

## **Supplementary Information**

### **Decarboxylative C(sp<sup>3</sup>)-N Cross Coupling via Synergetic Photoredox and Copper Catalysis**

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# Supplementary Methods

## General Analytical Information

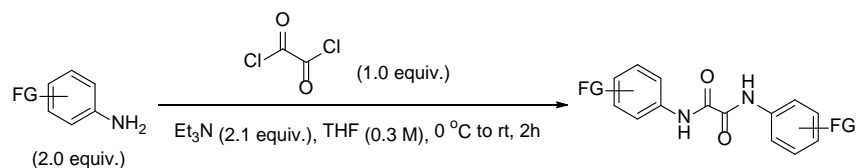
Nuclear Magnetic Resonance spectra were recorded on a Bruker Avance 400 MHz instruments at ambient temperature. All  $^1\text{H}$  NMR spectra were measured in part per million (ppm) relative to the signals of tetramethylsilane (TMS) added into the deuterated chloroform ( $\text{CDCl}_3$ ) (0.00 ppm) unless otherwise stated.<sup>1</sup> Data for  $^1\text{H}$  NMR were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qu = quintet, sex = sextet, m = multiplet, br = broad), coupling constants, and integration. All  $^{13}\text{C}$  NMR spectra were reported in ppm relative to  $\text{CDCl}_3$  (77.16 ppm) unless otherwise stated, and were obtained with complete  $^1\text{H}$  decoupling. All GC analyses were performed on a Perkin-Elmer Clarus 400 GC system with a FID detector. All GC-MS analyses were performed on an Agilent Technologies 7890A GC system equipped with a 5975C MS detector. High-resolution mass spectra (HRMS) by electrospray ionization (ESI) and atmospheric pressure photoionization (APPI) method were performed at the EPFL ISIC Mass Spectroscopy Service with a Micro Mass QTOF Ultima spectrometer.

## General Manipulation Considerations

All manipulations for the decarboxylative  $\text{C}(\text{sp}^3)\text{-N}$  cross coupling via synergetic photoredox and copper catalyzed reactions were set up in a 15 mL Teflon-screw capped test tubes (unless otherwise noted) under an inert nitrogen ( $\text{N}_2$ ) atmosphere using glove-box techniques. The test tubes were then sealed with airtight electrical tapes and the reaction mixtures were stirred under the irradiation of blue LEDs with a fan cooling down the temperature. Blue LEDs were purchased from Kessil Co., Ltd. (40 W max., product No. A160WE). Table fan was purchased from Galaxus Co., Ltd. (35 W max.). Flash column chromatography was performed using silica gel (Silicycle, ultra-pure grade). Preparative thin-layer chromatography (preparative TLC) was performed using preparative TLC plate (Merck Millipore, TLC Silica gel 60 F254, 20 x 20 cm, catalogue number: 1.05715.0001) in a developing tank. Notably, the TLC plates used for the purification of amine products were washed with hexanes/triethylamine solution (volume ratio ~40:1) prior to the use in order to minimize the product loss. The eluents for column chromatography and preparative TLC were presented as ratios of solvent volumes. Yields reported in the publication are of isolated materials unless otherwise noted.

## Synthesis of ligands

### Preparation of *N,N'*-diaryloxalamides

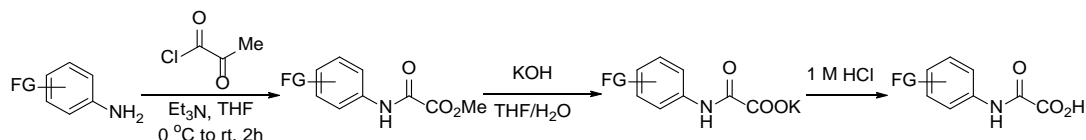


To a solution of the corresponding aniline (2.0 equiv.) in THF (0.3 M) was added Et<sub>3</sub>N (2.1 equiv.). Oxalyl chloride (1.0 equiv.) was then added to the solution slowly in an ice-water bath. After the resulting mixture was stirred at room temperature for 2 h, it was concentrated in vacuo to remove the solvent and water was added to the resulting residue to dissolve Et<sub>3</sub>N·HCl. Then the slurry was filtered and the solid on filter paper was washed with water and cold diethyl ether. These solids were dried in vacuo to afford the corresponding *N,N'*-diaryloxalamide. They were pure enough to be used without further purification.

**SI-L20** (product No. O0087 from TCI) is commercially available.

**SI-L21, SI-L22, SI-L23** were prepared according to the above procedure and spectral data match those previously reported.<sup>2,3</sup>

### Preparation of *N*-alkyl-*N'*-aryloxalamide



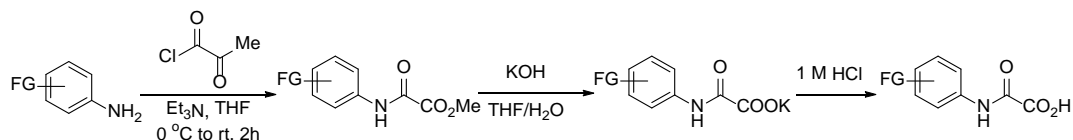
To a solution of the corresponding aniline in THF (0.2 M) was added Et<sub>3</sub>N (1.2 equiv.). Monomethyl oxalyl chloride (1.1 equiv.) was then added to the solution slowly in an ice-water bath. After the resulting mixture was stirred at room temperature for 2 h, the mixture was washed with the same volume of water and DCM. The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated. The crude product was purified with silica gel chromatography to afford the corresponding methyl *N*-aryloxamate.

To a magnetically stirred solution of the above monoamide in THF (1.0 M) was added BnNH<sub>2</sub> (1.2 equiv.) at room temperature. After the resulting mixture was stirred under 70 °C for 1 h, it was cooled to room temperature in the air and then to -18 °C in refrigerator. In most cases, the products would precipitate out as crystals. If no precipitate appeared, hexane was added to the

mixture until the products precipitated out. Then the mixture was filtered and the solids were collected and washed with small amount of cold diethyl ether to afford the corresponding *N*-benzyl-*N'*-aryloxalamide. They were pure enough to be used without further purification. (Note: BnNH<sub>2</sub> can be replaced by other aliphatic amines to afford the corresponding *N*-alkyl-*N'*-aryloxalamide.)

**SI-L24, SI-L25, SI-L26, SI-L27** were prepared according to the above procedure and spectral data match those previously reported.<sup>2-4</sup>

### Preparation of 2-oxo-2-(arylamino)acetic acids



To a solution of the corresponding aniline in THF (0.2 M) was added Et<sub>3</sub>N (1.2 equiv.). Methyl oxalyl chloride (1.1 equiv.) was then added to the solution slowly in an ice-water bath. After the resulting mixture was stirred at room temperature for 2 h, the mixture was washed with the same volume of water. The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated. The crude product was purified with silica gel chromatography to afford the corresponding methyl *N*-aryloxamate.

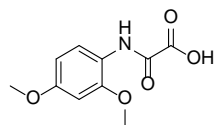
To a solution of the above methyl *N*-aryloxamate in THF (0.5 M) was added KOH (2.0 M aqueous solution, 1.0 equiv.) and the resulting mixture was stirred at room temperature until methyl *N*-aryloxamate was completely consumed as detected via TLC. Then it was concentrated *in vacuo* to remove THF and water to afford the corresponding potassium 2-oxo-2-(arylamino)acetate.

To a solution of the above 2-oxo-2-(arylamino)acetate in THF/H<sub>2</sub>O was added 1 M HCl (1.5 equiv.), the resulting mixture was stirred at room temperature for 10 min, after that the solvent was evaporated *in vacuo* to afford the corresponding 2-oxo-2-(arylamino)acetic acid.

**L2** (product No. 806412 from Aldrich) and **L3** (product No. 806455 from Aldrich) are commercially available.

**SI-L28, SI-L29** were prepared according to the above procedure and spectral data match those previously reported.<sup>2-6</sup>

### 2-((2,4-dimethoxyphenyl)amino)-2-oxoacetic acid (SI-L30)



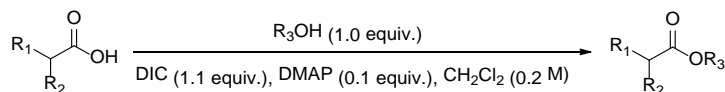
**<sup>1</sup>H NMR** (400 MHz, DMSO-*d*<sub>6</sub>): δ 9.51 (s, 1H), 7.87 (d, *J* = 8.8 Hz, 1H), 6.68 (d, *J* = 2.7 Hz, 1H), 6.55 (d, *J* = 8.9, 1H), 3.86 (s, 3H), 3.76 (s, 3H).

**<sup>13</sup>C NMR** (101 MHz, DMSO-*d*<sub>6</sub>): δ 162.0, 157.4, 155.5, 150.8, 121.7, 119.0, 104.4, 98.9, 56.0, 55.4.

**Physical State:** white solid

**HRMS** (ESI): calcd for C<sub>10</sub>H<sub>12</sub>NO<sub>5</sub> [M+H]<sup>+</sup> 226.0715; found 226.0715.

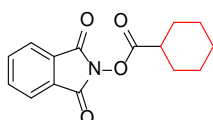
## General Procedure for the synthesis of NHPI esters (General Procedure A)



A round-bottom flask or culture tube was charged with (if solid) carboxylic acid (1.0 equiv), nucleophile (N-hydroxyphthalimide, 1.0 equiv) and DMAP (0.1 equiv). Dichloromethane was added (0.2 M), and the mixture was stirred vigorously. Carboxylic acid (1.0 equiv) was added via syringe (if liquid). DIC (1.1 equiv) was then added dropwise via syringe, and the mixture was allowed to stir until the carboxylic acid was consumed (determined by TLC). Typical reaction times were between 0.5 h and 12 h. The mixture was filtered over Celite and rinsed with additional  $\text{CH}_2\text{Cl}_2$ . The solvent was removed under reduced pressure, and purification by column chromatography afforded corresponding activated esters, which were used without further purification unless otherwise noted.

Most of the NHPI esters have been previously reported. Unless otherwise specified, NHPI esters were prepared following General Procedure A.

### 1,3-dioxoisindolin-2-yl cyclohexanecarboxylate

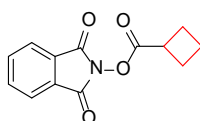


$^1\text{H NMR}$  (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.96 – 7.66 (m, 4H), 2.78 – 2.70 (m, 1H), 2.12 – 2.02 (m, 2H), 1.86 – 1.79 (m, 2H), 1.71 – 1.57 (m, 3H), 1.43 – 1.26 (m, 3H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  171.9, 162.2, 134.8, 129.2, 124.0, 40.6, 28.9, 25.6, 25.2.

Spectral data match those previously reported.<sup>7</sup>

### 1,3-dioxoisindolin-2-yl cyclobutanecarboxylate

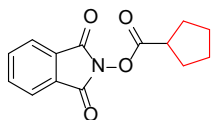


$^1\text{H NMR}$  (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.80 – 7.75 (m, 2H), 7.74 – 7.68 (m, 2H), 3.47 – 3.38 (m, 1H), 2.43 – 2.26 (m, 4H), 2.05 – 1.89 (m, 2H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  180.6, 171.5, 162.2, 134.8, 129.1, 124.0, 35.1, 25.5, 18.8.

Spectral data match those previously reported.<sup>7</sup>

### 1,3-dioxoisindolin-2-yl cyclopentanecarboxylate

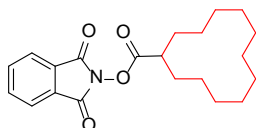


**<sup>1</sup>H NMR** (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 7.80 – 7.70 (m, 4H), 3.07 – 2.98 (m, 1H), 2.03 – 1.85 (m, 4H), 1.73 – 1.52 (m, 4H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 173.0, 162.2, 134.8, 129.1, 124.0, 40.8, 30.4, 26.1.

Spectral data match those previously reported.<sup>7</sup>

### 1,3-dioxoisindolin-2-yl cyclododecanecarboxylate

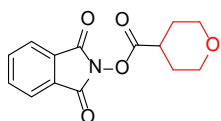


**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.89 – 7.75 (m, 4H), 2.90 – 2.86 (m, 1H), 1.83 – 1.36 (m, 22H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 172.9, 162.3, 134.8, 129.2, 124.0, 38.3, 26.8, 23.9, 23.8, 23.6, 23.5, 22.2.

Spectral data match those previously reported.<sup>7</sup>

### 1,3-dioxoisindolin-2-yl tetrahydro-2H-pyran-4-carboxylate

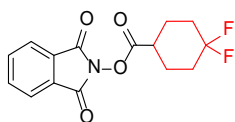


**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 8.00 – 7.74 (m, 4H), 4.02 (dt, *J* = 11.7, 3.8 Hz, 2H), 3.53 (ddd, *J* = 11.8, 9.9, 3.3 Hz, 2H), 3.03 – 2.96 (m, 1H), 2.09 – 1.93 (m, 4H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 170.7, 162.1, 134.9, 129.1, 124.1, 66.7, 37.8, 28.5.

Spectral data match those previously reported.<sup>7</sup>

### 1,3-dioxoisindolin-2-yl 4,4-difluorocyclohexane-1-carboxylate





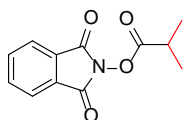
**<sup>1</sup>H NMR** (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 7.90 – 7.81 (m, 4H), 3.01 – 2.81 (m, 1H), 2.24 – 1.83 (m, 8H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 170.6, 162.0, 135.0, 129.0, 124.7, 124.2, 122.3, 119.9, 38.0, 32.4, 32.2, 31.9, 25.2, 25.1, 25.1.

**<sup>13</sup>C NMR** (101 MHz, Chloroform-d) δ 170.6, 162.0, 135.0, 129.0, 124.2, 122.3 (t, *J* = 241.3 Hz), 38.0, 32.2 (t, *J* = 24.8 Hz), 25.1 (t, *J* = 5.1 Hz).

Spectral data match those previously reported.<sup>7</sup>

### 1,3-dioxoisindolin-2-yl isobutyrate

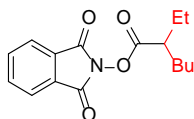


**<sup>1</sup>H NMR** (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 7.88 – 7.79 (m, 4H), 2.94 – 2.92 (m, 1H), 1.36 (s, 3H) 1.35 (s, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 173.1, 162.0, 134.7, 129.0, 123.9, 31.8, 18.8.

Spectral data match those previously reported.<sup>7</sup>

### 1,3-dioxoisindolin-2-yl 2-ethylhexanoate

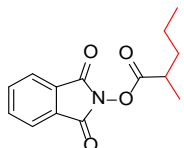


**<sup>1</sup>H NMR** (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 7.77 – 7.73 (m, 2H), 7.71 – 7.67 (m, 2H), 2.59 – 2.51 (m, 1H), 1.70 – 1.48 (m, 4H), 1.39 – 1.20 (m, 4H), 0.98 – 0.77 (m, 6H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 172.5, 162.2, 134.8, 129.1, 124.0, 45.0, 31.8, 29.3, 25.7, 22.6, 14.0, 11.7.

Spectral data match those previously reported.<sup>7</sup>

### 1,3-dioxoisindolin-2-yl 2-methylpentanoate



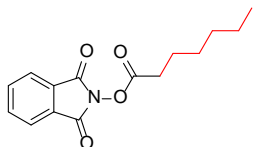
**<sup>1</sup>H NMR** (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 7.90 – 7.77 (m, 4H), 2.92 – 2.76 (m, 1H), 1.87 – 1.75 (m, 1H), 1.64 – 1.45 (m, 3H), 1.33 (d, *J* = 7.0 Hz, 3H), 0.97 (t, *J* = 7.3 Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  173.3, 162.4, 135.2, 129.4, 124.2, 37.3, 36.2, 20.5, 17.2, 14.0.

**Physical State:** colorless oil.

**HRMS** (ESI): calcd for  $\text{C}_{14}\text{H}_{15}\text{NO}_4\text{Na}$   $[\text{M}+\text{Na}]^+$  284.0899; found 284.0903.

### 1,3-dioxoisindolin-2-yl heptanoate



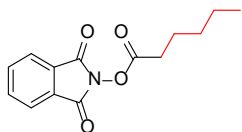
$^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.81 – 7.78 (m, 2H), 7.75 – 7.72 (m, 2H), 2.58 (t,  $J$  = 8.0 Hz, 2H), 1.72 – 1.64 (m, 2H), 1.38 – 1.23 (m, 6H), 0.84 – 0.81 (m, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  135.2, 129.3, 124.2, 31.7, 31.3, 28.9, 25.1, 22.8, 14.2.

**Physical State:** white solid.

**HRMS** (ESI): calcd for  $\text{C}_{15}\text{H}_{17}\text{NO}_4\text{Na}$   $[\text{M}+\text{Na}]^+$  298.1055; found 298.1059.

### 1,3-dioxoisindolin-2-yl hexanoate



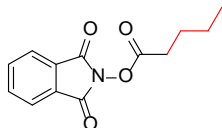
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.89 – 7.85 (m, 2H), 7.80 – 7.76 (m, 2H), 2.65 (t,  $J$  = 7.5 Hz, 2H), 1.79 (p,  $J$  = 7.5 Hz, 2H), 1.47 – 1.31 (m, 4H), 0.92 (t,  $J$  = 7.1 Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  169.8, 162.1, 134.8, 129.1, 124.1, 31.1, 31.1, 24.5, 22.3, 14.0.

**Physical State:** colorless oil.

**HRMS** (ESI): calcd for  $\text{C}_{14}\text{H}_{15}\text{NO}_4\text{Na}$   $[\text{M}+\text{Na}]^+$  284.0899; found 284.0905.

### 1,3-dioxoisindolin-2-yl pentanoate

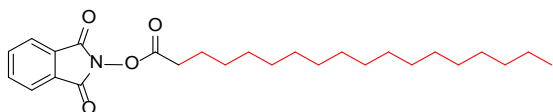


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.89 – 7.85 (m, 2H), 7.79 – 7.75 (m, 2H), 2.53 (d,  $J$  = 7.2 Hz, 2H), 2.30-2.20 (m, 1H), 1.09 (d,  $J$  = 6.7 Hz, 6H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  168.9, 162.1, 134.8, 129.0, 124.0, 39.9, 26.1, 22.3.

Spectral data match those previously reported.<sup>8</sup>

### 1,3-dioxoisindolin-2-yl stearate

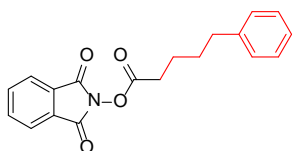


**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.91 – 7.87 (m, 2H), 7.81 – 7.77 (m, 2H), 2.66 (t, *J* = 7.4 Hz, 2H), 1.82 – 1.74 (m, 2H), 1.46 – 1.26 (s, 28H), 0.88 (t, *J* = 6.7 Hz, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 169.8, 162.2, 134.9, 129.1, 124.1, 32.1, 31.2, 29.9, 29.8, 29.8, 29.7, 29.5, 29.3, 29.0, 24.8, 22.9, 14.3.

Spectral data match those previously reported.<sup>9</sup>

### 1,3-dioxoisindolin-2-yl 5-phenylpentanoate

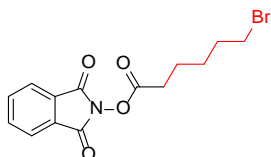


**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.82 – 7.79 (m, 2H), 7.73 – 7.70 (m, 2H), 7.23 – 7.10 (m, 5H), 2.63 – 2.59 (m, 4H), 1.78 – 1.69 (m, 4H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 169.6, 162.1, 141.9, 134.9, 129.1, 128.5, 128.5, 126.0, 124.1, 35.5, 31.0, 30.6, 24.4.

Spectral data match those previously reported.<sup>7</sup>

### 1,3-dioxoisindolin-2-yl 6-bromohexanoate

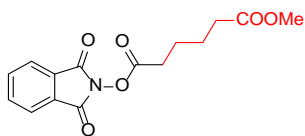


**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.91 – 7.77 (m, 4H), 3.43 (t, *J* = 6.7 Hz, 2H), 2.69 (t, *J* = 7.4 Hz, 2H), 2.02 – 1.74 (m, 4H), 1.67 – 1.55 (m, 2H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 169.5, 162.1, 134.9, 129.1, 124.1, 33.3, 32.4, 31.0, 27.5, 24.0.

Spectral data match those previously reported.<sup>10</sup>

### 1,3-dioxoisindolin-2-yl methyl adipate

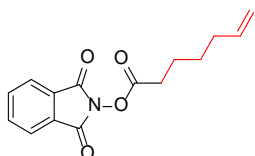


**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.93 – 7.88 (m, 2H), 7.84 – 7.79 (m, 2H), 3.71 (s, 3H), 2.72 (t,  $J$  = 7.1 Hz, 2H), 2.41 (t,  $J$  = 7.0 Hz, 2H), 1.88 – 1.77 (m, 4H).

**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  173.7, 169.4, 162.1, 134.9, 129.1, 124.1, 51.8, 33.6, 30.8, 24.2, 24.2.

Spectral data match those previously reported.<sup>11</sup>

### 1,3-dioxoisindolin-2-yl hept-6-enoate



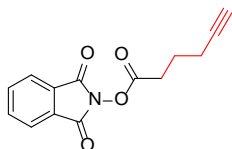
**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.89 – 7.84 (m, 2H), 7.79 – 7.74 (m, 2H), 5.85 – 5.75 (m, 1H), 5.06 – 4.95 (m, 2H), 2.66 (t,  $J$  = 7.4 Hz, 2H), 2.11 (q,  $J$  = 7.1 Hz, 2H), 1.79 (p,  $J$  = 7.4 Hz, 2H), 1.54 (p,  $J$  = 7.5 Hz, 2H).

**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  169.6, 162.1, 138.1, 134.8, 129.0, 124.0, 115.1, 33.2, 30.9, 28.0, 24.2.

**Physical State:** white solid

**HRMS** (ESI): calcd for  $\text{C}_{15}\text{H}_{15}\text{NO}_4\text{Na}$  [ $\text{M}+\text{Na}$ ]<sup>+</sup> 296.0893; found 296.0900.

### 1,3-dioxoisindolin-2-yl hex-5-ynoate

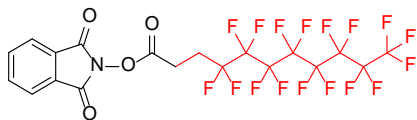


**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.91 – 7.87 (m, 2H), 7.82 – 7.77 (m, 2H), 2.84 (t,  $J$  = 7.4 Hz, 2H), 2.38 (td,  $J$  = 6.9, 2.7 Hz, 2H), 2.07 – 1.95 (m, 3H).

**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  169.3, 162.1, 134.9, 129.1, 124.1, 82.6, 70.0, 29.9, 23.6, 17.8.

Spectral data match those previously reported.<sup>12</sup>

**1,3-dioxoisindolin-2-yl 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecanoate**



**<sup>1</sup>H NMR** (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.30 – 7.23 (m, 2H), 6.80 – 6.71 (m, 2H), 2.30 (t, *J* = 7.8 Hz, 2H), 1.93 (tt, *J* = 17.9, 7.8 Hz, 2H).

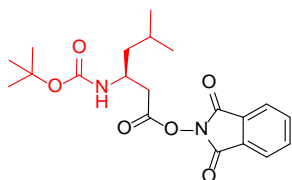
**<sup>19</sup>F NMR** (376 MHz, C<sub>6</sub>D<sub>6</sub>): δ -81.06 (t, *J* = 9.9 Hz), -114.62 (t, *J* = 14.5 Hz), -121.71, -121.92, -122.77, -123.38, -126.02 – -126.50 (m).

**<sup>13</sup>C NMR** (101 MHz, C<sub>6</sub>D<sub>6</sub>) δ 168.1, 161.8, 134.3, 129.1, 123.7, 26.0 (t, *J* = 22.1 Hz), 22.7 (t, *J* = 4.2 Hz).

**Physical State:** white solid.

**HRMS** (ESI): calcd for C<sub>19</sub>H<sub>8</sub>F<sub>17</sub>NO<sub>4</sub>Na [M+Na]<sup>+</sup> 660.0079; found 660.0095.

**1,3-dioxoisindolin-2-yl (S)-3-((tert-butoxycarbonyl)amino)-5-methylhexanoate**



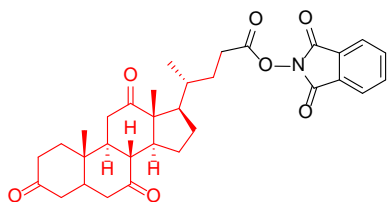
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.89 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.79 (dd, *J* = 5.5, 3.1 Hz, 2H), 5.02 – 4.71 (m, 1H), 4.18 – 4.01 (m, 1H), 3.00 – 2.80 (m, 2H), 1.78 – 1.52 (m, 3H), 1.44 (s, 9H), 0.95 (dd, *J* = 6.6, 2.5 Hz, 6H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 167.7, 162.0, 155.4, 135.0, 129.0, 124.2, 79.7, 45.9, 42.8, 36.6, 28.5, 25.1, 23.0, 22.2.

**Physical State:** colorless amorphous solid.

**HRMS** (ESI): calcd for C<sub>20</sub>H<sub>26</sub>N<sub>2</sub>O<sub>6</sub>Na [M+Na]<sup>+</sup> 413.1689; found 413.1683.

**1,3-dioxoisindolin-2-yl (4R)-4-((8R,9S,10S,13R,14S,17R)-10,13-dimethyl-3,7,12-trioxohexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoate**

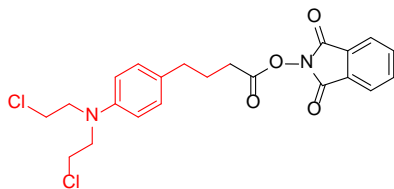


**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.89 – 7.86 (m, 2H), 7.82 – 7.76 (m, 2H), 4.11 (q, *J* = 7.2 Hz, 2H), 2.96 – 0.87 (m, 31H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 171.2, 169.9, 162.0, 134.8, 129.0, 124.0, 60.4, 57.0, 51.9, 49.0, 46.9, 45.7, 45.6, 45.0, 42.8, 42.2, 38.7, 36.5, 36.1, 35.3, 31.6, 30.4, 28.5, 27.7, 25.2, 23.5, 22.7, 21.9, 21.1, 18.6, 14.2, 14.1, 11.9.

Spectral data match those previously reported.<sup>11</sup>

### 1,3-dioxoisindolin-2-yl 4-(4-(bis(2-chloroethyl)amino)phenyl)butanoate

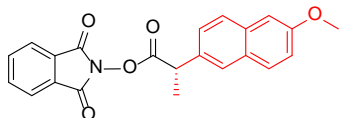


**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.89 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.82 – 7.76 (m, 2H), 7.17 – 7.08 (m, 2H), 6.72 – 6.64 (m, 2H), 3.77 – 3.60 (m, 8H), 2.67 (dt, *J* = 10.3, 7.4 Hz, 4H), 2.07 (p, *J* = 7.4 Hz, 2H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 169.6, 162.1, 134.7 (d, *J* = 42.6 Hz), 130.1 (d, *J* = 8.9 Hz), 129.1, 123.9 (d, *J* = 49.6 Hz), 113.6, 54.4, 40.1, 33.9 (d, *J* = 42.2 Hz), 33.0, 30.3, 26.6.

Spectral data match those previously reported.<sup>13</sup>

### 1,3-dioxoisindolin-2-yl (S)-2-(6-methoxynaphthalen-2-yl)propanoate

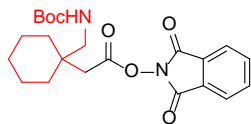


**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.86 (dt, *J* = 8.0, 4.0 Hz, 2H), 7.77 (tt, *J* = 6.6, 3.0 Hz, 5H), 7.48 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.19 – 7.12 (m, 2H), 4.26 (q, *J* = 7.2 Hz, 1H), 3.92 (s, 3H), 1.75 (d, *J* = 7.2 Hz, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 171.0, 162.0, 158.0, 134.8, 134.1, 133.6, 129.6, 129.1, 129.0, 127.7, 126.5, 126.0, 124.0, 119.3, 105.8, 55.5, 43.1, 19.2.

Spectral data match those previously reported.<sup>13</sup>

### 1,3-dioxoisindolin-2-yl 2-(1-(((*tert*-butoxycarbonyl)amino)methyl)cyclohexyl)acetate

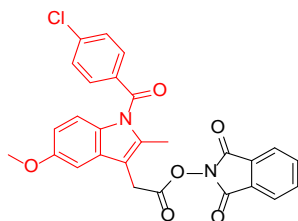


$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.88 (dt,  $J = 5.7, 3.6$  Hz, 2H), 7.79 (dd,  $J = 5.5, 3.1$  Hz, 2H), 4.87 (s, 1H), 3.31 (d,  $J = 13.4$  Hz, 1H), 3.10 (dt,  $J = 14.4, 7.4$  Hz, 1H), 2.64 (d,  $J = 6.4$  Hz, 2H), 2.35 – 2.19 (m, 1H), 1.79 – 1.68 (m, 1H), 1.43 (s, 9H), 1.29 (t,  $J = 6.9$  Hz, 2H), 0.99 – 0.79 (m, 6H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  168.9, 162.1, 156.3, 134.7, 129.1, 124.1, 79.5, 41.2, 34.3, 28.5, 25.3, 22.8.

Spectral data match those previously reported.<sup>13</sup>

### 1,3-dioxoisindolin-2-yl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate

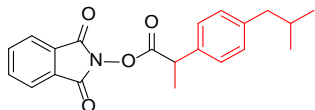


$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.91 – 7.86 (m, 2H), 7.79 (dd,  $J = 5.5, 3.1$  Hz, 2H), 7.71 – 7.65 (m, 2H), 7.50 – 7.46 (m, 2H), 7.03 (d,  $J = 2.5$  Hz, 1H), 6.96 – 6.90 (m, 1H), 6.71 (dd,  $J = 9.0, 2.5$  Hz, 1H), 4.04 (s, 2H), 3.89 (s, 3H), 2.42 (s, 3H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  168.5, 167.2, 161.9, 156.4, 139.6, 136.6, 135.0, 135.0, 134.6, 133.8, 131.7, 131.5, 130.9, 130.1, 129.5, 129.3, 129.0, 124.2, 123.7, 115.2, 112.6, 110.3, 100.8, 55.9, 29.9, 27.3, 13.6.

Spectral data match those previously reported.<sup>13</sup>

### 1,3-dioxoisindolin-2-yl 2-(4-isobutylphenyl)propanoate

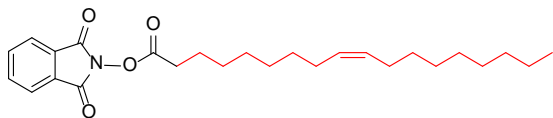


$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.87 – 7.84 (m, 2H), 7.78 – 7.74 (m, 2H), 7.35 – 7.28 (m, 2H), 7.18 – 7.16 (m, 2H), 4.10 (q,  $J = 7.2$  Hz, 1H), 2.48 (d,  $J = 7.1$  Hz, 2H), 1.87 (hept,  $J = 6.7$  Hz, 1H), 1.67 (d,  $J = 7.1$  Hz, 3H), 0.91 (d,  $J = 6.6$  Hz, 6H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  171.1, 141.4, 135.7, 134.9, 129.8, 129.6, 129.1, 127.4, 124.1, 45.2, 42.7, 30.3, 22.6, 19.2.

Spectral data match those previously reported.<sup>13</sup>

### 1,3-dioxoisindolin-2-yl oleate

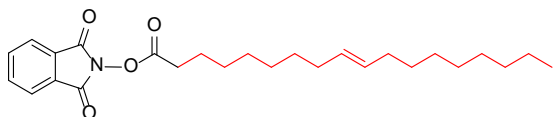


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.05 – 7.60 (m, 4H), 5.41 – 5.28 (m, 2H), 2.66 (t,  $J$  = 7.5 Hz, 2H), 2.11 – 1.95 (m, 4H), 1.85 – 1.72 (m, 2H), 1.47 – 1.24 (m, 20H), 0.87 (t,  $J$  = 6.6 Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  179.3, 169.8, 162.2, 134.7 (d,  $J$  = 30.1 Hz), 130.0 (d,  $J$  = 31.8 Hz), 129.1, 123.9 (d,  $J$  = 39.5 Hz), 34.0, 32.1, 31.1, 29.9, 29.8, 29.8, 29.7, 29.5, 29.3, 29.2, 29.2, 29.0, 27.4, 27.3, 24.8, 22.8, 14.3.

Spectral data match those previously reported.<sup>9</sup>

### 1,3-dioxoisindolin-2-yl (*E*)-octadec-9-enoate



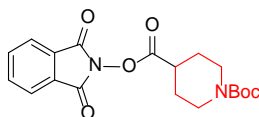
$^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  8.06 – 7.76 (m, 4H), 5.53 – 5.40 (m, 2H), 2.80-2.64 (m, 2H), 2.08-1.96 (m, 4H), 1.86-1.76 (m, 2H), 1.53-1.26 (m, 20H), 0.98-0.87 (m, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  170.2, 162.4, 135.2, 130.9, 130.6, 129.3, 124.2, 33.0, 33.0, 32.3, 31.3, 30.1, 30.0, 29.9, 29.7, 29.6, 29.4, 29.3, 29.2, 25.1, 23.1, 14.3.

**Physical State:** white solid.

**HRMS** (ESI): calcd for  $\text{C}_{26}\text{H}_{37}\text{NO}_4\text{Na}$  [ $\text{M}+\text{Na}$ ]<sup>+</sup> 450.2620; found 450.2618.

### 1-(*tert*-butyl) 4-(1,3-dioxoisindolin-2-yl) piperidine-1,4-dicarboxylate

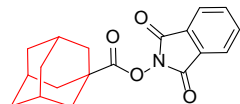


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.88 (dd,  $J$  = 5.5, 3.1 Hz, 2H), 7.79 (dd,  $J$  = 5.5, 3.1 Hz, 2H), 4.03 (d,  $J$  = 13.4 Hz, 2H), 3.00 (t,  $J$  = 11.4 Hz, 2H), 2.90 (tt,  $J$  = 10.4, 4.0 Hz, 1H), 2.06 (dt,  $J$  = 12.7, 3.9 Hz, 2H), 1.85 (dtd,  $J$  = 14.3, 10.5, 4.1 Hz, 2H).



**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  170.8, 162.0, 154.7, 134.9, 129.1, 124.1, 80.0, 38.7, 28.6.  
Spectral data match those previously reported.<sup>7</sup>

**1,3-dioxoisindolin-2-adamantane-1-carboxylate**



**$^1\text{H}$  NMR** (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.94 – 7.71 (m, 4H), 2.20 – 1.97 (m, 9H), 1.80 (d,  $J = 2.9$  Hz, 6H).

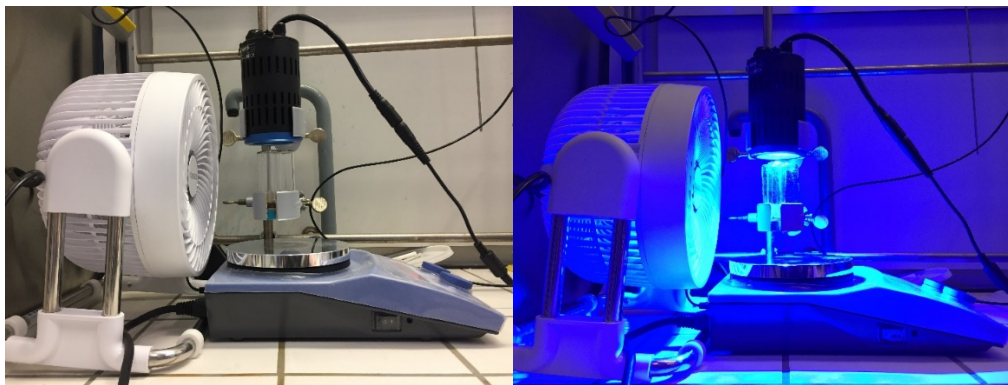
**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  170.8, 162.0, 154.7, 134.9, 129.1, 124.1, 80.0, 38.7, 28.6.  
Spectral data match those previously reported.<sup>11</sup>

### **General procedure for visible-light-mediated decarboxylative amination of aniline with secondary or tertiary NHPI esters (General Procedure B)**

An oven-dried 15 mL re-sealable screw-cap test tube equipped with a Teflon-coated magnetic stir bar was sequentially charged with NHPI ester, Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (1 mol%), CuBr (20 mol%), **L3** (7.5 mol%), MeCN (0.1 M), aniline (2 equiv), Et<sub>3</sub>N (5 equiv) in the glove box. The vial was sealed with a screw cap and removed from the glove box. Then the vial was placed 3 cm away from one blue LED, and irradiated under fan cooling (maintain the temperature at room temperature) for 12 h. After the reaction, the resulting dark brown reaction mixture was acidified with saturated NH<sub>4</sub>Cl solution (~1 mL) and then neutralized with saturated NaHCO<sub>3</sub> solution (~1.5 mL). The crude product in the aqueous fraction was extracted with EtOAc (~10 mL). The aqueous fraction was further washed with EtOAc (3 x ~5 mL). The combined organic fractions were concentrated *in vacuo* with the aid of a rotary evaporator. The crude product residue was purified by preparative TLC (pretreated with 3% triethylamine in hexanes in order to minimize the product loss) using a solvent mixture (EtOAc, hexanes) as an eluent to afford the purified product.

### **General procedure for visible-light-mediated decarboxylative amination of aniline with primary NHPI esters (General Procedure C)**

An oven-dried 15 mL re-sealable screw-cap test tube equipped with a Teflon-coated magnetic stir bar was sequentially charged with aniline, NHPI ester (2 equiv), Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (1 mol%), CuCl (20 mol%), MeCN (0.1 M), Et<sub>3</sub>N (3 equiv) in the glove box. The vial was sealed with a screw cap and removed from the glove box. Then the vial was placed 3 cm away from one blue LED, and irradiated under fan cooling (maintain the temperature at room temperature) for 12 h. After the reaction, the resulting dark brown reaction mixture was acidified with saturated NH<sub>4</sub>Cl solution (~1 mL) and then neutralized with saturated NaHCO<sub>3</sub> solution (~1.5 mL). The crude product in the aqueous fraction was extracted with EtOAc (~10 mL). The aqueous fraction was further washed with EtOAc (3 x ~5 mL). The combined organic fractions were concentrated *in vacuo* with the aid of a rotary evaporator. The crude product residue was purified by preparative TLC (pretreated with 3% triethylamine in hexanes in order to minimize the product loss) using a solvent mixture (EtOAc, hexanes) as an eluent to afford the purified product.

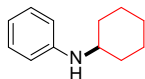


## General procedure for visible-light-mediated decarboxylative amination (General Procedure D: Gram-scale reaction)

An oven-dried 100 mL flask equipped with a Teflon-coated magnetic stir bar was sequentially charged with aniline (12.2 mmol, 1.2 mL), 1,3-dioxoisindolin-2-yl heptanoate (1.5 equiv, 5.1 g), Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (1 mol%, 105 mg), CuCl (20 mol%, 242 mg), MeCN (61 mL), Et<sub>3</sub>N (3 equiv, 5.1 mL) in the glove box. The flask was sealed and removed from the glove box. Then the flask was placed 10 cm away from two blue LED, and irradiated under fan cooling (maintain the temperature at room temperature) for 12 h. After the reaction, the resulting dark brown reaction mixture was acidified with saturated NH<sub>4</sub>Cl solution and then neutralized with saturated NaHCO<sub>3</sub> solution. The crude product in the aqueous fraction was extracted with EtOAc. The aqueous fraction was further washed with EtOAc. The combined organic fractions were concentrated *in vacuo* with the aid of a rotary evaporator. The crude product residue was purified by column chromatography using a solvent mixture (hexanes to 20:1 hexanes:EtOAc) as an eluent to afford 1.1 g (51%) of the purified product **5a**.



### ***N*-cyclohexylaniline (3a)**



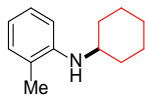
Following the General Procedure B with the corresponding NHPI ester (0.2 mmol) and aniline (0.4 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (40:1) as an eluent to afford 33 mg (94%) of the title compound **3a**.

**<sup>1</sup>H NMR** (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 7.11 (dd, *J* = 8.5, 7.3 Hz, 2H), 6.63 – 6.52 (m, 3H), 3.58 (br s, 1H), 3.28 – 3.21 (m, 1H), 2.06-2.00 (m, 2H), 1.78 – 1.62 (m, 3H), 1.41 – 1.11 (m, 5H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 147.5, 129.4, 117.0, 113.3, 51.8, 33.6, 26.1, 25.2.

Spectral data match those previously reported.<sup>14</sup>

### ***N*-cyclohexyl-2-methylaniline (3b)**



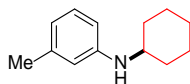
Following the General Procedure B with the corresponding NHPI ester (0.2 mmol) and *o*-toluidine (0.4 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (30:1) as an eluent to afford 30 mg (78%) of the title compound **3b**.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.11 (t, *J* = 7.8 Hz, 1H), 7.05 (d, *J* = 7.3 Hz, 1H), 6.68 – 6.58 (m, 2H), 3.37 – 3.27 (m, 1H), 2.13 (s, 3H), 2.11 – 2.04 (m, 2H), 1.82 – 1.63 (m, 3H), 1.47 – 1.15 (m, 5H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 145.4, 130.4, 127.2, 121.8, 116.4, 110.3, 51.7, 33.8, 26.2, 25.2, 17.7.

Spectral data match those previously reported.<sup>14</sup>

### ***N*-cyclohexyl-3-methylaniline (3c)**



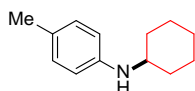
Following the General Procedure B with the corresponding NHPI ester (0.2 mmol) and *m*-toluidine (0.4 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (30:1) as an eluent to afford 26 mg (69%) of the title compound **3c**.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.06 (td, *J* = 7.3, 2.2 Hz, 1H), 6.50 (d, *J* = 7.5 Hz, 1H), 6.42 (d, *J* = 6.5 Hz, 2H), 3.55 (br s, 1H), 3.26 (tt, *J* = 10.2, 3.8 Hz, 1H), 2.28 (s, 3H), 2.11 – 2.00 (m, 2H), 1.82 – 1.61 (m, 3H), 1.44 – 1.32 (m, 2H), 1.28 – 1.11 (m, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 147.3, 139.2, 129.3, 118.2, 114.3, 110.6, 52.0, 33.6, 26.1, 25.2, 21.8.

Spectral data match those previously reported.<sup>14</sup>

### *N*-cyclohexyl-4-methylaniline (**3d**)



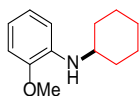
Following the General Procedure B with the corresponding NHPI ester (0.2 mmol) and *p*-toluidine (0.4 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (30:1) as an eluent to afford 21 mg (56%) of the title compound **3d**.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 6.98 (d, *J* = 8.1 Hz, 2H), 6.57 – 6.48 (m, 2H), 3.23 (tt, *J* = 10.1, 3.7 Hz, 1H), 2.24 (s, 3H), 2.06 (dd, *J* = 12.9, 3.9 Hz, 2H), 1.76 (dt, *J* = 13.2, 3.9 Hz, 2H), 1.65 (dt, *J* = 12.6, 3.8 Hz, 1H), 1.42 – 1.11 (m, 5H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 145.2, 129.9, 126.2, 113.6, 52.2, 33.7, 29.8, 26.1, 25.2, 20.5.

Spectral data match those previously reported.<sup>14</sup>

### *N*-cyclohexyl-2-methoxyaniline (**3e**)



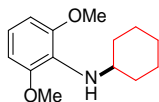
Following the General Procedure B with the corresponding NHPI ester (0.2 mmol) and *o*-anisidine (0.4 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (30:1) as an eluent to afford 39 mg (95%) of the title compound **3e**.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 6.85 (t, *J* = 7.7 Hz, 1H), 6.77 (d, *J* = 8.1 Hz, 1H), 6.69 – 6.58 (m, 2H), 4.14 (br s, 1H), 3.84 (s, 3H), 3.29 – 3.22 (m, 1H), 2.11 – 2.05 (m, 2H), 1.80 – 1.63 (m, 3H), 1.43 – 1.16 (m, 5H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 150.8, 147.4, 121.5, 120.9, 116.8, 112.5, 56.1, 32.2, 25.8, 24.3.

Spectral data match those previously reported.<sup>14</sup>

### *N*-cyclohexyl-2,6-dimethoxyaniline (**3f**)



Following the General Procedure B with the corresponding NHPI ester (0.2 mmol) and 2,6-dimethoxyaniline (0.4 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (25:1) as an eluent to afford 42 mg (88%) of the title compound **3f**.

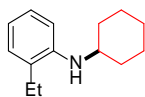
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 6.80 (t, *J* = 8.2 Hz, 1H), 6.53 (d, *J* = 8.3 Hz, 2H), 3.83 (s, 6H), 3.50 – 3.39 (m, 1H), 3.19 (br s, 1H), 1.91 (dd, *J* = 12.4, 4.0 Hz, 2H), 1.70 (dt, *J* = 12.9, 3.7 Hz, 2H), 1.63 – 1.54 (m, 1H), 1.34 – 1.01 (m, 5H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 151.5, 126.5, 119.8, 104.8, 56.1, 54.1, 34.4, 26.3, 25.3.

**Physical State:** reddish brown oil.

**HRMS** (ESI): calcd for C<sub>14</sub>H<sub>22</sub>NO<sub>2</sub> [M+H]<sup>+</sup> 236.1651; found 236.1656.

### *N*-cyclohexyl-2-ethylaniline (**3g**)



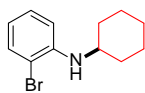
Following the General Procedure B with the corresponding NHPI ester (0.2 mmol) and 2-ethylaniline (0.4 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (30:1) as an eluent to afford 33 mg (80%) of the title compound **3g**.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.10 (t, *J* = 7.7 Hz, 1H), 7.07 (d, *J* = 7.4 Hz, 1H), 6.66 (t, *J* = 7.0 Hz, 2H), 3.39 – 3.28 (m, 1H), 2.47 (q, *J* = 7.5 Hz, 2H), 2.21 – 1.99 (m, 2H), 1.83 – 1.62 (m, 3H), 1.39 – 1.12 (m, 8H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 144.8, 128.2, 127.4, 127.0, 116.6, 110.7, 51.7, 33.7, 26.2, 25.2, 24.0, 13.0.

Spectral data match those previously reported.<sup>14</sup>

### 2-bromo-*N*-cyclohexylaniline (**3h**)



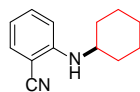
Following the General Procedure B with the corresponding NHPI ester (0.2 mmol) and 2-bromoaniline (0.4 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (30:1) as an eluent to afford 33 mg (65%) of the title compound **3h**.

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.40 (dd,  $J = 7.9, 1.6$  Hz, 1H), 7.14 (t,  $J = 7.8$  Hz, 1H), 6.70 – 6.60 (m, 1H), 6.51 (td,  $J = 7.7, 1.5$  Hz, 1H), 4.24 (br s, 1H), 3.33 – 3.28 (m, 1H), 2.07 – 2.02 (m, 2H), 1.81 – 1.75 (m, 2H), 1.68 – 1.61 (m, 1H), 1.48 – 1.18 (m, 5H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  144.3, 132.7, 128.5, 117.2, 111.9, 109.9, 51.7, 33.3, 26.0, 25.0.

Spectral data match those previously reported.<sup>15</sup>

### 2-(cyclohexylamino)benzonitrile (**3i**)



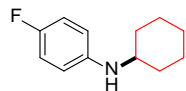
Following the General Procedure B with the corresponding NHPI ester (0.2 mmol) and 2-aminobenzonitrile (0.4 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (25:1) as an eluent to afford 16 mg (40%) of the title compound **3i**.

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.42 – 7.31 (m, 2H), 6.71 – 6.54 (m, 2H), 4.45 (br s, 1H), 3.35 (tt,  $J = 9.8, 3.7$  Hz, 1H), 2.10 – 2.00 (m, 2H), 1.85 – 1.75 (m, 2H), 1.69 – 1.59 (m, 1H), 1.46 – 1.20 (m, 5H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  149.4, 134.3, 133.1, 118.2, 116.3, 111.4, 95.8, 51.7, 33.1, 25.8, 24.9.

Spectral data match those previously reported.<sup>16</sup>

### N-cyclohexyl-4-fluoroaniline (**3j**)



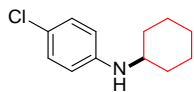
Following the General Procedure B with the corresponding NHPI ester (0.2 mmol) and 4-fluoroaniline (0.4 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (30:1) as an eluent to afford 35 mg (90%) of the title compound **3j**.

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.87 (t,  $J = 8.7$  Hz, 2H), 6.56 – 6.47 (m, 2H), 3.18 (tt,  $J = 10.2, 3.7$  Hz, 1H), 2.10 – 1.98 (m, 2H), 1.76 (d,  $J = 10.4$  Hz, 2H), 1.65 (d,  $J = 12.5$  Hz, 1H), 1.42 – 1.31 (m, 2H), 1.26 – 1.07 (m, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  156.8, 154.5, 143.9 (d,  $J = 1.8$  Hz), 115.7 (d,  $J = 22.2$  Hz), 114.2 (d,  $J = 7.2$  Hz), 52.6, 33.6, 26.1, 25.2.

Spectral data match those previously reported.<sup>17</sup>

#### 4-chloro-*N*-cyclohexylaniline (**3k**)



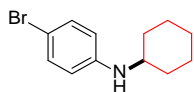
Following the General Procedure B with the corresponding NHPI ester (0.2 mmol) and 4-chloroaniline (0.4 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (30:1) as an eluent to afford 36 mg (85%) of the title compound **3k**.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.14 – 7.03 (m, 2H), 6.56 – 6.44 (m, 2H), 3.53 (br s, 1H), 3.20 (tt,  $J = 10.1, 3.8$  Hz, 1H), 2.10 – 1.98 (m, 2H), 1.80 – 1.62 (m, 3H), 1.41 – 1.08 (m, 5H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  146.1, 129.2, 121.4, 114.3, 52.0, 33.4, 26.0, 25.1.

Spectral data match those previously reported.<sup>18</sup>

#### 4-bromo-*N*-cyclohexylaniline (**3l**)



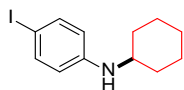
Following the General Procedure B with the corresponding NHPI ester (0.2 mmol) and 4-bromoaniline (0.4 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (30:1) as an eluent to afford 34 mg (66%) of the title compound **3l**.

$^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.21 – 7.18 (m, 2H), 6.48 – 6.44 (m, 2H), 3.80 (br s, 1H), 3.22 – 3.17 (m, 1H), 2.04 – 1.09 (m, 10H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  146.3, 132.1, 115.0, 108.6, 52.1, 42.5, 33.3, 26.0, 25.1, 23.6.

Spectral data match those previously reported.<sup>19</sup>

#### 4-iodo-*N*-cyclohexylaniline (**3m**)





Following the General Procedure B with the corresponding NHPI ester (0.2 mmol) and 4-iodoaniline (0.4 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (30:1) as an eluent to afford 36 mg (60%) of the title compound **3m**.

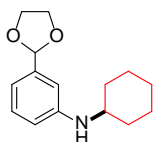
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.38 (d, *J* = 8.7 Hz, 2H), 6.36 (d, *J* = 8.7 Hz, 2H), 3.59 (br s, 1H), 3.23-3.17 (m, 1H), 2.02 (dd, *J* = 12.7, 3.1 Hz, 2H), 1.80-1.72 (m, 3H), 1.43 – 1.06 (m, 5H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 147.1, 137.9, 115.5, 77.1, 51.7, 33.4, 26.0, 25.1.

**Physical State:** dark brown solid.

**HRMS** (ESI): calcd for C<sub>12</sub>H<sub>17</sub>IN [M+H]<sup>+</sup> 302.0406; found 302.0407.

### ***N*-cyclohexyl-3-(1,3-dioxolan-2-yl)aniline (3n)**



Following the General Procedure B with the corresponding NHPI ester (0.2 mmol) and 3-(1,3-dioxolan-2-yl)aniline (0.4 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (20:1) as an eluent to afford 38 mg (76%) of the title compound **3n**.

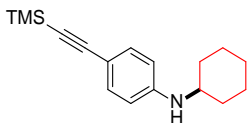
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.16 (t, *J* = 7.8 Hz, 1H), 6.77 (d, *J* = 7.5 Hz, 1H), 6.69 (t, *J* = 2.0 Hz, 1H), 6.58 (dd, *J* = 8.2, 2.4 Hz, 1H), 5.75 (s, 1H), 4.20 – 3.94 (m, 4H), 3.59 (s, 1H), 3.28 (tt, *J* = 10.1, 3.7 Hz, 1H), 2.05 (dd, *J* = 13.1, 3.9 Hz, 2H), 1.83 – 1.70 (m, 2H), 1.70 – 1.59 (m, 1H), 1.44 – 1.31 (m, 2H), 1.27 – 1.07 (m, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 147.6, 139.1, 129.4, 114.8, 113.8, 111.0, 104.0, 65.3, 51.7, 33.6, 26.0, 25.1.

**Physical State:** light yellow oil.

**HRMS** (ESI): calcd for C<sub>15</sub>H<sub>22</sub>NO<sub>2</sub> [M+H]<sup>+</sup> 248.1651; found 248.1651.

### ***N*-cyclohexyl-4-((trimethylsilyl)ethynyl)aniline (3o)**



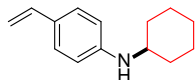
Following the General Procedure B with the corresponding NHPI ester (0.2 mmol) and methyl 4-((trimethylsilyl)ethynyl)aniline (0.4 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (20:1) as an eluent to afford 17 mg (32%) of the title compound **3o**.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.28 (d, *J* = 3.7 Hz, 1H), 6.47 (d, *J* = 8.2 Hz, 2H), 3.78 (br s, 1H), 3.32 – 3.20 (m, 1H), 2.08 – 2.00 (m, 2H), 1.81 – 1.62 (m, 3H), 1.45 – 1.11 (m, 5H), 0.23 (s, 9H).  
**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 147.6, 133.5, 112.6, 110.6, 106.7, 91.0, 51.6, 33.4, 26.0, 25.1.

**Physical State:** white solid.

**HRMS** (ESI): calcd for C<sub>17</sub>H<sub>26</sub>NSi [M+H]<sup>+</sup> 272.1834; found 272.1832.

### ***N*-cyclohexyl-4-vinylaniline (3p)**



Following the General Procedure B with the corresponding NHPI ester (0.2 mmol) and 4-vinylaniline (0.4 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (25:1) as an eluent to afford 17 mg (41%) of the title compound **3p**.

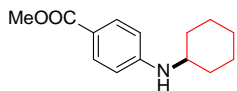
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.23 (d, *J* = 8.2 Hz, 1H), 6.65 – 6.51 (m, 3H), 5.50 (d, *J* = 17.6 Hz, 1H), 4.99 (d, *J* = 10.9 Hz, 1H), 3.58 (br s, 1H), 3.31 – 3.20 (m, 1H), 2.09 – 2.02 (m, 2H), 1.76 – 1.62 (m, 3H), 1.40 – 1.20 (m, 5H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 147.3, 136.8, 127.5, 126.8, 113.1, 109.2, 51.8, 33.6, 26.1, 25.1.

**Physical State:** brown oil.

**HRMS** (ESI): calcd for C<sub>14</sub>H<sub>20</sub>N [M+H]<sup>+</sup> 202.1596; found 202.1600.

### **Methyl 4-(cyclohexylamino)benzoate (3q)**



Following the General Procedure B with the corresponding NHPI ester (0.2 mmol) and methyl 4-aminobenzoate (0.4 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (25:1) as an eluent to afford 45 mg (96%) of the title compound **3q**.

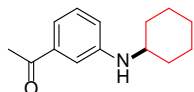
**<sup>1</sup>H NMR** (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 7.15 – 7.03 (m, 3H), 6.70 – 6.67 (m, 1H), 3.69 (br s, 1H), 3.26 – 3.21 (m, 1H), 2.44 (s, 3H), 1.98 – 1.92 (m, 2H), 1.70 – 1.65 (m, 2H), 1.60 – 1.54 (m, 1H), 1.37 – 1.26 (m, 2H), 1.21 – 1.03 (m, 3H).

**<sup>13</sup>C NMR** (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 198.7, 148.1, 138.7, 129.6, 117.9, 117.2, 112.0, 51.9, 33.7, 26.9, 26.3, 25.3.

**Physical State:** yellow solid.

**HRMS** (ESI): calcd for C<sub>14</sub>H<sub>20</sub>NO<sub>2</sub> [M+H]<sup>+</sup> 234.1489; found 234.1491.

### 1-(3-(cyclohexylamino)phenyl)ethan-1-one (**3r**)



Following the General Procedure B with the corresponding NHPI ester (0.2 mmol) and 4-aminoacetophenone (0.4 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (15:1) as an eluent to afford 39 mg (90%) of the title compound **3r**.

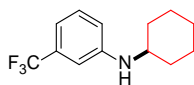
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.25 – 7.18 (m, 2H), 7.16 – 7.15 (m, 1H), 6.79 – 6.73 (m, 1H), 3.69 (br s, 1H), 3.31 (tt, *J* = 10.1, 3.8 Hz, 1H), 2.56 (s, 3H), 2.08 – 2.02 (m, 2H), 1.69 – 1.63 (m, 2H), 1.69 – 1.63 (m, 1H), 1.45 – 1.33 (m, 2H), 1.29 – 1.10 (m, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 198.9, 147.7, 138.3, 129.4, 117.9, 117.4, 112.0, 51.7, 33.5, 26.9, 26.0, 25.1.

**Physical State:** yellow oil.

**HRMS** (ESI): calcd for C<sub>14</sub>H<sub>20</sub>NO [M+H]<sup>+</sup> 218.1545; found 218.1547.

### *N*-cyclohexyl-3-(trifluoromethyl)aniline (**3s**)



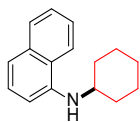
Following the General Procedure B with the corresponding NHPI ester (0.2 mmol) and 3-(trifluoromethyl)aniline (0.4 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (20:1) as an eluent to afford 41 mg (84%) of the title compound **3s**.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.22 (t, *J* = 7.7 Hz, 1H), 6.90 – 6.84 (m, 1H), 6.76 (s, 1H), 6.70 (dd, *J* = 8.2, 2.4 Hz, 1H), 3.74 (br s, 1H), 3.28 (tt, *J* = 10.1, 3.8 Hz, 1H), 2.09 – 2.00 (m, 2H), 1.81 – 1.74 (m, 2H), 1.72 – 1.63 (m, 1H), 1.46 – 1.33 (m, 2H), 1.28 – 1.13 (m, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 147.6, 131.7 (q, *J* = 31.6 Hz), 129.8, 124.5 (q, *J* = 272.3 Hz), 116.1, 113.2 (q, *J* = 4.0 Hz), 109.2 (q, *J* = 3.9 Hz), 51.7, 33.4, 26.0, 25.0.

Spectral data match those previously reported.<sup>20</sup>

### ***N*-cyclohexylnaphthalen-1-amine (3t)**



Following the General Procedure B with the corresponding NHPI ester (0.2 mmol) and naphthalen-1-amine (0.4 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (20:1) as an eluent to afford 25 mg (56%) of the title compound **3t**.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.83 – 7.74 (m, 2H), 7.47 – 7.39 (m, 2H), 7.34 (t, *J* = 7.9 Hz, 1H), 7.20 (d, *J* = 8.2 Hz, 1H), 6.65 (d, *J* = 7.6 Hz, 1H), 4.27 (br s, 1H), 3.48 (tt, *J* = 9.9, 3.7 Hz, 1H), 2.25 – 2.13 (m, 2H), 1.88 – 1.69 (m, 3H), 1.51 – 1.26 (m, 5H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 142.5, 134.7, 128.8, 126.8, 125.7, 124.6, 123.5, 119.9, 116.7, 104.8, 51.9, 33.4, 26.2, 25.2.

Spectral data match those previously reported.<sup>14</sup>

### ***N*-cyclohexylpyridin-2-amine (4a)**



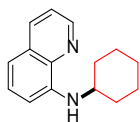
Following the General Procedure B with the corresponding NHPI ester (0.3 mmol) and 2-aminopyridine (3 equiv, 0.9 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (15:1) as an eluent to afford 26 mg (48%) of the title compound **4a**.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 8.05 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.42 – 7.31 (m, 1H), 6.54 – 6.46 (m, 1H), 6.34 (dd, *J* = 8.4, 1.0 Hz, 1H), 4.44 (br s, 1H), 3.62 – 3.42 (m, 1H), 2.11 – 1.95 (m, 2H), 1.82 – 1.68 (m, 2H), 1.69 – 1.58 (m, 1H), 1.45 – 1.32 (m, 2H), 1.28 – 1.13 (m, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 158.25, 148.42, 137.41, 112.47, 106.80, 50.25, 33.50, 25.93, 25.02.

Spectral data match those previously reported.<sup>21</sup>

### ***N*-cyclohexylquinolin-8-amine (4b)**

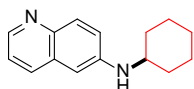


Following the General Procedure B with the corresponding NHPI ester (0.2 mmol) and quinolin-8-amine (0.4 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (20:1) as an eluent to afford 35 mg (78%) of the title compound **4b**.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 8.70 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.04 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.44 – 7.29 (m, 2H), 7.00 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.77 – 6.59 (m, 1H), 6.15 (br s, 1H), 3.55 – 3.39 (m, 1H), 2.24 – 2.12 (m, 2H), 1.91 – 1.79 (m, 2H), 1.72 – 1.64 (m, 1H), 1.57 – 1.07 (m, 6H).  
**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 146.5, 143.8, 136.4, 129.1, 128.0, 121.4, 113.2, 105.1, 51.5, 33.1, 26.2, 25.3.

Spectral data match those previously reported.<sup>14</sup>

#### ***N*-cyclohexylquinolin-6-amine (4c)**



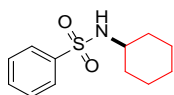
Following the General Procedure B with the corresponding NHPI ester (0.2 mmol) and quinolin-6-amine (0.4 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (20:1) as an eluent to afford 19 mg (43%) of the title compound **4c**.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 8.58 (dd, *J* = 4.3, 1.6 Hz, 1H), 7.93 – 7.72 (m, 2H), 7.28 – 7.24 (m, 1H), 7.07 (dd, *J* = 9.1, 2.6 Hz, 1H), 6.68 (d, *J* = 2.6 Hz, 1H), 3.96 (br s, 1H), 3.38 (tt, *J* = 10.1, 3.8 Hz, 1H), 2.17 – 2.10 (m, 2H), 1.80 (dt, *J* = 13.3, 3.9 Hz, 2H), 1.69 (dt, *J* = 12.8, 3.7 Hz, 1H), 1.48 – 1.17 (m, 5H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 145.6, 145.0, 142.0, 134.5, 134.4, 132.9, 130.5, 129.6, 123.7, 122.3, 121.4, 103.0, 51.9, 33.2, 26.0, 25.1.

Spectral data match those previously reported.<sup>2</sup>

#### ***N*-cyclohexylbenzenesulfonamide (4d)**



An oven-dried 15 mL vial equipped with a Teflon-coated magnetic stir bar was sequentially charged with corresponding NHPI ester (0.3 mmol), Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (1 mol%), Cu(MeCN)<sub>4</sub>PF<sub>6</sub> (50 mol%), **L3** (30 mol%), MeCN (0.1 M), benzenesulfonamide (0.9 mmol), Et<sub>3</sub>N (5 equiv) in the glove box. The vial was sealed with a screw cap and removed from the glove box. Then the

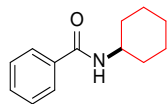
vial was placed 3 cm away from one blue LED, and irradiated under fan cooling (maintain the temperature at room temperature) for 20 h. After the reaction, the resulting dark brown reaction mixture was acidified with saturated  $\text{NH}_4\text{Cl}$  solution (~1 mL) and then neutralized with saturated  $\text{NaHCO}_3$  solution (~1.5 mL). The crude product in the aqueous fraction was extracted with EtOAc (~10 mL). The aqueous fraction was further washed with EtOAc (3 x ~5 mL). The combined organic fractions were concentrated *in vacuo* with the aid of a rotary evaporator. The crude product residue was purified by preparative TLC (pretreated with 3% triethylamine in hexanes in order to minimize the product loss) using hexanes / EtOAc (20:1) as an eluent to afford 26 mg (36%) of the title compound **4d**.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.97 – 7.82 (m, 2H), 7.61 – 7.47 (m, 3H), 4.59 (d,  $J = 7.7$  Hz, 1H), 3.20 – 3.11 (m, 1H), 1.78 – 1.70 (m, 2H), 1.66 – 1.61 (m, 2H), 1.53 – 1.47 (m, 1H), 1.27 – 1.09 (m, 5H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  141.6, 132.6, 129.2, 127.0, 52.8, 34.1, 25.3, 24.8.

Spectral data match those previously reported.<sup>22</sup>

#### ***N*-cyclohexylbenzamide (4e)**



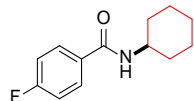
An oven-dried 15 mL vial equipped with a Teflon-coated magnetic stir bar was sequentially charged with corresponding NHPI ester (0.5 mmol),  $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$  (1 mol%),  $\text{Cu}(\text{MeCN})_4\text{PF}_6$  (50 mol%), **L3** (30 mol%), MeCN (0.1 M), benzamide (1.5 mmol),  $\text{Et}_3\text{N}$  (5 equiv) in the glove box. The vial was sealed with a screw cap and removed from the glove box. Then the vial was placed 3 cm away from one blue LED, and irradiated under fan cooling (maintain the temperature at room temperature) for 20 h. After the reaction, the resulting dark brown reaction mixture was acidified with saturated  $\text{NH}_4\text{Cl}$  solution (~1 mL) and then neutralized with saturated  $\text{NaHCO}_3$  solution (~1.5 mL). The crude product in the aqueous fraction was extracted with EtOAc (~10 mL). The aqueous fraction was further washed with EtOAc (3 x ~5 mL). The combined organic fractions were concentrated *in vacuo* with the aid of a rotary evaporator. The crude product residue was purified by preparative TLC (pretreated with 3% triethylamine in hexanes in order to minimize the product loss) using hexanes / EtOAc (10:1) as an eluent to afford 42 mg (41%) of the title compound **4e**.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.80 – 7.68 (m, 2H), 7.49 – 7.42 (m, 1H), 7.42 – 7.34 (m, 2H), 6.16 (br s, 1H), 4.04 – 3.86 (m, 1H), 2.03 – 1.95 (m, 2H), 1.80 – 1.57 (m, 3H), 1.47 – 1.09 (m, 5H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 166.7, 135.2, 131.3, 128.5, 126.9, 48.8, 33.3, 25.6, 25.0.

Spectral data match those previously reported.<sup>23</sup>

#### ***N*-cyclohexyl-4-fluorobenzamide (4f)**



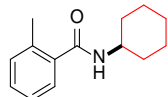
An oven-dried 15 mL vial equipped with a Teflon-coated magnetic stir bar was sequentially charged with corresponding NHPI ester (0.5 mmol), Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (1 mol%), Cu(MeCN)<sub>4</sub>PF<sub>6</sub> (50 mol%), **L3** (30 mol%), MeCN (0.1 M), 4-fluorobenzamide (1.5 mmol), Et<sub>3</sub>N (5 equiv) in the glove box. The vial was sealed with a screw cap and removed from the glove box. Then the vial was placed 3 cm away from one blue LED, and irradiated under fan cooling (maintain the temperature at room temperature) for 20 h. After the reaction, the resulting dark brown reaction mixture was acidified with saturated NH<sub>4</sub>Cl solution (~1 mL) and then neutralized with saturated NaHCO<sub>3</sub> solution (~1.5 mL). The crude product in the aqueous fraction was extracted with EtOAc (~10 mL). The aqueous fraction was further washed with EtOAc (3 x ~5 mL). The combined organic fractions were concentrated *in vacuo* with the aid of a rotary evaporator. The crude product residue was purified by preparative TLC (pretreated with 3% triethylamine in hexanes in order to minimize the product loss) using hexanes / EtOAc (10:1) as an eluent to afford 33 mg (30%) of the title compound **4f**.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.84 – 7.66 (m, 2H), 7.18 – 7.02 (m, 2H), 5.93 (s, 1H), 4.05 – 3.84 (m, 1H), 2.13 – 1.93 (m, 2H), 1.80 – 1.60 (m, 3H), 1.51 – 1.35 (m, 2H), 1.31 – 1.11 (m, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 165.95, 165.68, 163.46, 131.39 (d, *J* = 3.3 Hz), 129.25 (d, *J* = 8.9 Hz), 115.63 (d, *J* = 21.9 Hz), 48.94, 33.38, 25.70, 25.05.

Spectral data match those previously reported.<sup>24</sup>

#### ***N*-cyclohexyl-2-methylbenzamide (4g)**



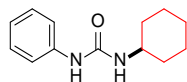
An oven-dried 15 mL vial equipped with a Teflon-coated magnetic stir bar was sequentially charged with corresponding NHPI ester (0.5 mmol), Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (1 mol%), Cu(MeCN)<sub>4</sub>PF<sub>6</sub> (50 mol%), **L3** (30 mol%), MeCN (0.1 M), 2-methylbenzamide (1.5 mmol), Et<sub>3</sub>N (5 equiv) in the glove box. The vial was sealed with a screw cap and removed from the glove box. Then the vial was placed 3 cm away from one blue LED, and irradiated under fan cooling (maintain the temperature at room temperature) for 20 h. After the reaction, the resulting dark brown reaction mixture was acidified with saturated NH<sub>4</sub>Cl solution (~1 mL) and then neutralized with saturated NaHCO<sub>3</sub> solution (~1.5 mL). The crude product in the aqueous fraction was extracted with EtOAc (~10 mL). The aqueous fraction was further washed with EtOAc (3 x ~5 mL). The combined organic fractions were concentrated *in vacuo* with the aid of a rotary evaporator. The crude product residue was purified by preparative TLC (pretreated with 3% triethylamine in hexanes in order to minimize the product loss) using hexanes / EtOAc (10:1) as an eluent to afford 36 mg (33%) of the title compound **4g**.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.36 – 7.27 (m, 2H), 7.23 – 7.16 (m, 2H), 5.60 (s, 1H), 4.05 – 3.90 (m, 1H), 2.44 (s, 3H), 2.10 – 1.97 (m, 2H), 1.81 – 1.60 (m, 3H), 1.51 – 1.37 (m, 2H), 1.29 – 1.13 (m, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 169.4, 137.2, 135.9, 131.0, 129.8, 126.7, 125.8, 48.6, 33.4, 25.7, 25.0, 19.8.

Spectral data match those previously reported.<sup>25</sup>

### 1-cyclohexyl-3-phenylurea (**4h**)



An oven-dried 15 mL vial equipped with a Teflon-coated magnetic stir bar was sequentially charged with corresponding NHPI ester (0.5 mmol), Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (1 mol%), Cu(MeCN)<sub>4</sub>PF<sub>6</sub> (50 mol%), **L3** (30 mol%), MeCN (0.1 M), *N*-phenylurea (1.5 mmol), Et<sub>3</sub>N (5 equiv) in the glove box. The vial was sealed with a screw cap and removed from the glove box. Then the vial was placed 3 cm away from one blue LED, and irradiated under fan cooling (maintain the temperature at room temperature) for 20 h. After the reaction, the resulting dark brown reaction mixture was acidified with saturated NH<sub>4</sub>Cl solution (~1 mL) and then neutralized with saturated NaHCO<sub>3</sub> solution (~1.5 mL). The crude product in the aqueous fraction was extracted with



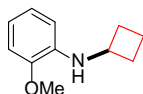
EtOAc (~10 mL). The aqueous fraction was further washed with EtOAc (3 x ~5 mL). The combined organic fractions were concentrated *in vacuo* with the aid of a rotary evaporator. The crude product residue was purified by preparative TLC (pretreated with 3% triethylamine in hexanes in order to minimize the product loss) using hexanes / EtOAc (10:1) as an eluent to afford 31 mg (28%) of the title compound **4h**.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.27 (d, *J* = 5.4 Hz, 4H), 7.15 – 6.94 (m, 1H), 6.81 (s, 1H), 4.99 (s, 1H), 3.65 (tt, *J* = 10.5, 3.9 Hz, 1H), 2.02 – 1.86 (m, 2H), 1.73 – 1.54 (m, 3H), 1.43 – 1.25 (m, 2H), 1.25 – 0.93 (m, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 155.5, 138.9, 129.4, 123.7, 121.0, 49.1, 33.8, 25.7, 25.0.

Spectral data match those previously reported.<sup>26</sup>

#### ***N*-cyclobutyl-2-methoxyaniline (5a)**



Following the General Procedure B with the corresponding NHPI ester (0.2 mmol) and *o*-anisidine (0.4 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (25:1) as an eluent to afford 29 mg (81%) of the title compound **5a**.

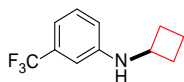
**<sup>1</sup>H NMR** (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 6.81 (td, *J* = 7.6, 1.4 Hz, 1H), 6.75 (dd, *J* = 8.0, 1.4 Hz, 1H), 6.61 (td, *J* = 7.7, 1.6 Hz, 1H), 6.49 (dd, *J* = 7.8, 1.6 Hz, 1H), 4.36 (br s, 1H), 3.95 – 3.88 (m, 1H), 3.83 (s, 3H), 2.49 – 2.37 (m, 2H), 1.90 – 1.75 (m, 4H).

**<sup>13</sup>C NMR** (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 147.1, 137.7, 121.6, 116.6, 110.5, 109.8, 55.7, 49.1, 31.6, 15.7.

**Physical State:** yellow oil.

**HRMS** (ESI): calcd for C<sub>11</sub>H<sub>16</sub>NO [M+H]<sup>+</sup> 178.1232; found 178.1236.

#### ***N*-cyclobutyl-3-(trifluoromethyl)aniline (5b)**



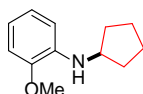
Following the General Procedure B with the corresponding NHPI ester (0.2 mmol) and 2-(trifluoromethyl)aniline (0.4 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (25:1) as an eluent to afford 31 mg (71%) of the title compound **5b**.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.23 (t, *J* = 7.9 Hz, 1H), 6.92 (d, *J* = 7.7 Hz, 1H), 6.73 (s, 1H), 6.67 (dd, *J* = 8.2, 2.3 Hz, 1H), 4.13 (br s, 1H), 3.97 – 3.88 (m, 1H), 2.49 – 2.40 (m, 2H), 1.89 – 1.78 (m, 4H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 147.4, 131.7 (q, *J* = 31.6 Hz), 129.7, 124.5 (q, *J* = 272.2 Hz), 116.0 (d, *J* = 1.5 Hz), 113.8 (q, *J* = 4.0 Hz), 109.2 (q, *J* = 4.0 Hz), 48.9, 31.2, 15.4.

Spectral data match those previously reported.<sup>27</sup>

### ***N*-cyclopentyl-2-methoxyaniline (5c)**



Following the General Procedure B with the corresponding NHPI ester (0.2 mmol) and *o*-anisidine (0.4 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (25:1) as an eluent to afford 16 mg (41%) of the title compound **5c**.

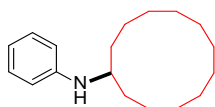
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 6.87 (td, *J* = 7.5, 1.4 Hz, 1H), 6.76 (dd, *J* = 8.3, 1.4 Hz, 1H), 6.68 – 6.62 (m, 2H), 4.21 (s, 1H), 3.84 (s, 3H), 3.82 – 3.74 (m, 1H), 2.11 – 1.97 (m, 2H), 1.83 – 1.67 (m, 2H), 1.68 – 1.59 (m, 2H), 1.56 – 1.48 (m, 2H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 146.9, 138.1, 121.4, 116.1, 110.6, 109.4, 55.5, 54.5, 33.8, 24.3.

**Physical State:** brown solid.

**HRMS** (ESI): calcd for C<sub>12</sub>H<sub>18</sub>NO [M+H]<sup>+</sup> 192.1388; found 192.1391.

### ***N*-phenylcyclododecanamine (5d)**



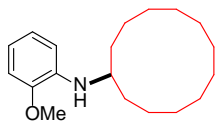
Following the General Procedure B with the corresponding NHPI ester (0.2 mmol) and aniline (0.4 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (25:1) as an eluent to afford 34 mg (66%) of the title compound **5d**.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.17 (t, *J* = 7.8 Hz, 2H), 6.67 (t, *J* = 7.3 Hz, 1H), 6.60 (d, *J* = 7.9 Hz, 2H), 3.57 – 3.48 (m, 1H), 3.42 (br s, 1H), 1.69 – 1.57 (m, 2H), 1.51 – 1.30 (m, 20H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 148.0, 129.4, 116.8, 113.2, 49.6, 29.9, 24.5, 24.1, 23.5, 23.4, 21.4.

Spectral data match those previously reported.<sup>28</sup>

### *N*-(2-methoxyphenyl)cyclododecanamine (**5e**)



Following the General Procedure B with the corresponding NHPI ester (0.2 mmol) and *o*-anisidine (0.4 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (20:1) as an eluent to afford 44 mg (76%) of the title compound **5e**.

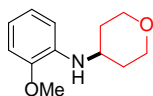
**<sup>1</sup>H NMR** (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 6.82 (td, *J* = 7.6, 1.4 Hz, 1H), 6.75 (dd, *J* = 7.8, 1.4 Hz, 1H), 6.62 – 6.54 (m, 2H), 4.04 (d, *J* = 32.8 Hz, 1H), 3.82 (br s, 3H), 3.53 – 3.48 (m, 1H), 1.69 – 1.59 (m, 2H), 1.52 – 1.33 (m, 20H).

**<sup>13</sup>C NMR** (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 147.2, 138.3, 121.6, 115.8, 110.2, 110.0, 55.8, 49.4, 30.1, 24.8, 24.4, 23.8, 23.8, 21.8.

**Physical State:** pale brown solid.

**HRMS** (ESI): calcd for C<sub>19</sub>H<sub>32</sub>NO [M+H]<sup>+</sup> 290.2484; found 290.2483.

### *N*-(2-methoxyphenyl)tetrahydro-2*H*-pyran-4-amine (**5f**)



Following the General Procedure B with the corresponding NHPI ester (0.2 mmol) and *o*-anisidine (0.4 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (15:1) as an eluent to afford 34 mg (82%) of the title compound **5f**.

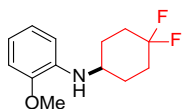
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 6.86 (td, *J* = 7.6, 1.4 Hz, 1H), 6.78 (dd, *J* = 7.9, 1.4 Hz, 1H), 6.69 – 6.63 (m, 2H), 4.18 (br s, 1H), 4.03 – 3.99 (m, 2H), 3.85 (s, 3H), 3.57 – 3.45 (m, 3H), 2.08 – 2.02 (m, 2H), 1.58 – 1.47 (m, 2H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 147.0, 136.7, 121.3, 116.6, 110.5, 109.9, 67.1, 55.5, 48.9, 33.7.

**Physical State:** reddish brown oil.

**HRMS** (ESI): calcd for C<sub>12</sub>H<sub>18</sub>NO<sub>2</sub> [M+H]<sup>+</sup> 208.1338; found 208.1340.

### *N*-(4,4-difluorocyclohexyl)-2-methoxyaniline (**5g**)



Following the General Procedure B with the corresponding NHPI ester (0.2 mmol) and *o*-anisidine (0.4 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (15:1) as an eluent to afford 35 mg (73%) of the title compound **5g**.

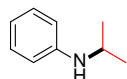
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 6.87 (td, *J* = 7.6, 1.5 Hz, 1H), 6.79 (dd, *J* = 8.0, 1.4 Hz, 1H), 6.68 (td, *J* = 7.7, 1.5 Hz, 1H), 6.62 (dd, *J* = 7.8, 1.6 Hz, 1H), 4.16 (br s, 1H), 3.85 (s, 3H), 3.46 – 3.41 (m, 1H), 2.16 – 1.63 (m, 8H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 147.0, 136.9, 121.4, 123.1, 116.7, 110.4, 109.8, 77.4, 55.6, 49.3, 32.2 (t, *J* = 24.2 Hz), 29.1 – 28.1 (m).

**Physical State:** brown oil.

**HRMS** (ESI): calcd for C<sub>13</sub>H<sub>18</sub>F<sub>2</sub>NO [M+H]<sup>+</sup> 242.1357; found 242.1362.

### *N*-isopropylaniline (**5h**)



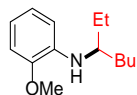
Following the General Procedure B with the corresponding NHPI ester (0.4 mmol) and aniline (0.8 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (30:1) as an eluent to afford 20 mg (37%) of the title compound **5h**.

**<sup>1</sup>H NMR** (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 7.12 (dd, *J* = 8.6, 7.2 Hz, 2H), 6.68 – 6.47 (m, 3H), 3.64 – 3.58 (m, 1H), 3.50 (br s, 1H), 1.20 (s, 3H), 1.18 (s, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 147.6, 129.4, 117.1, 113.4, 44.4, 23.1.

Spectral data match those previously reported.<sup>29</sup>

### *N*-(heptan-3-yl)-2-methoxyaniline (**5i**)



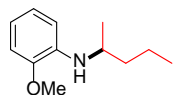
Following the General Procedure B with the corresponding NHPI ester (0.2 mmol) and *o*-anisidine (0.4 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (25:1) as an eluent to afford 27 mg (60%) of the title compound **5i**.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 6.84 (td, *J* = 7.6, 1.2 Hz, 1H), 6.76 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.60 (ddd, *J* = 7.6, 6.8, 1.2 Hz, 1H), 6.58 (dd, *J* = 6.8, 1.2 Hz, 1H), 4.06 (br s, 1H), 3.84 (s, 3H), 3.30 – 3.24 (m, 1H), 1.71 – 0.87 (m, 14H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  146.8, 138.3, 121.4, 115.4, 110.0, 109.7, 55.6, 53.9, 34.3, 28.4, 27.4, 23.0, 14.2, 10.2.

Spectral data match those previously reported.<sup>30</sup>

### 2-methoxy-*N*-(pentan-2-yl)aniline (**5j**)



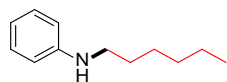
Following the General Procedure B with the corresponding NHPI ester (0.2 mmol) and *o*-anisidine (0.4 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (25:1) as an eluent to afford 22 mg (56%) of the title compound **5j**.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.87 (td,  $J = 7.6, 1.4$  Hz, 1H), 6.77 (dd,  $J = 7.8, 1.4$  Hz, 1H), 6.67 – 6.58 (m, 2H), 4.04 (br s, 1H), 3.85 (s, 3H), 3.48 (h,  $J = 6.3$  Hz, 1H), 1.68 – 1.54 (m, 1H), 1.51 – 1.37 (m, 3H), 1.20 (d,  $J = 6.3$  Hz, 3H), 0.95 (t,  $J = 7.1$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  146.8, 137.8, 121.4, 115.7, 110.1, 109.6, 55.5, 48.0, 39.6, 20.9, 19.5, 14.3.

Spectral data match those previously reported.<sup>30</sup>

### *N*-hexylaniline (**6a**)



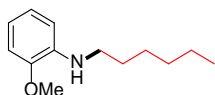
Following the General Procedure C with the corresponding NHPI ester (0.4 mmol) and aniline (0.2 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (30:1) as an eluent to afford 23 mg (64%) of the title compound **6a**.

$^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.13 (dd,  $J = 8.6, 7.3$  Hz, 2H), 6.63 (t,  $J = 7.3$  Hz, 1H), 6.60 – 6.54 (m, 2H), 3.66 (br s, 1H), 3.08 (t,  $J = 7.1$  Hz, 2H), 1.64 – 1.57 (m, 2H), 1.43 – 1.29 (m, 6H), 0.93 – 0.85 (m, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  172.86, 162.27, 134.81, 129.18, 124.03, 38.34, 26.78, 23.90, 23.81, 23.61, 23.52, 22.21.

Spectral data match those previously reported.<sup>31</sup>

### ***N*-hexyl-2-methoxyaniline (6b)**



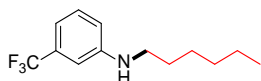
Following the General Procedure C with the corresponding NHPI ester (0.4 mmol) and *o*-anisidine (0.2 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (25:1) as an eluent to afford 29 mg (70%) of the title compound **6b**.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 6.88 (td, *J* = 7.6, 1.4 Hz, 1H), 6.77 (dd, *J* = 7.9, 1.4 Hz, 1H), 6.66 (td, *J* = 7.7, 1.6 Hz, 1H), 6.62 (dd, *J* = 7.8, 1.5 Hz, 1H), 4.17 (s, 1H), 3.85 (s, 3H), 3.13 (t, *J* = 7.1 Hz, 2H), 1.67 (p, *J* = 7.2 Hz, 2H), 1.43 – 1.32 (m, 5H), 0.95 – 0.88 (m, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 146.9, 138.7, 121.4, 116.2, 109.9, 109.5, 55.5, 43.9, 31.8, 29.7, 27.1, 22.8, 14.2.

Spectral data match those previously reported.<sup>32</sup>

### ***N*-hexyl-3-(trifluoromethyl)aniline (6c)**



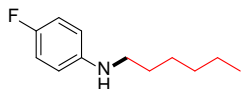
Following the General Procedure C with the corresponding NHPI ester (0.4 mmol) and 3-(trifluoromethyl)aniline (0.2 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (20:1) as an eluent to afford 27 mg (55%) of the title compound **6c**.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.23 (t, *J* = 7.9 Hz, 1H), 6.90 (d, *J* = 7.6 Hz, 1H), 6.78 (s, 1H), 6.72 (dd, *J* = 8.3, 2.3 Hz, 1H), 3.82 (s, 1H), 3.12 (t, *J* = 7.1 Hz, 2H), 1.68 – 1.60 (m, 2H), 1.43 – 1.29 (m, 6H), 0.95 – 0.87 (m, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 148.7, 131.8, 131.5, 129.7, 125.9, 123.2, 115.8, 113.6, 108.8, 44.0, 31.7, 29.5, 26.9, 22.8, 14.2.

Spectral data match those previously reported.<sup>33</sup>

### **4-fluoro-*N*-hexylaniline (6d)**



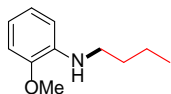
Following the General Procedure C with the corresponding NHPI ester (0.4 mmol) and 4-fluoroaniline (0.2 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (25:1) as an eluent to afford 24 mg (62%) of the title compound **6d**.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 6.93 – 6.85 (m, 2H), 6.60 – 6.53 (m, 2H), 3.06 (t, *J* = 7.2 Hz, 2H), 1.61 (p, *J* = 7.1 Hz, 2H), 1.43 – 1.28 (m, 6H), 0.92 – 0.87 (m, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 156.4 (d, *J* = 237.4 Hz), 144.0, 115.9 (d, *J* = 22.2 Hz), 114.6 (d, *J* = 8.1 Hz), 45.6, 31.8, 29.4, 26.9, 22.8, 14.2.

Spectral data match those previously reported.<sup>32</sup>

### ***N*-butyl-2-methoxyaniline (6e)**



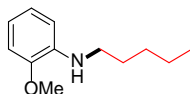
Following the General Procedure C with the corresponding NHPI ester (0.4 mmol) and *o*-anisidine (0.2 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (25:1) as an eluent to afford 22 mg (62%) of the title compound **6e**.

**<sup>1</sup>H NMR** (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 6.82 (td, *J* = 7.6, 1.4 Hz, 1H), 6.76 (dd, *J* = 7.9, 1.4 Hz, 1H), 6.60 (td, *J* = 7.7, 1.6 Hz, 1H), 6.56 (dd, *J* = 8.0, 1.6 Hz, 1H), 4.31 (br s, 1H), 3.83 (s, 3H), 2.94 (d, *J* = 6.8 Hz, 2H), 1.97 – 1.85 (m, 1H), 0.99 (d, *J* = 6.7 Hz, 6H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 146.8, 138.7, 121.4, 116.1, 109.9, 109.5, 55.6, 51.8, 28.1, 20.7.

Spectral data match those previously reported.<sup>34</sup>

### **2-methoxy-*N*-pentylaniline (6f)**



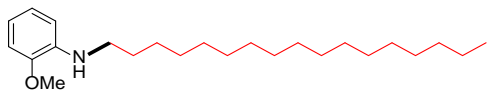
Following the General Procedure C with the corresponding NHPI ester (0.4 mmol) and *o*-anisidine (0.2 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (25:1) as an eluent to afford 22 mg (58%) of the title compound **6f**.

**<sup>1</sup>H NMR** (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 6.82 (td, *J* = 7.6, 1.4 Hz, 1H), 6.75 (dd, *J* = 7.9, 1.4 Hz, 1H), 6.63 – 6.54 (m, 2H), 4.17 (br s, 1H), 3.82 (s, 3H), 3.10 (t, *J* = 7.1 Hz, 2H), 1.68 – 1.61 (m, 2H), 1.41 – 1.33 (m, 4H), 0.96 – 0.90 (m, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 146.9, 138.6, 121.4, 116.2, 110.0, 109.6, 55.6, 51.8, 28.1, 20.7.

Spectral data match those previously reported.<sup>35</sup>

### ***N*-heptadecyl-2-methoxyaniline (6g)**



Following the General Procedure C with the corresponding NHPI ester (0.4 mmol) and *o*-anisidine (0.2 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (20:1) as an eluent to afford 64 mg (88%) of the title compound **6g**.

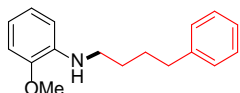
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 6.88 (t, *J* = 7.3 Hz, 1H), 6.78 (d, *J* = 7.6 Hz, 1H), 6.71 – 6.61 (m, 2H), 3.85 (s, 3H), 3.12 (t, *J* = 7.2 Hz, 2H), 1.70 – 1.63 (m, 3H), 1.46 – 1.27 (m, 27H), 0.89 (t, *J* = 6.6 Hz, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 147.0, 138.3, 121.4, 116.6, 109.6, 110.4, 55.6, 44.1, 32.1, 29.9, 29.8, 29.8, 29.8, 29.6, 29.6, 29.5, 27.4, 22.9, 14.3.

**Physical State:** reddish brown solid.

**HRMS** (ESI): calcd for C<sub>24</sub>H<sub>44</sub>NO [M+H]<sup>+</sup> 362.3423; found 362.3423.

### **2-methoxy-*N*-(4-phenylbutyl)aniline (6h)**



Following the General Procedure C with the corresponding NHPI ester (0.4 mmol) and *o*-anisidine (0.2 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (20:1) as an eluent to afford 38 mg (75%) of the title compound **6h**.

**<sup>1</sup>H NMR** (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 7.34 – 7.16 (m, 5H), 6.83 (td, *J* = 7.6, 1.5 Hz, 1H), 6.76 (dd, *J* = 7.9, 1.4 Hz, 1H), 6.61 (td, *J* = 7.6, 1.5 Hz, 1H), 6.57 (dd, *J* = 7.8, 1.5 Hz, 1H), 4.19 (br s, 1H), 3.82 (s, 3H), 3.14 (t, *J* = 6.8 Hz, 2H), 2.68 (t, *J* = 7.4 Hz, 2H), 1.79 – 1.64 (m, 4H).

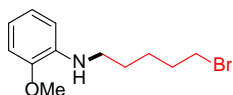
**<sup>13</sup>C NMR** (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 147.2, 143.0, 139.0, 128.8, 128.7, 126.1, 121.6, 116.3, 109.9, 109.8, 55.8, 43.9, 36.1, 29.6, 29.5.

**Physical State:** colorless oil.

**HRMS** (ESI): calcd for C<sub>17</sub>H<sub>22</sub>NO [M+H]<sup>+</sup> 256.1701; found 256.1708.



### ***N*-(5-bromopentyl)-2-methoxyaniline (6i)**



Following the General Procedure C with the corresponding NHPI ester (0.4 mmol) and *o*-anisidine (0.2 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (20:1) as an eluent to afford 22 mg (40%) of the title compound **6i**.

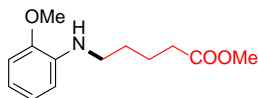
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.01 – 6.88 (m, 3H), 6.85 (dd, *J* = 7.8, 1.6 Hz, 1H), 3.87 (s, 3H), 2.98 (t, *J* = 5.3 Hz, 4H), 1.76 (p, *J* = 5.6 Hz, 4H), 1.60 – 1.55 (m, 2H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 152.5, 142.9, 122.6, 121.0, 118.5, 111.2, 55.5, 52.5, 26.5, 24.6.

**Physical State:** colorless oil.

**HRMS** (ESI): calcd for C<sub>12</sub>H<sub>19</sub>BrNO [M+H]<sup>+</sup> 272.0650; found 272.0648.

### **Methyl 5-((2-methoxyphenyl)amino)pentanoate (6j)**



Following the General Procedure C with the corresponding NHPI ester (0.4 mmol) and *o*-anisidine (0.2 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (20:1) as an eluent to afford 19 mg (41%) of the title compound **6j**.

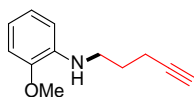
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 6.87 (td, *J* = 7.6, 1.4 Hz, 1H), 6.77 (dd, *J* = 7.9, 1.4 Hz, 1H), 6.66 (td, *J* = 7.7, 1.5 Hz, 1H), 6.60 (dd, *J* = 7.9, 1.5 Hz, 1H), 4.18 (br s, 1H), 3.84 (s, 3H), 3.68 (s, 3H), 3.15 (t, *J* = 6.8 Hz, 2H), 2.38 (t, *J* = 7.2 Hz, 2H), 1.84 – 1.63 (m, 4H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 174.0, 146.9, 138.4, 121.4, 116.4, 109.9, 109.5, 55.5, 51.7, 43.4, 33.9, 29.1, 22.7.

**Physical State:** brown oil.

**HRMS** (ESI): calcd for C<sub>13</sub>H<sub>20</sub>NO<sub>3</sub> [M+H]<sup>+</sup> 238.1443; found 238.1446.

### ***N*-(hex-5-yn-1-yl)-2-methoxyaniline (6k)**



Following the General Procedure C with the corresponding NHPI ester (0.4 mmol) and *o*-anisidine (0.2 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (20:1) as an eluent to afford 12 mg (31%) of the title compound **6k**.

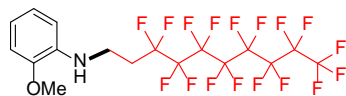
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 6.87 (td, *J* = 7.6, 1.4 Hz, 1H), 6.77 (dd, *J* = 7.9, 1.4 Hz, 1H), 6.71 – 6.62 (m, 2H), 3.84 (s, 3H), 3.28 (t, *J* = 6.9 Hz, 2H), 2.33 (td, *J* = 7.0, 2.7 Hz, 2H), 1.99 (t, *J* = 2.7 Hz, 1H), 1.88 (p, *J* = 6.9 Hz, 2H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 147.0, 138.1, 121.4, 116.7, 110.1, 109.6, 83.9, 69.0, 55.6, 42.7, 28.2, 16.4.

**Physical State:** brown oil.

**HRMS** (ESI): calcd for C<sub>12</sub>H<sub>16</sub>NO [M+H]<sup>+</sup> 190.1232; found 190.1230.

#### *N*-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptafluorodecyl)-2-methoxyaniline (**6l**)



Following the General Procedure C with the corresponding NHPI ester (0.4 mmol) and *o*-anisidine (0.2 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (15:1) as an eluent to afford 57 mg (50%) of the title compound **6l**.

**<sup>1</sup>H NMR** (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 6.87 (td, *J* = 7.6, 1.4 Hz, 1H), 6.80 (dd, *J* = 8.0, 1.4 Hz, 1H), 6.69 (td, *J* = 7.7, 1.5 Hz, 1H), 6.61 (dd, *J* = 7.8, 1.5 Hz, 1H), 4.39 (br s, 1H), 3.84 (s, 3H), 3.57 – 3.52 (m, 2H), 2.51 – 2.37 (m, 2H).

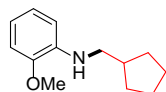
**<sup>13</sup>C NMR** (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 147.5, 137.5, 121.7, 117.5, 110.2, 109.8, 55.9, 54.4, 54.1, 53.8, 53.6, 53.3, 35.9, 31.4, 31.2, 30.9.

**<sup>19</sup>F NMR** (376 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ -81.17 (t, *J* = 10.4 Hz), -114.17 (t, *J* = 14.1 Hz), -121.90, -122.12, -122.93, -123.74, -126.3 – -126.43 (m).

**Physical State:** light pink solid

**HRMS** (ESI): calcd for C<sub>17</sub>H<sub>13</sub>F<sub>17</sub>NO [M+H]<sup>+</sup> 570.0726; found 570.0729.

#### *N*-(cyclopentylmethyl)-2-methoxyaniline (**6m**)



Following the General Procedure C with the corresponding NHPI ester (0.4 mmol) and *o*-anisidine (0.2 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (20:1) as an eluent to afford 24 mg (59%) of the title compound **6m**.

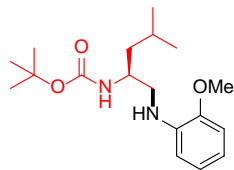
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 6.88 (td, *J* = 7.6, 1.4 Hz, 1H), 6.77 (dd, *J* = 8.0, 1.4 Hz, 1H), 6.68 – 6.62 (m, 2H), 4.34 (br s, 1H), 3.86 (s, 3H), 3.05 (d, *J* = 7.2 Hz, 2H), 2.26 – 2.16 (m, 1H), 1.89 – 1.81 (m, 2H), 1.68 – 1.53 (m, 4H), 1.34 – 1.25 (m, 2H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 146.9, 138.7, 121.4, 116.3, 110.0, 109.5, 55.6, 49.4, 39.6, 30.9, 25.4.

**Physical State:** pale yellow oil.

**HRMS** (ESI): calcd for C<sub>13</sub>H<sub>20</sub>NO [M+H]<sup>+</sup> 206.1545; found 206.1547.

***tert*-butyl (*S*)-1-((2-methoxyphenyl)amino)-4-methylpentan-2-yl)carbamate (**7a**)**



Following the General Procedure C with the corresponding NHPI ester (0.4 mmol) and *o*-anisidine (0.2 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (10:1) as an eluent to afford 38 mg (59%) of the title compound **7a**.

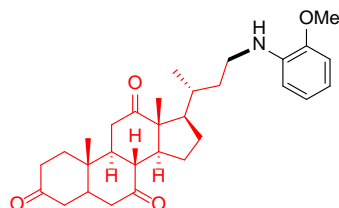
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 6.86 (td, *J* = 7.6, 1.4 Hz, 1H), 6.76 (dd, *J* = 8.1, 1.4 Hz, 1H), 6.70 – 6.58 (m, 2H), 4.68 (br s, 1H), 4.46 (s, 1H), 3.94 (s, 1H), 3.83 (s, 3H), 3.33 – 2.94 (m, 2H), 1.82 – 1.65 (m, 1H), 1.45 (s, 9H), 1.42 – 1.32 (m, 2H), 0.99 – 0.89 (m, 6H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 156.1, 147.0, 138.3, 121.4, 116.7, 110.0, 109.6, 79.4, 55.5, 49.2, 48.8, 42.5, 28.5, 25.1, 23.3, 22.3.

**Physical State:** pale brown solid.

**HRMS** (ESI): calcd for C<sub>18</sub>H<sub>31</sub>N<sub>2</sub>O<sub>3</sub> [M+H]<sup>+</sup> 323.2335; found 323.2332.

**(8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-17-((*R*)-4-((2-methoxyphenyl)amino)butan-2-yl)-10,13-dimethyldodecahydro-3*H*-cyclopenta[*a*]phenanthrene-3,7,12(2*H*,4*H*)-trione (7b)**



Following the General Procedure C with the corresponding NHPI ester (0.4 mmol) and *o*-anisidine (0.2 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (5:1) as an eluent to afford 41 mg (43%) of the title compound **7b**.

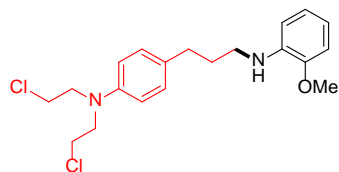
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 6.86 (td, *J* = 7.7, 1.4 Hz, 1H), 6.75 (dd, *J* = 7.9, 1.4 Hz, 1H), 6.68 – 6.55 (m, 2H), 4.08 (br s, 1H), 3.83 (s, 3H), 3.28 – 3.13 (m, 1H), 3.07 (dt, *J* = 11.8, 7.8 Hz, 1H), 2.92 – 2.83 (m, 3H), 2.41 – 0.91 (m, 28H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 146.8, 138.6, 134.4, 121.4, 116.3, 109.9, 109.4, 57.0, 55.5, 51.9, 49.1, 49.0, 47.0, 46.1, 45.7, 45.1, 42.9, 41.6, 38.8, 36.6, 36.1, 35.5, 35.4, 34.5, 28.0, 25.3, 22.0, 19.4, 12.0.

**Physical State:** light brown solid.

**HRMS** (ESI): calcd for C<sub>30</sub>H<sub>42</sub>NO<sub>4</sub> [M+H]<sup>+</sup> 480.3114; found 480.3113.

***N,N*-bis(2-chloroethyl)-4-(3-((2-methoxyphenyl)amino)propyl)aniline (7c)**



Following the General Procedure C with the corresponding NHPI ester (0.4 mmol) and *o*-anisidine (0.2 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (10:1) as an eluent to afford 38 mg (50%) of the title compound **7c**.

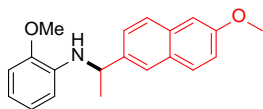
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.10 (d, *J* = 8.6 Hz, 2H), 6.87 (td, *J* = 7.6, 1.5 Hz, 1H), 6.78 (dd, *J* = 8.0, 1.4 Hz, 1H), 6.73 – 6.60 (m, 4H), 3.85 (s, 3H), 3.72 – 3.60 (m, 8H), 3.16 (t, *J* = 7.1 Hz, 2H), 2.66 (t, *J* = 7.6 Hz, 2H), 1.96 (dt, *J* = 15.2, 7.3 Hz, 2H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 147.2, 144.4, 131.0, 129.8, 129.6, 121.4, 117.1, 112.4, 109.7, 55.6, 53.8, 43.7, 40.7, 32.3, 31.1.

**Physical State:** colorless oil.

**HRMS** (ESI): calcd for C<sub>20</sub>H<sub>27</sub>N<sub>2</sub>OCl<sub>2</sub> [M+H]<sup>+</sup> 381.1501; found 381.1505.

**2-methoxy-*N*-(1-(6-methoxynaphthalen-2-yl)ethyl)aniline (7d)**



Following the General Procedure B with the corresponding NHPI ester (0.2 mmol) and *o*-anisidine (0.4 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (10:1) as an eluent to afford 34 mg (55%) of the title compound **7d**.

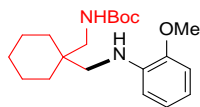
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.76 (d, *J* = 1.8 Hz, 1H), 7.71 (dd, *J* = 9.0, 5.9 Hz, 2H), 7.48 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.17 – 7.10 (m, 2H), 6.78 (dd, *J* = 7.8, 1.5 Hz, 1H), 6.68 (td, *J* = 7.7, 1.5 Hz, 1H), 6.61 (td, *J* = 7.7, 1.7 Hz, 1H), 6.40 (dd, *J* = 7.7, 1.7 Hz, 1H), 4.71 (s, 1H), 4.60 (q, *J* = 6.8 Hz, 1H), 3.91 (2s, *J* = 1.4 Hz, 6H), 1.62 (d, *J* = 6.7 Hz, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 157.5, 146.7, 140.8, 137.5, 133.9, 129.4, 129.2, 127.4, 125.1, 124.2, 121.3, 118.8, 116.5, 111.3, 109.4, 105.8, 55.6, 55.5, 53.6, 25.3.

**Physical State:** colorless oil.

**HRMS** (ESI): calcd for C<sub>20</sub>H<sub>21</sub>NO<sub>2</sub>Na [M+H]<sup>+</sup> 330.1470; found 330.1467.

***tert*-butyl ((1-(((2-methoxyphenyl)amino)methyl)cyclohexyl)methyl)carbamate (7e)**



Following the General Procedure C with the corresponding NHPI ester (0.4 mmol) and *o*-anisidine (0.2 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (15:1) as an eluent to afford 33 mg (48%) of the title compound **7e**.

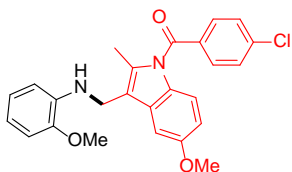
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 6.87 (td, *J* = 7.6, 1.4 Hz, 1H), 6.77 (dd, *J* = 7.9, 1.4 Hz, 1H), 6.66 (td, *J* = 7.7, 1.5 Hz, 1H), 6.60 (dd, *J* = 7.8, 1.5 Hz, 1H), 4.74 (br s, 1H), 4.39 (br s, 1H), 3.85 (s, 3H), 3.31 (dt, *J* = 12.3, 5.5 Hz, 1H), 3.16 – 2.95 (m, 3H), 1.93 (h, *J* = 5.9 Hz, 1H), 1.72 (qd, *J* = 11.9, 10.3, 5.1 Hz, 1H), 1.45 (s, 9H), 1.21 (t, *J* = 7.1 Hz, 2H), 0.92 (dd, *J* = 6.6, 3.7 Hz, 6H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 156.4, 147.1, 138.5, 121.4, 116.5, 109.9, 109.7, 79.2, 55.6, 46.3, 43.0, 40.0, 36.2, 28.5, 25.6, 23.1, 23.0.

**Physical State:** reddish brown oil.

**HRMS** (APPI): calcd for C<sub>20</sub>H<sub>33</sub>N<sub>2</sub>O<sub>3</sub> [M+H] 349.2486; found 349.2504.

**(4-chlorophenyl)(5-methoxy-3-(((2-methoxyphenyl)amino)methyl)-2-methyl-1H-indol-1-yl)methanone (7f)**



Following the General Procedure C with the corresponding NHPI ester (0.4 mmol) and *o*-anisidine (0.2 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (10:1) as an eluent to afford 35 mg (40%) of the title compound **7f**.

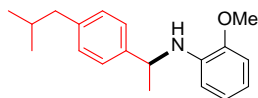
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.72 – 7.65 (m, 2H), 7.52 – 7.46 (m, 2H), 7.03 (d, *J* = 2.5 Hz, 1H), 6.97 (td, *J* = 7.6, 1.5 Hz, 1H), 6.90 (d, *J* = 8.9 Hz, 1H), 6.83 (ddd, *J* = 11.0, 7.9, 1.5 Hz, 2H), 6.75 (td, *J* = 7.6, 1.5 Hz, 1H), 6.69 (dd, *J* = 9.0, 2.6 Hz, 1H), 4.37 (s, 2H), 4.31 (s, 1H), 3.81 (s, 3H), 3.80 (s, 3H), 2.44 (s, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 168.5, 156.2, 147.0, 139.5, 138.5, 136.3, 134.0, 131.3, 131.1, 130.6, 129.3, 121.4, 117.0, 116.8, 115.1, 112.0, 110.0, 109.6, 101.4, 55.9, 55.5, 38.5, 13.4.

**Physical State:** light yellow oil.

**HRMS** (ESI): calcd for C<sub>25</sub>H<sub>23</sub>ClN<sub>2</sub>O<sub>3</sub>Na [M+Na]<sup>+</sup> 457.1295; found 457.1290.

***N*-(1-(4-isobutylphenyl)ethyl)-2-methoxyaniline (7g)**



Following the General Procedure B with the corresponding NHPI ester (0.2 mmol) and *o*-anisidine (0.4 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (10:1) as an eluent to afford 23 mg (41%) of the title compound **7g**.

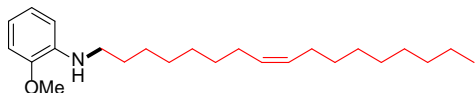
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.28 – 7.24 (m, 2H), 7.09 (d, *J* = 7.7 Hz, 2H), 6.77 (dd, *J* = 7.9, 1.4 Hz, 1H), 6.72 (td, *J* = 7.7, 1.5 Hz, 1H), 6.61 (td, *J* = 7.7, 1.6 Hz, 1H), 6.38 (dd, *J* = 7.8, 1.6 Hz, 1H), 4.60 (br s, 1H), 4.46 (q, *J* = 6.7 Hz, 1H), 3.89 (s, 3H), 2.44 (d, *J* = 7.2 Hz, 2H), 1.84 (dp, *J* = 13.6, 6.8 Hz, 1H), 1.54 (d, *J* = 6.6 Hz, 3H), 0.89 (d, *J* = 6.6 Hz, 6H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): 146.7, 142.8, 140.3, 137.5, 129.4, 125.7, 121.3, 116.3, 111.1, 109.4, 55.6, 53.1, 45.3, 30.4, 25.2, 22.6.

**Physical State:** colorless oil.

**HRMS** (ESI): calcd for C<sub>19</sub>H<sub>26</sub>NO [M+H]<sup>+</sup> 284.2014; found 284.2017.

**(Z)-N-(heptadec-8-en-1-yl)-2-methoxyaniline (7h)**



Following the General Procedure C with the corresponding NHPI ester (0.4 mmol) and *o*-anisidine (0.2 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (20:1) as an eluent to afford 29 mg (40%) of the title compound **7h**.

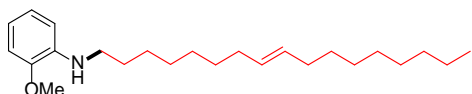
**<sup>1</sup>H NMR** (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 6.83 (td, *J* = 7.8, 2.6 Hz, 1H), 6.75 (dd, *J* = 8.0, 2.7 Hz, 1H), 6.65 – 6.50 (m, 2H), 5.47 – 5.33 (m, 2H), 4.17 (br s, 1H), 3.87 (s, 3H), 3.22 – 2.98 (m, 2H), 2.18 – 1.98 (m, 4H), 1.68 – 1.62 (m, 2H), 1.46 – 1.26 (m, 20H), 0.95 – 0.85 (m, 3H).

**<sup>13</sup>C NMR** (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 147.2, 139.1, 130.4, 130.2, 121.6, 116.2, 109.9, 109.8, 55.8, 44.1, 32.4, 30.2, 30.2, 30.0, 30.0, 29.8, 29.8, 29.7, 27.7, 27.6, 27.6, 26.0, 23.1, 14.3.

**Physical State:** pale yellow oil.

**HRMS** (ESI): calcd for C<sub>24</sub>H<sub>42</sub>NO [M+H]<sup>+</sup> 360.3266; found 360.3265.

**(E)-N-(heptadec-8-en-1-yl)-2-methoxyaniline (7i)**



Following the General Procedure C with the corresponding NHPI ester (0.4 mmol) and *o*-anisidine (0.2 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (20:1) as an eluent to afford 23 mg (32%) of the title compound **7i**.

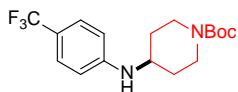
**<sup>1</sup>H NMR** (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 6.82 (td, *J* = 7.7, 2.6 Hz, 1H), 6.75 (dd, *J* = 7.5, 2.3 Hz, 1H), 6.63 – 6.55 (m, 2H), 5.42–5.31 (m, 2H), 4.17 (br s, 1H), 3.82 (s, 3H), 3.10 (t, *J* = 7.1 Hz, 2H), 2.00 – 1.96 (m, 4H), 1.66 – 1.62 (m, 2H), 1.43 – 1.28 (m, 20H), 0.89 (t, *J* = 6.9 Hz, 3H).

**<sup>13</sup>C NMR** (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 147.2, 139.1, 130.9, 130.7, 121.6, 116.2, 109.9, 109.7, 55.8, 44.1, 33.0, 33.0, 32.4, 30.1, 30.1, 30.0, 30.0, 29.8, 29.6, 29.5, 27.6, 23.1, 14.3.

**Physical State:** pale yellow solid.

**HRMS** (ESI): calcd for C<sub>24</sub>H<sub>42</sub>NO [M+H]<sup>+</sup> 360.3266; found 360.3268.

***tert*-butyl 4-((4-(trifluoromethyl)phenyl)amino)piperidine-1-carboxylate (8a)**



Following the General Procedure B with the corresponding NHPI ester (0.2 mmol) and 4-(trifluoromethyl)aniline (0.4 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (10:1) as an eluent to afford 52 mg (75%) of the title compound **8a**.

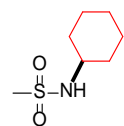
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.40 (d,  $J = 8.5$  Hz, 2H), 6.61 (d,  $J = 8.3$  Hz, 2H), 4.12 – 4.00 (m, 2H), 3.46 (tt,  $J = 10.3, 4.0$  Hz, 1H), 2.93 (t,  $J = 12.6$  Hz, 2H), 2.06 – 1.98 (m, 2H), 1.47 (s, 9H), 1.40 – 1.33 (m, 2H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  154.9, 134.5, 126.9 (q,  $J = 3.7$  Hz), 123.7, 79.9, 32.2, 28.6, 28.6.

**Physical State:** white solid.

Spectral data match those previously reported.<sup>36</sup>

### ***N*-cyclohexylmethanesulfonamide (S1)**



An oven-dried 15 mL vial equipped with a Teflon-coated magnetic stir bar was sequentially charged with corresponding NHPI ester (0.5 mmol),  $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$  (1 mol%),  $\text{Cu}(\text{MeCN})_4\text{PF}_6$  (50 mol%), **L3** (30 mol%), MeCN (0.1 M), methanesulfonamide (1.5 mmol),  $\text{Et}_3\text{N}$  (5 equiv) in the glove box. The vial was sealed with a screw cap and removed from the glove box. Then the vial was placed 3 cm away from one blue LED, and irradiated under fan cooling (maintain the temperature at room temperature) for 20 h. After the reaction, the resulting dark brown reaction mixture was acidified with saturated  $\text{NH}_4\text{Cl}$  solution (~1 mL) and then neutralized with saturated  $\text{NaHCO}_3$  solution (~1.5 mL). The crude product in the aqueous fraction was extracted with EtOAc (~10 mL). The aqueous fraction was further washed with EtOAc (3 x ~5 mL). The combined organic fractions were concentrated *in vacuo* with the aid of a rotary evaporator. The crude product residue was purified by flash chromatography column using hexanes / EtOAc (40:1) as an eluent to afford 14 mg (16%) of the title compound **S1**.

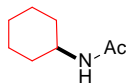
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  4.21 (s, 1H), 3.31 (dt,  $J = 10.7, 7.6, 4.0$  Hz, 1H), 2.97 (s, 3H), 2.05 – 1.88 (m, 2H), 1.73 (dt,  $J = 13.5, 3.9$  Hz, 2H), 1.65 – 1.58 (m, 1H), 1.42 – 1.10 (m, 5H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  53.0, 42.3, 34.6, 25.3, 24.9.

Spectral data match those previously reported.



### ***N*-cyclohexylacetamide (S2)**



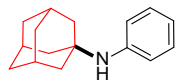
An oven-dried 15 mL vial equipped with a Teflon-coated magnetic stir bar was sequentially charged with corresponding NHPI ester (1 mmol), Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (1 mol%), Cu(MeCN)<sub>4</sub>PF<sub>6</sub> (50 mol%), **L3** (30 mol%), MeCN (0.1 M), acetamide (3 mmol), Et<sub>3</sub>N (5 equiv) in the glove box. The vial was sealed with a screw cap and removed from the glove box. Then the vial was placed 3 cm away from one blue LED, and irradiated under fan cooling (maintain the temperature at room temperature) for 20 h. After the reaction, the resulting dark brown reaction mixture was acidified with saturated NH<sub>4</sub>Cl solution (~1 mL) and then neutralized with saturated NaHCO<sub>3</sub> solution (~1.5 mL). The crude product in the aqueous fraction was extracted with EtOAc (~10 mL). The aqueous fraction was further washed with EtOAc (3 x ~5 mL). The combined organic fractions were concentrated *in vacuo* with the aid of a rotary evaporator. The crude product residue was purified by flash chromatography column using hexanes / EtOAc (40:1) as an eluent to afford 13 mg (9%) of the title compound **S2**.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 5.33 (s, 1H), 3.84 – 3.66 (m, 1H), 1.95 (s, 5H), 1.72 – 1.57 (m, 3H), 1.44 – 1.27 (m, 2H), 1.23 – 1.02 (m, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 169.2, 48.4, 33.4, 25.7, 25.0, 23.8.

Spectral data match those previously reported.

### ***N*-phenyladamantan-1-amine (S3)**



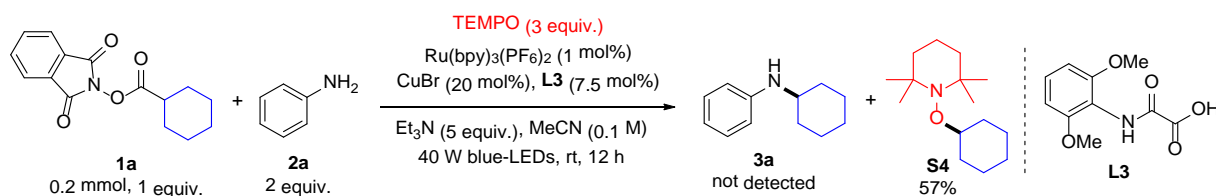
Following the General Procedure B with the corresponding NHPI ester (1.0 mmol) and 4-(trifluoromethyl)aniline (2.0 mmol). The crude product was purified by preparative TLC using hexanes / EtOAc (20:1) as an eluent to afford 21 mg (9%) of the title compound **S3**.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.20 – 7.10 (m, 2H), 6.80 (d, *J* = 7.7 Hz, 3H), 3.05 (br s, 1H), 2.15 – 2.03 (m, 3H), 1.88 (d, *J* = 2.9 Hz, 6H), 1.75 – 1.60 (m, 6H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 146.2, 128.9, 119.3, 119.2, 52.4, 43.6, 36.6, 29.9.

Spectral data match those previously reported.<sup>36</sup>

## TEMPO trapping experiment

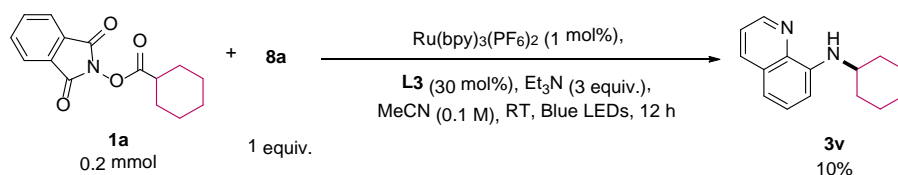


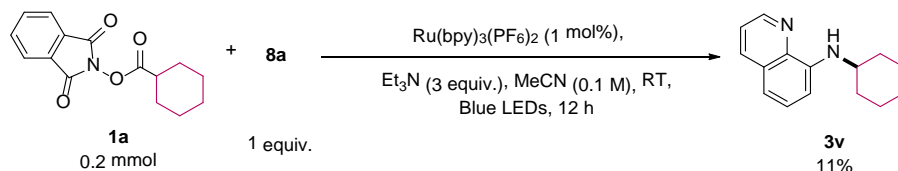
An oven-dried 15 mL vial equipped with a Teflon-coated magnetic stir bar was sequentially charged with NHPI ester **1a** (0.2 mmol),  $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$  (1 mol%, 2  $\mu\text{mol}$ , 1.8 mg),  $\text{CuBr}$  (20 mol%, 0.04 mmol, 5.8 mg), ligand **L3** (30 mol%, 0.06 mmol, 13.5 mg), MeCN (2 mL), **2a** (2 equiv, 0.4 mmol),  $\text{Et}_3\text{N}$  (5 equiv, 1 mmol, 139  $\mu\text{L}$ ), TEMPO (3 equiv., 0.6 mmol) in the glove box. The vial was sealed with a screw cap and removed from the glove box. Then the vial was placed 3 cm away from one blue LED, and irradiated under fan cooling (maintain the temperature at room temperature) for 12 h. After irradiation, the brown reaction mixture was submitted to mass spectrometry (LC-MS) without any further work-up. Desired product **3a** was not detected and TEMPO trapped product **S4** (57% GC yield) was found through mass spectrometry (Supplementary Figure 4).

## Preparation of Cu(II) complex (**9a**)

To a test tube was added a solution of 8-aminoquinoline (0.144 g, 1.00 mmol) in  $\text{CH}_2\text{Cl}_2$  (15  $\text{cm}^3$ ) before layer MeOH solvent (2 mL) on the top, then a methanolic solution (5  $\text{cm}^3$ ) of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (0.170 g, 1.00 mmol) was carefully layered on the top, the tube was sealed and stood at room temperature for a week. Green block-like crystal **9a** were observed on the wall of the tube, and collected by decanting the solvent, washed with methanol and dried in air. The structure of the compound was confirmed by X-ray crystallography (Supplementary Figure 5), and is identical to the literature report.<sup>37</sup>

## Reactivity of Cu(II) complex (**9a**)

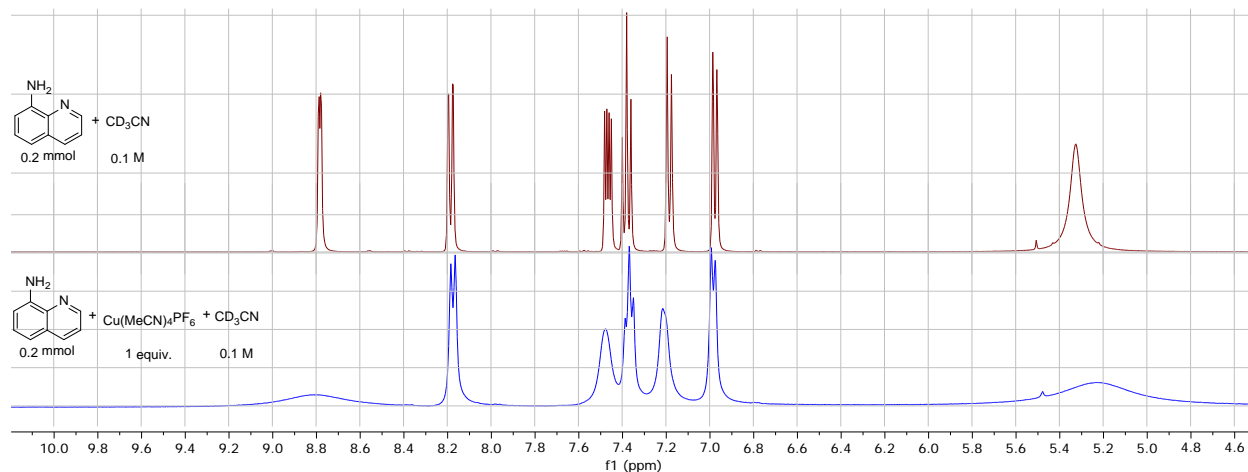




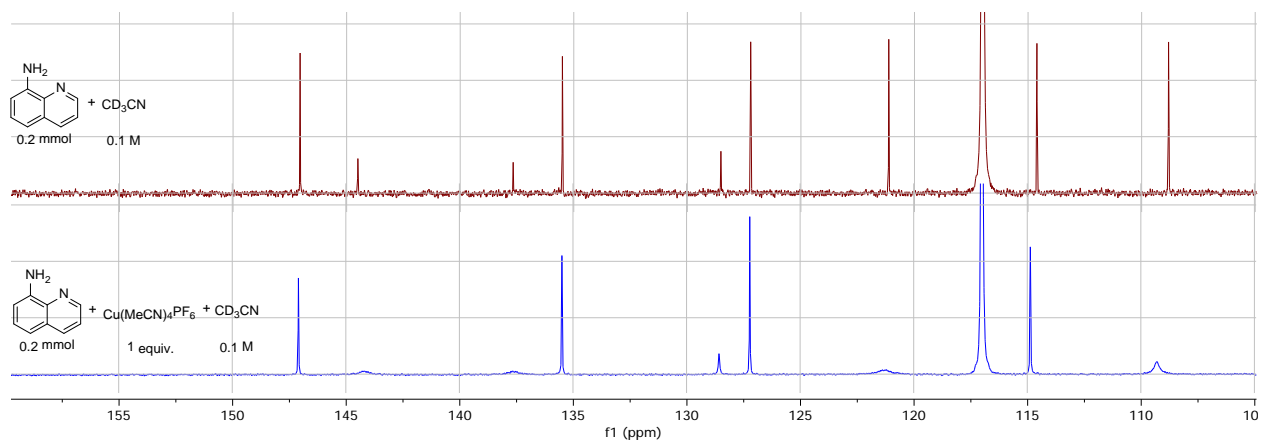
An oven-dried 15 mL vial equipped with a Teflon-coated magnetic stir bar was sequentially charged with NHPI ester **1a** (0.2 mmol, 55 mg),  $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$  (1 mol%, 2  $\mu\text{mol}$ , 1.8 mg), **L3** (30 mol%, 6.8 mg) or without **L3**, **9a** (1 equiv, 0.2 mmol), MeCN (2 mL),  $\text{Et}_3\text{N}$  (3 equiv, 80  $\mu\text{L}$ ), dodecane (1 equiv, 45  $\mu\text{L}$ , internal standard) in the glove box. The vial was sealed with a screw cap and removed from the glove box. Then the vial was placed 3 cm away from one blue LED, and irradiated under fan cooling (maintain the temperature at room temperature) for 12 h. After the reaction, GC analysis of the mixture.

### Preparation of Cu(I) complex

An oven-dried 15 mL vial equipped with a Teflon-coated magnetic stir bar was charged 8-aminoquinoline (0.2 mmol, 29 mg) and  $\text{CD}_3\text{CN}$  (1 mL) in the glove box. The vial was stirring until all 8-aminoquinoline dissolved and transferred the solution to a NMR tube. Then analysis of  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR were conducted (red spectra). Afterwards, the solution was transferred to previous vial,  $\text{Cu}(\text{MeCN})_4\text{PF}_6$  (0.2 mmol, 76 mg) was added in the glove box. The vial was stirring vigorously until a transparent solution to obtain the Cu(I)-amido complex solution (solution color changed to light yellow). Then transferred the solution to a NMR tube and analysis of  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR were conducted (blue spectra).

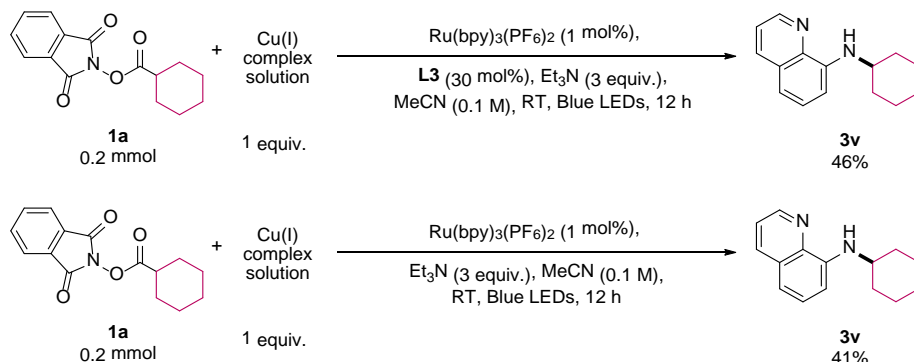


$^1\text{H}$  NMR spectra showing formation of a Cu(I) complex



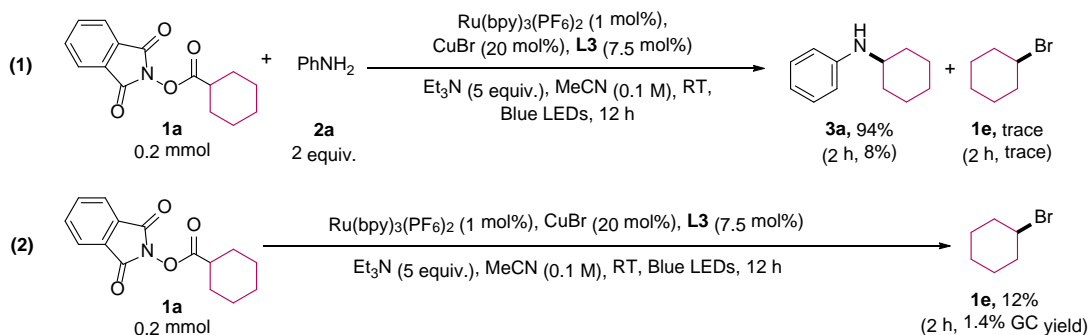
$^{13}\text{C}$  NMR spectra showing formation of a Cu(I) complex.

### Reactivity of in-situ generated Cu(I) complex.



An oven-dried 15 mL vial equipped with a Teflon-coated magnetic stir bar was sequentially charged with  $\text{Cu}(\text{MeCN})_4\text{PF}_6$  (0.2 mmol, 76 mg), 8-aminoquinoline (1 equiv, 29 mg) and MeCN (1 mL) in the glove box, stirring vigorously for 15 min to obtain the Cu(I) complex solution (solution color changed to light yellow). Another oven-dried 15 mL vial equipped with a Teflon-coated magnetic stir bar was sequentially charged with NHPI ester **1a** (0.2 mmol, 55 mg),  $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$  (1 mol%, 2  $\mu\text{mol}$ , 1.8 mg), **L3** (30 mol%, 6.8 mg) or without **L3**, MeCN (1 mL),  $\text{Et}_3\text{N}$  (3 equiv, 80  $\mu\text{L}$ ), dodecane (1 equiv, 45  $\mu\text{L}$ , internal standard) in the glove box. Then add Cu(I) complex solution into this mixture. The vial was sealed with a screw cap and removed from the glove box. Then the vial was placed 3 cm away from one blue LED, and irradiated under fan cooling (maintain the temperature at room temperature) for 12 h. After the reaction, GC analysis of the mixture.

## Probing the reactions of alkyl radical with CuBr prior the Cu-amido complex formation

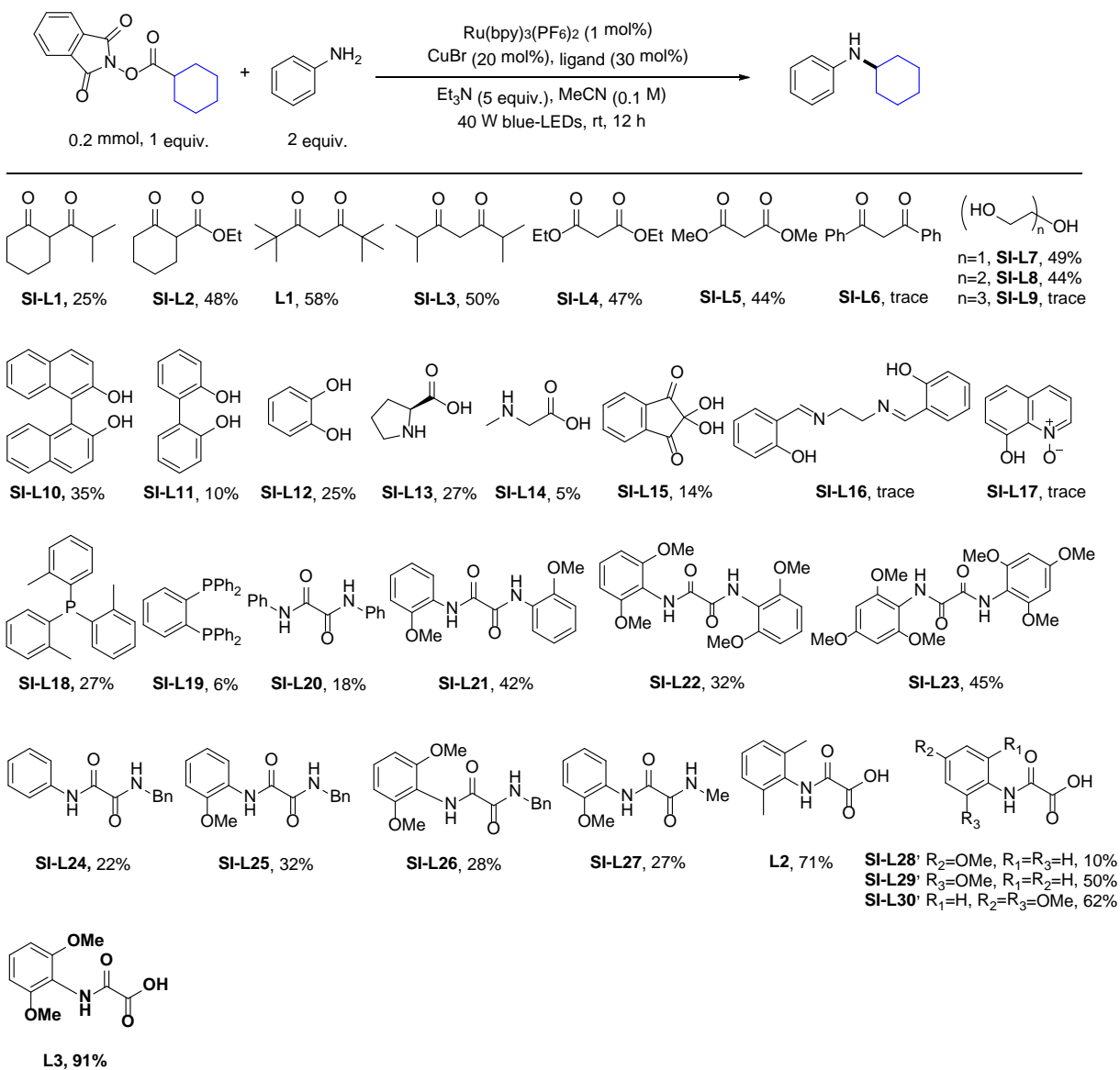


Follow the General Procedure B, An oven-dried 15 mL vial equipped with a Teflon-coated magnetic stir bar was sequentially charged with NHPI ester (0.2 mmol), Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (1 mol%), CuBr (20 mol%), **L3** (7.5 mol%), MeCN (0.1 M), aniline (2 equiv) or without aniline, Et<sub>3</sub>N (5 equiv) in the glove box. The vial was sealed with a screw cap and removed from the glove box. Then the vial was placed 3 cm away from one blue LED, and irradiated under fan cooling (maintain the temperature at room temperature) for 12 h or 2 h. After the reaction, GC analysis of the mixture.

In the test reaction under standard conditions, the amination has a yield of 94% (8% in 2 h), while bromocyclohexane **1e** has less than 1% GC yield (trace in 2 h). However, in the absence of aniline, i.e., Cu-amido complex, **1e** was obtained in 12% yield (1.4% in 2 h). This result suggests that if alkyl radical react with Cu(I) prior to the amido-complex, then a certain amount of alkyl bromide would be formed, from a Cu(II) alkyl bromide intermediate.

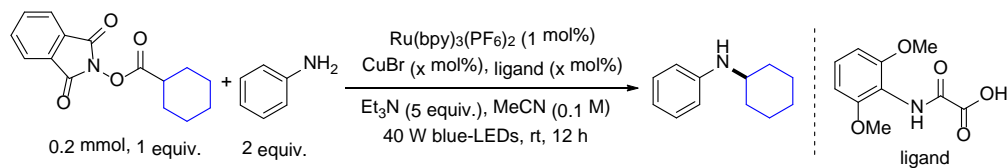
# Supplementary Tables

## Supplementary Table 1. Optimization of ligands



\* Corrected GC yield using *n*-dodecane as an internal standard

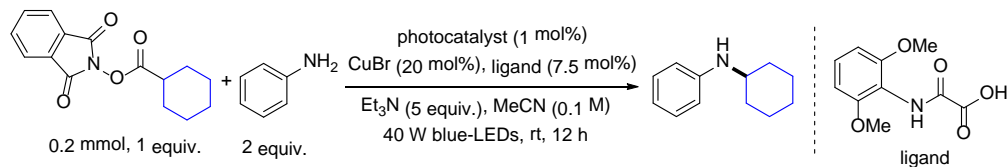
## Supplementary Table 2. Optimization of Cu(I)/ligand ratio.



entry	CuBr/ligand ratio	GC yield <sup>a</sup>
1	20/30	91%
2	10/20	70%
3	5/10	48%
4	<b>20/7.5</b>	<b>94%</b>
5	20/5	81%
6	20/0	15%

<sup>a</sup>Corrected GC yield using *n*-dodecane as an internal standard

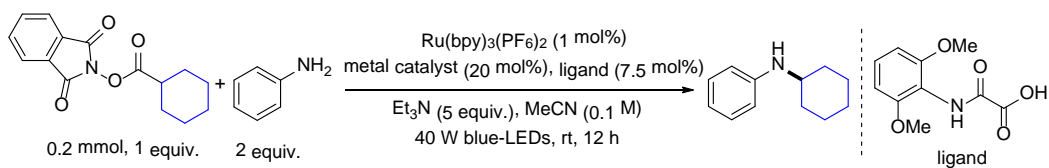
## Supplementary Table 3. Optimization of photocatalysts.



entry	Photocatalyst	GC yield <sup>a</sup>
1	Ru(bpy) <sub>3</sub> (PF <sub>6</sub> ) <sub>2</sub>	94%
2	Ru(bpy) <sub>3</sub> Cl <sub>2</sub> •6H <sub>2</sub> O	70%
3	[Ir{dF(CF <sub>3</sub> )ppy} <sub>2</sub> (dtbpy)]PF <sub>6</sub>	40%
4	<i>fac</i> -Ir(ppy) <sub>3</sub>	55%
5	Ru(Phen) <sub>3</sub> Cl <sub>2</sub>	29%
6	Ru(bpz) <sub>3</sub> (PF <sub>6</sub> ) <sub>2</sub>	trace
7	Ru(bpm) <sub>3</sub> (Cl) <sub>2</sub>	trace
8	Eosin	trace
9	Eosin B	trace
10	Eosin Y	trace
11	9,10-anthracenedicarbonitrile	trace

<sup>a</sup>Corrected GC yield using *n*-dodecane as an internal standard

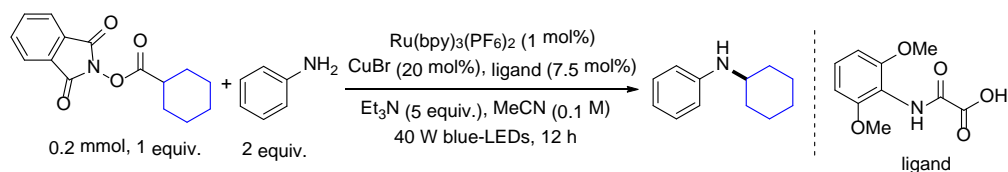
### Supplementary Table 4. Optimization of transition metal catalysts.



entry	transition metal	GC yield <sup>a</sup>
1	CuBr	94%
2	CuCl	83%
3	CuI	76%
4	Cu	trace
5	CuBr <sub>2</sub>	43%
6	NiCl <sub>2</sub> •6H <sub>2</sub> O	trace
7	CoCl <sub>2</sub> •6H <sub>2</sub> O	trace
8	FeCl <sub>2</sub> •4H <sub>2</sub> O	trace
9	FeCl <sub>2</sub>	trace

<sup>a</sup>Corrected GC yield using *n*-dodecane as an internal standard

### Supplementary Table 5. Optimization of temperatures.

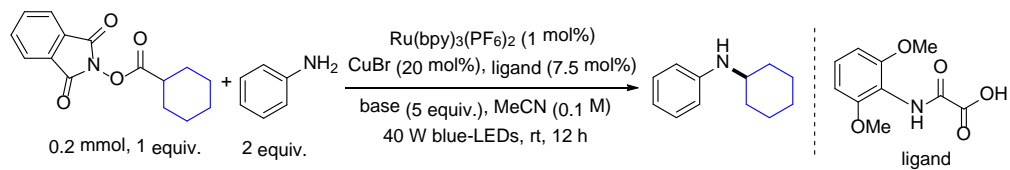


entry	temperature	GC yield <sup>a</sup>
1	rt	94%
2	55 °C	35%
3	0	68%

<sup>a</sup>Corrected GC yield using *n*-dodecane as an internal standard



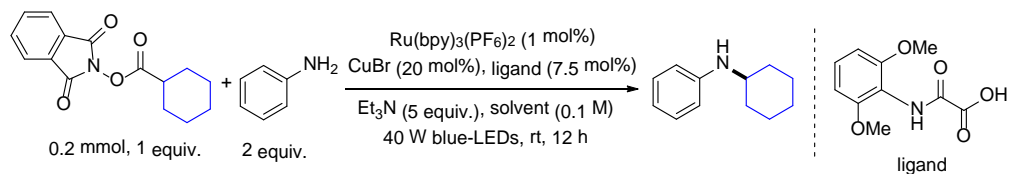
## Supplementary Table 6. Optimization of bases.



entry	base	GC yield <sup>a</sup>
1	Et <sub>3</sub> N	94%
2	DIPEA	trace
3	DABCO	trace
4	triethanoamine	trace
5	Na <sub>2</sub> CO <sub>3</sub>	trace
6	K <sub>2</sub> CO <sub>3</sub>	trace
7	K <sub>3</sub> PO <sub>4</sub>	trace
8	KO <sup>t</sup> Bu	trace
9	NaO <sup>t</sup> Bu	trace
10	KOH	trace
11	Cs <sub>2</sub> CO <sub>3</sub>	trace

<sup>a</sup>Corrected GC yield using *n*-dodecane as an internal standard

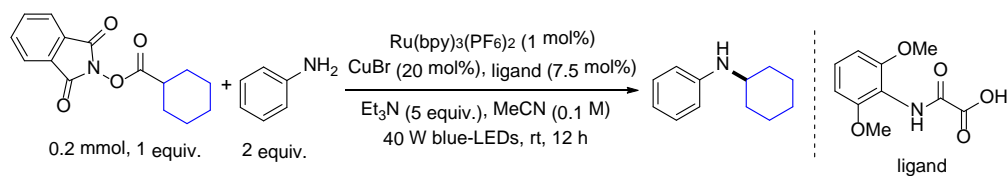
## Supplementary Table 7. Optimization of solvents.



entry	solvent	GC yield <sup>a</sup>
1	MeCN	94%
2	CH <sub>2</sub> Cl <sub>2</sub>	trace
3	benzene	21%
4	toluene	trace
5	DMA	32%
6	dioxane	trace

<sup>a</sup>Corrected GC yield using *n*-dodecane as an internal standard

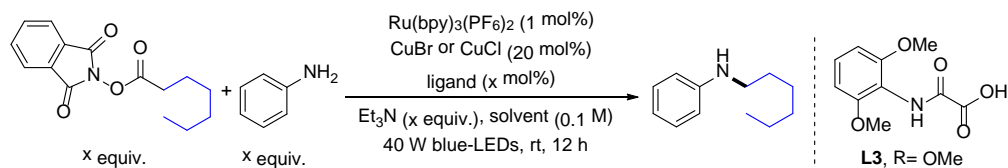
## Supplementary Table 8. Control experiments



entry	variation from the "standard conditions"	GC yield <sup>a</sup>
1	none	94%
2	no light	NR
3	no Ru(bpy) <sub>3</sub> (PF <sub>6</sub> ) <sub>2</sub>	NR
4	no CuBr	NR
5	no ligand	15%

<sup>a</sup>Corrected GC yield using *n*-dodecane as an internal standard

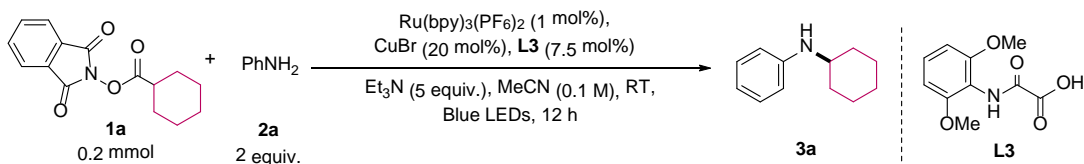
## Supplementary Table 9. Optimization of reaction parameters for primary NHPI ester

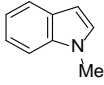


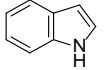


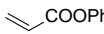





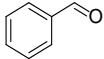


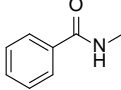




entry	RAE <sup>a</sup> /aniline ratio	copper source	ligand	base loading	GC yield <sup>b</sup>
1	1/2	CuBr	L3 (30 mol%)	5 equiv.	23%
2	2/1	CuBr	L3 (30 mol%)	3 equiv.	35%
3	2/1	CuCl	-	3 equiv.	64%

<sup>a</sup>REA (redox active ester). <sup>b</sup>Corrected GC yield using *n*-dodecane as an internal standard

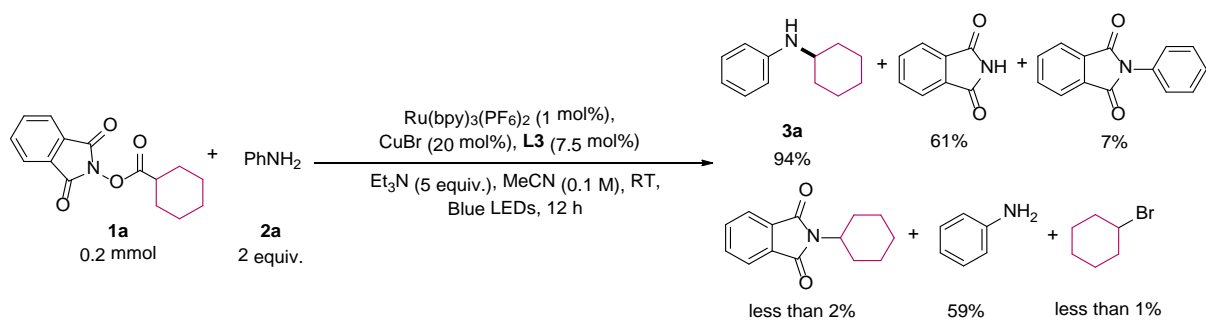
## Supplementary Table 10. Further test of functional-group tolerance using the screening method developed by Glorius



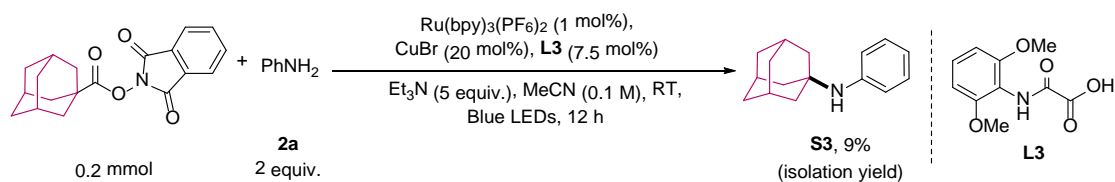
Entry	Additive	Yield of <b>3a</b> (%) <sup>*</sup>	Additive remaining (%) <sup>*</sup>
1	None	94	-
2		85 	100 
3		49 	64 
4		25 	20 
5		80 	95 
6		62 	36 
7		26 	70 

The standard reaction is undertaken in the presence of one molar equivalent of the given additive. The yield of **3a**, and the additive remaining after reaction is given. Color coding: green '✓' (above 66%), yellow '−' (34 - 66%), red '✗' (below 34%). \* GC yield.

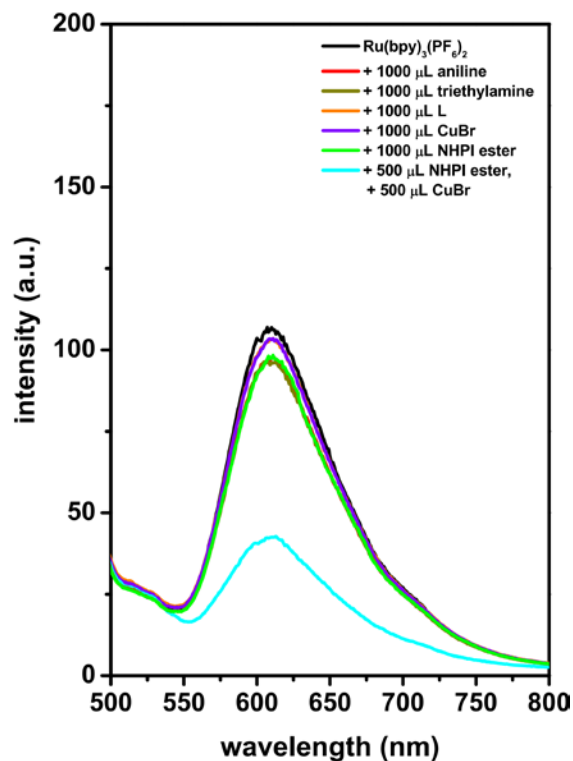
## Supplementary Figures



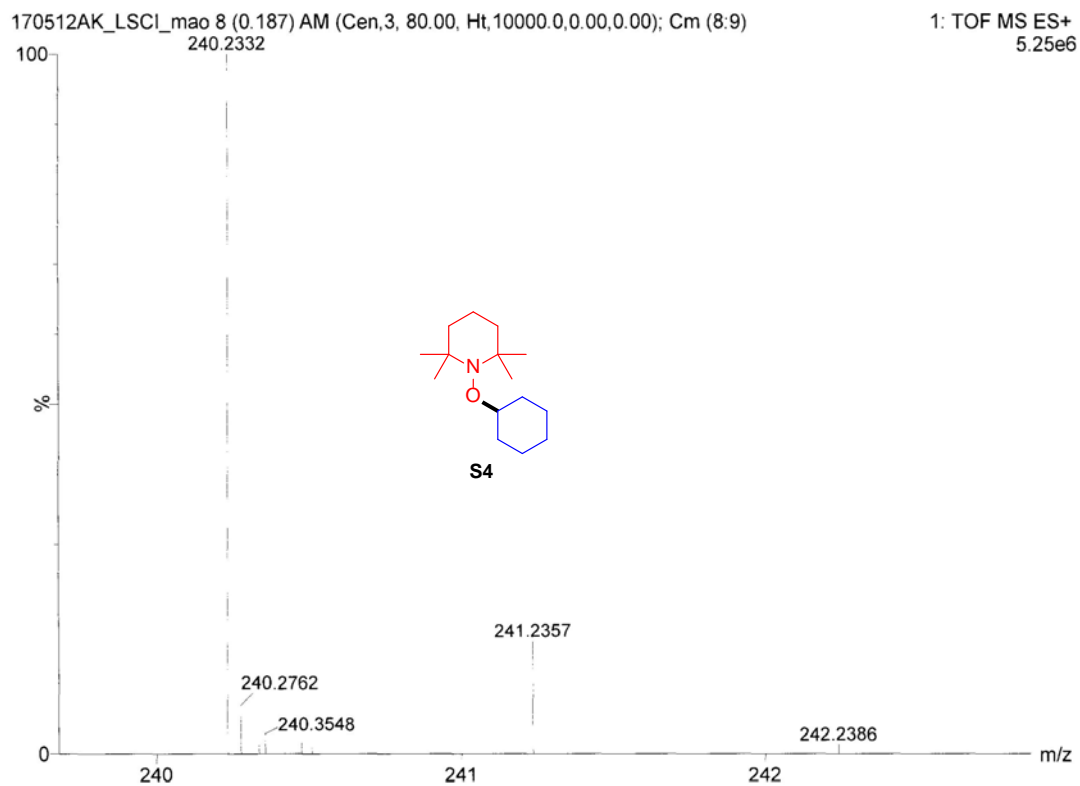
**Supplementary Figure 1. Conversion and product distribution for the test reaction.**



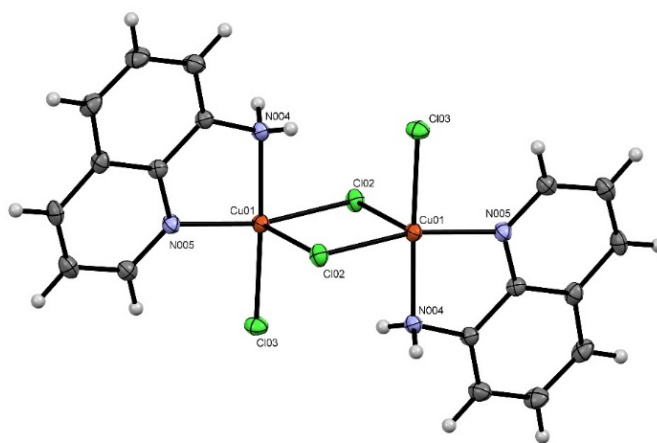
**Supplementary Figure 2. Decarboxylative amination of a tertiary alkyl redox-active ester.**



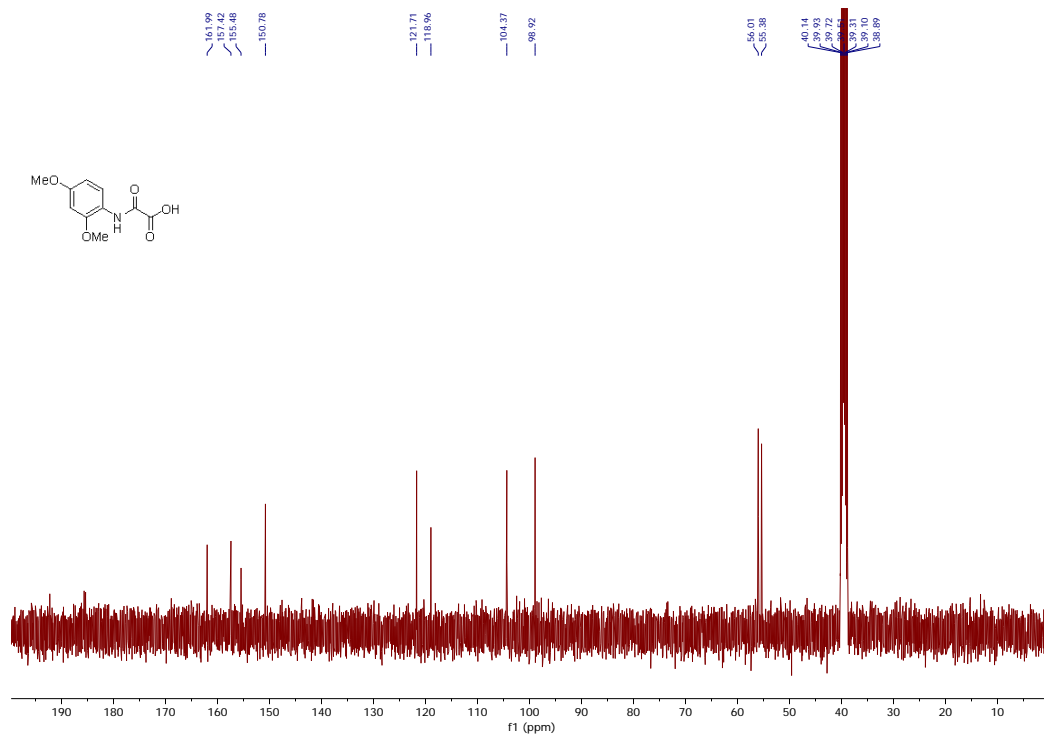
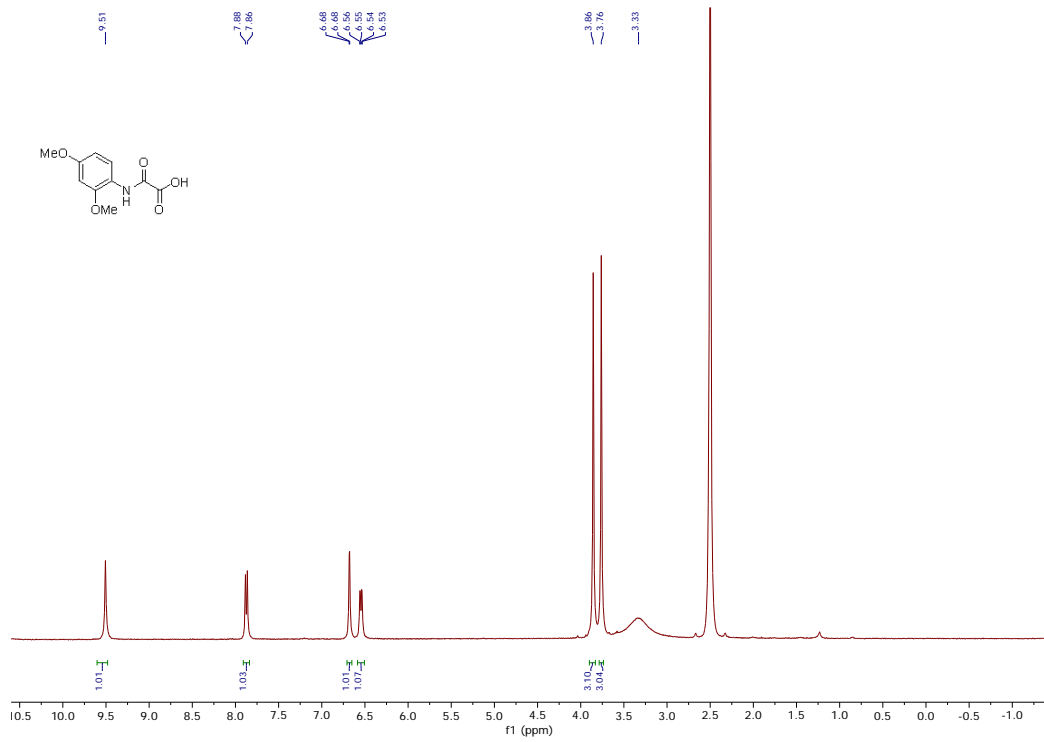
**Supplementary Figure 3. Fluorescence quenching experiments.** Fluorescence spectra of 1000 μL [Ru(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> (15 μM in MeCN) upon addition of 1000 μL aniline (100 mM in MeCN); 1000 μL triethylamine (100 mM in MeCN); 1000 μL L3 (10 mM in MeCN); 1000 μL CuBr (10 mM in MeCN); 1000 μL NHPI ester (50 mM in MeCN); 500 μL NHPI ester (50 mM in MeCN) + 500 μL CuBr (10 mM in MeCN), respectively.



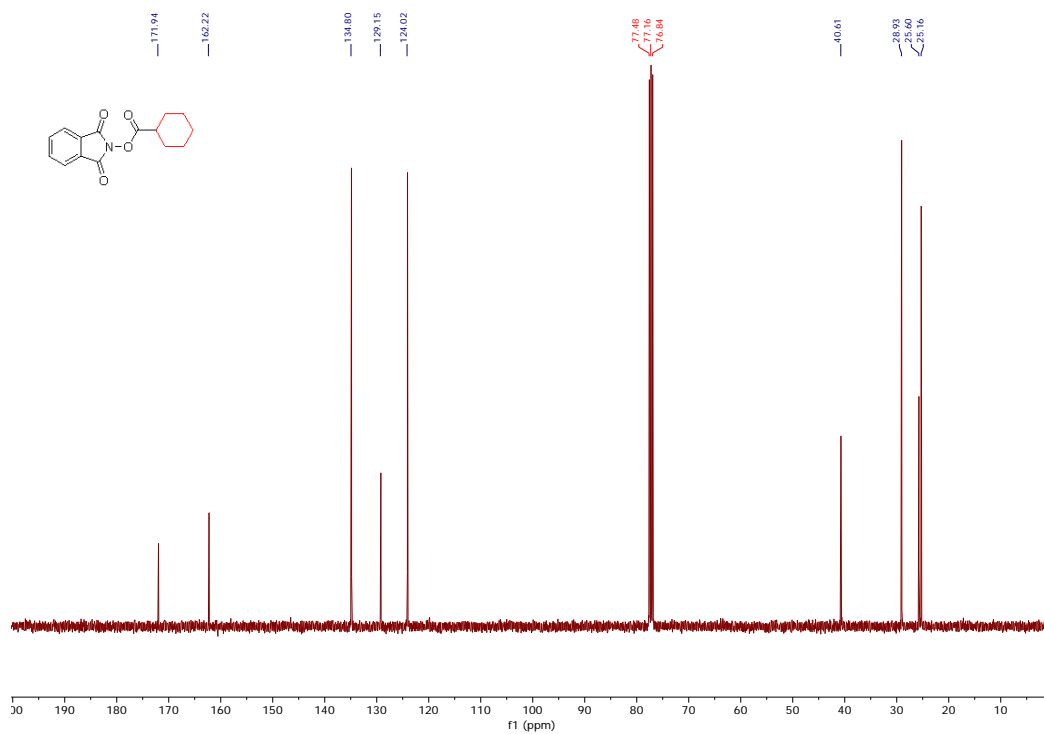
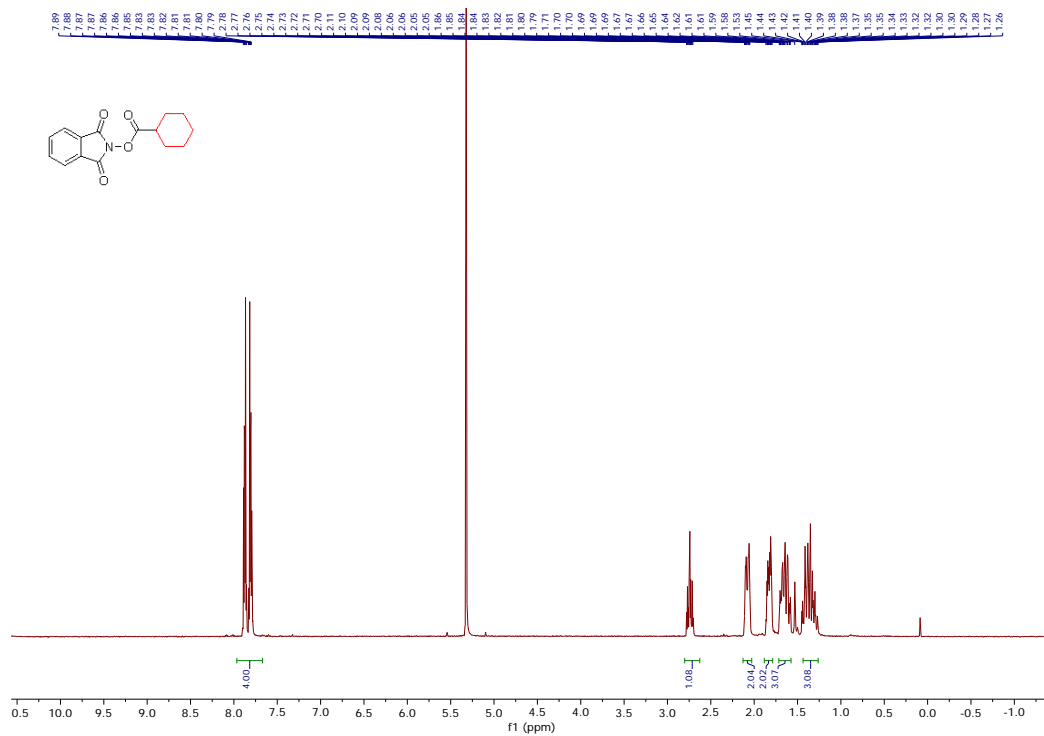
**Supplementary Figure 4. TEMPO trapping mass spectrum. HRMS (ESI):** calcd for  $C_{15}H_{30}NO$   $[M+H]^+$  240.2327; found 240.2332.



**Supplementary Figure 5. X-ray crystallography of 9a**

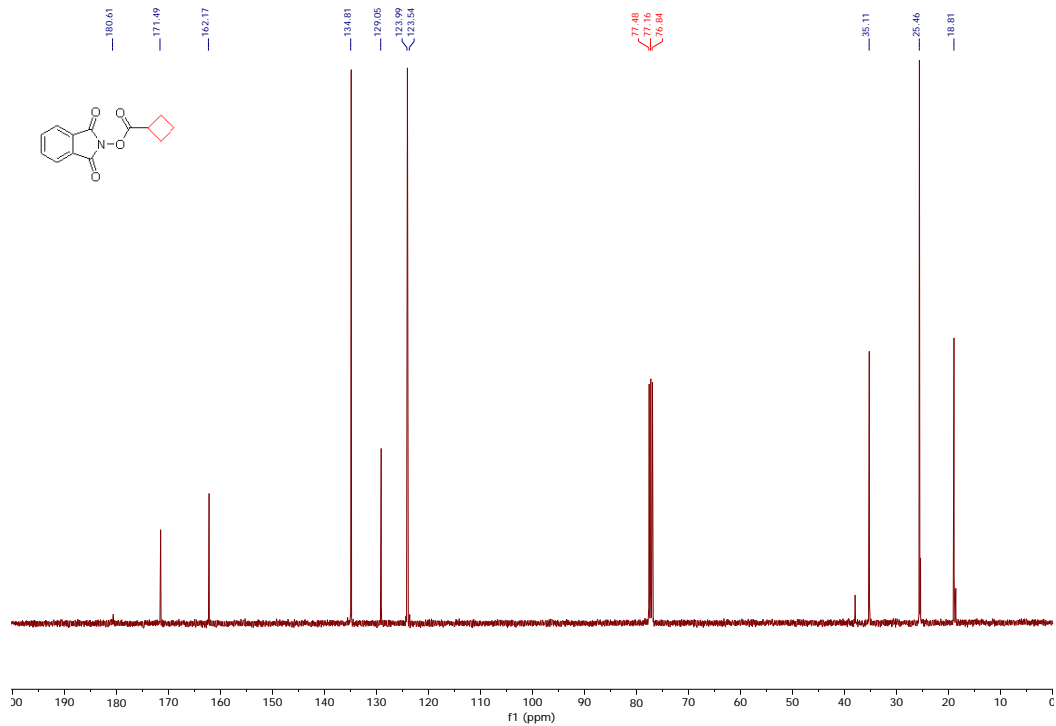
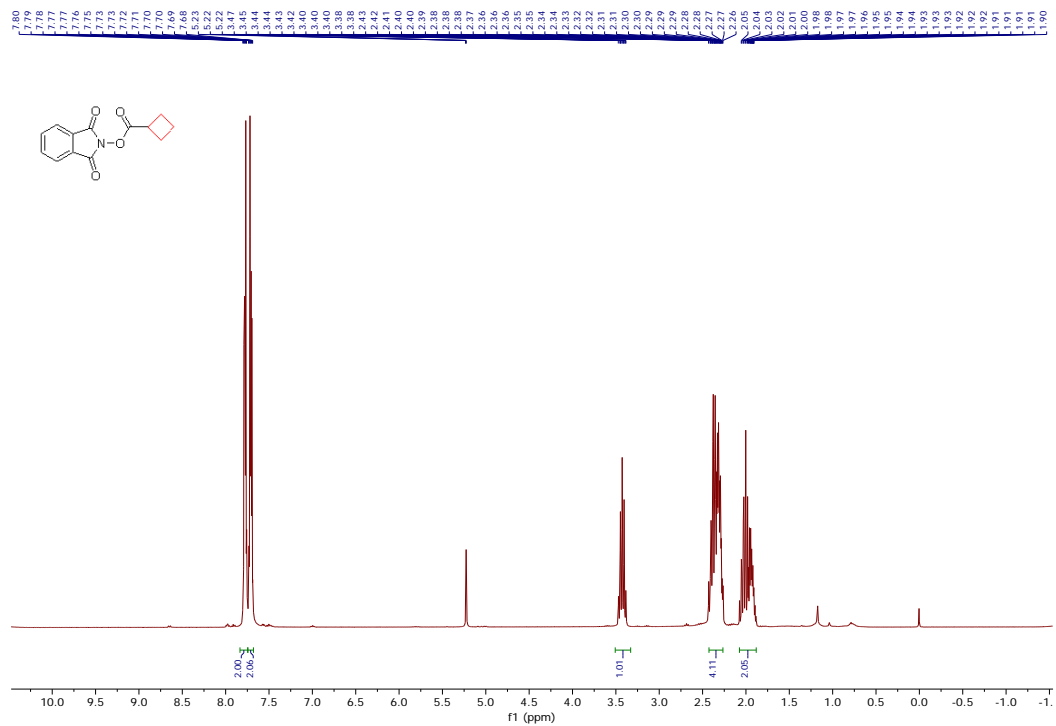


**Supplementary Figure 6. NMR spectra of 2-((2,4-dimethoxyphenyl)amino)-2-oxoacetic acid (SI-L30)**

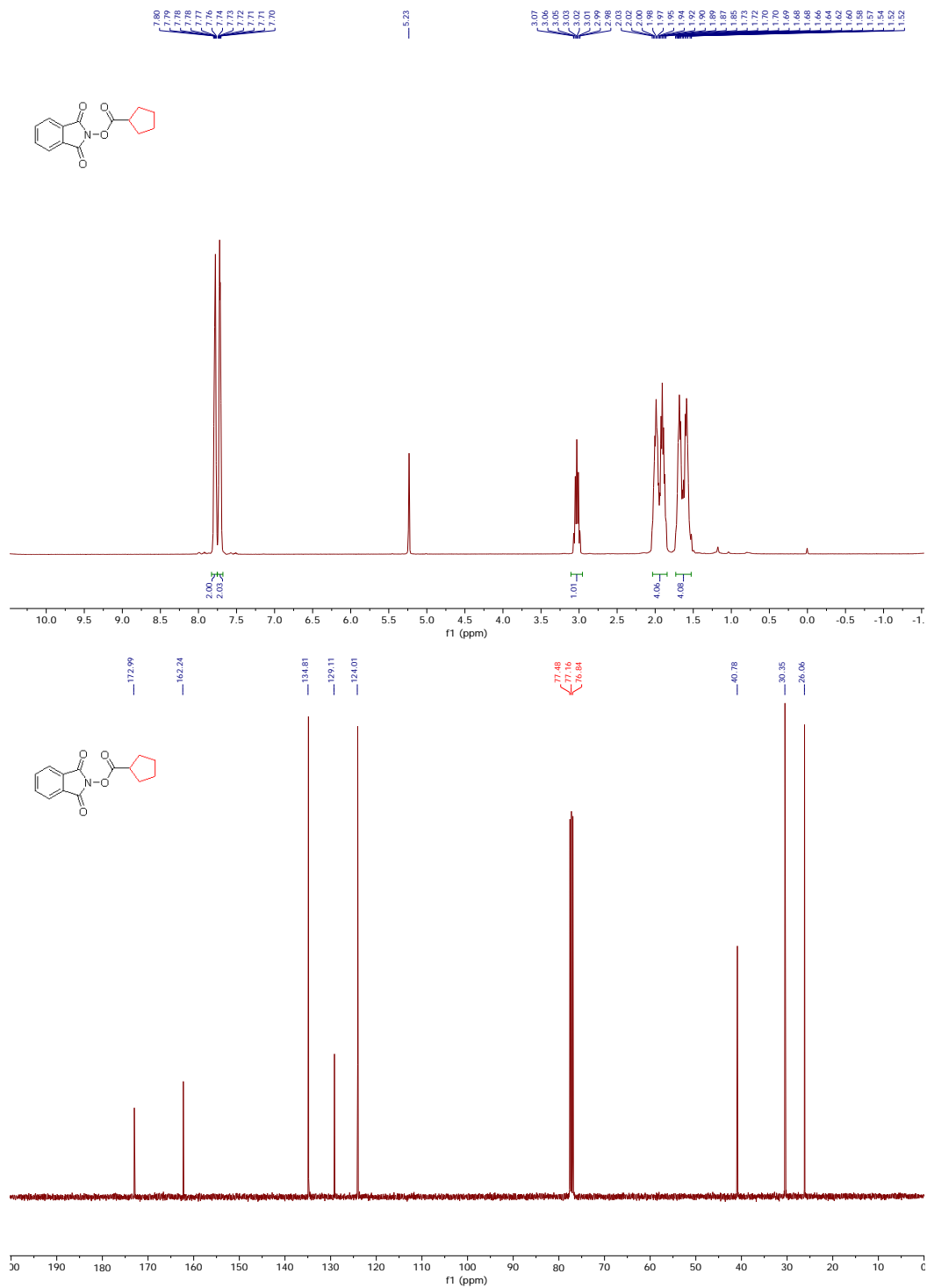


**Supplementary Figure 7. NMR spectra of 1,3-dioxoisindolin-2-yl cyclohexanecarboxylate**

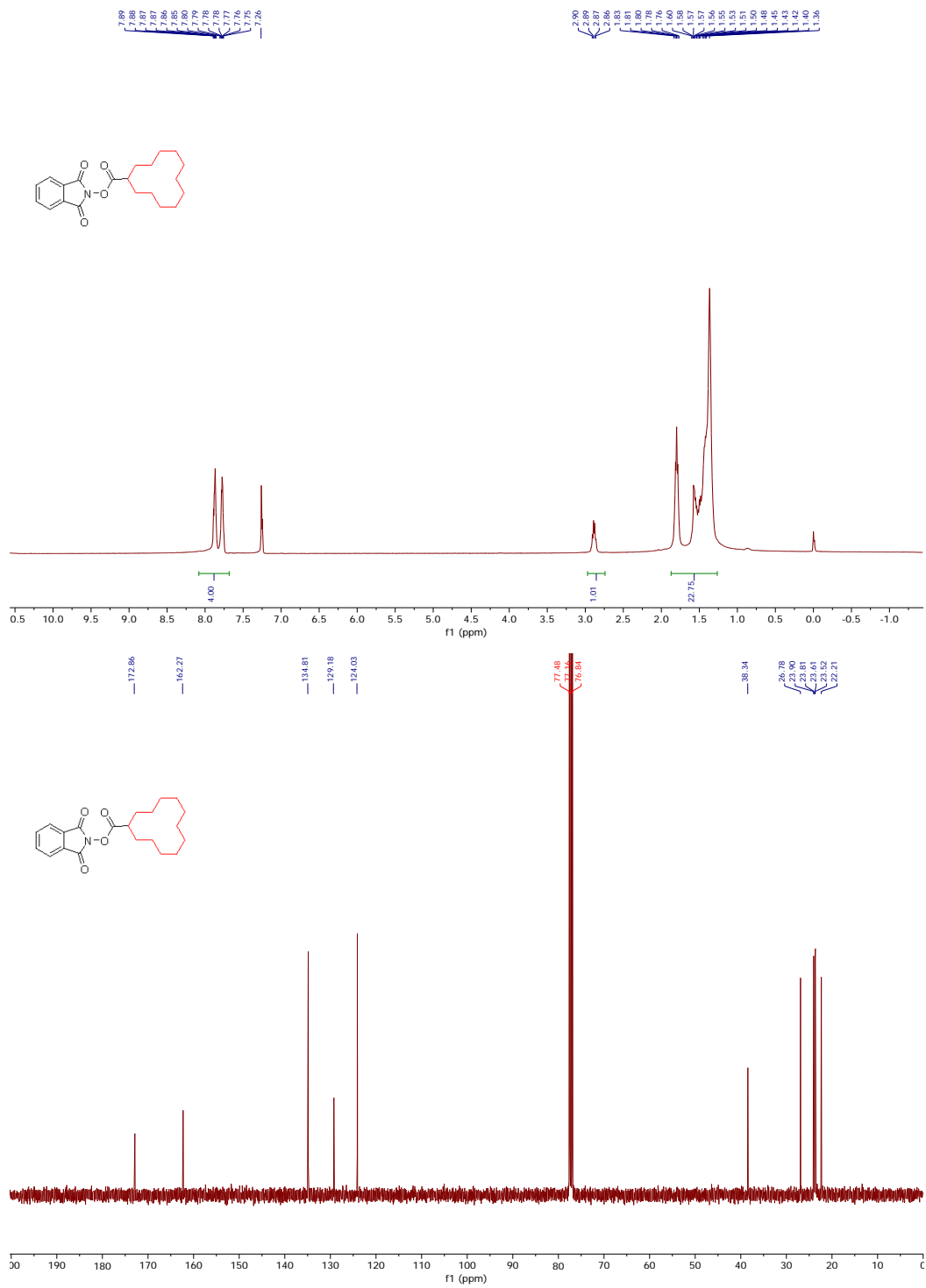




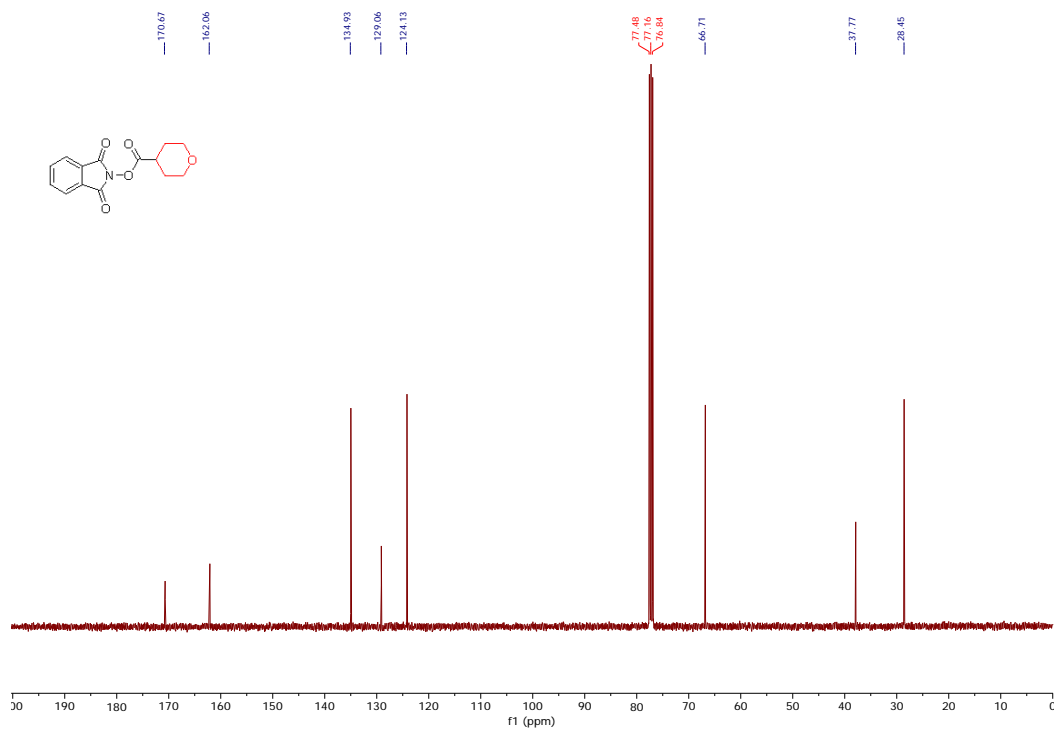
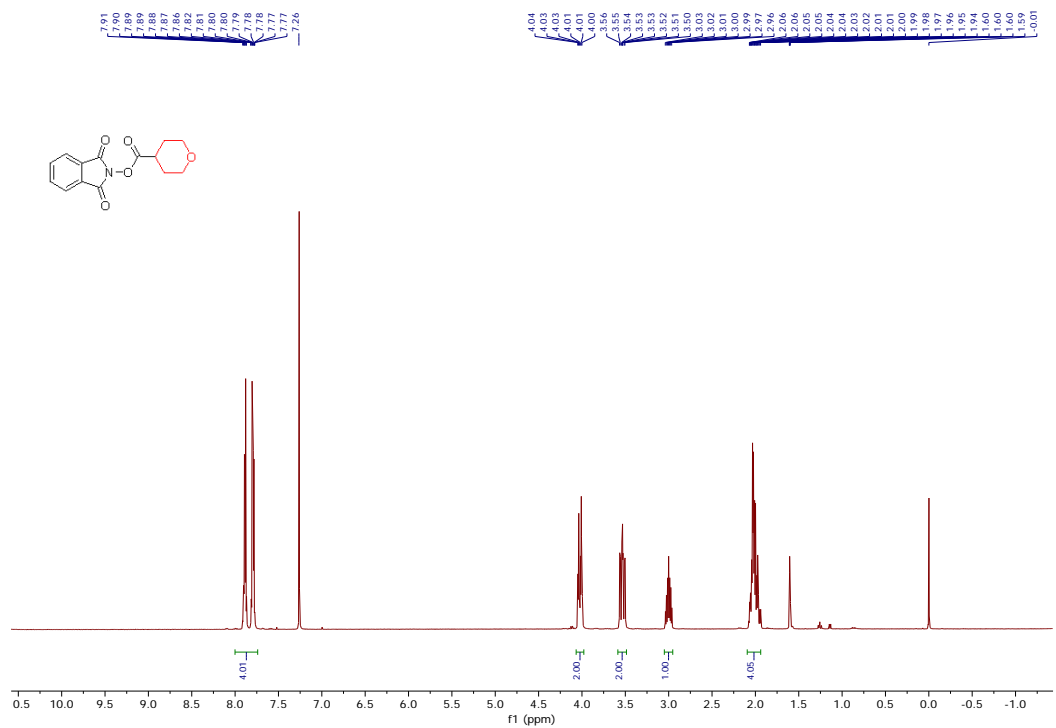
**Supplementary Figure 8. NMR spectra of 1,3-dioxoisindolin-2-yl cyclobutanecarboxylate**



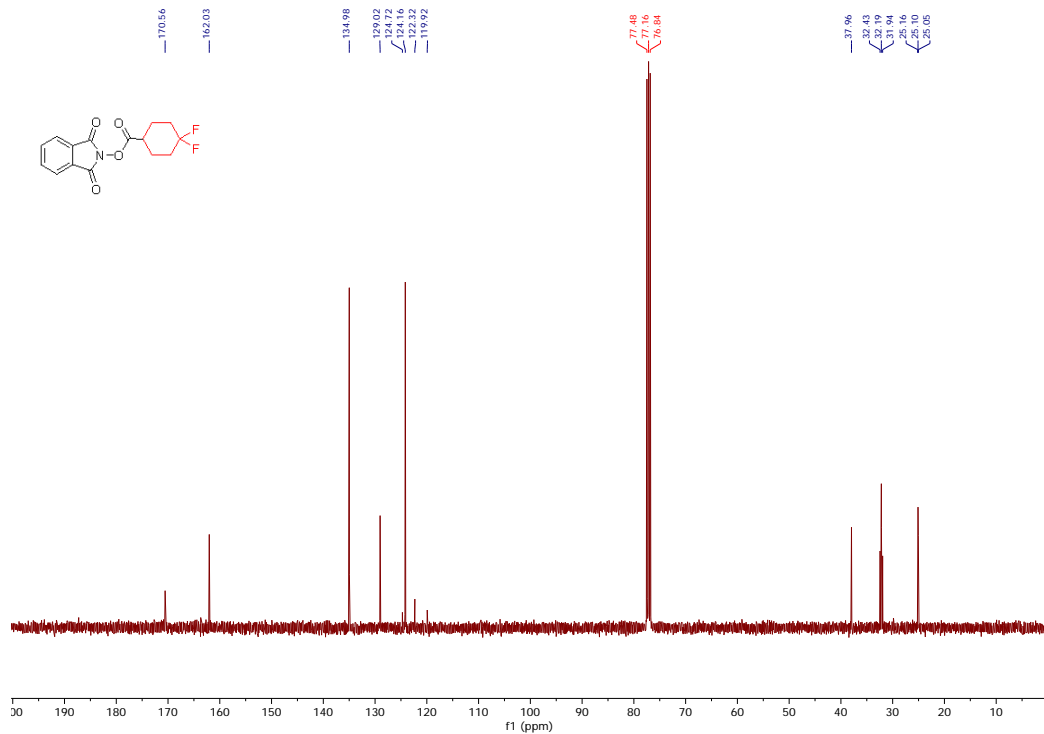
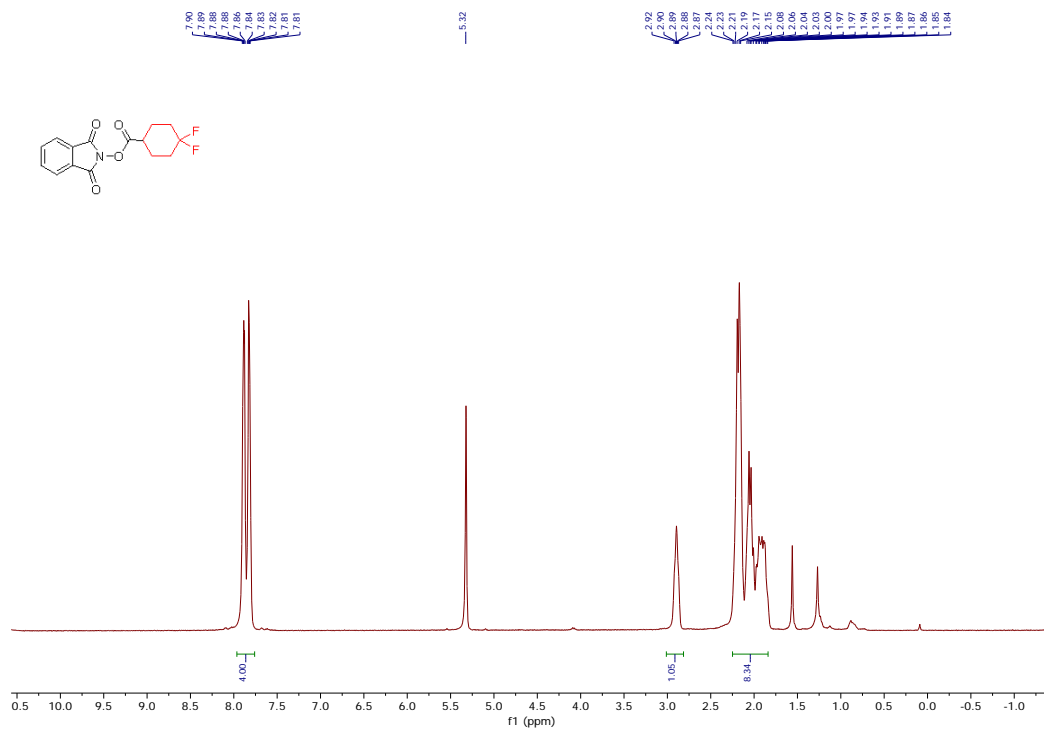
**Supplementary Figure 9. NMR spectra of 1,3-dioxoisindolin-2-yl cyclopentanecarboxylate**



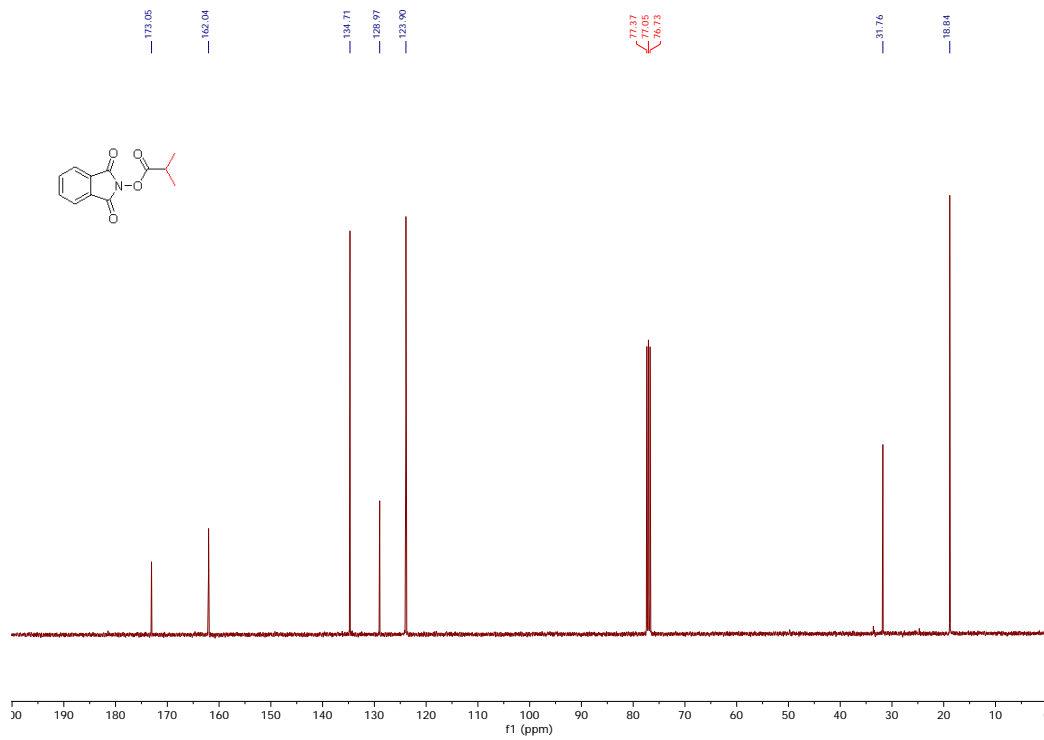
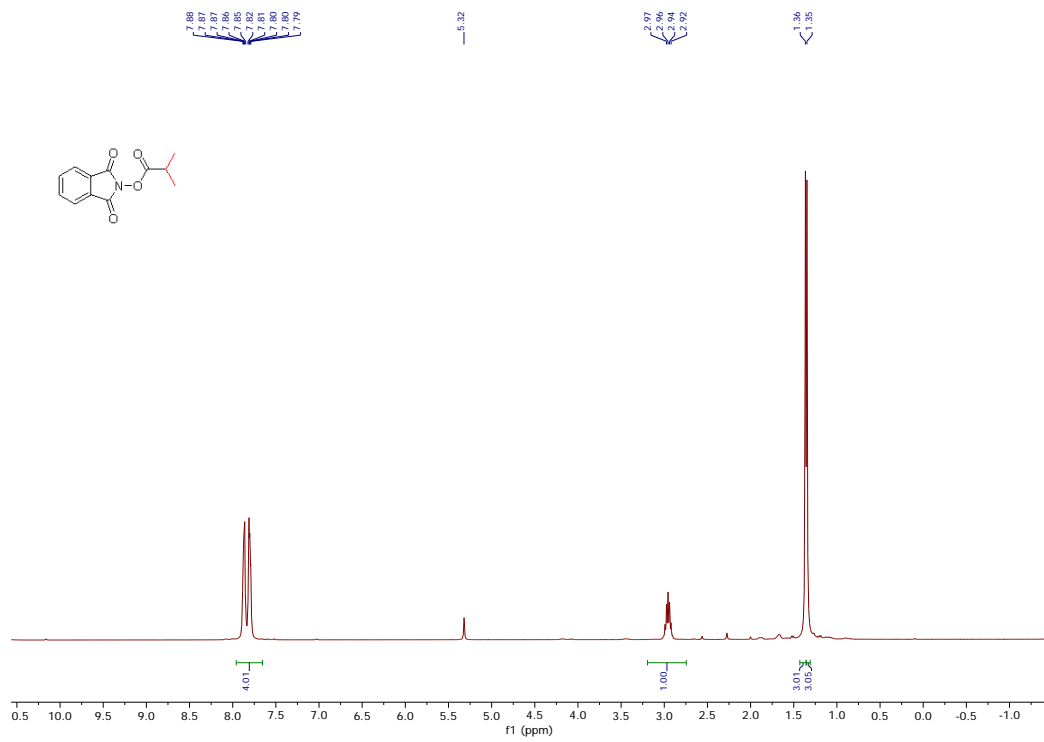
**Supplementary Figure 10. NMR spectra of 1,3-dioxoisindolin-2-yl cyclododecanecarboxylate**



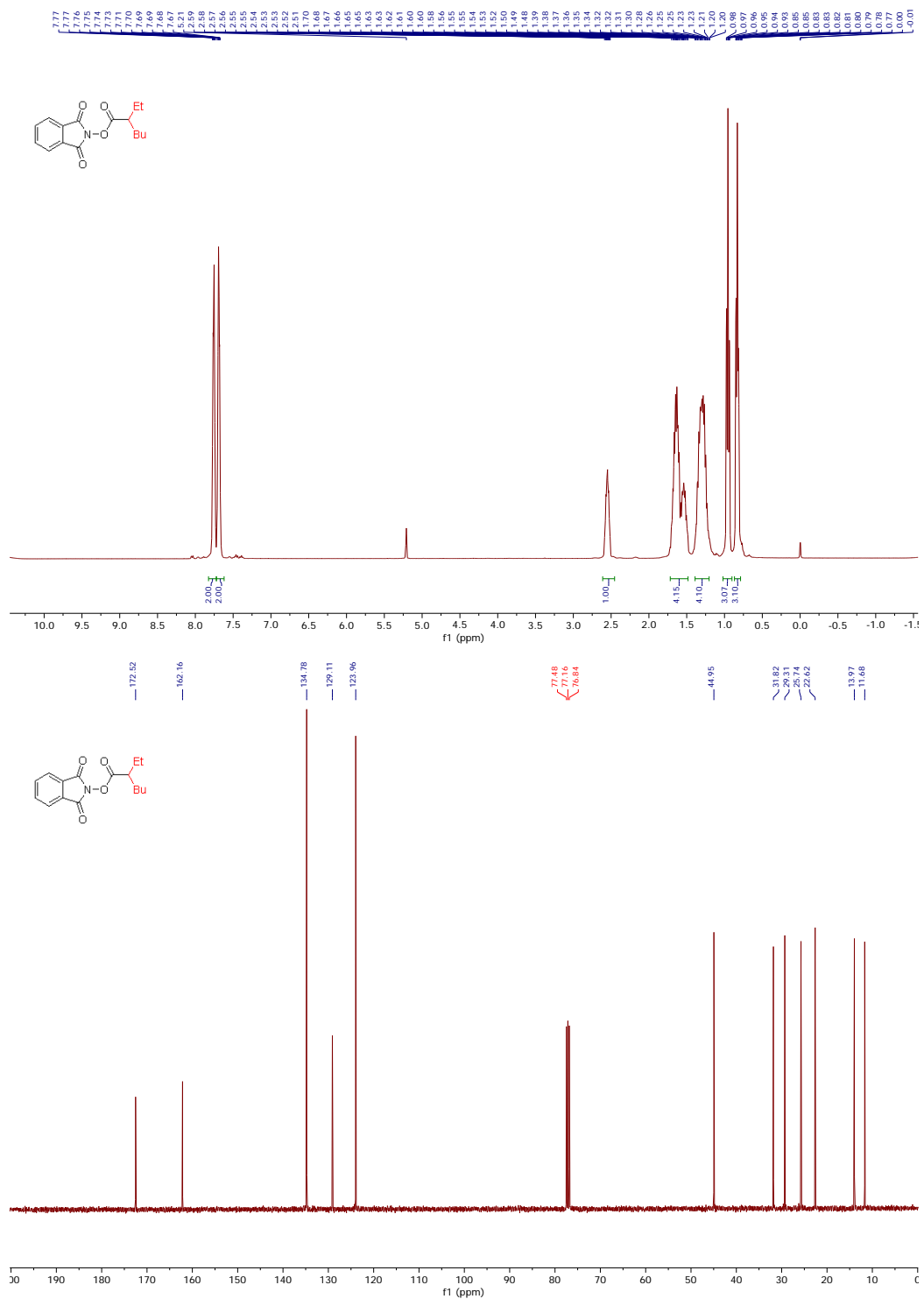
**Supplementary Figure 11. NMR spectra of 1,3-dioxoisindolin-2-yl tetrahydro-2H-pyran-4-carboxylate**



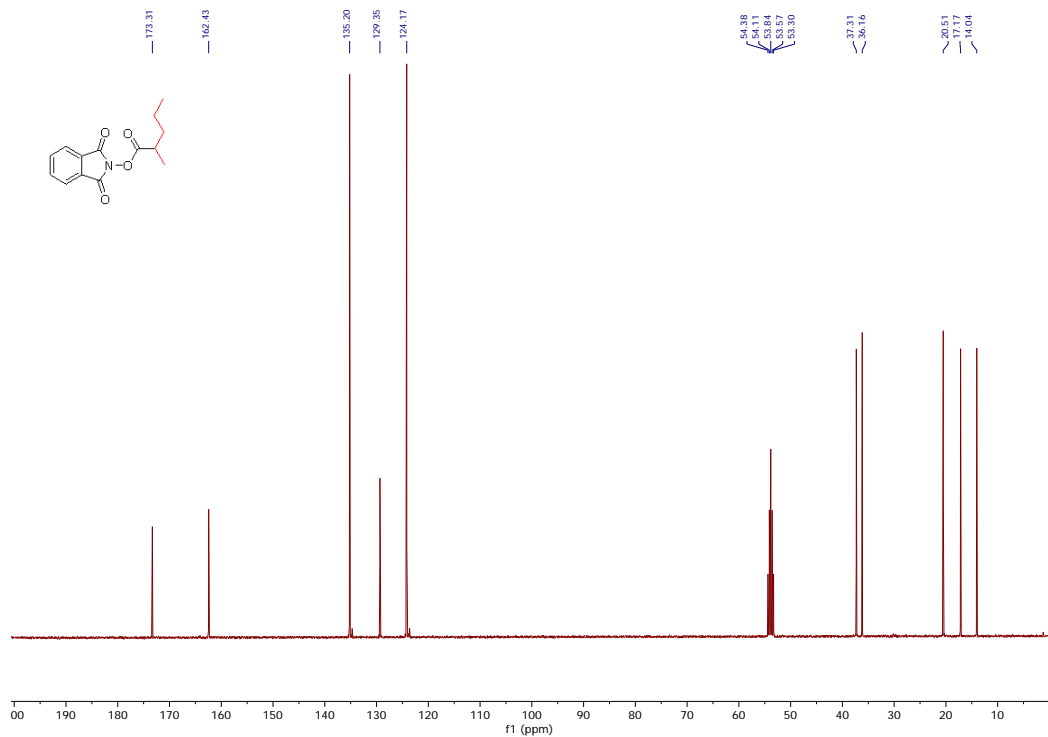
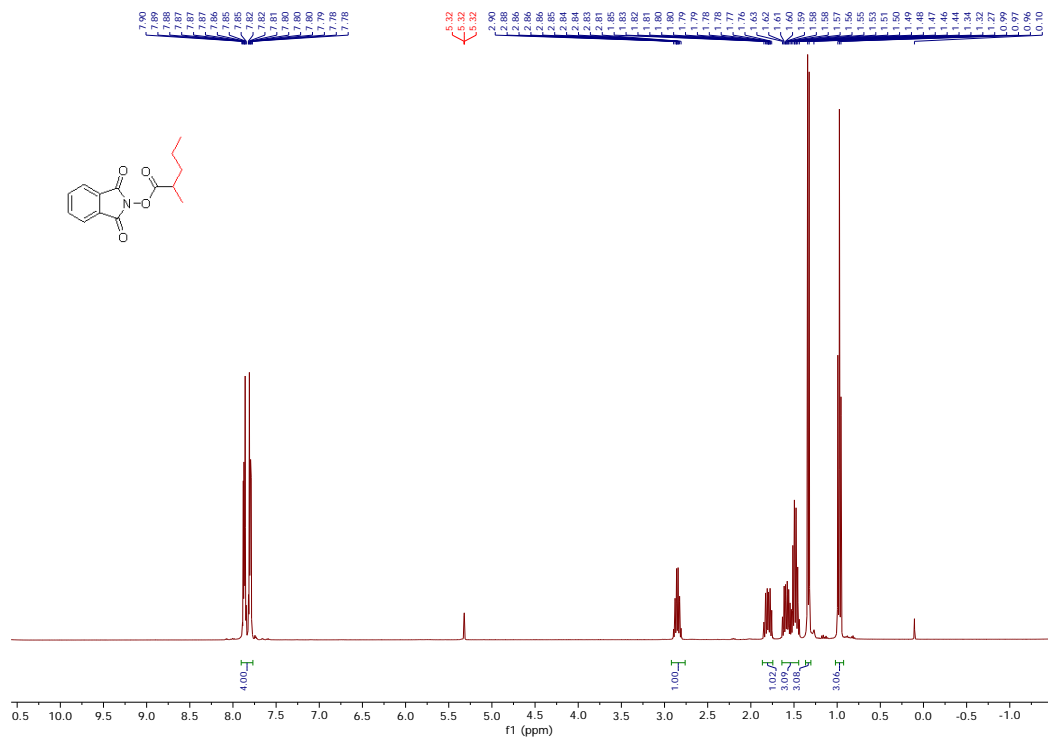
**Supplementary Figure 12. NMR spectra of 1,3-dioxoisindolin-2-yl 4,4-difluorocyclohexane-1-carboxylate**



**Supplementary Figure 13. NMR spectra of 1,3-dioxoisindolin-2-yl isobutyrate**

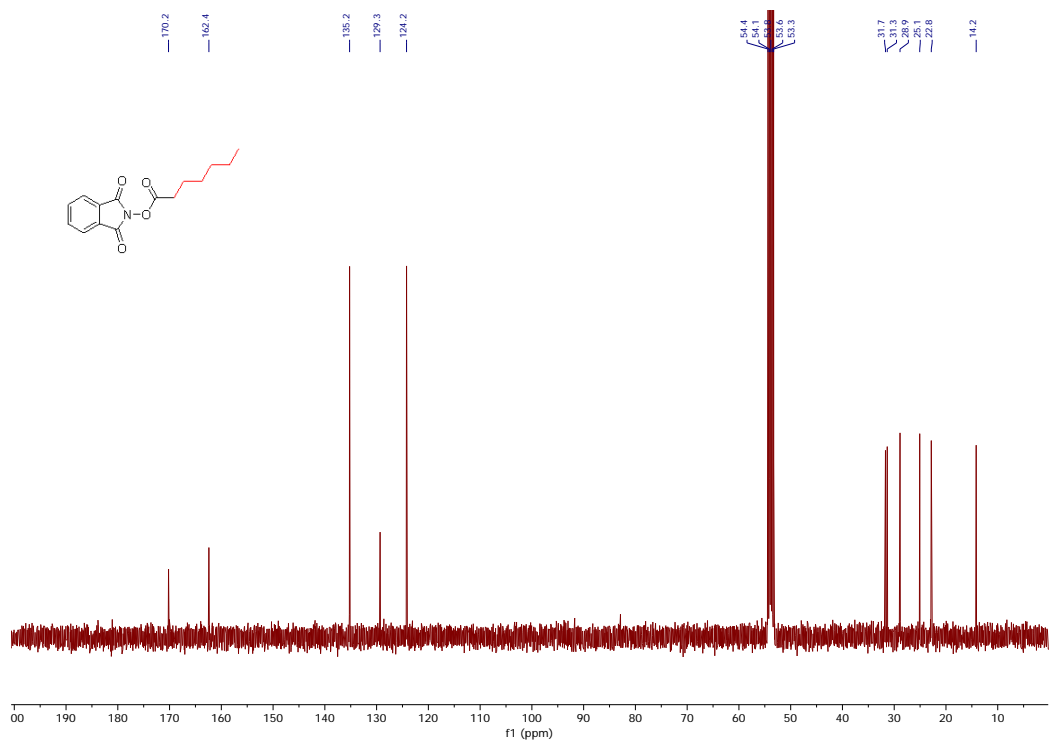
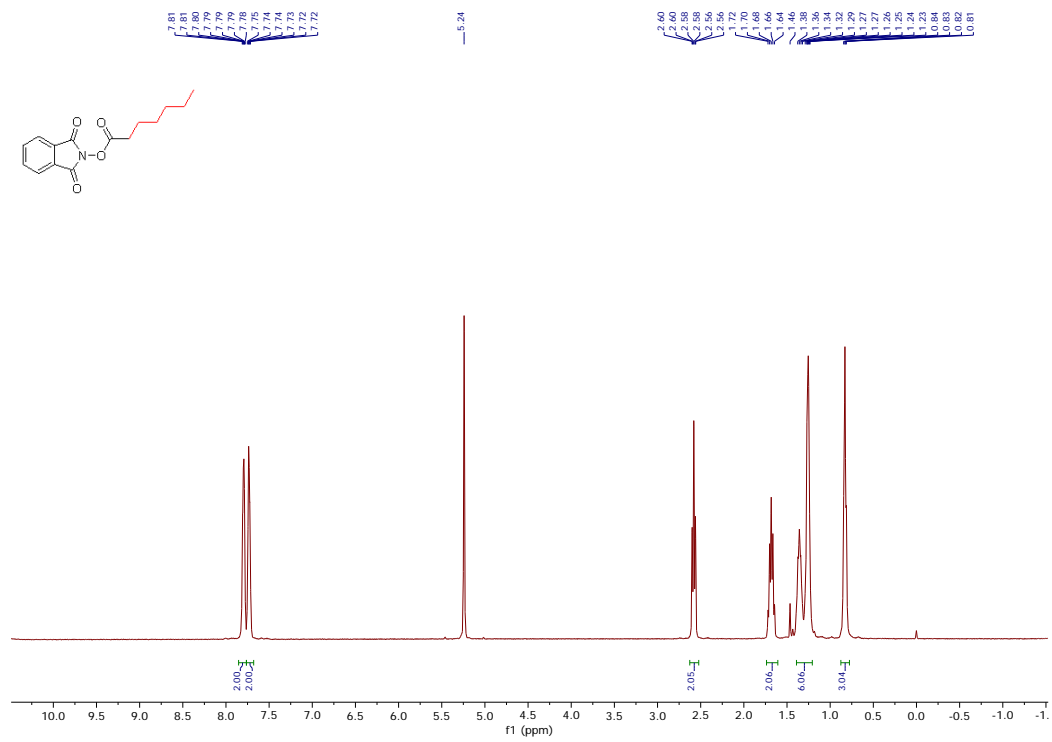


**Supplementary Figure 14. NMR spectra of 1,3-dioxisoindolin-2-yl 2-ethylhexanoate**

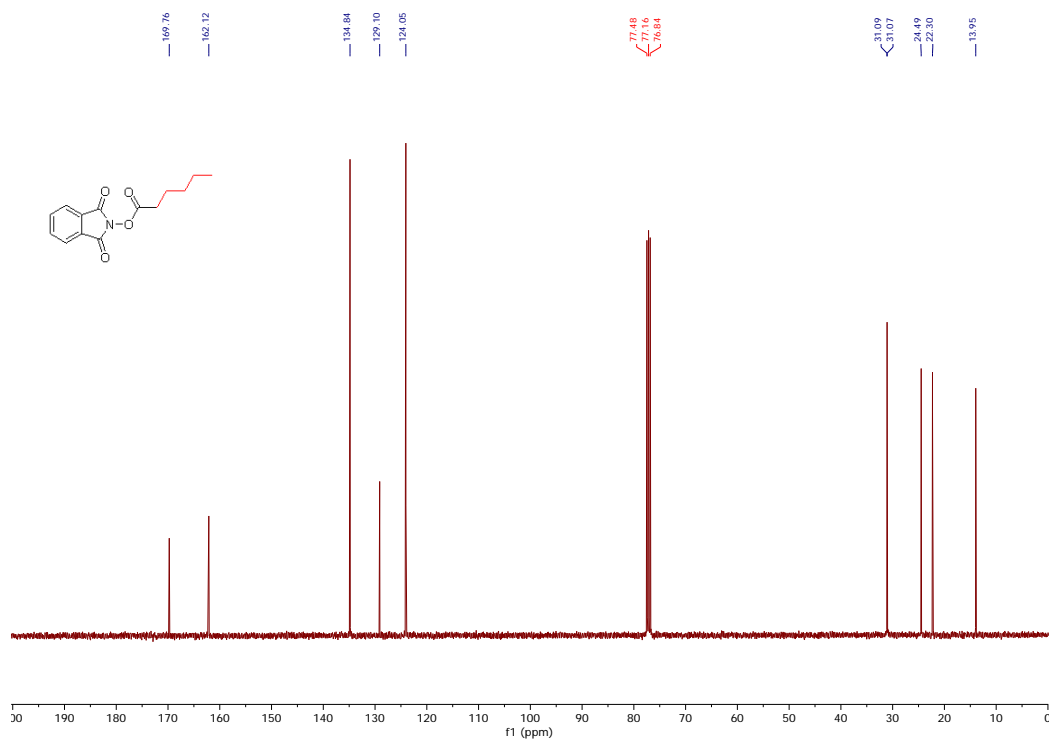
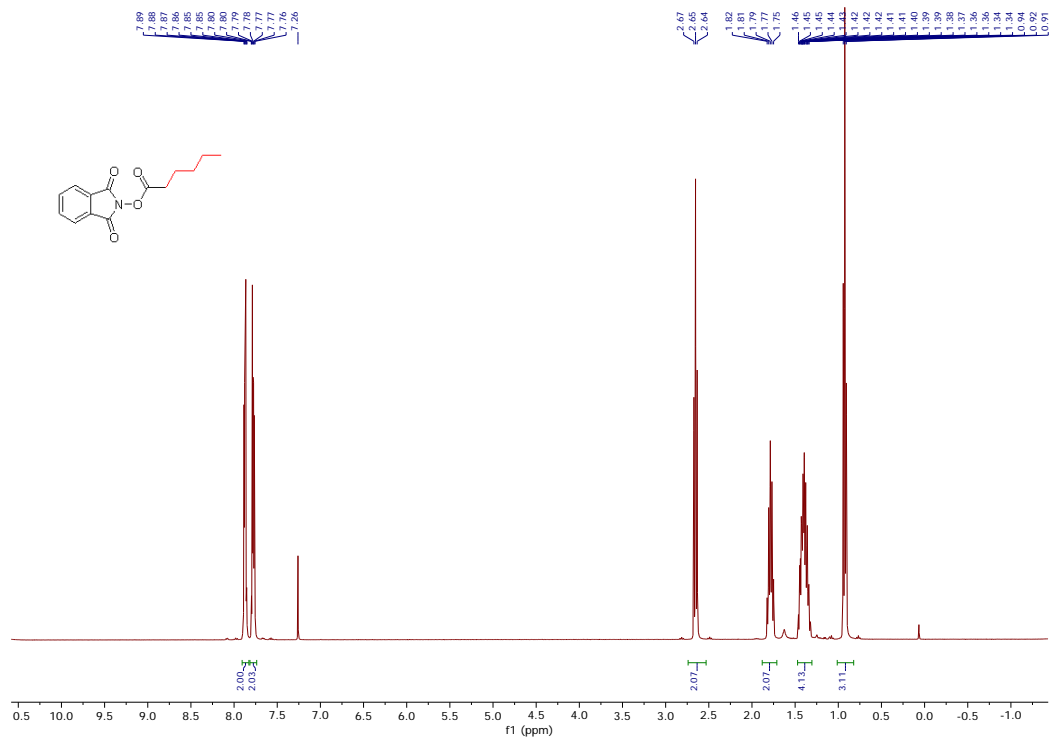


**Supplementary Figure 15. NMR spectra of 1,3-dioxoisindolin-2-yl 2-methylpentanoate**

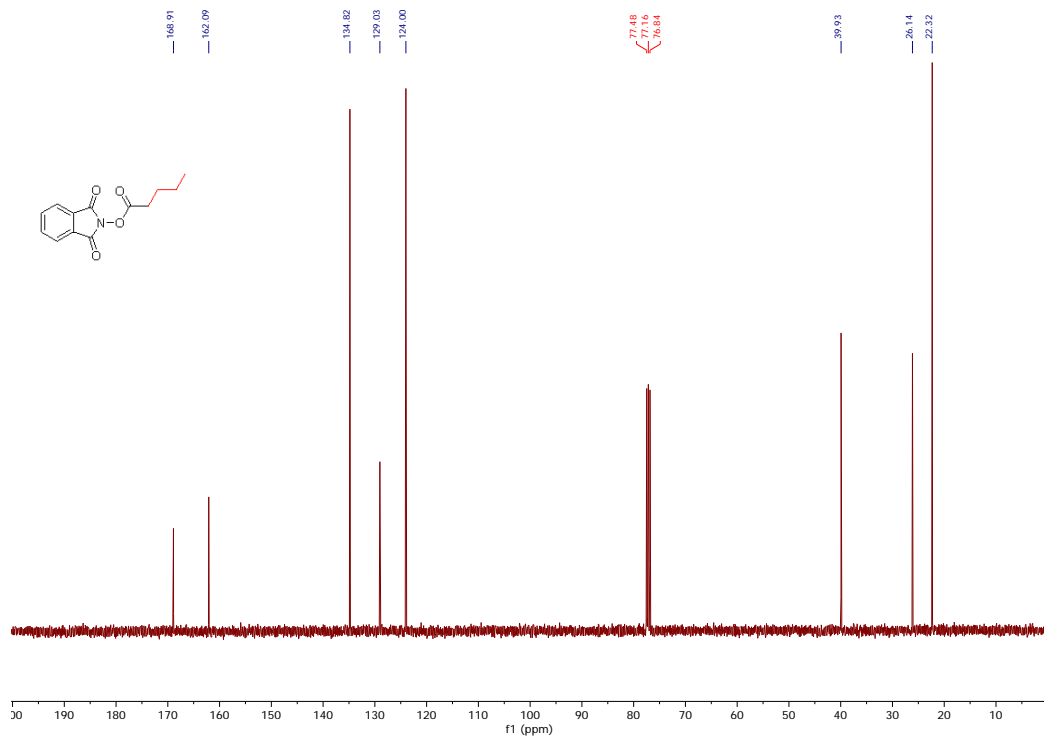
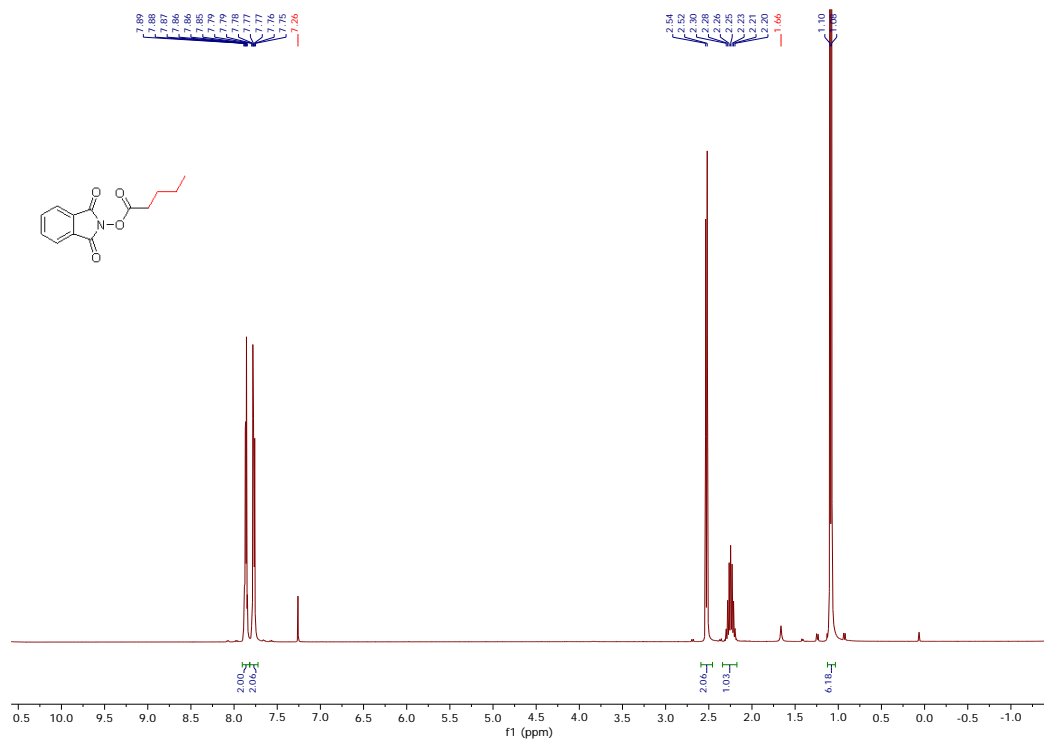




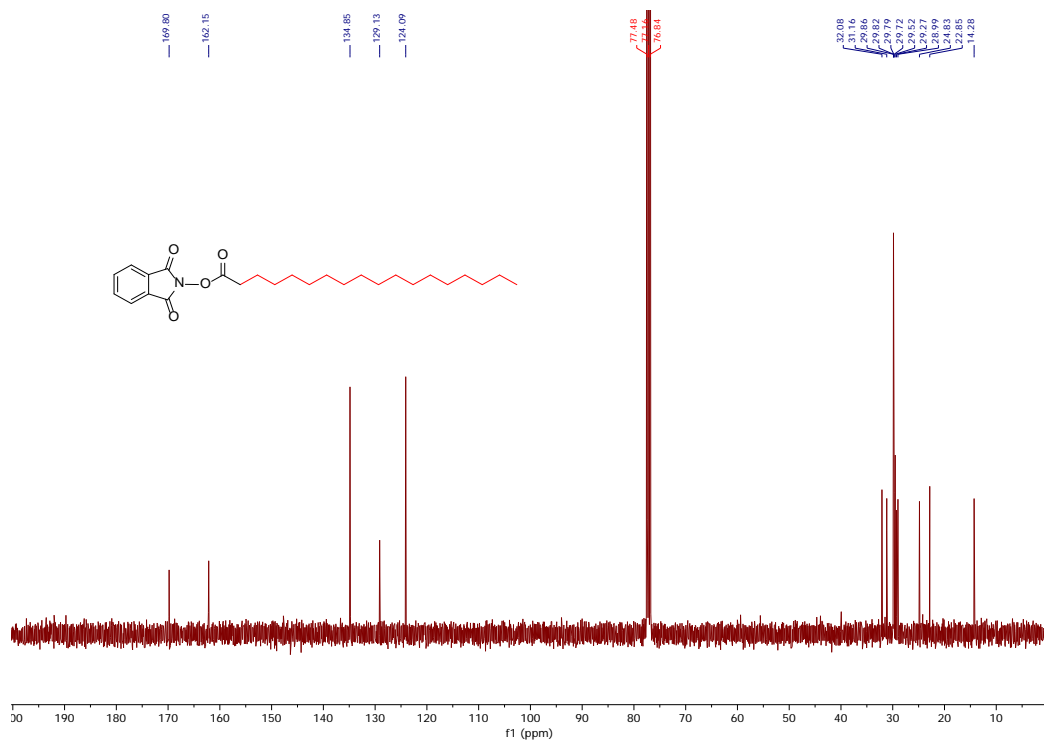
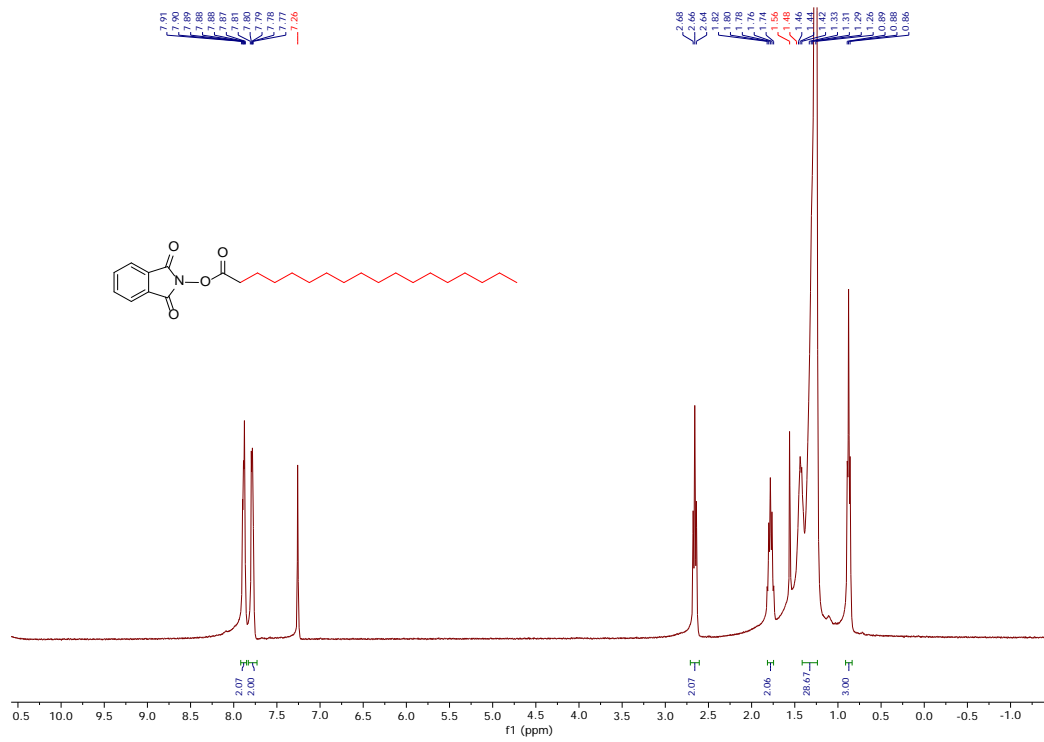
**Supplementary Figure 16. NMR spectra of 1,3-dioxoisindolin-2-yl heptanoate**



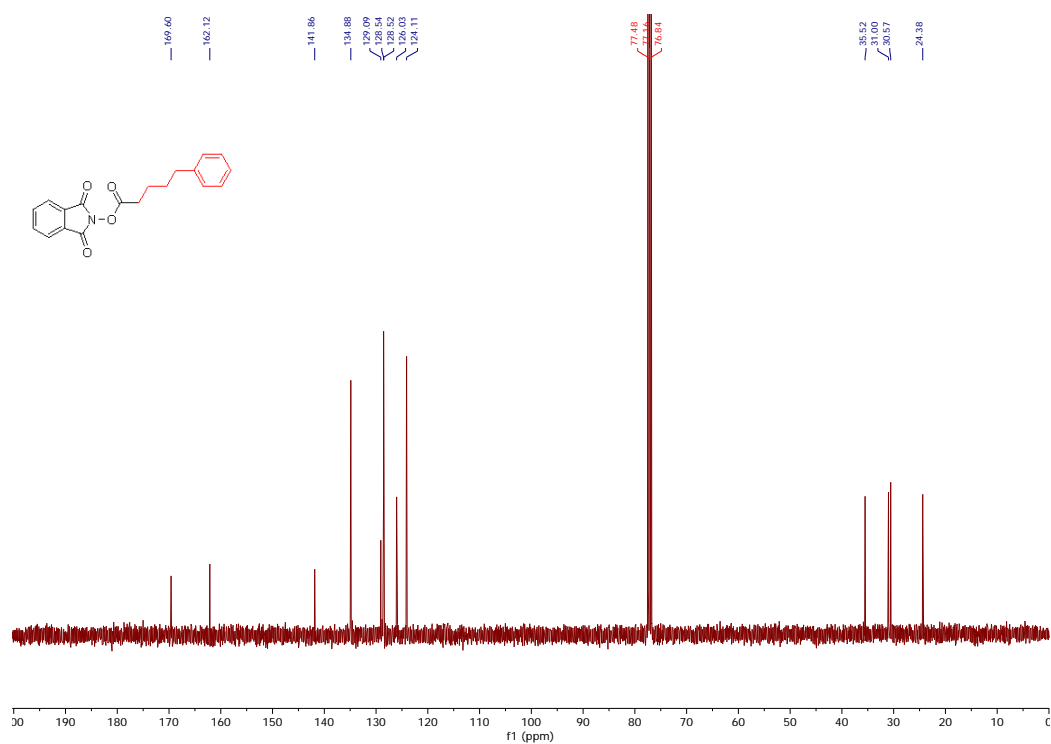
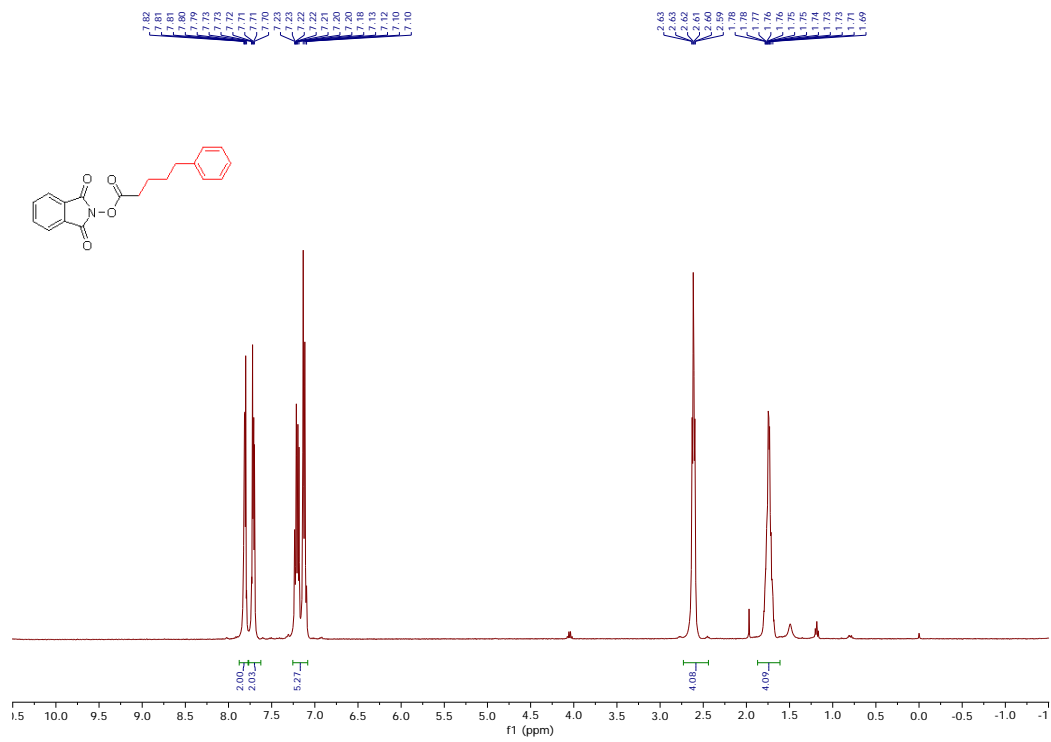
**Supplementary Figure 17. NMR spectra of 1,3-dioxoisindolin-2-yl hexanoate**



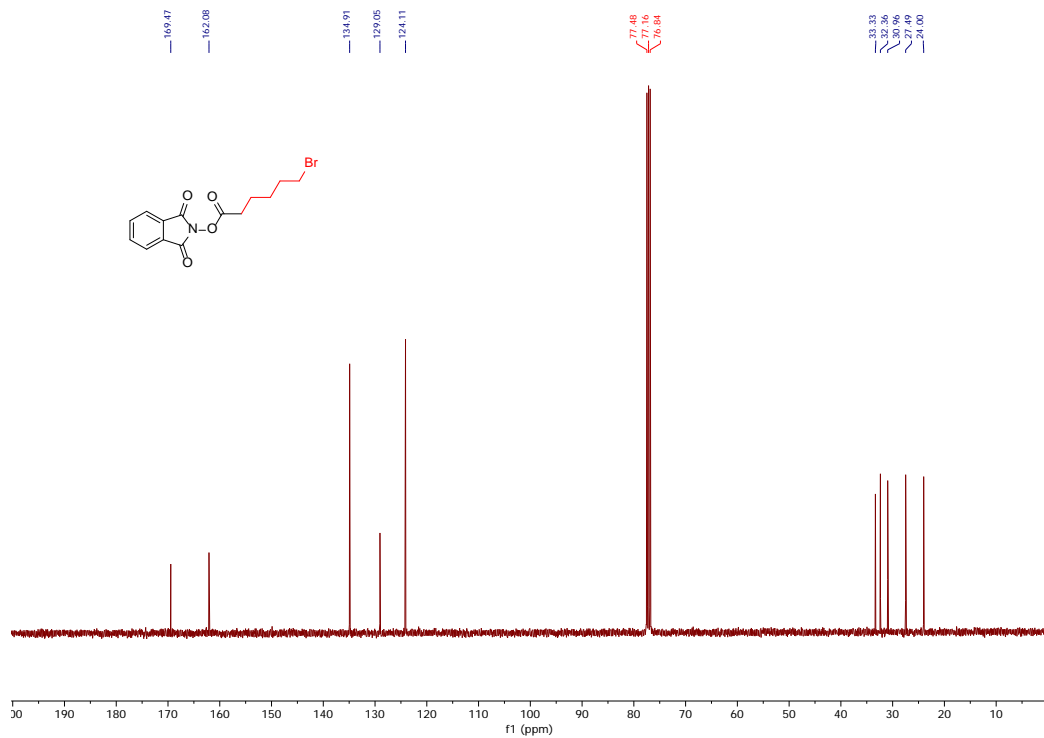
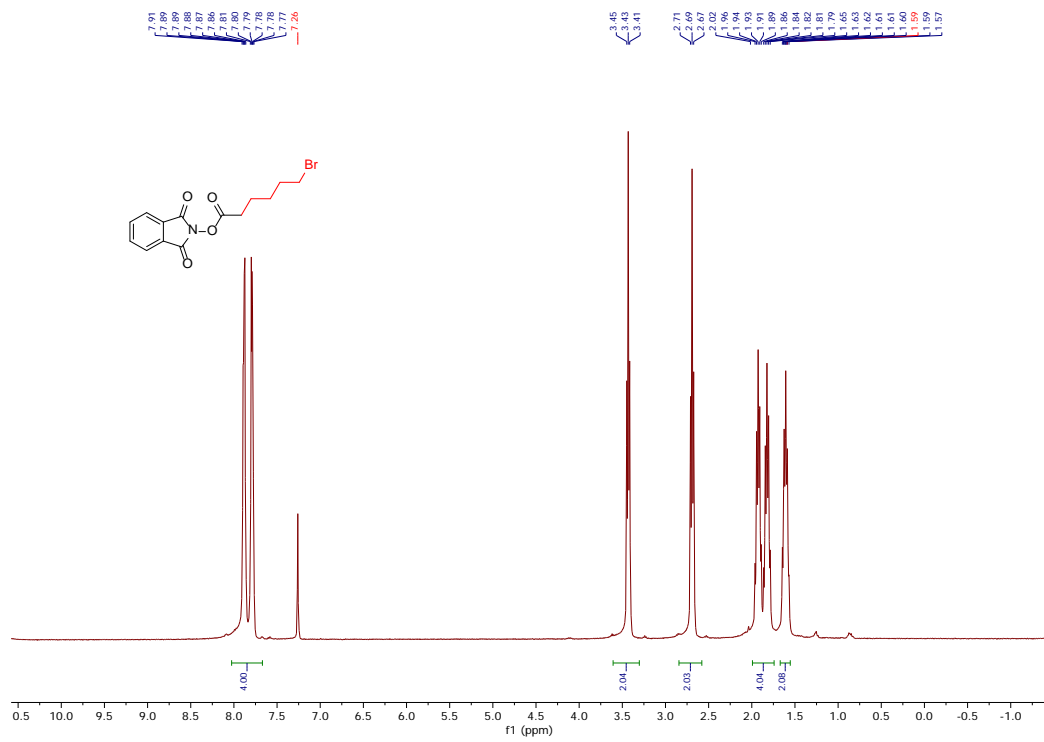
**Supplementary Figure 18. NMR spectra of 1,3-dioxoisindolin-2-yl pentanoate**



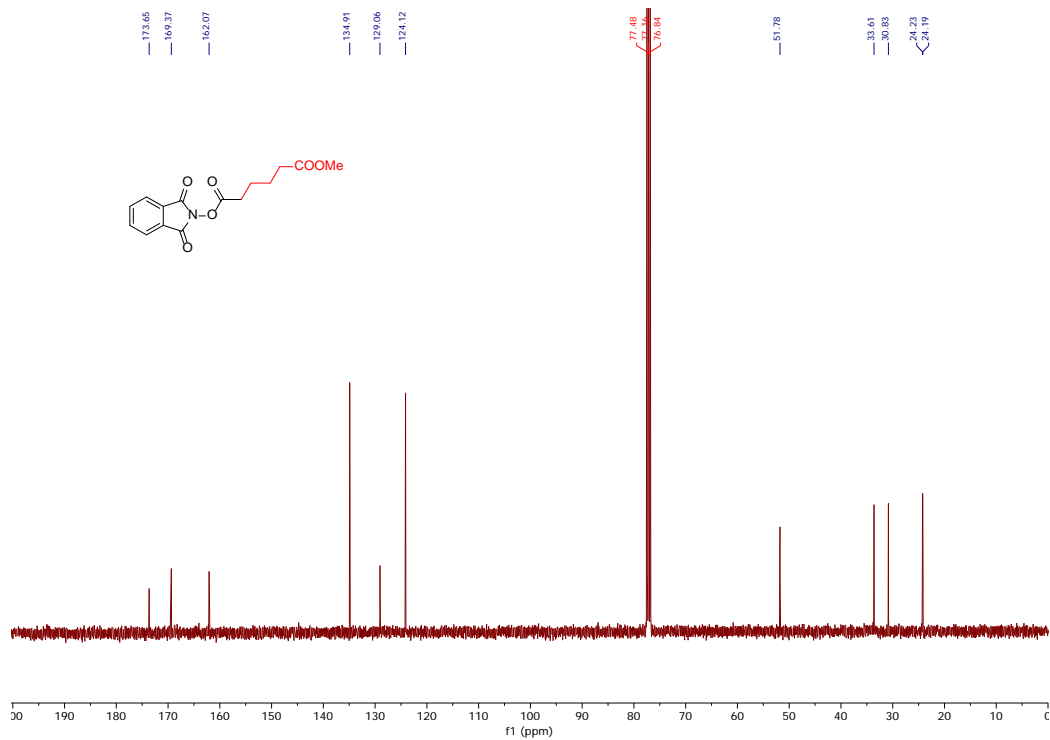
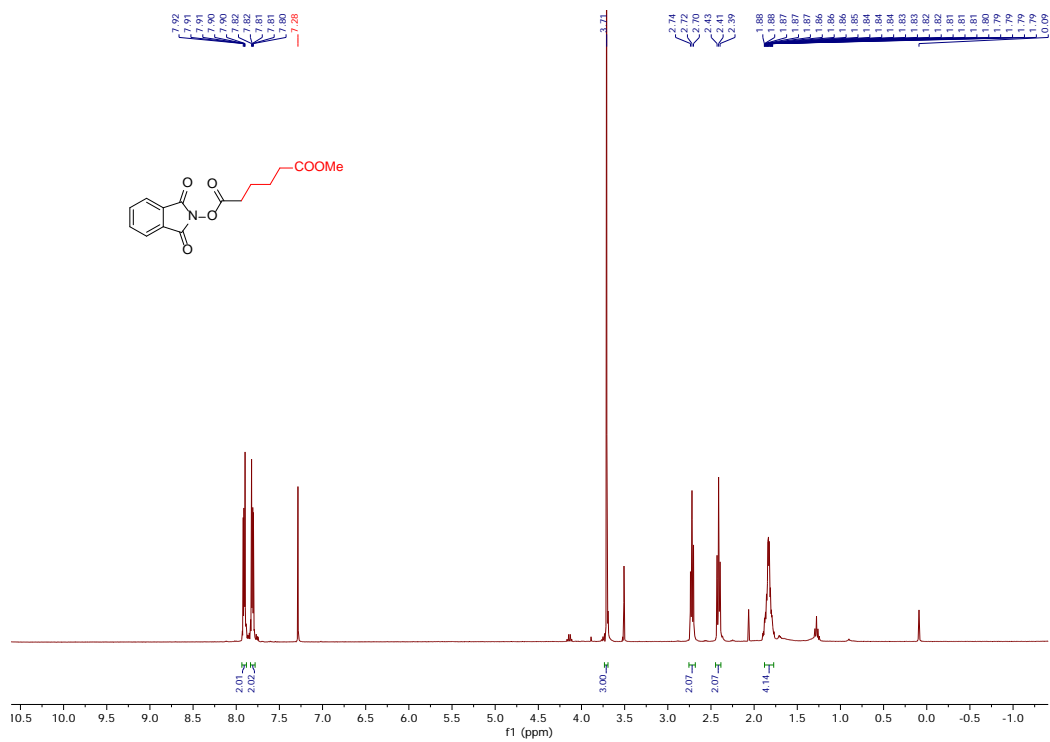
**Supplementary Figure 19. NMR spectra of 1,3-dioxisoindolin-2-yl stearate**



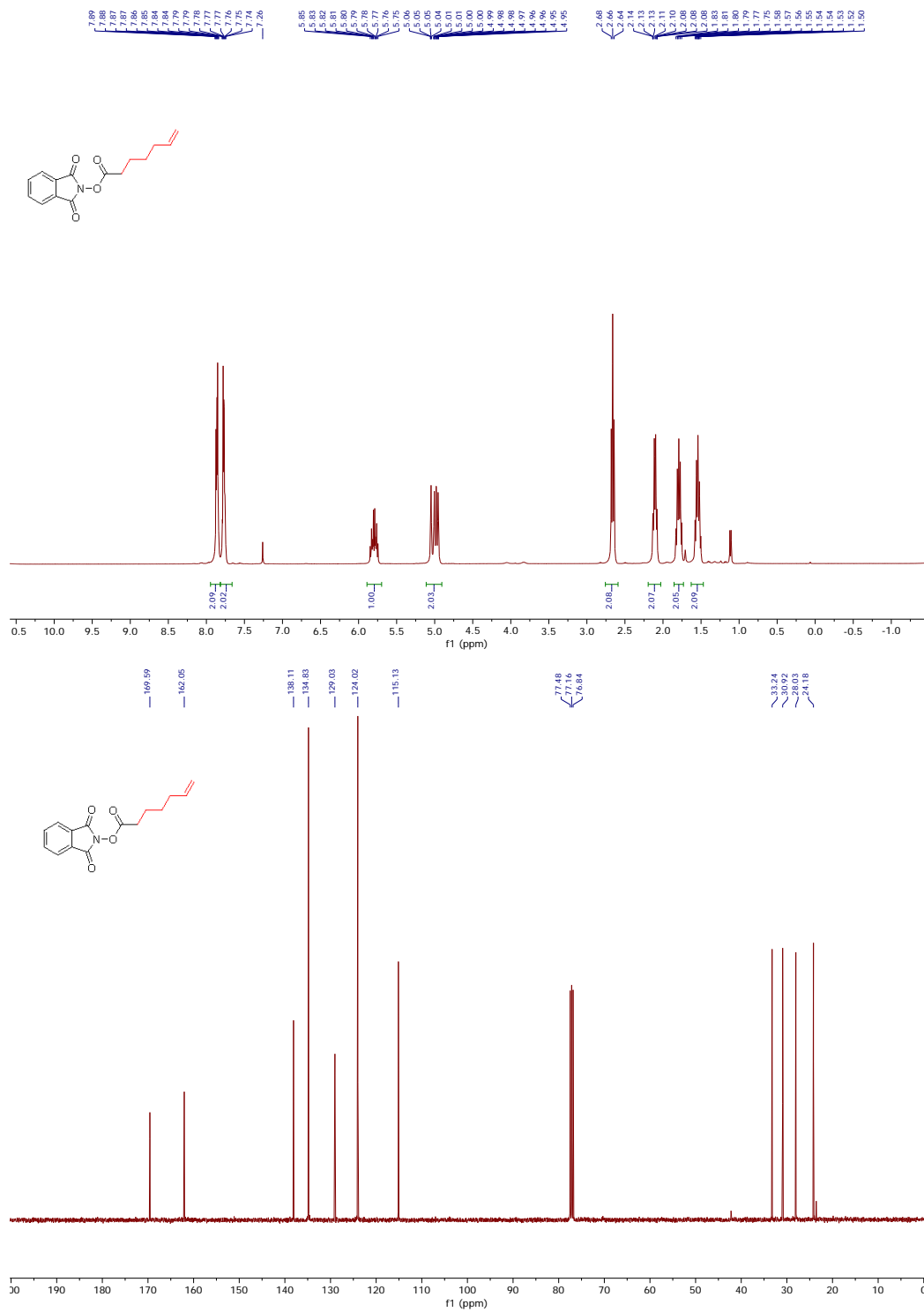
**Supplementary Figure 20. NMR spectra of 1,3-dioxoisindolin-2-yl 5-phenylpentanoate**



**Supplementary Figure 21. NMR spectra of 1,3-dioxisoindolin-2-yl 6-bromohexanoate**

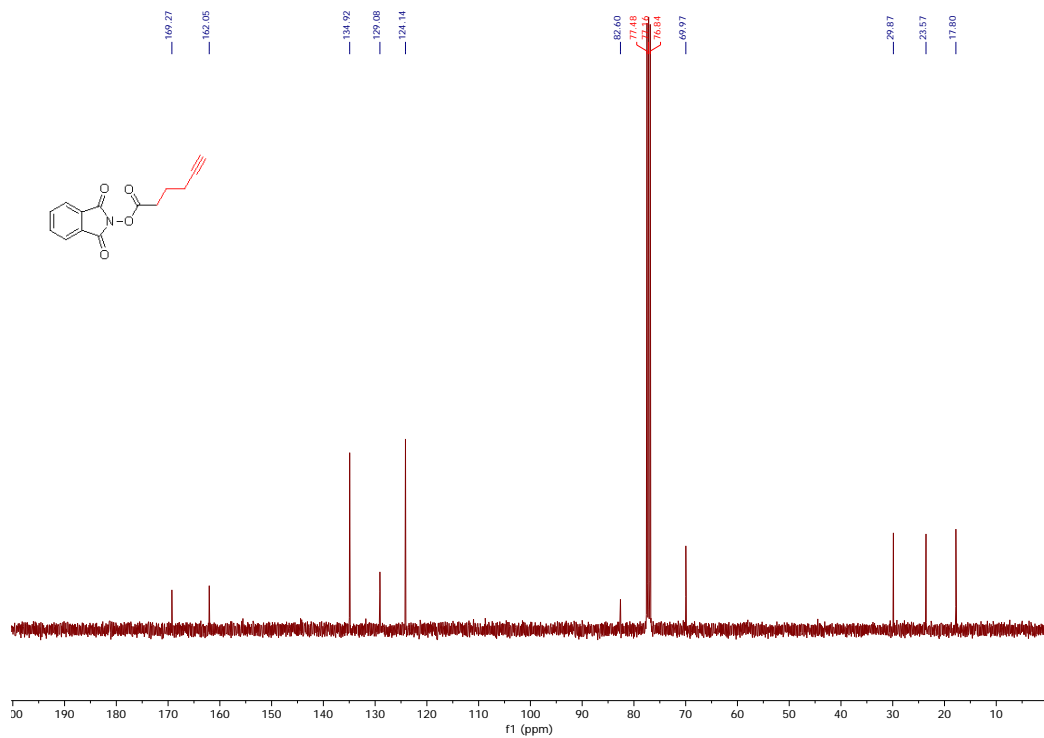
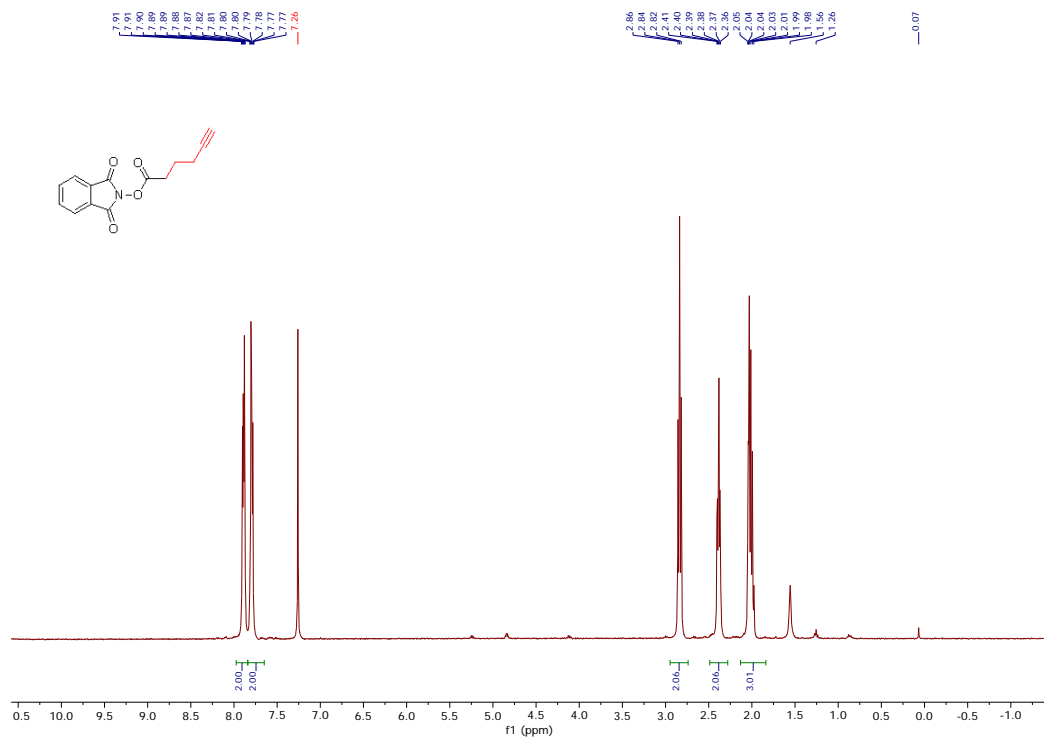


**Supplementary Figure 22. NMR spectra of 1,3-dioxoisindolin-2-yl methyl adipate**

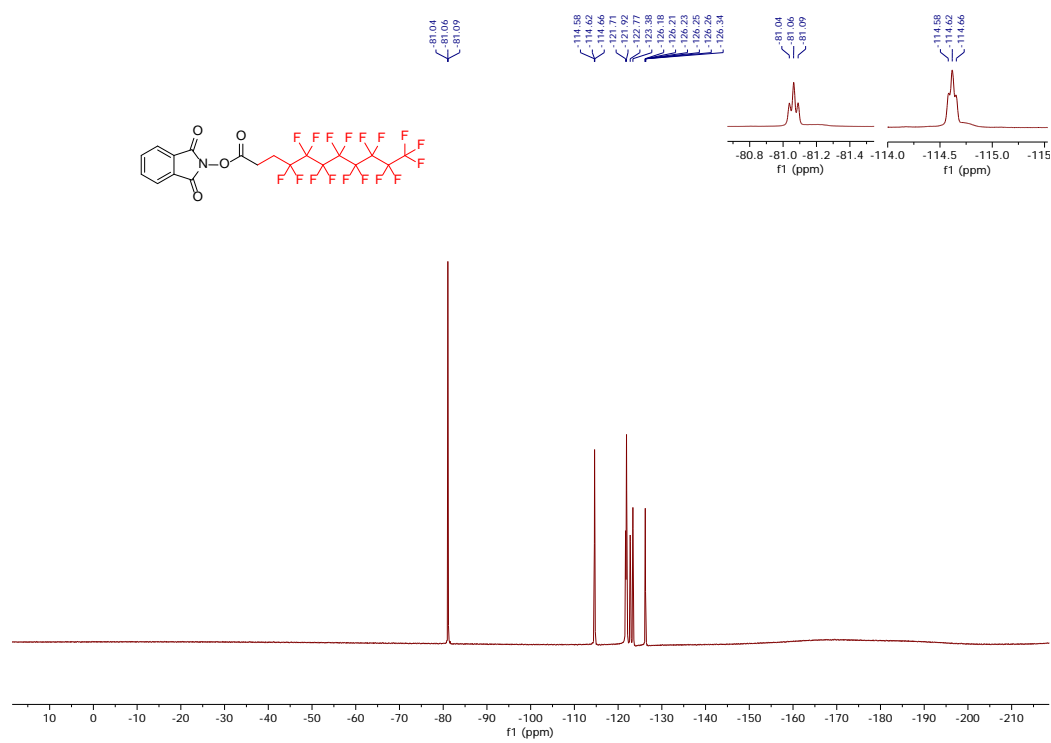
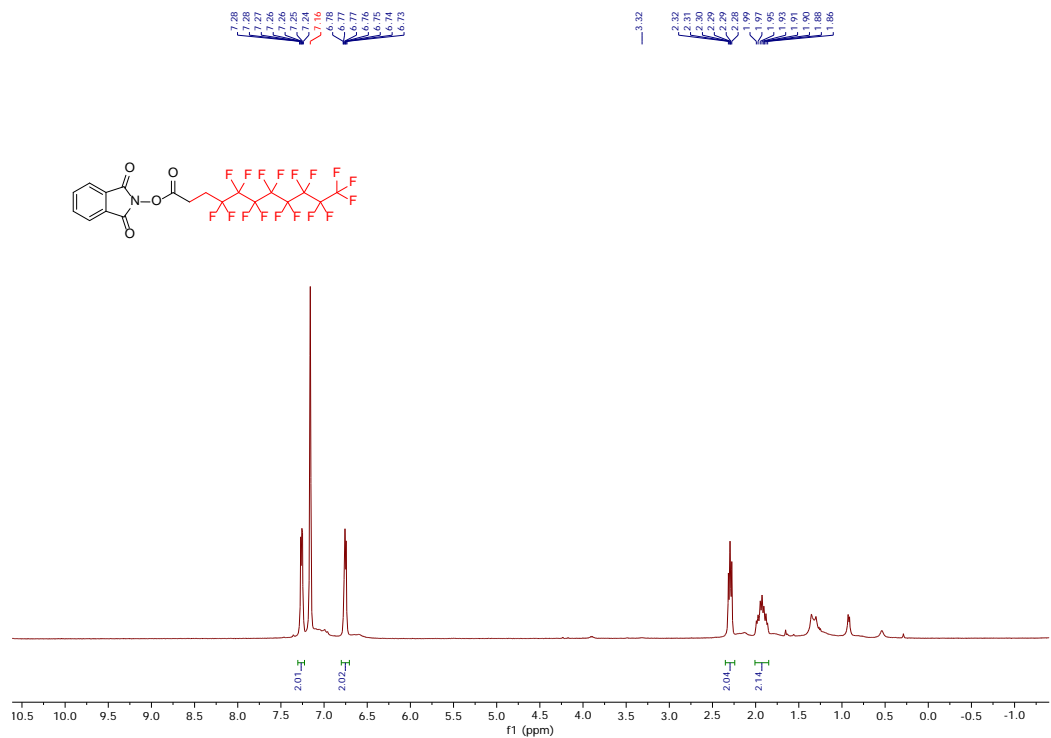


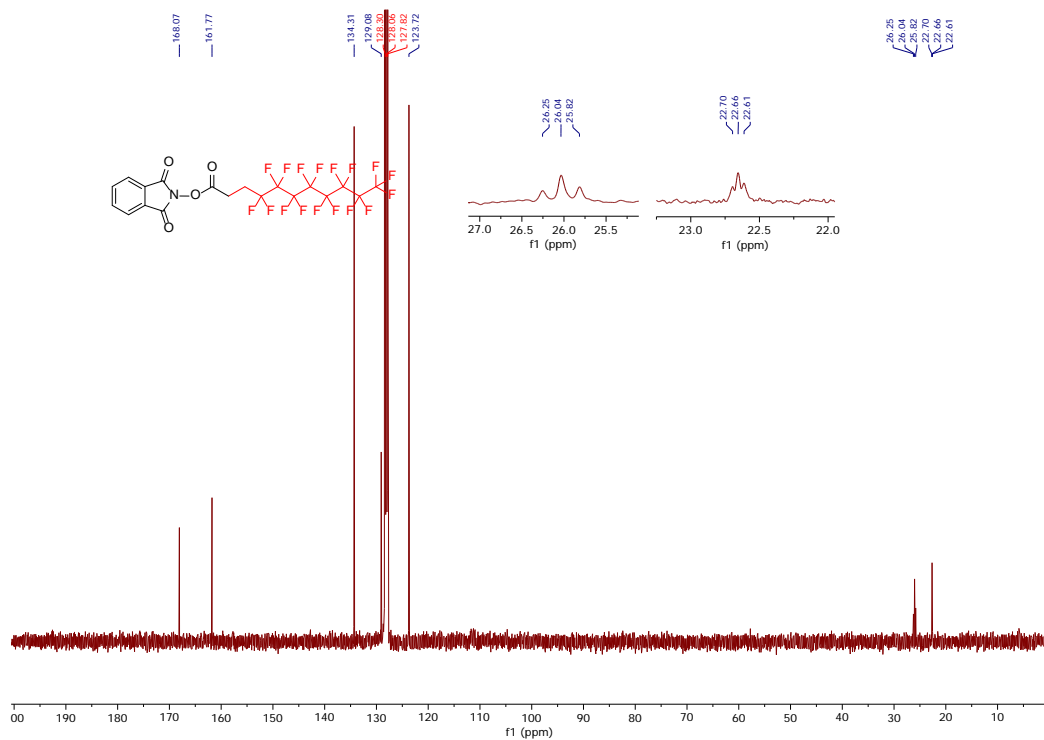
**Supplementary Figure 23. NMR spectra of 1,3-dioxoisindolin-2-yl hept-6-enoate**



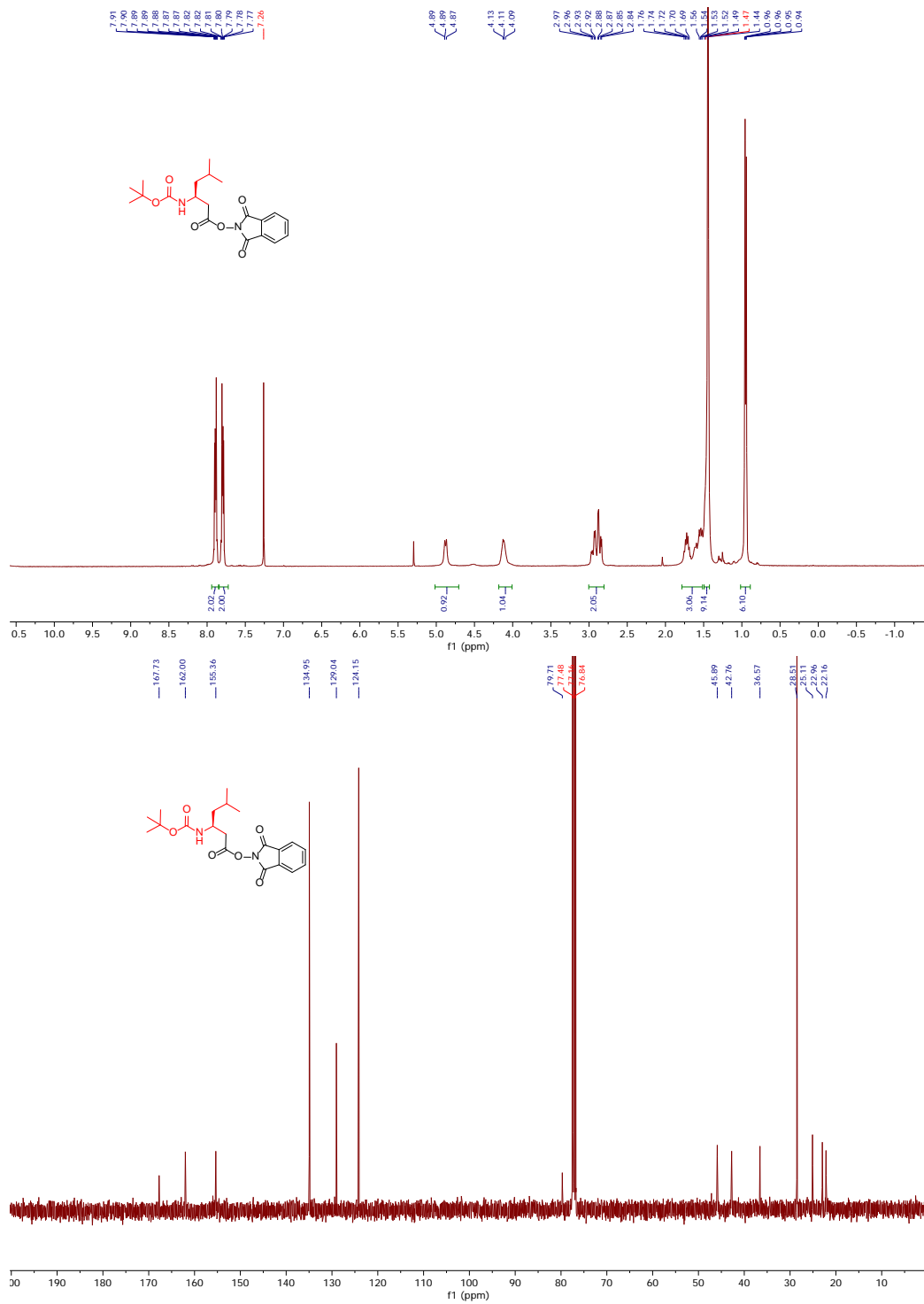


**Supplementary Figure 24. NMR spectra of 1,3-dioxoisindolin-2-yl hex-5-ynoate**

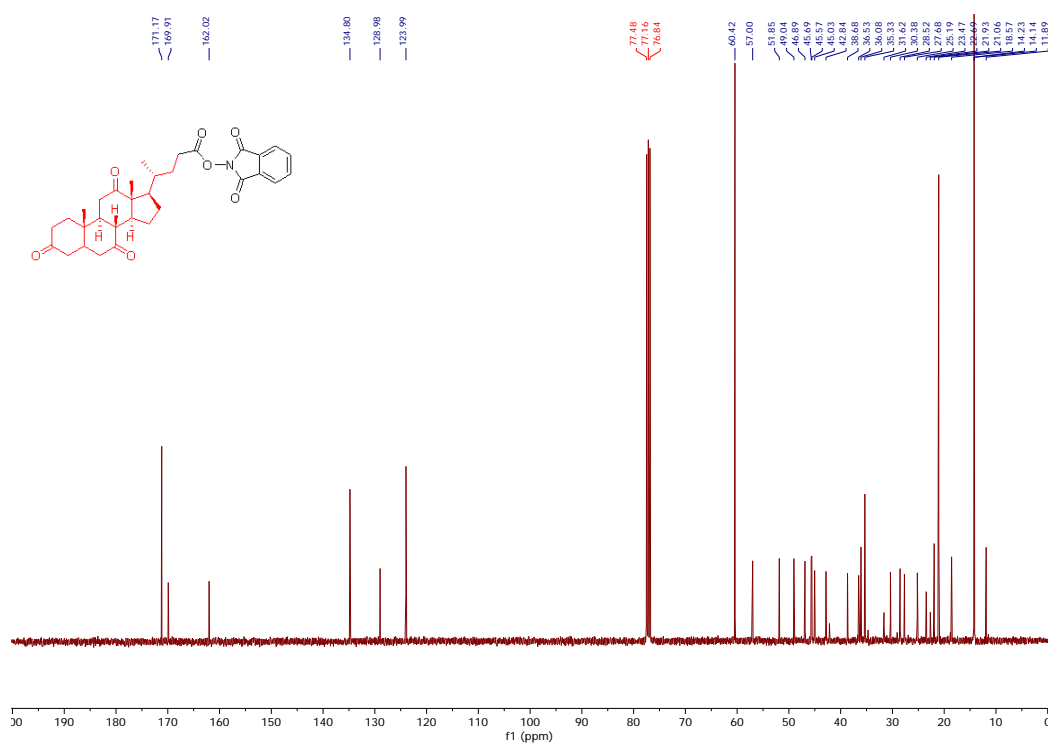
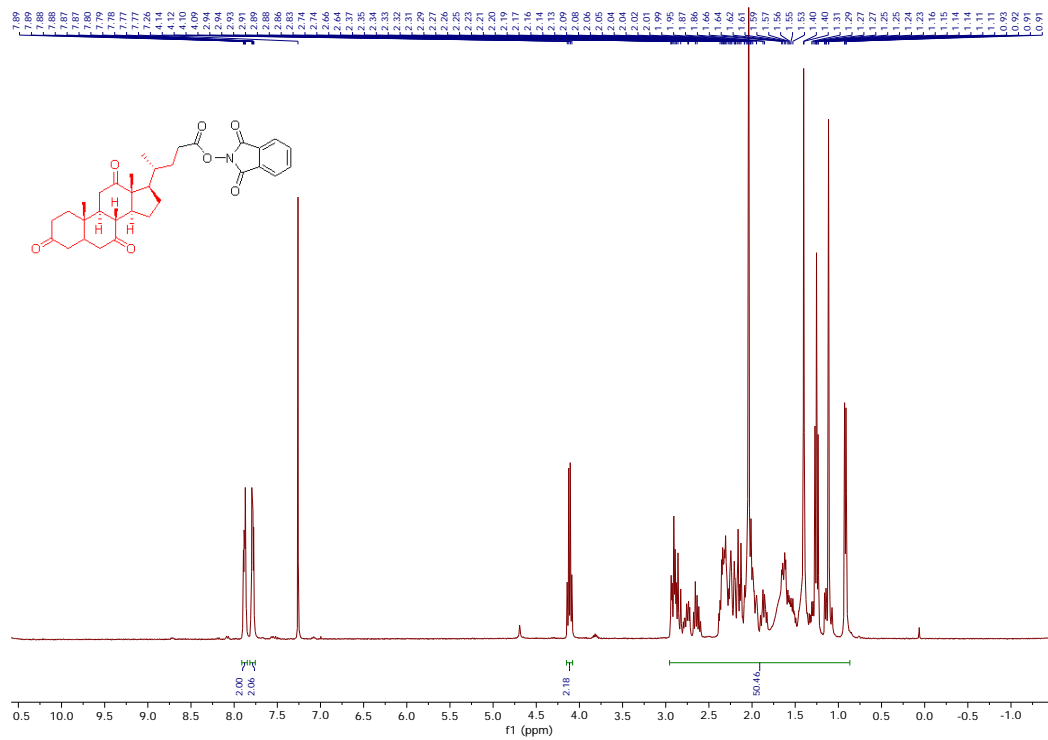




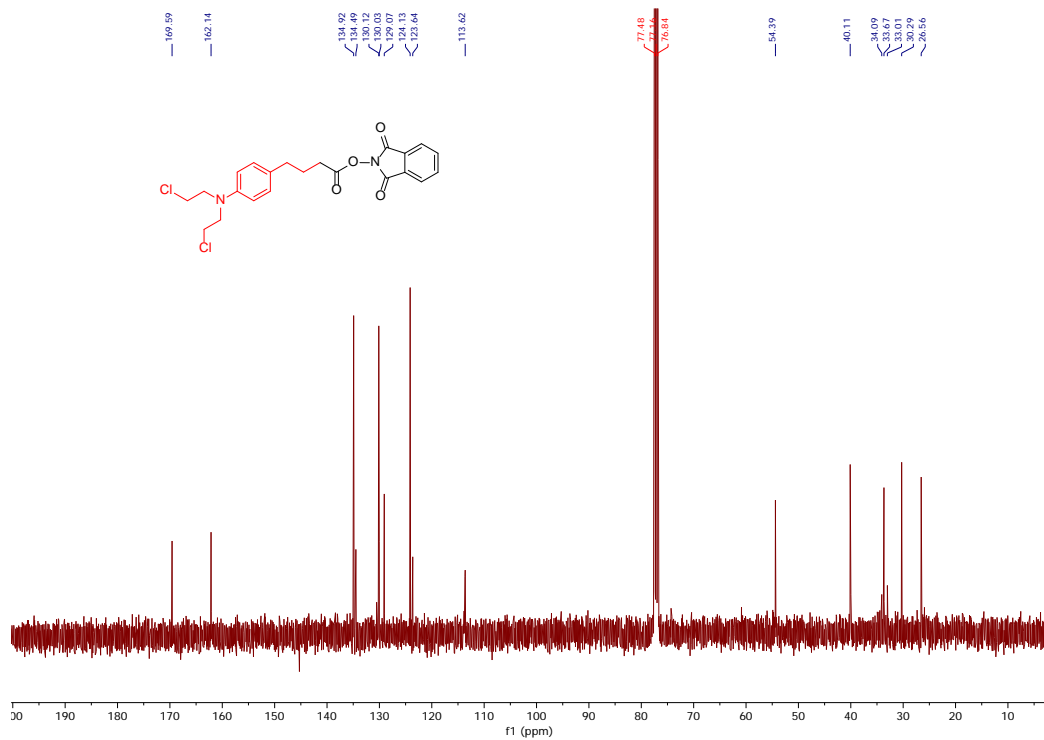
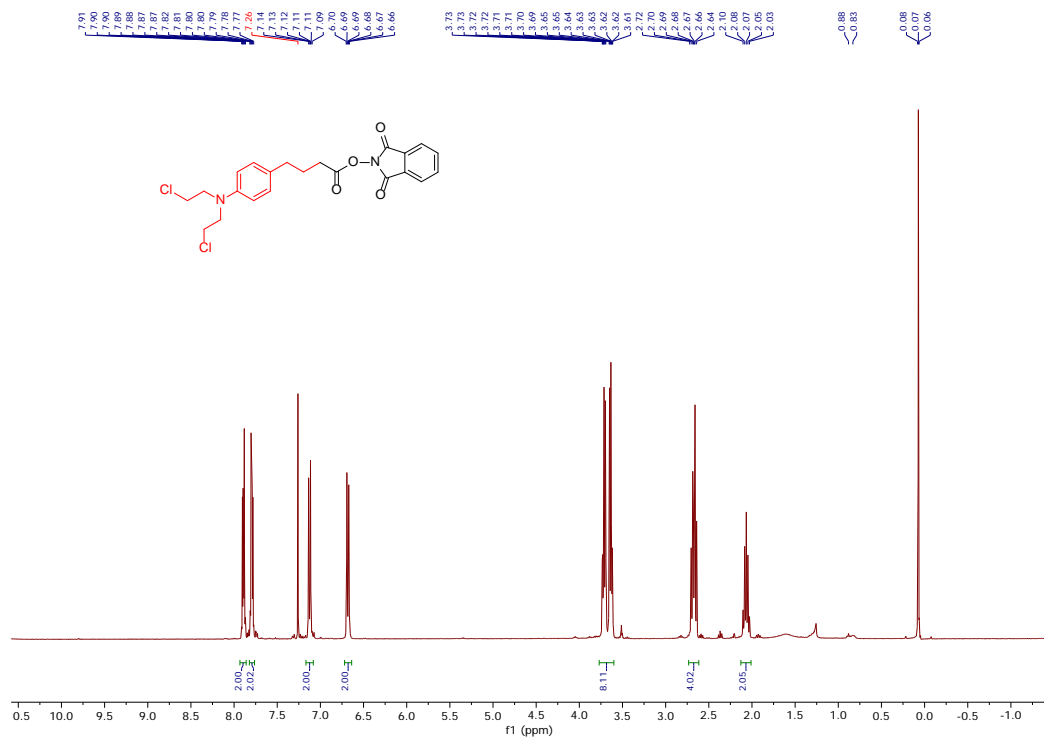
**Supplementary Figure 25. NMR spectra of 1,3-dioxoisindolin-2-yl 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptafluoroundecanoate**



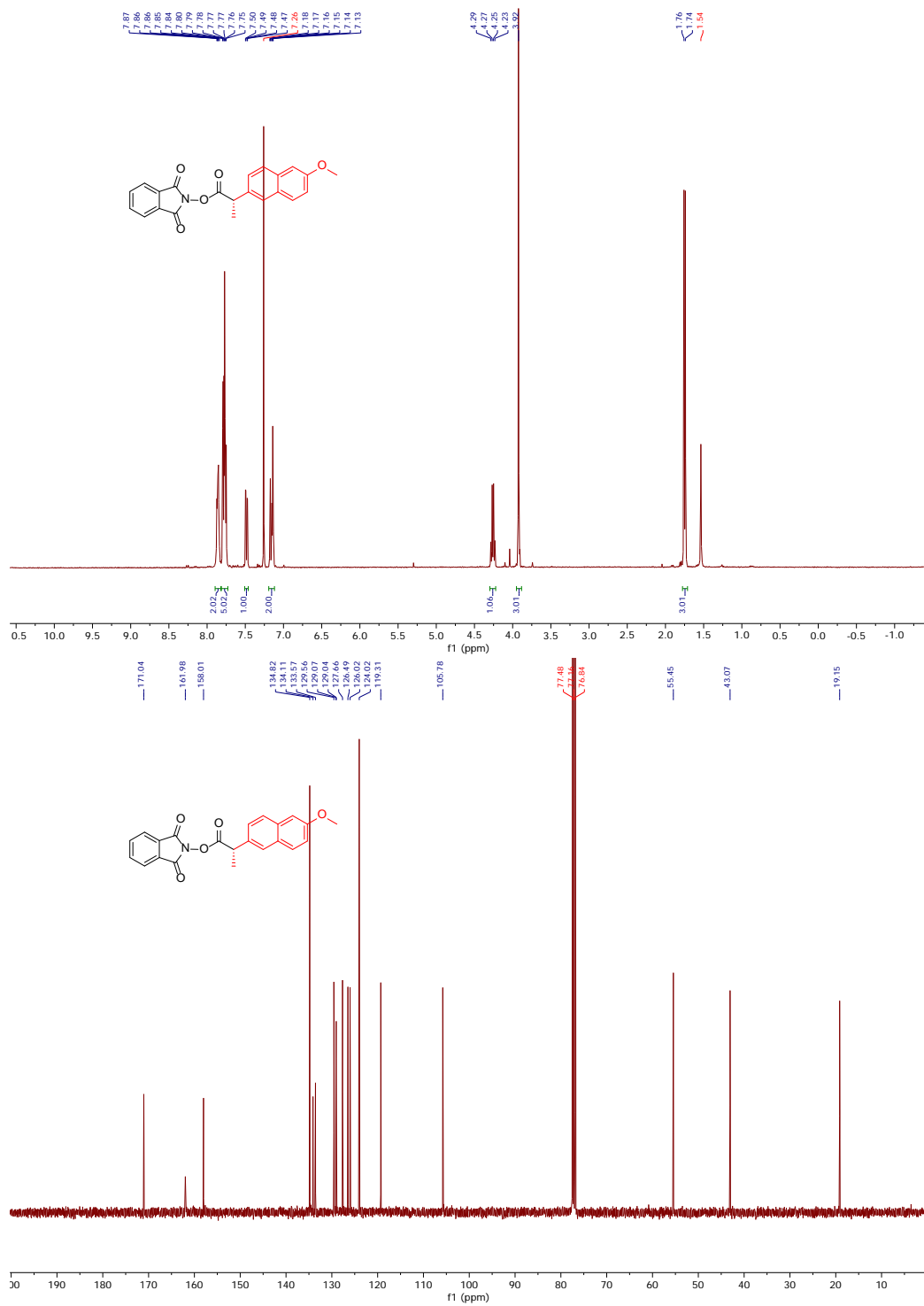
**Supplementary Figure 26. NMR spectra of 1,3-dioxoisindolin-2-yl (*S*)-3-((*tert*-butoxycarbonyl)amino)-5-methylhexanoate**



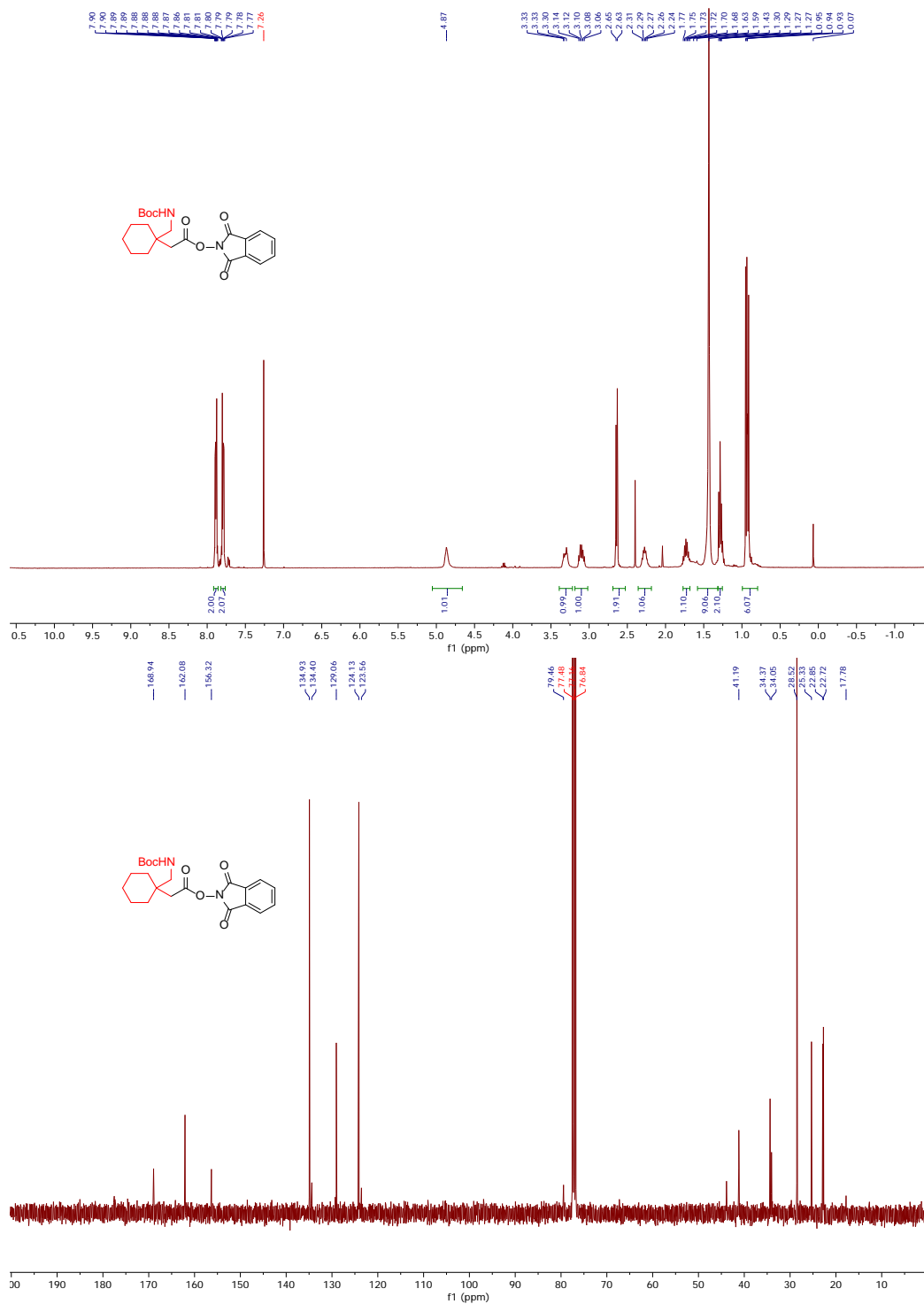
**Supplementary Figure 27. NMR spectra of 1,3-dioxoisindolin-2-yl (4R)-4-((8R,9S,10S,13R,14S,17R)-10,13-dimethyl-3,7,12 trioxohexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoate**



**Supplementary Figure 28. NMR spectra of 1,3-dioxoisindolin-2-yl 4-(4-(bis(2-chloroethyl)amino)phenyl)butanoate**

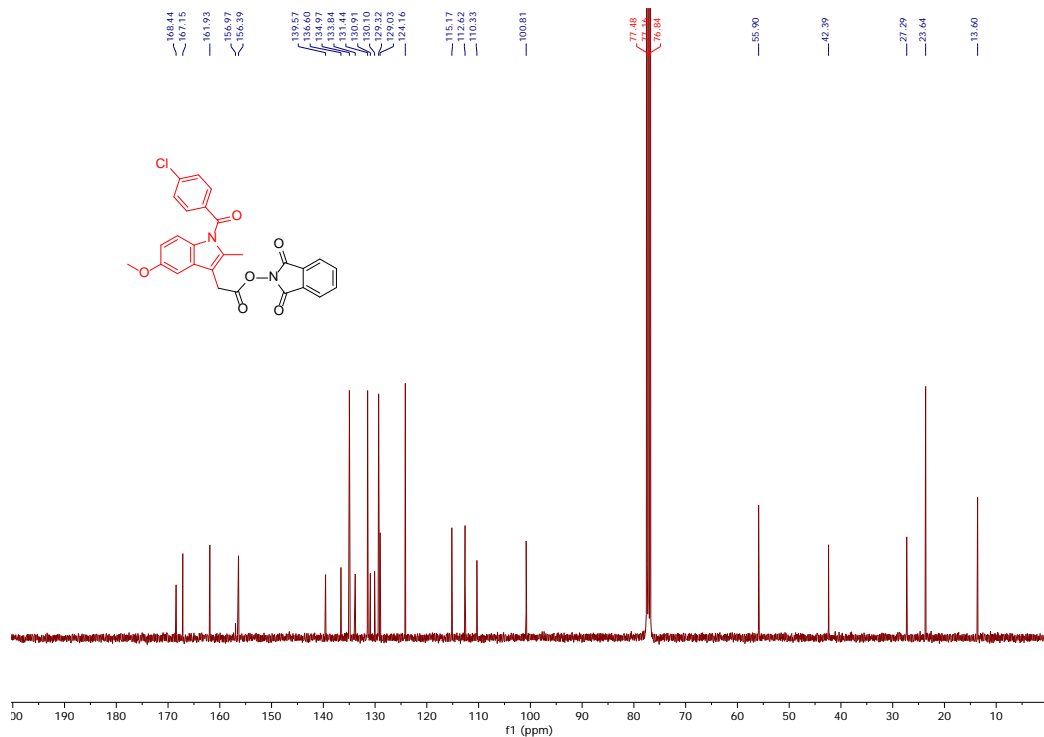
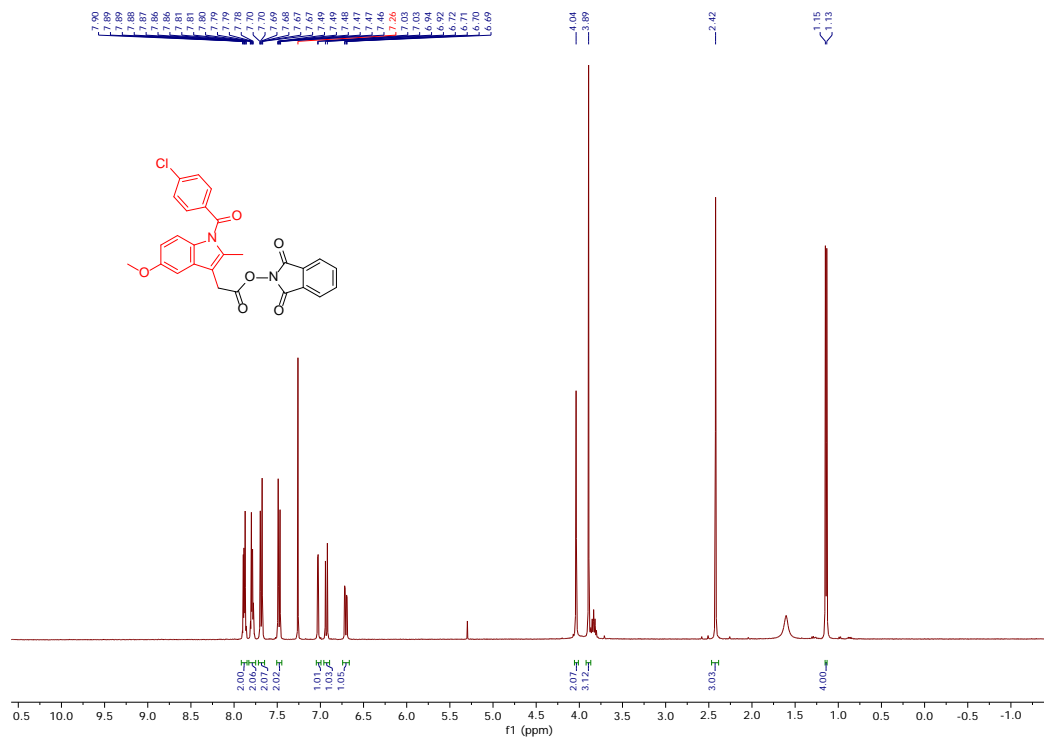


**Supplementary Figure 29. NMR spectra of 1,3-dioxoisindolin-2-yl (*S*)-2-(6-methoxynaphthalen-2-yl)propanoate**

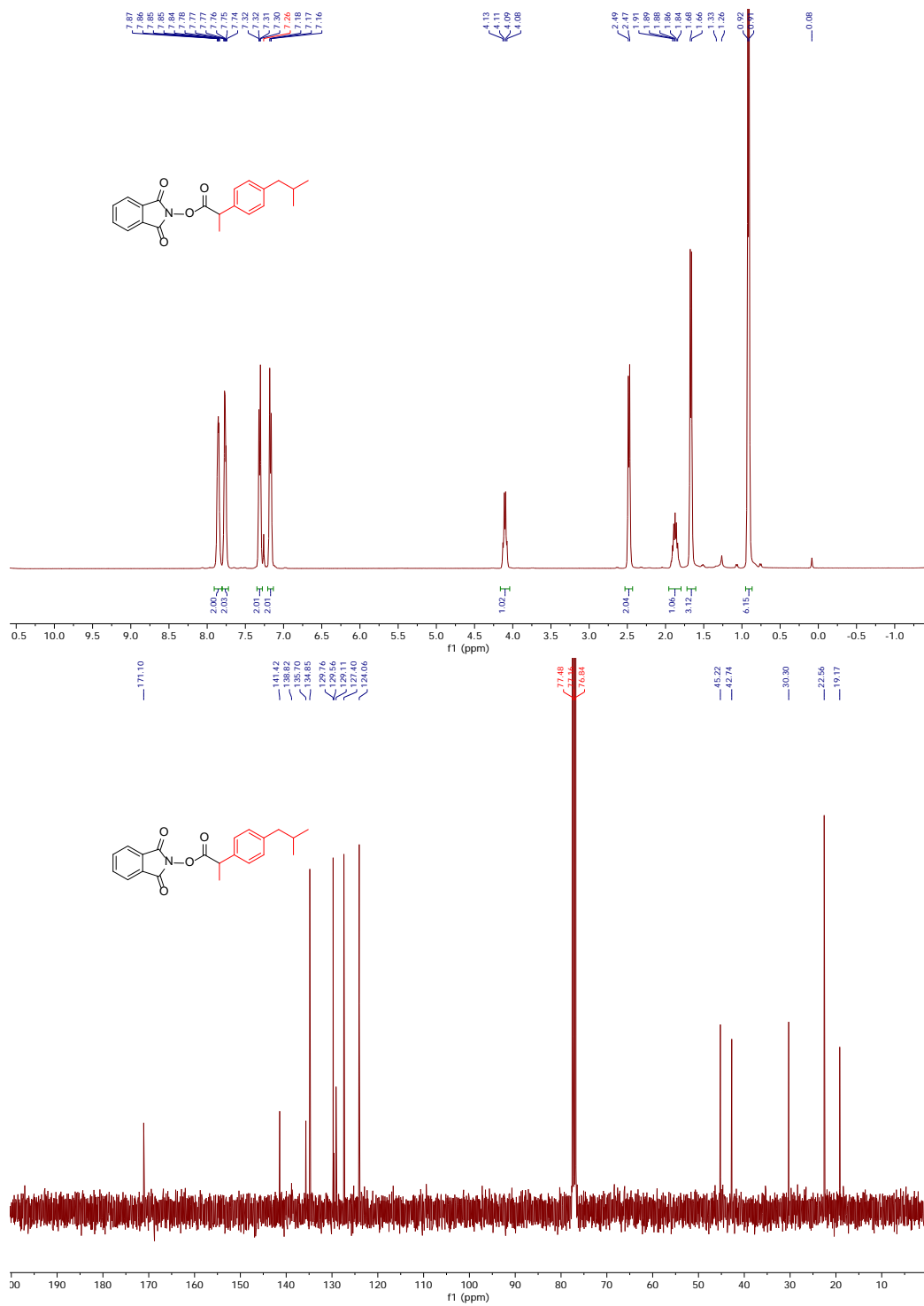


**Supplementary Figure 30. NMR spectra of 1,3-dioxoisindolin-2-yl 2-(((*tert*-butoxycarbonyl)amino)methyl)cyclohexyl)acetate**

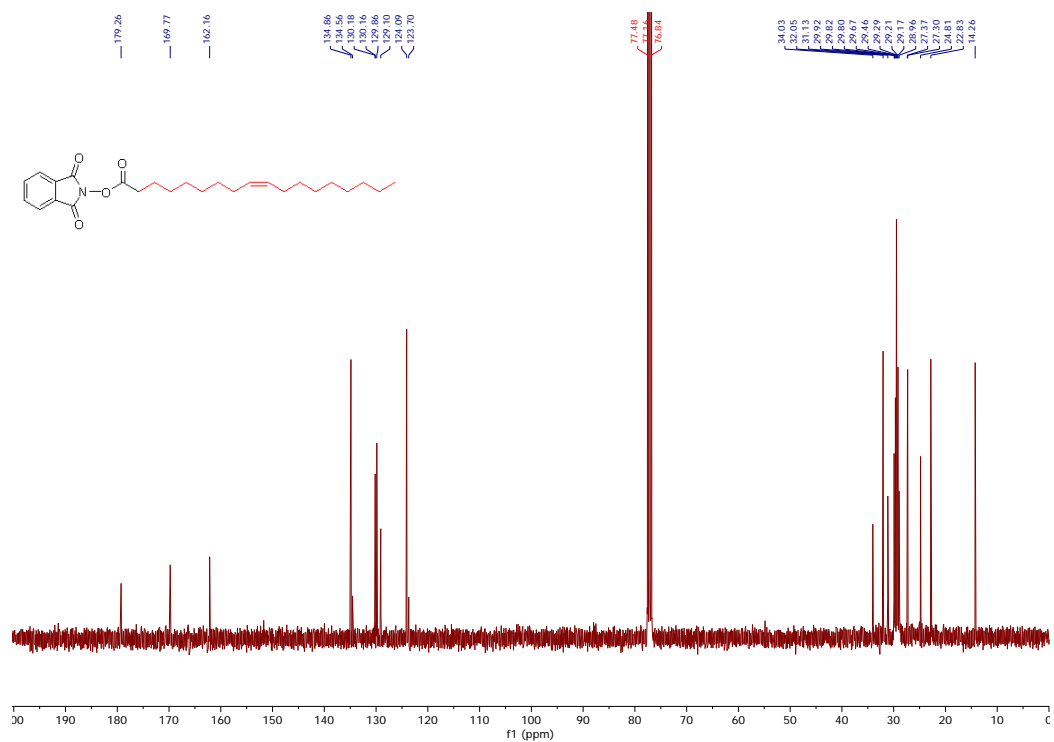
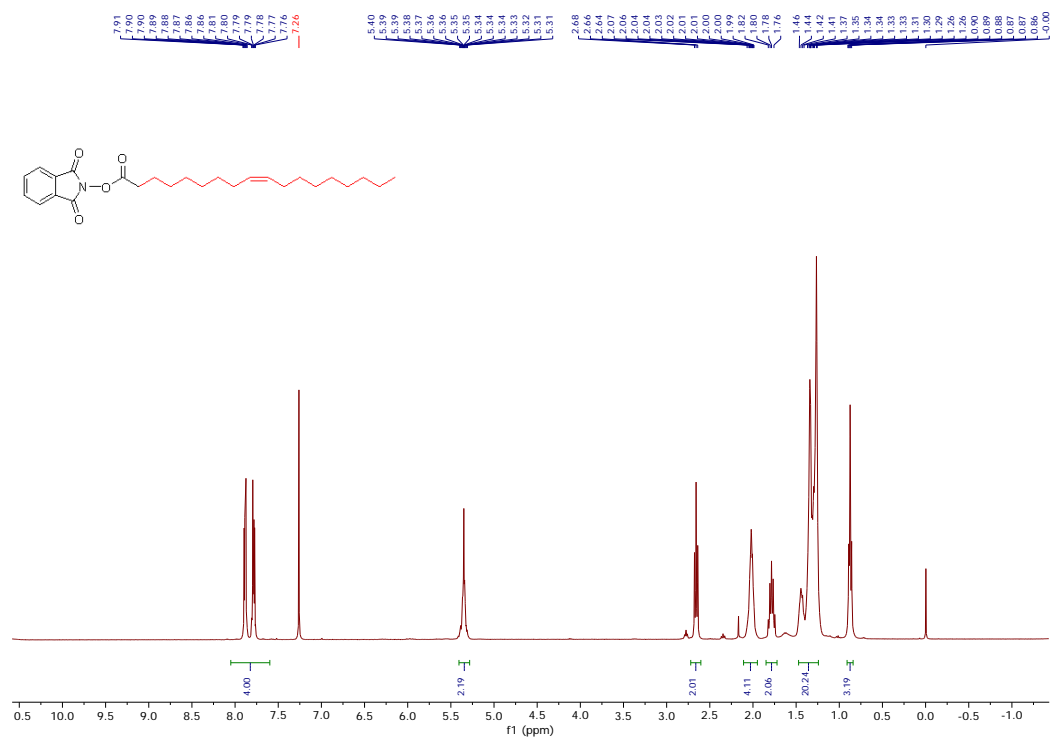




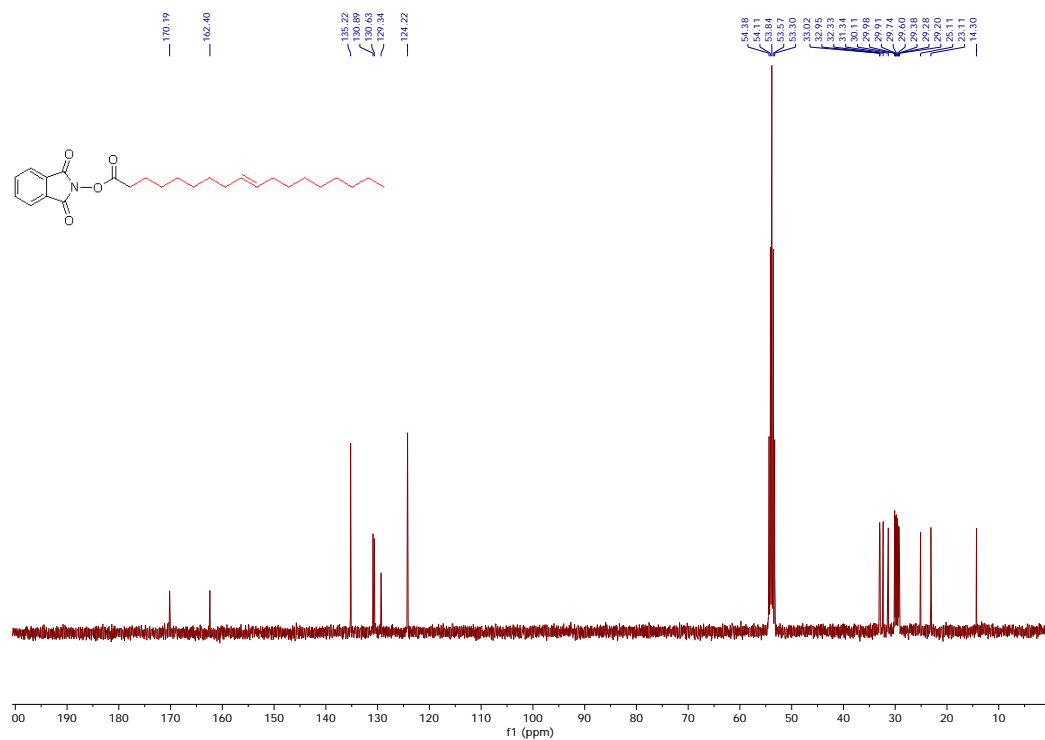
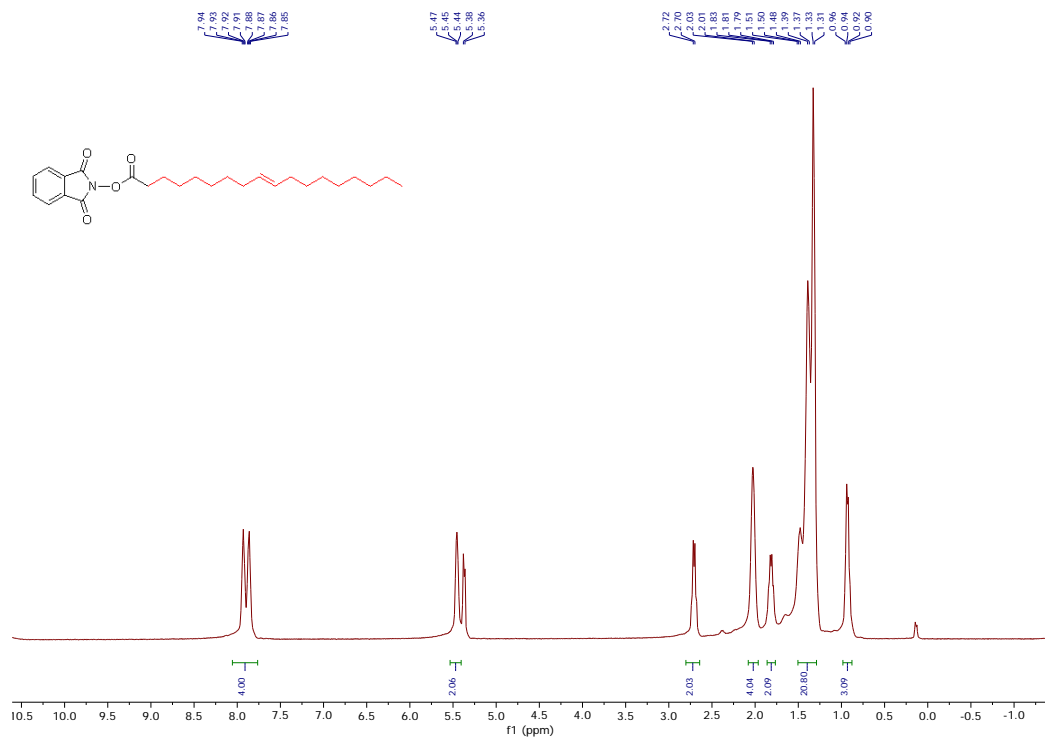
**Supplementary Figure 31. NMR spectra of 1,3-dioxisoindolin-2-yl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate**



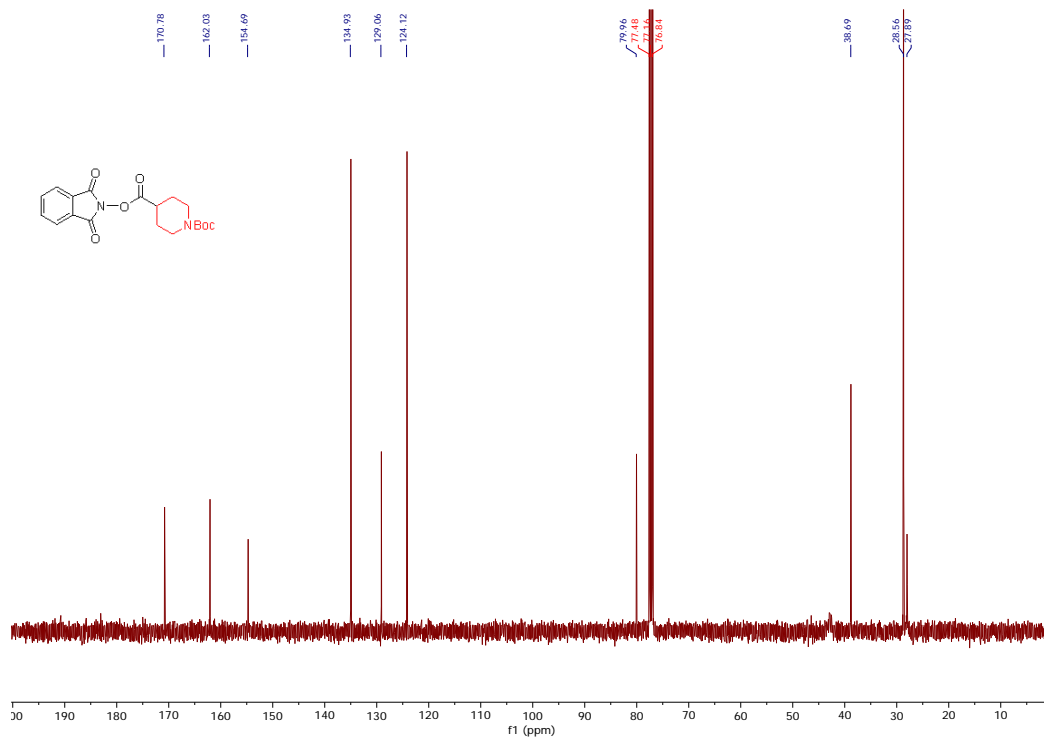
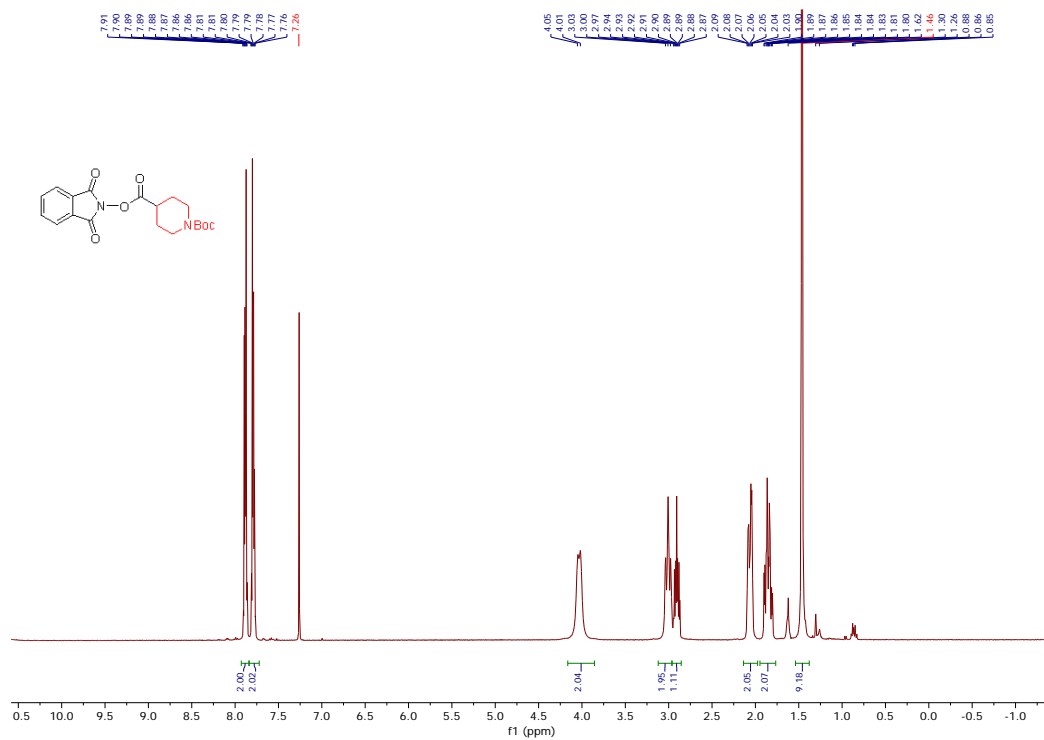
**Supplementary Figure 32. NMR spectra of 1,3-dioxoisindolin-2-yl 2-(4-isobutylphenyl)propanoate**



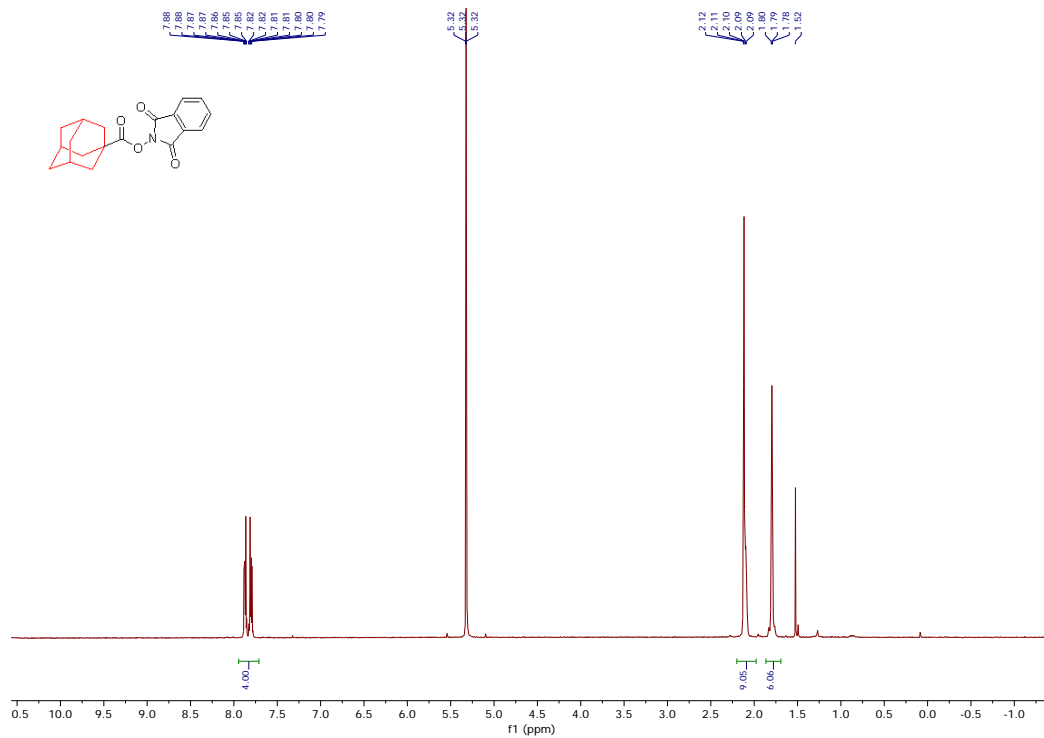
Supplementary Figure 33. NMR spectra of 1,3-dioxoisindolin-2-yl oleate



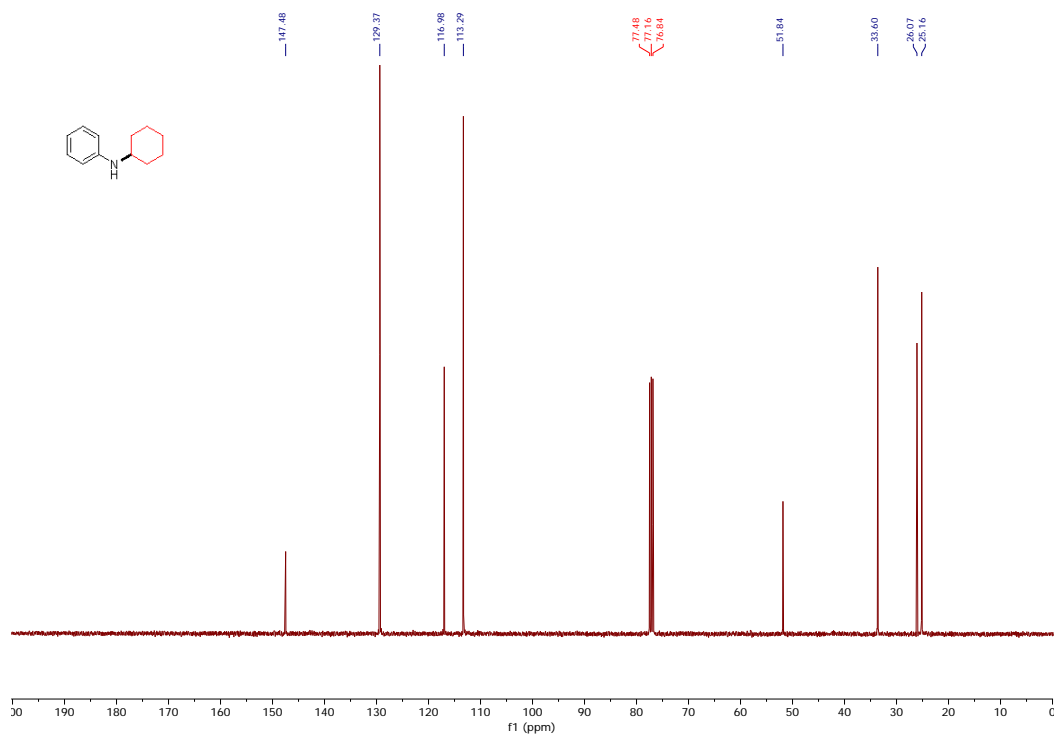
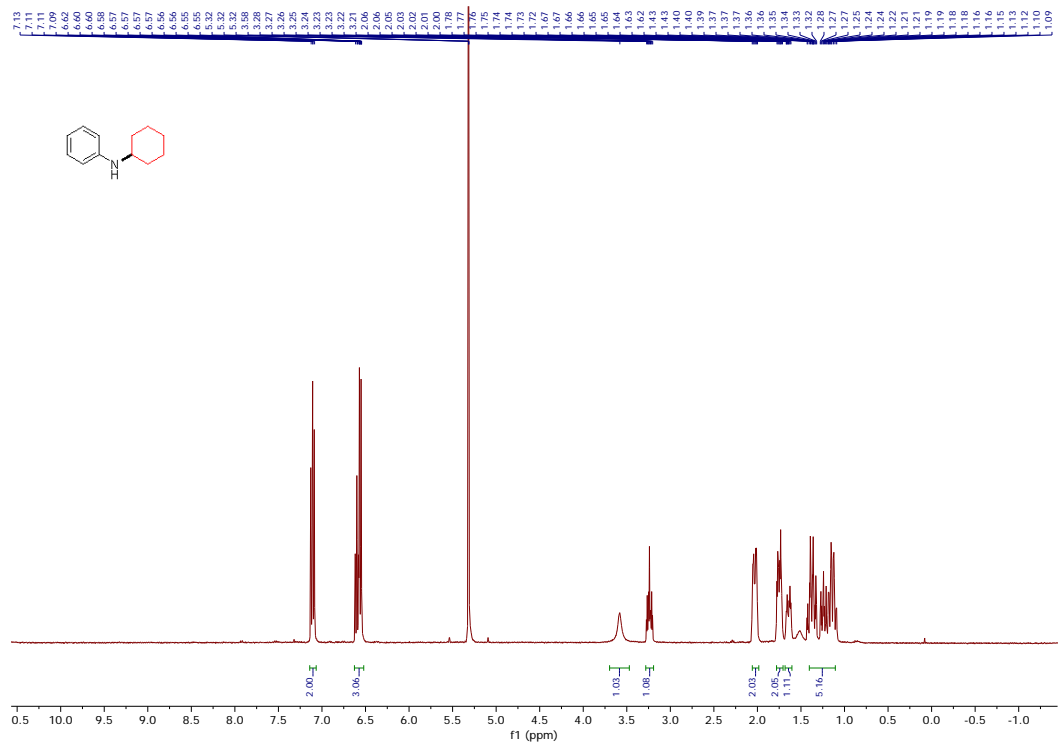
**Supplementary Figure 34. NMR spectra of 1,3-dioxoisindolin-2-yl (*E*)-octadec-9-enoate**



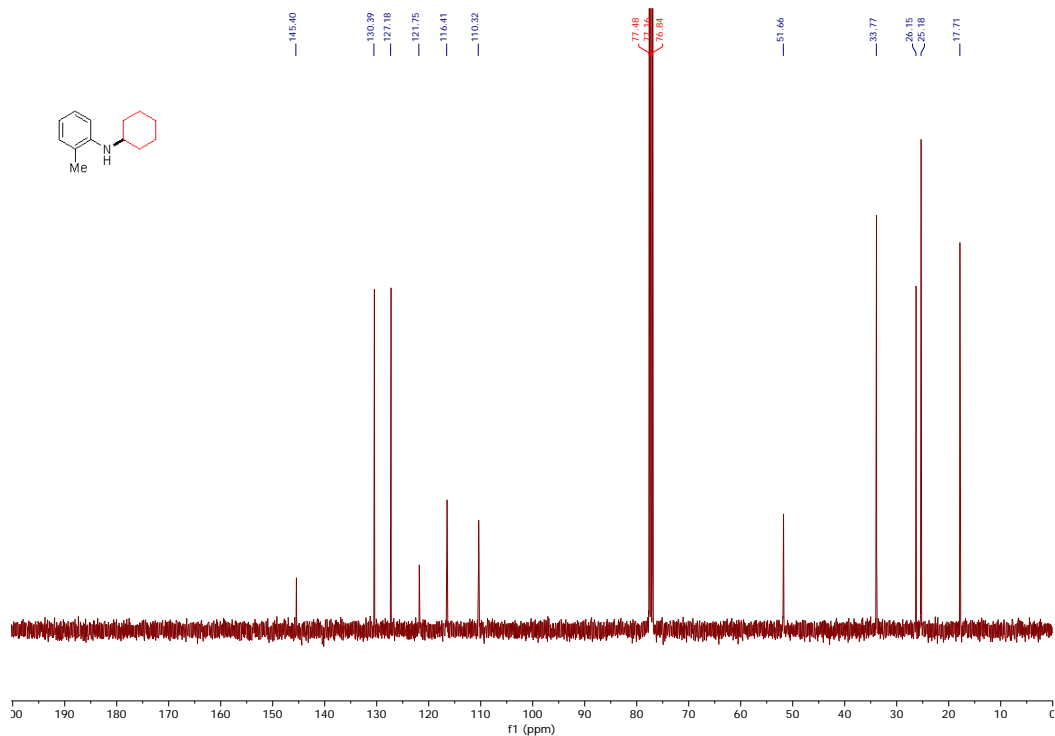
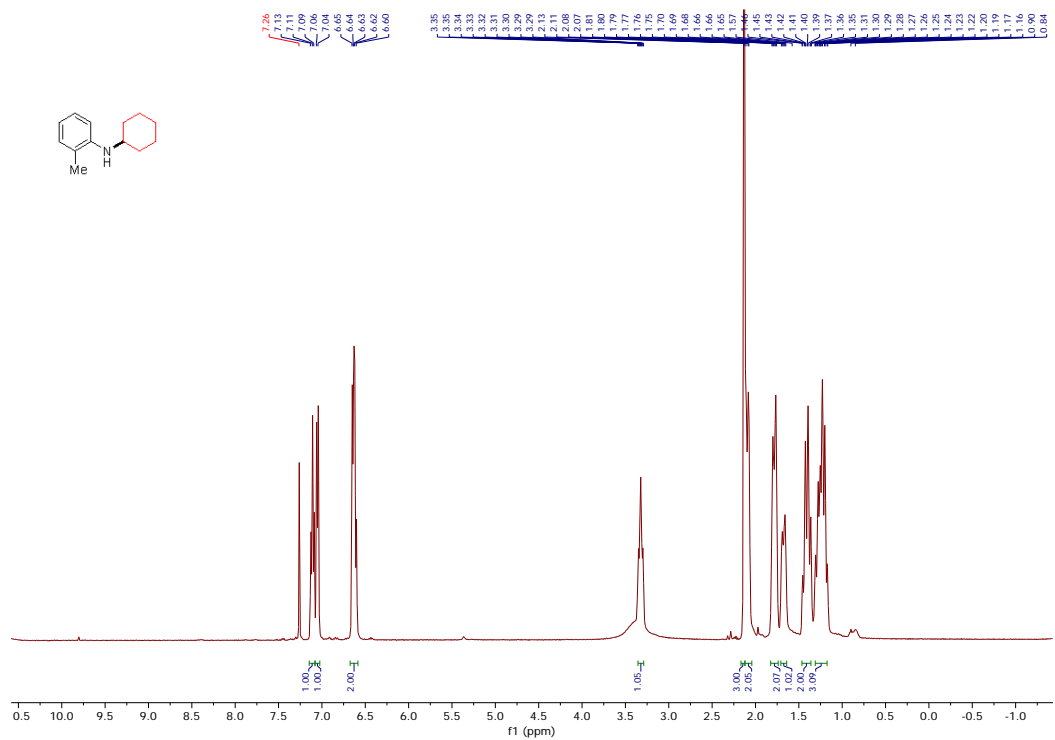
**Supplementary Figure 35. NMR spectra of 1-(*tert*-butyl) 4-(1,3-dioxisoindolin-2-yl) piperidine-1,4-dicarboxylate**



**Supplementary Figure 36. NMR spectra of 1,3-dioxoisindolin-2-adamantane-1-carboxylate**

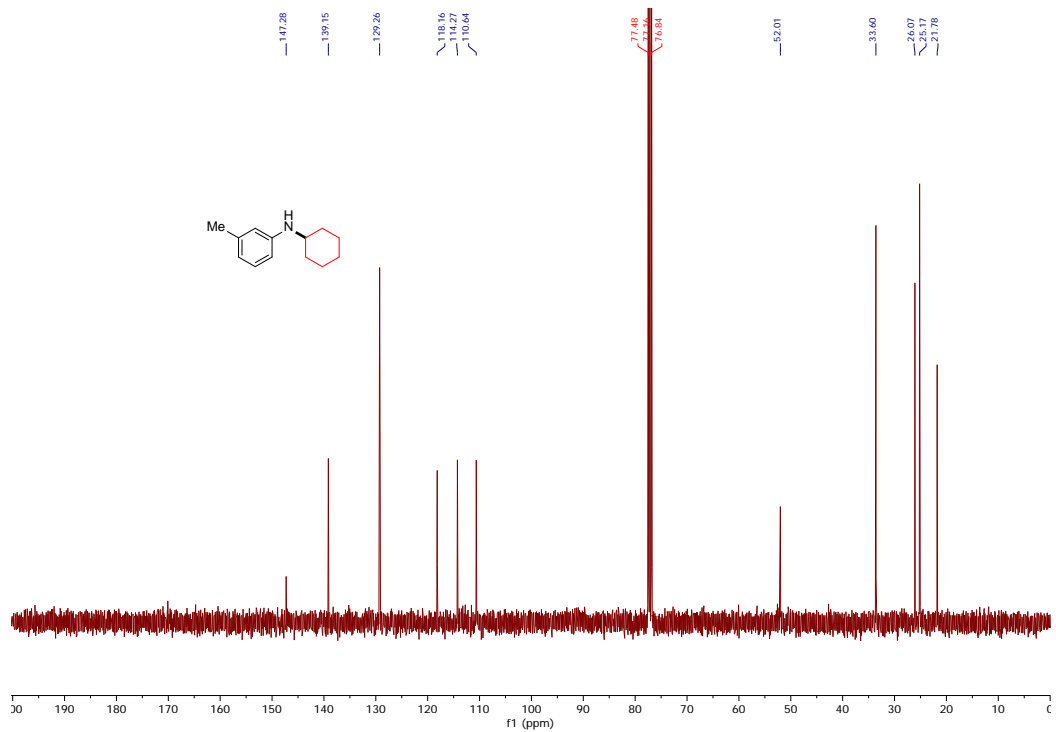
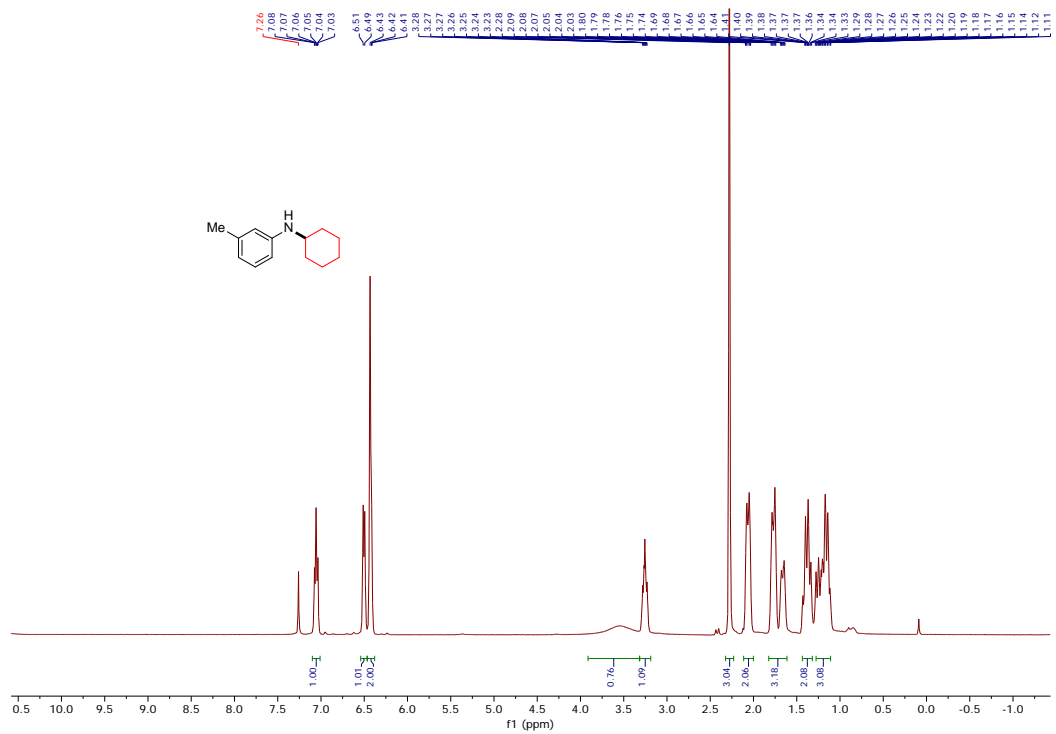


**Supplementary Figure 37. NMR spectra of N-cyclohexylaniline (3a)**

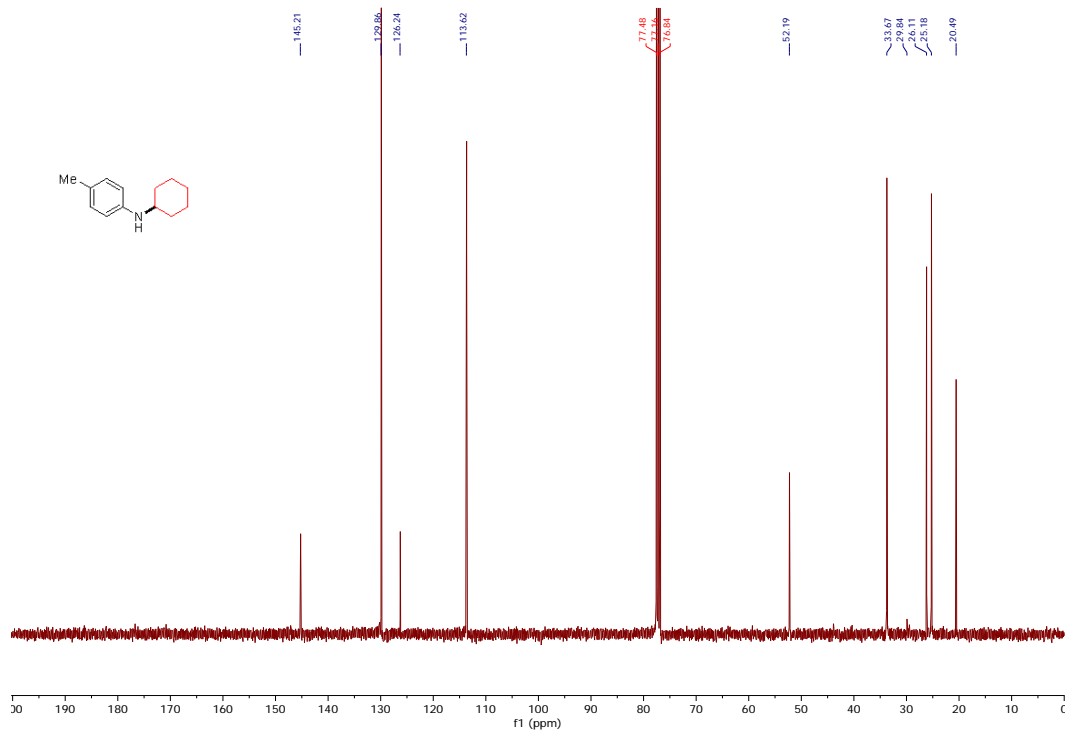
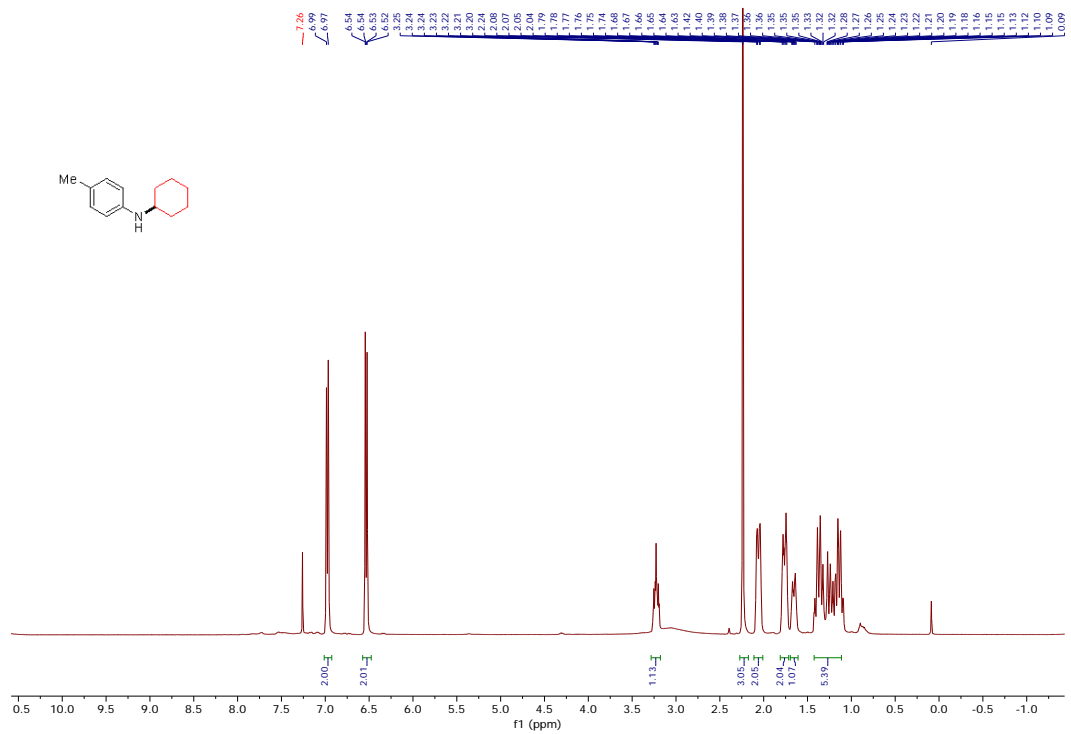


**Supplementary Figure 38. NMR spectra of N-cyclohexyl-2-methylaniline (3b)**

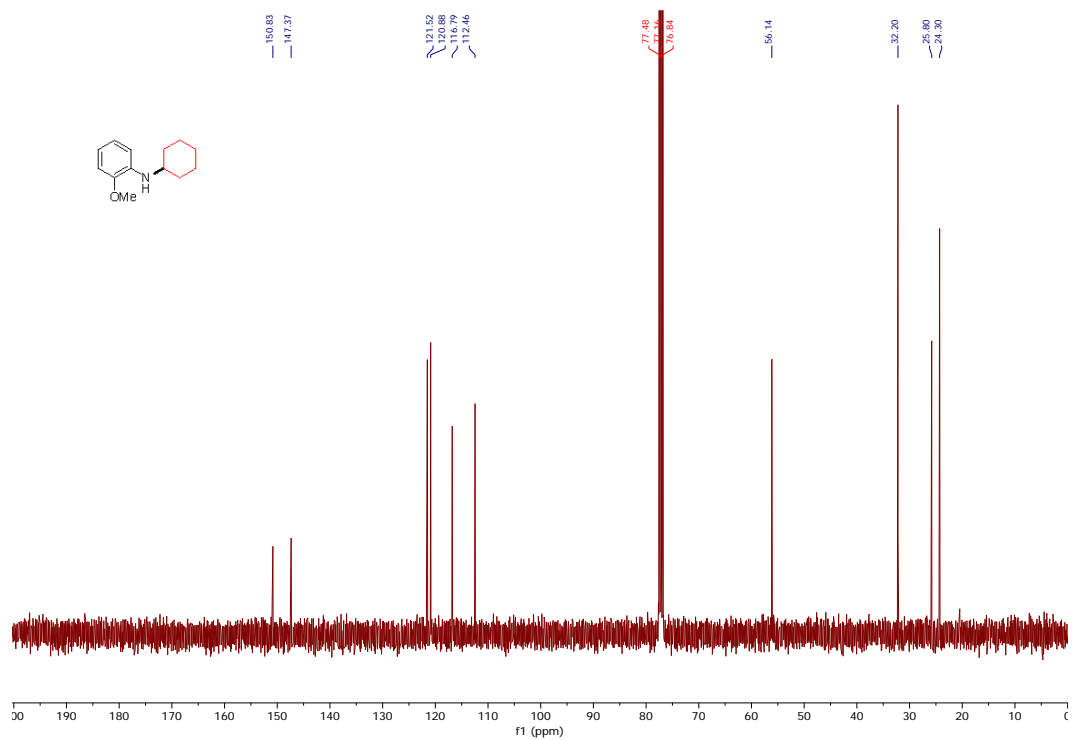
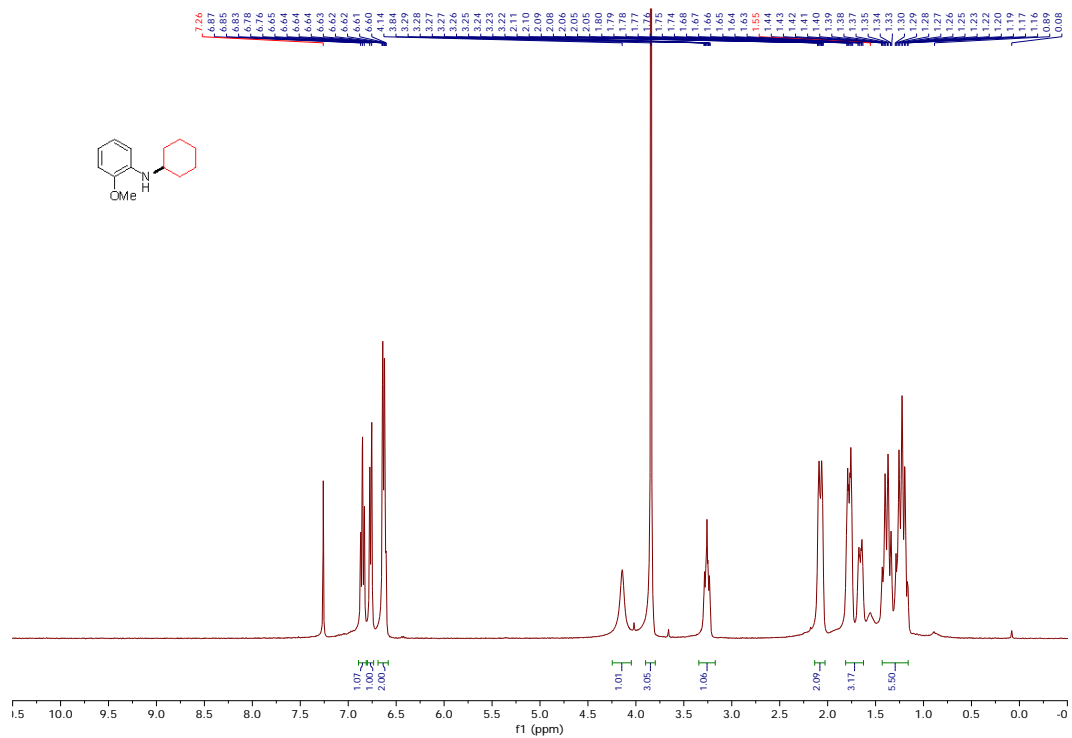




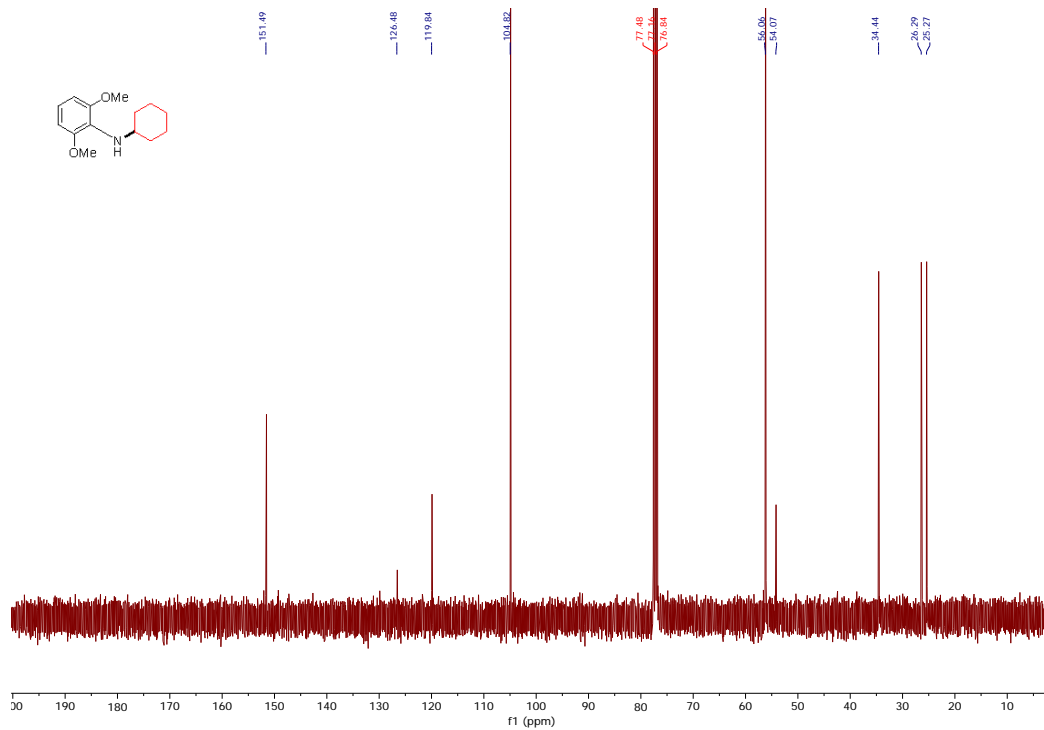
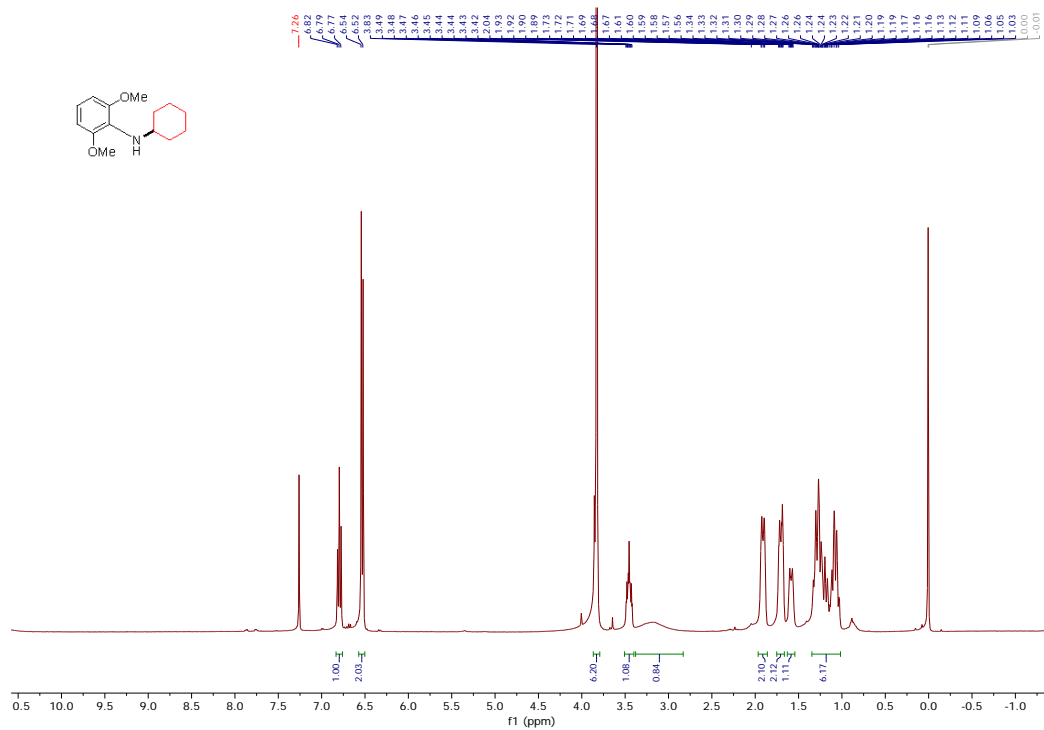
Supplementary Figure 39. NMR spectra of *N*-cyclohexyl-3-methylaniline (3c)



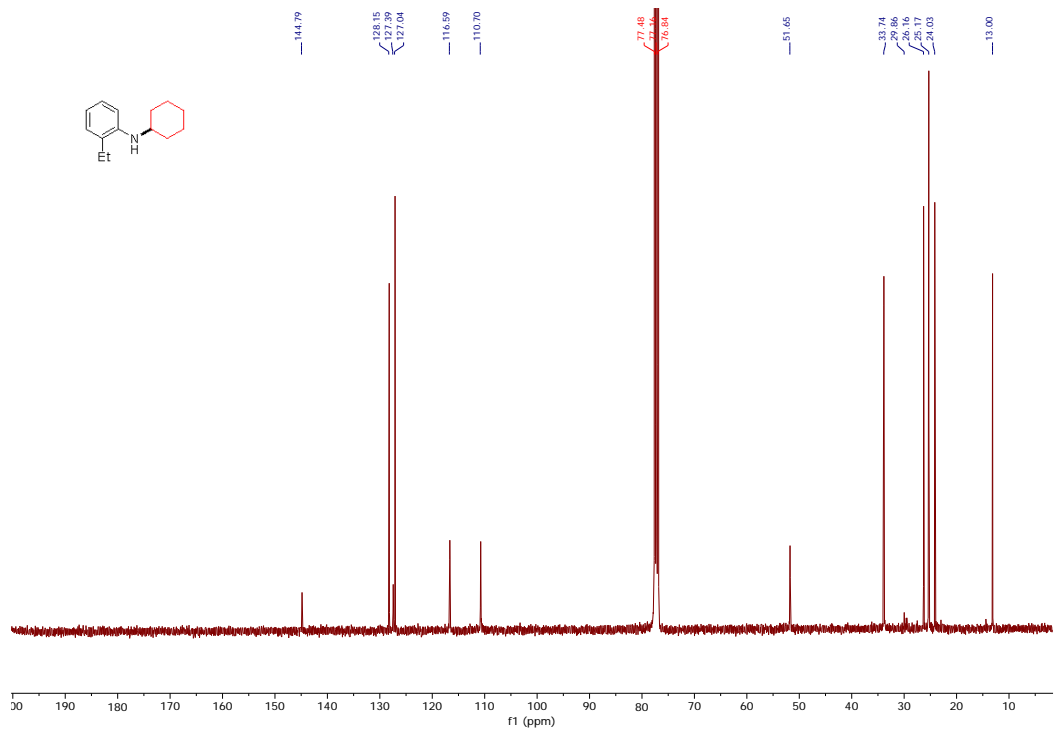
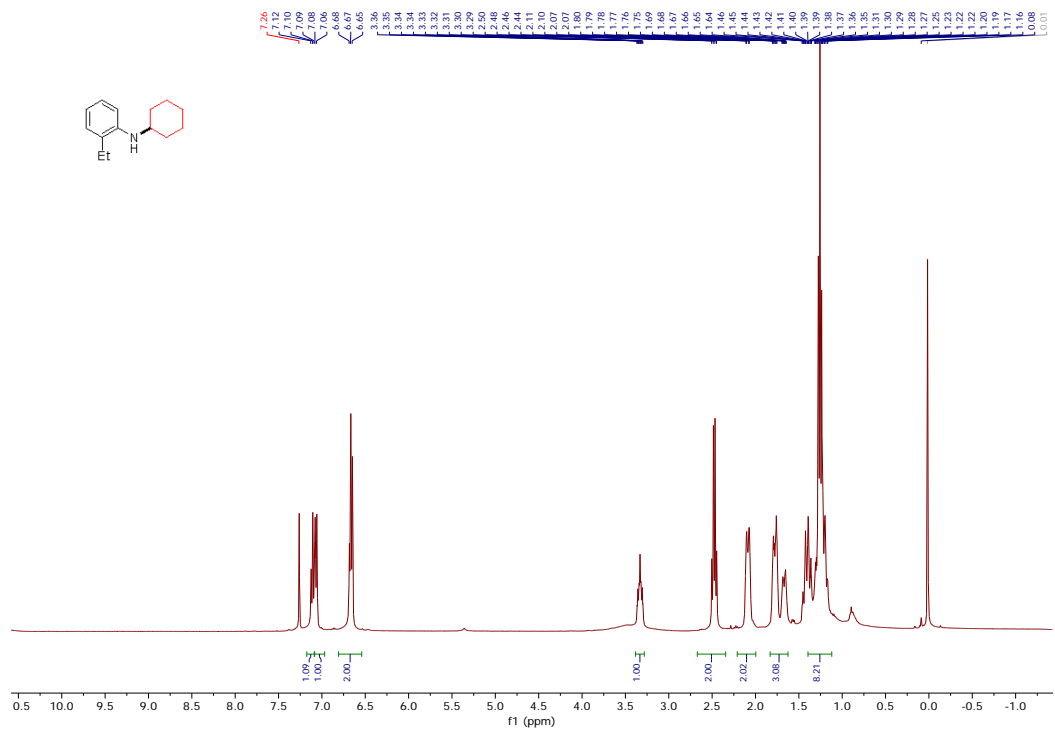
Supplementary Figure 40. NMR spectra of *N*-cyclohexyl-4-methylaniline (3d)



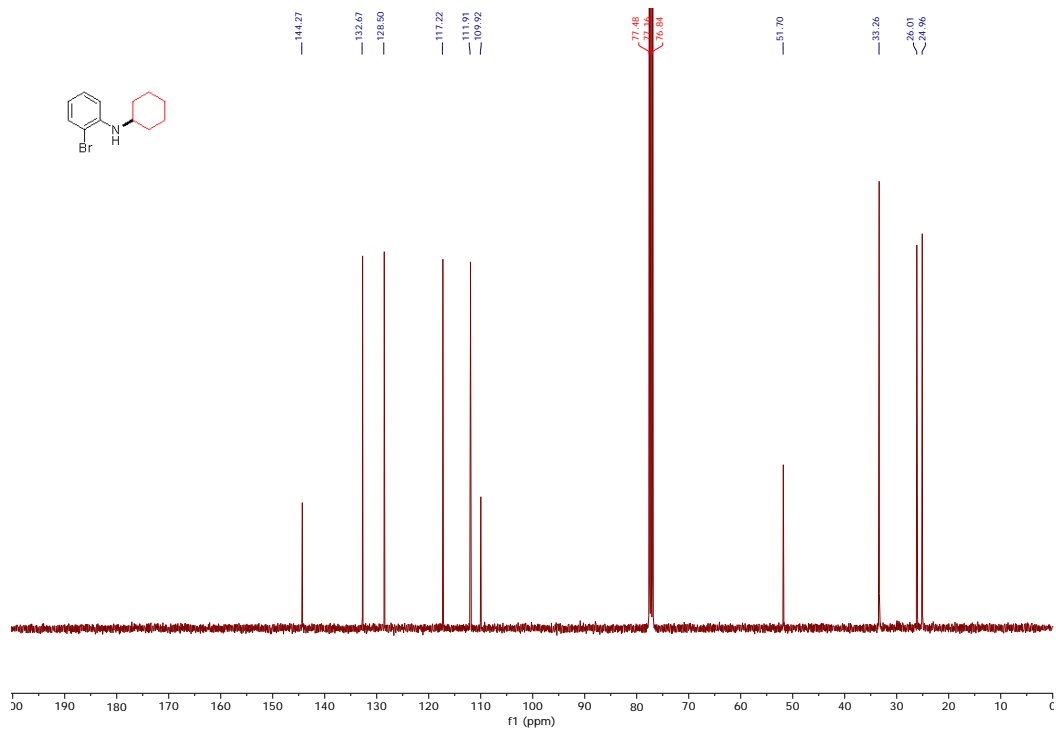
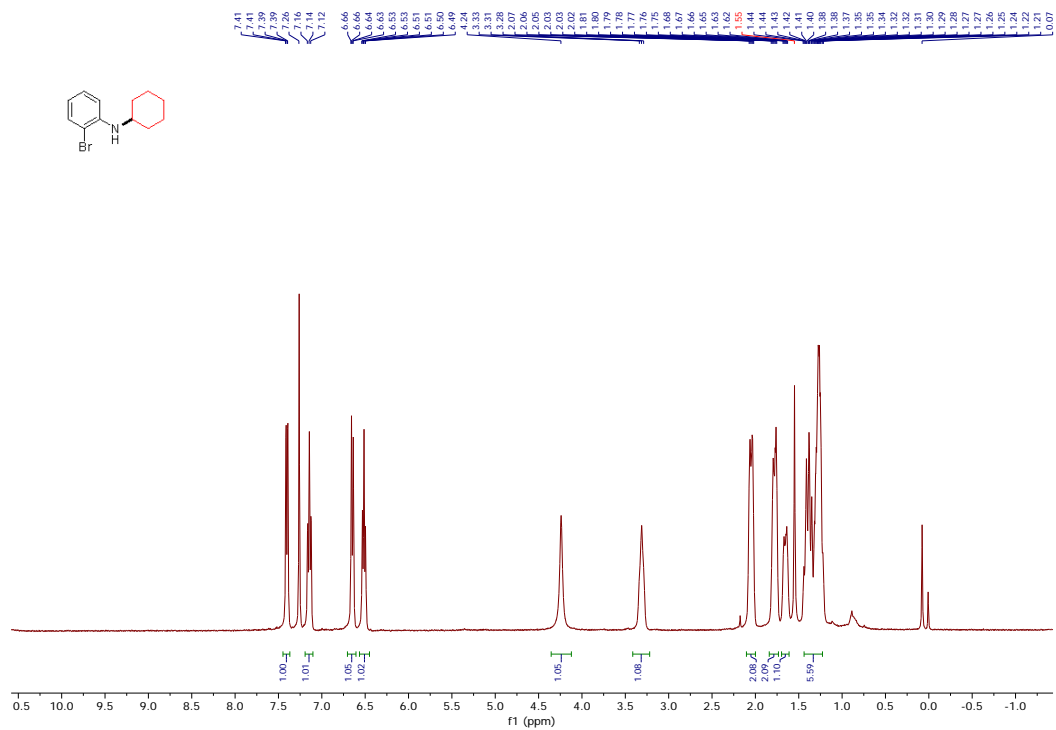
**Supplementary Figure 41. NMR spectra of *N*-cyclohexyl-2-methoxyaniline (3e)**



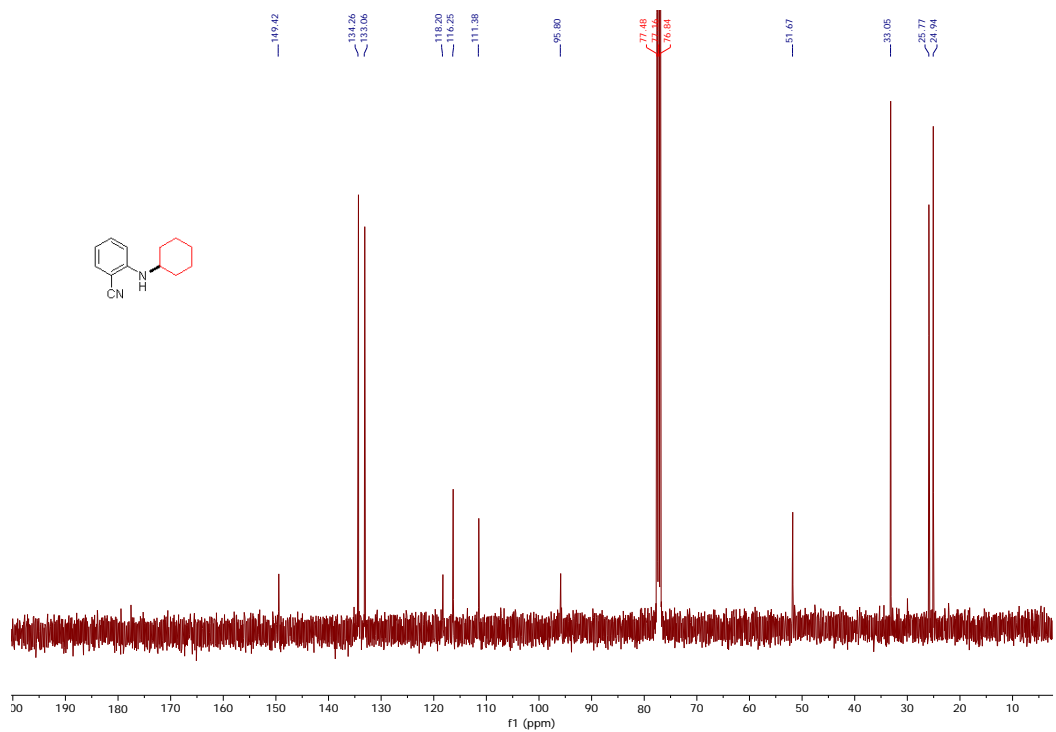
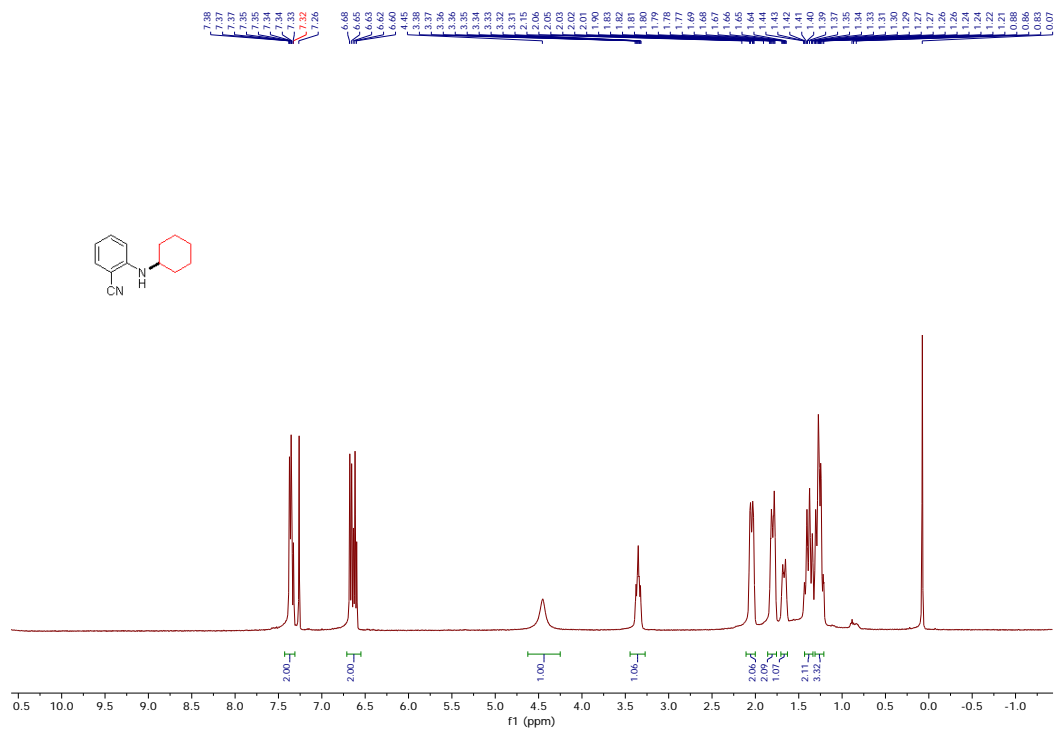
**Supplementary Figure 42. NMR spectra of *N*-cyclohexyl-2,6-dimethoxyaniline (3f)**



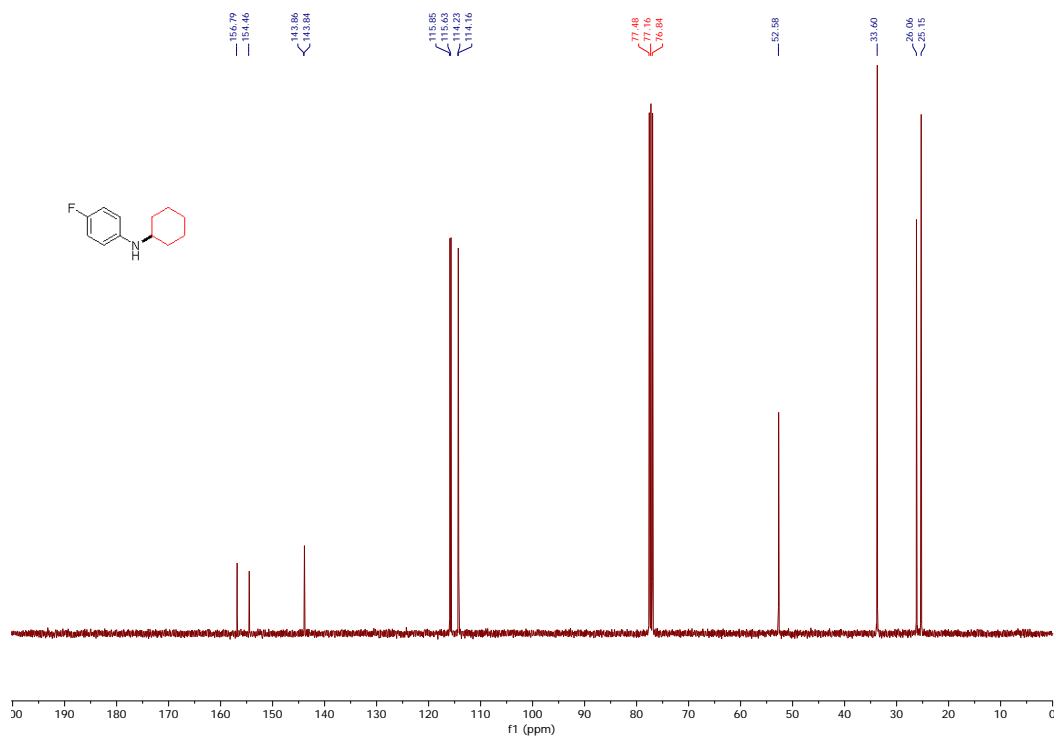
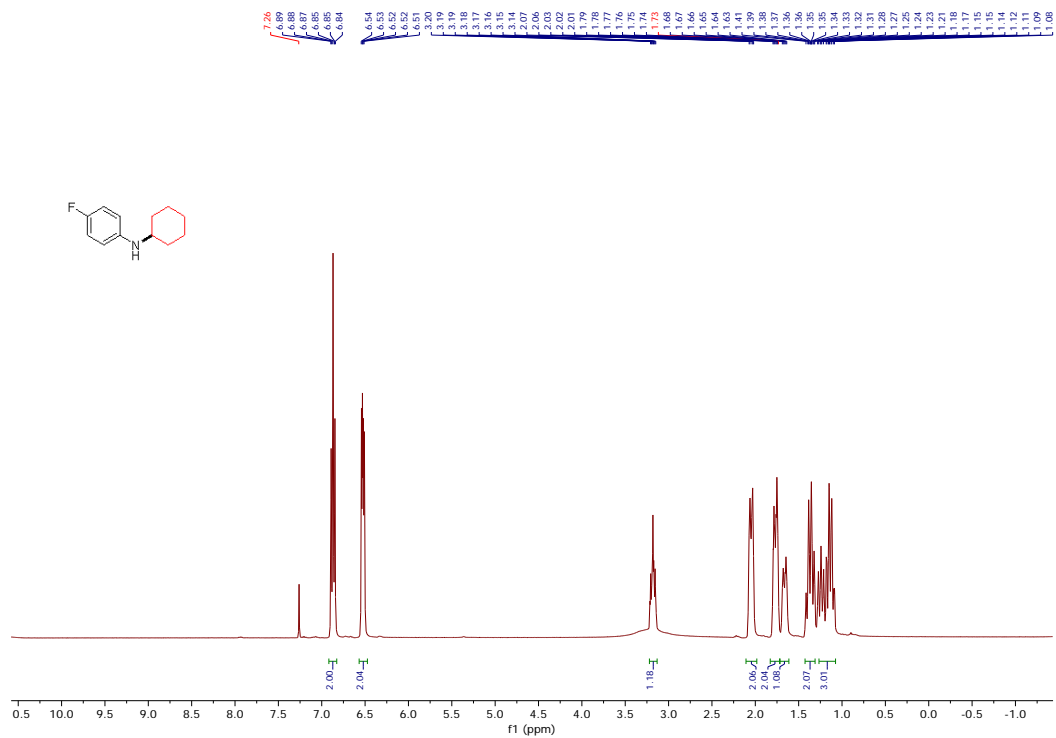
**Supplementary Figure 43. NMR spectra of *N*-cyclohexyl-2-ethylaniline (3g)**



Supplementary Figure 44. NMR spectra of 2-bromo-N-cyclohexylaniline (3h)

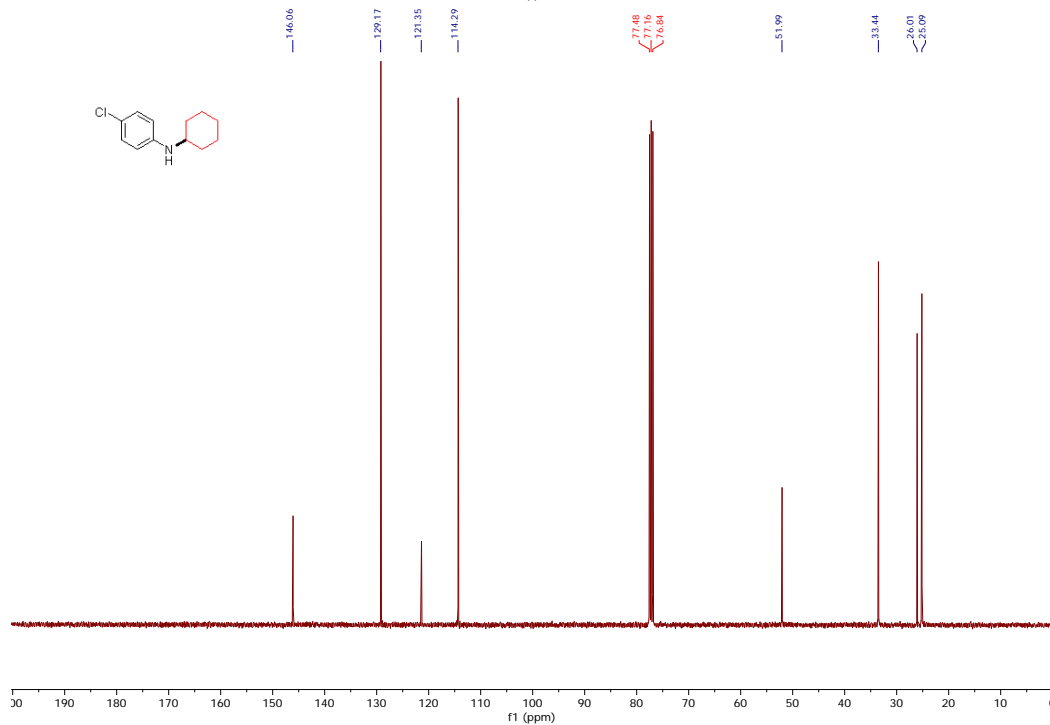
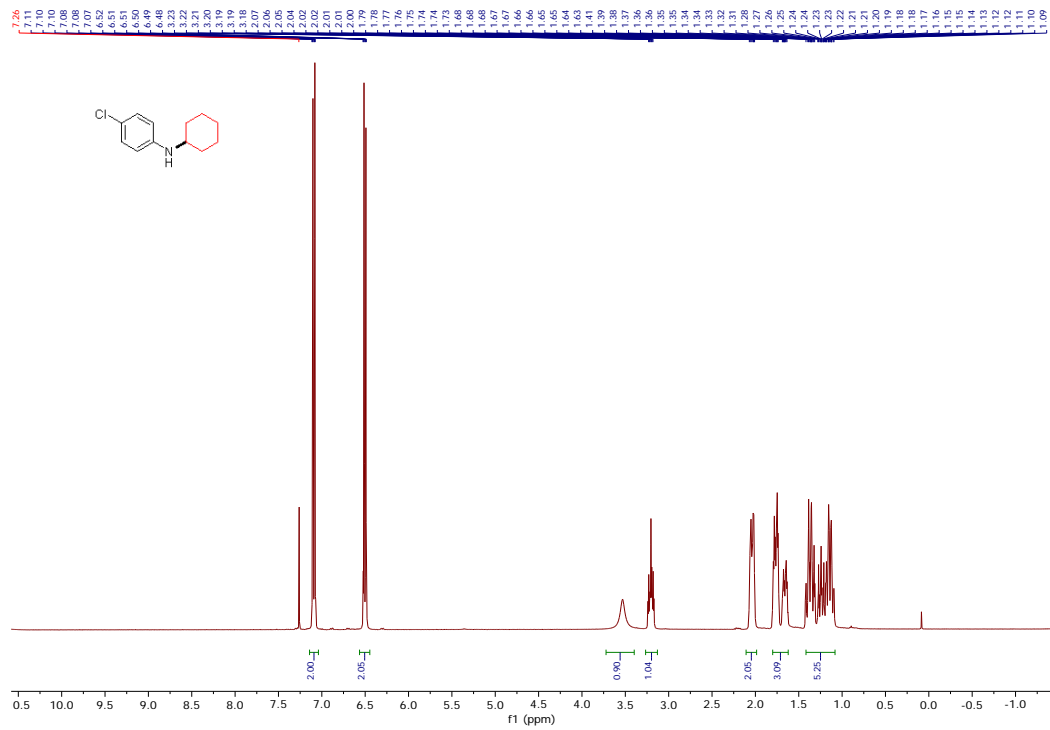


**Supplementary Figure 45. NMR spectra of 2-(cyclohexylamino)benzonitrile (3i)**

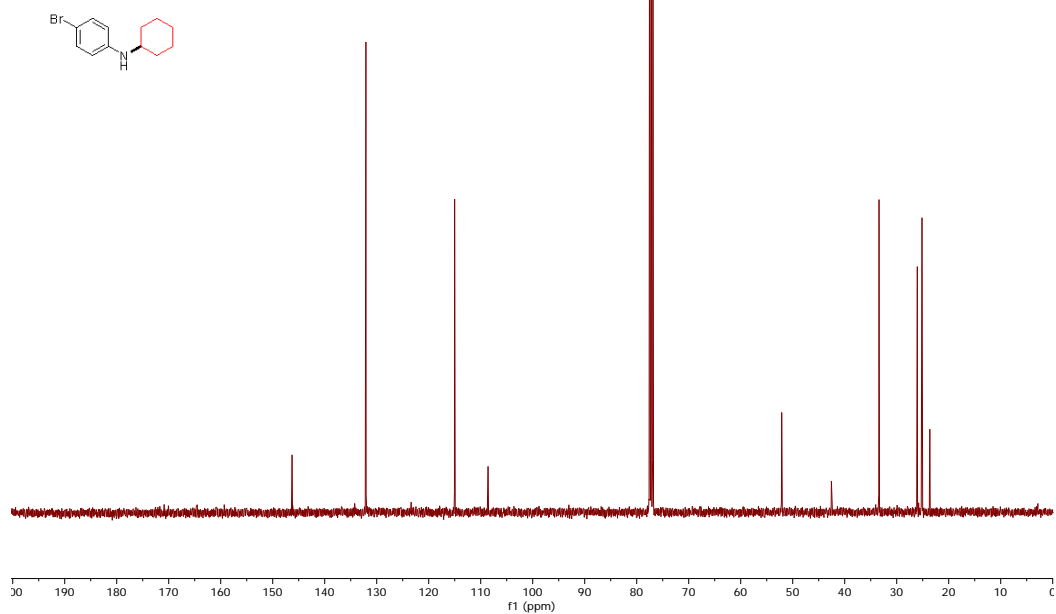
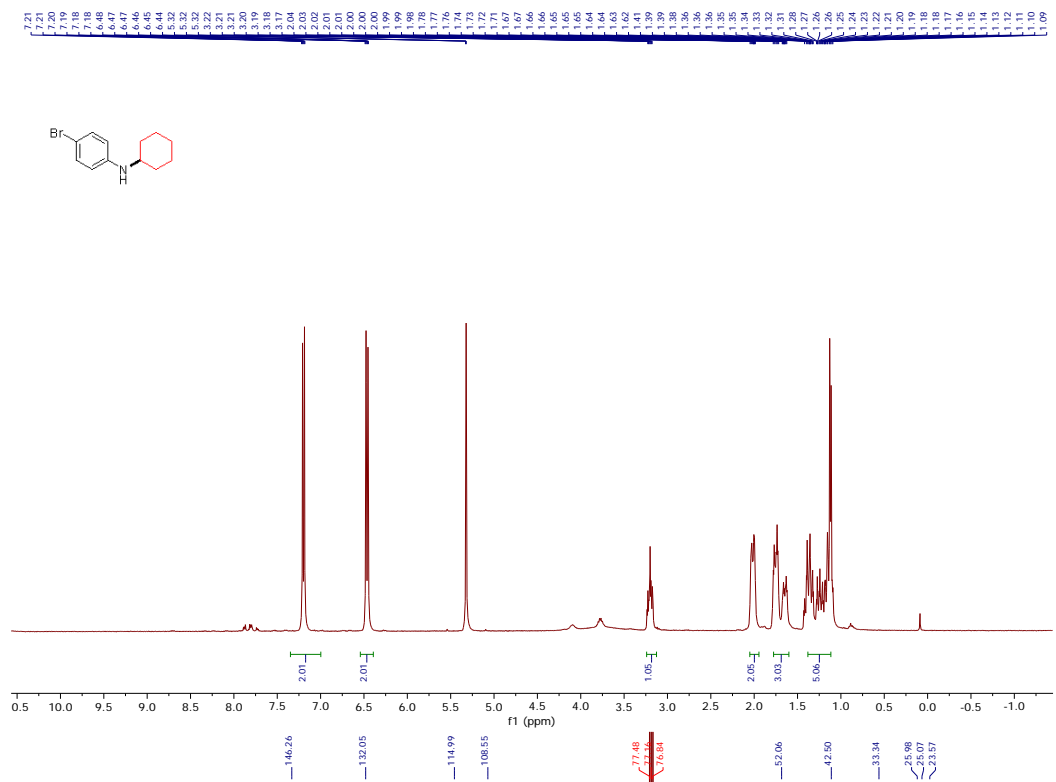


**Supplementary Figure 46. NMR spectra of *N*-cyclohexyl-4-fluoroaniline (3j)**

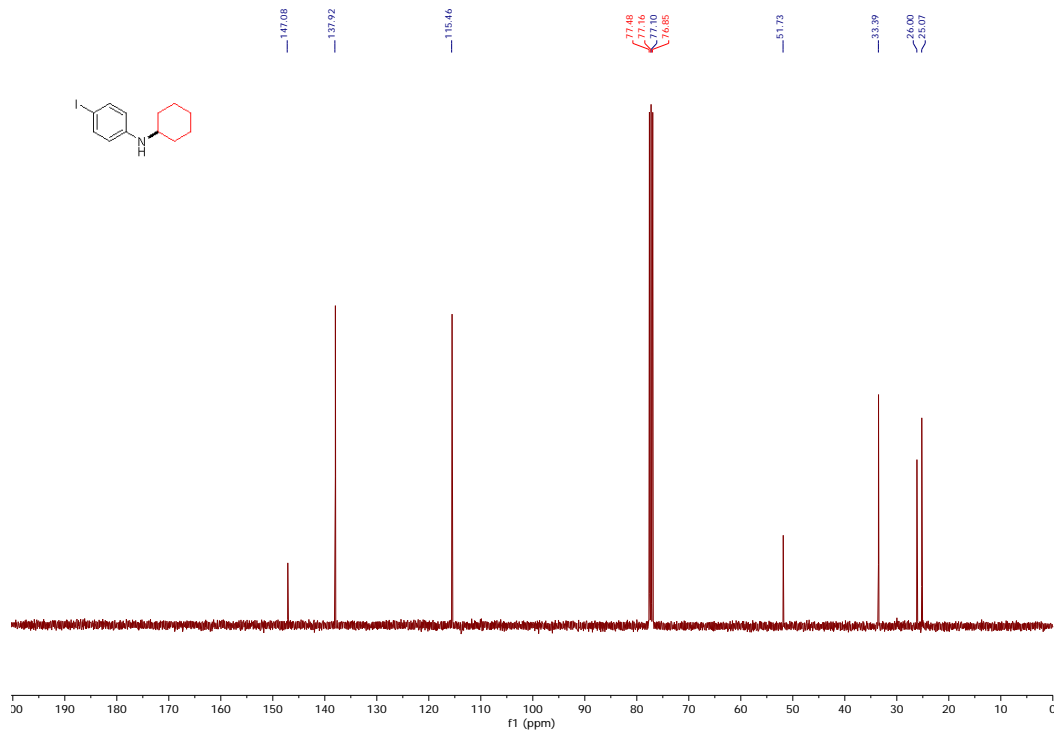
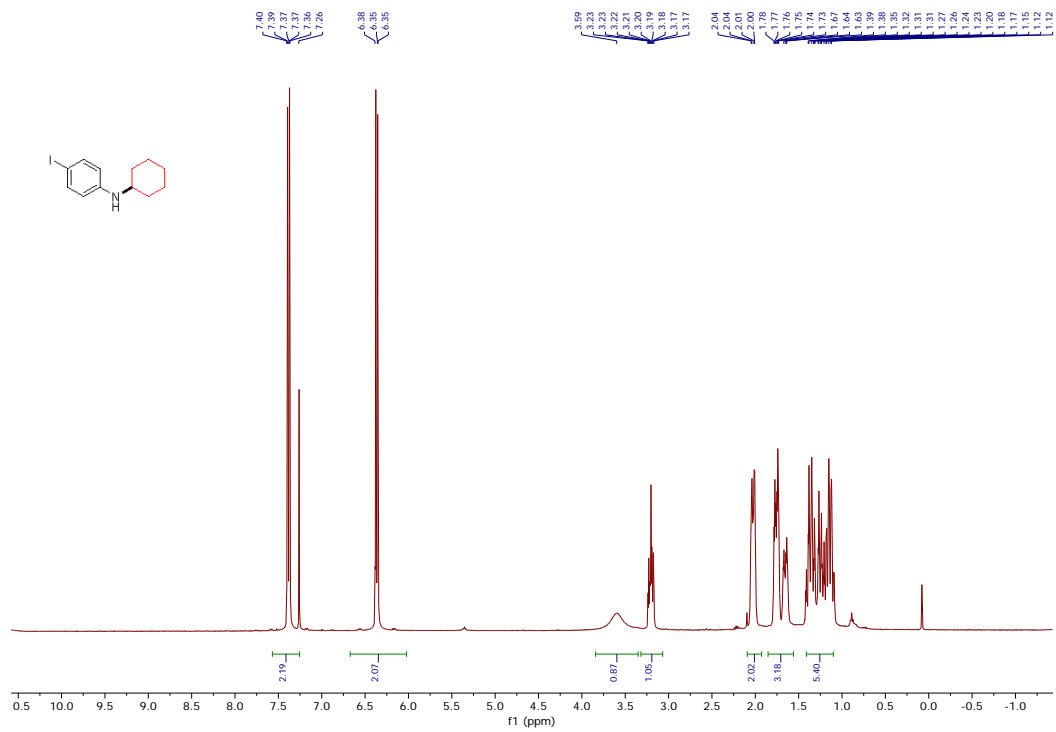




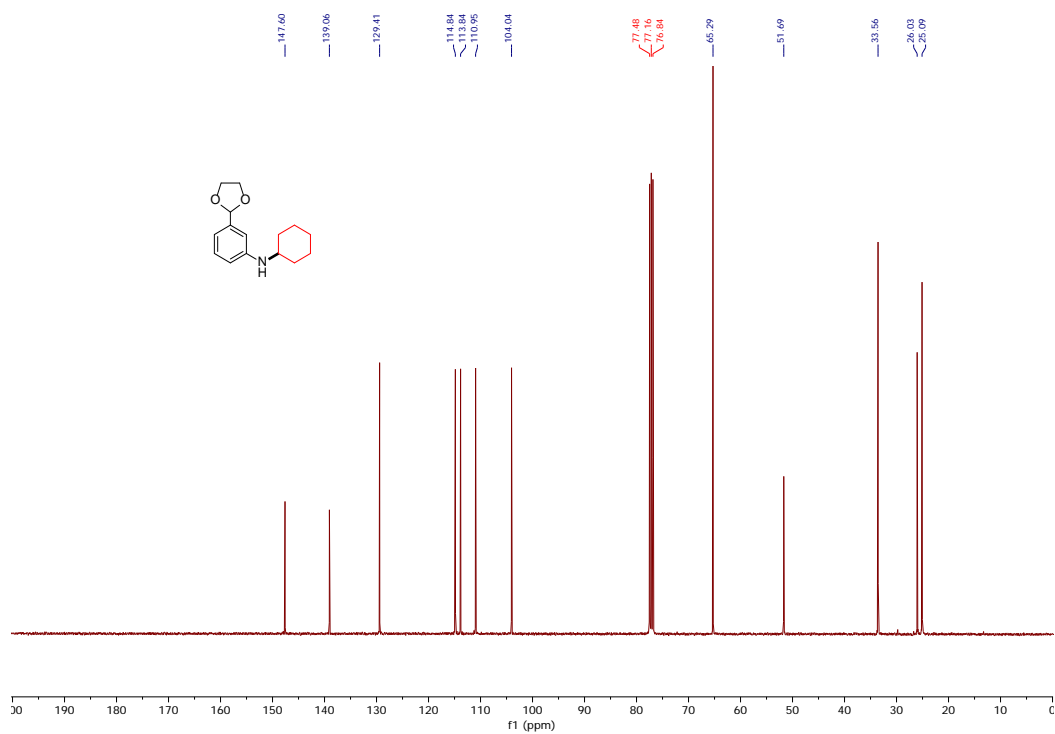
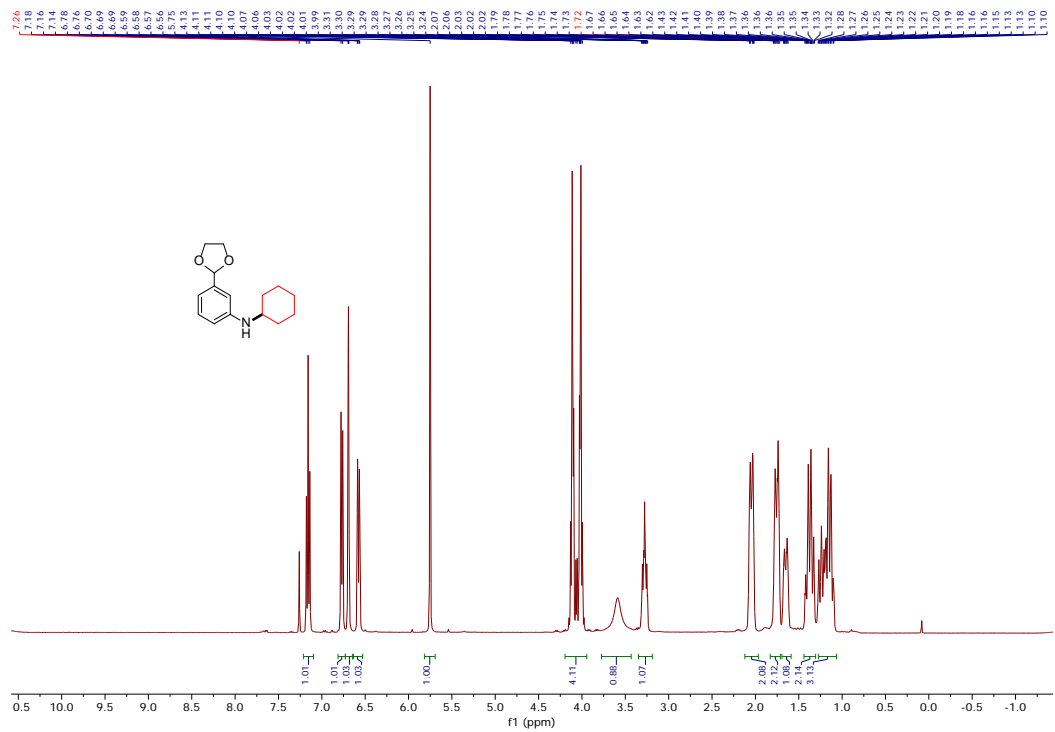
Supplementary Figure 47. NMR spectra of 4-chloro-N-cyclohexylaniline (3k)



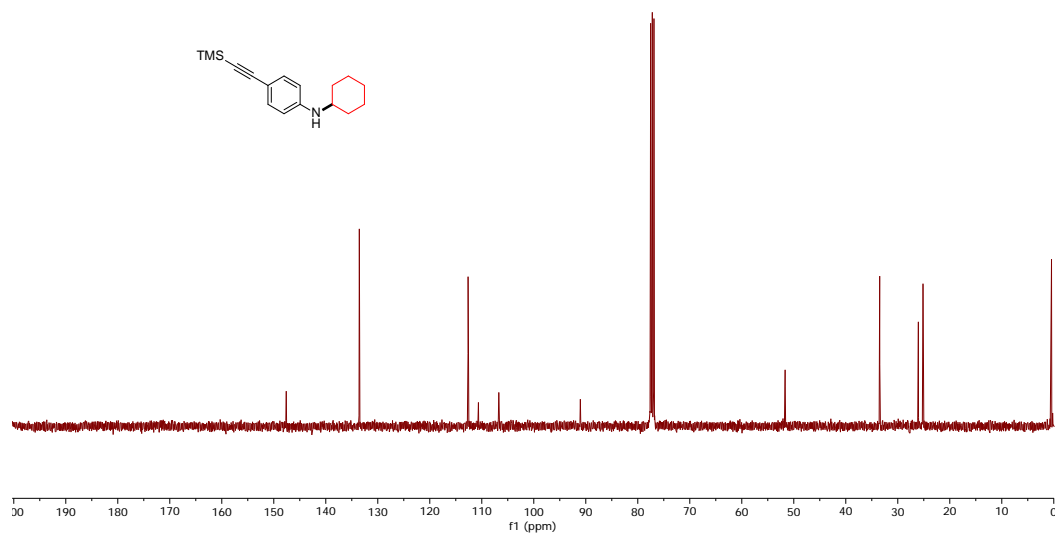
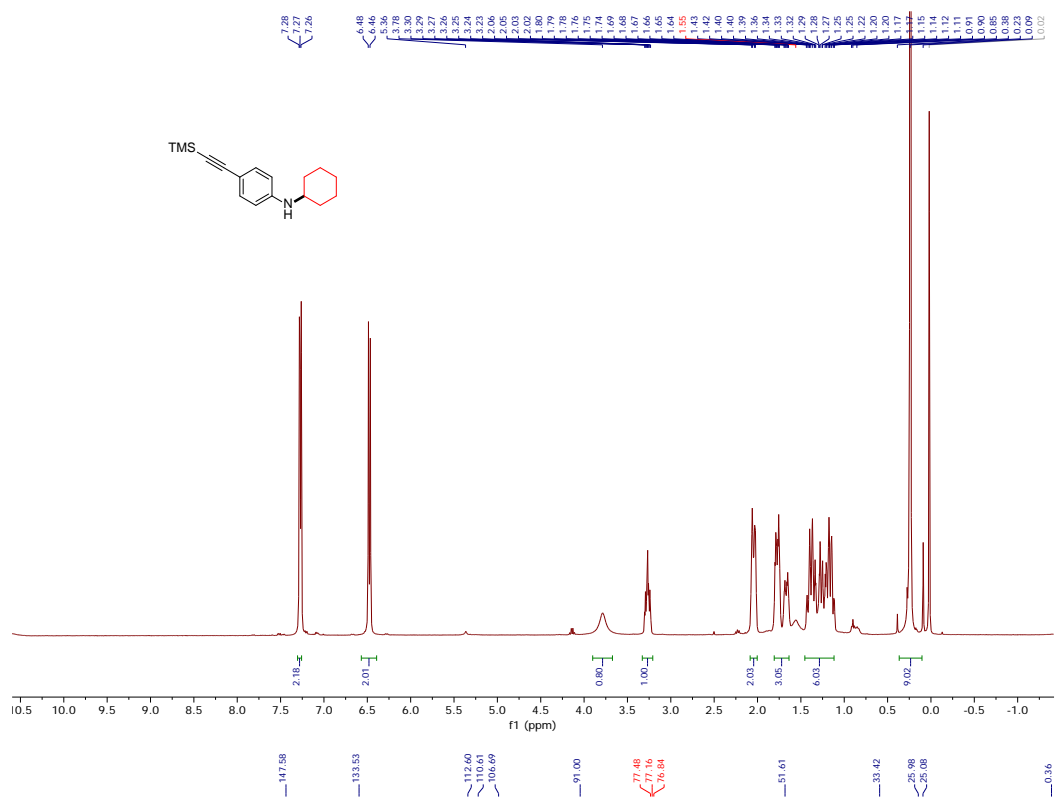
**Supplementary Figure 48. NMR spectra of 4-bromo-*N*-cyclohexylaniline (31)**



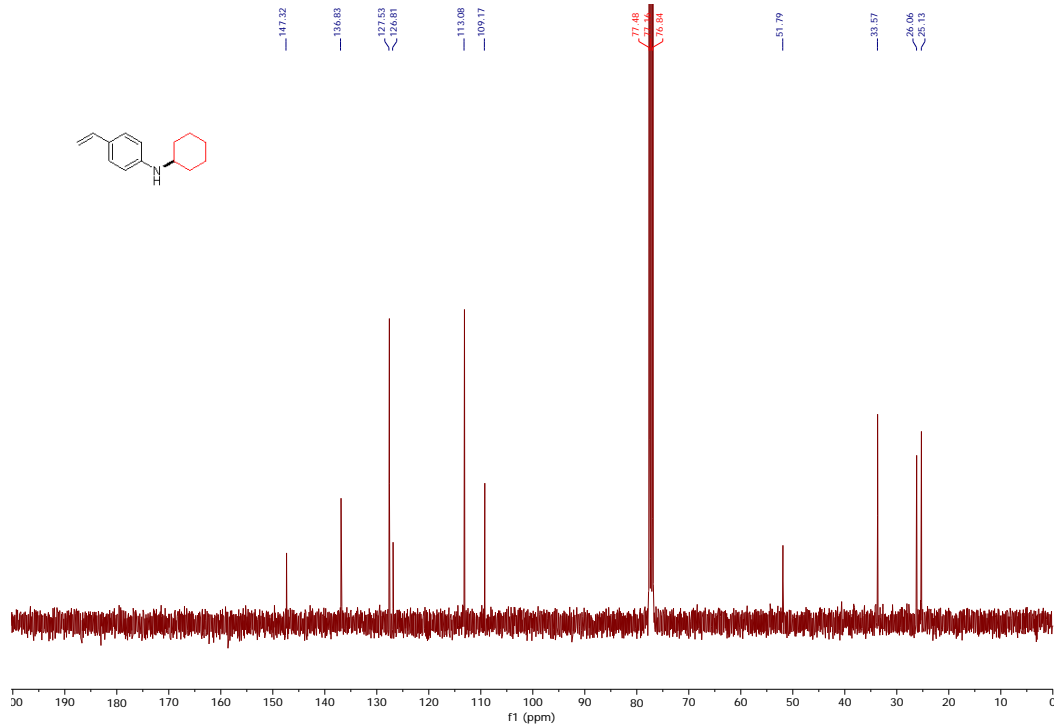
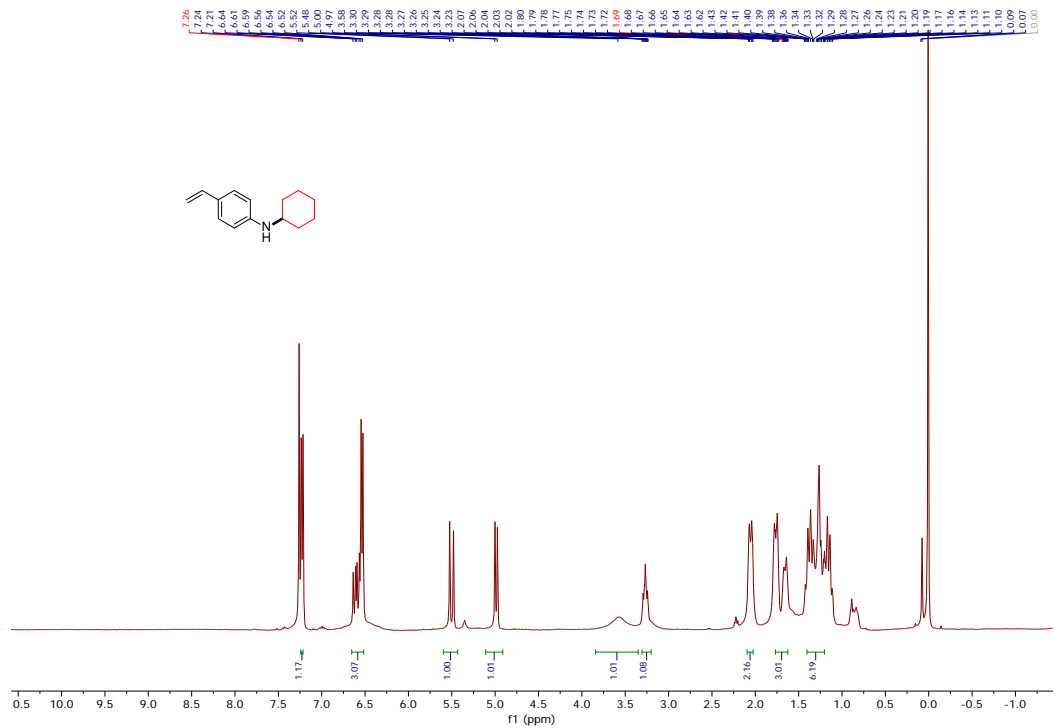
**Supplementary Figure 49. NMR spectra of 4-iodo-N-cyclohexylaniline (3m)**



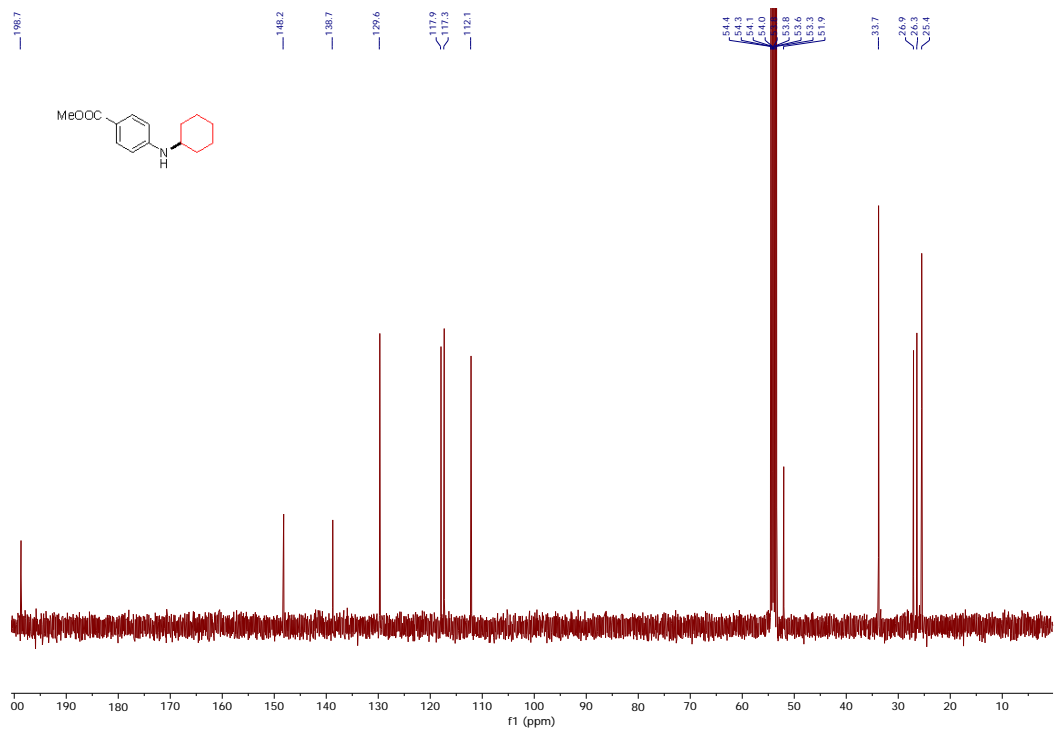
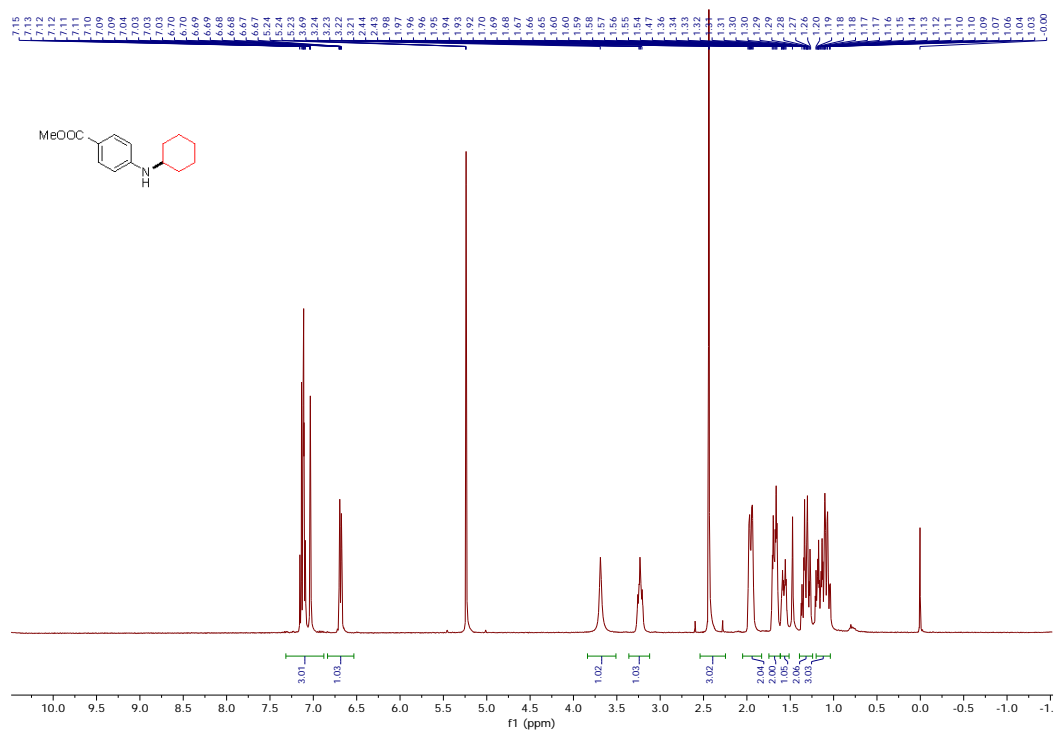
**Supplementary Figure 50. NMR spectra of *N*-cyclohexyl-3-(1,3-dioxolan-2-yl)aniline (3n)**



**Supplementary Figure 51. NMR spectra of *N*-cyclohexyl-4-((trimethylsilyl)ethynyl)aniline (30)**



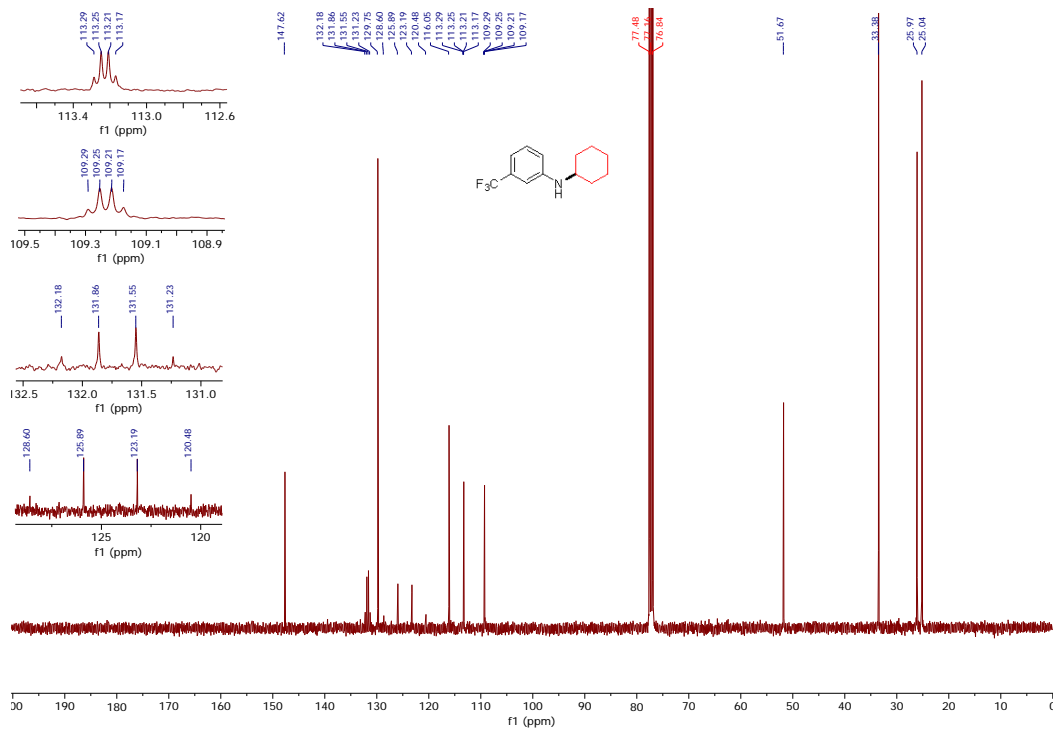
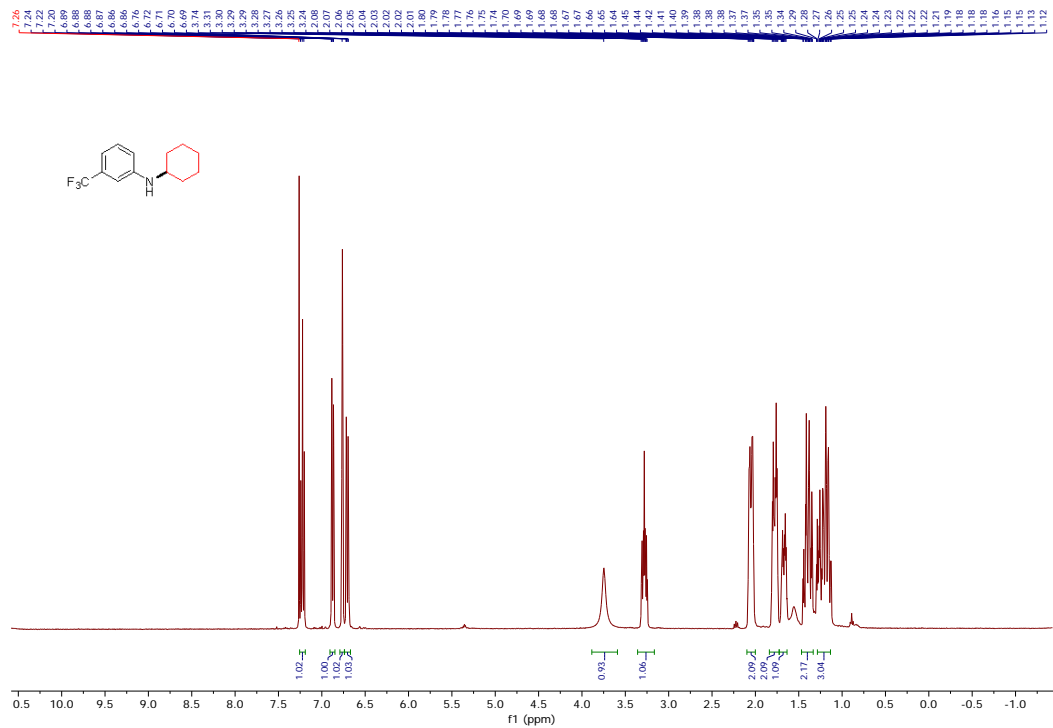
**Supplementary Figure 52. NMR spectra of *N*-cyclohexyl-4-vinylaniline (3p)**



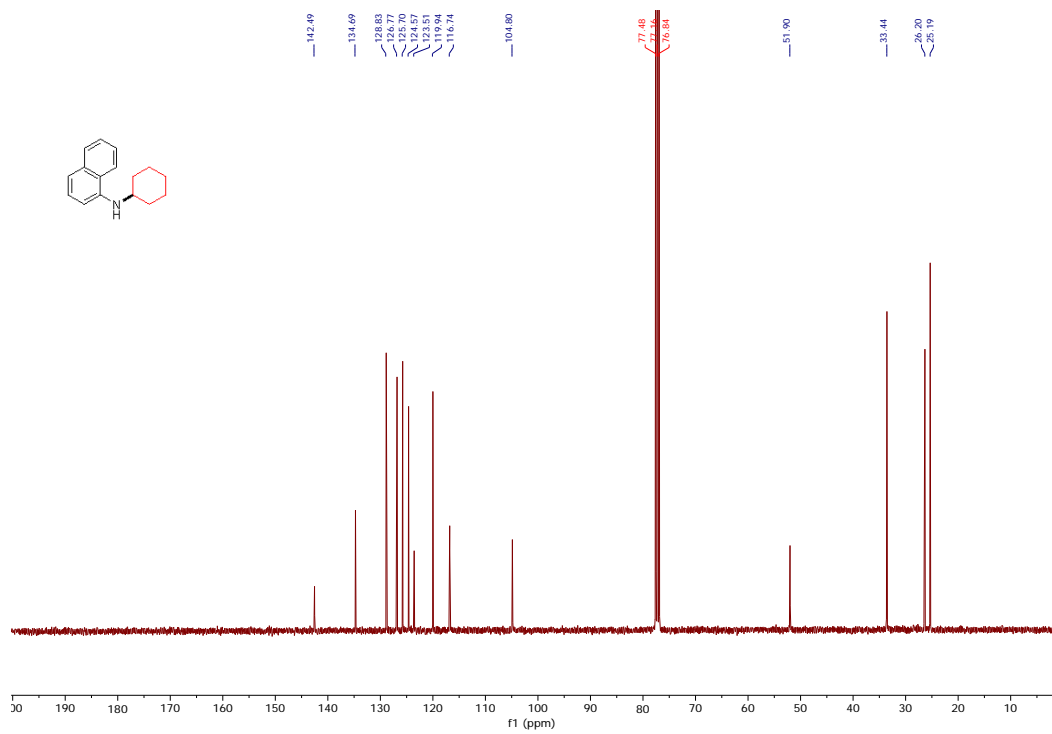
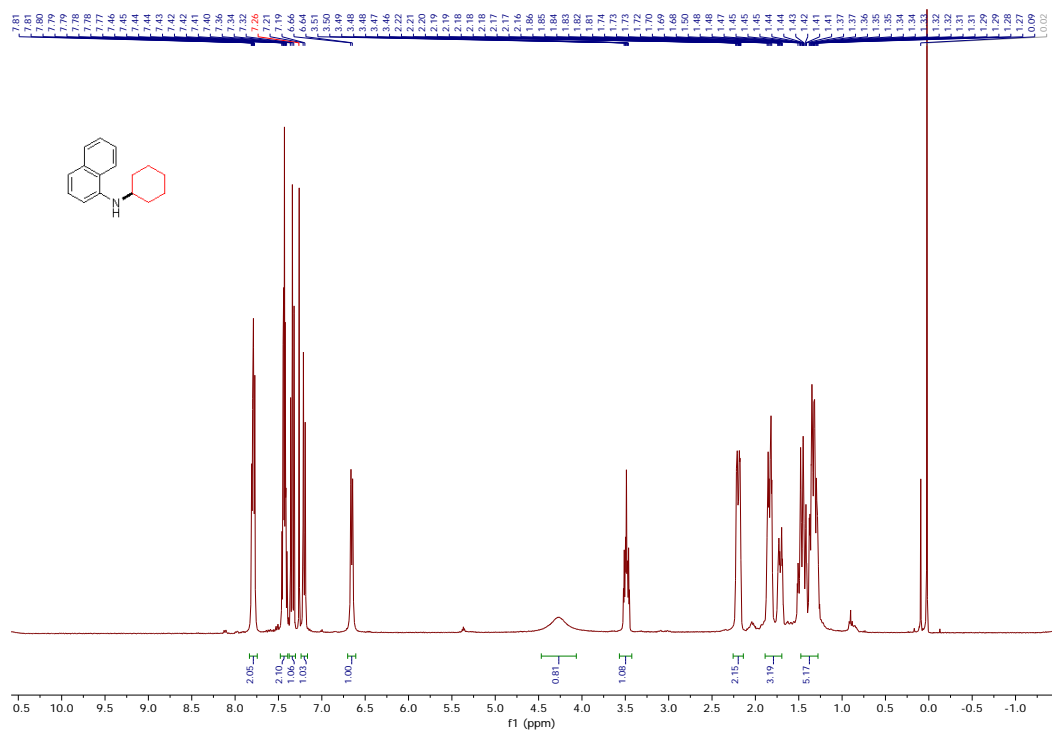
**Supplementary Figure 53. NMR spectra of Methyl 4 (cyclohexylamino)benzoate (3q)**



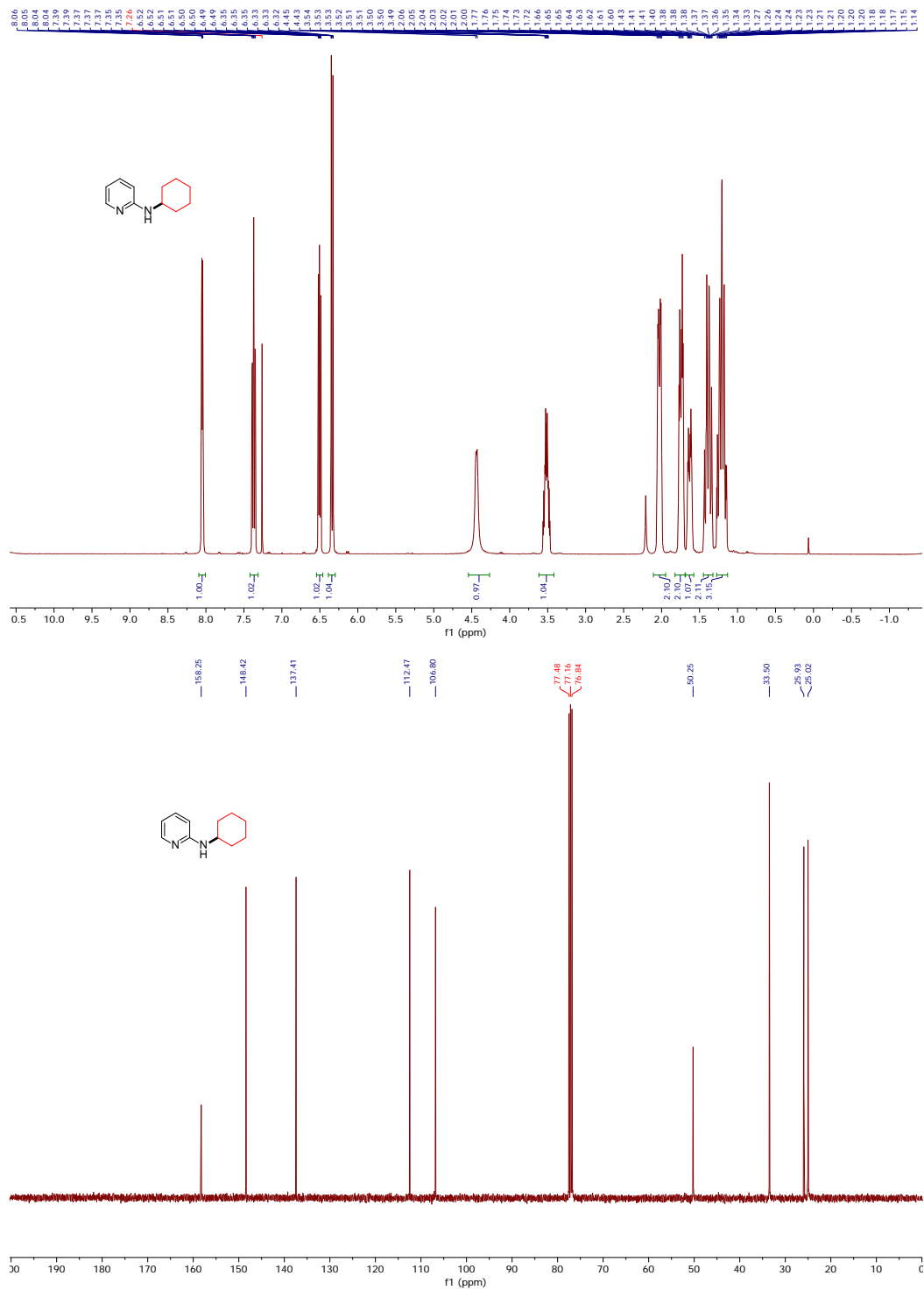




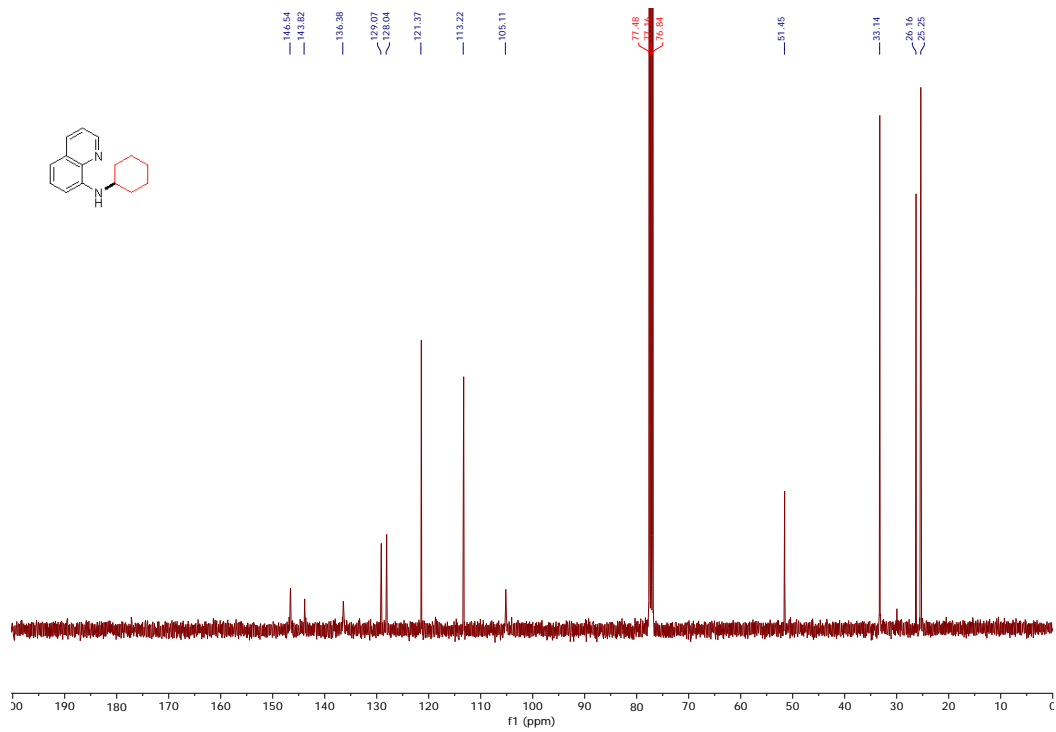
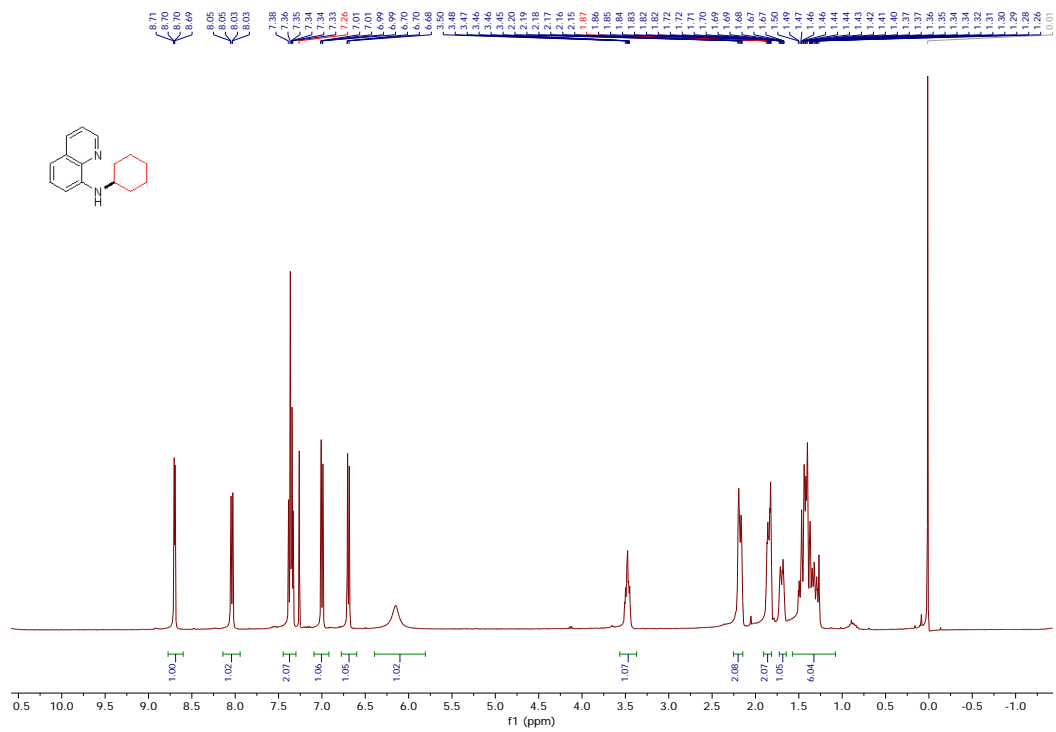
**Supplementary Figure 55. NMR spectra of *N*-cyclohexyl-3-(trifluoromethyl)aniline (3s)**



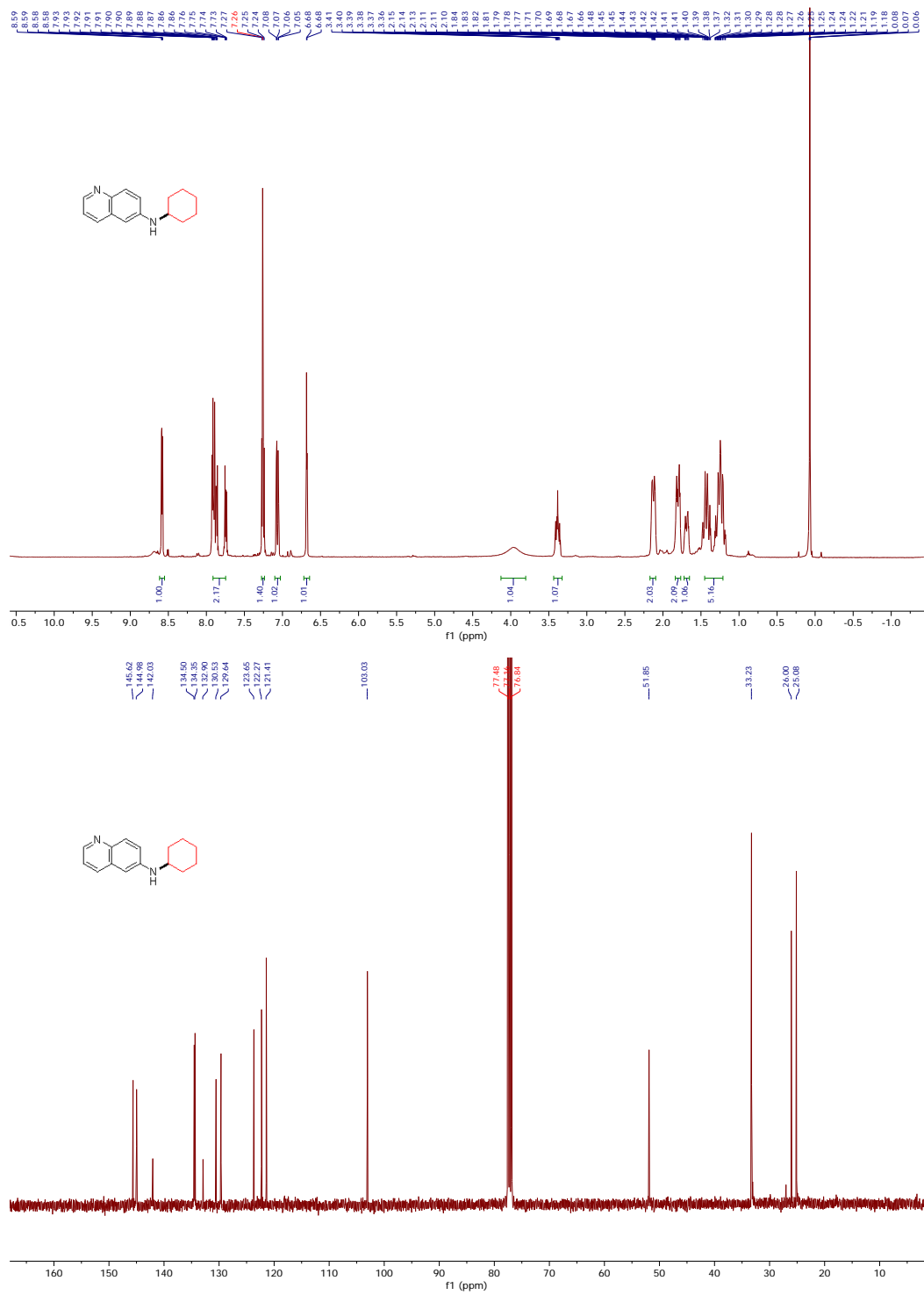
**Supplementary Figure 56. NMR spectra of *N*-cyclohexylnaphthalen-1-amine (3t)**



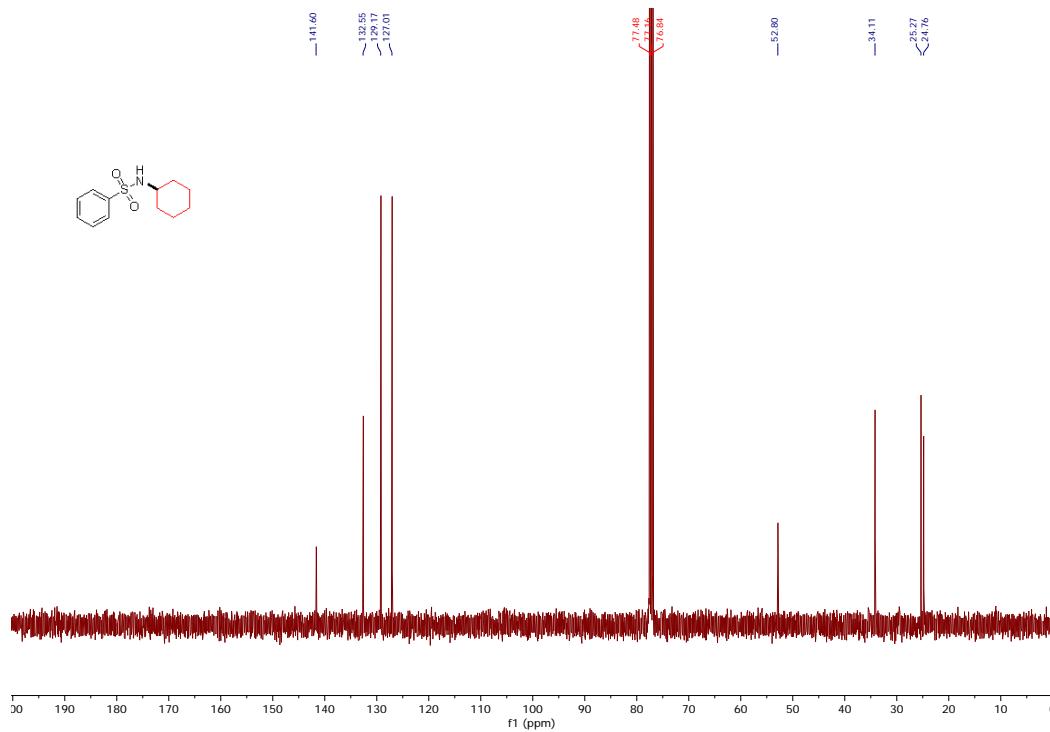
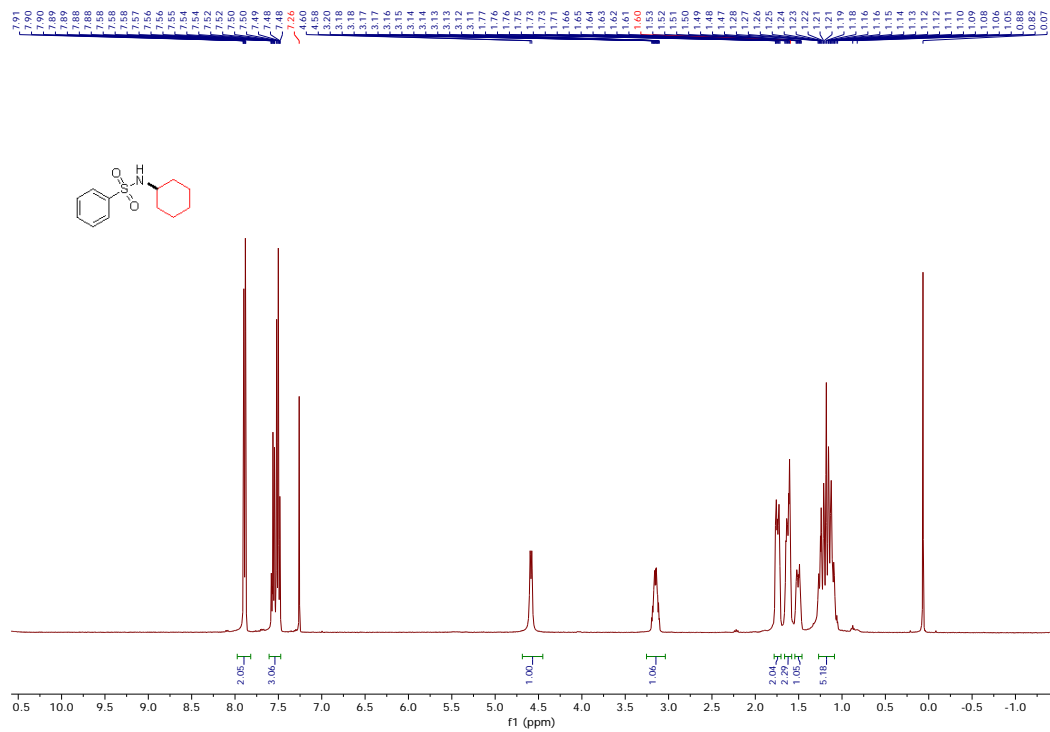
Supplementary Figure 57. NMR spectra of *N*-cyclohexylpyridin-2-amine (4a)



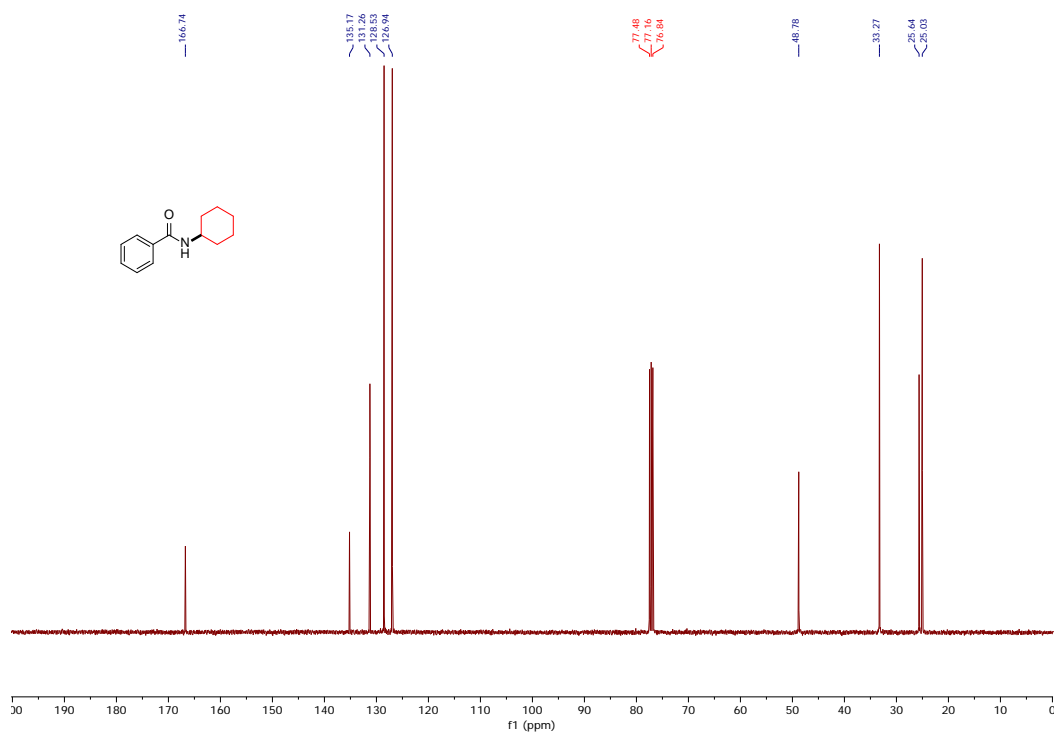
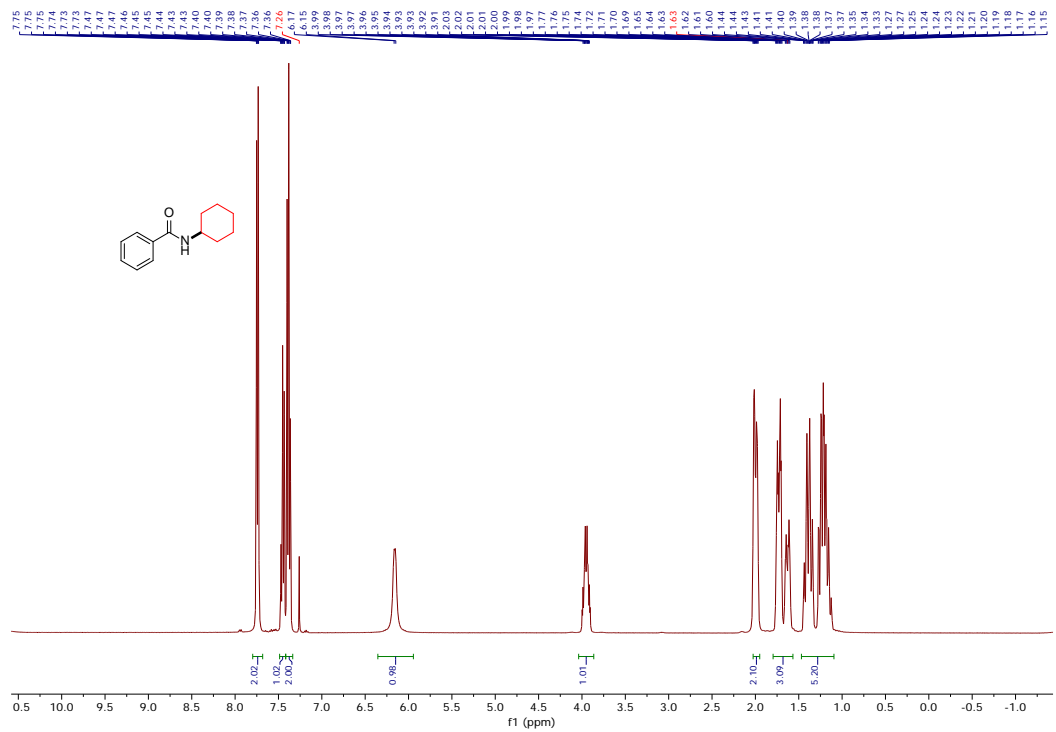
**Supplementary Figure 58. NMR spectra of *N*-cyclohexylquinolin-8-amine (4b)**



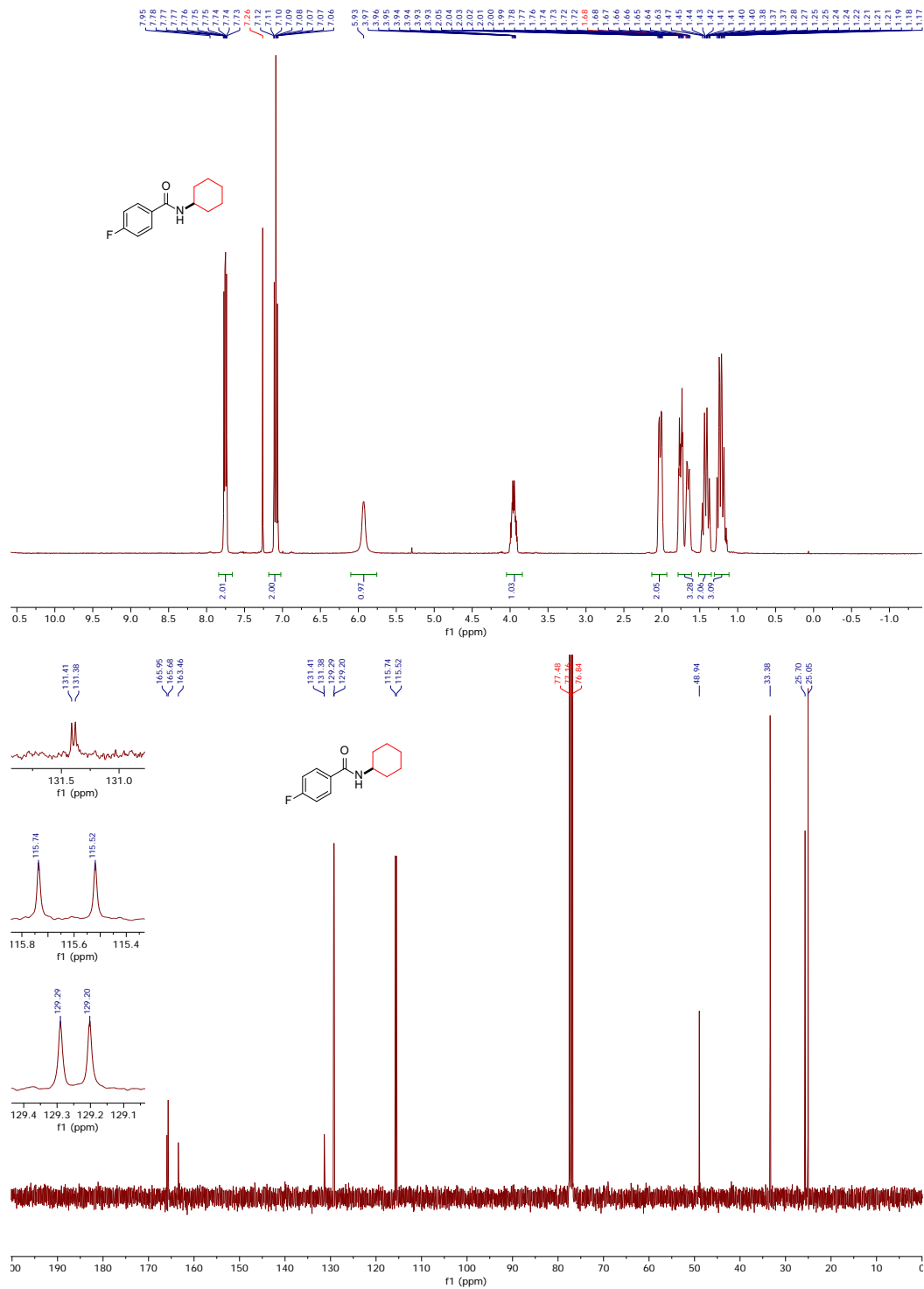
**Supplementary Figure 59. NMR spectra of *N*-cyclohexylquinolin-6-amine (4c)**



**Supplementary Figure 60. NMR spectra of *N*-cyclohexylbenzenesulfonamide (4d)**

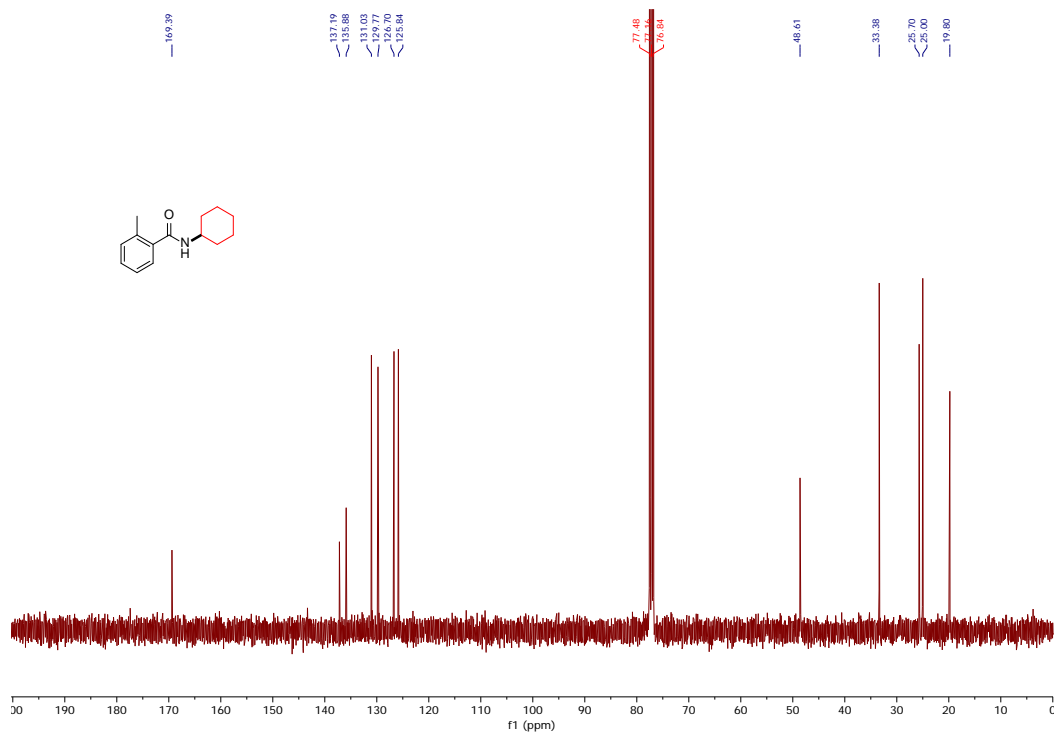
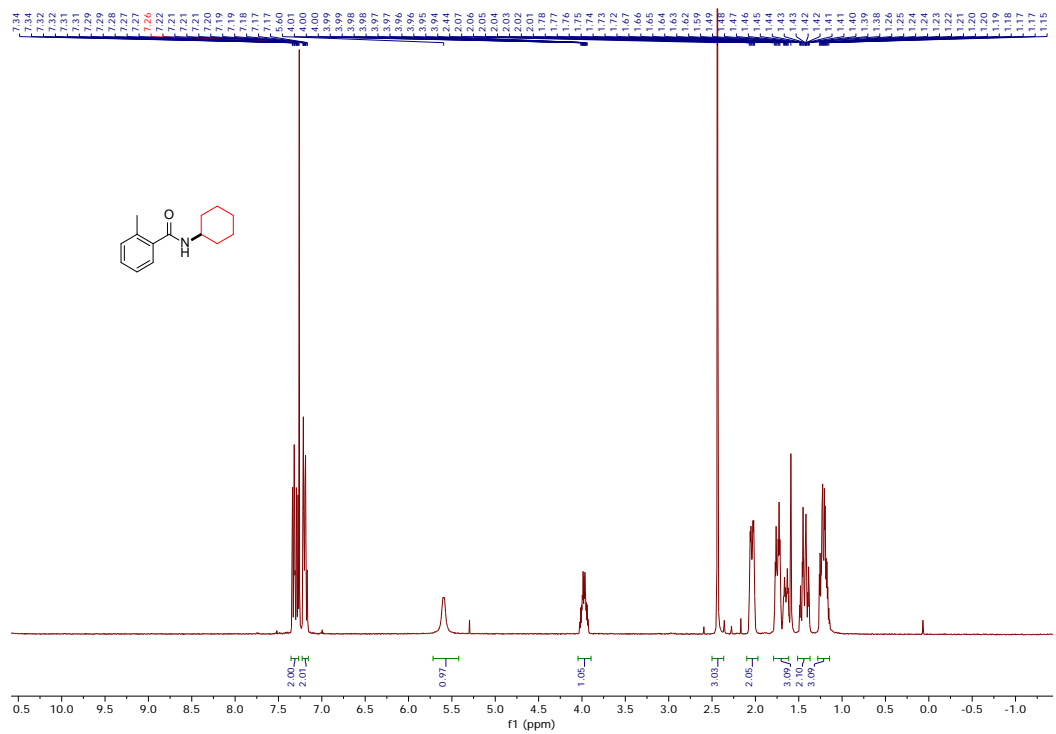


**Supplementary Figure 61. NMR spectra of N-cyclohexylbenzamide (4e)**

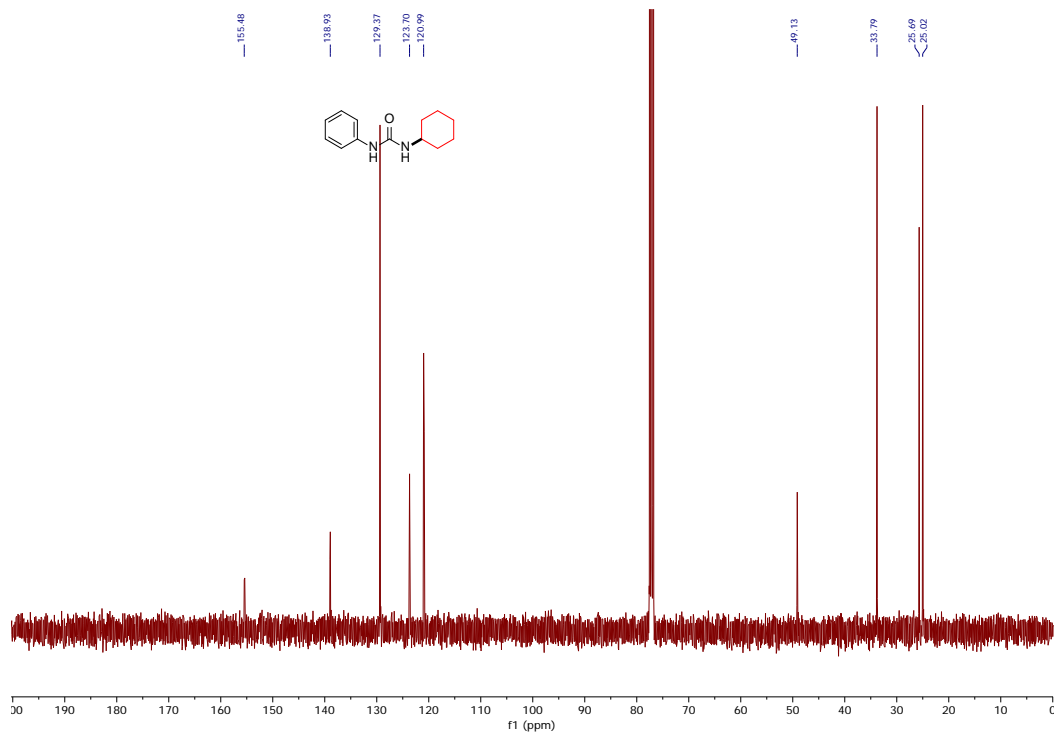
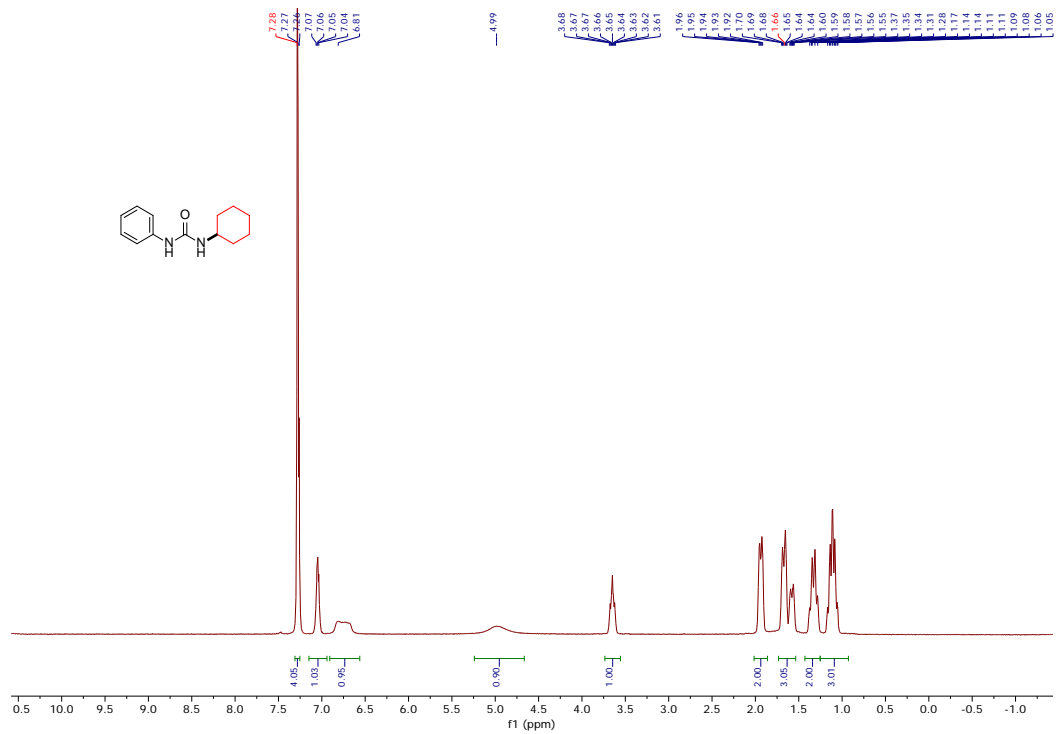


**Supplementary Figure 62. NMR spectra of *N*-cyclohexyl-4-fluorobenzamide (4f)**

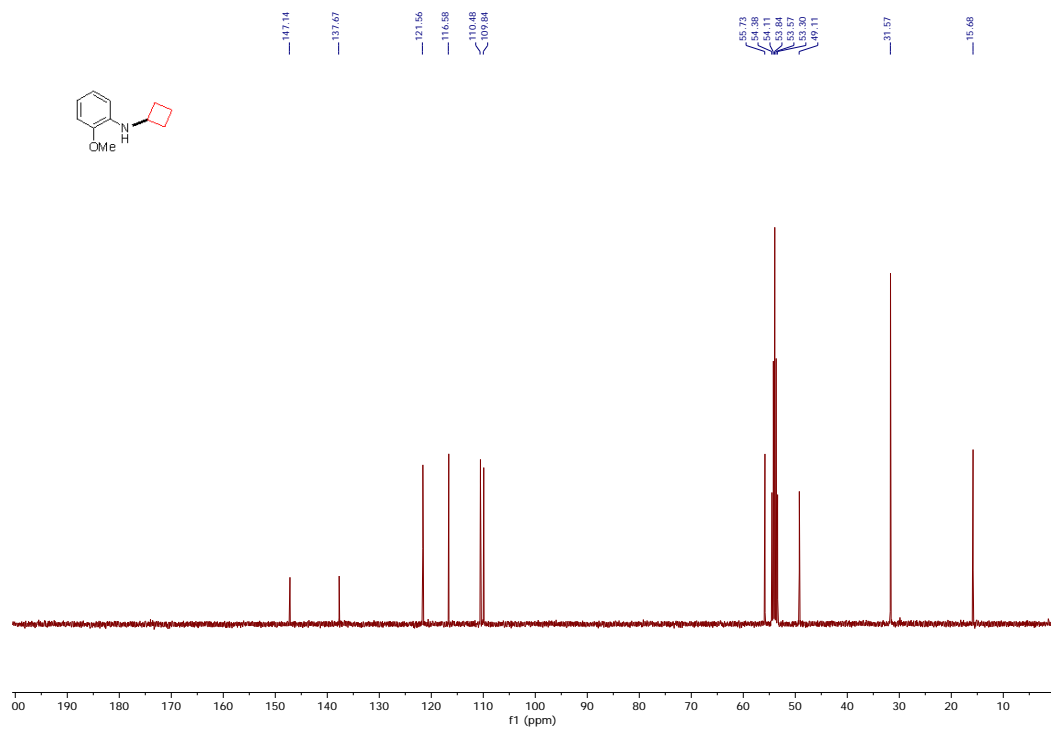
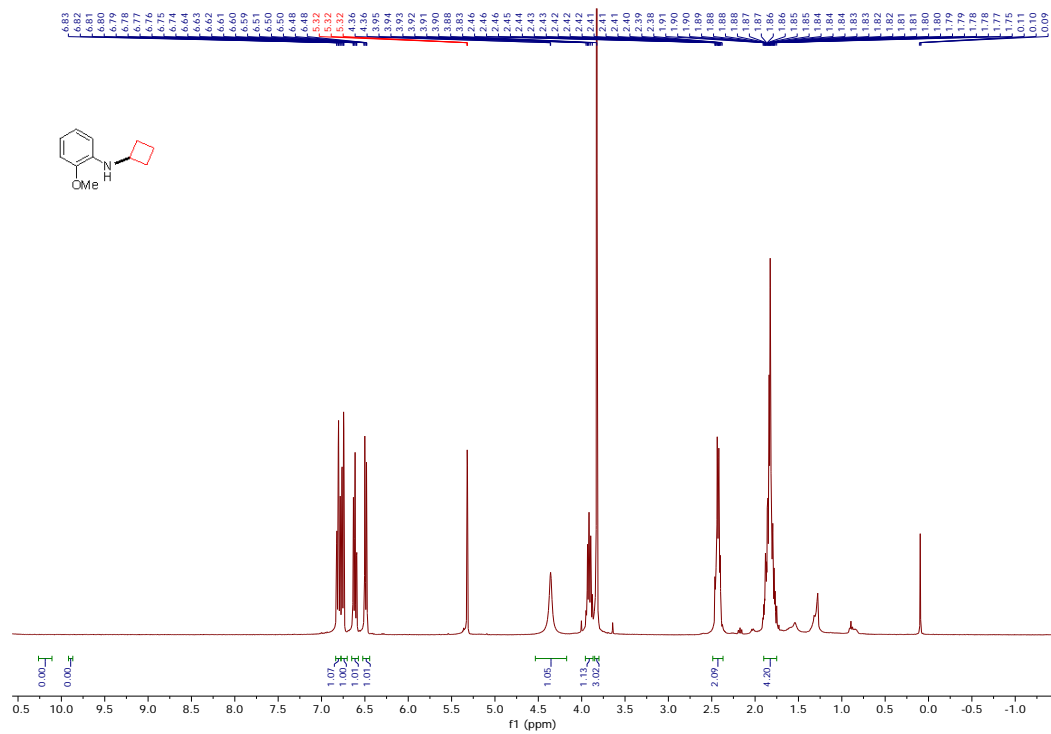




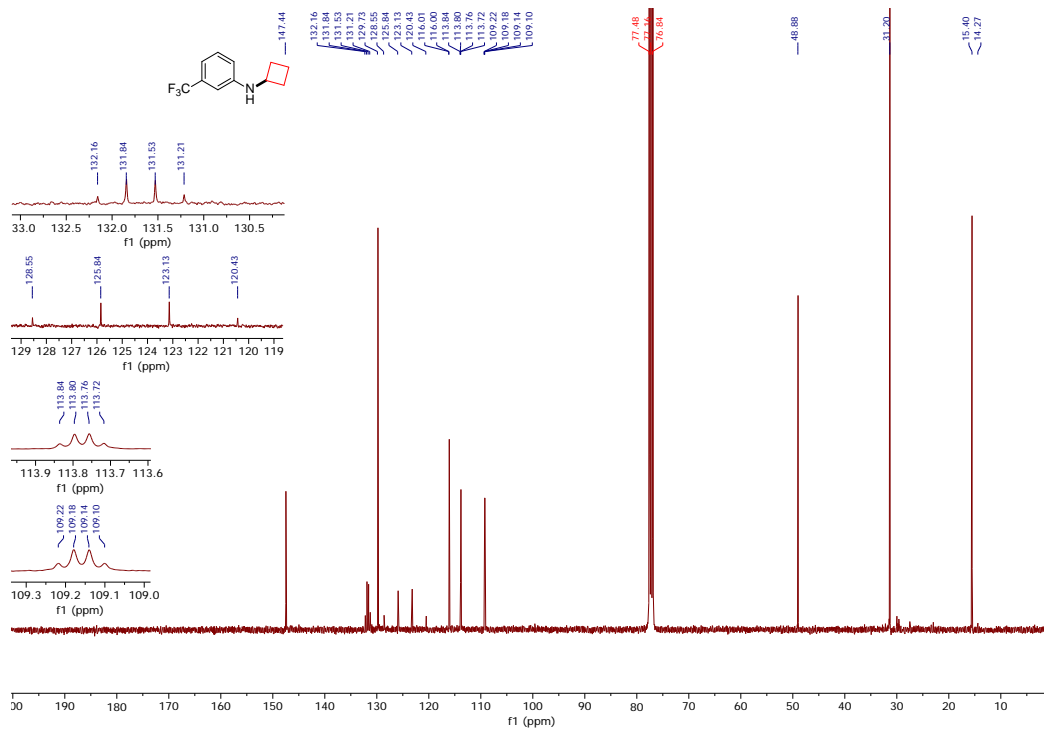
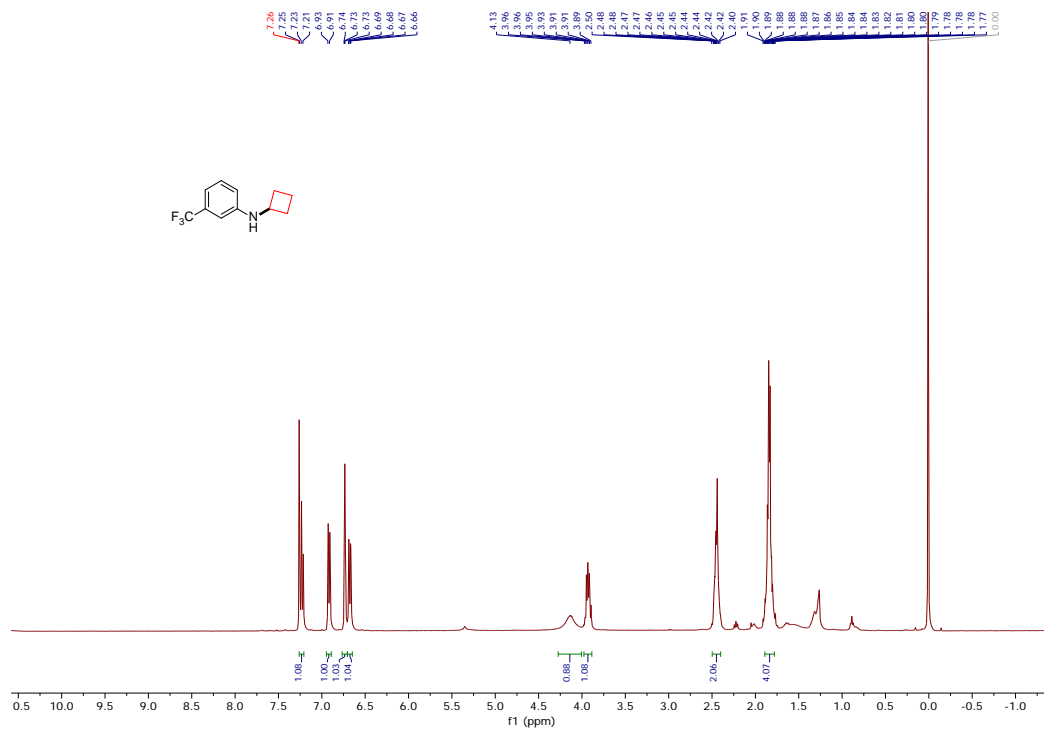
**Supplementary Figure 63. NMR spectra of *N*-cyclohexyl-2-methylbenzamide (4g)**



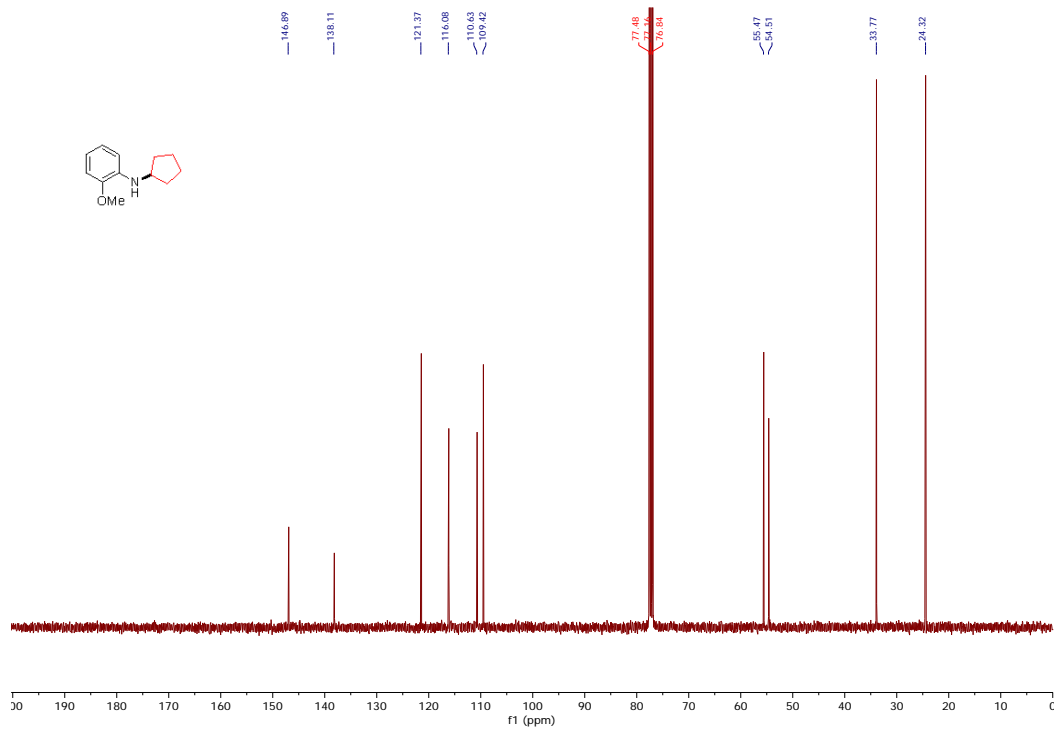
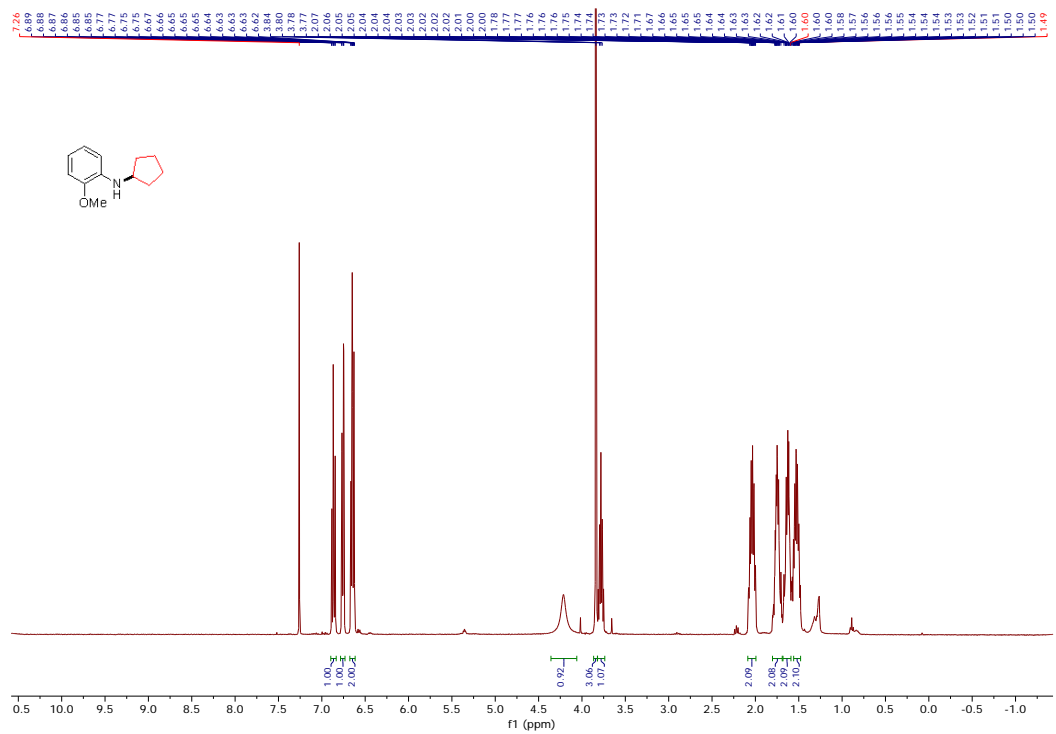
**Supplementary Figure 64. NMR spectra of 1-cyclohexyl-3-phenylurea (4h)**



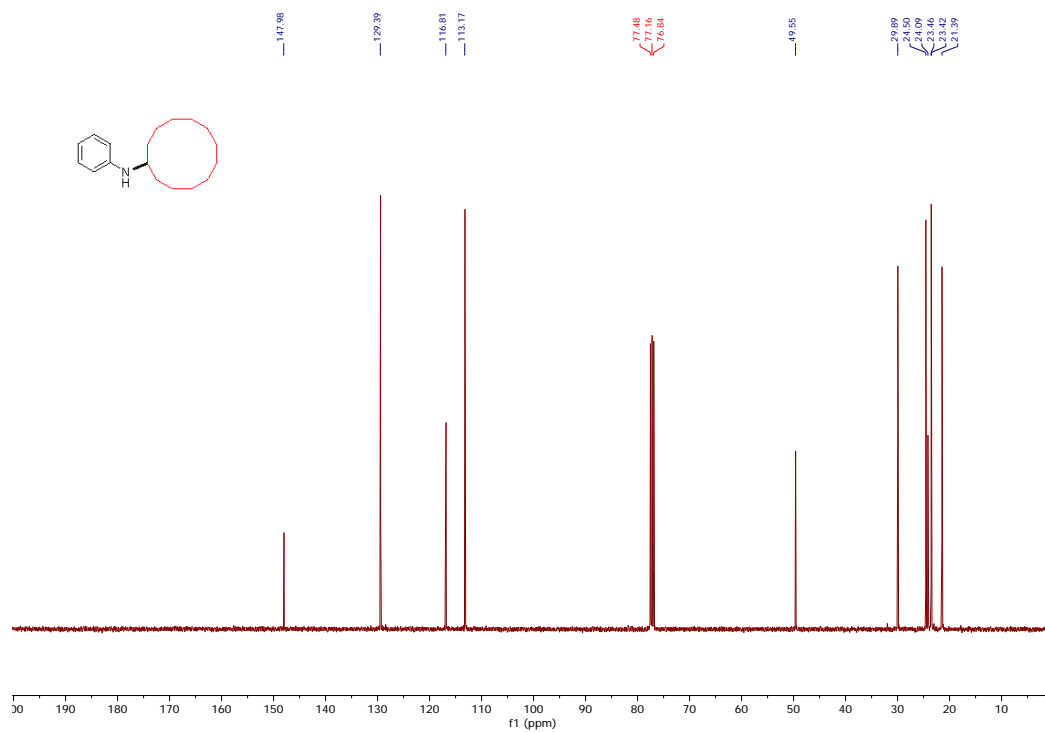
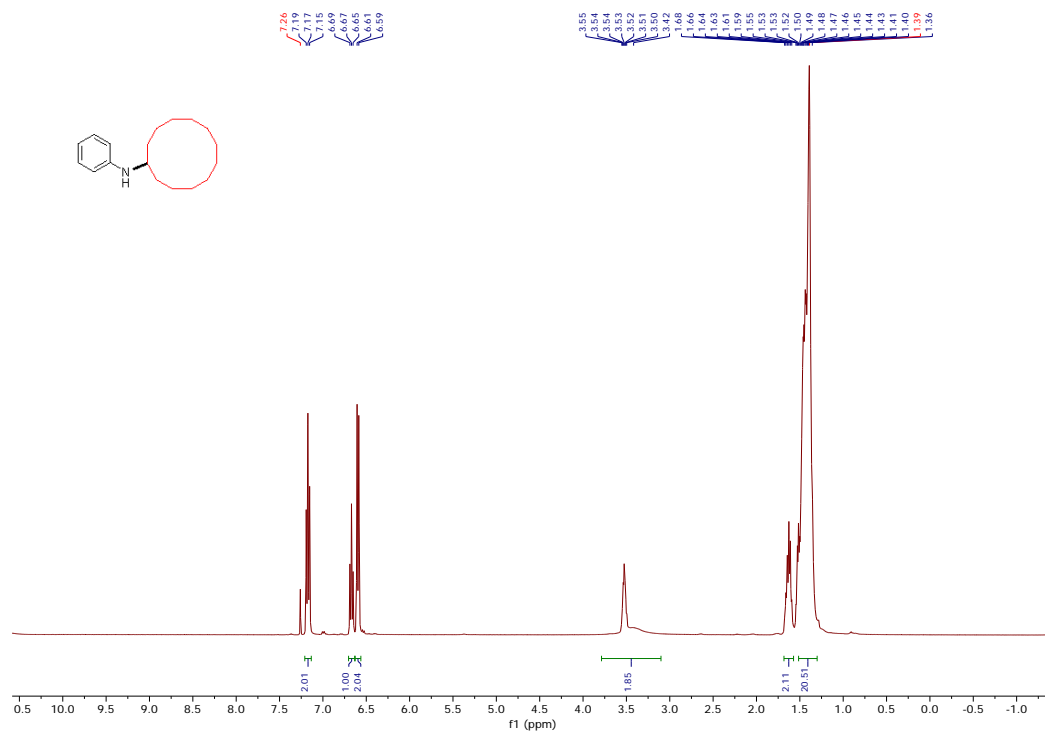
**Supplementary Figure 65. NMR spectra of *N*-cyclobutyl-2-methoxyaniline (5a)**



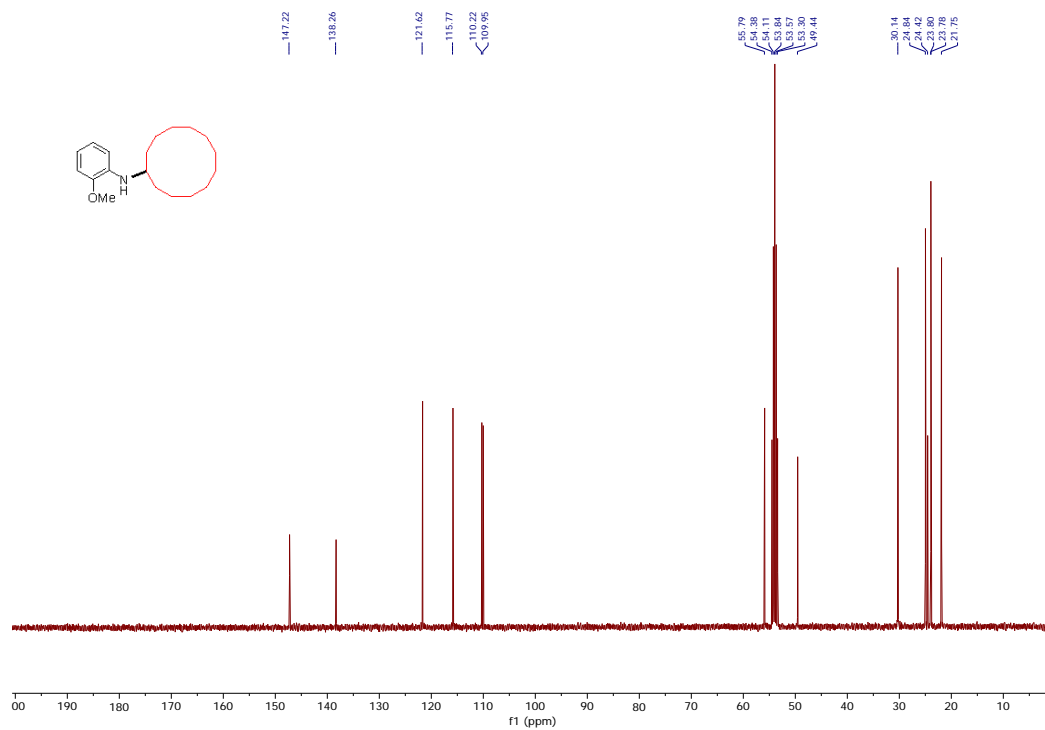
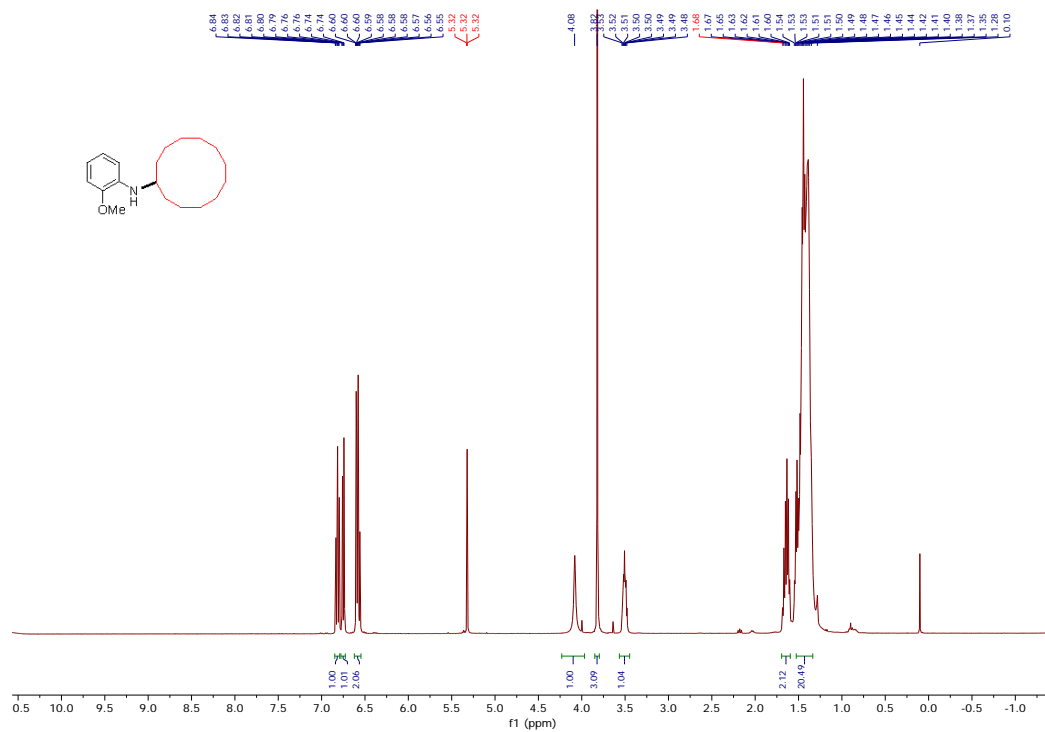
**Supplementary Figure 66. NMR spectra of *N*-cyclobutyl-3-(trifluoromethyl)aniline (5b)**



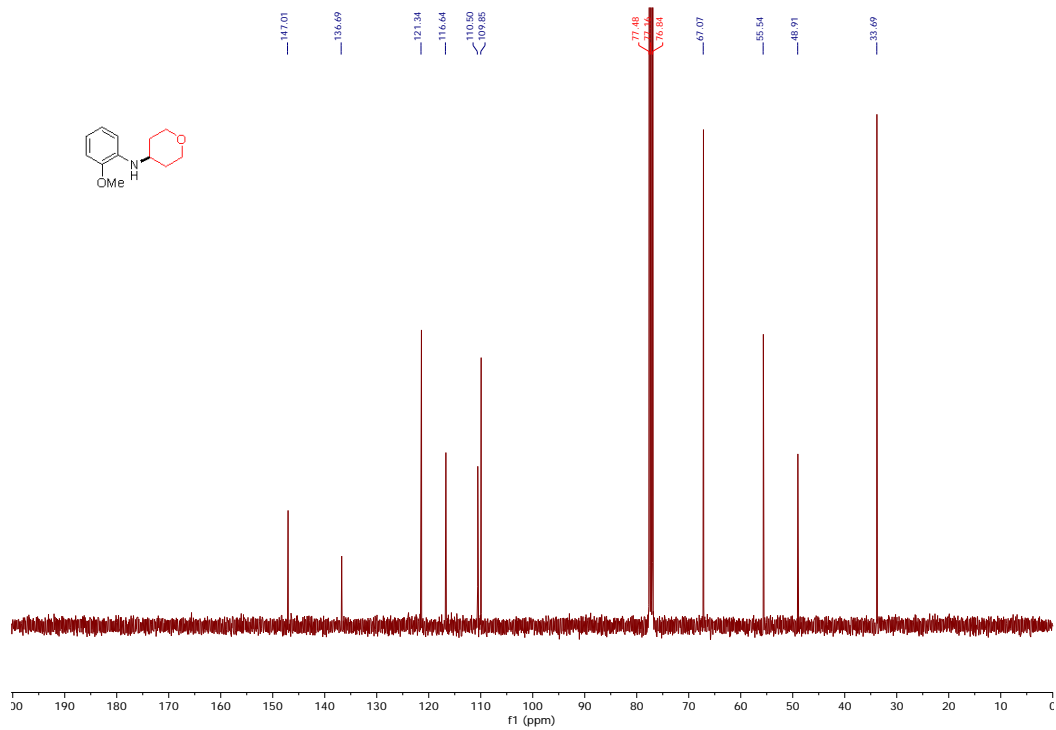
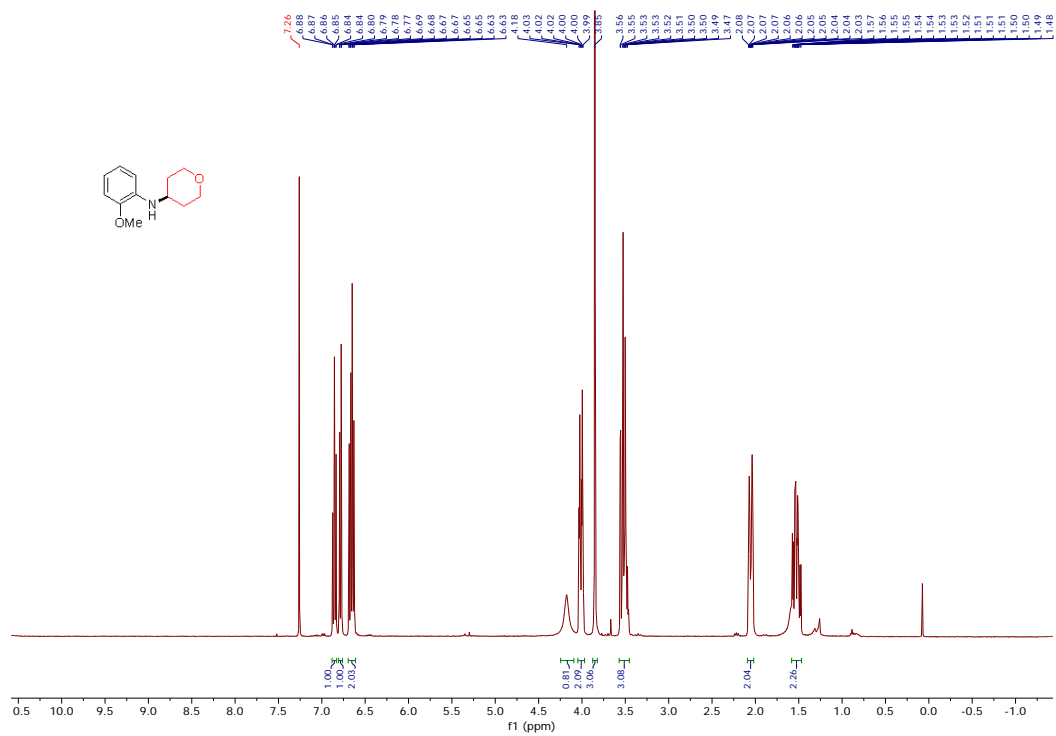
**Supplementary Figure 67. NMR spectra of *N*-cyclopentyl-2-methoxyaniline (5c)**



**Supplementary Figure 68. NMR spectra of *N*-cyclododecanamine (5d)**

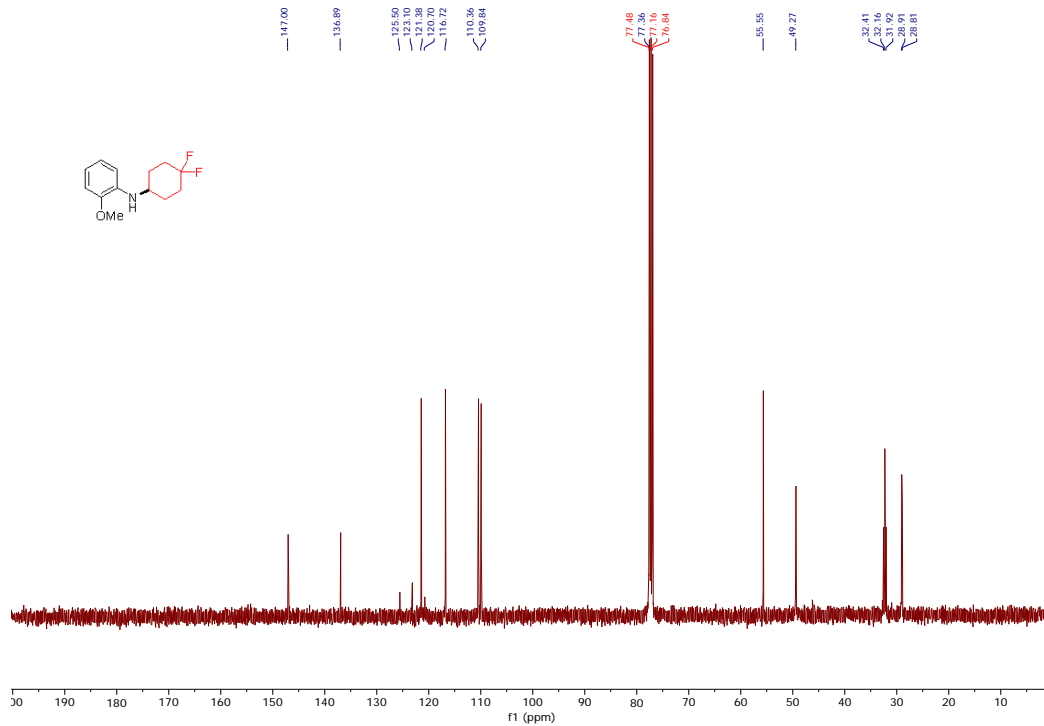
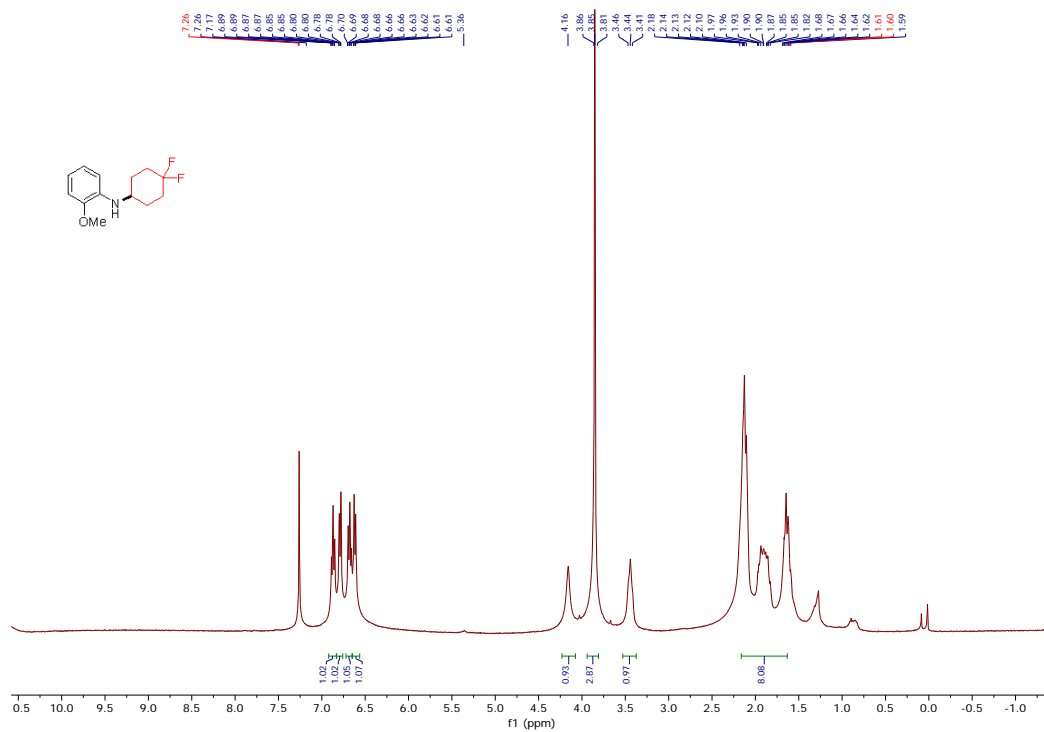


**Supplementary Figure 69. NMR spectra of *N*-(2-methoxyphenyl)cyclododecanamine (5e)**

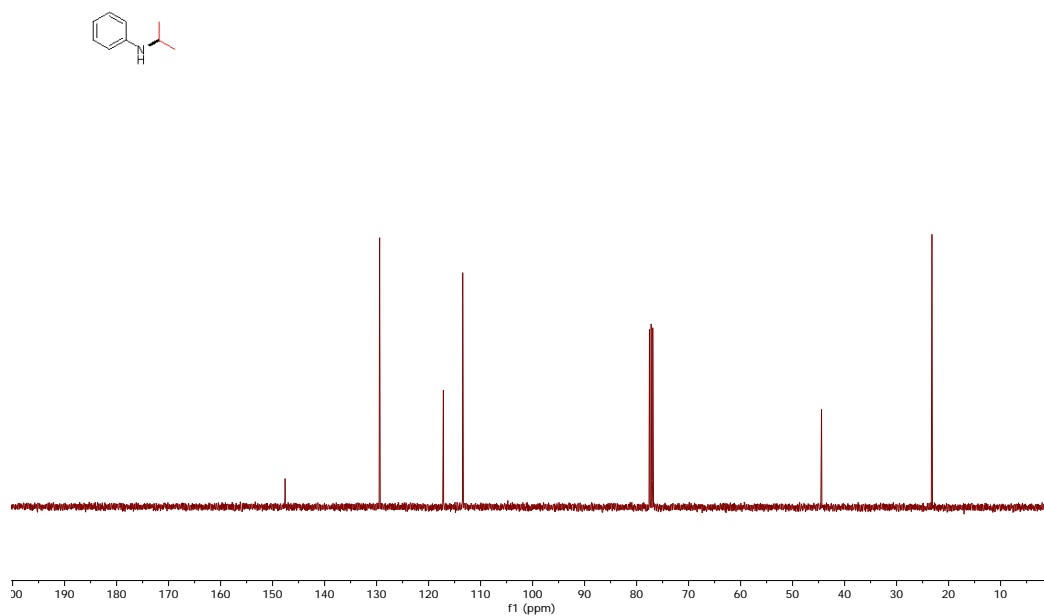
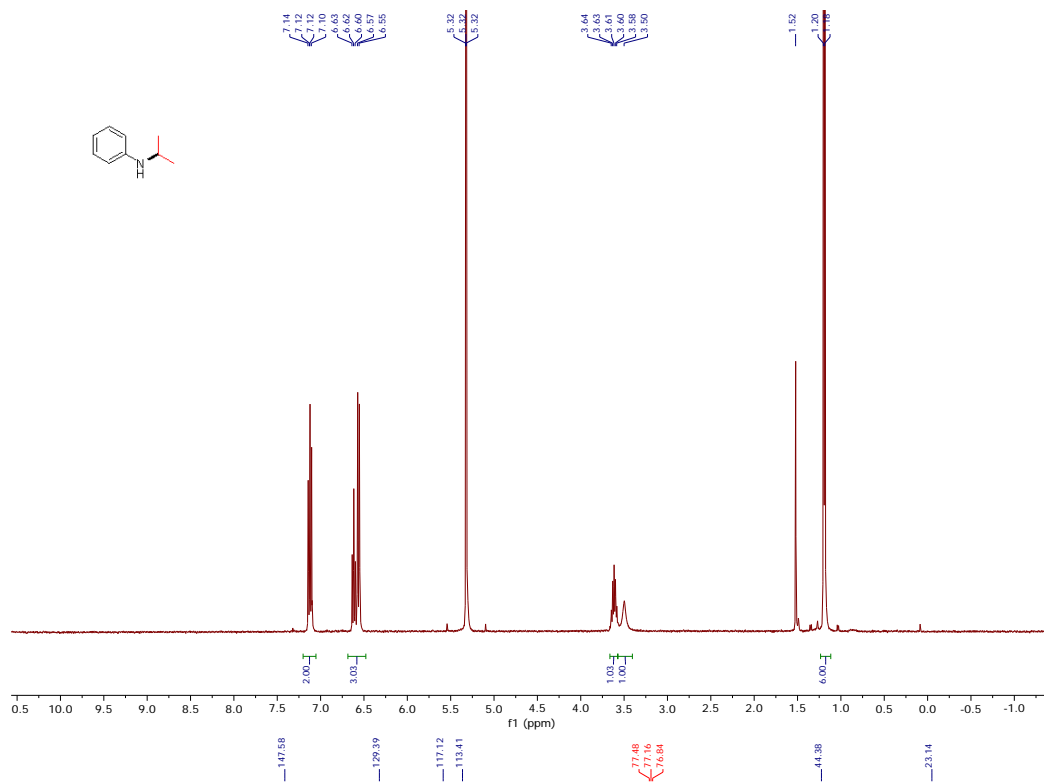


**Supplementary Figure 70. NMR spectra of *N*-(2-methoxyphenyl)tetrahydro-2H-pyran-4-amine (5f)**

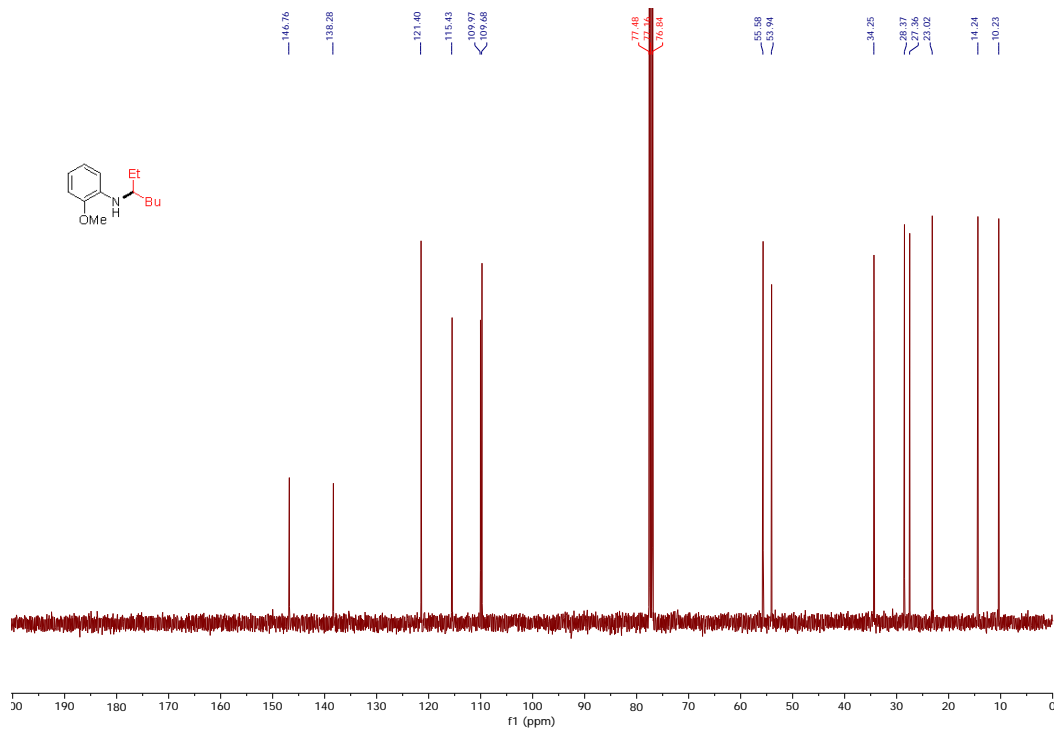
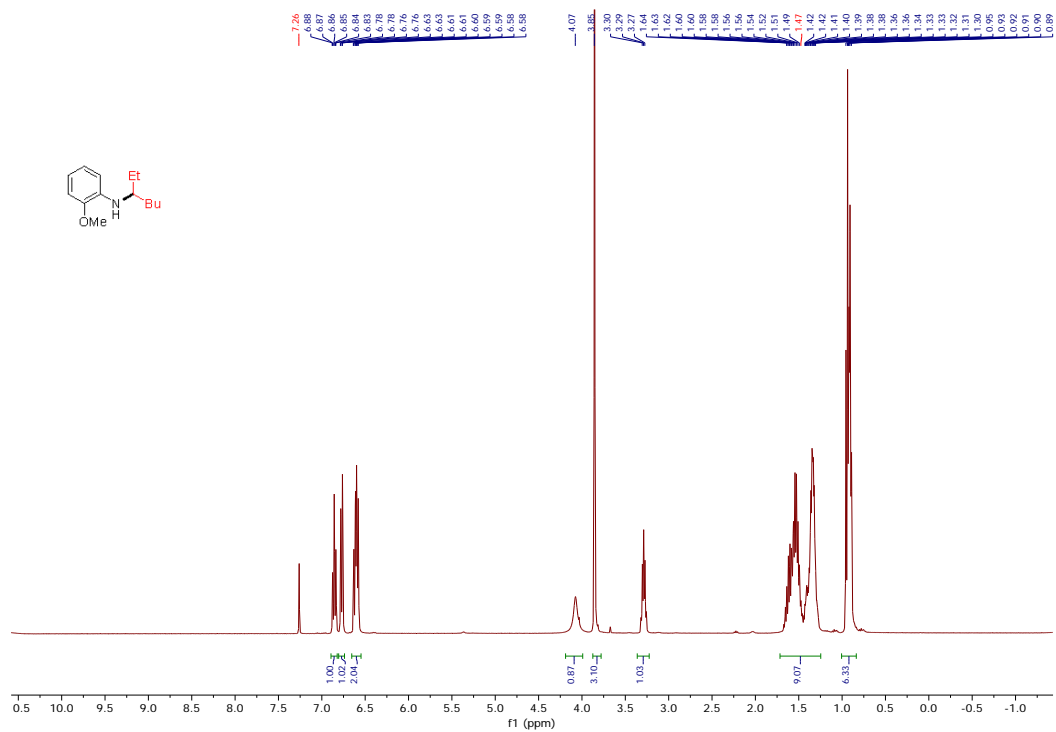




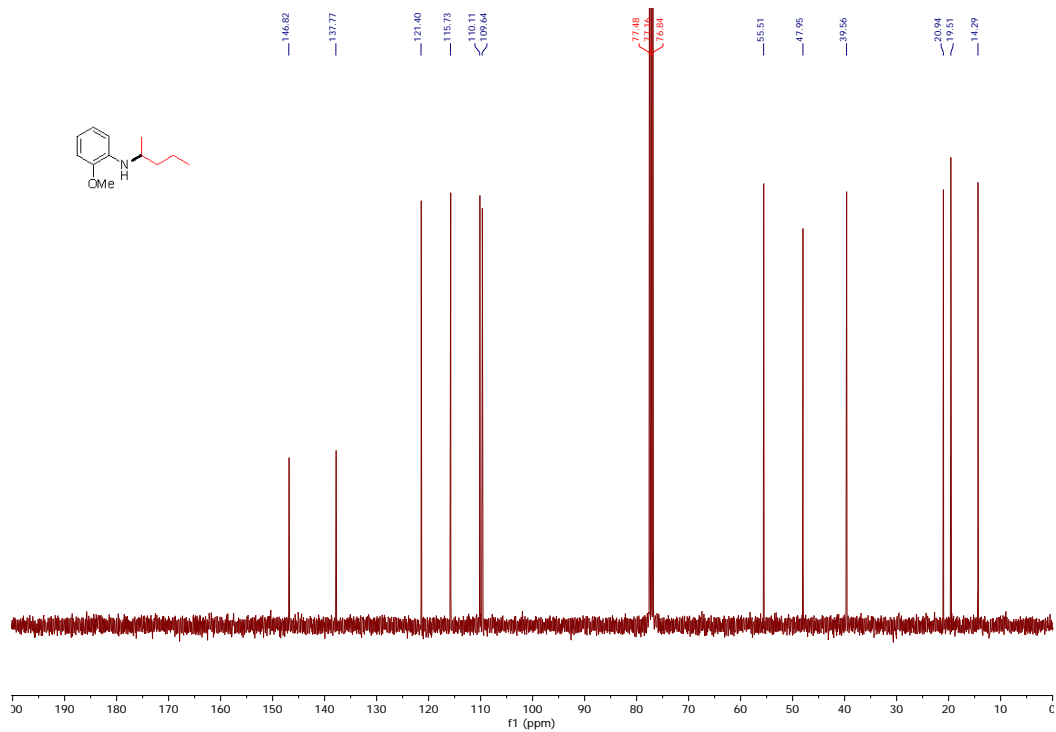
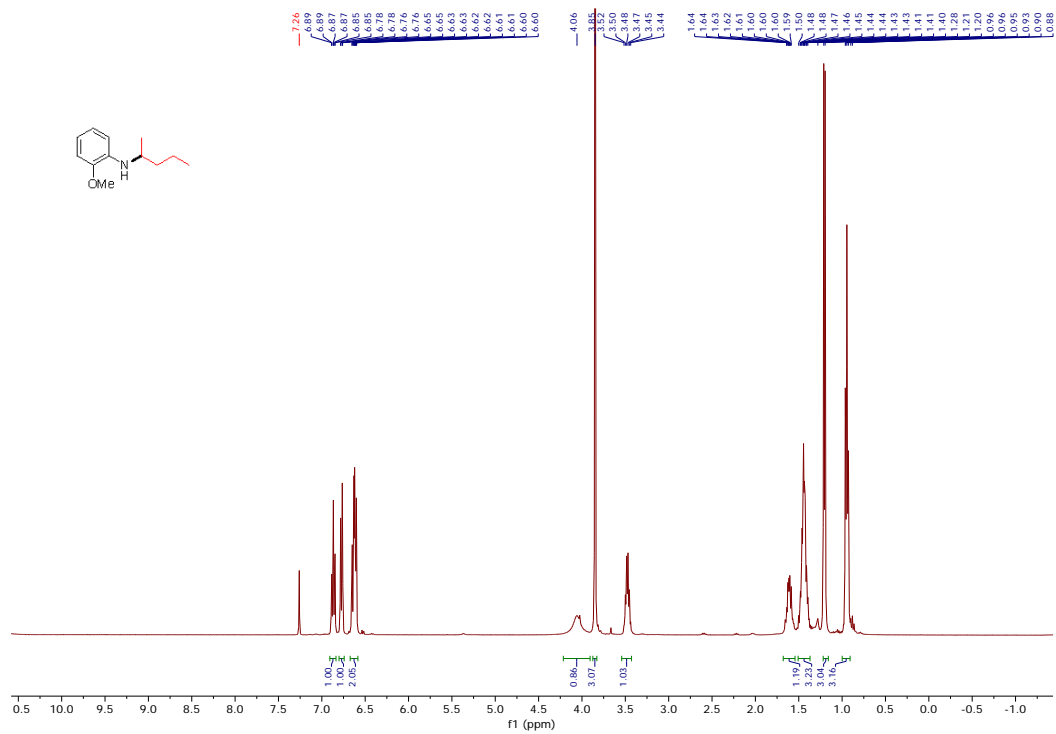
**Supplementary Figure 71. NMR spectra of *N*-(4,4-difluorocyclohexyl)-2-methoxyaniline (5g)**



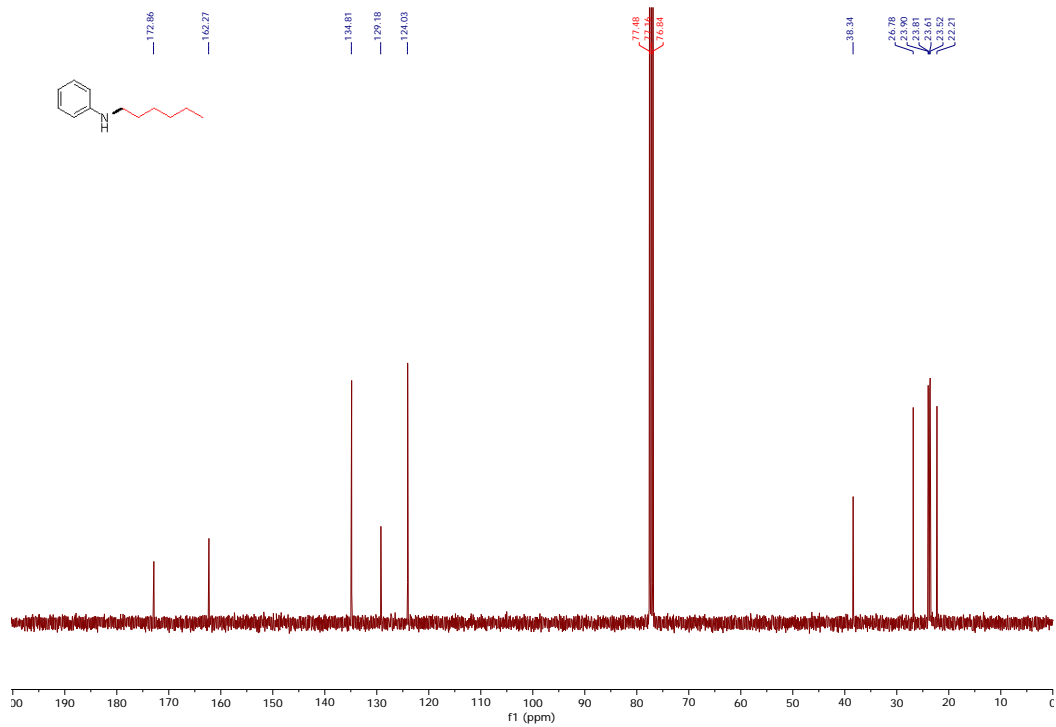
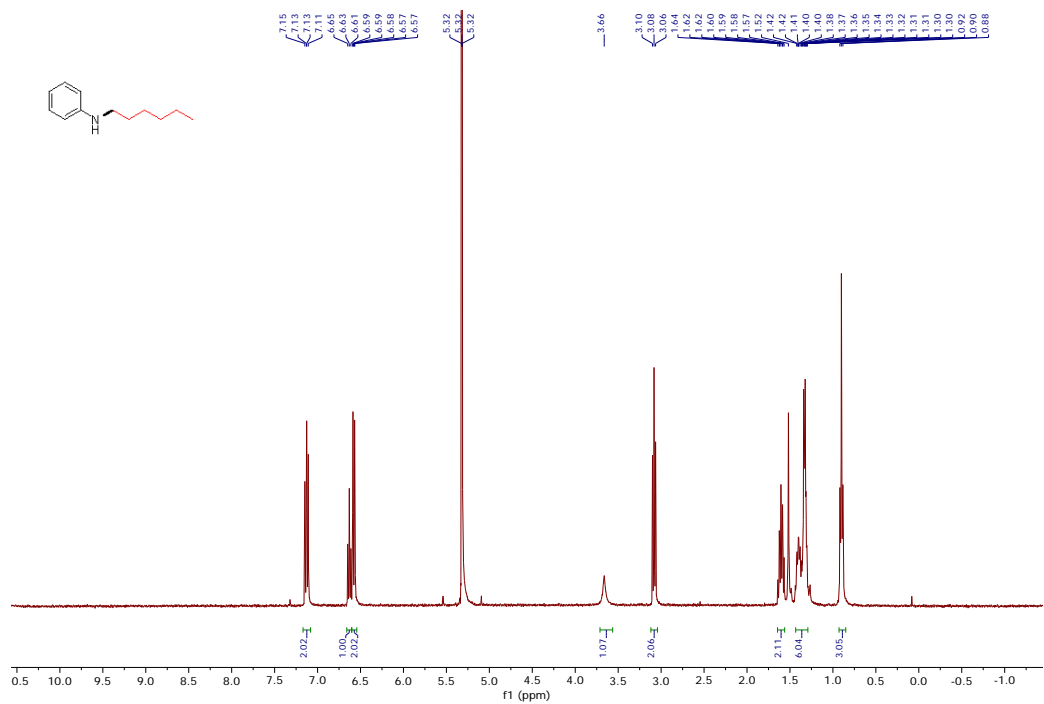
**Supplementary Figure 72. NMR spectra of *N*-isopropylaniline (5h)**



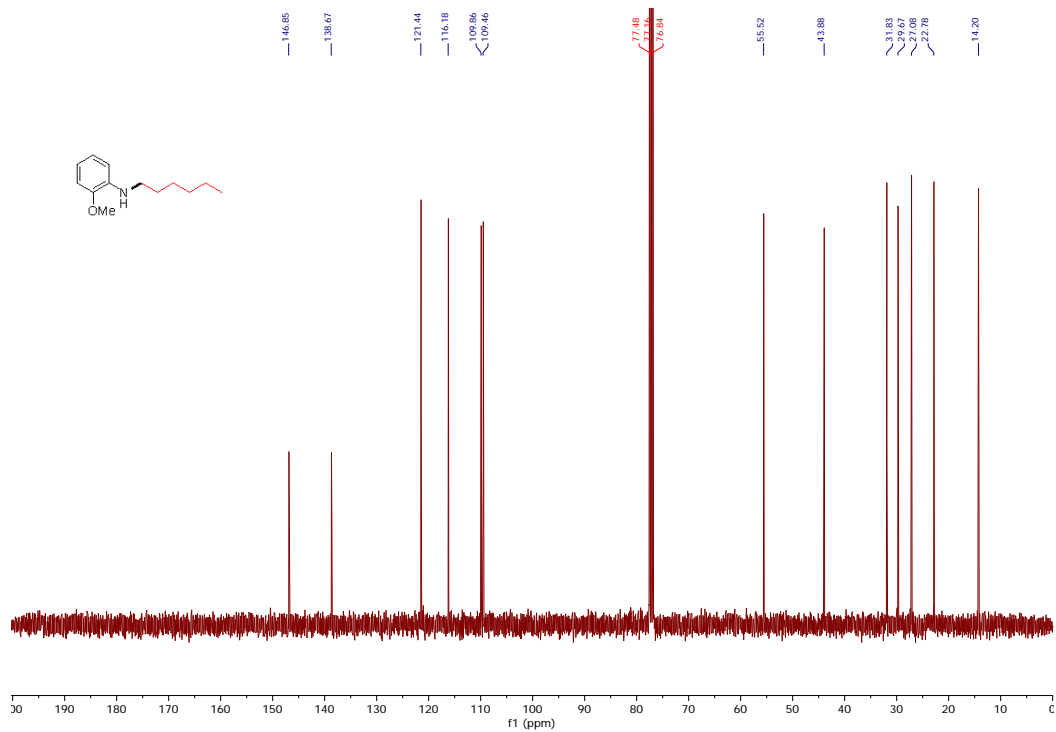
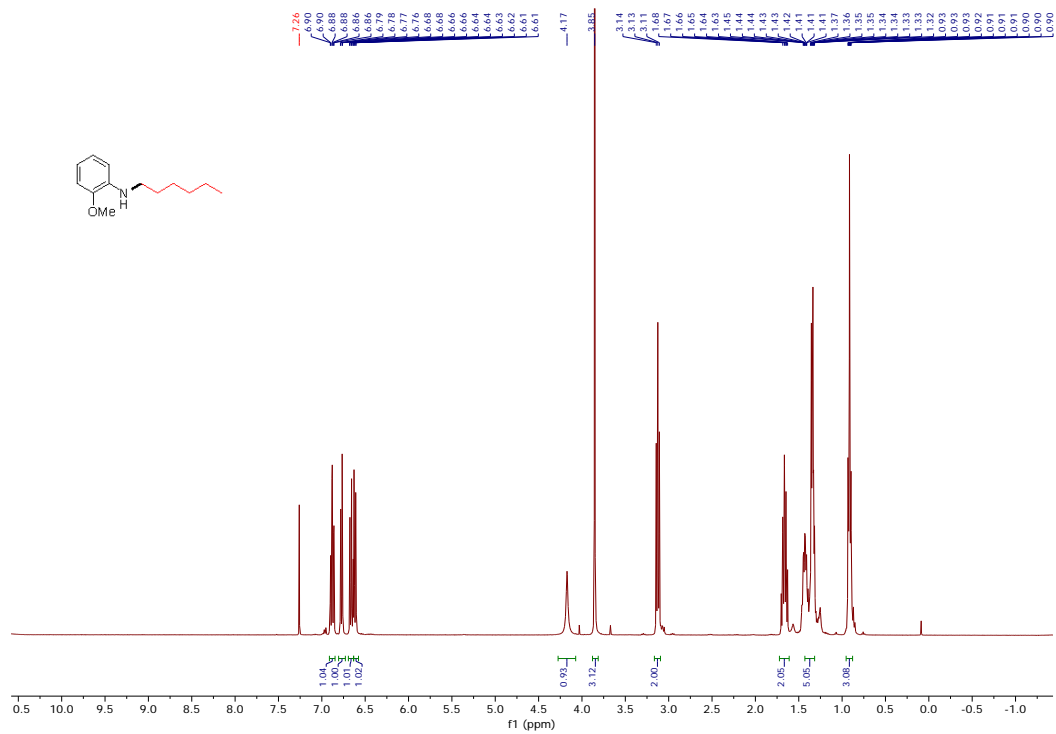
**Supplementary Figure 73. NMR spectra of *N*-(heptan-3-yl)-2-methoxyaniline (5i)**



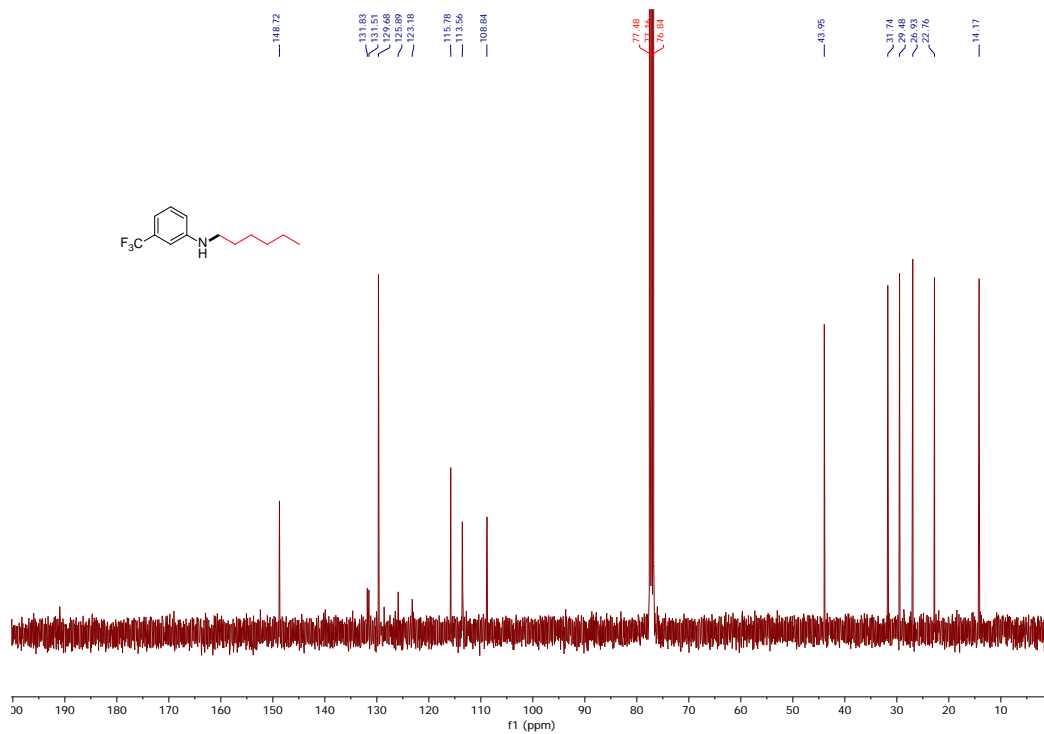
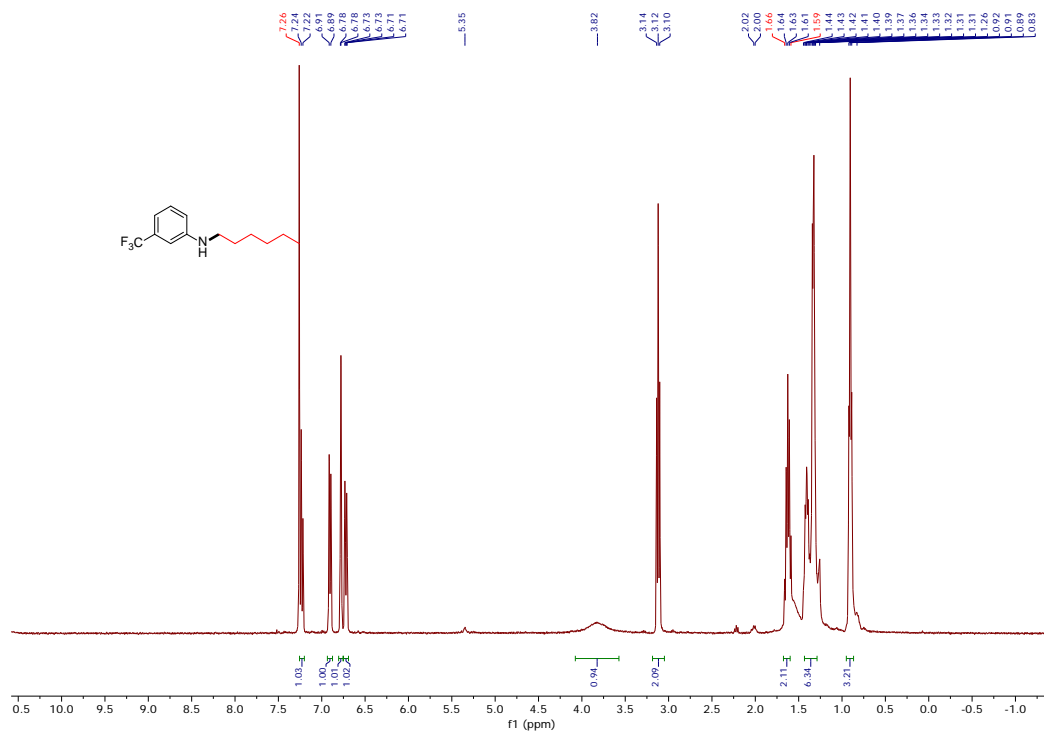
**Supplementary Figure 74. NMR spectra of 2-methoxy-N-(pentan-2-yl)aniline (5j)**



**Supplementary Figure 75. NMR spectra of N-hexylaniline (6a)**



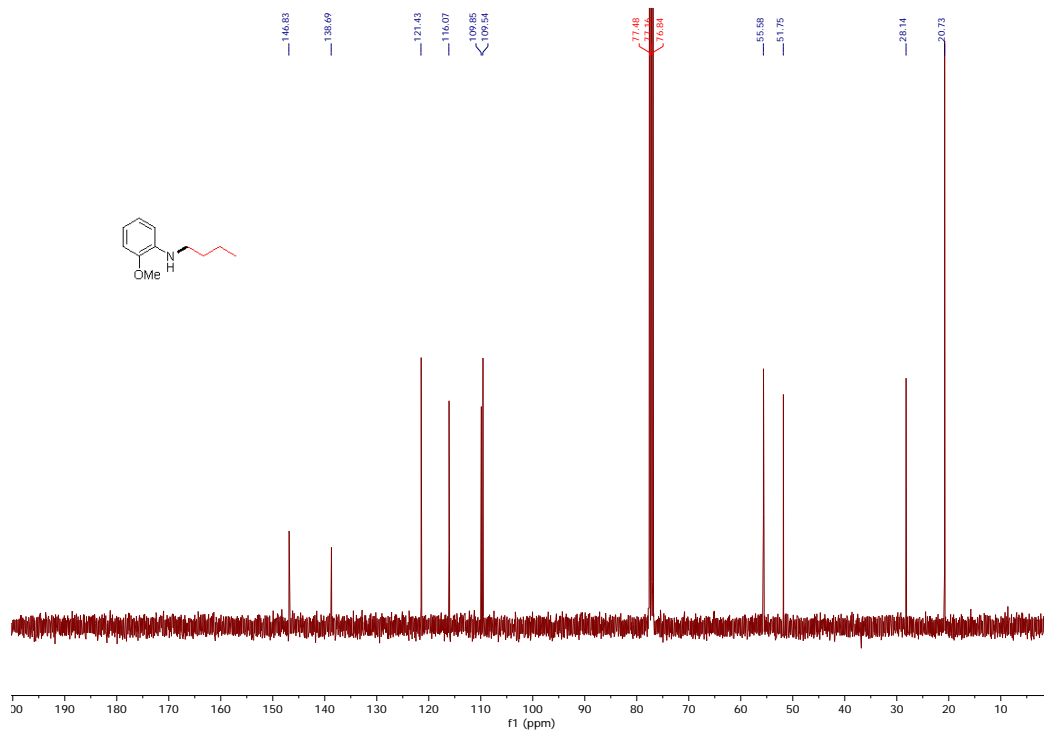
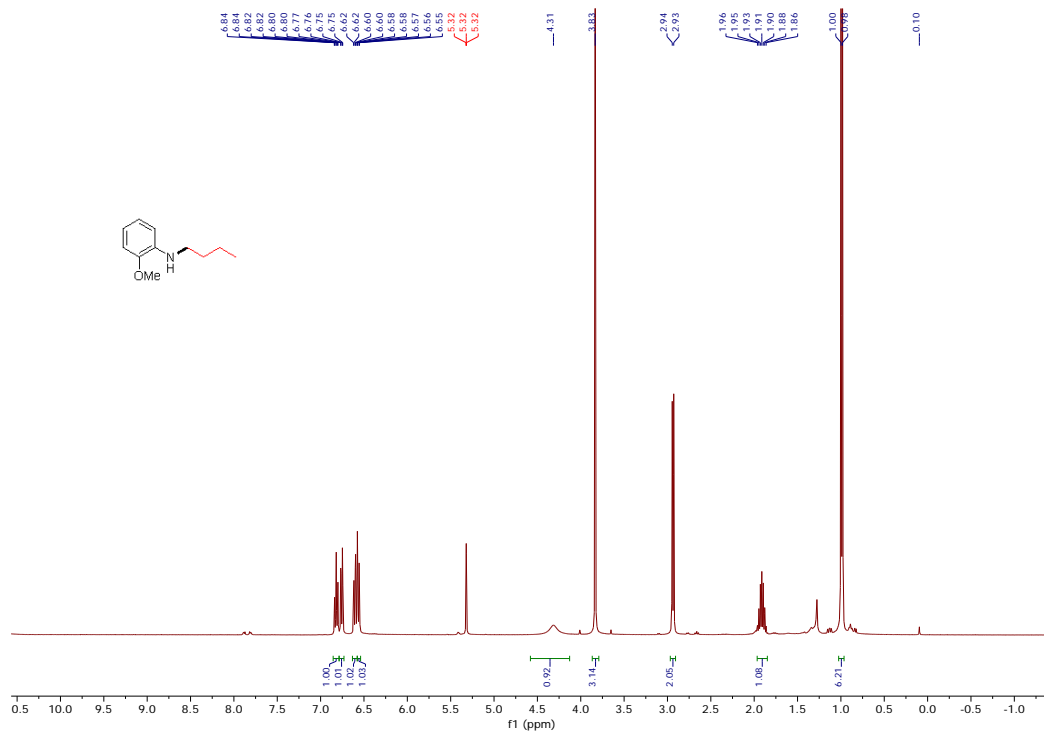
**Supplementary Figure 76. NMR spectra of *N*-hexyl-2-methoxyaniline (6b)**



**Supplementary Figure 77. NMR spectra of *N*-hexyl-3-(trifluoromethyl)aniline (6c)**

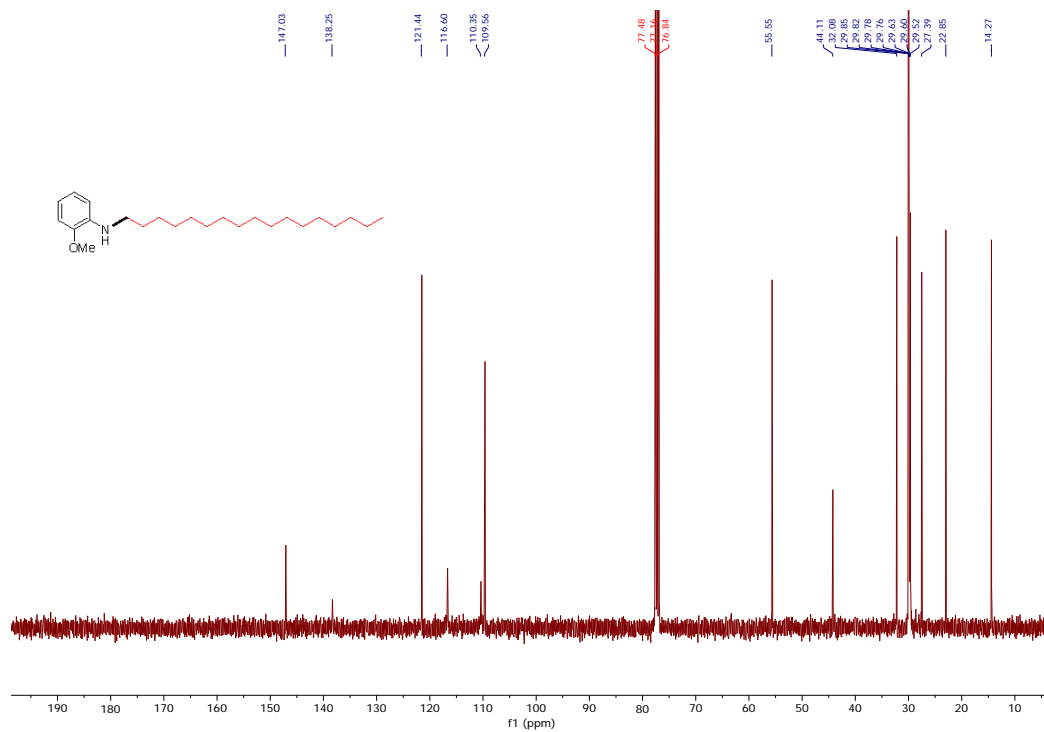
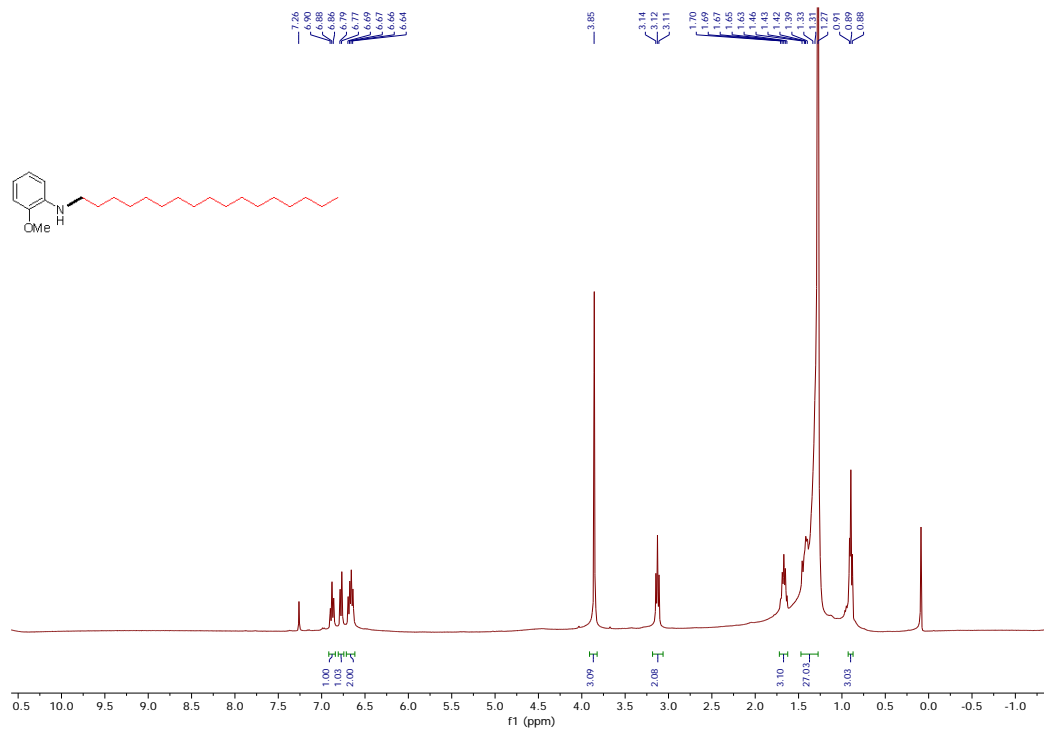






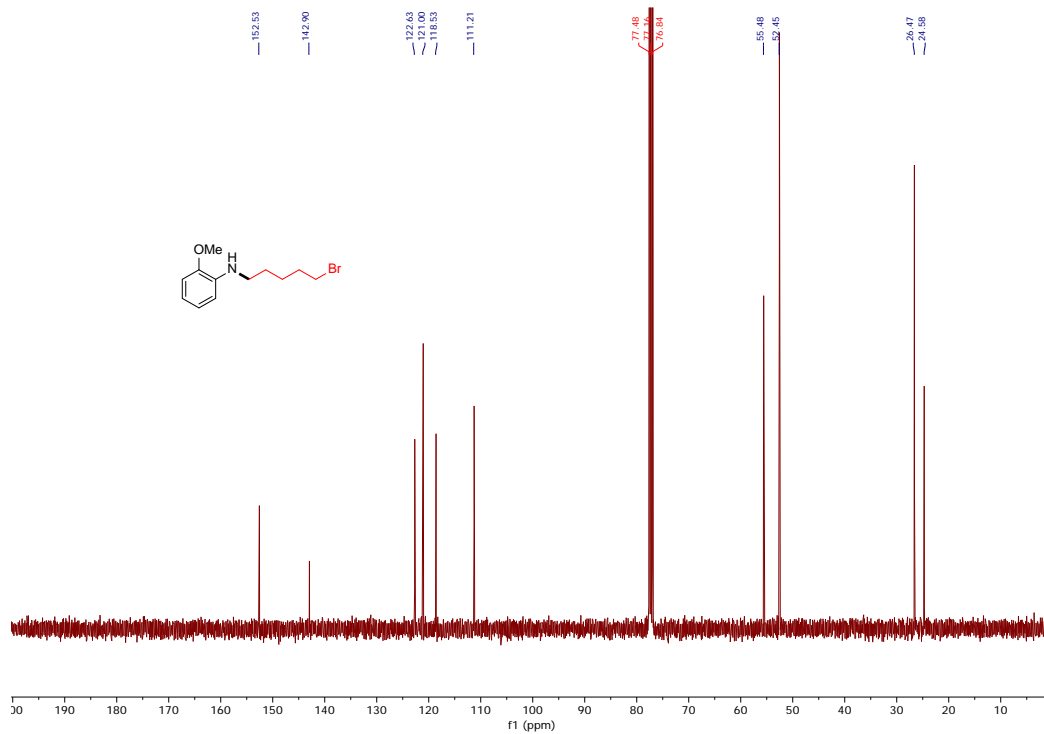
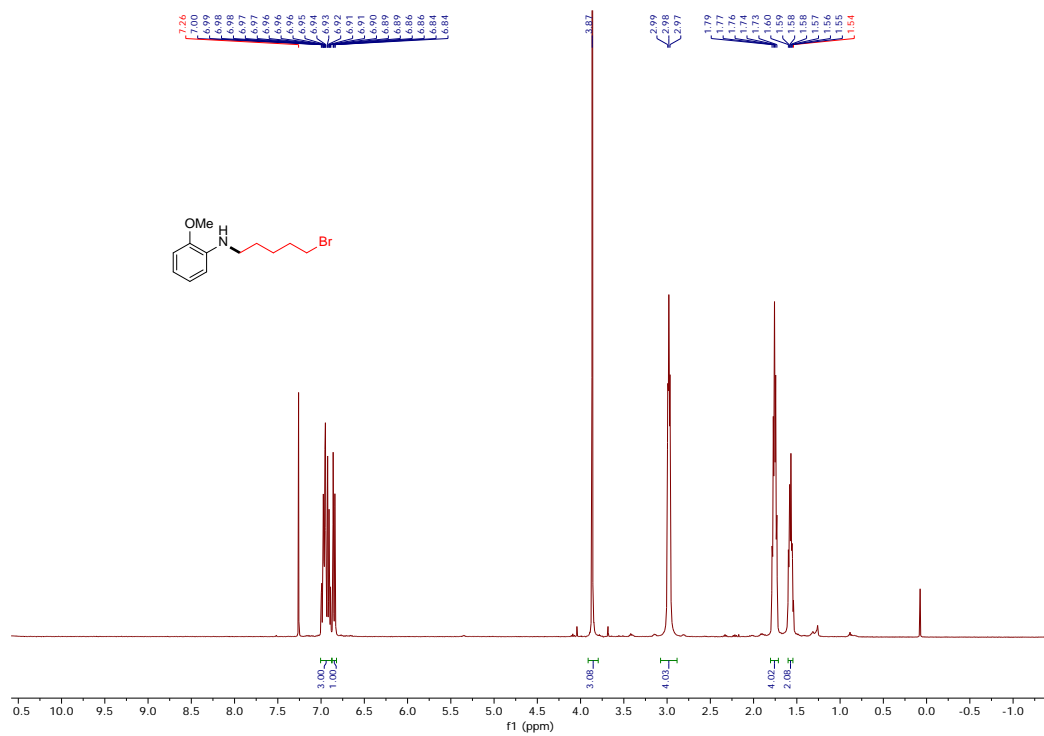
**Supplementary Figure 79. NMR spectra of *N*-butyl-2-methoxyaniline (6e)**



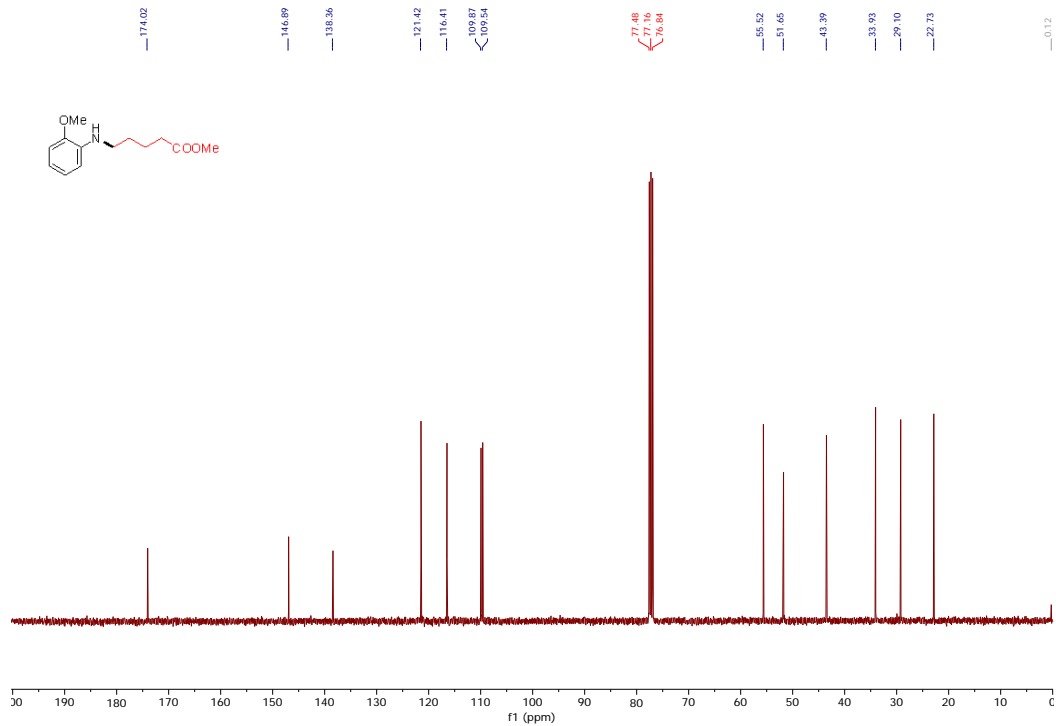
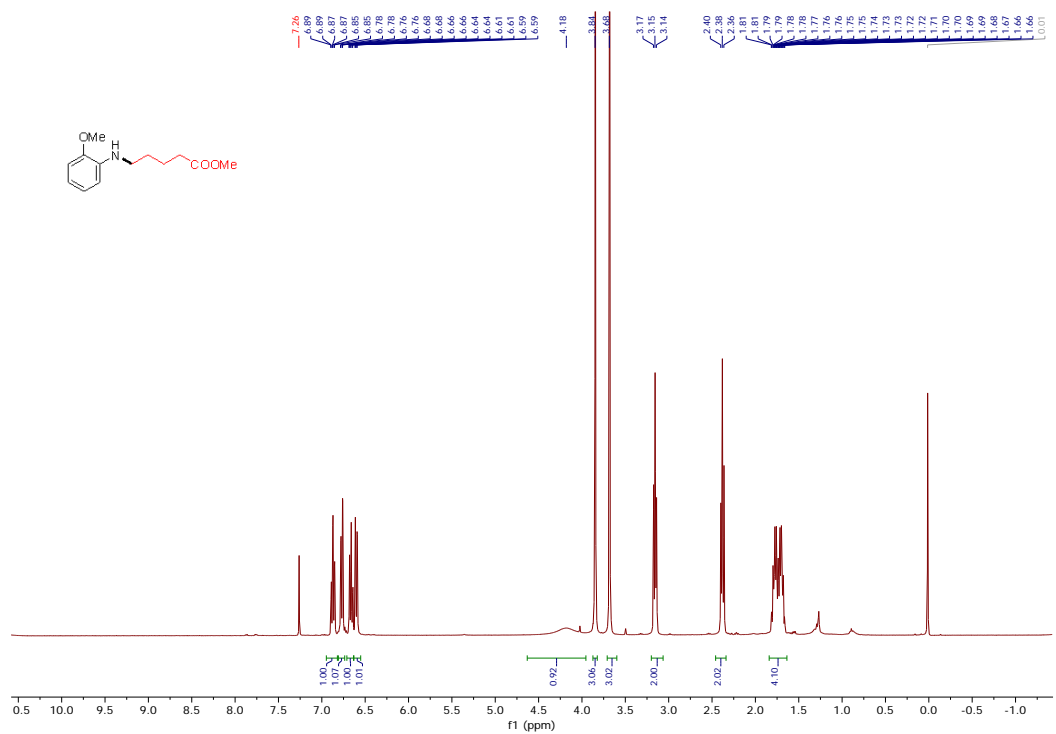


**Supplementary Figure 81. NMR spectra of *N*-heptadecyl-2-methoxyaniline (6g)**

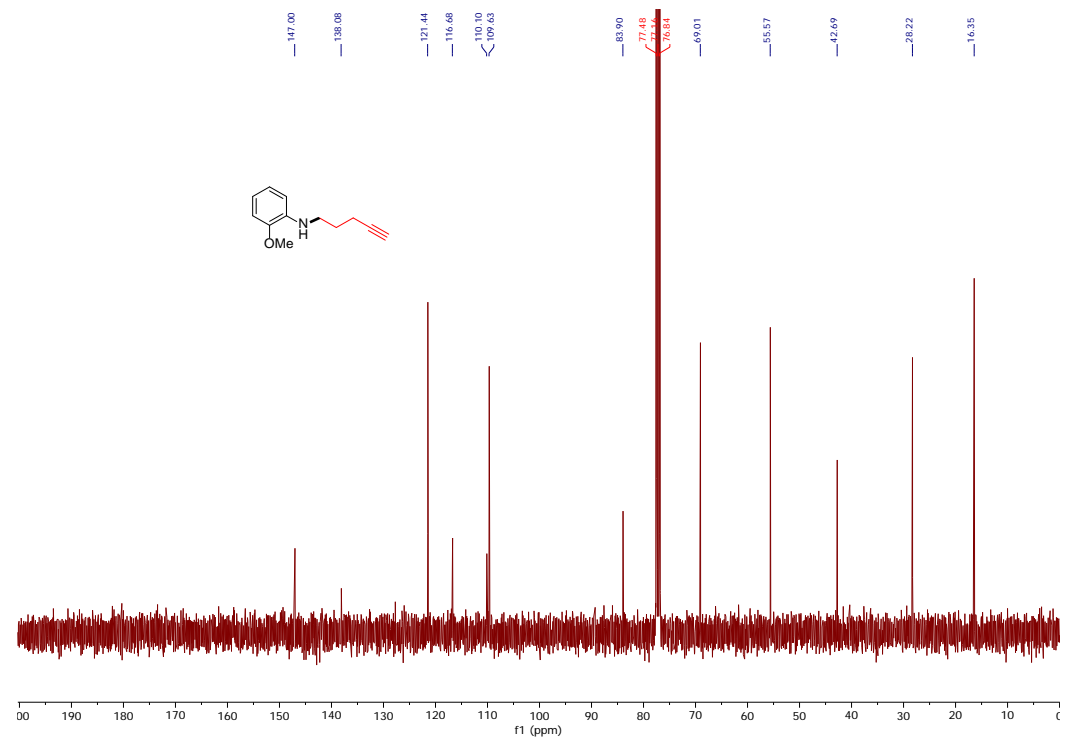
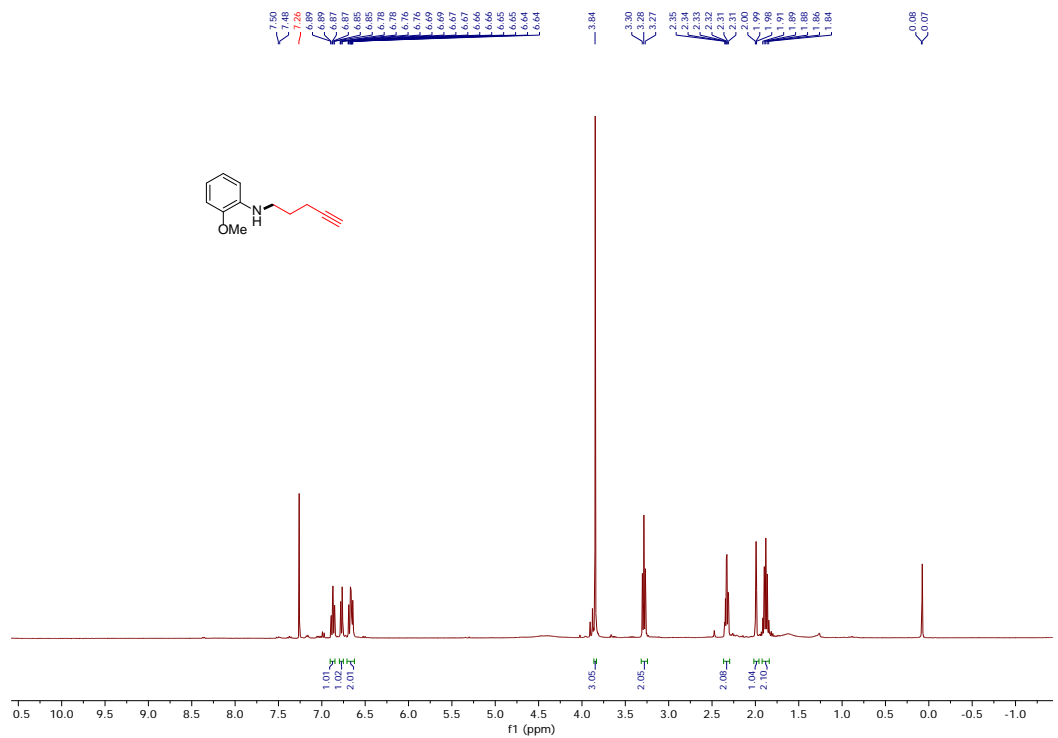




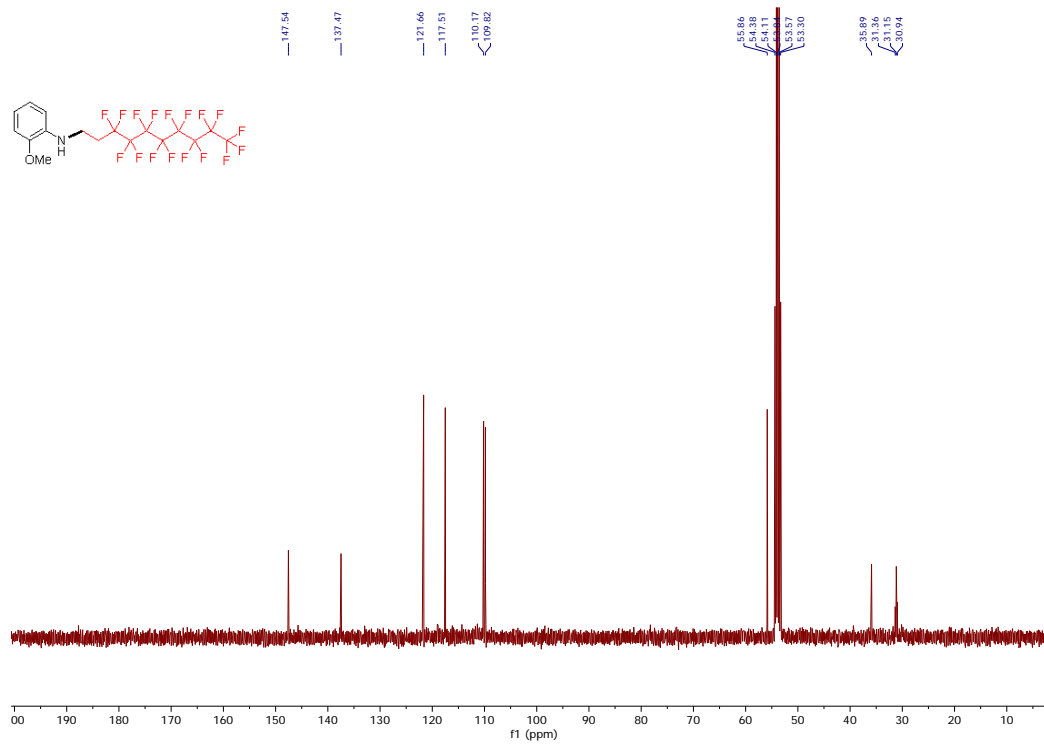
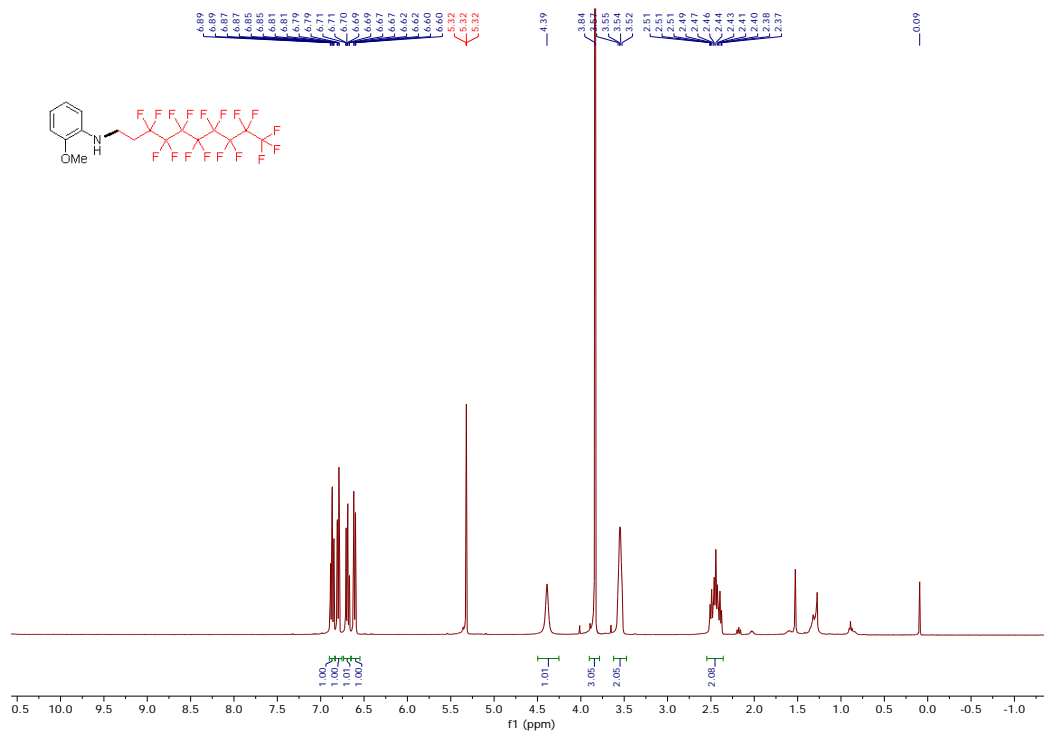
**Supplementary Figure 83. NMR spectra of *N*-(5-bromopentyl)-2-methoxyaniline (6i)**



**Supplementary Figure 84. NMR spectra of Methyl 5-((2-methoxyphenyl)amino)pentanoate (6j)**

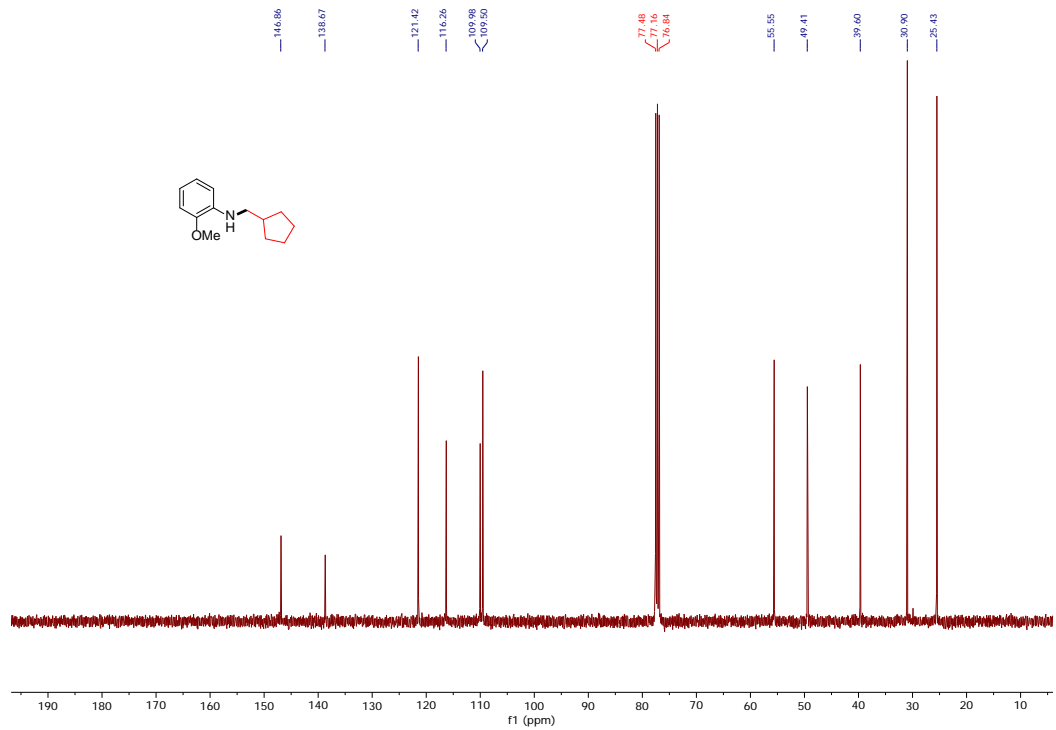
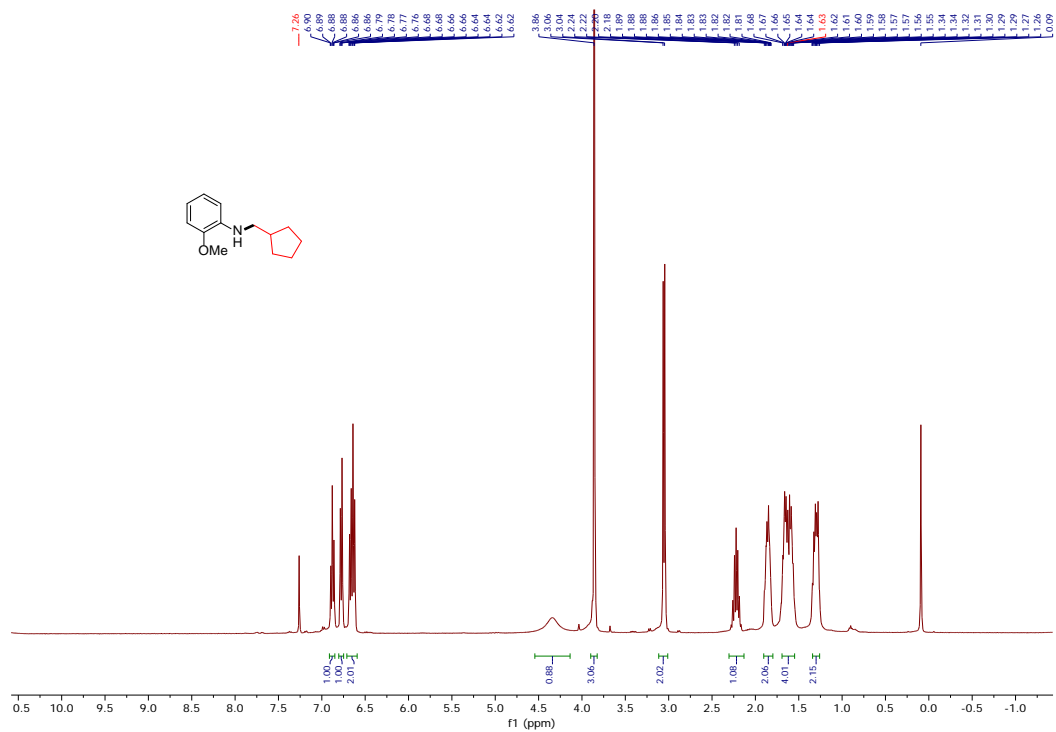


**Supplementary Figure 85. NMR spectra of N-(hex-5-yn-1-yl)-2-methoxyaniline (6k)**

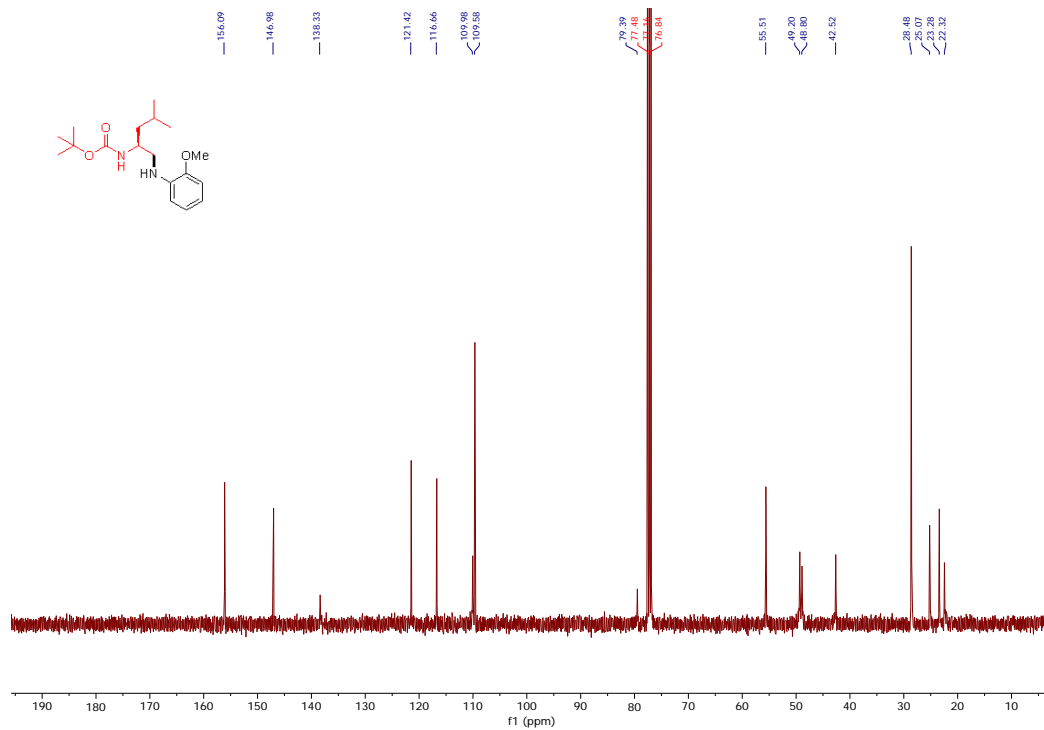
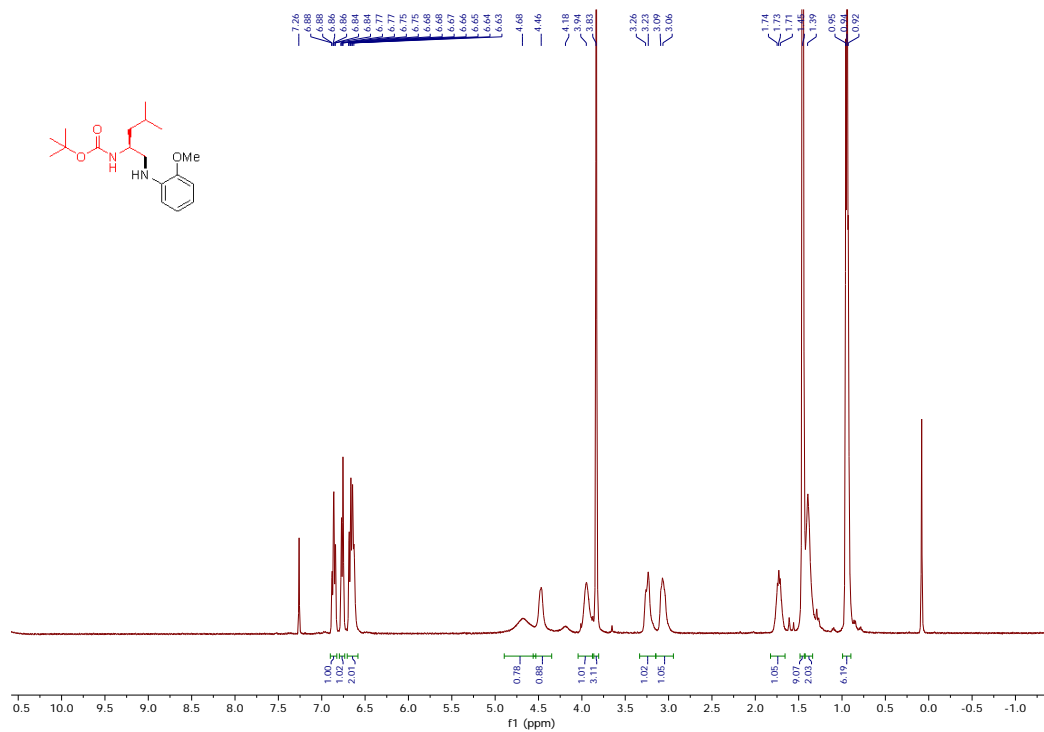






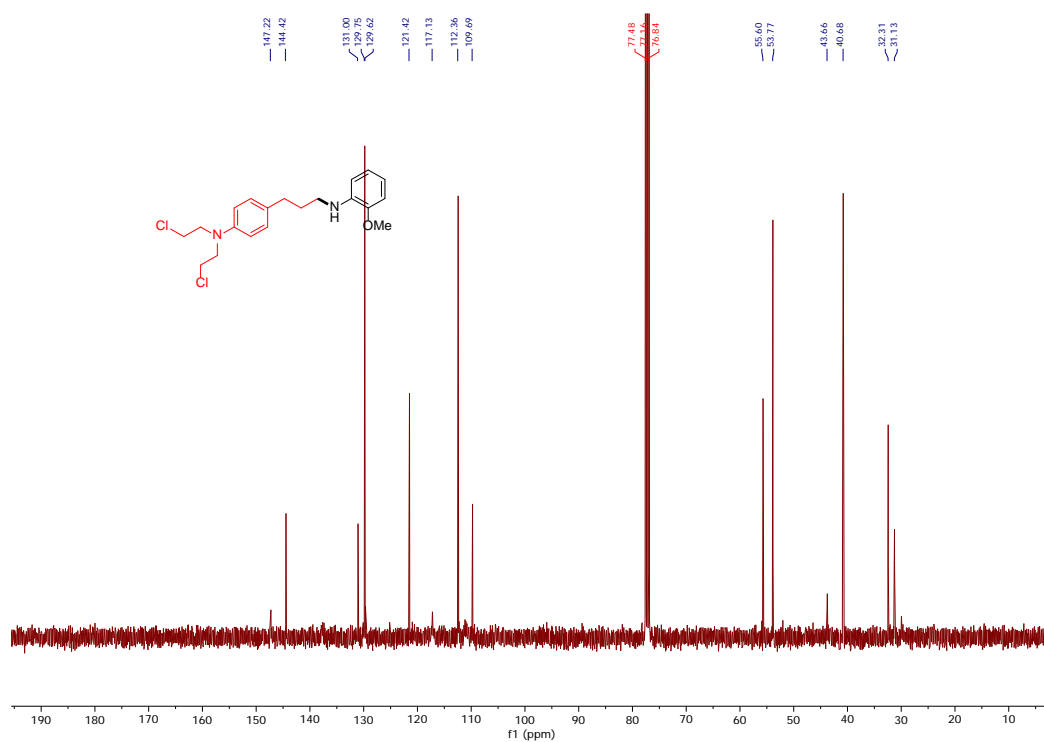
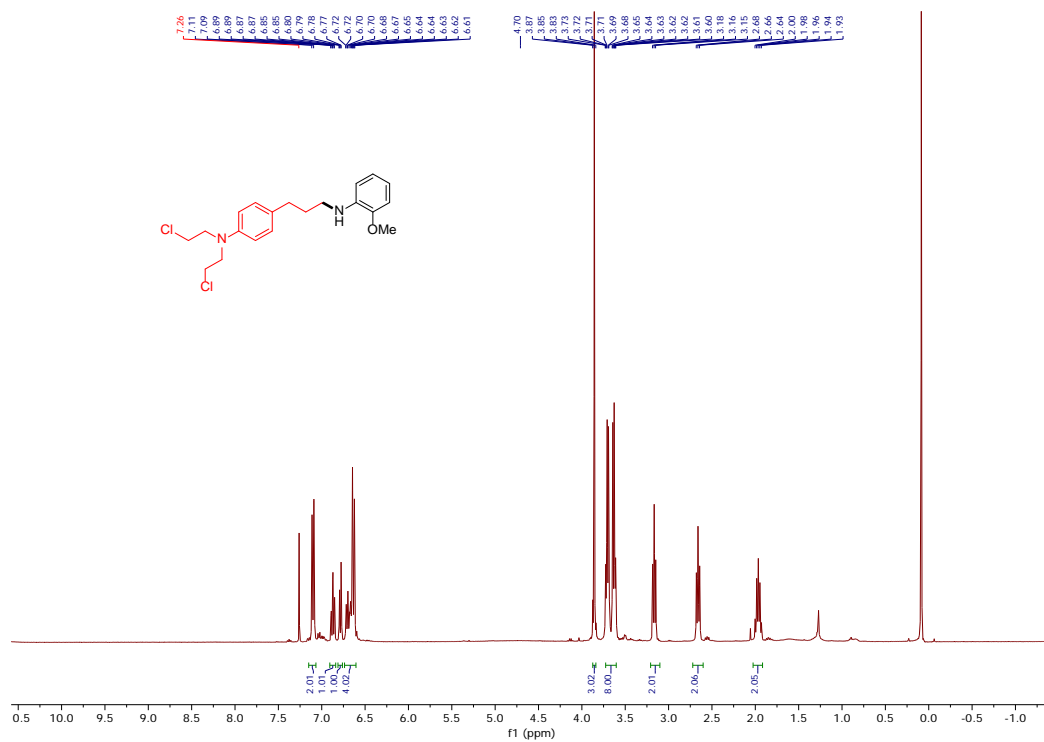


**Supplementary Figure 87. NMR spectra of *N*-(cyclopentylmethyl)-2-methoxyaniline (6m)**

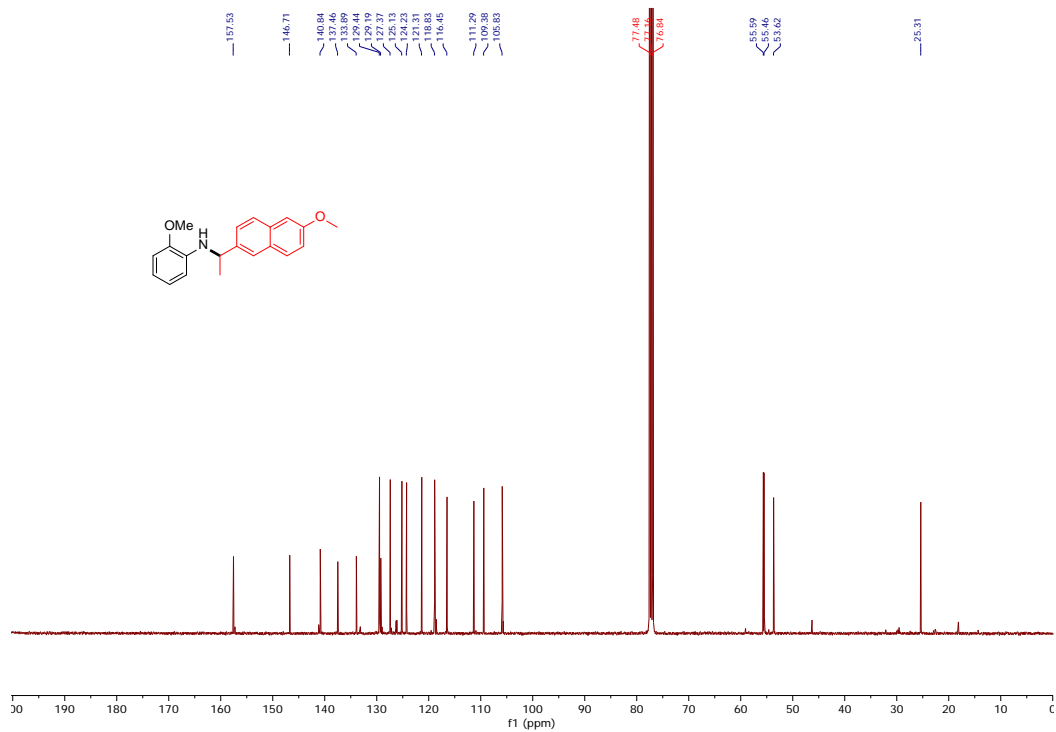
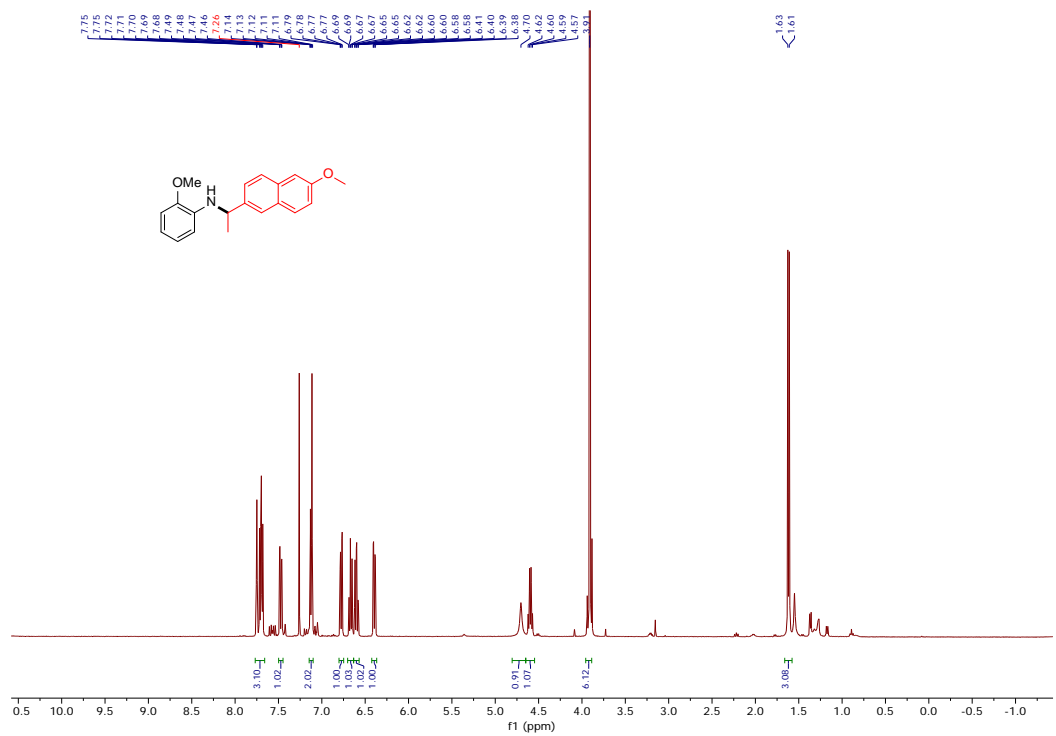


**Supplementary Figure 88. NMR spectra of *tert*-butyl (S)-1-((2-methoxyphenyl)amino)-4-methylpentan-2-yl)carbamate (7a)**

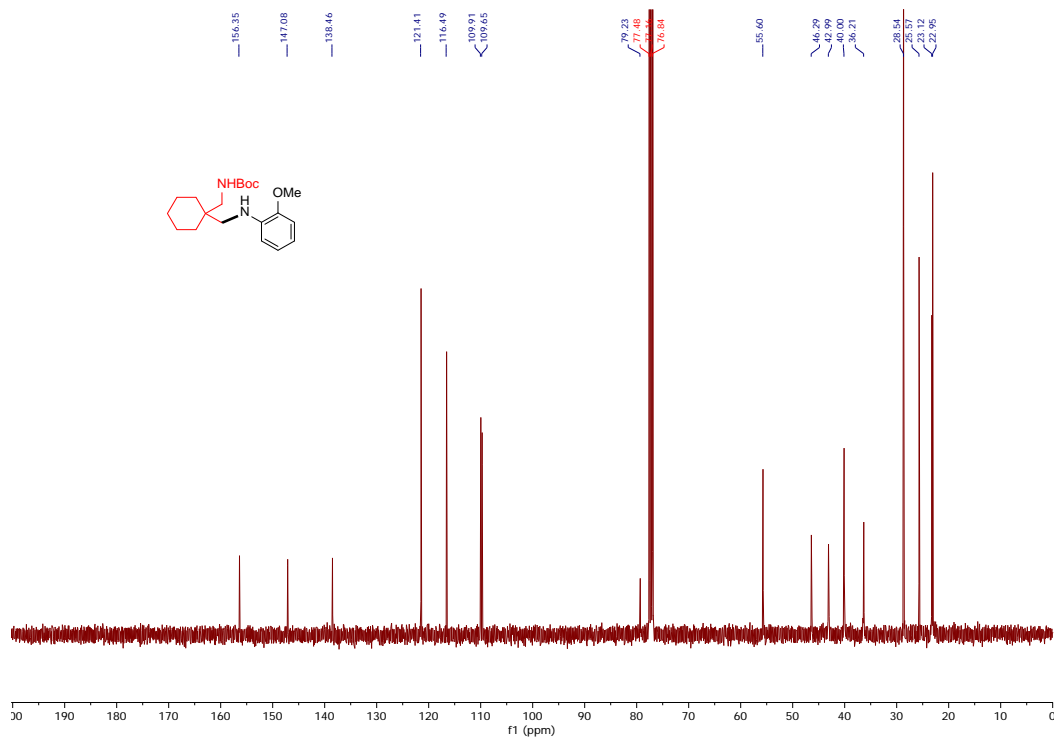
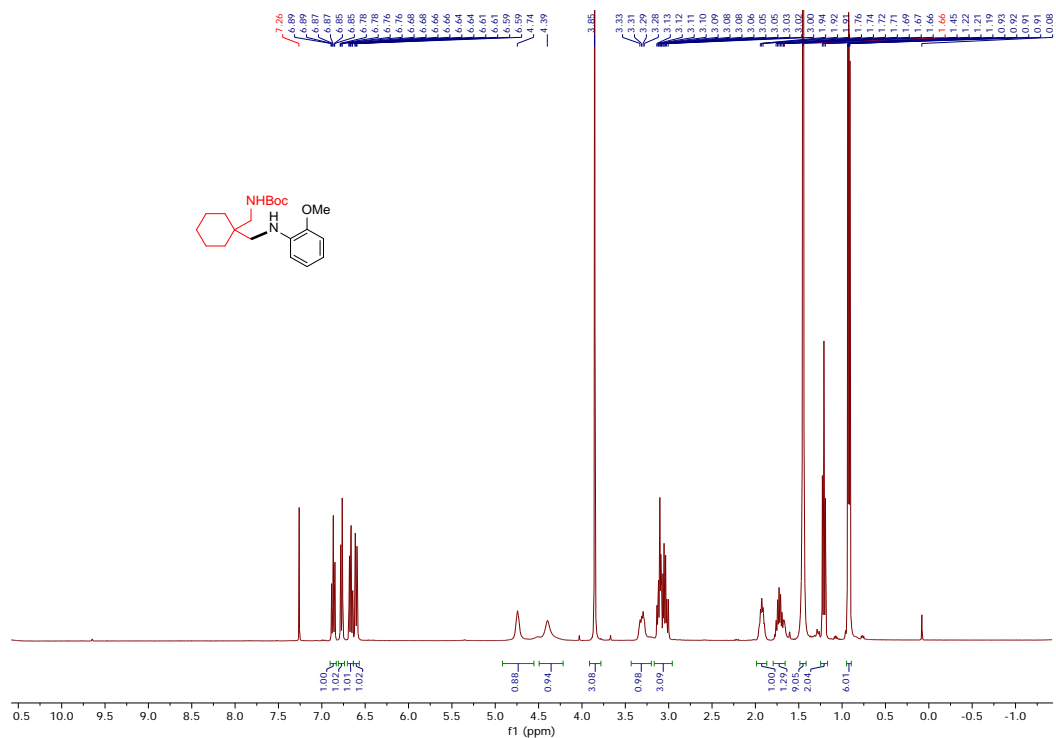




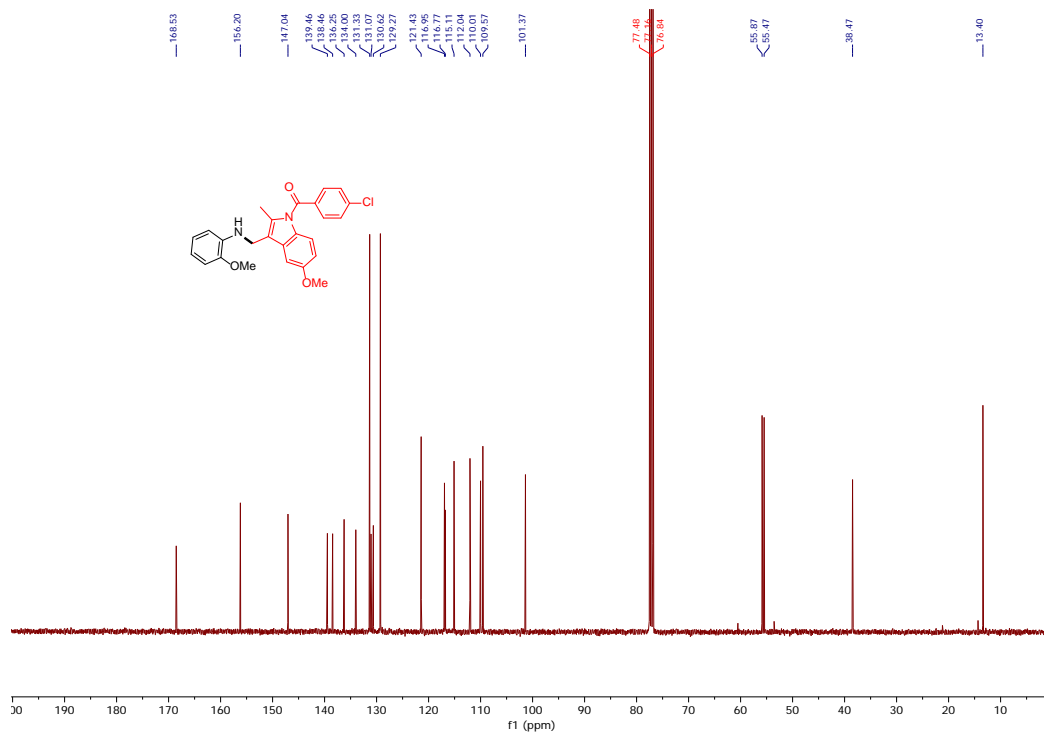
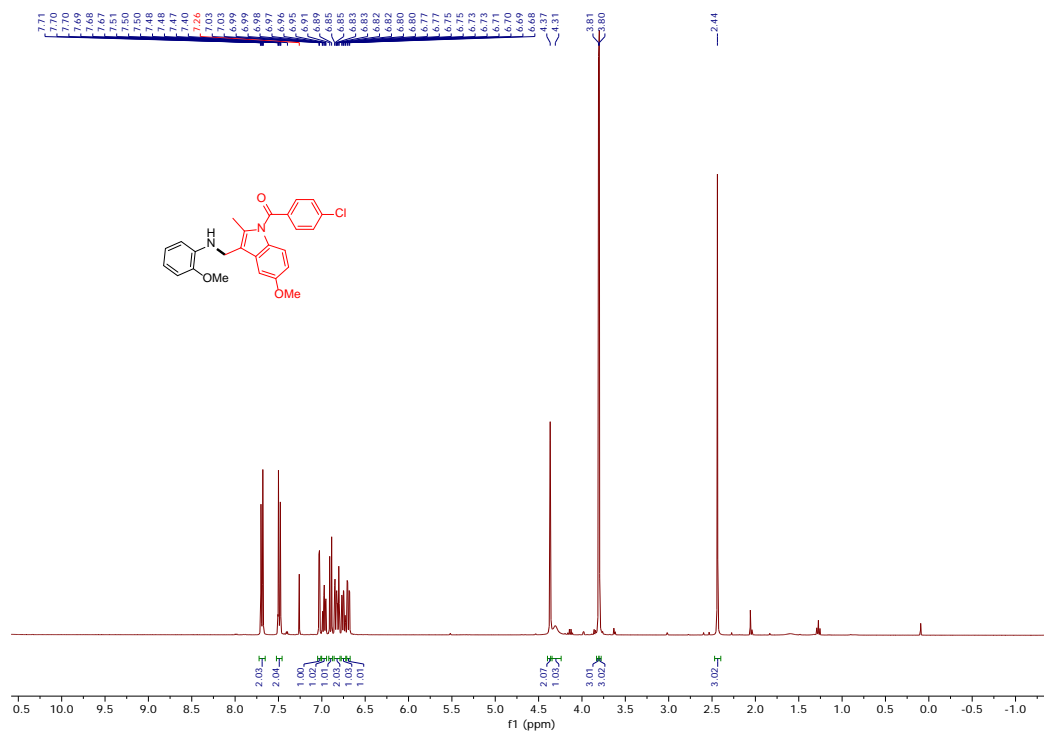
**Supplementary Figure 90. NMR spectra of *N,N*-bis(2-chloroethyl)-4-(3-((2-methoxyphenyl)amino)propyl)aniline (7c)**



**Supplementary Figure 91. NMR spectra of 2-methoxy-N-(1-(6-methoxynaphthalen-2-yl)ethyl)aniline (7d)**

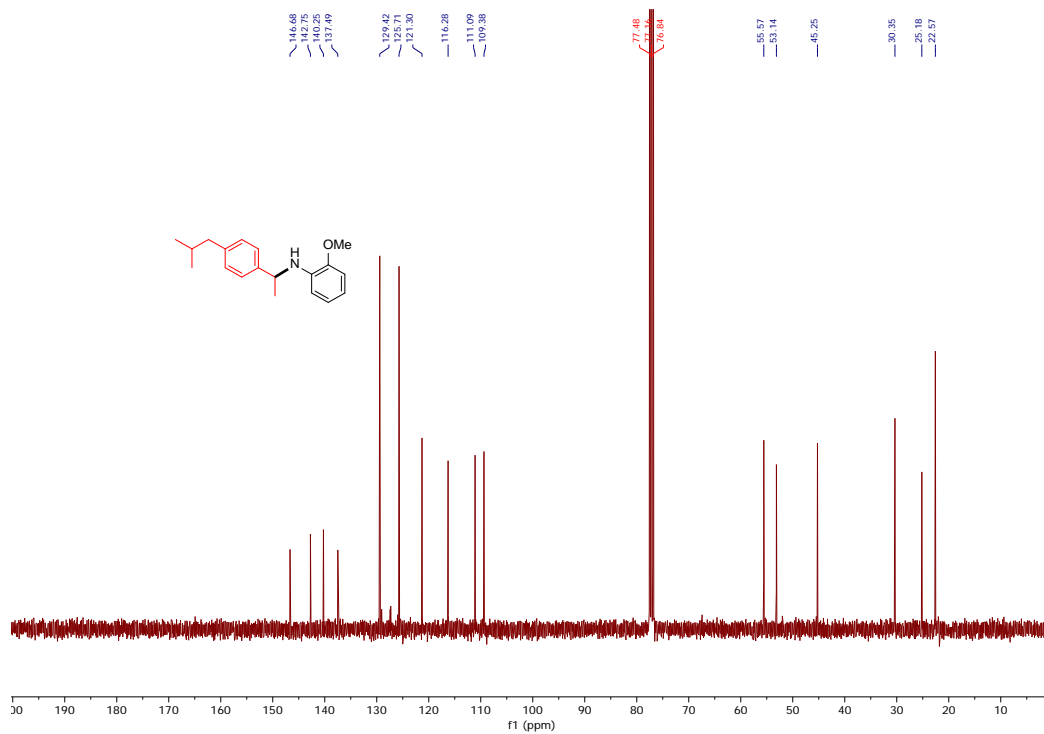
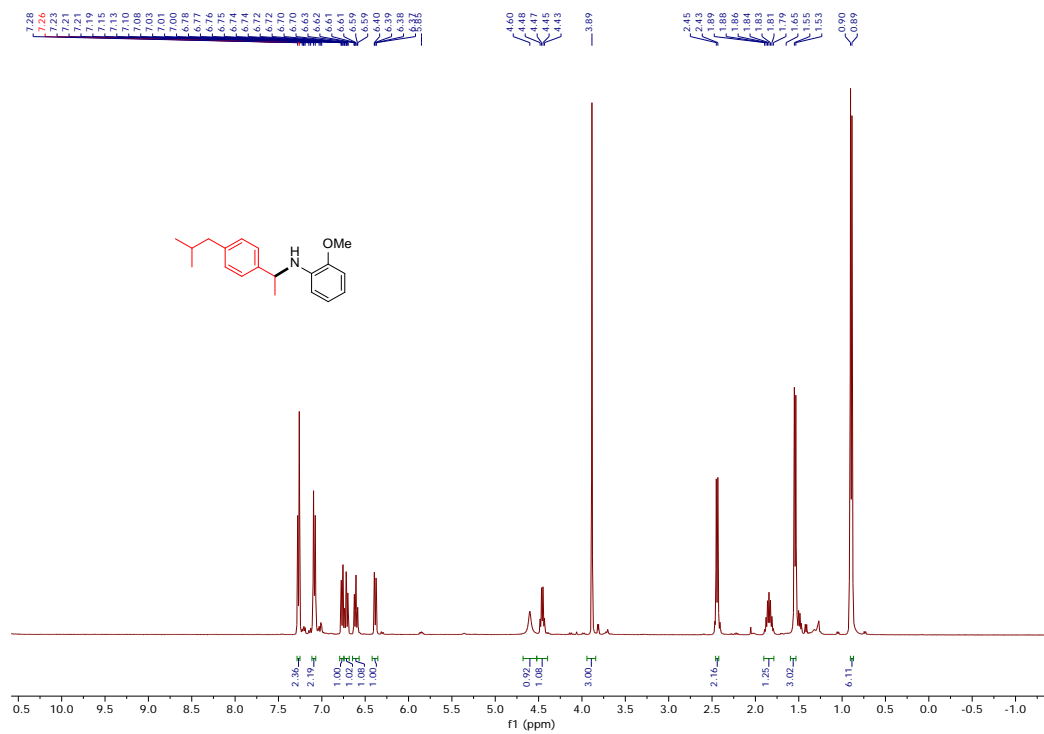


**Supplementary Figure 92. NMR spectra of *tert*-butyl ((1-(((2-methoxyphenyl)amino)methyl)cyclohexyl)methyl)carbamate (7e)**

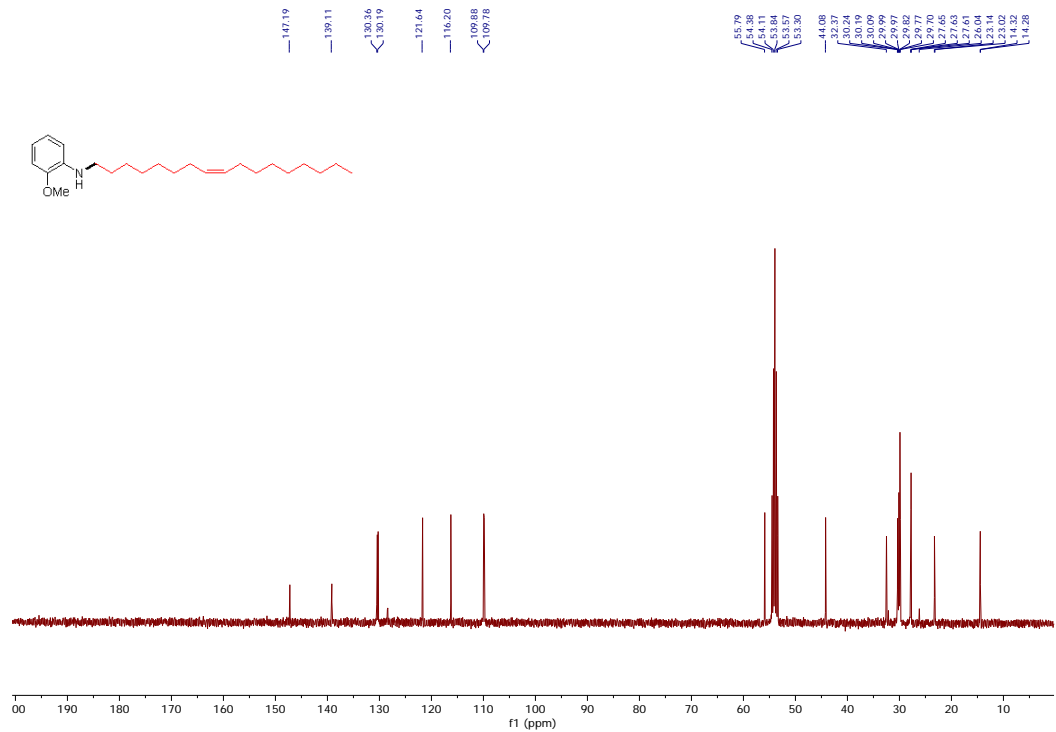
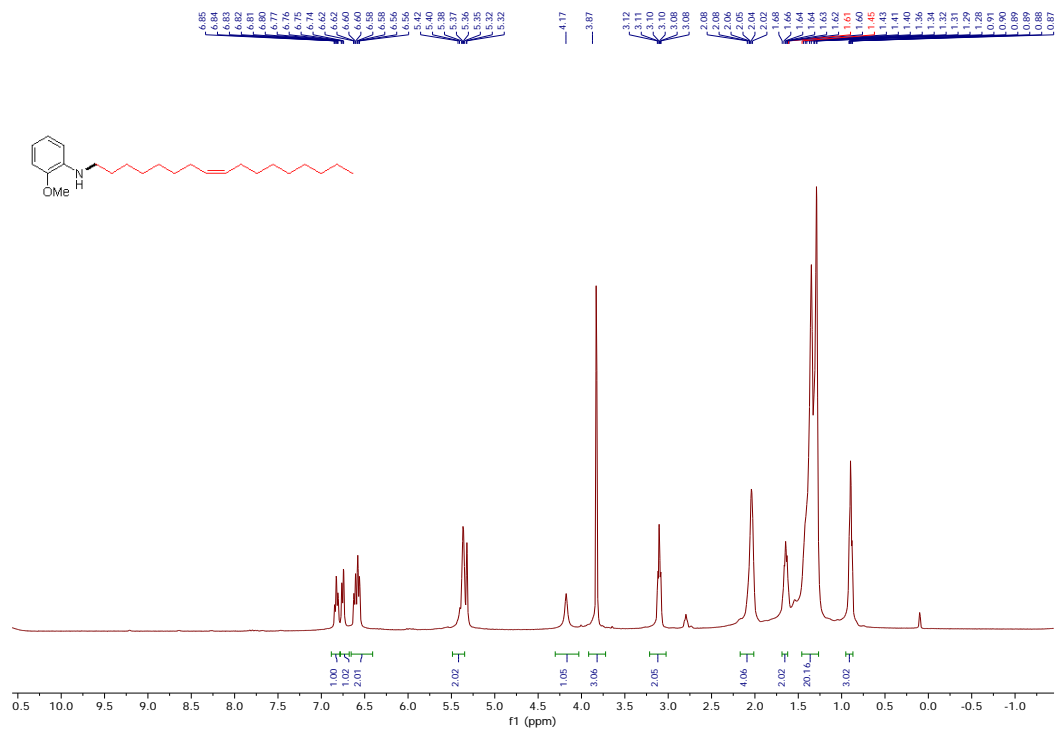


**Supplementary Figure 93. NMR spectra of (4-chlorophenyl)(5-methoxy-3-(((2-methoxyphenyl)amino)methyl)-2-methyl-1*H*-indol-1-yl)methanone (7f)**

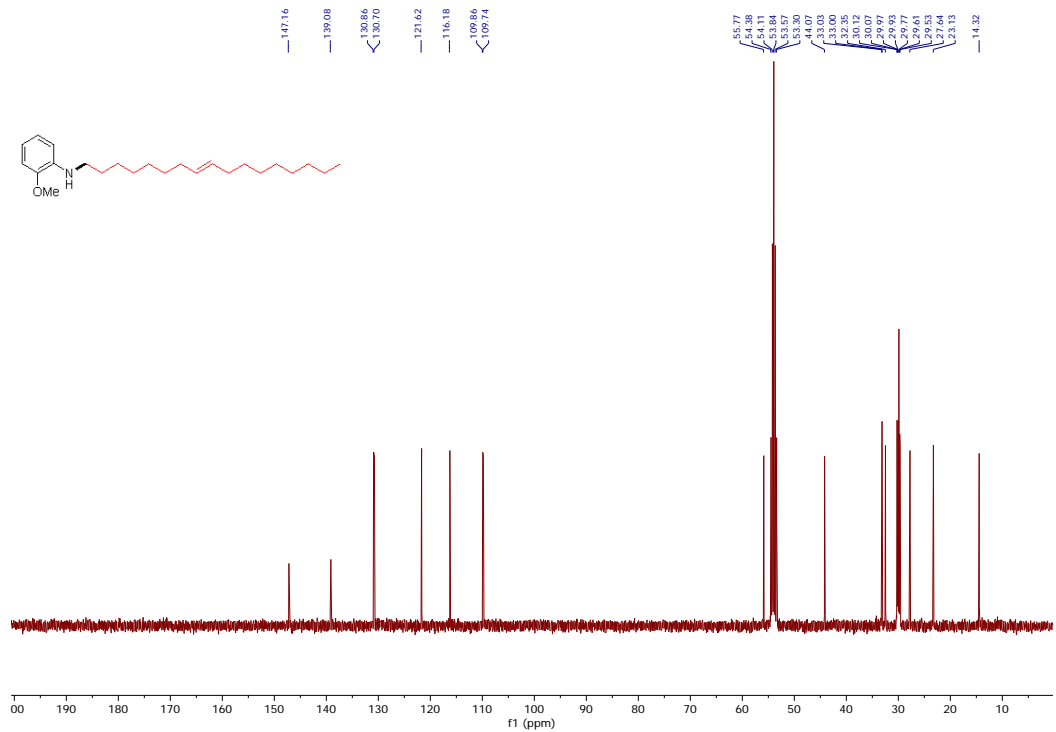
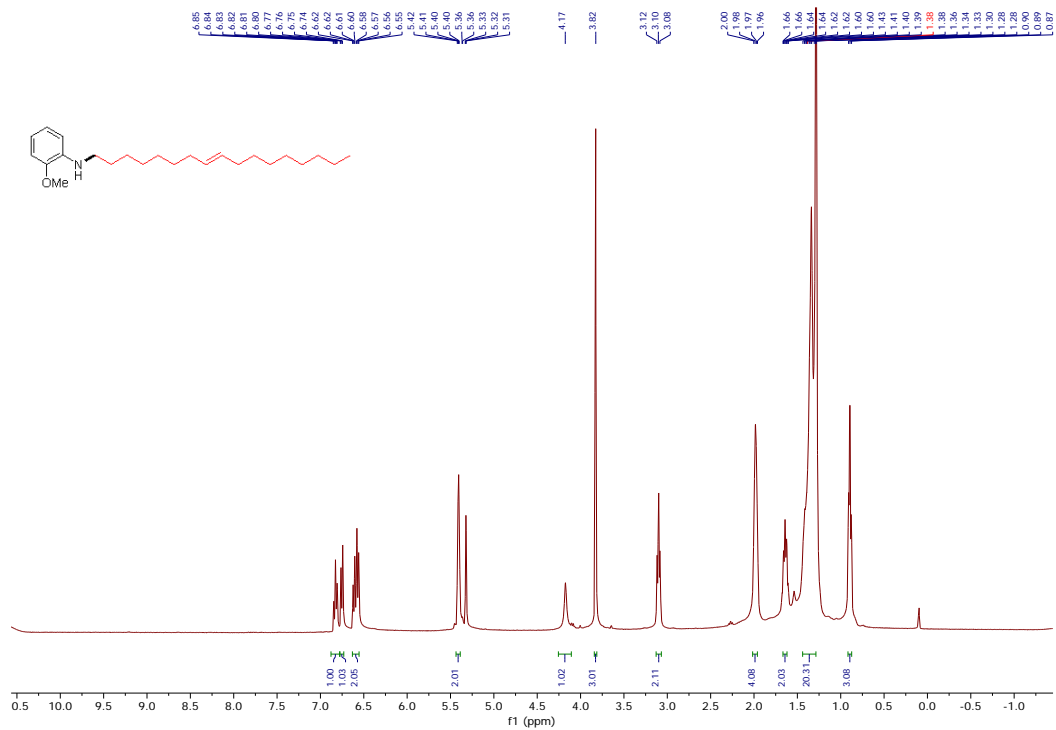




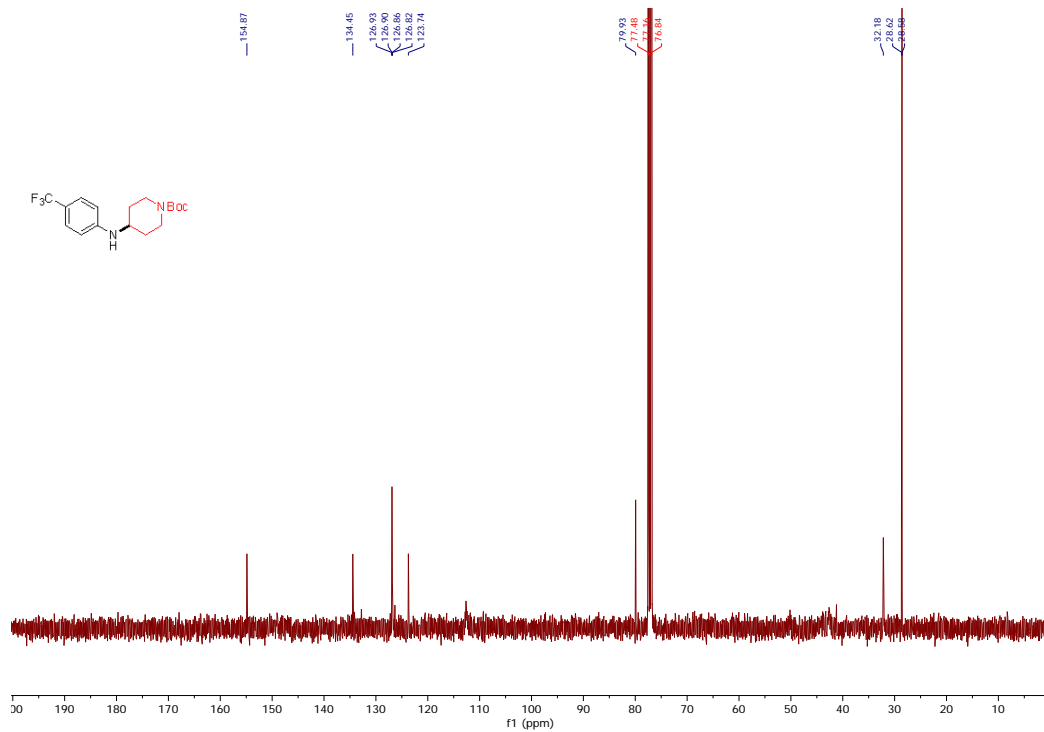
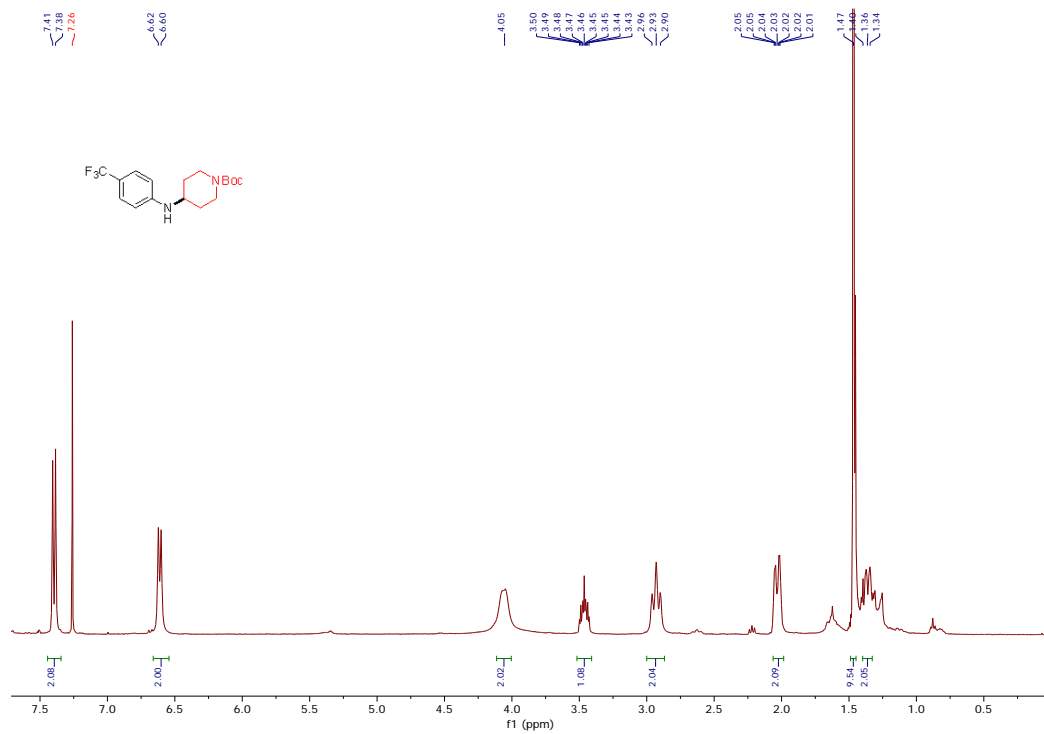
**Supplementary Figure 94. NMR spectra of *N*-(1-(4-isobutylphenyl)ethyl)-2-methoxyaniline (7g)**



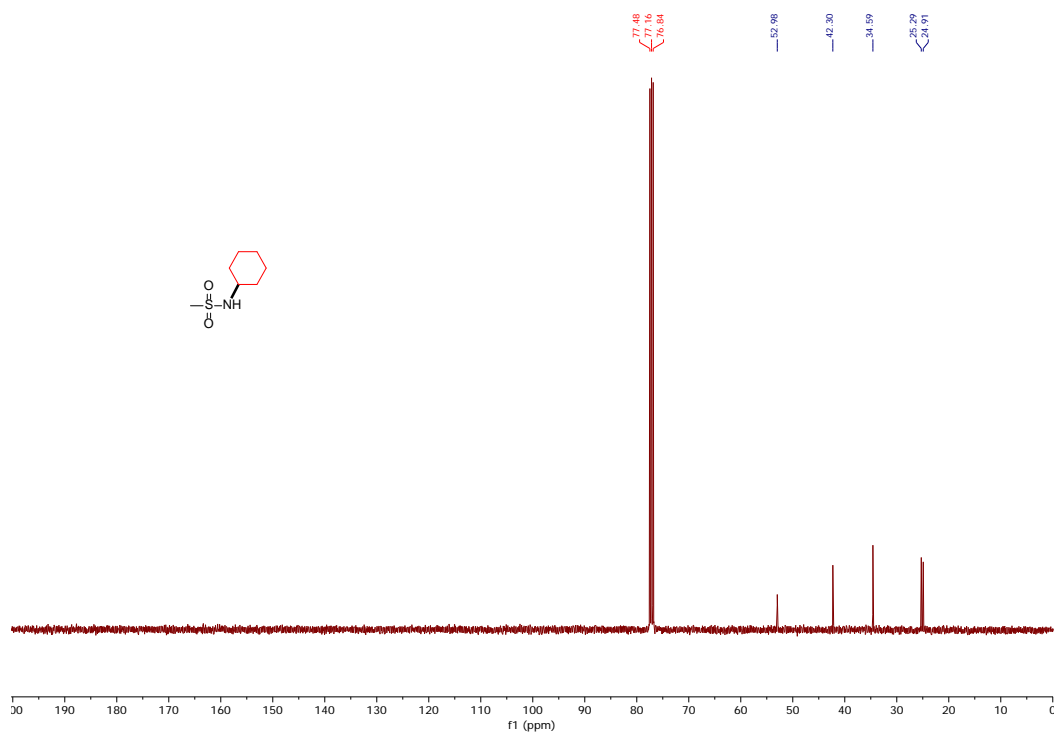
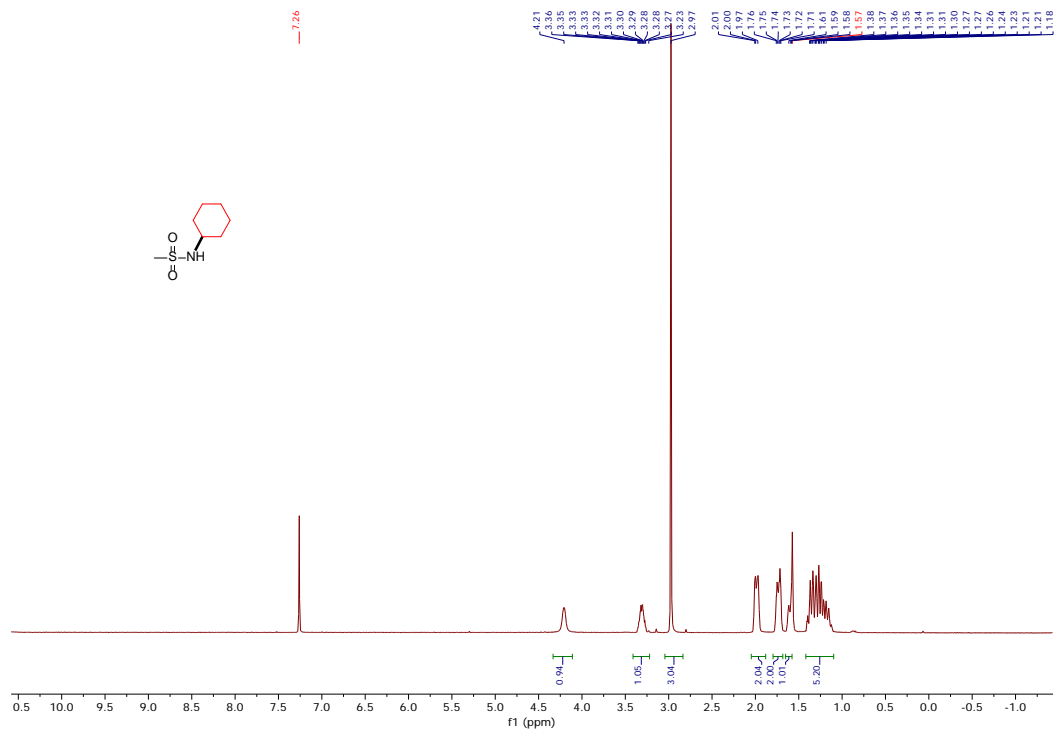
**Supplementary Figure 95. NMR spectra of (Z)-N-(heptadec-8-en-1-yl)-2-methoxyaniline (7h)**



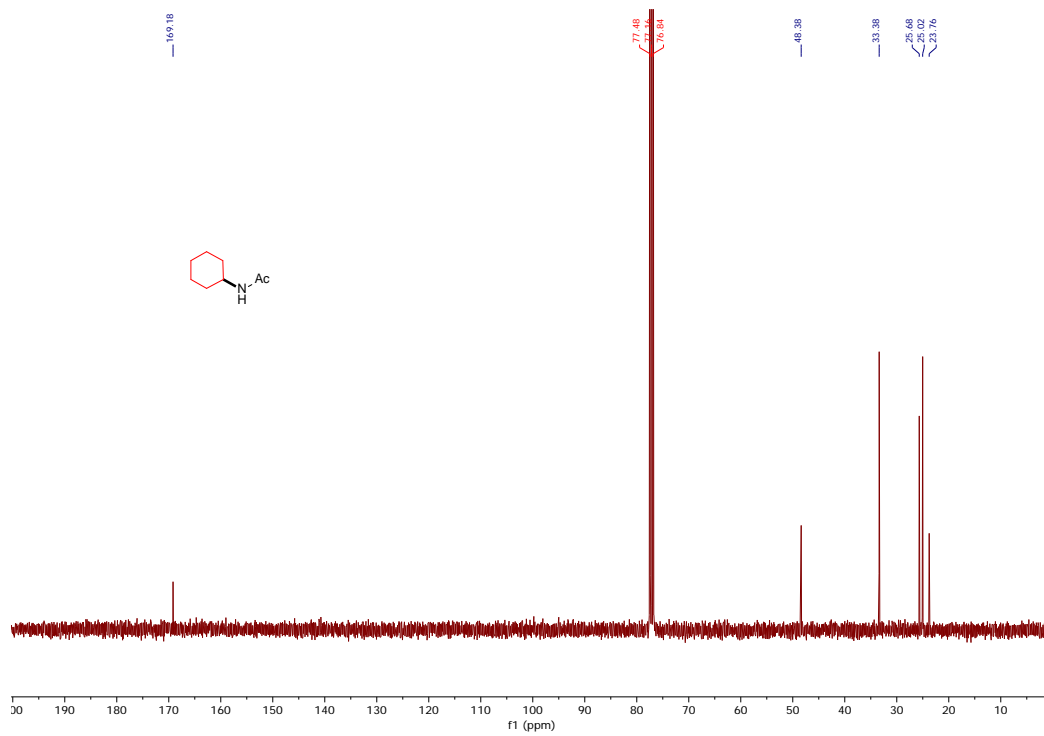
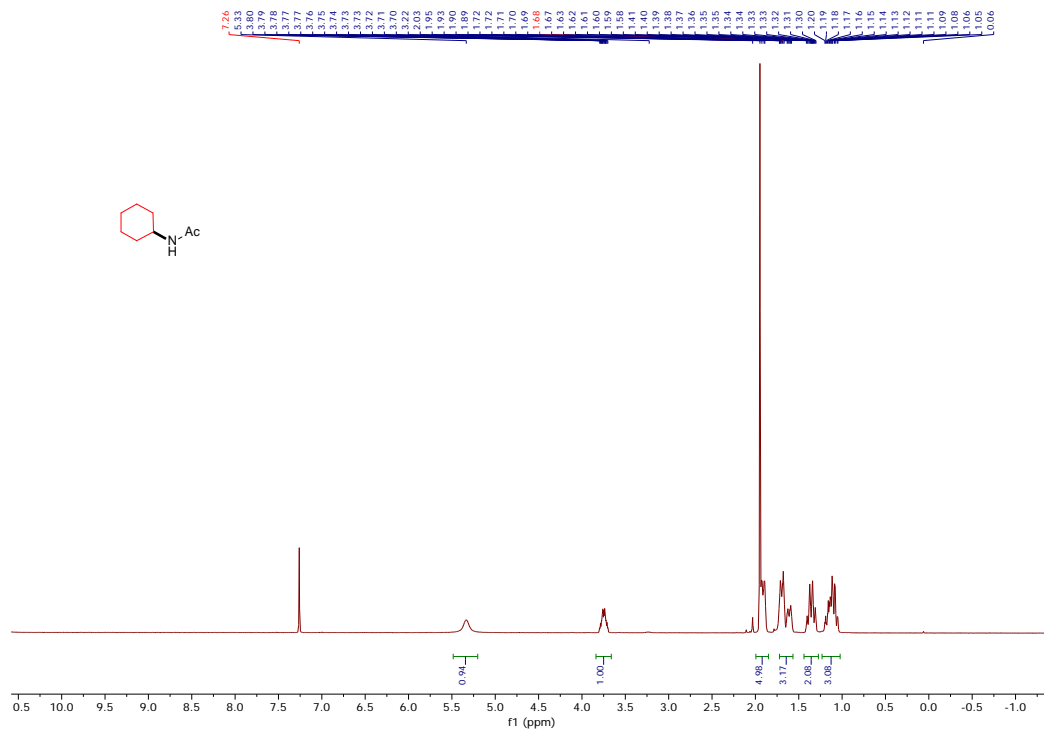
**Supplementary Figure 96. NMR spectra of (*E*)-*N*-(heptadec-8-en-1-yl)-2-methoxyaniline (7i)**



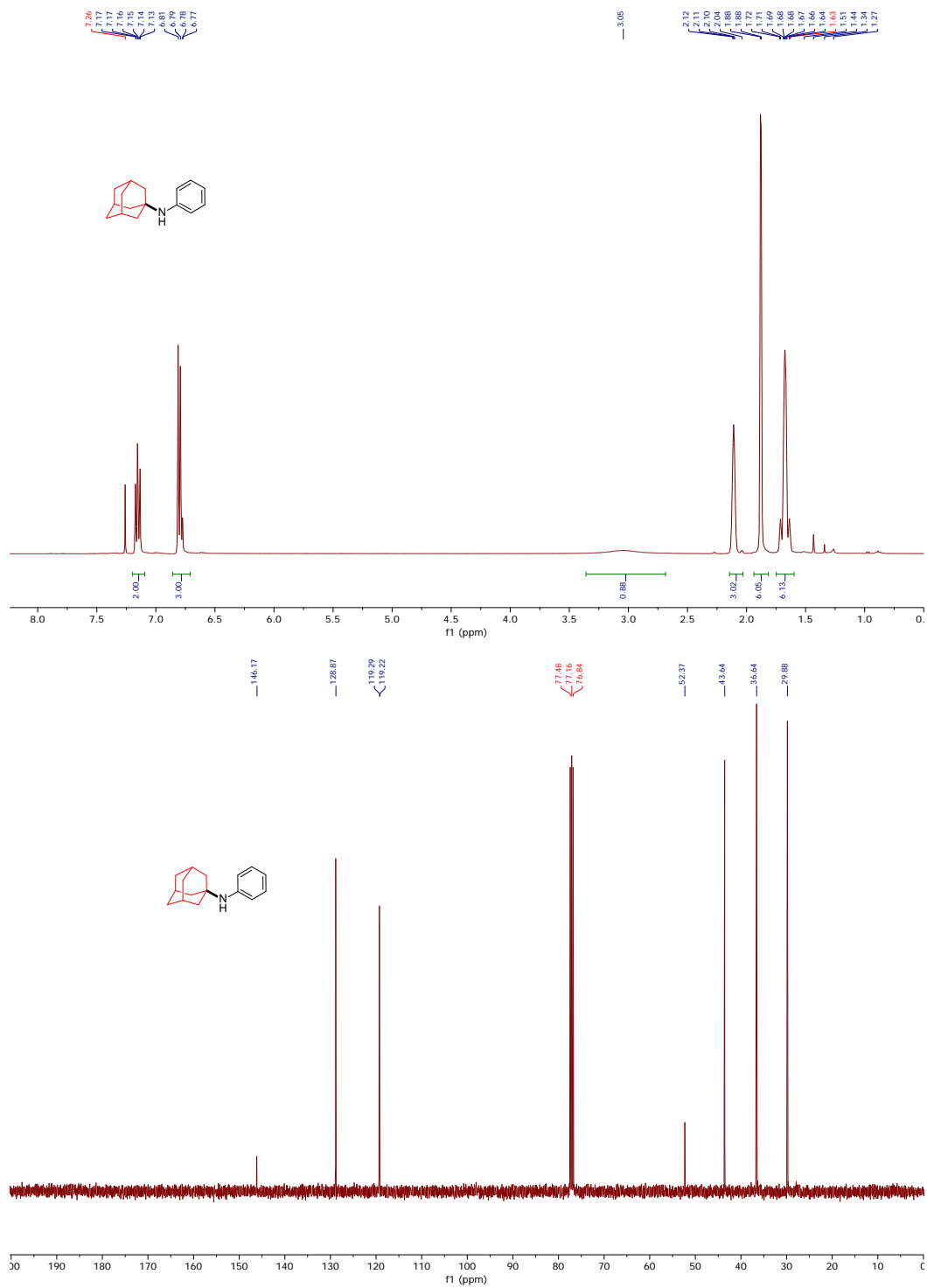
**Supplementary Figure 97. NMR spectra of *tert*-butyl 4-((4-(trifluoromethyl)phenyl)amino)piperidine-1-carboxylate (8a)**



**Supplementary Figure 98. NMR spectra of *N*-cyclohexylmethanesulfonamide (S1)**



**Supplementary Figure 99. NMR spectra of *N*-cyclohexylacetamide (S2)**



**Supplementary Figure 100. NMR spectra of *N*-phenyladamantan-1-amine (S3)**

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