# Supporting Information

# Electrochemical *α*-Deuteration of Amides

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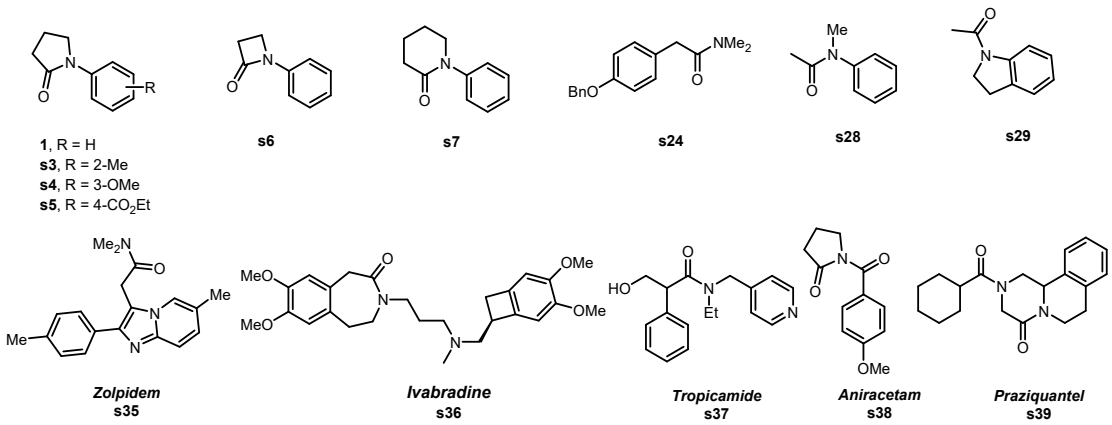
# I. General Information

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 $CDCl_3$ 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. High-resolution mass spectra (HRMS) were obtained with a time-of-flight (TOF) mass spectrometer (ESI).

***Electrode materials/dimensions:***

The graphite electrodes, steel electrodes and molybdenum electrodes are purchased from Zhongnuotansu (Tianjin). 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：**



## II. Substrates Synthesis and Characterization

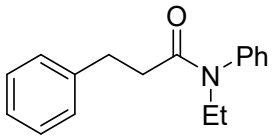
Synthesis of compounds **s8-s23**, **s25-s27** and **s30-s34**.


**s8-s23**, **s25-s27** and **s30-s34**

At room temperature, corresponding carboxylic acid (5 mmol, 1.0 eq.) was dissolved in DCM (30 mL) in a 50 mL round bottom flask, then EDCI (1.4 g, 7.5 mmol, 1.5 eq.) and DMAP (92 mg, 0.75 mmol, 0.15 eq.) were added, and then the corresponding secondary amine (7.5 mmol, 1.5 eq.) was added dropwise to the above solution, and the obtained solution was stirred at room temperature for 3 hours. 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 **s8-s23**, **s25-s27** and **s30-s34**.

***N*-Ethyl-*N*,3-diphenylpropanamide (s8)**

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

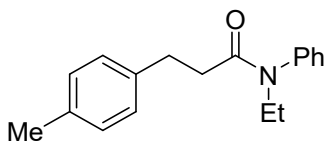



**s8**

Colourless liquid (1.16 g, 92% yield);

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.45 – 7.29 (m, 3H), 7.26 – 7.11 (m, 3H), 7.08 – 7.03 (m, 2H), 7.02 – 6.85 (m, 2H), 3.73 (q, *J* = 7.1 Hz, 2H), 2.90 (t, *J* = 7.8 Hz, 2H), 2.35 – 2.18 (m, 2H), 1.08 (td, *J* = 7.1, 0.6 Hz, 3H).

***N*-Ethyl-*N*-phenyl-3-(*p*-tolyl)propanamide (s9)**




**s9**

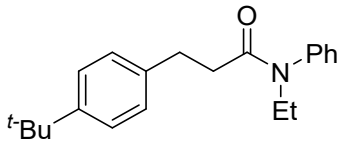
Colourless liquid (1.23 g, 92% yield);

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.49 – 7.26 (m, 3H), 7.11 – 6.74 (m, 6H), 3.75 (q, *J* = 7.1 Hz, 2H), 3.08 – 2.72 (m, 2H), 2.46 – 2.18 (m, 5H), 1.10 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 171.4, 142.1, 138.0, 135.2, 129.4, 128.8, 128.2, 128.1, 127.6, 43.8, 36.3, 31.1, 20.8, 12.9.

**HRMS (ESI)**: Calcd. for $C_{18}H_{22}NO^+$ $[M + H]^+$: 268.1696, found: 268.1690.

**3-(4-(*tert*-Butyl)phenyl)-*N*-ethyl-*N*-phenylpropanamide (s10)**




**s10**

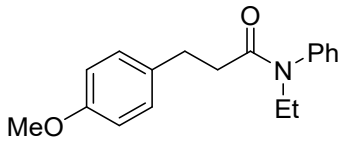
Colourless liquid (1.41 g, 91% yield);

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.42 – 7.30 (m, 3H), 7.30 – 7.22 (m, 2H), 7.05 – 6.82 (m, 4H), 3.74 (q, *J* = 7.1 Hz, 2H), 2.88 (dd, *J* = 9.1, 6.7 Hz, 2H), 2.38 – 2.17 (m, 2H), 1.29 (s, 9H), 1.10 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 171.5, 148.6, 142.1, 138.0, 129.3, 128.2, 127.9, 127.6, 124.9, 43.8, 36.1, 34.1, 31.1, 31.0, 12.8.

**HRMS (ESI)**: Calcd. for $C_{21}H_{28}NO^+$ $[M + H]^+$: 310.2165, found: 310.2161.

***N*-Ethyl-3-(4-methoxyphenyl)-*N*-phenylpropanamide (s11)**




**s11**

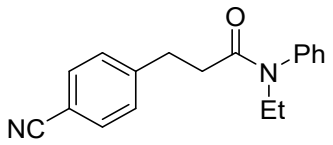
Colourless liquid (1.34 g, 95% yield);

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.45 – 7.28 (m, 3H), 7.07 – 6.87 (m, 4H), 6.88 – 6.67 (m, 2H), 3.74 (d, *J* = 13.0 Hz, 5H), 2.84 (t, *J* = 7.8 Hz, 2H), 2.52 – 2.04 (m, 2H), 1.14 – 0.86 (m, 3H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 171.4, 157.7, 142.0, 133.1, 129.4, 129.2, 128.2, 127.6, 113.4, 55.0, 43.8, 36.3, 30.7, 12.8.

**HRMS (ESI)**: Calcd. for $C_{18}H_{22}NO_2^+$ $[M + H]^+$: 284.1645, found: 284.1643.

**3-(4-Cyanophenyl)-*N*-ethyl-*N*-phenylpropanamide (s12)**




**s12**

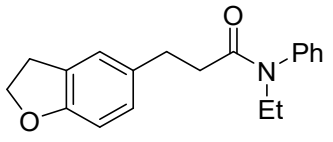
Colourless liquid (1.18 g, 85% yield);

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.61 – 7.43 (m, 2H), 7.43 – 7.32 (m, 3H), 7.17 (d, *J* = 7.9 Hz, 2H), 7.03 – 6.89 (m, 2H), 3.71 (q, *J* = 7.1 Hz, 2H), 2.94 (t, *J* = 7.5 Hz, 2H), 2.30 (t, *J* = 7.5 Hz, 2H), 1.07 (td, *J* = 7.2, 0.7 Hz, 3H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 170.4, 146.8, 141.7, 131.8, 129.5, 129.1, 128.0, 127.8, 118.7, 109.6, 43.8, 35.2, 31.3, 12.8.

**HRMS (ESI)**: Calcd. for $C_{18}H_{19}N_2O^+$ $[M + H]^+$: 279.1492, found: 279.1495.

**3-(2,3-Dihydrobenzofuran-5-yl)-*N*-ethyl-*N*-phenylpropanamide (s13)**




**s13**

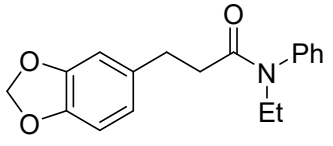
Colourless liquid (1.39 g, 94% yield);

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.51 – 7.27 (m, 3H), 7.14 – 6.87 (m, 3H), 6.82 – 6.71 (m, 1H), 6.64 (d, *J* = 8.1 Hz, 1H), 4.51 (t, *J* = 8.7 Hz, 2H), 3.73 (q, *J* = 7.1 Hz, 2H), 3.13 (t, *J* = 8.6 Hz, 2H), 2.92 – 2.63 (m, 2H), 2.26 (dd, *J* = 8.5, 7.0 Hz, 2H), 1.08 (t, *J* = 7.2 Hz, 3H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 171.5, 158.1, 142.1, 133.0, 129.3, 128.2, 127.6, 127.5, 126.7, 124.9, 108.6, 70.9, 43.8, 36.6, 31.0, 29.5, 12.8.

**HRMS (ESI)**: Calcd. for $C_{19}H_{22}NO_2^+$ $[M + H]^+$: 296.1645, found: 296.1647.

**3-(Benzo[*d*][1,3]dioxol-5-yl)-*N*-ethyl-*N*-phenylpropanamide (s14)**




**s14**

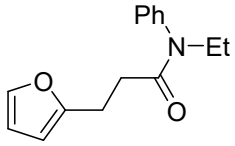
Colourless liquid (1.38 g, 93% yield);

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.56 – 7.25 (m, 3H), 7.10 – 6.89 (m, 2H), 6.79 – 6.60 (m, 1H), 6.56 – 6.35 (m, 2H), 5.89 (s, 2H), 3.73 (q, *J* = 7.2 Hz, 2H), 2.98 – 2.76 (m, 2H), 2.25 (dd, *J* = 8.6, 7.0 Hz, 2H), 1.09 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 171.3, 147.2, 145.4, 142.0, 134.9, 129.4, 128.2, 127.7, 121.0, 108.7, 107.8, 100.5, 43.8, 36.3, 31.2, 12.8.

**HRMS (ESI)**: Calcd. for $C_{18}H_{20}NO_3^+$ $[M + H]^+$: 298.1438, found: 298.1438.

***N*-Ethyl-3-(furan-2-yl)-*N*-phenylpropanamide (s15)**




**s15**

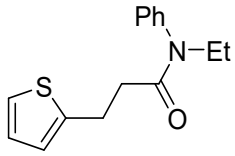
Yellow liquid (1.08 g, 89% yield);

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.51 – 7.28 (m, 3H), 7.28 – 7.21 (m, 1H), 7.10 – 6.98 (m, 2H), 6.22 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.00 – 5.79 (m, 1H), 3.74 (q, *J* = 7.1 Hz, 2H), 2.92 (dd, *J* = 8.7, 6.5 Hz, 2H), 2.32 (dd, *J* = 8.6, 6.6 Hz, 2H), 1.09 (t, *J* = 7.2 Hz, 3H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 171.0, 154.8, 142.1, 140.7, 129.6, 128.3, 127.8, 110.0, 105.1, 44.0, 32.9, 23.8, 13.0.

**HRMS (ESI)**: Calcd. for $C_{15}H_{18}NO_2^+$ $[M + H]^+$: 244.1332, found: 244.1341.

***N*-Ethyl-*N*-phenyl-3-(thiophen-2-yl)propanamide (s16)**




**s16**

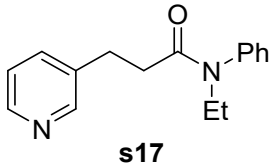
Colourless liquid (1.09 g, 84% yield);

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.48 – 7.28 (m, 3H), 7.19 – 6.92 (m, 3H), 6.84 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.68 (dt, *J* = 3.5, 1.0 Hz, 1H), 3.73 (q, *J* = 7.1 Hz, 2H), 3.22 – 3.01 (m, 2H), 2.33 (dd, *J* = 8.2, 6.8 Hz, 2H), 1.08 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 170.8, 143.7, 142.0, 129.5, 128.2, 127.8, 126.5, 124.4, 123.0, 43.9, 36.3, 25.5, 12.9.

**HRMS (ESI)**: Calcd. for $C_{15}H_{18}NOS^+$ $[M + H]^+$: 260.1104, found: 260.1106.

***N*-Ethyl-*N*-phenyl-3-(pyridin-3-yl)propanamide (s17)**




**s17**

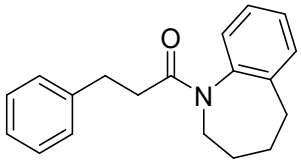
Colourless liquid (1.05 g, 83% yield);

**$^{1}$H NMR** (300 MHz, $CDCl_3$): δ 8.41 (d, *J* = 5.1 Hz, 2H), 7.50 – 7.28 (m, 3H), 7.12 – 6.86 (m, 4H), 3.70 (q, *J* = 7.2 Hz, 2H), 2.86 (t, *J* = 7.5 Hz, 2H), 2.28 (t, *J* = 7.6 Hz, 2H), 1.06 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 170.5, 150.1, 149.4, 141.8, 129.6, 128.1, 127.9, 123.7, 43.9, 34.7, 30.6, 12.8.

**HRMS (ESI)**: Calcd. for $C_{16}H_{19}N_2O^+$ $[M + H]^+$: 255.1492, found: 255.1490.

**3-Phenyl-1-(2,3,4,5-tetrahydro-1*H*-benzo[*b*]azepin-1-yl)propan-1-one (s18)**




**s18**

Colourless liquid (1.13 g, 81% yield);

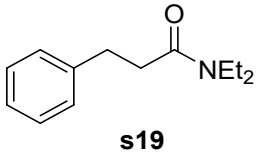
**$^{1}$H NMR** (300 MHz, $CDCl_3$): δ 7.36 – 6.78 (m, 9H), 4.91 – 4.48 (m, 1H), 2.89 (td, *J* = 7.9, 7.4, 1.8 Hz, 2H), 2.74 – 2.35 (m, 4H), 2.22 (ddd, *J* = 15.6, 8.6, 7.3 Hz, 1H), 2.08 – 1.68 (m, 3H), 1.49 – 1.11 (m, 1H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 170.9, 142.9, 141.2, 140.5, 129.9, 128.3, 128.1, 127.7, 127.4, 127.0, 125.8, 47.0, 35.9, 34.1, 31.4, 28.9, 26.3.

**HRMS (ESI)**: Calcd. for $C_{19}H_{22}NO^+$ $[M + H]^+$: 280.1696, found: 280.1694.

***N*,*N*-Diethyl-3-phenylpropanamide (s19)**

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

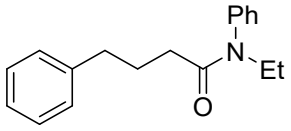



**s19**

Colourless liquid (0.98 g, 96% yield);

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.39 – 7.12 (m, 5H), 3.39 (q, *J* = 7.1 Hz, 2H), 3.23 (q, *J* = 7.2 Hz, 2H), 3.08 – 2.88 (m, 2H), 2.75 – 2.47 (m, 2H), 1.11 (td, *J* = 7.1, 2.7 Hz, 6H).

***N*-Ethyl-*N*,4-diphenylbutanamide (s20)**




**s20**

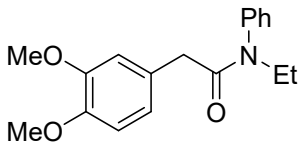
Colourless liquid (1.27 g, 95% yield);

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.51 – 7.32 (m, 3H), 7.28 – 6.97 (m, 7H), 3.75 (q, *J* = 7.1 Hz, 2H), 2.97 – 2.42 (m, 2H), 2.25 – 1.99 (m, 2H), 1.93 – 1.77 (m, 2H), 1.10 (t, *J* = 7.2 Hz, 3H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 172.1, 142.3, 141.7, 129.5, 128.3, 128.1, 127.7, 125.6, 43.9, 35.1, 33.8, 26.9, 13.0.

**HRMS (ESI)**: Calcd. for $C_{18}H_{22}NO^+$ $[M + H]^+$: 268.1696, found: 268.1689.

**2-(3,4-Dimethoxyphenyl)-*N*-ethyl-*N*-phenylacetamide (s21)**




**s21**

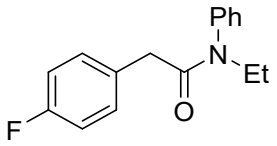
Colourless liquid (1.34 g, 90% yield);

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.47 – 7.31 (m, 3H), 7.14 – 7.00 (m, 2H), 6.72 (d, *J* = 8.2 Hz, 1H), 6.60 (d, *J* = 2.0 Hz, 1H), 6.52 (dd, *J* = 8.2, 2.0 Hz, 1H), 3.84 (s, 3H), 3.81 (s, 3H), 3.75 (q, *J* = 7.1 Hz, 2H), 3.35 (s, 2H), 1.10 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 170.5, 148.5, 147.5, 142.1, 129.4, 128.7, 127.9, 120.9, 112.1, 110.8, 55.7, 55.6, 44.2, 40.8, 12.9.

**HRMS (ESI)**: Calcd. for $C_{18}H_{22}NO_3^+$ $[M + H]^+$: 300.1594, found: 300.1598.

***N*-Ethyl-2-(4-fluorophenyl)-*N*-phenylacetamide (s22)**




**s22**

Colourless liquid (1.19 g, 93% yield);

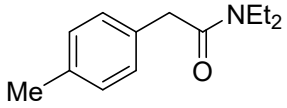
**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.45 – 7.32 (m, 3H), 7.14 – 6.78 (m, 6H), 3.75 (q, *J* = 7.2 Hz, 2H), 3.36 (s, 2H), 1.10 (t, *J* = 7.2 Hz, 3H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 170.1, 163.2, 160.0, 142.0, 131.2, 131.1, 130.5, 130.4, 129.5, 128.6, 128.0, 115.1, 114.8, 44.2, 40.4, 12.9.

**HRMS (ESI)**: Calcd. for $C_{16}H_{17}FNO^+$ $[M + H]^+$: 258.1289, found: 258.1292.

***N*,*N*-Diethyl-2-(*p*-tolyl)acetamide (s23)**

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



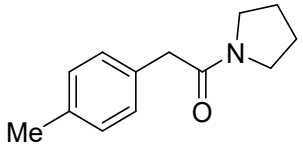

**s23**

Colourless liquid (0.97 g, 95% yield);

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.23 – 6.97 (m, 4H), 3.65 (s, 2H), 3.33 (dq, *J* = 29.0, 7.1 Hz, 4H), 2.32 (s, 3H), 1.10 (dt, *J* = 9.2, 7.1 Hz, 6H).

**1-(Pyrrolidin-1-yl)-2-(*p*-tolyl)ethan-1-one (s25)**

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



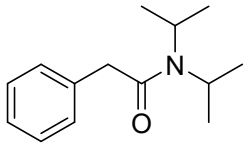

**s25**

Colourless liquid (0.91 g, 90% yield);

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.21 – 7.02 (m, 4H), 3.61 (s, 2H), 3.45 (dt, *J* = 20.5, 6.8 Hz, 4H), 2.32 (s, 3H), 1.99 – 1.74 (m, 4H).

***N*,*N*-Diisopropyl-2-phenylacetamide (s26)**

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

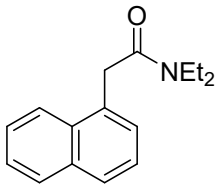


**s26**

Colourless liquid (0.99 g, 90% yield);

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.49 – 7.03 (m, 5H), 3.93 (p, *J* = 6.7 Hz, 1H), 3.66 (s, 2H), 3.34 (s, 1H), 1.39 (d, *J* = 6.8 Hz, 6H), 0.98 (d, *J* = 6.7 Hz, 6H).

***N*,*N*-Diethyl-2-(naphthalen-1-yl)acetamide (s27)**



**s27**

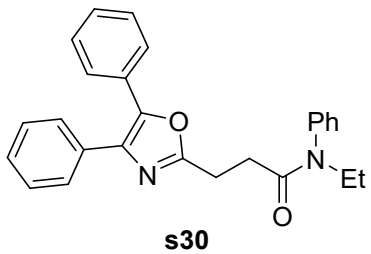
Yellow liquid (1.1 g, 90% yield);

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 8.00 – 7.91 (m, 1H), 7.84 (dd, *J* = 7.3, 2.0 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.60 – 7.28 (m, 4H), 4.11 (s, 2H), 3.44 (q, *J* = 7.1 Hz, 2H), 3.30 (q, *J* = 7.1 Hz, 2H), 1.13 (dt, *J* = 20.0, 7.1 Hz, 6H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 170.0, 133.6, 131.9, 131.7, 128.6, 127.4, 126.1, 126.0, 125.5, 125.4, 123.3, 42.3, 40.1, 38.2, 14.1, 12.8.

**HRMS (ESI)**: Calcd. for $C_{16}H_{20}NO^+$ $[M + H]^+$: 242.1539, found: 242.1545.

**3-(4,5-Diphenyloxazol-2-yl)-*N*-ethyl-*N*-phenylpropanamide (s30)**



**s30**

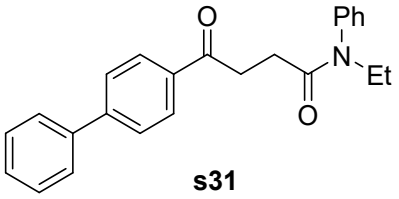
Colourless liquid (1.6 g, 80% yield);

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.73 – 7.50 (m, 4H), 7.47 – 7.30 (m, 9H), 7.19 (ddt, *J* = 7.5, 1.4, 0.8 Hz, 2H), 3.78 (q, *J* = 7.1 Hz, 2H), 3.16 (dd, *J* = 8.4, 6.7 Hz, 2H), 2.57 (dd, *J* = 8.4, 6.7 Hz, 2H), 1.12 (t, *J* = 7.2 Hz, 3H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 170.1, 162.3, 144.9, 141.7, 134.7, 132.3, 129.5, 128.8, 128.3, 128.2, 128.0, 127.7, 127.6, 127.6, 126.1, 43.9, 31.2, 23.7, 12.8.

**HRMS (ESI)**: Calcd. for $C_{26}H_{25}N_2O_2^+$ $[M + H]^+$: 397.1911, found: 397.1901.

**4-([1,1'-Biphenyl]-4-yl)-*N*-ethyl-4-oxo-*N*-phenylbutanamide (s31)**




**s31**

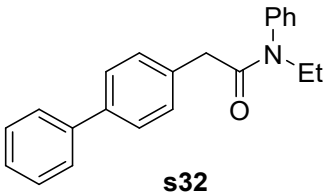
White solid (1.64 g, 92% yield); m.p. 105.1-106.9°C;

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 8.12 – 7.92 (m, 2H), 7.75 – 7.54 (m, 4H), 7.54 – 7.35 (m, 6H), 7.35 – 7.18 (m, 2H), 3.78 (q, *J* = 7.2 Hz, 2H), 3.31 (t, *J* = 6.5 Hz, 2H), 2.47 (t, *J* = 6.5 Hz, 2H), 1.12 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 198.4, 171.1, 145.3, 142.2, 139.7, 135.3, 129.5, 128.2, 128.4, 128.4, 127.7, 127.8, 127.0, 126.9, 43.9, 33.5, 28.5, 12.9.

**HRMS (ESI)**: Calcd. for $C_{24}H_{24}NO_2^+$ $[M + H]^+$: 358.1802, found: 358.1798.

**2-([1,1'-Biphenyl]-4-yl)-*N*-ethyl-*N*-phenylacetamide (s32)**




**s32**

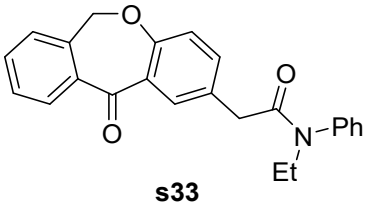
Colourless liquid (1.42 g, 90% yield);

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.61 – 7.52 (m, 2H), 7.50 – 7.29 (m, 8H), 7.17 – 7.06 (m, 4H), 3.78 (q, *J* = 7.1 Hz, 2H), 3.45 (s, 2H), 1.13 (t, *J* = 7.2 Hz, 3H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 170.2, 142.2, 140.9, 139.3, 134.6, 129.8, 129.5, 129.4, 128.7, 128.6, 128.0, 127.0, 126.9, 44.2, 40.9, 12.9.

**HRMS (ESI)**: Calcd. for $C_{22}H_{22}NO^+$ $[M + H]^+$: 316.1696, found: 316.1696.

***N*-Ethyl-2-(11-oxo-6,11-dihydrodibenzo[*b*,*e*]oxepin-2-yl)-*N*-phenylacetamide (s33)**




**s33**

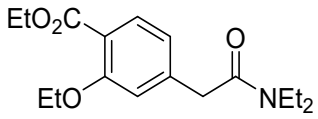
White solid (1.45 g, 78% yield); m.p. 154.5-155.1°C;

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.87 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.75 (d, *J* = 2.4 Hz, 1H), 7.61 – 7.33 (m, 7H), 7.18 – 7.11 (m, 2H), 6.97 (d, *J* = 8.4 Hz, 1H), 5.16 (s, 2H), 3.76 (d, *J* = 7.1 Hz, 2H), 3.40 (s, 2H), 1.12 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 190.3, 169.9, 159.9, 141.4, 140.1, 136.3, 135.2, 132.9, 132.1, 131.9, 129.5, 129.3, 128.9, 128.3, 128.0, 127.4, 124.6, 120.5, 73.2, 44.1, 40.0, 12.7.

**HRMS (ESI)**: Calcd. for $C_{24}H_{22}NO_3^+$ $[M + H]^+$: 372.1594, found: 372.1601.

**Ethyl 4-(2-(diethylamino)-2-oxoethyl)-2-ethoxybenzoate (s34)**




**s34**

Colourless liquid (1.38 g, 90% yield);

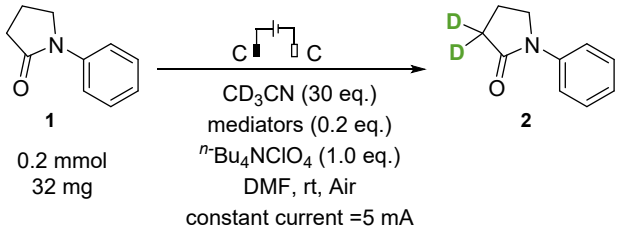
**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.74 (d, *J* = 7.9 Hz, 1H), 6.91 (d, *J* = 1.5 Hz, 1H), 6.87 – 6.72 (m, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 4.10 (q, *J* = 7.0 Hz, 2H), 3.69 (s, 2H), 3.39 (q, *J* = 7.1 Hz, 2H), 3.26 (q, *J* = 7.2 Hz, 2H), 1.40 (dt, *J* = 22.2, 7.0 Hz, 6H), 1.11 (td, *J* = 7.2, 5.7 Hz, 6H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 169.1, 166.1, 158.6, 141.1, 131.6, 120.2, 118.9, 113.2, 64.4, 60.4, 42.2, 40.9, 40.0, 14.5, 14.1, 14.0, 12.6.

**HRMS (ESI)**: Calcd. for $C_{17}H_{26}NO_4^+$ $[M + H]^+$: 308.1856, found: 308.1862.

## III. Investigation of Reaction Conditions

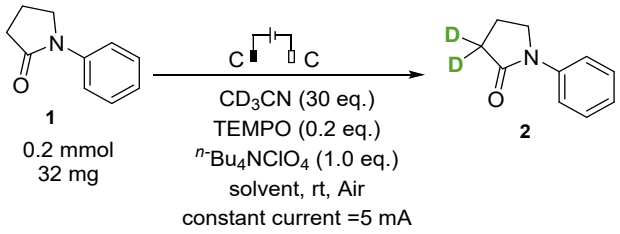
**Table S1.** Investigation of mediators[a]:




| entry | variation of mediators | D % of **2** [b] |
|---|---|---|
| 1 | NHPI | 65 |
| 2 | $Et_3N$ | 80 |
| 3 | $PPh_3$ | 70 |
| 4 | Ferrocene | 90 |
| 5 | TEMPO | 97 (82)[c] |

[a]Reaction conditions: graphite anode (d = 5 mm), graphite cathode (d = 5 mm), **1** (0.2 mmol), $^{n}$-$Bu_4NClO_4$ (1.0 eq.), mediators (0.2 eq.), $CD_3CN$ (30 eq.), DMF (3.0 mL), undivided cell, constant current = 5 mA, room temperature, 1-3 h (0.9 – 2.8 F/mol). [b]Degree of deuteration. [c]Isolated yield in parentheses.

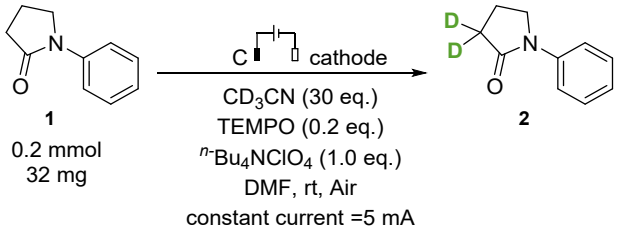
**Table S2.** Investigation of solvent[a]:




| entry | solvent (3 mL) | D % of **2** [b] |
|---|---|---|
| 1 | MeCN | 0 |
| 2 | DCM | trace |
| 3 | DMA | 46 |

[a]Reaction conditions: graphite anode (d = 5 mm), graphite cathode (d = 5 mm), **1** (0.2 mmol), $^{n}$-$Bu_4NClO_4$ (1.0 eq.), TEMPO (0.2 eq.), $CD_3CN$ (30 eq.), solvent (3.0 mL), undivided cell, constant current = 5 mA, room temperature, 1-3 h (0.9 – 2.8 F/mol). [b]Degree of deuteration.

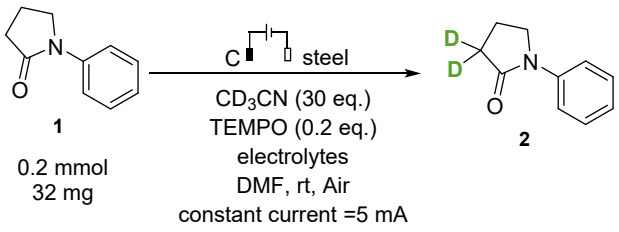
**Table S3.** Investigation of cathode[a]:




| entry | variation of cathode | D % of **2** [b] |
|---|---|---|
| 1 | RVC | 95 |
| 2 | Ni | 85 |
| 3 | Pt | 96 (82)[c] |
| 4 | steel | 97 (85)[c] |

[a]Reaction conditions: graphite anode (d = 5 mm), cathode (d = 5 mm), **1** (0.2 mmol), $^{n}$-$Bu_4NClO_4$ (1.0 eq.), TEMPO (0.2 eq.), $CD_3CN$ (30 eq.), DMF (3.0 mL), undivided cell, constant current = 5 mA, room temperature, 1-3 h (0.9 – 2.8 F/mol). [b]Degree of deuteration. [c]Isolated yield in parentheses.

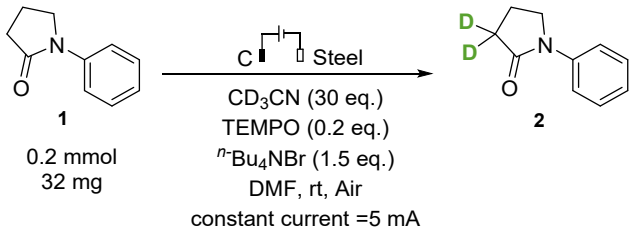
**Table S4.** Investigation of electrolytes[a]:




| entry | variation of electrolytes | D % of **2** [b] |
|---|---|---|
| 1 | $^{n}$-$Bu_4NPF_6$ (1.0 eq.) | 92 |
| 2 | $^{n}$-$Bu_4NBF_4$ (1.0 eq.) | 96 |
| 3 | $LiClO_4$ (1.0 eq.) | 0 |
| 4 | $NaSbF_6$ (1.0 eq.) | 0 |
| 5 | $^{n}$-$Bu_4NBr$ (0.2 eq.) | 97 (82)[c] |
| 6 | $^{n}$-$Bu_4NBr$ (0.5 eq.) | 97 (85)[c] |
| 7 | $^{n}$-$Bu_4NBr$ (1.0 eq.) | 97 (89)[c] |
| 8 | $^{n}$-$Bu_4NBr$ (1.5 eq.) | 99 (94)[c] |

[a]Reaction conditions: graphite anode (d = 5 mm), steel cathode (d = 5 mm), **1** (0.2 mmol), electrolytes, TEMPO (0.2 eq.), $CD_3CN$ (30 eq.), DMF (3.0 mL), undivided cell, constant current = 5 mA, room temperature, 1-3 h (0.9 – 2.8 F/mol). [b]Degree of deuteration. [c]Isolated yield in parentheses.

**Table S5.** Investigation of other conditions[a]:

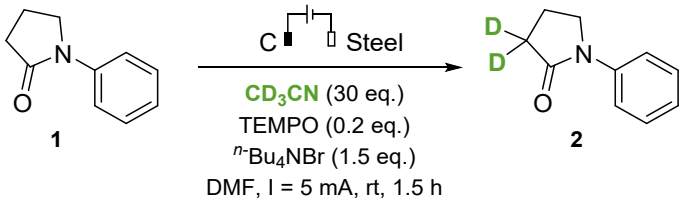



| entry | variation from standard conditions | D % of **2** [b] |
|---|---|---|
| 1 | none | 99 (94%) [c] |
| 2 | no TEMPO | 96 (67%) [c] |
| 3 | $D_2O$ instead of $CD_3CN$ | 10 |
| 4 | DMSO-$d_6$ instead of $CD_3CN$ | 95 (80%) [c] |
| 5 | $CD_3CN$ (20 eq.) instead of $CD_3CN$ (30 eq.) | 95 (81%) [c] |
| 6 | $CD_3CN$ (10 eq.) instead of $CD_3CN$ (30 eq.) | 80 |
| 7 | 10 mA instead of 5 mA | 96 (40%) [c] |
| 8 | TEMPO (0.1 eq.) instead of TEMPO (0.2 eq.) | 97 (85%) [c] |
| 9 | no electric current | 0 |

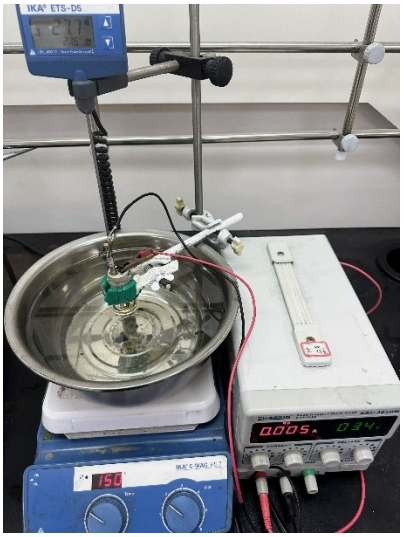
[a]Standard conditions: graphite anode (d = 5 mm), steel cathode (d = 5 mm), **1** (0.2 mmol), $^{n}$-$Bu_4NBr$ (1.5 eq.), TEMPO (0.2 eq.), $CD_3CN$ (30 eq.), DMF (3.0 mL), undivided cell, constant current = 5 mA, room temperature, 1.5 h (1.4 F/mol). [b]Degree of deuteration. [c]Isolated yield in parentheses.

# IV. Experimental Procedures and Compound Characterization

**General procedure for electrochemical *α*-deuteration of amides (Procedure A):**

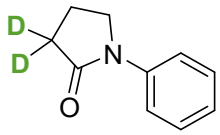



A 10 mL distillation flask equipped with a magnetic stir bar was charged with compound **1** (32.2 mg, 0.2 mmol, 1.0 eq.), $CD_3CN$ (0.32 mL, 30 eq.), TEMPO (6.5 mg, 0.04 mmol, 0.2 eq.), $^n$-$Bu_4NBr$ (96.7 mg, 0.3 mmol, 1.5 eq.) and DMF (3.0 mL). The flask equipped with graphite rod anode (d = 5 mm) and steel 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, the voltage range is 3.4 V – 3.9 V) for 1.5 h (1.4 F/mol) 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 = 5/1) as eluent afforded the desired product **2**.



Electrochemical setup for 0.2 mmol scale

**1-Phenylpyrrolidin-2-one-3,3-$d_2$ (2)**




**2**

White solid (30.6 mg, 94% yield, 99% D); m.p. 55.1−56.8 °C.

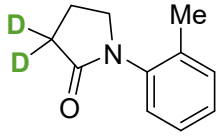
**$^{1}$H NMR** (300 MHz, $CDCl_3$): δ 7.72 – 7.55 (m, 2H), 7.54 – 7.29 (m, 2H), 7.26 – 6.99 (m, 1H), 3.88 (dd, *J* = 7.3, 6.7 Hz, 2H), 2.62 (s, 0.02H), 2.16 (t, *J* = 6.9 Hz, 2H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 174.1, 139.4, 128.7, 124.3, 119.8, 48.6, 32.8 – 31.8 (m), 17.7.

**HRMS (ESI)**: Calcd. for $C_{10}H_{10}D_2NO^+$ $[M + H]^+$: 164.1039, found: 164.1048.

**1-(*o*-Tolyl)pyrrolidin-2-one-3,3-$d_2$ (3)**

Following Procedure A, using 2.0 h (1.9 F/mol) instead of 1.5 h (1.4 F/mol).




**3**

Colourless liquid (25.5 mg, 72% yield, 97% D);

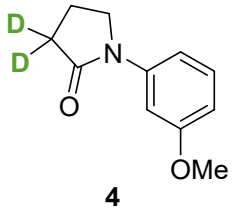
**$^{1}$H NMR** (300 MHz, $CDCl_3$): δ 7.34 – 7.17 (m, 3H), 7.19 – 7.04 (m, 1H), 3.83 – 3.35 (m, 2H), 2.58 (s, 0.06H), 2.23 (d, *J* = 7.4 Hz, 5H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 174.1, 137.3, 135.3, 130.9, 127.6, 126.6, 126.4, 50.5, 31.0 – 29.9 (m), 18.6, 17.7.

**HRMS (ESI)**: Calcd. for $C_{11}H_{12}D_2NO^+$ $[M + H]^+$: 178.1195, found: 178.1199.

**1-(3-Methoxyphenyl)pyrrolidin-2-one-3,3-$d_2$ (4)**

Following Procedure A, using 2.0 h (1.9 F/mol) instead of 1.5 h (1.4 F/mol).




**4**

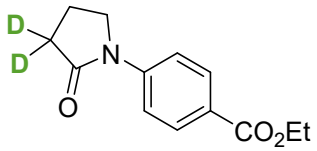
Colourless liquid (31.7 mg, 82% yield, 99% D);

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.41 – 7.18 (m, 2H), 7.12 (ddt, *J* = 8.2, 2.1, 0.7 Hz, 1H), 6.77 – 6.48 (m, 1H), 4.05 – 3.64 (m, 5H), 2.62 (s, 0.02H), 2.14 (t, *J* = 7.1 Hz, 2H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 174.1, 159.6, 140.4, 129.2, 111.7, 109.7, 105.7, 55.0, 48.6, 32.6 – 31.7 (m), 17.4.

**HRMS (ESI)**: Calcd. for $C_{11}H_{12}D_2NO_2^+$ $[M + H]^+$: 194.1145, found: 194.1153.

**Ethyl 4-(2-oxopyrrolidin-1-yl-3,3-*d*$_2$)benzoate (5)**




**5**

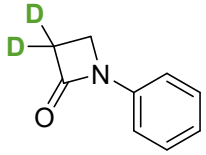
White solid (36.2 mg, 77% yield, 96% D); m.p. 91.1−92.5 °C.

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 8.19 – 7.91 (m, 2H), 7.84 – 7.60 (m, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.90 (dd, *J* = 7.3, 6.8 Hz, 2H), 2.63 (d, *J* = 8.5 Hz, 0.08H), 2.18 (t, *J* = 7.0 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 174.4, 165.8, 143.0, 130.0, 125.4, 118.2, 60.5, 48.1, 32.6 – 32.0 (m), 17.3, 14.1.

**HRMS (ESI)**: Calcd. for $C_{13}H_{14}D_2NO_3^+$ $[M + H]^+$: 236.1250, found: 236.1258.

**1-Phenylazetidin-2-one-3,3-*d*$_2$ (6)**




**6**

White solid (21.2 mg, 84% yield, 77% D); m.p. 70.5-72.1 °C.

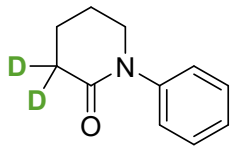
**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.45 – 7.29 (m, 4H), 7.22 – 6.96 (m, 1H), 3.73 – 3.47 (m, 2H), 3.11 (t, *J* = 4.5 Hz, 0.46H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 164.3, 138.4, 128.9, 123.6, 115.9, 37.6, 35.9 – 35.3 (m).

**HRMS (ESI)**: Calcd. for $C_9H_8D_2NO^+$ $[M + H]^+$: 150.0882, found: 150.0890.

**1-Phenylpiperidin-2-one-3,3-*d*$_2$ (7)**

Following Procedure A, using 2.0 h (1.9 F/mol) instead of 1.5 h (1.4 F/mol).




**7**

White solid (21.2 mg, 60% yield, 98% D); m.p. 95.1-96.7 °C.

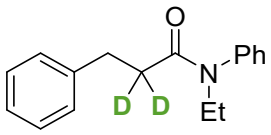
**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.51 – 7.33 (m, 2H), 7.31 – 7.11 (m, 3H), 3.64 (ddd, *J* = 6.3, 4.5, 1.4 Hz, 2H), 2.56 (s, 0.04H), 1.94 (dd, *J* = 6.0, 3.6 Hz, 4H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 169.8, 143.1, 128.9, 126.5, 126.0, 51.5, 32.6 – 32.0 (m), 23.3, 21.0.

**HRMS (ESI)**: Calcd. for $C_{11}H_{12}D_2NO^+$ $[M + H]^+$: 178.1195, found: 178.1207.

***N*-Ethyl-*N*,3-diphenylpropanamide-2,2-*d*$_2$ (8)**

Following Procedure A, using 2.5 h (2.3 F/mol) instead of 1.5 h (1.4 F/mol).




**8**

Colourless liquid (47.4 mg, 93% yield, 98% D);

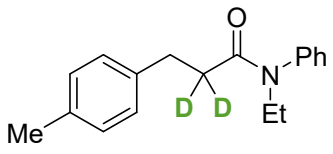
**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.45 – 7.27 (m, 3H), 7.27 – 7.12 (m, 3H), 7.09 – 6.87 (m, 4H), 3.74 (q, *J* = 7.2 Hz, 2H), 2.89 (s, 2H), 2.30 (s, 0.04H), 1.09 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 171.3, 142.0, 141.0, 129.3, 128.2, 128.1, 128.0, 127.6, 125.7, 43.8, 36.0 – 35.1 (m), 31.4, 12.8.

**HRMS (ESI)**: Calcd. for $C_{17}H_{18}D_2NO^+$ $[M + H]^+$: 256.1665, found: 256.1663.

***N*-Ethyl-*N*-phenyl-3-(*p*-tolyl)propanamide-2,2-*d*$_2$ (9)**

Following Procedure A, using 2.0 h (1.9 F/mol) instead of 1.5 h (1.4 F/mol).




**9**

Colourless liquid (49.5 mg, 92% yield, 98% D);

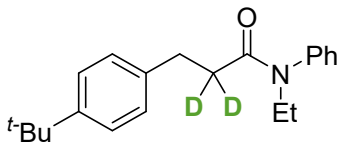
**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.46 – 7.28 (m, 3H), 7.12 – 6.70 (m, 6H), 3.74 (q, *J* = 7.1 Hz, 2H), 2.85 (s, 2H), 2.29 (s, 3.04H), 1.10 (td, *J* = 7.1, 0.7 Hz, 3H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 171.4, 142.1, 138.0, 135.2, 129.4, 128.8, 128.2, 128.1, 127.6, 43.8, 36.2 – 35.2 (m), 31.0, 20.8, 12.8.

**HRMS (ESI)**: Calcd. for $C_{18}H_{20}D_2NO^+$ $[M + H]^+$: 270.1821, found: 270.1815.

**3-(4-(*tert*-Butyl)phenyl)-*N*-ethyl-*N*-phenylpropanamide-2,2-$d_2$ (10)**

Following Procedure A, using 2.5 h (2.3 F/mol) instead of 1.5 h (1.4 F/mol).




**10**

Colourless liquid (56.0 mg, 90% yield, 99% D);

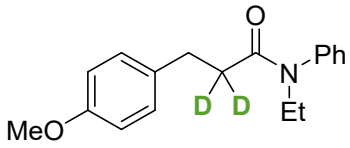
**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.60 – 7.17 (m, 5H), 6.98 (t, $J$ = 7.5 Hz, 4H), 3.74 (q, $J$ = 7.1 Hz, 2H), 2.86 (s, 2H), 2.30 (s, 0.02H), 1.29 (s, 9H), 1.09 (t, $J$ = 7.2 Hz, 3H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 171.5, 148.6, 142.1, 138.0, 129.4, 128.2, 127.9, 127.6, 125.0, 43.8, 35.8 – 34.1 (m), 34.1, 31.2, 31.0, 12.8.

**HRMS (ESI)**: Calcd. for $C_{21}H_{26}D_2NO^+$ $[M + H]^+$: 312.2291, found: 312.2287.

***N*-Ethyl-3-(4-methoxyphenyl)-*N*-phenylpropanamide-2,2-$d_2$ (11)**

Following Procedure A, using 2.0 h (1.9 F/mol) instead of 1.5 h (1.4 F/mol).




**11**

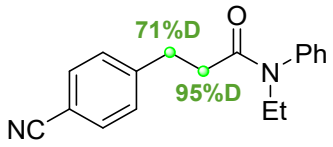
Colourless liquid (51.3 mg, 90% yield, 98% D);

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.45 – 7.27 (m, 3H), 7.03 – 6.82 (m, 4H), 6.76 (d, $J$ = 8.5 Hz, 2H), 3.74 (d, $J$ = 13.1 Hz, 5H), 2.82 (s, 2H), 2.25 (s, 0.04H), 1.08 (td, $J$ = 7.1, 0.5 Hz, 3H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 171.5, 157.8, 142.2, 133.2, 129.5, 129.3, 128.3, 127.7, 113.6, 55.1, 43.9, 36.3 – 35.3 (m), 30.7, 13.0.

**HRMS (ESI)**: Calcd. for $C_{18}H_{20}D_2NO_2^+$ $[M + H]^+$: 286.1771, found: 286.1766.

**3-(4-Cyanophenyl)-*N*-ethyl-*N*-phenylpropanamide-2,2,3,3-$d_4$ (12)**




**12**

Colourless liquid (40.3 mg, 72% yield);

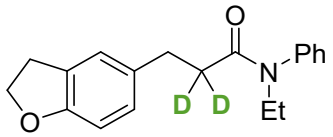
**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.59 – 7.46 (m, 2H), 7.46 – 7.33 (m, 3H), 7.23 – 7.11 (m, 2H), 7.02 – 6.89 (m, 2H), 3.71 (q, *J* = 7.2 Hz, 2H), 2.92 (d, *J* = 5.5 Hz, 0.58H, 71% D), 2.28 (s, 0.1H, 95% D), 1.07 (t, *J* = 7.2 Hz, 3H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 170.6, 146.9, 141.9, 132.0, 129.7, 129.2, 128.2, 128.0, 118.9, 109.7, 44.0, 31.4, 31.1 – 30.7 (m), 12.9.

**HRMS (ESI)**: Calcd. for $C_{18}H_{15}D_4N_2O^+$ [M + H] $^+$: 283.1743, found: 283.1749.

**3-(2,3-Dihydrobenzofuran-5-yl)-*N*-ethyl-*N*-phenylpropanamide-2,2-$d_2$ (13)**

Following Procedure A, using 2.0 h (1.9 F/mol) instead of 1.5 h (1.4 F/mol).




**13**

Colourless liquid (53.5 mg, 90% yield, 95% D);

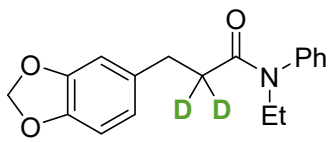
**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.42 – 7.26 (m, 3H), 7.04 – 6.86 (m, 3H), 6.76 (d, *J* = 8.1 Hz, 1H), 6.64 (d, *J* = 8.1 Hz, 1H), 4.52 (t, *J* = 8.7 Hz, 2H), 3.73 (q, *J* = 7.1 Hz, 2H), 3.13 (t, *J* = 8.7 Hz, 2H), 2.80 (s, 2H), 2.25 (s, 0.1H), 1.08 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 171.4, 158.1, 142.1, 132.9, 129.3, 128.2, 127.6, 127.5, 126.6, 124.8, 108.6, 70.8, 43.7, 36.4 – 35.6 (m), 30.9, 29.5, 12.8.

**HRMS (ESI)**: Calcd. for $C_{19}H_{20}D_2NO_2^+$ [M + H] $^+$: 298.1771, found: 298.1770.

**3-(Benzo[*d*][1,3]dioxol-5-yl)-*N*-ethyl-*N*-phenylpropanamide-2,2-$d_2$ (14)**

Following Procedure A, using 2.0 h (1.9 F/mol) instead of 1.5 h (1.4 F/mol).




**14**

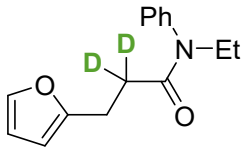
Colourless liquid (50.2 mg, 84% yield, 99% D);

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.45 – 7.27 (m, 3H), 7.16 – 6.97 (m, 2H), 6.86 – 6.61 (m, 1H), 6.51 (d, *J* = 6.9 Hz, 2H), 5.89 (s, 2H), 3.73 (q, *J* = 7.2 Hz, 2H), 2.79 (s, 2H), 2.24 (s, 0.02H), 1.09 (t, *J* = 7.2 Hz, 3H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 171.4, 147.3, 145.6, 142.1, 134.9, 129.5, 128.3, 127.8, 121.1, 108.8, 108.0, 100.6, 43.9, 36.3 – 35.5 (m), 31.2, 13.0.

**HRMS (ESI)**: Calcd. for $C_{18}H_{18}D_2NO_3^+$ $[M + H]^+$: 300.1563, found: 300.1565.

***N*-Ethyl-3-(furan-2-yl)-*N*-phenylpropanamide-2,2-$d_2$ (15)**




**15**

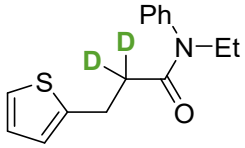
Colourless liquid (43.1 mg, 88% yield, 99% D);

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.52 – 7.28 (m, 3H), 7.29 – 7.18 (m, 1H), 7.12 – 6.88 (m, 2H), 6.23 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.05 – 5.79 (m, 1H), 3.75 (q, *J* = 7.1 Hz, 2H), 2.91 (s, 2H), 2.32 (s, 0.02H), 1.10 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 171.0, 154.8, 142.1, 140.8, 129.6, 128.3, 127.8, 110.1, 105.1, 44.0, 32.7 – 31.7 (m), 23.7, 13.0.

**HRMS (ESI)**: Calcd. for $C_{15}H_{16}D_2NO_2^+$ $[M + H]^+$: 246.1458, found: 246.1468.

***N*-Ethyl-*N*-phenyl-3-(thiophen-2-yl)propanamide-2,2-$d_2$ (16)**




**16**

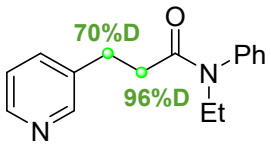
Colourless liquid (48.0 mg, 92% yield, 98% D);

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.51 – 7.29 (m, 3H), 7.13 – 6.92 (m, 3H), 6.87 (dd, *J* = 5.2, 3.4 Hz, 1H), 6.80 – 6.63 (m, 1H), 3.75 (q, *J* = 7.2 Hz, 2H), 3.12 (s, 2H), 2.34 (s, 0.04H), 1.11 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 170.7, 143.6, 141.9, 129.4, 128.1, 127.7, 126.4, 124.3, 122.9, 43.8, 36.7 – 35.3 (m), 25.3, 12.8.

**HRMS (ESI)**: Calcd. for $C_{15}H_{16}D_2NOS^+$ $[M + H]^+$: 262.1229, found: 262.1236.

***N*-Ethyl-*N*-phenyl-3-(pyridin-3-yl)propanamide-2,2,3,3-$d_4$ (17)**




**17**

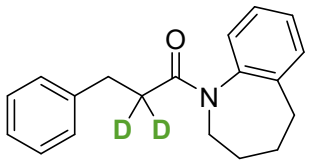
Colourless liquid (40.8 mg, 79% yield);

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 8.54 – 8.30 (m, 2H), 7.58 – 7.28 (m, 3H), 7.11 – 6.80 (m, 4H), 3.72 (q, *J* = 7.1 Hz, 2H), 2.88 (s, 0.6H, 70% D), 2.27 (s, 0.08H, 96% D), 1.27 – 0.87 (m, 3H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 170.4, 149.9, 149.4, 149.3, 141.7, 129.4, 128.0, 127.8, 123.6, 43.8, 30.3, 30.0 – 29.4 (m), 12.7.

**HRMS (ESI)**: Calcd. for $C_{16}H_{15}D_4N_2O^+$ $[M + H]^+$: 259.1743, found: 259.1748.

**3-Phenyl-1-(2,3,4,5-tetrahydro-1*H*-benzo[b]azepin-1-yl)propan-1-one-2,2-$d_2$ (18)**




**18**

Colourless liquid (53.4 mg, 86% yield, 95% D);

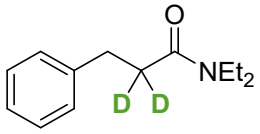
**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.32 – 6.89 (m, 9H), 4.81 – 4.57 (m, 1H), 2.89 (s, 2H), 2.67 – 2.32 (m, 3H), 2.24 (s, 0.1H), 1.94 – 1.69 (m, 3H), 1.45 – 1.08 (m, 1H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 170.9, 143.0, 141.2, 140.6, 130.0, 128.4, 128.2, 127.8, 127.5, 127.1, 125.9, 47.1, 36.0 – 35.1 (m), 34.1, 31.3, 29.0, 26.4.

**HRMS (ESI)**: Calcd. for $C_{19}H_{20}D_2NO^+$ $[M + H]^+$: 282.1821, found: 282.1816.

***N*,*N*-Diethyl-3-phenylpropanamide-2,2-$d_2$ (19)**

Following Procedure A, using molybdenum rod instead of steel, using 10 mA instead of 5 mA, using 4.0 h (7.5 F/mol) instead of 1.5 h (1.4 F/mol).




**19**

Colourless liquid (29.0 mg, 70% yield, 92% D);

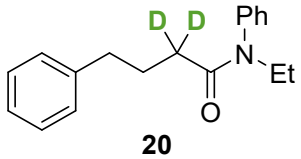
**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.30 – 7.07 (m, 5H), 3.35 (q, *J* = 7.1 Hz, 2H), 3.19 (q, *J* = 7.2 Hz, 2H), 2.94 (s, 2H), 2.63 – 2.44 (m, 0.16H), 1.08 (dt, *J* = 7.2, 3.6 Hz, 6H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 171.1, 141.3, 128.2, 125.9, 123.9, 41.7, 40.0, 34.9 – 33.9 (m), 31.3, 14.1, 12.9.

**HRMS (ESI)**: Calcd. for $C_{13}H_{18}D_2NO^+$ $[M + H]^+$: 208.1665, found: 208.1669.

***N*-Ethyl-*N*,4-diphenylbutanamide-2,2-$d_2$ (20)**

Following Procedure A, using 2.0 h (1.9 F/mol) instead of 1.5 h (1.4 F/mol).




**20**

Colourless liquid (51.1 mg, 95% yield, 95% D);

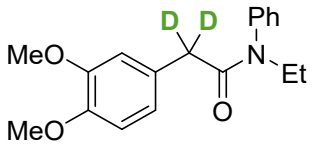
**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.46 – 7.31 (m, 3H), 7.31 – 7.03 (m, 7H), 3.74 (q, *J* = 7.1 Hz, 2H), 2.51 (dd, *J* = 8.8, 6.6 Hz, 2H), 2.04 (s, 0.1H), 1.87 (t, *J* = 7.8 Hz, 2H), 1.10 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 171.9, 142.1, 141.5, 129.3, 128.1, 127.9, 127.5, 125.4, 43.7, 34.9, 33.6 – 32.6 (m), 26.6, 12.9.

**HRMS (ESI)**: Calcd. for $C_{18}H_{20}D_2NO^+$ $[M + H]^+$: 270.1821, found: 270.1809.

**2-(3,4-Dimethoxyphenyl)-*N*-ethyl-*N*-phenylacetamide-$d_2$ (21)**

Following Procedure A, using 1.0 h (0.9 F/mol) instead of 1.5 h (1.4 F/mol).




**21**

Colourless liquid (43.3 mg, 72% yield, 97% D);

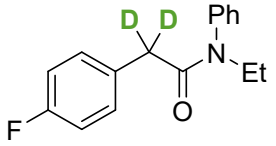
**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.42 – 7.29 (m, 3H), 7.11 – 6.92 (m, 2H), 6.71 (d, *J* = 8.2 Hz, 1H), 6.59 (d, *J* = 2.0 Hz, 1H), 6.51 (dd, *J* = 8.2, 2.1 Hz, 1H), 3.83 (s, 3H), 3.80 (s, 3H), 3.74 (q, *J* = 7.2 Hz, 2H), 3.34 (s, 0.06H), 1.09 (t, *J* = 7.2 Hz, 3H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 170.2, 148.4, 147.4, 141.9, 129.2, 128.5, 127.7, 125.1, 120.7, 112.0, 110.8, 55.6, 55.4, 43.9, 40.5 – 39.8 (m), 12.7.

**HRMS (ESI)**: Calcd. for $C_{18}H_{20}D_2NO_3^+$ $[M + H]^+$: 302.1720, found: 302.1719.

***N*-Ethyl-2-(4-fluorophenyl)-*N*-phenylacetamide-$d_2$ (22)**

Following Procedure A, using 0.5 h (0.5 F/mol) instead of 1.5 h (1.4 F/mol).




**22**

Colourless liquid (42.0 mg, 81% yield, 97% D);

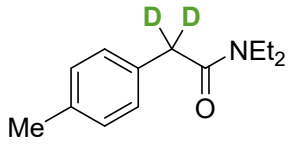
**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.49 – 7.30 (m, 3H), 7.19 – 6.68 (m, 6H), 3.75 (q, *J* = 7.2 Hz, 2H), 3.36 (s, 0.06H), 1.10 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 169.9, 163.0, 159.8, 141.8, 130.9, 130.3, 130.2, 129.4, 128.4, 127.8, 114.9, 114.6, 44.0, 40.1 – 39.6 (m), 12.7.

**HRMS (ESI)**: Calcd. for $C_{16}H_{15}D_2FNO^+$ $[M + H]^+$: 260.1414, found: 260.1415.

***N*,*N*-Diethyl-2-(*p*-tolyl)acetamide-$d_2$ (23)**

Following Procedure A, using 1.0 h (0.9 F/mol) instead of 1.5 h (1.4 F/mol).




**23**

Colourless liquid (34.4 mg, 83% yield, 98% D);

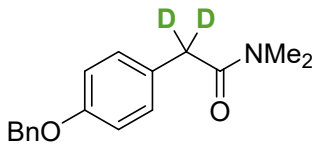
**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.20 – 6.96 (m, 4H), 3.63 (s, 0.04H), 3.33 (dq, *J* = 28.9, 7.1 Hz, 4H), 2.32 (d, *J* = 0.6 Hz, 3H), 1.45 – 0.58 (m, 6H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 170.1, 135.8, 132.0, 129.0, 128.2, 127.0, 124.1, 42.0, 40.7 – 40.4 (m), 39.8, 20.7, 13.9, 12.6.

**HRMS (ESI)**: Calcd. for $C_{13}H_{18}D_2NO^+$ $[M + H]^+$: 208.1665, found: 208.1675.

**2-(4-(Benzyloxy)phenyl)-*N*,*N*-dimethylacetamide-$d_2$ (24)**

Following Procedure A, using 0.5 h (0.5 F/mol) instead of 1.5 h (1.4 F/mol).




**24**

White solid (45.5 mg, 84% yield, 97% D); m.p. 100.5-101.1 °C.

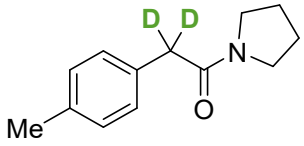
**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.54 – 7.25 (m, 5H), 7.22 – 7.13 (m, 2H), 7.01 – 6.78 (m, 2H), 5.04 (s, 2H), 3.65 (s, 0.06H), 2.98 (d, *J* = 11.8 Hz, 6H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 171.1, 157.4, 136.8, 129.5, 128.3, 127.7, 127.2, 125.6, 114.8, 69.7, 39.8 – 39.2 (m), 37.4, 35.3.

**HRMS (ESI)**: Calcd. for $C_{17}H_{18}D_2NO_2^+$ $[M + H]^+$: 272.1614, found: 272.1619.

**1-(Pyrrolidin-1-yl)-2-(*p*-tolyl)ethan-1-one-2,2-$d_2$ (25)**

Following Procedure A, using 0.5 h (0.5 F/mol) instead of 1.5 h (1.4 F/mol).




**25**

Colourless liquid (33.2 mg, 81% yield, 96% D);

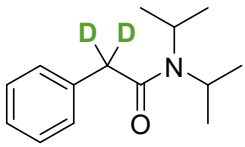
**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.15 (q, *J* = 8.2 Hz, 4H), 3.61 (s, 0.08H), 3.45 (dt, *J* = 19.2, 6.8 Hz, 4H), 2.32 (s, 3H), 1.99 – 1.76 (m, 4H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 169.5, 135.9, 131.5, 129.0, 128.5, 46.6, 45.6, 41.7 – 41.1 (m), 25.9, 24.1, 20.8.

**HRMS (ESI)**: Calcd. for $C_{13}H_{16}D_2NO^+$ $[M + H]^+$: 206.1508, found: 206.1517.

***N*,*N*-Diisopropyl-2-phenylacetamide-$d_2$ (26)**

Following Procedure A, using 1.0 h (0.9 F/mol) instead of 1.5 h (1.4 F/mol).




**26**

Colourless liquid (35.4 mg, 80% yield, 97% D);

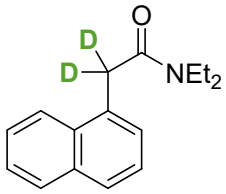
**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.43 – 7.00 (m, 5H), 3.95 (p, *J* = 6.6 Hz, 1H), 3.67 (s, 0.06H), 3.36 (s, 1H), 1.41 (d, *J* = 6.8 Hz, 6H), 1.00 (d, *J* = 6.7 Hz, 6H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 169.4, 135.3, 128.1, 128.0, 126.1, 48.9, 45.3, 43.9 – 41.5 (m), 20.1, 20.0.

**HRMS (ESI)**: Calcd. for $C_{14}H_{20}D_2NO^+$ $[M + H]^+$: 222.1821, found: 222.1826.

***N*,*N*-Diethyl-2-(naphthalen-1-yl)acetamide-$d_2$ (27)**

Following Procedure A, using 0.5 h (0.5 F/mol) instead of 1.5 h (1.4 F/mol).




**27**

Yellow liquid (37.9 mg, 78% yield, 93% D);

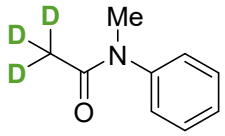
**$^1$H NMR** (300 MHz, $CDCl_3$): δ 8.01 – 7.95 (m, 1H), 7.92 – 7.84 (m, 1H), 7.78 (dt, *J* = 8.2, 1.1 Hz, 1H), 7.62 – 7.31 (m, 4H), 4.14 (s, 0.14H), 3.47 (q, *J* = 7.1 Hz, 2H), 3.33 (q, *J* = 7.1 Hz, 2H), 1.16 (dt, *J* = 20.4, 7.1 Hz, 6H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 169.9, 133.6, 131.9, 131.6, 128.5, 127.3, 126.0, 125.9, 125.4, 125.3, 123.2, 42.2, 40.0, 38.1 – 37.2 (m), 14.0, 12.8.

**HRMS (ESI)**: Calcd. for $C_{16}H_{18}D_2NO^+$ $[M + H]^+$: 244.1665, found: 244.1667.

***N*-Methyl-*N*-phenylacetamide-$d_3$ (28)**

Following Procedure A, using 2.5 h (2.3 F/mol) instead of 1.5 h (1.4 F/mol).




**28**

White solid (27.4 mg, 90% yield, 96% D); m.p. 91.6-93.2 °C.

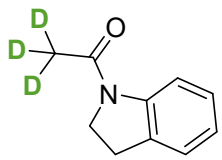
**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.51 – 7.27 (m, 3H), 7.24 – 7.09 (m, 2H), 3.26 (s, 3H), 1.84 (s, 0.12H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 170.4, 144.5, 129.6, 127.6, 126.9, 37.0, 22.6 – 21.6 (m).

**HRMS (ESI)**: Calcd. for $C_9H_9D_3NO^+$ $[M + H]^+$: 153.1102, found: 153.1106.

**1-(Indolin-1-yl)ethan-1-one-2,2,2-$d_3$ (29)**

Following Procedure A, using 2.0 h (1.9 F/mol) instead of 1.5 h (1.4 F/mol).




**29**

Colourless liquid (27.9 mg, 85% yield, 96% D);

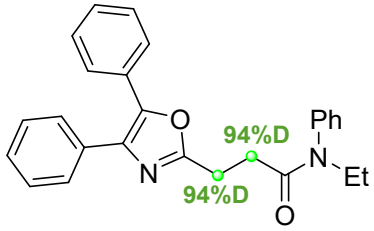
**$^1$H NMR** (300 MHz, $CDCl_3$, rotamers): δ 8.26 – 8.04 (m, 1H), 7.24 – 7.07 (m, 2H), 6.98 (td, *J* = 7.5, 1.1 Hz, 1H), 4.02 (dd, *J* = 9.0, 8.0 Hz, 2H), 3.26 – 2.88 (m, 2H), 2.20 – 2.16 (m, 0.12H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$, rotamers): δ 169.1, 168.5, 142.7, 141.6, 131.0, 127.2, 125.7, 124.4, 123.3, 122.9, 116.6, 113.8, 48.5, 47.7, 27.7, 26.6, 24.0 – 23.0 (m).

**HRMS (ESI)**: Calcd. for $C_{10}H_9D_3NO^+$ $[M + H]^+$: 165.1102, found: 165.1108.

**3-(4,5-Diphenyloxazol-2-yl)-*N*-ethyl-*N*-phenylpropanamide-2,2,3,3-$d_4$ (30)**

Following Procedure A, using 0.1 mmol substrate instead of 0.2 mmol, using 2.0 h (3.7 F/mol) instead of 1.5 h (1.4 F/mol).




**30**

Colourless liquid (28.0 mg, 70% yield);

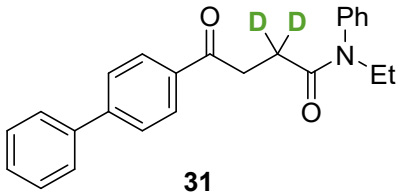
**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.68 – 7.48 (m, 4H), 7.45 – 7.24 (m, 9H), 7.23 – 7.14 (m, 2H), 3.78 (q, *J* = 7.2 Hz, 2H), 3.14 (s, 0.12H, 94% D), 2.54 (s, 0.12H, 94% D), 1.12 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 170.1, 162.2, 144.8, 141.6, 134.6, 132.2, 129.4, 128.7, 128.2, 128.16, 128.13, 128.0, 127.7, 127.6, 127.5, 126.1, 43.8, 31.1 – 29.3 (m), 23.6 – 22.3 (m), 12.7.

**HRMS (ESI)**: Calcd. for $C_{26}H_{21}D_4N_2O_2^+$ $[M + H]^+$: 401.2162, found: 401.2151.

**4-([1,1'-Biphenyl]-4-yl)-*N*-ethyl-4-oxo-*N*-phenylbutanamide-2,2-$d_2$ (31)**

Following Procedure A, using 2.0 h (1.9 F/mol) instead of 1.5 h (1.4 F/mol).




**31**

Colourless liquid (30.2 mg, 42% yield, 90% D);

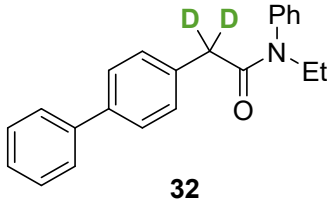
**$^1$H NMR** (300 MHz, $CDCl_3$): δ 8.05 (d, *J* = 8.3 Hz, 2H), 7.76 – 7.53 (m, 4H), 7.53 – 7.30 (m, 8H), 3.77 (q, *J* = 7.2 Hz, 2H), 3.27 (s, 0.2H), 2.46 (s, 2H), 1.39 – 0.86 (m, 3H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 198.6, 171.0, 145.3, 142.0, 139.7, 135.3, 129.5, 128.7, 128.4, 128.4, 127.9, 127.8, 127.0, 126.9, 43.9, 33.6 – 32.8 (m), 28.5, 12.9.

**HRMS (ESI)**: Calcd. for $C_{24}H_{21}D_2NNaO_2^+$ $[M + Na]^+$: 382.1752, found: 382.1739.

**2-([1,1'-Biphenyl]-4-yl)-*N*-ethyl-*N*-phenylacetamide-$d_2$ (32)**

Following Procedure A, using 3.0 h (2.8 F/mol) instead of 1.5 h (1.4 F/mol).




**32**

Colourless liquid (35.5 mg, 56% yield, 95% D);

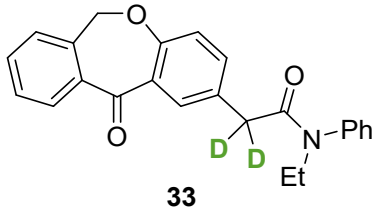
**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.62 – 7.51 (m, 2H), 7.51 – 7.27 (m, 8H), 7.21 – 7.00 (m, 4H), 3.78 (q, *J* = 7.2 Hz, 2H), 3.43 (s, 0.1H), 1.13 (t, *J* = 7.2 Hz, 3H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 170.1, 142.1, 140.8, 139.2, 134.4, 129.8, 129.4, 129.3, 128.8, 128.5, 127.9, 126.9, 126.8, 44.1, 40.8 – 40.0 (m), 12.9.

**HRMS (ESI)**: Calcd. for $C_{22}H_{20}D_2NO^+$ $[M + H]^+$: 318.1821, found: 318.1815.

***N*-Ethyl-2-(11-oxo-6,11-dihydrodibenzo[*b*,*e*]oxepin-2-yl)-*N*-phenylacetamide-$d_2$ (33)**

Following Procedure A, using 3.0 h (2.8 F/mol) instead of 1.5 h (1.4 F/mol).




**33**

White solid (38.8 mg, 52% yield, 92% D); m.p. 149.5-152.1 °C.

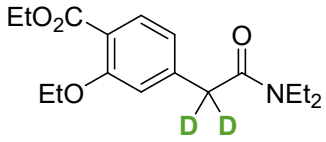
**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.93 – 7.79 (m, 1H), 7.75 (d, *J* = 2.4 Hz, 1H), 7.57 – 7.32 (m, 7H), 7.18 – 7.11 (m, 2H), 6.97 (d, *J* = 8.4 Hz, 1H), 5.16 (s, 2H), 3.76 (q, *J* = 7.2 Hz, 2H), 3.38 (s, 0.16H), 1.11 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 190.6, 169.9, 159.9, 141.8, 140.2, 136.3, 135.4, 132.9, 132.4, 131.9, 129.5, 129.1, 128.9, 128.4, 128.0, 127.5, 124.6, 120.5, 73.3, 44.0, 40.0 – 39.5 (m), 12.8.

**HRMS (ESI)**: Calcd. for $C_{24}H_{20}D_2NO_3^+$ $[M + H]^+$: 374.1720, found: 374.1721.

**Ethyl 4-(2-(diethylamino)-2-oxoethyl-1,1-*d*$_2$)-2-ethoxybenzoate (34)**

Following Procedure A, using 3.0 h (2.8 F/mol) instead of 1.5 h (1.4 F/mol).




**34**

Colourless liquid (37.1 mg, 60% yield, 95% D);

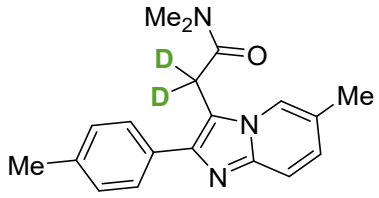
**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.73 (d, *J* = 7.9 Hz, 1H), 7.09 – 6.52 (m, 2H), 4.33 (q, *J* = 7.1 Hz, 2H), 4.09 (q, *J* = 7.0 Hz, 2H), 3.67 (s, 0.1H), 3.38 (q, *J* = 7.1 Hz, 2H), 3.25 (q, *J* = 7.1 Hz, 2H), 1.69 – 1.25 (m, 6H), 1.10 (td, *J* = 7.2, 5.4 Hz, 6H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 169.2, 166.2, 158.7, 141.1, 131.7, 120.3, 119.0, 113.3, 64.5, 60.6, 42.3, 40.7 – 40.5 (m), 40.0, 14.6, 14.2, 14.2, 12.8.

**HRMS (ESI)**: Calcd. for $C_{17}H_{24}D_2NO_4^+$ $[M + H]^+$: 310.1982, found: 310.1992.

***N*,*N*-Dimethyl-2-(6-methyl-2-(*p*-tolyl)imidazo[1,2-*a*]pyridin-3-yl)acetamide-*d*$_2$ (35)**

Following Procedure A, using 1.0 h (0.9 F/mol) instead of 1.5 h (1.4 F/mol).




**35**

White solid (45.1 mg, 73% yield, 97% D); mp: 186.2-188.1 °C;

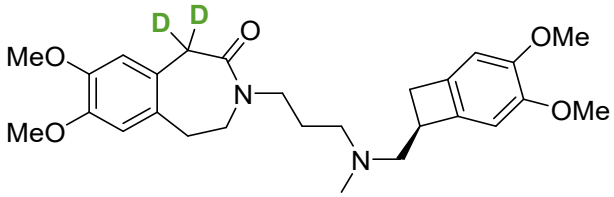
**$^1$H NMR** (300 MHz, $CDCl_3$): δ 8.02 (dt, *J* = 2.0, 1.1 Hz, 1H), 7.64 – 7.44 (m, 3H), 7.34 – 7.19 (m, 2H), 7.04 (dd, *J* = 9.2, 1.7 Hz, 1H), 4.07 (s, 0.06H), 2.94 (s, 3H), 2.86 (s, 3H), 2.40 (s, 3H), 2.34 (s, 3H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 168.0, 143.8, 143.5, 137.0, 131.5, 129.0, 128.0, 127.1, 121.9, 121.3, 116.2, 113.4, 37.1, 35.4, 29.6 – 28.7 (m), 20.9, 18.1.

**HRMS (ESI)**: Calcd. for $C_{19}H_{20}D_2N_3O^+$ $[M + H]^+$: 310.1883, found: 310.1881.

**(*S*)-3-(3-(((3,4-Dimethoxybicyclo[4.2.0]octa-1(6),2,4-trien-7-yl)methyl)(methyl)amino)propyl)-7,8-dimethoxy-1,3,4,5-tetrahydro-2*H*-benzo[*d*]azepin-2-one-1,1-$d_2$ (36)**

Following Procedure A, using molybdenum rod instead of steel, using TEMPO (1.0 eq.) instead of TEMPO (0.2 eq.).




**36**

Yellow liquid (28.2 mg, 30% yield, 92% D);

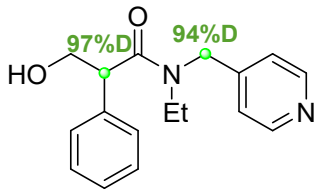
**$^1$H NMR** (300 MHz, $CDCl_3$): δ 6.69 (s, 1H), 6.65 (s, 1H), 6.57 (s, 1H), 6.53 (s, 1H), 3.82 – 3.79 (m, 9H), 3.78 (s, 3.16H), 3.73 – 3.65 (m, 2H), 3.58 – 3.38 (m, 3H), 3.21 (dd, *J* = 13.6, 4.9 Hz, 1H), 3.02 (t, *J* = 6.1 Hz, 2H), 2.80 – 2.65 (m, 2H), 2.61 – 2.53 (m, 1H), 2.44 (s, 2H), 2.32 (s, 3H), 1.80 (q, *J* = 7.3 Hz, 2H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 171.5, 149.3, 148.8, 147.3, 146.6, 138.2, 134.4, 127.0, 122.8, 113.4, 112.7, 106.9, 106.3, 61.3, 55.8, 55.7, 55.4, 55.3, 54.6, 46.0, 44.4, 42.1 – 41.7 (m), 39.9, 34.6, 31.8, 25.6.

**HRMS (ESI)**: Calcd. for $C_{27}H_{35}D_2N_2O_5^+$ $[M + H]^+$: 471.2823, found: 471.2824.

***N*-Ethyl-3-hydroxy-2-phenyl-*N*-(pyridin-4-ylmethyl)propanamide-$d_3$ (37)**

Following Procedure A, using 2.0 h (1.9 F/mol) instead of 1.5 h (1.4 F/mol).




**37**

White solid (30.4 mg, 53% yield); mp: 96.2-97.6 °C;

**$^1$H NMR** (300 MHz, $CDCl_3$, rotamers): δ 8.51 (s, 2H), 7.50 – 7.13 (m, 5H), 7.10 – 6.83 (m, 2H), 4.73 and 4.44 (2s, 0.05H and 0.07H, 94%D), [4.10 (t, *J* = 11.9 Hz) and 3.84 –

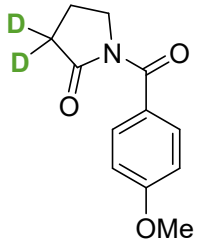
3.55 (m, total 2.03H, 97%D)], 3.31 (dt, $J$ = 14.3, 7.2 Hz, 0.6H), 3.13 (dq, $J$ = 15.0, 7.4 Hz, 1.4H), 1.10 (t, $J$ = 7.2 Hz, 0.83H), 0.93 (t, $J$ = 7.1 Hz, 1.94H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$, rotamers): δ 172.5, 172.3, 149.8, 149.5, 146.6, 145.7, 135.9, 135.6, 128.9, 128.8, 127.8, 127.6, 127.4, 122.0, 121.2, 65.4, 51.8 – 50.9 (m), 47.2 – 46.6 (m), 41.9, 41.0, 13.3, 12.1.

**HRMS (ESI)**: Calcd. for $C_{17}H_{18}D_3N_2O_2^+$ $[M + H]^+$: 288.1786, found: 288.1787.

**1-(4-Methoxybenzoyl)pyrrolidin-2-one-3,3-$d_2$ (38)**

Following Procedure A, using molybdenum rod instead of steel, using 10 mA instead of 5 mA, using 3.0 h (5.6 F/mol) instead of 1.5 h (1.4 F/mol).




**38**

White solid (15.0 mg, 34% yield, 93% D); mp: 118.2-119.1 °C;

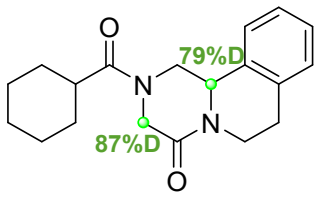
**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.72 – 7.49 (m, 2H), 7.13 – 6.74 (m, 2H), 3.96 – 3.88 (m, 2H), 3.84 (s, 3H), 2.58 (d, $J$ = 7.6 Hz, 0.14H), 2.11 (t, $J$ = 7.0 Hz, 2H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 174.4, 169.8, 162.6, 131.5, 126.0, 112.8, 55.1, 46.6, 33.2 – 32.5 (m), 17.3.

**HRMS (ESI)**: Calcd. for $C_{12}H_{12}D_2NO_3^+$ $[M + H]^+$: 222.1094, found: 222.1083.

**2-(Cyclohexanecarbonyl)-1,2,3,6,7,11b-hexahydro-4*H*-pyrazino[2,1-*a*]isoquinolin-4-one-3,3,11b-$d_3$ (39)**

Following Procedure A, using molybdenum rod instead of steel, using 2.0 h (1.9 F/mol) instead of 1.5 h (1.4 F/mol).




**39**

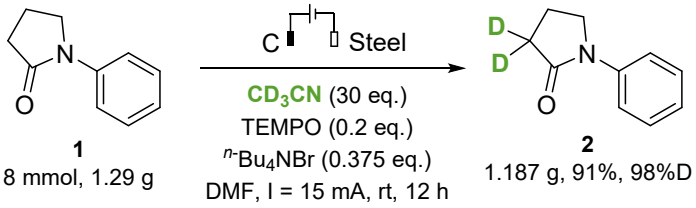
White solid (35.3 mg, 56% yield); mp: 112.1-113.8 °C;

**$^1$H NMR** (300 MHz, $CDCl_3$, rotamers): δ 7.51 – 6.81 (m, 4H), 5.30 – 5.01 (m, 0.72H), 4.87 – 4.63 (m, 1.49H, 79%D), [4.49 – 4.24 (m), 4.09 (s) and 3.89 (s, total 0.26H, 87%D)], 3.21 – 2.67 (m, 4H), 2.46 (dd, *J* = 9.1, 5.8 Hz, 1H), 1.94 – 1.65 (m, 4H), 1.53 (tt, *J* = 12.5, 6.1 Hz, 2H), 1.25 (q, *J* = 9.5, 8.7 Hz, 4H).

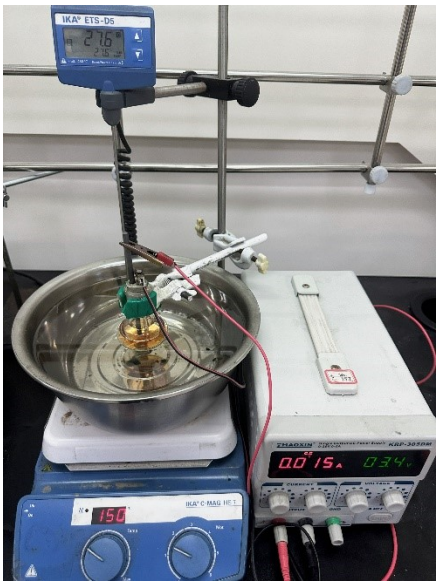
**$^{13}$C NMR** (75 MHz, $CDCl_3$, rotamers): δ 174.6, 164.3, 135.4, 134.7, 132.7, 132.1, 129.6, 129.2, 127.6, 127.4, 126.9, 125.4, 125.2, 55.7, 54.8, 54.4 – 53.6 (m), 49.4, 48.9 – 48.4 (m), 45.0, 40.7, 39.0, 38.6, 29.5, 29.2, 28.9, 28.7, 25.7.

**HRMS (ESI)**: Calcd. for $C_{19}H_{22}D_3N_2O_2^+$ $[M + H]^+$: 316.2099, found: 316.2111.

**Procedure for gram-scale experiment (Procedure B):**

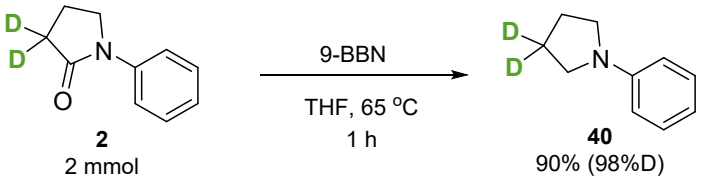



A 50 mL distillation flask equipped with a magnetic stir bar was charged with compound **1** (1.29 g, 8 mmol, 1.0 eq.), $CD_3CN$ (12.8 mL, 30 eq.), TEMPO (0.25 g, 1.6 mmol, 0.2 eq.), $^n$-$Bu_4NBr$ (0.97 g, 3 mmol, 0.375 eq.) and DMF (30 mL). The flask equipped with graphite rod anode (d = 5 mm) and steel 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 15 mA (Single Output DC Power Supply: KRP-305DM, the voltage range is 3.4 V – 4.0 V) for 12 h (0.8 F/mol) 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 = 5/1) as eluent afforded the desired product **2** (1.187 g, 91%, 98%D). **$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.70 – 7.55 (m, 2H), 7.44 – 7.31 (m, 2H), 7.25 – 7.05 (m, 1H), 3.87 (t, *J* = 7.0 Hz, 2H), 2.60 (s, 0.04H), 2.16 (t, *J* = 7.0 Hz, 2H).



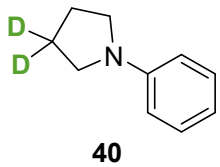
Electrochemical setup for 8 mmol scale

**Procedure for transformation of amide (Procedure C):**




A dry 50 mL three-necked bottle flask was charged with 9-BBN (8.8 mL, 4.4 mmol, 2.2 eq., 0.5 mol/L in anhydrous THF) and compound **2** (326 mg, 2 mmol, 1.0 eq.) under nitrogen atmosphere. The reaction mixture was heated to 65 °C and refluxed for 1.0 h. The solution was cooled to room temperature under nitrogen, ethanolamine (0.27 mL, 4.4 mmol, 2.2 eq.) was added and the residue concentrated in *vacuo*. The resulting solid was then triturated with pentane (20 mL) and the suspension was filtered over a short plug of Celite and rinsed with ice cold pentane (20 mL). The filtrate was concentrated in *vacuo*. Purification by flash column chromatography using PE/EtOAc (v/v = 150/1) as eluent afforded the desired product **40** (268 mg, 90%, 98% D).

**1-Phenylpyrrolidine-3,3-$d_2$ (40)**




**40**

Colourless liquid (268 mg, 90% yield, 98%D);

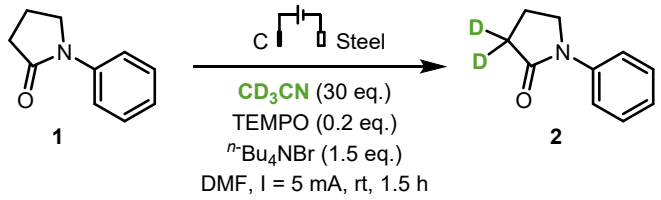
**$^{1}$H NMR** (300 MHz, $CDCl_3$): δ 7.38 – 7.10 (m, 2H), 6.69 (tt, $J$ = 7.2, 1.1 Hz, 1H), 6.65 – 6.44 (m, 2H), 3.37 – 3.15 (m, 4H), 2.10 – 1.91 (m, 2.04H).

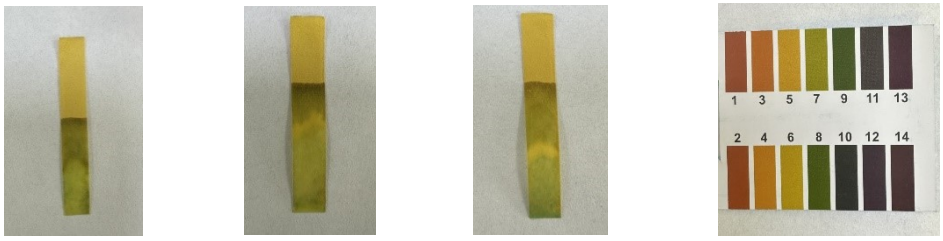
**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 147.9, 129.0, 115.3, 111.6, 47.5, 47.3, 25.3 – 24.5 (m).

**HRMS (ESI)**: Calcd. for $C_{10}H_{12}D_2N^+$ $[M + H]^+$: 150.1246, found: 150.1253.

## V Mechanism Research

**Scheme S1**: 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.

## VI References


1 S. Ning, L. Zheng, Y. Bai, S.-T. Wang, S.-Y. Wang, L. Shi, Q. Gao, X. Che, Z. Zhang and J. Xiang, *Tetrahedron*, 2021, **102**, 132535.

2 J.-S. Li, Y.-D. Da, G.-Q. Chen, Q. Yang, Z.-W. Li, F. Yang and P.-M. Huang, *ChemistrySelect*, 2017, **2**, 1770–1773.

3 S.-M. Wang, C. Zhao, X. Zhang and H.-L. Qin, *Org. Biomol. Chem.*, 2019, **17**, 4087–4101.

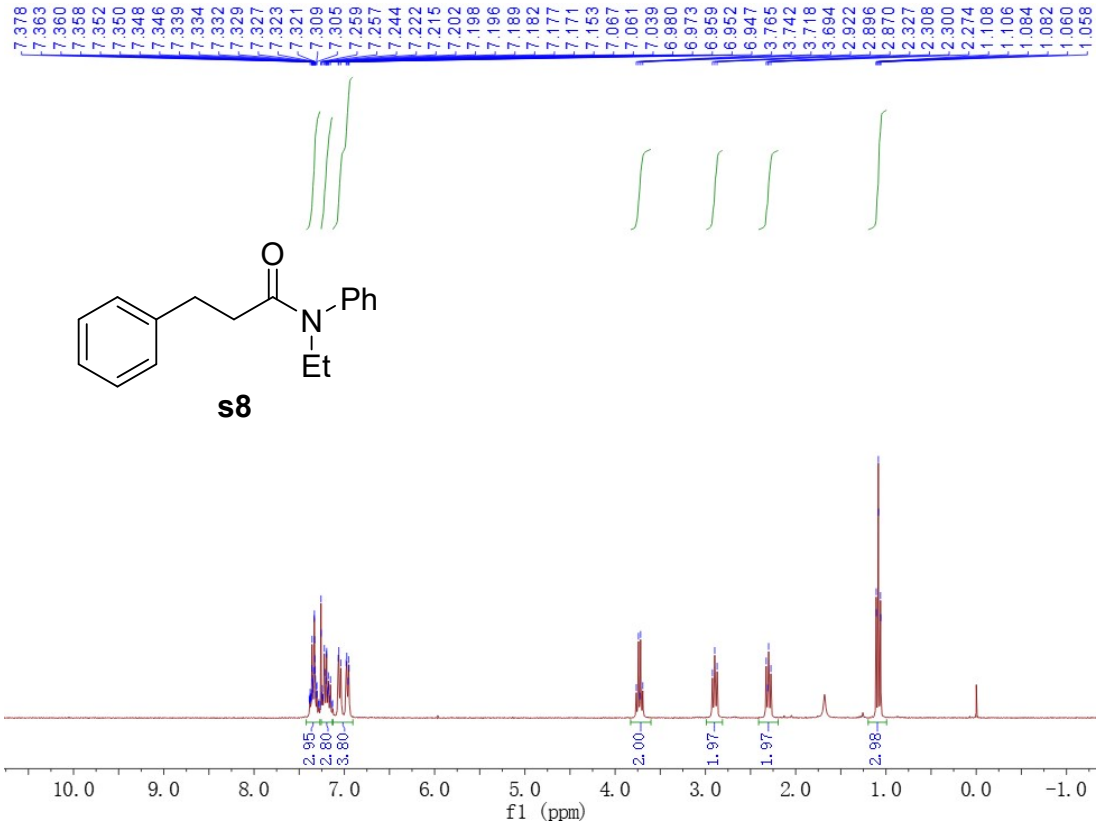
4 Z.-W. Chen, H.-F. Jiang, X.-Y. Pan and Z.-J. He, *Tetrahedron*, 2011, **67**, 5920–5927.

5 N. Oku, M. Murakami and T. Miura, *Org. Lett.*, 2022, **24**, 1616–1619.

6 V. Rathore, M. Sattar and R. Kumar, S. Kumar, *J. Org. Chem.*, 2016, **81**, 9206–9218.

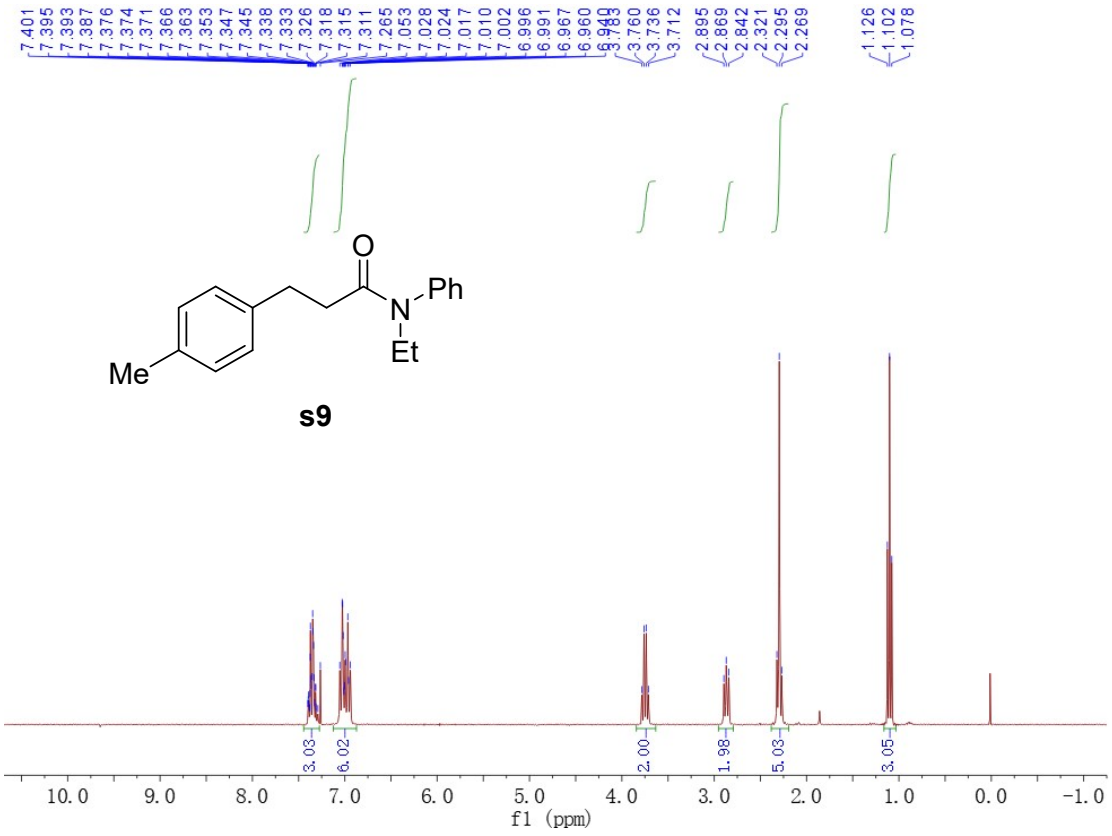
# VII. Spectra

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



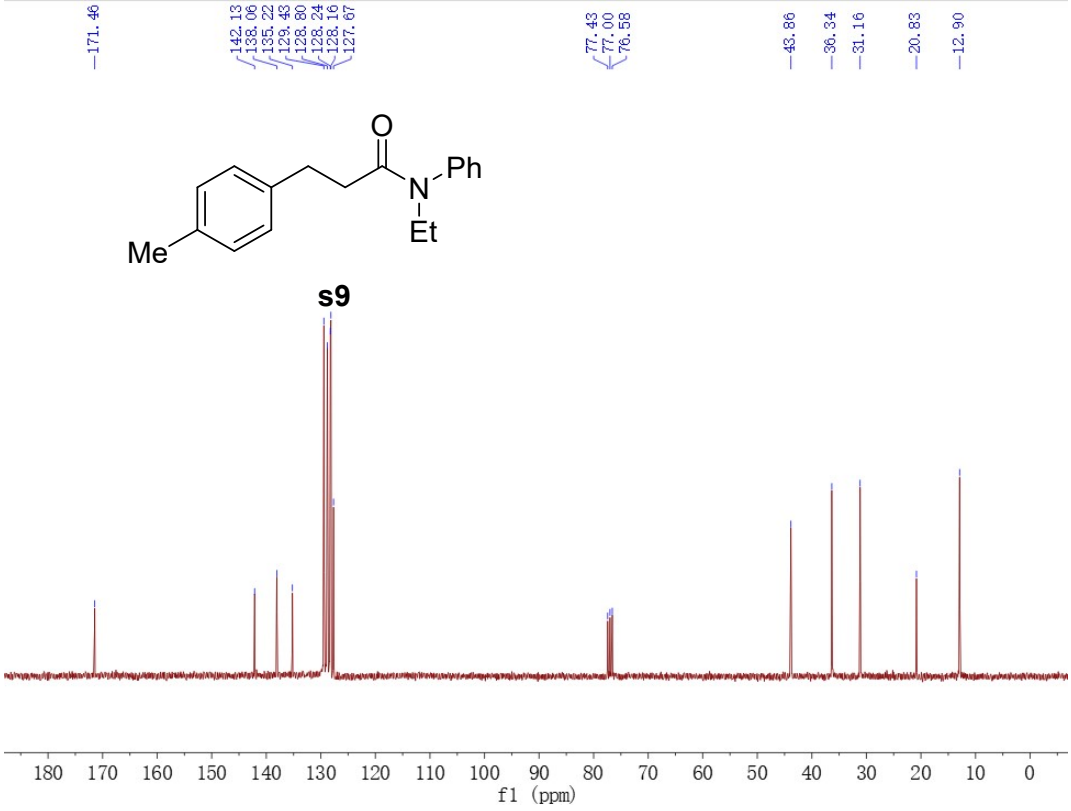

**s8**

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

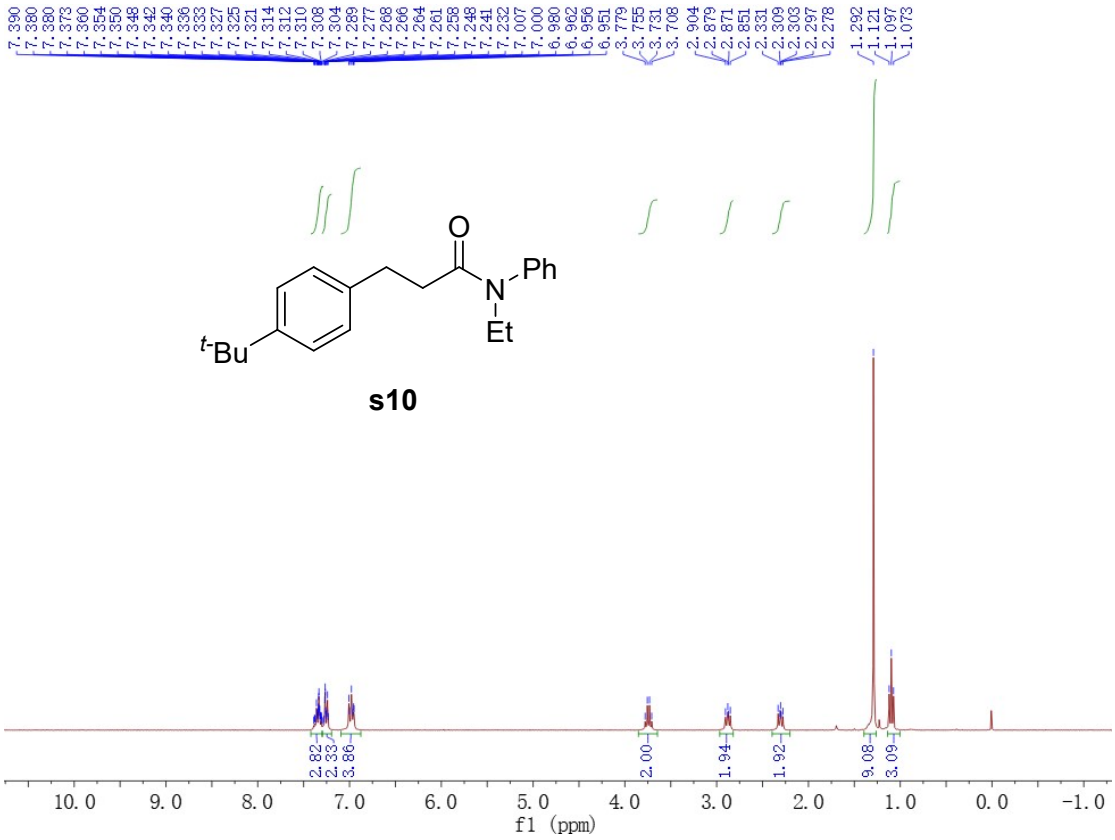



**s9**

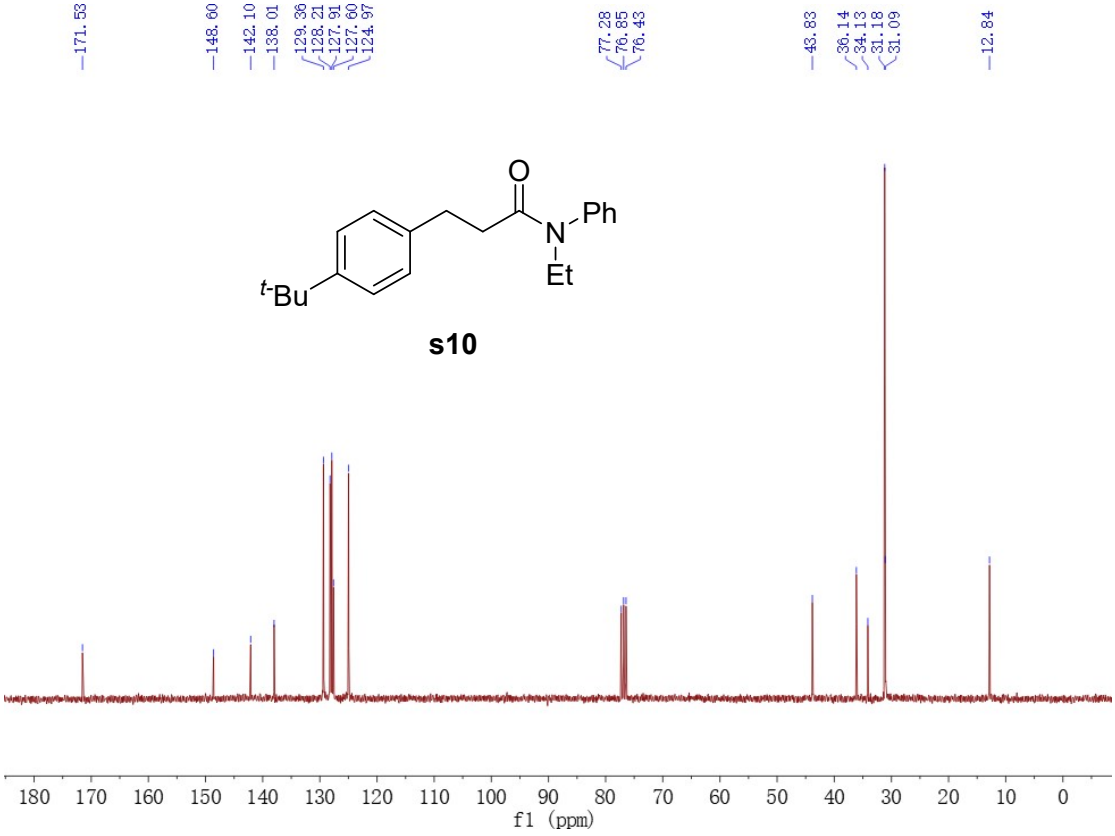
**$^{13}$C NMR (75 MHz, $CDCl_3$):**




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

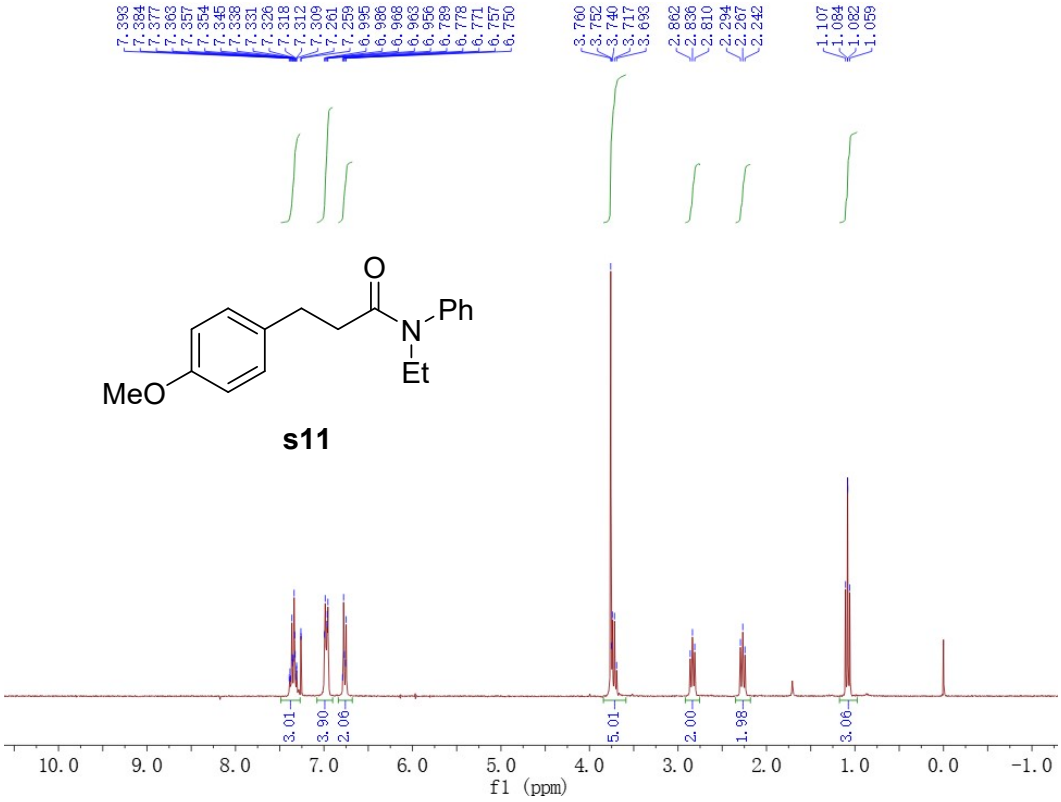


**$^{13}$C NMR (75 MHz, $CDCl_3$):**



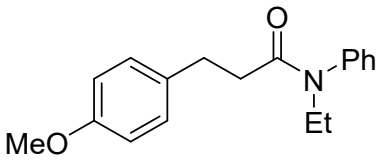

**s10**

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

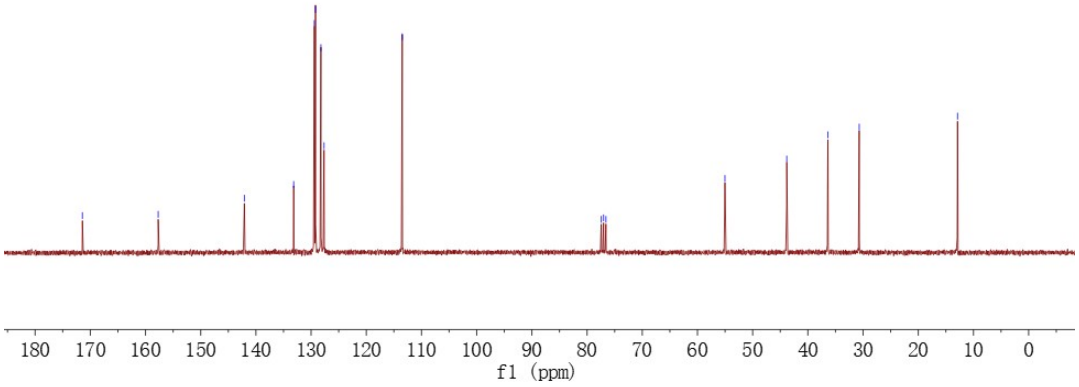



**s11**

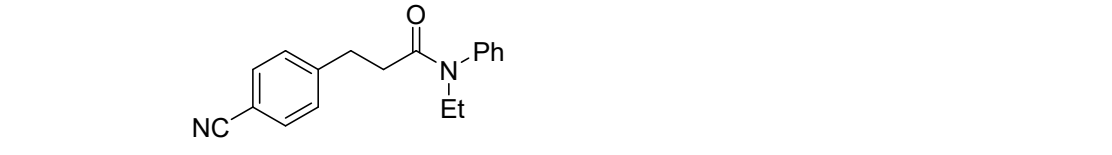
**$^{13}$C NMR (75 MHz, $CDCl_3$):**


**s11**

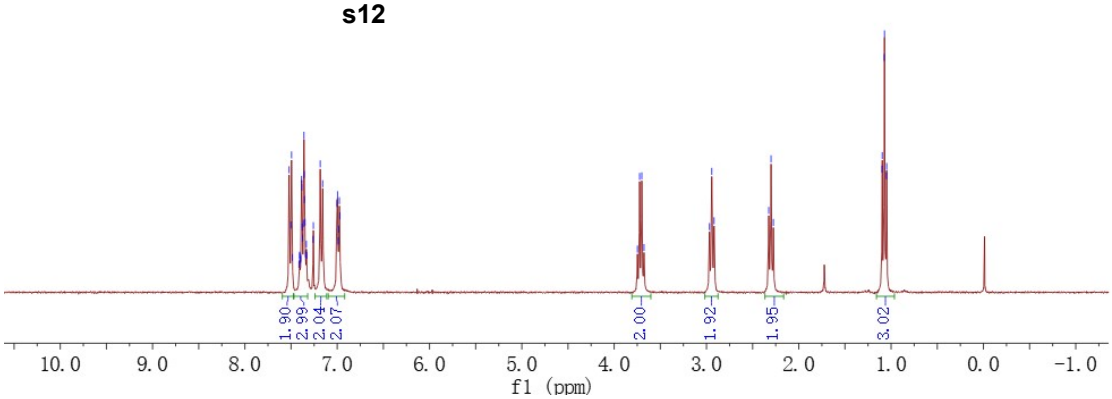



**$^{1}$H NMR (300 MHz, $CDCl_3$):**

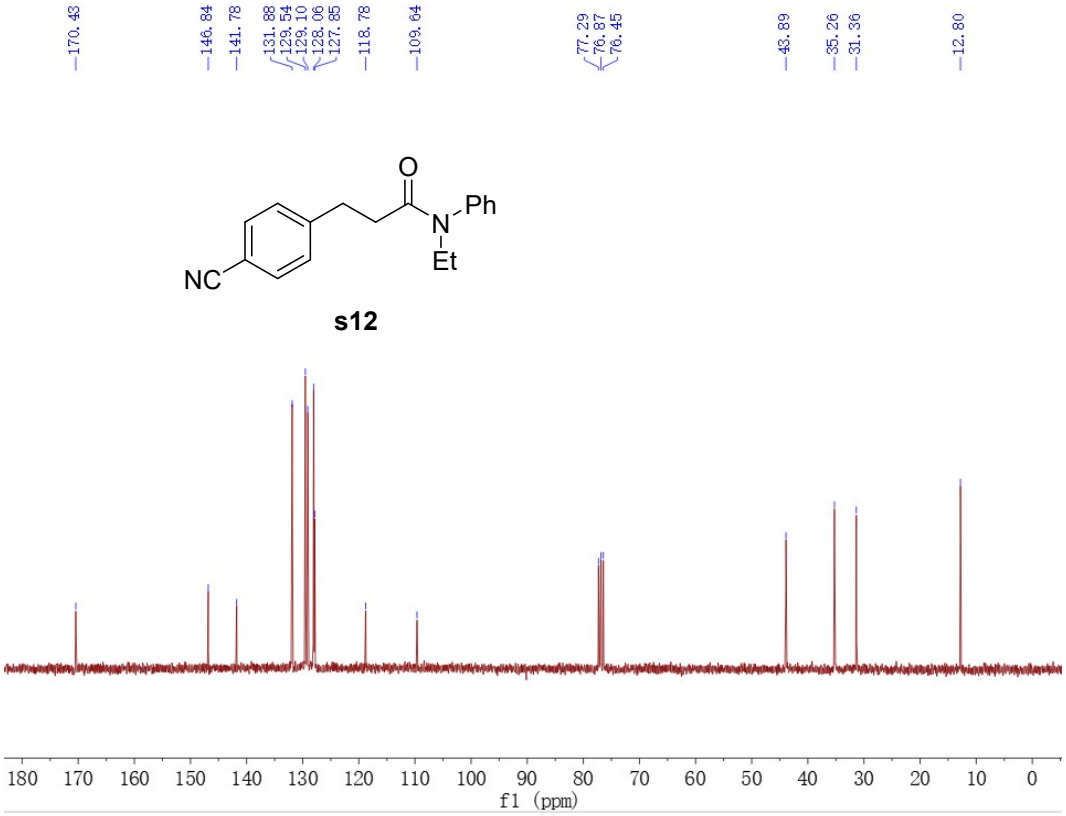





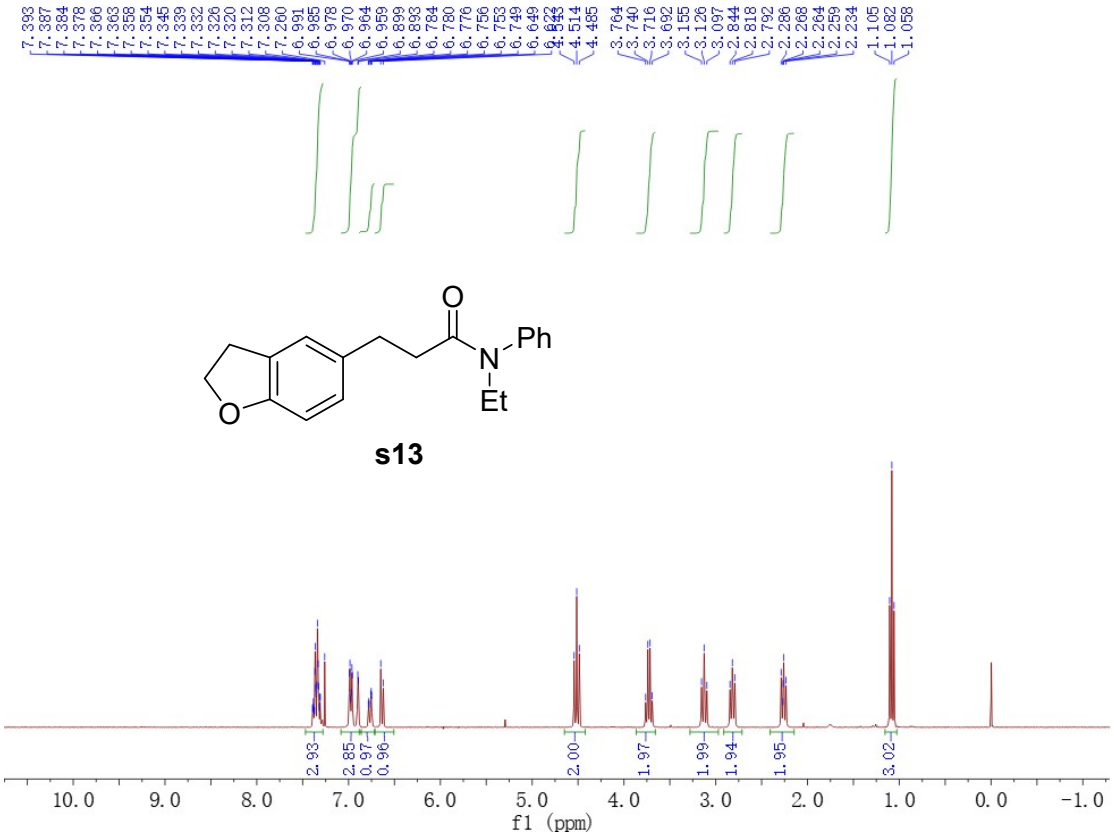

**s12**



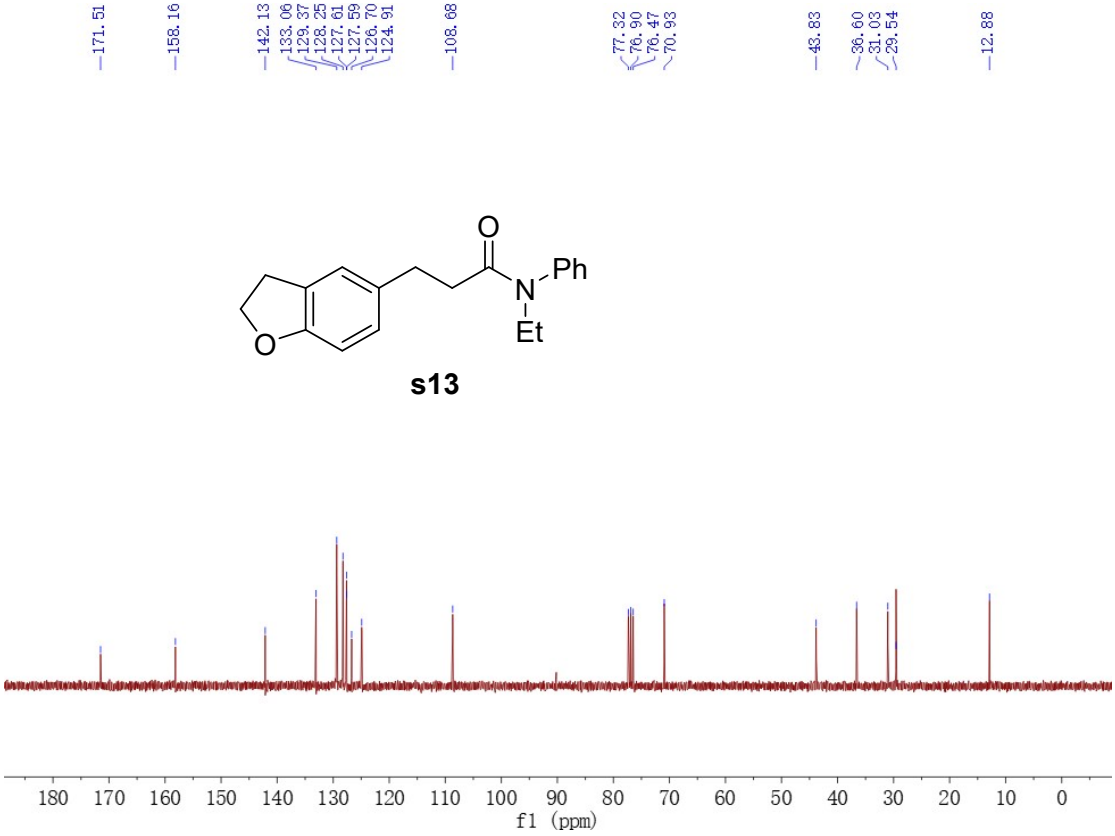
**$^{13}$C NMR (75 MHz, $CDCl_3$):**




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



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

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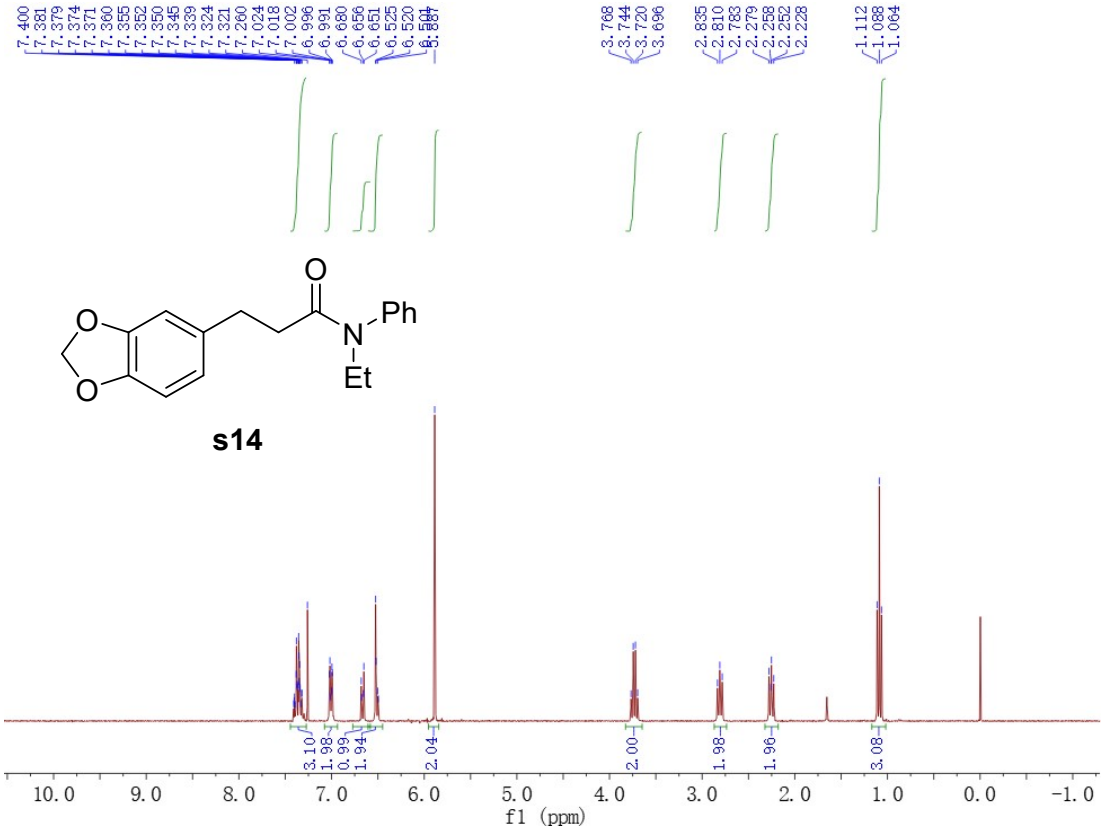

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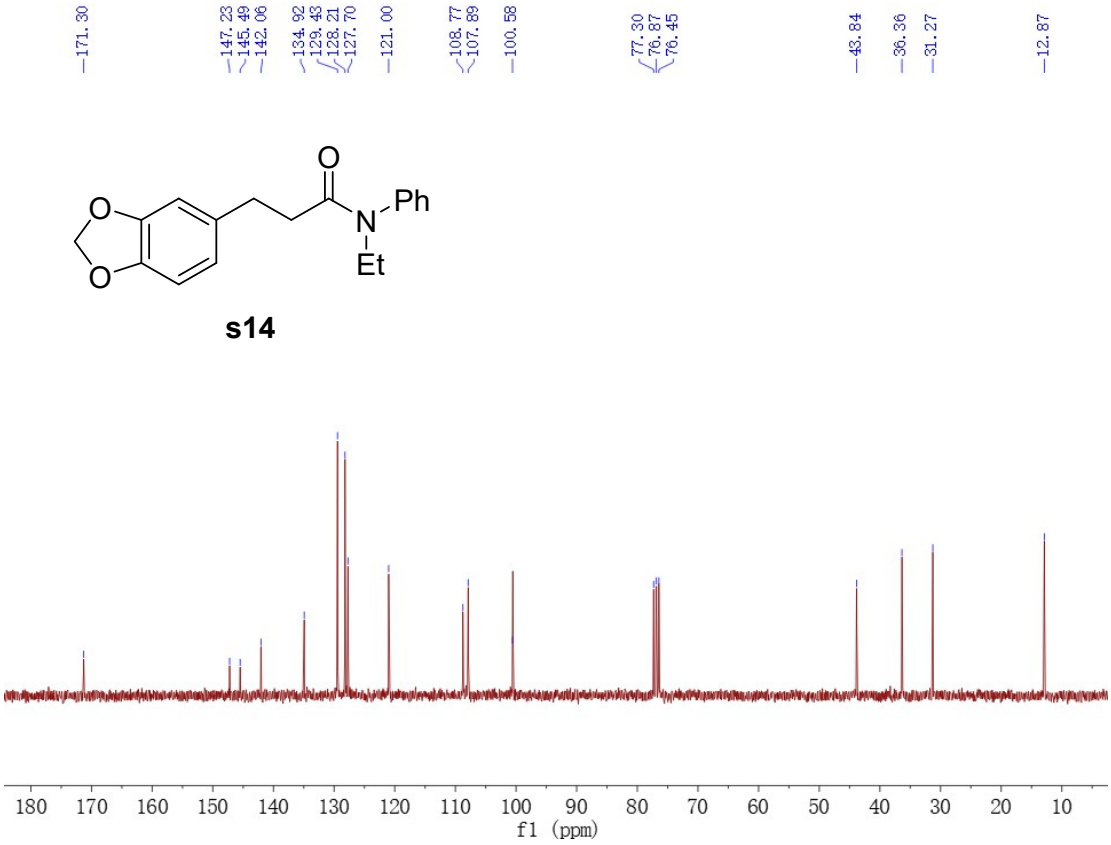


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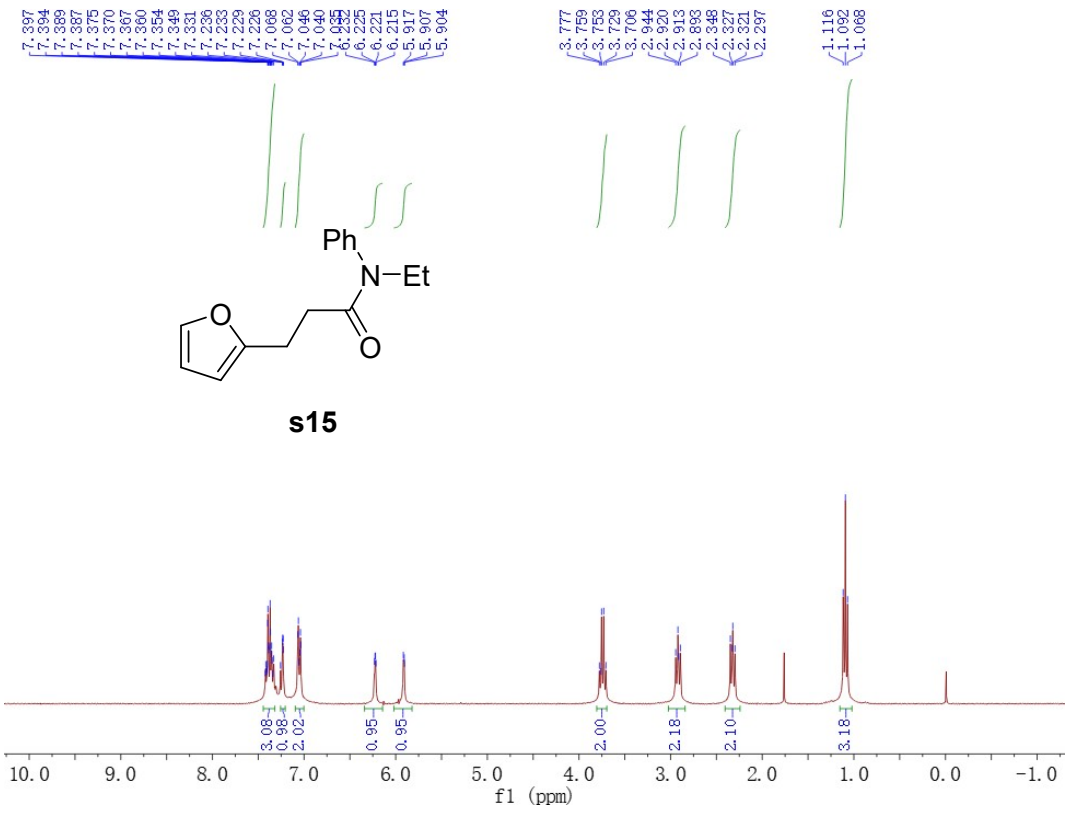
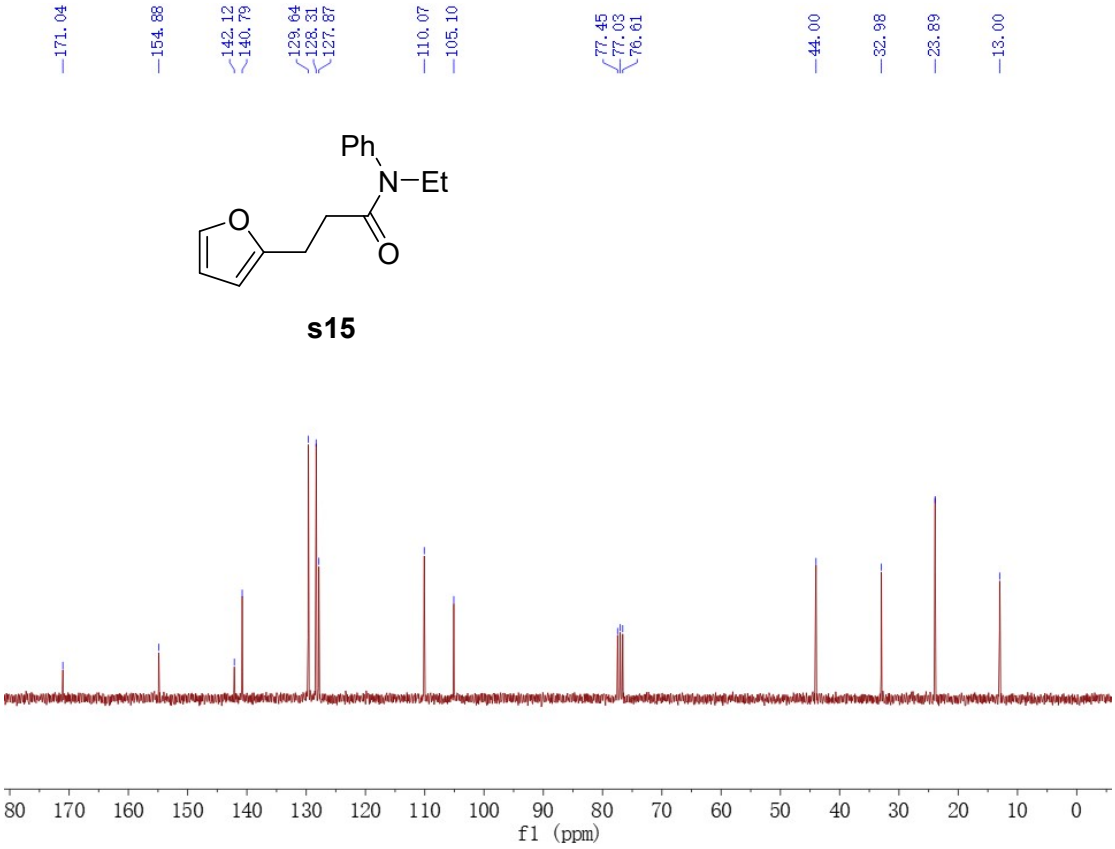
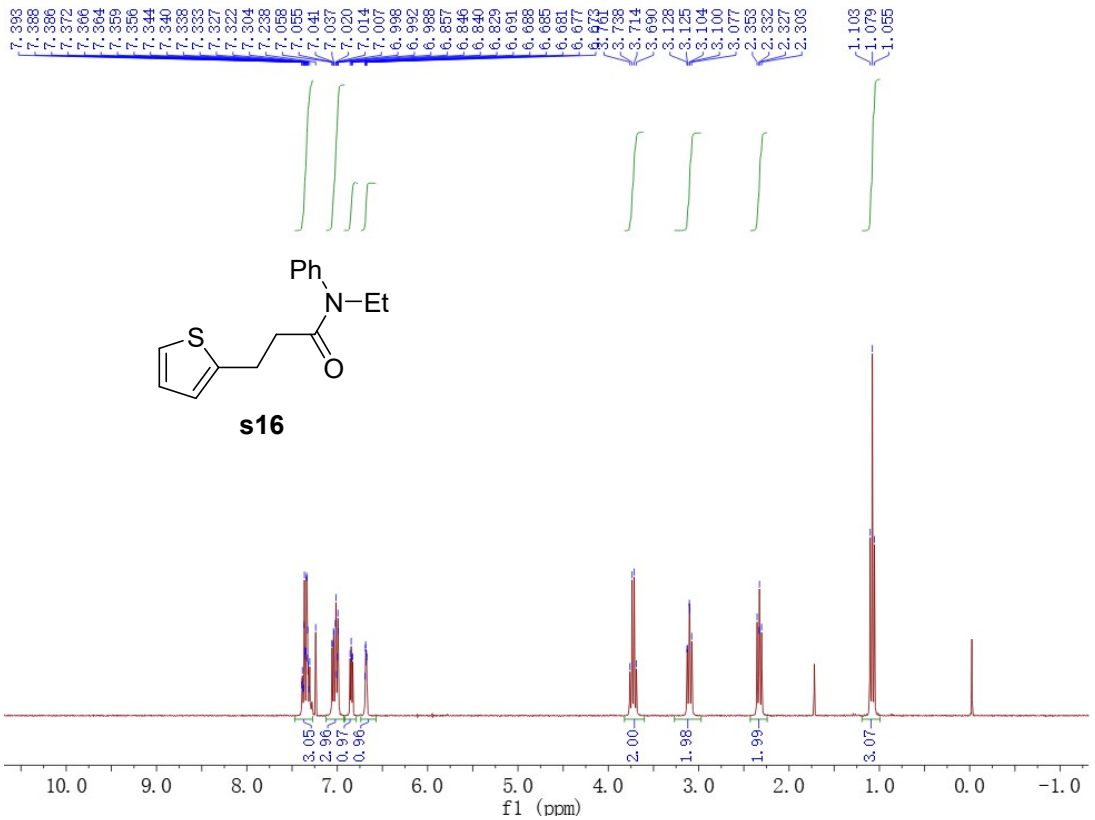


**$^{13}$C NMR (75 MHz, $CDCl_3$):**



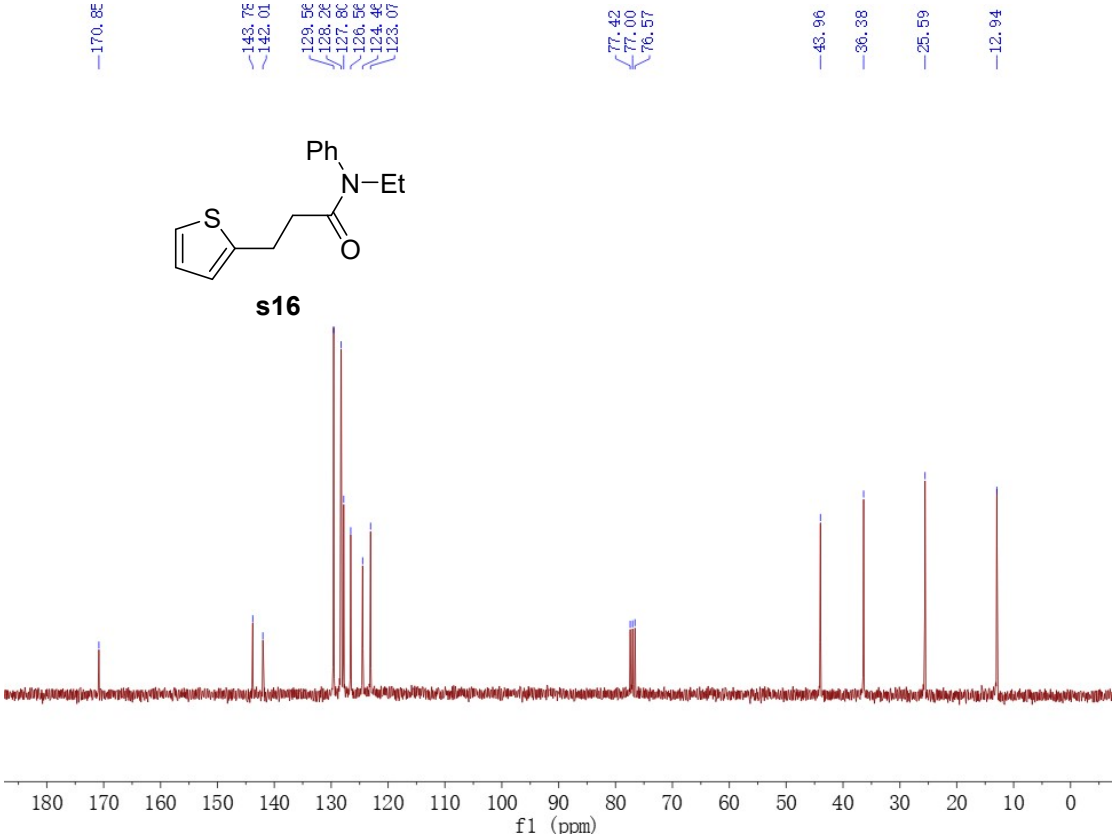

**s15**

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



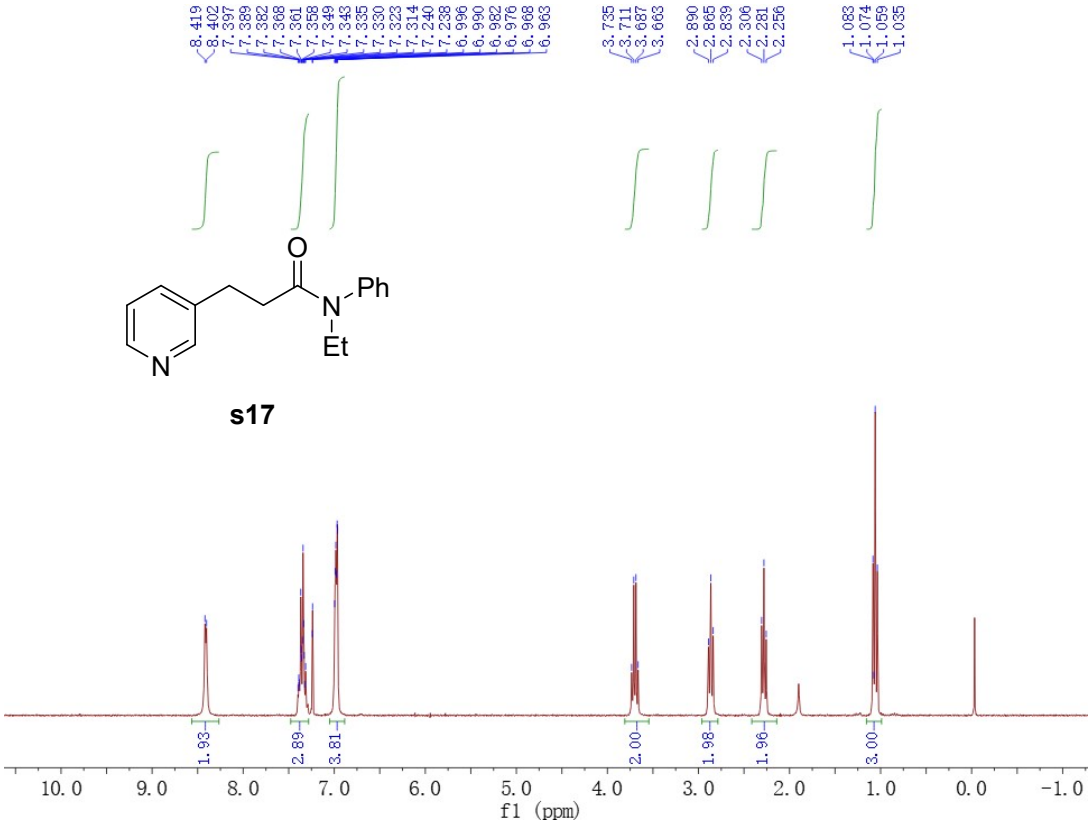

**s16**

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



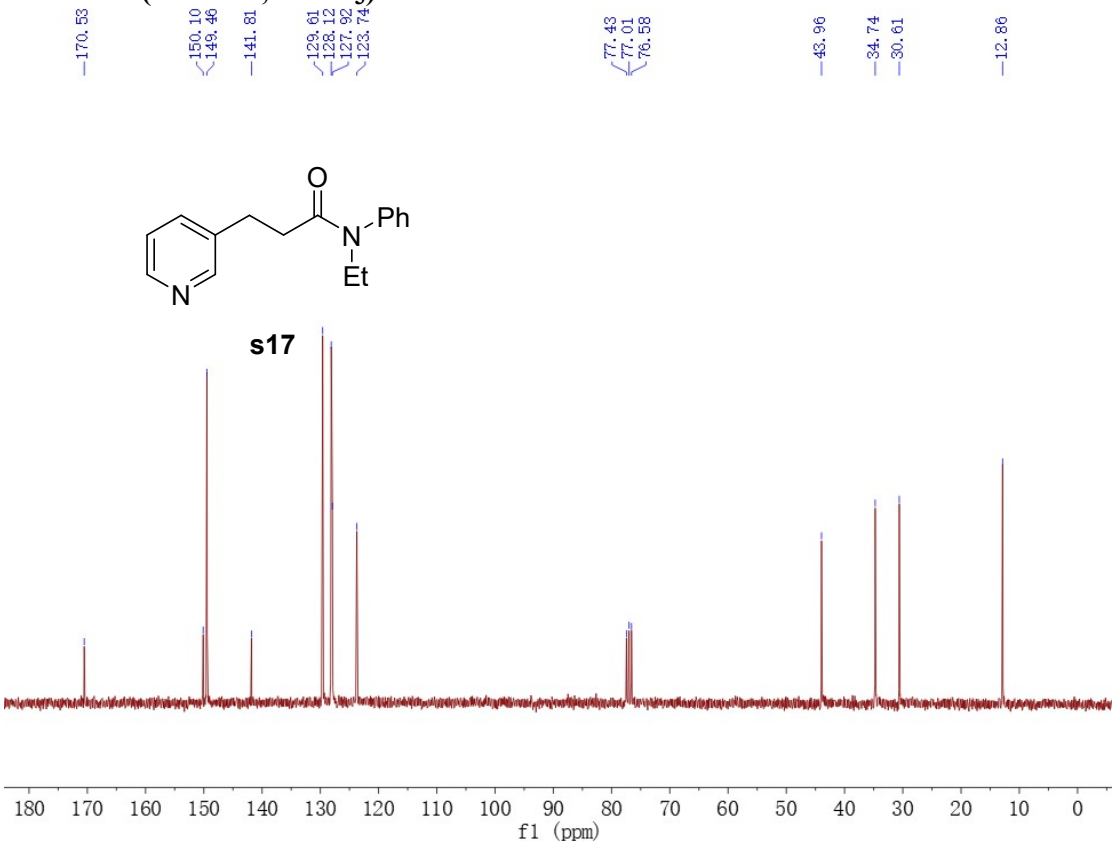

**s16**

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




**s17**

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




**s17**

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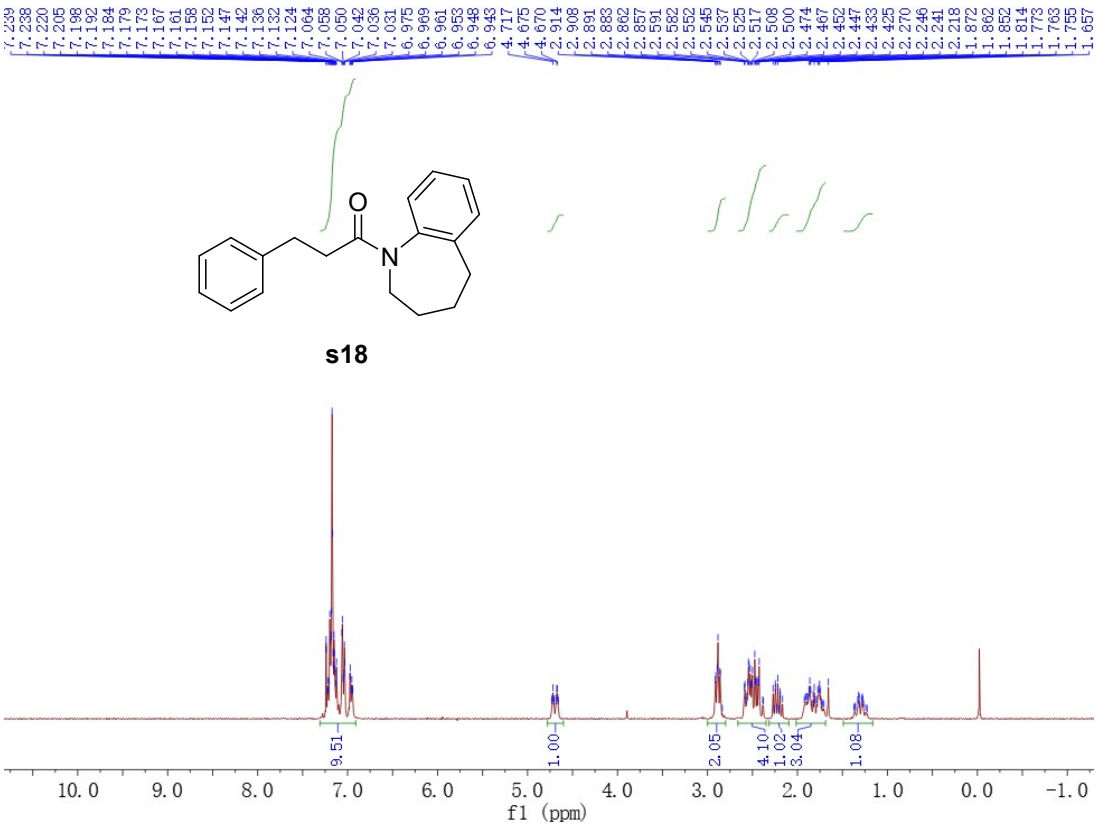
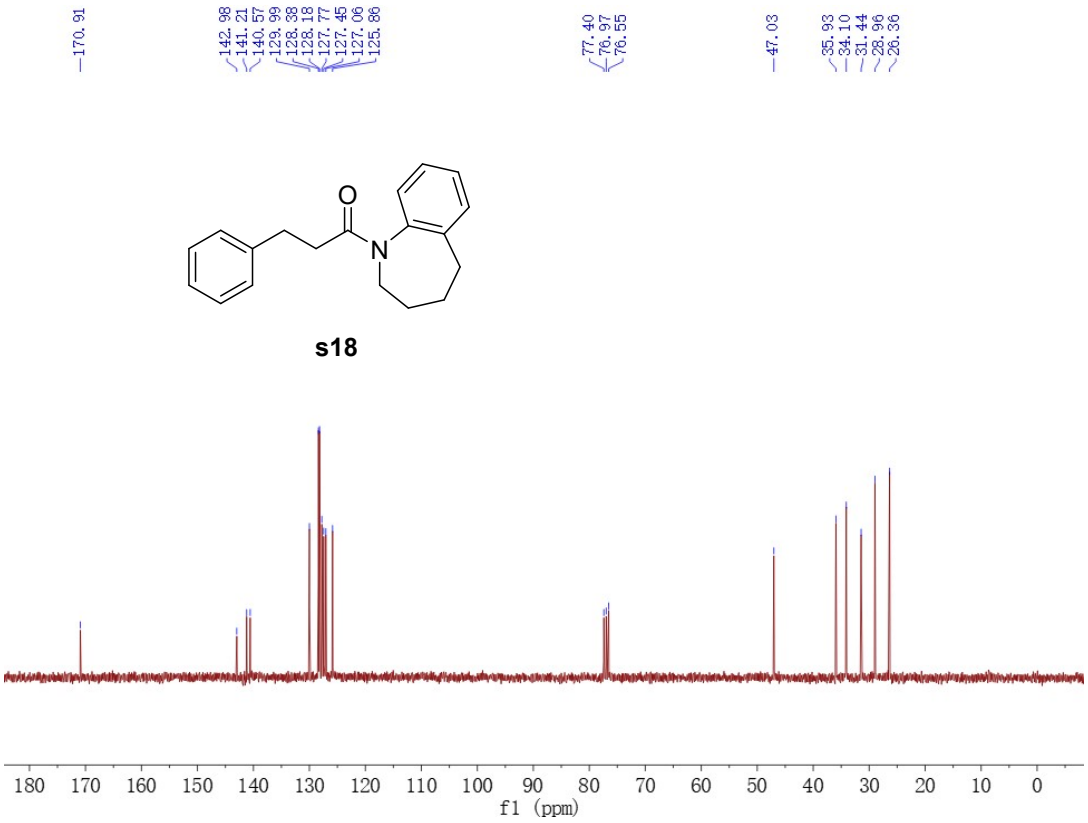


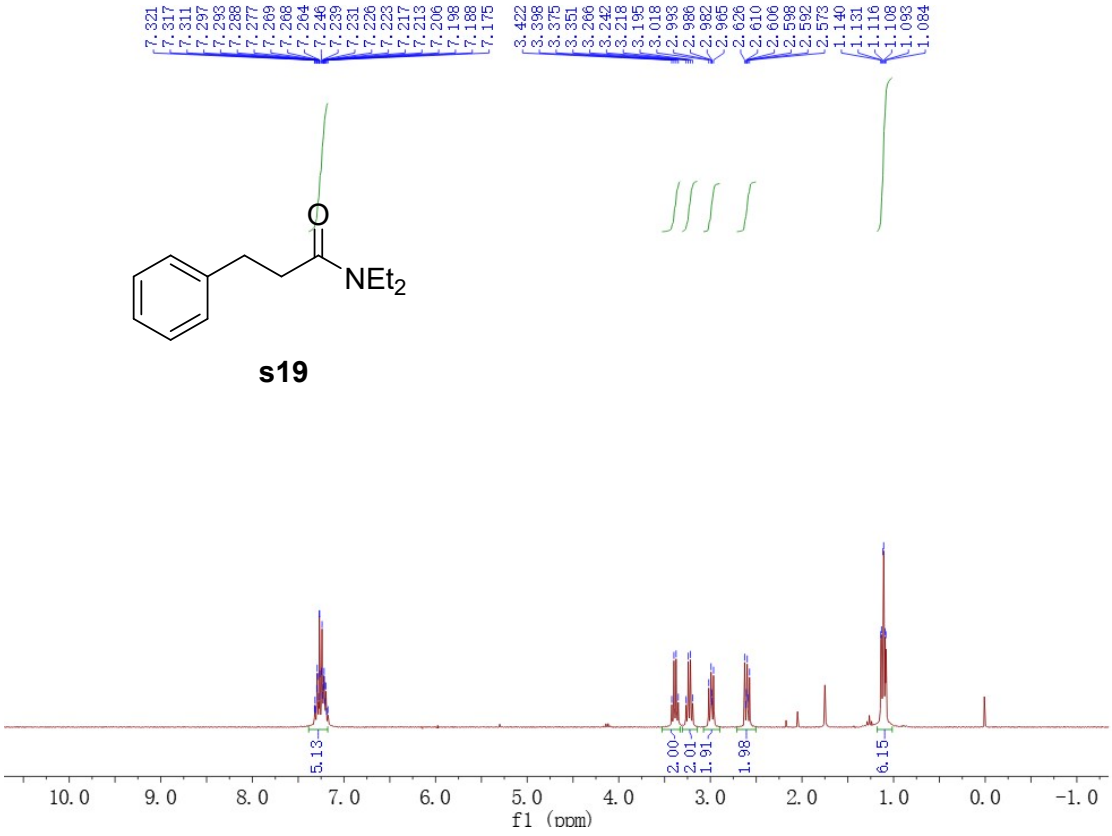

**s18**

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



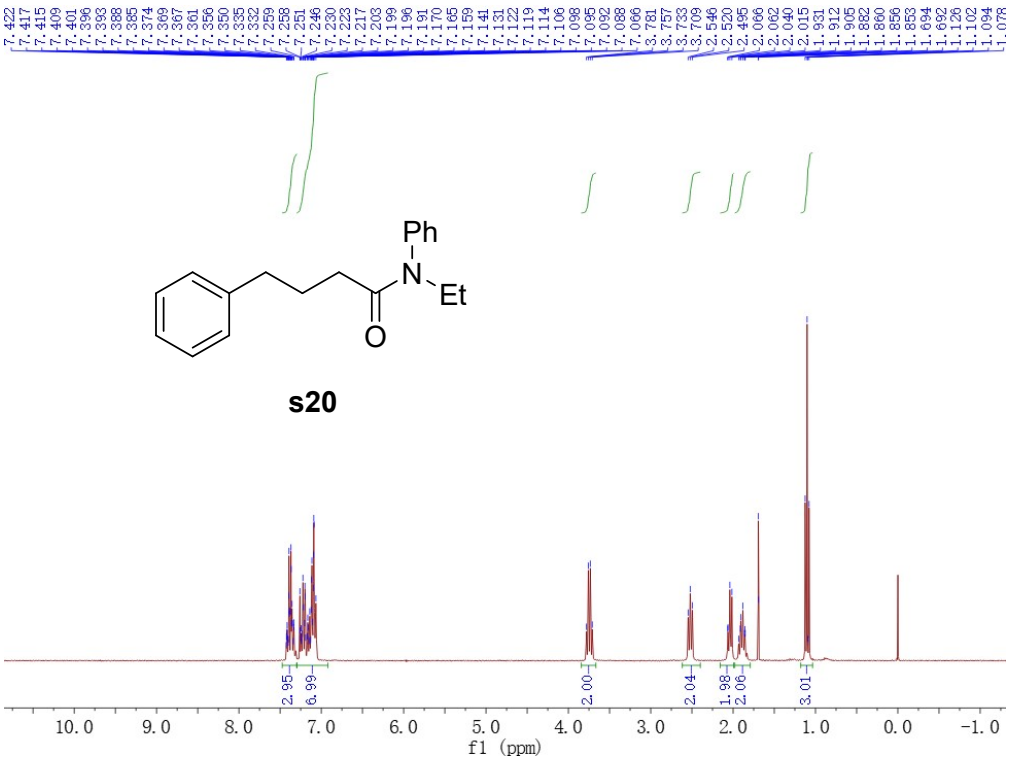

**s18**

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

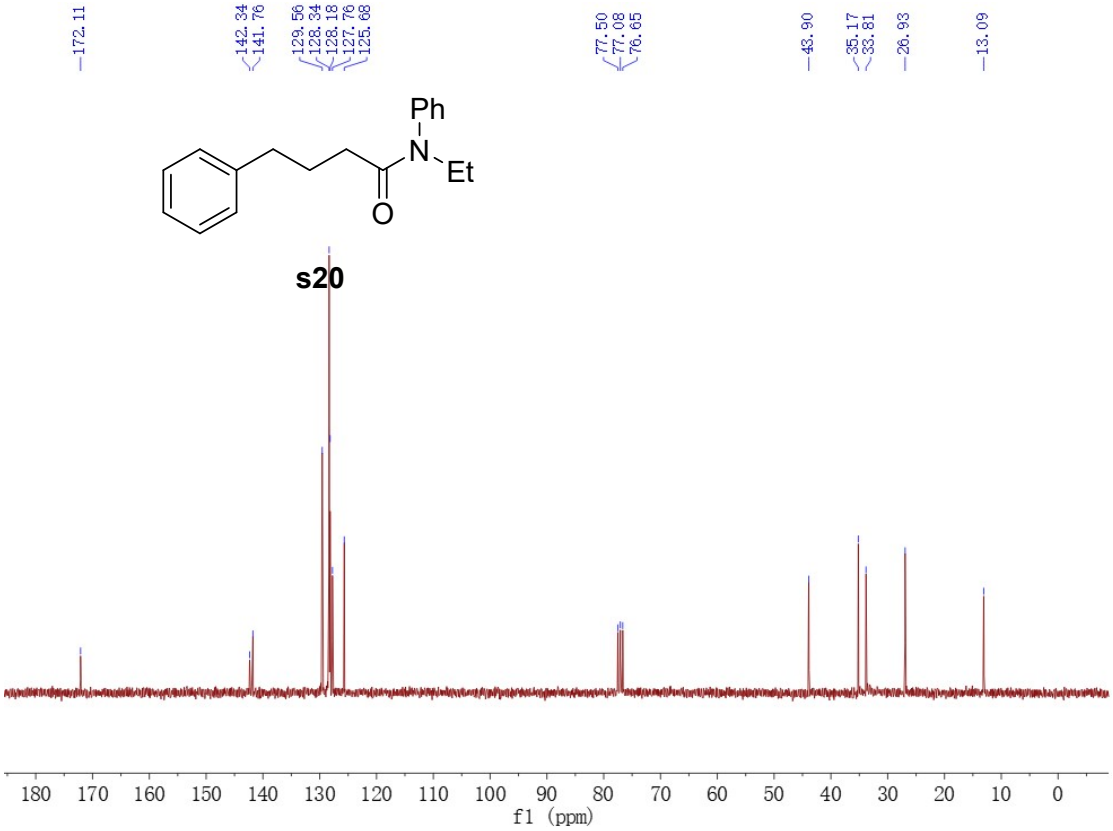



**s19**

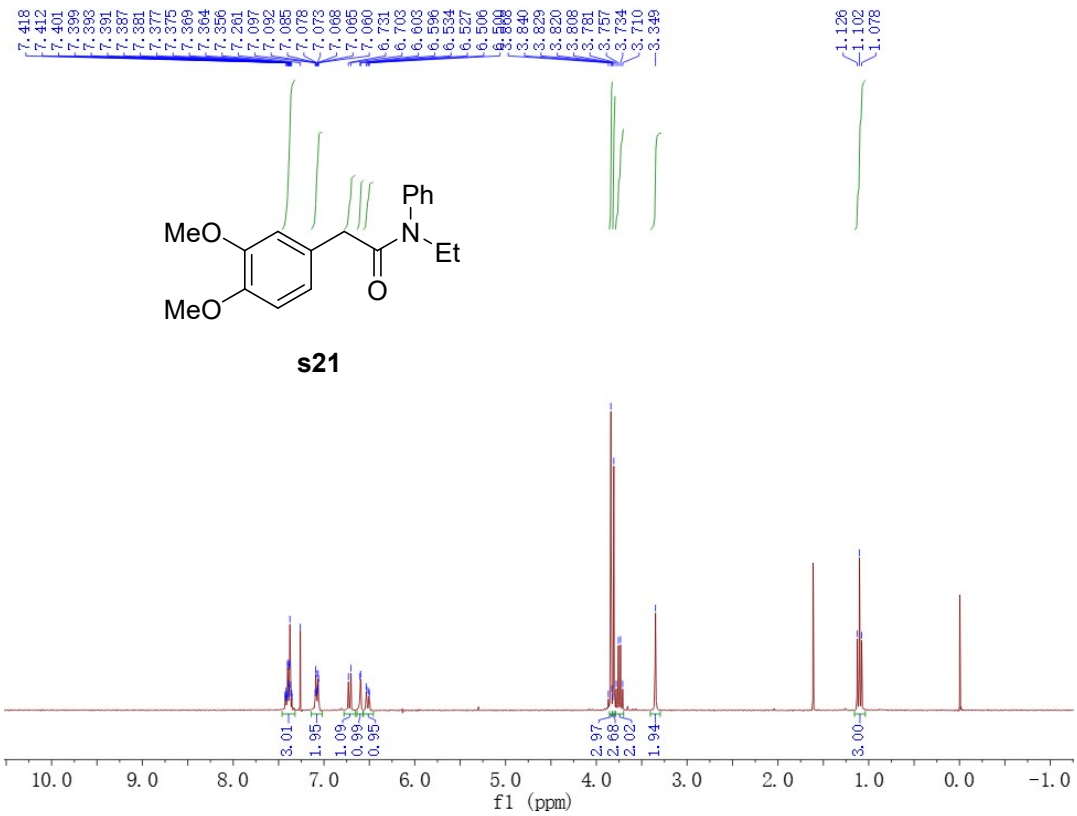
**$^1$H NMR (300 MHz, $CDCl_3$):**




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

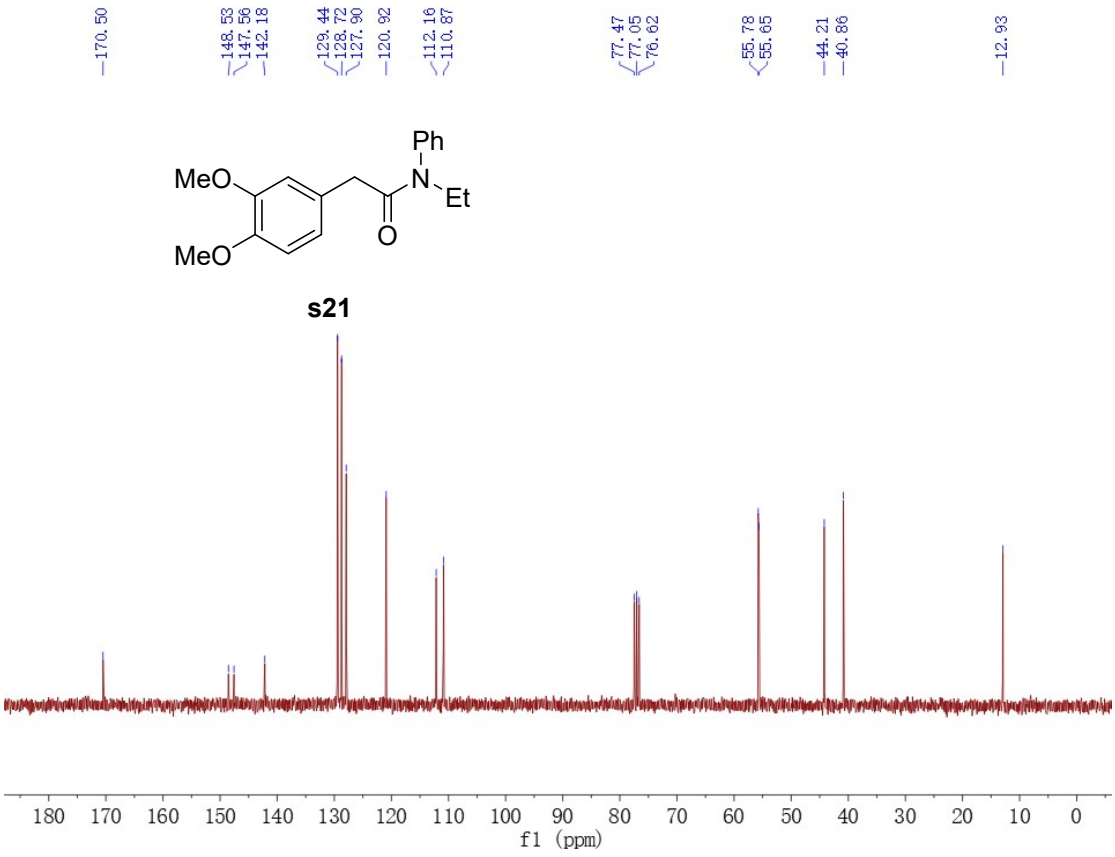



**$^{1}$H NMR (300 MHz, $CDCl_3$):**



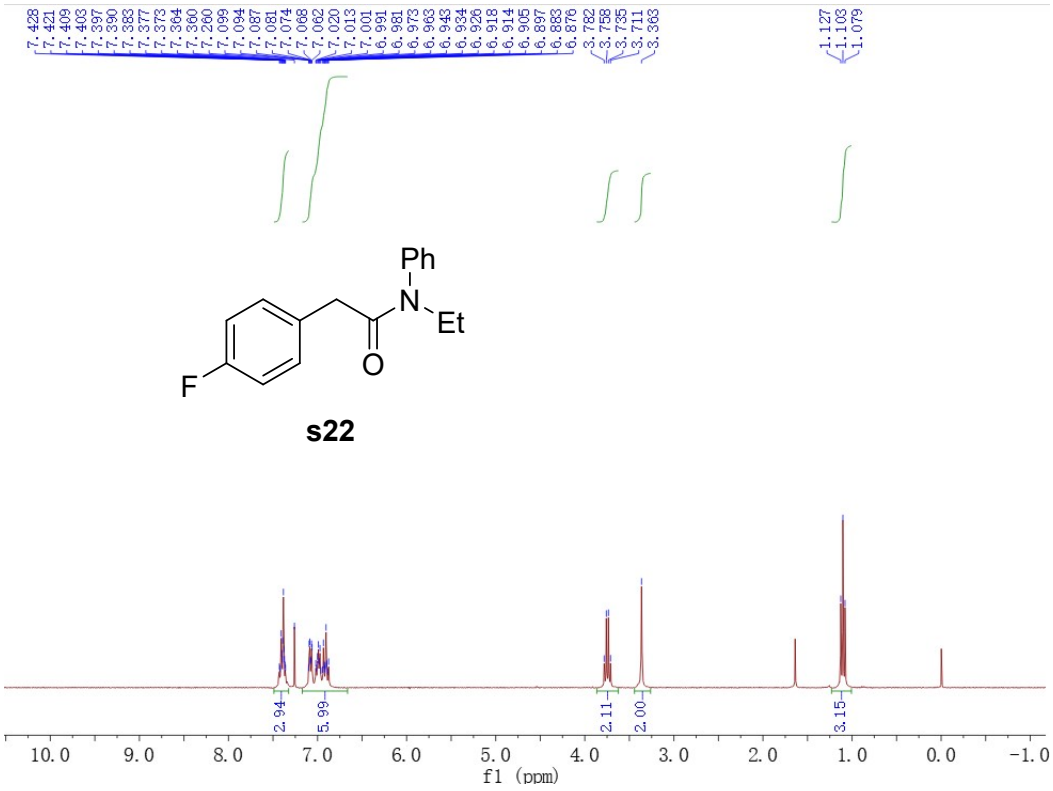

**s21**

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



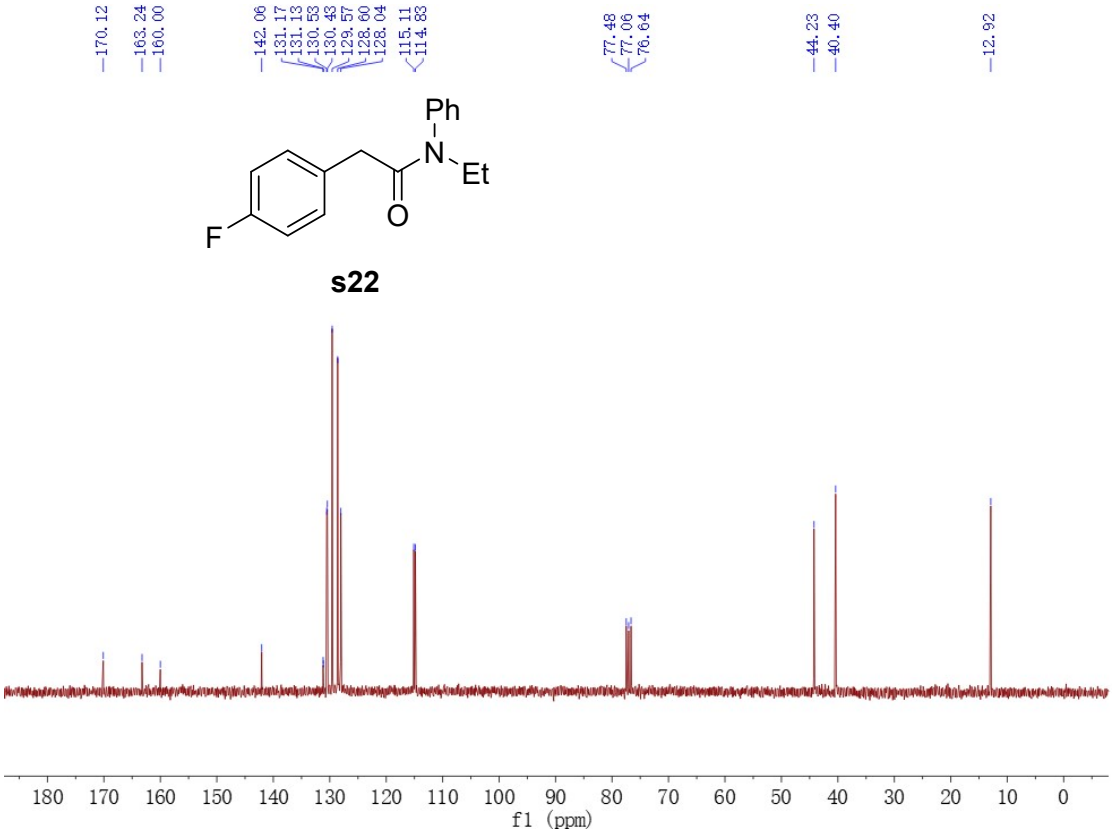

**s21**

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



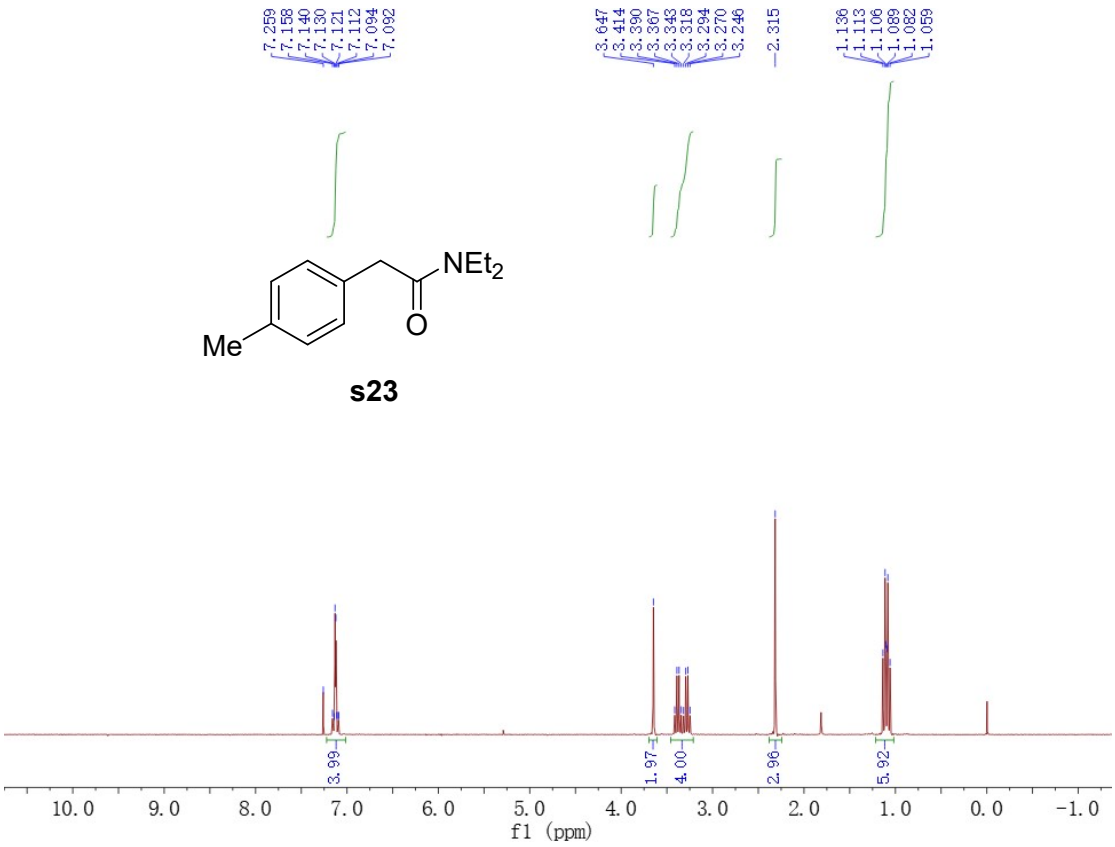

**s22**

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



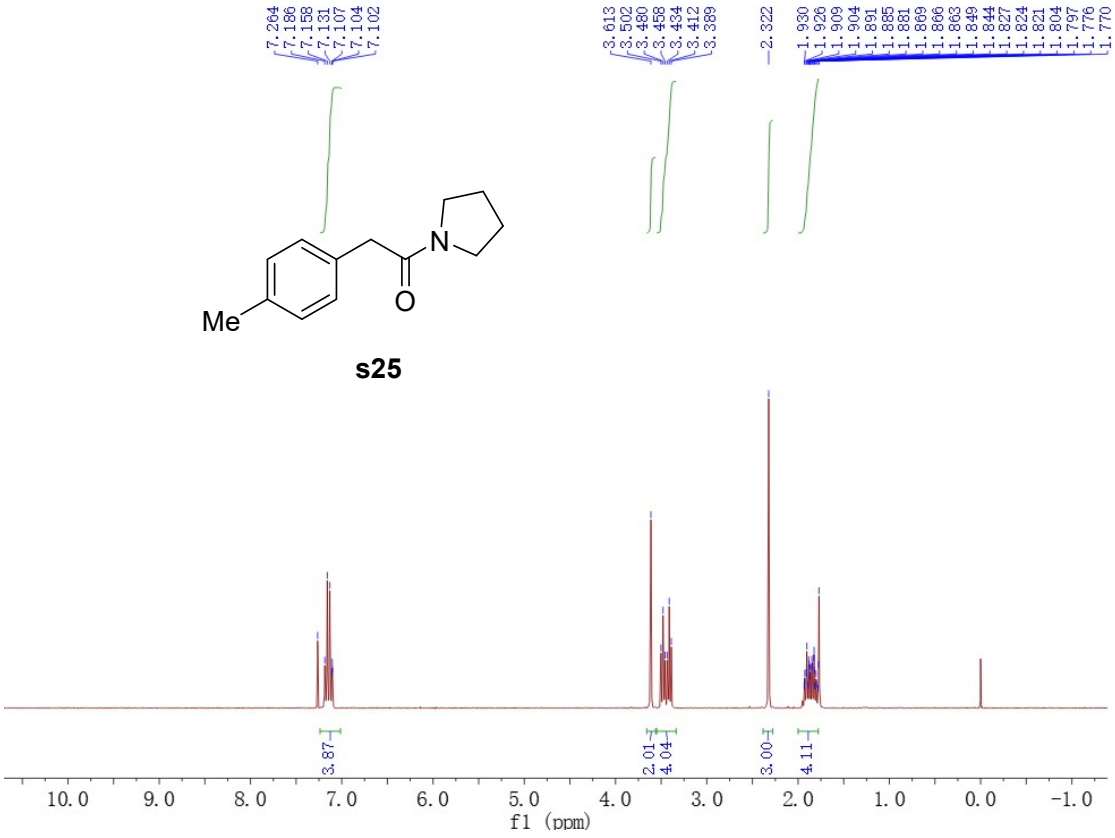

**s22**

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



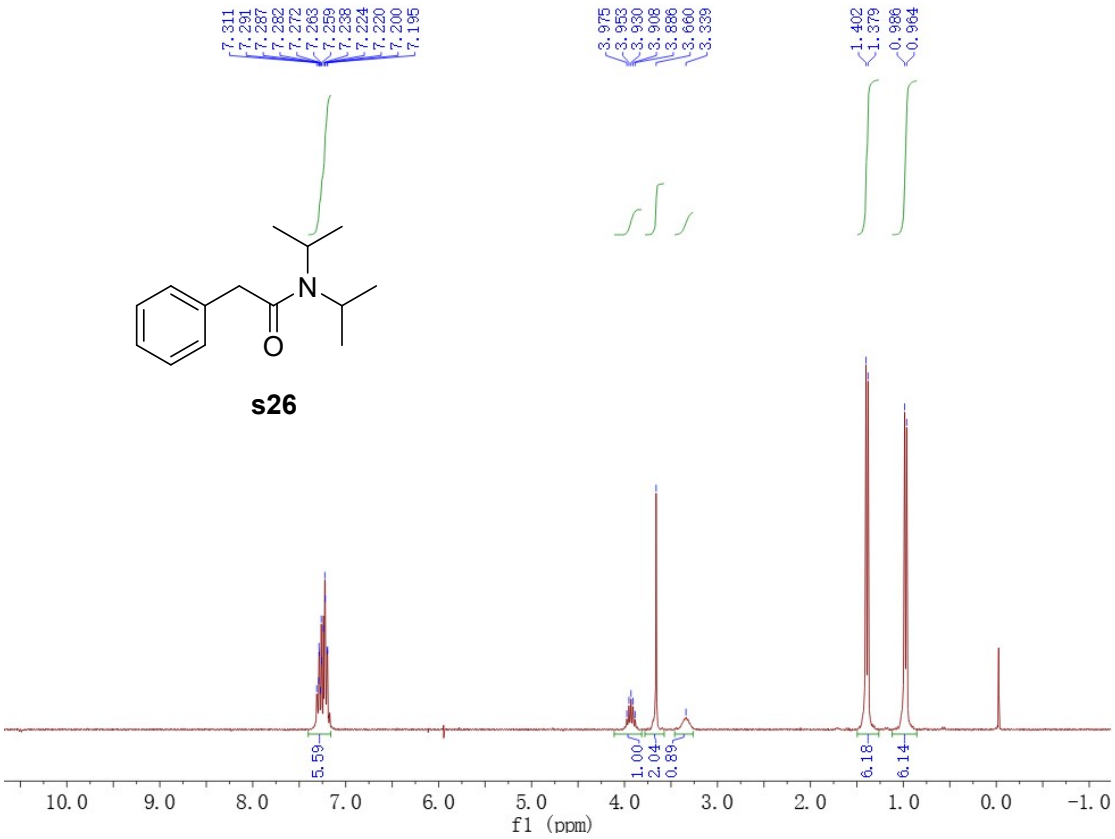

**s23**

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



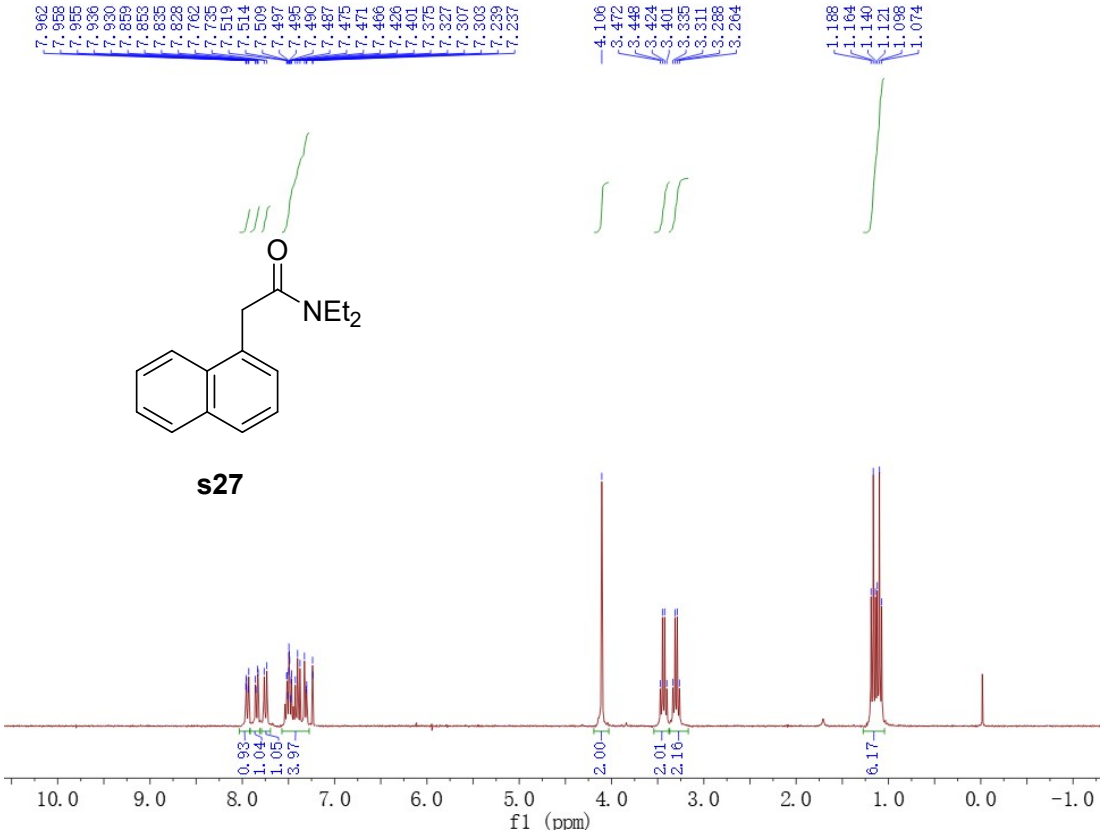

**s25**

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



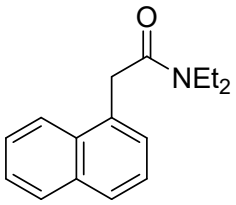

s26

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

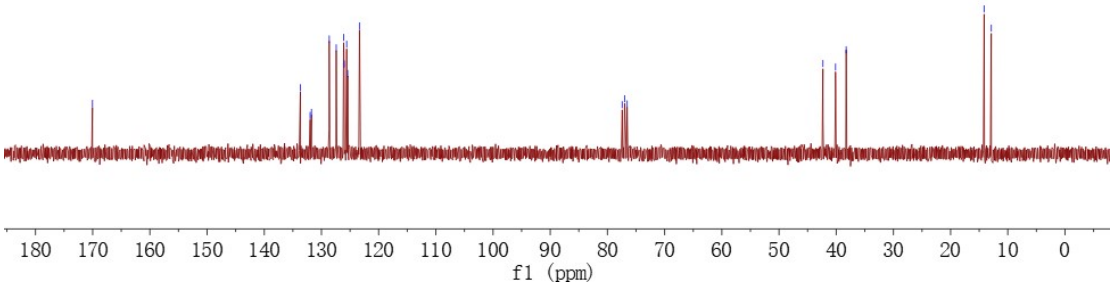



s27

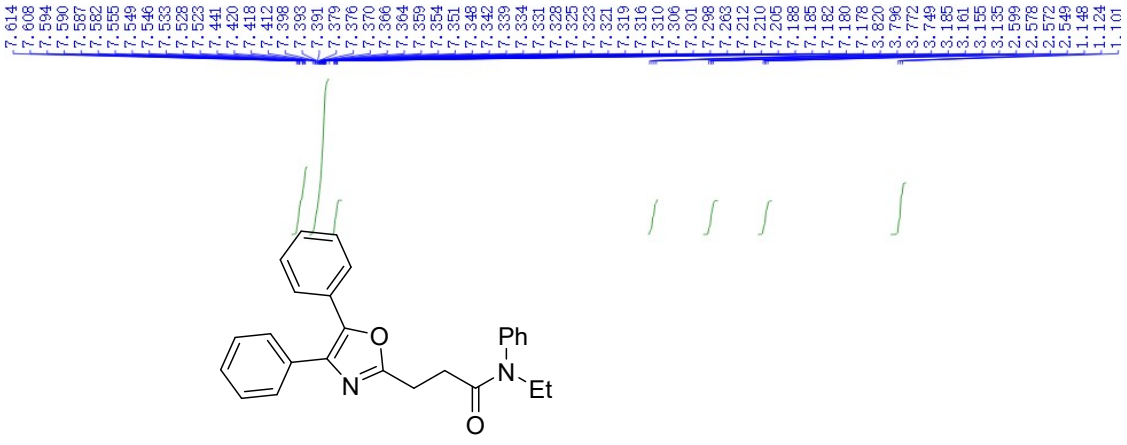
**$^{13}$C NMR (75 MHz, $CDCl_3$):**

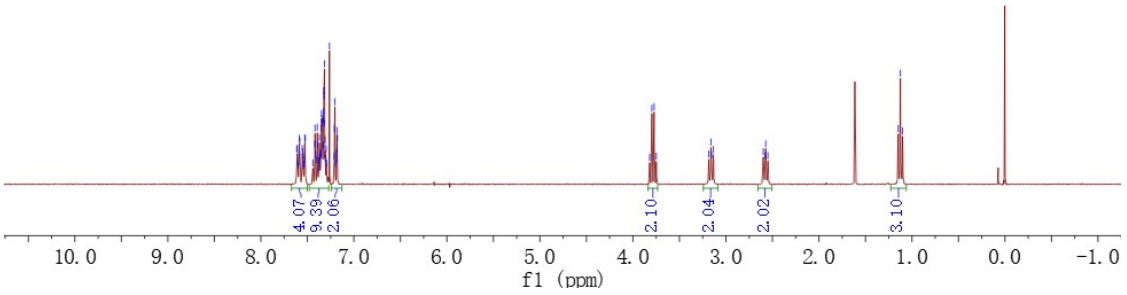

**s27**



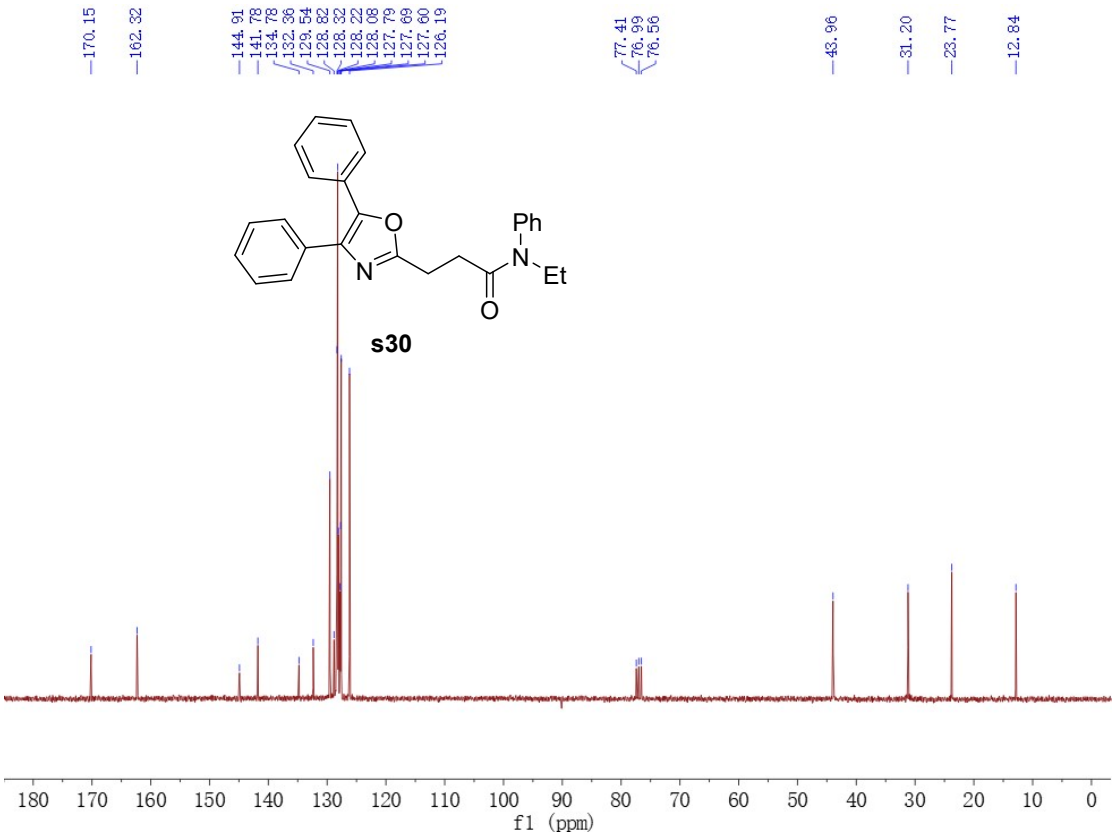

**$^{1}$H NMR (300 MHz, $CDCl_3$):**



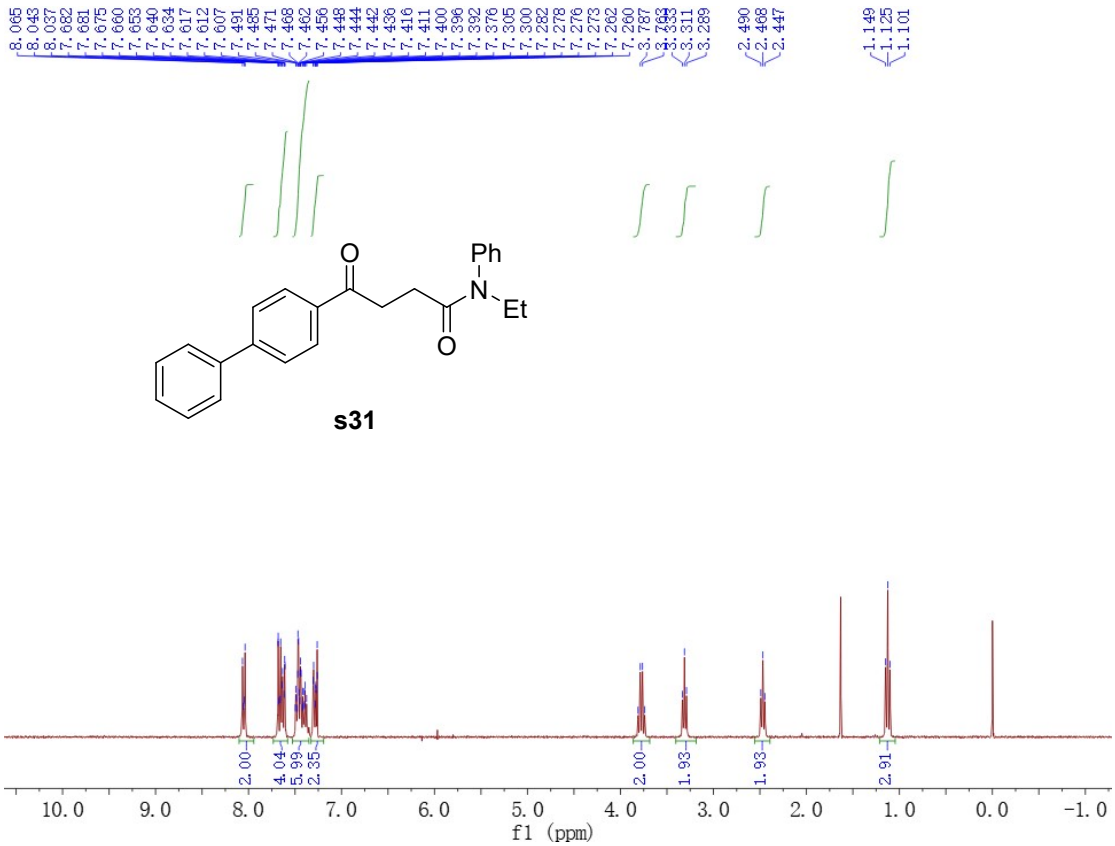

**s30**



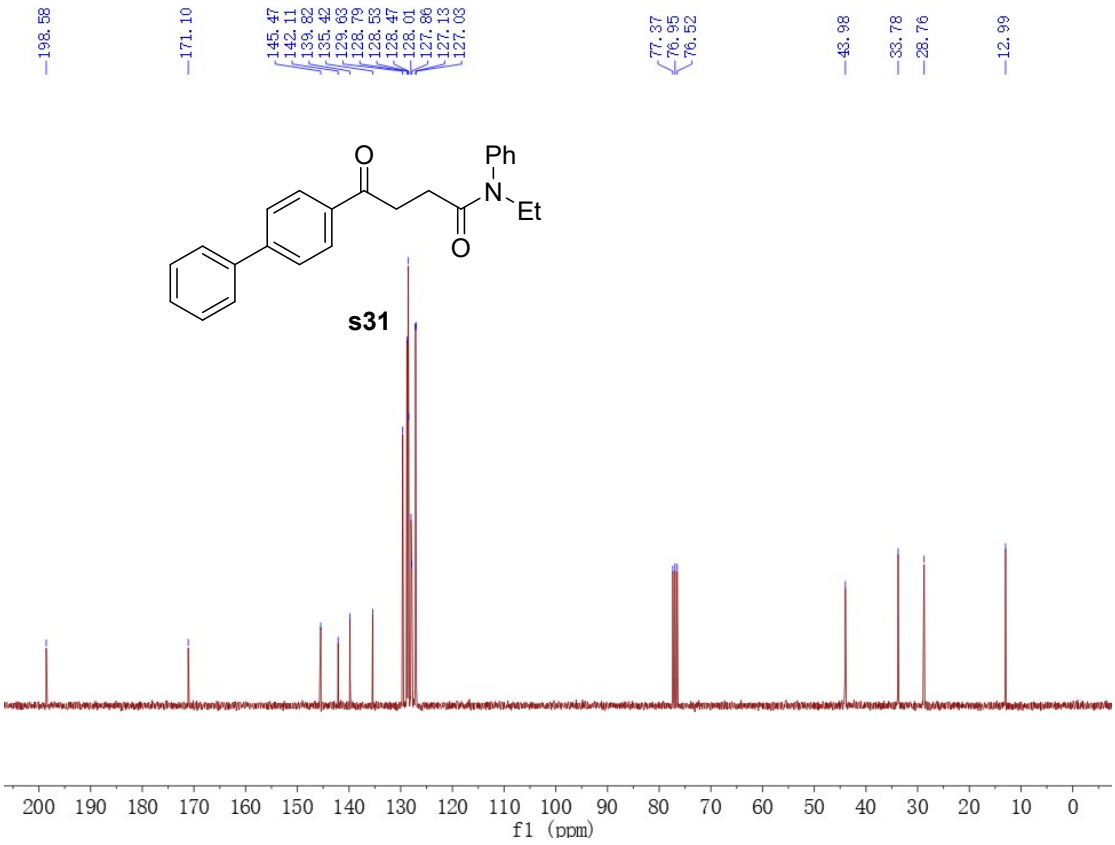

**$^{13}$C NMR (75 MHz, $CDCl_3$):**



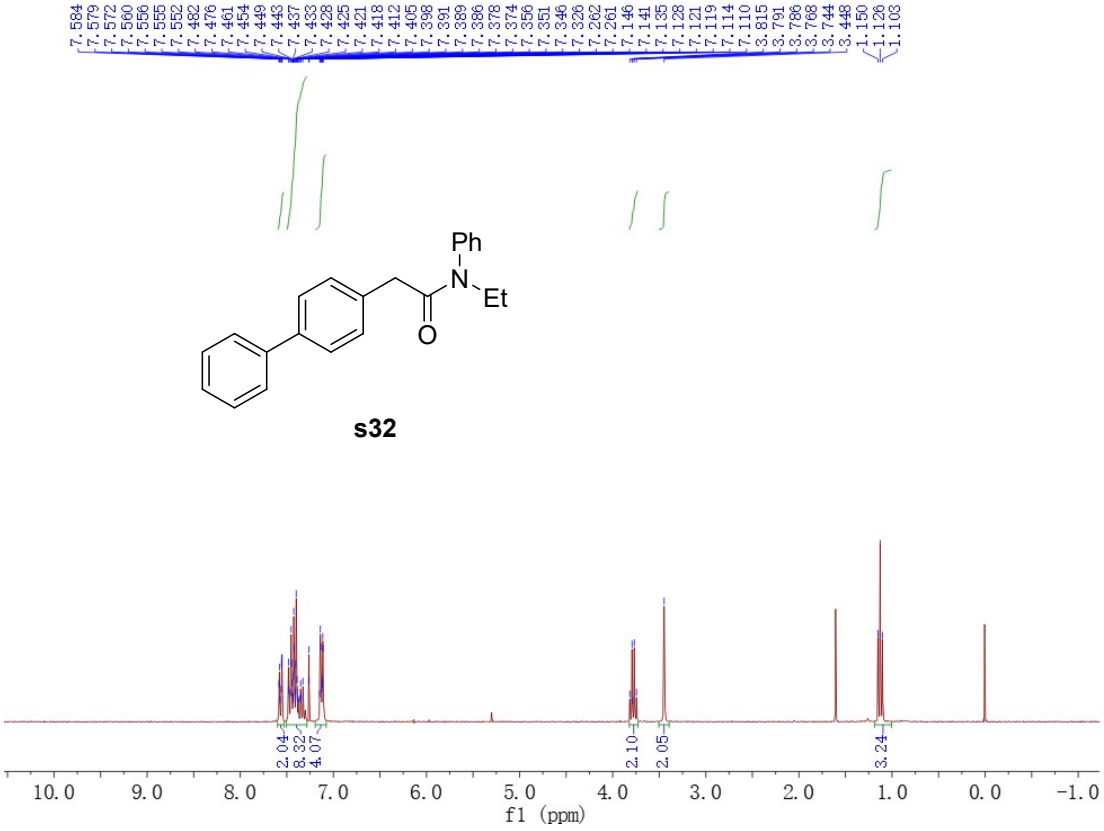

**$^{1}$H NMR (300 MHz, $CDCl_3$):**



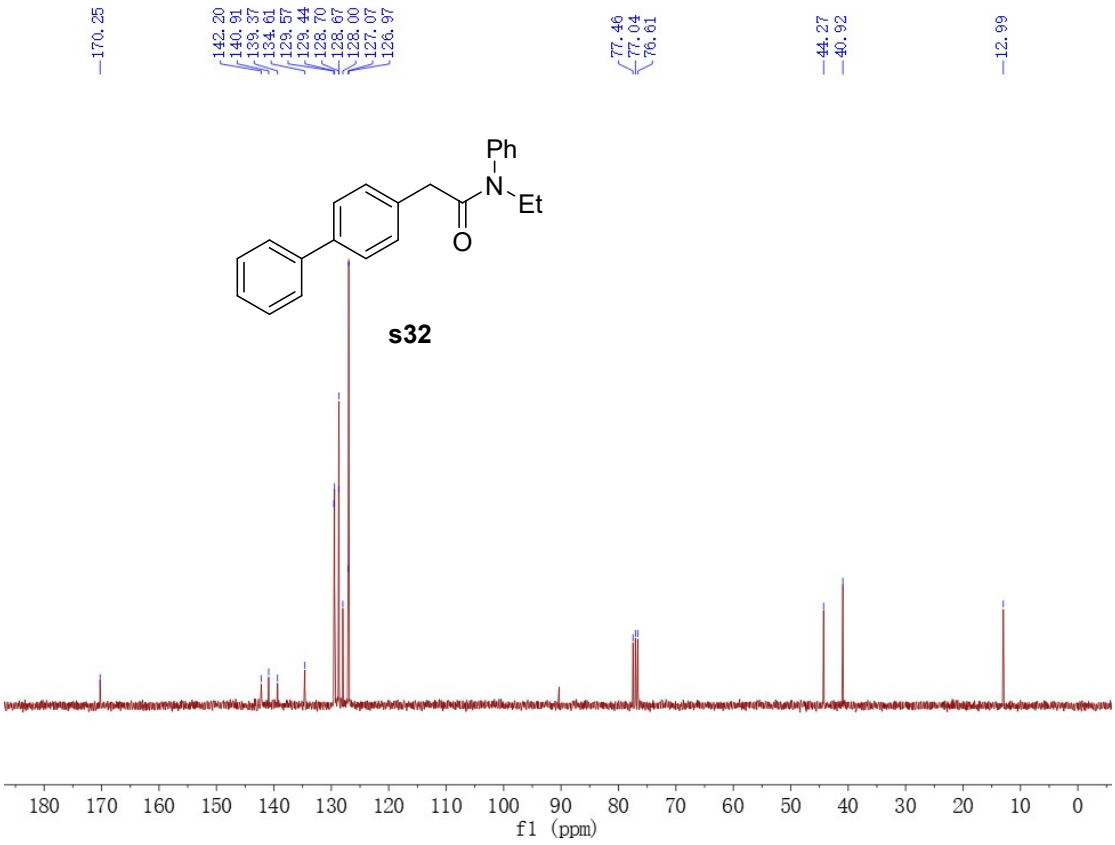

**$^{13}$C NMR (75 MHz, $CDCl_3$):**




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




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

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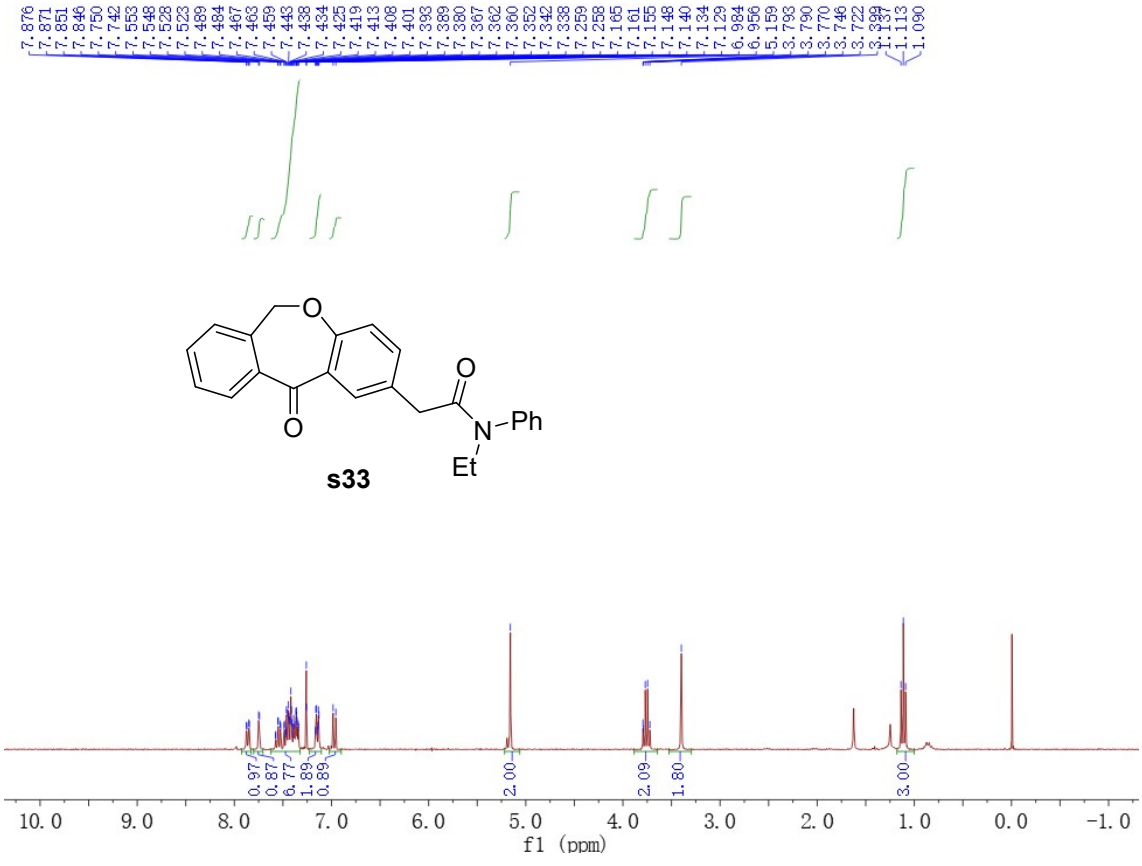
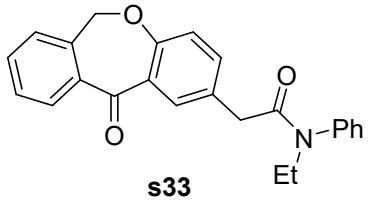
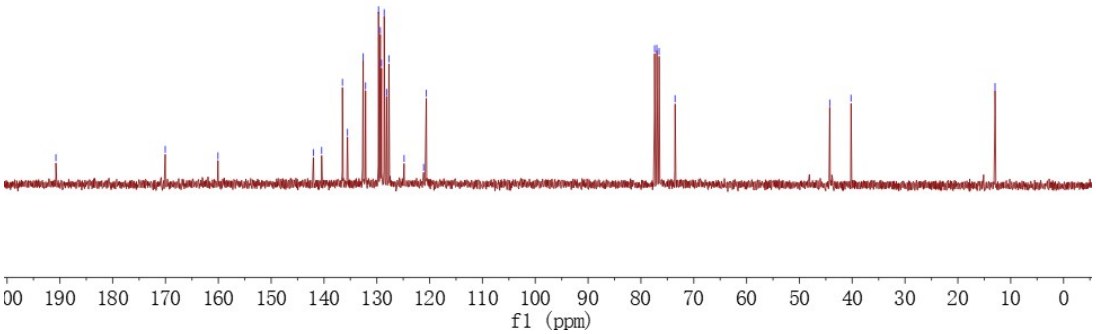


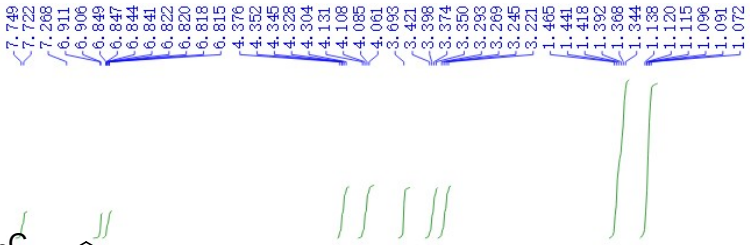

**$^{13}$C NMR (75 MHz, $CDCl_3$):**

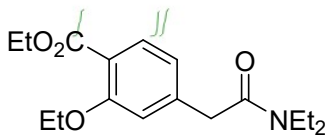




**s33**

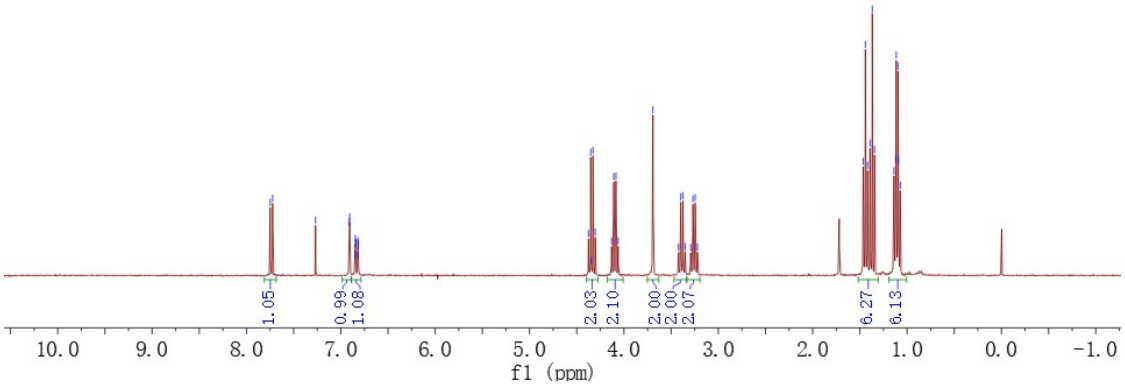



**$^{1}$H NMR (300 MHz, $CDCl_3$):**

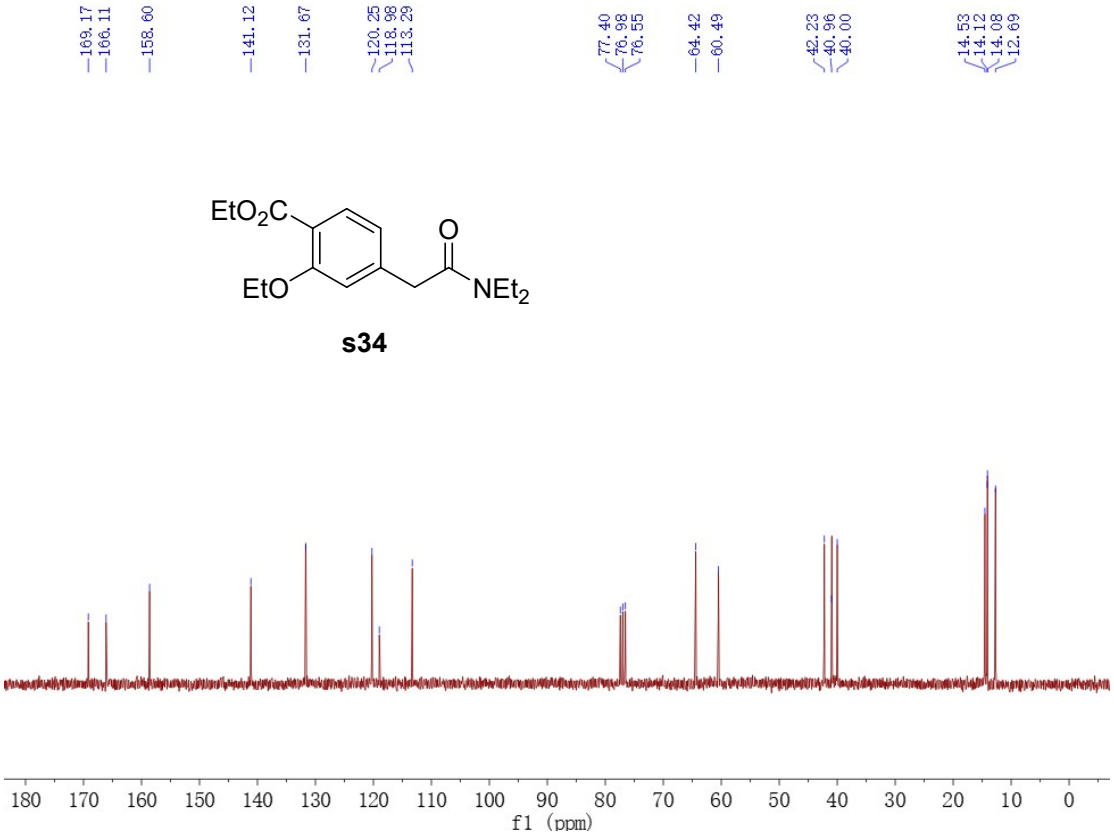


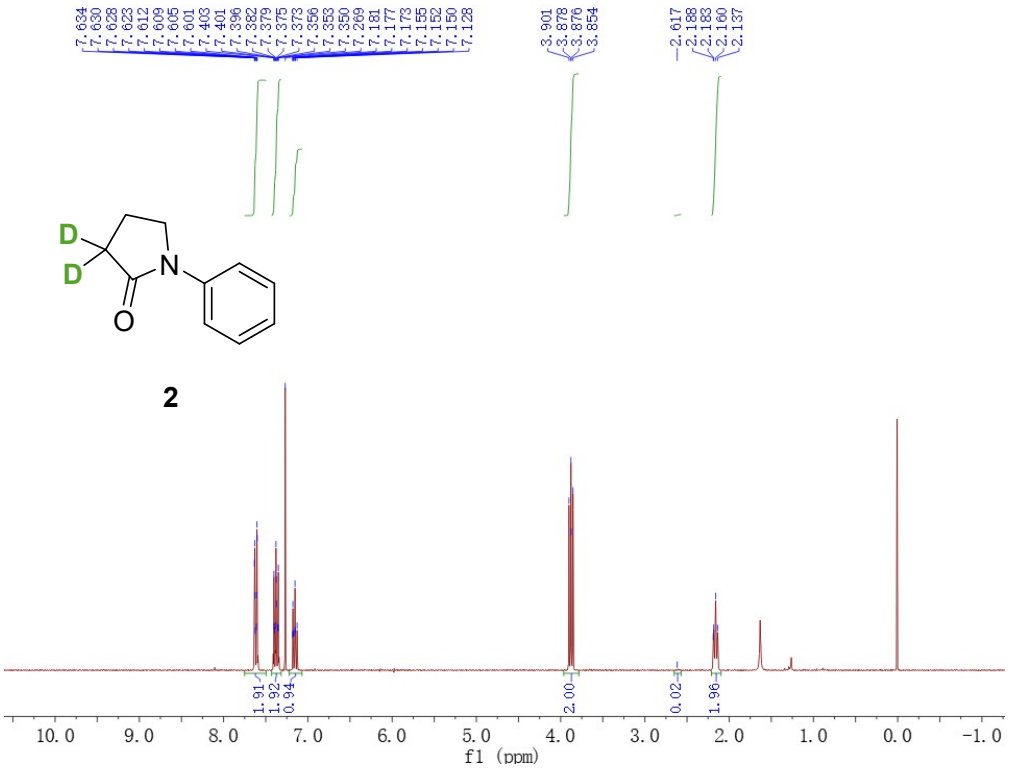

**s34**



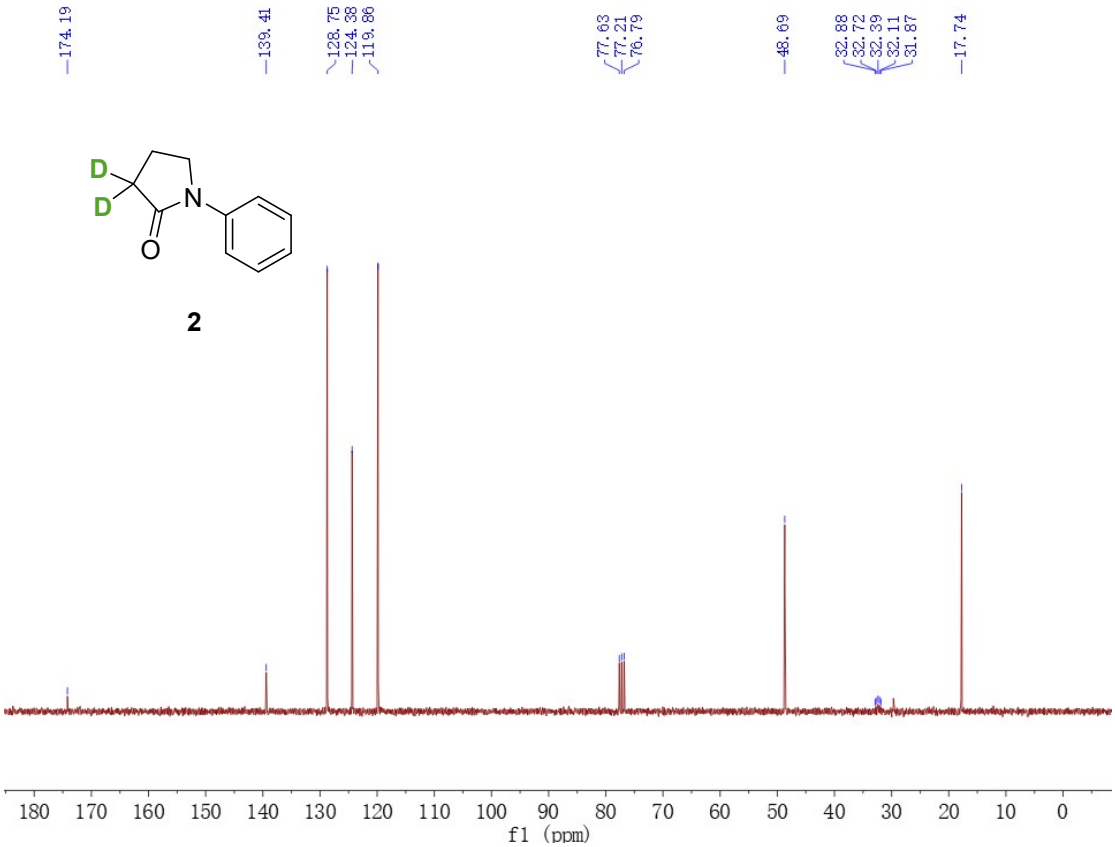

**$^{13}$C NMR (75 MHz, $CDCl_3$):**




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

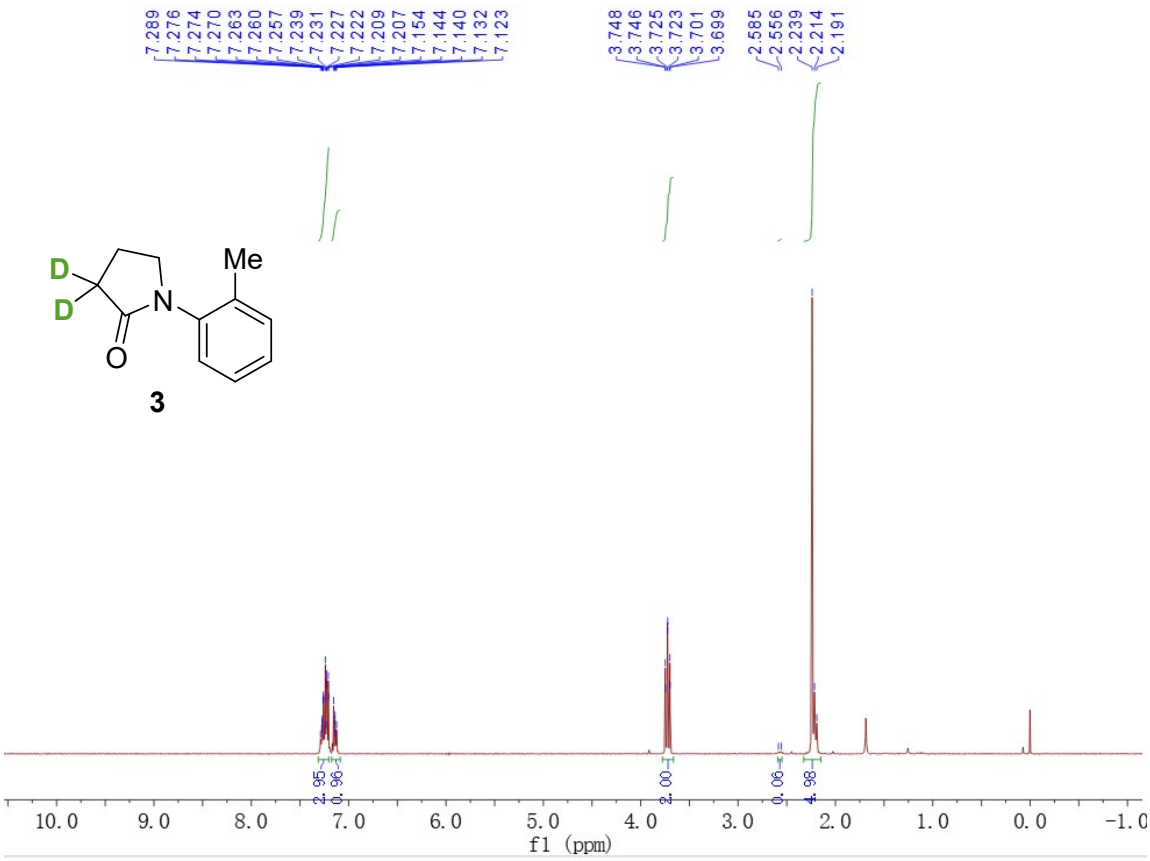



**$^{13}$C NMR (75 MHz, $CDCl_3$):**




2

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

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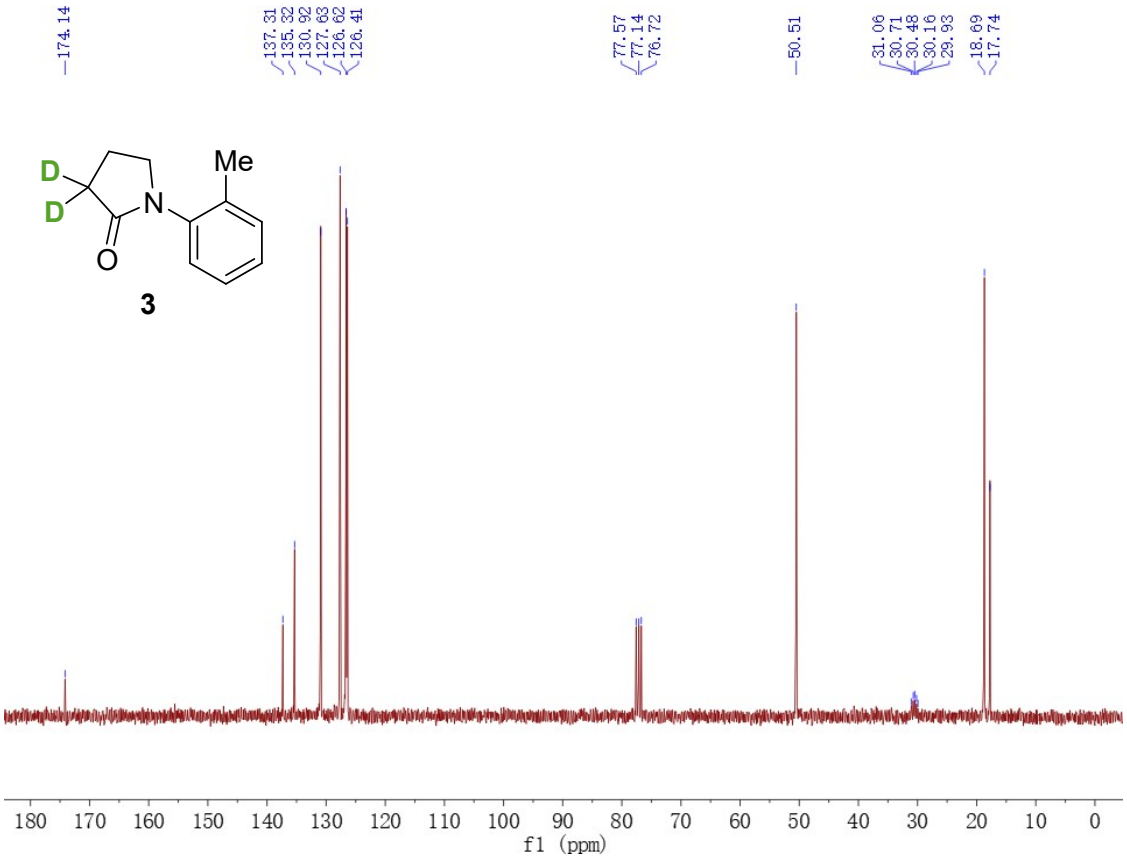
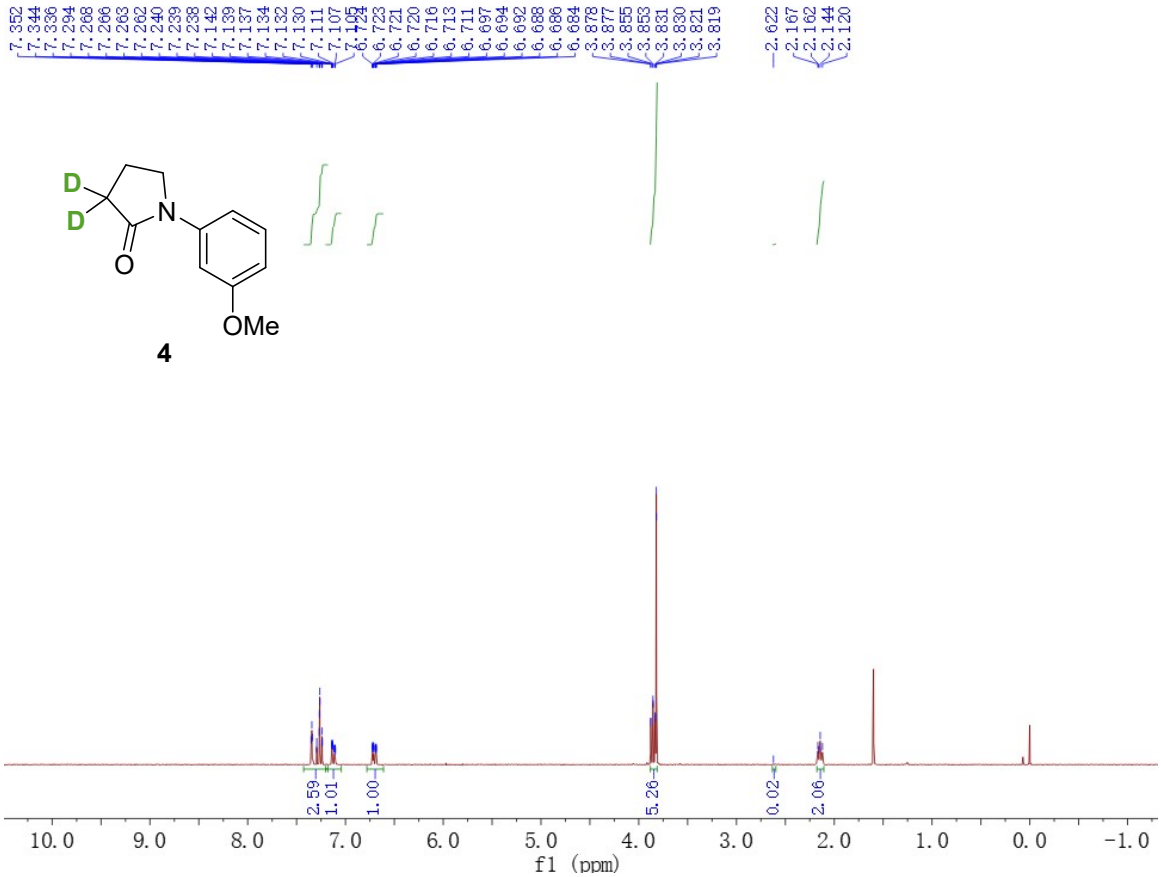


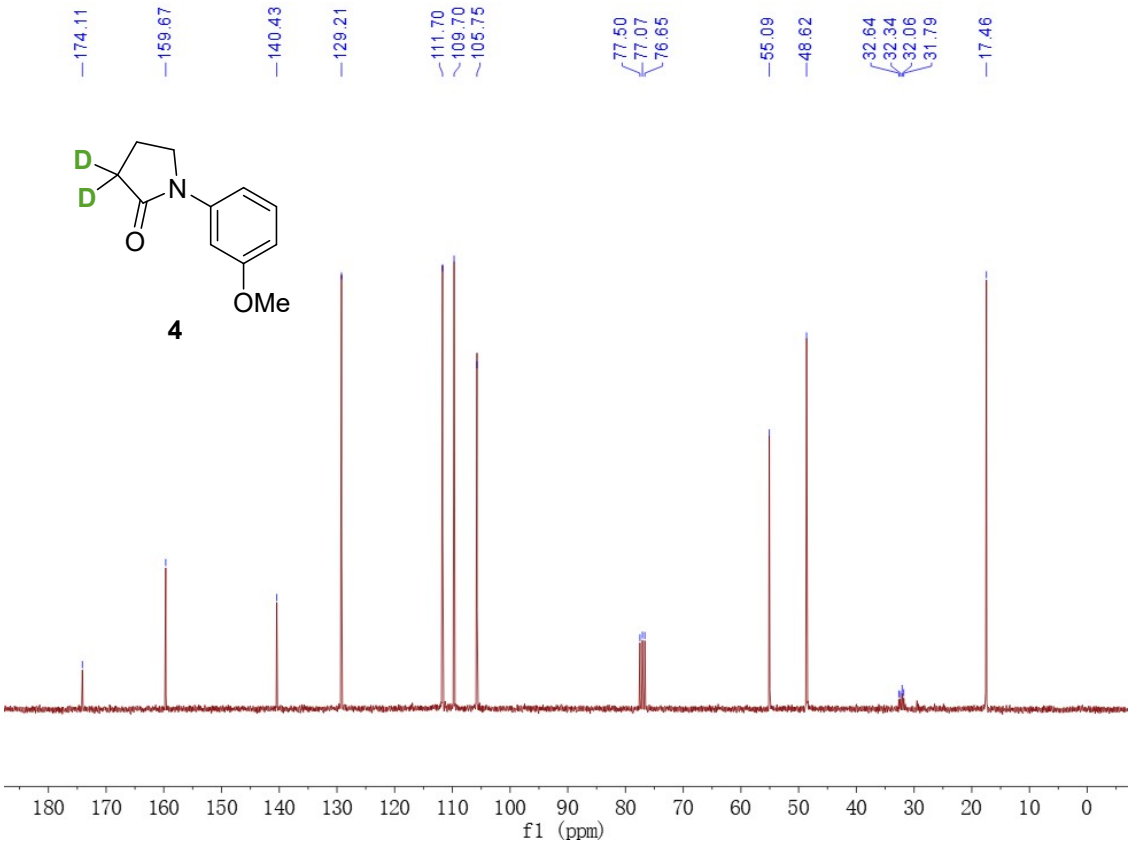

**3**

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




**4**

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

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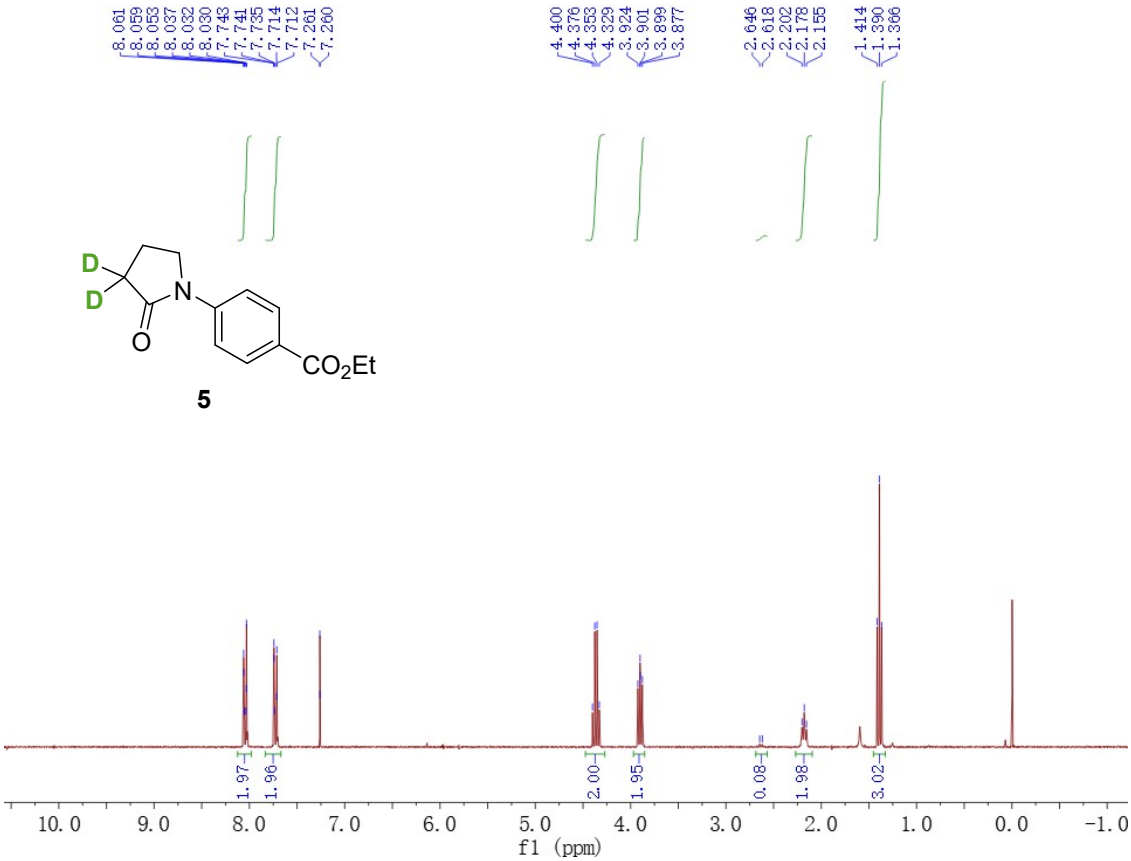
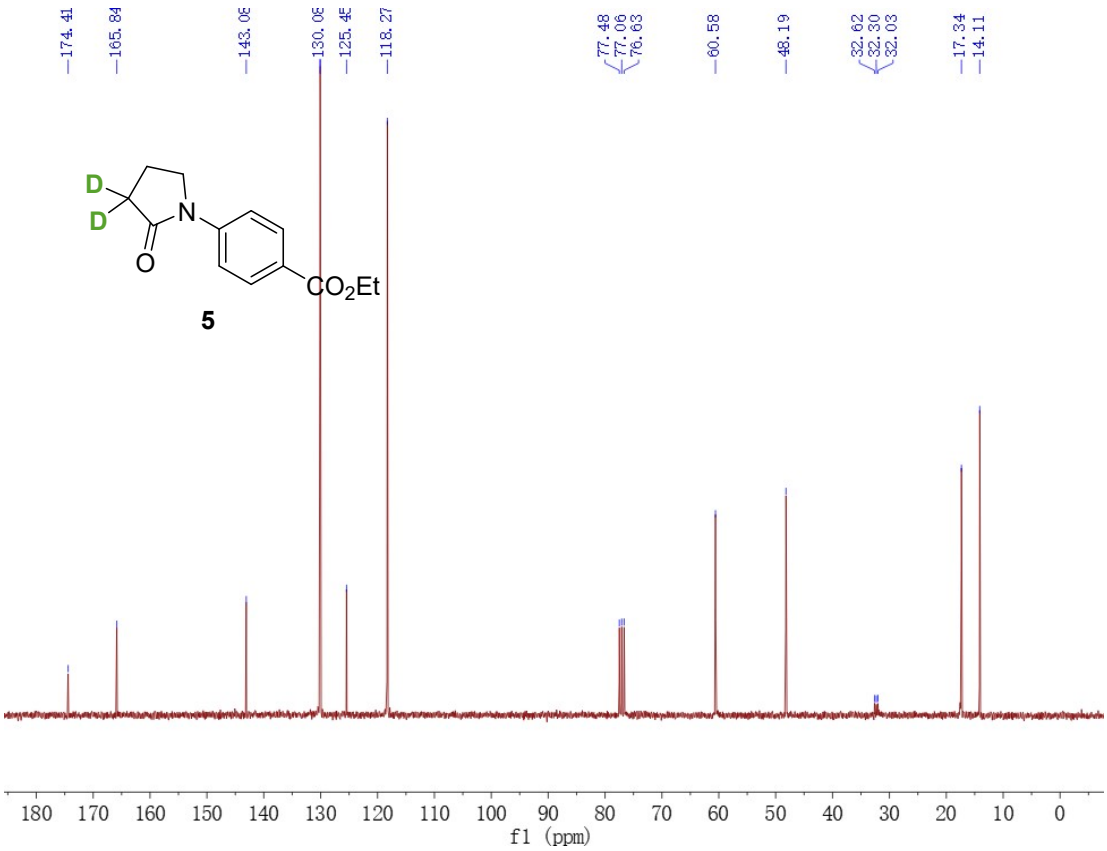
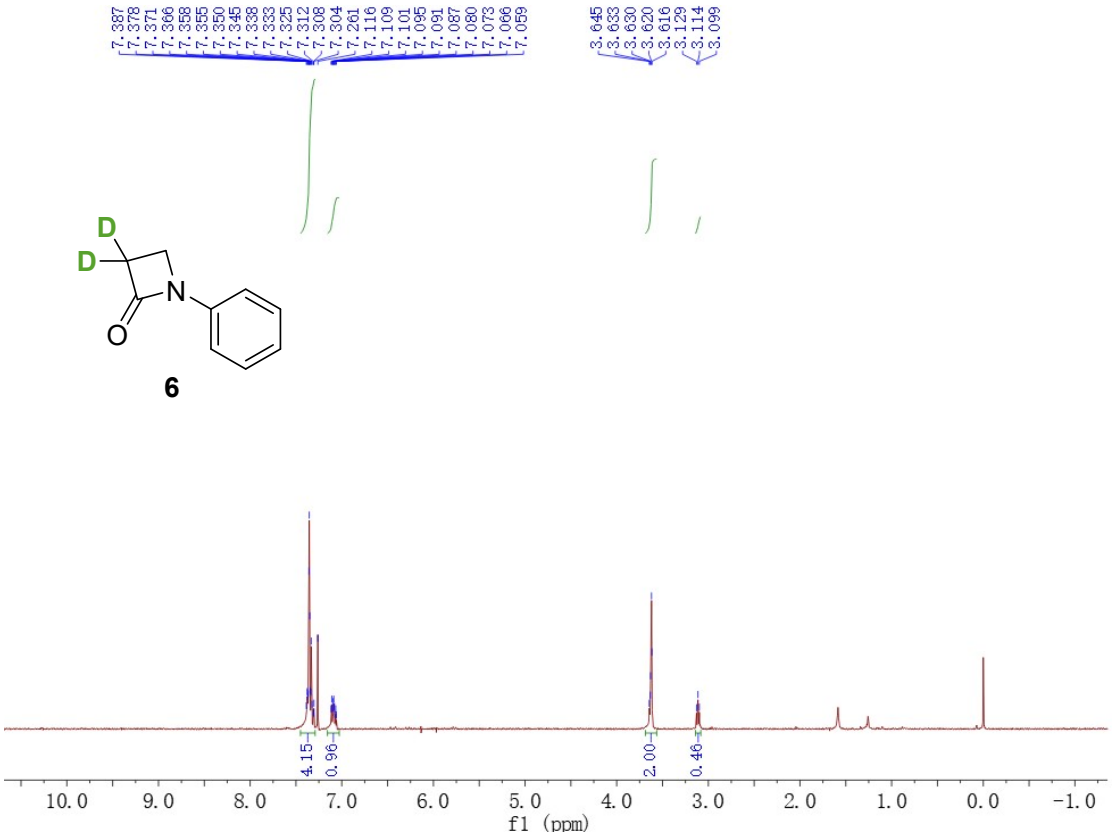


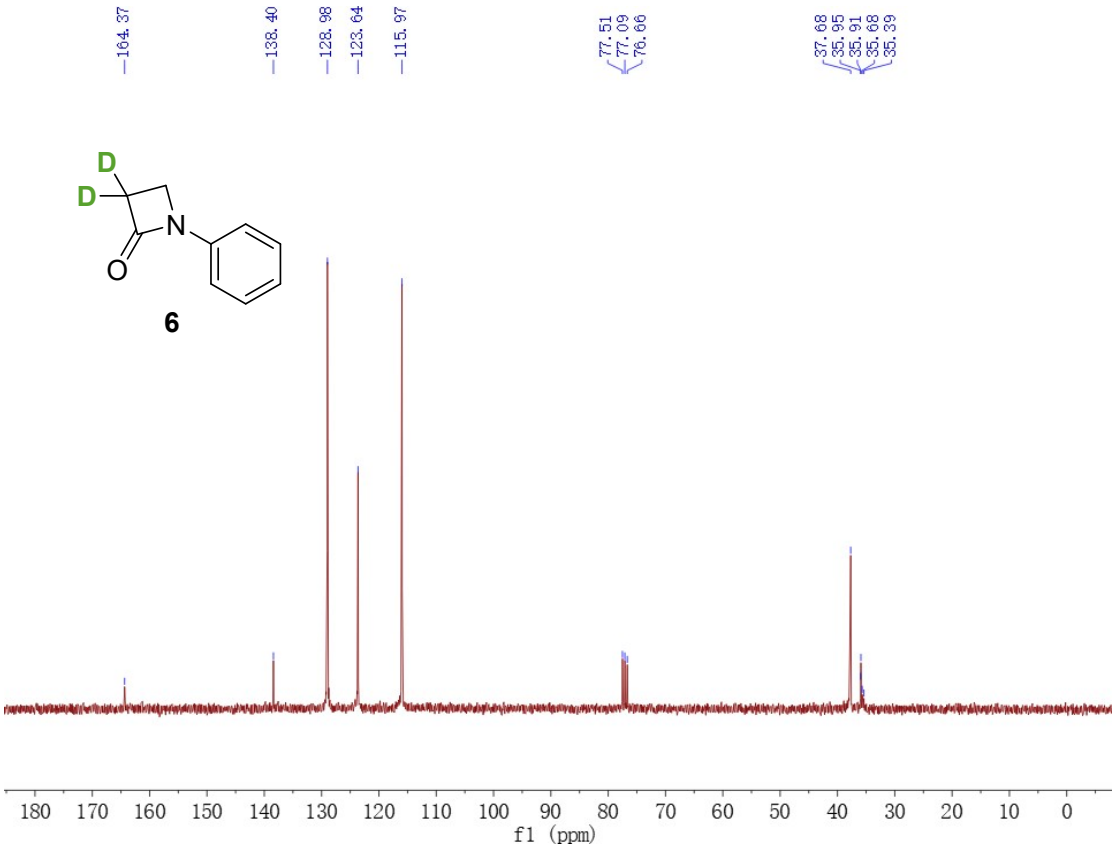

**$^{13}$C NMR (75 MHz, $CDCl_3$):**




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




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

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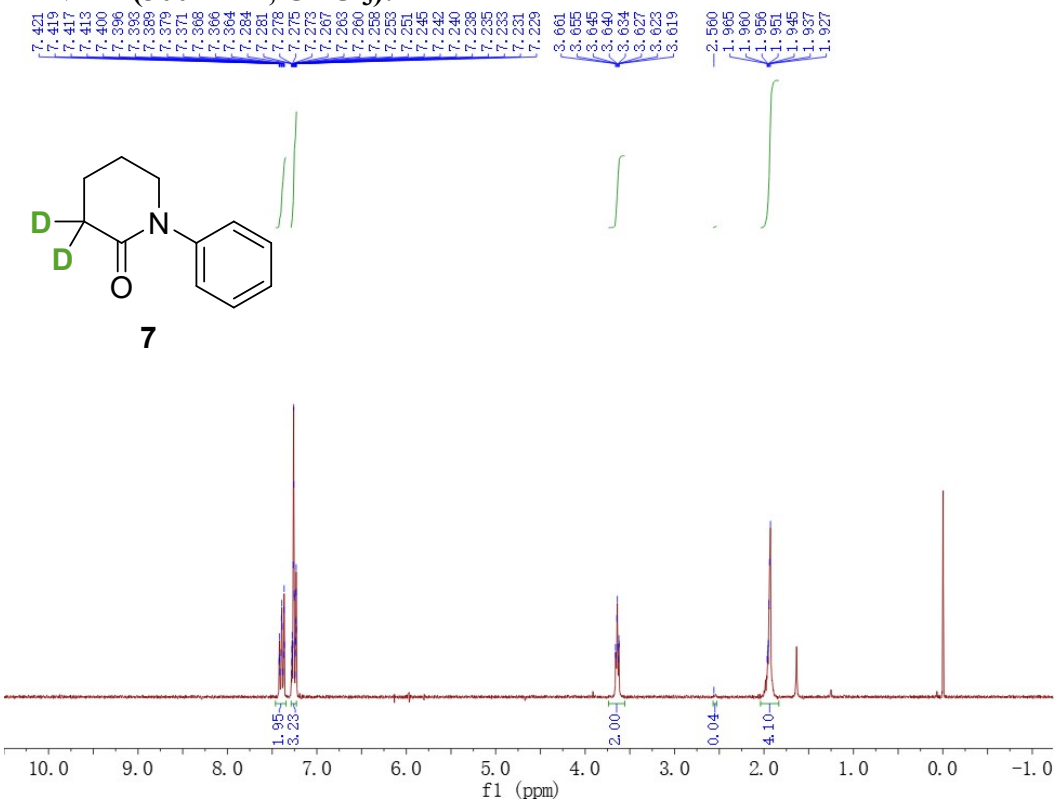


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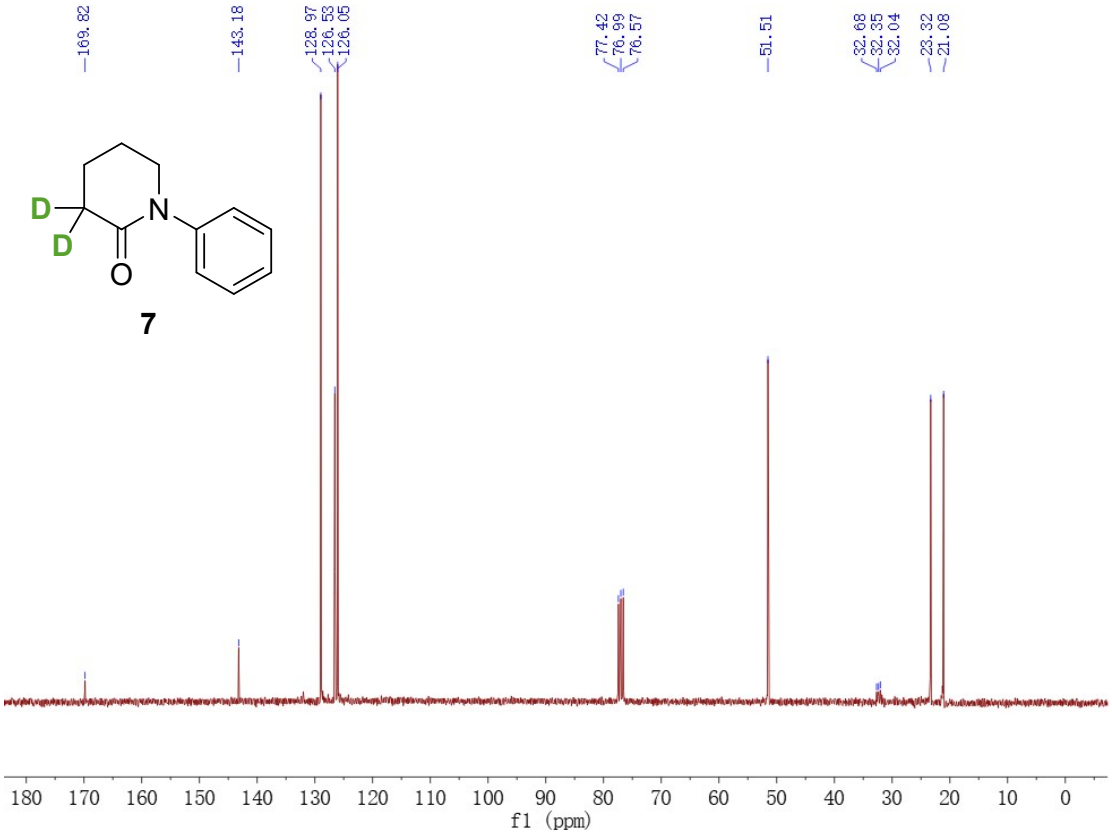


7

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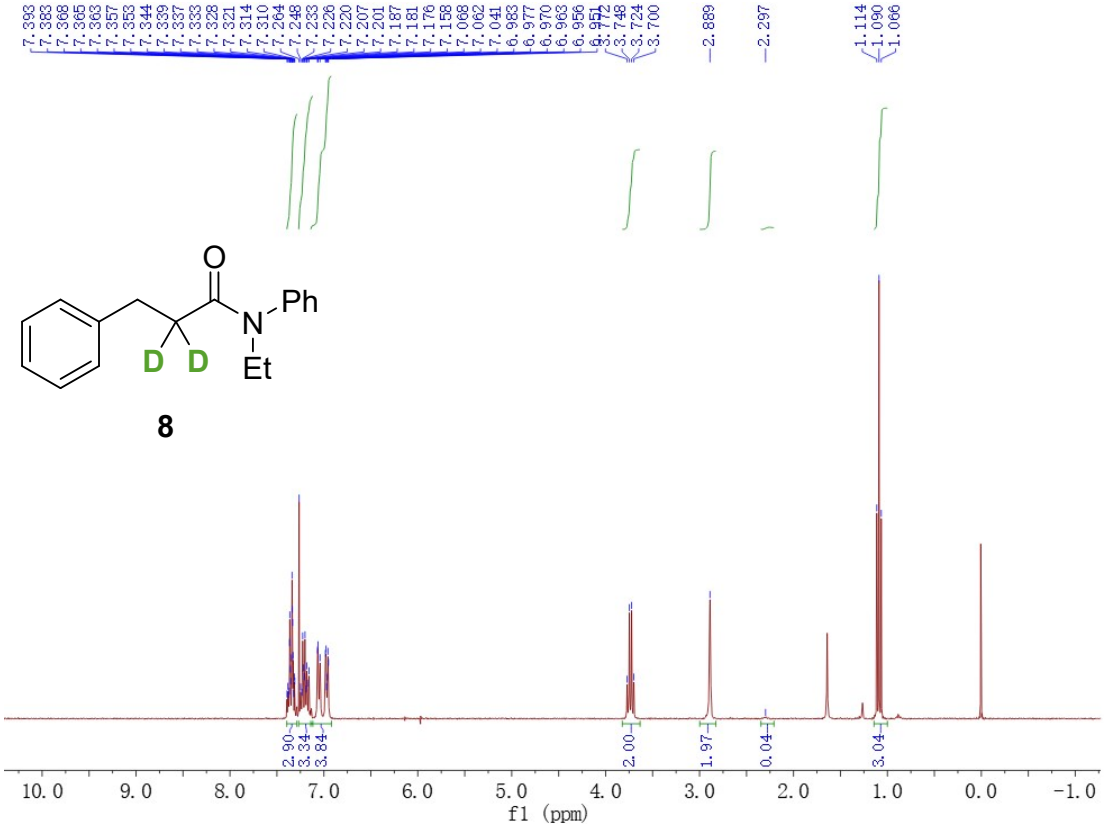
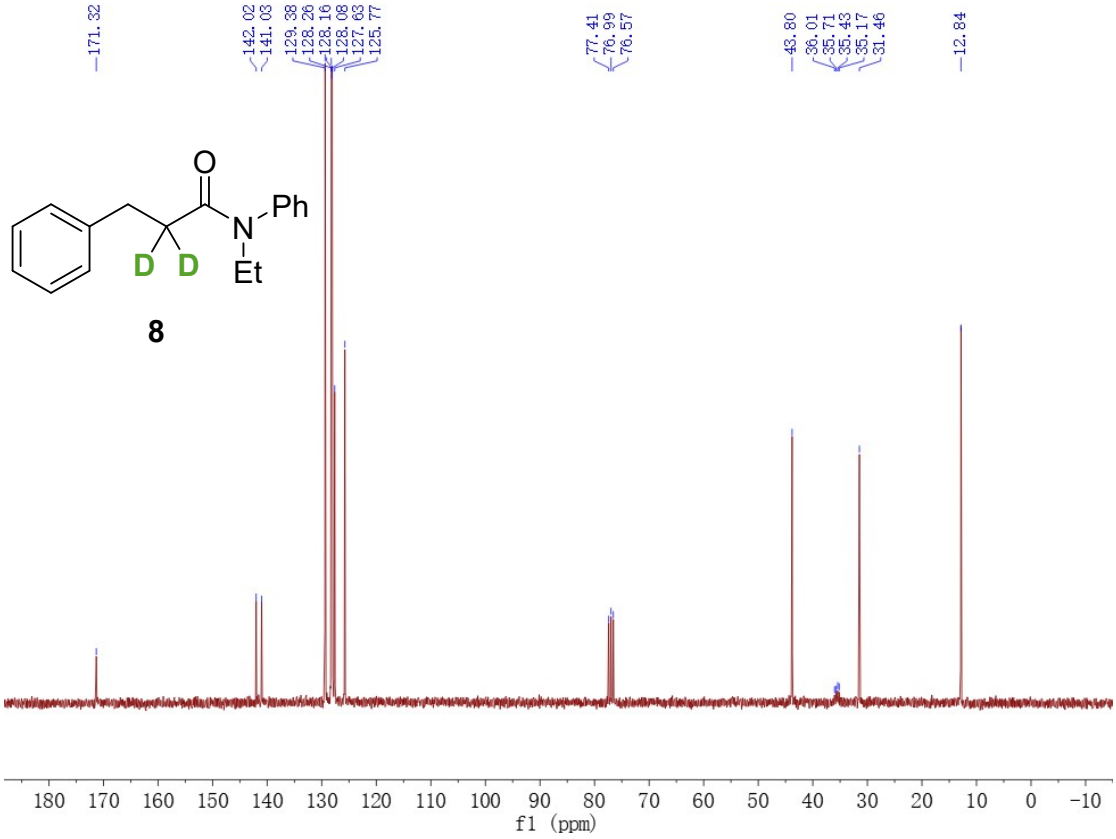


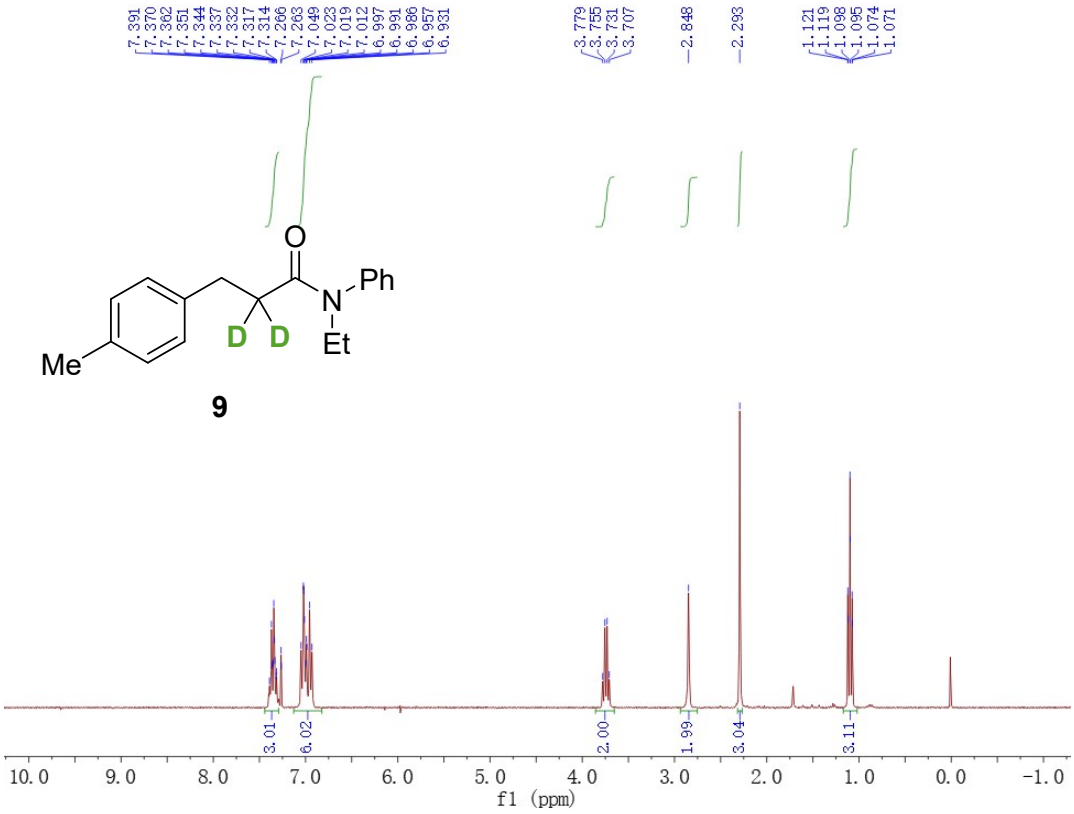

8

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



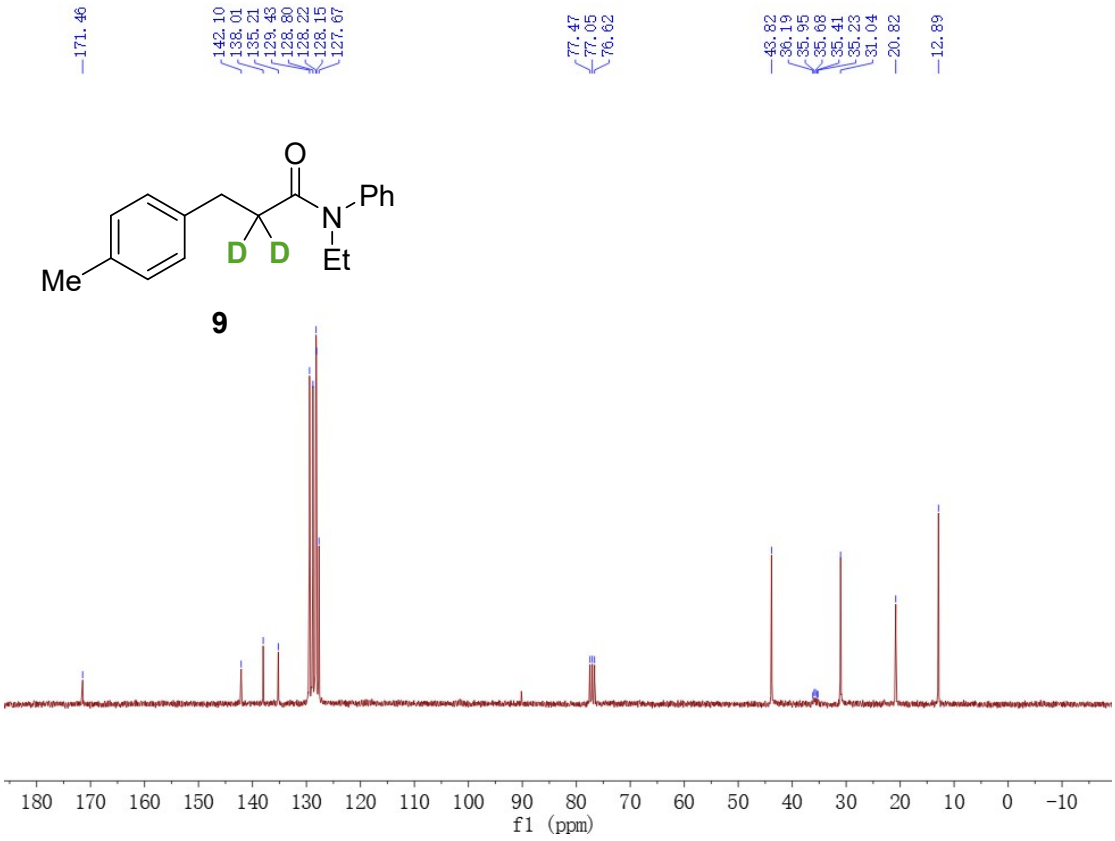

8

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



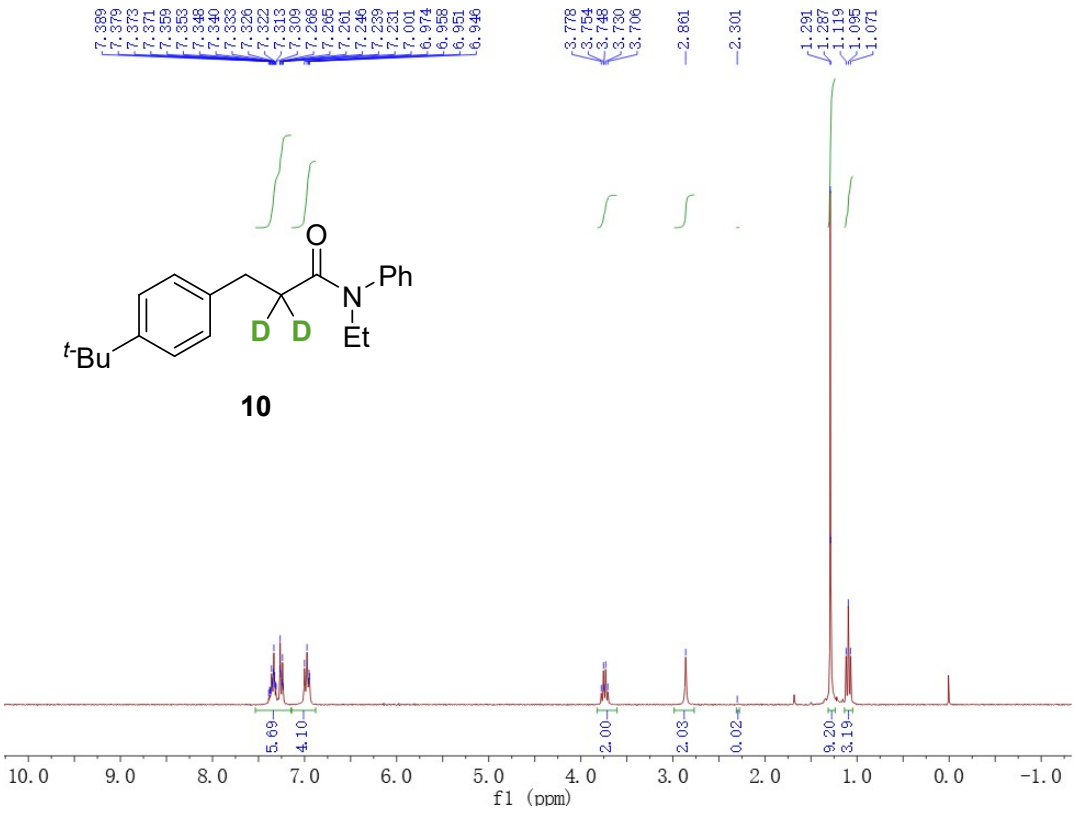

9

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



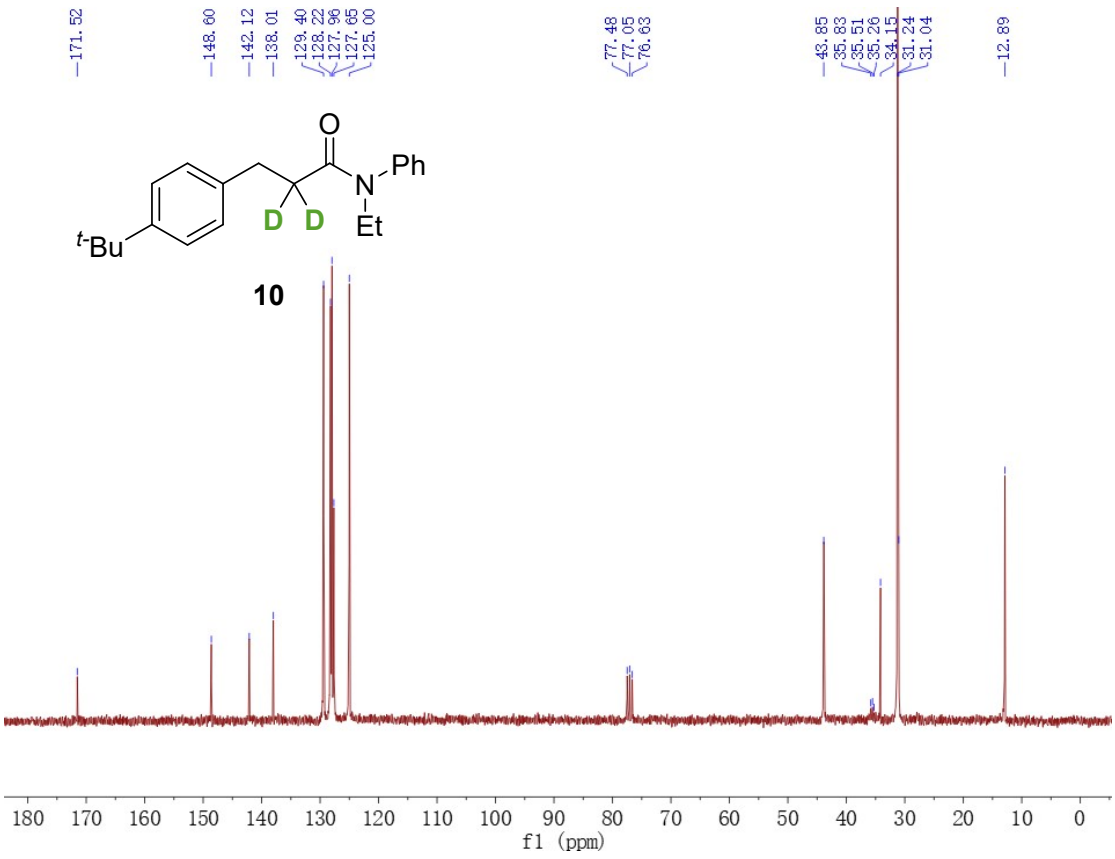

**9**

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




**10**

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

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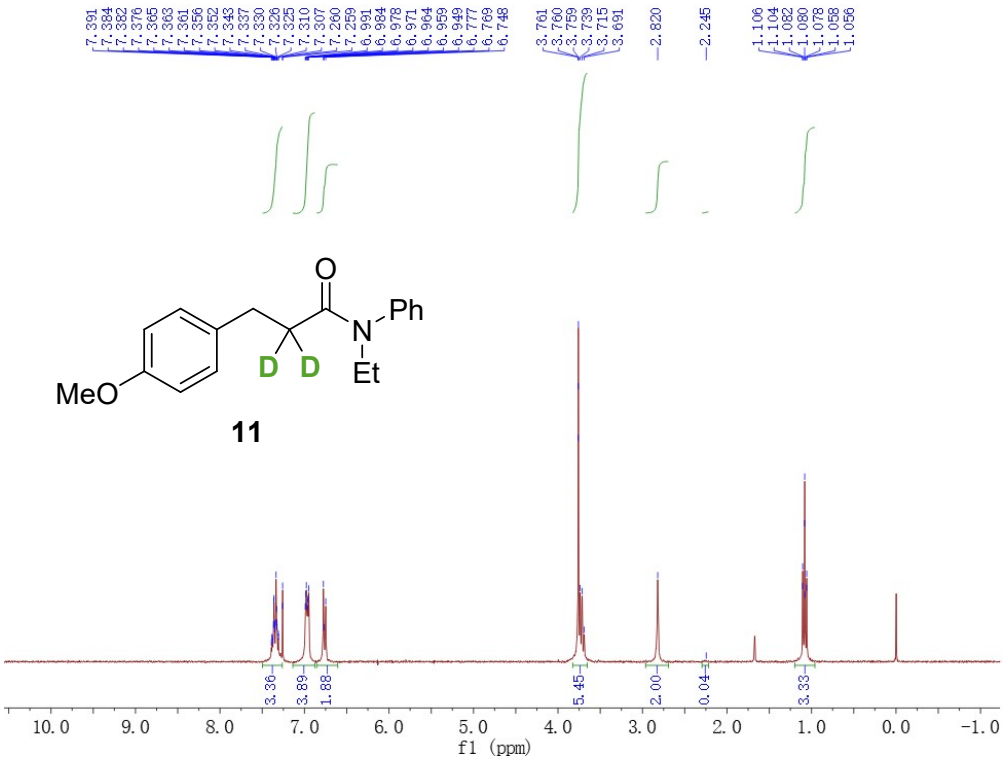


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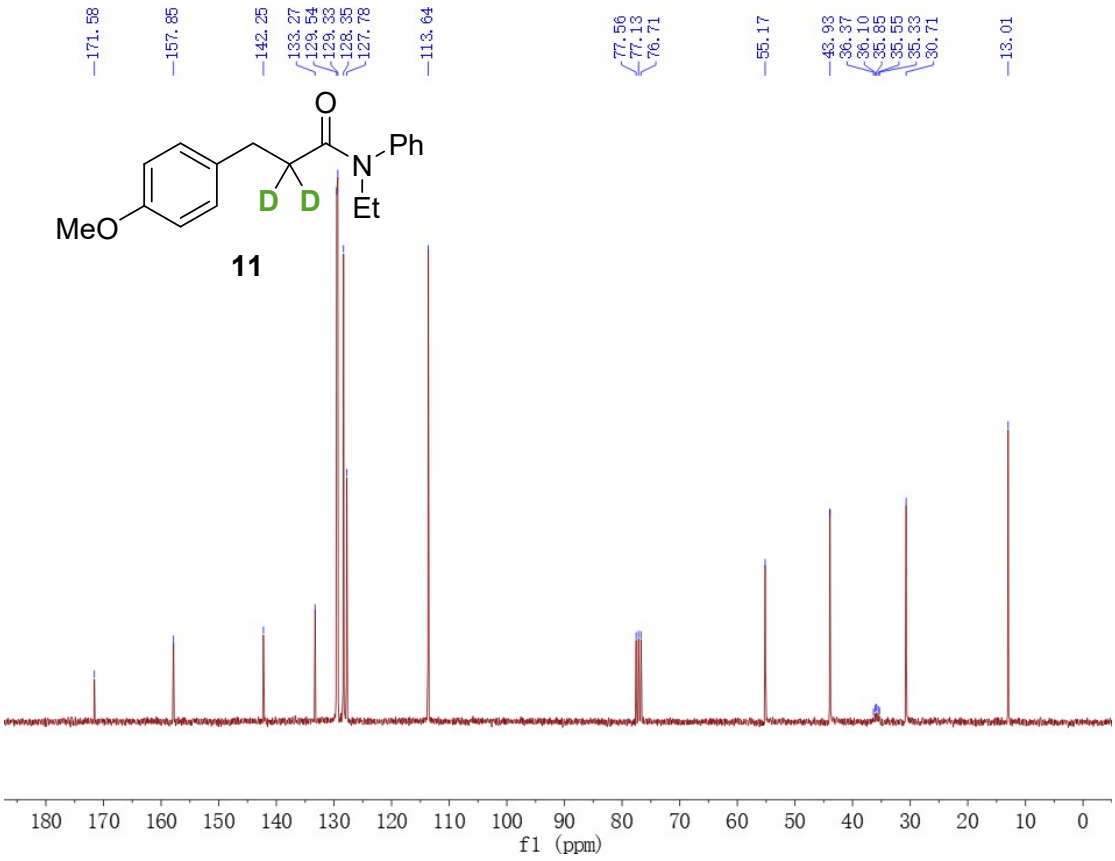


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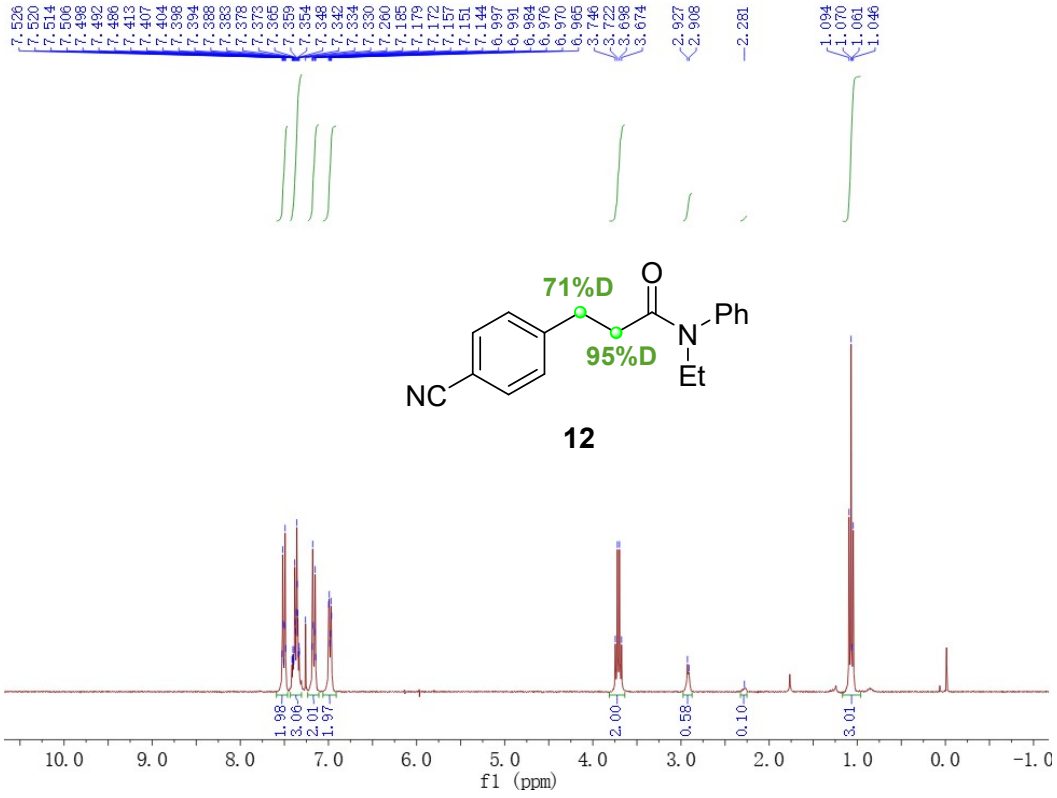


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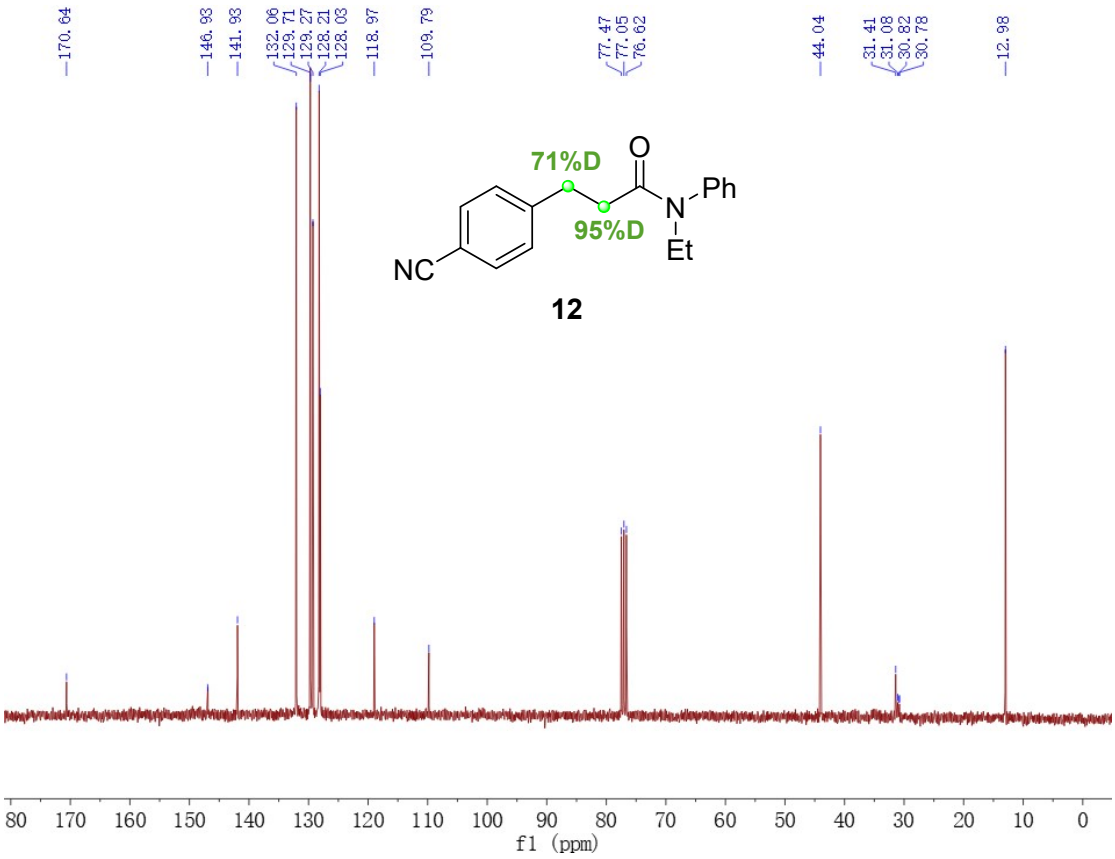
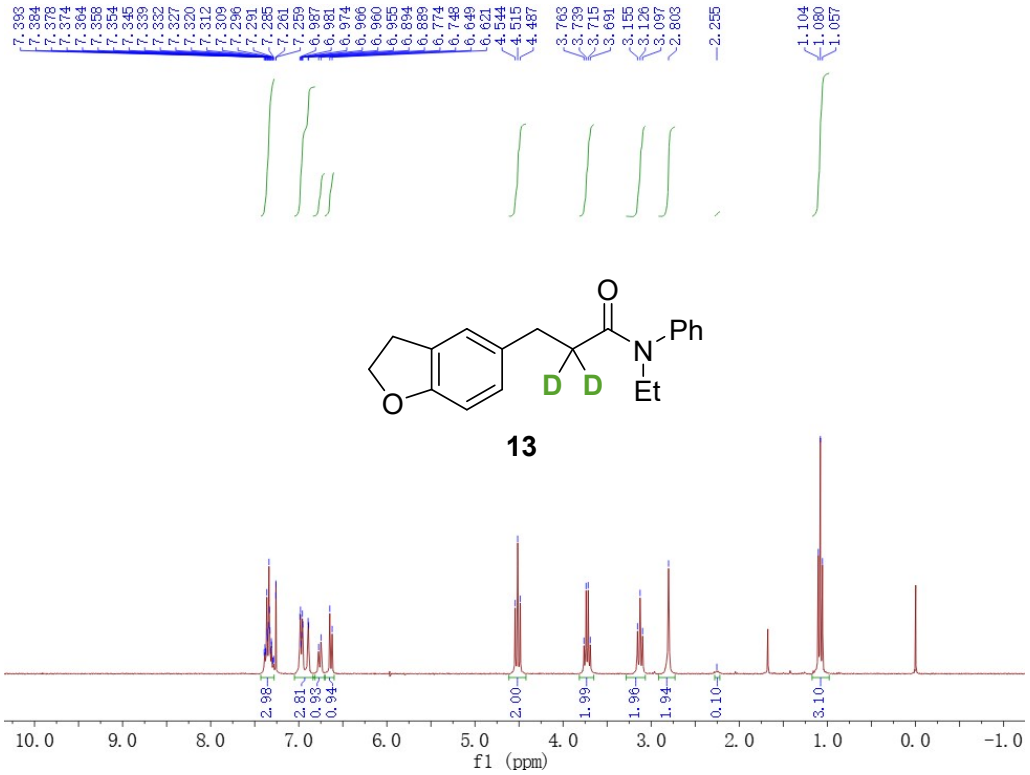



**$^{1}$H NMR (300 MHz, $CDCl_3$):**

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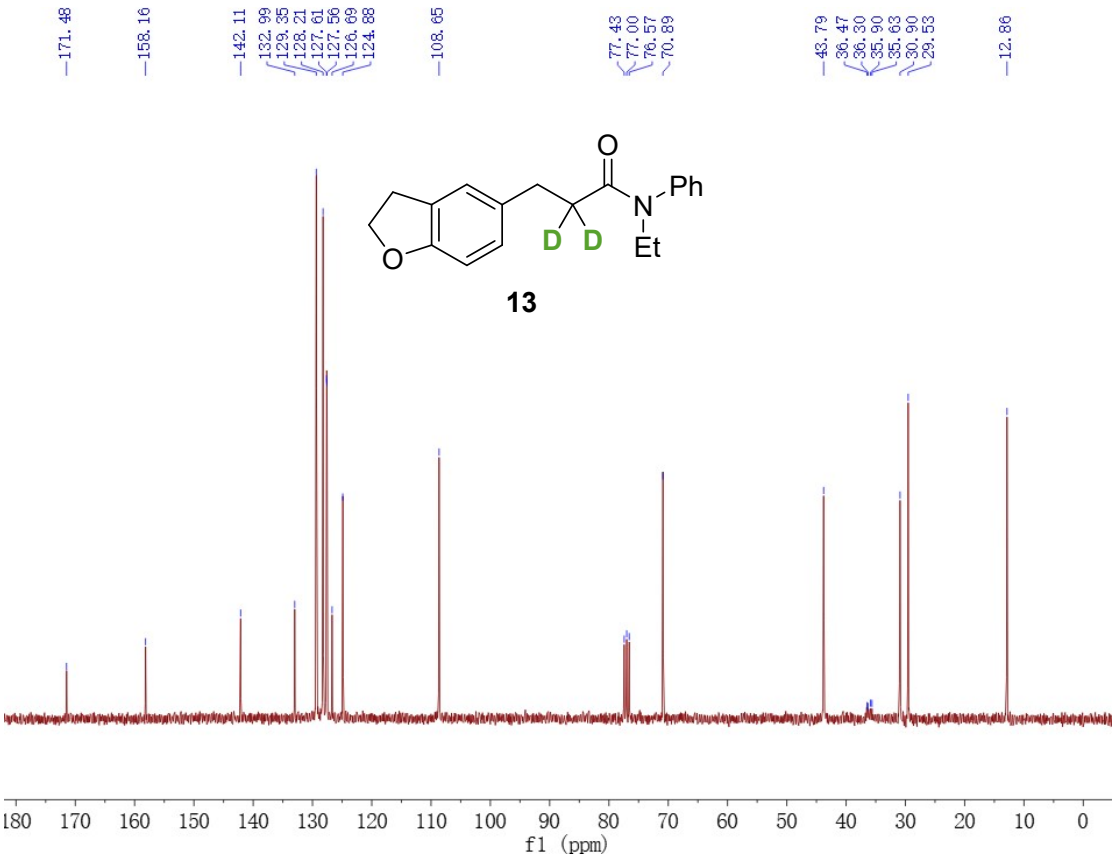


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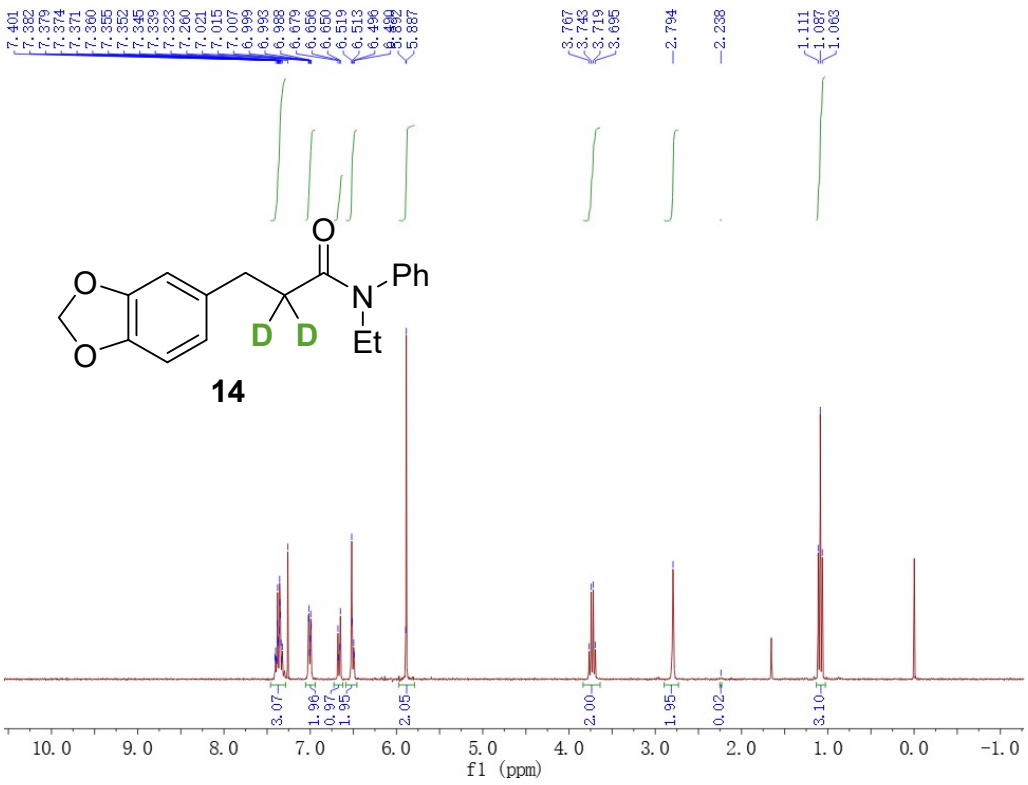


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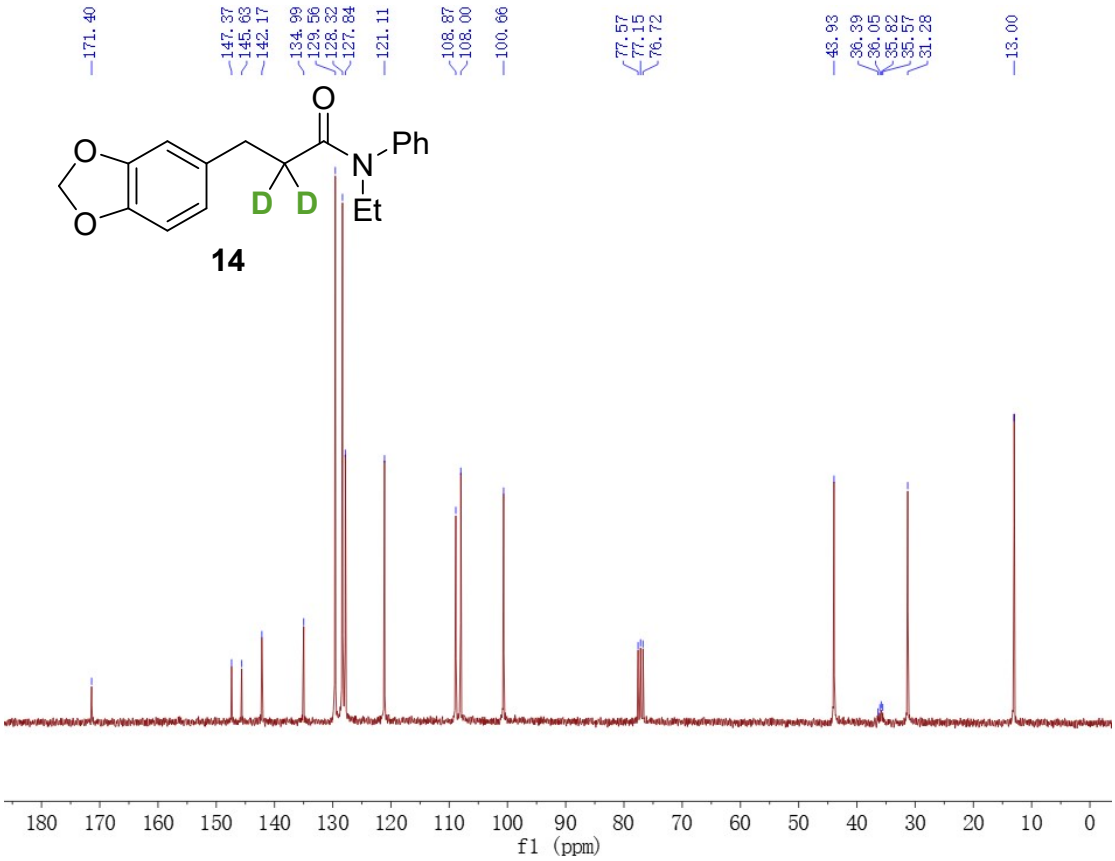


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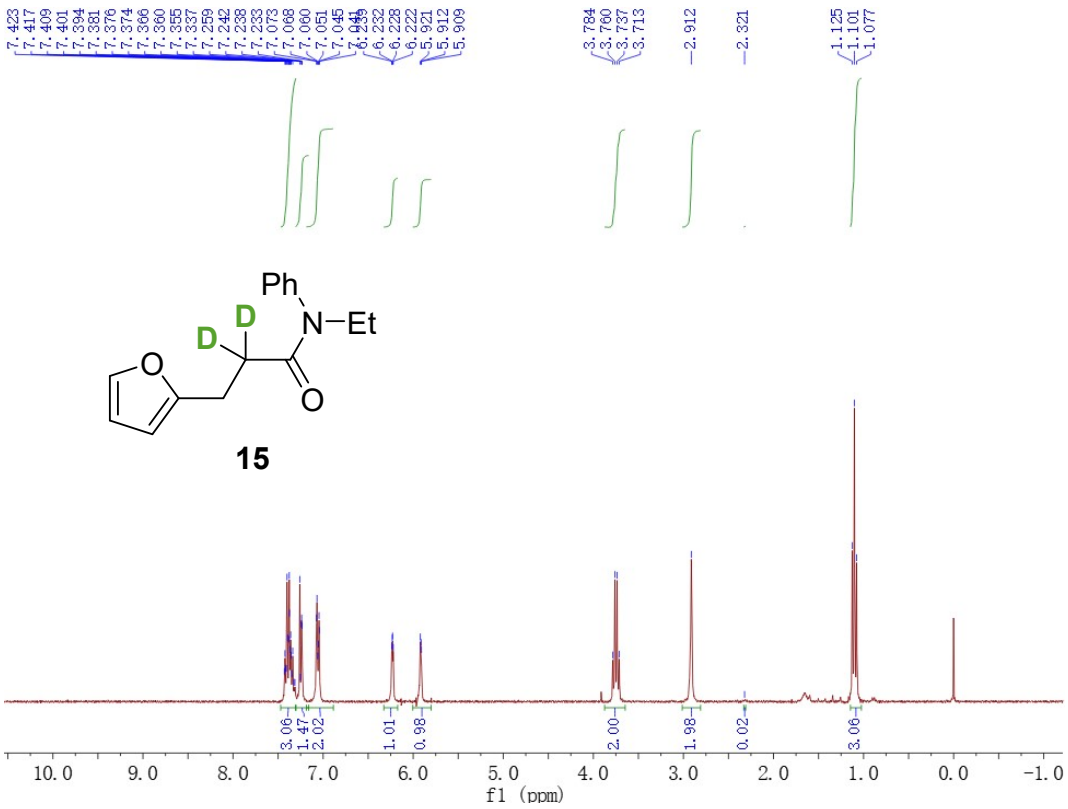


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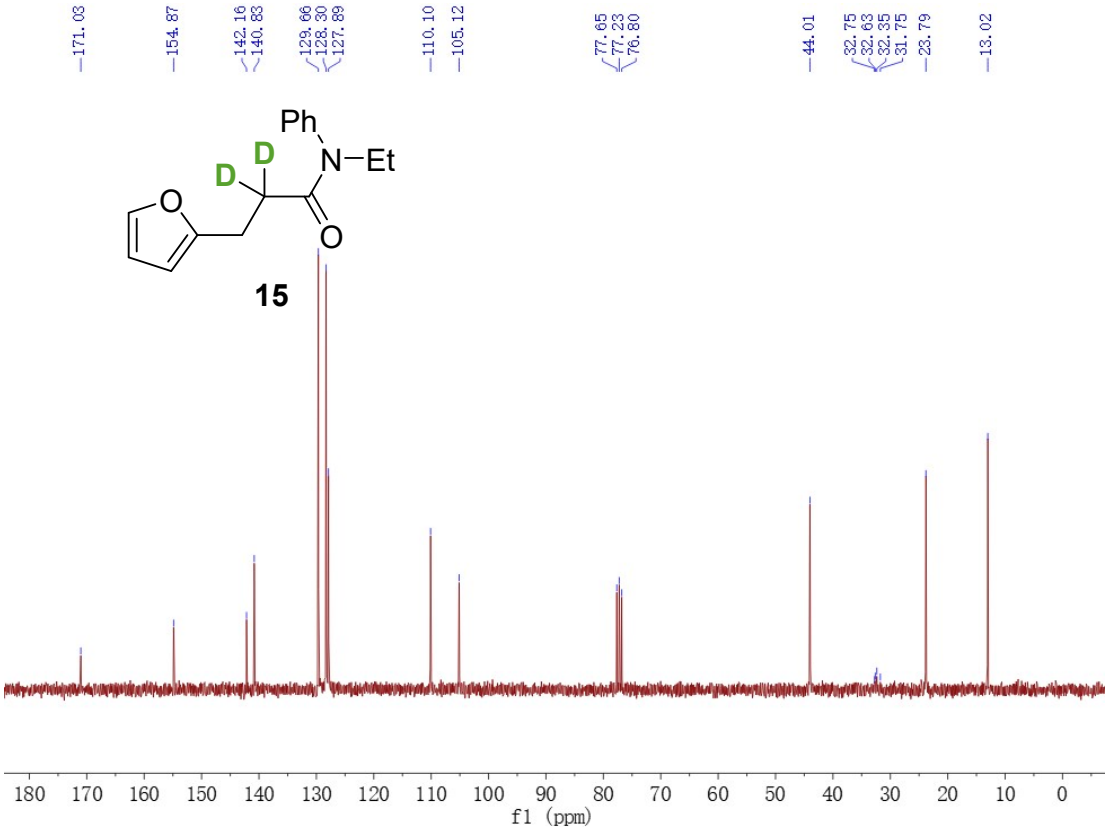


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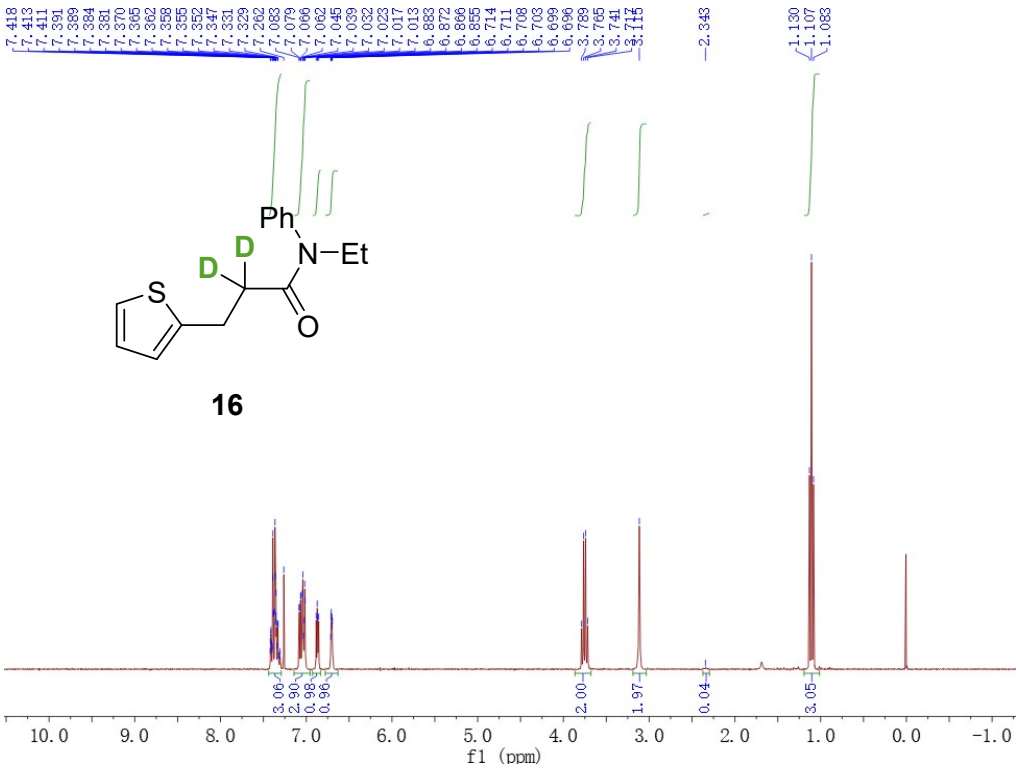


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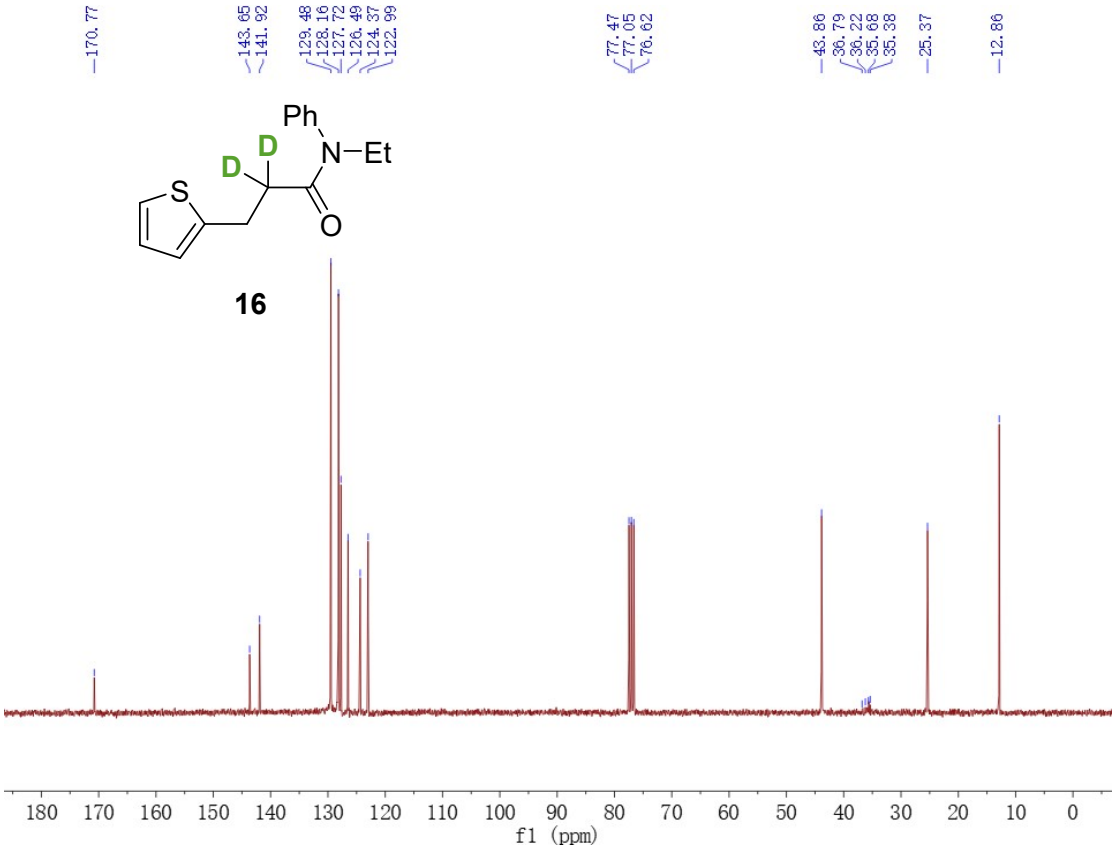


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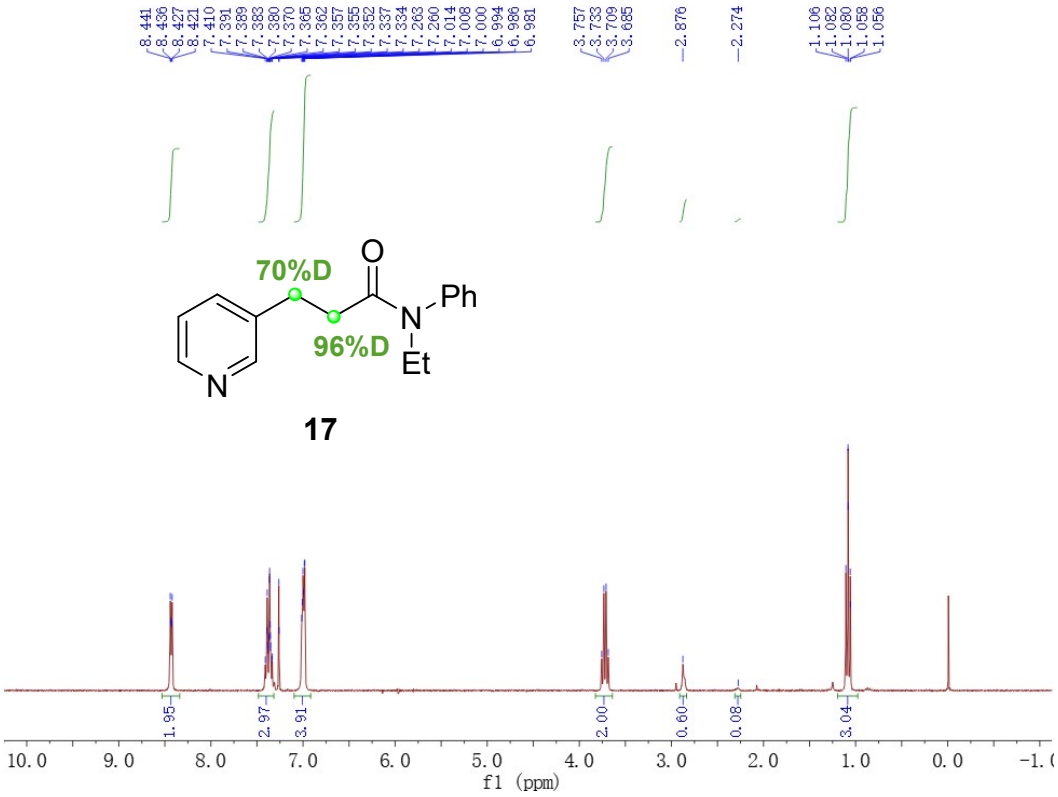


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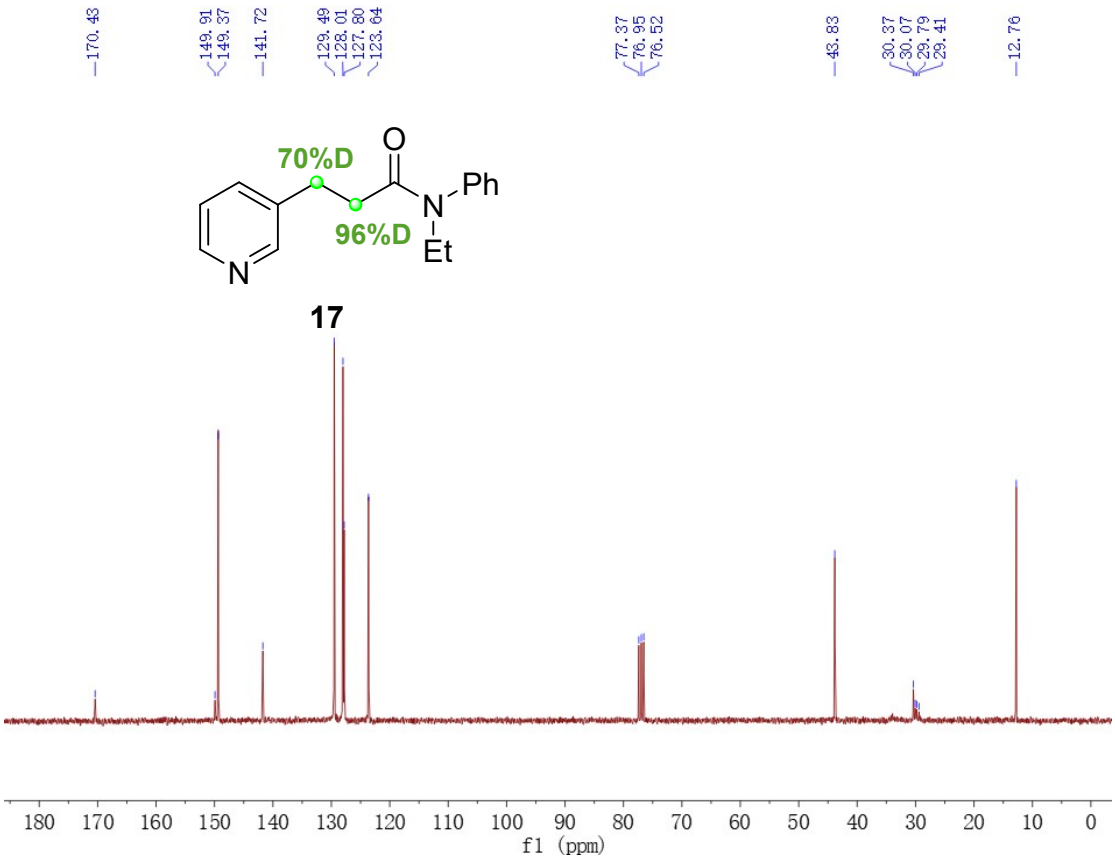


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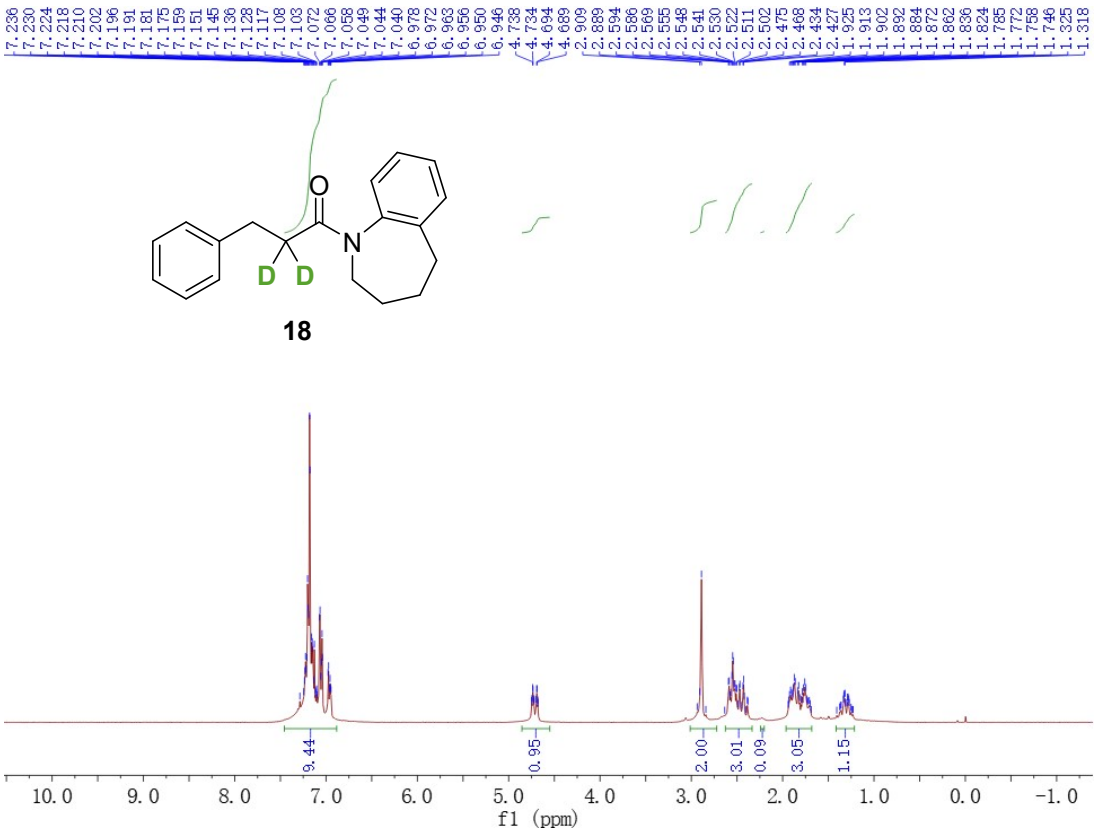


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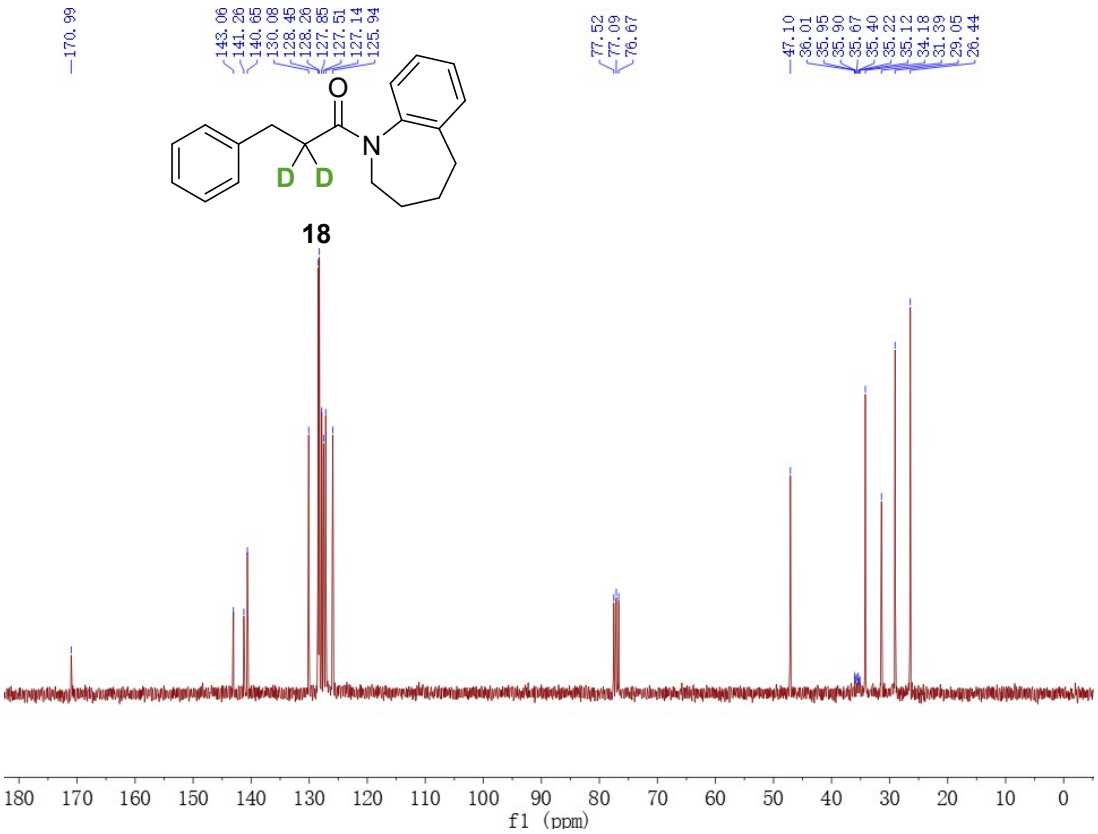


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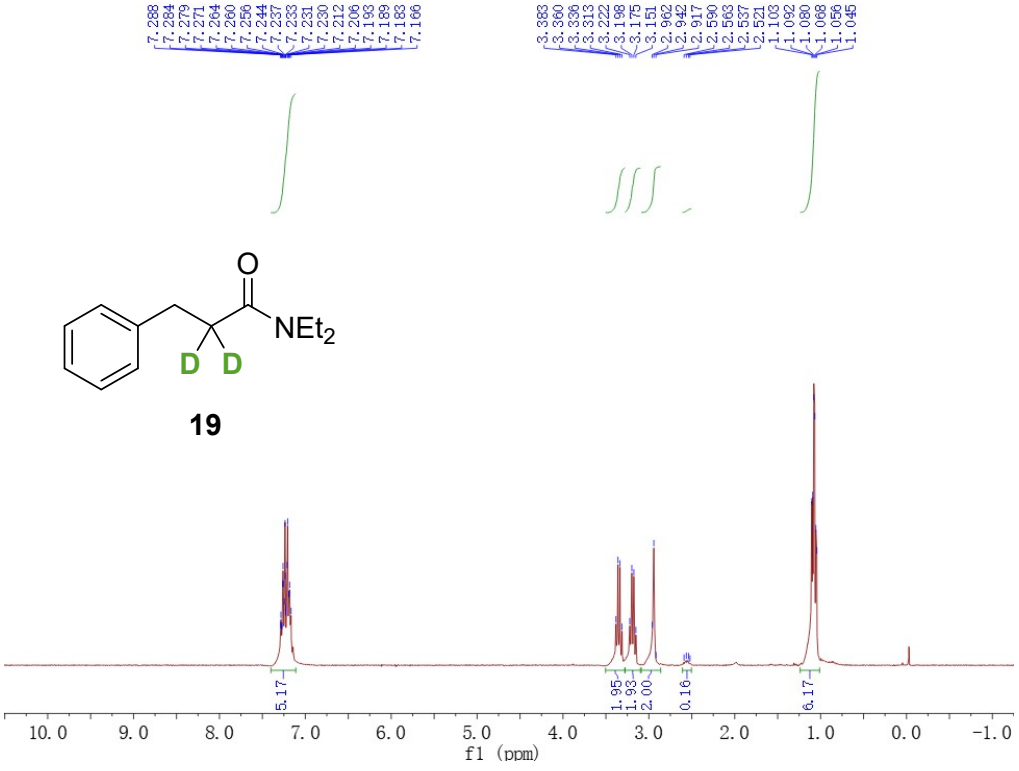


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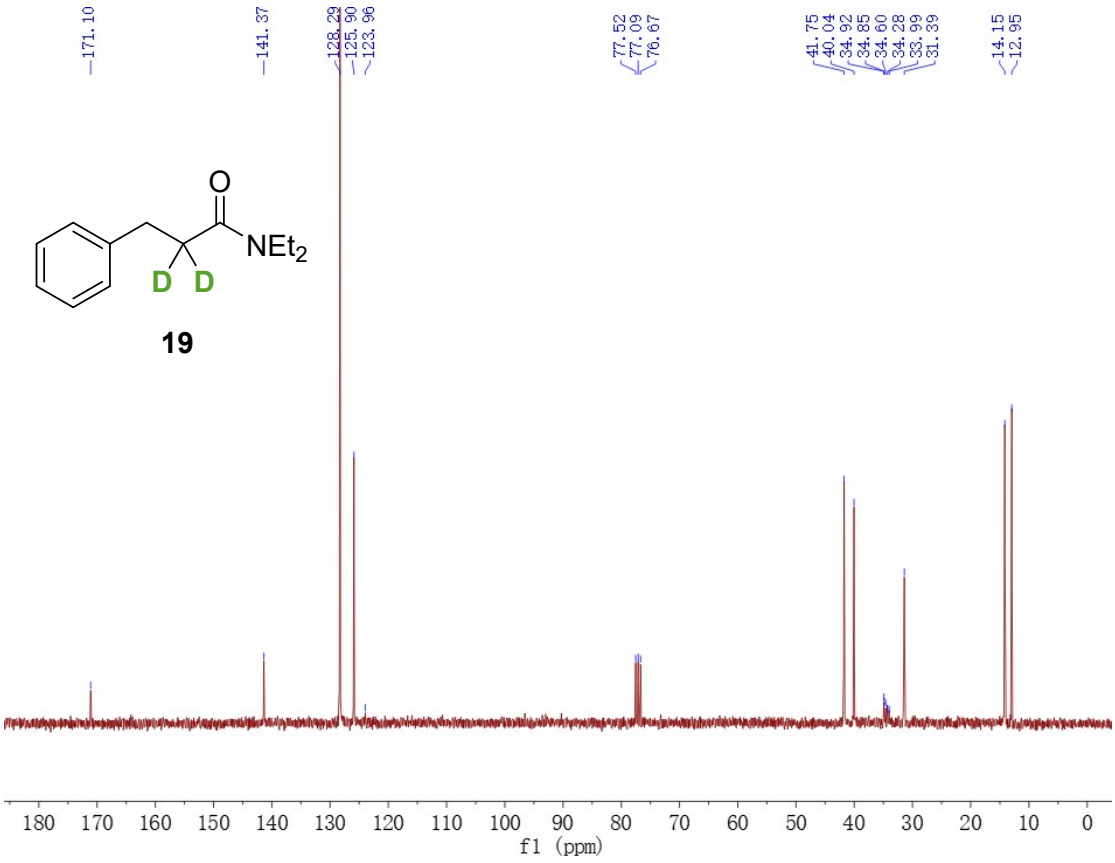


19

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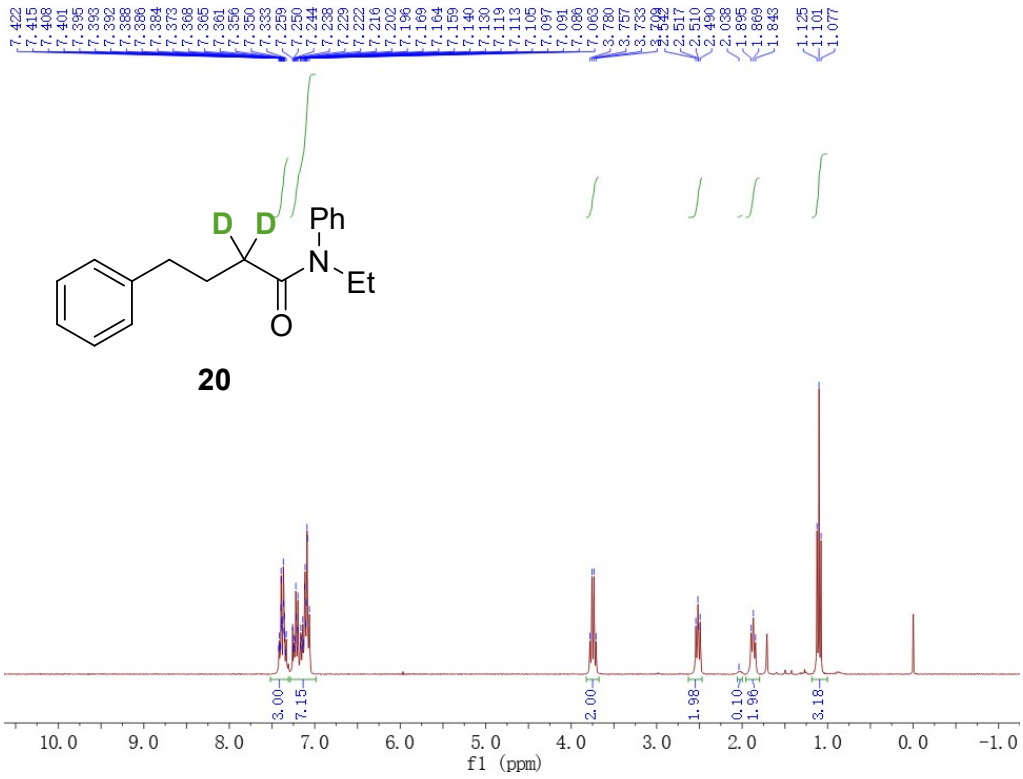


20

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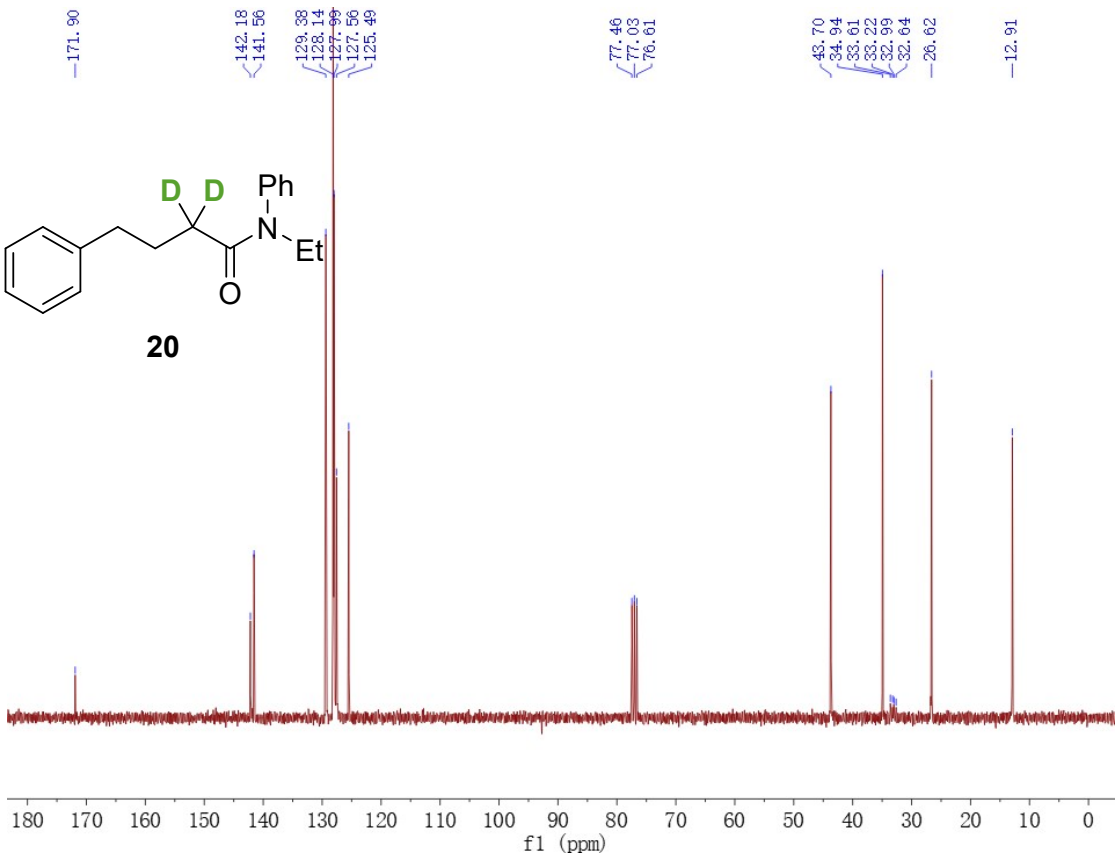


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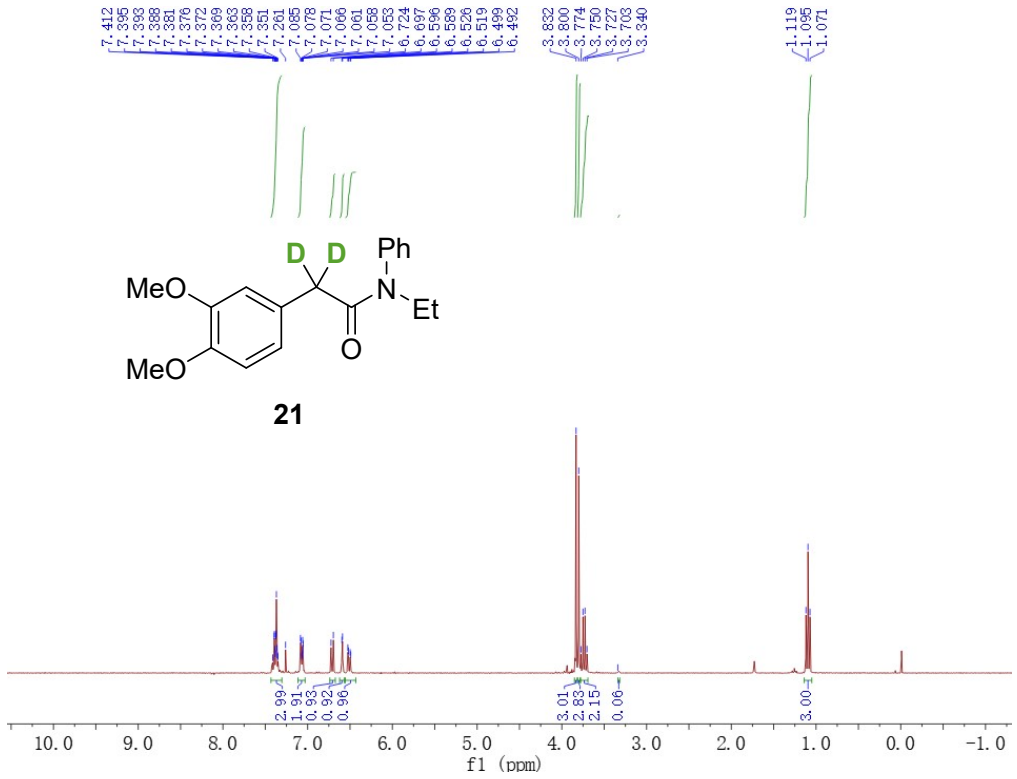


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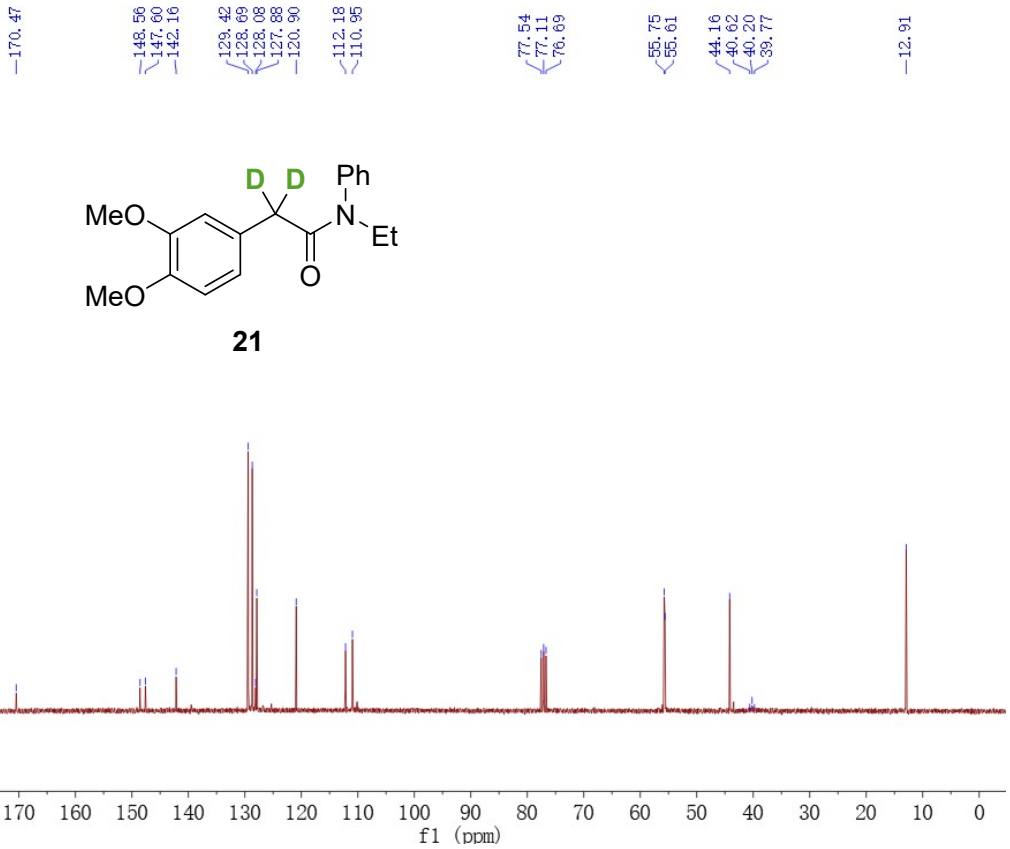
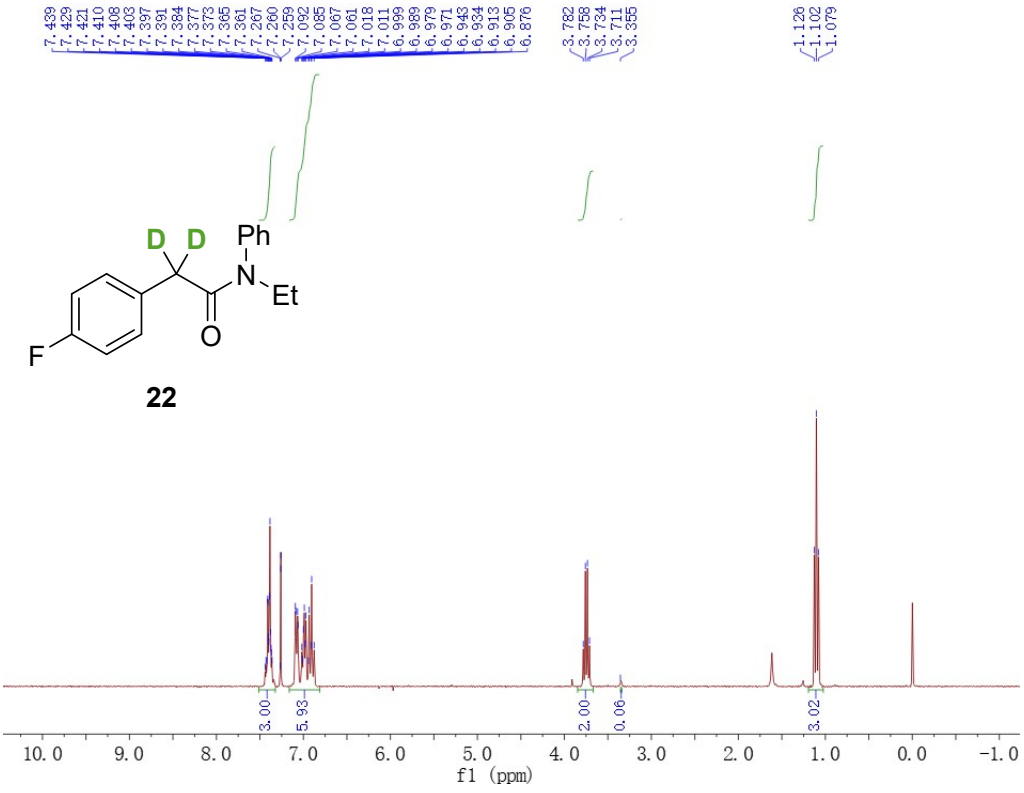


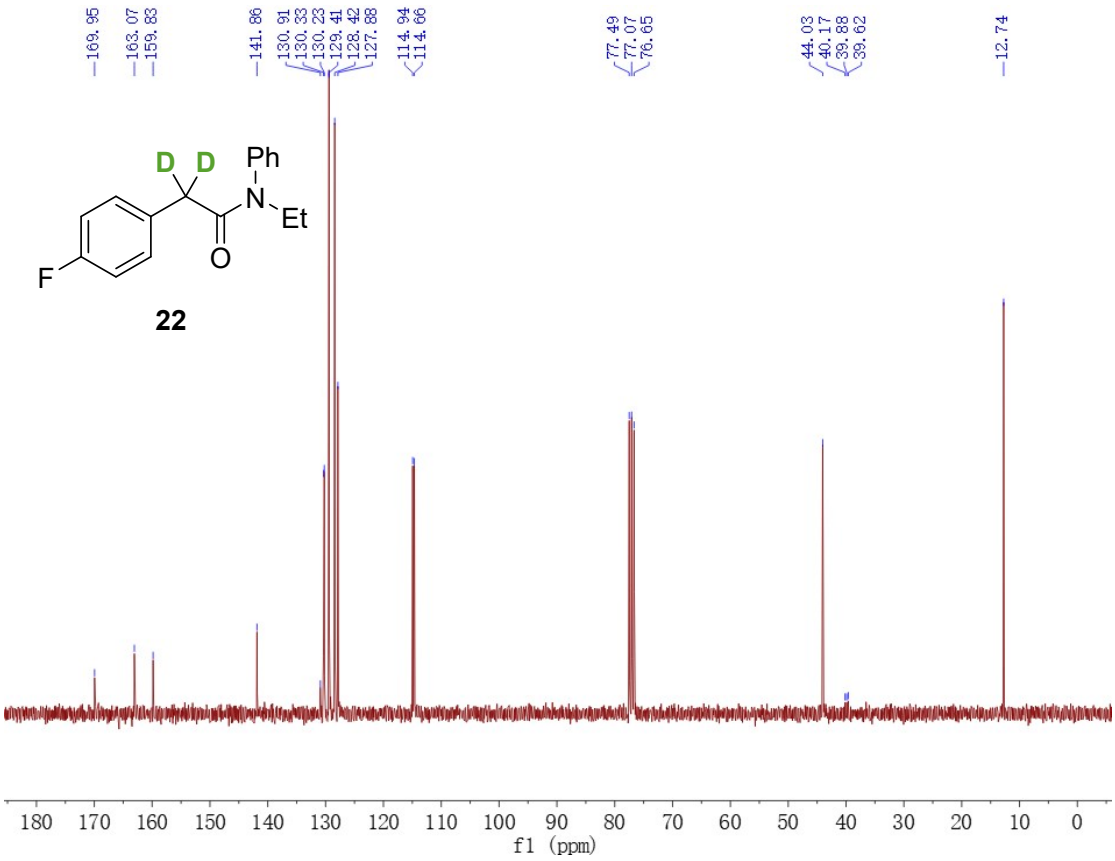

**21**

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

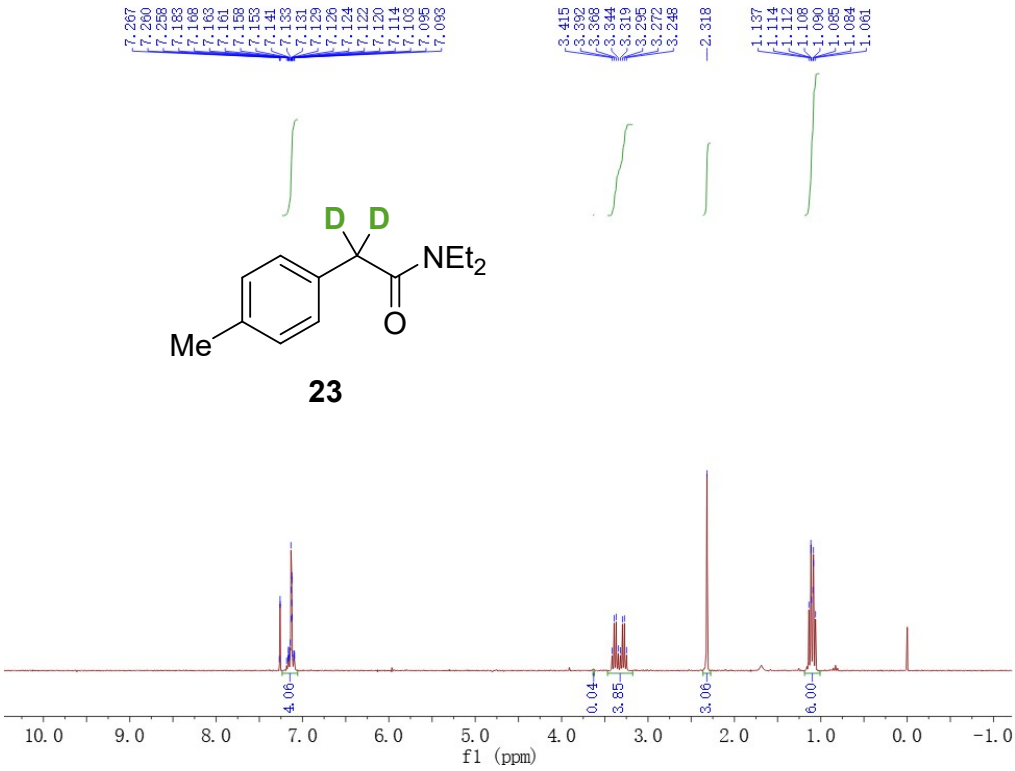



**22**

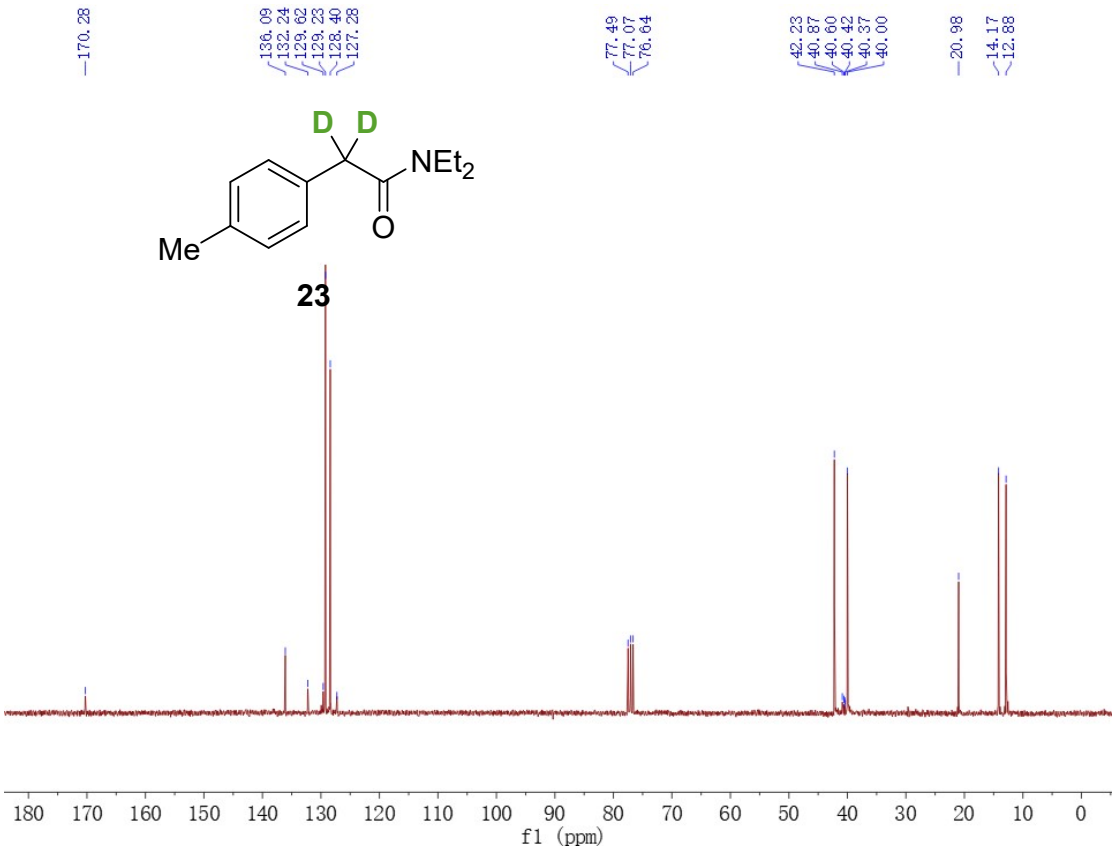
**$^{13}$C NMR (75 MHz, $CDCl_3$):**



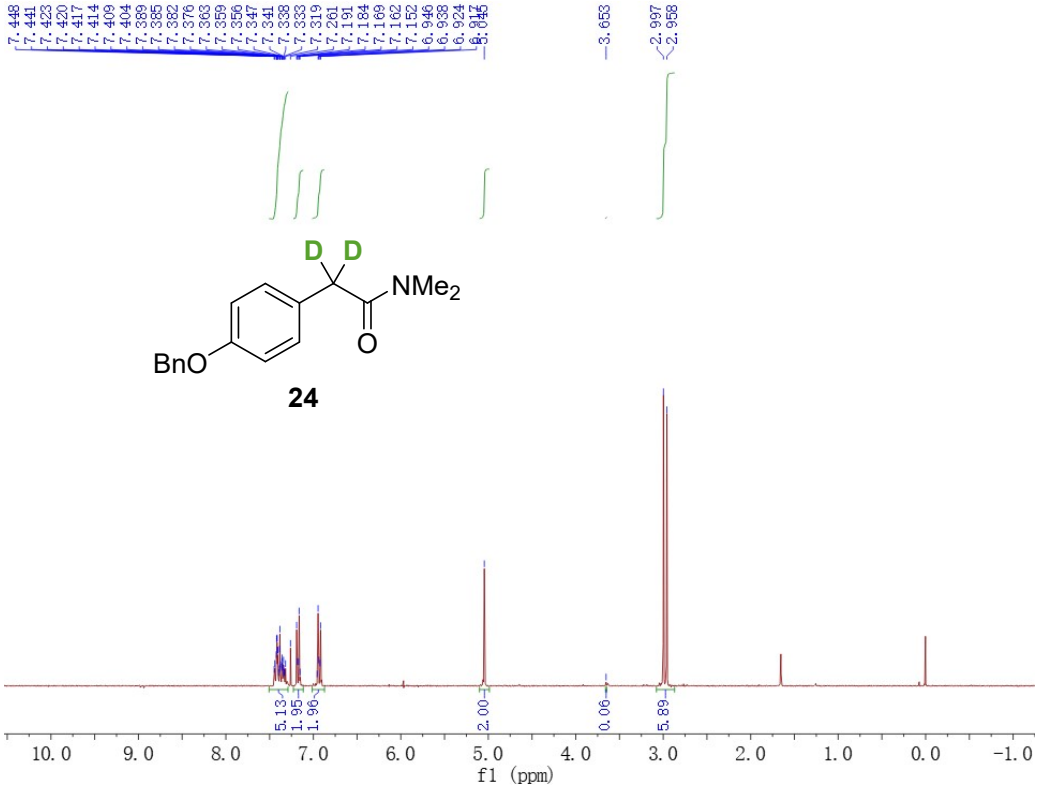

**$^{1}$H NMR (300 MHz, $CDCl_3$):**



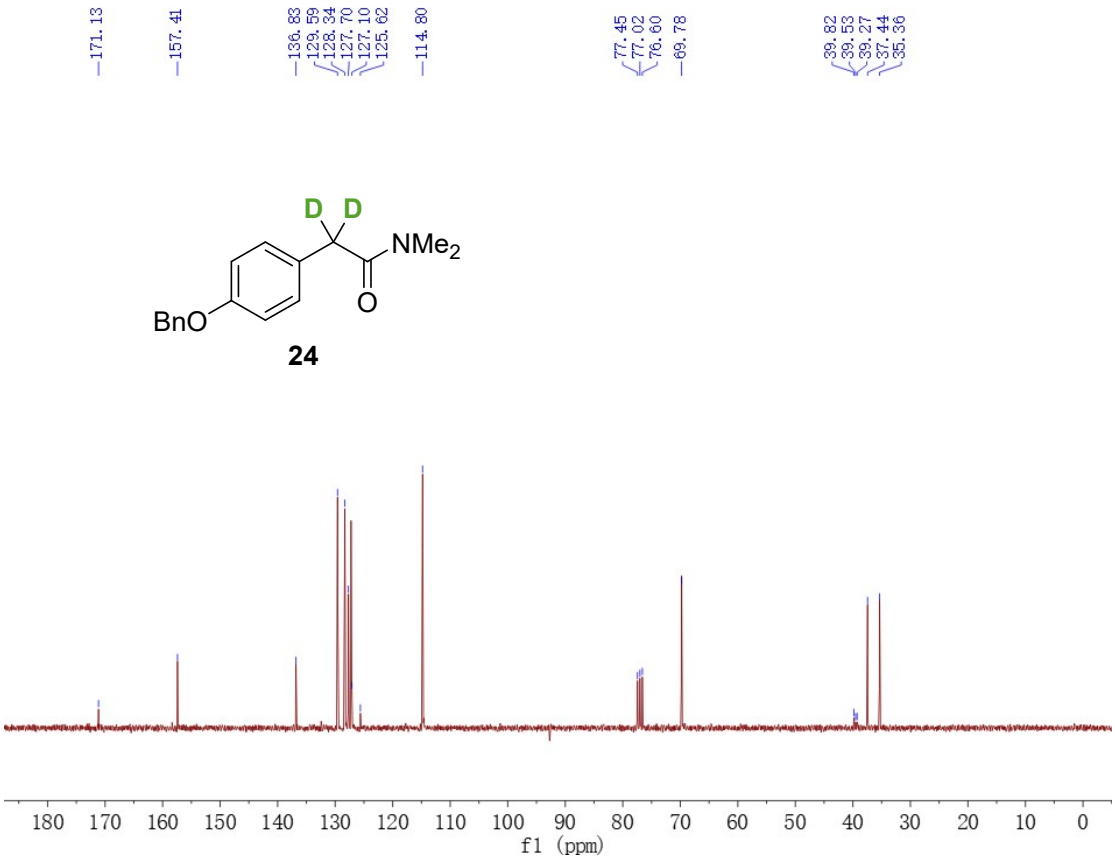

**$^{13}$C NMR (75 MHz, $CDCl_3$):**



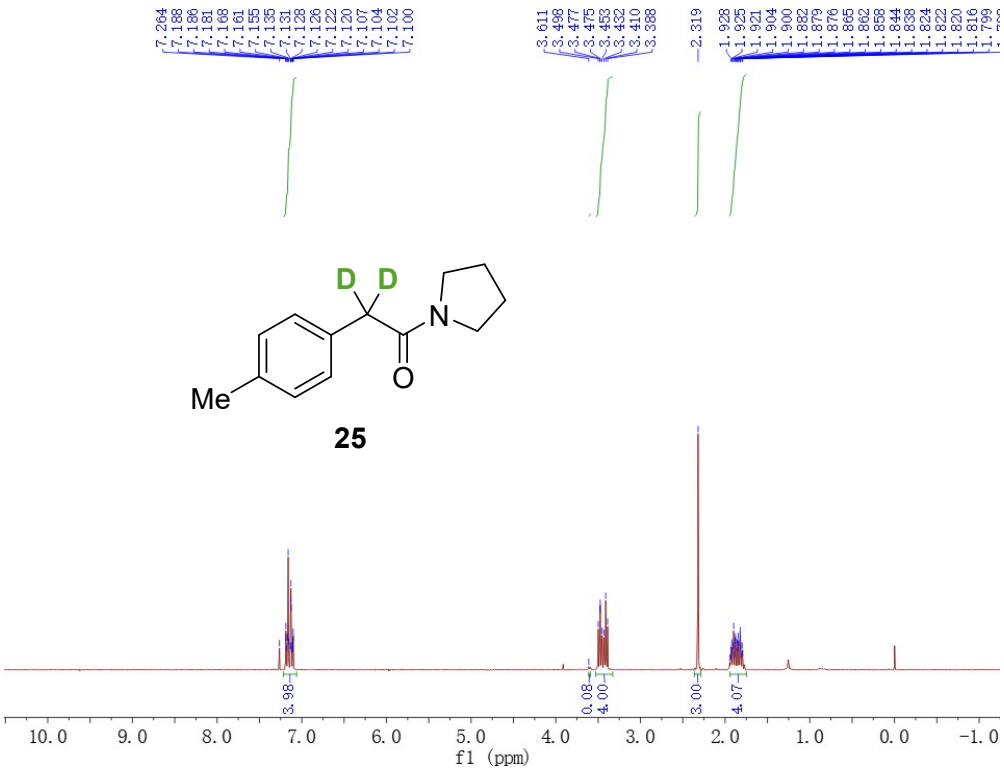

**$^{1}$H NMR (300 MHz, $CDCl_3$):**



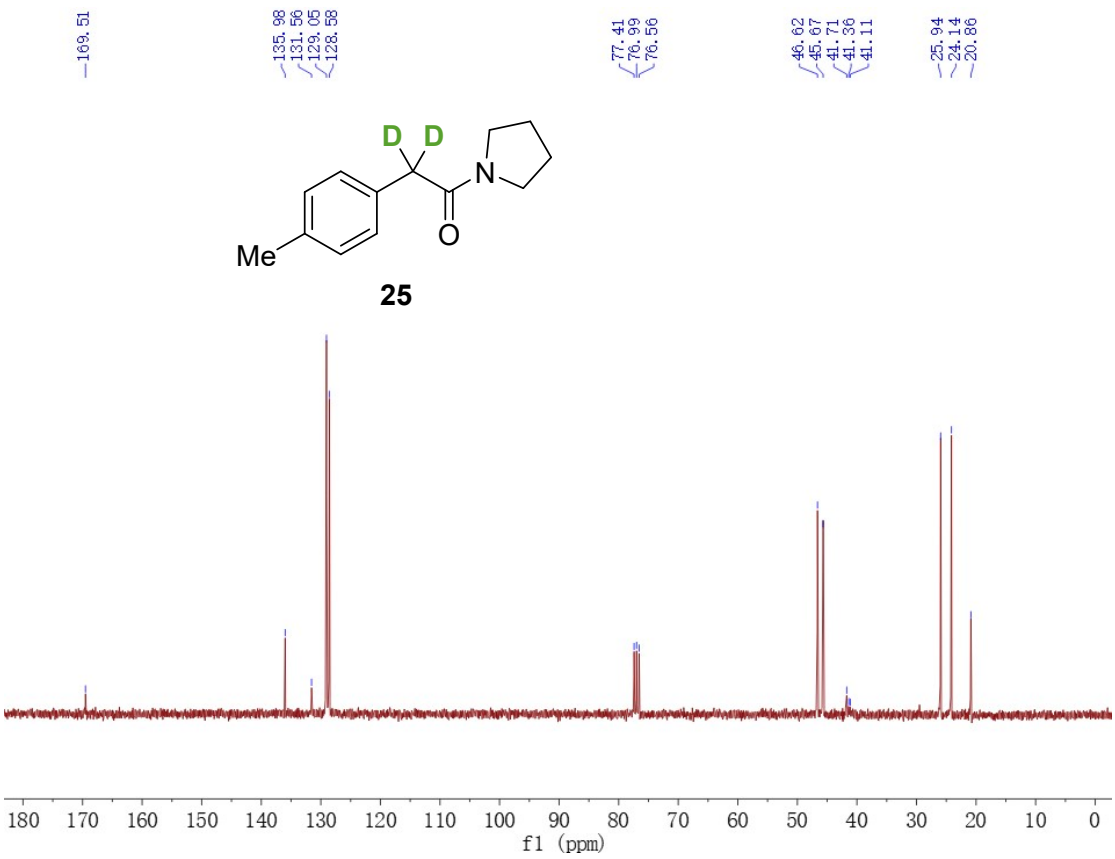

**$^{13}$C NMR (75 MHz, $CDCl_3$):**




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

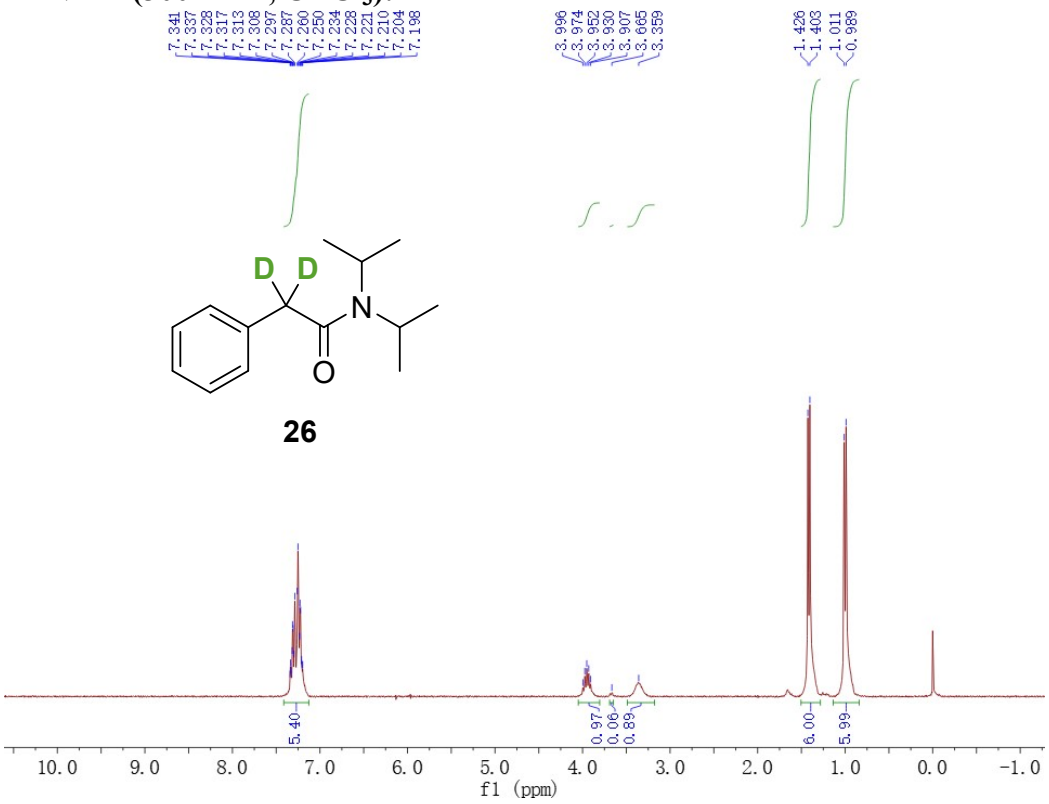



**$^{13}$C NMR (75 MHz, $CDCl_3$):**



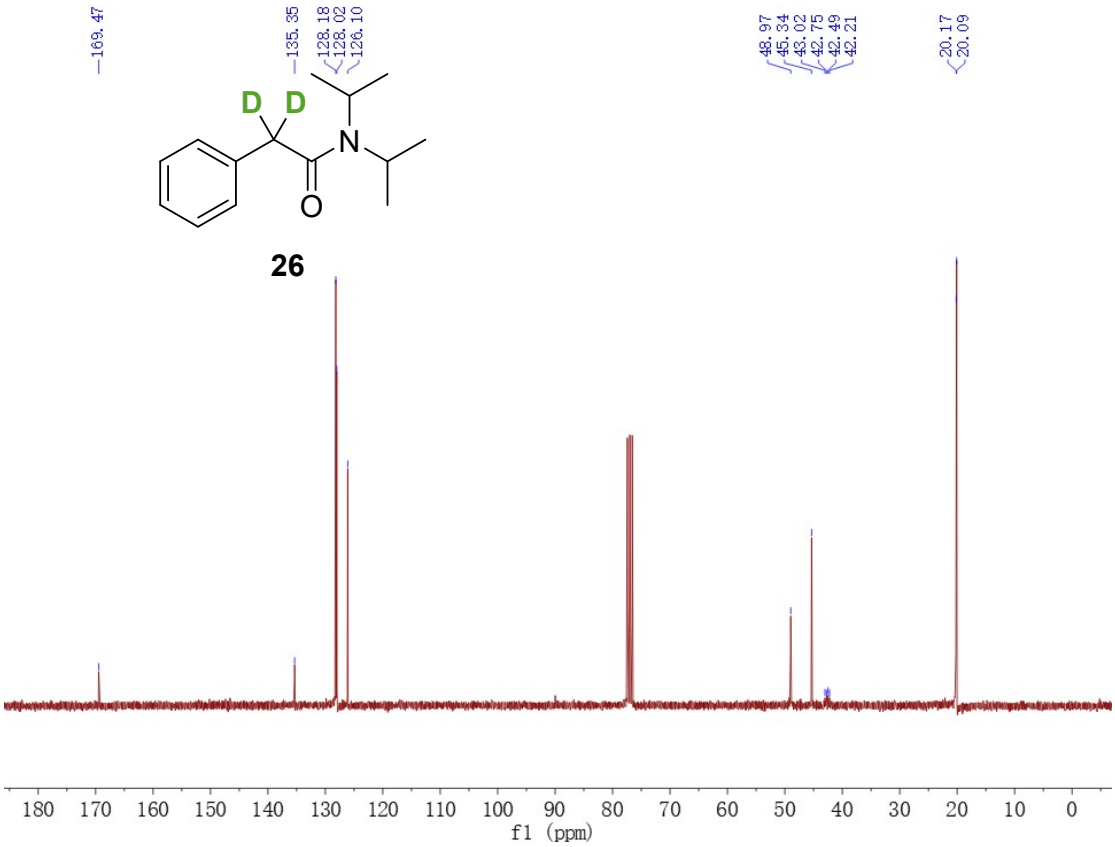

**25**

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



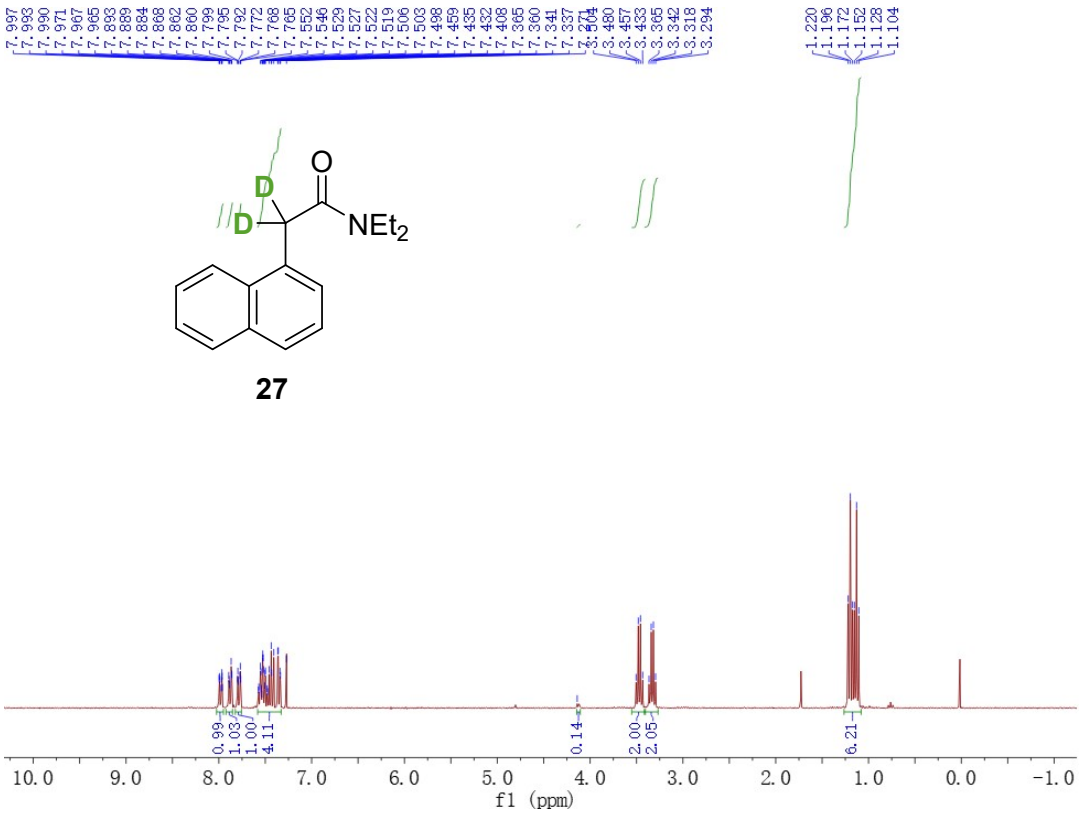

**26**

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



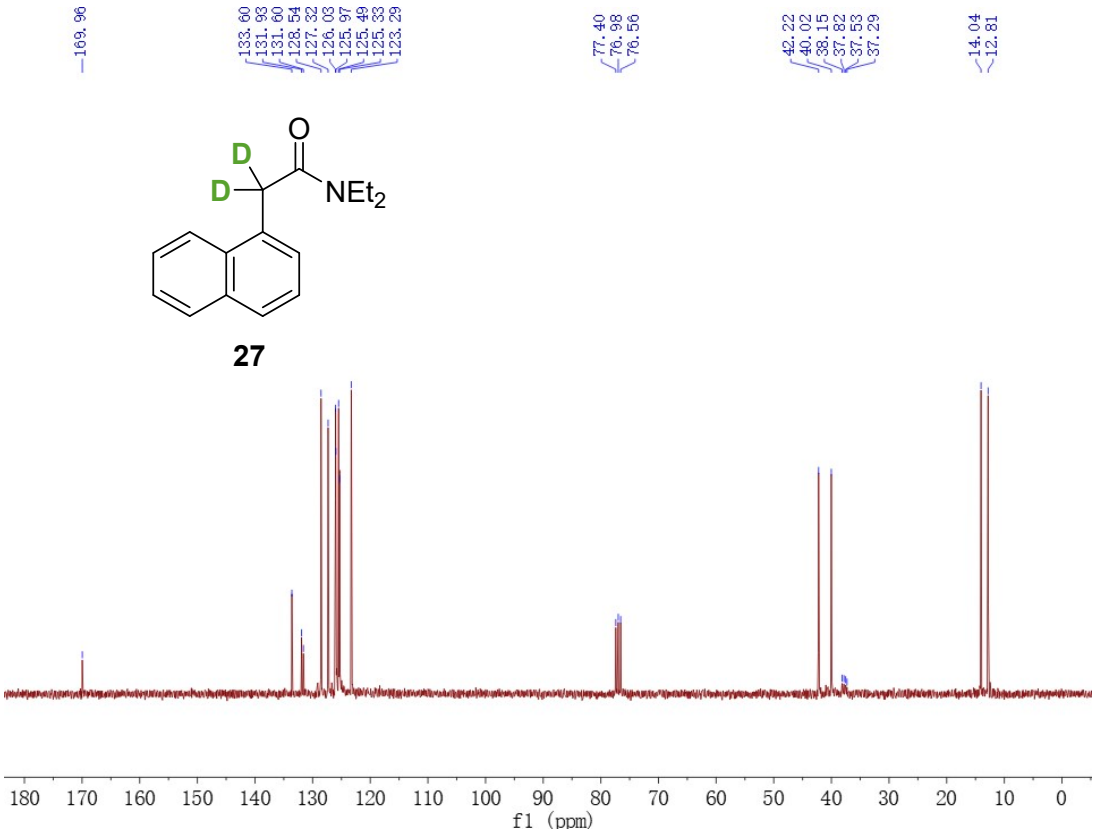

**26**

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



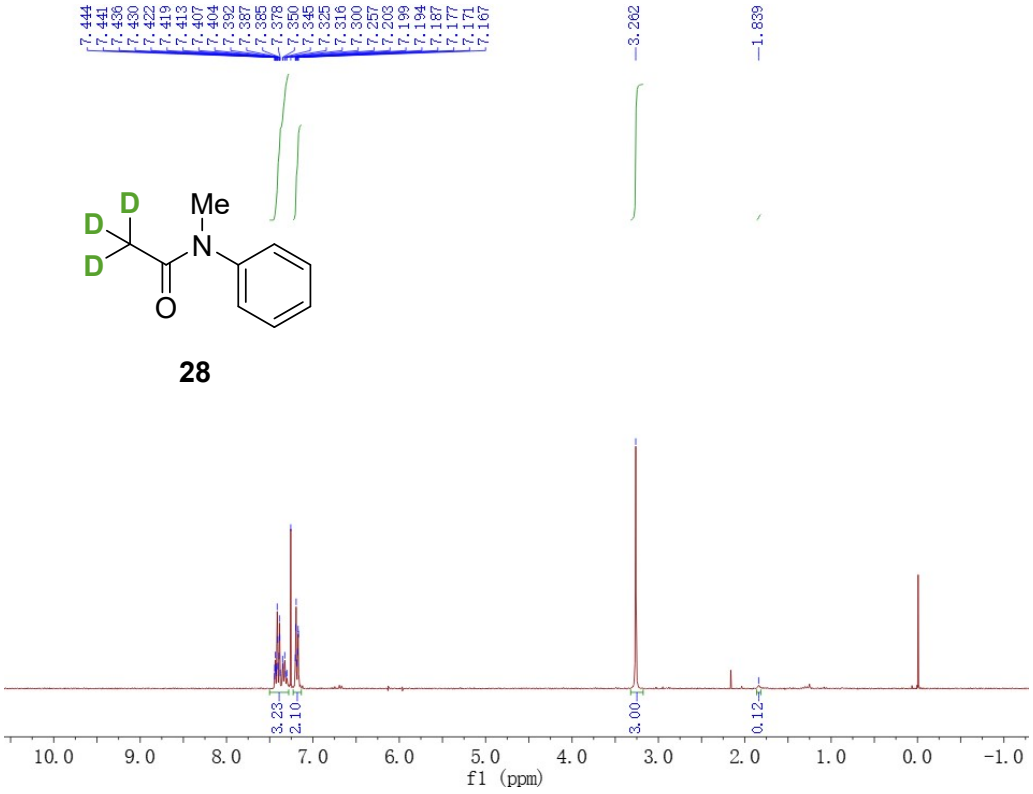

**27**

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



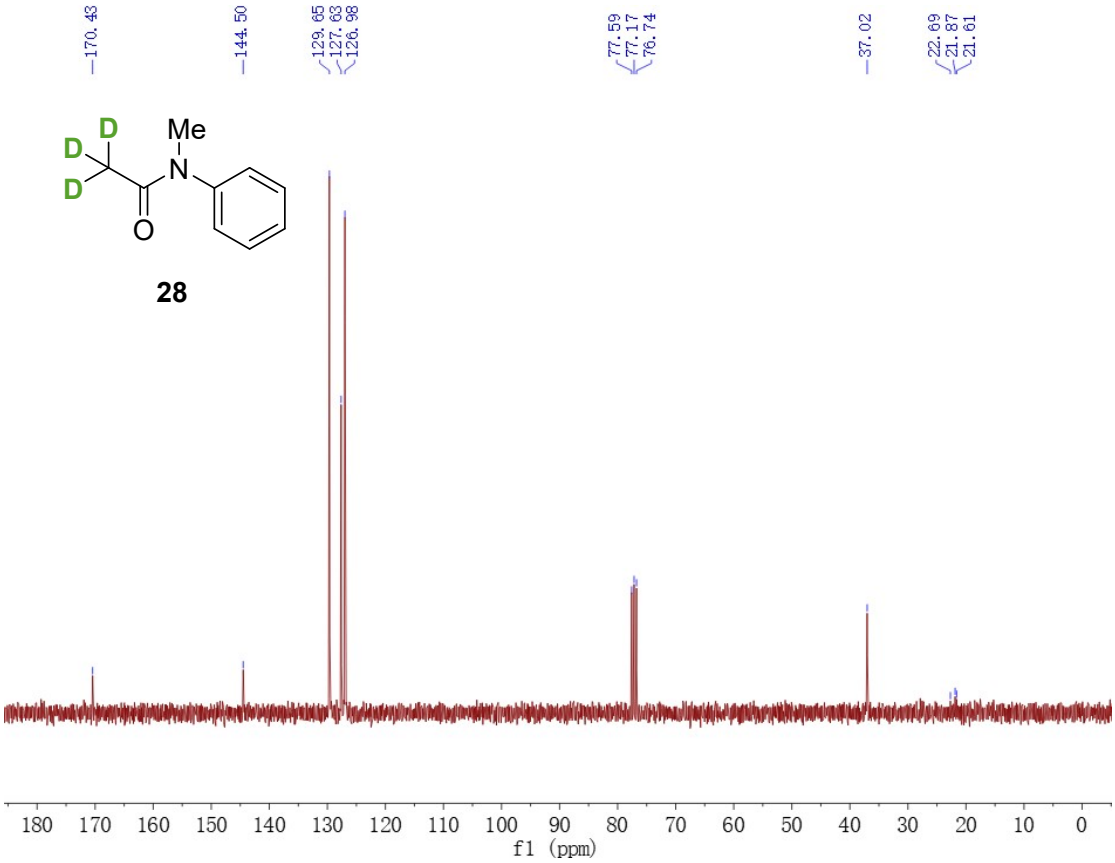

**27**

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



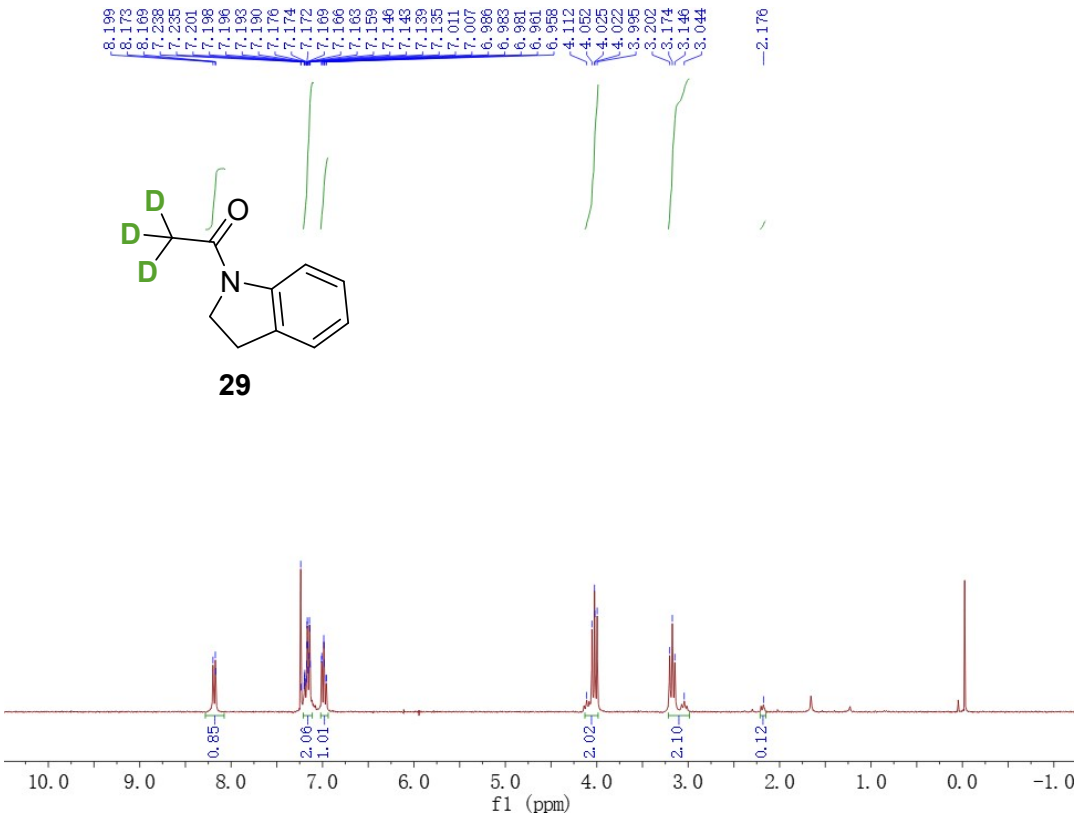

**28**

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



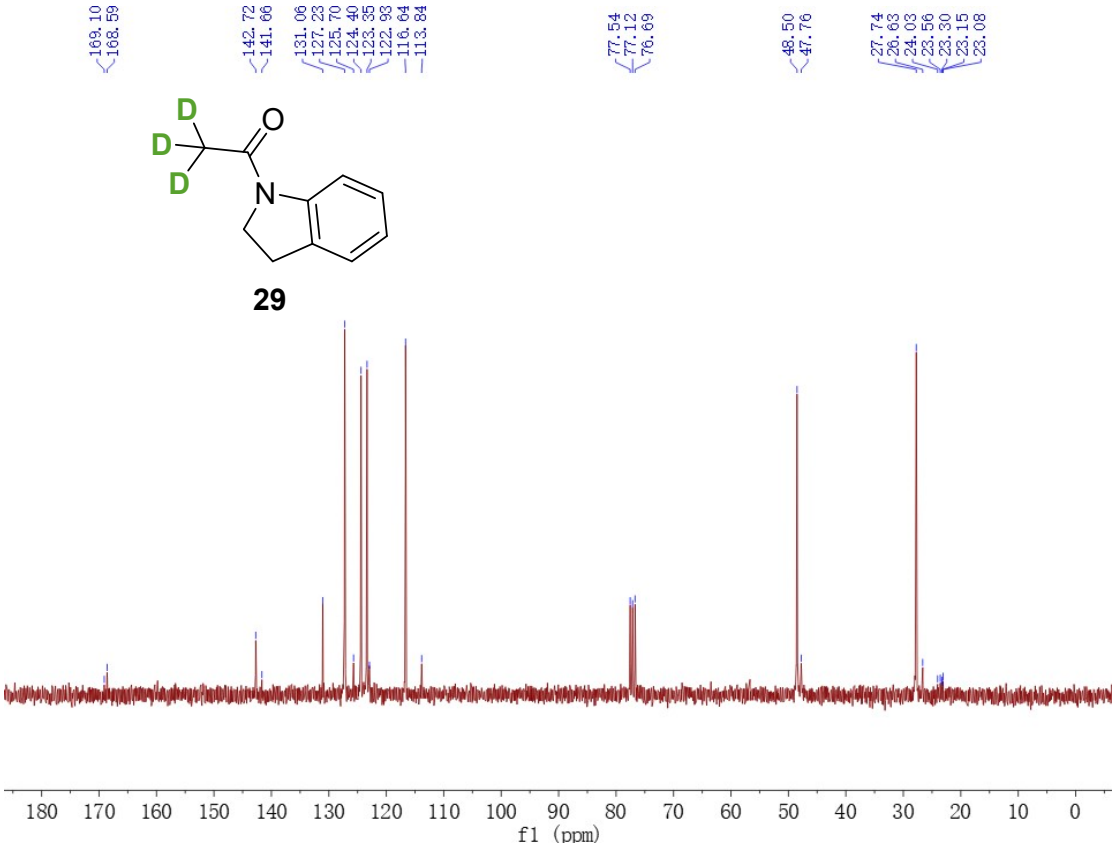

**28**

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



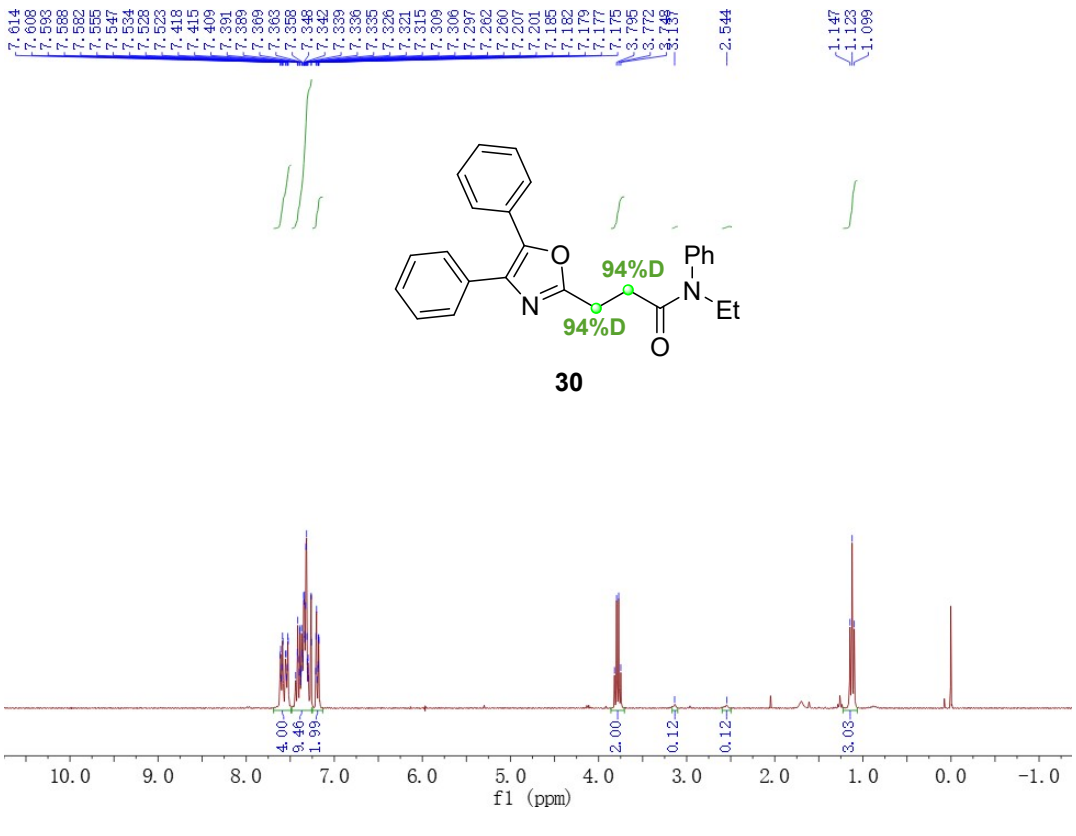

**29**

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



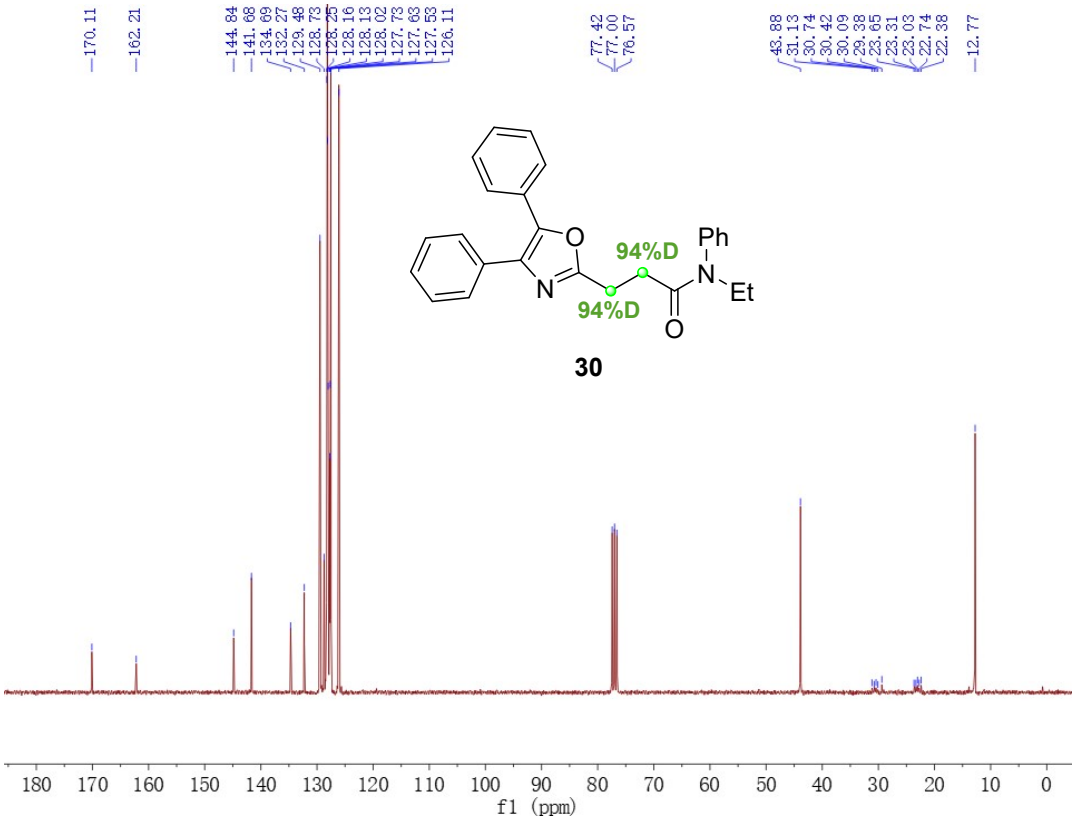

**29**

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



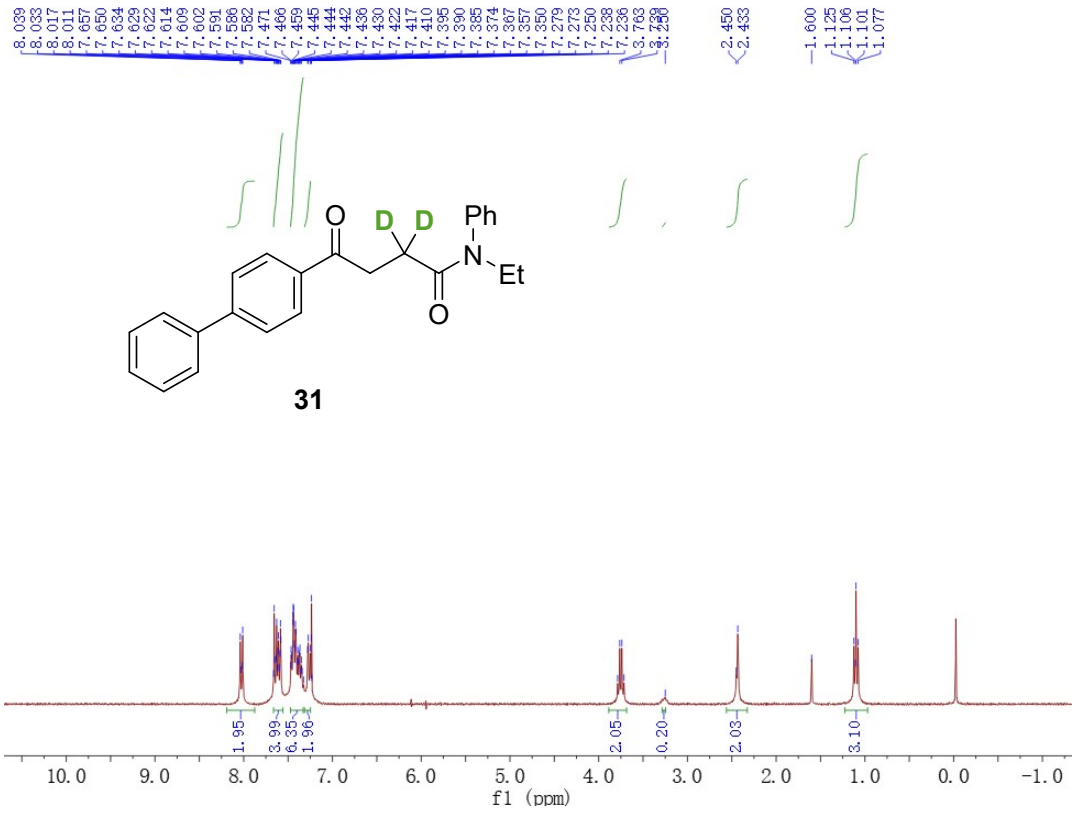

**30**

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



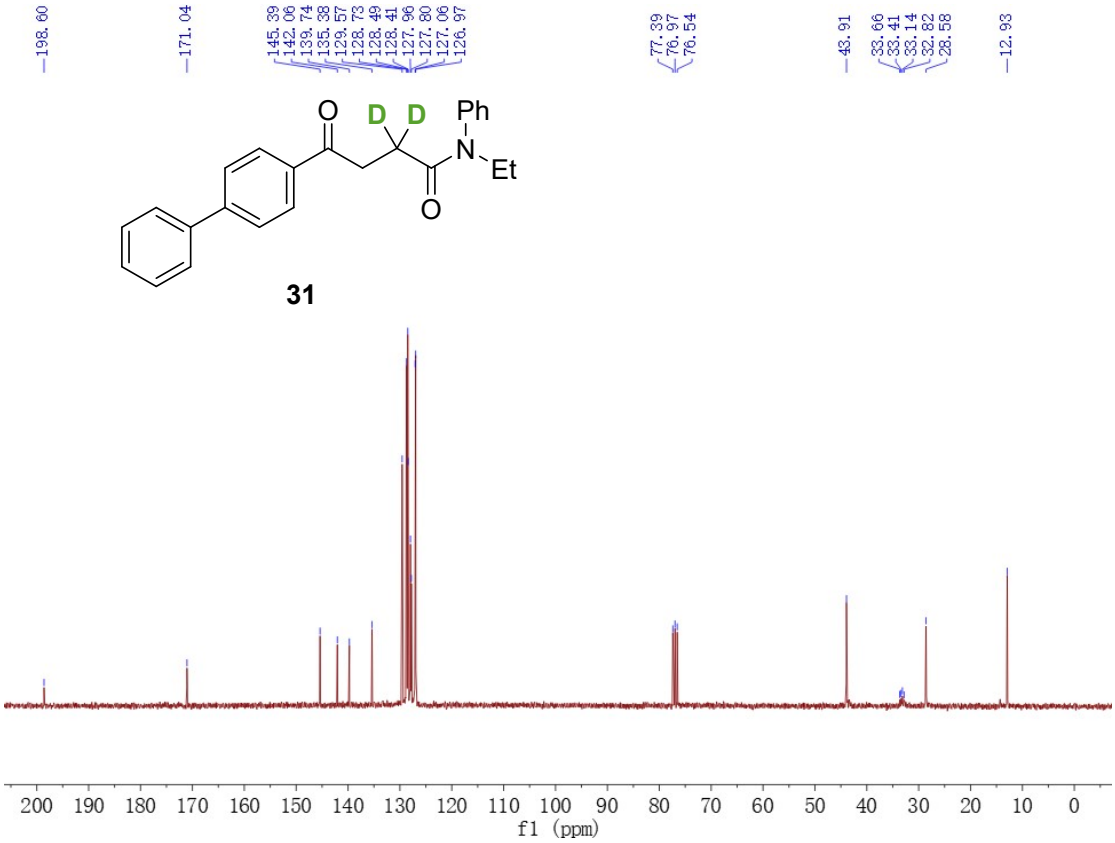

30

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



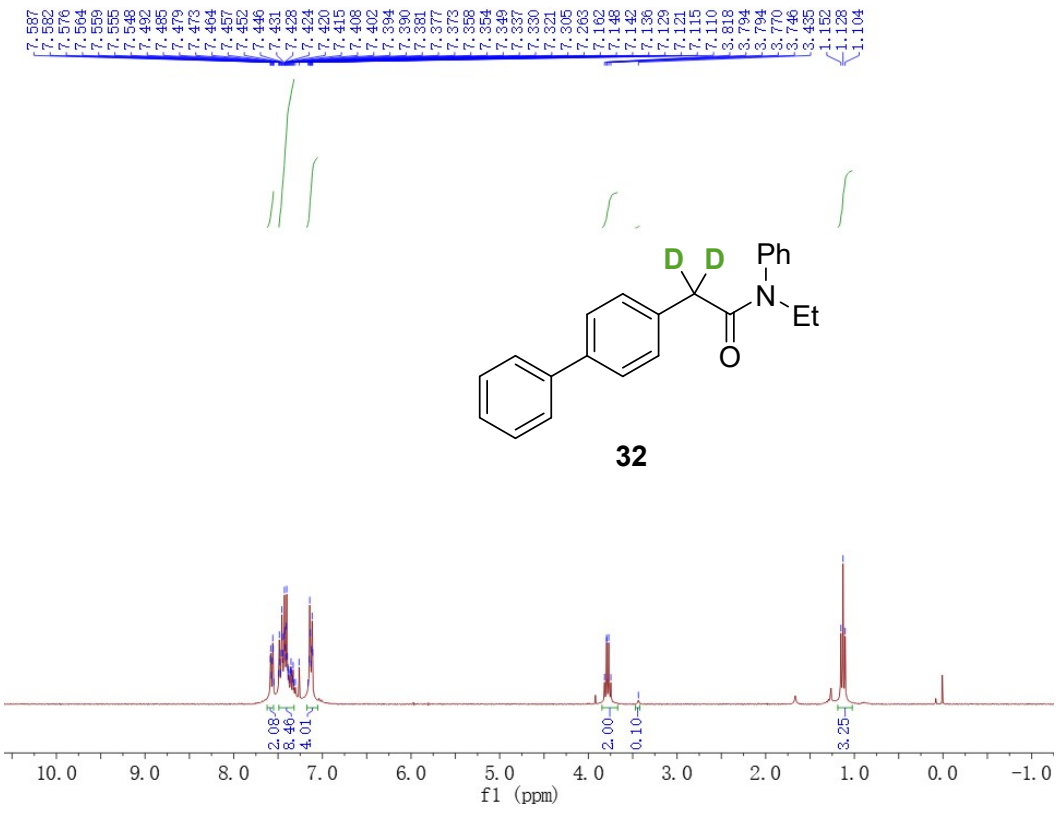

31

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



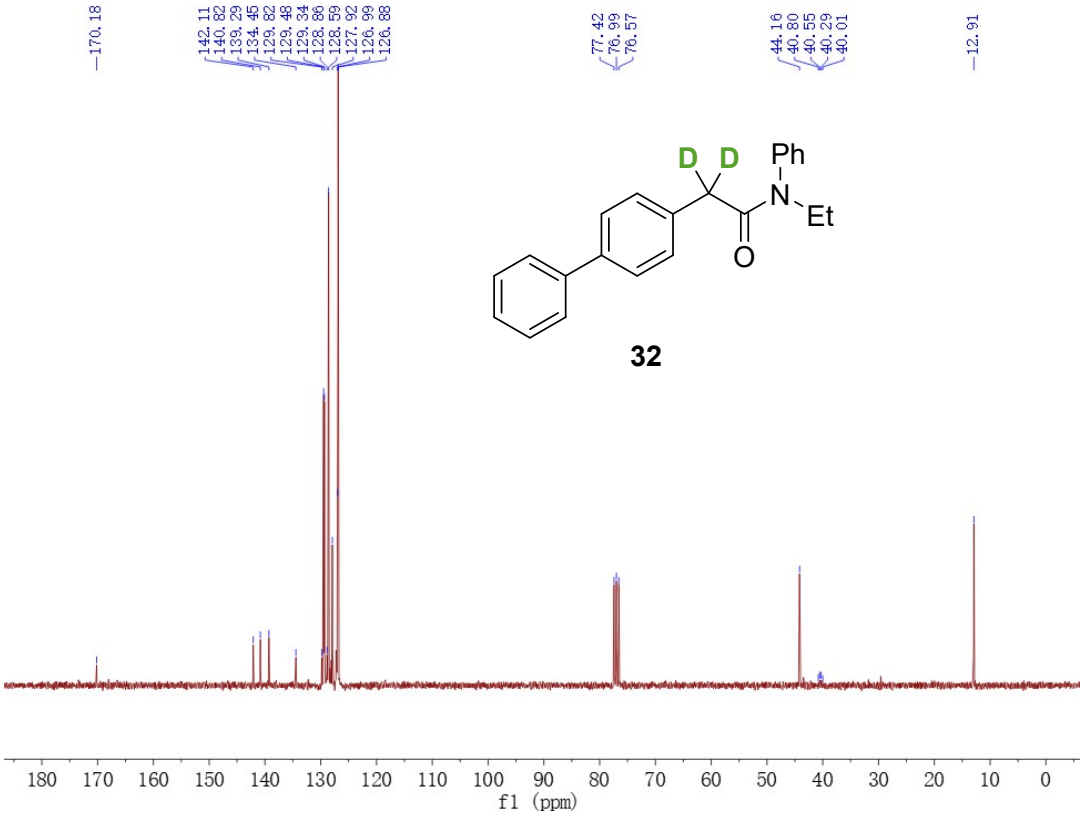

31

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



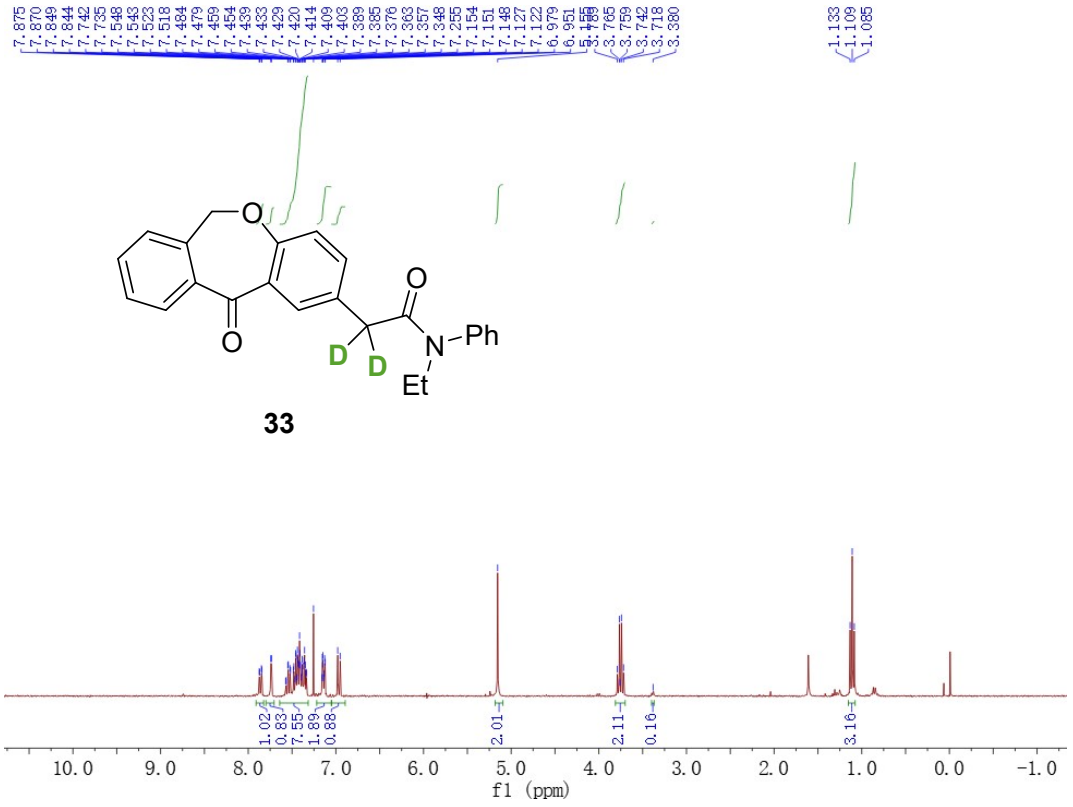

32

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



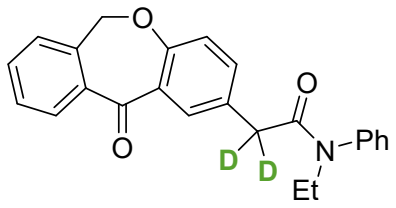

**32**

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

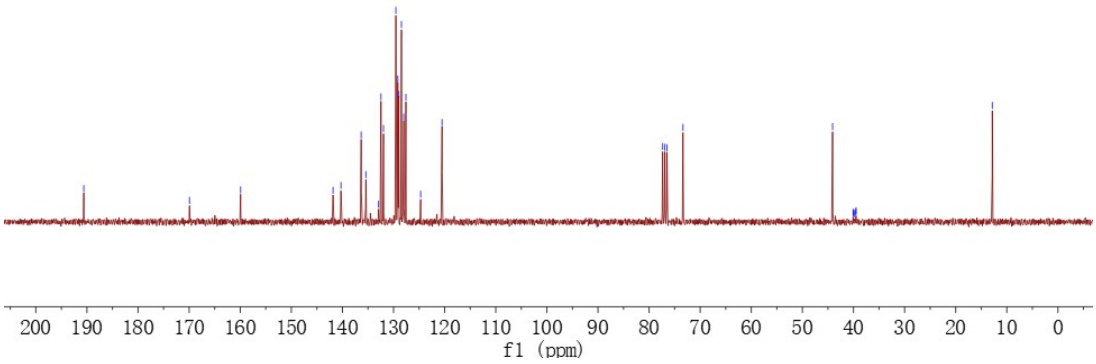



**33**

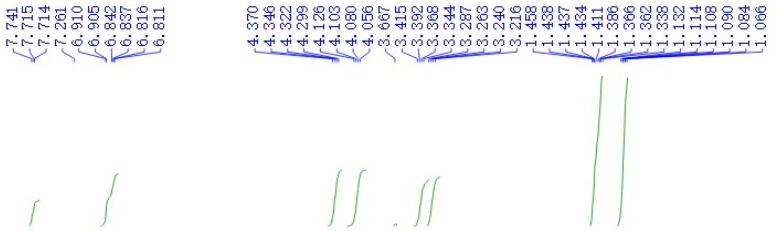
**$^{13}$C NMR (75 MHz, $CDCl_3$):**

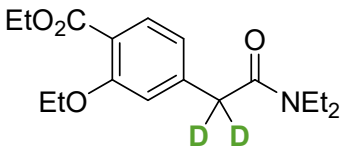




**33**

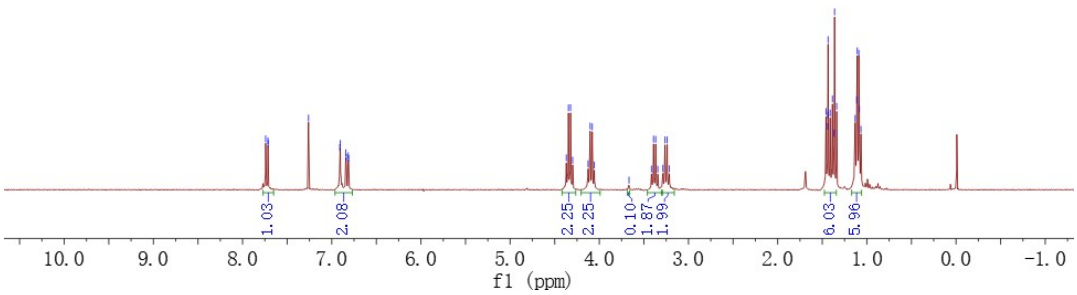



**$^{1}$H NMR (300 MHz, $CDCl_3$):**

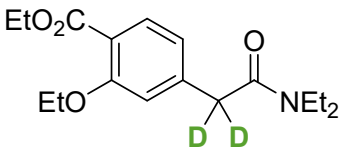


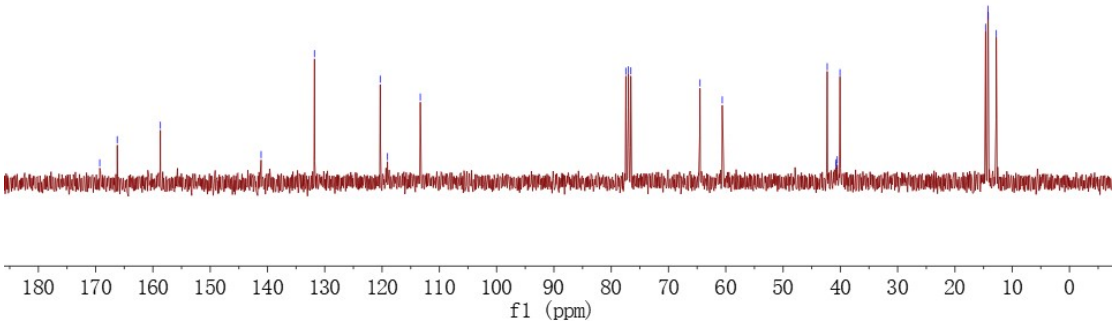

**34**



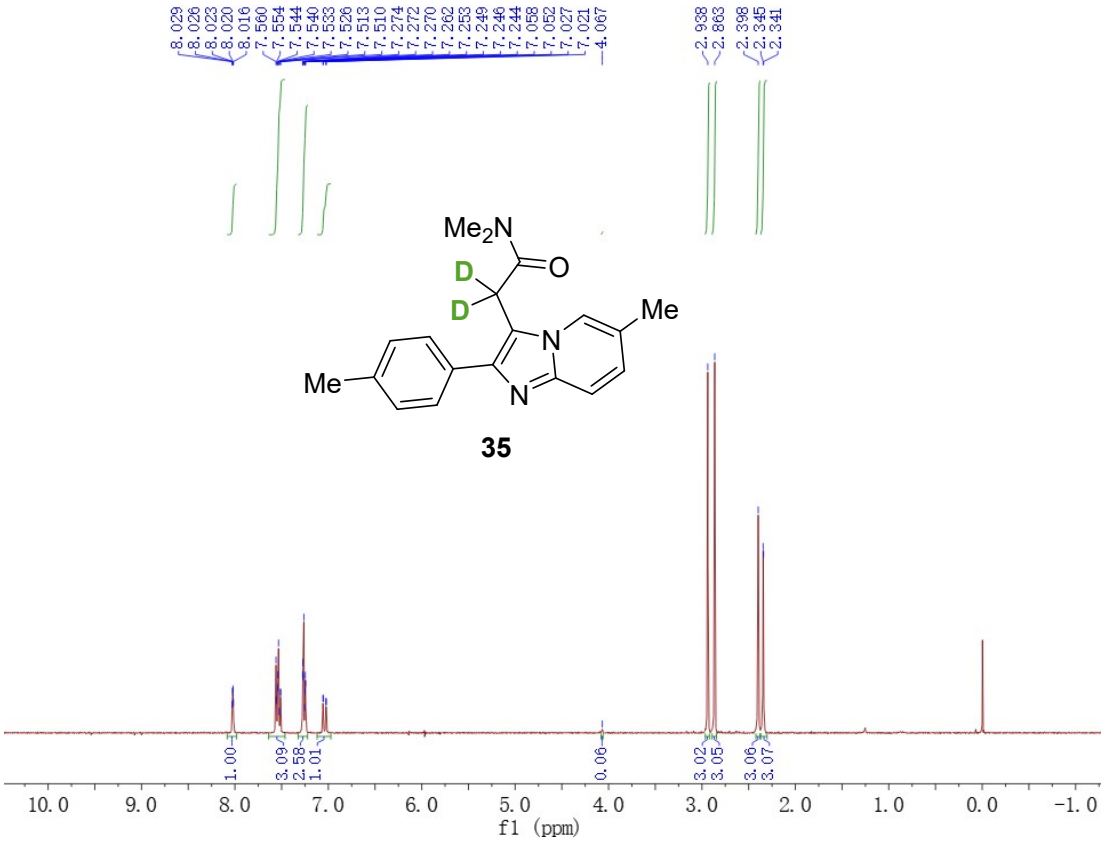

**$^{13}$C NMR (75 MHz, $CDCl_3$):**




**34**

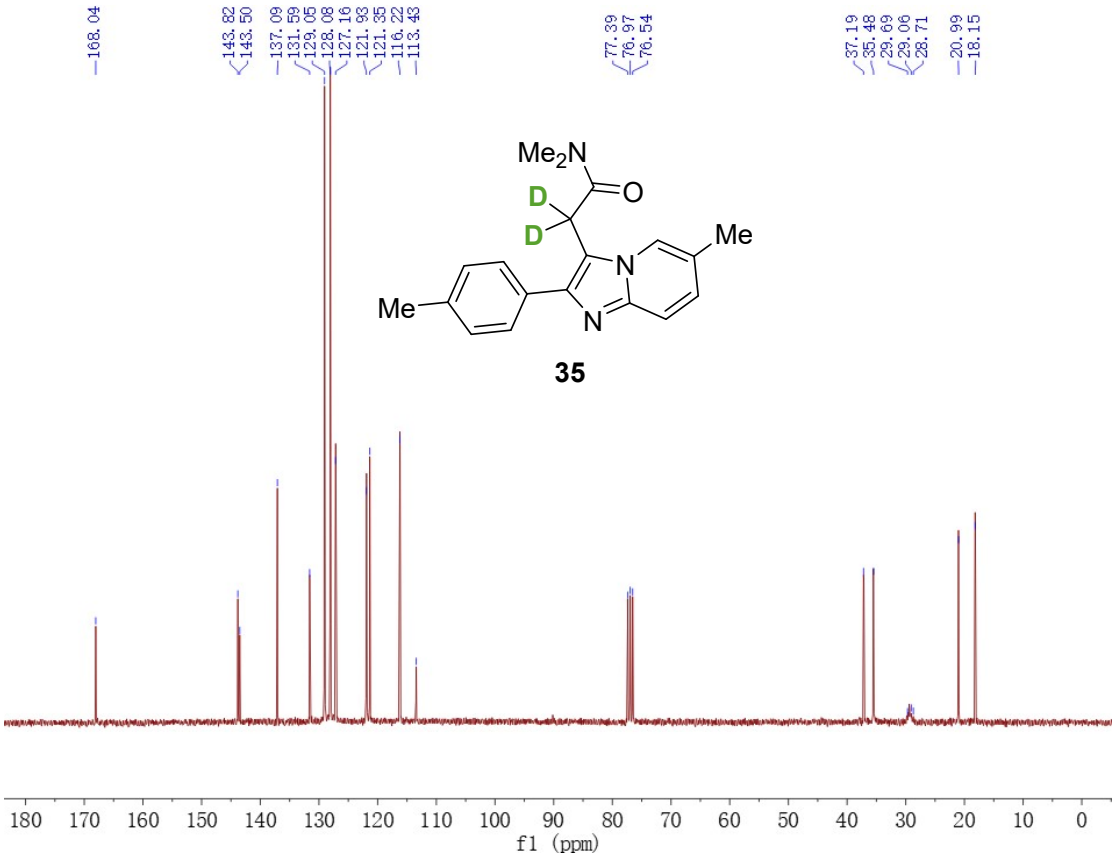



**$^{1}$H NMR (300 MHz, $CDCl_3$):**

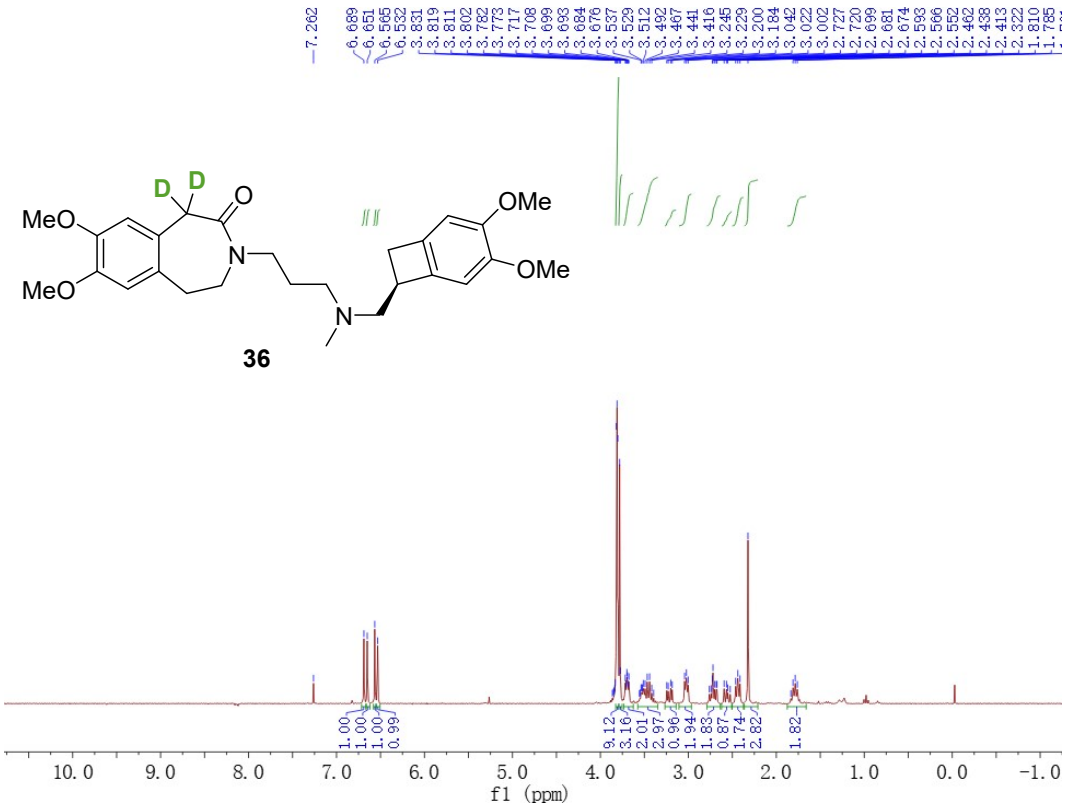



**35**

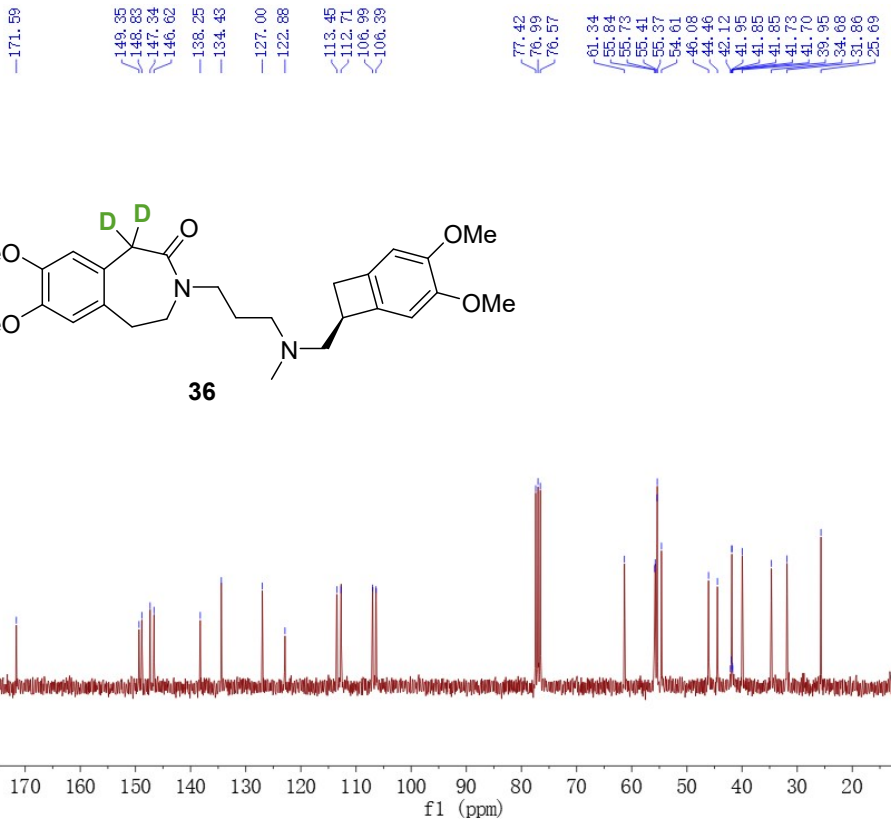
**$^{13}$C NMR (75 MHz, $CDCl_3$):**



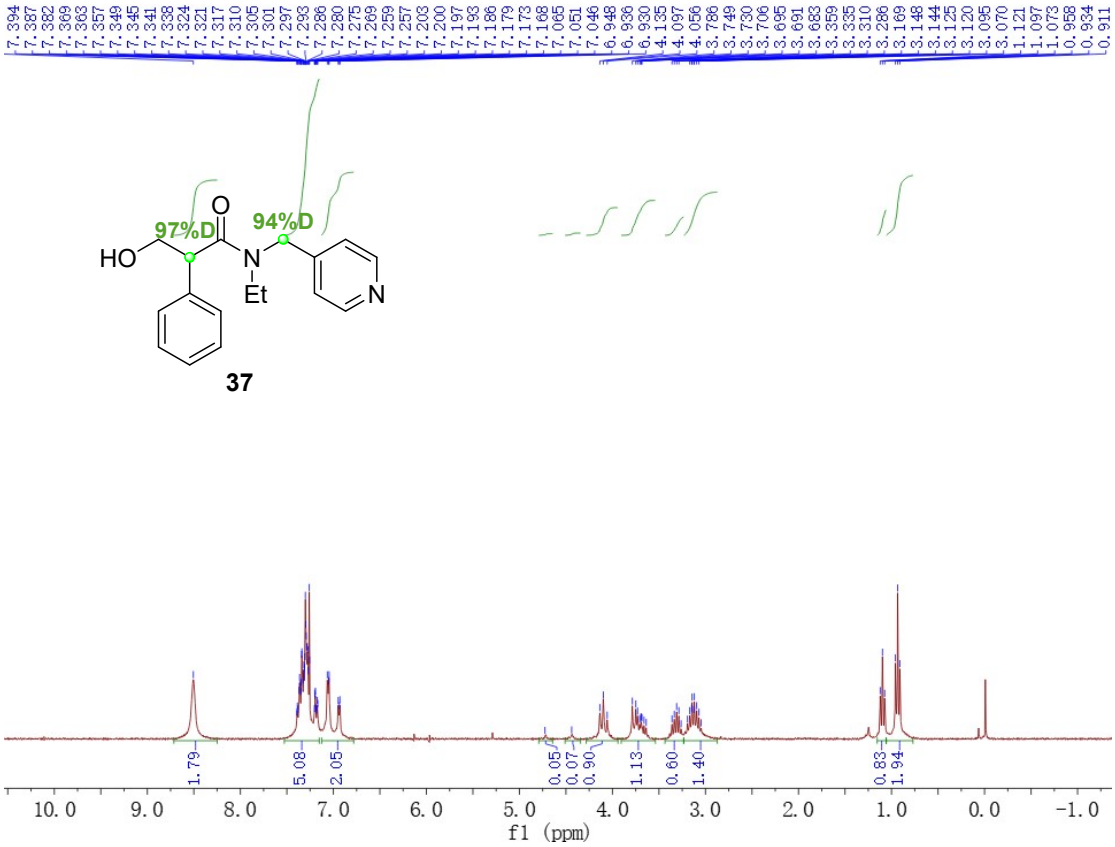

**$^{1}$H NMR (300 MHz, $CDCl_3$):**



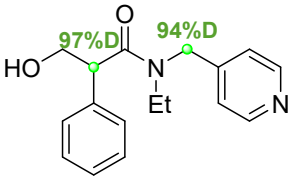

**$^{13}$C NMR (75 MHz, $CDCl_3$):**



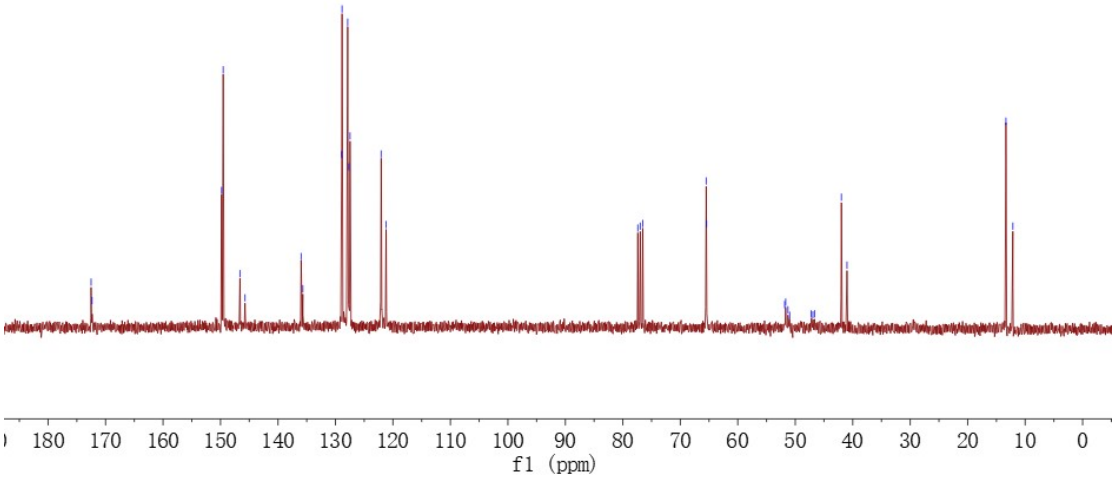

**$^{1}$H NMR (300 MHz, $CDCl_3$):**



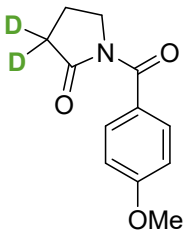

**$^{13}$C NMR (75 MHz, $CDCl_3$):**

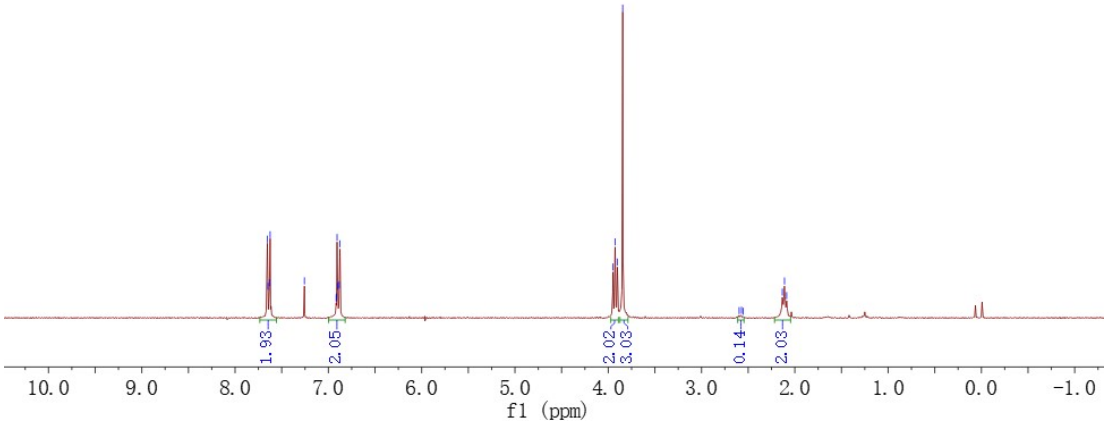

**37**



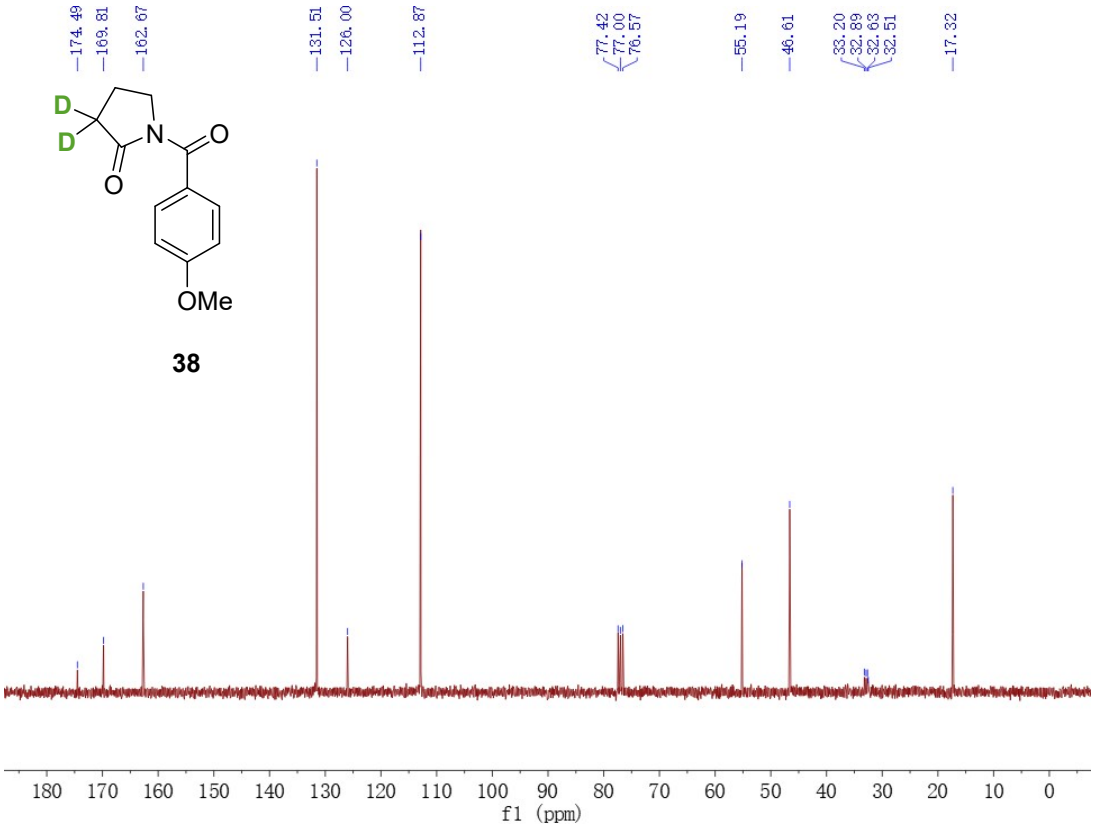

**$^{1}$H NMR (300 MHz, $CDCl_3$):**


**38**

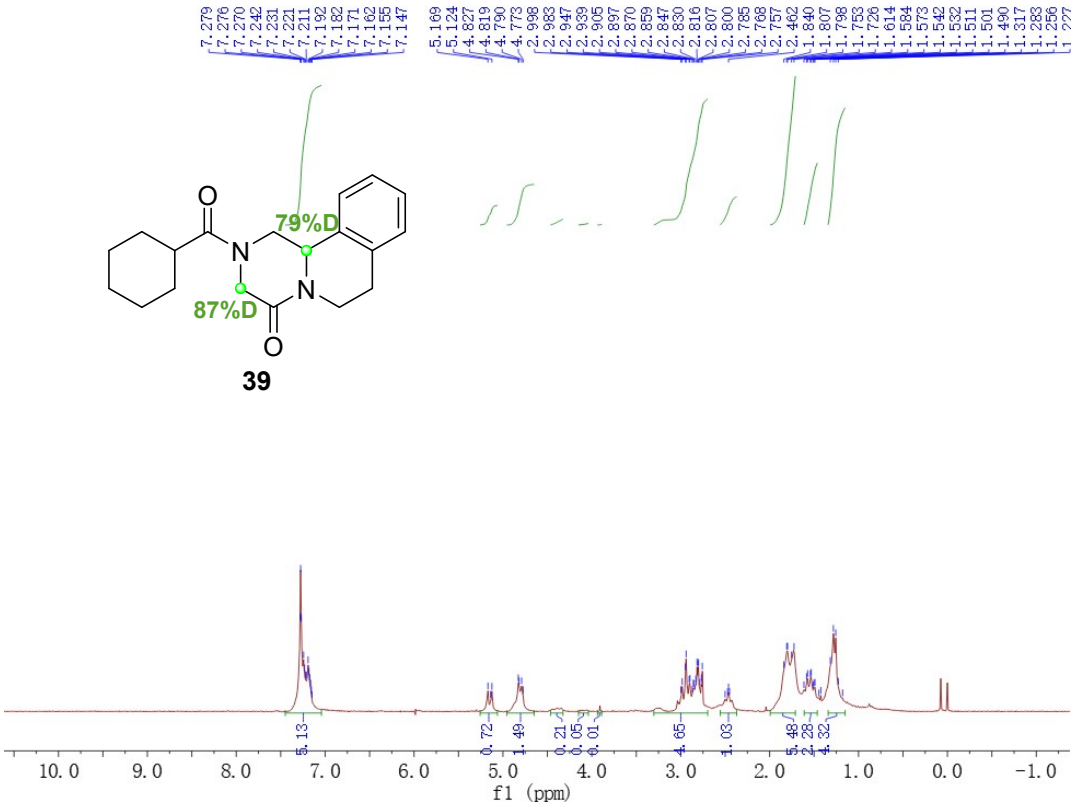



**$^{13}$C NMR (75 MHz, $CDCl_3$):**



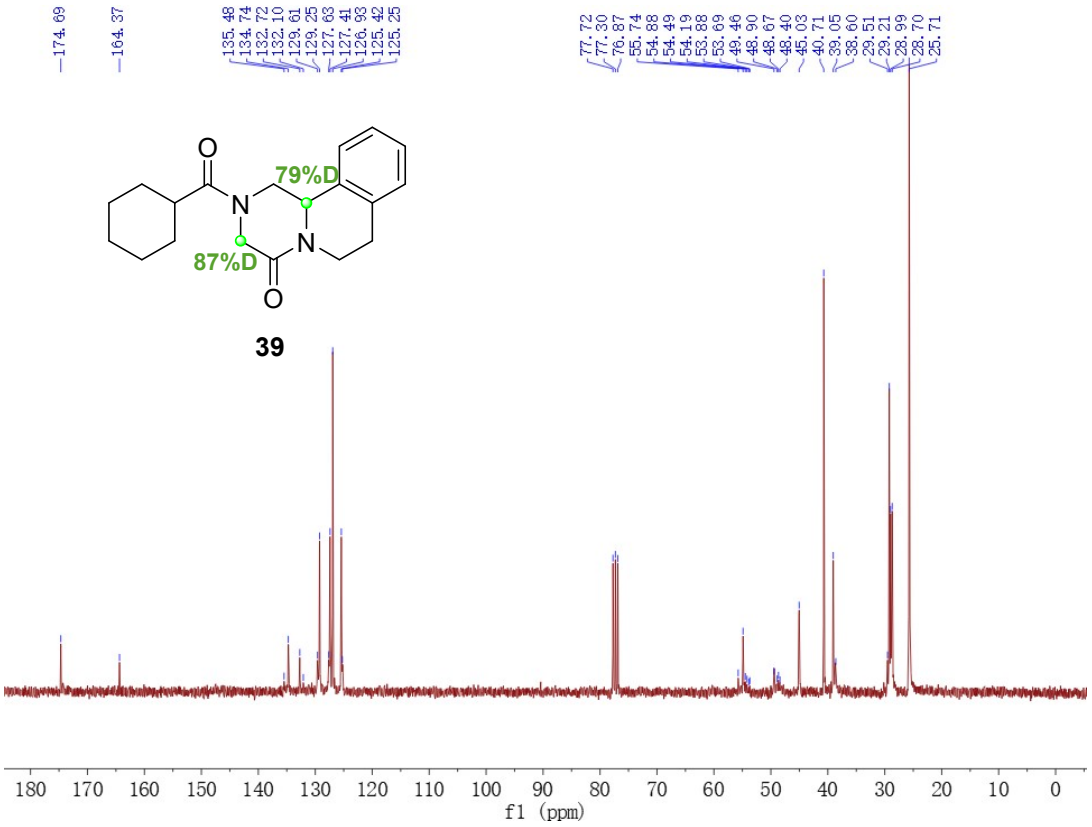

**38**

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

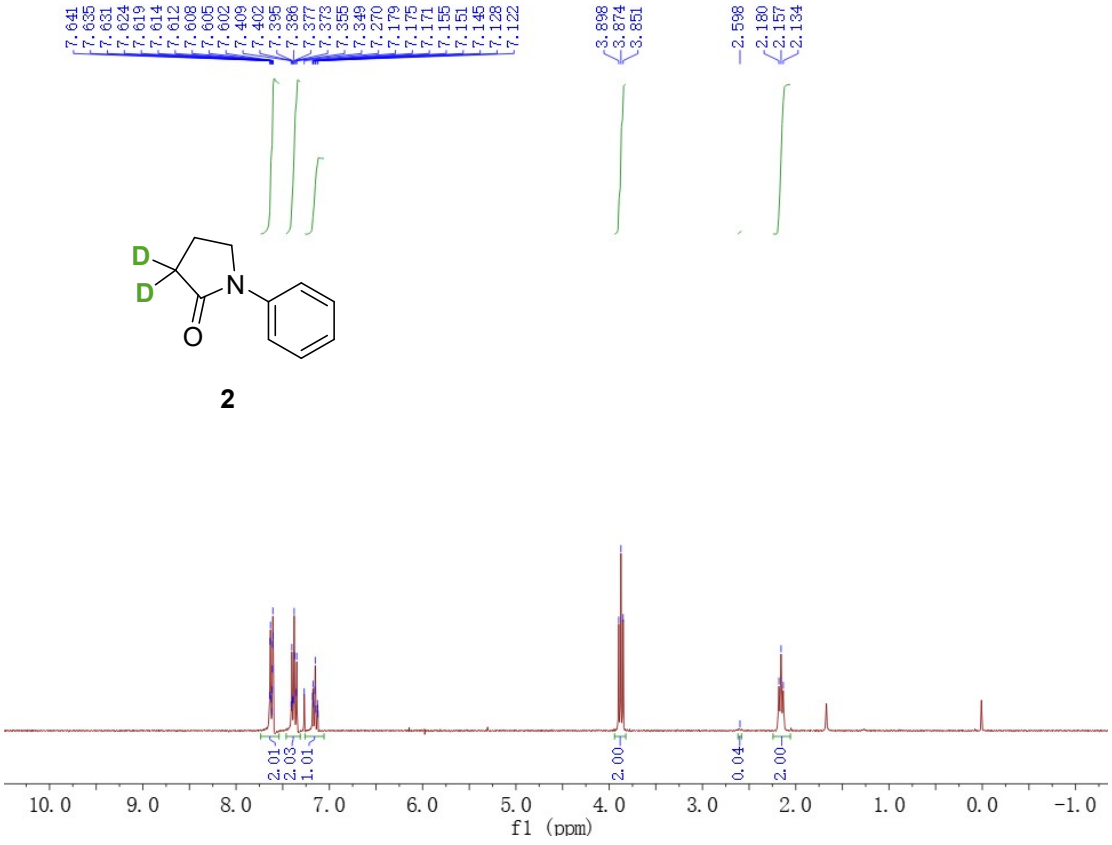



**39**

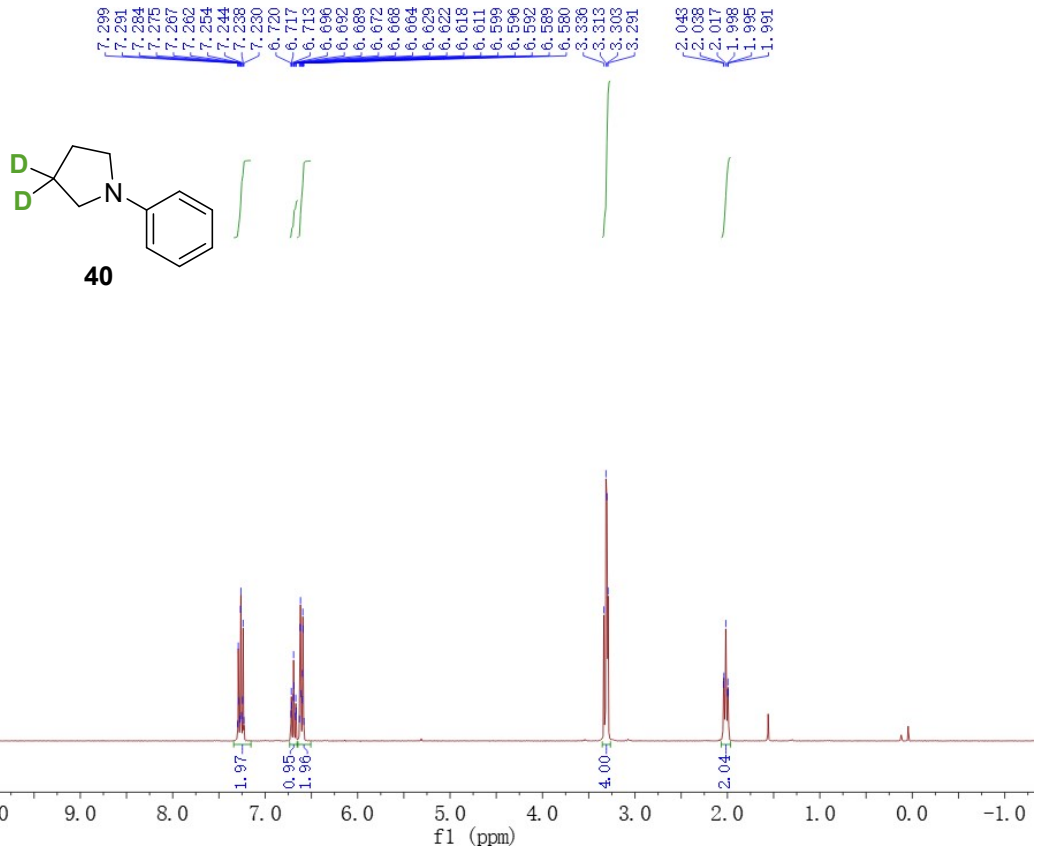
**$^{13}$C NMR (75 MHz, $CDCl_3$):**




**$^1$H NMR (300 MHz, $CDCl_3$): 8 mmol scale**




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




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