

Supplemental Information

Electroreductive Deuteration of *N*-Propynylamides to Enamides

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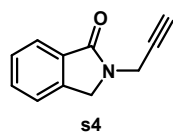
I. General Information

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 aluminium sheets of silica gel 60 (F254). Melting points were uncorrected. The ¹H and ¹³C NMR data were obtained on 300 MHz or 400 MHz NMR spectrometer with TMS as the internal standard and CDCl₃ 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). LC-MS data were obtained by high-performance liquid chromatography (HPLC, Agilent 1260 Infinity II) equipped with a quadrupole mass spectrometer (Agilent 6125).

Electrode materials/dimensions:

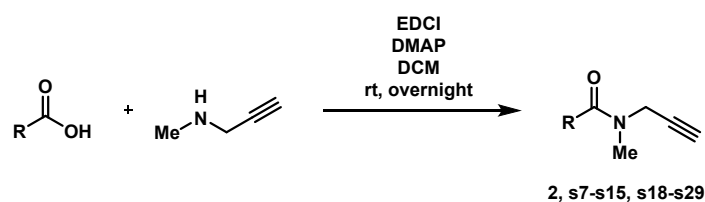
The aluminium electrodes are purchased from Tianjin Zhongnuotansu Technology Co., Ltd. The dimensions of the electrodes are 5 mm × 100 mm (the submerged height of the electrode is approximately 5 mm).

List of available substrates from our group's pervious work²:



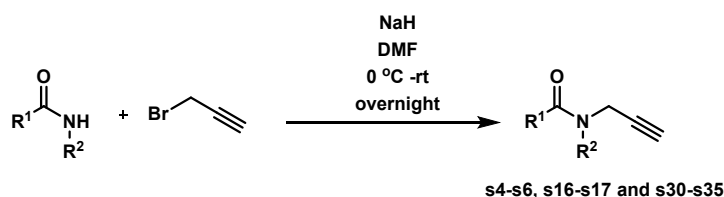
II. Substrates Synthesis and Characterization

Method A: Synthesis of compounds **2**, **s7-s15**, **s18-s29**.



At room temperature, corresponding carboxylic acid (3 mmol, 1.0 eq.) was dissolved in DCM (20 mL) in a 50 mL round bottom flask, then EDCI (4.5 mmol, 1.5 eq.) and DMAP (0.45 mmol, 0.15 eq.) was added. Then *N*-methylpropargylamine (3.6 mmol, 1.2 eq.) was added dropwise to the above solution, and the obtained solution was stirred at room temperature for overnight. After the completion of the reaction, the solution was diluted with DCM (30 mL) and quenched with 1*N* HCl aqueous or water (30 mL). The aqueous layer was extracted with DCM (3 × 30 mL). The combined DCM layers were washed with brine (3 × 30 mL), dried over Na₂SO₄, and concentrated *in vacuo*. Purification by flash column chromatography using PE/EtOAc as eluent afforded the desired product **2**, **s7-s15**, **s18-s29**.

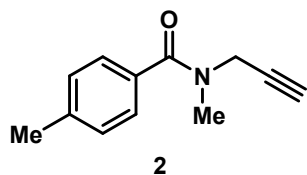
Method B: Synthesis of compounds **s5-s6**, **s16-s17** and **s30-s35**.



Add sodium hydride (60% dispersion in mineral oil, 3.6 mmol, 1.2 eq.) to a solution of amide substrate (3 mmol, 1.0 eq.) in anhydrous DMF (10 mL) at 0 °C, stir the reaction mixture for 15 minutes. Then 3-bromo-propyne (3.6 mmol, 1.2 eq.) was added dropwise to the above solution, and the obtained solution was stirred at room temperature for overnight. After the completion of the reaction, ice water was added into solution. The solution was diluted with EtOAc (30 mL) and quenched with water (30 mL). The aqueous layer was extracted with EtOAc (3 × 30 mL). The combined EtOAc layers were washed with brine (3 × 30 mL), dried over Na₂SO₄, and concentrated *in vacuo*. Purification by flash column chromatography using PE/EtOAc as eluent afforded the desired product **s4-s6**, **s16-s17** and **s30-s35**.

***N*,4-Dimethyl-*N*-(prop-2-yn-1-yl)benzamide (**2**)**

The ¹H spectra data matched with values reported in the literature³.

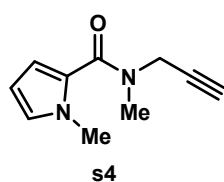


Yellow liquid (505 mg, 90% yield);

¹H NMR (400 MHz, CDCl₃): δ 7.38 (s, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 4.44 – 4.22 (s, 1H), 4.02 (s, 1H), 3.11 (s, 3H), 2.38 (s, 3H), 2.31 (s, 1H).

***N*,1-Dimethyl-*N*-(prop-2-yn-1-yl)-1*H*-pyrrole-2-carboxamide (s4)**

The ¹H spectra data matched with values reported in the literature⁴.

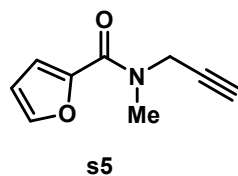


Yellow liquid (425 mg, 80% yield);

¹H NMR (400 MHz, CDCl₃): δ 6.71 (s, 1H), 6.57 (s, 1H), 6.09 (s, 1H), 4.33 (s, 2H), 3.80 (s, 3H), 3.20 (s, 3H), 2.31 (s, 1H).

***N*-Methyl-*N*-(prop-2-yn-1-yl)furan-2-carboxamide (s5)**

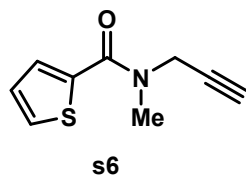
The ¹H spectra data matched with values reported in the literature³.



Brown liquid (440 mg, 90% yield);

¹H NMR (400 MHz, CDCl₃): δ 7.52 (s, 1H), 7.09 (d, *J* = 3.2 Hz, 1H), 6.49 (q, *J* = 3.2 Hz, 1H), 4.37 (s, 2H), 3.31 (s, 3H), 2.29 (s, 1H).

***N*-Methyl-*N*-(prop-2-yn-1-yl)thiophene-2-carboxamide (s6)**



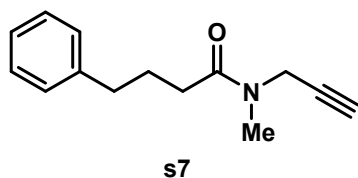
Yellow liquid (483 mg, 90% yield);

¹H NMR (400 MHz, CDCl₃): δ 7.48 (d, *J* = 4.5 Hz, 2H), 7.06 (t, *J* = 4.5 Hz, 1H), 4.32 (s, 2H), 3.25 (s, 3H), 2.34 (s, 1H).

¹³C NMR (101 MHz, CDCl₃): δ 164.3, 137.3, 129.6, 129.4, 127.0, 78.6, 73.0, 35.4, 8.8.

HRMS (ESI): Calcd. for C₉H₁₀NO⁺ [M + H]⁺: 180.0478, found: 180.0483.

***N*-Methyl-4-phenyl-*N*-(prop-2-yn-1-yl)butanamide (s7)**



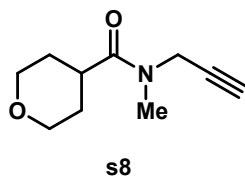
Colourless liquid (613 mg, 95% yield);

¹H NMR (400 MHz, CDCl₃): δ 7.29 (d, *J* = 7.1 Hz, 2H), 7.19 (d, *J* = 7.1 Hz, 3H), 4.23 (s, 1.37H), 3.98 (s, 0.63H), 3.00 (s, 3H), 2.68 (t, *J* = 7.6 Hz, 2H), 2.39 (t, *J* = 7.5 Hz, 0.64H), 2.32 (t, *J* = 7.5 Hz, 1.36H), 2.27 (s, 0.3H), 2.19 (s, 0.6H), 2.00 (m, 2H).

¹³C NMR (101 MHz, CDCl₃): δ 172.5, 141.8, 128.6, 128.5, 126.0, 79.0, 72.8, 71.7, 39.5, 36.3, 35.3, 34.4, 33.4, 32.5, 32.3, 26.6, 26.4.

HRMS (ESI): Calcd. for C₁₄H₁₈NO⁺ [M + H]⁺: 216.1383, found: 216.1385.

***N*-Methyl-*N*-(prop-2-yn-1-yl)tetrahydro-2*H*-pyran-4-carboxamide (s8)**



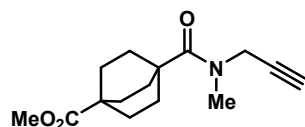
Colourless liquid (490 mg, 90% yield);

¹H NMR (400 MHz, CDCl₃): δ 4.23 (d, *J* = 2.3 Hz, 1.4H), δ 4.10 (d, *J* = 2.3 Hz, 0.6H), 4.04 (dd, *J* = 4.0, 2.1 Hz, 1H), 4.01 (dd, *J* = 4.0, 2.1 Hz, 1H), 3.45 (t, *J* = 11.0 Hz, 2H), δ 3.13 (s, 2H), δ 3.00 (s, 1H), 2.83 – 2.69 (m, 1H), δ 2.32 (s, 0.3H), δ 2.20 (s, 0.9H), 1.96 – 1.83 (m, 2H), 1.63 (m, 2H).

¹³C NMR (101 MHz, CDCl₃): δ 174.4, 78.9, 73.1, 71.9, 67.3, 39.3, 38.0, 36.5, 34.3, 33.7, 29.2, 28.8.

HRMS (ESI): Calcd. for C₁₀H₁₆NO₂⁺ [M + H]⁺: 182.1176, found: 182.1173.

Methyl-4-(methyl(prop-2-yn-1-yl)carbamoyl)bicyclo[2.2.2]octane-1-carboxylate (s9)



s9

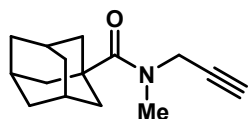
White solid (550 mg, 70% yield); m.p. 110 – 111 °C;

¹H NMR (400 MHz, CDCl₃): δ 4.19 (s, 2H), 3.65 (s, 3H), 3.13 (s, 3H), 2.22 (s, 1H), 1.93 (d, *J* = 8.0 Hz, 6H), 1.84 (d, *J* = 8.0 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 178.0, 176.1, 79.1, 72.1, 51.9, 39.8, 39.4, 38.7, 36.2, 28.0, 27.7.

HRMS (ESI): Calcd. for C₁₅H₂₂NO₃⁺ [M + H]⁺: 264.1594, found: 264.1600.

(1R,3R,5S)-N-Methyl-N-(prop-2-yn-1-yl)adamantane-1-carboxamide (s10)



s10

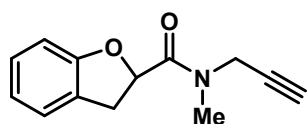
White solid (550 mg, 80% yield); m.p. 118 – 120 °C;

¹H NMR (400 MHz, CDCl₃): δ 4.22 (s, 2H), 3.17 (s, 3H), 2.21 (s, 1H), 2.03 (d, *J* = 10.2 Hz, 9H), 1.72 (s, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 176.8, 79.4, 71.9, 41.9, 39.5, 38.9, 36.7, 36.2, 28.5.

HRMS (ESI): Calcd. for C₁₅H₂₂NO⁺ [M + H]⁺: 232.1696, found: 232.1707.

N-Methyl-N-(prop-2-yn-1-yl)-2,3-dihydrobenzofuran-2-carboxamide (s11)



s11

Yellow liquid (520 mg, 80% yield);

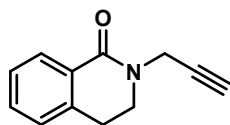
¹H NMR (400 MHz, CDCl₃) δ 7.19 (d, *J* = 7.5 Hz, 1H), 7.12 (t, *J* = 7.7 Hz, 1H), 6.88 (t, *J* = 7.7 Hz, 1H), 6.81 (m, 1H), 5.41 (m, 1H), 4.56 (dd, *J* = 17.3, 2.5 Hz, 0.4H), 4.42 (dd, *J* = 17.3, 2.5 Hz, 0.6H), 4.12 (m, 1H), 3.82 (m, 0.4H), 3.76 – 3.68 (m, 0.6H), 3.35 (m, 1H), 3.26 (s, 2H), 3.07 (s, 1H), 2.34 (t, *J* = 2.5 Hz, 0.4H), 2.24 (t, *J* = 2.5 Hz, 0.6H).

¹³C NMR (101 MHz, CDCl₃): δ 168.8, 158.4, 128.2, 128.1, 125.8, 125.0, 121.3, 121.2, 109.6, 79.2, 79.0, 73.1, 72.4, 39.2, 37.2, 34.4, 34.0, 32.3, 32.2.

HRMS (ESI): Calcd. for C₁₃H₁₄NO₂⁺ [M + H]⁺: 216.1019, found: 216.1028.

2-(Prop-2-yn-1-yl)-3,4-dihydroisoquinolin-1(2H)-one (s13)

The ^1H spectra data matched with values reported in the literature⁵.



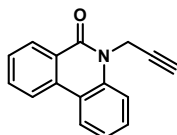
s13

Yellow liquid (477 mg, 86% yield);

$^1\text{H NMR}$ (300 MHz, CDCl_3): δ 8.09 (dd, $J = 7.4, 1.5$ Hz, 1H), 7.43 (td, $J = 7.4, 1.5$ Hz, 1H), 7.37 – 7.30 (m, 1H), 7.18 (dt, $J = 7.2, 1.0$ Hz, 1H), 4.43 (d, $J = 2.5$ Hz, 2H), 3.69 (t, $J = 6.6$ Hz, 2H), 3.05 (t, $J = 6.6$ Hz, 2H), 2.23 (t, $J = 2.5$ Hz, 1H).

5-(Prop-2-yn-1-yl)phenanthridin-6(5H)-one (s14)

The ^1H spectra data matched with values reported in the literature⁶.



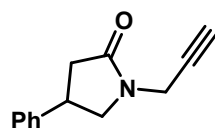
s14

White solid (490 mg, 70% yield); m.p. 159 – 160 °C;

$^1\text{H NMR}$ (300 MHz, CDCl_3): δ 8.55 (dd, $J = 7.9, 1.5$ Hz, 1H), 8.34 – 8.23 (m, 2H), 7.77 (m, 1H), 7.65 – 7.53 (m, 3H), 7.36 (m, 1H), 5.22 (d, $J = 2.5$ Hz, 2H), 2.26 (t, $J = 2.5$ Hz, 1H).

4-Phenyl-1-(prop-2-yn-1-yl)pyrrolidin-2-one (s15)

The ^1H spectra data matched with values reported in the literature⁷.

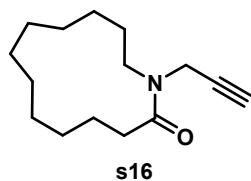


s15

Yellow liquid (360 mg, 60% yield);

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.35 (t, $J = 7.6$ Hz, 2H), 7.25 (m, 3H), 4.18 (s, 2H), 3.88 (t, $J = 8.0$ Hz, 1H), 3.62 (p, $J = 8.0$ Hz, 1H), 3.55 – 3.49 (m, 1H), 2.86 (m, 1H), 2.58 (m, 1H), 2.25 (s, 1H).

1-(Prop-2-yn-1-yl)azacyclotridecan-2-one (s16)



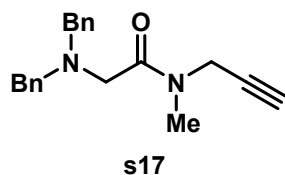
Yellow liquid (420 mg, 60% yield);

¹H NMR (400 MHz, CDCl₃): δ 4.40 (t, *J* = 12.3 Hz, 0.3H), 4.20 (s, 2H), 3.93 (d, *J* = 18.4 Hz, 0.3H), 3.41 (t, *J* = 8.0 Hz, 2H), 2.79 – 2.64 (m, 0.5H), 2.35 (t, *J* = 8.0 Hz, 2H), 2.26 (s, 0.4H), 2.16 (s, 1H), 1.83 – 1.64 (m, 4H), 1.50 – 1.16 (m, 12H).

¹³C NMR (101 MHz, CDCl₃): δ 173.3, 79.7, 72.5, 71.4, 45.7, 44.7, 37.8, 34.3, 33.4, 32.2, 26.8, 26.6, 26.3, 25.9, 25.8, 25.7, 25.5, 25.4, 25.3, 25.1, 24.9, 24.6, 24.6, 24.3, 23.7, 23.6.

HRMS (ESI): Calcd. for C₁₅H₂₆NO⁺ [M + H]⁺: 236.2009, found: 236.2016.

2-(Dibenzylamino)-*N*-methyl-*N*-(prop-2-yn-1-yl)acetamide (s17)



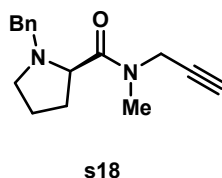
Colourless liquid (620 mg, 40% yield);

¹H NMR (400 MHz, CDCl₃): δ 7.38 – 7.25 (m, 10H), 4.13 (d, *J* = 9.1 Hz, 2H), 3.70 (s, 2.27H), 3.64 (s, 1.73H), 3.28 (d, *J* = 10.4 Hz, 2H), 2.91 (d, *J* = 4.2 Hz, 3H), 2.16 (d, *J* = 5.6 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃): δ 170.5, 138.9, 138.4, 129.4, 129.4, 128.5, 128.4, 127.4, 127.3, 72.4, 71.8, 58.9, 58.6, 57.1, 55.8, 39.0, 36.4, 34.4.

HRMS (ESI): Calcd. for C₂₀H₂₃N₂O⁺ [M + H]⁺: 307.1805, found: 307.1818.

(*R*)-1-Benzyl-*N*-methyl-*N*-(prop-2-yn-1-yl)pyrrolidine-2-carboxamide (s18)



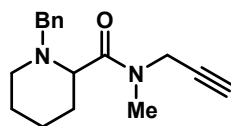
Colourless liquid (610 mg, 80% yield);

¹H NMR (400 MHz, CDCl₃): δ 7.34 – 7.21 (m, 5H), 4.85 (d, *J* = 18.0 Hz, 0.38H), 4.31 – 4.10 (m, 1H), 4.06 (d, *J* = 18.0 Hz, 0.62H), 3.91 (m, 1H), 3.55 – 3.36 (m, 2H), 3.09 (t, *J* = 7.6 Hz, 0.46H), 3.04 (s, 2H), 2.93 (s, 1H), 2.41 (q, *J* = 7.6 Hz, 0.54H), 2.30 – 2.07 (m, 2H), 2.03 – 1.75 (m, 3H), 1.67 (s, 1H)

^{13}C NMR (101 MHz, CDCl_3): δ 172.9, 138.4, 129.3, 129.2, 128.3, 127.2, 127.1, 79.0, 72.7, 71.8, 67.2, 63.8, 58.6, 57.9, 53.1, 52.8, 38.5, 36.7, 34.0, 33.9, 28.5, 22.9, 22.8.

HRMS (ESI): Calcd. for $\text{C}_{16}\text{H}_{21}\text{N}_2\text{O}^+$ $[\text{M} + \text{H}]^+$: 257.1648, found: 257.1661.

1-Benzyl-N-methyl-N-(prop-2-yn-1-yl)piperidine-2-carboxamide (s19)



s19

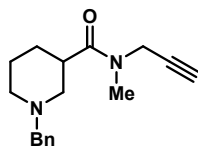
Brown liquid (560 mg, 70% yield);

^1H NMR (400 MHz, CDCl_3): δ 7.30 (s, 5H), 4.38 (d, $J = 17.8$ Hz, 0.5H), 4.31 (d, $J = 17.2$ Hz, 0.5H), 4.17 (d, $J = 17.2$ Hz, 0.5H), 3.81 (dd, $J = 13.2, 5.3$ Hz, 1H), 3.34 (d, $J = 13.2$ Hz, 0.5H), 3.25 (d, $J = 9.5$ Hz, 2H), 3.21 (d, $J = 5.3$ Hz, 1H), 2.98 (s, 2H), 2.92 (d, $J = 11.7$ Hz, 0.5H), 2.30 (s, 0.5H), 2.20 (s, 0.5H), 2.06 (s, 0.5H), 1.85 (s, 2H), 1.76 (s, 2H), 1.54 (s, 2H), 1.31 (s, 1H).

^{13}C NMR (101 MHz, CDCl_3): δ 172.8, 172.6, 138.0, 129.5, 129.1, 128.3, 128.2, 127.1, 127.1, 79.1, 78.9, 72.9, 71.8, 60.0, 59.6, 52.1, 51.6, 38.6, 36.9, 34.3, 33.7, 28.1, 27.9, 24.9, 23.9, 23.4.

HRMS (ESI): Calcd. for $\text{C}_{17}\text{H}_{23}\text{N}_2\text{O}^+$ $[\text{M} + \text{H}]^+$: 271.1805, found: 271.1816.

1-Benzyl-N-methyl-N-(prop-2-yn-1-yl)piperidine-3-carboxamide (s20)



s20

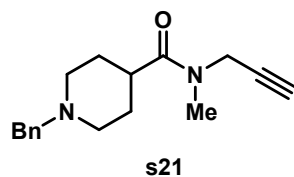
Brown liquid (405 mg, 30% yield);

^1H NMR (400 MHz, CDCl_3): δ 7.30 (s, 5H), 4.26 – 4.12 (m, 1.4H), 4.05 (s, 0.6H), 3.50 (d, $J = 13.7$ Hz, 2H), 3.07 (s, 2H), 2.95 (s, 1H), 2.88 (s, 2H), 2.78 (m, 1H), 2.16 (d, $J = 12.8$ Hz, 2H), 1.97 (d, $J = 12.5$ Hz, 1H), 1.82 (d, $J = 12.5$ Hz, 1H), 1.73 (d, $J = 12.8$ Hz, 1H), 1.64 (s, 2H), 1.48 (d, $J = 12.8$ Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3): δ 174.0, 138.3, 129.3, 128.3, 127.1, 79.0, 72.9, 71.8, 63.5, 56.1, 55.8, 53.9, 53.8, 39.9, 39.4, 36.3, 34.3, 33.5, 27.7, 27.4, 25.1.

HRMS (ESI): Calcd. for $\text{C}_{17}\text{H}_{23}\text{N}_2\text{O}^+$ $[\text{M} + \text{H}]^+$: 271.1805, found: 271.1816.

1-Benzyl-N-methyl-N-(prop-2-yn-1-yl)piperidine-4-carboxamide (s21)



Brown liquid (650 mg, 80% yield);

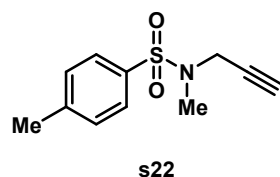
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.32 (s, 5H), 4.22 (s, 1.36H), 4.07 (s, 0.64H), 3.52 (s, 2H), 3.10 (s, 2H), 2.99 (s, 1H), 2.95 (d, $J = 10.8$ Hz, 2H), 2.48 (s, 1H), 2.29 (s, 0.3H), 2.19 (s, 0.6H), 2.01 (s, 2H), 1.88 (m, 2H), 1.70 (s, 2H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 164.6, 138.5, 129.2, 128.3, 127.1, 71.8, 63.3, 53.2, 39.1, 36.4, 34.3, 28.9, 28.5.

HRMS (ESI): Calcd. for $\text{C}_{17}\text{H}_{23}\text{N}_2\text{O}^+$ $[\text{M} + \text{H}]^+$: 271.1805, found: 271.1817.

***N*,4-Dimethyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (s22)**

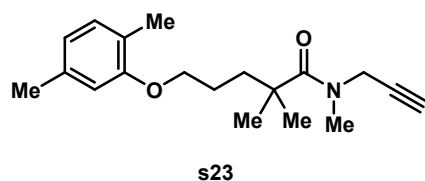
The ^1H spectra data matched with values reported in the literature⁸.



White solid (335 mg, 50% yield); m.p. 89 – 91 °C;

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.71 (d, $J = 7.9$ Hz, 2H), 7.31 (d, $J = 7.9$ Hz, 2H), 4.02 (s, 2H), 2.82 (s, 3H), 2.43 (s, 3H), 2.08 (s, 1H).

5-(2,5-Dimethylphenoxy)-*N*,2,2-trimethyl-*N*-(prop-2-yn-1-yl)pentanamide (s23)



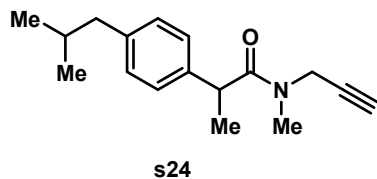
Colourless liquid (700 mg, 78% yield);

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.00 (d, $J = 7.5$ Hz, 1H), 6.66 (d, $J = 7.5$ Hz, 1H), 6.61 (s, 1H), 4.19 (s, 2H), 3.93 (s, 2H), 3.16 (s, 3H), 2.30 (s, 3H), 2.19 (s, 1H), 2.17 (s, 3H), 1.81 (m, 4H), 1.32 (s, 6H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 176.4, 157.0, 136.6, 130.4, 123.5, 120.8, 111.9, 79.2, 71.9, 67.8, 42.5, 39.2, 37.4, 35.7, 27.0, 25.3, 21.5, 16.0.

HRMS (ESI): Calcd. for $\text{C}_{19}\text{H}_{27}\text{NO}_2\text{Na}^+$ $[\text{M} + \text{Na}]^+$: 324.1934, found: 324.1930.

2-(4-Isobutylphenyl)-*N*-methyl-*N*-(prop-2-yn-1-yl)propanamide (s24)



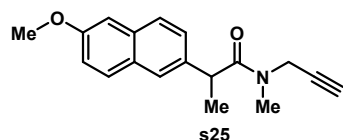
Yellow liquid (690 mg, 89% yield);

¹H NMR (400 MHz, CDCl₃): δ 7.14 (d, *J* = 7.8 Hz, 2H), 7.08 (d, *J* = 7.8 Hz, 2H), 4.36 (dd, *J* = 17.3, 2.5 Hz, 0.6H), 4.14 (ddd, *J* = 22.3, 17.3, 2.5 Hz, 1H), 3.91 (t, *J* = 6.8 Hz, 0.4H), 3.84 (q, *J* = 6.8 Hz, 0.6H), 3.68 (dd, *J* = 18.3, 2.5 Hz, 0.4H), 3.00 (s, 1H), 2.93 (s, 2H), 2.43 (d, *J* = 7.2 Hz, 2H), 2.19 (dt, *J* = 20.2, 2.5 Hz, 1H), 1.83 (m, 1H), 1.43 (m, 3H), 0.89 (d, *J* = 6.6 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 174.4, 173.9, 140.5, 140.3, 138.9, 138.7, 129.8, 129.7, 127.1, 79.0, 72.6, 71.8, 45.1, 43.2, 39.2, 36.8, 34.5, 33.9, 30.3, 22.5, 21.0, 20.8.

HRMS (ESI): Calcd. for C₁₇H₂₄NO⁺ [M + H]⁺: 258.1852, found: 258.1863.

2-(6-Methoxynaphthalen-2-yl)-N-methyl-N-(prop-2-yn-1-yl)propanamide (s25)



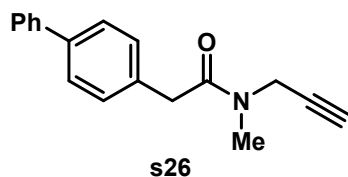
White solid (720 mg, 85% yield); m.p. 131 – 132 °C;

¹H NMR (400 MHz, CDCl₃): δ 7.70 (t, *J* = 8.6 Hz, 2H), 7.63 – 7.60 (m, 1H), 7.40 – 7.34 (m, 1H), 7.16 – 7.10 (m, 2H), 4.33 (dd, *J* = 17.2, 2.5 Hz, 0.7H), 4.21 (m, 1H), 4.06 (q, *J* = 6.8 Hz, 0.3H), 3.99 (q, *J* = 6.8 Hz, 0.7H), 3.91 (s, 3H), 3.65 (dd, *J* = 17.2, 2.5 Hz, 0.3H), 3.02 (s, 1H), 2.94 (s, 2H), 2.19 (dt, *J* = 25.0, 2.5 Hz, 1H), 1.51 (m, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 173.6, 157.7, 136.7, 133.6, 129.3, 127.7, 126.3, 125.7, 119.2, 105.7, 79.0, 71.8, 55.4, 43.5, 36.9, 34.6, 20.9.

HRMS (ESI): Calcd. for C₁₈H₂₀NO₂⁺ [M + H]⁺: 282.1489, found: 282.1494.

2-([1,1'-Biphenyl]-4-yl)-N-methyl-N-(prop-2-yn-1-yl)acetamide (s26)



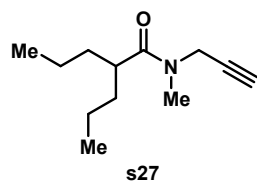
White solid (630 mg, 80% yield); m.p. 112 – 113 °C;

¹H NMR (400 MHz, CDCl₃): δ 7.60 – 7.52 (t, *J* = 8.6 Hz, 4H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.33 (m, 3H), 4.28 (d, *J* = 2.5 Hz, 1.4H), 4.06 (d, *J* = 2.5 Hz, 0.6H), 3.83 (s, 0.7H), 3.77 (s, 1.3H), 3.10 (s, 2H), 3.04 (s, 1H), 2.31 (t, *J* = 2.5 Hz, 0.3H), 2.22 (t, *J* = 2.5 Hz, 0.6H).

¹³C NMR (101 MHz, CDCl₃): δ 170.8, 140.9, 139.9, 133.7, 129.4, 128.9, 127.5, 127.4, 127.1, 78.7, 73.1, 72.0, 40.6, 40.5, 36.5, 35.0, 33.7.

HRMS (ESI): Calcd. for C₁₈H₁₈NO⁺ [M + H]⁺: 264.1383, found: 264.1394.

***N*-Methyl-*N*-(prop-2-yn-1-yl)-2-propylpentanamide (s27)**



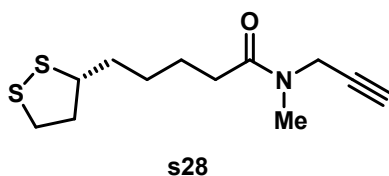
Colourless liquid (520 mg, 89% yield);

¹H NMR (400 MHz, CDCl₃): δ 4.25 (d, *J* = 2.5 Hz, 1.4H), 4.10 (d, *J* = 2.5 Hz, 0.6H), 3.11 (s, 2H), 3.00 (s, 1H), 2.66 (m, 1H), 2.28 (t, *J* = 2.5 Hz, 0.3H), 2.17 (t, *J* = 2.5 Hz, 0.6H), 1.73 – 1.57 (m, 2H), 1.47 – 1.34 (m, 2H), 1.30 – 1.19 (m, 4H), 0.87 (t, *J* = 7.2 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 176.4, 72.6, 71.6, 41.0, 39.4, 36.5, 35.4, 34.7, 33.6, 20.9, 20.8, 14.4.

HRMS (ESI): Calcd. for C₁₂H₂₂NO⁺ [M + H]⁺: 196.1696, found: 196.1698.

(*R*)-5-(1,2-Dithiolan-3-yl)-*N*-methyl-*N*-(prop-2-yn-1-yl)pentanamide (s28)



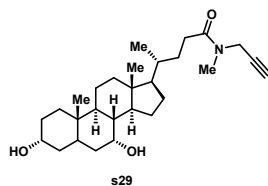
Yellow liquid (650 mg, 85% yield);

¹H NMR (400 MHz, CDCl₃): δ 4.23 (d, *J* = 2.7 Hz, 1.4H), 4.04 (d, *J* = 2.7 Hz, 0.6H), 3.59 (p, *J* = 6.9 Hz, 1H), 3.20 – 3.09 (m, 2H), 3.06 (s, 2H), 2.99 (s, 1H), 2.46 (m, 1H), 2.39 (t, *J* = 7.3 Hz, 1H), 2.33 (t, *J* = 7.3 Hz, 1H), 2.29 (d, *J* = 2.6 Hz, 0.3H), 2.20 (d, *J* = 2.6 Hz, 0.7H), 1.92 (m, 1H), 1.70 (m, 4H), 1.55 – 1.46 (m, 2H).

¹³C NMR (101 MHz, CDCl₃): δ 172.5, 72.9, 71.8, 56.6, 40.4, 38.6, 36.3, 34.9, 34.5, 33.3, 29.2, 24.8.

HRMS (ESI): Calcd. for C₁₂H₂₀NOS₂⁺ [M + H]⁺: 258.0981, found: 258.0993.

(4*R*)-4-((3*R*,7*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3,7-Dihydroxy-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)-*N*-methyl-*N*-(prop-2-yn-1-yl)pentanamide (s29)



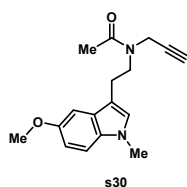
White solid (800 mg, 60% yield); m.p. 95 – 96 °C;

¹H NMR (400 MHz, CDCl₃): δ 4.22 (s, 1.4H), 4.04 (s, 0.6H), 3.85 (s, 1H), 3.45 (s, 1H), 3.07 (s, 2H), 2.99 (s, 1H), 2.43 – 2.14 (m, 3H), 1.99 – 1.59 (m, 9H), 1.54 – 1.10 (m, 12H), 0.95 (d, *J* = 6.3 Hz, 3H), 0.90 (s, 3H), 0.66 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 173.4, 79.1, 72.8, 72.1, 71.8, 68.6, 55.9, 50.6, 42.8, 41.6, 40.0, 39.8, 39.5, 36.3, 35.6, 35.5, 35.2, 34.7, 34.6, 32.9, 31.3, 31.0, 30.8, 30.3, 28.3, 23.8, 22.9, 20.7, 18.6, 11.9.

HRMS (ESI): Calcd. for C₂₈H₄₆NO₃⁺ [M + H]⁺: 444.3472, found: 444.3473.

***N*-(2-(5-Methoxy-1-methyl-1*H*-indol-3-yl)ethyl)-*N*-(prop-2-yn-1-yl)acetamide (s30)**



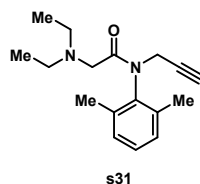
Brown liquid (170 mg, 20% yield);

¹H NMR (400 MHz, CDCl₃): δ 7.19 (m, 1H), 7.12 (d, *J* = 2.5 Hz, 0.4H), 7.01 (d, *J* = 2.5 Hz, 0.6H), 6.91 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.86 (d, *J* = 9.0 Hz, 1H), 4.28 (d, *J* = 2.5 Hz, 1.2H), 3.91 (d, *J* = 2.5 Hz, 0.8H), 3.87 (d, *J* = 3.5 Hz, 3H), 3.72 (d, *J* = 3.5 Hz, 4H), 3.71 – 3.66 (m, 1H), 3.02 (q, *J* = 7.6 Hz, 2H), 2.28 (t, *J* = 2.6 Hz, 0.3H), 2.24 (t, *J* = 2.6 Hz, 0.6H), 2.19 (s, 1H), 1.95 (s, 2H).

¹³C NMR (101 MHz, CDCl₃): δ 170.4, 154.0, 132.6, 127.8, 112.0, 110.4, 110.1, 110.0, 100.8, 100.5, 79.6, 72.6, 71.8, 56.1, 48.8, 47.6, 39.2, 34.4, 33.0, 24.5, 23.7, 22.0, 21.4.

HRMS (ESI): Calcd. for C₁₇H₂₁N₂O₂⁺ [M + H]⁺: 285.1598, found: 285.1607.

2-(Diethylamino)-*N*-(2,6-dimethylphenyl)-*N*-(prop-2-yn-1-yl)acetamide (s31)



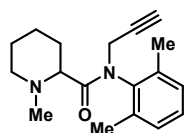
Yellow liquid (604 mg, 74% yield);

¹H NMR (400 MHz, CDCl₃): δ 7.20 – 7.15 (m, 1H), 7.12 (d, *J* = 7.4 Hz, 2H), 4.41 (s, 2H), 2.84 (s, 2H), 2.55 (q, *J* = 7.2 Hz, 4H), 2.27 (s, 6H), 2.12 (s, 1H), 0.89 (t, *J* = 7.2 Hz, 6H).

^{13}C NMR (101 MHz, CDCl_3): δ 170.9, 138.8, 136.8, 129.0, 128.6, 78.5, 72.6, 54.5, 47.5, 37.1, 18.5, 12.1.

HRMS (ESI): Calcd. for $\text{C}_{17}\text{H}_{25}\text{N}_2\text{O}^+$ $[\text{M} + \text{H}]^+$: 273.1961, found: 273.1967.

***N*-(2,6-Dimethylphenyl)-1-methyl-*N*-(prop-2-yn-1-yl)piperidine-2-carboxamide (s32)**



s32

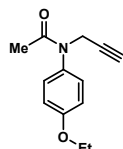
Yellow liquid (511 mg, 60% yield);

^1H NMR (400 MHz, CDCl_3): δ 7.07 (s, 2H), 7.04 (s, 1H), 3.59 (d, $J = 11.7$ Hz, 0.3H), 3.37 (t, $J = 10.8$ Hz, 0.3H), 3.01 (t, $J = 11.3$ Hz, 1H), 2.65 (dd, $J = 10.8$ Hz, 0.7H), 2.42 (d, $J = 2.8$ Hz, 2H), 2.25 (d, $J = 2.8$ Hz, 6H), 2.19 (d, $J = 11.7$ Hz, 0.7H), 2.14 (q, $J = 8.3, 7.5$ Hz, 3H), 1.79 (q, $J = 8.3, 6.2$ Hz, 2H), 1.71 (s, 2H), 1.61 (m, 2H), 1.34 – 1.24 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3): δ 172.7, 135.4, 128.5, 128.3, 127.2, 77.4, 70.3, 55.8, 45.6, 36.0, 31.7, 25.6, 24.1, 23.8, 23.5, 19.0, 18.8.

HRMS (ESI): Calcd. for $\text{C}_{18}\text{H}_{25}\text{N}_2\text{O}^+$ $[\text{M} + \text{H}]^+$: 285.1961, found: 285.1972.

***N*-(4-Ethoxyphenyl)-*N*-(prop-2-yn-1-yl)acetamide (s33)**



s33

Yellow liquid (326 mg, 50% yield);

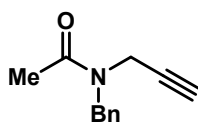
^1H NMR (400 MHz, CDCl_3): δ 7.17 (d, $J = 8.8$ Hz, 2H), 6.91 (d, $J = 8.8$ Hz, 2H), 4.44 (d, $J = 2.5$ Hz, 2H), 4.04 (q, $J = 7.0$ Hz, 2H), 2.19 (t, $J = 2.5$ Hz, 1H), 1.85 (s, 2H), 1.43 (t, $J = 7.0$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ 170.6, 158.8, 134.9, 129.2, 115.3, 79.4, 72.0, 63.8, 38.4, 22.4, 14.9.

HRMS (ESI): Calcd. for $\text{C}_{13}\text{H}_{16}\text{NO}_2^+$ $[\text{M} + \text{H}]^+$: 218.1176, found: 218.1182.

***N*-Benzyl-*N*-(prop-2-yn-1-yl)acetamide (s34)**

The ^1H spectra data matched with values reported in the literature⁹.

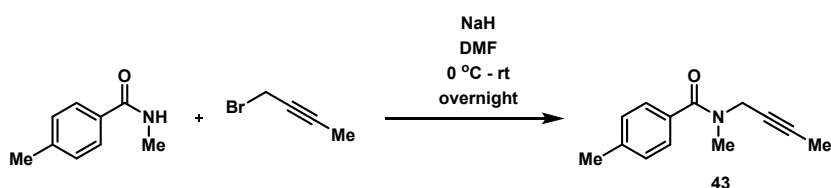


s34

Colourless liquid (393 mg, 70% yield);

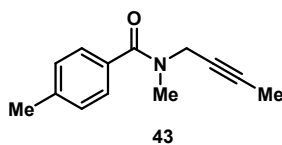
¹H NMR (400 MHz, CDCl₃): δ 7.38 – 7.15 (m, 5H), 4.66 (d, *J* = 2.8 Hz, 2H), 4.20 (d, *J* = 2.5 Hz, 1H), 3.90 (d, *J* = 2.5 Hz, 1H), 2.28 (t, *J* = 2.5 Hz, 0.4H), 2.24 (s, 1.5H), 2.20 (t, *J* = 2.5 Hz, 0.6H), 2.16 (s, 1.5H).

Method C: Synthesis of compound **43**.



Add sodium hydride (60% dispersion in mineral oil, 3.6 mmol, 1.2 eq.) to a solution of *N*,4-dimethylbenzamide (3 mmol, 1.0 eq.) in anhydrous DMF (10 mL) at 0 °C, stir the reaction mixture for 15 minutes. Then 1-bromo-2-butyne (3.6 mmol, 1.2 eq.) was added dropwise to the above solution, and the obtained solution was stirred at room temperature for overnight. After the completion of the reaction, ice water was added into solution. The solution was diluted with EtOAc (30 mL) and quenched with water (30 mL). The aqueous layer was extracted with EtOAc (3 × 30 mL). The combined EtOAc layers were washed with brine (3 × 30 mL), dried over Na₂SO₄, and concentrated *in vacuo*. Purification by flash column chromatography using PE/EtOAc as eluent afforded the desired product **43**.

***N*-(but-2-yn-1-yl)-*N*,4-dimethylbenzamide (43)**



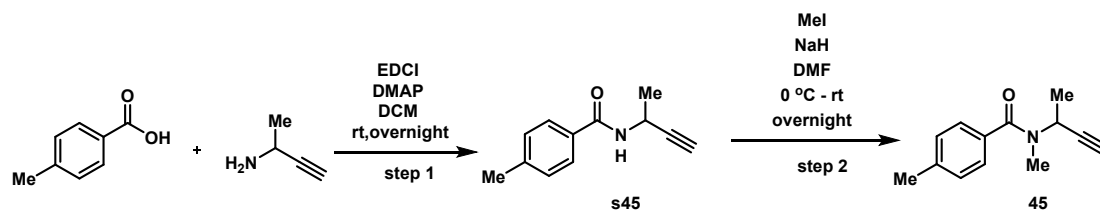
43

Yellow liquid (400 mg, 63% yield);

¹H NMR (400 MHz, CDCl₃): δ 7.40 (s, 2H), 7.20 (d, *J* = 7.2 Hz, 2H), 4.31 (s, 1H), 3.96 (s, 1H), 3.08 (d, *J* = 26.8 Hz, 3H), 2.37 (s, 3H), 1.85 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 171.5, 140.0, 132.8, 129.0, 127.3, 73.8, 42.1, 36.9, 32.8, 21.5, 3.6.

Method D: Synthesis of compound **45**.

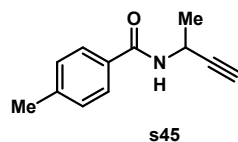


Step 1: At room temperature, *p*-toluic acid (5 mmol, 1.0 eq.) was dissolved in DCM (20 mL) in a 50 mL round bottom flask, then EDCI (7.5 mmol, 1.5 eq.) and DMAP (0.75 mmol, 0.15 eq.) was added. Then But-3-yn-2-amine (3.6 mmol, 1.2 eq.) was added dropwise to the above solution, and the obtained solution was stirred at room temperature for overnight. After the completion of the reaction, the solution was diluted with DCM (30 mL) and quenched with 1N HCl aqueous or water (30 mL). The aqueous layer was extracted with DCM (3 × 30 mL). The combined DCM layers were washed with brine (3 × 30 mL), dried over Na₂SO₄, and concentrated *in vacuo*. Purification by flash column chromatography using PE/EtOAc as eluent afforded the desired product **s45**.

Step 2: Add sodium hydride (60% dispersion in mineral oil, 3.6 mmol, 1.2 eq.) to a solution of **s45** (3 mmol, 1.0 eq.) in anhydrous DMF (10 mL) at 0 °C, stir the reaction mixture for 15 minutes. Then MeI (3.6 mmol, 1.2 eq.) was added dropwise to the above solution, and the obtained solution was stirred at room temperature for overnight. After the completion of the reaction, ice water was added into solution. The solution was diluted with EtOAc (30 mL) and quenched with water (30 mL). The aqueous layer was extracted with EtOAc (3 × 30 mL). The combined EtOAc layers were washed with brine (3 × 30 mL), dried over Na₂SO₄, and concentrated *in vacuo*. Purification by flash column chromatography using PE/EtOAc as eluent afforded the desired product **45**.

***N*-(But-3-yn-2-yl)-4-methylbenzamide (s45)**

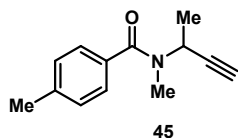
The ¹H spectra data matched with values reported in the literature¹⁰.



Colourless liquid (560 mg, 60% yield);

¹H NMR (400 MHz, CDCl₃): δ 7.71 (d, *J* = 7.5 Hz, 2H), 7.31–7.23 (m, 2H), 6.29 (s, 1H), 5.06 (s, 1H), 2.43 (s, 3H), 2.34 (s, 1H), 1.56 (d, *J* = 6.7 Hz, 3H).

***N*-(But-3-yn-2-yl)-*N*,4-dimethylbenzamide (45)**

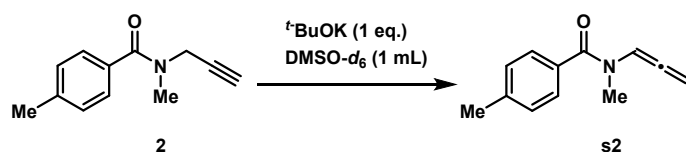


Colourless liquid (300 mg, 60% yield);

¹H NMR (400 MHz, CDCl₃): δ 7.34 (d, *J* = 7.5 Hz, 2H), 7.21 (d, *J* = 7.2 Hz, 2H), 5.64 (s, 0.5H), 4.75 (s, 0.5H), 3.01 (s, 3H), 2.38 (s, 3H), 2.34 (s, 1H), 1.42 (s, 3H).

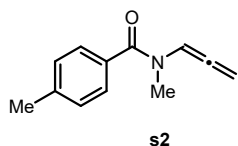
¹³C NMR (101 MHz, CDCl₃): δ 171.5, 140.1, 133.2, 129.3, 127.3, 126.9, 72.3, 59.73, 47.1, 41.5, 32.6, 28.0, 21.6, 20.6, 19.3.

Method E: Synthesis of compound **s2**.



At room temperature, *N*-propynylamide (1 mmol, 1.0 eq.) was dissolved in DMSO (1 mL) in a 10 mL round bottom flask, then *t*-BuOK (1 mmol, 1.0 eq.) was added. After the completion of the reaction, 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 Na₂SO₄, and concentrated *in vacuo*. Purification by flash column chromatography using PE/EtOAc (v/v = 10/1) as eluent afforded the desired product **s2**.

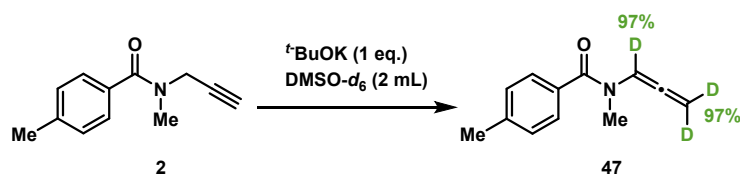
***N*,4-Dimethyl-*N*-(propa-1,2-dien-1-yl)benzamide (s2)**



Yellow liquid (100 mg, 52% yield);

¹H NMR (400 MHz, CDCl₃): δ 7.69 (s, 0.2H), 7.38 (s, 2H), 7.22 (d, *J* = 7.8 Hz, 2H), 6.78 (s, 0.45H), 5.37 (s, 2H), 3.08 (d, *J* = 47.8 Hz, 3H), 2.38 (s, 3H).

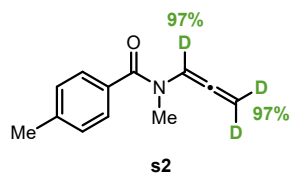
Method F: Synthesis of compound **47**.



At room temperature, *N*-propynylamide (2 mmol, 1.0 eq.) was dissolved in DMSO-*d*₆ (2 mL) in a 10 mL

round bottom flask, then *t*-BuOK (2 mmol, 1.0 eq.) was added. After the completion of the reaction, 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 Na₂SO₄, and concentrated *in vacuo*. Purification by flash column chromatography using PE/EtOAc (v/v = 10/1) as eluent afforded the desired product 47.

***N*,4-Dimethyl-*N*-(propa-1,2-dien-1-yl-*d*₃)benzamide (47)**



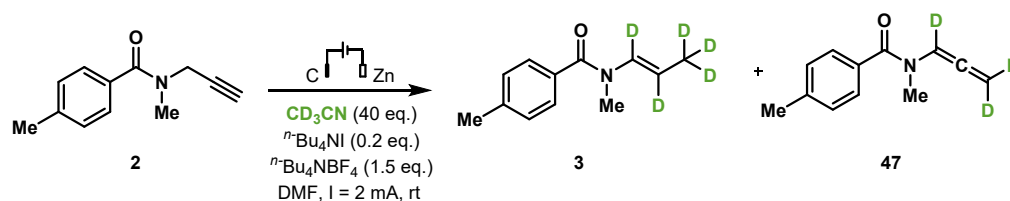
Yellow liquid (228 mg, 60% yield, 2.91 D/molecule);

¹H NMR (400 MHz, CDCl₃): δ 7.64 (s, 0.01H), 7.39 (d, *J* = 7.7 Hz, 2H), 7.22 (d, *J* = 7.7 Hz, 2H), 6.79 (s, 0.02H), 5.38 (s, 0.06H), 3.08 (d, *J* = 43.8 Hz, 3H), 2.38 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 200.0, 172.5, 169.7, 164.5-164.0 (m), 143.1, 140.5, 131.9, 129.6, 129.1, 128.1, 103.7, 86.8, 35.7, 31.3, 27.5, 21.4.

III. Investigation of Reaction Conditions

Characterization the ratio of **3** and **47**.



A 10 mL distillation flask equipped with a magnetic stir bar was charged with compound **2** (37 mg, 0.2 mmol, 1.0 eq.), CD_3CN (0.42 mL, 40.0 eq.), $n\text{-Bu}_4\text{NI}$ (15 mg, 0.04 mmol, 0.2 eq.), $n\text{-Bu}_4\text{NBF}_4$ (99 mg, 0.3 mmol, 1.5 eq.) and DMF (3 mL). The flask equipped with graphite anode ($d = 5 \text{ mm}$) and zinc cathode ($d = 5 \text{ mm}$). The resulting solution was stirred and electrolyzed at a constant current of 2 mA (Single Output DC Power Supply: KRP-305DM) for 1 h at room temperature. The solution was diluted with EtOAc (5 mL) and brine (20 mL), and extracted with EtOAc ($3 \times 20 \text{ mL}$). The combined organic layers were washed with brine ($3 \times 20 \text{ mL}$), dried over Na_2SO_4 , and concentrated *in vacuo*. Purification by flash column chromatography using PE/EtOAc ($v/v = 10/1$) as eluent afforded the mixture product **3** and **47** (22mg) as yellow oil.

Because of the ^1H NMR of the mixture product **3** and **47** can't display the ratio of **3** and **47** (Figure S1), we represented the ratio of **3** and **47** by calculating the m/z peak height ratio of **3** and **47** detected by LC/MS. As shown in Figure S2, DAD of the mixture product **3** and **47** just displays singlet, the ratio of **3** and **47** can't be judged by the peak area ratio. Then, we use the option of "averaging the selected position spectra" for the MS region of the mixture, the m/z peak height of **3** is 2.58, the m/z peak height of **47** is 5.02, the m/z peak height ratio of **3** and **47** is 1 : 1.95.

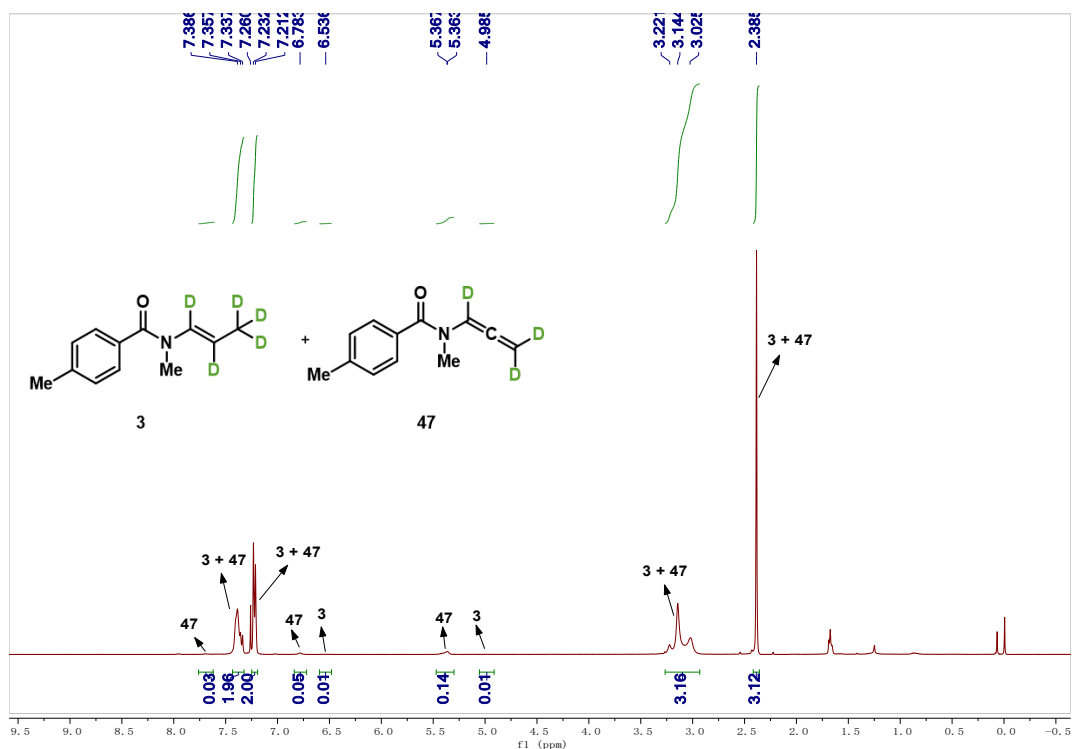


Figure S1: ^1H NMR (400 Hz, CDCl_3) of the mixture product **3** and **47**

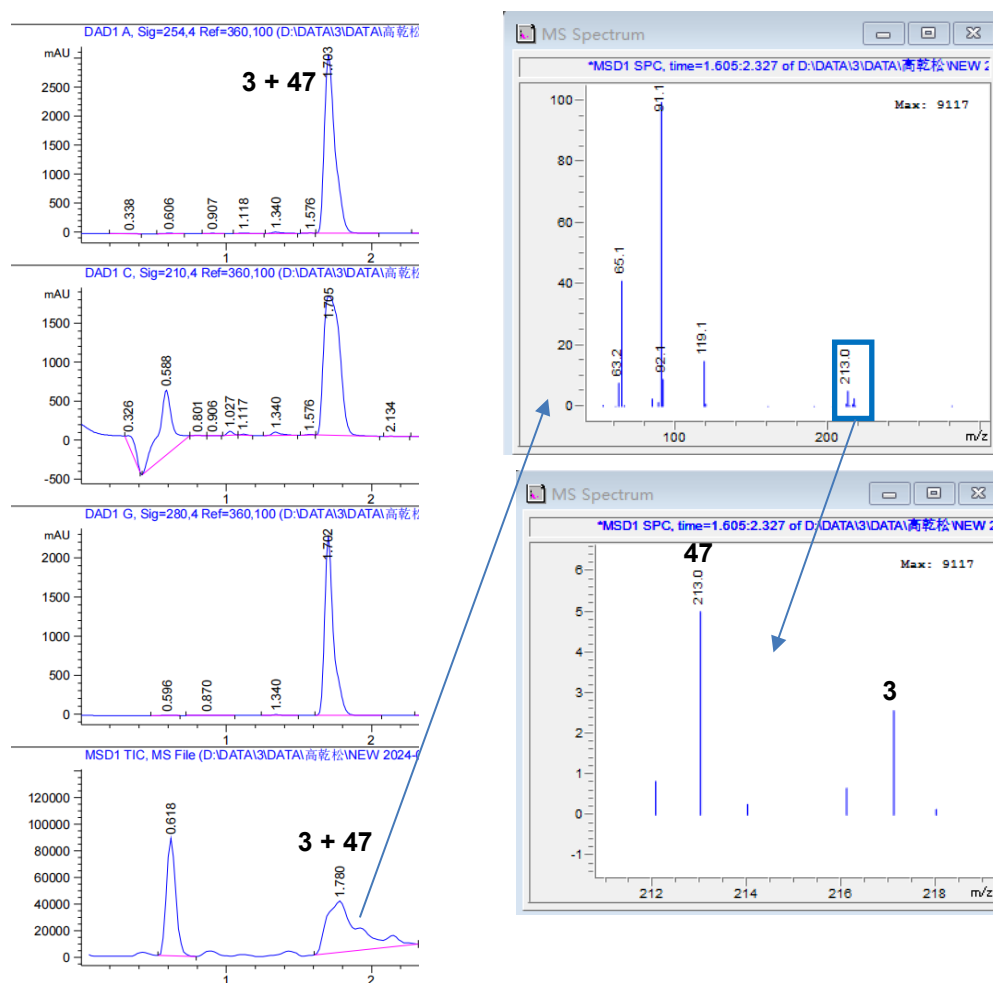
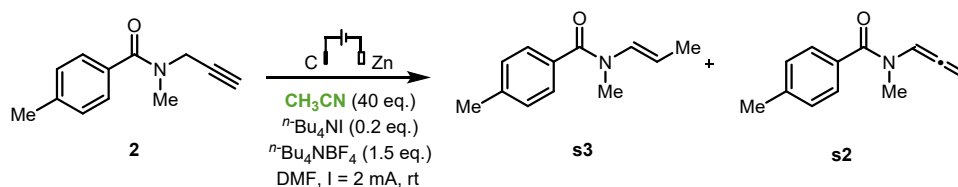


Figure S2: The m/z peak height ratio of **3** and **47** detected by LC/MS.

Characterization the ratio of s3 and s2.



A 10 mL distillation flask equipped with a magnetic stir bar was charged with compound **2** (37 mg, 0.2 mmol, 1.0 eq.), CH_3CN (0.42 mL, 40.0 eq.), $n\text{-Bu}_4\text{NI}$ (15 mg, 0.04 mmol, 0.2 eq.), $n\text{-Bu}_4\text{NBF}_4$ (99 mg, 0.3 mmol, 1.5 eq.) and DMF (3 mL). The flask equipped with graphite anode ($d = 5 \text{ mm}$) and zinc cathode ($d = 5 \text{ mm}$). The resulting solution was stirred and electrolyzed at a constant current of 2 mA (Single Output DC Power Supply: KRP-305DM) for 1 h at room temperature. The solution was diluted with EtOAc (5 mL) and brine (20 mL), and extracted with EtOAc ($3 \times 20 \text{ mL}$). The combined organic layers were washed with brine ($3 \times 20 \text{ mL}$), dried over Na_2SO_4 , and concentrated *in vacuo*. Purification by flash column chromatography using PE/EtOAc ($v/v = 10/1$) as eluent afforded the mixture product **s3** and **s2** (22mg) as yellow oil. The structure of **s2** in the reaction mixture was verified by comparison of the ^1H NMR spectrum of **s2** and Figure S3.

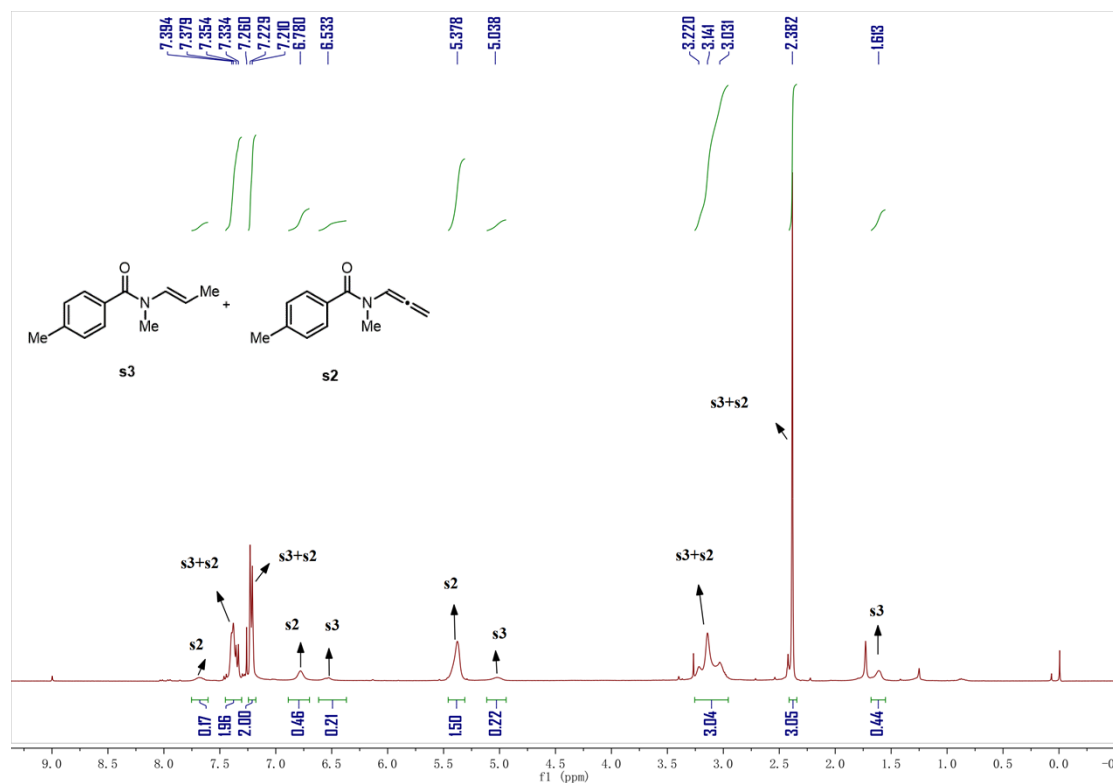
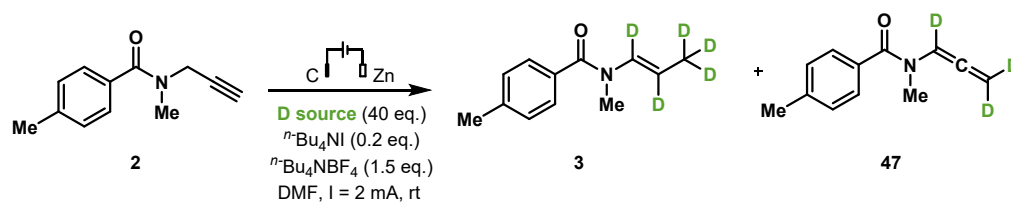
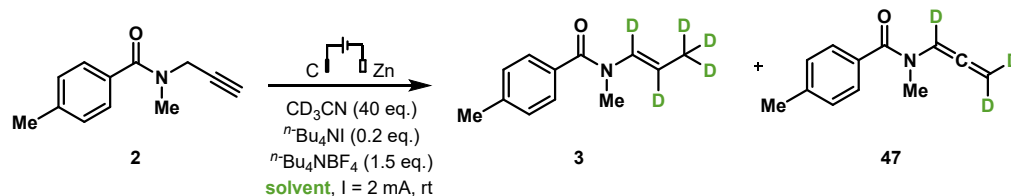


Figure S3: ^1H NMR (400 HZ, CDCl_3) of the mixture product **s3** and **s2**

Table S1. Investigation of deuterium source^a:

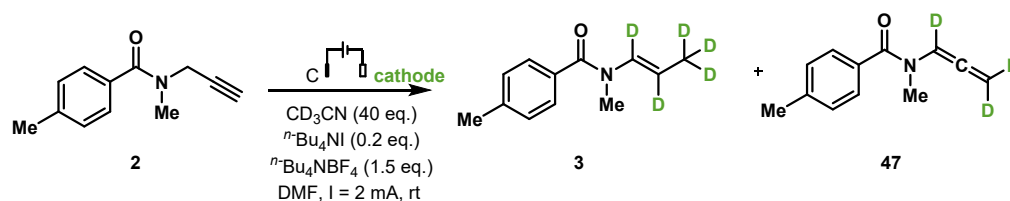
entry	variation of deuterium source	yield ^b (3:47) ^c	D/molecule
1	CD ₃ CN	56 (1:1.95)	ND ^d
2	CD ₃ OD	0	ND ^d
3	EtOD	0	ND ^d
4	D ₂ O	0	ND ^d
5	(CD ₃) ₂ SO	39 (1:0.83)	ND ^d
6	(CD ₃) ₂ CO	0	ND ^d

^aReaction conditions: Graphite anode (d = 5 mm), zinc cathode (d = 5 mm), **2** (0.2 mmol), deuterium source (40 eq.), *n*-Bu₄NI (0.2 eq.), *n*-Bu₄NBF₄ (1.5 eq.), DMF (3 mL), undivided cell, constant current = 2 mA, room temperature, 1 h. ^bIsolated yield. ^cThe m/z peak height ratio of **3** and **47** was detected by LC/MS. ^dND = not determined by ¹H NMR.

Table S2. Investigation of solvent^a:

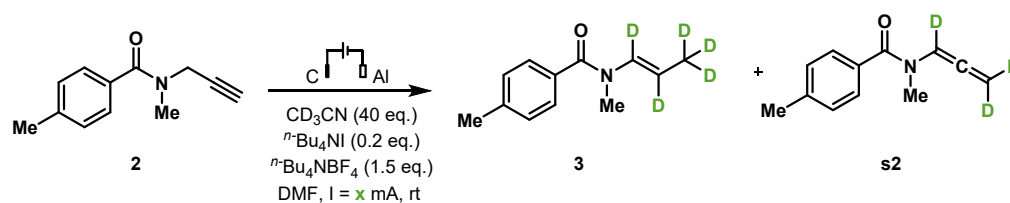
entry	variation of solvent (3 mL)	yield ^b (3:47) ^c	D/molecule
1	MeCN	0	ND ^d
2	DCM	0	ND ^d
3	NMP	trace	ND ^d
4	THF	0	ND ^d
5	DMA	39 (1:1)	ND ^d

^aReaction conditions: Graphite anode (d = 5 mm), zinc cathode (d = 5 mm), **2** (0.2 mmol), CD₃CN (40 eq.), *n*-Bu₄NI (0.2 eq.), *n*-Bu₄NBF₄ (1.5 eq.), solvent (3 mL), undivided cell, constant current = 2 mA, room temperature, 1 h. ^bIsolated yield. ^cThe m/z peak height ratio of **3** and **47** was detected by LC/MS. ^dND = not determined by ¹H NMR.

Table S3. Investigation of cathode^a:

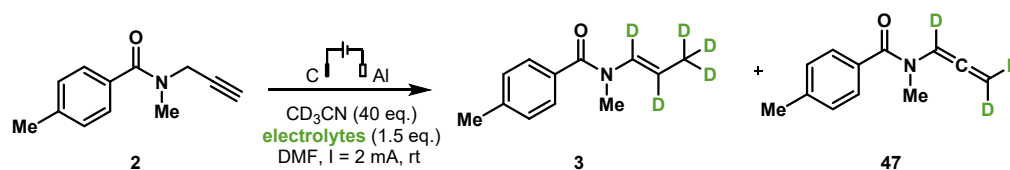
entry	variation of cathode	yield ^b (3 : 47) ^c	D/molecule
1	Pt	52 (1:1.5)	ND ^d
2	Cu	52 (1:1.3)	ND ^d
3	Mo	52 (1:1.8)	ND ^d
4	steel	58 (1:1.1)	ND ^d
5	Ti	58 (1:1.3)	ND ^d
6	Mg	55 (1:2)	ND ^d
7	Al	58 (1:1)	ND ^d

^aReaction conditions: Graphite anode (d = 5 mm), cathode (d = 5 mm), **2** (0.2 mmol), CD_3CN (40 eq.), $n\text{-Bu}_4\text{NI}$ (0.2 eq.), $n\text{-Bu}_4\text{NBF}_4$ (1.5 eq.), DMF (3 mL), undivided cell, constant current = 2 mA, room temperature, 1 h. ^bIsolated yield. ^cThe m/z peak height ratio of **3** and **47** was detected by LC/MS. ^dND = not determined by ¹H NMR.

Table S4. Investigation of current and time^a:

entry	variation of current and time	yield ^b (3 : 47) ^c	D/molecule
2	4 mA, 3h	28% (1:0.1)	ND ^d
3	3 mA, 4h	32% (1:0.03)	ND ^d
4	2 mA, 6h	36% (1:0)	4.85

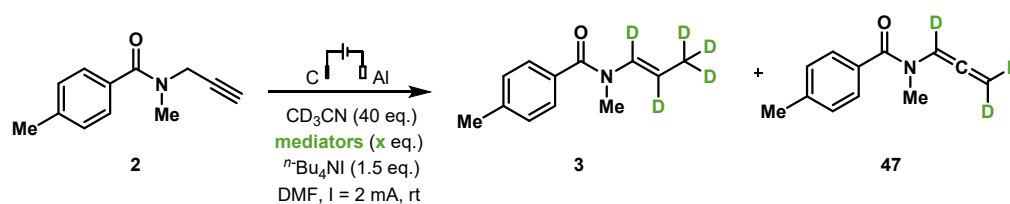
^aReaction conditions: Graphite anode (d = 5 mm), aluminium cathode (d = 5 mm), **2** (0.2 mmol), CD_3CN (40 eq.), $n\text{-Bu}_4\text{NI}$ (0.2 eq.), $n\text{-Bu}_4\text{NBF}_4$ (1.5 eq.), DMF (3 mL), undivided cell, constant current = x mA, room temperature, 3-6 h. ^bIsolated yield. ^cThe m/z peak height ratio of **3** and **47** was detected by LC/MS. ^dND = not determined by ¹H NMR.

Table S5. Investigation of electrolytes^a:

entry	variation of electrolytes	yield ^b (3 : 47) ^c	D/molecule
1	<i>n</i> -Bu ₄ NPF ₆	72% (1:0.4)	ND ^d
2	<i>n</i> -Bu ₄ NClO ₄	39% (1:0.3)	ND ^d
3	LiClO ₄	0	ND ^d
4	<i>n</i> -Bu ₄ NBr	39% (1:0.3)	ND ^d
5	<i>n</i> -Bu ₄ NI	62% (1:0.25)	ND ^d
6 ^d	<i>n</i> -Bu ₄ NI	39% (1:0)	4.88

^aReaction conditions: Graphite anode (d = 5 mm), aluminium cathode (d = 5 mm), **2** (0.2 mmol), CD₃CN (40 eq.), electrolytes (1.5 eq.), DMF (3 mL), undivided cell, constant current = 2 mA, room temperature, 3 h. ^bIsolated yield.

^cThe m/z peak height ratio of **3** and **47** was detected by LC/MS. ^dND = not determined by ¹H NMR.

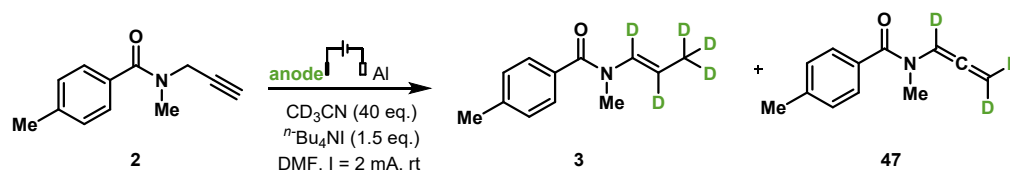
Table S6. Investigation of mediators^a:

entry	variation of mediators	yield ^b (3 : 47) ^c	D/molecule
1	TEMPO (0.2 eq.)	28 (1:0)	ND ^d
2	FeCl ₃ (0.2 eq.)	34 (1:0)	ND ^d
3	Phenanthrene (2 eq.)	39 (1:0)	ND ^d
4 ^e	PPh ₃ (2 eq.)	52 (1:0)	4.88
5	DIPEA (2 eq.)	31 (1:0)	ND ^d

^aReaction conditions: Graphite anode (d = 5 mm), aluminium cathode (d = 5 mm), **2** (0.2 mmol), CD₃CN (40 eq.), mediators (x eq.), *n*-Bu₄NI (1.5 eq.), DMF (3 mL), undivided cell, constant current = 2 mA, room temperature, 6 h.

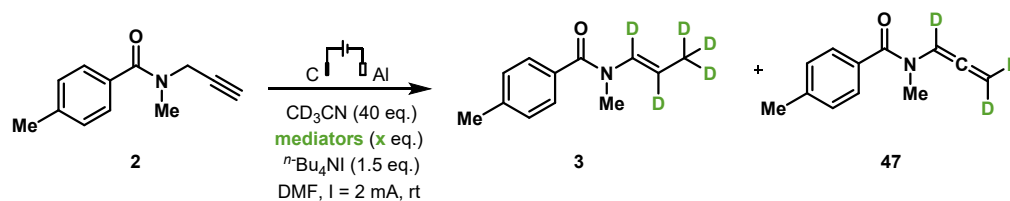
^bIsolated yield. ^cThe m/z peak height ratio of **3** and **47** was detected by LC/MS. ^dND = not determined by ¹H NMR.

^e7h instead of 6h.

Table S7. Investigation of anode^a:

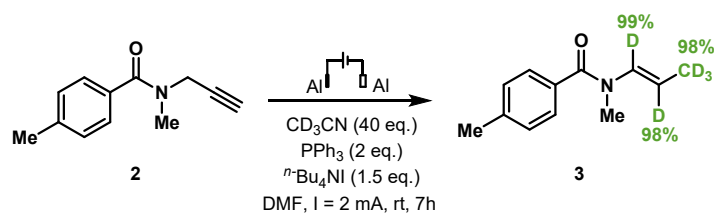
entry	variation of anode	yield ^b (3:47) ^c	D/molecule
1	Zn	49 (1:0)	ND ^d
2	Cu	28 (1:0)	ND ^d
3	Pt	42 (1:0)	ND ^d
4	Mo	15 (1:0)	ND ^d
5	Ti	26 (1:0)	ND ^d
6	Mg	31 (1:0)	ND ^d
7	Al	52 (1:0)	ND ^d

^aReaction conditions: Anode (d = 5 mm), aluminium cathode (d = 5 mm), **2** (0.2 mmol), CD₃CN (40 eq.), ⁿBu₄NI (1.5 eq.), DMF (3 mL), undivided cell, constant current = 2 mA, room temperature, 6 h. ^bIsolated yield. ^cThe m/z peak height ratio of **3** and **47** was detected by LC/MS. ^dND = not determined by ¹H NMR.

Table S8. Investigation of the amount of PPh₃^a:

entry	variation of the amount of PPh ₃	yield ^b (3:47) ^c	D/molecule
1	PPh ₃ (1 eq.)	62 (1:0)	ND ^d
2	PPh ₃ (2 eq.)	72 (1:0)	4.91
3	PPh ₃ (3 eq.)	72 (1:0)	ND ^d

^aReaction conditions: Aluminium anode (d = 5 mm), aluminium cathode (d = 5 mm), **2** (0.2 mmol), CD₃CN (40 eq.), mediators (x eq.), ⁿBu₄NI (1.5 eq.), DMF (3 mL), undivided cell, constant current = 2 mA, room temperature, 7 h. ^bIsolated yield. ^cThe m/z peak height ratio of **3** and **47** was detected by LC/MS. ^dND = not determined by ¹H NMR.

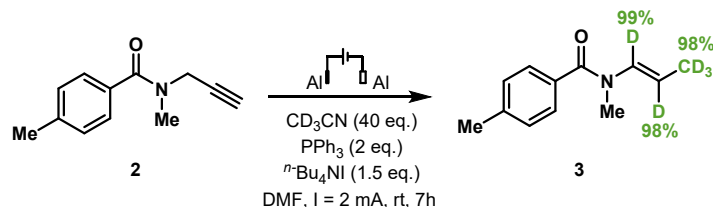
Table S9. Control reactions of optimized conditions^a:

entry	variation from standard conditions	D/molecule of 3 ^b
1	none	4.91 (72%) ^c
2	no PPh ₃	4.87 (49 %) ^c
3	<i>n</i> -Bu ₄ NBF ₄ instead of <i>n</i> -Bu ₄ NI	4.88 (28 %) ^d
4	D ₂ O instead of CD ₃ CN	trace ^c
5	DMSO- <i>d</i> ₆ instead of CD ₃ CN	4.83 (52%) ^c
6	CH ₂ Cl ₂ instead of DMF	-
7	EtOH instead of DMF	-
8	graphite (+) instead of aluminium (+)	4.88 (52%) ^c
9	3 mA, 4.7 h instead of 2mA, 7h	4.90 (59%) ^c
10	no electric current	0

^aStandard conditions: Aluminium anode (d = 5 mm), aluminium cathode (d = 5 mm), **2** (0.2 mmol), CD₃CN (40 eq.), PPh₃ (2 eq.), *n*-Bu₄NI (1.5 eq.), DMF (3 mL), undivided cell, constant current = 2 mA, room temperature, 7 h. ^bThe number of incorporated deuterium atoms per molecule. ^cIsolated yields in parentheses. ^dYield was determined by ¹H NMR spectroscopy with 1,3,5-trimethoxybenzene as an internal standard. ^e7% yield of *N*,4-dimethylbenzamide was obtained and 79% yield of the substrate **2** was recovered.

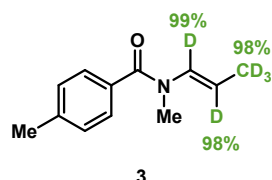
IV. Experimental Procedures and Compound Characterization

General procedure for electroreductive deuteration of *N*-propynylamides to enamides (Procedure A):



A 10 mL distillation flask equipped with a magnetic stir bar was charged with compound **2** (37 mg, 0.2 mmol, 1.0 eq.), CD_3CN (0.42 mL, 40.0 eq.), PPh_3 (105 mg, 0.4 mmol, 2.0 eq.), $n\text{-Bu}_4\text{NI}$ (111 mg, 0.3 mmol, 1.5 eq.) and DMF (3 mL). The flask equipped with aluminium anode ($d = 5 \text{ mm}$) and aluminium cathode ($d = 5 \text{ mm}$). The resulting solution was stirred and electrolyzed at a constant current of 2 mA (Single Output DC Power Supply: KRP-305DM) for 7 h at room temperature. The solution was diluted with EtOAc (5 mL) and brine (20 mL), and extracted with EtOAc ($3 \times 20 \text{ mL}$). The combined organic layers were washed with brine ($3 \times 20 \text{ mL}$), dried over Na_2SO_4 , and concentrated *in vacuo*. Purification by flash column chromatography using PE/EtOAc ($v/v = 10/1$) as eluent afforded the desired product **3**.

(*E*)-*N*,4-Dimethyl-*N*-(prop-1-en-1-yl- d_5)benzamide (**3**)



Colourless liquid (28 mg, 72% yield, 4.91 D/molecule);

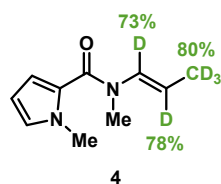
$^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.34 (d, $J = 8.0 \text{ Hz}$, 2H), 7.21 (d, $J = 8.0 \text{ Hz}$, 2H), 6.53 (s, 0.01H), 5.00 (s, 0.02H), 3.20 (s, 3H), 2.38 (s, 3H), 1.58 (s, 0.06H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 170.2, 140.3, 132.8, 129.6, 129.2, 129.0, 128.1, 105.1, 30.4, 21.5, 14.7.

HRMS (ESI): Calcd. for $\text{C}_{12}\text{H}_{11}\text{D}_5\text{NO}^+$ [$\text{M} + \text{H}$] $^+$: 195.1540, found: 195.1547.

(*E*)-*N*,1-Dimethyl-*N*-(prop-1-en-1-yl- d_5)-1*H*-pyrrole-2-carboxamide (**4**)

Following Procedure A, using 13 h instead of 7 h.



Colourless liquid (22 mg, 60% yield, 3.91 D/molecule);

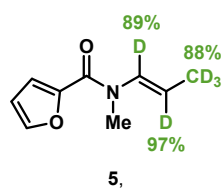
¹H NMR (400 MHz, CDCl₃): δ 6.71 (d, *J* = 10.9 Hz, 1H), 6.47 (m, 1H), 6.09 (d, *J* = 15.9 Hz, 1H), 5.85 (s, 0.27H), 5.01 (s, 0.22H), 3.94 (s, 1.9H), 3.80 (s, 1.1H), 3.22 (s, 1.1H), 2.92 (s, 1.9H), 2.43 (d, *J* = 9.8 Hz, 0.6H).

¹³C NMR (101 MHz, CDCl₃): δ 162.5, 130.9, 127.3, 125.2, 115.5, 107.2, 104.9, 36.1, 31.7, 14.3.

HRMS (ESI): Calcd. for C₁₀H₁₀D₅N₂O⁺ [M + H]⁺: 184.1493, found: 184.1500.

(*E*)-*N*-Methyl-*N*-(prop-1-en-1-yl-*d*₅)furan-2-carboxamide (5)

Following Procedure A, using 11.5 h instead of 7 h.



Colourless liquid (18 mg, 53% yield, 4.50 D/molecule);

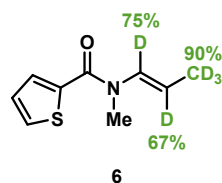
¹H NMR (400 MHz, CDCl₃): δ 7.55 (s, 1H), 7.09 (s, 0.11H), 7.01 (s, 1H), 6.50 (s, 1H), 5.45 (s, 0.03H), 3.26 (s, 3H), 1.73 (s, 0.36H).

¹³C NMR (101 MHz, CDCl₃): δ 158.9, 147.6, 144.6, 117.7, 117.3, 111.4, 107.5, 31.6, 14.9.

HRMS (ESI): Calcd. for C₉H₇D₅NO₂⁺ [M + H]⁺: 171.1176, found: 171.1173.

(*E*)-*N*-Methyl-*N*-(prop-1-en-1-yl-*d*₅)thiophene-2-carboxamide (6)

Following Procedure A, using 18 h instead of 7 h.



Colourless liquid (15 mg, 40% yield, 4.12 D/molecule);

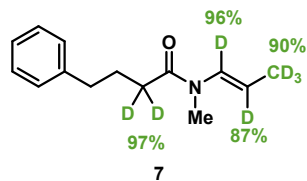
¹H NMR (400 MHz, CDCl₃): δ 7.51 – 7.46 (m, 1H), 7.40 (d, *J* = 3.6 Hz, 1H), 7.13 – 7.02 (m, 1H), 6.84 (s, 0.25H), 5.36 (m, 0.33H), 3.24 (d, *J* = 21.4 Hz, 3H), 1.70 (s, 0.3H).

¹³C NMR (101 MHz, CDCl₃): δ 163.1, 137.7, 130.7, 130.0, 127.0, 120.4, 115.5, 29.8, 14.9.

HRMS (ESI): Calcd. for C₉H₇D₅NOS⁺ [M + H]⁺: 187.0948, found: 187.0944.

(*E*)-*N*-Methyl-4-phenyl-*N*-(prop-1-en-1-yl-*d*₅)butanamide-2,2-*d*₂ (7)

Following Procedure A.



Colourless liquid (27 mg, 61% yield, 6.47 D/molecule);

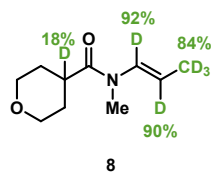
¹H NMR (300 MHz, CDCl₃): δ 7.30 (m, 2H), 7.20 (d, *J* = 6.9 Hz, 3H), 6.51 (s, 0.04H), 4.97 (s, 0.13H), 3.08 – 2.95 (m, 3H), 2.69 (t, *J* = 7.5 Hz, 2H), 2.42 – 2.38 (m, 0.06H), 1.99 (t, *J* = 7.5 Hz, 2H), 1.66 (s, 0.3H).

¹³C NMR (101 MHz, CDCl₃): δ 171.0, 141.6, 128.5, 128.4, 126.3, 126.0, 106.3, 35.2, 32.2, 29.8, 26.4, 14.9.

HRMS (ESI): Calcd. for C₁₄H₁₃D₇NO⁺ [M + H]⁺: 225.1979, found: 225.1980.

(*E*)-*N*-Methyl-*N*-(prop-1-en-1-yl-*d*₅)tetrahydro-2*H*-pyran-4-carboxamide-4-*d* (8)

Following Procedure A, using 11 h instead of 7 h.



Colourless liquid (23 mg, 61% yield, 4.52 D/molecule);

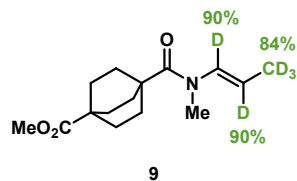
¹H NMR (400 MHz, CDCl₃): δ 6.67 (s, 0.08H), 5.03 (s, 0.1H), 4.03 (d, *J* = 11.3 Hz, 2H), 3.48 (t, *J* = 11.3 Hz, 2H), 3.12 (s, 1H), 3.07 (s, 2H), 2.86 (d, *J* = 11.8 Hz, 0.82H), 1.90 (t, *J* = 11.3 Hz, 2H), 1.71 – 1.64 (m, 2.48 H).

¹³C NMR (101 MHz, CDCl₃): δ 172.8, 172.3, 128.3, 128.1, 107.5, 67.2, 38.6, 38.2, 32.2, 30.4, 28.9, 28.9, 14.9.

HRMS (ESI): Calcd. for C₁₀H₁₁D₆NO₂Na⁺ [M + Na]⁺: 212.1528, found: 212.1531.

Methyl (*E*)-4-(methyl(prop-1-en-1-yl-*d*₅)carbamoyl)bicyclo[2.2.2]octane-1-carboxylate (9)

Following Procedure A, using 11 h instead of 7 h.



White solid (33 mg, 61% yield, 4.32 D/molecule); m.p. 97 – 99 °C;

¹H NMR (400 MHz, CDCl₃): δ 7.01 (s, 0.1H), 4.97 (s, 0.1H), 3.65 (s, 3H), 3.09 (s, 3H), 1.95 (d, *J* =

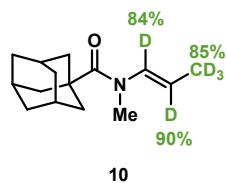
8.0 Hz, 6H), 1.85 (d, $J = 8.0$ Hz, 6H), 1.69 (s, 0.48H).

^{13}C NMR (101 MHz, CDCl_3): δ 177.9, 174.9, 130.4, 106.2, 51.8, 40.4, 40.2, 38.8, 33.2, 28.0, 14.8.

HRMS (ESI): Calcd. for $\text{C}_{15}\text{H}_{19}\text{D}_5\text{NO}_3^+$ [$\text{M} + \text{H}$] $^+$: 271.2065, found: 271.2068.

(1R,3R,5S)-N-Methyl-N-((E)-prop-1-en-1-yl- d_5)adamantane-1-carboxamide (10)

Following Procedure A, using 12 h instead of 7 h.



White solid (29 mg, 61% yield, 4.29 D/molecule); m.p. 90 – 92 °C;

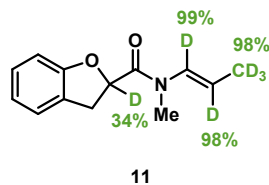
^1H NMR (400 MHz, CDCl_3): δ 7.16 (s, 0.16H), 4.95 (s, 0.1H), 3.11 (s, 3H), 2.05 (s, 9H), 1.73 (s, 6H), 1.70 (s, 0.45H).

^{13}C NMR (101 MHz, CDCl_3): δ 175.6, 130.7, 105.5, 42.5, 39.1, 36.7, 33.1, 28.5, 15.1.

HRMS (ESI): Calcd. for $\text{C}_{15}\text{H}_{19}\text{D}_5\text{NO}^+$ [$\text{M} + \text{H}$] $^+$: 239.2166, found: 239.2157.

(E)-N-Methyl-N-(prop-1-en-1-yl- d_5)-2,3-dihydrobenzofuran-2-carboxamide- $2-d$ (11)

Following Procedure A, using 11 h instead of 7 h.



Yellow liquid (27 mg, 61% yield, 5.25 D/molecule);

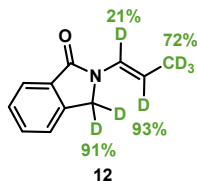
^1H NMR (400 MHz, CDCl_3): δ 7.20 (d, $J = 7.5$ Hz, 1H), 7.13 (t, $J = 7.5$ Hz, 1H), 6.91 – 6.86 (m, 1H), 6.83 (t, $J = 7.5$ Hz, 1H), 5.95 (s, 0.01H), 5.45 (m, 0.66H), 5.00 (s, 0.02H), 3.77 (t, $J = 14.8$ Hz, 1H), 3.38 (dd, $J = 14.8, 7.1$ Hz, 1H), 3.21 (s, 1.4H), 3.07 (s, 1.6H), 1.55 (s, 0.06H).

^{13}C NMR (101 MHz, CDCl_3): δ 167.2, 158.5, 129.7, 128.3, 125.8, 125.7, 125.0, 121.4, 121.3, 115.5, 109.7, 109.6, 33.0, 32.3, 32.2, 31.9, 14.6 – 13.8(m).

HRMS (ESI): Calcd. for $\text{C}_{10}\text{H}_{12}\text{D}_6\text{NO}_2^+$ [$\text{M} + \text{H}$] $^+$: 190.1709, found: 190.1703.

(E)-2-(Prop-1-en-1-yl- d_5)isoindolin-1-one-3,3- d_2 (12)

Following Procedure A, using 6 h instead of 7 h.



Colourless liquid (22 mg, 61% yield, 5.12 D/molecule);

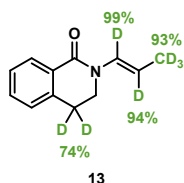
¹H NMR (300 MHz, DMSO-*d*₆): δ 7.72 (dt, *J* = 7.5, 1.0 Hz, 1H), 7.66 – 7.59 (m, 2H), 7.50 (dd, *J* = 7.5, 1.9 Hz, 1H), 6.97 (s, 0.79H), 5.26 (s, 0.07H), 4.60 (s, 0.18H), 1.71 (s, 0.84H).

¹³C NMR (101 MHz, CDCl₃): δ 166.0, 140.6, 132.6, 132.0, 128.3, 124.1, 123.9, 122.8, 106.2 – 105.7 (m), 48.2 – 47.5 (m), 15.2 – 14.51 (m).

HRMS (ESI): Calcd. for C₁₁H₅D₇NO⁺ [M + H]⁺: 181.1353, found: 181.1357.

(*E*)-2-(Prop-1-en-1-yl-*d*₃)-3,4-dihydroisoquinolin-1(2*H*)-one-4,4-*d*₂ (13)

Following Procedure A, using 10 h instead of 7 h.



Colourless liquid (27 mg, 70% yield, 6.20 D/molecule);

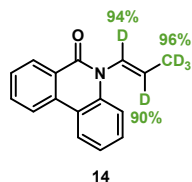
¹H NMR (300 MHz, CDCl₃): δ 8.09 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.42 (td, *J* = 7.4, 1.5 Hz, 1H), 7.33 (td, *J* = 7.6, 1.4 Hz, 1H), 7.19 (dd, *J* = 7.4, 1.4 Hz, 1H), 6.91 (s, 0.01H), 5.13 (s, 0.06H), 3.70 (d, *J* = 5.1 Hz, 2H), 3.08 – 2.98 (m, 0.52H), 1.77 – 1.72 (s, 0.21H).

¹³C NMR (101 MHz, CDCl₃): δ 162.1, 137.7, 132.0, 129.2, 128.7, 127.5, 127.2, 126.9, 106.4, 42.8, 27.4, 27.1, 14.2.

HRMS (ESI): Calcd. for C₁₂H₇D₇NO⁺ [M + H]⁺: 195.1509, found: 195.1513.

(*E*)-5-(Prop-1-en-1-yl-*d*₃)phenanthridin-6(5*H*)-one (14)

Following Procedure A, using 12 h instead of 7 h.



Colourless liquid (30 mg, 63% yield, 4.72 D/molecule);

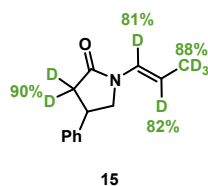
¹H NMR (300 MHz, CDCl₃): δ 8.57 (d, *J* = 7.8 Hz, 1H), 8.30 (d, *J* = 8.3 Hz, 2H), 7.78 (t, *J* = 7.8 Hz, 1H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 8.3 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 6.01 (s, 0.06H), 5.04 (s, 0.10H), 1.54 (s, 0.12H).

¹³C NMR (101 MHz, CDCl₃): δ 161.3, 137.1, 133.7, 132.7, 132.5, 129.4, 128.9, 127.9, 125.4, 123.2, 122.8, 122.4, 121.6, 119.3, 115.7, 44.4.

HRMS (ESI): Calcd. for C₁₆H₉D₅NO⁺ [M + H]⁺: 241.1384, found: 241.1395.

(*E*)-4-Phenyl-1-(prop-1-en-1-yl-*d*₅)pyrrolidin-2-one-3,3-*d*₂ (15)

Following Procedure A, using 12 h instead of 7 h.



Colourless liquid (29 mg, 70% yield, 6.07 D/molecule);

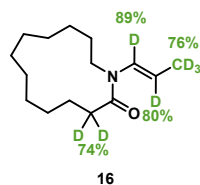
¹H NMR (400 MHz, CDCl₃): δ 7.35 (t, *J* = 7.5 Hz, 2H), δ 7.28 (d, *J* = 7.5 Hz, 1H), 7.23 (d, *J* = 7.5 Hz, 2H), 6.94 (s, 0.19H), 4.93 (s, 0.18H), 3.89 (t, *J* = 9.1 Hz, 1H), 3.61 (t, *J* = 9.1 Hz, 1H), 3.51 – 3.46 (m, 1H), 2.62 (s, 0.2H), 1.70 (s, 0.36H).

¹³C NMR (101 MHz, CDCl₃): δ 171.4, 142.4, 129.0, 127.3, 126.8, 124.1, 106.9, 53.0, 52.6, 36.8, 14.7.

HRMS (ESI): Calcd. for C₁₃H₉D₇NO⁺ [M + H]⁺: 209.1666, found: 209.1673.

(*E*)-1-(Prop-1-en-1-yl-*d*₅)azacyclotridecan-2-one-3,3-*d*₂ (16)

Following Procedure A, using 11 h instead of 7 h.



Colourless liquid (33 mg, 68% yield, 5.45 D/molecule);

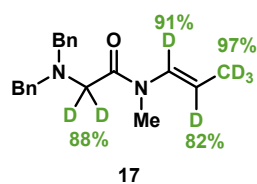
¹H NMR (400 MHz, CDCl₃): δ 6.53 (s, 0.11H), 5.02 (s, 0.2H), 4.49 (t, *J* = 11.9 Hz, 1H), 3.43 (t, *J* = 8.1 Hz, 1H), 2.99 (d, *J* = 11.9 Hz, 1H), 2.27 (s, 0.52H), 1.74 (m, 4.72H), 1.48 (s, 4H), 1.28 (s, 9H).

¹³C NMR (101 MHz, CDCl₃): δ 172.6, 171.8, 128.5, 107.4, 43.8, 42.2, 33.9 – 33.5(m), 26.9, 26.7, 26.4, 26.0, 25.4, 24.9, 24.7, 24.4, 24.3, 24.2, 23.9, 23.5, 23.2, 15.2.

HRMS (ESI): Calcd. for C₁₅H₂₁D₇NO⁺ [M + H]⁺: 245.2605, found: 245.2614.

(*E*)-2-(Dibenzylamino)-*N*-methyl-*N*-(prop-1-en-1-yl-*d*₅)acetamide-*d*₂ (17)

Following Procedure A, using 21 h instead of 7 h.



Colourless liquid (40 mg, 63% yield, 6.40 D/molecule);

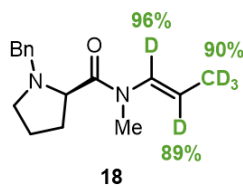
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.39 – 7.19 (m, 10H), 6.67 (s, 0.09H), 4.90 (s, 0.18H), 3.69 (s, 1H), 3.65 (s, 3H), 3.35 (s, 0.24H), 2.99 (s, 2.28H), 2.93 (s, 0.72H), 1.67 (s, 0.09H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 169.0, 168.7, 138.7, 129.3, 129.3, 128.4, 127.3, 105.4, 58.6, 58.4, 56.8 – 55.9(m), 32.1, 29.6, 14.7 – 14.3(m).

HRMS (ESI): Calcd. for $\text{C}_{20}\text{H}_{18}\text{D}_7\text{N}_2\text{O}^+$ $[\text{M} + \text{H}]^+$: 316.2401, found: 316.2408.

(R,E)-1-Benzyl-N-methyl-N-(prop-1-en-1-yl- d_5)pyrrolidine-2-carboxamide (18)

Following Procedure A, using 10 h instead of 7 h.



Colourless liquid (32 mg, 60% yield, 4.55 D/molecule);

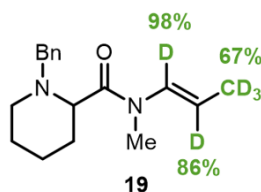
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.28 (s, 5H), 6.92 (s, 0.04H), 4.98 (s, 0.11H), 3.94 (t, $J = 14.6$ Hz, 1H), 3.52 – 3.43 (m, 2H), 3.09 (s, 1H), 3.06 (s, 3H), 2.35 (d, $J = 9.0$ Hz, 1H), 2.15 (s, 1H), 1.91 (m, 2H), 1.81 (t, $J = 9.0$ Hz, 1H), 1.67 (s, 0.3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 171.5, 138.5, 129.3, 128.9, 128.2, 127.0, 106.5, 65.1, 58.1, 52.7, 31.9, 30.5, 29.0, 22.8.

HRMS (ESI): Calcd. for $\text{C}_{16}\text{H}_{18}\text{D}_5\text{N}_2\text{O}^+$ $[\text{M} + \text{H}]^+$: 264.2119, found: 264.2118.

(E)-1-Benzyl-N-methyl-N-(prop-1-en-1-yl- d_5)piperidine-2-carboxamide (19)

Following Procedure A, using 13 h instead of 7 h.



Colourless liquid (28 mg, 50% yield, 3.85 D/molecule);

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.28 (s, 5H), 6.99 (s, 0.02H), 5.01 (0.14H), 3.80 (t, $J = 13.2$ Hz, 1H),

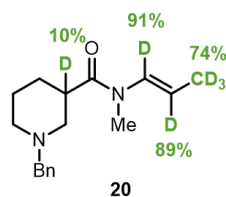
3.38 –3.09 (m, 5H), 2.96 (d, $J = 12.4$ Hz, 1H), 1.97 (s, 1H), 1.77 (m, 3.99H), 1.55 (s, 2H), 1.33 (s, 1H).

^{13}C NMR (101 MHz, CDCl_3): δ 171.6, 171.1, 138.2, 138.0, 129.2, 128.2, 127.0, 105.7, 59.8, 51.6, 32.1, 30.4, 28.3, 28.1, 24.9, 24.8, 23.7, 23.6, 14.9.

HRMS (ESI): Calcd. for $\text{C}_{17}\text{H}_{20}\text{D}_5\text{N}_2\text{O}^+$ [$\text{M} + \text{H}$] $^+$: 278.2275, found: 278.2280.

(*E*)-1-Benzyl-*N*-methyl-*N*-(prop-1-en-1-yl- d_5)piperidine-3-carboxamide (20)

Following Procedure A, using 12 h instead of 7 h.



Colourless liquid (28 mg, 51% yield, 4.12 D/molecule);

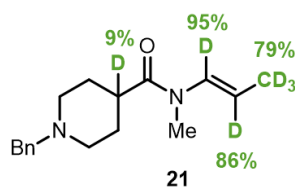
^1H NMR (400 MHz, CDCl_3): δ 7.28 (m, 5H), 6.65 (s, 0.09H), 4.98 (s, 0.11H), 3.59 – 3.41 (m, 2H), 3.05 (s, 0.78H), 3.01 (s, 2.22H), 2.91 (m, 2.9H), 2.16 (d, $J = 11.1$ Hz, 1H), 2.00 (t, $J = 11.1$ Hz, 1H), 1.82 (s, 1H), 1.77 – 1.63 (m, 2.78H), 1.52 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3): δ 172.8, 138.4, 129.3, 128.6, 128.3, 127.1, 107.2, 63.5, 55.9, 54.0, 40.3, 32.2, 30.2, 27.6, 25.1.

HRMS (ESI): Calcd. for $\text{C}_{17}\text{H}_{20}\text{D}_5\text{N}_2\text{O}^+$ [$\text{M} + \text{H}$] $^+$: 278.2275, found: 278.2283.

(*E*)-1-Benzyl-*N*-methyl-*N*-(prop-1-en-1-yl- d_5)piperidine-4-carboxamide (21)

Following Procedure A, using 27 h instead of 7 h.



Colourless liquid (19 mg, 35% yield, 4.27 D/molecule);

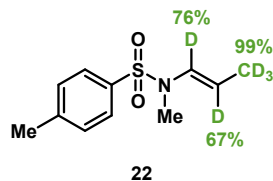
^1H NMR (400 MHz, CDCl_3): δ 7.33 (s, 5H), 6.64 (s, 0.05H), 5.03 (s, 0.14H), 3.57 (s, 2H), 3.09 (s, 0.8H), 3.05 (s, 2.2H), 2.99 (d, $J = 11.1$ Hz, 2H), 2.62 (s, 0.91H), 2.10 (s, 2H), 1.87 (m, 2.63H), 1.76 (s, 2H).

^{13}C NMR (101 MHz, CDCl_3): δ 173.5, 173.1, 138.3, 129.1, 128.5, 128.2, 127.0, 106.9, 63.2, 53.1, 39.7, 39.3, 32.1, 30.2, 28.6, 15.3 – 14.6 (m).

HRMS (ESI): Calcd. for $\text{C}_{17}\text{H}_{20}\text{D}_5\text{N}_2\text{O}^+$ [$\text{M} + \text{H}$] $^+$: 278.2275, found: 278.2283.

(*E*)-*N*,4-Dimethyl-*N*-(prop-1-en-1-yl- d_5)benzenesulfonamide (22)

Following Procedure A, using 8 h instead of 7 h.



Colourless liquid (28 mg, 60% yield, 4.40 D/molecule);

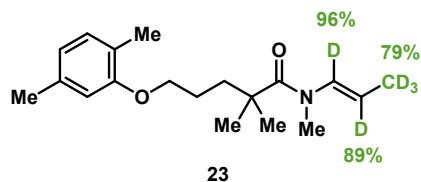
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.67 (d, $J = 8.2$ Hz, 2H), 7.32 (d, $J = 8.2$ Hz, 2H), 6.90 (s, 0.24H), 5.28 (s, 0.33H), 2.71 (s, 3H), 2.43 (s, 3H), 2.04 (s, 0.03H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 144.0, 133.8, 129.8, 127.5, 101.9, 87.4, 33.3, 21.7, 15.2.

HRMS (ESI): Calcd. for $\text{C}_{11}\text{H}_{11}\text{D}_5\text{NO}_2\text{S}^+$ $[\text{M} + \text{H}]^+$: 231.1210, found: 231.1200.

(E)-5-(2,5-Dimethylphenoxy)-N,2,2-trimethyl-N-(prop-1-en-1-yl- d_5)pentanamide (23)

Following Procedure A, using 17 h instead of 7 h.



Colourless liquid (31 mg, 50% yield, 4.22 D/molecule);

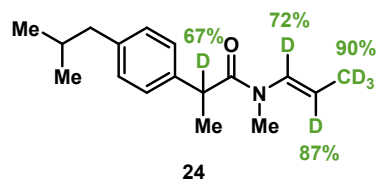
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.00 (d, $J = 7.5$ Hz, 1H), 6.85 (s, 0.04H), 6.65 (d, $J = 7.5$ Hz, 1H), 6.59 (s, 1H), 4.99 (s, 0.11H), 3.91 (t, $J = 5.9$ Hz, 2H), 3.11 (s, 3H), 2.30 (s, 3H), 2.16 (s, 3H), 1.86 (m, 2H), 1.78 – 1.67 (m, 2.63H), 1.34 (s, 6H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 175.3, 157.0, 136.5, 133.9, 130.3, 123.5, 120.7, 111.8, 106.4, 67.8, 43.2, 37.6, 33.0, 32.9, 27.3, 25.3, 21.5, 15.9, 15.2 – 14.8(m).

HRMS (ESI): Calcd. for $\text{C}_{19}\text{H}_{24}\text{D}_5\text{NO}_2\text{Na}^+$ $[\text{M} + \text{Na}]^+$: 331.2404, found: 331.2392.

(E)-2-(4-Isobutylphenyl)-N-methyl-N-(prop-1-en-1-yl- d_5)propanamide-2- d (24)

Following Procedure A, using 10.5 h instead of 7 h.



Colourless liquid (27 mg, 51% yield, 4.96 D/molecule);

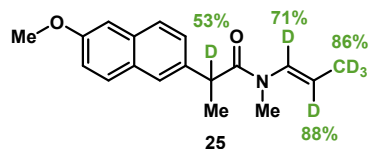
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.15 (d, $J = 7.8$ Hz, 2H), 7.08 (d, $J = 7.8$ Hz, 2H), 6.66 (s, 0.28H), 4.95 (s, 0.13H), 3.95 (q, $J = 6.6$ Hz, 0.33H), 3.07 (s, 2H), 2.93 (s, 1H), 2.43 (d, $J = 7.1$ Hz, 2H), 1.84 (m, 1H), 1.70 – 1.63 (s, 0.3H), 1.45 (d, $J = 6.6$ Hz, 3H), 0.89 (d, $J = 6.8$, 6H).

^{13}C NMR (101 MHz, CDCl_3): δ 172.6, 172.1, 140.4, 138.7, 129.8, 129.7, 127.0, 107.5, 45.2, 32.4, 30.8, 30.3, 22.5, 21.0 – 20.7(m), 15.0.

HRMS (ESI): Calcd. for $\text{C}_{17}\text{H}_{20}\text{D}_6\text{NO}^+$ $[\text{M} + \text{H}]^+$: 266.2386, found: 266.2375.

(E)-2-(6-Methoxynaphthalen-2-yl)-N-methyl-N-(prop-1-en-1-yl- d_5)propanamide-2- d (25)

Following Procedure A, using 16 h instead of 7 h.



Colourless liquid (26 mg, 45% yield, 4.70 D/molecule);

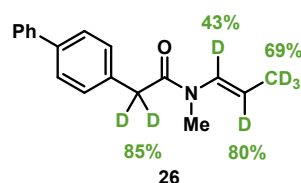
^1H NMR (400 MHz, CDCl_3): δ 7.70 (t, $J = 7.7$ Hz, 2H), 7.61 (d, $J = 7.7$ Hz, 1H), 7.37 (d, $J = 9.0$ Hz, 1H), 7.20 – 7.09 (m, 2H), 6.70 (s, 0.29H), 4.94 (s, 0.12H), 4.11 (m, 0.47H), 3.91 (s, 3H), 3.10 (s, 2H), 2.95 (s, 1H), 1.68 (s, 0.42H).

^{13}C NMR (101 MHz, CDCl_3): δ 172.5, 172.0, 157.7, 136.8, 133.6, 129.4, 129.3, 129.3, 127.8, 127.7, 126.2, 126.2, 125.7, 120.4, 119.2, 119.1, 115.5, 105.7, 55.5, 44.4, 43.7, 32.4, 30.9, 30.8, 21.1 – 20.8(m), 15.0.

HRMS (ESI): Calcd. for $\text{C}_{18}\text{H}_{16}\text{D}_6\text{NO}_2^+$ $[\text{M} + \text{H}]^+$: 290.2022, found: 290.2009.

(E)-2-([1,1'-Biphenyl]-4-yl)-N-methyl-N-(prop-1-en-1-yl- d_5)acetamide- d_2 (26)

Following Procedure A, using 24 h instead of 7 h.



Colourless liquid (27 mg, 50% yield, 5.00 D/molecule);

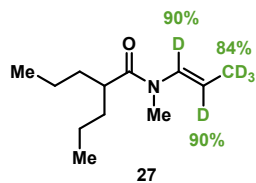
^1H NMR (400 MHz, CDCl_3): δ 7.57 (t, $J = 8.8$ Hz, 4H), 7.43 (t, $J = 7.6$ Hz, 2H), 7.33 (m, 3H), 6.72 (s, 0.57H), 5.30 (s, 0.2H), 3.84 (s, 0.3H), 3.12 (s, 2H), 3.08 (s, 1H), 1.69 (s, 0.93H).

^{13}C NMR (101 MHz, CDCl_3): δ 169.5, 141.0, 140.0, 133.8, 129.5, 129.2, 128.9, 127.6, 127.6, 127.4, 127.4, 127.2, 106.6, 33.0, 30.5, 15.2.

HRMS (ESI): Calcd. for $\text{C}_{18}\text{H}_{13}\text{D}_7\text{NO}^+$ $[\text{M} + \text{H}]^+$: 273.1979, found: 273.1983.

(E)-N-Methyl-N-(prop-1-en-1-yl- d_5)-2-propylpentanamide (27)

Following Procedure A, using 12 h instead of 7 h.



Colourless liquid (25 mg, 61% yield, 4.32 D/molecule);

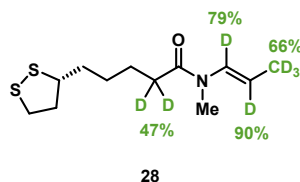
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 6.75 (s, 0.1H), 5.00 (s, 0.1H), 3.12 (s, 1H), 3.08 (s, 2H), 2.91 – 2.75 (m, 1H), 1.72 – 1.61 (m, 2.48H), 1.45 – 1.37 (m, 2H), 1.30 – 1.20 (m, 4H), 0.88 (t, $J = 7.3$ Hz, 6H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 175.0, 129.1, 107.0, 41.3, 35.1, 32.4, 30.4, 20.7, 14.3.

HRMS (ESI): Calcd. for $\text{C}_{12}\text{H}_{19}\text{D}_5\text{NO}^+$ [$\text{M} + \text{H}$] $^+$: 203.2166, found: 203.2167.

(*R,E*)-5-(1,2-Dithiolan-3-yl)-*N*-methyl-*N*-(prop-1-en-1-yl-*d*₅)pentanamide-2,2-*d*₂ (28)

Following Procedure A, using 12 h instead of 7 h.



Colourless liquid (25 mg, 48% yield, 4.61 D/molecule);

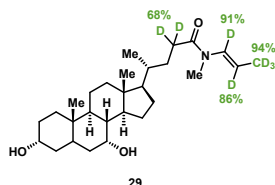
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 6.61 (s, 0.21H), 5.00 (s, 0.1H), 3.64 – 3.51 (m, 1H), 3.22 – 3.09 (m, 2H), 3.06 (s, 3H), 2.45 (m, 2H), 1.92 (m, 1.06H), 1.69 (m, 5.02H), 1.54 – 1.44 (m, 2H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 171.2, 128.9, 106.7, 56.5, 40.4, 38.6, 34.9, 34.0 – 33.4(m), 29.9, 29.1, 24.8 – 24.7(m), 15.4.

HRMS (ESI): Calcd. for $\text{C}_{12}\text{H}_{15}\text{D}_7\text{NOS}_2^+$ [$\text{M} + \text{H}$] $^+$: 267.1577, found: 267.1573.

(4*R*)-4-((3*R*,7*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3,7-Dihydroxy-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)-*N*-methyl-*N*-((*E*)-prop-1-en-1-yl-*d*₅)pentanamide-2,2-*d*₂ (29)

Following Procedure A, using 18 h instead of 7 h.



Colourless liquid (42 mg, 47% yield, 5.95 D/molecule);

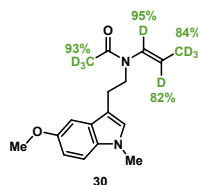
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 6.63 (s, 0.09H), 4.99 (s, 0.14H), 3.85 (s, 1H), 3.46 (s, 1H), 3.06 (s, 2H), 2.80 (s, 1H), 2.48 – 2.28 (m, 0.64H), 2.20 (q, $J = 12.4$ Hz, 1H), 2.02 – 1.76 (m, 6.18H), 1.74 – 1.56 (m, 4H), 1.54 – 1.08 (m, 15H), 0.96 (d, $J = 7.0$ Hz, 3H), 0.90 (s, 3H), 0.66 (d, $J = 4.5$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ 172.0, 171.7, 132.9, 106.3, 71.8, 68.3, 55.9, 55.8, 50.4, 42.7, 41.6, 39.8, 39.7, 39.4, 35.5, 35.4, 35.1, 34.7, 32.8, 31.0, 30.7, 29.8, 28.2, 23.7, 22.8, 20.6, 18.6, 18.5, 15.1 – 14.7(m), 14.2, 11.8.

HRMS (ESI): Calcd. for $\text{C}_{28}\text{H}_{41}\text{D}_7\text{NO}_3^+$ $[\text{M} + \text{H}]^+$: 453.4068, found: 453.4050.

(E)-N-(2-(5-Methoxy-1-methyl-1H-indol-3-yl)ethyl)-N-(prop-1-en-1-yl- d_5)acetamide- d_3 (30)

Following Procedure A, using 11.5 h instead of 7 h.



Yellow liquid (36 mg, 62% yield, 7.08 D/molecule);

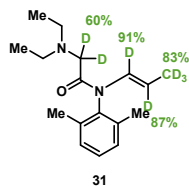
^1H NMR (400 MHz, CDCl_3): δ 7.18 (m, 1.6H), 7.03 – 6.79 (m, 2.4H), 6.48 (s, 0.05H), 5.16 (s, 0.18H), 3.88 (s, 3H), 3.84 (m, 1H), 3.75 (m, 1H), 3.72 (s, 3H), 2.99 – 2.93 (m, 2H), 2.05 (m, 0.21H), 1.72 (s, 0.48H).

^{13}C NMR (101 MHz, CDCl_3): δ 168.8, 154.0, 153.8, 132.4, 128.2, 127.9, 127.6, 127.2, 111.9, 111.3, 110.3, 110.0, 107.2, 100.8, 100.5, 56.0, 46.4, 43.8, 32.9, 32.8, 23.2, 22.7, 15.4 – 14.8(m).

HRMS (ESI): Calcd. for $\text{C}_{17}\text{H}_{15}\text{D}_8\text{N}_2\text{O}_2^+$ $[\text{M} + \text{H}]^+$: 295.2256, found: 295.2262.

(E)-2-(Diethylamino)-N-(2,6-dimethylphenyl)-N-(prop-1-en-1-yl- d_5)acetamide- d_2 (31)

Following Procedure A, using 11h instead of 7 h.



Colourless liquid (28 mg, 50% yield, 5.47 D/molecule);

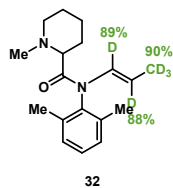
^1H NMR (400 MHz, CDCl_3): δ 7.20 (m, 1H), 7.15 – 7.07 (m, 2H), 4.98 (s, 0.09H), 4.28 (s, 0.13H), 2.89 – 2.66 (m, 0.8H), 2.54 (q, $J = 7.2$ Hz, 4H), 2.15 (m, 6H), 1.67 (s, 0.51H), 0.90 (t, $J = 7.2$ Hz, 6H).

^{13}C NMR (101 MHz, CDCl_3): δ 168.5, 136.5, 136.4, 136.3, 129.1, 128.7, 125.7, 106.4, 55.0, 54.9, 54.7, 54.5, 47.5, 17.7, 14.7 – 14.2(m), 12.1.

HRMS (ESI): Calcd. for $\text{C}_{17}\text{H}_{20}\text{D}_7\text{N}_2\text{O}^+$ $[\text{M} + \text{H}]^+$: 282.2557, found: 282.2547.

(E)-N-(2,6-Dimethylphenyl)-1-methyl-N-(prop-1-en-1-yl- d_5)piperidine-2-carboxamide (32)

Following Procedure A, using 12h instead of 7 h.



Colourless liquid (29 mg, 50% yield, 4.47 D/molecule);

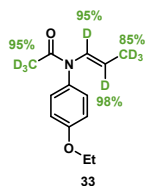
¹H NMR (400 MHz, CDCl₃): δ 7.22 (d, *J* = 7.5 Hz, 1H), 7.15 (t, *J* = 7.5 Hz, 2H), 7.08 (s, 0.11H), 4.26 (s, 0.12H), 2.90 (d, *J* = 11.5 Hz, 1H), 2.24 (s, 3H), 2.19 (s, 3H), 2.13 (s, 3H), 2.09 – 2.06 (m, 1H), 1.86 (t, *J* = 11.5 Hz, 1H), 1.71 – 1.52 (m, 5.3H), 1.46 (d, *J* = 13.6 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃): δ 171.2, 170.0, 137.2, 136.5, 136.3, 136.1, 129.2, 129.0, 128.6, 107.6, 66.2, 55.6, 44.7, 44.1, 28.6, 25.4, 25.0, 23.4, 23.3, 18.2, 18.0, 17.9, 17.7, 14.6.

HRMS (ESI): Calcd. for C₁₈H₂₂D₅N₂O⁺ [M + H]⁺: 292.2432, found: 292.2437.

(E)-N-(4-Ethoxyphenyl)-N-(prop-1-en-1-yl-d₅)acetamide-d₃ (33)

Following Procedure A, using 11h instead of 7 h.



Colourless liquid (23 mg, 51% yield, 7.33 D/molecule);

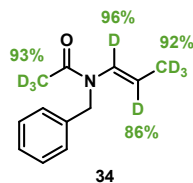
¹H NMR (400 MHz, CDCl₃): δ 7.05 (d, *J* = 8.5 Hz, 2H), 6.95 (d, *J* = 8.5 Hz, 2H), 6.57 (s, 0.05H), 4.99 (s, 0.02H), 4.06 (q, *J* = 6.8 Hz, 2H), 1.80 (s, 0.15H), 1.61 (s, 0.45H), 1.44 (t, *J* = 6.8 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 168.7, 158.8, 132.5, 129.8, 129.1, 115.5, 108.6, 63.8, 29.5, 22.7, 14.8.

HRMS (ESI): Calcd. for C₁₃H₁₀D₈NO₂⁺ [M + H]⁺: 228.1834, found: 228.1832.

(E)-N-Benzyl-N-(prop-1-en-1-yl-d₅)acetamide-d₃ (34)

Following Procedure A.



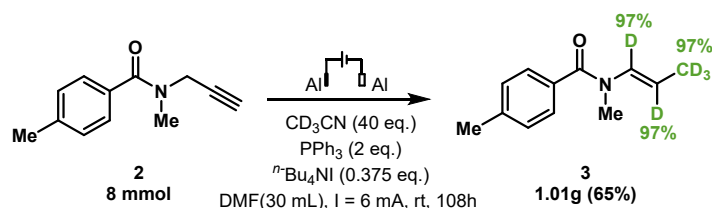
Colourless liquid (25 mg, 64% yield, 7.37 D/molecule);

¹H NMR (400 MHz, CDCl₃): δ 7.37 – 7.31 (m, 1H), 7.29 (d, *J* = 7.2 Hz, 1H), 7.23 (d, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 7.5 Hz, 2H), 6.53 (s, 0.04H), 4.98 (s, 0.14H), 4.88 – 4.62 (m, 2H), 2.19 (m, 0.21H), 1.60 (s, 0.24H).

¹³C NMR (101 MHz, CDCl₃): δ 169.2, 137.4, 136.4, 128.9, 128.5, 127.3, 126.9, 126.8, 125.6, 108.5, 106.8, 49.7, 46.6, 21.8 – 21.4(m), 14.9 – 14.71(m).

HRMS (ESI): Calcd. for C₁₂H₈D₈NO⁺ [M + H]⁺: 198.1729, found: 198.1734.

Procedure for gram-scale experiment (Procedure B):

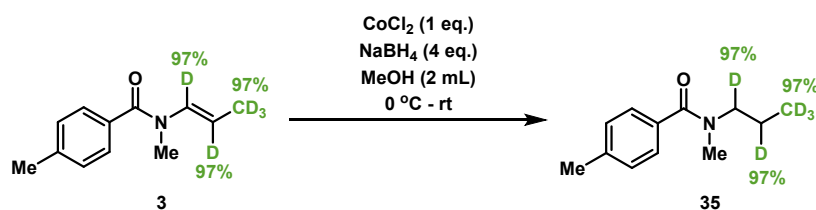


A 50 mL distillation flask equipped with a magnetic stir bar was charged with compound **2** (1.496 g, 8 mmol, 1.0 eq.), CD_3CN (16.7 mL, 40.0 eq.), PPh_3 (4.197 g, 16 mmol, 2.0 eq.), $n\text{-Bu}_4\text{NI}$ (1.108 g, 3 mmol, 0.375 eq.) and DMF (30 mL). The flask equipped with aluminium anode ($d = 5$ mm) and aluminium cathode ($d = 5$ mm) (the submerged height of the electrode is approximately 3 cm). The resulting solution was stirred and electrolyzed at a constant current of 6 mA (Single Output DC Power Supply: KRP-305DM) for 108 hours at room temperature. The solution was diluted with EtOAc (20 mL) and brine (20 mL), and extracted with EtOAc (3×30 mL). The combined organic layers were washed with brine (3×50 mL), dried over Na_2SO_4 , and concentrated *in vacuo*. Purification by flash column chromatography using PE/EtOAc ($v/v = 10/1$) as eluent afforded the desired product **3** (1.01 g, 65%, 4.85 D/molecule).

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.34 (d, $J = 8.0$ Hz, 2H), 7.21 (d, $J = 8.0$ Hz, 2H), 6.53 (s, 0.03H), 5.00 (s, 0.03H), 3.20 (s, 3H), 2.38 (s, 3H), 1.58 (s, 0.09H).

V Application of Enamides

N,4-Dimethyl-*N*-(propyl-1,2,3,3-*d*₅)benzamide (35)

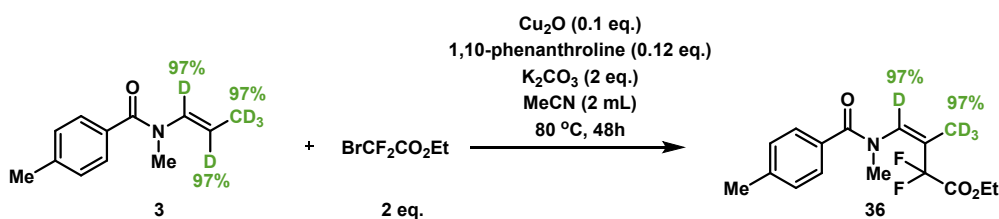


A procedure adopted from literature was used¹¹. CoCl_2 (26 mg, 0.2 mmol, 1.0 eq.) was added to a stirred solution of enamide **3** (39 mg, 0.2 mmol, 1.0 eq.) in MeOH (2 mL) at 0 °C. After 10 min, NaBH_4 (30 mg, 0.8 mmol, 4.0 eq.) was added to the reaction mixture, and the mixture was allowed to warm to room temperature and stirred for 48 h. The reaction mixture was quenched by slowly adding cold H_2O (20 mL), the solution was diluted with DCM (20 mL) and brine (20 mL), and extracted with DCM (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 = 3/1) as eluent afforded the desired product **35** (32 mg, 82%, 4.85 D/molecule) as colourless oil.

¹H NMR (400 MHz, CDCl_3): δ 7.27 (d, $J = 7.4$ Hz, 2H), 7.18 (d, $J = 7.4$ Hz, 2H), 3.45 (s, 0.43H), 3.18 (s, 0.6H), 3.05 (s, 1.8H), 2.93 (s, 1.2H), 2.36 (s, 3H), 1.64 (s, 0.43H), 1.52 (s, 0.6H), 1.25 (s, 0.09H).

¹³C NMR (101 MHz, CDCl_3): δ 172.3, 171.5, 139.3, 134.0, 129.0, 127.0, 126.8, 52.6, 48.7, 37.6, 32.7, 21.4.

Ethyl (*Z*)-4-(*N*,4-dimethylbenzamido)-2,2-difluoro-3-(methyl-*d*₃)but-3-enoate-4-*d* (36)



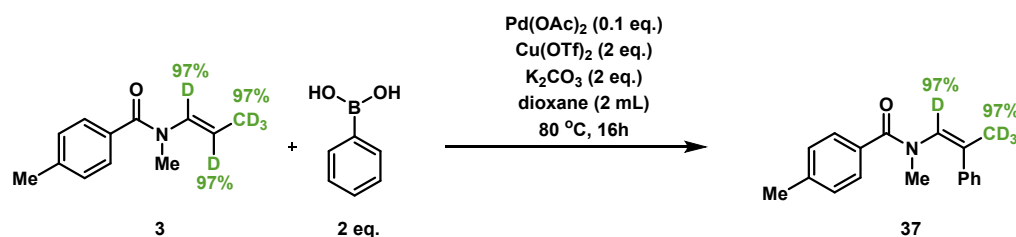
A procedure adopted from literature was used¹². A screw-cap vial was loaded with enamide **3** (39 mg, 0.2 mmol, 1.0 eq.), Cu_2O (3 mg, 0.02 mmol, 0.1 eq.), 1,10-phenanthroline (4 mg, 0.024 mmol, 0.12 eq.) and K_2CO_3 (55 mg, 0.4 mmol, 2 eq.). Anhydrous acetonitrile (2 mL) was added, the mixture was stirred under N_2 for a few seconds and ethyl bromodifluoroacetate (81 mg, 0.4 mmol, 2.0 eq.) was added. The tube was sealed and placed in an oil bath at 80 °C for 48h. After cooling to room temperature, the solution was diluted with DCM (20 mL) and brine (20 mL), and extracted with DCM (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 = 20/1) as eluent afforded the desired product **36** (31 mg, 49%, 3.88 D/molecule) as colourless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.39 (d, *J* = 7.2 Hz, 2H), 7.17 (d, *J* = 7.2 Hz, 2H), 6.72 (s, 0.03H), 4.22 (d, *J* = 6.8 Hz, 2H), 3.26 (s, 3H), 2.37 (s, 3H), 1.67 (s, 0.09H), 1.25 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 171.3, 163.4, 141.4, 134.2, 132.2, 129.5, 129.2, 128.9, 128.7, 127.1, 127.0, 114.0, 63.2, 36.0, 21.6, 14.6, 14.0.

(Z)-N,4-Dimethyl-N-(2-phenylprop-1-en-1-yl-1,3,3,3-*d*₄)benzamide (37)

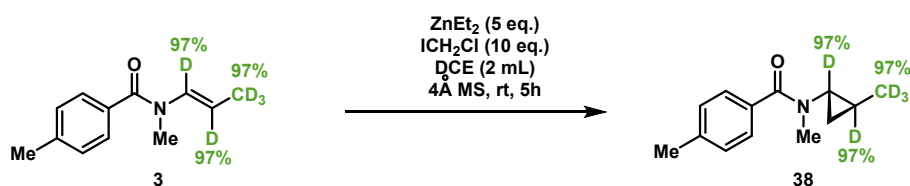


A procedure adopted from literature was used¹². A screw-cap vial was loaded with enamide **3** (39 mg, 0.2 mmol, 1.0 eq.), Cu(OTf)₂ (145 mg, 0.4 mmol, 2.0 eq.), K₂CO₃ (55 mg, 0.4 mmol, 2.0 eq.), phenylboronic acid (49 mg, 0.4 mmol, 2.0 eq.). Anhydrous 1,4-dioxane (2 ml) was added, the mixture was stirred under N₂ for a few seconds and Pd(OAc)₂ (5 mg, 0.02 mmol, 0.1 eq.) was added. The tube was sealed and placed in an oil bath at 80 °C for 16h. After cooling to 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 Na₂SO₄, and concentrated in vacuo. Purification by flash column chromatography using PE/EtOAc (v/v = 10/1) as eluent afforded the desired product **37** (15 mg, 27%, 3.88 D/molecule) as colourless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.44 (d, *J* = 7.2 Hz, 2H), 7.38 (d, *J* = 7.4 Hz, 4H), 7.32 (d, *J* = 7.4 Hz, 1H), 6.97 (d, *J* = 7.2 Hz, 2H), 6.71 (s, 0.03H), 3.18 (s, 3H), 2.28 (s, 3H), 1.48 (s, 0.09H).

¹³C NMR (101 MHz, CDCl₃): δ 171.9, 142.5, 140.3, 136.9, 133.2, 129.0, 128.3, 128.1, 127.6, 125.6, 121.5, 35.7, 29.9 – 29.8 (m), 21.5.

N,4-Dimethyl-N-((1*S*,2*S*)-2-(methyl-*d*₃)cyclopropyl-1,2-*d*₂)benzamide (38)



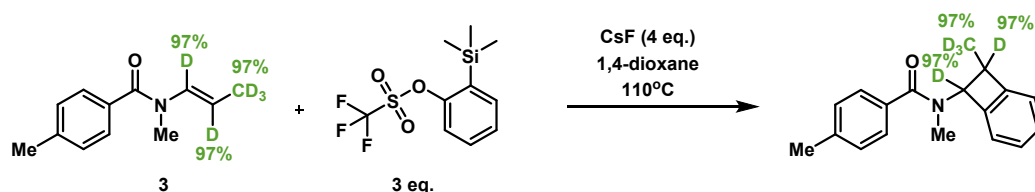
A procedure adopted from literature was used¹³. Molecular sieves (4 Å, 50 mg) and ICH₂Cl (353 mg, 2

mmol, 10.0 eq.) were added to a solution of the enamide **3** (39 mg, 0.2 mmol, 1.0 eq.) in anhydrous DCE (2 mL), and the resulting mixture was stirred at room temperature for 30 min. A solution of ZnEt₂ (1 mL, 1.0M in hexane, 1 mmol, 5.0 eq.) was then added carefully dropwise. After further stirring at room temperature for 5 h, TLC analysis showed that **2** had been consumed entirely. The reaction mixture was quenched with saturated aqueous NaHCO₃ (5 mL). The solution was diluted with DCM (20 mL) and brine (20 mL), and extracted with DCM (3 × 30 mL). The combined organic layers were washed with brine (3 × 50 mL), dried over Na₂SO₄, and concentrated in vacuo. Purification by flash column chromatography using PE/EtOAc (v/v = 3/1) as eluent afforded the desired product **38** (33 mg, 80%, 4.85 D/molecule) as colourless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.37 (d, *J* = 7.5 Hz, 2H), 7.19 (d, *J* = 7.5 Hz, 2H), 3.04 (s, 3H), 2.92 (s, 0.03H), 2.37 (s, 3H), 1.89 (s, 0.09H), 1.02 (s, 0.03H), 0.61 (s, 1.3H), 0.35 (s, 0.7H).

¹³C NMR (101 MHz, CDCl₃): δ 172.9, 139.5, 134.8, 128.8, 127.4, 34.8, 26.87, 26.8, 21.5, 16.6, 16.0.

***N*,4-Dimethyl-*N*-(8-(methyl-*d*₃)bicyclo[4.2.0]octa-1(6),2,4-trien-7-yl-7,8-*d*₂)benzamide (39)**



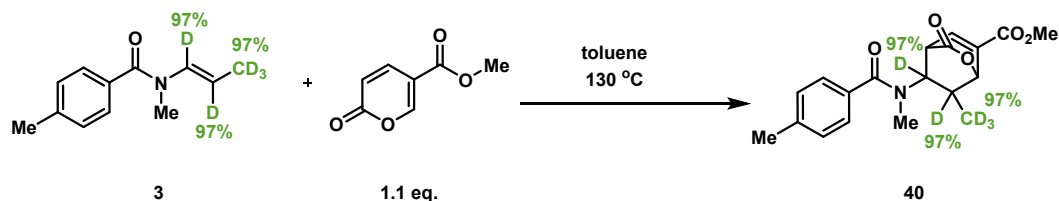
A modified procedure adopted from literature was used¹⁴. A screw-cap vial was loaded with CsF (122 mg, 0.8 mmol, 4.0 eq.), enamide **3** (39 mg, 0.2 mmol, 1.0 eq.) and anhydrous 1,4-dioxane (2 mL). Then, 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (179 mg, 0.6 mmol, 3.0 eq.) was added dropwise using a gastight syringe. The reaction mixture was heated at 110 °C for 16 h. After cooling to 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 Na₂SO₄, and concentrated in vacuo. Purification by flash column chromatography using PE/EtOAc (v/v = 3/1) as eluent afforded the desired product **39** (27 mg, 50%, 4.85 D/molecule) as colourless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.36 (d, *J* = 7.7 Hz, 2H), 7.23 (d, *J* = 12.4 Hz, 2H), 7.18 (d, *J* = 7.7 Hz, 2H), 7.10 (d, *J* = 12.4 Hz, 2H), 4.83 (s, 0.03H), 3.56 (s, 0.03H), 2.86 (s, 3H), 2.33 (s, 3H), 1.38 (s, 0.09H).

¹³C NMR (101 MHz, CDCl₃): δ 172.2, 142.2, 139.9, 133.5, 129.4, 129.1, 128.7, 128.0, 127.4, 123.2, 122.3, 66.0, 34.3, 29.0, 21.5, 16.1.

Methyl **8-(*N*,4-dimethylbenzamido)-7-(methyl-*d*₃)-3-oxo-2-oxabicyclo[2.2.2]oct-5-ene-6-**

carboxylate-7,8-*d*₂ (**40**)

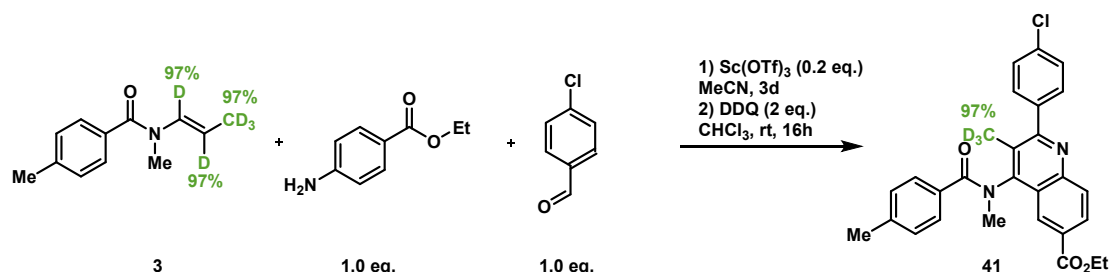


A procedure adopted from literature was used¹⁴. A screw-cap vial was loaded with methyl coumalate (34 mg, 0.22 mmol, 1.1 eq.), followed by the addition of enamide **3** (39 mg, 0.2 mmol, 1.0 eq.) dissolved in toluene (1 mL). The mixture was heated at 130 °C for 48 h. After cooling to room temperature, 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 Na₂SO₄, and concentrated in vacuo. Purification by flash column chromatography using PE/EtOAc (v/v = 3/1) as eluent afforded the desired product **40** (24 mg, 35%, 4.85 D/molecule) as yellow oil.

¹H NMR (400 MHz, CDCl₃): δ 7.53 (s, 1H), 7.31 (m, 2H), 7.25 (d, *J* = 7.7 Hz, 2H), 5.52 (s, 1H), 4.15 (s, 0.03H), 3.86 (s, 3H), 3.69 (s, 1H), 2.97 (s, 3H), 2.56 (s, 0.03H), 2.42 (s, 3H), 2.08 (s, 0.09H).

¹³C NMR (101 MHz, CDCl₃): δ 186.9, 173.3, 163.1, 140.9, 140.5, 135.5, 132.9, 129.4, 127.1, 78.2, 76.8, 52.6, 47.8, 21.6, 17.2.

Ethyl 2-(4-chlorophenyl)-4-(*N*,4-dimethylbenzamido)-3-(methyl-*d*₃)quinoline-6-carboxylate (**41**)



A procedure adopted from literature was used¹⁴. Ethyl 4-aminobenzoate (50 mg, 0.3 mmol, 1.0 eq.) and *p*-chlorobenzaldehyde (42 mg, 0.3 mmol, 1.0 eq.) were dissolved in anhydrous MeCN (1 mL) in an oven-dried round bottom flask. Then, molecular sieves (4 Å, 50 mg) were added, followed by Sc(OTf)₃ (30 mg, 0.06 mmol, 0.2 eq.). The resulting mixture was stirred at room temperature for 5 min. Then, the enamide **3** (58 mg, 0.3 mmol, 1.0 eq.) dissolved in MeCN (1 mL) was added. The mixture was stirred for 3 d at room temperature. Then, the reaction was stopped by the addition of aqueous saturated solution of NaHCO₃ (5 mL) and filtered. The aqueous phase was extracted with EtOAc (3 × 10 mL). The combined organic phases were dried over anhydrous Na₂SO₄ and the solvent was removed under reduced pressure. The crude material was used directly in the next oxidative step and was dissolved in

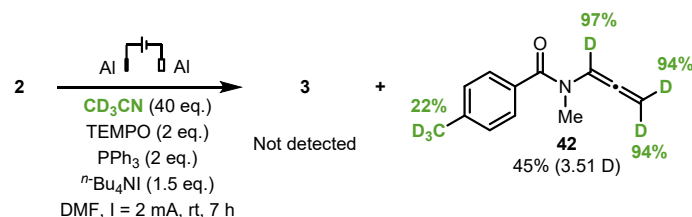
anhydrous CHCl_3 (2 mL). Next, DDQ (136 mg, 0.6 mmol, 2.0 eq.) was added. The reaction was stirred for 16 h at room temperature. The solution was diluted with DCM (20 mL) and brine (20 mL), and extracted with DCM (3×30 mL). The combined organic layers were washed with brine (3×50 mL), dried over Na_2SO_4 , and concentrated in vacuo. Purification by flash column chromatography using PE/EtOAc ($v/v = 2/1$) as eluent afforded the desired product **41** (43 mg, 30%, 2.91 D/molecule) as yellow oil.

^1H NMR (400 MHz, CDCl_3): δ 8.76 (s, 1H), 8.35 (d, $J = 8.0$ Hz, 1H), 8.24 (d, $J = 8.0$ Hz, 1H), 7.42 (d, $J = 7.7$ Hz, 2H), 7.27 (d, $J = 7.7$ Hz, 2H), 7.15 (d, $J = 7.7$ Hz, 2H), 6.86 (d, $J = 7.7$ Hz, 2H), 4.51 (d, $J = 7.0$ Hz, 2H), 3.51 (s, 3H), 2.21 (s, 3H), 2.10 (s, 0.09H), 1.49 (t, $J = 7.0$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ 171.6, 166.0, 162.8, 149.2, 141.1, 138.3, 135.3, 132.2, 130.6, 130.5, 130.3, 129.9, 129.4, 128.8, 128.6, 127.8, 127.5, 125.6, 124.0, 61.8, 37.3, 21.4, 16.2, 15.8, 15.4, 14.6.

V Mechanism Research

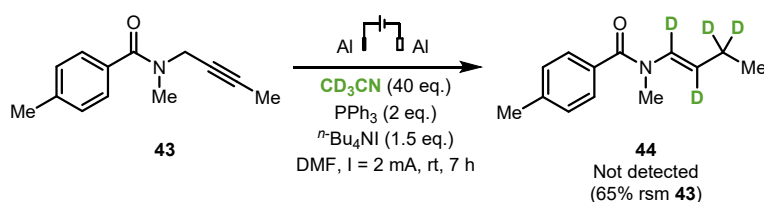
Control Experiment



A 10 mL distillation flask equipped with a magnetic stir bar was charged with compound **2** (37 mg, 0.2 mmol, 1.0 eq.), CD₃CN (0.42 mL, 40.0 eq.), TEMPO (63 mg, 0.4 mmol, 2.0 eq.), PPh₃ (105 mg, 0.4 mmol, 2.0 eq.), ⁿBu₄NI (111 mg, 0.3 mmol, 1.5 eq.) and DMF (3 mL). The flask equipped with aluminium anode (d = 5 mm) and aluminium cathode (d = 5 mm). The resulting solution was stirred and electrolyzed at a constant current of 2 mA (Single Output DC Power Supply: KRP-305DM) for 7 h at room temperature. The solution was diluted with EtOAc (5 mL) and brine (20 mL), and extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine (3 × 20 mL), dried over Na₂SO₄, and concentrated *in vacuo*. Purification by flash column chromatography using PE/EtOAc (v/v = 10/1) as eluent afforded the product **42** (17 mg, 45%, 3.51 D/molecule) as colourless oil.

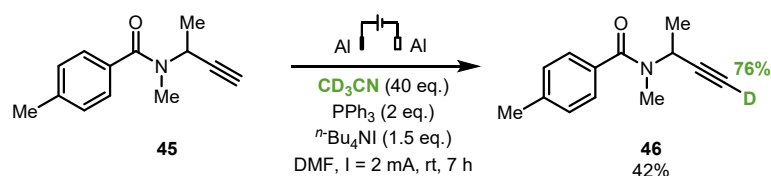
¹H NMR (400 MHz, CDCl₃): δ 7.39 (s, 2H), 7.23 (d, *J* = 7.3 Hz, 2H), 6.78 (s, 0.03H), 5.38 (s, 0.12H), 3.15 (s, 1H), 3.02 (s, 1H), 2.39 (s, 2.34H).

¹³C NMR (101 MHz, CDCl₃): δ 169.7, 140.4, 131.8, 129.0, 128.0, 127.5, 103.6, 86.7, 35.7, 31.3, 21.4.



A 10 mL distillation flask equipped with a magnetic stir bar was charged with compound **43** (40 mg, 0.2 mmol, 1.0 eq.), CD₃CN (0.42 mL, 40.0 eq.), PPh₃ (105 mg, 0.4 mmol, 2.0 eq.), ⁿBu₄NI (111 mg, 0.3 mmol, 1.5 eq.) and DMF (3 mL). The flask equipped with aluminium anode (d = 5 mm) and aluminium cathode (d = 5 mm). The resulting solution was stirred and electrolyzed at a constant current of 2 mA (Single Output DC Power Supply: KRP-305DM) for 7 h at room temperature. The solution was diluted with EtOAc (5 mL) and brine (20 mL), and extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine (3 × 20 mL), dried over Na₂SO₄, and concentrated *in vacuo*. Purification by flash column chromatography using PE/EtOAc (v/v = 10/1) as eluent afforded the product **43** (26

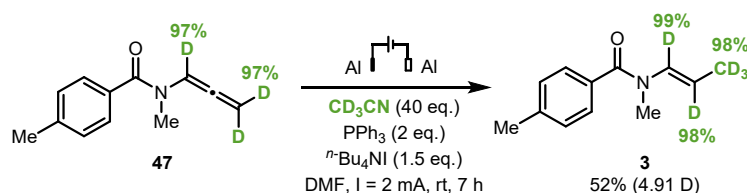
mg, 65%) as colourless oil.



A 10 mL distillation flask equipped with a magnetic stir bar was charged with compound **45** (40 mg, 0.2 mmol, 1.0 eq.), CD₃CN (0.42 mL, 40.0 eq.), PPh₃ (105 mg, 0.4 mmol, 2.0 eq.), *n*-Bu₄NI (111 mg, 0.3 mmol, 1.5 eq.) and DMF (3 mL). The flask equipped with aluminium anode (d = 5 mm) and aluminium cathode (d = 5 mm). The resulting solution was stirred and electrolyzed at a constant current of 2 mA (Single Output DC Power Supply: KRP-305DM) for 7 h at room temperature. The solution was diluted with EtOAc (5 mL) and brine (20 mL), and extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine (3 × 20 mL), dried over Na₂SO₄, and concentrated *in vacuo*. Purification by flash column chromatography using PE/EtOAc (v/v = 10/1) as eluent afforded the product **46** (17 mg, 42%, 0.76 D/molecule) as colourless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.34 (d, *J* = 7.5 Hz, 2H), 7.21 (d, *J* = 7.5 Hz, 2H), 5.70 (s, 0.5H), 4.70 (s, 0.5H), 3.03 (s, 3H), 2.38 (s, 3H), 2.35 (s, 0.24H), 1.42 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 171.4, 140.1, 133.1, 129.2, 127.2, 72.1 71.8, 66.9, 47.0, 41.7, 32.5, 28.1, 21.5, 19.3.



A 10 mL distillation flask equipped with a magnetic stir bar was charged with compound **47** (38 mg, 0.2 mmol, 1.0 eq.), CD₃CN (0.42 mL, 40.0 eq.), PPh₃ (105 mg, 0.4 mmol, 2.0 eq.), *n*-Bu₄NI (111 mg, 0.3 mmol, 1.5 eq.) and DMF (3 mL). The flask equipped with aluminium anode (d = 5 mm) and aluminium cathode (d = 5 mm). The resulting solution was stirred and electrolyzed at a constant current of 2 mA (Single Output DC Power Supply: KRP-305DM) for 7 h at room temperature. The solution was diluted with EtOAc (5 mL) and brine (20 mL), and extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine (3 × 20 mL), dried over Na₂SO₄, and concentrated *in vacuo*. Purification by flash column chromatography using PE/EtOAc (v/v = 10/1) as eluent afforded the product **3** (20 mg, 52%, 4.91 D/molecule) as colourless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.34 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.53 (s, 0.01H), 5.00 (s, 0.02H), 3.20 (s, 3H), 2.38 (s, 3H), 1.58 (s, 0.06H).

pH Detection

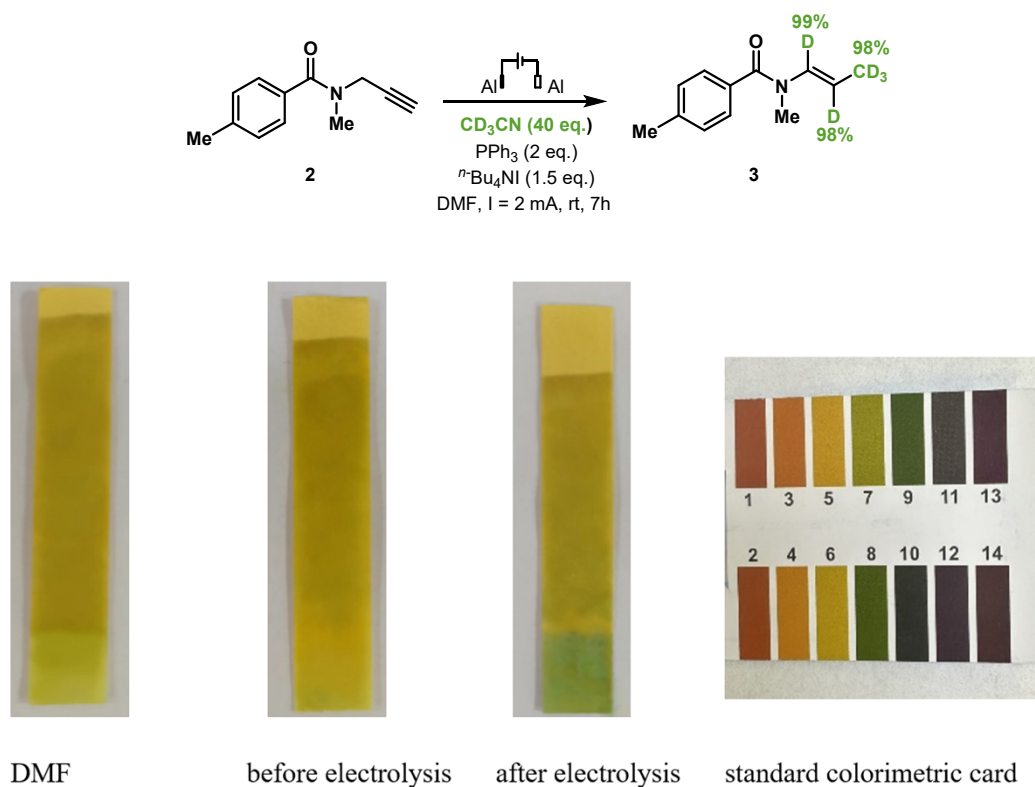


Figure S4: pH Detection

- (1) The pH test paper was moistened with water and anhydrous DMF was dropped on it. The color did not change obviously.
- (2) The pH test paper was moistened with water and the reaction mixture before electrolysis was dropped on the pH test paper. The color did not change 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 change obviously.

Cyclic Voltammetry Experiment

Cyclic voltammetry was carried out in a glass cell with CHI760E electrochemical workstation. Cyclic voltammetry of compound **2** at a scan rate of $100 \text{ mV}\cdot\text{s}^{-1}$. The electrochemical experiments were performed in a three-compartment cell fitted with a glassy carbon as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a graphite rod (diameter is 5 mm) as the counter electrode.

Electrolyte: $0.1 \text{ M } n\text{-Bu}_4\text{NI}$ in DMF; Concentration of sample: 0.01 M .

Discussion: The reduction potentials of the substrate **2** is -2.339 V and -2.421 V (Figure S5, red line). The reduction potentials of the **47** is -2.418 V (Figure S5, blue line), the results indicated that **47** is an intermediate reduced from **2**. In the mixture of **2** with PPh_3 , the reduction potential of **2** did not change significantly (Figure S6, green line). In the mixture of **2** with O=PPh_3 , the reduction potential of **2** did not change significantly (Figure S7, green line). These results showed that PPh_3 and O=PPh_3 did not change the reduction potential of **2** indicating that there is no interaction between PPh_3 or O=PPh_3 and substrate **2** in the electrochemical system. We observed that the reaction voltage range of model reaction was $2.6\text{-}2.7 \text{ V}$ without adding PPh_3 , and the voltage decreased to $2.0\text{-}2.1 \text{ V}$ under standard conditions (with PPh_3). In addition, we obtained O=PPh_3 in 23% yield from model reaction under standard conditions. Based on these results, we speculated that PPh_3 is oxidized in the electrochemical system, reducing the reaction voltage to make the reaction condition milder than the model reaction without adding PPh_3 .

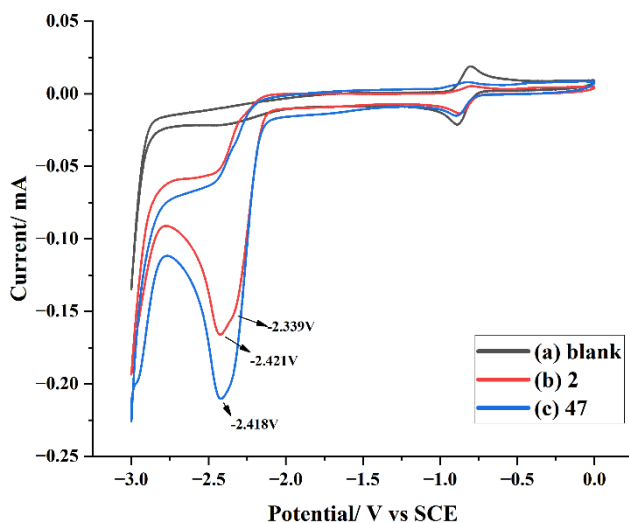


Figure S5: Cyclic voltammograms obtained in $0.1 \text{ M } n\text{-Bu}_4\text{NI}/\text{DMF}$ using glass carbon (diameter, 3 mm) as the working electrode, graphite rod, and saturated calomel electrode (SCE) as the auxiliary and reference electrode, respectively, at a scan rate of $100 \text{ mV}\cdot\text{s}^{-1}$: (a) blank, (b) $10 \text{ mM } \mathbf{2}$, (c) $10 \text{ mM } \mathbf{47}$.

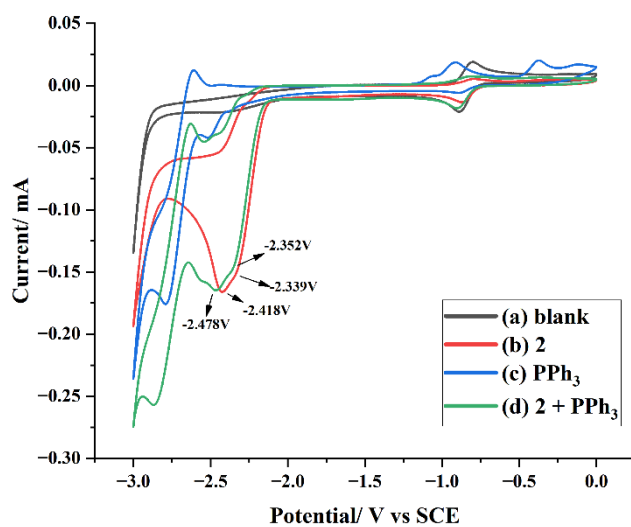


Figure S6: Cyclic voltammograms obtained in 0.1 M $n\text{-Bu}_4\text{NI}/\text{DMF}$ using glass carbon (diameter, 3 mm) as the working electrode, graphite rod, and saturated calomel electrode (SCE) as the auxiliary and reference electrode, respectively, at a scan rate of $100\text{ mV}\cdot\text{s}^{-1}$: (a) blank, (b) 10 mM **2**, (c) 10 mM PPh_3 , (d) 10 mM **2** + 10 mM PPh_3 .

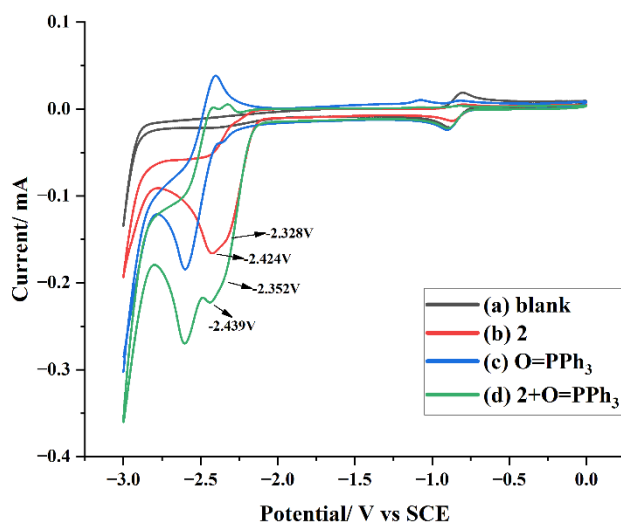


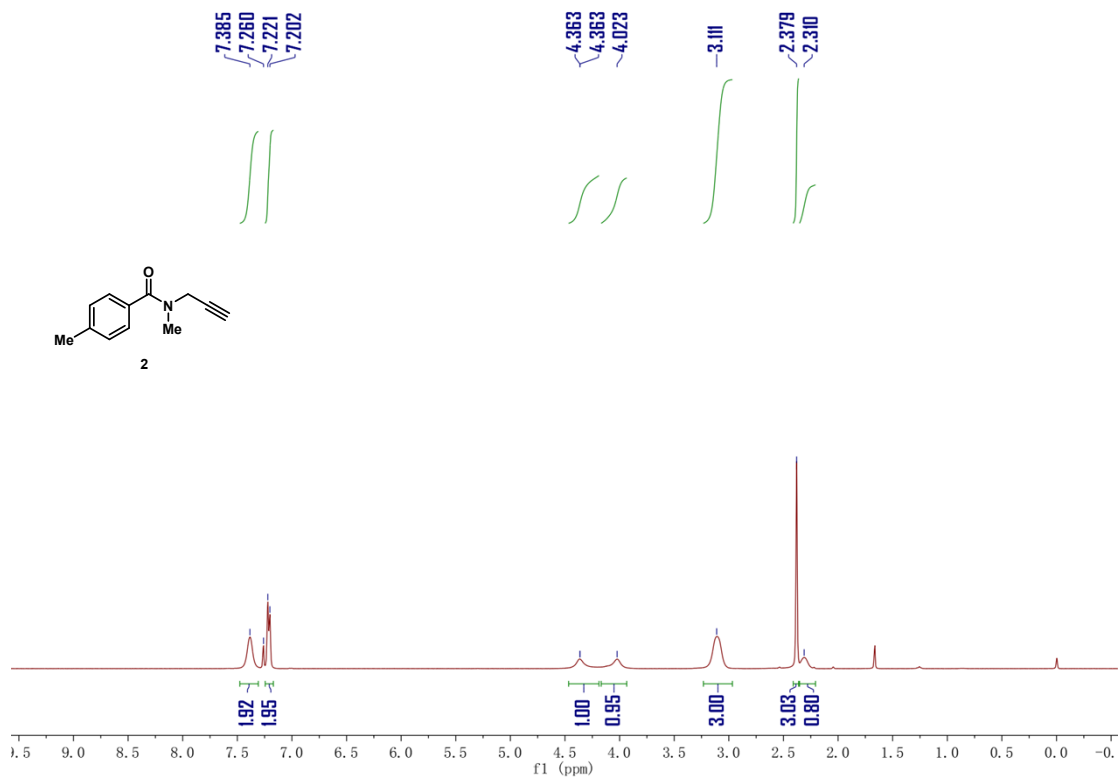
Figure S7: Cyclic voltammograms obtained in 0.1 M $n\text{-Bu}_4\text{NI}/\text{DMF}$ using glass carbon (diameter, 3 mm) as the working electrode, graphite rod, and saturated calomel electrode (SCE) as the auxiliary and reference electrode, respectively, at a scan rate of $100\text{ mV}\cdot\text{s}^{-1}$: (a) blank, (b) 10 mM **2**, (c) 10 mM O=PPh_3 , (d) 10 mM **2** + 10 mM O=PPh_3 .

VI References

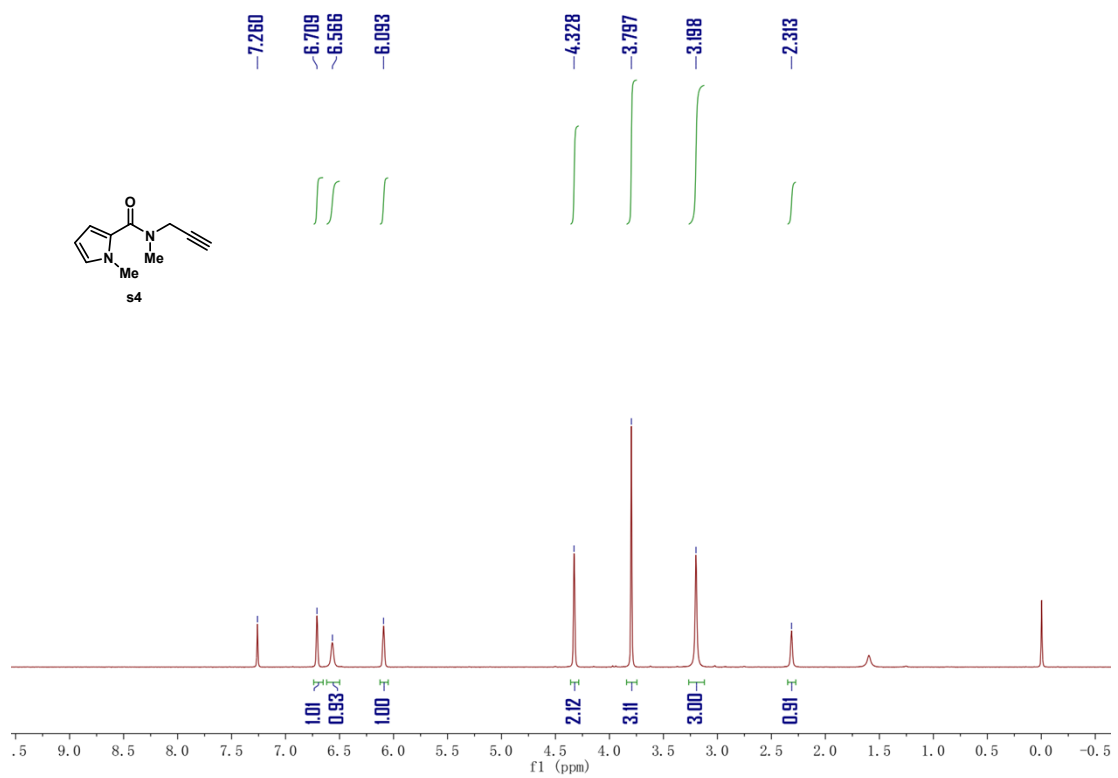
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VII. Spectra

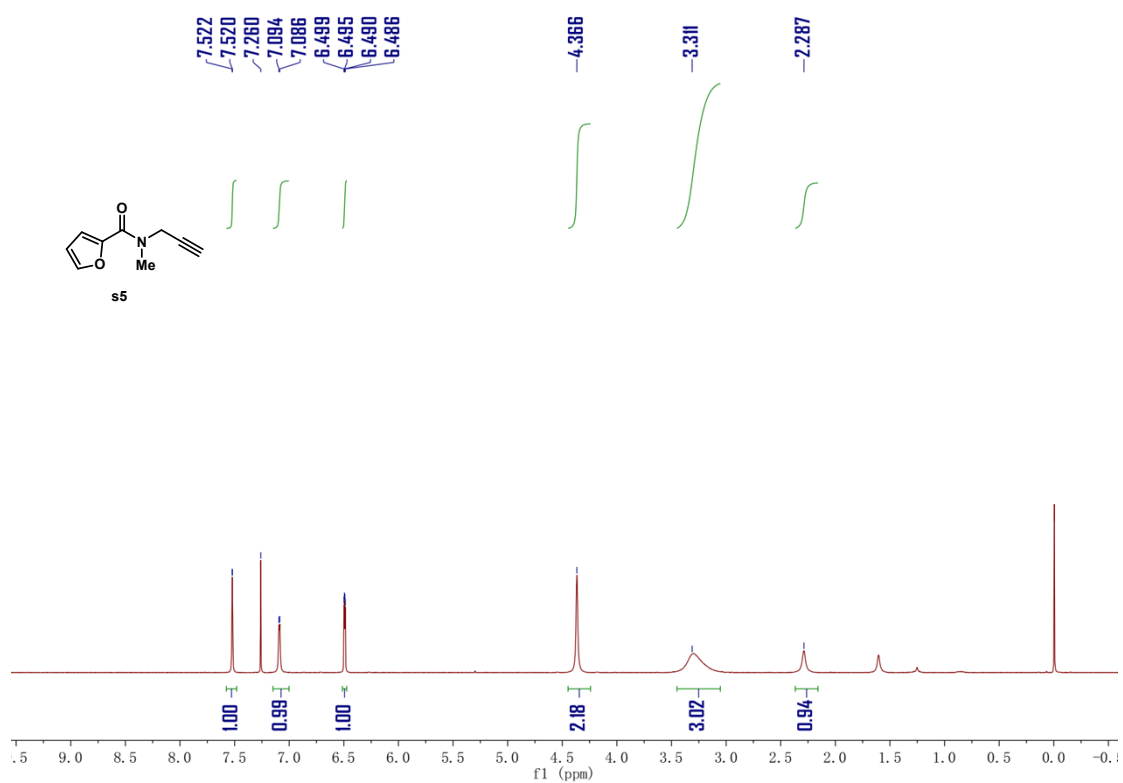
$^1\text{H NMR}$ (400 MHz, CDCl_3):



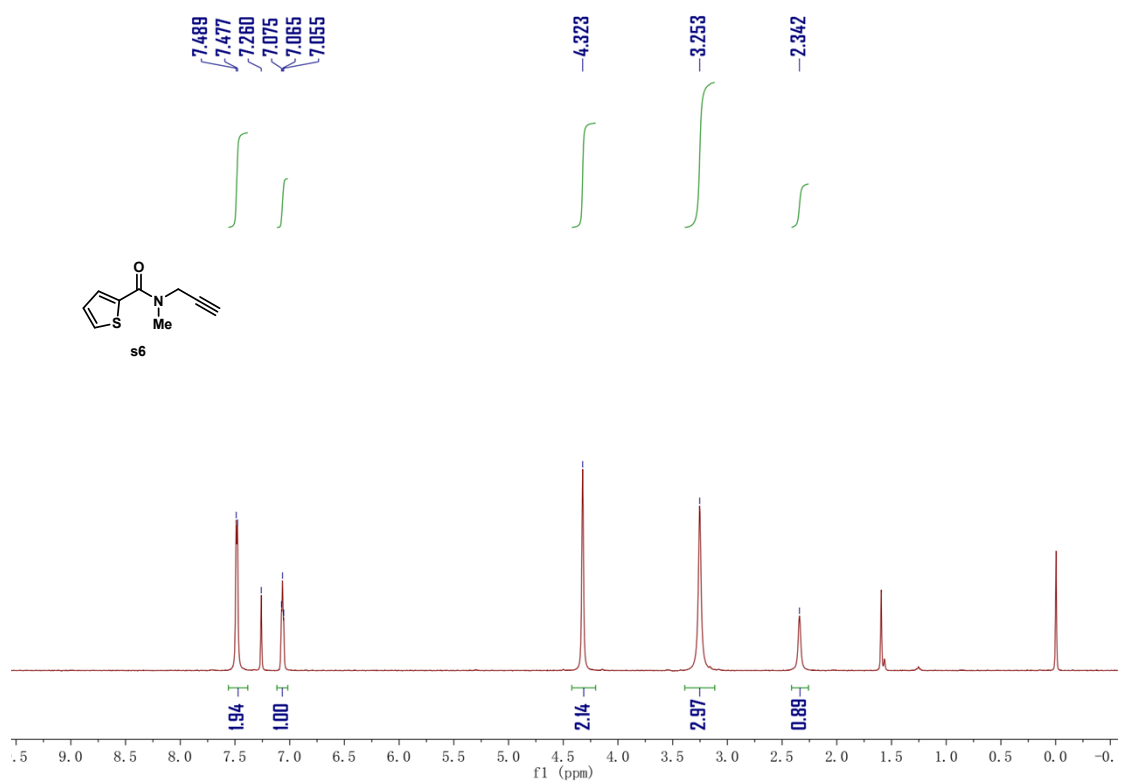
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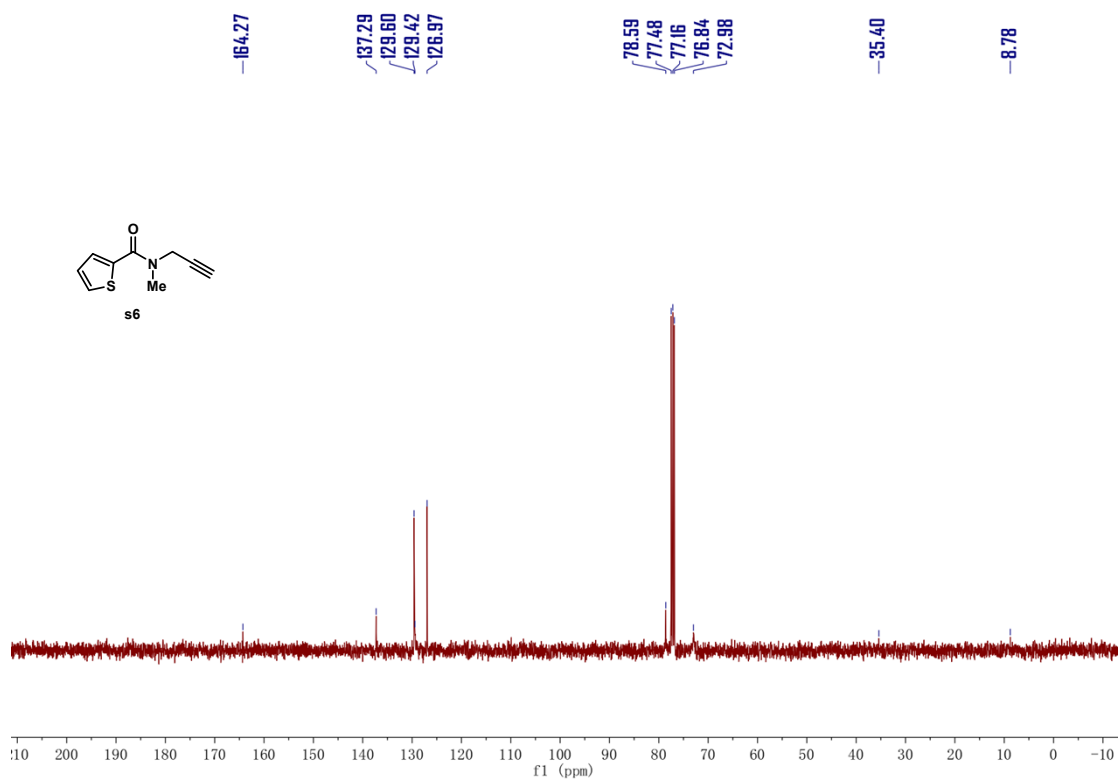
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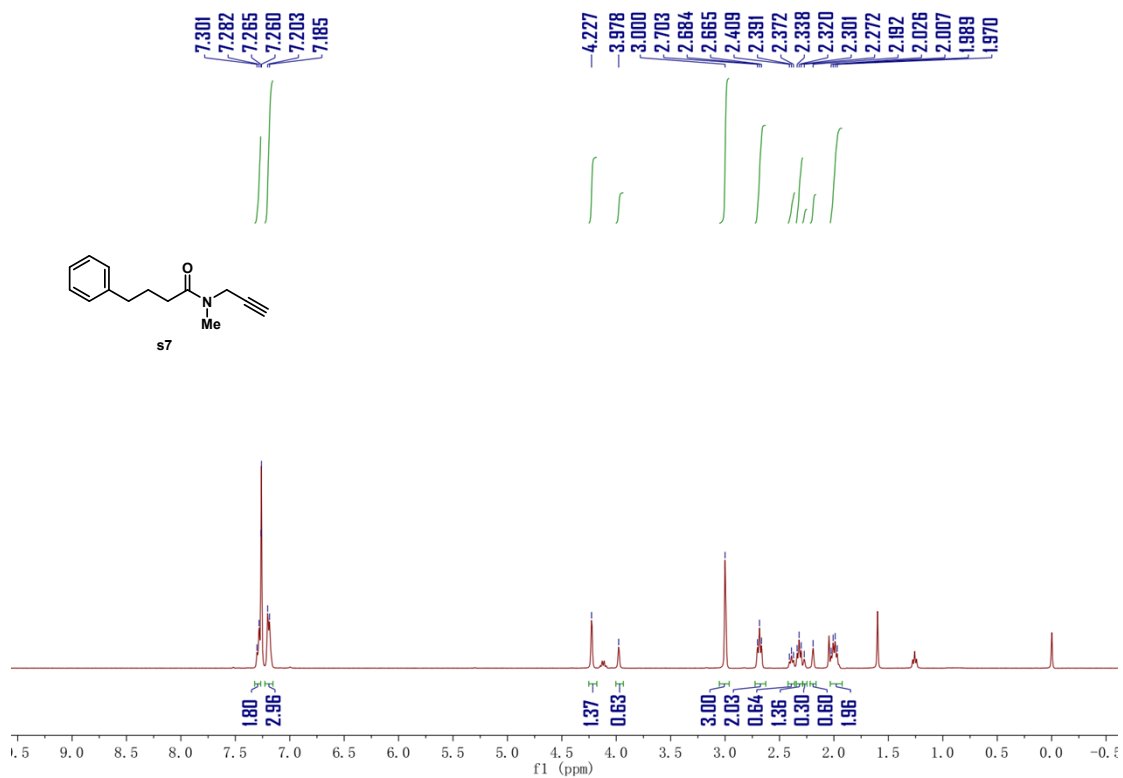
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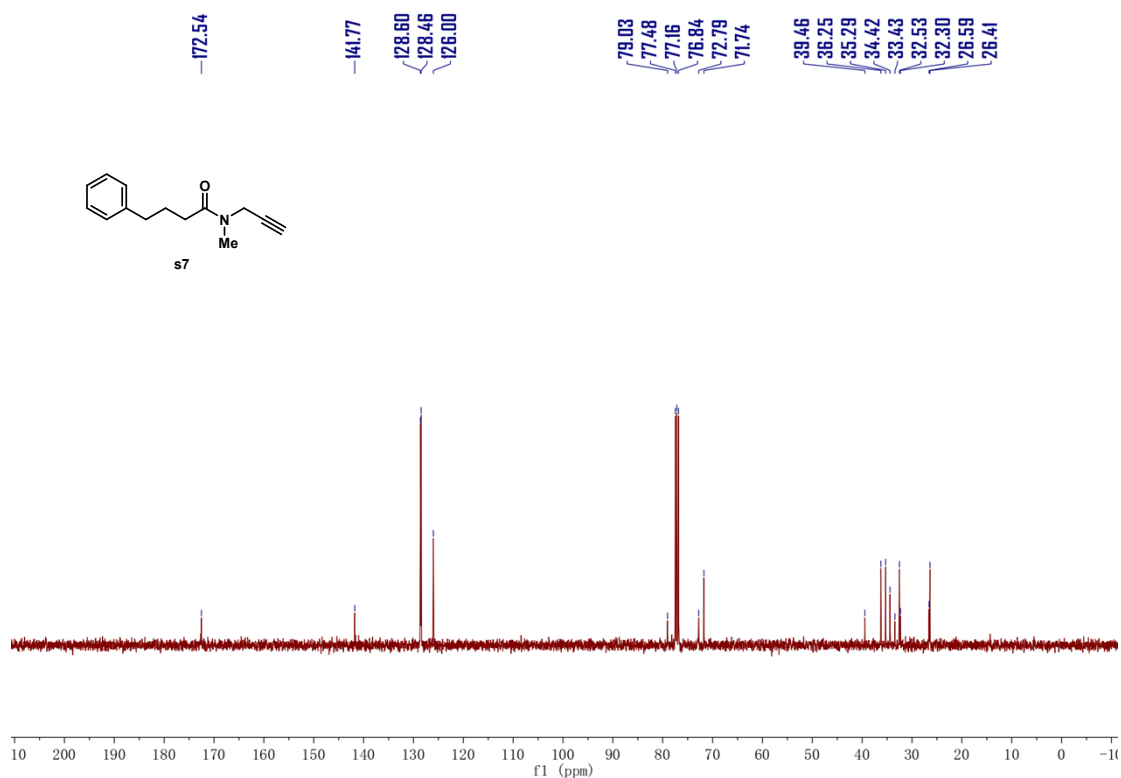
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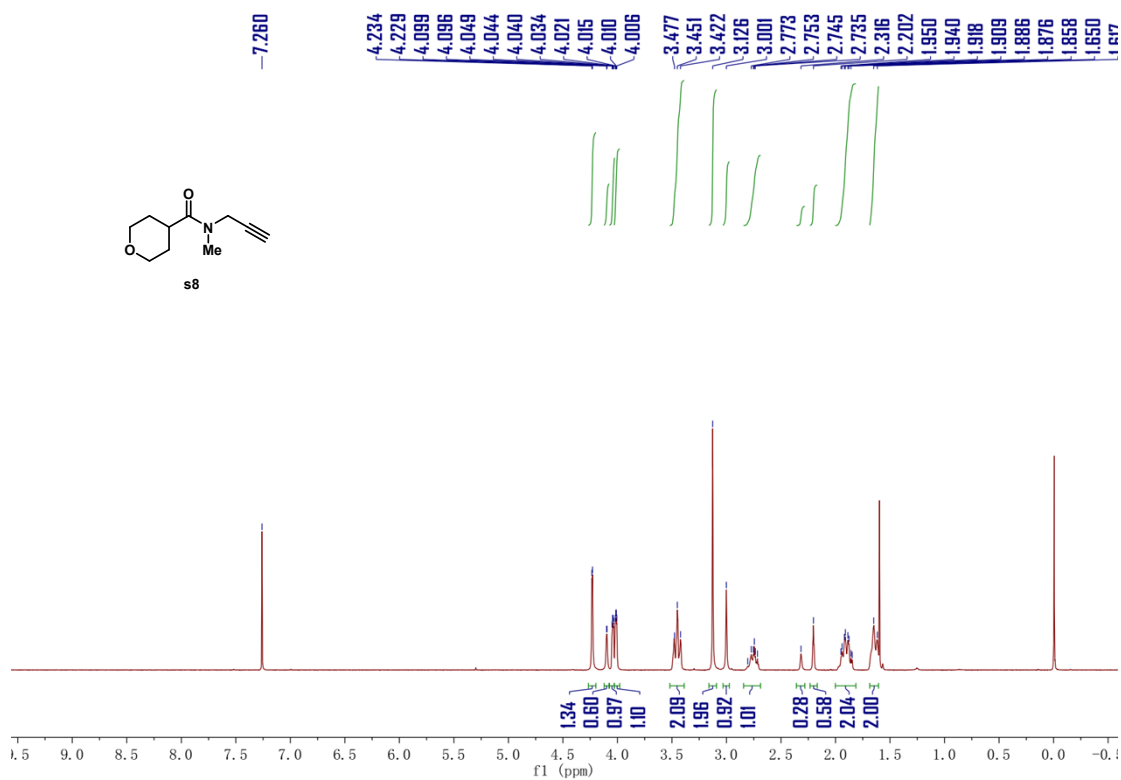
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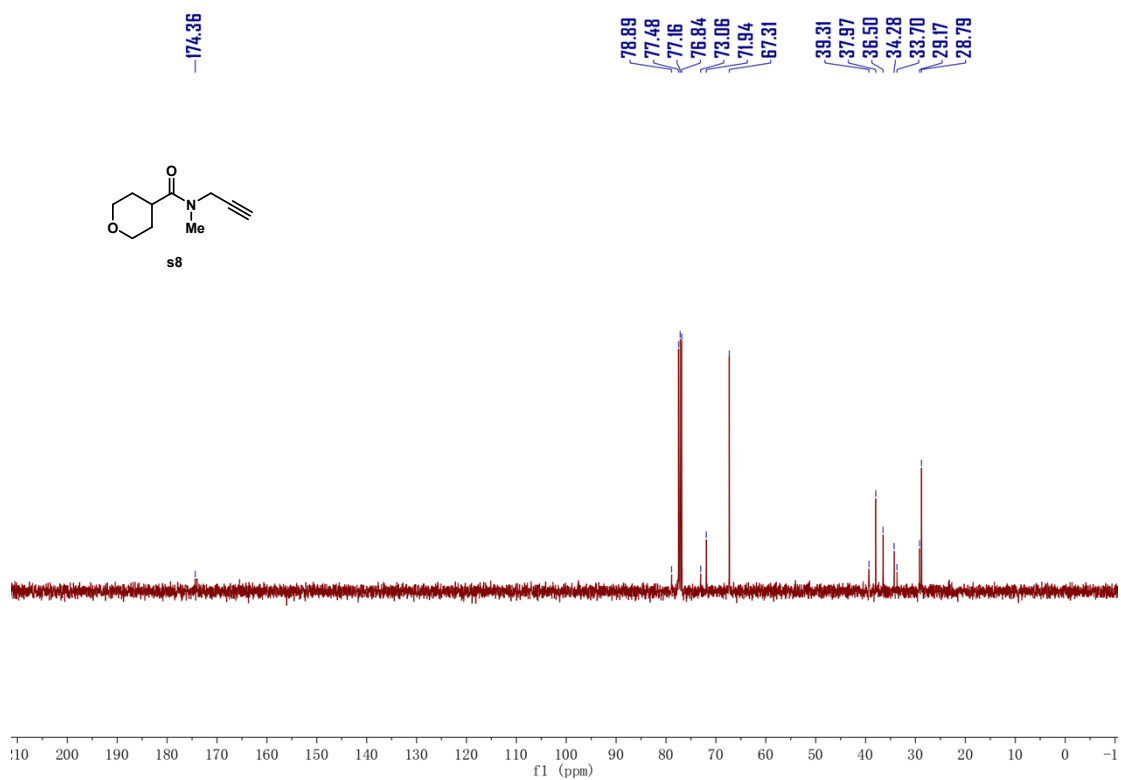
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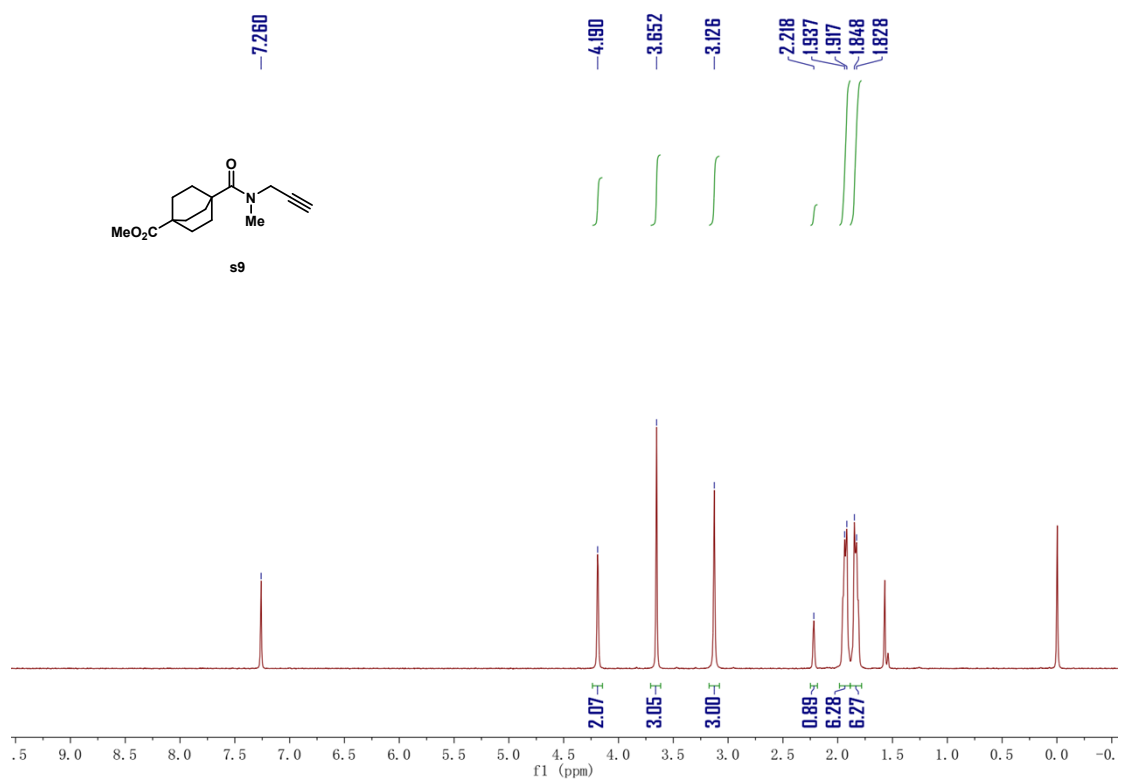
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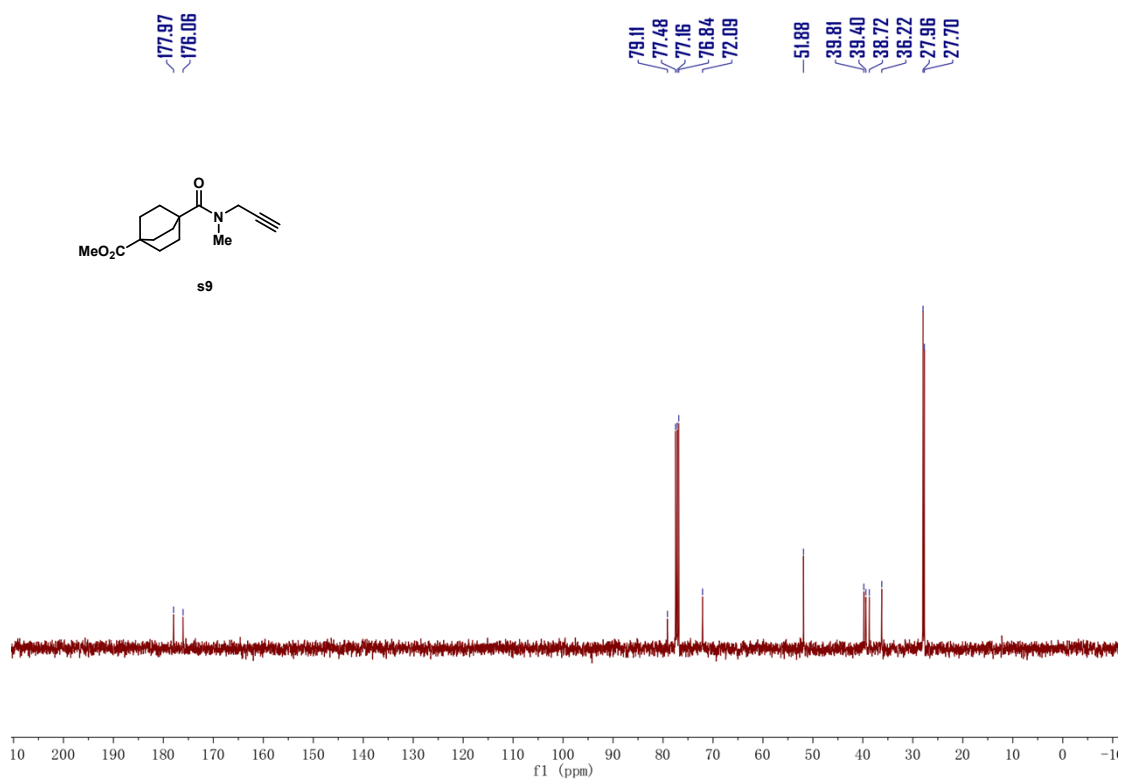
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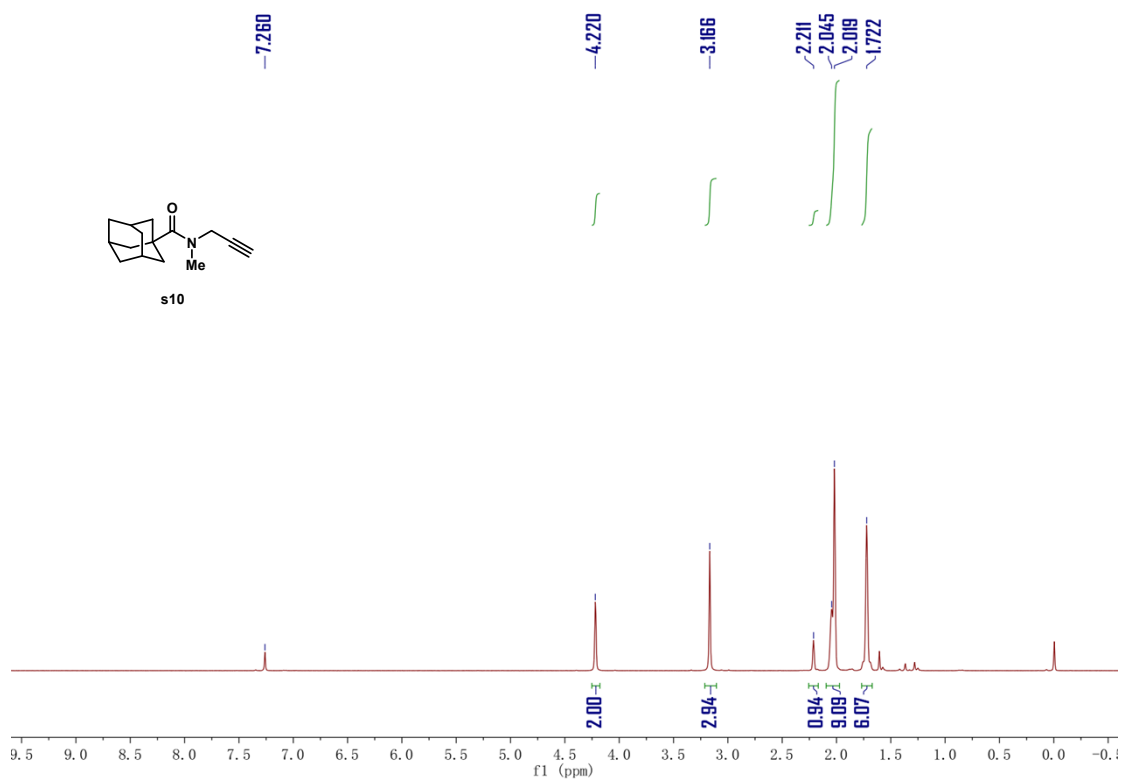
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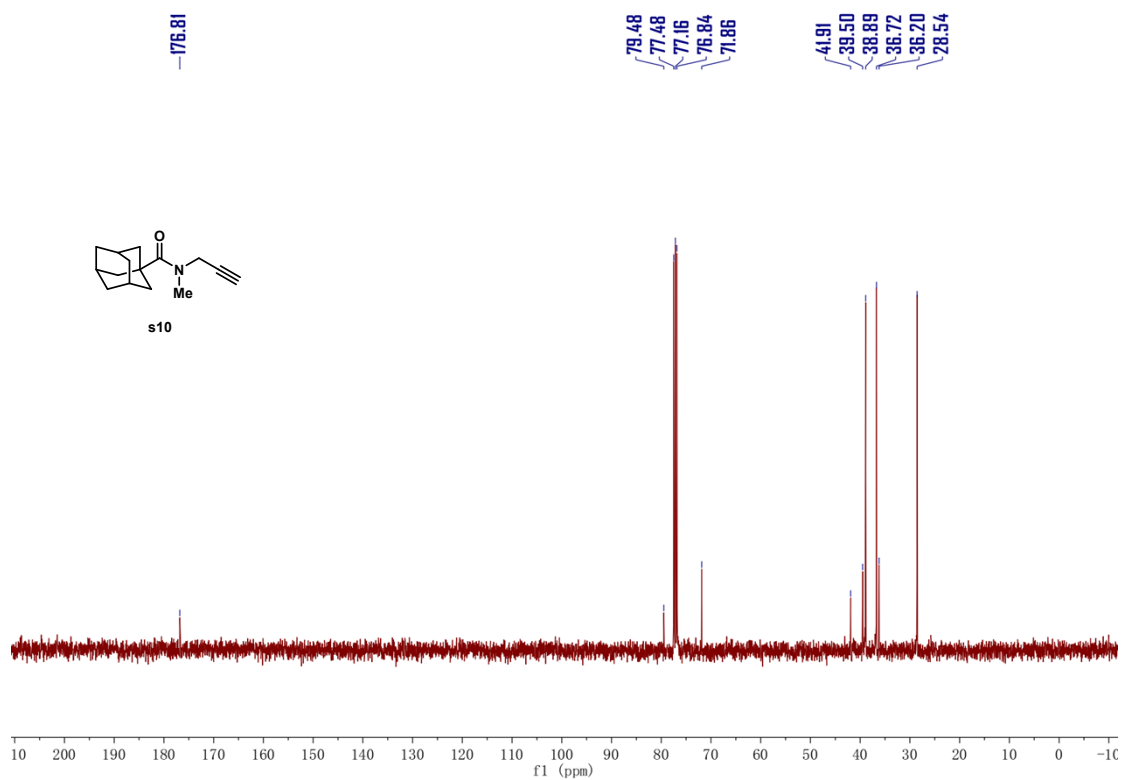
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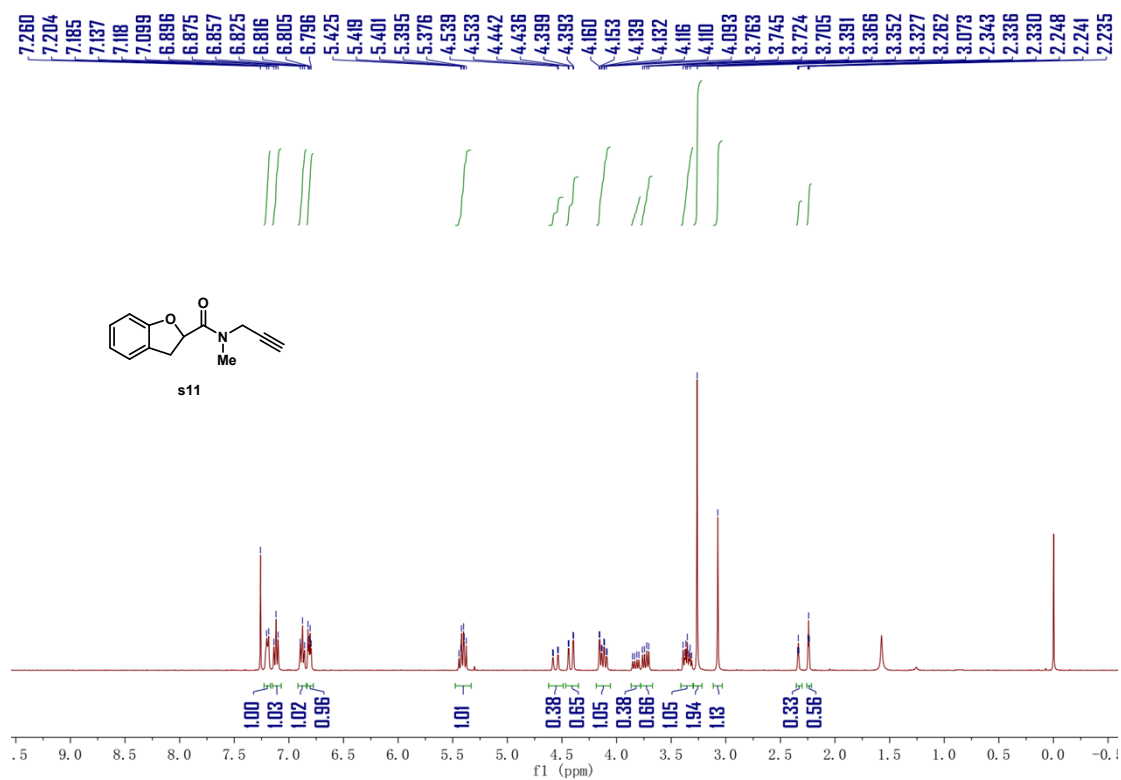
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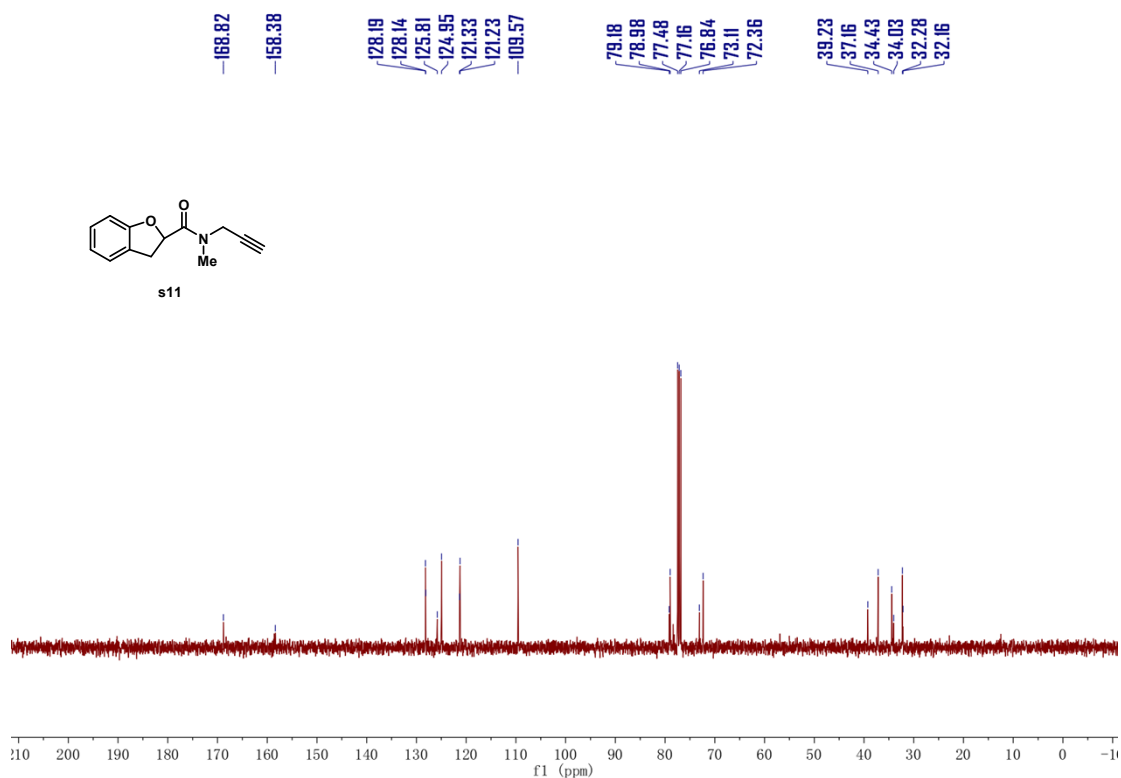
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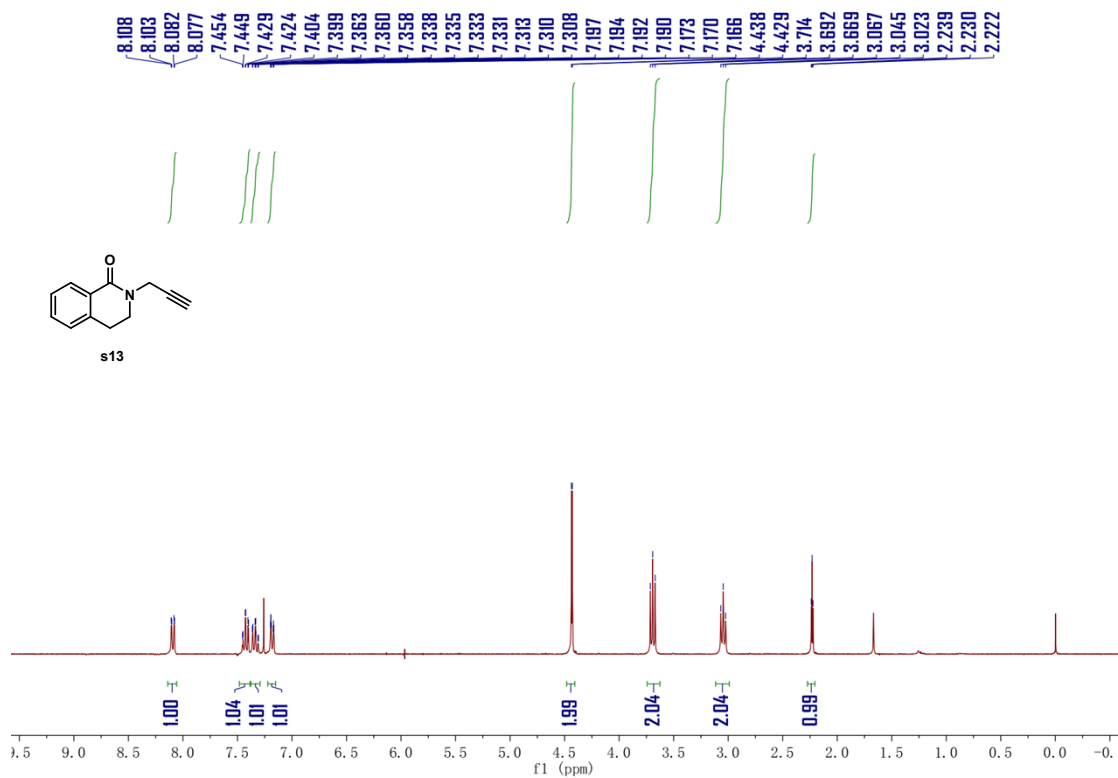
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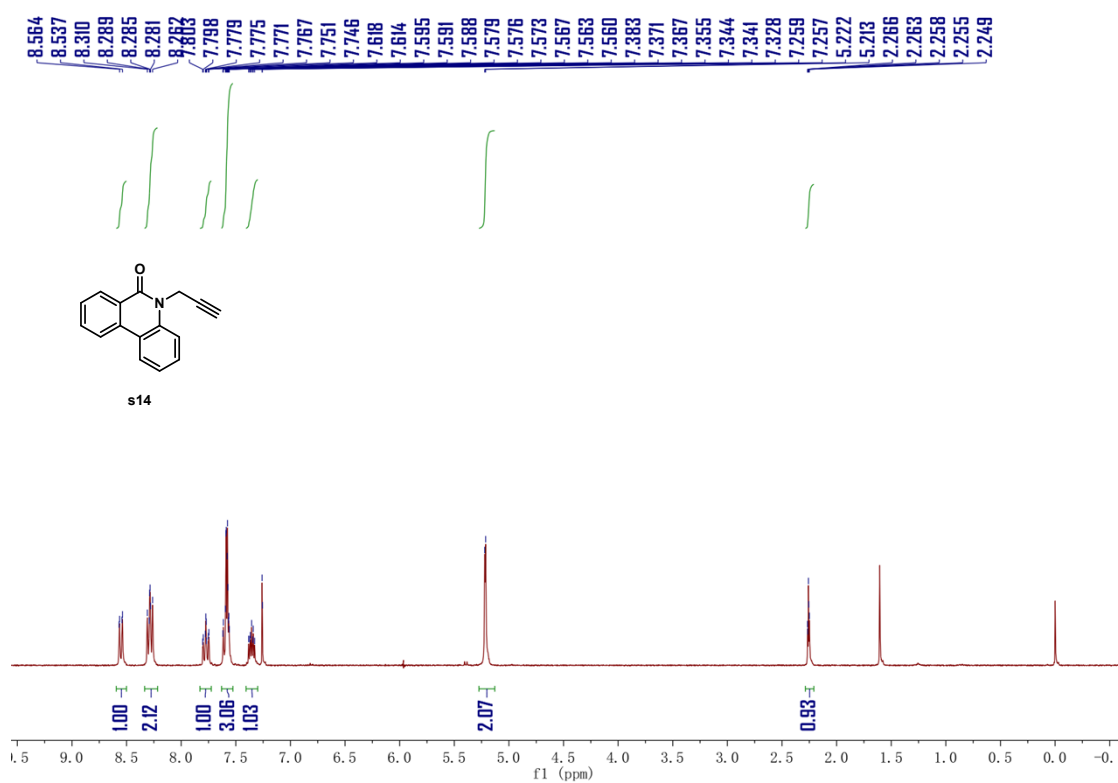
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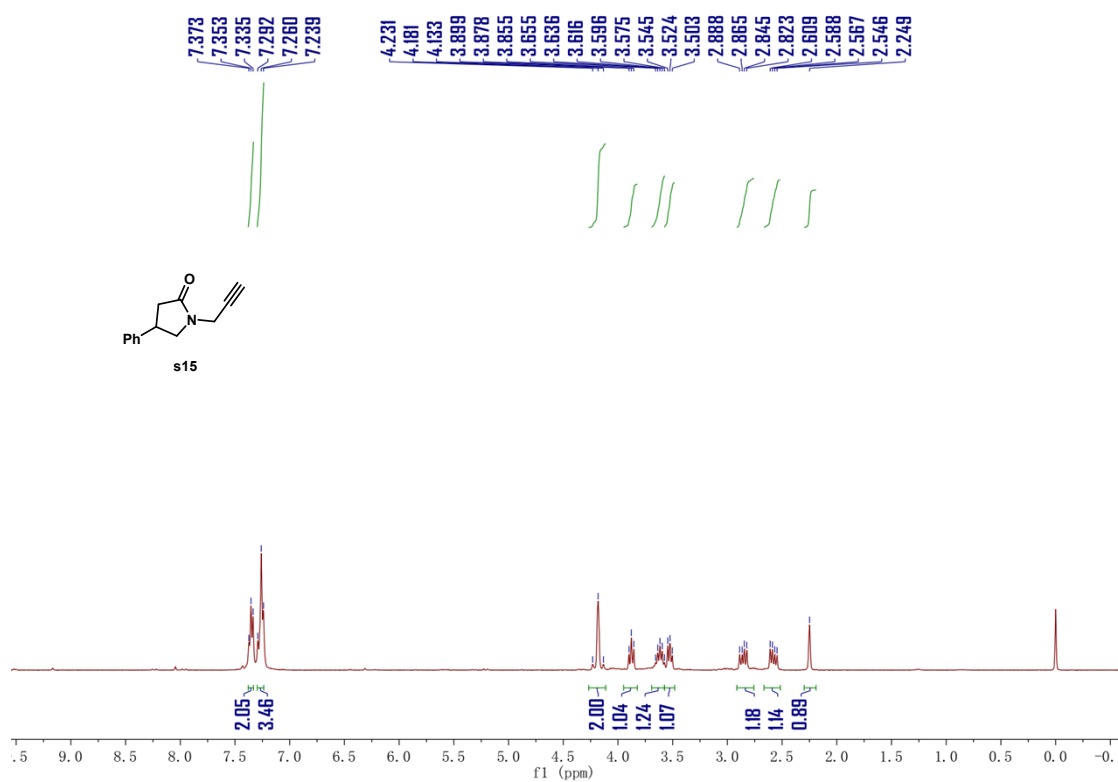
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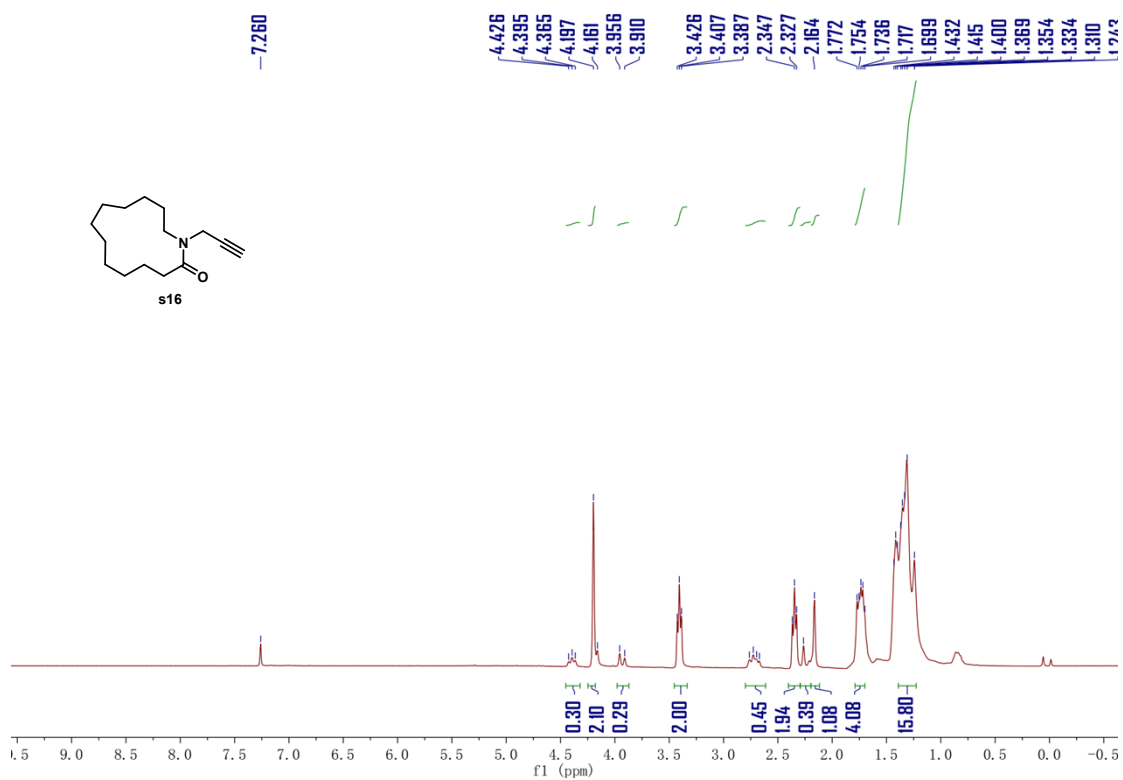
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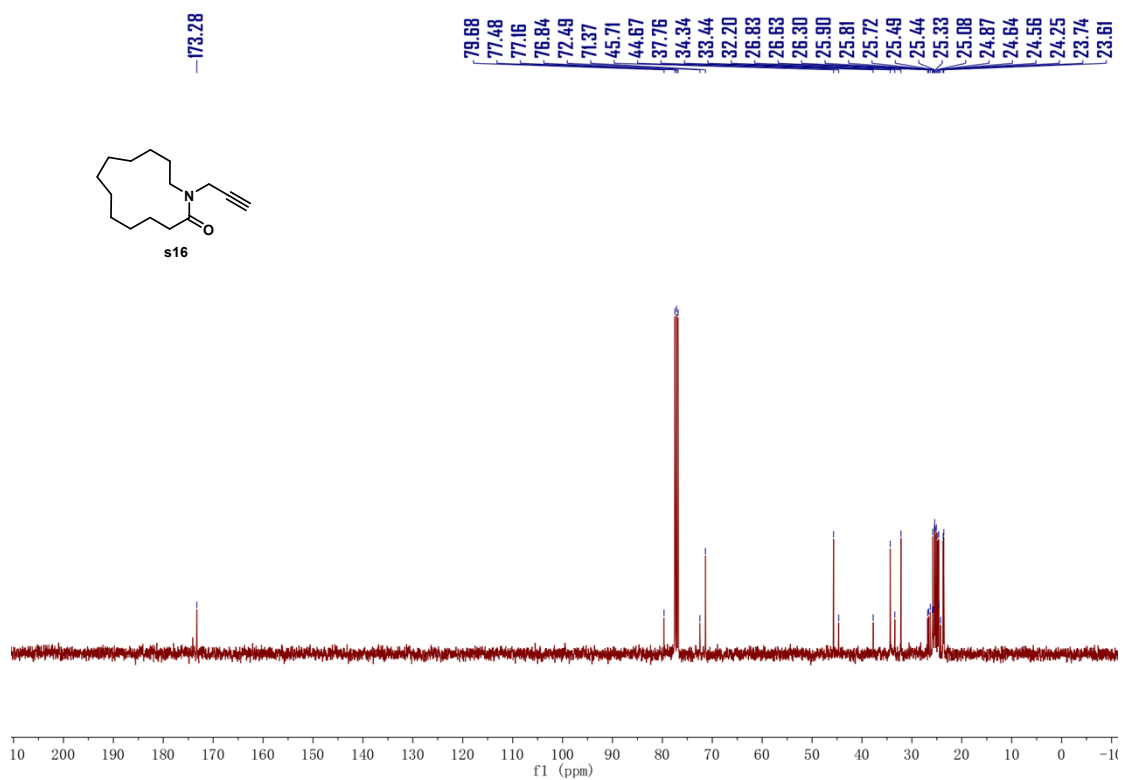
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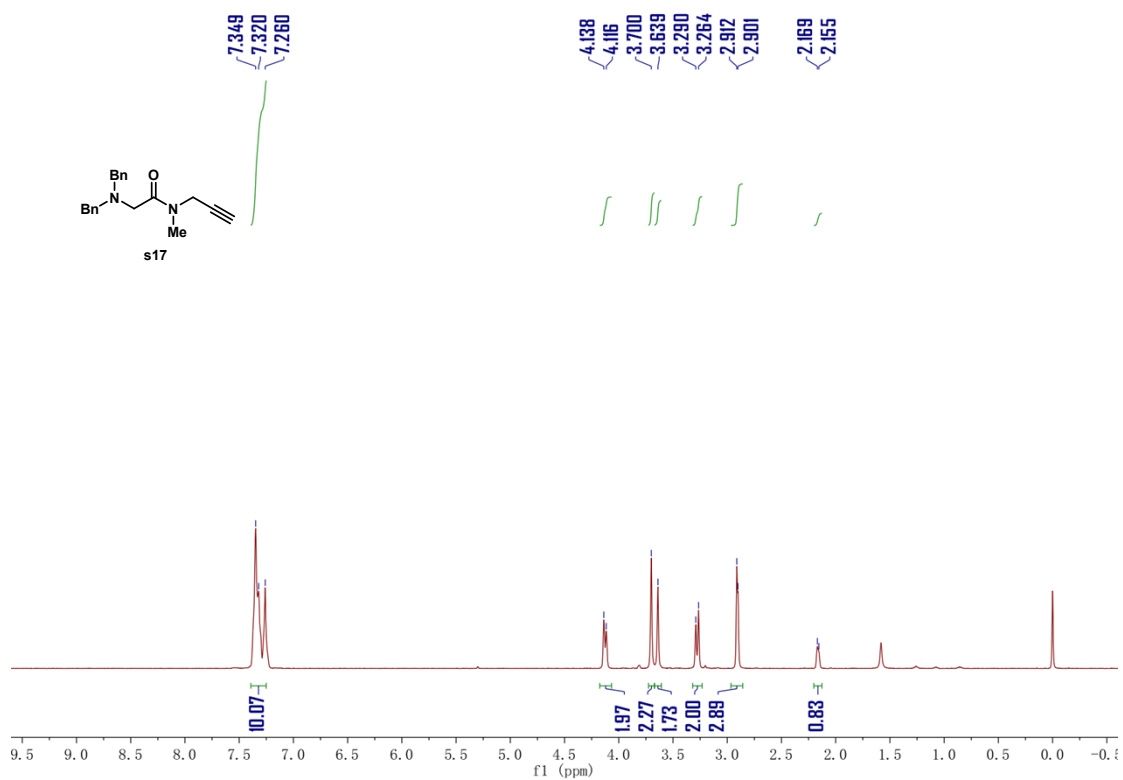
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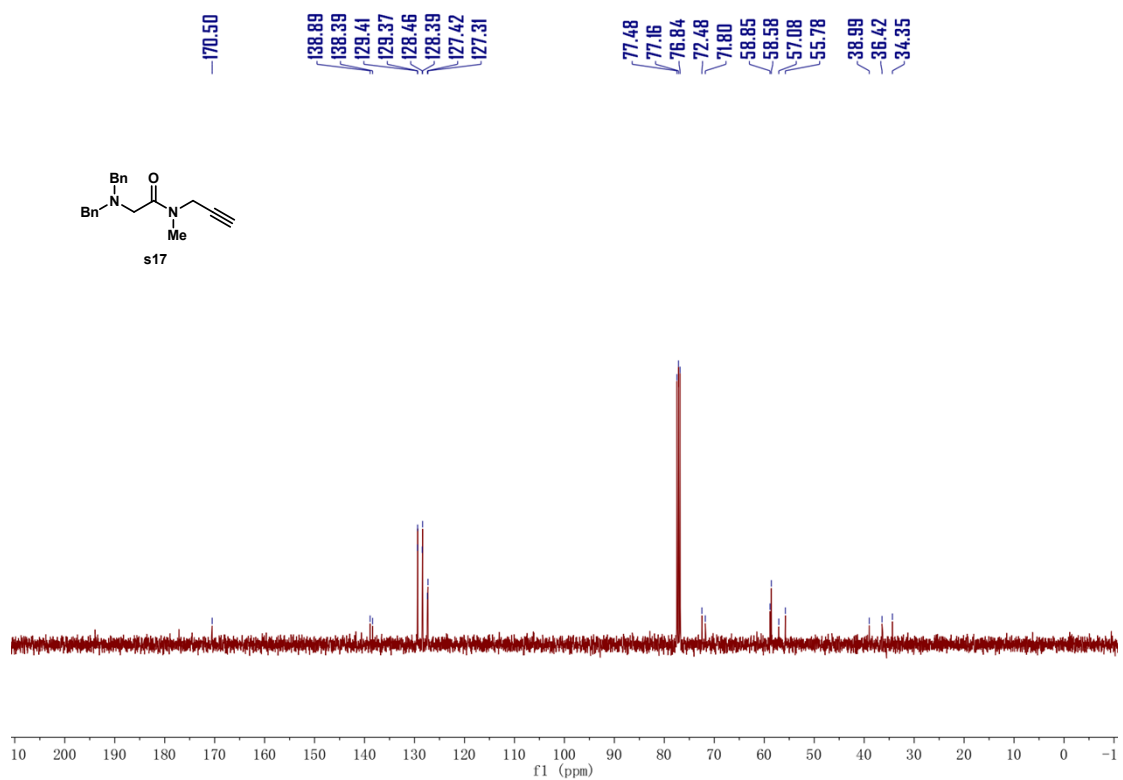
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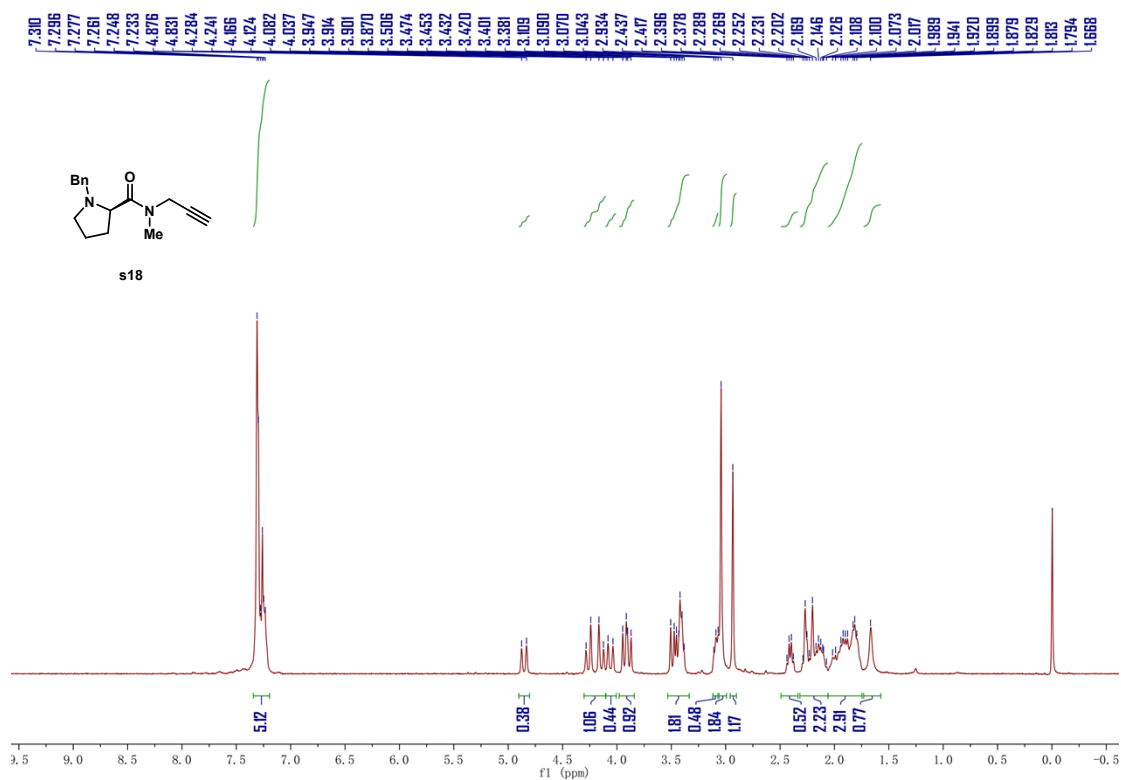
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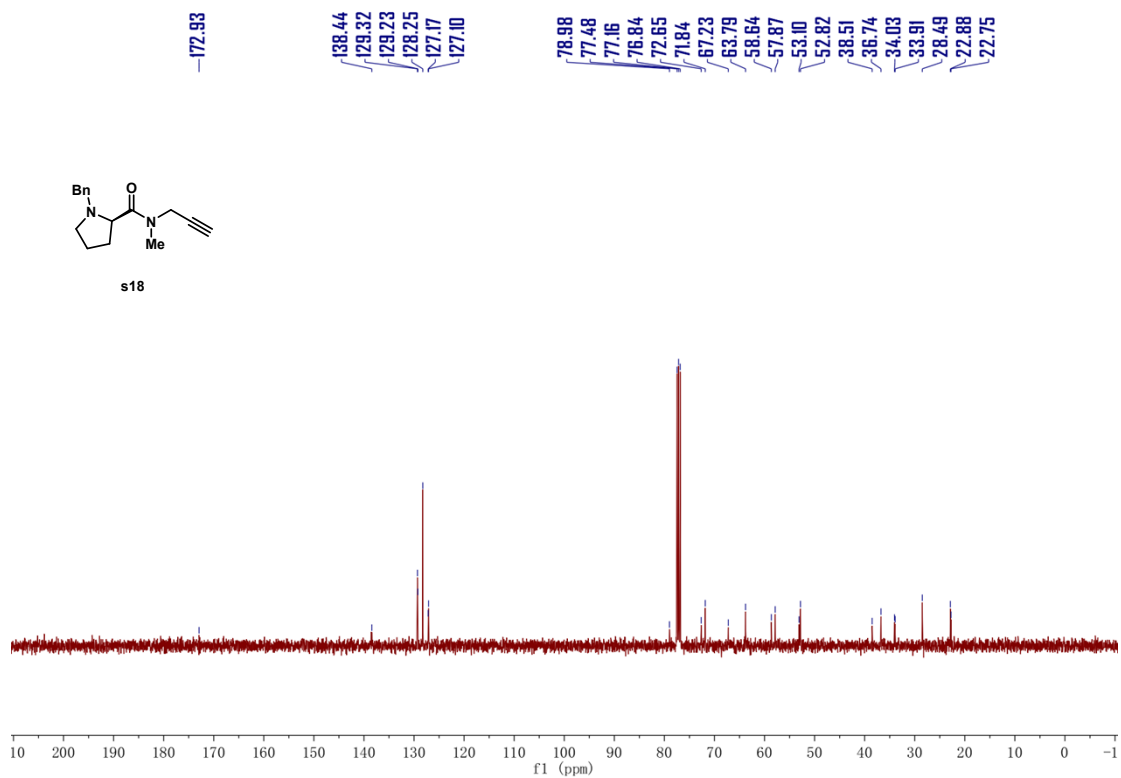
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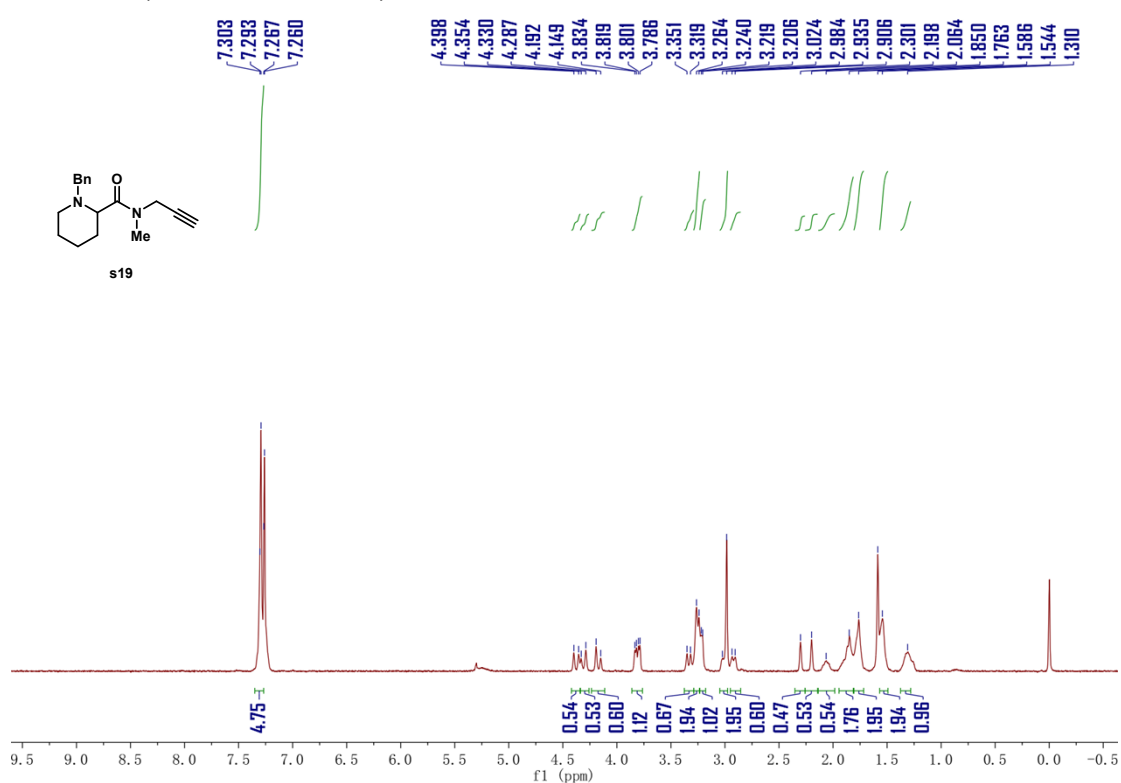
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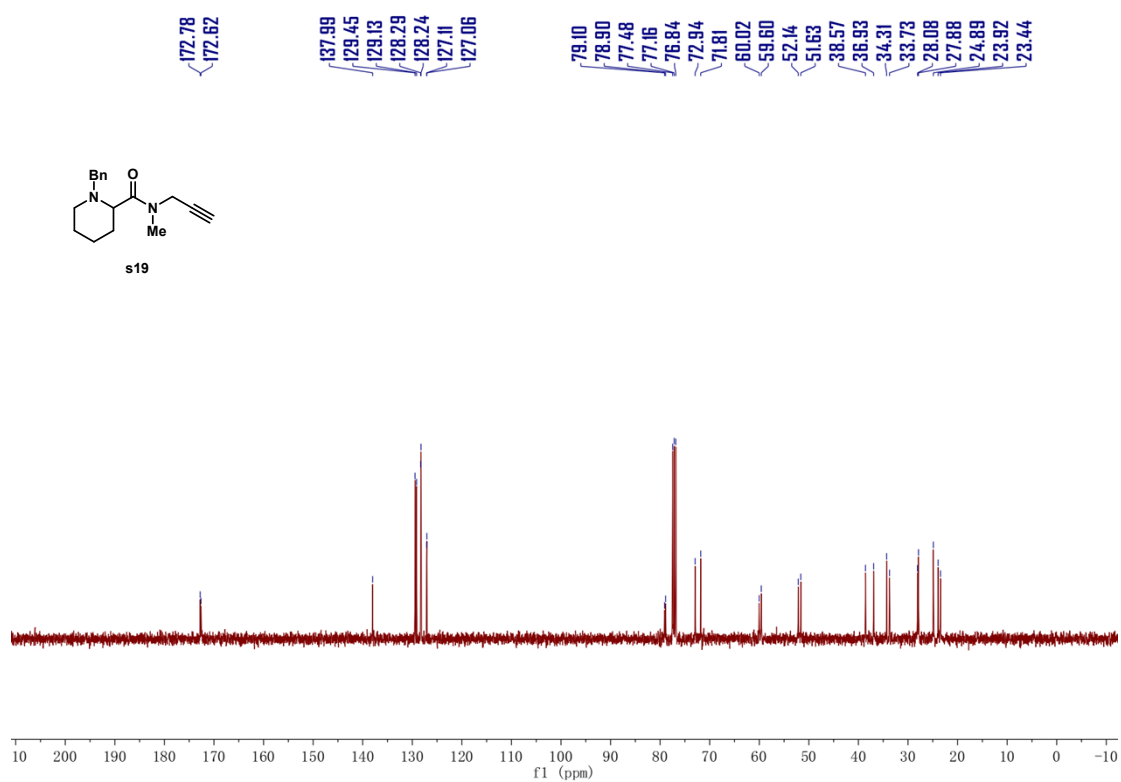
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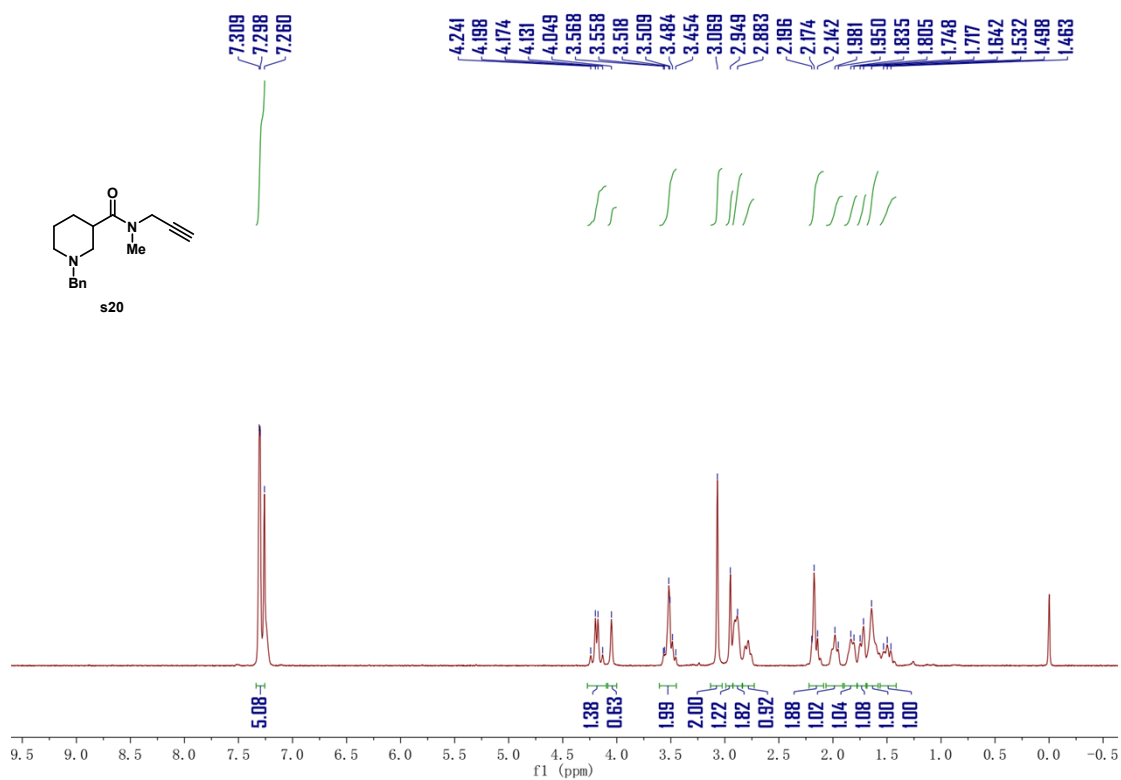
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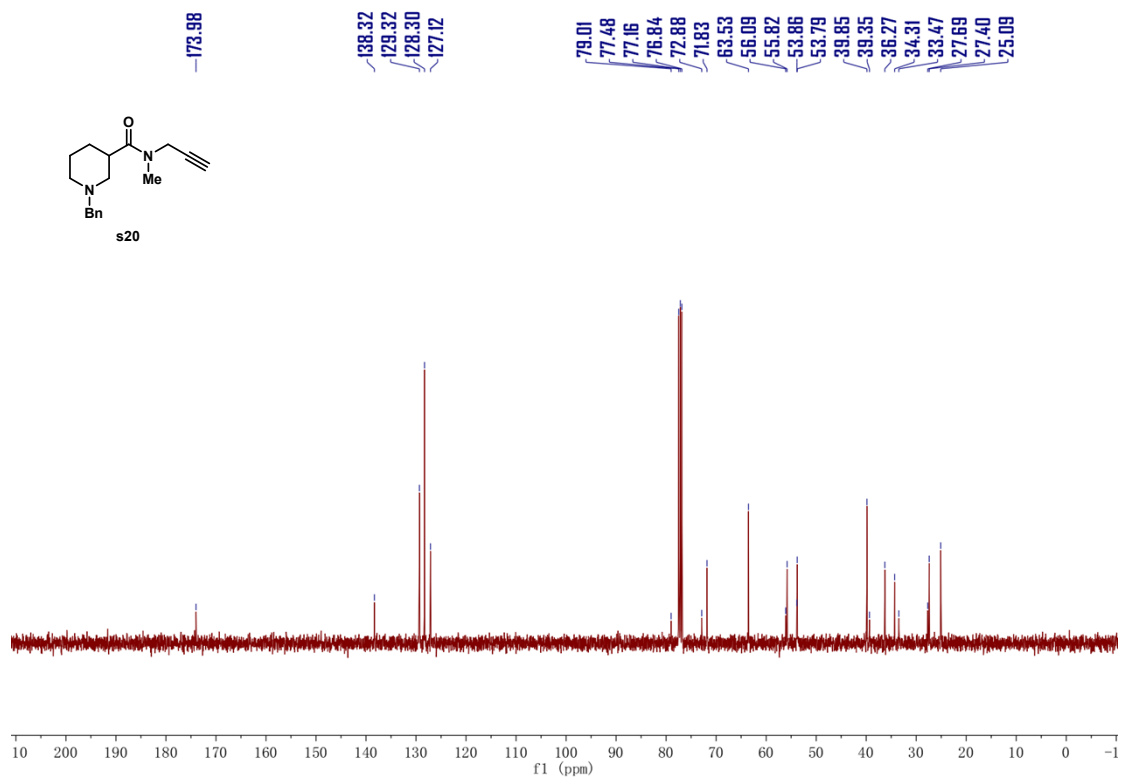
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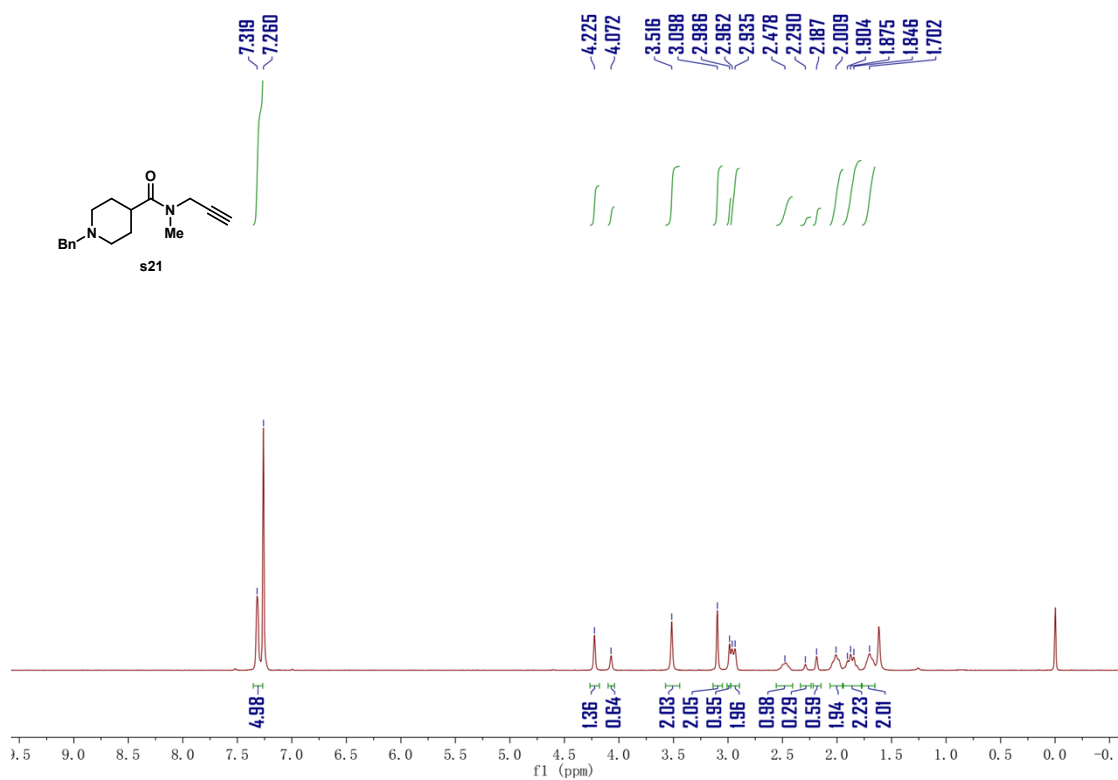
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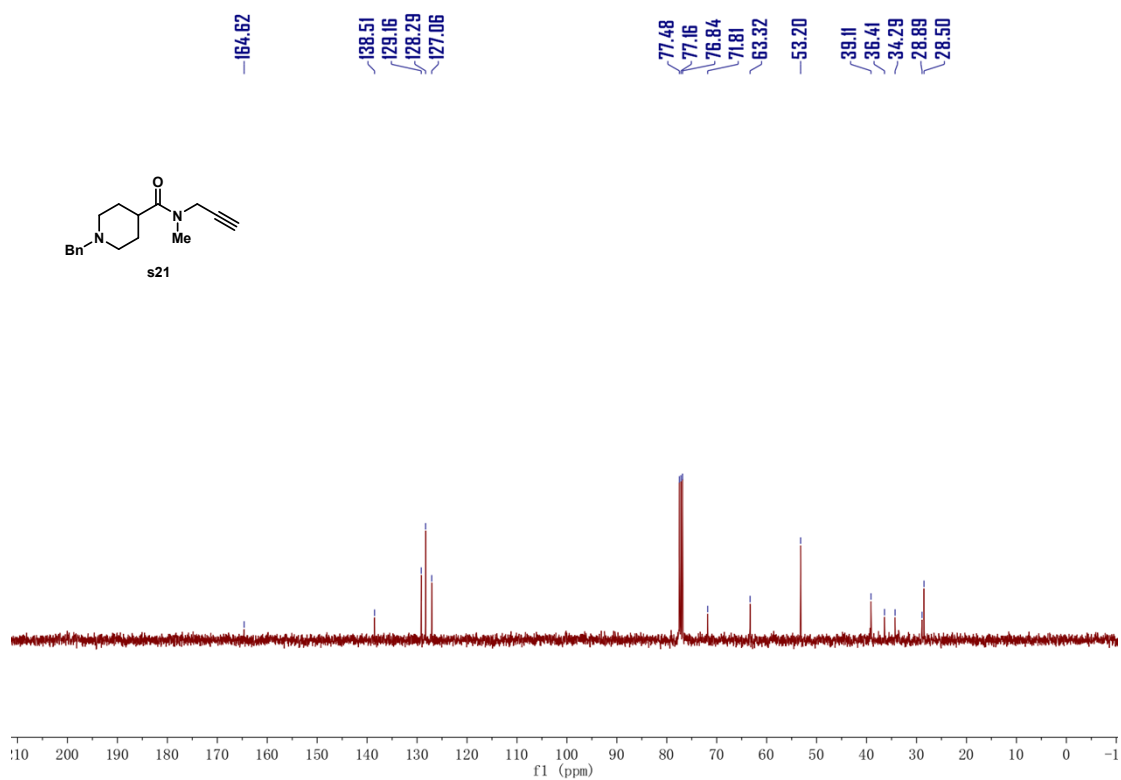
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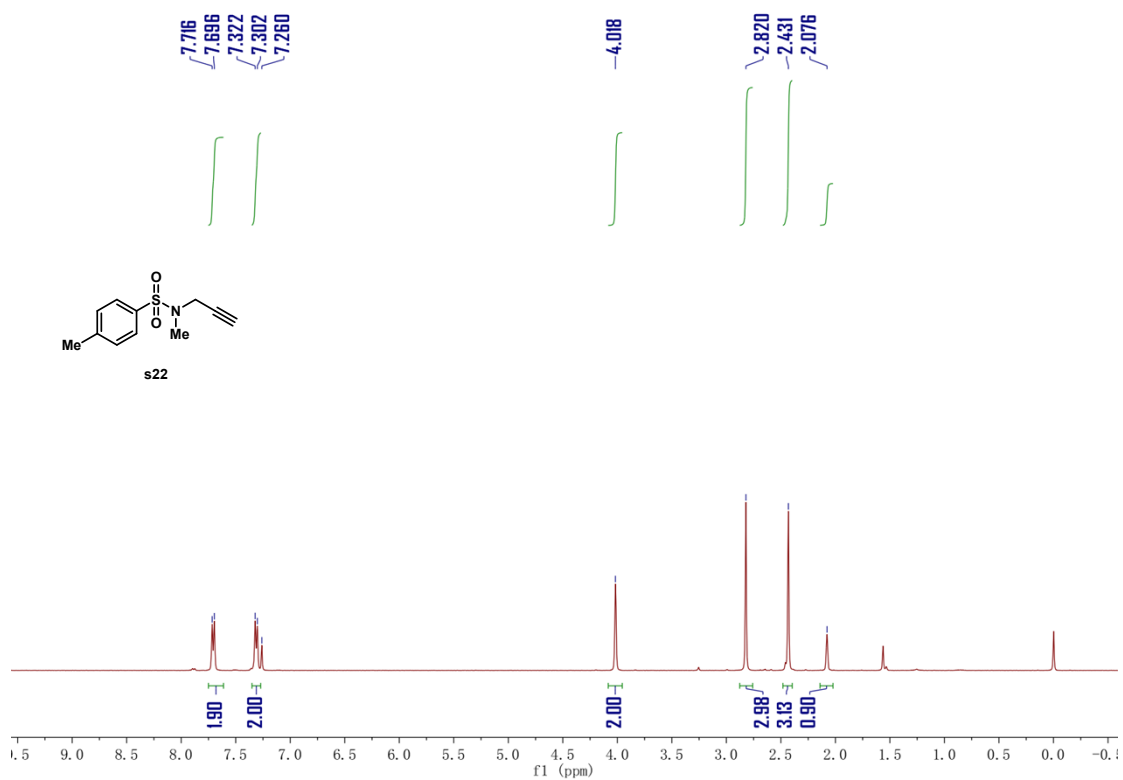
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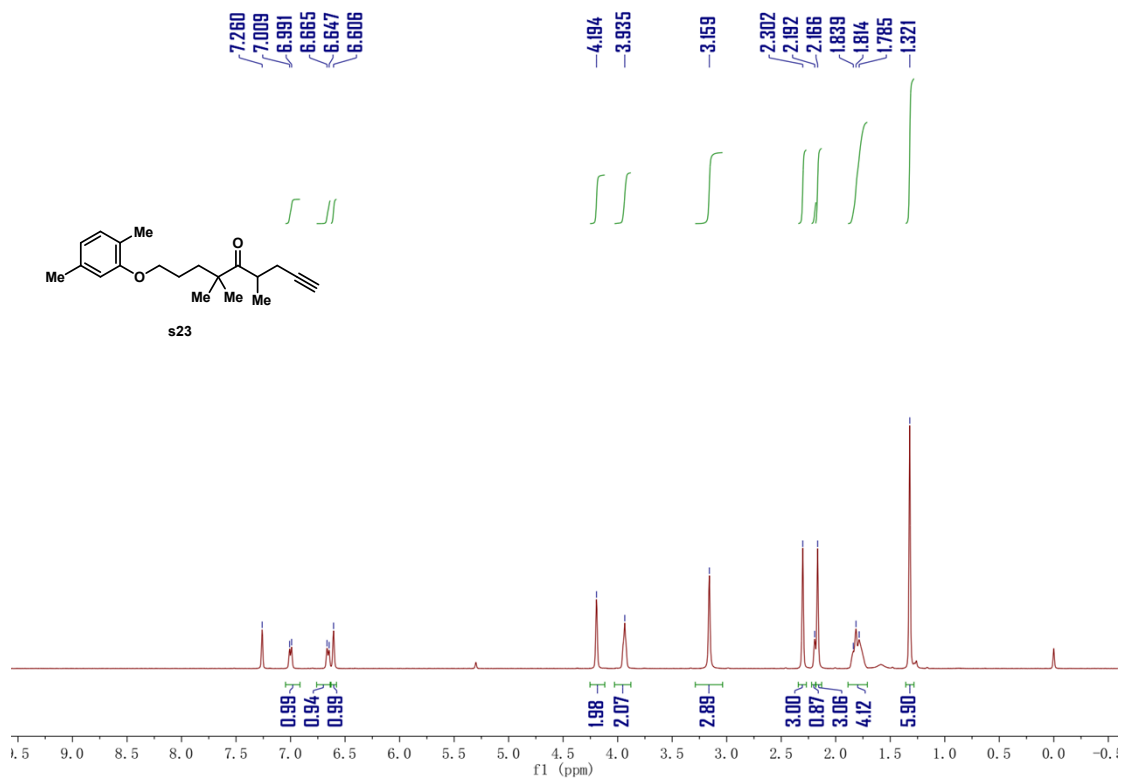
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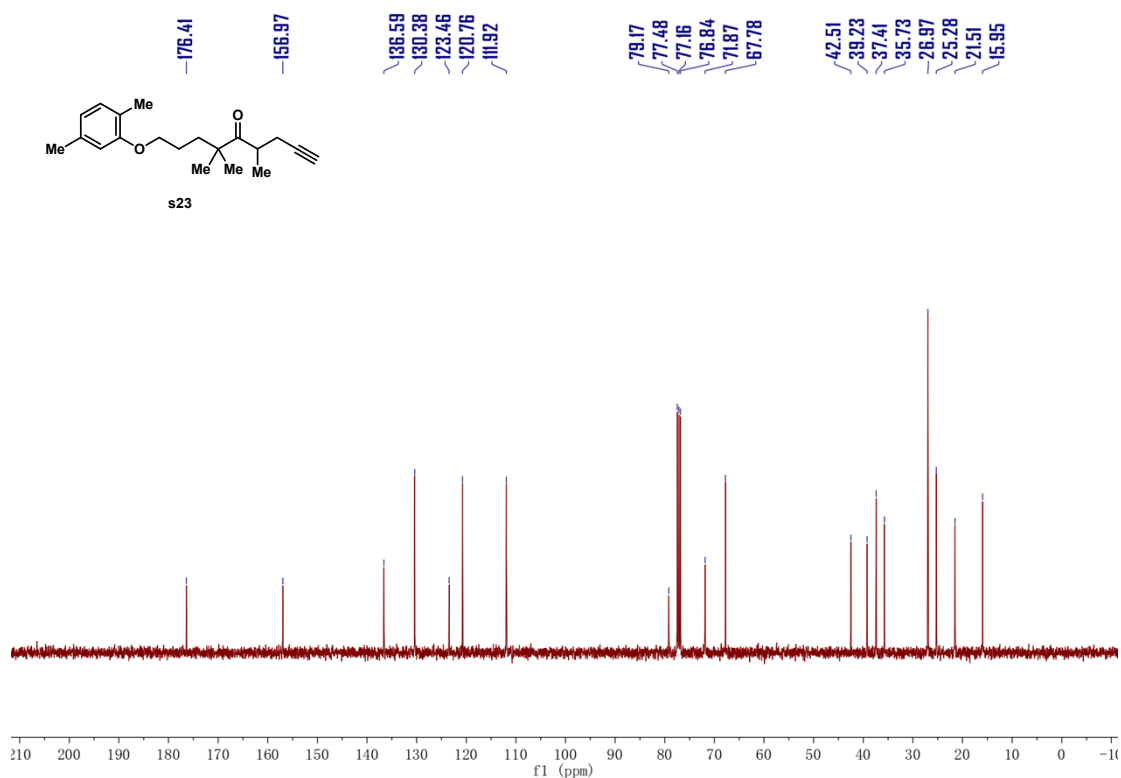
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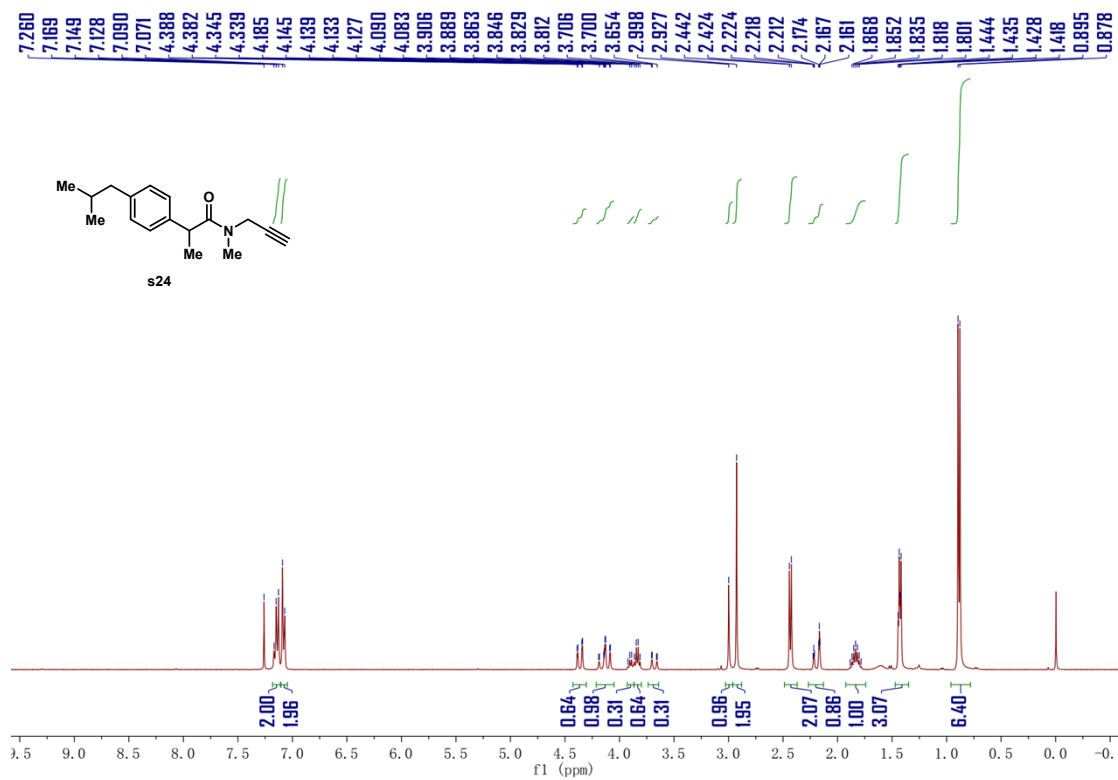
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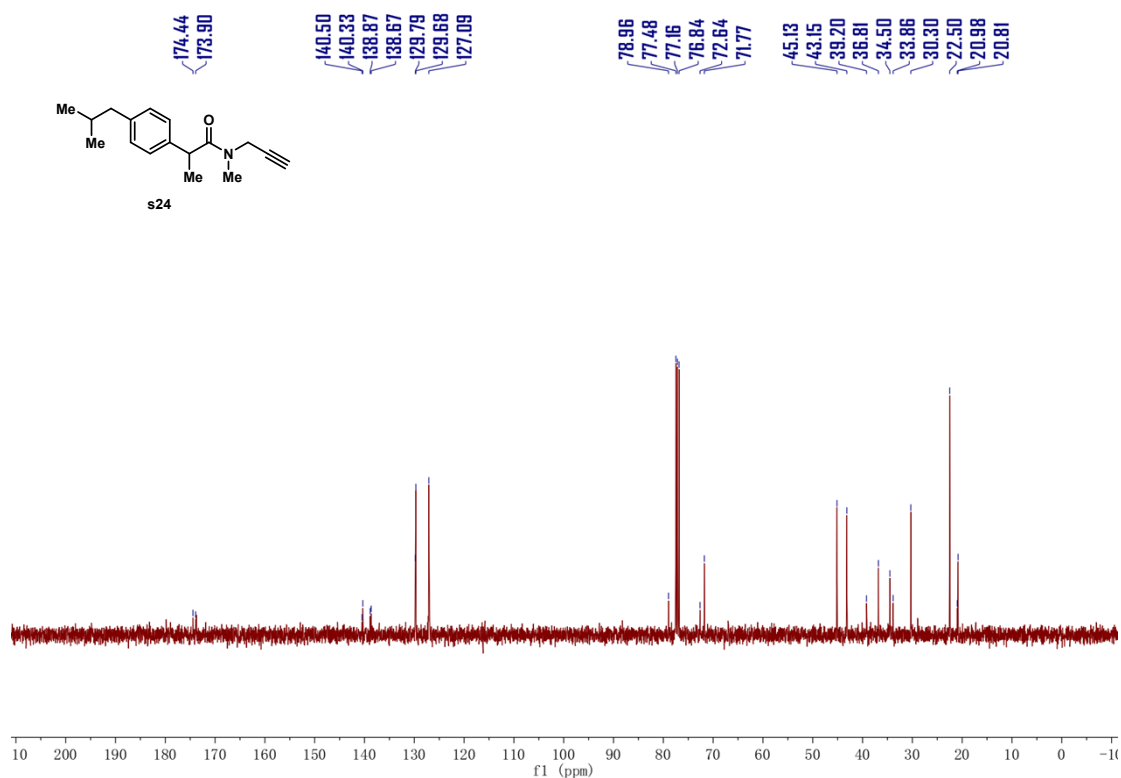
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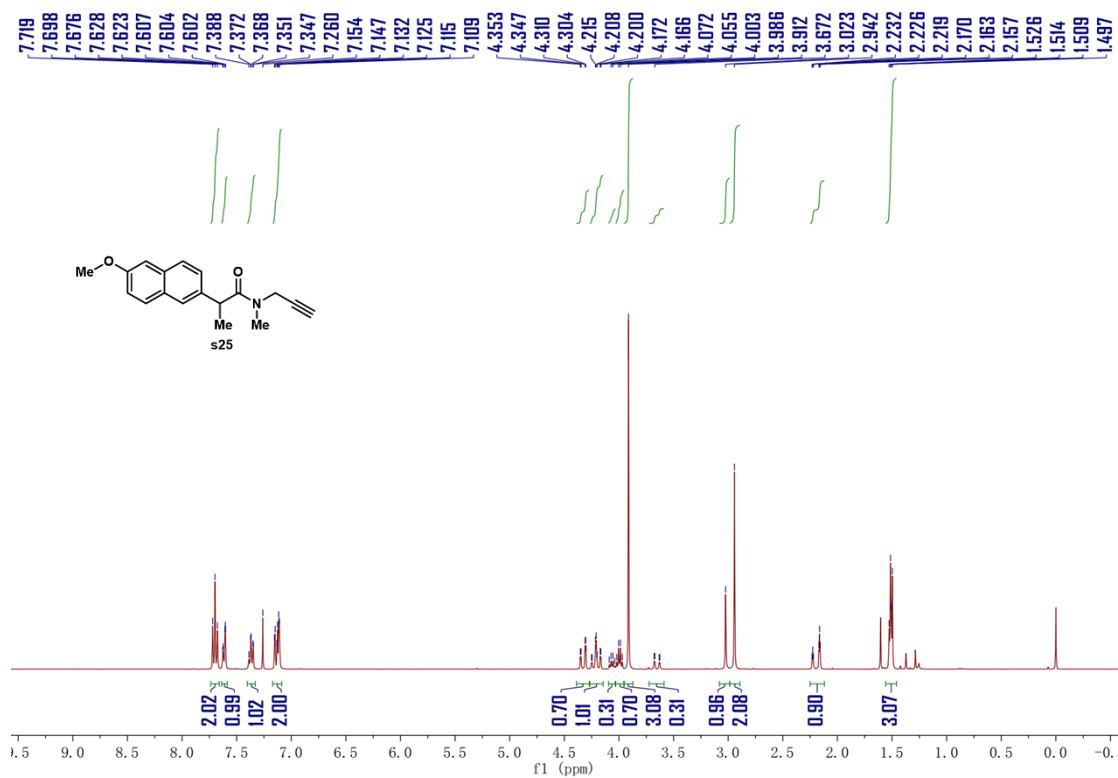
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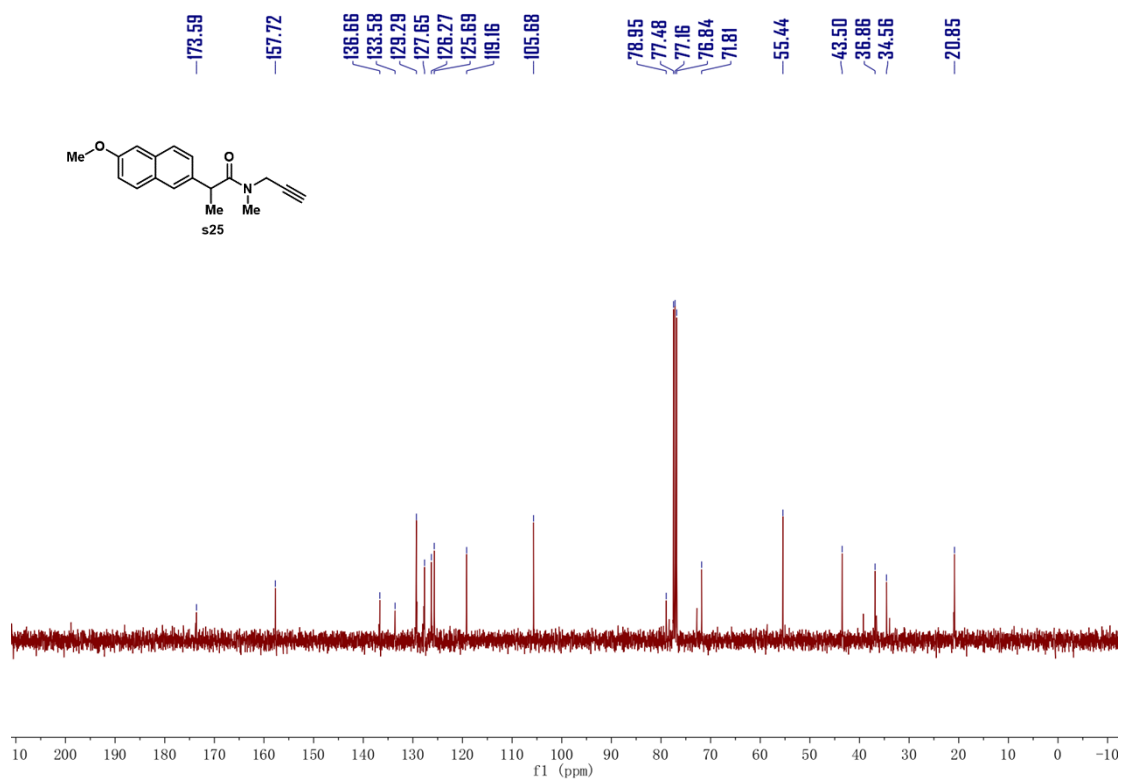
¹³C NMR (101 MHz, CDCl₃):



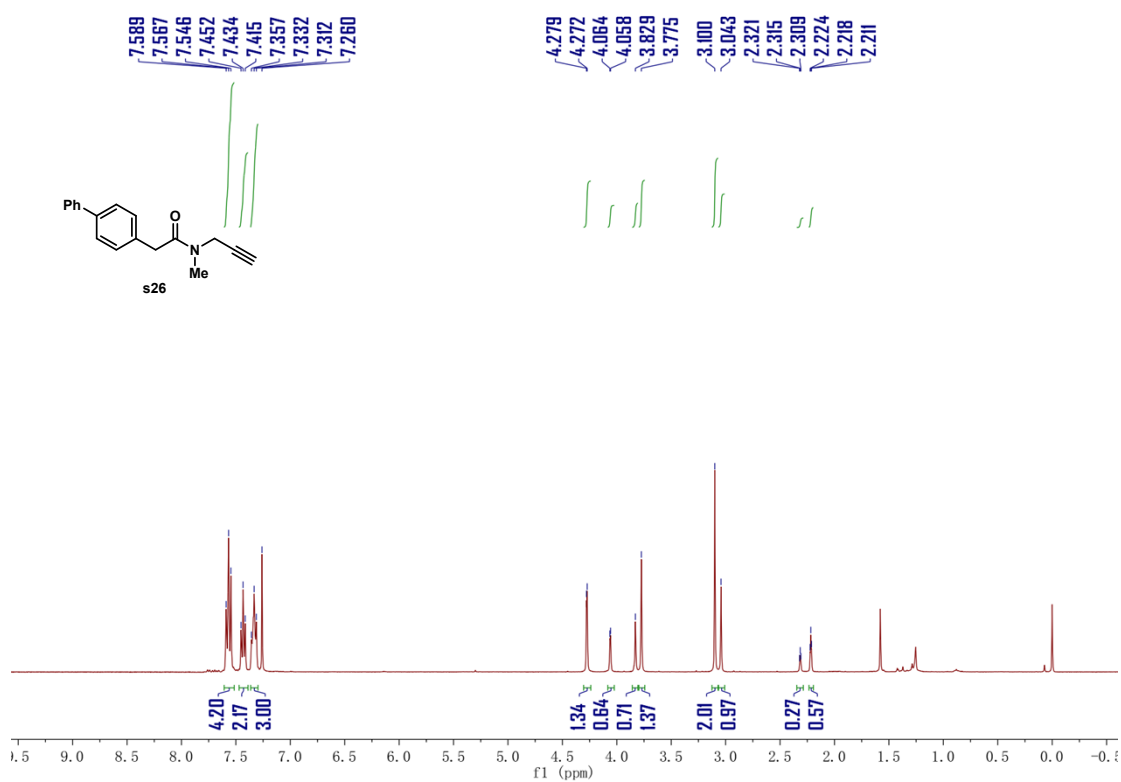
¹H NMR (400 MHz, CDCl₃):



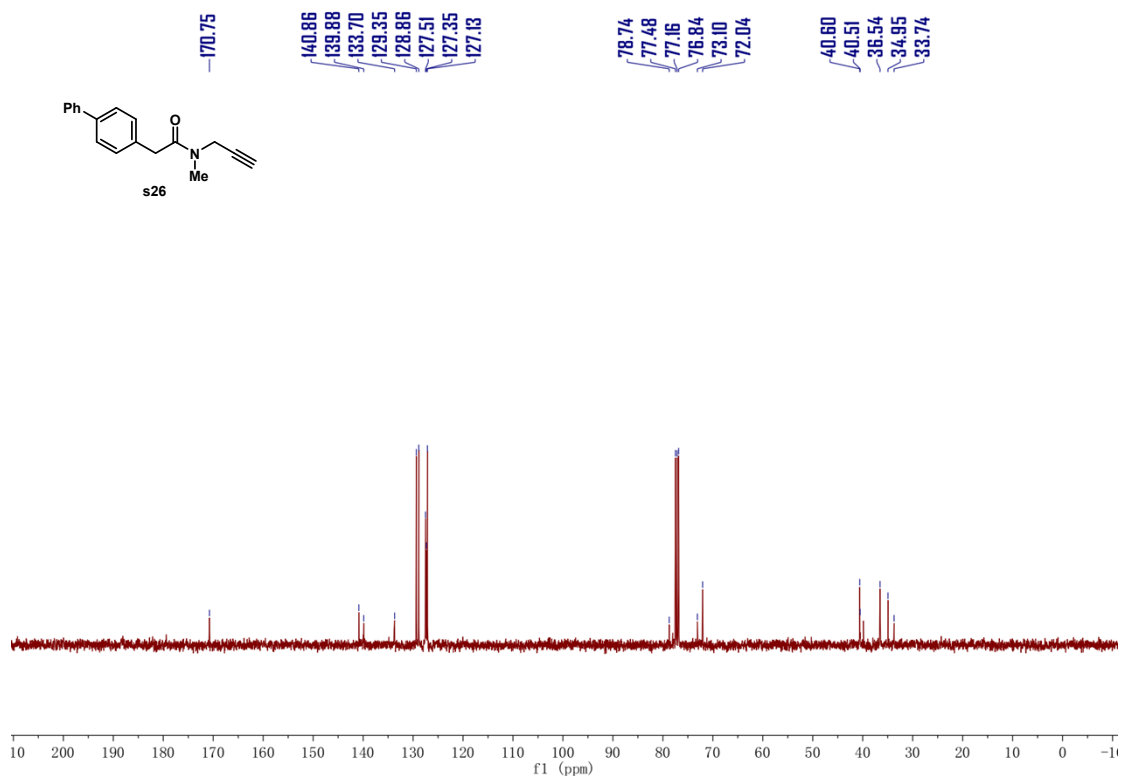
^{13}C NMR (101 MHz, CDCl_3):



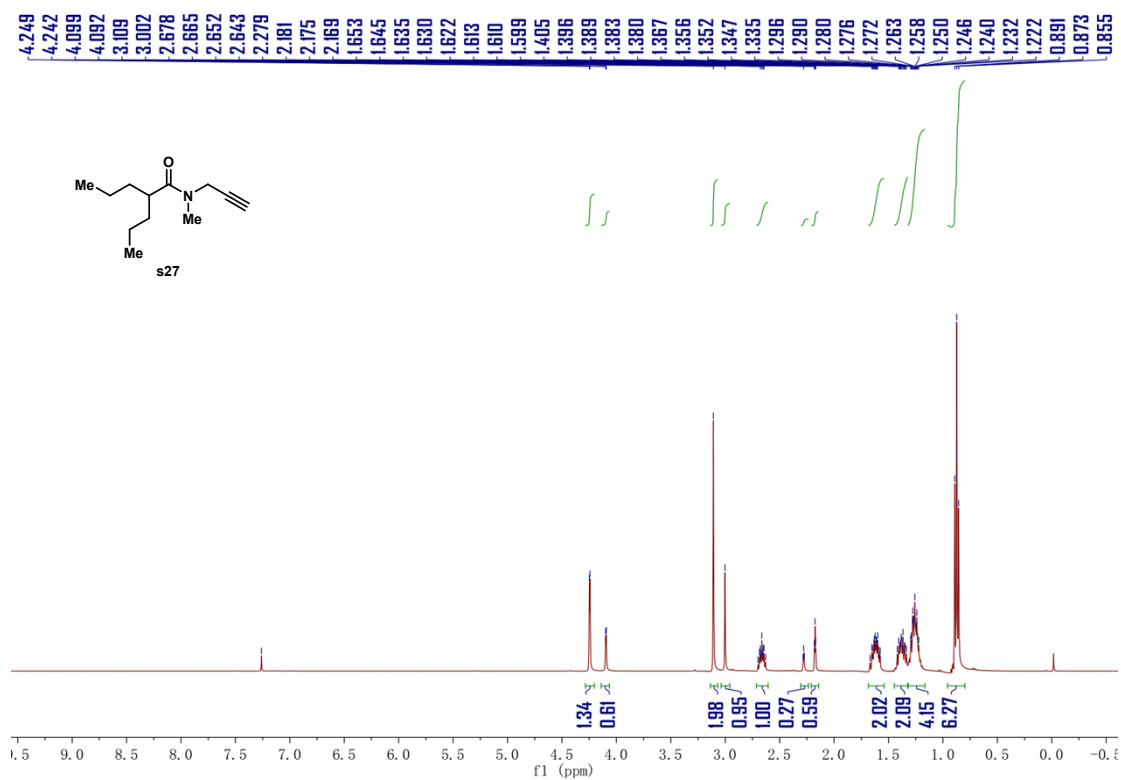
^1H NMR (400 MHz, CDCl_3):



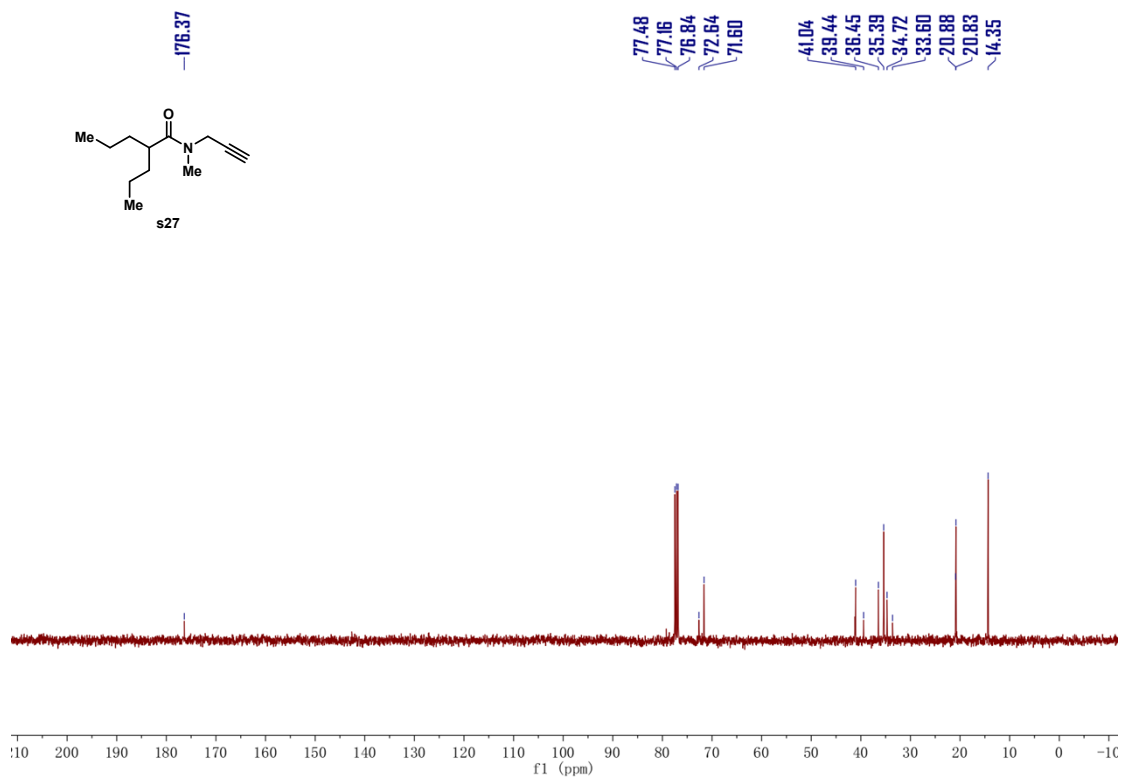
¹³C NMR (101 MHz, CDCl₃):



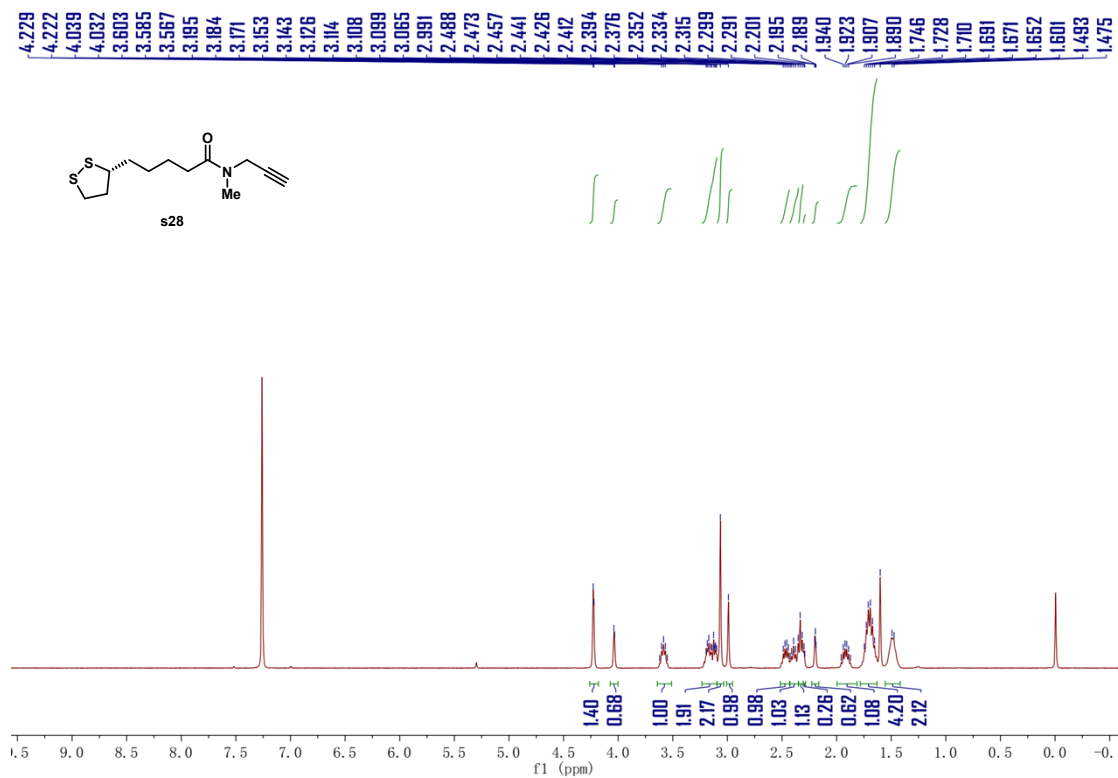
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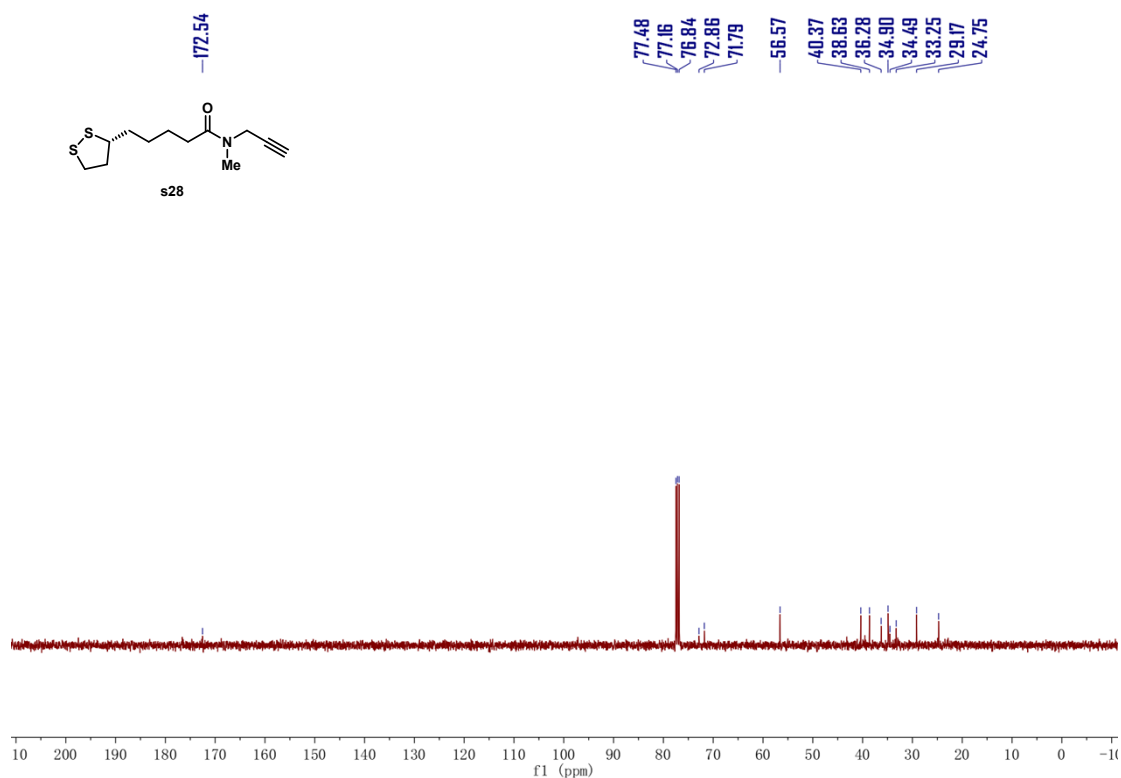
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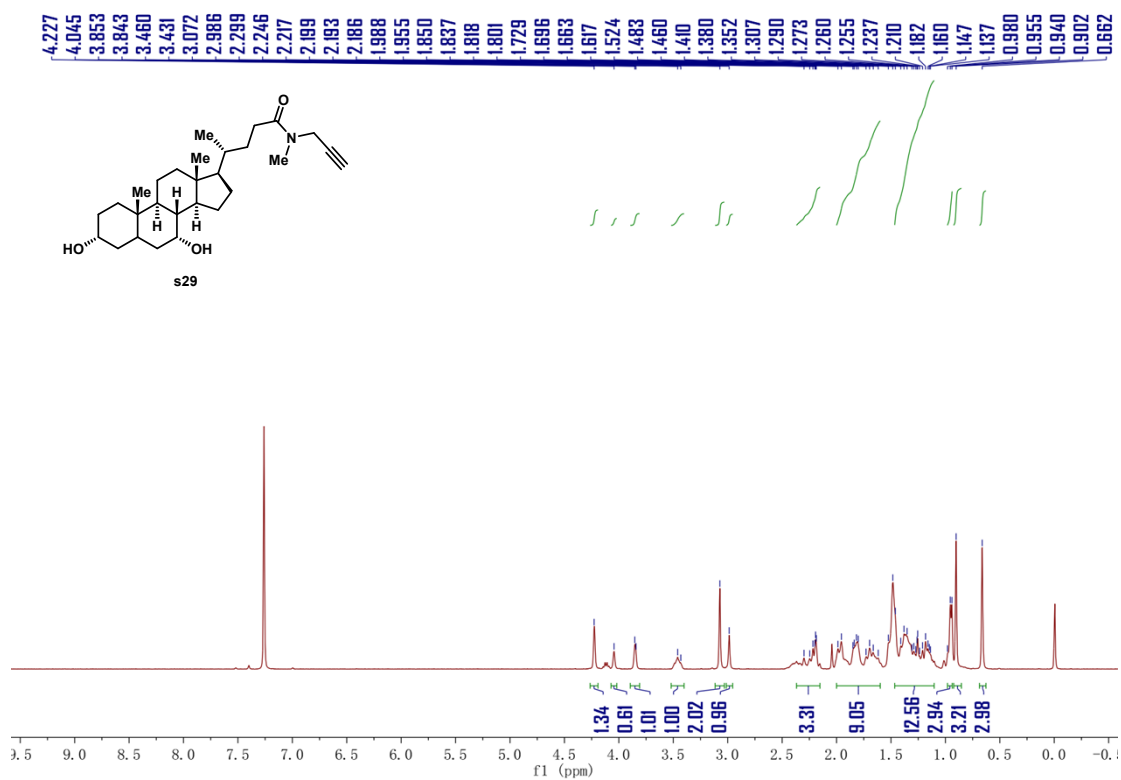
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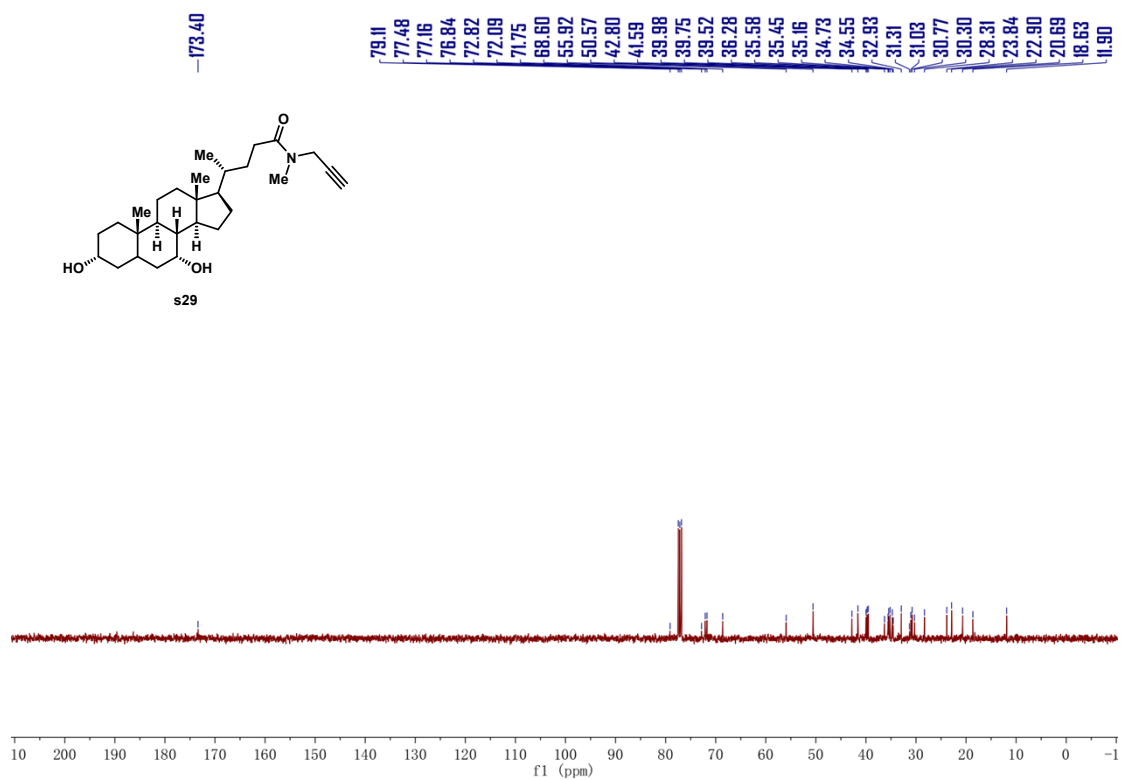
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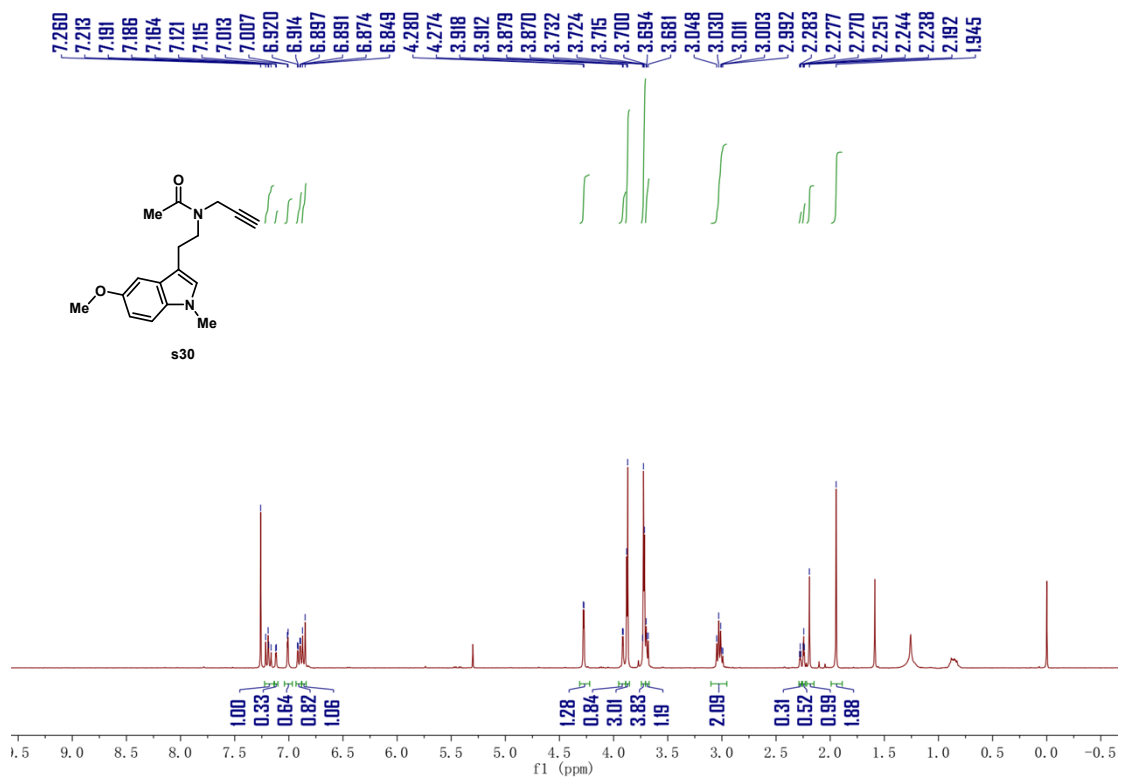
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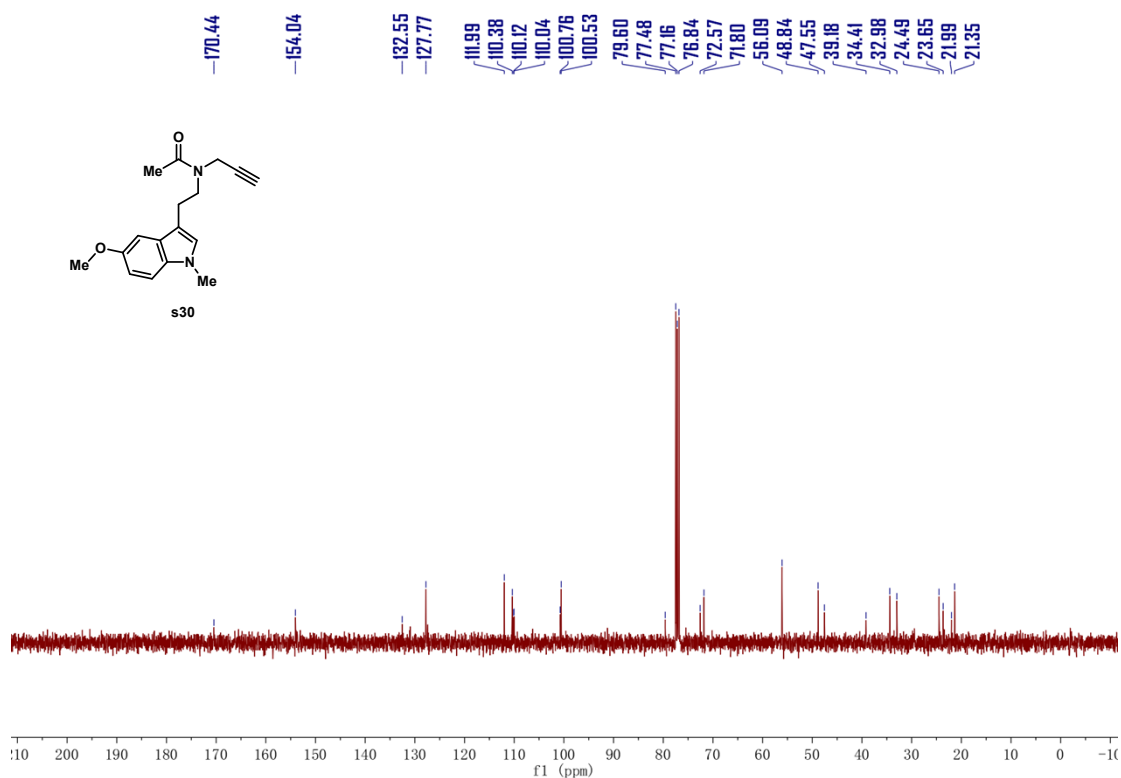
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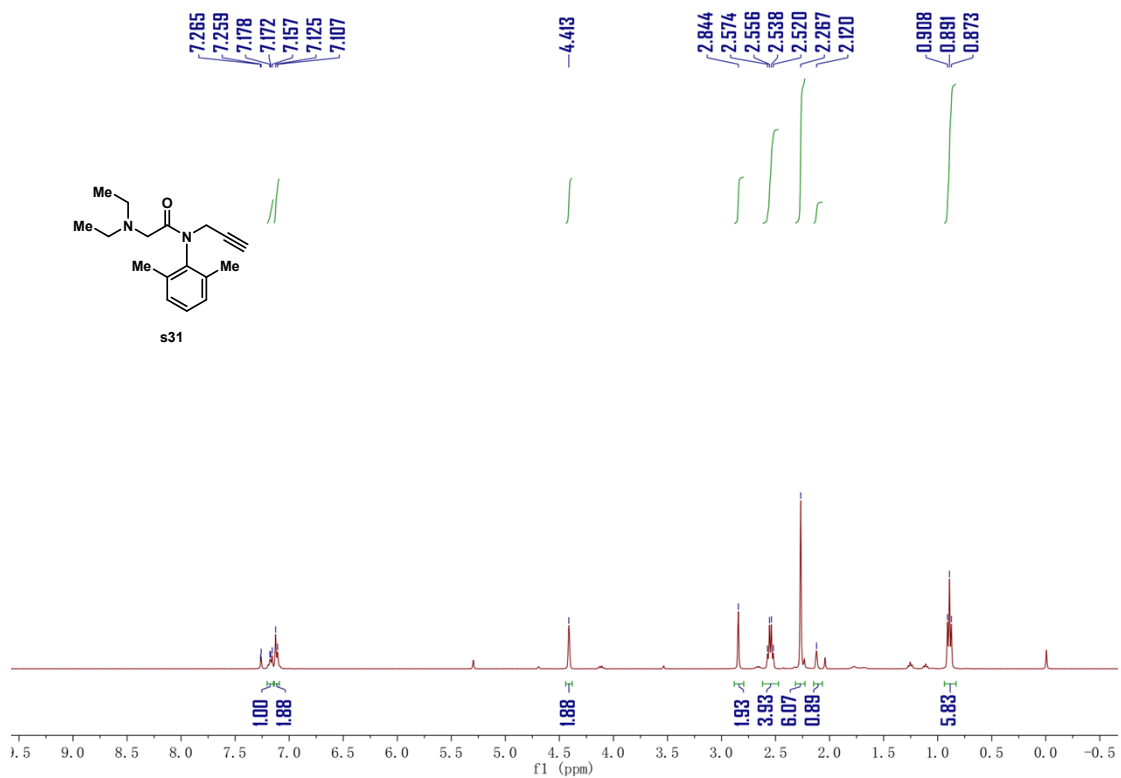
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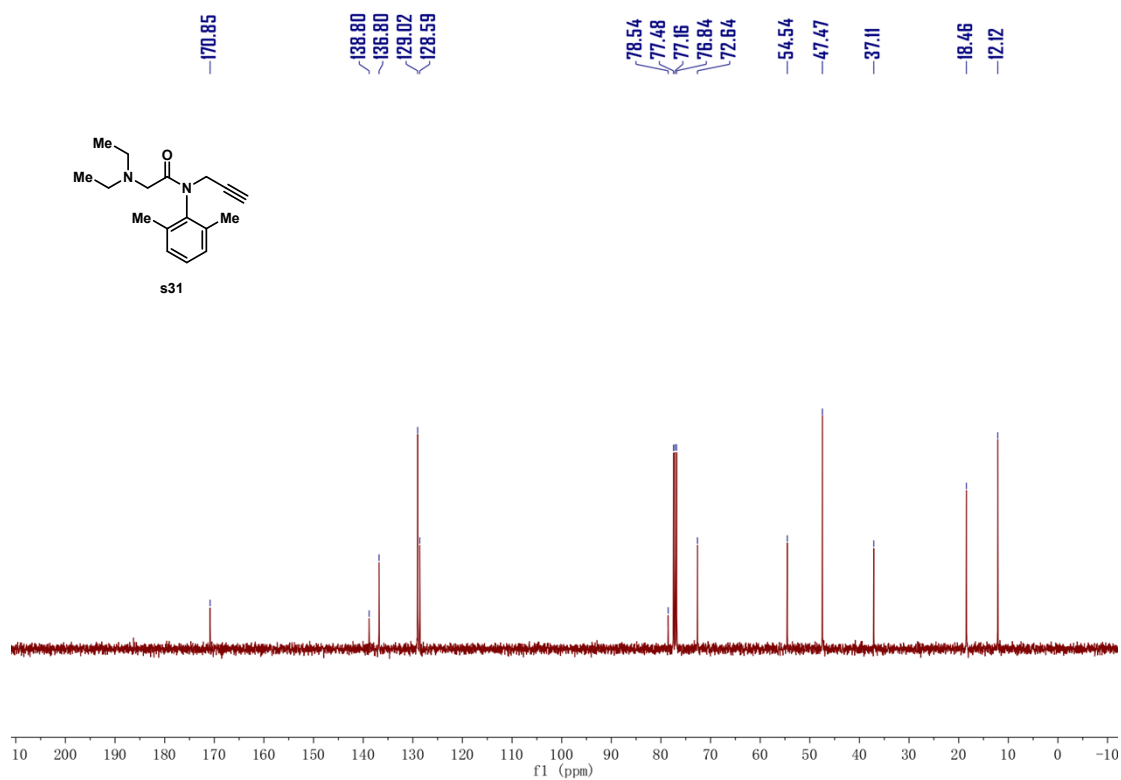
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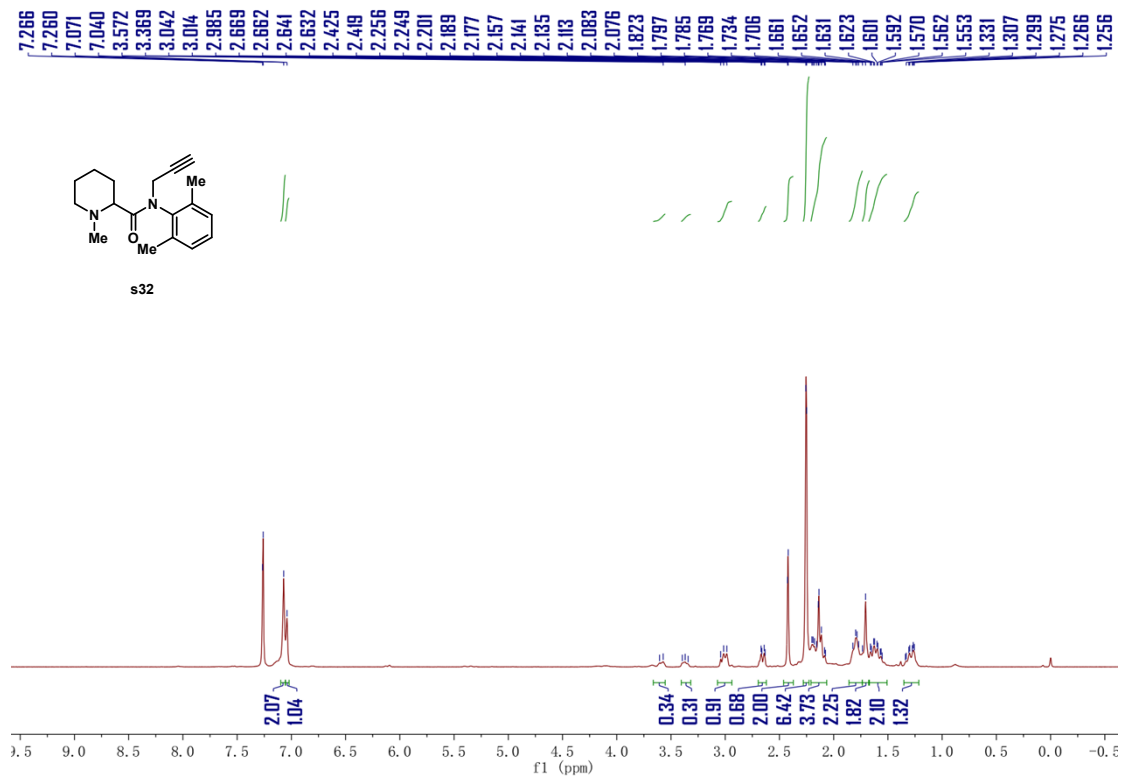
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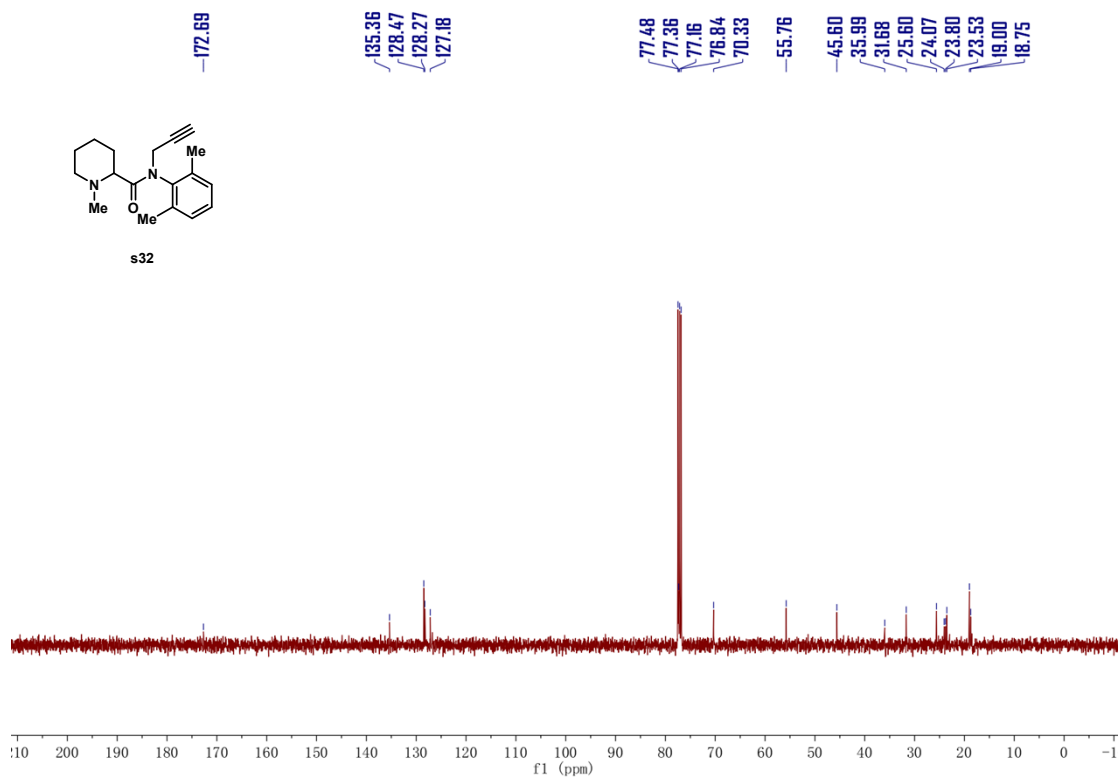
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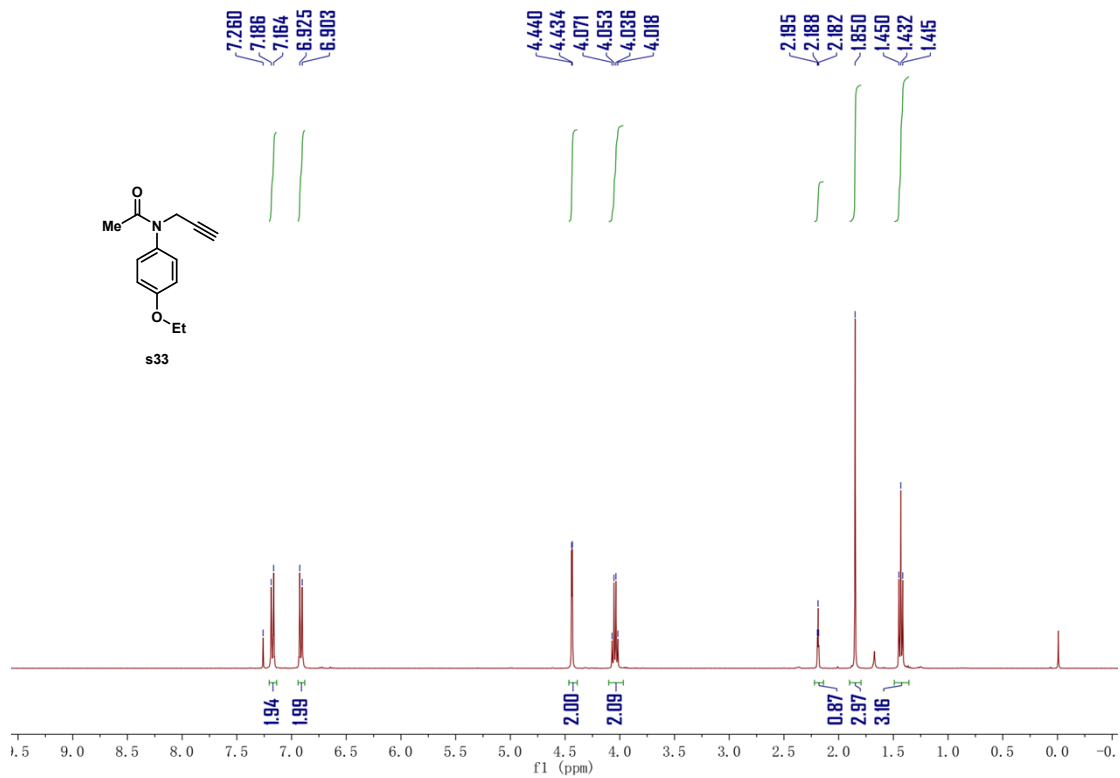
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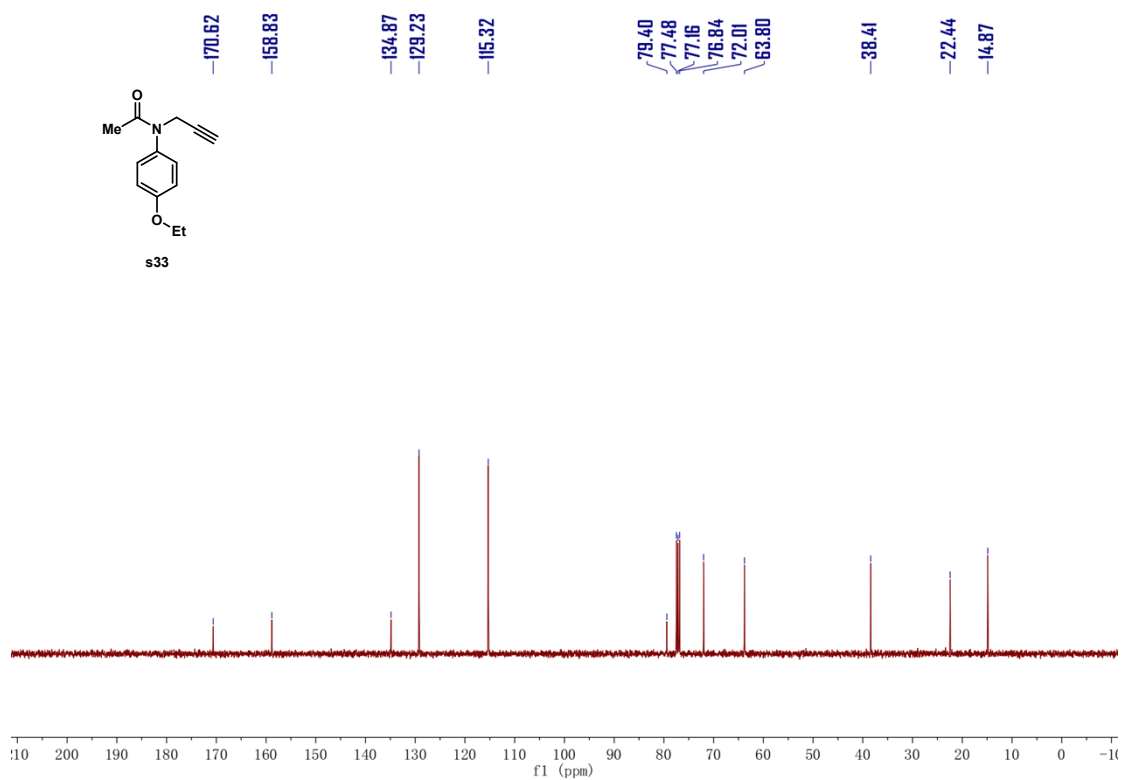
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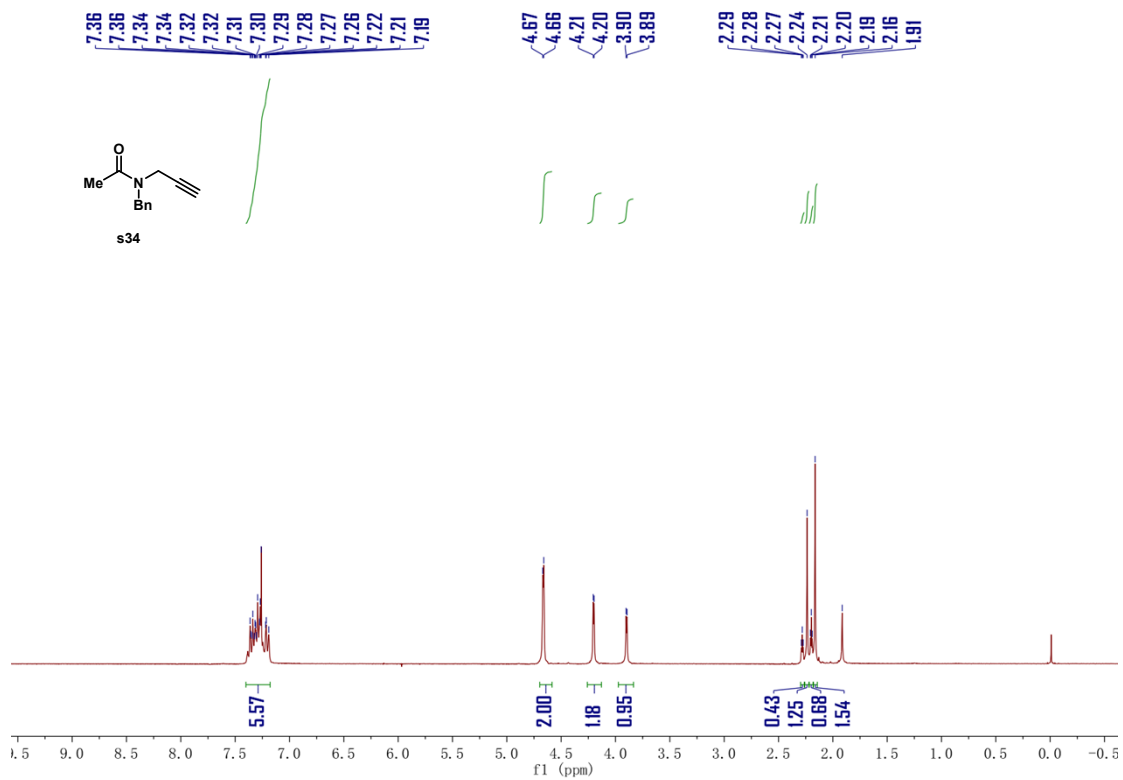
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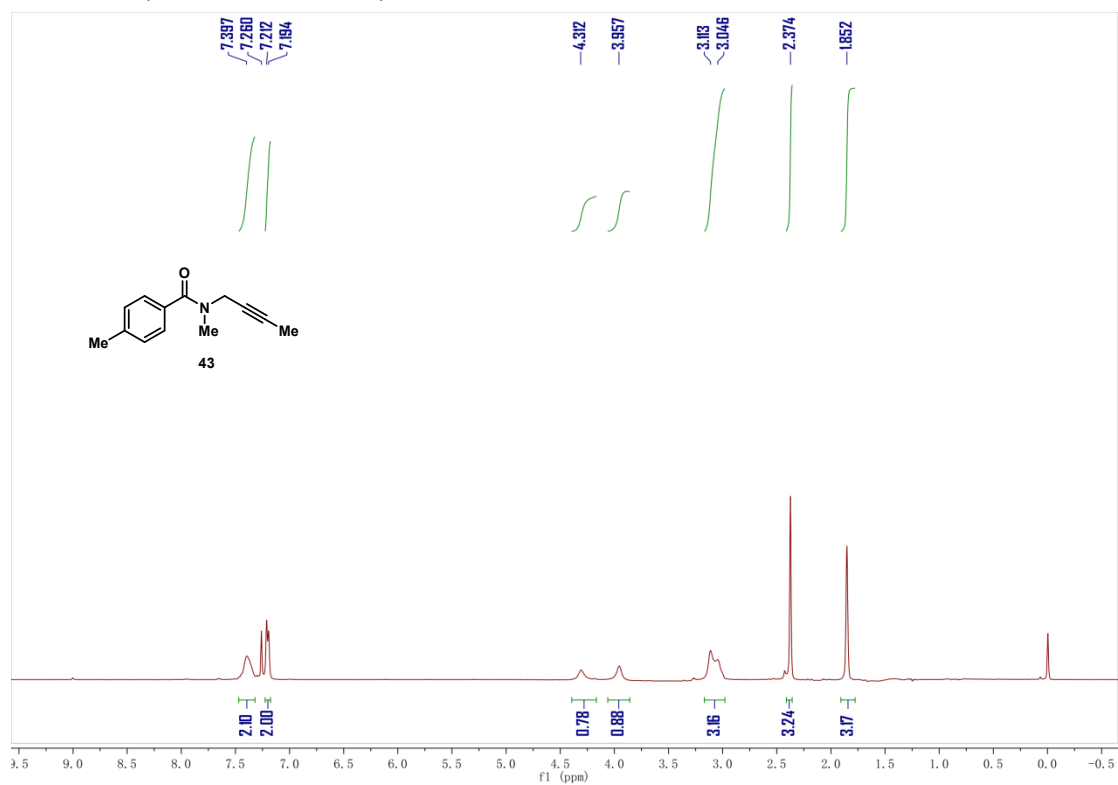
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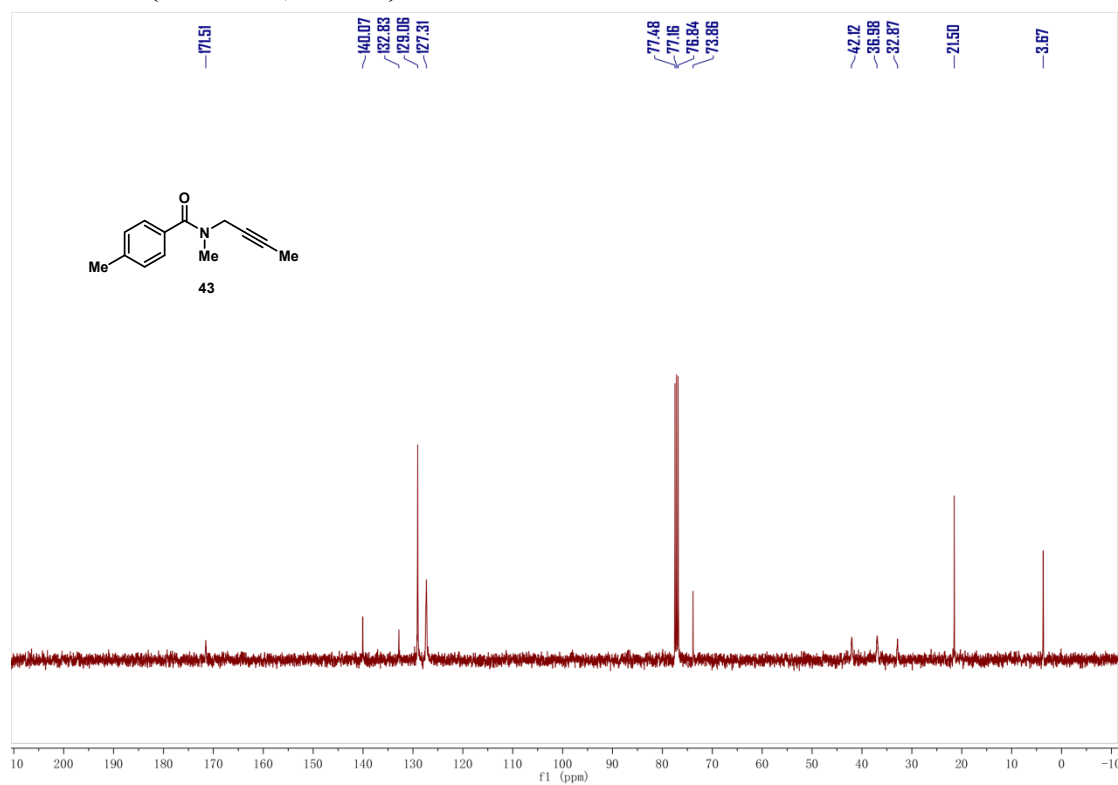
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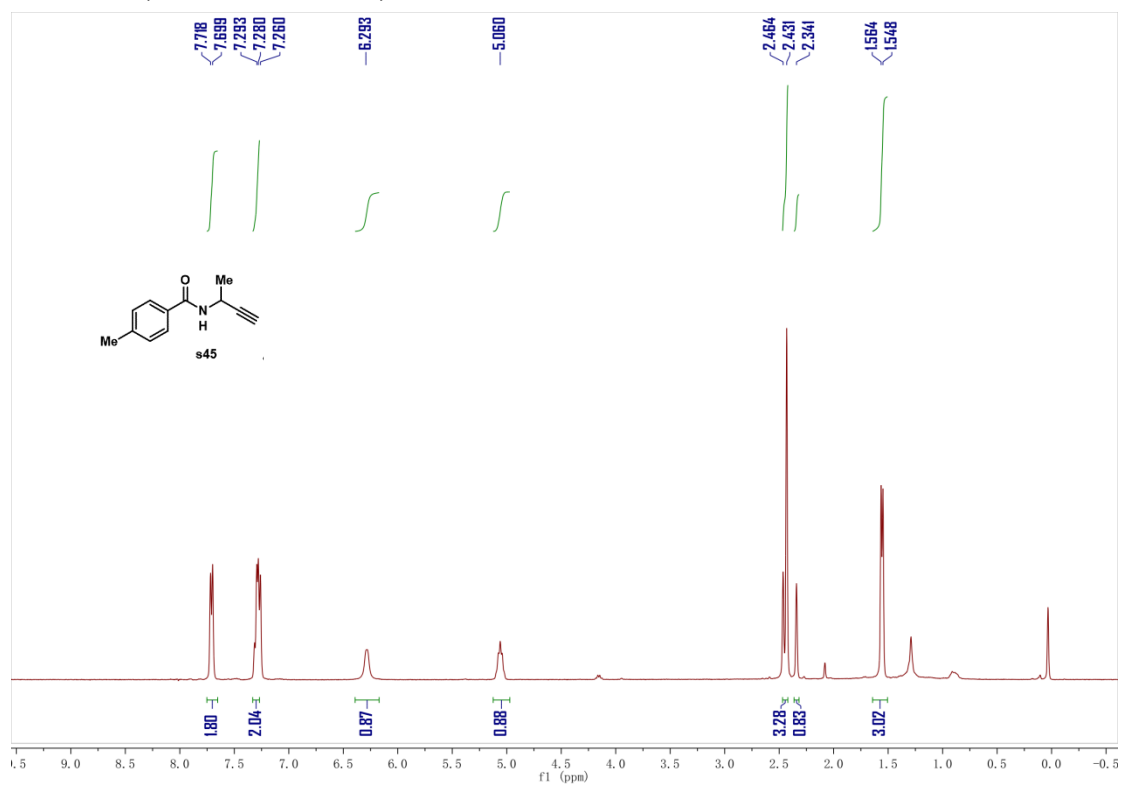
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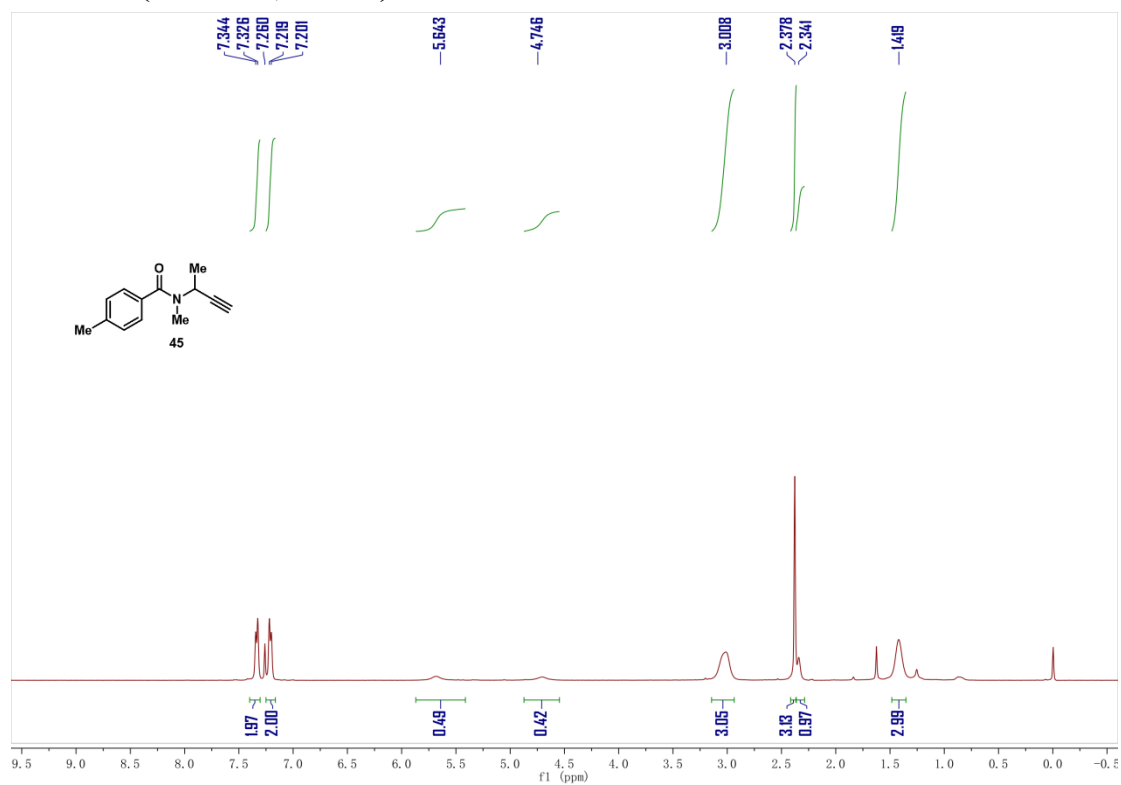
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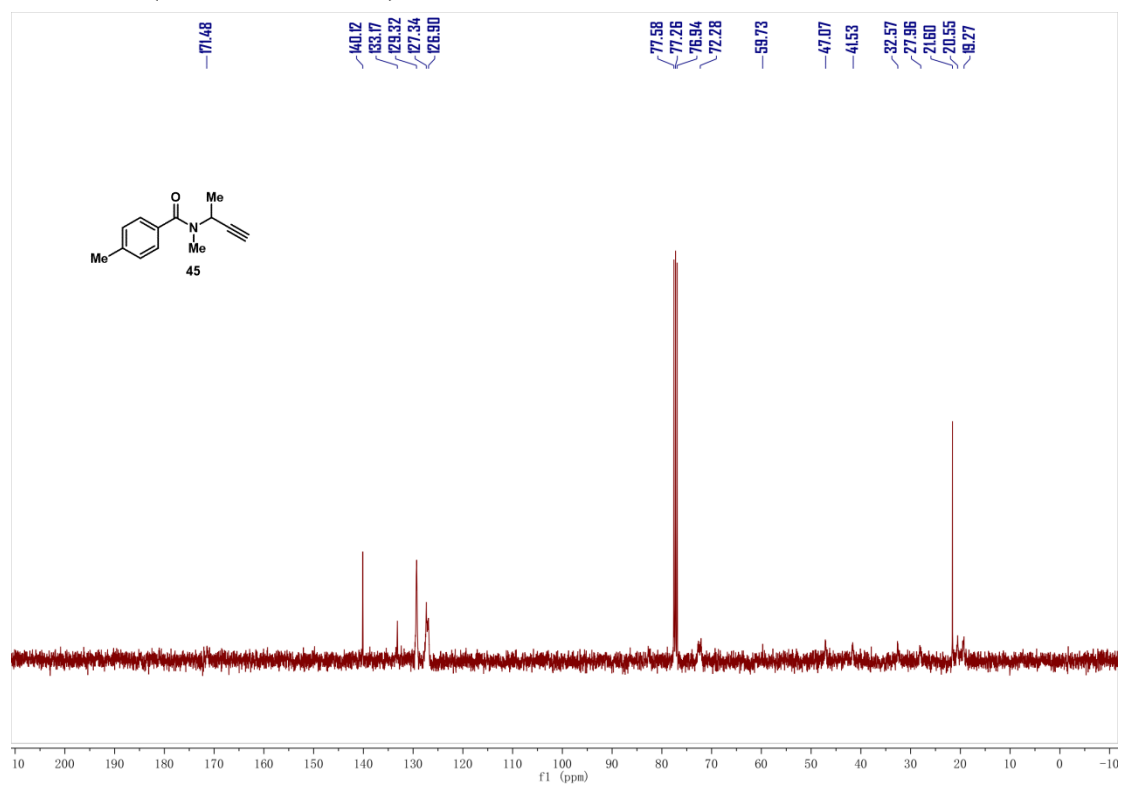
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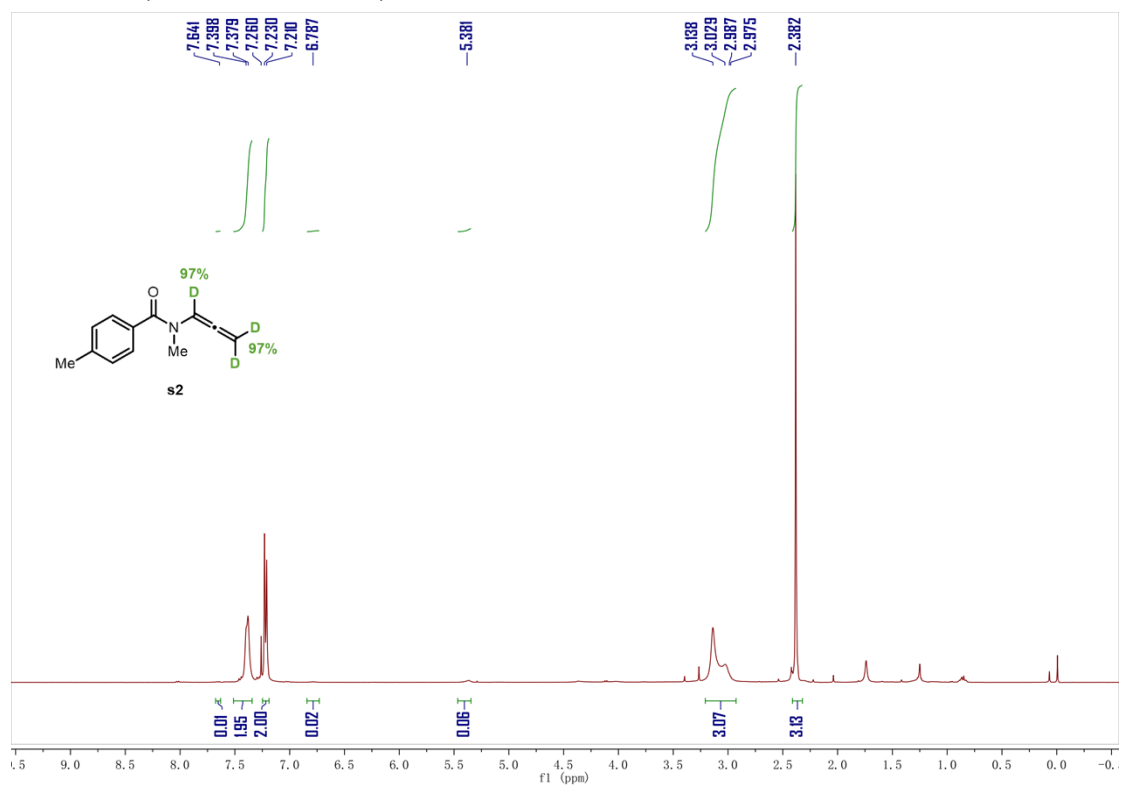
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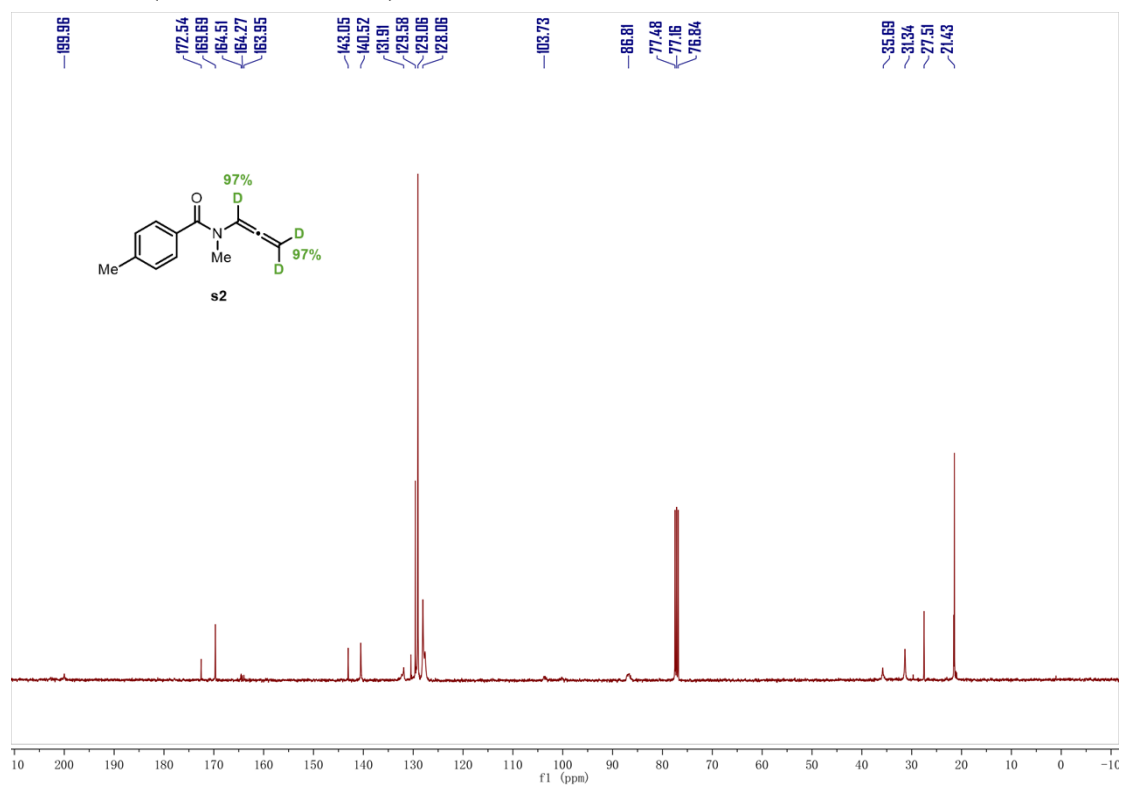
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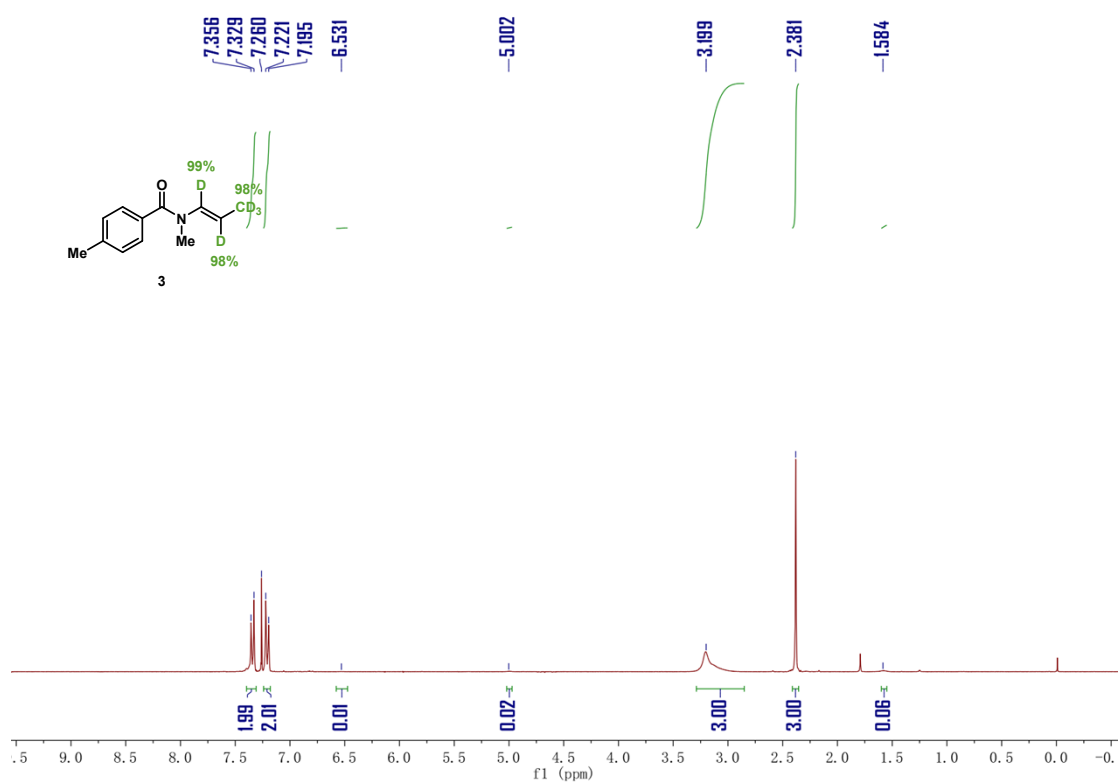
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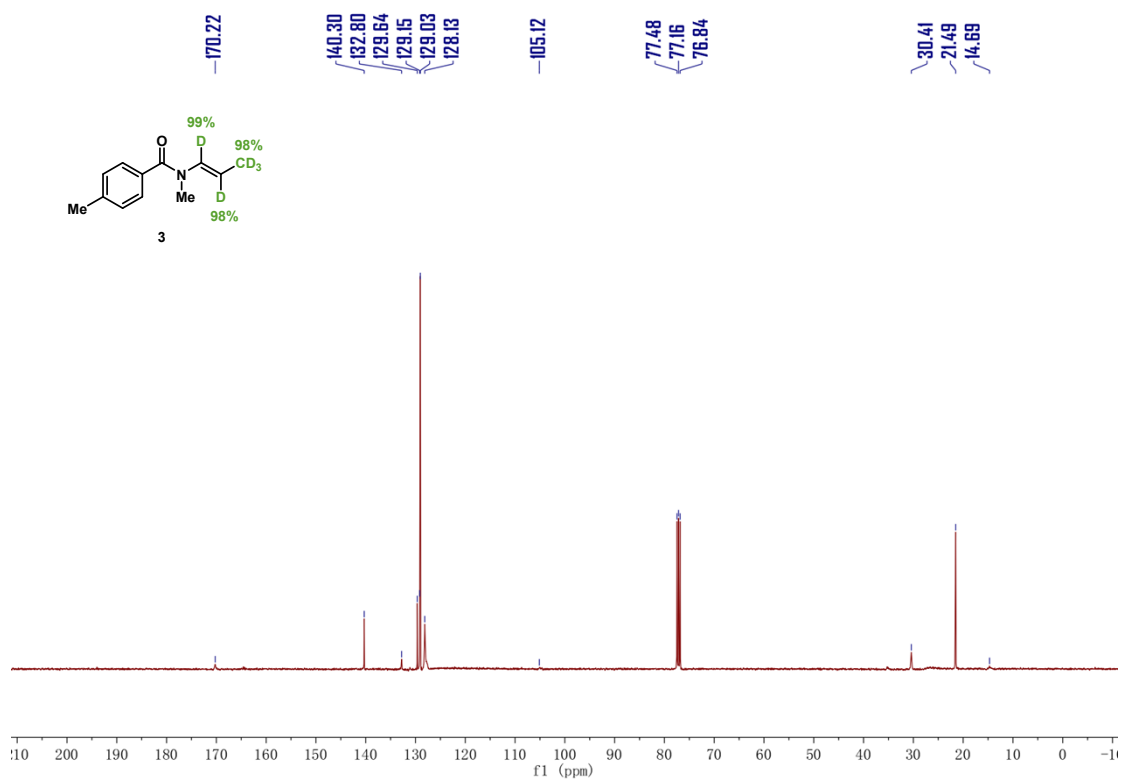
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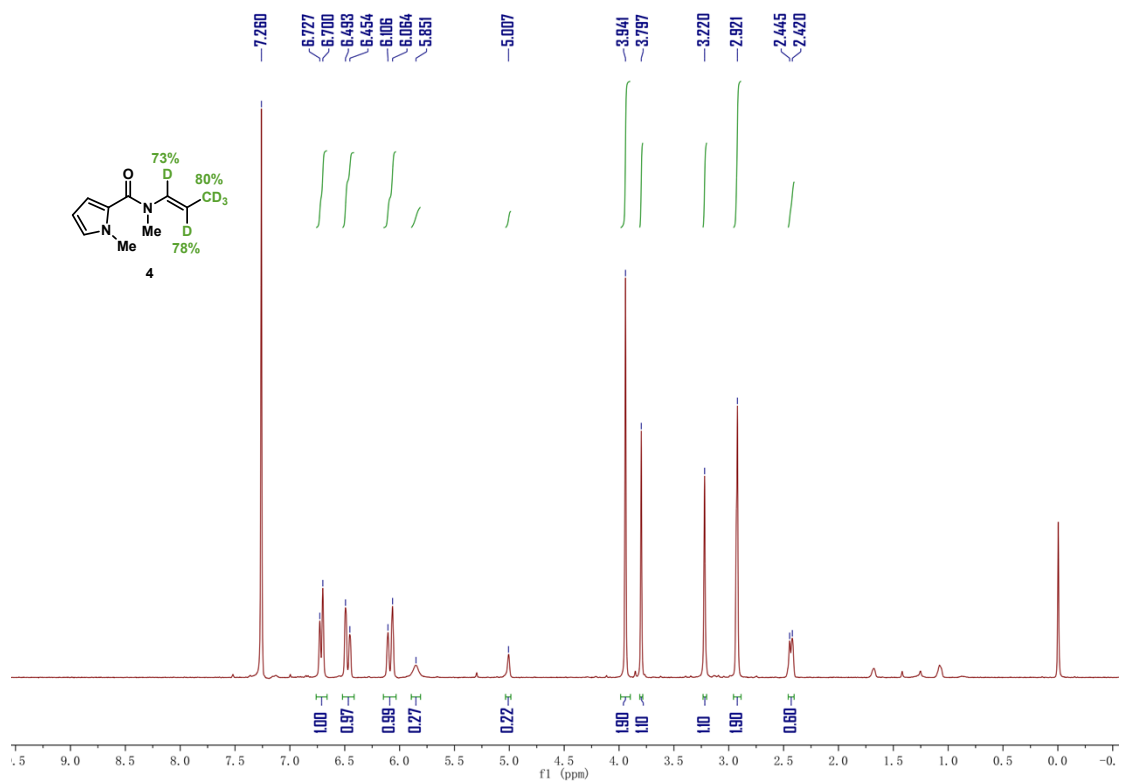
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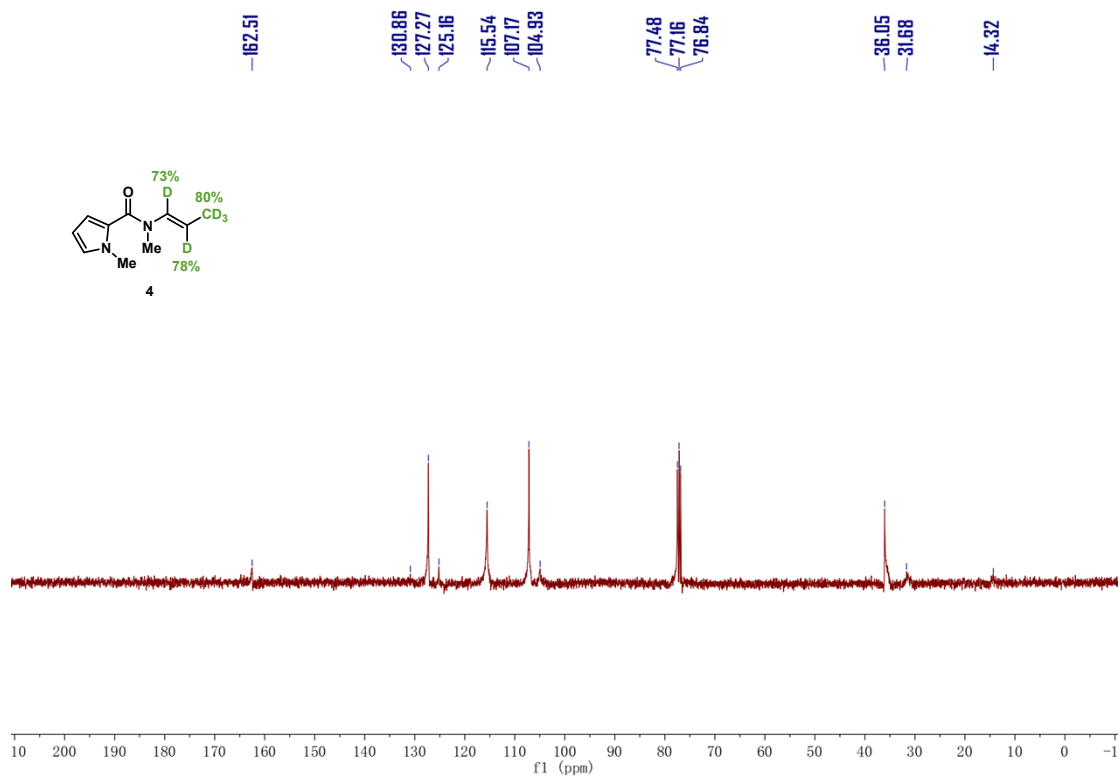
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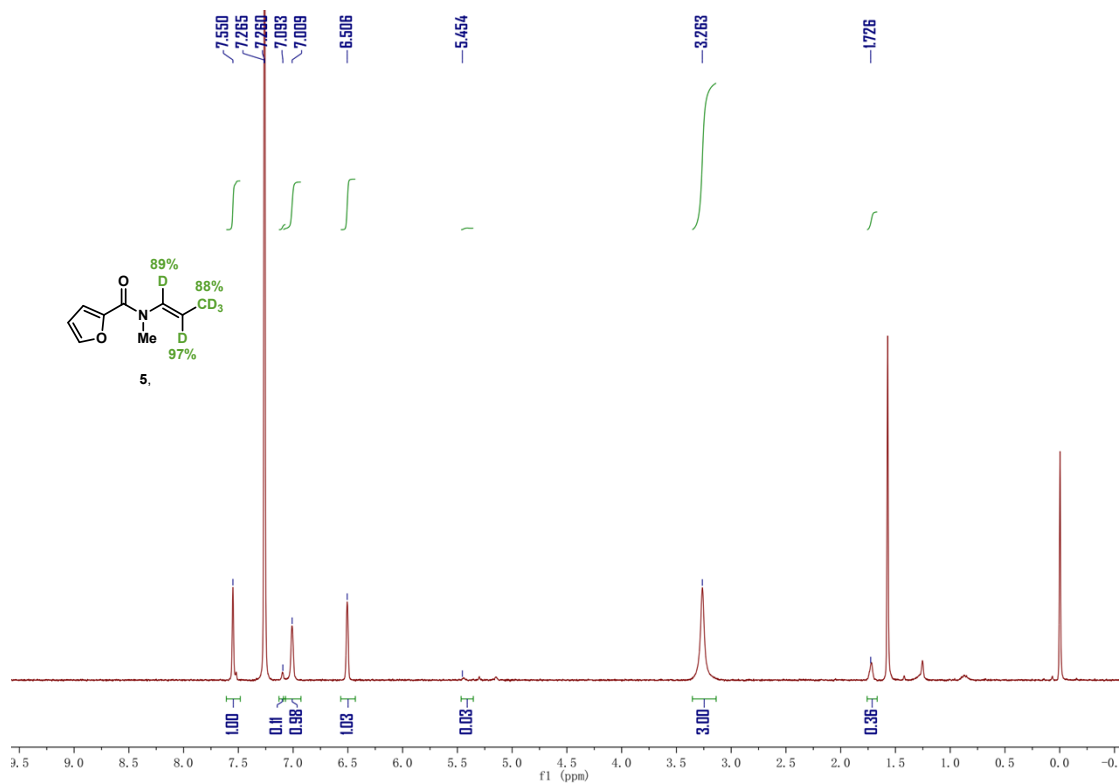
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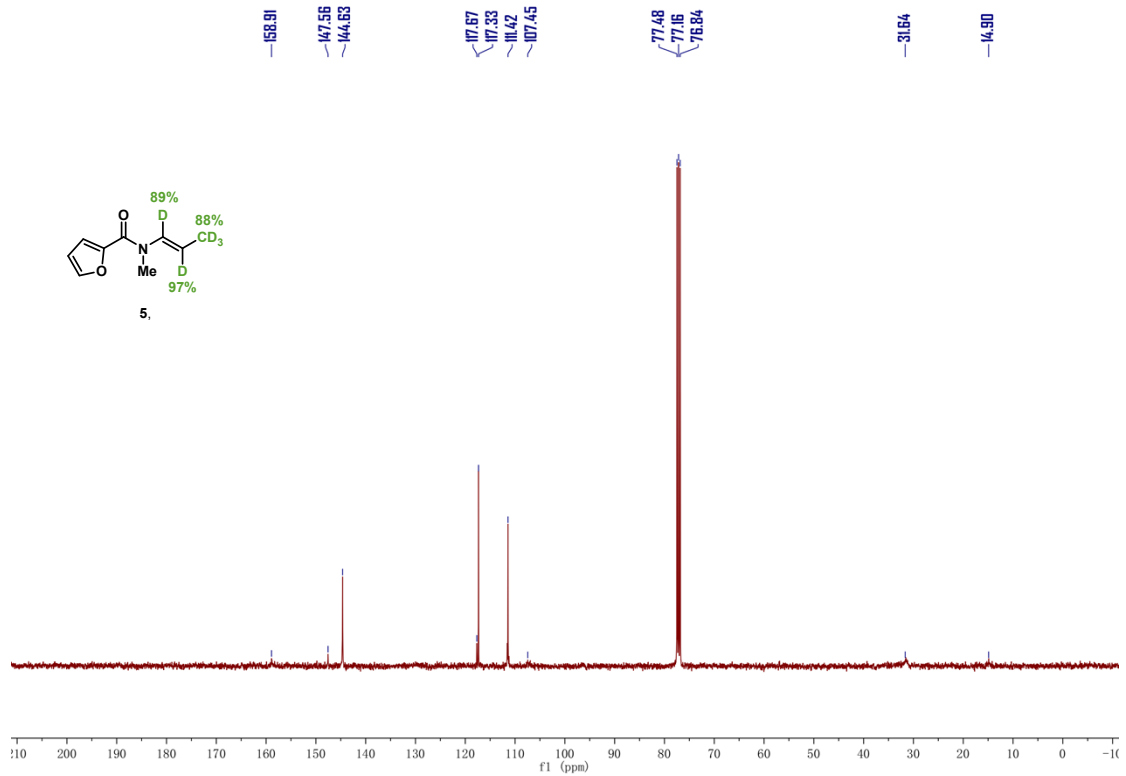
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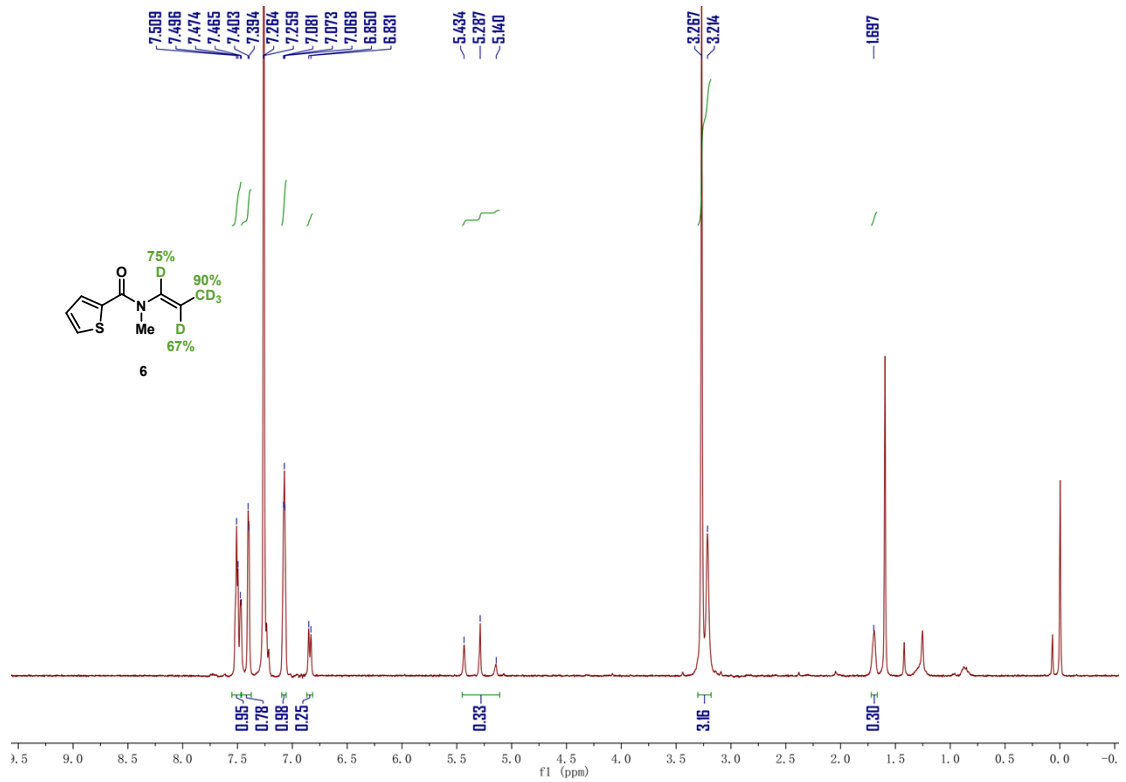
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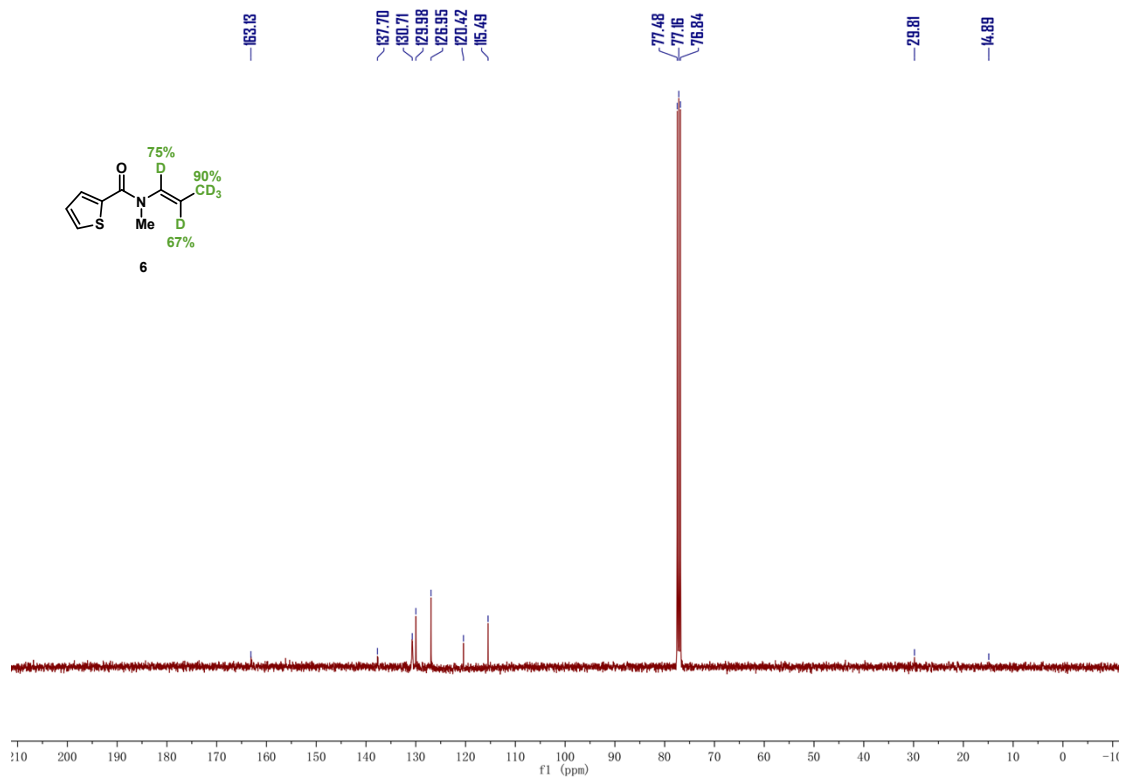
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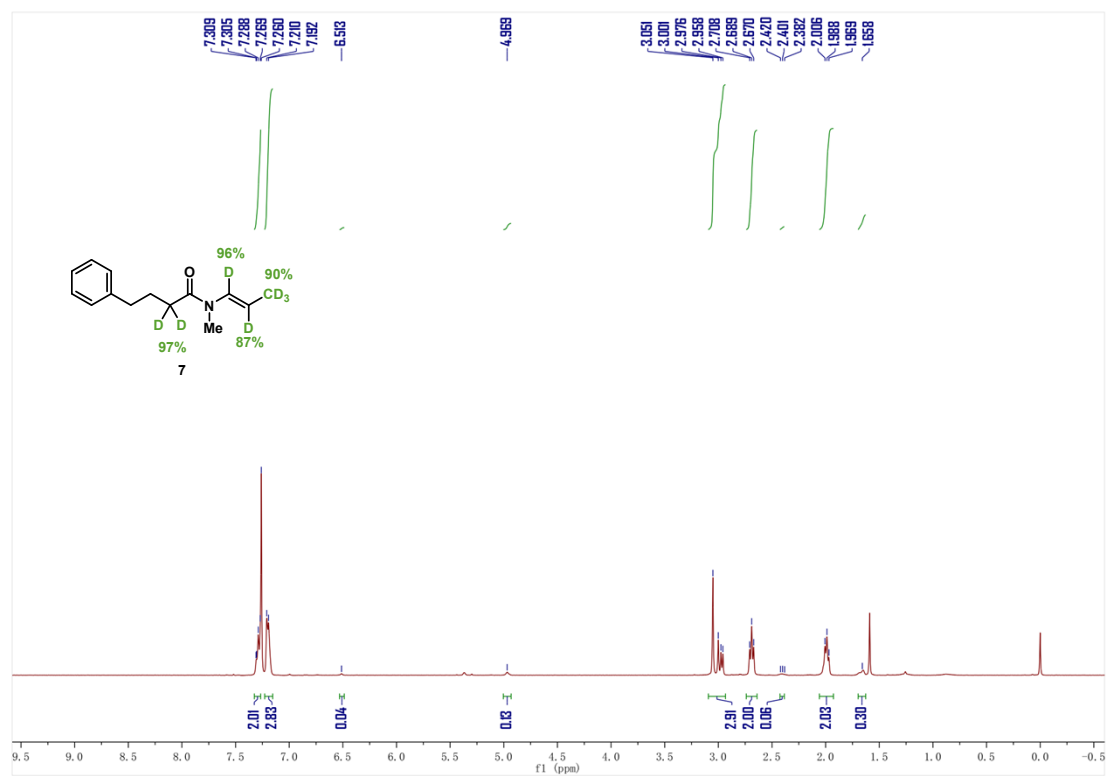
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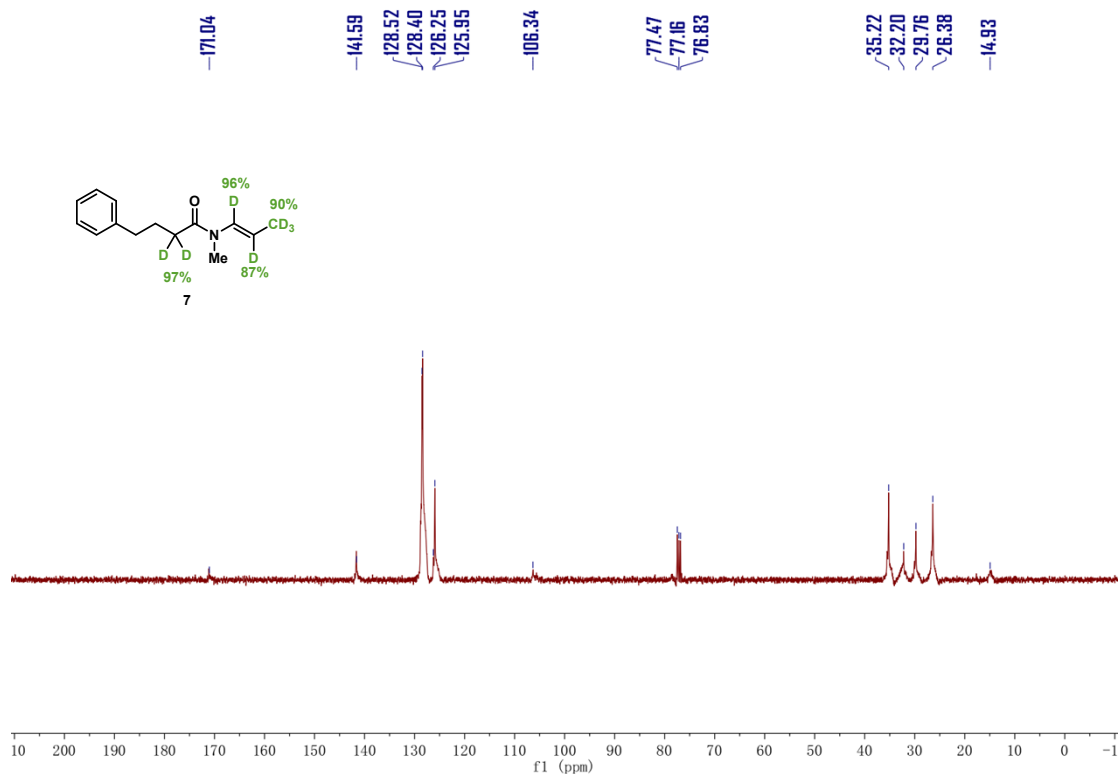
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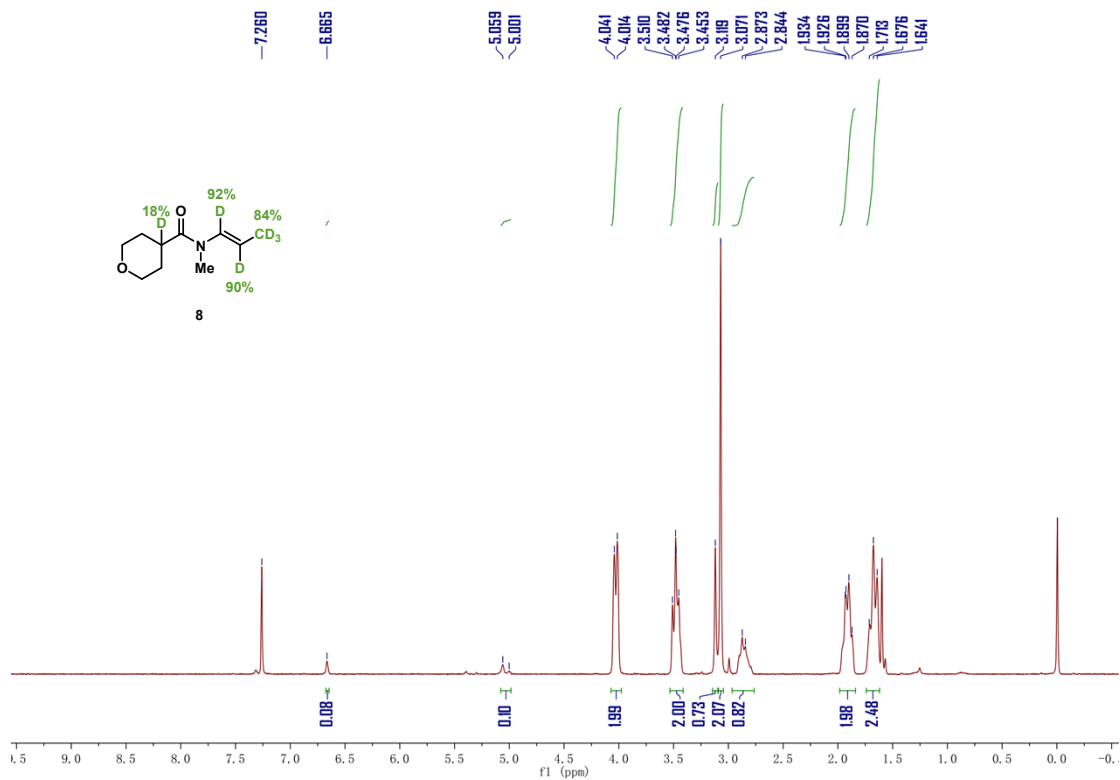
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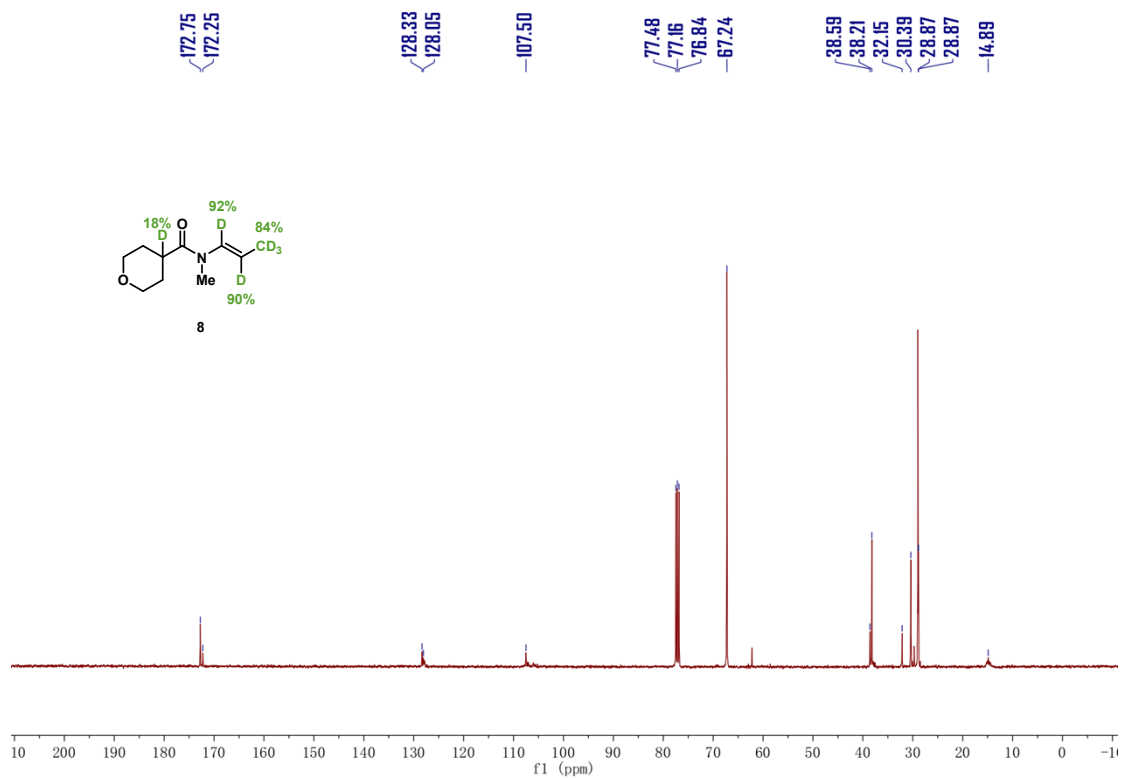
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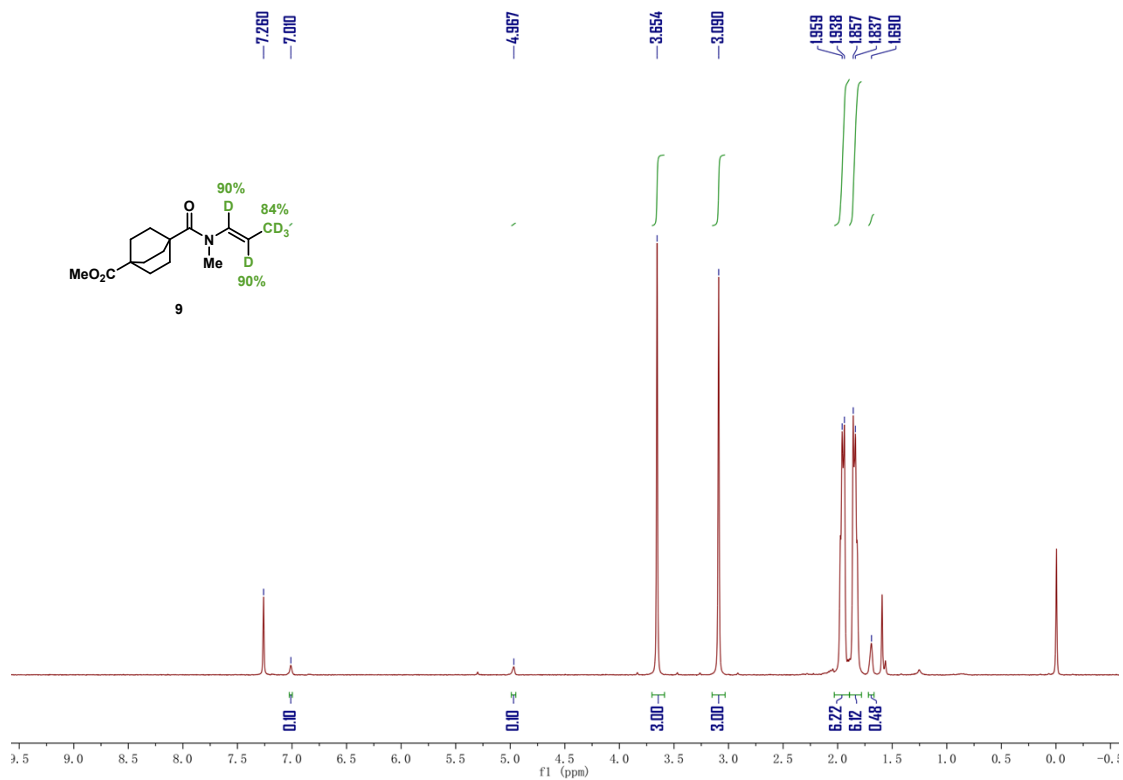
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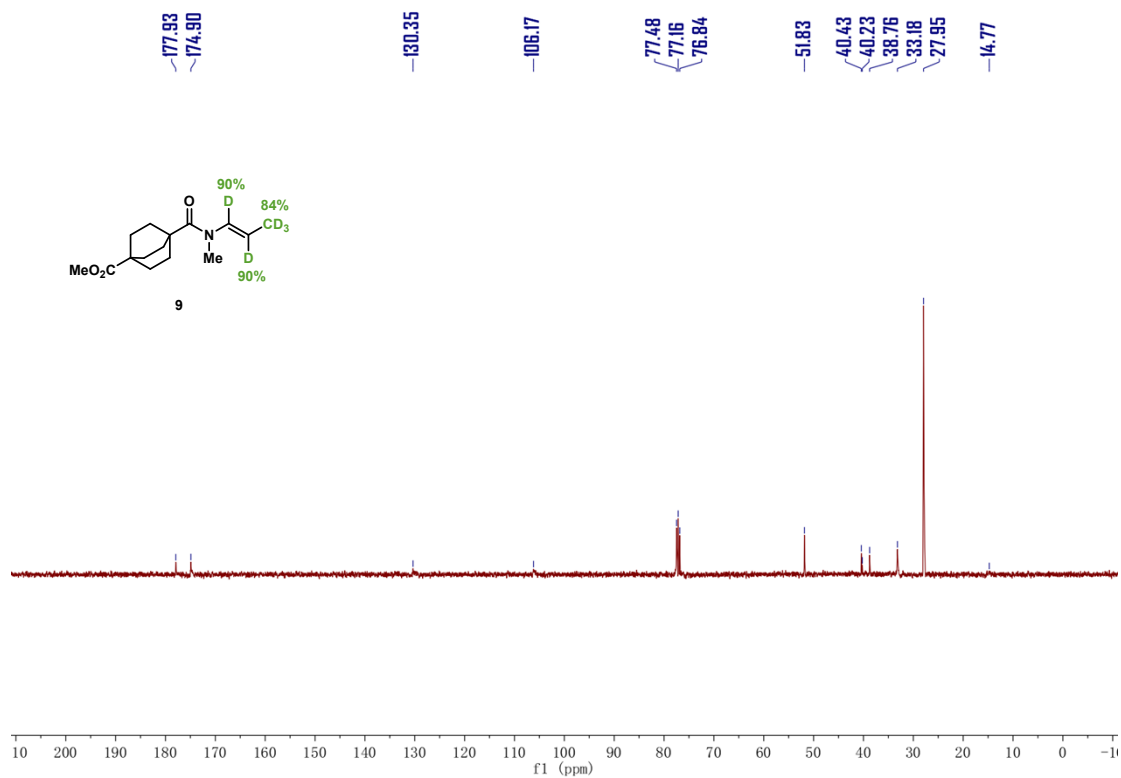
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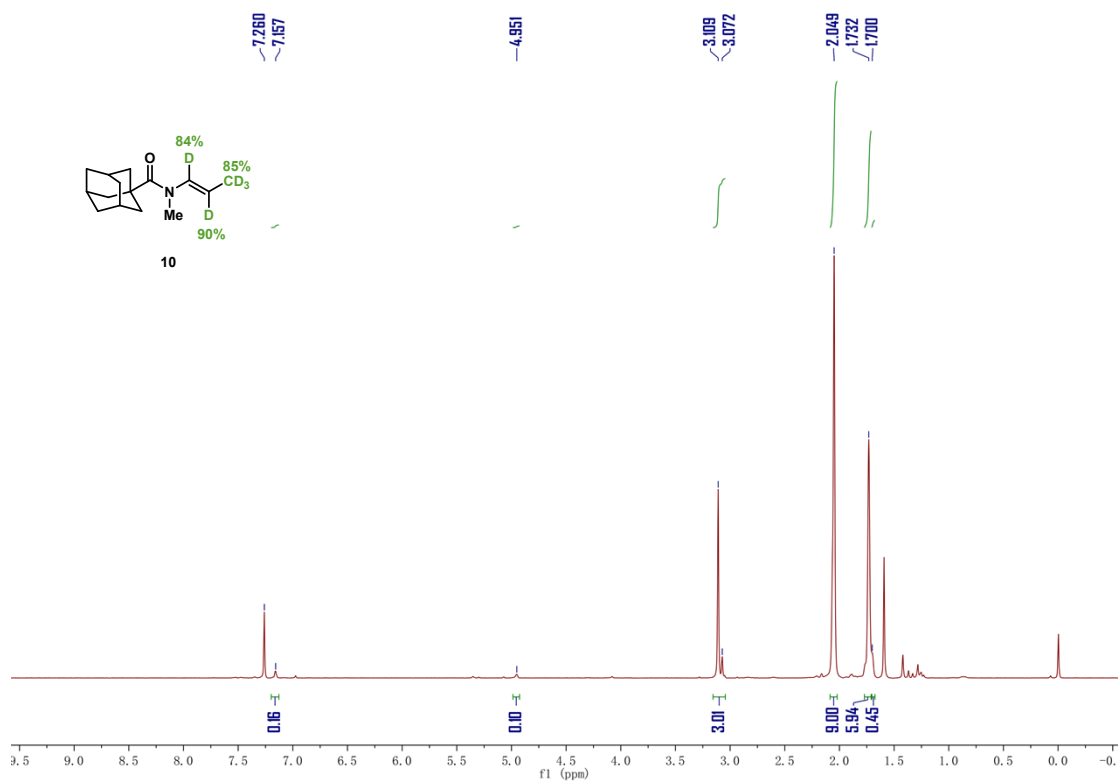
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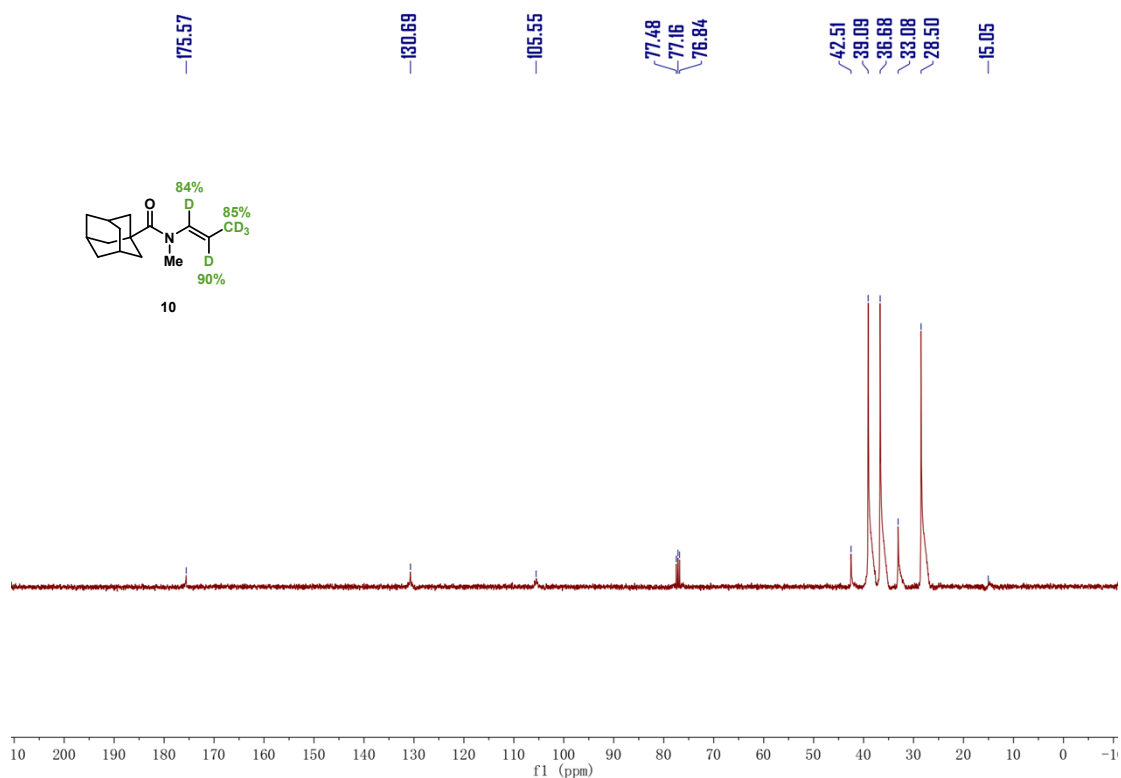
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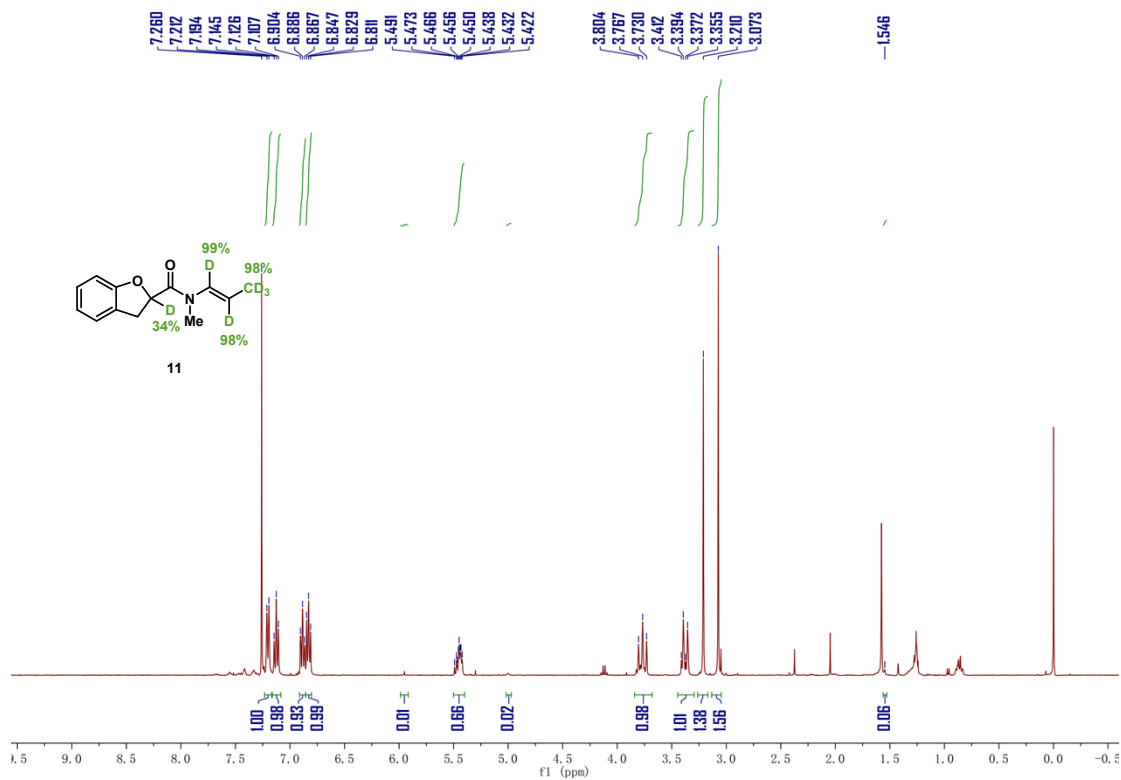
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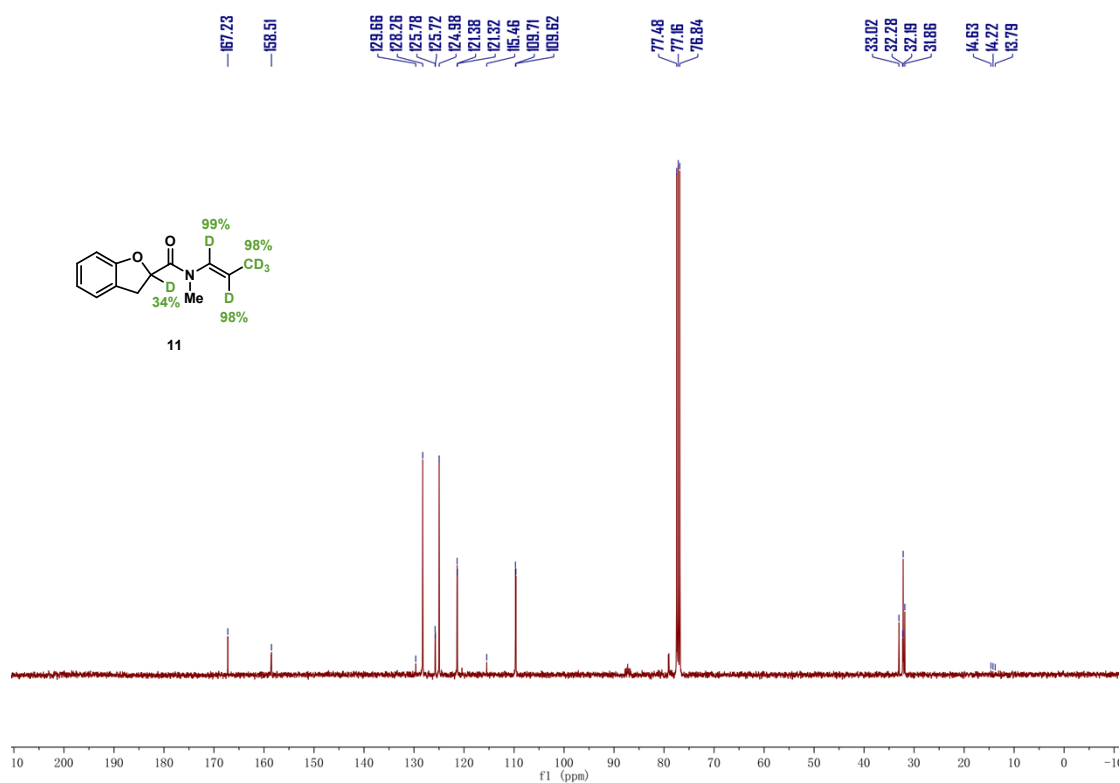
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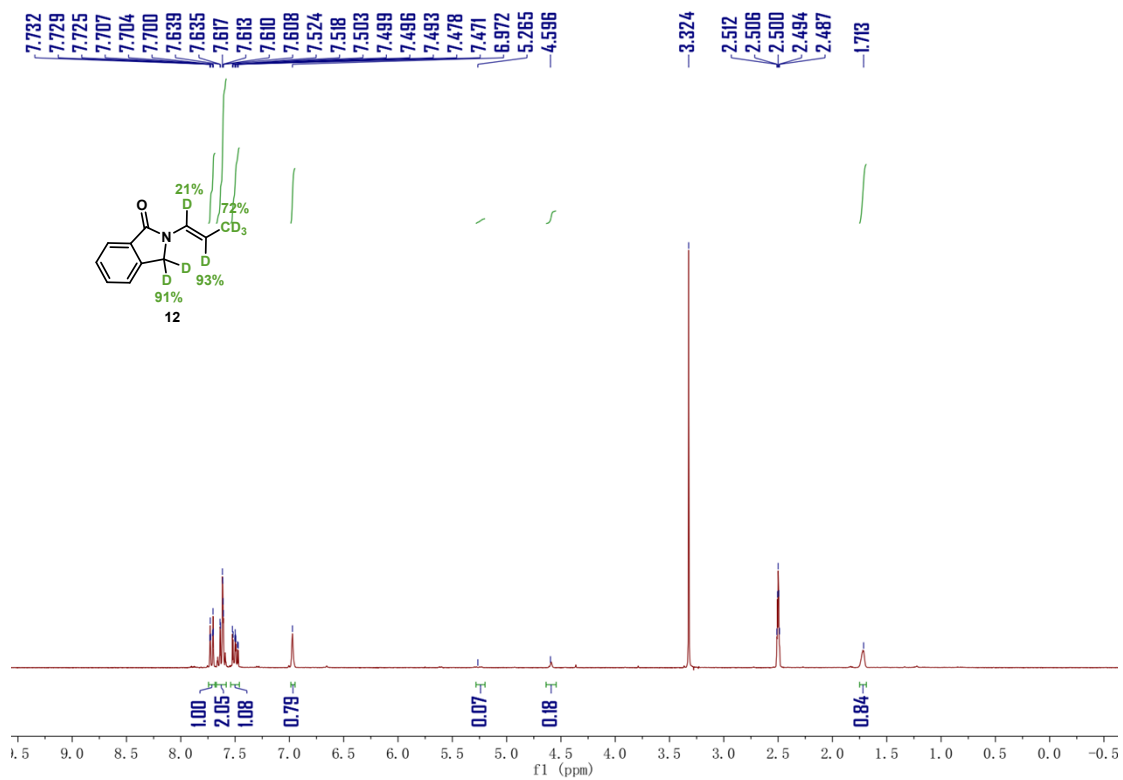
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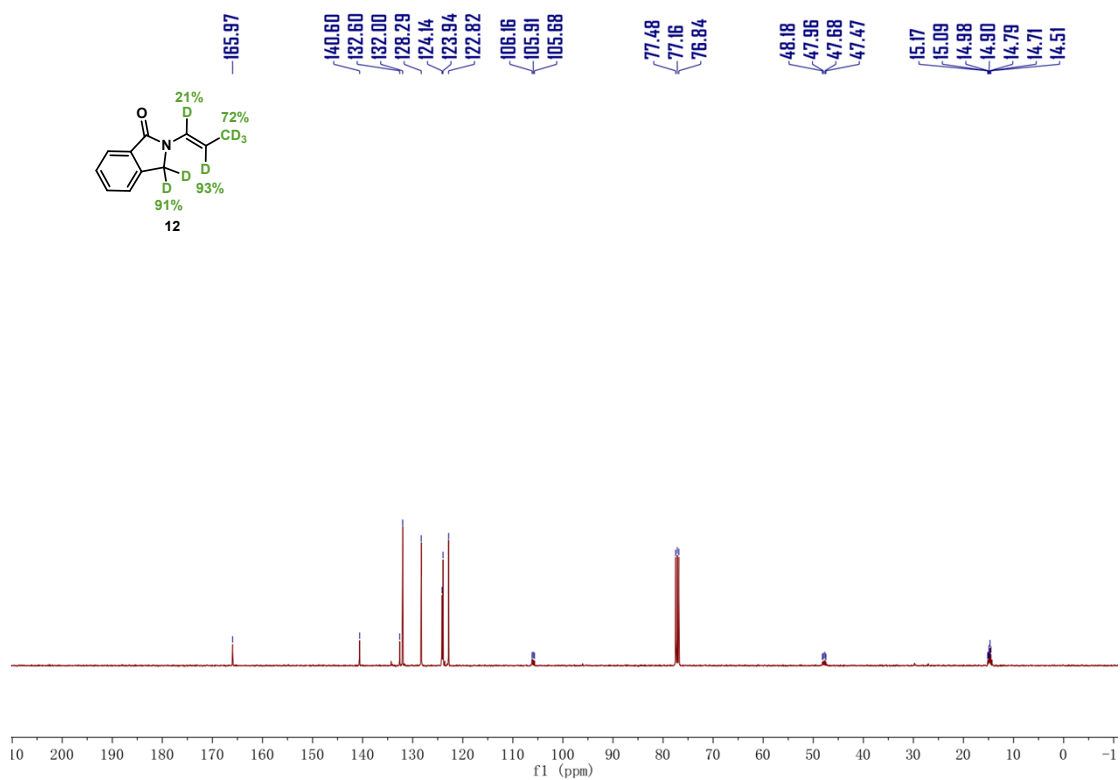
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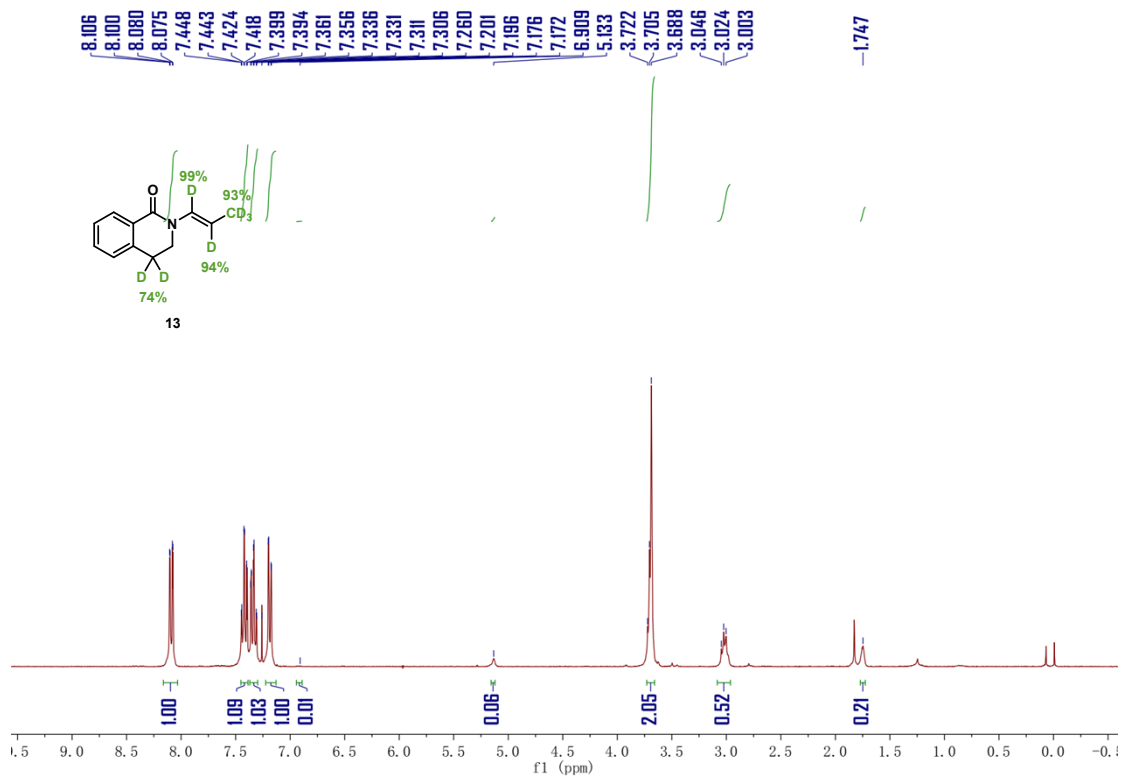
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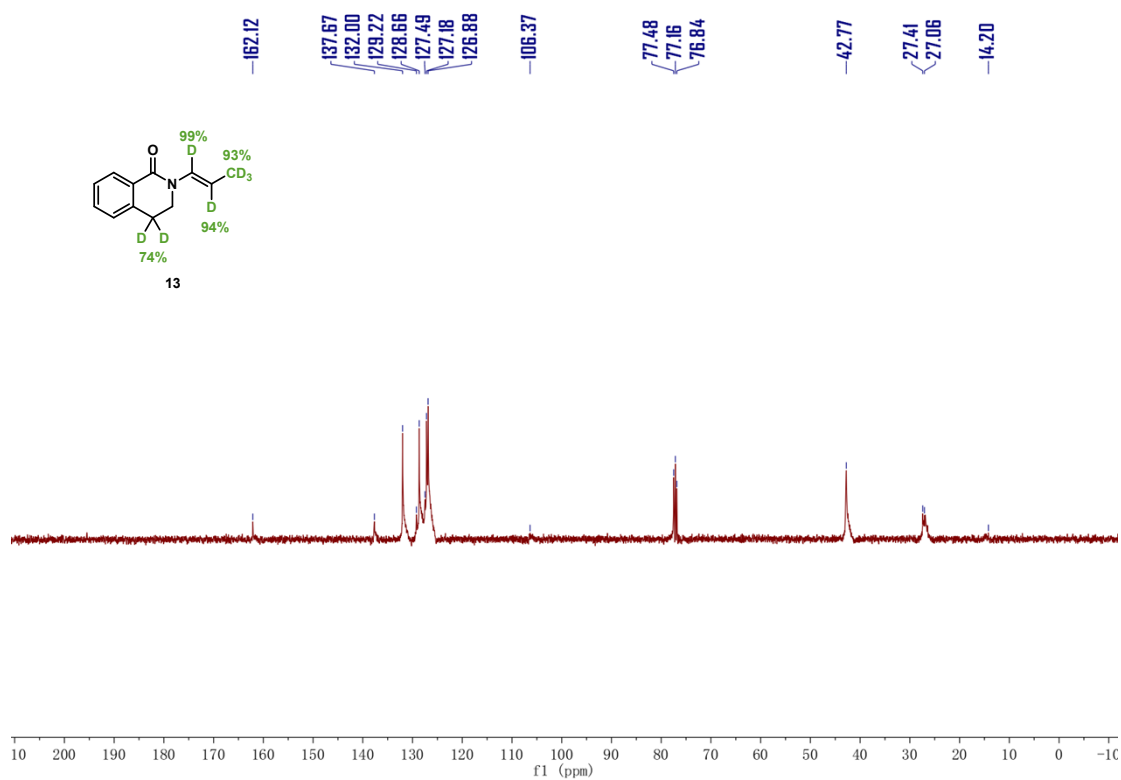
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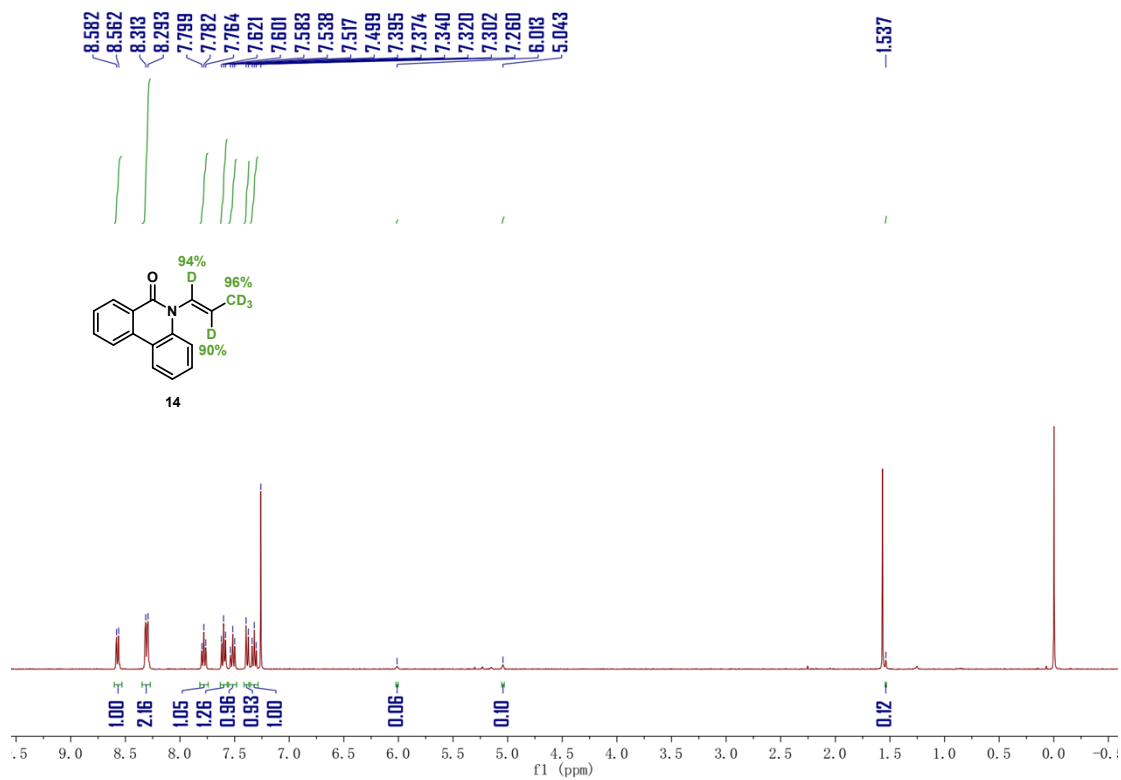
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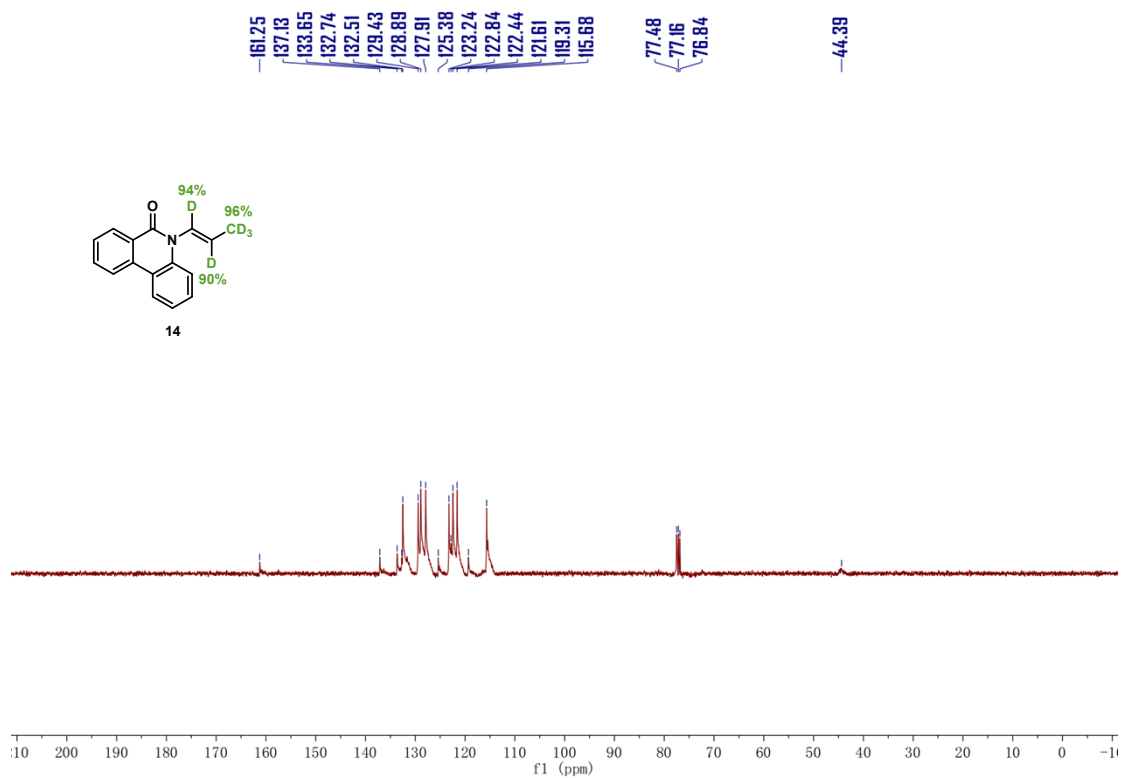
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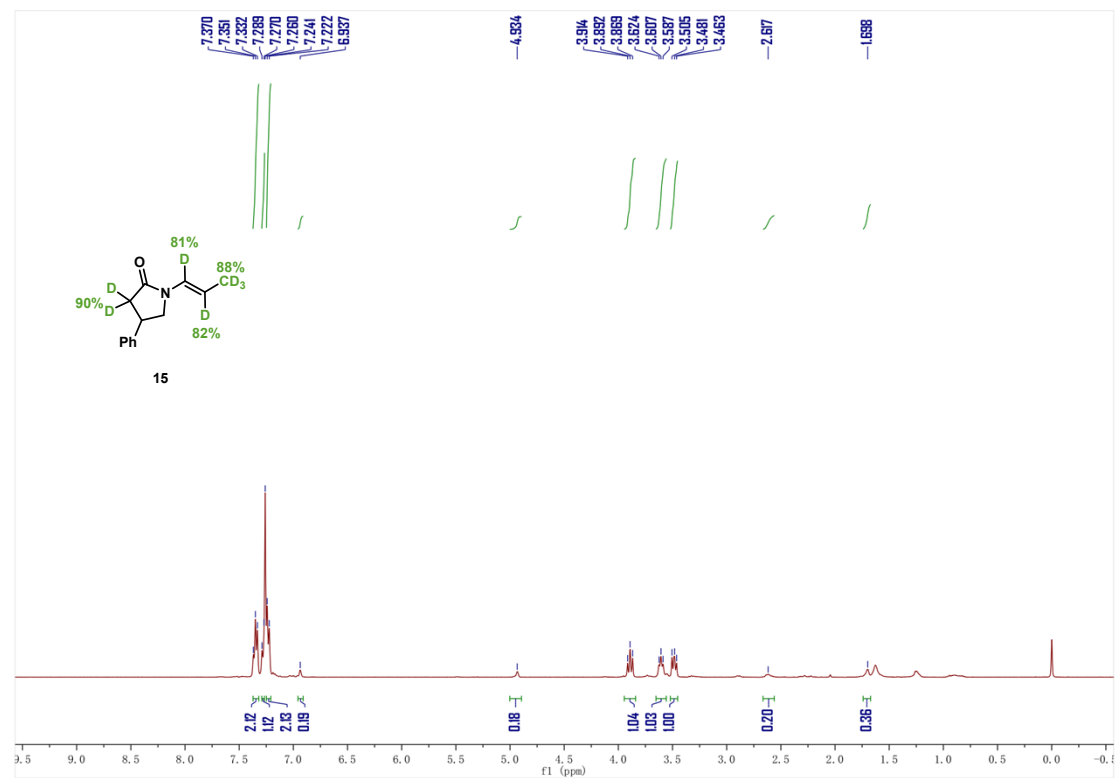
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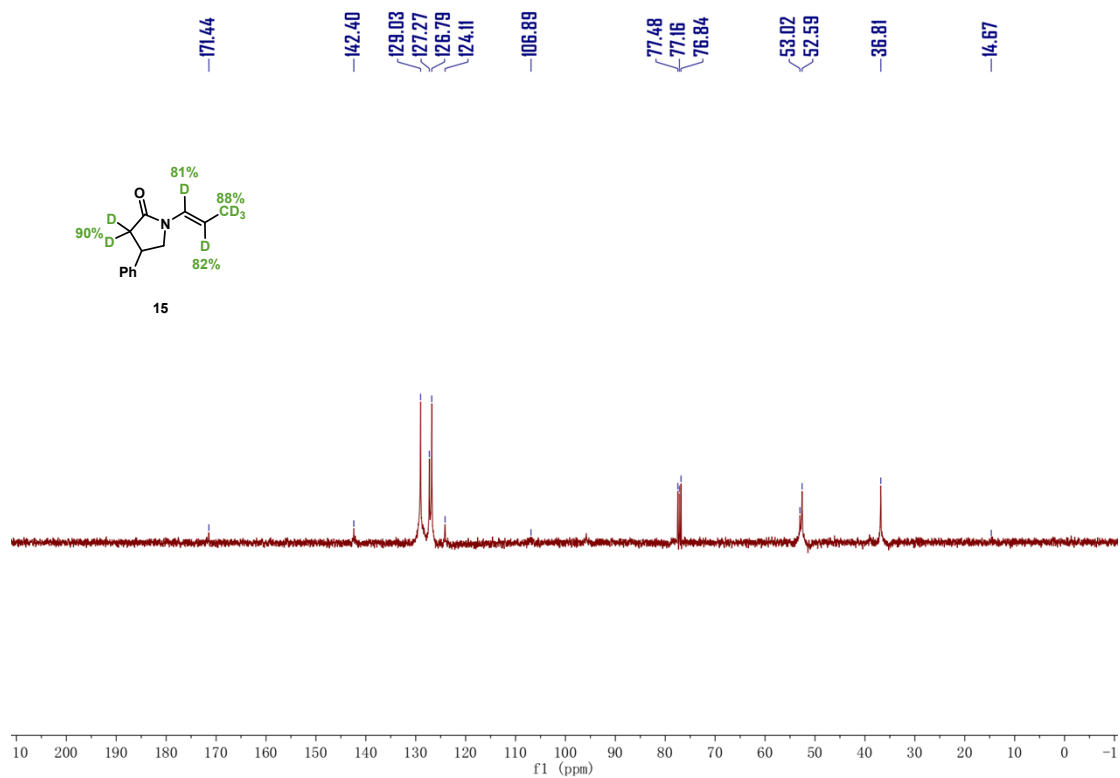
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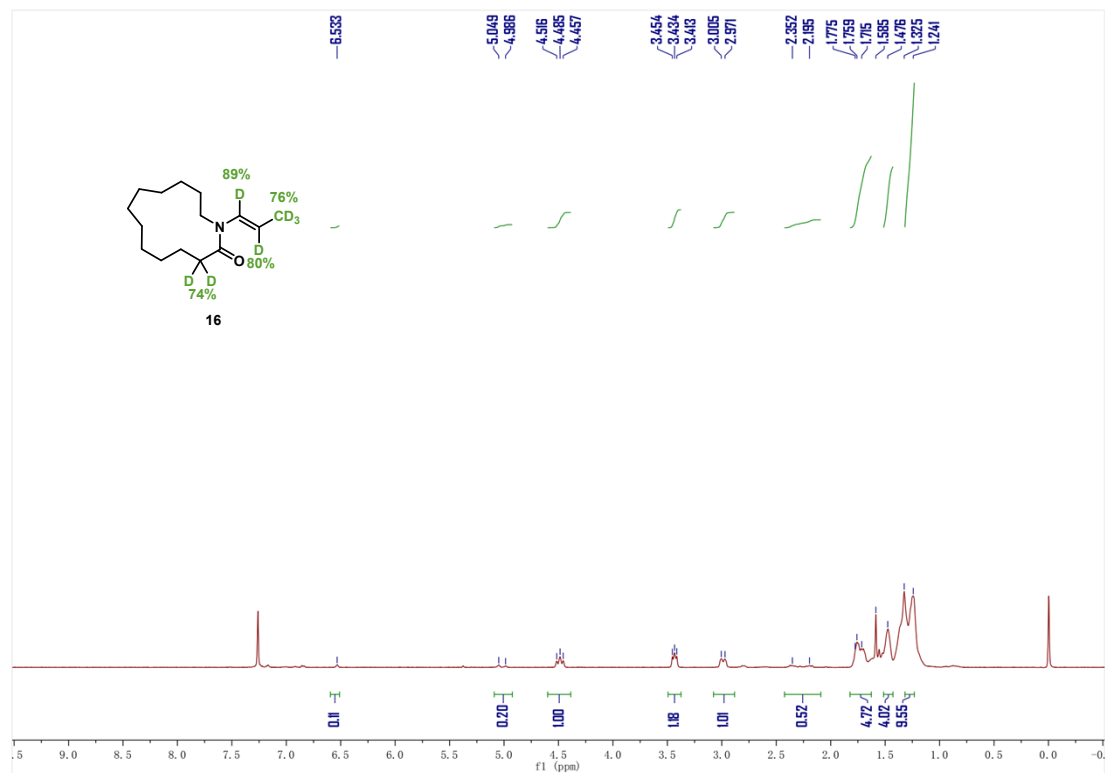
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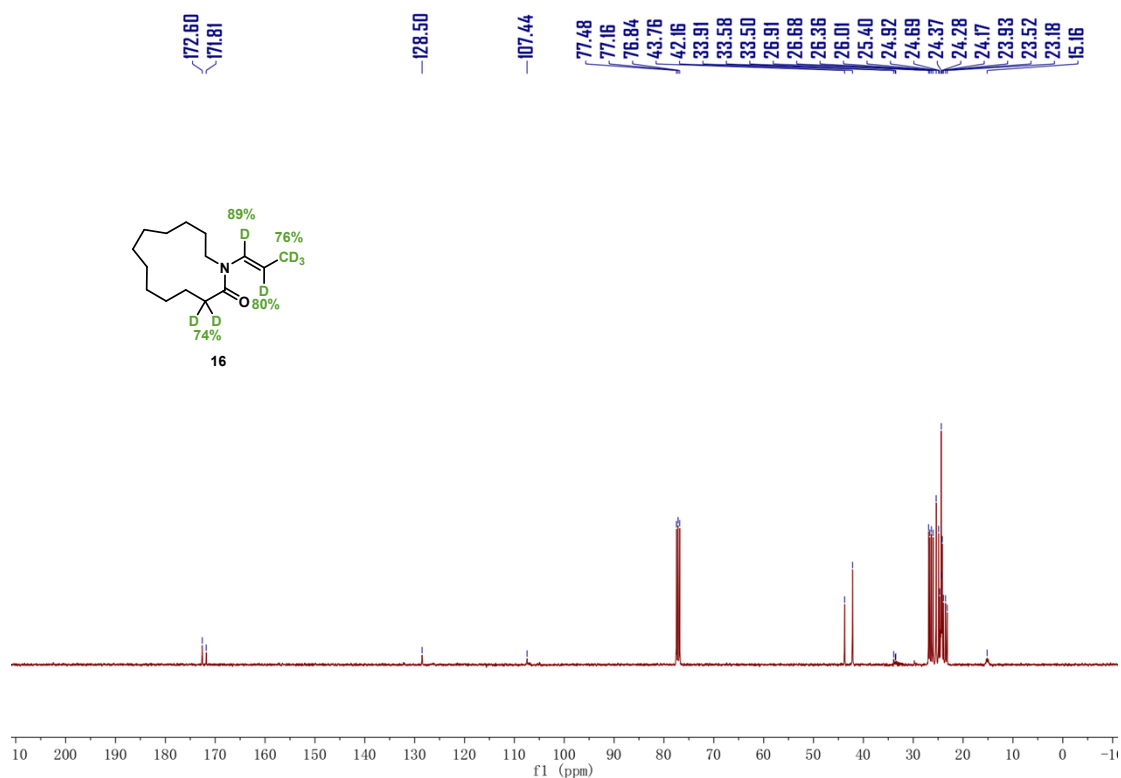
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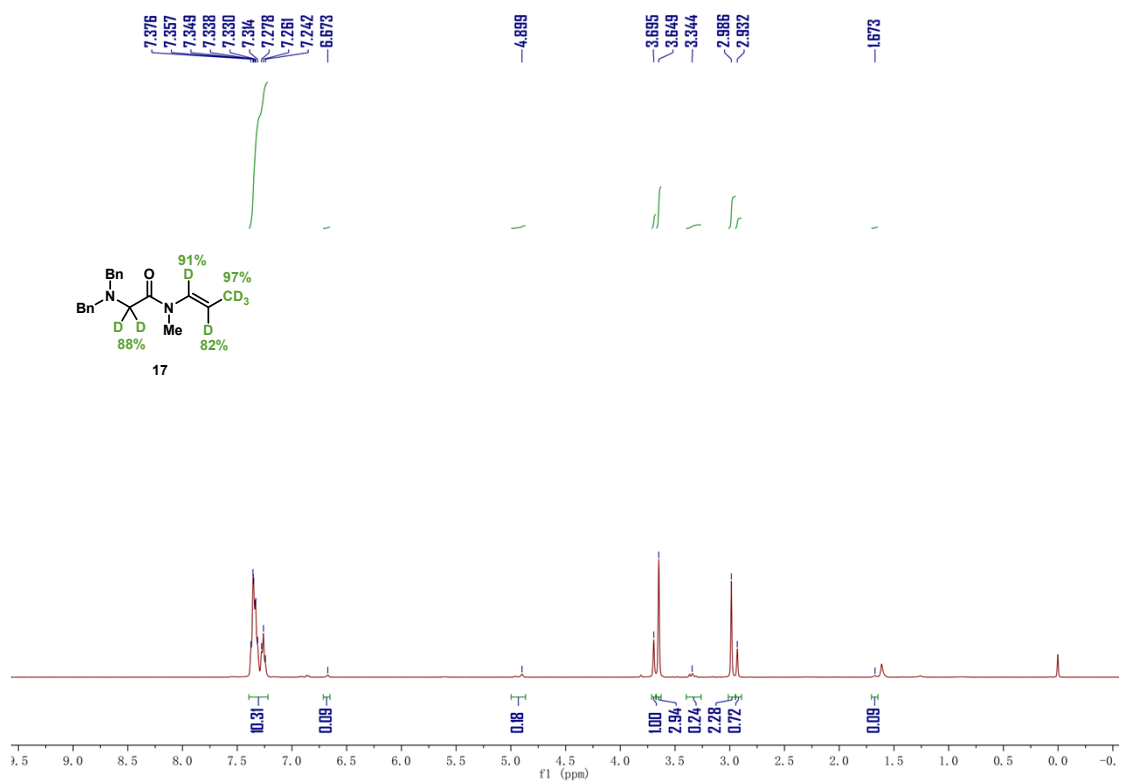
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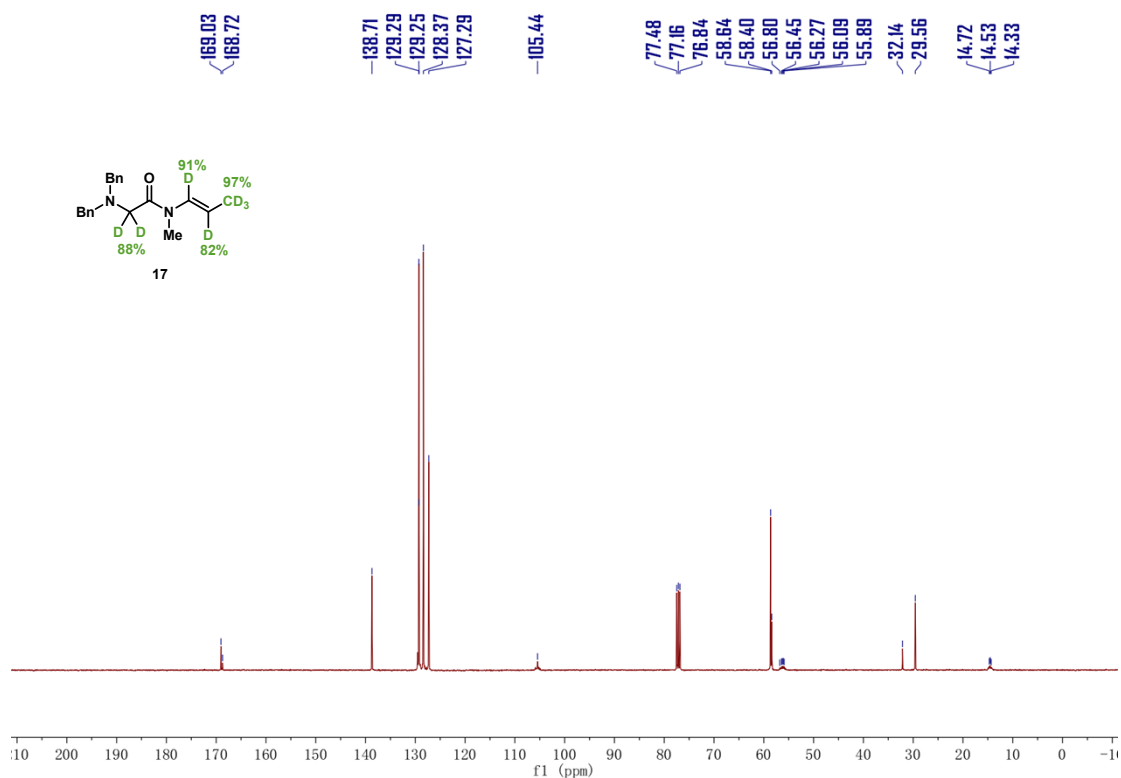
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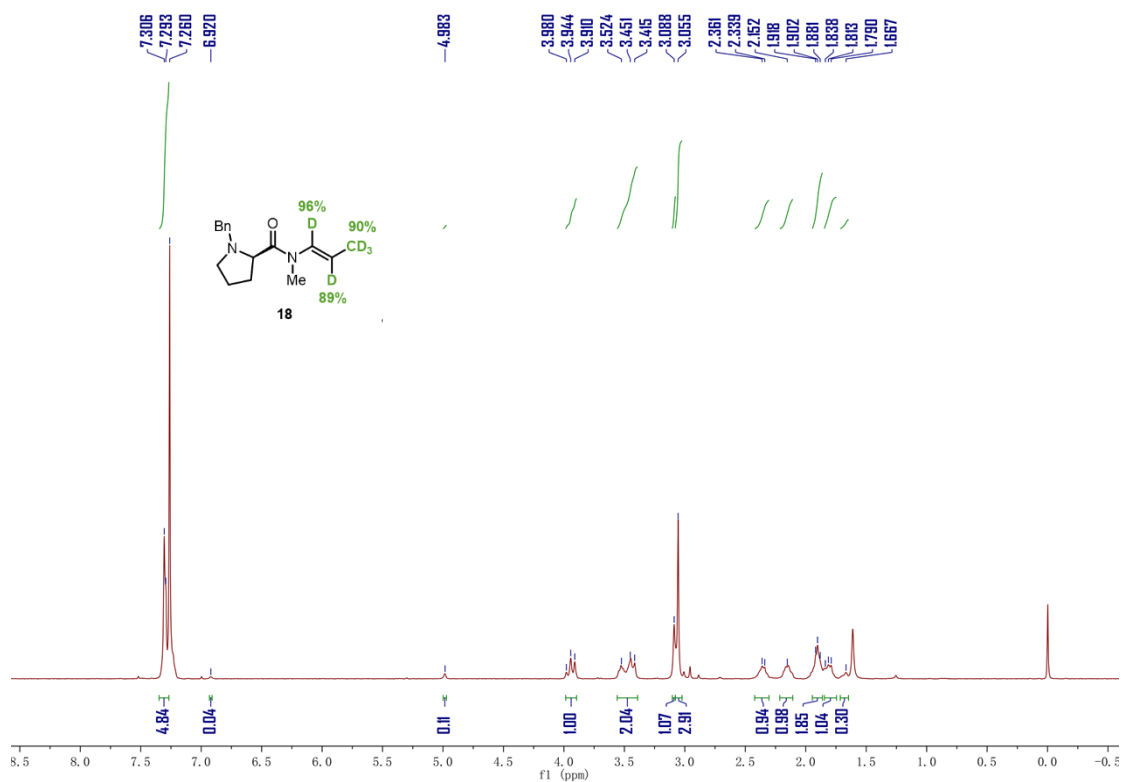
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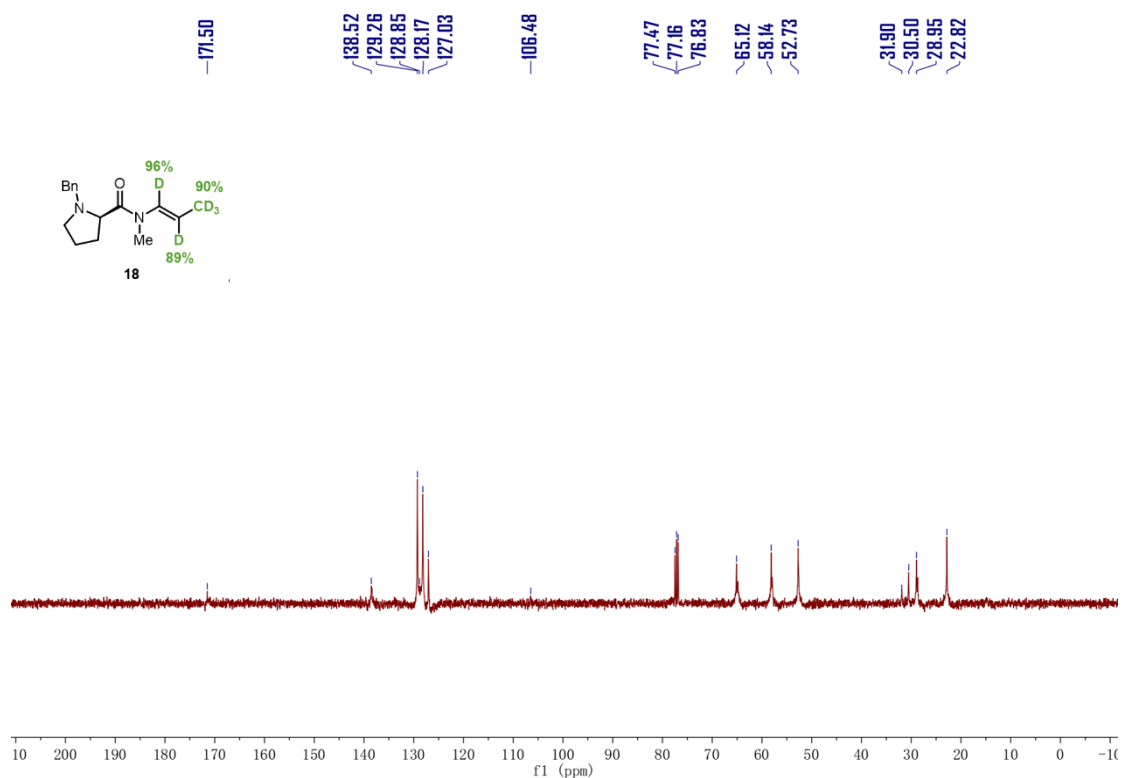
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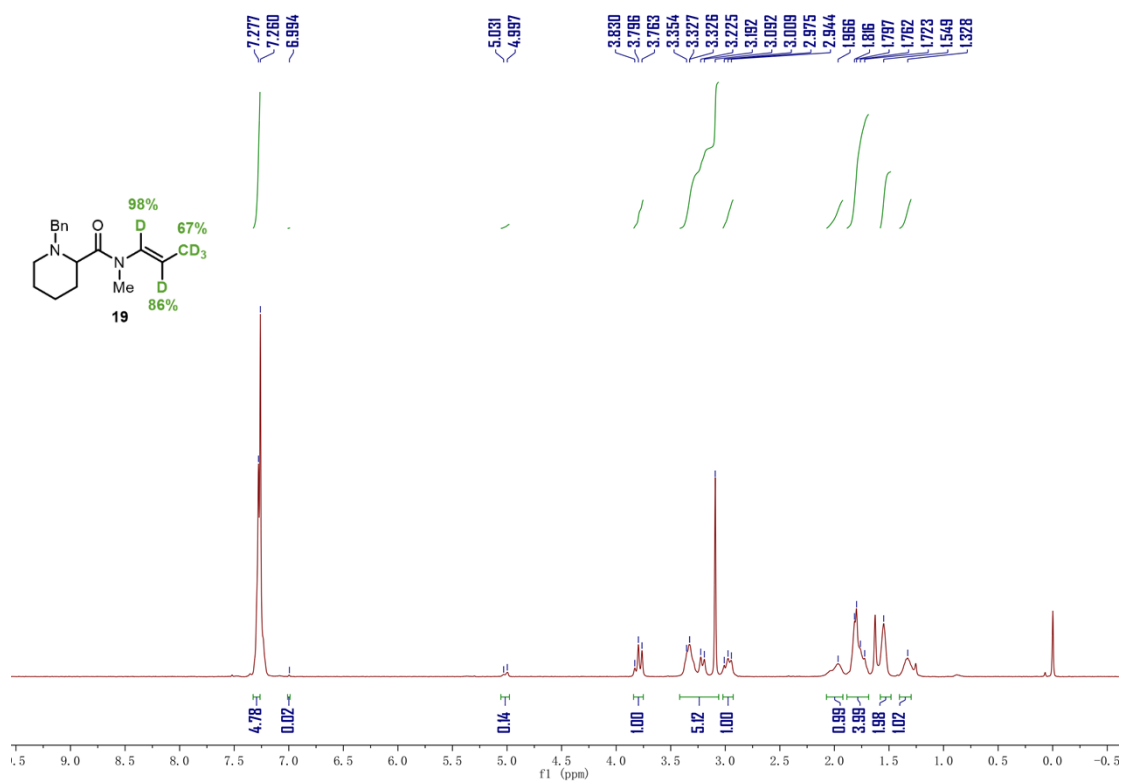
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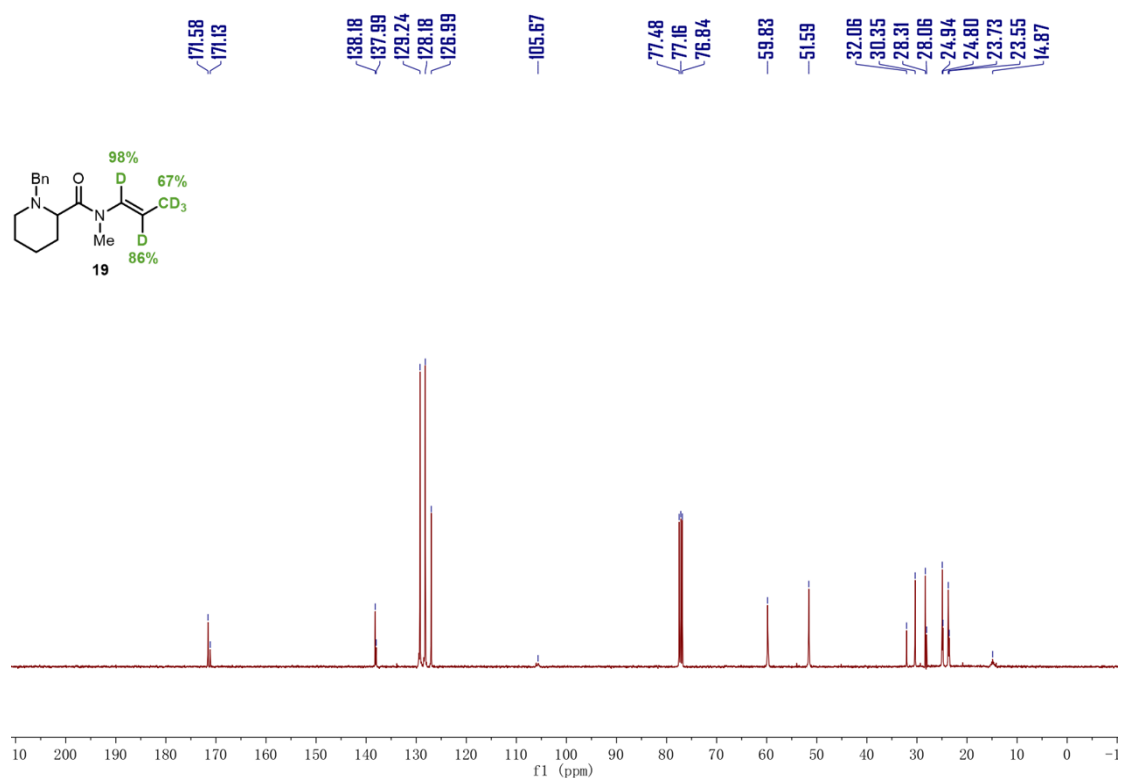
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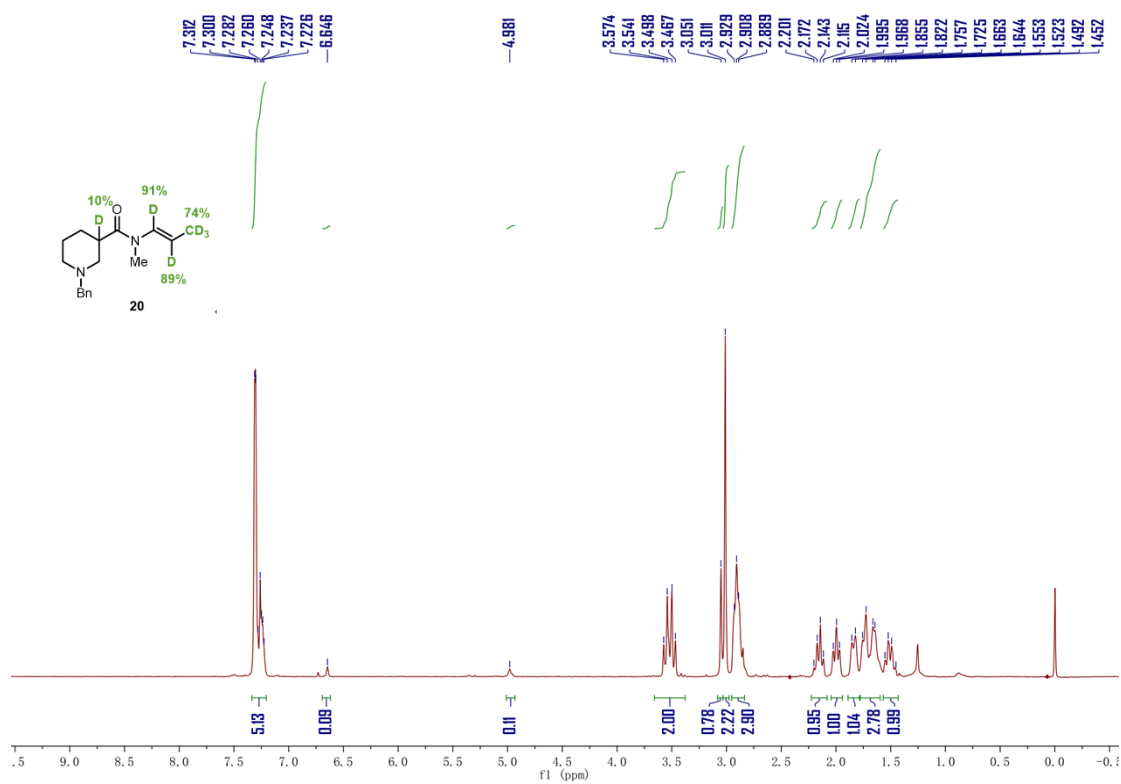
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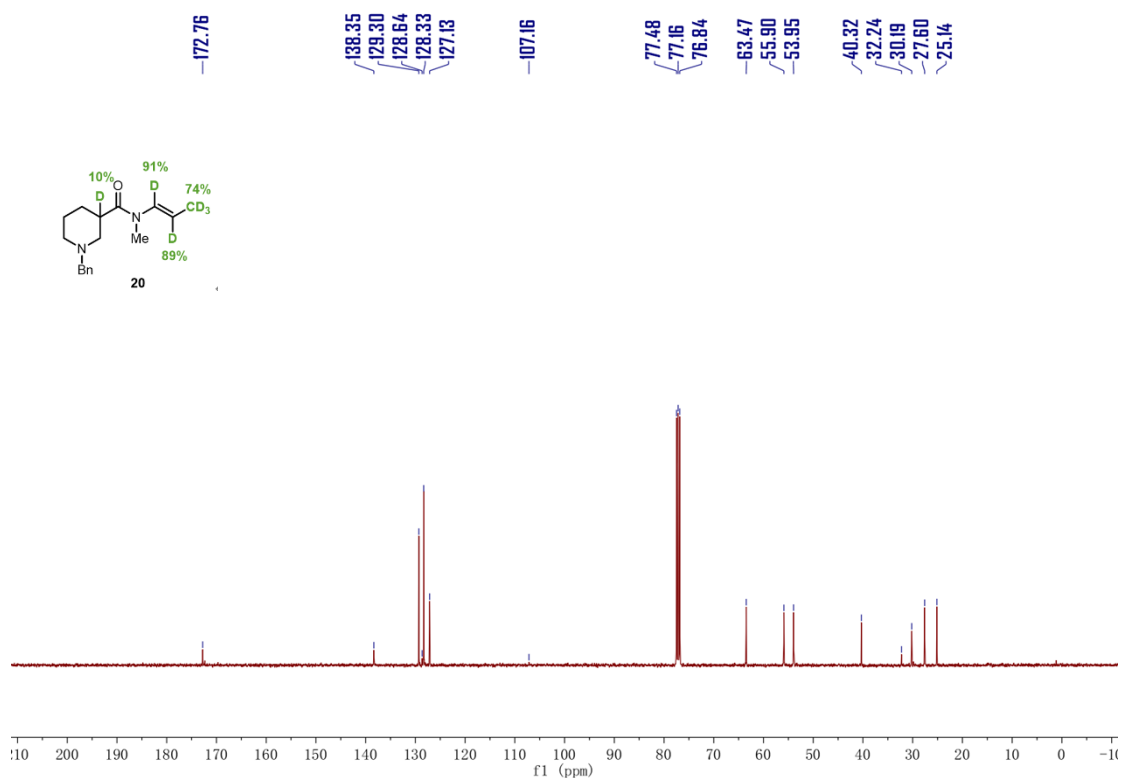
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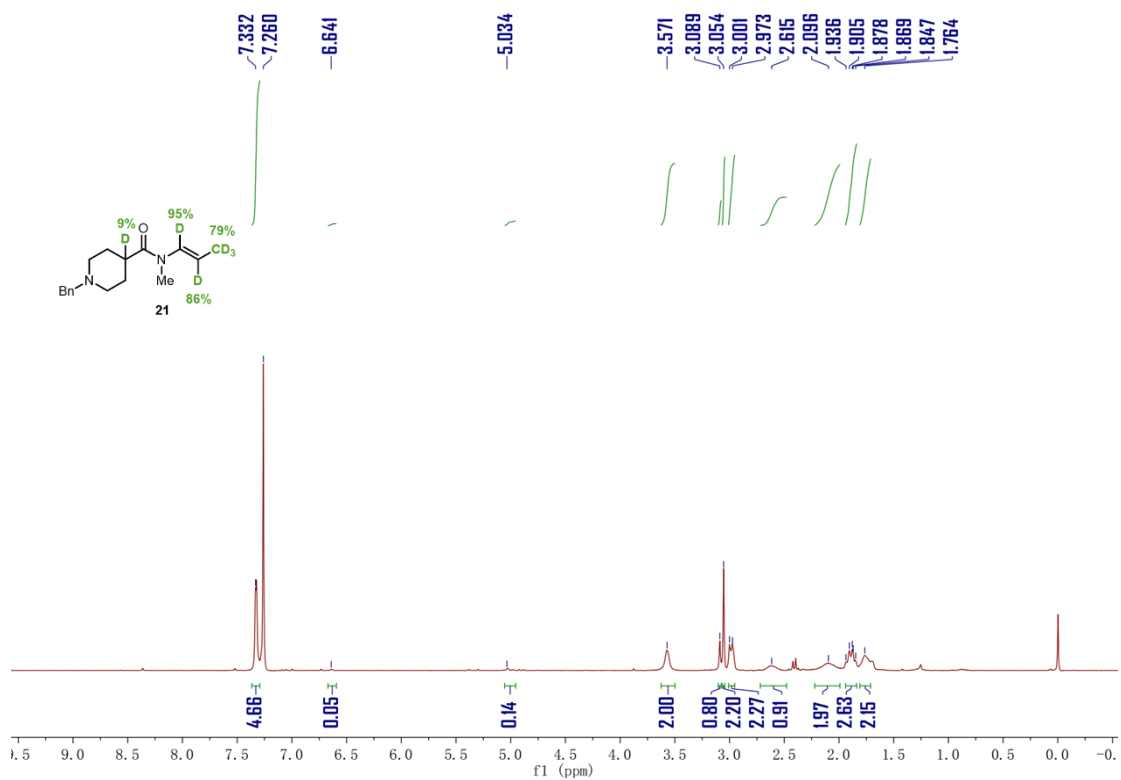
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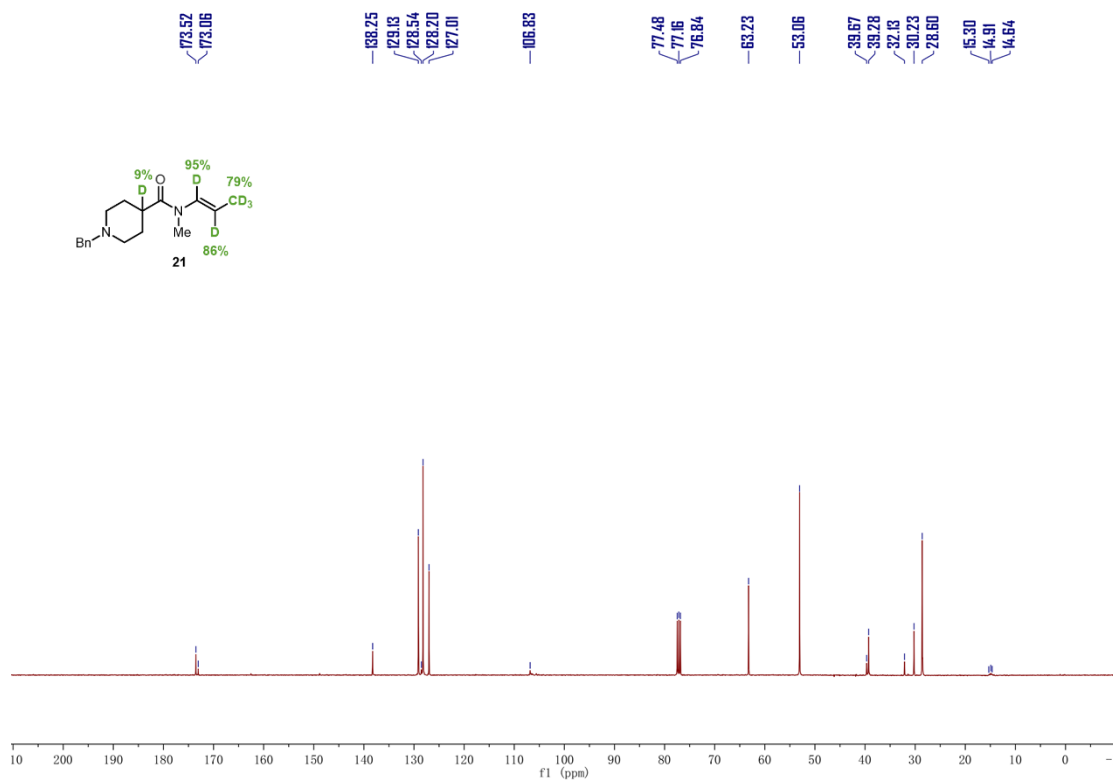
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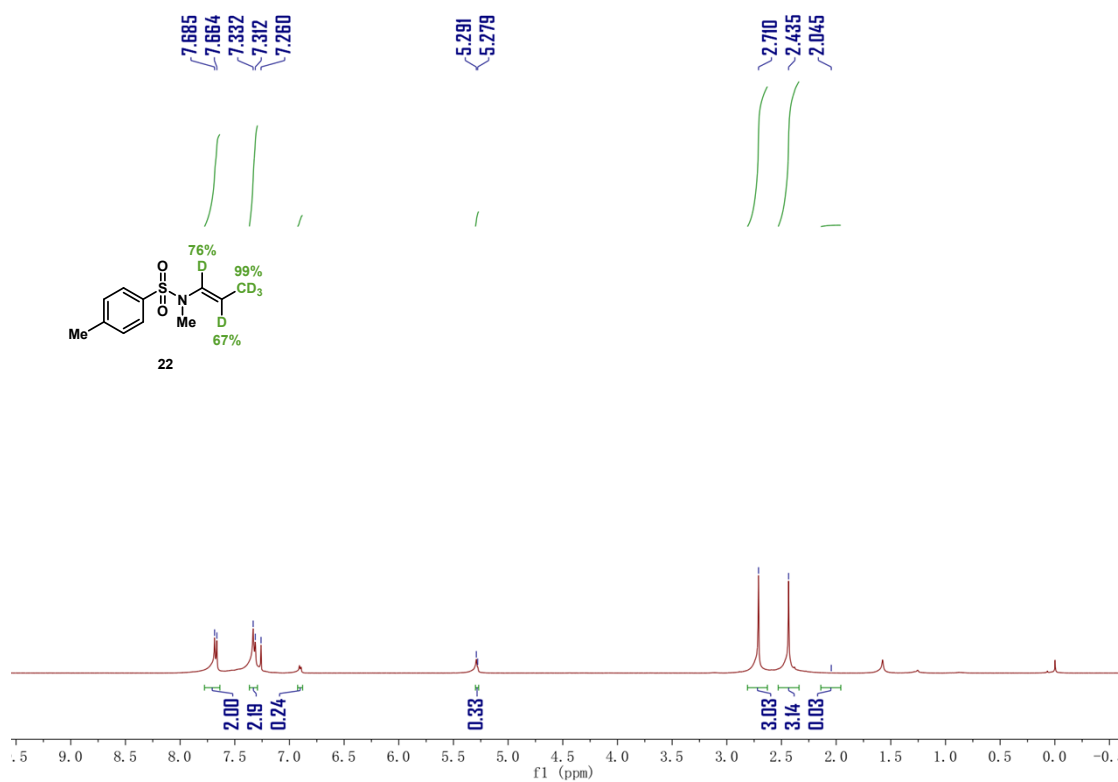
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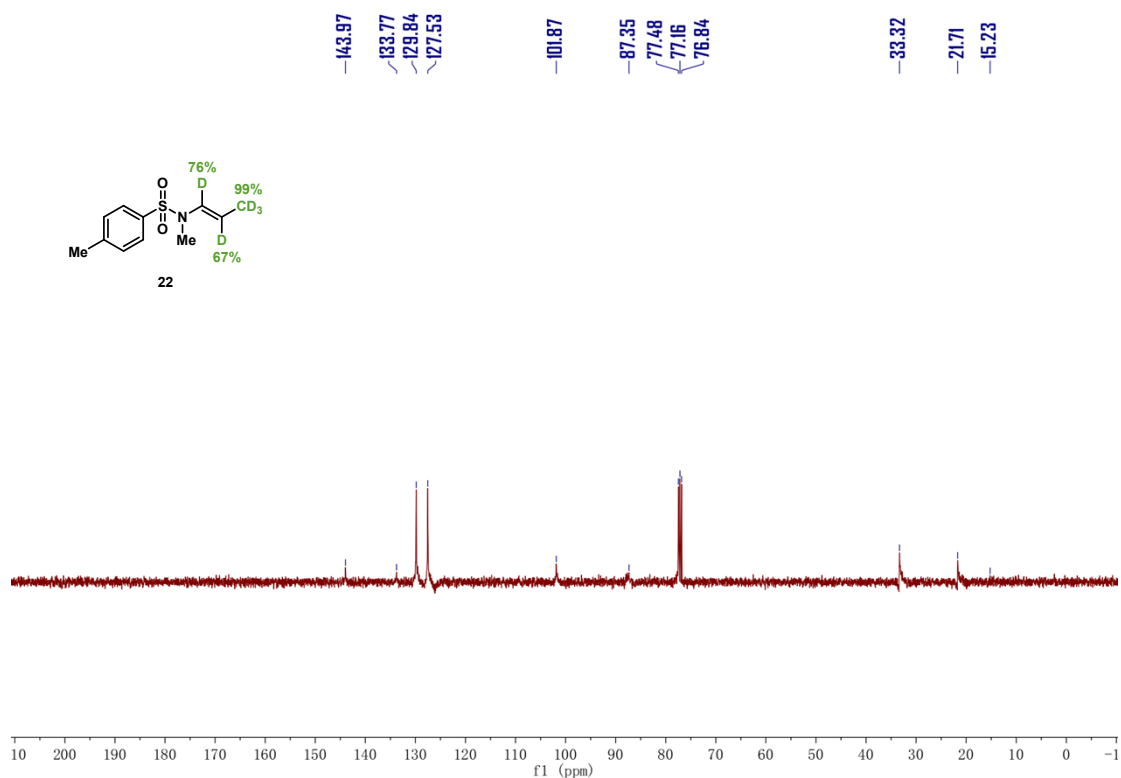
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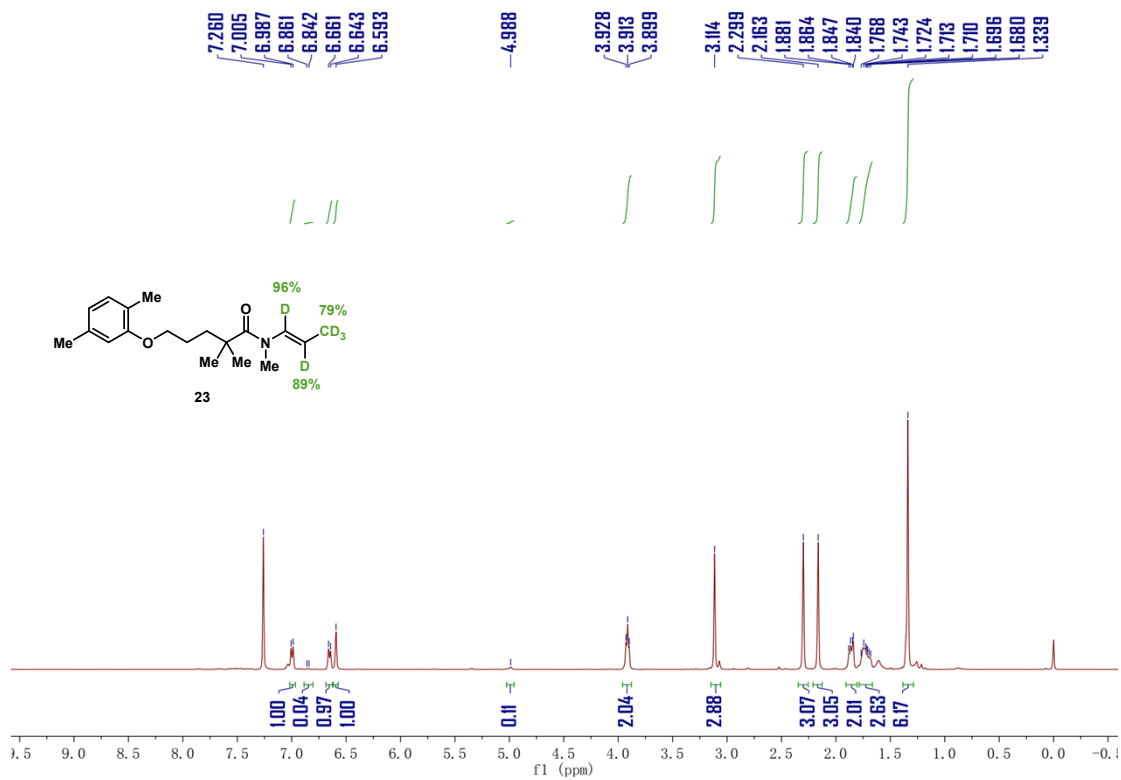
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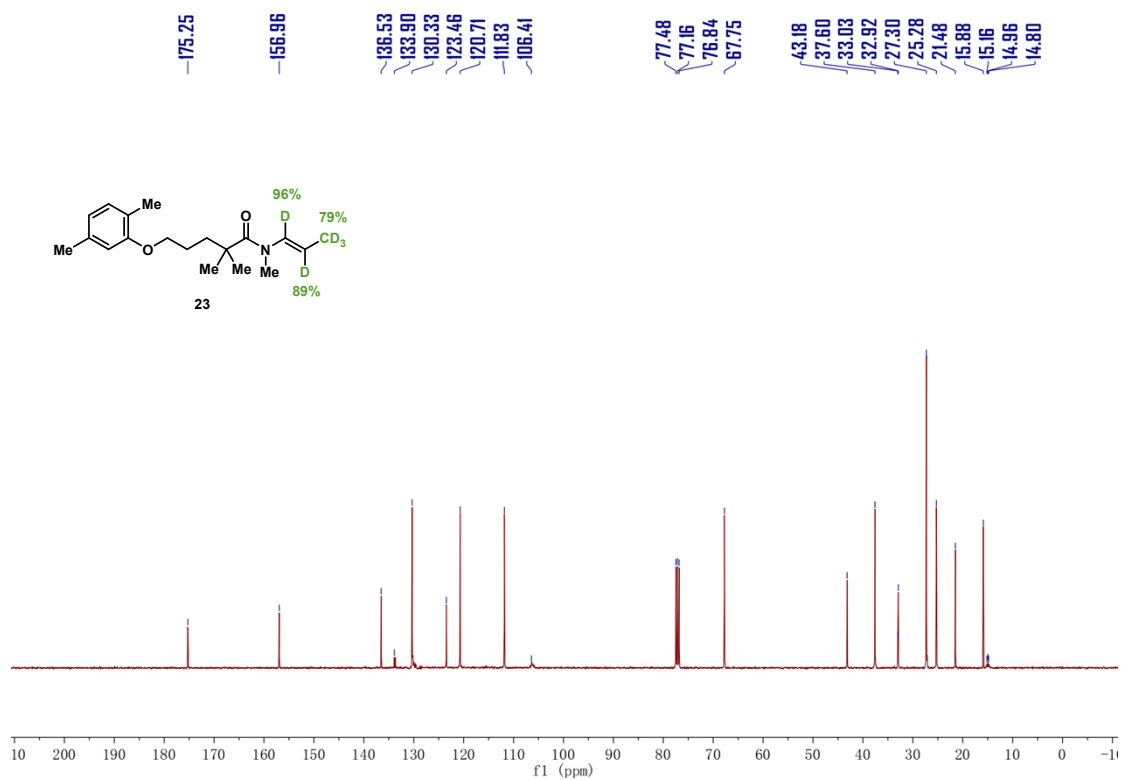
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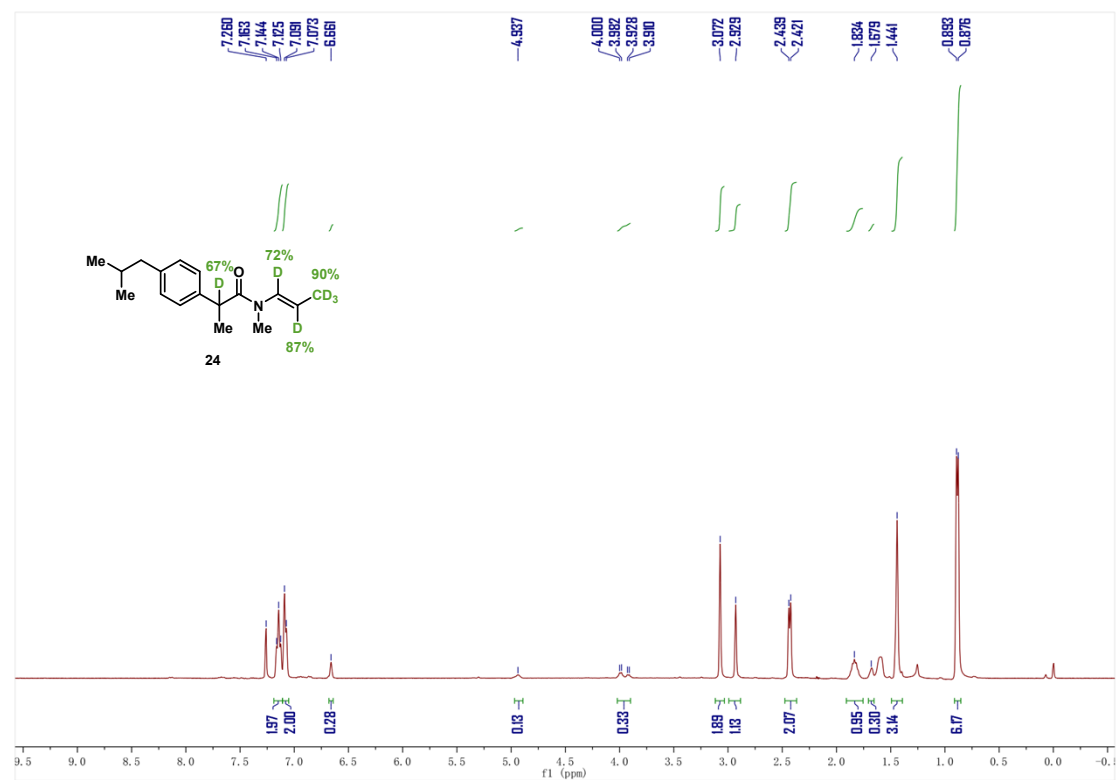
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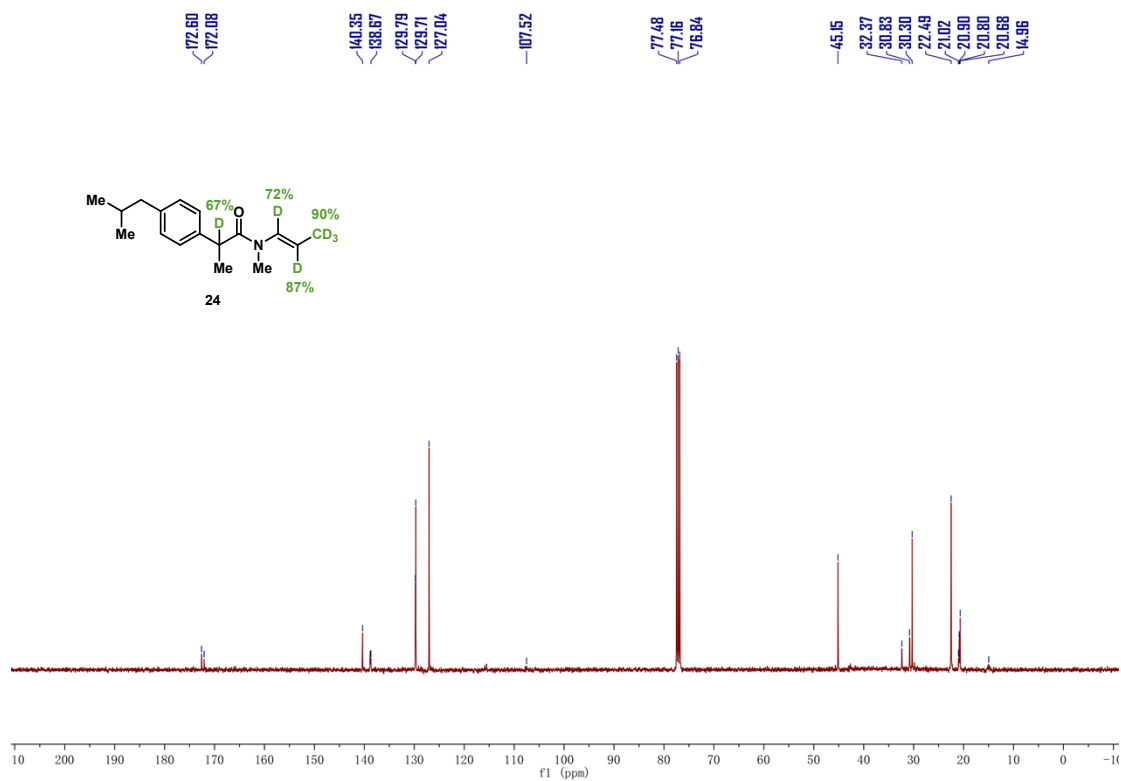
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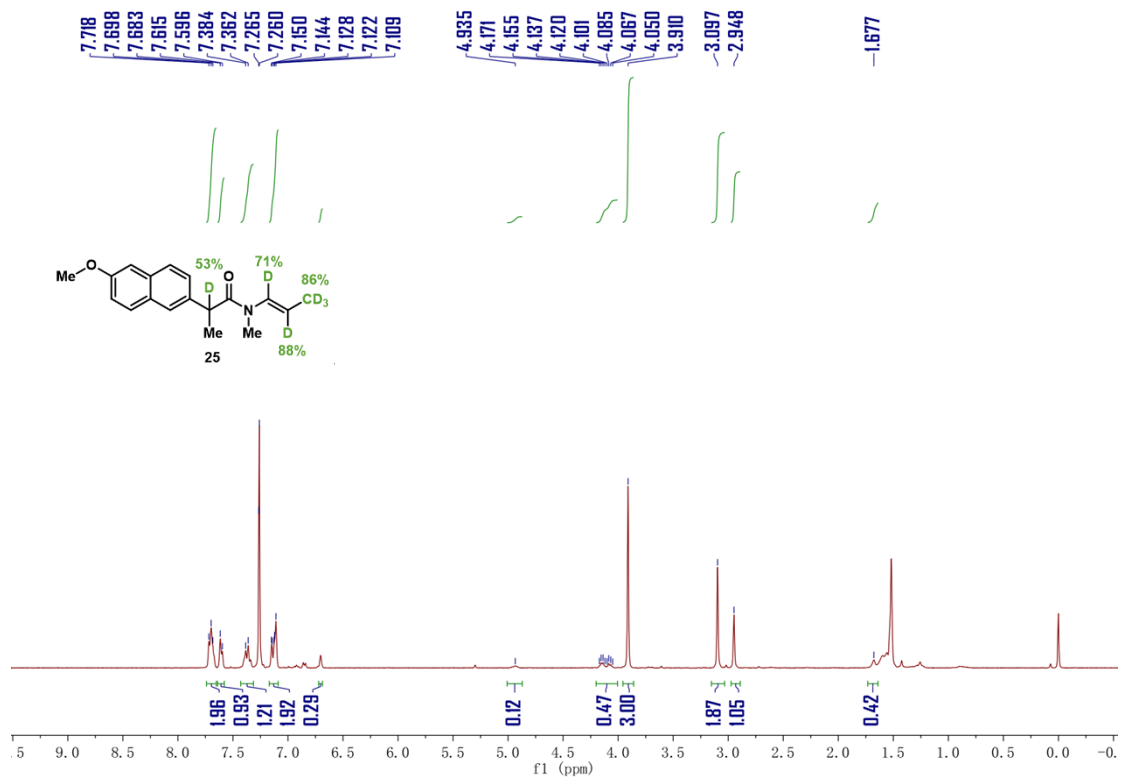
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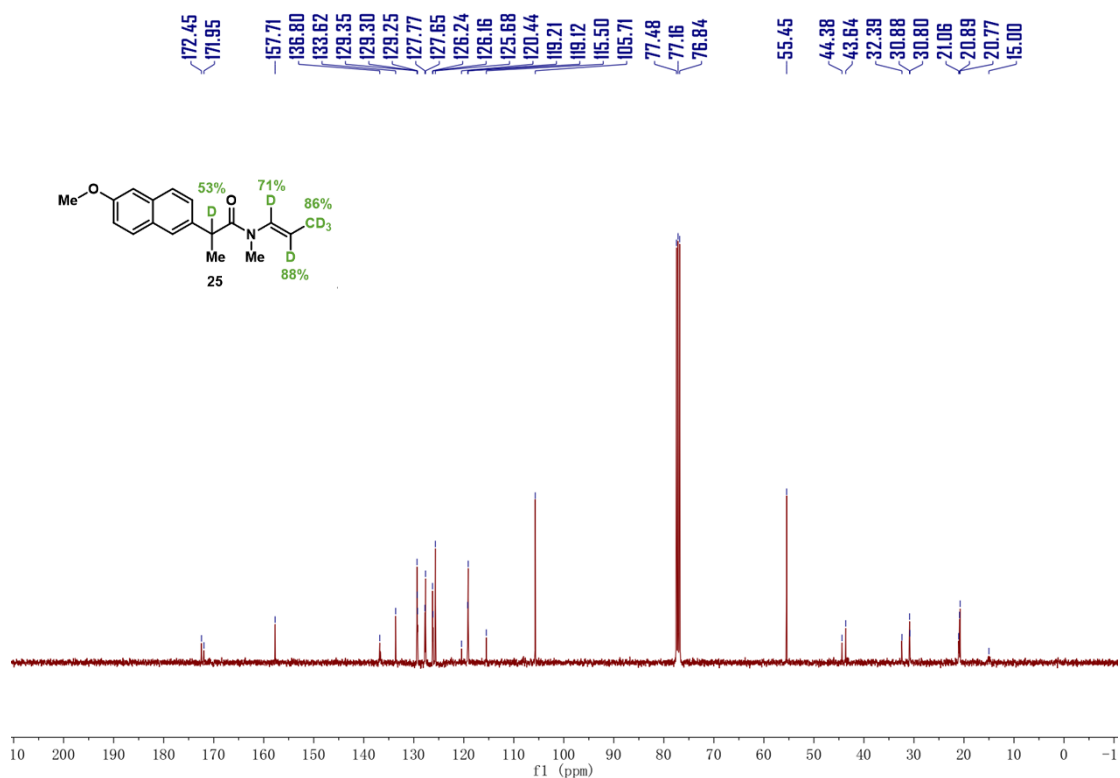
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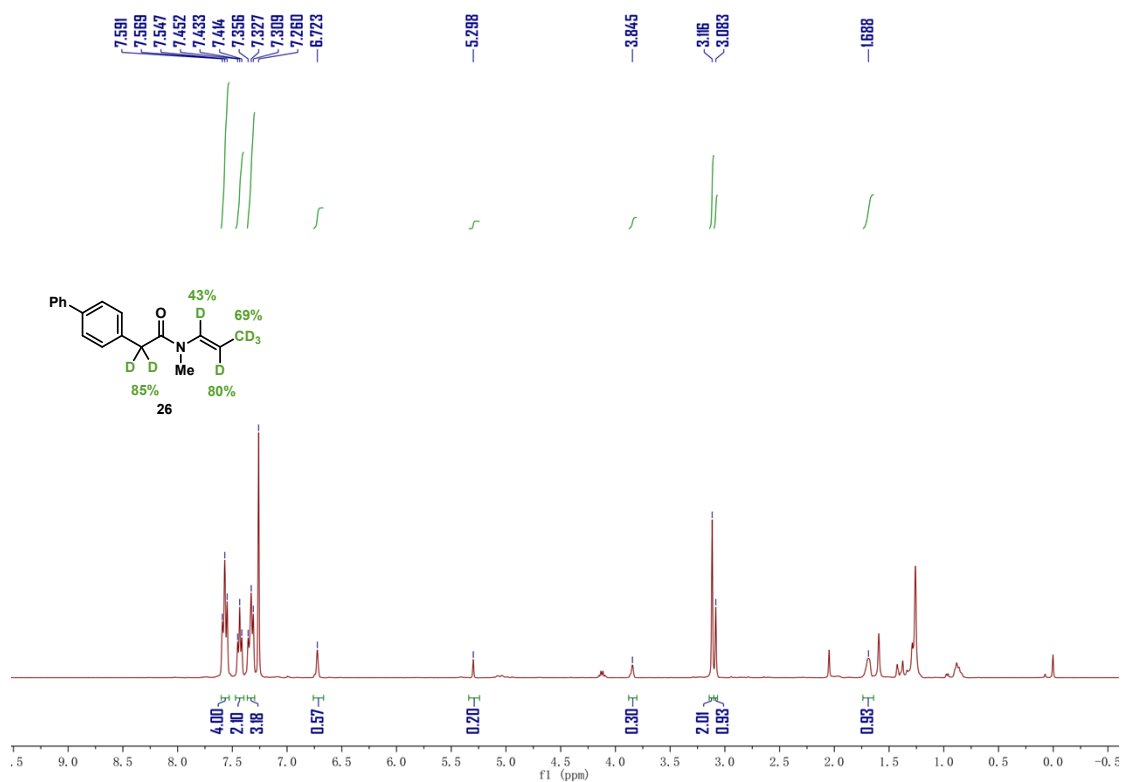
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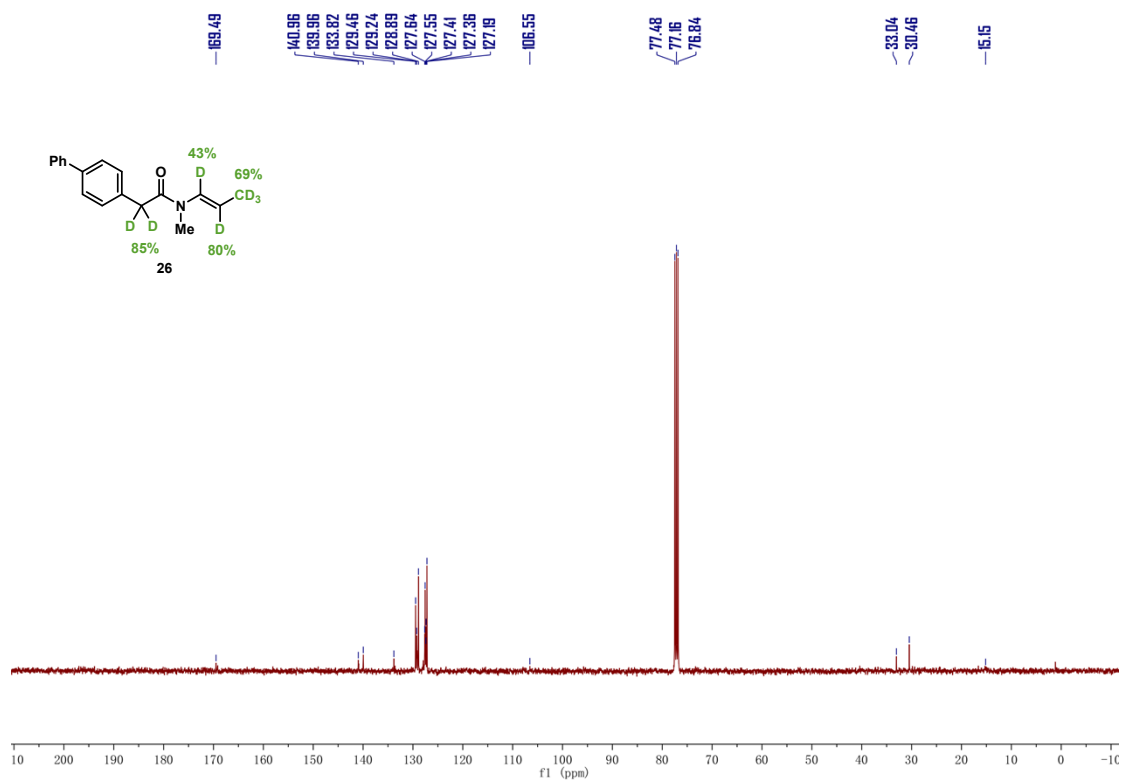
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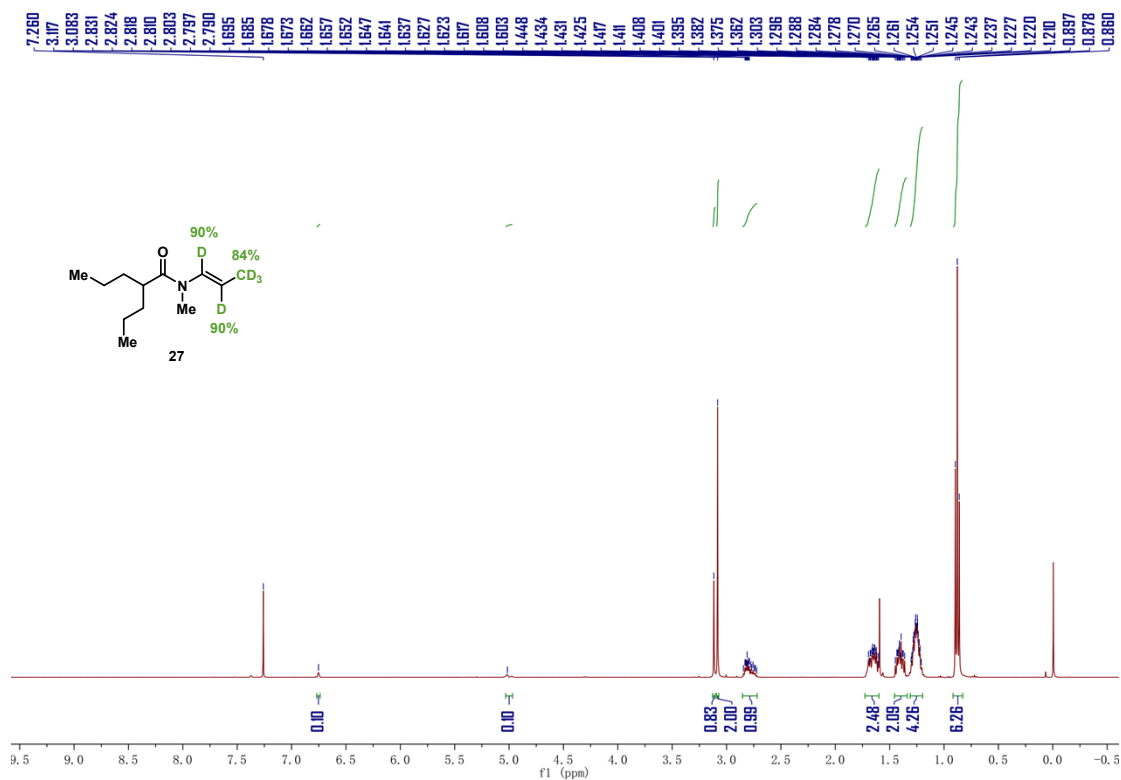
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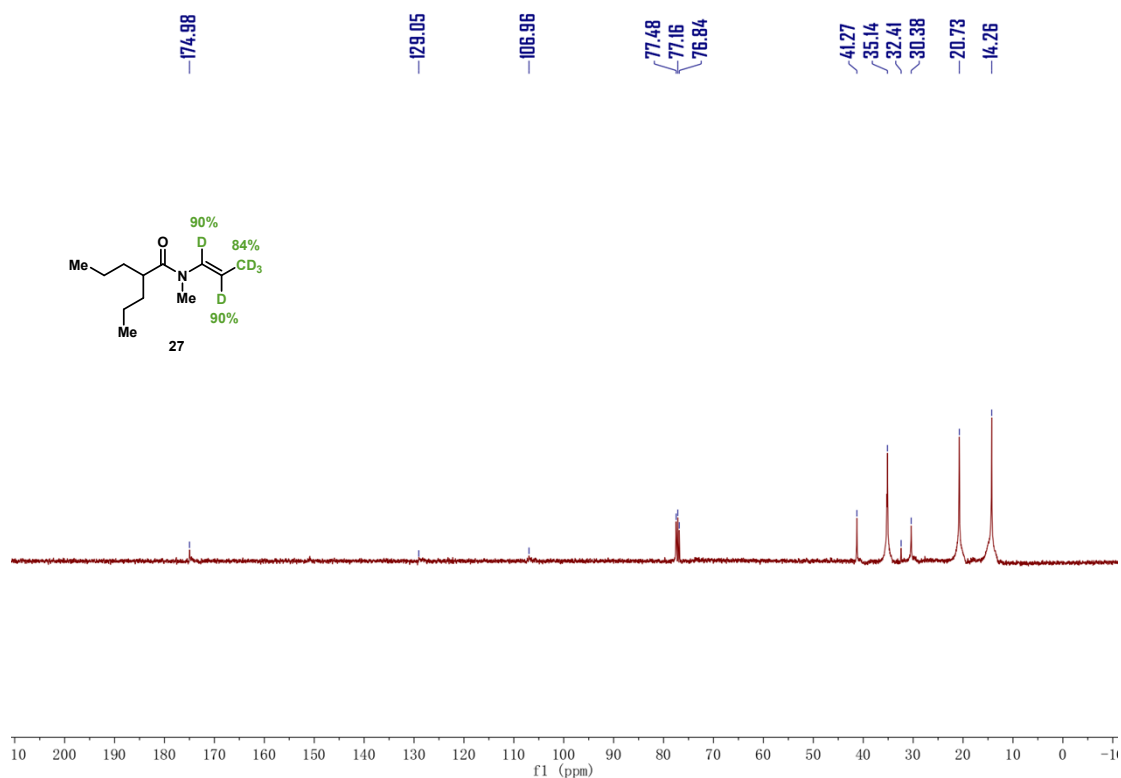
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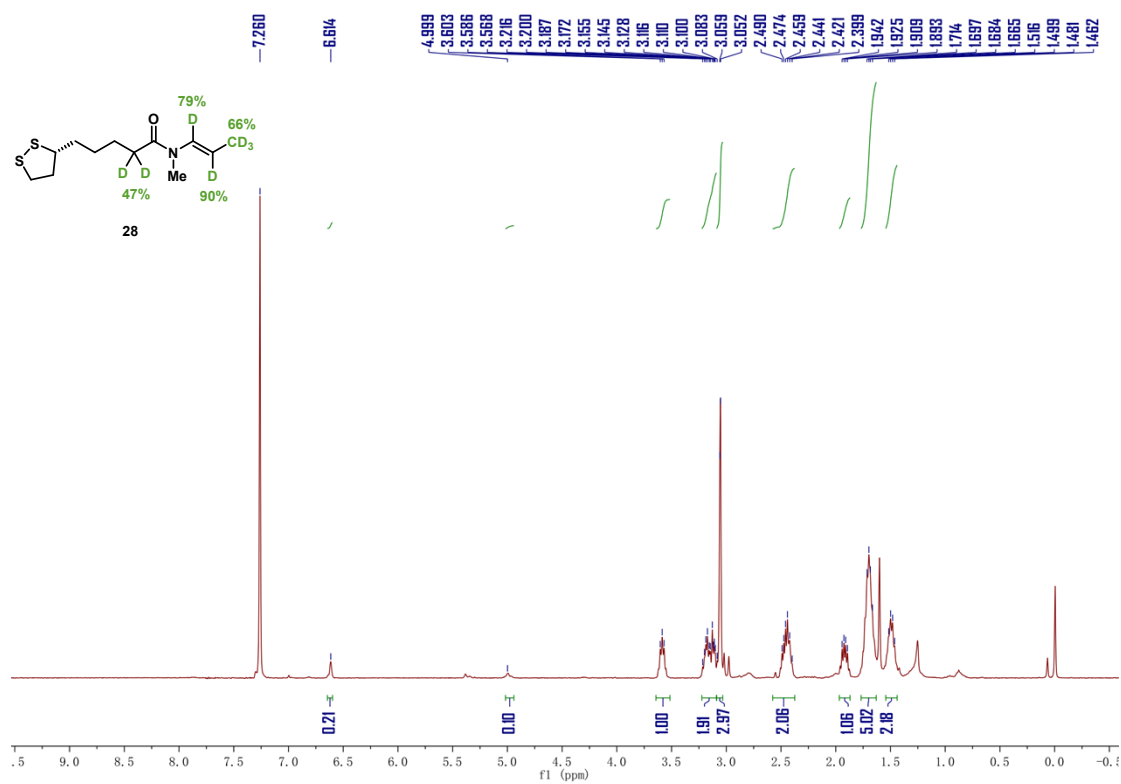
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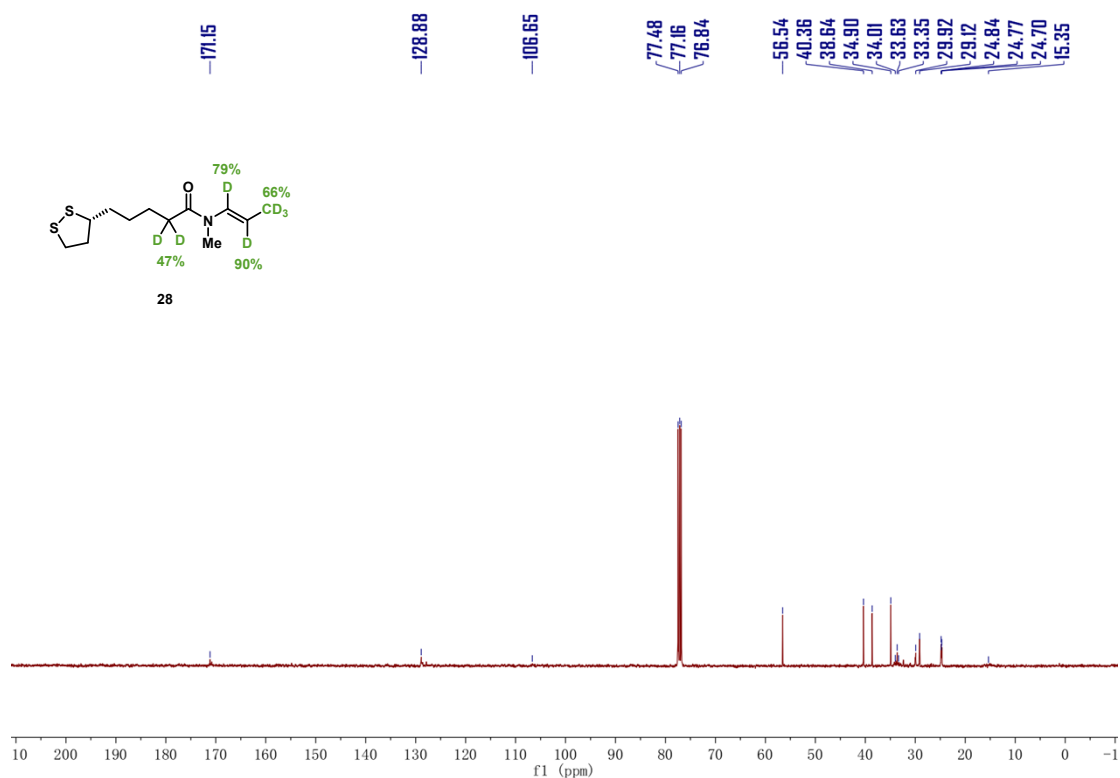
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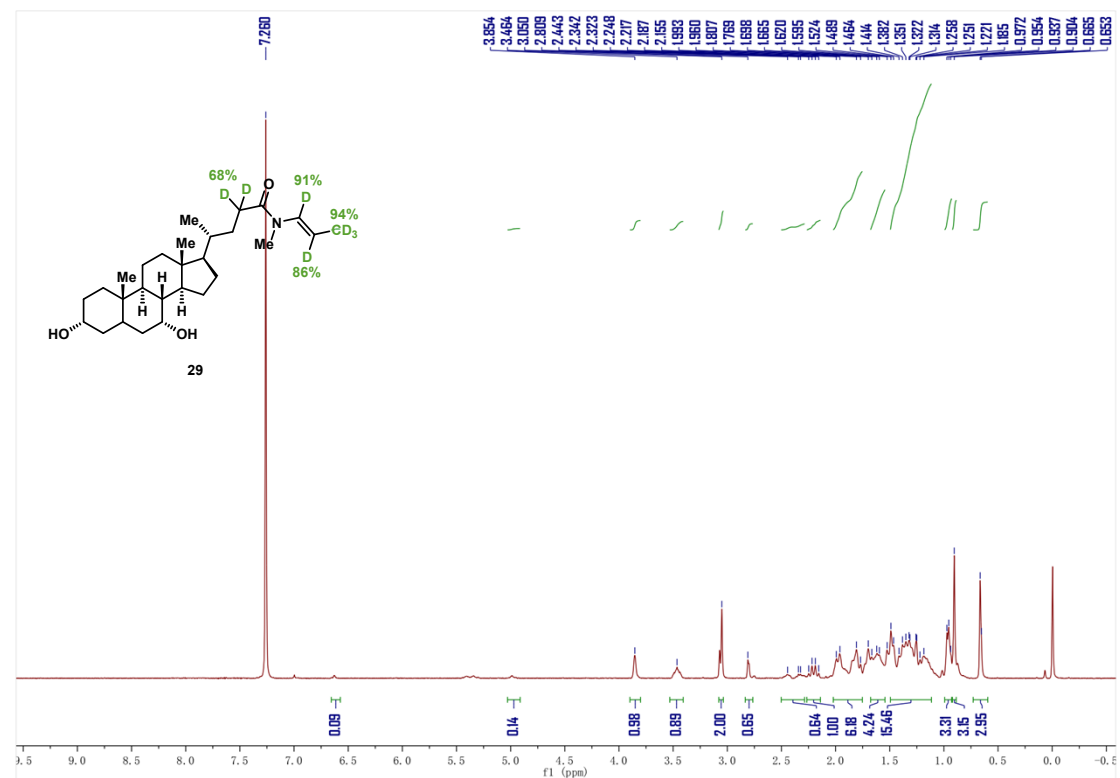
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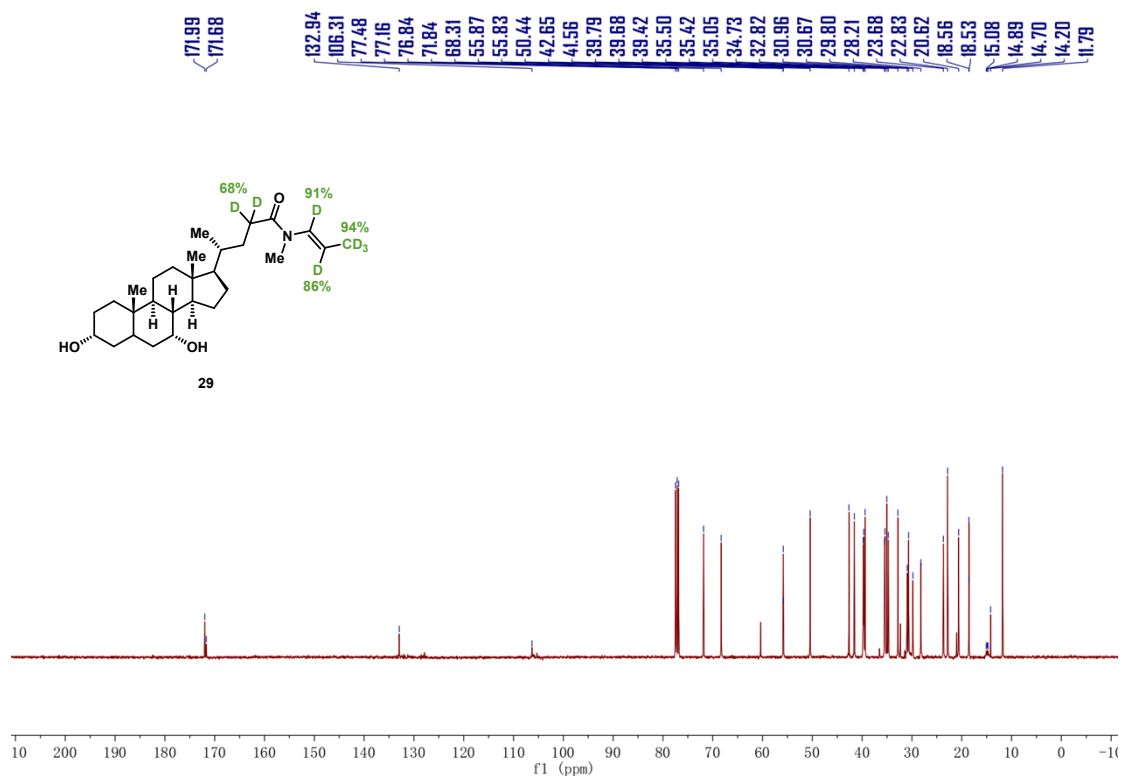
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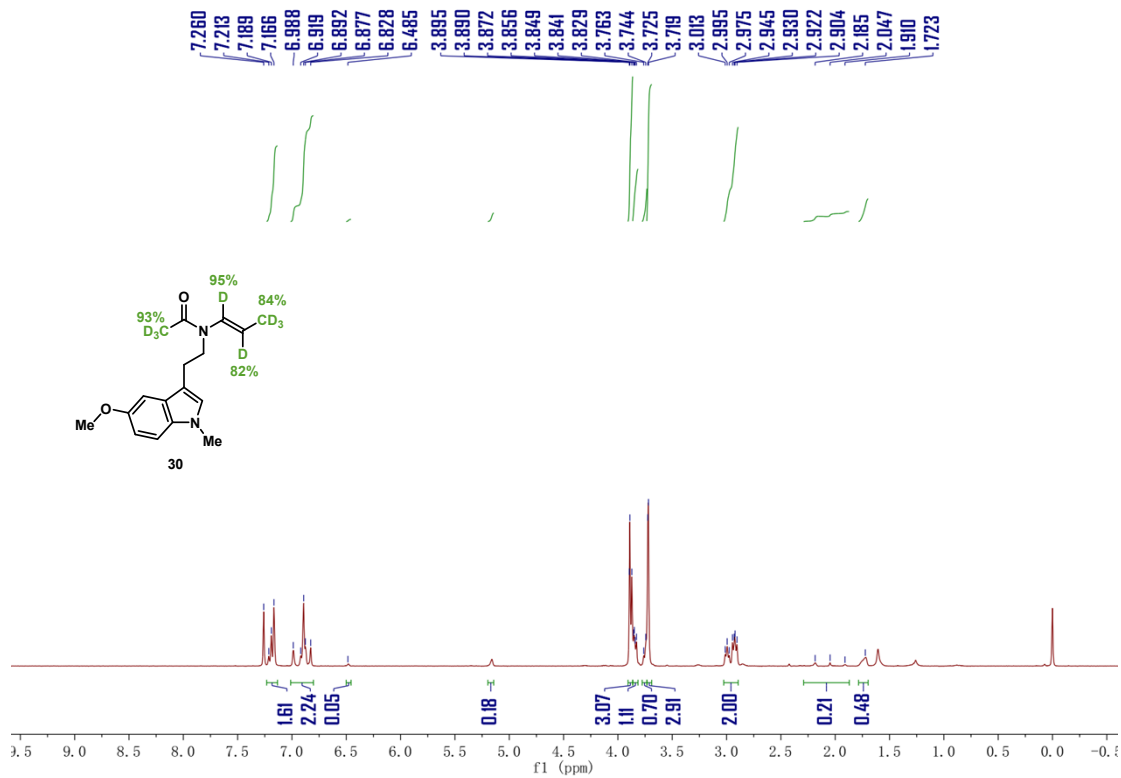
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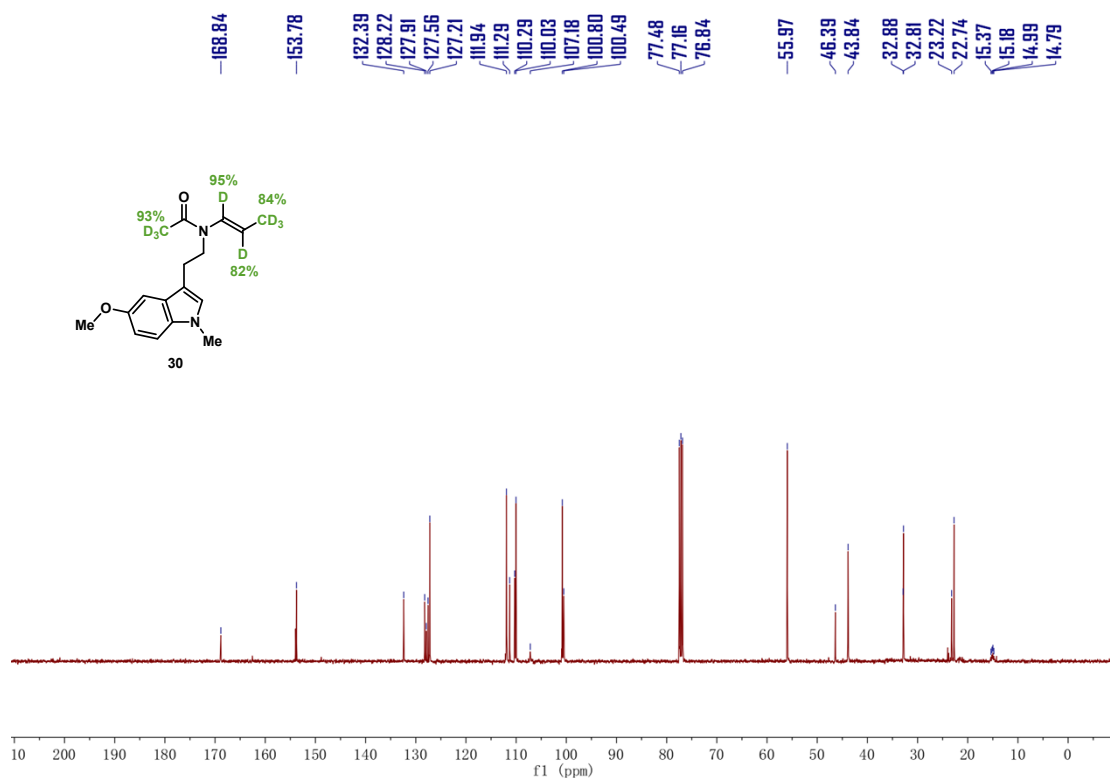
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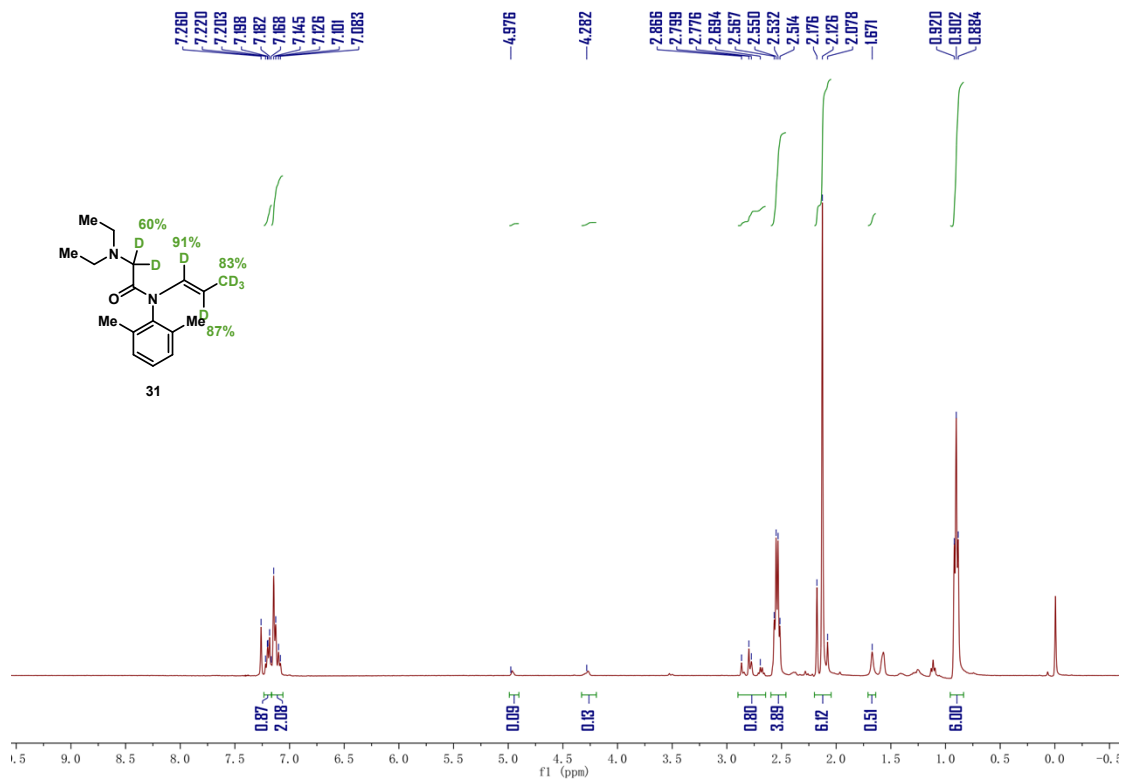
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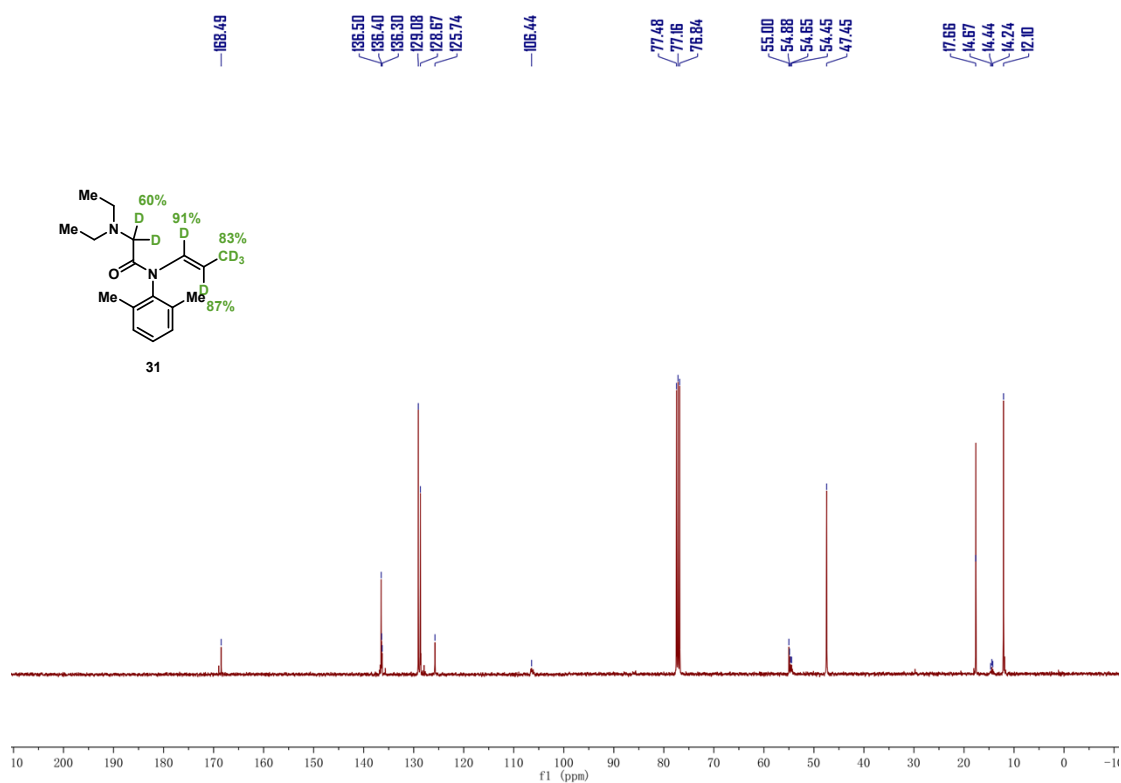
^{13}C NMR (101 MHz, CDCl_3):



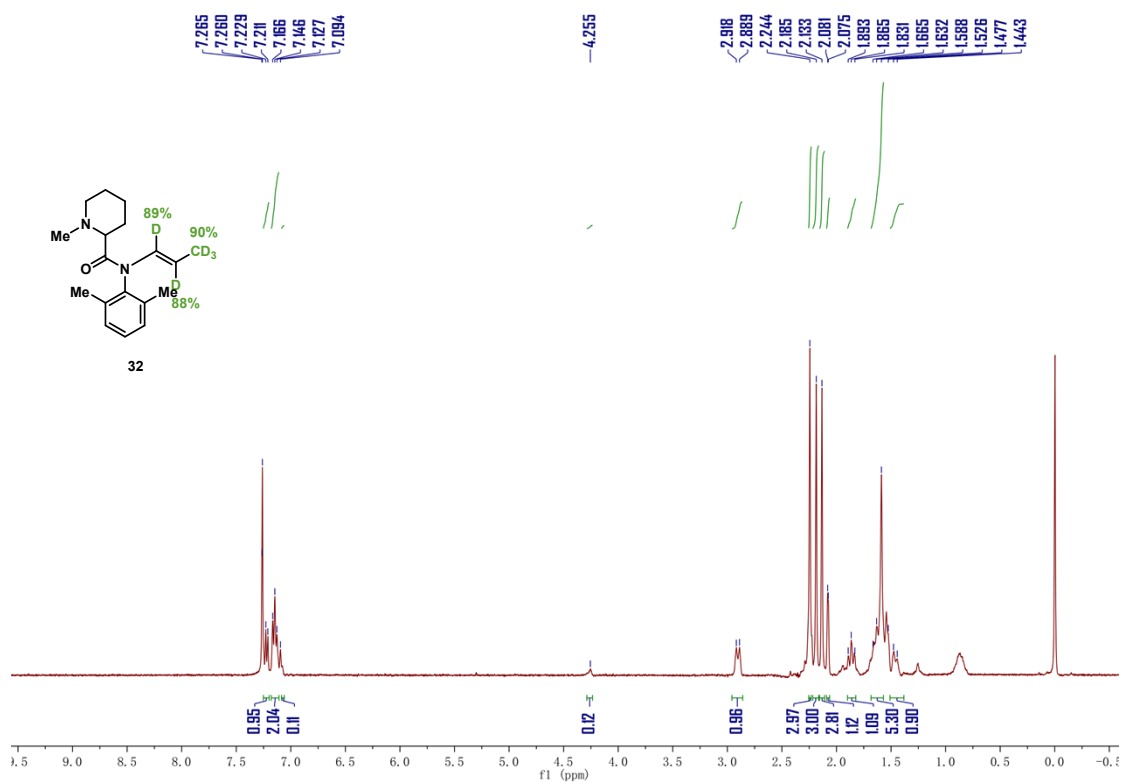
^1H NMR (400 MHz, CDCl_3):



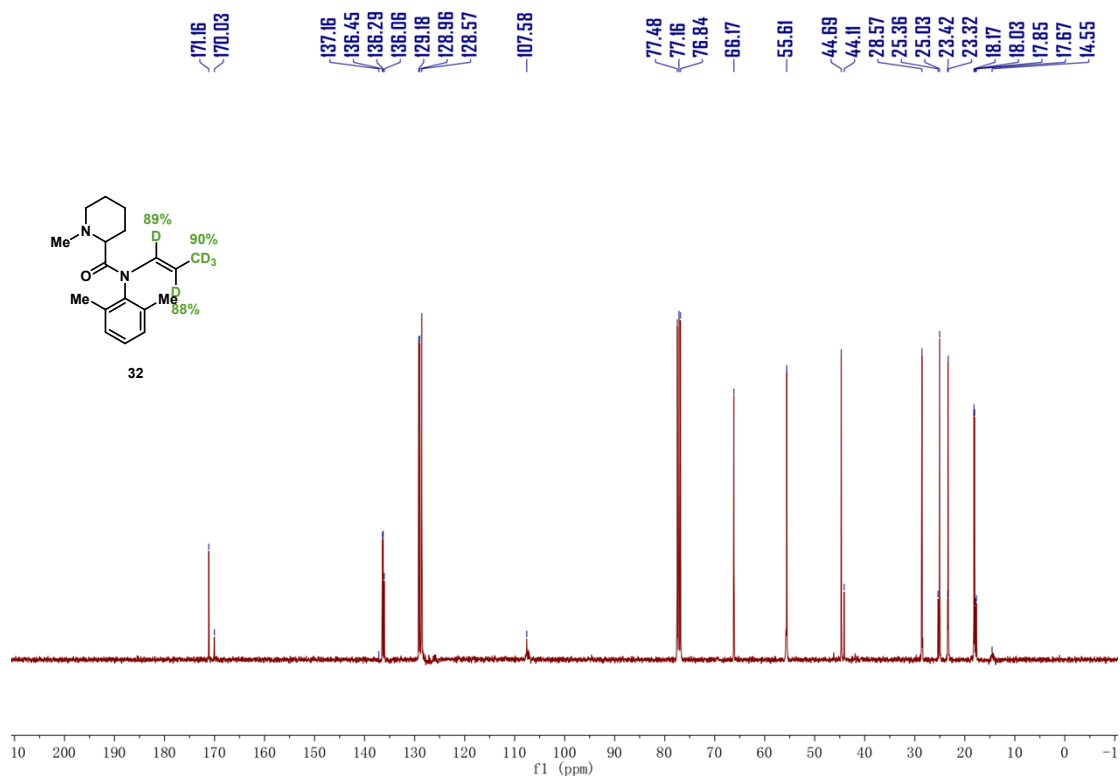
^{13}C NMR (101 MHz, CDCl_3):



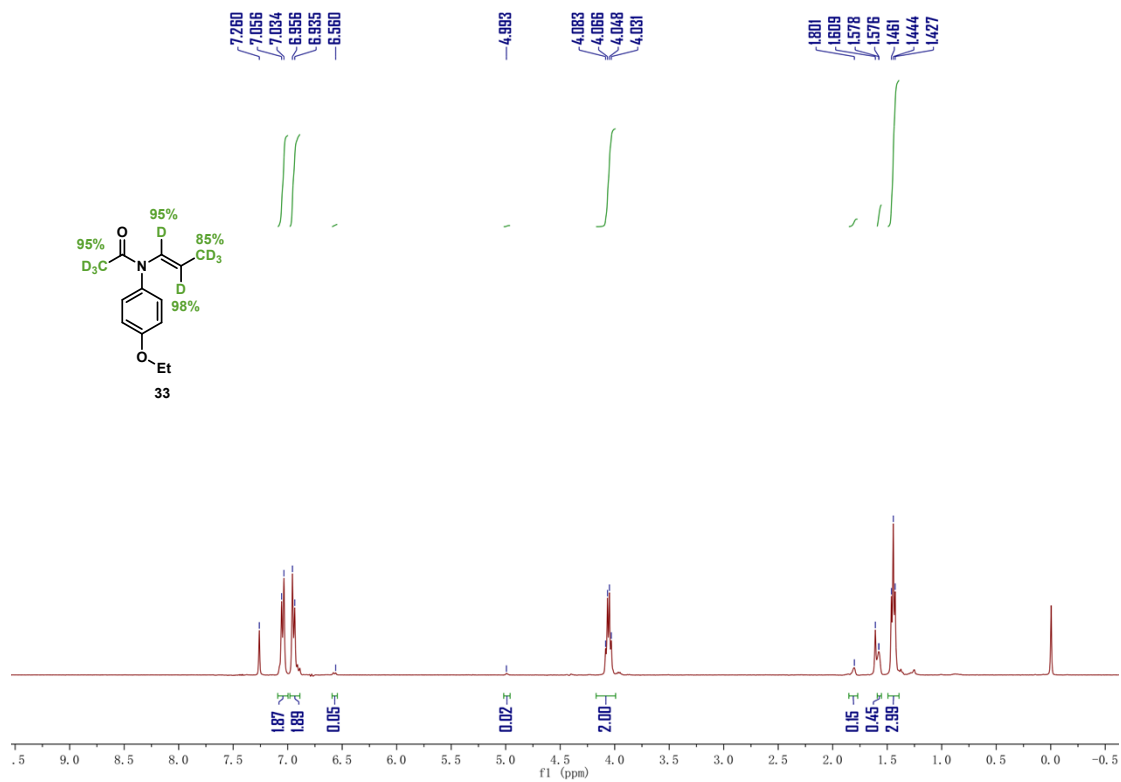
^1H NMR (400 MHz, CDCl_3):



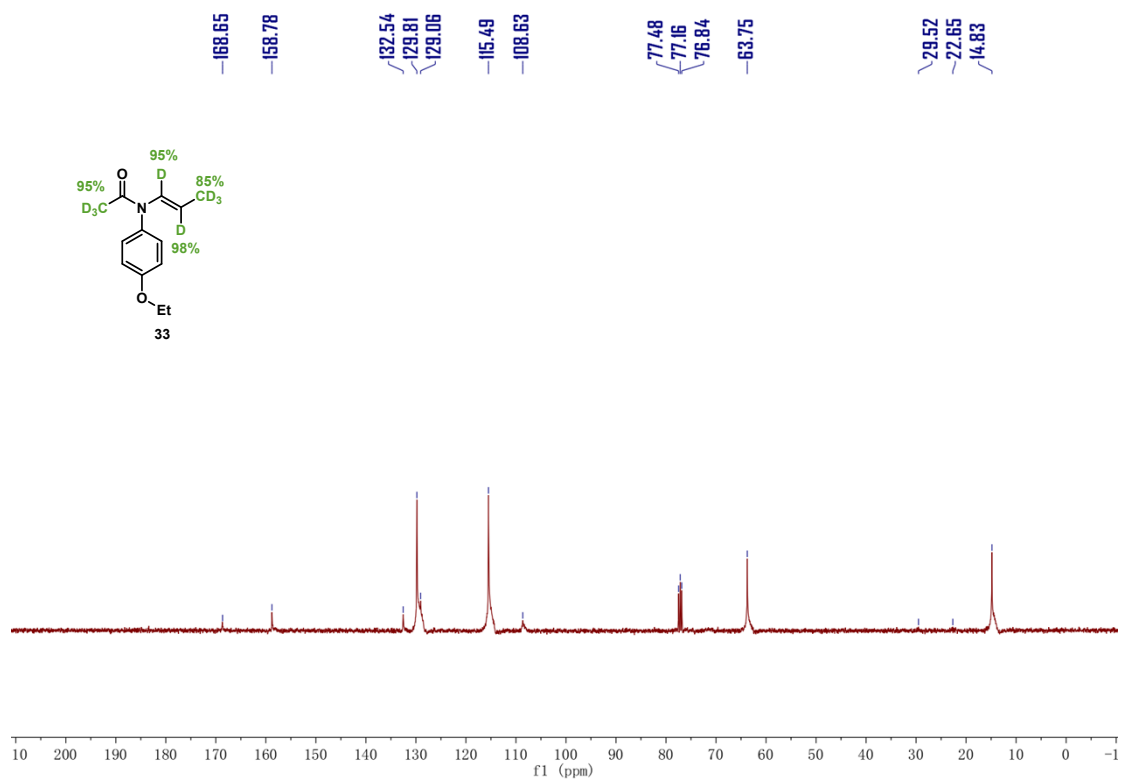
^{13}C NMR (101 MHz, CDCl_3):



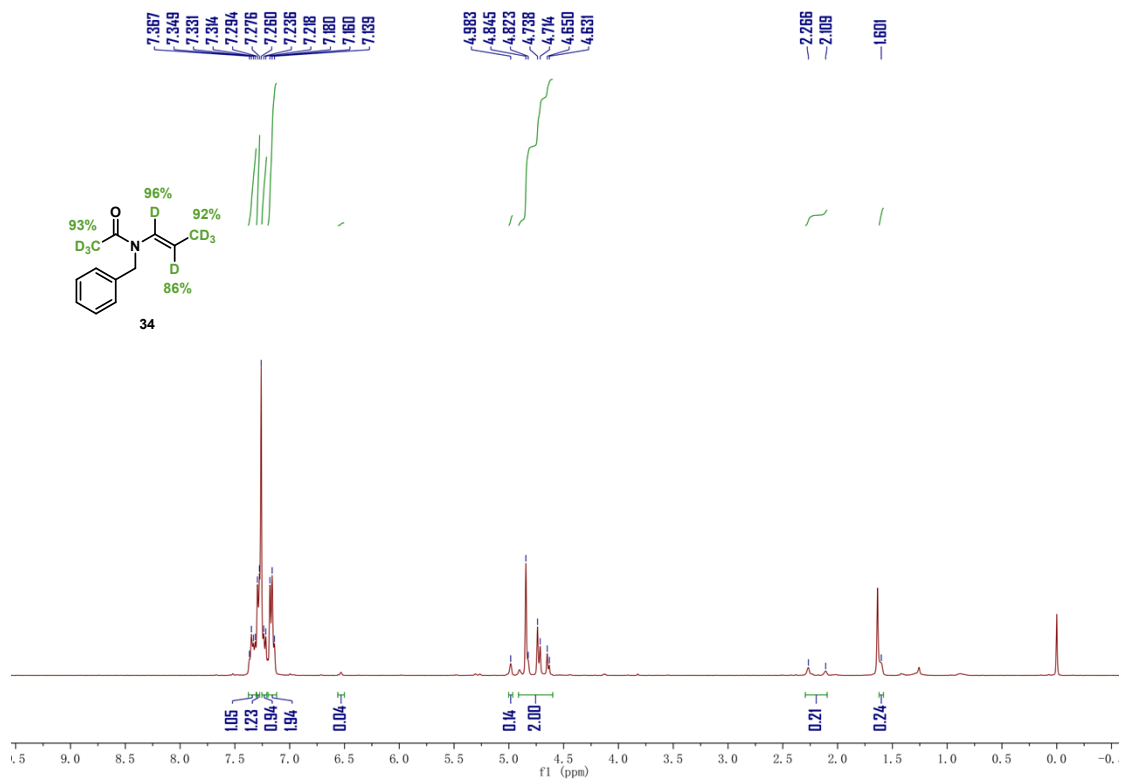
^1H NMR (400 MHz, CDCl_3):



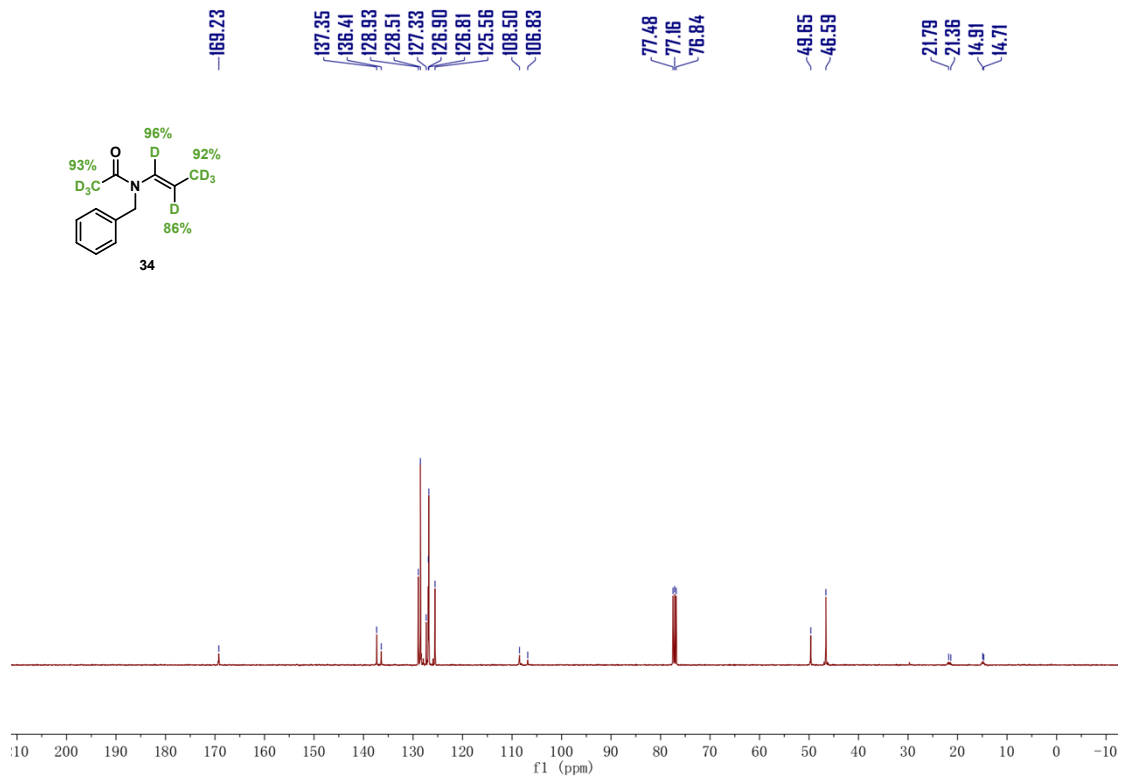
^{13}C NMR (101 MHz, CDCl_3):



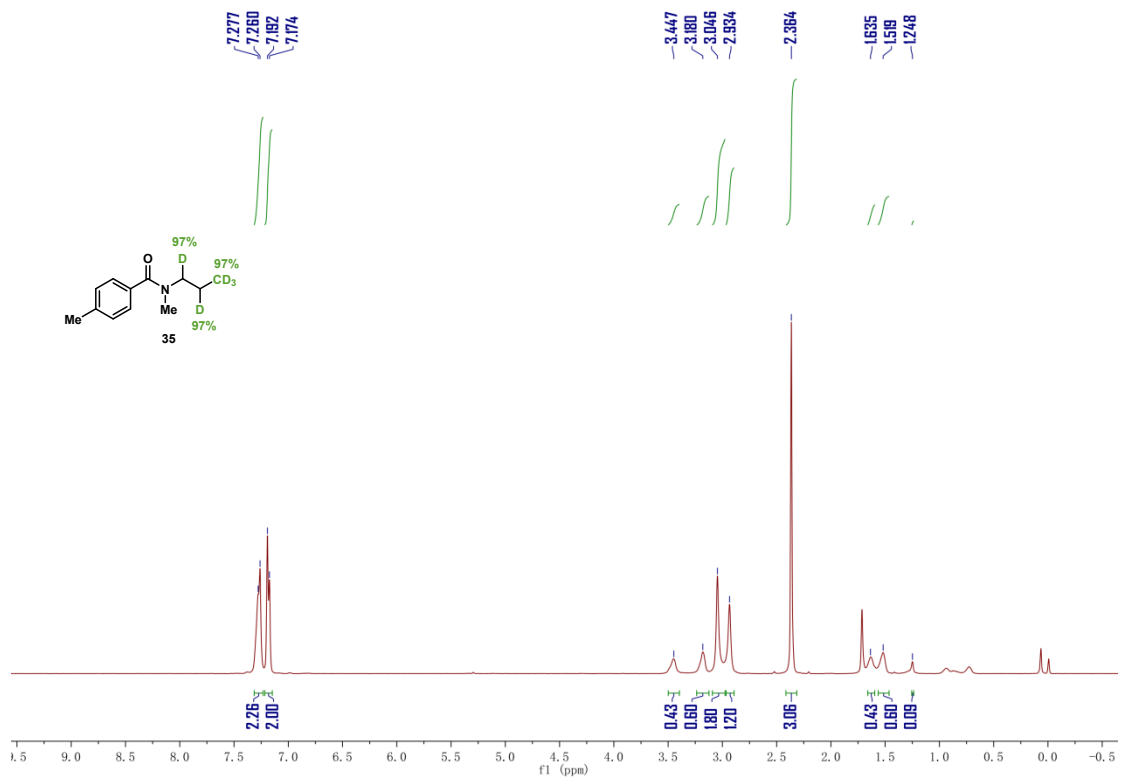
^1H NMR (400 MHz, CDCl_3):



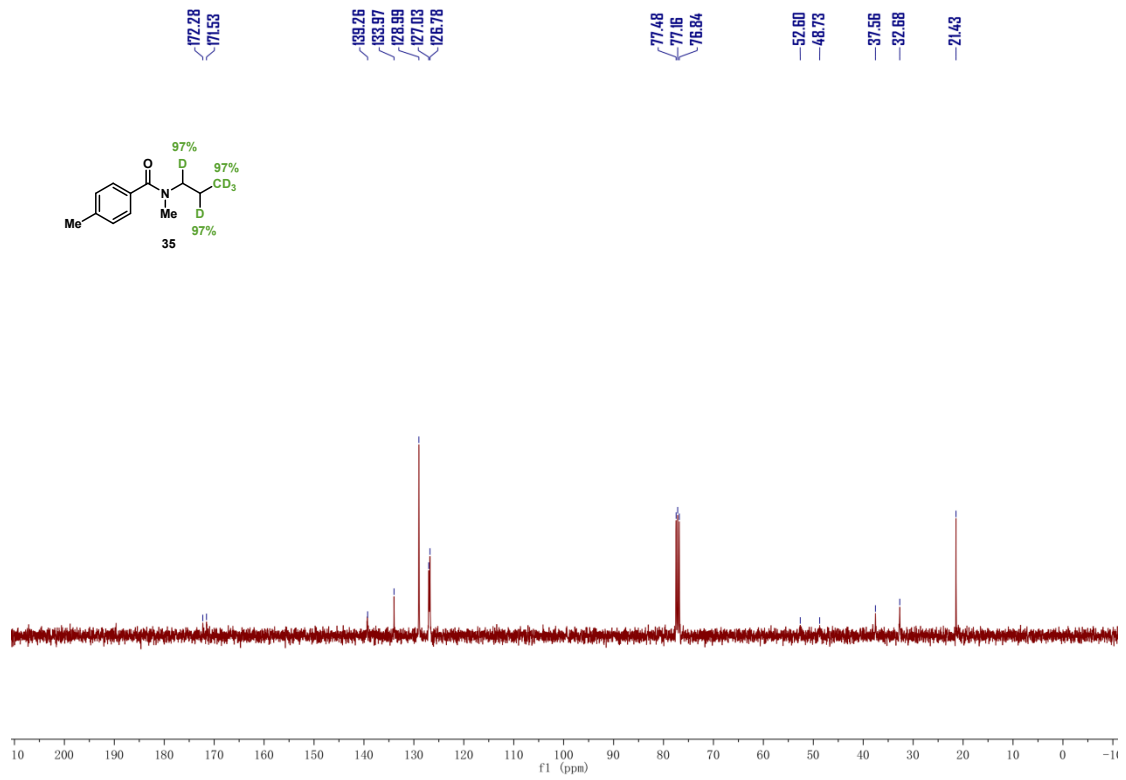
^{13}C NMR (101 MHz, CDCl_3):



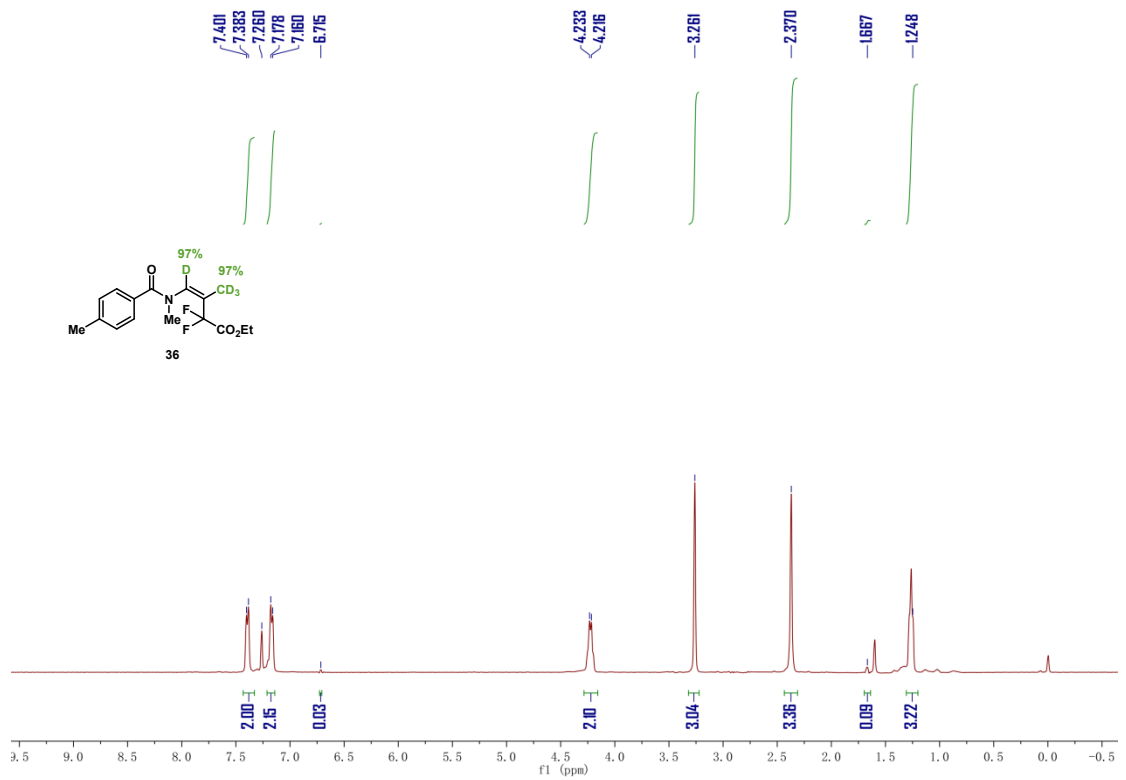
^1H NMR (400 MHz, CDCl_3):



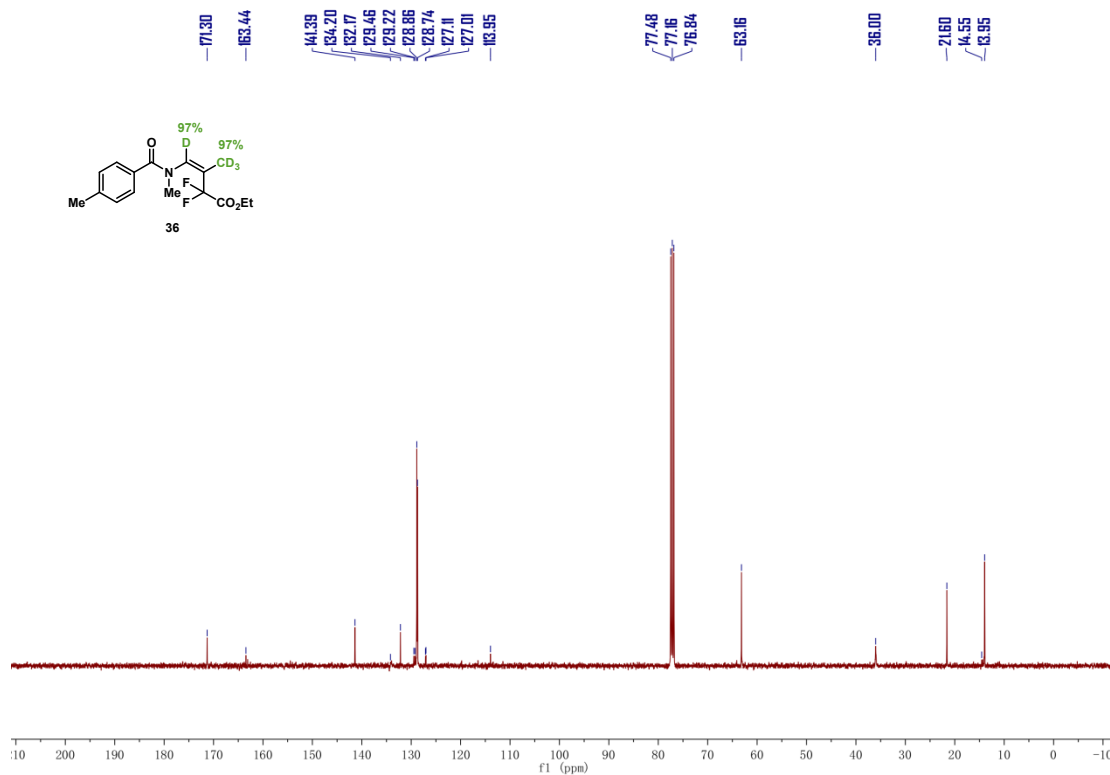
¹³C NMR (101 MHz, CDCl₃):



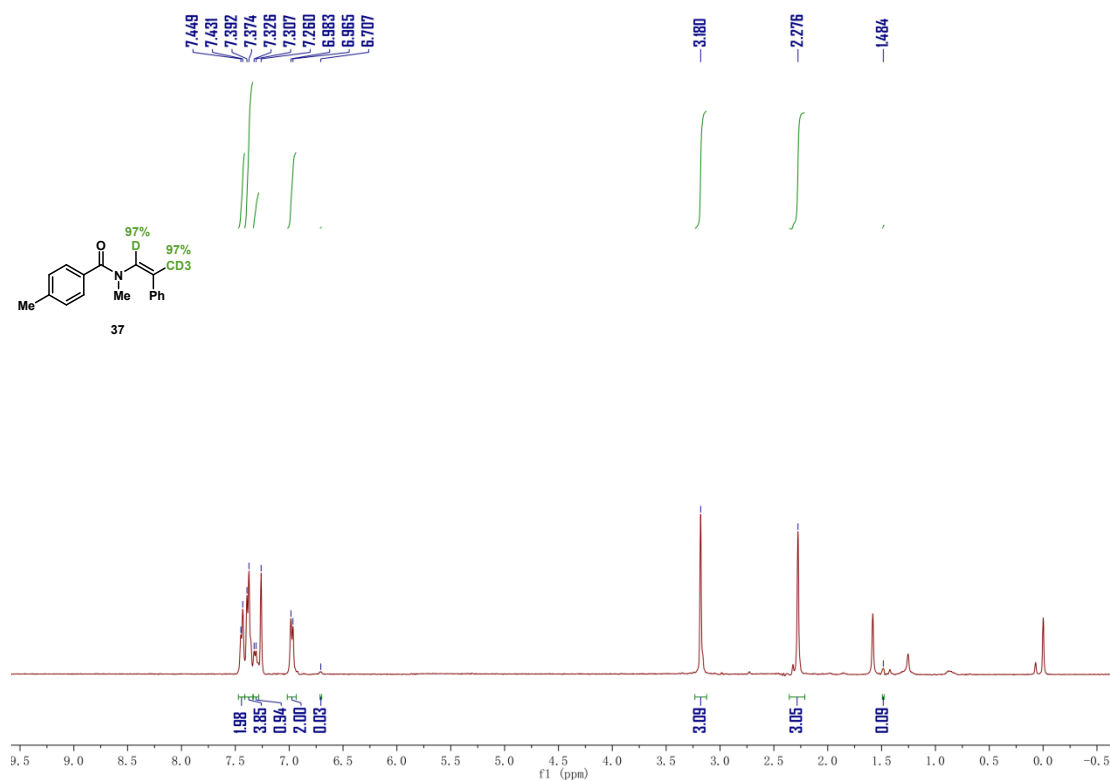
¹H NMR (400 MHz, CDCl₃):



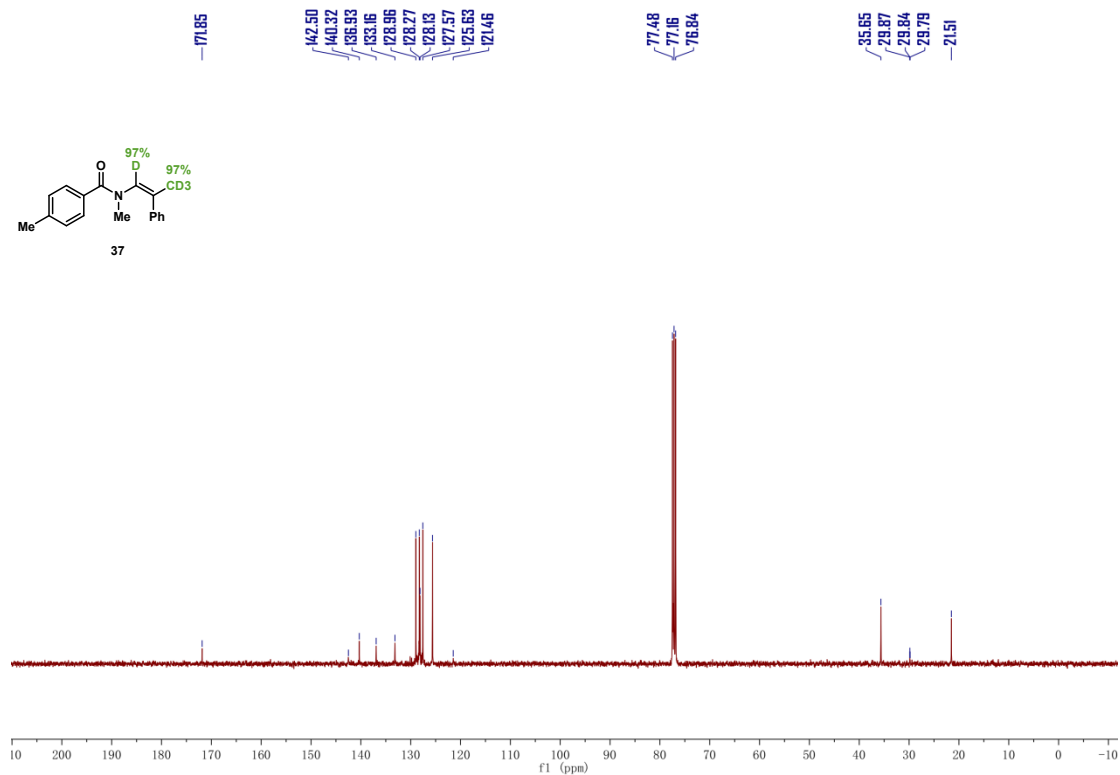
¹³C NMR (101 MHz, CDCl₃):



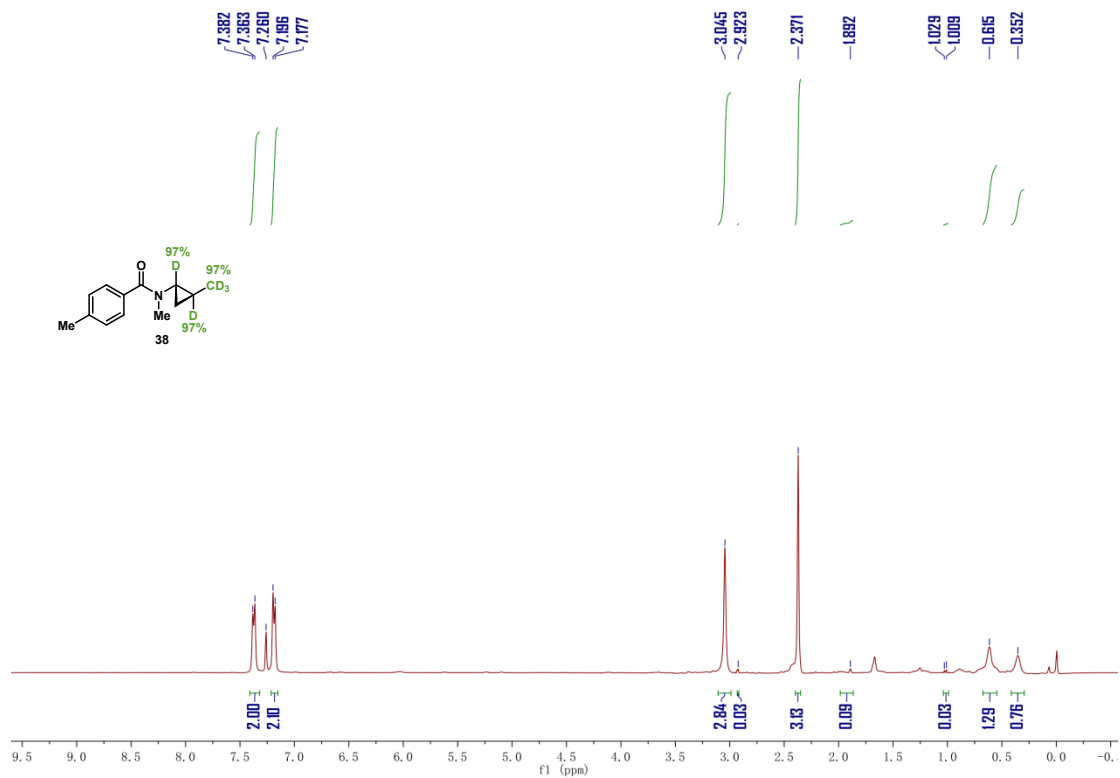
¹H NMR (400 MHz, CDCl₃):



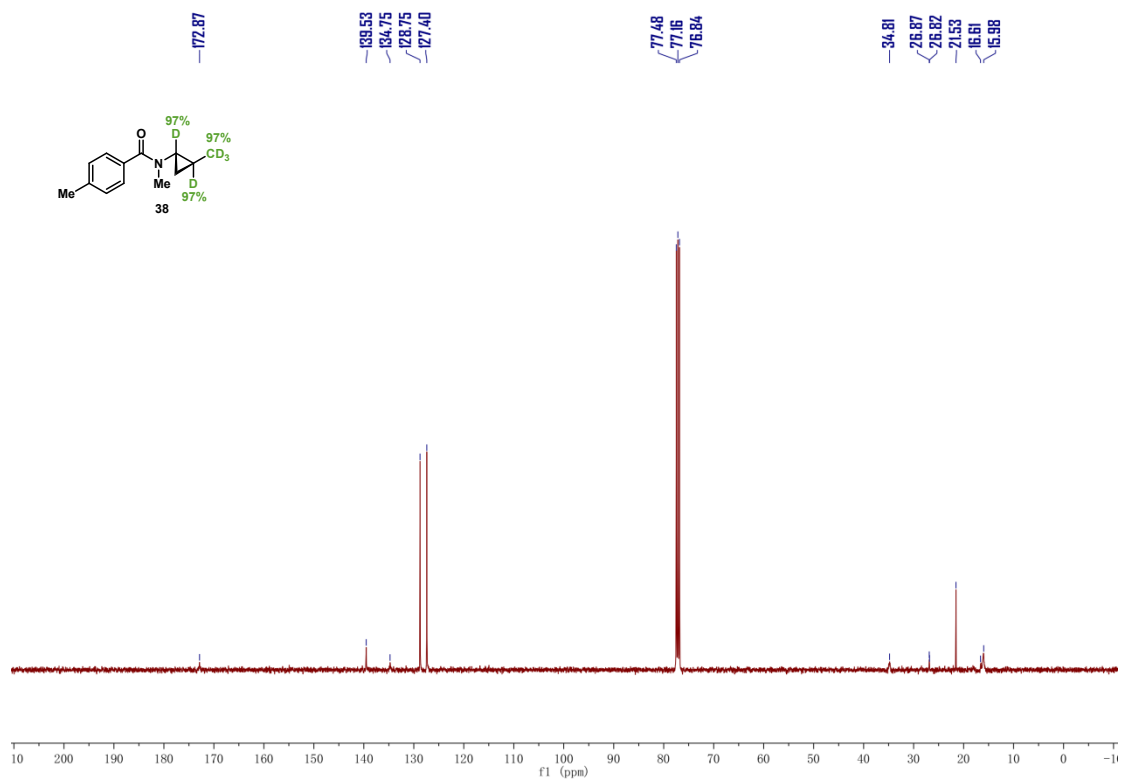
^{13}C NMR (101 MHz, CDCl_3):



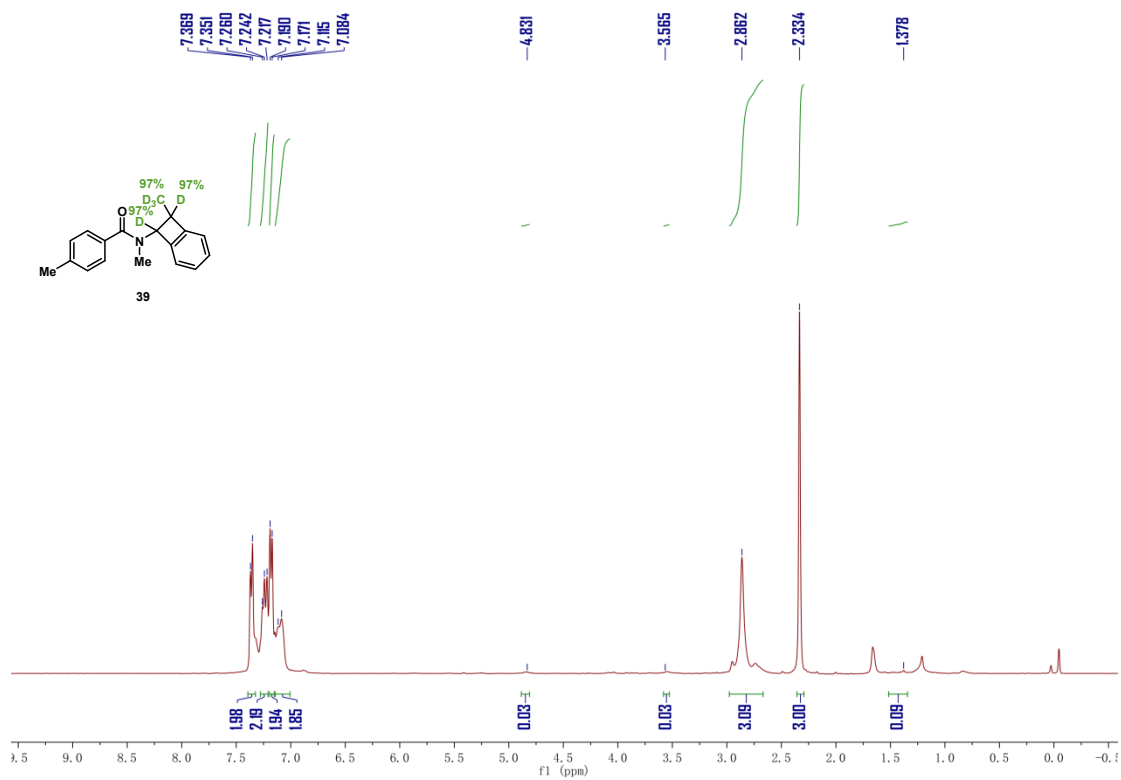
^1H NMR (400 MHz, CDCl_3):



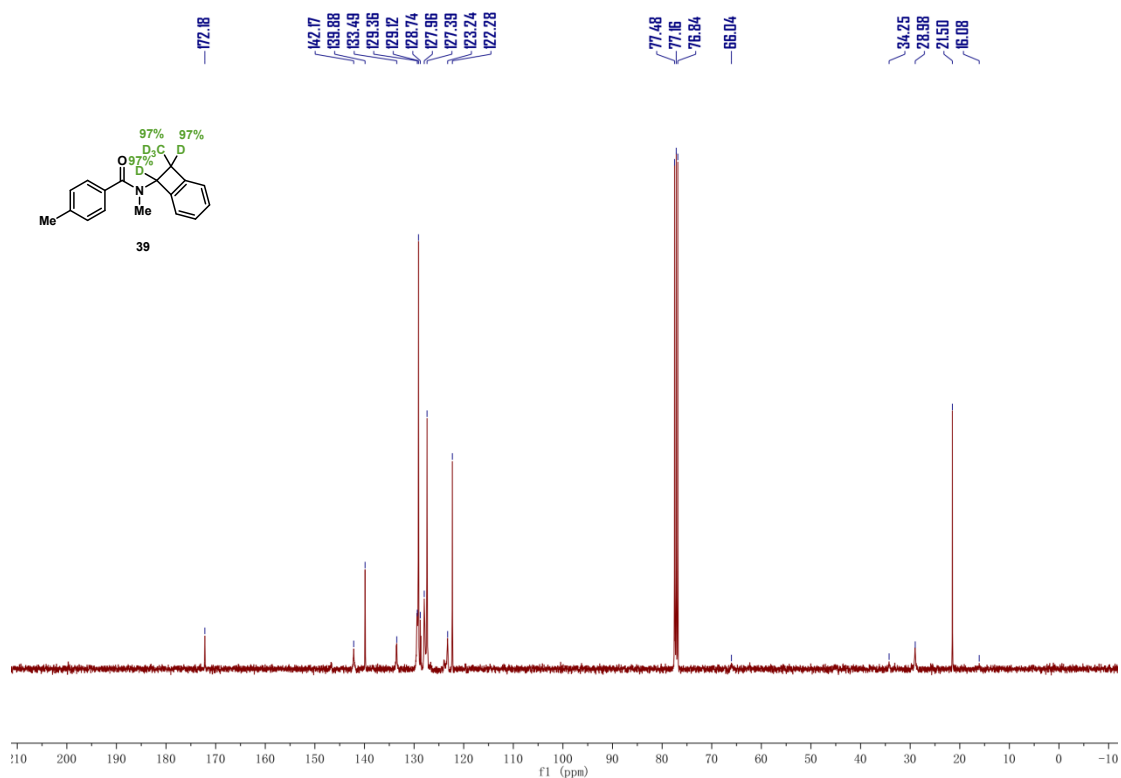
^{13}C NMR (101 MHz, CDCl_3):



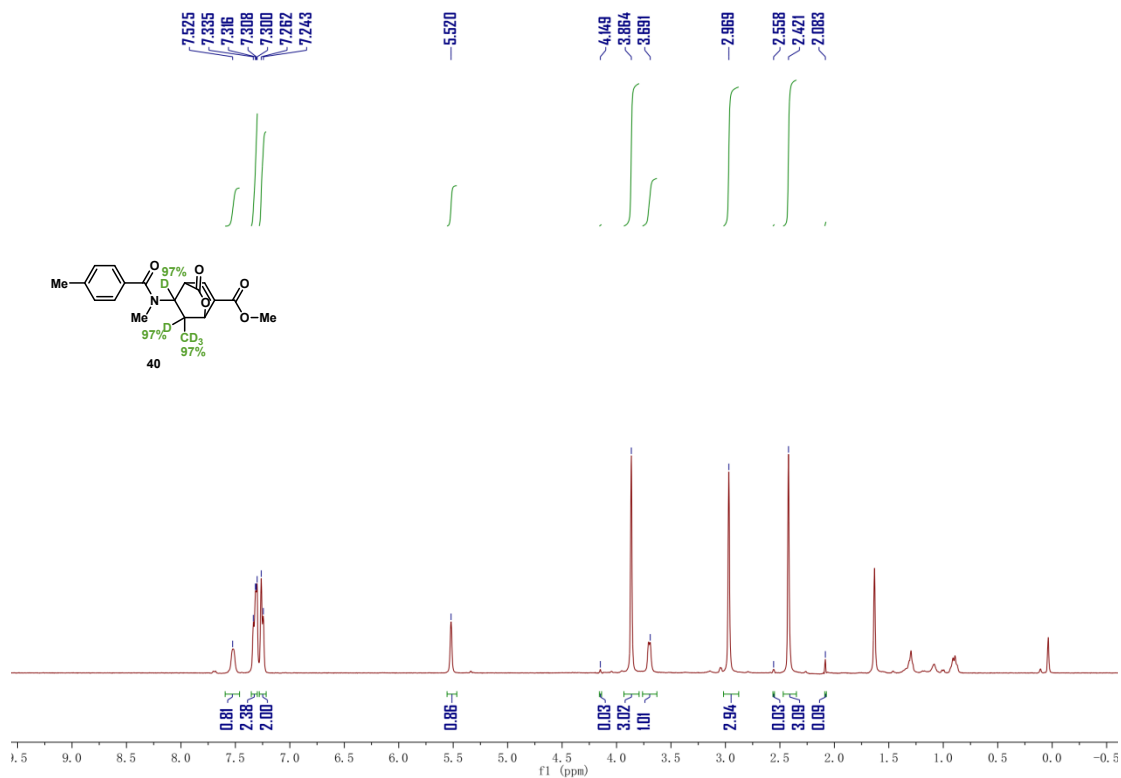
^1H NMR (400 MHz, CDCl_3):



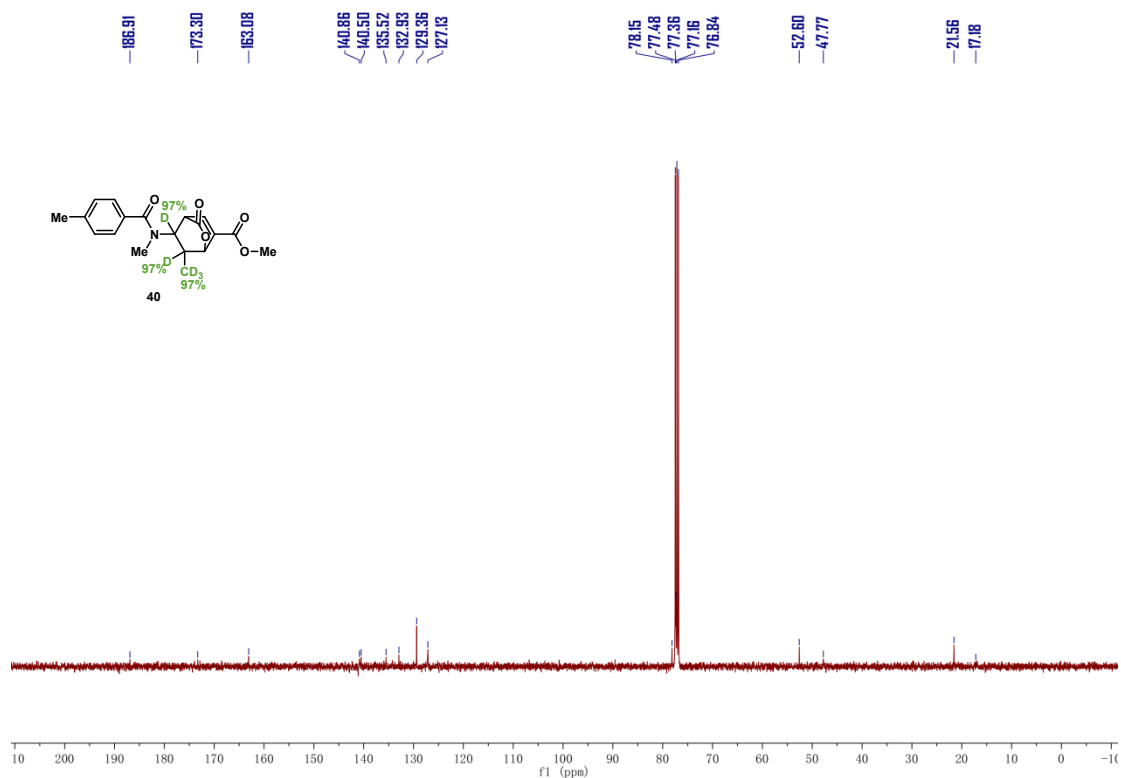
¹³C NMR (101 MHz, CDCl₃):



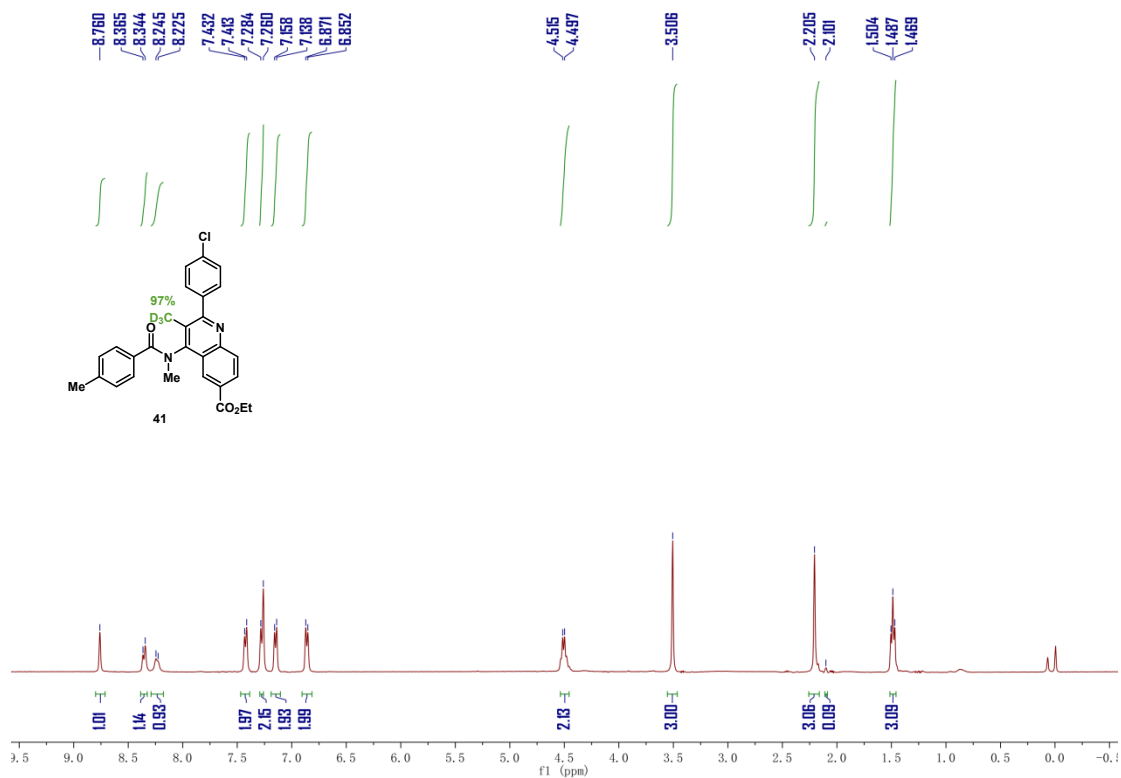
¹H NMR (400 MHz, CDCl₃):



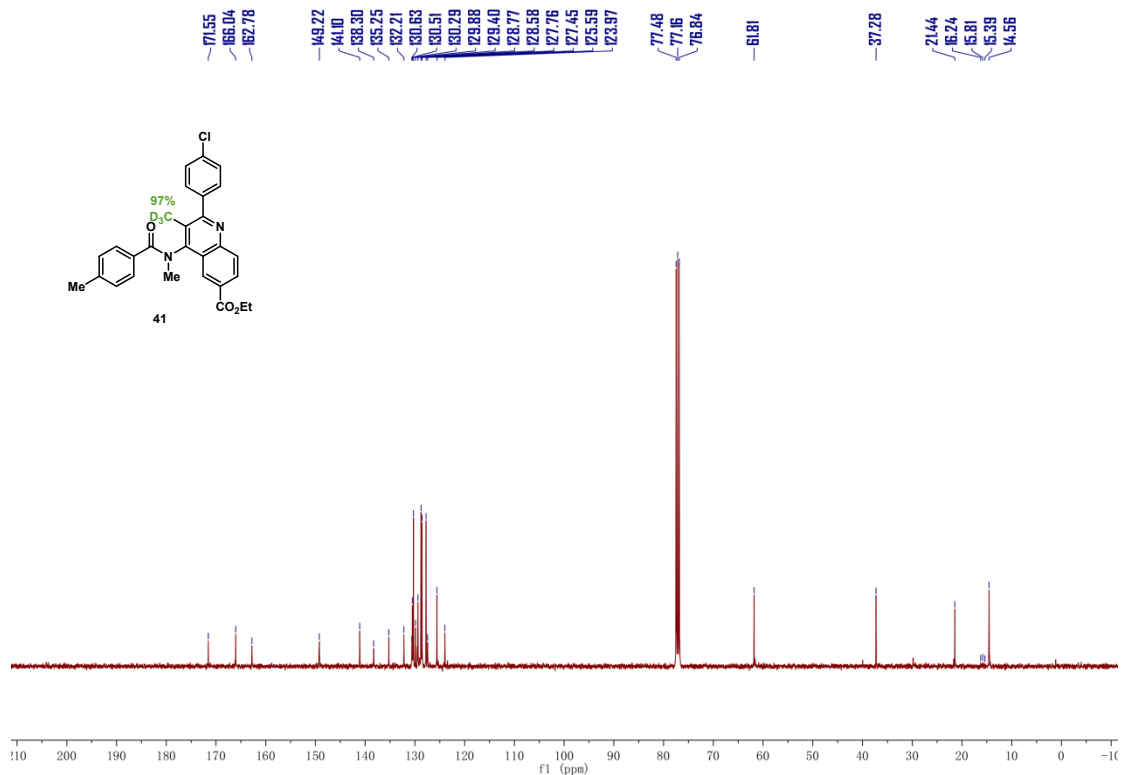
^{13}C NMR (101 MHz, CDCl_3):



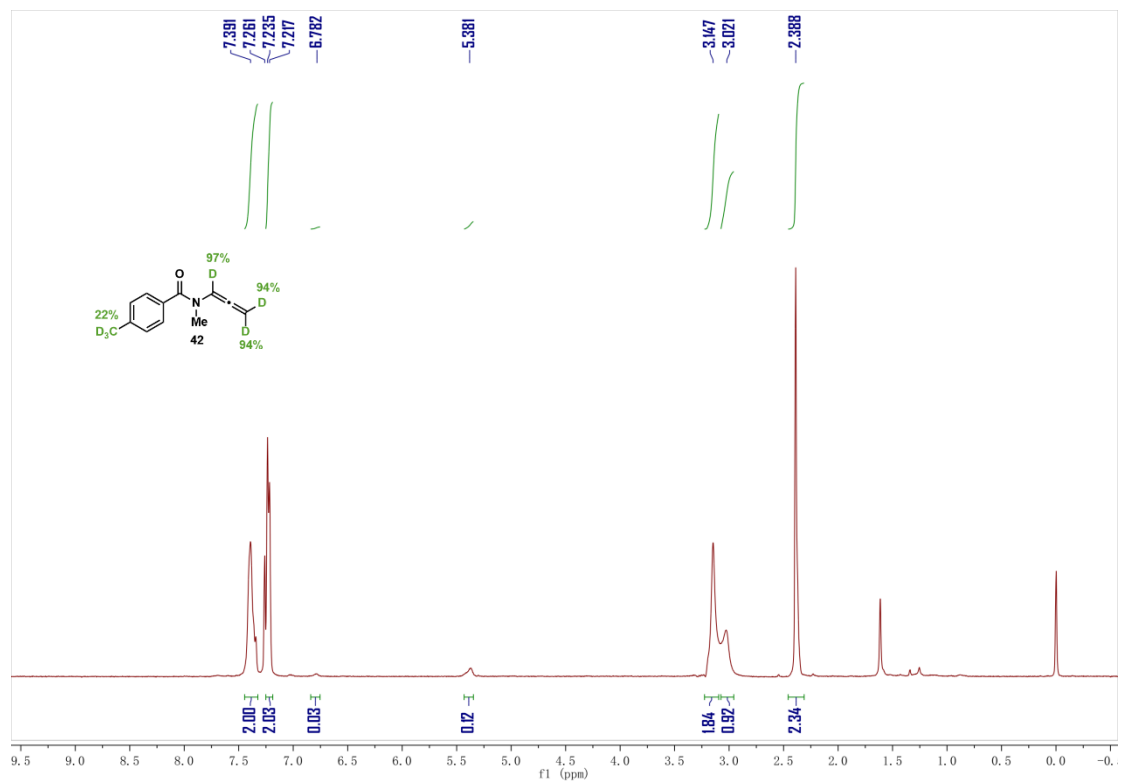
^1H NMR (400 MHz, CDCl_3):



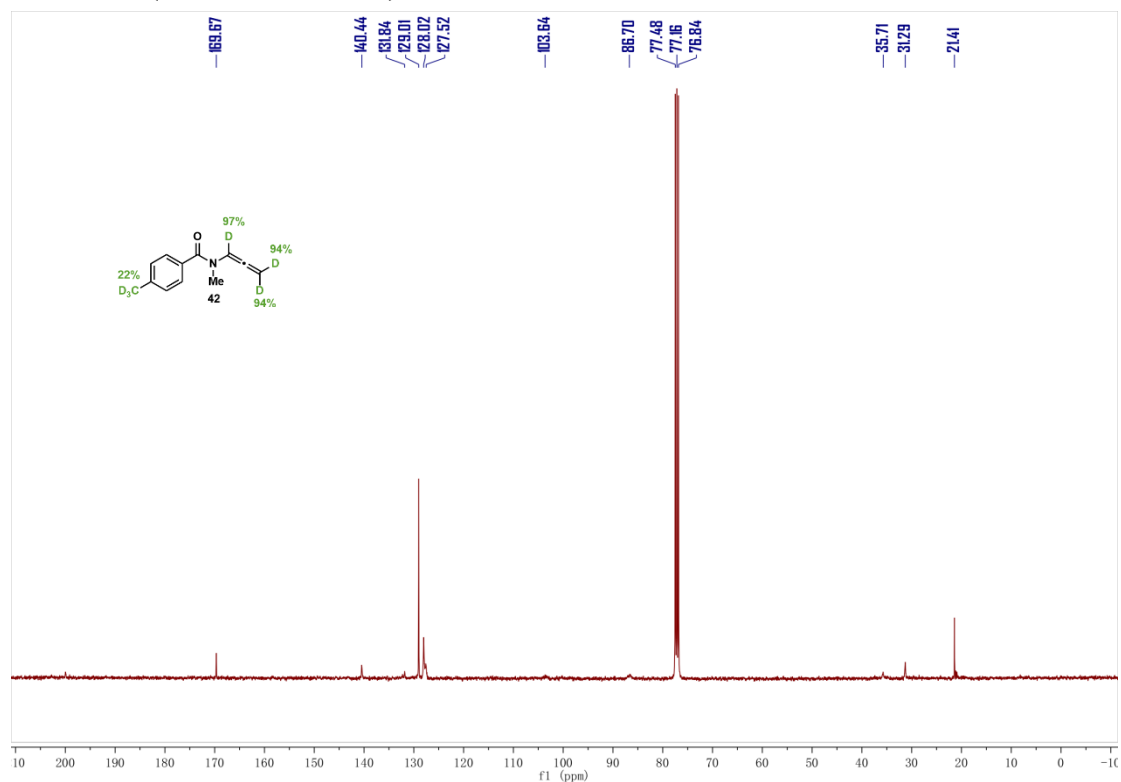
¹³C NMR (101 MHz, CDCl₃):



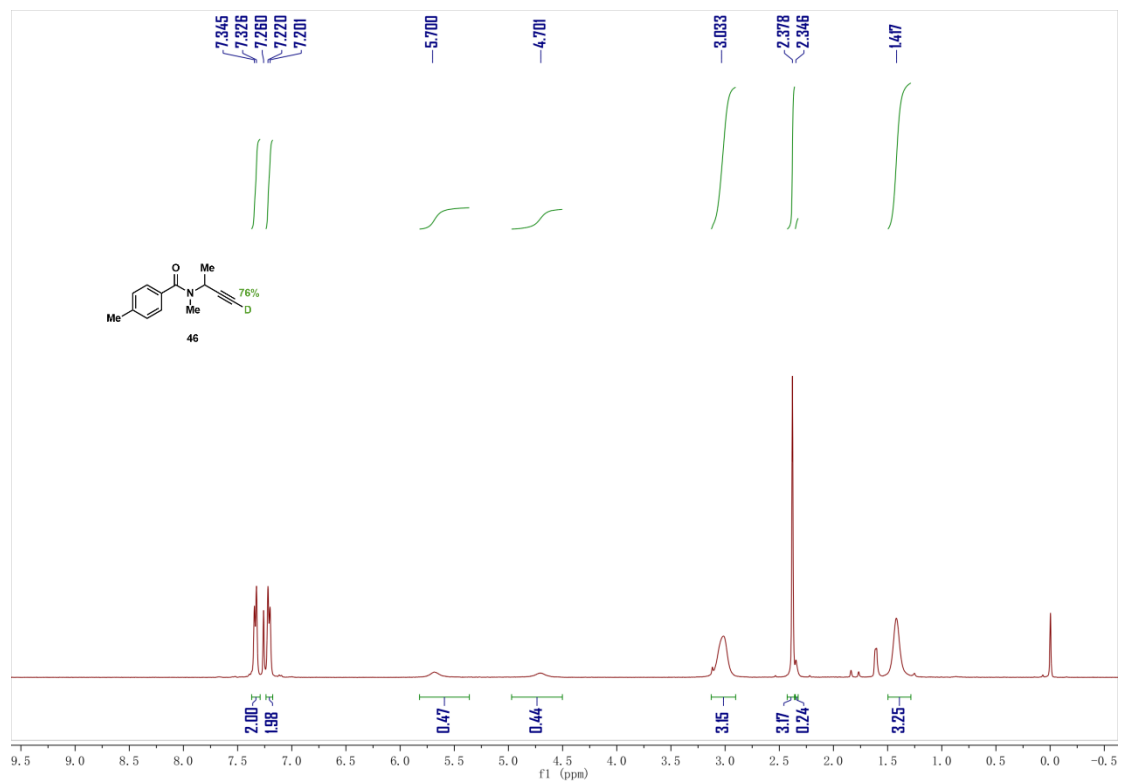
¹H NMR (400 MHz, CDCl₃):



¹³C NMR (101 MHz, CDCl₃):



¹H NMR (400 MHz, CDCl₃):



¹³C NMR (101 MHz, CDCl₃):

