Supporting Information

Palladium-catalyzed reductive Heck cyclization of alkene-tethered carbamoyl chlorides to access CH_3 and CH_2D-functionalized oxindoles

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Table of Contents

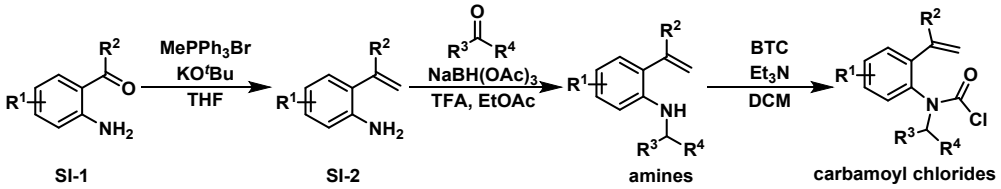
General Information

The ^{1}H NMR, ^{13}C NMR, ^{19}F NMR were recorded with Bruker 400 MHz and 600 MHz spectrometer instruments in $CDCl_3$. The chemical shifts (δ) of ^{1}H NMR, ^{13}C NMR, ^{19}F NMR were measured in ppm, referenced to residual ^{1}H and ^{13}C signals of nondeuterated $CDCl_3$ (δ = 7.26 and 77.00) as internal standards. All solvents were obtained from commercial sources and were purified according to standard procedures. Purification of products was accomplished by flash chromatography using silica gel (200~300 mesh). Thin layer chromatography (TLC) was performed on Merck silica gel GF254 plates and visualized by UV-light (254 nm). Melting points were obtained on a Yanaco-241 apparatus and are uncorrected. HRMS were recorded on Agilent 6520 Q-TOF mass spectrometer with ESI resource.

General Procedures for the Synthesis of Substrates

General Procedures for the Synthesis of Amines and Carbamoyl Chlorides

General Procedure 1



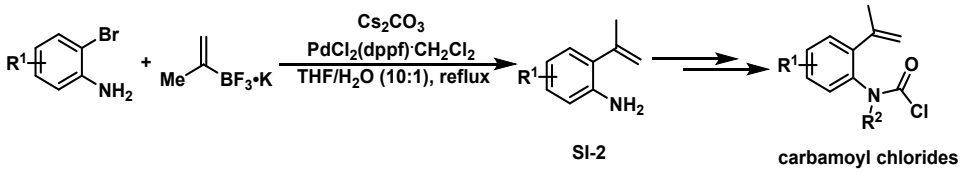
A mixture of $MePPh_3Br$ (1.5 equiv) and KO^tBu (1.5 equiv) in THF (0.3 M) was stirred at room temperature for 1 h. Then **SI-1** (1.0 equiv) was added dropwise to the reaction mixture at 0 °C. The reaction was stirred at room temperature until the starting material was disappeared. After that the solvents were evaporated under reduced pressure. The residue was purified by column chromatography to give **SI-2**.

The **SI-2** (1.0 equiv) was dissolved in EtOAc (0.25 M). The aldehyde or ketone (1.2 equiv) was added followed by TFA (2.0 equiv). The reaction was stirred for 30 minutes then $NaBH(OAc)_3$ (2.0 equiv) was added. The reduction was stirred for 2 h then quenched with 4 M NaOH. The reaction was diluted with EtOAc and washed twice with brine. The organic layer was dried over magnesium sulfate, filtered, and

concentrated under reduced pressure. The crude was purified by flash column chromatography to give amines.

The amine (1.0 equiv) was dissolved in DCM (0.3 M) and cooled to 0 °C. Then Et_3N (2.0 equiv) was added followed by BTC (0.6 equiv). The reaction was warmed to room temperature and stirred until completion indicated by TLC. The reaction was quenched with water and extracted twice with DCM. The organic layers were dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The crude starting materials were purified by flash column chromatography in EA/PE mixtures to give carbamoyl chlorides.

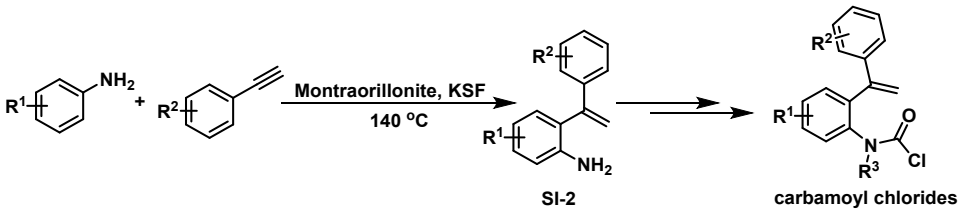
General Procedure 2



To a suspension of potassium isopropenyltrifluoroborate (1.1 equiv), Cs_2CO_3 (3.0 equiv), $PdCl_2(dppf)\cdot CH_2Cl_2$ (9 mol%) in a solvent mixture (THF/H_2O = 10/1) was added 2-bromoaniline (1.0 equiv). The reaction mixture was stirred at reflux for 16 h, then cooled to room temperature and diluted with water followed by extraction with EtOAc. The combined organic layer was washed with saturated NaCl solution, dried over $MgSO_4$, concentrated under reduced pressure and the crude product was purified by flash column chromatography in EA/PE mixtures to give **SI-2**.

(Note: The remaining procedure follows the **General Procedure 1**.)

General Procedure 3

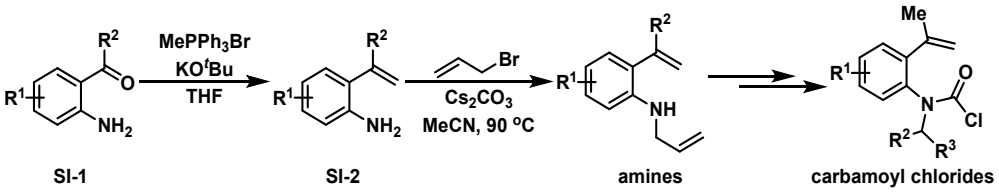


Aniline (1.0 equiv), phenylacetylene (1.1 equiv) and montraorillonite KSF (100.0 mg/mmol) are introduced in a round bottomed flask equipped with magnetic stirrer and a reflux condenser. The reaction mixture is heated at 140 °C for 5 hours and then cooled

to room temperature. The crude mixtures were dissolved with dichloromethane and filtered. Then the solvents were concentrated in vacuo and the crude was purified by flash column chromatography in EA/PE mixtures to give **SI-2**.

(Note: The remaining procedure follows the **General Procedure 1**.)

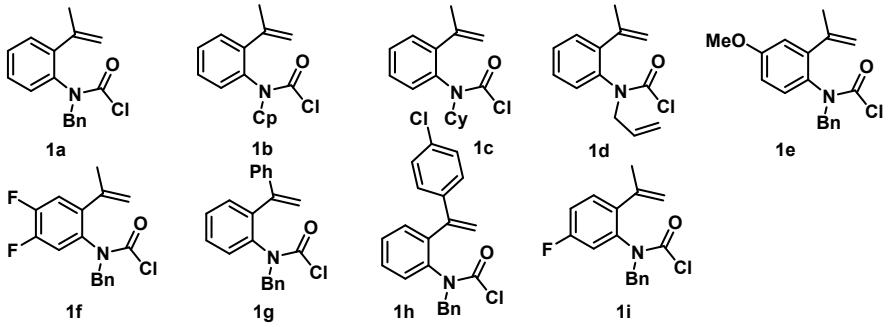
General Procedure 4



A mixture of $MePPh_3Br$ (1.5 equiv) and KO^{t}Bu (1.5 equiv) in THF (0.3 M) was stirred at room temperature for 1 h. Then **SI-1** (1.0 equiv) was added dropwise to the reaction mixture at 0 °C. The reaction was stirred at room temperature until the starting material was disappeared. After that the solvents were evaporated under reduced pressure. The residue was purified by column chromatography to give **SI-2**.

The mixture of **SI-2** (1.0 equiv), 3-bromoprop-1-ene (1.5 equiv), Cs_2CO_3 (6.0 equiv) and an appropriate amount of KI in MeCN was stirred at 90 °C and stirred until the starting material disappeared. After that the solvents were evaporated under reduced pressure. The residue was purified by column chromatography to give amines.

(Note: The remaining procedure follows the **General Procedure 1**.)



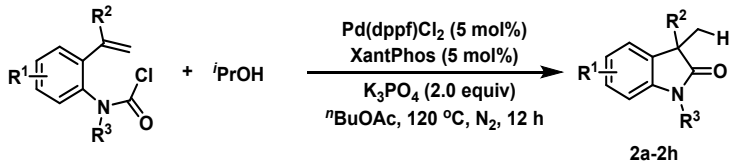
1a to **1c**, **1g** were synthesized by **general procedure 1**

1e, **1f**, **1i** were synthesized by **general procedure 2**

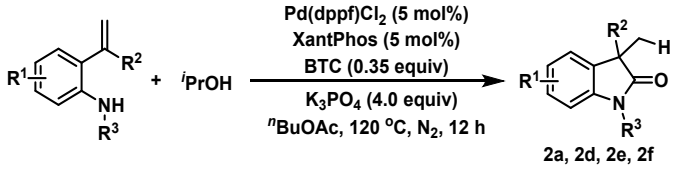
1h was synthesized by **general procedure 3**

1d was synthesized by **general procedure 4**

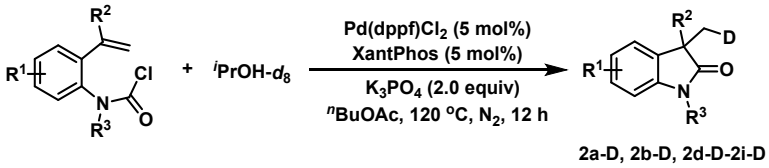
General Procedures for the Synthesis of Products



In a 25 mL sealed tube, the mixture of alkene-tethered carbamoyl chlorides (0.2 mmol, 1.0 equiv), ^{i}PrOH (0.4 mmol, 2.0 equiv), Pd(dppf)Cl_2 (5 mol%), XantPhos (5 mol%), K_3PO_4 (0.4 mmol, 2.0 equiv), were added in anhydrous ^{n}BuOAc (2.0 mL). Then, the tube was purged with N_2 for three times and sealed with PTEF cap. The reaction mixture was heated to 120 °C for 12 h. When the reaction was finished, the mixture was cooled to room temperature and the solvents were removed under reduced pressure. The residue was purified by silica gel column chromatography to give the products **2a-2h**.

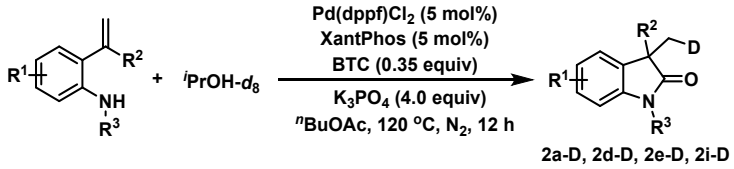


In a 25 mL sealed tube, the mixture of amines (0.2 mmol, 1.0 equiv), ^{i}PrOH (0.4 mmol, 2.0 equiv), BTC (0.07 mmol, 0.35 equiv), Pd(dppf)Cl_2 (5 mol%), XantPhos (5 mol%), K_3PO_4 (0.8 mmol, 4.0 equiv), were added in anhydrous ^{n}BuOAc (2.0 mL). Then, the tube was purged with N_2 for three times and sealed with PTEF cap. The reaction mixture was heated to 120 °C for 12 h. When the reaction was finished, the mixture was cooled to room temperature and the solvents were removed under reduced pressure. The residue was purified by silica gel column chromatography to give the products **2a, 2d, 2e, 2f**.



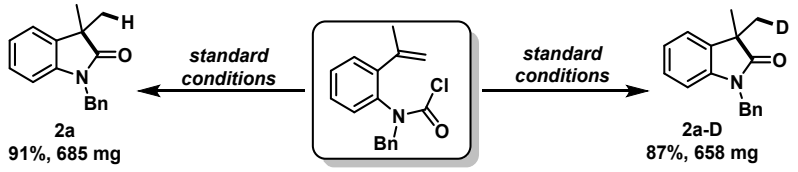
In a 25 mL sealed tube, the mixture of alkene-tethered carbamoyl chlorides (0.2 mmol, 1.0 equiv), ^{i}PrOH-d_8 (0.24 mmol, 1.2 equiv), Pd(dppf)Cl_2 (5 mol%), XantPhos (5 mol%), K_3PO_4 (0.4 mmol, 2.0 equiv), were added in anhydrous ^{n}BuOAc (2.0 mL). Then, the tube was purged with N_2 for three times and sealed with PTEF cap. The reaction mixture was heated to 120 °C for 12 h. When the reaction was finished, the

mixture was cooled to room temperature and the solvents were removed under reduced pressure. The residue was purified by silica gel column chromatography to give the products **2a-D**, **2b-D, 2d-D-2i-D**.



In a 25 mL sealed tube, the mixture of amines (0.2 mmol, 1.0 equiv), ^{i}PrOH-d_8 (0.24 mmol, 1.2 equiv), BTC (0.07 mmol, 0.35 equiv), Pd(dppf)Cl_2 (5 mol%), XantPhos (5 mol%), K_3PO_4 (0.8 mmol, 4.0 equiv), were added in anhydrous ^{n}BuOAc (2.0 mL). Then, the tube was purged with N_2 for three times and sealed with PTEF cap. The reaction mixture was heated to 120 °C for 12 h. When the reaction was finished, the mixture was cooled to room temperature and the solvents were removed under reduced pressure. The residue was purified by silica gel column chromatography to give the products **2a-D, 2d-D, 2e-D, 2i-D**.

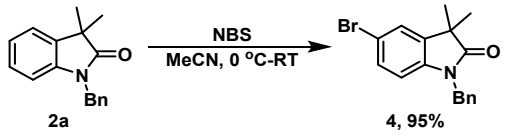
Scale-up Experiments and Synthetic Transformations



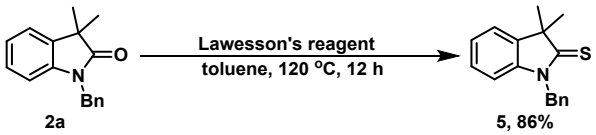
To a flame-dried 100 mL pressure reaction vessel was charged sequentially with: alkene-tethered carbamoyl chlorides (3.0 mmol, 1.0 equiv), ^{i}PrOH (6.0 mmol, 2.0 equiv), Pd(dppf)Cl_2 (5 mol%), XantPhos (5 mol%), K_3PO_4 (6.0 mmol, 2.0 equiv), were added in anhydrous ^{n}BuOAc (20.0 mL). Then, the tube was purged with N_2 for three times and sealed with PTEF cap. The reaction mixture was heated to 120 °C for 12 h. When the reaction was finished, the mixture was cooled to room temperature and the solvents were removed under reduced pressure. The residue was purified by silica gel column chromatography to give the products **2a** in 91% yield (685 mg).

To a flame-dried 100 mL pressure reaction vessel was charged sequentially with: alkene-tethered carbamoyl chlorides (3.0 mmol, 1.0 equiv), ^{i}PrOH-d_8 (6.0 mmol, 2.0 equiv), Pd(dppf)Cl_2 (5 mol%), XantPhos (5 mol%), K_3PO_4 (6.0 mmol, 2.0 equiv), were added in anhydrous ^{n}BuOAc (20.0 mL). Then, the tube was purged with N_2 for three

times and sealed with PTEF cap. The reaction mixture was heated to 120 °C for 12 h. When the reaction was finished, the mixture was cooled to room temperature and the solvents were removed under reduced pressure. The residue was purified by silica gel column chromatography to give the products **2a-D** in 87% yield (658 mg).



In a 25 mL sealed tube, the mixture of **2a** (0.2 mmol, 1.0 equiv), NBS (0.2 mmol, 1.0 equiv) were added in 2.0 mL MeCN in 0 °C over 3 min. Then, the tube sealed with PTEF cap. The reaction mixture was heated to room temperature for 12 h. When the reaction was finished, the mixture was warmed to room temperature and the solvents were removed under reduced pressure. The crude mixture was purified by silica gel flash column chromatography using EA/PE as the eluent to afford the product **4** in 95% yield.



In a 25 mL sealed tube, **2a** (0.2 mmol, 1.0 equiv) in toluene (6.0 mL) was added Lawesson's reagent (0.8 mmol, 4.0 equiv). The reaction was stirring at 120 °C for 16 h. The reaction mixture was filtered through a pad of celite and washed with DCM. The crude mixture was purified by silica gel flash column chromatography using EA/PE as the eluent to afford the products **5** in 86% yield.

Characterization of Products

1-benzyl-3,3-dimethylindolin-2-one (2a)[1]

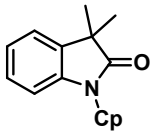
Yield: 98%, 49.2 mg; appearance: colorless oil; R_f = 0.2 (PE/EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 5H), 7.25 (d, *J* = 7.2 Hz, 1H), 7.19 –

7.15 (m, 1H), 7.08 – 7.03 (m, 1H), 6.75 (d, *J* = 7.6 Hz, 1H), 4.95 (s, 2H), 1.48 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 181.4, 141.6, 136.0, 135.7, 128.7, 127.51, 127.47, 127.1, 122.4, 122.3, 109.0, 44.1, 43.5, 24.5.

1-cyclopentyl-3,3-dimethylindolin-2-one (2b)



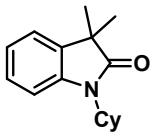
Yield: 96%, 44.0 mg; appearance: colorless oil; R_f = 0.2 (PE/EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.20 (m, 2H), 7.06 – 7.01 (m, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 4.86 – 4.77 (m, 1H), 2.11 – 2.03 (m, 2H), 1.98 – 1.87 (m, 4H), 1.77 – 1.66 (m, 2H), 1.35 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 181.3, 140.9, 136.3, 127.2, 122.5, 121.9, 109.7, 51.9, 43.8, 27.5, 25.3, 24.5.

ESI-MS: Calcd for $C_{15}H_{20}NO$: [M+H$^+$] 230.1539, found 230.1542.

1-cyclohexyl-3,3-dimethylindolin-2-one (2c)[2]

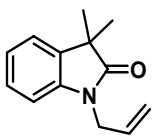


Yield: 95%, 46.2 mg; appearance: colorless oil; R_f = 0.2 (PE/EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.19 (m, 2H), 7.08 – 7.00 (m, 2H), 4.23 – 4.16 (m, 1H), 2.20 – 2.10 (m, 2H), 1.91 – 1.87 (m, 2H), 1.77 – 1.73 (m, 3H), 1.47 – 1.23 (m, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 181.2, 141.6, 136.3, 127.2, 122.4, 121.7, 110.1, 51.8, 43.7, 29.1, 26.0, 25.4, 24.5.

1-cyclohexyl-3,3-dimethylindolin-2-one (2d)[3]

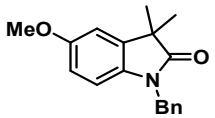


Yield: 90%, 36.2 mg; appearance: colorless oil; R_f = 0.2 (PE/EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.20 (m, 2H), 7.08 – 7.03 (m, 1H), 6.85 – 6.82 (m, 1H), 5.89 – 5.79 (m, 1H), 5.22 – 5.16 (m, 2H), 4.36 – 4.33 (m, 2H), 1.39 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 181.1, 141.7, 135.8, 131.6, 127.5, 122.4, 122.3, 117.2, 108.9, 44.1, 42.1, 24.5.

1-benzyl-5-methoxy-3,3-dimethylindolin-2-one (2e)[4]

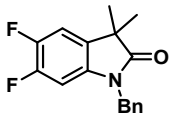


Yield: 94%, 52.9 mg; appearance: yellow oil; R_f = 0.2 (PE/EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.13 (m, 5H), 6.75 (d, *J* = 2.4 Hz, 1H), 6.57 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.51 (d, *J* = 8.8 Hz, 1H), 4.81 (s, 2H), 3.67 (s, 3H), 1.35 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 181.1, 156.0, 137.1, 136.1, 135.0, 128.7, 127.4, 127.1, 111.5, 110.0, 109.3, 55.7, 44.6, 43.5, 24.5.

1-benzyl-5,6-difluoro-3,3-dimethylindolin-2-one (2f)



Yield: 95%, 54.6 mg; appearance: white solid, M.P.: 99-101ºC; R_f = 0.2 (PE/EA = 20:1).

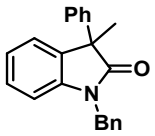
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.26 (m, 5H), 7.09 – 7.04 (m, 1H), 5.58 – 5.53 (m, 1H), 4.90 (s, 2H), 1.45 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 181.0, 151.0 (d, *J* = 14.0 Hz), 148.5 (d, *J* = 14.0 Hz), 147.9 (d, *J* = 13.0 Hz), 145.5 (d, *J* = 13.0 Hz), 137.6 (d, *J* = 7.0 Hz), 135.3, 131.1 – 130.9 (m), 128.9, 127.8, 127.1, 112.1, 111.9, 99.4, 99.2, 44.3, 43.7, 24.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -137.93 to -138.01 (m, 1F), -146.05 to -146.12 (m, 1F).

ESI-MS: Calcd for $C_{17}H_{16}F_2NO$: $[M+H^+]$ 288.1194, found 288.1193.

1-benzyl-3-methyl-3-phenylindolin-2-one (2g)[5]

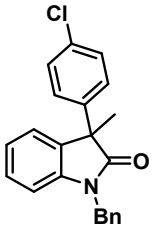


Yield: 82%, 51.4 mg; appearance: colorless oil; R_f = 0.2 (PE/EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 10H), 7.26 – 7.21 (m, 2H), 7.12 – 7.07 (m, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 5.03 (d, *J* = 15.6 Hz, 1H), 4.95 (d, *J* = 15.6 Hz, 1H), 1.90 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 179.5, 142.2, 140.8, 136.0, 135.0, 128.8, 128.6, 128.0, 127.6, 127.3, 127.2, 126.6, 124.2, 122.8, 109.3, 52.1, 43.8, 23.8.

1-benzyl-3-methyl-3-phenylindolin-2-one (2h)



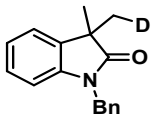
Yield: 73%, 50.7 mg; appearance: yellow oil; R_f = 0.2 (PE/EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.15 (m, 9H), 7.15 – 7.07 (m, 2H), 7.00 – 6.96 (m, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 4.89 (d, *J* = 15.6 Hz, 1H), 4.81 (d, *J* = 15.6 Hz, 1H), 1.75 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 179.1, 142.2, 139.3, 135.8, 134.3, 133.3, 128.8, 128.7, 128.22, 128.15, 127.7, 127.2, 124.1, 122.9, 109.5, 51.7, 43.8, 23.9.

ESI-MS: Calcd for $C_{22}H_{19}ClNO$: [M+H$^+$] 348.1150, found 348.1155.

1-benzyl-3-methyl-3-(methyl-*d*)indolin-2-one (2a-D)[6]

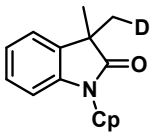


Yield: 95%, 47.9 mg; appearance: colorless oil; R_f = 0.2 (PE/EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.12 (m, 6H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.96 – 6.92 (m, 1H), 6.64 (d, *J* = 7.6 Hz, 1H), 4.84 (s, 2H), 1.36 – 1.34 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 181.4, 141.6, 136.0, 135.7, 128.7, 127.51, 127.41, 127.1, 122.5, 122.3, 109.0, 44.1, 43.5, 24.5 – 24.0 (m).

1-cyclopentyl-3-methyl-3-(methyl-*d*)indolin-2-one (2b-D)



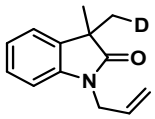
Yield: 90%, 41.4 mg; appearance: colorless oil; R_f = 0.2 (PE/EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.20 (m, 2H), 7.06 – 7.02 (m, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 4.86 – 4.74 (m, 1H), 2.10 – 2.02 (m, 2H), 1.94 – 1.87 (m, 4H), 1.74 – 1.70 (m, 2H), 1.36 – 1.33 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 181.3, 140.9, 136.3, 127.2, 122.5, 121.9, 109.7, 51.9, 43.8, 27.5, 25.3, 24.5 – 24.0 (m).

ESI-MS: Calcd for $C_{15}H_{19}DNO$: [M+H$^+$] 231.1602, found 231.1602.

1-allyl-3-methyl-3-(methyl-*d*)indolin-2-one (2d-D)



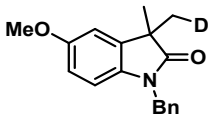
Yield: 85%, 34.4 mg; appearance: colorless oil; R_f = 0.2 (PE/EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.20 (m, 2H), 7.08 – 7.03 (m, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 5.89 – 5.79 (m, 1H), 5.22 – 5.16 (m, 2H), 4.36 – 4.33 (m, 2H), 1.40 – 1.37 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 181.1, 141.7, 135.8, 131.6, 127.5, 122.4, 122.3, 117.2, 108.9, 44.0, 42.1, 24.5 – 24.0 (m).

ESI-MS: Calcd for $C_{13}H_{15}DNO$: [M+H$^+$] 203.1289, found 203.1289.

1-benzyl-5-methoxy-3-methyl-3-(methyl-*d*)indolin-2-one (2e-D)



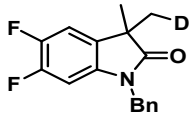
Yield: 89%, 50.2 mg; appearance: colorless oil; R_f = 0.2 (PE/EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.14 (m, 5H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.46 – 6.43 (m, 1H), 6.25 – 6.23 (m, 1H), 4.81 (s, 2H), 3.64 (s, 3H), 1.33 – 1.31 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 182.0, 159.6, 142.8, 136.09, 128.7, 127.8, 127.5, 127.1, 122.7, 106.0, 97.2, 55.4, 43.6, 43.5, 24.7 – 24.2 (m).

ESI-MS: Calcd for $C_{18}H_{19}DNO_2$: [M+H$^+$] 283.1551, found 283.1550.

1-benzyl-5,6-difluoro-3-methyl-3-(methyl-*d*)indolin-2-one (2f-D)



Yield: 91%, 52.4 mg; appearance: colorless oil; R_f = 0.2 (PE/EA = 20:1).

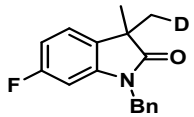
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.29 – 7.15 (m, 5H), 6.96 (dd, *J* = 9.2, 7.6 Hz, 1H), 6.44 (dd, *J* = 10.4, 6.4 Hz, 1H), 4.80 (s, 2H), 1.35 – 1.32 (m, 5H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 181.1, 151.0 (d, *J* = 14.0 Hz), 148.6 (d, *J* = 13.0 Hz), 145.5 (d, *J* = 14.0 Hz), 137.6 (d, *J* = 10.0 Hz), 135.3, 131.1 – 130.0 (m), 129.0, 127.9, 127.1, 112.1, 111.9, 99.4, 99.2, 44.3, 43.8, 24.5 – 24.0 (m).

^{19}F NMR (376 MHz, CDCl$_3$) δ -137.93 to -138.00 (m, 1F), -146.03 to -146.10 (m, 1F).

ESI-MS: Calcd for $C_{17}H_{15}DF_2NO$: [M+H$^+$] 289.1257, found 289.1263.

1-benzyl-6-fluoro-3-methyl-3-(methyl-*d*)indolin-2-one (2i-D)



Yield: 88%, 47.5 mg; appearance: yellow oil; R_f = 0.2 (PE/EA = 20:1).

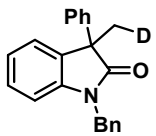
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.28 – 7.17 (m, 5H), 7.05 (dd, *J* = 8.4, 5.6 Hz, 1H), 6.65 – 6.59 (m, 1H), 6.37 (dd, *J* = 9.2, 2.4 Hz, 1H), 4.81 (s, 2H), 1.35 – 1.33 (m, 5H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 181.7, 163.7, 161.3, 143.0 (d, *J* = 11.0 Hz), 135.6, 128.9, 127.7, 127.1, 123.1 (d, *J* = 9.0 Hz), 108.6, 108.4, 98.0, 97.7, 43.8, 43.7, 24.6 – 24.1 (m).

^{19}F NMR (376 MHz, CDCl$_3$) δ -113.08 (s, 1F).

ESI-MS: Calcd for $C_{17}H_{16}DFNO$: [M+H$^+$] 271.1351, found 271.1352.

1-benzyl-3-(methyl-*d*)-3-phenylindolin-2-one (2g-D)[7]

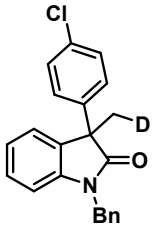


Yield: 73%, 45.9 mg; appearance: yellow oil; R_f = 0.2 (PE/EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 10H), 7.26 – 7.21 (m, 2H), 7.12 – 7.07 (m, 1H), 6.84 (d, *J* = 7.6 Hz, 1H), 5.02 (d, *J* = 15.6 Hz, 1H), 4.95 (d, *J* = 15.6 Hz, 1H), 1.91 – 1.88 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 179.5, 142.3, 140.8, 136.0, 135.0, 128.8, 128.6, 128.5, 128.0, 127.6, 127.23, 127.21, 126.6, 124.2, 122.8, 109.3, 52.1, 43.8, 23.8 – 23.3 (m).

1-benzyl-3-(4-chlorophenyl)-3-(methyl-*d*)indolin-2-one (2h-D)



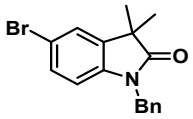
Yield: 68%, 47.3 mg; appearance: yellow oil; R_f = 0.2 (PE/EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.07 (m, 11H), 7.01 – 6.97 (m, 1H), 6.73 (d, *J* = 7.6 Hz, 1H), 4.90 (d, *J* = 15.6 Hz, 1H), 4.81 (d, *J* = 15.6 Hz, 1H), 1.76 – 1.73 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 179.1, 142.2, 139.3, 135.8, 135.8, 134.3, 133.3, 128.8, 128.7, 128.6, 128.2, 128.2, 127.7, 127.2, 124.1, 123.0, 109.5, 51.6, 43.9, 23.9 – 23.4 (m).

ESI-MS: Calcd for $C_{22}H_{18}DClNO$: [M+H$^+$] 349.1212, found 349.1212.

1-benzyl-5-bromo-3,3-dimethylindolin-2-one (4)



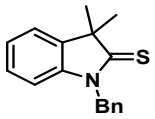
Yield: 95%, 62.5 mg; appearance: yellow oil; R_f = 0.2 (PE/EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.25 (m, 7H), 6.61 (d, *J* = 8.4 Hz, 1H), 4.93 (s, 2H), 1.47 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 180.7, 140.6, 137.8, 135.5, 130.4, 128.8, 127.6, 127.0, 125.7, 115.2, 110.5, 53.4, 44.4, 43.5, 24.4.

ESI-MS: Calcd for $C_{17}H_{17}BrNO$: [M+H$^+$] 330.0488, found 330.0488.

1-benzyl-3,3-dimethylindoline-2-thione (5)[8]



Yield: 86%, 45.9 mg; appearance: yellow oil; R_f = 0.2 (PE/EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.17 (m, 6H), 7.15 – 7.05 (m, 2H), 6.84 (d, *J* = 7.6 Hz, 1H), 5.42 (s, 2H), 1.43 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 212.8, 143.1, 140.3, 134.9, 128.8, 127.70, 127.67, 127.0, 124.2, 122.7, 110.4, 55.1, 47.9, 28.3.

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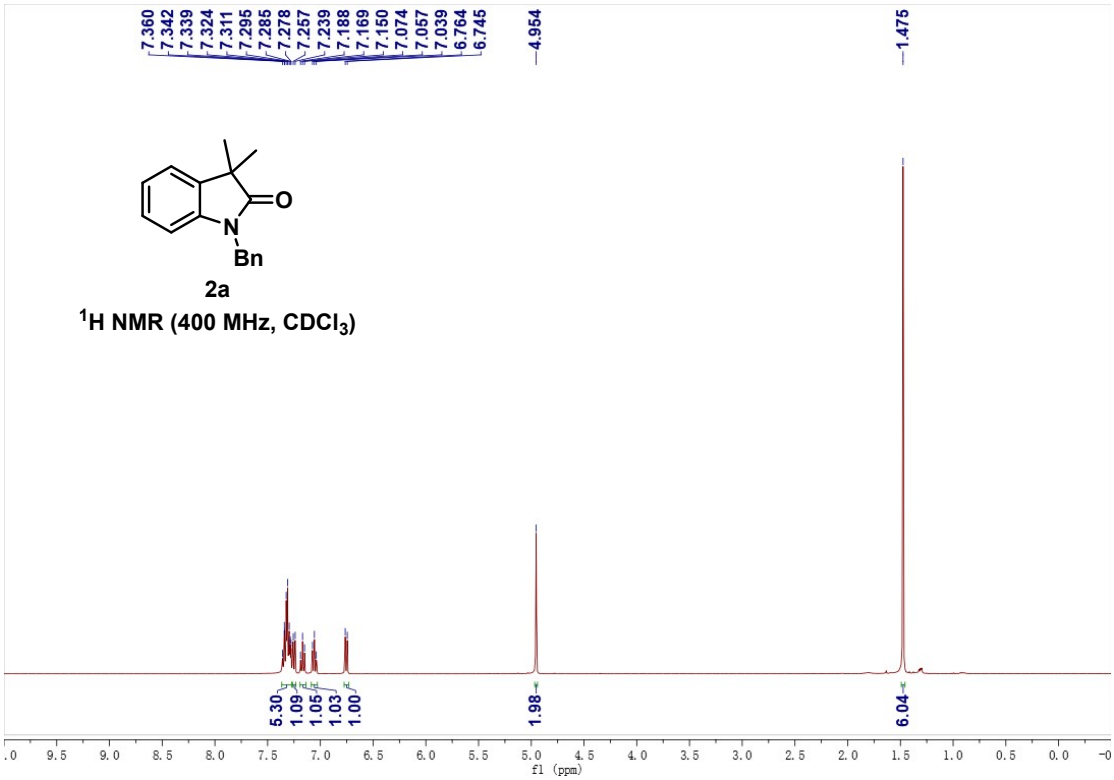
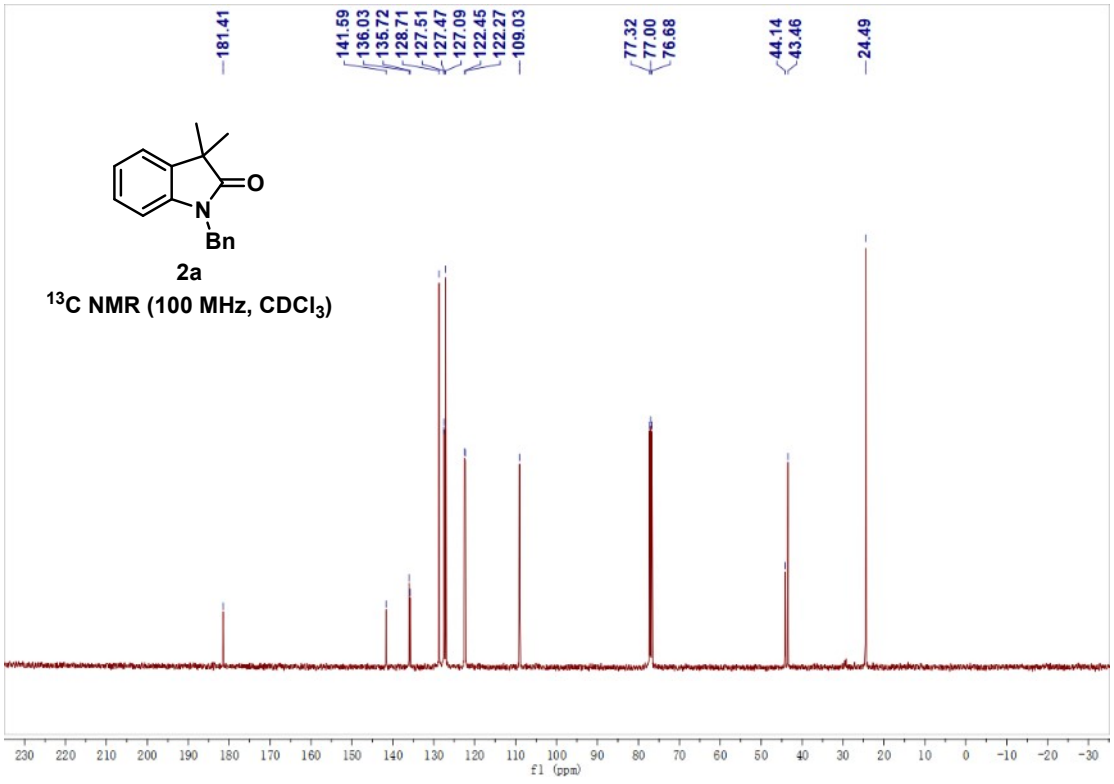
NMR Spectra



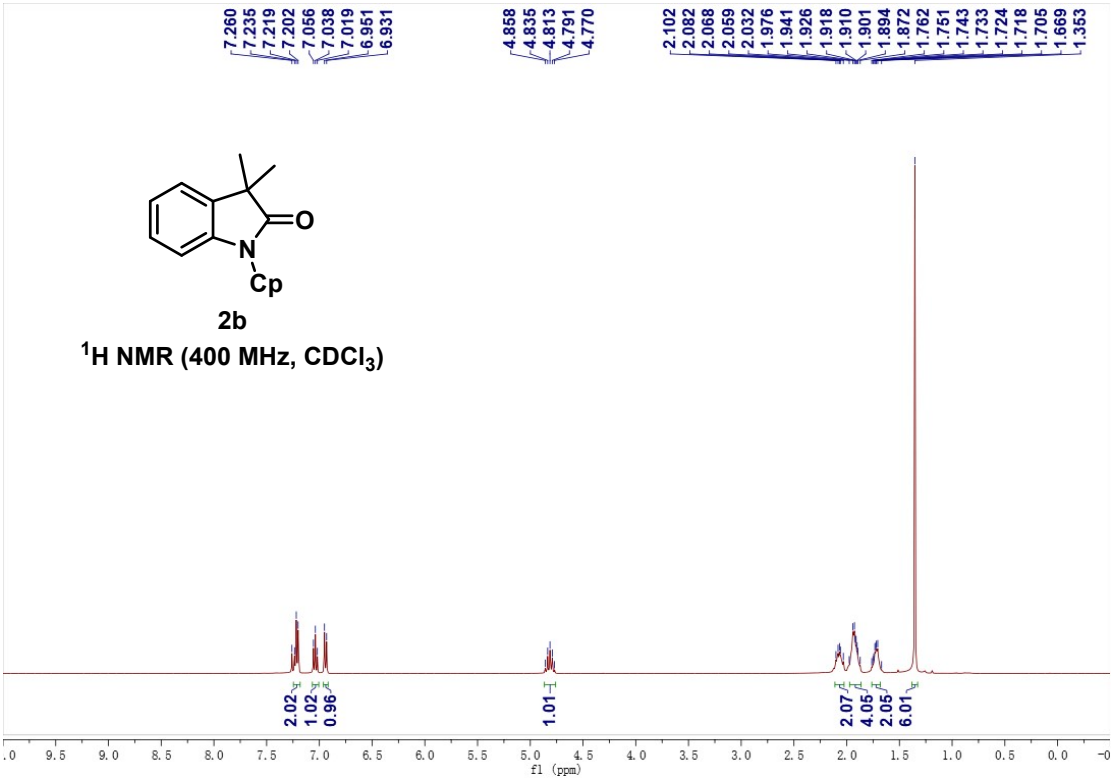
2a

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



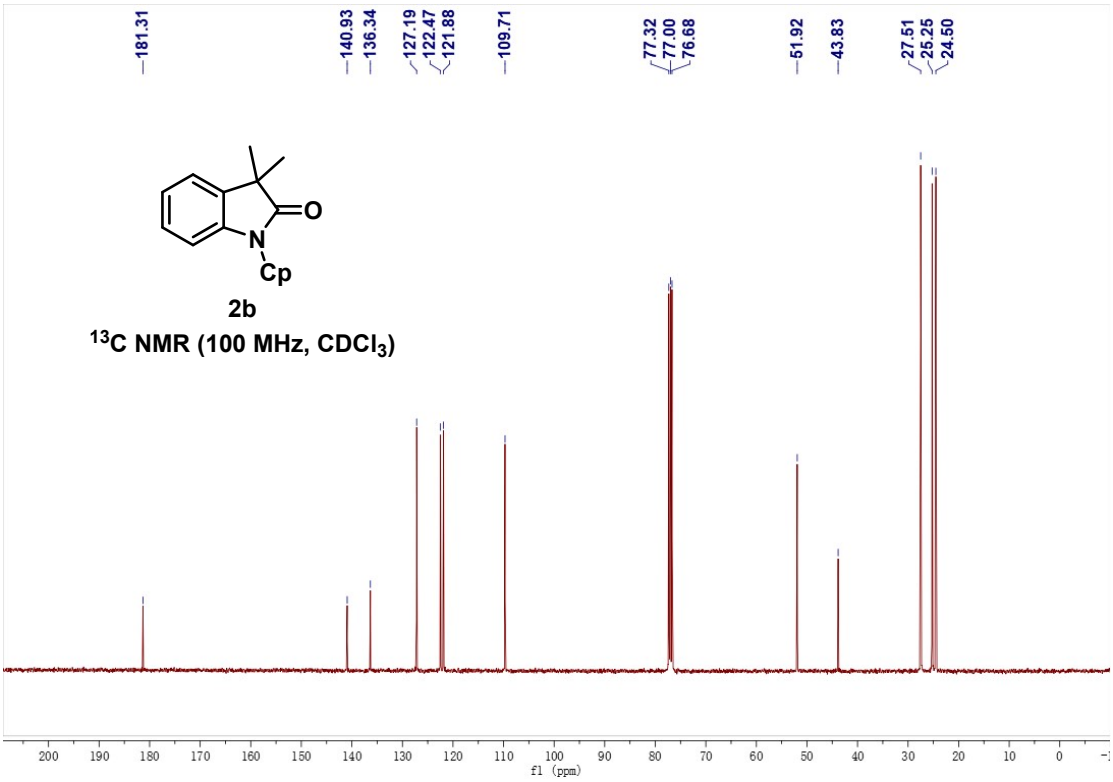
2a

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



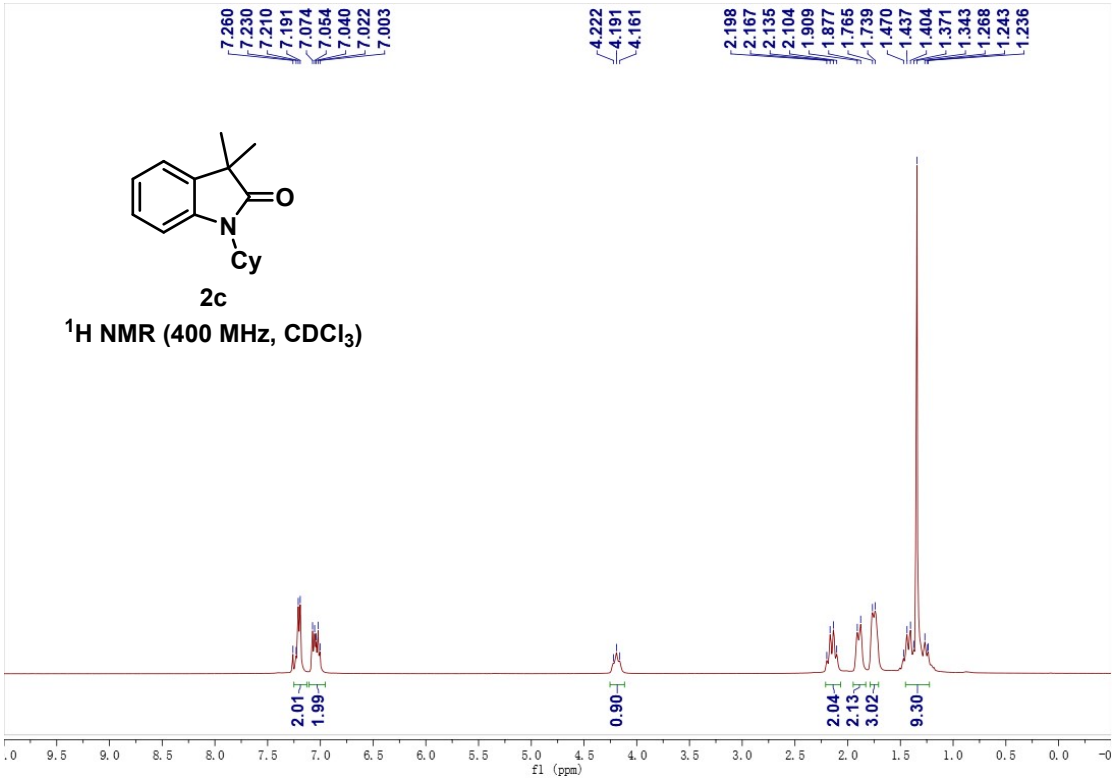
2b

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



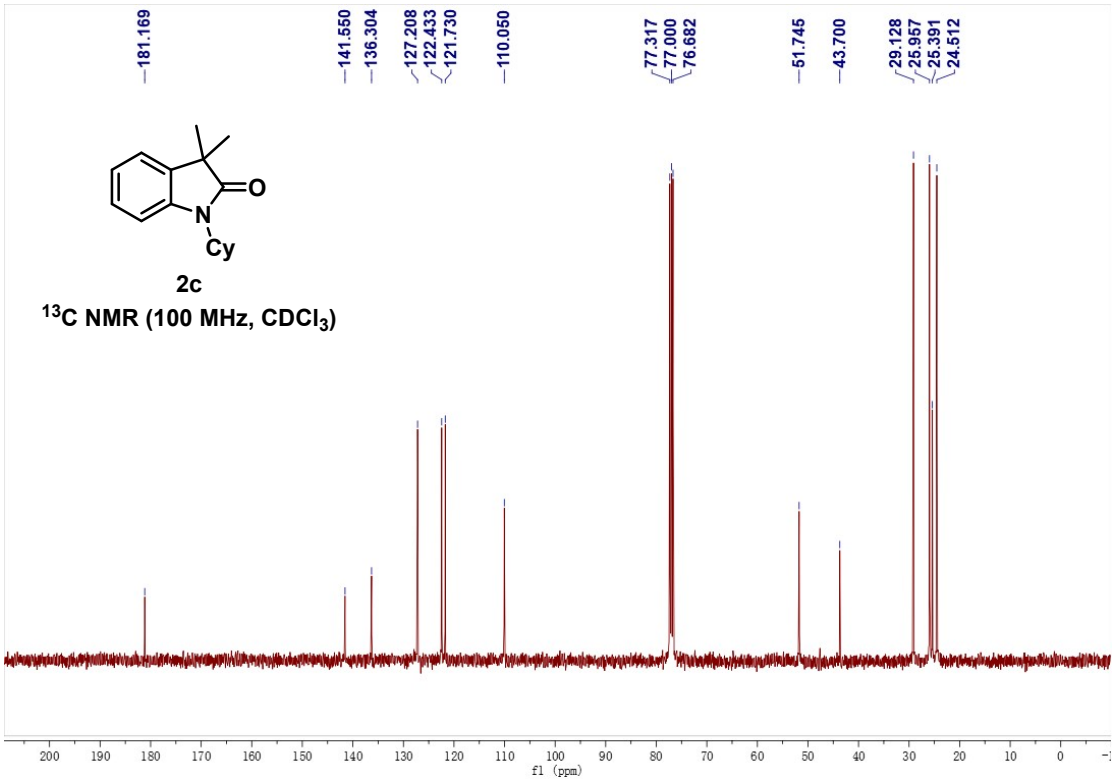
2b

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



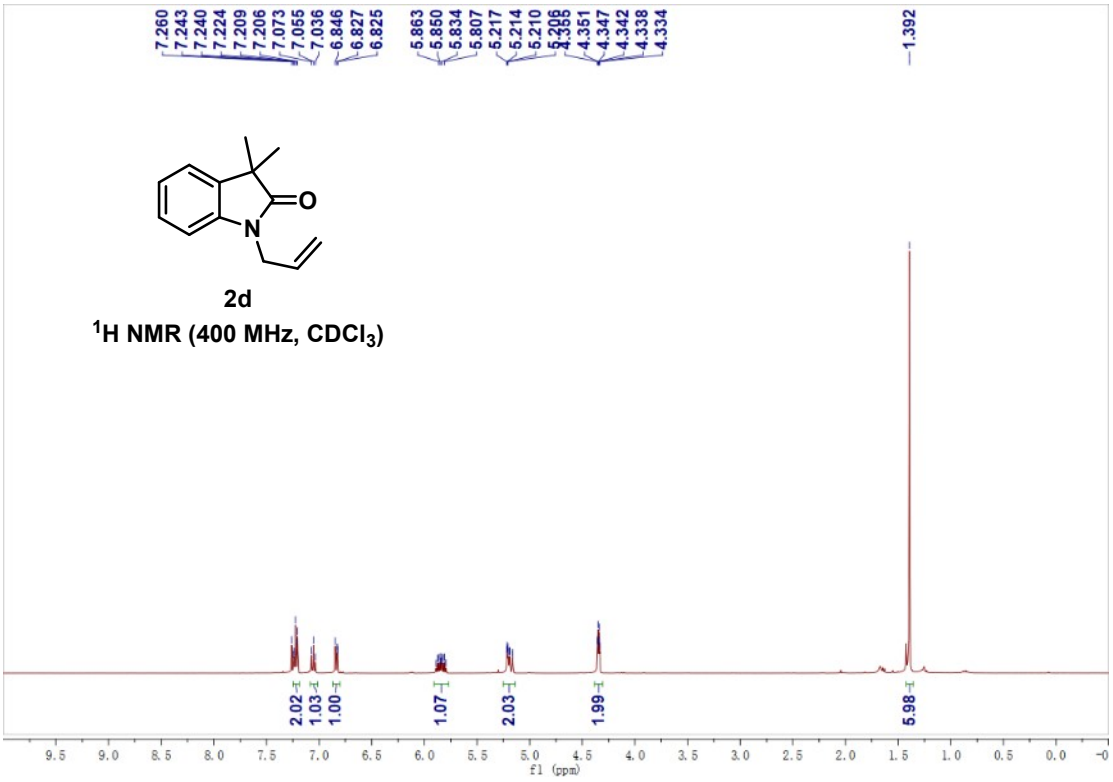
2c

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



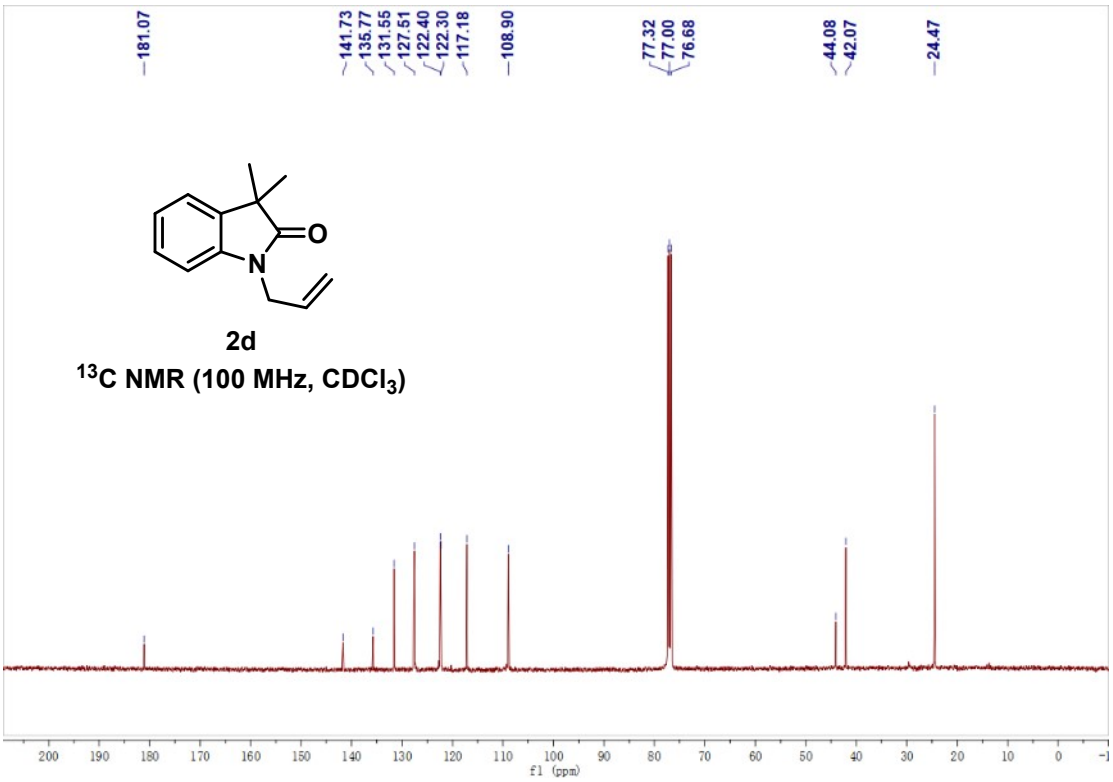
2c

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



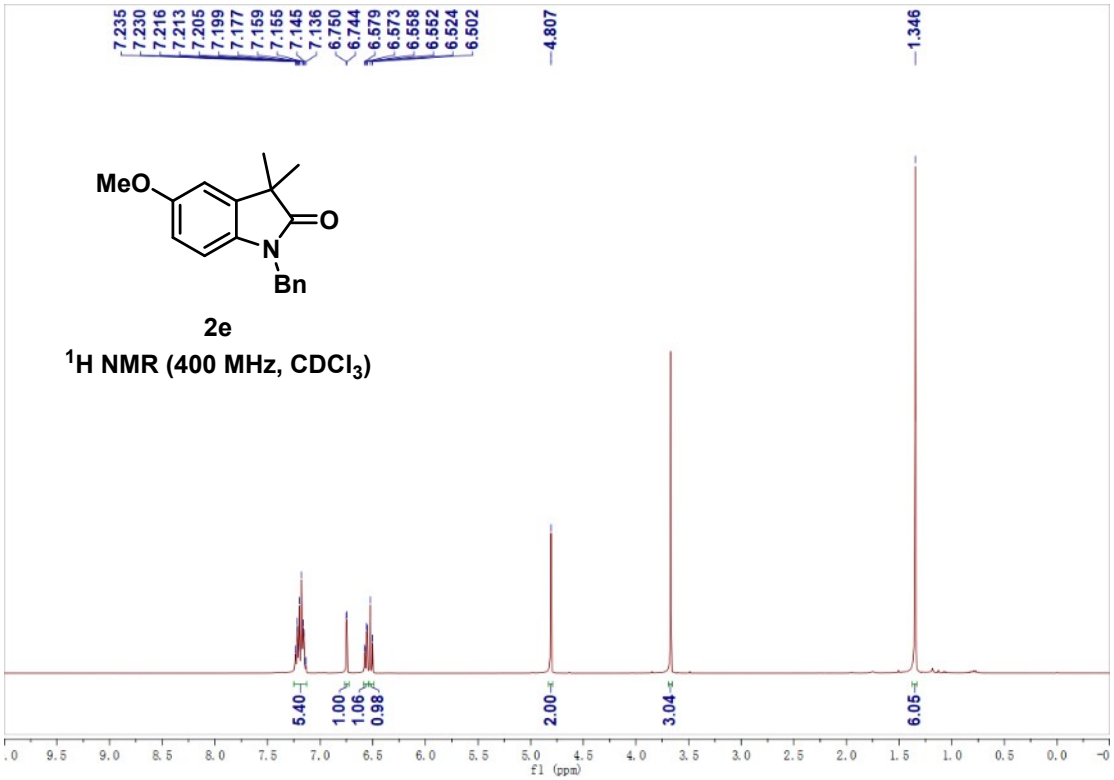
2d

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



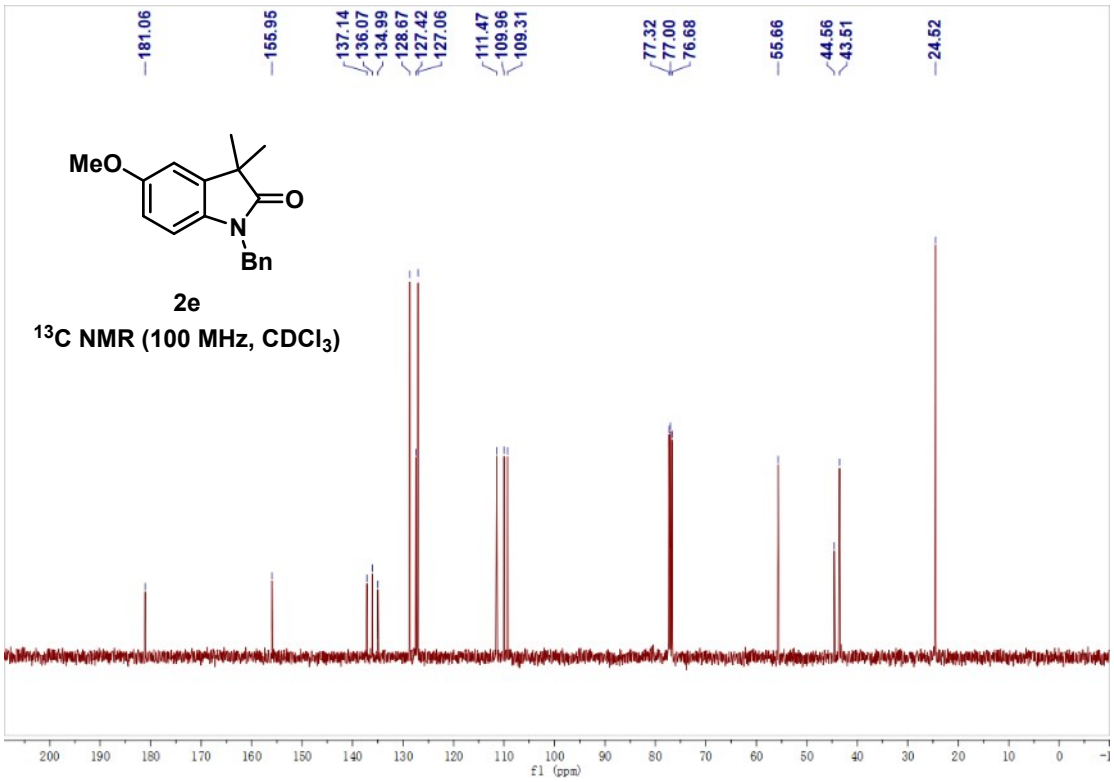
2d

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



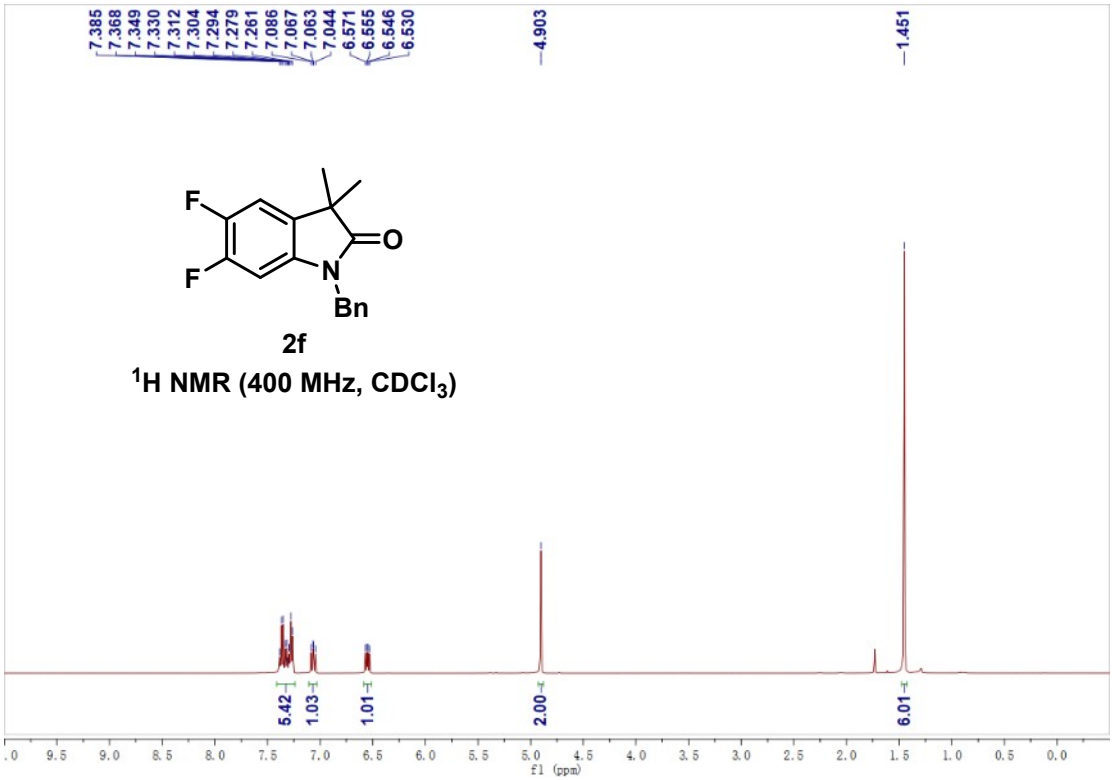
2e

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



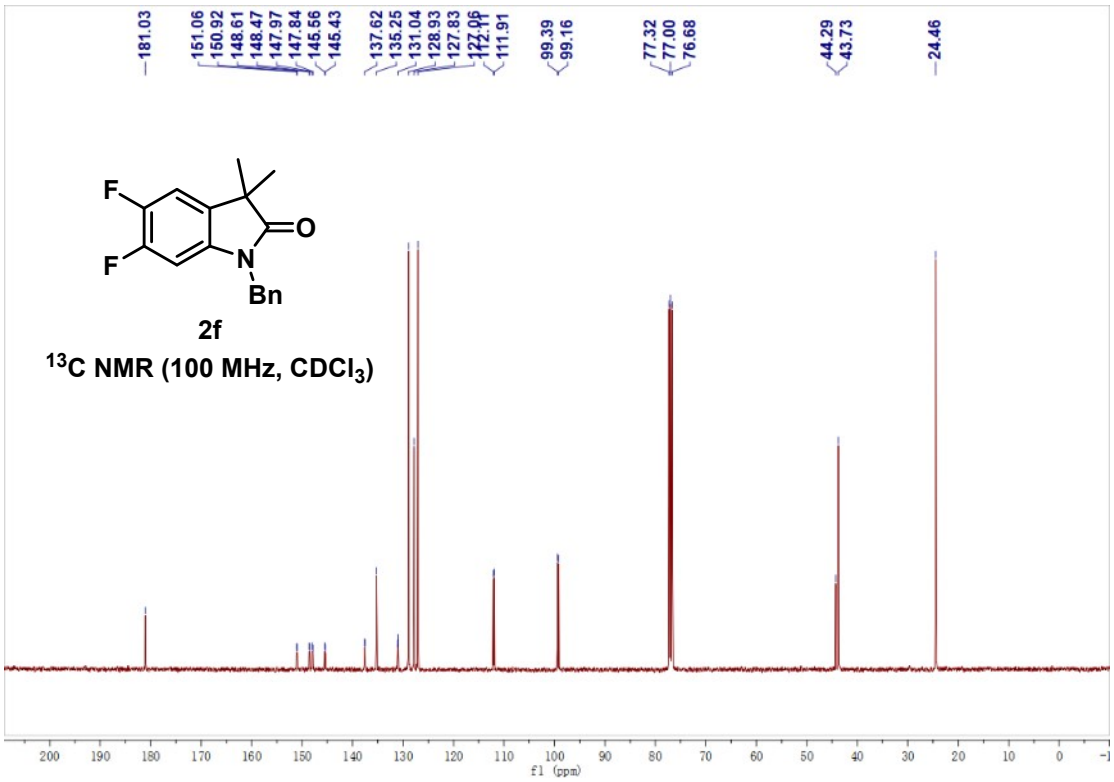
2e

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



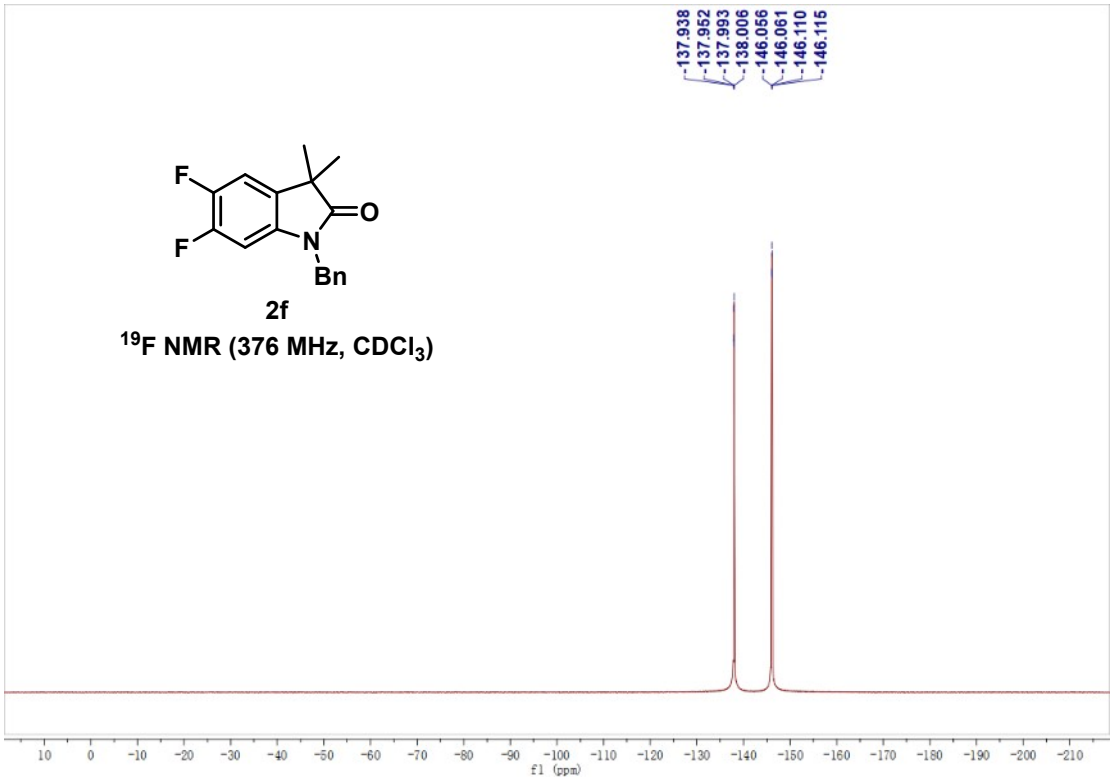
2f

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



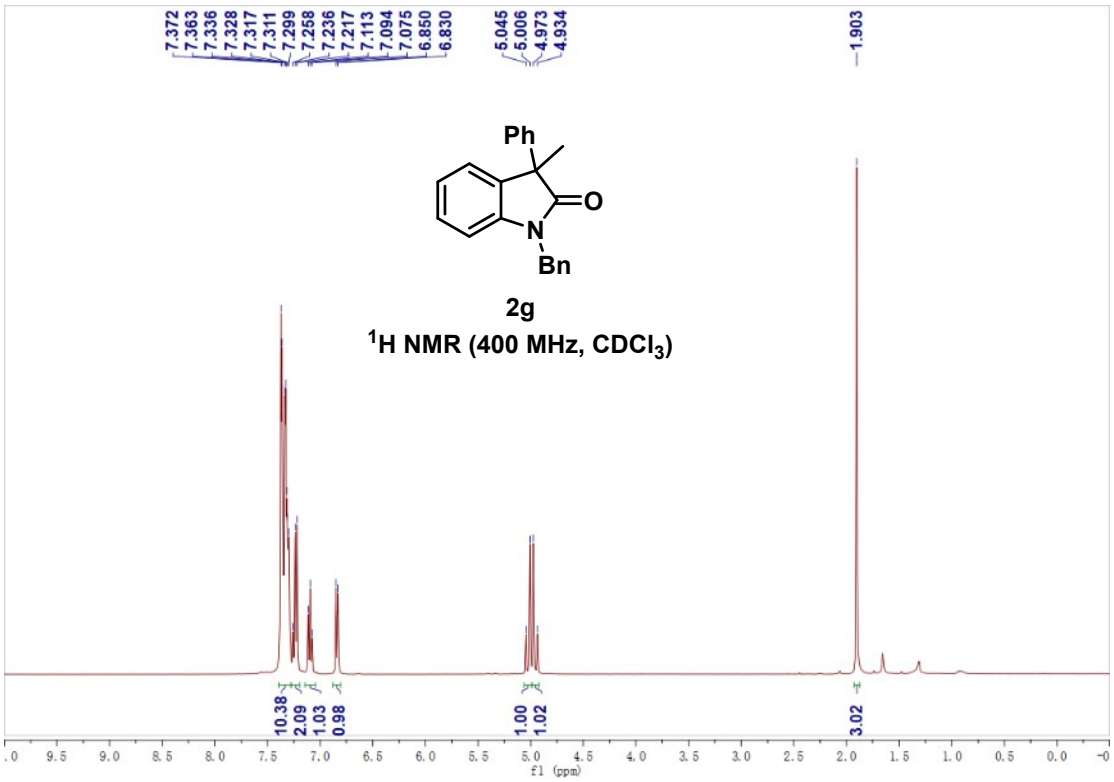
2f

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



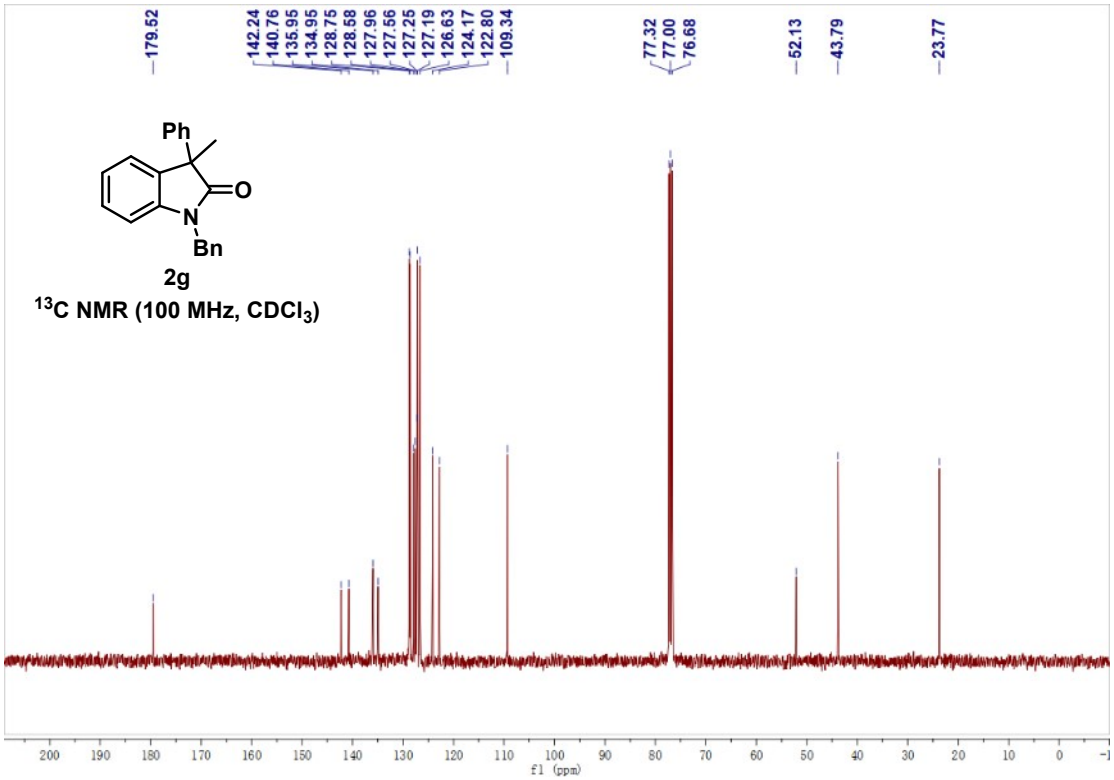
2f

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



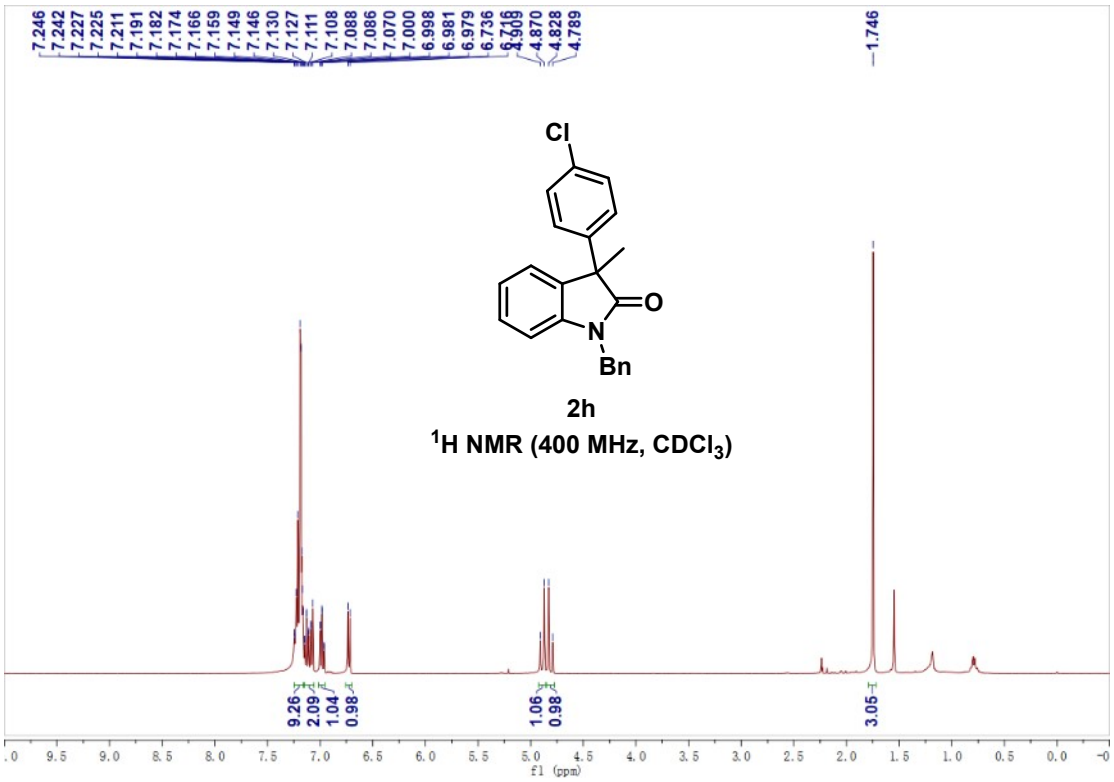
2g

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



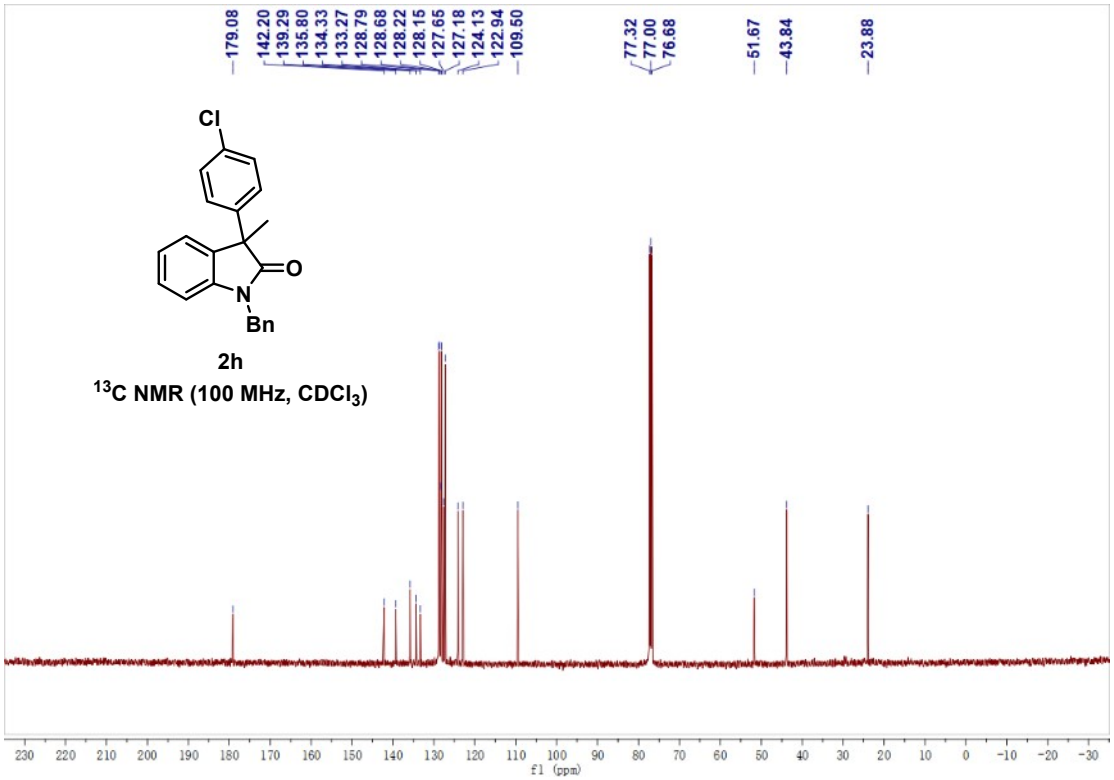
2g

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



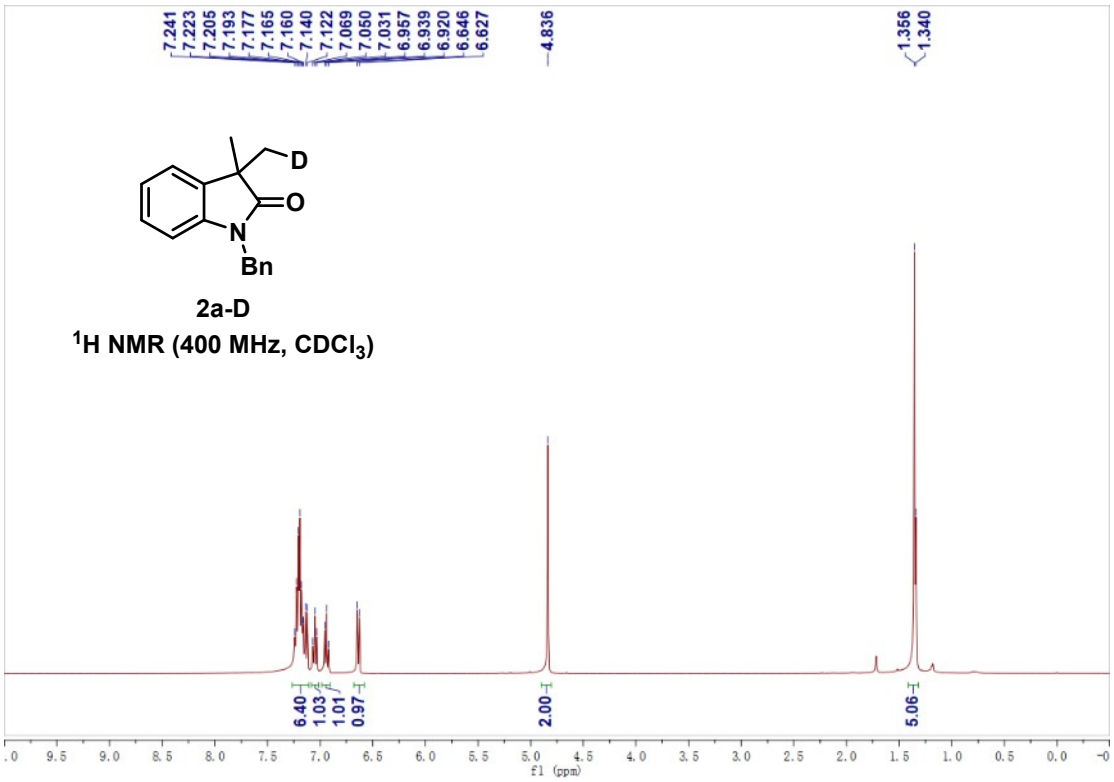
2h

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



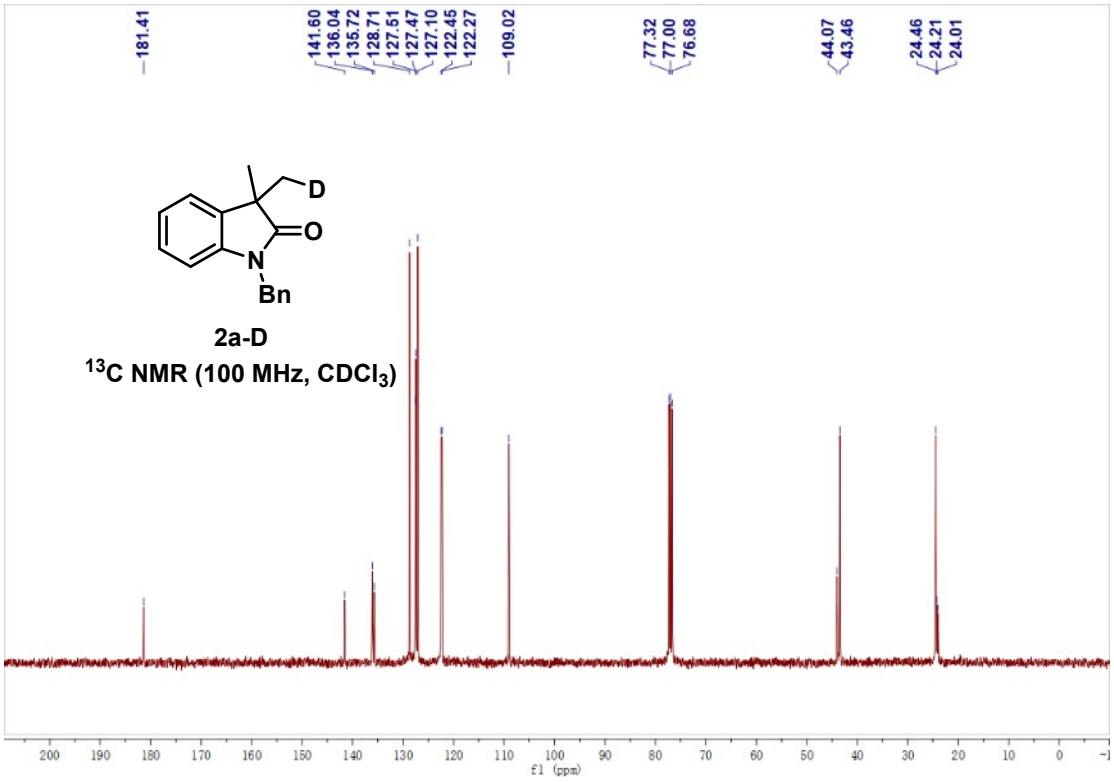
2h

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



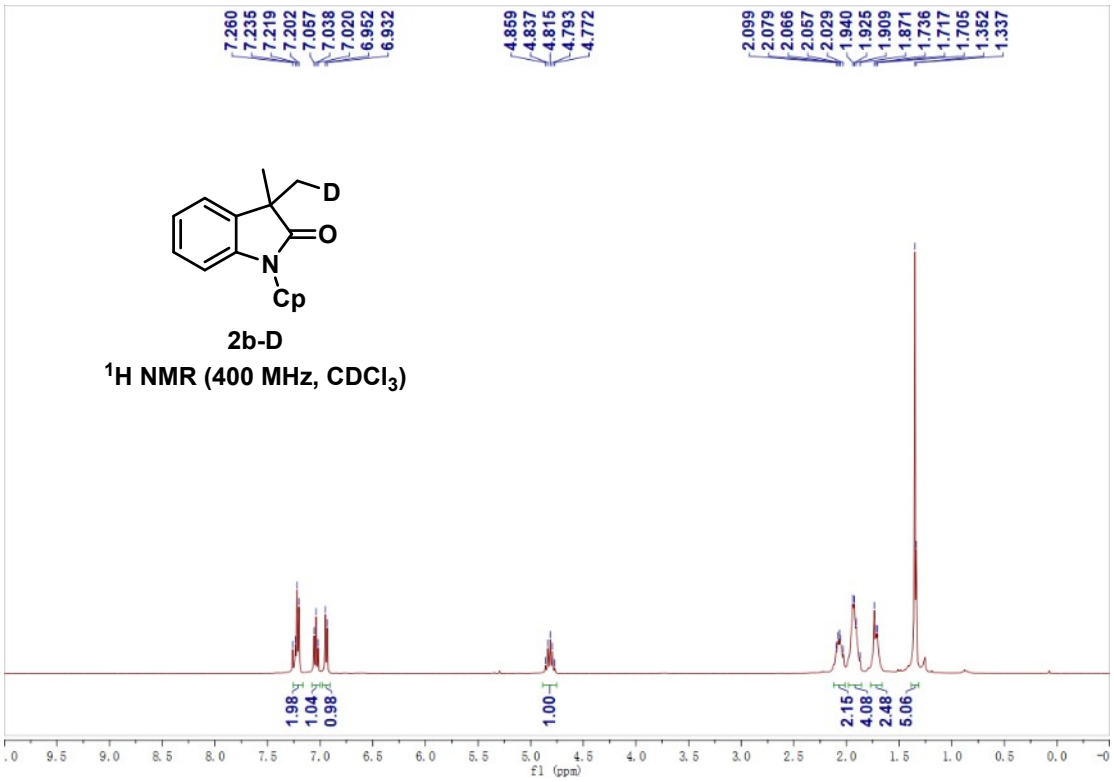
2a-D

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



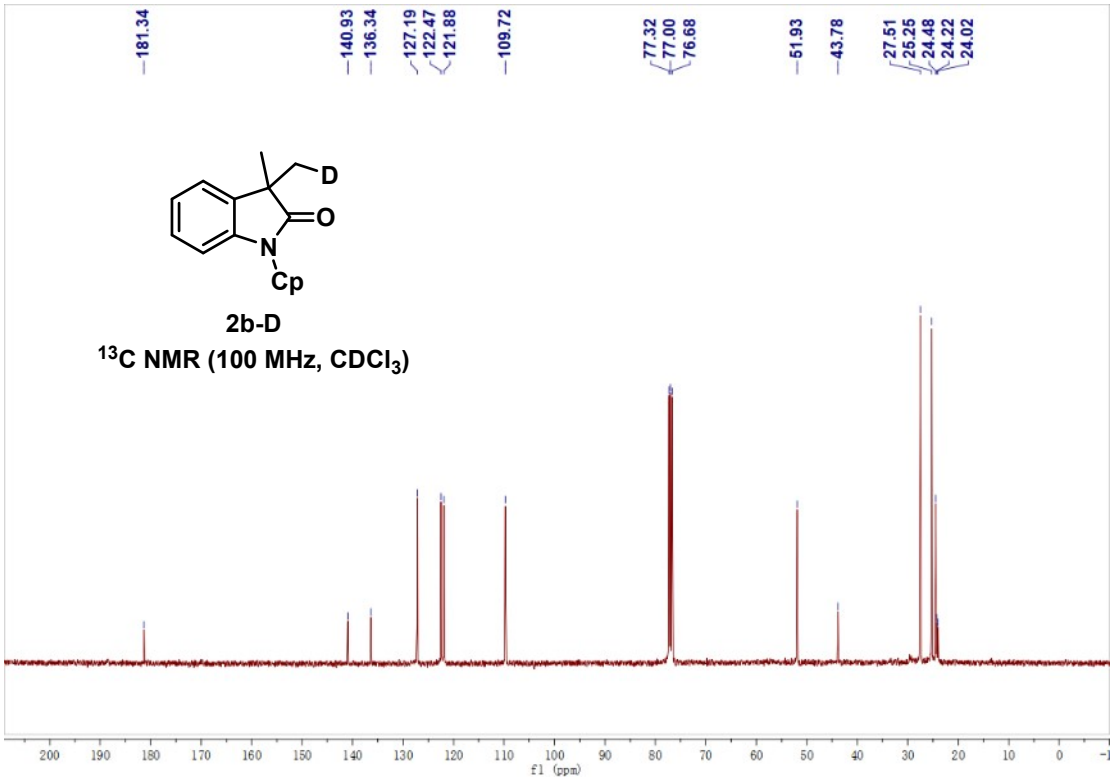
2a-D

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



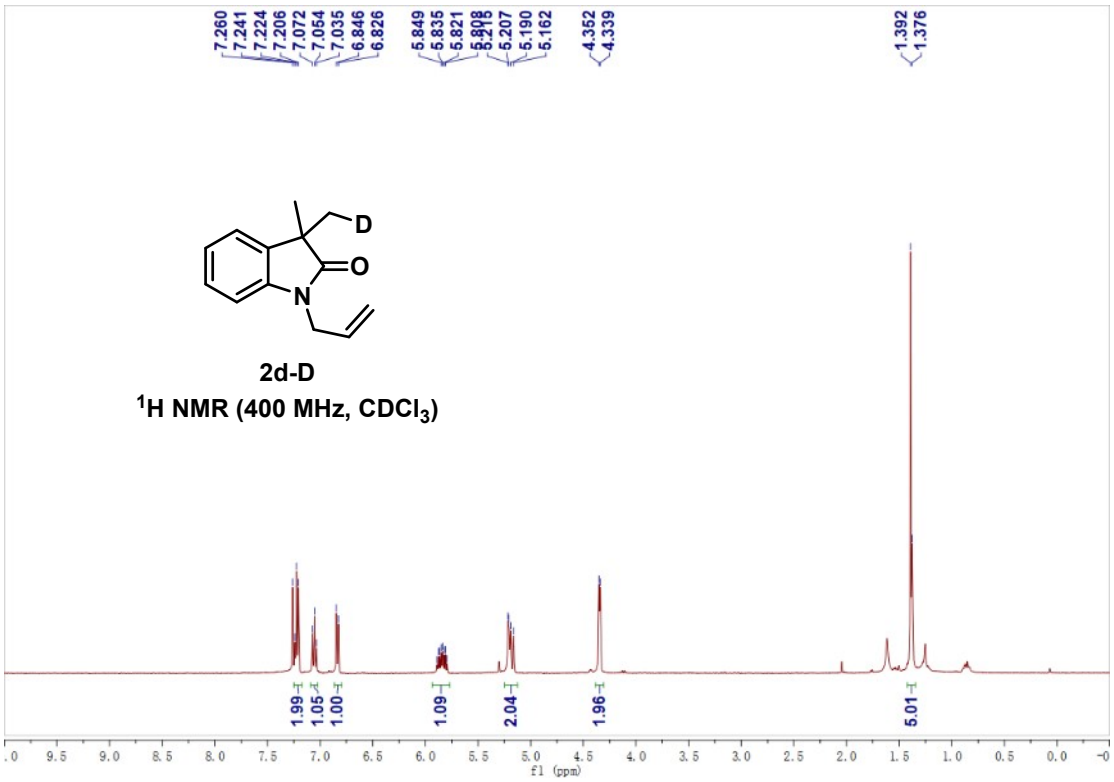
2b-D

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



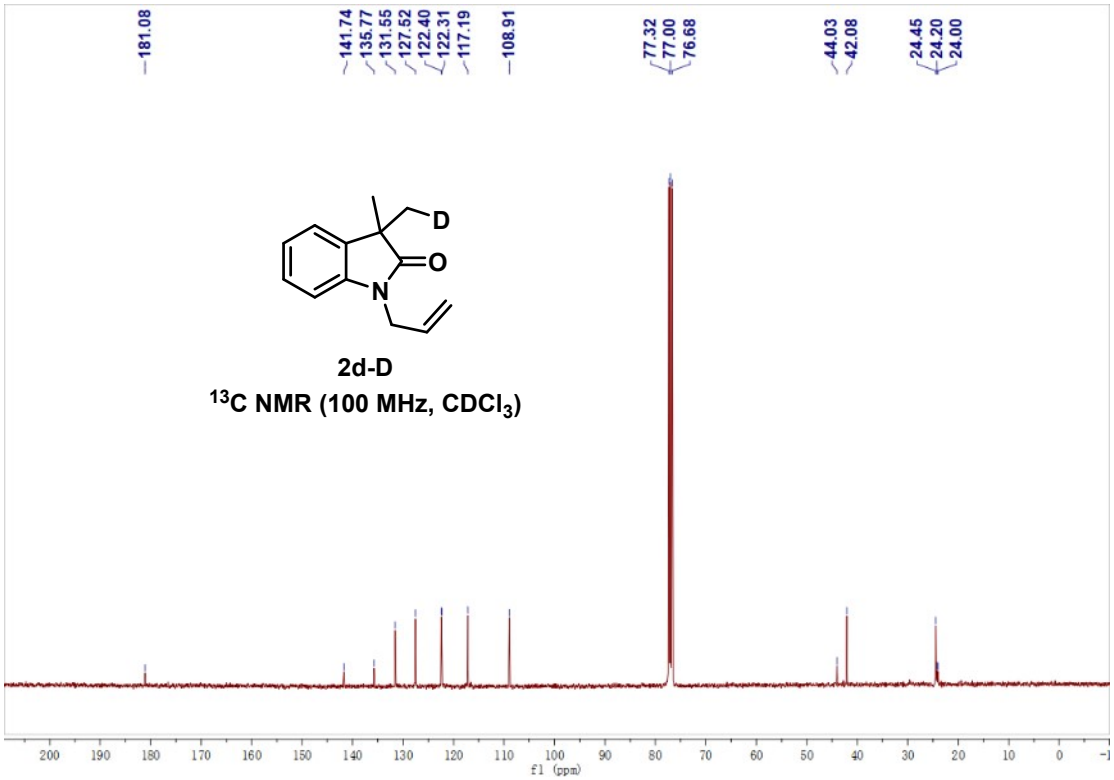
2b-D

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



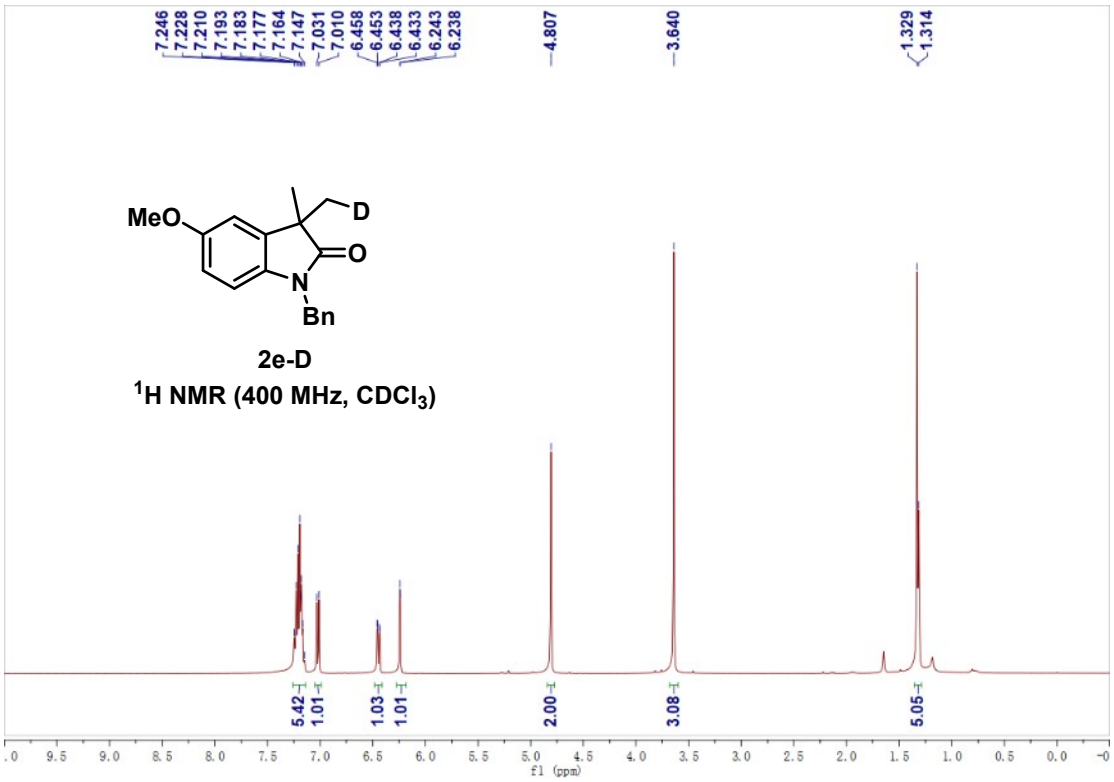
2d-D

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



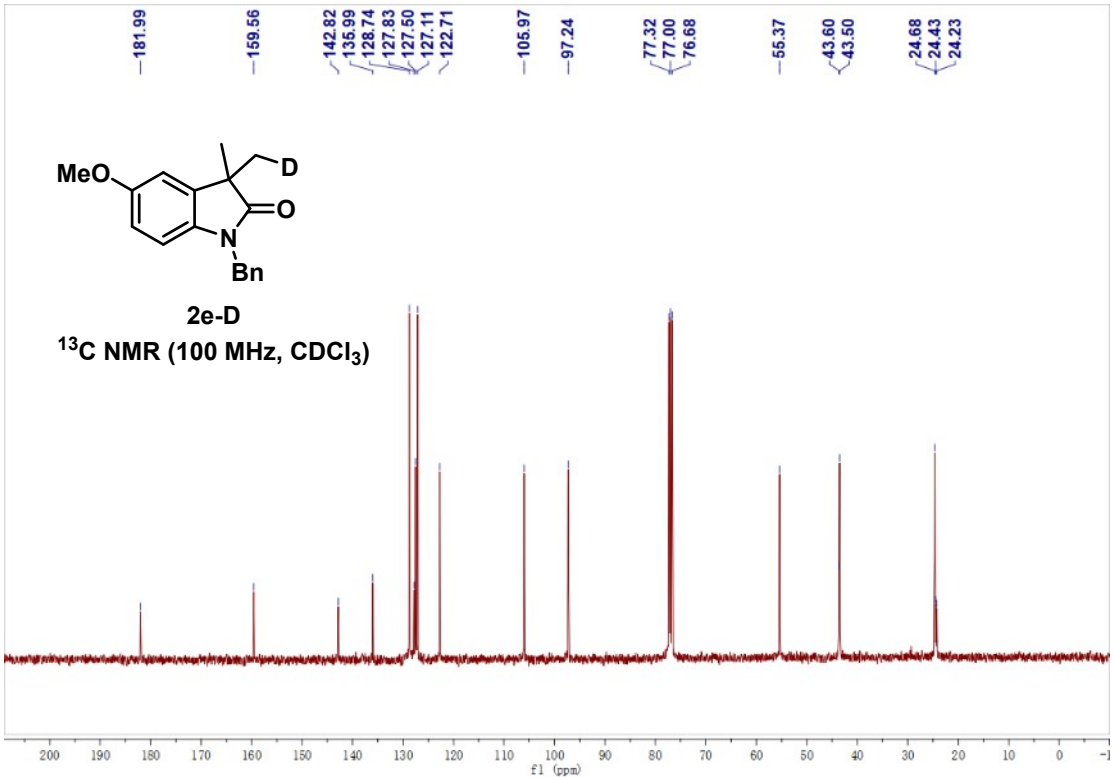
2d-D

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



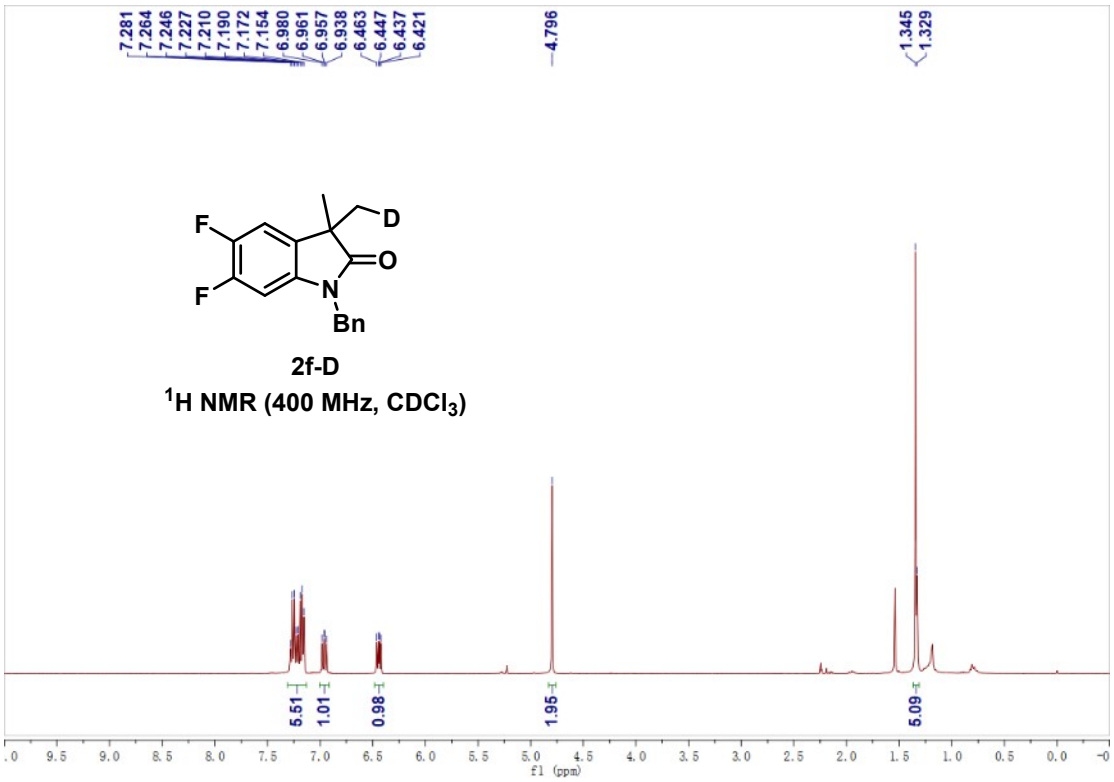
2e-D

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



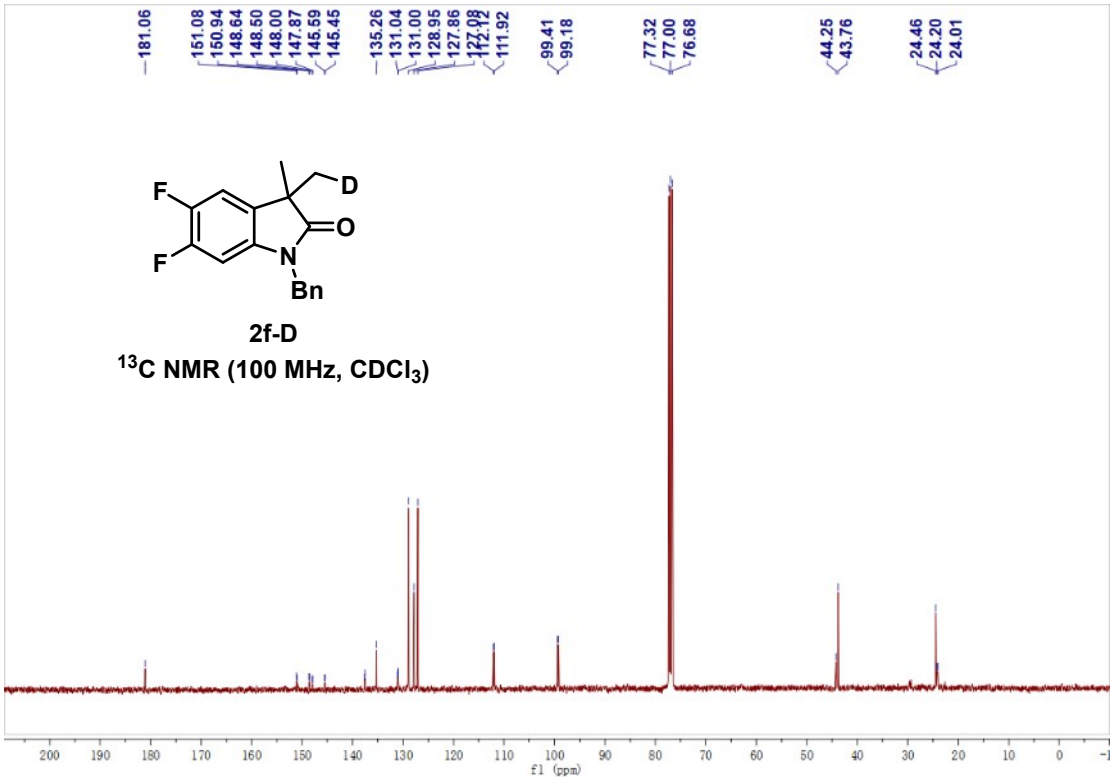
2e-D

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



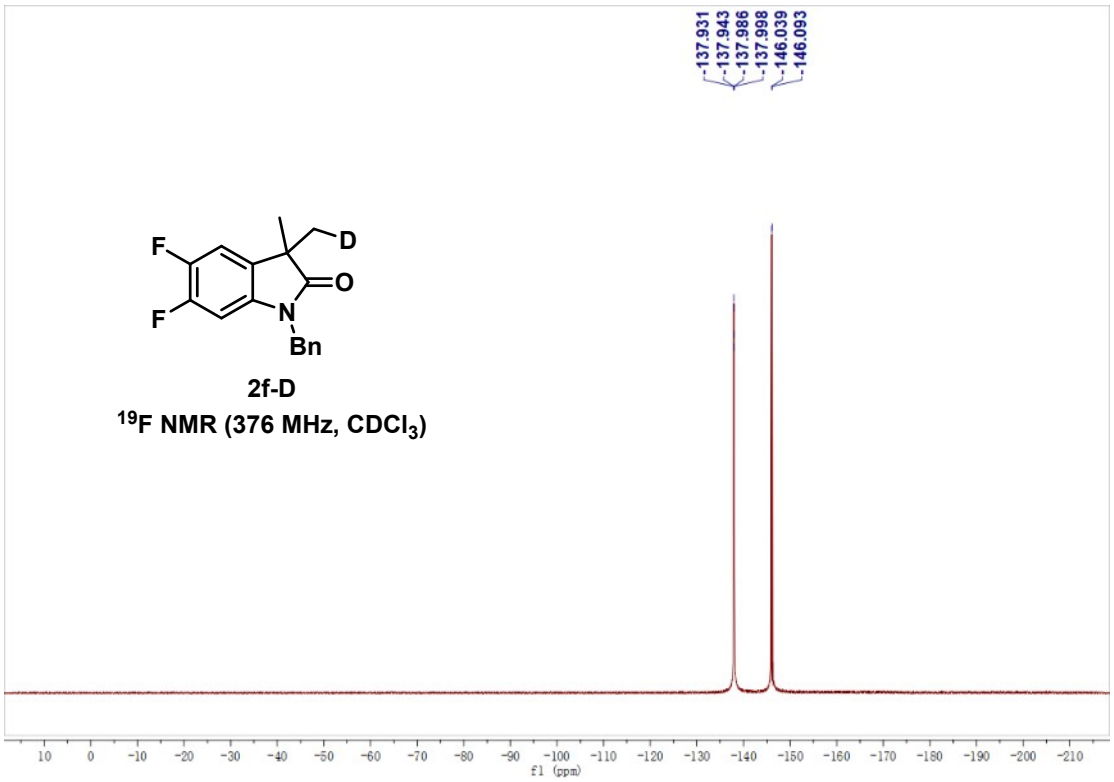
2f-D

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



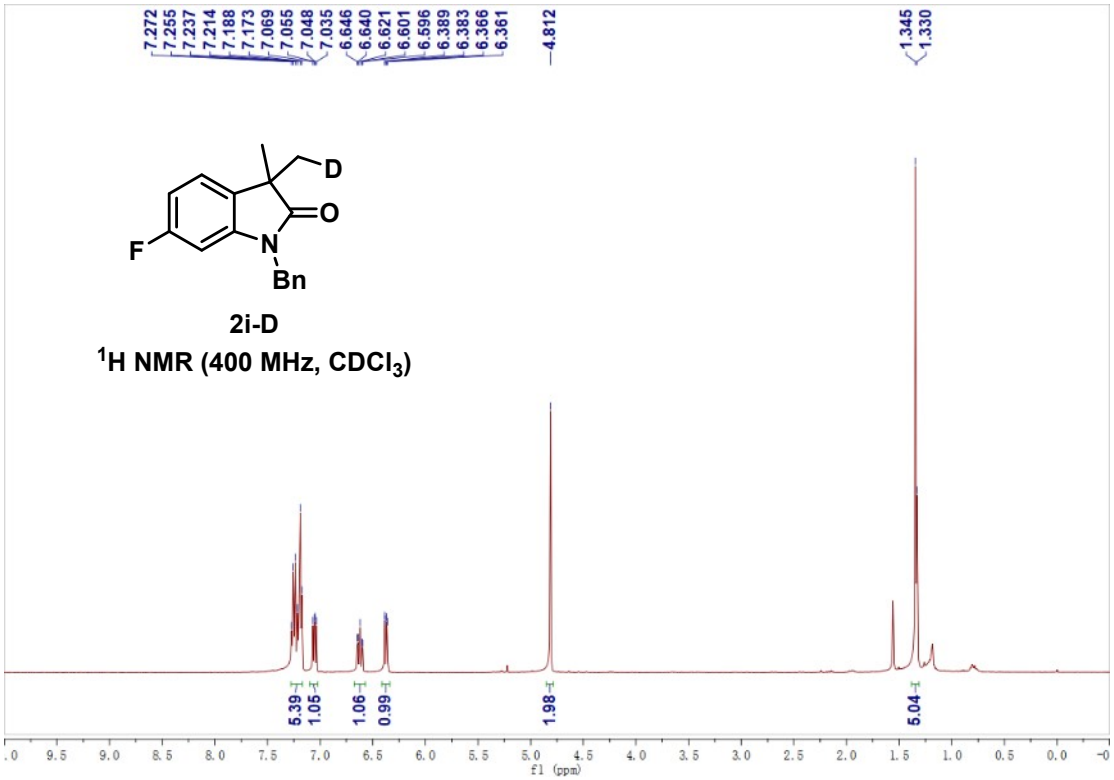
2f-D

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



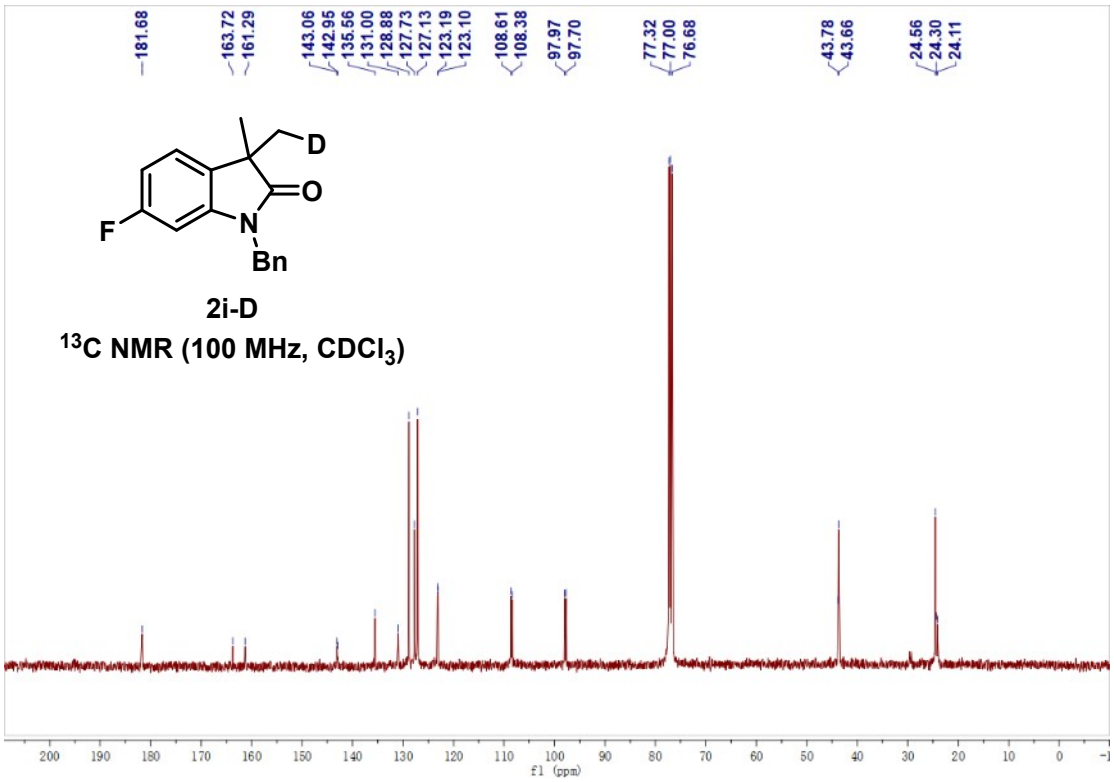
2f-D

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



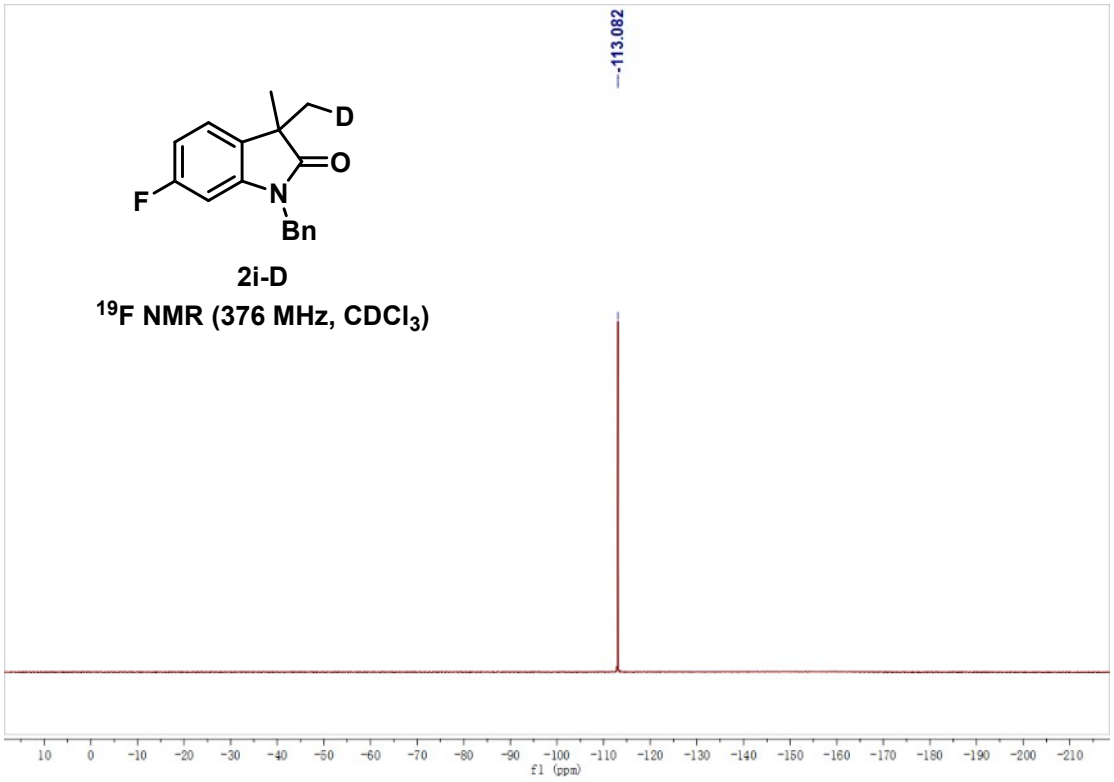
2i-D

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



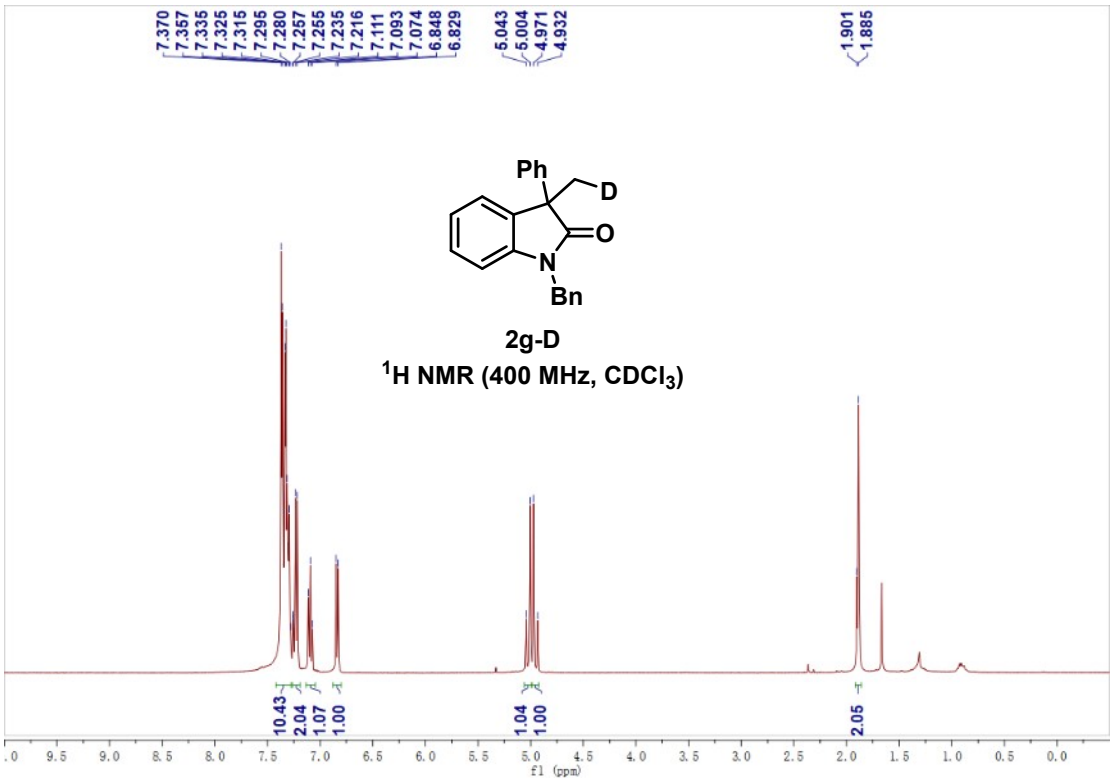
2i-D

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



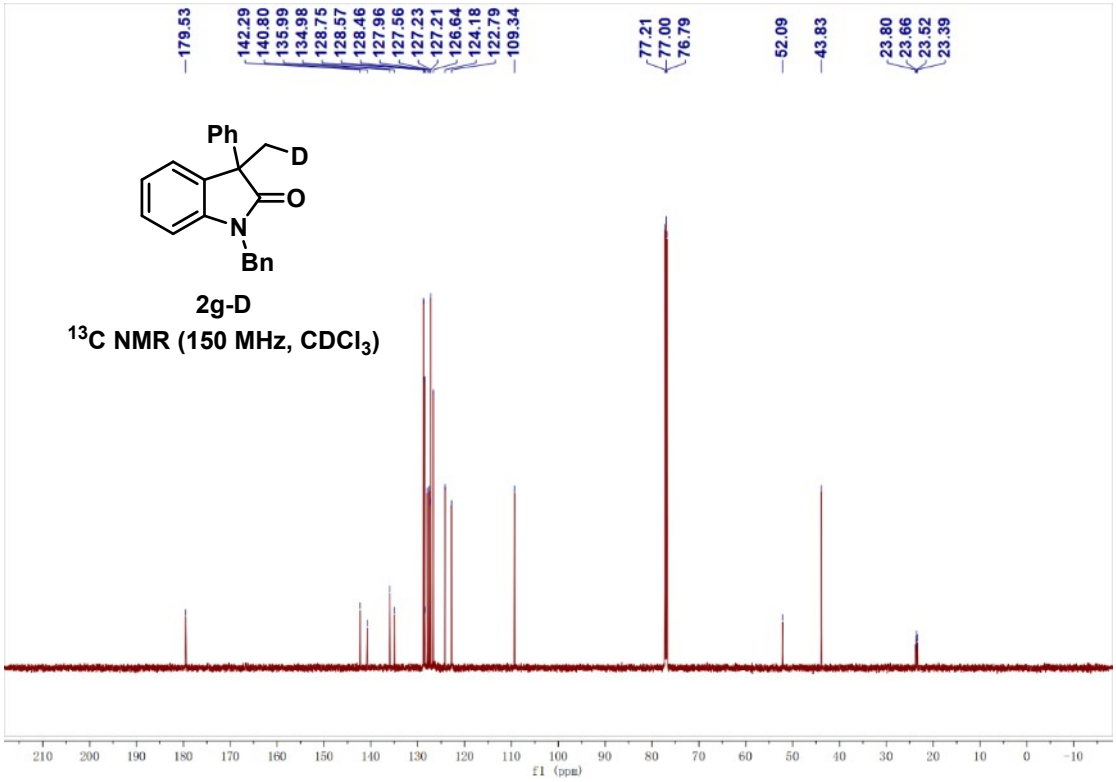
2i-D

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



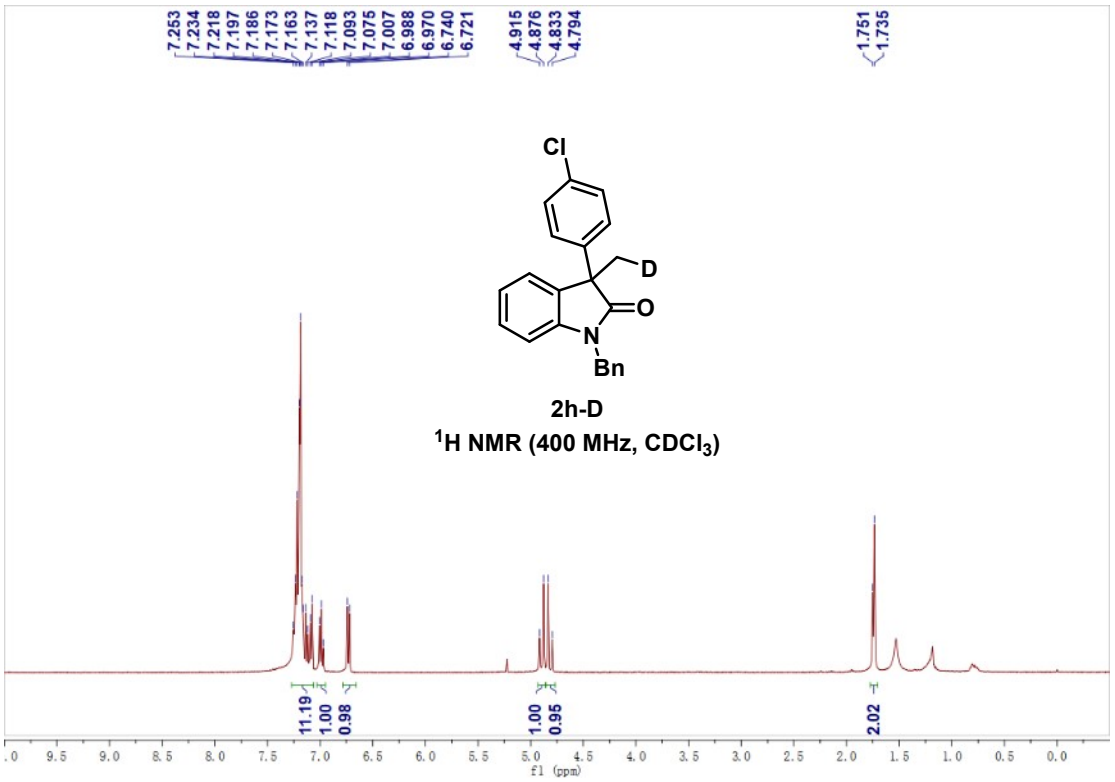
2g-D

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



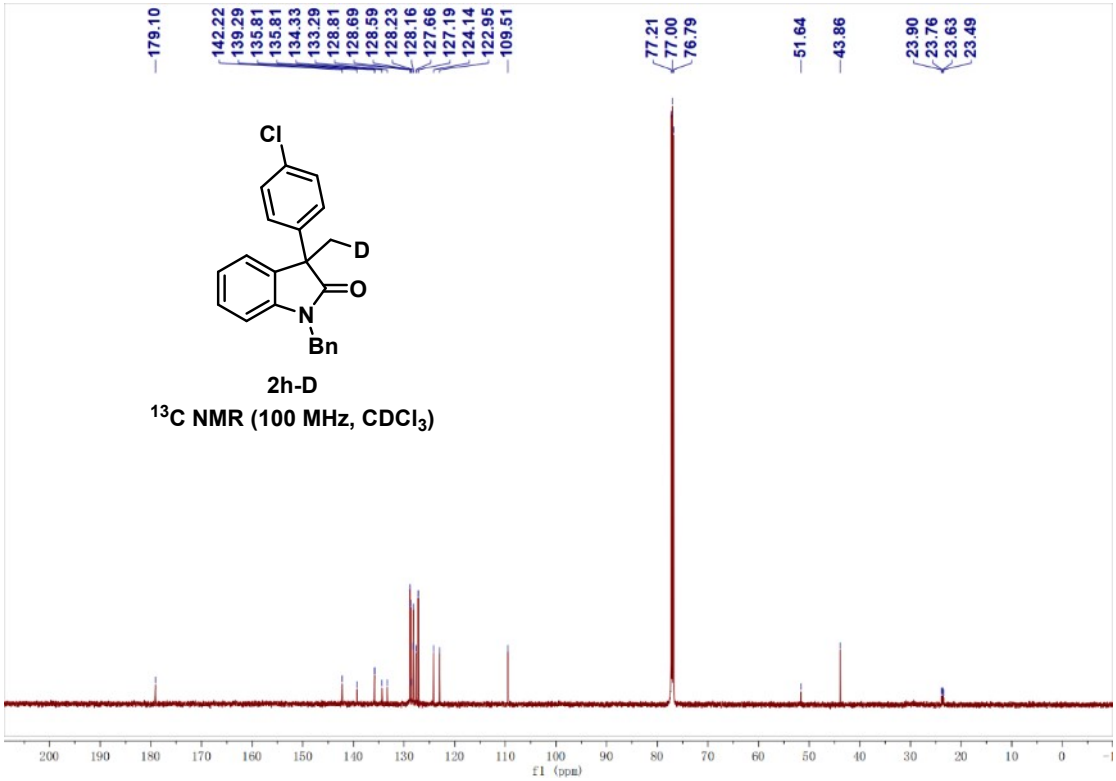
2g-D

^{13}C NMR (150 MHz, $CDCl_3$)



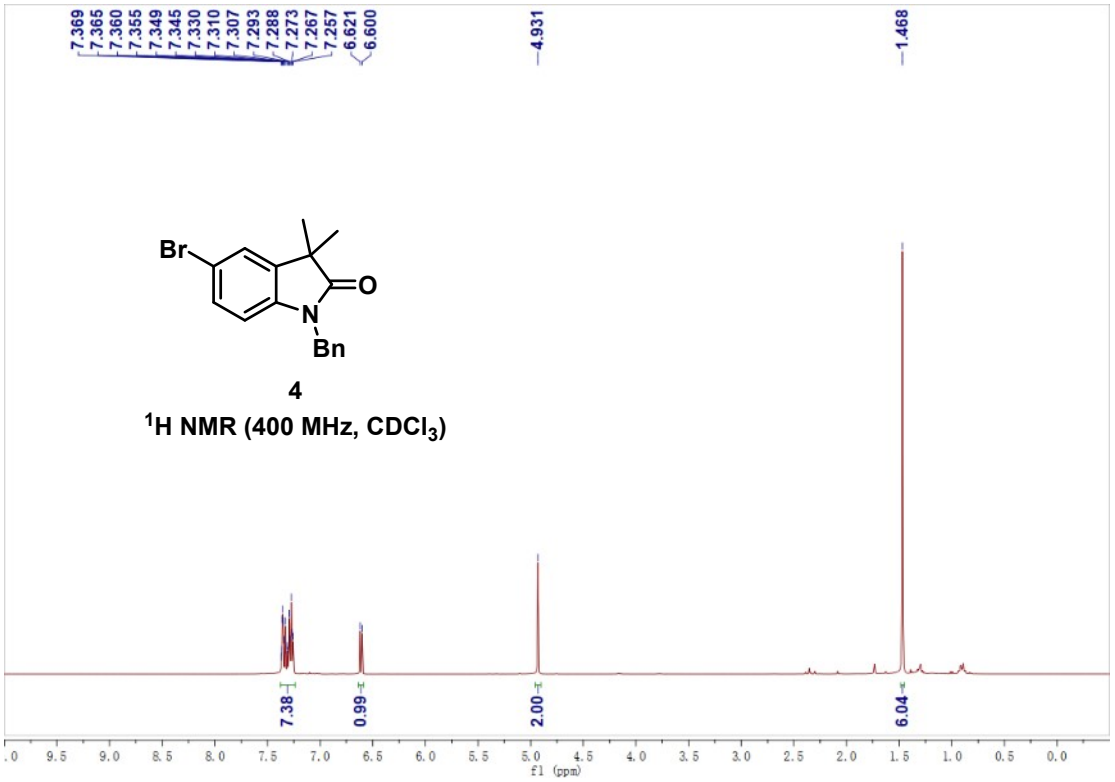
2h-D

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



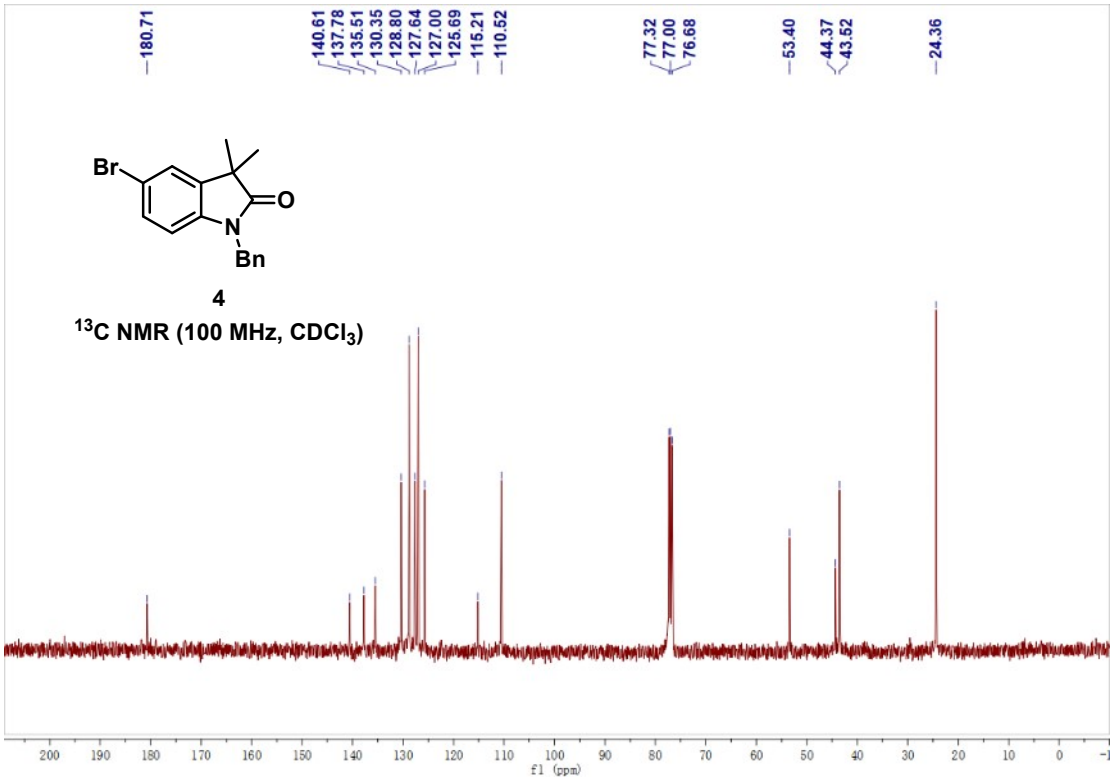
2h-D

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



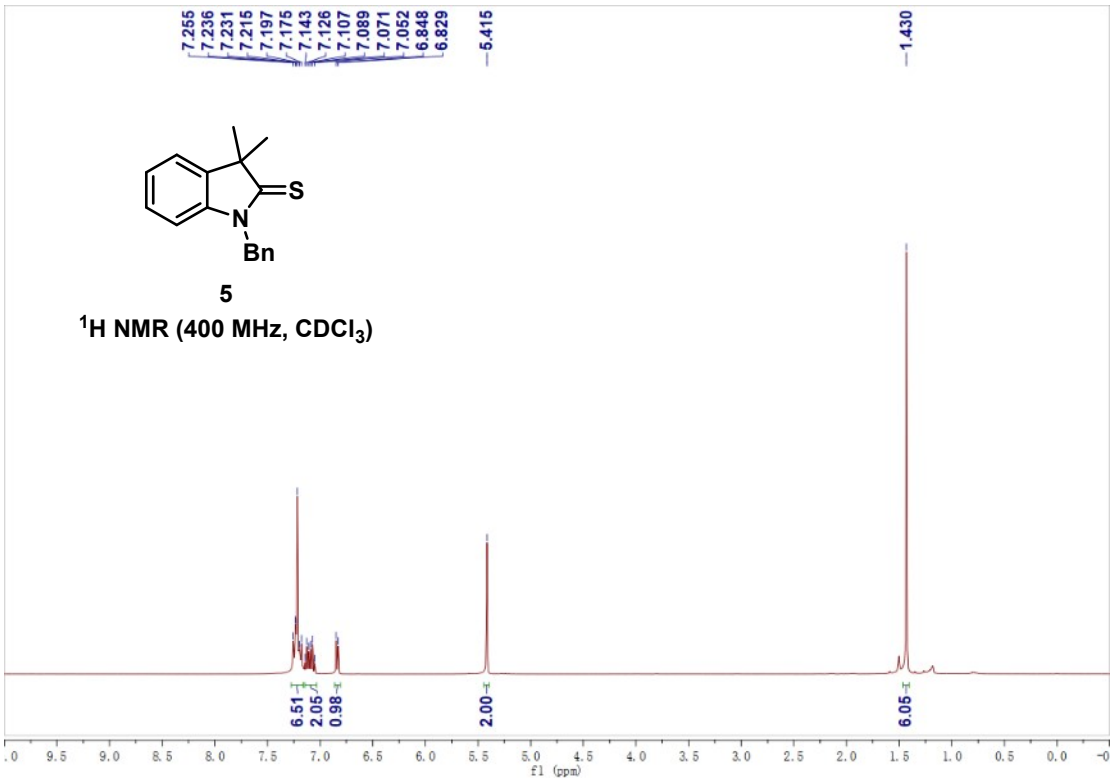
4

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



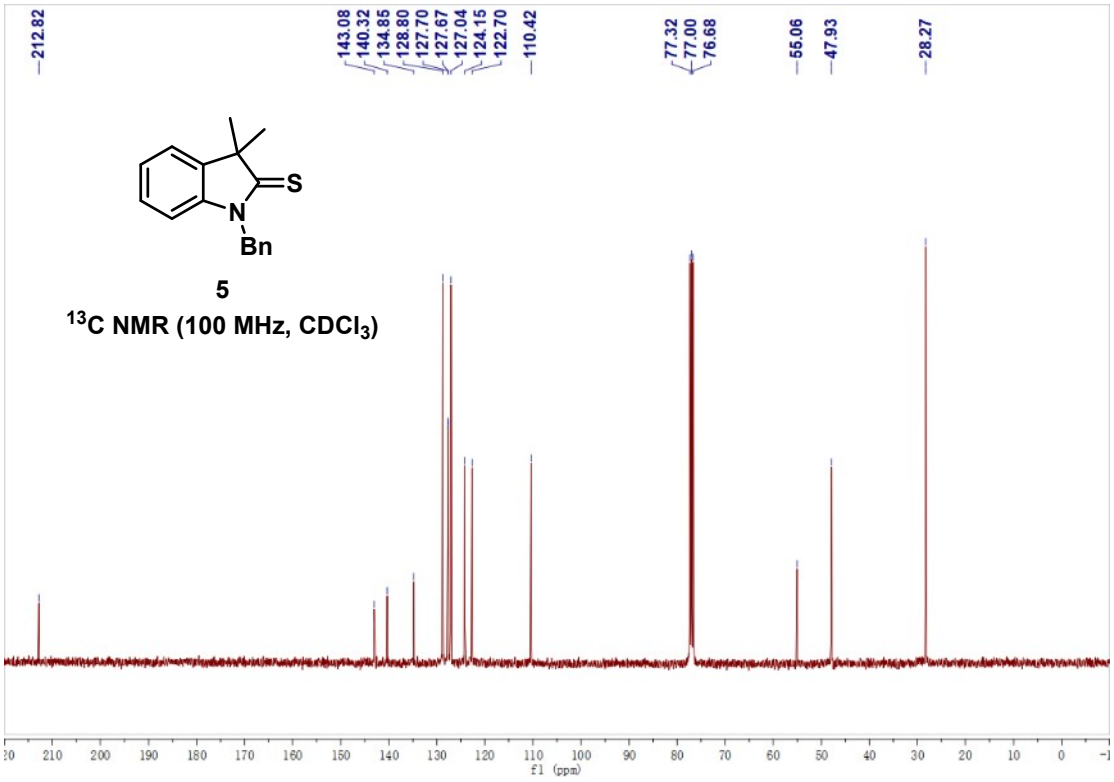
4

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



5

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



5

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