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SUPPLEMENTARY INFORMATION

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**Zinc Acetate-Promoted Blocking of ATRA Process with Alkyl Halides Enabling Photochemical Alkylamination of Olefins**

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## 1. General Information:

All commercially available chemicals and reagents were used without any further purification unless otherwise stated. Solvents for extraction or column chromatography were of technical quality. All water used was purified via a Merck Millipore reverse osmosis purification system prior to use. All reactions were performed in oven-dried glassware under a positive pressure of argon with freshly distilled anhydrous solvents.<sup>1</sup> Solvents were transferred *via* syringe and were introduced into the reaction vessels through a rubber septum. Solvents were removed under reduced pressure using Büchi Rotavapor apparatus.

**Thin-layer chromatography (TLC):** The progress of the reaction was monitored by thin layer chromatography (TLC) using SiO<sub>2</sub>-60 UV254 coated aluminium sheets (Merck, TLC Silica gel 60 F<sub>254</sub>). Visualization was achieved using UV light, iodine, and/or chemical staining with vanillin or basic potassium permanganate solutions as appropriate.

**Flash column chromatography (FC):** Purification of reaction mixture was carried out with flash column chromatography on silica gel 230-400 mesh (Merck, 37-63 µm). Solvents for extraction and chromatography were of technical quality. Eluting solvent mixtures are individually reported in parenthesis.

**NMR spectra:** Proton, Carbon, and Fluorine nuclear magnetic resonance (<sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR) spectra were recorded on a Bruker Avance III HD (400, 101, and 377 MHz) spectrometer at 25 °C. Chemical shifts (δ) are given in ppm and reported as follows: multiplicity [s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), dt (doublet of triplets), and m (multiplet)], coupling constants (*J*) in Hz, number of protons; suggested assignment. The residual deuterated solvent was used as internal standard (CDCl<sub>3</sub>: δ<sub>H</sub> = 7.26 ppm; δ<sub>C</sub> = 77.16 ppm).

**Melting point (Mp):** Melting points were measured by 'Tempstar' melting point instrument using open glass capillaries in a Remco-Kolkata apparatus and are reported uncorrected.

**High-resolution mass spectrometry (HRMS):** HRMS were recorded using a QTOF micro MS system by ESI technique.

**GC-MS:** GC-MS analysis was done by a Thermo Scientific ISQ QD single quadrupole GC-MS system using a TG-5MS column (30 m × 0.25 mm × 0.25 µm).

**Photoreactions:** Photoreactions were carried out in borosilicate made culture tube using blue light source (PAR38 12W blue LED bulb).

**Luminescence spectrometer:** Fluorescence quenching studies were carried out using a PerkinElmer LS 55 Fluorescence Spectrometer.

**Electrochemical Measurements:** Cyclic Voltammetry was performed using a CH Instruments (model: CHI1140C).

**Energy Dispersive X-Ray Analysis (EDX):** The elemental analysis was investigated using Field Emission Scanning Microscopy (FESEM/EDX, Make-Zeiss, Germany).

**Powder X-Ray Diffraction Study:** Powder XRD was carried out using X-Ray diffractometer (Model-Smartlab, Make-Rigaku, Japan).

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<sup>1</sup> W. L. F. Armarego, C. Chai. *Purification of Laboratory Chemicals*; 7th ed. Butterworth-Heinemann: Oxford, 2012.

## 2. Preparation of Starting Materials:

**2.1 General procedure for  $\alpha$ -bromination of ketones (GP-1):**<sup>2</sup> Ketones (5.0 mmol.) was dissolved in dry  $\text{CH}_2\text{Cl}_2$  (10 mL) and the solution was cooled to 0 °C. Bromine (5.0 mmol.) was then added dropwise to the solution under vigorous stirring. After complete addition, the dark reaction mixture was stirred for 3-4 h at room temperature (dark red solution turned into light yellow). After completion of the reaction (as confirmed by TLC), the mixture was quenched with saturated  $\text{Na}_2\text{S}_2\text{O}_3$  (5 mL) solution and was extracted with  $\text{CH}_2\text{Cl}_2$  (10 mL  $\times$  3). Then the combined organic layer was washed with brine solution, dried over  $\text{Na}_2\text{SO}_4$  and concentrated under reduced pressure. The residue was further purified by silica gel column chromatography to give the corresponding  $\alpha$ -bromoketone.

### Preparation of substrates 2o:

Following the general procedure for bromination (GP-1), **2o** was synthesized using 4-Chlorophenacyl cyclopropyl ketone (900 mg, 5 mmol).

#### 2,4-Dibromo-1-(4-chlorophenyl)butan-1-one (2t):

<sup>3</sup>

**Yield:** 70% (1.18 g).

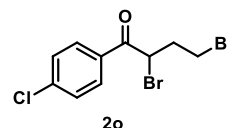
**Nature:** white solid

**Mp:** 80 – 83 °C

**R<sub>f</sub> value** = 0.5 [EtOAc:Petroleum ether = 1:19 (v/v)].

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm):** 7.98 (d,  $J$  = 8.7 Hz, 2H), 7.48 (d,  $J$  = 8.7 Hz, 2H), 5.41 (dd,  $J$  = 8.1, 5.7 Hz, 1H), 3.70 – 3.59 (m, 2H), 2.63 (tt,  $J$  = 7.8, 5.4 Hz, 2H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm):** 191.4, 140.7, 132.4, 130.5, 129.4, 44.8, 35.6, 30.9



### 2.2 General procedure for preparation of alkenes:

**General Procedure (GP-A):** 4-Vinylbenzyl chloride (1.2 mmol) was added to the suspension of respective alcohol/acid (1.0 mmol) and  $\text{K}_2\text{CO}_3$  (1.5 mmol) in 10 mL DMF solvent at room temperature. Then the resulting mixture was allowed to be stirred for 10-12h at room temperature. After completion of the reaction (checked by TLC), 10 mL water was added to the reaction mixture and the whole organic layer was extracted with EtOAc (10 mL $\times$ 3), washed with Brine solution and dried over  $\text{MgSO}_4$ . The residue was concentrated under vacuo and purified by column chromatography.

#### (8S,9R,13R,14R)-13-Methyl-3-((4-vinylbenzyl)oxy)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (1u):

<sup>4</sup>

<sup>2</sup> M. Günther, J. Lategahn, M. Juchum, E. Döring, M. Keul, J. Engel, H. L. Tumbrink, D. Rauh, S. Laufer, *J. Med. Chem.* **2017**, *60*, 5613–5637.

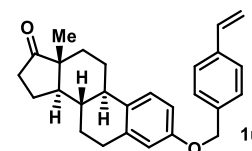
<sup>3</sup> M. Takahashi, N. Takeshi, K. Myojoh, H. Sano, T. Morisawa, *J. Heterocyclic Chem.* **1983**, *20*, 209.

<sup>4</sup> Y. Chen, Y. Ma, L. Li, H. Jiang, Z. Li, *Org. Lett.* **2019**, *21*, 1480–1483.

**Yield:** 58% (226 mg)

**Nature:** white solid.

**R<sub>f</sub> value** = 0.4 [EtOAc:Petroleum ether = 1:9 (v/v)].



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 7.44 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 8.6 Hz, 1H), 6.83 – 6.69 (m, 3H), 5.77 (d, *J* = 17.6 Hz, 1H), 5.27 (d, *J* = 10.9 Hz, 1H), 5.03 (s, 2H), 2.91 (dd, *J* = 11.1, 4.5 Hz, 2H), 2.52 (dd, *J* = 18.8, 8.5 Hz, 1H), 2.40 (dt, *J* = 8.4, 3.4 Hz, 1H), 2.25 (dd, *J* = 13.7, 7.2 Hz, 1H), 2.19 – 1.93 (m, 4H), 1.68 – 1.42 (m, 6H), 0.92 (s, 3H).

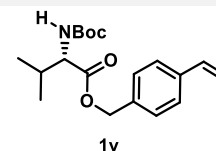
**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 221.1, 156.9, 137.9, 137.3, 136.9, 136.5, 132.4, 127.7, 126.5, 115.0, 114.1, 112.4, 69.7, 50.5, 48.1, 44.1, 38.4, 36.0, 31.6, 29.7, 26.6, 26.0, 21.7, 13.9.

#### 4-Vinylbenzyl (*tert*-butoxycarbonyl)-L-valinate (1v):<sup>5</sup>

**Yield:** 62% (207 mg)

**Nature:** colourless oil.

**R<sub>f</sub> value** = 0.3 [EtOAc:Petroleum ether = 1:9 (v/v)].



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 7.39 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 1H), 6.70 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.75 (d, *J* = 17.6 Hz, 1H), 5.26 (d, *J* = 10.9 Hz, 1H), 5.11 (m, 3H), 4.27 (dd, *J* = 9.1, 4.6 Hz, 1H), 2.13 (dt, *J* = 13.3, 6.7 Hz, 1H), 1.44 (s, 9H), 0.93 (d, *J* = 6.9 Hz, 3H), 0.84 (d, *J* = 6.9 Hz, 3H).

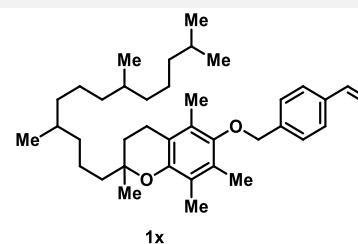
**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 172.4, 155.8, 137.8, 136.4, 135.0, 128.7, 126.5, 114.5, 79.8, 77.5, 66.7, 58.6, 31.4., 28.4, 19.1, 17.6.

#### 2,5,7,8-Tetramethyl-2-(4,8,12-trimethyltridecyl)-6-((4-vinylbenzyl)oxy)chromane (1x):<sup>6</sup>

**Yield:** 55% (302 mg)

**Nature:** gummy liquid.

**R<sub>f</sub> value** = 0.4 [EtOAc:Petroleum ether = 1:9 (v/v)].



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 7.58 – 7.44 (m, 4H), 6.79 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.82 (dd, *J* = 17.6, 0.7 Hz, 1H), 5.30 (dd, *J* = 10.9, 0.7 Hz, 1H), 4.73 (s, 2H), 2.64 (t, *J* = 6.7 Hz, 2H), 2.27 (s, 3H), 2.22 (s, 3H), 2.16 (s, 3H), 1.84 (ddt, *J* = 20.0, 13.3, 6.6 Hz, 2H), 1.70 – 1.51 (m, 4H), 1.45 (td, *J* = 10.2, 5.1 Hz, 4H), 1.34 – 1.24 (m, 9H), 1.23 – 1.02 (m, 7H), 0.92 (dd, *J* = 9.0, 5.6 Hz, 12H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 148.2, 148.0, 137.8, 137.2, 136.7, 128.1, 128.0, 126.4, 126.1, 123.1, 117.7, 114.0, 75.0, 74.6, 40.2, 40.1, 39.5, 37.8, 37.7, 37.6, 37.5, 37.4, 33.1, 33.0, 32.9, 32.8, 31.5, 31.4, 28.13, 25.0, 24.9, 24.6, 24.0, 22.9, 22.8, 21.2, 20.8, 19.9, 19.8, 19.8, 19.7, 13.0, 12.2, 12.1

<sup>5</sup> K. Matsubara, A. Kurimaru, M. Yamanaka, T. Hirashima, Y. Onishi, E. Murakami, E.; Kawachi, Y. Koga, S. Ando, *J Polym Sci Part A: Polym Chem.* **2010**, *48*, 5593–5602.

<sup>6</sup> Y. Chen, L. Li, X. He, Z. Li, *ACS Catal.* **2019**, *9*, 9098–9102.



**General Procedure (GP-B):** In a 50 mL round bottom flask equipped with stir bar was charged with corresponding acid (5 mmol, 1 equiv.), followed by alcohols (6 mmol, 1.2 equiv), 4-dimethylaminopyridine (31 mg, 0.25 mmol, 0.05 equiv.) and DCM (20 mL). Then the flask was sealed with septum and placed in N<sub>2</sub> atmosphere. DCC (6 mmol, 1.4 equiv. ) was added to the reaction mixture *via* syringe at once and stirred for overnight. After completion the reaction, the reaction mixture was filtered and the solid filtrate were rinsed with DCM (5mL×3). The combined filtrate were concentrated under vacuo and purified by column chromatography.

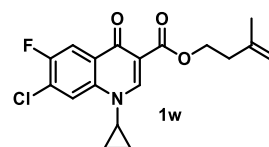
**3-Methylbut-3-en-1-yl 7-chloro-1-cyclopropyl-6-fluoro-4-oxo-1,4-dihydroquinoline-3-carboxylate (1w):**

**Yield:** 50% (436 mg)

**Nature:** white solid.

**Mp:** 180 - 183 °C

**R<sub>f</sub> value** = 0.4 [EtOAc:Petroleum ether = 4:6 (v/v)].



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 8.52 (s, 1H), 8.15 (dd, *J* = 9.0, 1.6 Hz, 1H), 7.98 (d, *J* = 5.9 Hz, 1H), 4.81 (d, *J* = 10.2 Hz, 2H), 4.40 (q, *J* = 6.7 Hz, 2H), 3.71 (q, *J* = 7.0 Hz, 1H), 3.45 (dt, *J* = 10.9, 3.6 Hz, 1H), 2.48 (t, *J* = 7.0 Hz, 2H), 1.80 (s, 3H), 1.36 (d, *J* = 6.5 Hz, 2H), 1.22 (d, *J* = 7.1 Hz, 1H), 1.14 (dd, *J* = 3.6, 1.9 Hz, 2H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 172.9, 164.9, 157.0(d, *J* = 251.2 Hz), 154.5, 148.9, 142.1, 137.3, 128.7, 127.0 (d, *J* = 20.2 Hz), 119.04, 114.1, 113.9 (d, *J* = 25.3 Hz), 112.4, 110.7, 63.3, 36.9, 34.9, 22.7, 8.3.

**{<sup>19</sup>F} NMR (377 MHz, CDCl<sub>3</sub>) δ (ppm):** -118.0

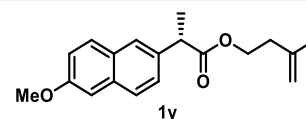
**HRMS (ESI) *m/z*** calcd for C<sub>18</sub>H<sub>18</sub>ClFNO<sub>3</sub> [M+H]<sup>+</sup>: 350.0959; found: 350.0959.

**3-Methylbut-3-en-1-yl (S)-2-(6-methoxynaphthalen-2-yl)propanoate (1y):**

**Yield:** 70% (500 mg)

**Nature:** gummy liquid.

**R<sub>f</sub> value** = 0.4 [EtOAc:Petroleum ether = 1:9 (v/v)].



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 7.71 (dd, *J* = 10.8, 5.0 Hz, 3H), 7.44 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.19 – 7.12 (m, 2H), 4.75 (s, 1H), 4.67 (s, 1H), 4.27 – 4.17 (m, 2H), 3.91 (s, 3H), 3.86 (dd, *J* = 8.1, 6.2 Hz, 1H), 2.31 (t, *J* = 6.8 Hz, 2H), 1.70 (s, 3H), 1.60 (d, *J* = 7.2 Hz, 3H).

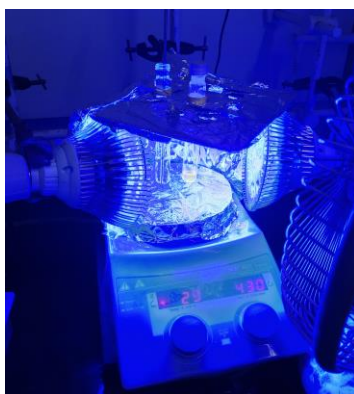
**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 174.7, 157.7, 141.6, 135.8, 133.7, 129.3, 129.0, 127.1, 126.4, 126.0, 119.0, 112.4, 105.6, 63.0, 55.3, 45.5, 36.7, 22.4, 18.6.

**HRMS (ESI) *m/z*** calcd for C<sub>19</sub>H<sub>23</sub>O<sub>3</sub> [M+H]<sup>+</sup>: 299.1647; found: 299.1635.

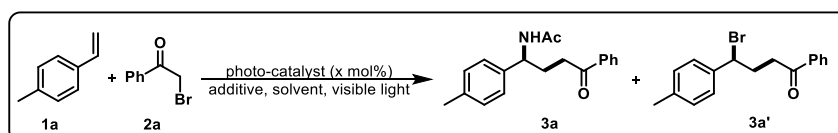
### 3. Reaction Optimization:

#### General procedure for optimization of reaction conditions:

In a flame dried culture tube equipped with a magnetic stirring bar was charged with photocatalyst (2 mol %), phenacyl bromide **2a** (40 mg, 0.2 mmol), additive (x mmol) and dry acetonitrile (1 mL), then the tube was sealed with a Teflon screw cap, evacuated and backfilled with argon. 4-Methylstyrene **1a** (40  $\mu$ L, 0.3 mmol), H<sub>2</sub>O (4  $\mu$ L, 1 equiv.) was added *via* a syringe under argon atmosphere. Afterwards, the reaction mixture was degassed by Freeze-Pump-Thaw cycles two times with argon *via* syringe needle and irradiated at room temperature with 12 W blue LED bulb at a distance of approximately 5 cm and simultaneously cooled by a fan to maintain the reaction at RT.



#### Optimized reaction conditions:



**Table S1.** Different photocatalyst screening

Entry	PC	Yield <b>3a</b> (%)	Yield <b>3a'</b> (%) <sup>[a]</sup>
1	Ru(bpy) <sub>3</sub> .Cl <sub>2</sub>	0	7
2	<i>fac</i> -Ir(ppy) <sub>3</sub>	16	31
3	Eosin Y	0	0
4	Acr <sup>+</sup> -Mes ClO <sub>4</sub> <sup>-</sup>	0	0
<b>5</b>	<b>4CzIPN</b>	<b>18</b>	<b>35</b>

<sup>[a]</sup> NMR Yield using 1,1,2,2-tetrachloroethane as internal standard

In a flame dried culture tube equipped with a magnetic stirring bar was charged with 4CzIPN (3 mg, 2 mol %), phenacyl bromide **2a** (40 mg, 0.2 mmol), additive (1.0 equiv.) and dry acetonitrile (1 mL), then the tube was sealed with a Teflon screw cap, evacuated and backfilled with argon. 4-Methylstyrene **1a** (40  $\mu$ L, 0.3 mmol), H<sub>2</sub>O (4  $\mu$ L, 1 equiv.) was added *via* a syringe under argon atmosphere. Afterwards, the reaction mixture was degassed by Freeze-Pump-Thaw cycles two times with argon *via* syringe needle and irradiated at room

temperature with 12 W blue LED bulb at a distance of approximately 5 cm and simultaneously cooled by fan to maintain the reaction at RT.

**Table S2.** Additive screening

Entry	Additive (1 equiv.)	Yield 3a (%)	Yield 3a' (%) <sup>[a]</sup>
1	Na <sub>2</sub> CO <sub>3</sub>	18	0
2	KH <sub>2</sub> PO <sub>4</sub>	18	5
3	Ag <sub>2</sub> CO <sub>3</sub>	32	trace
4	BF <sub>3</sub> .OEt	38	12
5	FeCl <sub>3</sub>	30	22
6	ZnCl <sub>2</sub>	50	trace
7	Zn(OTf) <sub>2</sub>	12	0
<b>8</b>	<b>Zn(OAc)<sub>2</sub>.H<sub>2</sub>O</b>	<b>58</b>	<b>0</b>
9	Zn dust	42	trace

<sup>[a]</sup> NMR Yield using 1,1,2,2-tetrachloroethane as internal standard.

**Table S3.** Loading amount of additive

Entry	additive (x equiv.)	Yield 3a (%)	Yield 3a' (%)
<b>1</b>	<b>0.5</b>	<b>58</b>	<b>0</b>
2	2.0	57	0

A flame dried culture tube equipped with a magnetic stirring bar was charged with photocatalyst (3 mg, 2 mol %), phenacyl bromide **2a** (40 mg, 0.2 mmol), Zn(OAc)<sub>2</sub> (21 mg, 0.1 mmol.) and dry acetonitrile (1 mL), then the tube was sealed with a Teflon screw cap, evacuated and backfilled with argon. 4-Methylstyrene **1a** (40 μL, 0.3 mmol), H<sub>2</sub>O (4 μL, 1.0 equiv.) and acid (1.0 equiv.) were added *via* syringe under argon atmosphere. Afterwards, the reaction mixture was degassed by Freeze-Pump-Thaw cycles two times with argon *via* syringe needle and irradiated at room temperature with 12 W blue LED bulb at a distance of approximately 5 cm and simultaneously cooled by fan to maintain the reaction at RT.

**Table S4.** Acid screening

Entry	Acid (1 equiv.)	Yield 3a (%)	Yield 3a' (%)
1	CH <sub>3</sub> COOH	66	0
2	H <sub>2</sub> SO <sub>4</sub>	69	0
3	HPF <sub>6</sub>	64	0
4	TsOH	60	0
5	H <sub>3</sub> PO <sub>4</sub>	67	0
<b>6</b>	<b>CF<sub>3</sub>COOH</b>	<b>70</b>	<b>0</b>

**Table S5.** Loading amount of acid.

Entry	Acid (x equiv.)	Yield 3a (%)	Yield 3a' (%)
1	1	70	0
2	3	72	0
<b>3</b>	<b>5</b>	<b>74</b>	<b>0</b>
4	10	70	0

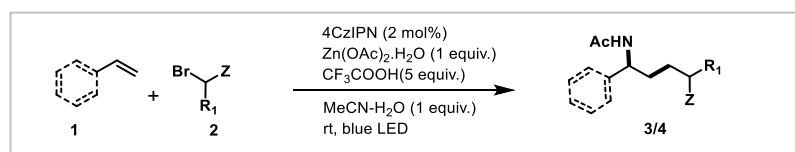
In a flame dried culture tube equipped with a magnetic stirring bar was charged with 4CzIPN (3 mg, 2 mol %), phenacyl bromide **2a** (40 mg, 0.2 mmol), Zinc acetate (21 mg, 0.1 mmol) and dry acetonitrile (1 mL), the tube was sealed with a Teflon screw cap, evacuated and backfilled with argon. 4-Methylstyrene **1a** (40  $\mu$ L, 0.3 mmol), H<sub>2</sub>O (4  $\mu$ L, 1 equiv.) and CF<sub>3</sub>COOH (5 equiv.) were added *via* syringe under argon atmosphere. Afterwards, the reaction mixture was degassed by Freeze-Pump-Thaw cycles two times with argon *via* syringe needle and irradiated at room temperature with 12 W blue LED bulb at a distance of approximately 5 cm and simultaneously cooled by fan to maintain the reaction at RT.

**Table S6.** Control reaction conditions

Entry	PC	additive	acid	Light	Air	Yield of 3a (%)
1	✓	✓	✓	✓	✗	74
2	✓	✗	✗	✓	✗	18
3	✗	✓	✓	✓	✗	0
4	✓	✓	✓	✗	✗	0
5	✓	✓	✓	✓	✓	60

## 4. Experimental procedures

### 4.1 General Procedure for Photoredox carboamination of alkenes:



In a flame dried culture tube equipped with a magnetic stirring bar was charged with 4CzIPN (3 mg, 2 mol %), alkyl bromide **2** (0.2 mmol, 1 equiv.), Zinc acetate (21 mg, 0.1 mmol) and dry acetonitrile (1 mL), then the tube was sealed with a Teflon screw cap, evacuated and backfilled with argon. alkene **1** (0.3 mmol, 1.5 equiv.), H<sub>2</sub>O (4  $\mu$ L, 1 equiv.) and CF<sub>3</sub>COOH (80  $\mu$ L, 5 equiv.) were added *via* syringe under argon atmosphere. Afterwards, the reaction mixture was degassed by Freeze-Pump-Thaw cycles two times with argon *via* syringe needle and irradiated at room temperature with 12 W blue LED bulb at a distance of approximately 5 cm and simultaneously cooled by fan to maintain the reaction at RT. After 6 h, completion

the reaction (checked by TLC), the reaction mixture was poured into 2 mL Saturated NaHCO<sub>3</sub> solution and extracted with EtOAc (5 mL × 2). The combined organic layer was washed with brine solution, dried over MgSO<sub>4</sub> and concentrated under reduced pressure. Finally, the crude residue was purified by flash column chromatography on silica gel 230-400 mesh (EtOAc:Petroleum ether = 40:60 – 80:20) to get the corresponding aminoalkylation product **3/4**.

#### 4.2 Compound characterization data:

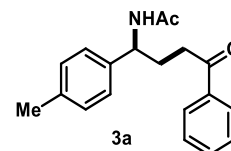
##### ***N*-(4-Oxo-4-phenyl-1-(*p*-tolyl)butyl)acetamide: (3a)**

**Yield:** 74% (44 mg).

**Nature:** white solid.

**Mp:** 165-168 °C

**R<sub>f</sub> value** = 0.3 [EtOAc:Petroleum ether = 4:6 (v/v)].



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 7.91 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.59 – 7.53 (m, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 6.06 (d, *J* = 8.2 Hz, 1H), 5.02 (td, *J* = 8.5, 6.4 Hz, 1H), 3.09 (ddd, *J* = 17.9, 7.8, 6.5 Hz, 1H), 2.97 (ddd, *J* = 17.9, 7.8, 6.2 Hz, 1H), 2.39 – 2.33 (m, 1H), 2.33 – 2.30 (m, 3H), 2.21 – 2.14 (m, 1H), 1.92 (s, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 200.3, 169.6, 138.9, 137.4, 136.8, 133.4, 129.6, 128.7, 128.2, 126.6, 53.3, 35.8, 30.0, 23.6, 21.2.

**HRMS (ESI) *m/z*** calcd for C<sub>19</sub>H<sub>21</sub>NO<sub>2</sub>K [M+K]<sup>+</sup>: 334.1209; found: 334.1210.

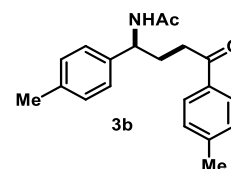
##### ***N*-(4-Oxo-4-phenyl-1-(*p*-tolyl)butyl)acetamide: (3b)**

**Yield:** 81% (50 mg).

**Nature:** white solid.

**Mp:** 180 - 183 °C

**R<sub>f</sub> value** = 0.3 [EtOAc:Petroleum ether = 6:4 (v/v)].



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 7.81(d, 2H), 7.25 – 7.18 (m, 4H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.29 (d, *J* = 8.2 Hz, 1H), 5.01 (dt, *J* = 8.4, 4.2 Hz, 1H), 3.05 (ddd, *J* = 17.8, 7.9, 6.5 Hz, 1H), 2.94 (ddd, *J* = 17.8, 7.9, 6.2 Hz, 1H), 2.39 (s, 3H), 2.32 (s, 3H), 2.31 – 2.25 (m, 1H), 2.19 – 2.11 (m, 1H), 1.90 (s, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 200.0, 169.6, 144.2, 139.1, 137.2, 134.3, 129.5, 129.4, 128.2, 126.6, 53.2, 35.6, 30.1, 23.5, 21.7, 21.2.

**HRMS (ESI) *m/z*** calcd for C<sub>20</sub>H<sub>23</sub>NO<sub>2</sub>Na [M+Na]<sup>+</sup>: 332.1626; found:332.1597.

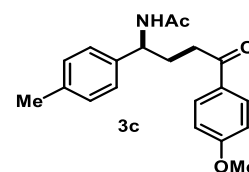
##### ***N*-(4-(4-Methoxyphenyl)-4-oxo-1-(*p*-tolyl)butyl)acetamide: (3c)**

**Yield:** 60% (39 mg).

**Nature:** white solid.

**Mp:** 168 – 171 °C

**R<sub>f</sub> value** = 0.1 [EtOAc:Petroleum ether = 1:1 (v/v)].



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 7.90 (d, *J* = 8.9 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 6.16 (d, *J* = 8.2 Hz, 1H), 5.01 (td, *J* = 8.5, 6.3 Hz, 1H), 3.86 (s, 3H), 3.10 – 3.00 (m, 1H), 2.96 – 2.86 (m, 1H), 2.32 (s, 3H), 2.31 – 2.23 (m, 1H), 2.15 (dd, *J* = 14.0, 7.7 Hz, 1H), 1.91 (s, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 198.9, 169.6, 163.7, 139.1, 137.3, 130.5, 129.9, 129.5, 126.6, 113.9, 55.6, 53.4, 35.4, 30.1, 23.6, 21.2.

**HRMS (ESI) *m/z* calcd for C<sub>20</sub>H<sub>24</sub>NO<sub>3</sub> [M+H]<sup>+</sup>:** 326.1756; found: 326.1758.

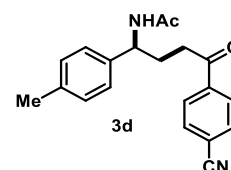
#### ***N*-4-(4-Cyanophenyl)-4-oxo-1-(*p*-tolyl)butylacetamide: (3d)**

**Yield:** 85% (54 mg).

**Nature:** white solid.

**Mp:** 185-188 °C

**R<sub>f</sub> value** = 0.2 [EtOAc:Petroleum ether = 1:1 (v/v)].



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 7.98 (d, *J* = 8.6 Hz, 2H), 7.74 (d, *J* = 8.6 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 5.95 (d, *J* = 8.3 Hz, 1H), 5.02 (dd, *J* = 15.0, 8.4 Hz, 1H), 3.07 (ddd, *J* = 18.1, 8.2, 6.2 Hz, 1H), 2.96 (ddd, *J* = 18.1, 8.1, 6.1 Hz, 1H), 2.33 (s, 3H), 2.30 (dd, *J* = 8.3, 6.2 Hz, 1H), 2.24 – 2.16 (m, 1H), 1.92 (s, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 198.6, 169.6, 139.7, 138.5, 137.7, 132.6, 129.7, 128.5, 126.6, 118.0, 116.5, 53.0, 36.1, 29.9, 23.6, 21.2.

**HRMS (ESI) *m/z* calcd for C<sub>20</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>Na [M+Na]<sup>+</sup>:** 343.1422; found: 343.1407.

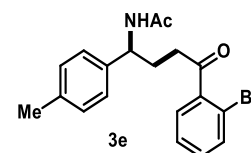
#### ***N*-4-(2-Bromophenyl)-4-oxo-1-(*p*-tolyl)butylacetamide: (3e)**

**Yield:** 74% (55 mg).

**Nature:** white solid.

**Mp:** 150 - 153 °C

**R<sub>f</sub> value** = 0.3 [EtOAc:Petroleum ether = 1:1 (v/v)].



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 7.57 (dd, *J* = 8.3, 0.6 Hz, 1H), 7.34 – 7.30 (m, 2H), 7.27 (ddd, *J* = 7.9, 6.1, 3.1 Hz, 1H), 7.22 – 7.17 (m, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.28 (d, *J* = 8.4 Hz, 1H), 4.99 (td, *J* = 8.5, 6.5 Hz, 1H), 2.99 (ddd, *J* = 18.3, 8.1, 6.3 Hz, 1H), 2.90 (ddd, *J* = 18.3, 7.9, 6.3 Hz, 1H), 2.31 (s, 3H), 2.30 – 2.23 (m, 1H), 2.19 – 2.12 (m, 1H), 1.93 (s, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 203.9, 169.4, 141.3, 138.6, 137.2, 133.6, 131.6, 129.3, 128.2, 127.4, 126.4, 118.4, 52.8, 39.7, 29.7, 23.3, 21.0.

**HRMS (ESI) *m/z* calcd for C<sub>19</sub>H<sub>21</sub>NO<sub>2</sub>Br [M+H]<sup>+</sup>:** 374.0756; found: 374.0749.

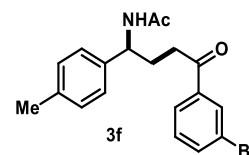
#### ***N*-4-(3-Bromophenyl)-4-oxo-1-(*p*-tolyl)butylacetamide: (3f)**

**Yield:** 70% (52 mg).

**Nature:** white solid.

**Mp:** 145-148 °C

**R<sub>f</sub> value** = 0.3 [EtOAc:Petroleum ether = 1:1 (v/v)].



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 8.02 (s, 1H), 7.83 – 7.79 (m, 1H), 7.67 (ddd, *J* = 7.9, 1.9, 1.0 Hz, 1H), 7.32 (t, *J* = 7.9 Hz, 1H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 5.98 (d, *J* = 8.3 Hz, 1H), 5.02 (dd, *J* = 14.9, 8.4 Hz, 1H), 3.07 – 2.99 (m, 1H), 2.97 – 2.90 (m, 1H), 2.33 (s, 3H), 2.32 – 2.26 (m, 1H), 2.21 – 2.14 (m, 1H), 1.93 (s, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 198.9, 169.7, 138.8, 138.6, 137.7, 136.3, 131.3, 130.5, 129.8, 126.8, 126.7, 123.2, 53.2, 36.0, 30.0, 23.7, 21.3.

**HRMS (ESI) *m/z*** calcd for C<sub>19</sub>H<sub>21</sub>NO<sub>2</sub>Br [M+H]<sup>+</sup>: 374.0756; found: 374.0748.

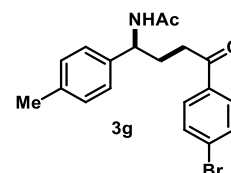
#### ***N*-(4-(4-Bromophenyl)-4-oxo-1-(*p*-tolyl)butyl)acetamide: (3g)**

**Yield:** 76% (57 mg).

**Nature:** white solid.

**Mp:** 198 - 200 °C

**R<sub>f</sub> value** = 0.2 [EtOAc:Petroleum ether = 1:1 (v/v)].



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 7.77 (d, *J* = 8.6 Hz, 2H), 7.58 (d, *J* = 8.6 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 5.96 (d, *J* = 8.2 Hz, 1H), 5.02 (dd, *J* = 14.9, 8.5 Hz, 1H), 3.04 (ddd, *J* = 17.9, 8.0, 6.4 Hz, 1H), 2.92 (ddd, *J* = 17.9, 8.0, 6.2 Hz, 1H), 2.33 (s, 3H), 2.33 – 2.28 (m, 1H), 2.20 – 2.13 (m, 1H), 1.92 (s, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 199.2, 169.5, 138.7, 137.6, 135.5, 132.1, 129.7, 129.7, 128.5, 126.6, 53.2, 35.7, 29.9, 23.6, 21.2.

**HRMS (ESI) *m/z*** calcd for C<sub>19</sub>H<sub>21</sub>BrNO<sub>2</sub> [M+H]<sup>+</sup>: 374.0756; found: 374.0740.

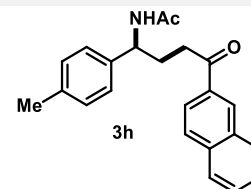
#### ***N*-(4-(Naphthalen-2-yl)-4-oxo-1-(*p*-tolyl)butyl)acetamide: (3h)**

**Yield:** 58% (40 mg).

**Nature:** white solid.

**Mp:** 209-212 °C

**R<sub>f</sub> value** = 0.3 [EtOAc:Petroleum ether = 1:1 (v/v)].



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 8.42 (s, 1H), 8.01 – 7.94 (m, 2H), 7.87 (dd, *J* = 8.3, 4.4 Hz, 2H), 7.62 – 7.53 (m, 2H), 7.25 (d, *J* = 7.3 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.10 (d, *J* = 8.2 Hz, 1H), 5.08 (dt, *J* = 14.8, 7.5 Hz, 1H), 3.27 – 3.19 (m, 1H), 3.15 – 3.07 (m, 1H), 2.43 – 2.37 (m, 1H), 2.33 (s, 3H), 2.27 – 2.22 (m, 1H), 1.93 (s, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 200.3, 169.6, 139.0, 137.4, 135.8, 134.1, 132.6, 129.9, 129.7, 129.6, 128.7, 128.6, 127.9, 127.0, 126.6, 123.9, 53.3, 35.8, 30.1, 23.6, 21.2.

**HRMS** (ESI)  $m/z$  calcd for  $C_{23}H_{24}NO_2$   $[M+H]^+$ : 346.1807; found: 346.1801.

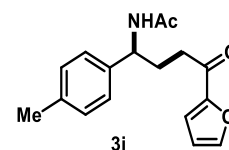
***N*-4-(Furan-2-yl)-4-oxo-1-(*p*-tolyl)butylacetamide: (3i)**

**Yield:** 72% (42 mg).

**Nature:** white solid.

**Mp:** 90 – 93 °C

**R<sub>f</sub> value** = 0.1 [EtOAc:Petroleum ether = 1:1 (v/v)].



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** δ 7.57 (dd,  $J$  = 1.6, 0.5 Hz, 1H), 7.20 (d,  $J$  = 8.1 Hz, 2H), 7.16 (dd,  $J$  = 3.5, 0.6 Hz, 1H), 7.13 (d,  $J$  = 8.1 Hz, 2H), 6.52 (dd,  $J$  = 3.6, 1.7 Hz, 1H), 6.15 (d,  $J$  = 8.3 Hz, 1H), 5.00 (dd,  $J$  = 8.5, 2.3 Hz, 1H), 2.98 – 2.90 (m, 1H), 2.86 – 2.80 (m, 1H), 2.32 (s, 3H), 2.30 – 2.25 (m, 1H), 2.15 (dd,  $J$  = 7.8, 6.3 Hz, 1H), 1.91 (s, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 189.3, 169.6, 152.5, 146.7, 138.8, 137.3, 129.5, 126.5, 117.6, 112.4, 53.1, 35.5, 29.8, 23.5, 21.2.

**HRMS** (ESI)  $m/z$  calcd for  $C_{17}H_{20}NO_3$   $[M+H]^+$ : 286.1443; found: 286.1438.

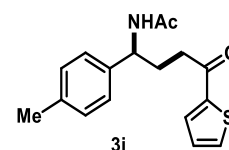
***N*-4-(Thiophene-2-yl)-4-oxo-1-(*p*-tolyl)butylacetamide: (3j)**

**Yield:** 70% (42 mg).

**Nature:** light yellow solid.

**Mp:** 172-175 °C

**R<sub>f</sub> value** = 0.2 [EtOAc:Petroleum ether = 1:1 (v/v)].



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 7.67 (dd,  $J$  = 3.8, 1.1 Hz, 1H), 7.63 (dd,  $J$  = 5.0, 1.1 Hz, 1H), 7.20 (d,  $J$  = 8.1 Hz, 2H), 7.14 (d,  $J$  = 8.1 Hz, 2H), 7.11 (dd,  $J$  = 4.9, 3.8 Hz, 1H), 6.17 (d,  $J$  = 8.3 Hz, 1H), 5.01 (td,  $J$  = 8.6, 6.2 Hz, 1H), 3.07 – 2.98 (m, 1H), 2.94 – 2.85 (m, 1H), 2.33 – 2.30 (m, 4H), 2.16 (ddd,  $J$  = 14.0, 6.4, 1.3 Hz, 1H), 1.90 (s, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 193.3, 169.6, 144.0, 138.8, 137.4, 134.0, 132.4, 129.6, 128.4, 126.6, 53.2, 36.4, 30.2, 23.5, 21.2.

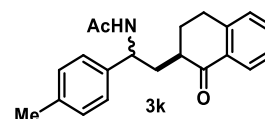
**HRMS** (ESI)  $m/z$  calcd for  $C_{17}H_{19}NO_2SNa$   $[M+Na]^+$ : 324.1034; found: 324.1028.

***N*-2-(1-Oxo-1,2,3,4-tetrahydronaphthalen-2-yl)-1-(*p*-tolyl)butylacetamide: (3k)**

**Yield:** 60% (39 mg).

**Nature:** gummy colourless oil.

**R<sub>f</sub> value** = 0.3 [EtOAc:Petroleum ether = 1:1 (v/v)].





**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** (for diastereomeric mixing) 8.08 – 7.97 (m, 1H), 7.50 – 7.43 (m, 1H), 7.31 (t, *J* = 7.8 Hz, 1H), 7.27 – 7.24 (m, 2H), 7.21 (d, *J* = 7.9 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.57 (dd, *J* = 50.5, 8.0 Hz, 1H), 5.17 – 5.04 (m, 1H), 3.08 – 2.90 (m, 2H), 2.62 – 2.55 (m, 1H), 2.39 – 2.35 (m, 1H), 2.31 (d, *J* = 2.8 Hz, 3H), 2.24 – 2.15 (m, 1H), 1.96 – 1.66 (m, 5H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** (for diastereomeric mixing) 201.4, 201.0, 169.9, 169.3, 144.4, 144.2, 140.1, 138.6, 137.2, 137.1, 133.7, 133.6, 132.4, 129.5, 129.4, 128.9, 127.6, 127.5, 126.8, 126.7, 126.6, 126.4, 51.9, 51.0, 45.9, 45.1, 37.0, 35.4, 29.8, 29.1, 28.5, 23.5, 21.2.

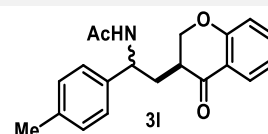
**HRMS (ESI) *m/z*** calcd for C<sub>21</sub>H<sub>24</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 322.1807; found: 322.1788.

### ***N*-(2-(4-Oxocroman-3-yl)-1-(*p*-tolyl)butyl)acetamide: (3l)**

**Yield:** 58% (38 mg).

**Nature:** low melting solid.

**R<sub>f</sub> value** = 0.2 [EtOAc:Petroleum ether = 1:1 (v/v)].



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** (for diastereomeric mixing) 7.90 -7.86 (m, 1H), 7.50 – 7.44 (m, 1H), 7.21 (dd, *J* = 12.3, 8.1 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.04 – 6.91 (m, 2H), 6.53 (dd, *J* = 72.2, 7.9 Hz, 1H), 5.12 – 5.08 (m, 1H), 4.59 - 4.44 (m, 1H), 4.36 – 4.18 (m, 1H), 2.88 – 2.59 (m, 1H), 2.41 – 2.33 (m, 1H), 2.32 (d, *J* = 2.5 Hz, 3H), 1.97 (d, *J* = 1.1 Hz, 3H), 1.75 – 1.68 (m, 1H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** (for diastereomeric mixing) 195.34, 195.1, 170.0, 169.4, 161.9, 161.8, 139.3, 137.7, 137.6, 137.5, 136.4, 136.3, 129.6, 129.7, 127.6, 127.5, 126.6, 126.5, 121.6, 120.6, 120.5, 118.0, 117.9, 70.5, 70.2, 51.4, 51.0, 43.7, 42.8, 32.8, 31.5, 23.6, 23.5, 21.18.

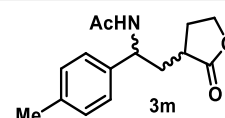
**HRMS (ESI) *m/z*** calcd for C<sub>20</sub>H<sub>22</sub>NO<sub>3</sub> [M+H]<sup>+</sup>: 324.1600; found: 324.1582.

### ***N*-(2-(2-Oxotetrahydrofuran-3-yl)-1-(*p*-tolyl)ethyl)acetamide: (3m)**

**Yield:** 62% (32 mg).

**Nature:** colourless oil.

**R<sub>f</sub> value** = 0.1 [EtOAc: Petroleum ether = 1:1 (v/v)].



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** (for diastereomeric mixing) 7.21 – 7.17 (m, 4H), 7.14 (dd, *J* = 7.9, 5.7 Hz, 4H), 6.54 (d, *J* = 8.2 Hz, 1H), 6.40 (d, *J* = 8.6 Hz, 1H), 5.11 – 5.01 (m, 2H), 4.36 (m, 2H), 4.23 – 4.16 (m, 1H), 4.14 – 4.08 (m, 1H), 2.69 – 2.55 (m, 2H), 2.36 (ddd, *J* = 8.6, 4.7, 2.5 Hz, 2H), 2.32 (d, *J* = 2.0 Hz, 6H), 2.32 – 2.27 (m, 2H), 2.16 – 2.02 (m, 3H), 1.98 (d, *J* = 4.1 Hz, 3H), 1.96 (s, 3H), 1.81 – 1.75 (m, 1H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** (for diastereomeric mixing) 180.2, 180.1, 170.2, 169.5, 138.9, 137.8, 137.6, 137.4, 129.8, 129.6, 126.7, 126.4, 67.1, 67.0, 51.5, 51.3, 37.6, 37.3, 36.9, 35.8, 29.7, 28.2, 23.5, 23.4, 21.2.

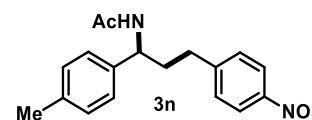
**HRMS (ESI) *m/z*** calcd for C<sub>15</sub>H<sub>19</sub>NNaO<sub>3</sub> [M+Na]<sup>+</sup>: 284.1263; found: 284.1265.

### ***N*-(3-(4-Nitrophenyl)-1-(*p*-tolyl)propyl)acetamide: (3n)**

**Yield:** 75% (47 mg).

**Nature:** yellow oil.

**R<sub>f</sub> value** = 0.2 [EtOAc:Petroleum ether = 1:1 (v/v)].



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 8.09 (d, *J* = 8.5 Hz, 2H), 7.31 – 7.25 (m, 2H), 7.16 (q, *J* = 8.3 Hz, 4H), 6.09 (d, *J* = 8.1 Hz, 1H), 4.94 (q, *J* = 7.6 Hz, 1H), 2.73 – 2.59 (m, 2H), 2.32 (s, 3H), 2.21 (ddd, *J* = 16.7, 8.3, 5.4 Hz, 1H), 2.06 (ddd, *J* = 11.9, 6.8, 3.1 Hz, 1H), 1.95 (s, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 169.5, 149.5, 146.4, 138.3, 137.7, 129.7, 129.3, 126.7, 123.7, 53.0, 37.1, 32.6, 23.5, 21.2.

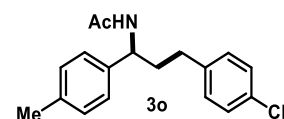
**HRMS (ESI) *m/z*** calcd for C<sub>18</sub>H<sub>20</sub>N<sub>2</sub>NaO<sub>3</sub> [*M*+Na] 335.1372; found: 335.1365.

### ***N*-(3-(4-Cyanophenyl)-1-(*p*-tolyl)propyl)acetamide: (3o)**

**Yield:** 60% (35 mg).

**Nature:** Colourless oil.

**R<sub>f</sub> value** = 0.1 [EtOAc:Petroleum ether = 1:1 (v/v)].



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 7.49 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 7.17 – 7.08 (m, 4H), 6.47 (d, *J* = 8.3 Hz, 1H), 4.92 (q, *J* = 7.6 Hz, 1H), 2.69 – 2.53 (m, 2H), 2.31 (s, 3H), 2.20 – 2.11 (m, 1H), 2.06 – 1.98 (m, 1H), 1.93 (s, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 169.5, 147.3, 138.5, 137.3, 132.2, 129.5, 129.2, 126.6, 119.1, 109.6, 52.9, 37.1, 32.8, 23.3, 21.1.

**HRMS (ESI) *m/z*** calcd for C<sub>19</sub>H<sub>21</sub>N<sub>2</sub>O [*M*+H]<sup>+</sup>: 293.1654; found: 293.1653.

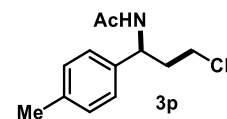
### ***N*-(3-Cyano-1-(*p*-tolyl)propyl)acetamide: (3p)<sup>7</sup>**

**Yield:** 55% (24 mg).

**Nature:** white solid.

**Mpt:** 121-123 °C

**R<sub>f</sub> value** = 0.1 [EtOAc: Petroleum ether = 1:1(v/v)].



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 7.26 – 7.13 (m, 4H), 5.81 (s, 1H), 4.99 (q, *J* = 7.4 Hz, 1H), 2.35 (d, *J* = 5.3 Hz, 3H), 2.31 (dt, *J* = 5.5, 3.1 Hz, 2H), 2.28 – 2.21 (m, 1H), 2.16 – 2.07 (m, 1H), 2.00 (d, *J* = 3.8 Hz, 3H)

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 169.8, 138.3, 136.9, 130.0, 126.6, 119.5, 52.7, 31.7, 23.5, 21.2, 14.6.

<sup>7</sup> N. Zhu, T. Wang, L. Ge, Y. Li, X. Zang, H. Bao, *Org. Lett.* **2017**, *19*, 4718.

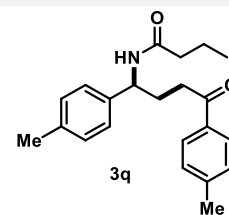
***N*-(4-Oxo-1,4-di-*p*-tolylbutyl)butyramide: (3q)**

**Yield:** 70% (47 mg).

**Nature:** white solid.

**Mp:** 154-156 °C

**R<sub>f</sub> value** = 0.2 [EtOAc:Petroleum ether = 1:1 (v/v)].



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 7.82 (d, *J* = 8.2 Hz, 2H), 7.23 (dd, *J* = 14.9, 6.8 Hz, 4H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.03 (d, *J* = 8.1 Hz, 1H), 5.00 – 5.06 (m, 1H), 3.09 – 2.91 (m, 2H), 2.40 (s, 3H), 2.36 – 2.29 (m, 4H), 2.20 – 2.13 (m, 1H), 2.12 – 2.06 (m, 2H), 1.59 (dd, *J* = 14.9, 7.4 Hz, 2H), 0.87 (t, *J* = 7.4 Hz, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 200.0, 172.5, 144.2, 139.2, 137.3, 134.4, 129.6, 129.4, 128.3, 126.6, 53.2, 38.9, 35.7, 30.0, 21.8, 21.2, 19.2, 13.9.

**HRMS (ESI) *m/z*** calcd for C<sub>22</sub>H<sub>28</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 338.2120; found: 338.2119.

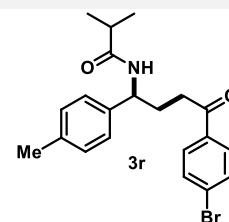
***N*-(4-(4-Bromophenyl)-4-oxo-1-(*p*-tolyl)butyl)isobutyramide: (3r)**

**Yield:** 72% (58 mg).

**Nature:** white solid.

**Mp:** 183 – 186 °C

**R<sub>f</sub> value** = 0.2 [EtOAc:Petroleum ether = 1:1 (v/v)].



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 7.77 (d, *J* = 8.6 Hz, 2H), 7.58 (d, *J* = 8.6 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 5.93 (d, *J* = 8.1 Hz, 1H), 5.01 (dt, *J* = 14.7, 7.4 Hz, 1H), 3.06 - 2.98 (m, 2H), 2.36 – 2.25 (m, 5H), 2.20 – 2.12 (m, 1H), 1.08 (dd, *J* = 6.9, 0.5 Hz, 6H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 199.2, 176.4, 139.0, 137.4, 135.5, 132.1, 129.7, 129.6, 128.6, 126.5, 52.9, 35.9, 35.8, 29.8, 21.2, 19.6, 19.7.

**HRMS (ESI) *m/z*** calcd for C<sub>21</sub>H<sub>25</sub>BrNO<sub>2</sub> [M+H]<sup>+</sup>: 402.1069; found: 402.1053.

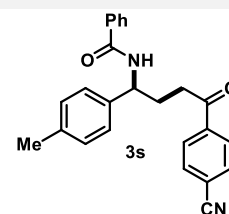
***N*-(4-(4-Bromophenyl)-4-oxo-1-(*p*-tolyl)butyl)benzamide: (3s)**

**Yield:** 60% (43 mg).

**Nature:** white solid.

**Mp:** 190-193 °C

**R<sub>f</sub> value** = 0.2 [EtOAc:Petroleum ether = 1:1 (v/v)].



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 8.09 – 7.89 (m, 2H), 7.79 – 7.65 (m, 4H), 7.50 – 7.45 (m, 1H), 7.42 – 7.37 (m, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 6.71 (d, *J* = 8.0 Hz, 1H), 5.24 (td, *J* = 8.5, 6.1 Hz, 1H), 3.22 – 2.99 (m, 2H), 2.47 (ddt, *J* = 14.0, 8.8, 6.9 Hz, 1H), 2.33 (s, 3H), 2.32 – 2.27 (m, 1H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 199.0, 166.9, 139.7, 138.6, 137.7, 134.2, 132.6, 131.7, 129.7, 128.6, 128.7, 127.0, 126.6, 118.0, 116.6, 53.6, 36.2, 29.8, 21.2.

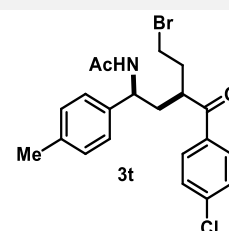
**HRMS (ESI) *m/z* calcd for C<sub>25</sub>H<sub>23</sub>N<sub>2</sub>O<sub>2</sub> [M+Na]<sup>+</sup>:** 383.1760; found: 383.1762.

#### ***N*-(5-Bromo-3-(4-chlorobenzoyl)-1-(*p*-tolyl)pentyl)acetamide: (3t)**

**Yield:** 50% (44 mg).

**Nature:** colourless gummy oil.

**R<sub>f</sub> value** = 0.3 [EtOAc:Petroleum ether = 1:1 (v/v)].



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** (for diastereomeric mixing) 7.76 (dd, *J* = 110.0, 8.6 Hz, 2H), 7.39 (dd, *J* = 47.6, 8.6 Hz, 2H), 7.19 – 7.08 (m, 4H), 6.13 (d, *J* = 156.9 Hz, 1H), 5.09 – 4.85 (m, 1H), 3.84 – 3.59 (m, 1H), 3.55 – 3.35 (m, 1H), 3.25 – 3.30 (m, 1H), 2.40 – 2.57 (m, 1H), 2.33 (d, *J* = 4.6 Hz, 3H), 2.20 – 2.26 (m, 1H), 2.12 – 2.03 (m, 2H), 1.96 (s, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** (for diastereomeric mixing) 201.1, 169.4, 140.4, 139.8, 138.7, 138.0, 137.8, 137.7, 134.6, 131.0, 130.0, 129.7, 129.6, 129.3, 129.0, 127.0, 126.5, 52.4, 52.2, 42.5, 41.4, 38.0, 37.9, 36.0, 34.4, 31.9, 30.9, 23.5, 23.2, 21.2.

**HRMS (ESI) *m/z* calcd for C<sub>21</sub>H<sub>24</sub>BrClNO<sub>2</sub> [M+H]<sup>+</sup>:** 436.0679; found: 436.0648.

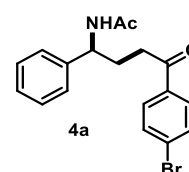
#### ***N*-(4-(4-Bromophenyl)-4-oxo-1-phenylbutyl)acetamide: (4a)**

**Yield:** 60% (43 mg).

**Nature:** white solid.

**Mp:** 209–212 °C

**R<sub>f</sub> value** = 0.3 [EtOAc:Petroleum ether = 1:1 (v/v)].



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 7.78 (d, *J* = 8.6 Hz, 2H), 7.59 (d, *J* = 8.6 Hz, 2H), 7.38 – 7.27 (m, 5H), 5.98 (d, *J* = 8.1 Hz, 1H), 5.06 (td, *J* = 8.6, 6.2 Hz, 1H), 3.10 – 3.02 (m, 1H), 2.98 – 2.90 (m, 1H), 2.36 – 2.29 (m, 1H), 2.23 – 2.16 (m, 1H), 1.94 (s, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 199.1, 169.63, 141.8, 135.5, 132.1, 129.7, 129.0, 127.8, 126.7, 53.5, 35.7, 29.9, 23.6.

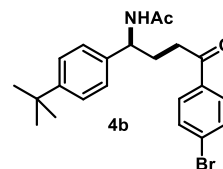
**HRMS (ESI) *m/z* calcd for C<sub>18</sub>H<sub>19</sub>BrNO<sub>2</sub> [M+H]<sup>+</sup>:** 360.0599; found: 360.0579.

#### ***N*-(4-(4-Bromophenyl)-1-(4-*tert*-butyl)phenyl)-4-oxobutyl)acetamide: (4b)**

**Yield:** 82% (69 mg).

**Nature:** low melting solid.

**R<sub>f</sub> value** = 0.3 [EtOAc:Petroleum ether = 1:1 (v/v)].



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 7.75 (d, *J* = 8.6 Hz, 2H), 7.56 (d, *J* = 8.6 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.3 Hz, 2H), 6.23 (d, *J* = 8.4 Hz, 1H), 5.03 (td, *J* = 8.5, 6.5 Hz, 1H), 3.09 – 2.85 (m, 2H), 2.36 – 2.10 (m, 2H), 1.90 (s, 3H), 1.9 (s, 9H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 199.1, 169.7, 150.6, 138.6, 135.5, 132.0, 129.7, 128.5, 126.4, 125.8, 53.0, 35.7, 34.6, 31.4, 30.0, 23.5.

**HRMS (ESI) *m/z*** calcd for C<sub>22</sub>H<sub>26</sub>BrNNaO<sub>2</sub> [M+Na]<sup>+</sup>: 438.1045, found: 438.1039

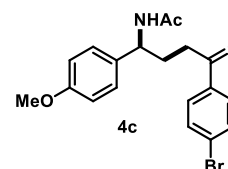
#### ***N*-(4-(4-Bromophenyl)-1-(4-methoxyphenyl)-4-oxobutyl)acetamide: (4c)**

**Yield:** 70% (55 mg).

**Nature:** white solid

**Mp:** 160-163 °C

**R<sub>f</sub> value** = 0.1 [EtOAc:Petroleum ether = 1:1 (v/v)].



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 7.77 (d, *J* = 8.6 Hz, 2H), 7.58 (d, *J* = 8.6 Hz, 2H), 7.25 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 5.90 (d, *J* = 8.2 Hz, 1H), 5.00 (dd, *J* = 14.9, 8.4 Hz, 1H), 3.79 (s, 3H), 3.08 – 2.99 (m, 1H), 2.92 (ddd, *J* = 17.9, 7.9, 6.1 Hz, 1H), 2.32 (ddd, *J* = 10.1, 7.9, 1.7 Hz, 1H), 2.16 (td, *J* = 7.8, 1.6 Hz, 1H), 1.92 (s, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 199.2, 169.5, 159.2, 135.5, 133.8, 132.1, 129.7, 128.6, 127.9, 114.3, 55.5, 52.9, 35.7, 29.9, 23.6.

**HRMS (ESI) *m/z*** calcd for C<sub>19</sub>H<sub>20</sub>BrNNaO<sub>3</sub> [M+Na]<sup>+</sup>: 412.0524; found: 412.0520.

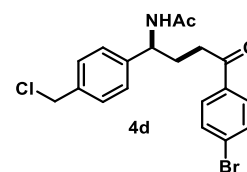
#### ***N*-(4-(4-Bromophenyl)-1-(4-(chloromethyl)phenyl)-4-oxobutyl)acetamide: (4d)**

**Yield:** 72% (59 mg).

**Nature:** white solid.

**Mp:** 193 – 196 °C

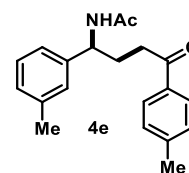
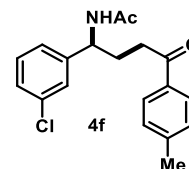
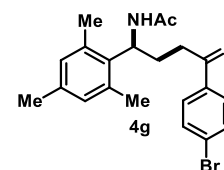
**R<sub>f</sub> value** = 0.2 [EtOAc:Petroleum ether = 1:1 (v/v)].



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 7.77 (d, *J* = 8.6 Hz, 2H), 7.59 (d, *J* = 8.6 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 6.10 (d, *J* = 8.2 Hz, 1H), 5.05 (td, *J* = 8.6, 6.0 Hz, 1H), 4.57 (s, 2H), 3.01 (dtd, *J* = 18.2, 11.1, 6.9 Hz, 2H), 2.35 – 2.26 (m, 1H), 2.17 (dd, *J* = 13.9, 7.4 Hz, 1H), 1.93 (s, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 199.1, 169.6, 142.2, 137.0, 135.4, 132.1, 129.7, 129.2, 128.7, 127.1, 53.2, 46.0, 35.7, 29.7, 23.6.

**HRMS (ESI) *m/z*** calcd for C<sub>19</sub>H<sub>20</sub>BrClNO<sub>2</sub> [M+H]<sup>+</sup>: 408.0366; found: 408.0351.

***N*-(4-Oxo-1-(*m*-tolyl)-4-(*p*-tolyl)butyl)acetamide: (4e)****Yield:** 66% (41 mg).**Nature:** white solid.**Mp:** 105- 108 °C**R<sub>f</sub> value** = 0.3 [EtOAc:Petroleum ether = 1:1 (v/v)].**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 7.82 (d, *J* = 8.2 Hz, 2H), 7.23 (t, *J* = 8.5 Hz, 3H), 7.12 (d, *J* = 8.3 Hz, 2H), 7.08 (d, *J* = 7.6 Hz, 1H), 6.14 (d, *J* = 6.7 Hz, 1H), 5.01 (td, *J* = 8.6, 6.1 Hz, 1H), 3.10 – 2.91 (m, 2H), 2.40 (s, 3H), 2.36 – 2.33 (m, 3H), 2.33 – 2.27 (m, 1H), 2.16 (dd, *J* = 14.0, 7.7 Hz, 1H), 1.92 (s, 3H).**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 200.1, 169.6, 144.2, 142.0, 138.6, 134.4, 129.4, 128.8, 128.5, 128.4, 127.5, 123.6, 53.6, 35.7, 30.1, 23.6, 21.8, 21.6.**HRMS (ESI) *m/z*** calcd for C<sub>20</sub>H<sub>24</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 310.1807; found: 310.1788.***N*-(1-(3-Chlorophenyl)-4-oxo-4-(*p*-tolyl)butyl)acetamide: (4f)****Yield:** 52% (35 mg).**Nature:** white solid.**Mp:** 150 – 153 °C**R<sub>f</sub> value** = 0.3 [EtOAc:Petroleum ether = 1:1 (v/v)].**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 7.82 (d, *J* = 8.1 Hz, 2H), 7.30 (s, 1H), 7.25 (dd, *J* = 9.3, 1.3 Hz, 4H), 7.20 (d, *J* = 7.2 Hz, 1H), 6.38 (d, *J* = 7.8 Hz, 1H), 5.00 (td, *J* = 8.7, 5.7 Hz, 1H), 3.10 – 2.95 (m, 2H), 2.41 (s, 3H), 2.34 – 2.25 (m, 1H), 2.18 – 2.10 (m, 1H), 1.93 (s, 3H).**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 200.0, 169.8, 144.5, 144.4, 134.2, 134.2, 130.1, 129.5, 128.3, 127.8, 126.7, 124.9, 53.4, 35.5, 29.9, 23.5, 21.8.**HRMS (ESI) *m/z*** calcd for C<sub>19</sub>H<sub>21</sub>ClNO<sub>2</sub> [M+H]<sup>+</sup>: 330.1261; found: 330.1266.***N*-(4-(4-Bromophenyl)-1-mesityl-4-oxobutyl)acetamide: (4g)****Yield:** 59% (47 mg).**Nature:** white solid.**Mp:** 190-193 °C**R<sub>f</sub> value** = 0.2 [EtOAc:Petroleum ether = 1:1 (v/v)].**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 7.78 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 6.83 (s, 2H), 6.12 (d, *J* = 8.0 Hz, 1H), 5.45 (dd, *J* = 15.6, 8.8 Hz, 1H), 3.12 – 2.95 (m, 2H), 2.57 – 2.48 (m, 1H), 2.46 (s, 6H), 2.23 (s, 3H), 2.13 – 2.06 (m, 1H), 1.87 (s, 3H).**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 199.5, 169.5, 136.9, 135.9, 135.6, 134.9, 132.1, 130.5, 129.7, 128.6, 50.1, 36.1, 27.9, 23.4, 21.2, 20.8.**HRMS (ESI) *m/z*** calcd for C<sub>21</sub>H<sub>24</sub>BrKNO<sub>2</sub> [(M+2)+K]<sup>+</sup>: 442.0607; found: 442.0610

***N*-(4-(4-Bromophenyl)-4-oxo-1-(thiophen-3-yl)butyl)acetamide: (4h)**

**Yield:** 65% (48 mg).

**Nature:** white solid.

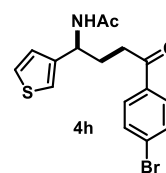
**Mp:** 183-186 °C

**R<sub>f</sub> value** = 0.2 [EtOAc:Petroleum ether = 1:1 (v/v)].

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 7.79 (d, *J* = 8.6 Hz, 2H), 7.59 (d, *J* = 8.6 Hz, 2H), 7.31 (dd, *J* = 5.0, 2.9 Hz, 1H), 7.21 – 7.13 (m, 1H), 7.05 (dd, *J* = 5.0, 1.3 Hz, 1H), 5.87 (d, *J* = 8.7 Hz, 1H), 5.22 – 5.16 (m, 1H), 3.10 – 2.95 (m, 2H), 2.33 – 2.25 (m, 2H), 1.93 (s, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 199.0, 169.6, 142.8, 135.5, 132.1, 129.7, 128.6, 126.7, 126.4, 121.5, 49.0, 35.6, 29.6, 23.6.

**HRMS (ESI) *m/z*** calcd for C<sub>16</sub>H<sub>17</sub>BrNO<sub>2</sub>S [(M+2)+H]<sup>+</sup>: 368.0143; found: 368.0129

***N*-(4-Oxo-4-(*p*-tolyl)-1-(1-tosyl-1*H*-indol-3-yl)butyl)acetamide: (4i)**

**Yield:** 30% (29 mg).

**Nature:** white solid.

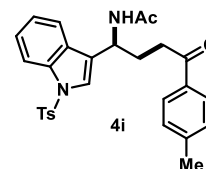
**Mp:** 175-178 °C

**R<sub>f</sub> value** = 0.1 [EtOAc:Petroleum ether = 1:1 (v/v)].

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 7.97 (d, *J* = 8.3 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.53 (s, 1H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.26 (s, 1H), 7.23 (d, *J* = 9.8 Hz, 2H), 7.18 (d, *J* = 8.2 Hz, 2H), 5.86 (d, *J* = 8.9 Hz, 1H), 5.40 (dt, *J* = 14.7, 7.4 Hz, 1H), 3.18 – 2.97 (m, 2H), 2.44 – 2.35 (m, 5H), 2.32 (s, 3H), 1.91 (s, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 199.7, 169.8, 145.2, 144.3, 135.5, 135.3, 134.3, 130.1, 129.5, 129.4, 128.4, 127.0, 125.2, 123.6, 123.1, 120.3, 113.8, 45.4, 35.4, 28.3, 23.5, 21.8, 21.7.

**HRMS (ESI) *m/z*** calcd for C<sub>28</sub>H<sub>29</sub>N<sub>2</sub>O<sub>4</sub>S [M+H]<sup>+</sup>: 489.1848; found: 489.1823.

***N*-((1*S*,2*R*)-4-(4-Bromophenyl)-1-(4-fluorophenyl)-2-methyl-4-oxobutyl)acetamide: (4j)**

**Yield:** 56% (44 mg).

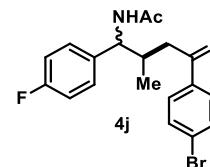
**Nature:** white solid.

**Mp:** 165 – 168 °C

**R<sub>f</sub> value** = 0.3 [EtOAc:Petroleum ether = 1:1 (v/v)].

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):**(for diastereomeric mixing) 7.88 – 7.65 (m, 2H), 7.64 – 7.44 (m, 2H), 7.29 (dd, *J* = 8.7, 5.3 Hz, 1H), 7.25 – 7.20 (m, 1H), 7.01 (ddd, *J* = 12.8, 11.7, 8.7 Hz, 2H), 6.20 (dd, *J* = 61.9, 8.9 Hz, 1H), 5.03 – 4.70 (m, 1H), 3.26 – 2.63 (m, 3H), 1.88 (d, *J* = 110.8 Hz, 3H), 0.94 (dd, *J* = 64.6, 6.7 Hz, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** (for diastereomeric mixing) 200.1, 198.7, 169.6, 169.4, 163.4 (d, *J* = 249.5 Hz), 160.9 (d, *J* = 249.5 Hz), 137.4 (d, *J* = 3.5 Hz), 136.5 (d, *J* = 3.5 Hz), 135.7, 132.2,



132.1, 129.8, 129.6, 128.9 (d,  $J = 8.2$  Hz), 128.7 (d,  $J = 8.1$  Hz), 115.8 (d,  $J = 21.6$  Hz), 115.6 (d,  $J = 21.6$  Hz), 58.7, 57.0, 43.2, 42.8, 34.3, 23.6, 23.4, 18.7, 17.1.

{ $^{19}\text{F}$ } NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): (for diastereomeric mixing) -114.7, -114.9.

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{19}\text{H}_{20}\text{BrFNO}_2$   $[\text{M}+\text{H}]^+$ : 392.0661; found: 392.0645

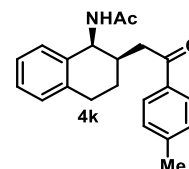
***N*-(1*S*,2*R*)-2-(2-Oxo-2-(*p*-tolyl)ethyl)-1,2,3,4-tetrahydronaphthalen-1-yl)acetamide: (4k)(syn)**

Yield: 53% (34 mg).

Nature: white solid.

Mp: 190-193 °C

$R_f$  value = 0.3 [EtOAc:Petroleum ether = 1:1 (v/v)].



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.88 (d,  $J = 8.2$  Hz, 2H), 7.27 (dd,  $J = 9.4, 1.0$  Hz, 3H), 7.21 (td,  $J = 7.4, 1.8$  Hz, 2H), 7.13 (d,  $J = 8.2$  Hz, 1H), 5.72 (d,  $J = 8.9$  Hz, 1H), 5.38 (dd,  $J = 9.3, 4.2$  Hz, 1H), 3.35 (dd,  $J = 16.7, 4.4$  Hz, 1H), 2.85 (ddd,  $J = 25.5, 13.8, 7.0$  Hz, 3H), 2.72 – 2.59 (m, 1H), 2.43 (s, 3H), 2.03 (s, 3H), 1.97 – 1.91 (m, 1H), 1.61 – 1.50 (m, 1H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 199.1, 169.5, 143.9, 136.9, 136.6, 134.7, 130.1, 129.4, 129.2, 128.4, 127.8, 126.5, 50.3, 40.9, 34.9, 28.8, 24.3, 23.7, 21.8.

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{21}\text{H}_{23}\text{NNaO}_2$   $[\text{M}+\text{Na}]^+$ : 344.1626; found: 344.1633

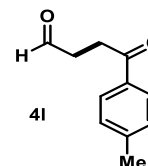
**4-Oxo-4-(*p*-tolyl)butanal: (4l)<sup>8</sup>**

Yield: 75% (26 mg).

Nature: light yellow solid.

Mp: 44- 47 °C

$R_f$  value = 0.3 [EtOAc:Petroleum ether = 1:9 (v/v)].



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 9.90 (d,  $J = 0.5$  Hz, 1H), 7.88 (d,  $J = 8.3$  Hz, 2H), 7.37 – 7.15 (m, 2H), 3.33 – 3.25 (m, 2H), 2.99 – 2.85 (m, 2H), 2.41 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 201.0, 197.6, 144.3, 134.0, 129.4, 128.3, 37.7, 31.0, 21.8.

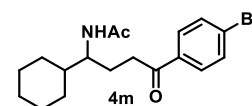
***N*-(4-(4-Bromophenyl)-1-cyclohexyl-4-oxobutyl)acetamide: (4m)**

Yield: 50% (37 mg).

Nature: white solid.

Mp: 189-192 °C

$R_f$  value = 0.2 [EtOAc:Petroleum ether = 1:1 (v/v)].



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): (for mixture of product) 7.80 (d,  $J = 8.6$  Hz, 6H), 7.59 (d,  $J = 8.6$  Hz, 6H), 5.28 (d,  $J = 9.8$  Hz, 2H), 5.11 (s, 1H), 3.89 – 3.81 (m, 2H), 2.98 (td,  $J = 7.1, 3.9$  Hz, 4H), 2.93 (t,  $J = 7.3$  Hz, 2H), 2.05 (dd,  $J = 12.8, 10.8$  Hz, 2H), 1.97 (d,  $J = 2.8$  Hz, 3H), 1.88 (d,  $J = 8.5$  Hz, 6H),

<sup>8</sup> W. H. G. Santos, J. B. M. Ruiz, A. C. Vargas, *Org. Lett.* **2019**, *21*, 4092–4096.



1.83 (t,  $J = 3.5$  Hz, 2H), 1.77 (dd,  $J = 17.0, 7.2$  Hz, 8H), 1.65 (dt,  $J = 14.4, 7.6$  Hz, 8H), 1.59 – 1.51 (m, 4H), 1.39 (dd,  $J = 11.5, 6.0$  Hz, 6H), 1.23 – 1.15 (m, 4H), 1.12 (dd,  $J = 12.8, 3.3$  Hz, 2H), 1.05 – 0.91 (m, 4H).

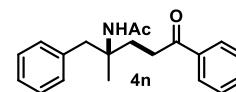
$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): (for mixture of product) 199.7, 199.5, 169.7, 170.2, 135.8, 135.6, 132.1, 132.0, 129.7, 129.6, 128.5, 128.2, 58.6, 56.1, 54.0, 42.8, 35.9, 34.9, 29.7, 28.8, 26.5, 26.3, 26.2, 25.8, 24.7, 23.6, 21.9, 18.6, 17.9.

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{18}\text{H}_{25}\text{BrNO}_2$   $[\text{M}+\text{H}]^+$ : 366.1069; found: 366.1067.

#### ***N*-(2-Methyl-5-oxo-1,5-diphenylpentan-2-yl)acetamide: (4n)**

**Yield:** 56% (35 mg).

**Nature:** colourless oil.



**R<sub>f</sub> value** = 0.3 [EtOAc:Petroleum ether = 4:6 (v/v)].

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 8.00 – 7.94 (m, 2H), 7.57 (m, 1H), 7.50 – 7.44 (m, 2H), 7.30 – 7.22 (m, 3H), 7.18 – 7.12 (m, 2H), 5.35 (s, 1H), 3.28 (d,  $J = 13.3$  Hz, 1H), 3.13 – 2.99 (m, 2H), 2.94 (d,  $J = 13.3$  Hz, 1H), 2.50 (ddd,  $J = 15.0, 8.7, 6.6$  Hz, 1H), 1.93 (s, 3H), 1.92 – 1.86 (m, 1H), 1.26 (s, 3H).

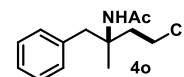
$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 200.7, 170.3, 137.6, 136.9, 133.3, 130.7, 128.8, 128.3, 128.2, 126.6, 56.5, 44.1, 33.7, 33.4, 24.6, 24.4.

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{20}\text{H}_{24}\text{NO}_2$   $[\text{M}+\text{H}]^+$ : 310.1807; found: 310.1801.

#### ***N*-(4-Cyano-2-methyl-1-phenylbutan-2-yl)acetamide: (4o)**

**Yield:** 68% (31 mg).

**Nature:** colourless oil.



**R<sub>f</sub> value** = 0.3 [EtOAc:Petroleum ether = 1:1 (v/v)].

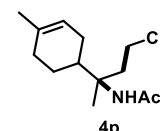
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.32 – 7.24 (m, 3H), 7.15 – 7.08 (m, 2H), 5.50 (s, 1H), 3.33 (d,  $J = 13.3$  Hz, 1H), 2.78 – 2.67 (m, 2H), 2.44 – 2.35 (m, 2H), 2.07 (s, 3H), 1.86 (dd,  $J = 14.4, 7.5$  Hz, 1H), 1.19 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 170.6, 136.6, 130.7, 128.3, 126.9, 120.1, 56.1, 43.9, 33.4, 24.4, 24.3, 12.4.

#### ***N*-((2R)-4-Cyano-2-(4-methylcyclohex-3-en-1-yl)butan-2-yl)acetamide: (4p)**

**Yield:** 45% (21 mg).

**Nature:** colourless oil.



**R<sub>f</sub> value** = 0.3 [EtOAc:Petroleum ether = 4:6 (v/v)].

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): (for the mixing) 5.37 – 5.24 (m, 2H), 2.60 – 2.43 (m, 1H), 2.32 (tdd,  $J = 9.5, 6.0, 3.7$  Hz, 2H), 2.16 – 2.10 (m, 1H), 2.04 – 1.99 (m, 2H), 1.98 – 1.92 (m, 5H), 1.81 – 1.75 (m, 1H), 1.73 – 1.67 (m, 1H), 1.62 (s, 3H), 1.30 – 1.21 (m, 1H), 1.13 (d,  $J = 12.8$  Hz, 3H).

**$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm):** (for the mixing) 170.1, 170.1, 134.4, 134.2, 120.4, 120.3, 120.0, 119.9, 58.4, 58.3, 40.11, 39.9, 31.6, 31.4, 31.0, 31.1, 26.4, 26.3, 24.4, 24.3, 24.2, 23.8, 23.3, 23.3, 20.2, 19.9, 12.4, 12.2.

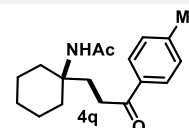
**HRMS (ESI)  $m/z$  calcd for  $\text{C}_{14}\text{H}_{23}\text{N}_2\text{O}$   $[\text{M}+\text{H}]^+$ :** 235.1810; found: 235.1809.

***N*-(1-(3-Oxo-3-(*p*-tolyl)propyl)cyclohexyl)acetamide: (4q)**

**Yield:** 52% (30 mg).

**Nature:** gummy liquid.

**$R_f$  value** = 0.3 [EtOAc:Petroleum ether = 4:6 (v/v)].



**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm):** 7.85 (d,  $J$  = 8.2 Hz, 2H), 7.25 (d,  $J$  = 8.2 Hz, 2H), 5.11 (s, 1H), 2.92 (dd,  $J$  = 8.7, 7.0 Hz, 2H), 2.40 (s, 3H), 2.22 – 2.16 (m, 2H), 2.06 – 2.09 (m, 2H), 1.97 (s, 3H), 1.58 – 1.51 (m, 4H), 1.43 – 1.34 (m, 4H).

**$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm):** 200.7, 169.7, 143.9, 129.4, 128.5, 58.6, 55.9, 34.9, 33.4, 25.7, 24.7, 21.9, 21.8, 18.6.

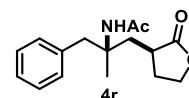
**HRMS (ESI)  $m/z$  calcd for  $\text{C}_{18}\text{H}_{25}\text{NaNO}_2$   $[\text{M}+\text{Na}]^+$ :** 310.1783; found: 310.1788.

***N*-(*(R)*-2-Methyl-1-(*(R)*-2-oxotetrahydrofuran-3-yl)-3-phenylpropan-2-yl)acetamide: (4r)**

**Yield:** 64% (35 mg).

**Nature:** colourless oil.

**$R_f$  value** = 0.2 [EtOAc:Petroleum ether = 1:1 (v/v)].



**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm):** (for the mixing) 7.28 – 7.21 (m, 6H), 7.14 – 7.10 (m, 4H), 6.65 (s, 1H), 5.68 (s, 1H), 4.34 (tt,  $J$  = 8.7, 4.4 Hz, 2H), 4.23 – 4.12 (m, 2H), 3.53 (d,  $J$  = 13.4 Hz, 1H), 3.23 (d,  $J$  = 13.3 Hz, 1H), 2.99 (d,  $J$  = 13.3 Hz, 1H), 2.77 – 2.74 (m, 1H), 2.74 – 2.68 (m, 1H), 2.60 – 2.56 (m, 1H), 2.49 – 2.43 (m, 1H), 2.43 – 2.37 (m, 2H), 2.23 – 2.16 (m, 1H), 2.07 – 1.98 (m, 4H), 1.92 (d,  $J$  = 0.9 Hz, 6H), 1.54 (dd,  $J$  = 14.6, 4.3 Hz, 1H), 1.45 (s, 3H), 1.19 (s, 3H).

**$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm):** (for the mixing) 181.2, 180.6, 170.7, 170.6, 137.5, 137.2, 130.7, 128.2, 126.6, 67.2, 67.0, 56.4, 56.0, 44.5, 43.3, 40.3, 39.3, 36.0, 35.7, 31.3, 30.4, 25.0, 24.6, 24.5, 23.9.

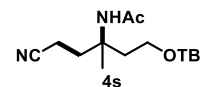
**HRMS (ESI)  $m/z$  calcd for  $\text{C}_{16}\text{H}_{21}\text{NO}_3$   $[\text{M}+\text{H}]^+$ :** 276.1600; found: 276.1604.

***N*-(1-(*tert*-Butyldimethylsilyloxy)-5-cyano-3-methylpentan-3-yl)acetamide: (4s)**

**Yield:** 68% (40 mg).

**Nature:** colourless oil.

**$R_f$  value** = 0.3 [EtOAc:Petroleum ether = 4:6 (v/v)].



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 6.82 (s, 1H), 3.92 – 3.86 (m, 1H), 3.82 – 3.75 (m, 1H), 2.59 – 2.50 (m, 1H), 2.36 – 2.28 (m, 2H), 2.01 – 1.89 (m, 5H), 1.47 (ddd, *J* = 14.7, 5.6, 2.7 Hz, 1H), 1.41 (s, 3H), 0.91 (s, 9H), 0.09 (d, *J* = 1.6 Hz, 6H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 170.0, 120.4, 77.5, 76.8, 59.8, 55.7, 40.8, 34.1, 26.0, 24.6, 23.6, 18.3, 12.4, -5.4

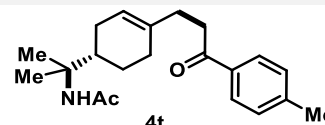
**HRMS (ESI) *m/z* calcd for C<sub>15</sub>H<sub>30</sub>N<sub>2</sub>O<sub>2</sub>SiNa [M+Na]<sup>+</sup>:** 321.1974; found: 321.1982.

***N*-(2-(4-(3-Oxo-3-(*p*-tolyl)propyl)cyclohex-3-en-1-yl)propan-2-yl)acetamide: (4t)**

**Yield:** 60% (39 mg).

**Nature:** Colourless oil.

**R<sub>f</sub> value** = 0.3 [EtOAc:Petroleum ether = 4:6 (v/v)].



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 7.85 (d, *J* = 8.2 Hz, 2H), 7.26 – 7.23 (m, 2H), 5.45 – 5.38 (m, 1H), 5.23 (s, 1H), 3.02 (ddd, *J* = 8.0, 6.8, 3.1 Hz, 2H), 2.40 (s, 3H), 2.35 (t, *J* = 7.5 Hz, 2H), 2.22 – 2.14 (m, 1H), 2.04 – 1.97 (m, 2H), 1.92 (s, 3H), 1.80 – 1.73 (m, 3H), 1.29 (s, 3H), 1.27 (s, 3H), 1.21 (dd, *J* = 11.9, 6.4 Hz, 1H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 200.0, 169.5, 143.8, 136.8, 134.6, 129.4, 128.3, 120.9, 56.4, 40.9, 37.2, 31.9, 29.7, 26.7, 24.7, 24.3, 24.2, 24.0, 21.7.

**HRMS (ESI) *m/z* calcd for C<sub>21</sub>H<sub>29</sub>NO<sub>2</sub> [M+H]<sup>+</sup>:** 328.2277; found: 328.2282.

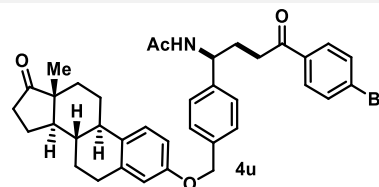
***N*-(4-(4-Bromophenyl)-1-(4-(((8*S*,9*R*,13*R*,14*R*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)methyl)phenyl)-4-oxobutyl)acetamide: (4u)**

**Yield:** 40% (51 mg)

**Nature:** white solid.

**Mp:** 175-178 °C

**R<sub>f</sub> value** = 0.3 [EtOAc:Petroleum ether = 1:1 (v/v)].



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 7.85 – 7.71 (m, 2H), 7.64 – 7.53 (m, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.6 Hz, 1H), 6.78 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.72 (d, *J* = 2.5 Hz, 1H), 5.99 (d, *J* = 8.2 Hz, 1H), 5.07 (dt, *J* = 14.7, 7.4 Hz, 1H), 5.02 (d, *J* = 8.9 Hz, 2H), 3.11 – 2.85 (m, 4H), 2.50 (dd, *J* = 18.8, 8.5 Hz, 1H), 2.41 – 1.99 (m, 7H), 1.93 (s, 3H), 1.63 (dd, *J* = 12.0, 3.3 Hz, 2H), 1.57 – 1.38 (m, 5H), 0.91 (s, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 221.1, 199.1, 169.6, 156.9, 141.5, 138.0, 136.9, 135.5, 132.6, 132.1, 129.7, 128.1, 126.9, 126.5, 115.0, 112.5, 69.7, 53.3, 50.6, 48.2, 44.1, 38.5, 36.0, 35.7, 31.7, 29.9, 29.8, 26.7, 26.1, 23.6, 21.7, 14.0.

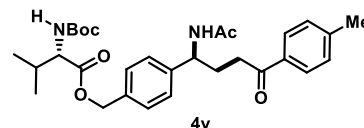
**HRMS (ESI) *m/z* calcd for C<sub>37</sub>H<sub>41</sub>BrNO<sub>4</sub> [M+H]<sup>+</sup>:** 642.2219; found: 642.2202.

**4-(1-Acetamido-4-oxo-4-(*p*-tolyl)butyl)benzyl (*tert*-butoxycarbonyl)-*L*-valinate: (4v)**

**Yield:** 45% (48 mg)

**Nature:** colourless oil.

**R<sub>f</sub> value** = 0.1 [EtOAc:Petroleum ether = 1:1 (v/v)].



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 7.84 (d, *J* = 8.2 Hz, 2H), 7.35 (s, 4H), 7.26 (s, 2H), 6.19 (d, *J* = 5.9 Hz, 1H), 5.16 (d, *J* = 6.8 Hz, 2H), 5.12 – 5.02 (m, 2H), 4.32 – 4.26 (m, 1H), 3.13 – 2.96 (m, 2H), 2.43 (s, 3H), 2.40 – 2.33 (m, 1H), 2.22 – 2.15 (m, 2H), 1.95 (s, 3H), 1.46 (s, 9H), 0.96 (d, *J* = 6.8 Hz, 3H), 0.87 (d, *J* = 6.8 Hz, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 200.0, 172.4, 169.6, 155.8, 144.4, 134.8, 134.3, 129.4, 128.9, 128.3, 126.9, 79.9, 66.7, 58.7, 53.5, 35.6, 31.4, 29.9, 28.5, 23.5, 21.8, 19.2, 17.6.

**HRMS (ESI) *m/z*** calcd for C<sub>30</sub>H<sub>40</sub>N<sub>2</sub>NaO<sub>6</sub> [M+Na]<sup>+</sup>: 547.2784; found: 547.2773.

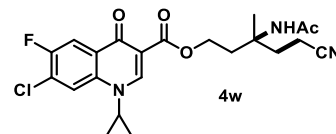
### 3-Acetamido-5-cyano-3-methylpentyl 7-chloro-1-cyclopropyl-6-fluoro-4-oxo-1,4-dihydroquinoline-3-carboxylate: (4w)

**Yield:** 41% (37 mg).

**Nature:** white solid.

**Mp:** 183-185 °C

**R<sub>f</sub> value** = 0.3 [EtOAc:Petroleum ether = 4:6 (v/v)].



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 8.65 (s, 1H), 8.15 (d, *J* = 8.9 Hz, 1H), 8.05 (d, *J* = 5.9 Hz, 1H), 7.40 (s, 1H), 4.52 – 4.40 (m, 2H), 3.52 – 3.46 (m, 1H), 2.59 – 2.50 (m, 1H), 2.40 (dd, *J* = 8.3, 7.1 Hz, 2H), 2.37 – 2.30 (m, 1H), 2.19 (dd, *J* = 13.6, 7.6 Hz, 1H), 1.99 (s, 3H), 1.74 – 1.68 (m, 1H), 1.64 (s, 1H), 1.47 (s, 3H), 1.41 (d, *J* = 6.5 Hz, 2H), 1.18 (q, *J* = 6.4 Hz, 2H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 172.9, 171.7, 165.7, 156.1 (d, *J* = 251.6 Hz), 149.7, 137.4, 128.8, 127.7 (d, *J* = 20.3 Hz), 120.8, 119.4, 113.8 (d, *J* = 22.9 Hz), 110.1, 61.4, 54.8, 37.5, 35.1, 34.8, 24.2, 23.4, 12.4, 8.5.

**{<sup>19</sup>F} NMR (377 MHz, CDCl<sub>3</sub>) δ (ppm):** -116.9.

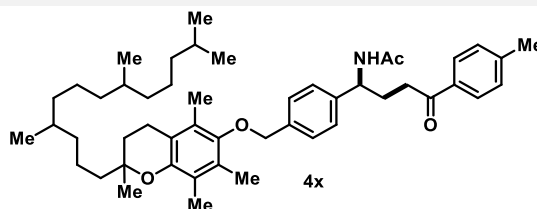
**HRMS (ESI) *m/z*** calcd for C<sub>22</sub>H<sub>24</sub>ClFN<sub>3</sub>O<sub>4</sub> [M+H]<sup>+</sup>: 448.1439; found: 448.1441.

### N-(4-Oxo-1-(4-(((2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)chroman-6-yl)oxy)methyl)phenyl)-4-(*p*-tolyl)butyl)acetamide: (4x)

**Yield:** 42% (62 mg)

**Nature:** gummy colourless oil.

**R<sub>f</sub> value** = 0.3 [EtOAc:Petroleum ether = 1:1 (v/v)].



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 7.86 (d, *J* = 8.2 Hz, 2H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.3 Hz, 2H), 6.16 (d, *J* = 7.8 Hz, 1H), 5.10 (dd, *J* = 14.5, 8.5 Hz, 1H), 4.69 (s, 2H), 3.17 – 3.07 (m, 1H), 3.01 (dt, *J* = 17.9, 6.7 Hz, 1H), 2.61 (t, *J* = 6.7 Hz, 2H), 2.43 (s, 3H), 2.37 (dd, *J* =

15.7, 7.1 Hz, 1H), 2.27 – 2.21 (m, 4H), 2.19 (s, 3H), 2.12 (s, 3H), 1.96 (s, 3H), 1.82 (ddd,  $J = 20.1, 13.5, 6.7$  Hz, 2H), 1.56 (dt,  $J = 13.2, 5.5$  Hz, 3H), 1.41 (dd,  $J = 11.1, 5.2$  Hz, 4H), 1.27 (d,  $J = 3.7$  Hz, 9H), 1.18 – 1.03 (m, 7H), 0.91 – 0.86 (m, 13H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 200.0, 169.6, 148.2, 144.3, 141.6, 137.6, 134.4, 129.5, 128.3, 128.2, 128.0, 126.8, 126.1, 123.1, 117.8, 75.0, 74.4, 53.5, 40.3, 39.5, 37.5, 37.4, 35.6, 32.9, 32.8, 31.4, 30.0, 28.1, 24.9, 24.6, 24.0, 23.6, 22.9, 22.8, 21.8, 21.2, 20.8, 19.9, 19.8, 13.0, 12.1, 12.0.

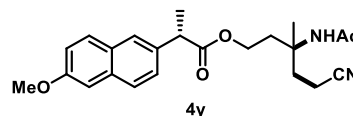
HRMS (ESI)  $m/z$  calcd for  $\text{C}_{49}\text{H}_{71}\text{NO}_4$   $[\text{M}]^+$ : 737.5383; found: 737.5369.

### 3-Acetamido-5-cyano-3-methylpentyl (2S)-2-(6-methoxynaphthalen-2-yl)propanoate: (4y)

Yield: 55% (44 mg).

Nature: colourless oil.

$R_f$  value = 0.2 [EtOAc:Petroleum ether = 1:1 (v/v)].



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.70 (dd,  $J = 8.6, 5.7$  Hz, 2H), 7.64 (s, 1H), 7.36 (dd,  $J = 8.5, 1.8$  Hz, 1H), 7.18 – 7.08 (m, 2H), 5.27 (d,  $J = 10.5$  Hz, 1H), 4.17 – 4.07 (m, 2H), 3.91 (s, 3H), 3.82 (qd,  $J = 7.1, 2.0$  Hz, 1H), 2.28 – 2.12 (m, 4H), 1.90 – 1.83 (m, 2H), 1.83 – 1.79 (m, 3H), 1.57 (d,  $J = 7.1$  Hz, 3H), 1.12 (d,  $J = 13.3$  Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 174.7, 170.2, 157.9, 135.4, 129.3, 129.0, 127.5, 126.1, 119.9, 119.4, 105.7, 61.1, 55.5, 54.8, 45.7, 45.6, 36.8, 33.5, 24.3, 24.2, 18.6, 18.5, 12.1.

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{23}\text{H}_{28}\text{N}_2\text{O}_4\text{K}$   $[\text{M}+\text{K}]^+$ : 435.1686; found: 435.1688.

## 4.2 Gram-scale reaction of compound 3b:

A flame dried 50 mL round bottom flask equipped with a magnetic stirring bar was charged with 4CzIPN (74 mg, 2 mol %), 4-methyl phenacyl bromide **2b** (1.0 g, 4.7 mmol), zinc acetate (515 mg, 2.35 mmol) and dry acetonitrile (24 mL), then the tube was sealed with a rubber septum, evacuated and backfilled with argon. 4-methylstyrene **1a** (0.94 mL, 7.05 mmol),  $\text{H}_2\text{O}$  (84  $\mu\text{L}$ , 1 equiv.) and  $\text{CF}_3\text{COOH}$  (1.9 mL, 5 equiv.) were added *via* syringe under argon atmosphere. Afterwards, the reaction mixture was degassed by Freeze-Pump-Thaw cycles two times with argon *via* syringe needle and irradiated at room temperature with 12 W blue LED bulb at a distance of approximately 5 cm and simultaneously cooled by fan to maintain the reaction at RT. After 10 h, completion the reaction (checked by TLC). The reaction mixture was poured into 20 mL Saturated  $\text{NaHCO}_3$  solution and extracted with EtOAc (20 mL  $\times$  2). The combined organic layer was washed with brine solution, dried over  $\text{MgSO}_4$  and concentrated under reduced pressure. Finally, the crude residue was purified by flash column chromatography on silica gel 230-400 mesh (EtOAc:Petroleum ether = 40:60 – 80:20) to get the corresponding product **3b** (1.1 g, 74%).

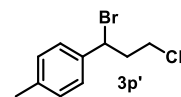
## 4.3 Photocatalytic ATRA reaction:

#### 4-Bromo-4-(p-tolyl)butanenitrile: (3p')<sup>9</sup>

**Yield:** 33% (16 mg).

**Nature:** colourless oil.

**R<sub>f</sub> value** = 0.3 [EtOAc:Petroleum ether = 1:9 (v/v)].



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 7.72 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 5.03 (dd, *J* = 8.2, 6.0 Hz, 1H), 2.59 – 2.39 (m, 4H), 2.35 (s, 3H).

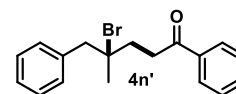
**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 139.2, 137.3, 129.8, 127.2, 118.5, 52.5, 35.4, 21.3, 16.6

#### 4-Bromo-4-methyl-1,5-diphenylpentan-1-one: (4n')

**Yield:** 50% (33 mg).

**Nature:** colourless oil.

**R<sub>f</sub> value** = 0.5 [EtOAc:Petroleum ether = 1:9 (v/v)].



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 8.03 – 7.95 (m, 2H), 7.58 (dd, *J* = 10.4, 4.4 Hz, 1H), 7.48 (dd, *J* = 10.3, 4.8 Hz, 2H), 7.34 – 7.27 (m, 5H), 3.44 – 3.28 (m, 3H), 3.26 – 3.21 (m, 1H), 2.36 – 2.19 (m, 2H), 1.74 (s, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 199.3, 136.9, 136.6, 133.4, 131.1, 128.8, 128.3, 128.2, 127.2, 71.5, 52.1, 38.8, 36.0, 31.1.

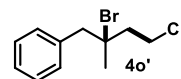
**HRMS (ESI) *m/z* calcd for C<sub>18</sub>H<sub>20</sub>BrO [M+H]<sup>+</sup>:** 331.0698; found: 331.0619.

#### 4-Bromo-4-methyl-5-phenylpentanenitrile: (4o')

**Yield:** 65% (33 mg).

**Nature:** colourless oil.

**R<sub>f</sub> value** = 0.5 [EtOAc:Petroleum ether = 1:9 (v/v)].

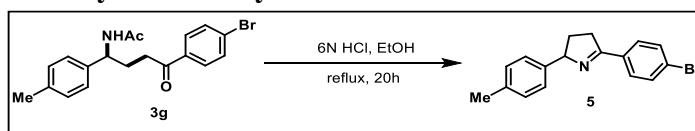


**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 7.41 – 7.27 (m, 3H), 7.27 – 7.22 (m, 2H), 3.28 (d, *J* = 13.9 Hz, 1H), 3.20 (d, *J* = 13.9 Hz, 1H), 2.76 – 2.67 (m, 1H), 2.66 – 2.56 (m, 1H), 2.25 – 2.17 (m, 1H), 2.10 – 2.02 (m, 1H), 1.72 (s, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 135.8, 130.9, 128.4, 127.5, 119.5, 68.3, 51.8, 40.1, 30.6, 14.9.

## 5. Synthetic transformations of aminoalkylation products

### Reaction procedure for the synthesis of Pyrolline derivative 5:



Compound **3g** (74 mg, 0.2 mmol), 6N HCl (0.5 mL) and 1 mL EtOH was taken sequentially to the 5 mL pear-shaped flask and the reaction mixture was heated to reflux for 20 hours. After completion (as monitored

<sup>9</sup> W. Pu, D. Sun, W. Fan, W. Pan, Q. Chai, X. Wang, Y. Lv, Chem. Commun., **2019**, 55, 4821-4824.

by TLC), the reaction mixture was quenched by 1 mL saturated NaHCO<sub>3</sub> solution and extracted with EtOAc (5 mL × 2). Then the organic layer was washed with brine solution, dried over Na<sub>2</sub>SO<sub>4</sub>, concentrated under reduced pressure and purified by silica gel column chromatography (EtOAc:Petroleum ether = 0:100 – 10:90) to afford the desired product **5**.

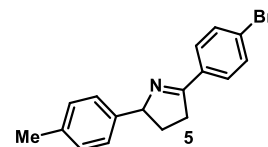
#### 5-(4-Bromophenyl)-2-(*p*-tolyl)-3,4-dihydro-2*H*-pyrrole: (**5**)

**Yield:** 80% (49 mg).

**Nature:** white solid.

**Mp:** 140 – 142 °C

**R<sub>f</sub> value** = 0.3 [EtOAc:Petroleum ether = 1:9 (v/v)].

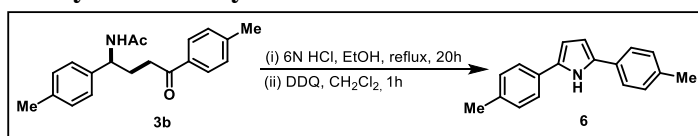


**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 7.80 (d, *J* = 8.6 Hz, 2H), 7.56 (d, *J* = 8.6 Hz, 2H), 7.17 (q, *J* = 8.2 Hz, 4H), 5.26 (t, *J* = 7.7 Hz, 1H), 3.16 – 3.10 (m, 1H), 3.01 – 2.91 (m, 1H), 2.63 – 2.51 (m, 1H), 2.34 (s, 3H), 1.95 – 1.83 (m, 1H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 172.6, 141.4, 136.6, 133.5, 131.8, 129.6, 129.3, 126.6, 125.2, 76.1, 35.6, 32.6, 21.2.

**HRMS (ESI) *m/z*** calcd for C<sub>17</sub>H<sub>17</sub>BrN [M+H]<sup>+</sup>: 314.0544; found: 314.0534.

#### Reaction procedure for the synthesis of Pyrrole derivative **6**:



Compound **3b** (64 mg, 0.2 mmol), and 6(N) HCl (0.5 mL) were added sequentially to the 1 mL EtOH in 5 mL pear-shaped flask and the reaction mixture was heated to reflux for 20 hours. After completion, the reaction mixture was quenched by 1 mL saturated NaHCO<sub>3</sub> solution and extracted with EtOAc (5 mL × 2). Then the organic layer was washed with brine solution, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuum. The crude reaction mixture thus obtained was dissolved in 1 mL CH<sub>2</sub>Cl<sub>2</sub> and DDQ (23 mg, 0.1 mmol) was added. The reaction mixture was then stirred at room temperature for 1 hour. Then the solvent was concentrated under reduced pressure and purified by silica gel column chromatography (EtOAc:Petroleum ether = 0:100 – 10:90) to afford the desired product **6**.

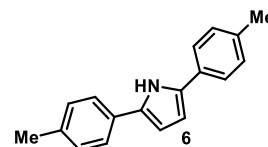
#### 2,5-Di-*p*-tolyl-1*H*-pyrrole: (**6**)<sup>10</sup>

**Yield:** 70% (36 mg).

**Nature:** white solid.

**Mp:** 202-204 °C

**R<sub>f</sub> value** = 0.5 [EtOAc:Petroleum ether = 1:9 (v/v)].

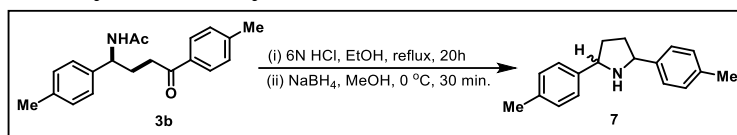


<sup>10</sup> H. Surya Prakash Rao, S. Jothilingam, H. W. Scheeren, *Tetrahedron*. **2004**, *60*, 1625.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 8.52 (s, 1H), 7.42 (d, *J* = 8.0 Hz, 4H), 7.20 (d, *J* = 7.9 Hz, 4H), 6.53 (d, *J* = 2.1 Hz, 2H), 2.37 (s, 6H)

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 136.2, 133.0, 129.9, 129.7, 123.8, 107.4, 21.3.

### Reaction procedure for the synthesis of Pyrrolidine derivative 7:



Compound 3b (64 mg, 0.2 mmol), and 6(N) HCl (0.5 mL) were added sequentially to the 1 mL EtOH in 5 mL pear-shape flask and the reaction mixture was heated to reflux for 20 hours. After completion, the reaction mixture was quenched by 1 mL saturated NaHCO<sub>3</sub> solution and extracted with EtOAc (5 mL × 2). Then the organic layer was washed with brine solution, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuum, the residue was dissolved in 2mL MeOH and added NaBH<sub>4</sub> (20 mg, 0.6 mmol) to this solution and stirred at 0 °C for 30 min. Then the solvent was concentrated under reduced pressure and purified by silica gel column chromatography (EtOAc:Petroleum ether = 0:100 – 10:90) to afford the desired product 7.

### 2,5-Di-*p*-tolylpyrrolidine: (7)

**Yield:** 68% (34 mg).

**Nature:** white solid.

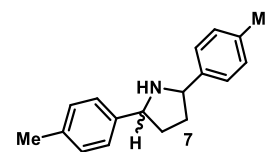
**Mp:** 132-135 °C

**R<sub>f</sub> value** = 0.2 [EtOAc:Petroleum ether = 1:9 (v/v)].

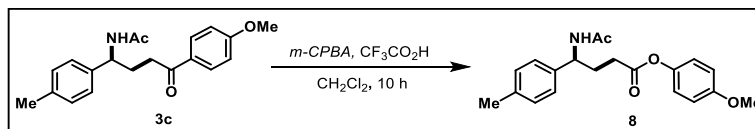
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** (for diastereomeric mixing) 7.35 (dd, *J* = 37.0, 8.0 Hz, 4H), 7.15 (d, *J* = 7.8 Hz, 4H), 4.39 (m, 2H), 2.37 (m, 1H), 2.35 (d, *J* = 2.0 Hz, 6H), 1.89 (m, 1H), 1.80 (m, 2H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** (for diastereomeric mixing) 143.0, 142.4, 136.5, 129.3, 129.1, 126.8, 126.4, 62.3, 62.1, 35.7, 34.7, 21.2, 21.1

**HRMS (ESI) *m/z*** calcd for C<sub>18</sub>H<sub>22</sub>N [M+H]<sup>+</sup>: 252.1752; found: 252.1750.



### Reaction procedure for the synthesis of GABA derivative 8:



Compound 3c (66 mg, 0.2 mmol) and *m*-chloroperbenzopic acid (≤ 77% purity, 45 mg, 0.2 mmol) were dissolved in 2 mL CH<sub>2</sub>Cl<sub>2</sub> in a 10 mL round bottom flask, equipped with a magnetic stirring bar and sealed with septum. The solution was stirred vigorously at 0 °C for 5 min. then trifluoroacetic acid (20 μL, 0.3 mmol) was added dropwise via syringe to the reaction mixture and stirred overnight allowing to reach room temperature slowly. After consumption of all starting materials (monitored by the TLC) the reaction mixture was quenched with 2 mL saturated NaHCO<sub>3</sub> (2 mL) solution, extracted with CH<sub>2</sub>Cl<sub>2</sub> (5 mL × 3). The combined organic layer was washed with brine solution, dried over Na<sub>2</sub>SO<sub>4</sub>, concentrated under reduced pressure purified



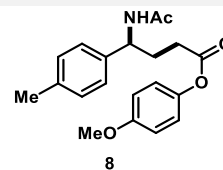
by silica gel column chromatography (EtOAc:Petroleum ether = 40:60 – 80:20) to afford the desired product **8**.

#### 4-Methoxyphenyl (*S*)-4-acetamido-4-(*p*-tolyl)butanoate : (**8**)

**Yield:** 85% (58 mg).

**Nature:** colourless oil.

**R<sub>f</sub> value** = 0.2 [EtOAc:Petroleum ether = 1:1 (v/v)].

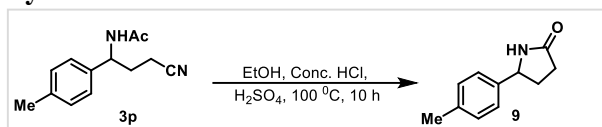


**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 7.20 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 6.98 – 6.94 (m, 2H), 6.89 – 6.85 (m, 2H), 6.09 (d, *J* = 8.3 Hz, 1H), 5.02 (dd, *J* = 15.1, 8.2 Hz, 1H), 3.78 (s, 3H), 2.62 – 2.50 (m, 2H), 2.34 (s, 3H), 2.20 (dddd, *J* = 14.0, 8.2, 7.5, 1.6 Hz, 2H), 1.96 (s, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 172.6, 169.6, 157.4, 144.2, 138.4, 137.6, 129.6, 126.6, 122.3, 114.5, 55.7, 52.9, 31.4, 30.9, 23.5, 21.2.

**HRMS (ESI) *m/z*** calcd for C<sub>20</sub>H<sub>24</sub>NO<sub>4</sub> [M+H]<sup>+</sup>: 342.1705; found: 342.1706.

#### Reaction procedure for the synthesis of Lactum derivative **9**:



In a flame-dried Schlenk tube equipped with stir bar was charged with compound **3p** (43 mg, 0.2 mmol), EtOH (1.0 mL) and Conc. HCl (1.5 mL) in nitrogen atmosphere. Then the reaction mixture was heated to 100 ° C for 2 hour and then another portion of Conc. HCl (0.5 mL) was added to this reaction mixture. After 4 hour, H<sub>2</sub>SO<sub>4</sub> (30%, 1.5 mL) was added to this reaction mixture and allowed to heat another 2 hour at same temperature. Finally, another portion of H<sub>2</sub>SO<sub>4</sub> (30%, 0.5 mL) was added to this reaction mixture and heated for another 4 hour. Then the reaction mixture was cooled and neutralised with ammonium hydroxide (10 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (30 mL, 10 mL×3) . The combined organic layer was washed with brine solution, dried over Na<sub>2</sub>SO<sub>4</sub>, concentrated under reduced pressure and purified by silica gel column chromatography (EtOAc:Petroleum ether = 50:50 – 100:0) to afford the desired product **9**.

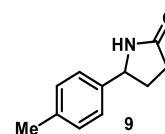
#### 5-(*p*-Tolyl)pyrrolidin-2-one (**9**):<sup>11</sup>

**Yield:** 75% (20 mg).

**Nature:** white solid

**Mpt:** 90-92 °C

**R<sub>f</sub> value** = 0.3 [EtOAc: Petroleum ether = 1:1 (v/v)].

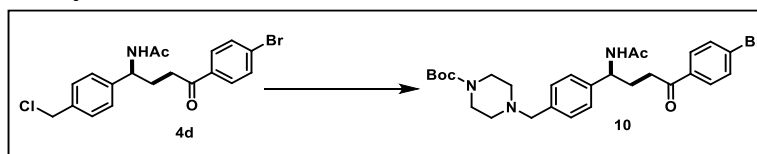


**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 7.18 (s, 4H), 6.05 (s, 1H), 4.72 (t, *J* = 7.1 Hz, 1H), 2.60 – 2.51 (m, 1H), 2.49 – 2.38 (m, 2H), 2.34 (s, 3H), 1.99 – 1.94 (m, 1H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 178.6, 139.5, 37.9, 129.7, 125.7, 58.0, 31.6, 30.5, 21.2.

<sup>11</sup> Y. L. Su, J. W. Liu, L. Tram, H. Qiu, M. P. Doyle, *J. Am. Chem. Soc.* **2020**, *142*, 13846–13855.

## Reaction procedure for synthesis of 10:



Compound **4d** (41 mg, 0.1 mmol), 1-Boc-piperazine (28 mg, 0.15 mmol) and  $\text{Cs}_2\text{CO}_3$  (20 mg, 0.2 mmol) were dissolved in 2 mL  $\text{CH}_3\text{CN}$  and stirred for 16 hrs under argon at room temperature. After full consumption of starting materials (monitored by TLC), the reaction mixture was diluted with 10 mL EtOAc, concentrated under reduced pressure and purified by silica gel column chromatography (MeOH/ $\text{CH}_2\text{Cl}_2$  = 2:98 – 10:90) to afford the desired product **10**.

### **tert-Butyl-4-(4-(1-acetamido-4-(4-bromophenyl)-4-oxobutyl)benzyl)piperazine-1-carboxylate: (10)**

**Yield:** 90% (50 mg).

**Nature:** white solid.

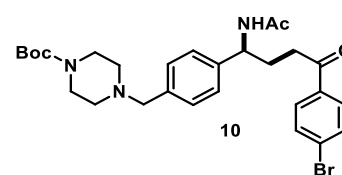
**Mp:** 160 - 163 °C

**R<sub>f</sub> value** = 0.1 [EtOAc:Petroleum ether = 1:1 (v/v)].

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 7.77 (d, *J* = 8.7 Hz, 2H), 7.58 (d, *J* = 8.6 Hz, 2H), 7.29 – 7.25 (m, 4H), 6.09 (d, *J* = 8.4 Hz, 1H), 5.03 (td, *J* = 8.6, 6.1 Hz, 1H), 3.47 (s, 2H), 3.43 – 3.38 (m, 4H), 3.05 (ddd, *J* = 17.9, 7.6, 6.5 Hz, 1H), 2.94 (td, *J* = 7.5, 1.2 Hz, 1H), 2.38 – 2.33 (m, 4H), 2.29 (dd, *J* = 7.7, 1.0 Hz, 1H), 2.17 (dd, *J* = 13.3, 7.0 Hz, 1H), 1.92 (s, 3H), 1.44 (s, 9H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 199.1, 169.7, 154.9, 140.8, 137.4, 135.5, 132.1, 129.6, 129.7, 128.6, 126.6, 79.7, 77.5, 76.8, 62.7, 53.2, 52.9, 35.7, 23.0, 28.5, 23.5.

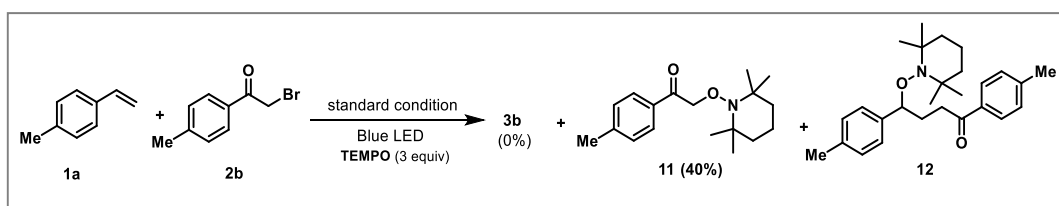
**HRMS (ESI) *m/z* calcd for C<sub>28</sub>H<sub>37</sub>BrN<sub>3</sub>O<sub>4</sub> [M+H]<sup>+</sup>:** 558.1967; found: 558.1982.



## 6. Controlled experiments and Mechanistic studies:

### 6.1. Radical inhibition experiment:

To explore the reaction mechanism towards the radical pathway a radical trapping experiment was performed with TEMPO (3 equiv.) free radical in the reaction of 4-methylstyrene **1a** (2 equiv.) and 4-methylphenacyl bromide **2b** (1 equiv.) under the standard reaction condition (Scheme 6.1). Surprisingly, no desired product **3b** was observed but a trace of TEMPO adducts **11** was isolated with 40% yield and analyzed by NMR and **12** was detected in GCMS analysis from the crude reaction mixture which demonstrated that the mechanism of this photo-reaction involves the generation of phenacyl radical from **2b**, which coupled with TEMPO to give adduct **11** and existence of another adduct **12** suggests that the benzyl radical species is the intermediate of this reaction.



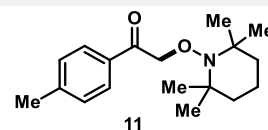
**Reaction procedure:** A flame dried culture tube equipped with a magnetic stirring bar was charged with 4CzIPN (3 mg, 2 mol %), 4-methylphenacyl bromide **2b** (42 mg, 0.2 mmol), Zn(OAc)<sub>2</sub> (21 mg, 0.1 mmol) and dry acetonitrile (1 mL). The tube was sealed with a Teflon screw cap, evacuated and backfilled with argon, before styrene **1a** (40 μL, 0.3 mmol) and TEMPO free radical (94 mg, 0.6 mmol) was added to it. Then the reaction mixture was degassed by Freeze-Pump-Thaw cycles with argon and irradiated at room temperature with 12 W blue LED bulb at a distance of approximately 5 cm. A high-speed fan was used to maintain the temperature. After 6h no desired carbo-amination product **3b** was formed, a trace amount of the TEMPO adducts **12** were detected in GCMS analysis from the crude reaction mixture. These results suggested that the reaction passes through the radical pathway.

**2-((2,2,6,6-Tetramethylpiperidin-1-yl)oxy)-1-(p-tolyl)ethan-1-one: (11)**<sup>12</sup>

**Yield:** 40% (23mg).

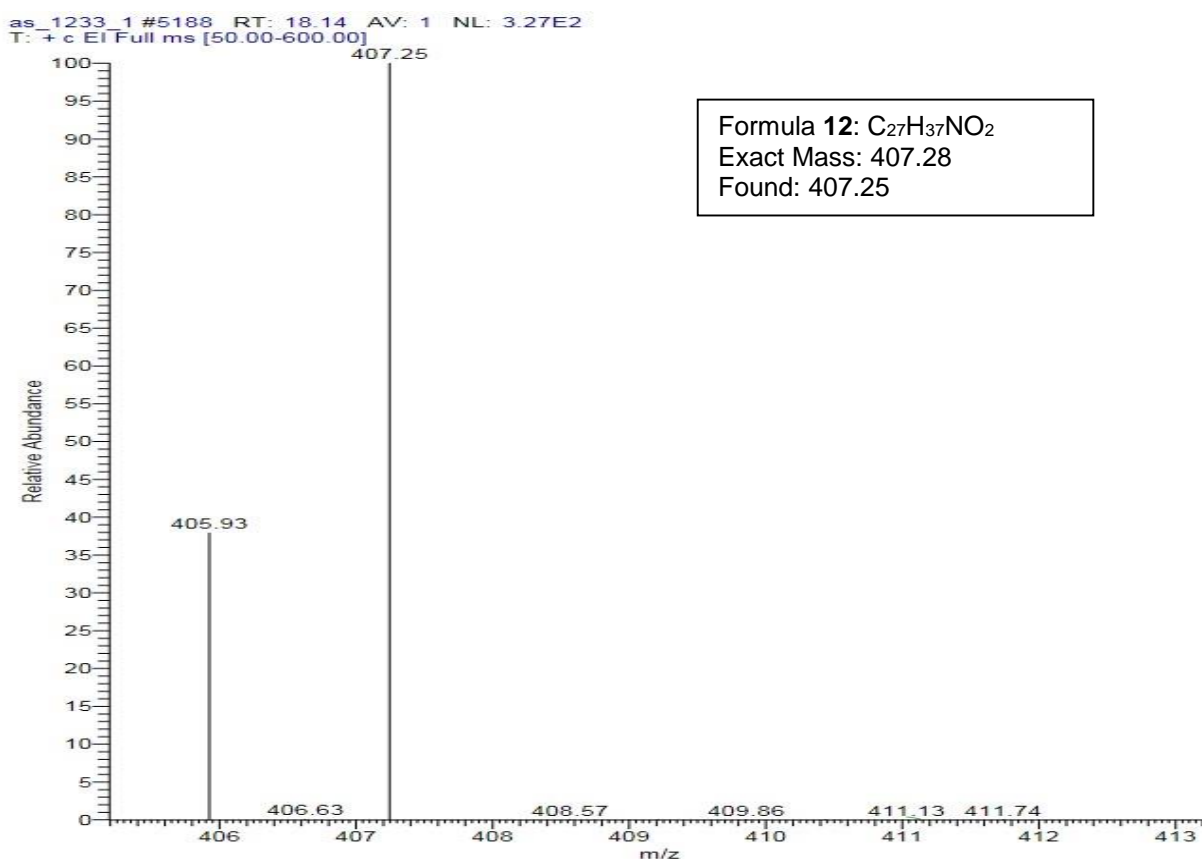
**Nature:** colourless oil.

**Rf value** = 0.5 [EtOAc:Petroleum ether =1:9 (v/v)].



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 7.84 (d, *J* = 8.2 Hz, 2H), 7.27 – 7.23 (m, 2H), 5.09 (s, 2H), 2.41 (s, 3H), 1.64 – 1.53 (m, 2H), 1.45 – 1.47 (m, 4.2 Hz, 4H), 1.17 (s, 12H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 195.5, 144.2, 133.0, 129.4, 128.2, 81.4, 60.2, 39.8, 32.9, 21.8, 20.4, 17.2.



**Figure S1.** GCMS spectra of crude reaction mixture (compound **12**)

<sup>12</sup> J.-L. Liu, S.-W. Wu, Q.-Y. Wu, F. Liu, *J. Org. Chem.* **2018**, *83*, 8183–8192.

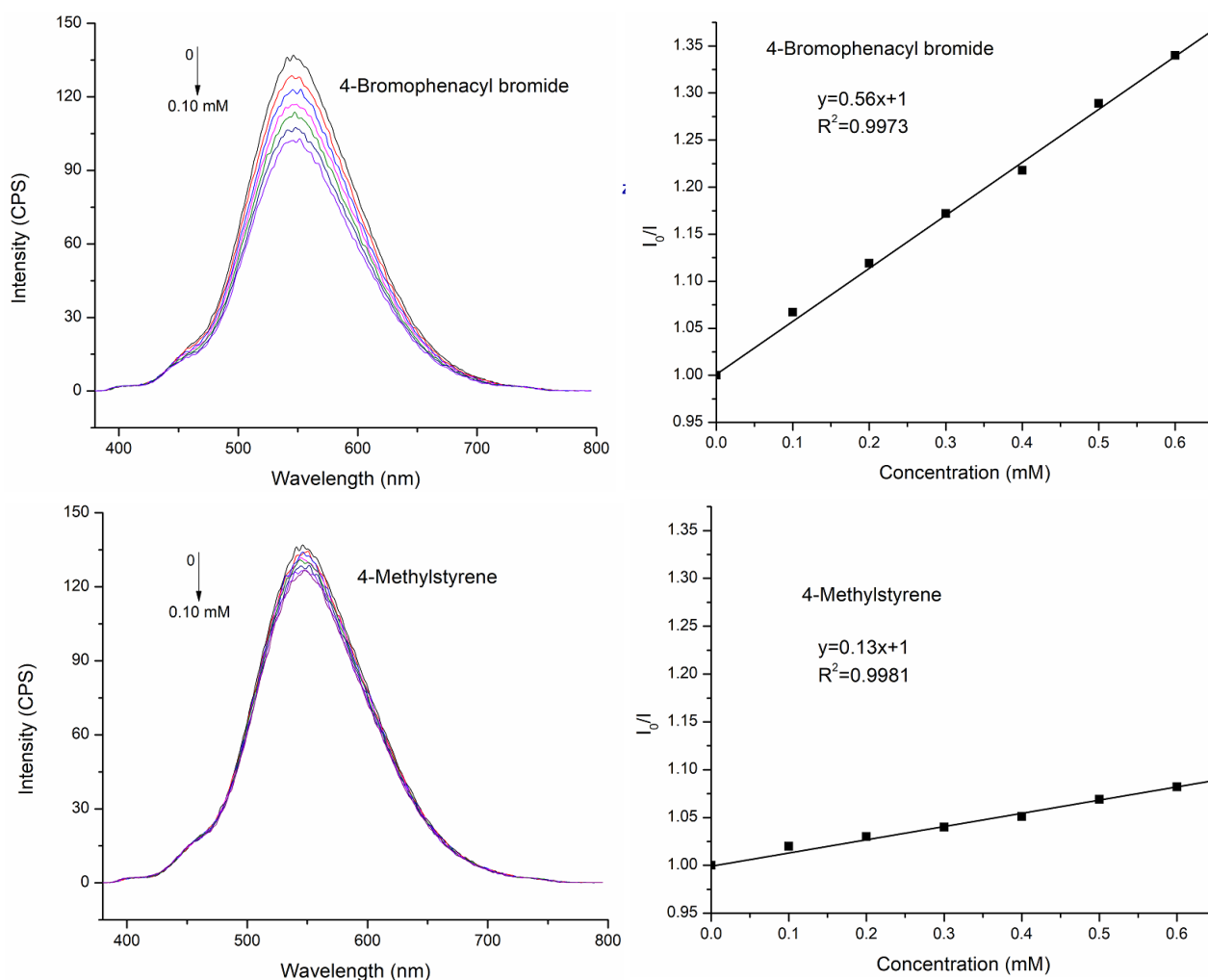
## 6.2. Stern-Volmer Fluorescence Quenching Experiments:

Fluorescence quenching studies were carried out using a PerkinElmer LS 55 Fluorescence Spectrometer and the Stern-Volmer Fluorescence Quenching Experiments were run with a freshly prepared solution of  $5.0 \times 10^{-5}$  M 4CzIPN in degassed anhydrous  $\text{CH}_3\text{CN}$  in 10 mm length quartz cuvette at room temperature. The solutions were irradiated at 378 nm (maximum absorption wavelength of 4CzIPN) and luminescence was measured at 540 nm. Plots were derived according to the Stern-Volmer equation and  $K_{sv}$  calculated.

$$\text{Stern-Volmer equation: } I_0/I = 1 + K_{sv}[Q]$$

Where  $I_0$  is the luminescence intensity without the quencher,  $I$  is the intensity with the quencher,  $[Q]$  is the concentration of added quencher and  $K_{sv}$  is the Stern-Volmer quenching constant.

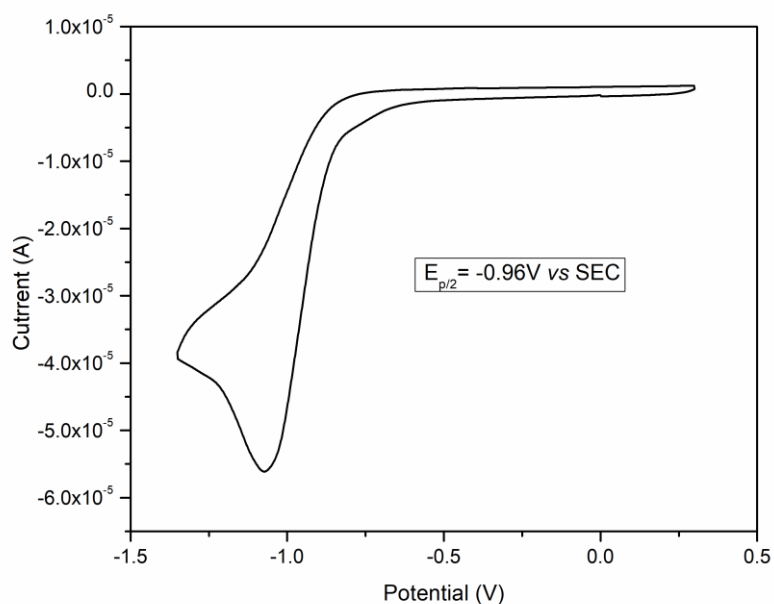
All the emission spectra were recorded after each addition of the quencher. The result of Figure S8 shows a significant change in emission intensity for 4-bromophenacyl bromide than the styrene (calculated  $K_{sv}$  value of 4-bromophenacyl bromide and 4-methylstyrene are  $0.56 \text{ mM}^{-1}$  and  $0.13 \text{ mM}^{-1}$  respectively).



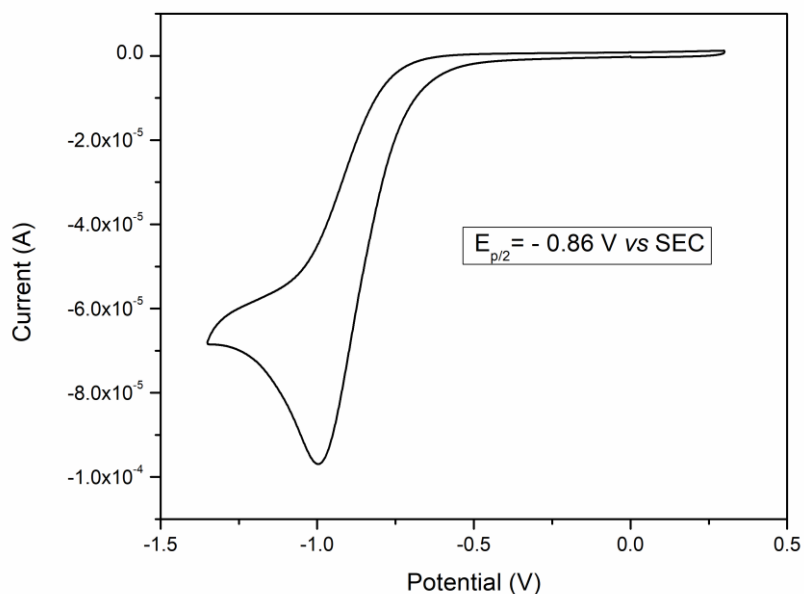
**Figure S2:** Emission spectra and Stern-Volmer plots of 4CzIPN, quenching with varying concentrations of phenacyl bromide and styrene.

### 6.3. Electrochemical Measurements

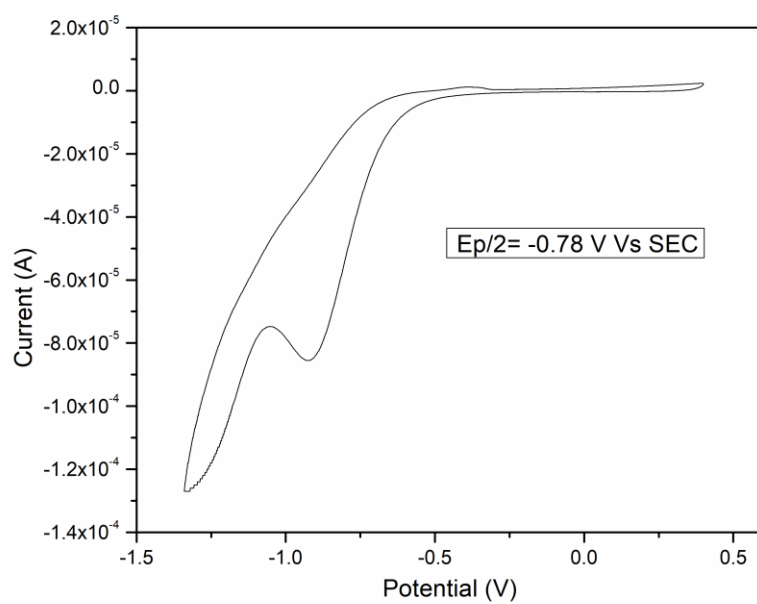
Cyclic Voltammetry was performed using a CH Instruments (model: CHI1140C) using a glassy carbon working electrode, saturated calomel reference electrode and a platinum wire counter electrode. The sample was prepared with 2.0 mmol of a substrate in 5 mL of 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) in dry and degassed acetonitrile. The potential range scanned was normally 0.2 V and -2.2 V at a scan rate 100 mV/s.  $E_{p/2}$  is given as the half-wave potential for irreversible reduction where the current is equal to one-half the peak current of the reduction event.



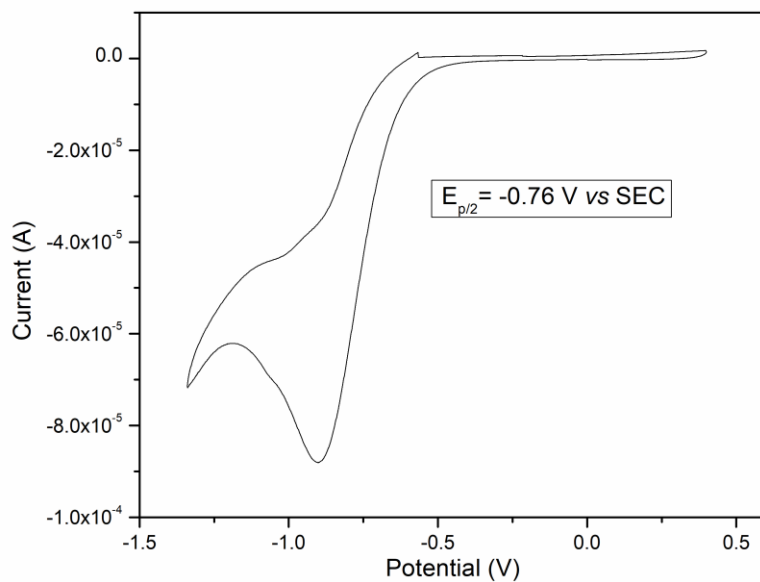
**Figure S3:** Cyclic voltammogram of 4-bromophenacyl bromide (**2g**)



**Figure S4:** Cyclic voltammogram of 4-bromophenacyl bromide (**2g**) and Zn(OAc)<sub>2</sub>.



**Figure S5:** Cyclic voltammogram of 4-bromophenacyl bromide (**2g**) and TFA



**Figure S6:** Cyclic voltammogram of 4-bromophenacyl bromide (**2g**), TFA and Zn(OAc)<sub>2</sub>.

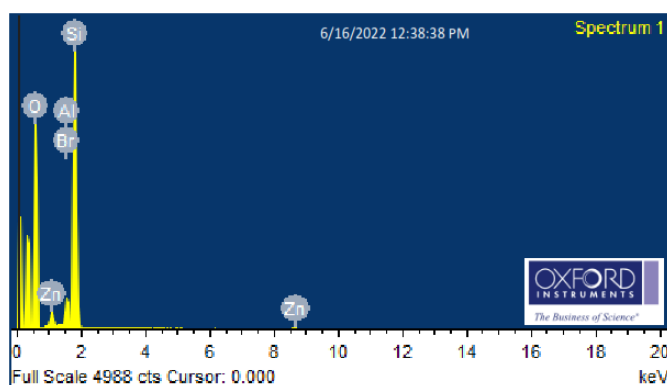
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#### 6.4. Analysis with Aqueous Extract of Crude Reaction Mixture

After completion of the photo-amination reaction, the crude reaction mixture was extracted with ethyl acetate and water. The water extract was evaporated in rotary under heat and then dried by a high vacuum pump with temperature to get an off-white solid. The solid material is highly hygroscopic and transformed into liquid upon exposure to air. All the following experiments were conducted with this crude solid.

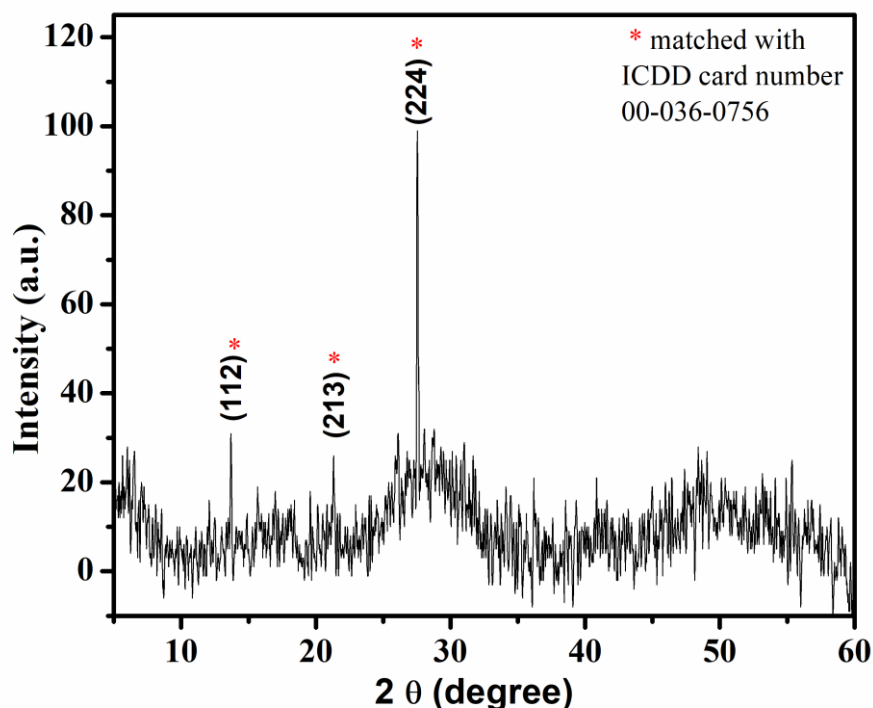
##### a) Energy dispersive X-ray (EDX) analysis:

As the material is highly hygroscopic, the EDX analysis was conducted by mixing the crude solid with dry silica gel. As extra elements (O, Si, and Al) are from silica gel, the spectrum indicates the presence of Zn and Br in the crude solid.

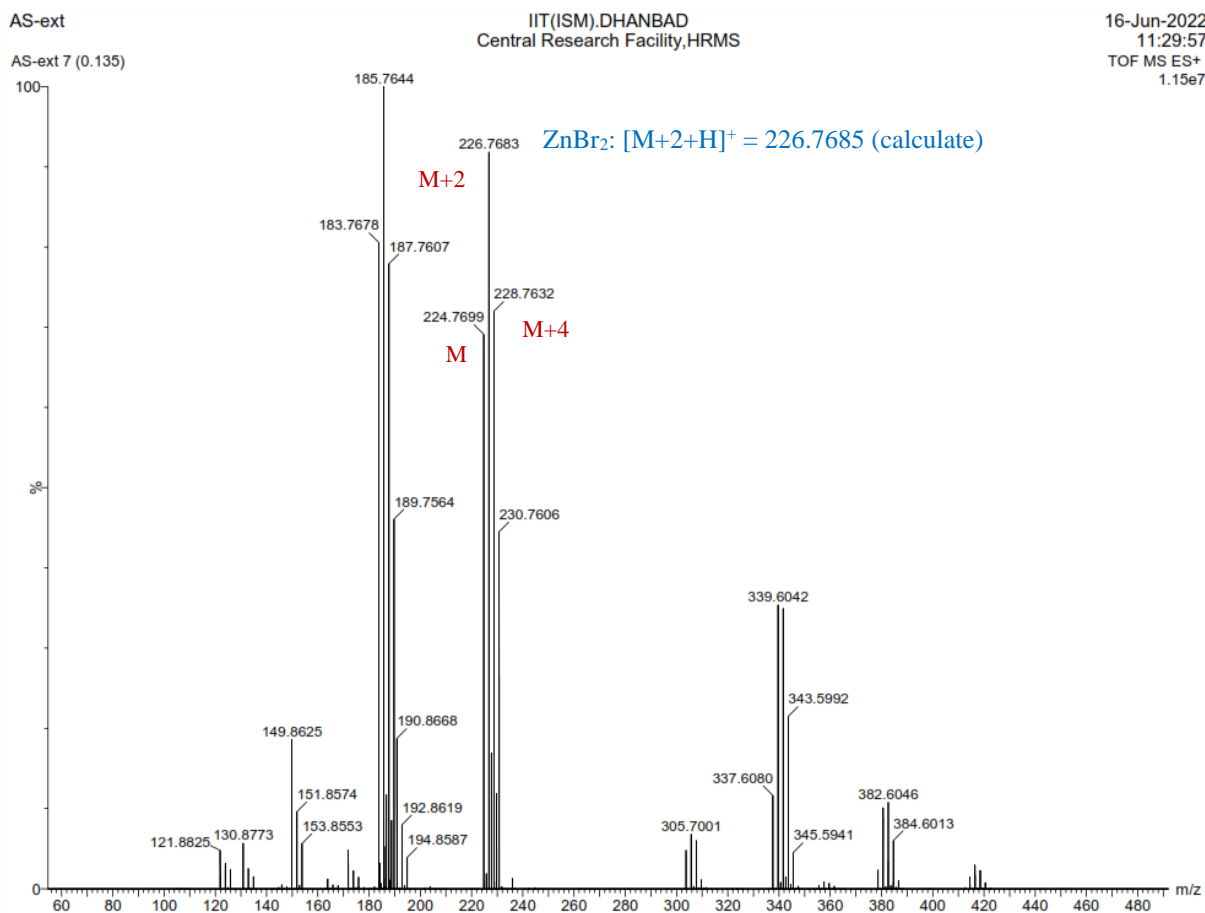


##### b) Powder X-Ray Diffraction (PXRD) analysis:

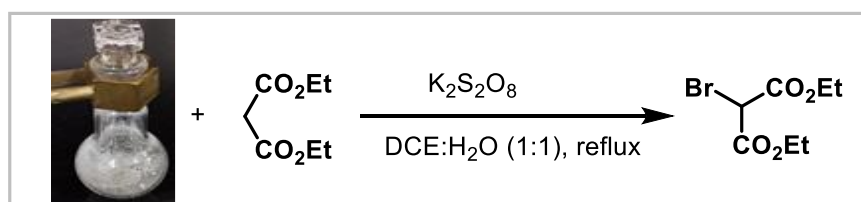
The crude solid was analysed through PXRD analysis to find out its material composition. The obtained pattern was matched with the ICDD database and found to be matched with  $\text{ZnBr}_2$  (card number 00-036-0756). Hence, the presence of  $\text{ZnBr}_2$  in the solid is confirmed.



### c) HRMS analysis



### d) Bromination of Malonate:



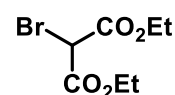
**Reaction Procedure:** To the crude solid (obtained from water extract) (~110 mg, 1 mmol) in 4 mL of co-solvent DCE: H<sub>2</sub>O (1:1), diethyl malonate (40  $\mu$ L, 0.25 mmol), and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (135 mg, 1 mmol) were added. Then the reaction mixture was heated to reflux for 10 h. After that, the reaction mixture was quenched by Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution and was extracted with EtOAc. The combined organic layer was washed with brine solution, dried over MgSO<sub>4</sub>, and concentrated under reduced pressure. Finally, the crude residue was purified by flash column chromatography.

#### Diethyl 2-bromomalonate:

**Yield:** 42% (25 mg).

**Nature:** Colourless oil.

**R<sub>f</sub> value** = 0.3 [EtOAc:Petroleum ether = 1:19 (v/v)].



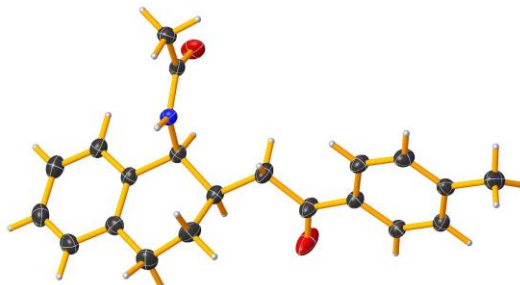


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$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 4.82 (s, 1H), 4.29 (q,  $J = 7.1$  Hz, 4H), 1.31 (t,  $J = 7.1$  Hz, 6H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 164.7, 63.4, 42.5, 14.0.

## 7. X-ray crystal structure and data for Compound 4k.



**Figure S7.** ORTEP plot of compound **4k** with 50% ellipsoid probability.

**Crystal data for 4k:** X-ray single crystal data were collected using  $\text{MoK}\alpha$  ( $\lambda = 0.71073$  Å) radiation on a Rigaku SuperNova diffractometer equipped with an Eos S2 detector. Structure solution/refinement were carried out using Shelx-2013. The structure was solved by direct method and refined in a routine manner. Non-hydrogen atoms were treated anisotropically. All hydrogen atoms were geometrically fixed. CCDC (CCDC No: 2164564) contains the supplementary crystallographic data of **4k**. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

**Table S7: Crystal data and structure refinement for compound 4k.**

Identification code	CCDC 2164564
Empirical formula	$\text{C}_{21}\text{H}_{23}\text{NO}_2$
Formula weight	321.40
Temperature/K	293(2)
Crystal system	monoclinic
Space group	P 21/c
$a/\text{Å}$	9.537(3)
$b/\text{Å}$	19.937(3)
$c/\text{Å}$	9.6171(19)
$\alpha/^\circ$	90
$\beta/^\circ$	95.72(3)
$\gamma/^\circ$	90
Volume/ $\text{Å}^3$	1819.6(7)
Z	4
$\rho_{\text{calc}}/\text{g}/\text{cm}^3$	1.173

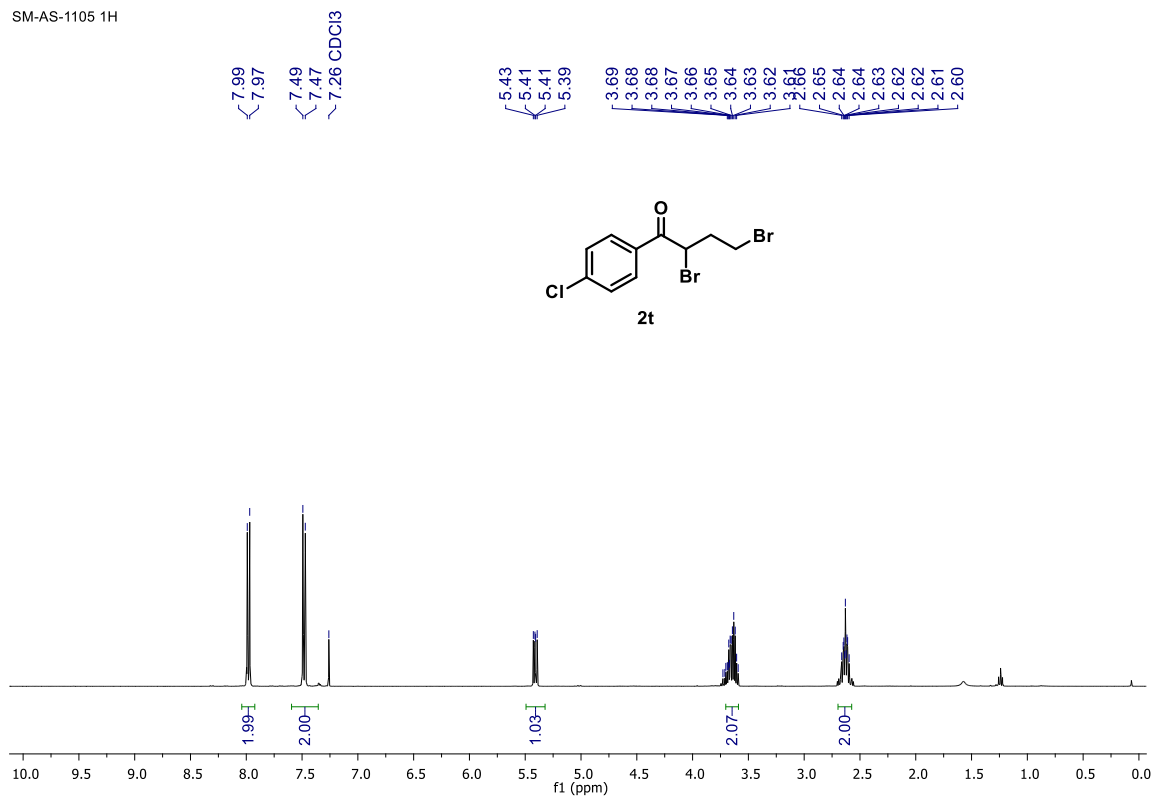
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$\mu/\text{mm}^{-1}$	0.075
F(000)	688.0
h, k, lmax	12, 25, 12
Theta (max)	27.000
R (reflections)	0.0544 ( 2346)
wR2 (reflections)	0.1633 ( 3948)
Radiation	MoK $\alpha$ ( $\lambda = 0.71073$ )

## 8. NMR Spectra

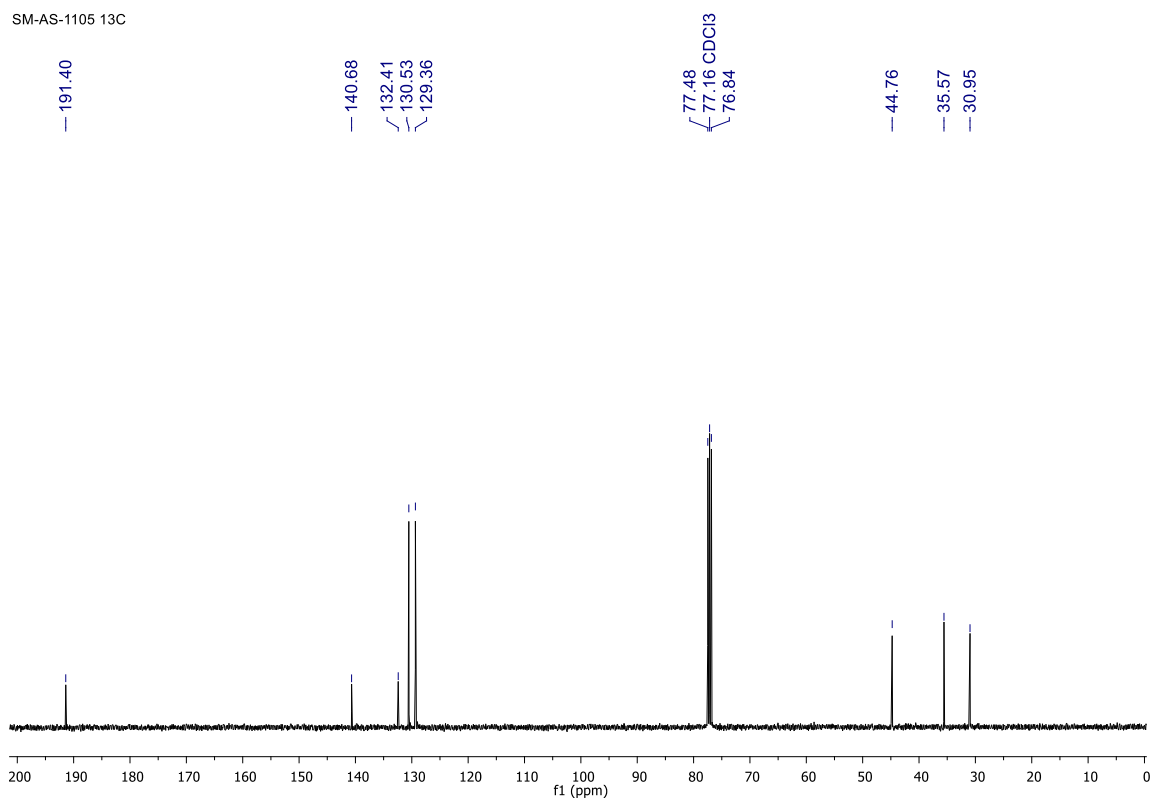
$^1\text{H}$  NMR of **2t** (400 MHz,  $\text{CDCl}_3$ ):

SM-AS-1105 1H



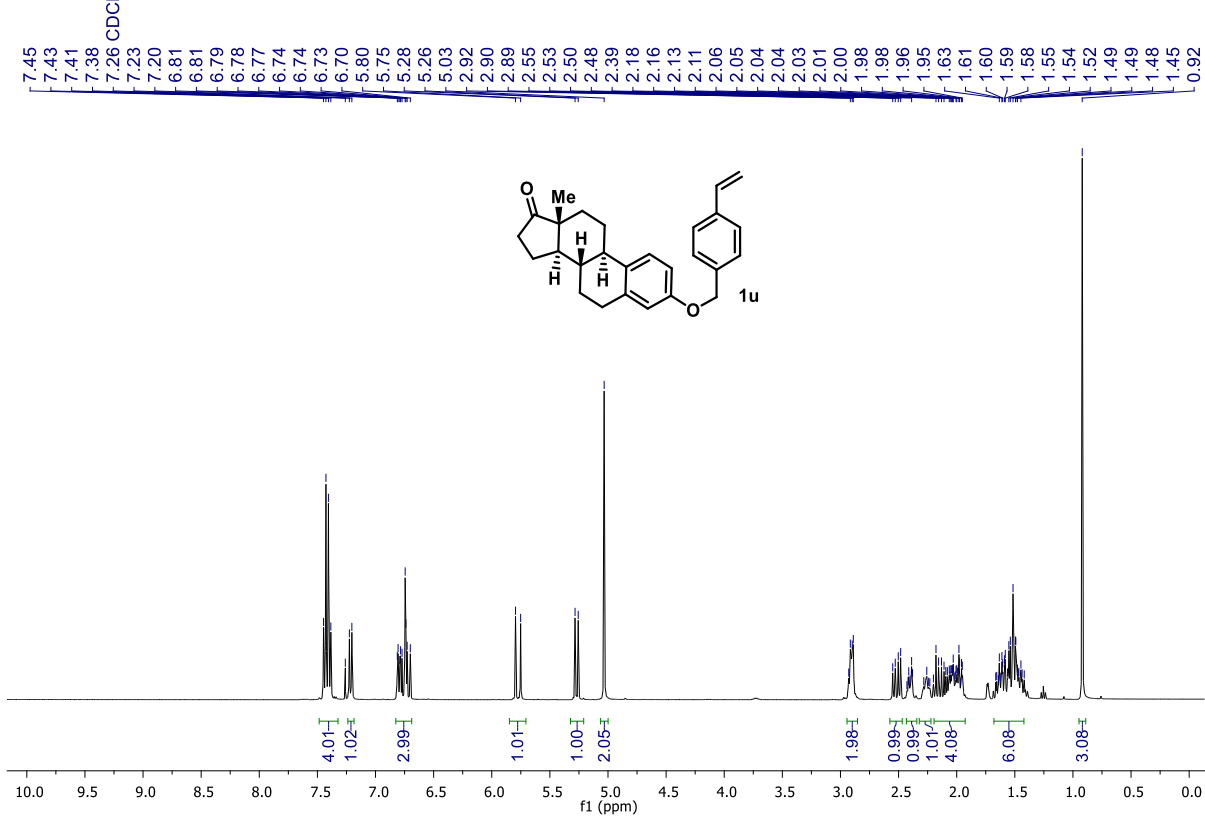
$^{13}\text{C}\{^1\text{H}\}$  NMR of **2t** (101 MHz,  $\text{CDCl}_3$ ):

SM-AS-1105 13C



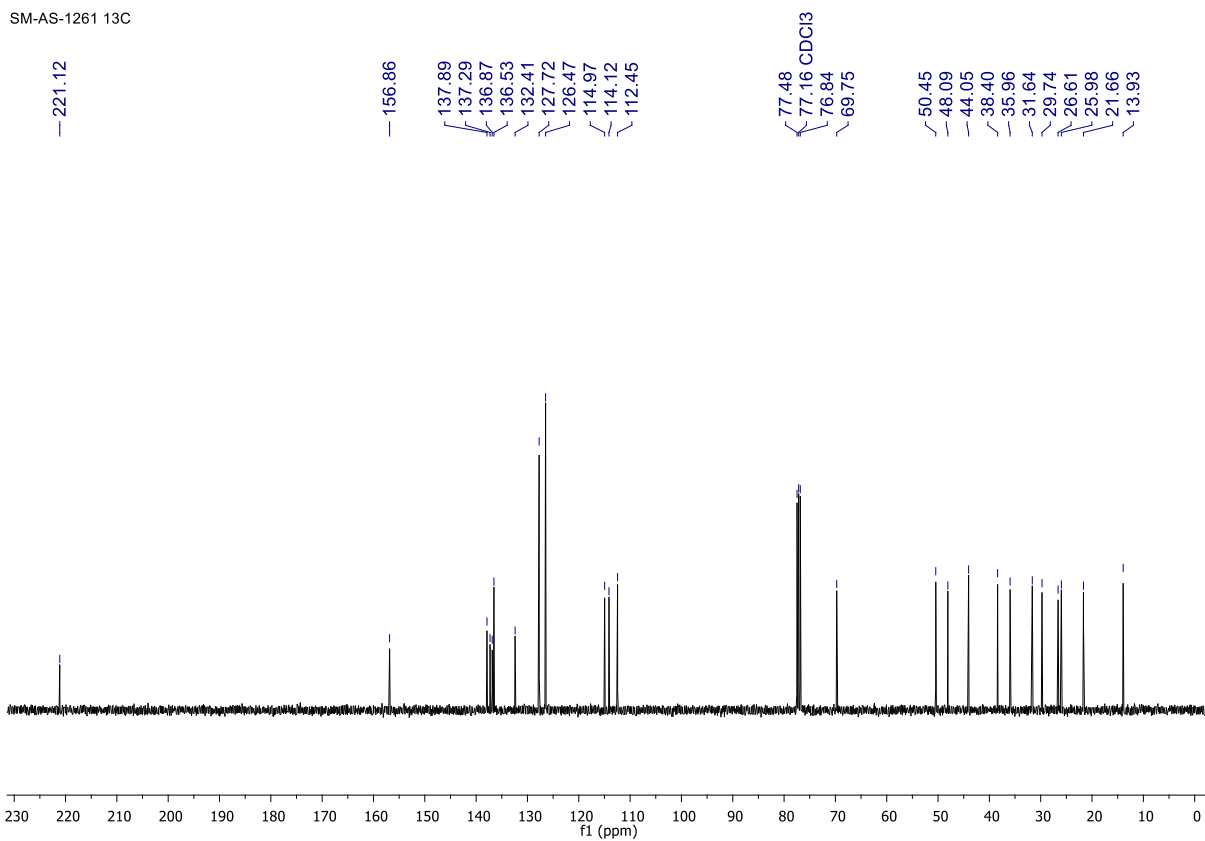
<sup>1</sup>H NMR of **1u** (400 MHz, CDCl<sub>3</sub>):

SM-AS-1261



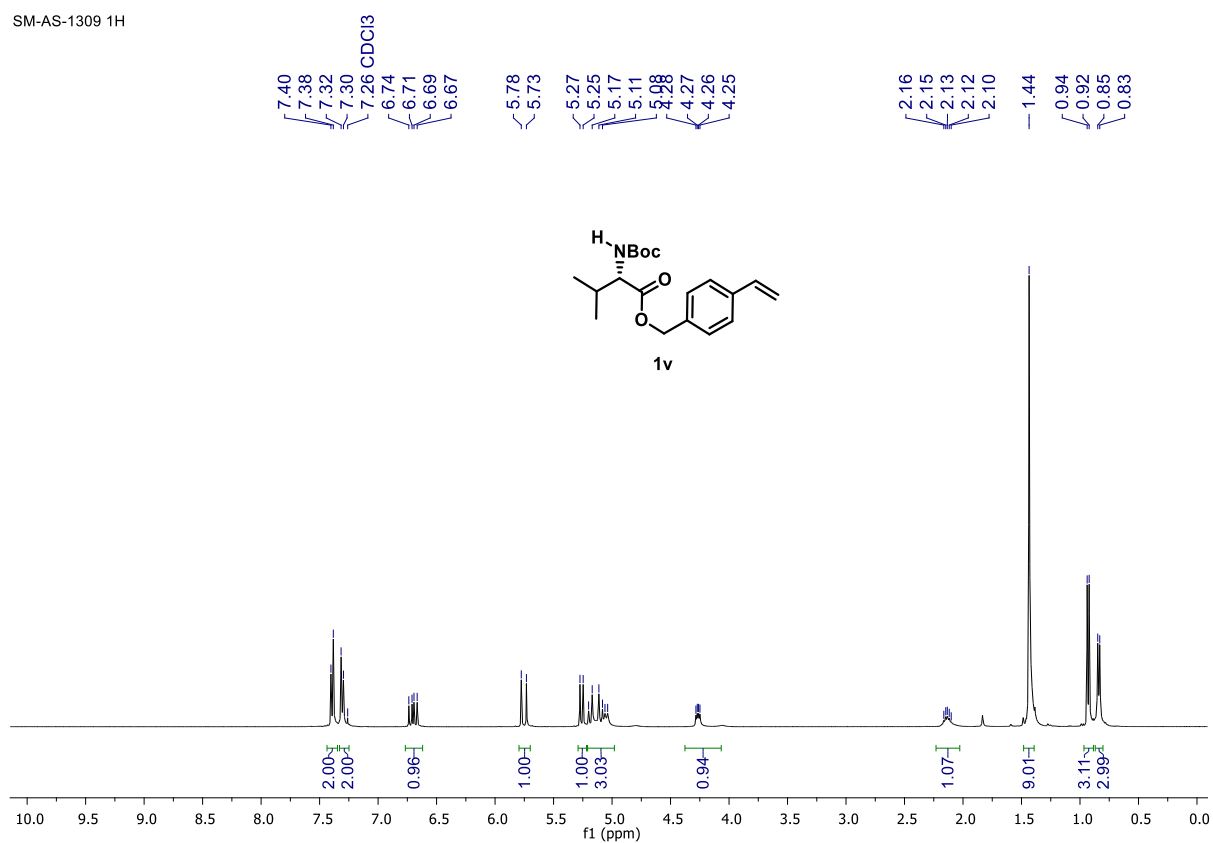
<sup>13</sup>C{<sup>1</sup>H} NMR of **1u** (101 MHz, CDCl<sub>3</sub>):

SM-AS-1261 13C



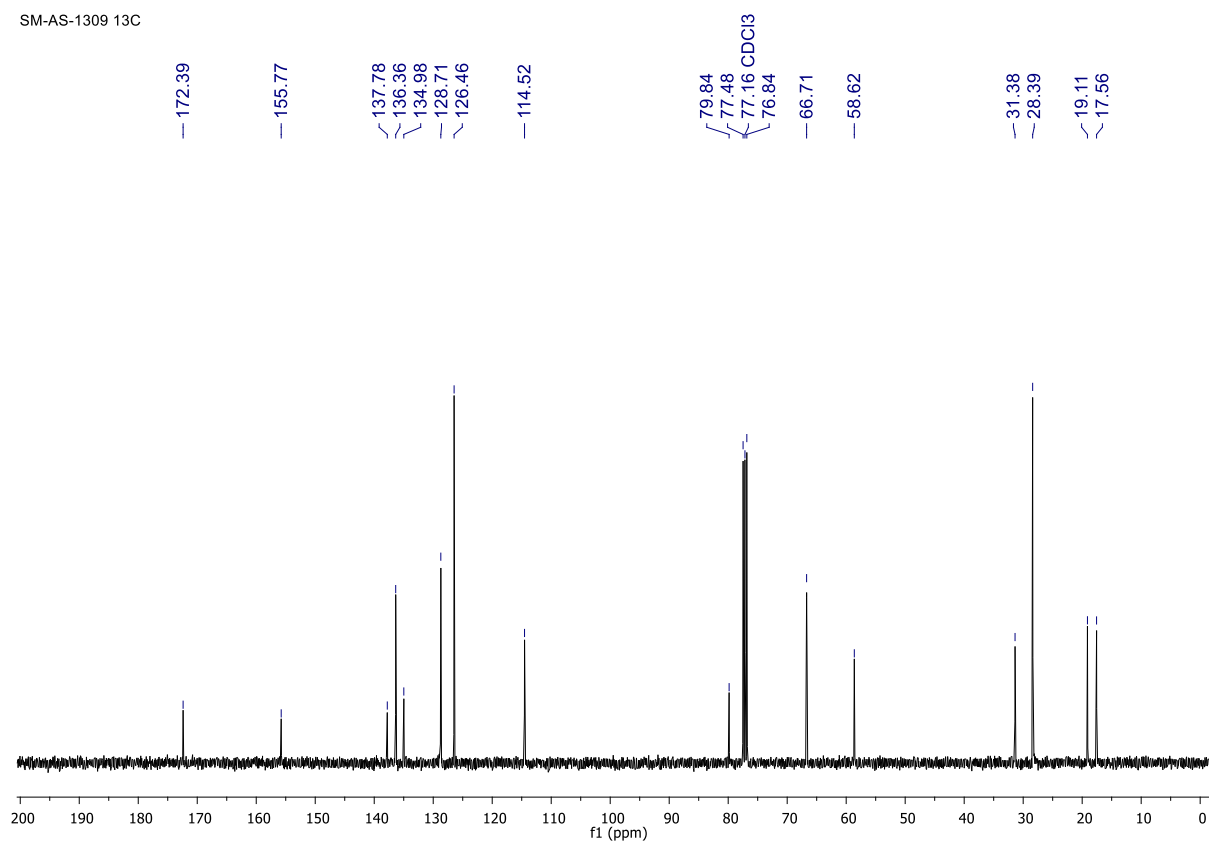
<sup>1</sup>H NMR of **1v** (400 MHz, CDCl<sub>3</sub>):

SM-AS-1309 1H



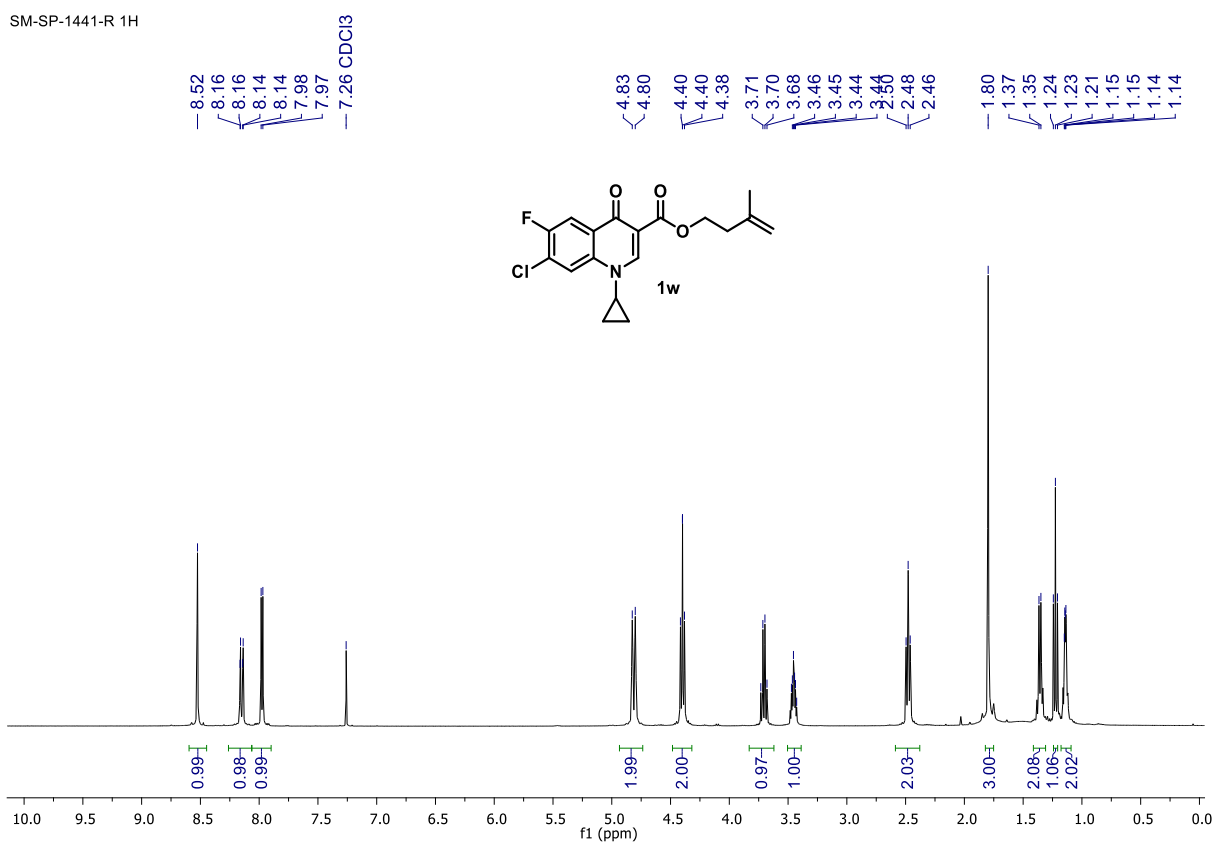
<sup>13</sup>C{<sup>1</sup>H} NMR of **1v** (101 MHz, CDCl<sub>3</sub>):

SM-AS-1309 13C



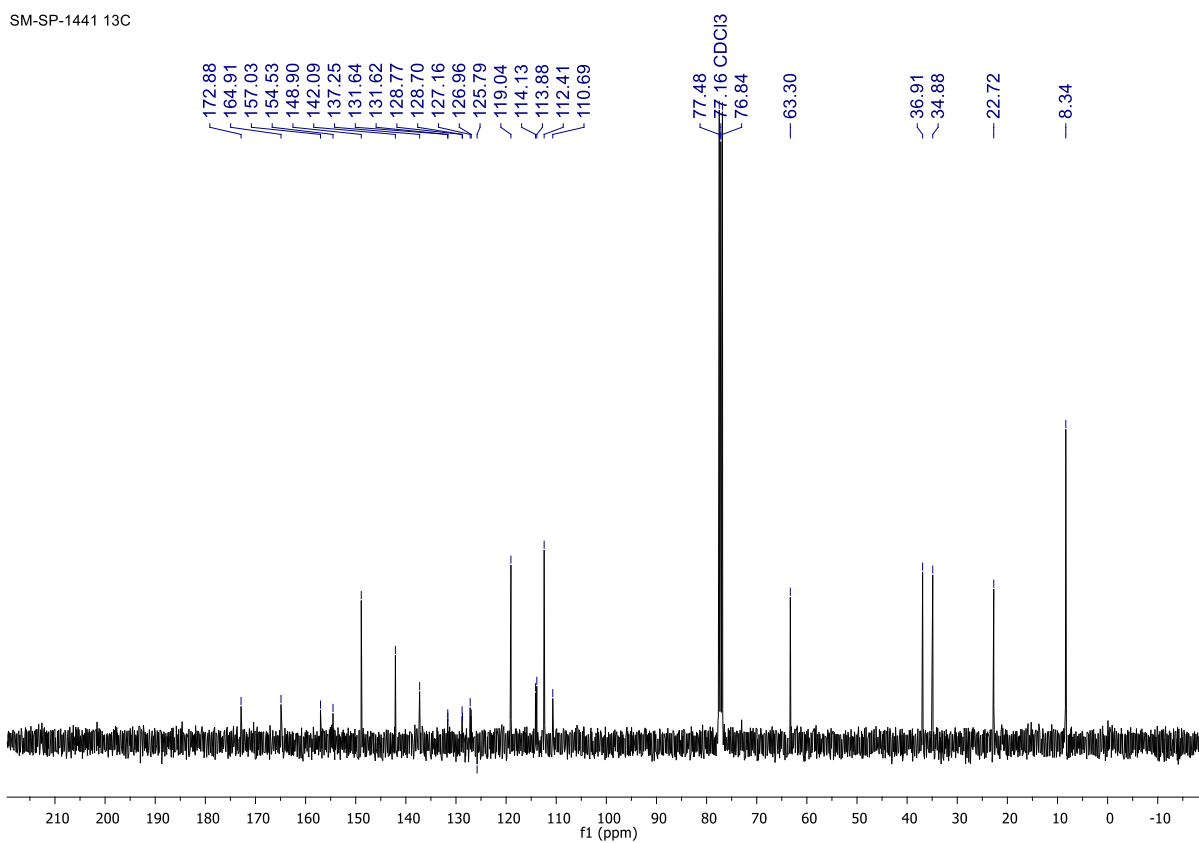
<sup>1</sup>H NMR of **1w** (400 MHz, CDCl<sub>3</sub>):

SM-SP-1441-R 1H



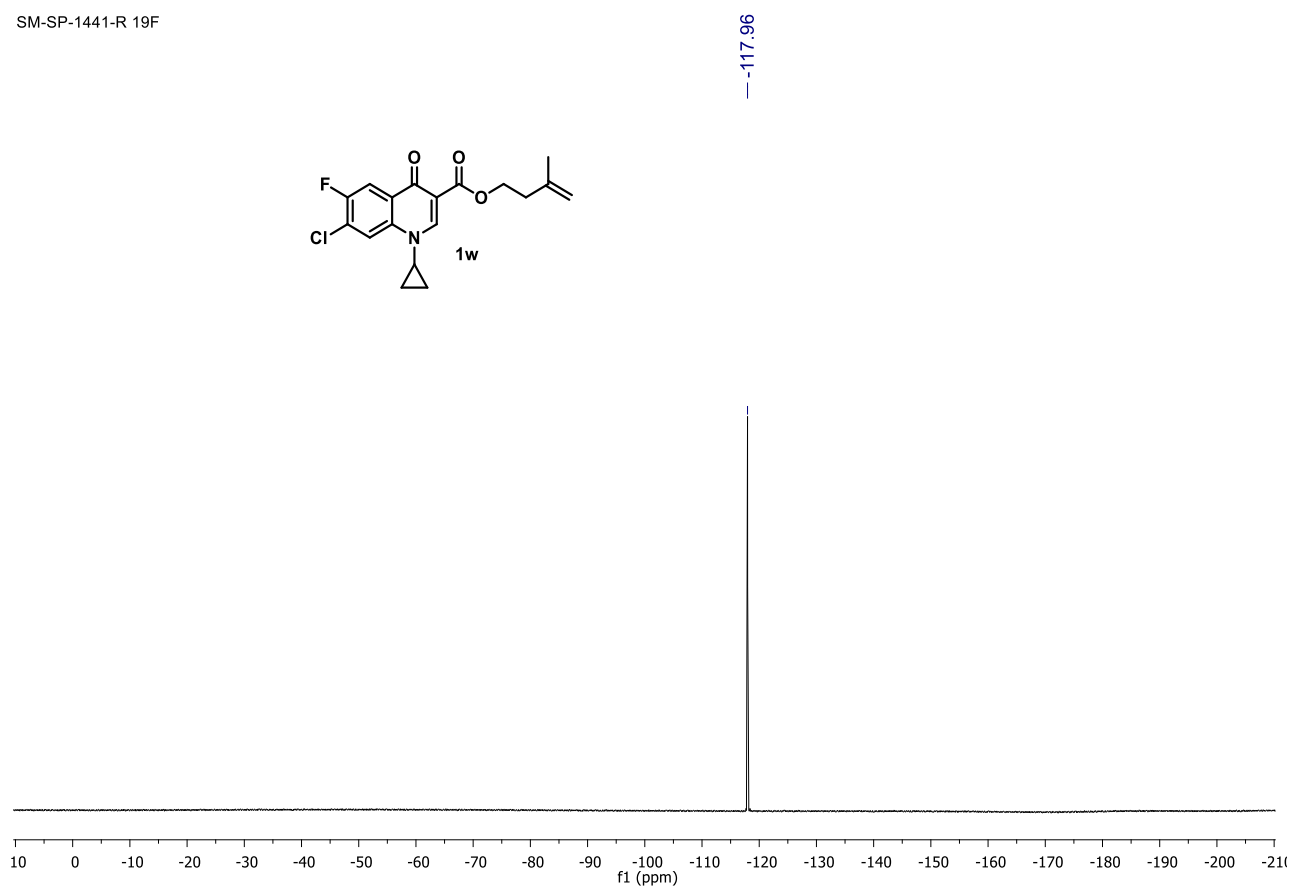
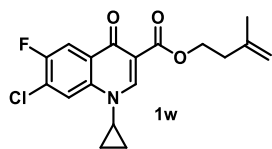
<sup>13</sup>C{<sup>1</sup>H} NMR of **1w** (101 MHz, CDCl<sub>3</sub>):

SM-SP-1441 13C



<sup>19</sup>F NMR of **1w** (377 MHz, CDCl<sub>3</sub>):

SM-SP-1441-R 19F

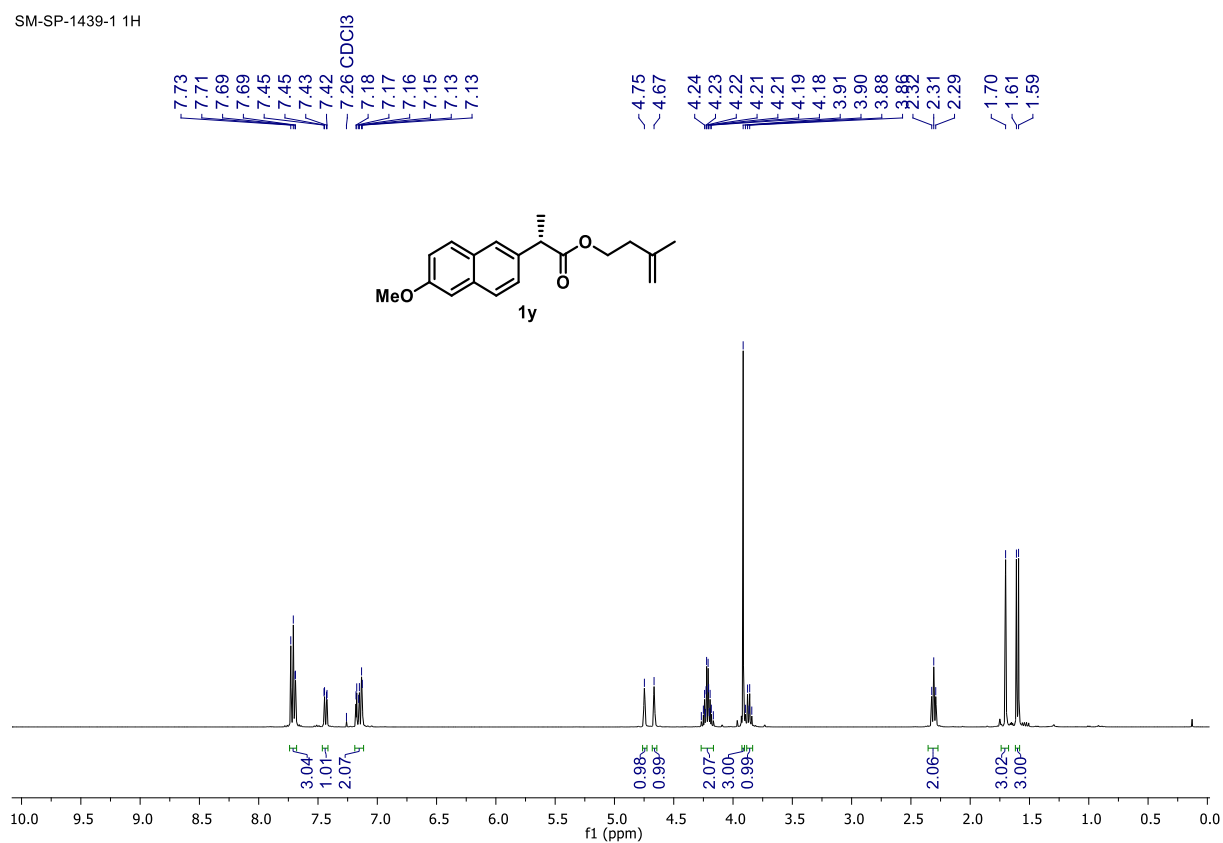






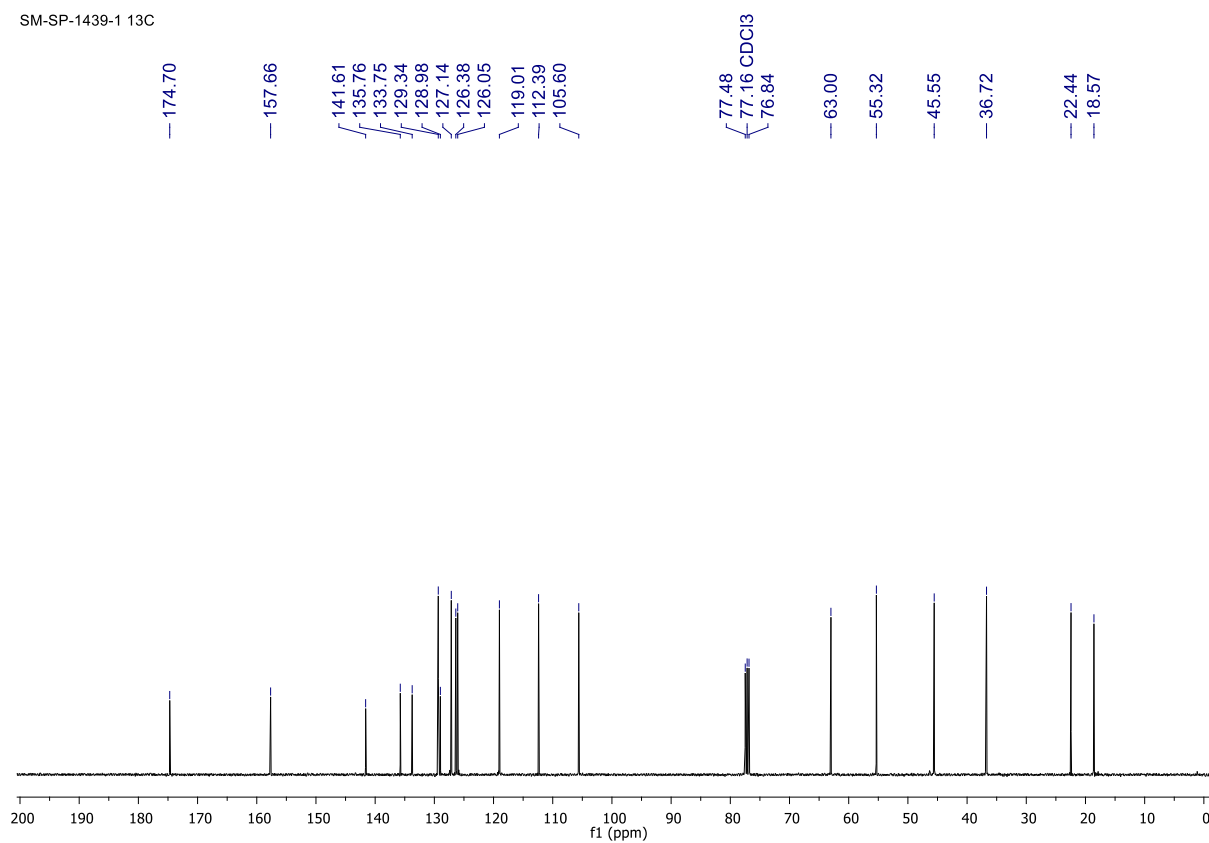
<sup>1</sup>H NMR of **1y** (400 MHz, CDCl<sub>3</sub>):

SM-SP-1439-1 1H



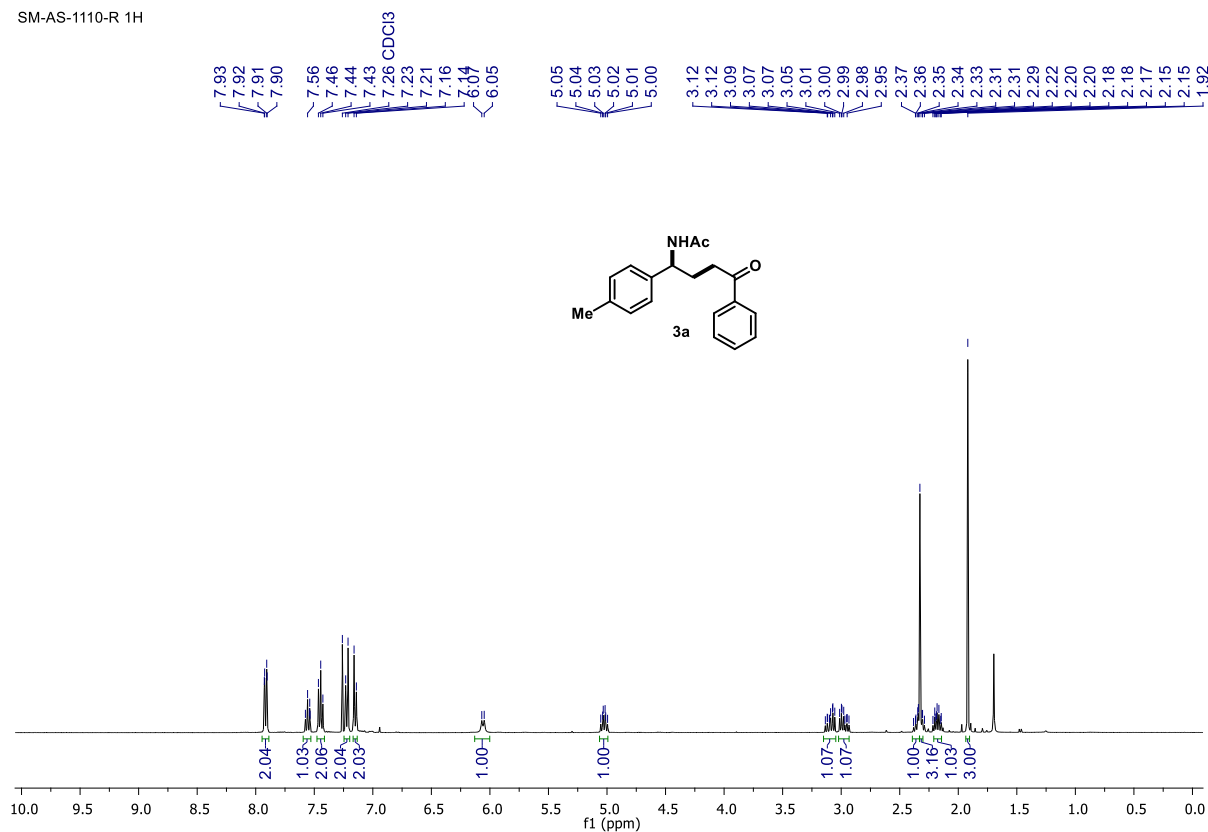
<sup>13</sup>C{<sup>1</sup>H} NMR of **1y** (101 MHz, CDCl<sub>3</sub>):

SM-SP-1439-1 13C



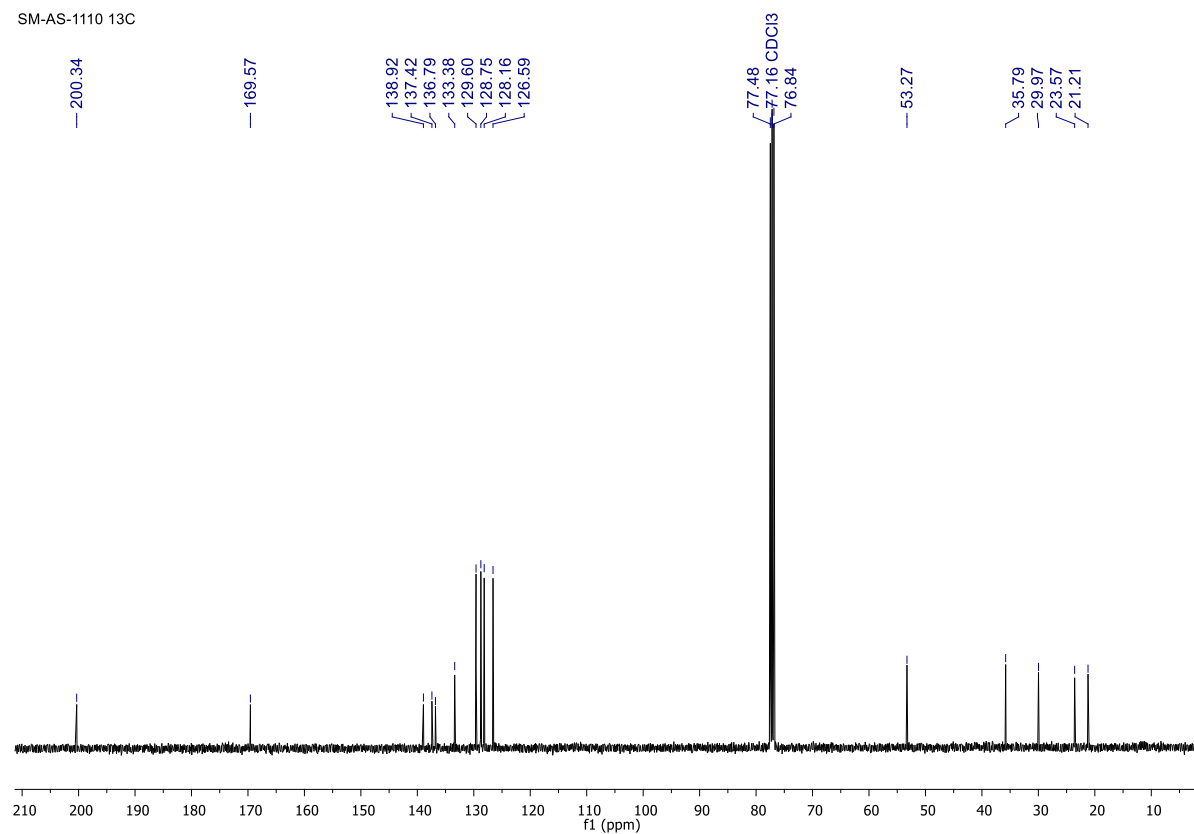
<sup>1</sup>H NMR of **3a** (400 MHz, CDCl<sub>3</sub>):

SM-AS-1110-R 1H



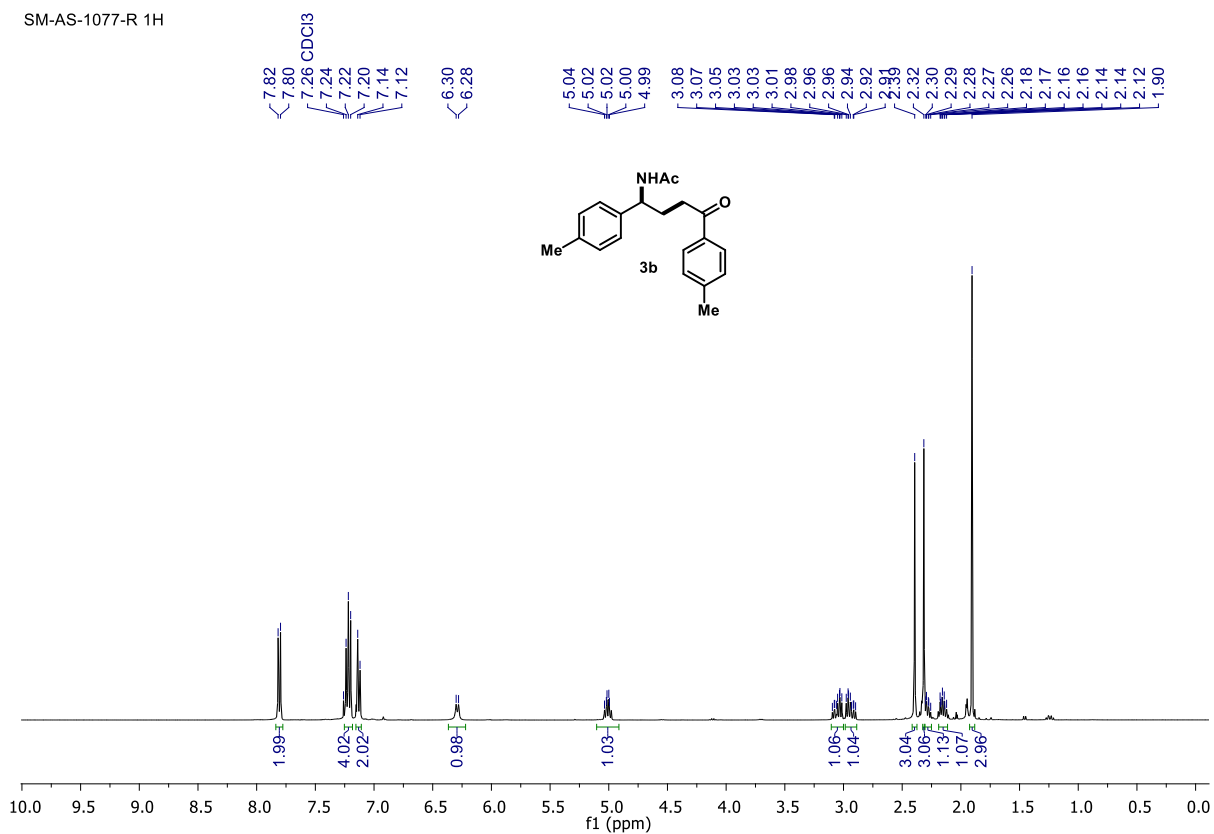
<sup>13</sup>C{<sup>1</sup>H} NMR of **3a** (101 MHz, CDCl<sub>3</sub>):

SM-AS-1110 13C



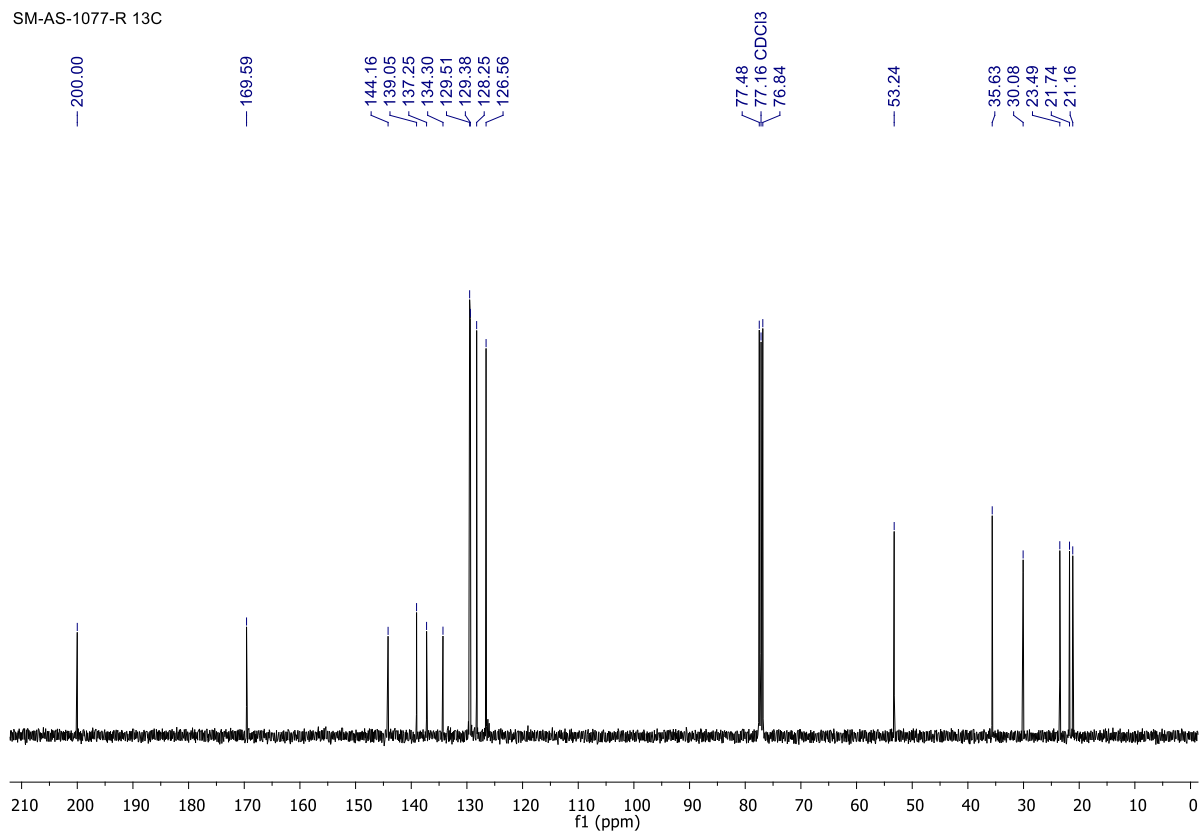
<sup>1</sup>H NMR of **3b** (400 MHz, CDCl<sub>3</sub>):

SM-AS-1077-R 1H



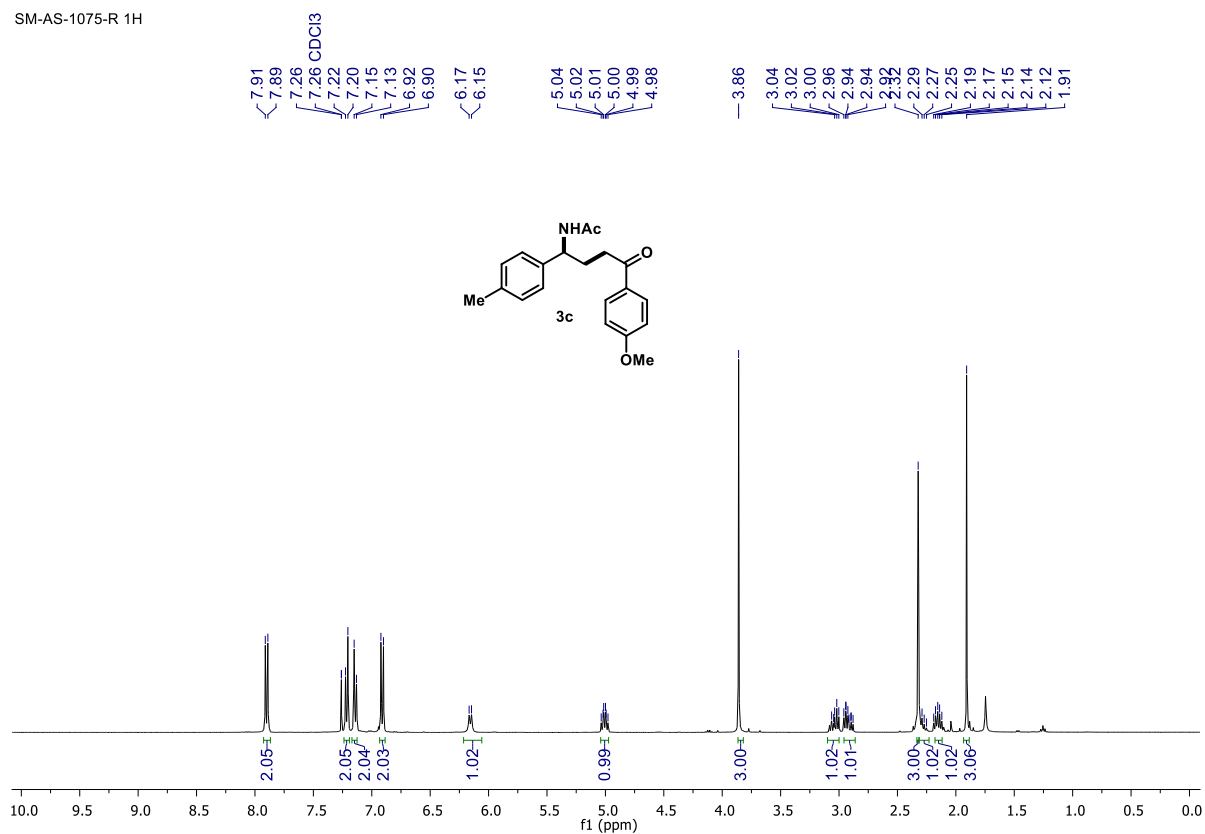
<sup>13</sup>C{<sup>1</sup>H} NMR of **3b** (101 MHz, CDCl<sub>3</sub>):

SM-AS-1077-R 13C



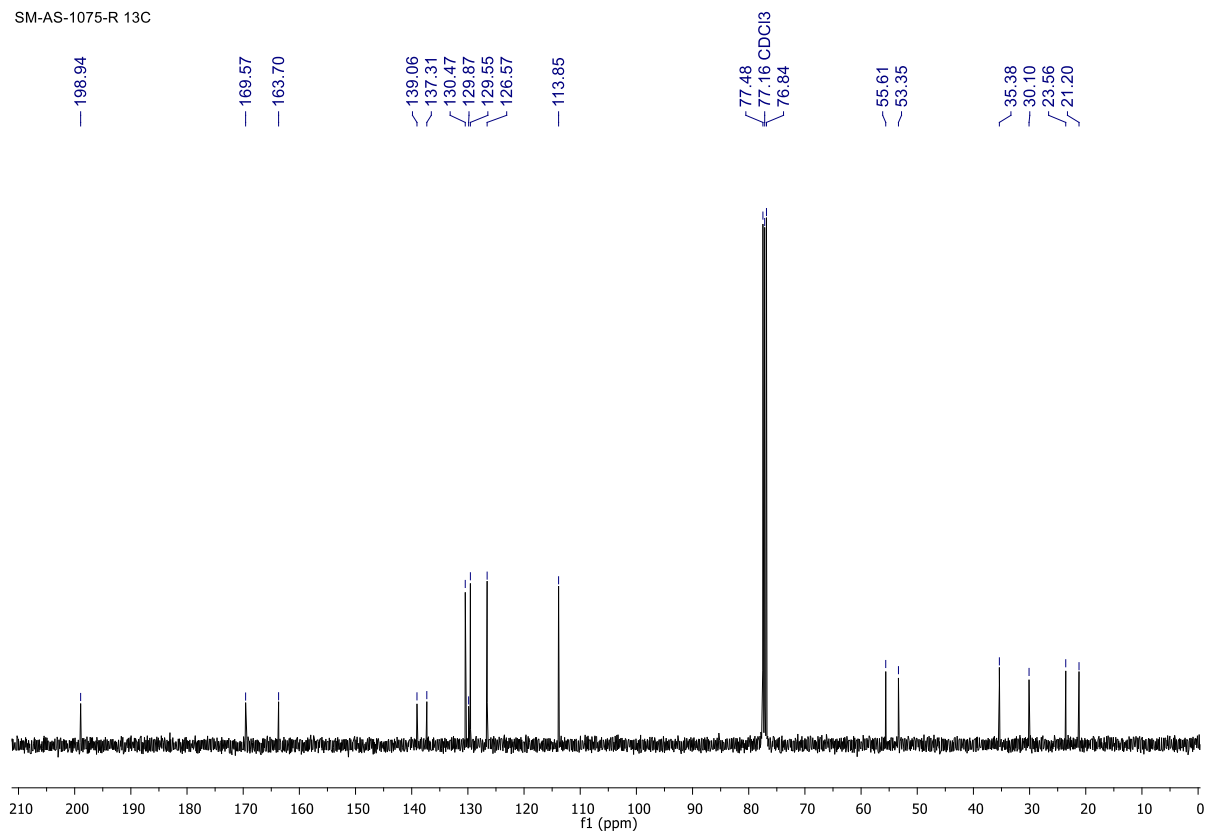
<sup>1</sup>H NMR of **3c** (400 MHz, CDCl<sub>3</sub>):

SM-AS-1075-R 1H



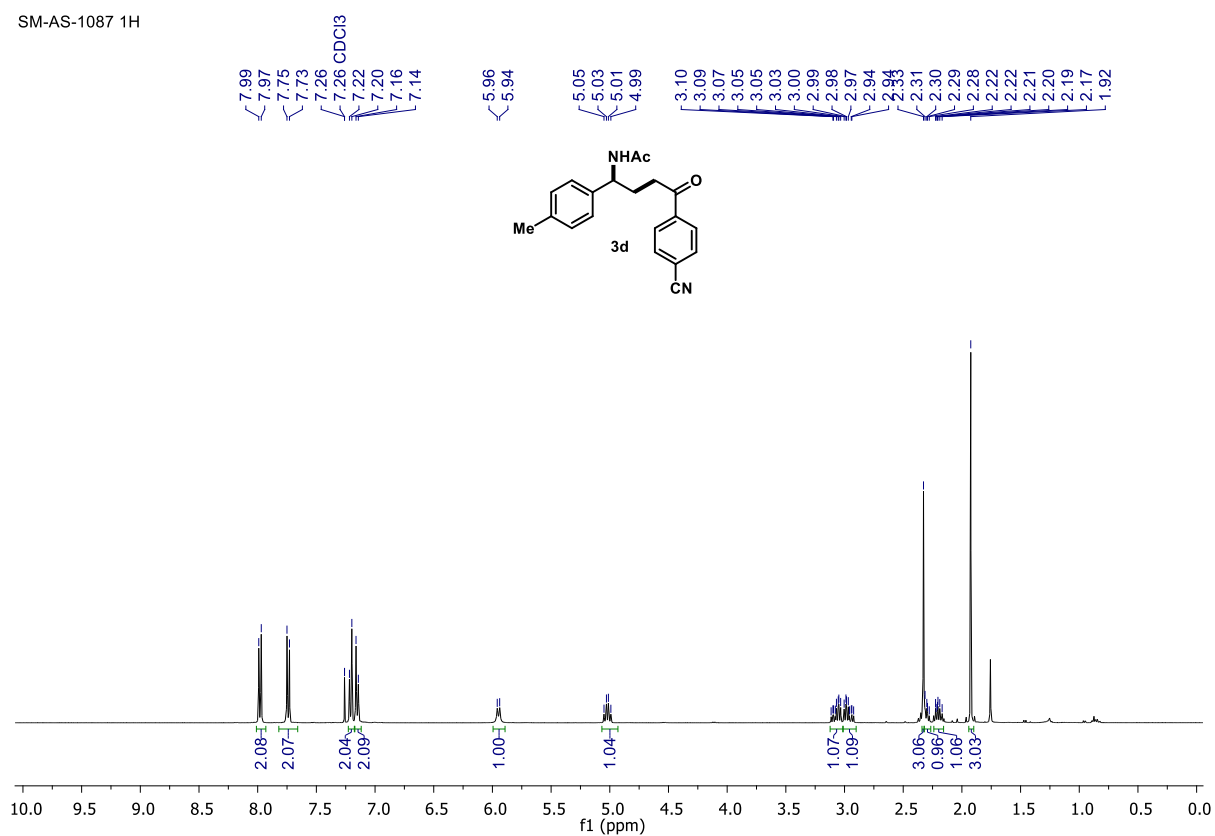
<sup>13</sup>C{<sup>1</sup>H} NMR of **3c** (101 MHz, CDCl<sub>3</sub>):

SM-AS-1075-R 13C



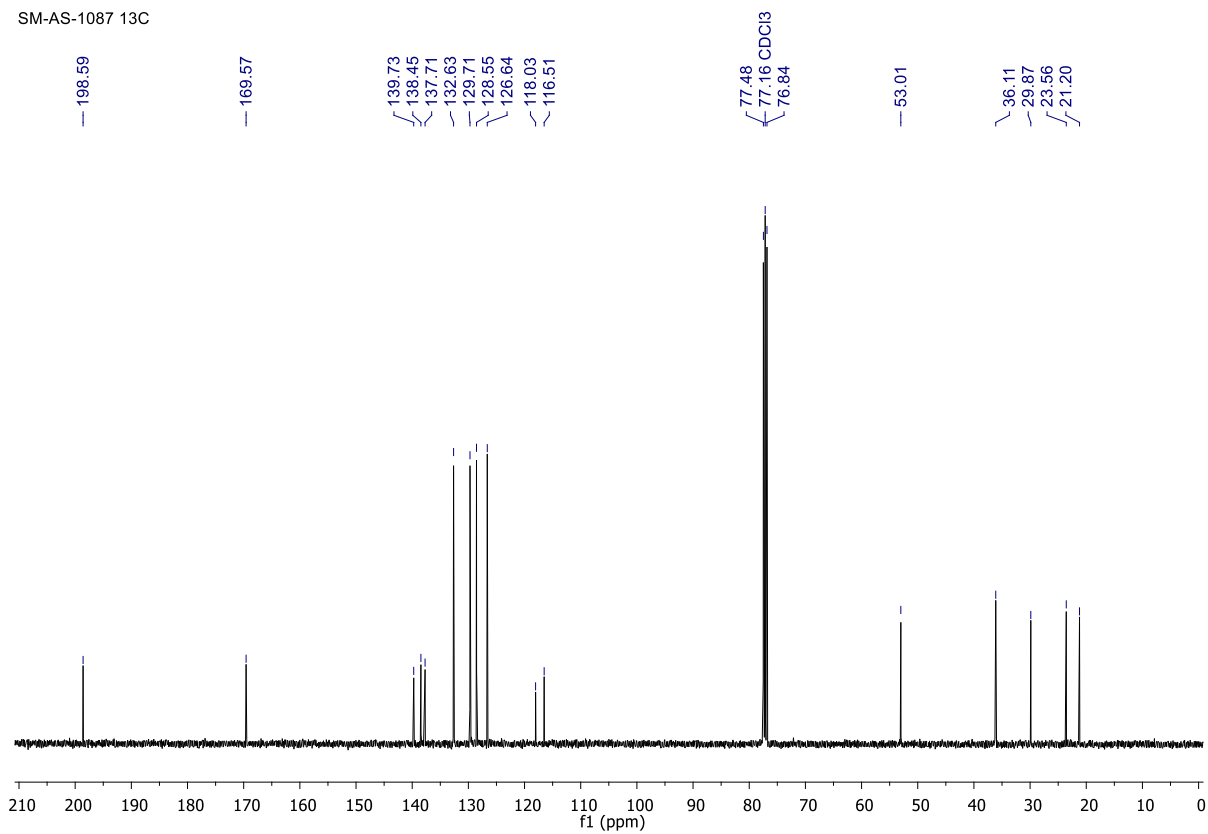
<sup>1</sup>H NMR of **3d** (400 MHz, CDCl<sub>3</sub>):

SM-AS-1087 1H



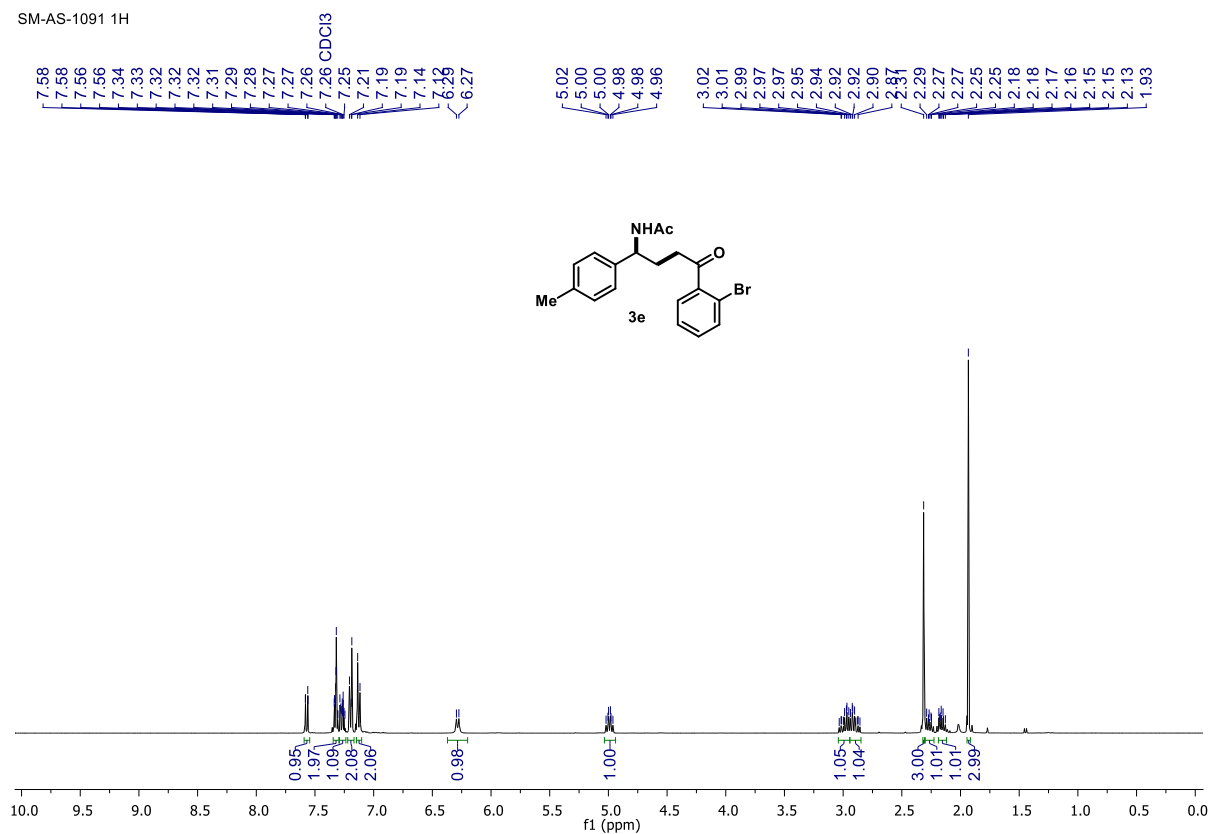
<sup>13</sup>C{<sup>1</sup>H} NMR of **3d** (101 MHz, CDCl<sub>3</sub>):

SM-AS-1087 13C



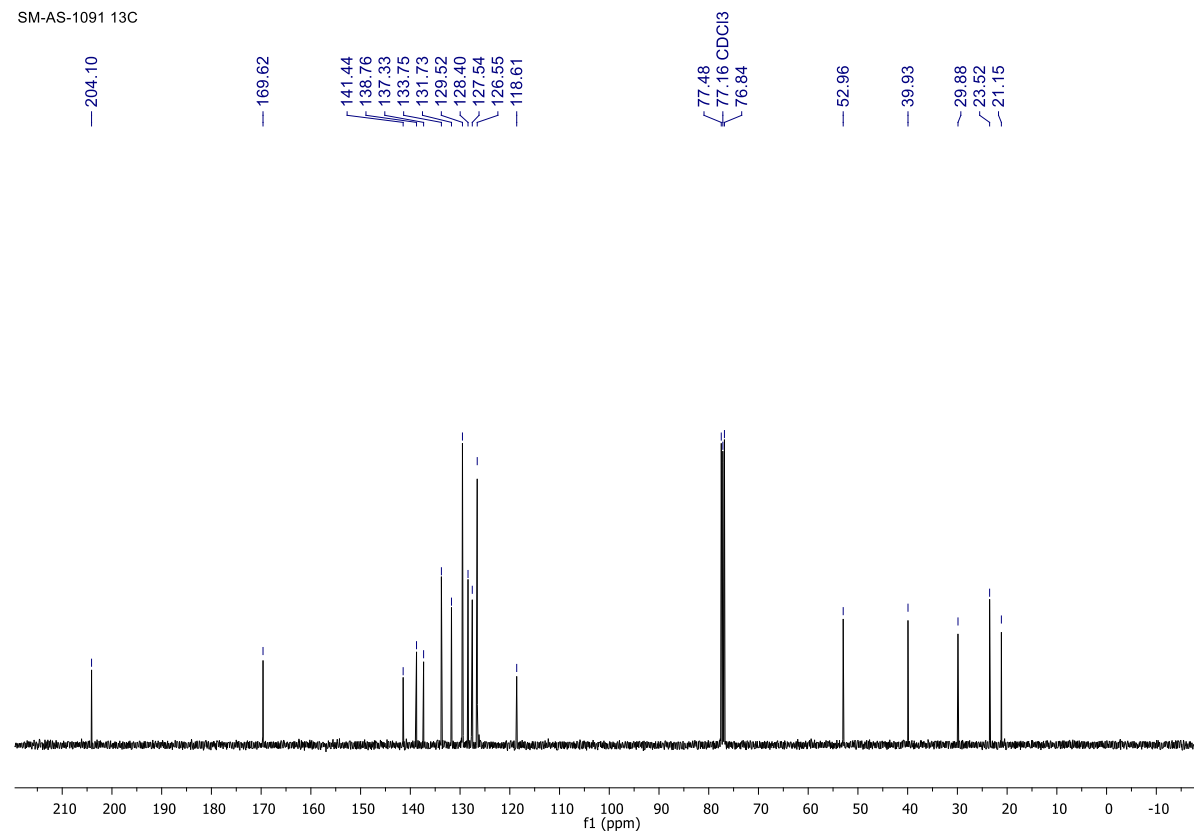
<sup>1</sup>H NMR of **3e** (400 MHz, CDCl<sub>3</sub>):

SM-AS-1091 1H



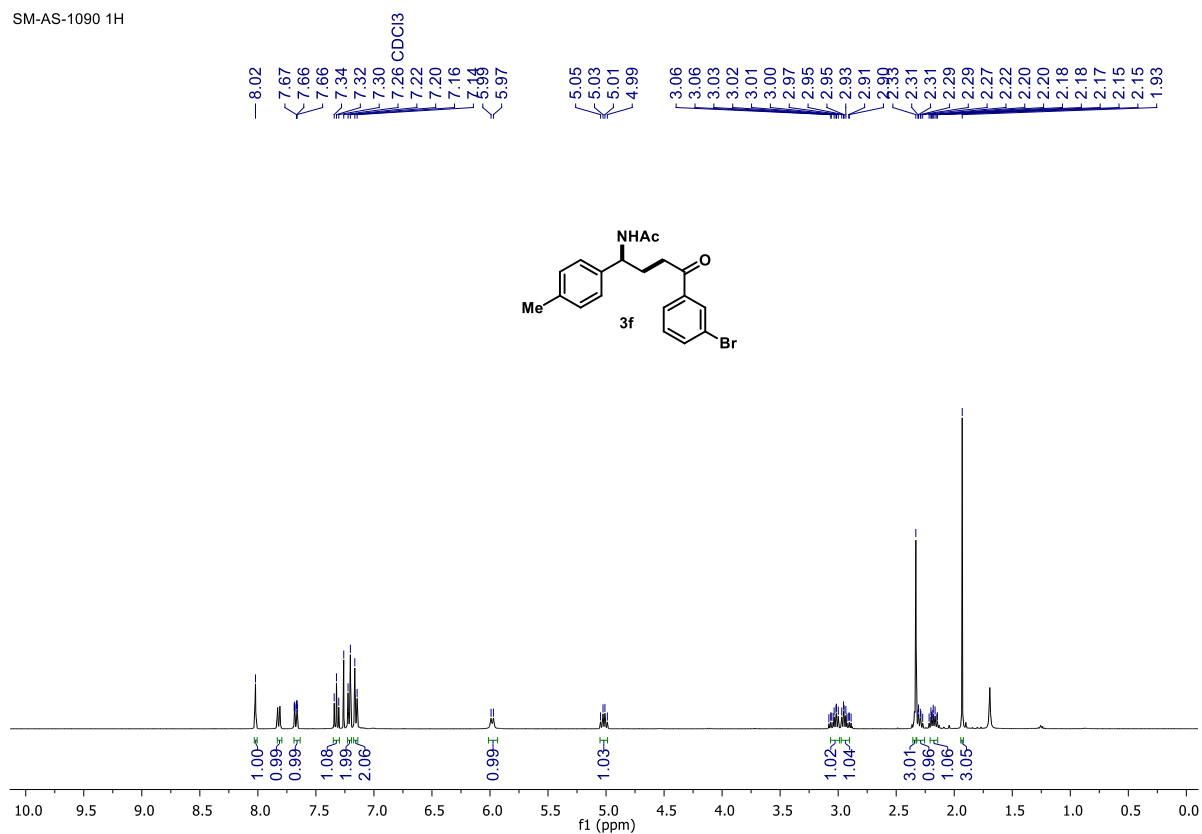
<sup>13</sup>C{<sup>1</sup>H} NMR of **3e** (101 MHz, CDCl<sub>3</sub>):

SM-AS-1091 13C



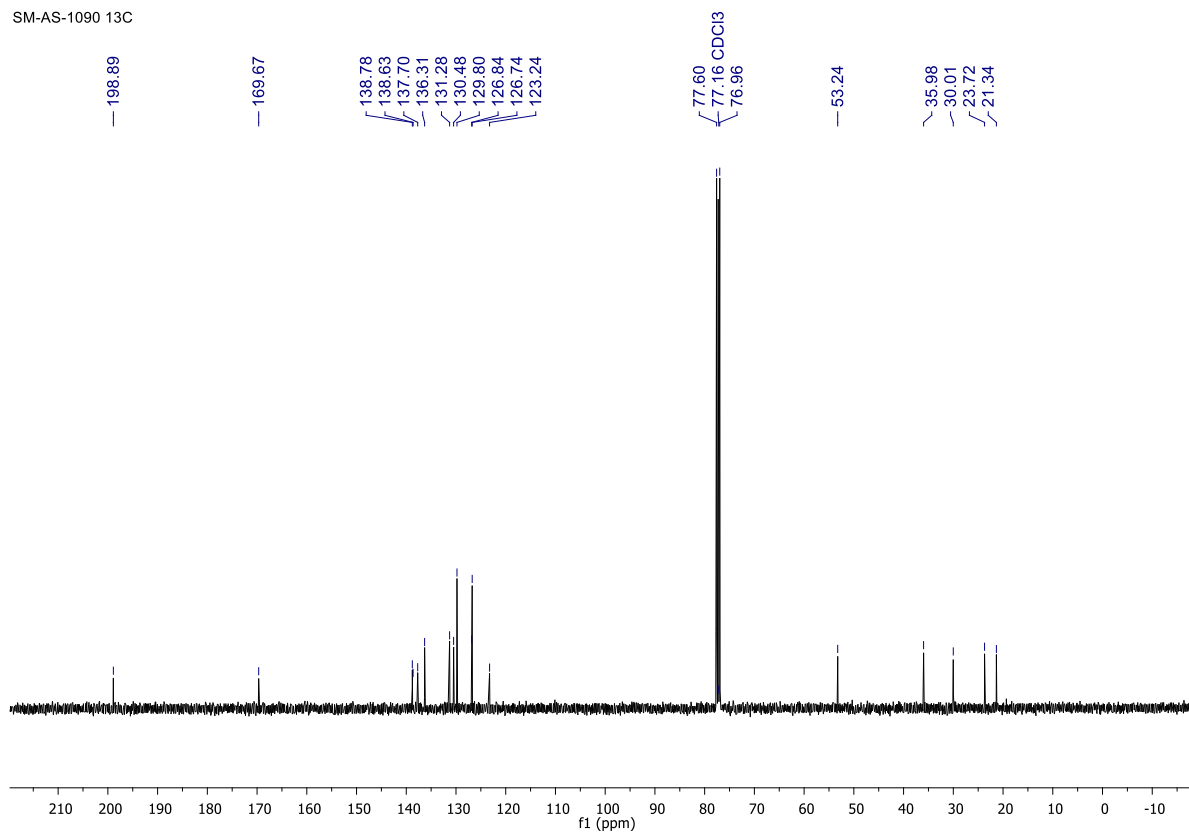
$^1\text{H}$  NMR of **3f** (400 MHz,  $\text{CDCl}_3$ ):

SM-AS-1090 1H



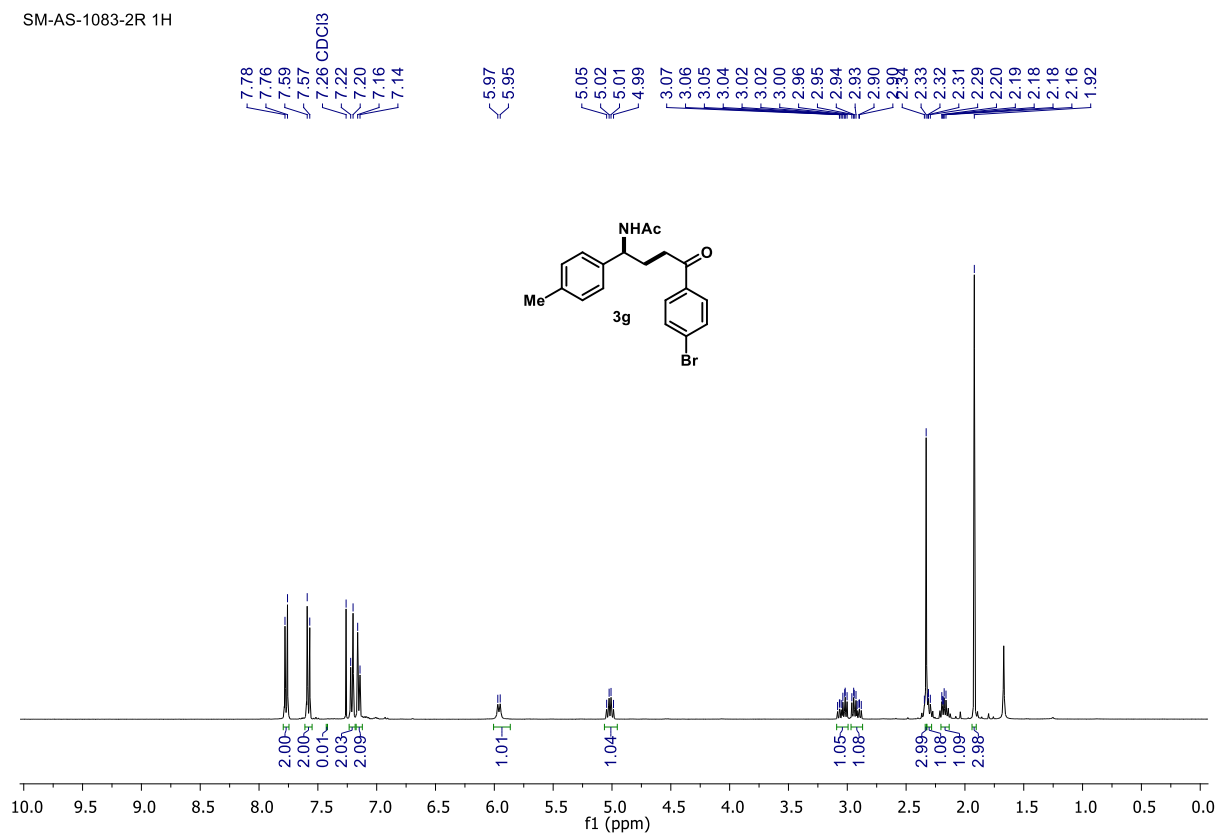
$^{13}\text{C}\{^1\text{H}\}$  NMR of **3f** (101 MHz,  $\text{CDCl}_3$ ):

SM-AS-1090 13C



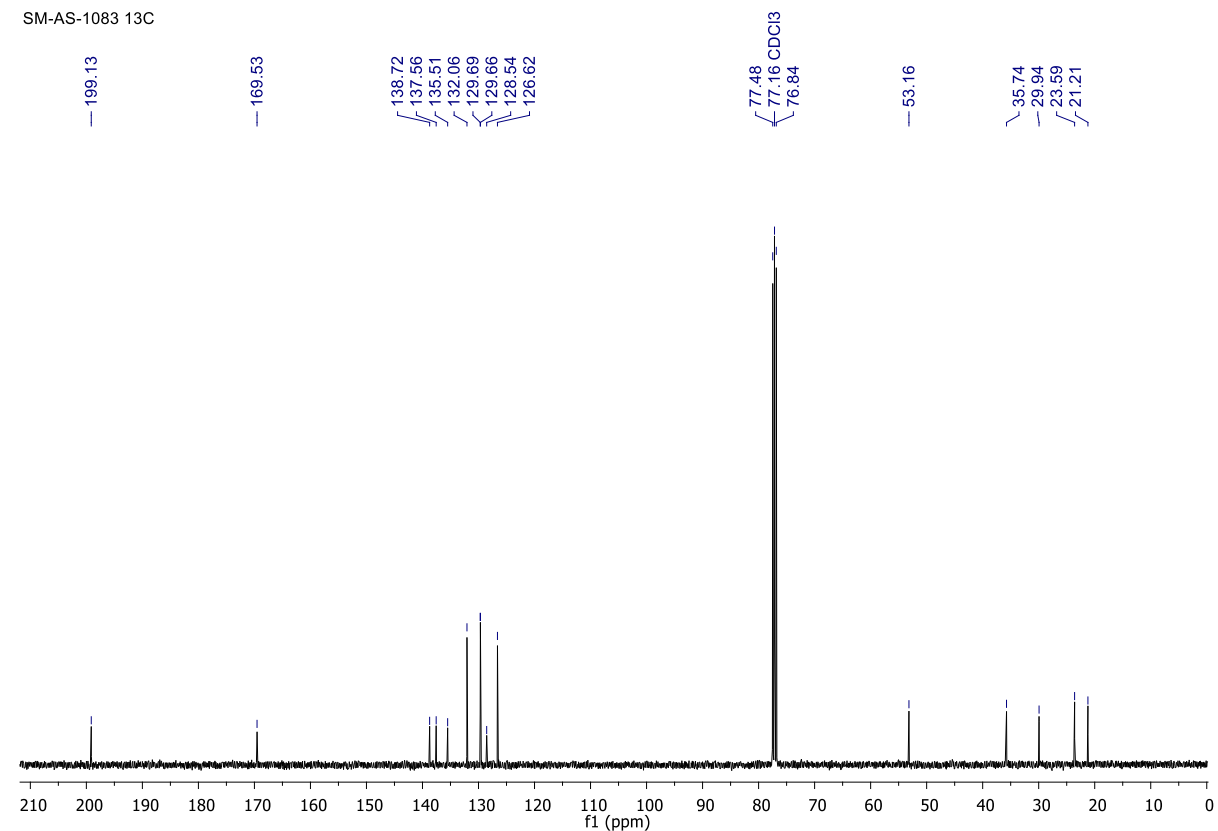
<sup>1</sup>H NMR of **3g** (400 MHz, CDCl<sub>3</sub>):

SM-AS-1083-2R 1H



<sup>13</sup>C{<sup>1</sup>H} NMR of **3g** (101 MHz, CDCl<sub>3</sub>):

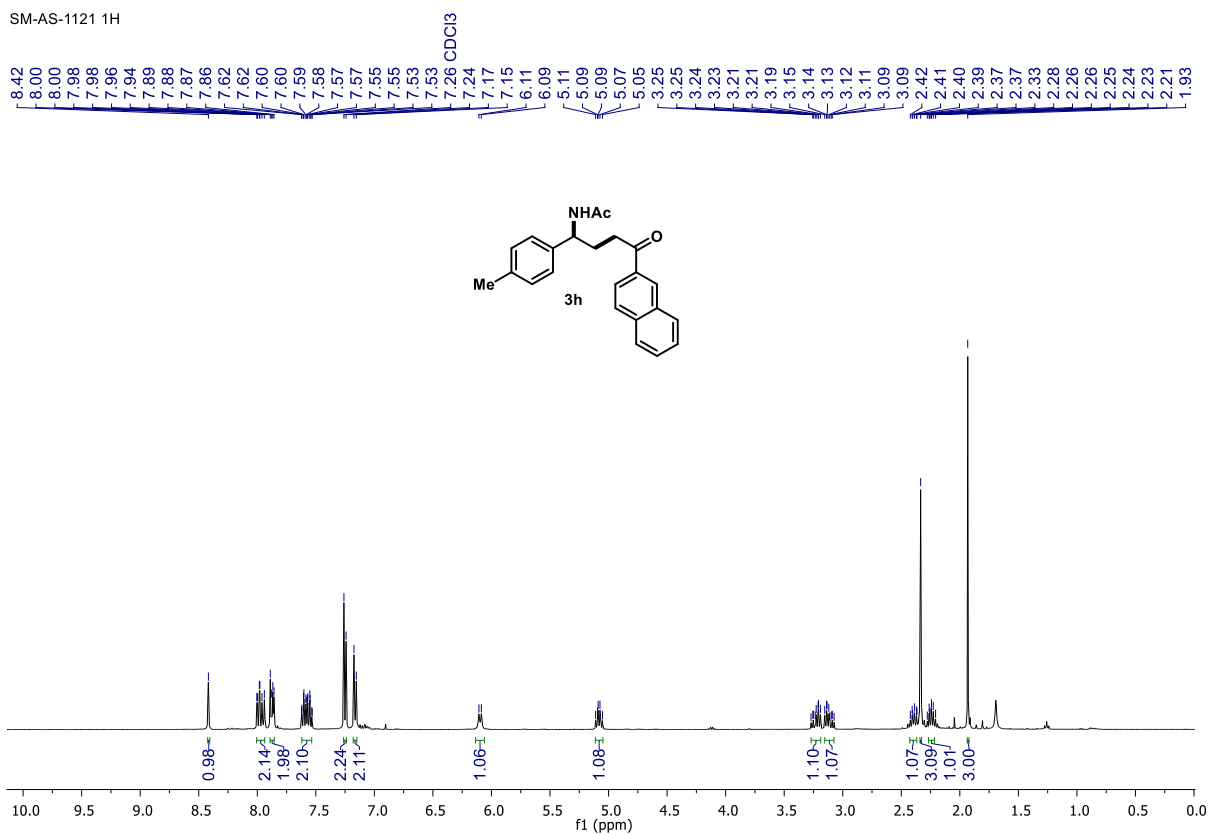
SM-AS-1083 13C





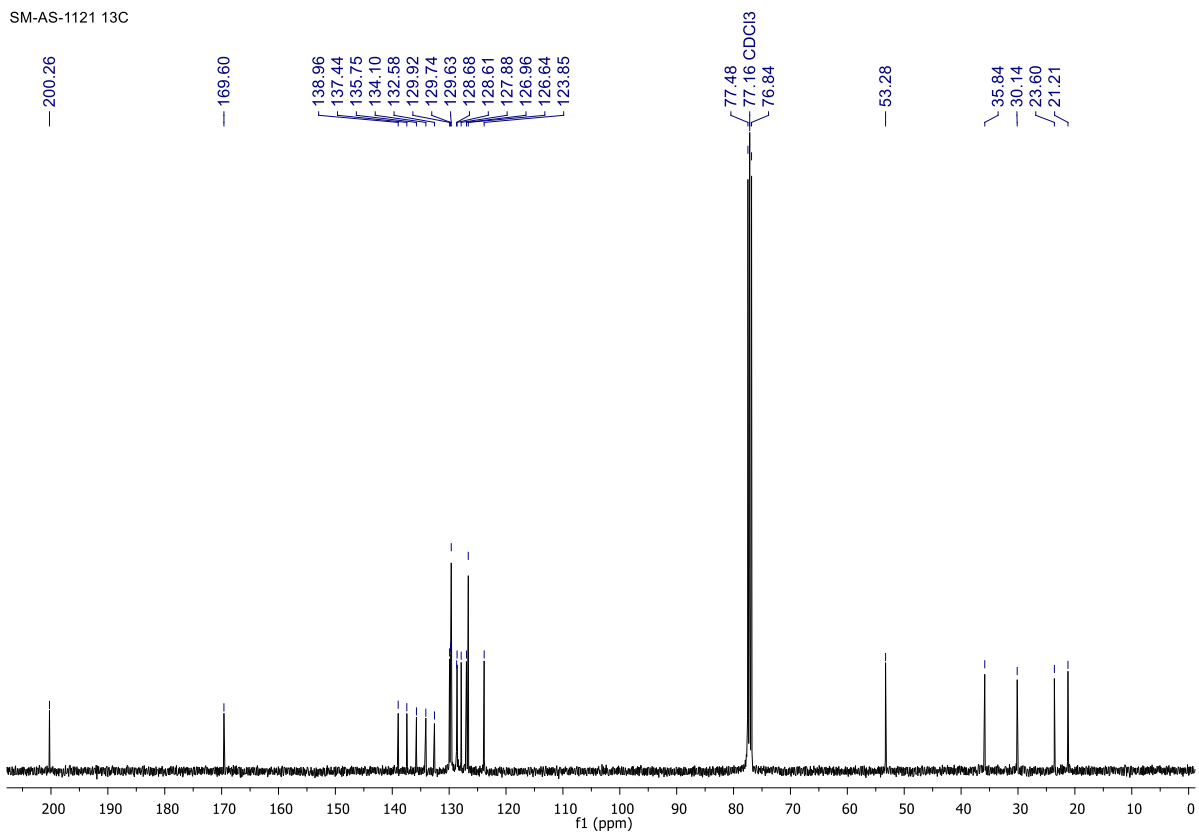
<sup>1</sup>H NMR of **3h** (400 MHz, CDCl<sub>3</sub>):

SM-AS-1121 1H



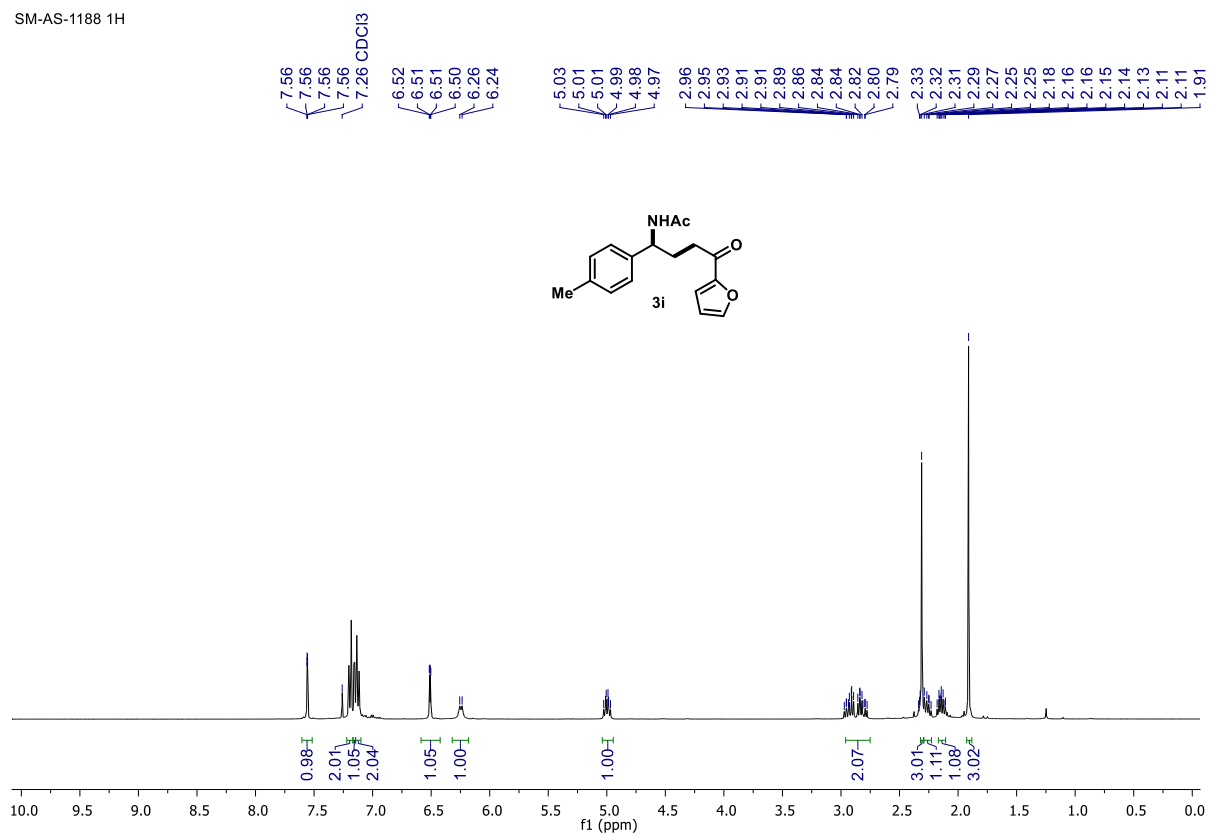
<sup>13</sup>C{<sup>1</sup>H} NMR of **3h** (101 MHz, CDCl<sub>3</sub>):

SM-AS-1121 13C



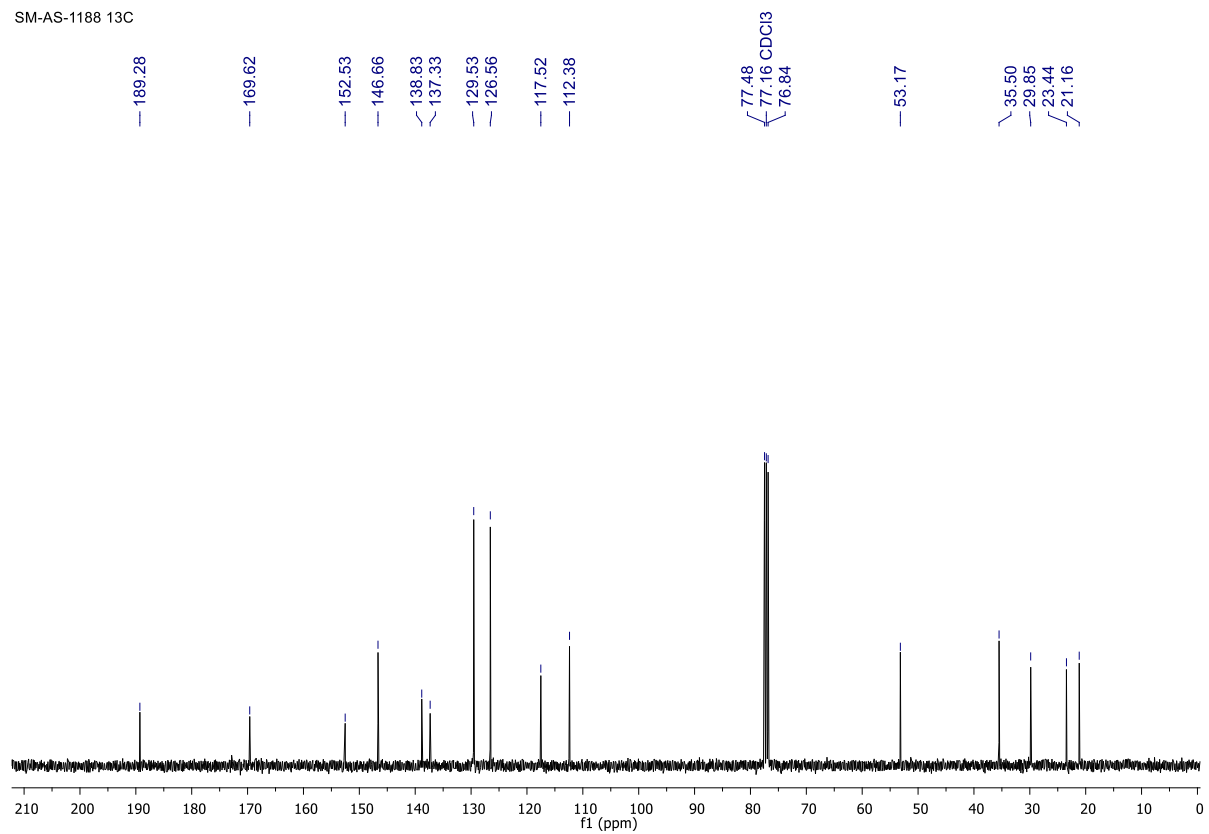
<sup>1</sup>H NMR of **3i** (400 MHz, CDCl<sub>3</sub>):

SM-AS-1188 1H



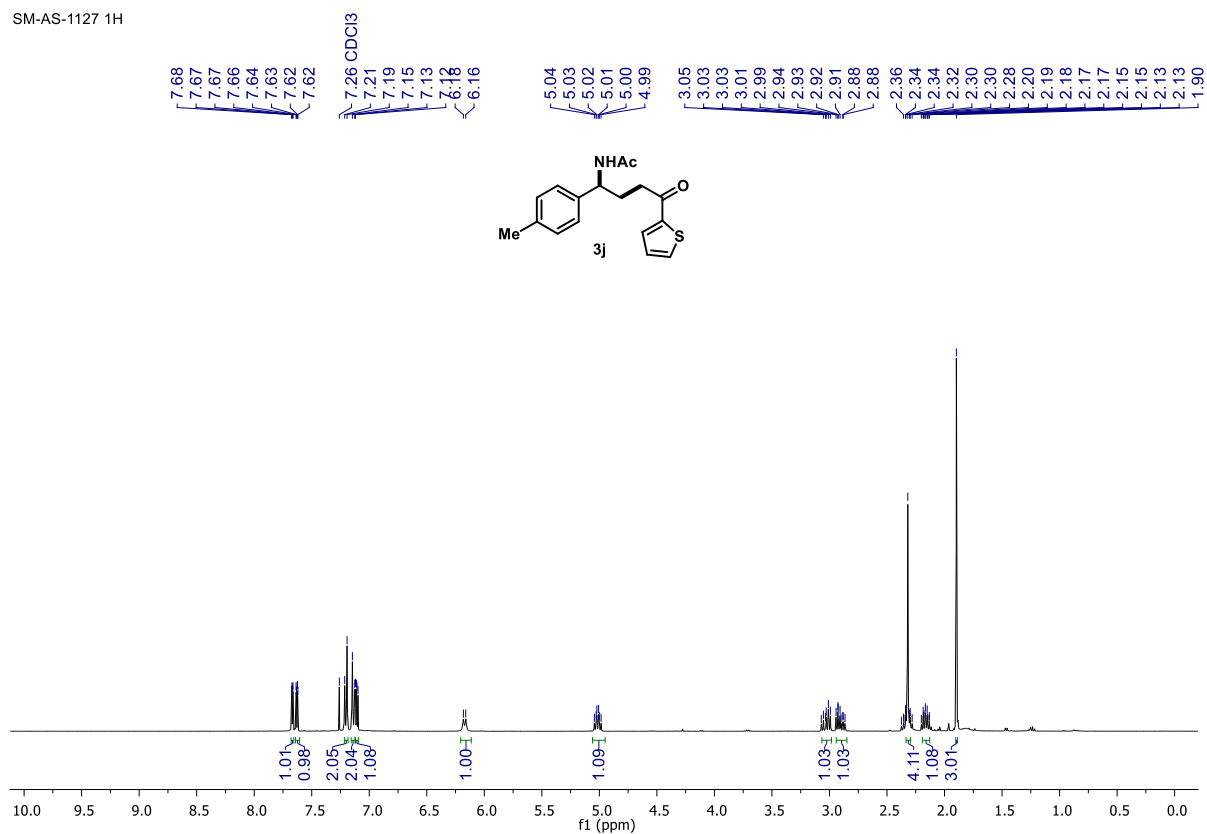
<sup>13</sup>C{<sup>1</sup>H} NMR of **3i** (101 MHz, CDCl<sub>3</sub>):

SM-AS-1188 13C



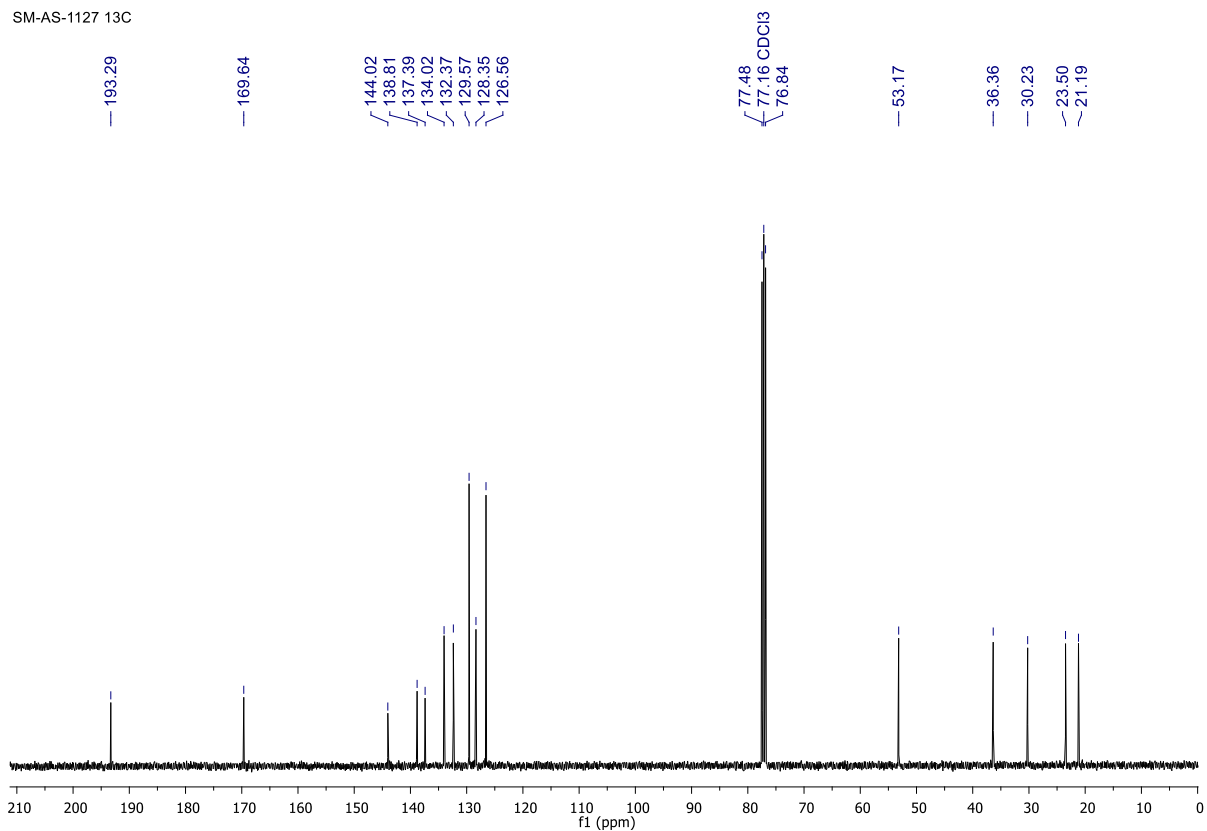
<sup>1</sup>H NMR of **3j** (400 MHz, CDCl<sub>3</sub>):

SM-AS-1127 1H



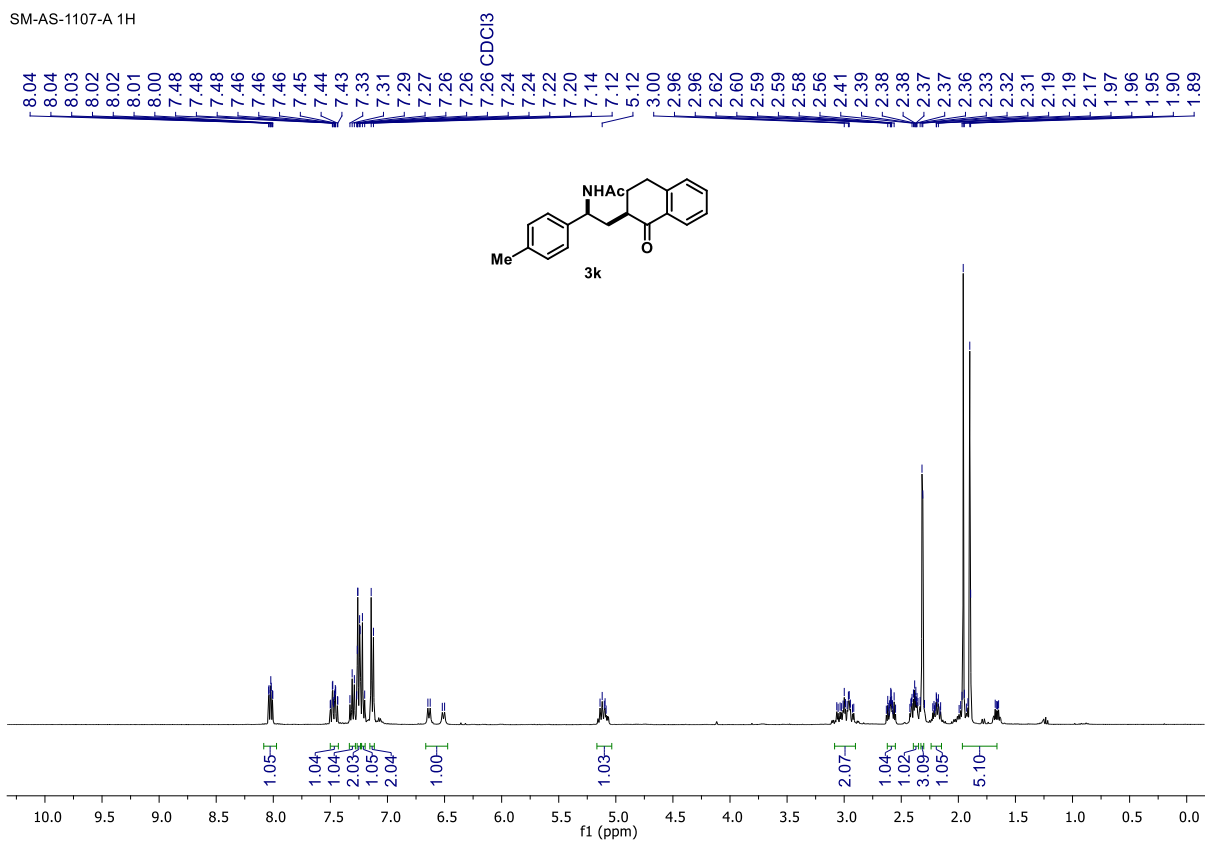
<sup>13</sup>C{<sup>1</sup>H} NMR of **3j** (101 MHz, CDCl<sub>3</sub>):

SM-AS-1127 13C



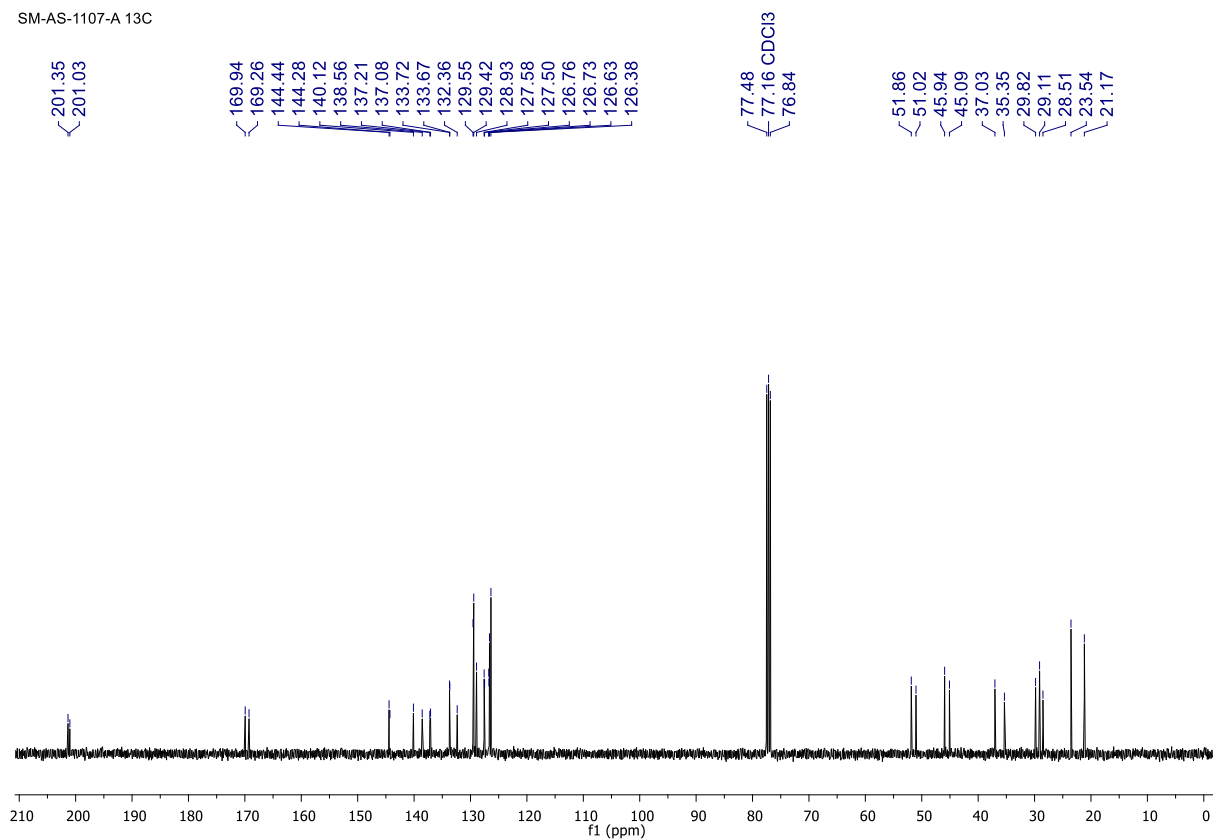
<sup>1</sup>H NMR of **3k** (400 MHz, CDCl<sub>3</sub>):

SM-AS-1107-A 1H



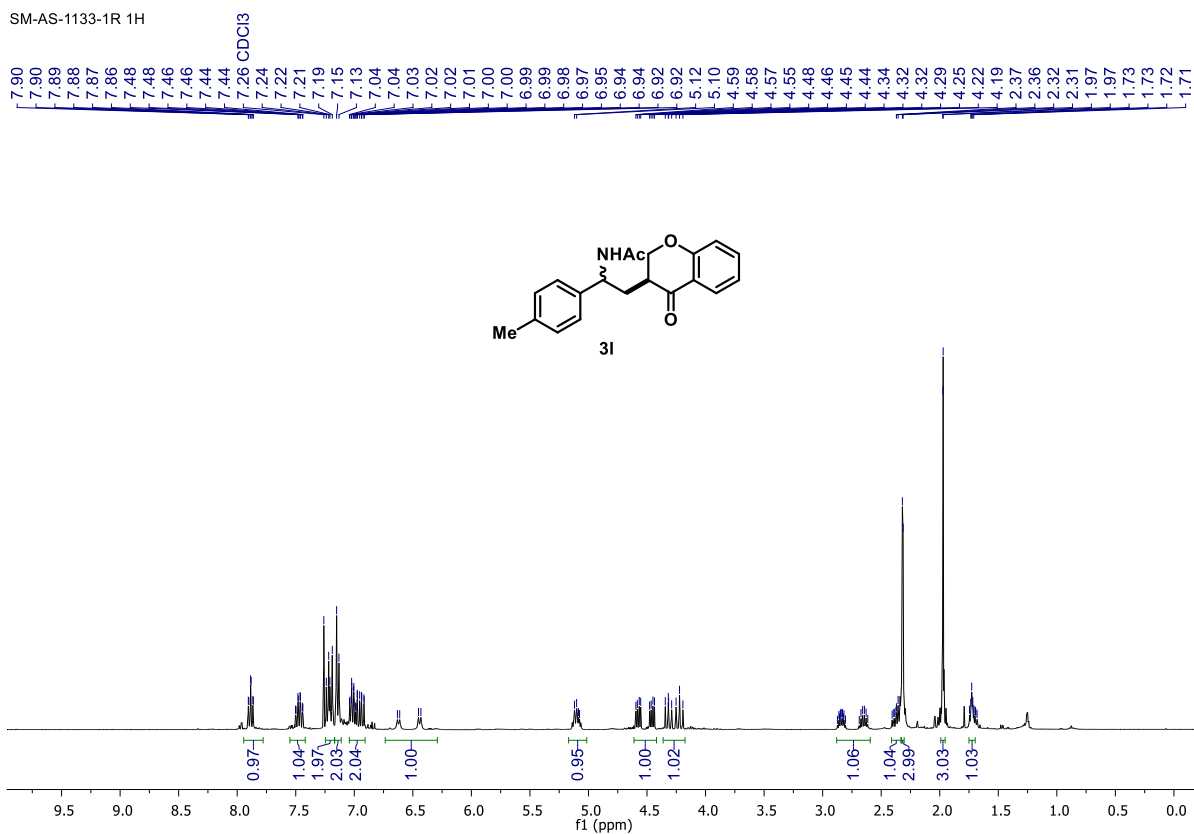
<sup>13</sup>C{<sup>1</sup>H} NMR of **3k** (101 MHz, CDCl<sub>3</sub>):

SM-AS-1107-A 13C



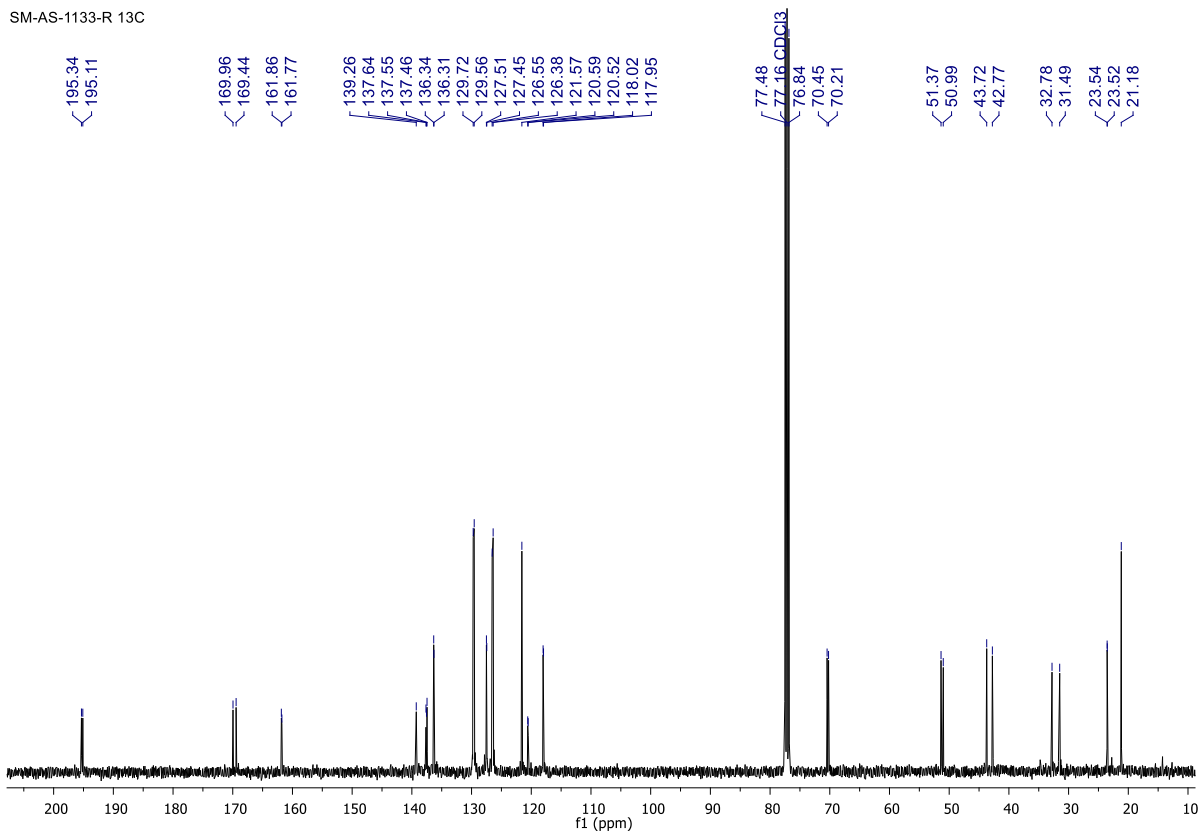
<sup>1</sup>H NMR of **31** (400 MHz, CDCl<sub>3</sub>):

SM-AS-1133-1R 1H

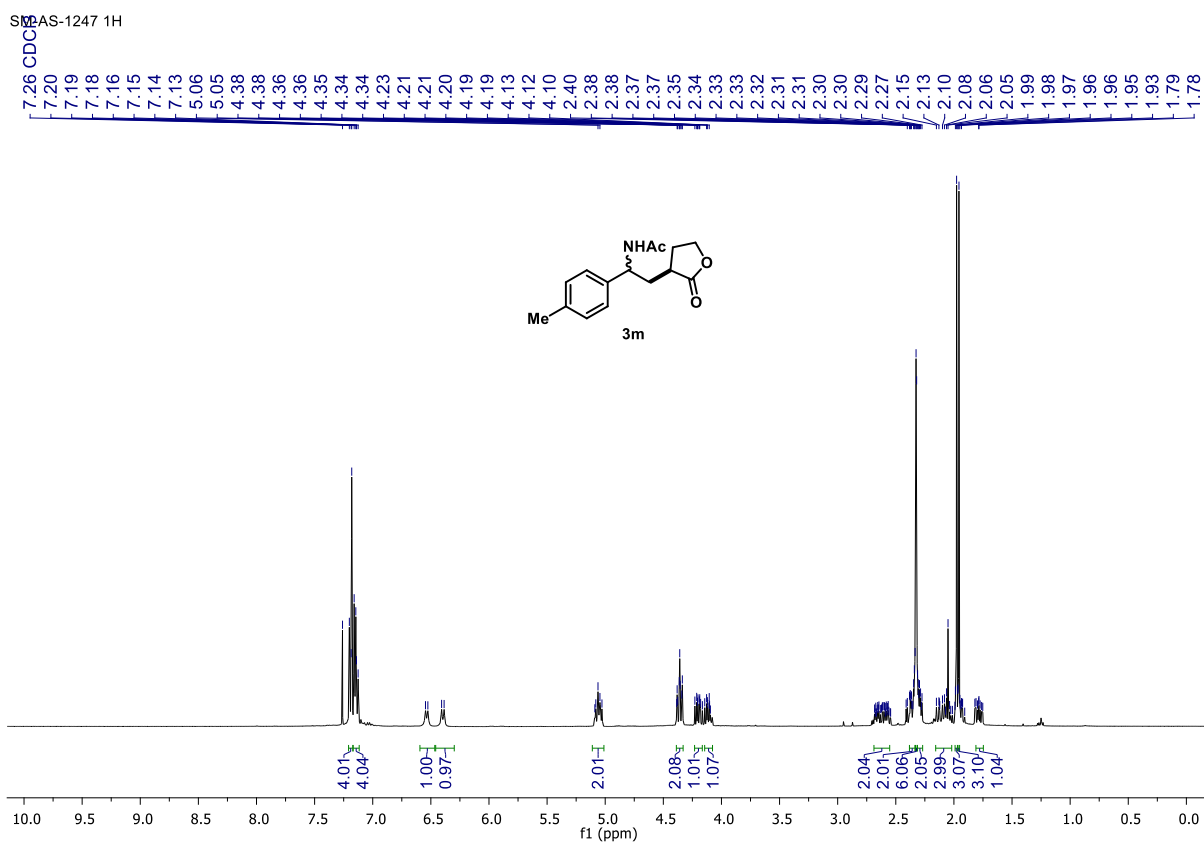


<sup>13</sup>C{<sup>1</sup>H} NMR of **31** (101 MHz, CDCl<sub>3</sub>):

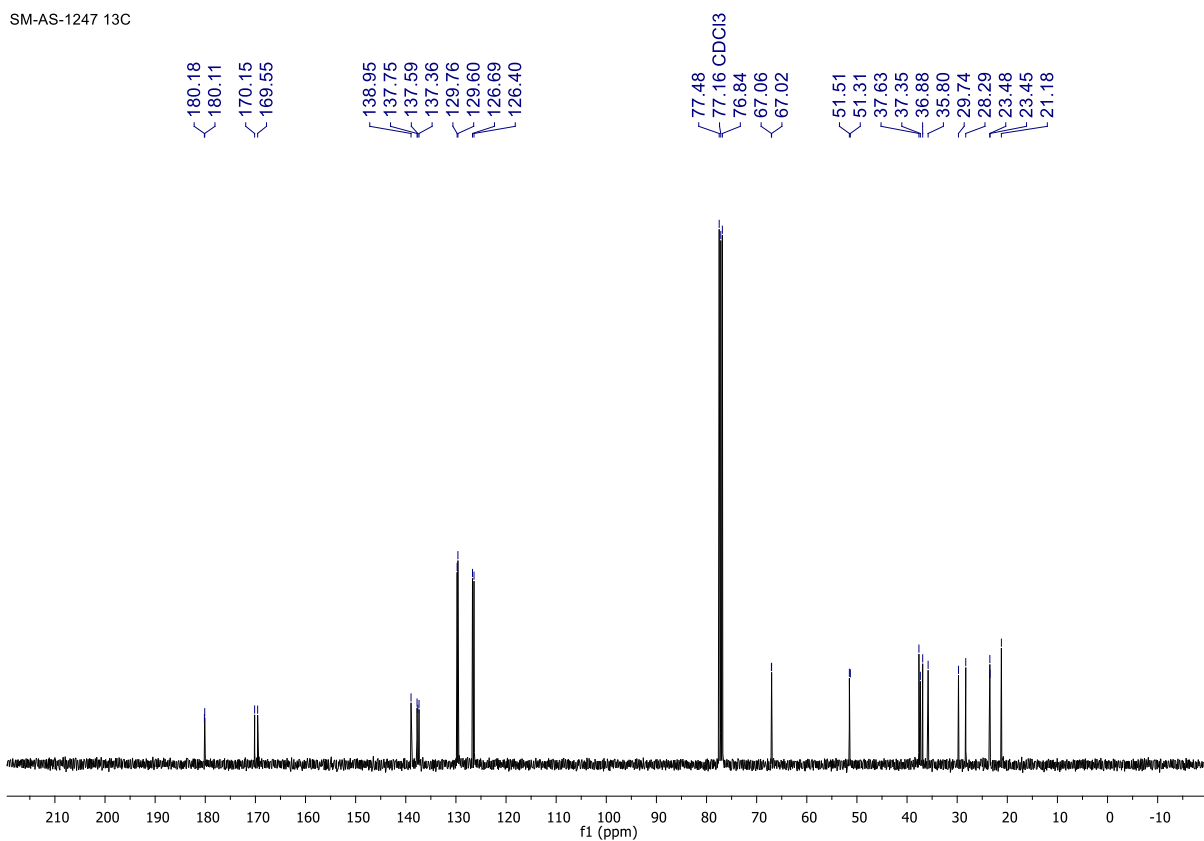
SM-AS-1133-R 13C



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

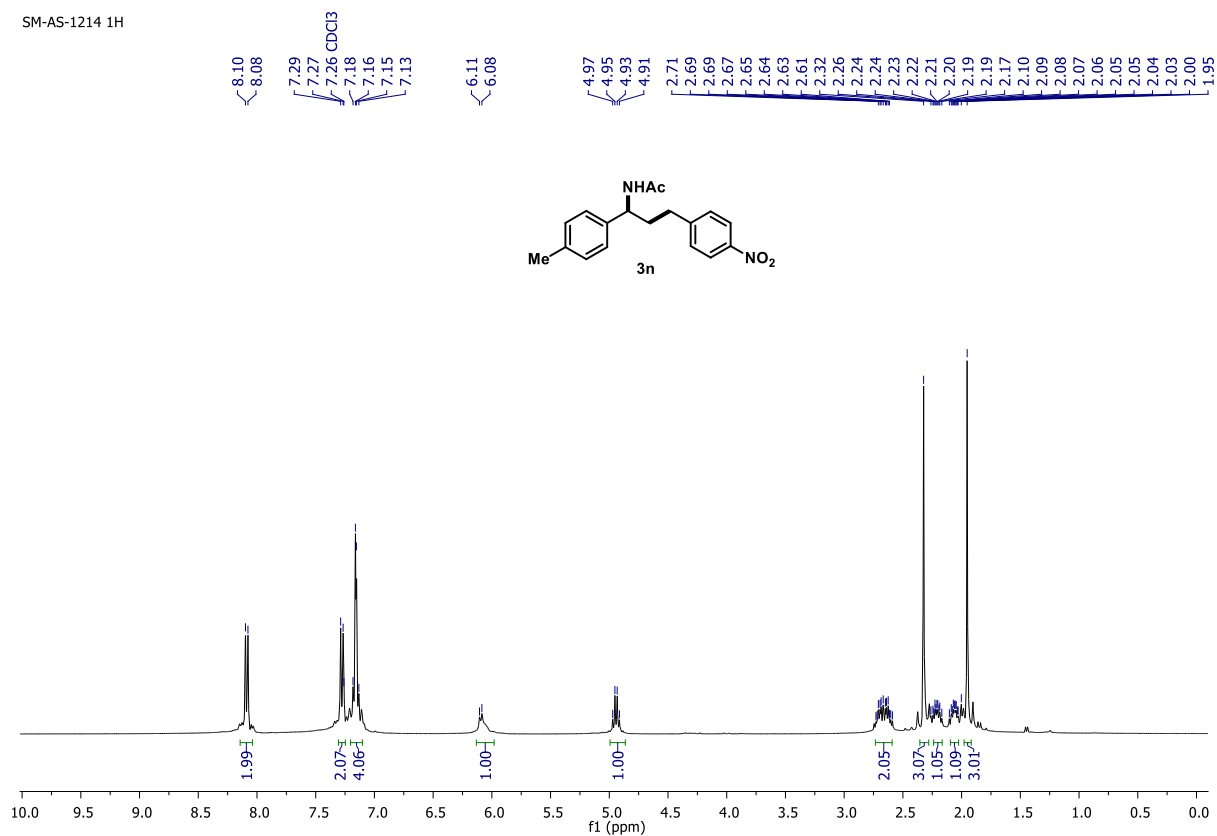


<sup>13</sup>C{<sup>1</sup>H} NMR of **3m** (101 MHz, CDCl<sub>3</sub>):



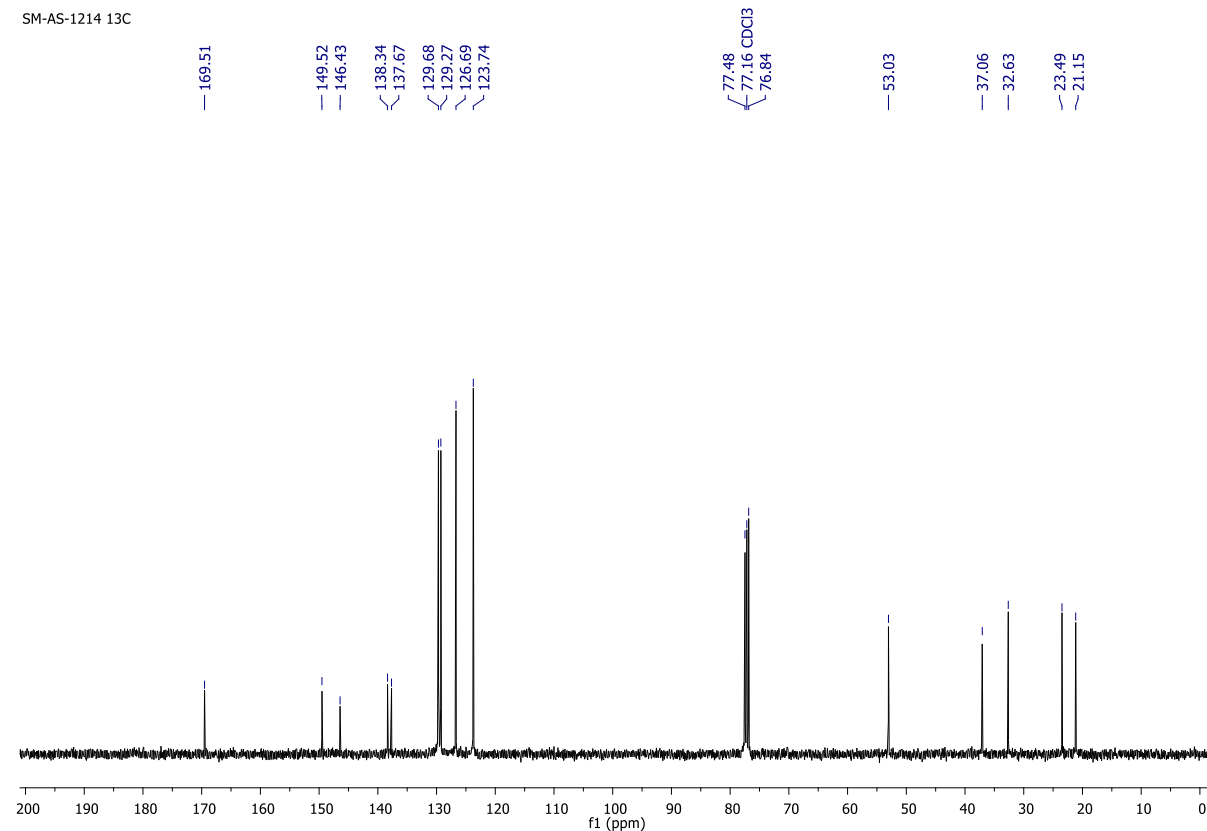
<sup>1</sup>H NMR of **3n** (400 MHz, CDCl<sub>3</sub>):

SM-AS-1214 1H

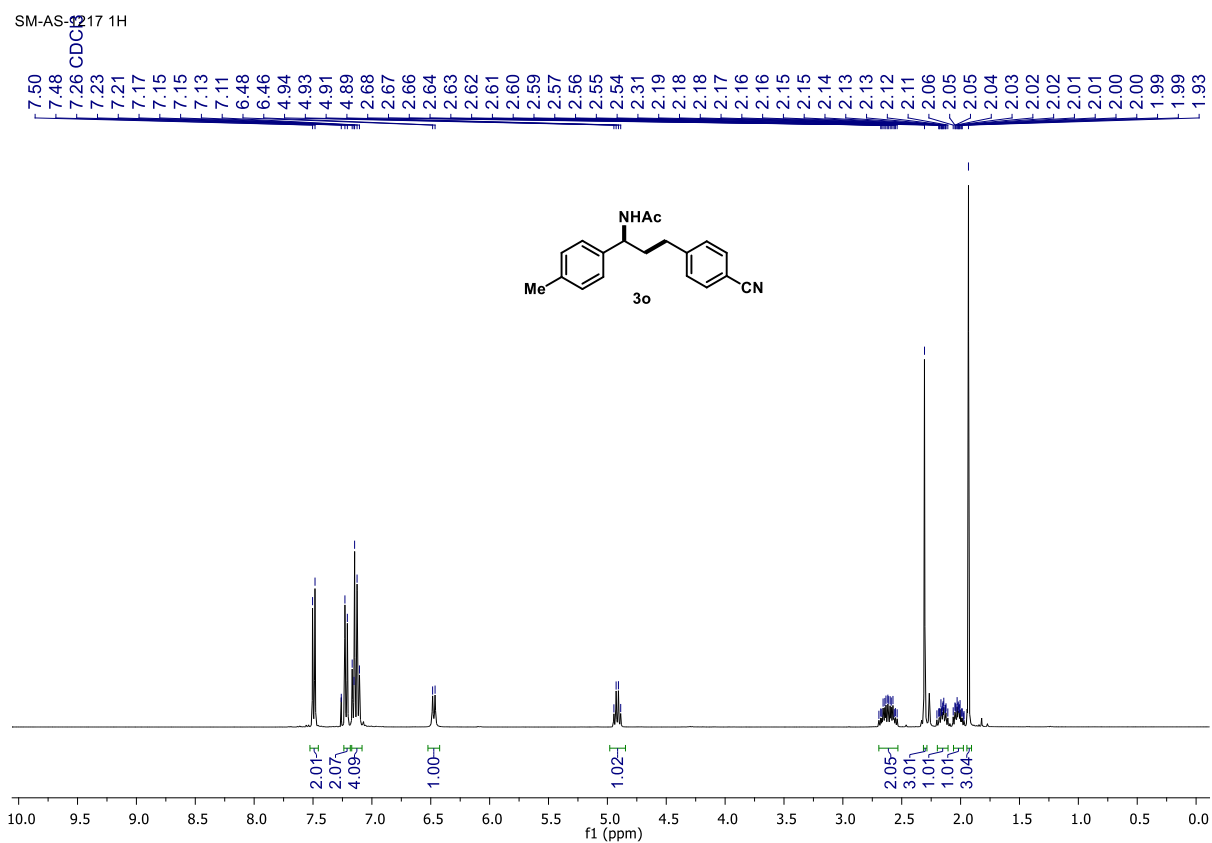


<sup>13</sup>C{<sup>1</sup>H} NMR of **3n** (101 MHz, CDCl<sub>3</sub>):

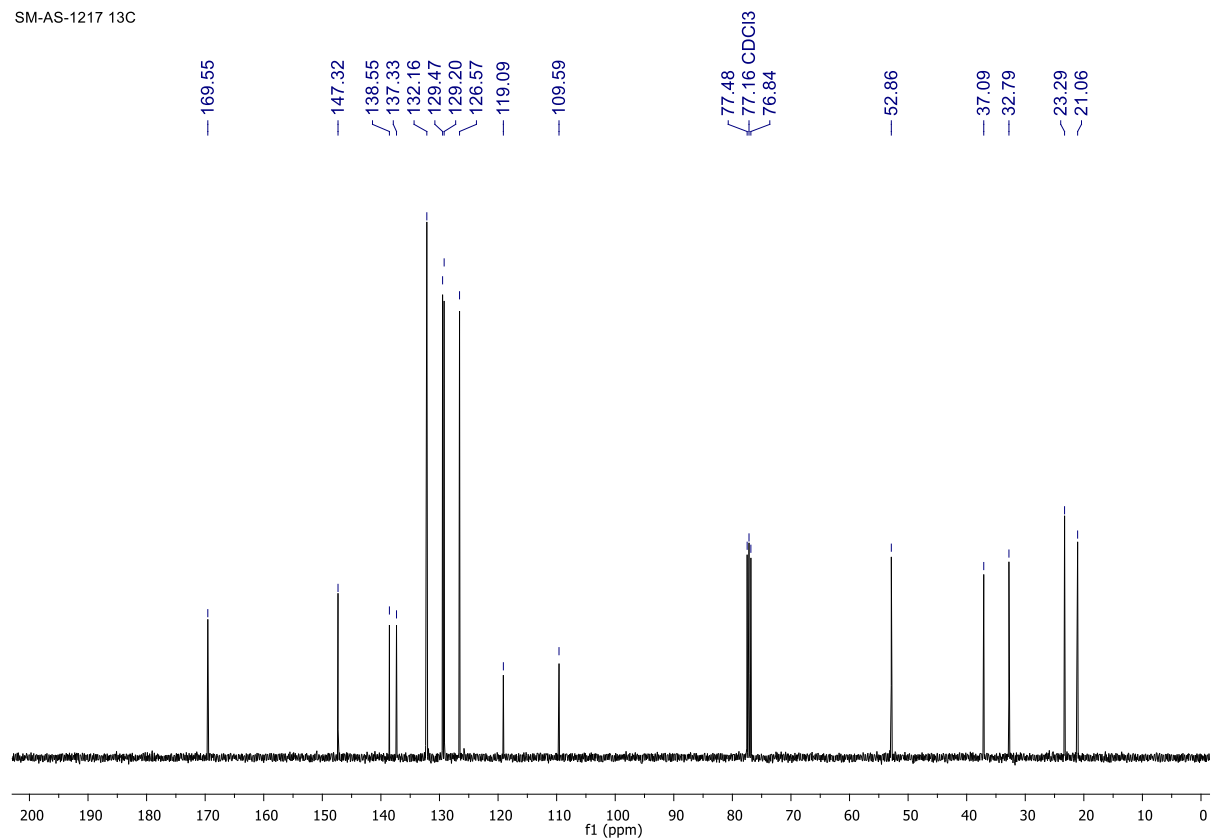
SM-AS-1214 13C



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



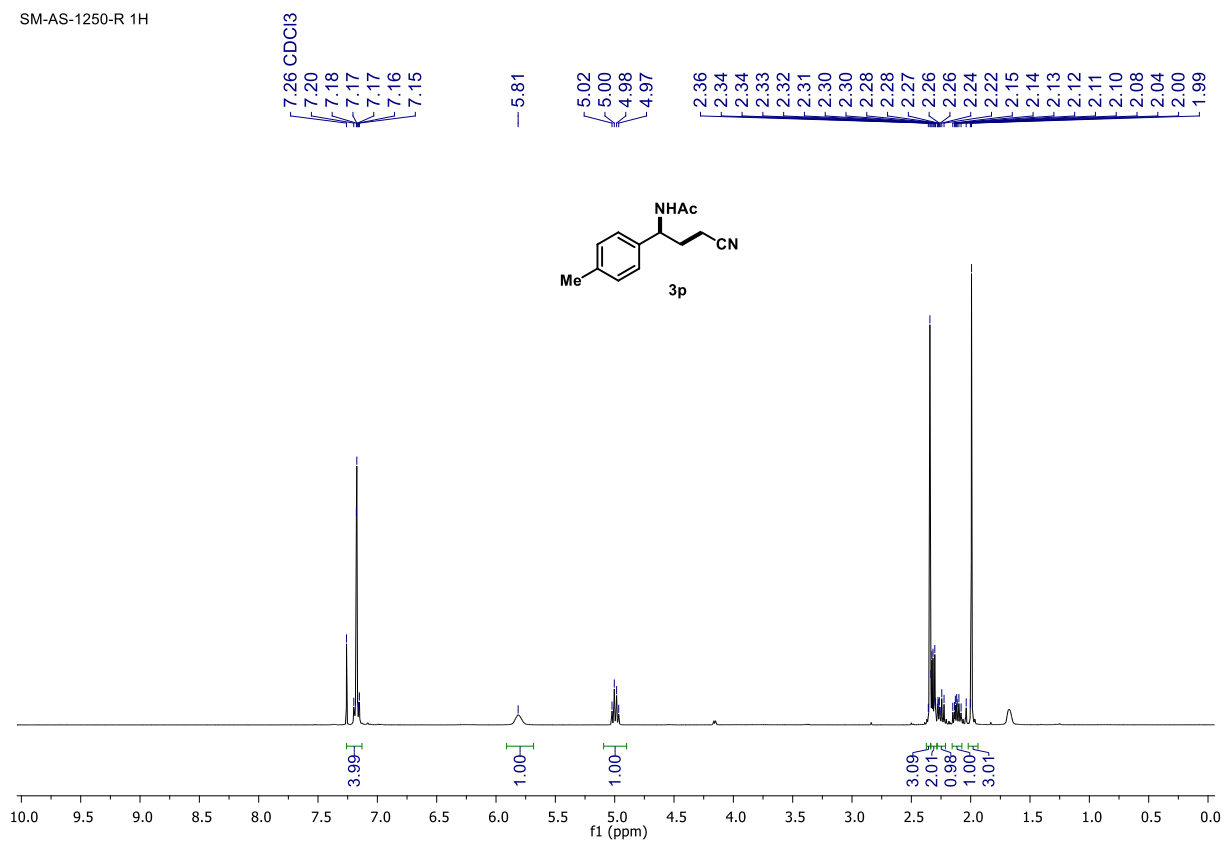
<sup>13</sup>C{<sup>1</sup>H} NMR of **3o** (101 MHz, CDCl<sub>3</sub>):





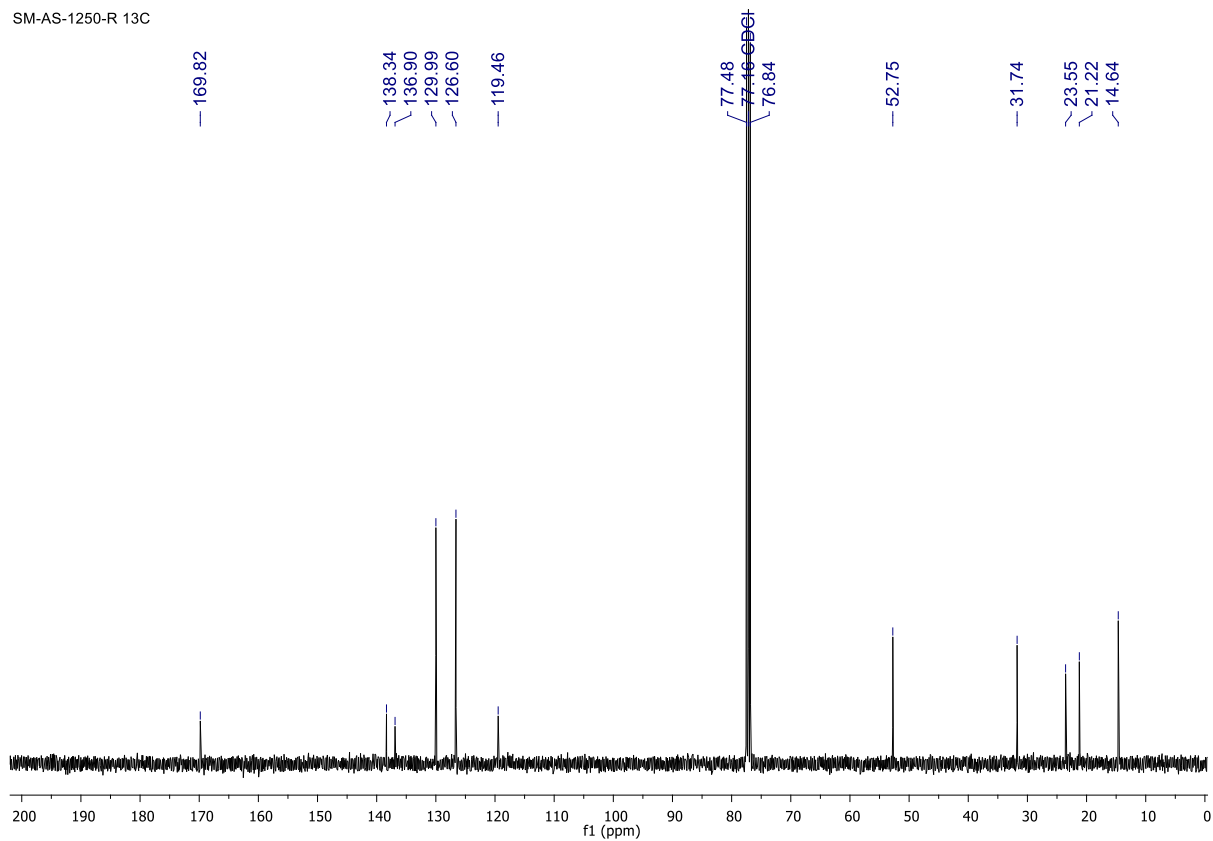
<sup>1</sup>H NMR of **3p** (400 MHz, CDCl<sub>3</sub>):

SM-AS-1250-R 1H



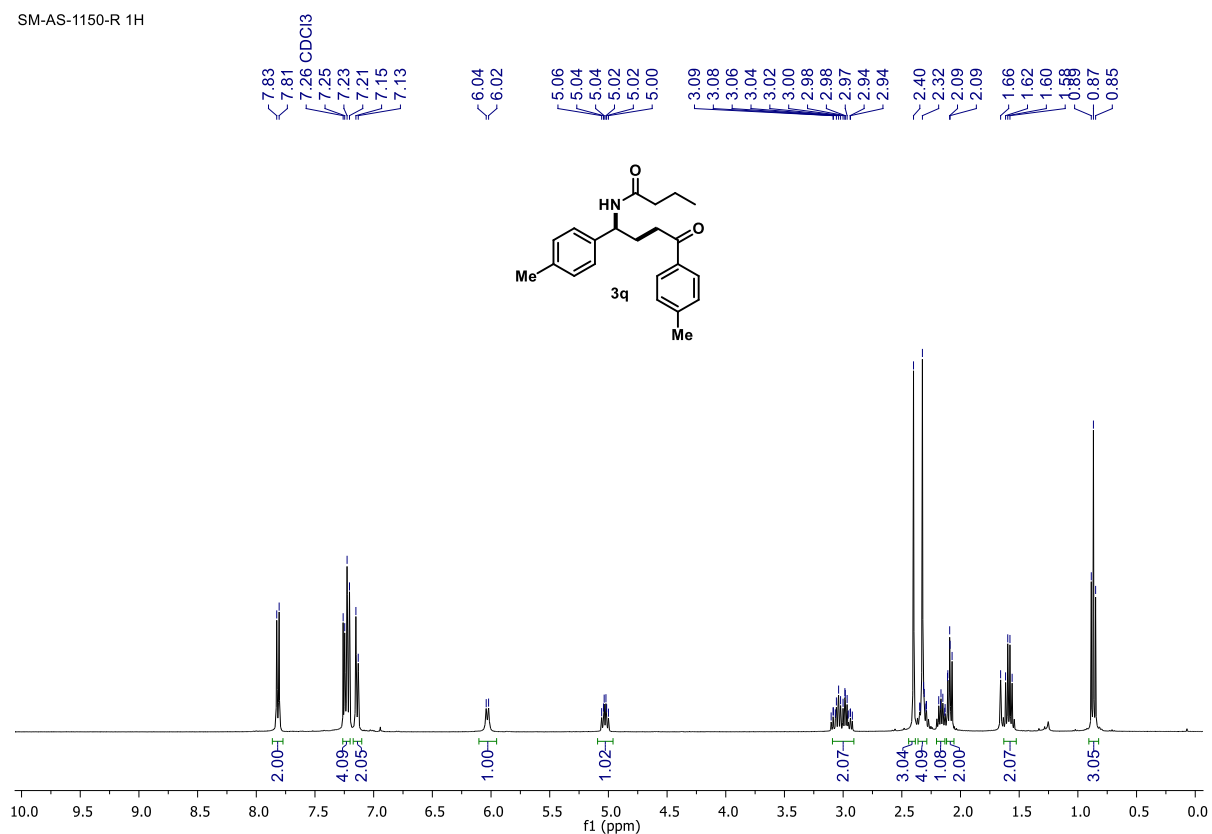
<sup>13</sup>C{<sup>1</sup>H} NMR of **3p** (101 MHz, CDCl<sub>3</sub>):

SM-AS-1250-R 13C



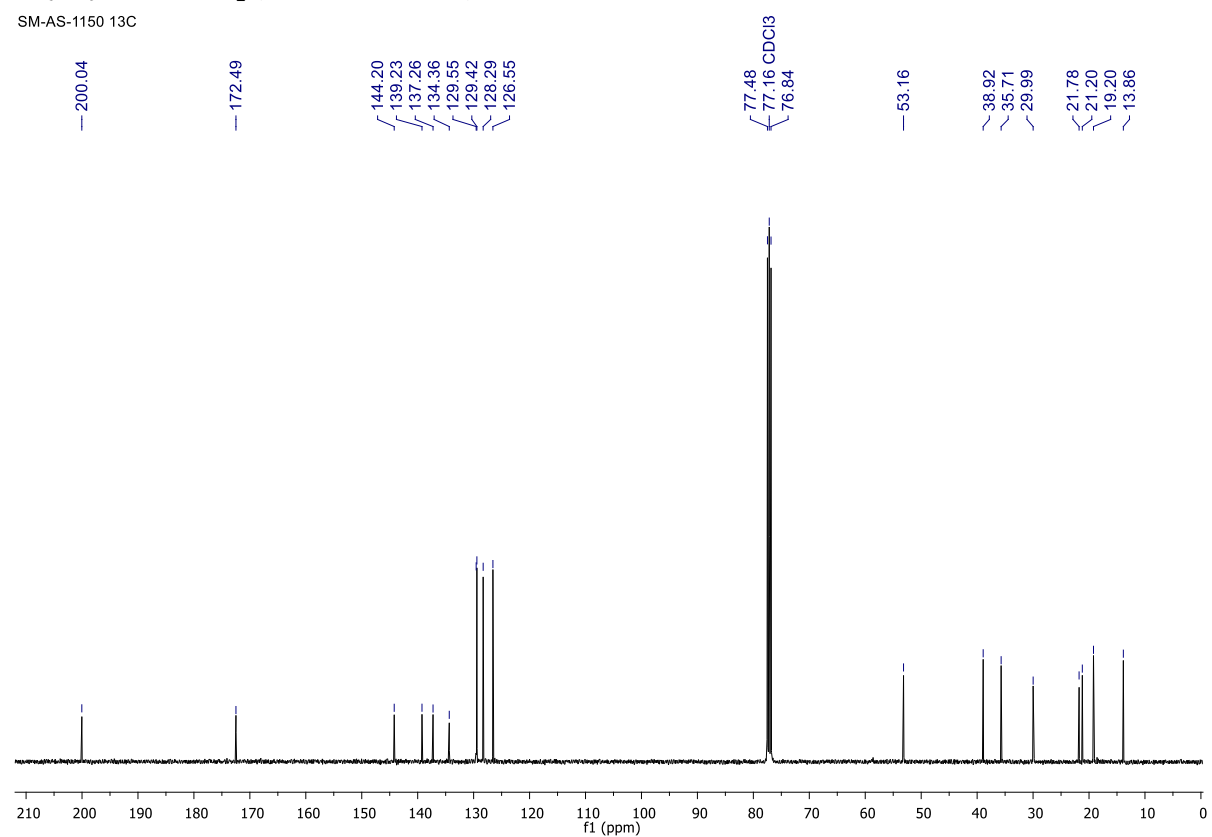
<sup>1</sup>H NMR of **3q** (400 MHz, CDCl<sub>3</sub>):

SM-AS-1150-R 1H



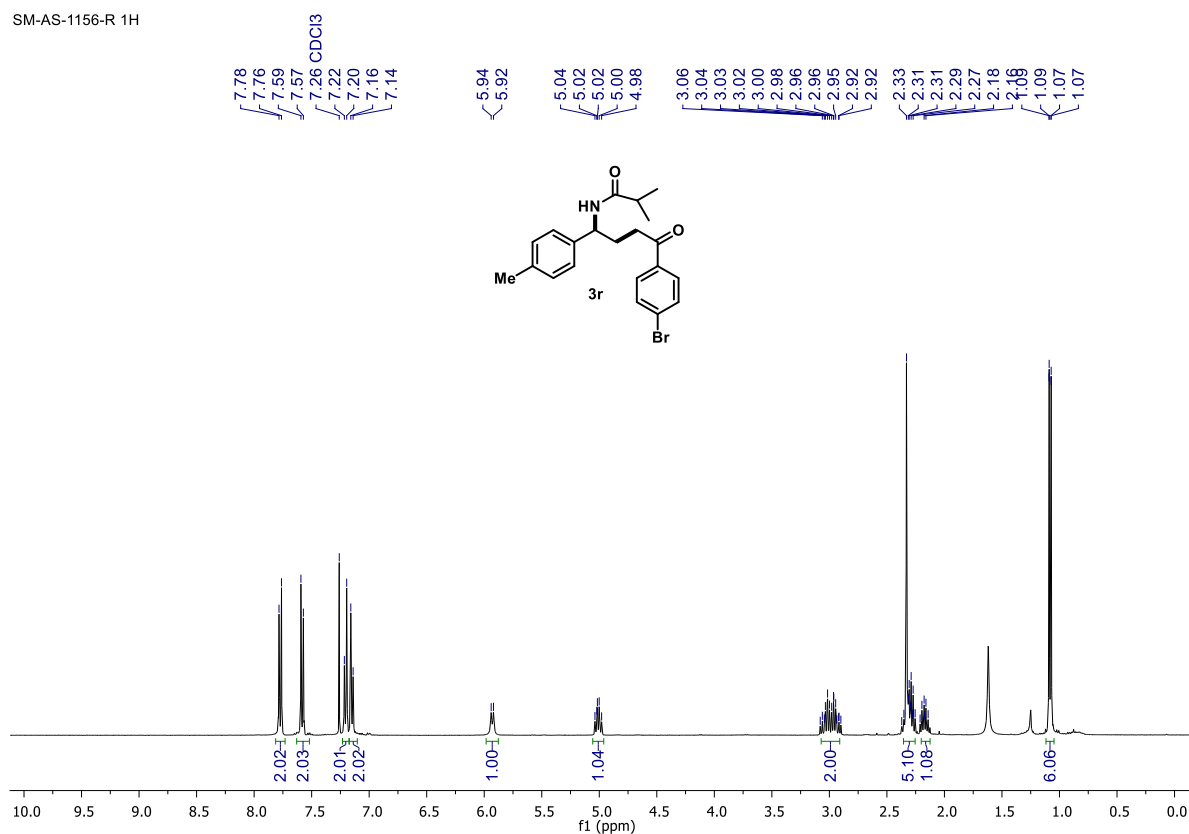
<sup>13</sup>C{<sup>1</sup>H} NMR of **3q** (101 MHz, CDCl<sub>3</sub>):

SM-AS-1150 13C



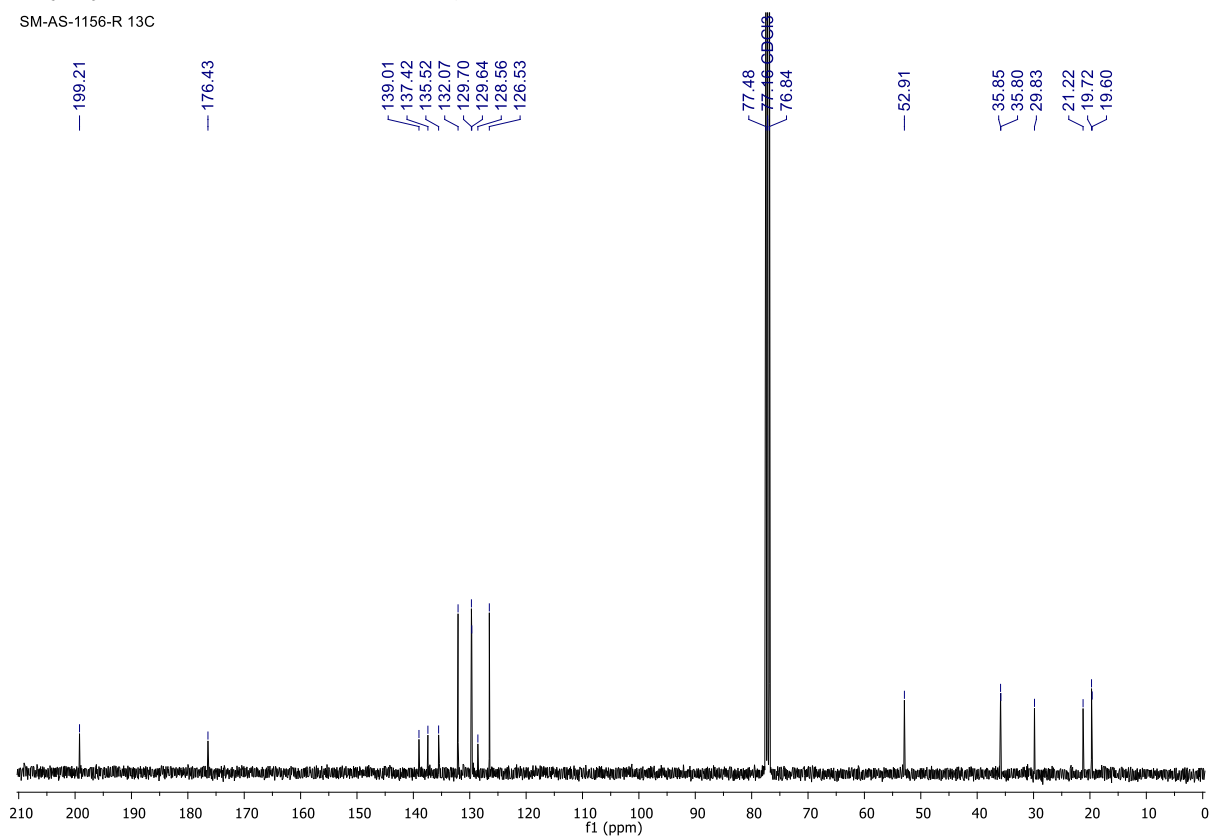
<sup>1</sup>H NMR of **3r** (400 MHz, CDCl<sub>3</sub>):

SM-AS-1156-R 1H



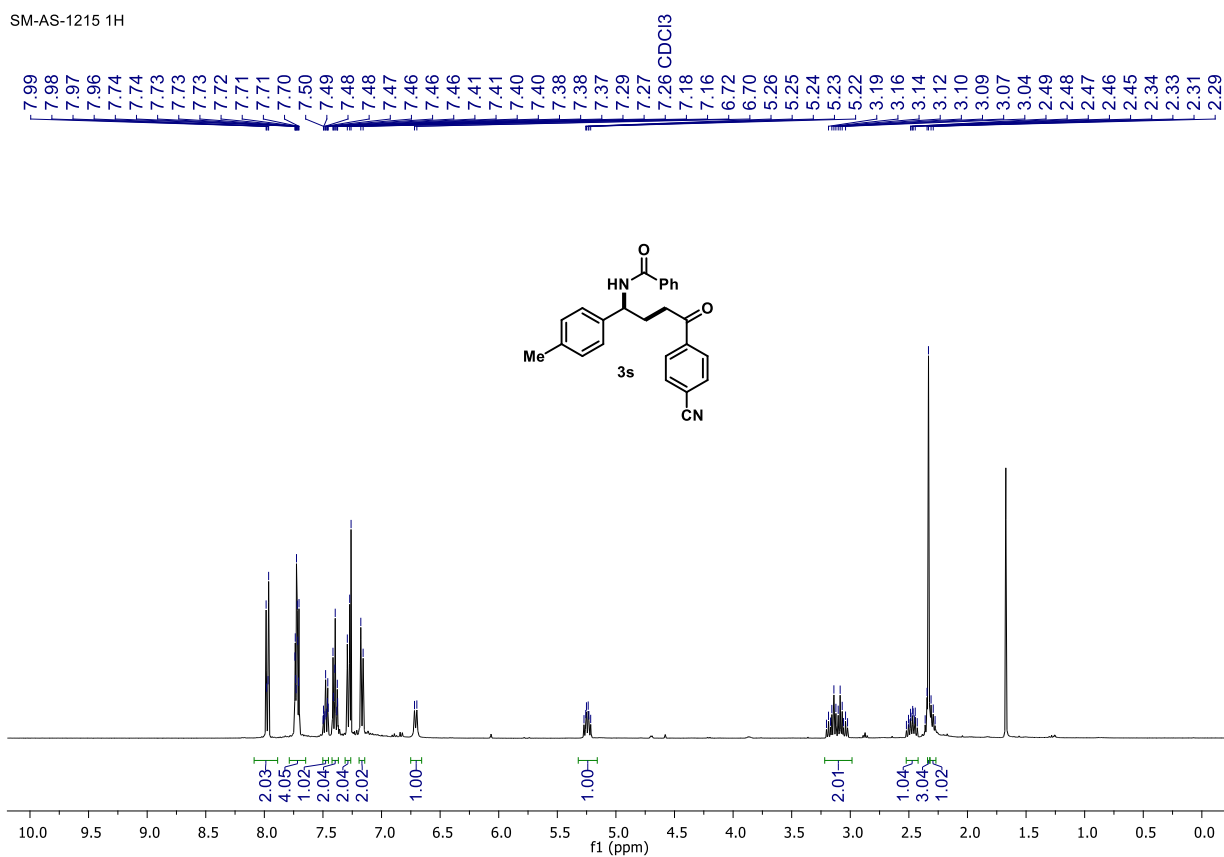
<sup>13</sup>C{<sup>1</sup>H} NMR of **3r** 101 MHz, CDCl<sub>3</sub>):

SM-AS-1156-R 13C



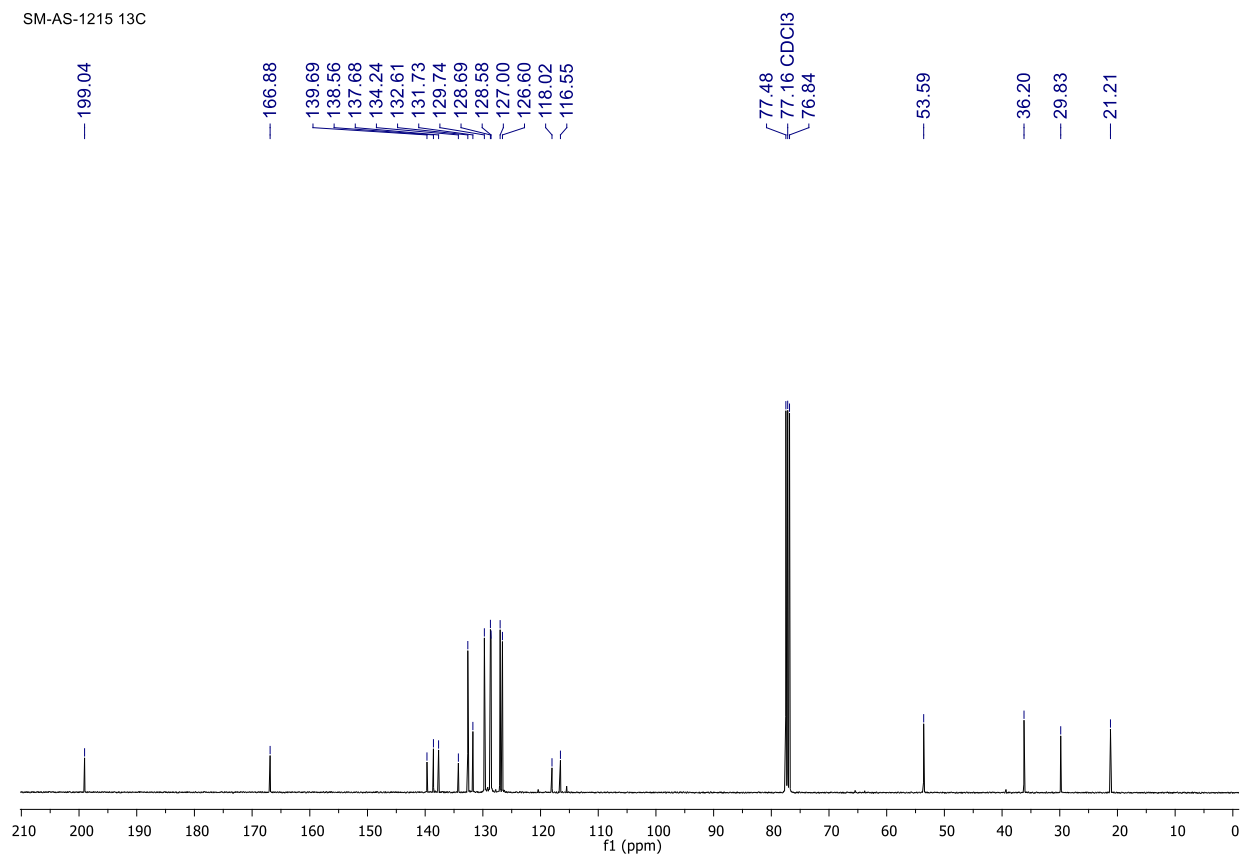
<sup>1</sup>H NMR of **3s** (400 MHz, CDCl<sub>3</sub>):

SM-AS-1215 1H

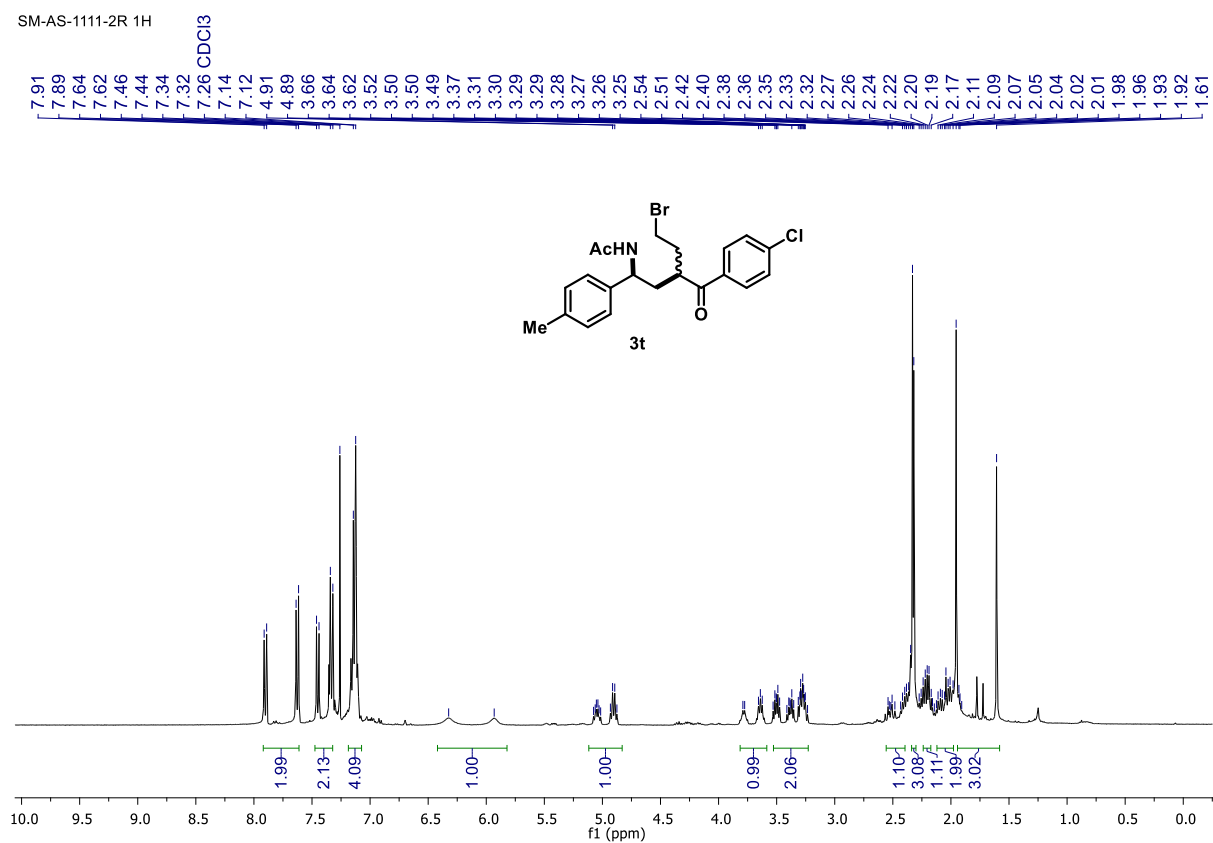


<sup>13</sup>C{<sup>1</sup>H} NMR of **3s** (101 MHz, CDCl<sub>3</sub>):

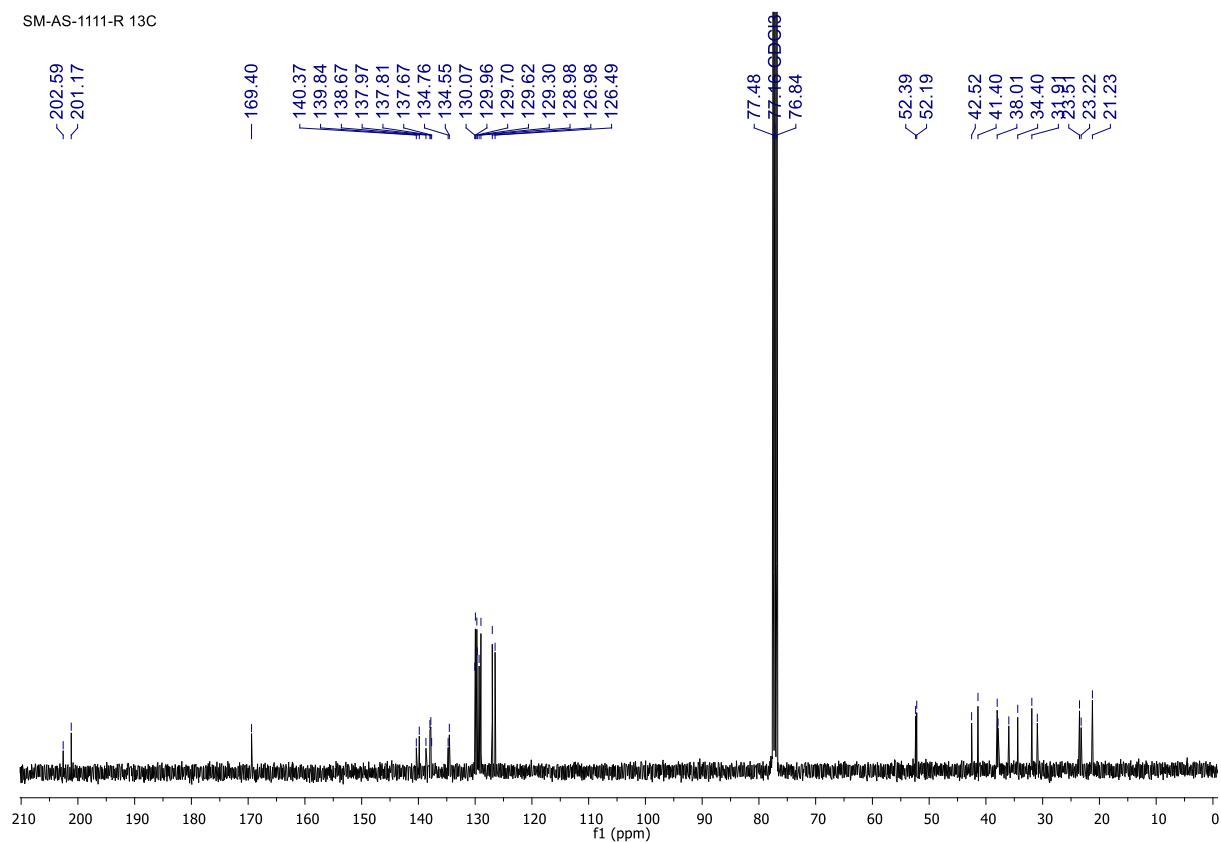
SM-AS-1215 13C



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

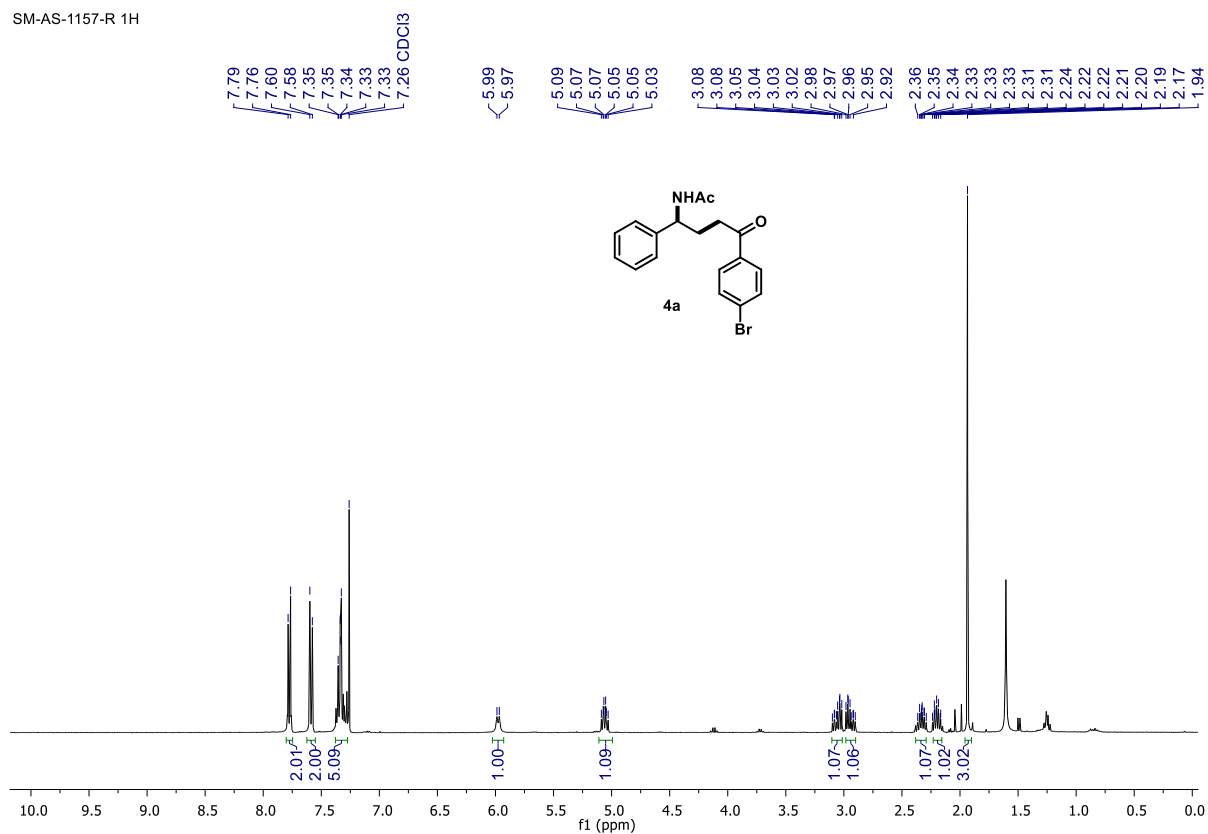


<sup>13</sup>C{<sup>1</sup>H} NMR of **3t** (101 MHz, CDCl<sub>3</sub>):



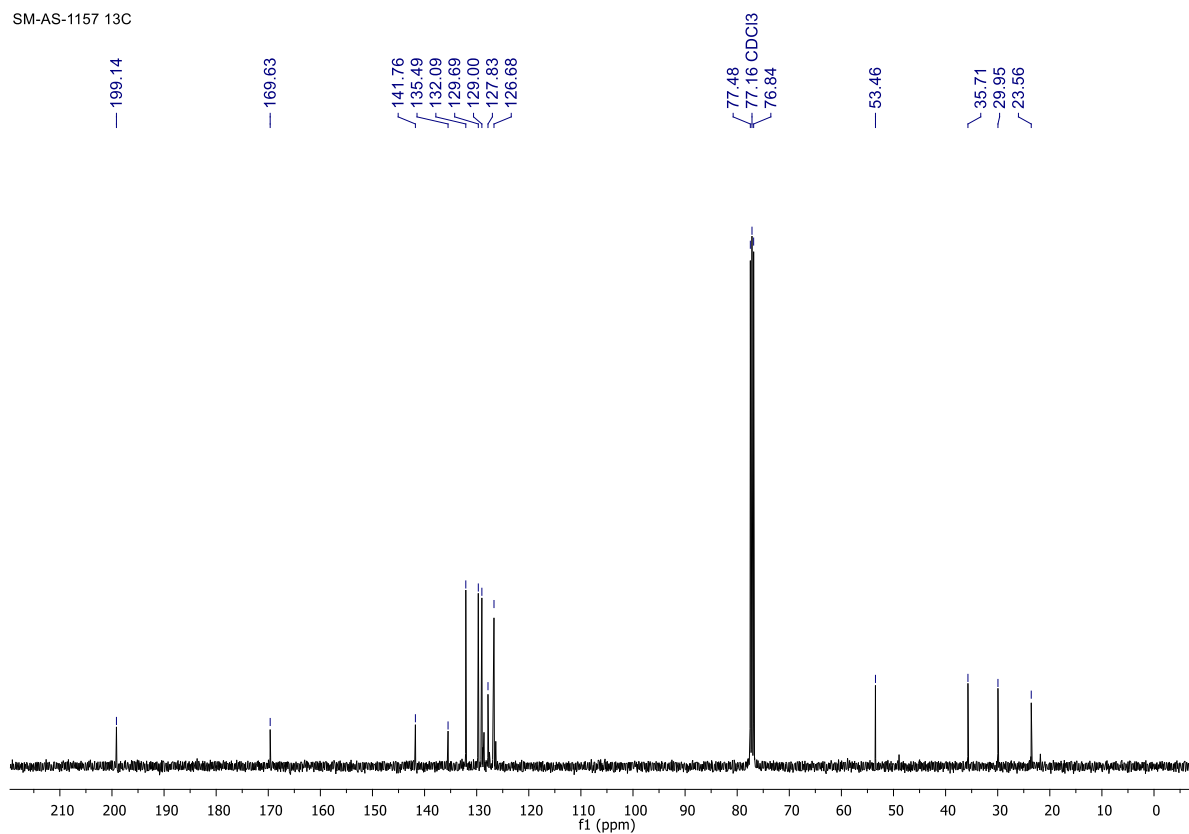
<sup>1</sup>H NMR of **4a** (400 MHz, CDCl<sub>3</sub>):

SM-AS-1157-R 1H



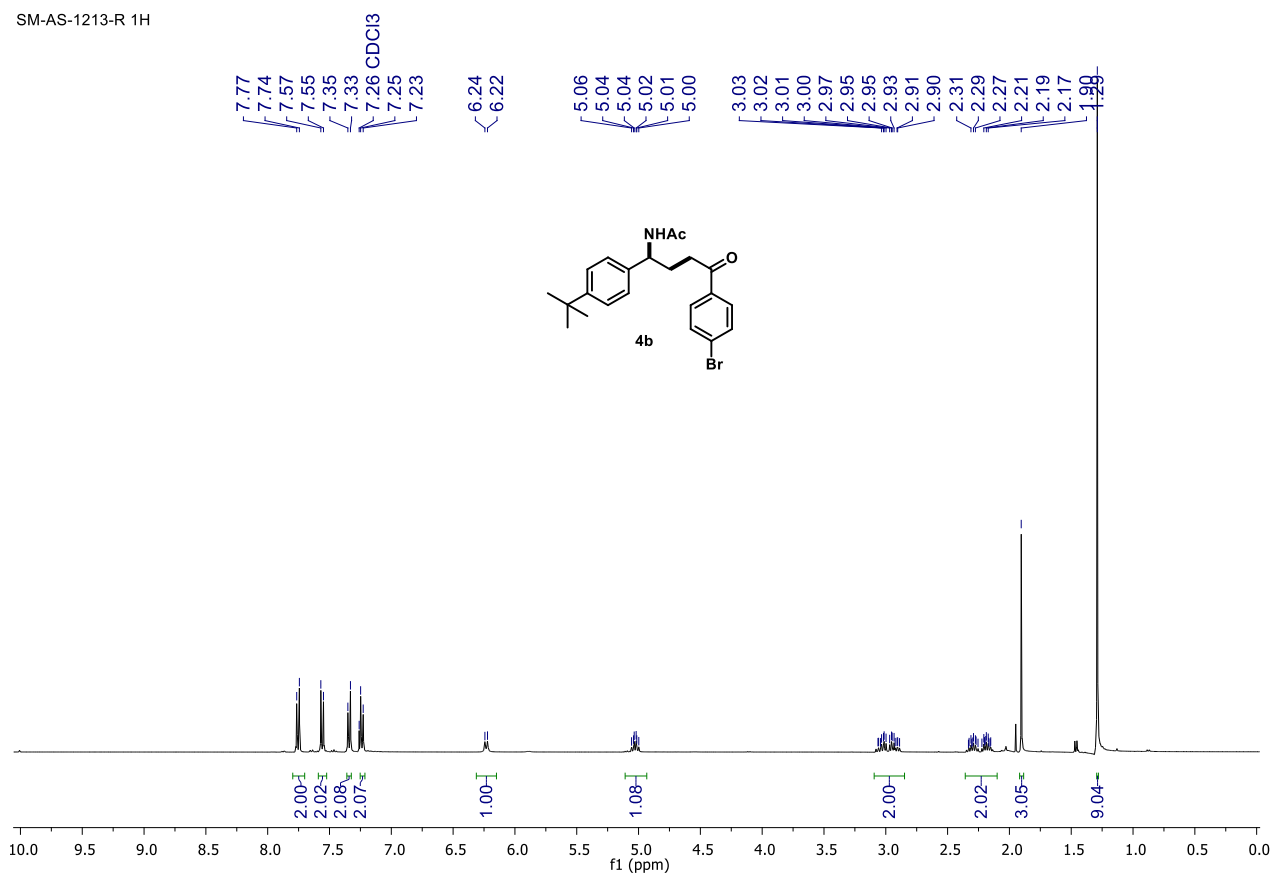
<sup>13</sup>C{<sup>1</sup>H} NMR of **4a** (101 MHz, CDCl<sub>3</sub>):

SM-AS-1157 13C



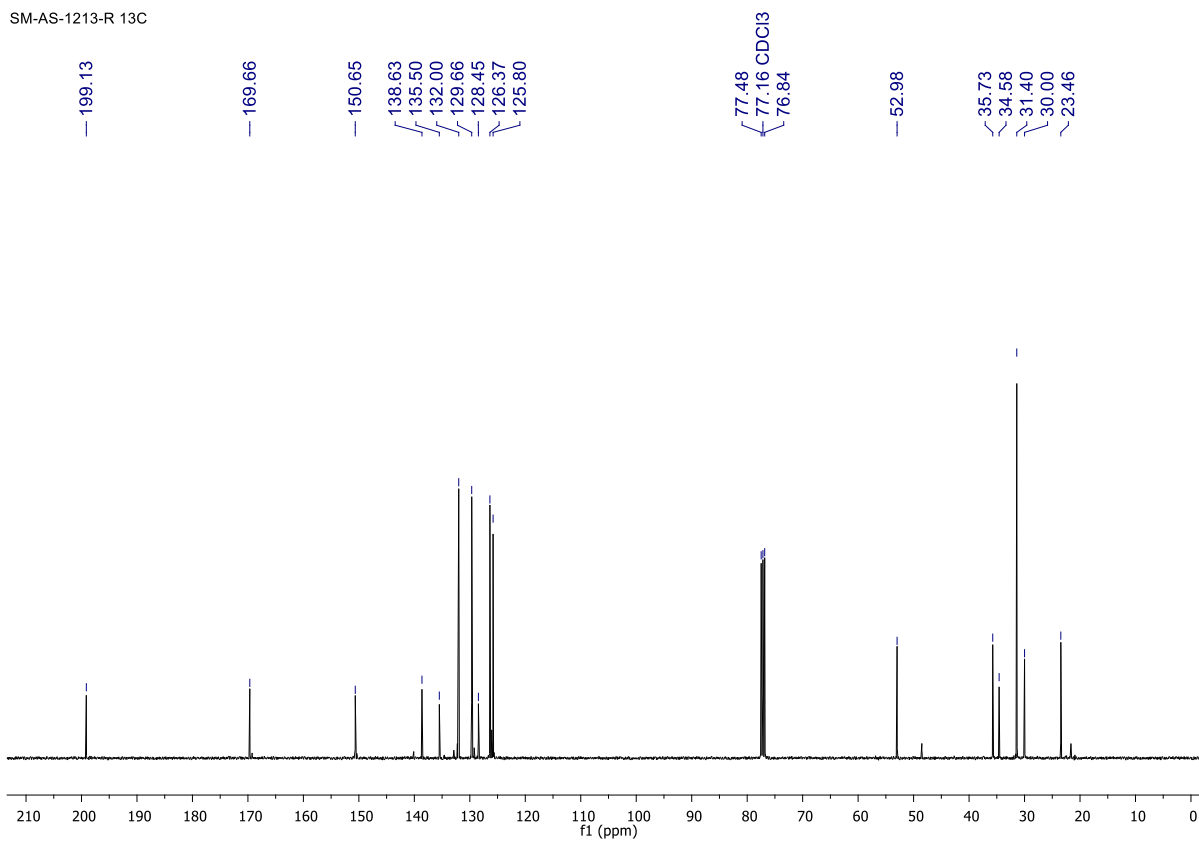
<sup>1</sup>H NMR of **4b** (400 MHz, CDCl<sub>3</sub>):

SM-AS-1213-R 1H



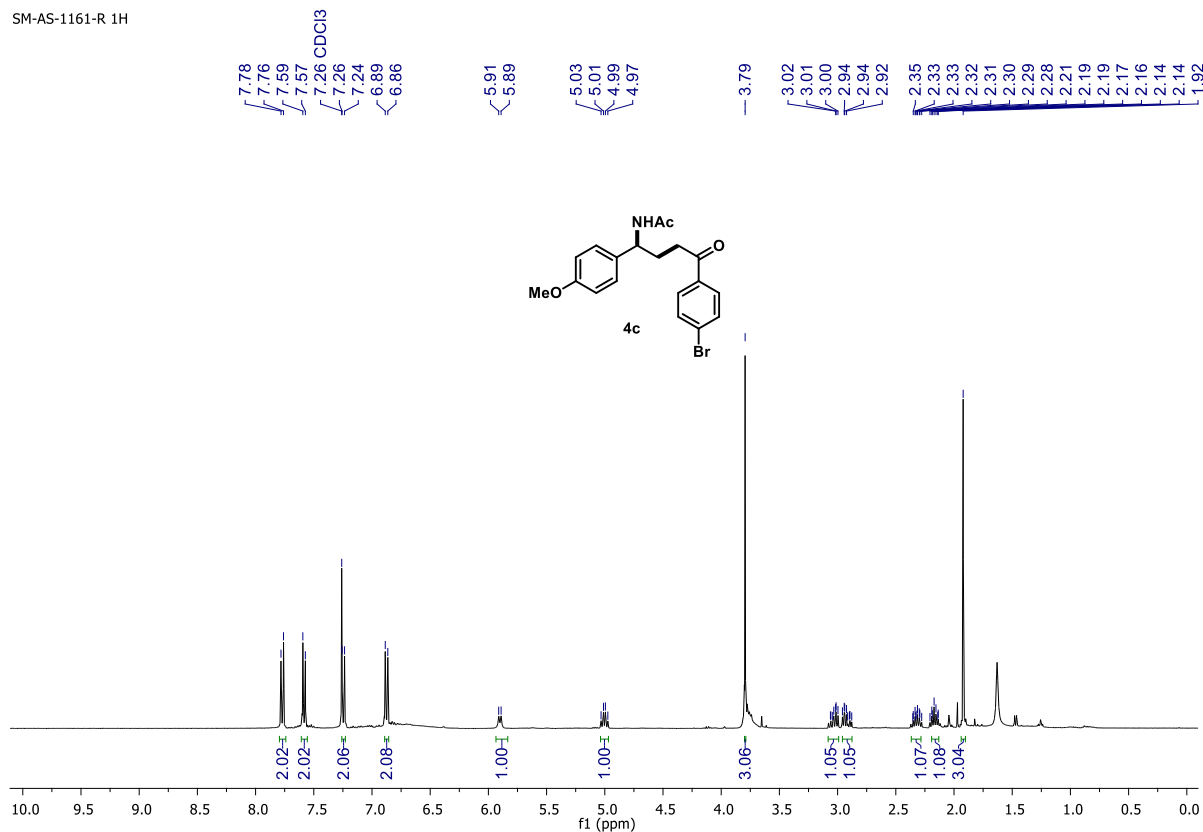
<sup>13</sup>C{<sup>1</sup>H} NMR of **4b** (101 MHz, CDCl<sub>3</sub>):

SM-AS-1213-R 13C



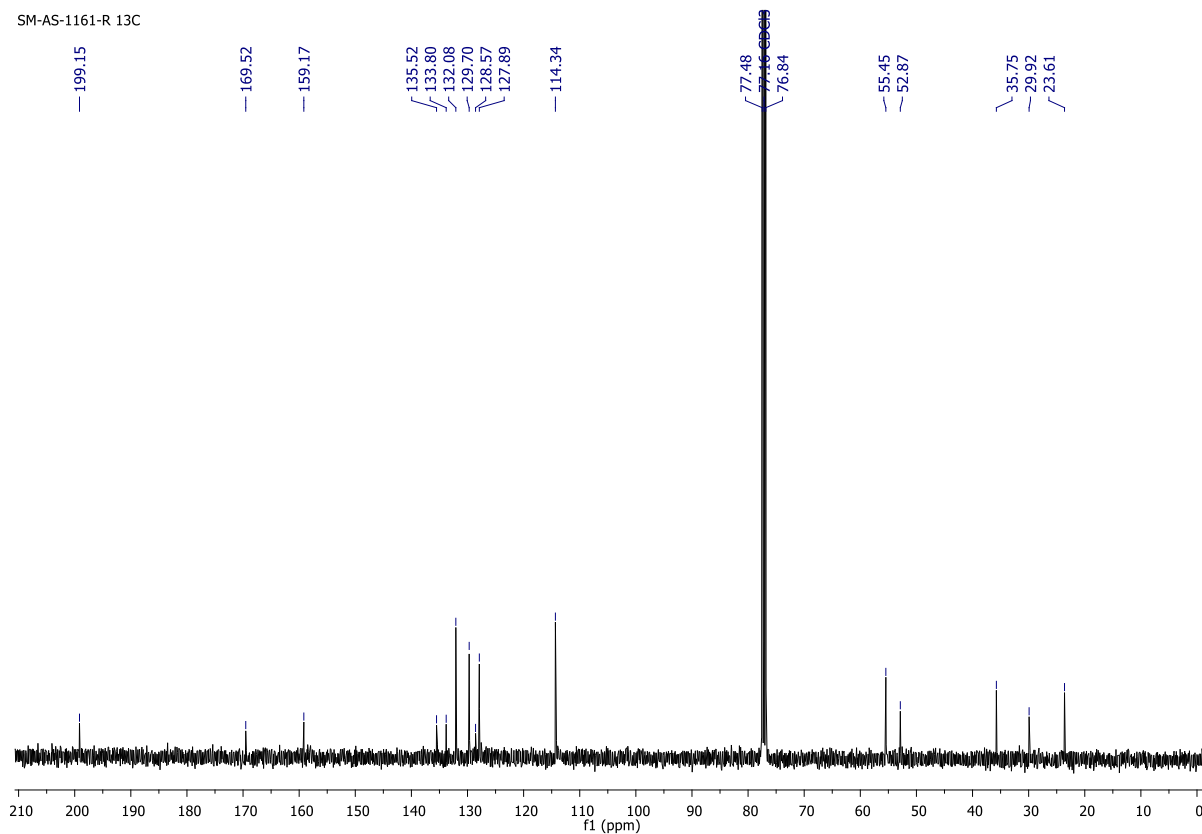
<sup>1</sup>H NMR of **4c** (400 MHz, CDCl<sub>3</sub>):

SM-AS-1161-R 1H



<sup>13</sup>C{<sup>1</sup>H} NMR of **4c** (101 MHz, CDCl<sub>3</sub>):

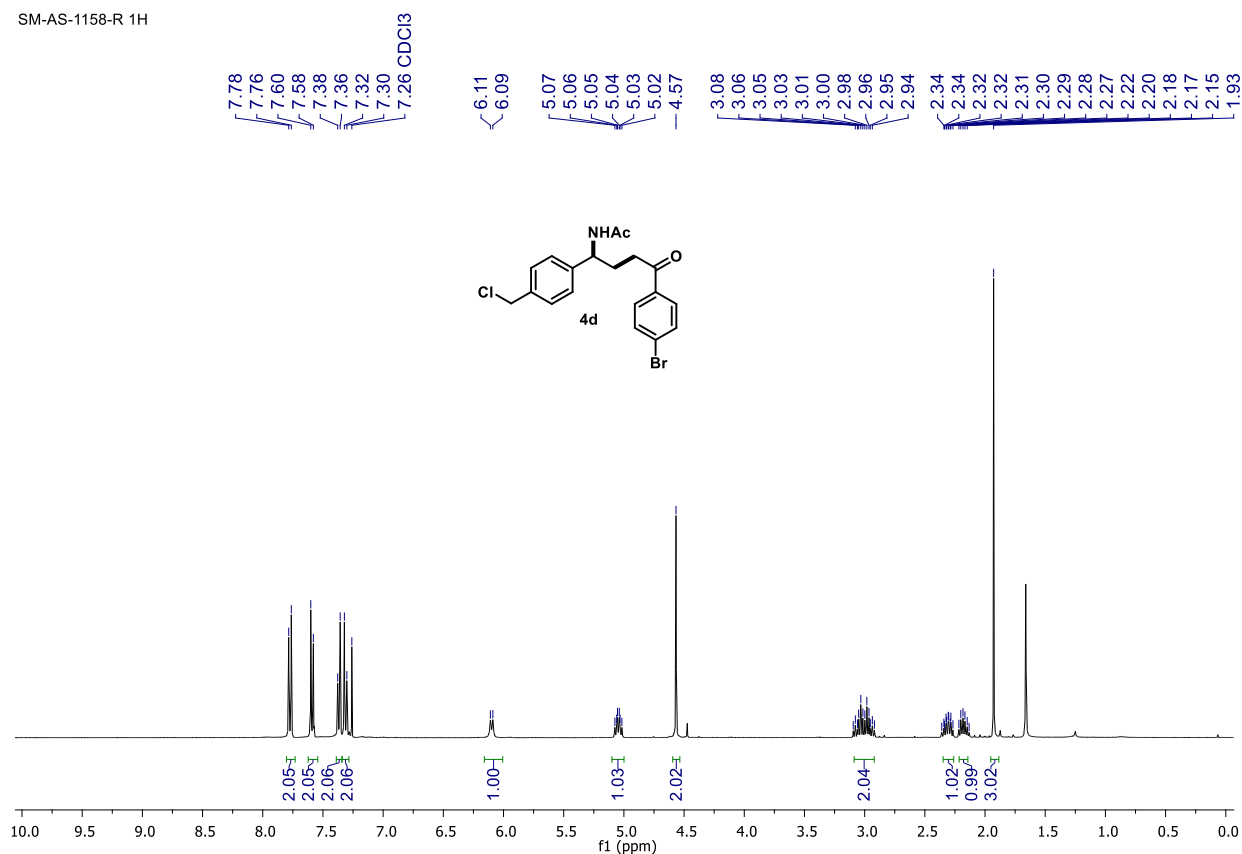
SM-AS-1161-R 13C





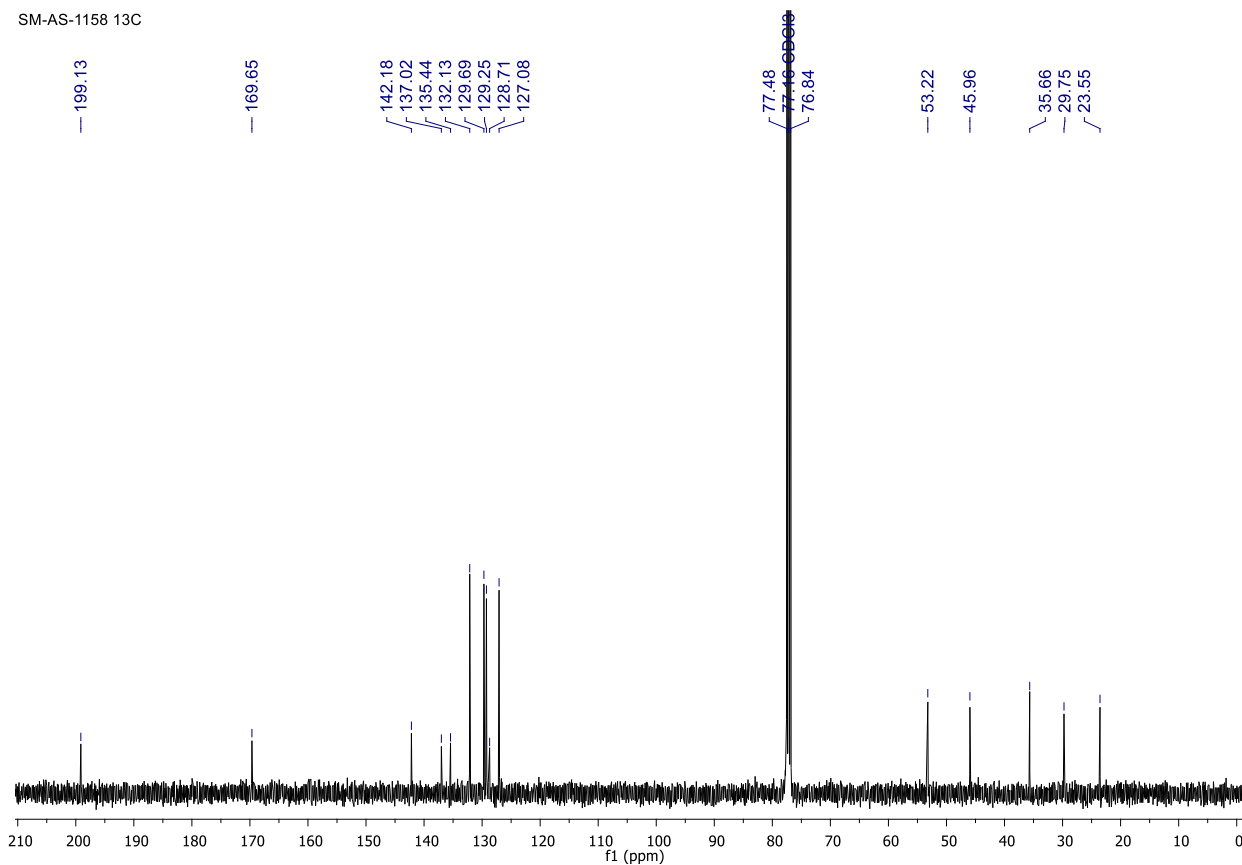
<sup>1</sup>H NMR of **4d** (400 MHz, CDCl<sub>3</sub>):

SM-AS-1158-R 1H



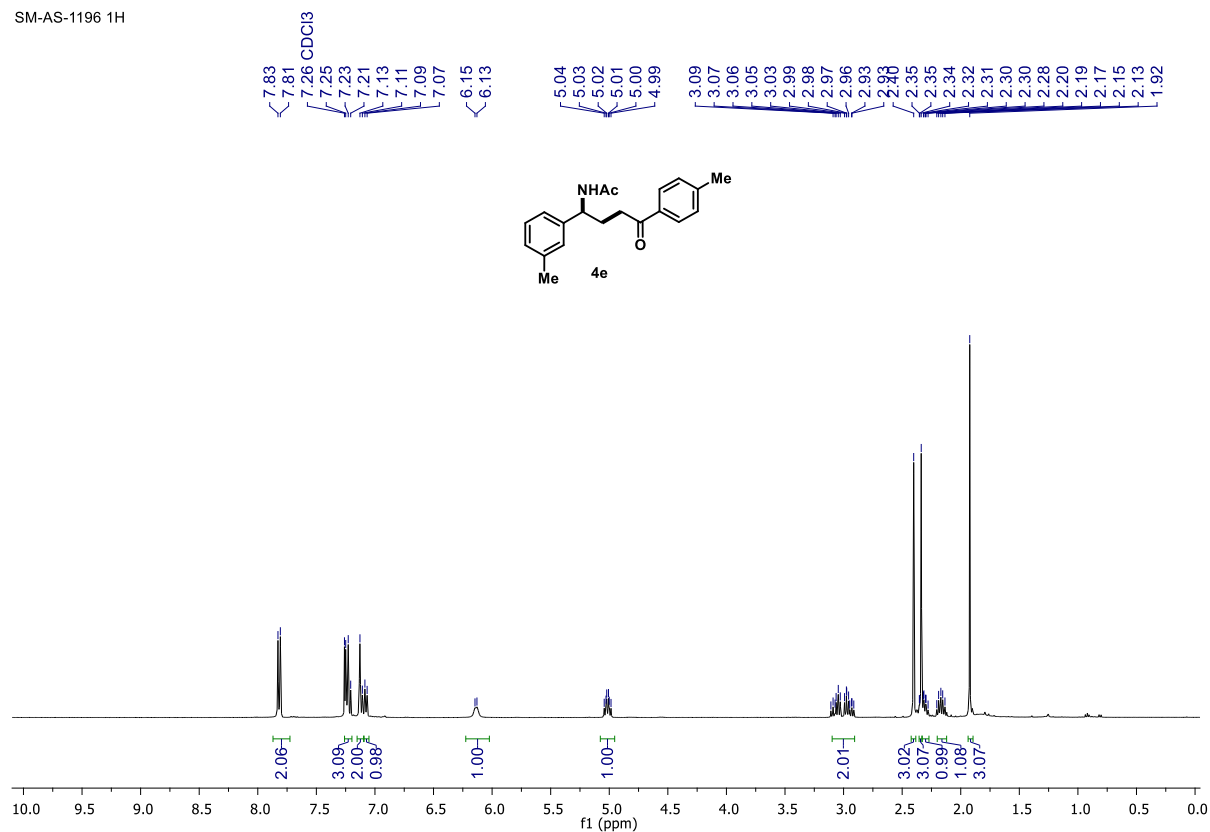
<sup>13</sup>C{<sup>1</sup>H} NMR of **4d** (101 MHz, CDCl<sub>3</sub>):

SM-AS-1158 13C



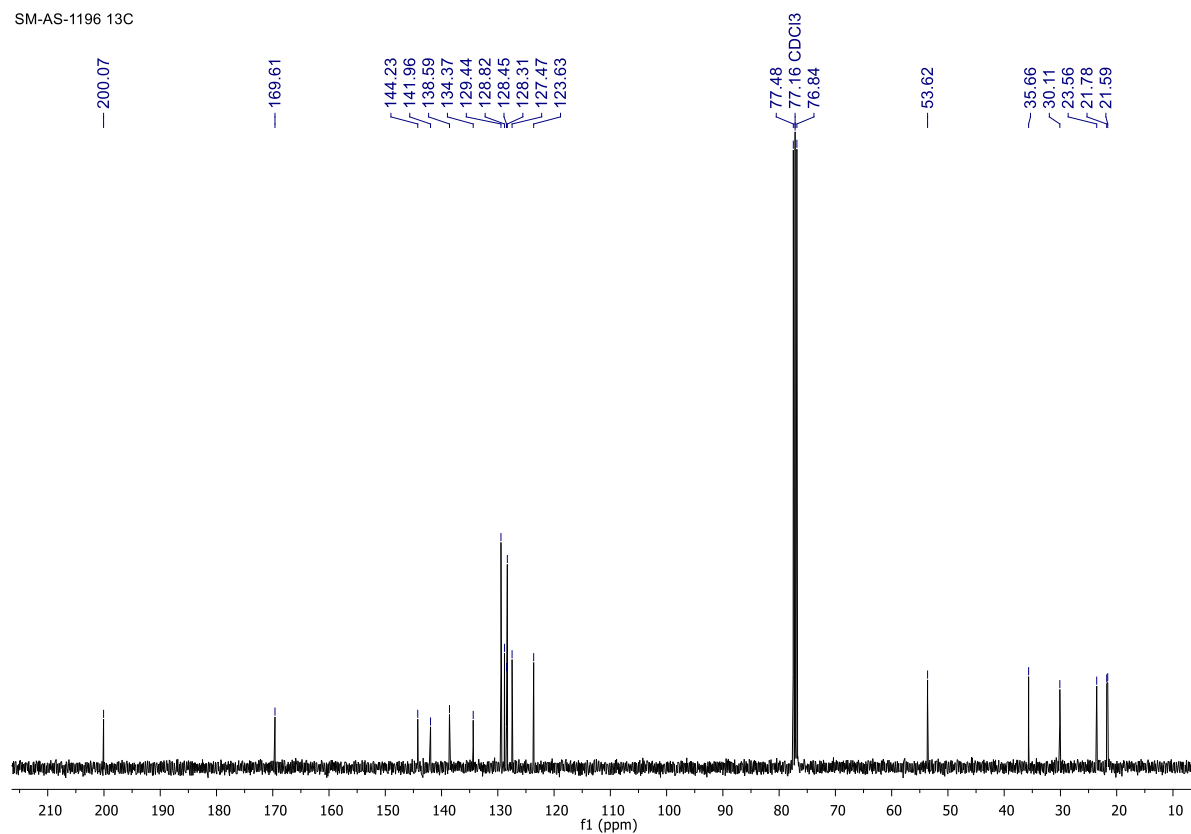
$^1\text{H}$  NMR of **4e** (400 MHz,  $\text{CDCl}_3$ ):

SM-AS-1196 1H



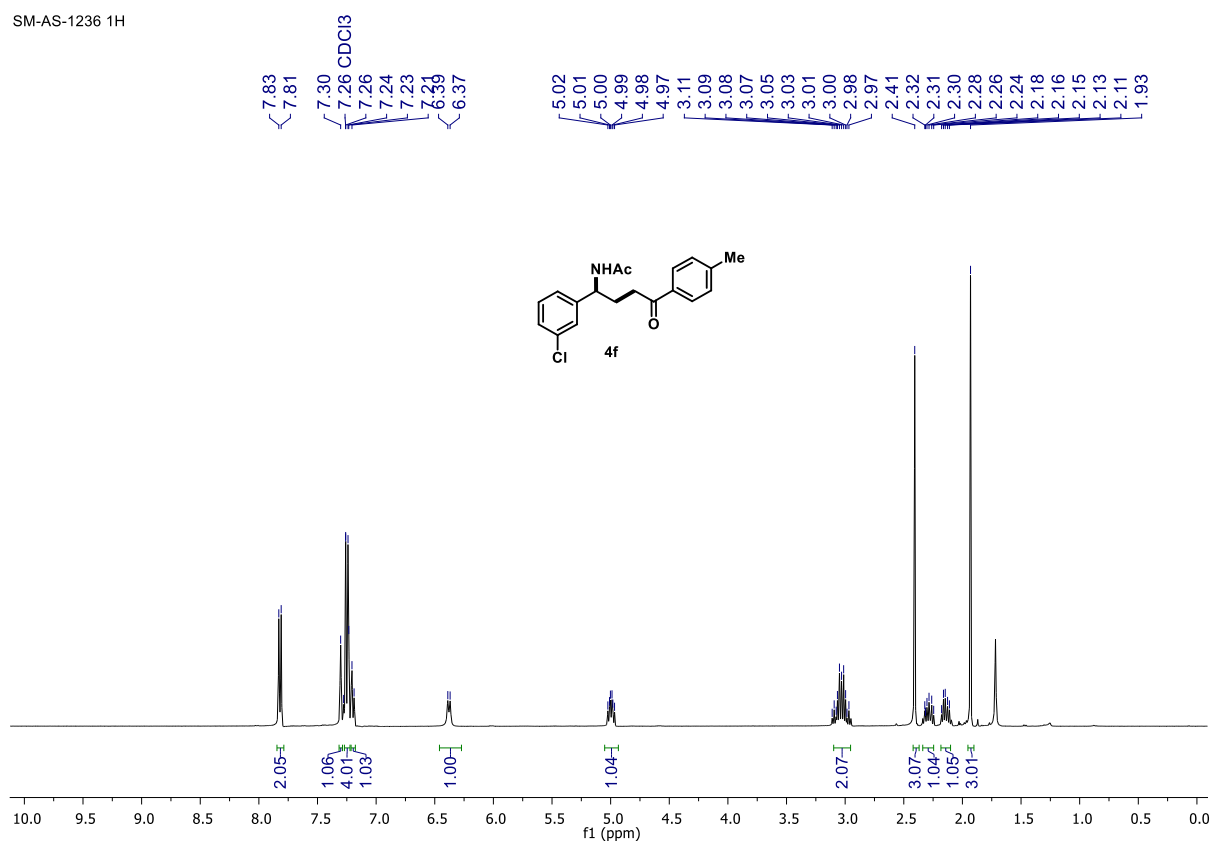
$^{13}\text{C}\{^1\text{H}\}$  NMR of **4e** (101 MHz,  $\text{CDCl}_3$ ):

SM-AS-1196 13C



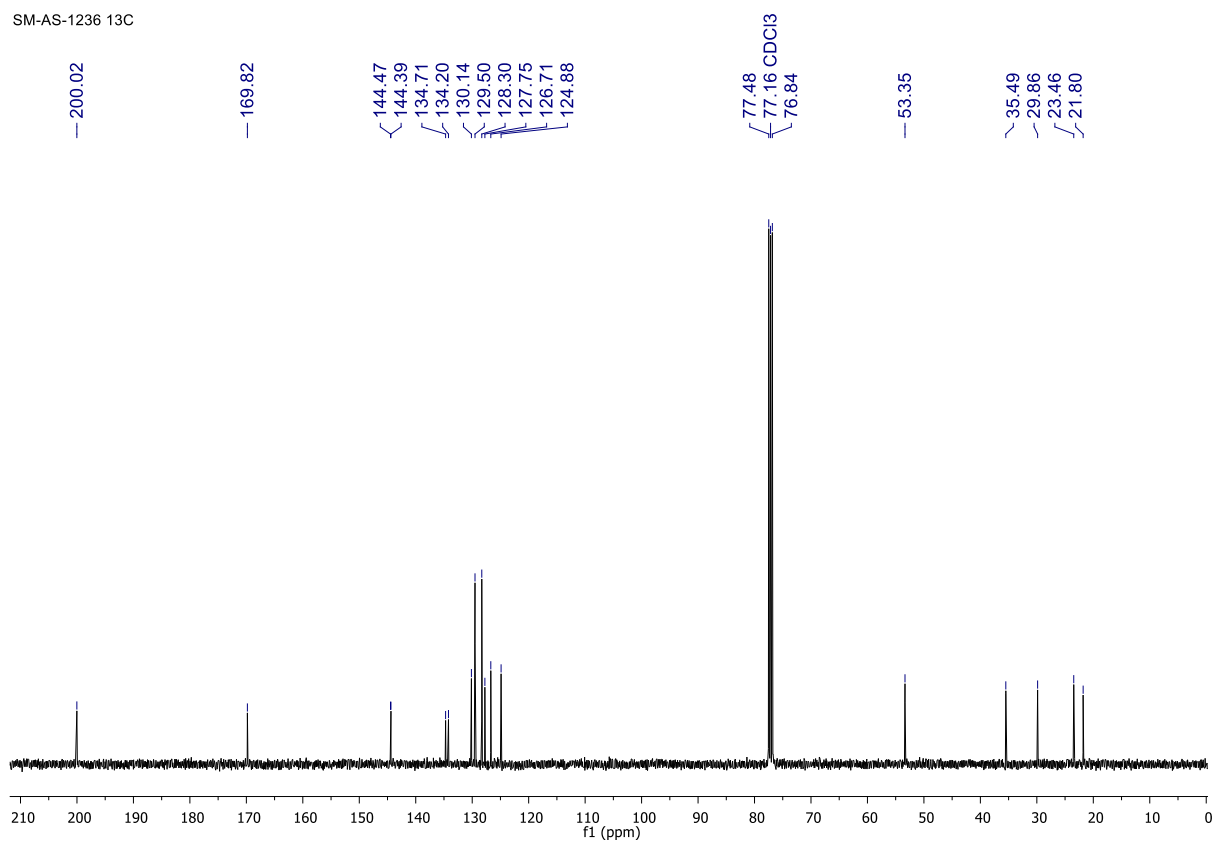
<sup>1</sup>H NMR of **4f** (400 MHz, CDCl<sub>3</sub>):

SM-AS-1236 1H



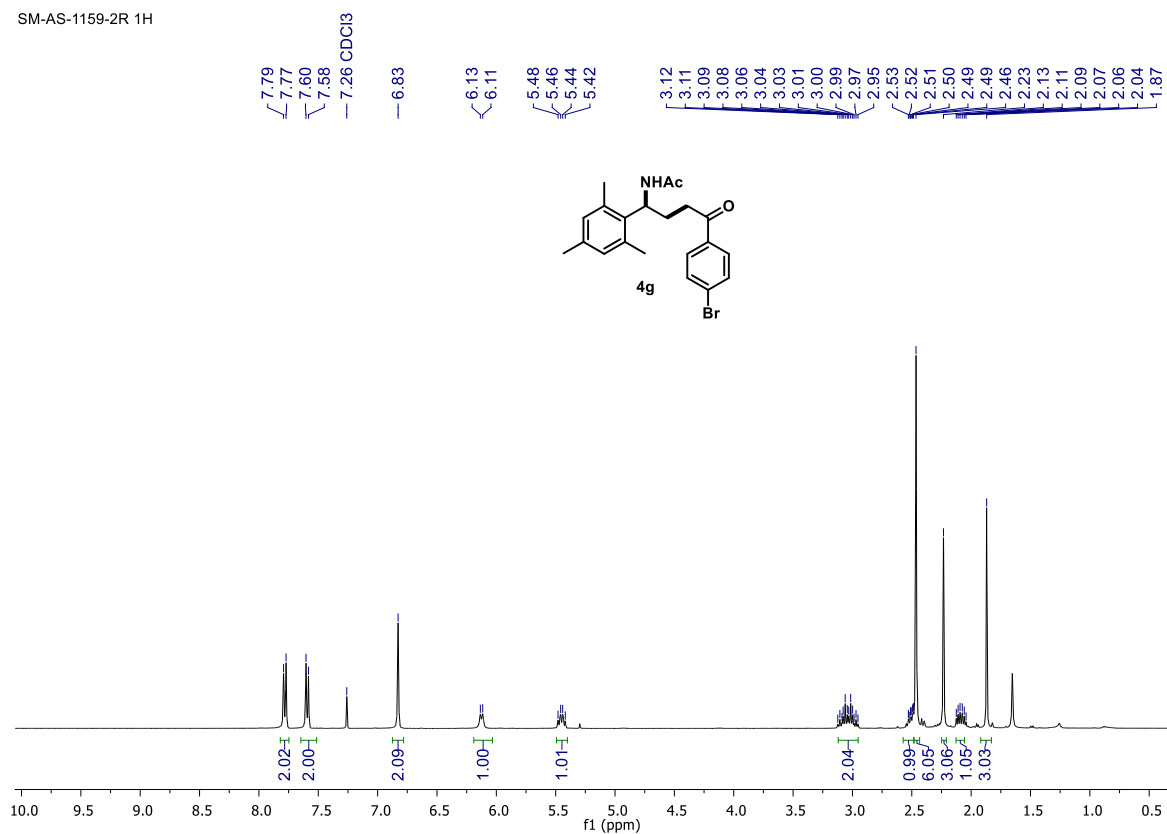
<sup>13</sup>C{<sup>1</sup>H} NMR of **4f** (101 MHz, CDCl<sub>3</sub>):

SM-AS-1236 13C



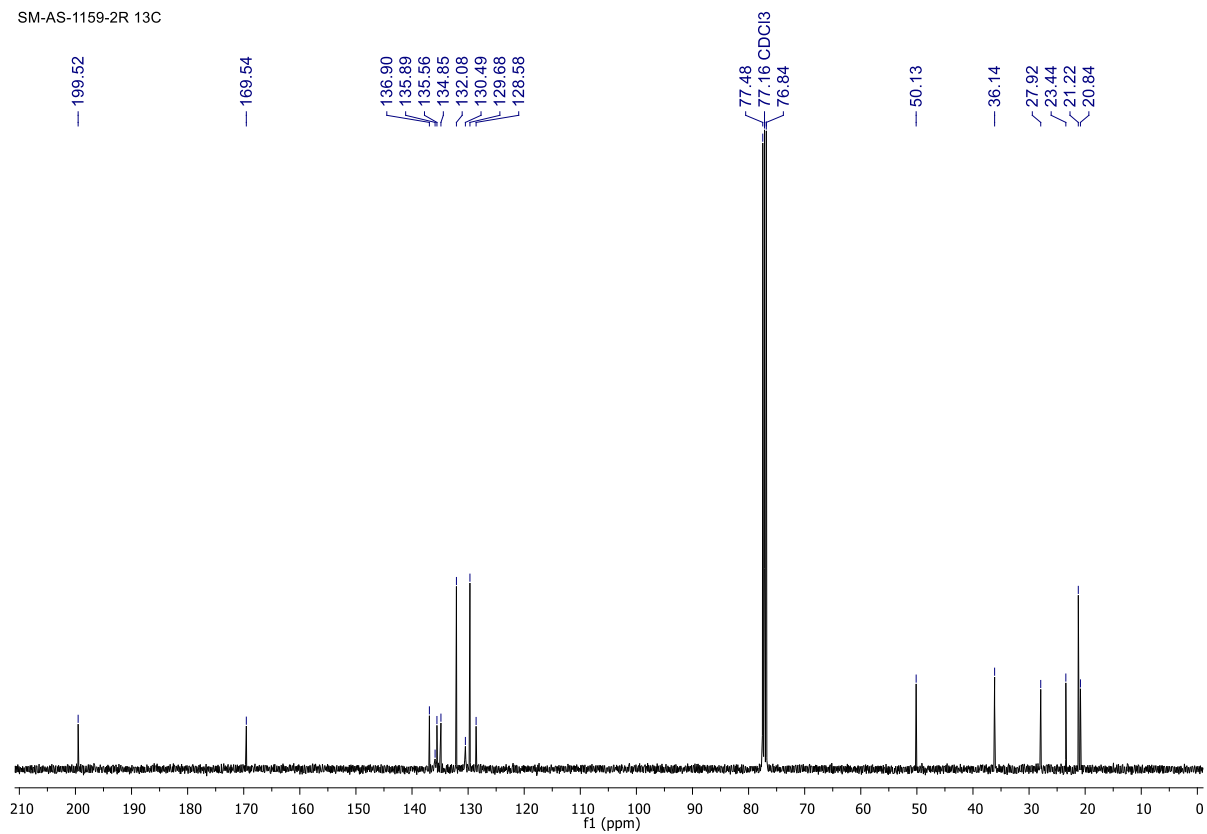
<sup>1</sup>H NMR of **4g** (400 MHz, CDCl<sub>3</sub>):

SM-AS-1159-2R 1H



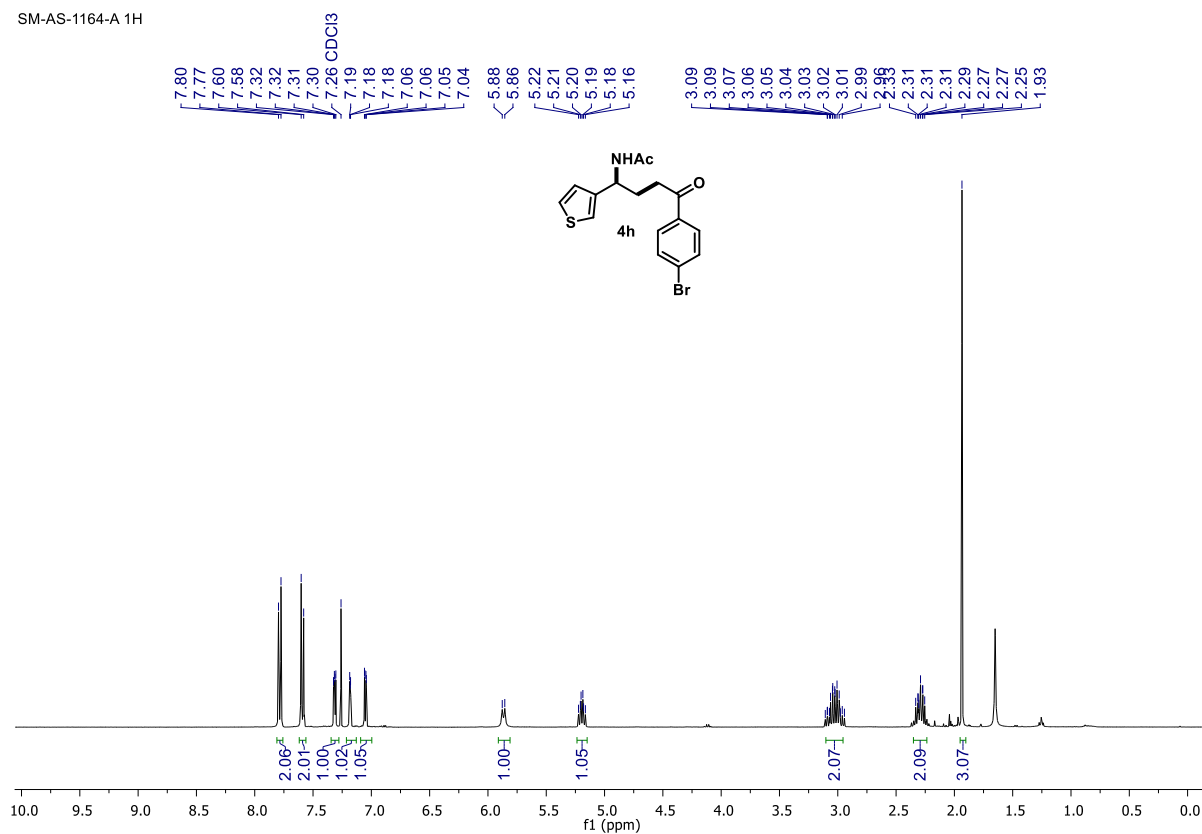
<sup>13</sup>C{<sup>1</sup>H} NMR of **4g** (101 MHz, CDCl<sub>3</sub>):

SM-AS-1159-2R 13C



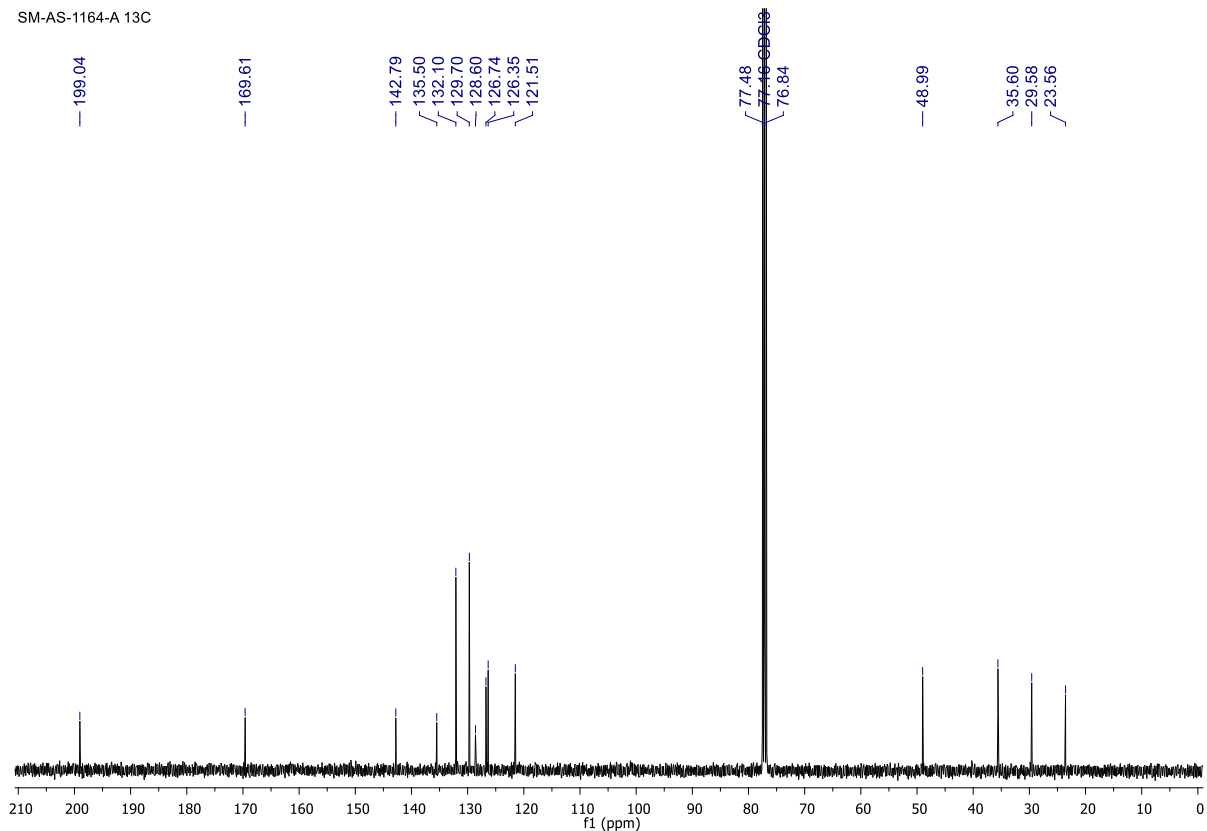
<sup>1</sup>H NMR of **4h** (400 MHz, CDCl<sub>3</sub>):

SM-AS-1164-A 1H



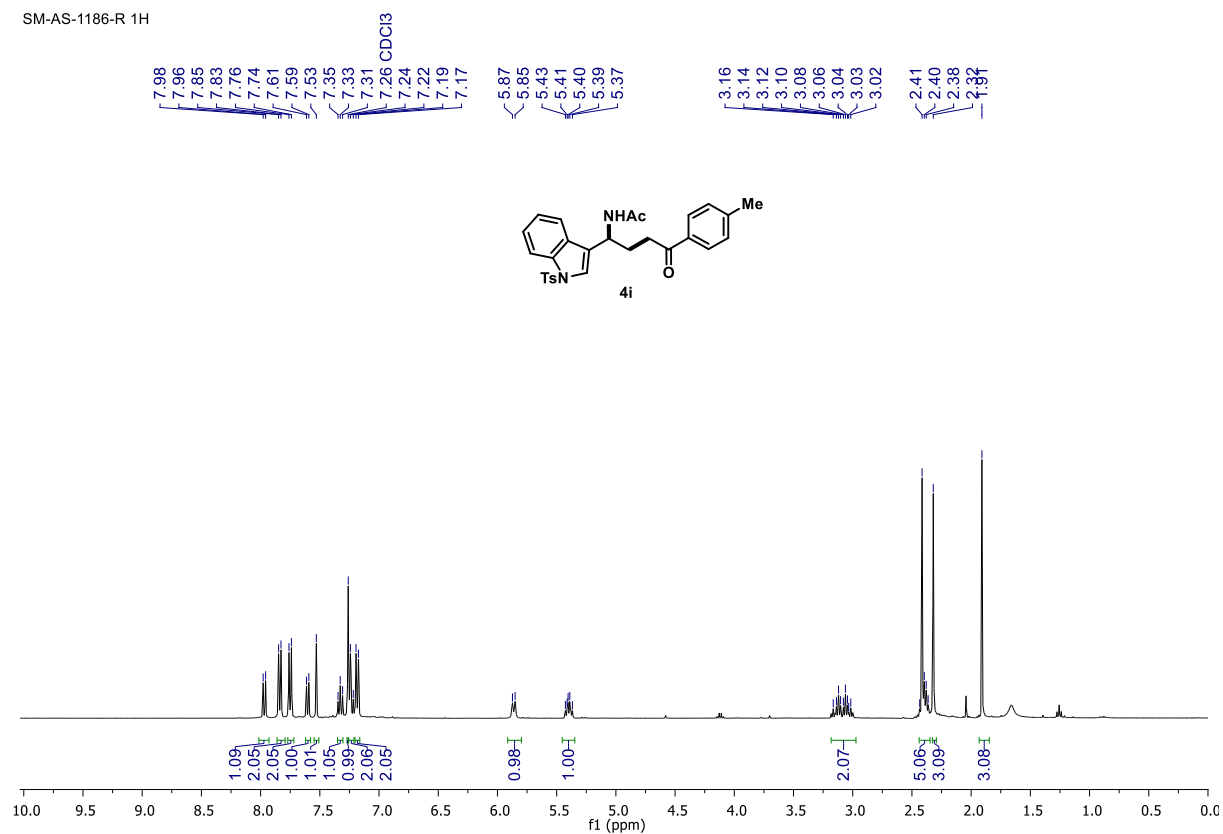
<sup>13</sup>C{<sup>1</sup>H} NMR of **4h** (101 MHz, CDCl<sub>3</sub>):

SM-AS-1164-A 13C



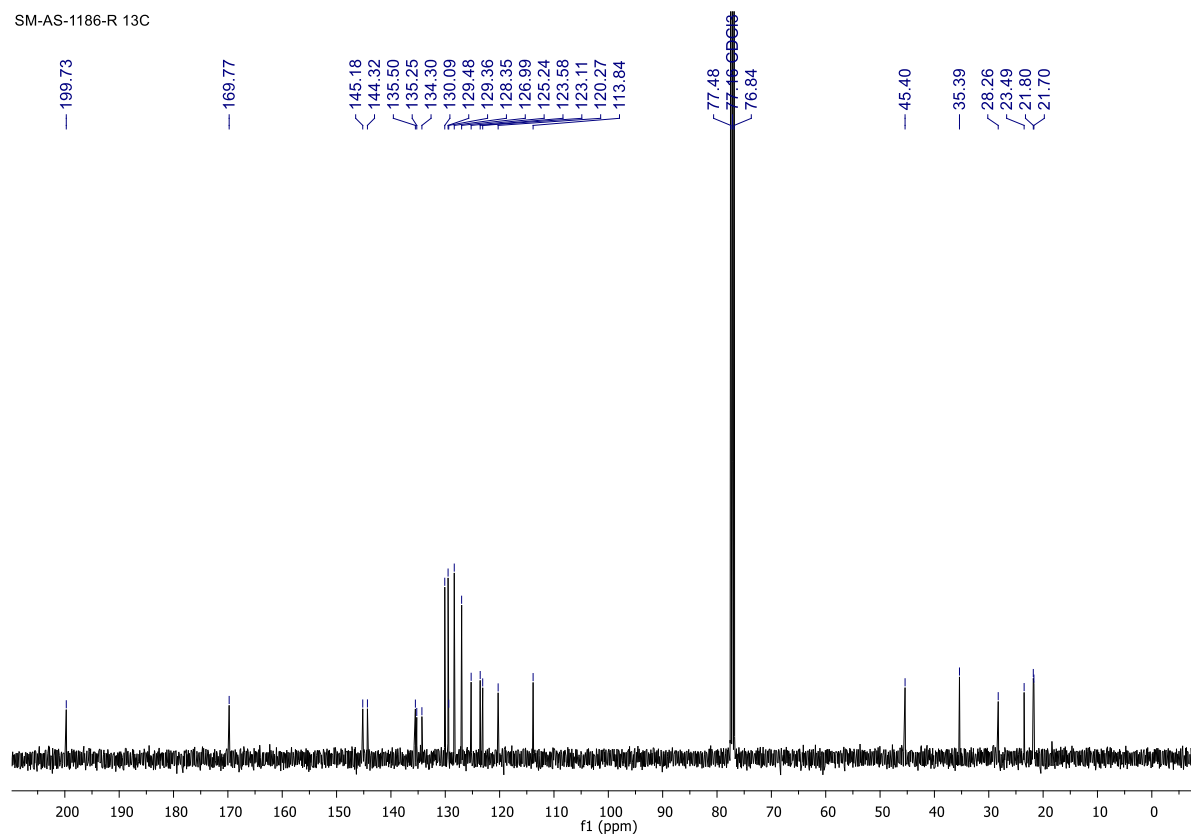
<sup>1</sup>H NMR of **4i** (400 MHz, CDCl<sub>3</sub>):

SM-AS-1186-R 1H



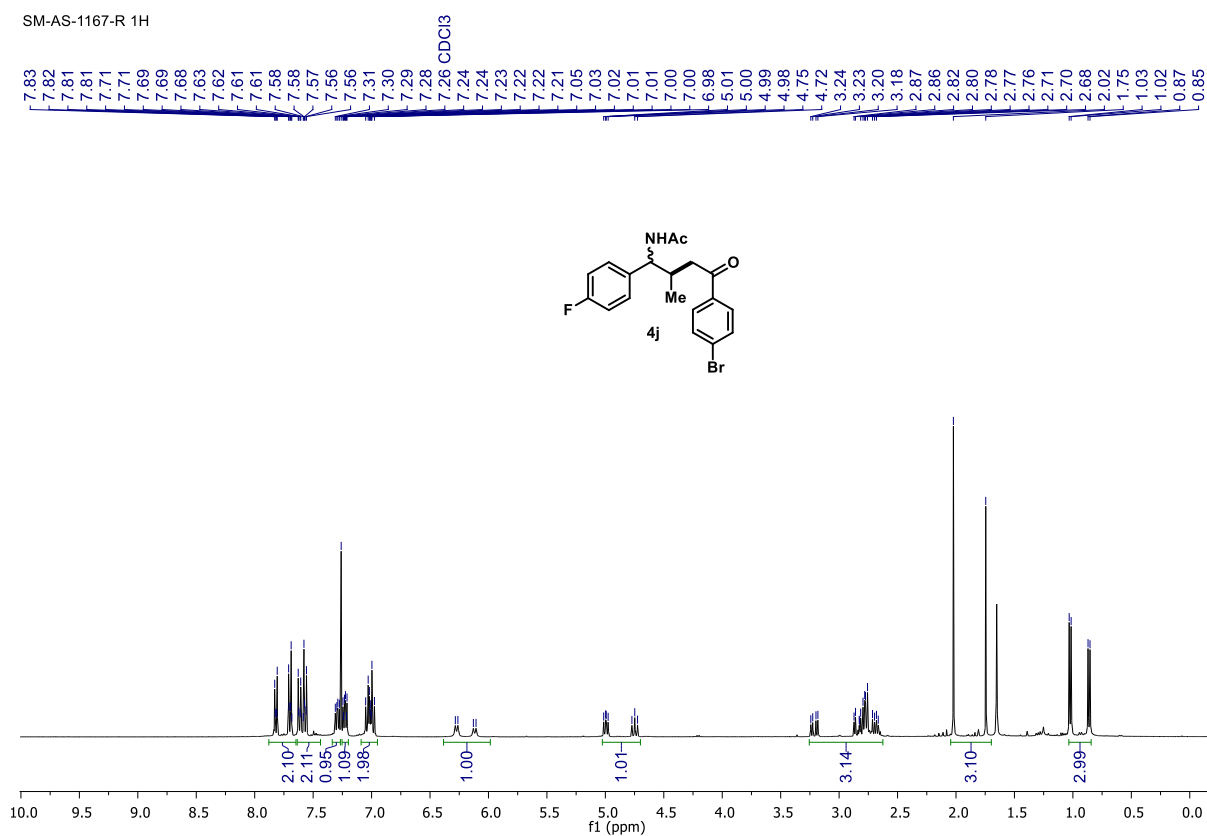
<sup>13</sup>C{<sup>1</sup>H} NMR of **4i** (101 MHz, CDCl<sub>3</sub>):

SM-AS-1186-R 13C



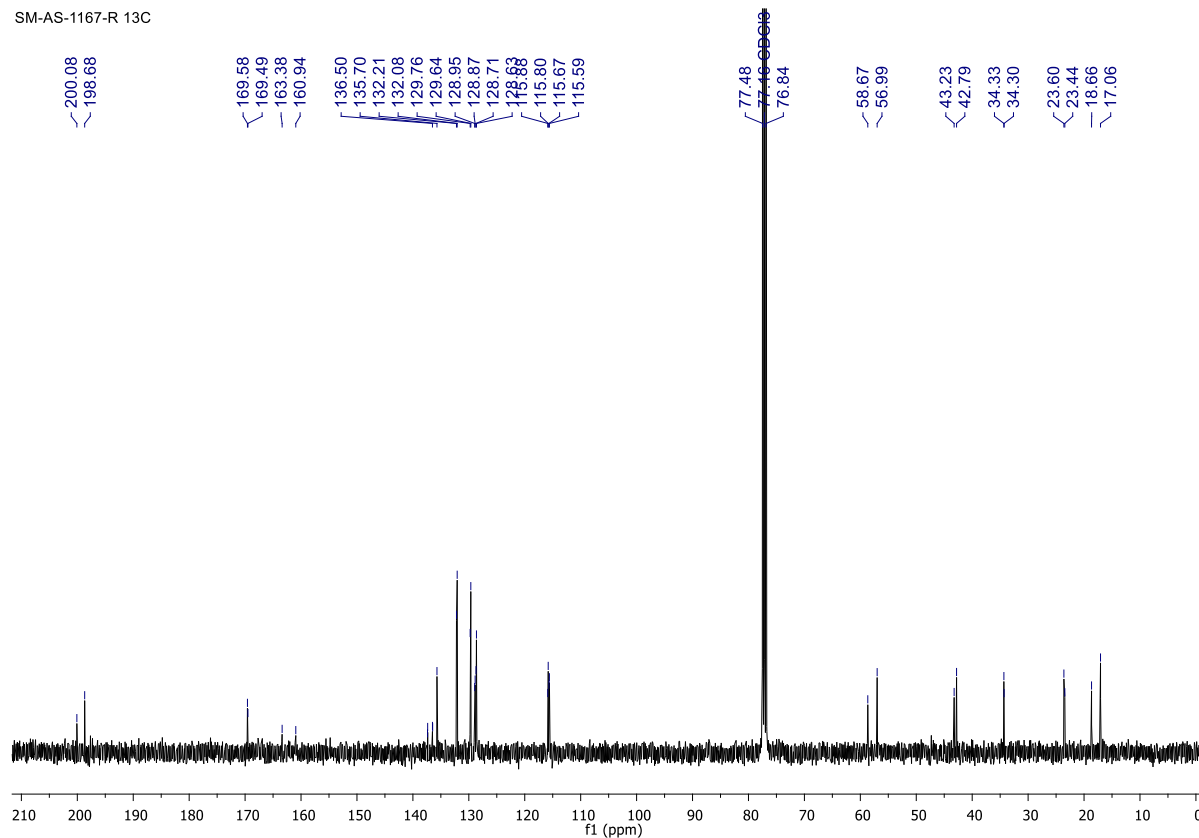
<sup>1</sup>H NMR of **4j** (400 MHz, CDCl<sub>3</sub>):

SM-AS-1167-R 1H



<sup>13</sup>C{<sup>1</sup>H} NMR of **4j** (101 MHz, CDCl<sub>3</sub>):

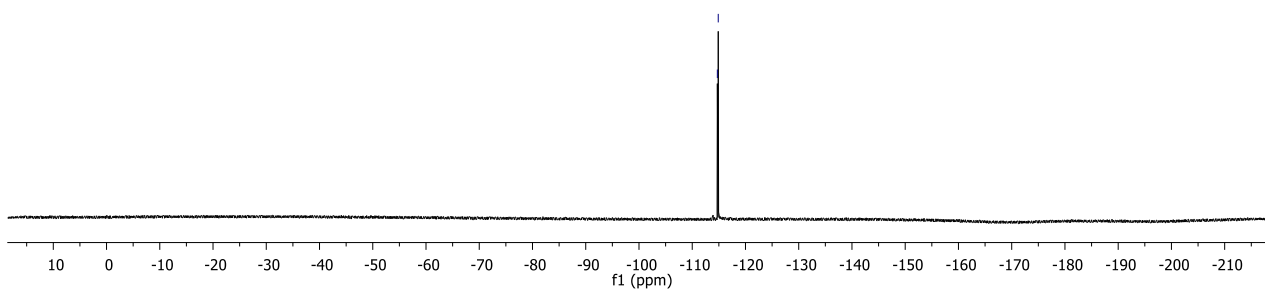
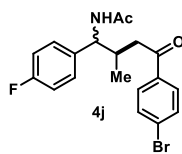
SM-AS-1167-R 13C



{<sup>19</sup>F} NMR of **4j** (377 MHz, CDCl<sub>3</sub>):

SM-AS-1167-R 19F

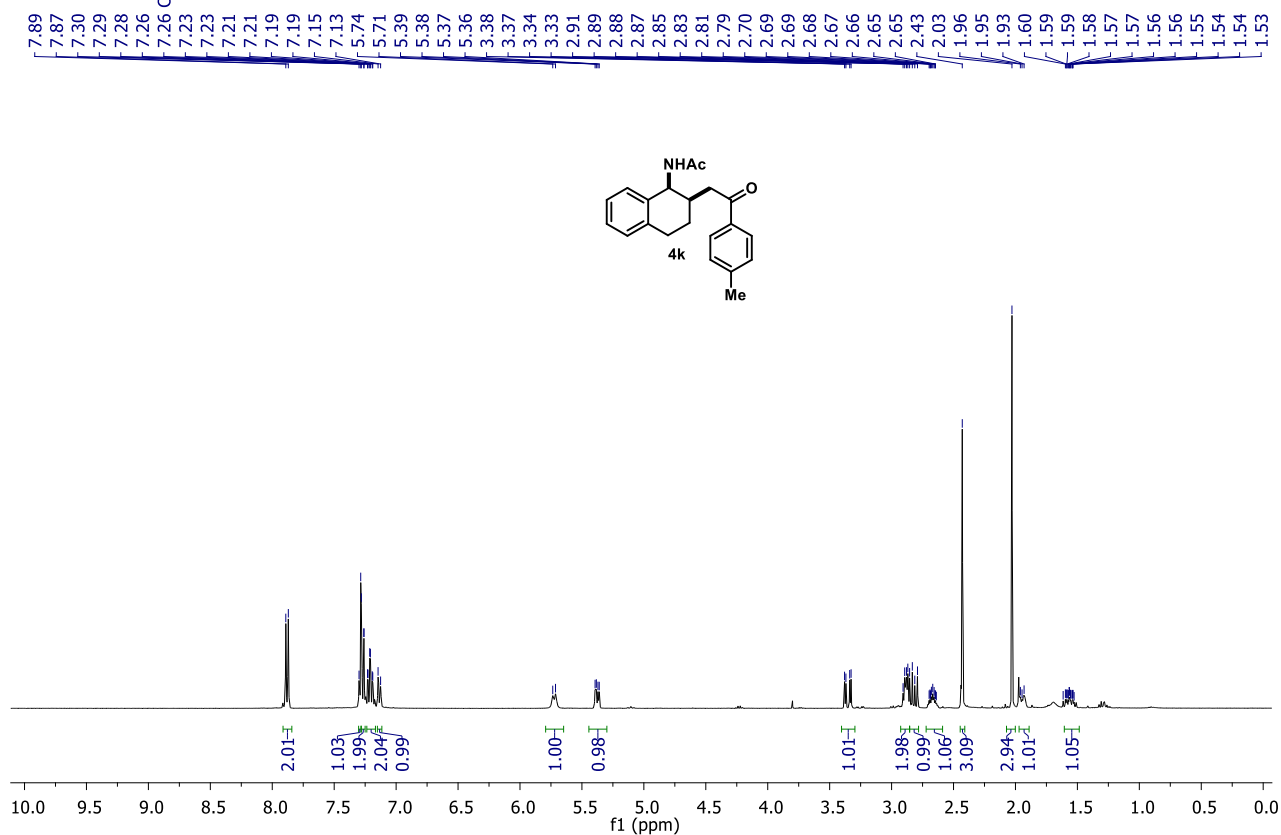
-114.72  
-114.89





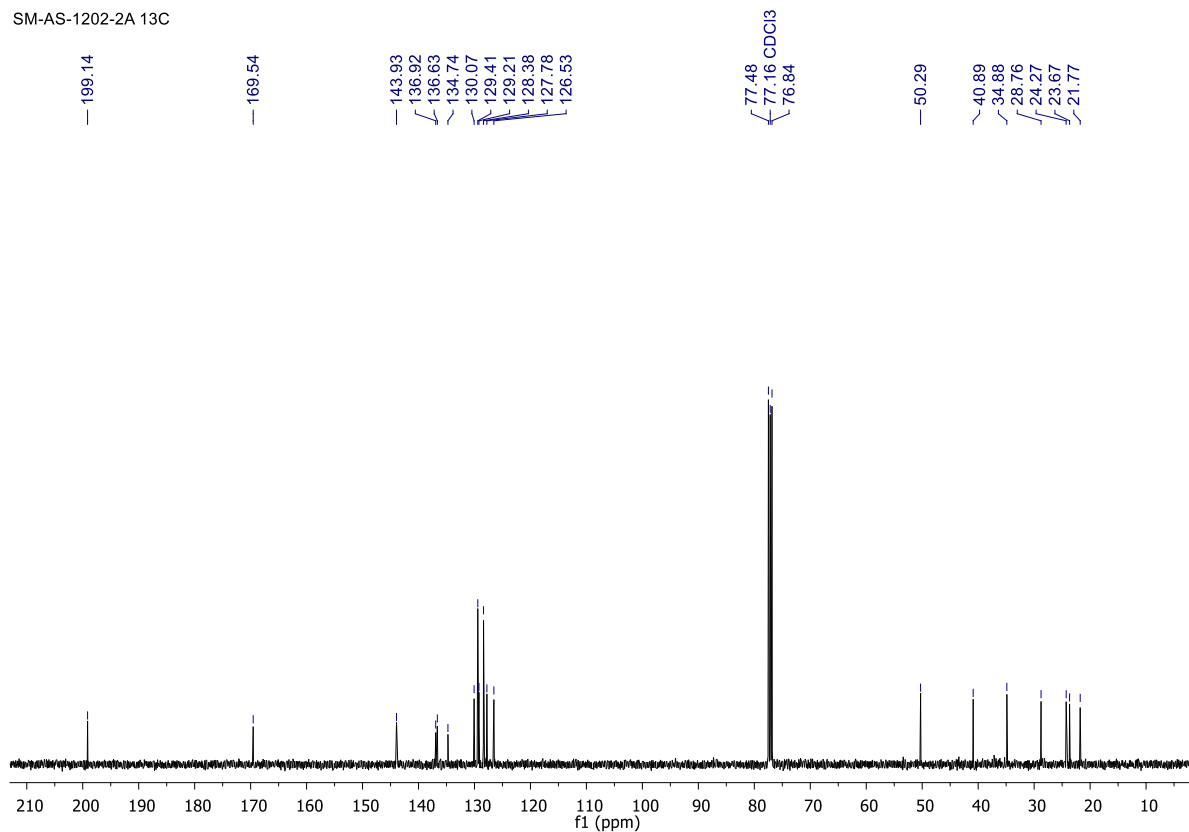
<sup>1</sup>H NMR of **4k** (400 MHz, CDCl<sub>3</sub>):

SM-AS-1202-2A  
CDCl<sub>3</sub>

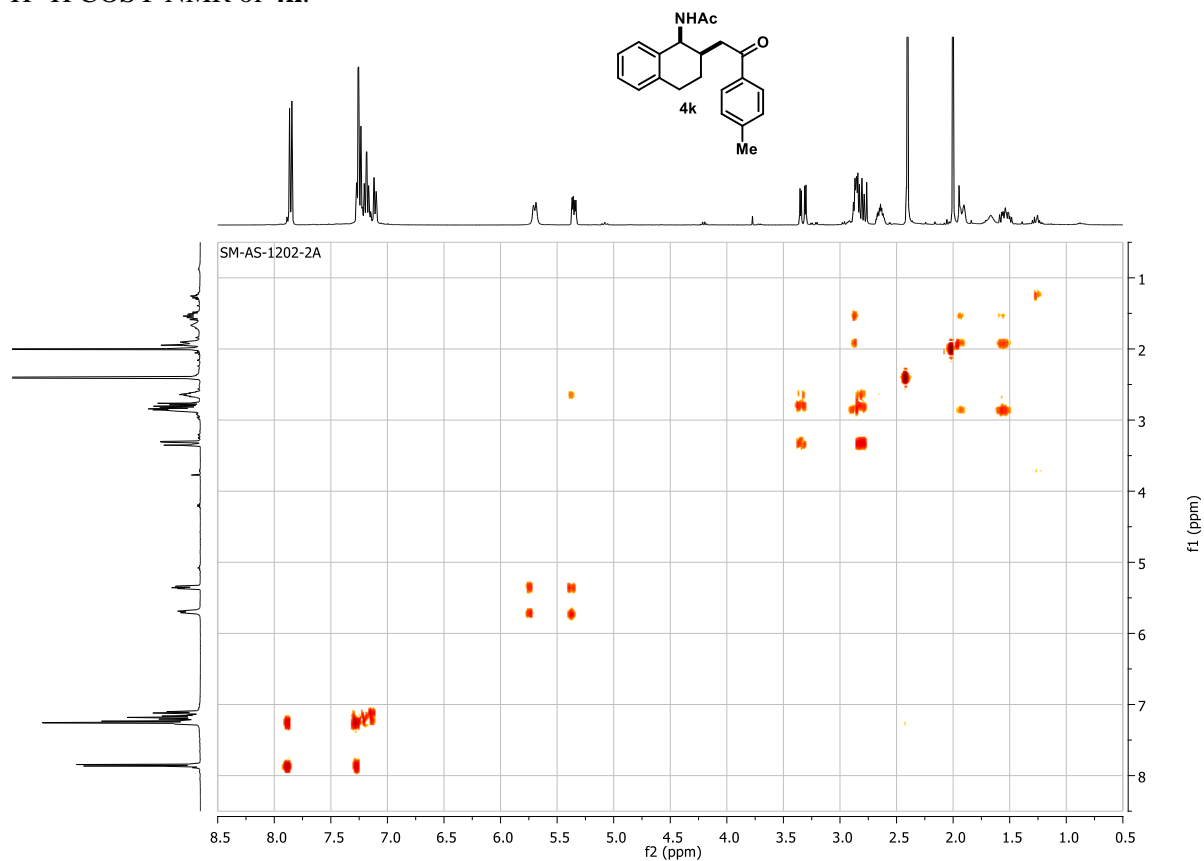


<sup>13</sup>C{<sup>1</sup>H} NMR of **4k** (101 MHz, CDCl<sub>3</sub>):

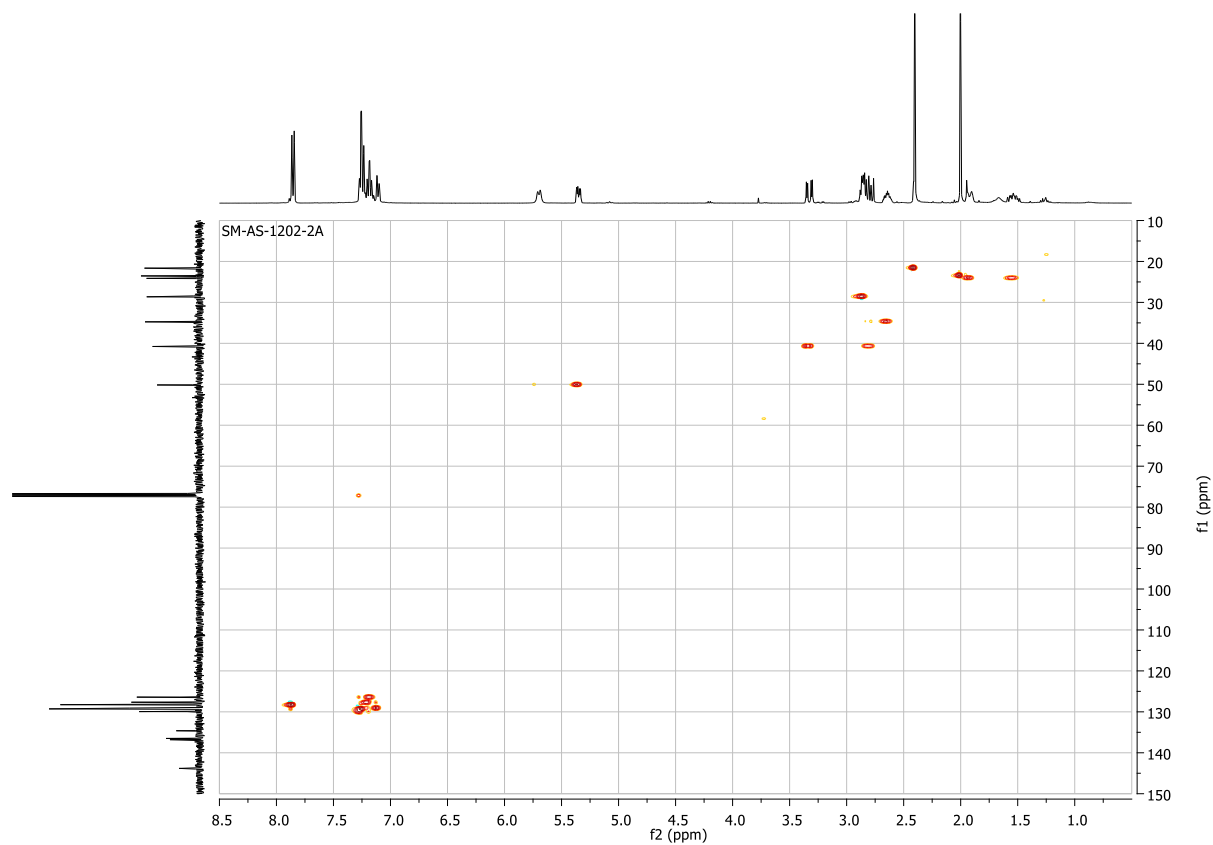
SM-AS-1202-2A 13C



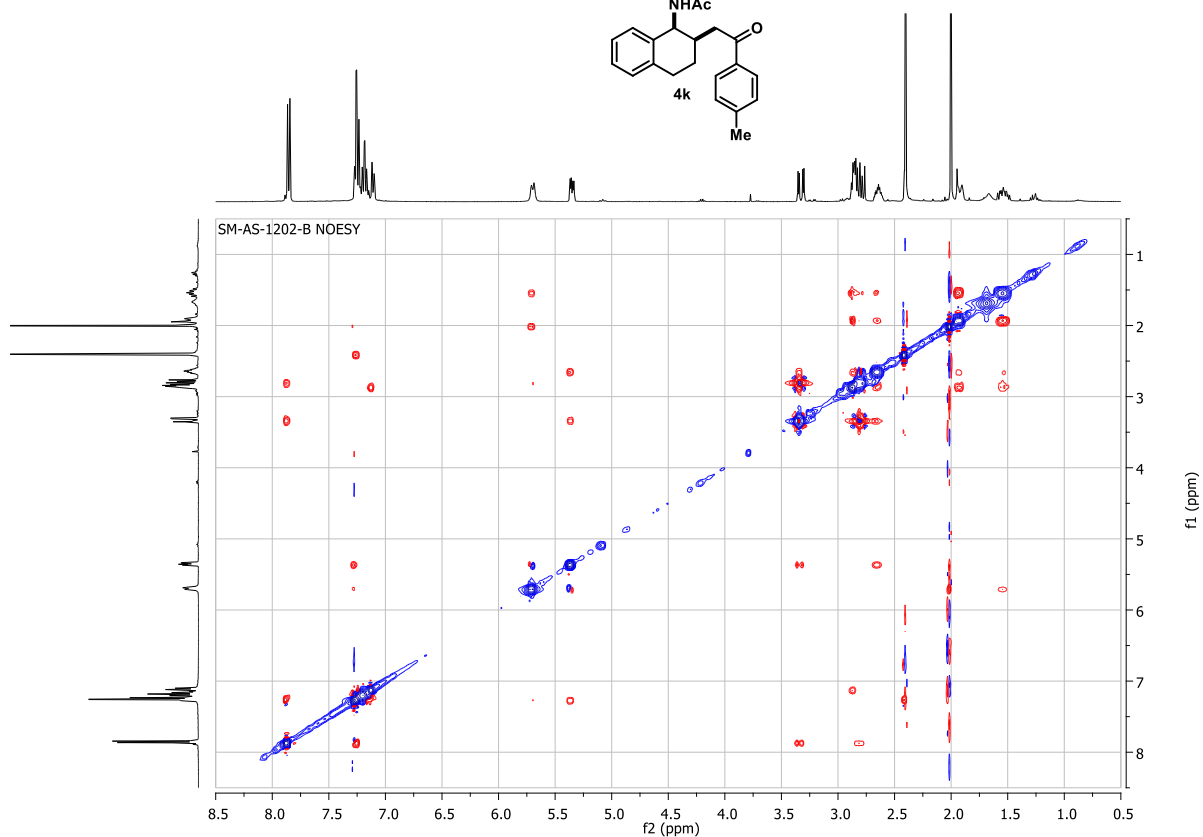
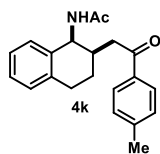
$^1\text{H}$ - $^1\text{H}$  COSY NMR of **4k**:



$^1\text{H}$ - $^{13}\text{C}$  HSQC NMR of **4k**:

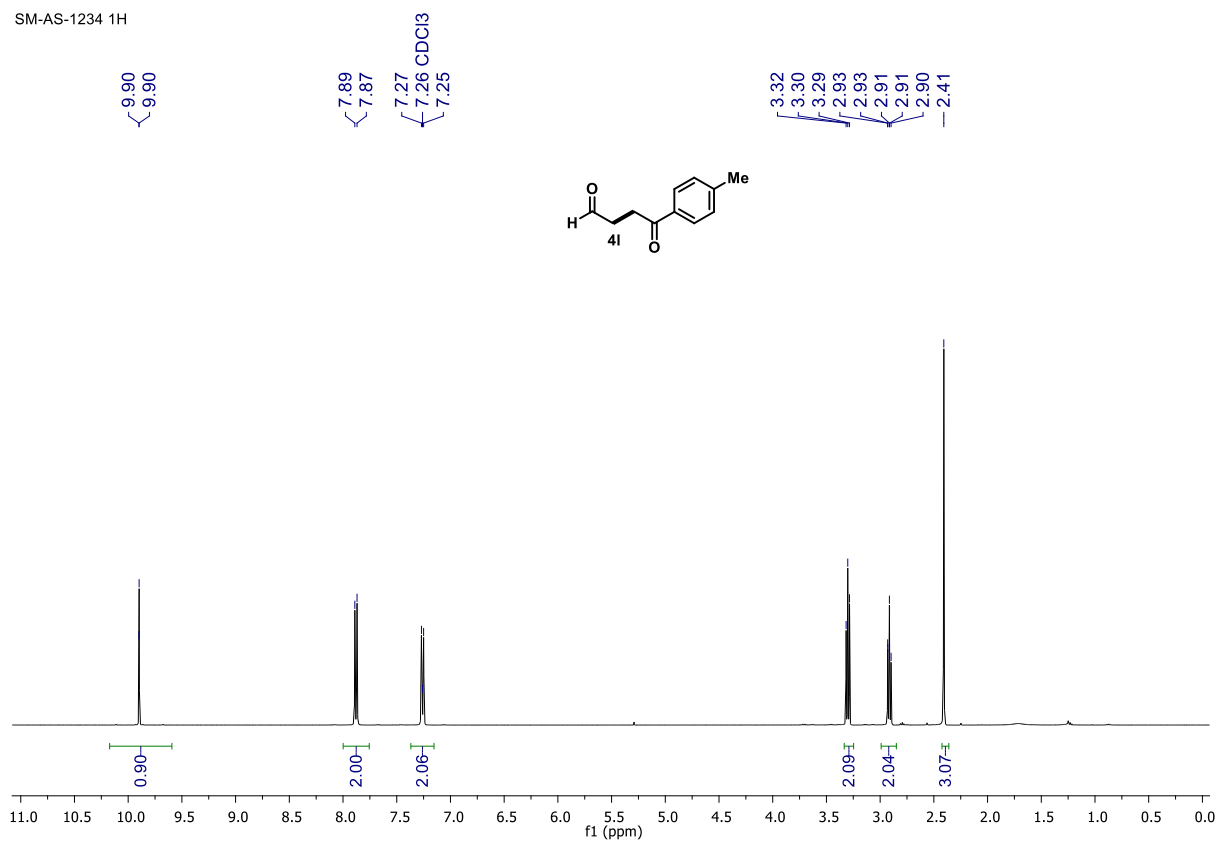


NOESY NMR of **4k**:



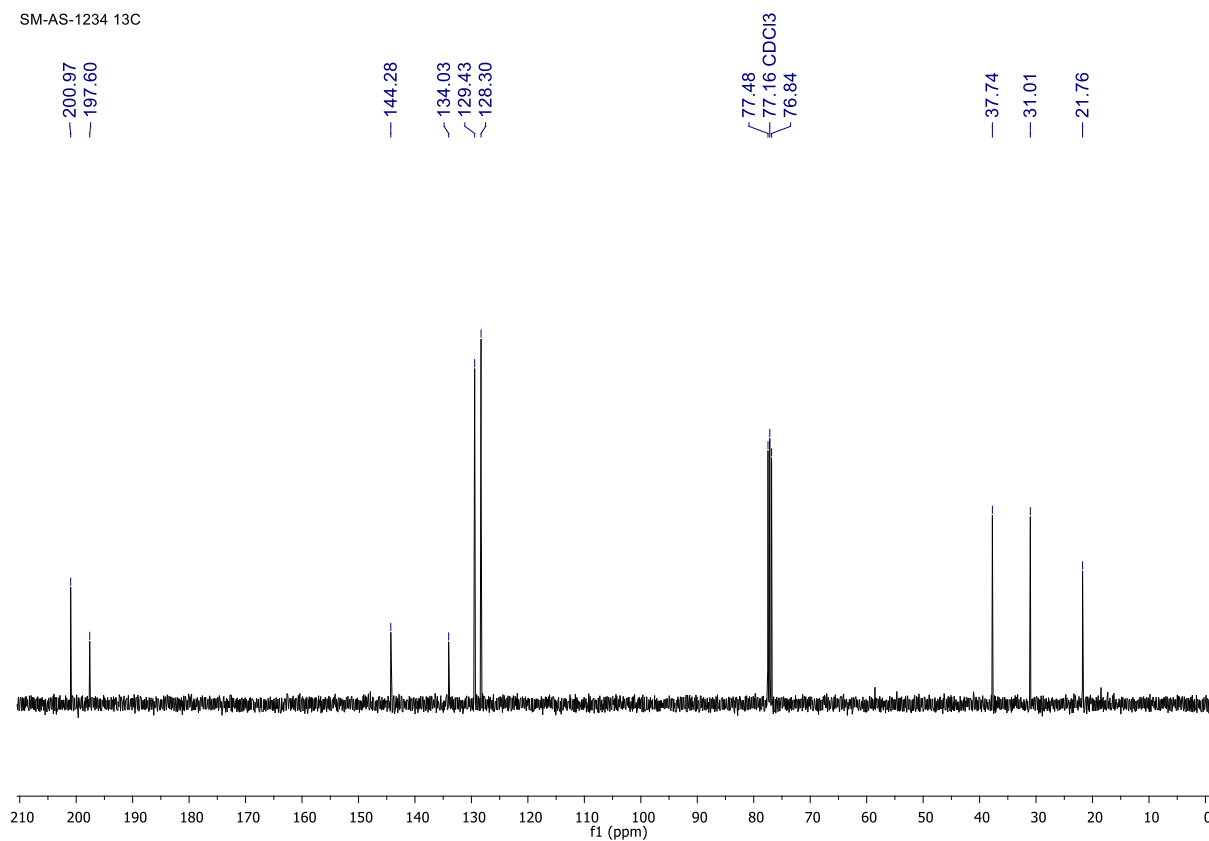
$^1\text{H}$  NMR of **41** (400 MHz,  $\text{CDCl}_3$ ):

SM-AS-1234 1H

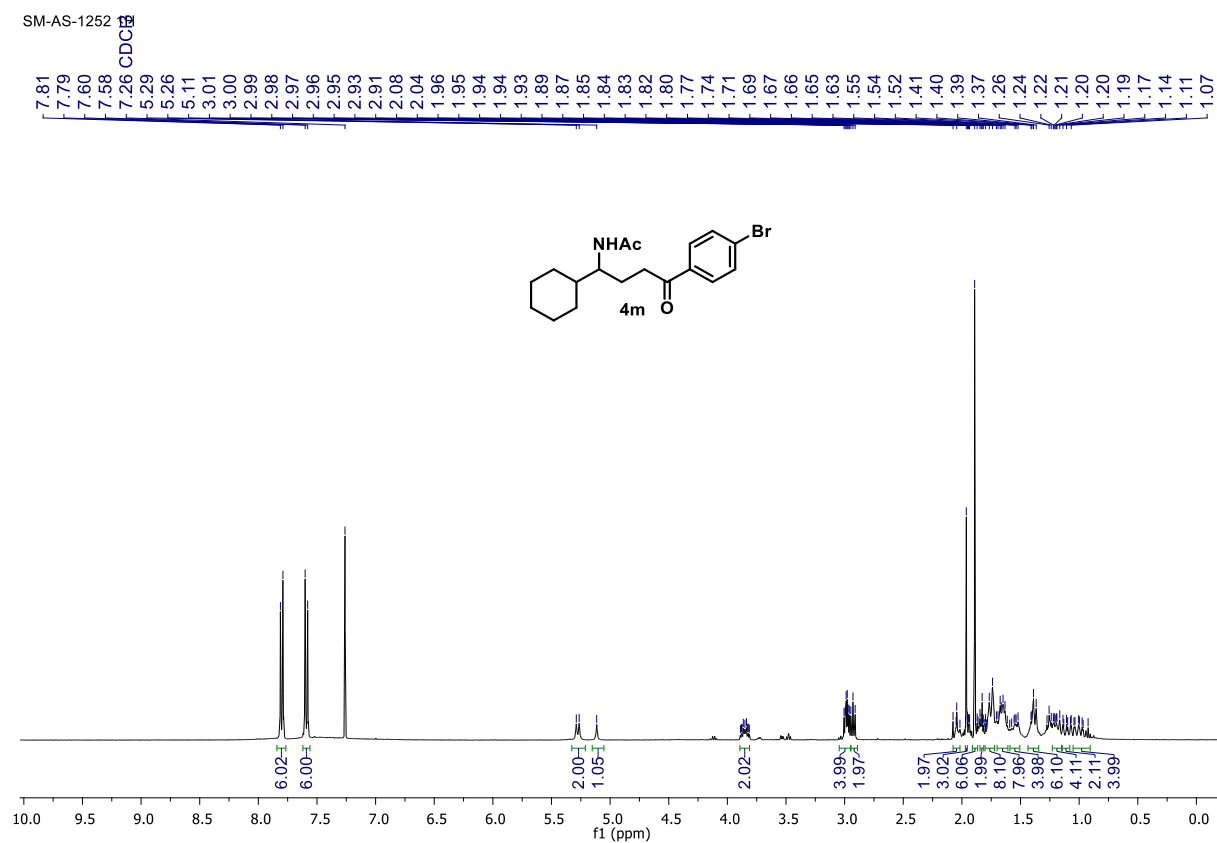


$^{13}\text{C}\{^1\text{H}\}$  NMR of **41** (101 MHz,  $\text{CDCl}_3$ ):

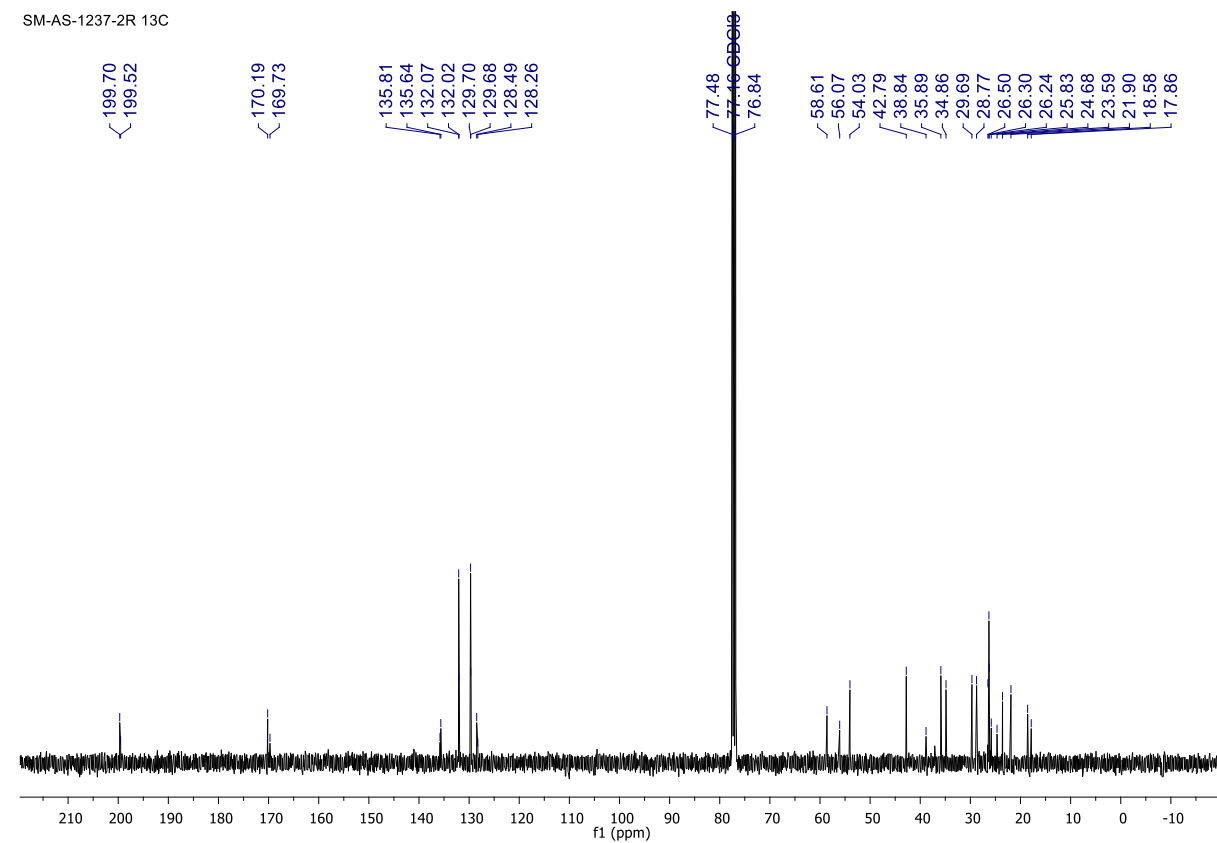
SM-AS-1234 13C



<sup>1</sup>H NMR of **4m** (400 MHz, CDCl<sub>3</sub>):

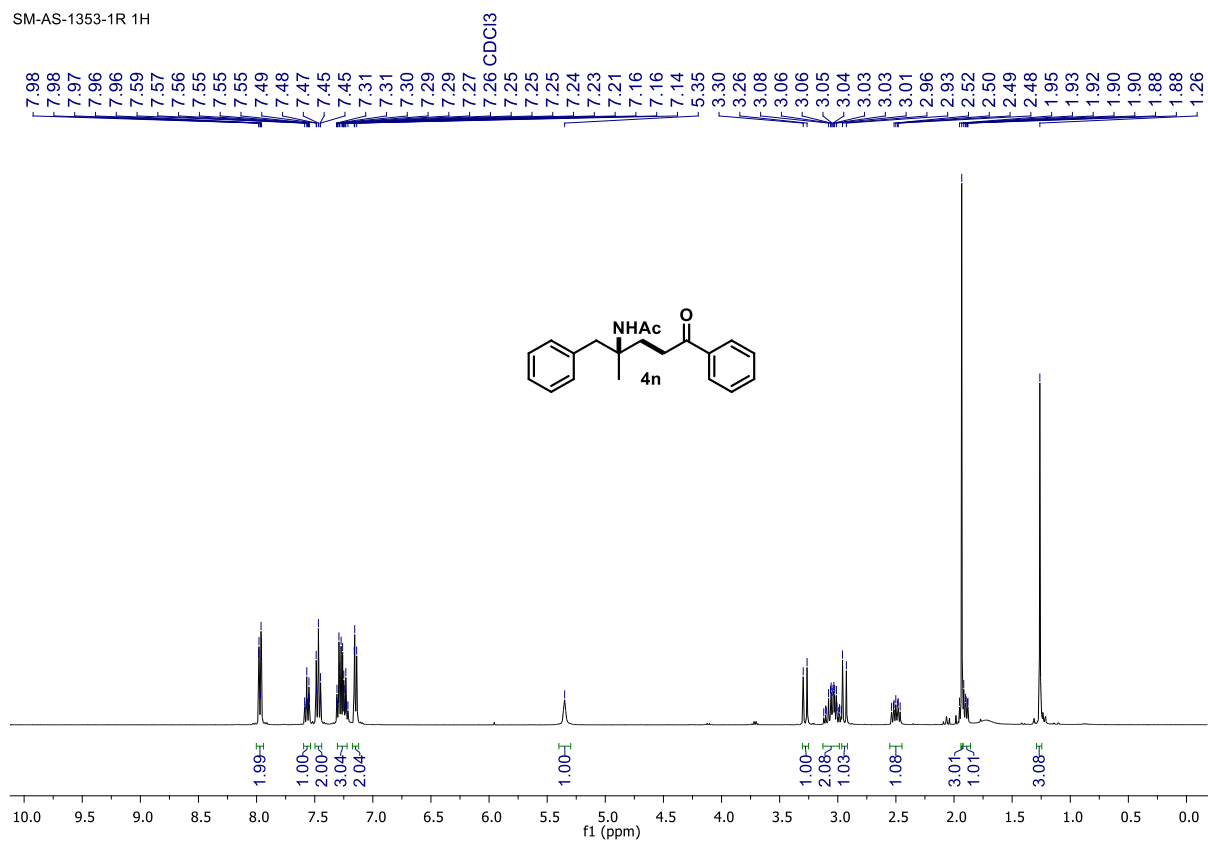


<sup>13</sup>C{<sup>1</sup>H} NMR of **4m** (101 MHz, CDCl<sub>3</sub>):



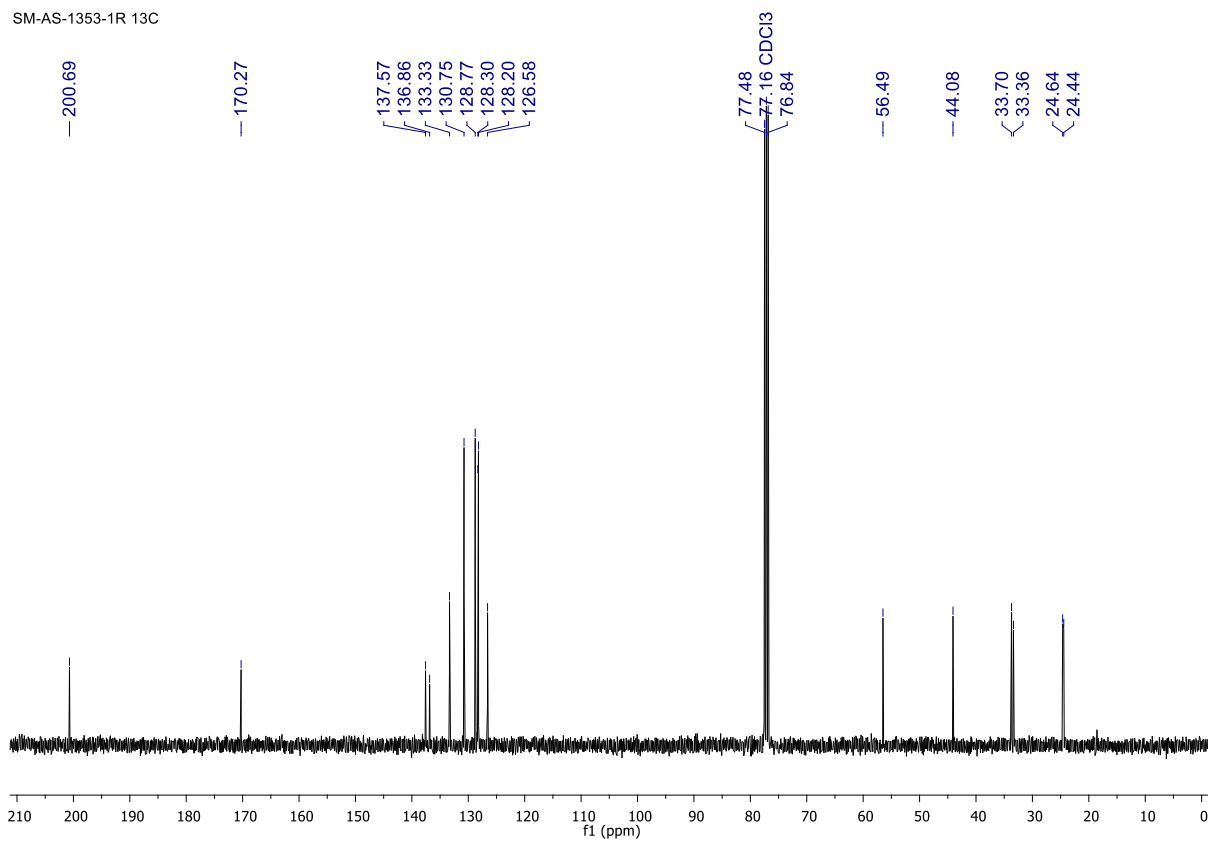
<sup>1</sup>H NMR of **4n** (400 MHz, CDCl<sub>3</sub>):

SM-AS-1353-1R 1H



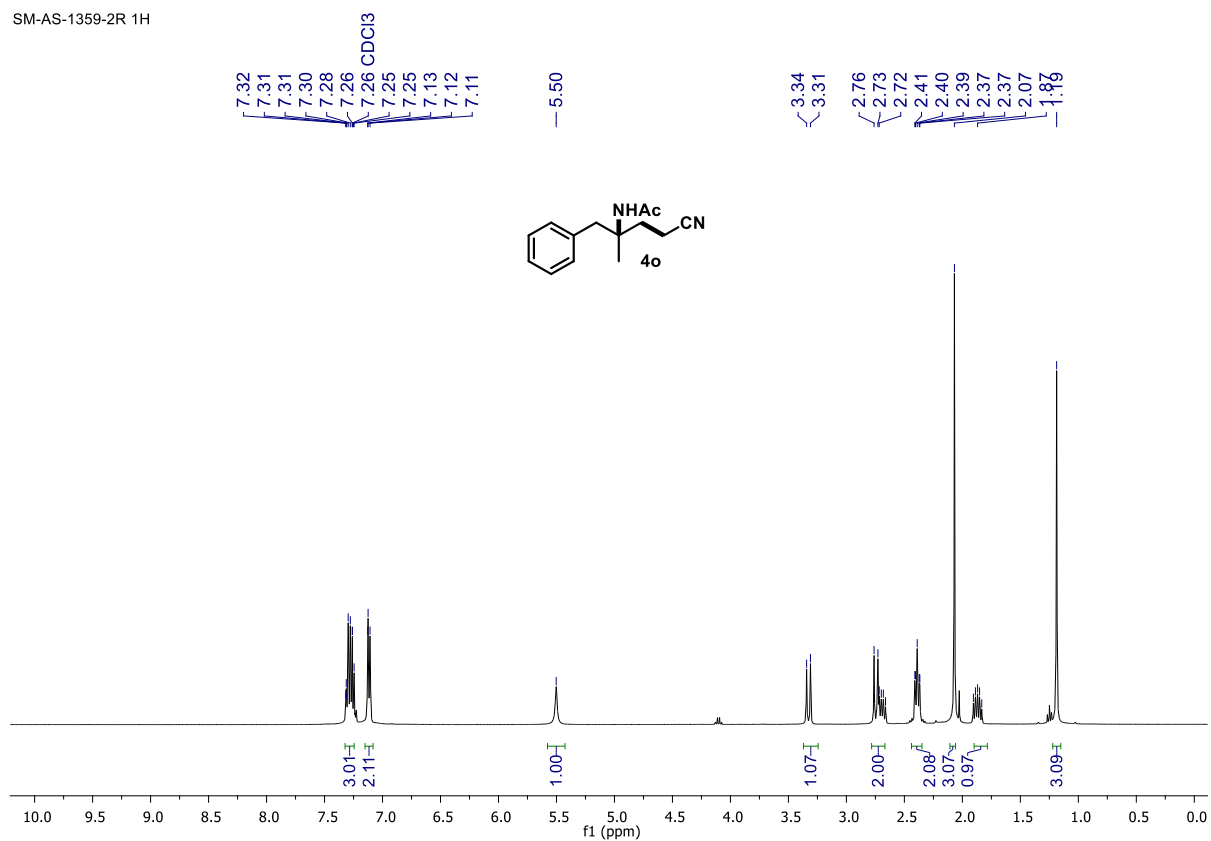
<sup>13</sup>C{<sup>1</sup>H} NMR of **4n** (101 MHz, CDCl<sub>3</sub>):

SM-AS-1353-1R 13C



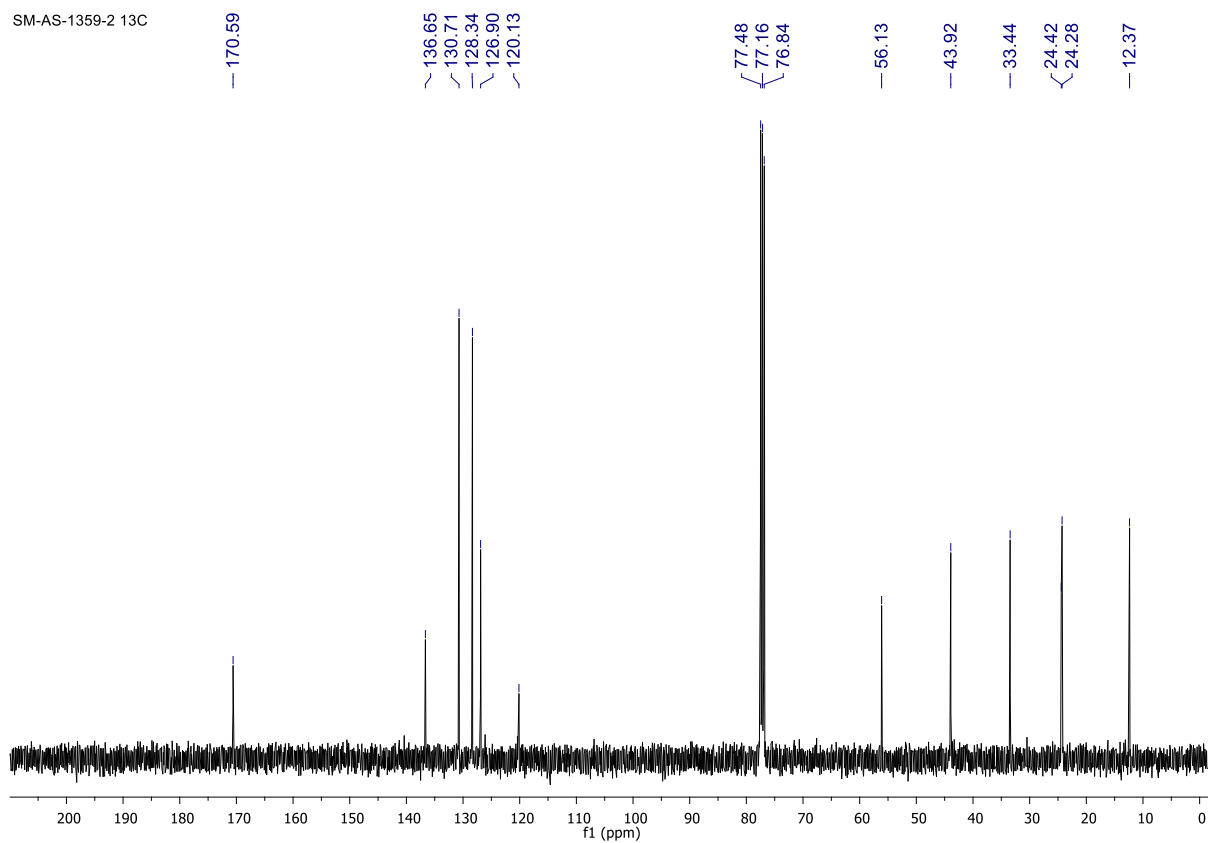
<sup>1</sup>H NMR of **4o** (400 MHz, CDCl<sub>3</sub>):

SM-AS-1359-2R 1H

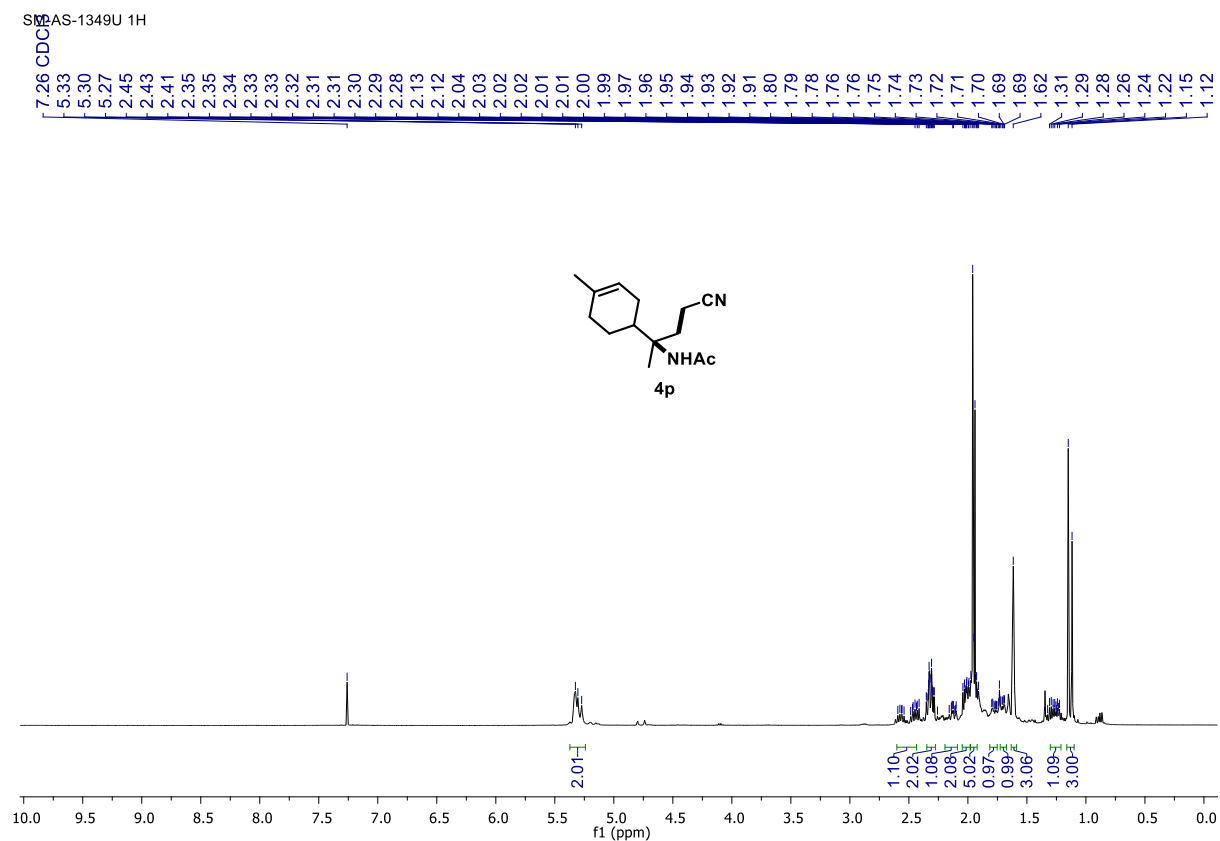


<sup>13</sup>C{<sup>1</sup>H} NMR of **4o** (101 MHz, CDCl<sub>3</sub>):

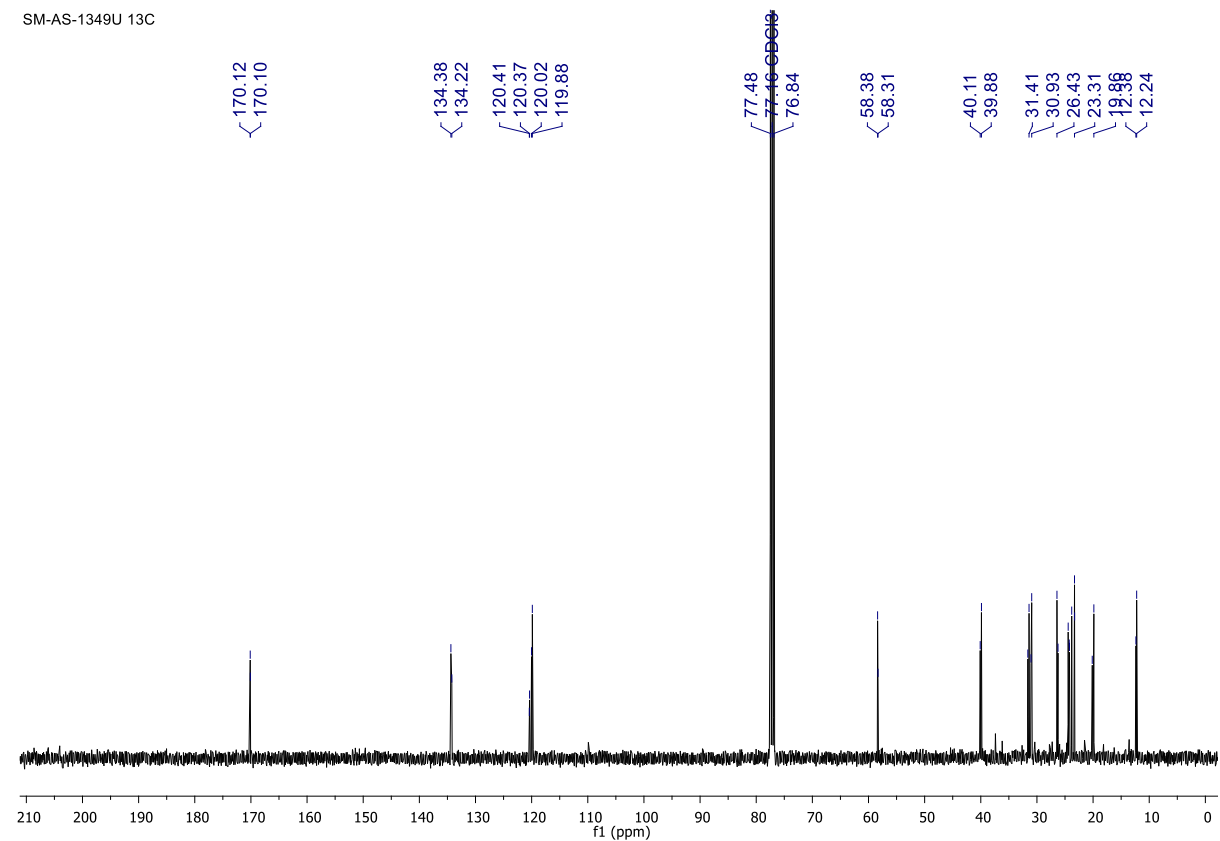
SM-AS-1359-2 13C



<sup>1</sup>H NMR of **4p** (400 MHz, CDCl<sub>3</sub>):



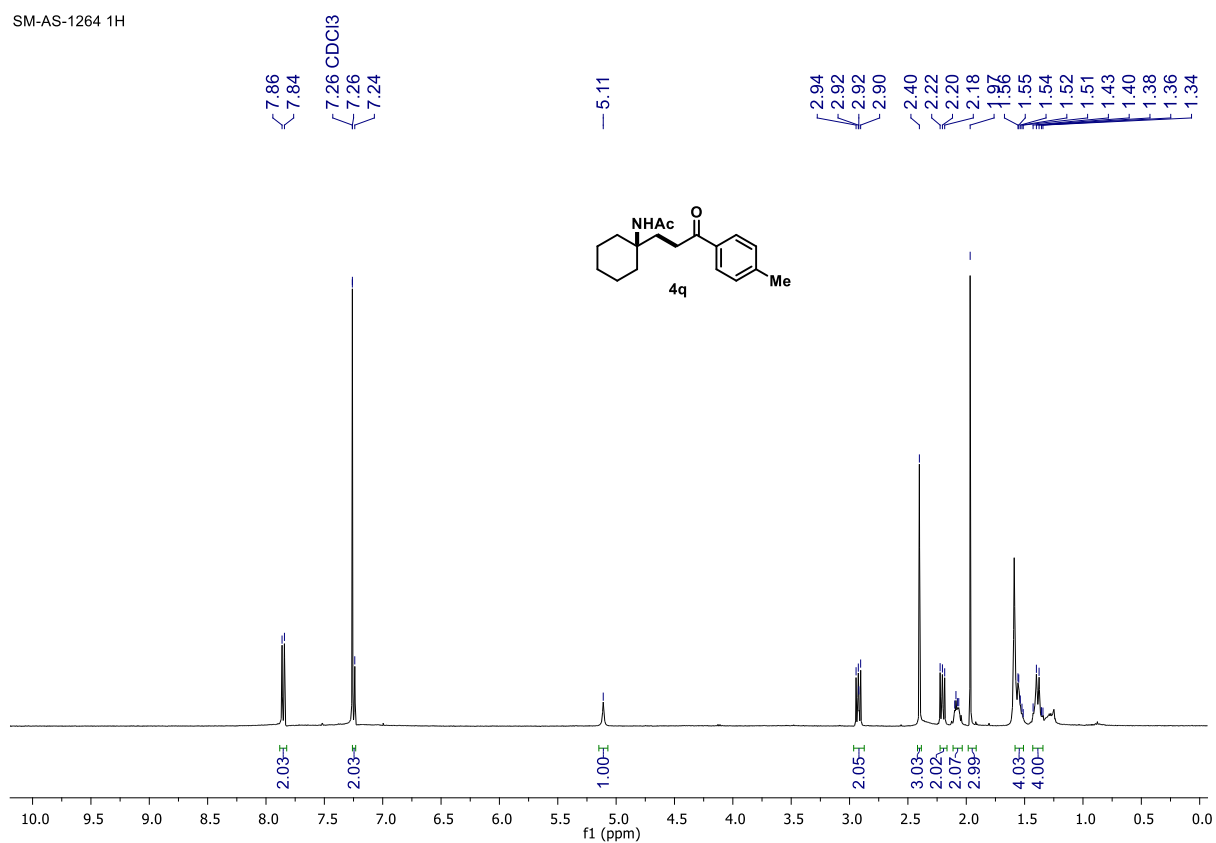
<sup>13</sup>C{<sup>1</sup>H} NMR of **4p** (101 MHz, CDCl<sub>3</sub>):





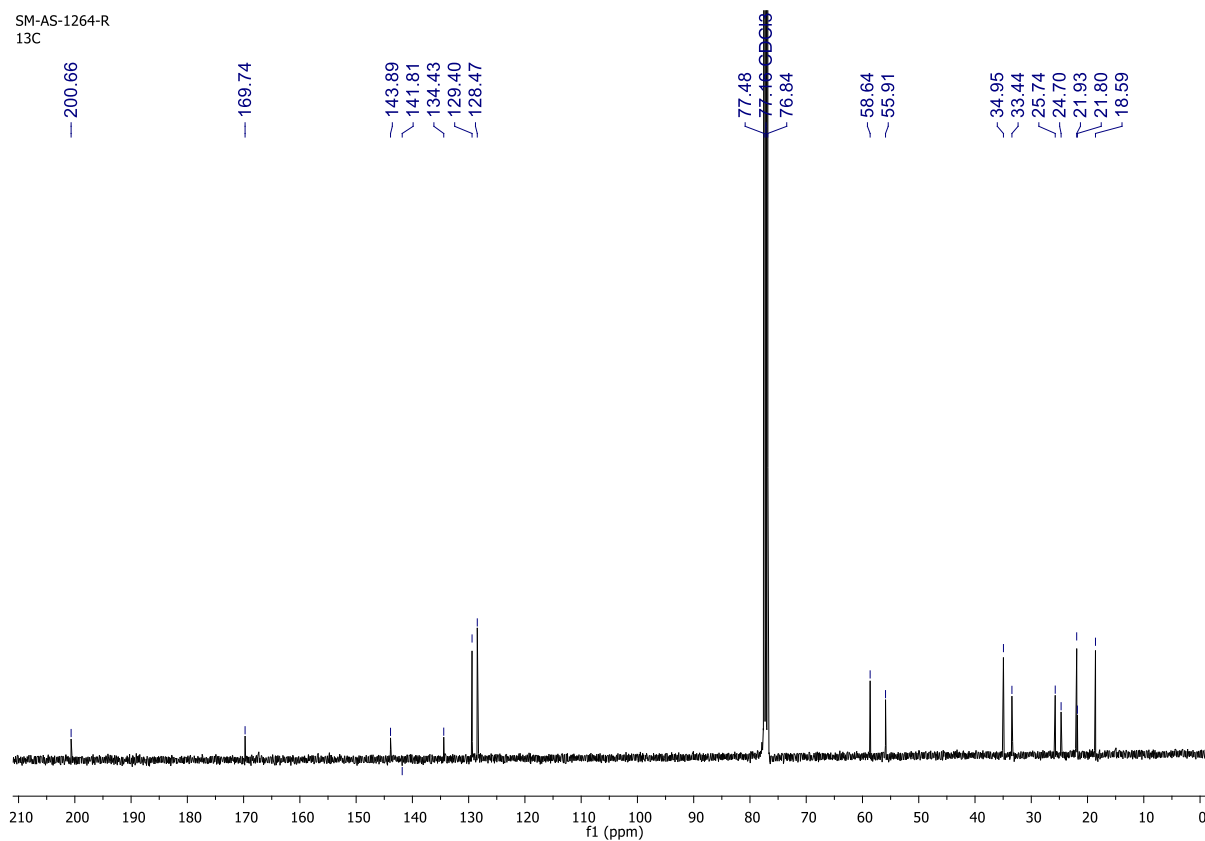
<sup>1</sup>H NMR of **4q** (400 MHz, CDCl<sub>3</sub>):

SM-AS-1264 1H

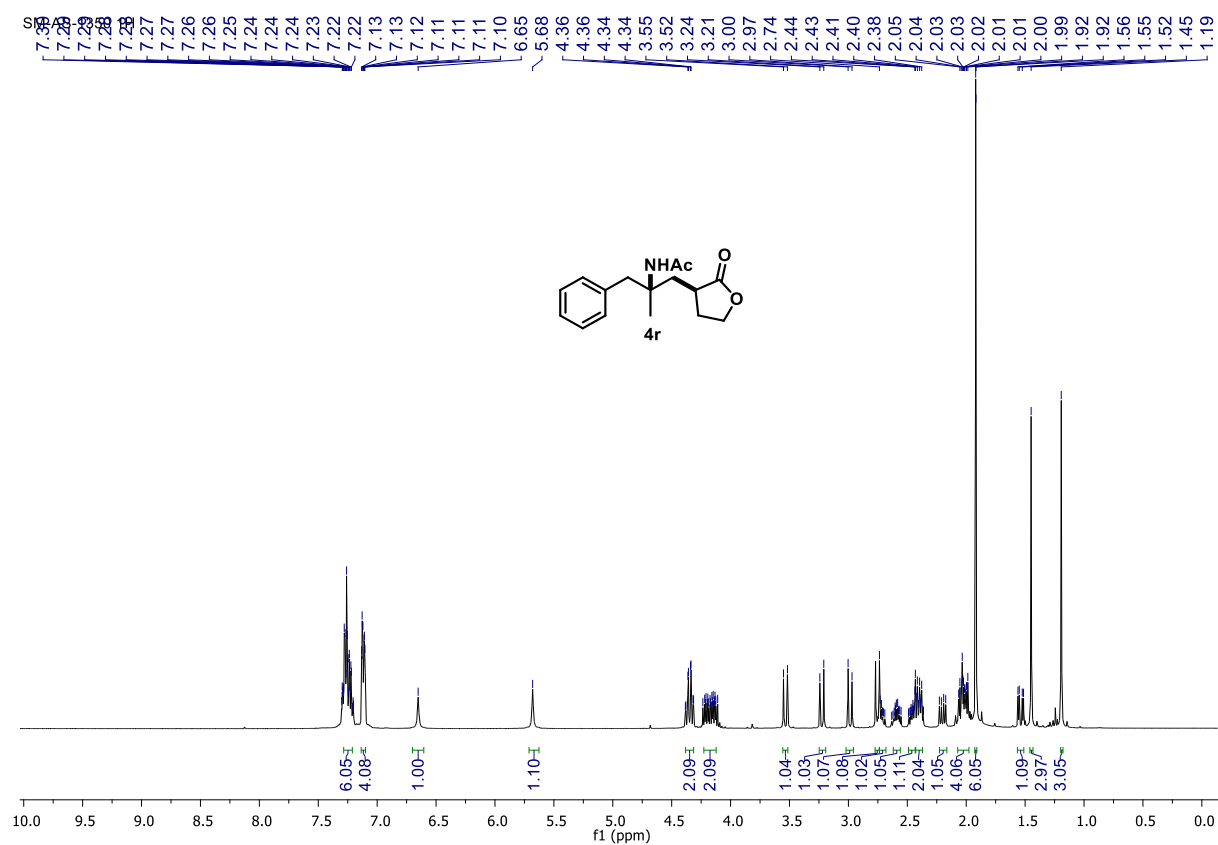


<sup>13</sup>C{<sup>1</sup>H} NMR of **4q** (101 MHz, CDCl<sub>3</sub>):

SM-AS-1264-R  
13C

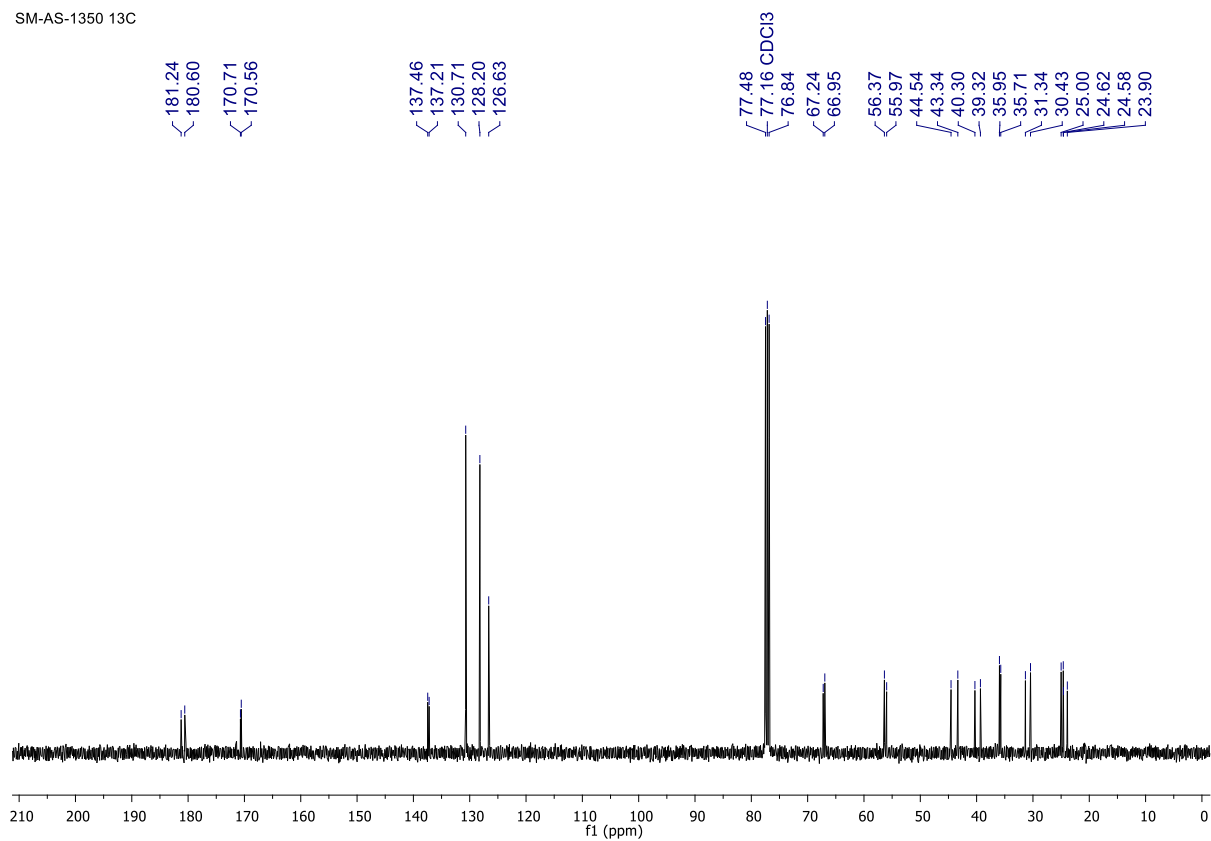


<sup>1</sup>H NMR of **4r** (400 MHz, CDCl<sub>3</sub>):



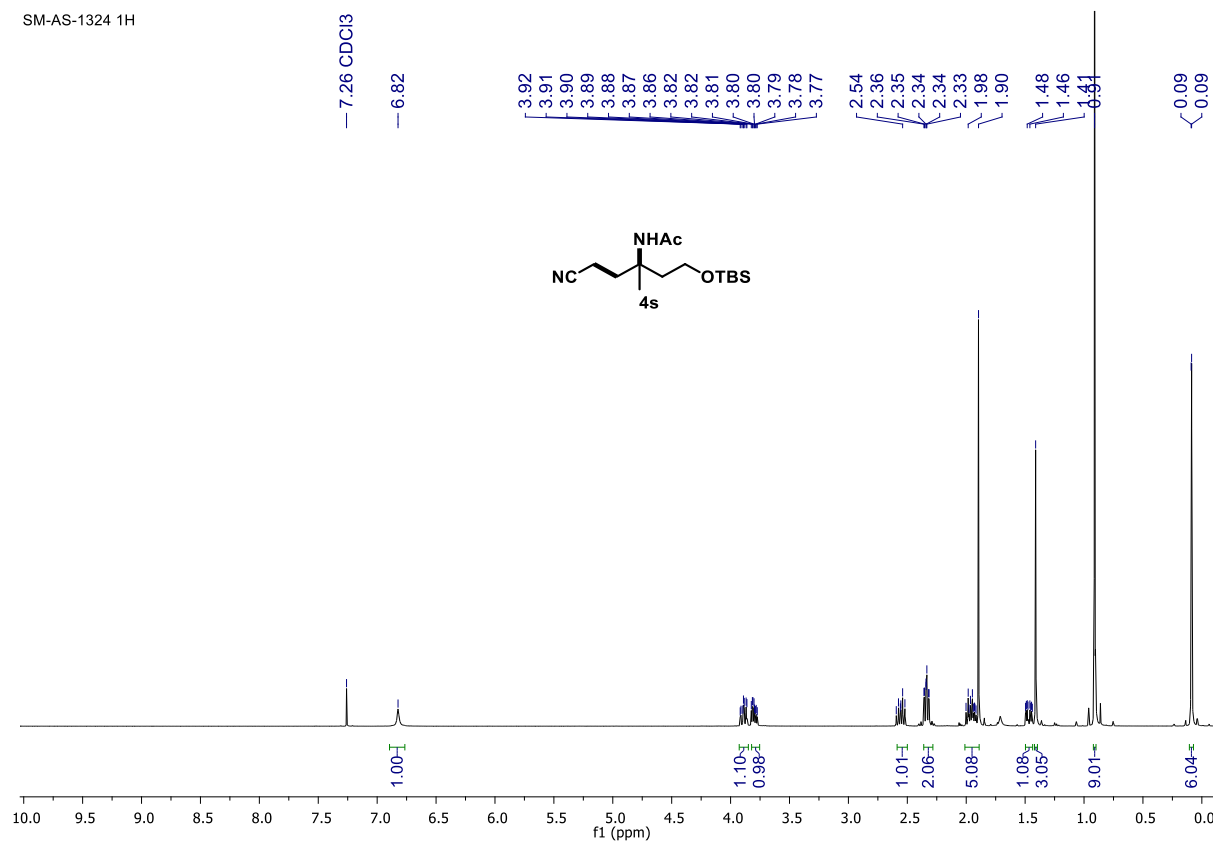
<sup>13</sup>C{<sup>1</sup>H} NMR of **4r** (101 MHz, CDCl<sub>3</sub>):

SM-AS-1350 13C



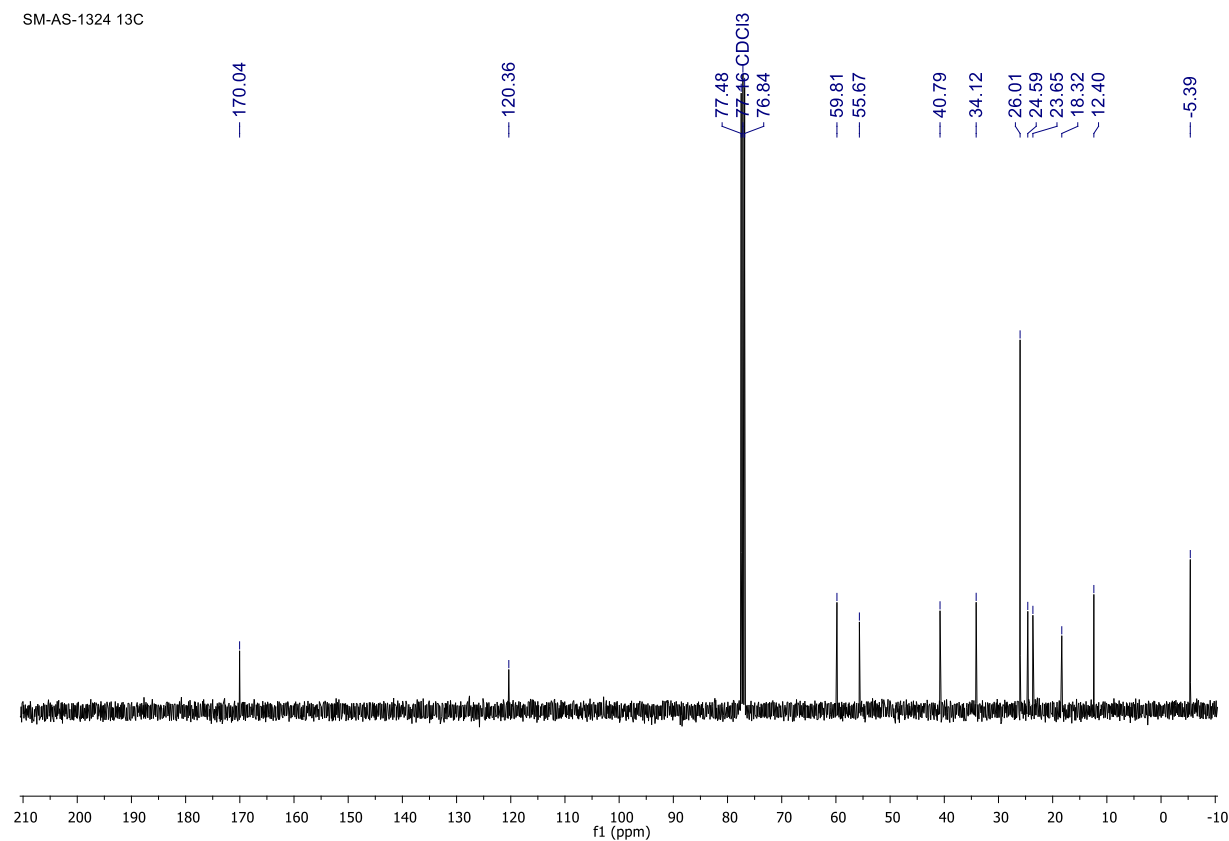
<sup>1</sup>H NMR of **4s** (400 MHz, CDCl<sub>3</sub>):

SM-AS-1324 1H



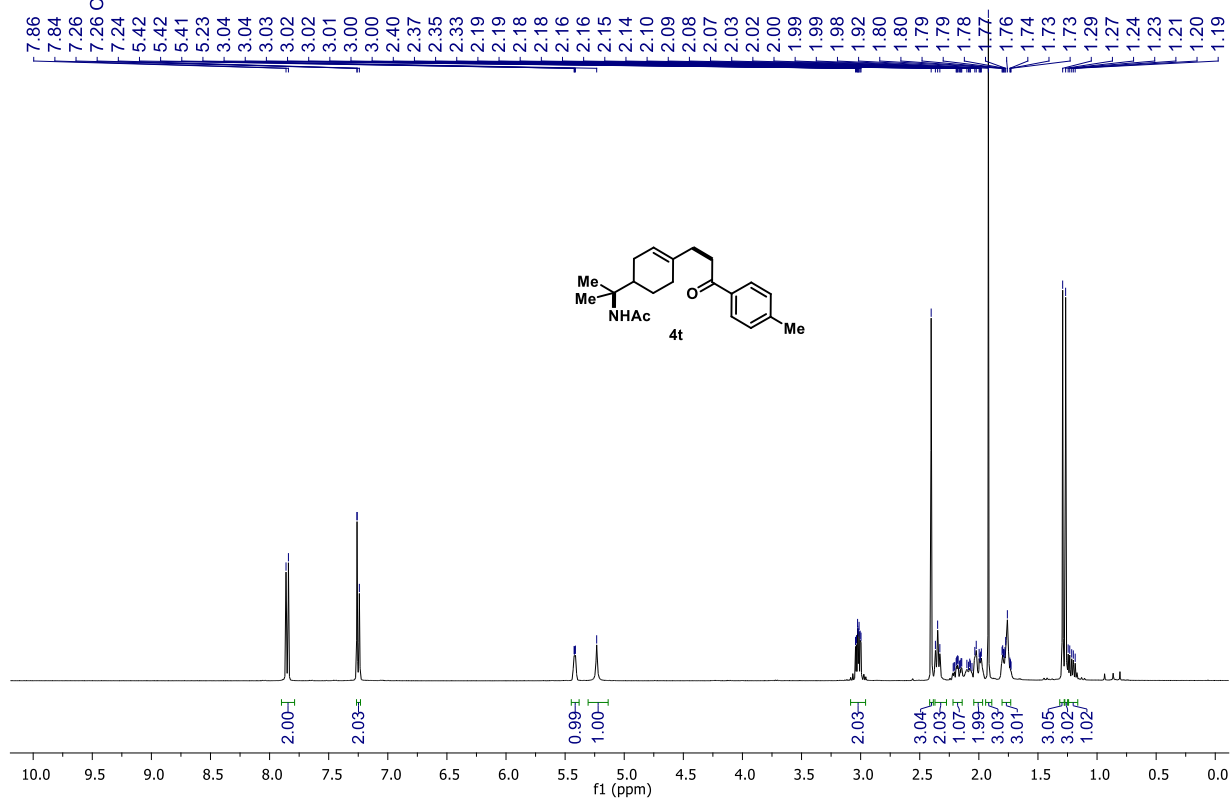
<sup>13</sup>C{<sup>1</sup>H} NMR of **4s** (101 MHz, CDCl<sub>3</sub>):

SM-AS-1324 13C



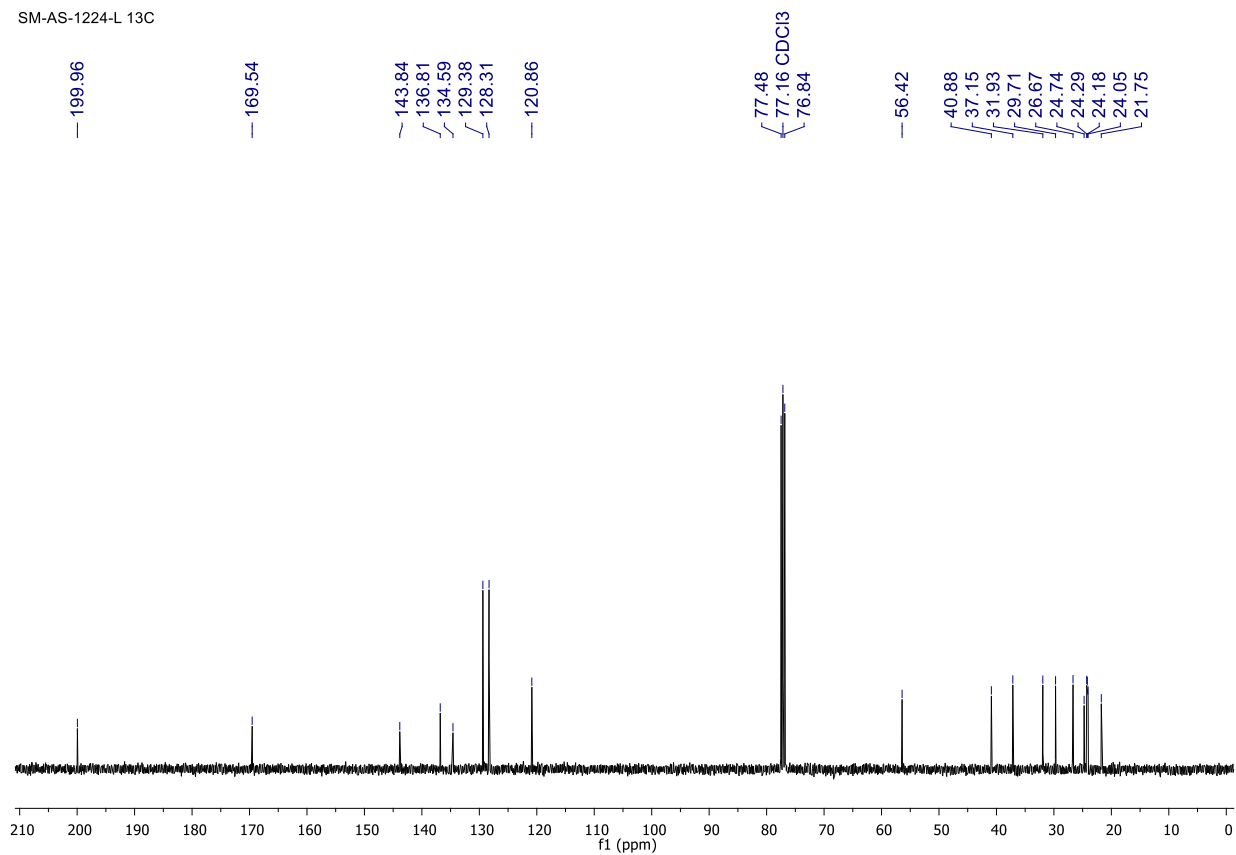
<sup>1</sup>H NMR of **4t** (400 MHz, CDCl<sub>3</sub>):

SM-AS-1224-L 1H

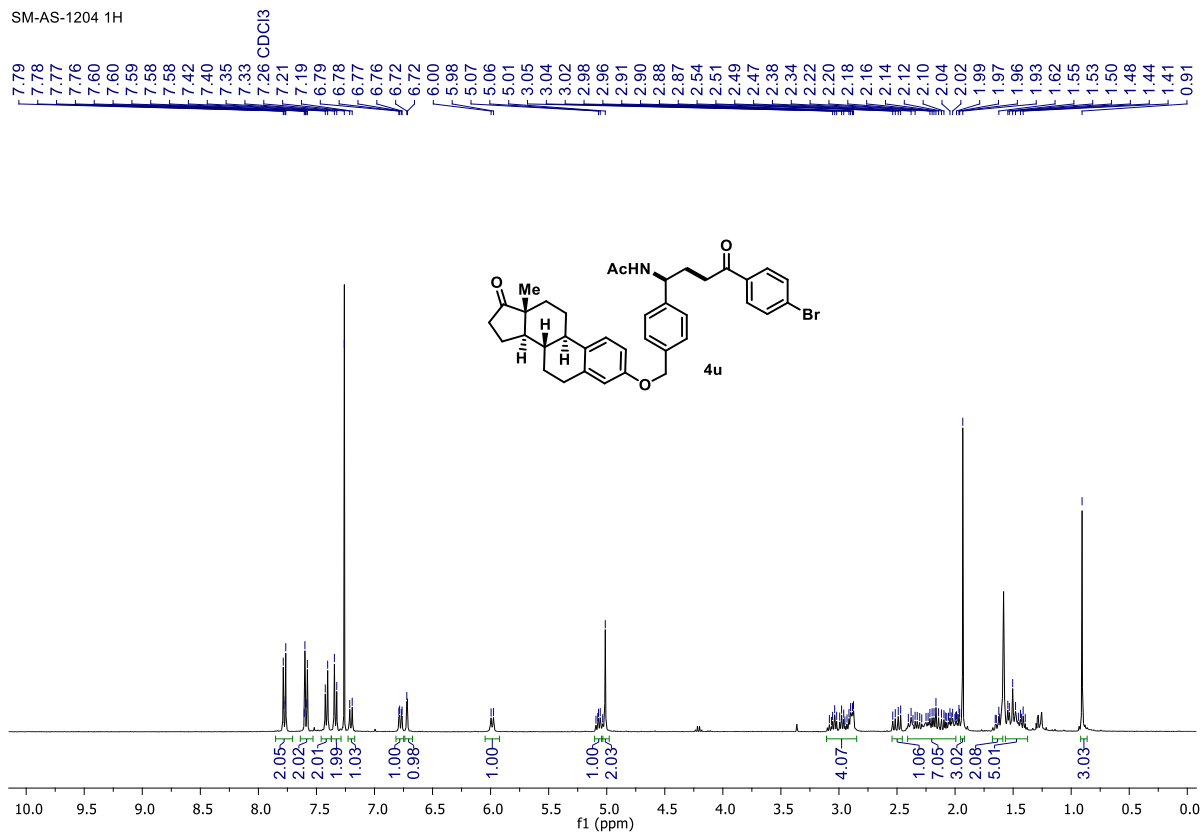


<sup>13</sup>C{<sup>1</sup>H} NMR of **4t** (101 MHz, CDCl<sub>3</sub>):

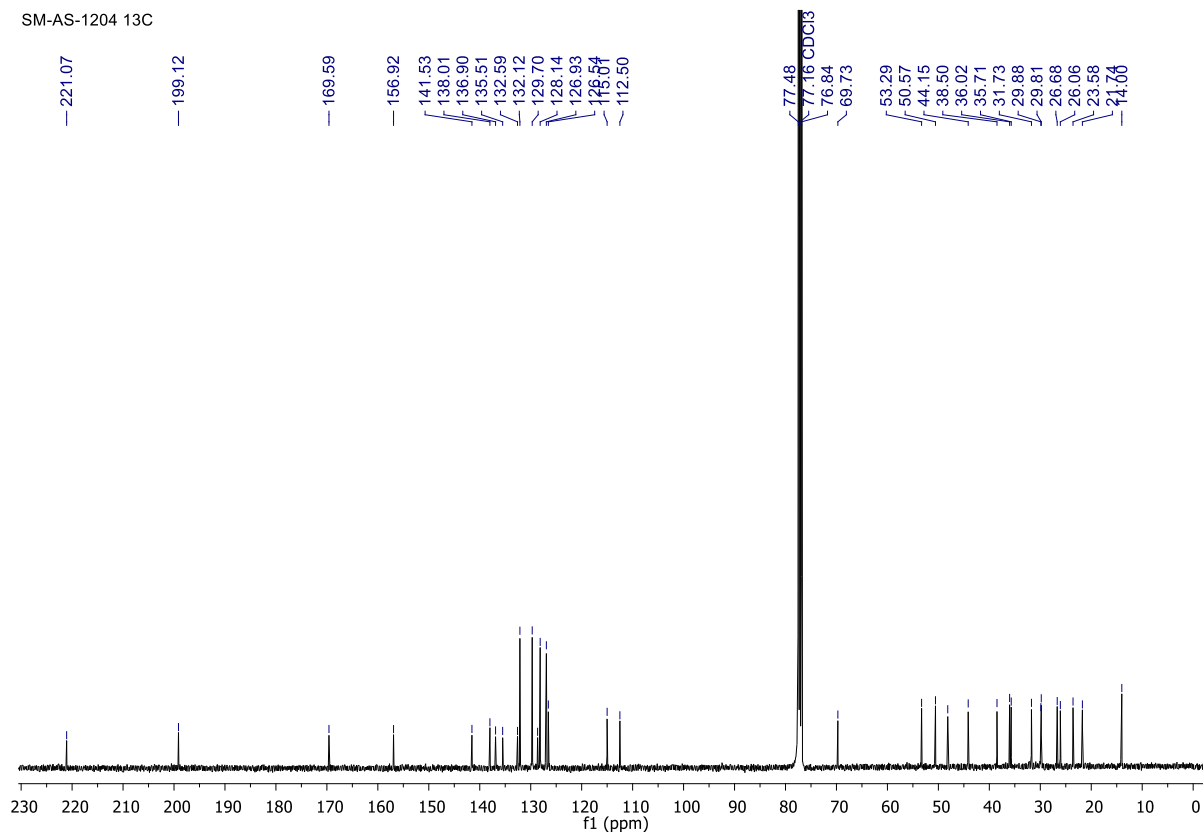
SM-AS-1224-L 13C



<sup>1</sup>H NMR of **4u** (400 MHz, CDCl<sub>3</sub>):

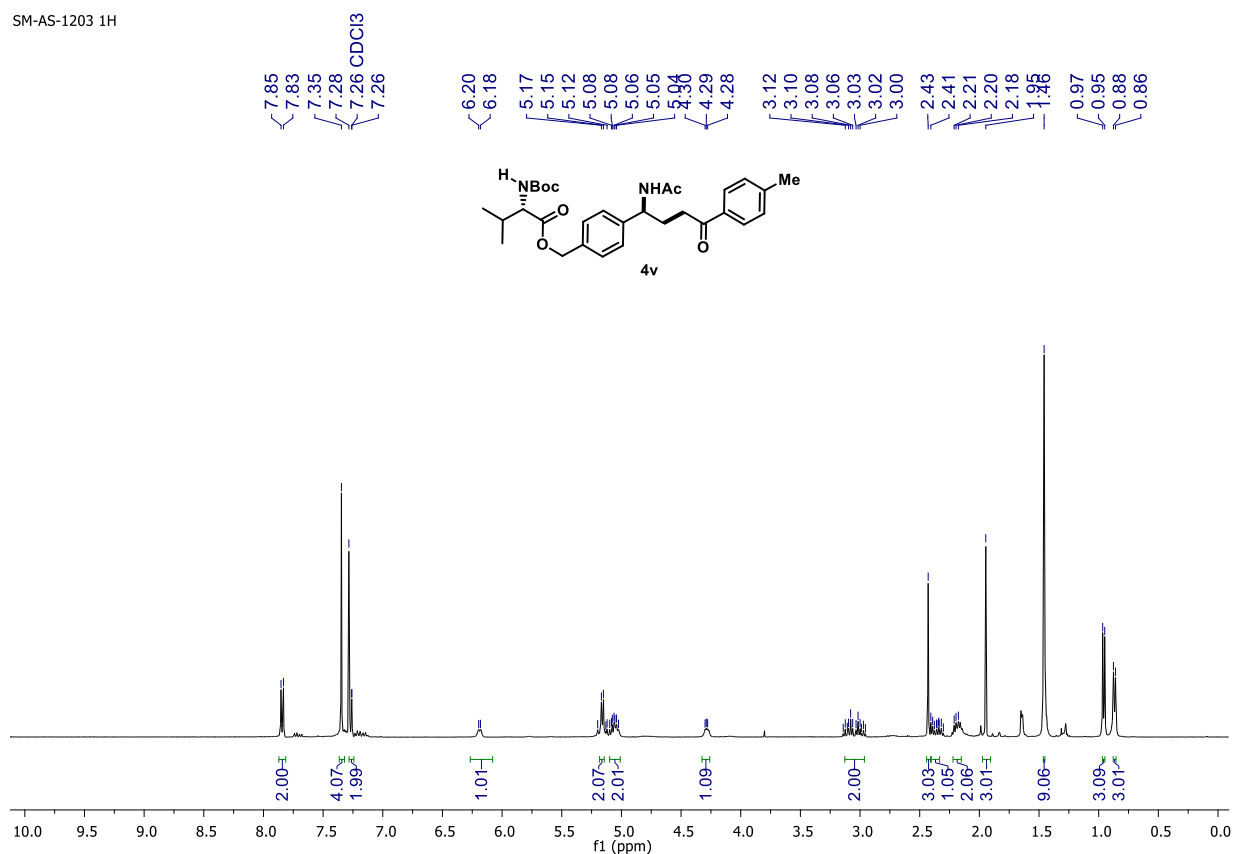


<sup>13</sup>C{<sup>1</sup>H} NMR of **4u** (101 MHz, CDCl<sub>3</sub>):



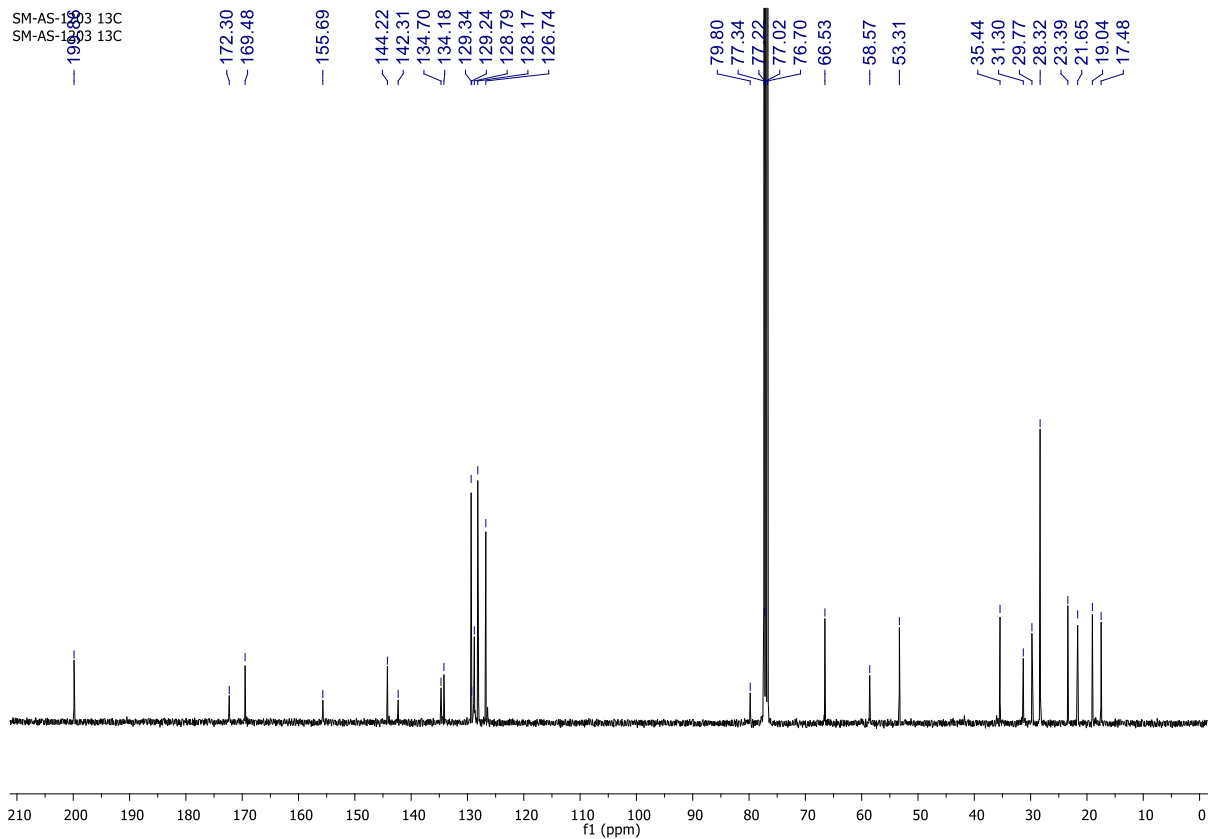
<sup>1</sup>H NMR of **4v** (400 MHz, CDCl<sub>3</sub>):

SM-AS-1203 1H

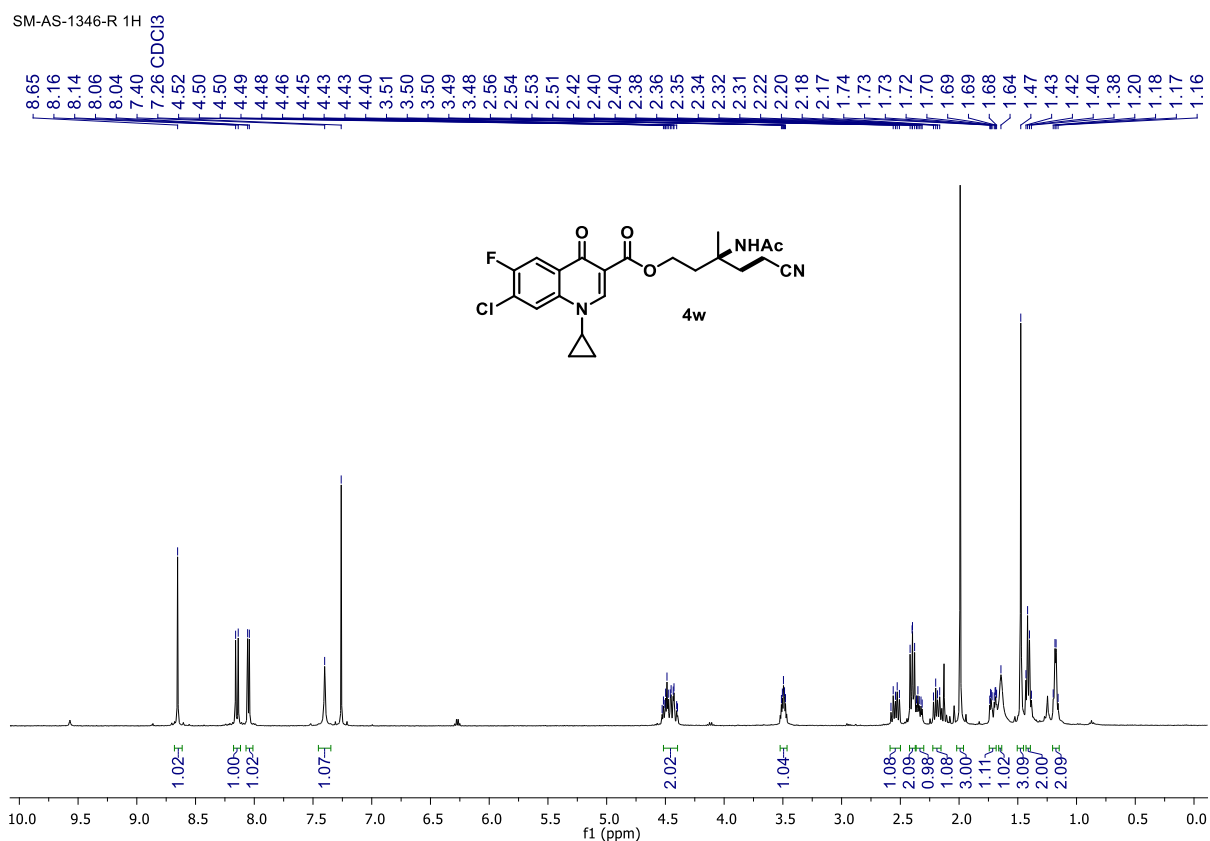


<sup>13</sup>C{<sup>1</sup>H} NMR of **4v** (101 MHz, CDCl<sub>3</sub>):

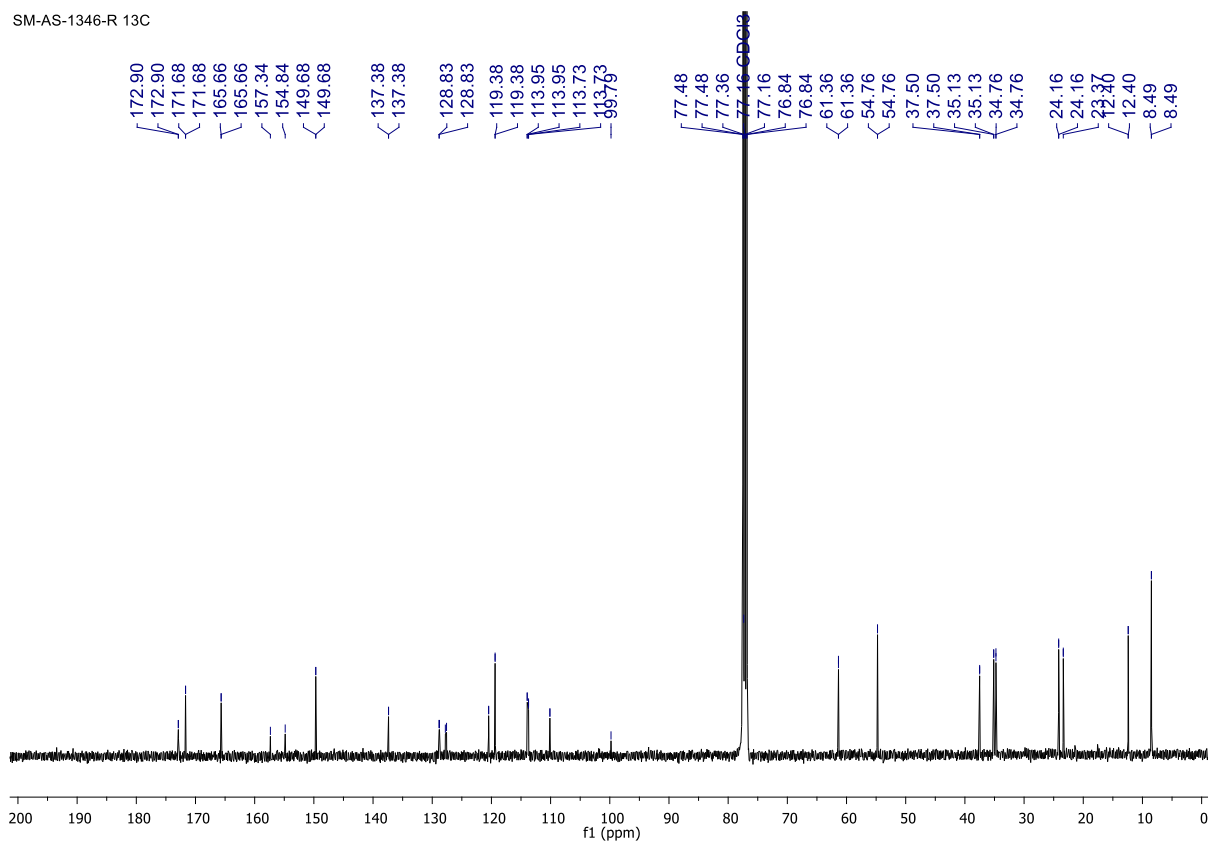
SM-AS-1203 13C  
SM-AS-1203 13C



<sup>1</sup>H NMR of **4w** (400 MHz, CDCl<sub>3</sub>):



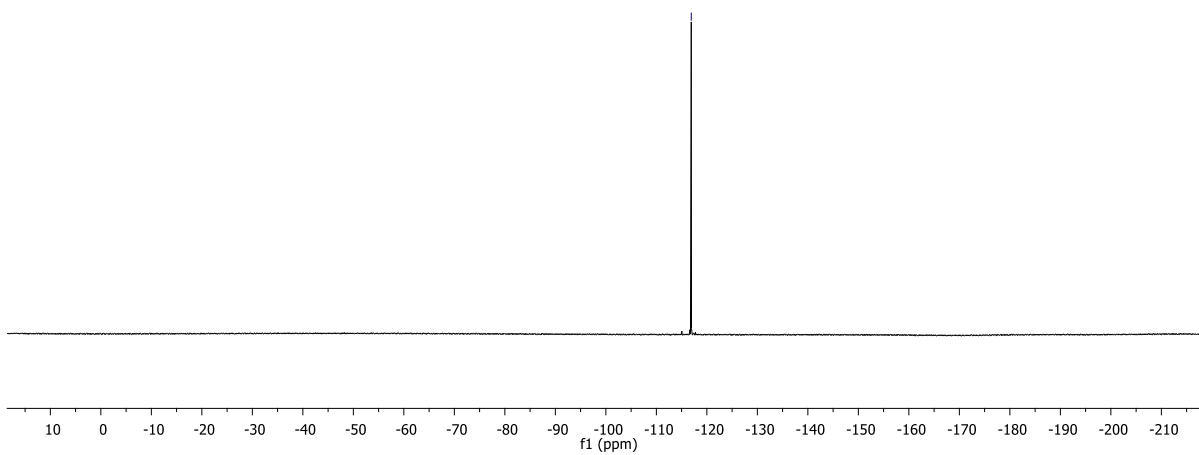
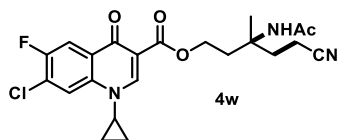
<sup>13</sup>C{<sup>1</sup>H} of **4w** (101 MHz, CDCl<sub>3</sub>):



{<sup>19</sup>F} NMR of **4w** (377 MHz, CDCl<sub>3</sub>):

SM-AS-1346-R 19F

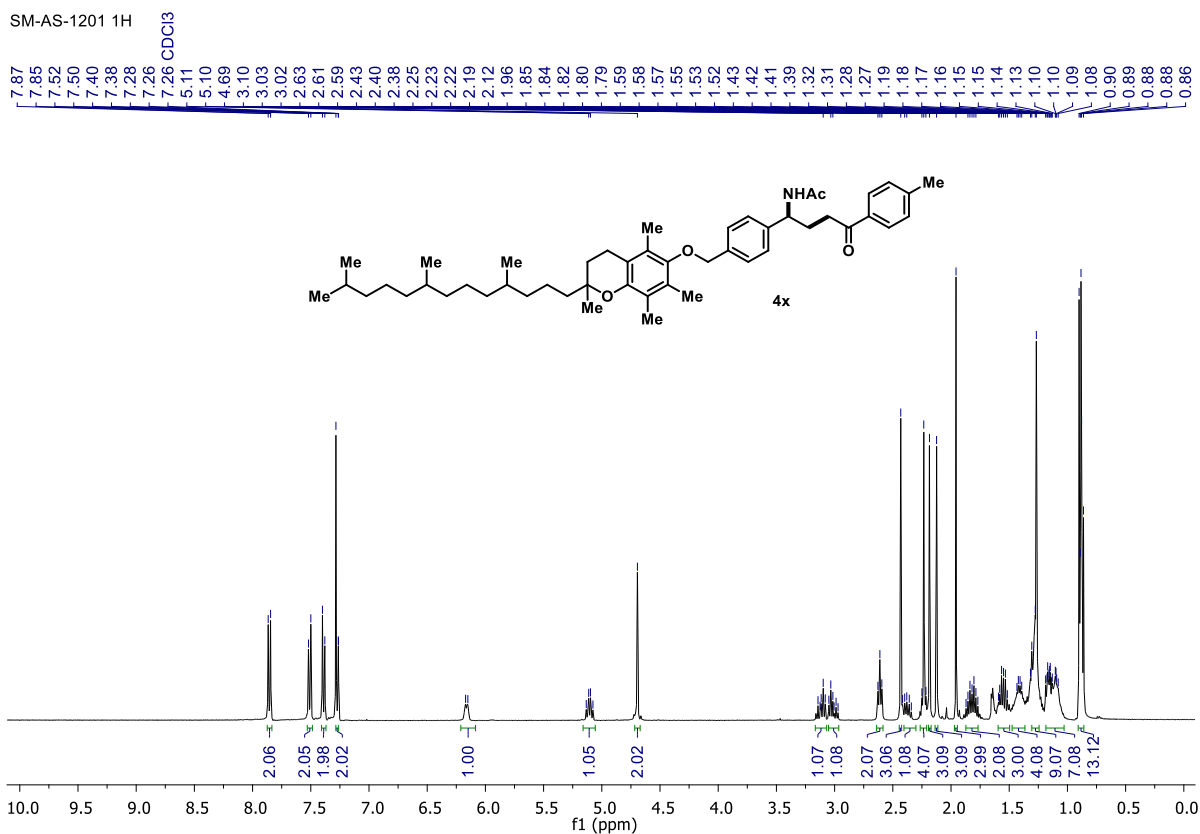
— -116.91





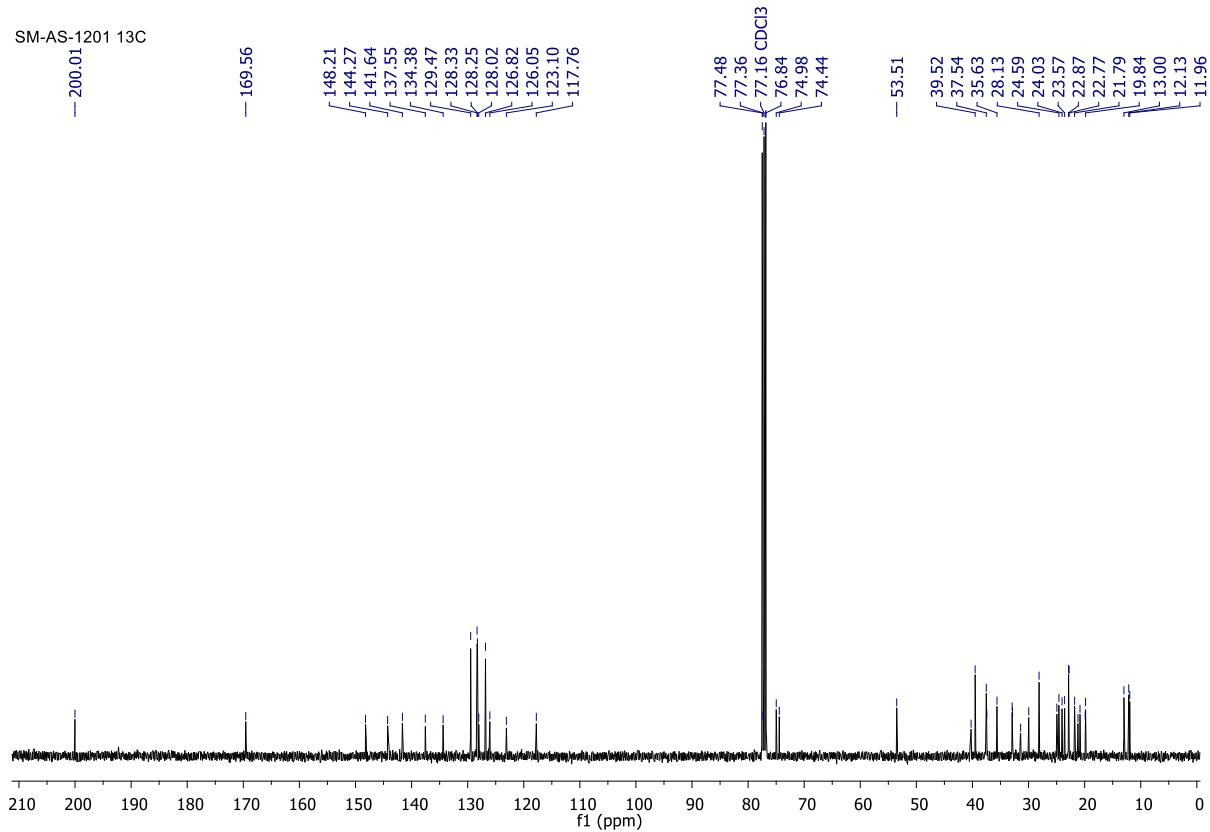
<sup>1</sup>H NMR of **4x** (400 MHz, CDCl<sub>3</sub>):

SM-AS-1201 1H



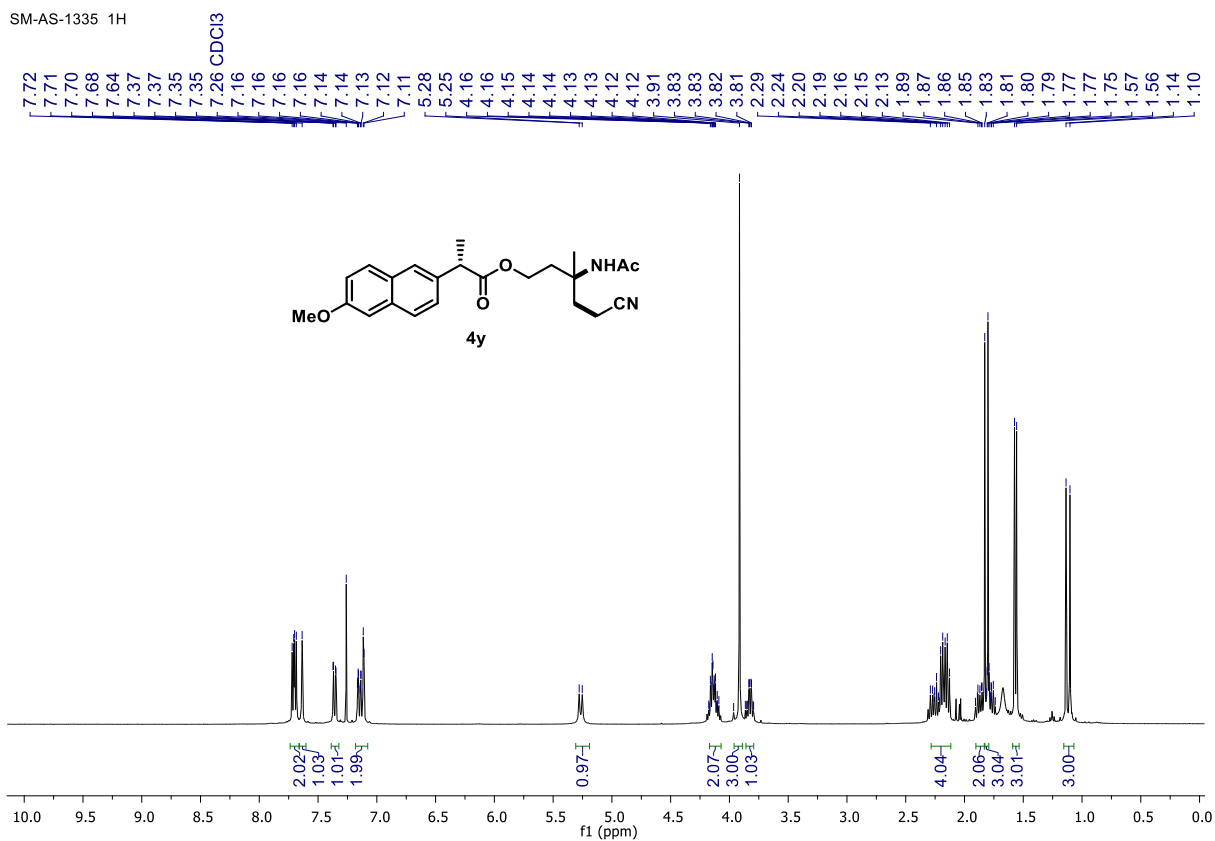
<sup>13</sup>C{<sup>1</sup>H} NMR of **4x** (101 MHz, CDCl<sub>3</sub>):

SM-AS-1201 13C



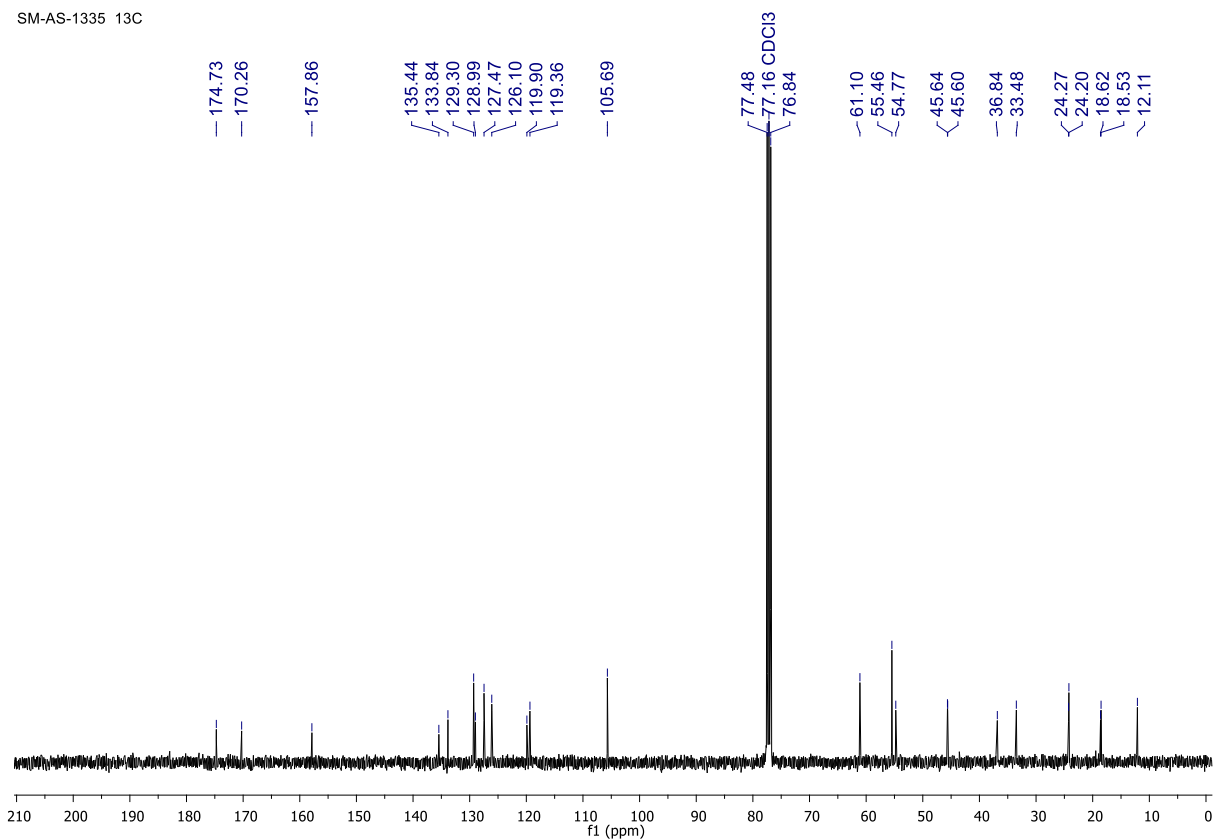
<sup>1</sup>H NMR of **4y** (400 MHz, CDCl<sub>3</sub>):

SM-AS-1335 1H



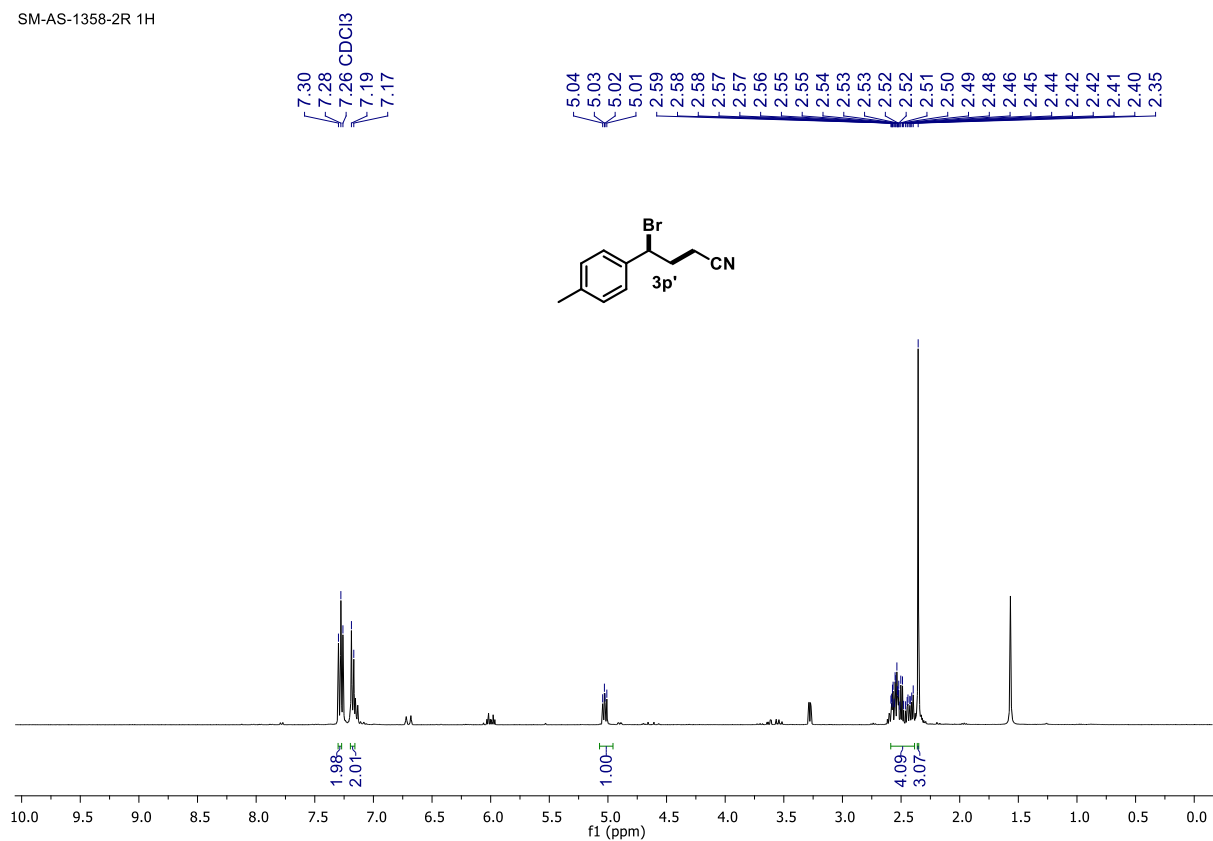
<sup>13</sup>C{<sup>1</sup>H} NMR of **4y** (101 MHz, CDCl<sub>3</sub>):

SM-AS-1335 13C



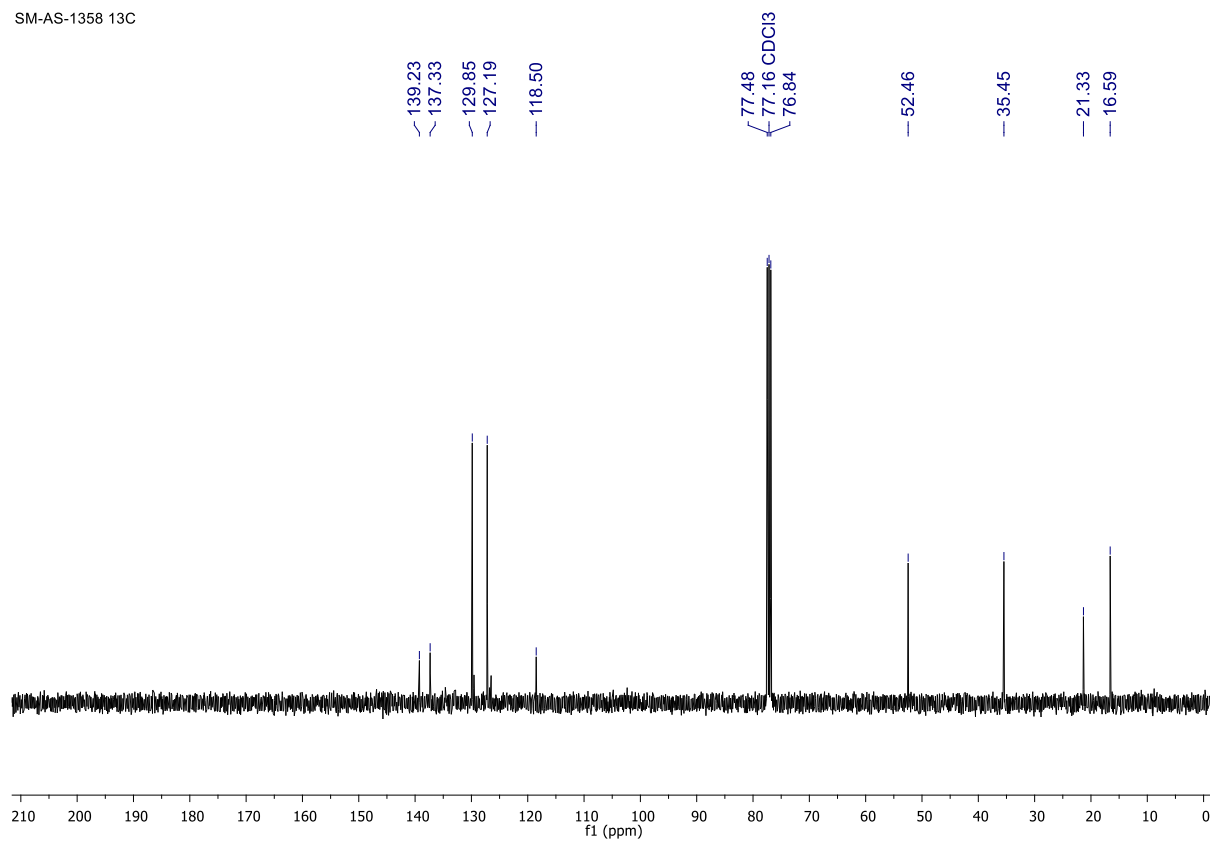
<sup>1</sup>H NMR of **3p'** (400 MHz, CDCl<sub>3</sub>):

SM-AS-1358-2R 1H



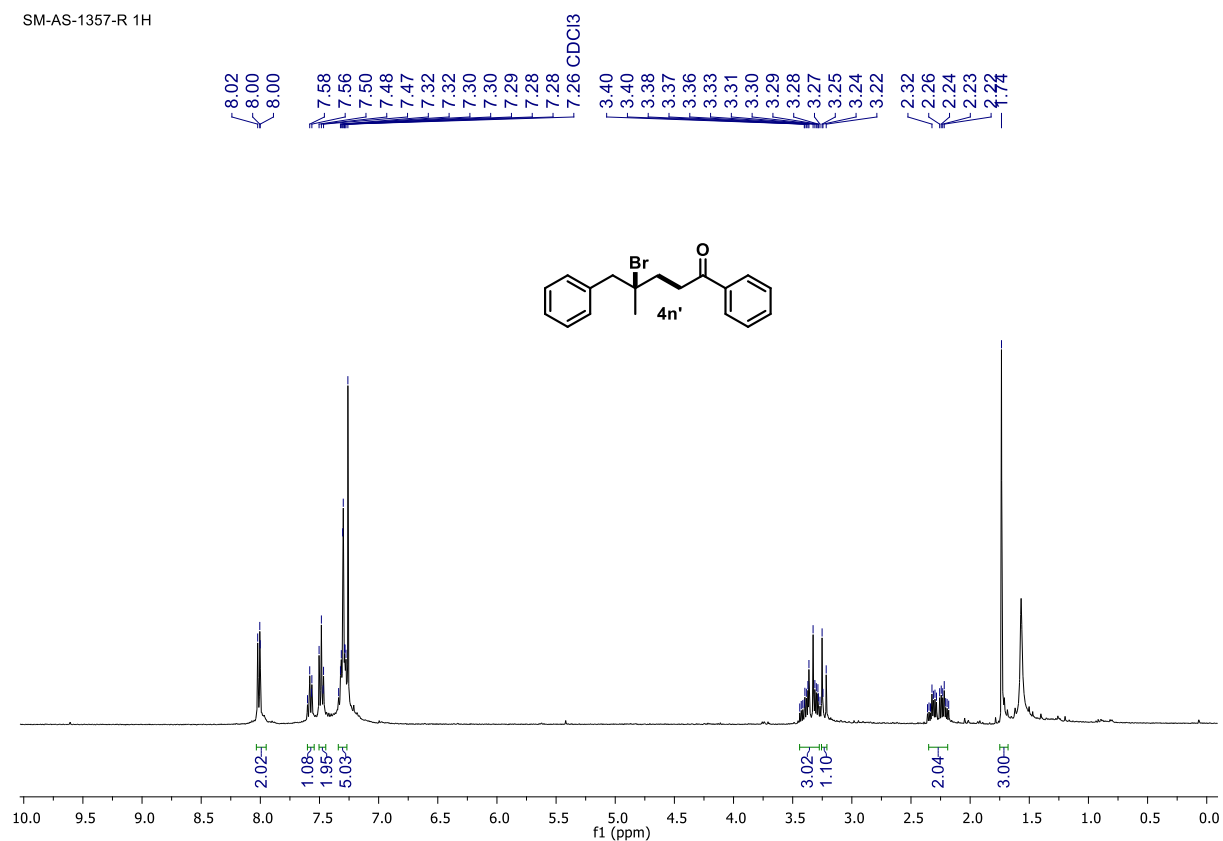
<sup>13</sup>C{<sup>1</sup>H} NMR of **3p'** (101 MHz, CDCl<sub>3</sub>):

SM-AS-1358 13C



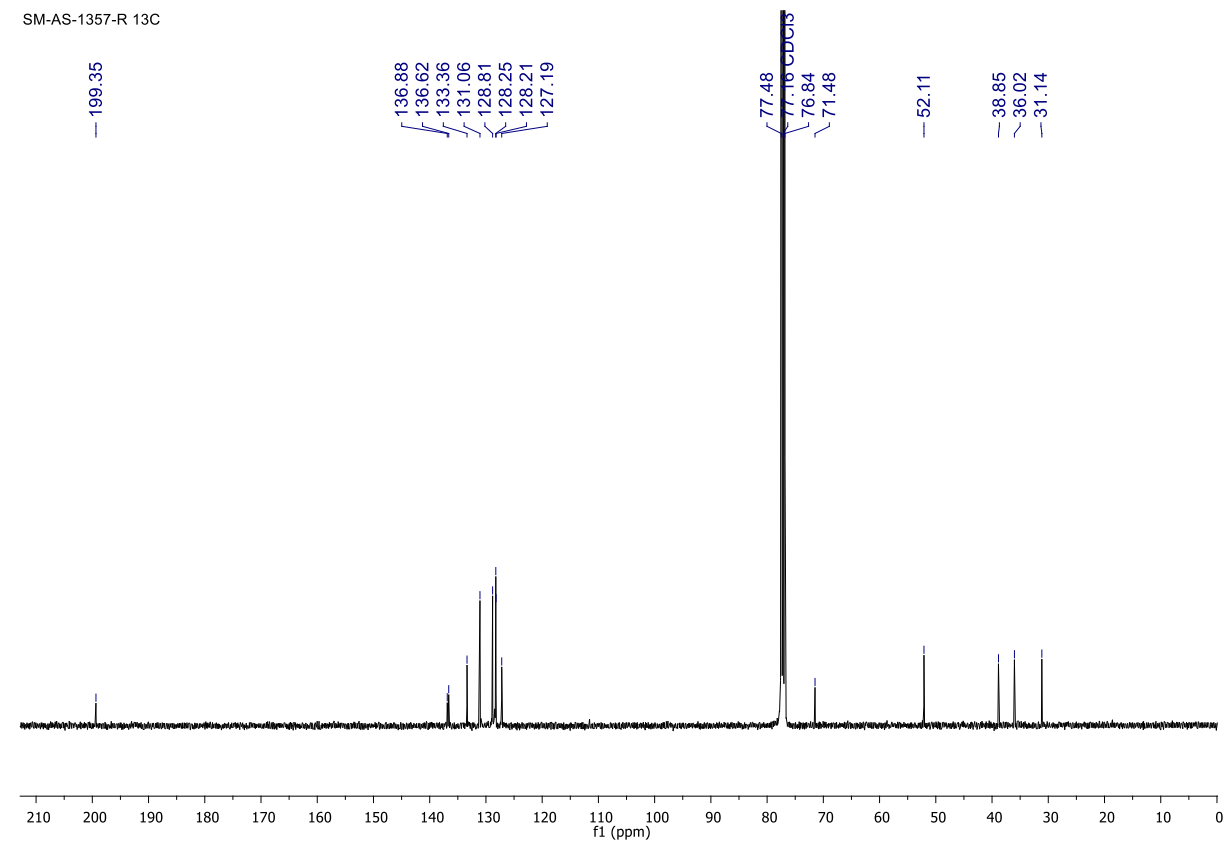
<sup>1</sup>H NMR of **4n'** (400 MHz, CDCl<sub>3</sub>):

SM-AS-1357-R 1H



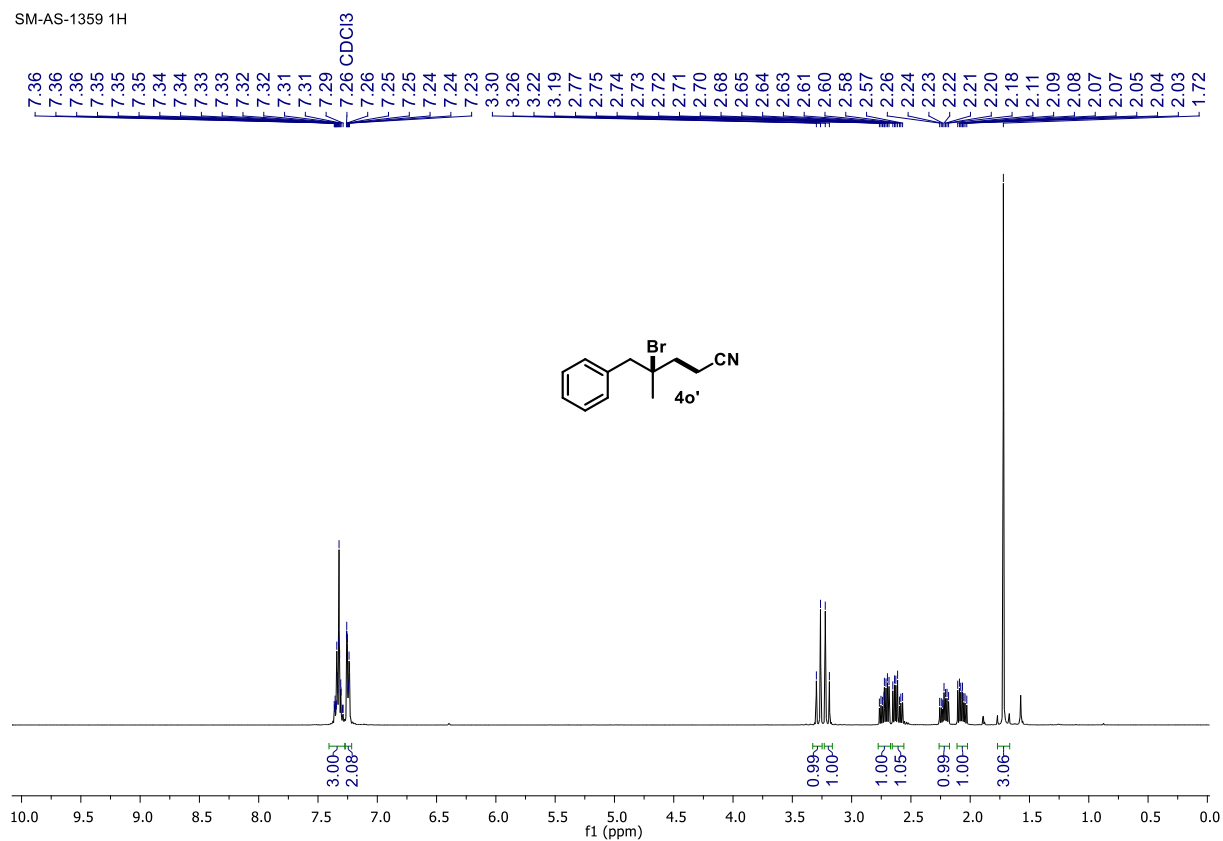
<sup>13</sup>C{<sup>1</sup>H} NMR of **4n'** (101 MHz, CDCl<sub>3</sub>):

SM-AS-1357-R 13C



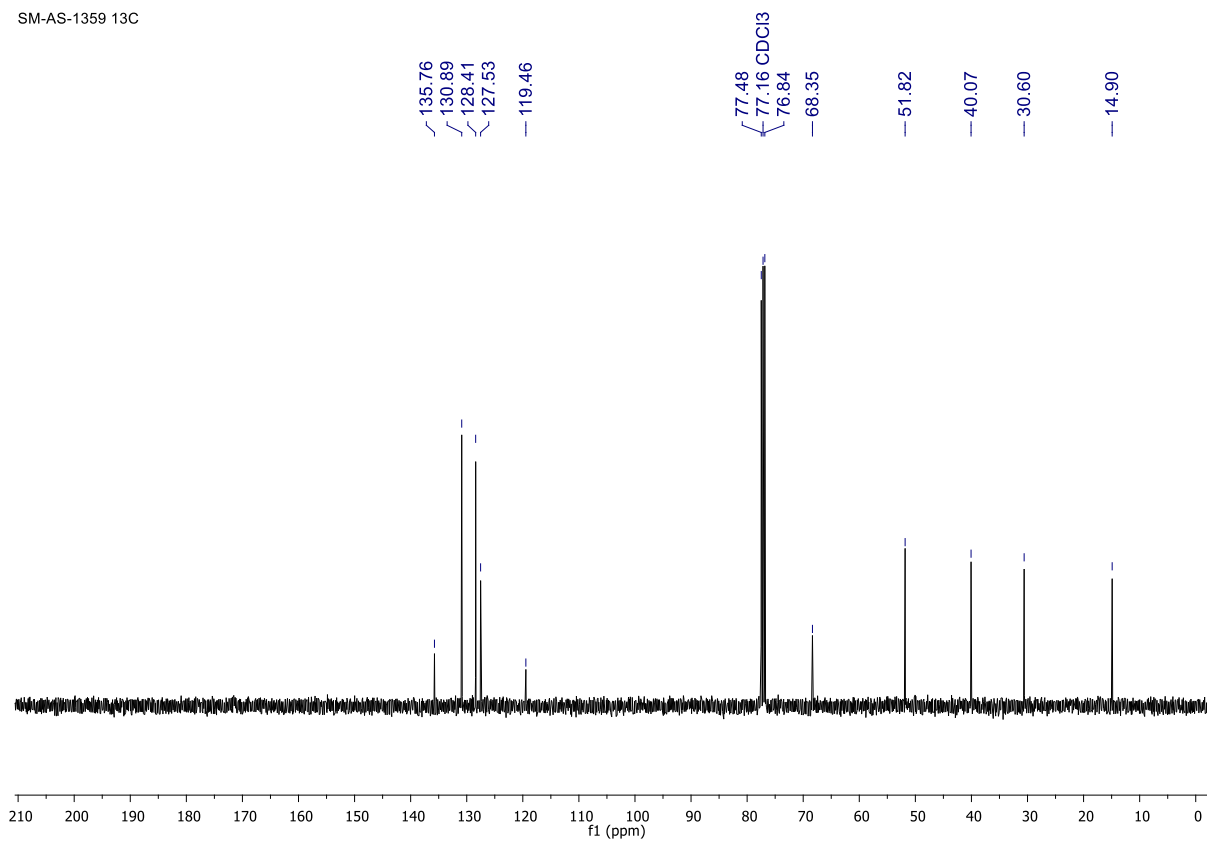
<sup>1</sup>H NMR of **4o'** (400 MHz, CDCl<sub>3</sub>):

SM-AS-1359 1H



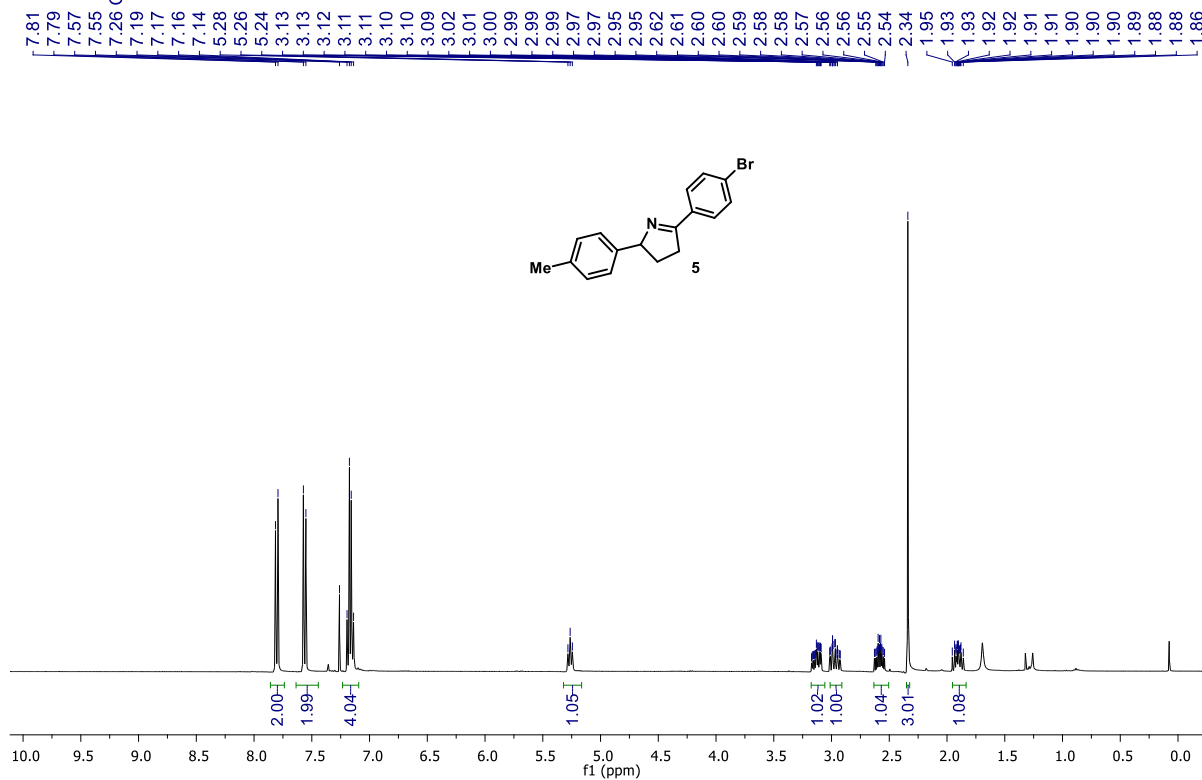
<sup>13</sup>C{<sup>1</sup>H} NMR of **4o'** (101 MHz, CDCl<sub>3</sub>):

SM-AS-1359 13C



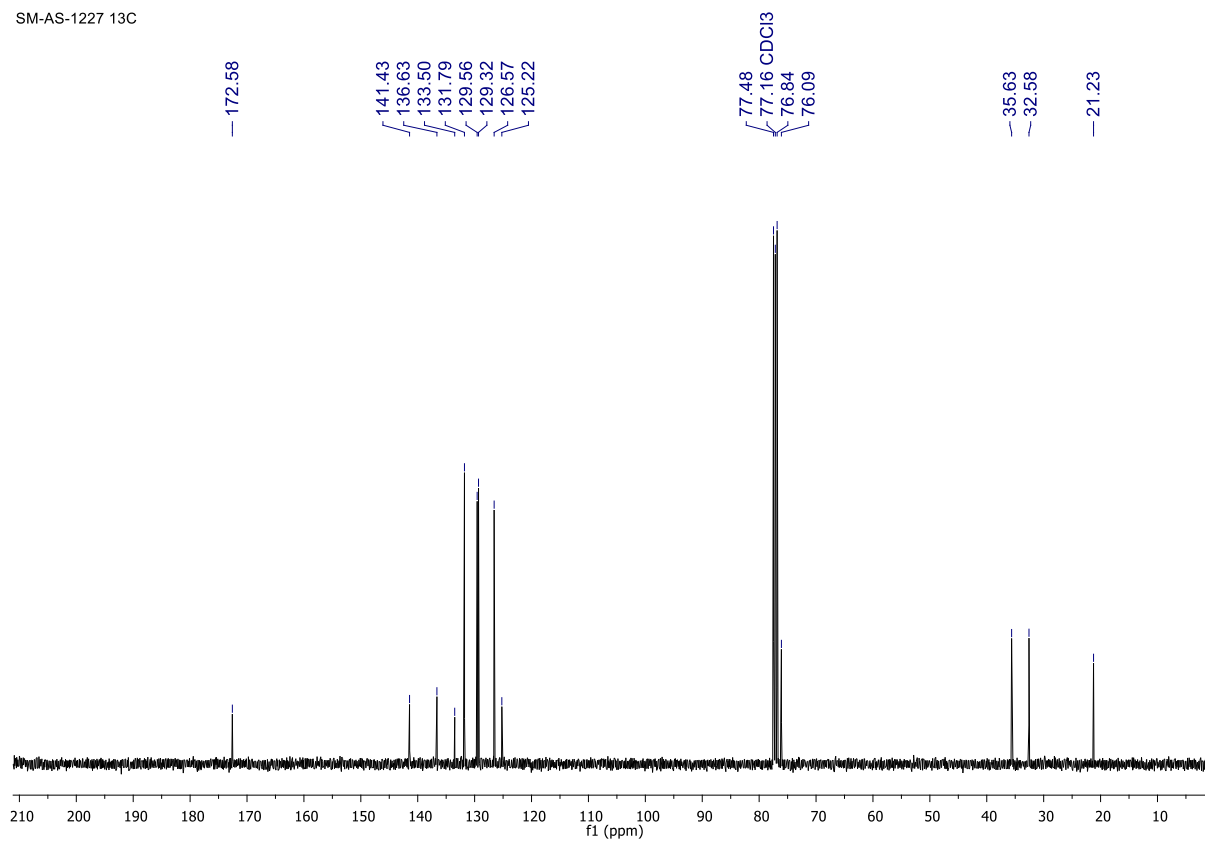
$^1\text{H}$  NMR of **5** (400 MHz,  $\text{CDCl}_3$ ):

SM-AS-1227



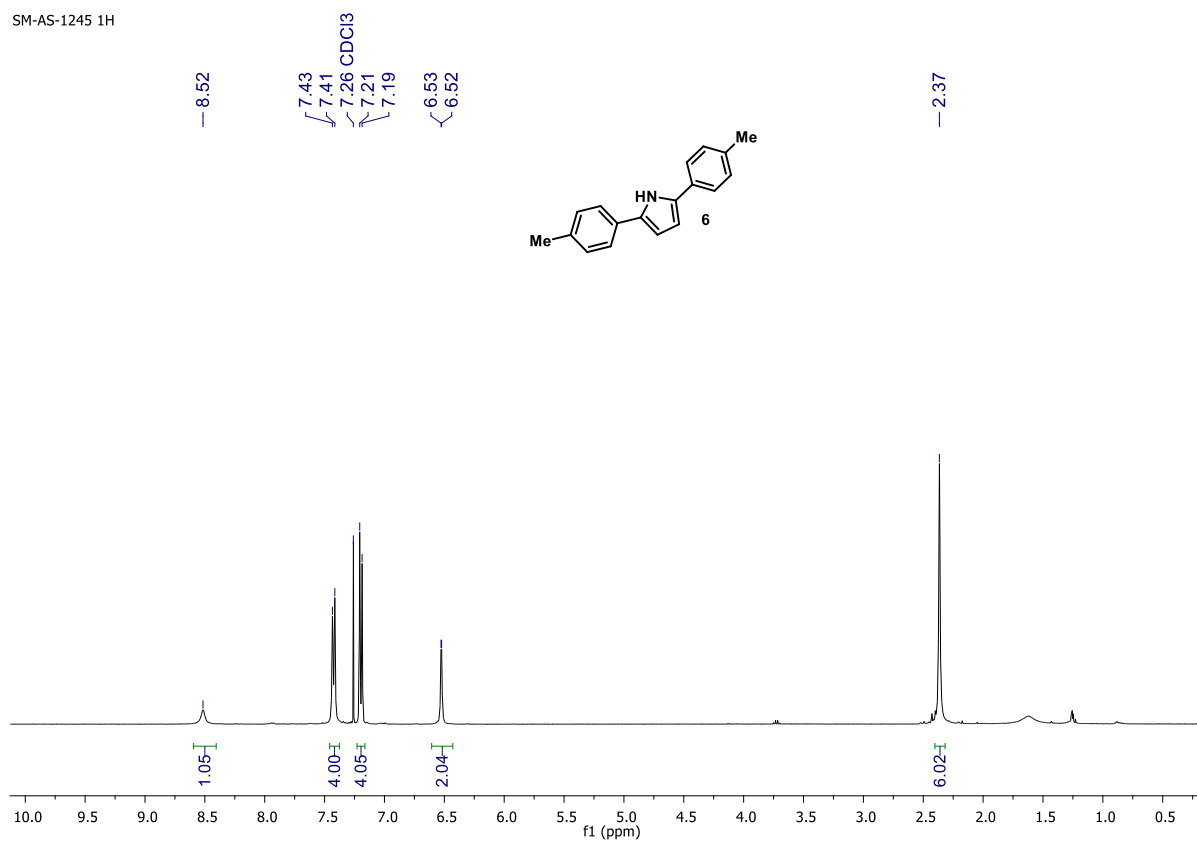
$^{13}\text{C}\{^1\text{H}\}$  NMR of **5** (101 MHz,  $\text{CDCl}_3$ ):

SM-AS-1227 13C



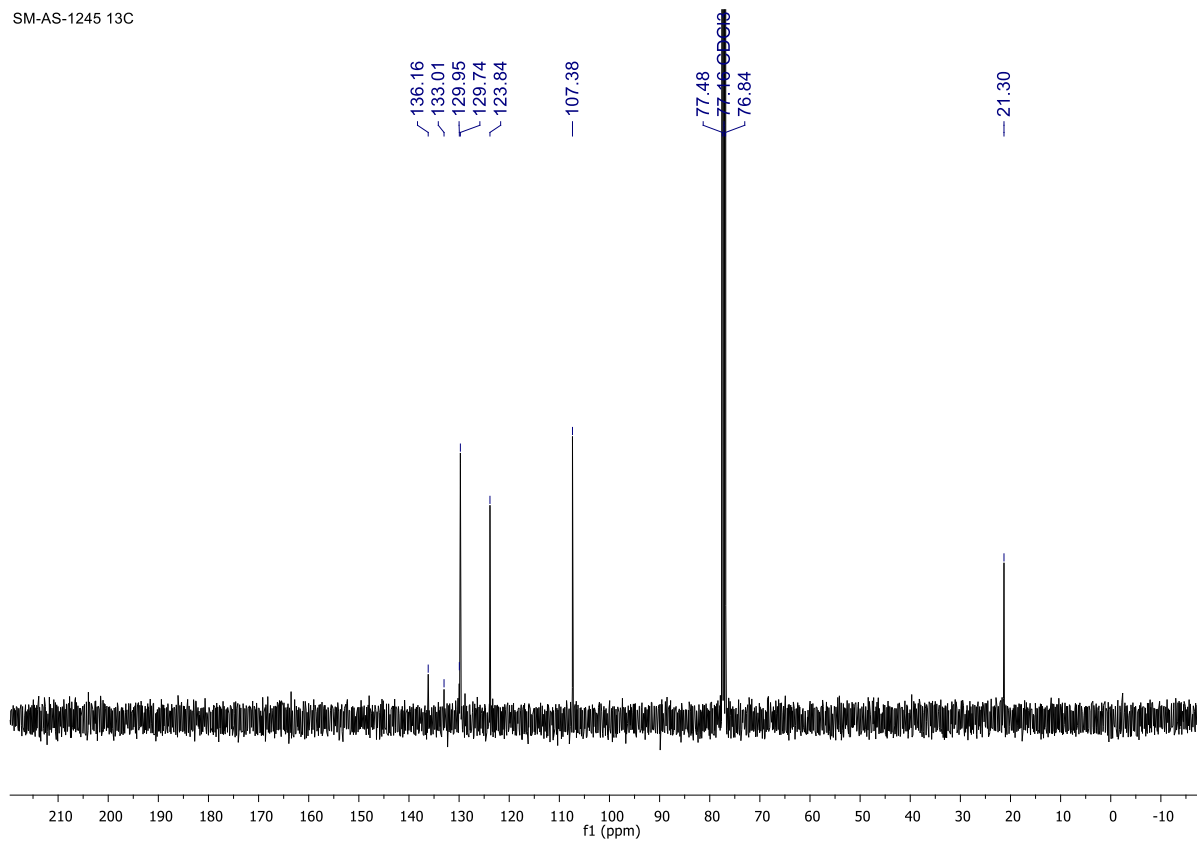
<sup>1</sup>H NMR of **6** (400 MHz, CDCl<sub>3</sub>):

SM-AS-1245 1H



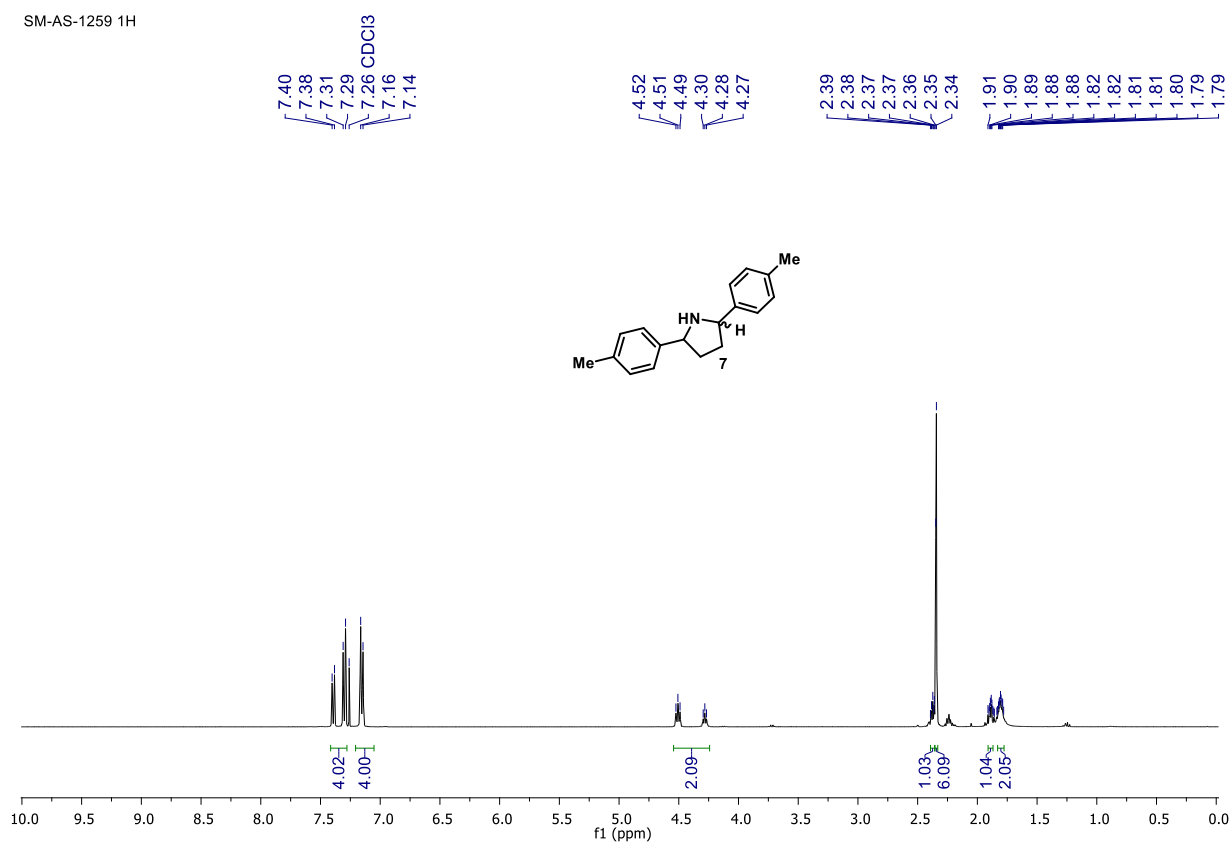
<sup>13</sup>C{<sup>1</sup>H} NMR of **6** (101 MHz, CDCl<sub>3</sub>):

SM-AS-1245 13C



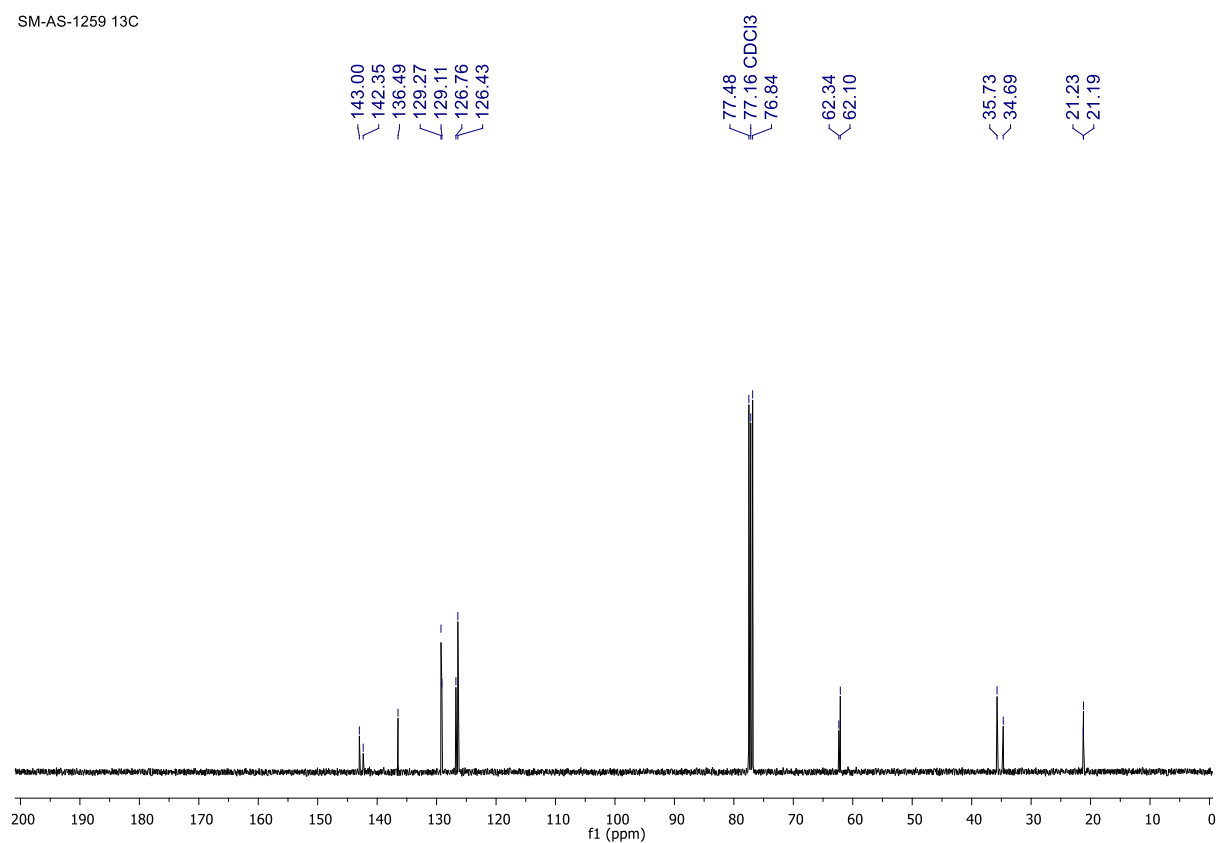
<sup>1</sup>H NMR of **7** (400 MHz, CDCl<sub>3</sub>):

SM-AS-1259 1H



<sup>13</sup>C{<sup>1</sup>H} NMR of **7** (101 MHz, CDCl<sub>3</sub>):

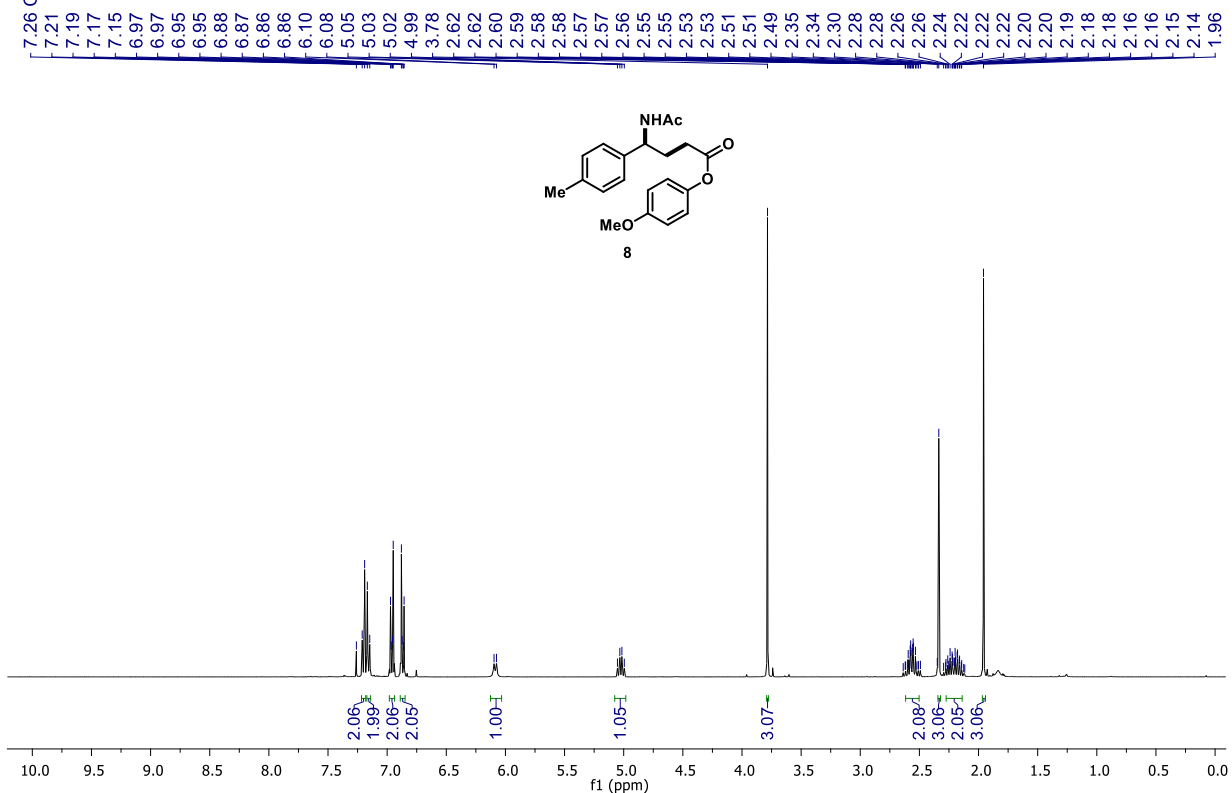
SM-AS-1259 13C





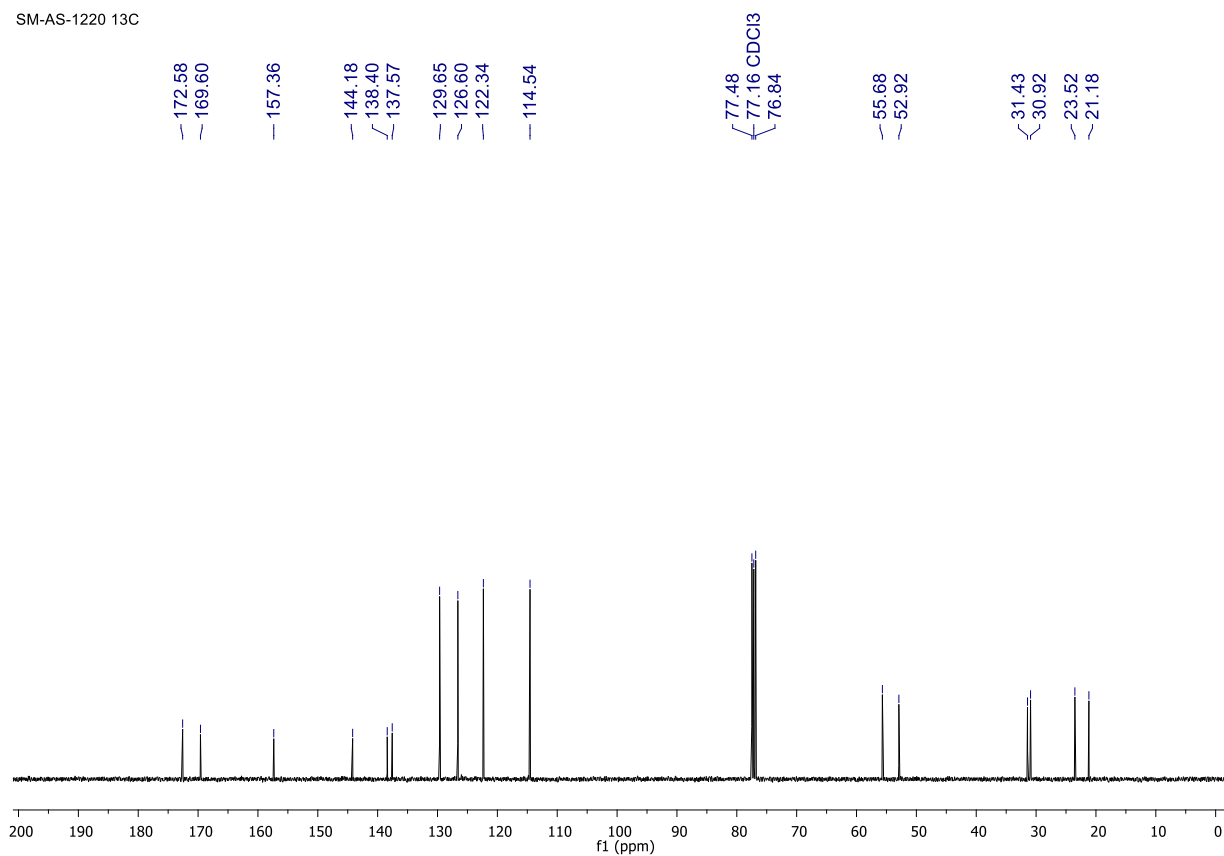
<sup>1</sup>H NMR of **8** (400 MHz, CDCl<sub>3</sub>):

SM-AS-1220 1H



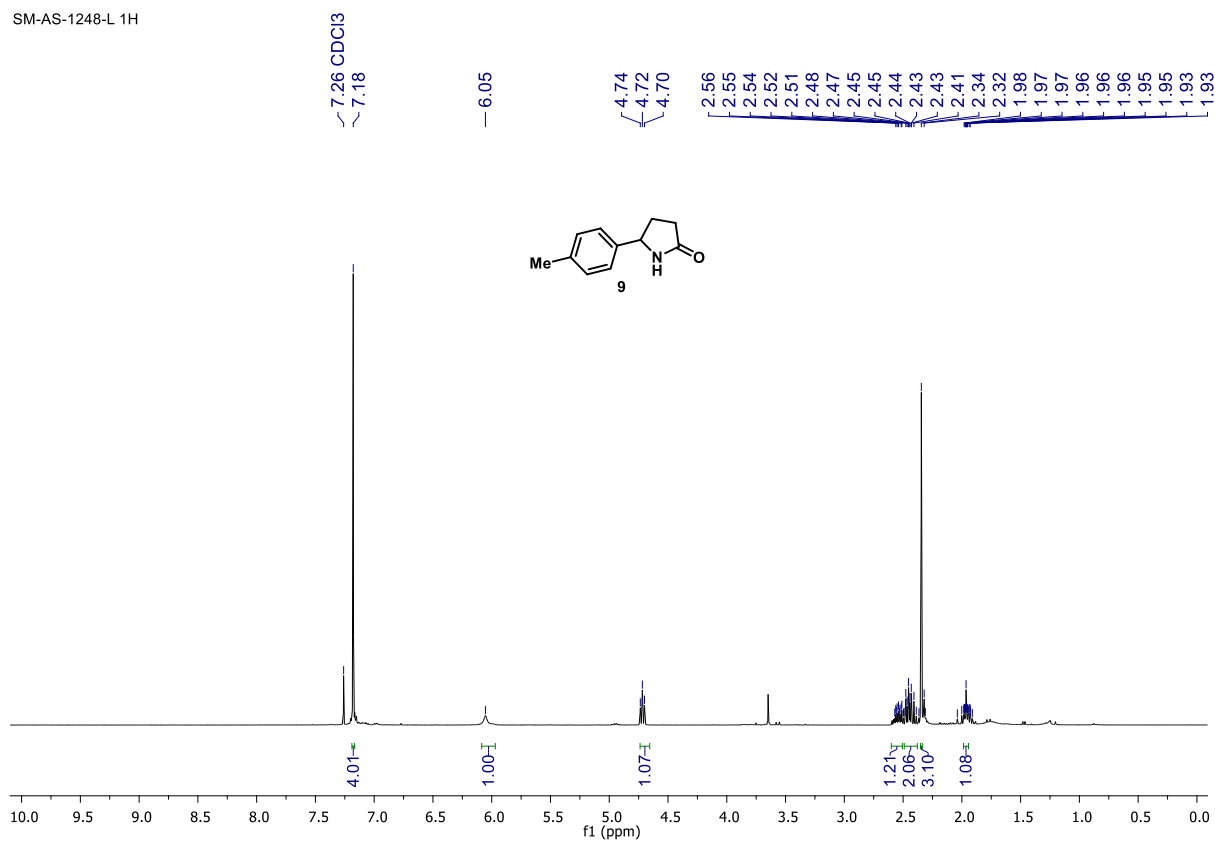
<sup>13</sup>C{<sup>1</sup>H} NMR of **8** (101 MHz, CDCl<sub>3</sub>):

SM-AS-1220 13C



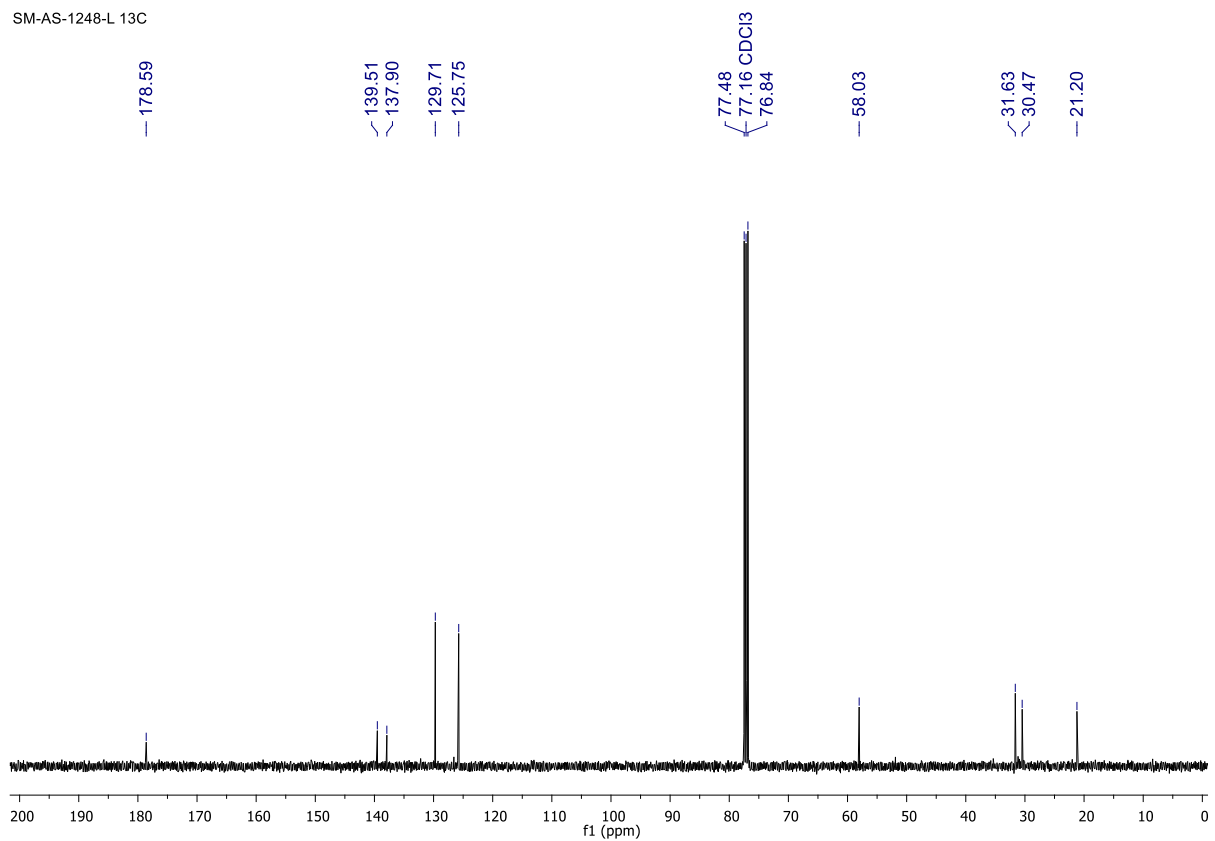
<sup>1</sup>H NMR of **9** (400 MHz, CDCl<sub>3</sub>):

SM-AS-1248-L 1H



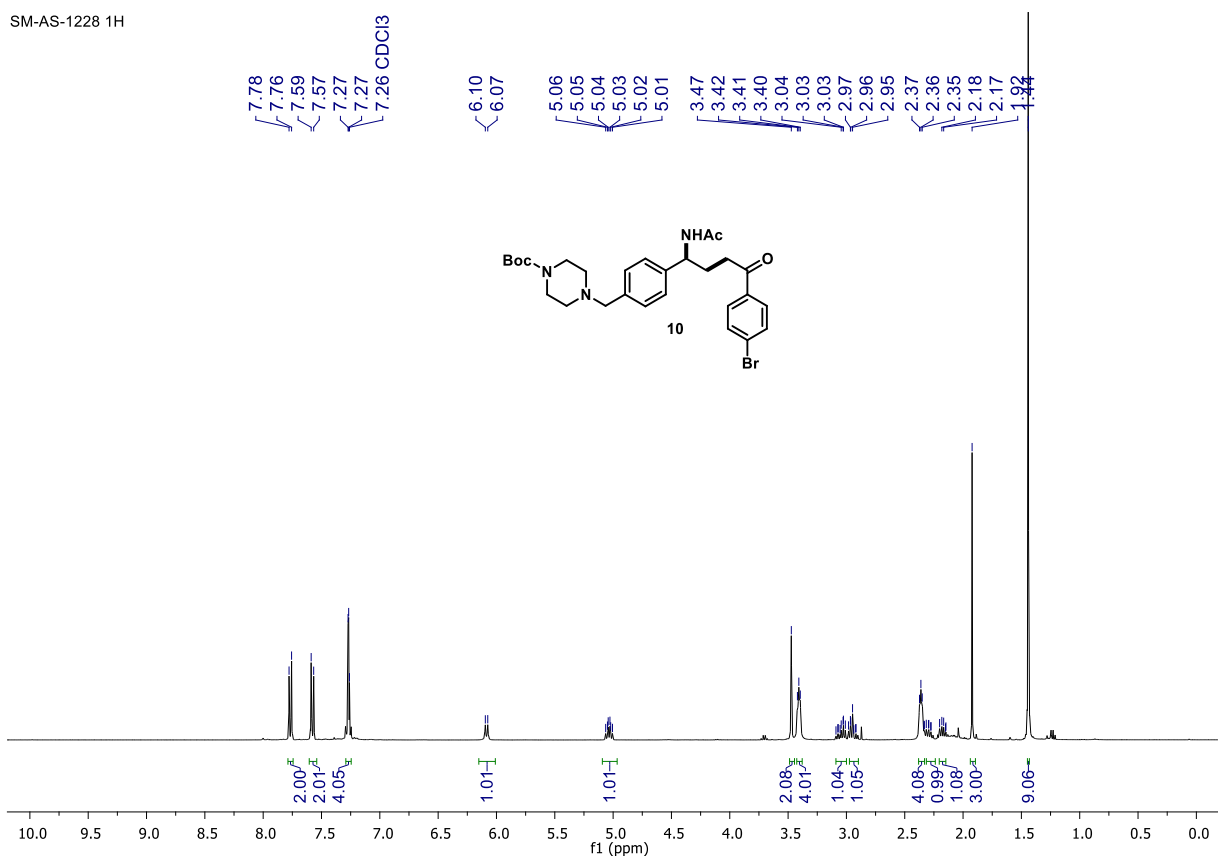
<sup>13</sup>C{<sup>1</sup>H} NMR of **9** (101 MHz, CDCl<sub>3</sub>):

SM-AS-1248-L 13C



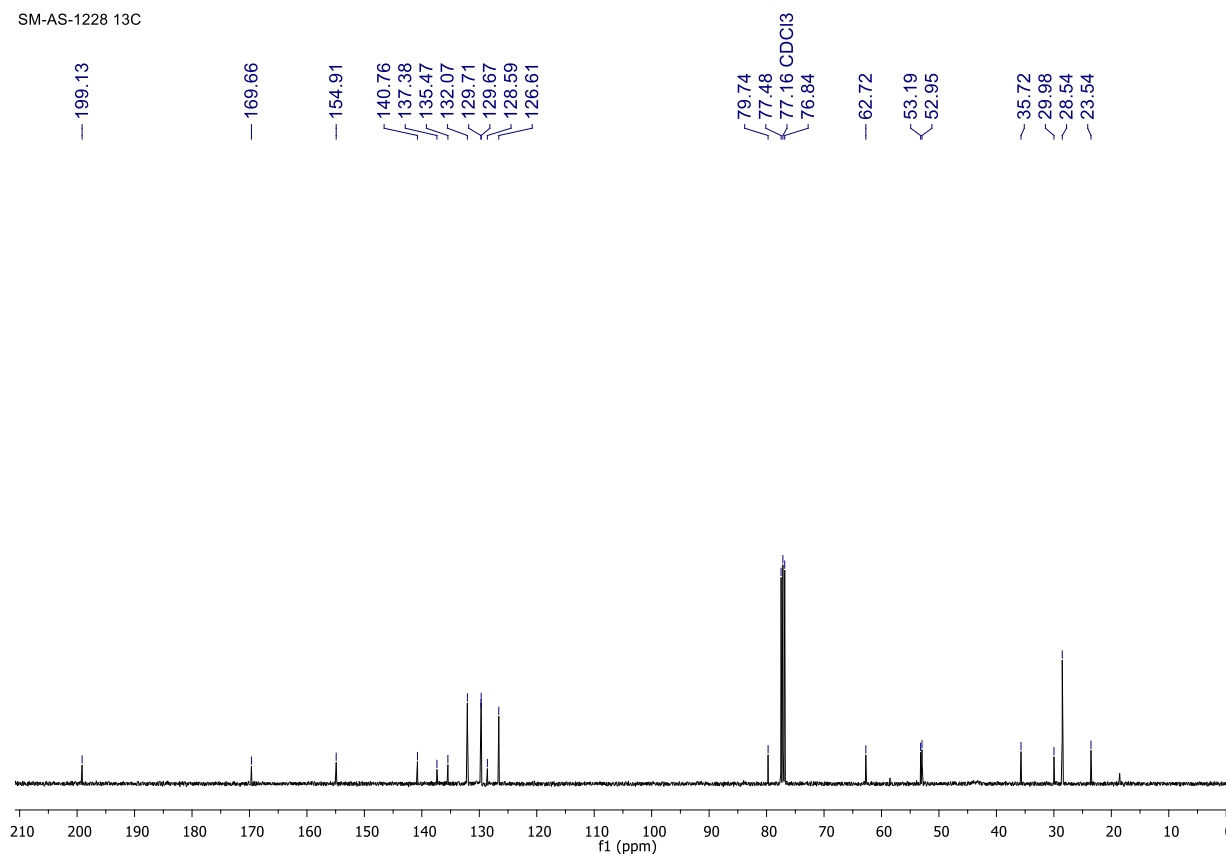
<sup>1</sup>H NMR of **10** (400 MHz, CDCl<sub>3</sub>):

SM-AS-1228 1H



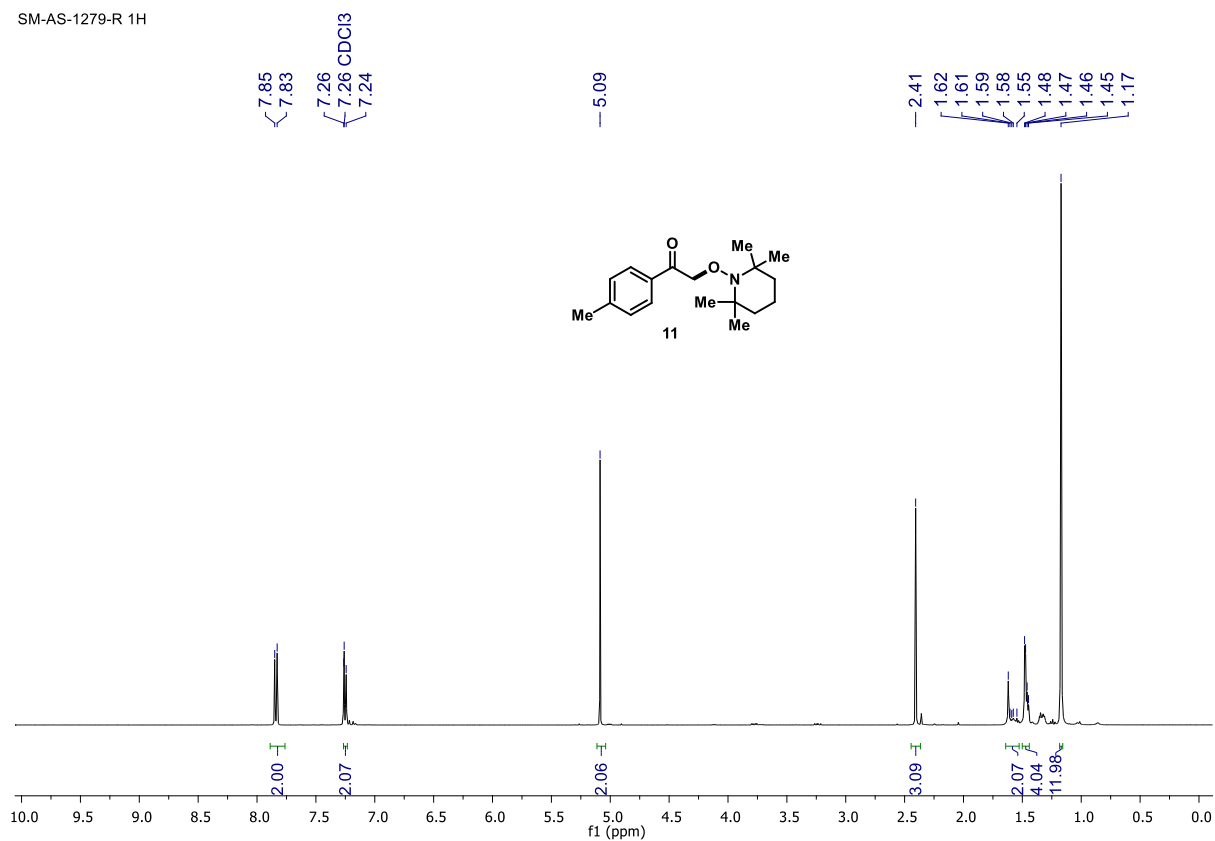
<sup>13</sup>C{<sup>1</sup>H} NMR of **10** (101 MHz, CDCl<sub>3</sub>):

SM-AS-1228 13C



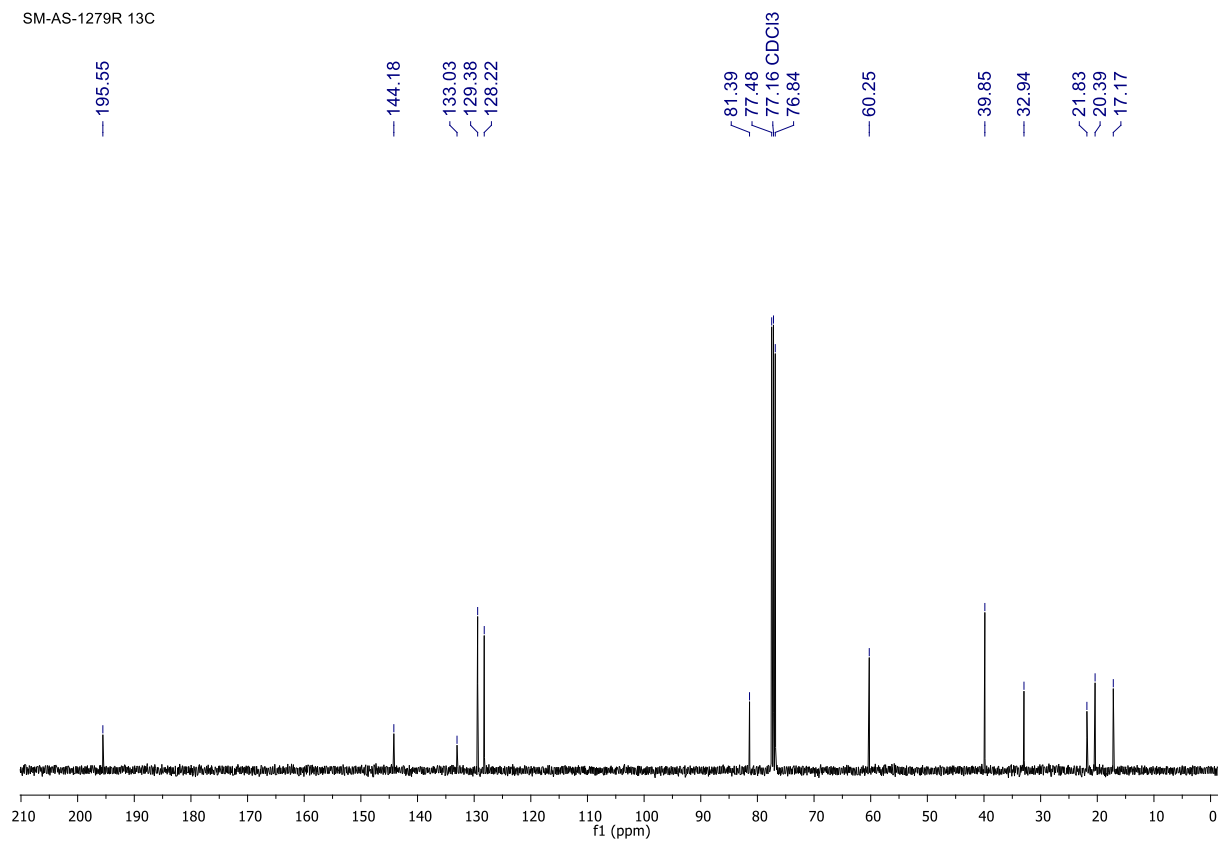
<sup>1</sup>H NMR of **11** (400 MHz, CDCl<sub>3</sub>):

SM-AS-1279-R 1H



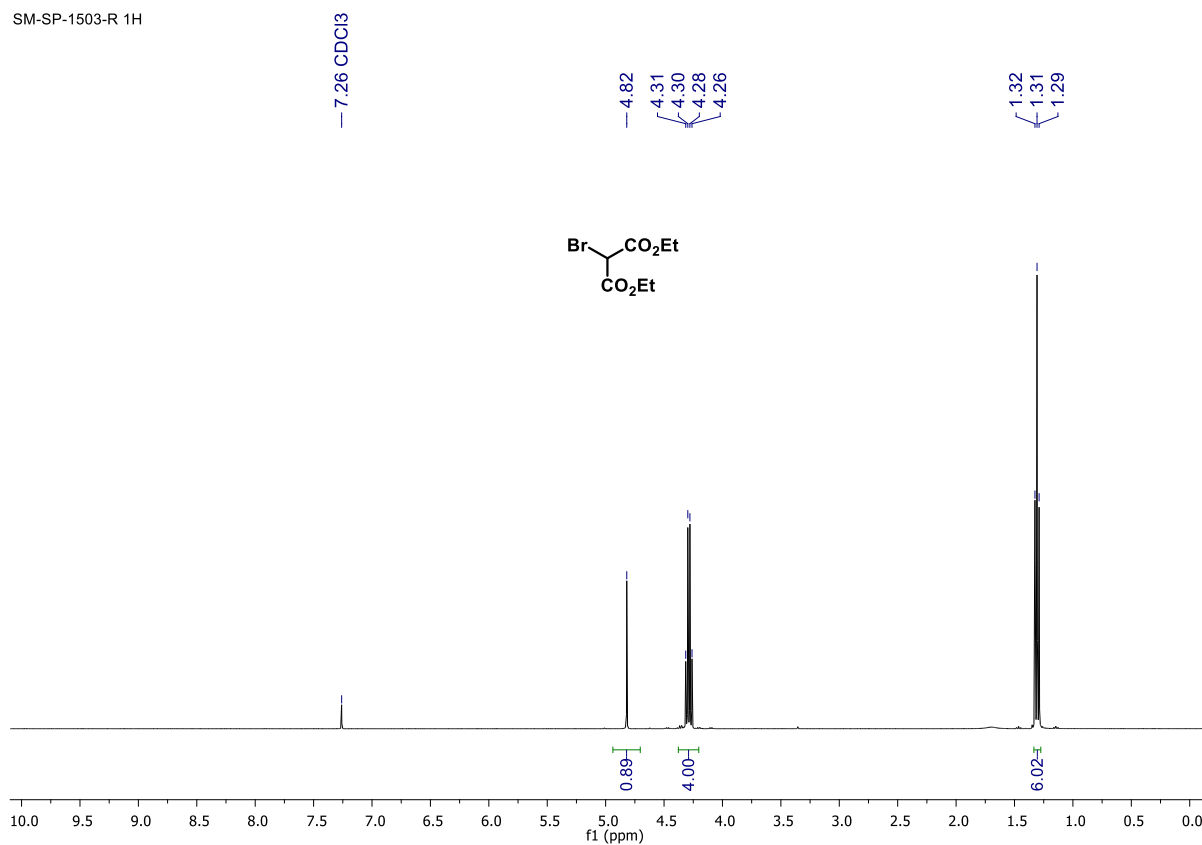
<sup>13</sup>C{<sup>1</sup>H} NMR of **11** (101 MHz, CDCl<sub>3</sub>):

SM-AS-1279R 13C



<sup>1</sup>H NMR of Diethyl bromomalonate (400 MHz, CDCl<sub>3</sub>):

SM-SP-1503-R 1H



<sup>13</sup>C{<sup>1</sup>H} NMR of Diethyl bromomalonate (101 MHz, CDCl<sub>3</sub>):

SM-SP-1503-R 13C

