Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Electroselective C(sp^3)–H Deuteration of Isoindolinones

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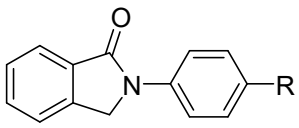
I. General Information

All reactions were performed under air atmosphere, using round bottom flasks. All substrates were obtained from the commercial sources or synthesized following literature procedures. All reagents were commercial and were used without further purification. The electrochemical reaction device follows our previous work.[1] The instrument for electrolysis is Single Output DC Power Supply (KRP-305DM) (made in China). Chromatography was carried on flash silica gel (300-400 mesh). All reactions were monitored by TLC, which was performed on percolated aluminum sheets of silica gel 60 (F254). Melting points were uncorrected. The ^{1}H and ^{13}C NMR data were obtained on a 300 MHz NMR spectrometer with TMS as the internal standard and $CDCl_3$ or DMSO - d_6 as solvent. Multiplicities are indicated as it follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, doubled doublet; br, broad. Coupling constants (*J* values) where noted are quoted in Hertz. Highresolution mass spectra (HRMS) were obtained with a time-of-flight (TOF) mass spectrometer (ESI).

Electrode materials/dimensions:

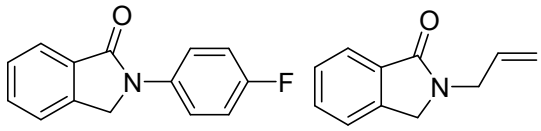
The graphite electrodes, alumium electrodes and znic electrodes are purchased from Tianjin Zhongnuotansu Technology Co., Ltd. The dimensions of the electrodes are 5 mm × 50 mm (the submerged height of the electrode is approximately 5 mm).

List of commercially available substrates：



1, R = H
s3, R = OMe
s4, R = Me
s7, R = Br
s10, R = CO_2Et

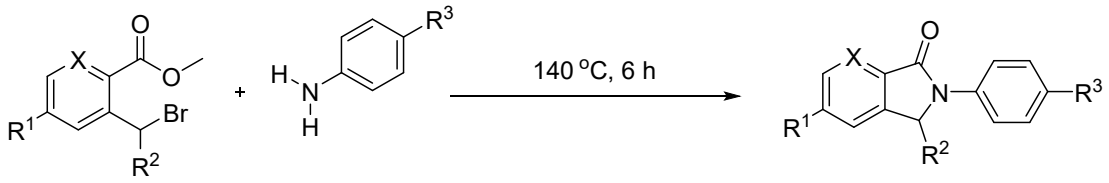
List of available substrates from our group's pervious work[2]：



s5 **s23**

II. Substrates Synthesis and Characterization

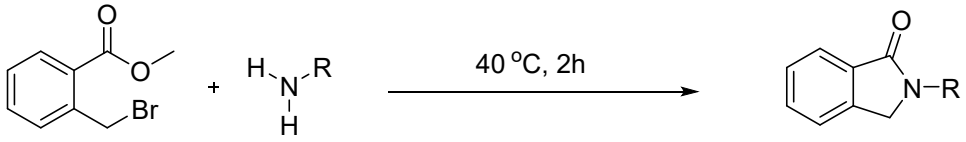
Method A : Synthesis of compounds **s6**, **s8-s9, s11-s12, s25-s29** and **s36**.



s6, s8-s9, s11-s12, s25-s29 and s36

A mixture of corresponding substituted methyl 2-(bromomethyl)benzoate (5 mmol, 1.0 eq.) and substituted amine (6 mmol, 1.2 eq.) in a 100 mL round bottom flask was stirred at 140 °C for 6 hours. The HBr tail gas absorbtion device was connected to this system throughout. After the completion of the reaction, the mixture was cooled to room temperature. The solution was diluted with DCM (30 mL) and quenched with 1*N* HCl aqueous or water (30 mL). The aqueous layer was extracted with DCM (3 × 30 mL). The combined DCM layers were washed with brine (3 × 30 mL), dried over Na_2SO_4, and concentrated *in vacuo*. Purification by flash column chromatography using PE/EtOAc as eluent afforded the desired product **s6**, **s8-s9, s11-s12, s25-s29** and **s36**.

Method B : Synthesis of compounds **s13-s15**, **s17-s22** and **s24**.

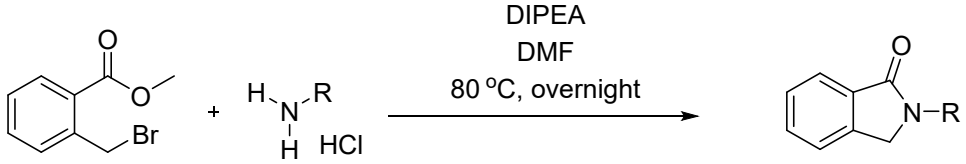


s13-s15, s17-s22 and s24

A mixture of methyl 2-(bromomethyl)benzoate (5 mmol, 1.0 eq.) and substituted amine (6 mmol, 1.2 eq.) in a 100 mL round bottom flask was stirred at 40 °C for 2 hours. The HBr tail gas absorbtion device was connected to this system throughout. After the completion of the reaction, the mixture was cooled to room temperature. The solution was diluted with DCM (30 mL) and quenched with 1*N* HCl aqueous (30 mL). The

aqueous layer was extracted with DCM (3 × 30 mL). The combined DCM layers were washed with brine (3 × 30 mL), dried over Na_2SO_4, and concentrated *in vacuo*. Purification by flash column chromatography using PE/EtOAc as eluent afforded the desired product **s13-s15**, **s17-s22** and **s24**.

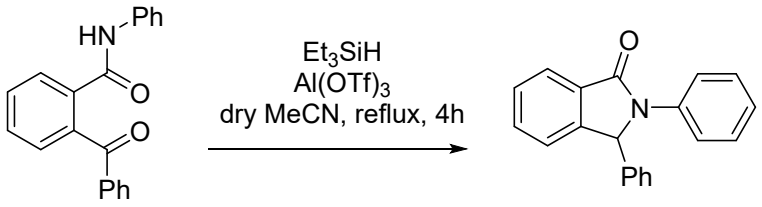
Method C : Synthesis of compounds **s32-s34**.



s32-s34

A mixture of corresponding substituted methyl 2-(bromomethyl)benzoate (5 mmol, 1.0 eq.) , substituted amine hydrochloride (6 mmol, 1.2 eq.), DIPEA (15 mmol, 3 eq.) and DMF (15 mL) in a 100 mL round bottom flask was stirred at 80 °C for overnight. After the completion of the reaction, the mixture was cooled to room temperature. The solution was diluted with EtOAc (30 mL) and quenched with 1*N* HCl aqueous (30 mL). The aqueous layer was extracted with EtOAc (3 × 30 mL). The combined EtOAc layers were washed with brine (3 × 30 mL), dried over Na_2SO_4, and concentrated *in vacuo*. Purification by flash column chromatography using PE/EtOAc as eluent afforded the desired product **s32-s34**.

Method D : Synthesis of compounds **s30**.

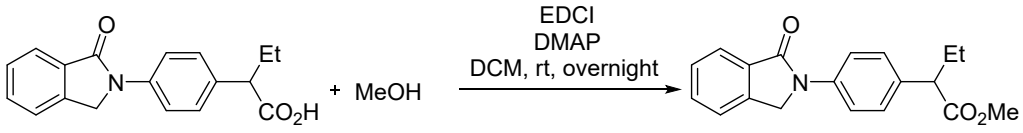


s30

To a solution of 2-benzoyl-N-phenylbenzamide (3.0 mmol, 1.0 eq.) in CH_3CN (5 mL) were added Et_3SiH (6.0 mmol, 2.0 eq.) and $Al(OTf)_3$ (1.5 mmol, 0.5 eq.) at room temperature. The reaction mixture was heated at reflux for 4 hours and then concentrated *in vacuo*. The solution was diluted with DCM (30 mL) and quenched with 1*N* HCl aqueous (30 mL). The aqueous layer was extracted with DCM (3 × 30 mL). The combined DCM layers were washed with brine (3 × 30 mL), dried over Na_2SO_4,

and concentrated *in vacuo*. Purification by flash column chromatography using PE/EtOAc (v/v = 3/1) as eluent afforded the desired product **s30**.

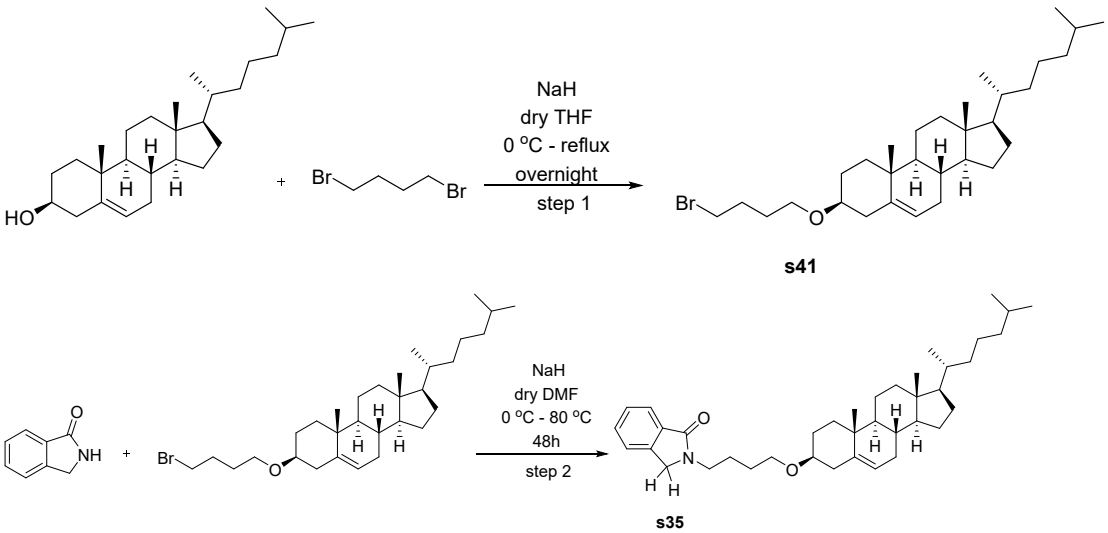
Method E : Synthesis of compounds **s31**.



s31

At room temperature, indobufen (2 mmol, 1.0 eq.) was dissolved in DCM (20 mL) in a 50 mL round bottom flask, then EDCI (3 mmol, 1.5 eq.) and DMAP (2.4 mmol, 1.2 eq.) were added, and then the MeOH (4 mmol, 2 eq.) was added dropwise to the above solution, and the obtained solution was stirred at room temperature for overnight. The solution was diluted with DCM (30 mL) and quenched with 1*N* HCl aqueous (30 mL). The aqueous layer was extracted with DCM (3 × 30 mL). The combined DCM layers were washed with brine (3 × 30 mL), dried over Na_2SO_4, and concentrated *in vacuo*. Purification by flash column chromatography using PE/EtOAc (v/v = 10/1) as eluent afforded the desired product **s31**.

Method F : Synthesis of compounds **s35**.



s41

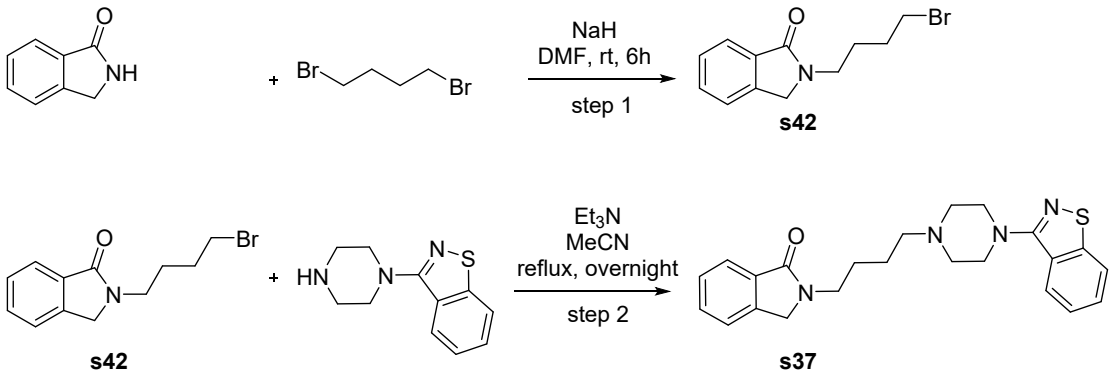
s35

Step 1: At room temperature, cholesterol (10 mmol, 1.0 eq.) was dissolved in THF (10 mL) in a 50 mL round bottom flask, then at 0 °C NaH (20 mmol, 2 eq.) were added, then the 1,4-dibromobutane (50 mmol, 5 eq.) was added dropwise to the above solution,

and the obtained solution heated at reflux for overnight. After the completion of the reaction, the mixture was cooled to room temperature and added ice water into solution, then concentrated *in vacuo*.The solution was diluted with DCM (30 mL) and quenched with water (30 mL). The aqueous layer was extracted with DCM (3 × 30 mL). The combined DCM layers were washed with brine (3 × 30 mL), dried over Na_2SO_4, and concentrated *in vacuo*. Purification by flash column chromatography using PE/EtOAc (v/v = 10/1) as eluent afforded the desired product **s41**.

Step 2: At room temperature, isoindolin-1-one (2 mmol, 1.0 eq.) was dissolved in DMF (10 mL) in a 50 mL round bottom flask, then at 0 °C NaH (4 mmol, 2.0 eq.) were added, and then the **s41** (2.4 mmol, 1.2 eq.) was added dropwise to the above solution, and the obtained solution heated at 80 °C for 48 hours. After the completion of the reaction, the mixture was cooled to room temperature and added ice water into solution.The solution was diluted with Et_2O (30 mL) and quenched with water (30 mL). The aqueous layer was extracted with Et_2O (3 × 30 mL). The combined Et_2O layers were washed with brine (3 × 30 mL), dried over Na_2SO_4, and concentrated *in vacuo*. Purification by flash column chromatography using PE/EtOAc (v/v = 3/1) as eluent afforded the desired product **s35**.

Method G : Synthesis of compounds **s37**.

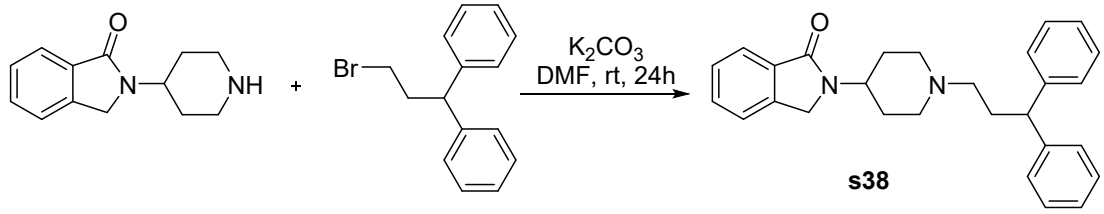


Step 1: At room temperature, isoindolin-1-one (10 mmol, 1.0 eq.) was dissolved in DMF (10 mL) in a 50 mL round bottom flask, then at 0 °C NaH (12 mmol, 1.2 eq.) were added, and then the 1,4-dibromobutane (50 mmol, 5 eq.) was added dropwise to the above solution, and the obtained solution was stirred at room temperature for 6

hours. After the completion of the reaction, the mixture was cooled to room temperature and added ice water into solution. The solution was diluted with EtOAc (30 mL) and quenched with water (30 mL). The aqueous layer was extracted with EtOAc (3 × 30 mL). The combined EtOAc layers were washed with brine (3 × 30 mL), dried over Na_2SO_4, and concentrated *in vacuo*. Purification by flash column chromatography using PE/EtOAc = (v/v = 3/1) as eluent afforded the desired product **s42**.

Step 2: A mixture of **s42** (5 mmol, 1.0 eq.) , 3-(piperazin-1-yl)benzo[d]isothiazole (5.5 mmol, 1.1 eq.), Et_3N (6 mmol, 1.2 eq.) and MeCN (10 mL) in a 100 mL round bottom flask was heated at reflux for overnight. After the completion of the reaction, the mixture was cooled to room temperature and then concentrated *in vacuo*.The solution was diluted with DCM (30 mL) and quenched with 1*N* HCl aqueous (30 mL). The aqueous layer was extracted with DCM (3 × 30 mL). The combined DCM layers were washed with brine (3 × 30 mL), dried over Na_2SO_4, and concentrated *in vacuo*. Purification by flash column chromatography using PE/EtOAc (v/v = 1/3) as eluent afforded the desired product **s37**.

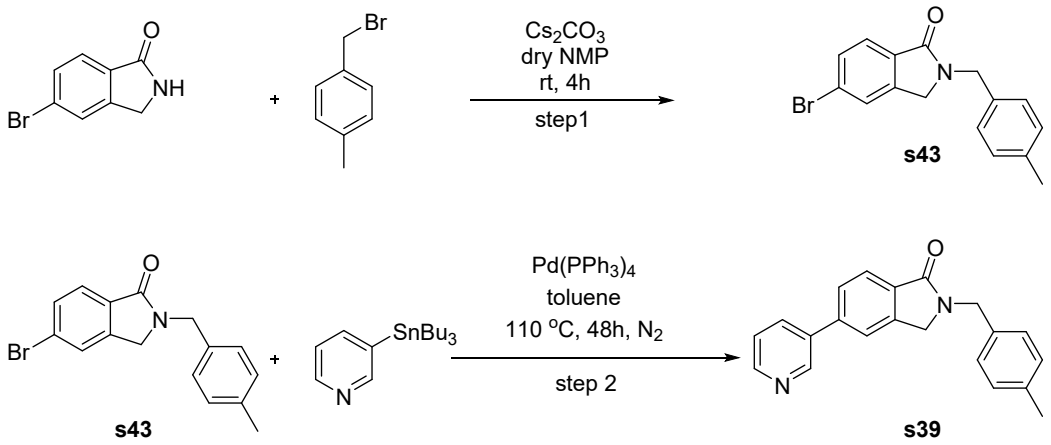
Method H : Synthesis of compounds **s38**.



s38

A mixture of (3-bromopropane-1,1-diyl)dibenzene (2 mmol, 1.0 eq.), 2-(piperidin-4-yl)isoindolin-1-one (2.2 mmol, 1.1 eq.), K_2CO_3 (4 mmol, 2.0 eq.) and DMF (10 mL) in a 100 mL round bottom flask was at room temperature for 24 hours. After the completion of the reaction, the solution was diluted with EtOAc (30 mL) and quenched with 1*N* HCl aqueous (30 mL). The aqueous layer was extracted with EtOAc (3 × 30 mL). The combined EtOAc layers were washed with brine (3 × 30 mL), dried over Na_2SO_4, and concentrated *in vacuo*. Purification by flash column chromatography using PE/EtOAc (v/v = 1/1) as eluent afforded the desired product **s38**.

Method I : Synthesis of compounds **s39**.

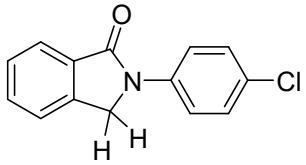


Step 1: A mixture of 5-bromoisoindolin-1-one (10 mmol, 1.0 eq.) , 1-(bromomethyl)-4-methylbenzene (15 mmol, 1.5 eq.), Cs_2CO_3 (16 mmol, 2 eq.) and NMP (10 mL) in a 100 mL round bottom flask was at 60 °C for 4 hours. After the completion of the reaction, the solution was diluted with EtOAc (30 mL) and quenched with 1*N* HCl aqueous (30 mL). The aqueous layer was extracted with EtOAc (3 × 30 mL). The combined EtOAc layers were washed with brine (3 × 30 mL), dried over Na_2SO_4, and concentrated *in vacuo*. Purification by flash column chromatography using PE/EtOAc (v/v = 10/1) as eluent afforded the desired product **s43**.

Step 2: At room temperature, a mixture of **s43** (5 mmol, 1.0 eq.) and 3-(tributylstannyl)pyridine (7.5 mmol, 1.5 eq.) was dissolved in toluene (10 mL) in a 100 mL three-compartment cell, the reaction system was purged with N_2 three times, followed by the addition of $Pd(PPh_3)_4$ (1 mmol, 0.2 eq.). The mixture was refluxed at 110 °C for 48 h. . The solution was diluted with EtOAc (30 mL) and quenched with water (30 mL). The aqueous layer was extracted with EtOAc (3 × 30 mL). The combined EtOAc layers were washed with brine (3 × 30 mL), dried over Na_2SO_4, and concentrated *in vacuo*. Purification by flash column chromatography using PE/EtOAc (v/v = 10/1) as eluent afforded the desired product **s39**.

2-(4-Chlorophenyl)isoindolin-1-one (s6)

The ^{1}H spectra data matched with values reported in the literature.[3]



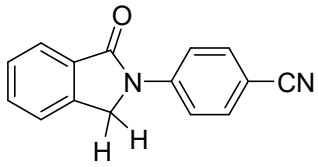
s6

White solid (900 mg, 75% yield); m.p. 184 – 186 °C;

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.3 Hz, 1H), 7.86 – 7.79 (m, 2H), 7.65 – 7.56 (m, 1H), 7.54 – 7.47 (m, 2H), 7.41 – 7.32 (m, 2H), 4.82 (s, 2H).

4-(1-Oxoisoindolin-2-yl)benzonitrile (s8)

The ^{1}H spectra data matched with values reported in the literature.[4]



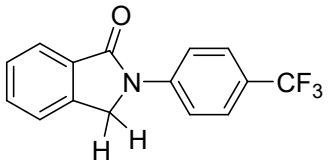
s8

White solid (780 mg, 67% yield); m.p. 204 – 206 °C;

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.09 – 8.03 (m, 2H), 7.96 – 7.92 (m, 1H), 7.74 – 7.69 (m, 2H), 7.69 – 7.62 (m, 1H), 7.58 – 7.51 (m, 2H), 4.89 (s, 2H).

2-(4-(Trifluoromethyl)phenyl)isoindolin-1-one (s9)

The ^{1}H spectra data matched with values reported in the literature.[4]



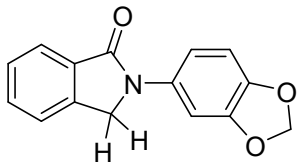
s9

White solid (970 mg, 70% yield); m.p. 231 – 232 °C;

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.04 (d, *J* = 8.4 Hz, 2H), 7.94 (d, *J* = 7.3 Hz, 1H), 7.72 – 7.66 (m, 2H), 7.65 – 7.60 (m, 1H), 7.58 – 7.49 (m, 2H), 4.90 (s, 2H).

2-(Benzo[*d*][1,3]dioxol-5-yl)isoindolin-1-one (s11)

The ^{1}H spectra data matched with values reported in the literature.[5]



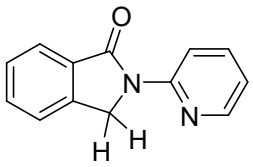
s11

White solid (830 mg, 66% yield); m.p. 167 – 169 °C;

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.94 – 7.88 (m, 1H), 7.63 – 7.55 (m, 2H), 7.53 – 7.45 (m, 2H), 7.10 (dd, *J* = 8.4, 2.3 Hz, 1H), 6.85 (dd, *J* = 8.4, 0.4 Hz, 1H), 5.99 (s, 2H), 4.80 (s, 2H).

2-(Pyridin-2-yl)isoindolin-1-one (s12)

The ^{1}H spectra data matched with values reported in the literature.[4]



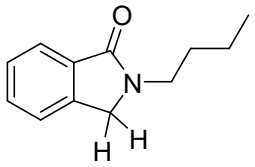
s12

White solid (300 mg, 29% yield); m.p. 176 – 177 °C;

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.67 (dt, *J* = 8.5, 0.9 Hz, 1H), 8.40 (ddd, *J* = 5.0, 2.0, 0.9 Hz, 1H), 7.96 – 7.90 (m, 1H), 7.81 – 7.72 (m, 1H), 7.62 (ddd, *J* = 7.6, 7.1, 1.2 Hz, 1H), 7.58 – 7.45 (m, 2H), 7.10 – 7.01 (m, 1H), 5.11 (s, 2H).

2-Butylisoindolin-1-one (s13)

The ^{1}H spectra data matched with values reported in the literature.[2]



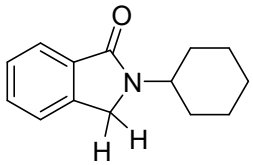
s13

Colourless liquid (800 mg, 85% yield);

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.86 – 7.78 (m, 1H), 7.54 – 7.47 (m, 1H), 7.46 – 7.40 (m, 2H), 4.36 (s, 2H), 3.64 (dt, *J* = 19.2, 7.4 Hz, 2H), 1.73 – 1.48 (m, 2H), 1.46 – 1.29 (m, 2H), 1.07 – 0.82 (m, 3H).

2-Cyclohexylisoindolin-1-one (s14)

The ^{1}H spectra data matched with values reported in the literature.[3]



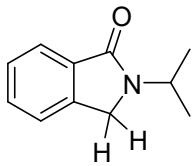
s14

Colourless liquid (750 mg, 70% yield);

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.89 – 7.74 (m, 1H), 7.55 – 7.48 (m, 1H), 7.48 – 7.41 (m, 2H), 4.35 (s, 2H), 4.30 – 4.17 (m, 1H), 1.87 (s, 4H), 1.73 (d, *J* = 13.1 Hz, 1H), 1.57 – 1.38 (m, 4H), 1.27 – 1.11 (m, 1H).

2-Isopropylisoindolin-1-one (s15)

The ^{1}H spectra data matched with values reported in the literature.[3]



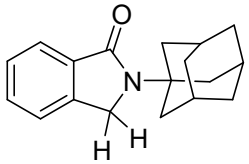
s15

Colourless liquid (825 mg, 94% yield);

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.84 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.55 – 7.49 (m, 1H), 7.44 (ddd, *J* = 6.7, 4.0, 1.4 Hz, 2H), 4.77 – 4.50 (m, 1H), 4.34 (s, 2H), 1.29 (d, *J* = 6.8 Hz, 6H).

2-(Adamantan-1-yl)isoindolin-1-one (s16)

The ^{1}H spectra data matched with values reported in the literature.[6]



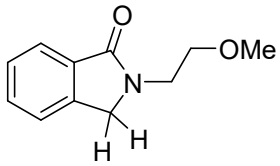
s16

White solid (1.1 g, 82% yield); m.p. 202 – 204 °C;

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.81 – 7.75 (m, 1H), 7.49 (td, *J* = 7.3, 1.4 Hz, 1H), 7.45 – 7.37 (m, 2H), 4.46 (s, 2H), 2.31 (d, *J* = 3.0 Hz, 6H), 2.16 (s, 3H), 1.74 (dd, *J* = 7.5, 4.2 Hz, 6H).

2-(2-Methoxyethyl)isoindolin-1-one (s17)

The ^{1}H spectra data matched with values reported in the literature.[2]



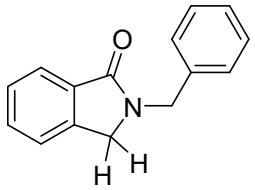
s17

Colourless liquid (700 mg, 73% yield);

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.85 – 7.77 (m, 1H), 7.54 – 7.46 (m, 1H), 7.44 – 7.36 (m, 2H), 4.49 (s, 2H), 3.80 – 3.72 (m, 2H), 3.63 – 3.57 (m, 2H), 3.32 (s, 3H).

2-Benzylisoindolin-1-one (s18)

The ^{1}H spectra data matched with values reported in the literature.[2]



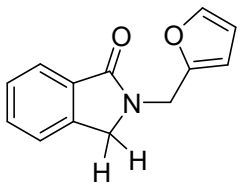
s18

White solid (900 mg, 81% yield); m.p. 88 – 89 °C;

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.95 – 7.85 (m, 1H), 7.56 – 7.42 (m, 2H), 7.38 (ddt, *J* = 7.3, 1.5, 0.8 Hz, 2H), 7.35 – 7.27 (m, 4H), 4.81 (s, 2H), 4.27 (s, 2H).

2-(Furan-2-ylmethyl)isoindolin-1-one (s19)

The ^{1}H spectra data matched with values reported in the literature.[7]

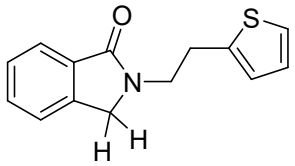


s19

Yellow liquid (500 mg, 47% yield);

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.84 (dt, *J* = 7.3, 1.1 Hz, 1H), 7.50 (td, *J* = 7.3, 1.7 Hz, 1H), 7.45 – 7.36 (m, 2H), 7.34 (dd, *J* = 1.7, 1.1 Hz, 1H), 6.34 – 6.25 (m, 2H), 4.77 (s, 2H), 4.35 (s, 2H).

2-(2-(Thiophen-2-yl)ethyl)isoindolin-1-one (s20)



s20

White solid (970 mg, 80% yield); m.p. 102 – 104 °C;

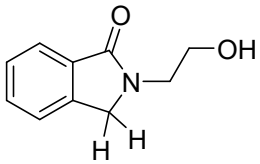
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.89 – 7.78 (m, 1H), 7.54 – 7.48 (m, 1H), 7.46 (ddd, *J* = 7.3, 1.4, 0.6 Hz, 1H), 7.41 – 7.36 (m, 1H), 7.14 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.91 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.86 (dt, *J* = 3.5, 1.0 Hz, 1H), 4.25 (s, 2H), 3.90 (t, *J* = 7.0 Hz, 2H), 3.23 (t, *J* = 7.0, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 168.6, 141.3, 132.9, 131.3, 128.1, 127.2, 125.5, 124.1, 123.7, 122.7, 50.8, 44.4, 29.1.

HRMS (ESI): Calcd. for $C_{14}H_{14}NOS^+$ $[M + H]^+$: 244.0791, found: 244.0785.

2-(2-Hydroxyethyl)isoindolin-1-one (s21)

The ^{1}H spectra data matched with values reported in the literature.[2]



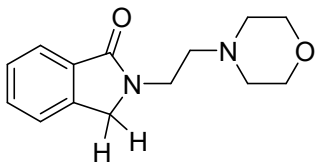
s21

White solid (800 mg, 90% yield); m.p. 113 – 115 °C;

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.82 (dt, *J* = 7.5, 1.1 Hz, 1H), 7.57 – 7.49 (m, 1H), 7.48 – 7.38 (m, 2H), 4.51 (s, 2H), 3.92 (dd, *J* = 5.6, 4.3 Hz, 2H), 3.77 (dd, *J* = 5.6, 4.3 Hz, 2H).

2-(2-Morpholinoethyl)isoindolin-1-one (s22)

The ^{1}H spectra data matched with values reported in the literature.[8]



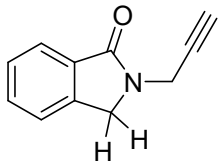
s22

Colourless liquid (740 mg, 60% yield);

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.89 – 7.82 (m, 1H), 7.58 – 7.50 (m, 1H), 7.49 – 7.41 (m, 2H), 4.50 (s, 2H), 3.75 (t, *J* = 6.4 Hz, 2H), 3.71 – 3.61 (m, 4H), 2.64 (t, *J* = 6.4 Hz, 2H), 2.57 – 2.43 (m, 4H).

2-(Prop-2-yn-1-yl)isoindolin-1-one (s24)

The ^{1}H spectra data matched with values reported in the literature.[2]



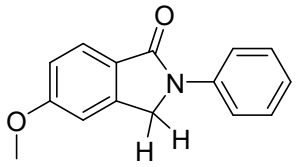
s24

Colourless liquid (700 mg, 82% yield);

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90 – 7.81 (m, 1H), 7.60 – 7.51 (m, 1H), 7.49 – 7.43 (m, 2H), 4.50 (s, 2H), 4.45 (d, *J* = 2.6 Hz, 2H), 2.28 (t, *J* = 2.6 Hz, 1H).

5-Methoxy-2-phenylisoindolin-1-one (s25)

The ^{1}H spectra data matched with values reported in the literature.[2]



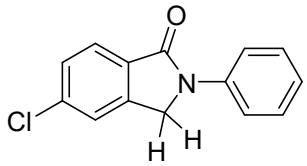
s25

White solid (600 mg, 50% yield); m.p. 142 – 144 °C;

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.88 – 7.75 (m, 3H), 7.48 – 7.34 (m, 2H), 7.18 – 7.08 (m, 1H), 7.04 – 6.90 (m, 2H), 4.74 (s, 2H), 3.87 (s, 3H).

5-Chloro-2-phenylisoindolin-1-one (s26)

The ^{1}H spectra data matched with values reported in the literature.[7]

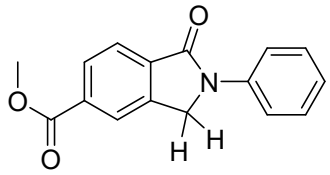


s26

Yellow solid (400 mg, 30% yield); m.p. 155 – 156 °C;

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90 – 7.81 (m, 3H), 7.55 – 7.47 (m, 2H), 7.44 (dd, *J* = 8.7, 7.4 Hz, 2H), 7.21 (d, *J* = 7.4 Hz, 1H), 4.85 (s, 2H).

Methyl 1-oxo-2-phenylisoindoline-5-carboxylate (s27)



s27

White solid (670 mg, 50% yield); m.p. 142 – 144 °C;

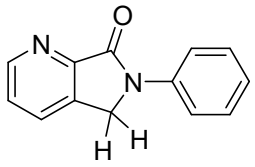
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.27 – 8.15 (m, 2H), 8.02 – 7.95 (m, 1H), 7.90 – 7.82 (m, 2H), 7.45 (t, *J* = 7.9 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 4.91 (s, 2H), 3.98 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 166.5, 165.5, 140.1, 139.3, 137.2, 133.7, 130.0, 129.4, 125.1, 124.3, 124.2, 119.8, 52.7, 50.8.

HRMS (ESI): Calcd. for $C_{16}H_{14}NO_3^+$ $[M + H]^+$: 268.0968, found: 268.0971.

6-Phenyl-5,6-dihydro-7*H*-pyrrolo[3,4-*b*]pyridin-7-one (s28)

The ^{1}H spectra data matched with values reported in the literature.[9]



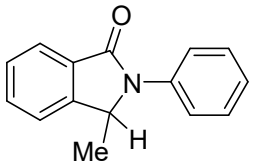
s28

Yellow solid (400 mg, 64% yield); m.p. 192 – 194 °C;

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.84 (d, *J* = 4.8 Hz, 1H), 7.92 – 7.77 (m, 3H), 7.60 – 7.38 (m, 3H), 7.25 – 7.18 (m, 1H), 4.89 (s, 2H).

3-Methyl-2-phenylisoindolin-1-one (s29)

The ^{1}H spectra data matched with values reported in the literature.[3]



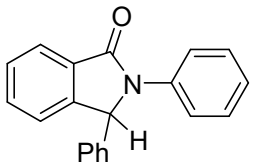
s29

Colourless liquid (1.03 g, 92% yield);

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.99 – 7.85 (m, 1H), 7.67 – 7.55 (m, 3H), 7.55 – 7.41 (m, 4H), 7.28 – 7.19 (m, 1H), 5.21 (q, *J* = 6.7 Hz, 1H), 1.46 (d, *J* = 6.7, 3H).

2,3-Diphenylisoindolin-1-one (s30)

The ^{1}H spectra data matched with values reported in the literature.[10]



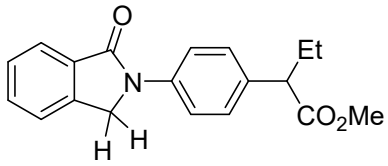
s30

White solid (600 mg, 70% yield); m.p. 198 – 199 °C;

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.01 – 7.95 (m, 1H), 7.64 – 7.58 (m, 2H), 7.56 – 7.47 (m, 2H), 7.35 – 7.18 (m, 8H), 7.13 – 7.04 (m, 1H), 6.10 (s, 1H).

Methyl 2-(4-(1-oxoisoindolin-2-yl)phenyl)butanoate (s31)

The ^{1}H spectra data matched with values reported in the literature.[11]



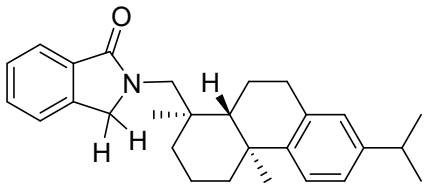
s31

Colourless liquid (560 mg, 90% yield);

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.96 – 7.89 (m, 1H), 7.83 (d, *J* = 8.6 Hz, 2H), 7.63 – 7.56 (m, 1H), 7.52 (d, *J* = 7.2 Hz, 2H), 7.37 (d, *J* = 8.6 Hz, 2H), 4.85 (s, 2H), 3.67 (s, 3H), 3.47 (t, *J* = 14.0 Hz, 1H), 2.19 – 2.00 (m, 1H), 1.81 (dt, *J* = 14.0, 7.4 Hz, 1H), 0.91 (t, *J* = 7.4 Hz, 3H).

2-(((1*R*,4a*S*,10a*R*)-7-Isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)isoindolin-1-one (s32)

The ^{1}H spectra data matched with values reported in the literature.[12]



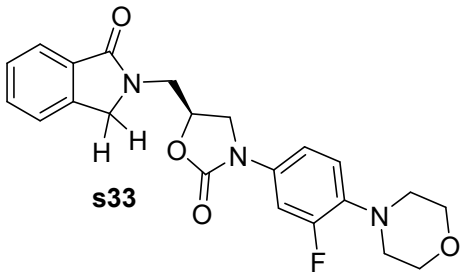
s32

Yellow liquid (1.2 g, 60% yield);

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.85 (dt, *J* = 7.4, 1.1 Hz, 1H), 7.52 (td, *J* = 7.4, 1.1 Hz, 1H), 7.48 – 7.38 (m, 2H), 7.19 (d, *J* = 8.1 Hz, 1H), 7.01 (dd, *J* = 8.1, 2.1 Hz, 1H), 6.94 (d, *J* = 2.1 Hz, 1H), 4.51 (s, 2H), 3.50 (s, 2H), 3.06 – 2.94 (m, 2H), 2.85 (dt, *J* = 13.8,

6.4 Hz, 1H), 2.31 (dt, *J* = 12.9, 3.4 Hz, 1H), 2.17 (ddt, *J* = 12.9, 6.4, 2.2 Hz, 1H), 1.97 – 1.67 (m, 3H), 1.61 (q, *J* = 2.7 Hz, 2H), 1.56 (d, *J* = 2.2 Hz, 1H), 1.39 (td, *J* = 12.7, 4.1 Hz, 1H), 1.27 (d, *J* = 2.5 Hz, 6H), 1.24 (s, 3H), 1.09 (s, 3H).

(*S*)-3-(3-Fluoro-4-morpholinophenyl)-5-((1-oxoisoindolin-2-yl)methyl)oxazolidin-2-one (s33)



s33

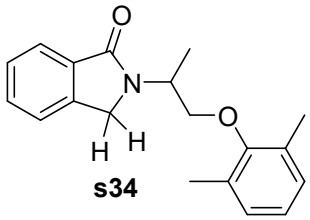
Yellow solid (800 mg, 40% yield); m.p. 233 – 236 °C;

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.88 – 7.80 (m, 1H), 7.61 – 7.53 (m, 1H), 7.50 – 7.42 (m, 2H), 7.39 (d, *J* = 2.6 Hz, 1H), 7.05 (dd, *J* = 2.6, 1.1 Hz, 1H), 6.92 (d, *J* = 9.1 Hz, 1H), 5.01 – 4.85 (m, 1H), 4.63 (d, *J* = 1.8 Hz, 2H), 4.10 (d, *J* = 9.1 Hz, 1H), 4.06 – 4.02 (m, 1H), 3.98 – 3.93 (m, 1H), 3.92 – 3.89 (m, 1H), 3.88 – 3.83 (m, 4H), 3.07 – 2.96 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 169.8, 157.2, 154.2, 153.9, 141.9, 136.6, 133.1, 132.1, 131.6, 128.3, 123.9, 123.0, 118.9, 114.1, 107.9, 107.5, 72.7, 67.0, 52.5, 51.0, 47.9, 45.6.

HRMS (ESI): Calcd. for $C_{22}H_{23}FN_3O_4^+$ $[M + H]^+$: 412.1667, found: 412.1677.

2-(1-(2,6-Dimethylphenoxy)propan-2-yl)isoindolin-1-one (s34)



s34

Colourless liquid (800 mg, 54% yield);

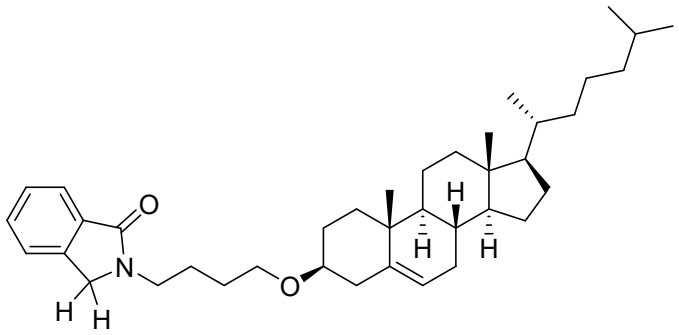
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.88 (m, 1H), 7.60 – 7.51 (m, 1H), 7.47 (m, 2H), 6.97 (m, 2H), 6.92 (s, 1H), 4.84 (tdd, *J* = 7.1, 4.7, 2.4 Hz, 1H), 4.72 (d, *J* = 17.1 Hz, 1H), 4.54 (d, *J* = 17.1 Hz, 1H), 4.03 – 3.89 (m, 2H), 2.26 – 2.15 (m, 6H), 1.56 (dd, *J* = 7.1, 0.8 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 168.6, 155.3, 141.7, 133.0, 131.3, 130.8, 129.0, 128.0,

124.1, 123.7, 122.8, 74.0, 47.9, 47.5, 16.3, 15.5.

HRMS (ESI): Calcd. for $C_{19}H_{22}NO_2^+$ $[M + H]^+$: 296.1645, found: 296.1658.

2-((((3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)methyl)isoindolin-1-one (s35)



s35

Colourless liquid (800 mg, 54% yield);

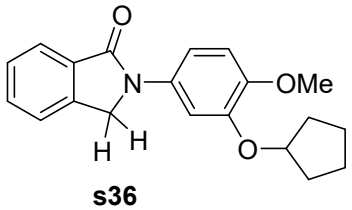
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90 – 7.73 (m, 1H), 7.59 – 7.50 (m, 1H), 7.48 – 7.38 (m, 2H), 5.33 (s, 1H), 4.45 – 4.32 (m, 2H), 3.70 – 3.60 (m, 2H), 3.57 – 3.44 (m, 2H), 3.14 (m, 1H), 2.33 (m, 1H), 2.18 (d, *J* = 12.1 Hz, 1H), 2.08 – 1.94 (m, 2H), 1.91 – 1.62 (m, 5H), 1.62 – 1.06 (m, 21H), 1.00 (td, *J* = 5.4, 4.9, 2.8 Hz, 4H), 0.95 – 0.89 (m, 4H), 0.86 (m, 6H), 0.71 – 0.65 (m, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 168.6, 141.2, 141.1, 133.2, 131.2, 128.1, 123.7, 122.7, 121.6, 79.1, 67.4, 56.9, 56.3, 50.3, 50.1, 42.4, 42.2, 39.9, 39.6, 39.3, 37.3, 37.0, 36.3, 35.9, 32.0, 28.6, 28.3, 28.1, 27.5, 25.4, 24.4, 23.9, 22.9, 22.7, 21.2, 19.5, 18.8, 12.0.

HRMS (ESI): Calcd. for $C_{39}H_{60}NO_2^+$ $[M + H]^+$: 574.4619, found: 574.4612.

2-(3-(Cyclopentyloxy)-4-methoxyphenyl)isoindolin-1-one (s36)

The ^{1}H spectra data matched with values reported in the literature.[3]



s36

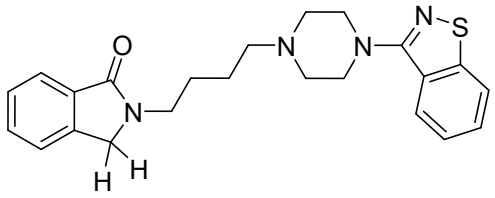
White solid (950 mg, 60% yield); m.p. 137 – 139 °C;

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.97 – 7.84 (m, 2H), 7.59 (ddd, *J* = 7.8, 7.1, 1.2 Hz,

1H), 7.54 – 7.44 (m, 2H), 7.06 – 6.98 (m, 1H), 6.94 – 6.84 (m, 1H), 4.92 – 4.85 (m, 1H), 4.82 (s, 2H), 3.86 (s, 3H), δ 2.04 (m, 2H), 1.98 – 1.88 (m, 2H), 1.85 (m, 2H), 1.61 (m, 2H).

2-(4-(4-(Benzo[*d*]isothiazol-3-yl)piperazin-1-yl)butyl)isoindolin-1-one (s37)

The ^{1}H spectra data matched with values reported in the literature.[13]



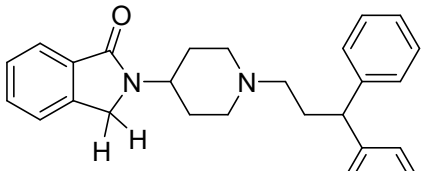
s37

White solid (1.4 g, 69% yield); m.p. 233 – 234 °C;

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.1 Hz, 1H), 7.85 – 7.81 (m, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.55 – 7.48 (m, 1H), 7.48 – 7.41 (m, 3H), 7.37 – 7.29 (m, 1H), 4.38 (s, 2H), 3.66 (t, *J* = 7.0 Hz, 2H), 3.54 (t, *J* = 4.9 Hz, 4H), 2.65 (t, *J* = 4.9 Hz, 4H), 2.47 (t, *J* = 7.0 Hz, 2H), 1.80 – 1.67 (m, 2H), 1.61 (m, 2H).

2-(1-(3,3-Diphenylpropyl)piperidin-4-yl)isoindolin-1-one (s38)

The ^{1}H spectra data matched with values reported in the literature.[14]



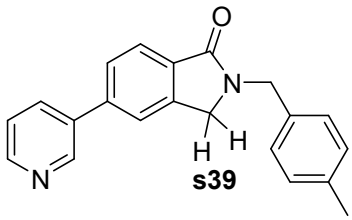
s38

Colourless liquid (400 mg, 50% yield);

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.84 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.56 – 7.49 (m, 1H), 7.48 – 7.41 (m, 2H), 7.32 – 7.22 (m, 8H), 7.21 – 7.14 (m, 2H), 4.36 (s, 2H), 4.34 – 4.15 (m, 1H), 3.98 (t, *J* = 7.0 Hz, 1H), 3.00 (d, *J* = 7.0 Hz, 2H), 2.29 (m, 4H), 2.16 – 2.00 (m, 2H), 1.83 (p, *J* = 4.0 Hz, 4H).

2-(4-Methylbenzyl)-5-(pyridin-3-yl)isoindolin-1-one (s39)

The ^{1}H spectra data matched with values reported in the literature.[15]



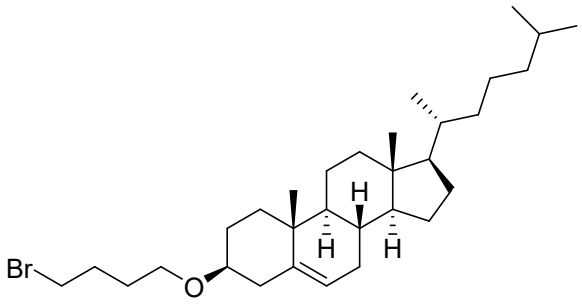
s39

Yellow solid (800 mg, 40% yield); m.p. 145 – 147 °C;

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.87 – 8.82 (m, 1H), 8.63 (dd, *J* = 4.9, 1.7 Hz, 1H), 7.99 (dd, *J* = 7.9, 0.8 Hz, 1H), 7.88 (ddd, *J* = 7.9, 2.4, 1.7 Hz, 1H), 7.67 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.56 (dd, *J* = 1.6, 0.8 Hz, 1H), 7.43 – 7.36 (m, 1H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.18 – 7.13 (m, 2H), 4.79 (s, 2H), 4.33 (s, 2H), 2.33 (s, 3H).

(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-3-(4-Bromobutoxy)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthrene (s41)

The ^{1}H spectra data matched with values reported in the literature.[16]



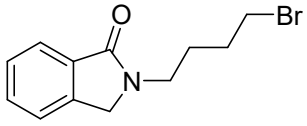
s41

Colourless liquid (1.3 g, 25% yield);

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.34 (d, *J* = 5.1 Hz, 1H), 3.56 – 3.38 (m, 4H), 3.12 (tt, *J* = 11.3, 4.4 Hz, 1H), 2.40 – 2.27 (m, 1H), 2.24 – 2.11 (m, 1H), 2.04 – 1.79 (m, 6H), 1.70 (dd, *J* = 8.8, 6.0 Hz, 2H), 1.54 – 0.82 (m, 34H), 0.68 (s, 3H).

2-(4-Bromobutyl)isoindolin-1-one (s42)

The ^{1}H spectra data matched with values reported in the literature.[17]



s42

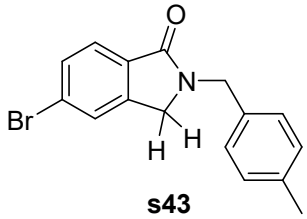
Colourless liquid (2.1 g, 80% yield);

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.80 – 7.72 (m, 1H), 7.50 – 7.43 (m, 1H), 7.42 – 7.34

(m, 2H), 4.32 (s, 2H), 3.59 (t, *J* = 6.6 Hz, 2H), 3.45 – 3.34 (m, 3H), 2.02 – 1.91 (m, 1H), 1.89 – 1.69 (m, 4H).

5-Bromo-2-(4-methylbenzyl)isoindolin-1-one (s43)

The ^{1}H spectra data matched with values reported in the literature.[15]



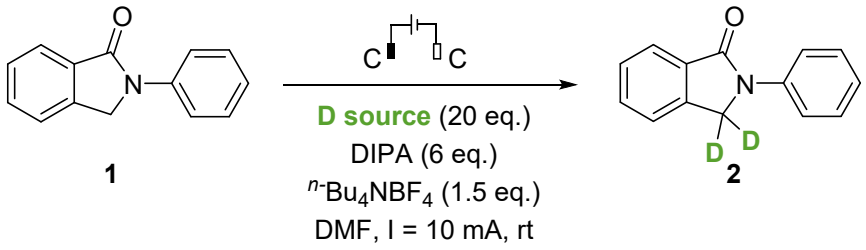
s43

Yellow solid (1.4 g, 70% yield); m.p. 95 – 96 °C;

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.71 (d, *J* = 7.9 Hz, 1H), 7.62 – 7.46 (m, 2H), 7.15 (m, 4H), 4.72 (s, 2H), 4.20 (s, 2H), 2.32 (s, 3H).

III. Investigation of Reaction Conditions

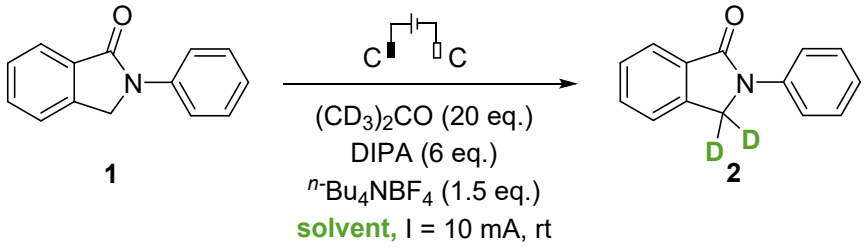
Table S1. Investigation of deuterium source[a]:



entry	variation of deuterium source	D % of **2** [b]
1	$(CD_3)_2SO$	30
2	CD_3OD	60
3	EtOD	70
4	D_2O	75
5	CD_3CN	77
6	$(CD_3)_2CO$	82 (64%)[c]

[a]Reaction conditions: graphite anode (d = 5 mm), graphite cathode (d = 5 mm), **1** (0.2 mmol), deuterium source (20 eq.), DIPA (6 eq.), ^{n}-Bu_4NBF_4 (1.5 eq.), DMF (3.0 mL), undivided cell, constant current = 10 mA, room temperature, 3 h. [b]Degree of deuteration. [c]Isolated yield in parentheses.

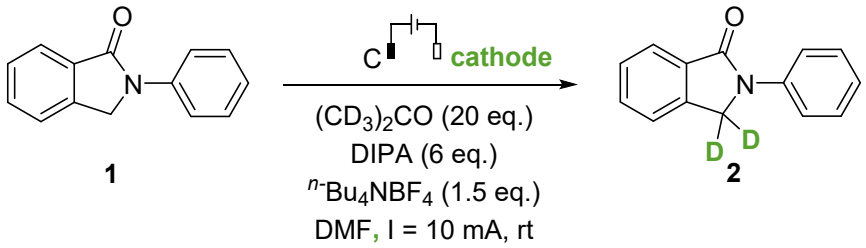
Table S2. Investigation of solvent[a]:



entry	variation of solvent (3 mL)	D % of **2** [b]
1	MeCN	10
2	DCM	15
3	NMP	70
4	THF	75
5	DMA	80

[a]Reaction conditions: graphite anode (d = 5 mm), graphite cathode (d = 5 mm), **1** (0.2 mmol), $(CD_3)_2CO$ (20 eq.), DIPA (6 eq.), ^{n}-Bu_4NBF_4 (1.5 eq.), solvent (3.0 mL), undivided cell, constant current = 10 mA, room temperature, 3 h. [b]Degree of deuteration. [c]Isolated yield in parentheses.

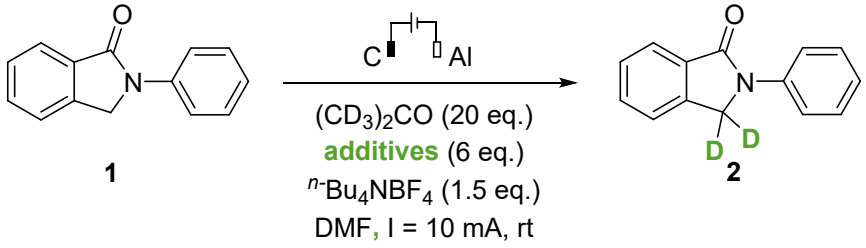
Table S3. Investigation of cathode[a]:



entry	variation of cathode	D % of **2** [b]
1	Pt	80
2	Ni	75
3	Mo	80
4	steel	80
5	Zn	85
6	Mg	85
7	Al	90 (66%)[c]

[a]Reaction conditions: graphite anode (d = 5 mm), cathode (d = 5 mm), **1** (0.2 mmol), $(CD_3)_2CO$ (20 eq.), DIPA (6 eq.), ^{n}-Bu_4NBF_4 (1.5 eq.), DMF (3.0 mL), undivided cell, constant current = 10 mA, room temperature, 3 h. [b]Degree of deuteration. [c]Isolated yield in parentheses.

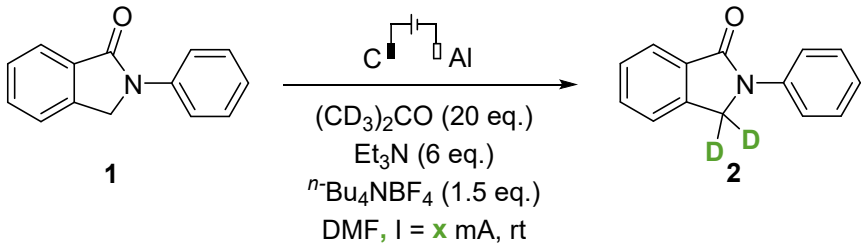
Table S4. Investigation of additives[a]:



entry	variation of additives	D % of **2** [b]
1	PivOH	0
2	DIPEA	95 (36%)[c]
3	Et_3N	96 (36%)[c]
4	PMP	95 (30%)[c]

[a]Reaction conditions: graphite anode (d = 5 mm), aluminium cathode (d = 5 mm), **1** (0.2 mmol), $(CD_3)_2CO$ (20 eq.), additives (6 eq.), ^{n}-Bu_4NBF_4 (1.5 eq.), DMF (3.0 mL), undivided cell, constant current = 10 mA, room temperature, 1.5 h. [b]Degree of deuteration. [c]Isolated yield in parentheses.

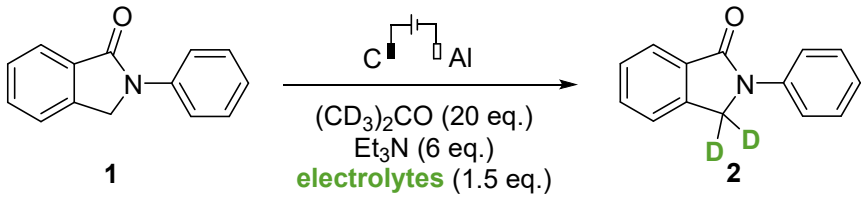
Table S5. Investigation of current[a]:



entry	variation of current	D % of **2** [b]
1	3	90
2	5	96 (60%)[c]
3	20	96 (20%)[c]

[a]Reaction conditions: graphite anode (d = 5 mm), aluminium cathode (d = 5 mm), **1** (0.2 mmol), $(CD_3)_2CO$ (20 eq.), Et_3N (6 eq.), ^{n}-Bu_4NBF_4 (1.5 eq.), DMF (3.0 mL), undivided cell, constant current = x mA, room temperature, 1.5 h. [b]Degree of deuteration. [c]Isolated yield in parentheses.

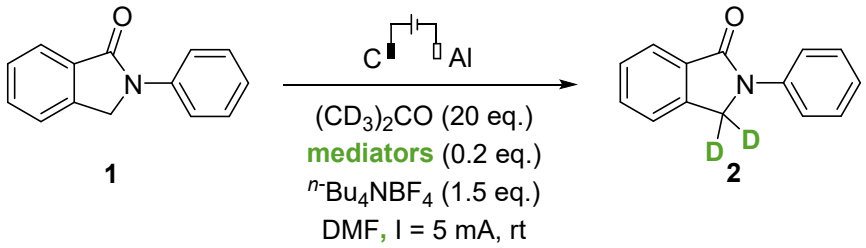
Table S6. Investigation of electrolytes[a]:



entry	variation of electrolytes	D % of **2** [b]
1	^{n}-Bu_4NPF_6	95 (55%)[c]
2	^{n}-Bu_4NClO_4	95 (47%)[c]
3	$LiClO_4$	0
4	$NaSbF_6$	0
5	^{n}-Bu_4NBr	96 (53%)[c]
6	^{n}-Bu_4NI	96 (55%)[c]

[a]Reaction conditions: graphite anode (d = 5 mm), aluminium cathode (d = 5 mm), **1** (0.2 mmol), $(CD_3)_2CO$ (20 eq.), Et_3N (6 eq.), electrolytes (1.5 eq.), DMF (3.0 mL), undivided cell, constant current = 5 mA, room temperature, 1.5 h. [b]Degree of deuteration. [c]Isolated yield in parentheses.

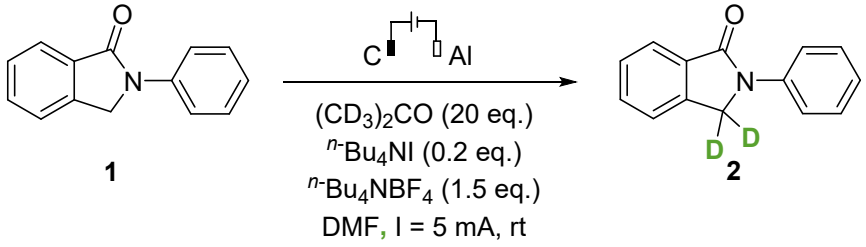
Table S7. Investigation of mediators[a]:



entry	variation of mediators	D % of **2** [b]
1	KI	90
2	NHPI	95 (47%)[c]
3	TEMPO	94 (66%)[c]
4	^{n}-Bu_4NI	96 (81%)[c]

[a]Reaction conditions: graphite anode (d = 5 mm), aluminium cathode (d = 5 mm), **1** (0.2 mmol), $(CD_3)_2CO$ (20 eq.), mediators (0.2 eq.), ^{n}-Bu_4NBF_4 (1.5 eq.), DMF (3.0 mL), undivided cell, constant current = 5 mA, room temperature, 1.5 h. [b]Degree of deuteration. [c]Isolated yield in parentheses.

Table S8. Investigation of other conditions[a]:



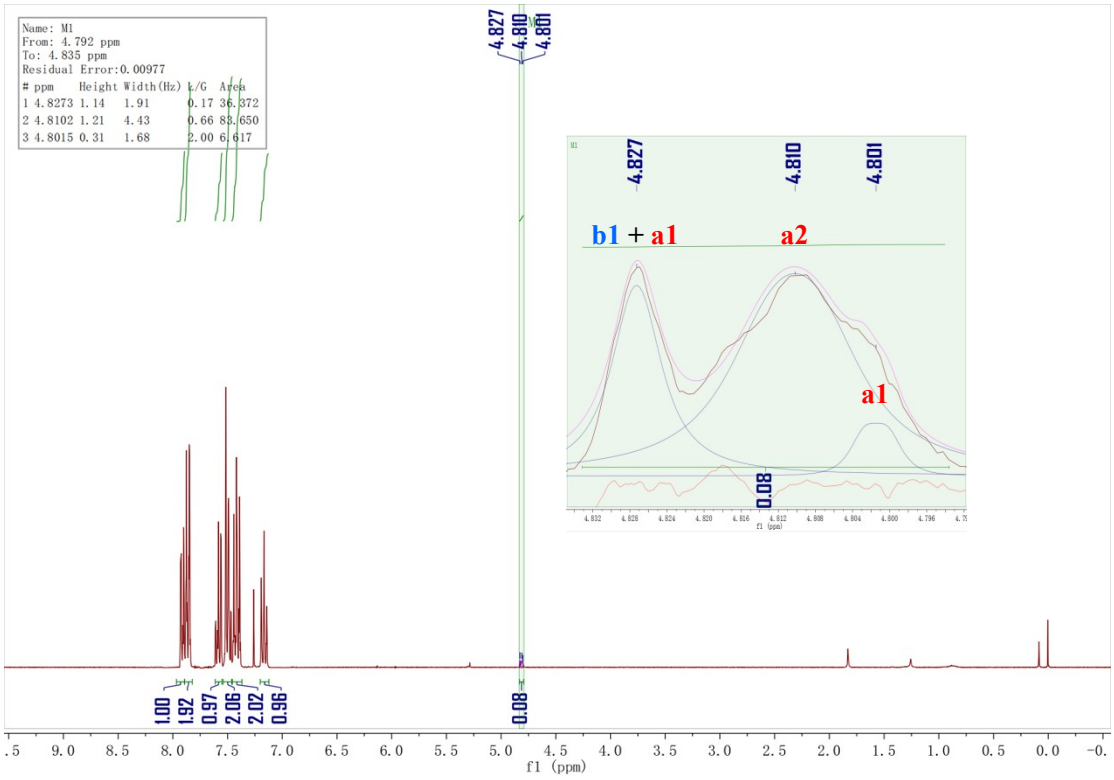
entry	variation from standard conditions	D % of **2** [b]
1	none	96 (81%)[c]
2	no ^{n}-Bu_4NI	95 (50%) [c]
3	no ^{n}-Bu_4NBF_4	95 (62%) [c]
4	D_2O instead of $(CD_3)_2CO$	90 (71%) [c]
5	DMSO-d_6 instead of $(CD_3)_2CO$	27 (60%) [c]
6	DCM instead of DMF	92 (69%) [c]
7	EtOH instead of DMF	0
8	graphite instead of aluminium	93 (71%) [c]
9	10 mA, 45min instead of 5 mA, 1.5h	95 (57%) [c]
10	no electric current	0

[a]Reaction conditions: graphite anode (d = 5 mm), aluminium cathode (d = 5 mm), **1** (0.2 mmol), $(CD_3)_2CO$ (20 eq.), ^{n}-Bu_4NI (0.2 eq.), ^{n}-Bu_4NBF_4 (1.5 eq.), DMF (3.0 mL), undivided cell, constant

current = 5 mA, room temperature, 1.5 h. [b]Degree of deuteration. [c]Isolated yield in parentheses.

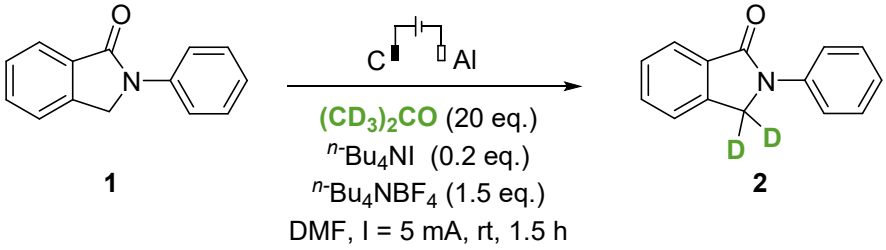
Scheme S1: Peak fitting function analyzing the ratio of CD_2/CDH/CH_2.

Peak fitting function in Mestrenova software was adopted to analyzed the residue ^{1}H signal around 4.81 ppm. It was found that the residue benzylic hydrogen in product **2a** exists in the major form of Ar-CDH (triplet). Another existence is the Ar-CH_2 (single). By the analysis of the peak area of Ar-CDH (consisting 2*a1 + a2) and Ar-CH_2 (consisting b1), it was deduced the ratio to be 6.5:1. Take the overall peak area 0.08 (0 for Ar-CD_2, and 2.0 for Ar-CH_2) in account, the ratio of Ar-CD_2/Ar-CDH/Ar-CH_2 was 93:6:1.



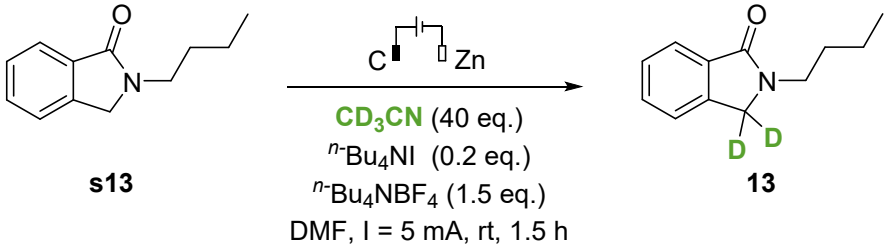
IV. Experimental Procedures and Compound Characterization

General procedure for electrochemical deuteration of isolindolinoes (Procedure A):



A 10 mL distillation flask equipped with a magnetic stir bar was charged with compound **1** (42 mg, 0.2 mmol, 1.0 eq.), $(CD_3)_2CO$ (0.3 mL, 20 eq.), ^{n}-Bu_4NI (15 mg, 0.04 mmol), ^{n}-Bu_4NBF_4 (99 mg, 0.3 mmol, 1.5 eq.) and DMF (3.0 mL). The flask equipped with graphite rod anode (d = 5 mm) and aluminium rod cathode (d = 5 mm). The resulting solution was stirred and electrolyzed at a constant current of 5 mA (Single Output DC Power Supply: KRP-305DM) for 1.5 h at room temperature. The solution was diluted with EtOAc (5 mL) and brine (20 mL), and extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine (3 × 20 mL), dried over Na_2SO_4, and concentrated *in vacuo*. Purification by flash column chromatography using PE/EtOAc (v/v = 10/1) as eluent afforded the desired product **2**

(Procedure B):

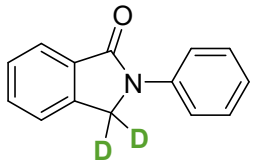


A 10 mL distillation flask equipped with a magnetic stir bar was charged with compound **s13** (38 mg, 0.2 mmol, 1.0 eq.), CD_3CN (0.43 mL, 40 eq.), ^{n}-Bu_4NI (15 mg, 0.04 mmol), ^{n}-Bu_4NBF_4 (99 mg, 0.3 mmol, 1.5 eq.) and DMF (3.0 mL). The flask equipped with graphite rod anode (d = 5 mm) and znic rod cathode (d = 5 mm). The resulting solution was stirred and electrolyzed at a constant current of 5 mA (Single Output DC Power Supply: KRP-305DM) for 1.5 h at room temperature. The solution

was diluted with EtOAc (5 mL) and brine (20 mL), and extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine (3 × 20 mL), dried over Na_2SO_4, and concentrated *in vacuo*. Purification by flash column chromatography using PE/EtOAc (v/v = 10/1) as eluent afforded the desired product **13**.

2-Phenylisoindolin-1-one-3,3-*d*$_2$ (2)

Following Procedure A.



2

White solid (34 mg, 81% yield, 96% D); m.p. 161 – 163 °C;

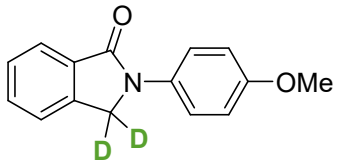
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.95 – 7.89 (m, 1H), 7.89 – 7.82 (m, 2H), 7.63 – 7.55 (m, 1H), 7.54 – 7.47 (m, 2H), 7.46 – 7.38 (m, 2H), 7.22 – 7.13 (m, 1H), 4.85 – 4.82 (s, 0.08H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 167.4, 139.9, 139.4, 133.1, 131.9, 129.0, 128.2, 124.2, 123.9, 122.5, 119.2, 50.5 – 49.6 (m).

HRMS (ESI): Calcd. for $C_{14}H_{10}D_2NO^+$ $[M + H]^+$: 212.1039, found: 212.1037.

2-(4-Meoxyphenyl)isoindolin-1-one-3,3-*d*$_2$ (3)

Following Procedure A, using 2.0 h instead of 1.5 h.



3

White solid (35 mg, 73% yield, 95% D); m.p. 147 – 149 °C;

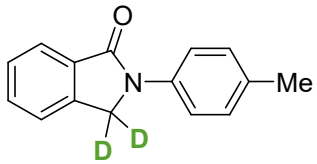
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.94 – 7.84 (m, 1H), 7.78 – 7.66 (m, 2H), 7.62 – 7.49 (m, 1H), 7.54 – 7.42 (m, H), 6.99 – 6.87 (m, 2H), 4.75 (s, 0.10H), 3.80 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 167.0, 156.3, 139.9, 133.1, 132.5, 131.6, 128.0, 123.6, 122.4, 121.0, 114.0, 55.2, 51.2 – 49.9 (m).

HRMS (ESI): Calcd. for $C_{15}H_{12}D_2NO_2^+$ $[M + H]^+$: 242.1145, found: 242.1156.

2-(*p*-Tolyl)isoindolin-1-one-3,3-d_2 (4)

Following Procedure A.



4

White solid (36 mg, 80% yield, 95% D); m.p. 128 – 130 °C;

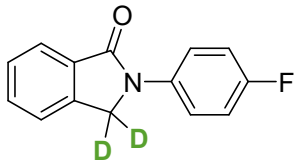
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.96 – 7.88 (m, 1H), 7.77 – 7.70 (m, 2H), 7.59 (ddd, *J* = 7.7, 7.0, 1.3 Hz, 1H), 7.54 – 7.46 (m, 2H), 7.26 – 7.19 (m, 2H), 4.81 (s, 0.10H), 2.35 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 167.2, 139.9, 136.8, 133.8, 133.2, 131.7, 129.4, 128.1, 123.7, 122.4, 119.2, 50.6 – 50.0 (m), 20.7.

HRMS (ESI): Calcd. for $C_{15}H_{12}D_2NO^+$ $[M + H]^+$: 226.1195, found: 226.1190.

2-(4-Fluorophenyl)isoindolin-1-one-3,3-d_2 (5)

Following Procedure A.



5

White solid (38 mg, 82% yield, 96% D); m.p. 172 – 174 °C;

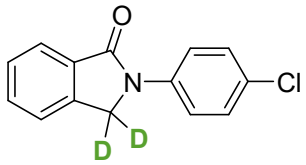
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.95 – 7.87 (m, 1H), 7.86 – 7.75 (m, 2H), 7.63 – 7.55 (m, 1H), 7.54 – 7.42 (m, 2H), 7.15 – 6.95 (m, 2H), 4.80 (s, 0.08H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 167.3, 161.0, 157.7, 139.8, 135.5, 135.5, 132.9, 132.0, 128.3, 123.9, 122.6, 121.0, 115.8, 115.5, 50.8 – 50.2 (m).

HRMS (ESI): Calcd. for $C_{14}H_9D_2FNO^+$ $[M + H]^+$: 230.0945, found: 230.0942.

2-(4-Chlorophenyl)isoindolin-1-one-3,3-d_2 (6)

Following Procedure A.



6

White solid (37 mg, 75% yield, 95% D); m.p. 184 – 186 °C;

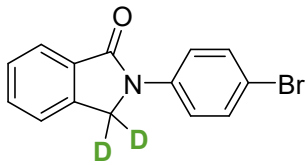
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91 – 7.85 (m, 1H), 7.84 – 7.76 (m, 2H), 7.64 – 7.55 (m, 1H), 7.53 – 7.44 (m, 2H), 7.37 – 7.30 (m, 2H), 4.78 (s, 0.10H).

^{13}C NMR (75 MHz, $CDCl_3$):δ 167.4, 139.7, 138.0, 132.8, 132.2, 129.3, 129.0, 128.4, 124.0, 122.6, 120.2, 50.5 – 49.4 (m).

HRMS (ESI): Calcd. for $C_{14}H_9D_2ClNO^+$ $[M + H]^+$: 246.0649, found: 246.0650.

2-(4-Bromophenyl)isoindolin-1-one-3,3-*d*$_2$ (7)

Following Procedure A, using ^{n}-Bu_4NI (3.0 eq.) instead of ^{n}-Bu_4NI (0.2 eq.), using 1.0 h instead of 1.5 h.



7

White solid (41 mg, 70% yield, 95% D); m.p. 188 – 189 °C;

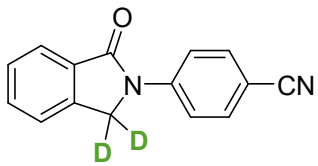
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.94 – 7.86 (m, 1H), 7.81 – 7.73 (m, 2H), 7.60 (m, 1H), 7.54 – 7.46 (m, 4H), 4.79 (s, 0.10H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 167.4, 139.7, 138.5, 132.8, 132.2, 132.0, 128.4, 124.0, 122.6, 120.4, 117.0, 50.5 – 49.8 (m).

HRMS (ESI): Calcd. for $C_{14}H_9D_2BrNO^+$ $[M + H]^+$: 290.0144, found: 290.0133.

4-(1-Oxoisoindolin-2-yl-3,3-*d*$_2$)benzonitrile (8)

Following Procedure A.



8

White solid (33 mg, 70% yield, 95% D); m.p. 207 – 209 °C;

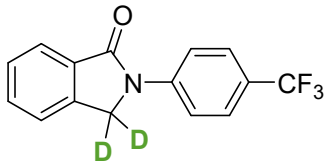
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.06 – 7.97 (m, 2H), 7.93 – 7.85 (m, 1H), 7.70 – 7.58 (m, 3H), 7.56 – 7.47 (m, 2H), 4.83 (s, 0.10H).

^{13}C NMR (75 MHz, DMSO-d_6): δ167.3, 143.3, 140.9, 133.2, 132.9, 131.8, 128.3, 123.5, 123.4, 118.9, 118.7, 105.5, 50.2 – 48.6 (m).

HRMS (ESI): Calcd. for $C_{15}H_9D_2N_2O^+$ $[M + H]^+$: 237.0991, found: 237.0983.

2-(4-(Trifluoromethyl)phenyl)isoindolin-1-one-3,3-d_2 (9)

Following Procedure A, using 3.5 h instead of 1.5 h.



9

White solid (34 mg, 61% yield, 91% D); m.p. 233 – 235 °C;

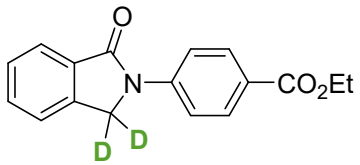
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.03 (d, J = 8.5 Hz, 2H), 7.92 (d, J = 7.5 Hz, 1H), 7.73 – 7.59 (m, 3H), 7.54 (d, J = 7.5 Hz, 2H), 4.88 (s, 0.18H).

^{13}C NMR (75 MHz, $(CD_3)_2CO$): δ 174.3, 145.7, 141.0, 133.5, 129.2, 129.0, 127.2 – 127.0 (m),126.9, 124.5, 124.2 – 124.0 (m), 122.7, 120.0, 60.6 – 60.4(m).

HRMS (ESI): Calcd. for $C_{15}H_9D_2F_3NO^+$ $[M + H]^+$: 280.0913, found: 280.0918.

Ethyl 4-(1-oxoisoindolin-2-yl)benzoate-3,3-d_2 (10)

Following Procedure A.



10

White solid (40 mg, 71% yield, 95% D); m.p. 180 – 181 °C;

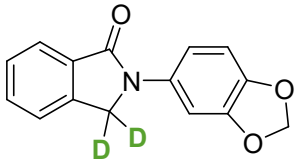
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.09 – 8.01 (m, 2H), 7.98 – 7.91 (m, 2H), 7.90 – 7.85 (m, 1H), 7.63 – 7.54 (m, 1H), 7.52 – 7.44 (m, 2H), 4.81 (s, 0.10H), 4.36 (t, J = 7.1 Hz, 2H), 1.39 (t, J = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 167.7, 166.0, 143.3, 139.8, 132.7, 132.5, 131.4, 130.6, 128.4, 125.6, 124.1, 122.6, 117.7, 113.6, 60.7, 58.2 – 57.51 (m), 14.3.

HRMS (ESI): Calcd. for $C_{17}H_{14}D_2NO_3^+$ $[M + H]^+$: 284.1250, found: 284.1244.

2-(Benzo[*d*][1,3]dioxol-5-yl)isoindolin-1-one-3,3-d_2 (11)

Following Procedure A.



11

White solid (26 mg, 50% yield, 92% D); m.p. 167 – 169 °C;

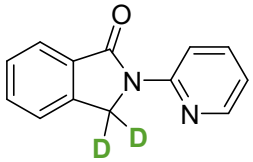
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.94 – 7.79 (m, 1H), 7.63 – 7.54 (m, 2H), 7.52 – 7.46 (m, 2H), 7.08 (dd, *J* = 8.4, 2.3 Hz, 1H), 6.83 (dd, *J* = 8.4, 0.4 Hz, 1H), 5.97 (s, 2H), 4.78 (s, 0.10H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 167.2, 147.9, 144.3, 139.8, 133.8, 133.1, 131.8, 128.2, 123.8, 122.5, 112.5, 108.0, 102.3, 101.3, 51.3 – 50.6 (m).

HRMS (ESI): Calcd. for $C_{15}H_{10}D_2NO_3^+$ $[M + H]^+$: 256.0937, found: 256.0936.

2-(Pyridin-2-yl)isoindolin-1-one-3,3-d_2 (12)

Following Procedure A, using 3.5 h instead of 1.5 h.



12

White solid (35 mg, 83% yield, 94% D); m.p. 177 – 179 °C;

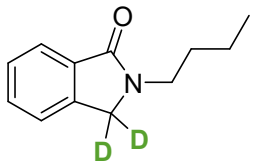
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.65 (dt, *J* = 8.5, 1.0 Hz, 1H), 8.37 (ddd, *J* = 4.9, 2.0, 1.0 Hz, 1H), 7.91 (dt, *J* = 7.6, 1.0 Hz, 1H), 7.73 (ddd, *J* = 8.5, 7.3, 2.0 Hz, 1H), 7.65 – 7.43 (m, 3H), 7.04 (ddd, *J* = 7.3, 4.9, 1.0 Hz, 1H), 5.06 (s, 0.12H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 167.7, 151.8, 147.6, 140.8, 137.8, 132.9, 132.4, 128.1, 124.0, 122.9, 119.3, 114.0, 49.7 – 49.2 (m).

HRMS (ESI): Calcd. for $C_{13}H_9D_2N_2O^+$ $[M + H]^+$: 213.0991, found: 213.0996.

2-Butylisoindolin-1-one-3,3-d_2 (13)

Following Procedure B.



13

Colourless liquid (34 mg, 89% yield, 96% D);

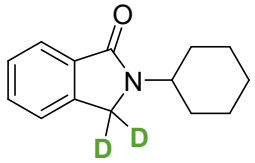
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.85 – 7.74 (m, 1H), 7.55 – 7.35 (m, 3H), 4.32 (s, 0.08H), 3.73 – 3.47 (m, 2H), 1.69 – 1.51 (m, 2H), 1.47 – 1.18 (m, 2H), 0.93 (t, J = 7.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 168.3, 140.8, 132.9, 130.9, 127.7, 123.3, 122.5, 49.7 – 49.1 (m), 41.8, 30.3, 19.8, 13.6.

HRMS (ESI): Calcd. for $C_{12}H_{14}D_2NO^+$ $[M + H]^+$: 192.1352, found: 192.1351.

2-Cyclohexylisoindolin-1-one-3,3-d_2 (14)

Following Procedure B, using 3.0 h instead of 1.5 h.



14

Colourless liquid (38 mg, 88% yield, 95% D);

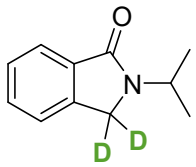
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90 – 7.72 (m, 1H), 7.57 – 7.38 (m, 3H), 4.31 (s, 0.10H), 4.23 (tt, J = 11.8, 3.3 Hz, 1H), 1.91 – 1.79 (m, 4H), 1.71 (m, 1H), 1.56 – 1.33 (m, 4H), 1.28 – 1.04 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 167.5, 140.9, 133.0, 130.6, 127.5, 123.0, 122.4, 50.15, 45.6 – 45.1 (m), 31.0, 25.2, 25.1.

HRMS (ESI): Calcd. for $C_{14}H_{16}D_2NO^+$ $[M + H]^+$: 218.1508, found: 218.1509.

2-Isopropylisoindolin-1-one-3,3-d_2 (15)

Following Procedure B.



15

Colourless liquid (27 mg, 77% yield, 97% D);

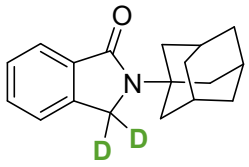
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.88 – 7.76 (m, 1H), 7.61 – 7.34 (m, 3H), 4.66 (pd, *J* = 6.8, 0.6 Hz, 1H), 4.30 (s, 0.06H), 1.27 (dd, *J* = 6.8, 0.6 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 167.5, 140.8, 133.1, 130.7, 127.6, 123.1, 122.5, 44.4 – 43.8 (m), 42.3, 20.5.

HRMS (ESI): Calcd. for $C_{11}H_{12}D_2NO^+$ $[M + H]^+$: 178.1195, found: 178.1195.

2-(Adamantan-1-yl)isoindolin-1-one-3,3-*d*$_2$ (16)

Following Procedure B, using 0.1 mmol substrate instead of 0.2 mmol, using 1.25 h instead of 1.5 h.



16

White solid (20 mg, 74% yield, 95% D); m.p. 202.5 – 205 °C;

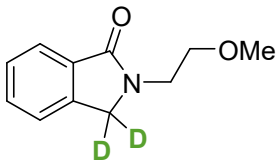
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.78 (dt, *J* = 7.3, 1.2 Hz, 1H), 7.53 – 7.35 (m, 3H), 4.46 (s, 0.10H), 2.30 (d, *J* = 3.0 Hz, 6H), 2.21 – 2.11 (m, 3H), 1.83 – 1.63 (m, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 168.6, 140.7, 134.6, 130.6, 127.6, 122.9, 122.2, 55.29, 47.5 – 46.7 (m), 39.9, 36.2, 29.5.

HRMS (ESI): Calcd. for $C_{18}H_{20}D_2NO^+$ $[M + H]^+$: 270.1821, found: 270.1824.

2-(2-Methoxyethyl)isoindolin-1-one-3,3-*d*$_2$ (17)

Following Procedure B.



17

Colourless liquid (30 mg, 78% yield, 97% D);

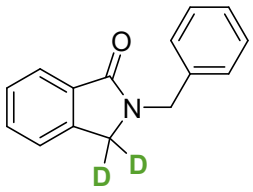
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.83 (dtd, *J* = 7.4, 1.3, 0.5 Hz, 1H), 7.55 – 7.47 (m, 1H), 7.46 – 7.38 (m, 2H), 4.48 (s, 0.06H), 3.81 – 3.72 (m, 2H), 3.62 (dd, *J* = 5.6, 4.5 Hz, 2H), 3.34 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 168.4, 141.4, 132.6, 131.0, 127.6, 123.3, 122.5, 77.4, 58.51, 51.4 – 50.2 (m), 42.1.

HRMS (ESI): Calcd. for $C_{11}H_{12}D_2NO_2^+$ $[M + H]^+$: 194.1145, found: 194.1145.

2-Benzylisoindolin-1-one-3,3-*d*$_2$ (18)

Following Procedure B, using 3.0 h instead of 1.5 h.



18

White solid (34 mg, 76% yield, 96% D); m.p. 88 – 89 °C;

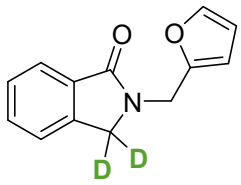
^{1}H NMR (300 MHz, $CDCl_3$): 7.90 – 7.82 (m, 1H), 7.53 – 7.38 (m, 2H), 7.37 – 7.21 (m, 6H), 4.77 (s, 2H), 4.22 (s, 0.08H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 168.3, 141.0, 136.9, 132.5, 131.2, 128.6, 127.9, 127.9, 127.5, 123.6, 122.6, 49.9 – 48.2 (m), 46.2.

HRMS (ESI): Calcd. for $C_{15}H_{12}D_2NO^+$ $[M + H]^+$: 226.1195, found: 226.1200.

2-(Furan-2-ylmethyl)isoindolin-1-one-3,3-*d*$_2$ (19)

Following Procedure B.



19

Yellow liquid (35 mg, 81% yield, 95% D);

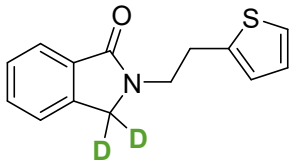
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.85 (ddd, *J* = 7.3, 1.4, 1.0 Hz, 1H), 7.56 – 7.37 (m, 3H), 7.35 (dd, *J* = 1.7, 1.0 Hz, 1H), 6.31 (t, *J* = 1.5 Hz, 2H), 4.78 (s, 2H), 4.35 (s, 0.10H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 168.0, 150.2, 142.3, 141.0, 132.3, 131.2, 127.8, 123.6, 122.6, 110.3, 108.3, 50.3 – 47.8 (m), 38.8.

HRMS (ESI): Calcd. for $C_{13}H_{10}D_2NO_2^+$ $[M + H]^+$: 216.0988, found: 216.0993.

2-(2-(Thiophen-2-yl)ethyl)isoindolin-1-one-3,3-*d*$_2$ (20)

Following Procedure B, using 1.0 h instead of 1.5 h.



20

White solid (43.1 mg, 88% yield, 95% D); m.p. 102 – 104 °C;

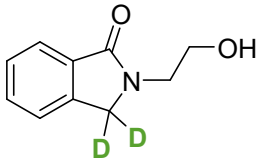
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.84 (d, *J* = 9 Hz, 1H), 7.56 – 7.33 (m, 3H), 7.13 (dt, *J* = 5.1, 1.0 Hz, 1H), 6.94 – 6.87 (m, 1H), 6.84 (dt, *J* = 3.1, 1.0 Hz, 1H), 4.22 (s, 0.10H), 4.02 – 3.65 (m, 2H), 3.21 (td, *J* = 7.0, 0.9 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 168.4, 141.0, 140.9, 132.6, 131.1, 127.8, 126.9, 125.2, 123.8, 123.4, 122.5, 52.1 – 48.7 (m), 44.1, 28.8.

HRMS (ESI): Calcd. for $C_{14}H_{12}D_2NOS^+$ $[M + H]^+$: 246.0916, found: 246.0922.

2-(2-Hydroxyethyl)isoindolin-1-one-3,3-*d*$_2$ (21)

Following Procedure B, using 3.0 h instead of 1.5 h.



21

White solid (25 mg, 70% yield, 95% D); m.p. 114 – 115 °C;

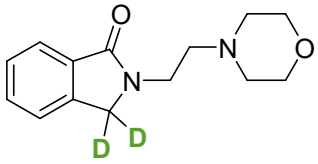
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.79 (dq, *J* = 7.4, 1.1 Hz, 1H), 7.56 – 7.47 (m, 1H), 7.45 – 7.37 (m, 2H), 4.48 (s, 0.10H), 3.94 – 3.84 (m, 2H), 3.80 – 3.69 (m, 2H), 3.45 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 169.5, 141.5, 132.5, 131.3, 127.9, 123.4, 122.7, 61.1, 51.8 – 50.7 (m), 45.7.

HRMS (ESI): Calcd. for $C_{10}H_{10}D_2NO_2^+$ $[M + H]^+$: 180.0988, found: 180.0982.

2-(2-Morpholinoethyl)isoindolin-1-one-3,3-d_2 (22)

Following Procedure B, using 1.25 h instead of 1.5 h.



22

Colourless liquid (37 mg, 75% yield, 97% D);

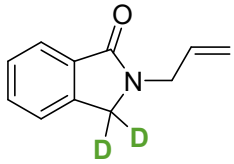
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.97 – 7.71 (m, 1H), 7.59 – 7.42 (m, 3H), 4.48 (s, 0.06H), 3.87 – 3.57 (m, 6H), 2.63 (t, J = 6.4 Hz, 2H), 2.51 (dd, J = 5.7, 3.7 Hz, 4H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 168.4, 141.2, 132.8, 131.1, 127.8, 123.5, 122.6, 66.8, 56.9, 53.5, 50.7 – 49.7 (m), 39.0.

HRMS (ESI): Calcd. for $C_{14}H_{17}D_2N_2O_2^+$ $[M + H]^+$: 249.1567, found: 249.1575.

2-Allylisoindolin-1-one-3,3-d_2 (23)

Following Procedure B, using 2.0 h instead of 1.5 h.



23

Colourless liquid (25 mg, 70% yield, 94% D);

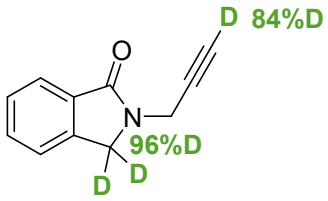
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.84 (dt, J = 7.3, 1.2 Hz, 1H), 7.57 – 7.38 (m, 3H), 5.85 (ddt, J = 17.4, 9.8, 6.0 Hz, 1H), 5.24 (m, 1H), 5.19 (t, J = 1.4 Hz, 1H), 4.33 (s, 0.12H), 4.22 (dt, J = 6.0, 1.4 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 168.0, 140.9, 132.8, 132.5, 131.1, 127.7, 123.4, 122.6, 117.6, 49.30 – 48.7 (m), 44.7.

HRMS (ESI): Calcd. for $C_{11}H_{10}D_2NO^+$ $[M + H]^+$: 176.1039, found: 176.1041.

2-(Prop-2-yn-1-yl-3-*d*)isoindolin-1-one-3,3-d_2 (24)

Following Procedure B.



24

Colourless liquid (25 mg, 29% yield);

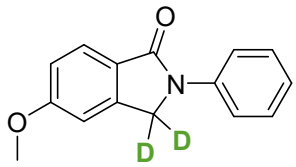
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.02 – 7.64 (m, 1H), 7.61 – 7.41 (m, 3H), 4.80 (s, 0.08H), 4.45 (s, 2H), 2.29 (s, 0.16H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 168.1, 141.2, 132.2, 131.7, 128.2, 123.9, 123.0, 77.4, 72.7-72.5 (m), 49.3 – 48.4 (m), 31.8.

HRMS (ESI): Calcd. for $C_{11}H_7D_3NO^+$ $[M + H]^+$: 175.0945, found: 175.0945.

5-Methoxy-2-phenylisoindolin-1-one-3,3-*d*$_2$ (25)

Following Procedure A, using 2.5 h instead of 1.5 h.



25

White solid (34 mg, 70% yield, 95% D); m.p. 144 – 146 °C;

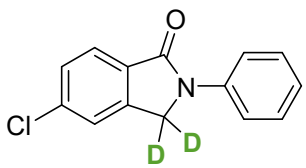
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.88 – 7.75 (m, 3H), 7.42 (dd, *J* = 8.7, 7.4 Hz, 2H), 7.20 – 7.10 (m, 1H), 7.07 – 6.95 (m, 2H), 4.80 (s, 0.10H), 3.90 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 167.5, 163.3, 142.4, 139.8, 129.2, 125.9, 125.6, 124.1, 119.2, 115.2, 107.4, 55.79, 50.5 – 49.0 (m).

HRMS (ESI): Calcd. for $C_{15}H_{12}D_2NO_2^+$ $[M + H]^+$: 242.1145, found: 242.1145.

5-Chloro-2-phenylisoindolin-1-one-3,3-*d*$_2$ (26)

Following Procedure A, using 3.0 h instead of 1.5 h.



26

yellow solid (35 mg, 71% yield, 93% D); m.p. 156 – 158 °C;

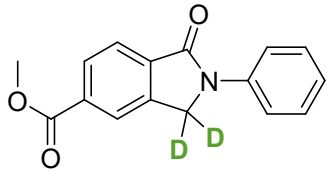
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.95 – 7.72 (m, 3H), 7.54 – 7.47 (m, 2H), 7.43 (dd, *J* = 8.7, 7.3 Hz, 2H), 7.23 – 7.16 (m, 1H), 4.84 (s, 0.14H).

^{13}C NMR (75 MHz, DMSO - d_6): δ 165.7, 143.0, 139.2, 137.0, 129.0, 128.6, 128.2, 125.0, 124.3, 123.6, 119.3, 50.2 – 49.2(m).

HRMS (ESI): Calcd. for $C_{14}H_9D_2ClNO^+$ $[M + H]^+$: 246.0649, found: 246.0654.

3-(Benzo[*d*][1,3]dioxol-5-yl)-*N*-ethyl-*N*-phenylpropanamide-2,2-d_2 (27)

Following Procedure A, using 0.1 mmol instead of 0.2 mmol, using 50 °C instead of rt.



27

White solid (27 mg, 50% yield, 95% D); m.p. 142 – 145 °C;

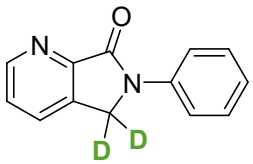
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.20 (d, *J* = 7.8 Hz, 2H), 7.99 (d, *J* = 8.3 Hz, 1H), 7.92 – 7.82 (d, *J* = 8.3 Hz, 2H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.30 – 7.11 (m, 1H), 4.91 (s, 0.10H), 3.98 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 166.6, 166.5, 140.0, 139.3, 137.3, 135.1, 133.7, 130.0, 129.4, 125.1, 124.3, 119.7, 52.7, 52.3 – 51.9 (m).

HRMS (ESI): Calcd. for $C_{16}H_{12}D_2NO_3^+$ $[M + H]^+$: 270.1094, found: 270.1088.

6-Phenyl-5,6-dihydro-7*H*-pyrrolo[3,4-*b*]pyridin-7-one-5,5-d_2 (28)

Following Procedure A.



28

Yellow solid (25 mg, 60% yield, 95% D); m.p. 193 – 195 °C;

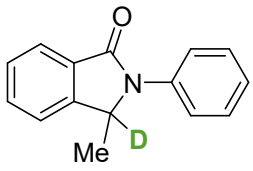
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.79 (dd, *J* = 4.8, 1.5 Hz, 1H), 7.99 – 7.83 (m, 3H), 7.61 – 7.38 (m, 3H), 7.19 (ddt, *J* = 8.7, 7.5, 1.2 Hz, 1H), 4.85 (s, 0.10H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 165.2, 151.1, 150.5, 138.9, 134.1, 131.3, 129.1, 125.7, 124.9, 119.3, 48.7 – 47.4 (m).

HRMS (ESI): Calcd. for $C_{13}H_9D_2N_2O^+$ $[M + H]^+$: 213.0991, found: 213.0994.

3-Methyl-2-phenylisoindolin-1-one-3-*d* (29)

Following Procedure A, using 6.0 h instead of 1.5 h.



29

Yellow liquid (36 mg, 80% yield, 93% D);

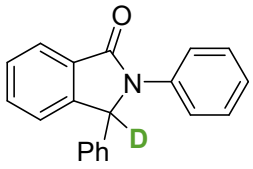
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.93 (dt, *J* = 7.5, 1.1 Hz, 1H), 7.66 – 7.56 (m, 3H), 7.55 – 7.40 (m, 4H), 7.27 – 7.20 (m, 1H), 5.21 (q, *J* = 6.7 Hz, 0.10H), 1.45 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 166.9, 146.2, 137.0, 132.0, 131.7, 129.0, 128.3, 125.3, 124.0, 123.3, 122.0, 56.8 – 56.2 (m), 18.6.

HRMS (ESI): Calcd. for $C_{15}H_{13}DNO^+$ $[M + H]^+$: 225.1133, found: 225.1142.

2,3-Diphenylisoindolin-1-one-3-*d* (30)

Following Procedure A, using 3.0 h instead of 1.5 h.



30

White solid (44 mg, 77% yield, 95% D); m.p. 198 – 199 °C;

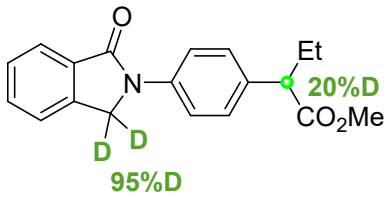
^{1}H NMR (300 MHz, $CDCl_3$):δ 8.02 – 7.93 (m, 1H), 7.68 – 7.59 (m, 2H), 7.57 – 7.45 (m, 2H), 7.36 – 7.18 (m, 8H), 7.10 (td, *J* = 7.3, 1.1 Hz, 1H), 6.10 (s, 0.05H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 167.9, 145.6, 137.6, 137.5, 132.4, 131.1, 129.1, 128.8, 128.5, 128.3, 126.8, 124.9, 124.0, 123.0, 122.4, 65.5 – 64.9 (m).

HRMS (ESI): Calcd. for $C_{20}H_{15}DNO^+$ $[M + H]^+$: 287.1289, found: 287.1300.

Methyl 2-(4-(1-oxoisoindolin-2-yl-3,3-*d*$_2$)phenyl)butanoate (31)

Following Procedure A.



31

Colourless liquid (50 mg, 80% yield);

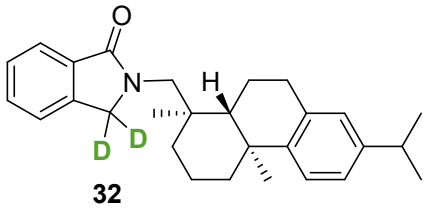
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.89 (dt, *J* = 7.4, 1.2 Hz, 1H), 7.85 – 7.78 (m, 2H), 7.61 – 7.53 (m, 1H), 7.52 – 7.43 (m, 2H), 7.39 – 7.31 (m, 2H), 4.81 (s, 0.10H), 3.66 (s, 3H), 3.46 (t, *J* = 7.7 Hz, 0.8H), 2.10 (ddd, *J* = 13.6, 7.7, 7.4 Hz, 1H), 1.82 (dq, *J* = 13.6, 7.4 Hz, 1H), 0.90 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 174.2, 167.3, 139.8, 138.4, 134.9, 133.0, 131.9, 128.5, 128.2, 123.8, 122.5, 119.3, 52.6, 51.7, 50.5 – 49.9 (m), 26.5, 12.0.

HRMS (ESI): Calcd. for $C_{19}H_{18}D_2NO_3^+$ $[M + H]^+$: 312.1563, found: 312.1552.

2-(((1*R*,4a*S*,10a*R*)-7-Isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)isoindolin-1-one-3,3-*d*$_2$ (32)

Following Procedure B, using 1.25 h instead of 1.5 h.



32

Yellow liquid (65 mg, 81% yield, 96% D);

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.88 – 7.78 (m, 1H), 7.56 – 7.33 (m, 3H), 7.16 (d, *J* = 8.2 Hz, 1H), 6.99 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.91 (d, *J* = 2.1 Hz, 1H), 4.66 – 4.37 (s, 0.08H), 3.49 (d, *J* = 2.8 Hz, 2H), 3.09 – 2.70 (m, 3H), 2.29 (d, *J* = 13.0 Hz, 1H), 2.13 (d, *J* = 6.5 Hz, 1H), 1.97 – 1.65 (m, 3H), 1.59 (q, *J* = 2.8, 2.3 Hz, 2H), 1.56 – 1.52 (m, 1H), 1.40 (dd, *J* = 17.6, 5.0 Hz, 1H), 1.24 (d, *J* = 4.4 Hz, 6H), 1.21 (s, 3H), 1.07 (s, 3H).

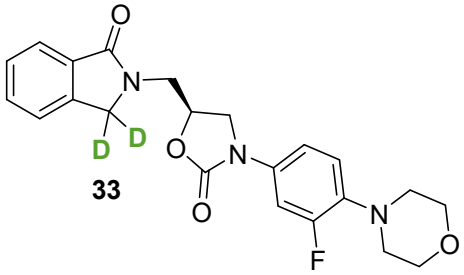
^{13}C NMR (75 MHz, $CDCl_3$): δ 169.9, 147.1, 145.4, 141.2, 134.4, 132.4, 131.1, 127.8, 126.8, 126.7, 123.9, 123.7, 123.5, 122.3, 54.8, 53.0 – 53.8 (m) 45.3, 39.4, 38.1, 37.4, 37.3, 33.3, 30.0, 25.5, 23.8, 23.8, 19.1, 19.0, 18.6.

HRMS (ESI): Calcd. for $C_{28}H_{34}D_2NO^+$ $[M + H]^+$: 404.2917, found: 404.2928.

(*S*)-3-(3-Fluoro-4-morpholinophenyl)-5-((1-oxoisoindolin-2-yl-3,3-

d_2)methyl)oxazolidin-2-one (33)

Following Procedure A, using 0.1 mmol instead of 0.2 mmol, using 50 °C instead of rt, using 3.0 h instead of 1.5 h.



33

White solid (25 mg, 60% yield, 95% D); m.p. 235 – 237 °C;

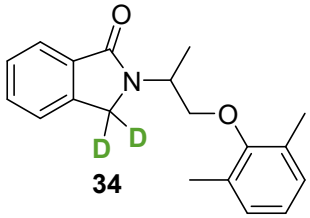
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.87 – 7.81 (m, 1H), 7.61 – 7.53 (m, 1H), 7.51 – 7.45 (m, 2H), 7.41 (dd, *J* = 14.3, 2.6 Hz, 1H), 7.06 (ddd, *J* = 8.8, 2.6, 1.1 Hz, 1H), 6.90 (d, *J* = 8.8 Hz, 1H), 5.05 – 4.84 (m, 1H), 4.60 (s, 0.10H), 4.16 – 4.00 (m, 2H), 3.97 – 3.77 (m, 6H), 3.07 – 2.89 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 169.4, 162.4, 156.8, 154.0, 153.5, 141.5, 136.1, 132.9, 131.7, 131.4, 127.9, 123.4, 122.7, 118.6, 113.8, 72.1, 66.6, 50.7, 49.8 – 49.1 (m), 47.7, 45.3.

HRMS (ESI): Calcd. for $C_{22}H_{21}D_2FN_3O_4^+$ $[M + H]^+$: 414.1793, found: 414.1784.

2-(1-(2,6-Dimethylphenoxy)propan-2-yl)isoindolin-1-one-3,3-d_2 (34)

Following Procedure B, using 10 mA instead of 5 mA.



34

Colourless liquid (48.1 mg, 81% yield, 95% D);

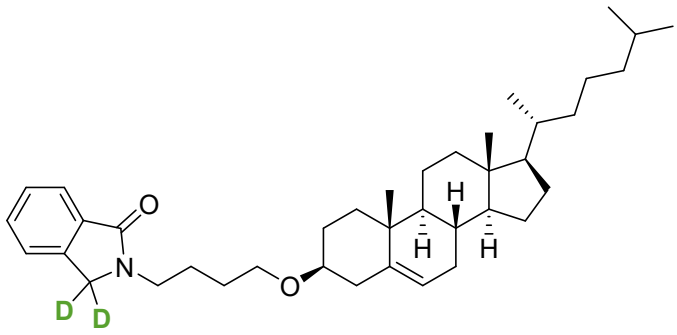
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.94 – 7.84 (m, 1H), 7.58 – 7.51 (m, 1H), 7.47 (m, 2H), 6.97 (ddd, *J* = 7.0, 1.6, 0.6 Hz, 2H), 6.92 – 6.86 (m, 1H), 4.83 (tdd, *J* = 7.1, 4.6, 2.5 Hz, 1H), 4.53 (s, 0.10H), 3.95 (h, *J* = 4.6 Hz, 2H), 2.20 – 2.13 (m, 6H), 1.56 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 168.5, 155.1, 141.5, 133.0, 131.2, 130.6, 128.9, 127.9, 124.0, 124.0, 123.5, 122.7, 73.9, 47.4, 46.9 – 46.3 (m), 16.1, 15.4.

HRMS (ESI): Calcd. for $C_{19}H_{20}D_2NO_2^+$ [M + H]$^+$: 298.1771, found: 298.1777.

2-(4-(((3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)butyl)isoindolin-1-one-3,3-d_2 (35)

Following Procedure B, using 2.0 h instead of 1.5 h.



35

Colourless liquid (95 mg, 82% yield, 97% D);

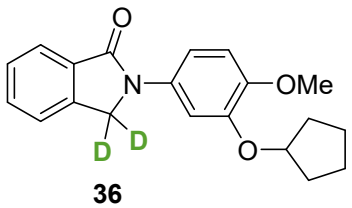
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.85 – 7.76 (m, 1H), 7.52 – 7.45 (m, 1H), 7.41 (m, 2H), 5.30 (m, 1H), 4.36 (s, 0.06H), 3.62 (t, *J* = 7.2 Hz, 2H), 3.48 (t, *J* = 7.2 Hz, 2H), 3.10 (m, 1H), 2.32 (m, 1H), 2.24 – 2.08 (m, 1H), 1.98 (m, 2H), 1.93 – 1.67 (m, 5H), 1.65 – 1.05 (m, 21H), 0.96 (s, 4H), 0.89 (d, *J* = 6.4 Hz, 4H), 0.84 (dd, *J* = 6.4, 1.3 Hz, 6H), 0.65 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 168.6, 141.2, 141.1, 133.2, 131.2, 128.1, 123.7, 122.7, 121.6, 79.1, 67.4, 56.9, 56.3, 50.3, 50.1 – 49.9 (m), 42.4, 42.2, 39.9, 39.6, 39.3, 37.3, 37.0, 36.3, 35.9, 32.0, 28.6, 28.3, 28.1, 27.5, 25.4, 24.4, 23.9, 22.9, 22.7, 21.2, 19.5, 18.8, 12.0.

HRMS (ESI): Calcd. for $C_{39}H_{58}D_2NO_2^+$ [M + H]$^+$: 576.4744, found: 576.4736.

2-(3-(Cyclopentyloxy)-4-methoxyphenyl)isoindolin-1-one-3,3-d_2 (36)

Following Procedure B.



36

White solid (41 mg, 62% yield, 95% D); mp: 137 – 140 °C;

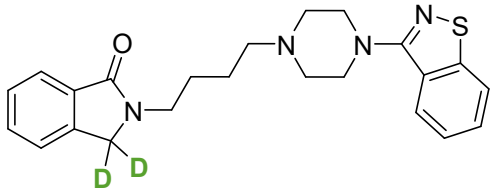
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.94 – 7.78 (m, 2H), 7.62 – 7.53 (m, 1H), 7.52 – 7.44 (m, 1H), 6.99 (dd, *J* = 8.7, 2.6 Hz, 1H), 6.87 (d, *J* = 8.7 Hz, 1H), 4.86 (dt, *J* = 6.3, 3.1 Hz, 1H), 4.78 (s, 0.10H), 3.84 (s, 3H), 2.14 – 1.74 (m, 6H), 1.70 – 1.53 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 167.1, 147.8, 146.8, 139.8, 133.2, 133.0, 131.7, 128.1, 123.6, 122.4, 111.9, 110.6, 107.7, 107.6, 80.4, 56.1, 50.6 – 49.9 (m), 32.7, 24.0.

HRMS (ESI): Calcd. for $C_{20}H_{20}D_2NO_3^+$ $[M + H]^+$: 326.1720, found: 326.1717.

2-(4-(4-(Benzo[*d*]isothiazol-3-yl)piperazin-1-yl)butyl)isoindolin-1-one-3,3-d_2 (37)

Following Procedure B, using 4.0 h instead of 1.5 h.



37

White solid (50 mg, 61% yield, 96% D); mp: 233.2 – 234.8 °C;

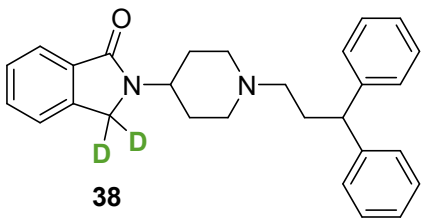
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.87 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.79 (ddt, *J* = 12.9, 8.1, 1.1 Hz, 2H), 7.55 – 7.38 (m, 4H), 7.36 – 7.29 (m, 1H), 4.36 (s, 0.08H), 3.64 (t, *J* = 7.0 Hz, 2H), 3.57 – 3.35 (m, 4H), 2.63 (t, *J* = 4.9 Hz, 4H), 2.45 (t, *J* = 7.0 Hz, 2H), 1.78 – 1.50 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 168.4, 163.7, 152.5, 140.8, 132.8, 131.0, 127.8, 127.3, 123.7, 123.4, 122.5, 120.3, 52.7, 49.7, 49.3 – 48.7 (m), 41.9, 26.1, 23.8.

HRMS (ESI): Calcd. for $C_{23}H_{25}D_2N_4OS^+$ $[M + H]^+$: 409.2026, found: 409.2037.

2-(1-(3,3-Diphenylpropyl)piperidin-4-yl)isoindolin-1-one-3,3-d_2 (38)

Following Procedure B, using 4.0 h instead of 1.5 h.



38

Colourless liquid (41 mg, 50% yield, 97% D);

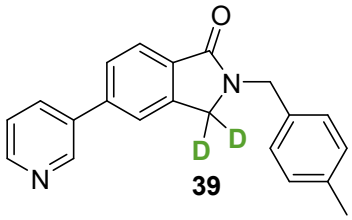
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.88 – 7.81 (m, 1H), 7.62 – 7.41 (m, 4H), 7.35 – 7.23 (m, 8H), 7.18 (m, 2H), 4.45 (s, 0.10H), 4.38 – 4.20 (m, 1H), 3.98 (t, *J* = 7.1 Hz, 1H), 3.01 (m, 2H), 2.46 – 2.23 (m, 4H), 2.19 – 2.07 (m, 2H), 1.89 – 1.72 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 168.2, 144.7, 141.2, 133.2, 131.2, 128.5, 128.0, 127.8, 126.2, 123.6, 122.8, 56.9, 53.0, 49.3, 48.9, 45.9 – 45.1 (m), 33.0, 30.3.

HRMS (ESI): Calcd. for $C_{28}H_{29}D_2N_2O^+$ $[M + H]^+$: 413.2556, found: 413.2558.

2-(4-Methylbenzyl)-5-(pyridin-3-yl)isoindolin-1-one-3,3-*d*$_2$ (39)

Following Procedure B, using 2.0 h instead of 1.5 h.



39

Yellow solid (53 mg, 84% yield, 94% D); mp: 145 – 147 °C;

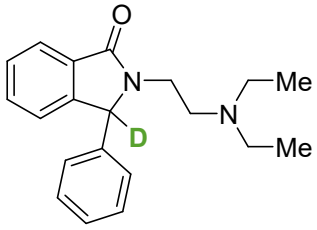
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.81 (d, *J* = 2.4 Hz, 1H), 8.60 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.95 (dd, *J* = 7.9, 0.8 Hz, 1H), 7.85 (dt, *J* = 7.9, 2.0 Hz, 1H), 7.63 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.54 – 7.51 (m, 1H), 7.36 (dd, *J* = 8.1, 4.8 Hz, 1H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 4.76 (s, 2H), 4.29 (s, 0.12H), 2.30 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$,): δ 167.9, 149.0, 148.3, 142.1, 141.0, 137.4, 135.9, 134.6, 133.8, 132.5, 129.4, 128.1, 127.3, 124.4, 123.7, 121.6, 49.3 – 48.1 (m), 46.1, 21.0.

HRMS (ESI): Calcd. for $C_{21}H_{17}D_2N_2O^+$ $[M + H]^+$: 317.1617, found: 317.1624.

2-(2-(Diethylamino)ethyl)-3-phenylisoindolin-1-one-3-*d* (40)

Following Procedure A, using ^{n}-Bu_4NI (1.5 eq.) instead of ^{n}-Bu_4NI (0.2 eq.), using 20 mA instead of 5 mA, using 3.0 h instead of 1.5 h.



40

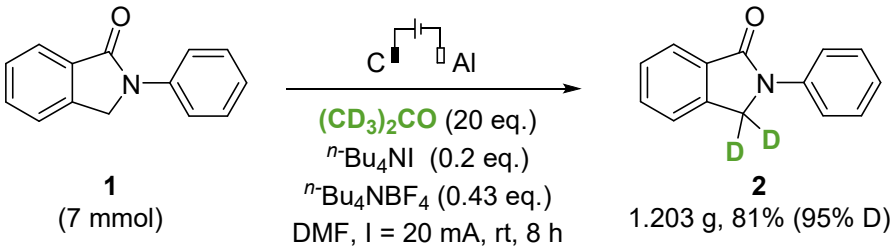
Colourless liquid (19 mg, 30% yield, 90% D);

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.97 – 7.81 (m, 1H), 7.53 – 7.42 (m, 2H), 7.35 (m, 3H), 7.20 – 7.09 (m, 3H), 5.68 (s, 0.10H), 3.95 (m, 1H), 3.17 (m, 1H), 2.85 (dt, *J* = 13.6, 7.1 Hz, 1H), 2.69 (qd, *J* = 7.1, 2.8 Hz, 5H), 1.05 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 169.3, 146.6, 136.8, 132.1, 131.3, 129.3, 128.9, 128.4, 127.8, 123.5, 123.3, 65.6 – 65.0 (m), 50.8, 47.4, 37.8, 10.8.

HRMS (ESI): Calcd. for $C_{20}H_{24}DN_2O^+$ $[M + H]^+$: 310.2024, found: 310.2039.

Procedure for gram-scale experiment (Procedure C):



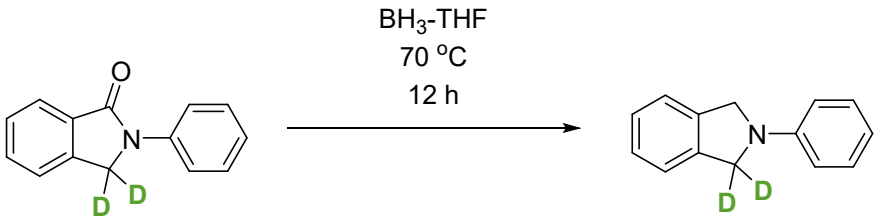
1
(7 mmol)

2
1.203 g, 81% (95% D)

A 50 mL distillation flask equipped with a magnetic stir bar was charged with compound **1** (1.463 g, 7 mmol, 1.0 eq.), $(CD_3)_2CO$ (10.5 mL, 20 eq.), ^{n}-Bu_4NBF_4 (0.988 g, 3 mmol, 0.43 eq.), ^{n}-Bu_4NI (0.517 g, 1.4 mmol, 0.2 eq.) and DMF (30 mL). The flask equipped with graphite rod anode (d = 5 mm) and aluminium rod cathode (d = 5 mm) (the submerged height of the electrode is approximately 2 cm). The resulting solution was stirred and electrolyzed at a constant current of 20 mA (Single Output DC Power Supply: KRP-305DM) for 8 hours at room temperature. The solution was diluted with EtOAc (20 mL) and brine (20 mL), and extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with brine (3 × 50 mL), dried over Na_2SO_4, and concentrated *in vacuo*. Purification by flash column chromatography using PE/EtOAc (v/v = 10/1) as eluent afforded the desired product **2** (1.203 g, 81%, 95%D).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.95 – 7.89 (m, 1H), 7.89 – 7.82 (m, 2H), 7.63 – 7.55 (m, 1H), 7.54 – 7.47 (m, 2H), 7.46 – 7.38 (m, 2H), 7.22 – 7.13 (m, 1H), 4.85 – 4.82 (s, 0.10 H).

Procedure for transformation of isoindolinones:

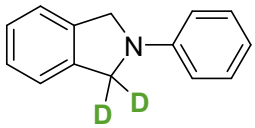


2
2 mmol

41
(80%, 95% D)

A dry 50 mL three-necked bottle flask was charged with BH_3-THF (12 mL, 12 mmol, 6 eq., 1 mol/L in anhydrous THF) and compound **2** (422 mg, 2 mmol, 1.0 eq.) under nitrogen atmosphere. The reaction mixture was heated to 70 °C and refluxed for 12 h. The solution was cooled to room temperature under nitrogen, then concentrated *in vacuo*. The solution was diluted with DCM (5 mL) and brine (20 mL), and extracted with DCM (3 × 20 mL). The combined organic layers were washed with brine (3 × 20 mL), dried over Na_2SO_4, and concentrated in vacuo. Purification by flash column chromatography using PE as eluent afforded the desired product **41**.

2-Phenylisoindoline-1,1-*d*$_2$ (41)



41

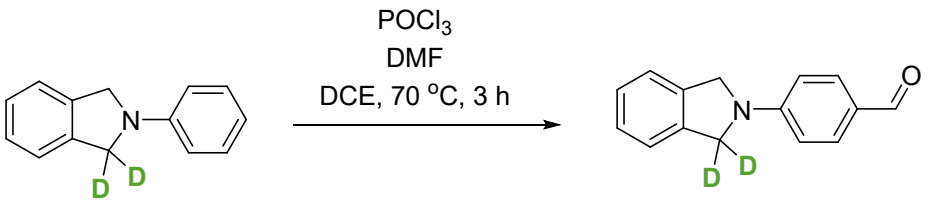
White solid (315 mg, 80% yield, 95% D); mp: 171 – 172 °C;

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38 – 7.28 (m, 6H), 6.76 (tt, *J* = 7.3, 0.9 Hz, 1H), 6.69 (dq, *J* = 7.3, 0.9 Hz, 2H), 4.66 (s, 2.10H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 147.1, 137.9, 137.7, 129.2, 127.0, 122.5, 116.0, 111.4, 53.6, 53.5 – 53.0 (m).

HRMS (ESI): Calcd. for $C_{14}H_{12}D_2N^+$ $[M + H]^+$: 198.1246, found: 198.1251.

Synthesis of compound 673A-*d*$_2$:

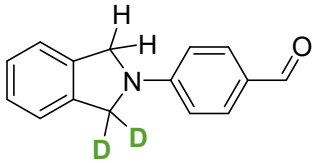


41
1 mmol

673A-d_2
90% (95%D)

A dry 50 mL three-necked bottle flask was charged with DMF (2 mmol, 2 eq.) in DCE (5 mL) and $POCl_3$ (2 mmol, 2.0 eq.) was added dropwise to the above solution at 0 °C under nitrogen atmosphere. The **41** (1 mmol, 1.0 eq.) was added after stir 20 minutes. The reaction mixture was at 70 °C for 3 h. The solution was cooled to room temperature and pour into ice water and saturated Na_2CO_3 solution. The solution was diluted with DCM (5 mL) and brine (20 mL), and extracted with DCM (3 × 20 mL). The combined organic layers were washed with brine (3 × 20 mL), dried over Na_2SO_4, and concentrated *in vacuo*. Purification by flash column chromatography using PE/EtOAc (v/v = 3/1) as eluent afforded the desired product **673A-d_2**.

4-(Isoindolin-2-yl-1,1-d_2)benzaldehyde (673A-d_2)



673A-d_2

White solid (202 mg, 90% yield, 95% D); mp: 174 – 176 °C;

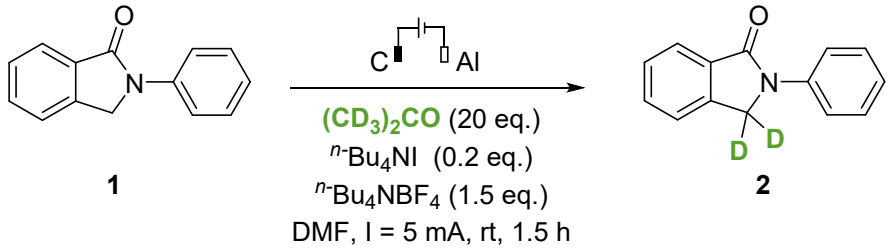
^{1}H NMR (300 MHz, $CDCl_3$): δ 9.77 (s, 1H), 7.87 – 7.74 (m, 2H), 7.34 (d, J = 1.7 Hz, 4H), 6.75 – 6.65 (m, 2H), 4.73 (s, 2.10H).

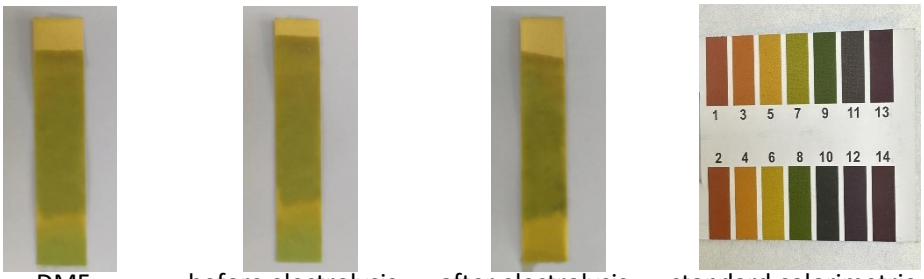
^{13}C NMR (75 MHz, $CDCl_3$): δ 190.1, 151.1, 136.5, 136.3, 132.0, 127.5, 125.4, 122.5, 111.0, 53.5 – 52.8 (m).

HRMS (ESI): Calcd. for $C_{15}H_{12}D_2NO^+$ $[M + H]^+$: 226.1195, found: 226.1198.

V Mechanism Research

Scheme S2: pH Detection.





DMF before electrolysis after electrolysis standard colorimetric card

(1) The pH test paper was moistened with water and anhydrous DMF was dropped on it. The color did not changed obviously.

(2) The pH test paper was moistened with water and the reaction mixture before electrification was dropped on the pH test paper. The color did not changed obviously.

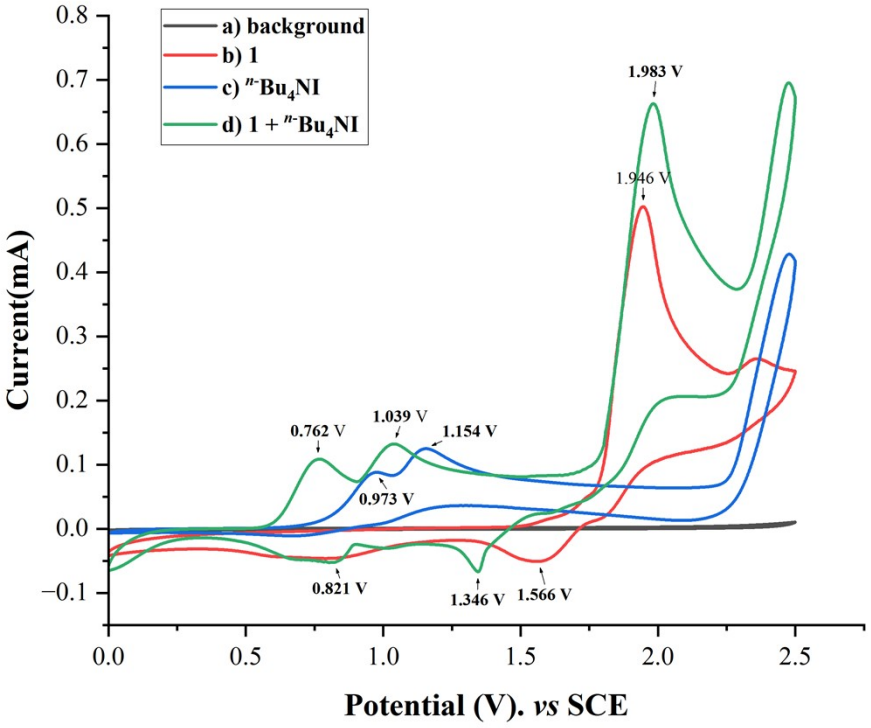
(3) After the reaction was completed under standard conditions, the pH test paper was moistened with water and the mixture was dropped on it. The color did not changed obviously.

Scheme S3: Cyclic Voltammetry Experiment

Cyclic voltammetry was carried out in a glass cell with CHI760E electrochemical workstation. Cyclic voltammetry of compound **1** at a scan rate of 100 $mV \cdot s^{-1}$.The electrochemical experiments were performed in a three-compartment cell fitted with a glassy carbon as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a graphite rod (diameter is 5 mm) as the counter electrode.

Electrolyte: 0.1 M ^{n}-Bu_4NBF_4 in MeCN; Concentration of a sample: 0.01 M.

In the mixture of **1** with ^{n}-Bu_4NI, the oxidation peak of ^{n}-Bu_4NI dramatically shifted from 0.973 V to 0.762 V and from 1.154 V to 1.039 V. In addition, the reduction peak of **1** shifted from 1.566 V to 1.346 V and the another reduction peak remained at 0.821V. (curve d)



Cyclic voltammograms obtained in 0.1 M ^{n}-Bu_4NBF_4/MeCN using glass carbon (diameter, 3 mm) as the working electrode, graphite rod, and saturated calomel electrode (SCE) as the auxiliary and reference electrode, respectively, at a scan rate of 100 $mV \cdot s^{-1}$: (a) background, (b) 10 mM **1**, (c) 10 mM ^{n}-Bu_4NI and (d) 10 mM **1** + 10 mM ^{n}-Bu_4NI.

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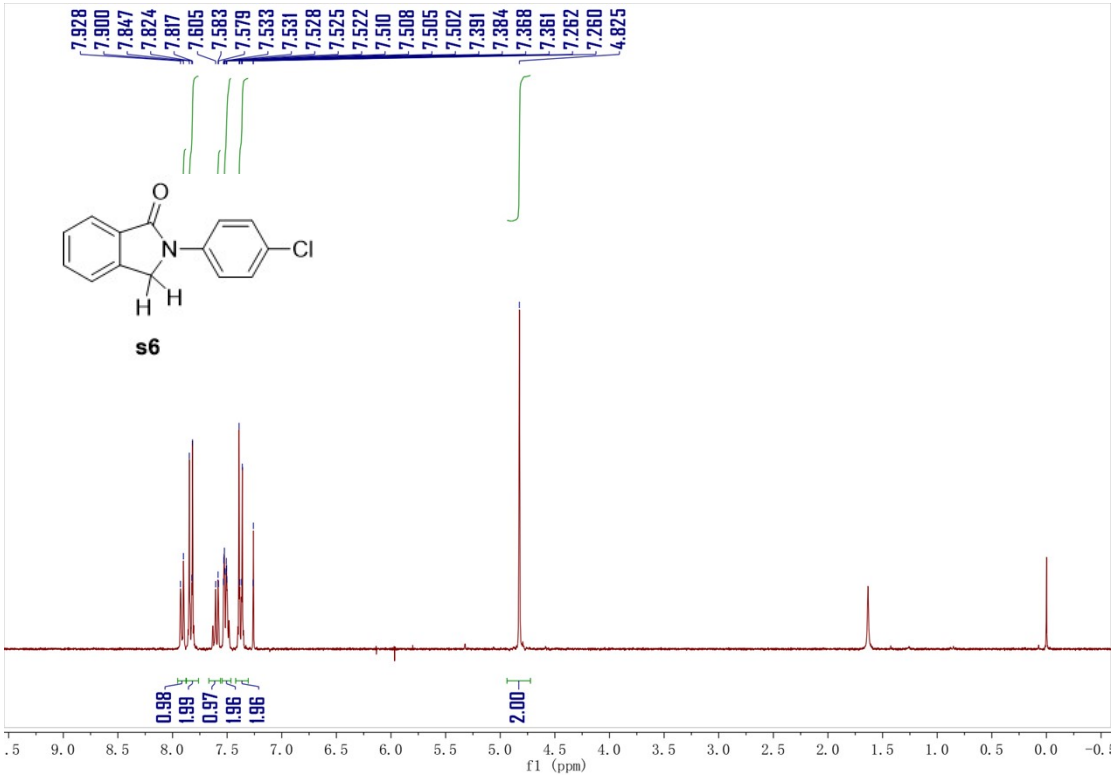
VII. Spectra

^{1}H NMR (300 MHz, $CDCl_3$):



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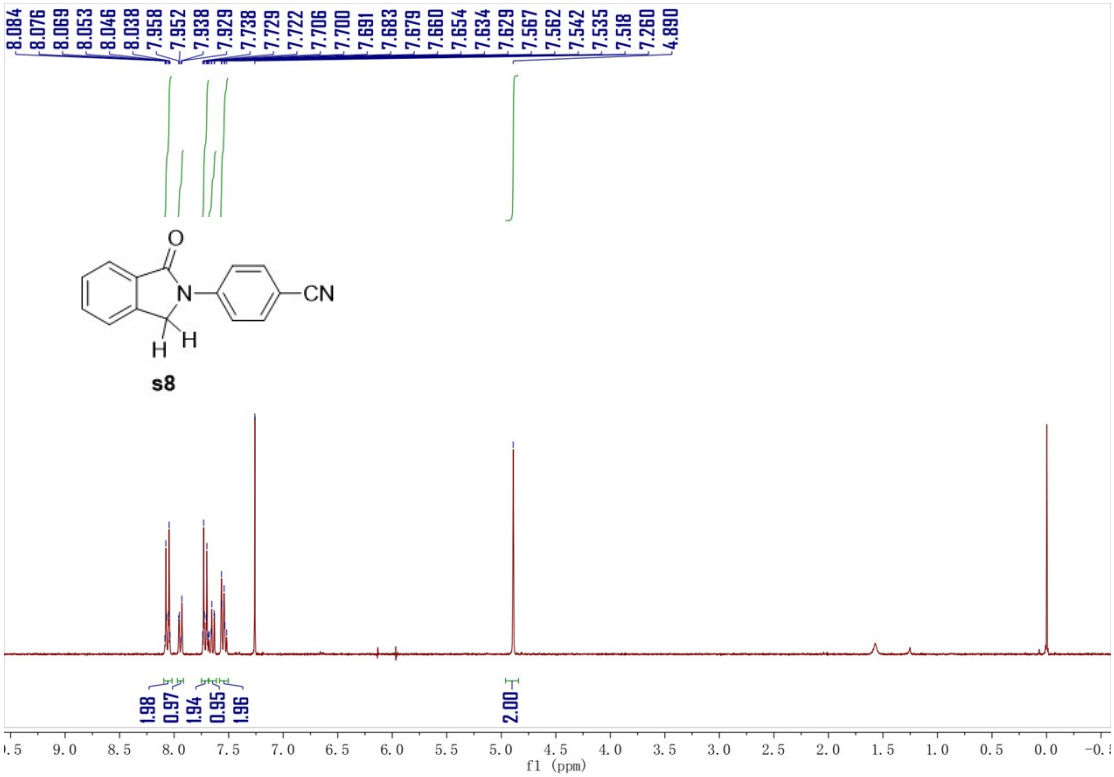

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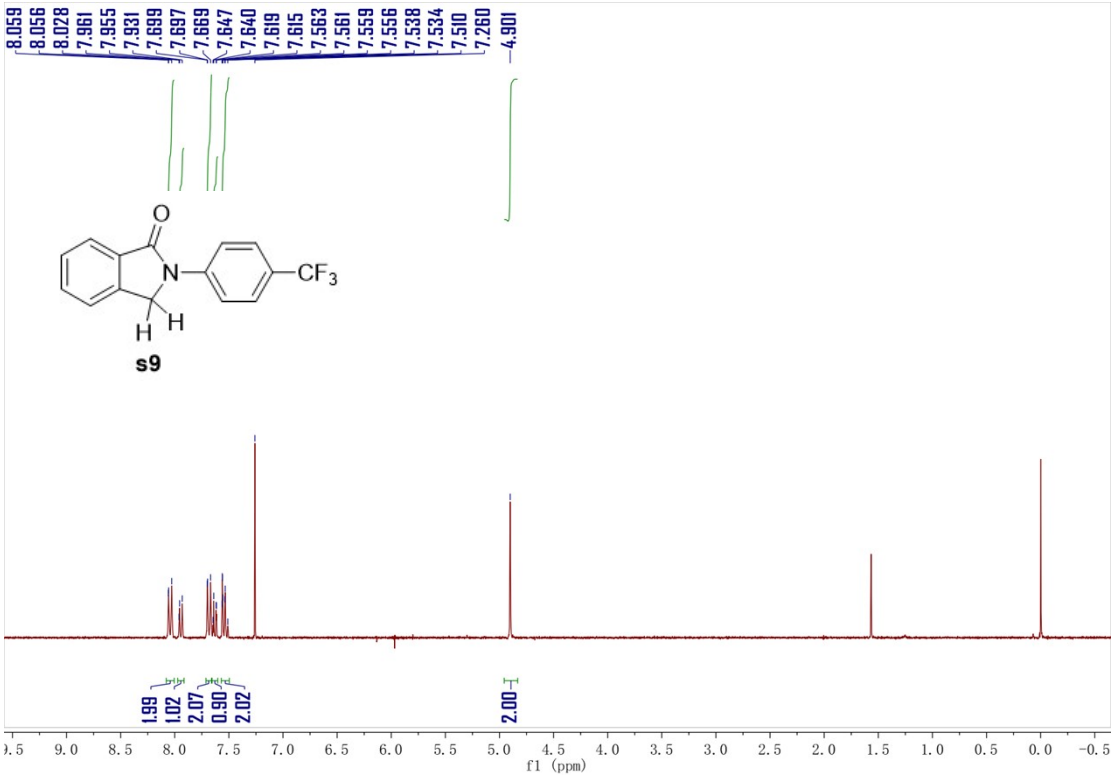

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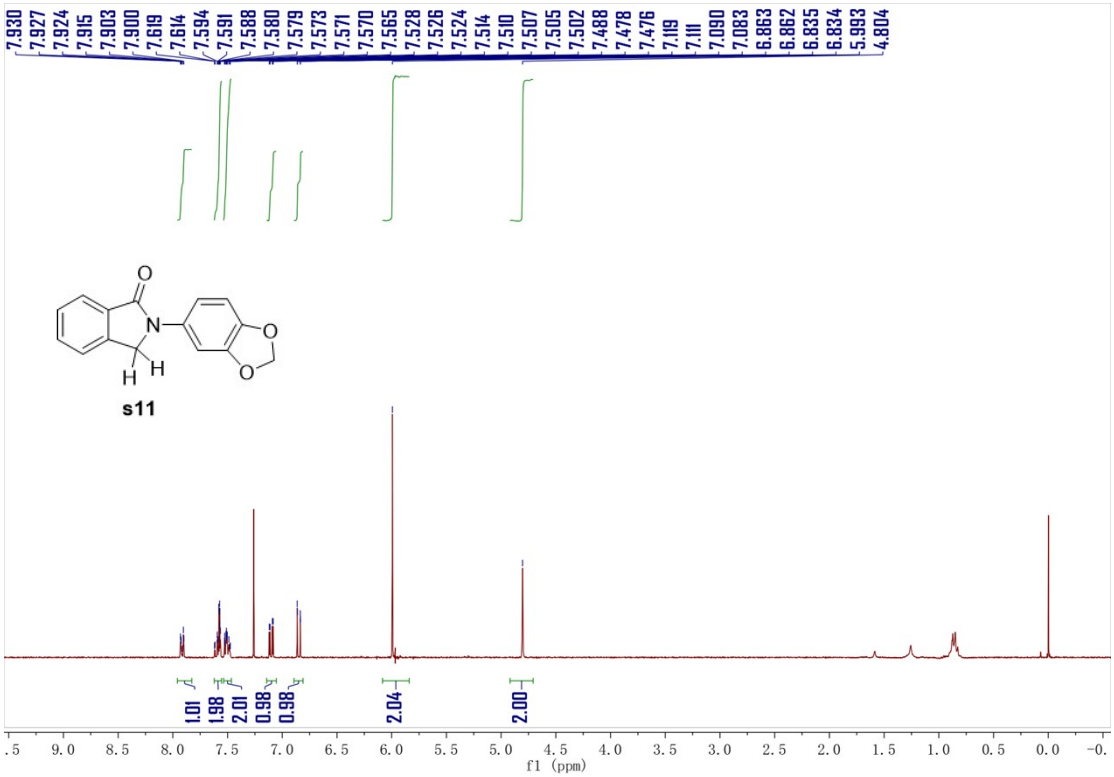

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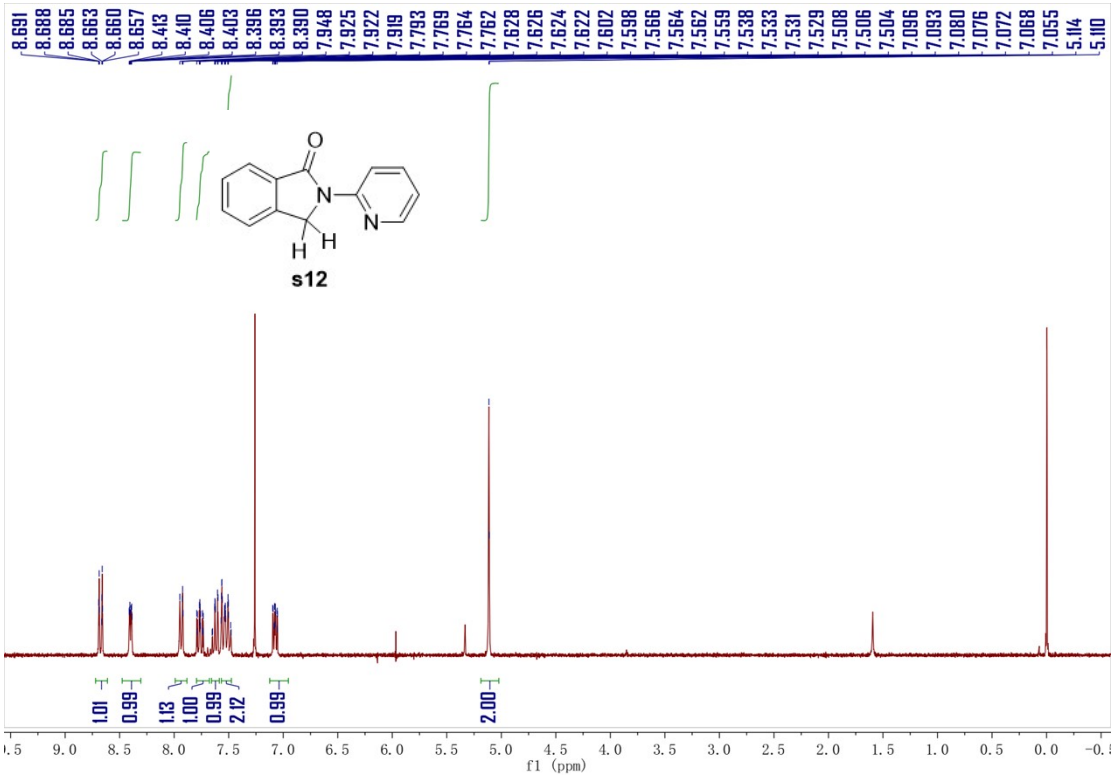

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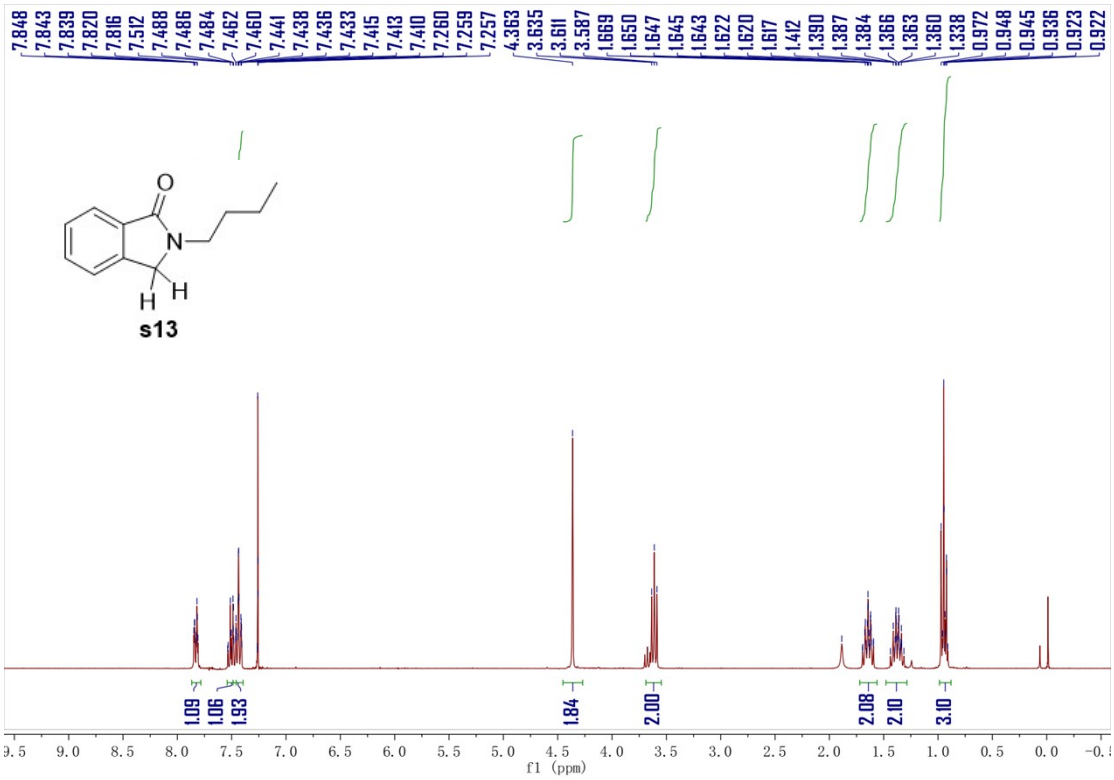

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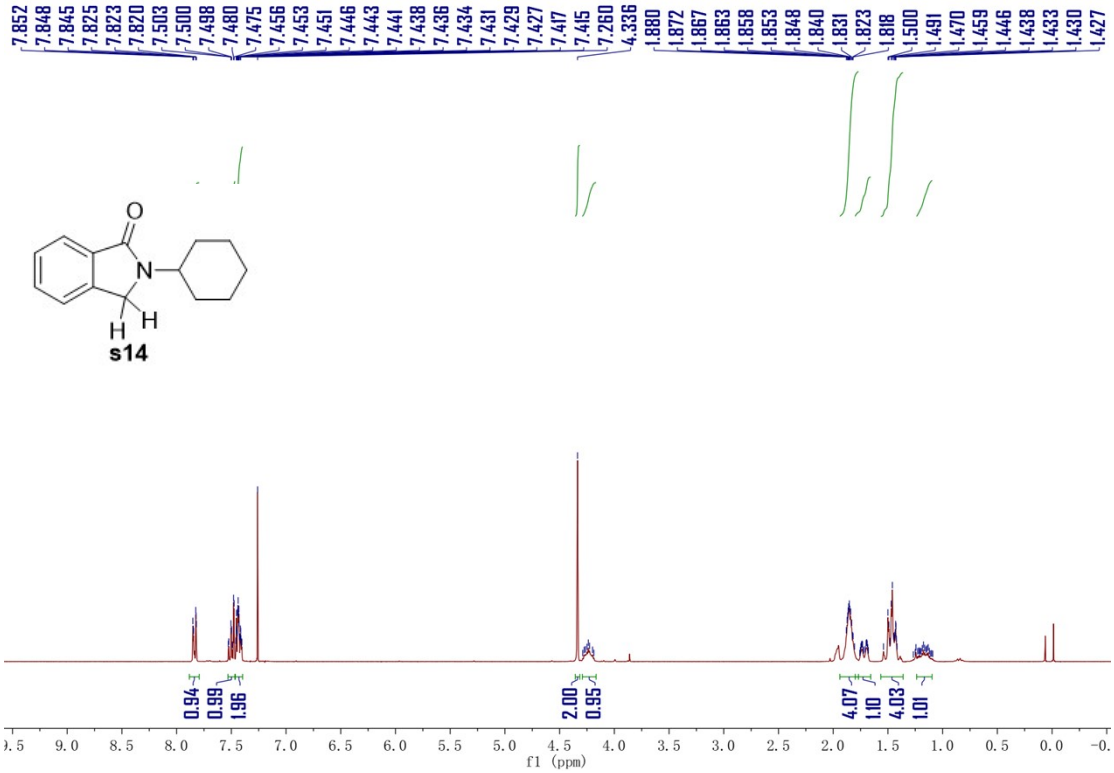

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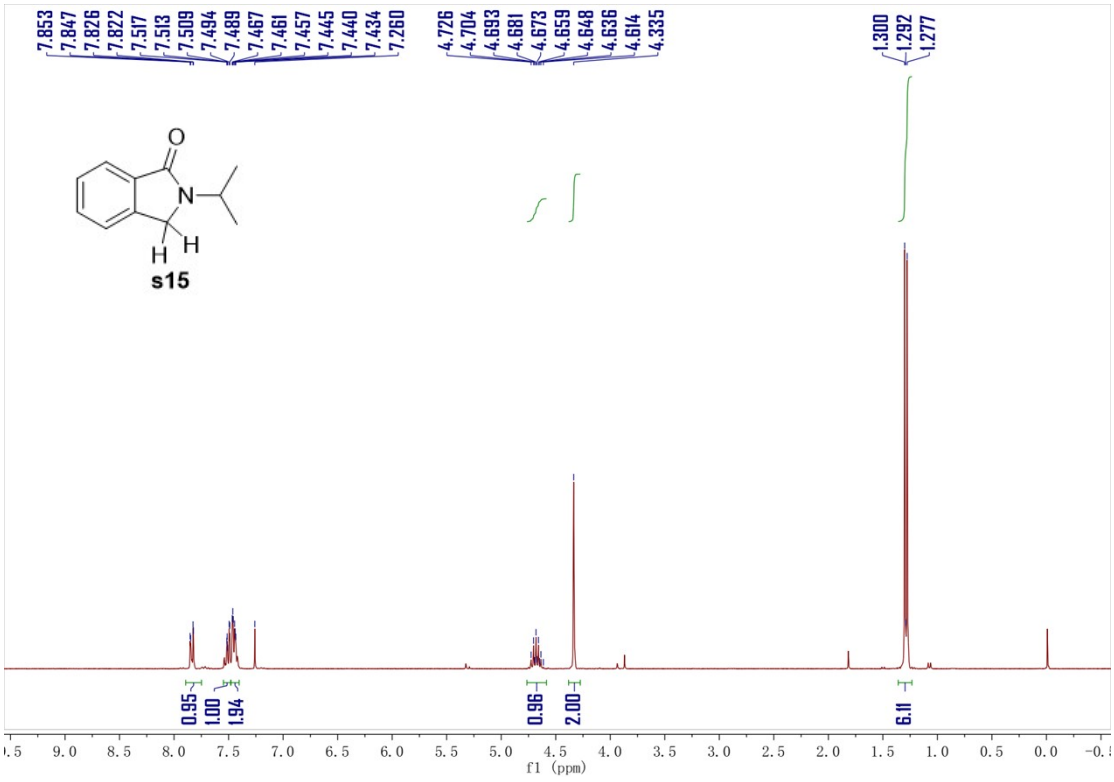

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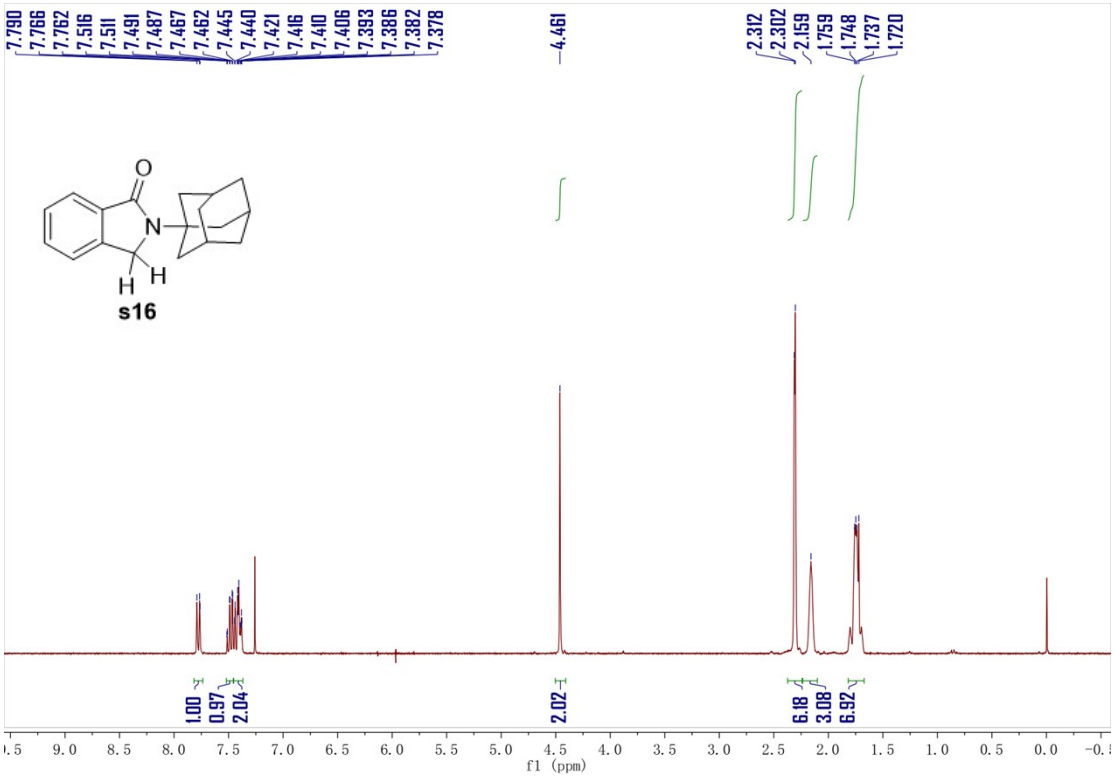

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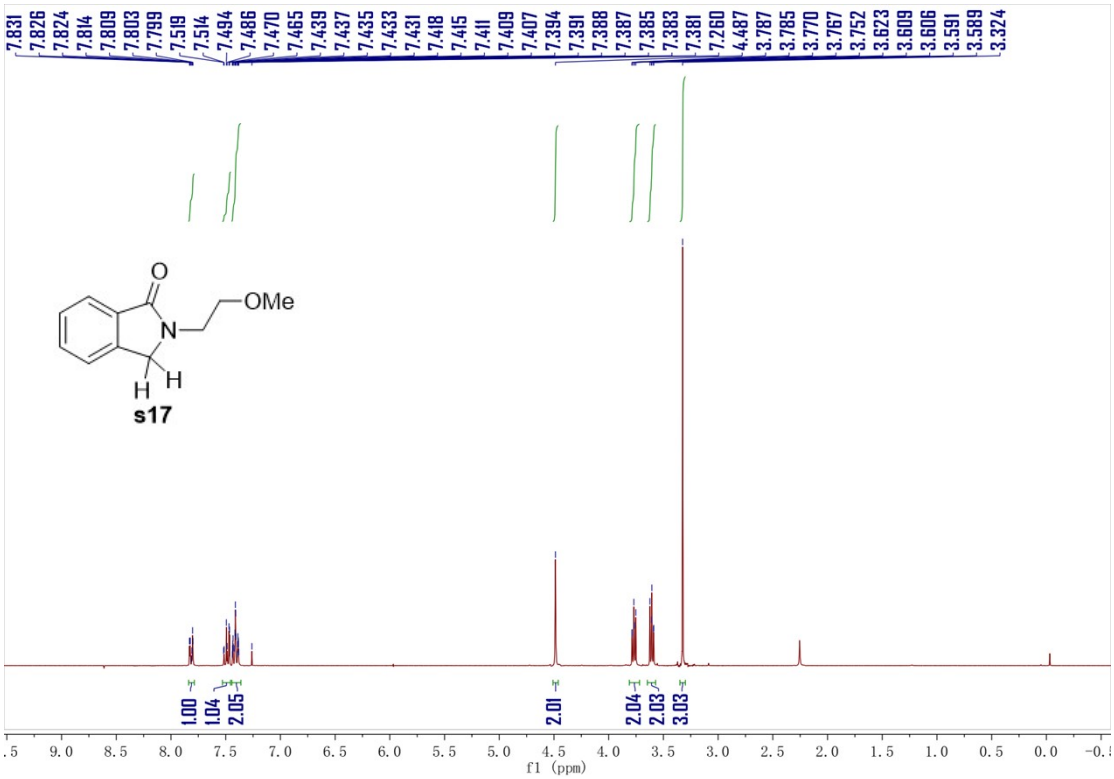

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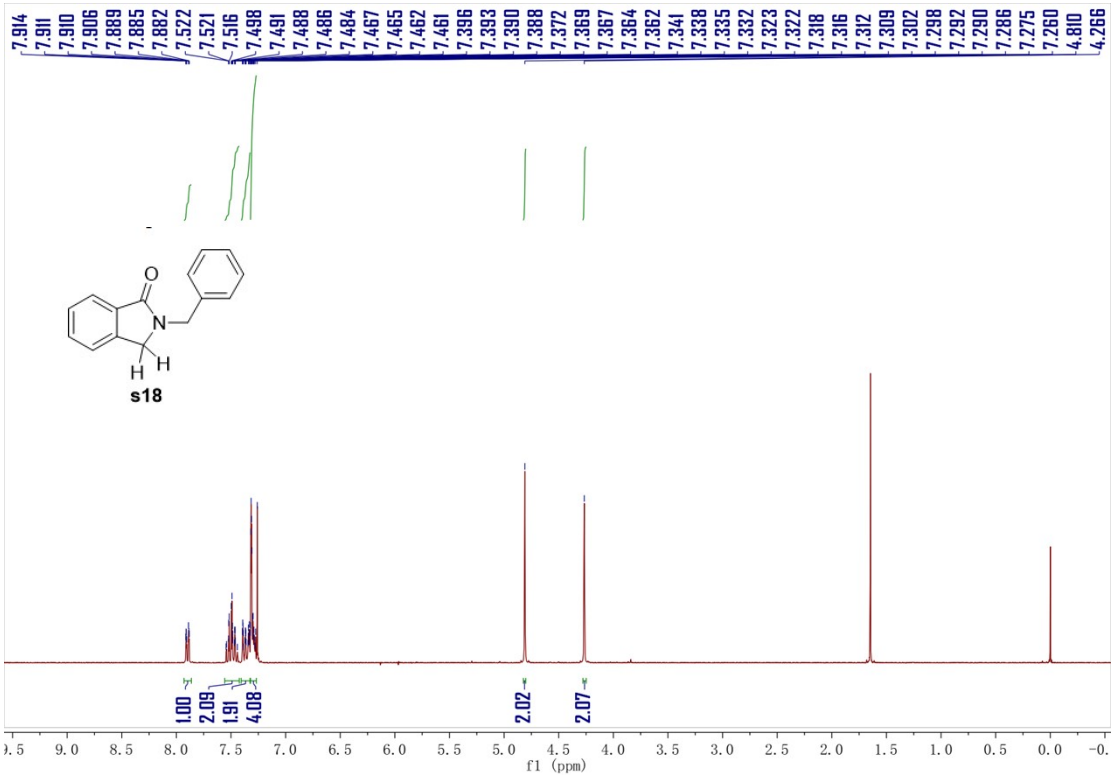

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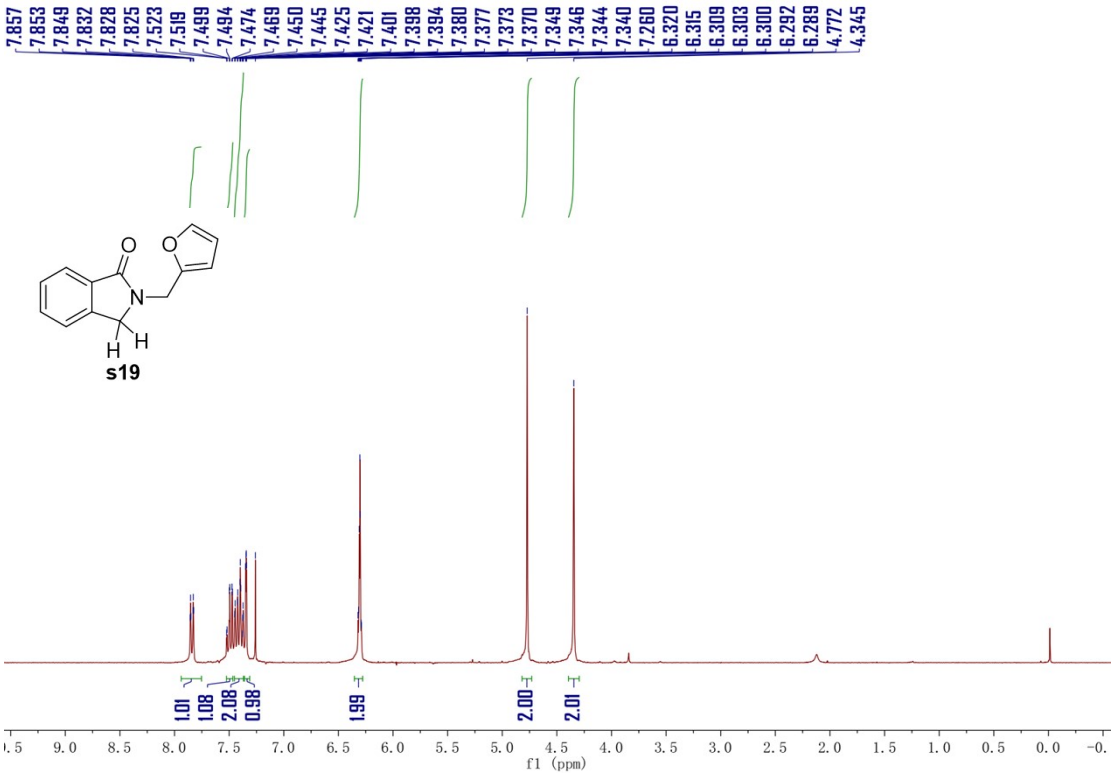

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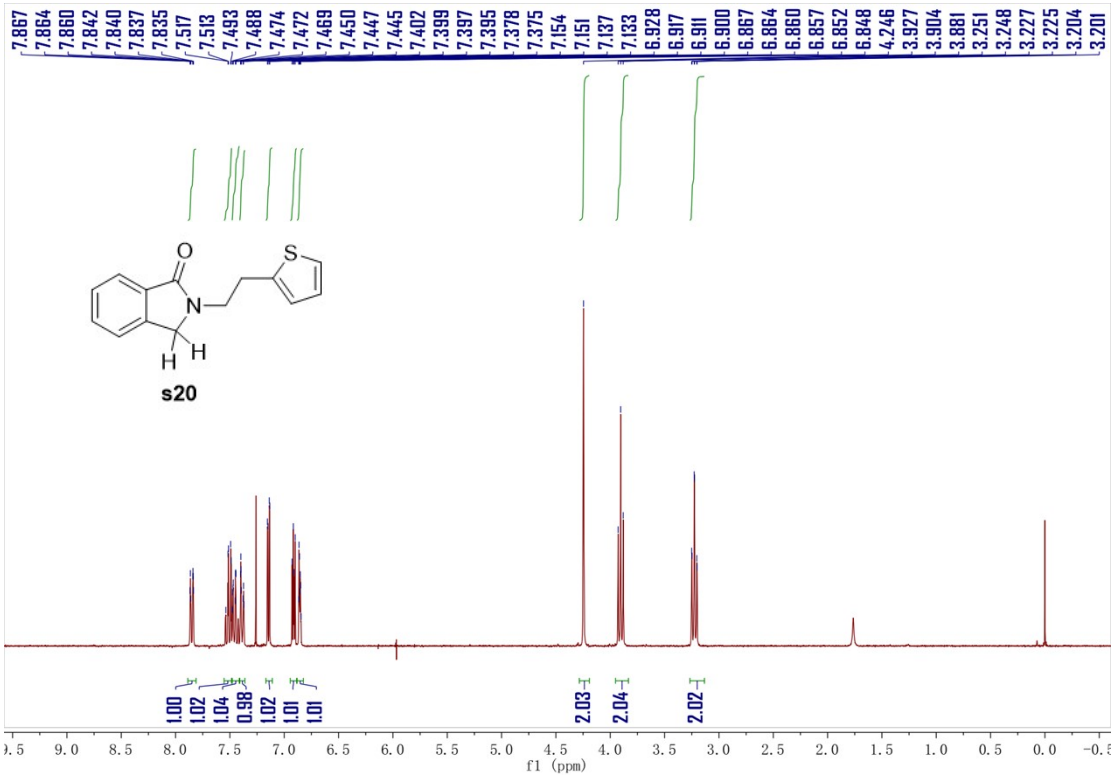

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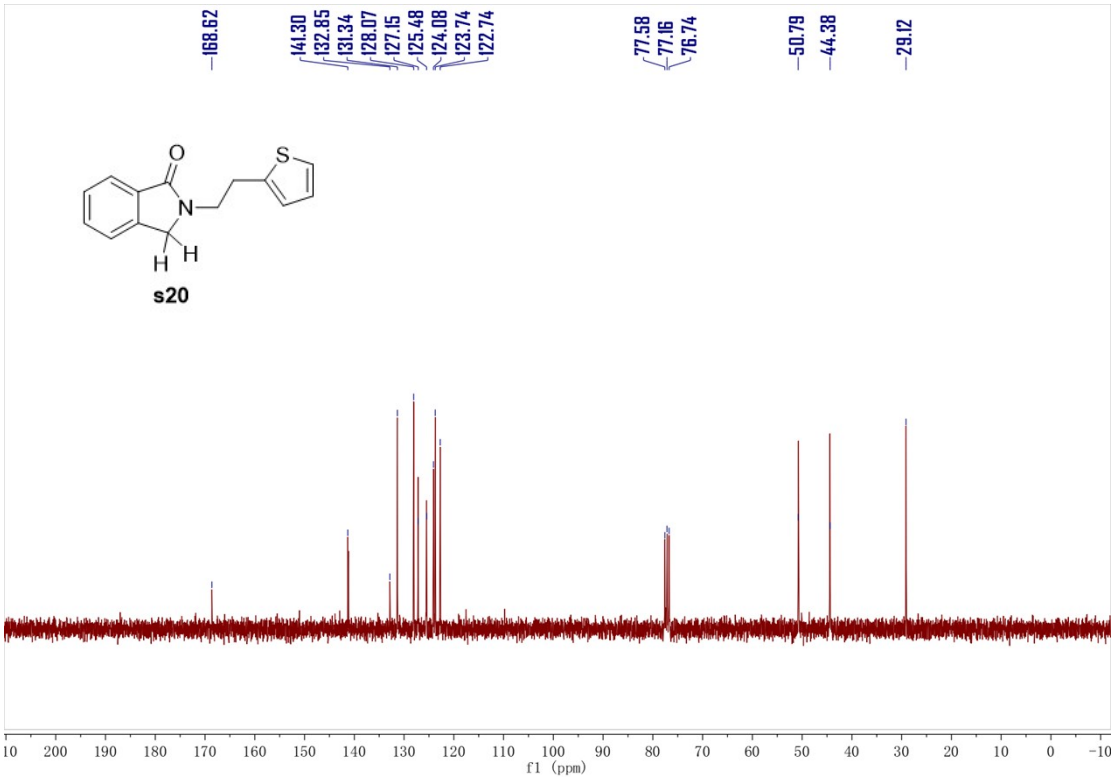

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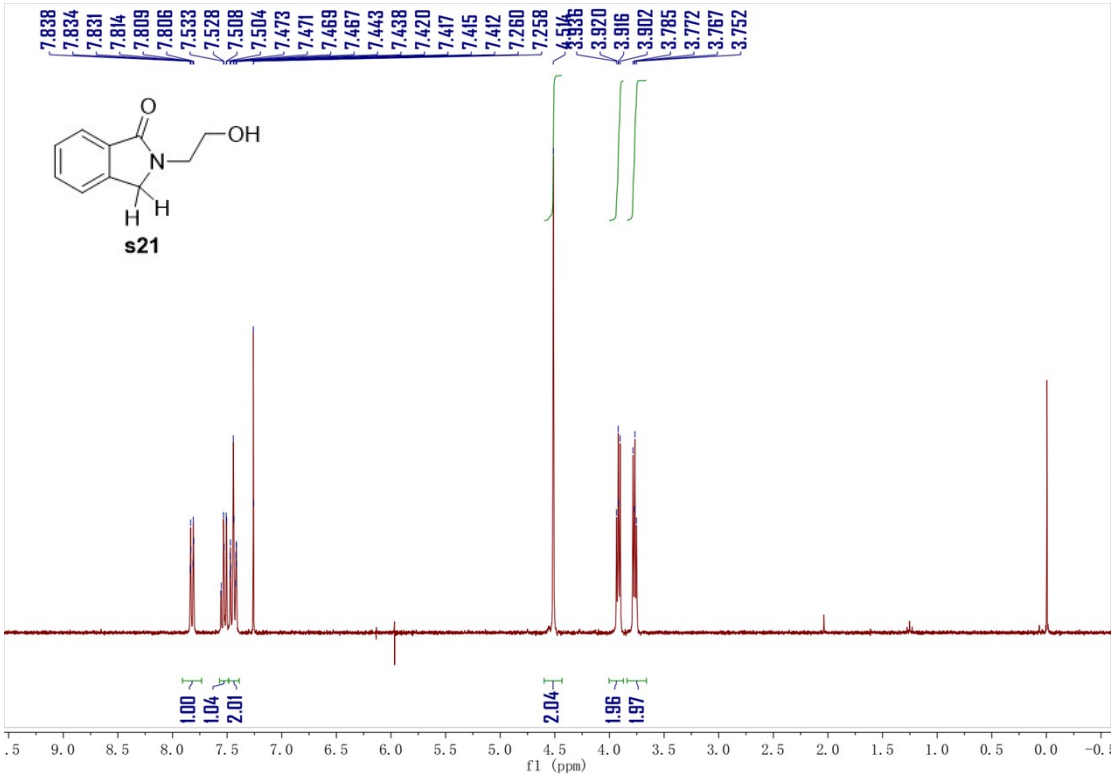

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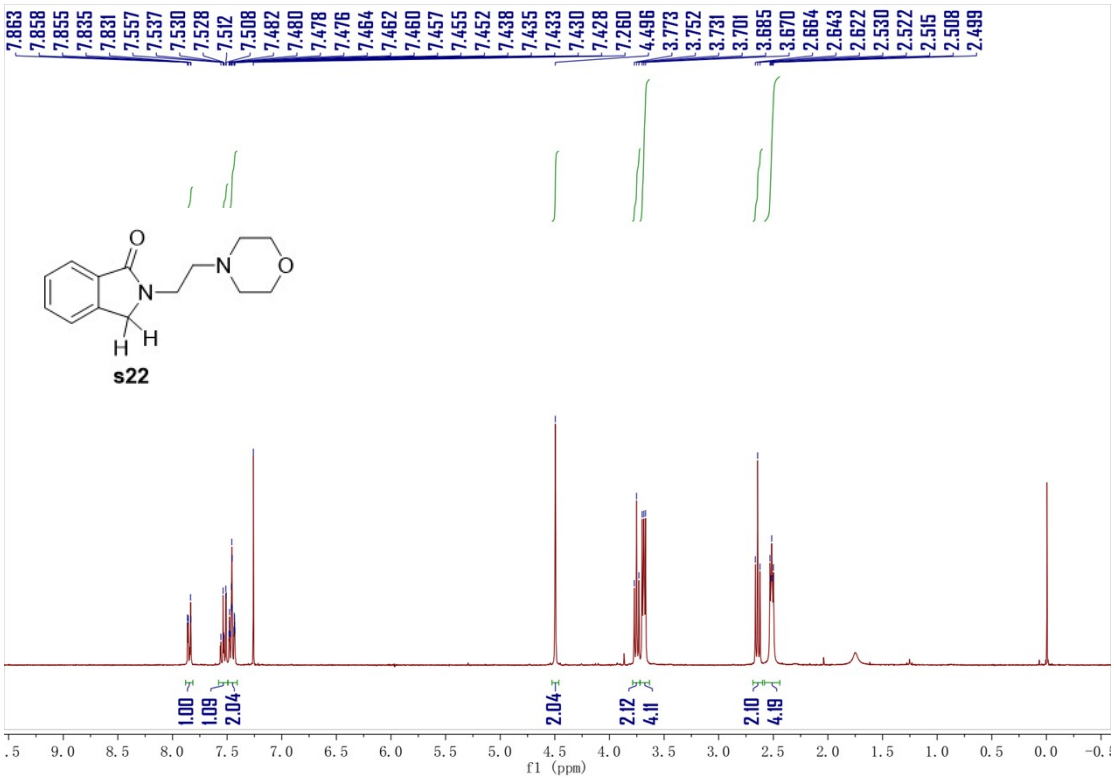

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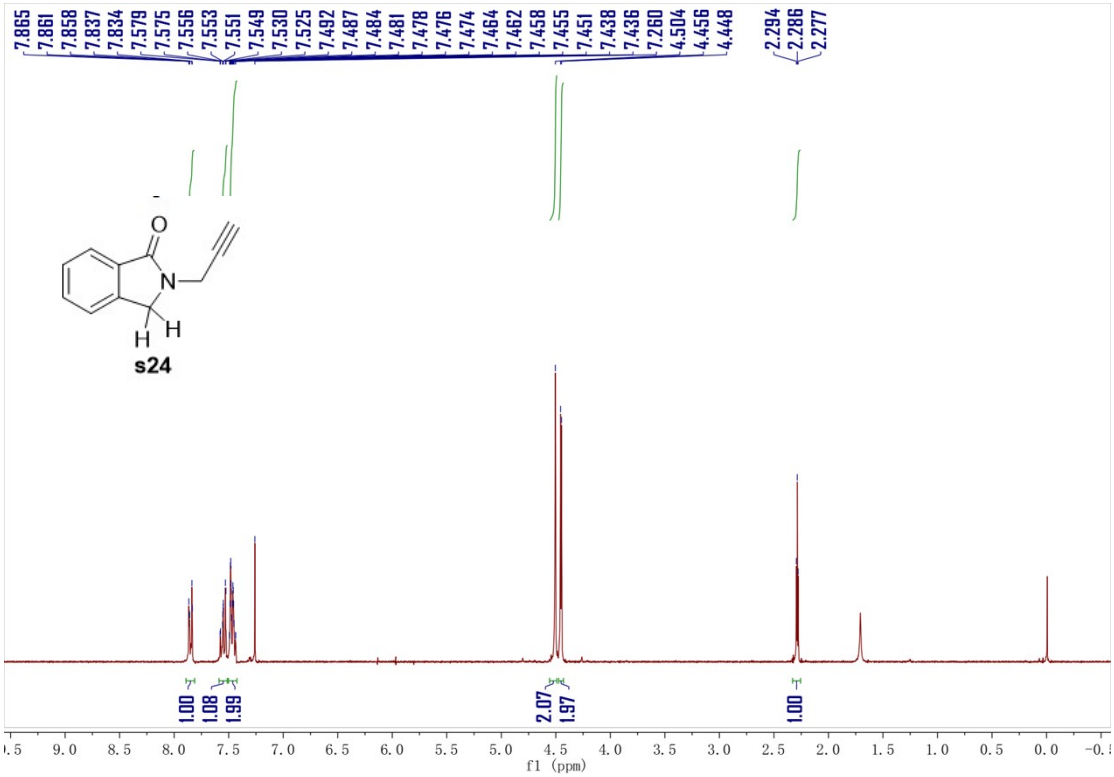

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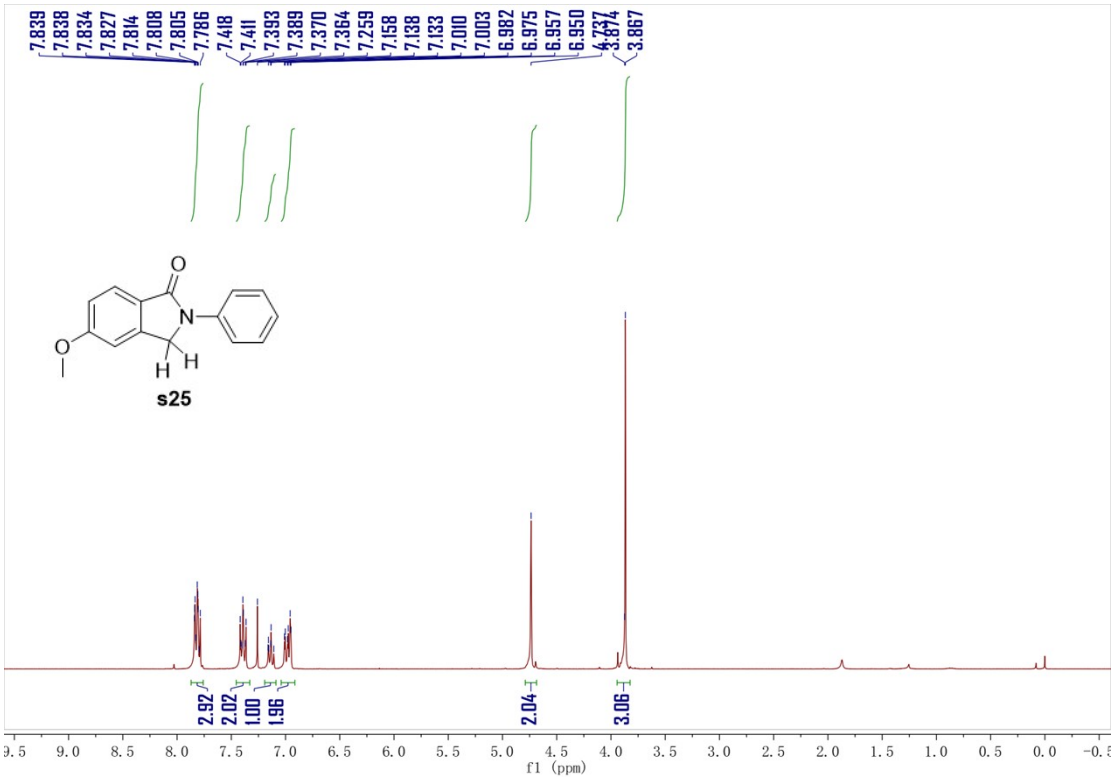

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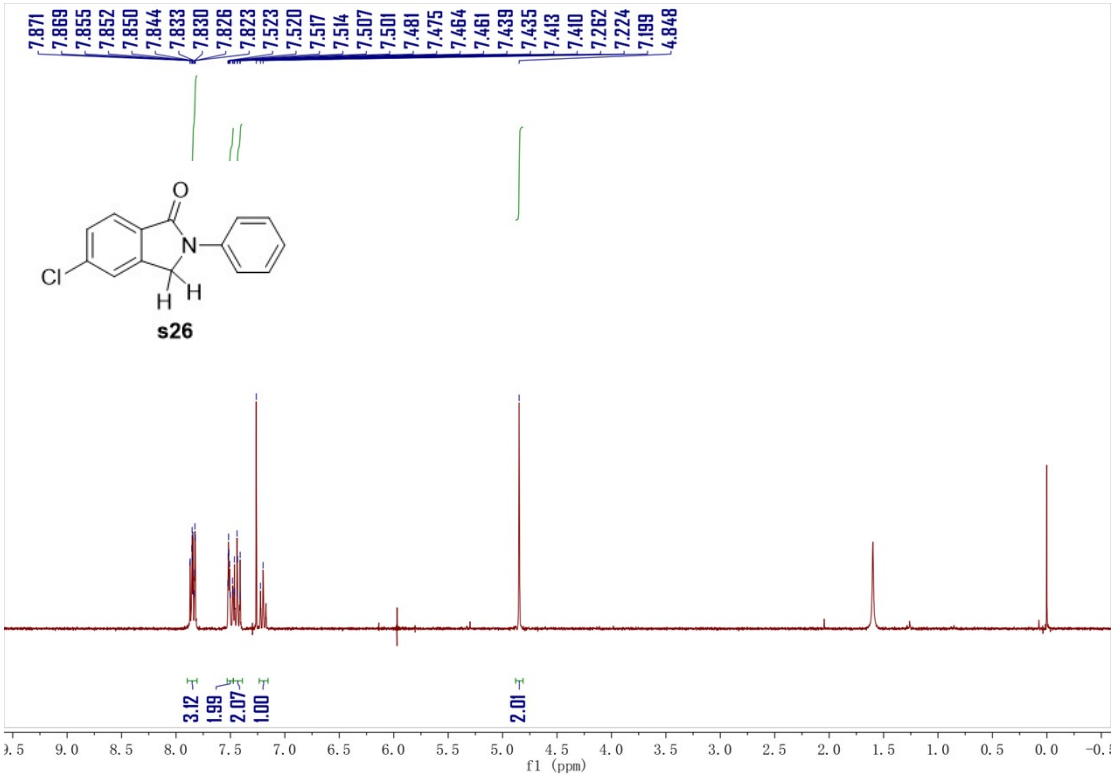

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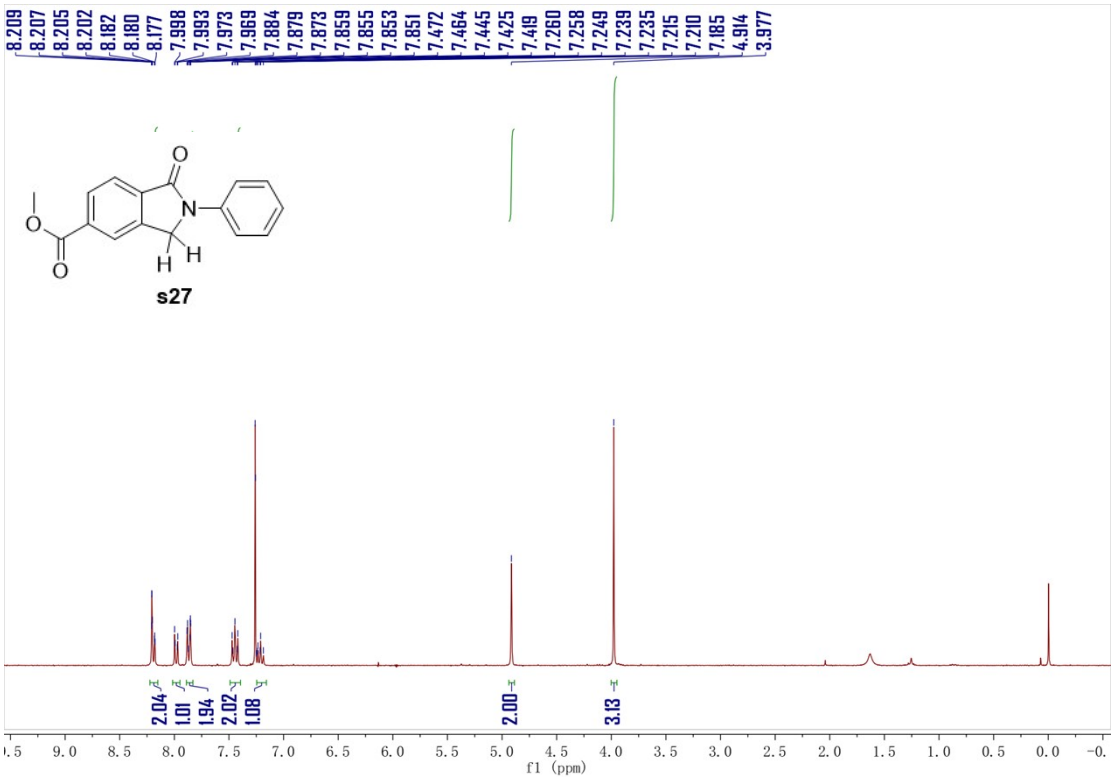

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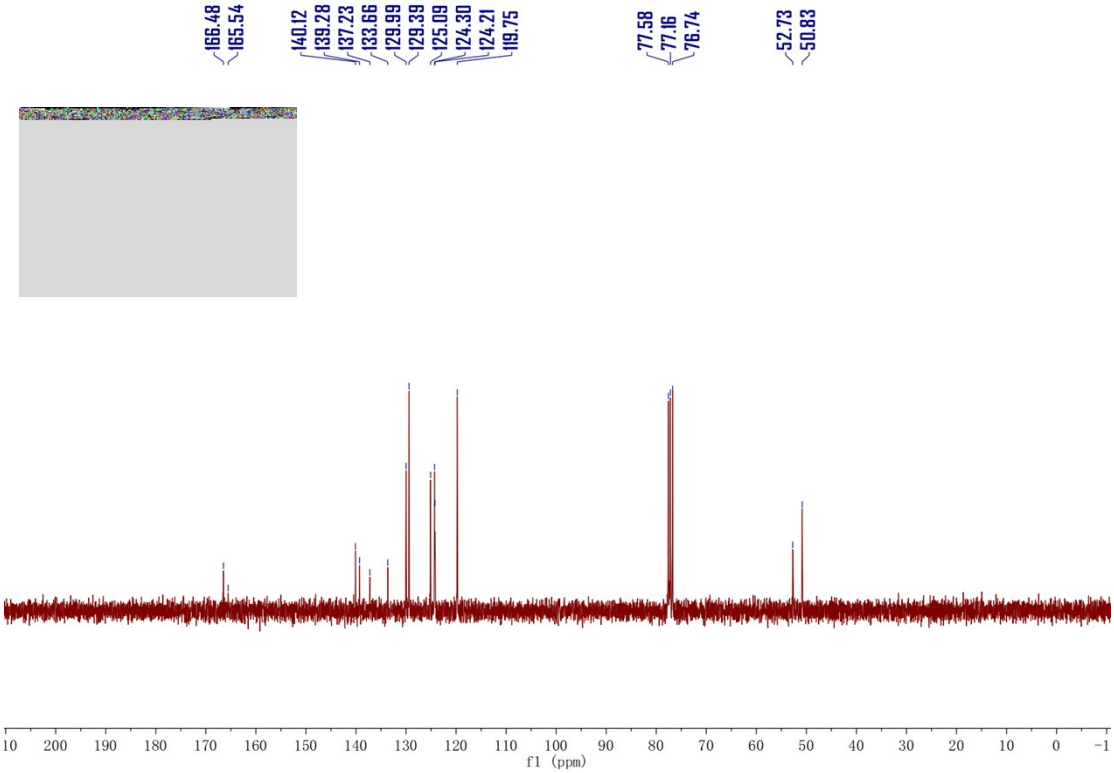

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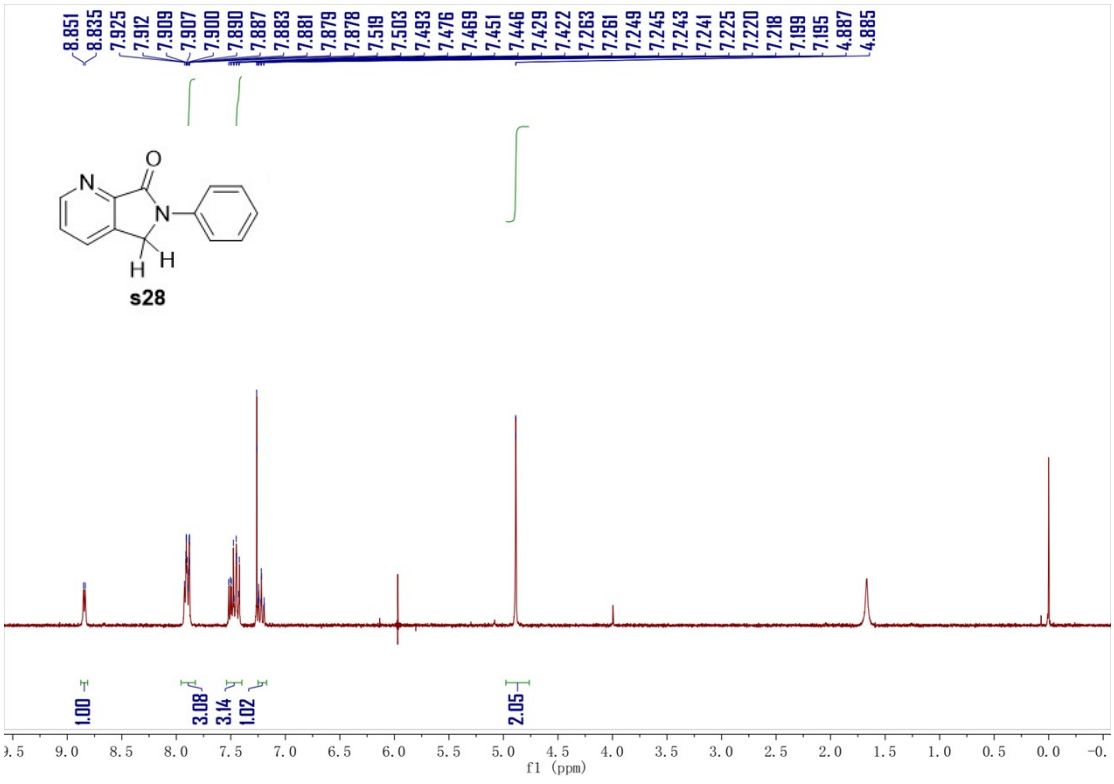

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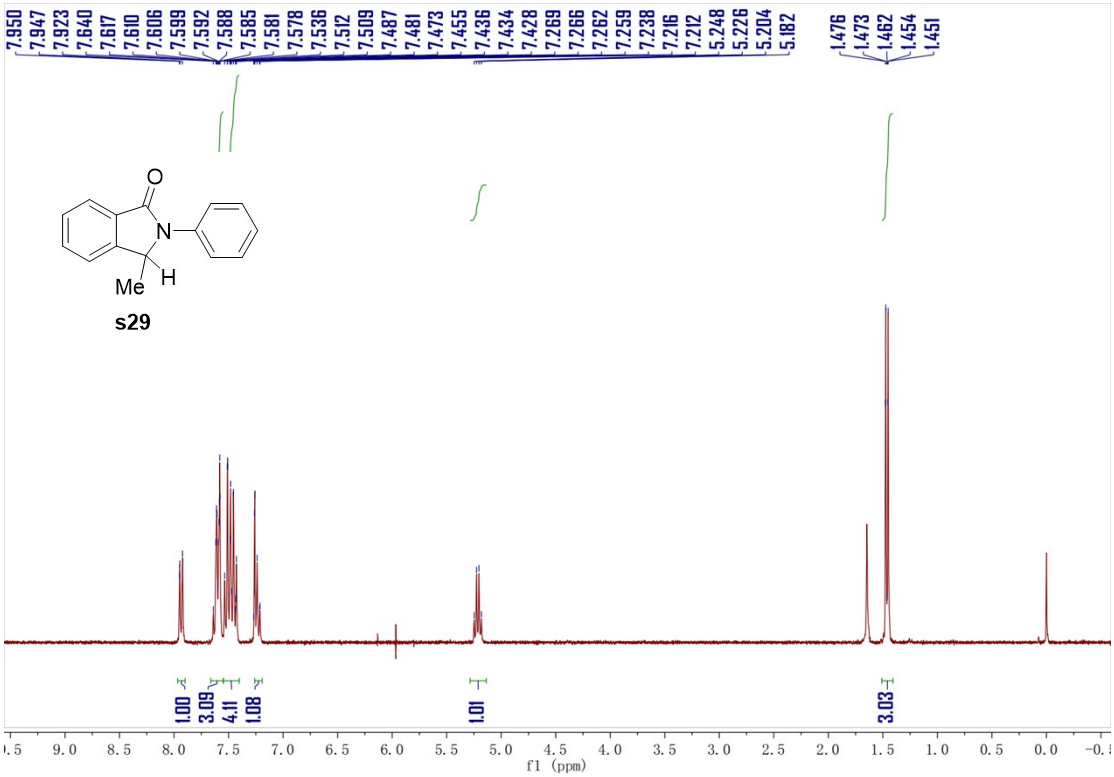

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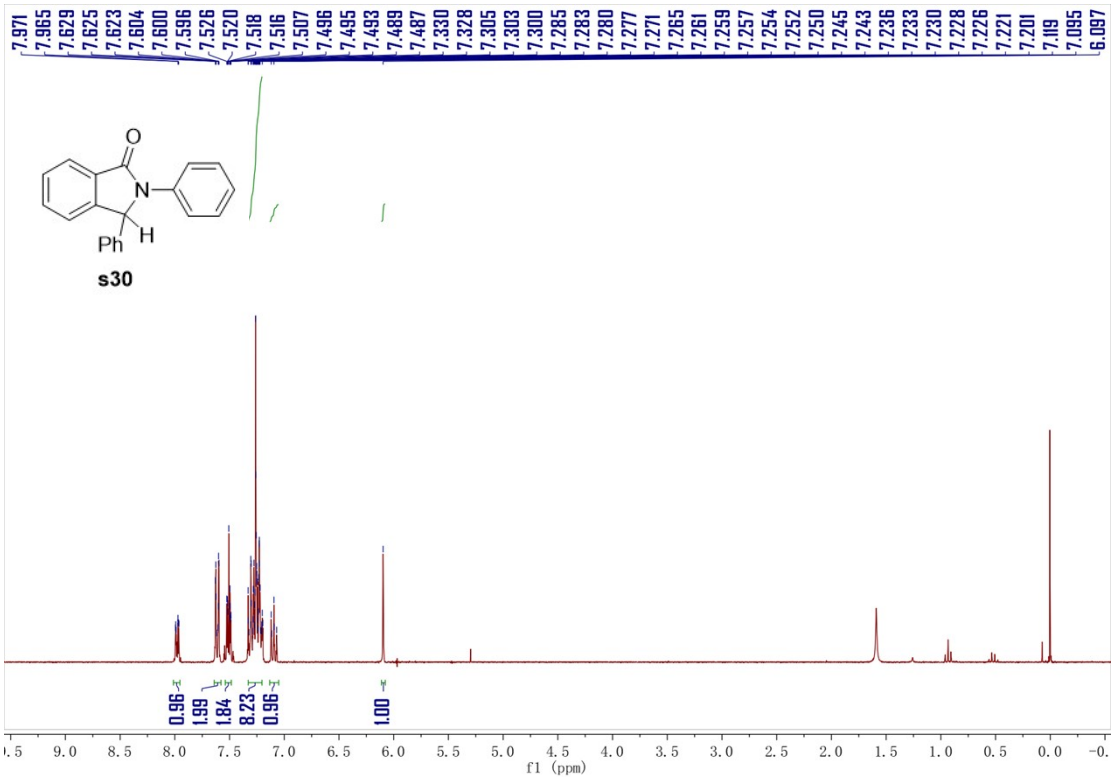

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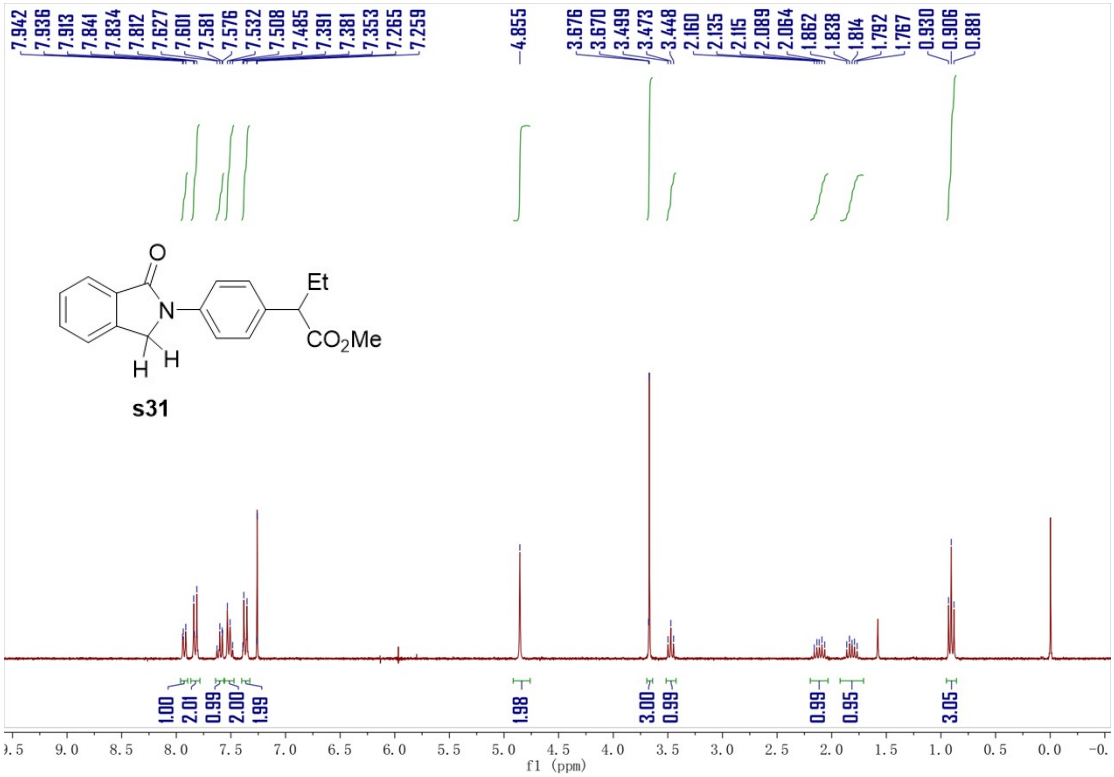

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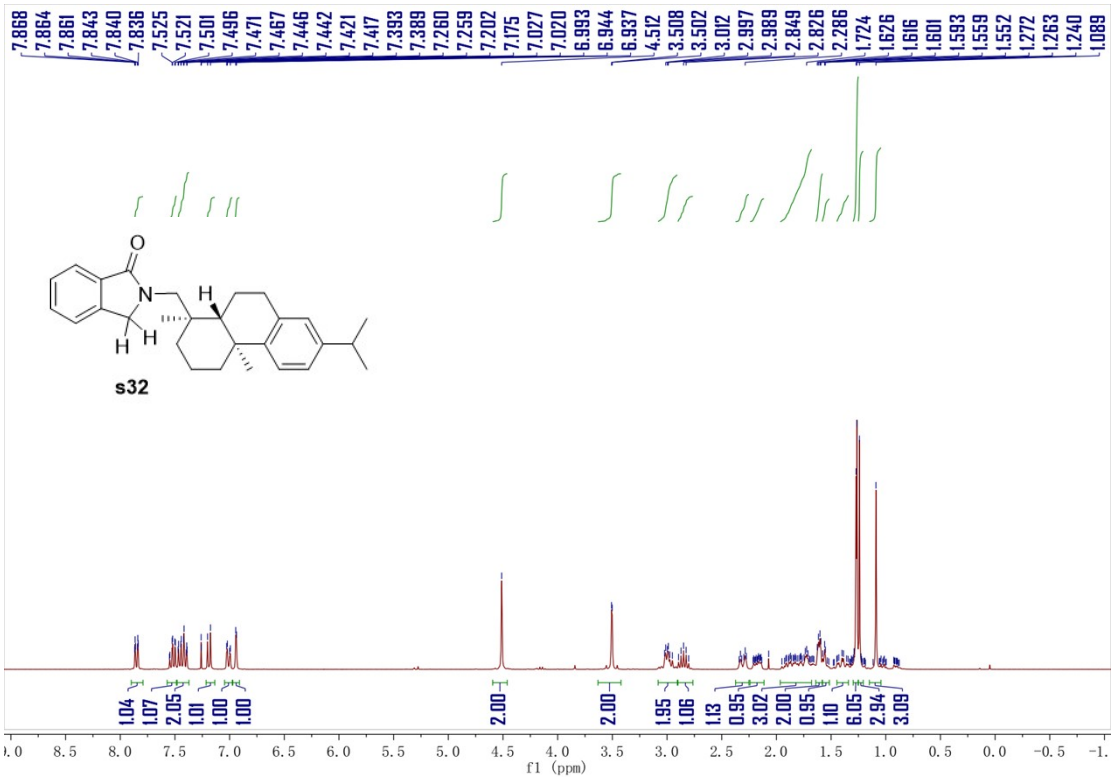
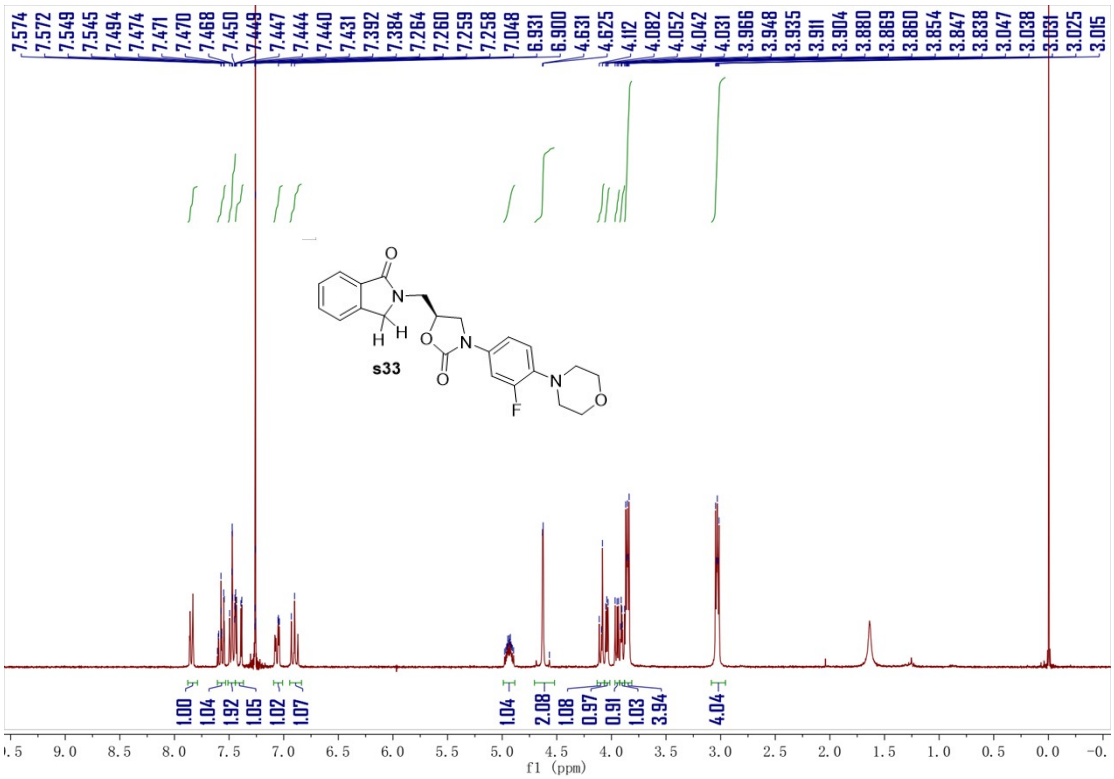
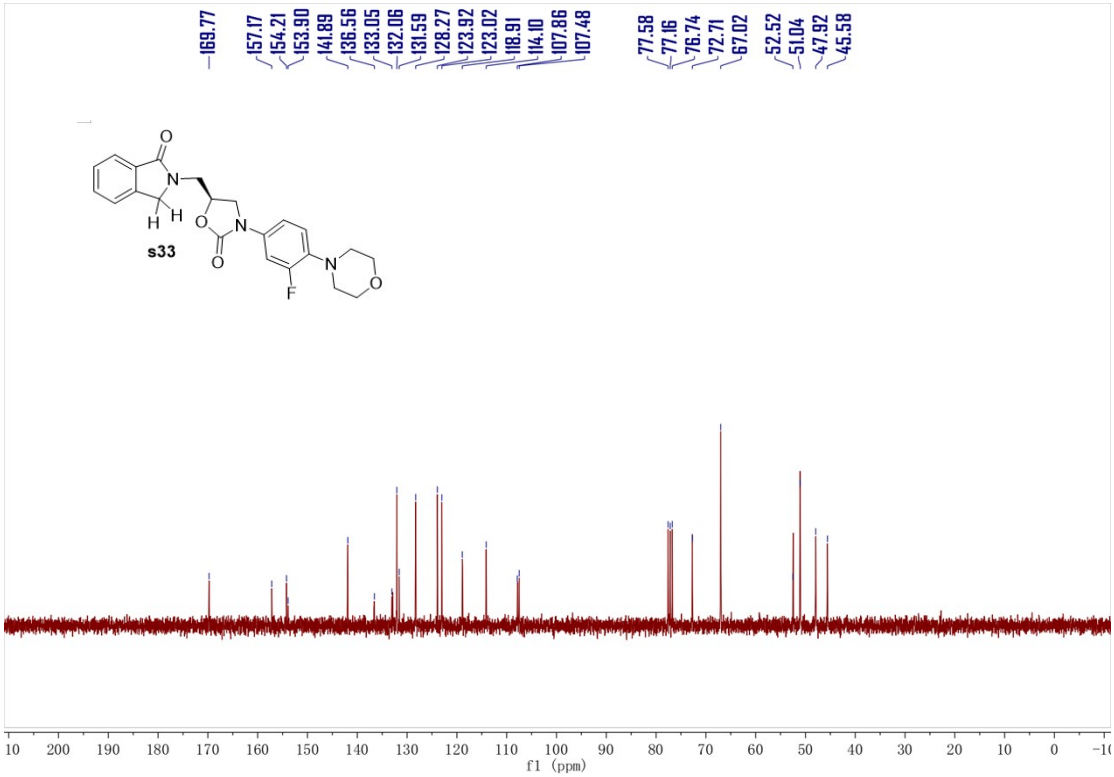


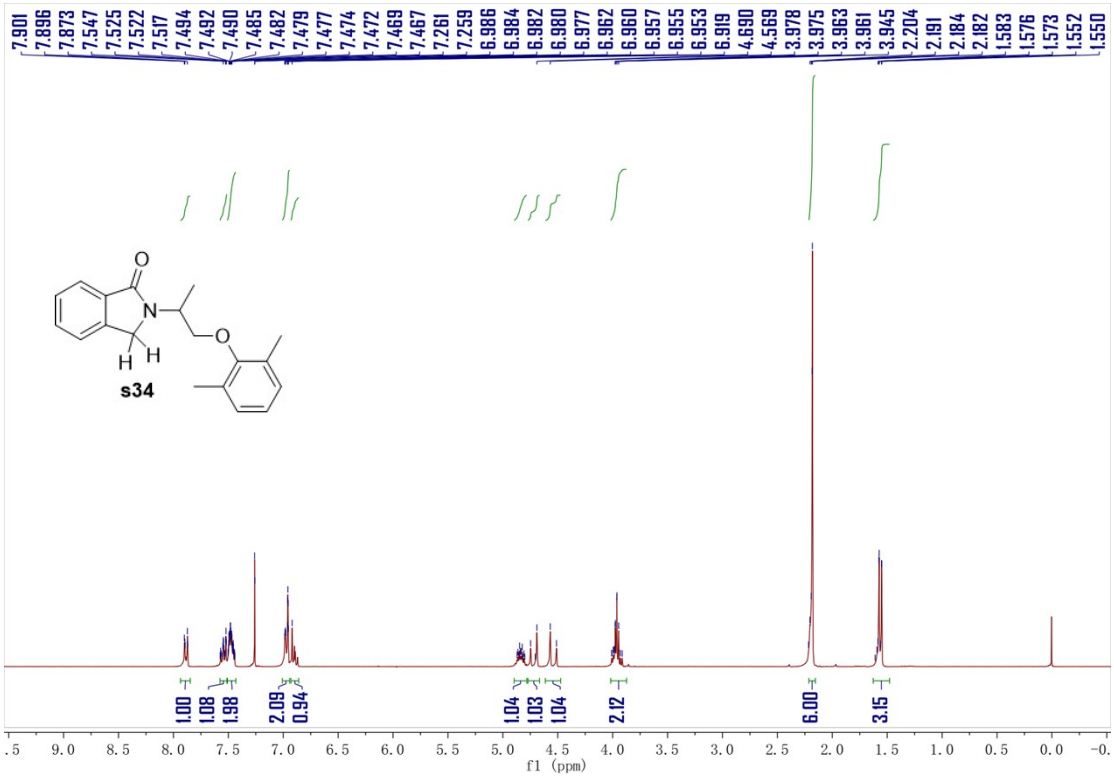
^{1}H NMR (300 MHz, $CDCl_3$):



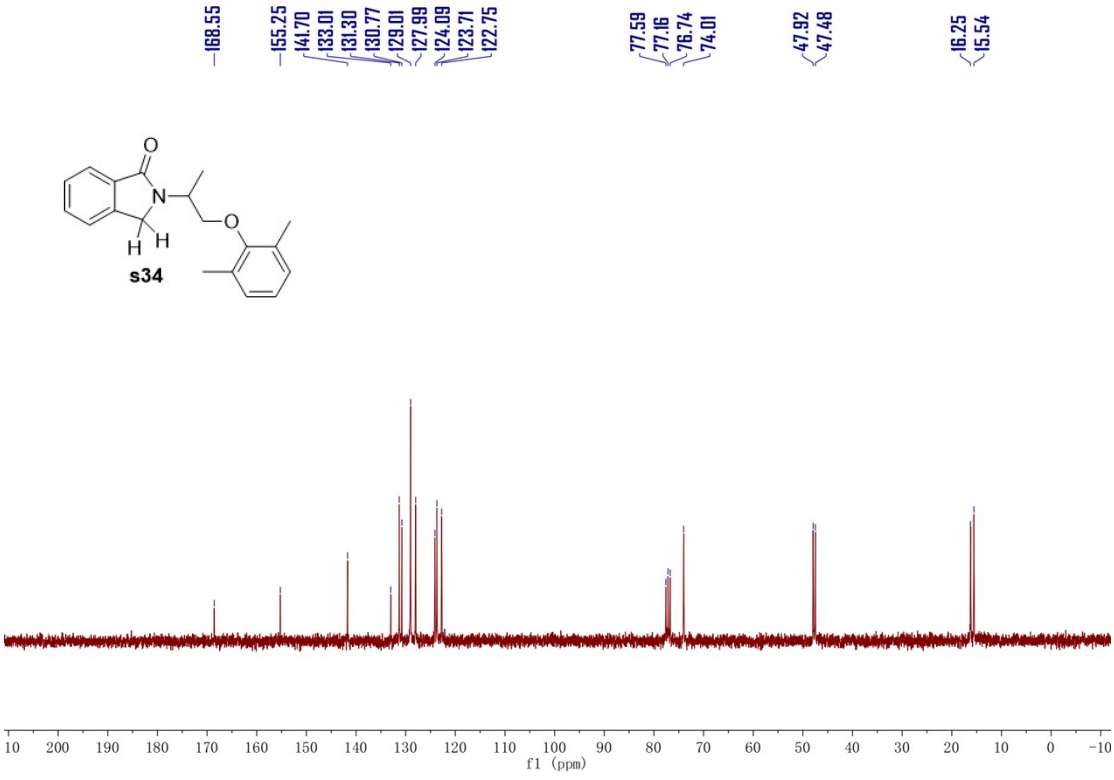
^{13}C NMR (75 MHz, $CDCl_3$):



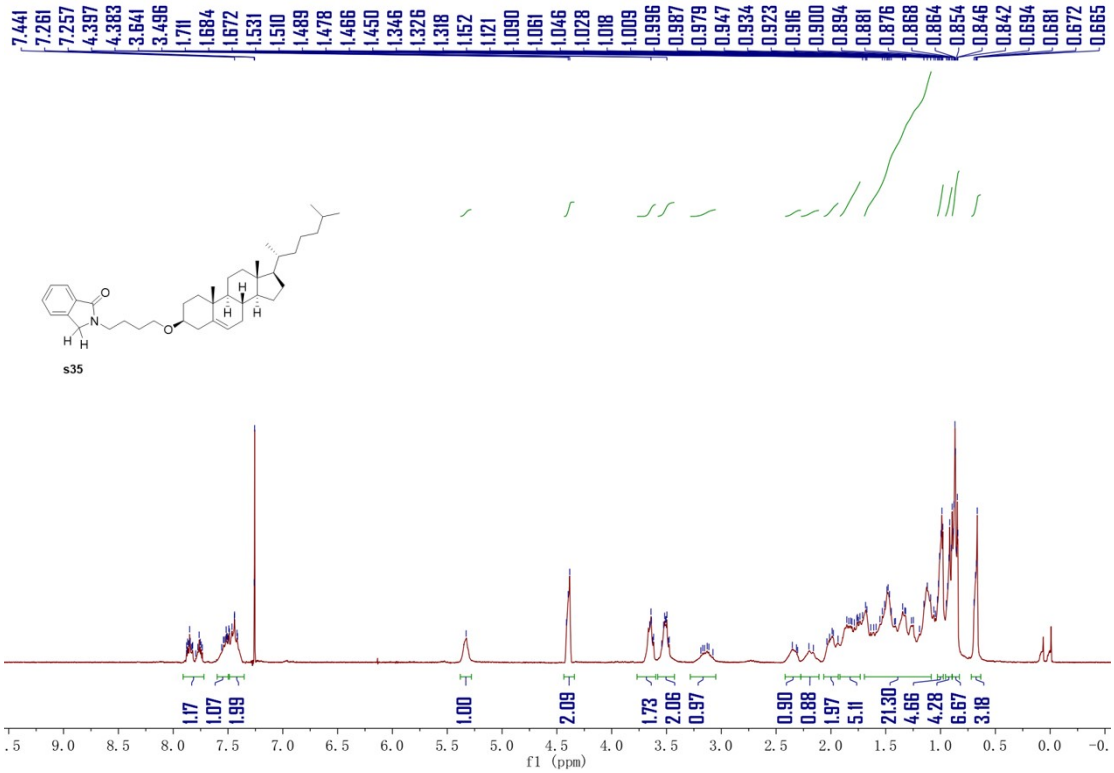
^{1}H NMR (300 MHz, $CDCl_3$):



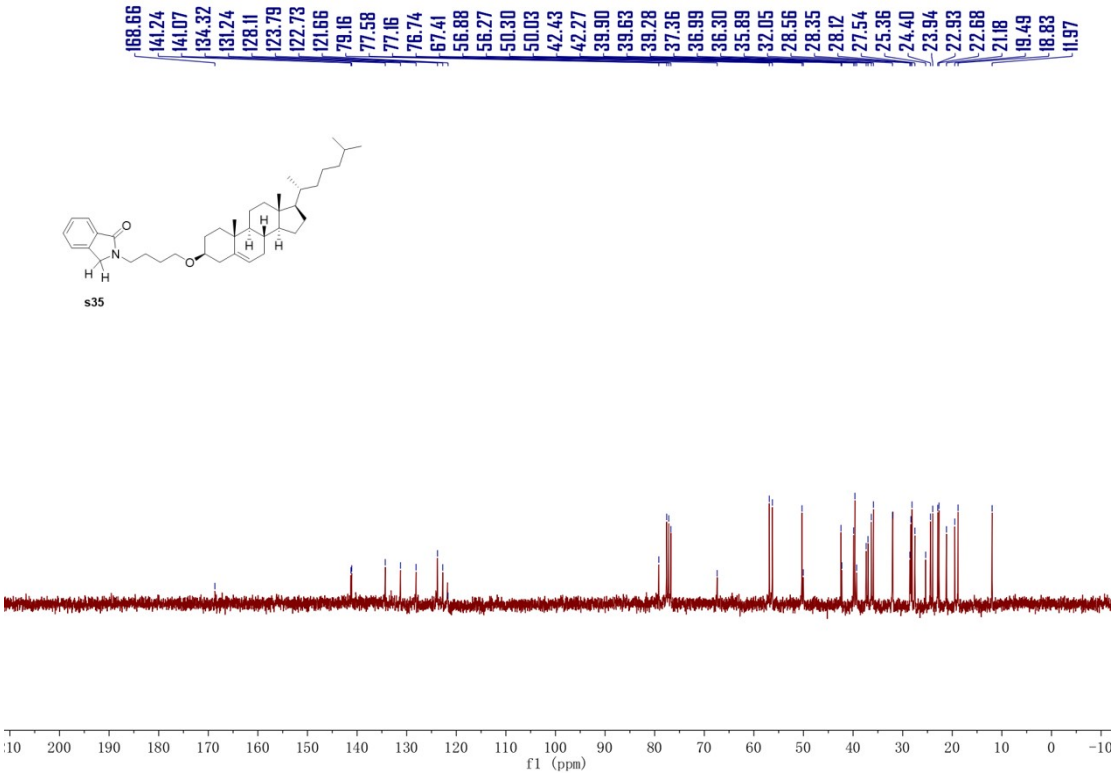
^{13}C NMR (75 MHz, $CDCl_3$):



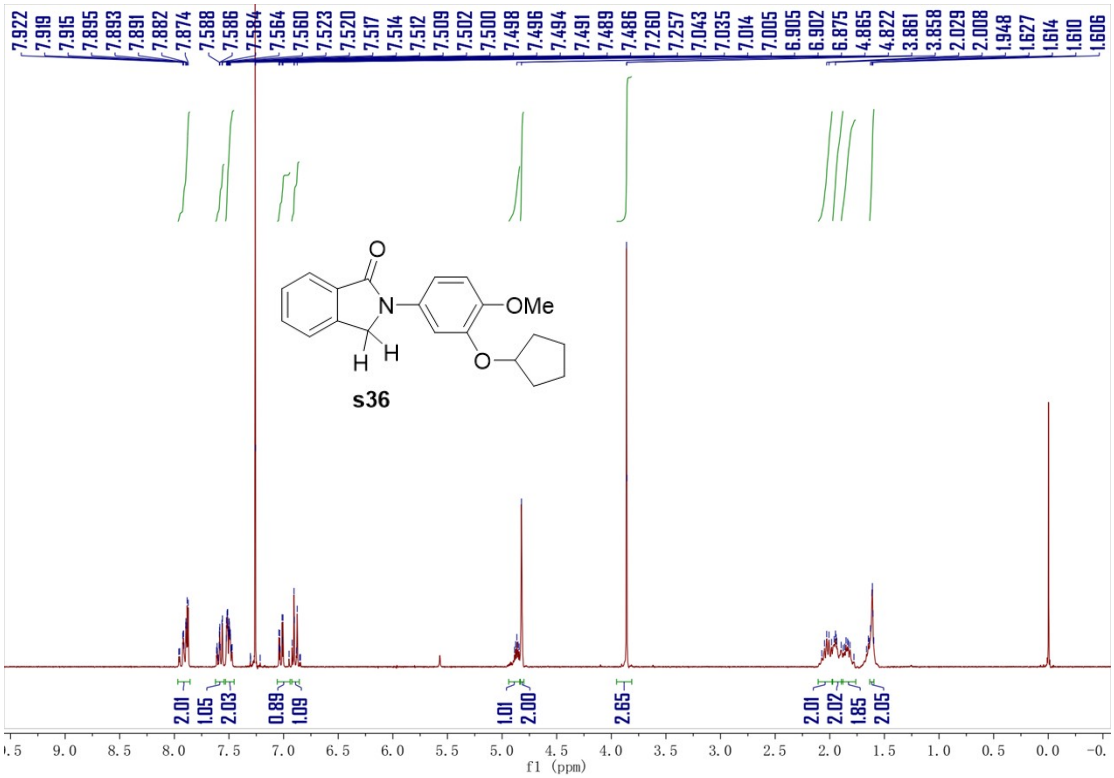
^{1}H NMR (300 MHz, $CDCl_3$):



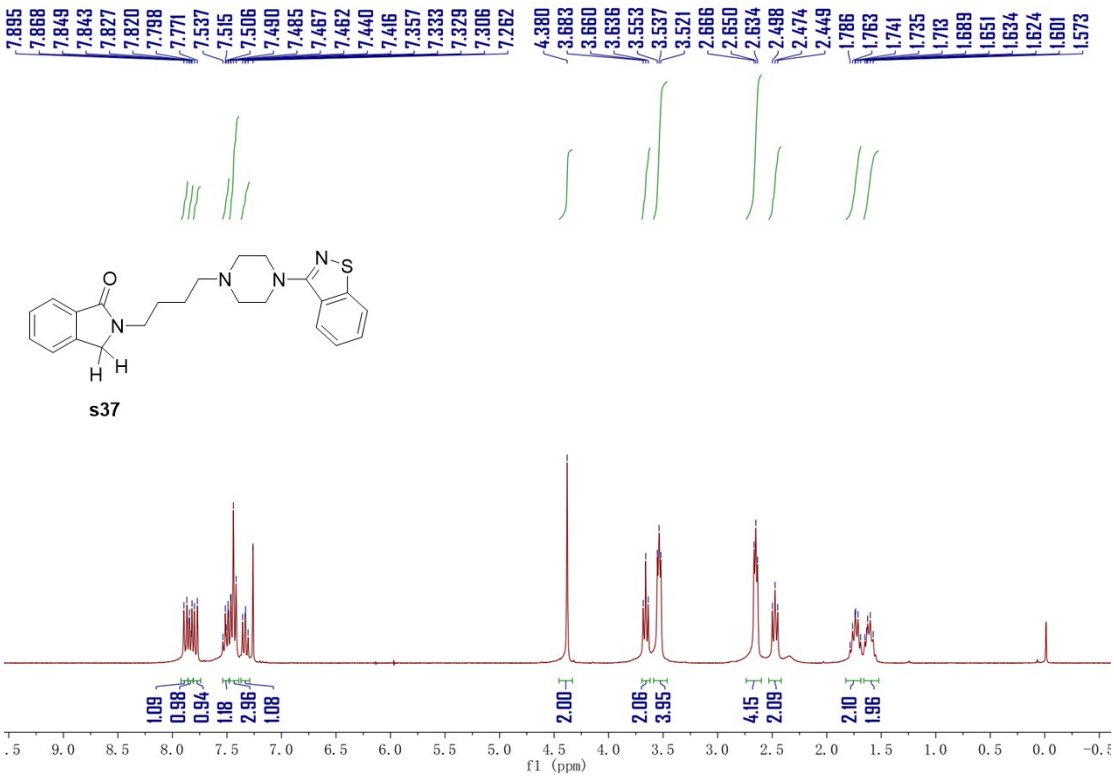
^{13}C NMR (75 MHz, $CDCl_3$):



^{1}H NMR (300 MHz, $CDCl_3$):



^{1}H NMR (300 MHz, $CDCl_3$):



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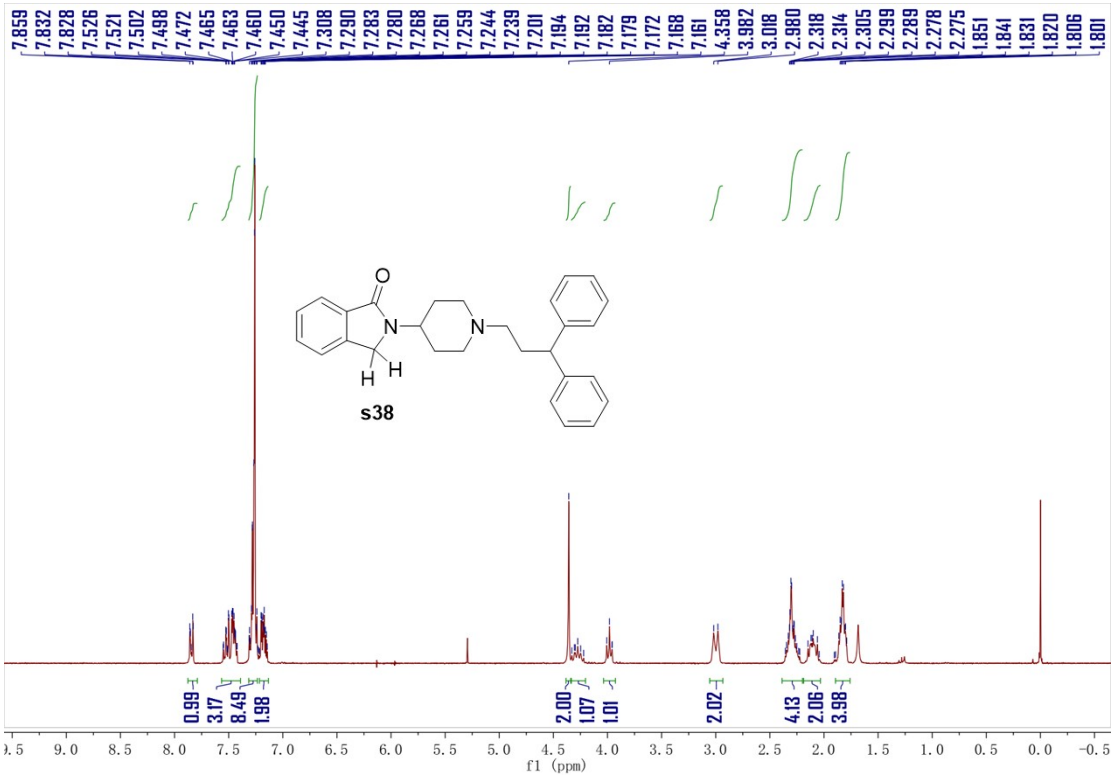
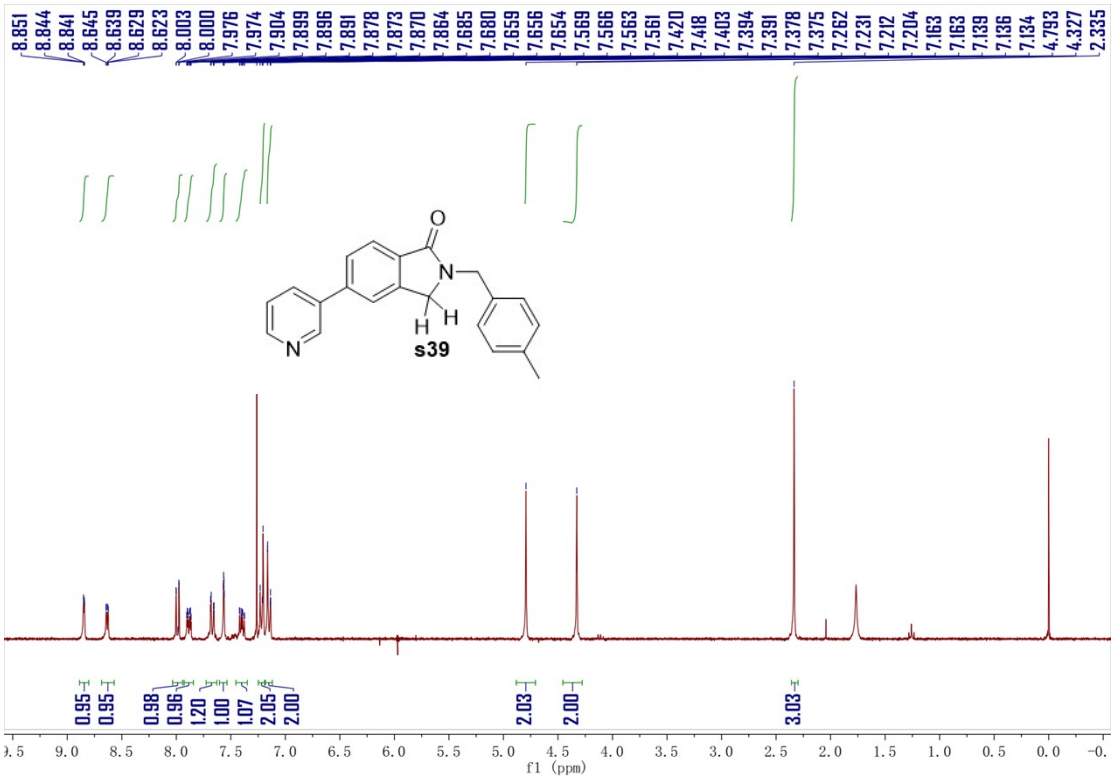
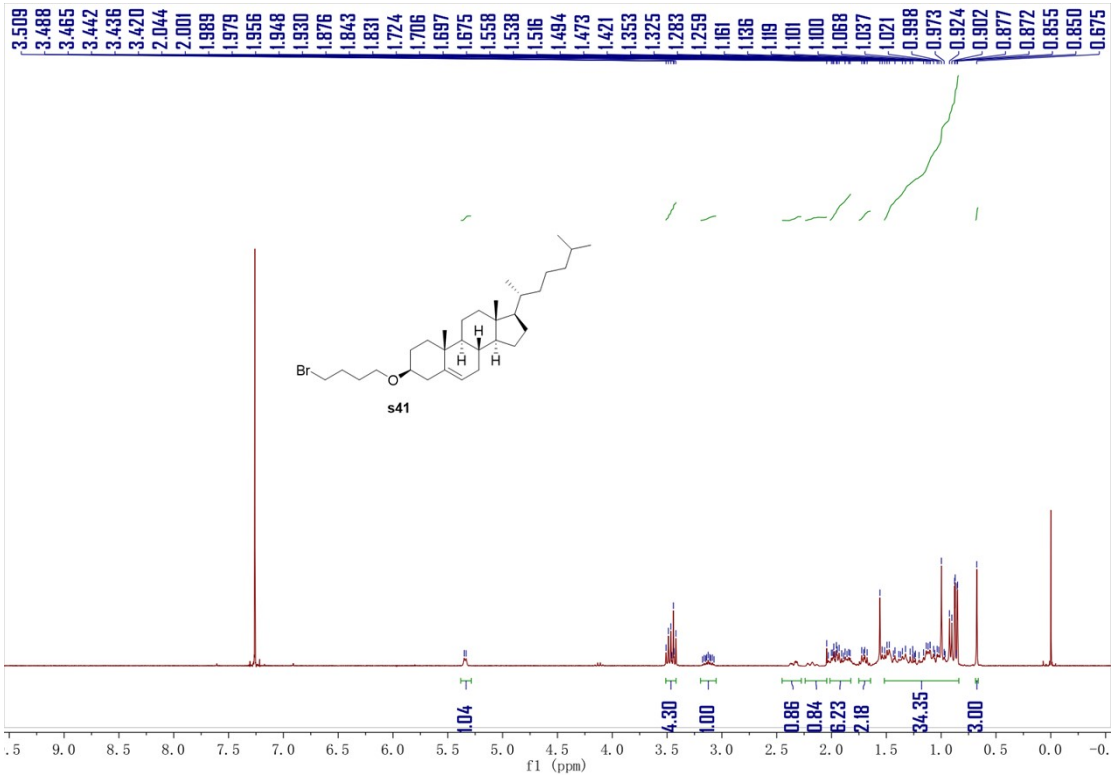


^{1}H NMR (300 MHz, $CDCl_3$):



^{1}H NMR (300 MHz, $CDCl_3$):



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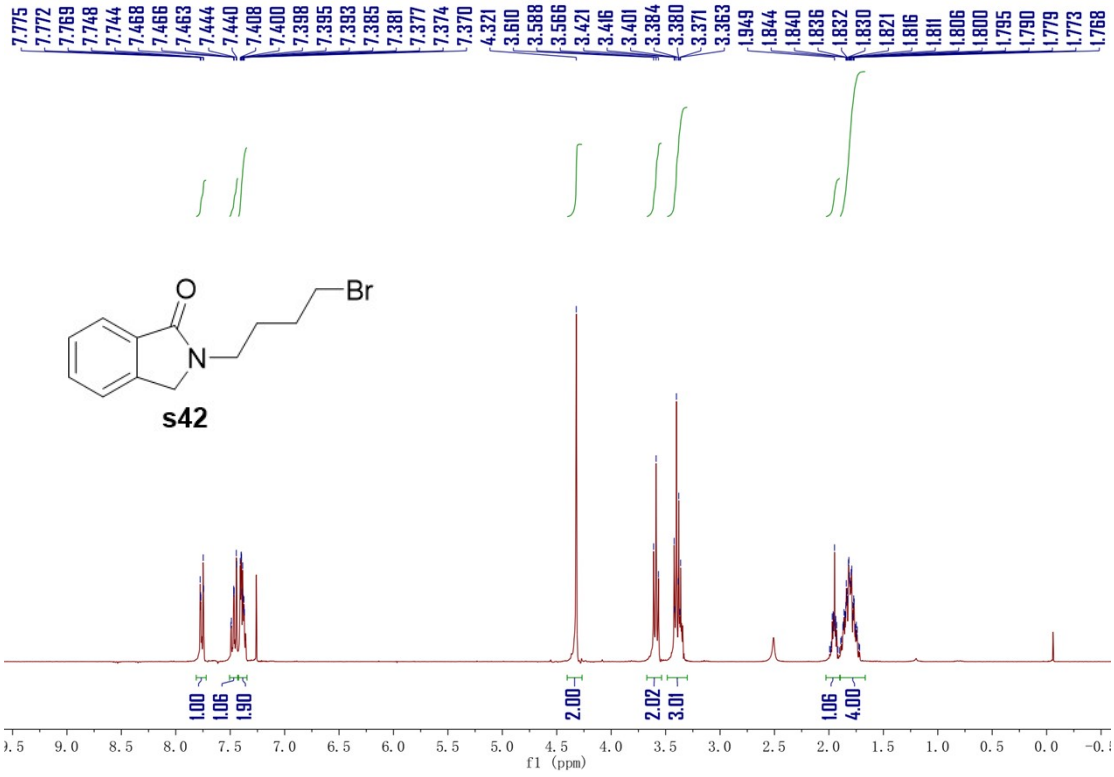

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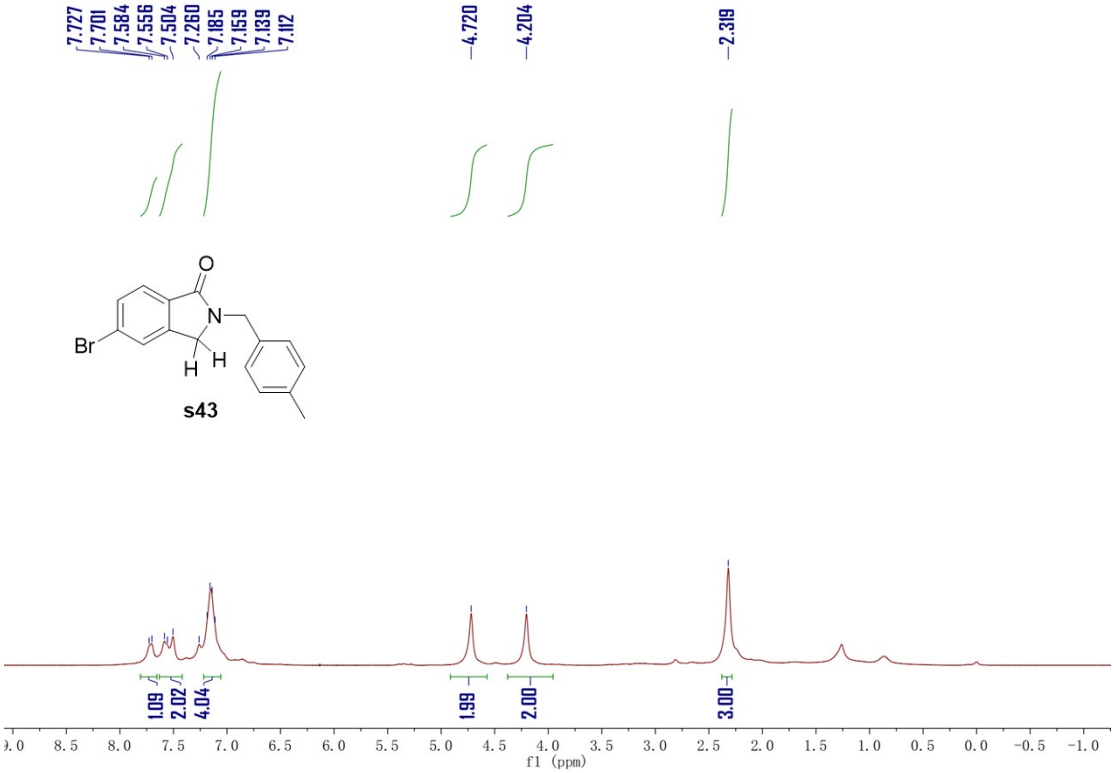
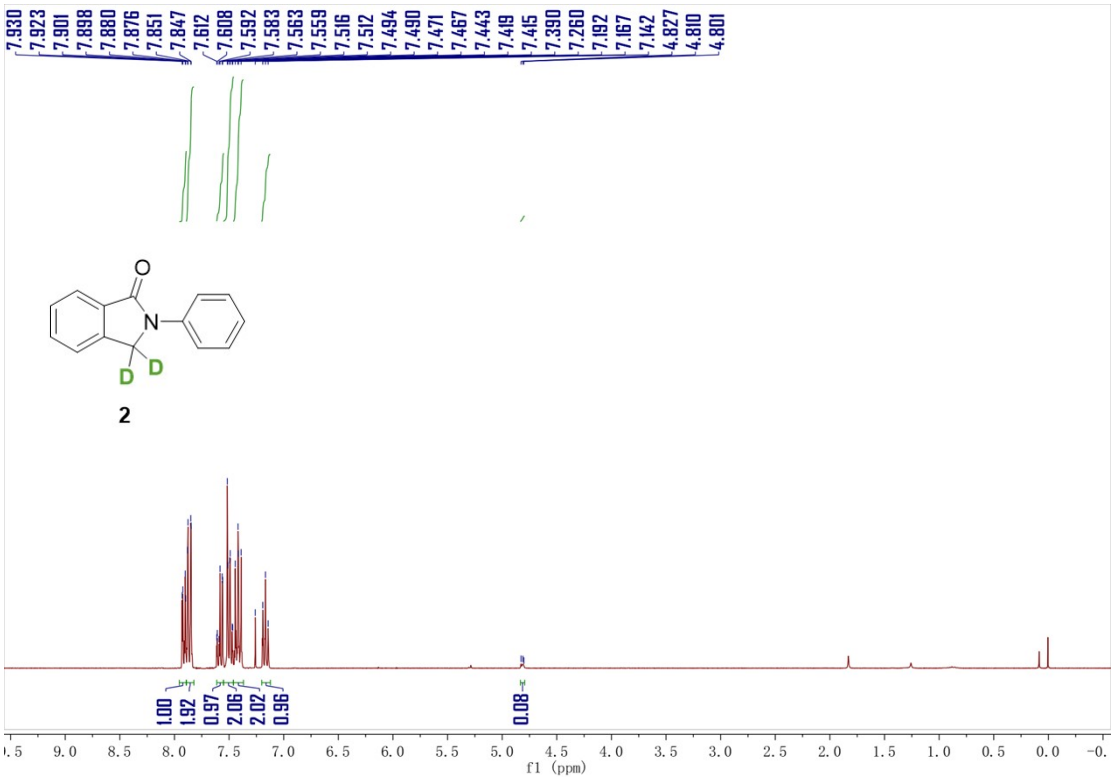


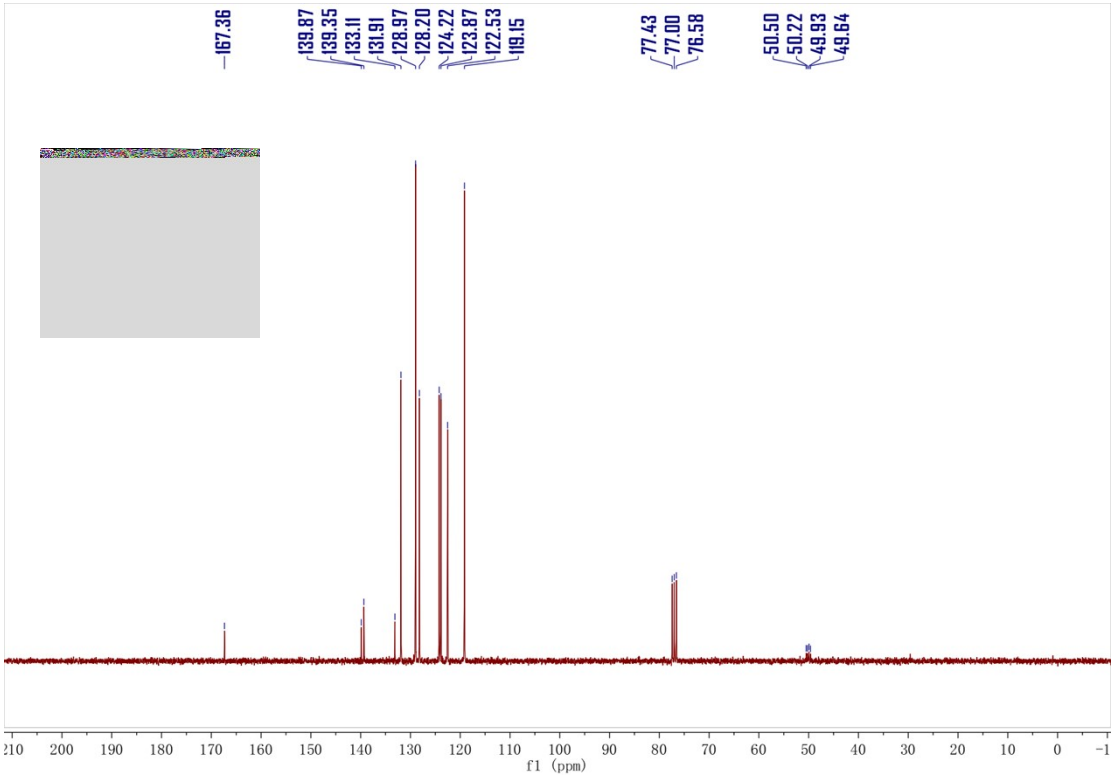
s43

^{1}H NMR (300 MHz, $CDCl_3$):

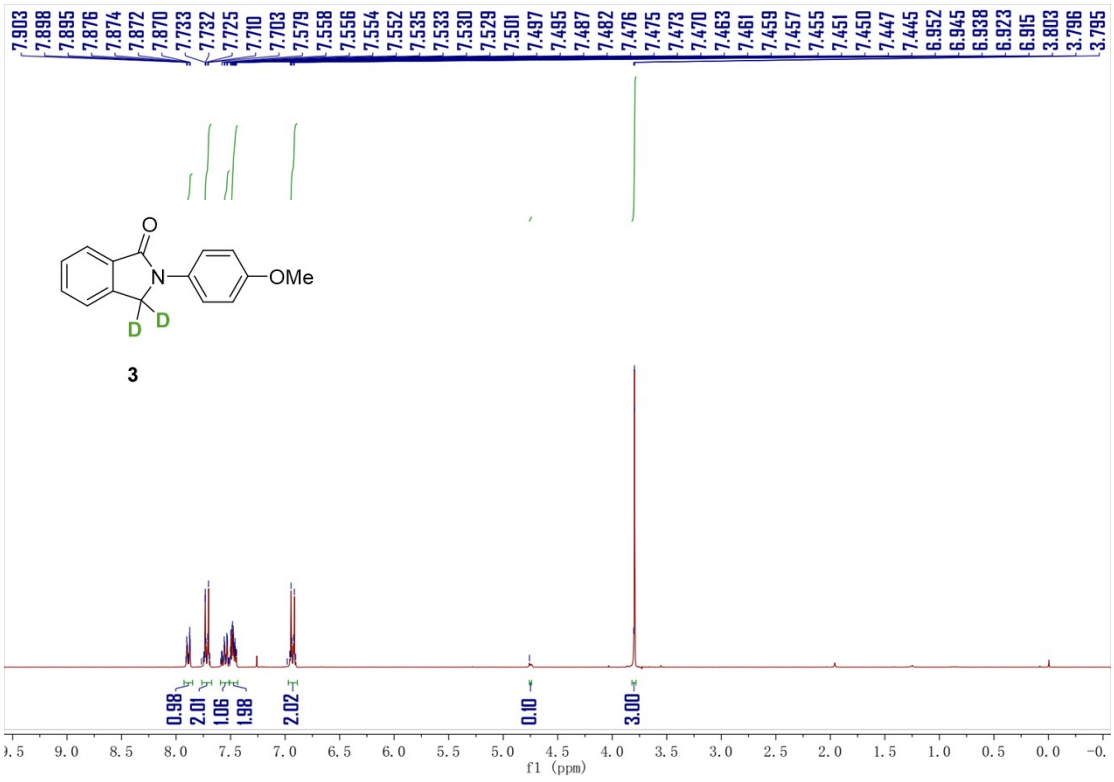


2

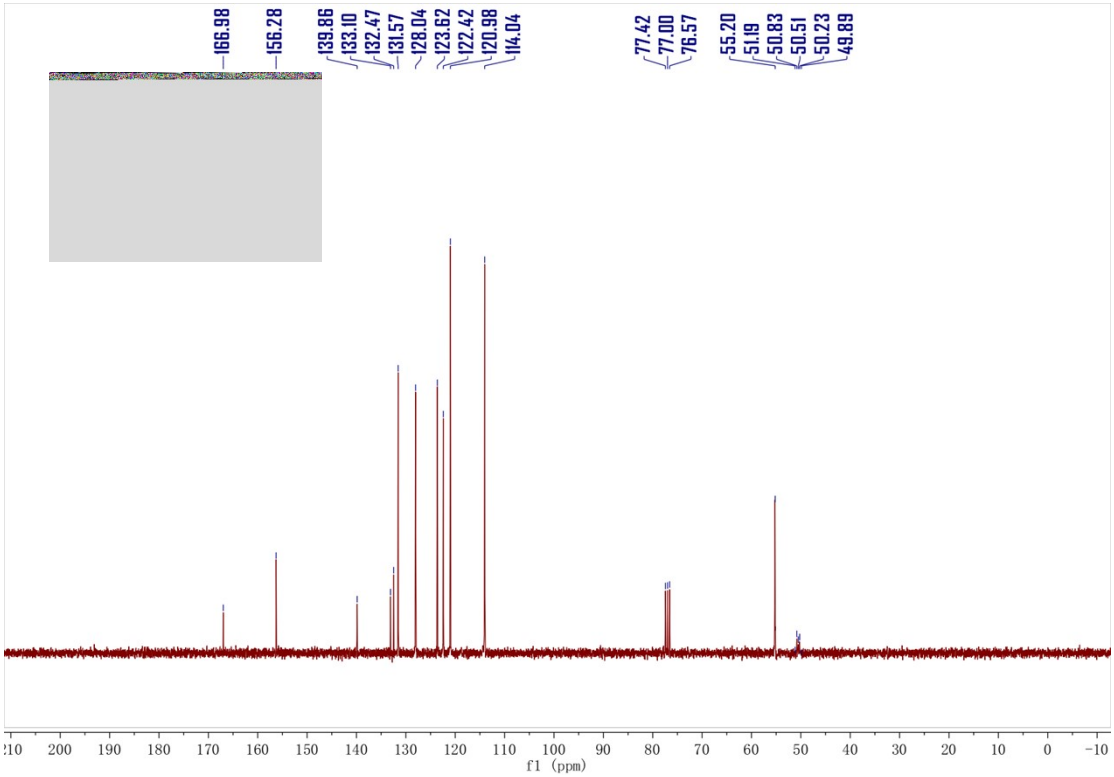
^{13}C NMR (75 MHz, $CDCl_3$):



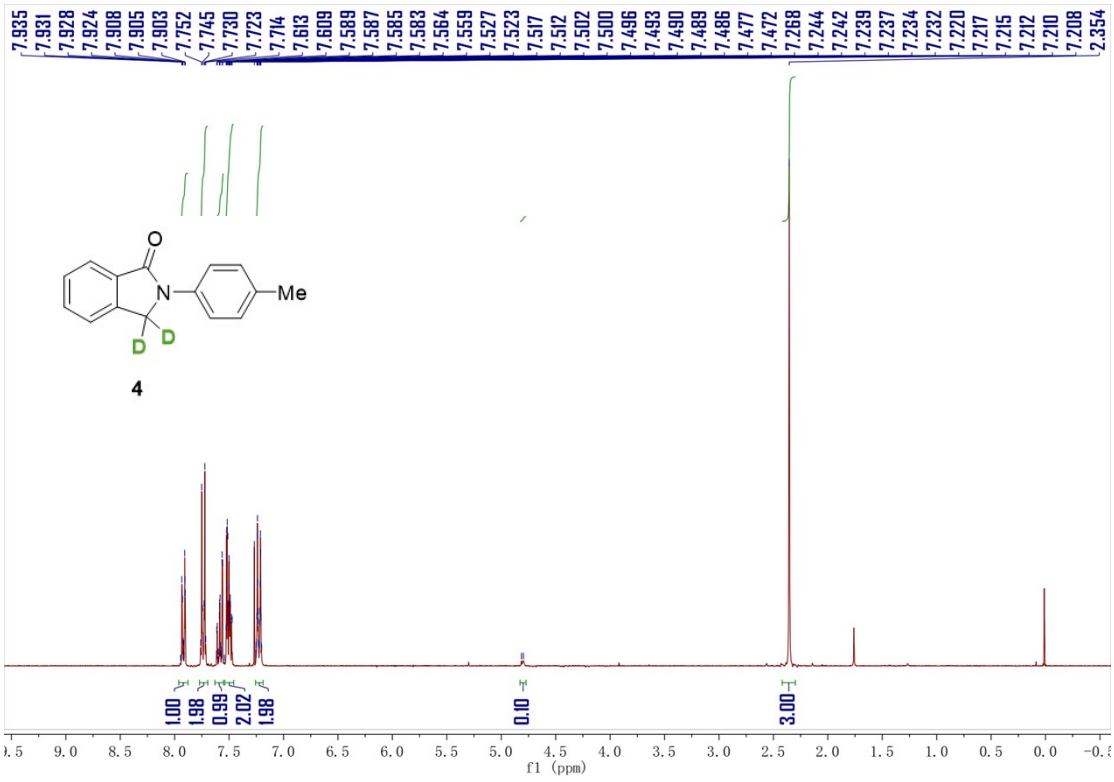
^{1}H NMR (300 MHz, $CDCl_3$):



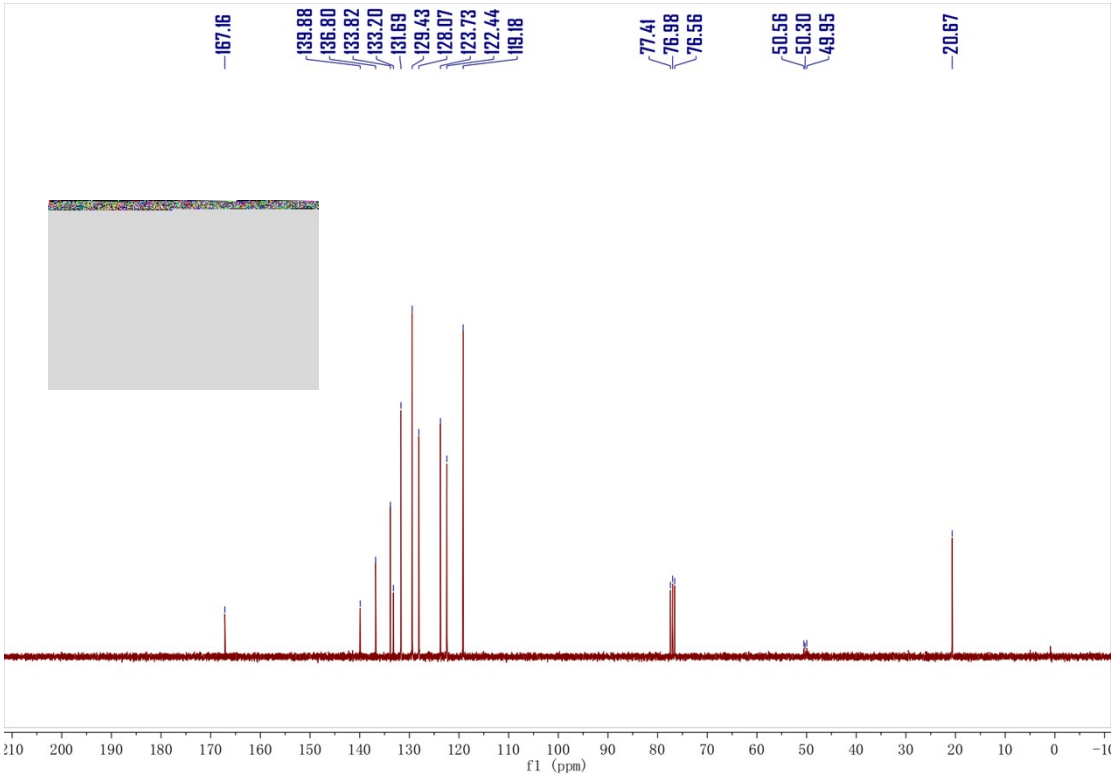
^{13}C NMR (75 MHz, $CDCl_3$):



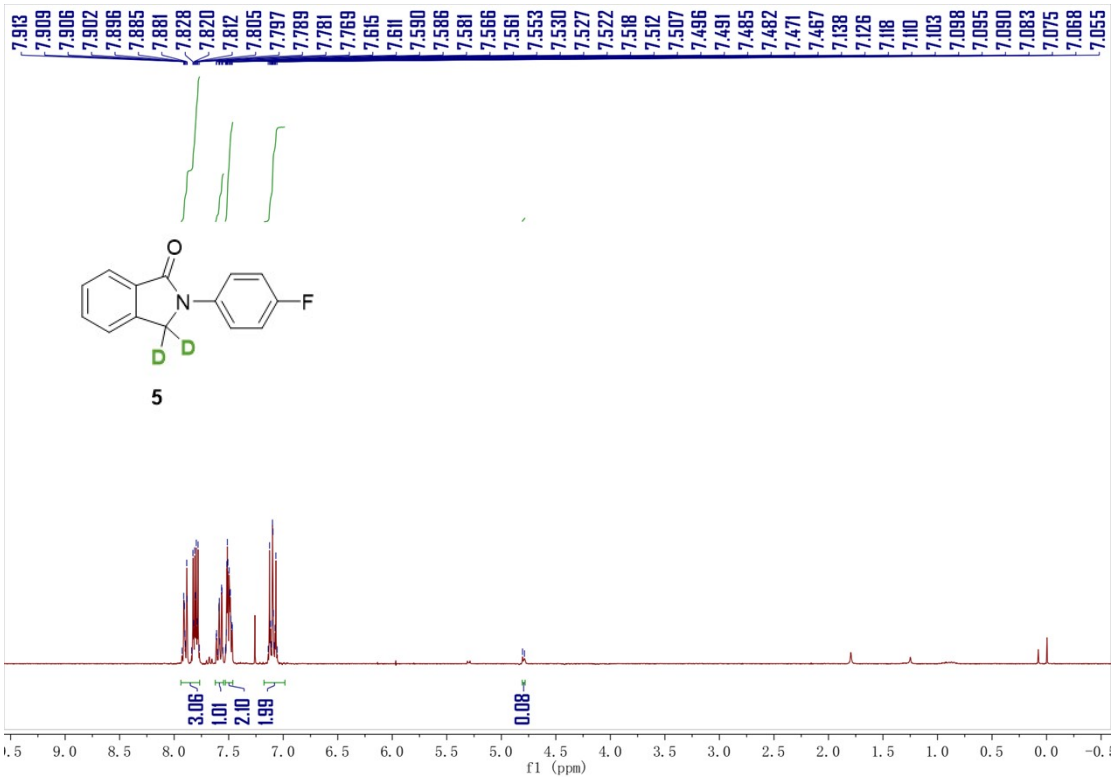
^{1}H NMR (300 MHz, $CDCl_3$):



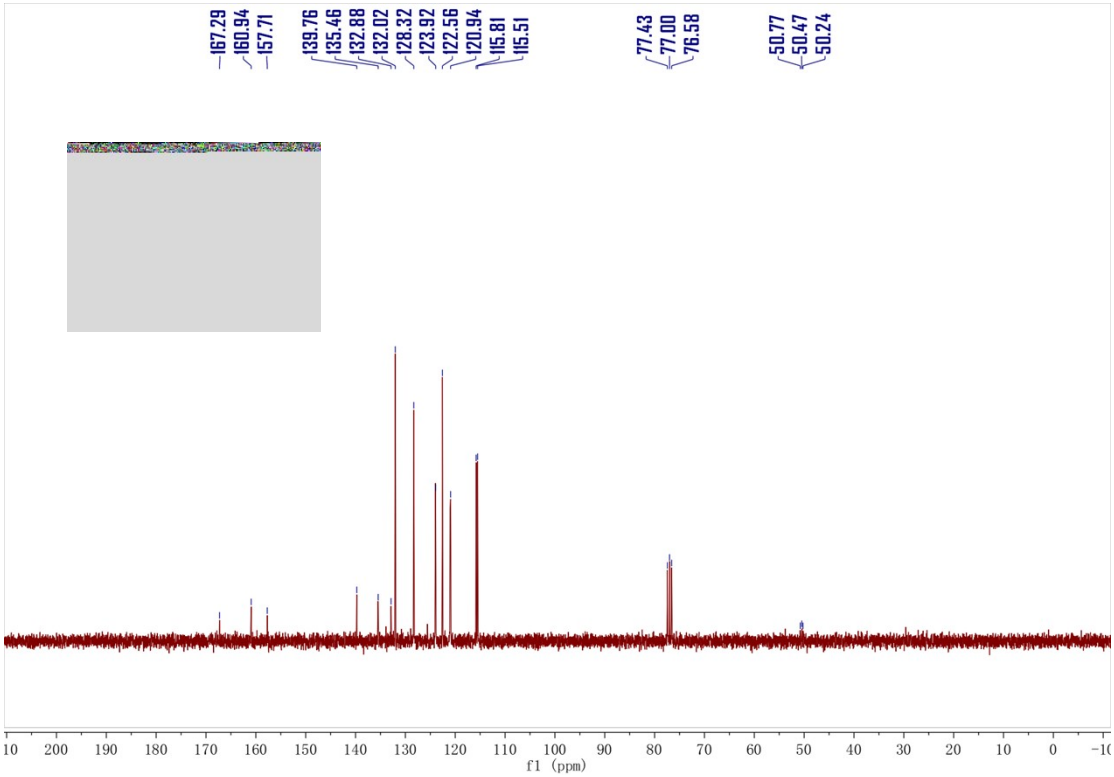
^{13}C NMR (75 MHz, $CDCl_3$):



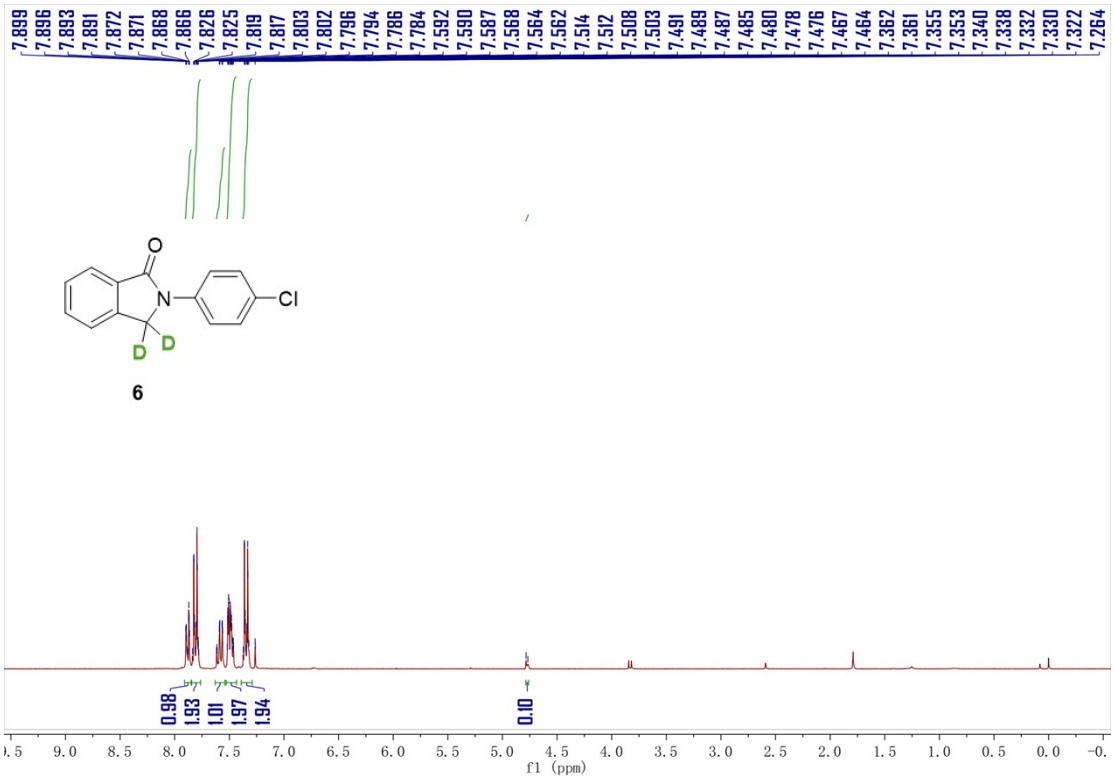
^{1}H NMR (300 MHz, $CDCl_3$):



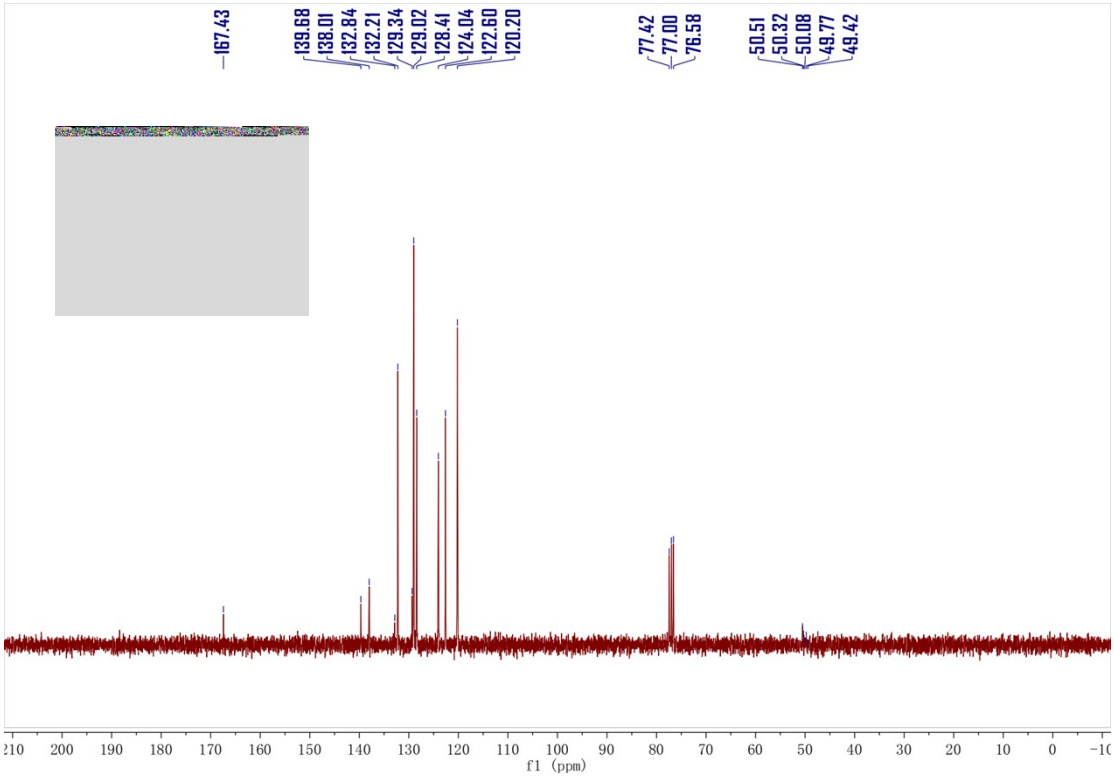
^{13}C NMR (75 MHz, $CDCl_3$):



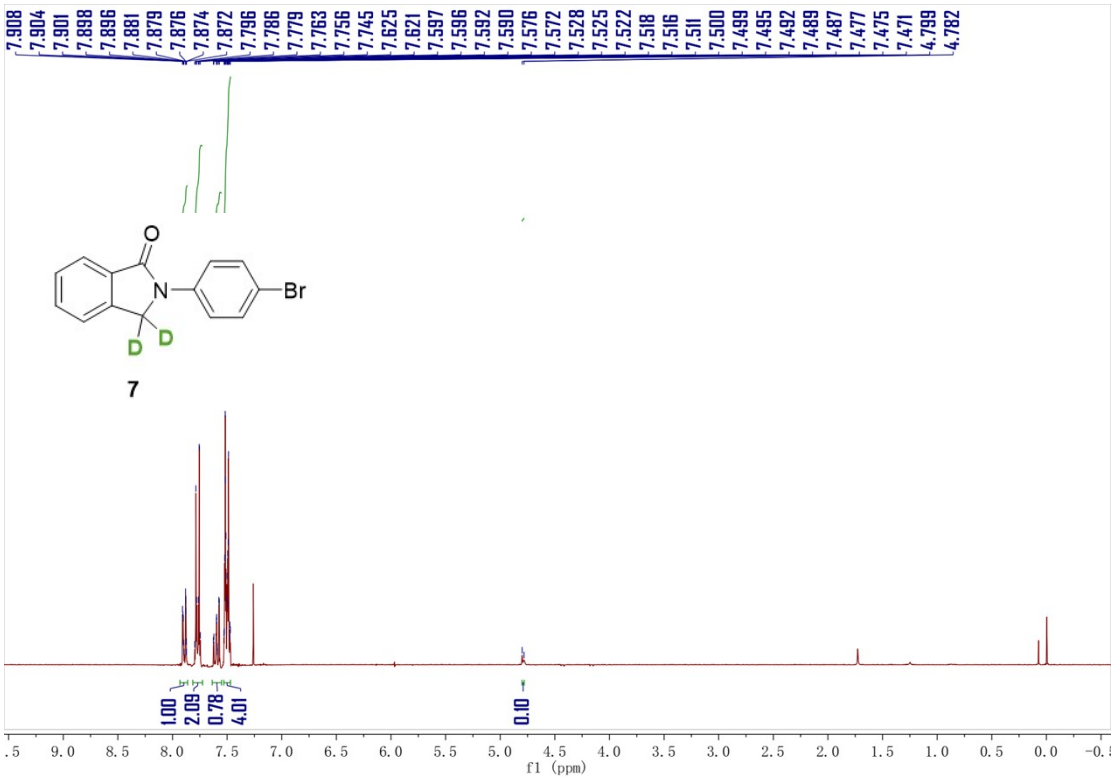
^{1}H NMR (300 MHz, $CDCl_3$):



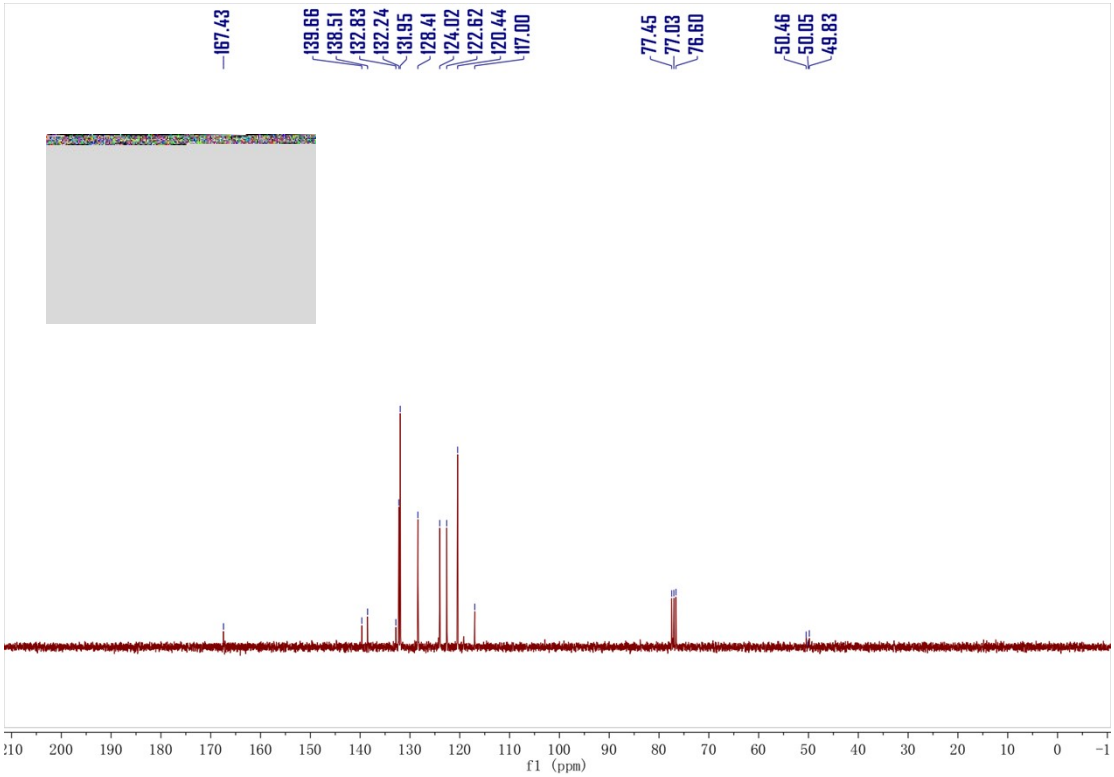
^{13}C NMR (75 MHz, $CDCl_3$):



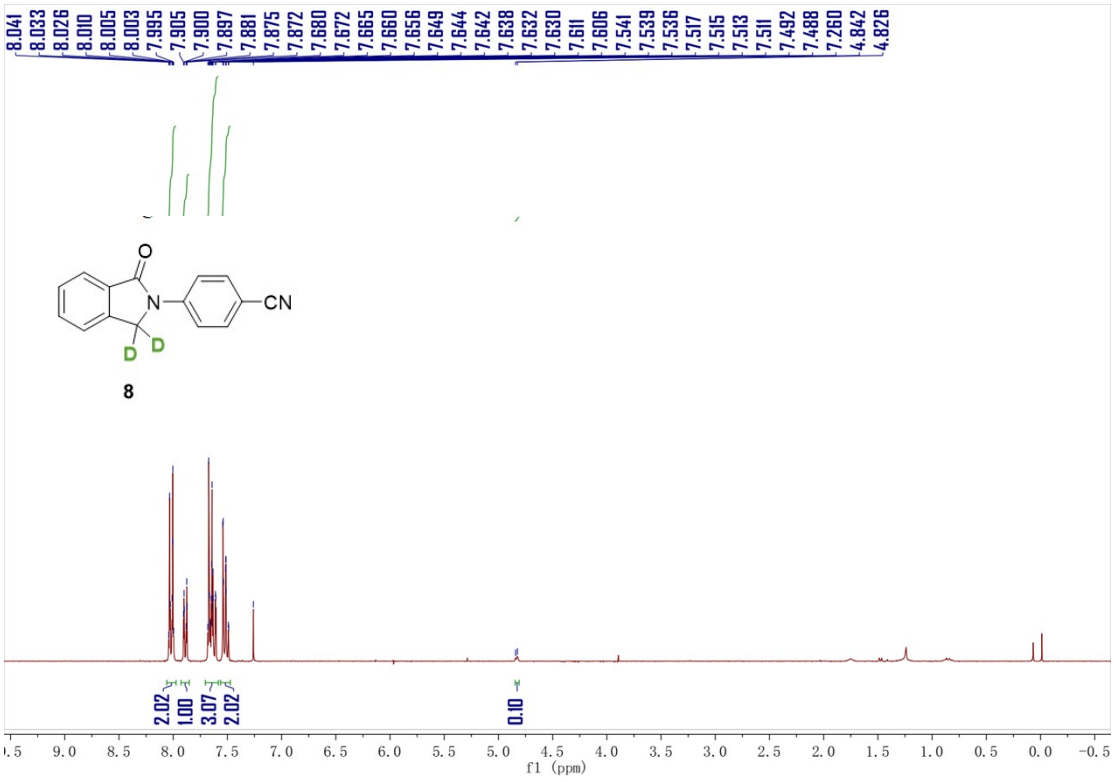
^{1}H NMR (300 MHz, $CDCl_3$):



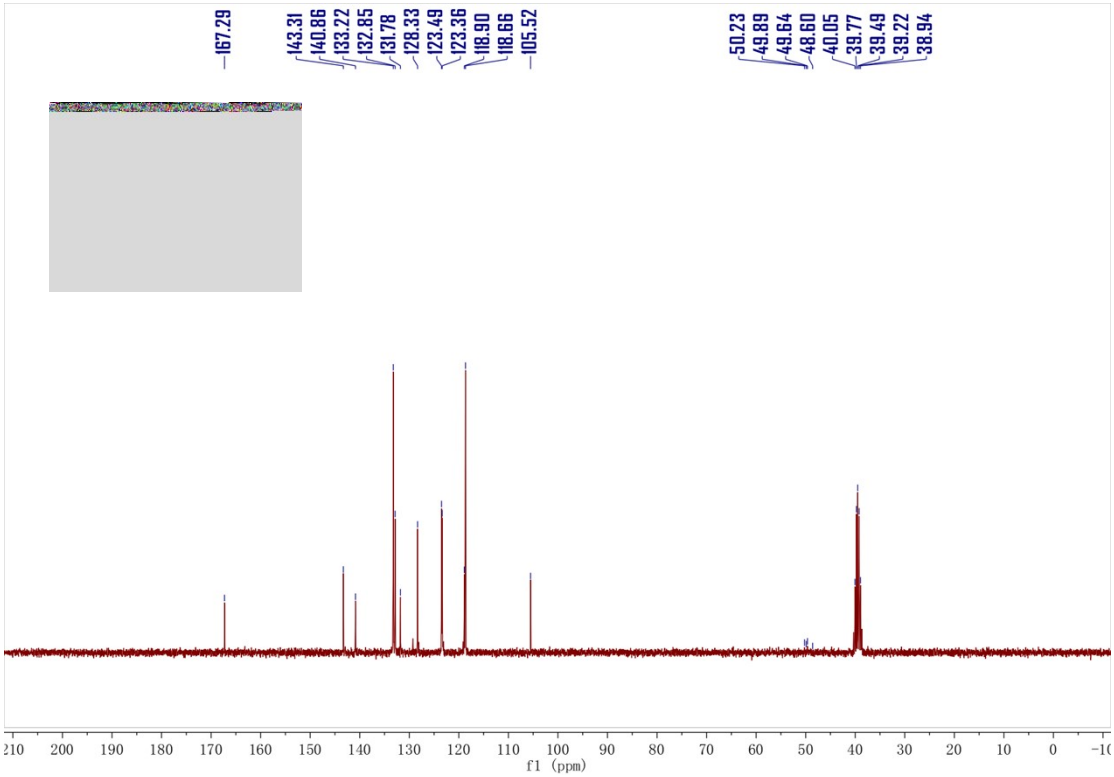
^{13}C NMR (75 MHz, $CDCl_3$):



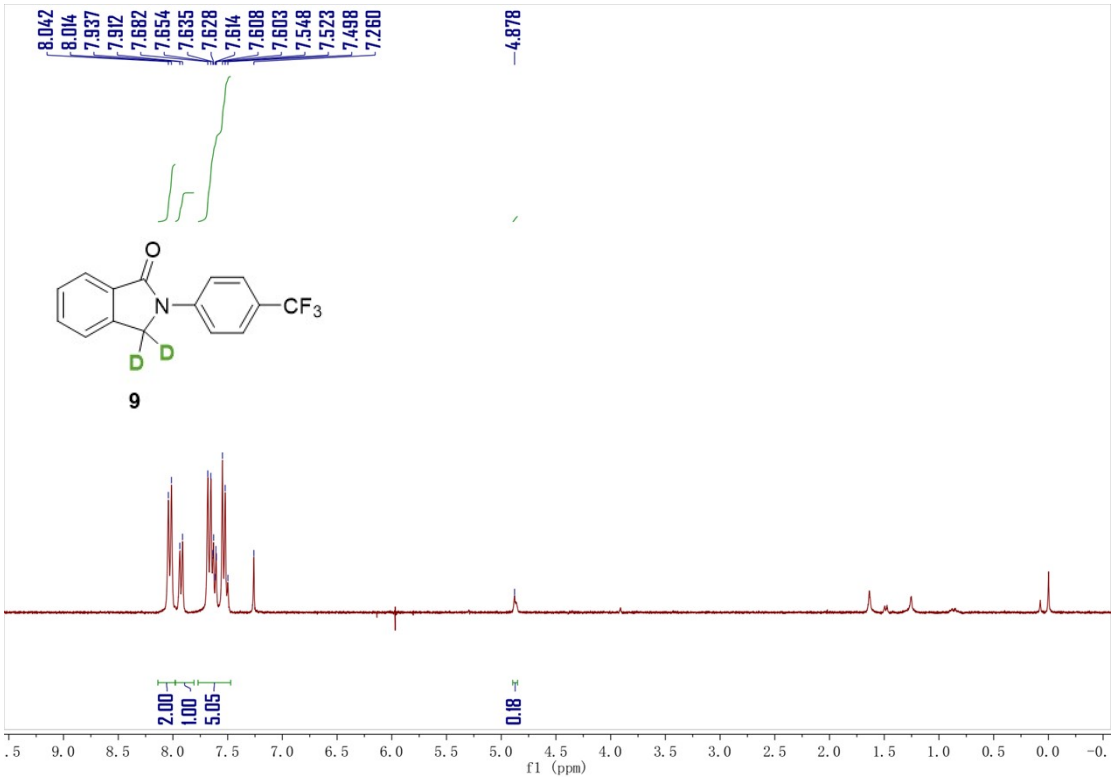
^{1}H NMR (300 MHz, $CDCl_3$):



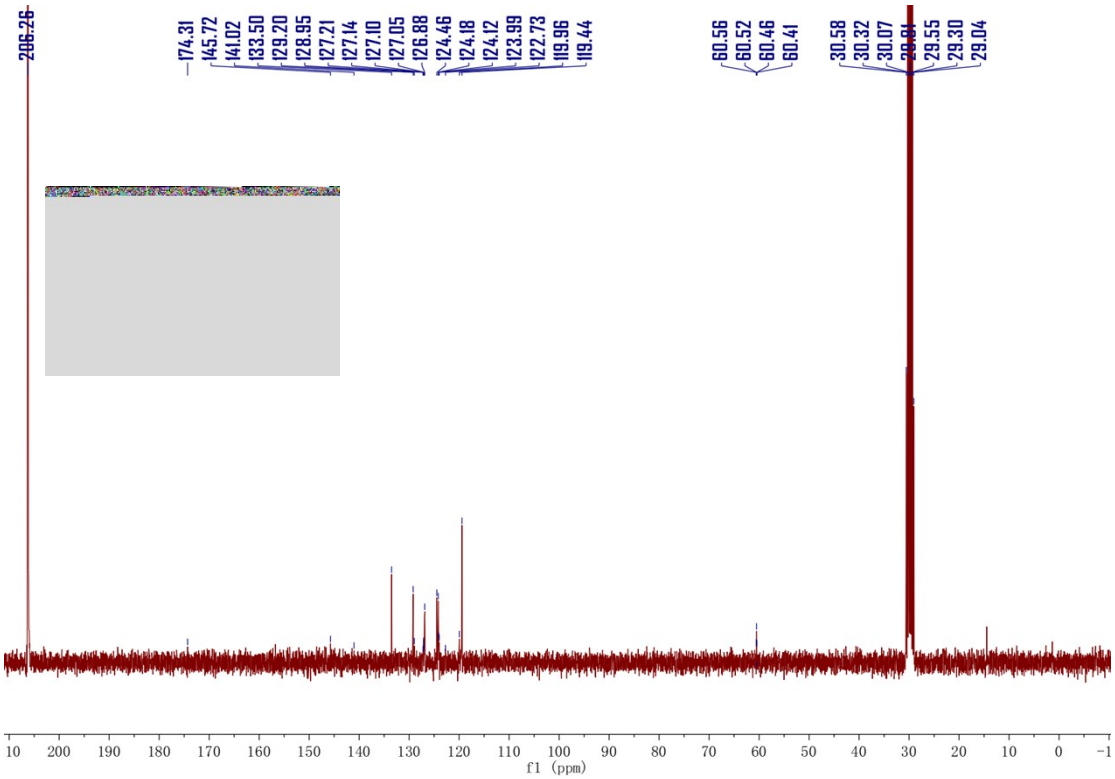
^{13}C NMR (75 MHz, DMSO-d_6):



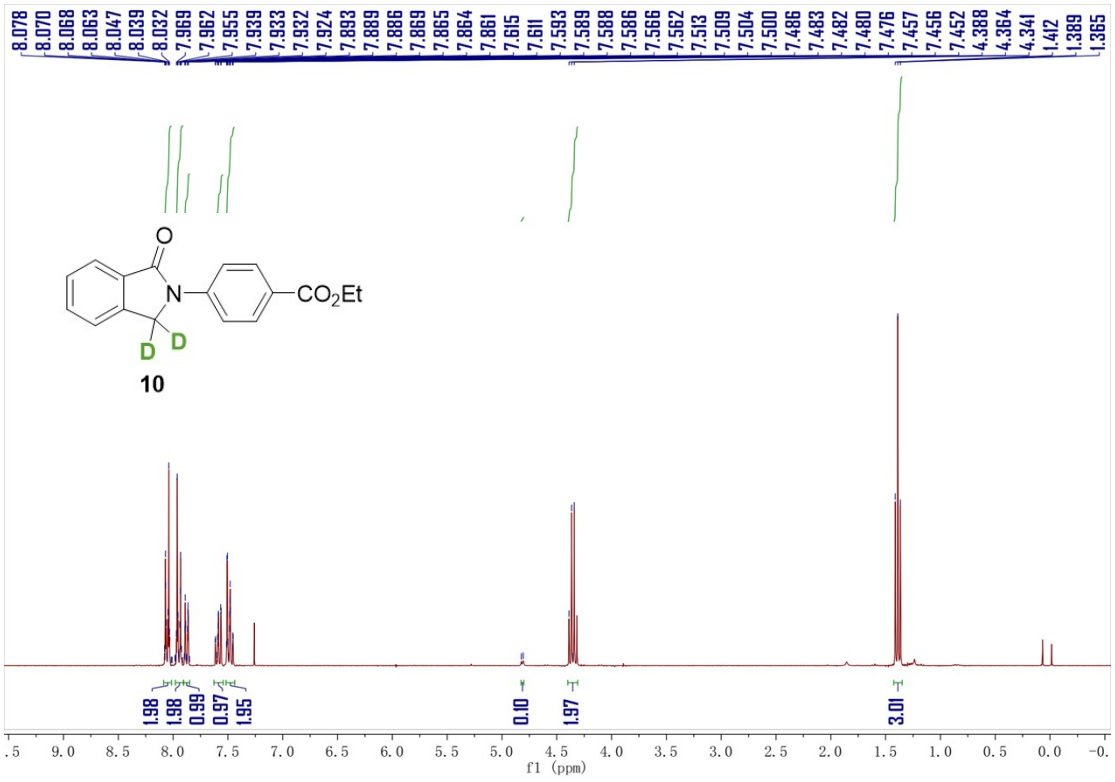
^{1}H NMR (300 MHz, $CDCl_3$):



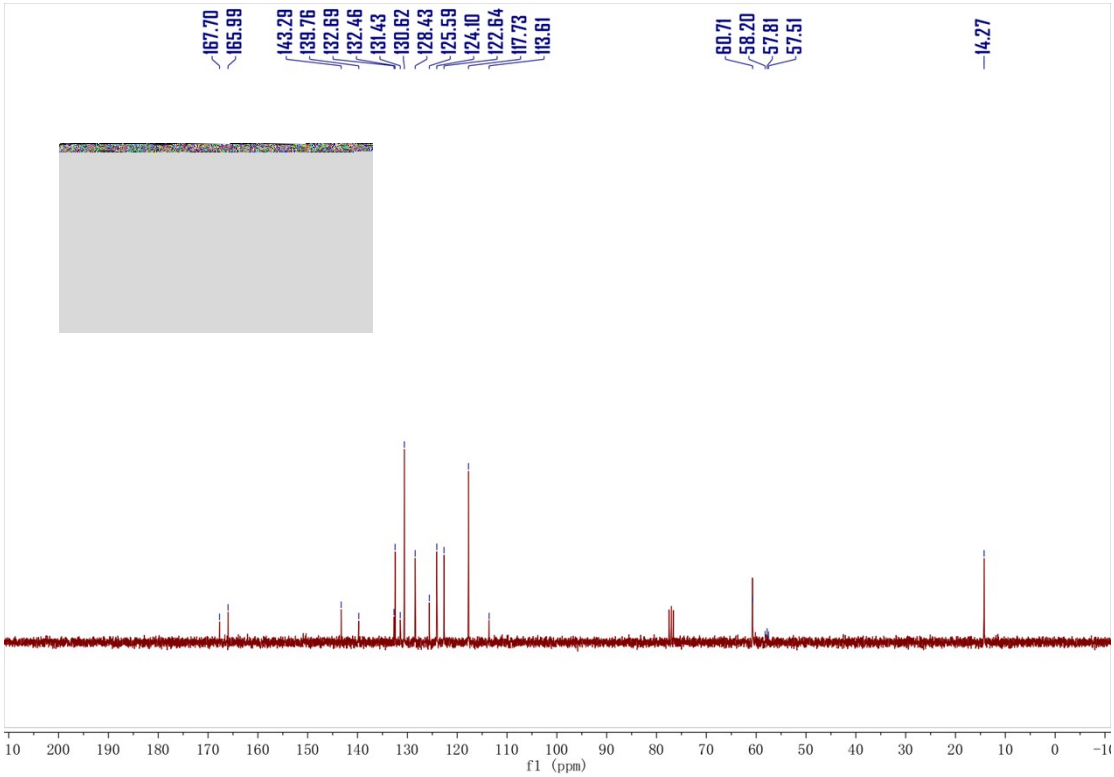
^{13}C NMR (75 MHz, $(CD_3)_2CO$):



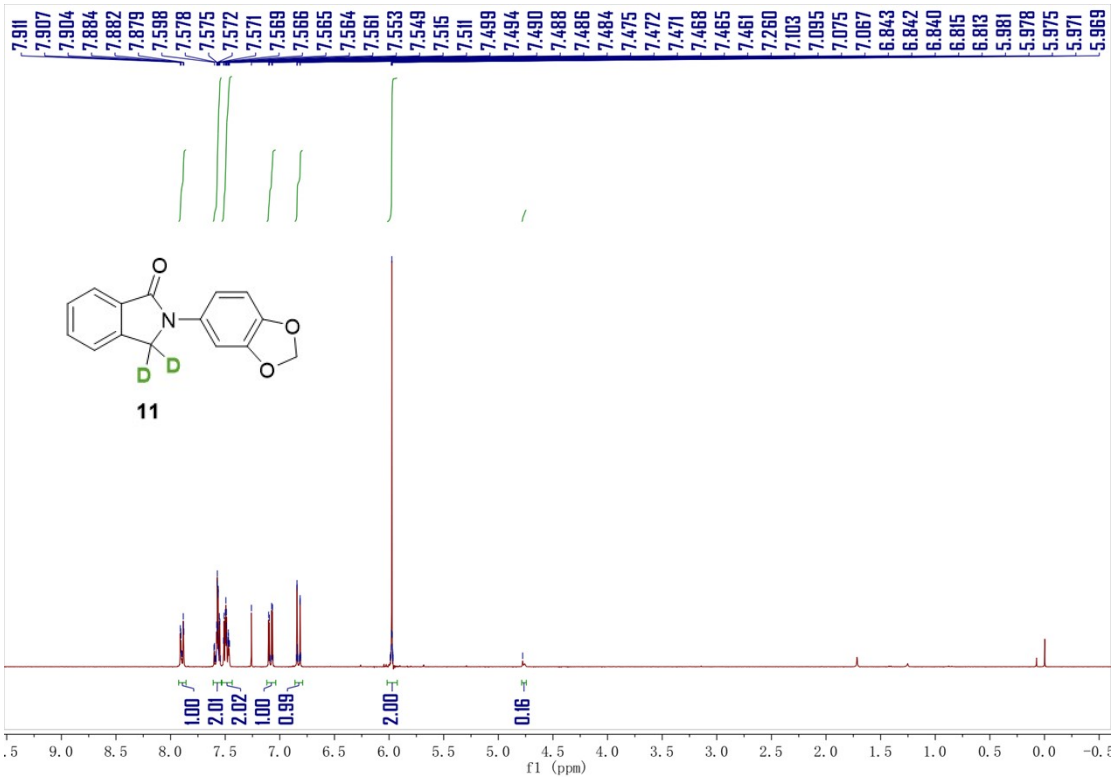
^{1}H NMR (300 MHz, $CDCl_3$):



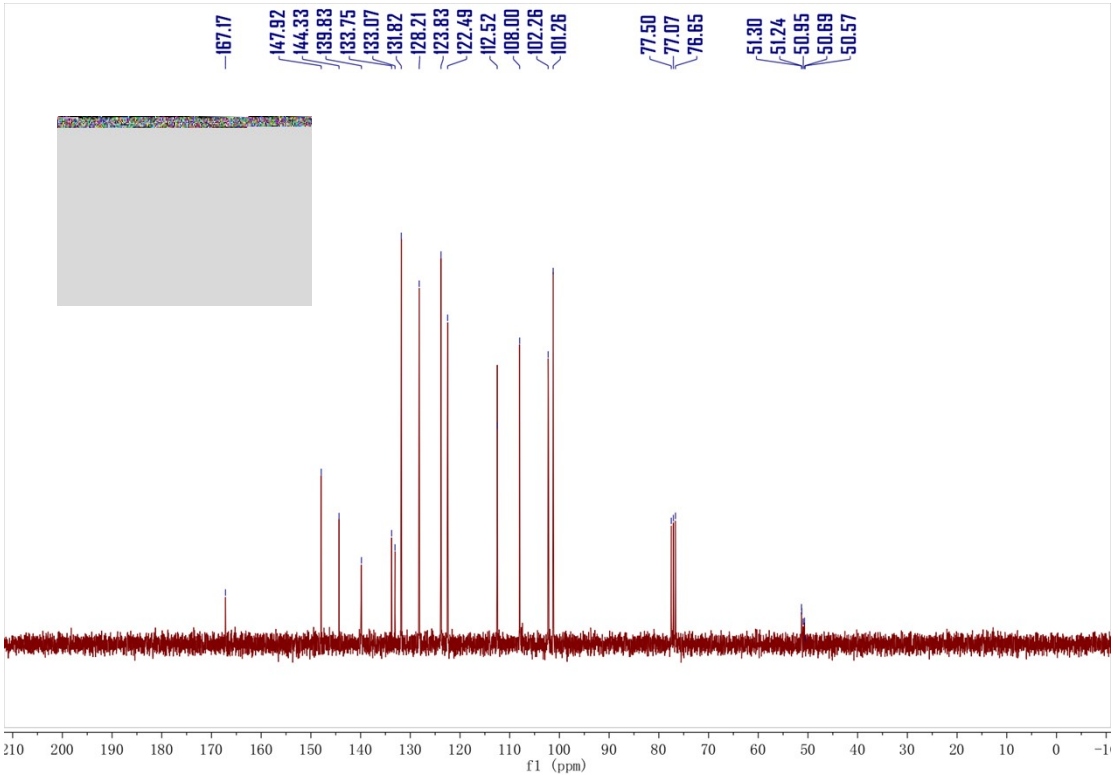
^{13}C NMR (75 MHz, $CDCl_3$):



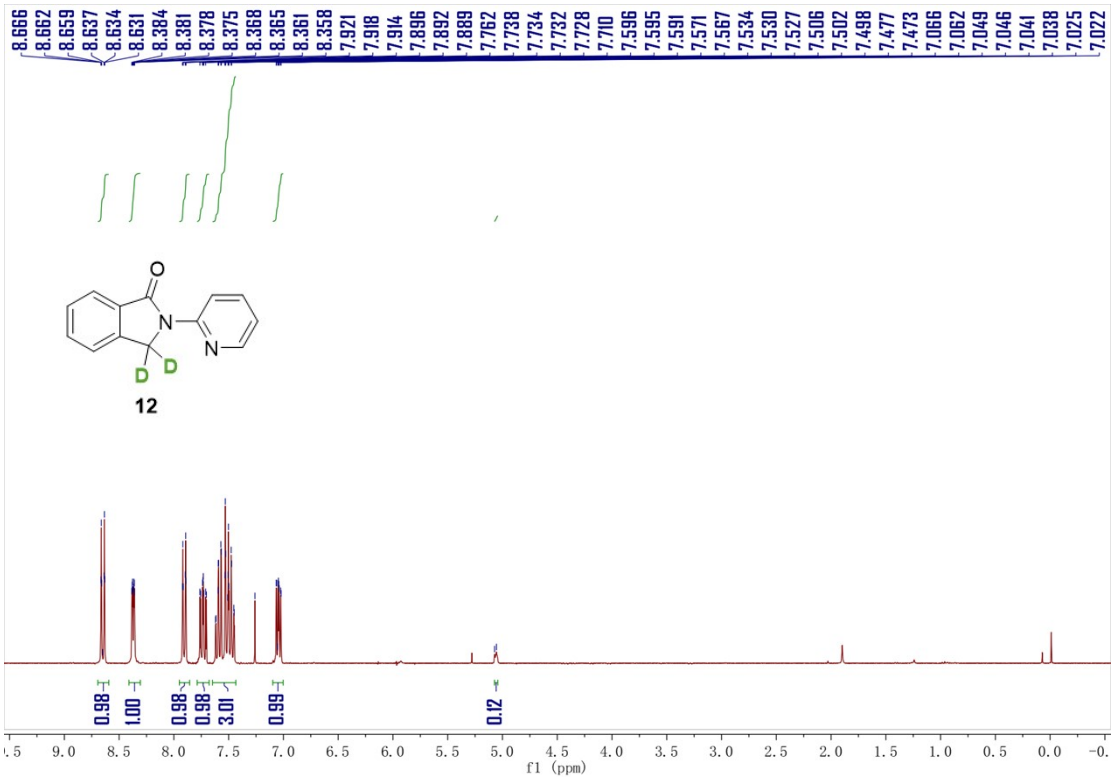
^{1}H NMR (300 MHz, $CDCl_3$):



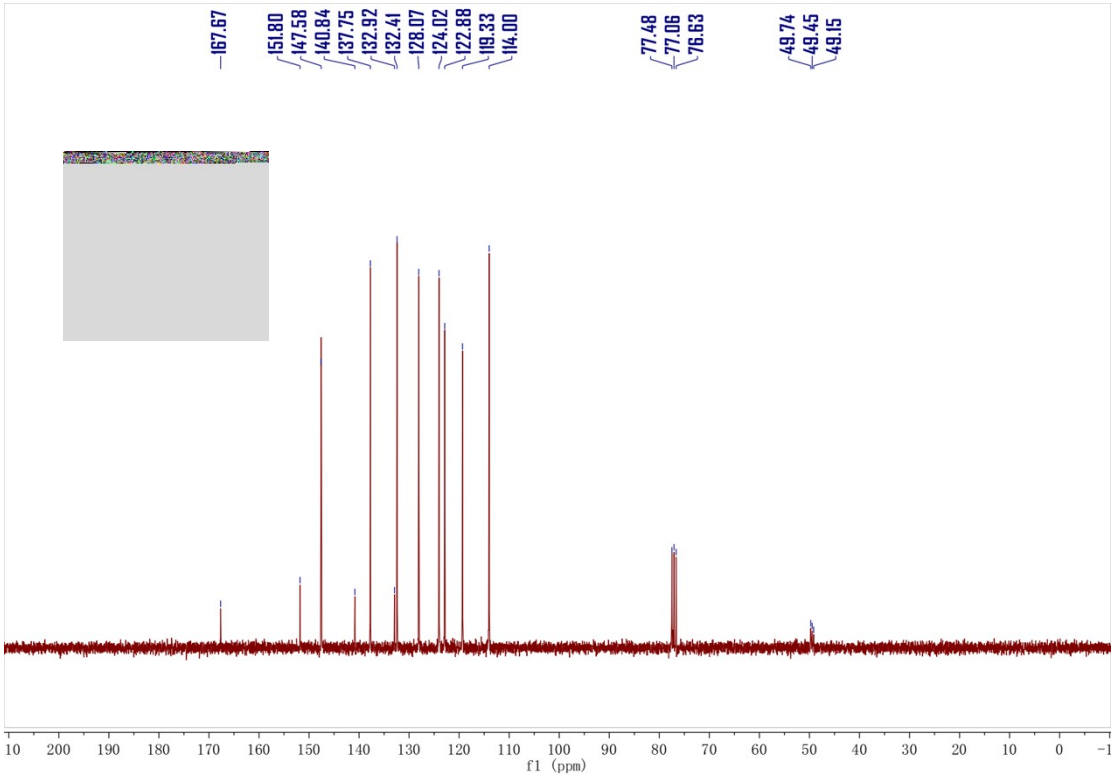
^{13}C NMR (75 MHz, $CDCl_3$):



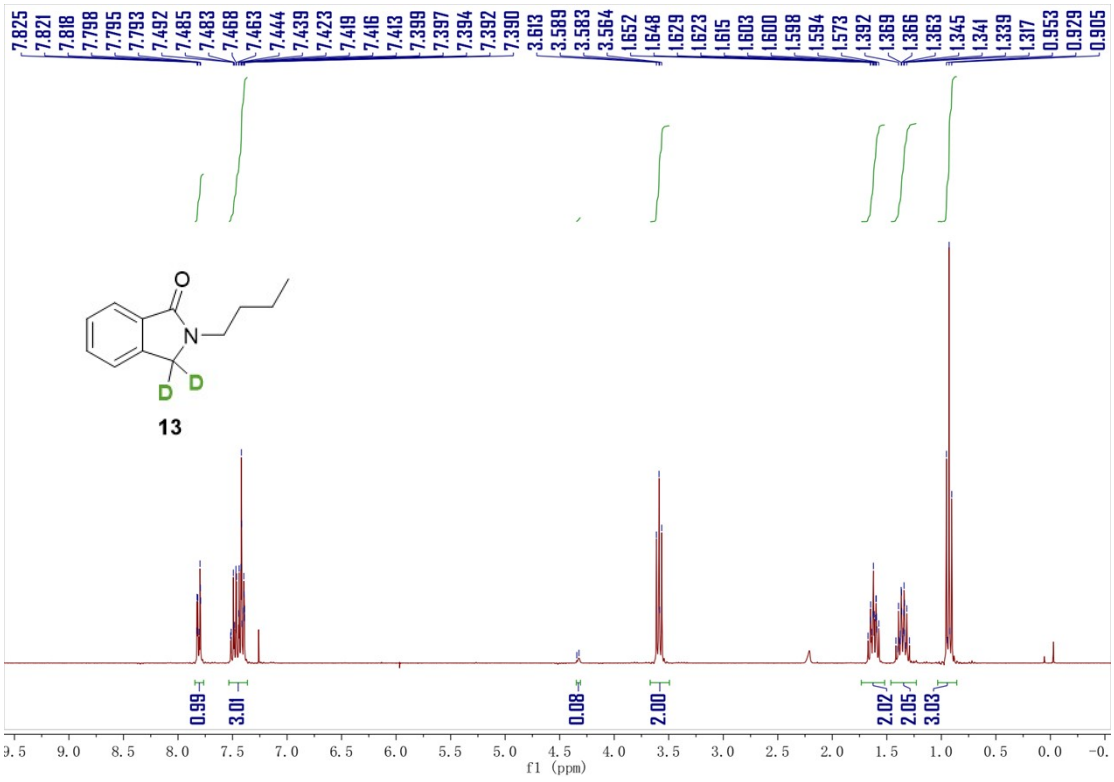
^{1}H NMR (300 MHz, $CDCl_3$):



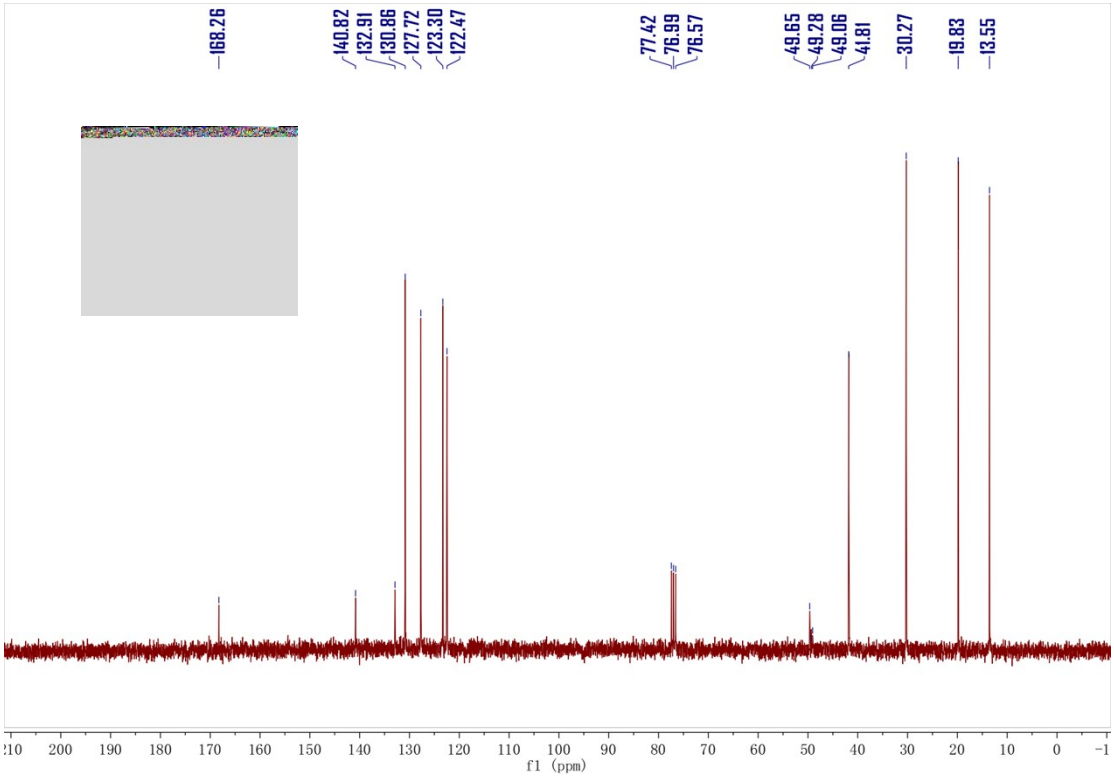
^{13}C NMR (75 MHz, $CDCl_3$):



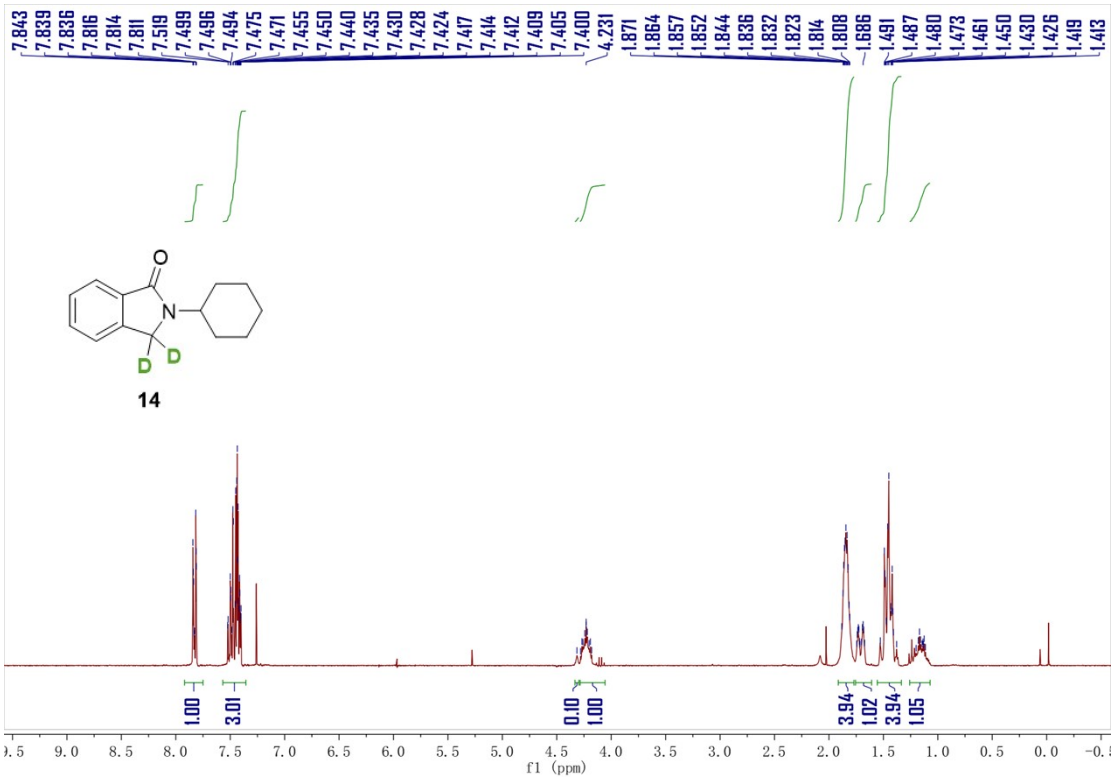
^{1}H NMR (300 MHz, $CDCl_3$):



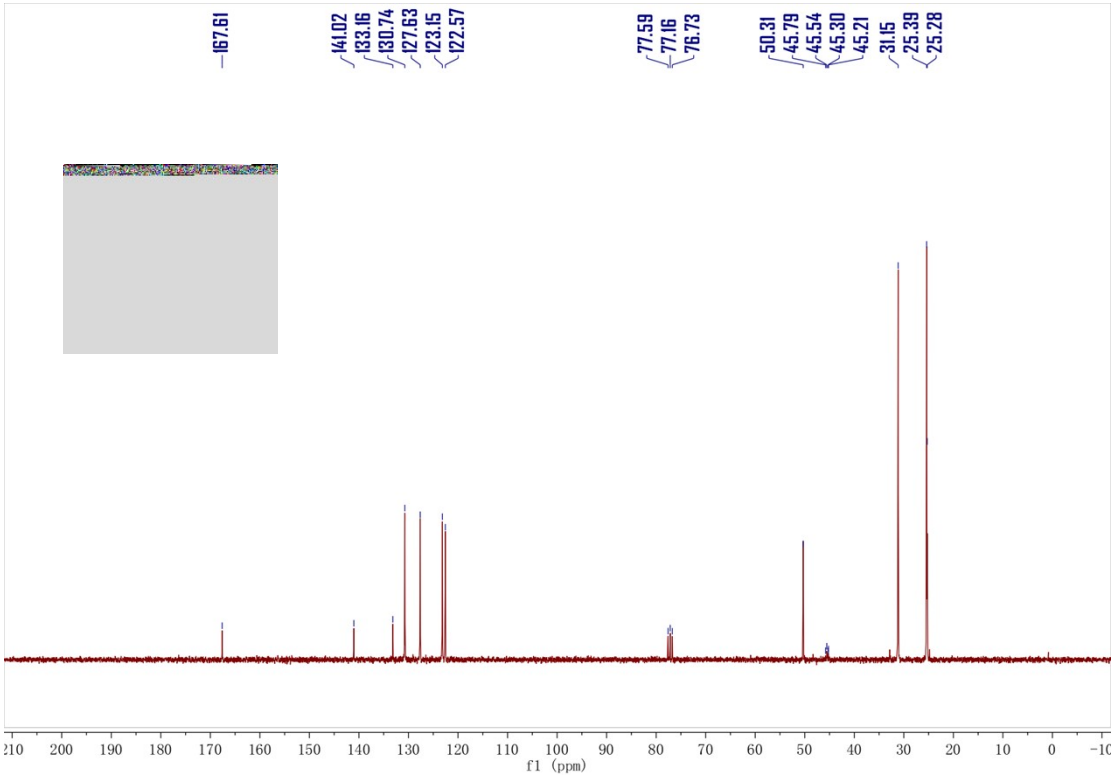
^{13}C NMR (75 MHz, $CDCl_3$):



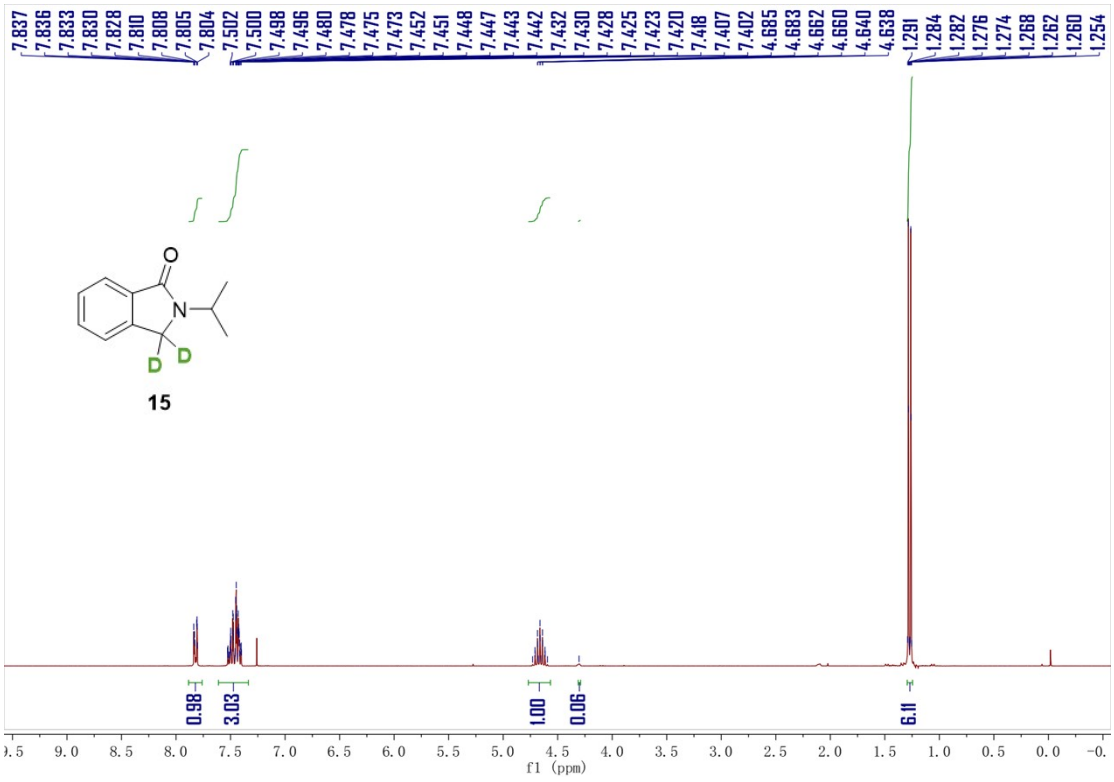
^{1}H NMR (300 MHz, $CDCl_3$):



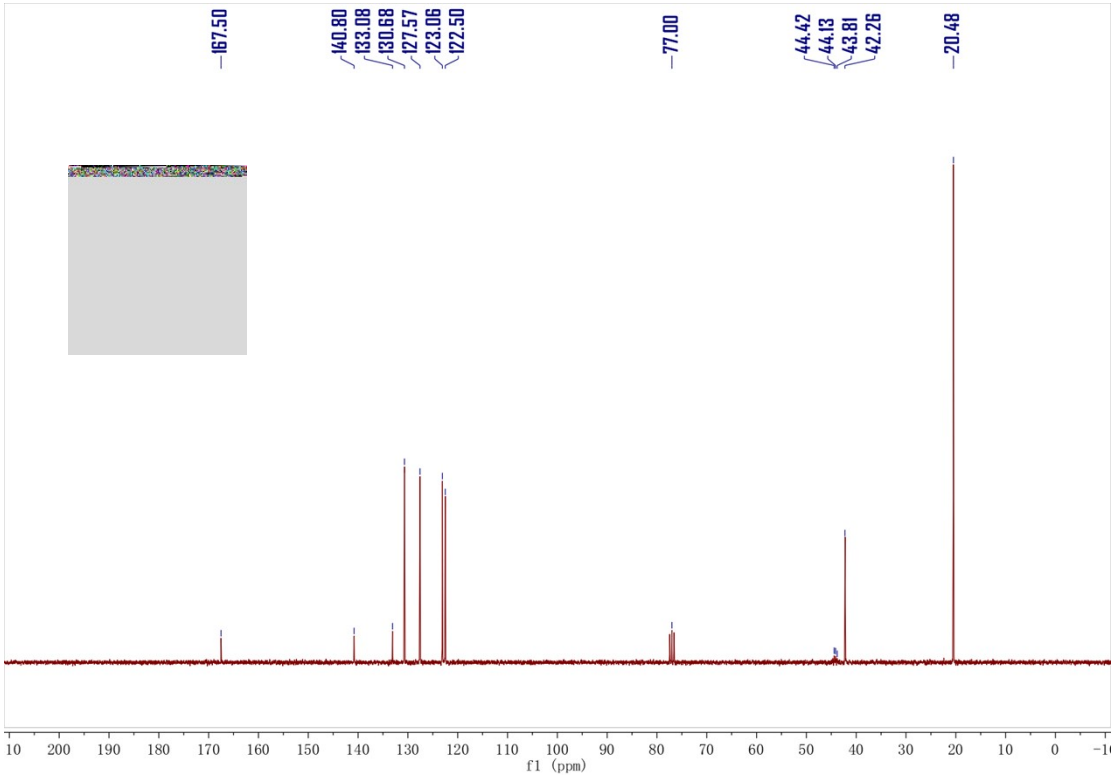
^{13}C NMR (75 MHz, $CDCl_3$):



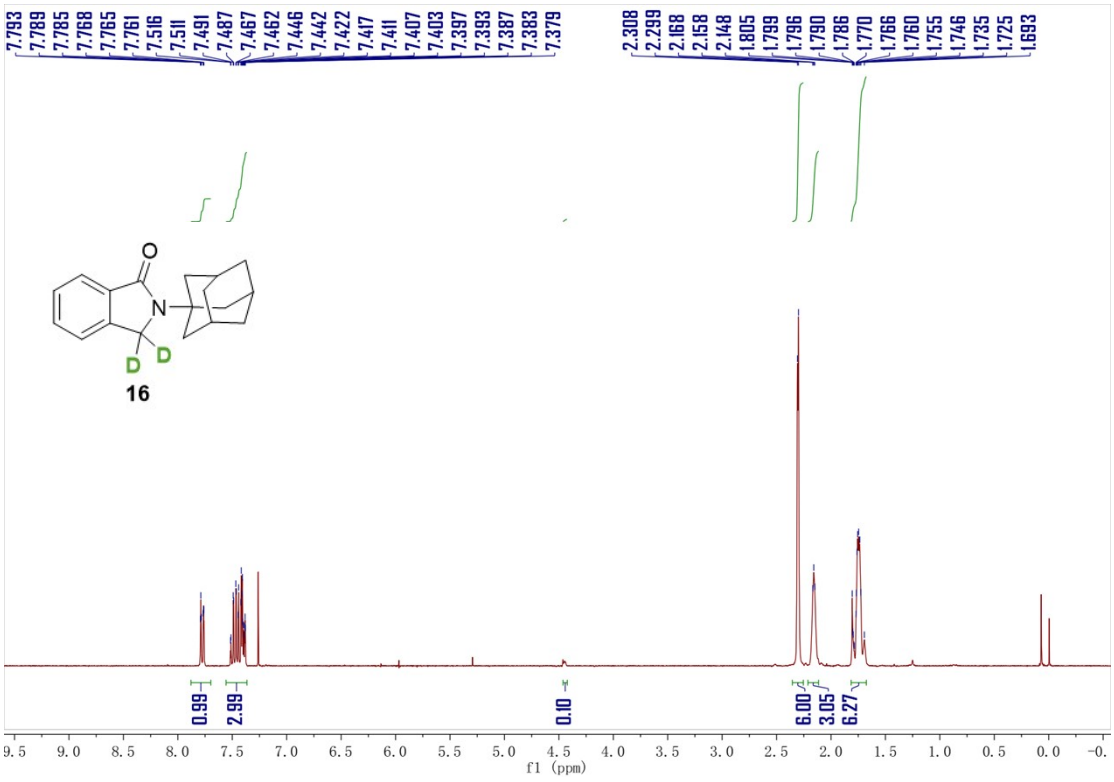
^{1}H NMR (300 MHz, $CDCl_3$):



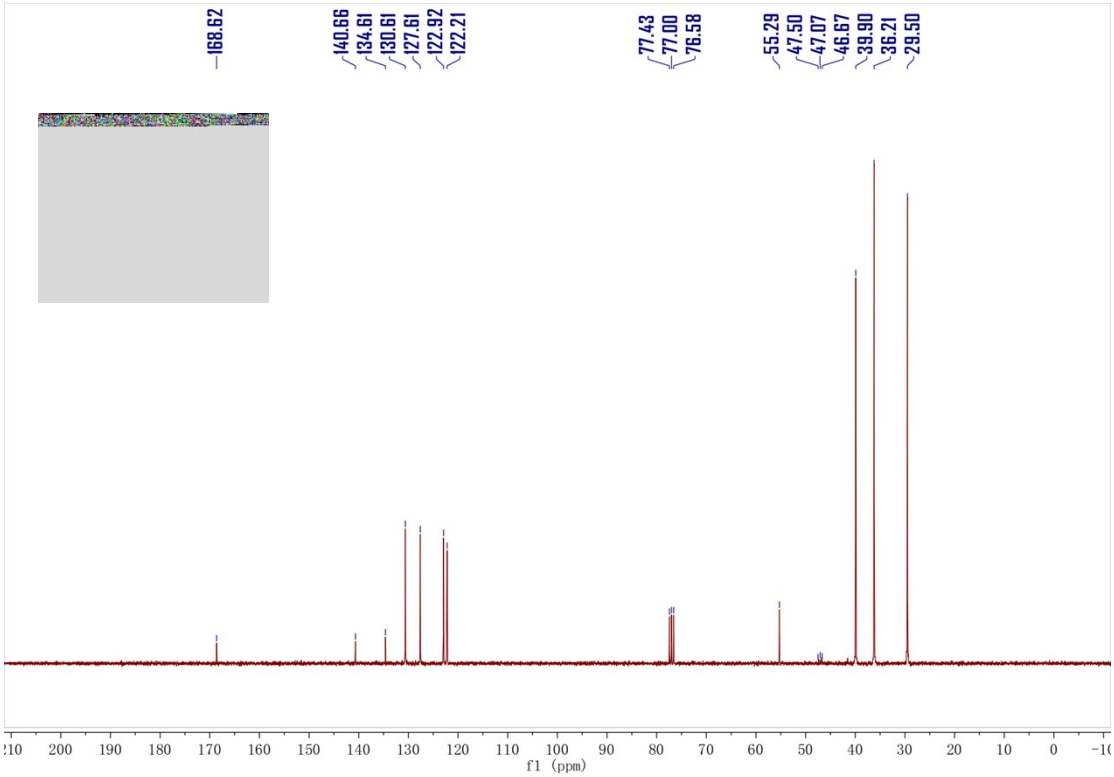
^{13}C NMR (75 MHz, $CDCl_3$):



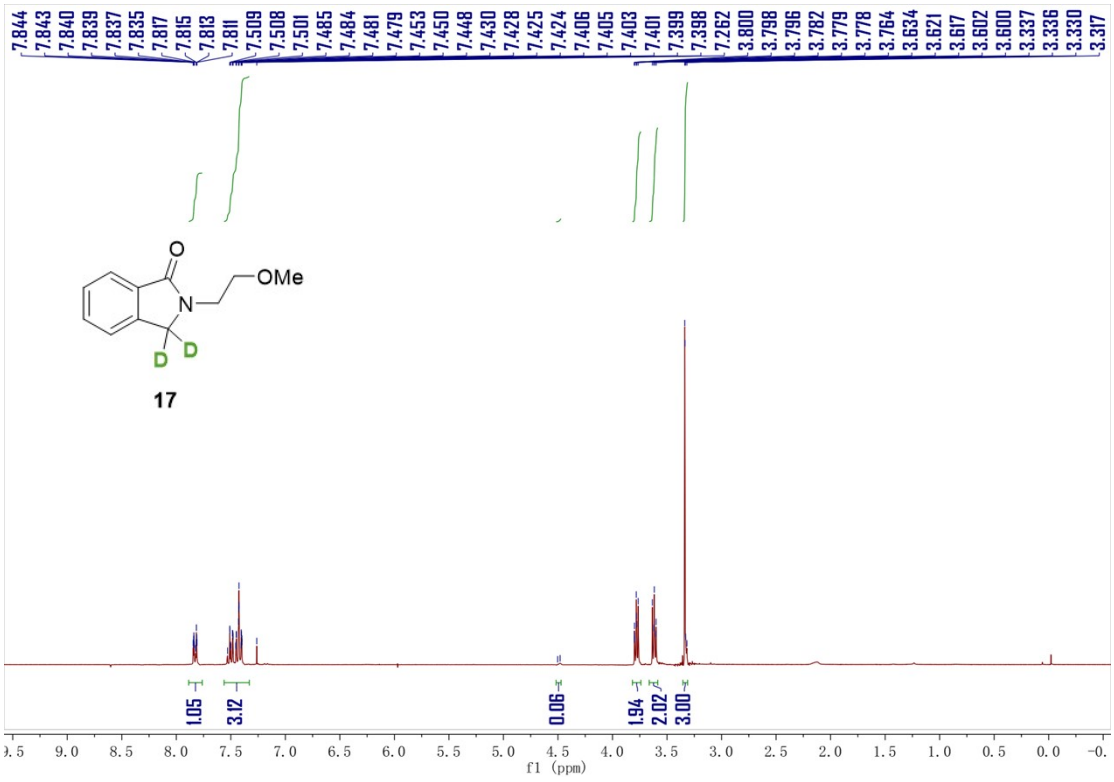
^{1}H NMR (300 MHz, $CDCl_3$):



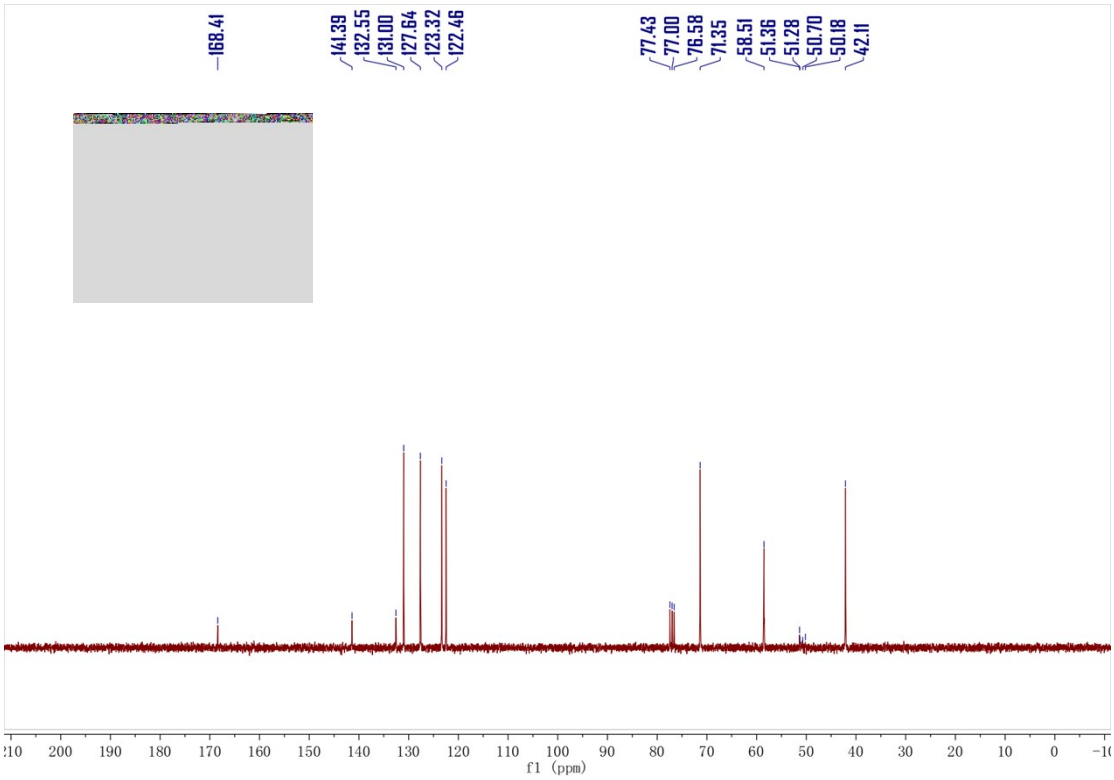
^{13}C NMR (75 MHz, $CDCl_3$):



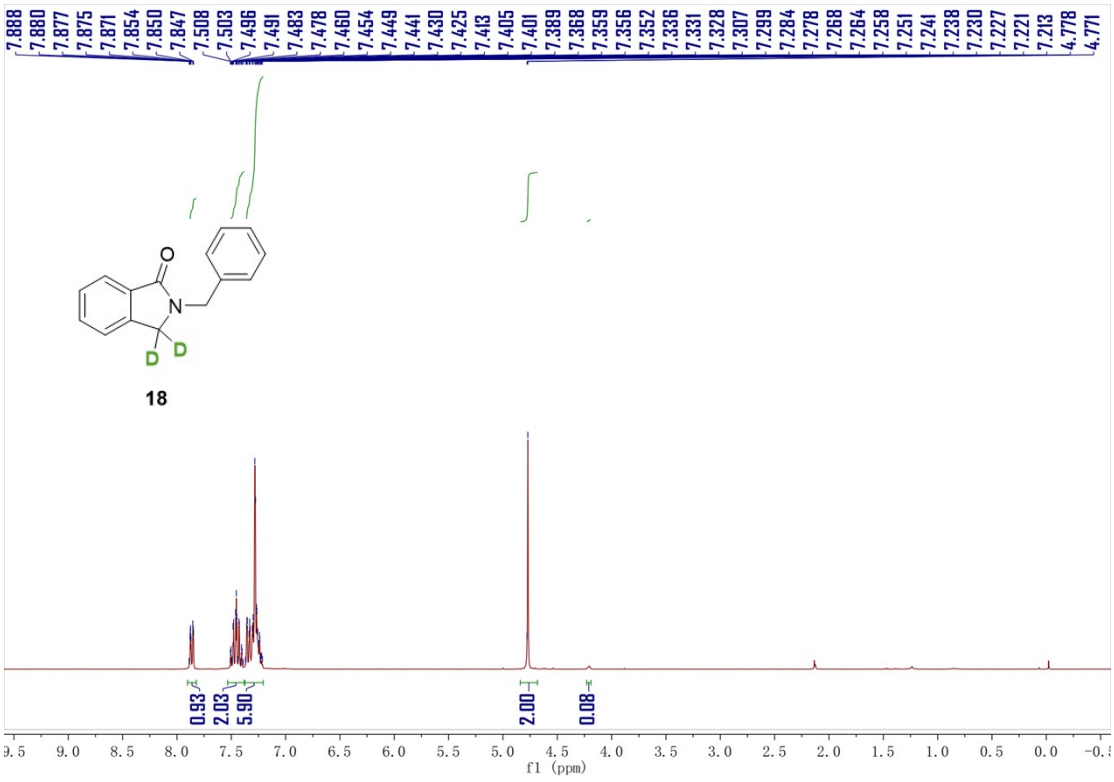
^{1}H NMR (300 MHz, $CDCl_3$):



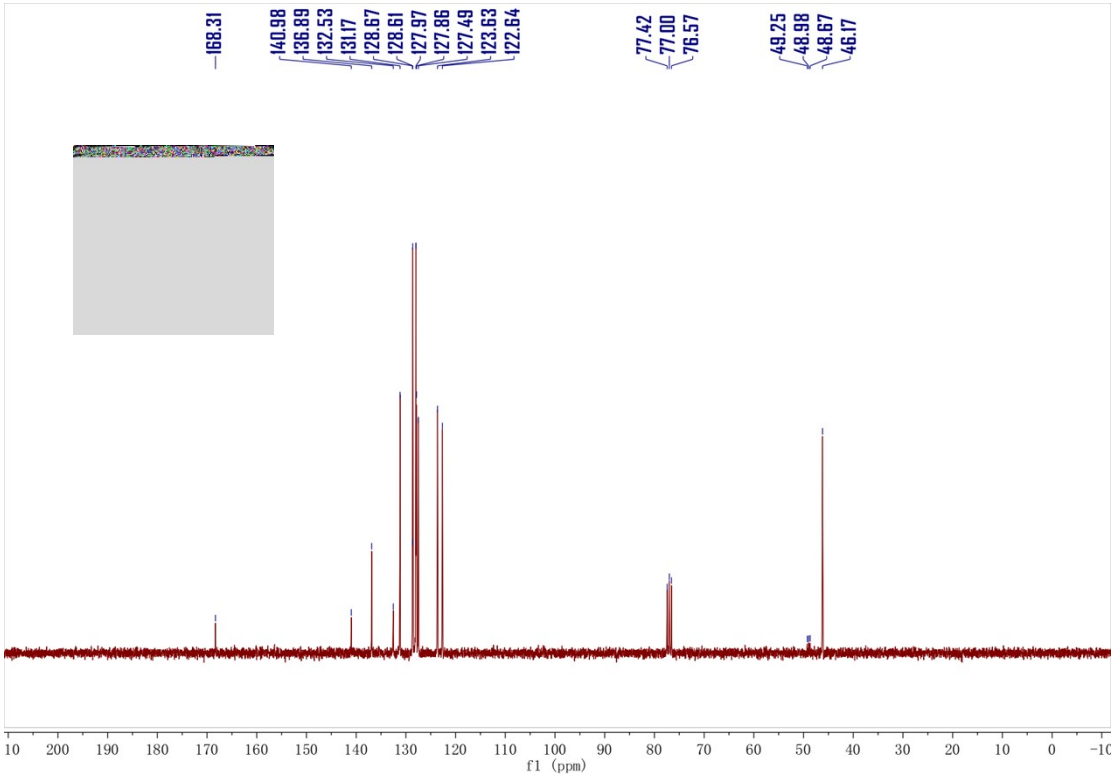
^{13}C NMR (75 MHz, $CDCl_3$):



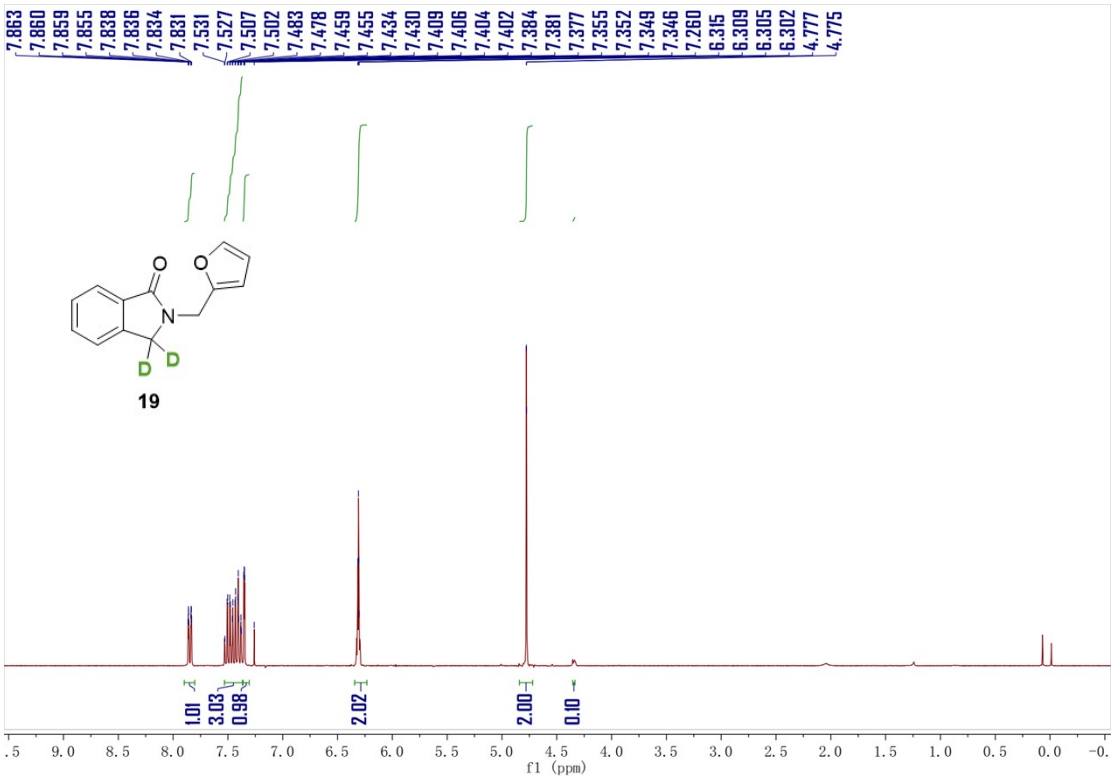
^{1}H NMR (300 MHz, $CDCl_3$):



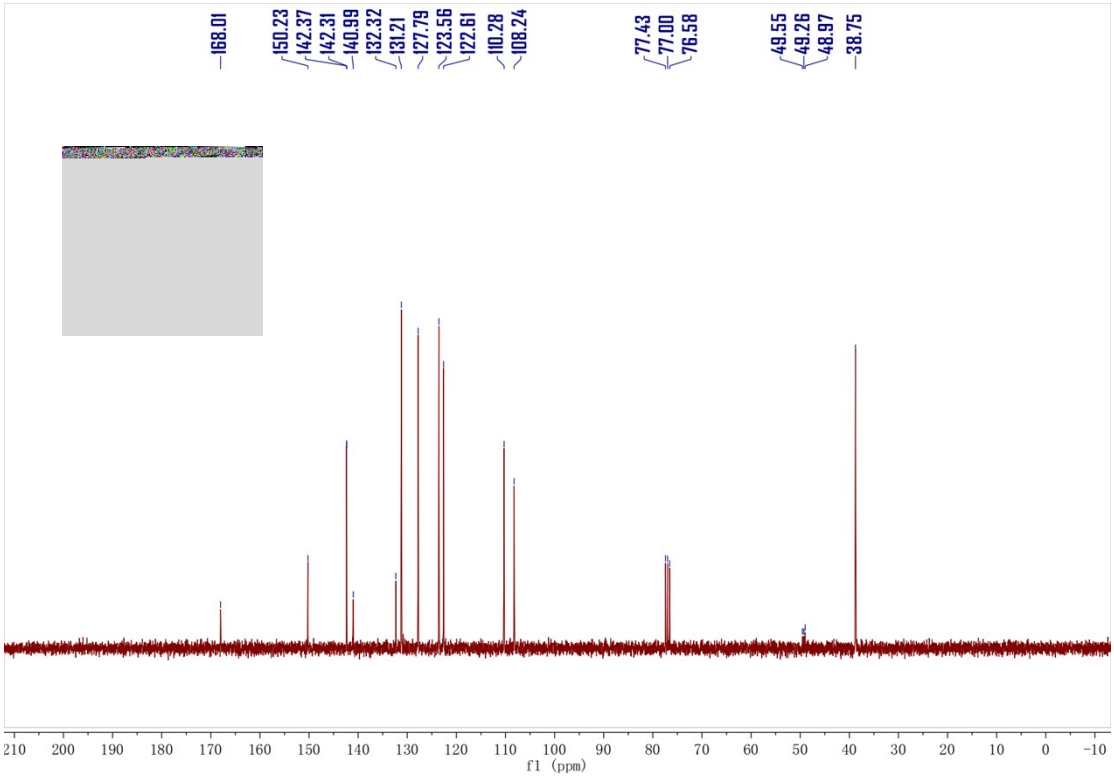
^{13}C NMR (75 MHz, $CDCl_3$):



^{1}H NMR (300 MHz, $CDCl_3$):



^{13}C NMR (75 MHz, $CDCl_3$):



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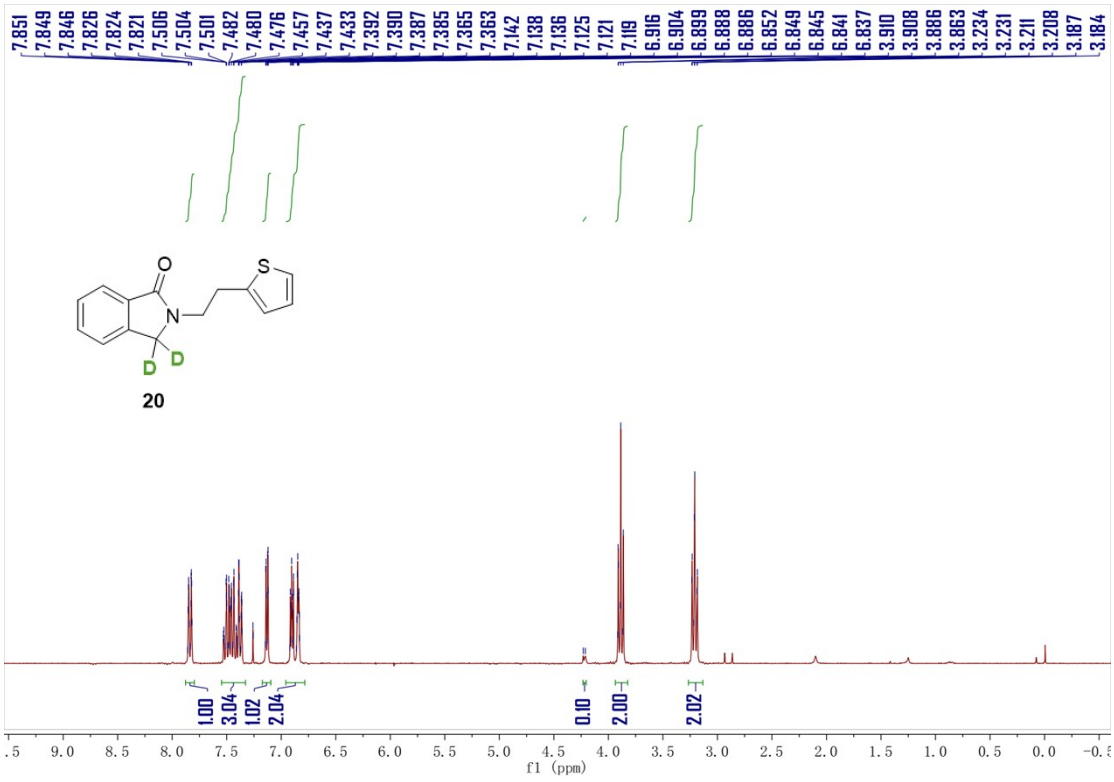
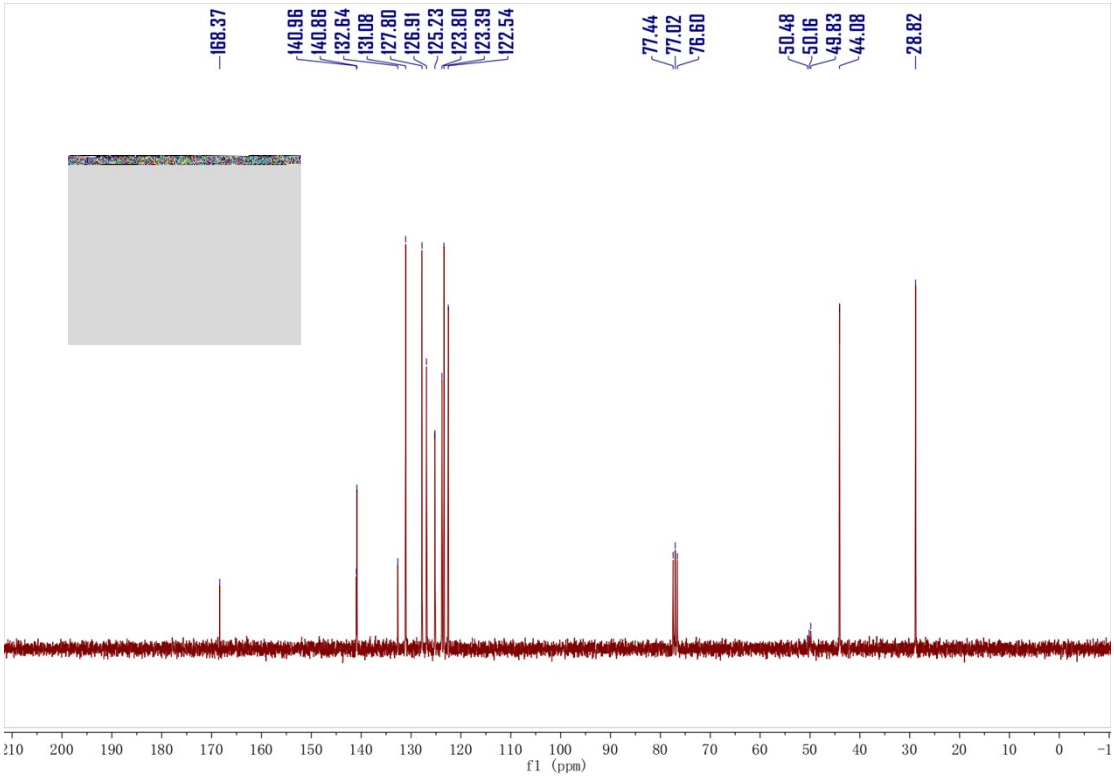


^{13}C NMR (75 MHz, $CDCl_3$):



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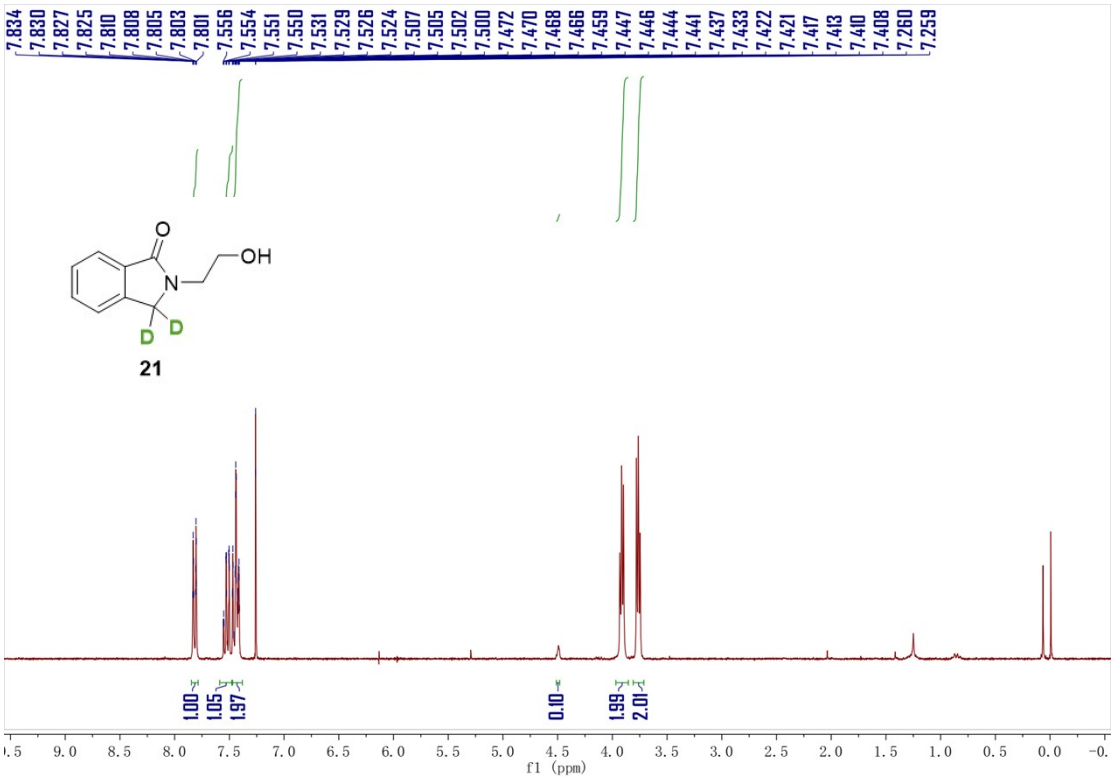
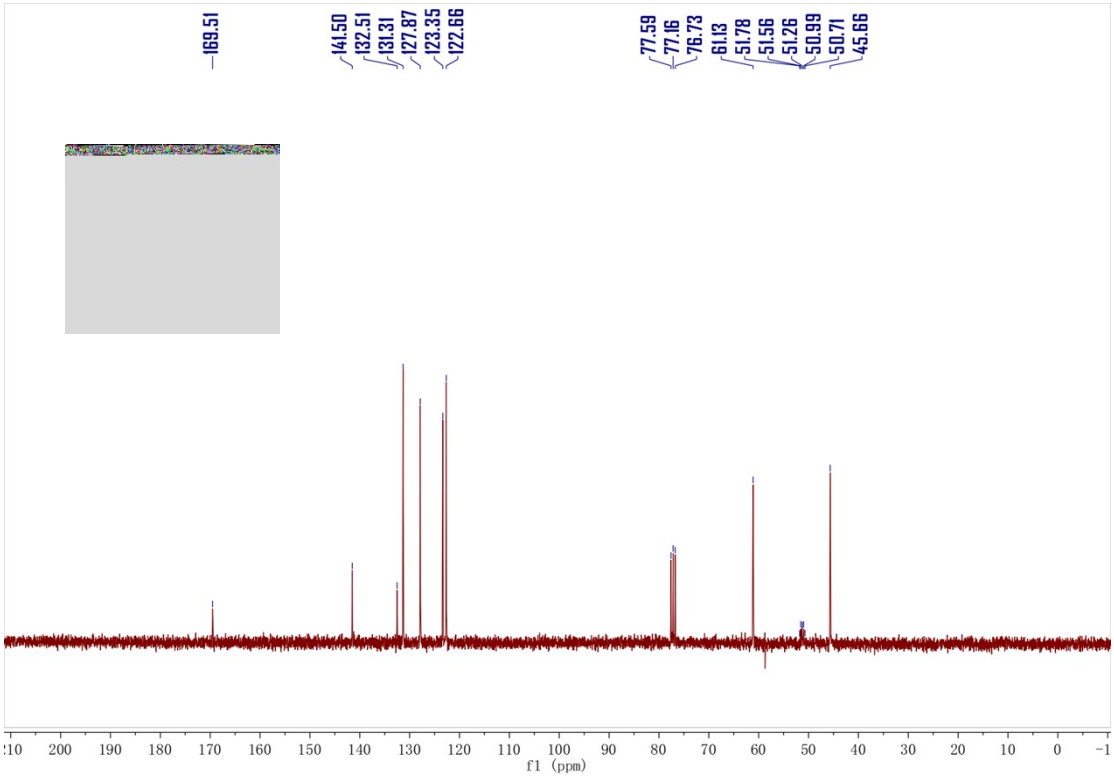
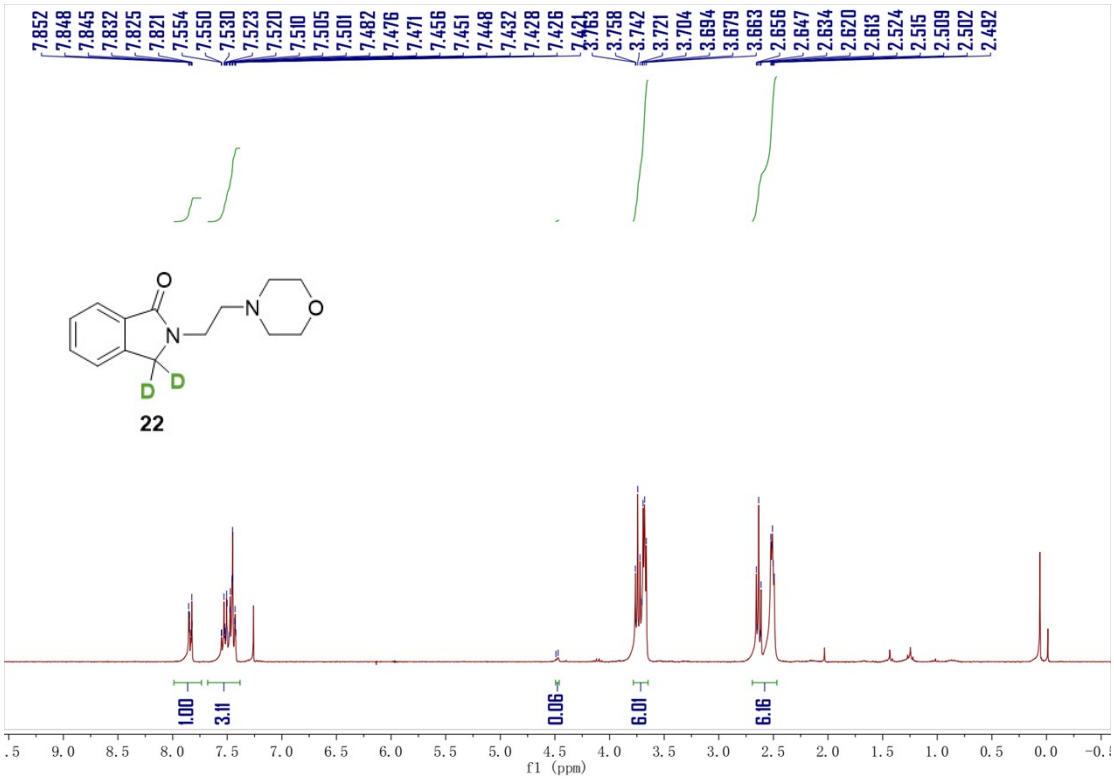


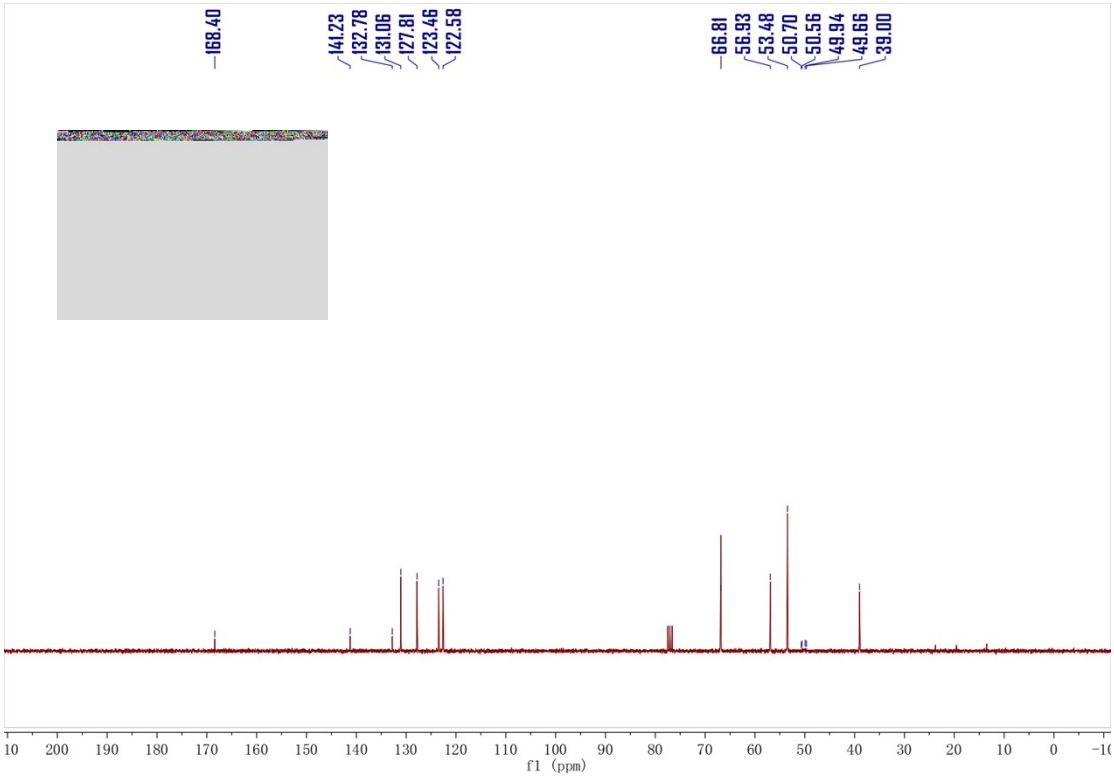
^{13}C NMR (75 MHz, $CDCl_3$):



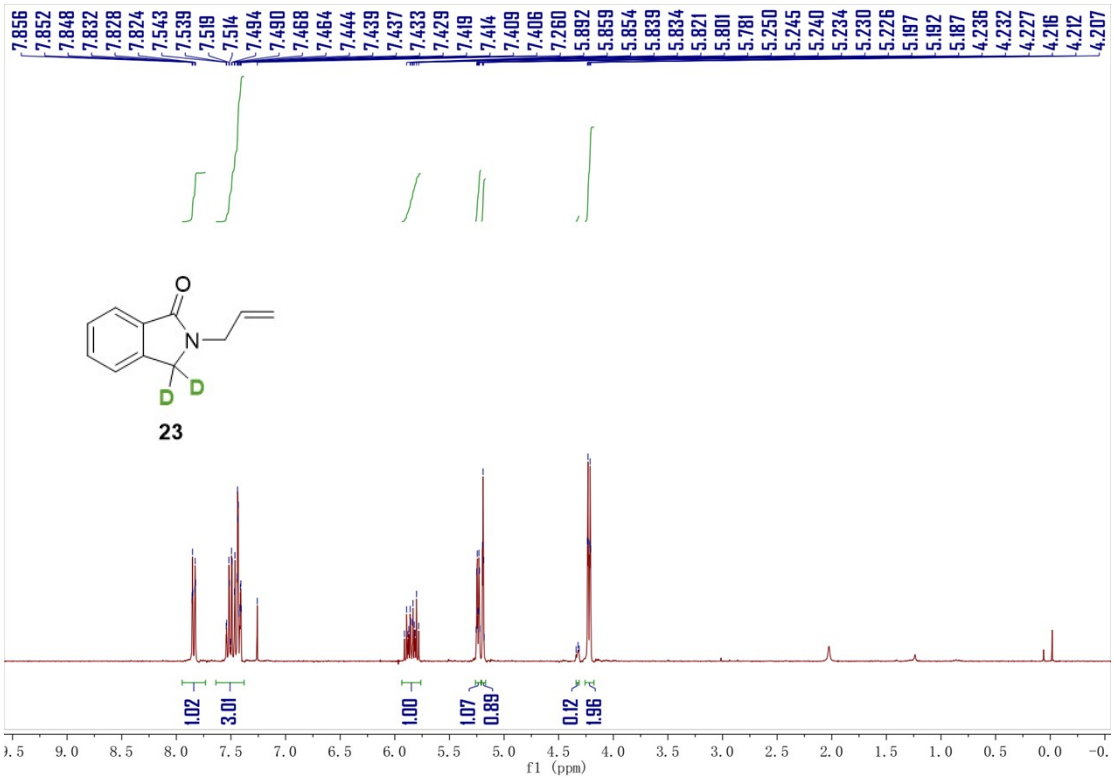
^{1}H NMR (300 MHz, $CDCl_3$):



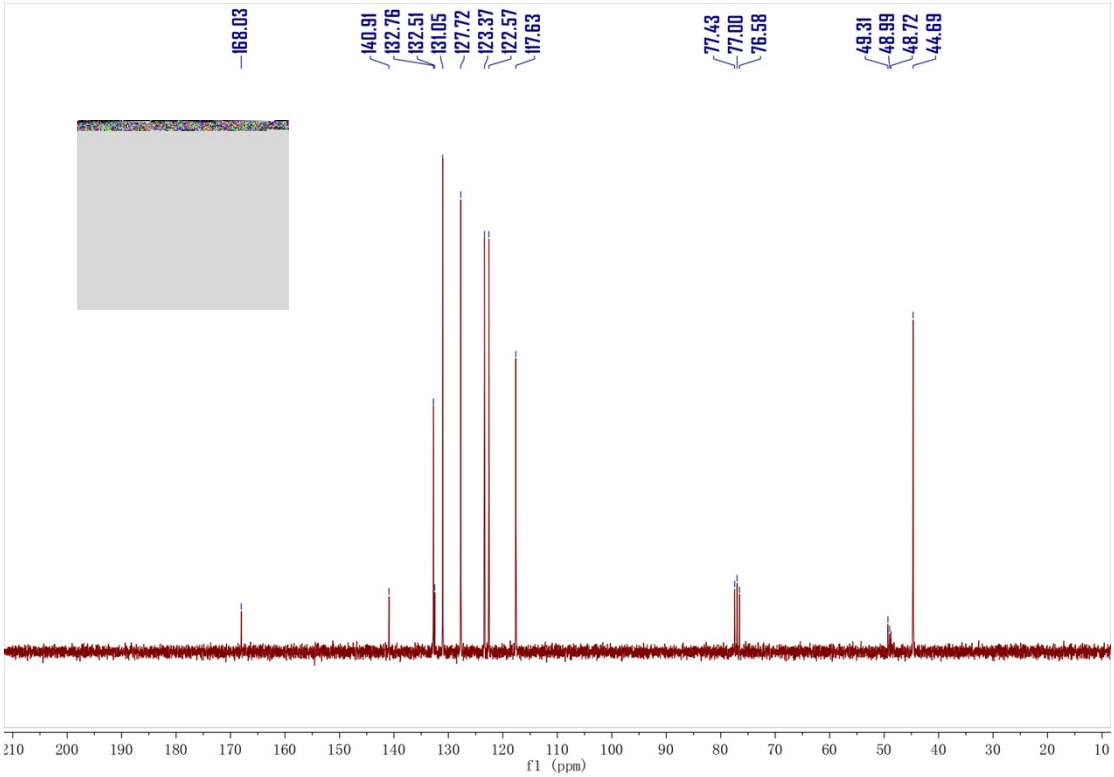
^{13}C NMR (75 MHz, $CDCl_3$):



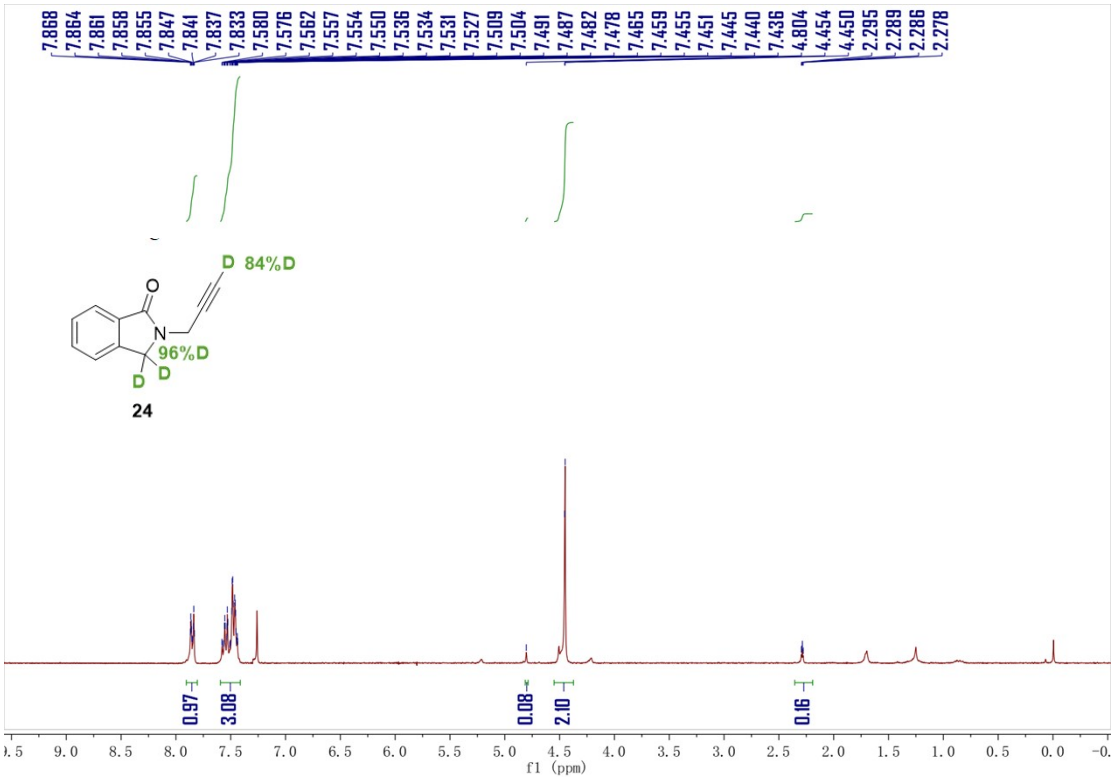
^{1}H NMR (300 MHz, $CDCl_3$):



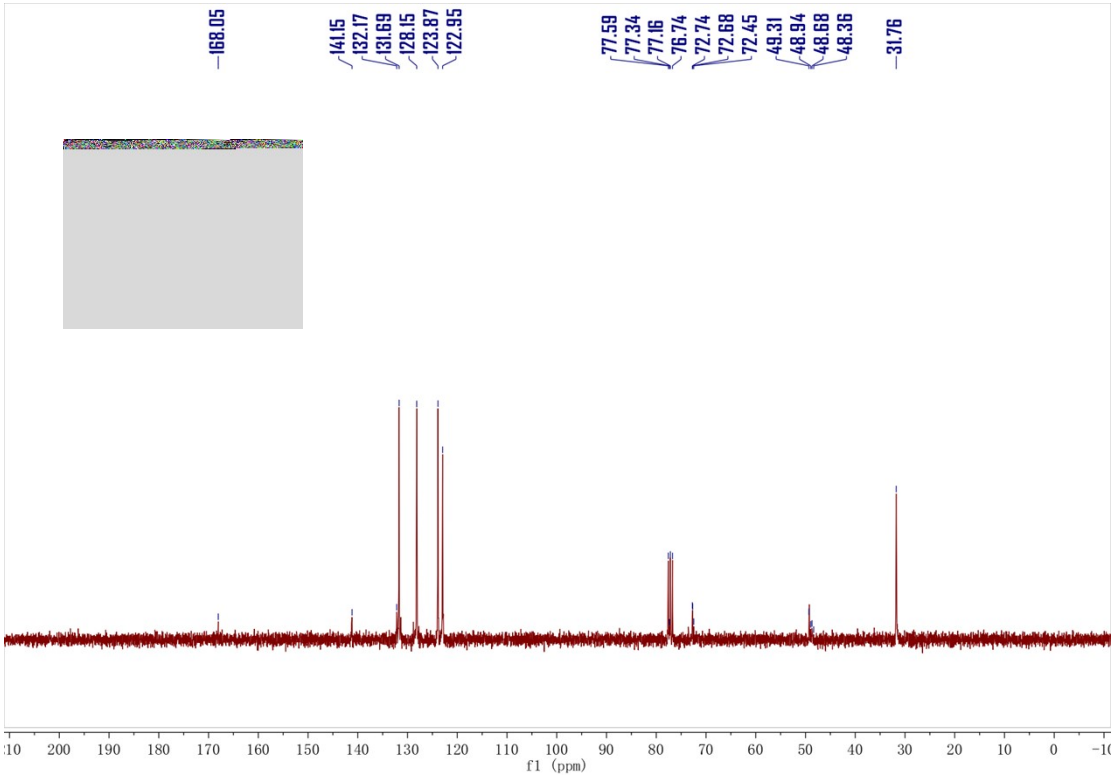
^{13}C NMR (75 MHz, $CDCl_3$):



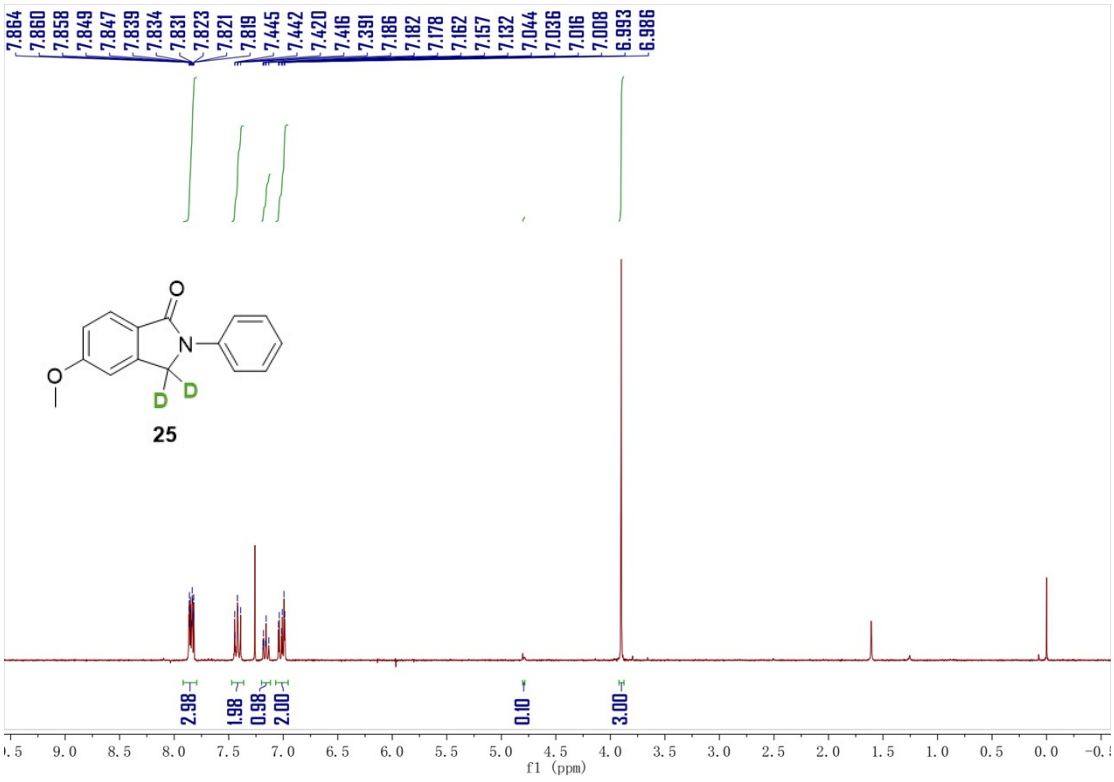
^{1}H NMR (300 MHz, $CDCl_3$):



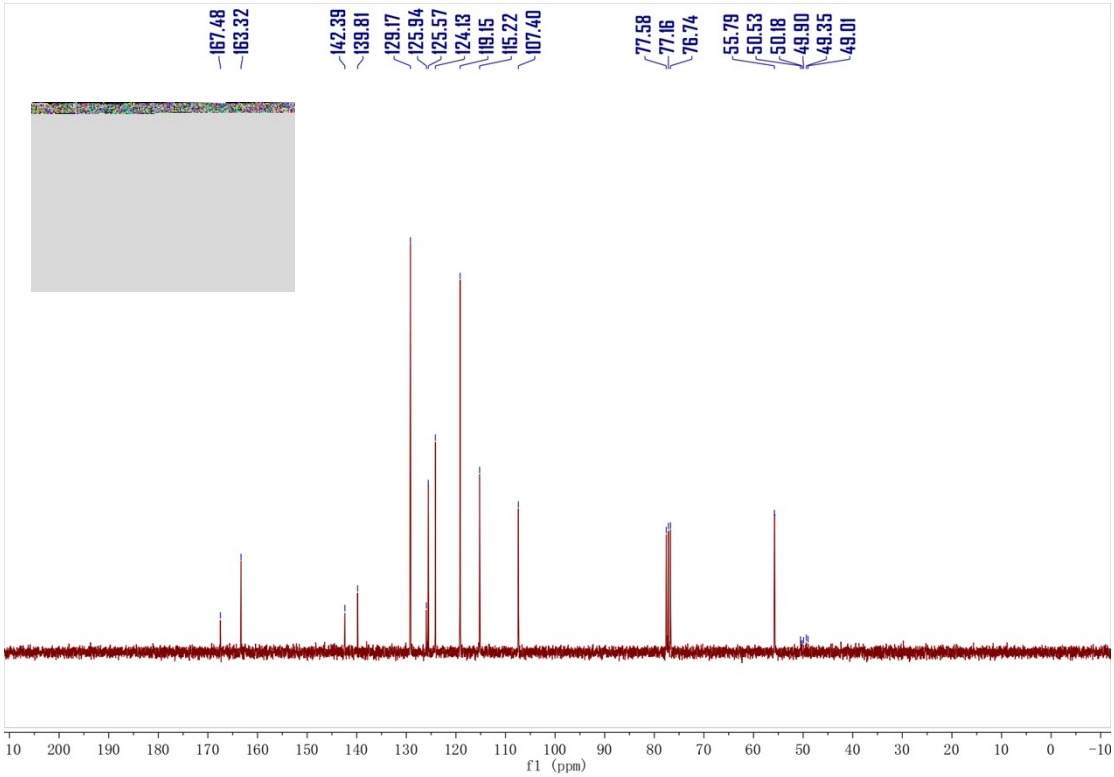
^{13}C NMR (75 MHz, $CDCl_3$):



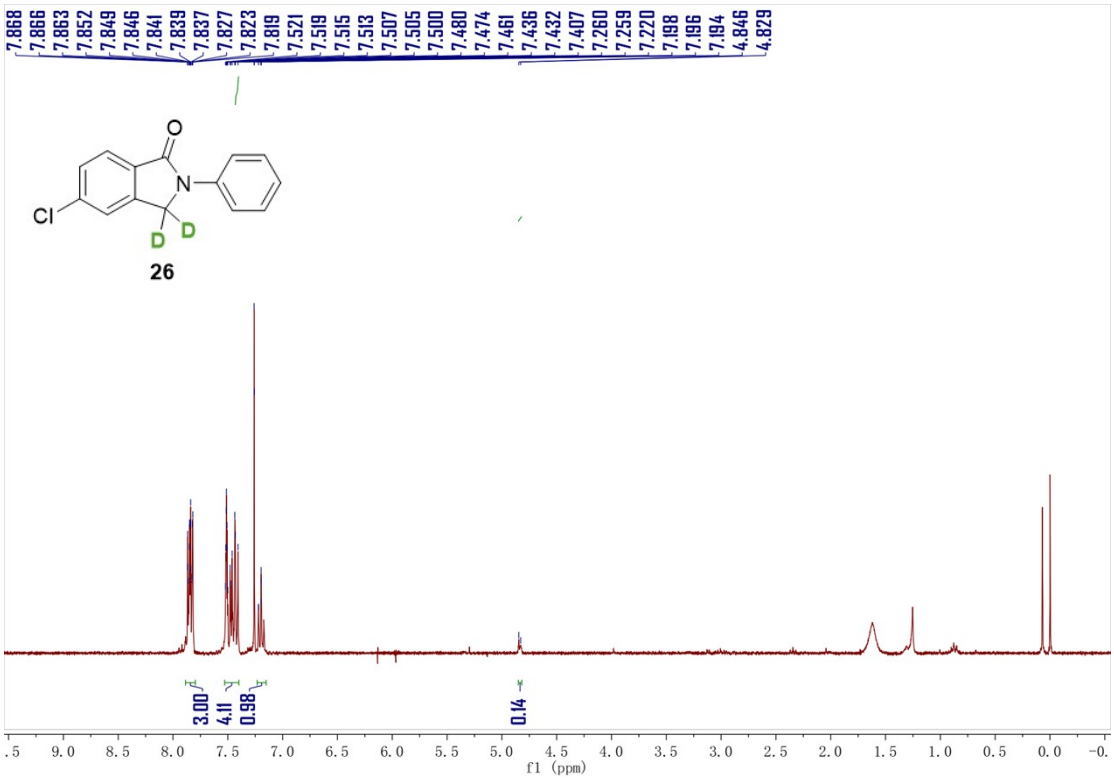
^{1}H NMR (300 MHz, $CDCl_3$):



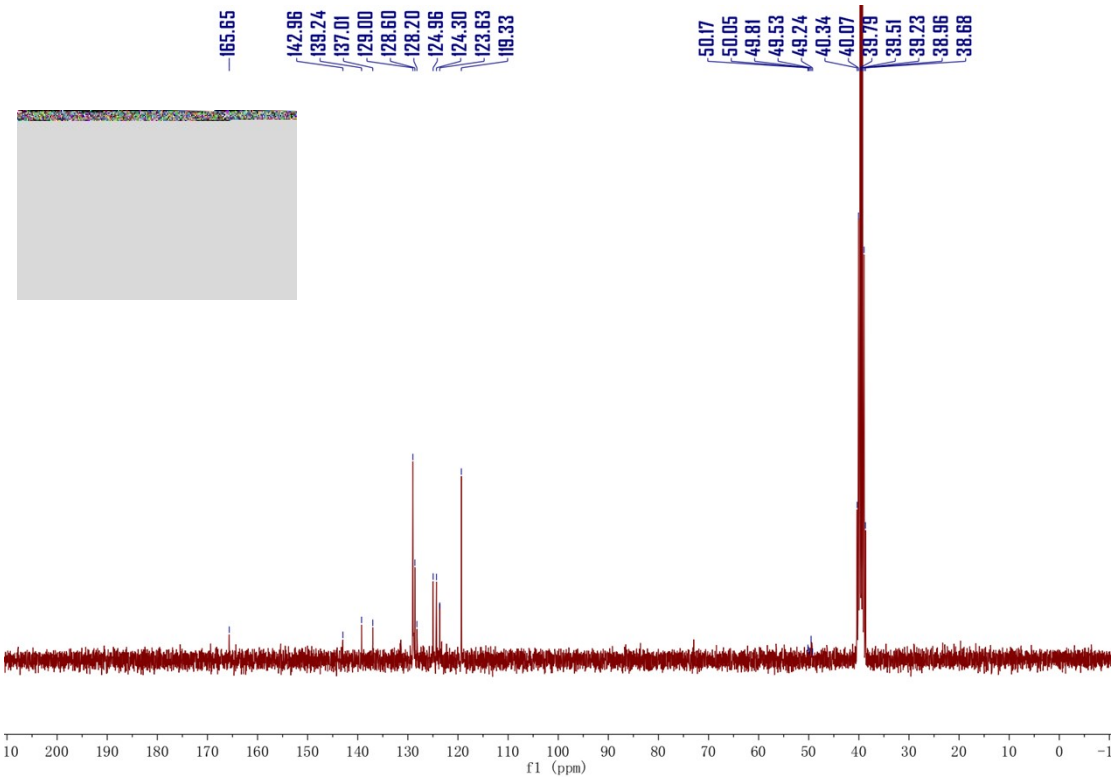
^{13}C NMR (75 MHz, $CDCl_3$):



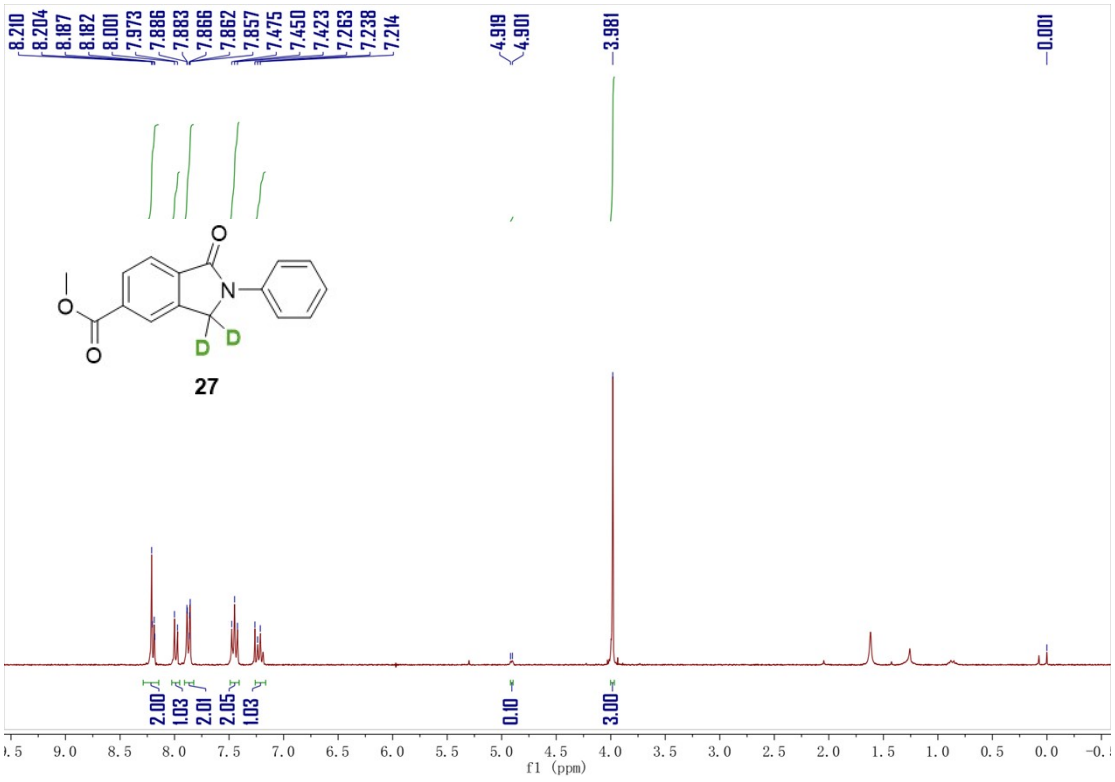
^{1}H NMR (300 MHz, $CDCl_3$):



^{13}C NMR (75 MHz, DMSO - d_6):



^{1}H NMR (300 MHz, $CDCl_3$):



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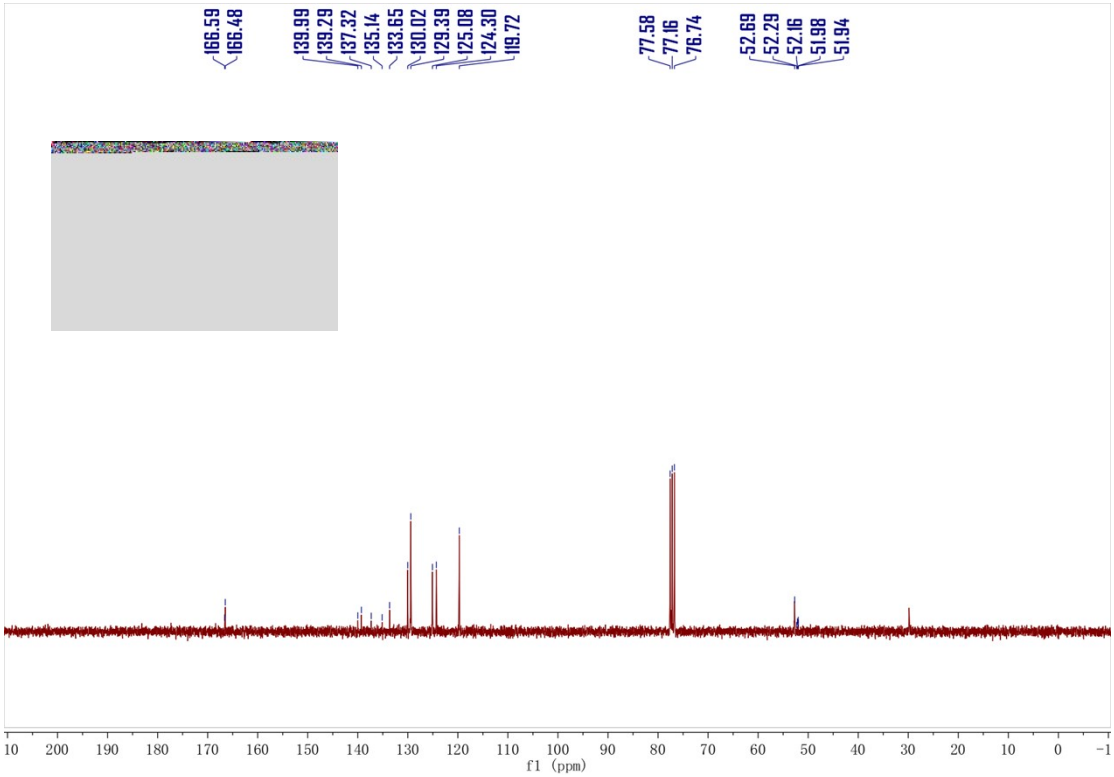

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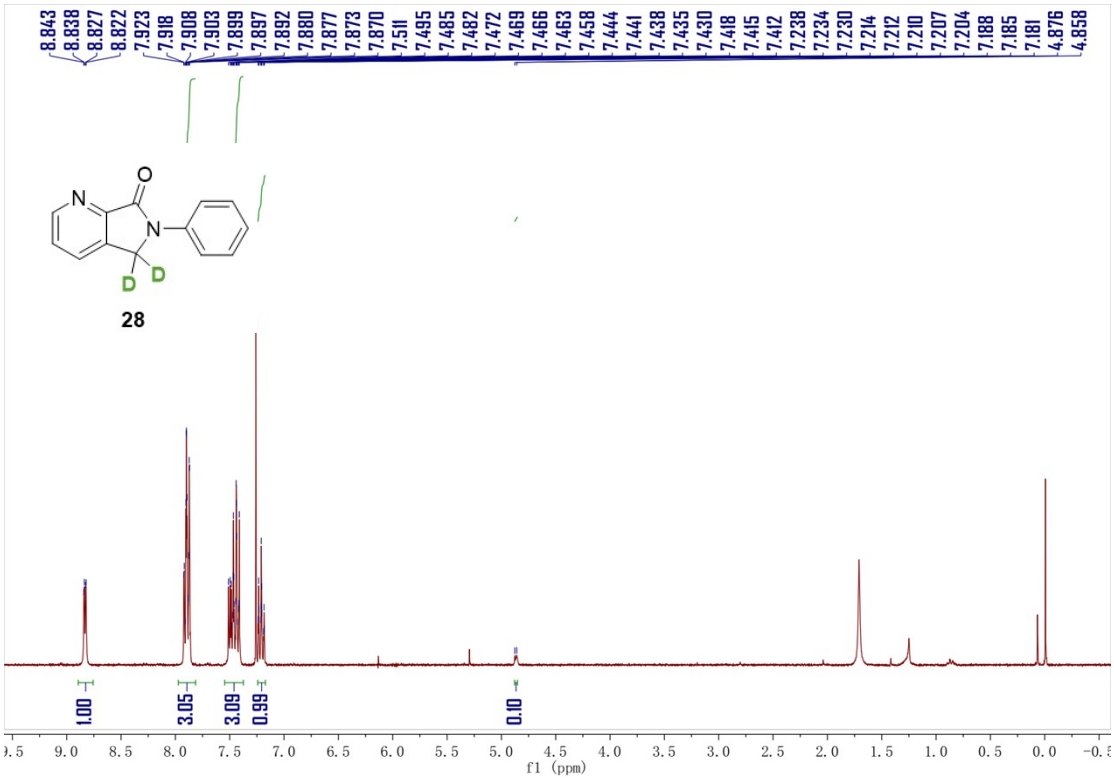
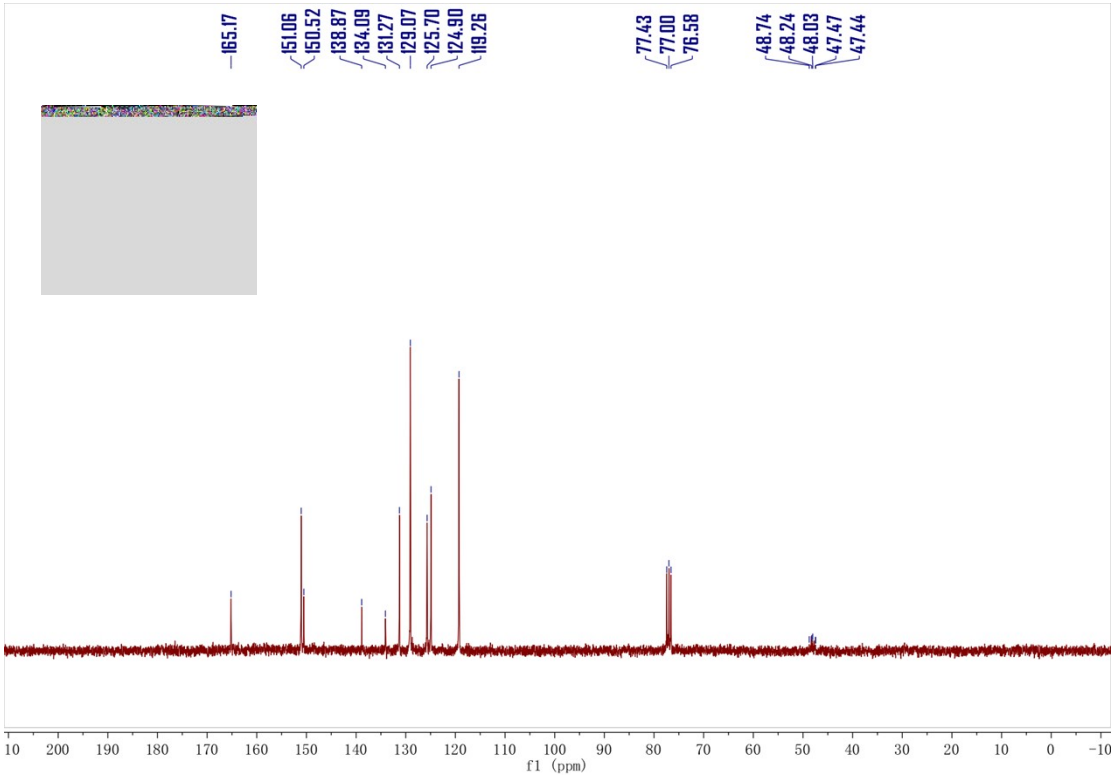
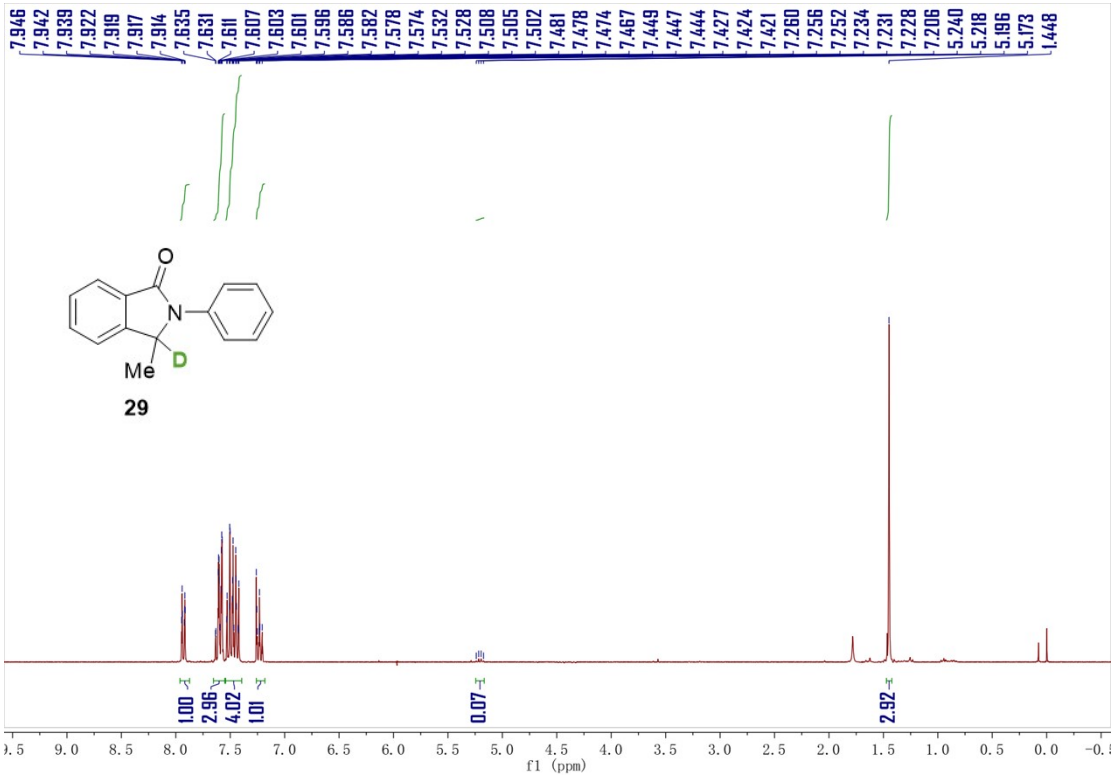


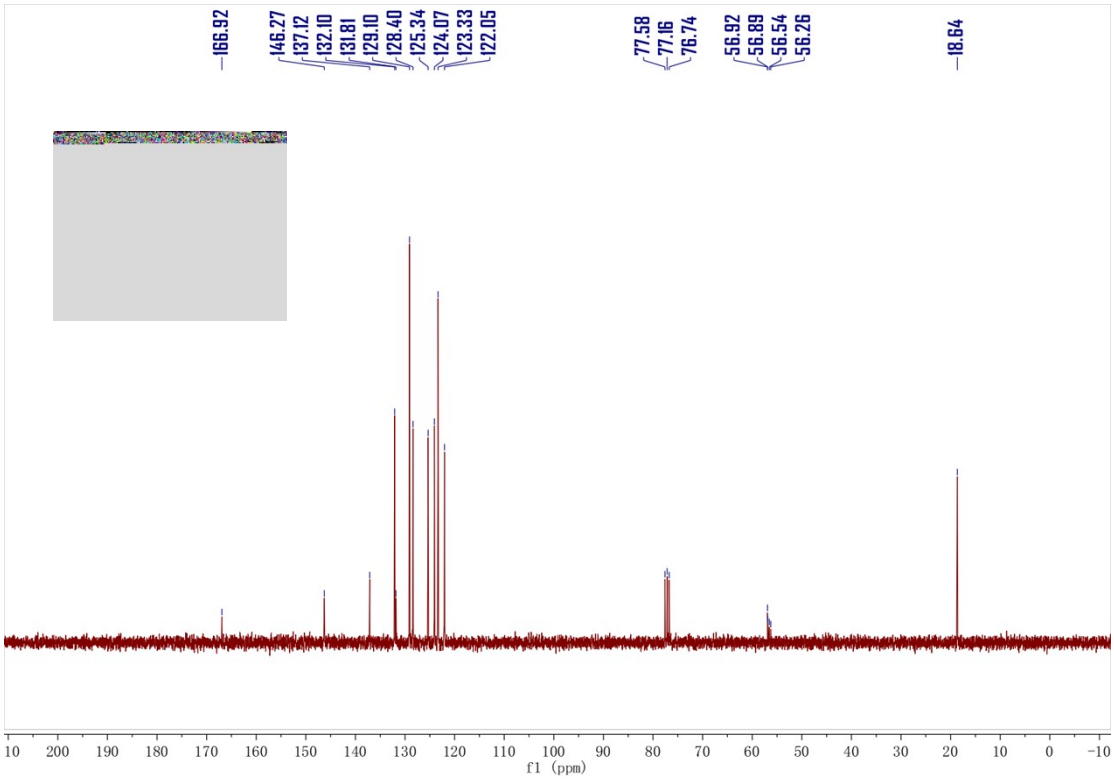
^{13}C NMR (75 MHz, $CDCl_3$):



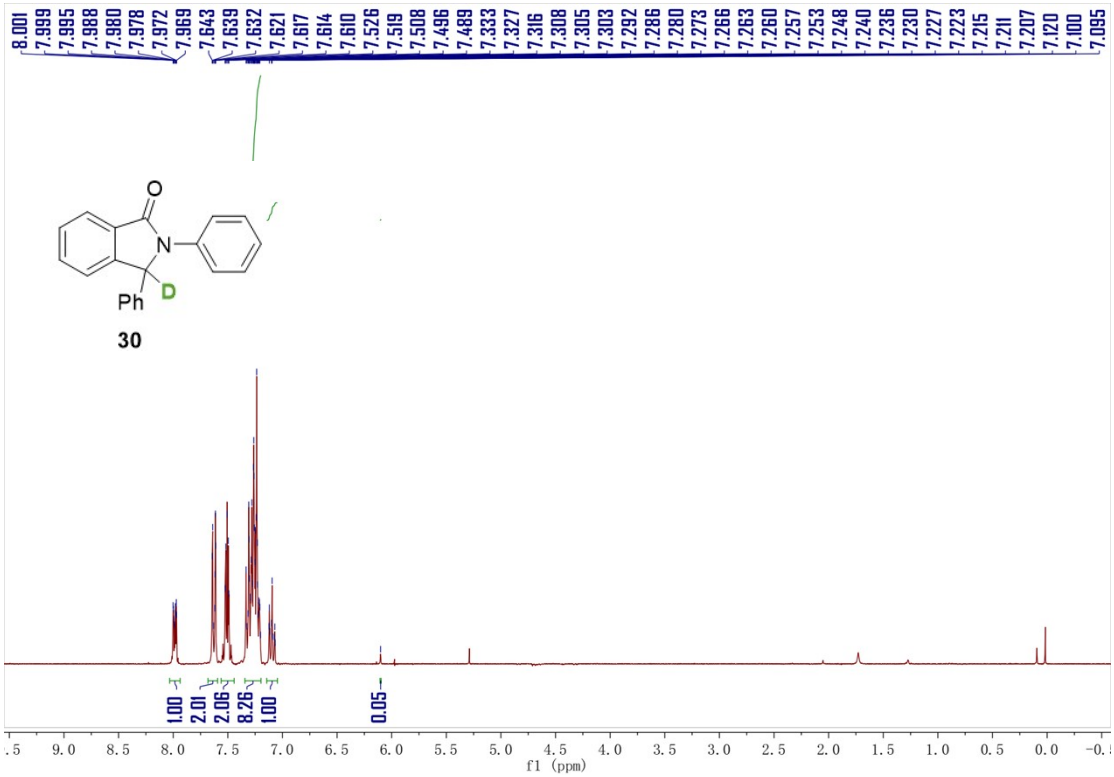
^{1}H NMR (300 MHz, $CDCl_3$):



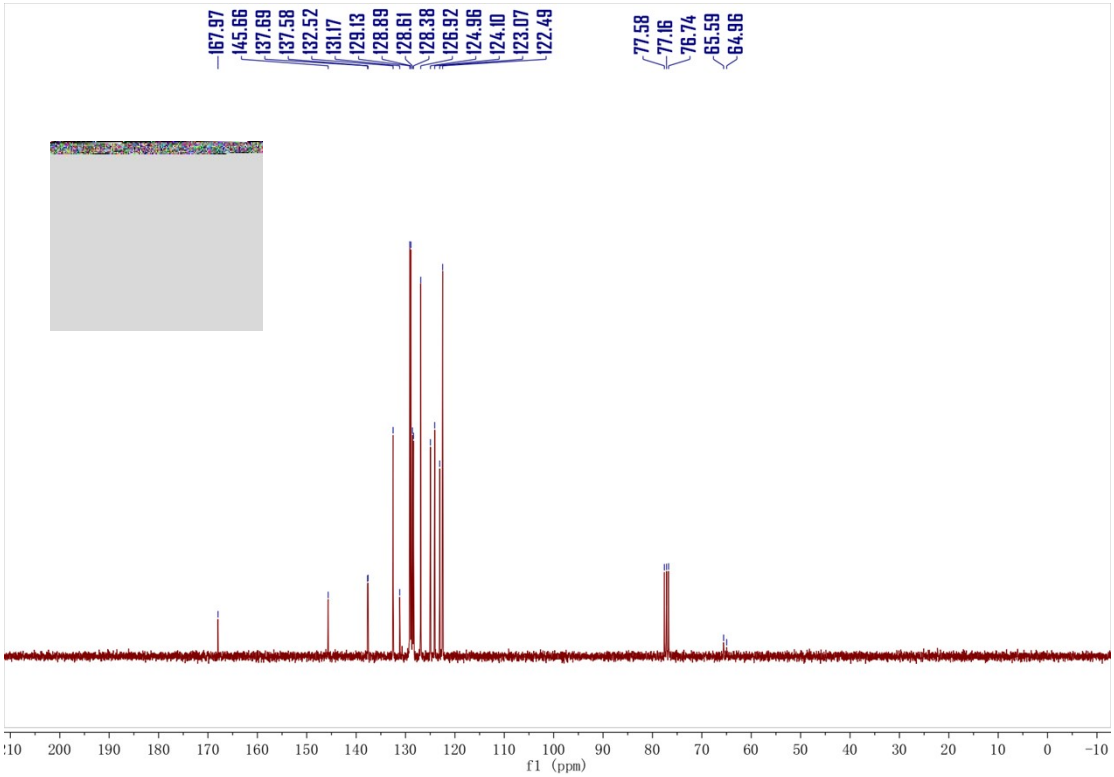
^{13}C NMR (75 MHz, $CDCl_3$):



^{1}H NMR (300 MHz, $CDCl_3$):



^{13}C NMR (75 MHz, $CDCl_3$):



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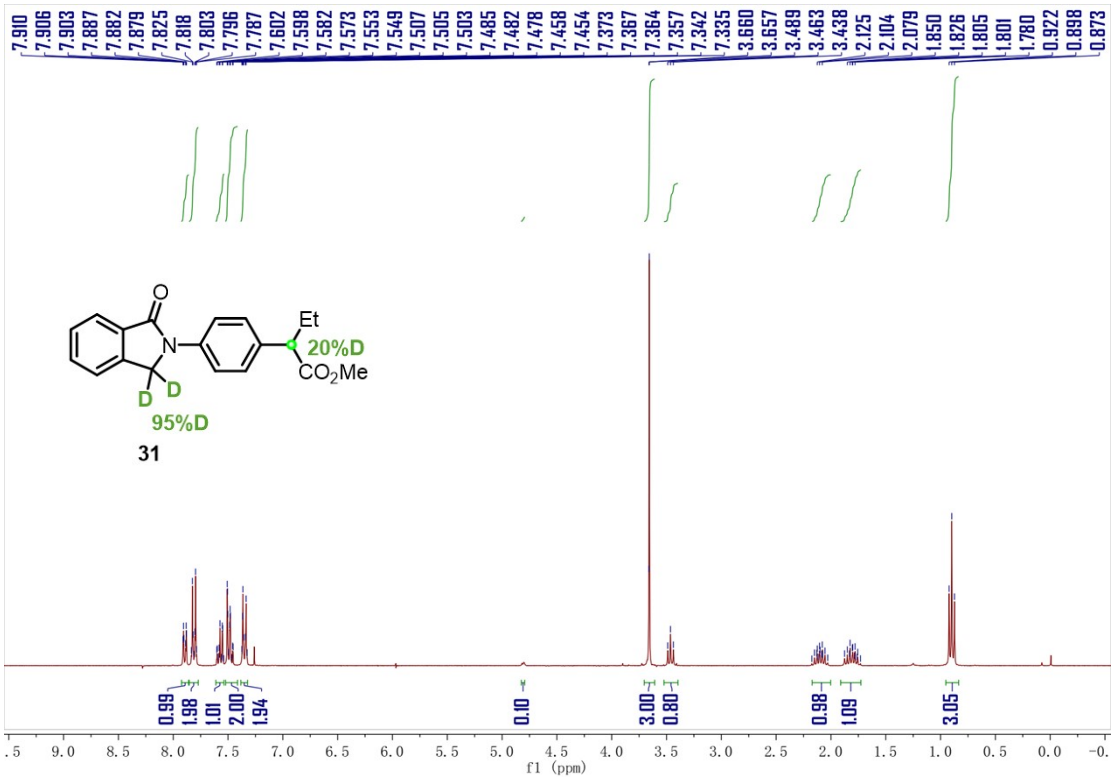
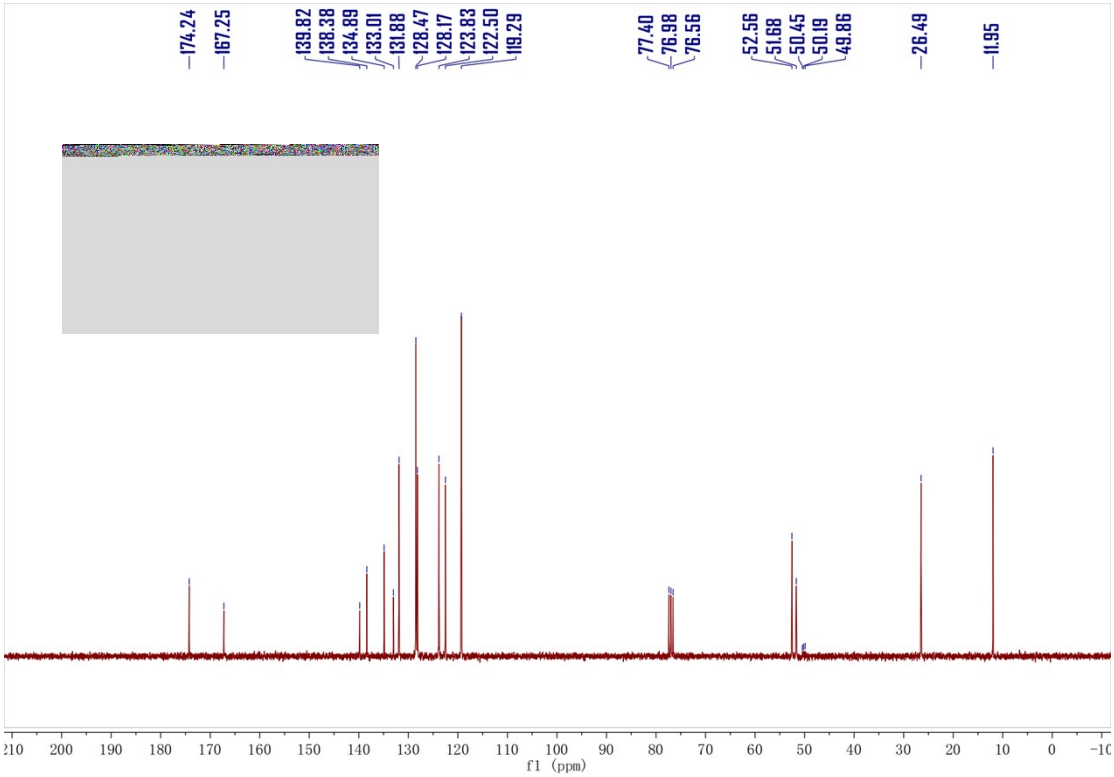


^{13}C NMR (75 MHz, $CDCl_3$):



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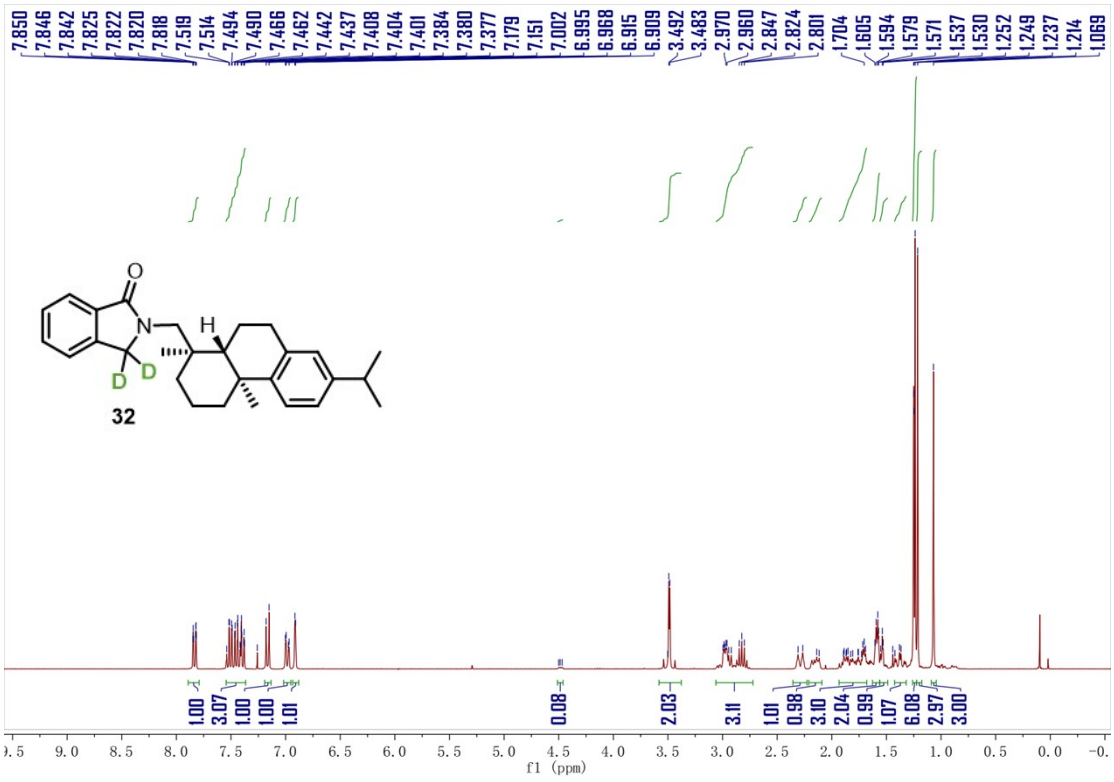

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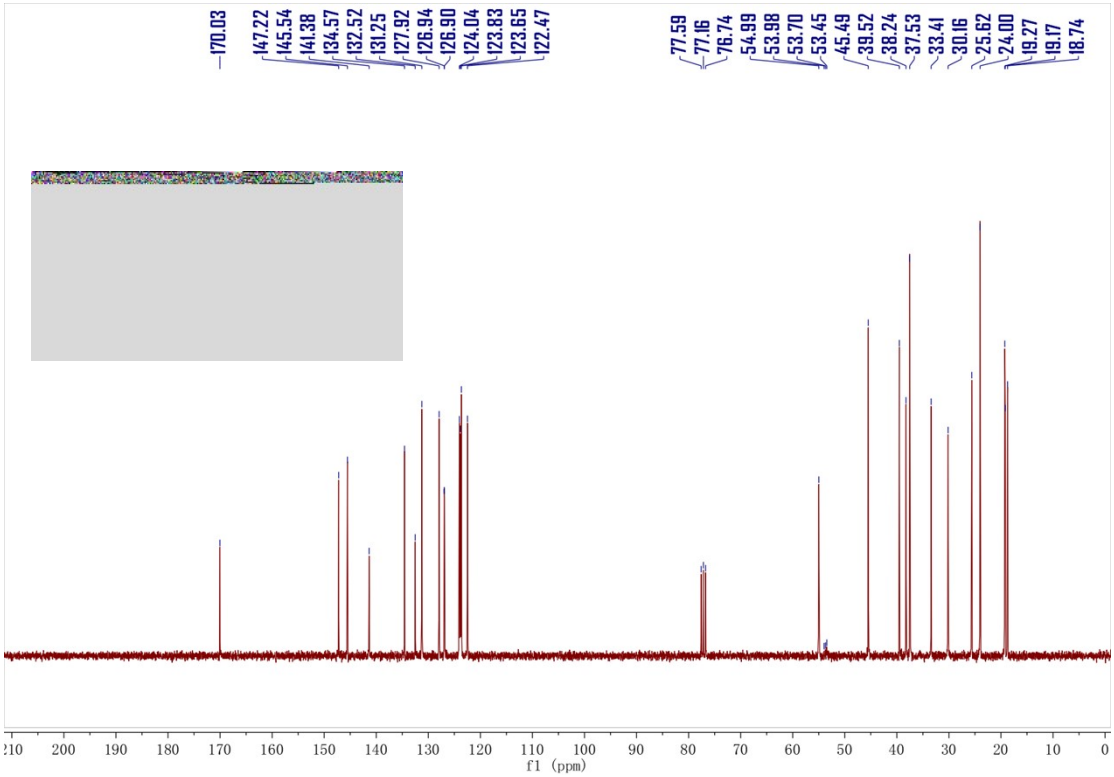

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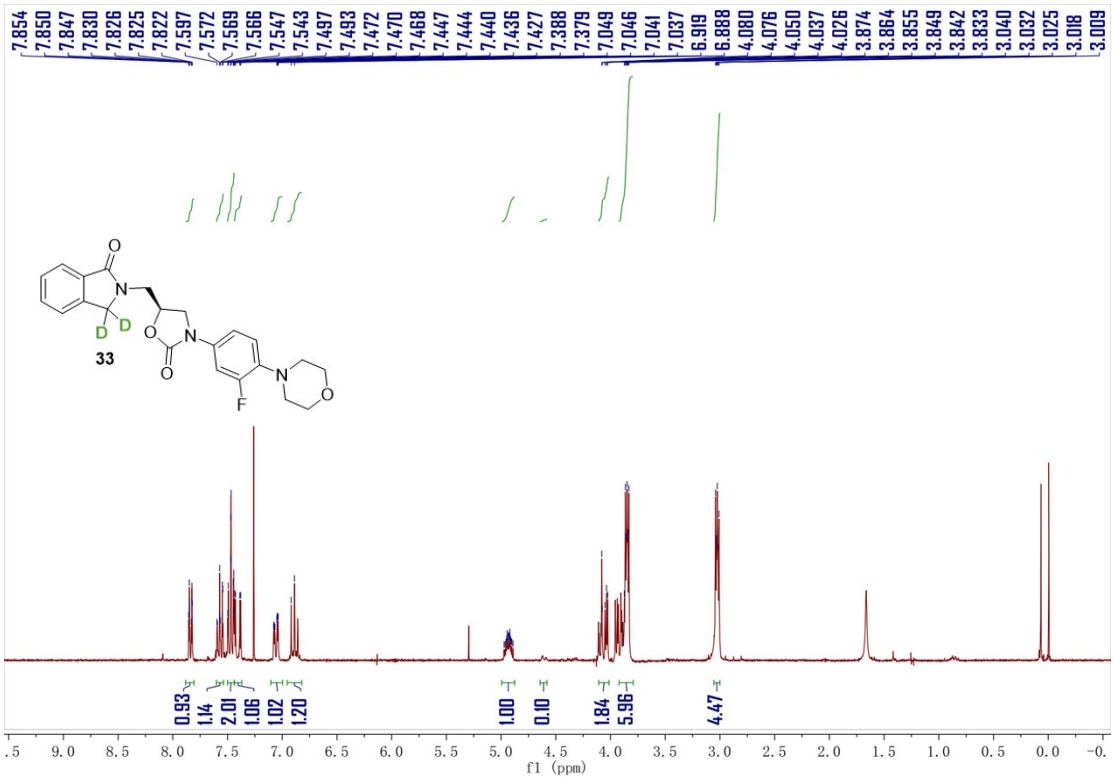

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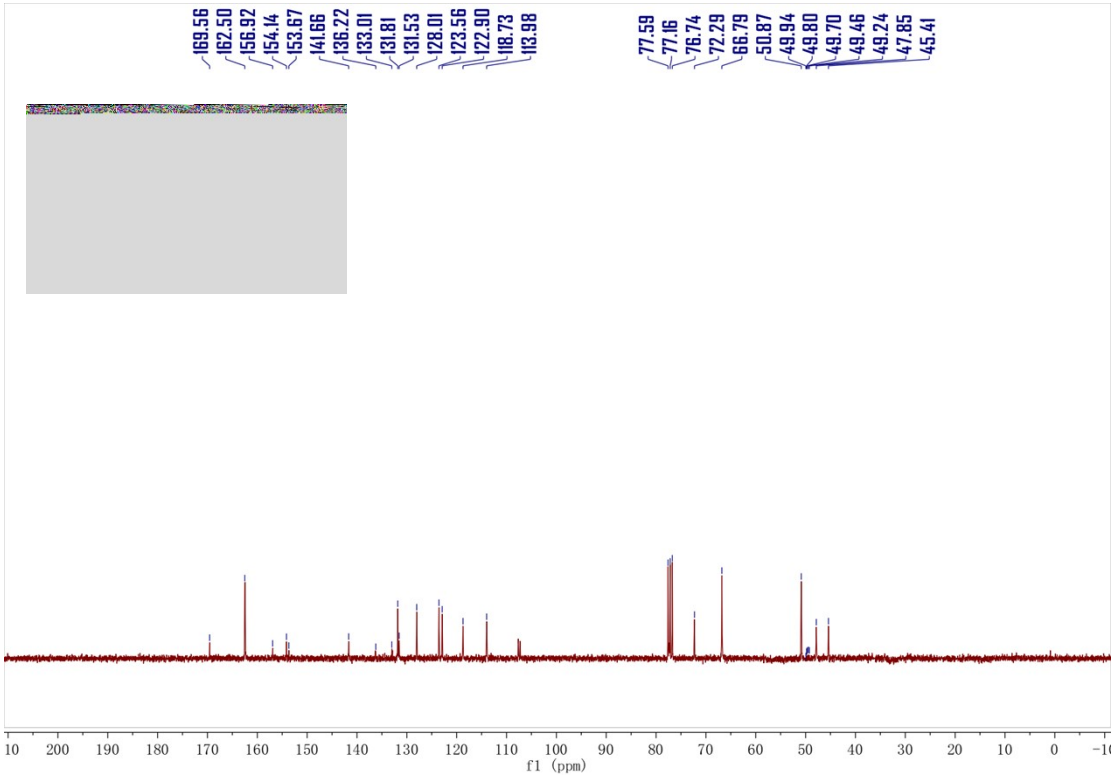
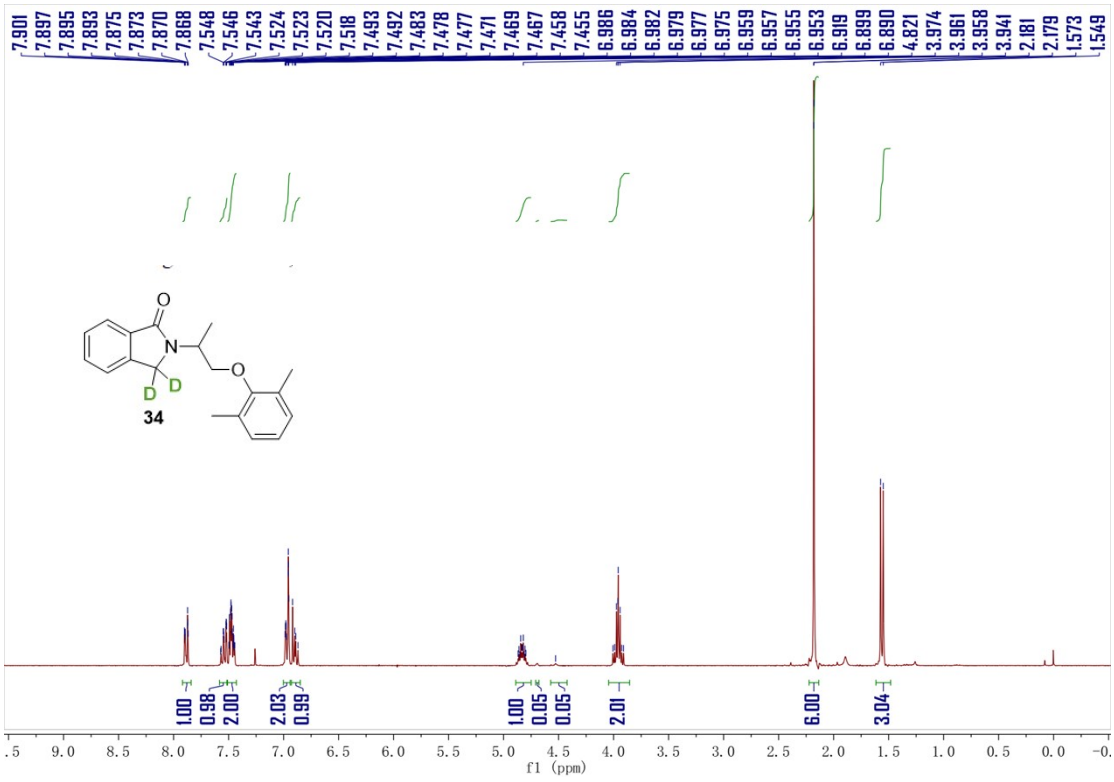


^{1}H NMR (300 MHz, $CDCl_3$):



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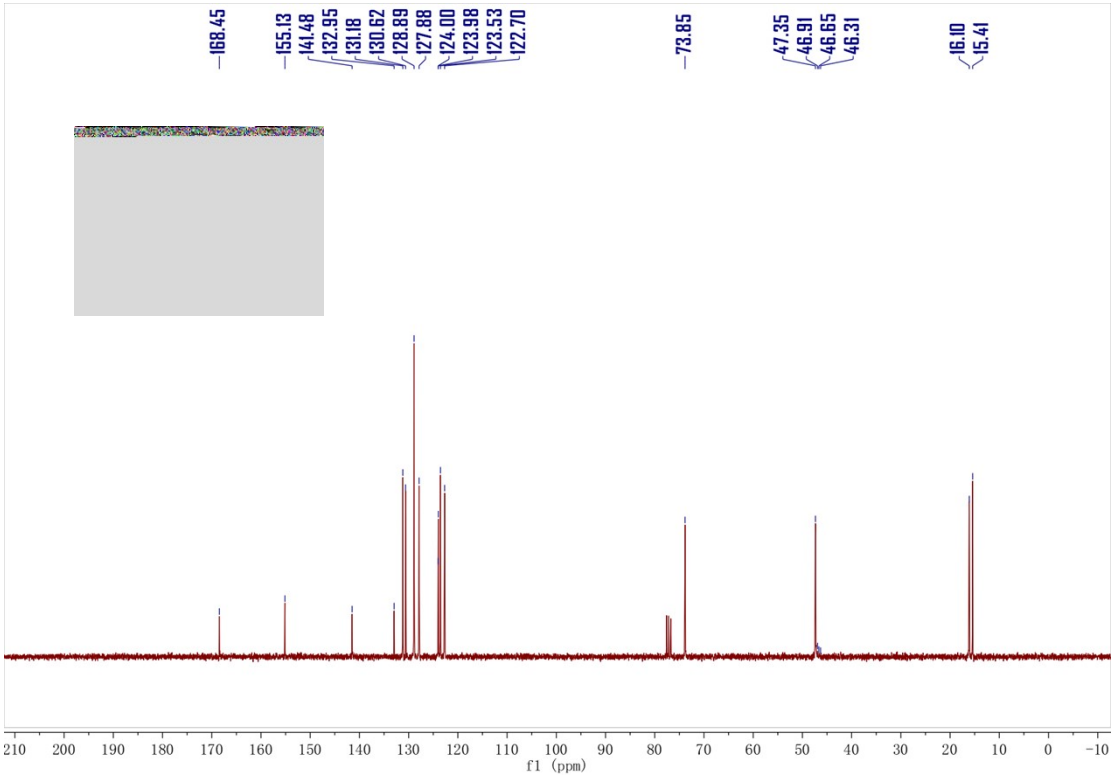
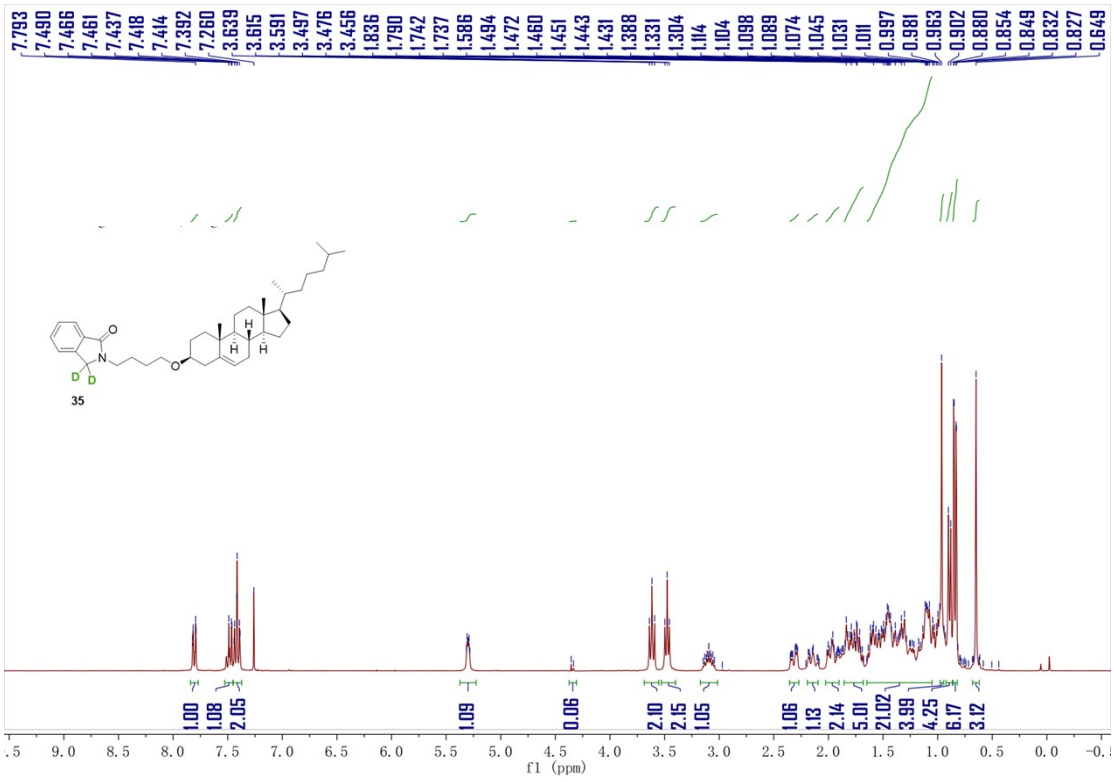


^{1}H NMR (300 MHz, $CDCl_3$):



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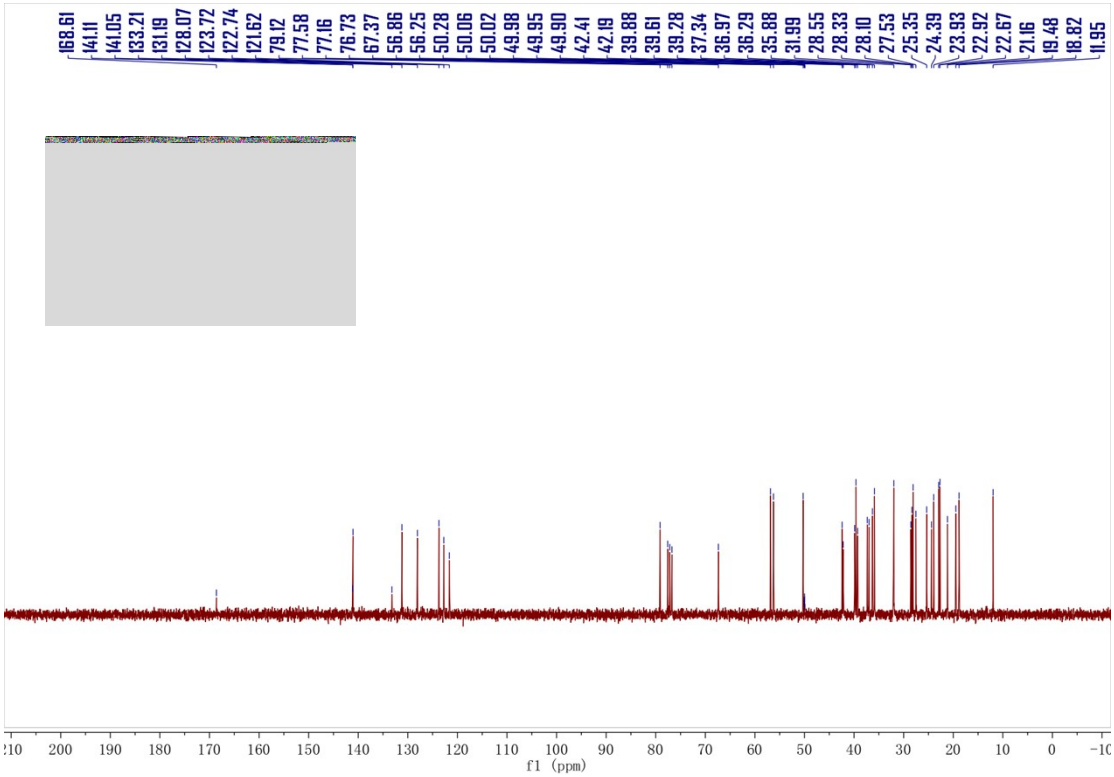

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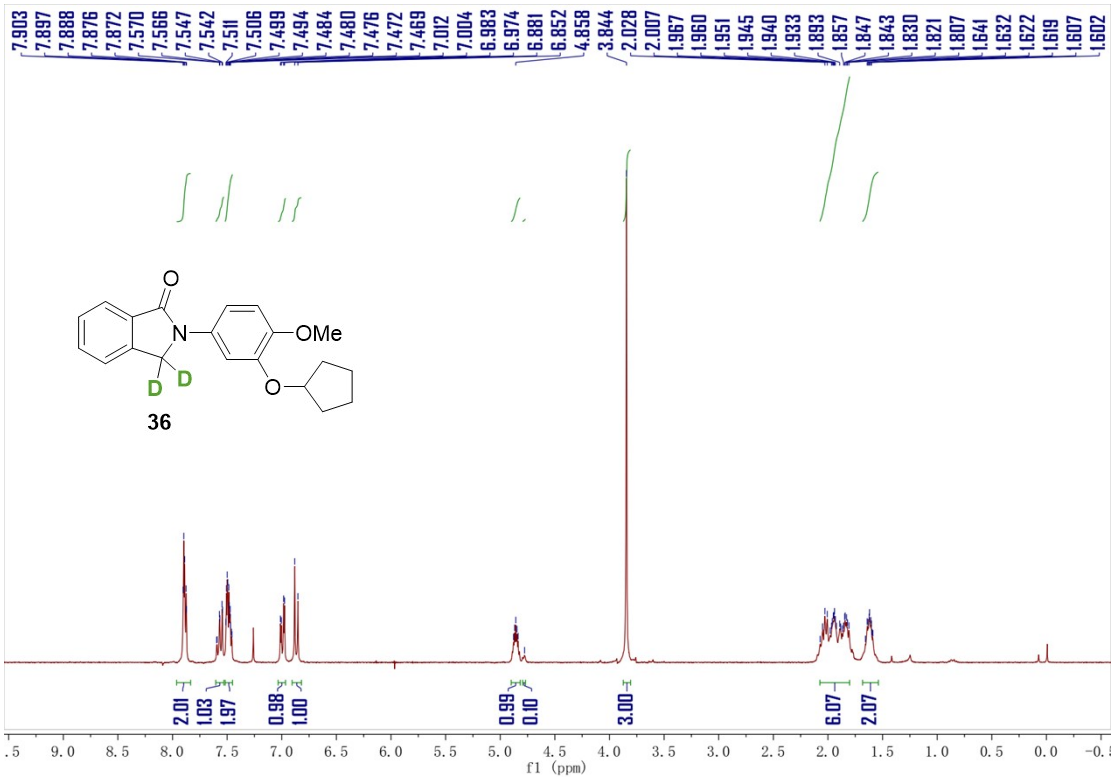

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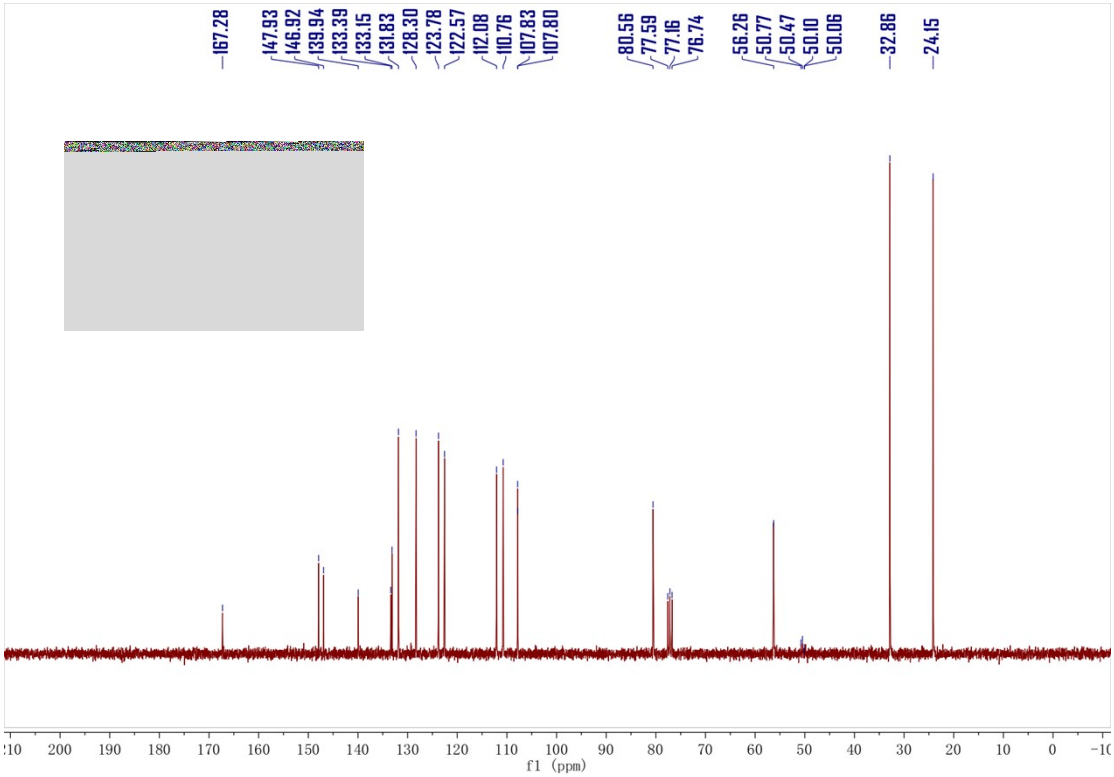
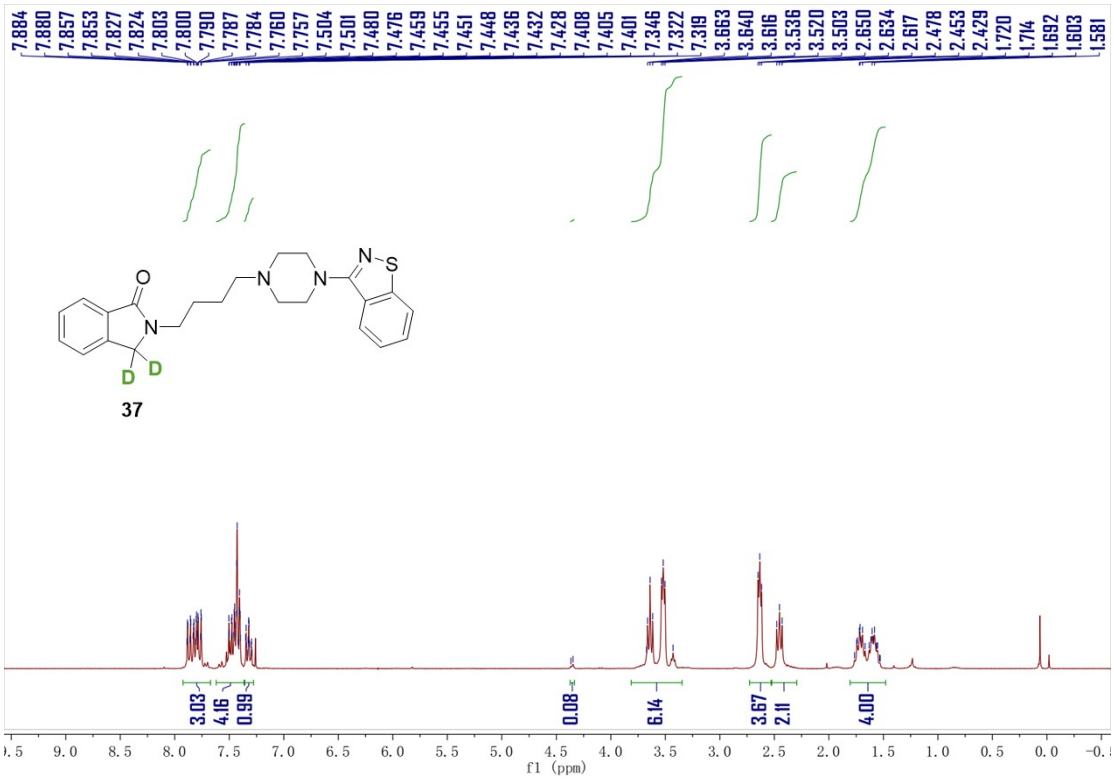


^{1}H NMR (300 MHz, $CDCl_3$):



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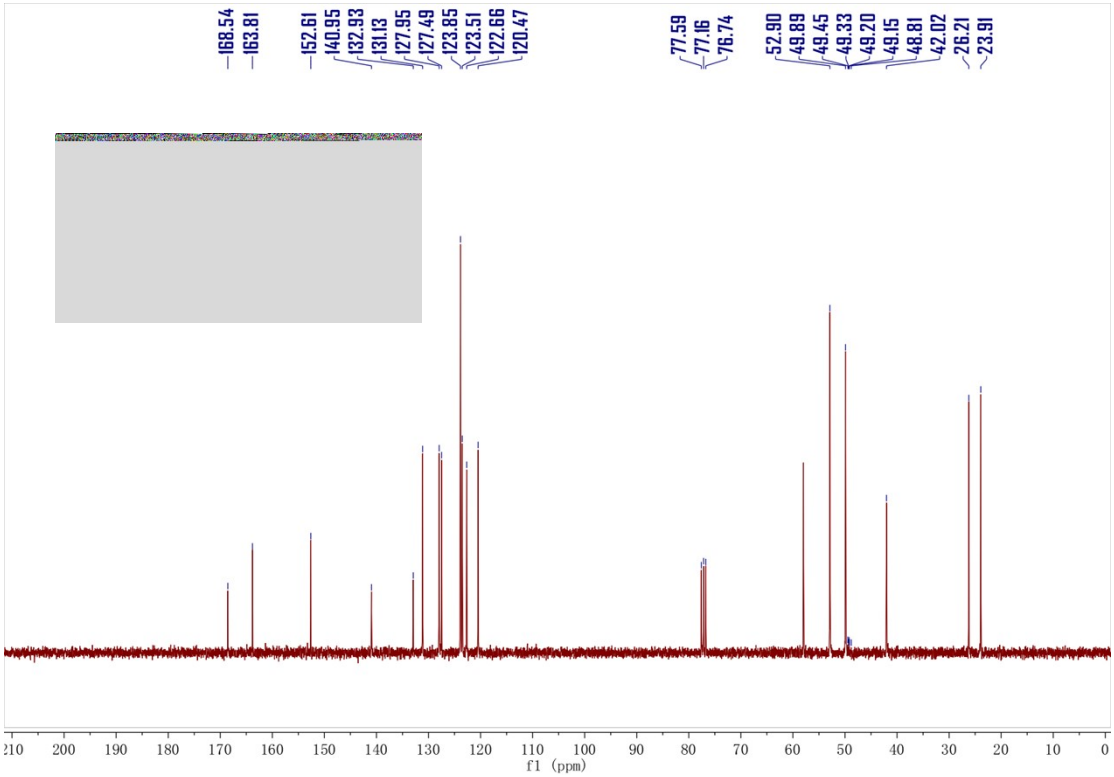

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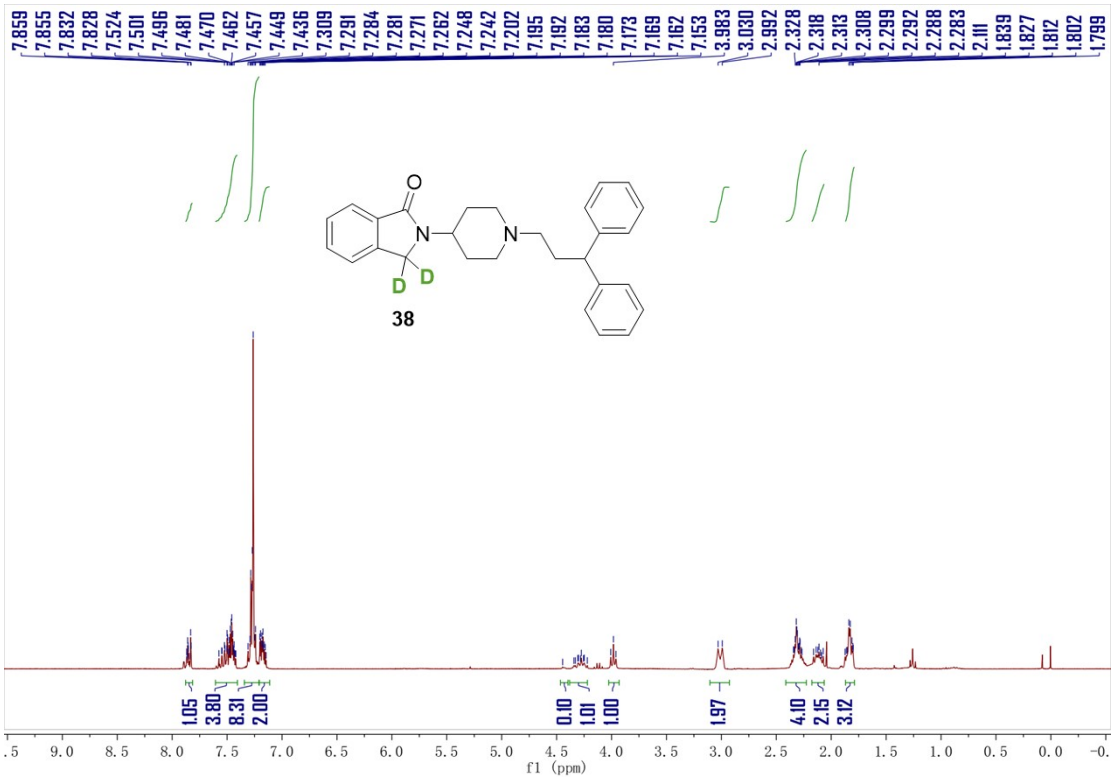

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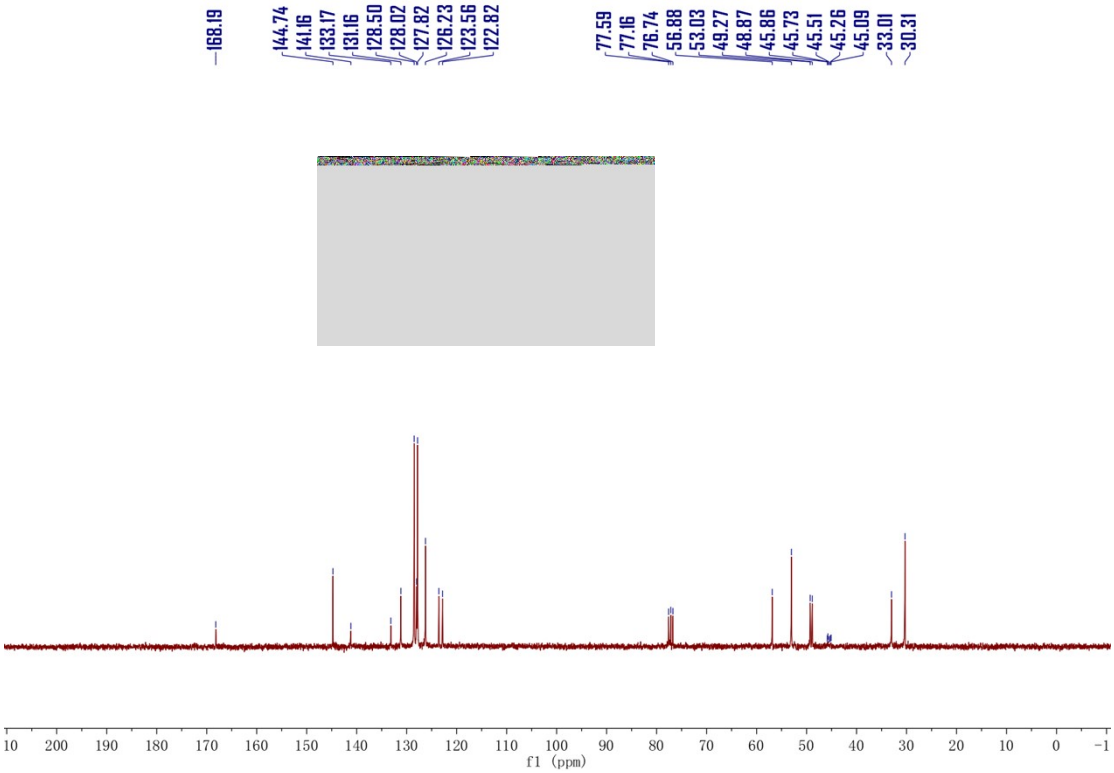

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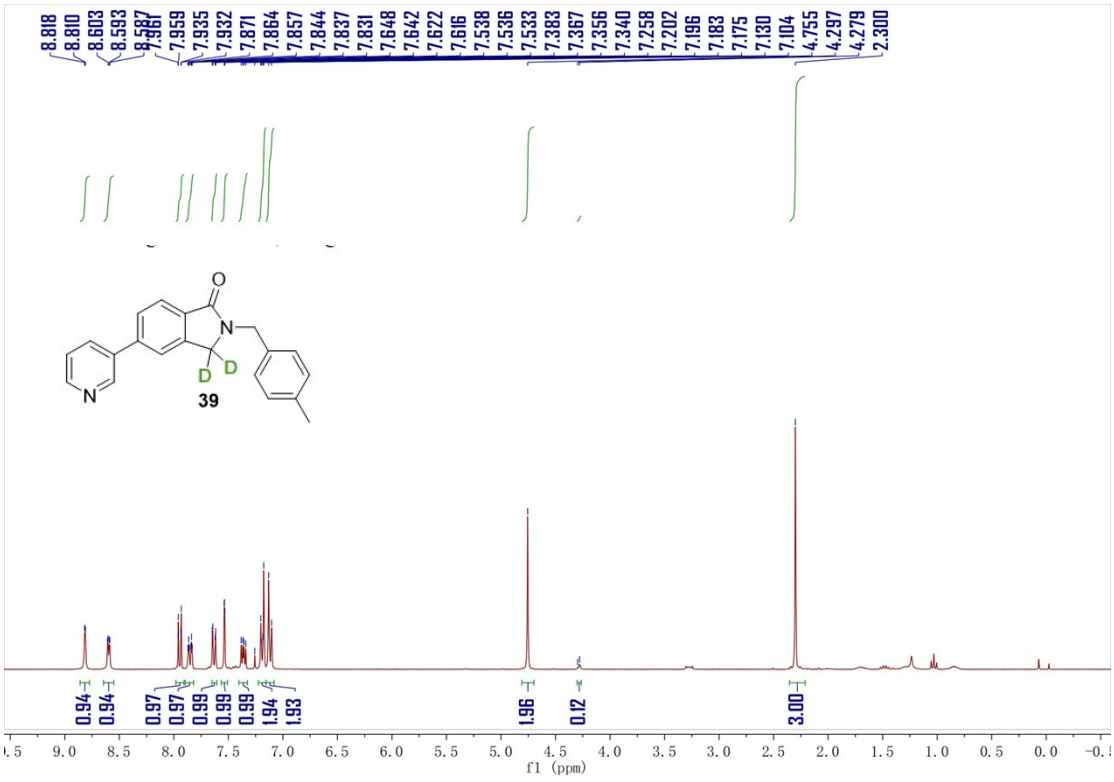

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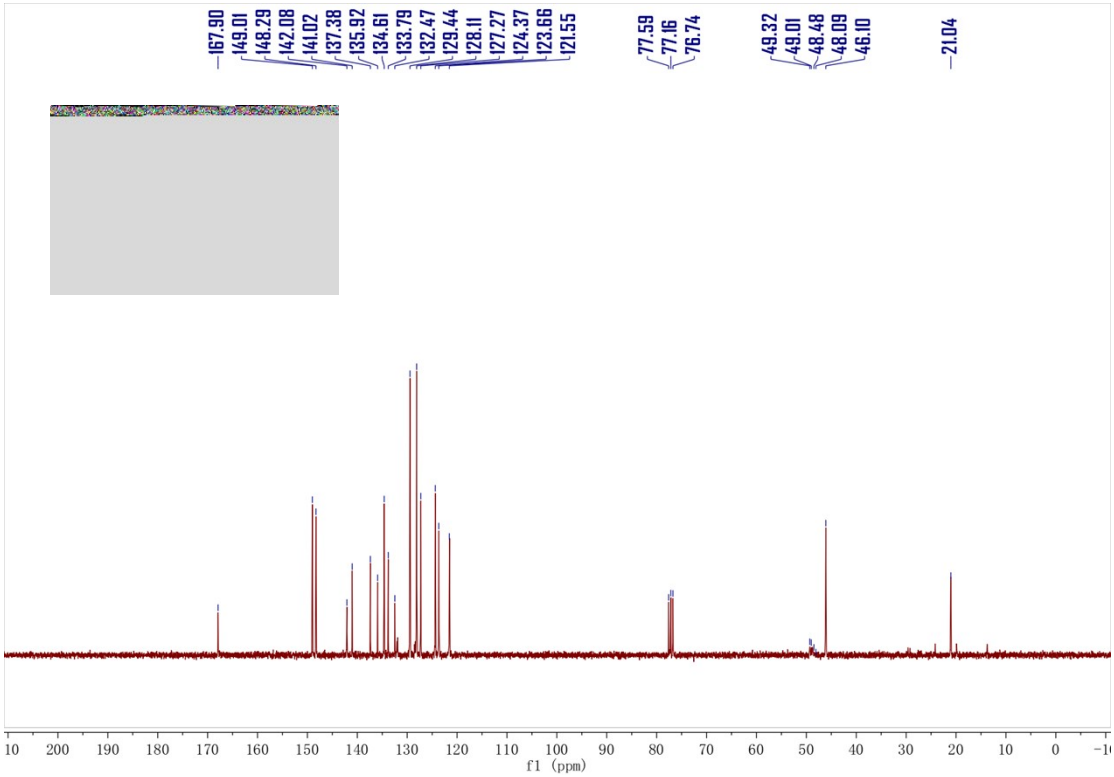

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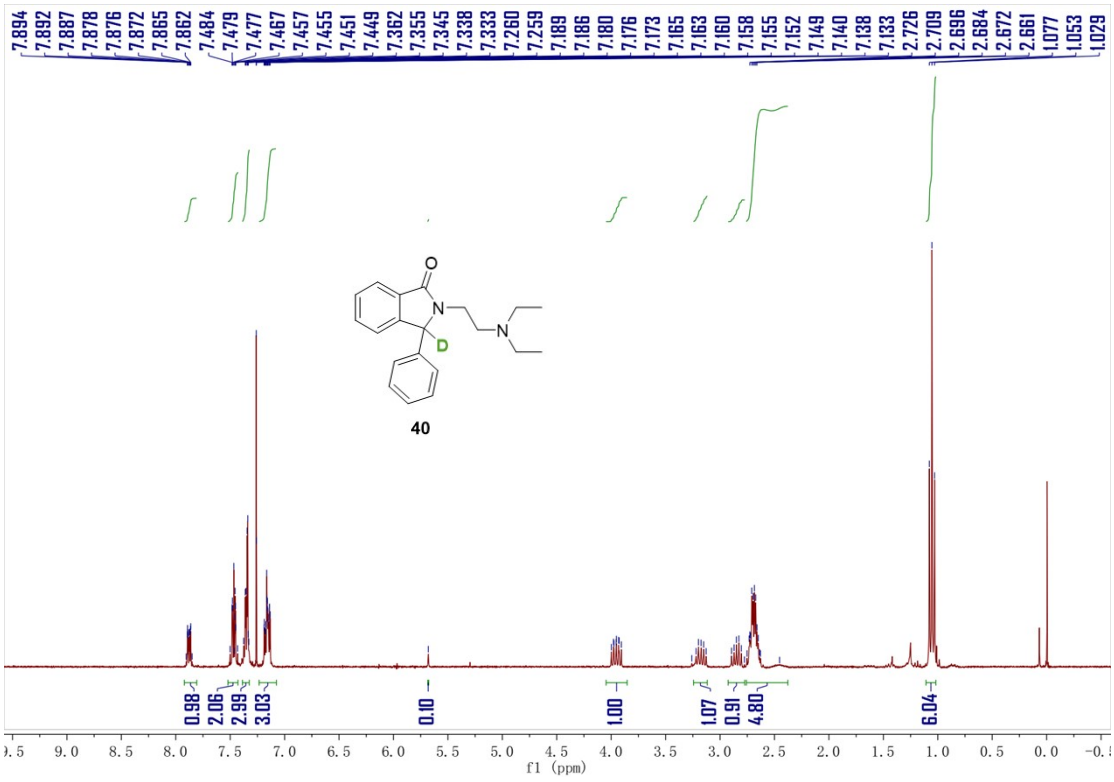

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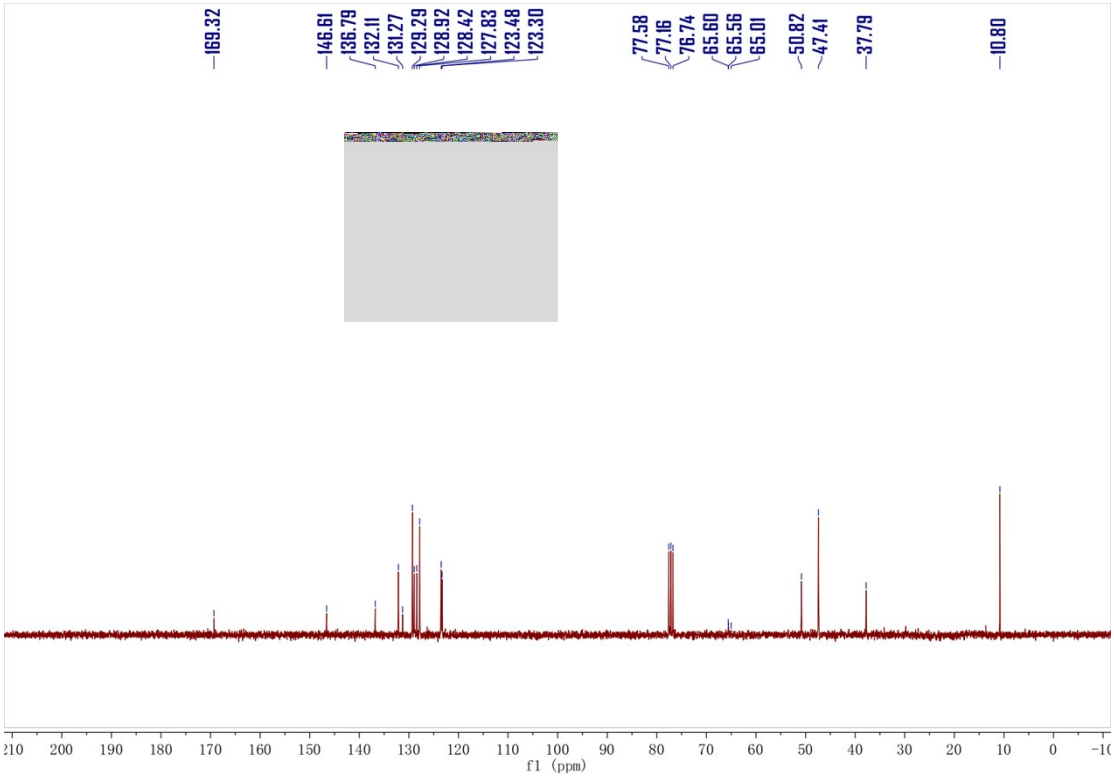

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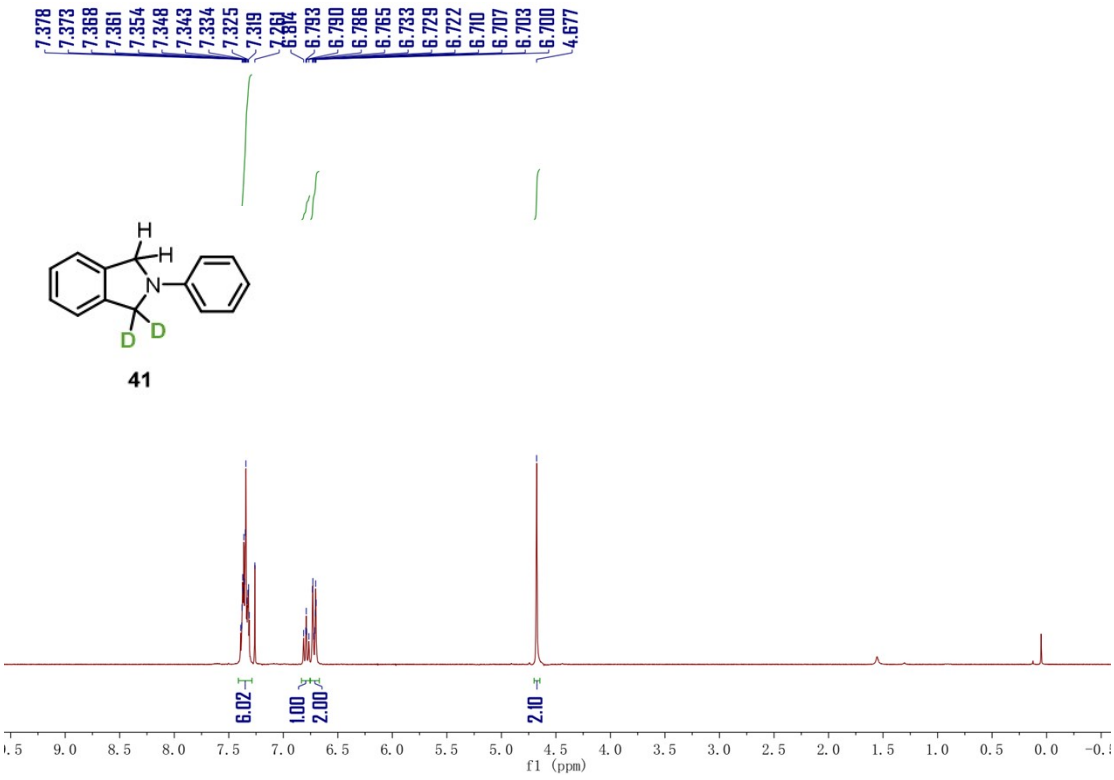

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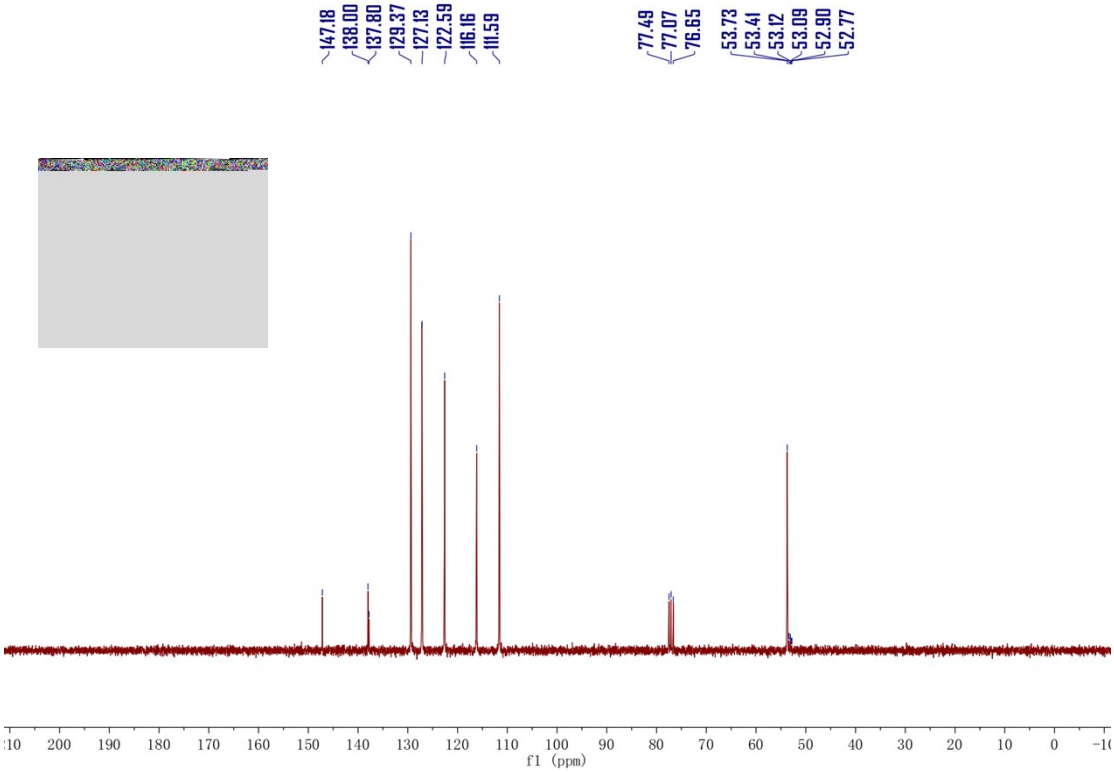

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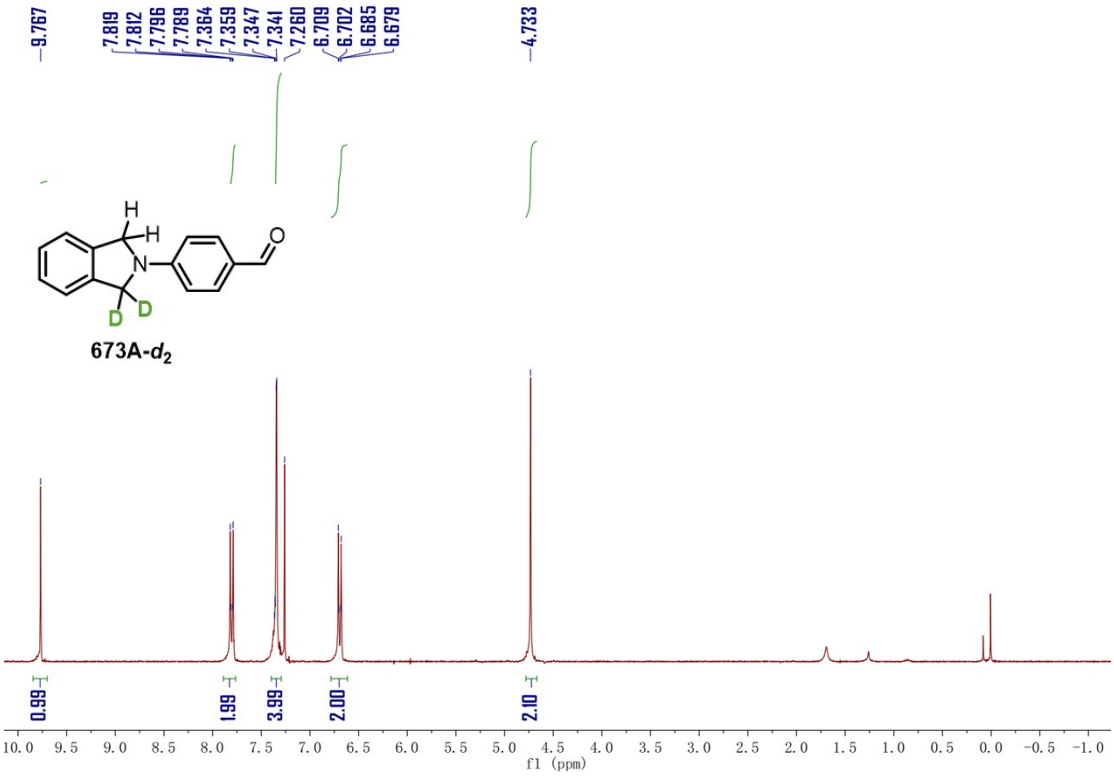

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