

## Supporting Information

### Photo-induced dehalogenative deuteration and elimination of alkyl halides enabled by phosphine-mediated halogen-atom transfer

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#### Supplemental Experimental Procedures

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## 1. General Consideration

All reactions were carried out with magnetic stirring under a N<sub>2</sub> atmosphere. <sup>1</sup>H NMR (400 MHz), <sup>13</sup>C NMR (100 MHz) and <sup>19</sup>F NMR (376 MHz) spectra were recorded on a Quantum-I Plus 400 NMR spectrometer with CDCl<sub>3</sub> as solvent and tetramethylsilane (TMS) as the internal standard. Chemical shifts were reported in parts per million (ppm, δ scale) downfield from TMS at 0.00 ppm and referenced to CDCl<sub>3</sub> at 7.26 ppm (for <sup>1</sup>H NMR) and 77.16 ppm (for <sup>13</sup>C NMR). The <sup>1</sup>H NMR spectra are reported as follows: δ, chemical shift; coupling constants (*J* are given in hertz, Hz); integration. Coupling constants are reported as follows: s = singlet, br. s = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, etc. High-resolution mass spectroscopy (HRMS) data of the products were collected on a Waters Xevo G2QTOF/UPLC mass spectrometer using electrospray ionization.

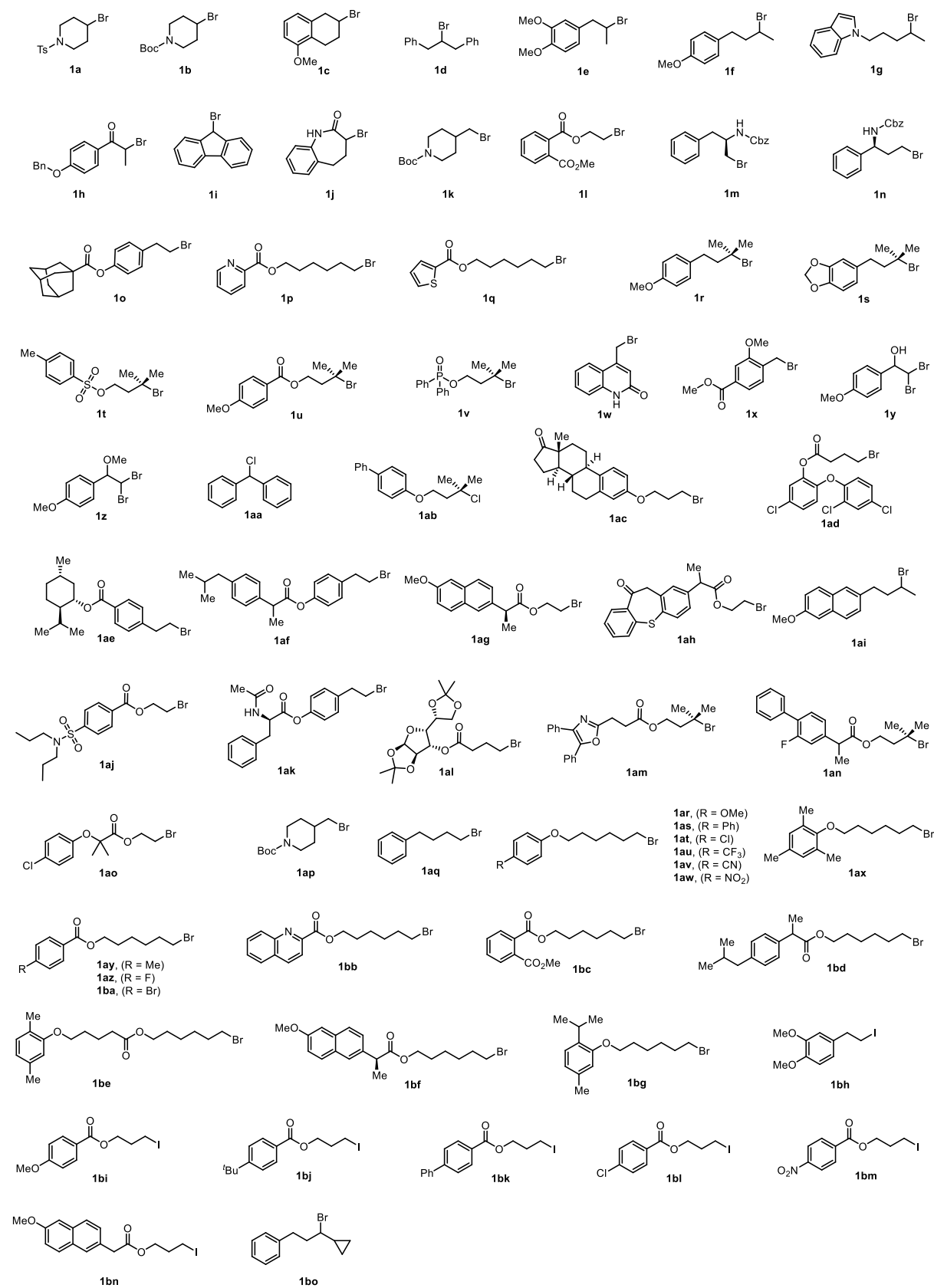
The chemicals and solvents were purchased from commercial suppliers without further purification unless otherwise specified. Analytical thin-layer chromatography (TLC) was performed on silicycle 250 mm silica gel F-254 plates. Products were purified by flash chromatography on 200-300 mesh silica gels, SiO<sub>2</sub>. All manipulations that require heating for starting materials were conducted with an oil bath. The photoreaction instrument (WPP-TEC-1020SL) was purchased from WATTCAS, China.

## 2. Photochemical Reaction Setup



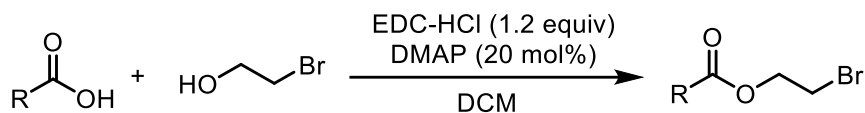
Figure S1.

### 3. Starting Materials

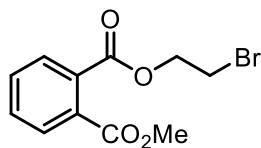


Compounds **1b**, **1h-1k**, **1w**, **1x**, **1aa**, **1ap**, **1aq** are commercially available, and used as received. Other alkyl halides were synthesized according to literature methods [1-12]. For the characterization of the new substrates, see the following:

#### For Synthesis of the Alkyl Bromides-GP1



To the mixture of acids (5.0 mmol, 1 equiv), DMAP (122.2 mg, 1.0 mmol, 0.2 equiv) and 2-bromoethanol (0.93 g, 7.5 mmol, 1.5 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was added 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC-HCl) (1.15 g, 6.0 mmol, 1.2 equiv). The resulting mixture was stirred at room temperature for 12 hours. After completion, the reaction mixture was quenched by water, the aqueous phase was then extracted with CH<sub>2</sub>Cl<sub>2</sub> three times. The combined organic phases were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, then the solvent was removed under vacuo. The residue was purified by flash column chromatography to yield the alkyl bromides **1l** and **1ah**.

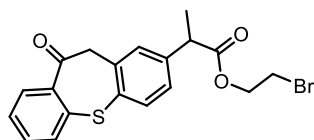


**2-bromoethyl methyl phthalate (1l)**: colorless oil, purified using flash chromatography (petroleum ether/EtOAc = 9:1).

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.76 – 7.74 (m, 2H), 7.57 – 7.55 (m, 2H), 4.62 (t, *J* = 6.2 Hz, 2H), 3.92 (s, 3H), 3.62 (t, *J* = 6.1 Hz, 2H).

<sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 167.7, 167.2, 131.7, 131.7, 131.3, 129.0, 128.9, 64.8, 52.7, 28.3.

HRMS (ESI) calcd C<sub>11</sub>H<sub>12</sub>BrO<sub>4</sub> [M + H]<sup>+</sup>: 286.9913, found: 286.9918.



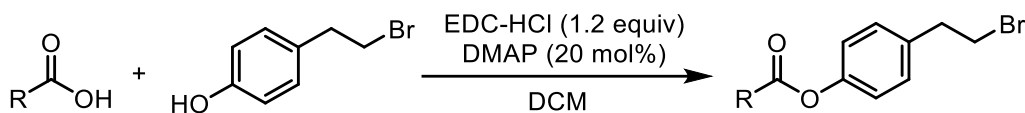
**2-bromoethyl 2-(10-oxo-10,11-dihydrodibenzo[b,f]thiepin-2-yl)propanoate (1ah)**: colorless oil, purified using flash chromatography (petroleum ether/EtOAc = 9:1).

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.20 (d, *J* = 7.9 Hz, 1H), 7.60 (d, *J* = 8.1 Hz, 2H), 7.44 – 7.40 (m, 2H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 7.9 Hz, 1H), 4.42 – 4.31 (m, *J* = 10.0 Hz, 4H), 3.76 (q, *J* = 7.2 Hz,

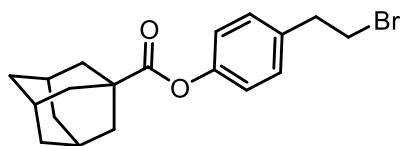
1H), 3.45 (t,  $J = 6.1$  Hz, 2H), 1.51 (d,  $J = 7.2$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  191.3, 173.4, 142.2, 140.1, 137.9, 136.1, 133.4, 132.5, 131.5, 130.8, 128.7, 126.8, 126.4, 64.1, 51.0, 45.0, 28.4, 18.3.

HRMS (ESI) calcd  $\text{C}_{19}\text{H}_{18}\text{BrO}_3\text{S}$   $[\text{M} + \text{H}]^+$ : 405.0155, found: 405.0157.



To the mixture of alkyl carboxylic acids (5.0 mmol, 1 equiv), DMAP (122.2 mg, 1.0 mmol, 0.2 equiv) and 4-(2-bromoethyl)phenol (1.21 g, 6.0 mmol, 1.2 equiv) in  $\text{CH}_2\text{Cl}_2$  (20 mL) was adding 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC-HCl) (1.15 g, 6.0 mmol, 1.2 equiv), and was allowed to stir at room temperature for 12 hours. After completion, the reaction mixture was quenched by water, the aqueous phase was then extracted with  $\text{CH}_2\text{Cl}_2$  three times. The combined organic phases were washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , then the solvent was removed under vacuo. The residue was purified by flash column chromatography to yield the alkyl bromides **1o**, **1af** and **1ak**.

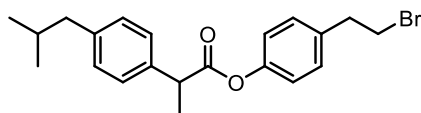


**4-(2-bromoethyl)phenyl (3r,5r,7r)-adamantane-1-carboxylate (1o)**: white solid, purified using flash chromatography (petroleum ether/EtOAc = 80:1).

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.20 (d,  $J = 8.4$  Hz, 2H), 6.99 (d,  $J = 8.4$  Hz, 2H), 3.54 (t,  $J = 7.6$  Hz, 2H), 3.15 (t,  $J = 7.6$  Hz, 2H), 2.08 – 2.05 (m, 9H), 1.80 – 1.73 (m, 6H).

$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  176.2, 150.0, 136.1, 129.5, 121.7, 41.0, 38.8, 38.7, 36.4, 32.8, 27.9.

HRMS (ESI) calcd  $\text{C}_{19}\text{H}_{24}\text{BrO}_2$   $[\text{M} + \text{H}]^+$ : 363.0954, found: 363.0958.



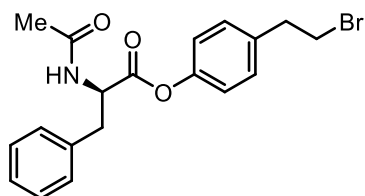
**4-(2-bromoethyl)phenyl 2-(4-isobutylphenyl)propanoate (1af)**: colorless oil, purified using flash chromatography (petroleum ether/EtOAc = 50:1).

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.29 (d,  $J = 8.0$  Hz, 2H), 7.17 – 7.12 (m, 4H), 6.94 (d,  $J = 8.4$  Hz, 2H), 3.92 (q,  $J = 7.1$  Hz, 1H), 3.52 (t,  $J = 7.6$  Hz, 2H), 3.12 (t,  $J = 7.6$  Hz, 2H), 2.47 (d,  $J = 7.2$  Hz, 2H),

1.91 – 1.81 (m, 1H), 1.59 (d,  $J = 7.1$  Hz, 3H), 0.91 (d,  $J = 6.6$  Hz, 6H).

$^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  173.2, 149.8, 140.80, 137.2, 136.3, 129.5, 127.2, 121.5, 45.2, 45.0, 38.7, 32.7, 22.4, 18.5.

HRMS (ESI) calcd  $\text{C}_{21}\text{H}_{26}\text{BrO}_2$   $[\text{M} + \text{H}]^+$ : 389.1111, found: 389.1115.

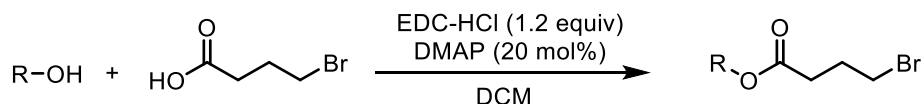


**4-(2-bromoethyl)phenyl acetyl-D-phenylalaninate (1ak):** white solid, purified using flash chromatography (petroleum ether/EtOAc = 2:1).

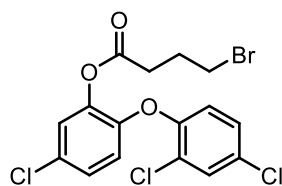
$^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.36 – 7.29 (m, 3H), 7.23 – 7.22 (m, 4H), 6.95 (d,  $J = 8.5$  Hz, 2H), 5.98 (s, 1H), 5.11 (q,  $J = 6.0$  Hz, 1H), 3.55 (t,  $J = 7.5$  Hz, 2H), 3.32 – 3.22 (m, 2H), 3.15 (t,  $J = 7.5$  Hz, 2H), 2.03 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  170.4, 169.7, 149.1, 136.9, 135.5, 129.7, 129.4, 128.7, 127.4, 121.4, 53.3, 38.7, 37.9, 32.6, 23.2.

HRMS (ESI) calcd  $\text{C}_{19}\text{H}_{21}\text{BrNO}_3$   $[\text{M} + \text{H}]^+$ : 390.0699, found: 390.0693.



To the mixture of 4-bromobutanoic acid (0.84 g, 5.0 mmol, 1 equiv), DMAP (122.2 mg, 1.0 mmol, 0.2 equiv) and phenols or alcohols (6.0 mmol, 1.2 equiv) in  $\text{CH}_2\text{Cl}_2$  (20 mL) was added 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC-HCl) (1.15 g, 6.0 mmol, 1.2 equiv). The resulting mixture was stirred at room temperature for 12 hours. After completion, the reaction mixture was quenched by water, the aqueous phase was then extracted with  $\text{CH}_2\text{Cl}_2$  three times. The combined organic phases were washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , then the solvent was removed under vacuo. The residue was purified by flash column chromatography to yield the alkyl bromides **1ad** and **1al**.

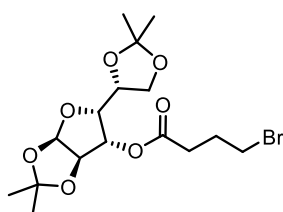


**5-chloro-2-(2,4-dichlorophenoxy)phenyl 4-bromobutanoate (1ad):** colorless oil, purified using flash chromatography (petroleum ether/EtOAc = 30:1).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.46 (d, *J* = 2.5 Hz, 1H), 7.20 (d, *J* = 2.4 Hz, 1H), 7.19 (d, *J* = 2.6 Hz, 1H), 7.17 (d, *J* = 2.5 Hz, 1H), 6.85 (t, *J* = 8.4 Hz, 2H), 3.46 (t, *J* = 6.4 Hz, 2H), 2.70 (t, *J* = 7.1 Hz, 2H), 2.24 – 2.17 (m, 2H).

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)**  $\delta$  170.0, 150.8, 146.5, 141.6, 130.5, 129.6, 129.3, 128.2, 127.1, 125.8, 124.3, 120.2, 120.1, 32.1, 32.0, 27.5.

**HRMS (ESI)** calcd C<sub>16</sub>H<sub>13</sub>BrCl<sub>3</sub>O<sub>3</sub> [M + H]<sup>+</sup>: 436.9108, found: 436.9105.

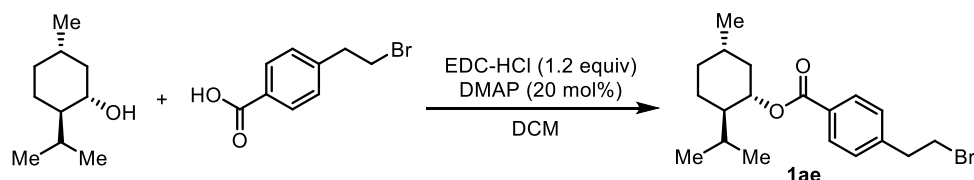


**(3aR,5R,6S,6aR)-5-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl 4-bromobutanoate (1al):** colorless oil, purified using flash chromatography (petroleum ether/EtOAc = 5:1).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**  $\delta$  5.88 (d, *J* = 3.4 Hz, 1H), 5.30 (s, 1H), 4.49 (d, *J* = 3.5 Hz, 1H), 4.21 – 4.18 (m, 2H), 4.13 – 4.08 (m, 1H), 4.03 – 3.99 (m, 2H), 3.47 (t, *J* = 5.9 Hz, 2H), 2.60 – 2.54 (m, 2H), 2.23 – 2.16 (m, 2H), 1.52 (s, 3H), 1.41 (s, 3H), 1.32 (s, 3H), 1.31 (s, 3H).

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)**  $\delta$  171.1, 112.3, 109.4, 105.1, 83.4, 79.9, 76.2, 72.4, 67.4, 32.4, 32.3, 27.6, 26.8, 26.1, 26.2, 25.2.

**HRMS (ESI)** calcd C<sub>16</sub>H<sub>26</sub>BrO<sub>7</sub> [M + H]<sup>+</sup>: 409.0856, found: 409.0852.



To the mixture of 4-(2-bromoethyl)benzoic acid (0.69 g, 3.0 mmol, 1 equiv), DMAP (73.3 mg, 0.6 mmol, 0.2 equiv) and (1S,2R,5S)-2-isopropyl-5-methylcyclohexan-1-ol (0.70 g, 4.5 mmol, 1.5 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was adding 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC-HCl) (0.69 g, 3.6 mmol, 1.2 equiv), and was allowed to stir at room temperature for 12 hours. After completion, the



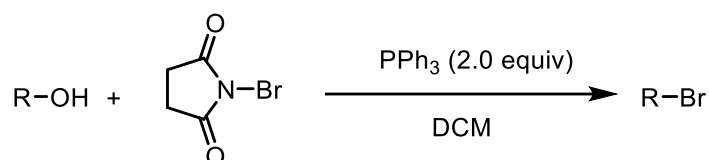
reaction mixture was quenched by water, the aqueous phase was then extracted with CH<sub>2</sub>Cl<sub>2</sub> three times. The combined organic phases were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, then the solvent was removed under vacuo. The residue was purified by flash column chromatography to afford **1ae** as a colorless oil.

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 8.00 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 4.92 (td, *J* = 10.8, 4.3 Hz, 1H), 3.58 (t, *J* = 7.4 Hz, 2H), 3.22 (t, *J* = 7.4 Hz, 2H), 2.12 (d, *J* = 11.9 Hz, 1H), 1.99 – 1.90 (m, 1H), 1.73 (d, *J* = 11.4 Hz, 2H), 1.57 – 1.52 (m, 2H), 1.18 – 1.05 (m, 2H), 0.97 – 0.88 (m, 7H), 0.79 (d, *J* = 6.9 Hz, 3H).

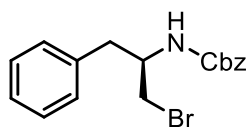
**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)** δ 165.9, 143.8, 129.9, 129.6, 128.6, 74.8, 47.3, 41.0, 39.1, 34.3, 32.2, 31.4, 26.5, 23.6, 22.0, 20.8, 16.5.

**HRMS (ESI)** calcd C<sub>19</sub>H<sub>28</sub>BrO<sub>2</sub> [M + H]<sup>+</sup>: 367.1267, found: 367.1269.

#### For Synthesis of the Alkyl Bromides **1m** and **1n-GP2**



To a solution of PPh<sub>3</sub> (2.62 g, 10.0 mmol, 2.0 equiv) in dry DCM (20 mL) was added N-bromosuccinimide (NBS) (1.78 g, 10.0 mmol, 2.0 equiv) in small portions under an ice-water bath. And the mixture was stirred for 30 min. Then amino alcohols (5.0 mmol, 1 equiv) was added. The reaction mixture was stirred overnight at room temperature. After completion, the reaction mixture was quenched by water, the aqueous phase was then extracted with CH<sub>2</sub>Cl<sub>2</sub> three times. The combined organic phases were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, then the solvent was removed under vacuo. The residue was purified by flash column chromatography to yield the alkyl bromides **1m** and **1n**.

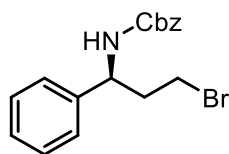


**benzyl (R)-(1-bromo-3-phenylpropan-2-yl)carbamate (1m)**: white solid, purified using flash chromatography (petroleum ether/EtOAc = 20:1).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 7.39 – 7.29 (m, 7H), 7.26 – 7.24 (m, 3H), 5.10 (s, 2H), 5.04 (d, *J* = 8.2 Hz, 1H), 4.18 – 4.09 (m, 1H), 3.56 (dd, *J* = 10.4, 4.0 Hz, 1H), 3.38 (dd, *J* = 10.4, 3.1 Hz, 1H), 2.99 – 2.86 (m, 2H).

<sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 155.4, 136.7, 136.2, 129.2, 128.7, 128.6, 128.2, 128.1, 126.9, 66.9, 52.0, 38.7, 37.0.

HRMS (ESI) calcd C<sub>17</sub>H<sub>19</sub>BrNO<sub>2</sub> [M + H]<sup>+</sup>: 348.0594, found: 348.0598.



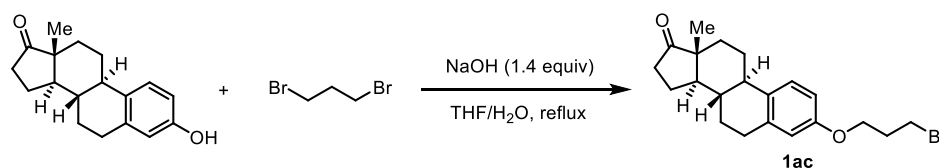
**benzyl (S)-(3-bromo-1-phenylpropyl)carbamate (1n)**: white solid, purified using flash chromatography (petroleum ether/EtOAc = 20:1).

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.27 (m, 10H), 5.13 – 5.04 (m, 3H), 4.90 (q, *J* = 7.3 Hz, 1H), 3.39 – 3.33 (m, 1H), 3.29 – 3.23 (m, 1H), 2.42 – 2.24 (m, 2H).

<sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 155.6, 136.2, 128.9, 128.5, 128.2, 127.9, 126.4, 67.0, 54.3, 39.5, 29.2.

HRMS (ESI) calcd C<sub>17</sub>H<sub>19</sub>BrNO<sub>2</sub> [M + H]<sup>+</sup>: 348.0594, found: 348.0599.

#### For Synthesis of the Alkyl Bromides 1ak-GP3



To the mixture of Estrone (1.35 g, 5.0 mmol, 1 equiv) and NaOH (240 mg, 6.0 mmol, 1.4 equiv) in THF (20 mL) and H<sub>2</sub>O (5 mL) was adding 1,3-dibromopropane (1.21 g, 6.0 mmol, 1.4 equiv). And heat the reaction mixture under reflux for 8 h. After completion, the reaction mixture was quenched by water, the aqueous phase was then extracted with EtOAc three times. The combined organic phases were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, then the solvent was removed under vacuo. The residue was purified by flash column chromatography to afford **1ac** as a white solid.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.20 (d, *J* = 8.6 Hz, 1H), 6.72 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.66 (s, 1H), 4.08 (t, *J* = 5.8 Hz, 2H), 3.60 (t, *J* = 6.4 Hz, 2H), 2.92 – 2.88 (m, 2H), 2.50 (dd, *J* = 18.7, 8.6 Hz, 1H), 2.42 – 2.38 (m, 1H), 2.33 – 2.23 (m, 3H), 2.19 – 1.94 (m, 4H), 1.60 – 1.41 (m, 6H), 0.91 (s, 3H).

<sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 220.9, 156.7, 137.8, 132.3, 126.4, 114.6, 112.2, 65.2, 50.4, 48.0, 44.0, 38.4, 35.9, 32.4, 31.6, 30.1, 29.6, 26.5, 25.9, 21.6, 13.9.

HRMS (ESI) calcd C<sub>21</sub>H<sub>28</sub>BrO<sub>2</sub> [M + H]<sup>+</sup>: 391.1267, found: 391.1262.

## 4. Dehalogenation Reactions

### 4.1 Dehalogenation of 1a

The dehalogenation of **1a** via XAT with **PCy<sub>3</sub>-OH** radical intermediate was attempted using three different protocols.

- 1) Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub>/visible-light
- 2) benzophenone/UV-light
- 3) persulfate/thermal

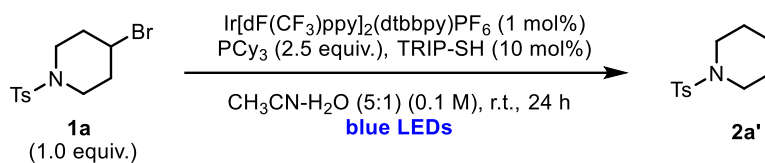
**Table S1.**

Entry	Reaction Conditions	Yield (%)
1	Ir[dF(CF <sub>3</sub> )ppy] <sub>2</sub> (dtbbpy)PF <sub>6</sub> (1 mol%), r.t., 24 h, blue LEDs	94
2*	Ir[dF(CF <sub>3</sub> )ppy] <sub>2</sub> (dtbbpy)PF <sub>6</sub> (1 mol%), r.t., 24 h, blue LEDs	-
3	benzophenone (1.0 equiv.), r.t., 20 h, UV-A LEDs	21
4*	benzophenone (1.0 equiv.), r.t., 20 h, UV-A LEDs	-
5	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (2.0 equiv.), 80 °C, 18 h	10
6*	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (2.0 equiv.), 80 °C, 18 h	-

\*The reaction was run without PCy<sub>3</sub>

All reactions have also been tested in the absence of PCy<sub>3</sub> and no product formation was observed.

### Dehalogenation of **1a** Under Photoredox Conditions



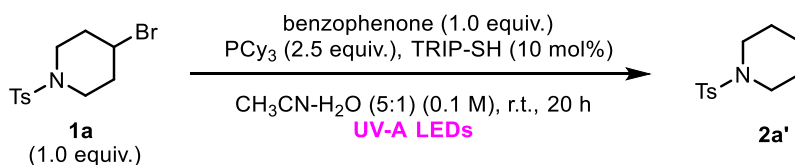
To a 10 mL quartz tube equipped with a magnetic stir bar was added **1a** (63.6 mg, 0.2 mmol), photocatalyst Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> (2.3 mg, 0.002 mmol, 1 mol%), PCy<sub>3</sub> (140.2 mg, 0.5 mmol, 2.5 equiv.), and the tube was evacuated and backfilled with Ar (three times). Thiol catalyst 2,4,6-triisopropylbenzenethiol (4.7 mg, 0.02 mmol, 10 mol%) in CH<sub>3</sub>CN/H<sub>2</sub>O (2.0 mL, 5:1 v/v) were added by syringe under Ar. The reaction mixture was stirred and irradiated using a 10 W blue LEDs lamp (WATTCAS: WP-TEC-1020SL) for 24 hours at room temperature. After completion, the mixture was quenched with water and extracted with EtOAc (3 x 10 mL). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, then the solvent was removed under vacuo. The residue was purified with chromatography column on silica gel (gradient eluent of petroleum ether/ ethyl acetate = 10:1) to give the corresponding product **2a'** (45.0 mg) in 94% yield.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 3.98 – 2.95 (m, 4H), 2.43 (s, 3H), 1.67 – 1.61 (m, 4H), 1.44 – 1.38 (m, 2H).

<sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 143.3, 133.2, 129.5, 127.7, 46.9, 25.1, 23.5, 21.5.

HRMS (ESI) calcd C<sub>21</sub>H<sub>28</sub>BrO<sub>2</sub> [M + H]<sup>+</sup>: 240.1053, found: 240.1051.

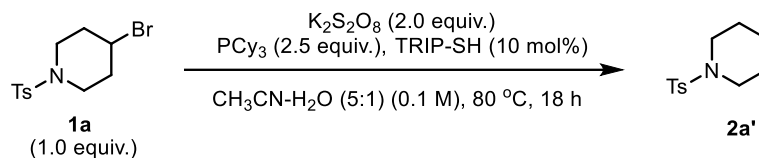
### Dehalogenation of **1a** Under Benzophenone/UV-light Conditions



To a 10 mL quartz tube equipped with a magnetic stir bar was added **1a** (63.6 mg, 0.2 mmol), benzophenone (36.4 mg, 0.2 mmol, 1.0 equiv.), PCy<sub>3</sub> (140.2 mg, 0.5 mmol, 2.5 equiv.), and the tube was evacuated and backfilled with Ar (three times). Thiol catalyst 2,4,6-triisopropylbenzenethiol (4.7 mg, 0.02 mmol, 10 mol%) in CH<sub>3</sub>CN/H<sub>2</sub>O (2.0 mL, 5:1 v/v) were added by syringe under Ar. The reaction mixture was stirred and irradiated using a 10 W blue LEDs lamp (WATTCAS: WP-TEC-1020SL) for 20 hours at room temperature. After completion, the mixture was quenched with water and extracted with EtOAc (3 x 10 mL). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, then the solvent was removed

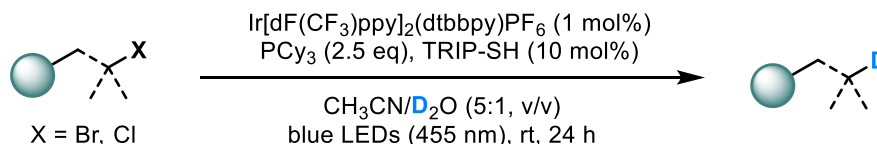
under vacuo. The residue was purified with chromatography column on silica gel (gradient eluent of petroleum ether/ ethyl acetate = 10:1) to give the corresponding product **2a'** (10.1 mg) in 21% yield.

#### Dehalogenation of **1a** Under Persulfate/Thermal Conditions



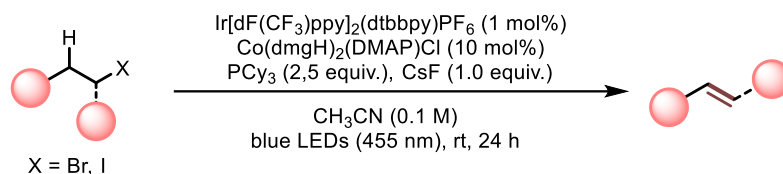
To a 10 mL quartz tube equipped with a magnetic stir bar was added **1a** (63.6 mg, 0.2 mmol),  $\text{K}_2\text{S}_2\text{O}_8$  (108.1 mg, 0.4 mmol, 2.0 equiv.),  $\text{PCy}_3$  (140.2 mg, 0.5 mmol, 2.5 equiv.), and the tube was evacuated and backfilled with Ar (three times). Thiol catalyst 2,4,6-triisopropylbenzenethiol (4.7 mg, 0.02 mmol, 10 mol%) in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (2.0 mL, 5:1 v/v) were added by syringe under Ar. The reaction mixture was stirred and irradiated using a 10 W blue LEDs lamp (WATTCAS: WP-TEC-1020SL) for 18 hours at room temperature. After completion, the mixture was quenched with water and extracted with EtOAc (3 x 10 mL). The combined organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$ , then the solvent was removed under vacuo. The residue was purified with chromatography column on silica gel (gradient eluent of petroleum ether/ ethyl acetate = 10:1) to give the corresponding product **2a'** (4.8 mg) in 10% yield.

#### General Procedure for the dehalogenative deuteration of alkyl halides -GP4



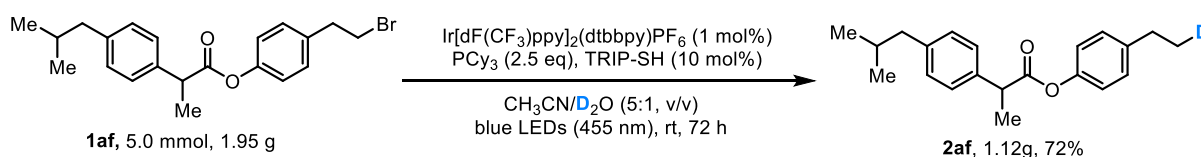
To a 20 mL quartz tube equipped with a magnetic stir bar was added alkyl halides (0.2 mmol, 1.0 equiv.), photocatalyst  $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$  (2.3 mg, 0.002 mmol, 1 mol%),  $\text{PCy}_3$  (140.2 mg, 0.5 mmol, 2.5 equiv.), and the tube was evacuated and backfilled with Ar (three times). Thiol catalyst 2,4,6-triisopropylbenzenethiol (4.7 mg, 0.02 mmol, 10 mol%) in dry and degassed  $\text{CH}_3\text{CN}/\text{D}_2\text{O}$  (2.0 mL, v/v = 5:1, 0.1 M) were added by syringe under Ar. The reaction mixture was stirred and irradiated using a 10 W blue LEDs lamp (WATTCAS: WP-TEC-1020SL) for 24 hours at room temperature. Brine (10 mL) and EtOAc (10 mL) were added and the mixture was shaken. Then, the aqueous layer was extracted with EtOAc (x 2), the combined organic layers were dried ( $\text{MgSO}_4$ ), filtered and evaporated. Purification by flash column chromatography on silica gel gave the products.

## General Procedure for the dehalogenative elimination of alkyl halides -GP5



To a 20 mL quartz tube equipped with a magnetic stir bar was added alkyl halides (0.2 mmol, 1.0 equiv.), photocatalyst Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> (2.3 mg, 0.002 mmol, 1 mol%), Co(dmgH)<sub>2</sub>(DMAP)Cl (8.9 mg, 0.02 mmol, 10 mol%), PCy<sub>3</sub> (140.2 mg, 0.5 mmol, 2.5 equiv.), CsF (30.4 mg, 0.2 mmol, 1.0 equiv.) and the tube was evacuated and backfilled with Ar (three times) in CH<sub>3</sub>CN (2.0 mL) were added by syringe under Ar. The reaction mixture was stirred and irradiated using a 10 W blue LEDs lamp (WATTCAS: WP-TEC-1020SL) for 24 hours at room temperature. Brine (10 mL) and EtOAc (10 mL) were added and the mixture was shaken. The aqueous layer was extracted with EtOAc (x 2), the combined organic layers were dried (MgSO<sub>4</sub>), filtered and evaporated. Purification by flash column chromatography on silica gel gave the products.

### Gram Scale Reaction

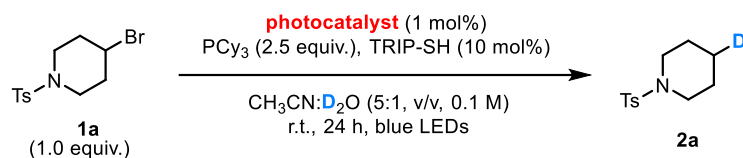


General procedure: To an oven-dried 250 mL flask equipped with a magnetic stir bar were sequentially added the corresponding **1af** (1.95 g, 5.0 mmol, 1.0 equiv.) Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> (57.5 mg, 0.05 mmol, 1 mol%), PCy<sub>3</sub> (2.1 g, 7.5 mmol, 2.5 equiv.), TRIP-SH (118.2 mg, 0.5 mmol, 10 mol%). The vial was degassed, backfilled with Argon three times and equipped with an Argon balloon, and then was added dry CH<sub>3</sub>CN (42 mL), D<sub>2</sub>O (8 mL). The flask was then put under the 50 W Blue light source and was irradiated and stirred for 72 h at around 32 °C. After the reaction was complete, Brine (50 mL) and EtOAc (50 mL) were added and the mixture was shaken. Then, the aqueous layer was extracted with EtOAc (x 2), the combined organic layers were dried (MgSO<sub>4</sub>), filtered and evaporated. Purification by flash column chromatography on silica gel to give the dehalogenative deuteration product **2af** in 1.12g, 72% yield.

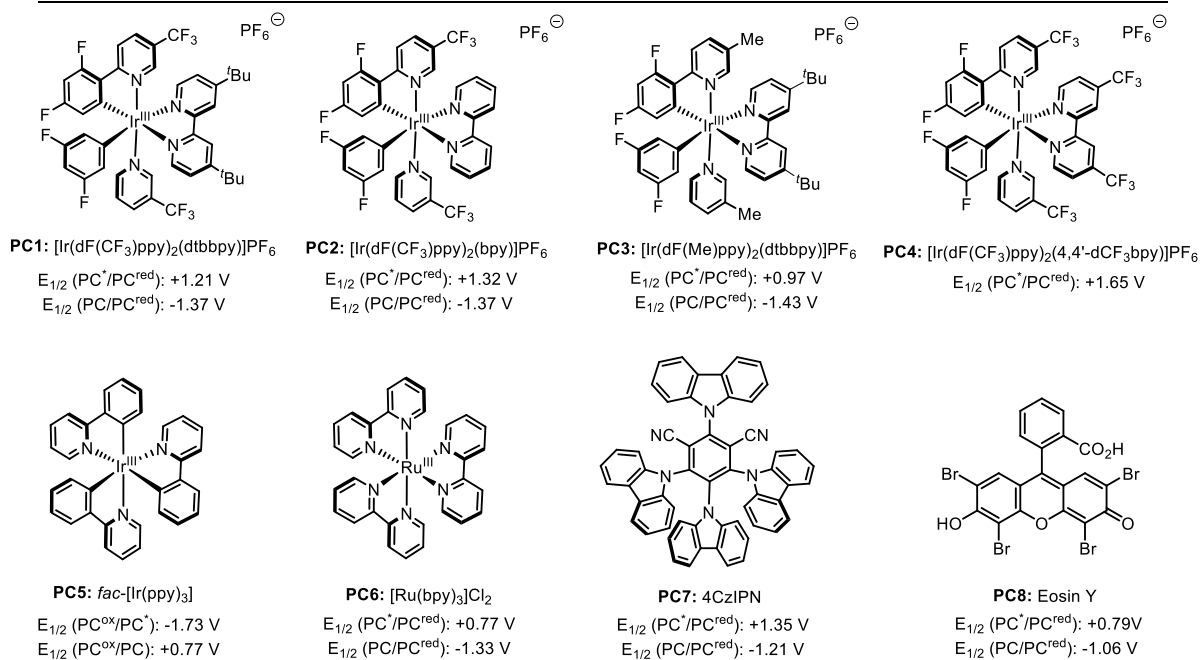
## 4.2 Reaction Condition Optimization

### Reaction condition optimization for dehalogenative deuteration

Table S2. Photocatalyst screening<sup>a</sup>

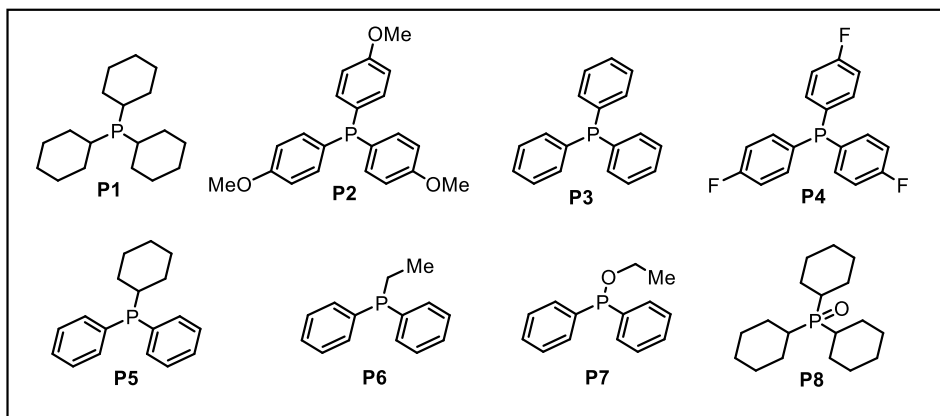


Entry	Photocatalyst	Redox potential (vs SCE)	Yield% <sup>b</sup>	D-inc. (%) <sup>c</sup>
1	PC1	Ir(II)/Ir(III)* = 1.21 V (ref. 13)	91	95
2	PC2	Ir(II)/Ir(III)* = 0.97 V (ref. 13)	79	93
3	PC3	Ir(II)/Ir(III)* = 0.97 V (ref. 14)	76	90
4	PC4	Ir(II)/Ir(III)* = 1.65 V (ref. 15)	12	--
5	PC5	Ir(II)/Ir(III)* = 0.31 V (ref. 13)	trace	--
6	PC6	Ru(II)/Ru(III)* = 0.77 V (ref. 16)	trace	--
7	PC7	1.35 V (ref. 13)	16	--
8	PC8	0.79 V (ref. 13)	trace	--



[a] Reaction conditions: **1a** (0.2 mmol, 1.0 equiv), photocatalyst (1 mol%), 2,4,6-triisopropylbenzenethiol (10 mol%), PCy<sub>3</sub> (2.5 equiv), CH<sub>3</sub>CN/D<sub>2</sub>O (5:1, v/v, 0.1M), 10 W blue LEDs, 24 h. [b] Isolated yield. [c] Deuterium incorporation was determined by <sup>1</sup>H NMR spectroscopy.

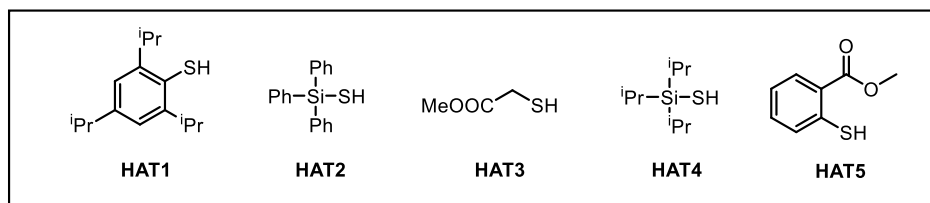
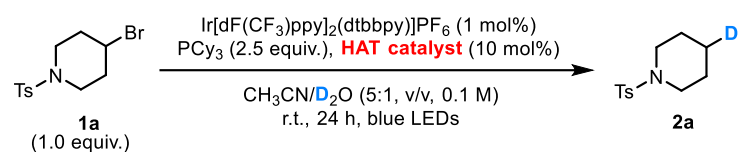
**Table S3. P reagent screening<sup>a</sup>**



entry	P reagent (2.5 equiv.)	yield (%) <sup>b</sup>	D-inc. (%) <sup>c</sup>
<b>1</b>	<b>P1</b>	<b>91</b>	<b>95</b>
2	P2	25	90
3	P3	trace	-
4	P4	trace	-
5	P5	trace	-
6	P6	trace	-
7	P7	n.d.	-
8	P8	n.d.	-
9 <sup>d</sup>	P1	trace	-
10 <sup>e</sup>	P1	89	95

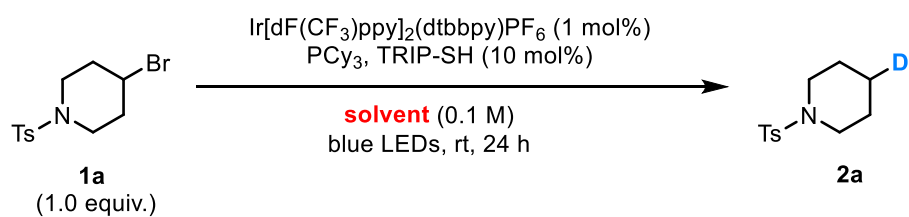
[a] Reaction conditions: **1a** (0.2 mmol, 1.0 equiv), Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)]PF<sub>6</sub> (1 mol%), 2,4,6-triisopropylbenzenethiol (10 mol%), P reagent (2.5 equiv), MeCN/D<sub>2</sub>O (5:1, v/v, 0.1 M), 10 W blue LEDs, 24 h. [b] Isolated yield. [c] Deuterium incorporation was determined by <sup>1</sup>H NMR spectroscopy. [d] P1 (20 mol%). [e] P2 (3.0 equiv.).



**Table S4. Thiol catalyst screening<sup>a</sup>**

entry	thiol catalyst (10 mol%)	yield (%) <sup>b</sup>	D-inc. (%) <sup>c</sup>
<b>1</b>	<b>HAT1</b>	<b>91</b>	<b>95</b>
2	HAT2	62	94
3	HAT3	71	91
4	HAT4	58	90
5	HAT5	83	87
6	/	35	95

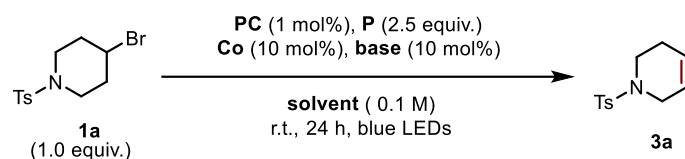
[a] Reaction conditions: **1a** (0.2 mmol, 1.0 equiv), Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)]PF<sub>6</sub> (1 mol%), HAT catalyst (10 mol%), PCy<sub>3</sub> (2.5 equiv), MeCN/D<sub>2</sub>O (5:1, v/v, 0.1M) (2.0 mL), 10 W blue LEDs, 24 h. [b] Isolated yield. [c] Deuterium incorporation was determined by <sup>1</sup>H NMR spectroscopy.

**Table S5. Solvent screening<sup>a</sup>**

entry	solvent	yield (%) <sup>b</sup>	D-inc. (%)
1	CH <sub>3</sub> CN/D <sub>2</sub> O (9:1)	90	86
2	PhCF <sub>3</sub> /D <sub>2</sub> O (9:1)	51	83
3	PhMe/D <sub>2</sub> O (9:1)	46	85
4	DCE/D <sub>2</sub> O (9:1)	42	88
5	DCM/D <sub>2</sub> O (9:1)	52	88
6	THF/D <sub>2</sub> O (9:1)	26	76
7	DMSO/D <sub>2</sub> O (9:1)	41	83
8	DMF/D <sub>2</sub> O (9:1)	38	85
9	CH <sub>3</sub> CN/D <sub>2</sub> O (5:1)	91	95
10	CH <sub>3</sub> CN/D <sub>2</sub> O (4:1)	85	95

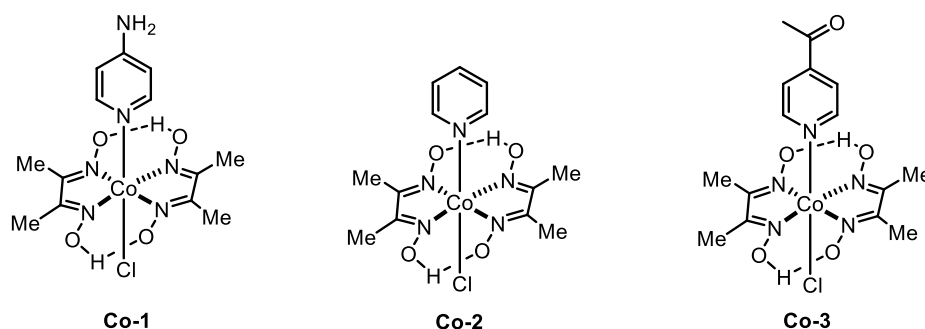
[a] Reaction conditions: **1a** (0.2 mmol, 1.0 equiv), Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)]PF<sub>6</sub> (1 mol%), HAT catalyst (10 mol%), PCy<sub>3</sub> (2.5 equiv) and solvent (0.1 M), 10 W blue LEDs, 24 h. [b] Isolated yield. [c] Deuterium incorporation was determined by <sup>1</sup>H NMR spectroscopy.

**Table S6. Reaction condition optimization for dehalogenative elimination<sup>a</sup>**



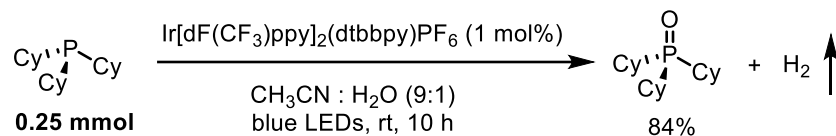
entry	PC	P reagent	Co	base	solvent	yield (%) <sup>b</sup>
<b>1</b>	<b>PC1</b>	<b>P1</b>	<b>Co-1</b>	<b>CsF</b>	<b>CH<sub>3</sub>CN</b>	<b>72</b>
2	PC5	P1	Co-1	CsF	CH <sub>3</sub> CN	trace
3	PC7	P1	Co-1	CsF	CH <sub>3</sub> CN	25
4	PC8	P1	Co-1	CsF	CH <sub>3</sub> CN	N.D.
5	PC1	P2	Co-1	CsF	CH <sub>3</sub> CN	44
6	PC1	P3	Co-1	CsF	CH <sub>3</sub> CN	trace
7	PC1	P1	Co-2	CsF	CH <sub>3</sub> CN	68
8	PC1	P1	Co-3	CsF	CH <sub>3</sub> CN	55
9	PC1	P1	Co-1	Na <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	40
10	PC1	P1	Co-1	KHCO <sub>3</sub>	CH <sub>3</sub> CN	34
11	PC1	P1	Co-1	K <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	35
12	PC1	P1	Co-1	Et <sub>3</sub> N	CH <sub>3</sub> CN	trace
13	PC1	P1	Co-1	DABCO	CH <sub>3</sub> CN	trace
14	PC1	P1	Co-1	CsF	DMF	55
15	PC1	P1	Co-1	CsF	DMSO	N.D.
16	PC1	P1	Co-1	CsF	toluene	N.D.
17	PC1	P1	Co-1	CsF	DCE	N.D.
18	PC1	P1	Co-1	CsF	THF	N.D.
19	PC1	P1	Co-1	CsF	dry CH <sub>3</sub> CN	31
20	PC1	P1	Co-1	--	CH <sub>3</sub> CN	51

Reaction conditions: **1a** (0.20 mmol, 1.0 equiv.), PC (0.002 mmol, 1 mol%), P reagent (0.50 mmol, 2.5 equiv.), Co catalyst (0.02 mmol, 10 mol%), base (1.0 equiv.) in CH<sub>3</sub>CN (0.1 M) at room temperature under Ar atmosphere, 455 nm LEDs (10 W), 24 h. Yields are of isolated products after chromatographic purification.



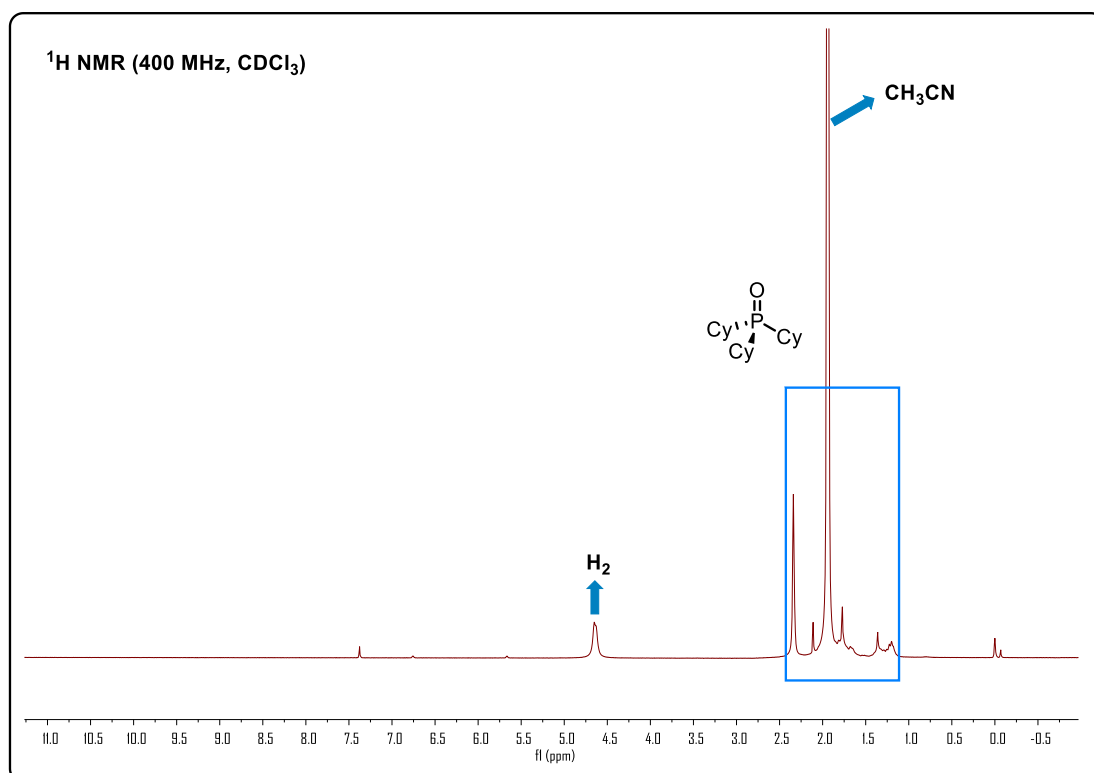
## 5. Mechanistic Study

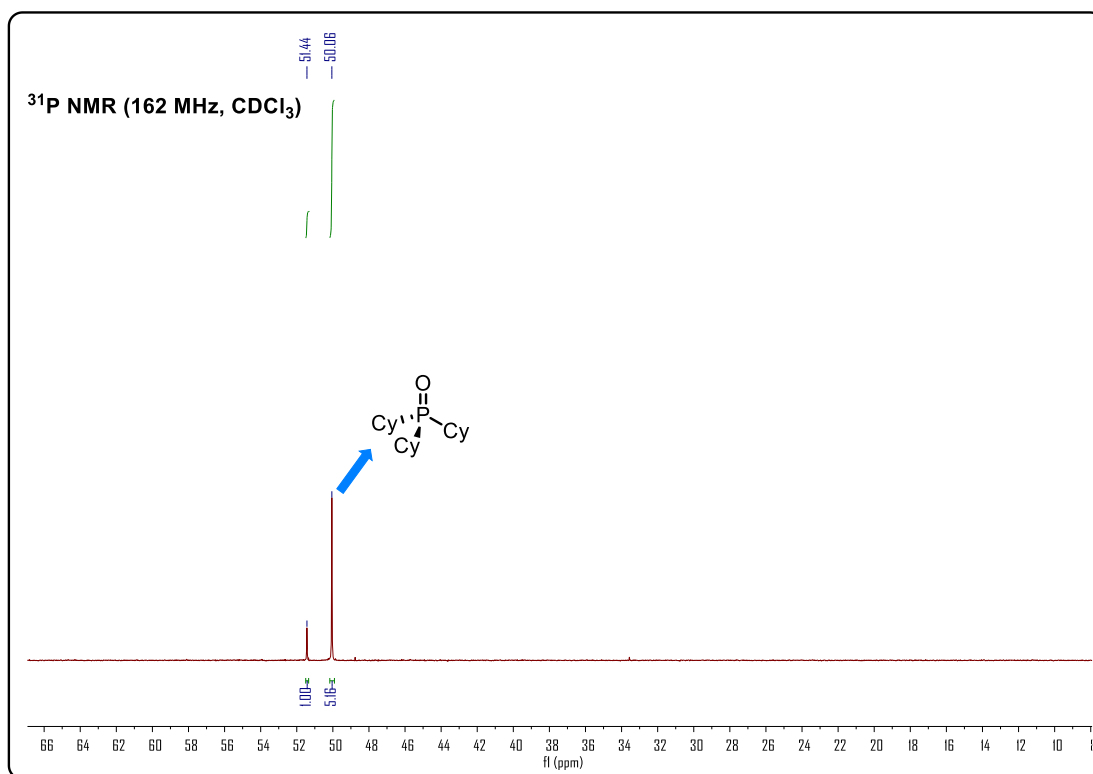
### 5.1 Detection of hydrogen gas H<sub>2</sub>



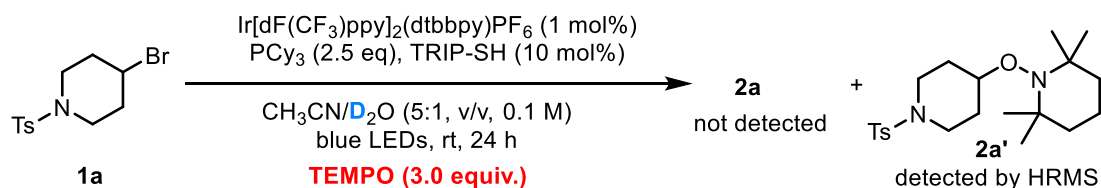
To an oven dried 20 mL quartz tube with a magnetic stirring bar, tricyclohexylphosphane (0.25 mmol), Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> (0.0025 mmol, 1 mol%), deionized water (0.2 mL) and acetonitrile (1.8 mL) were added under argon atmosphere at ambient temperature. The quartz tube was sealed and placed in the photoreactor, and then the reaction mixture was stirred and irradiated using a 10 W blue LEDs lamp for 10 h at room temperature. After the reaction, 5 mL of CDCl<sub>3</sub> was added and the mixture was analyzed by <sup>1</sup>H NMR and <sup>31</sup>P NMR.

**Detected by NMR:**

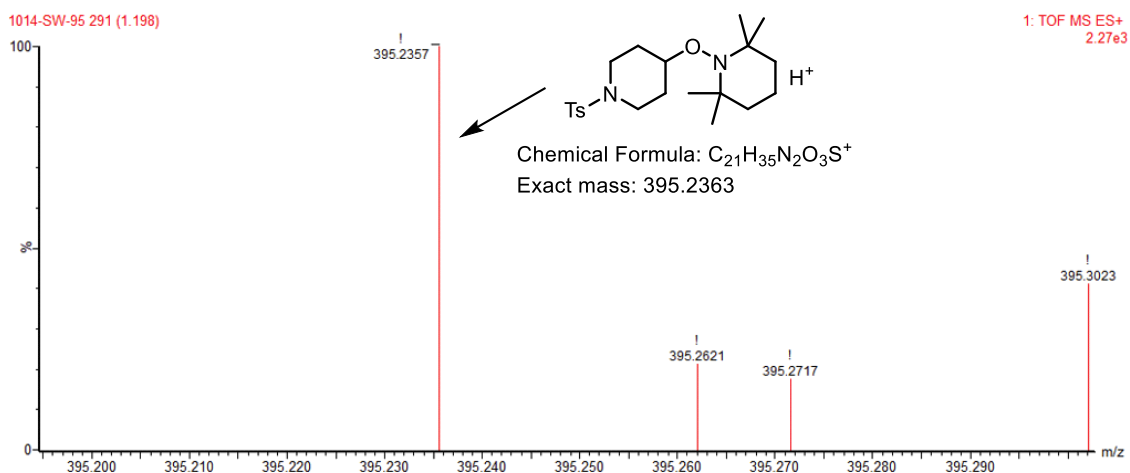




## 5.2 Control experiment

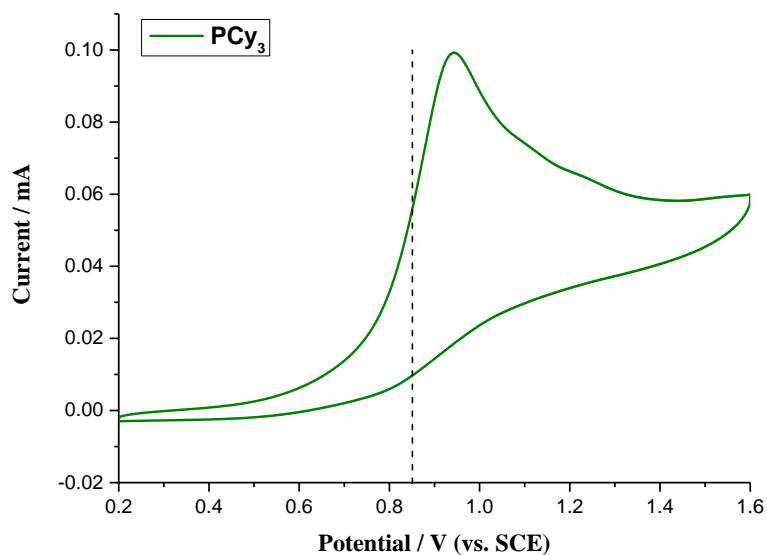


**Reaction procedure:** To a 20 mL quartz tube equipped with a magnetic stir bar was added 4-bromo-1-tosylpiperidine **1a** (63.6 mg, 0.2 mmol, 1.0 equiv.), photocatalyst Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> (2.3 mg, 0.002 mmol, 1 mol%), PCy<sub>3</sub> (140.2 mg, 0.5 mmol, 2.5 equiv.), 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO, 93.8 mg, 0.6 mmol, 3.0 equiv.), and the tube was evacuated and backfilled with Ar (three times). Thiol catalyst 2,4,6-triisopropylbenzenethiol (4.7 mg, 0.02 mmol, 10 mol%) in CH<sub>3</sub>CN/D<sub>2</sub>O (5:1, v/v 0.1 M) were added by syringe under Ar. The reaction mixture was stirred and irradiated using a 10 W blue LEDs lamp for 24 hours at room temperature. The trapping product **2a'** was detected by HRMS analysis.



### 5.3 The CV data of PCy<sub>3</sub>

The cyclic voltammogram was collected with a CHI 760E Potentiostat. Cyclic voltammetry (CV) experiments were conducted in a 30 mL three-necked cell set-up fitted with a glassy carbon working electrode, a saturated calomel electrode (SCE) reference electrode, and a platinum wire counter electrode. All measurements were carried out in anhydrous MeCN, using a scan rate of 200 mV/s.  $E_{1/2}$  was obtained using Origin.



**Figure S2.** Cyclic voltammogram of PCy<sub>3</sub>

Cyclic voltammogram of PCy<sub>3</sub> in 0.1 mol/L *n*-Bu<sub>4</sub>NPF<sub>6</sub> in MeCN. PCy<sub>3</sub> [ $E_{1/2}$  = + 0.86 V vs. SCE]. The photocatalyst Ir(dF(CF<sub>3</sub>)ppy)<sub>2</sub>(dtbbpy)]PF<sub>6</sub> [ $E_{1/2}^{\text{red}}$  (\*Ir<sup>III</sup>/Ir<sup>II</sup>) = + 1.21 V vs SCE] has higher oxidation potential to oxidize PCy<sub>3</sub>.

## 5.4 Stern–Volmer Luminescence Quenching Studies

The fluorescence quenching experiments were carried out in degassed  $\text{CH}_3\text{CN}$  at room temperature. An excitation wavelength of 380 nm was used for monitoring quenching of the iridium photocatalyst.

### 5.4.1 Quenching with $\text{PCy}_3$

**Emission quenching of  $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$  as a function of concentration of  $\text{PCy}_3$ .** A  $1.0 \times 10^{-3}$  M solution of  $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$  (11.2 mg, 0.01 mmol) in 10 mL anhydrous degassed MeCN were prepared in a nitrogen filled glovebox. And a  $2.0 \times 10^{-2}$  M solution of  $\text{PCy}_3$  (5.6 mg, 0.02 mmol) in 1.0 mL anhydrous degassed DCM were prepared in a nitrogen filled glovebox. To five sample vials were added 20  $\mu\text{L}$  of  $1.0 \times 10^{-3}$  M solution of Ir photocatalyst and 0  $\mu\text{L}$ , 10  $\mu\text{L}$ , 20  $\mu\text{L}$ , 30  $\mu\text{L}$ , 40  $\mu\text{L}$  of  $2.0 \times 10^{-2}$  M solution of  $\text{PCy}_3$ . Anhydrous degassed MeCN was then added to each sample vial to a quantity of 2.0 mL. These were then transferred to a 3.5 mL quartz cuvette (path length: 1 = 10 mm) sealed with Teflon caps under an atmosphere of nitrogen in the glove box. The emission quenching of  $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$  ( $1.0 \times 10^{-5}$  M) as a function of the concentration of  $\text{PCy}_3$  in MeCN is shown in Figure S3.

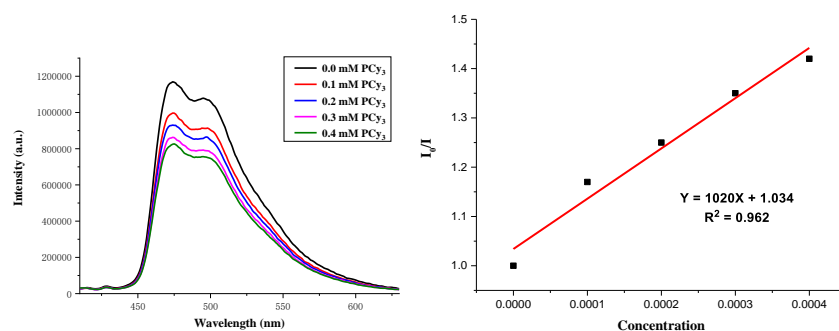


Figure S3. Characteristic plot of  $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$  emission quenching with  $\text{PCy}_3$

### 5.4.2 Quenching with alkyl bromide **1a**

The emission quenching of  $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$  ( $1.0 \times 10^{-5}$  M) as a function of the concentration of **1a** in MeCN is shown in Figure S4.

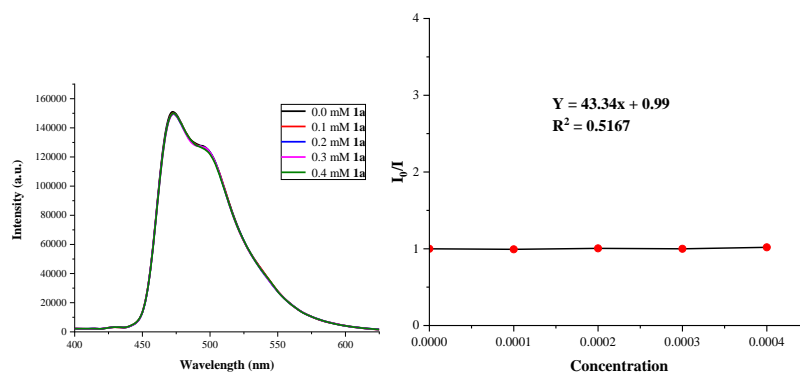
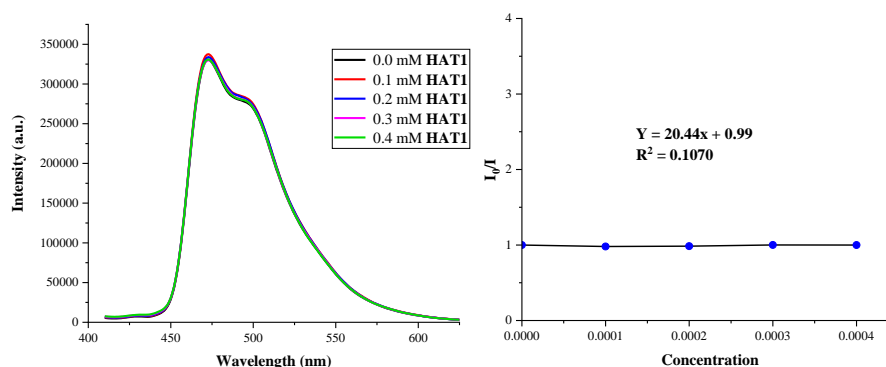


Figure S4. Characteristic plot of  $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$  emission quenching with **1a**

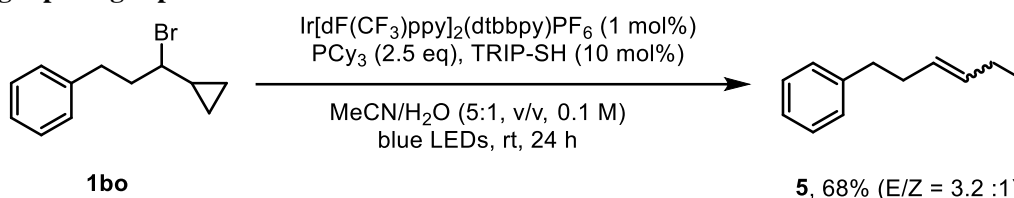
### 5.4.3 Quenching with HAT1

The emission quenching of  $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$  ( $1.0 \times 10^{-5}$  M) as a function of the concentration of **HAT1** in MeCN is shown in Figure S5.



**Figure S5. Characteristic plot of  $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$  emission quenching with HAT1**

### 5.5 Ring-Opening experiment



To a 20 mL quartz tube equipped with a magnetic stir bar was added (3-bromo-3-cyclopropylpropyl)benzene **1bo** (47.8 mg, 0.2 mmol, 1.0 equiv.), photocatalyst  $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$  (2.3 mg, 0.002 mmol, 1 mol%),  $\text{PCy}_3$  (140.2 mg, 0.5 mmol, 2.5 equiv.), and the tube was evacuated and backfilled with Ar (three times). Thiol catalyst 2,4,6-triisopropylbenzenethiol (4.7 mg, 0.02 mmol, 10 mol%) in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (5:1, v/v 0.1 M) were added by syringe under  $\text{N}_2$ . The reaction mixture was stirred and irradiated using a 10 W blue LEDs lamp for 24 hours at room temperature. Brine (10 mL) and EtOAc (10 mL) were added and the mixture was shaken. The aqueous layer was extracted with EtOAc (x 2), the combined organic layers were dried ( $\text{MgSO}_4$ ), filtered and evaporated. Purification by flash column chromatography on silica gel gave the products hex-3-en-1-ylbenzene **5** as colorless oil.

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.29 – 7.24 (m, 2H), 7.19 – 7.15 (m, 3H), 5.48 – 5.44 (m, 1.4H), 5.41 – 5.36 (m, 0.43H), 2.68 – 2.62 (m, 2H), 2.38 – 2.27 (m, 2H), 2.04 – 1.95 (m, 2H), 0.95 (t,  $J = 7.5$  Hz, 2.38H), 0.90 (t,  $J = 7.5$  Hz, 0.75H).

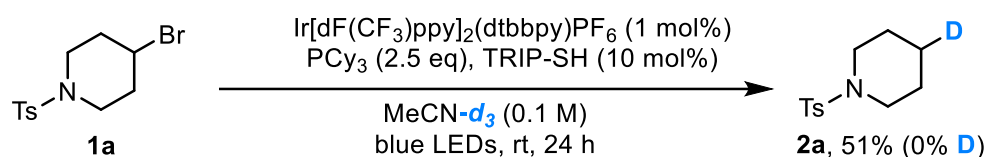
$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  142.2, 132.6, 132.3, 128.4, 128.3, 128.2, 128.0, 125.7, 125.7, 36.2, 36.0, 31.8, 29.1, 25.6, 23.2, 20.5, 14.2, 13.9.

HRMS (ESI) calcd  $\text{C}_{12}\text{H}_{17}$   $[\text{M} + \text{H}]^+$ : 161.1325, found: 161.1328.

### 5.6 Deuterium labeling experiment to rule out the deuterium atom from MeCN-*d*<sub>3</sub>



To a 20 mL quartz tube equipped with a magnetic stir bar was added 4-bromo-1-tosylpiperidine **1a** (63.6 mg, 0.2 mmol, 1.0 equiv.), photocatalyst Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> (2.3 mg, 0.002 mmol, 1 mol%), PCy<sub>3</sub> (140.2 mg, 0.5 mmol, 2.5 equiv.), and the tube was evacuated and backfilled with N<sub>2</sub> (three times). Thiol catalyst 2,4,6-triisopropylbenzenethiol (4.7 mg, 0.02 mmol, 10 mol%) in CH<sub>3</sub>CN-*d*<sub>3</sub> (2 mL) were added by syringe under N<sub>2</sub>. The reaction mixture was stirred and irradiated using a 10 W blue LEDs lamp for 24 hours at room temperature. Brine (10 mL) and EtOAc (10 mL) were added and the mixture was shaken. The aqueous layer was extracted with EtOAc (x 2), the combined organic layers were dried (MgSO<sub>4</sub>), filtered and evaporated. Purification by flash column chromatography on silica gel gave the hydrodebromination product **2a'** in 51% yield (0% D) which indicate CH<sub>3</sub>CN-*d*<sub>3</sub> was not act as a Deuterium atom donor.

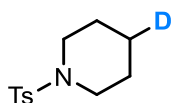


## 6. Reference

- [1] Zhao, H., MacMillan, A. J., Constantin, T., Mykura, R. C., Julia, F., and Leonori, D. (2021). Merging halogen-atom transfer (XAT) and cobalt catalysis to override E2-selectivity in the elimination of alkyl halides: A mild route towards *contra*-thermodynamic olefins. *J. Am. Chem. Soc.* *143*, 14806–14813.
- [2] Xia, A., Xie, X., Hu, X., Xu, W., and Liu, Y. (2019). Dehalogenative deuteration of unactivated alkyl halides using D<sub>2</sub>O as the deuterium source. *J. Org. Chem.* *84*, 13841–13857.
- [3] Atack, T. C., Lecker R. M., and Cook, S. P. (2014). Iron-catalyzed borylation of alkyl electrophiles. *J. Am. Chem. Soc.* *136*, 9521–9523.
- [4] Kaldas, S. J., Cannillo, A., McCallum, T., and Barriault, L. (2015). Indole functionalization via photoredox gold catalysis. *Org. Lett.* *17*, 2864–2866.
- [5] Huang, H.-M., Bellotti, P., Pflüger, P. M., Schwarz, J. L., Heidrich, B., Glorius, F. (2020). A three-component, interrupted radical heck/allylic substitution cascade involving unactivated alkyl bromides. *J. Am. Chem. Soc.* *142*, 10173–10183.
- [6] Lin, Q., Gong, H., and Wu, F. (2022). Ni-catalyzed reductive coupling of heteroaryl bromides with tertiary alkyl halides. *Org. Lett.* *24*, 8996–9000.
- [7] Ren, X., Ke, Q., Zhou, Y., Jiao, J., Li, G., Gao, S., Wang, X., Gao, Q., and Wang, X. (2023). Access to polysulfides through photocatalyzed dithiosulfonylation. *Angew. Chem. Int. Ed.* *62*, e202302199.
- [8] Singh, B., Gupta, P., Chaubey, A., Parshad, R., Sharma, S., and Taneja, S. C. (2008). Enantiomerically pure  $\alpha$ -methoxyaryl acetaldehydes as versatile precursors: A facile chemo-enzymatic methodology for their preparation, *Tetrahedron: Asymmetry.* *19*, 2579–2588.
- [9] Khamarui, S., Sarkar, D., Pandit, P., and Maiti, D. K. (2011). A fast and selective decarboxylative difunctionalization and cyclization for easy access to gem-dihalo alcohol, ether, ester and bromo-1,4-dioxane. *Chem. Commun.* *47*, 12667–12669.

- [10] Yang, S., Hu, H., and Chen, M. Photoinduced palladium-catalyzed regio- and chemoselective elimination of primary alkyl bromides: A mild route to synthesize unactivated terminal olefins. *Org. Lett.* *54*, 7968–7973.
- [11] Li, Y., Ye, Z., Lin, Y.-M., Liu, Y., Zhang, Y., and Gong, L. Organophotocatalytic selective deuterodehalogenation of aryl or alkyl chlorides. *Nat Commun.* *12*, 2894.
- [12] Caiger, L., Zhao, H., Constantin, T., Douglas, J. J., and Leonori, D. (2023). The merger of aryl radical-mediated halogen-atom transfer (XAT) and copper catalysis for the modular cross-coupling-type functionalization of alkyl iodides. *ACS Catal.* *13*, 4985–4991.
- [13] Lu, F.-D., Chen, J., Jiang, X., Chen, J.-R., Lu, L.-Q., and Xiao, W.-J. (2021). Recent advances in transition-metal-catalysed asymmetric coupling reactions with light intervention. *Chem. Soc. Rev.* *50*, 12808.
- [14] Teegardin, K., Day, J. I., Chan, J., and Weaver, J. (2016). Advances in photocatalysis: A microreview of visible light mediated ruthenium and iridium catalyzed organic transformations. *Org. Process Res. Dev.* *20*, 1156–1163.
- [15] Chinn, A. J., Sedillo, K., and Doyle, A. G. (2021). Phosphine/photoredox catalyzed anti-markovnikov hydroamination of olefins with primary sulfonamides via  $\alpha$ -scission from phosphoranyl radicals. *J. Am. Chem. Soc.* *143*, 18331–18338.
- [16] Corrigan, N., Shanmugam, S., Xu, J., and Boyer, C. (2016). Photocatalysis in organic and polymer synthesis. *Chem. Soc. Rev.* *45*, 6165–6212.

## 7. Characterization Data

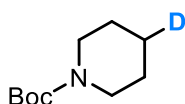


**1-tosylpiperidine-4-d (2a):** Followed the GP4 and purified using flash chromatography (petroleum ether/EtOAc = 10:1) to give 43.7 mg of the title compound (white solid; 91% yield); D-inc.: 95% (determined by  $^1\text{H}$  NMR).

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.64 (d,  $J$  = 8.2 Hz, 2H), 7.32 (d,  $J$  = 8.0 Hz, 2H), 2.96 (t,  $J$  = 5.5 Hz, 4H), 2.43 (s, 3H), 1.63 (q,  $J$  = 5.8 Hz, 4H), 1.43 – 1.35 (m, 1H).

$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  143.3, 133.1, 129.5, 127.6, 46.8, 25.0, 23.4 (C–H), 23.0 (t,  $J$  = 19.2 Hz, C–D), 21.5.

HRMS (ESI) calcd  $\text{C}_{12}\text{H}_{17}\text{DNO}_2\text{S}$   $[\text{M} + \text{H}]^+$ : 241.1116, found: 241.1113.

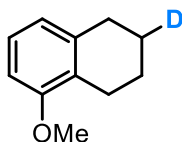


**tert-butyl piperidine-1-carboxylate-4-d (2b):** Followed the GP4 and purified using flash chromatography (petroleum ether/EtOAc = 10:1) to give 43.7 mg of the title compound (white solid; 92% yield.) D-inc.: 89% (determined by  $^1\text{H}$  NMR).

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  3.37 – 3.34 (m, 4H), 1.55 – 1.48 (m, 5H), 1.46 (s, 9H).

$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  155.0, 79.2, 44.6, 28.5, 25.7, 24.6 (C–H), 24.2 (t,  $J$  = 20.2 Hz, C–D).

HRMS (ESI) calcd  $\text{C}_{10}\text{H}_{19}\text{DNO}_2$   $[\text{M} + \text{H}]^+$ : 187.1551, found: 187.1554.

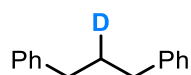


**5-methoxy-1,2,3,4-tetrahydronaphthalene-2-d (2c):** Followed the GP4 and purified using flash chromatography (petroleum ether/EtOAc = 100:1) to give 23.8 mg of the title compound (colorless oil; 73% yield); D-inc.: 90% (determined by  $^1\text{H}$  NMR).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 7.06 (t, *J* = 7.9 Hz, 1H), 6.69 (d, *J* = 7.6 Hz, 1H), 6.64 (d, *J* = 8.1 Hz, 1H), 3.80 (s, 3H), 2.74 (d, *J* = 5.9 Hz, 2H), 2.64 (t, *J* = 6.3 Hz, 2H), 1.80 – 1.70 (m, 3H).

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)** δ 157.3, 138.5, 125.9, 125.6, 121.4, 106.7, 55.2, 29.5, 23.0, 22.8 (C–H), 22.7, 22.4 (t, *J* = 19.2 Hz, C–D).

**HRMS (ESI)** calcd C<sub>11</sub>H<sub>14</sub>DO [M + H]<sup>+</sup>: 164.1180, found: 164.1177.

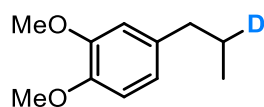


**(propane-1,3-diyl-2-d)dibenzene (2d)**: Followed the GP4 and purified using flash chromatography (petroleum ether/EtOAc = 100:1) to give 34.3 mg of the title compound (colorless oil; 87% yield); D-inc.: 96% (determined by <sup>1</sup>H NMR).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 7.30 – 7.26 (m, 4H), 7.19 – 7.16 (m, 6H), 2.64 (d, *J* = 7.7 Hz, 4H), 1.99 – 1.90 (m, 1H).

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)** δ 142.3, 128.4, 128.3, 125.7, 35.3, 32.5 (t, *J* = 20.2 Hz, C–D).

**HRMS (ESI)** calcd C<sub>15</sub>H<sub>16</sub>D [M + H]<sup>+</sup>: 198.1388, found: 198.1383.

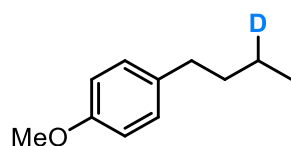


**1,2-dimethoxy-4-(propyl-2-d)benzene (2e)**: Followed the GP4 and purified using flash chromatography (petroleum ether/EtOAc = 50:1) to give 31.9 mg of the title compound (colorless oil; 88% yield); D-inc.: 97% (determined by <sup>1</sup>H NMR).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 6.79 (d, *J* = 8.7 Hz, 1H), 6.73 – 6.70 (m, 2H), 3.87 (s, 3H), 3.85 (s, 3H), 2.52 (d, *J* = 7.6 Hz, 2H), 1.65 – 1.57 (m, 1H), 0.93 (d, *J* = 7.3 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)** δ 148.6, 146.9, 135.3, 120.1, 111.7, 111.0, 55.8, 55.7, 37.5, 24.3 (t, *J* = 19.2 Hz, C–D), 13.7.

**HRMS (ESI)** calcd C<sub>11</sub>H<sub>16</sub>DO<sub>2</sub> [M + H]<sup>+</sup>: 182.1286, found: 182.1283.



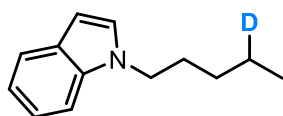
**1-(butyl-3-d)-4-methoxybenzene (2f)**: Followed the GP4 and purified using flash chromatography

(petroleum ether/EtOAc = 100:1) to give 30.1 mg of the title compound (colorless oil; 91% yield); D-inc.: 92% (determined by  $^1\text{H}$  NMR).

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.09 (d,  $J$  = 8.3 Hz, 2H), 6.82 (d,  $J$  = 8.1 Hz, 2H), 3.78 (s, 3H), 2.55 (t,  $J$  = 4.0 Hz, 2H), 1.58 – 1.54 (m, 2H), 1.37 – 1.27 (m, 1H), 0.91 (d,  $J$  = 7.3 Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  157.5, 135.0, 129.2, 113.6, 55.2, 34.7, 33.8, 22.3 (C–H), 21.9 (t,  $J$  = 19.2 Hz, C–D), 13.9.

HRMS (ESI) calcd  $\text{C}_{11}\text{H}_{16}\text{DO}$  [M + H] $^+$ : 166.1337, found: 166.1339.

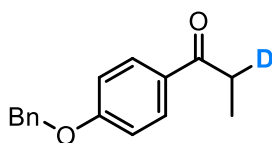


**1-(pentyl-4-d)-1H-indole (2g):** Followed the GP4 and purified using flash chromatography (petroleum ether/EtOAc = 100:1) to give 29.8 mg of the title compound (colorless oil; 79% yield); D-inc.: 92% (determined by  $^1\text{H}$  NMR).

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.63 (d,  $J$  = 7.9 Hz, 1H), 7.34 (d,  $J$  = 8.2 Hz, 1H), 7.22 – 7.17 (m, 1H), 7.11 – 7.07 (m, 2H), 6.48 (d,  $J$  = 3.6 Hz, 1H), 4.09 (t,  $J$  = 7.2 Hz, 2H), 1.86 – 1.79 (m, 2H), 1.34 – 1.25 (m, 3H), 0.87 (d,  $J$  = 6.5 Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  135.9, 128.5, 127.8, 121.2, 120.9, 119.1, 109.3, 100.7, 46.4, 29.9, 29.0, 22.3 (C–H), 21.92 (t,  $J$  = 19.2 Hz, C–D), 13.8.

HRMS (ESI) calcd  $\text{C}_{13}\text{H}_{17}\text{DN}$  [M + H] $^+$ : 189.1497, found: 189.1491.

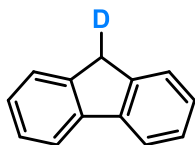


**1-(4-(benzyloxy)phenyl)propan-1-one-2-d (2h):** Followed the GP4 and purified using flash chromatography (petroleum ether/EtOAc = 80:1) to give 41.5 mg of the title compound (colorless oil; 86% yield); D-inc.: 76% (determined by  $^1\text{H}$  NMR).

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.94 (d,  $J$  = 8.9 Hz, 2H), 7.44 – 7.32 (m, 5H), 7.00 (d,  $J$  = 8.9 Hz, 2H), 5.12 (s, 2H), 2.97 – 2.88 (m, 1H), 1.20 (d,  $J$  = 7.0 Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  199.5, 162.4, 136.2, 130.2, 128.6, 128.2, 127.4, 114.5, 70.0, 31.4 (C–H), 31.1 (t,  $J$  = 19.2 Hz, C–D), 8.3.

**HRMS (ESI)** calcd C<sub>16</sub>H<sub>16</sub>DO<sub>2</sub> [M + H]<sup>+</sup>: 242.1286, found: 242.1290.

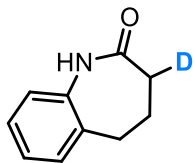


**9H-fluorene-9-d (2i):** Followed the GP4 and purified using flash chromatography (petroleum ether/EtOAc = 100:1) to give 27.8 mg of the title compound (colorless oil; 83% yield); D-inc.: 98% (determined by <sup>1</sup>H NMR).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 7.78 (d, *J* = 7.4 Hz, 2H), 7.54 (d, *J* = 7.3 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 2H), 7.29 (td, *J* = 7.4, 1.1 Hz, 2H), 3.89 – 3.85 (m, 1H).

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)** δ 143.2, 141.7, 126.7, 126.7, 125.0, 119.8, 36.9 (C–H), 36.6 (t, *J* = 19.2 Hz, C–D).

**HRMS (ESI)** calcd C<sub>13</sub>H<sub>10</sub>D [M + H]<sup>+</sup>: 167.0845, found: 167.0840.

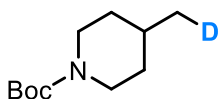


**1,3,4,5-tetrahydro-2H-benzo[b]azepin-2-one-3-d (2j):** Followed the GP4 and purified using flash chromatography (petroleum ether/EtOAc = 10:1) to give 31.1 mg of the title compound (colorless oil; 96% yield); D-inc.: 93% (determined by <sup>1</sup>H NMR).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 8.75 (s, 1H), 7.29 – 7.23 (m, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 7.7 Hz, 1H), 2.82 (t, *J* = 7.2 Hz, 2H), 2.37 (t, *J* = 7.2 Hz, 1H), 2.28 – 7.23 (m, 2H).

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)** δ 175.7, 137.9, 134.2, 129.7, 127.4, 125.5, 121.8, 32.7 (C–H), 32.4 (t, *J* = 20.2 Hz, C–D), 30.2, 28.4.

**HRMS (ESI)** calcd C<sub>10</sub>H<sub>11</sub>DNO [M + H]<sup>+</sup>: 163.0976, found: 163.0974.

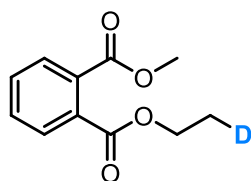


**(methylene-*d*)dibenzene (2k):** Followed the GP4 and purified using flash chromatography (petroleum ether/EtOAc = 10:1) to give 28.8 mg of the title compound (colorless oil; 72% yield); D-inc.: 92% (determined by <sup>1</sup>H NMR).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 4.05 (s, 2H), 2.67 (t, *J* = 13.0 Hz, 2H), 1.59 (d, *J* = 13.6 Hz, 3H), 1.45 (s, 9H), 1.12 – 1.02 (m, 2H), 0.94 – 0.91 (m, 2H).

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)** δ 154.9, 79.1, 44.0, 34.0, 30.9, 28.4, 21.9 (C–H), 21.6 (t, *J* = 19.2 Hz, C–D).

**HRMS (ESI)** calcd C<sub>11</sub>H<sub>21</sub>DNO<sub>2</sub> [M + H]<sup>+</sup>: 201.1708, found: 201.1705.

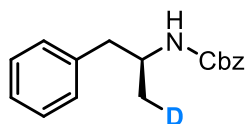


**ethyl-2-d methyl phthalate (2i):** Followed the GP4 and purified using flash chromatography (petroleum ether/EtOAc = 9:1) to give 31.4 mg of the title compound (colorless oil; 75% yield); D-inc.: 92% (determined by <sup>1</sup>H NMR).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 7.76 – 7.69 (m, 2H), 7.57 – 7.53 (m, 2H), 4.37 (t, *J* = 7.1 Hz, 2H), 3.91 (s, 3H), 1.38 – 1.33 (m, 2H).

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)** δ 168.2, 167.6, 132.2, 132.0, 131.1, 129.0, 128.9, 61.7, 52.6, 14.2 (C–H), 13.9 (t, *J* = 19.2 Hz, C–D).

**HRMS (ESI)** calcd C<sub>11</sub>H<sub>12</sub>DO<sub>4</sub> [M + H]<sup>+</sup>: 210.0871, found: 210.0876.

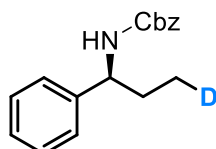


**benzyl (S)-(1-phenylpropan-2-yl-3-d)carbamate (2m):** Followed the GP4 and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 34.1 mg of the title compound (colorless oil; 63% yield); D-inc.: 98% (determined by <sup>1</sup>H NMR).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 7.37 – 7.23 (m, 8H), 7.16 (d, *J* = 7.0 Hz, 2H), 5.08 (s, 2H), 4.62 (s, 1H), 4.06 – 3.93 (m, 1H), 2.89 – 2.82 (m, 1H), 2.69 (dd, *J* = 13.3, 7.2 Hz, 1H), 1.12 – 1.09 (m, 2H).

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)** δ 155.6, 137.9, 136.6, 129.4, 128.5, 128.4, 128.0, 126.4, 66.5, 47.9, 19.9 (t, *J* = 20.2 Hz, C–D).

**HRMS (ESI)** calcd C<sub>17</sub>H<sub>19</sub>DNO<sub>2</sub> [M + H]<sup>+</sup>: 271.1551, found: 271.1553.

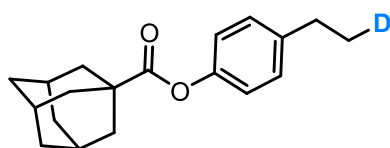


**benzyl (S)-(1-phenylpropyl-3-d)carbamate (2n):** Followed the GP4 and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 40.6 mg of the title compound (colorless oil; 75% yield); D-inc.: 94% (determined by  $^1\text{H}$  NMR).

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.34 – 7.23 (m, 10H), 5.12 – 5.02 (m, 3H), 4.61 (s, 1H), 1.84 – 1.73 (m, 2H), 0.89 – 0.85 (m, 2H).

$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  155.8, 136.5, 128.6, 128.5, 128.1, 127.3, 126.4, 66.7, 56.9, 29.6, 10.63 (C–H), 10.4 (t,  $J = 19.2$  Hz, C–D).

HRMS (ESI) calcd  $\text{C}_{17}\text{H}_{19}\text{DNO}_2$   $[\text{M} + \text{H}]^+$ : 271.1551, found: 271.1552.

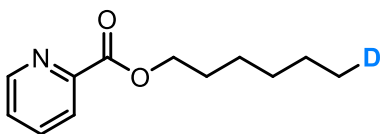


**4-(ethyl-2-d)phenyl (3r,5r,7r)-adamantane-1-carboxylate (2o):** Followed the GP4 and purified using flash chromatography (petroleum ether/EtOAc = 90:1) to give 46.2 mg of the title compound (colorless oil; 81% yield); D-inc.: 94% (determined by  $^1\text{H}$  NMR).

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.17 (d,  $J = 8.4$  Hz, 2H), 6.94 (d,  $J = 8.4$  Hz, 2H), 2.63 (t,  $J = 7.5$  Hz, 2H), 2.08 – 2.05 (m, 9H), 1.80 – 1.73 (m, 6H), 1.22 – 1.19 (m, 2H).

$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  176.4, 148.9, 141.4, 128.6, 121.2, 40.9, 38.7, 36.4, 28.2, 27.9, 15.6 (C–H), 15.3 (t,  $J = 19.2$  Hz, C–D).

HRMS (ESI) calcd  $\text{C}_{19}\text{H}_{24}\text{DO}_2$   $[\text{M} + \text{H}]^+$ : 286.1912, found: 286.1915.



**hexyl-6-d picolinate (2p):** Followed the GP4 and purified using flash chromatography (petroleum ether/EtOAc = 9:1) to give 46.2 mg of the title compound (colorless oil; 85% yield); D-inc.: 99% (determined by  $^1\text{H}$  NMR).

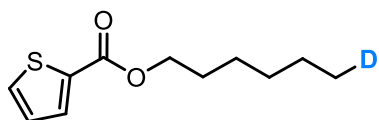
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.77 (d,  $J = 4.6$  Hz, 1H), 8.13 (d,  $J = 7.8$  Hz, 1H), 7.85 (td,  $J = 7.7$ , 1.6 Hz, 1H), 7.50 – 7.46 (m, 1H), 4.42 (t,  $J = 7.0$  Hz, 2H), 1.86 – 1.81 (m, 2H), 1.47 – 1.40 (m, 2H), 1.36 – 1.31 (m, 4H), 0.90 – 0.86 (m, 2H).

$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  165.2, 149.8, 148.2, 137.0, 126.8, 125.1, 66.1, 31.4, 28.6, 25.5,



22.4, 13.7 (t,  $J = 19.2$  Hz, C–D).

**HRMS (ESI)** calcd  $C_{16}H_{18}DNO_2$   $[M + H]^+$ : 209.1395, found: 209.1390.

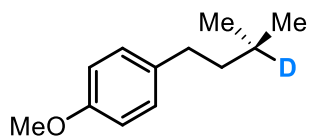


**hexyl-6-d thiophene-2-carboxylate (2q)**: Followed the GP4 and purified using flash chromatography (petroleum ether/EtOAc = 80:1) to give 26.0 mg of the title compound (colorless oil; 61% yield); D-inc.: 96% (determined by  $^1H$  NMR).

$^1H$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.80 (d,  $J = 3.6$  Hz, 1H), 7.55 (d,  $J = 5.0$  Hz, 0.54H), 7.11 – 7.09 (m, 1H), 4.29 (t,  $J = 6.7$  Hz, 2H), 1.78 – 1.71 (m, 2H), 1.44 – 1.39 (m, 2H), 1.35 – 1.29 (m, 4H), 0.92 – 0.87 (m, 2H).

$^{13}C$  NMR (101 MHz, Chloroform-*d*)  $\delta$  162.4, 133.2, 132.1, 127.7, 127.5, 65.3, 31.4, 28.6, 25.6, 22.4, 14.0 (C–H), 13.7 (t,  $J = 19.2$  Hz, C–D).

**HRMS (ESI)** calcd  $C_{11}H_{16}DO_2S$   $[M + H]^+$ : 214.1007, found: 214.1003.

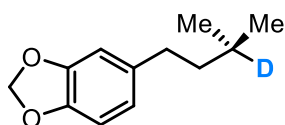


**methoxy-4-(3-methylbutyl-3-d)benzene (2r)**: Followed the GP4 and purified using flash chromatography (petroleum ether/EtOAc = 100:1) to give 33.3 mg of the title compound (colorless oil; 93% yield); D-inc.: 90% (determined by  $^{13}C$  NMR).

$^1H$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.09 (d,  $J = 8.6$  Hz, 2H), 6.82 (d,  $J = 8.6$  Hz, 2H), 3.78 (s, 3H), 2.57 – 2.53 (m, 2H), 1.48 – 1.44 (m, 2H), 0.91 (s, 6H).

$^{13}C$  NMR (101 MHz, Chloroform-*d*)  $\delta$  157.5, 136.2, 129.2, 113.6, 55.2, 41.0, 32.8, 27.6 (C–H), 27.1 (t,  $J = 19.2$  Hz, C–D), 22.4.

**HRMS (ESI)** calcd  $C_{12}H_{18}DO$   $[M + H]^+$ : 180.1493, found: 180.1495.

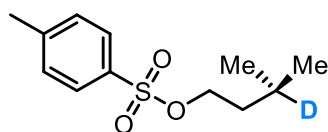


**methoxy-4-(3-methylbutyl-3-d)benzene (2s):** Followed the GP4 and purified using flash chromatography (petroleum ether/EtOAc = 100:1) to give 36.0 mg of the title compound (colorless oil; 93% yield); D-inc.: 82% (determined by  $^{13}\text{C}$  NMR).

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  6.72 (d,  $J$  = 7.9 Hz, 1H), 6.68 (s, 1H), 6.62 (d,  $J$  = 7.9 Hz, 1H), 5.91 (s, 2H), 2.54 – 2.50 (m, 2H), 1.47 – 1.43 (m, 2H), 0.91 (s, 6H).

$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  147.4, 145.3, 137.0, 120.9, 108.8, 108.0, 100.7, 41.0, 33.5, 27.5 (C–H), 27.0 (t,  $J$  = 20.2 Hz, C–D), 22.4.

HRMS (ESI) calcd  $\text{C}_{12}\text{H}_{16}\text{DO}_2$   $[\text{M} + \text{H}]^+$ : 194.1286, found: 194.1288.

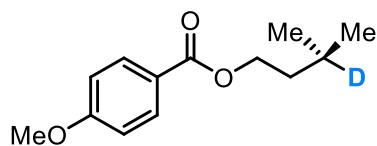


**3-methylbutyl-3-d 4-methylbenzenesulfonate (2t):** Followed the GP4 and purified using flash chromatography (petroleum ether/EtOAc = 80:1) to give 47.2 mg of the title compound (colorless oil; 97% yield); D-inc.: 92% (determined by  $^1\text{H}$  NMR).

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.82 (d,  $J$  = 8.1 Hz, 2H), 7.37 (d,  $J$  = 8.0 Hz, 2H), 4.07 (t,  $J$  = 6.6 Hz, 2H), 2.47 (s, 3H), 1.54 (t,  $J$  = 6.5 Hz, 2H), 0.85 (s, 6H).

$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  144.6, 133.0, 129.8, 127.8, 69.1, 37.2, 24.3 (C–H), 23.9 (t,  $J$  = 20.2 Hz, C–D), 21.9, 21.6.

HRMS (ESI) calcd  $\text{C}_{12}\text{H}_{18}\text{DO}_2\text{S}$   $[\text{M} + \text{H}]^+$ : 244.1112, found: 244.1117.

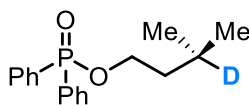


**3-methylbutyl-3-d 4-methylbenzenesulfonate (2u):** Followed the GP4 and purified using flash chromatography (petroleum ether/EtOAc = 50:1) to give 42.4 mg of the title compound (colorless oil; 95% yield); D-inc.: 86% (determined by  $^1\text{H}$  NMR).

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.02 (d,  $J$  = 8.9 Hz, 2H), 6.94 (d,  $J$  = 8.9 Hz, 2H), 4.35 (t,  $J$  = 6.8 Hz, 2H), 3.87 (s, 3H), 1.67 (t,  $J$  = 6.8 Hz, 2H), 0.99 (s, 6H).

$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  166.4, 163.2, 131.5, 122.9, 113.5, 63.2, 55.3, 37.3, 25.2 (C–H), 24.7 (t,  $J$  = 19.2 Hz, C–D), 22.3.

**HRMS (ESI)** calcd C<sub>13</sub>H<sub>18</sub>DO<sub>3</sub> [M + H]<sup>+</sup>: 224.1391, found: 224.1395.

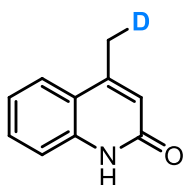


**3-methylbutyl-3-d diphenylphosphinate (2v):** Followed the GP4 and purified using flash chromatography (petroleum ether/EtOAc = 1:1) to give 55.5 mg of the title compound (colorless oil; 96% yield); D-inc.: 92% (determined by <sup>1</sup>H NMR).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 7.84 – 7.79 (m, 4H), 7.53 – 7.49 (m, 2H), 7.46 – 7.42 (m, 4H), 4.06 (q, *J* = 6.7 Hz, 2H), 1.61 (t, *J* = 6.7 Hz, 2H), 0.89 (s, 6H).

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)** δ 132.2, 132.0 (d, *J* = 3.0 Hz), 131.5 (d, *J* = 10.1 Hz), 130.8, 128.4 (d, *J* = 13.1 Hz), 63.3 (d, *J* = 6.1 Hz), 39.0 (d, *J* = 6.1 Hz), 24.5 (C–H), 24.1 (t, *J* = 20.2 Hz, C–D), 22.2.

**HRMS (ESI)** calcd C<sub>17</sub>H<sub>21</sub>DO<sub>2</sub>P [M + H]<sup>+</sup>: 290.1415, found: 290.1411.

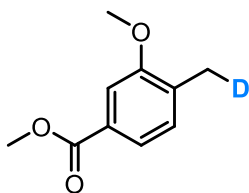


**4-(methyl-d)quinolin-2(1H)-one (2w):** Followed the GP4 and purified using flash chromatography (petroleum ether/EtOAc = 1:2) to give 26.3 mg of the title compound (yellow solid; 82% yield); D-inc.: 99% (determined by <sup>1</sup>H NMR).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 12.7 (s, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.53 – 7.46 (m, 2H), 7.26 – 7.22 (m, 1H), 6.60 (s, 1H), 2.51 (s, 2H).

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)** δ 164.4, 149.2, 138.2, 130.5, 124.3, 122.4, 120.4, 116.6, 19.1 (C–H), 18.9 (t, *J* = 20.2 Hz, C–D).

**HRMS (ESI)** calcd C<sub>10</sub>H<sub>9</sub>DNO [M + H]<sup>+</sup>: 161.0820, found: 161.0825.



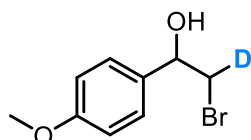
**ethyl-2-d methyl phthalate (2x):** Followed the GP4 and purified using flash chromatography (petroleum ether/EtOAc = 50:1) to give 26.1 mg of the title compound (colorless oil; 72% yield); D-inc.: 96%

(determined by  $^1\text{H}$  NMR).

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.56 (dd,  $J = 7.7, 1.3$  Hz, 1H), 7.48 (s, 1H), 7.18 (d,  $J = 7.7$  Hz, 1H), 3.91 (s, 3H), 3.88 (s, 3H), 2.26 – 2.24 (m, 2H).

$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  167.2, 157.5, 132.4, 130.4, 128.8, 121.8, 110.4, 55.4, 52.0, 16.3 (t,  $J = 20.2$  Hz, C–D).

HRMS (ESI) calcd  $\text{C}_{10}\text{H}_{12}\text{DO}_3$   $[\text{M} + \text{H}]^+$ : 182.0922, found: 182.0927.

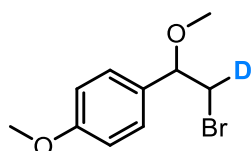


**2-bromo-1-(4-methoxyphenyl)ethan-2-d-1-ol (2y):** Followed the GP4 and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 38.5 mg of the title compound (colorless oil; 83% yield); D-inc.: 99% (determined by  $^1\text{H}$  NMR).

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.30 (d,  $J = 8.6$  Hz, 2H), 6.90 (d,  $J = 8.7$  Hz, 2H), 4.89 – 4.84 (m, 1H), 3.81 (s, 3H), 3.63 – 3.50 (m, 1H), 2.52 (s, 1H).

$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  159.6, 132.4, 127.2, 114.0, 73.4, 55.3, 40.0 (t,  $J = 24.2$  Hz, C–D).

HRMS (ESI) calcd  $\text{C}_9\text{H}_{11}\text{DBrO}_2$   $[\text{M} + \text{H}]^+$ : 233.1026, found: 233.1024.

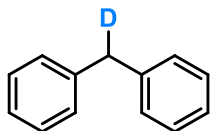


**1-methoxy-4-(1-methoxyethyl-2,2-d2)benzene (2z):** Followed the GP4 and purified using flash chromatography (petroleum ether/EtOAc = 60:1) to give 43.8 mg of the title compound (colorless oil; 89% yield); D-inc.: 99% (determined by  $^1\text{H}$  NMR).

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.24 (d,  $J = 8.6$  Hz, 2H), 6.91 (d,  $J = 8.7$  Hz, 2H), 4.34 – 4.32 (m, 1H), 3.81 (s, 3H), 3.51 (d,  $J = 8.4$  Hz, 0.51H), 3.42 (d,  $J = 4.0$  Hz, 0.50H), 3.28 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  159.7, 130.9, 128.0, 114.0, 82.8, 57.0, 55.2, 36.2 (t,  $J = 23.2$  Hz, C–D).

HRMS (ESI) calcd  $\text{C}_{10}\text{H}_{13}\text{DBrO}_2$   $[\text{M} + \text{H}]^+$ : 246.0234, found: 246.0231.

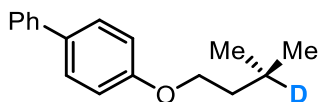


**(methylene-d)dibenzene (2aa):** Followed the GP4 and purified using flash chromatography (petroleum ether/EtOAc = 100:1) to give 24.0 mg of the title compound (colorless oil; 71% yield); D-inc.: 98% (determined by  $^1\text{H}$  NMR).

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.30 – 7.26 (m, 4H), 7.21 – 7.18 (m, 6H), 3.96 (s, 1H).

$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  141.1, 128.9, 128.4, 126.0, 41.6 (t,  $J = 20.2$  Hz, C–D).

HRMS (ESI) calcd  $\text{C}_{13}\text{H}_{12}\text{D}$   $[\text{M} + \text{H}]^+$ : 170.1075, found: 170.1070.

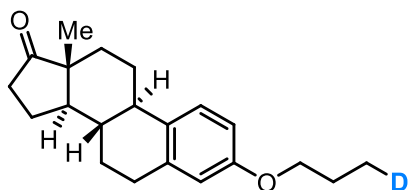


**4-(3-methylbutoxy-3-d)-1,1'-biphenyl (2ab):** Followed the GP4 and purified using flash chromatography (petroleum ether/EtOAc = 80:1) to give 15.4 mg of the title compound (colorless oil; 32% yield); D-inc.: 87% (determined by  $^1\text{H}$  NMR).

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.56 – 7.50 (m, 4H), 7.41 (t,  $J = 7.6$  Hz, 2H), 7.29 (t,  $J = 7.3$  Hz, 1H), 6.97 (d,  $J = 8.6$  Hz, 2H), 4.03 (t,  $J = 6.7$  Hz, 2H), 1.70 (t,  $J = 6.6$  Hz, 2H), 0.97 (s, 6H).

$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  158.7, 140.9, 133.5, 128.7, 128.1, 126.7, 126.6, 66.4, 37.9, 25.1 (C–H), 24.6 (t,  $J = 19.2$  Hz, C–D), 22.5.

HRMS (ESI) calcd  $\text{C}_{17}\text{H}_{20}\text{DO}$   $[\text{M} + \text{H}]^+$ : 242.1650, found: 242.1652.



**(8S,9R,13R,14R)-13-methyl-3-(propoxy-3-d)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-**

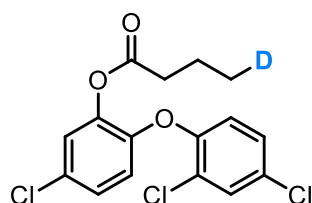
**cyclopenta[a]phenanthren-17-one (2ac):** Followed the GP4 and purified using flash chromatography (petroleum ether/EtOAc = 50:1) to give 49.5 mg of the title compound (colorless oil; 79% yield); D-inc.: 97% (determined by  $^1\text{H}$  NMR).

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.23 (d,  $J = 8.6$  Hz, 1H), 6.75 (dd,  $J = 8.6, 2.7$  Hz, 1H), 6.69 (s, 1H), 3.93 (t,  $J = 6.6$  Hz, 2H), 3.95 – 2.87 (m, 2H), 2.54 (dd,  $J = 18.7, 8.6$  Hz, 1H), 2.46 – 2.41 (m, 1H), 2.32 –

2.26 (m, 1H), 2.20 – 1.98 (m, 4H), 1.86 – 1.79 (m, 2H), 1.69 – 1.47 (m, 6H), 1.07 – 1.02 (m, 2H), 0.95 (s, 3H).

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)**  $\delta$  220.9, 157.1, 137.6, 131.8, 126.2, 114.6, 112.1, 69.4, 50.4, 48.0, 44.0, 38.4, 31.6, 29.6, 26.6, 25.9, 22.5, 21.6, 13.8, 10.5 (C–H), 10.2 (t,  $J$  = 20.2 Hz, C–D).

**HRMS (ESI)** calcd C<sub>21</sub>H<sub>28</sub>DO<sub>2</sub> [M + H]<sup>+</sup>: 314.2225, found: 314.2226.

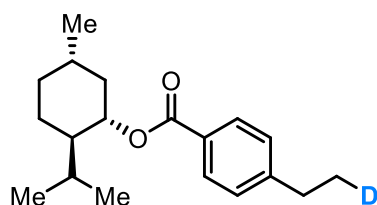


**5-chloro-2-(2,4-dichlorophenoxy)phenyl butanoate-4-d (2ad):** Followed the GP4 and purified using flash chromatography (petroleum ether/EtOAc = 30:1) to give 44.7 mg of the title compound (colorless oil; 62% yield); D-inc.: 97% (determined by <sup>1</sup>H NMR).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.48 (d,  $J$  = 2.5 Hz, 1H), 7.23 – 7.19 (m, 3H), 6.91 – 6.86 (m, 2H), 2.49 (t,  $J$  = 7.3 Hz, 2H), 1.76 – 1.68 (m, 2H), 1.00 – 0.96 (m, 2H).

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)**  $\delta$  171.0, 151.1, 146.6, 141.9, 130.4, 129.4, 129.3, 128.1, 126.9, 125.8, 124.5, 120.2, 120.2, 35.6, 18.2, 13.5 (C–H), 13.2 (t,  $J$  = 19.2 Hz, C–D).

**HRMS (ESI)** calcd C<sub>16</sub>H<sub>13</sub>DCl<sub>3</sub>O<sub>3</sub> [M + H]<sup>+</sup>: 360.0066, found: 360.0061.

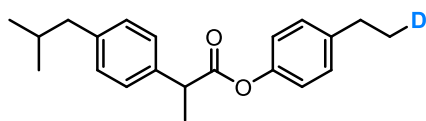


**(1S,2R,5S)-2-isopropyl-5-methylcyclohexyl 4-(ethyl-2-d)benzoate (2ae):** Followed the GP4 and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 45.7 mg of the title compound (colorless oil; 79% yield); D-inc.: 94% (determined by <sup>13</sup>C NMR).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**  $\delta$  8.00 (d,  $J$  = 8.2 Hz, 2H), 7.31 – 7.29 (m, 2H), 4.96 (td,  $J$  = 10.9, 4.4 Hz, 1H), 2.73 (t,  $J$  = 7.5 Hz, 2H), 2.16 (d,  $J$  = 12.0 Hz, 1H), 2.04 – 1.96 (m, 1H), 1.78 – 1.75 (m, 2H), 1.62 – 1.55 (m, 2H), 1.31 – 1.25 (m, 2H), 1.21 – 1.11 (m, 2H), 0.97 – 0.94 (m, 6H), 0.83 (d,  $J$  = 7.0 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)**  $\delta$  166.2, 149.5, 129.7, 128.4, 127.8, 74.6, 47.3, 41.0, 34.4, 31.4, 28.9, 26.5, 23.7, 22.0, 20.8, 16.5, 15.3 (C–H), 15.02 (t,  $J$  = 19.2 Hz, C–D).

**HRMS (ESI)** calcd C<sub>19</sub>H<sub>28</sub>DO<sub>2</sub> [M + H]<sup>+</sup>: 290.2225, found: 290.2226.

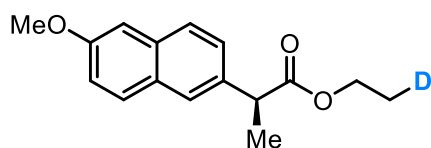


**4-(ethyl-2-d)phenyl 2-(4-isobutylphenyl)propanoate (2af):** Followed the GP4 and purified using flash chromatography (petroleum ether/EtOAc = 50:1) to give 51.1 mg of the title compound (colorless oil; 82% yield); D-inc.: 98% (determined by <sup>1</sup>H NMR).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 7.36 (d, *J* = 8.0 Hz, 2H), 7.21 – 7.18 (m, 4H), 6.96 (d, *J* = 8.5 Hz, 2H), 3.98 (q, *J* = 7.1 Hz, 1H), 2.66 (t, *J* = 7.5 Hz, 2H), 2.53 (d, *J* = 7.2 Hz, 2H), 1.98 – 1.88 (m, 1H), 1.66 (d, *J* = 7.2 Hz, 3H), 1.28 – 1.22 (m, 2H), 0.97 (d, *J* = 6.6 Hz, 6H).

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)** δ 173.4, 148.7, 141.6, 140.7, 137.3, 129.4, 128.6, 127.2, 121.1, 45.2, 45.0, 30.2, 28.2, 22.4, 18.5, 15.6 (C–H), 15.3 (t, *J* = 19.2 Hz, C–D).

**HRMS (ESI)** calcd C<sub>21</sub>H<sub>26</sub>DO<sub>2</sub> [M + H]<sup>+</sup>: 312.2068, found: 312.2069.

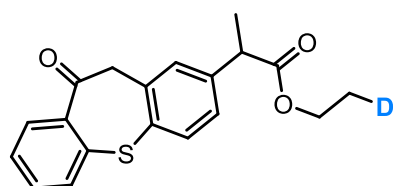


**ethyl-2-d (S)-2-(6-methoxynaphthalen-2-yl)propanoate (2ag):** Followed the GP4 and purified using flash chromatography (petroleum ether/EtOAc = 15:1) to give 36.8 mg of the title compound (white solid; 71% yield); D-inc.: 91% (determined by <sup>1</sup>H NMR).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 7.71 – 7.67 (m, 3H), 7.41 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.15 – 7.11 (m, 2H), 4.18 – 4.06 (m, 2H), 3.91 (s, 3H), 3.83 (q, *J* = 7.1 Hz, 1H), 1.57 (d, *J* = 7.2 Hz, 3H), 1.18 (ddd, *J* = 8.9, 4.4, 1.8 Hz, 2H).

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)** δ 174.8, 157.7, 135.9, 133.7, 129.3, 129.0, 127.2, 126.3, 126.0, 119.0, 105.6, 60.8, 55.4, 45.6, 18.7, 14.2 (C–H), 13.9 (t, *J* = 19.2 Hz, C–D).

**HRMS (ESI)** calcd C<sub>16</sub>H<sub>18</sub>DO<sub>3</sub> [M + H]<sup>+</sup>: 260.1391, found: 260.1392.



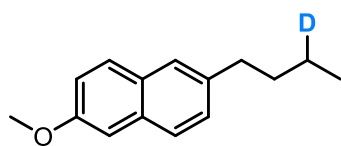
**ethyl-2-d 2-(10-oxo-10,11-dihydrodibenzo[b,f]thiepin-2-yl)propanoate (2ah):** Followed the GP4 and

purified using flash chromatography (petroleum ether/EtOAc = 7:1) to give 43.9 mg of the title compound (colorless oil; 67% yield); D-inc.: 92% (determined by  $^1\text{H}$  NMR).

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.20 (dd,  $J$  = 8.0, 1.5 Hz, 1H), 7.59 (d,  $J$  = 7.9 Hz, 2H), 7.42 (td,  $J$  = 7.7, 1.6 Hz, 1H), 7.38 (d,  $J$  = 1.7 Hz, 1H), 7.33 – 7.29 (m, 1H), 7.15 (dd,  $J$  = 8.0, 1.9 Hz, 1H), 4.36 (s, 2H), 4.16 – 4.05 (m, 2H), 3.70 (q,  $J$  = 7.3 Hz, 1H), 1.47 (d,  $J$  = 7.2 Hz, 3H), 1.22 – 1.16 (m, 2H).

$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  191.3, 173.9, 142.8, 140.2, 137.8, 136.1, 133.1, 131.5, 131.4, 130.8, 128.6, 126.8, 126.3, 60.9, 51.0, 18.5, 14.1 (C–H), 13.8 (t,  $J$  = 19.2 Hz, C–D).

HRMS (ESI) calcd  $\text{C}_{19}\text{H}_{18}\text{DO}_3\text{S}$  [ $\text{M} + \text{H}$ ] $^+$ : 328.1112, found: 328.1110.

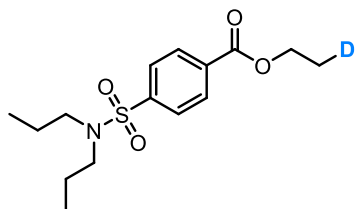


**2-(butyl-3-d)-6-methoxynaphthalene (2ai):** Followed the GP4 and purified using flash chromatography (petroleum ether/EtOAc = 80:1) to give 37.5 mg of the title compound (white solid; 87% yield); D-inc.: 92% (determined by  $^1\text{H}$  NMR).

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.72 (dd,  $J$  = 8.9, 3.3 Hz, 2H), 7.59 (s, 1H), 7.35 (d,  $J$  = 8.3 Hz, 1H), 7.18 – 7.16 (m, 2H), 3.96 (s, 3H), 2.81 – 2.77 (m, 2H), 1.72 (q,  $J$  = 7.6 Hz, 2H), 1.43 (dt,  $J$  = 14.8, 7.9 Hz, 1H), 0.99 (d,  $J$  = 7.3 Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  157.0, 138.1, 132.8, 129.1, 128.8, 127.9, 126.6, 126.1, 118.5, 105.6, 55.3, 35.6, 33.5, 22.4 (C–H), 22.0 (t,  $J$  = 19.2 Hz, C–D), 13.9.

HRMS (ESI) calcd  $\text{C}_{15}\text{H}_{18}\text{DO}$  [ $\text{M} + \text{H}$ ] $^+$ : 216.1493, found: 216.1496.



**ethyl-2-d 4-(N,N-dipropylsulfamoyl)benzoate (2aj):** Followed the GP4 and purified using flash chromatography (petroleum ether/EtOAc = 9:1) to give 40.9 mg of the title compound (colorless oil; 65% yield); D-inc.: 96% (determined by  $^1\text{H}$  NMR).

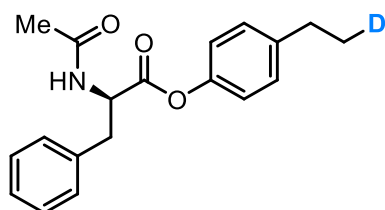
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.16 (d,  $J$  = 8.5 Hz, 2H), 7.87 (d,  $J$  = 8.5 Hz, 2H), 4.41 (t,  $J$  = 7.1



H<sub>z</sub>, 2H), 3.12 – 3.08 (m, 4H), 1.59 – 1.50 (m, 4H), 1.44 – 1.38 (m, 2H), 0.87 (t, *J* = 7.4 Hz, 6H).

<sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 165.2, 144.1, 133.7, 130.1, 126.9, 61.5, 49.9, 21.9, 14.2 (C–H), 14.0 (t, *J* = 19.2 Hz, C–D), 11.1.

HRMS (ESI) calcd C<sub>15</sub>H<sub>23</sub>DNO<sub>4</sub>S [M + H]<sup>+</sup>: 315.1483, found: 315.1488.

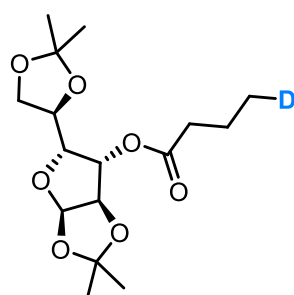


**4-(ethyl-2-d)phenyl acetyl-D-phenylalaninate (2ak):** Followed the GP4 and purified using flash chromatography (petroleum ether/EtOAc = 2:1) to give 46.9 mg of the title compound (colorless oil; 75% yield); D-inc.: 97% (determined by <sup>1</sup>H NMR).

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.28 (m, 3H), 7.22 (d, *J* = 6.7 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 6.04 (s, 1H), 5.15 – 5.09 (m, 1H), 3.32 – 3.22 (m, 2H), 2.63 (t, *J* = 7.5 Hz, 2H), 2.02 (s, 3H), 1.21 (t, *J* = 7.3 Hz, 2H).

<sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 170.5, 169.7, 148.1, 142.2, 135.6, 129.4, 128.8, 128.7, 127.3, 120.9, 53.2, 37.9, 28.2, 23.1, 15.5 (C–H), 15.2 (t, *J* = 19.2 Hz, C–D).

HRMS (ESI) calcd C<sub>19</sub>H<sub>21</sub>DNO<sub>3</sub> [M + H]<sup>+</sup>: 313.1657, found: 313.1655.



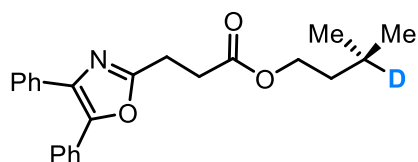
**(1S,2R,5S)-2-isopropyl-5-methylcyclohexyl 4-(ethyl-2-d)benzoate (2al):** Followed the GP4 and purified using flash chromatography (petroleum ether/EtOAc = 9:1) to give 43.1 mg of the title compound (colorless oil; 65% yield); D-inc.: 73% (determined by <sup>1</sup>H NMR).

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 5.87 (d, *J* = 3.6 Hz, 1H), 5.28 (s, 1H), 4.48 (d, *J* = 3.7 Hz, 1H), 4.22 – 4.18 (M, 2H), 4.11 – 4.07 (m, 1H), 4.02 – 3.99 (m, 1H), 2.33 (td, *J* = 7.3, 2.2 Hz, 2H), 1.69 – 1.65 (m,

2H), 1.52 (s, 3H), 1.41 (s, 3H), 1.31 (s, 6H), 0.98 – 0.92 (m, 2H).

<sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 172.2, 112.3, 109.3, 105.1, 83.4, 79.9, 75.8, 72.4, 67.3, 36.1, 26.8, 26.7, 26.2, 25.2, 18.4, 18.3, 13.6 (C–H), 13.3 (t, *J* = 19.2 Hz, C–D).

HRMS (ESI) calcd C<sub>16</sub>H<sub>26</sub>DO<sub>7</sub> [M + H]<sup>+</sup>: 332.1814, found: 332.1816.

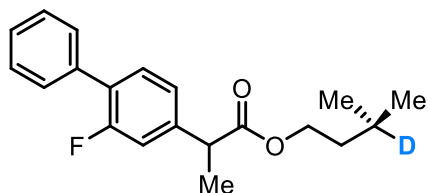


**3-methylbutyl-3-d 3-(4,5-diphenyloxazol-2-yl)propanoate (2am):** Followed the GP4 and purified using flash chromatography (petroleum ether/EtOAc = 9:1) to give 69.3 mg of the title compound (white solid; 95% yield); D-inc.: 92% (determined by <sup>13</sup>C NMR).

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.63 (dd, *J* = 8.0, 1.3 Hz, 2H), 7.57 (dd, *J* = 8.0, 1.4 Hz, 2H), 7.38 – 7.29 (m, 6H), 4.16 (t, *J* = 6.8 Hz, 2H), 3.19 (t, *J* = 7.5 Hz, 2H), 2.91 (t, *J* = 7.5 Hz, 2H), 1.52 (t, *J* = 6.8 Hz, 2H), 0.88 (s, 6H).

<sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 172.1, 161.8, 145.3, 135.1, 132.4, 128.9, 128.6, 128.5, 128.4, 128.0, 127.8, 126.4, 63.4, 37.1, 31.2, 24.9 (C–H), 24.5 (t, *J* = 19.2 Hz, C–D), 23.5, 22.3.

HRMS (ESI) calcd C<sub>23</sub>H<sub>25</sub>DNO<sub>3</sub> [M + H]<sup>+</sup>: 365.1970, found: 265.1974.



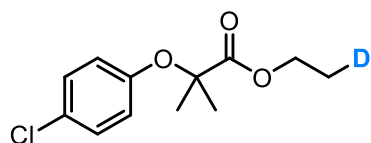
**3-methylbutyl-3-d 2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoate (2an):** Followed the GP4 and purified using flash chromatography (petroleum ether/EtOAc = 80:1) to give 61.8 mg of the title compound (colorless oil; 98% yield); D-inc.: 90% (determined by <sup>13</sup>C NMR).

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 8.1 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.40 – 7.33 (m, 2H), 7.16 – 7.10 (m, 2H), 4.12 (t, *J* = 6.8 Hz, 2H), 3.74 (q, *J* = 7.2 Hz, 1H), 1.53 (d, *J* = 7.2 Hz, 3H), 1.49 (t, *J* = 6.8 Hz, 2H), 0.87 (d, *J* = 3.6 Hz, 6H).

<sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 174.0, 160.8, 158.4, 141.9 (d, *J* = 8.1 Hz), 135.5, 130.7 (d, *J* = 4.0 Hz), 128.9 (d, *J* = 2.0 Hz), 128.4, 127.6, 123.5 (d, *J* = 4.0 Hz), 115.2 (d, *J* = 24.2 Hz), 63.6, 45.1, 37.0, 25.0 (C–H), 24.5 (t, *J* = 19.2 Hz, C–D), 22.2, 18.3.

<sup>19</sup>F NMR (376 MHz, Chloroform-*d*) δ -117.8.

HRMS (ESI) calcd C<sub>20</sub>H<sub>23</sub>DFO<sub>2</sub> [M + H]<sup>+</sup>: 316.1818, found: 316.1820.

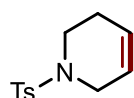


**ethyl-2-d 2-(4-chlorophenoxy)-2-methylpropanoate (2ao):** Followed the general procedure GP4 and purified using flash chromatography (petroleum ether/EtOAc = 50:1) to give 27.3 mg of the title compound (colorless oil; 56% yield); D-inc.: 90% (determined by <sup>1</sup>H NMR).

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.19 (d, *J* = 8.8 Hz, 2H), 6.78 (d, *J* = 8.8 Hz, 2H), 4.23 (t, *J* = 7.0 Hz, 2H), 1.58 (s, 6H), 1.25 – 1.21 (m, 2H).

<sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 174.0, 154.0, 129.1, 127.2, 120.5, 79.4, 61.5, 25.3, 14.1 (C–H), 13.8 (t, *J* = 20.2 Hz, C–D).

HRMS (ESI) calcd C<sub>12</sub>H<sub>15</sub>DClO<sub>3</sub> [M + H]<sup>+</sup>: 244.0845, found: 244.0850.

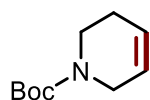


**1-tosyl-1,2,3,6-tetrahydropyridine (3a):** Followed the general procedure GP5 and purified using flash chromatography (petroleum ether/EtOAc = 25:1) to give 34.1 mg of the title compound (white solid.; 72% yield).

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 5.80 – 5.71 (m, 1H), 5.61 (d, *J* = 10.1 Hz, 1H), 3.60 – 3.54 (m, 2H), 3.17 (t, *J* = 5.7 Hz, 2H), 2.43 (s, 3H), 2.25 – 2.18 (m, 2H).

<sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 143.5, 133.4, 129.6, 127.7, 125.1, 122.7, 44.8, 42.6, 25.3, 21.51.

HRMS (ESI) calcd C<sub>12</sub>H<sub>16</sub>NO<sub>2</sub>S [M + H]<sup>+</sup>: 238.0896, found: 238.0894.

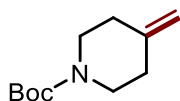


**tert-butyl 3,6-dihydropyridine-1(2H)-carboxylate (3b):** Followed the GP5 and purified using flash chromatography (petroleum ether/EtOAc = 100:1) to give 27.5 mg of the title compound (colorless oil; 75% yield).

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 5.80 (s, 1H), 5.65 (s, 1H), 3.87 (s, 2H), 3.47 (m, *J* = 5.7 Hz, 2H), 2.12 (s, 2H), 1.46 (s, 9H).

$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  155.1, 125.3, 124.5, 79.5, 43.7, 43.3, 41.0, 39.7, 28.5, 25.2.

HRMS (ESI) calcd  $\text{C}_{10}\text{H}_{18}\text{NO}_2$   $[\text{M} + \text{H}]^+$ : 184.1332, found: 184.1336.

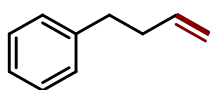


**tert-butyl 4-methylenepiperidine-1-carboxylate (3c):** Followed the GP5 and purified using flash chromatography (petroleum ether/EtOAc = 100:1) to give 31.9 mg of the title compound (colorless oil; 81% yield).

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  4.74 (s, 2H), 3.41 (t,  $J$  = 5.8 Hz, 4H), 2.17 (t,  $J$  = 5.8 Hz, 4H), 1.46 (s, 9H).

$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  154.8, 145.4, 109.1, 79.6, 45.5, 34.6, 28.5.

HRMS (ESI) calcd  $\text{C}_{11}\text{H}_{20}\text{NO}_2$   $[\text{M} + \text{H}]^+$ : 198.1489, found: 198.1487.

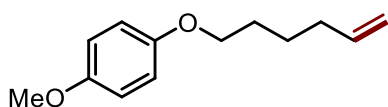


**but-3-en-1-ylbenzene (3d):** Followed the GP5 and purified using flash chromatography (petroleum ether/EtOAc = 100:1) to give 14.0 mg of the title compound (colorless oil; 53% yield).

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.32 – 7.26 (m, 2H), 7.22 – 7.16 (m, 3H), 6.03 – 5.70 (m, 1H), 5.20 – 4.83 (m, 2H), 2.75 – 2.68 (m, 2H), 2.38 (q,  $J$  = 7.2 Hz, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  141.9, 138.2, 128.5, 128.3, 125.9, 115.0, 35.6, 35.4.

HRMS (ESI) calcd  $\text{C}_{10}\text{H}_{13}$   $[\text{M} + \text{H}]^+$ : 133.1012, found: 133.1010.

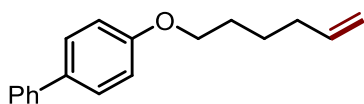


**1-(hex-5-en-1-yloxy)-4-methoxybenzene (3e):** Followed the GP5 and purified using flash chromatography (petroleum ether/EtOAc = 80:1) to give 30.5 mg of the title compound (colorless oil; 74% yield).

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  6.83 (s, 4H), 5.89 – 5.77 (m, 1H), 5.08 – 4.92 (m, 2H), 3.91 (t,  $J$  = 6.5 Hz, 2H), 3.77 (s, 3H), 2.12 (q,  $J$  = 7.2 Hz, 2H), 1.78 (dt,  $J$  = 15.1, 6.6 Hz, 2H), 1.57 – 1.52 (m, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  153.7, 153.3, 138.7, 115.5, 114.7, 68.5, 55.8, 33.5, 28.9, 25.4.

HRMS (ESI) calcd  $\text{C}_{13}\text{H}_{19}\text{O}_2$   $[\text{M} + \text{H}]^+$ : 207.1380, found: 207.1385.

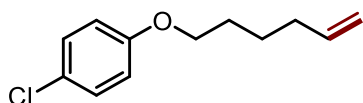


**4-(hex-5-en-1-yloxy)-1,1'-biphenyl (3f):** Followed the GP5 and purified using flash chromatography (petroleum ether/EtOAc = 50:1) to give 32.4 mg of the title compound (colorless oil; 64% yield).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 7.60 – 7.48 (m, 4H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 1H), 6.97 (d, *J* = 8.8 Hz, 2H), 5.92 – 5.77 (m, 1H), 5.10 – 4.95 (m, 2H), 4.01 (t, *J* = 6.2 Hz, 2H), 2.15 (d, *J* = 7.3 Hz, 2H), 1.88 – 1.79 (m, 2H), 1.65 – 1.55 (m, 2H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 158.6, 140.8, 138.5, 133.5, 128.7, 128.1, 126.7, 126.6, 114.7, 67.8, 33.4, 28.7, 25.3.

**HRMS (ESI)** calcd C<sub>18</sub>H<sub>21</sub>O [M + H]<sup>+</sup>: 253.1587, found: 253.1588.

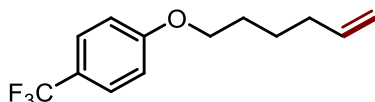


**1-chloro-4-(hex-5-en-1-yloxy)benzene (3g):** Followed the GP5 and purified using flash chromatography (petroleum ether/EtOAc = 50:1) to give 27.7 mg of the title compound (colorless oil; 66% yield).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 7.25 – 7.19 (m, 2H), 6.84 – 6.77 (m, 2H), 5.90 – 5.73 (m, 1H), 5.08 – 4.93 (m, 2H), 3.93 (t, *J* = 6.5 Hz, 2H), 2.18 – 2.07 (m, 2H), 1.78 (dt, *J* = 8.4, 6.6 Hz, 2H), 1.58 – 1.54 (m, 2H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 157.7, 138.5, 129.3, 125.4, 115.8, 114.8, 68.1, 33.5, 28.7, 25.3.

**HRMS (ESI)** calcd C<sub>12</sub>H<sub>16</sub>ClO [M + H]<sup>+</sup>: 211.0884, found: 211.0882.



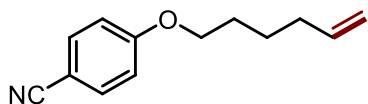
**1-(hex-5-en-1-yloxy)-4-(trifluoromethyl)benzene (3h):** Followed the GP5 and purified using flash chromatography (petroleum ether/EtOAc = 50:1) to give 31.2 mg of the title compound (colorless oil; 64% yield).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 7.53 (d, *J* = 8.5 Hz, 2H), 6.94 (d, *J* = 8.5 Hz, 2H), 5.90 – 5.76 (m, 1H), 5.09 – 4.93 (m, 2H), 4.00 (t, *J* = 6.4 Hz, 2H), 2.13 (q, *J* = 7.2 Hz, 2H), 1.88 – 1.77 (m, 2H), 1.63 – 1.52 (m, 2H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 161.57, 138.44, 126.9 (q, *J* = 4.0 Hz), 114.94, 114.44, 68.04, 33.43, 28.57, 25.28.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -61.4.

**HRMS (ESI)** calcd C<sub>13</sub>H<sub>16</sub>F<sub>3</sub>O [M + H]<sup>+</sup>: 245.1148, found: 245.1145.

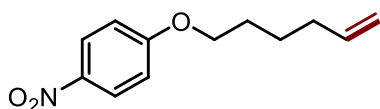


**4-(hex-5-en-1-yloxy)benzonitrile (3i):** Followed the GP5 and purified using flash chromatography (petroleum ether/EtOAc = 50:1) to give 27.3 mg of the title compound (colorless oil; 68% yield).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.61 (d, *J* = 8.8 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 5.93 – 5.78 (m, 1H), 5.12 – 4.98 (m, 2H), 4.04 (t, *J* = 6.4 Hz, 2H), 2.17 (q, *J* = 7.1 Hz, 2H), 1.92 – 1.80 (m, 2H), 1.61 (m, 2H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  162.4, 138.3, 134.0, 119.4, 115.2, 115.0, 103.7, 68.2, 33.4, 28.5, 25.2.

**HRMS (ESI)** calcd C<sub>13</sub>H<sub>16</sub>NO [M + H]<sup>+</sup>: 202.1226, found: 202.1228.

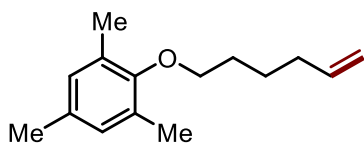


**1-(hex-5-en-1-yloxy)-4-nitrobenzene (3j):** Followed the GP5 and purified using flash chromatography (petroleum ether/EtOAc = 50:1) to give 29.6 mg of the title compound (yellow oil; 67% yield).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**  $\delta$  8.22 – 8.17 (m, 2H), 6.99 – 6.90 (m, 2H), 5.90 – 5.74 (m, 1H), 5.10 – 4.95 (m, 2H), 4.06 (t, *J* = 6.4 Hz, 2H), 2.14 (q, *J* = 7.0 Hz, 2H), 1.88 – 1.79 (m, 2H), 1.65 – 1.52 (m, 2H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  164.2, 141.4, 138.3, 126.0, 115.1, 114.4, 68.7, 33.4, 28.4, 25.2.

**HRMS (ESI)** calcd C<sub>12</sub>H<sub>16</sub>NO<sub>3</sub> [M + H]<sup>+</sup>: 222.1125, found: 222.1128.

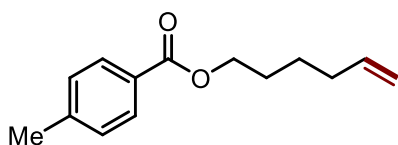


**2-(hex-5-en-1-yloxy)-1,3,5-trimethylbenzene (3k):** Followed the GP5 and purified using flash chromatography (petroleum ether/EtOAc = 50:1) to give 29.7 mg of the title compound (colorless oil; 68% yield).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**  $\delta$  6.81 (s, 2H), 5.91 – 5.78 (m, 1H), 5.08 – 4.93 (m, 2H), 3.73 (t, *J* = 6.5 Hz, 2H), 2.23 (s, 9H), 2.18 – 2.10 (m, 2H), 1.85 – 1.76 (m, 2H), 1.67 – 1.59 (m, 2H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  153.8, 138.7, 132.9, 130.6, 129.4, 114.7, 72.2, 33.7, 29.9, 25.6, 20.7, 16.2.

**HRMS (ESI)** calcd C<sub>15</sub>H<sub>23</sub>O [M + H]<sup>+</sup>: 219.1743, found: 219.1748.

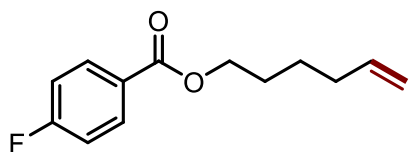


**hex-5-en-1-yl 4-methylbenzoate (3l):** Followed the GP5 and purified using flash chromatography (petroleum ether/EtOAc = 80:1) to give 27.5 mg of the title compound (colorless oil; 63% yield).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 7.95 – 7.91 (m, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 5.96 – 5.71 (m, 1H), 5.14 – 4.90 (m, 2H), 4.31 (t, *J* = 6.6 Hz, 2H), 2.41 (s, 3H), 2.13 (q, *J* = 7.1 Hz, 2H), 1.90 – 1.70 (m, 2H), 1.57 – 1.53 (m, 2H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 166.8, 143.5, 138.5, 129.6, 129.1, 127.8, 114.9, 64.8, 33.4, 28.3, 25.4, 21.7.

**HRMS (ESI)** calcd C<sub>14</sub>H<sub>19</sub>O<sub>2</sub> [M + H]<sup>+</sup>: 219.1380, found: 219.1385.



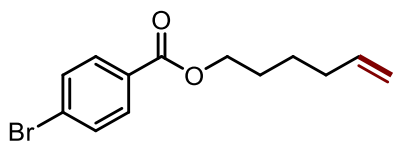
**hex-5-en-1-yl 4-fluorobenzoate (3m):** Followed the GP5 and purified using flash chromatography (petroleum ether/EtOAc = 50:1) to give 29.8 mg of the title compound (colorless oil; 67% yield).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 8.09 – 8.02 (m, 2H), 7.15 – 7.06 (m, 2H), 5.90 – 5.75 (m, 1H), 5.09 – 4.94 (m, 2H), 4.31 (t, *J* = 6.6 Hz, 2H), 2.17 – 2.09 (m, 2H), 1.83 – 1.74 (m, 2H), 1.61 – 1.50 (m, 2H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 165.8 (d, *J* = 254.5 Hz), 165.7, 138.4, 132.1 (d, *J* = 9.1 Hz), 126.7 (d, *J* = 3.0 Hz), 115.5 (d, *J* = 22.2 Hz), 115.0, 65.1, 33.4, 28.2, 25.3.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -105.9.

**HRMS (ESI)** calcd C<sub>13</sub>H<sub>16</sub>FO<sub>2</sub> [M + H]<sup>+</sup>: 223.1129, found: 223.1131.

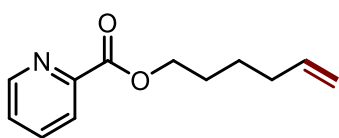


**hex-5-en-1-yl 4-bromobenzoate (3n):** Followed the GP5 and purified using flash chromatography (petroleum ether/EtOAc = 50:1) to give 35.0 mg of the title compound (colorless oil; 62% yield).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 7.93 – 7.87 (m, 2H), 7.60 – 7.55 (m, 2H), 6.02 – 5.64 (m, 1H), 5.14 – 4.87 (m, 2H), 4.32 (t, *J* = 6.6 Hz, 2H), 2.19 – 2.08 (m, 2H), 1.83 – 1.73 (m, 2H), 1.58 – 1.52 (m, 2H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 166.0, 138.3, 131.7, 131.1, 129.4, 128.0, 115.0, 65.2, 33.4, 28.2, 25.3.

**HRMS (ESI)** calcd C<sub>13</sub>H<sub>16</sub>BrO<sub>2</sub> [M + H]<sup>+</sup>: 283.0328, found: 283.0325.

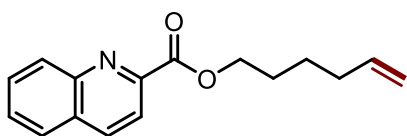


**hex-5-en-1-yl picolinate (3o):** Followed the GP5 and purified using flash chromatography (petroleum ether/EtOAc = 15:1) to give 29.9 mg of the title compound (colorless oil; 73% yield).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 8.77 (d, *J* = 4.8 Hz, 1H), 8.13 (d, *J* = 7.8 Hz, 1H), 7.84 (t, *J* = 6.9 Hz, 1H), 7.51 – 7.43 (m, 1H), 5.86 – 5.76 (m, 1H), 5.07 – 4.92 (m, 2H), 4.42 (t, *J* = 6.8 Hz, 2H), 2.12 (q, *J* = 7.1 Hz, 2H), 1.85 (dt, *J* = 15.1, 7.0 Hz, 2H), 1.58 – 1.52 (m, 2H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 165.3, 150.0, 148.3, 138.3, 137.0, 126.9, 125.2, 115.0, 66.0, 33.4, 28.2, 25.2.

**HRMS (ESI)** calcd C<sub>12</sub>H<sub>16</sub>NO<sub>2</sub> [M + H]<sup>+</sup>: 206.1176, found: 206.1173.

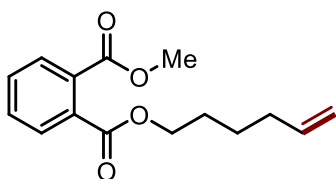


**hex-5-en-1-yl quinoline-2-carboxylate (3p):** Followed the GP5 and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 33.1 mg of the title compound (colorless oil; 65% yield).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 8.34 (t, *J* = 8.1 Hz, 2H), 8.20 (d, *J* = 8.6 Hz, 1H), 7.91 (d, *J* = 7.9 Hz, 1H), 7.86 – 7.77 (m, 1H), 7.68 (t, *J* = 7.6 Hz, 1H), 5.93 – 5.78 (m, 1H), 5.12 – 4.97 (m, 2H), 4.53 (t, *J* = 6.9 Hz, 2H), 2.18 (q, *J* = 7.2 Hz, 2H), 1.99 – 1.86 (m, 2H), 1.62 (q, *J* = 7.8 Hz, 2H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 165.5, 148.3, 147.7, 138.4, 137.3, 130.9, 130.3, 129.3, 128.6, 127.6, 121.1, 115.0, 66.2, 33.4, 28.2, 25.3.

**HRMS (ESI)** calcd C<sub>16</sub>H<sub>18</sub>NO<sub>2</sub> [M + H]<sup>+</sup>: 256.1332, found: 256.1336.



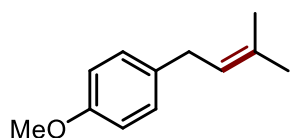
**hex-5-en-1-yl methyl phthalate (3q):** Followed the GP5 and purified using flash chromatography (petroleum ether/EtOAc = 10:1) to give 30.4 mg of the title compound (colorless oil; 58% yield).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 7.76 – 7.68 (m, 2H), 7.57 – 7.51 (m, 2H), 5.89 – 5.74 (m, 1H), 5.06 – 4.94 (m, 2H), 4.35 – 4.27 (m, 2H), 3.90 (s, 2H), 2.16 – 2.07 (m, 2H), 1.81 – 1.71 (m, 2H), 1.56 – 1.47 (m, 2H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 168.2, 167.7, 138.3, 132.2, 132.1, 131.1, 129.0, 115.0, 65.7, 52.7, 33.3, 28.0, 25.2.



**HRMS (ESI)** calcd C<sub>15</sub>H<sub>18</sub>O<sub>4</sub> [M + H]<sup>+</sup>: 263.1278, found: 263.1275.

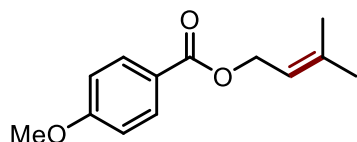


**1-methoxy-4-(3-methylbut-2-en-1-yl)benzene (3r):** Followed the GP5 and purified using flash chromatography (petroleum ether/EtOAc = 50:1) to give 26.1 mg of the title compound (colorless oil; 74% yield).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 7.09 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 8.3 Hz, 2H), 5.30 (t, *J* = 6.8 Hz, 1H), 3.78 (s, 3H), 3.28 (d, *J* = 7.3 Hz, 2H), 1.72 (d, *J* = 10.2 Hz, 6H).

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)** δ 157.7, 133.9, 132.2, 129.1, 123.6, 113.7, 55.3, 17.8.

**HRMS (ESI)** calcd C<sub>12</sub>H<sub>17</sub>O [M + H]<sup>+</sup>: 177.1274, found: 177.1272.

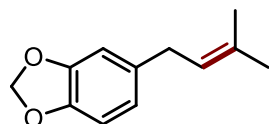


**3-methylbut-2-en-1-yl 4-methoxybenzoate (3s):** Followed the GP5 and purified using flash chromatography (petroleum ether/EtOAc = 50:1) to give 31.3 mg of the title compound (colorless oil; 71% yield).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 8.00 (d, *J* = 8.9 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 5.46 (t, *J* = 7.2 Hz, 1H), 4.79 (d, *J* = 7.2 Hz, 2H), 3.86 (s, 3H), 1.78 (d, *J* = 8.1 Hz, 6H).

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)** δ 166.4, 163.2, 138.9, 131.6, 122.9, 118.8, 113.5, 61.6, 55.4, 25.8, 18.1.

**HRMS (ESI)** calcd C<sub>13</sub>H<sub>17</sub>O<sub>3</sub> [M + H]<sup>+</sup>: 221.1172, found: 221.1175.

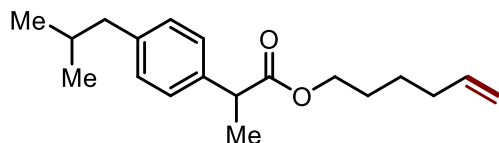


**3-methylbut-2-en-1-yl 4-methoxybenzoate (3t):** Followed the GP5 and purified using flash chromatography (petroleum ether/EtOAc = 100:1) to give 24.7 mg of the title compound (colorless oil; 65% yield).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 6.72 (d, *J* = 7.9 Hz, 1H), 6.67 (s, 1H), 6.63 (d, *J* = 8.5 Hz, 1H), 5.91 (s, 2H), 5.28 (t, *J* = 7.4 Hz, 1H), 3.25 (d, *J* = 7.4 Hz, 2H), 1.74 (s, 3H), 1.70 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  147.5, 145.5, 135.7, 132.5, 123.3, 120.8, 108.8, 108.1, 34.0, 25.7.

HRMS (ESI) calcd  $\text{C}_{12}\text{H}_{15}\text{O}_2$   $[\text{M} + \text{H}]^+$ : 191.1067, found: 191.1065.

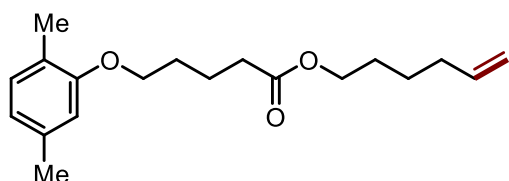


**hex-5-en-1-yl 2-(4-isobutylphenyl)propanoate (3u):** Followed the GP5 and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 25.9 mg of the title compound (colorless oil; 45% yield).

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.23 – 7.18 (m, 2H), 7.11 – 7.05 (m, 2H), 5.81 – 5.67 (m, 1H), 5.04 – 4.91 (m, 2H), 4.06 (t,  $J$  = 6.6 Hz, 2H), 3.68 (q,  $J$  = 7.2 Hz, 1H), 2.44 (d,  $J$  = 7.1 Hz, 2H), 2.05 – 1.96 (m, 2H), 1.90 – 1.78 (m, 1H), 1.60 – 1.57 (m, 2H), 1.49 (d,  $J$  = 7.2 Hz, 3H), 1.41 – 1.29 (m, 2H), 0.89 (d,  $J$  = 6.6 Hz, 6H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.9, 140.5, 138.4, 137.9, 129.3, 127.2, 114.8, 64.6, 45.3, 45.1, 33.2, 30.3, 28.0, 25.1, 22.5, 18.5.

HRMS (ESI) calcd  $\text{C}_{19}\text{H}_{29}\text{O}_2$   $[\text{M} + \text{H}]^+$ : 289.2162, found: 289.2166.

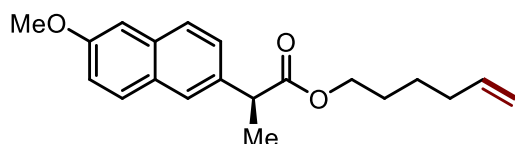


**hex-5-en-1-yl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (3v):** Followed the GP5 and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 26.2 mg of the title compound (colorless oil; 43% yield).

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.01 (d,  $J$  = 7.4 Hz, 1H), 6.66 (d,  $J$  = 6.9 Hz, 1H), 6.61 (s, 1H), 5.87 – 5.73 (m, 1H), 5.06 – 4.93 (m, 2H), 4.07 (t,  $J$  = 6.6 Hz, 2H), 3.96 – 3.88 (m, 2H), 2.31 (s, 3H), 2.18 (s, 3H), 2.12 – 2.05 (m, 2H), 1.73 (d,  $J$  = 2.2 Hz, 4H), 1.69 – 1.59 (m, 2H), 1.51 – 1.43 (m, 2H), 1.22 (s, 6H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  177.9, 157.0, 138.4, 136.5, 130.3, 123.6, 120.7, 114.9, 111.9, 68.0, 64.4, 42.2, 37.2, 33.3, 28.1, 25.3, 21.5, 15.9.

HRMS (ESI) calcd  $\text{C}_{32}\text{H}_{33}\text{O}_3$   $[\text{M} + \text{H}]^+$ : 305.2111, found: 305.2107.

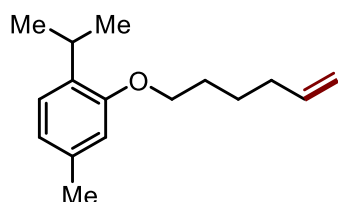


**hex-5-en-1-yl 2-(6-methoxynaphthalen-2-yl)propanoate (3w):** Followed the GP5 and purified using flash chromatography (petroleum ether/EtOAc = 50:1) to give 35.0 mg of the title compound (colorless oil; 56% yield).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.75 – 7.65 (m, 3H), 7.42 (d, *J* = 8.5 Hz, 1H), 7.18 – 7.10 (m, 2H), 5.77 – 5.64 (m, 1H), 4.99 – 4.88 (m, 2H), 4.08 (t, *J* = 6.6 Hz, 2H), 3.91 (s, 3H), 3.86 (q, *J* = 7.2 Hz, 1H), 2.04 – 1.96 (m, 2H), 1.62 – 1.54 (m, 5H), 1.40 – 1.30 (m, 2H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  174.8, 157.6, 138.4, 135.9, 133.7, 129.3, 129.0, 127.1, 126.3, 126.0, 119.0, 114.8, 105.6, 64.7, 55.4, 45.6, 33.2, 28.0, 25.1, 18.6.

**HRMS (ESI)** calcd C<sub>20</sub>H<sub>25</sub>O<sub>3</sub> [M + H]<sup>+</sup>: 313.1798, found: 313.1795.

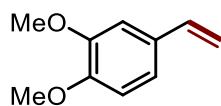


**2-(hex-5-en-1-yloxy)-1-isopropyl-4-methylbenzene (3x):** Followed the GP5 and purified using flash chromatography (petroleum ether/EtOAc = 80:1) to give 25.6 mg of the title compound (yellow oil; 55% yield).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.10 (d, *J* = 7.7 Hz, 1H), 6.74 (d, *J* = 7.7 Hz, 1H), 6.66 (s, 1H), 5.91 – 5.79 (m, 1H), 5.09 – 4.96 (m, 2H), 3.96 (t, *J* = 6.3 Hz, 2H), 3.33 – 3.26 (m, 1H), 2.33 (s, 3H), 2.15 (q, *J* = 7.4 Hz, 2H), 1.88 – 1.78 (m, 2H), 1.65 – 1.58 (m, 2H), 1.21 (d, *J* = 6.9 Hz, 6H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  156.2, 138.7, 136.3, 134.1, 125.9, 120.9, 114.7, 112.2, 67.6, 33.5, 29.0, 26.7, 25.6, 22.8, 21.4.

**HRMS (ESI)** calcd C<sub>16</sub>H<sub>25</sub>O [M + H]<sup>+</sup>: 233.1900, found: 233.1903.

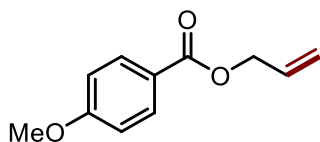


**1,2-dimethoxy-4-vinylbenzene (3y):** Followed the GP5 and purified using flash chromatography (petroleum ether/EtOAc = 50:1) to give 27.9 mg of the title compound (colorless oil; 85% yield).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.00 – 6.91 (m, 2H), 6.83 (d, *J* = 8.2 Hz, 1H), 6.66 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.62 (dd, *J* = 17.6, 0.9 Hz, 1H), 5.15 (d, *J* = 10.9 Hz, 1H), 3.90 (d, *J* = 9.1 Hz, 6H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  149.2, 149.1, 136.5, 130.8, 119.5, 111.9, 111.1, 108.5, 56.0, 55.9.

**HRMS (ESI)** calcd C<sub>10</sub>H<sub>13</sub>O<sub>2</sub> [M + H]<sup>+</sup>: 165.0910, found: 165.0912.

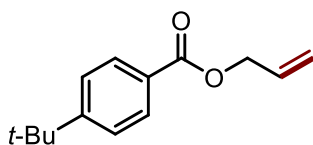


**allyl 4-methoxybenzoate (3z):** Followed the GP5 and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 30.4 mg of the title compound (colorless oil; 79% yield).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 8.02 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 6.09 – 5.98 (m, 1H), 5.40 (d, *J* = 17.2 Hz, 1H), 5.28 (d, *J* = 10.2 Hz, 1H), 4.80 (d, *J* = 5.7 Hz, 2H), 3.86 (s, 3H).

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)** δ 166.1, 163.4, 132.5, 131.7, 122.6, 118.1, 113.7, 65.3, 55.5.

**HRMS (ESI)** calcd C<sub>11</sub>H<sub>13</sub>O<sub>3</sub> [M + H]<sup>+</sup>: 193.0859, found: 193.0856.

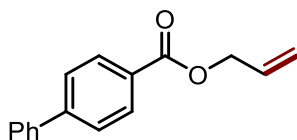


**allyl 4-(tert-butyl)benzoate (3aa):** Followed the GP5 and purified using flash chromatography (petroleum ether/EtOAc = 50:1) to give 31.8 mg of the title compound (colorless oil; 73% yield).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 7.99 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 6.15 – 5.95 (m, 1H), 5.40 (d, *J* = 17.2 Hz, 1H), 5.28 (d, *J* = 10.4 Hz, 1H), 4.82 (d, *J* = 5.6 Hz, 2H), 1.34 (s, 9H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 166.4, 156.7, 132.4, 129.6, 127.4, 125.4, 118.0, 65.4, 35.1, 31.2.

**HRMS (ESI)** calcd C<sub>14</sub>H<sub>19</sub>O<sub>2</sub> [M + H]<sup>+</sup>: 219.1308, found: 219.1309.

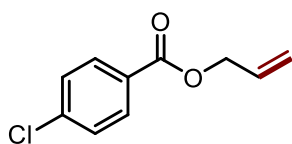


**allyl [1,1'-biphenyl]-4-carboxylate (3ab):** Followed the GP5 and purified using flash chromatography (petroleum ether/EtOAc = 50:1) to give 36.2 mg of the title compound (colorless oil; 76% yield).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 8.16 – 8.11 (m, 2H), 7.71 – 7.59 (m, 4H), 7.52 – 7.43 (m, 2H), 7.43 – 7.36 (m, 1H), 6.14 – 5.97 (m, 1H), 5.48 – 5.39 (m, 1H), 5.34 – 5.27 (m, 1H), 4.88 – 4.83 (m, 2H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 166.2, 145.8, 140.1, 132.3, 130.2, 129.0, 128.2, 127.4, 127.1, 118.3, 65.6.

**HRMS (ESI)** calcd C<sub>16</sub>H<sub>15</sub>O<sub>2</sub> [M + H]<sup>+</sup>: 239.1067, found: 239.1069.



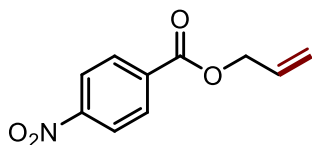
**allyl 4-chlorobenzoate (3ac):** Followed the GP5 and purified using flash chromatography (petroleum

ether/EtOAc = 50:1) to give 29.0 mg of the title compound (colorless oil; 74% yield).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 8.00 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 6.08 – 5.98 (m, 1H), 5.41 (d, *J* = 17.2 Hz, 1H), 5.30 (d, *J* = 10.4 Hz, 1H), 4.82 (d, *J* = 5.6 Hz, 2H).

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)** δ 165.5, 139.5, 132.0, 131.1, 128.8, 128.6, 118.6, 65.9.

**HRMS (ESI)** calcd C<sub>10</sub>H<sub>10</sub>O<sub>2</sub> [M + H]<sup>+</sup>: 197.0364, found: 197.0368.

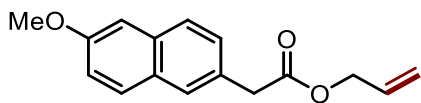


**allyl 4-nitrobenzoate (3ad):** Followed the GP5 and purified using flash chromatography (petroleum ether/EtOAc = 50:1) to give 31.0 mg of the title compound (colorless oil; 75% yield).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 8.30 (d, *J* = 8.7 Hz, 2H), 8.23 (d, *J* = 8.7 Hz, 2H), 6.12 – 5.97 (m, 1H), 5.44 (d, *J* = 17.1 Hz, 1H), 5.34 (d, *J* = 10.5 Hz, 1H), 4.87 (d, *J* = 5.8 Hz, 2H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 164.4, 150.6, 135.6, 131.6, 130.8, 123.6, 119.3, 66.5.

**HRMS (ESI)** calcd C<sub>10</sub>H<sub>10</sub>NO<sub>4</sub> [M + H]<sup>+</sup>: 208.0604, found: 208.0601.



**allyl 2-(6-methoxynaphthalen-2-yl)acetate (3ae):** Followed the GP5 and purified using flash chromatography (petroleum ether/EtOAc = 50:1) to give 36.3 mg of the title compound (colorless oil; 71% yield).

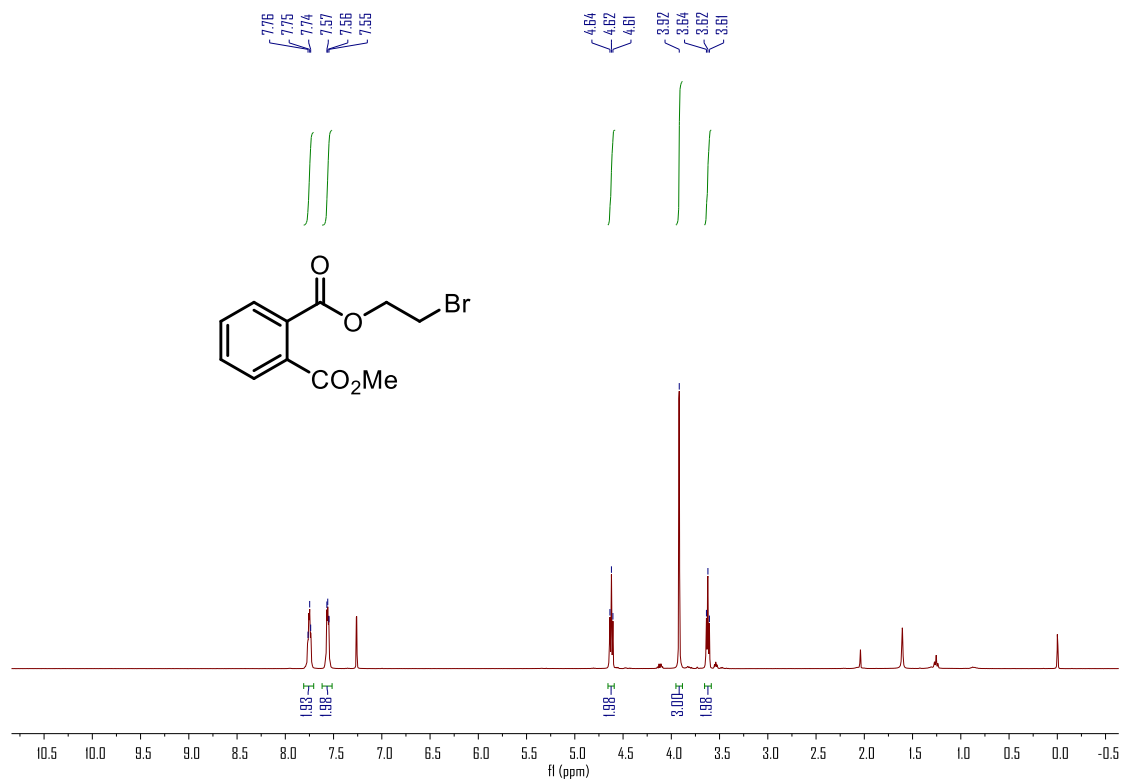
**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 7.73 – 7.66 (m, 3H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.14 (d, *J* = 9.5 Hz, 2H), 5.98 – 5.83 (m, 1H), 5.33 – 5.18 (m, 1H), 4.61 (d, *J* = 6.0 Hz, 2H), 3.92 (s, 3H), 3.78 (s, 2H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 171.5, 157.7, 133.7, 132.1, 129.2, 129.1, 129.0, 127.9, 127.9, 127.1, 119.0, 118.3, 105.6, 65.6, 55.4, 41.4.

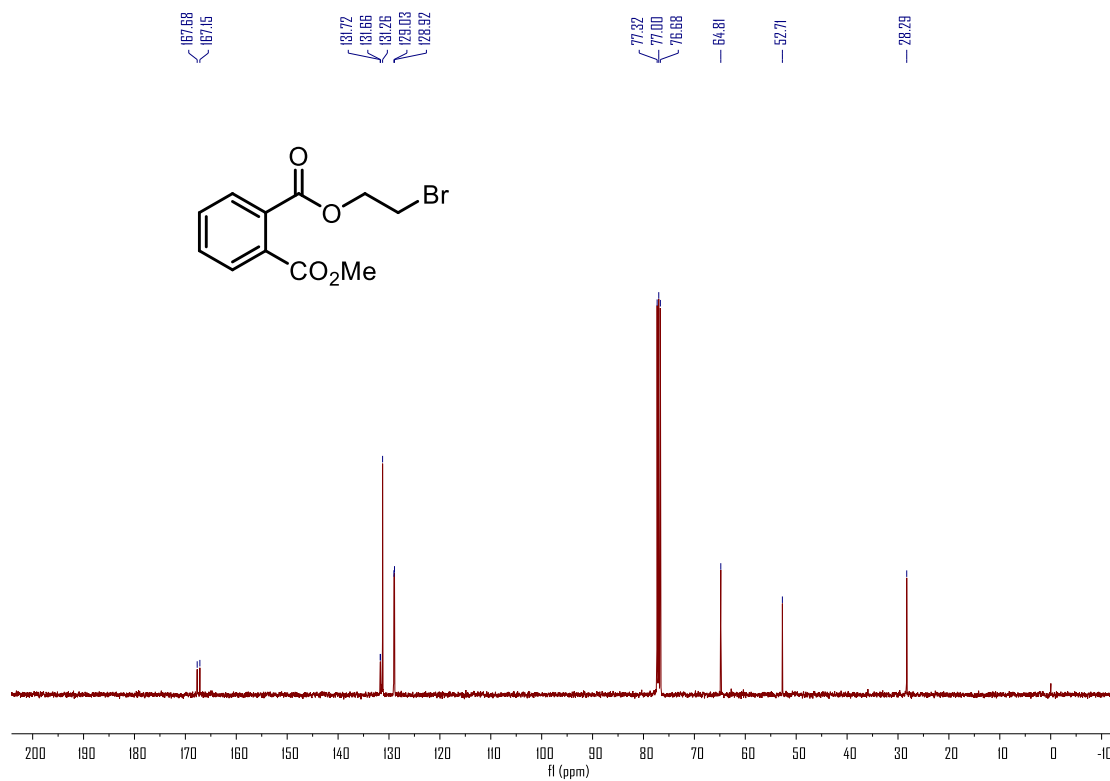
**HRMS (ESI)** calcd C<sub>16</sub>H<sub>16</sub>O<sub>3</sub> [M + H]<sup>+</sup>: 256.1099, found: 256.1097.

## 8. NMR Spectra

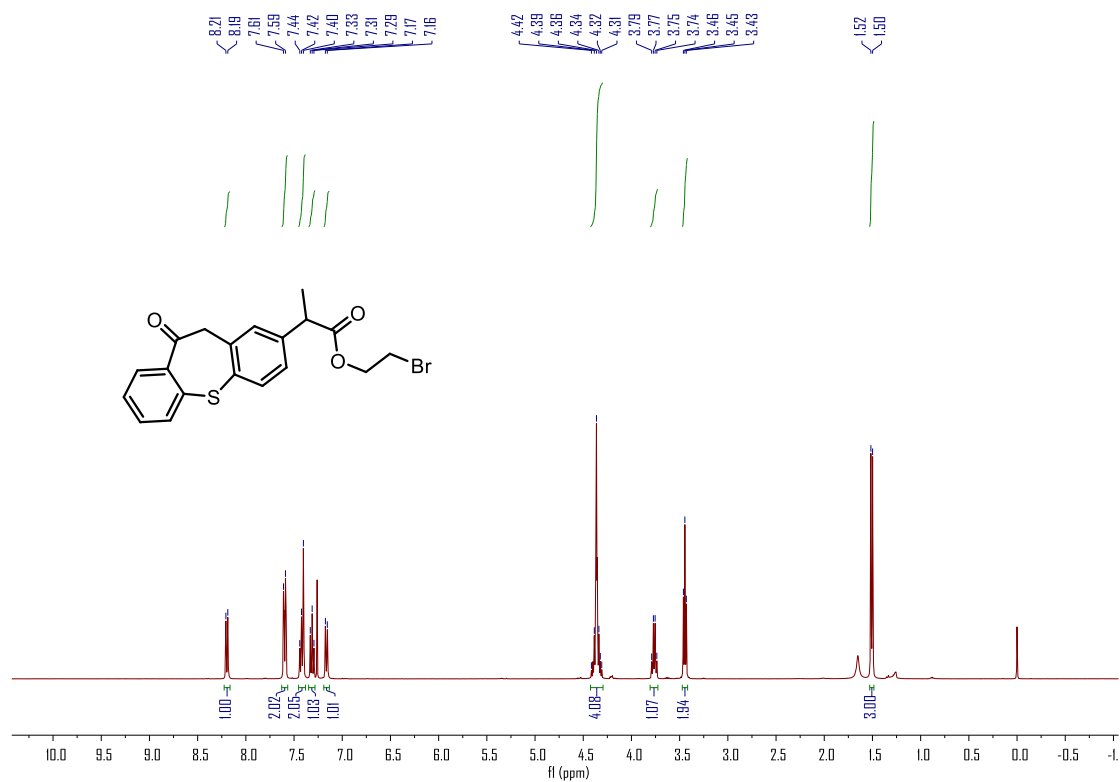
$^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of **11**



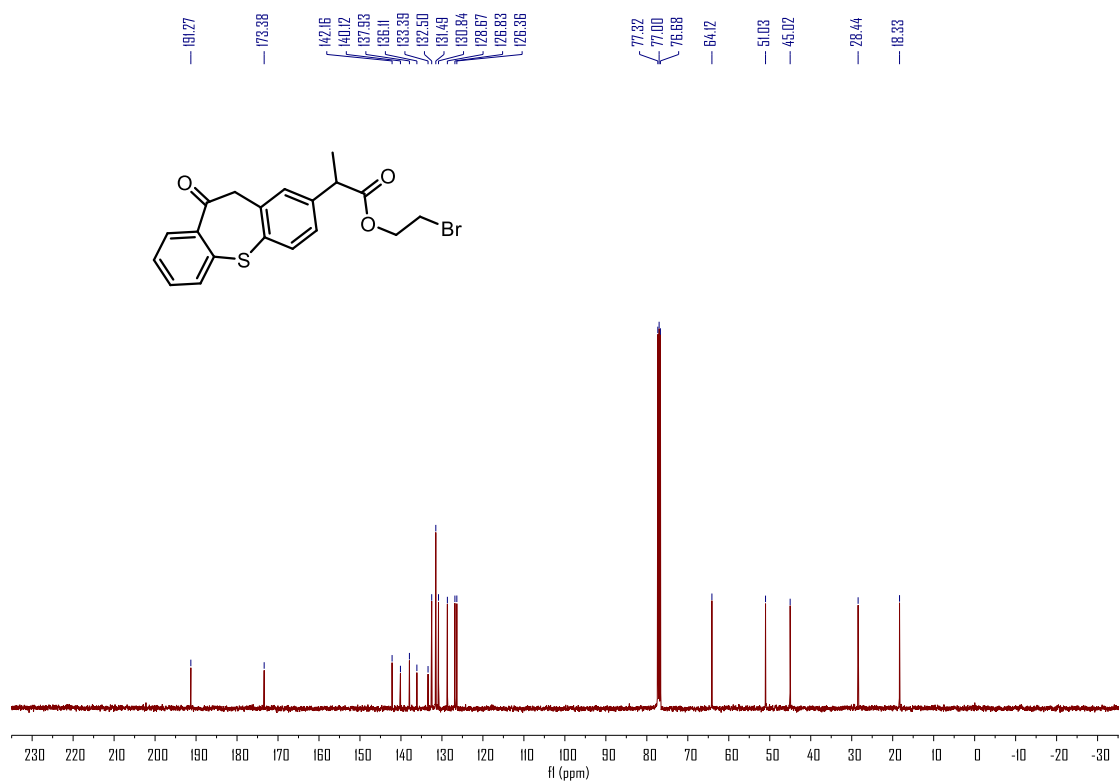
$^{13}\text{C}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of **11**



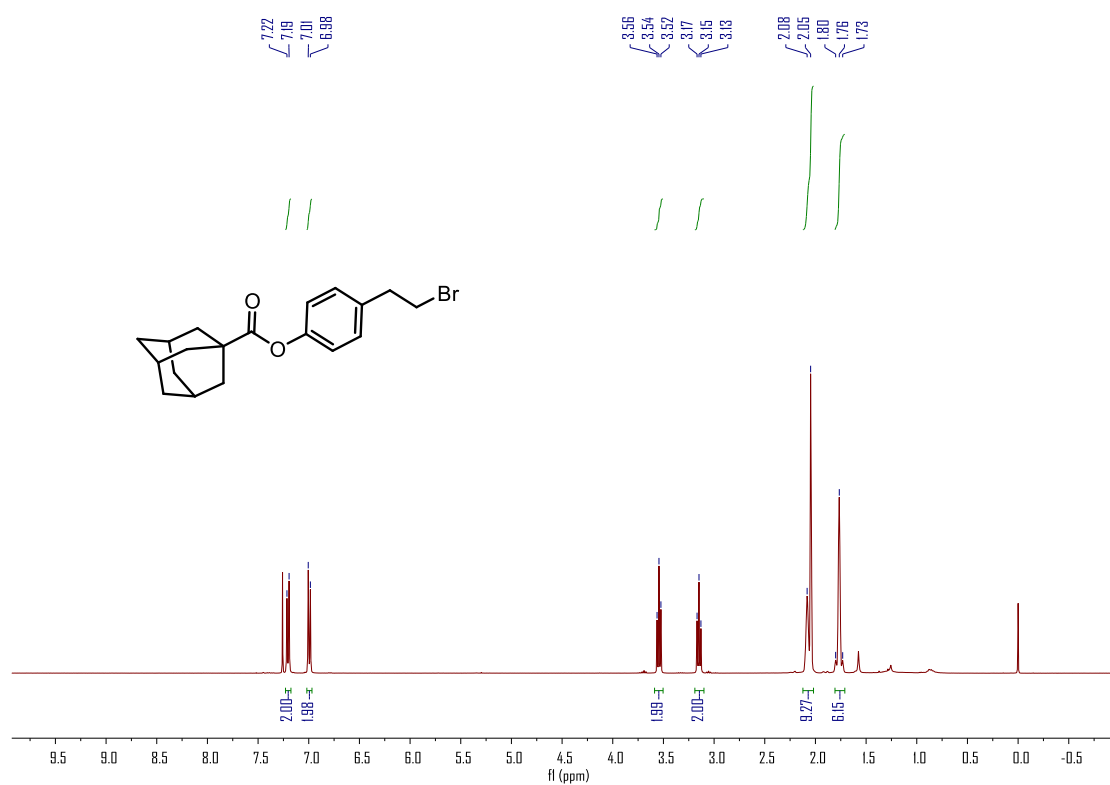
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **1ah**



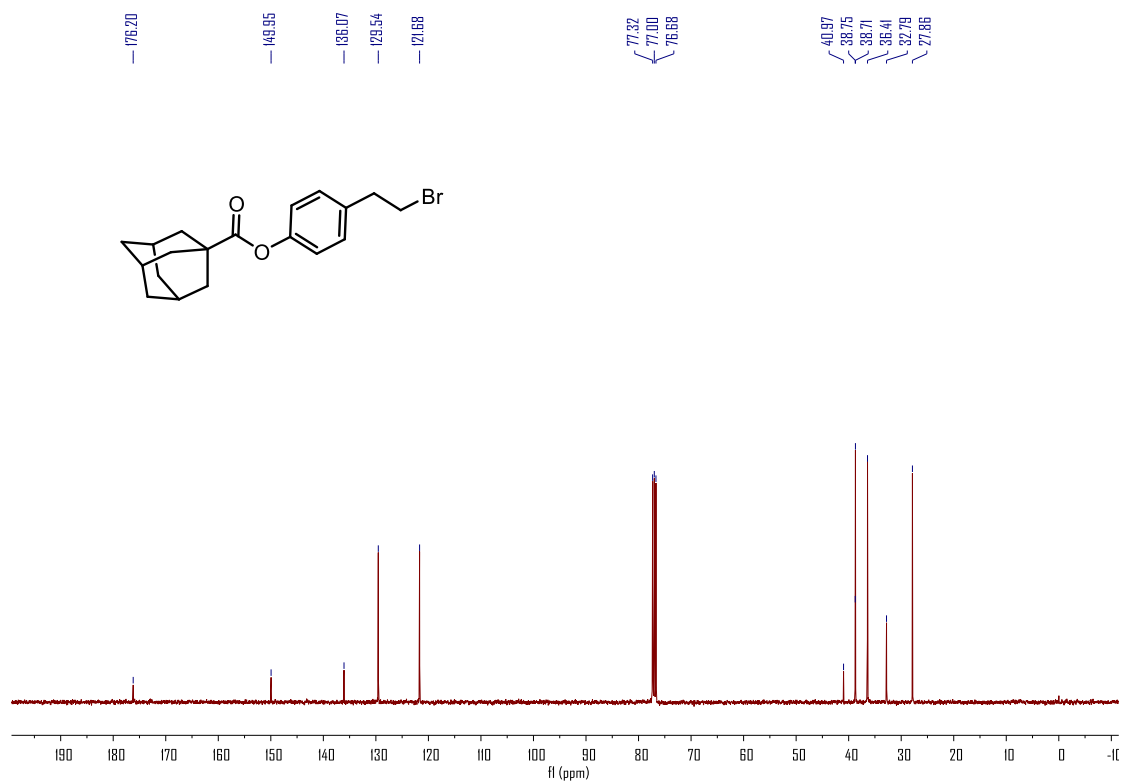
<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **1ah**



<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **1o**

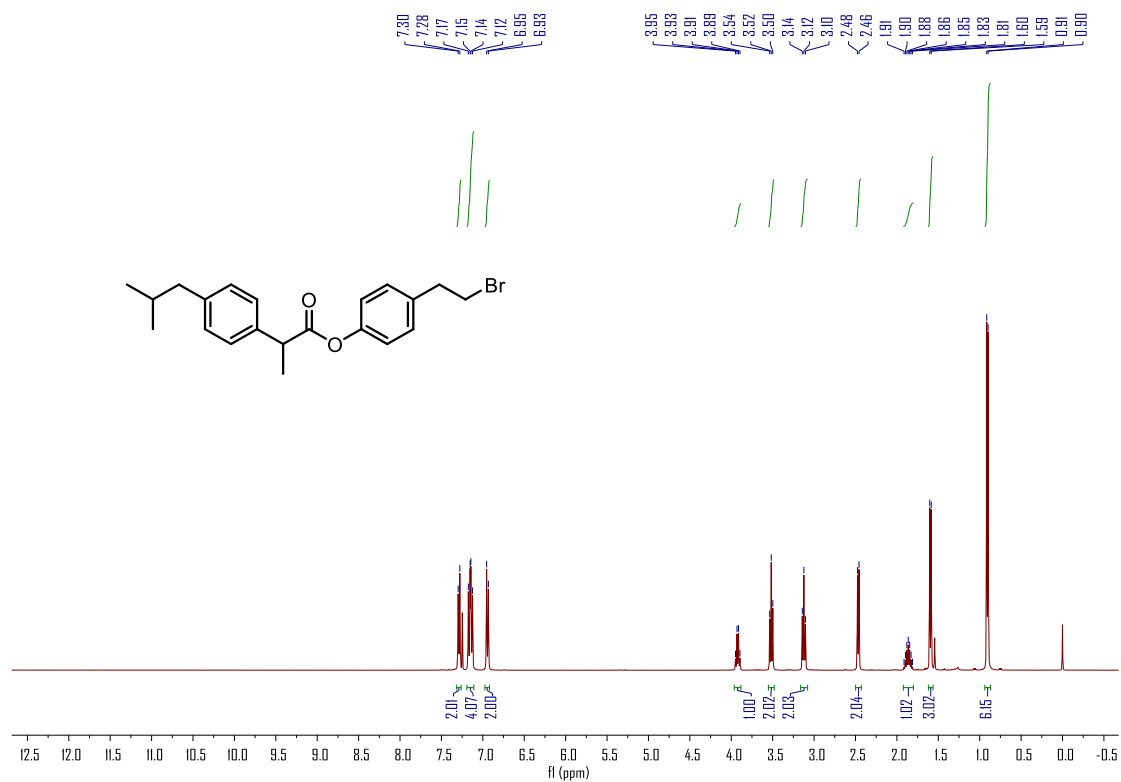


<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **1o**

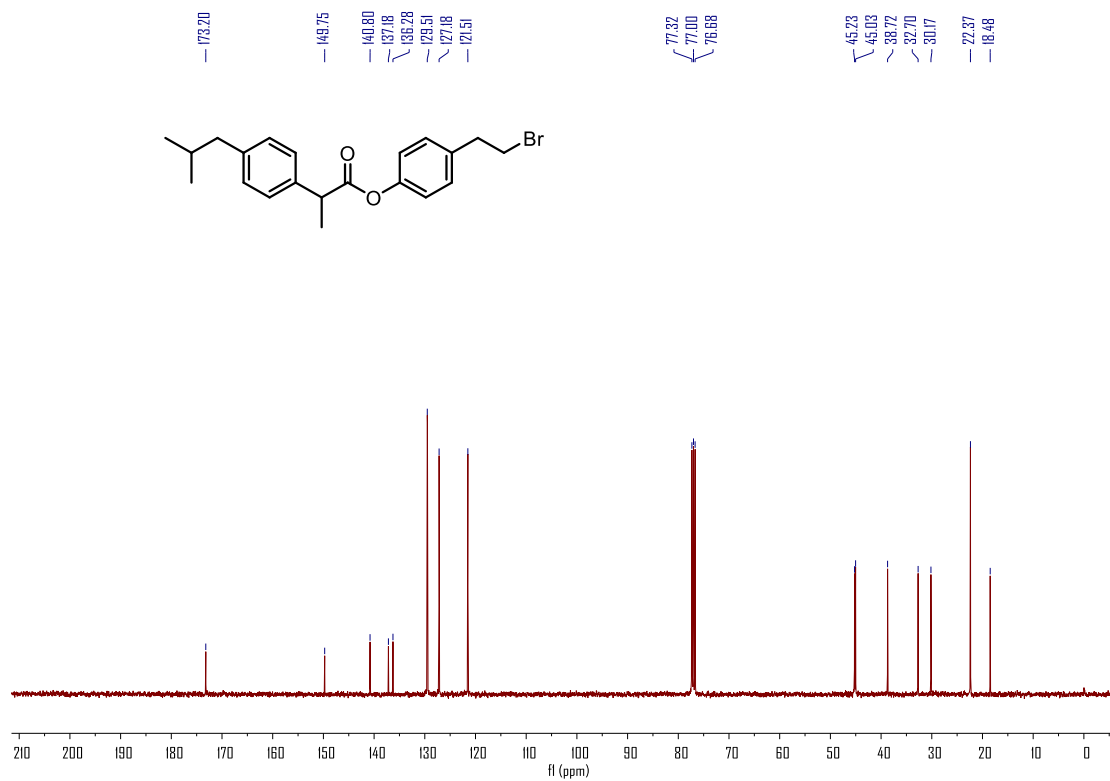




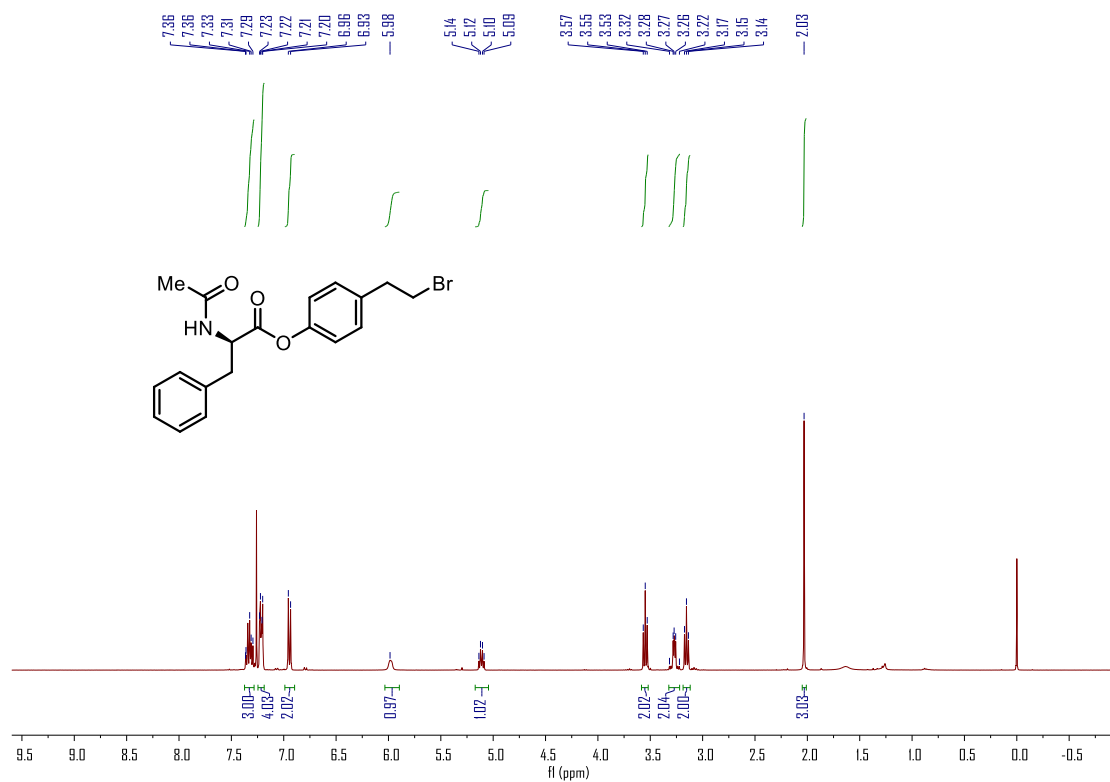
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **1af**



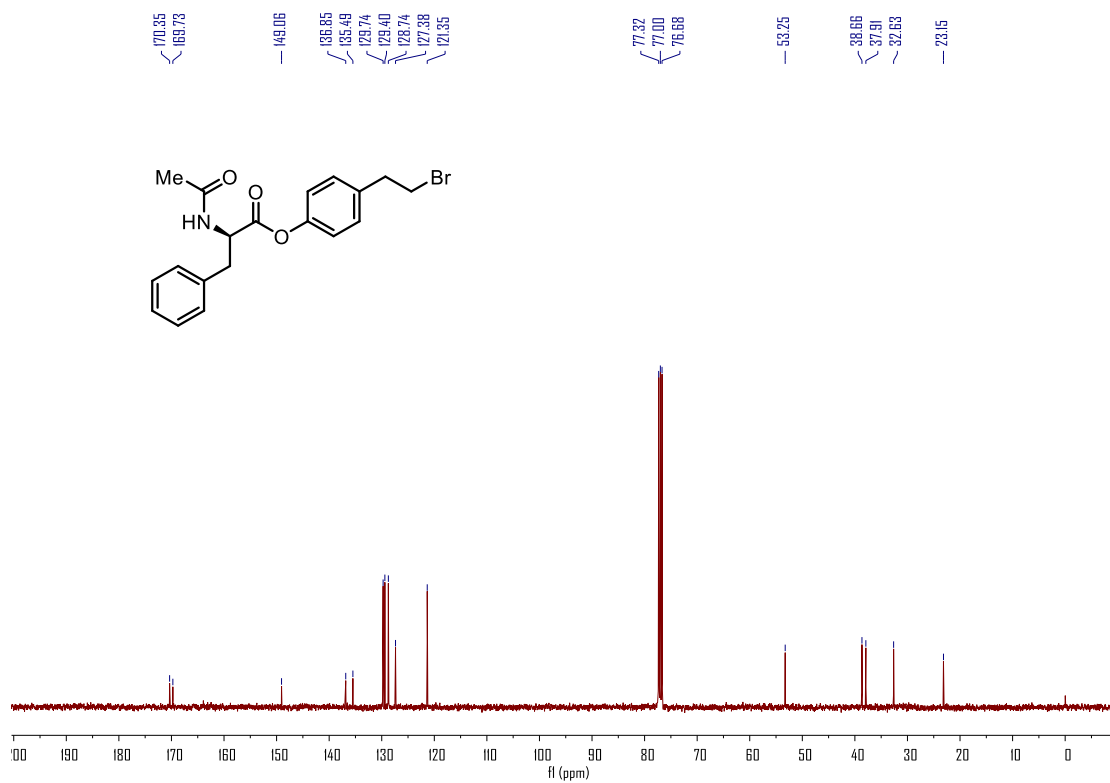
<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **1af**



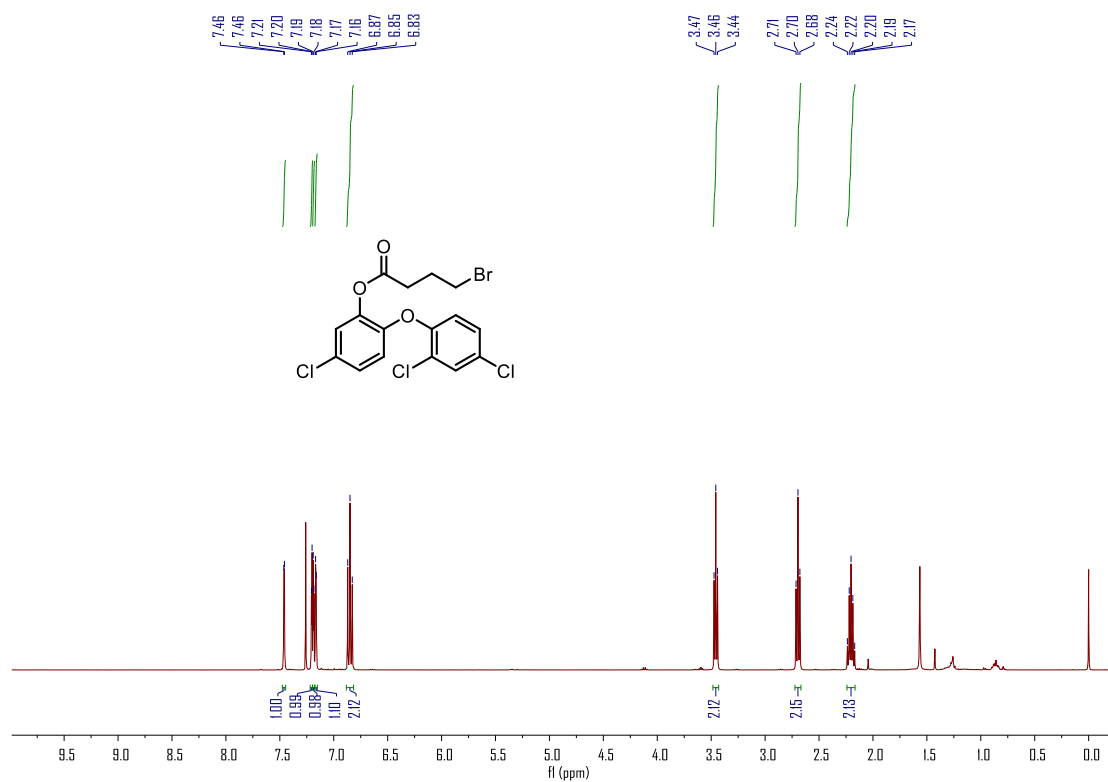
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **1ak**



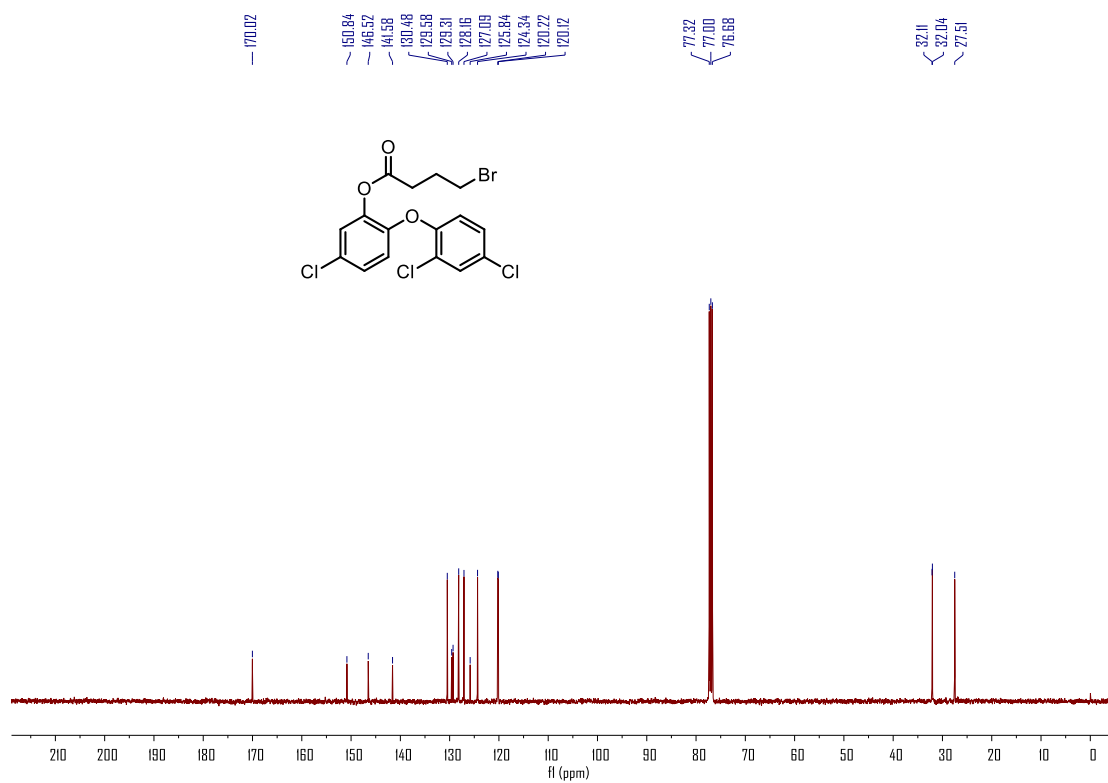
<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **1ak**



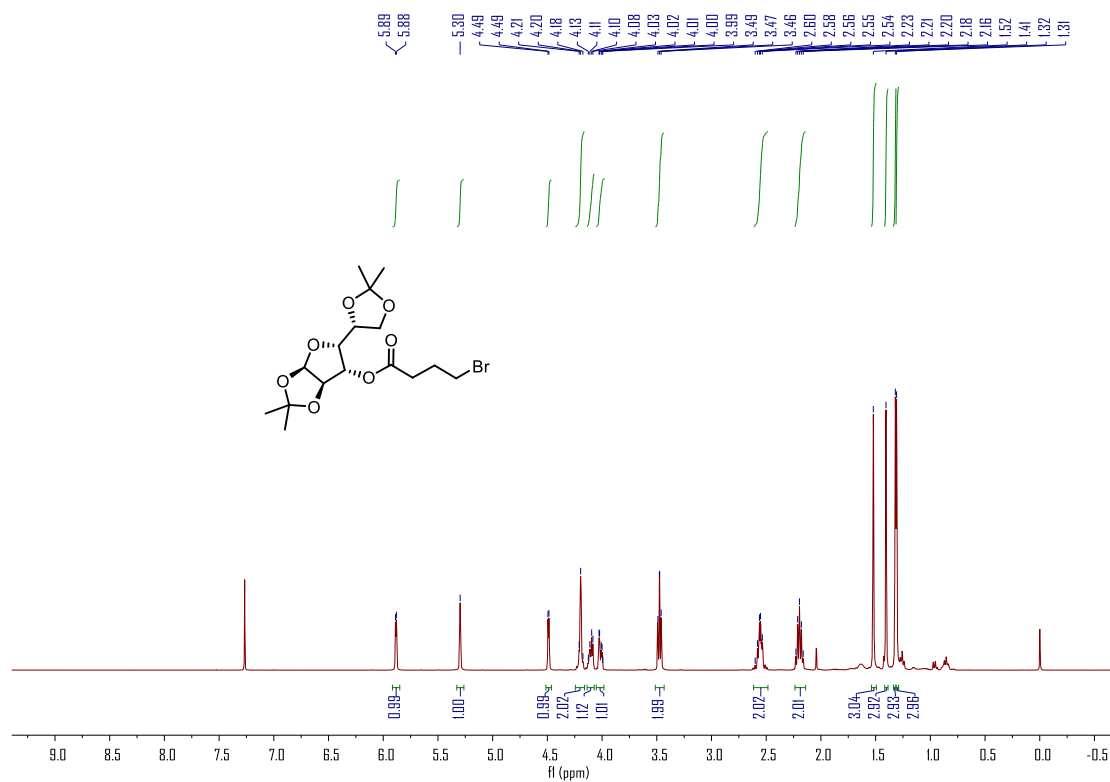
$^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of **1ad**



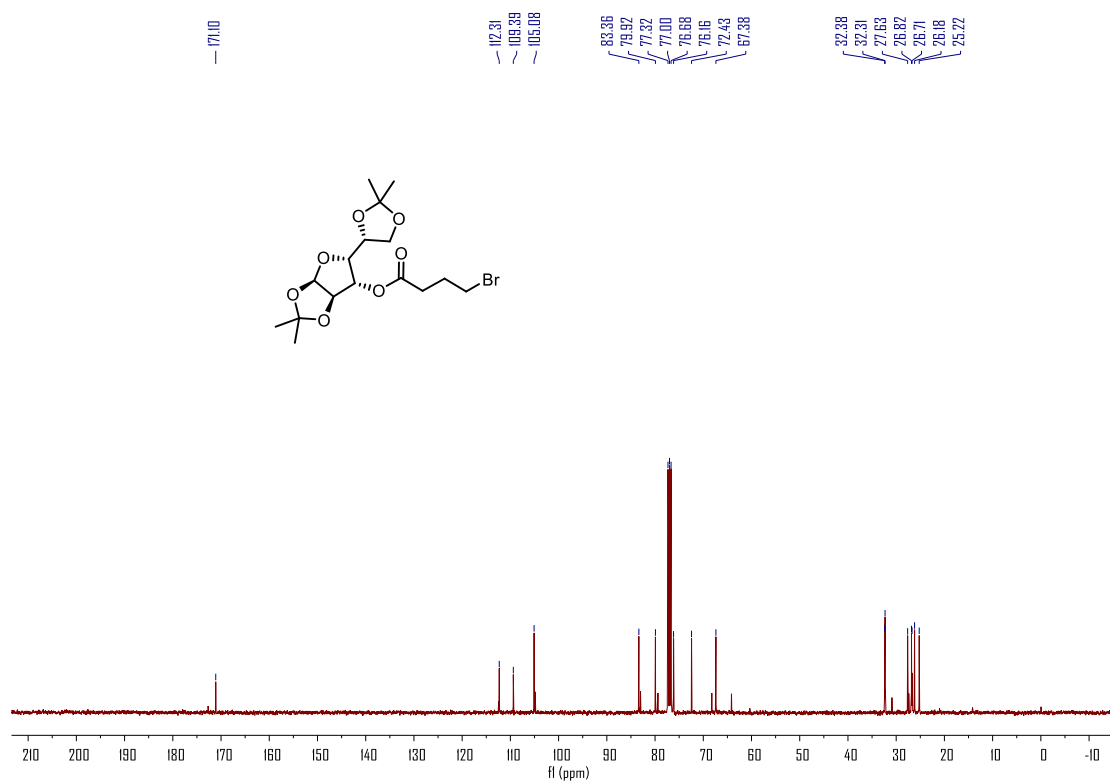
$^{13}\text{C}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of **1ad**



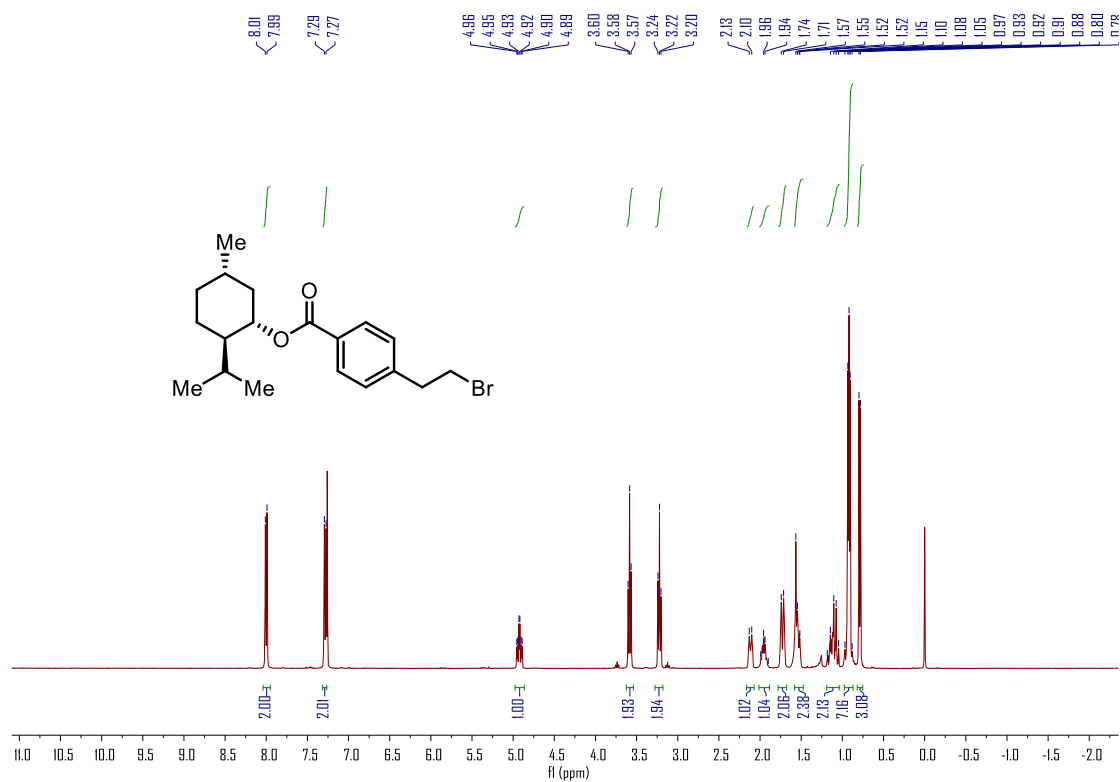
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **1a**



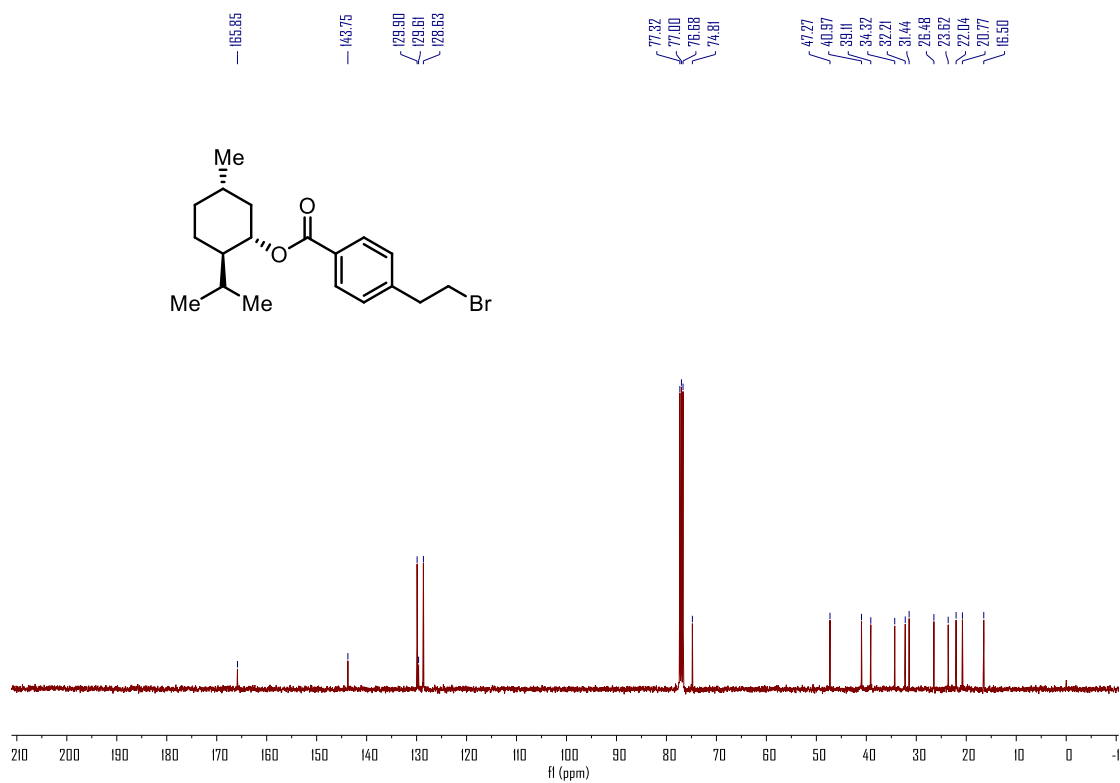
<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **1a**



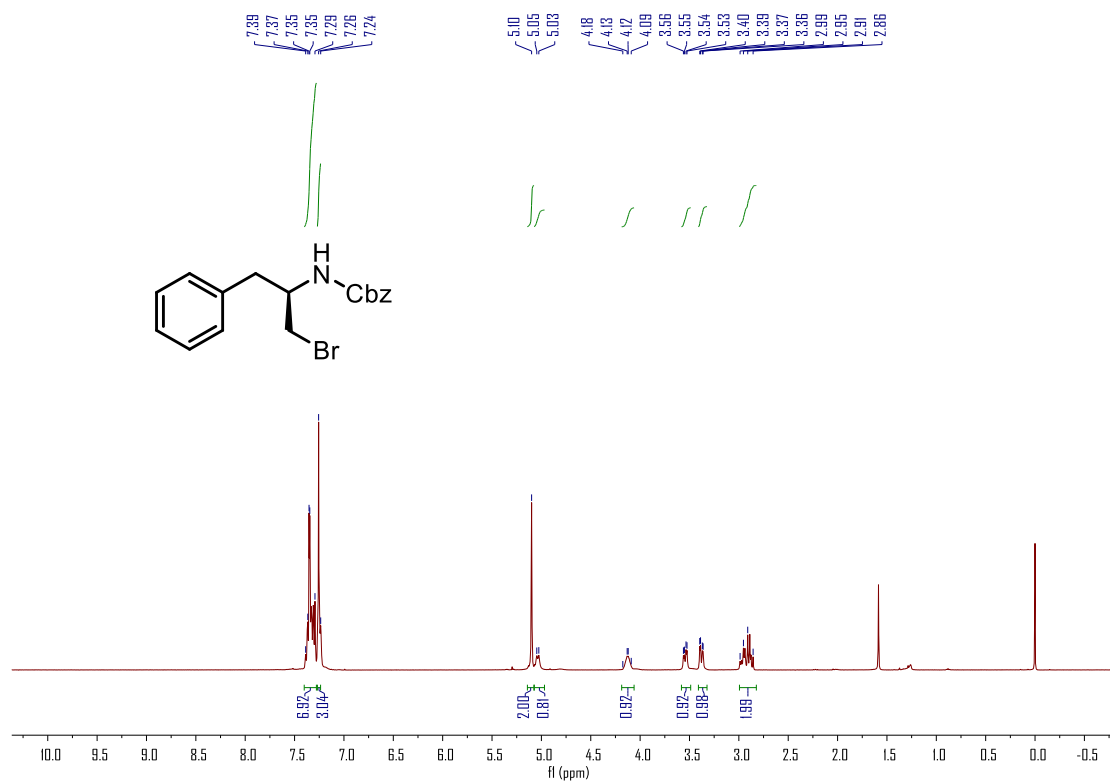
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **1ae**



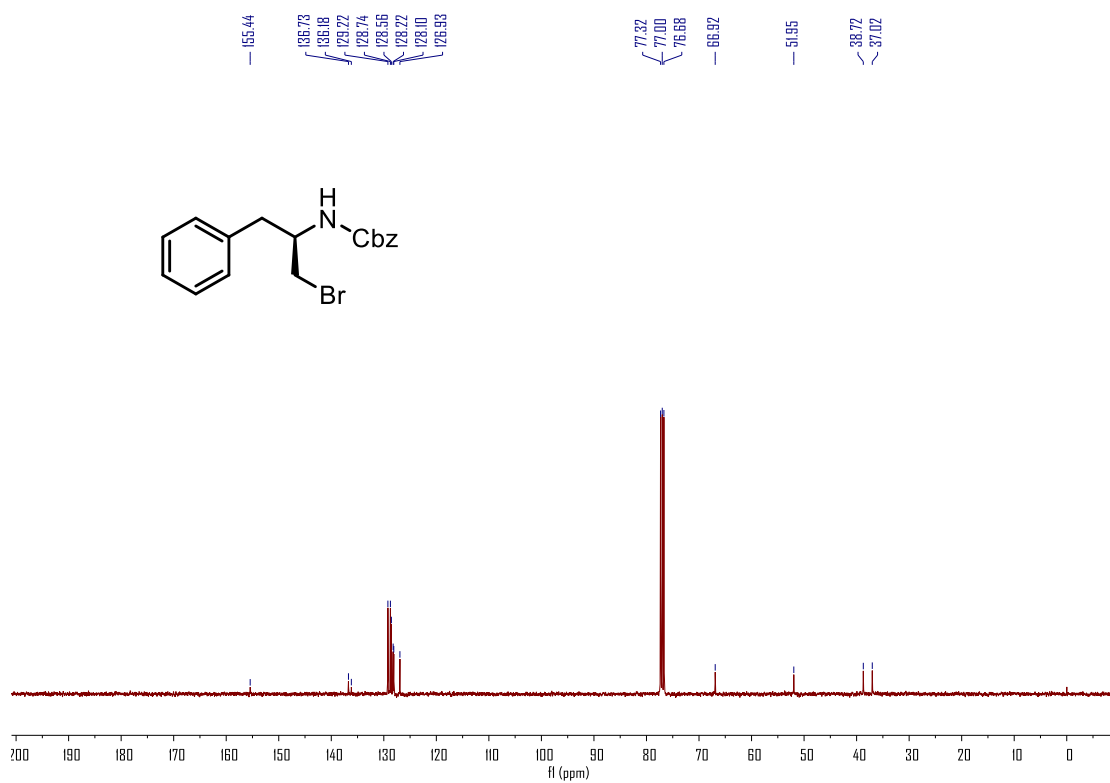
<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **1ae**



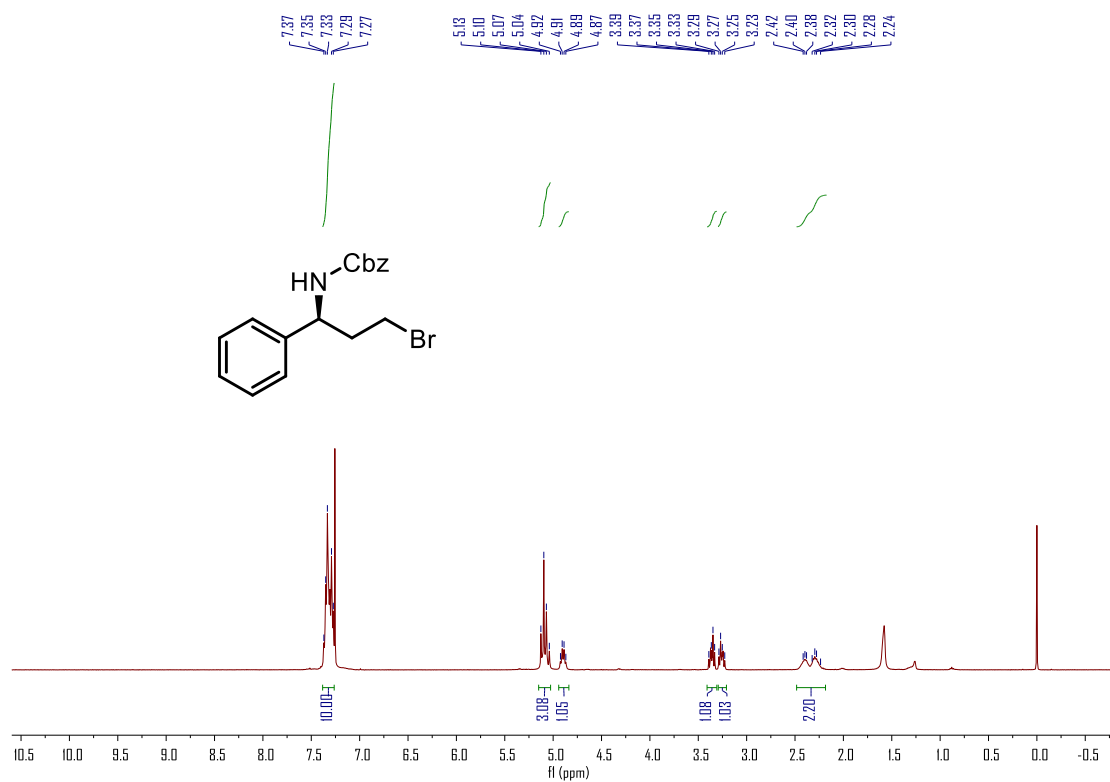
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **1m**



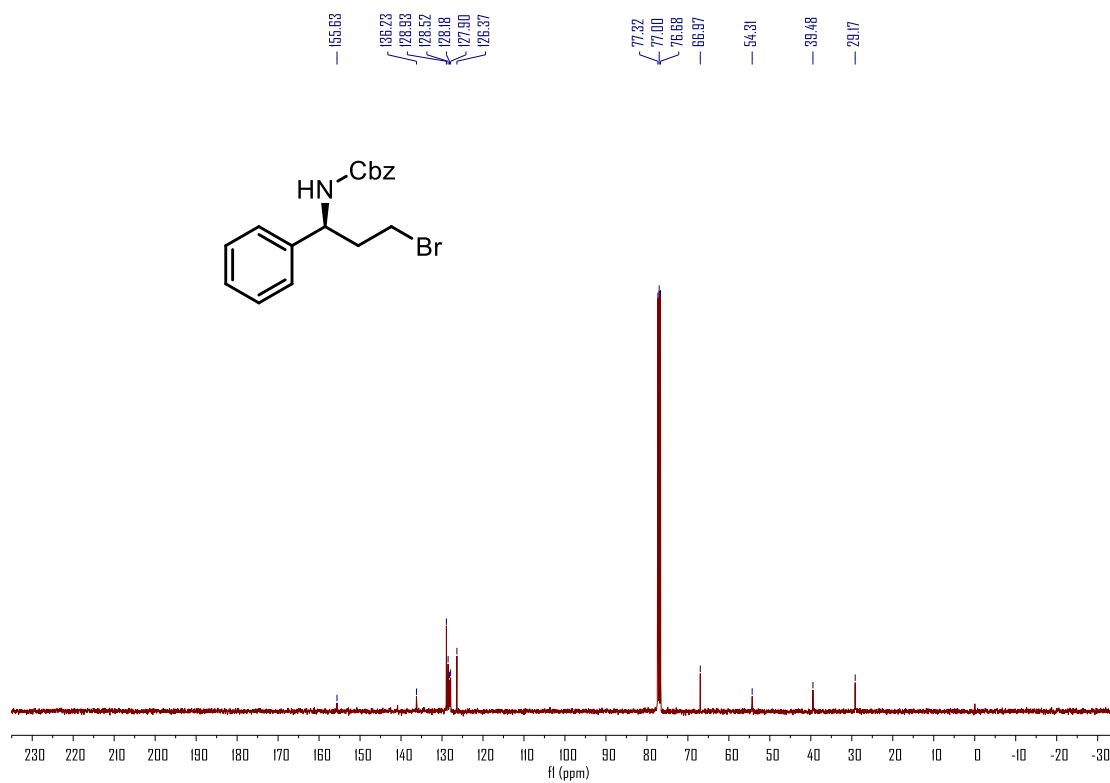
<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **1m**



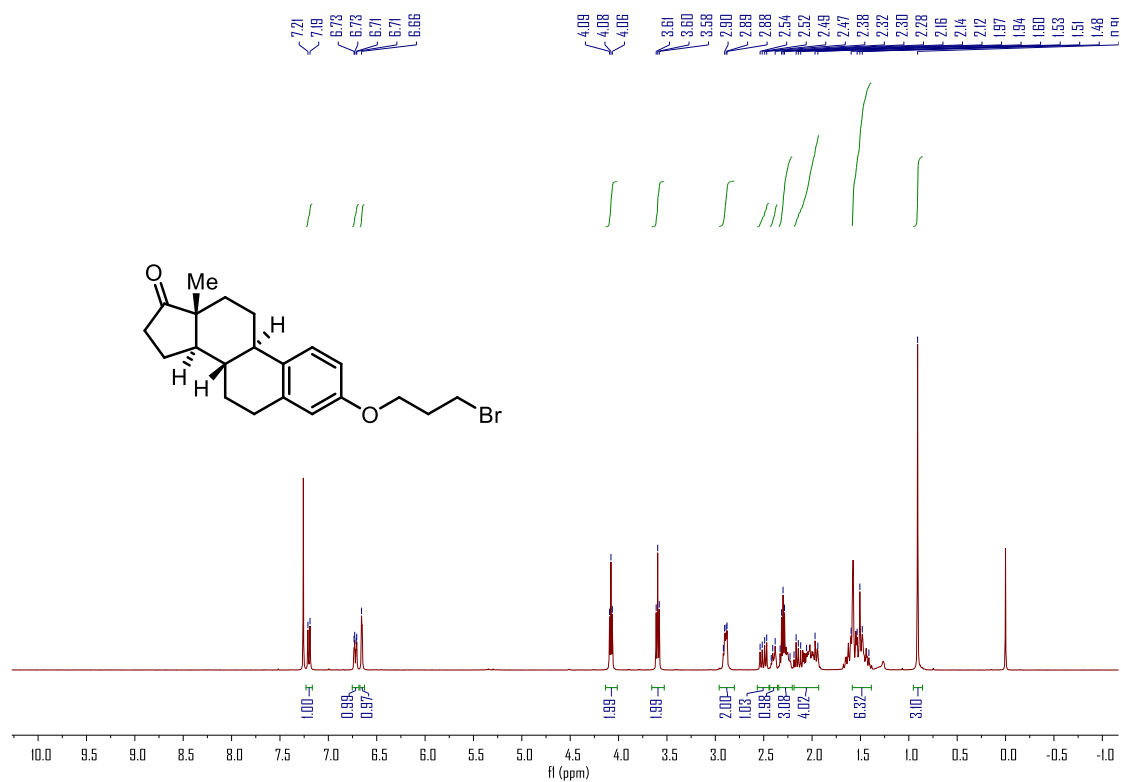
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **1n**



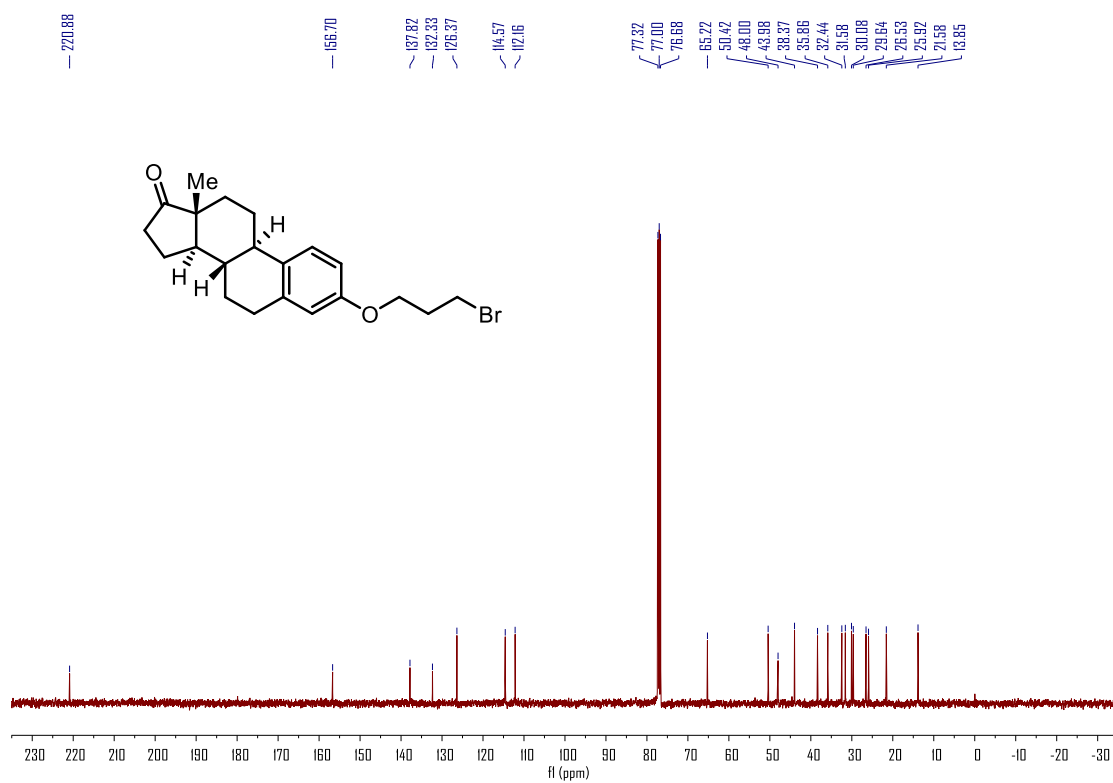
<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **1n**



<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **1ac**

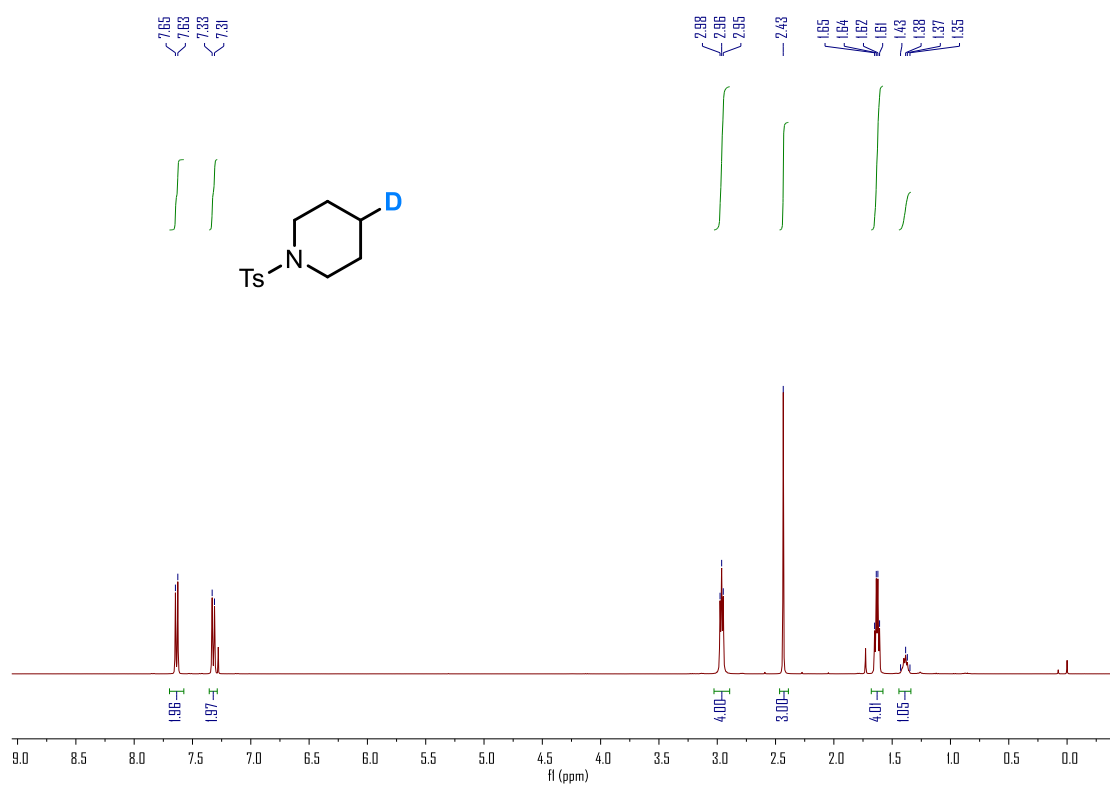


<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **1ac**

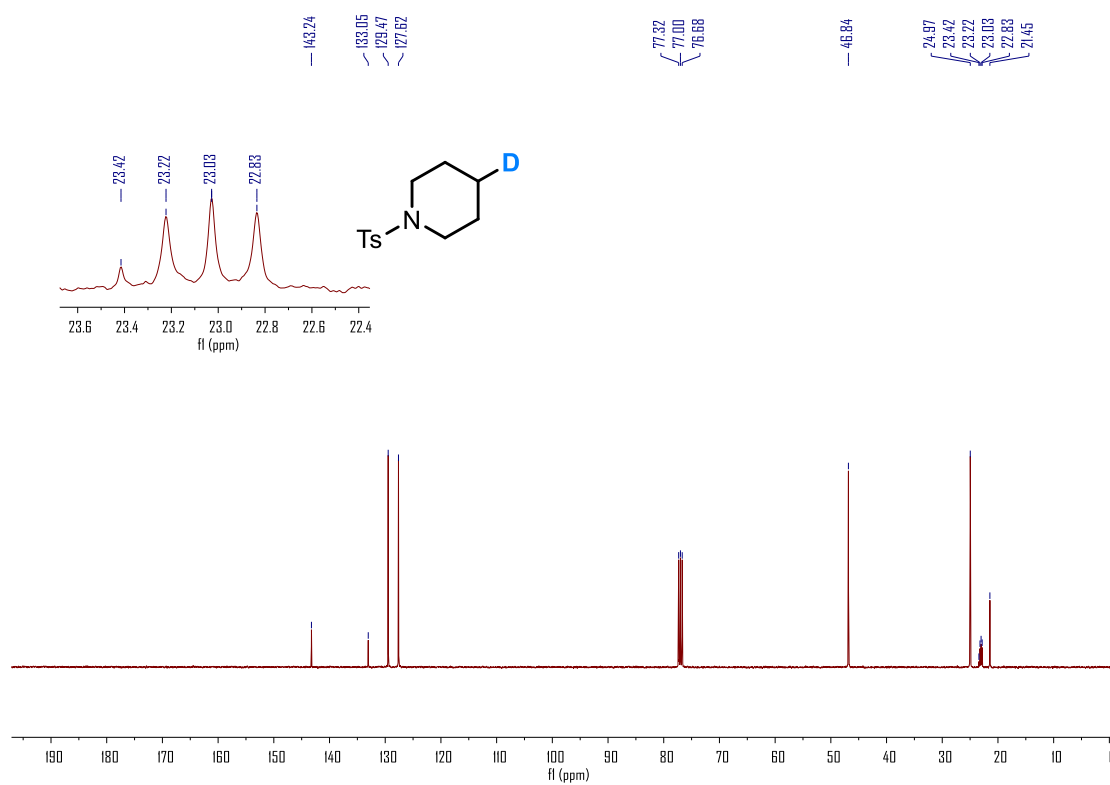




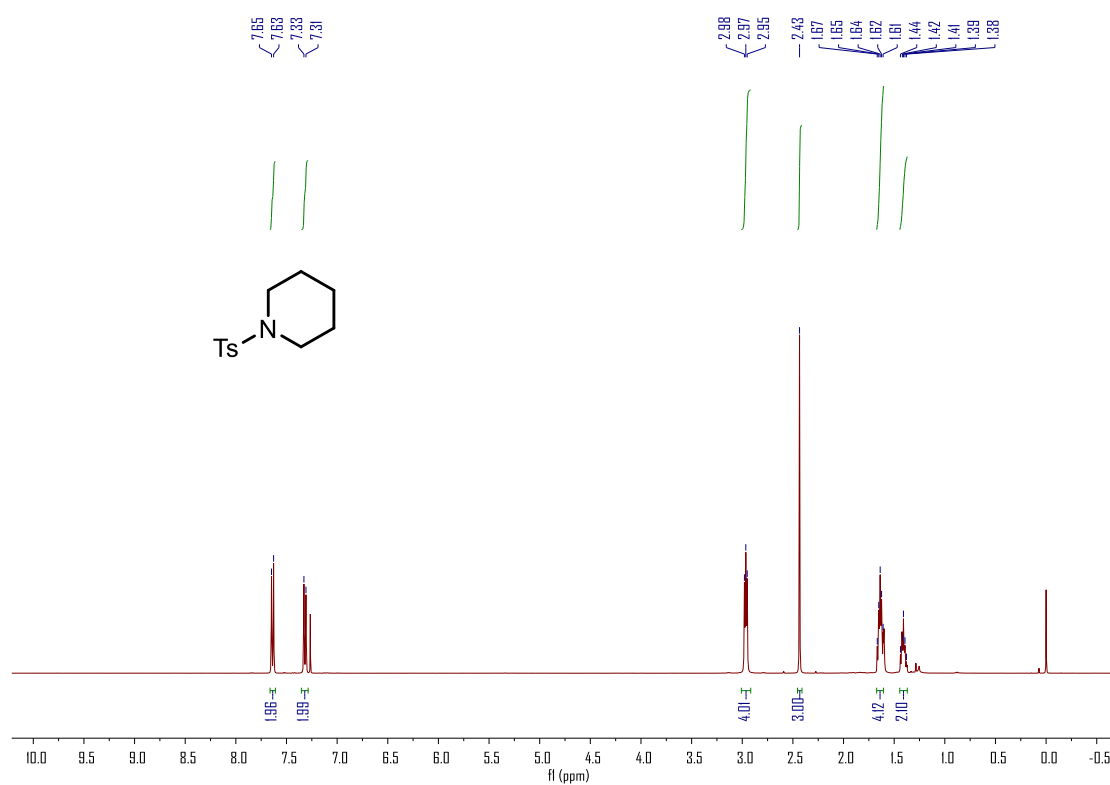
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **2a**



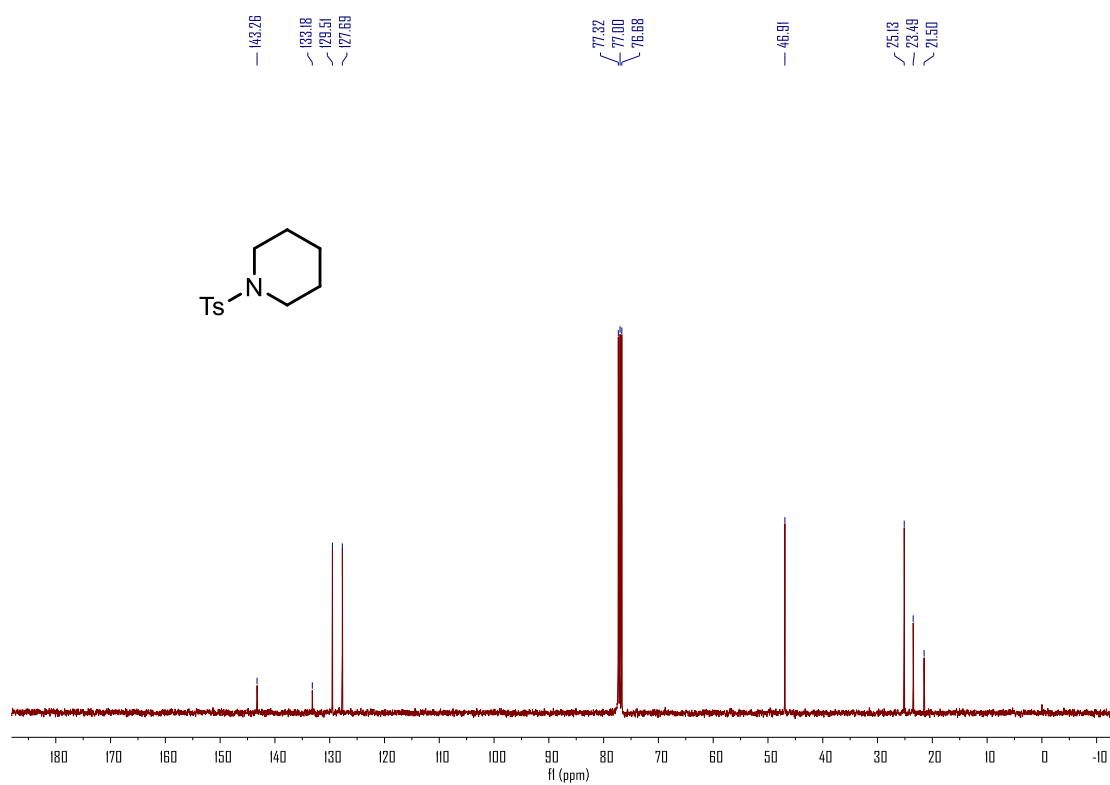
<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **2a**



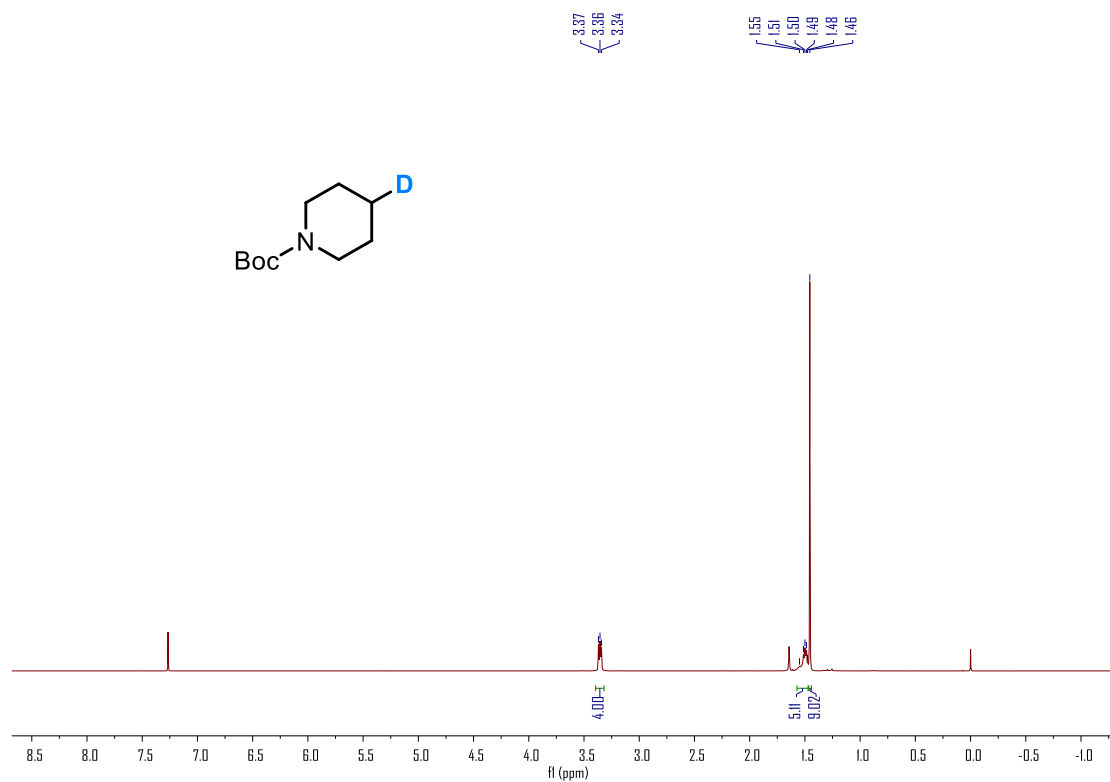
$^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of **2a'**



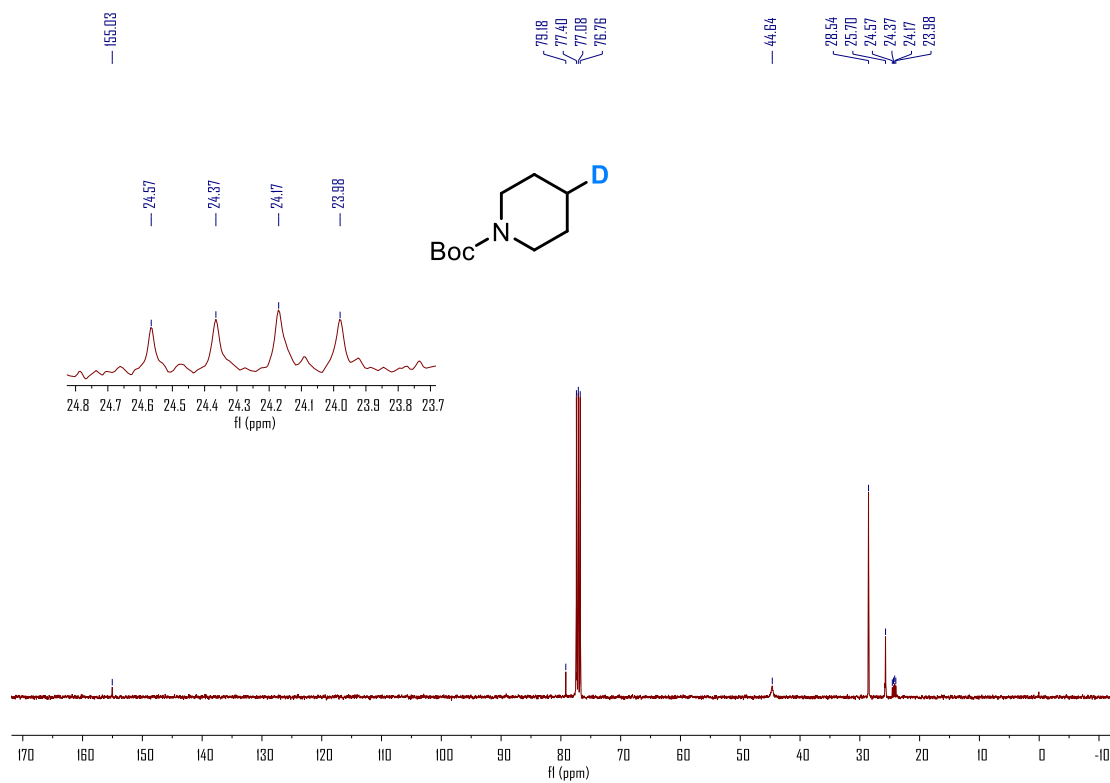
$^{13}\text{C}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of **2a'**



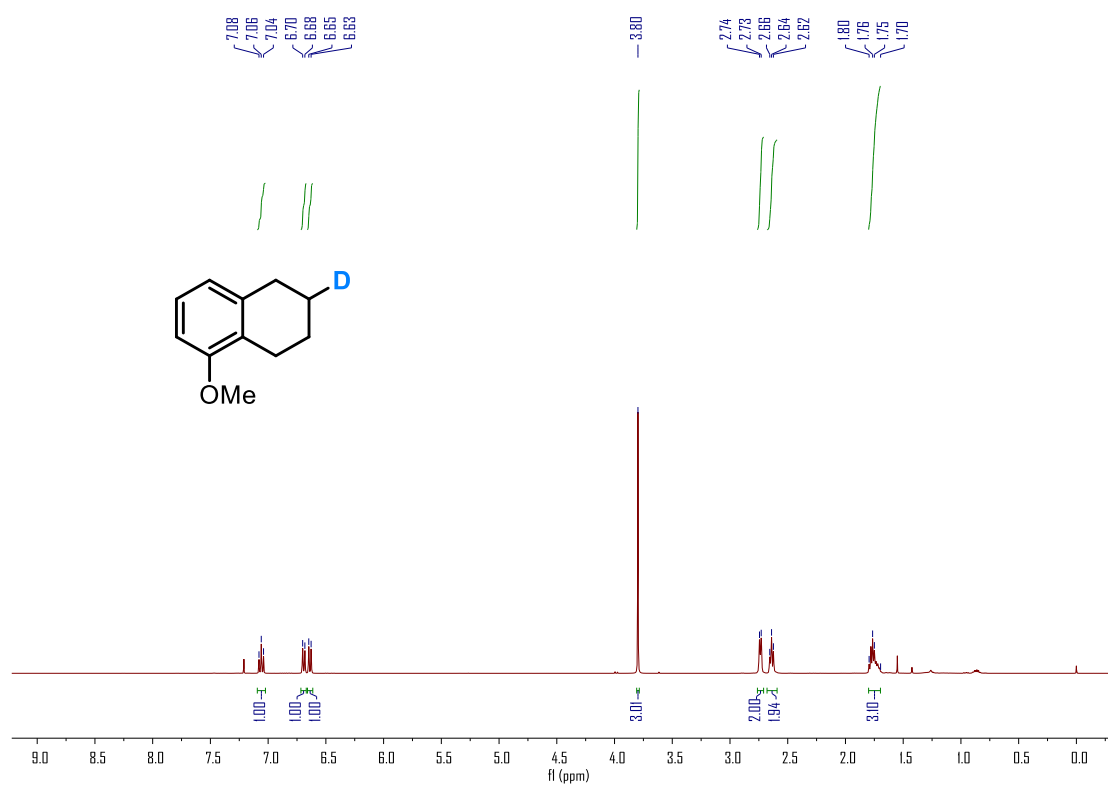
$^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of **2b**



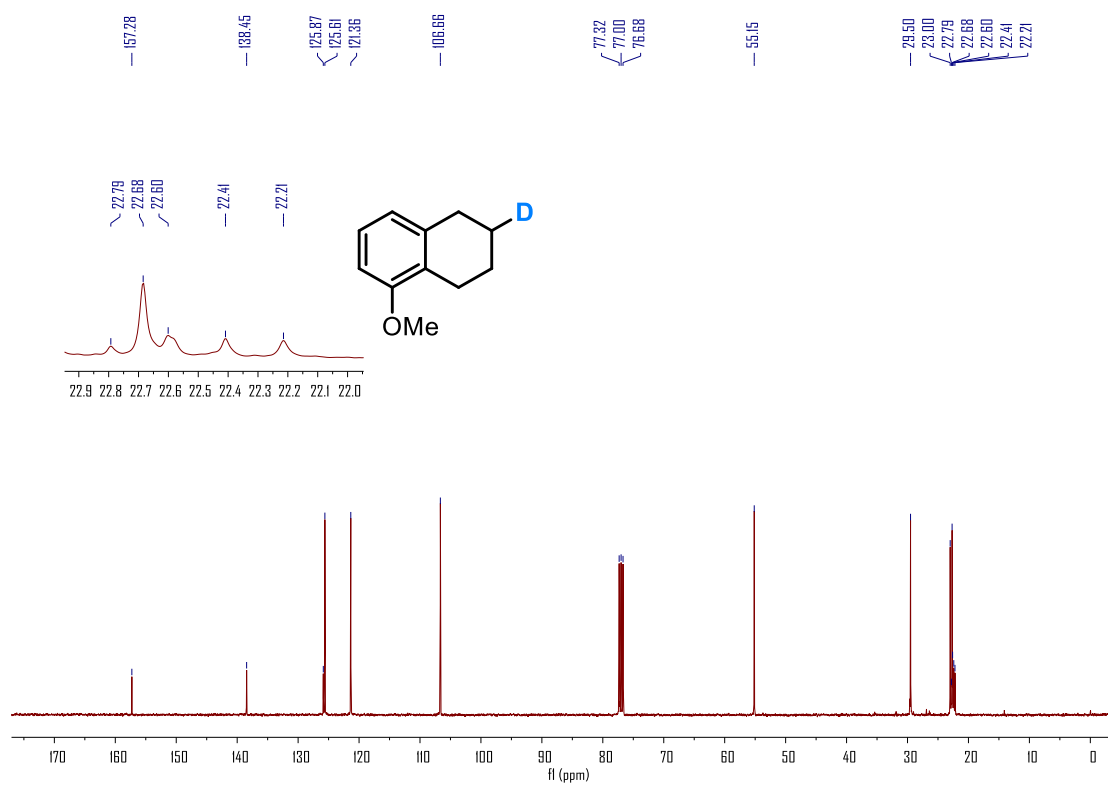
$^{13}\text{C}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of **2b**



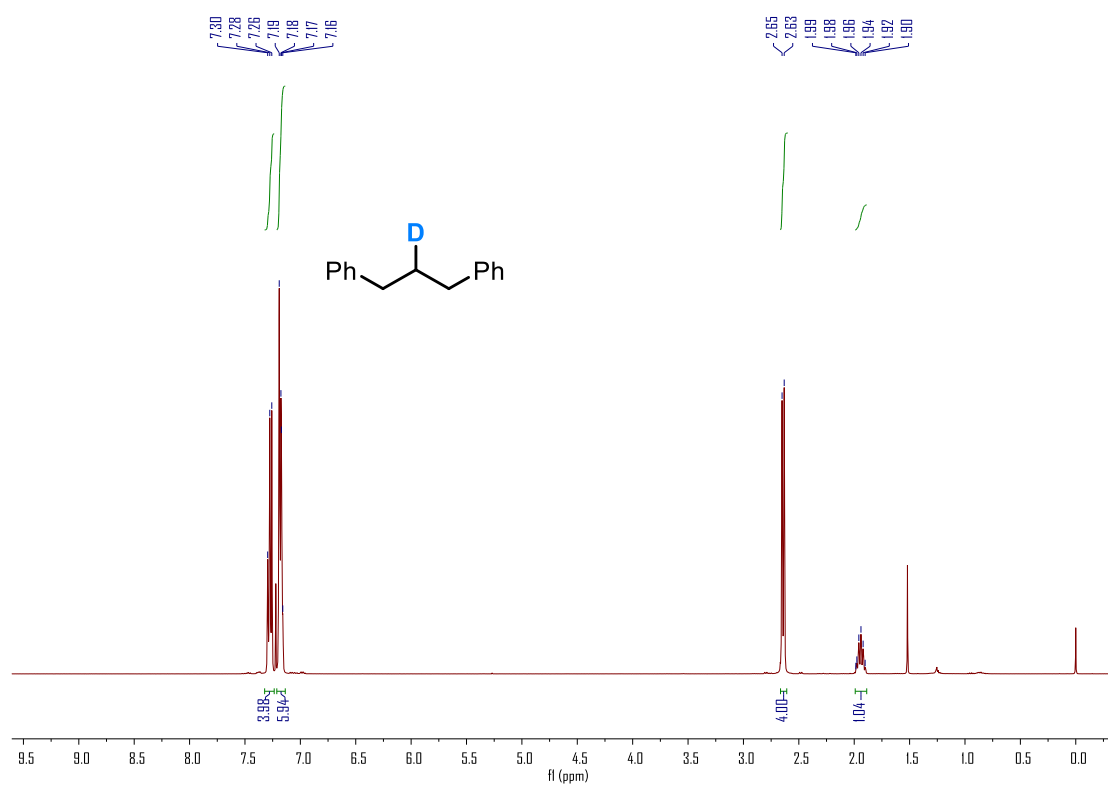
$^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of **2c**



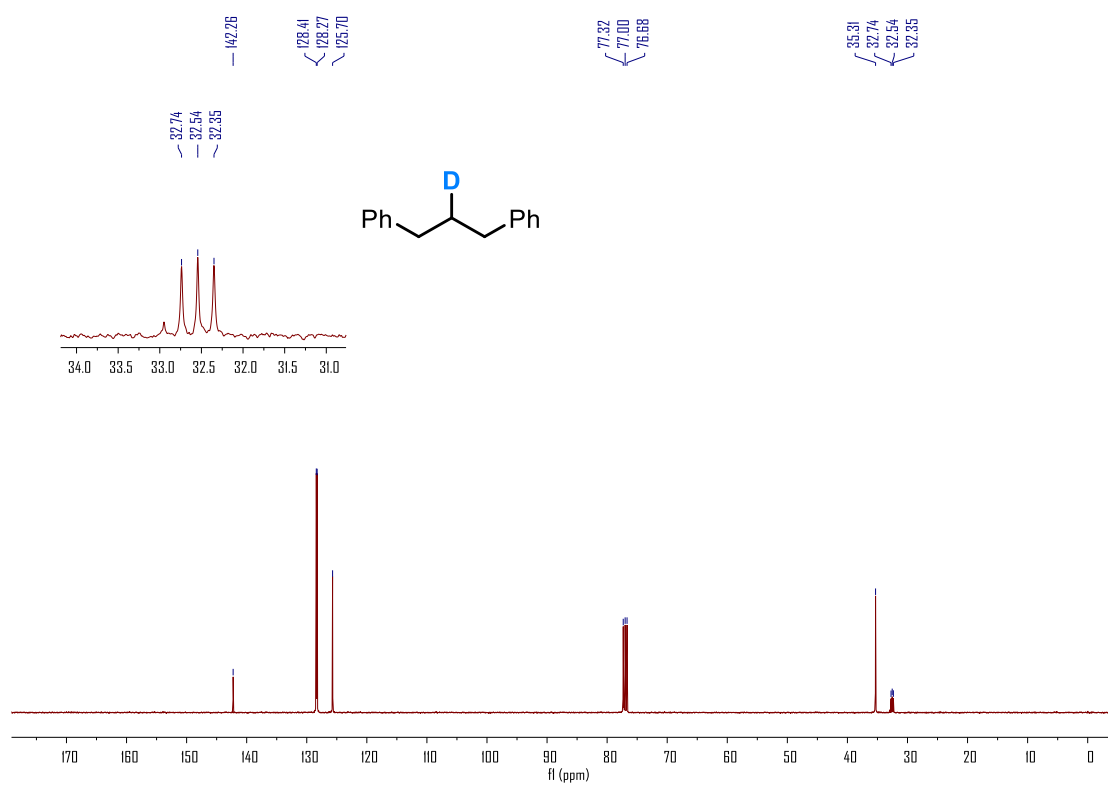
$^{13}\text{C}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of **2c**



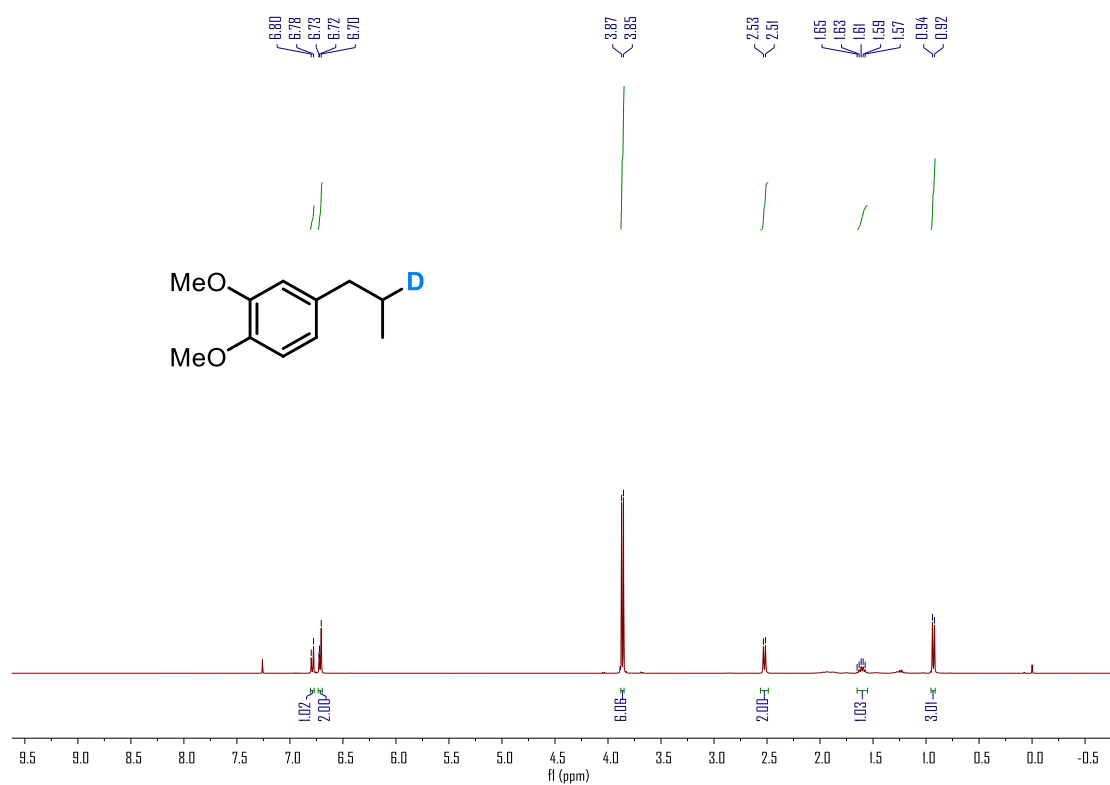
$^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of **2d**



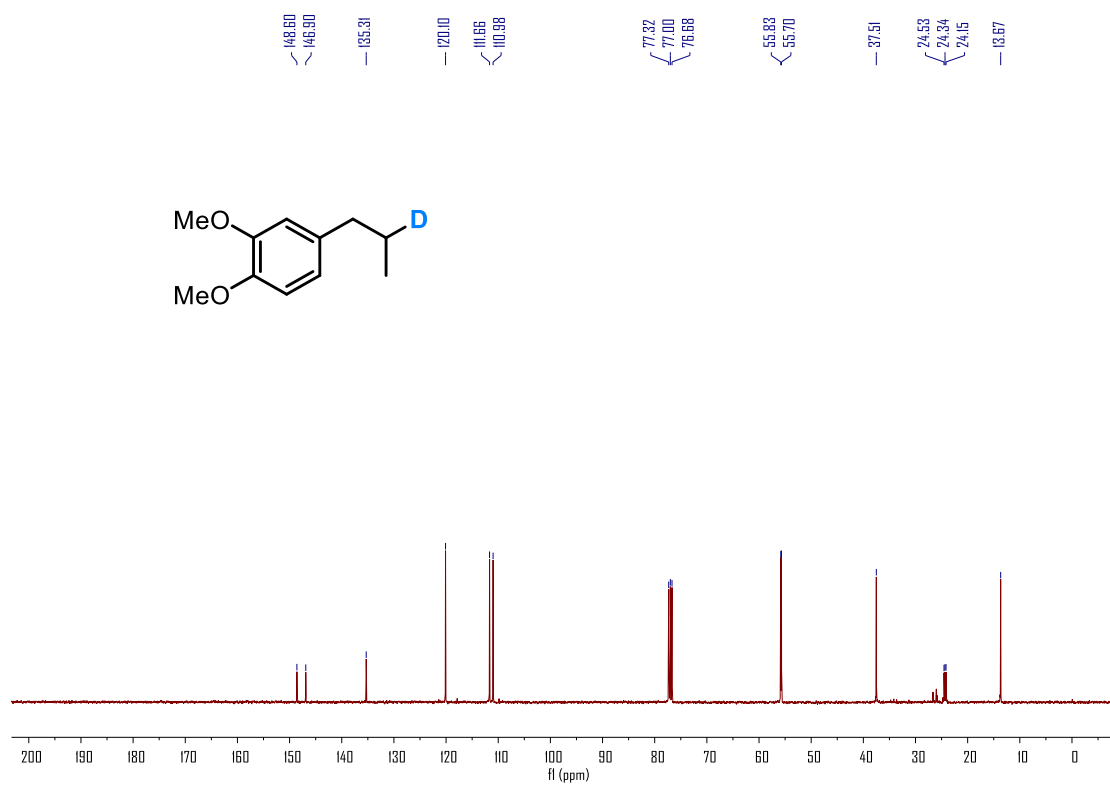
$^{13}\text{C}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of **2c**



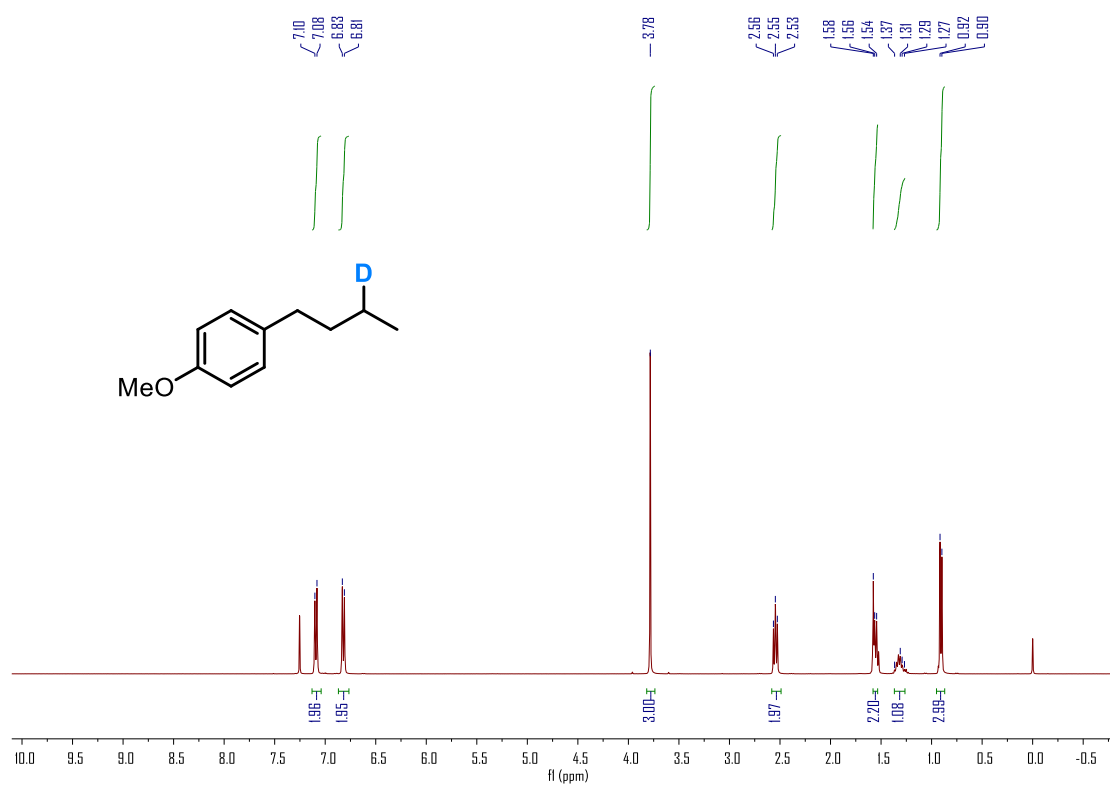
$^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of **2e**



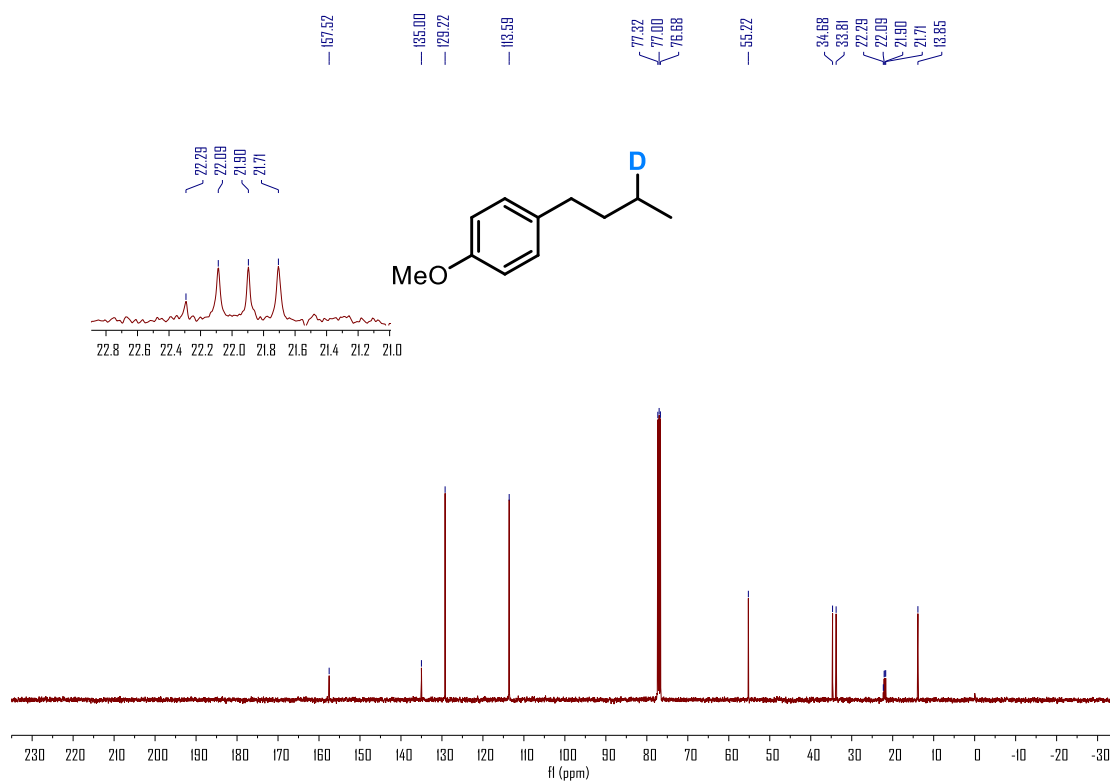
$^{13}\text{C}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of **2e**



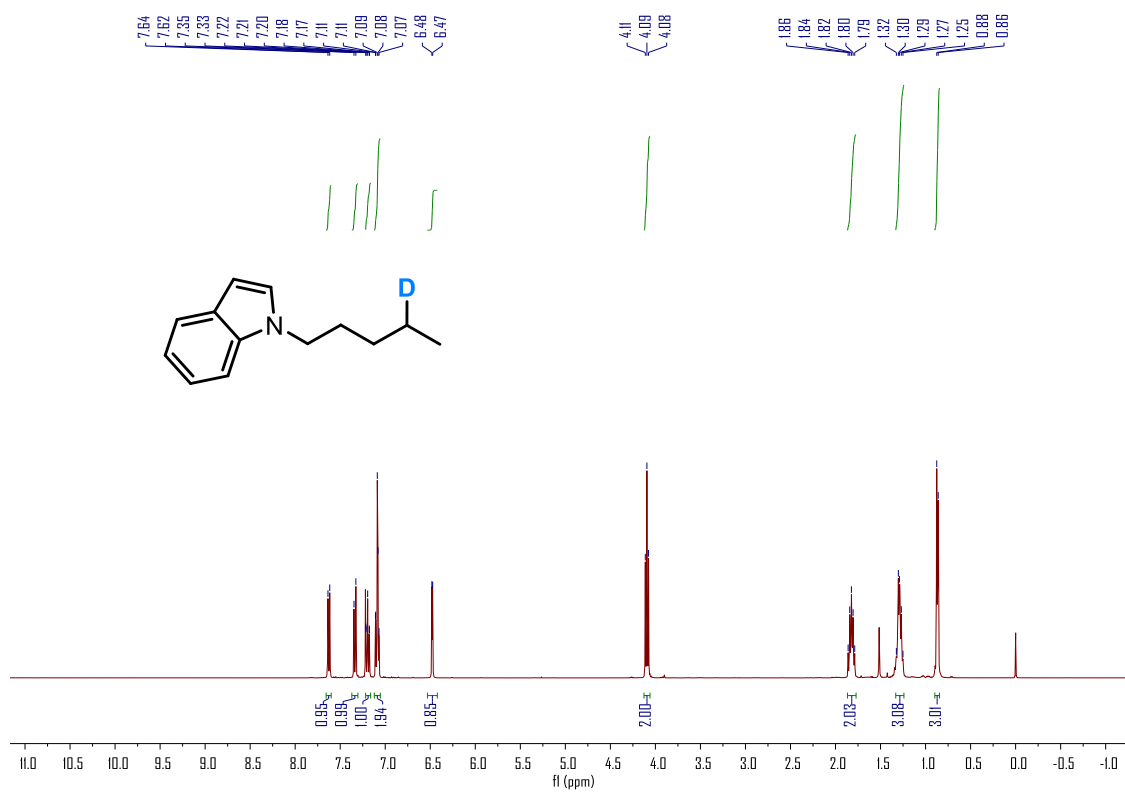
$^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of **2f**



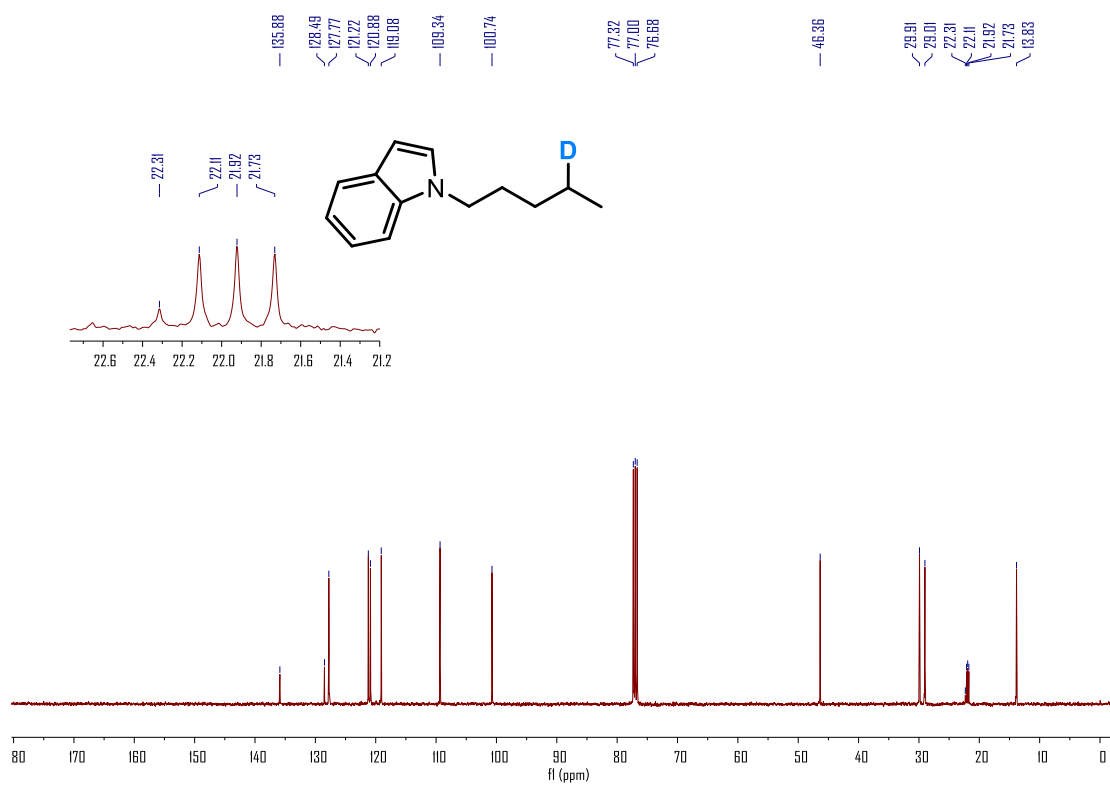
$^{13}\text{C}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of **2f**



$^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of **2g**

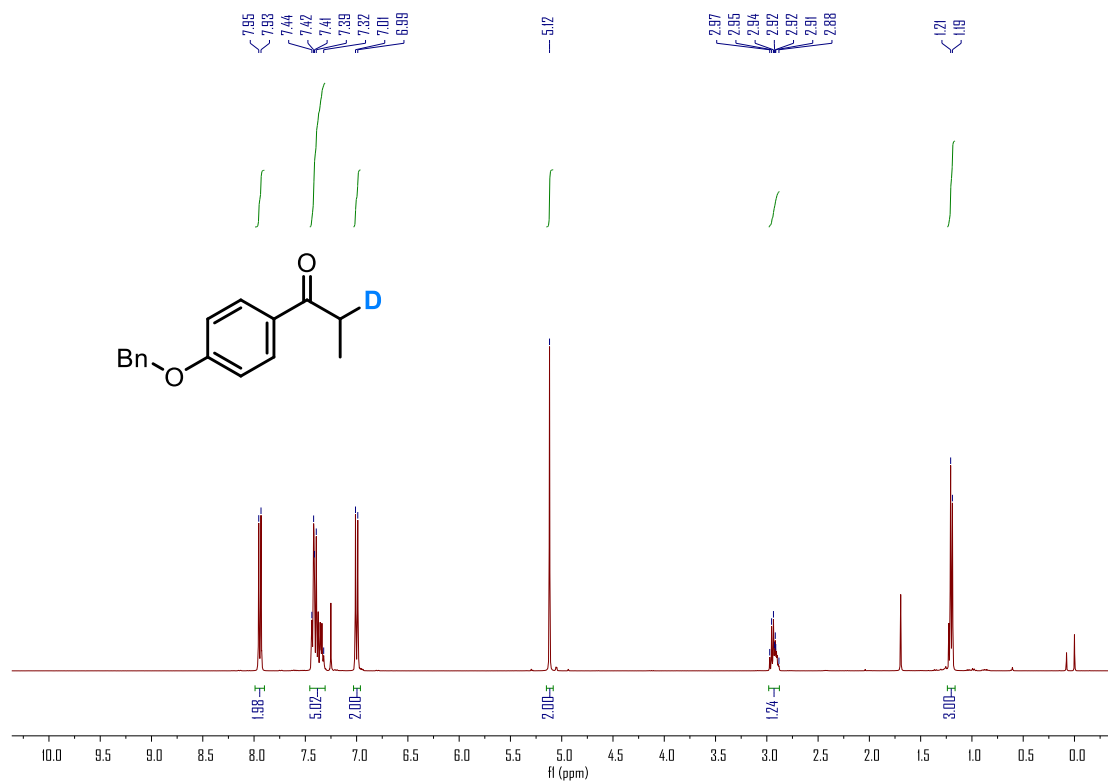


$^{13}\text{C}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of **2g**

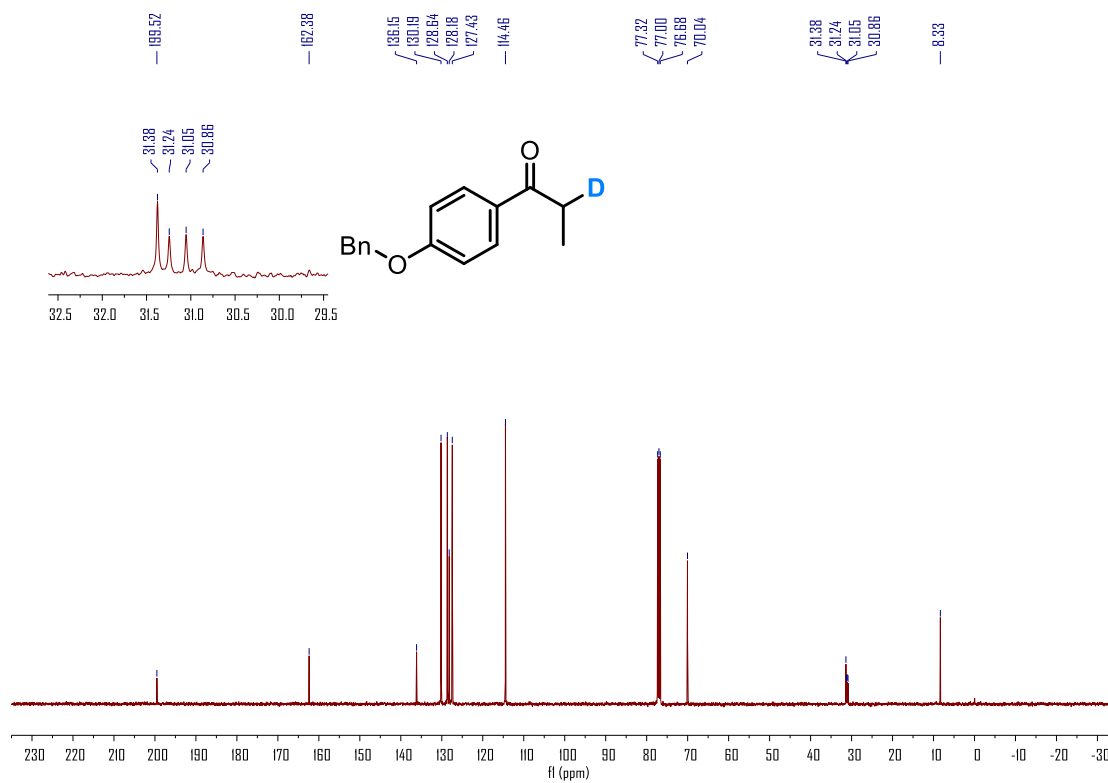




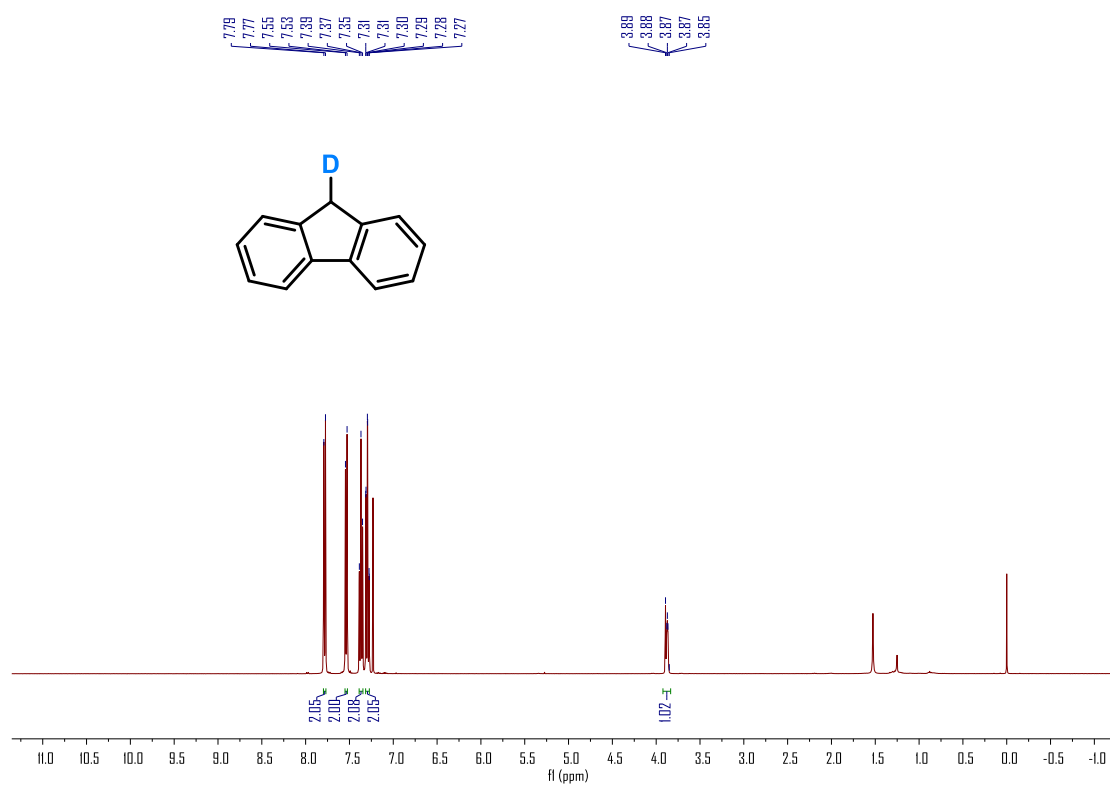
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **2h**



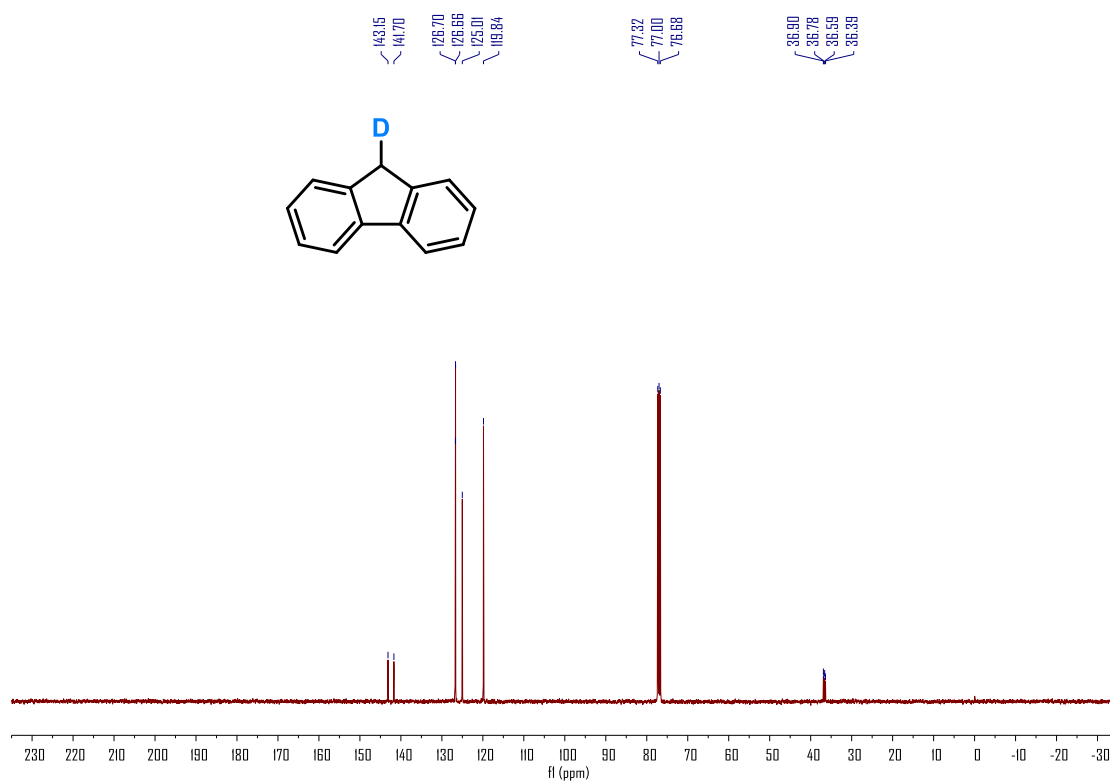
<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **2h**



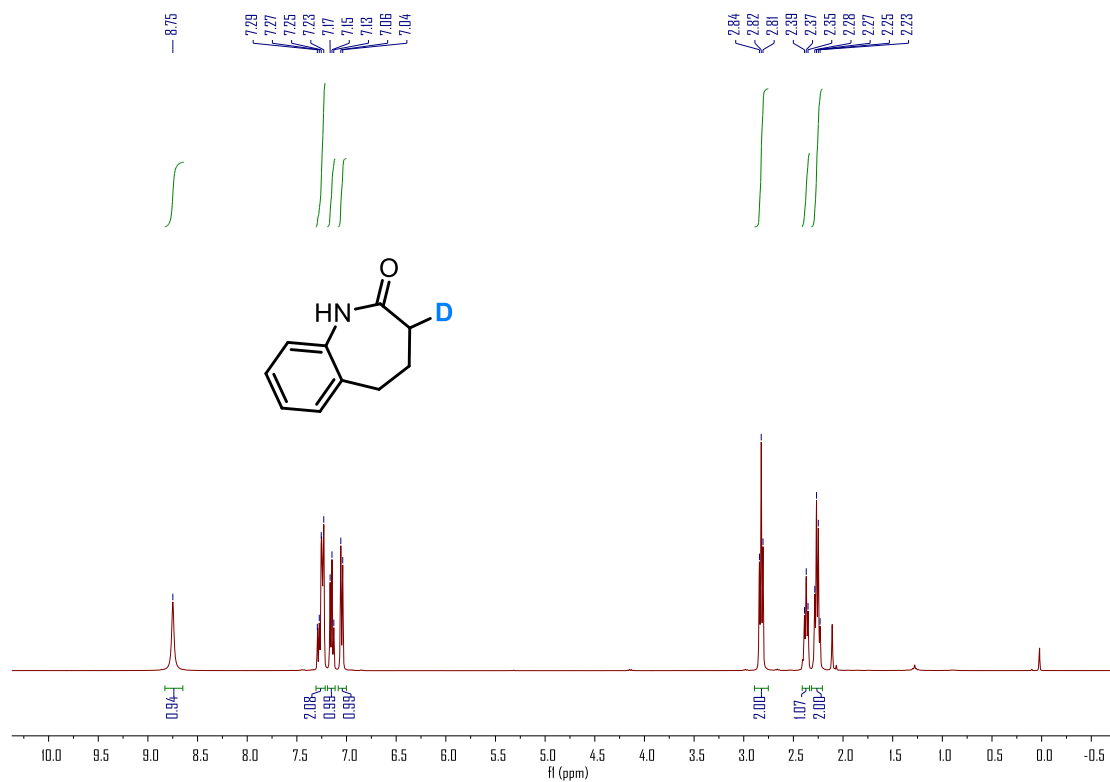
$^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of **2i**



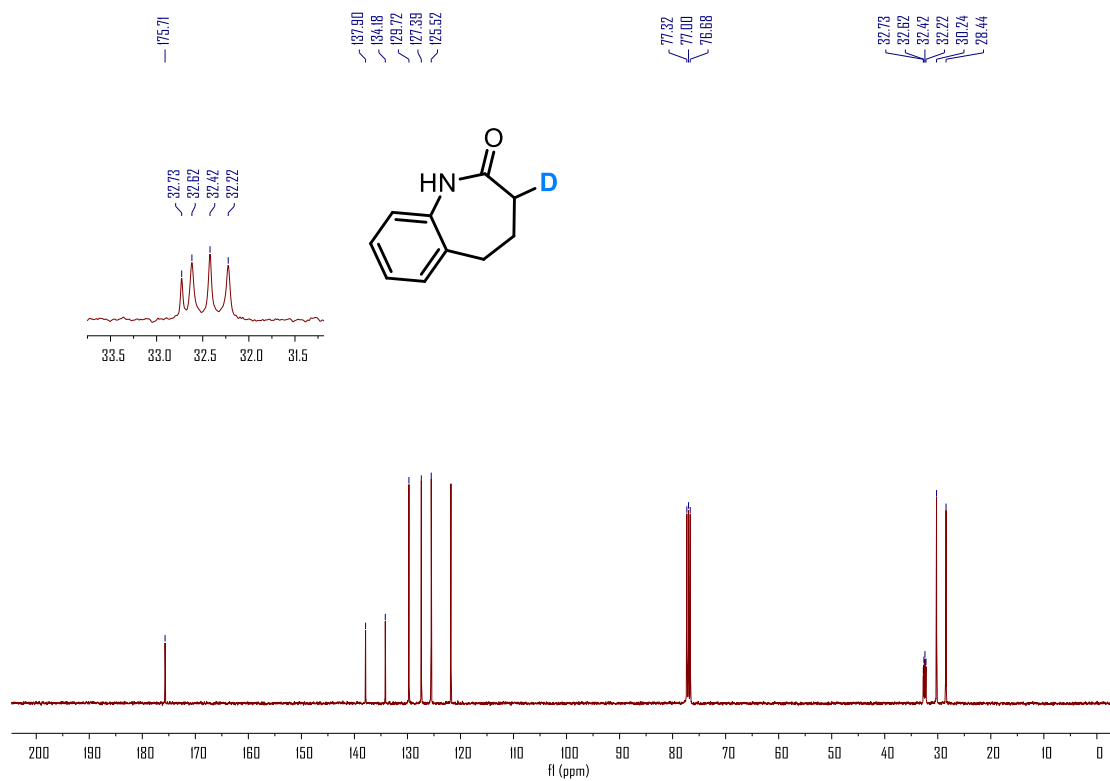
$^{13}\text{C}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of **2i**



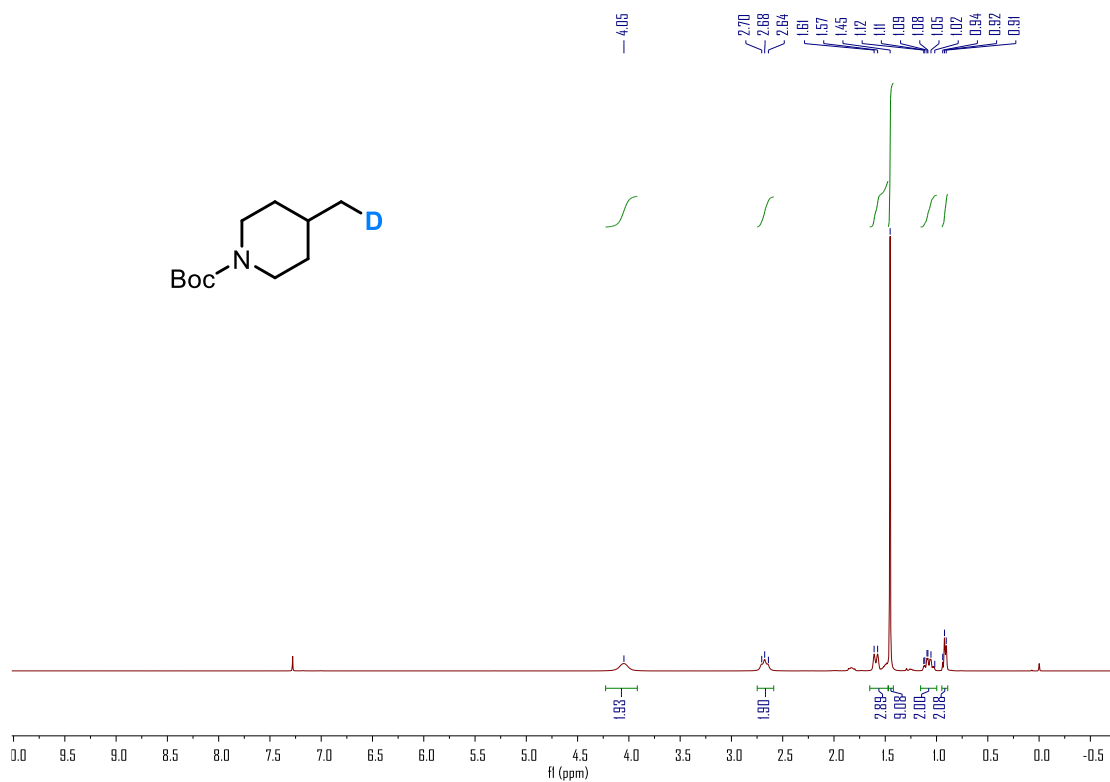
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **2j**



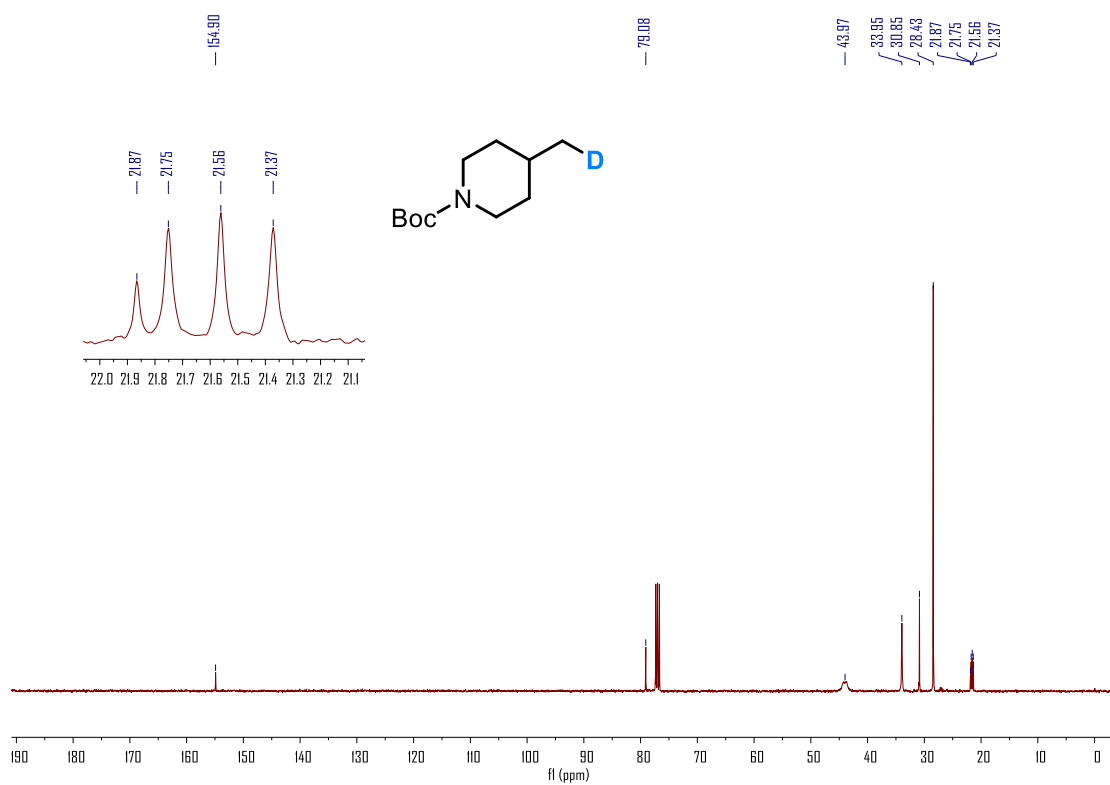
<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **2j**



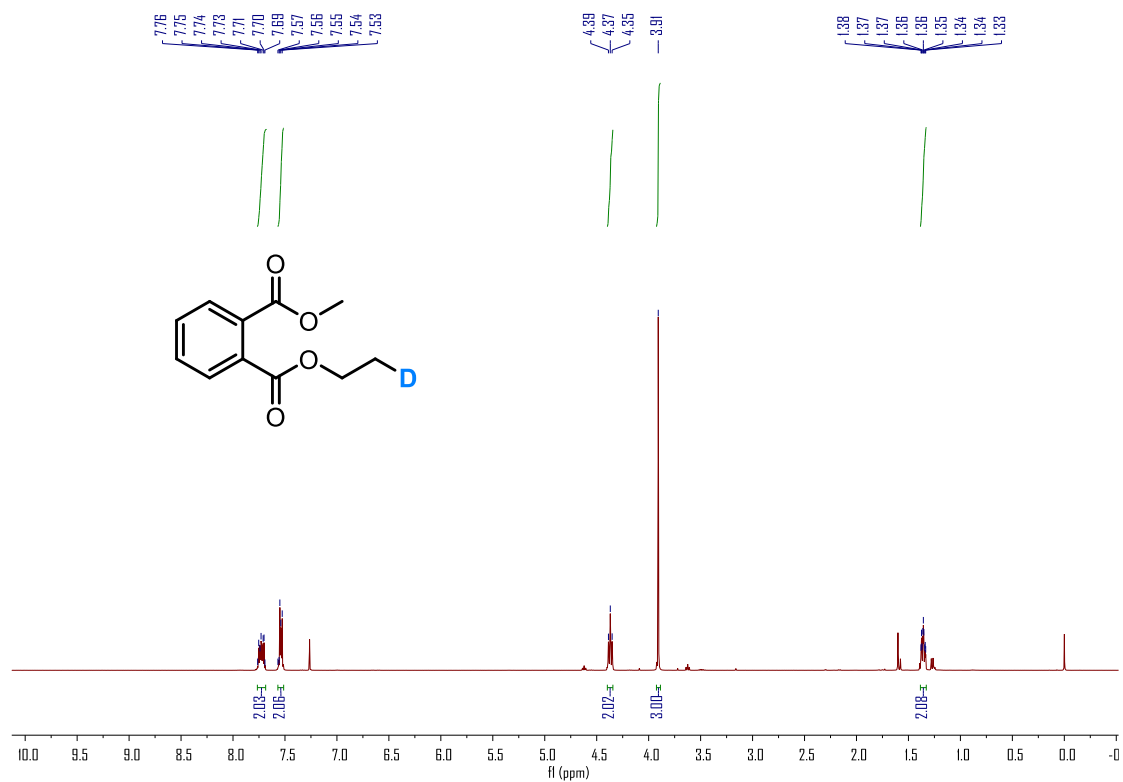
$^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of **2k**



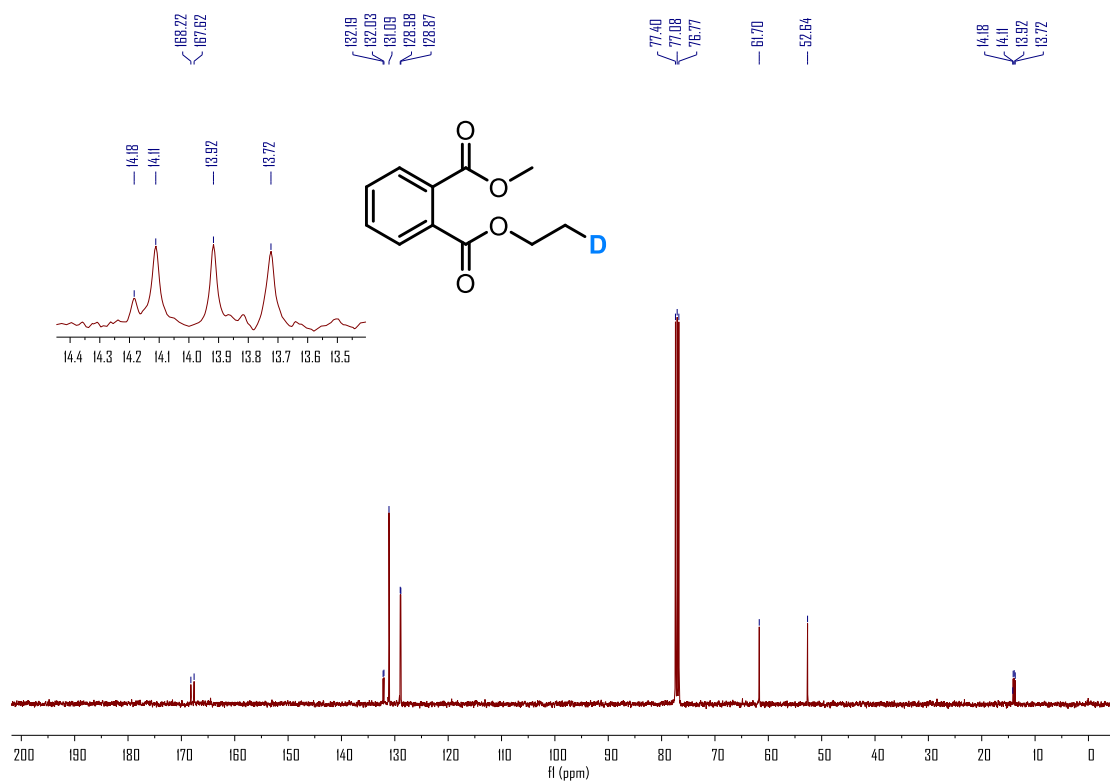
$^{13}\text{C}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of **2k**



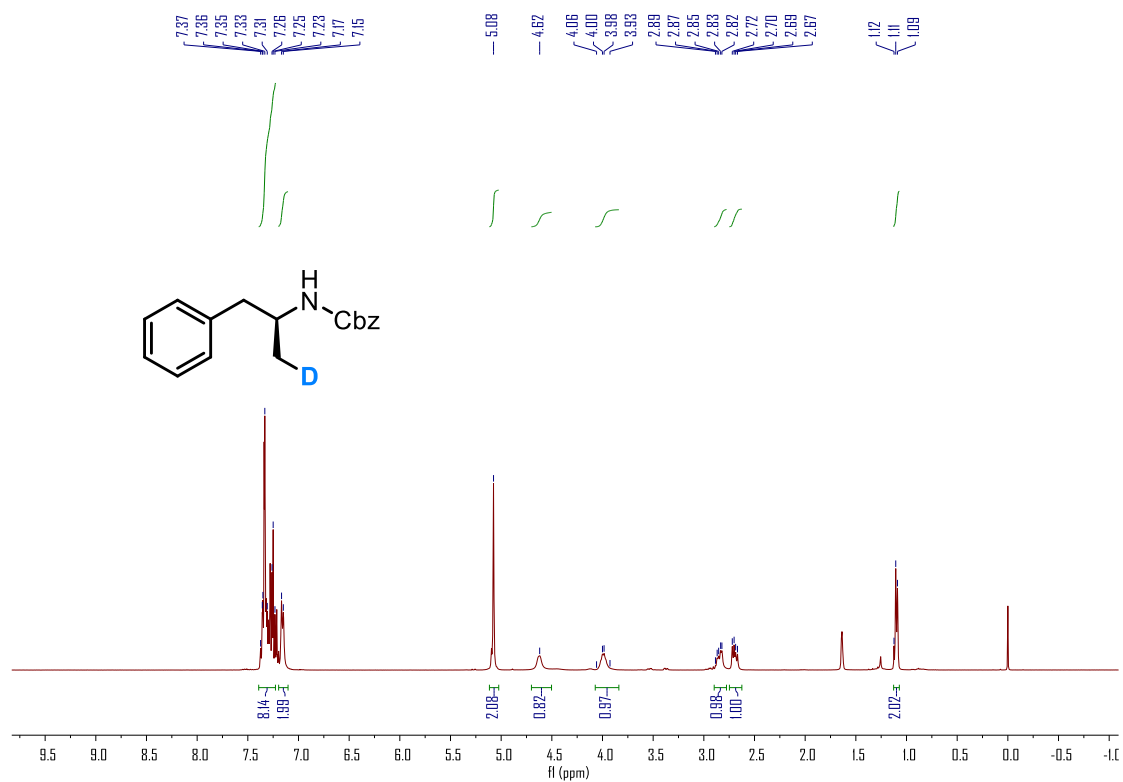
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **21**



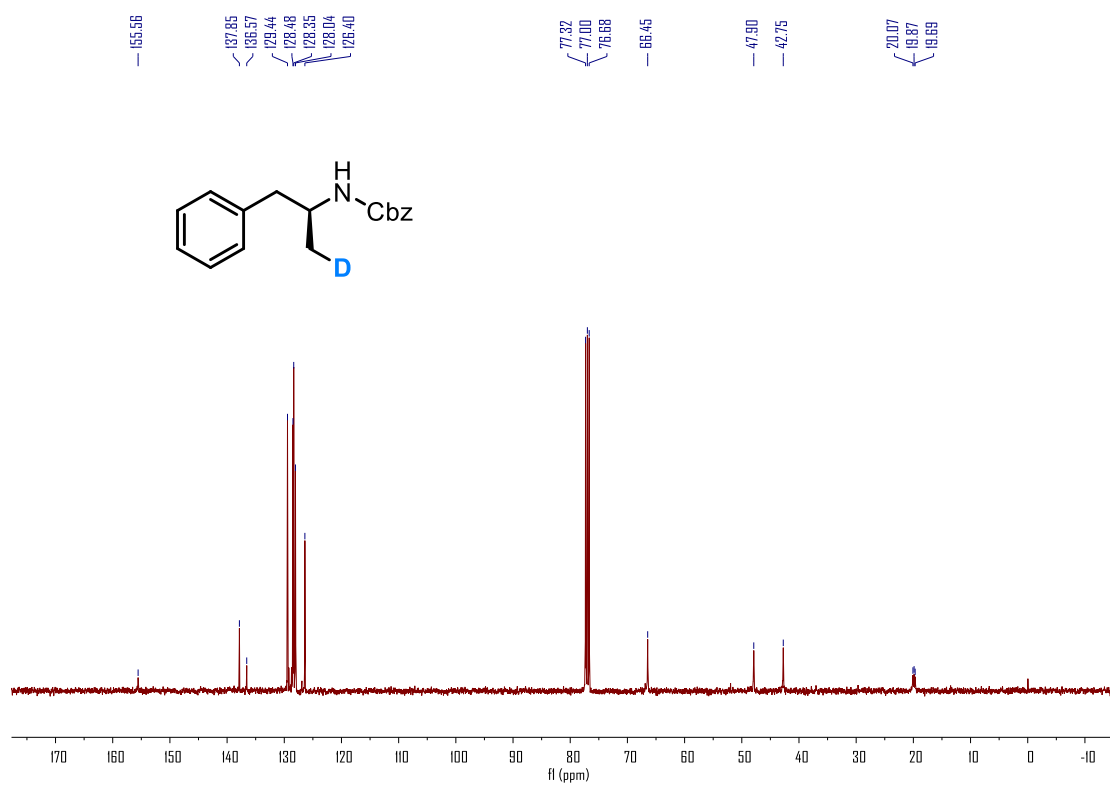
<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **21**



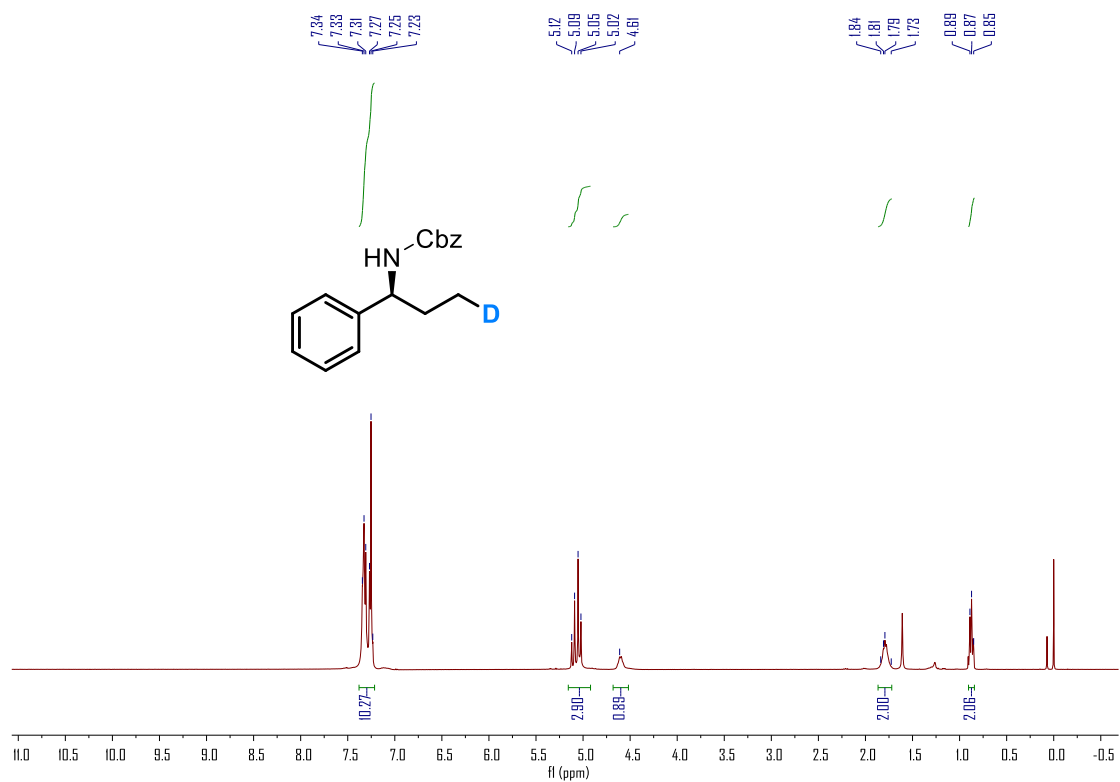
$^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of **2m**



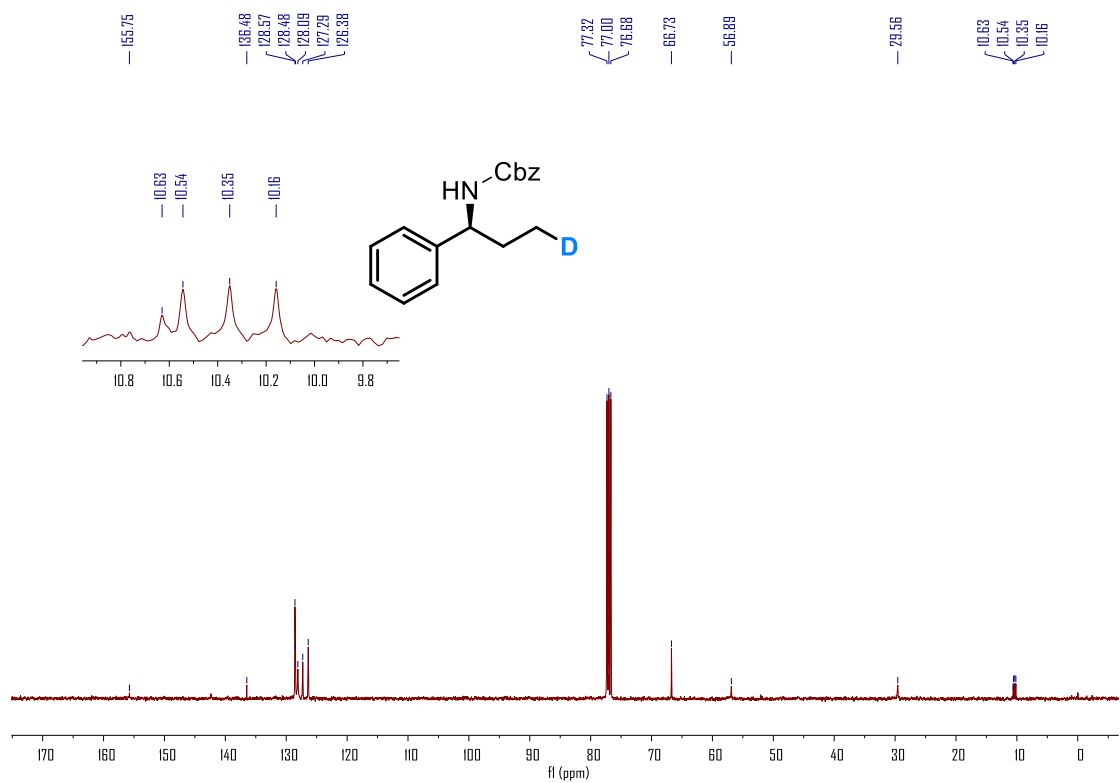
$^{13}\text{C}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of **2m**



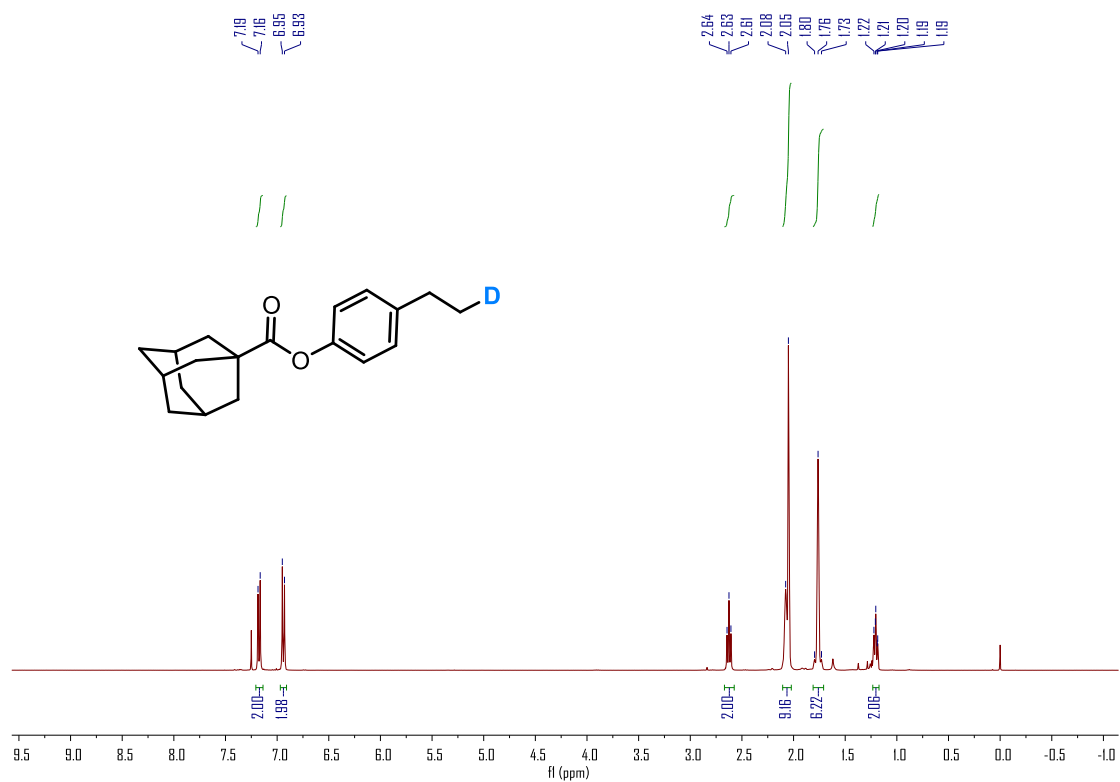
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **2n**



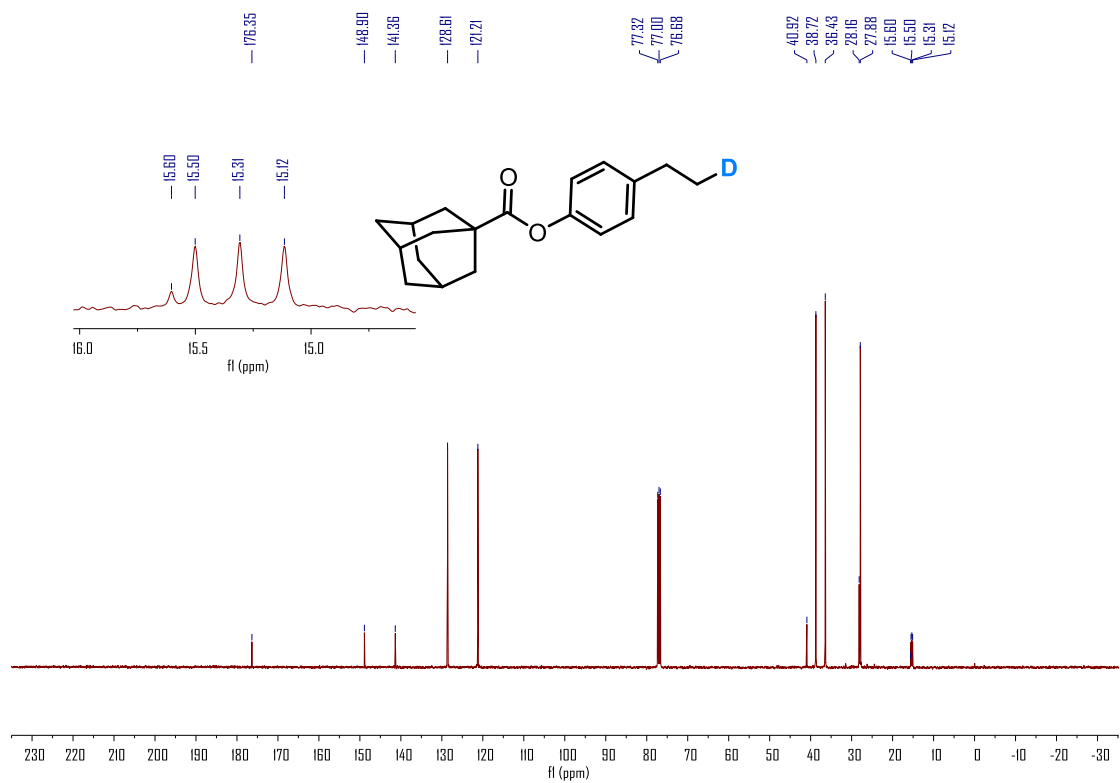
<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **2n**



<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **2o**



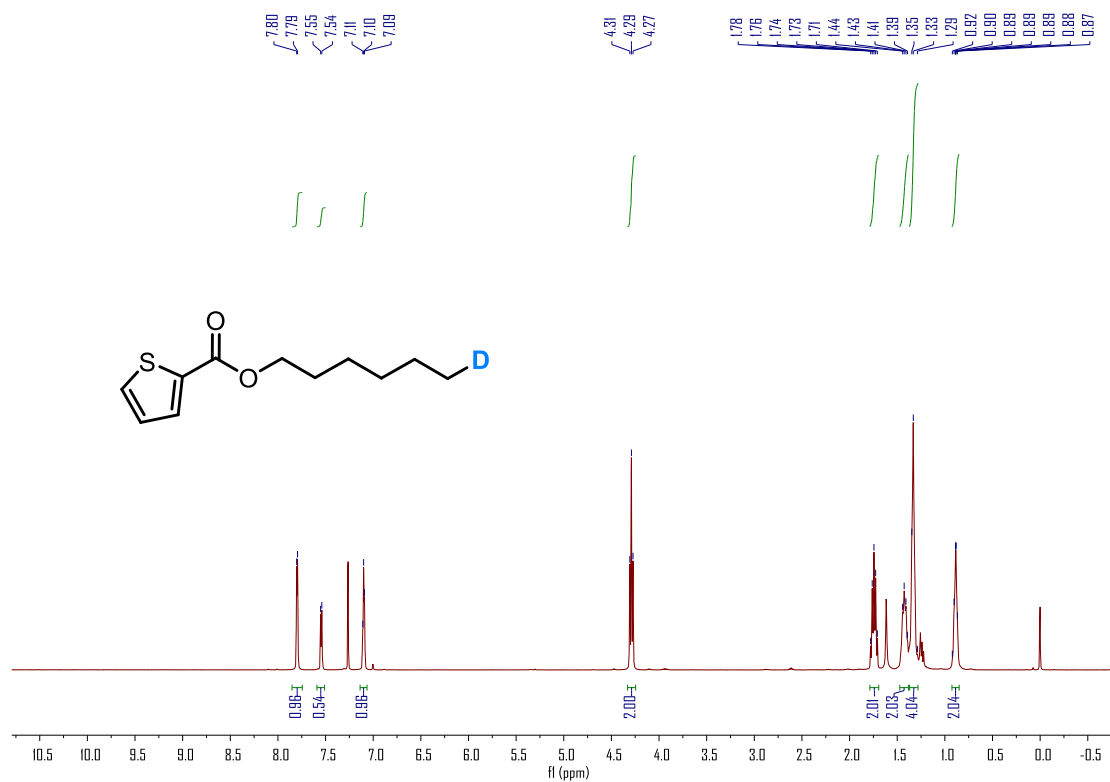
<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **2o**



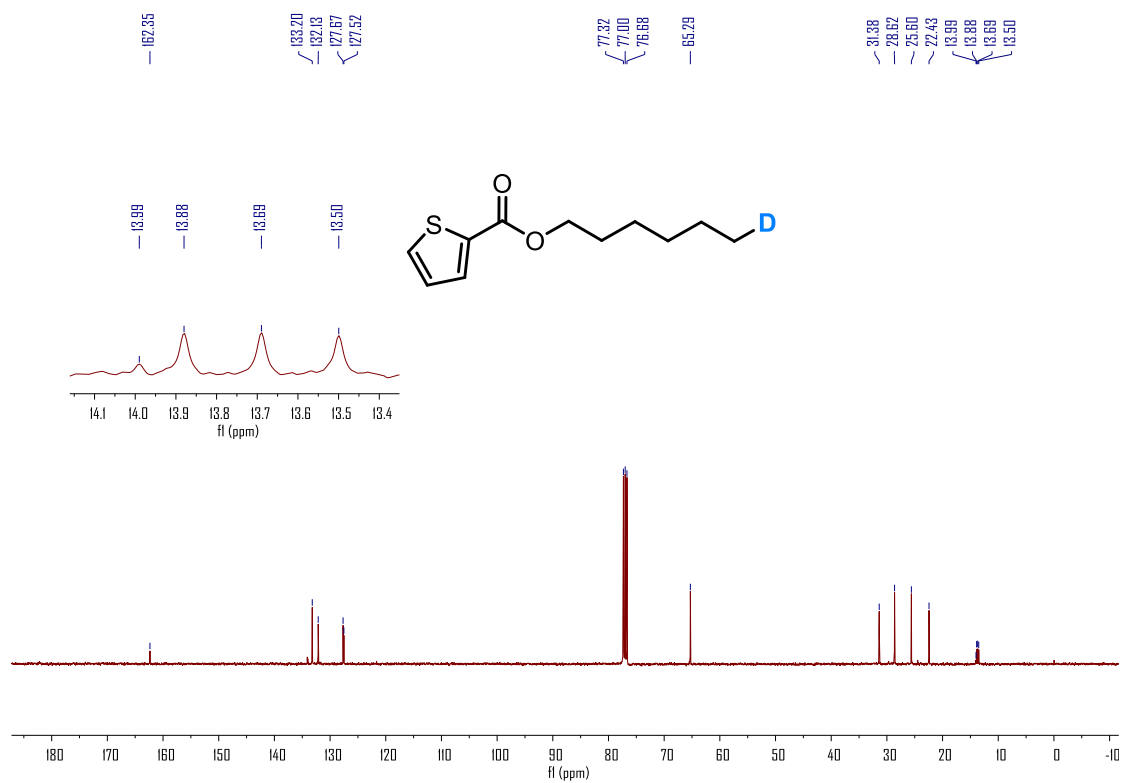




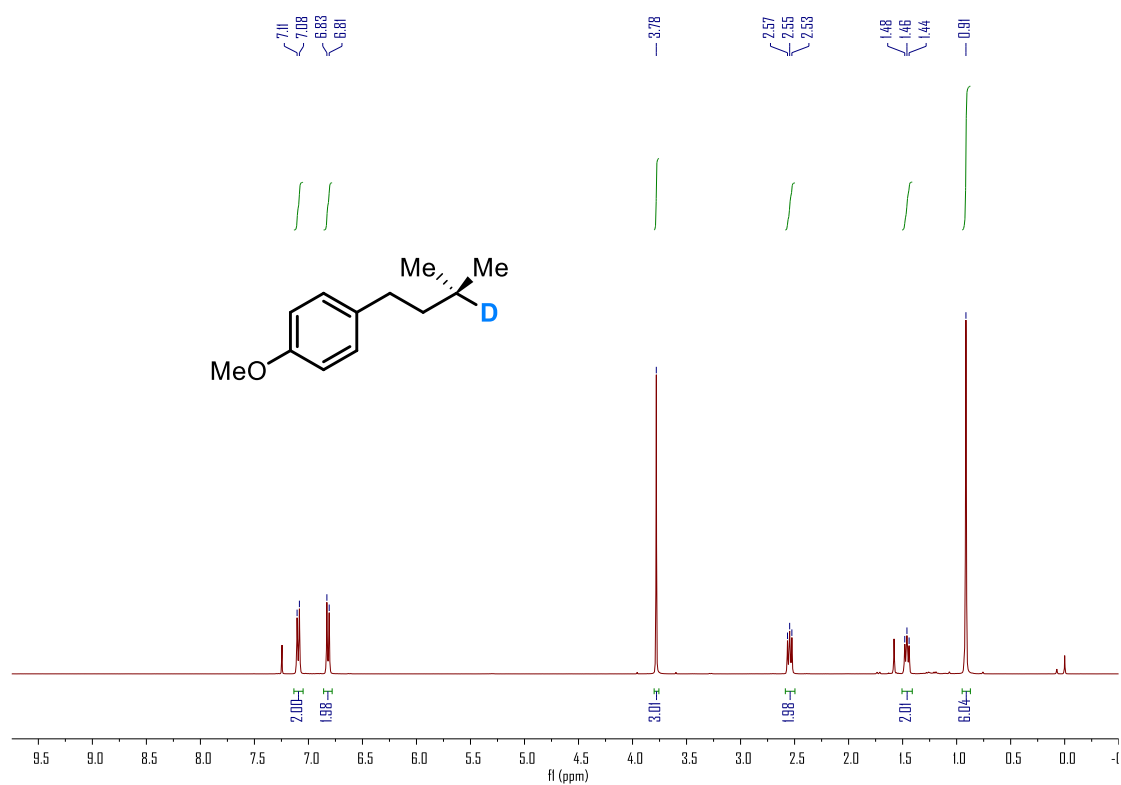
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **2q**



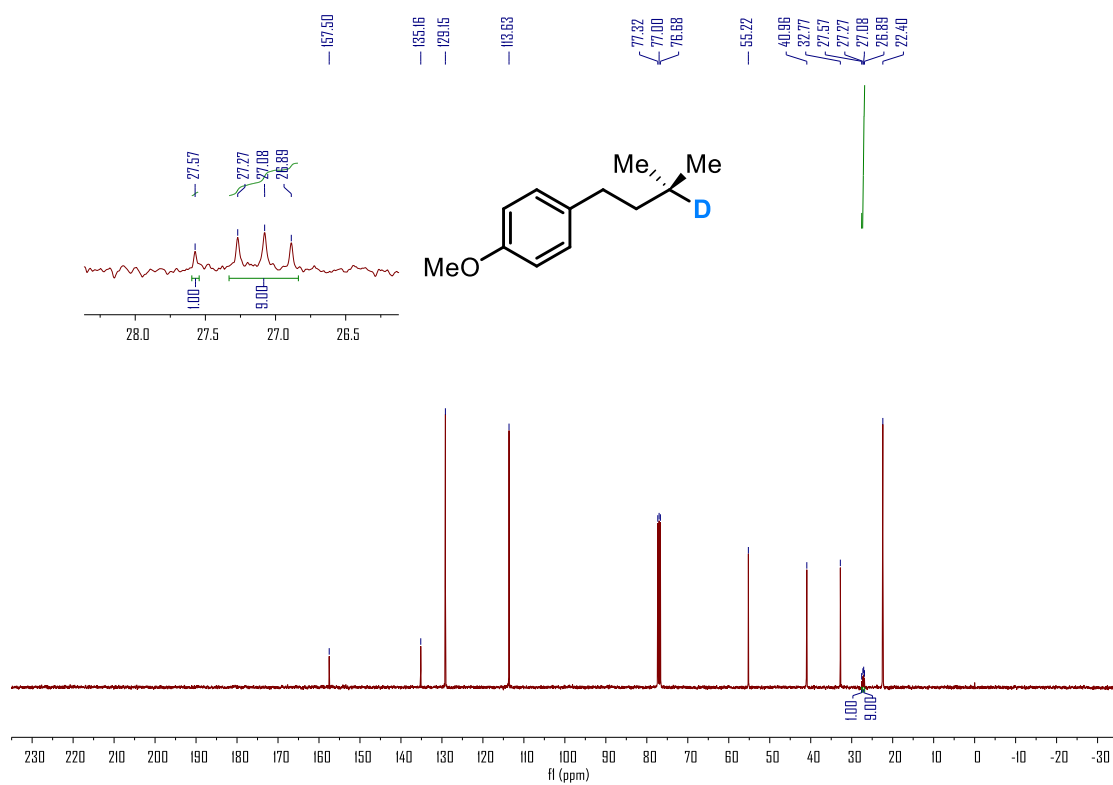
<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **2q**



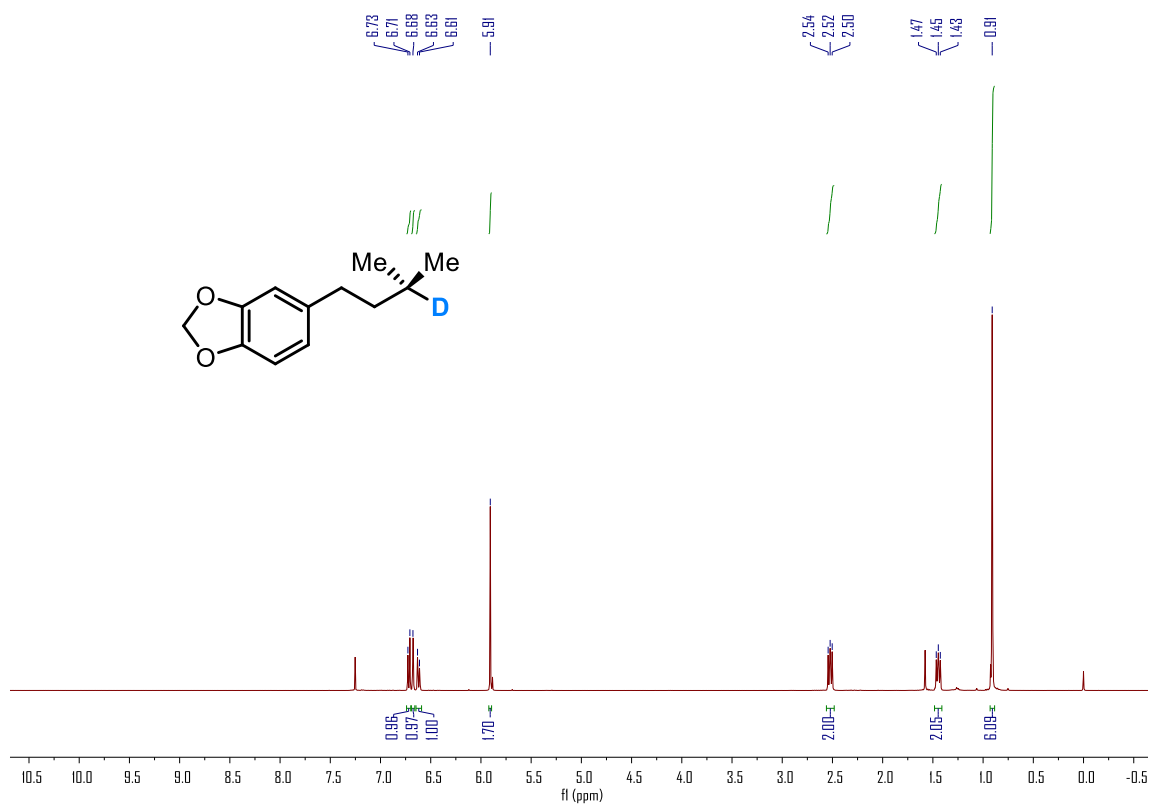
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **2r**



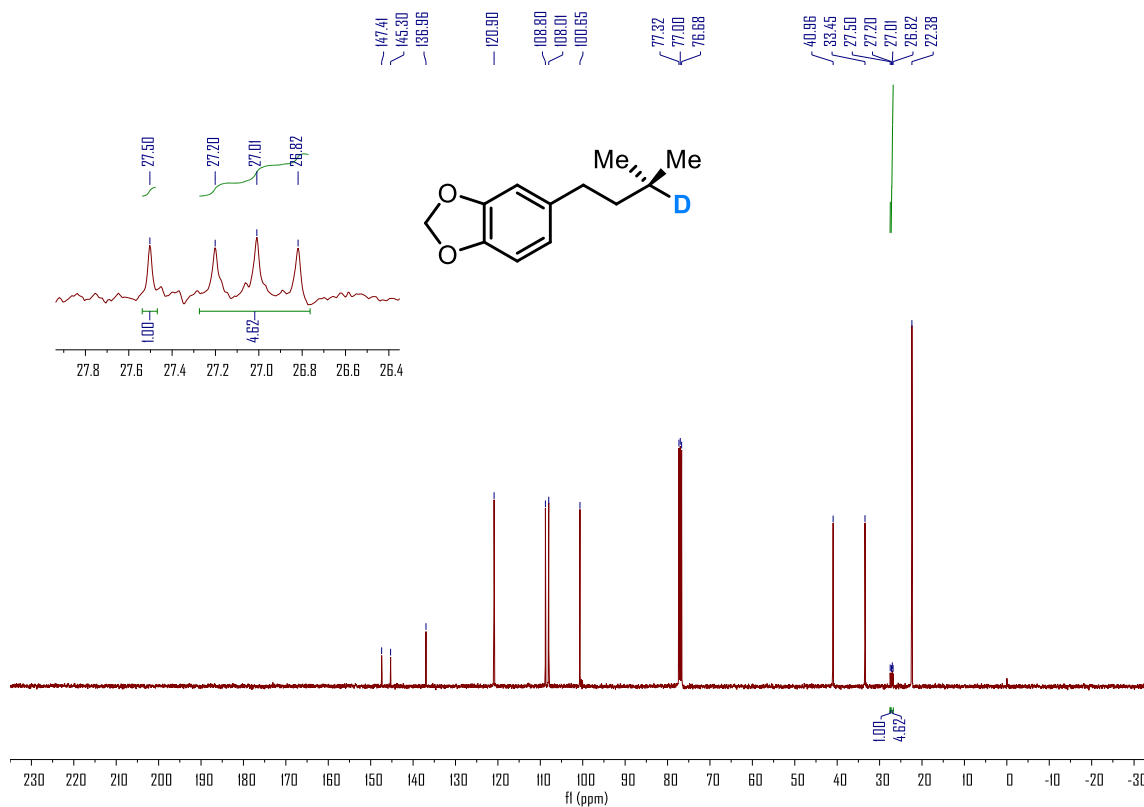
<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **2r**



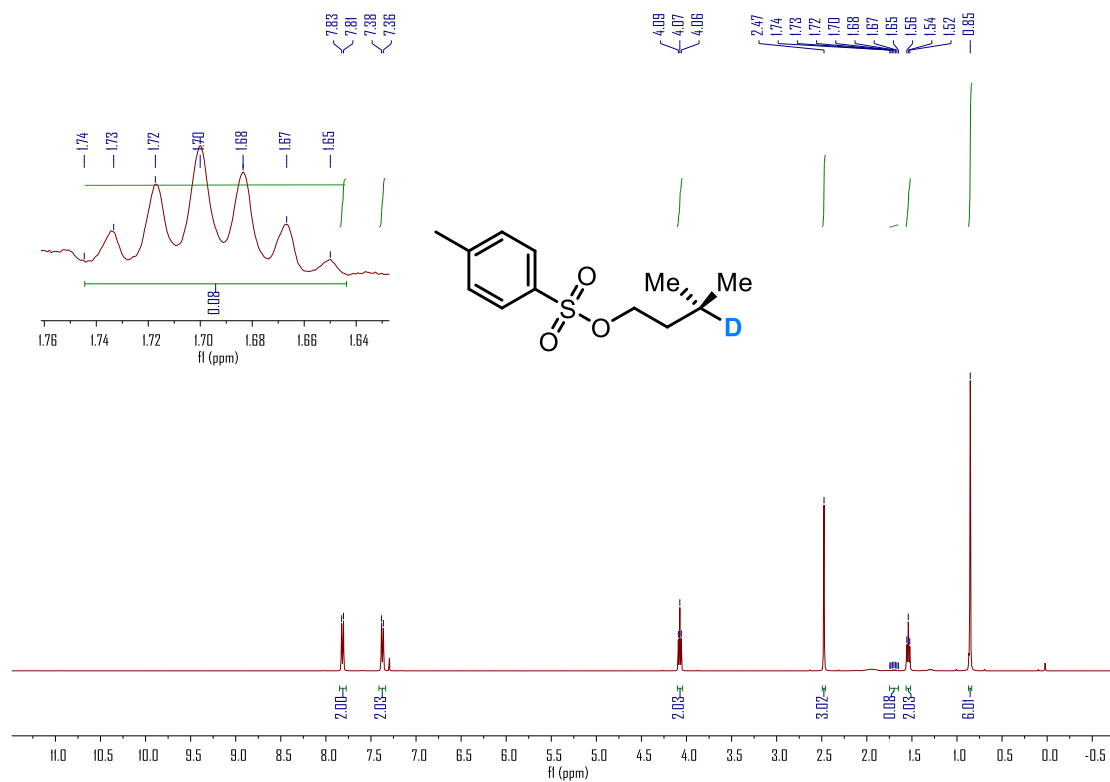
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **2s**



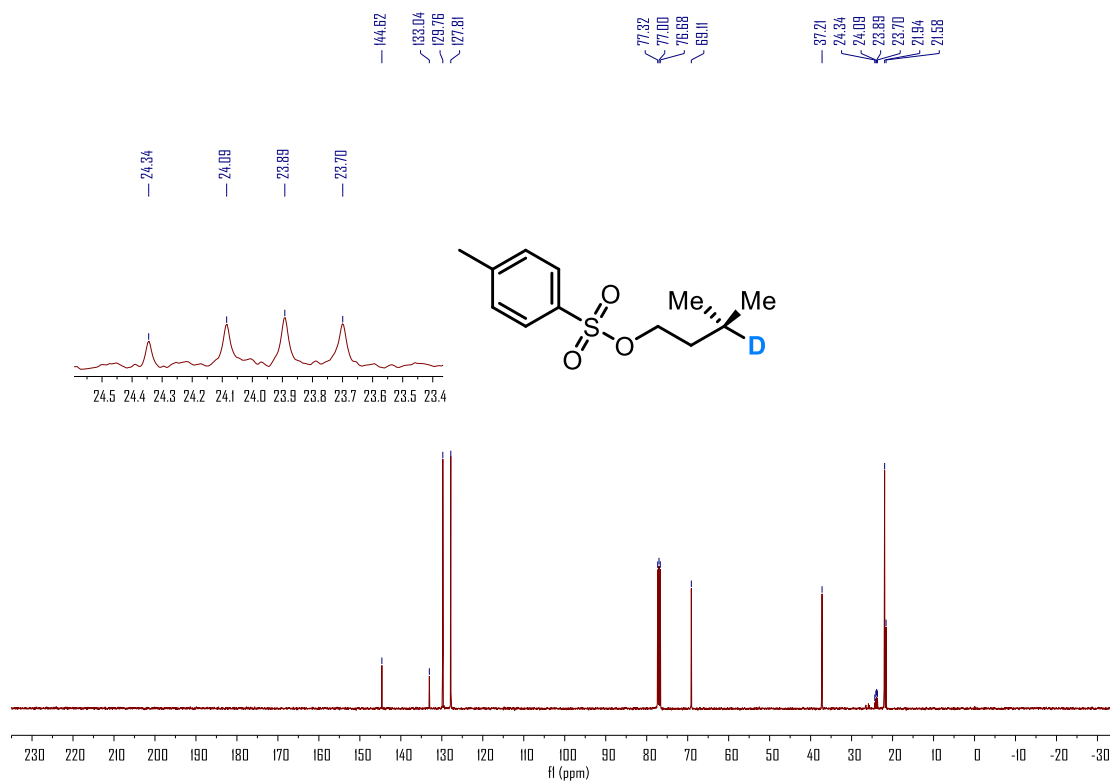
<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **2s**



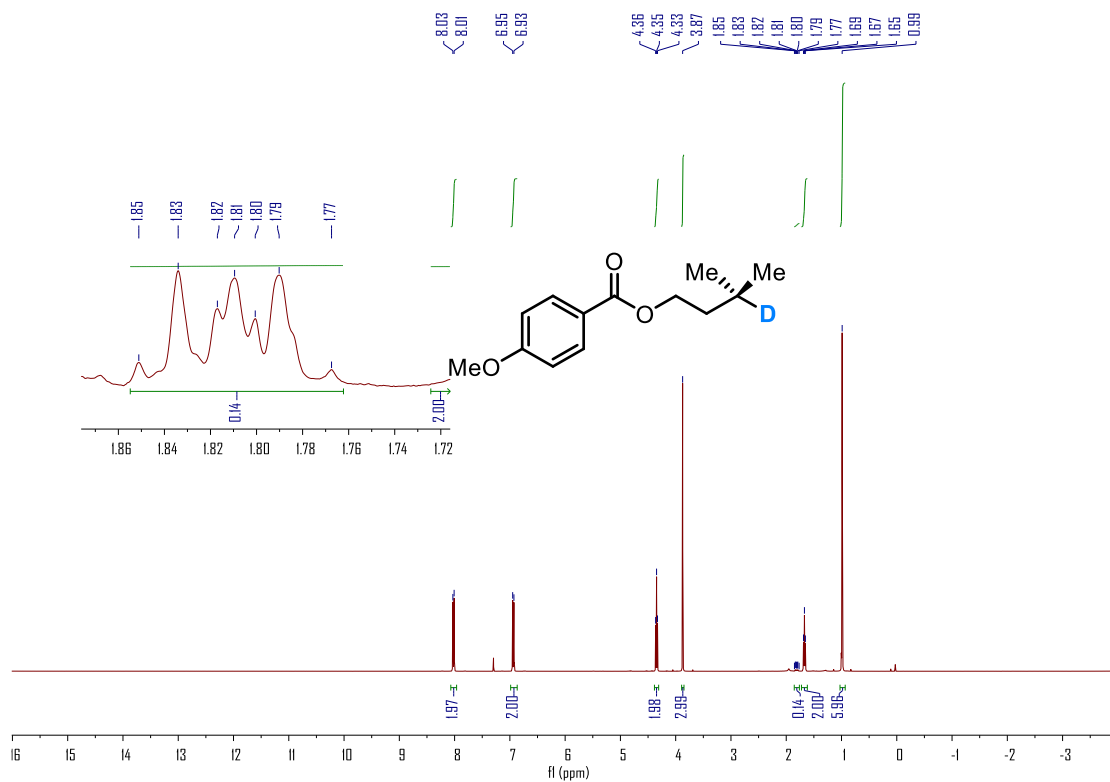
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **2t**



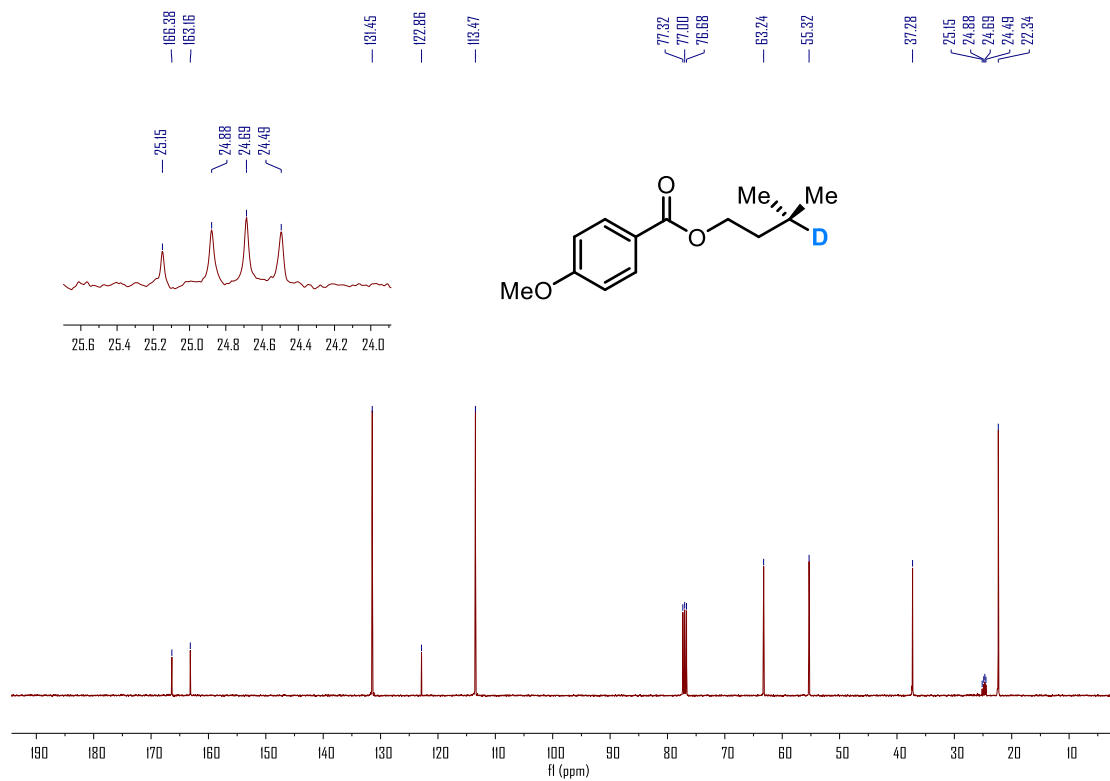
<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **2s**



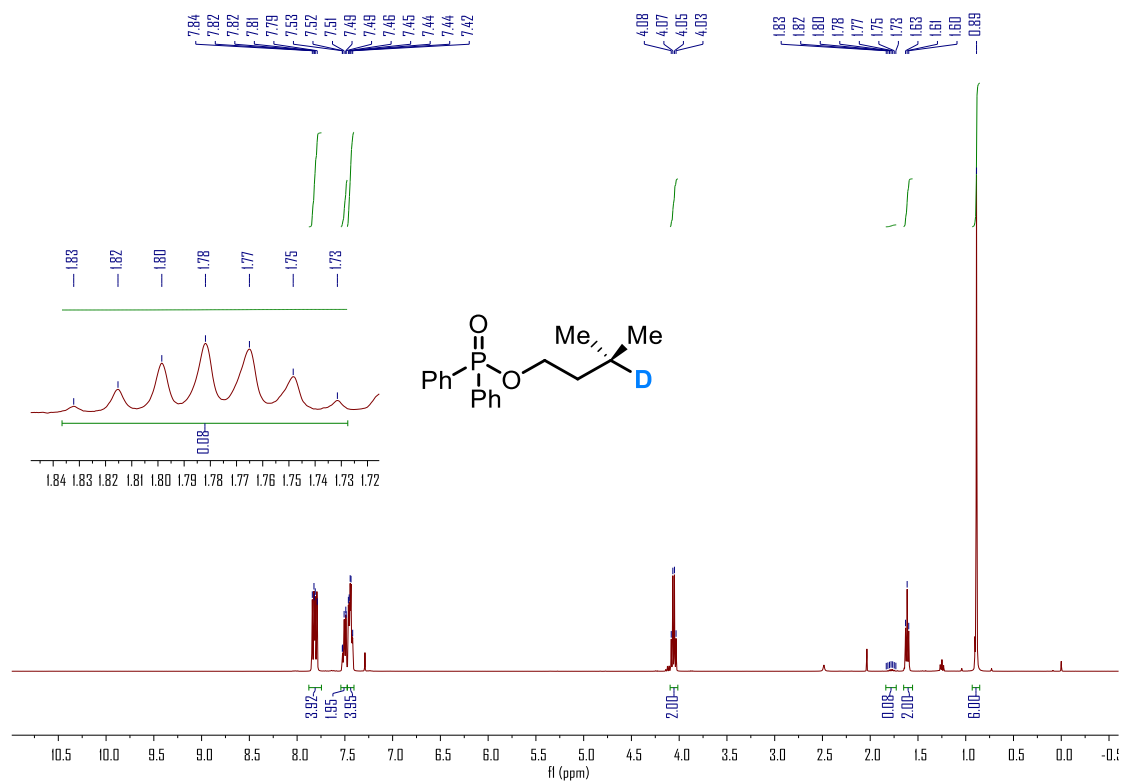
$^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of **2u**



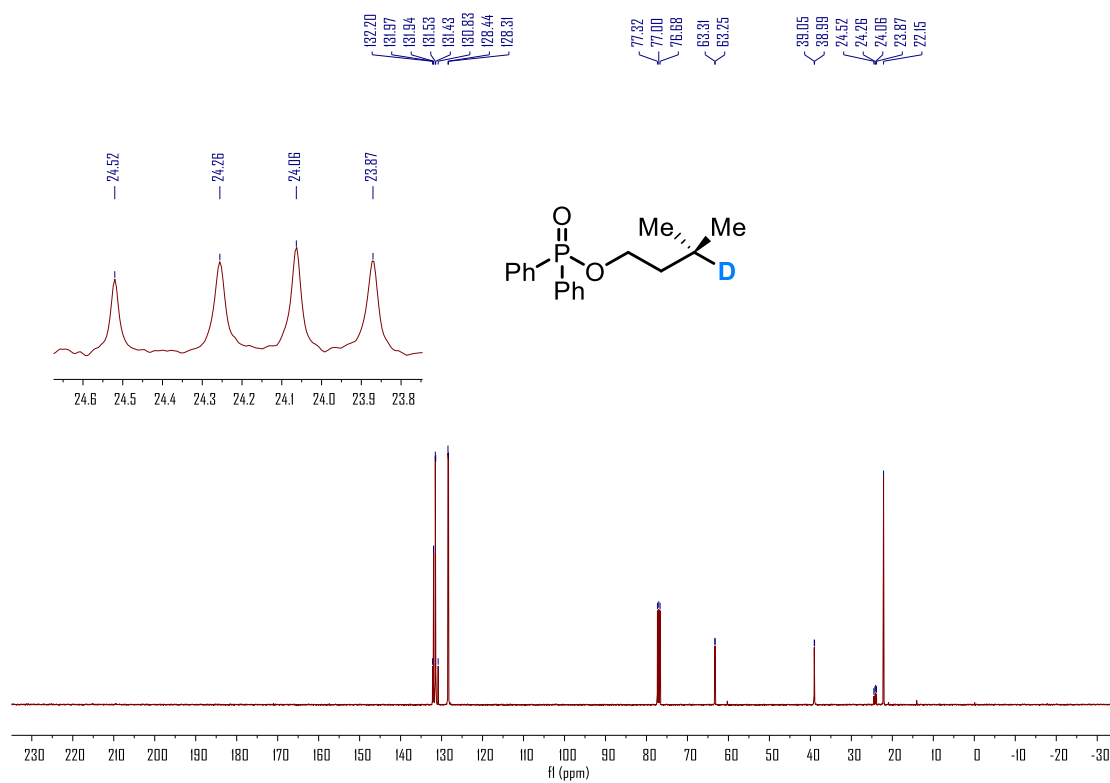
$^{13}\text{C}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of **2u**



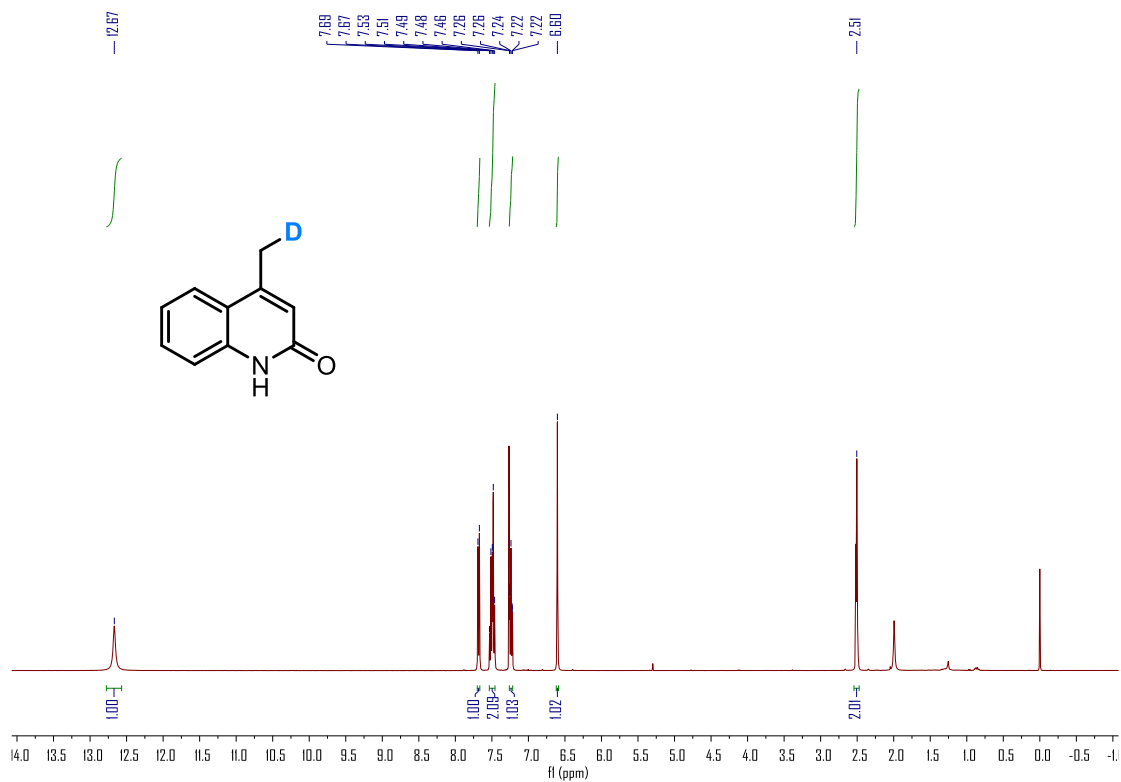
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **2v**



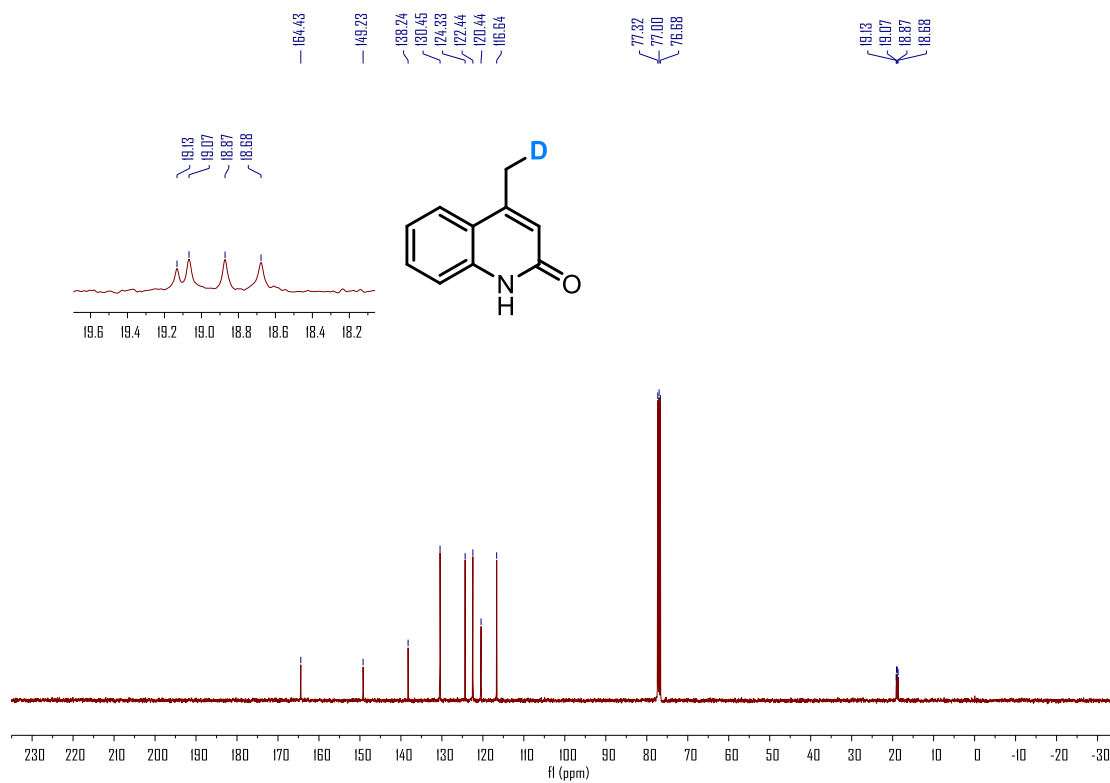
<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **2v**



$^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of **2w**

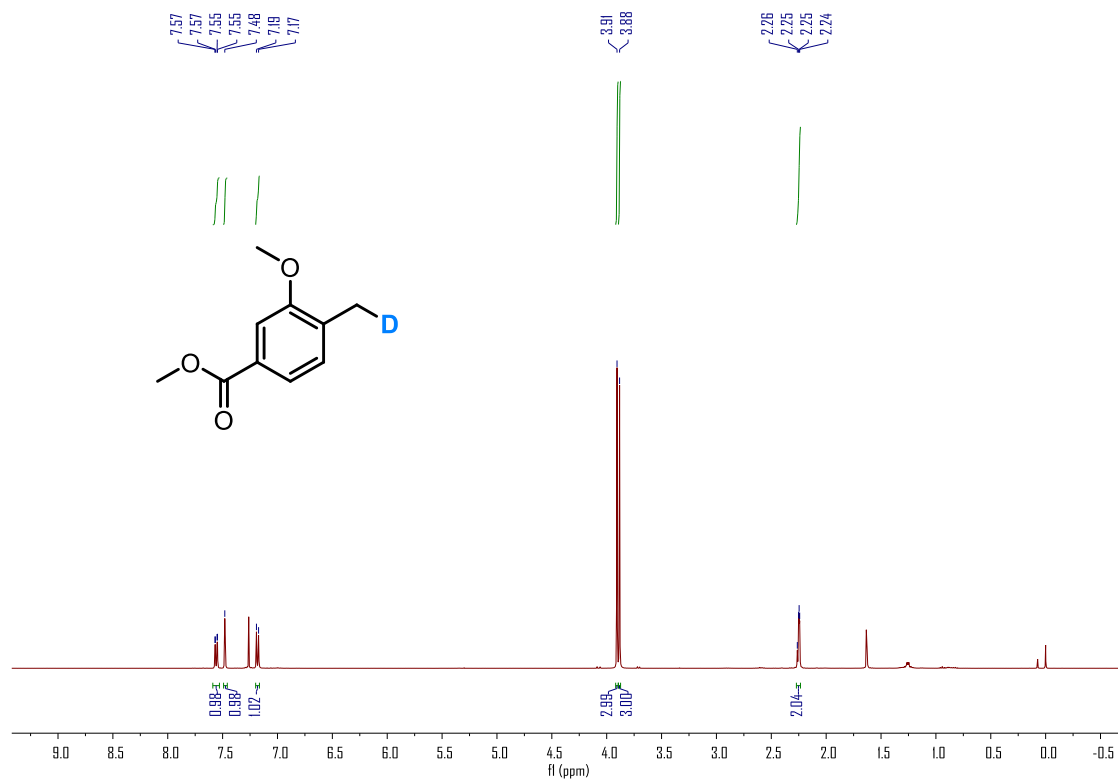


$^{13}\text{C}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of **2w**

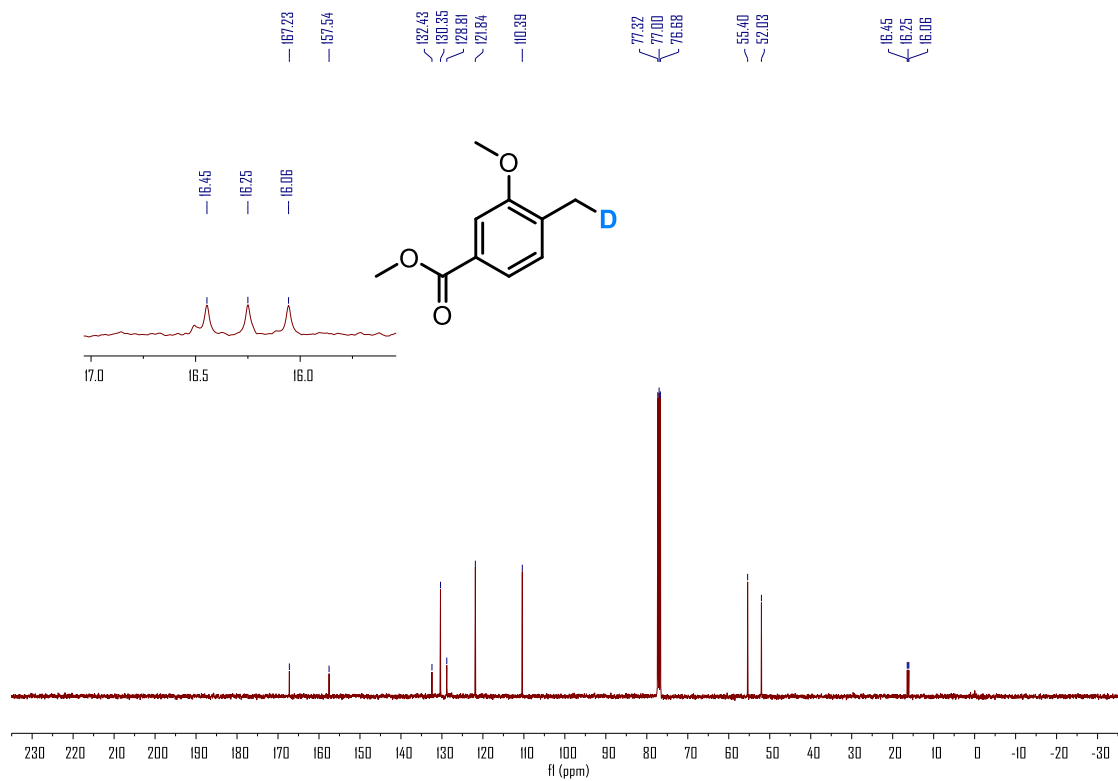




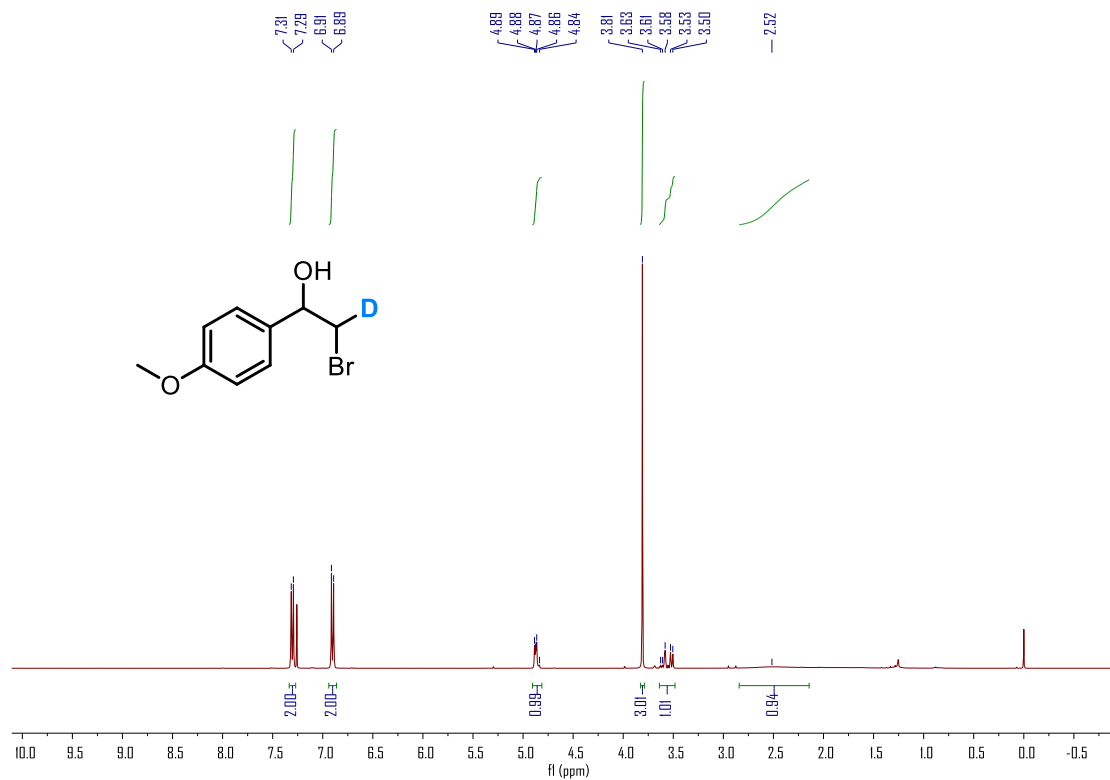
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **2x**



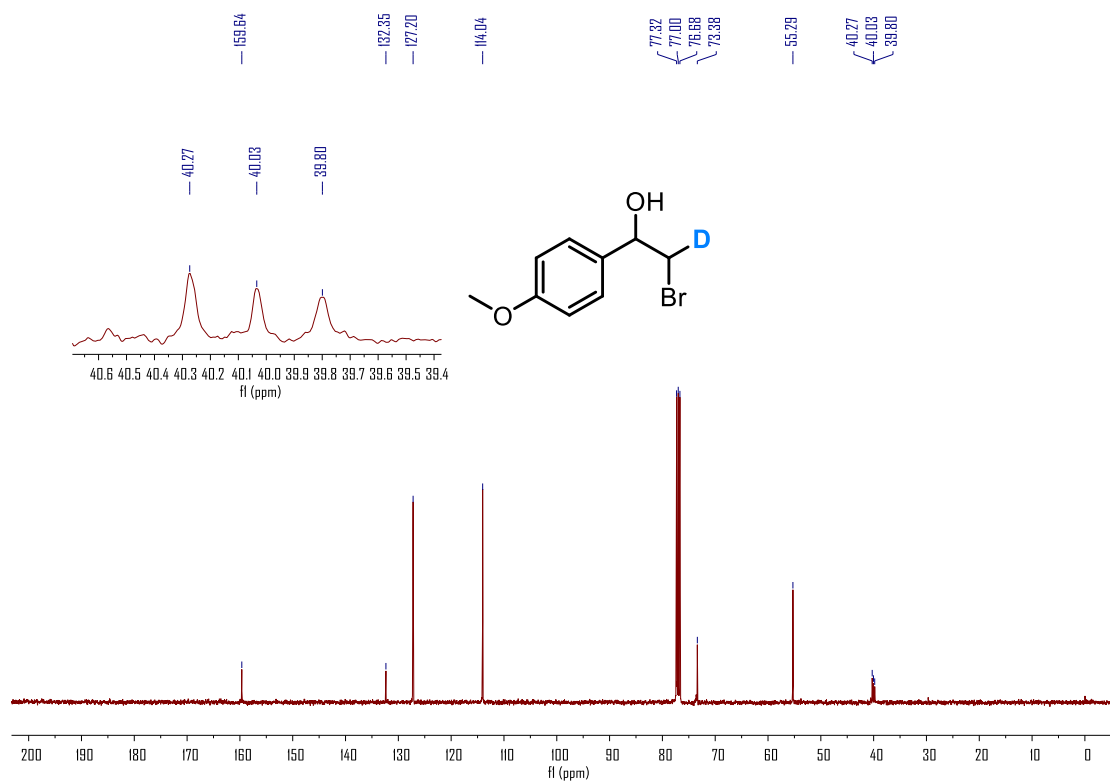
<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **2x**



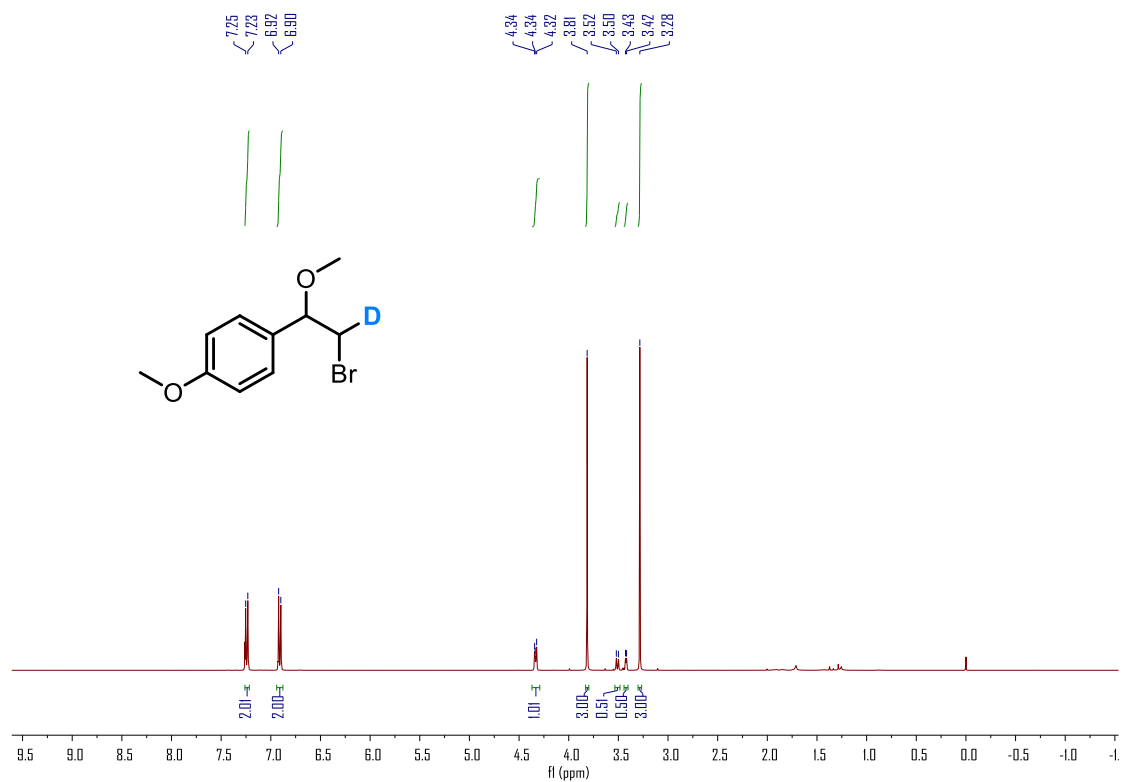
$^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of **2y**



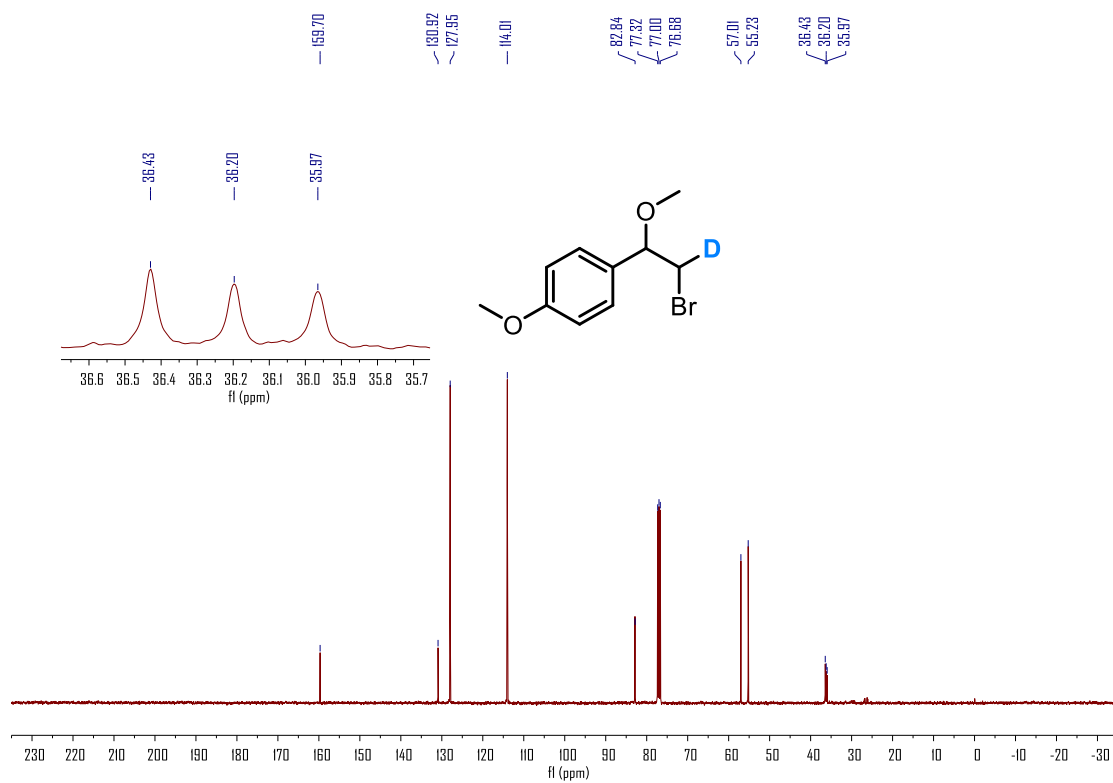
$^{13}\text{C}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of **2y**



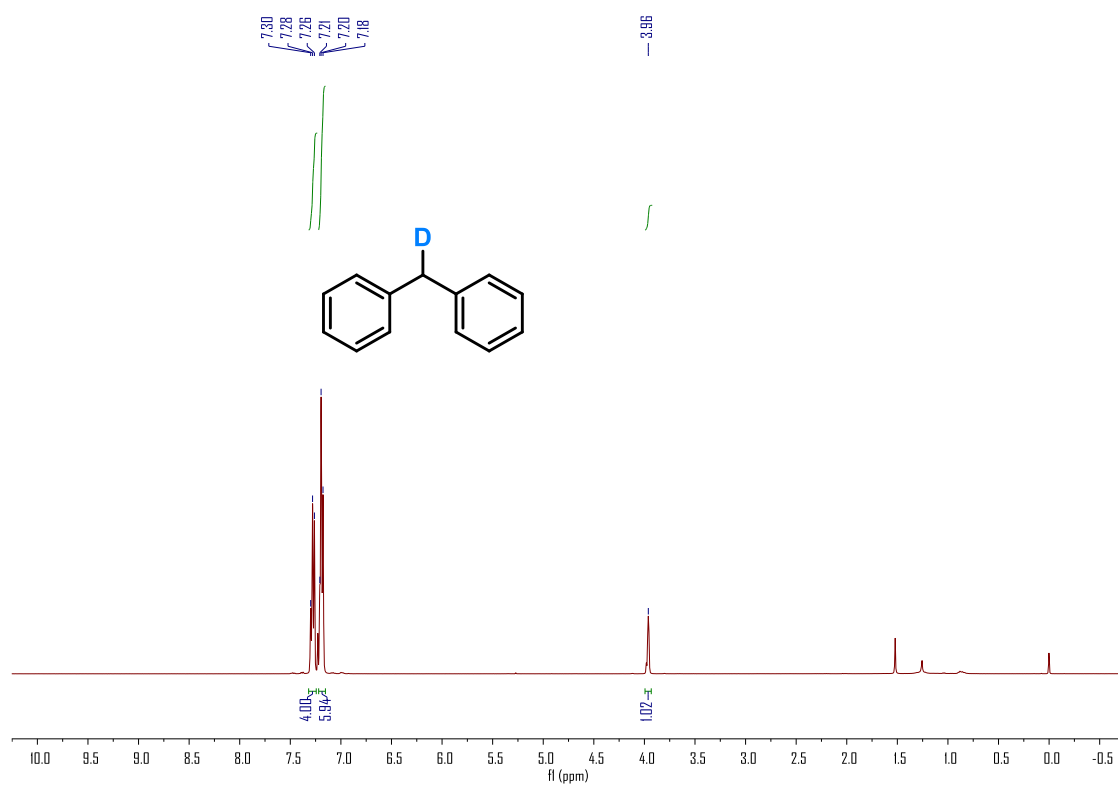
$^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of **2z**



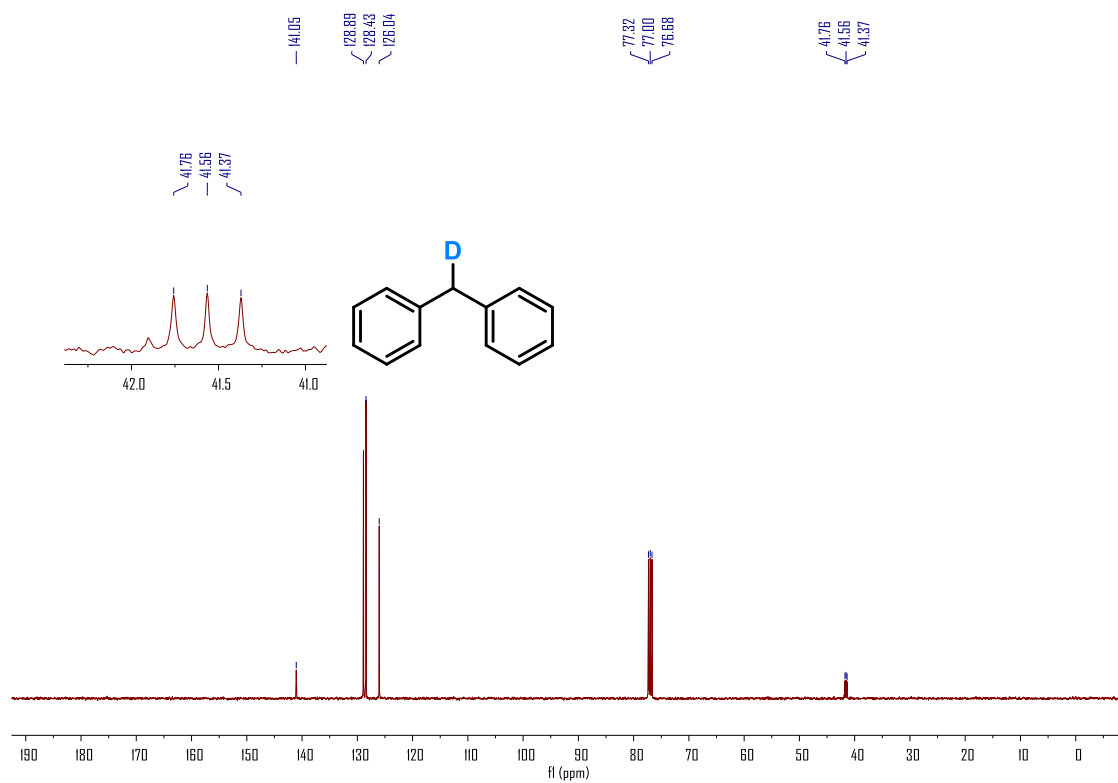
$^{13}\text{C}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of **2z**



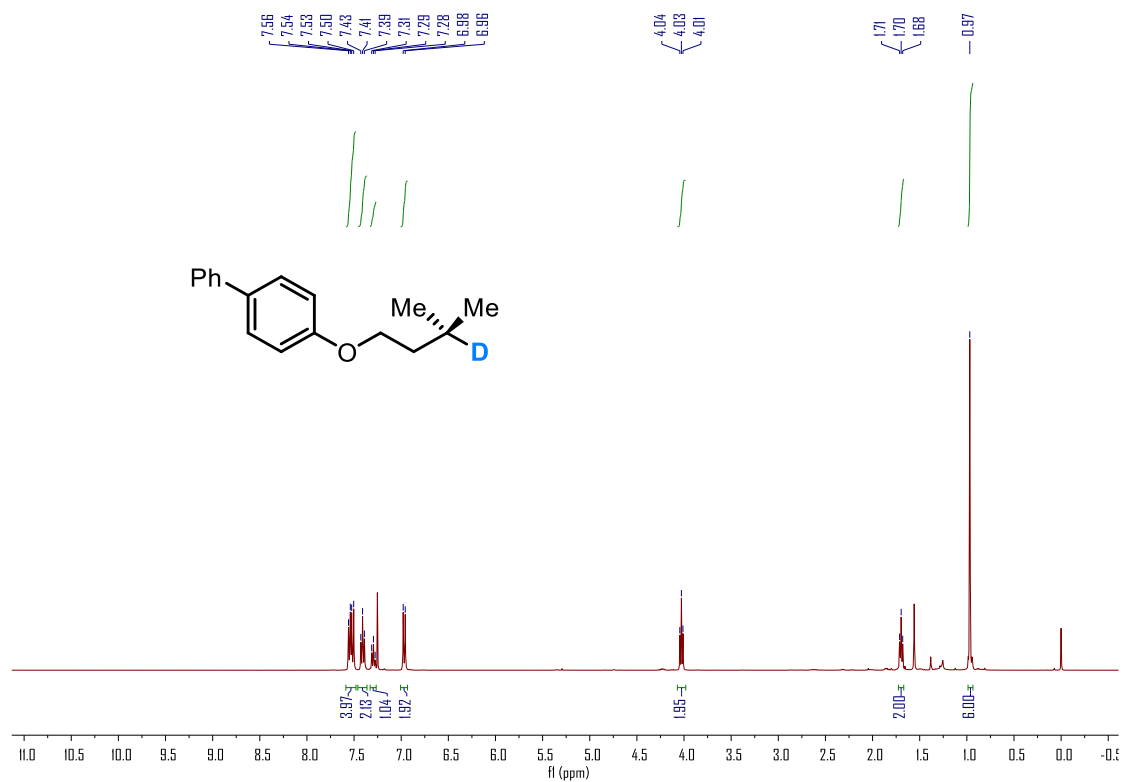
$^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of **2aa**



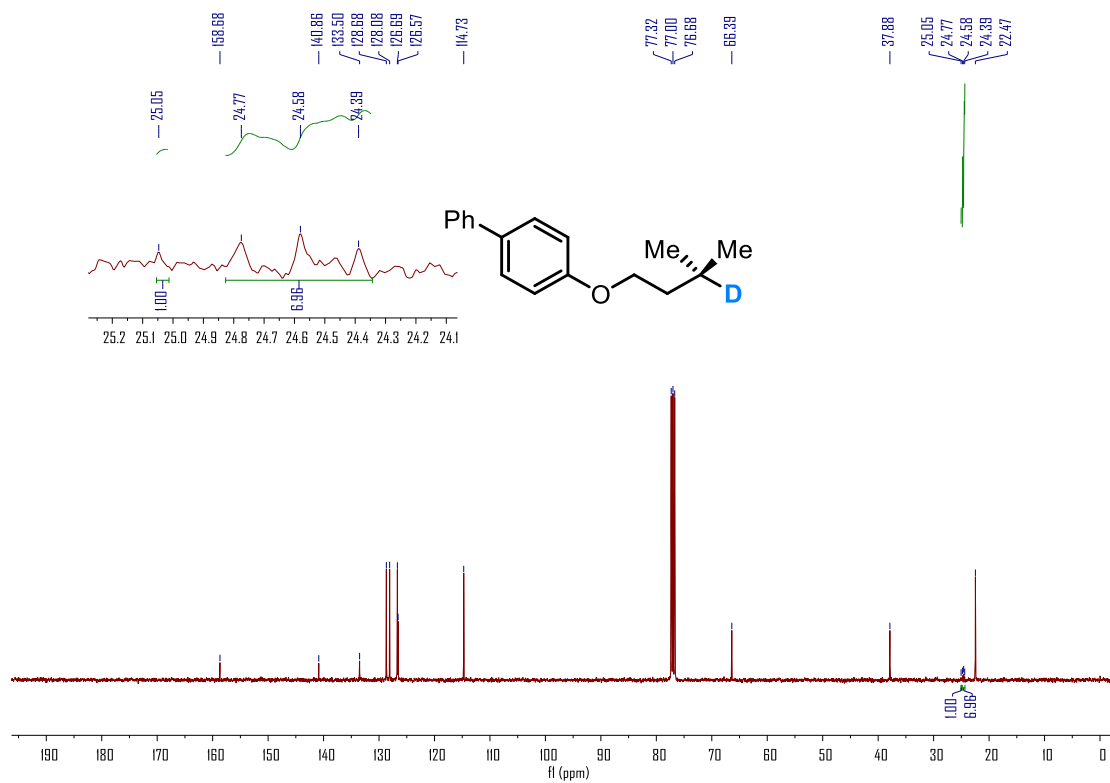
$^{13}\text{C}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of **2aa**



<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **2ab**

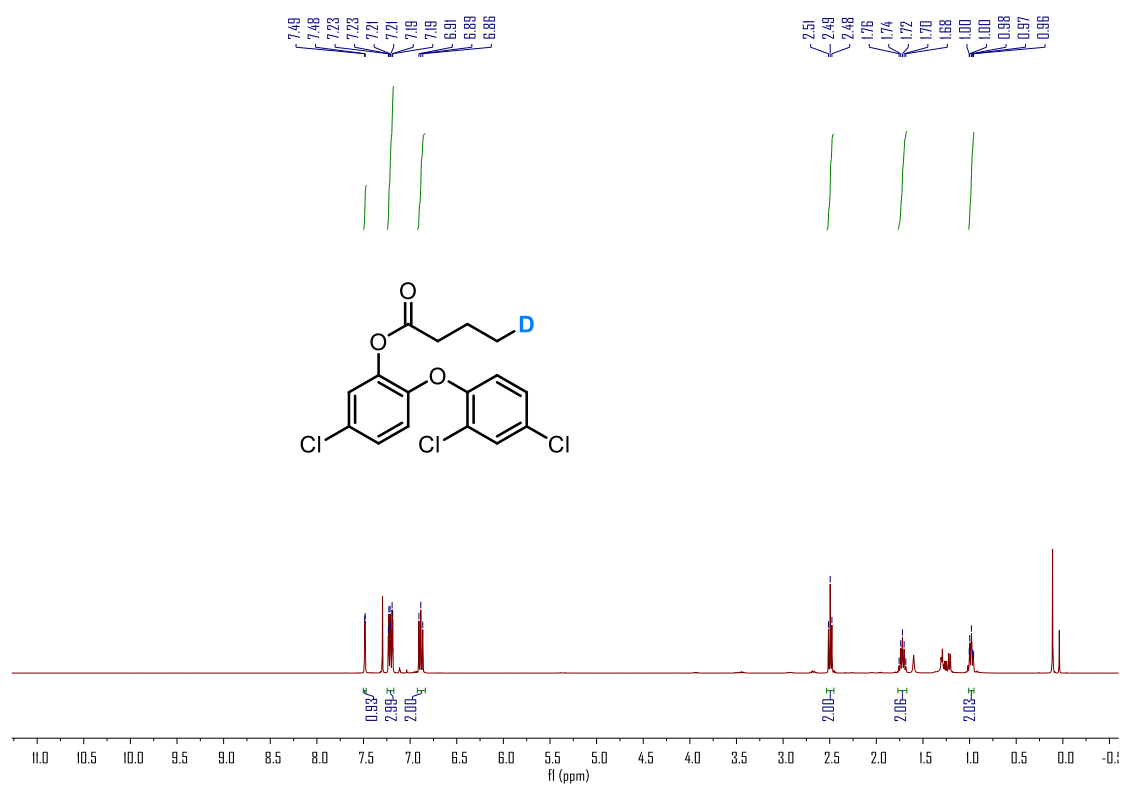


<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **2ab**

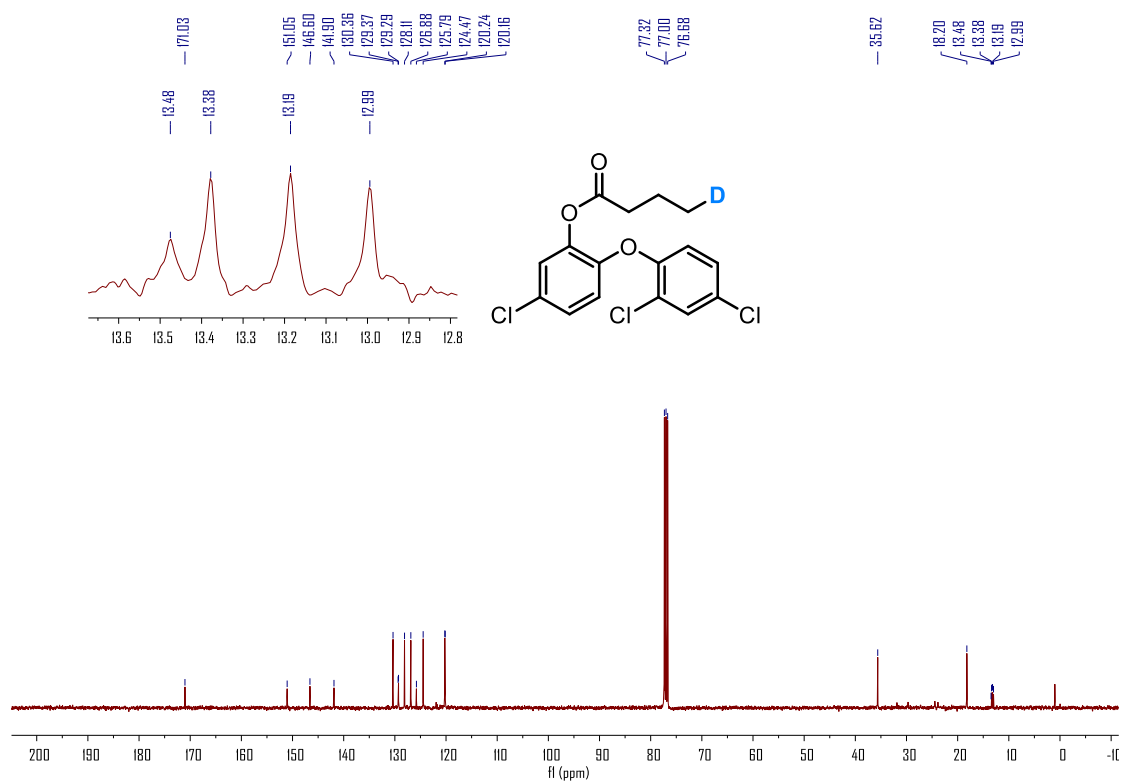




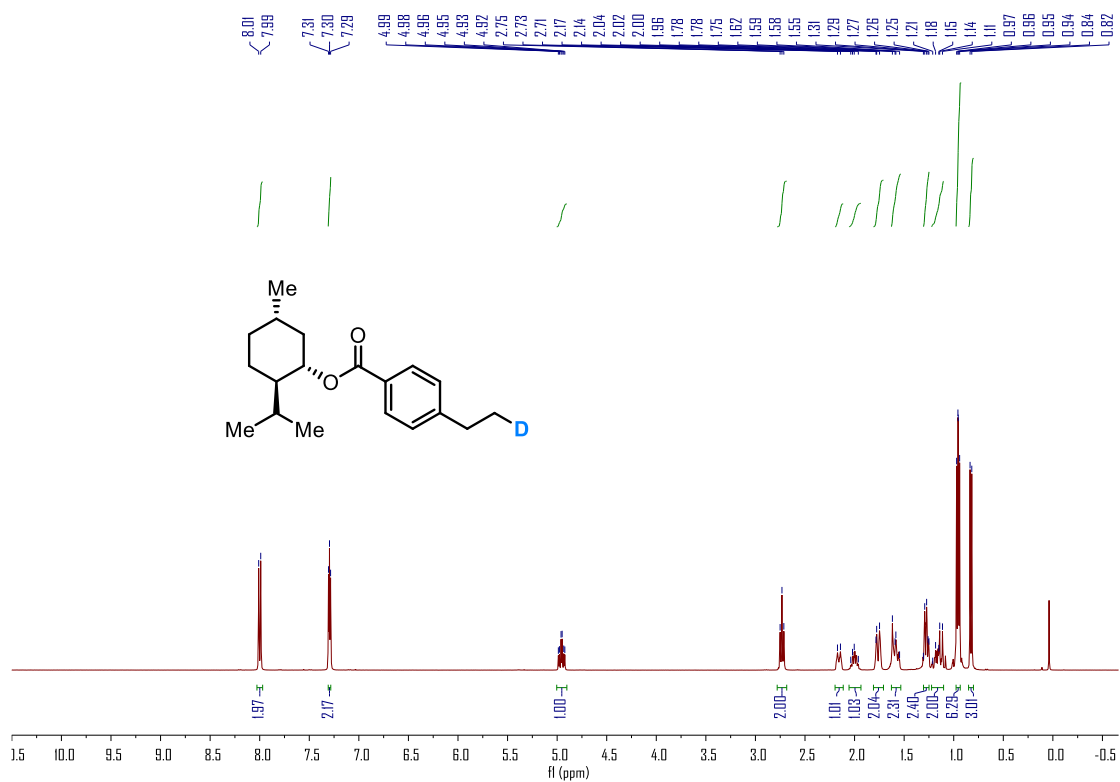
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **2ad**



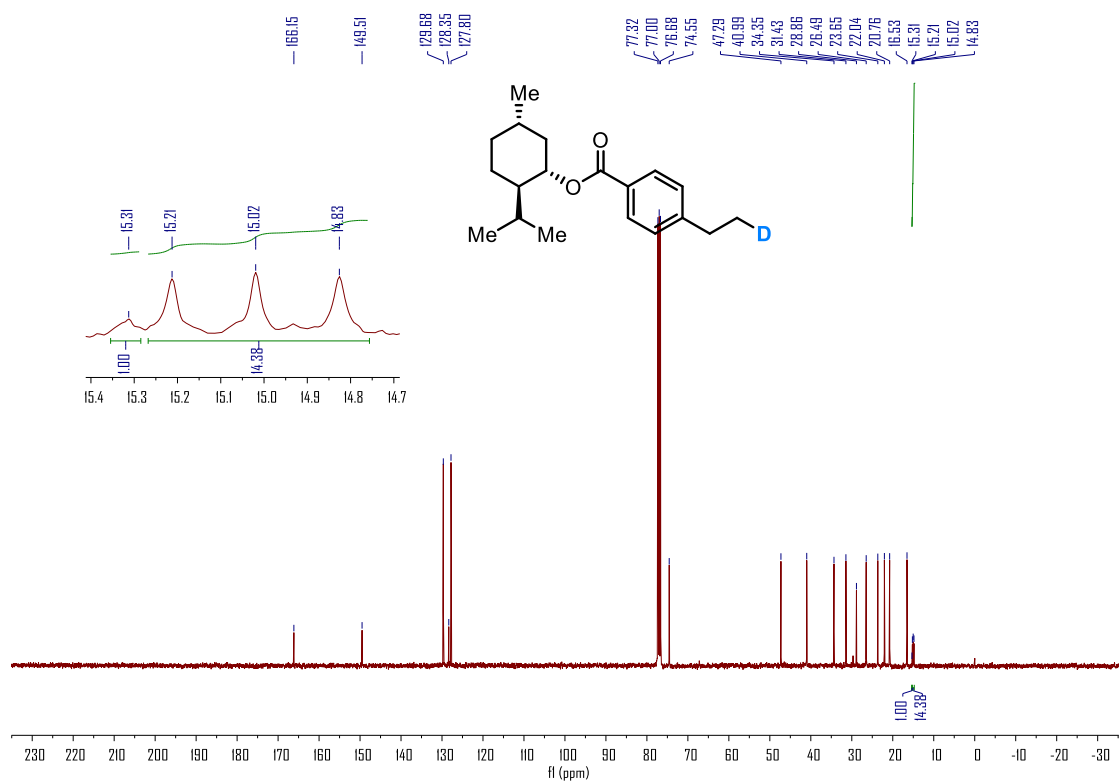
<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **2ad**



<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **2ae**

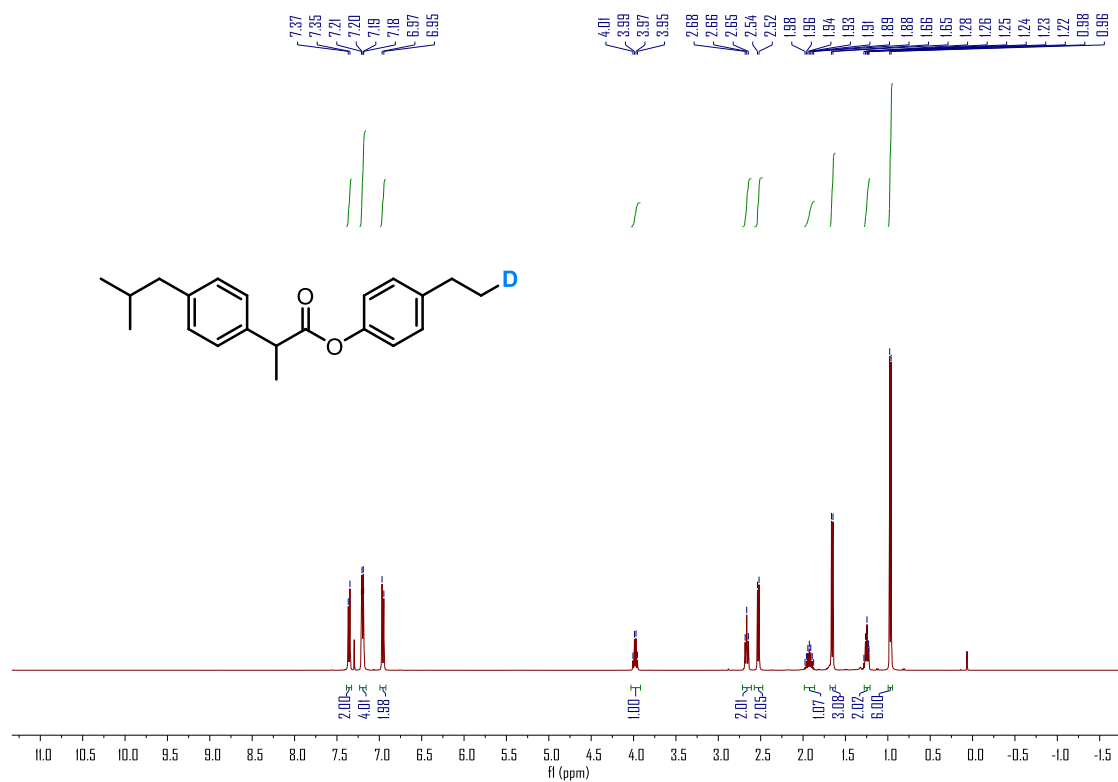


<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **2ae**

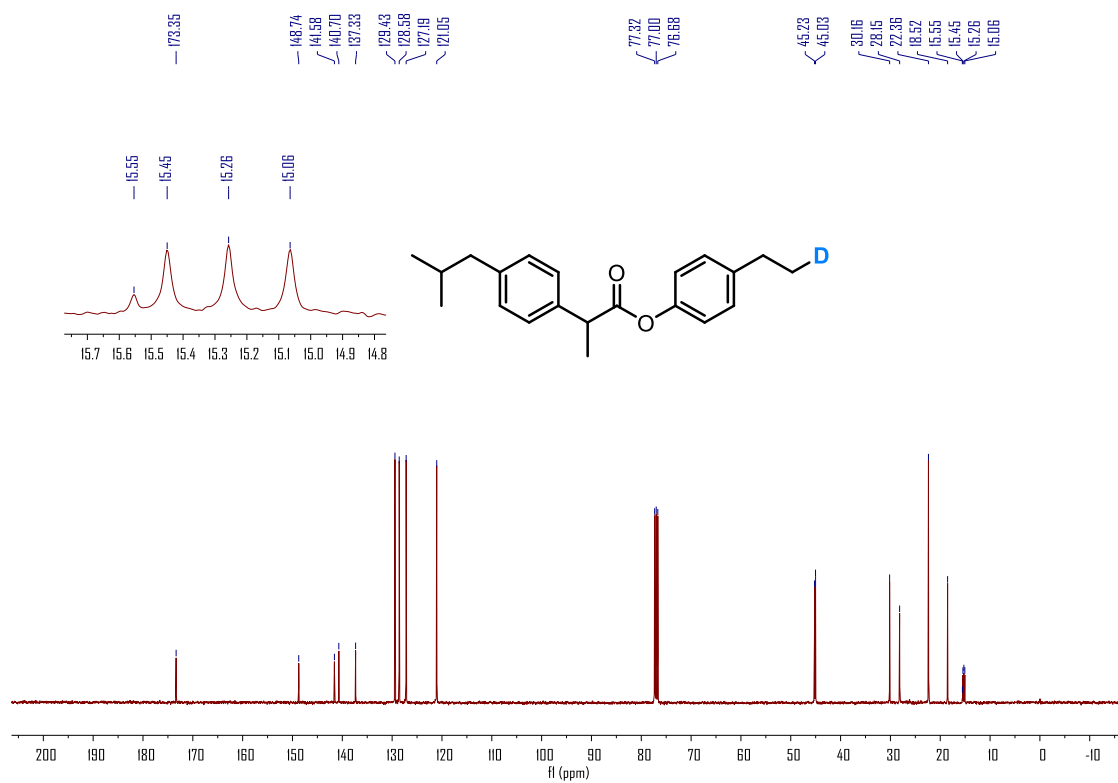




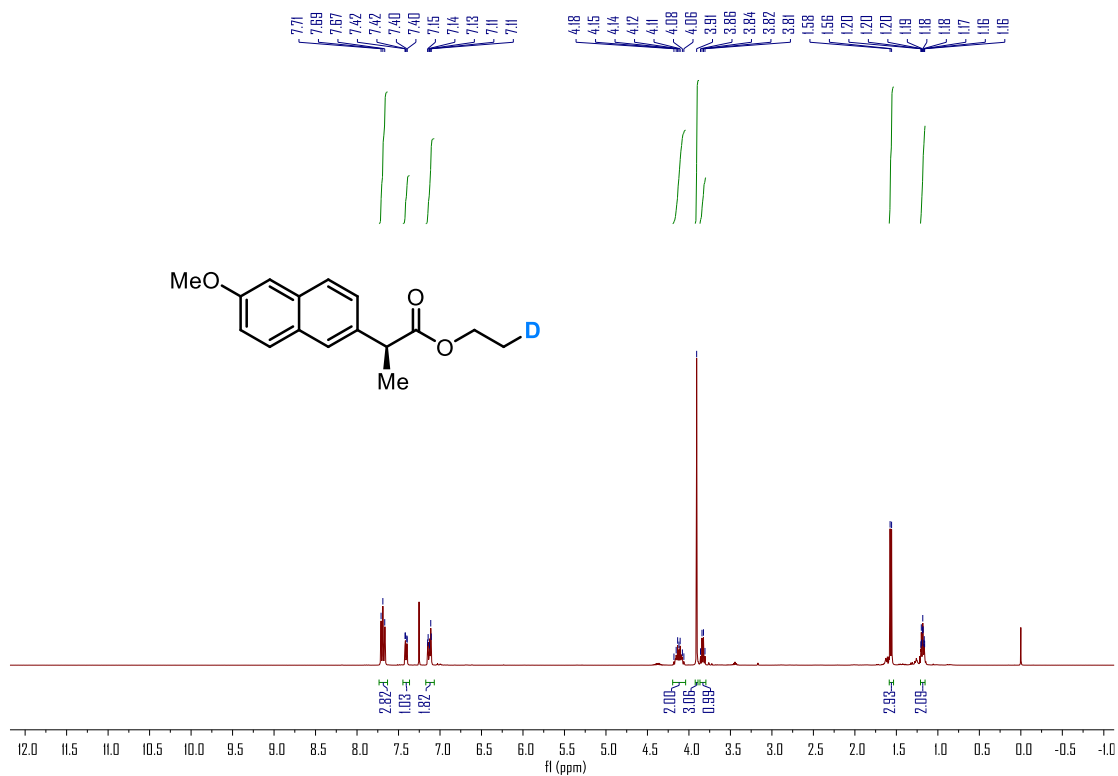
$^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of **2af**



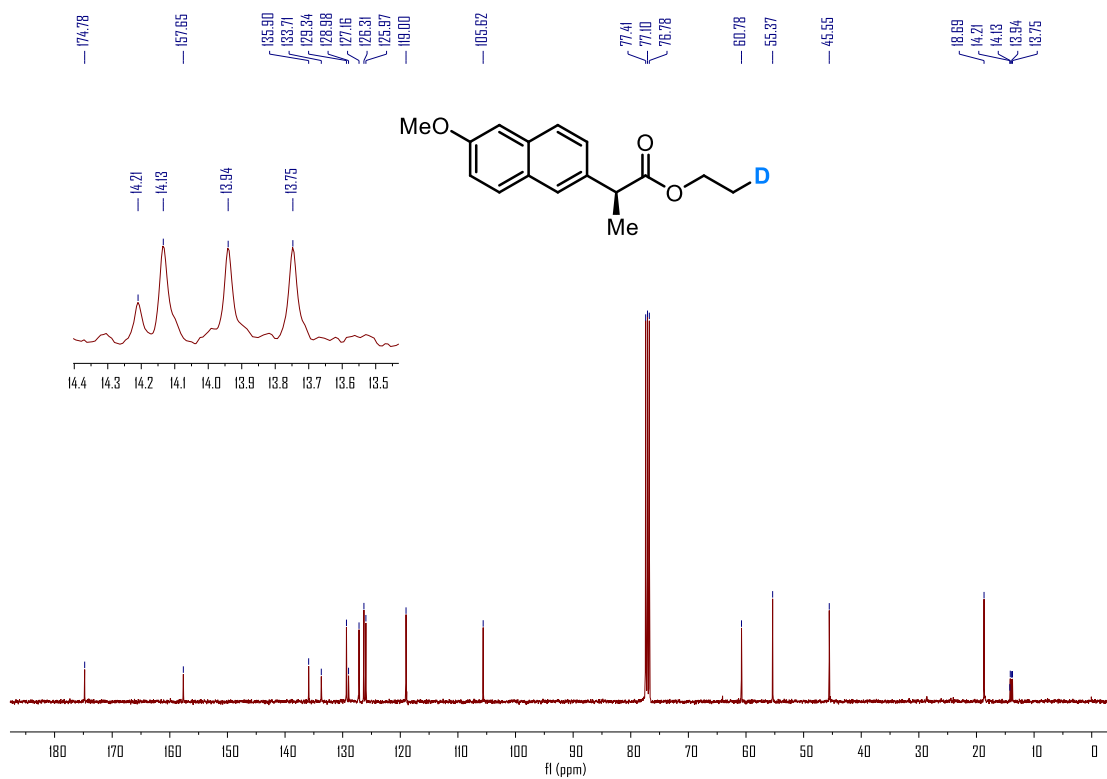
$^{13}\text{C}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of **2af**



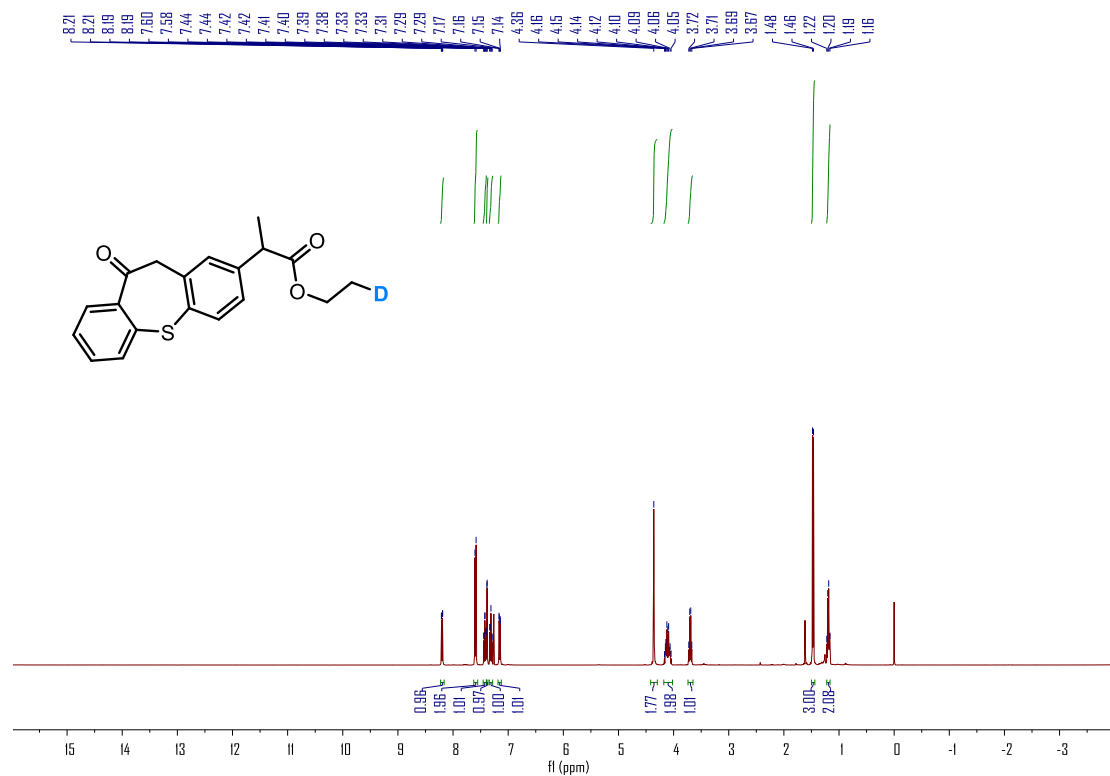
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **2ag**



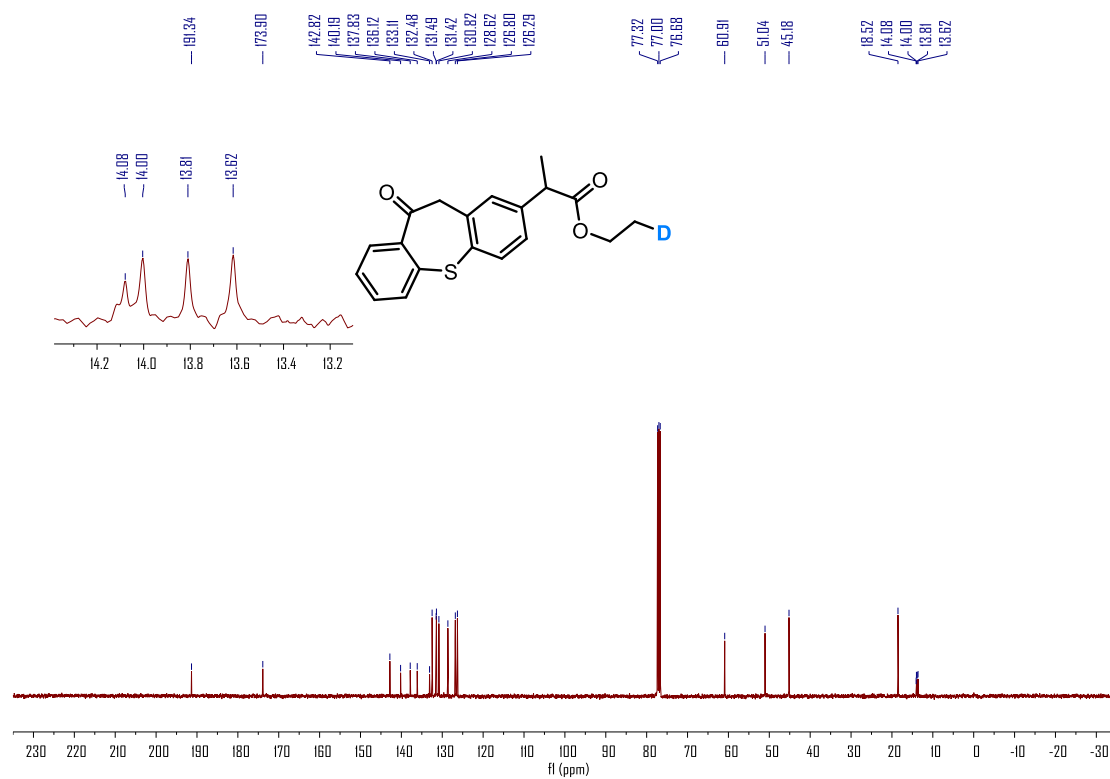
<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **2ag**



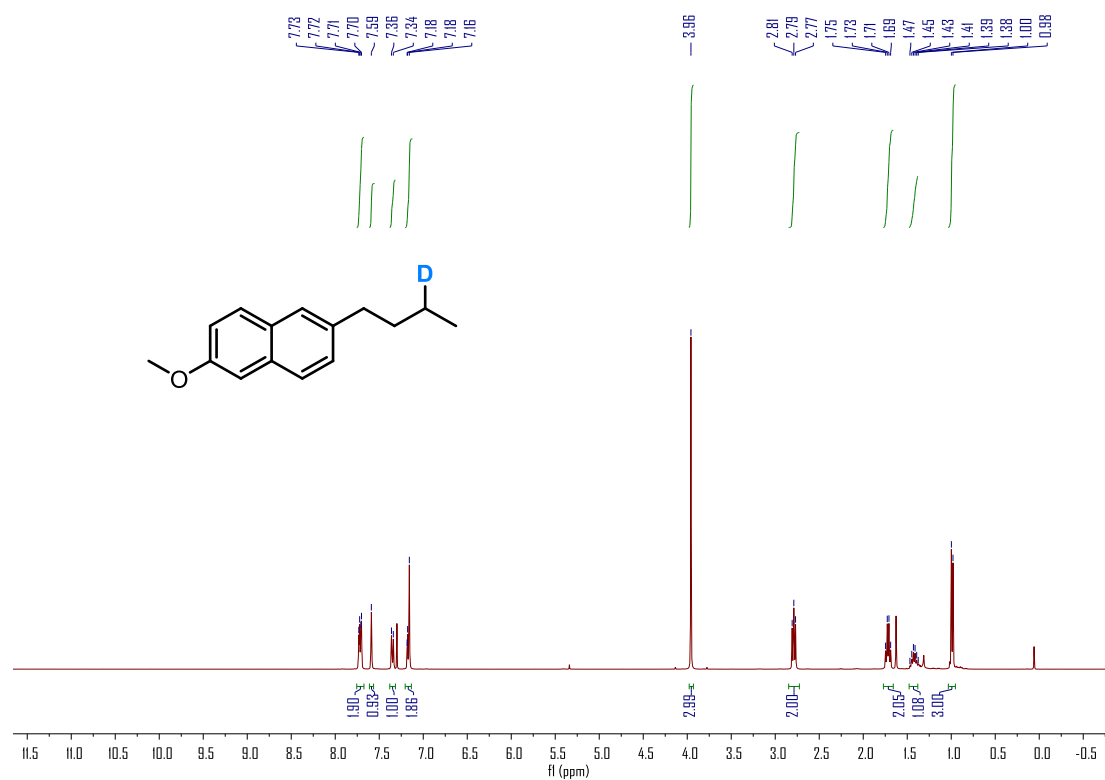
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **2ah**



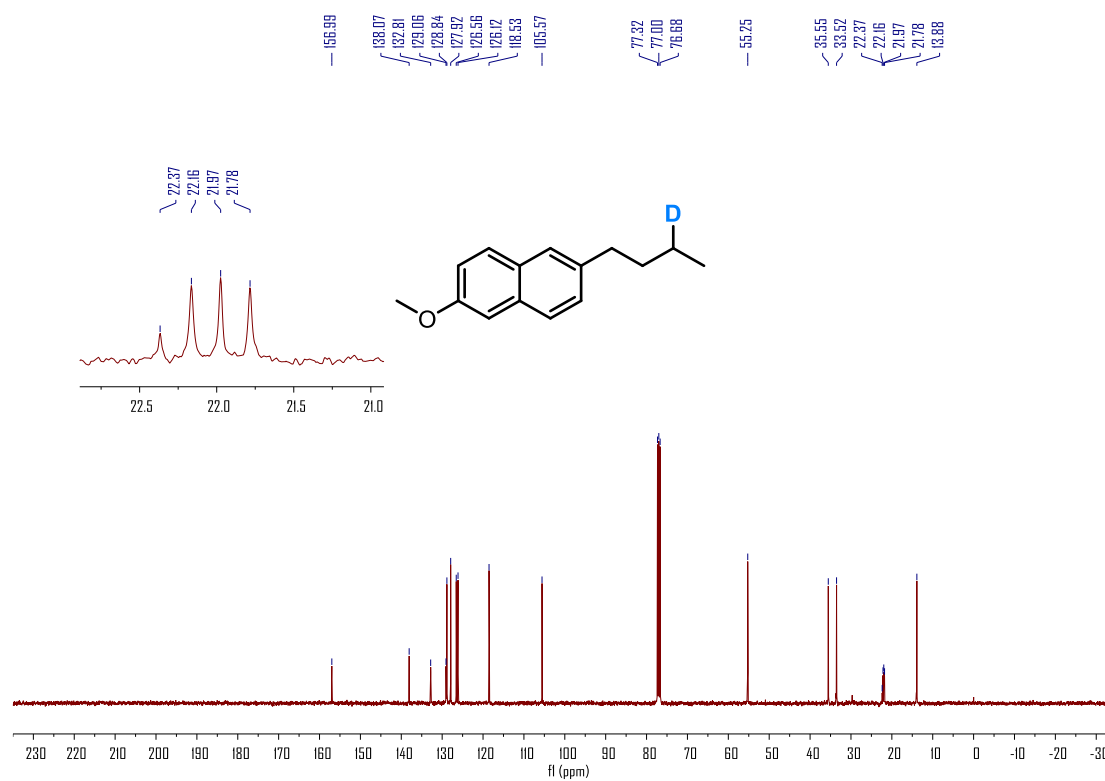
<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **2ah**



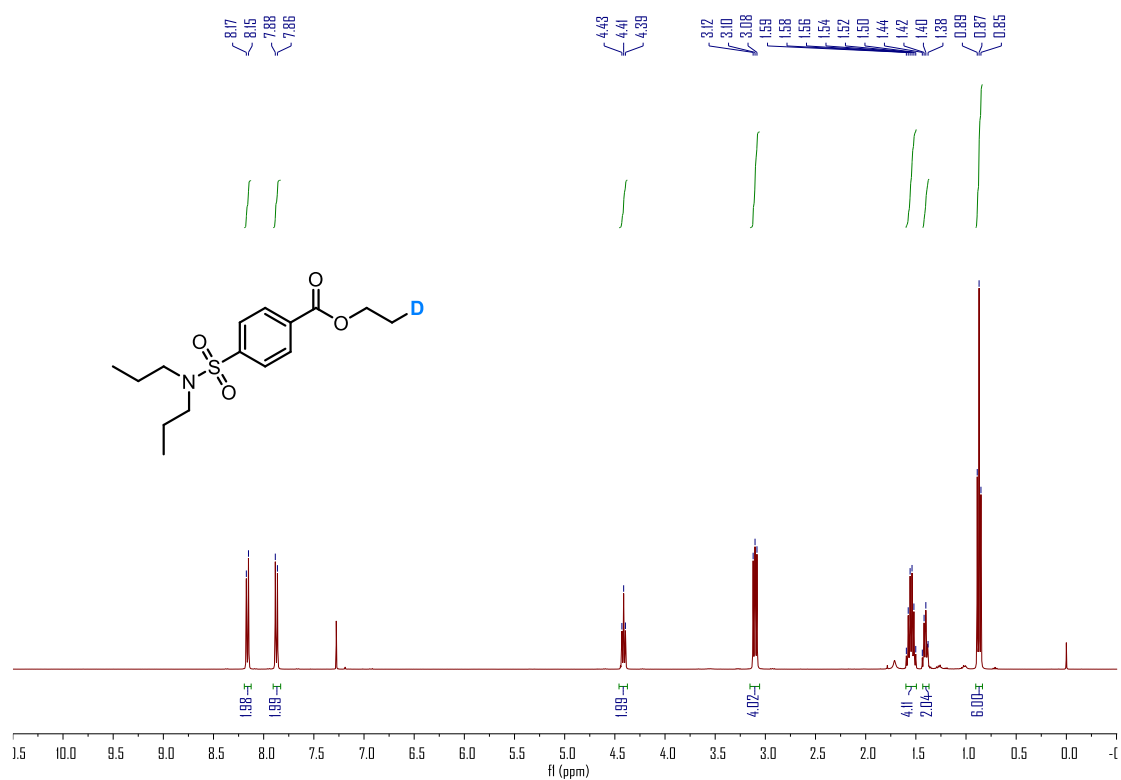
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **2ai**



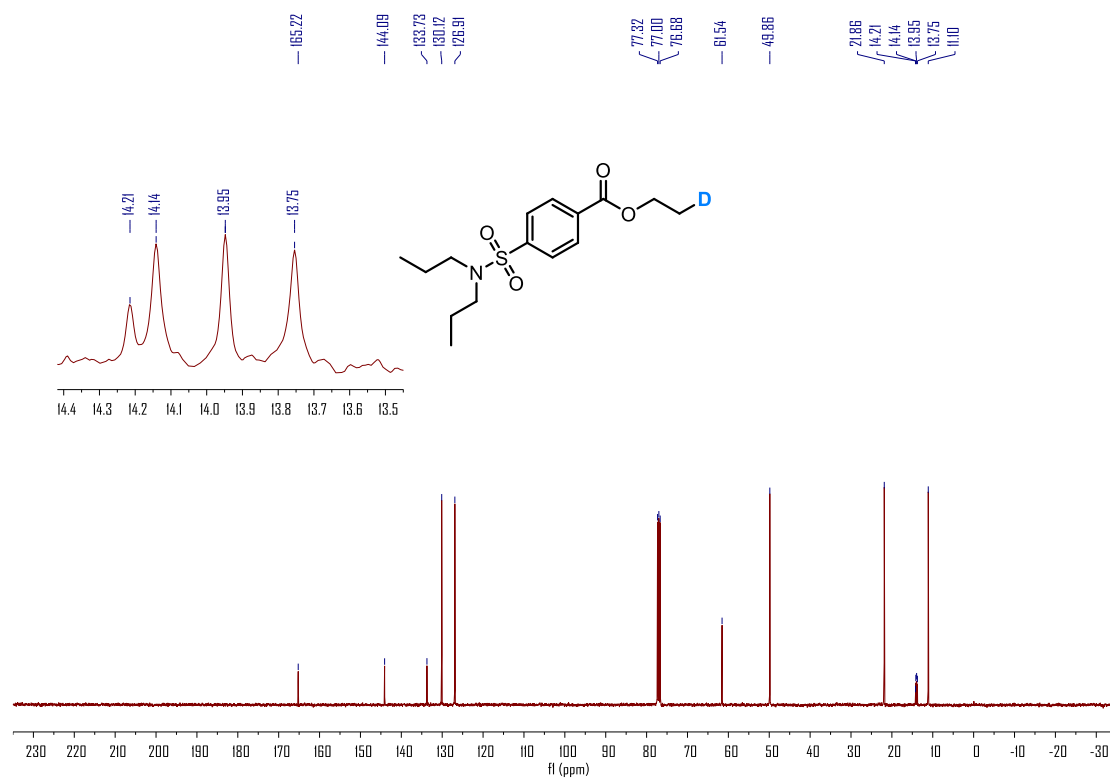
<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **2ai**



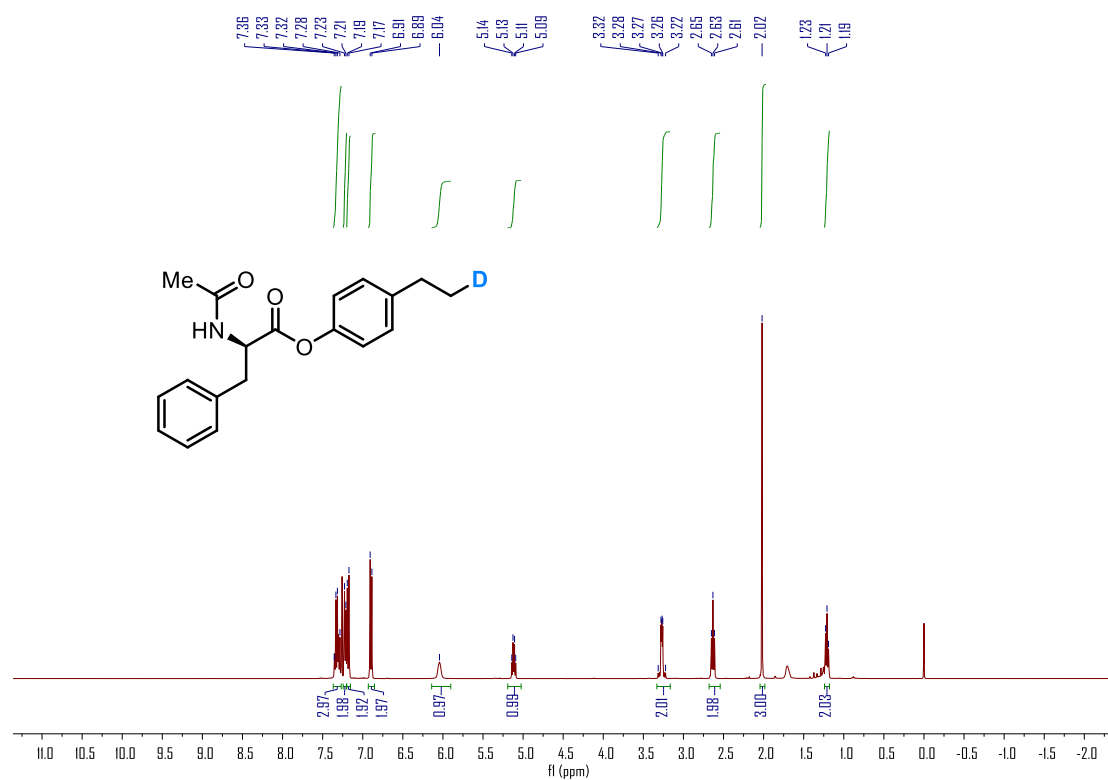
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **2aj**



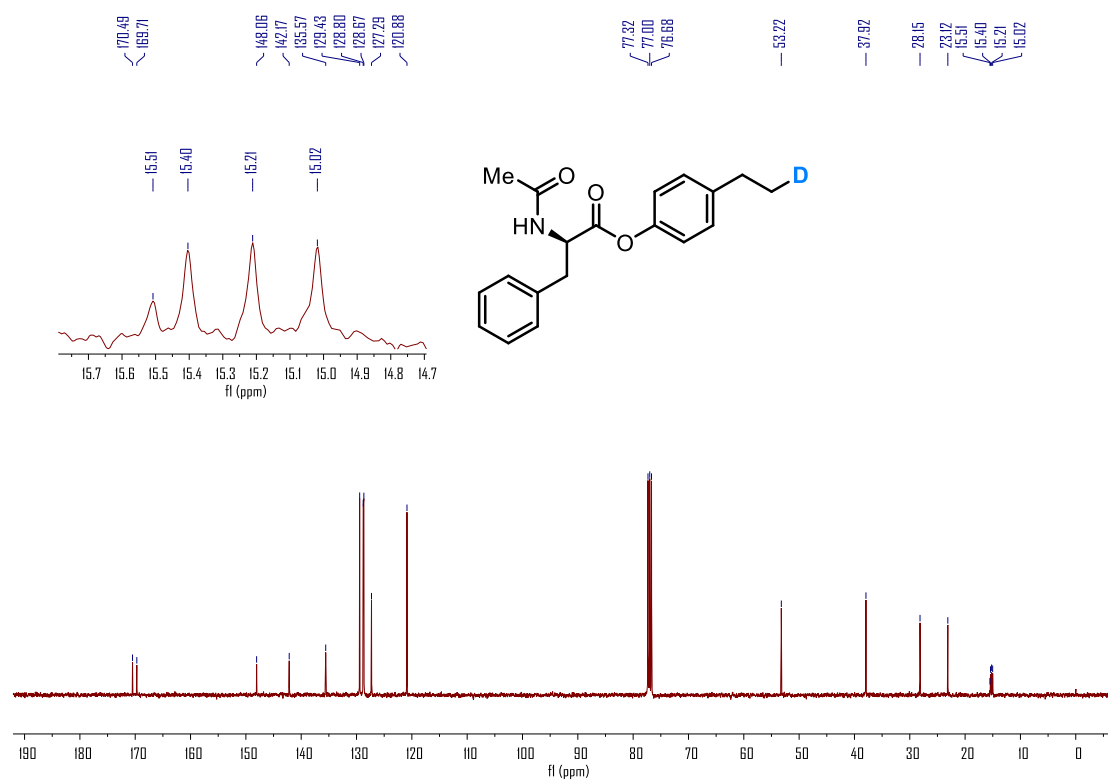
<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **2aj**



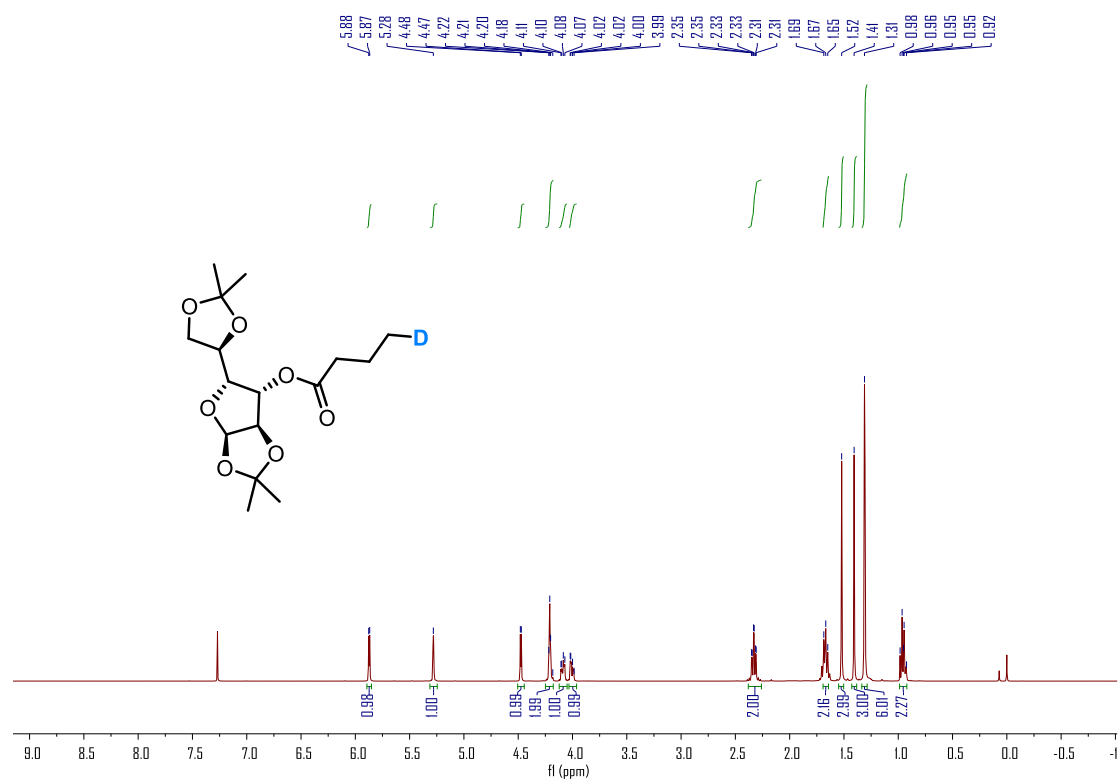
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **2ak**



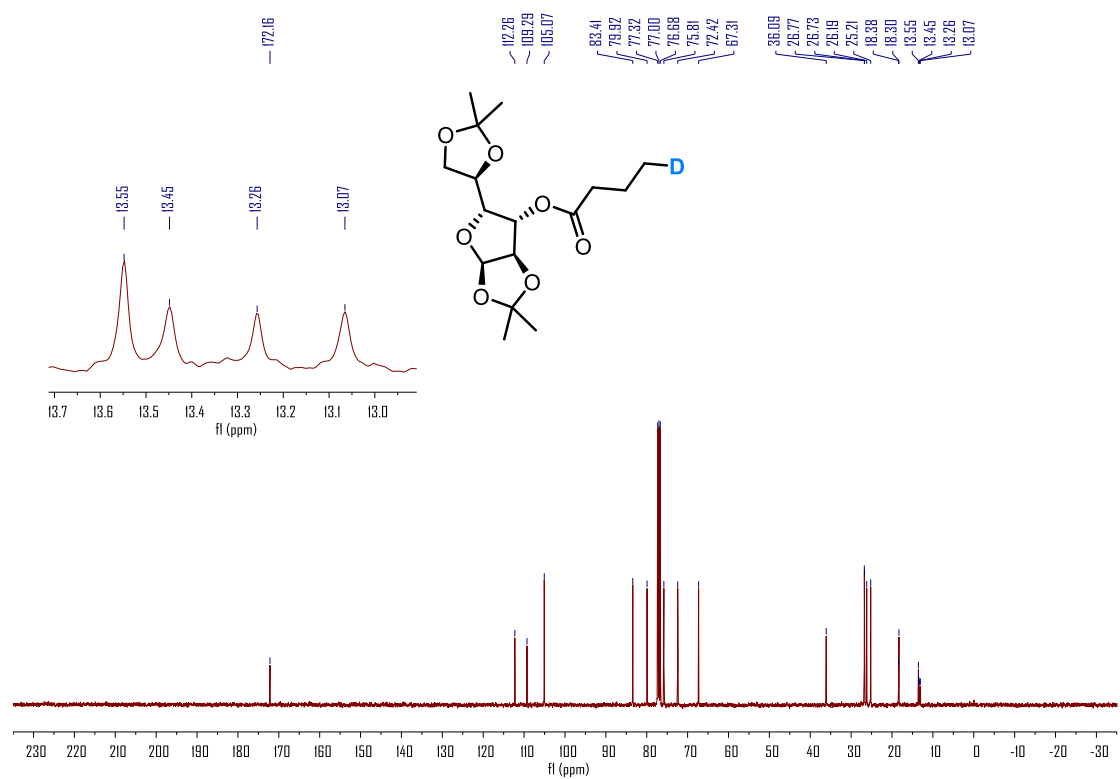
<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **2ak**



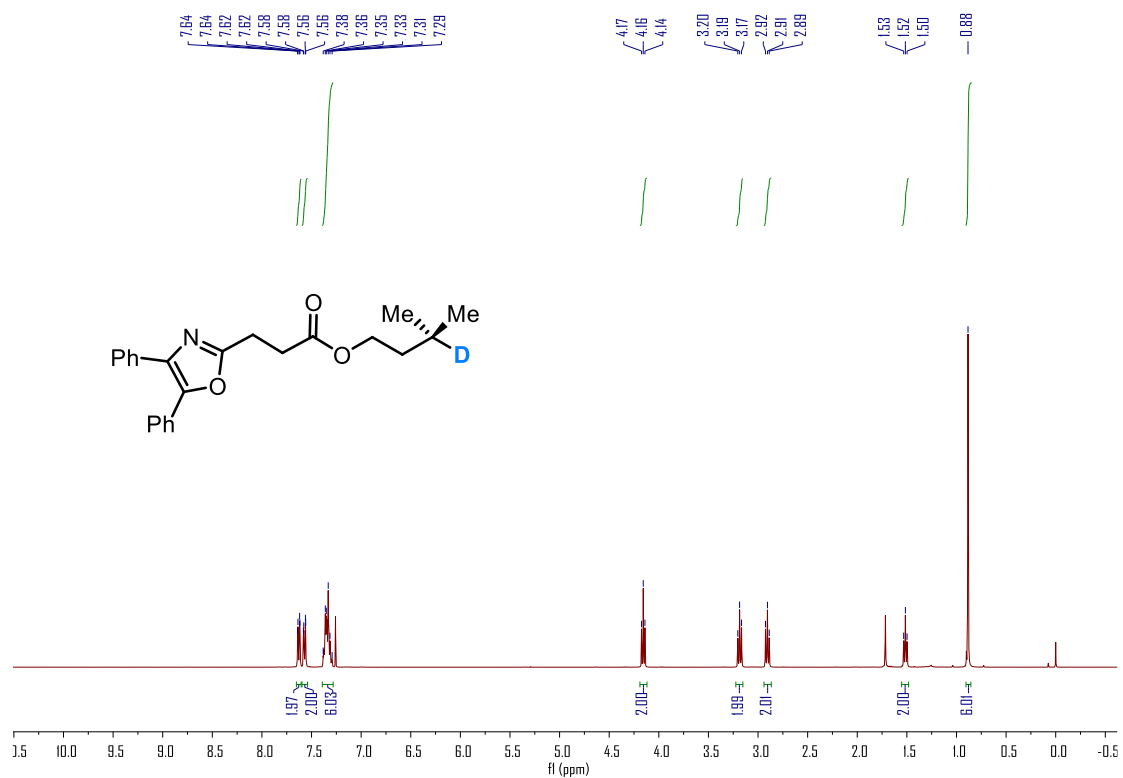
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **2a1**



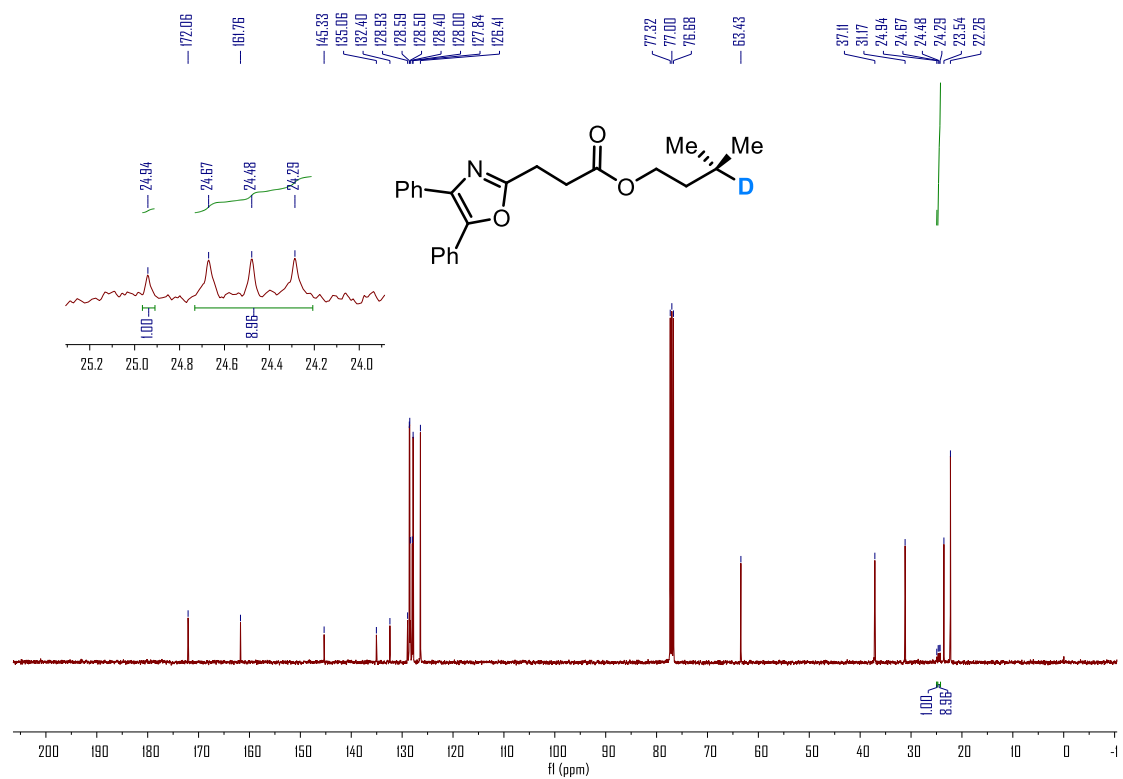
<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **2a1**



<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **2am**

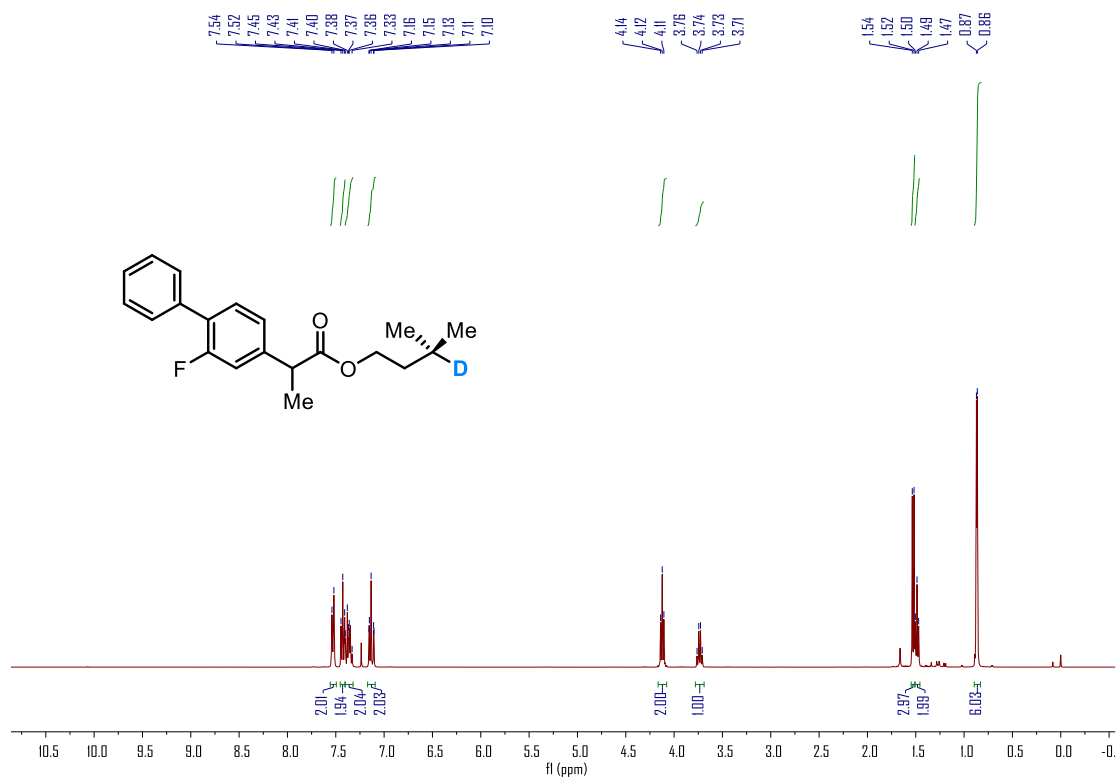


<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **2am**

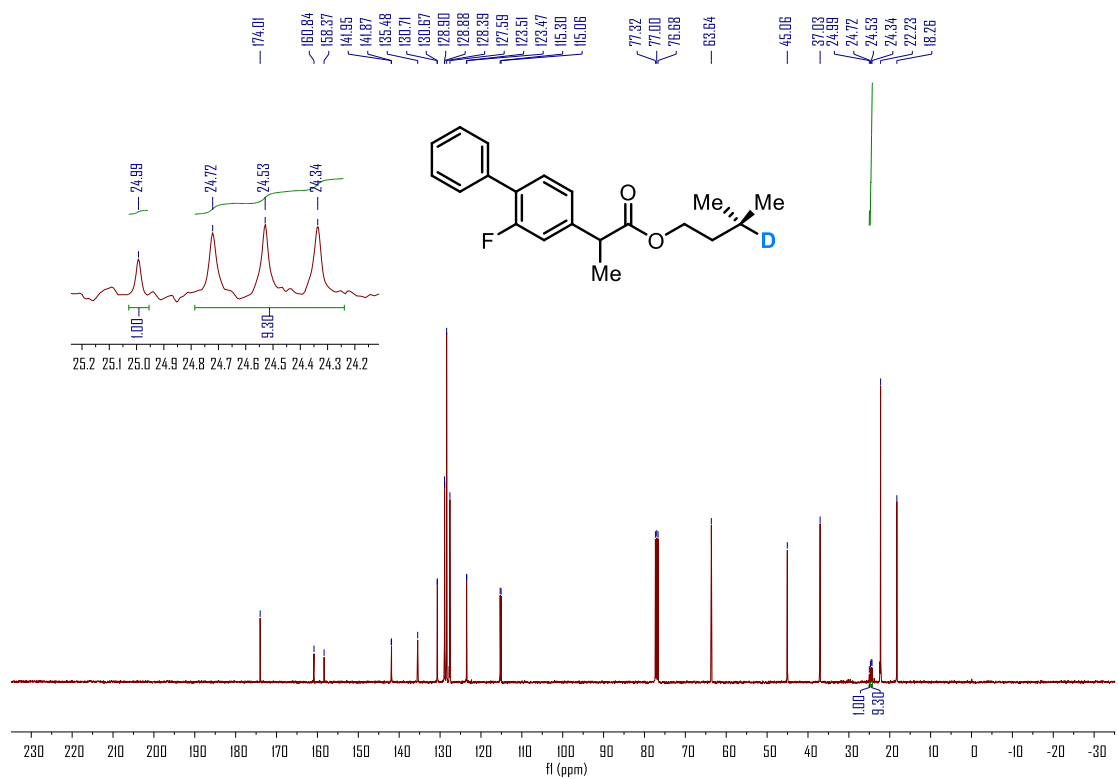




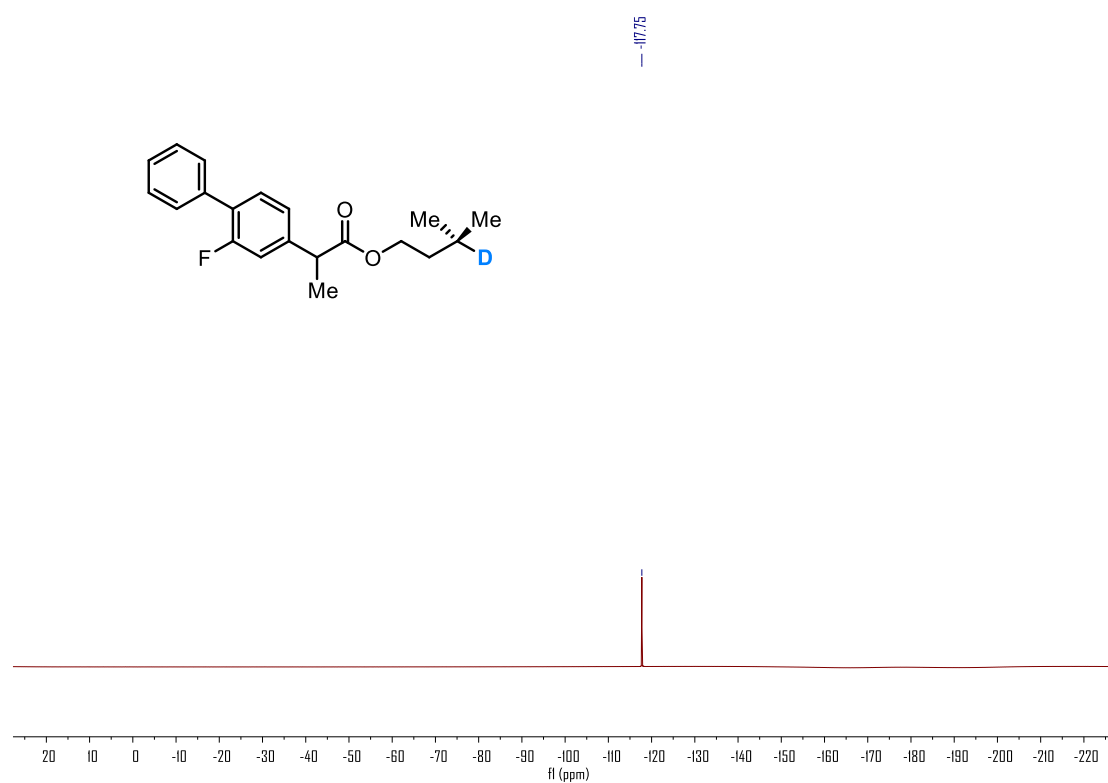
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **2an**



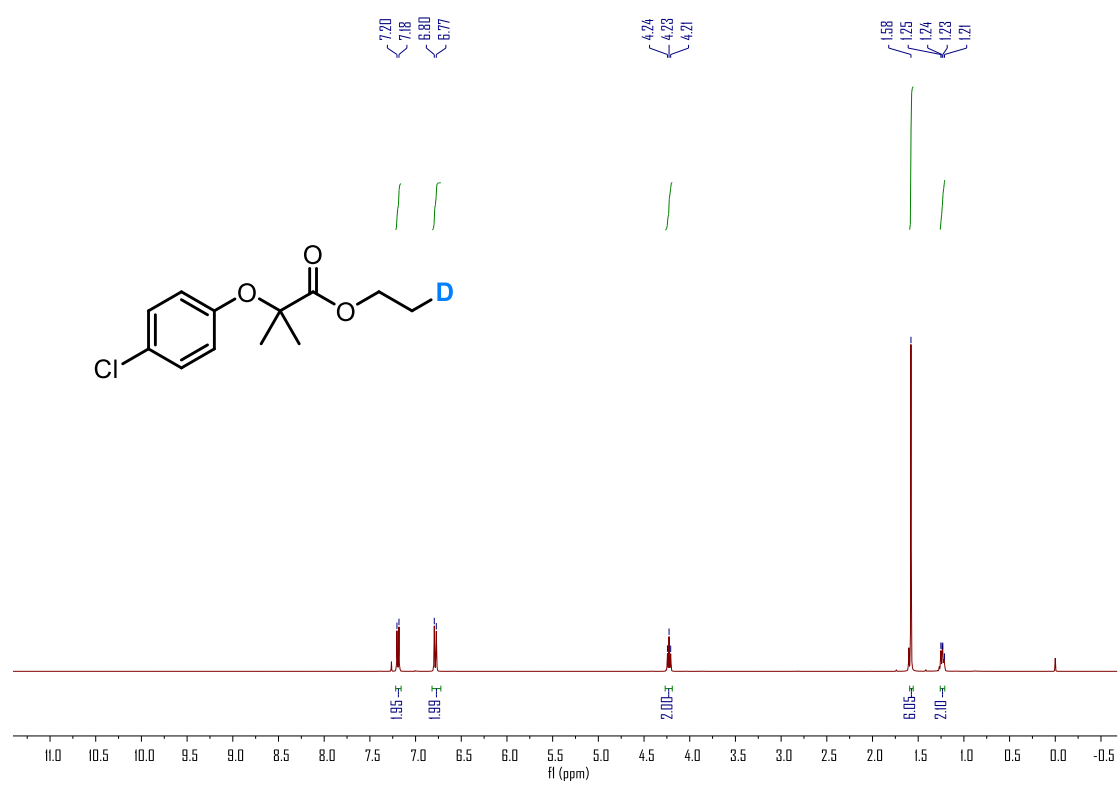
<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **2an**



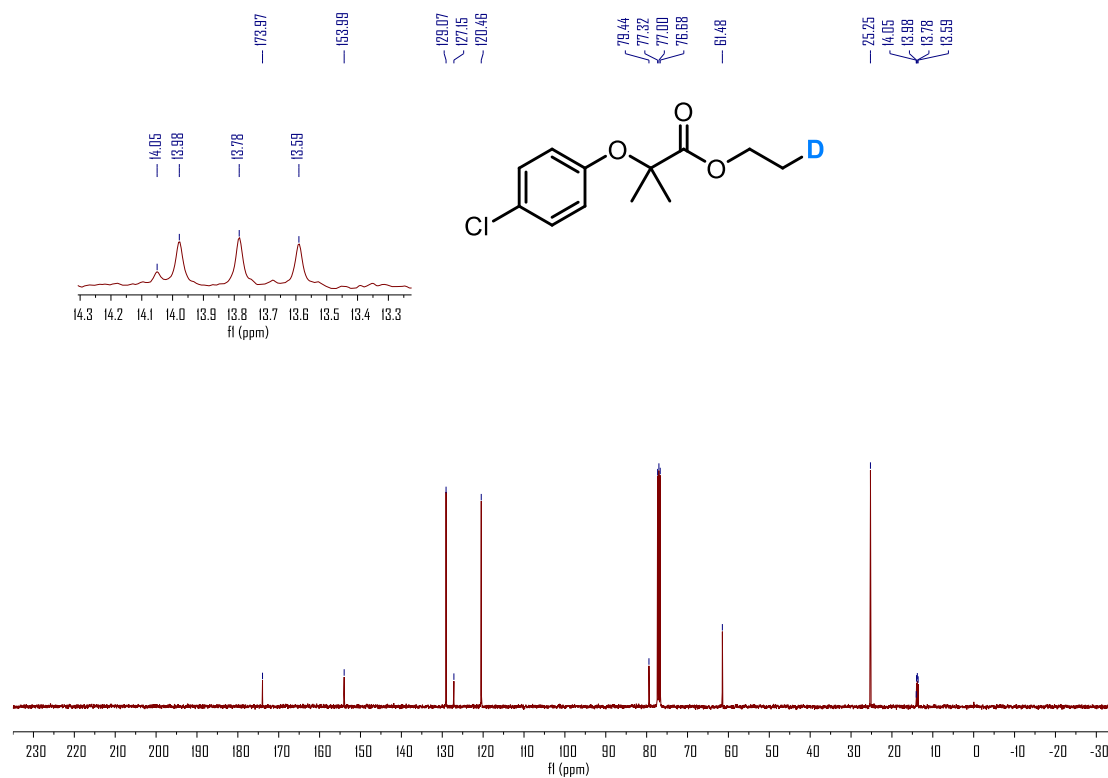
$^{19}\text{F}$  NMR spectrum (376 MHz,  $\text{CDCl}_3$ ) of **2an**



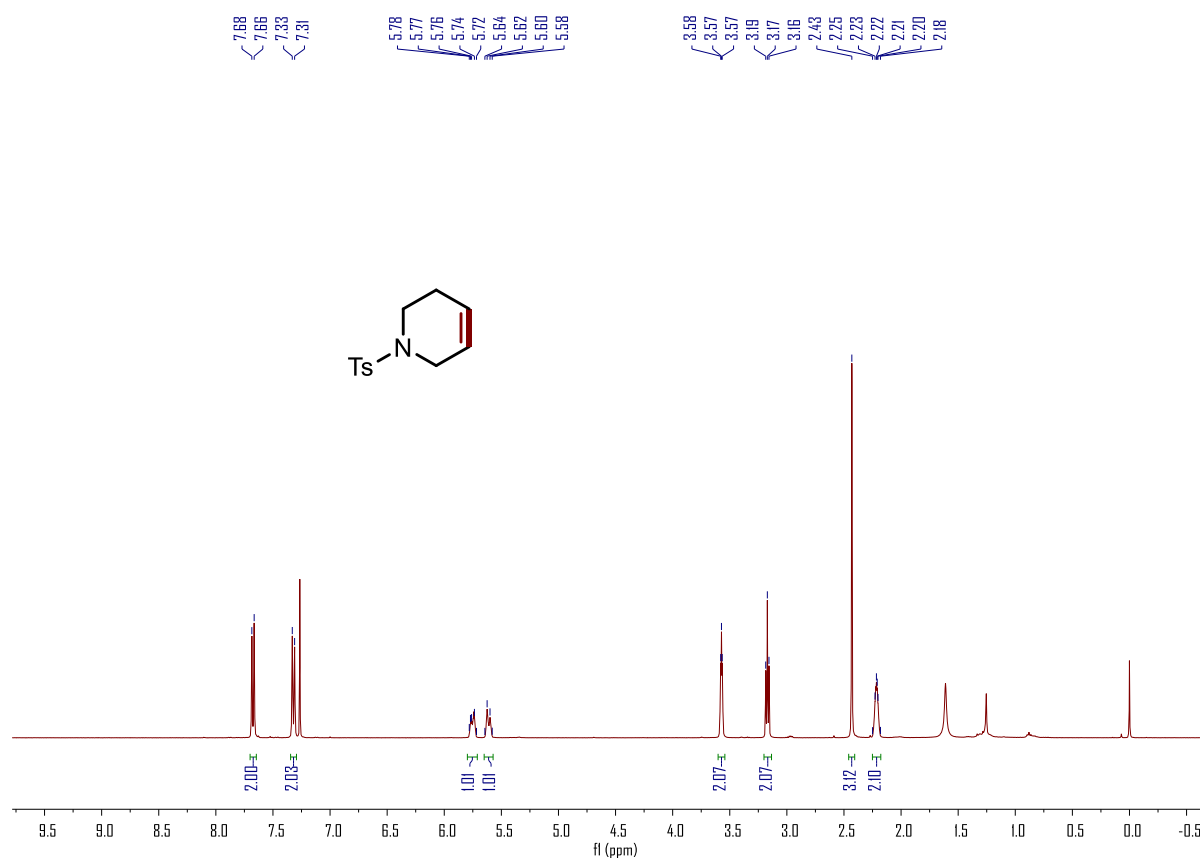
$^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of **2ao**



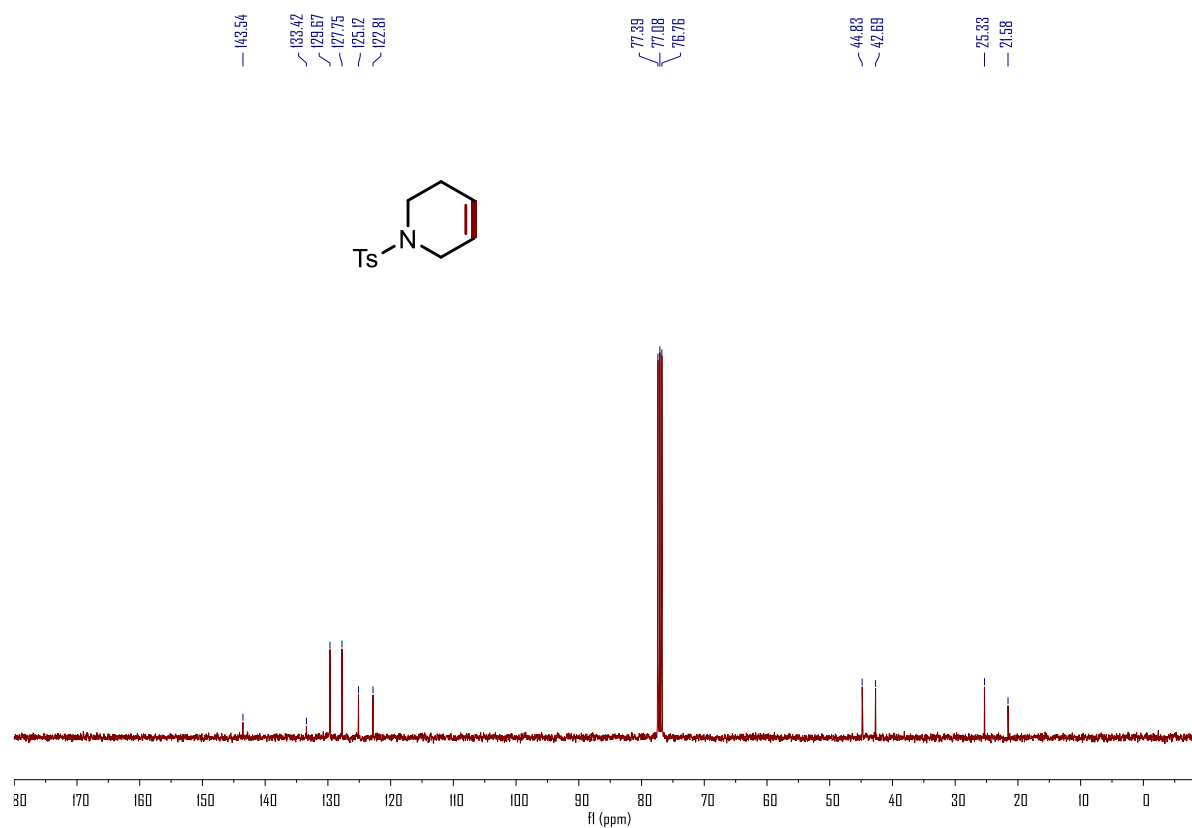
$^{13}\text{C}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of **2a**



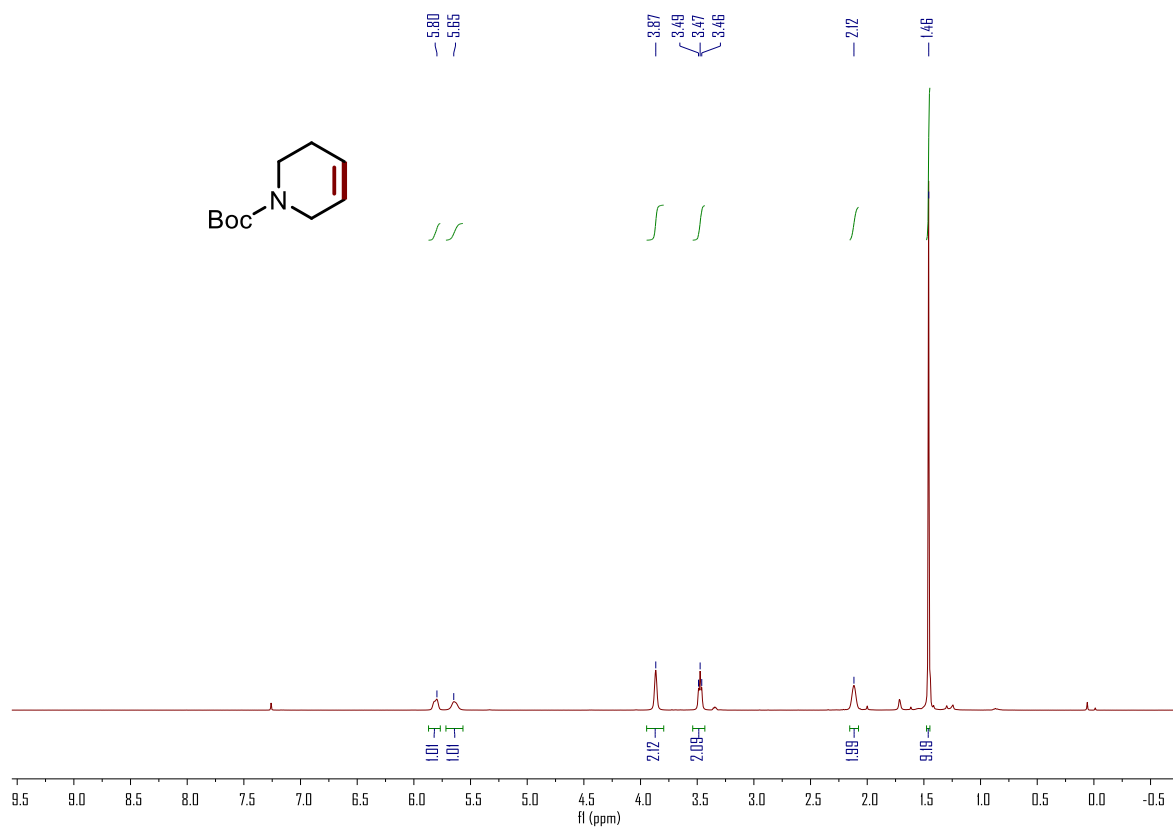
$^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of **3a**



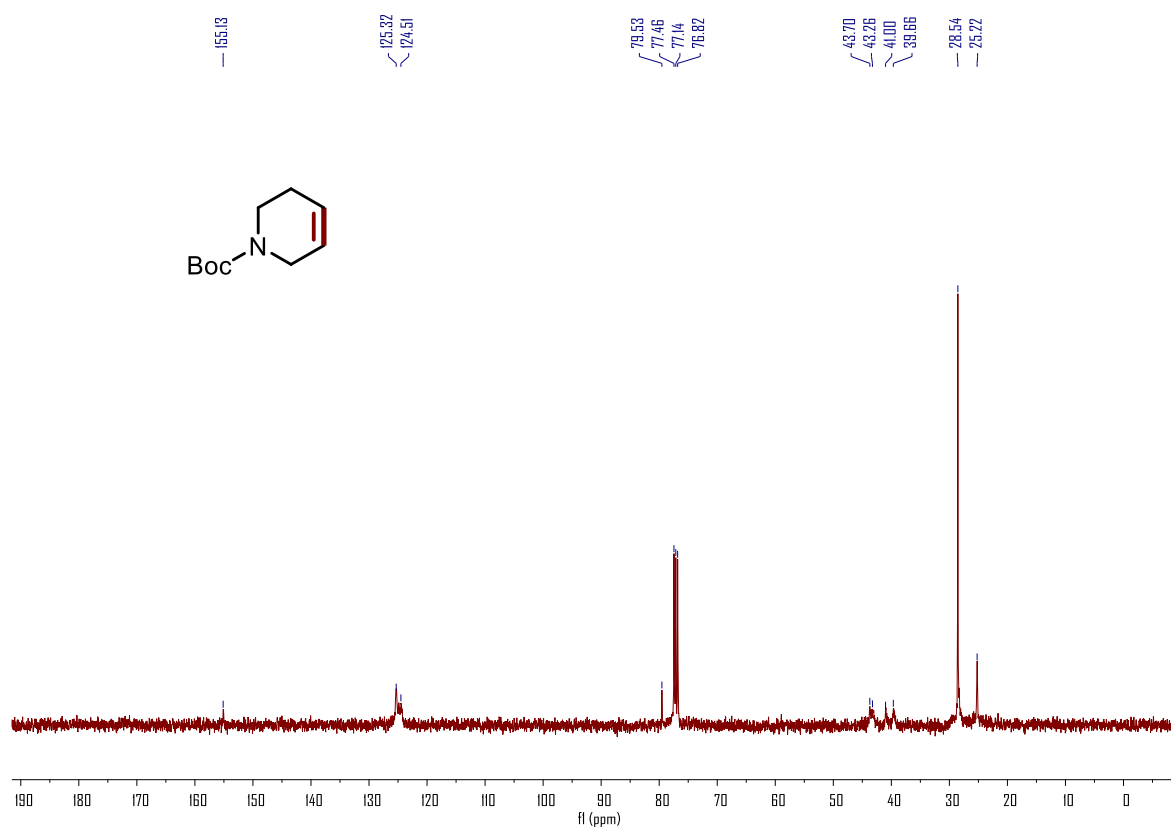
<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **3a**



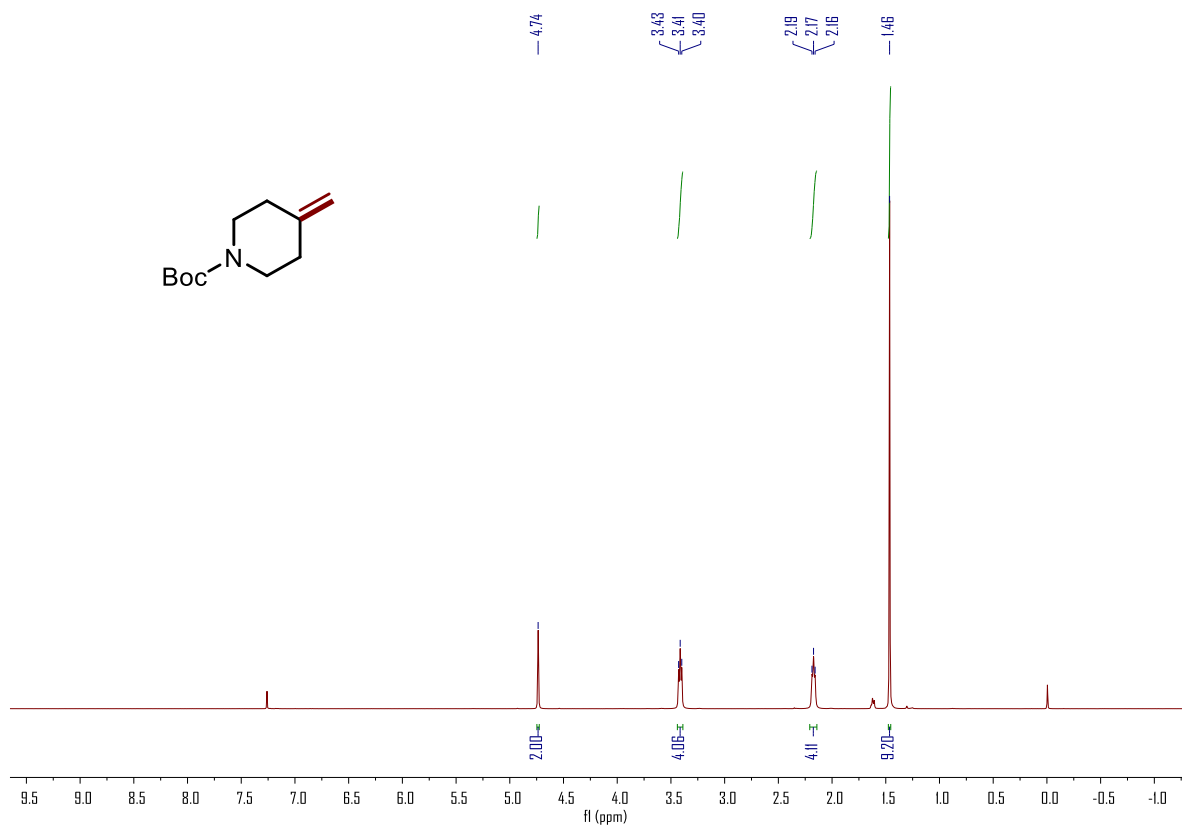
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **3b**



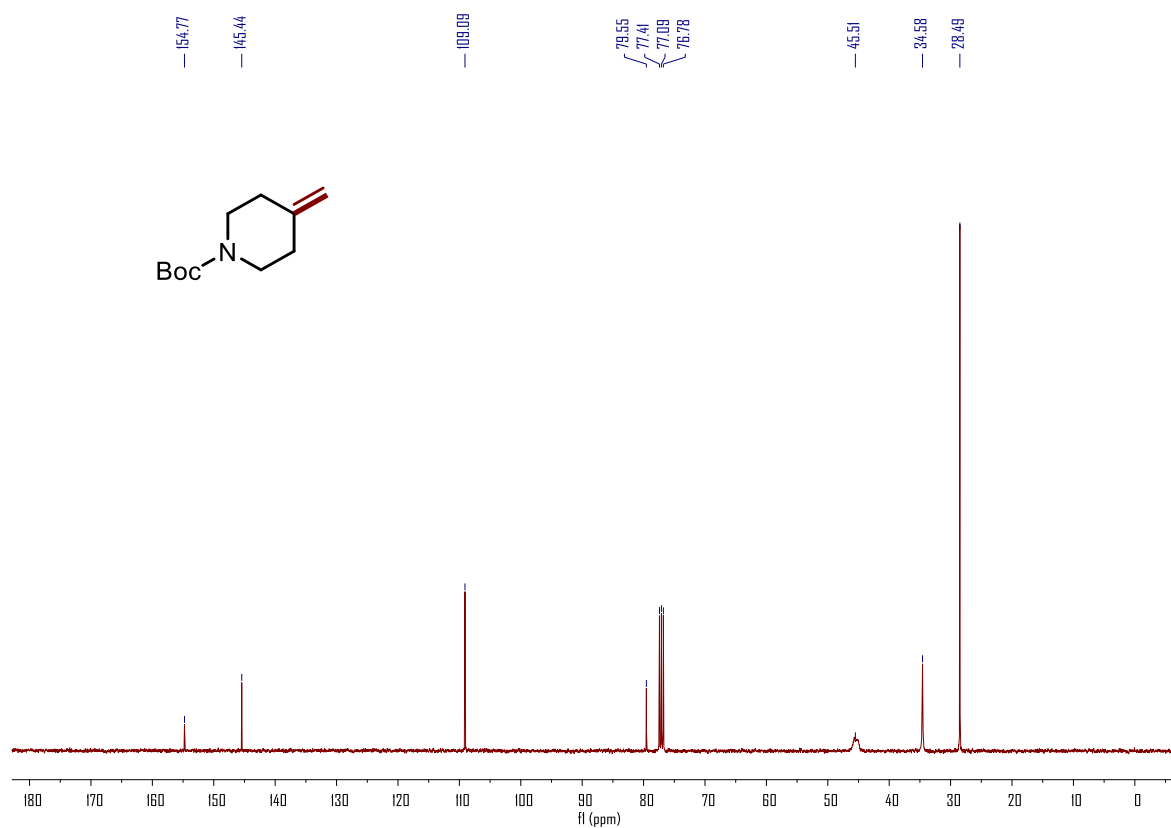
$^{13}\text{C}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of **3b**



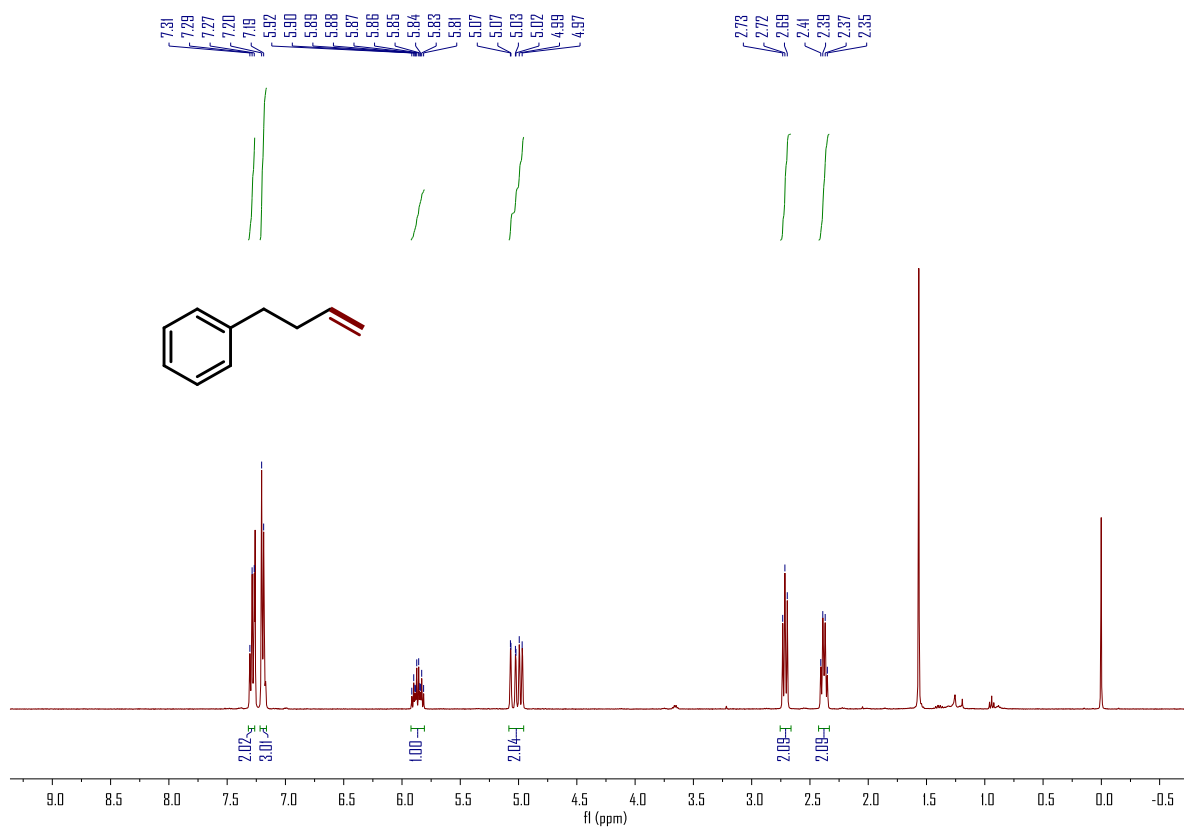
$^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of **3c**



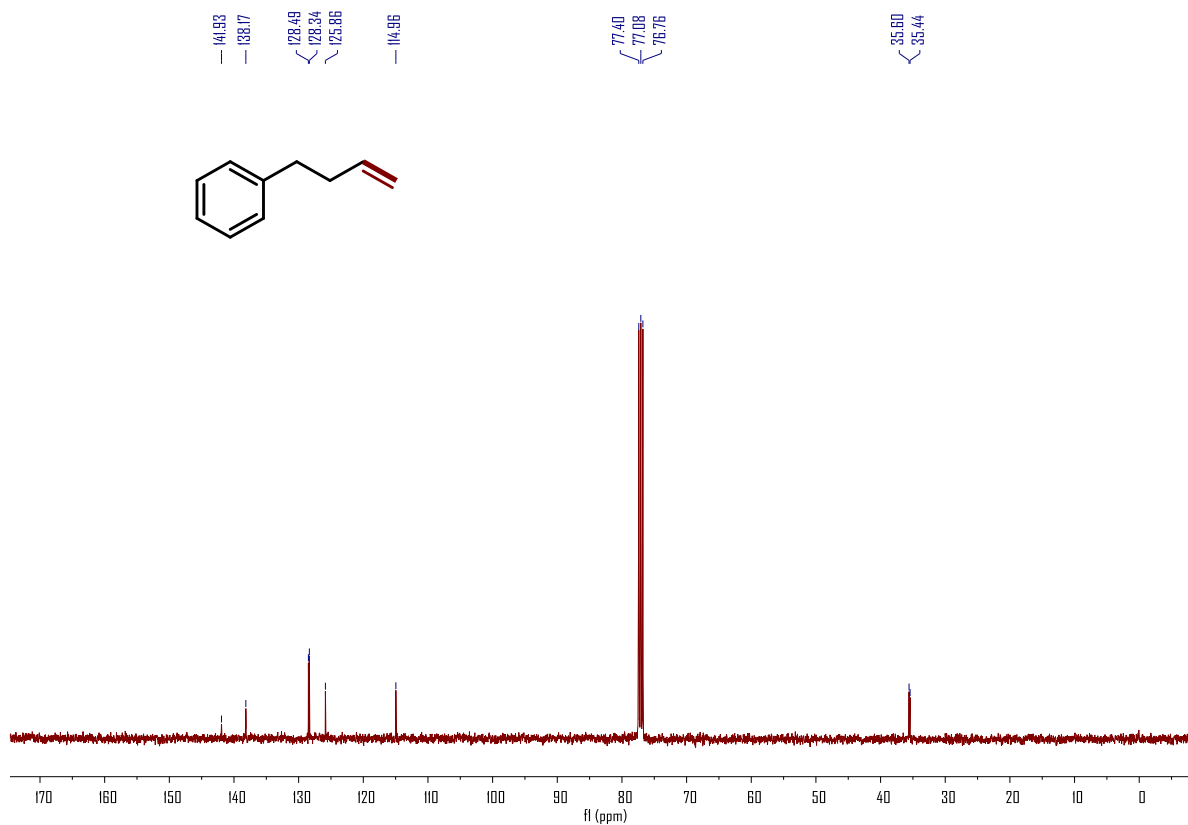
<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **3c**



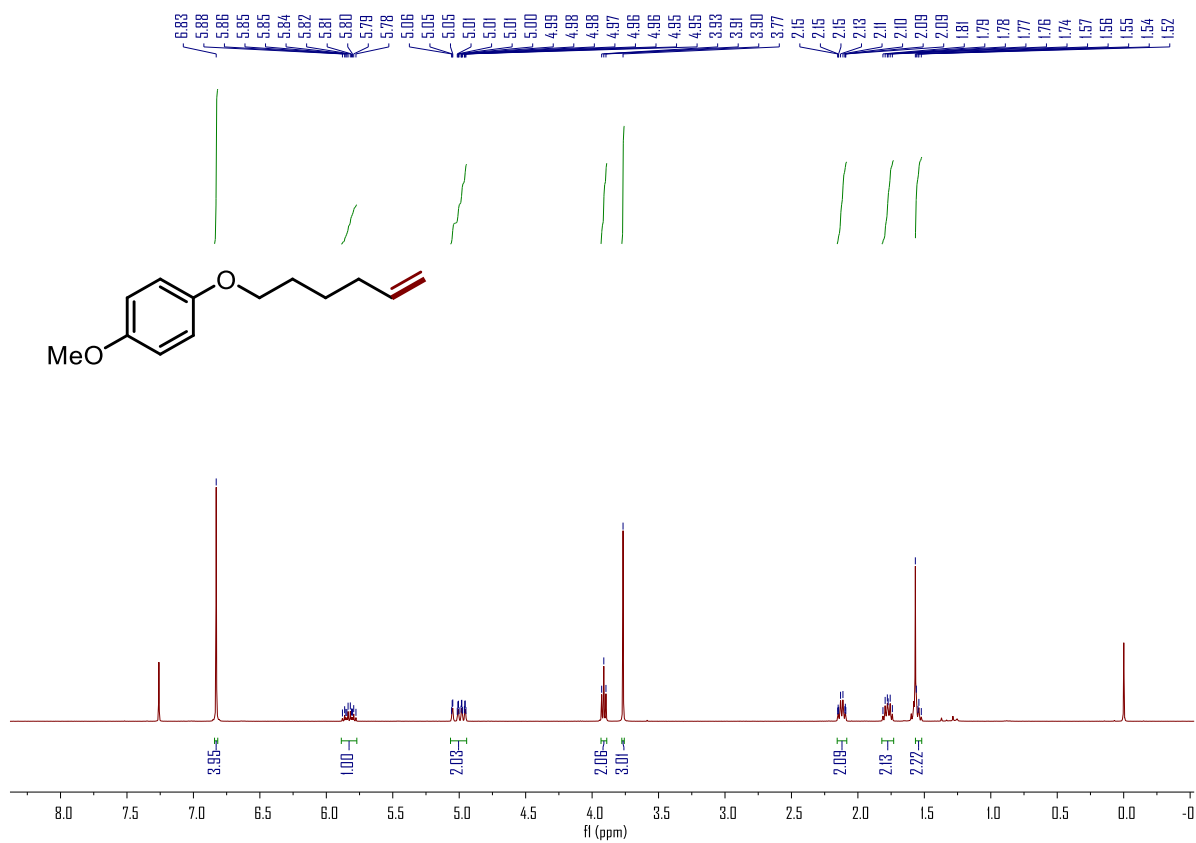
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **3d**



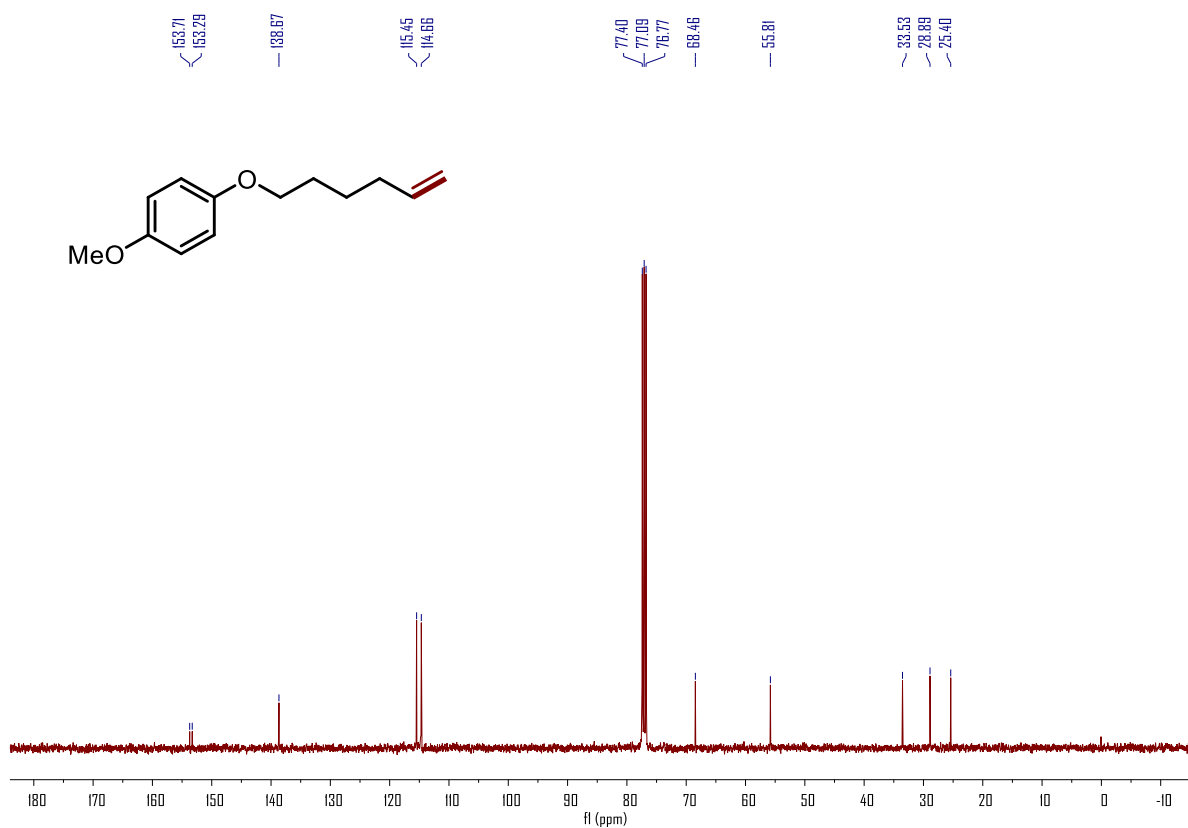
<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **3d**



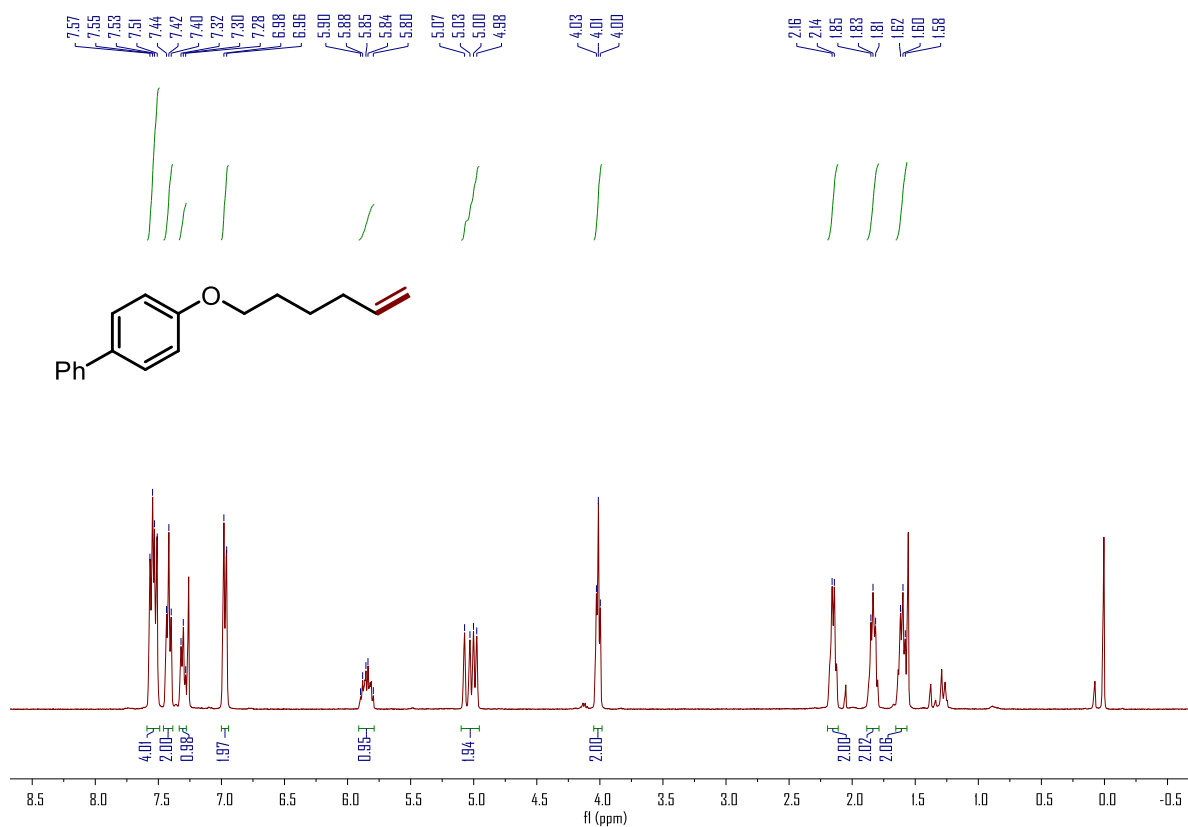
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **3e**



$^{13}\text{C}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of **3e**

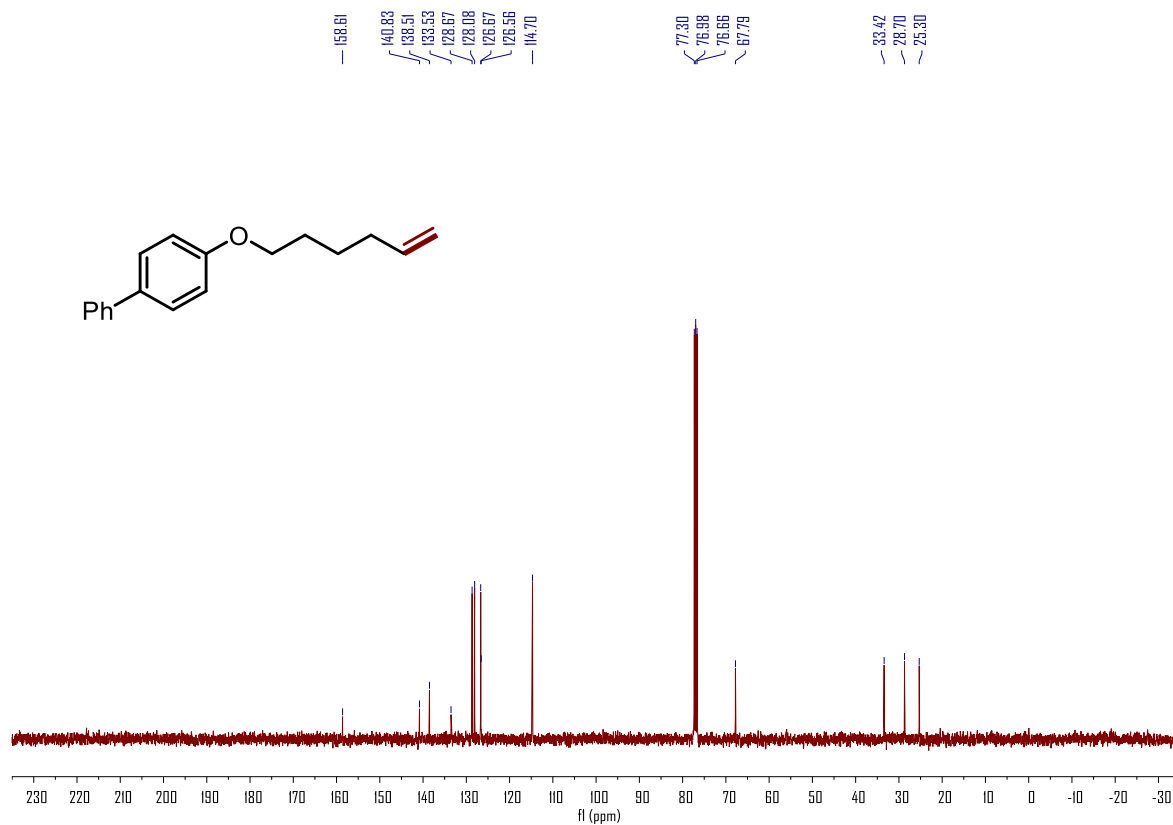


$^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of **3f**

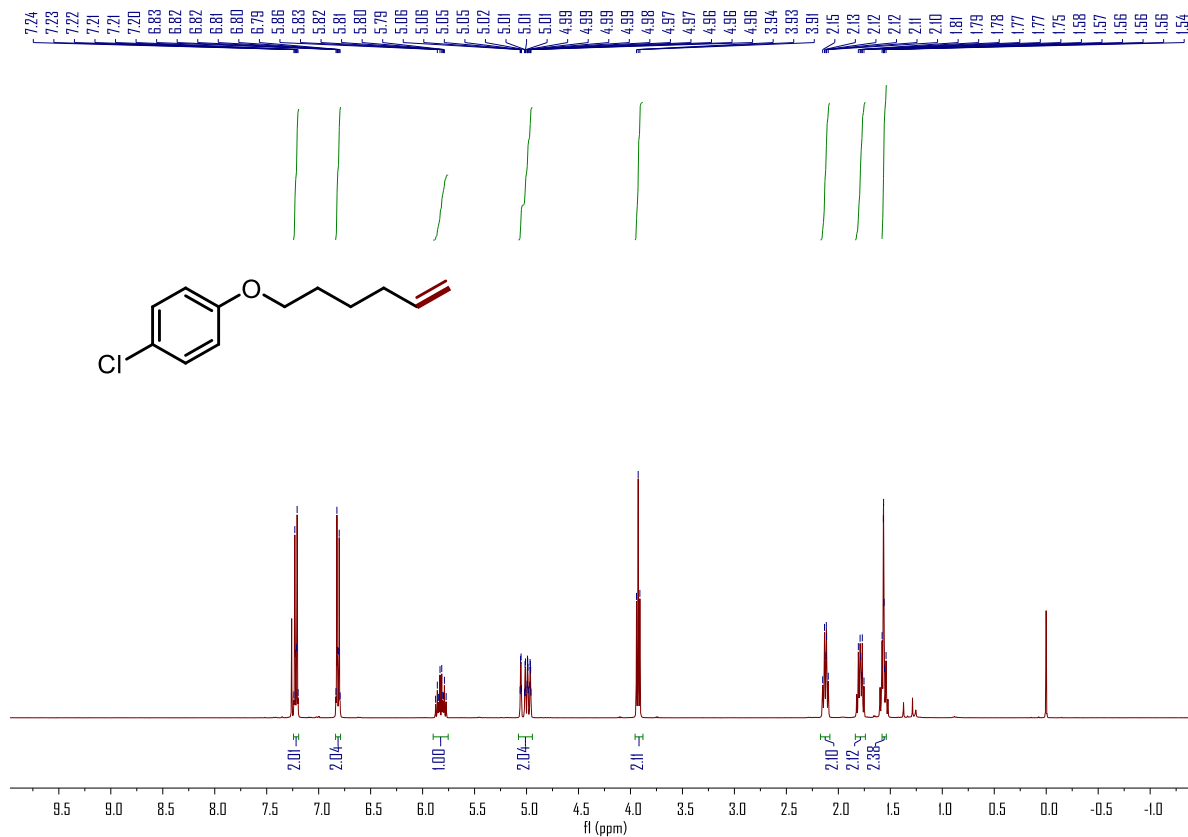




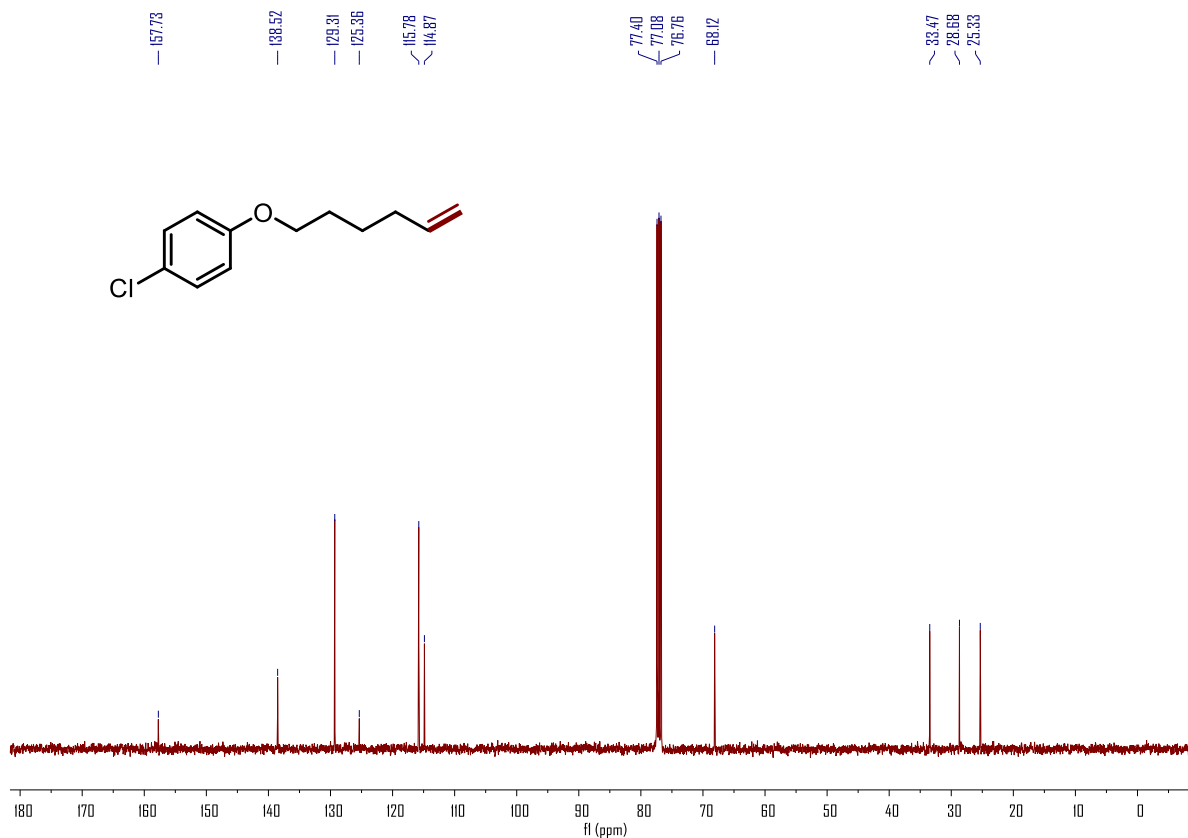
<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **3f**



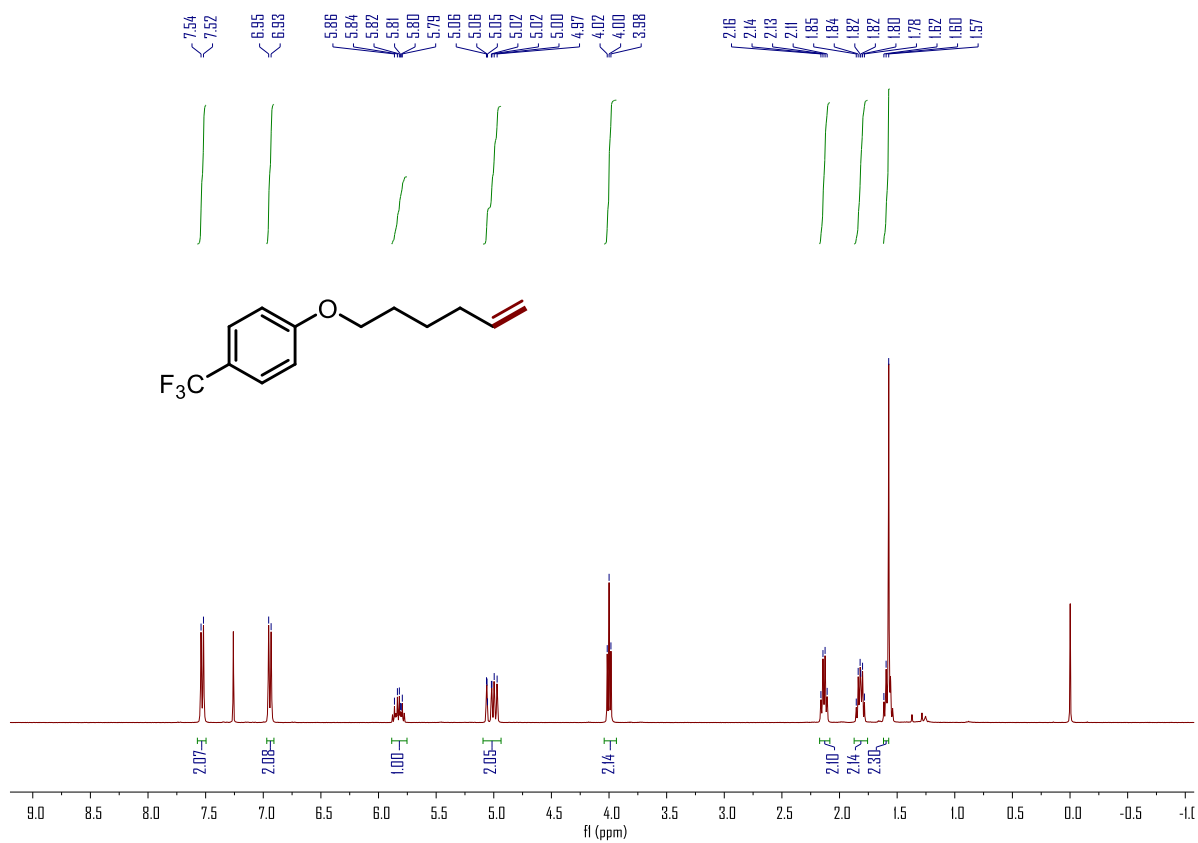
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **3g**



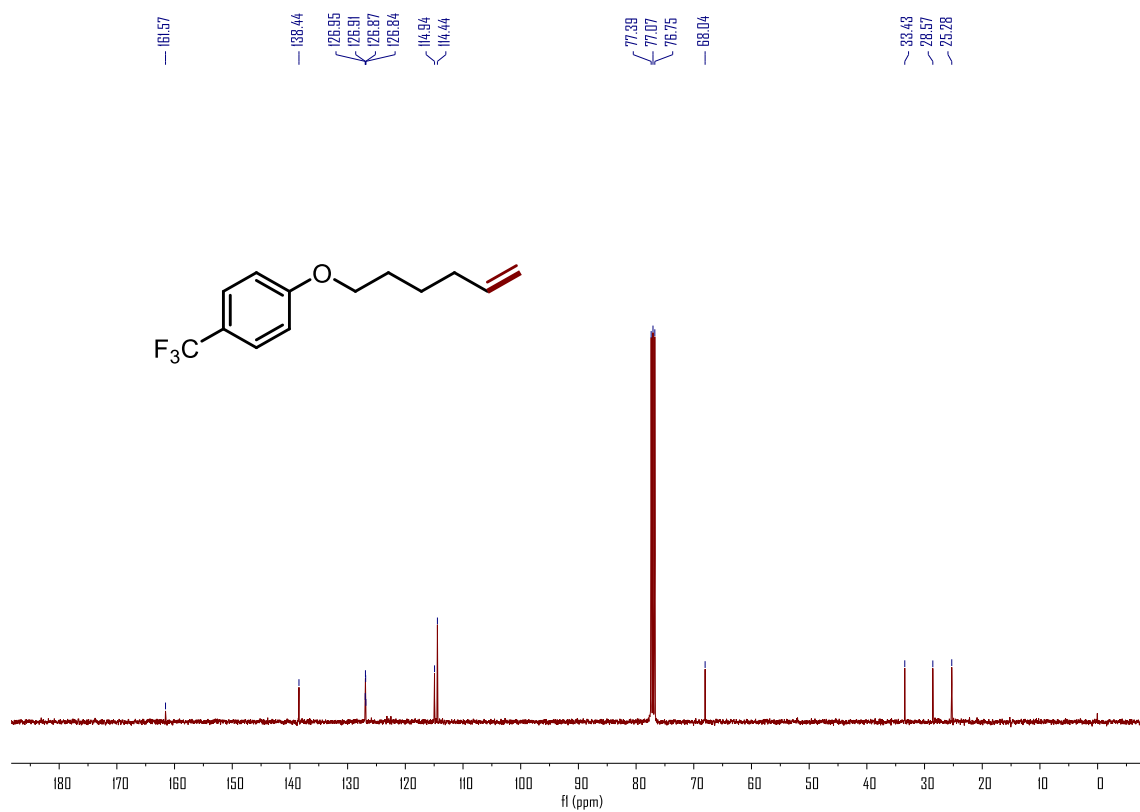
$^{13}\text{C}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of **3g**



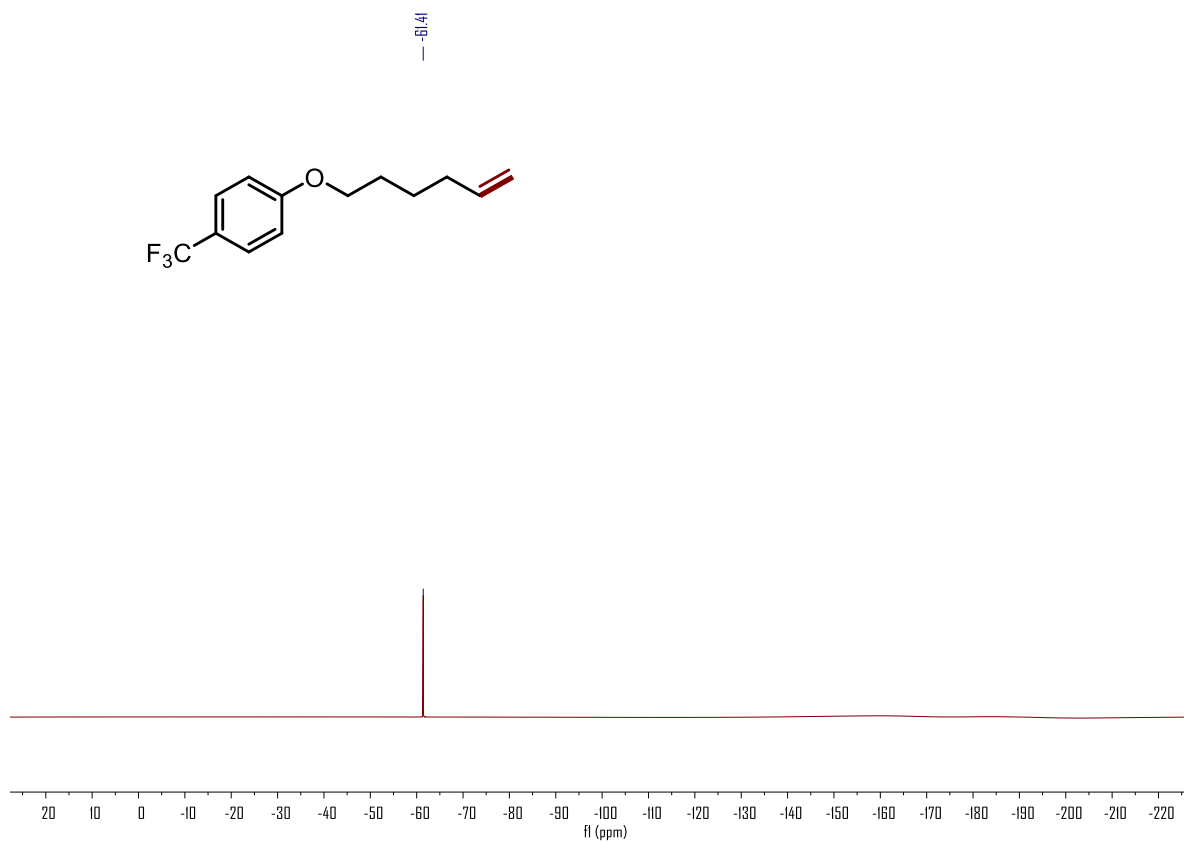
$^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of **3h**



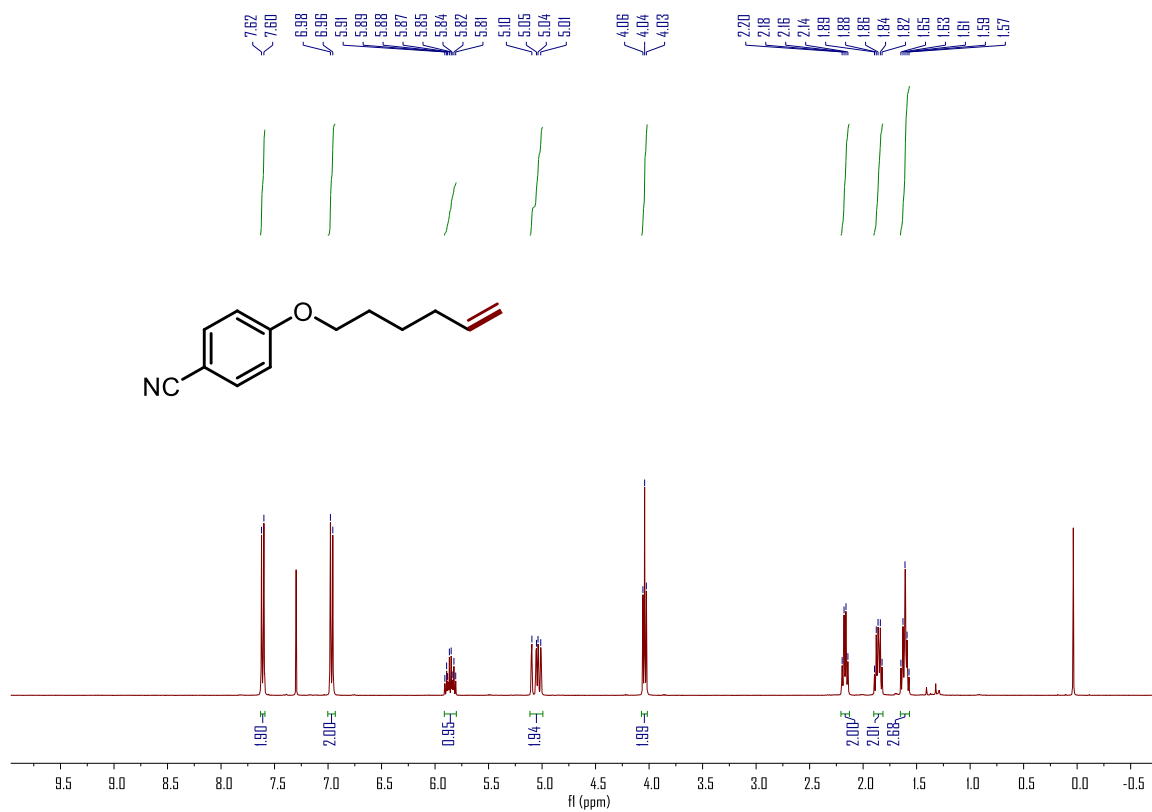
<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **3h**



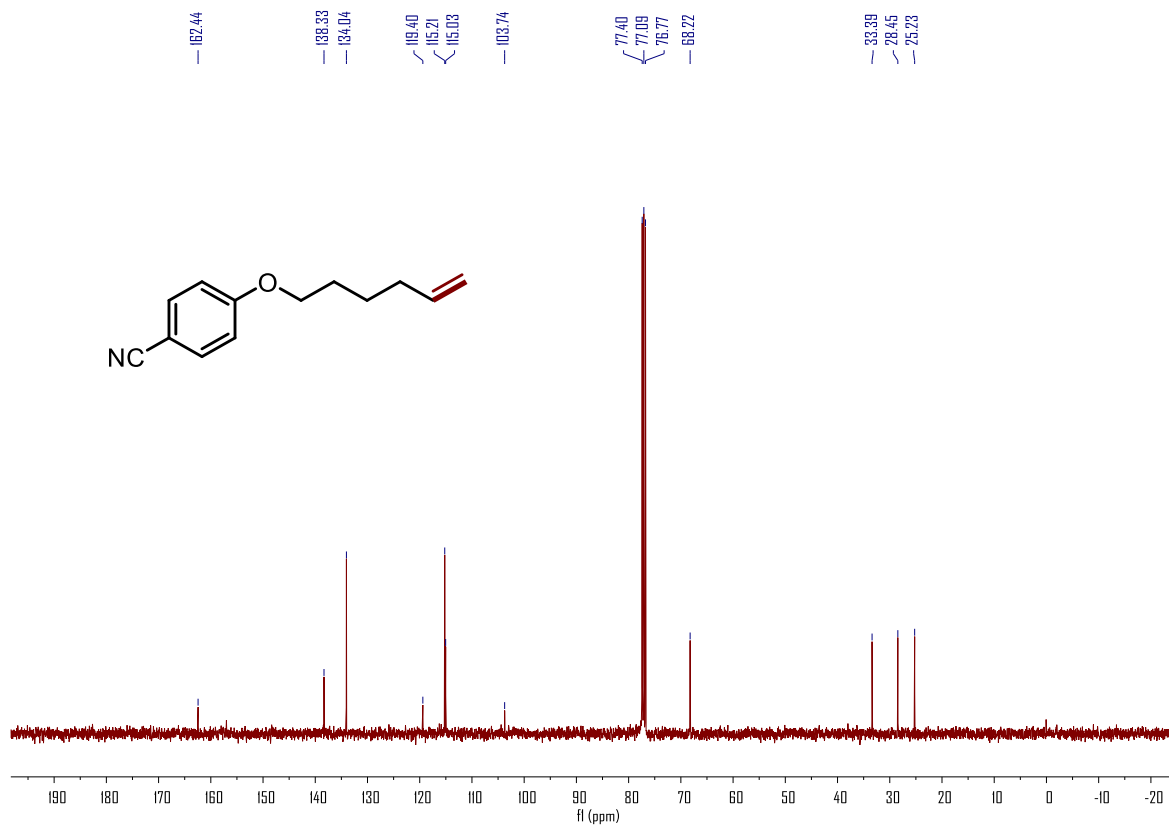
<sup>19</sup>F NMR spectrum (376 MHz, CDCl<sub>3</sub>) of **3h**



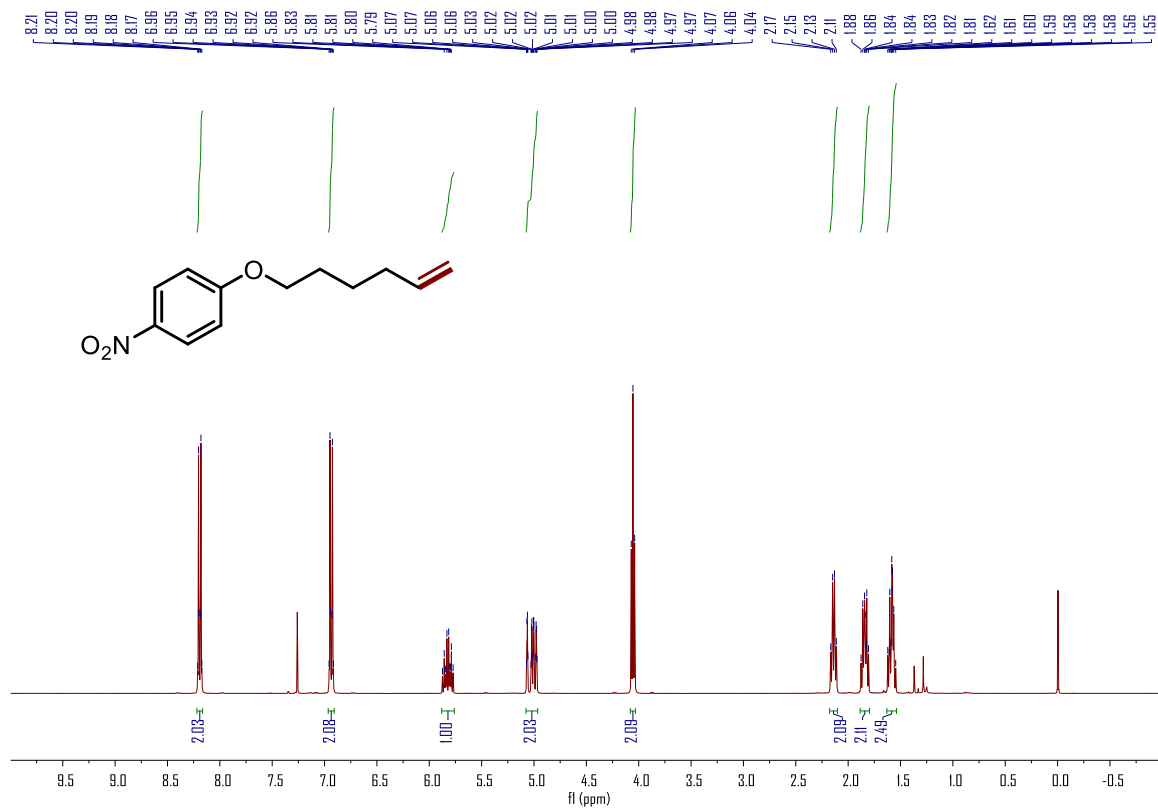
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **3i**



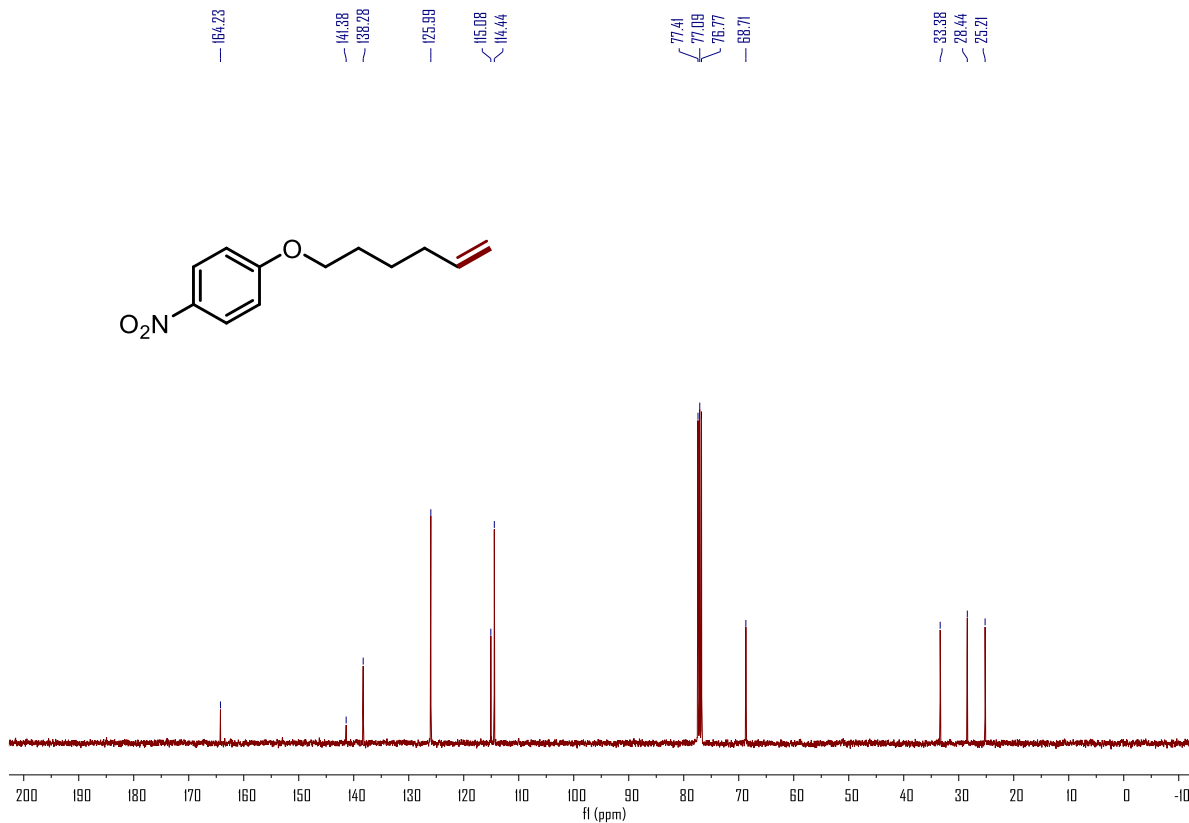
<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **3i**



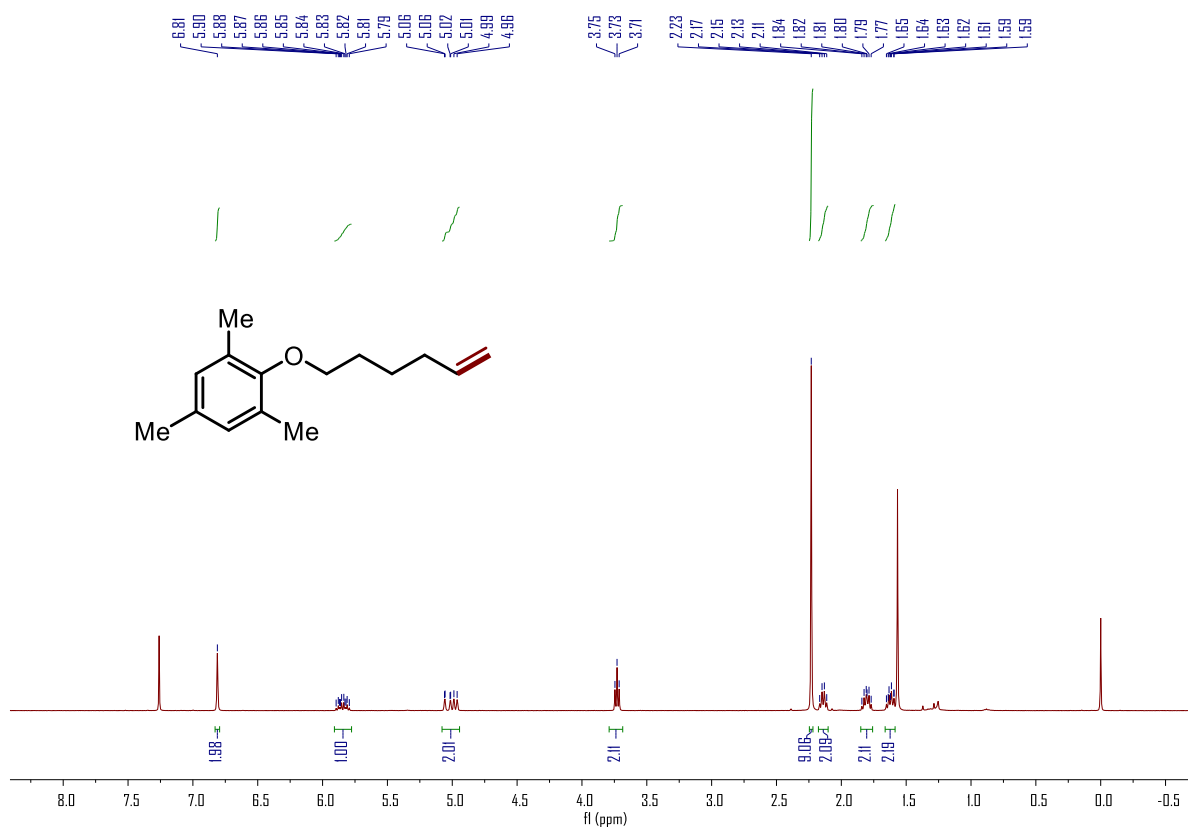
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **3j**



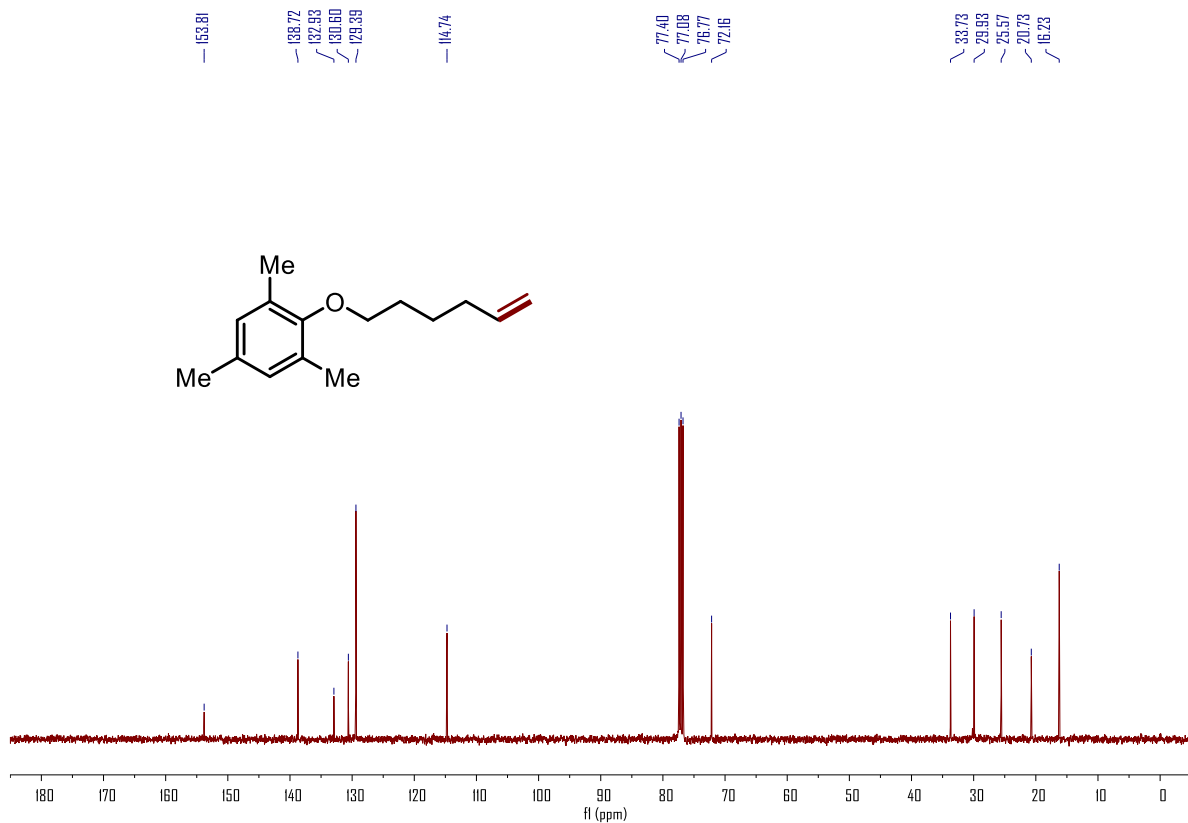
<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **3j**



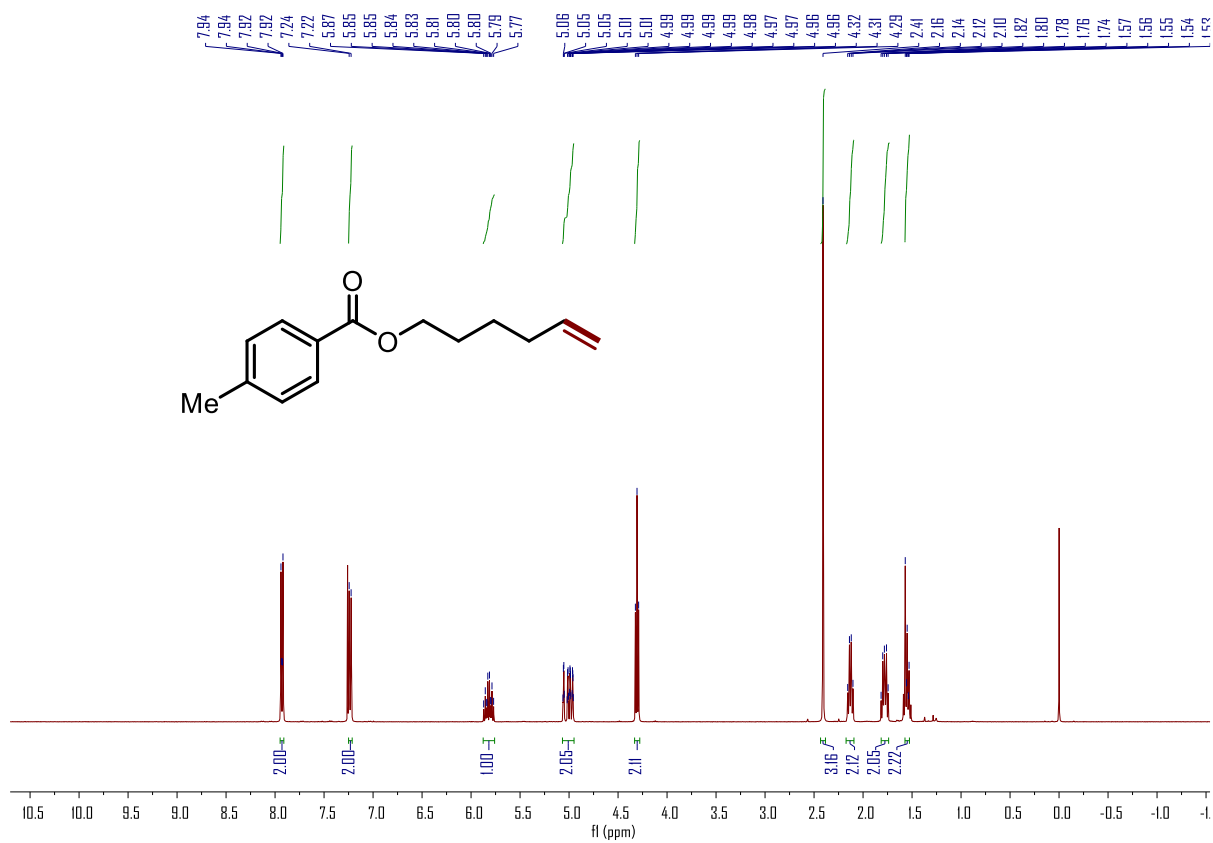
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **3k**



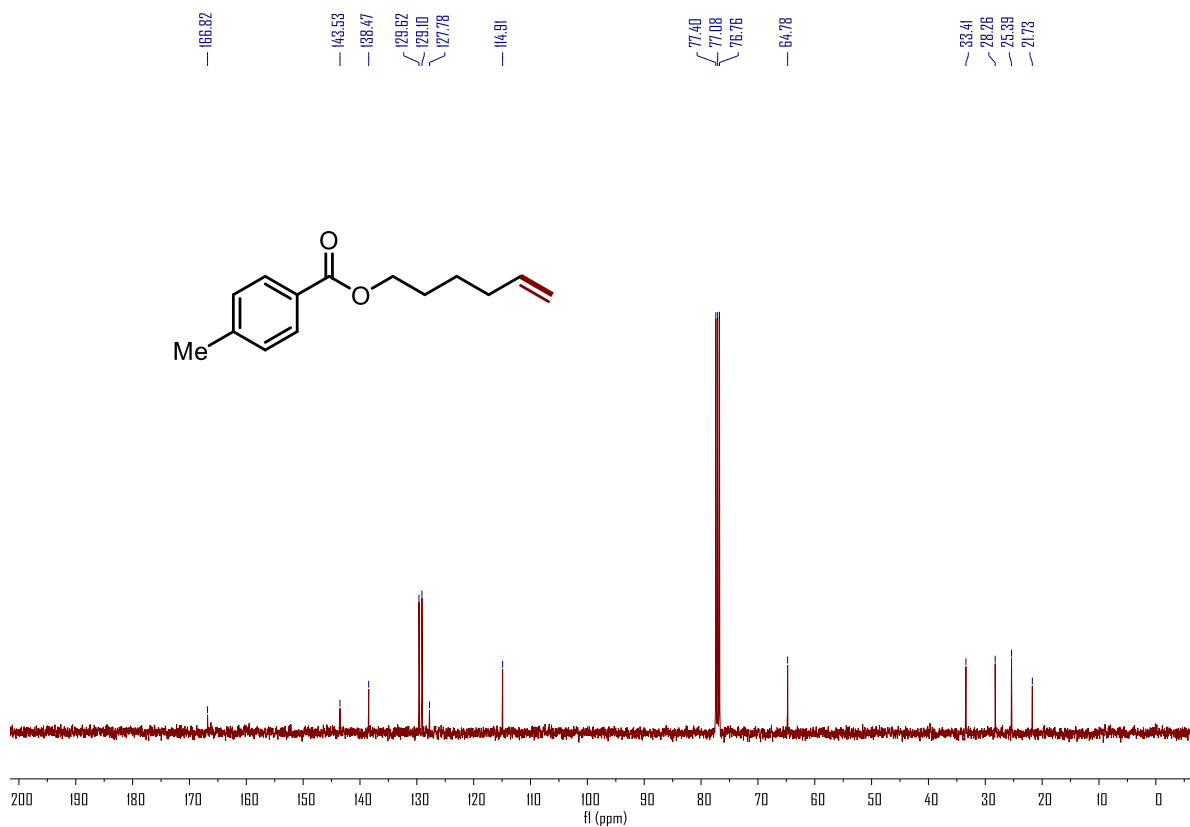
<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **3k**



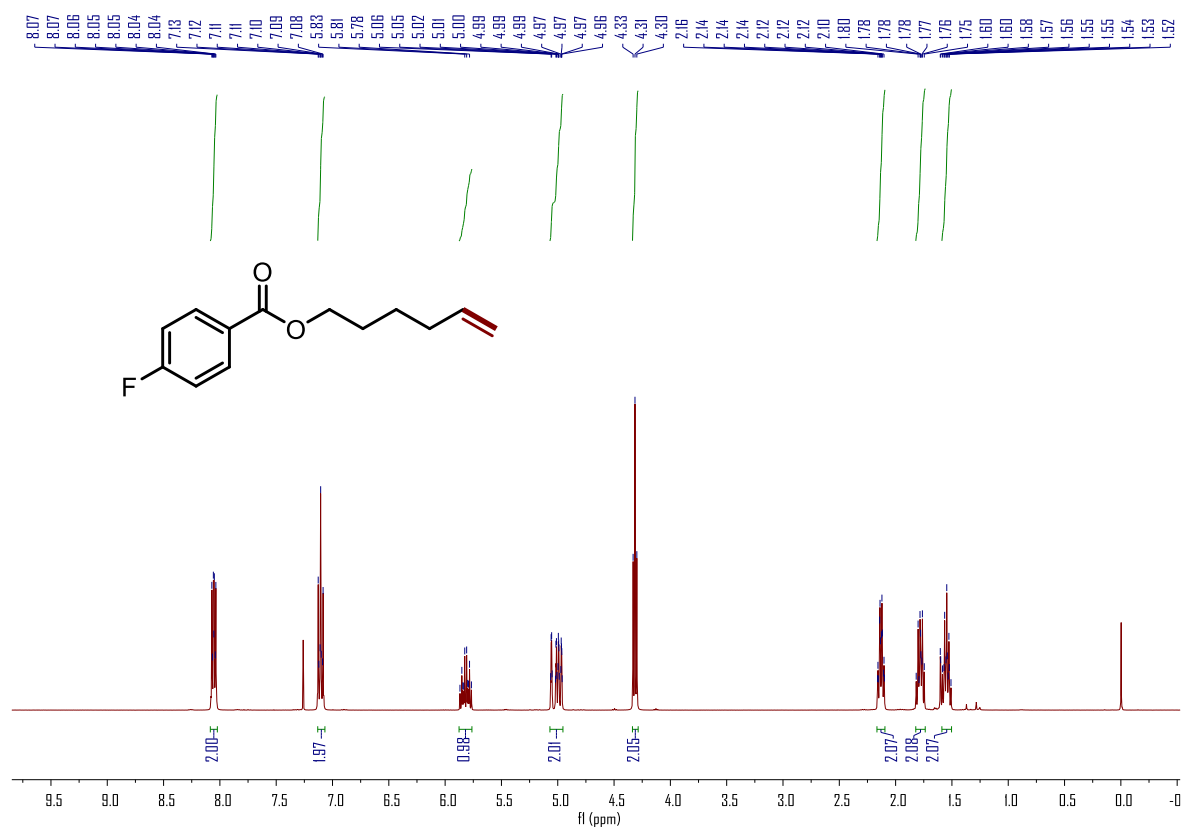
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **31**



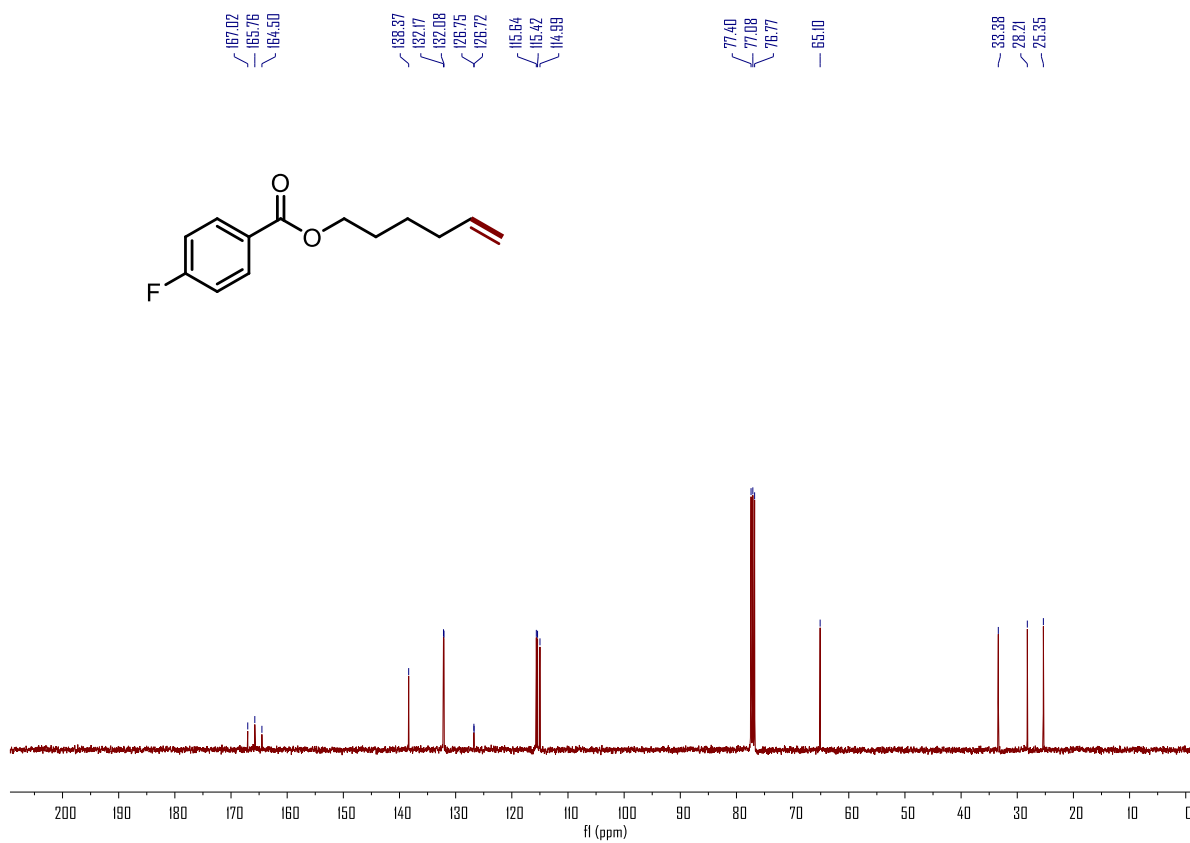
<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **31**



<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **3m**

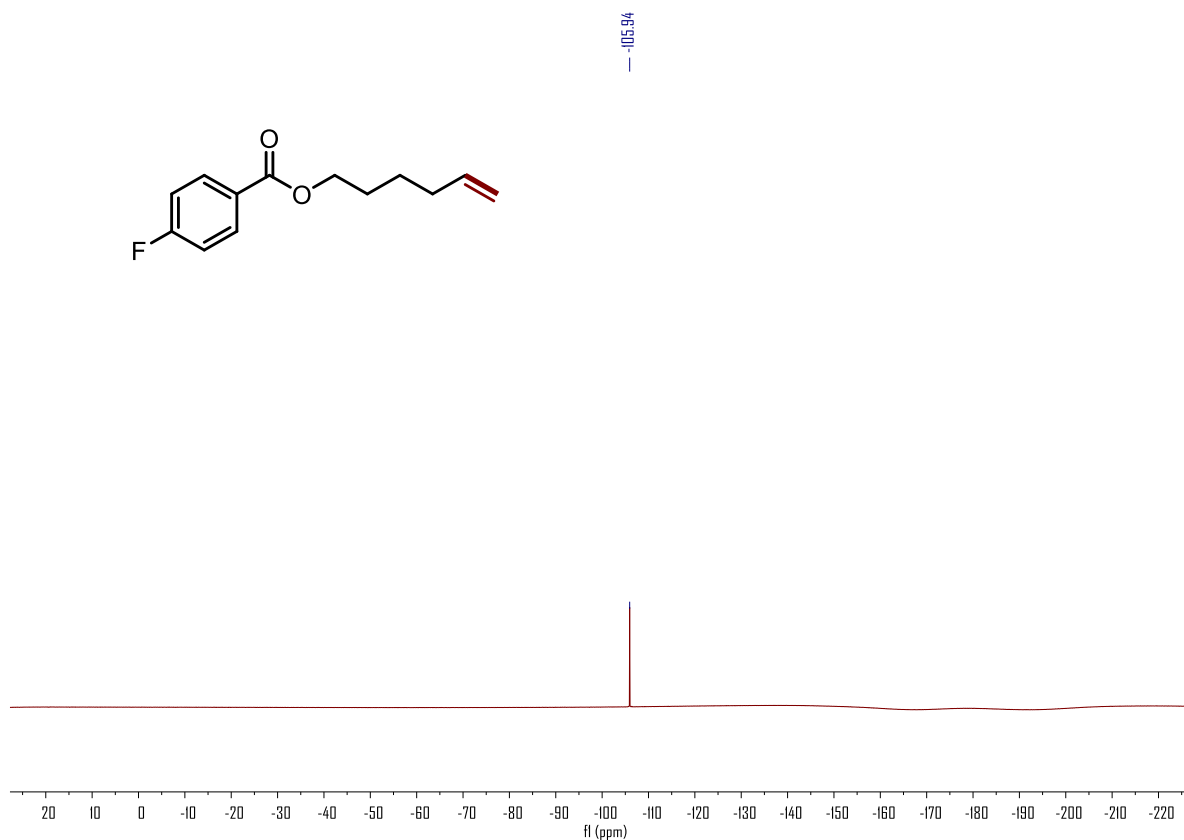


<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **3m**

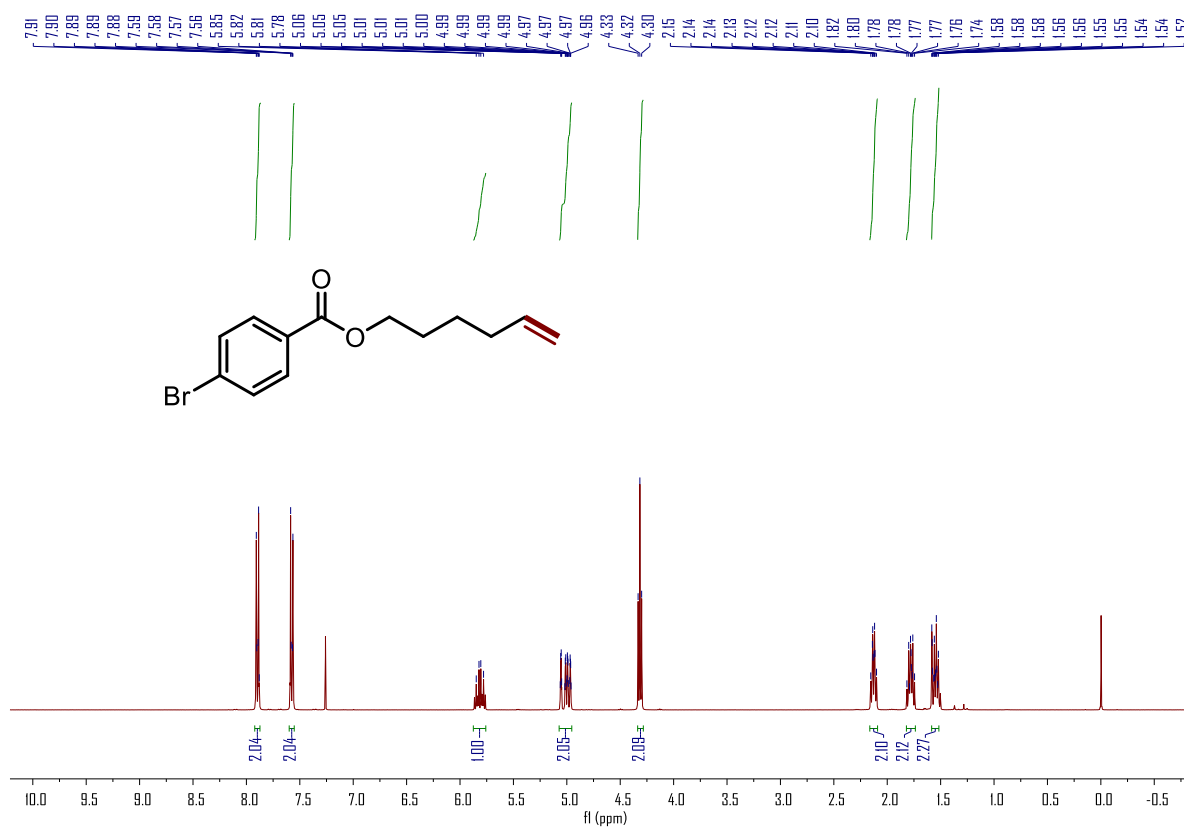




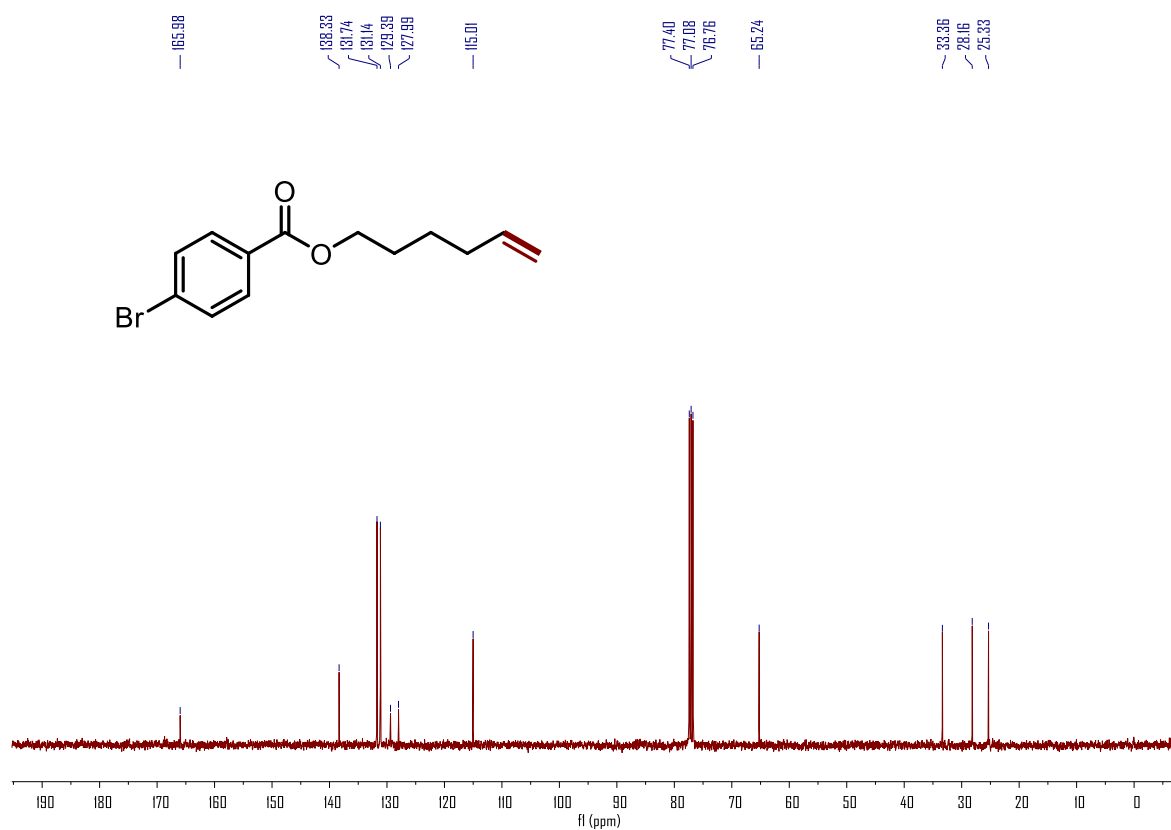
$^{19}\text{F}$  NMR spectrum (376 MHz,  $\text{CDCl}_3$ ) of **3m**



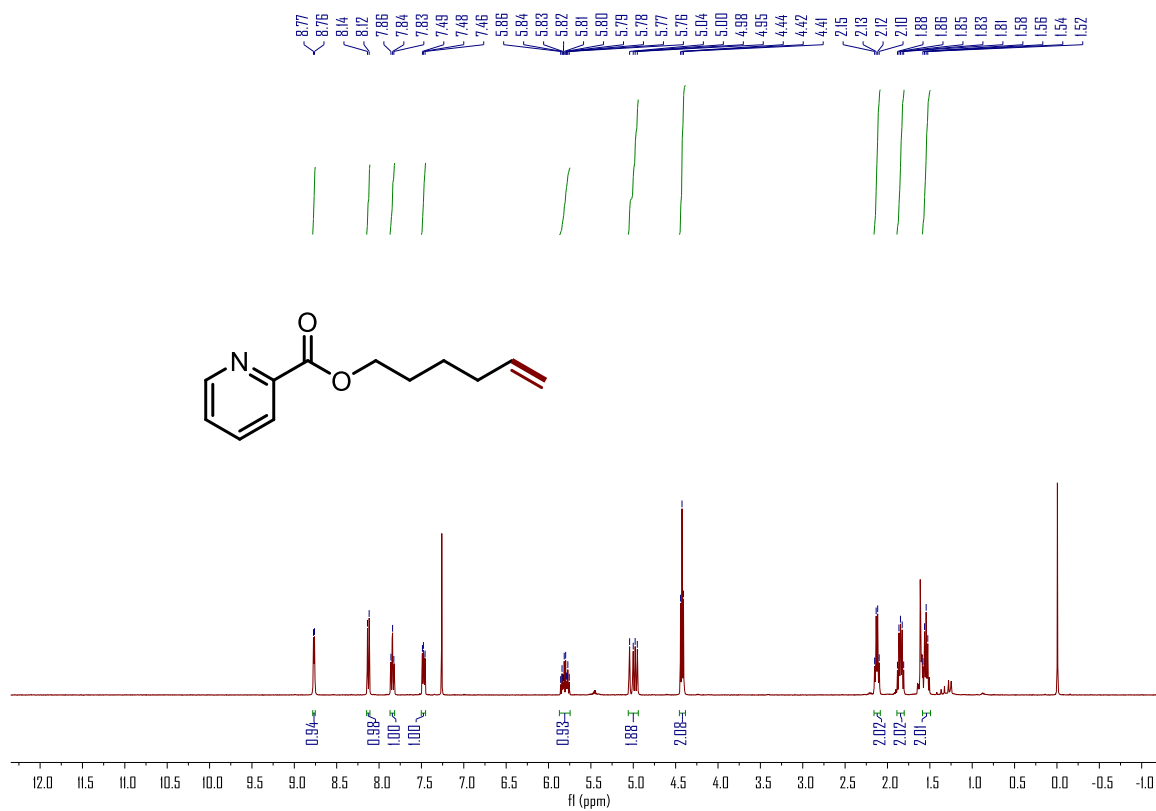
$^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of **3n**



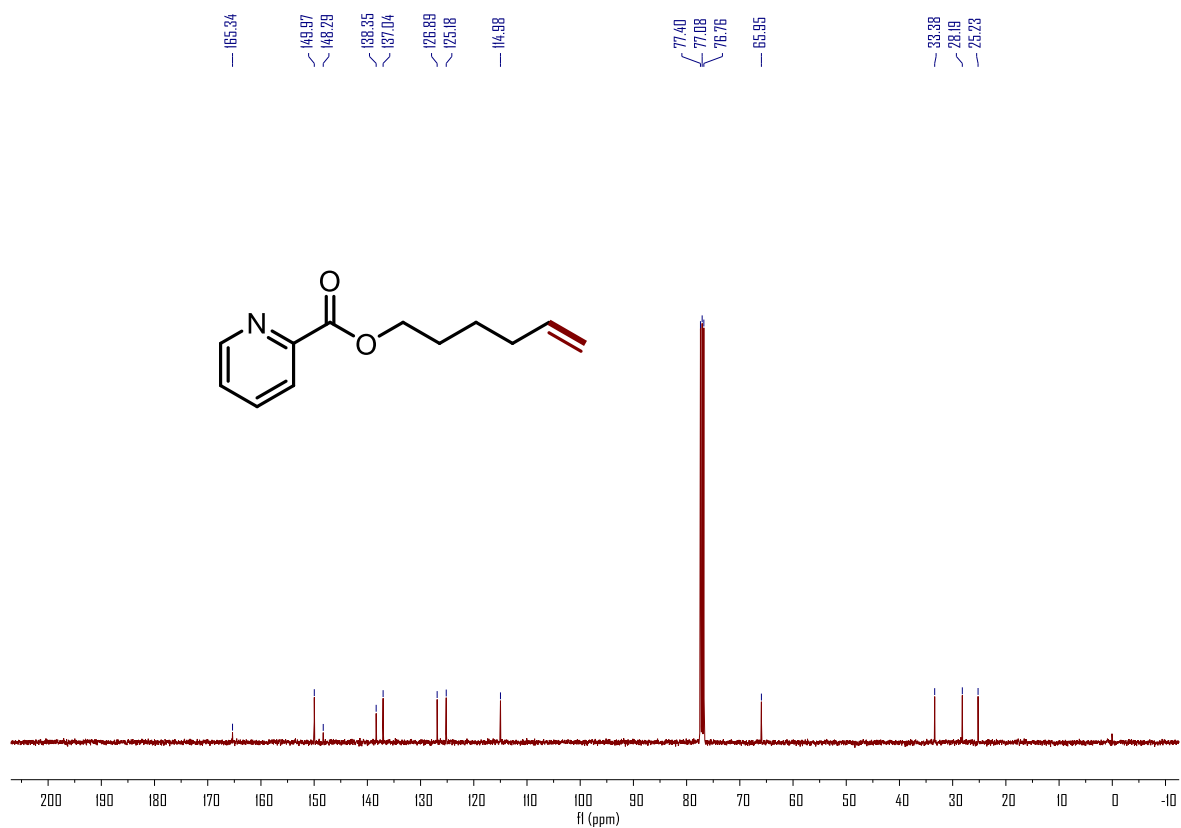
$^{13}\text{C}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of **3n**



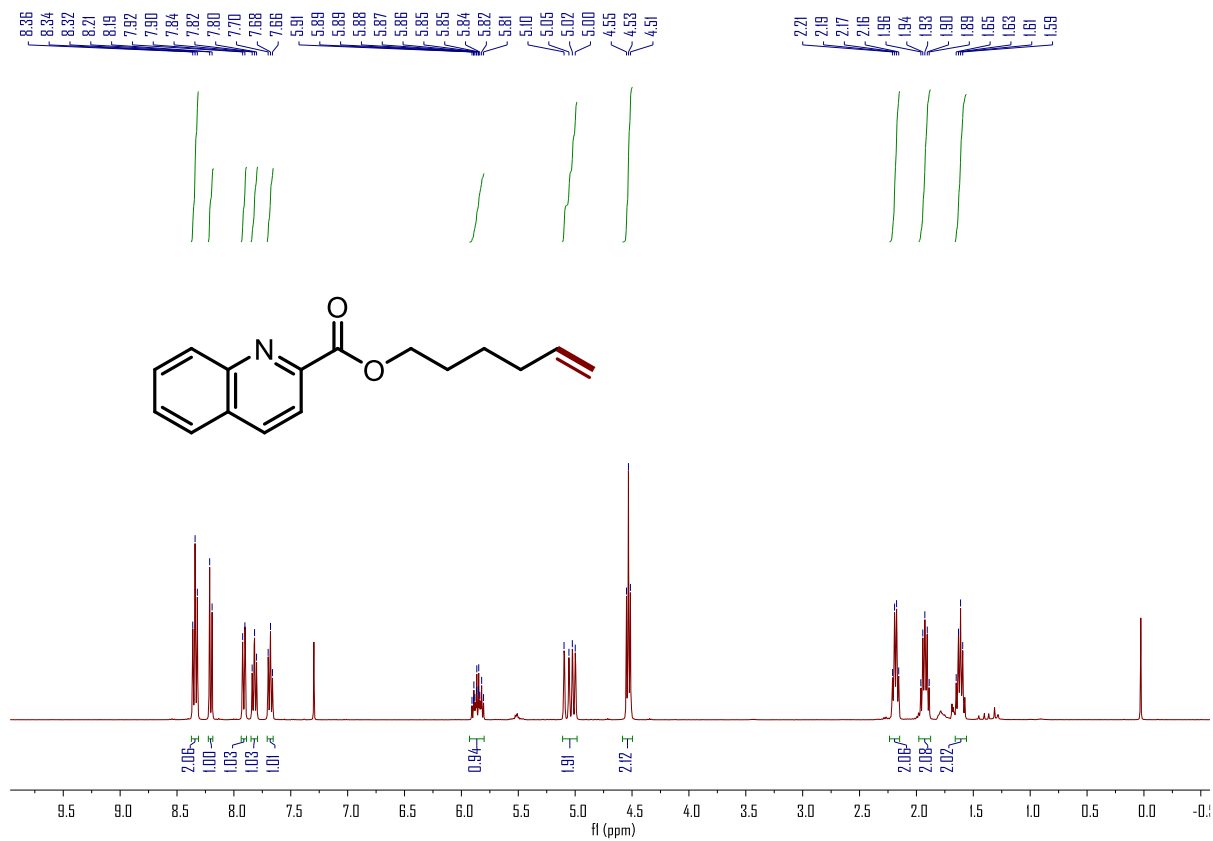
$^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of **3o**



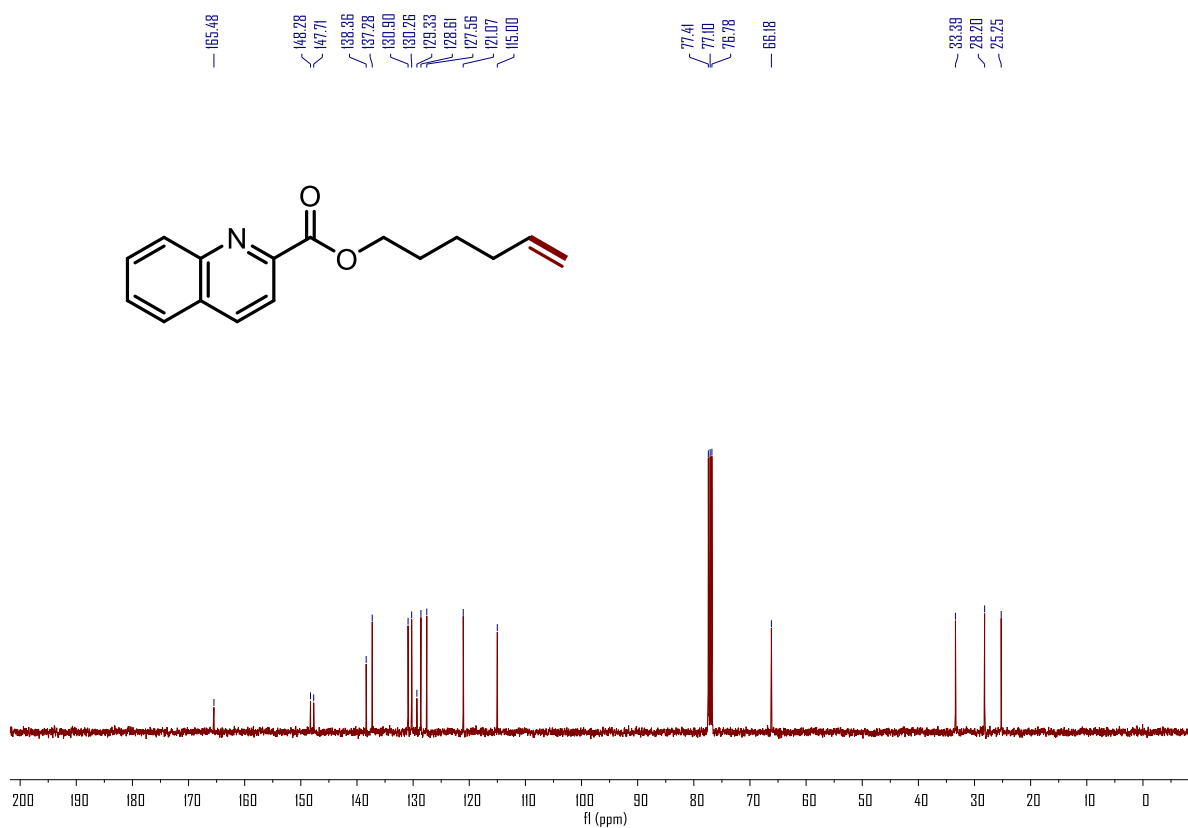
<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **3o**



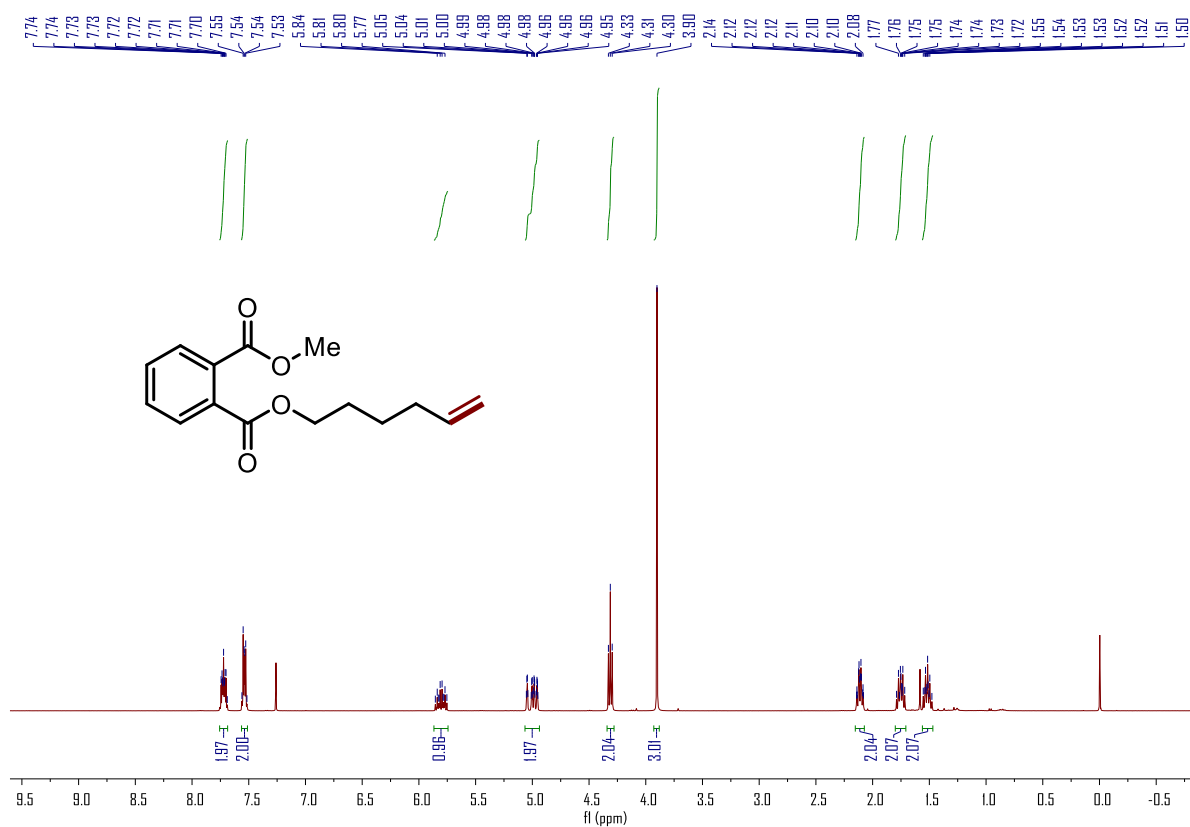
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **3p**



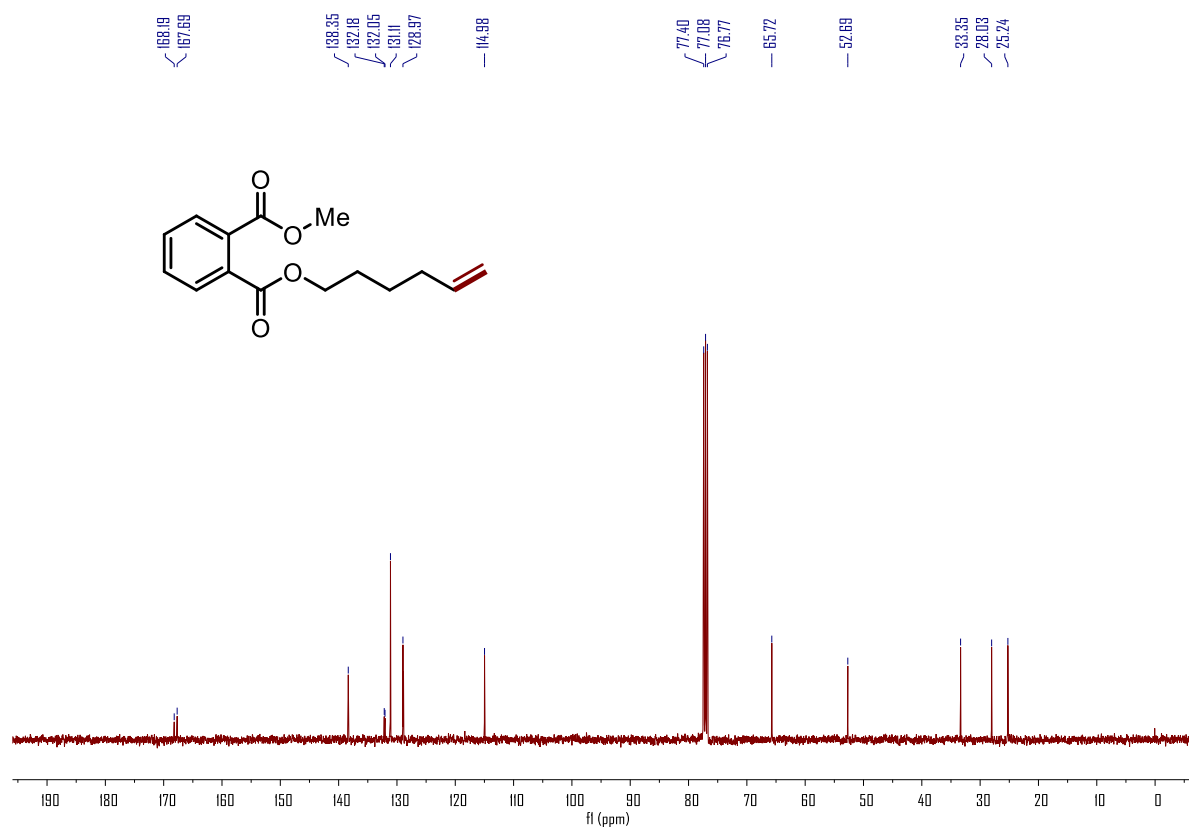
<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **3p**



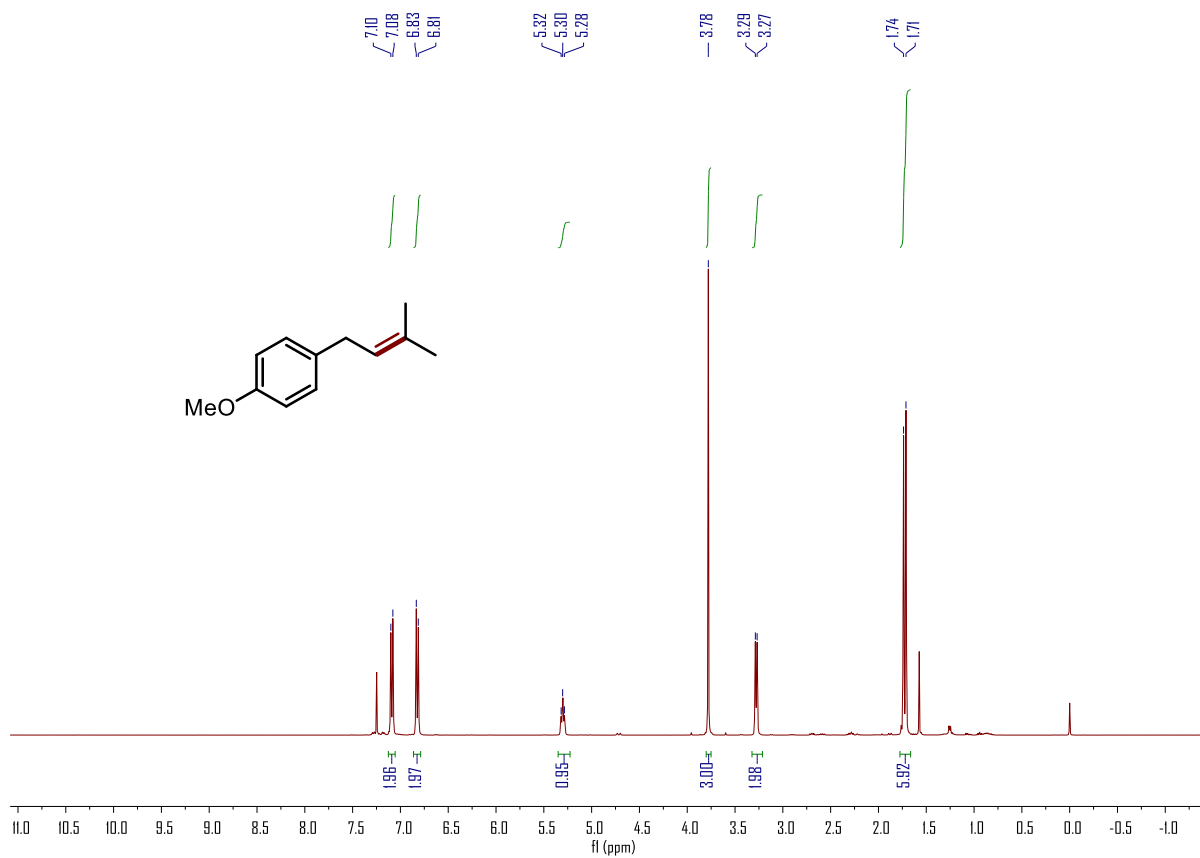
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **3q**



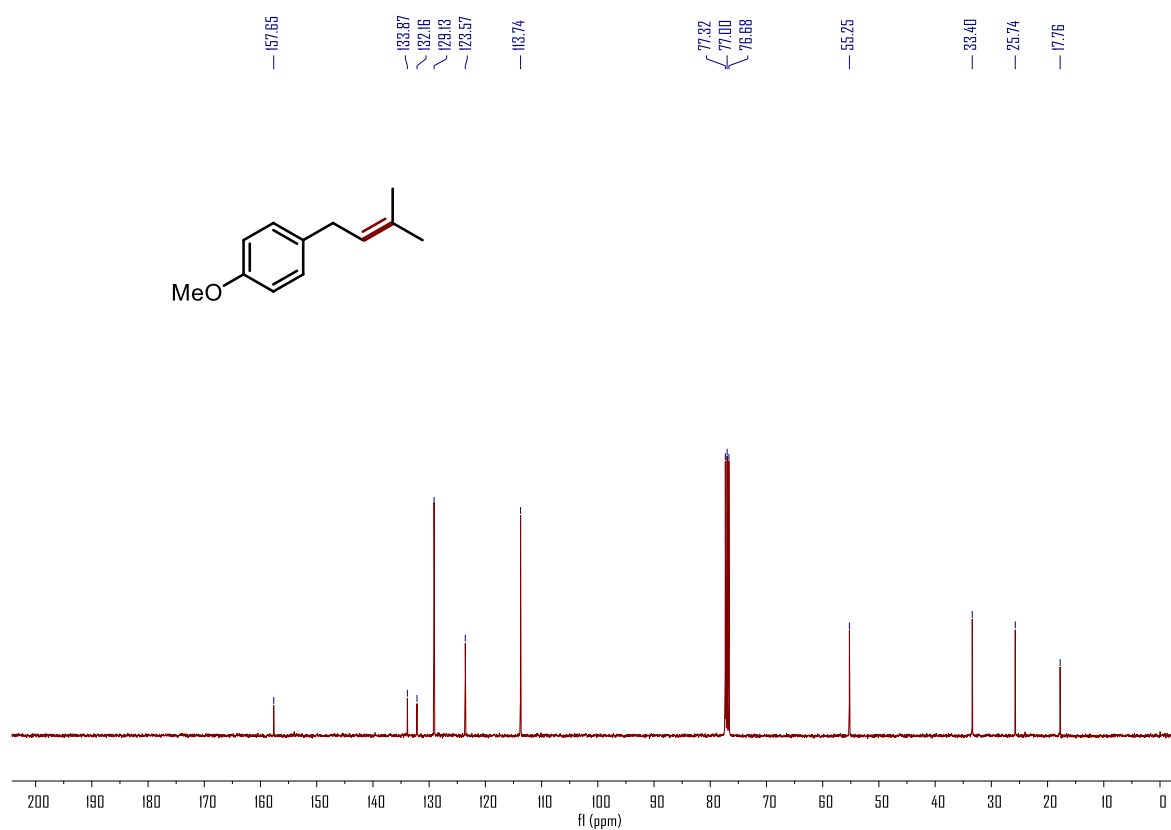
<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **3q**



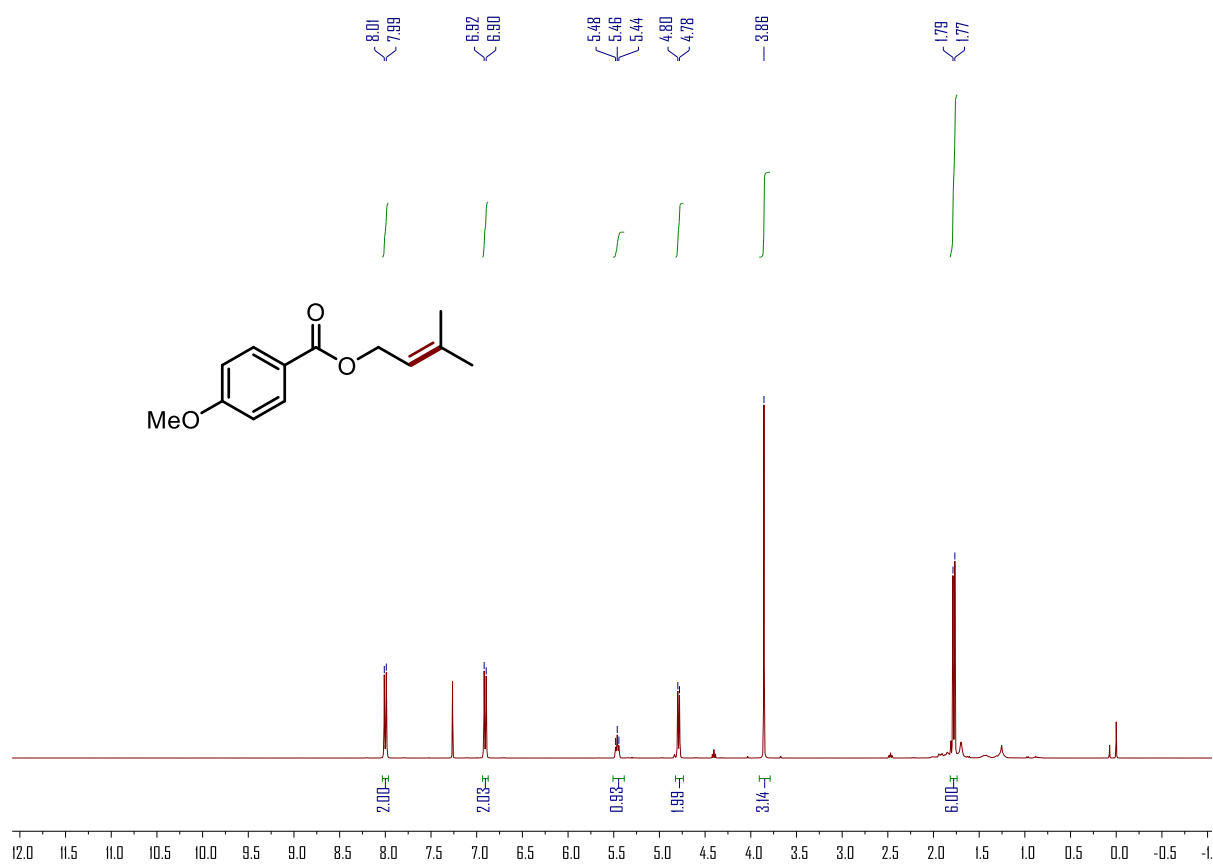
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **3r**



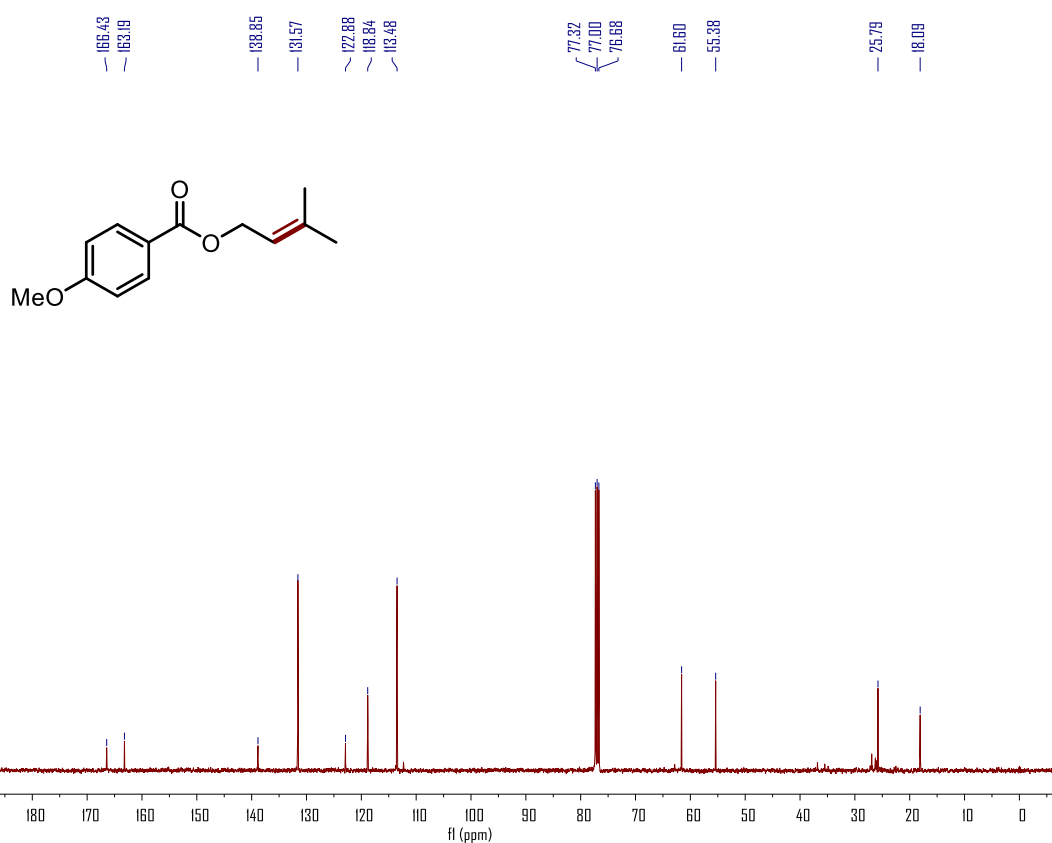
<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **3r**



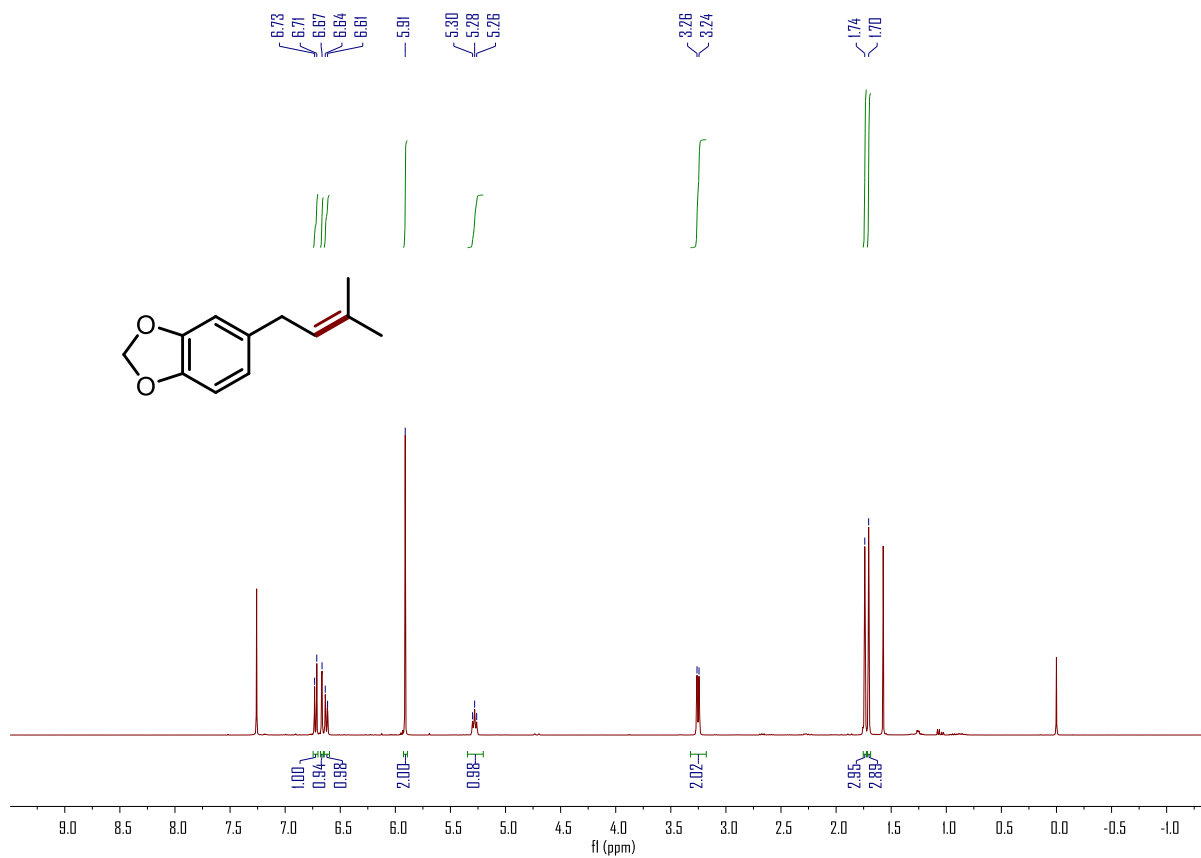
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **3s**



<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **3s**



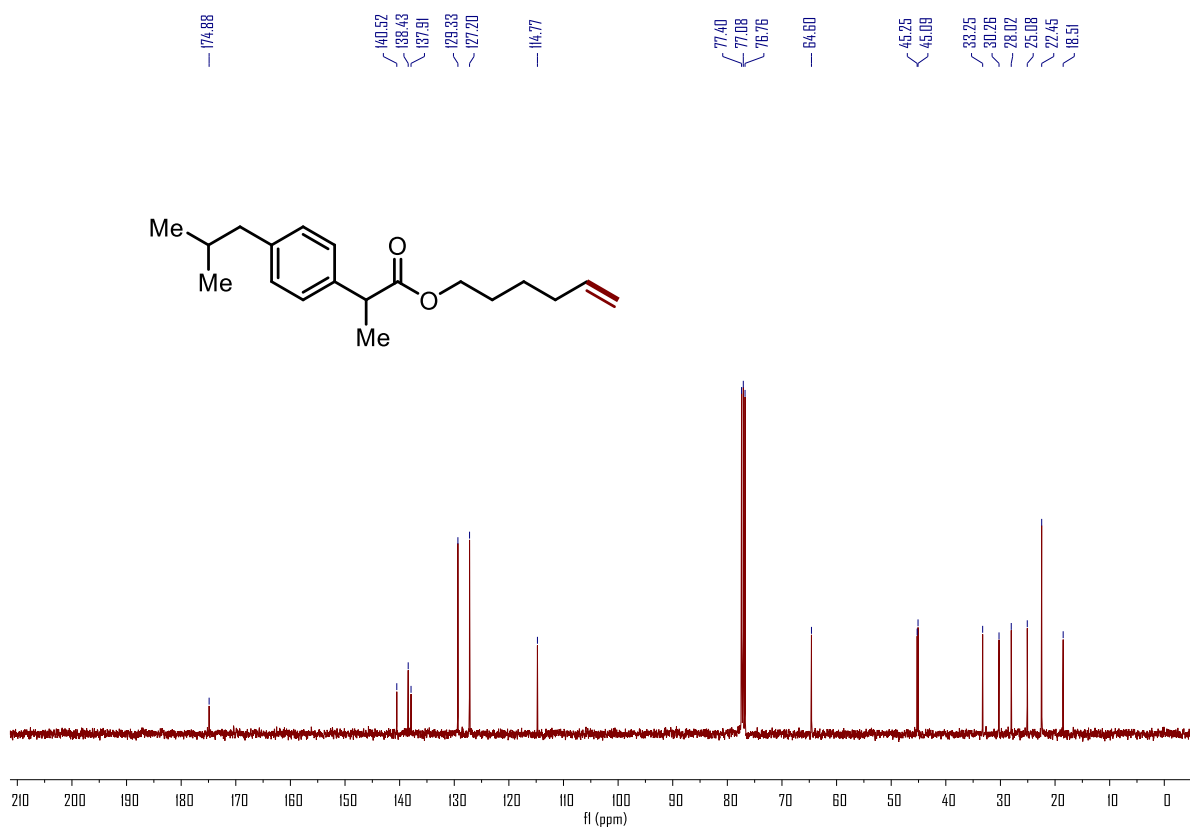
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **3t**



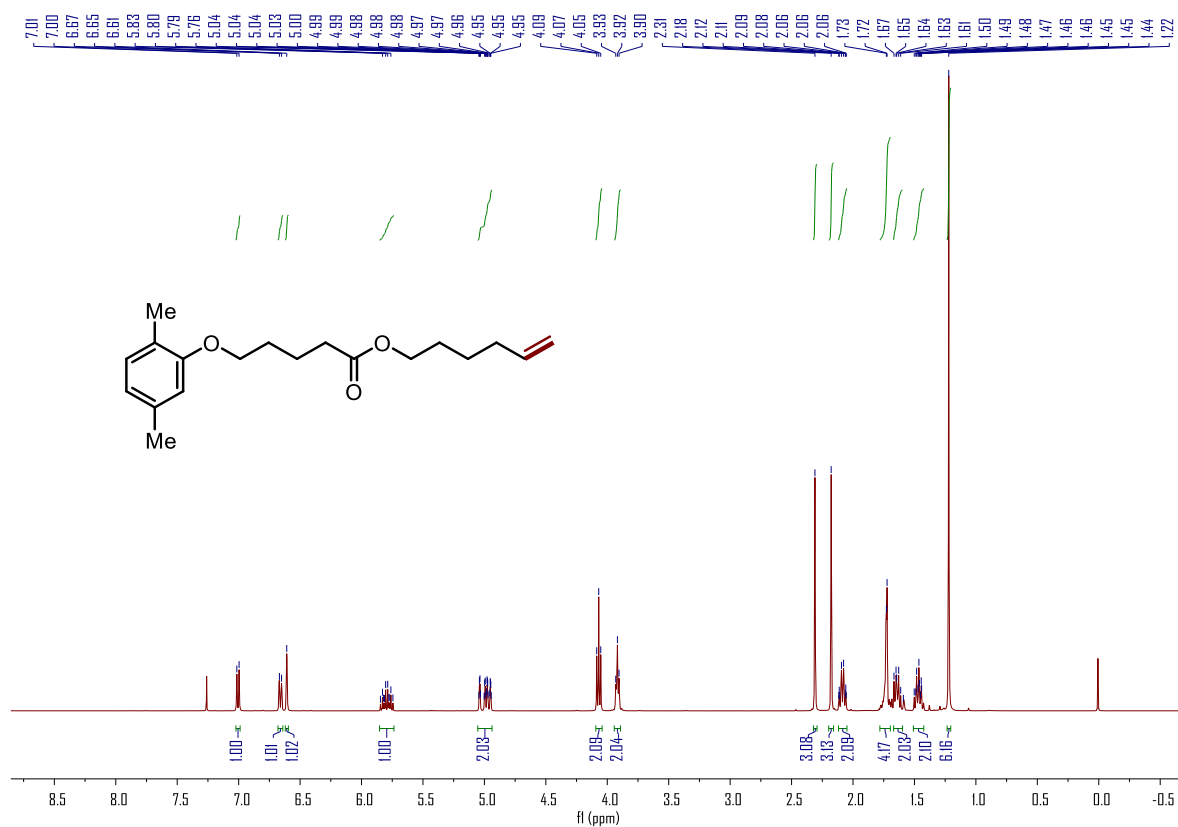




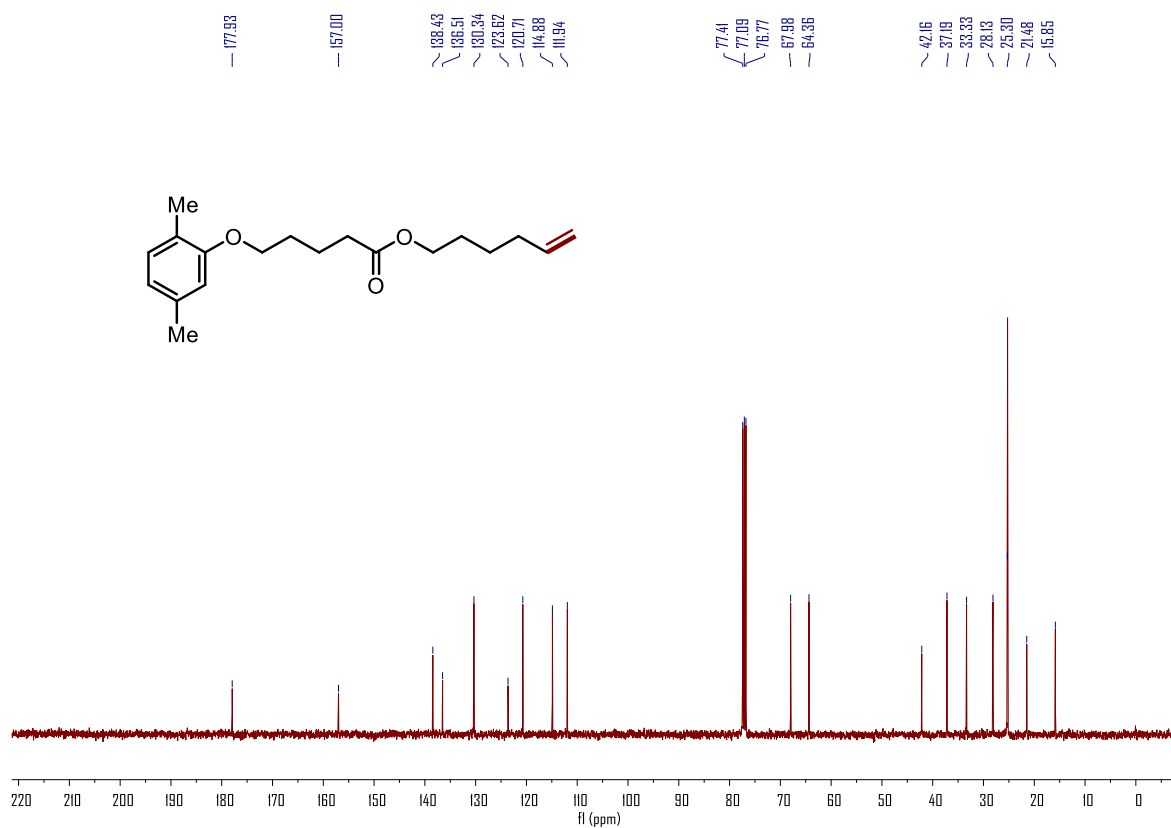
<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **3u**



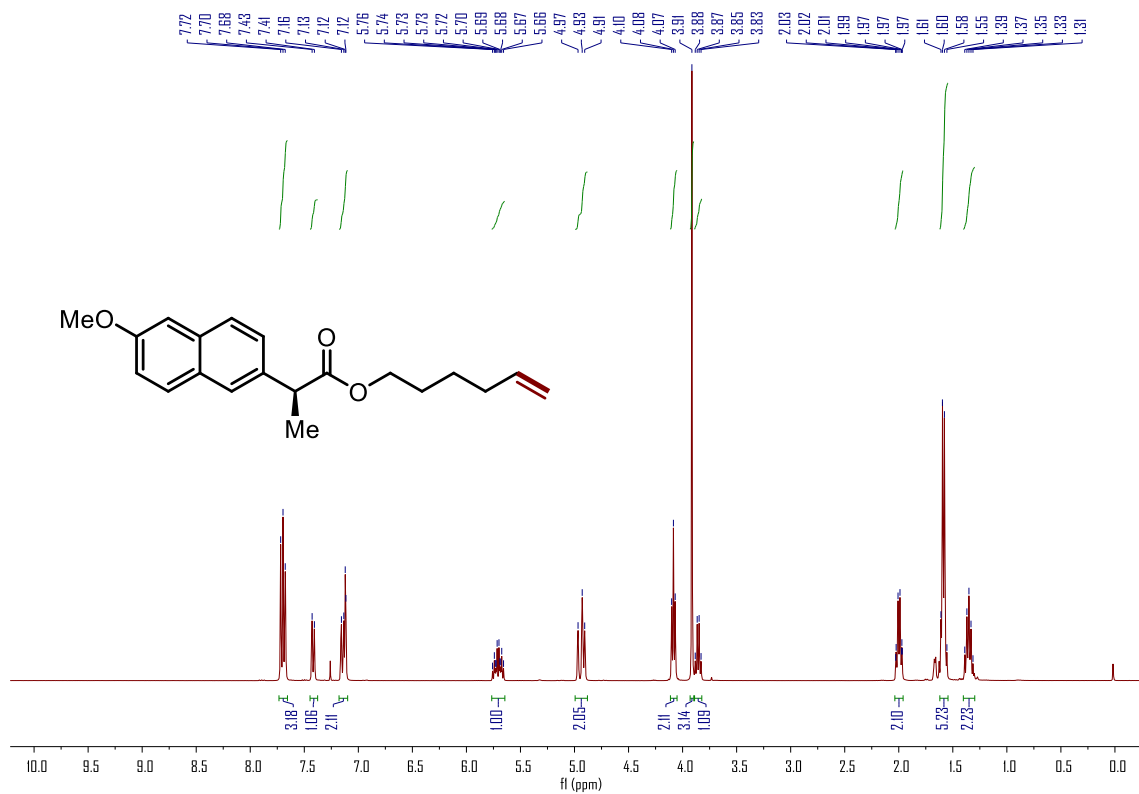
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **3v**



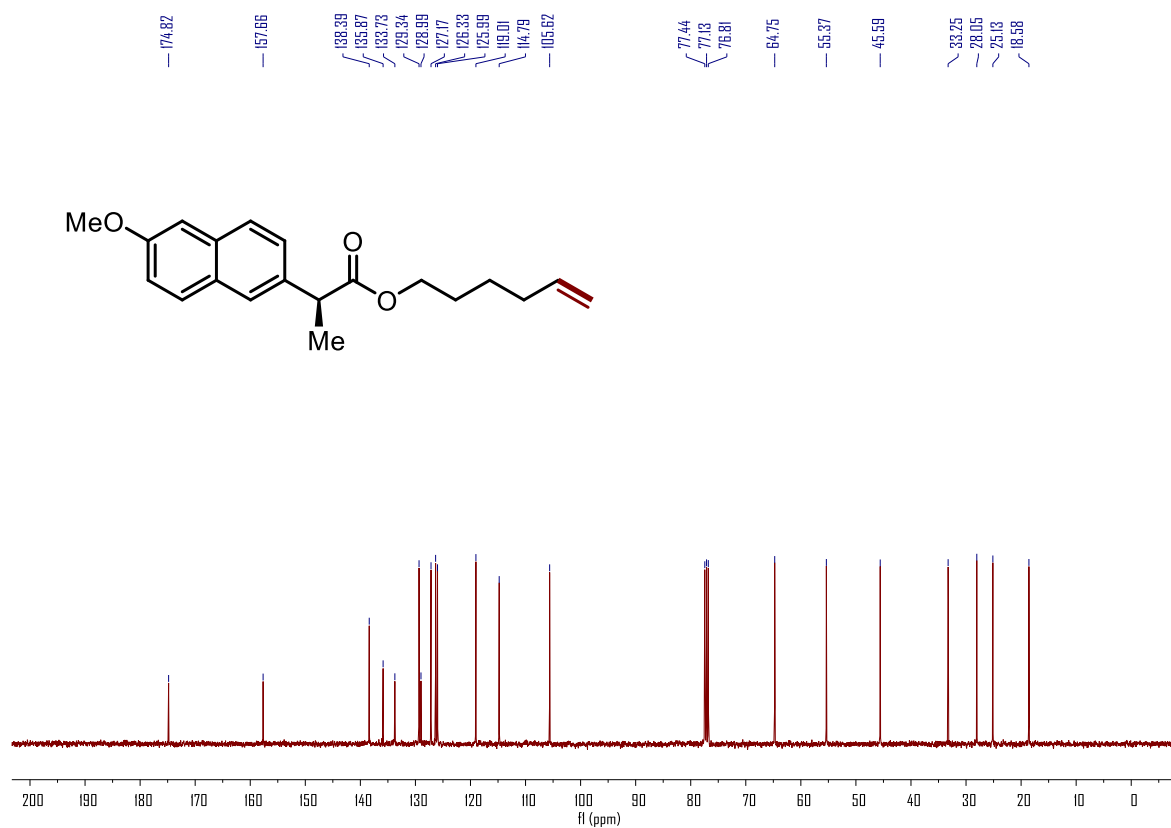
<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **3v**



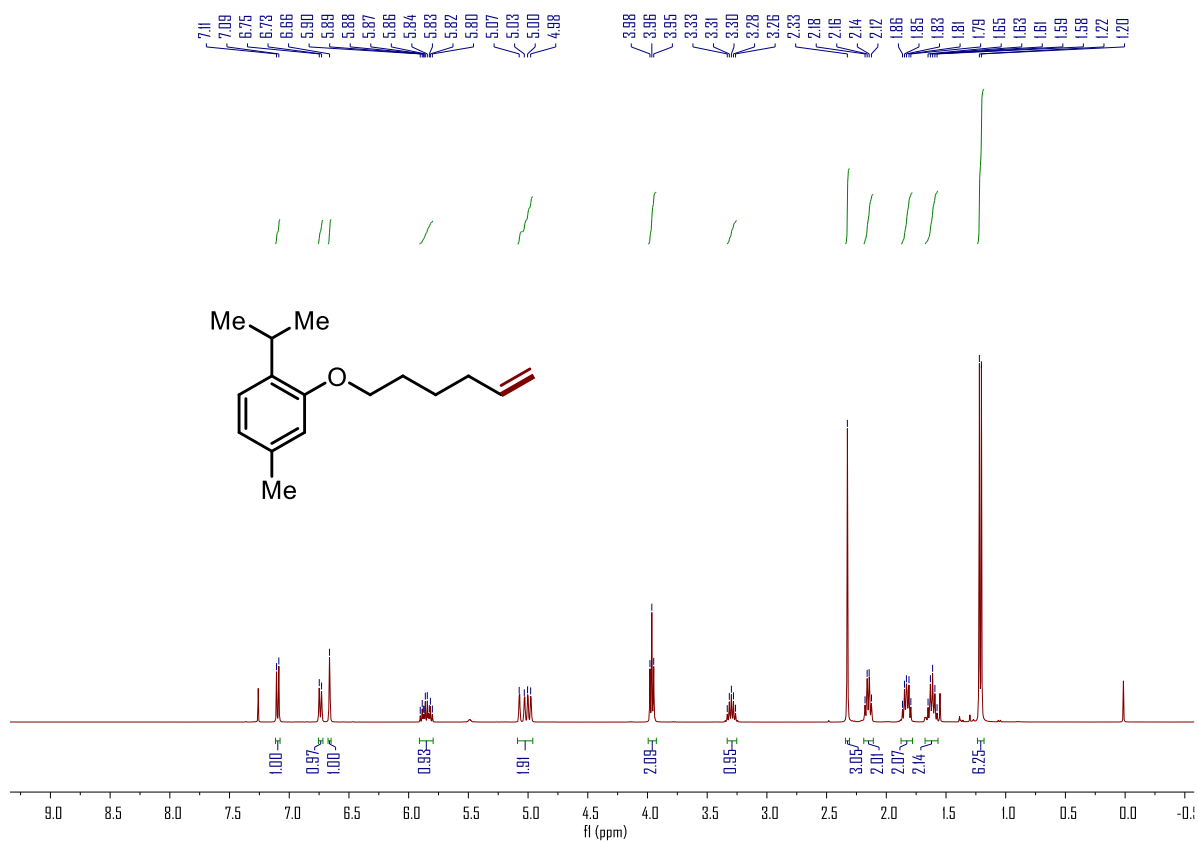
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **3w**



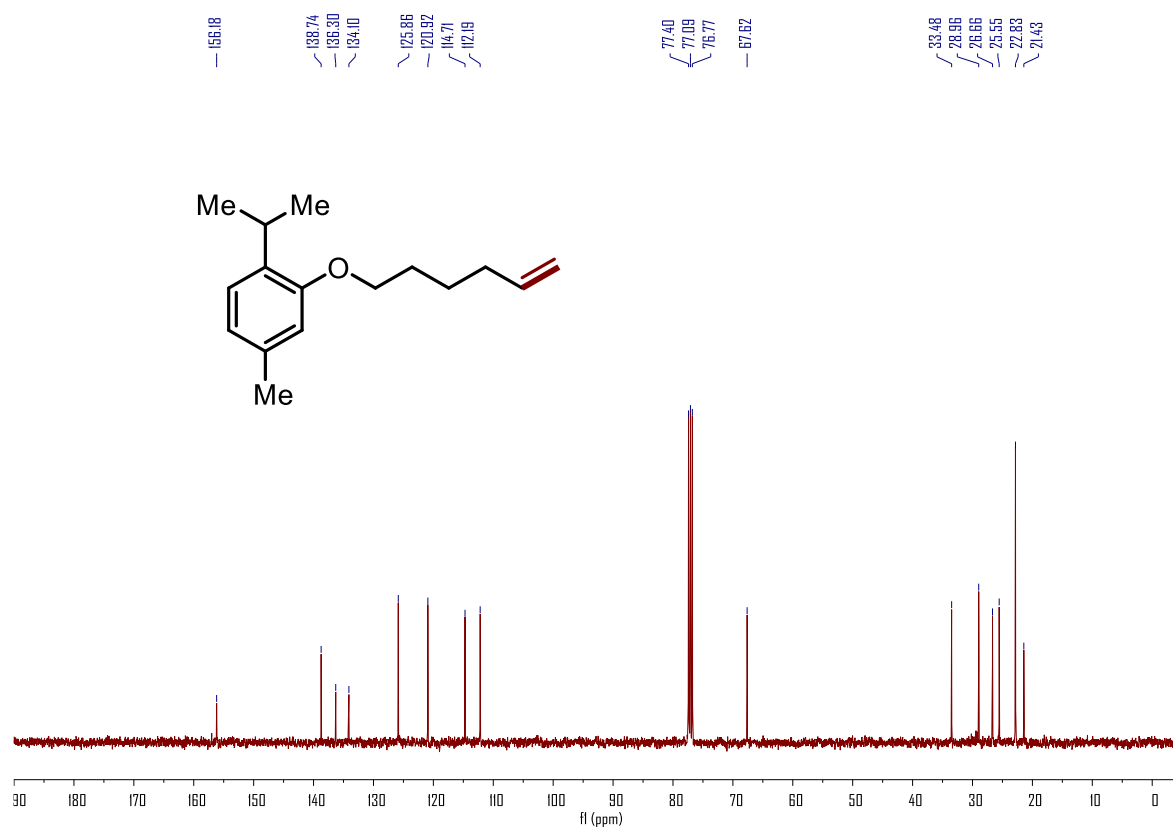
<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **3w**



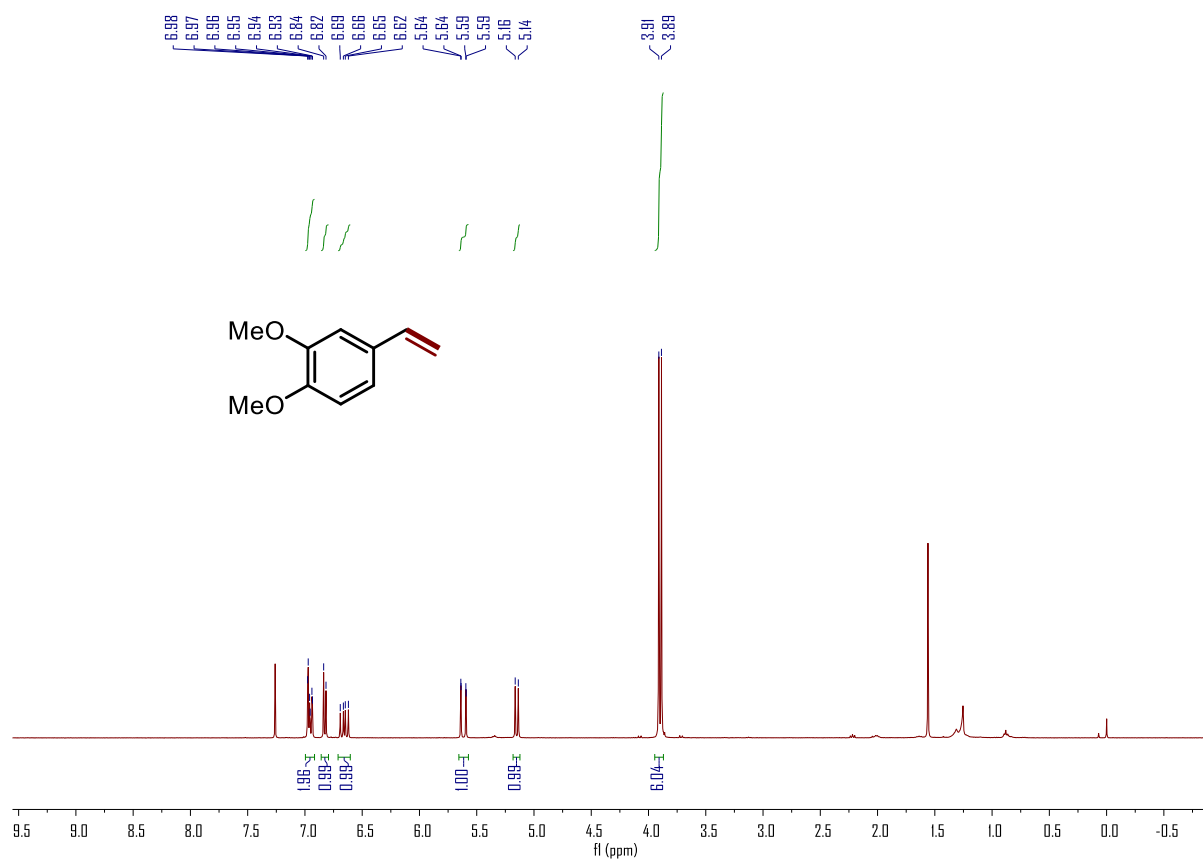
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **3x**



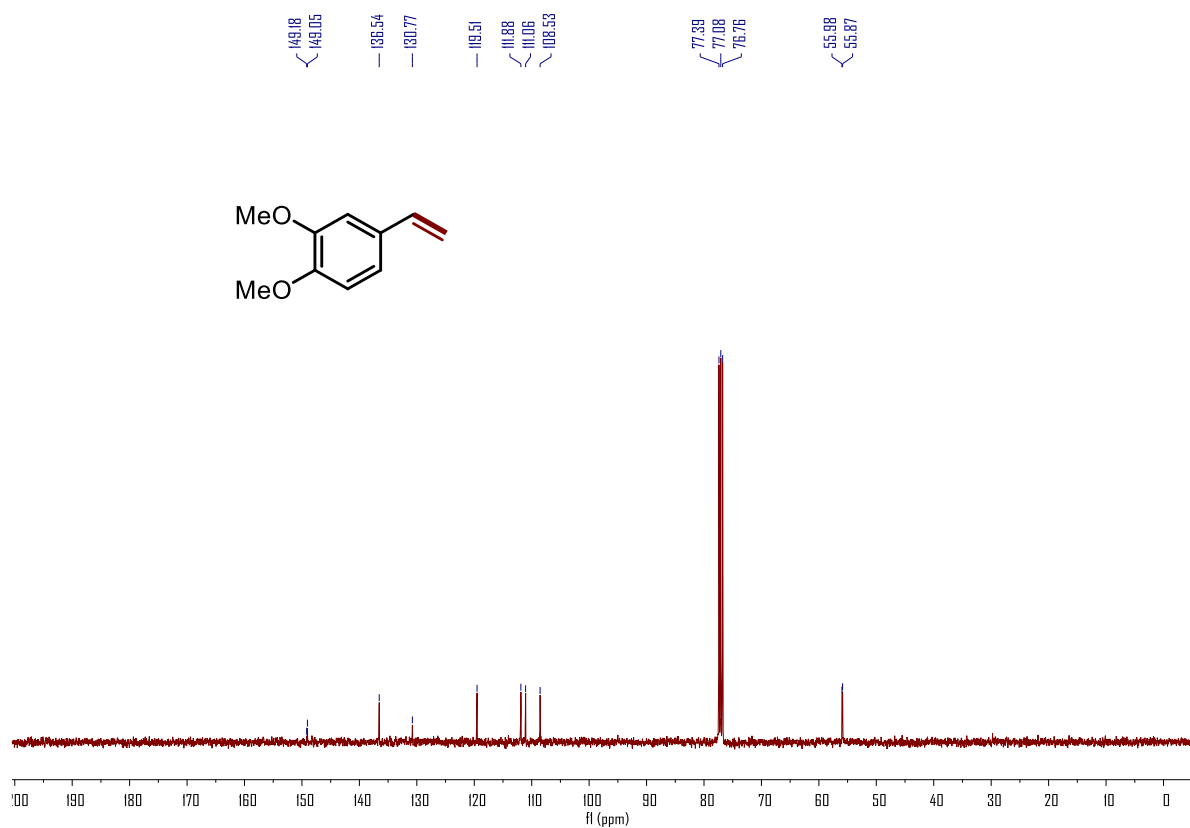
<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **3x**



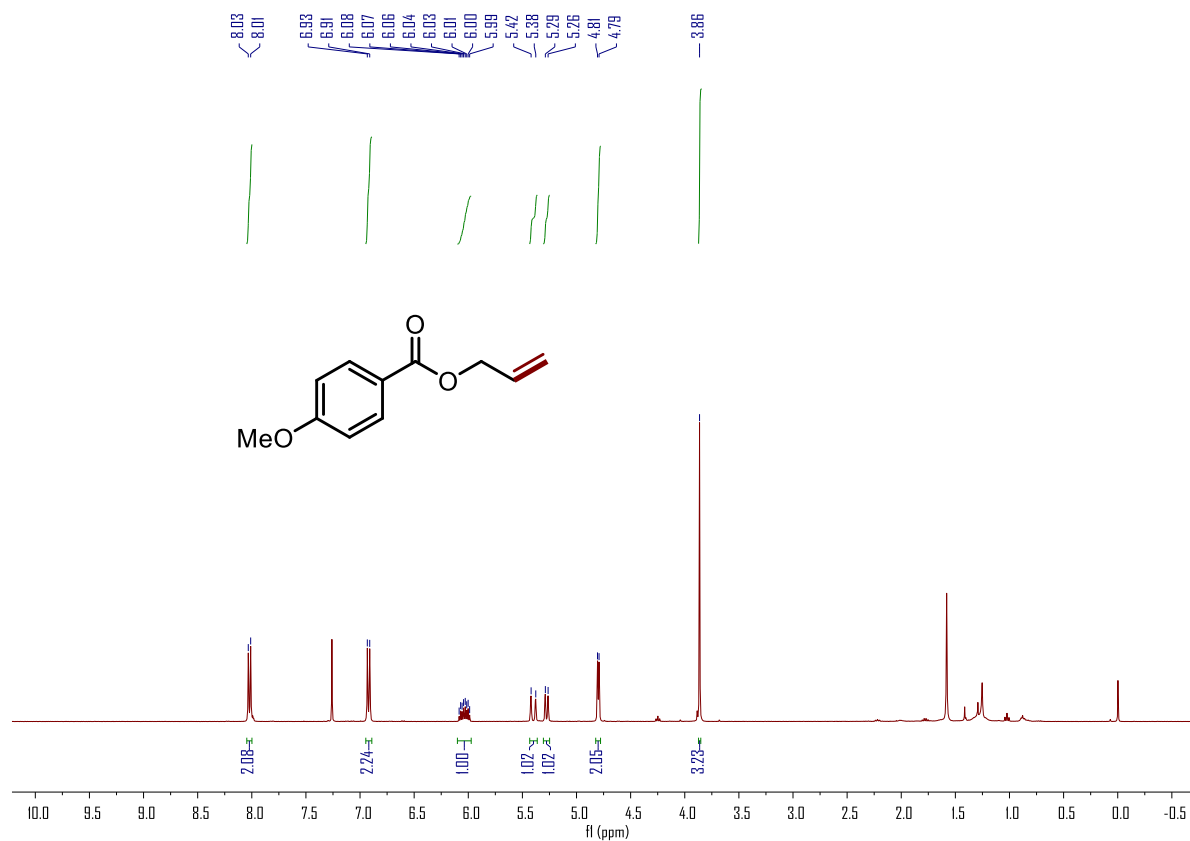
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **3y**



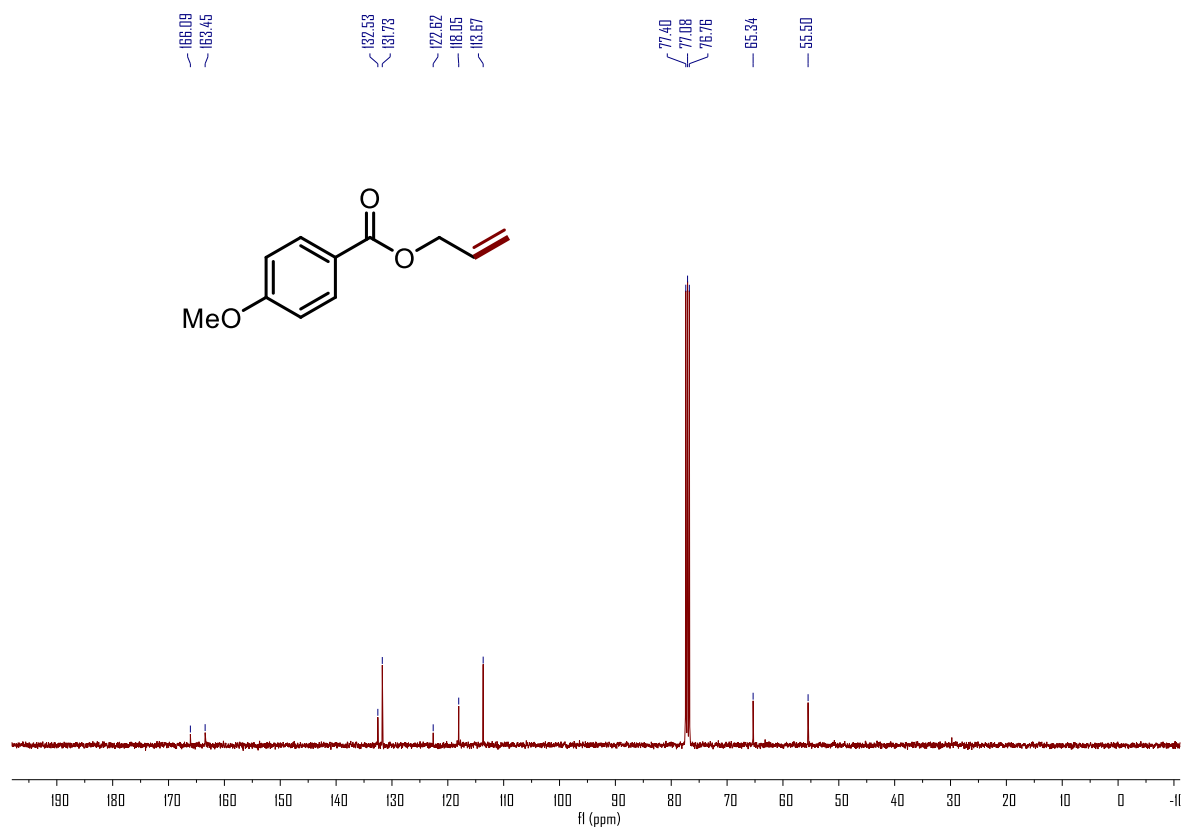
<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **3y**



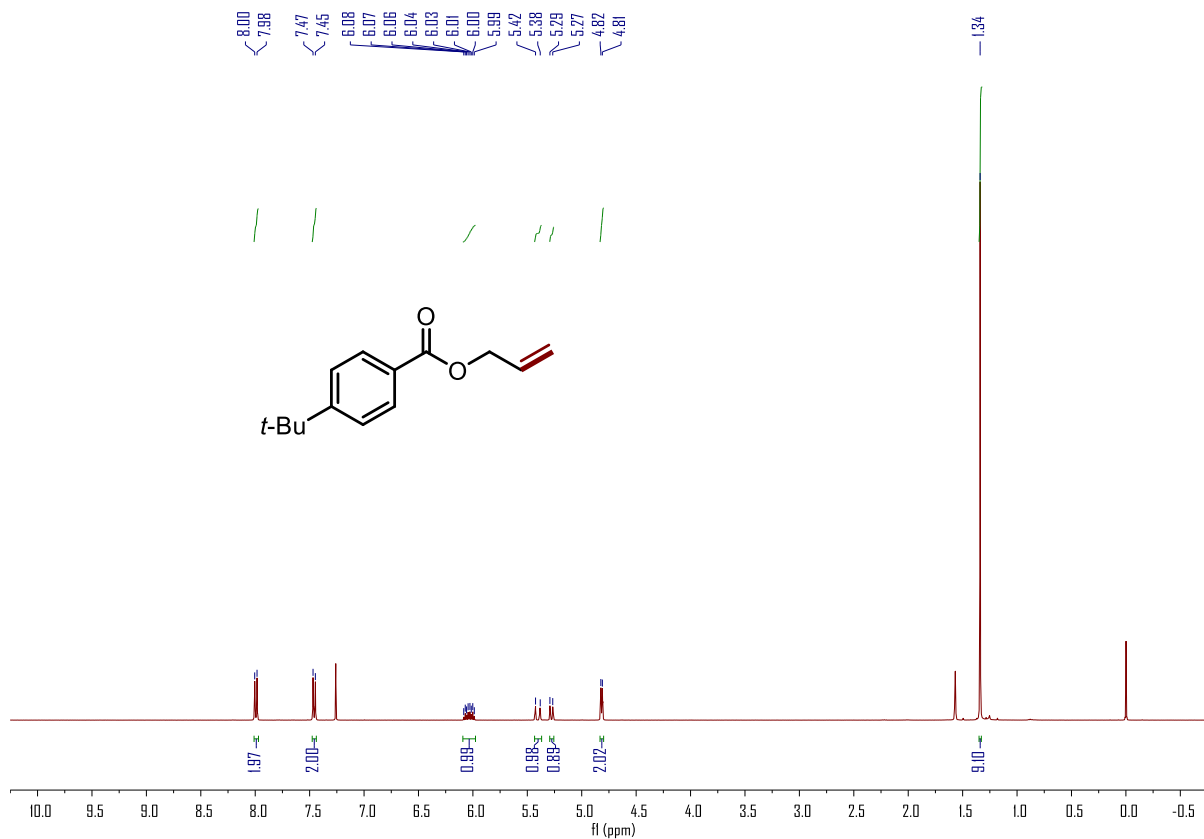
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **3z**



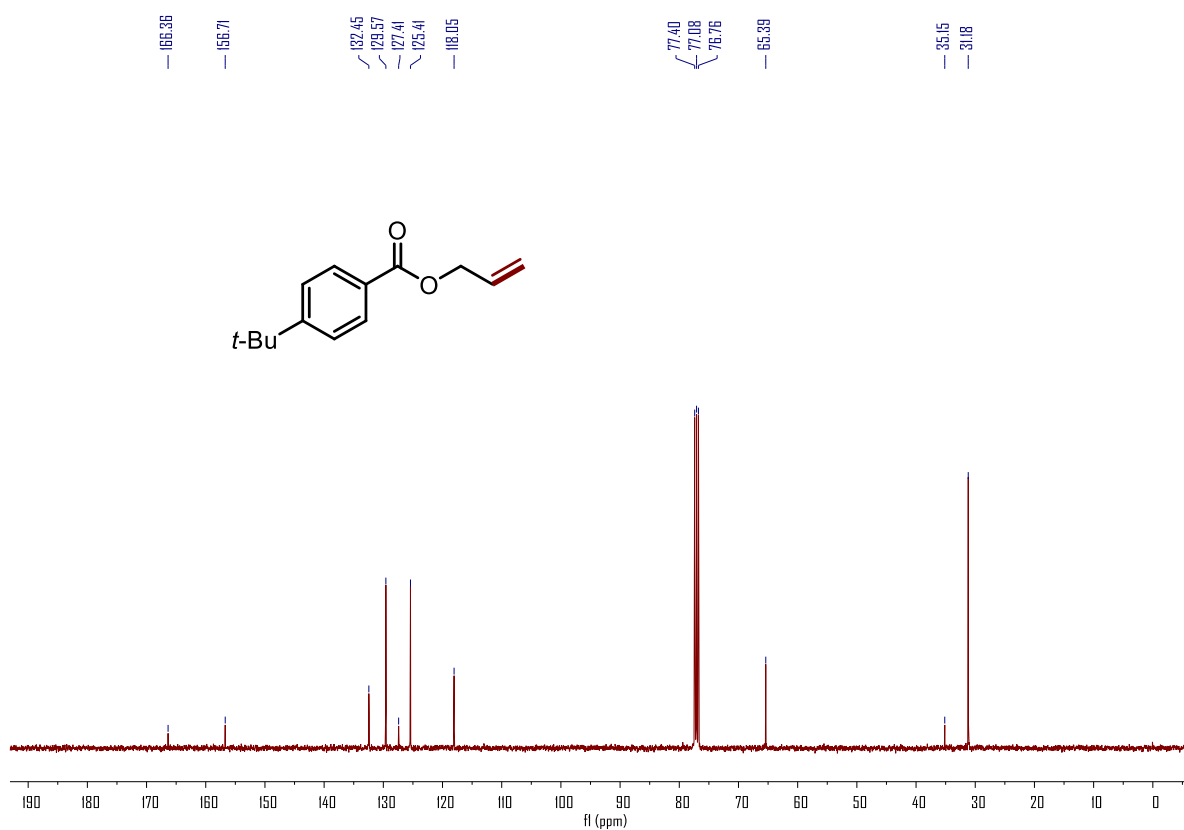
<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **3z**



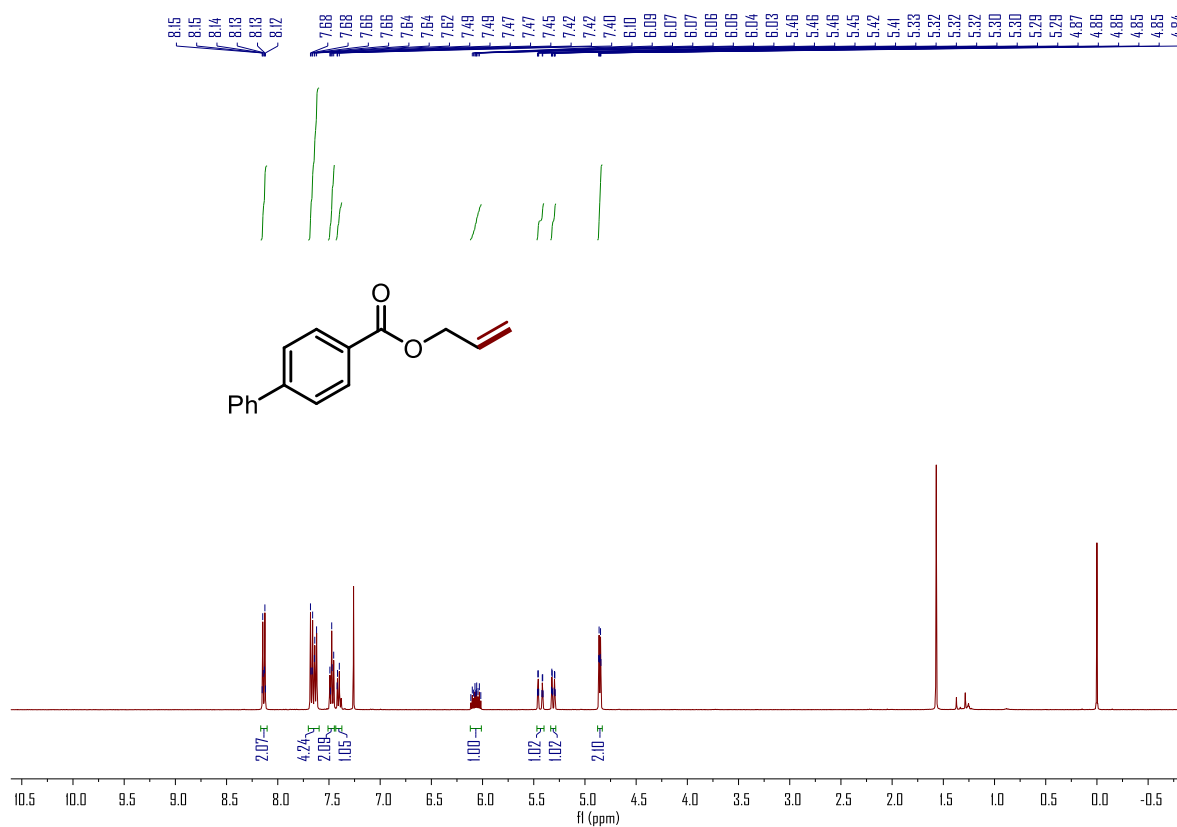
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **3aa**



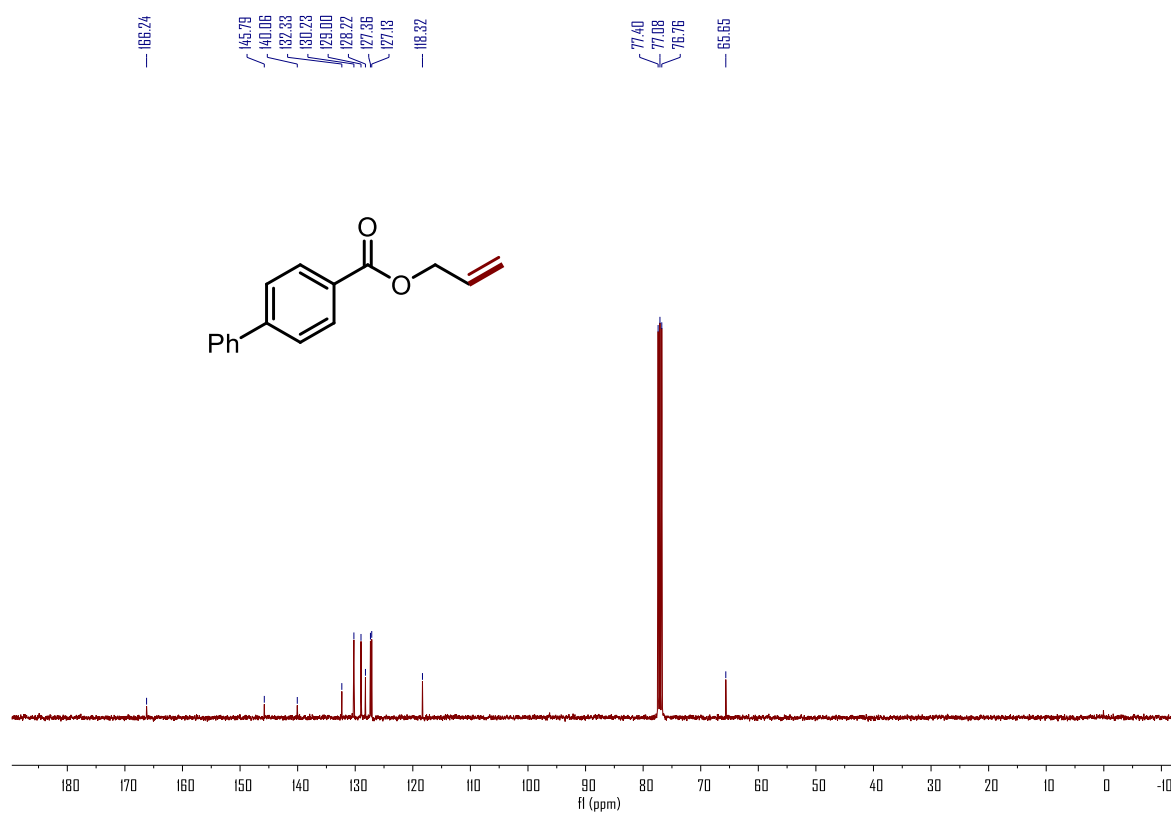
<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **3aa**



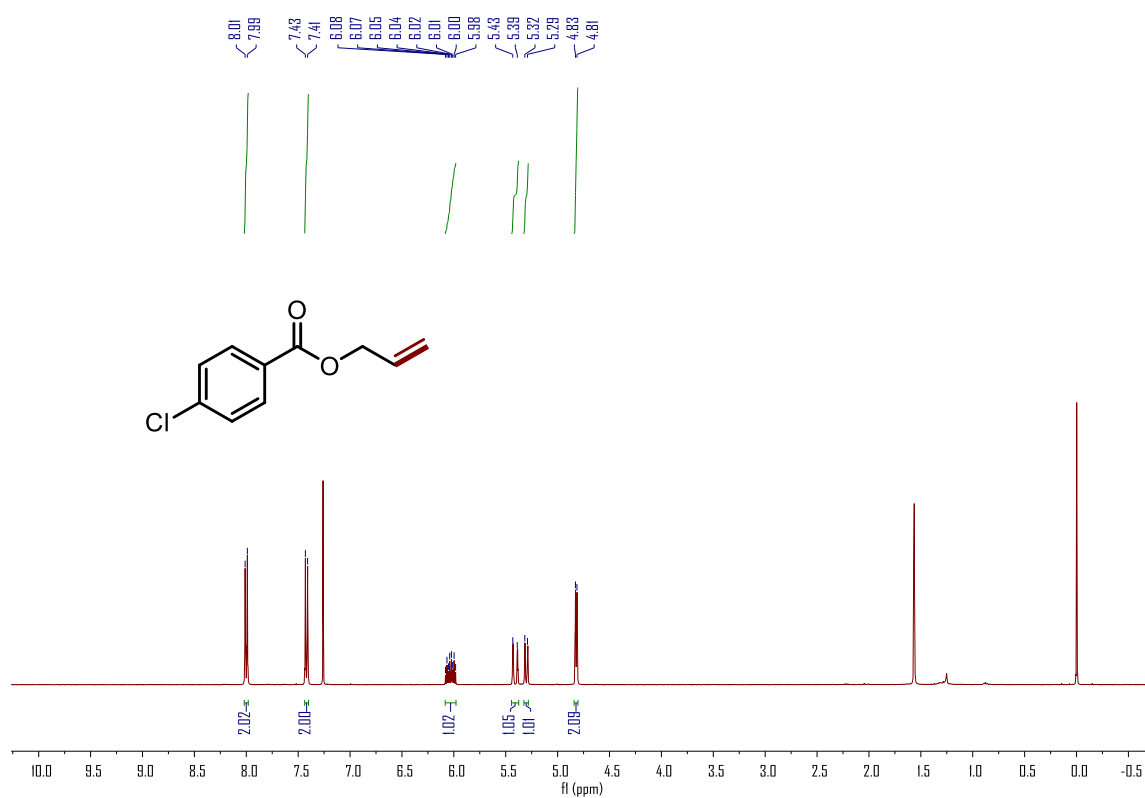
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **3ab**



$^{13}\text{C}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of **3ab**

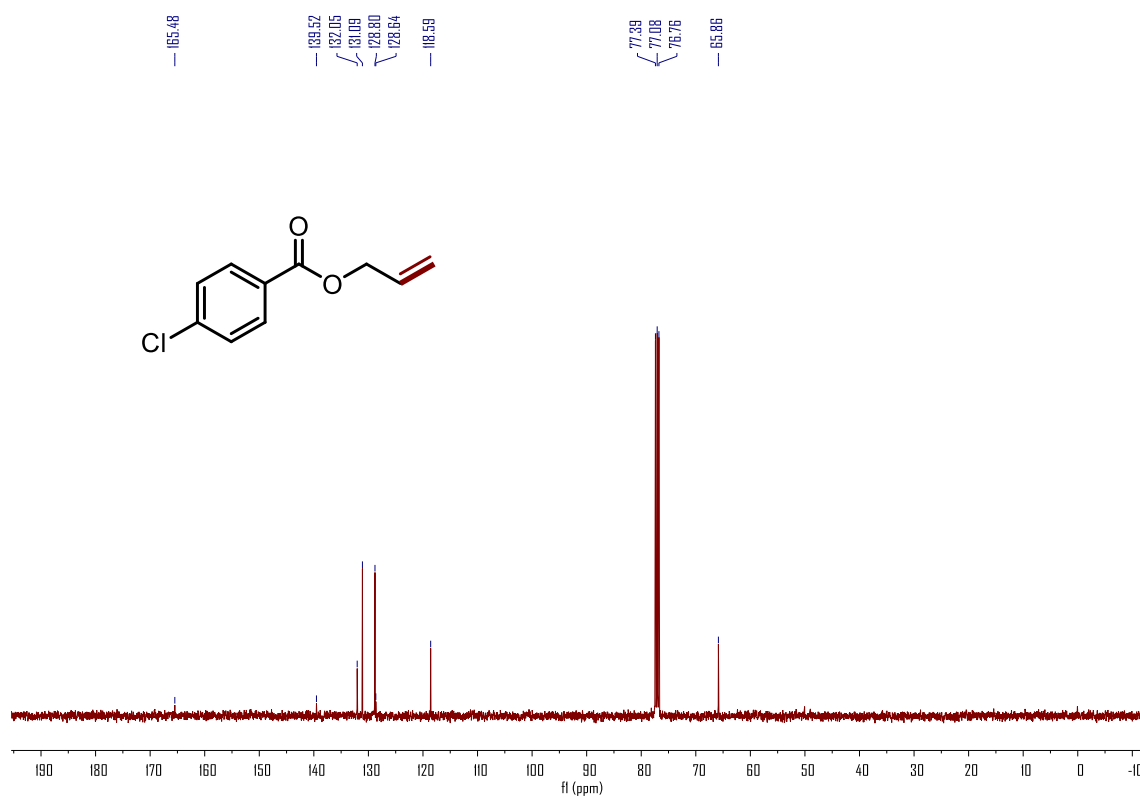


$^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of **3ac**

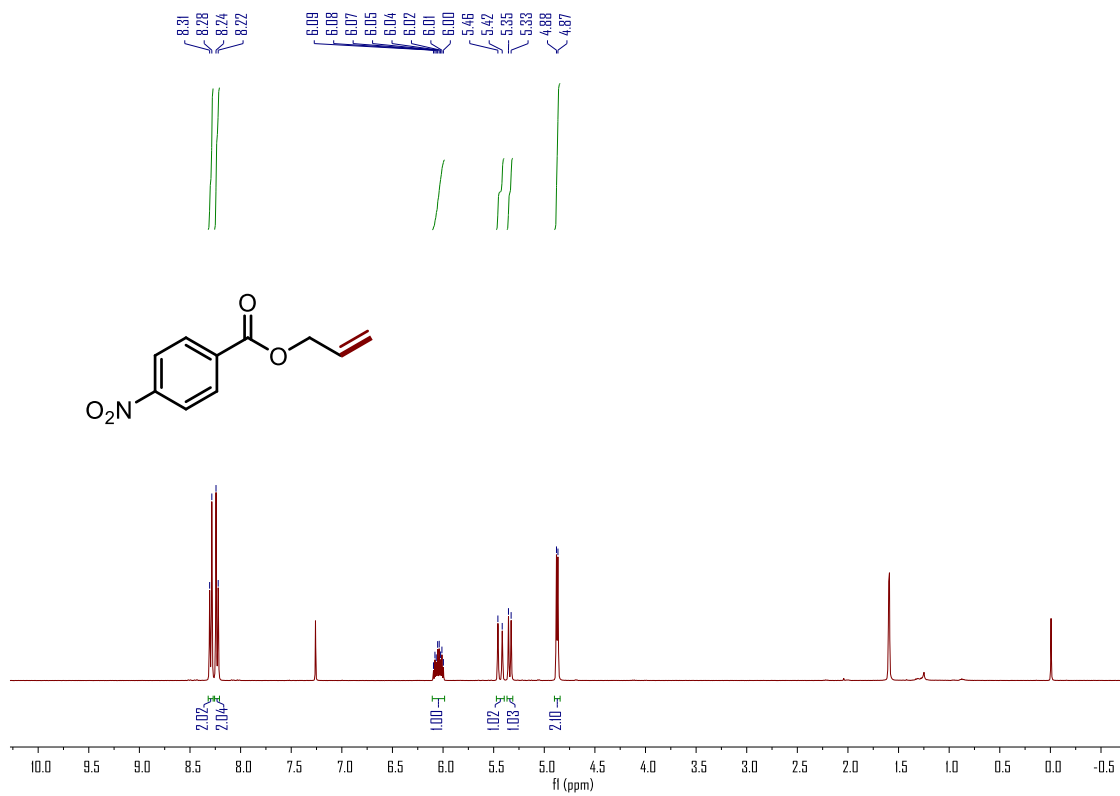




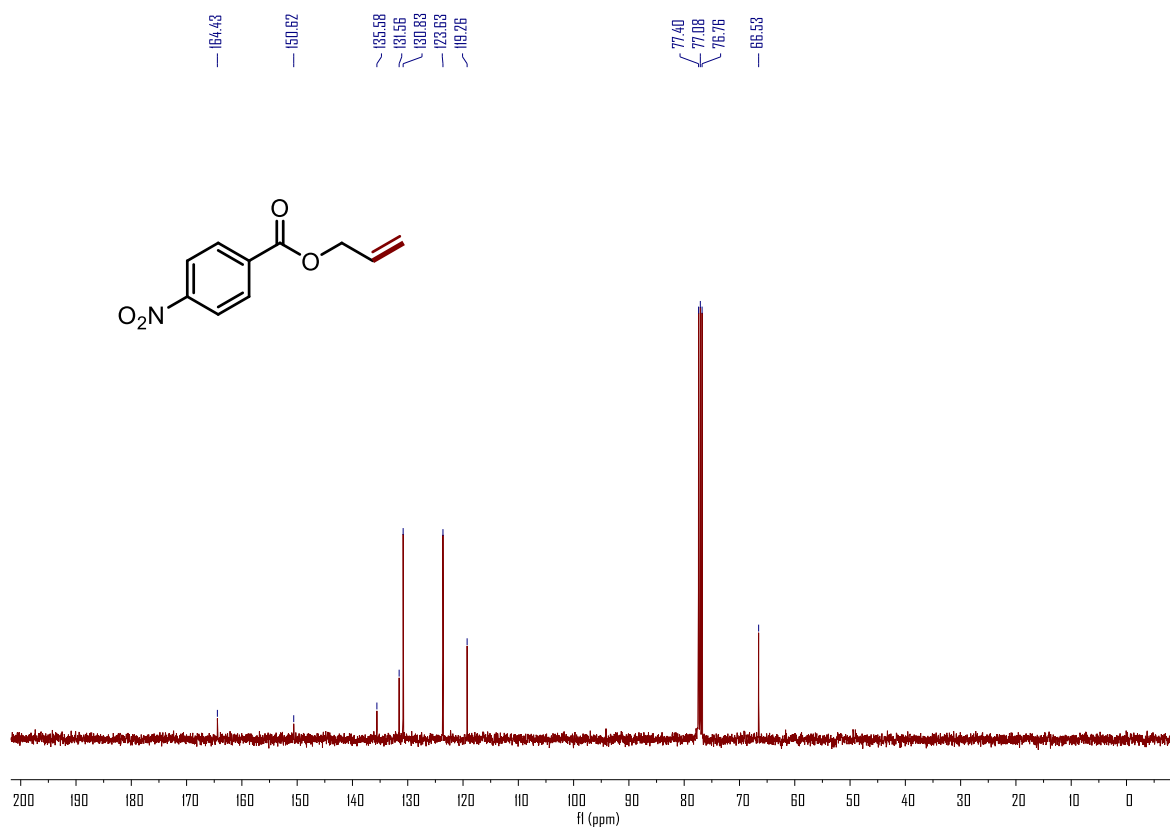
$^{13}\text{C}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of **3ac**



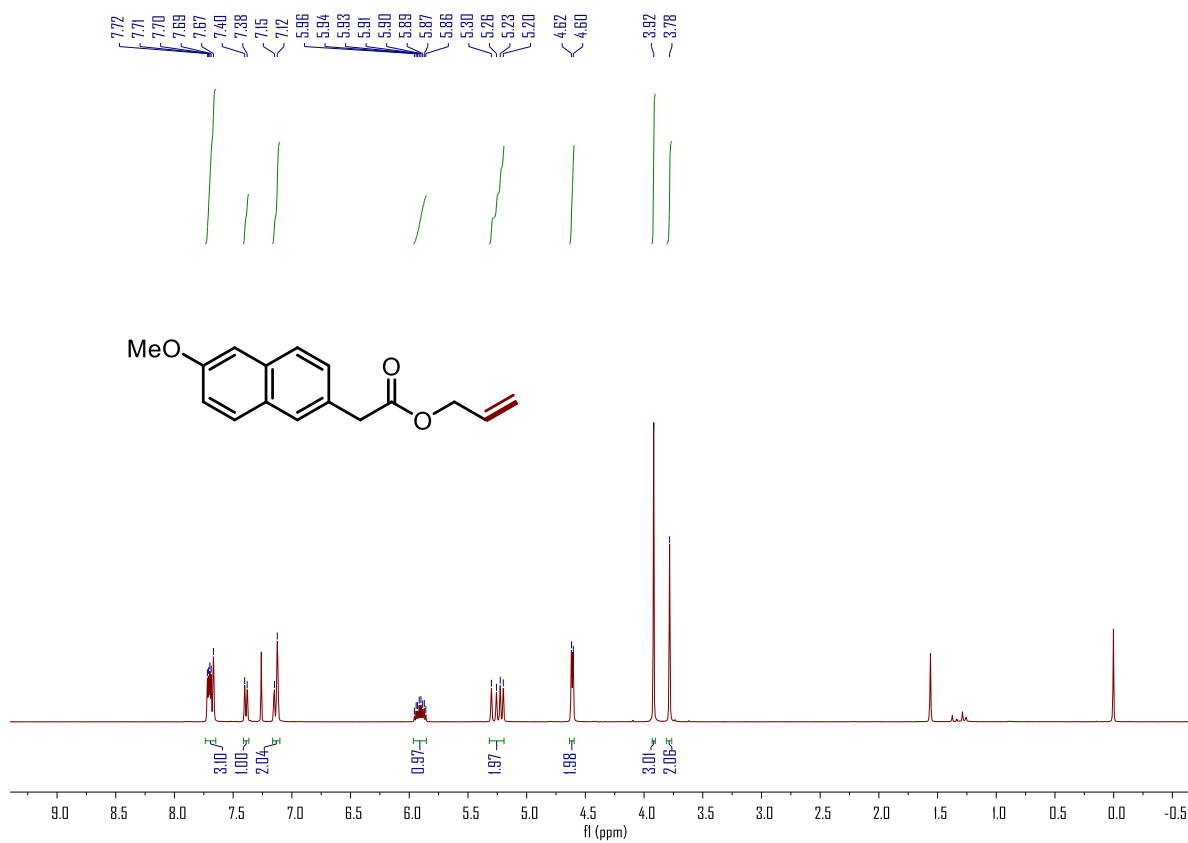
$^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of **3ad**



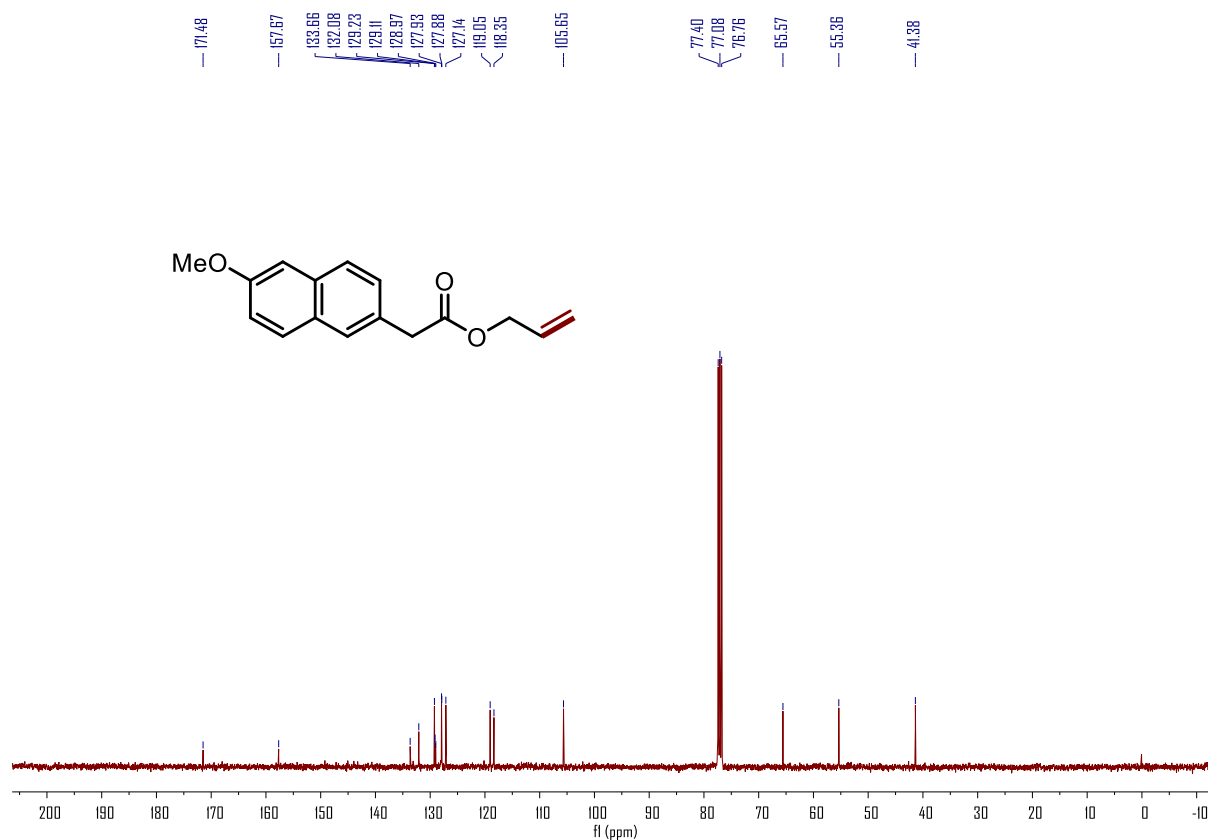
<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **3ad**



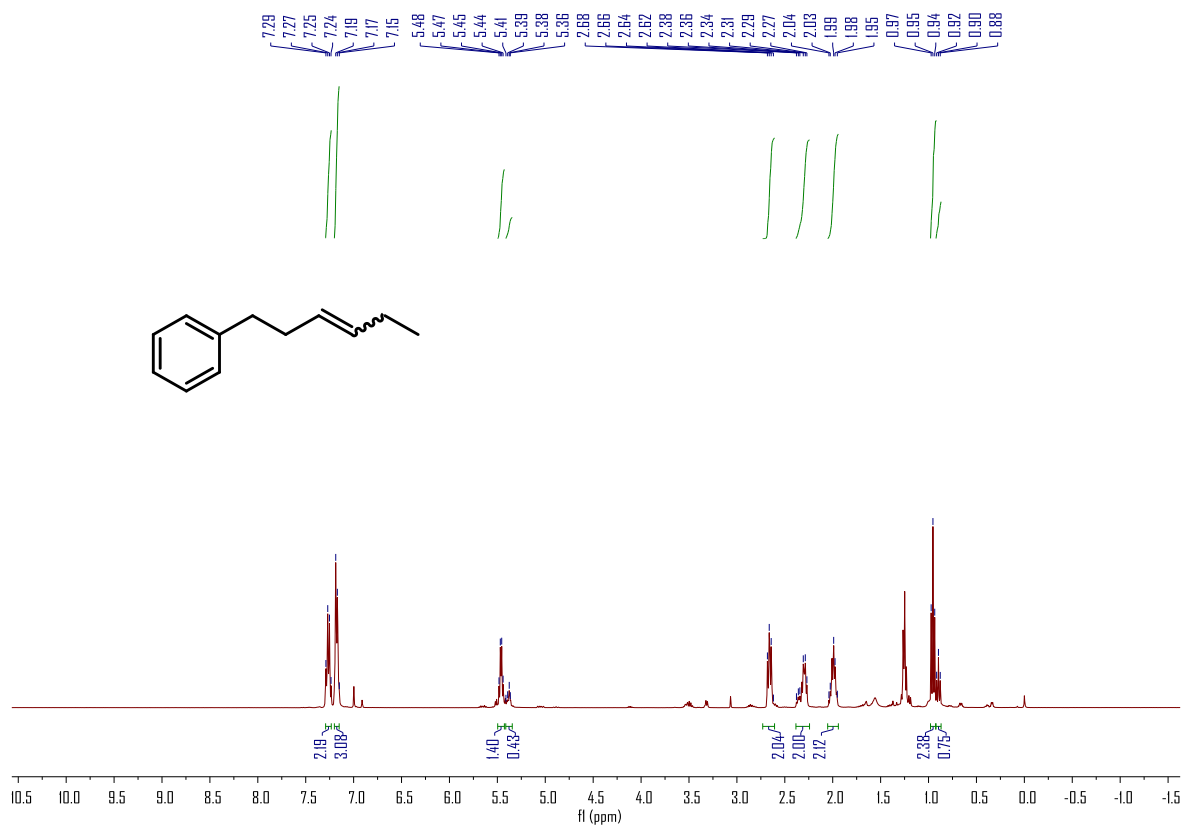
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **3ae**



<sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **3ae**



<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **5**



$^{13}\text{C}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of **5**

