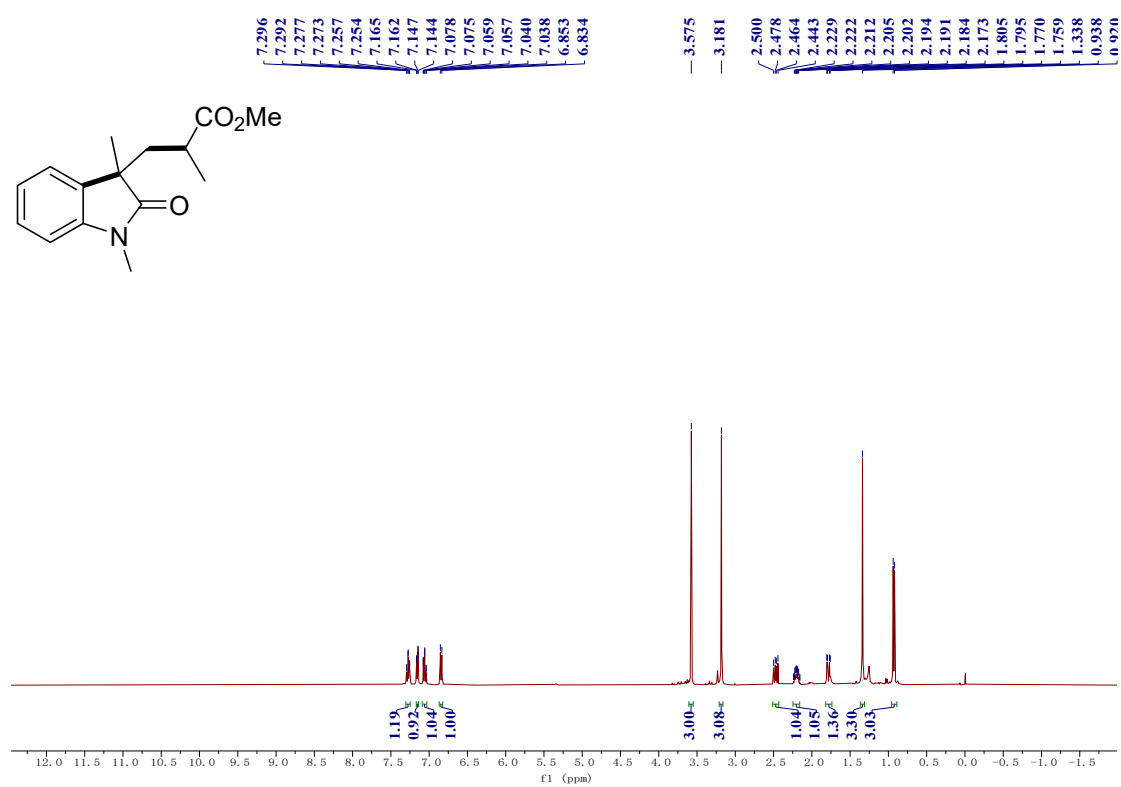
Substrate **30**: ^1H NMR (CDCl_3 , 400 MHz)



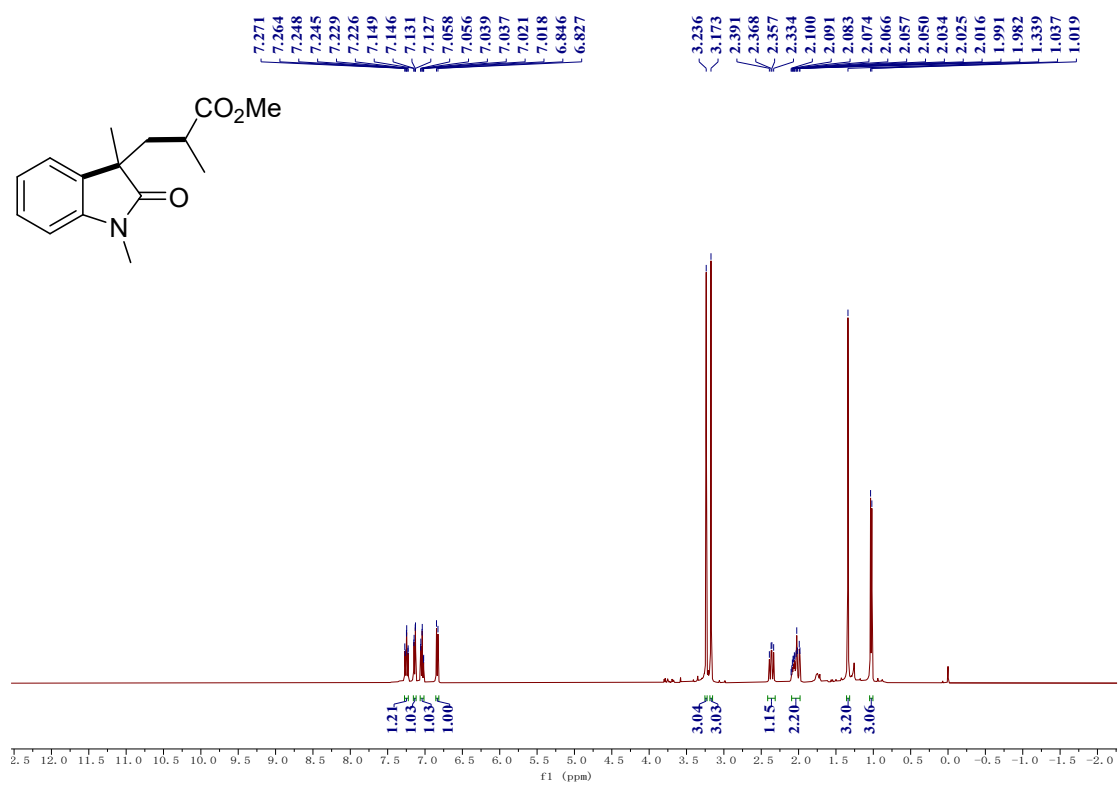
Substrate **31**: ^1H NMR (CDCl_3 , 400 MHz)



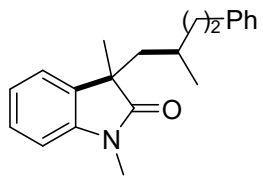
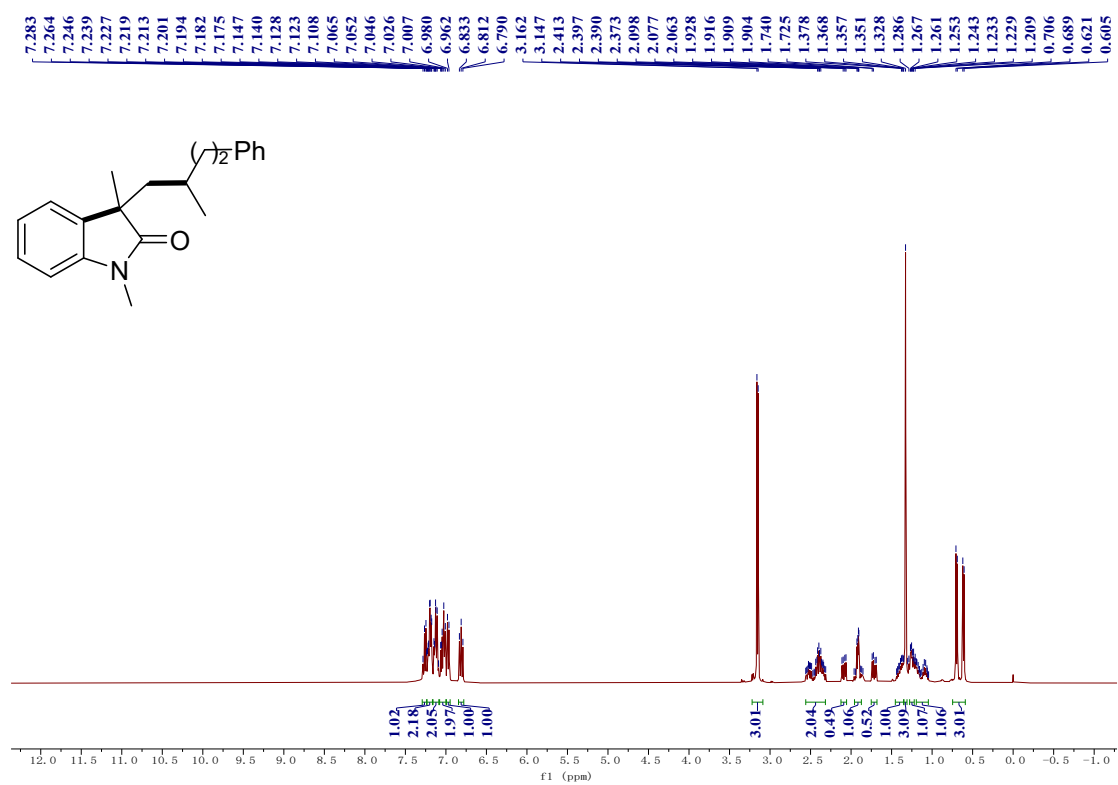
Substrate **32-1**: ^1H NMR (CDCl_3 , 400 MHz)



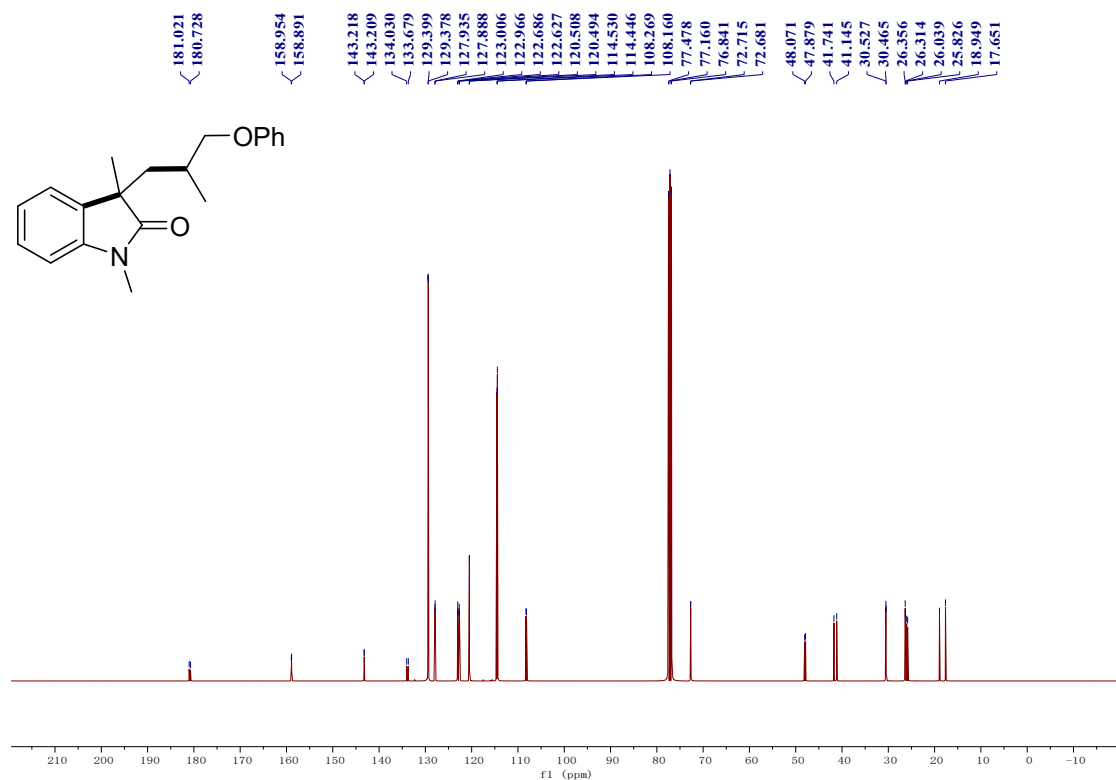
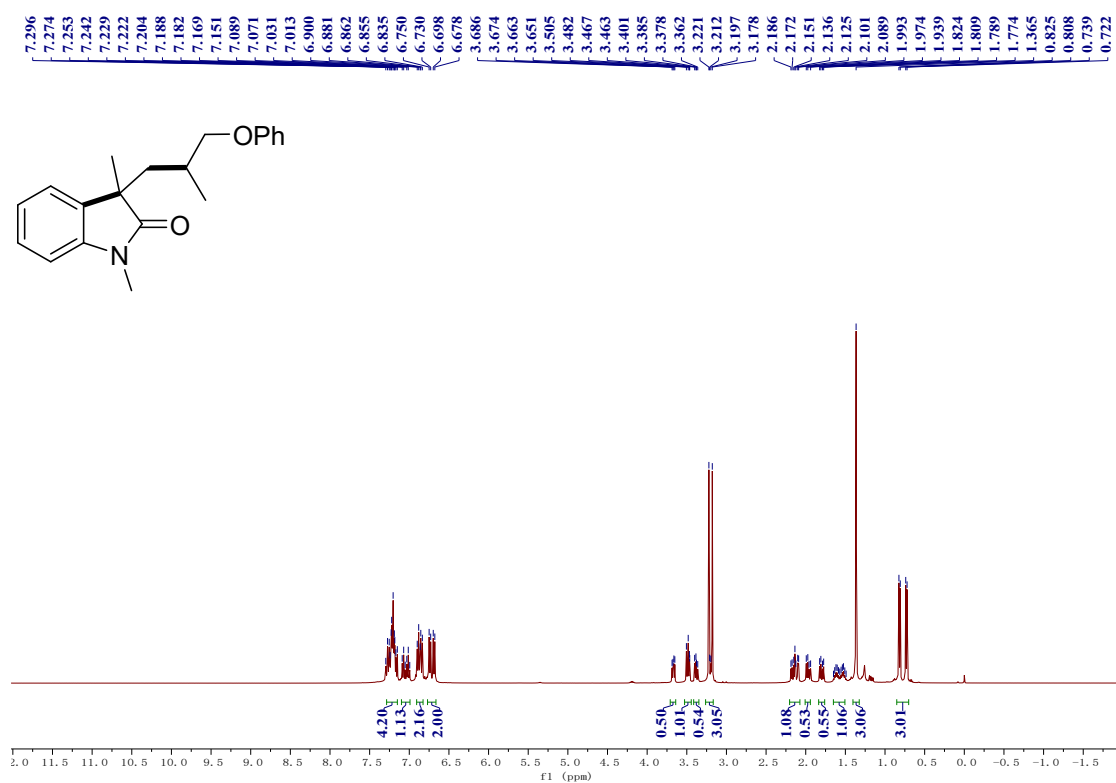
Substrate **32-2**: ^1H NMR (CDCl_3 , 400 MHz)



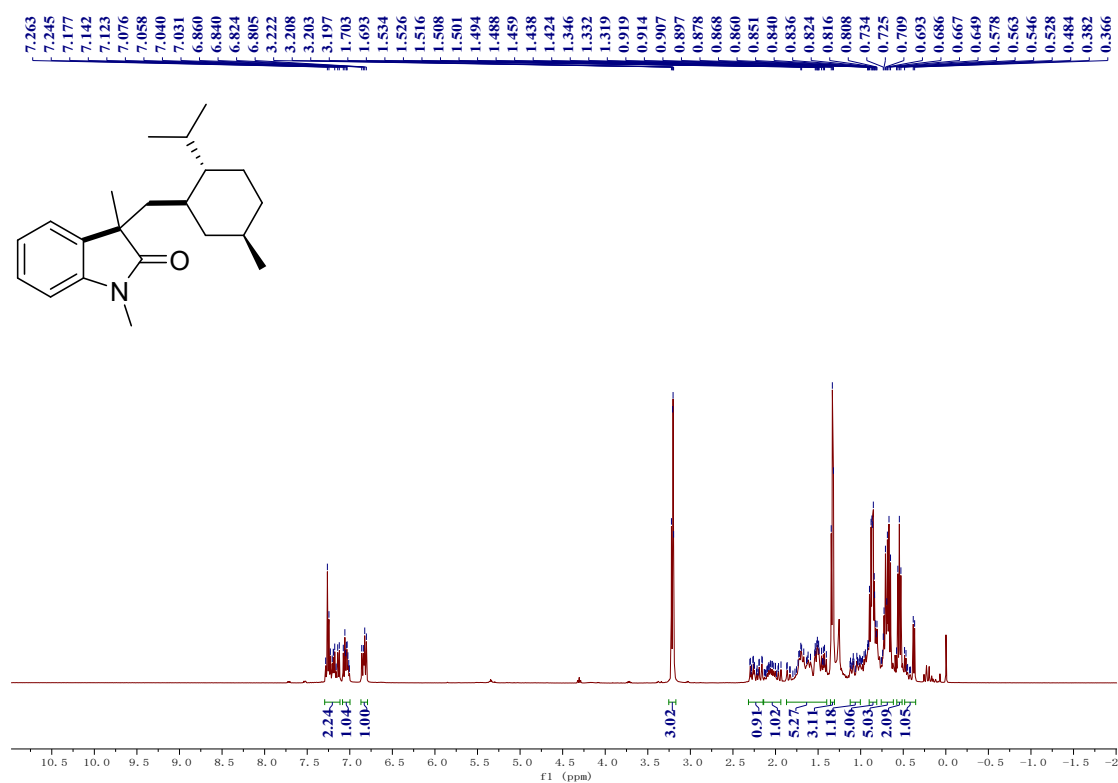
Substrate **33**: ^1H NMR (CDCl_3 , 400 MHz)



Substrate **34**: ^1H NMR (CDCl_3 , 400 MHz), ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz)



Substrate **35**: ^1H NMR (CDCl_3 , 400 MHz)



Reference of known compound:

Entry	Compounds	Reference
1	3, 15, 18-19, 25-32	10
2	4 8 12 21 24	11
3	5-6	12
4	9	13
5	10	3
6	14	14
7	20	15
8	22	16
9	23	17
10	33, 35	18

A comparison of the yields from our work and previous literatures.

Compounds	Yield	Reference	Yield in the corresponding reference
4	82%	11	71%
20	70%	15	20%
21	77%	11	51%
22	57%	16	40%
24	54%	11	46%
29	79%	10	42%

8. References

- [1] M. Zhang, X. Ding, A. Lu, J. Kang, Y. Gao, Z. Wang, H. Li, Q. Wang, *Org. Chem. Front.* **2021**, *8*, 961–967.
- [2] Z.-P. Ye, J.-S. Yang, S.-J. Yang, M. Guo, C.-P. Yuan, Y.-Q. Ye, H.-B. Chen, H.-Y. Xiang, K. Chen, H. Yang, *Org. Lett.* **2023**, *25*, 7062–7066.
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