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## SUPPLEMENTARY INFORMATION

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### A Two Carbon homologation of Friedel-Crafts alkylation enabled by Photochemical Alkene Stitching: Modular assembly of Cyclolignans

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## 1. General Information:

Unless otherwise mentioned, all commercially available chemicals and reagents were used without any further purification. Solvents for extraction or column chromatography were of technical quality. Water used during the reaction 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 IKA and Büchi rotary evaporators.

**Thin-layer chromatography (TLC):** The progress of the reaction was monitored by thin-layer chromatography (TLC) using a silica gel-aluminium sheets (Merck, TLC Silica gel 60 F254), and visualization was achieved under UV light, iodine, and/or chemical staining with vanillin, alkaline KMnO<sub>4</sub> solutions and magic stain as appropriate.

**Flash column chromatography:** Flash column chromatography was performed using silica gel (230–400 µm mesh size) to purify each reported compound. Solvents used during compound extraction was the mixture of ethyl acetate and petroleum ether of different proportions.

**NMR spectra:** A Bruker Avance III HD 400 instrument recorded nuclear magnetic resonance spectra. Chemical shifts ( $\delta$ ) are quoted in parts per million (ppm) relative to residual solvent signals, CDCl<sub>3</sub>, referenced at 7.26 ppm for <sup>1</sup>H and 77.16 ppm for <sup>13</sup>C{<sup>1</sup>H}. Coupling constants (*J*) are quoted in hertz (Hz). Multiplicity is reported with the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, dt = doublet of triplets, td = triplet of doublets and m = multiplets.

**Melting point (Mp):** Melting points were measured using Tempstar melting point instrument using open glass capillaries and are reported uncorrected.

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

**Photoreactions:** Photoreactions were carried out in a borosilicate-made culture tube using mentioned light sources [Kessil PR light ( $\lambda_{\text{max}}$  = 456 nm and 390 nm)]. A high-speed fan cooling was also attached to maintain the temperature.

**UV-Vis Spectrophotometer:** UV–vis absorption spectra were recorded using a Shimadzu UV-1800 Spectrophotometer

**Luminescence spectrometer:** Fluorescence quenching experiments were carried out using a Shimadzu RF-6000 spectrophotometer.

## 2. Preparation of Starting materials:

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

## 2.1. Preparation of alkene derivative 1ag and 1ah:

**General Procedure (GP-I):** In a 25 mL round bottom flask 4-vinylbenzyl chloride (1.2 equiv.) was added to the stirred solution of respective acids/alcohols (1 equiv.) and K<sub>2</sub>CO<sub>3</sub> (1.5 equiv.) in dry DMF (10 mL) at room temperature under argon atmosphere. Then the resultant mixture was allowed to stir for 10 hours at room temperature. After completion of the reaction (checked by TLC), 20 mL distilled water was added to reaction mixture and the organic part was extracted with ethyl acetate (3 x 10 mL). Combined organic layers were washed with brine solution (15 mL), passed over dried Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. Finally, the crude reaction mixture was purified *via* flash column chromatography to afford the corresponding alkenes.

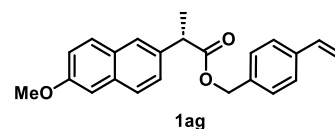
### 4-Vinylbenzyl (*S*)-2-(6-methoxynaphthalen-2-yl)propanoate (1ag):<sup>2</sup>

Following the general procedure **GP-I**, the reaction between (*S*)-naproxen (460 mg, 2 mmol), 4-vinylbenzyl chloride (338  $\mu$ L, 2.4 mmol) and K<sub>2</sub>CO<sub>3</sub> (414 mg, 3 mmol) provide the mentioned compound.

**Yield:** 71% yield (492 mg)

**Nature:** Colourless 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>)  $\delta$  (ppm):** 7.72 – 7.66 (m, 3H), 7.42 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.18 – 7.13 (m, 2H), 6.70 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.74 (d, *J* = 17.6 Hz, 1H), 5.26 (d, *J* = 10.8 Hz, 1H), 5.12 (q, *J* = 12.5 Hz, 2H), 3.95 – 3.90 (m, 4H), 1.61 (d, *J* = 7.2 Hz, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm):** 174.5, 157.7, 137.5, 136.5, 135.6, 135.6, 133.8, 129.4, 129.0, 128.3, 127.2, 126.4, 126.1, 119.1, 114.3, 105.7, 66.3, 55.4, 45.6, 18.6.

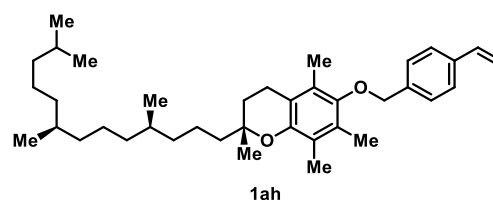
### (*R*)-2,5,7,8-Tetramethyl-2-((4*R*,8*S*)-4,8,12-trimethyltridecyl)-6-((4-vinylbenzyl)oxy)chromane (1ah):<sup>3</sup>

Following the general procedure **GP-I**, the reaction between DL- $\alpha$ -Tocopherol (861 mg, 2 mmol), 4-vinylbenzyl chloride (338  $\mu$ L, 2.4 mmol) and K<sub>2</sub>CO<sub>3</sub> (414 mg, 3 mmol) provide the mentioned compound.

**Yield:** 68% yield (744 mg)

**Nature:** Colourless sticky liquid.

**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>)  $\delta$  (ppm):** 7.50 – 7.44 (m, 4H), 6.76 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.79 (d, *J* = 17.6 Hz, 1H), 5.27 (d, *J* = 10.9 Hz, 1H), 4.70 (s, 2H), 2.61 (t, *J* = 6.7 Hz, 2H), 2.23 (s, 3H), 2.18 (s, 3H), 2.13 (s, 3H), 1.89 – 1.75 (m, 2H), 1.63 – 1.46 (m, 4H), 1.45 – 1.34 (m, 4H), 1.32 – 1.21 (m, 10H), 1.18 – 1.08 (m, 6H), 0.91 – 0.85 (m, 12H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm):** 148.3, 148.1, 137.8, 137.3, 136.7, 128.1, 128.0, 126.4, 126.1, 123.1, 117.7, 114.0, 75.0, 74.6, 40.2, 39.5, 37.7, 37.6, 37.5, 37.4, 32.9, 32.8, 31.5, 28.1, 25.0, 24.6, 24.0, 22.9, 22.8, 21.2, 20.8, 19.9, 19.8, 13.0, 12.1, 12.0.

## 2.2. Preparation of bromo-alkyl derivatives 2ai and 2aj:

<sup>2</sup> N. Katta, Q.-Q. Zhao, T. Mandal and O. Reiser, *ACS Catal.*, 2022, **12**, 14398–14407.

<sup>3</sup> H. Sahoo, L. Zhang, J. Cheng, M. Nishiura and Z. Hou, *J. Am. Chem. Soc.*, 2022, **144**, 23585–23594.

**General Procedure (GP-II):** An oven dried 50 mL round bottom flask equipped with magnetic stir bar was successively charged with bromoacetic acid (1.2 equiv.), catalytic amount of DMAP (0.2 equiv.) and respective alcohols (1.0 equiv.) in dry DCM (15 mL) under argon atmosphere. Then the mixture was allowed to cool to 0 °C in an ice-water bath and DCC (2.0 equiv.) was added at once under same condition. After that, the cooling condition was removed off and the reaction mixture was allowed to stirring for 8 hours at room temperature. After the completion of reaction (checked by TLC), the crude reaction mixture was filtered through a short pad of celite to remove the solid particles, washed with dichloromethane. Finally, the filtrate was concentrated under reduced pressure and purified by flash column chromatography to afford the corresponding bromo-alkyl derivatives.

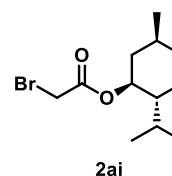
**(1*S*,2*R*,5*S*)-2-Isopropyl-5-methylcyclohexyl 2-bromoacetate (2ai):<sup>4</sup>**

Following the general procedure (GP-II), the reaction between menthol (469 mg, 3 mmol), bromoacetic acid (500 mg, 3.6 mmol), DCC (1.24 gm, 6.0 mmol) and DMAP (73 mg, 0.6 mmol) provide the mentioned compound.

**Yield:** 76% yield (632 mg)

**Nature:** Colourless liquid.

**R<sub>f</sub> value** = 0.6 [EtOAc/petroleum ether = 1:9 (v/v)]



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 4.71 (td, *J* = 10.9, 4.4 Hz, 1H), 3.82 – 3.75 (m, 2H), 2.02 – 1.96 (m, 1H), 1.93 – 1.85 (m, 1H), 1.67 (d, *J* = 11.4 Hz, 2H), 1.53 – 1.37 (m, 2H), 1.09 – 0.96 (m, 2H), 0.89 (dd, *J* = 6.6, 5.4 Hz, 6H), 0.83 (dd, *J* = 12.4, 2.6 Hz, 1H), 0.75 (d, *J* = 7.0 Hz, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 167.0, 76.5, 47.0, 40.6, 34.2, 31.5, 26.4, 26.2, 23.4, 22.1, 20.8, 16.3.

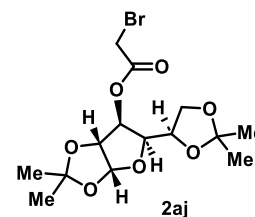
**(3*aR*,5*R*,6*S*,6*aR*)-5-((*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl 2-bromoacetate (2aj):<sup>5</sup>**

Following the general procedure (GP-II), the reaction between diacetone-d-glucose (781 mg, 3 mmol), bromoacetic acid (500 mg, 3.6 mmol), DCC (1.24 gm, 6.0 mmol) and DMAP (73 mg, 0.6 mmol) provide the mentioned compound.

**Yield:** 65% yield (743 mg)

**Nature:** Low-melting solid.

**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):** 5.88 (d, *J* = 3.7 Hz, 1H), 5.29 (d, *J* = 2.7 Hz, 1H), 4.49 (d, *J* = 3.7 Hz, 1H), 4.25 – 4.17 (m, 1H), 4.09 (dd, *J* = 8.7, 5.7 Hz, 1H), 3.99 (dd, *J* = 8.7, 4.5 Hz, 1H), 3.85 (s, 2H), 1.50 (s, 3H), 1.39 (s, 3H), 1.30 (d, *J* = 2.7 Hz, 6H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 166.1, 112.6, 109.6, 105.1, 83.1, 79.9, 77.7, 72.3, 67.5, 26.9, 26.8, 26.3, 25.33, 25.28.

### 2.3. Preparation of 1,2,5-Trimethoxy-3-vinylbenzene:

<sup>4</sup> S. P. Shankar, M. Jagodzinska, L. Malpezzi, P. Lazzari, I. Manca, I. R. Greig, M. Sani and M. Zanda, *Org. Biomol. Chem.*, 2013, **11**, 2273–2287.

<sup>5</sup> B. Zhao, Z. Li, Y. Wu, Y. Wang, J. Qian, Y. Yuan and Z. Shi, *Angew. Chem., Int. Ed.*, 2019, **58**, 9448–9452.

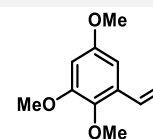
**Wittig Reaction:** An oven dried 250 mL round bottom flask equipped with magnetic stir bar was successively charged with methyltriphenylphosphonium bromide (6.43 gm, 18 mmol.) in dry THF (70 mL) under argon atmosphere and allowed to cool to 0 °C in an ice-water bath and stirred for 15 minutes. Then potassium tert-butoxide (2.0 gm, 18 mmol.) was added at once under the same condition. After the formation of the ylide (indicated by the appearance of yellow colour) the reaction mixture was stirred for another 15 minutes at room temperature and then further cooled to 0 °C before adding the 2,3,5-trimethoxybenzaldehyde (2.35 gm, 12 mmol.). Then the reaction was allowed to stir for 8 hours at room temperature. After completion of the reaction (checked by TLC), the crude reaction mixture was passed through the celite-pad, washed with diethyl ether and filtrate was concentrated under reduced pressure. Finally, flash column chromatography of the crude gives the target alkene.

### 1,2,5-Trimethoxy-3-vinylbenzene:<sup>6</sup>

**Yield:** 70% yield (1.63 gm)

**Nature:** Colourless oil.

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

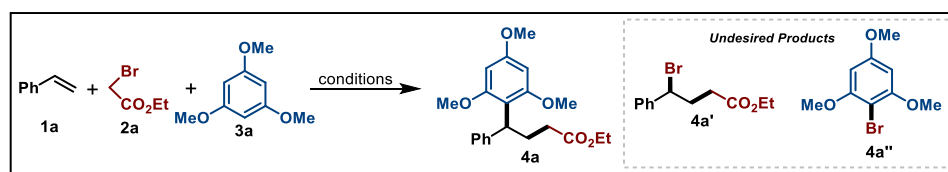


**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 7.04 (dd, *J* = 17.8, 11.0 Hz, 1H), 6.60 (d, *J* = 2.8 Hz, 1H), 6.43 (d, *J* = 2.8 Hz, 1H), 5.74 (dd, *J* = 17.8, 0.9 Hz, 1H), 5.31 (dd, *J* = 11.2, 0.8 Hz, 1H), 3.84 (s, 3H), 3.80 (s, 3H), 3.75 (s, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 156.2, 153.7, 141.2, 131.6, 131.3, 115.1, 100.1, 100.0, 61.2, 55.9, 55.6.

### 3. Reaction Optimization:

**General procedure for reaction optimization:** An oven-dried culture tube equipped with a magnetic stir bar was successively charged with the photocatalyst (2 mol%), styrene **1a** (47 μL, 0.4 mmol), ethyl bromoacetate **2a** (22 μL, 0.2 mmol), 1,3,5-trimethoxybenzene **3a** (34 mg, 0.2 mmol) and the additive (0.4 mmol, 2.0 equiv.) in dry solvent (2 mL). Then, the tube was sealed with a rubber screw cap, evacuated and backfilled with argon, placed under purple LEDs at an approximate distance of 5 cm and irradiated for a specific time. A high-speed fan was also applied to maintain the temperature. After completion of the reaction (checked by TLC), the crude reaction mixture was concentrated under reduced pressure, 5 mL of distilled water was added to it and the organic part was extracted with DCM (2 x 3 mL). Combined organic layers were washed with brine (3 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. Finally, flash column chromatography of the crude was carried out to isolate the mentioned compounds.



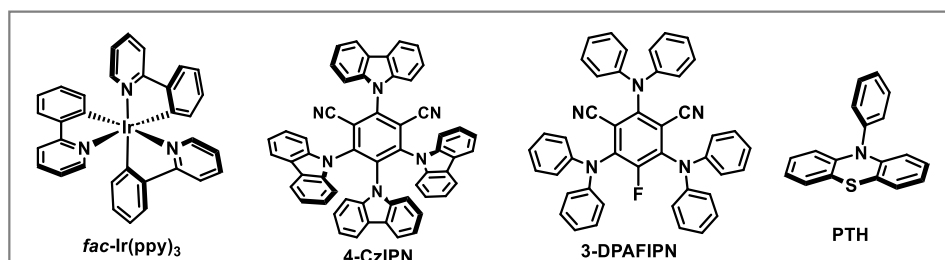
**Table S1: Optimization of the Alkylation reaction.<sup>a</sup>**

Entry	Photocatalyst (PC)	Solvent	Additive	4a: 4a': 4a'' (%) <sup>b</sup>
1.	<i>fac</i> -Ir(ppy) <sub>3</sub>	CH <sub>3</sub> CN	-	0: 47: 15
2.	<i>fac</i> -Ir(ppy) <sub>3</sub>	CH <sub>3</sub> CN	KF	0: 30: trace
3.	<i>fac</i> -Ir(ppy) <sub>3</sub>	CH <sub>3</sub> CN	LiCl	0: 35: 8
4.	<i>fac</i> -Ir(ppy) <sub>3</sub>	CH <sub>3</sub> CN	Zn(OAc) <sub>2</sub>	43: 0: 0
5.	<i>fac</i> -Ir(ppy) <sub>3</sub>	CH <sub>3</sub> CN	Zn(TFA) <sub>2</sub>	22: 6: 0

<sup>6</sup> B. Cheng, J. Yu, T. Arisawa, K. Hayashi, j. j. Richardson, Y. Shibuta and H. Ejima, *Nat. Commun.*, 2022,**13**, 1892.

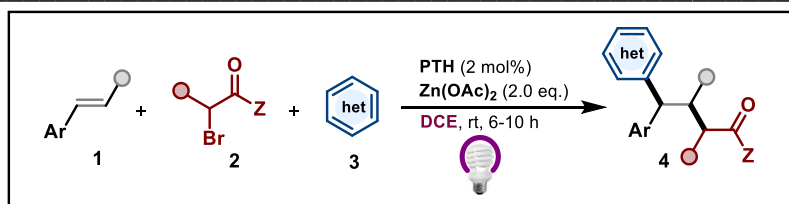
6.	<i>fac</i> -Ir(ppy) <sub>3</sub>	CH <sub>3</sub> CN	Zn(OTf) <sub>2</sub>	16: 0: 0
7.	<i>fac</i> -Ir(ppy) <sub>3</sub>	CH <sub>3</sub> CN	Zn-dust	25: 0: 0
8.	<i>fac</i> -Ir(ppy) <sub>3</sub>	CH <sub>3</sub> CN	BF <sub>3</sub> ·Et <sub>2</sub> O	NR
9.	<i>fac</i> -Ir(ppy) <sub>3</sub>	CH <sub>3</sub> CN	Yb(OTf) <sub>3</sub>	5: 7: trace
10.	<i>fac</i> -Ir(ppy) <sub>3</sub>	CH <sub>3</sub> CN	AlCl <sub>3</sub>	NR
11.	<i>fac</i> -Ir(ppy) <sub>3</sub>	CH <sub>3</sub> CN	Cu(OAc) <sub>2</sub>	0: 27: 8
12.	<i>fac</i> -Ir(ppy) <sub>3</sub>	CH <sub>3</sub> CN	[Cu(CH <sub>3</sub> CN) <sub>4</sub> ]PF <sub>6</sub>	15: 7: 13
13.	<i>fac</i> -Ir(ppy) <sub>3</sub>	CH <sub>3</sub> CN	Ag <sub>2</sub> CO <sub>3</sub>	18: trace: 0
14.	4-CzIPN	CH <sub>3</sub> CN	Zn(OAc) <sub>2</sub>	8: 0: 0
15.	3-DPAFIPN	CH <sub>3</sub> CN	Zn(OAc) <sub>2</sub>	12: 0: 0
16. <sup>c</sup>	PTH	CH <sub>3</sub> CN	Zn(OAc) <sub>2</sub>	49: 0: 0
17. <sup>c</sup>	PTH	DCE	Zn(OAc) <sub>2</sub>	80: 0: 0
18. <sup>c</sup>	PTH	THF	Zn(OAc) <sub>2</sub>	46: 0: 0
19. <sup>c</sup>	PTH	Toluene	Zn(OAc) <sub>2</sub>	65: 0: 0
20. <sup>c</sup>	PTH	DMSO	Zn(OAc) <sub>2</sub>	10: 0: 0
21. <sup>c</sup>	PTH	Acetone	Zn(OAc) <sub>2</sub>	77: 0: 0
22. <sup>c</sup>	PTH	Ethyl acetate	Zn(OAc) <sub>2</sub>	72: 0: 0
23. <sup>d</sup>	PTH	DCE	Zn(OAc) <sub>2</sub>	NR
24.	-	DCE	Zn(OAc) <sub>2</sub>	NR

<sup>a</sup> Conditions: **1a** (0.4 mmol), **2a** (0.2 mmol), **3a** (0.2 mmol), **PC** (2 mol%), additive (2.0 equiv.), solvent (0.1 M), degassed condition, irradiation with blue LEDs light in RT for 10 h. <sup>b</sup> isolated yield. <sup>c</sup> irradiation with LEDs light ( $\lambda_{\max}$  = 390 nm) for 6 h, <sup>d</sup> reactions performed in dark, NR= no reaction. *fac*-Ir(ppy)<sub>3</sub>: *fac*-Tris(2-phenylpyridine)iridium; 4CzIPN: 1,2,3,5-Tetrakis(carbazol-9-yl)-4,6-dicyanobenzene; 3-DPAFIPN: 2,4,6-Tris(diphenylamino)-5-fluoroisophthalonitrile; PTH: 10-phenylphenothiazine. DCE: 1,2-Dichloroethane.



#### 4. Experimental procedures and compound characterization data:

**4.1. General procedure of the alkylation reaction:** An oven-dried culture tube equipped with a magnetic stir bar was successively charged with the photocatalyst PTH (1 mg, 2 mol%), styrene **1** (0.4 mmol, 2.0 equiv.),  $\alpha$ -bromoalkyl **2** (0.2 mmol, 1.0 equiv.), (hetero)arenes **3** (0.2 mmol, 1.0 equiv.), and Zn(OAc)<sub>2</sub> (88 mg, 0.4 mmol) in dry DCE (2 mL). Then the tube was sealed with a rubber screw cap, evacuated and backfilled with argon, placed under purple LEDs at an approximate distance of 5 cm and irradiated for 6 h. A high-speed fan was also applied to maintain the temperature. After completion of the reaction (checked by TLC), 5 mL of distilled water was added to the reaction mixture and the organic part was extracted with DCM (2 x 3 mL). Combined organic layers were washed with brine (3 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. Finally, the crude residue was purified by flash column chromatography to get the corresponding alkylated products **4**.



## 4.2. Compound Characterization Data:

### Ethyl 4-bromo-4-phenylbutanoate (4a'):<sup>7</sup>

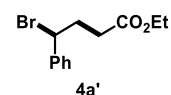
**Yield:** 47% yield (25 mg)

**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):** 7.40 (d, *J* = 7.2 Hz, 2H), 7.35 (t, *J* = 7.3 Hz, 2H), 7.31 – 7.27 (m, 1H), 5.06 – 5.02 (m, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.59 – 2.41 (m, 4H), 1.25 (t, *J* = 7.2 Hz, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 172.5, 141.6, 128.9, 128.7, 127.4, 60.7, 54.4, 35.1, 32.9, 14.3.



### 2-Bromo-1,3,5-trimethoxybenzene (4a''):<sup>8</sup>

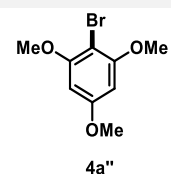
**Yield:** 15% yield (7 mg)

**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):** 6.17 (s, 2H), 3.87 (s, 6H), 3.81 (s, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 160.6, 157.6, 92.1, 91.8, 56.5, 55.7.



### Ethyl 4-phenyl-4-(2,4,6-trimethoxyphenyl)butanoate (4a):

**Yield:** 80% yield (57 mg)

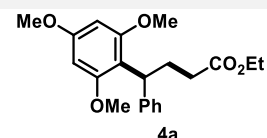
**Nature:** Colourless liquid.

**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):** 7.32 (d, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.6 Hz, 2H), 7.11 (t, *J* = 7.3 Hz, 1H), 6.11 (s, 2H), 4.59 (dd, *J* = 9.9, 6.3 Hz, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.78 (s, 3H), 3.71 (s, 6H), 2.62 – 2.42 (m, 2H), 2.31 – 2.16 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 174.2, 159.8, 159.4, 145.2, 127.9, 127.7, 125.3, 112.8, 91.2, 60.2, 55.7, 55.3, 38.8, 33.4, 27.1, 14.3.

**HRMS (ESI):** *m/z* calculated for C<sub>21</sub>H<sub>26</sub>NaO<sub>5</sub> [M+Na]<sup>+</sup>: 381.1678; found: 381.1674.



### Phenyl 4-phenyl-4-(2,4,6-trimethoxyphenyl)butanoate (4b):

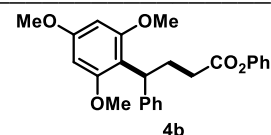
<sup>7</sup> X. Y. Dong, Y. F. Zhang, C. L. Ma, Q. S. Gu, F. L. Wang, Z. L. Li, S. P. Jiang and X. Y. Liu, *Nat. Chem.* 2019, **11**, 1158–1166.

<sup>8</sup> A. Frank, C. J. Seel, M. Groll and T. Gulder, *ChemBioChem*, 2016, **17**, 2028–2032.

**Yield:** 78% yield (63 mg)

**Nature:** Colourless liquid.

**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):** 7.39 – 7.34 (m, 4H), 7.26 – 7.19 (m, 3H), 7.13 (t, *J* = 7.3 Hz, 1H), 7.05 (d, *J* = 7.5 Hz, 2H), 6.14 (s, 2H), 4.70 (dd, *J* = 10.0, 6.0 Hz, 1H), 3.80 (s, 3H), 3.73 (s, 6H), 2.76 – 2.56 (m, 2H), 2.53 – 2.45 (m, 2H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 172.6, 159.9, 159.4, 151.0, 145.0, 129.4, 127.9, 127.8, 125.7, 125.4, 121.7, 112.5, 91.3, 55.7, 55.3, 38.8, 33.5, 27.1.

**HRMS (ESI): *m/z*** calculated for C<sub>25</sub>H<sub>27</sub>O<sub>5</sub> [M+H]<sup>+</sup>: 407.1858; found: 407.1849.

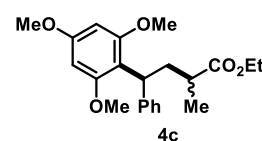
#### Ethyl 2-methyl-4-phenyl-4-(2,4,6-trimethoxyphenyl)butanoate (4c):

**Yield:** 73% yield (54 mg)

**Nature:** White solid.

**Mp:** 94-96 °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):** (for the mixture) 7.33 – 7.30 (m, 2H), 7.23 – 7.30 (m, 2H), 7.12 – 7.08 (m, 1H), 6.11 (s, 2H), 4.70 – 4.64 (m, 1H), 4.16 – 4.00 (m, 2H), 3.79 (s, 3H), 3.74 – 3.70 (m, 6H), 2.84 – 2.47 (m, 1H), 2.36 – 2.05 (m, 2H), 1.22 (q, *J* = 7.0 Hz, 3H), 1.17 – 1.14 (m, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** (for the mixture) 177.5, 177.2, 159.83, 159.77, 159.5, 159.4, 145.4, 145.3, 128.0, 127.8, 127.7, 125.4, 125.3, 113.0, 112.4, 91.29, 91.27, 60.09, 60.06, 55.75, 55.67, 55.3, 38.5, 38.4, 37.3, 37.1, 36.2, 35.9, 18.5, 16.7, 14.35, 14.32.

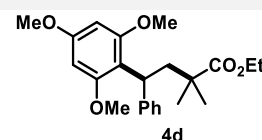
**HRMS (ESI): *m/z*** calculated for C<sub>22</sub>H<sub>28</sub>NaO<sub>5</sub> [M+Na]<sup>+</sup>: 395.1834; found: 395.1827.

#### Ethyl 2,2-dimethyl-4-phenyl-4-(2,4,6-trimethoxyphenyl)butanoate (4d):<sup>9</sup>

**Yield:** 68% yield (53 mg)

**Nature:** Colourless liquid.

**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):** 7.34 (d, *J* = 7.5 Hz, 2H), 7.21 – 7.17 (m, 2H), 7.09 – 7.05 (m, 1H), 6.07 (s, 2H), 4.70 (dd, *J* = 8.9, 4.7 Hz, 1H), 3.76 (s, 9H), 3.74 – 3.70 (m, 1H), 3.67 – 3.60 (m, 1H), 2.75 (dd, *J* = 13.9, 9.0 Hz, 1H), 2.33 (dd, *J* = 14.0, 4.7 Hz, 1H), 1.17 (s, 3H), 1.14 (s, 3H), 1.09 (t, *J* = 7.1 Hz, 3H).

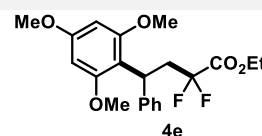
**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 178.0, 159.6, 146.2, 128.1, 127.6, 125.2, 114.1, 91.2, 60.1, 55.6, 55.3, 42.7, 42.4, 35.8, 26.7, 25.2, 14.1.

#### Ethyl 2,2-difluoro-4-phenyl-4-(2,4,6-trimethoxyphenyl)butanoate (4e):

**Yield:** 75% yield (59 mg)

**Nature:** Colourless liquid.

**R<sub>f</sub> value** = 0.3 [EtOAc/petroleum ether = 2:8 (v/v)]



<sup>9</sup> T. L. Buchanan, S. N. Gockel, A. M. Veatch, Y.-N. Wang and K. L. Hull, *Org. Lett.* 2021, **23**, 4538–4542.



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 7.32 (d, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.6 Hz, 2H), 7.12 (t, *J* = 7.3 Hz, 1H), 6.09 (s, 2H), 4.91 (dd, *J* = 8.7, 5.7 Hz, 1H), 3.95 – 3.82 (m, 2H), 3.77 (s, 9H), 3.30 – 3.16 (m, 1H), 3.02 – 2.88 (m, 1H), 1.19 (t, *J* = 7.1 Hz, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 164.3 (t, *J* = 32.9 Hz), 160.2, 159.1, 143.9, 127.9, 127.8, 125.9, 116.7 (t, *J* = 250.7 Hz), 111.8, 91.2, 62.6, 55.8, 55.4, 37.3 (t, *J* = 22.5 Hz), 33.00 (t, *J* = 5.2 Hz), 13.9.

**<sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ (ppm):** -102.5 (d, *J* = 257.2 Hz), -104.9 (d, *J* = 257.1 Hz).

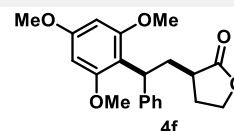
**HRMS (ESI): *m/z*** calculated for C<sub>21</sub>H<sub>25</sub>F<sub>2</sub>O<sub>5</sub> [M+H]<sup>+</sup>: 395.1670; found: 395.1652.

### 3-(2-Phenyl-2-(2,4,6-trimethoxyphenyl)ethyl)dihydrofuran-2(3H)-one (4f):

**Yield:** 64% yield (46 mg)

**Nature:** Viscous liquid.

**R<sub>f</sub> value** = 0.2 [EtOAc/petroleum ether = 3:7 (v/v)]



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** (for the mixture) 7.36 – 7.31 (m, 2H), 7.22 (t, *J* = 7.6 Hz, 2H), 7.12 (t, *J* = 7.3 Hz, 1H), 6.12 – 6.11 (m, 2H), 4.74 – 4.63 (m, 1H), 4.33 – 4.22 (m, 1H), 4.12 – 4.00 (m, 1H), 3.79 – 3.78 (m, 3H), 3.74 (s, 6H), 3.20 – 2.97 (m, 1H), 2.53 – 2.13 (m, 2H), 2.11 – 1.77 (m, 2H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** (for the mixture) 180.3, 180.1, 160.1, 159.9, 159.5, 159.2, 144.9, 144.1, 128.1, 127.9, 127.8, 125.61, 125.56, 113.4, 111.3, 91.3, 66.7, 66.6, 55.8, 55.3, 38.8, 38.5, 38.1, 37.1, 32.9, 32.7, 29.3, 29.2.

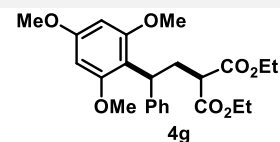
**HRMS (ESI): *m/z*** calculated for C<sub>21</sub>H<sub>24</sub>NaO<sub>5</sub> [M+Na]<sup>+</sup>: 379.1521; found: 379.1515.

### 3-(2-Phenyl-2-(2,4,6-trimethoxyphenyl)ethyl)dihydrofuran-2(3H)-one (4g):<sup>10</sup>

**Yield:** 71% yield (61 mg)

**Nature:** Colourless liquid.

**R<sub>f</sub> value** = 0.4 [EtOAc/petroleum ether = 2:8 (v/v)]



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 7.30 (d, *J* = 7.5 Hz, 2H), 7.21 (t, *J* = 7.6 Hz, 2H), 7.10 (t, *J* = 7.2 Hz, 1H), 6.10 (s, 2H), 4.64 (dd, *J* = 10.8, 5.8 Hz, 1H), 4.23 – 4.04 (m, 4H), 3.78 (s, 3H), 3.70 (s, 6H), 3.20 (dd, *J* = 9.3, 5.4 Hz, 1H), 2.93 – 2.86 (m, 1H), 2.76 – 2.69 (m, 1H), 1.23 (dt, *J* = 14.4, 7.1 Hz, 6H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 170.2, 169.7, 160.1, 159.5, 144.6, 127.9, 127.8, 125.5, 111.5, 91.2, 61.3, 61.2, 55.7, 55.3, 51.1, 37.2, 31.2, 14.22, 14.16.

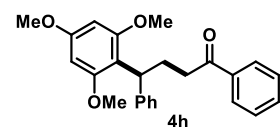
### 1,4-Diphenyl-4-(2,4,6-trimethoxyphenyl)butan-1-one (4h):<sup>10</sup>

**Yield:** 82% yield (64 mg)

**Nature:** White solid.

**Mp:** 72-74 °C.

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



<sup>10</sup> E. Richmond, V. D. Vuković and J. Moran, *Org. Lett.* 2018, **20**, 574–577.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 7.89 – 7.87 (m, 2H), 7.55 – 7.50 (m, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.36 (d, *J* = 7.4 Hz, 2H), 7.24 (t, *J* = 7.6 Hz, 2H), 7.13 (t, *J* = 7.3 Hz, 1H), 6.12 (s, 2H), 4.69 (dd, *J* = 10.0, 6.2 Hz, 1H), 3.80 (s, 3H), 3.68 (s, 6H), 3.01 – 2.93 (m, 1H), 2.89 – 2.81 (m, 1H), 2.74 – 2.60 (m, 2H).

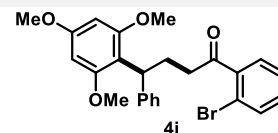
**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 201.0, 159.8, 159.3, 145.2, 137.2, 132.7, 128.4, 128.1, 127.9, 127.7, 125.3, 112.9, 91.1, 55.6, 55.3, 38.8, 37.6, 26.6.

**1-(2-Bromophenyl)-4-phenyl-4-(2,4,6-trimethoxyphenyl)butan-1-one (4i):**

**Yield:** 84% yield (79 mg)

**Nature:** Colourless liquid.

**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):** 7.56 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 7.6 Hz, 2H), 7.30 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.27 – 7.21 (m, 4H), 7.12 (t, *J* = 7.3 Hz, 1H), 6.12 (s, 2H), 4.66 (dd, *J* = 10.0, 6.3 Hz, 1H), 3.79 (s, 3H), 3.71 (s, 6H), 2.91 – 2.77 (m, 2H), 2.74 – 2.64 (m, 1H), 2.63 – 2.55 (m, 1H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 204.9, 159.8, 159.4, 145.1, 142.1, 133.6, 131.3, 128.4, 127.9, 127.7, 127.3, 125.4, 118.7, 112.5, 91.1, 55.7, 55.3, 41.9, 38.8, 26.3.

**HRMS (ESI): *m/z*** calculated for C<sub>25</sub>H<sub>25</sub>BrNaO<sub>4</sub> [M+Na]<sup>+</sup>: 491.0834; found: 491.0823.

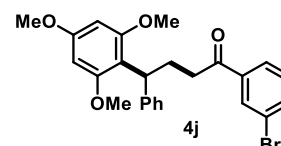
**1-(3-Bromophenyl)-4-phenyl-4-(2,4,6-trimethoxyphenyl)butan-1-one (4j):**

**Yield:** 78% yield (73 mg)

**Nature:** White solid.

**Mp:** 100-102 °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):** 7.94 (t, *J* = 1.5 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.63 (d, *J* = 8.5 Hz, 1H), 7.32 (d, *J* = 7.6 Hz, 2H), 7.28 (t, *J* = 7.7 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 2H), 7.11 (t, *J* = 7.3 Hz, 1H), 6.09 (s, 2H), 4.64 (dd, *J* = 10.2, 6.1 Hz, 1H), 3.79 (s, 3H), 3.67 (s, 6H), 2.92 – 2.76 (m, 2H), 2.73 – 2.64 (m, 1H), 2.60 – 2.52 (m, 1H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 199.7, 160.0, 159.4, 145.2, 139.1, 135.6, 131.3, 130.1, 127.9, 127.8, 126.7, 125.4, 122.8, 112.7, 91.2, 55.7, 55.4, 38.8, 37.6, 26.8.

**HRMS (ESI): *m/z*** calculated for C<sub>25</sub>H<sub>25</sub>BrNaO<sub>4</sub> [M+Na]<sup>+</sup>: 491.0834; found: 491.0830.

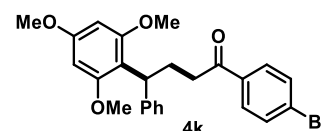
**1-(4-Bromophenyl)-4-phenyl-4-(2,4,6-trimethoxyphenyl)butan-1-one (4k):**

**Yield:** 73% yield (68 mg)

**Nature:** White solid.

**Mp:** 94-96 °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):** 7.70 (d, *J* = 8.5 Hz, 2H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.32 (d, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.6 Hz, 2H), 7.11 (t, *J* = 7.3 Hz, 1H), 6.08 (s, 2H), 4.64 (dd, *J* = 10.1, 6.2 Hz, 1H), 3.78 (s, 3H), 3.66 (s, 6H), 2.93 – 2.85 (m, 1H), 2.82 – 2.74 (m, 1H), 2.71 – 2.54 (m, 2H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 199.9, 159.9, 159.4, 145.1, 136.0, 131.7, 129.8, 127.9, 127.84, 127.77, 125.4, 112.8, 91.2, 55.7, 55.3, 38.8, 37.5, 26.7.

**HRMS (ESI): *m/z*** calculated for C<sub>25</sub>H<sub>25</sub>BrNaO<sub>4</sub> [M+Na+2]<sup>+</sup>: 493.0813; found: 493.0805.

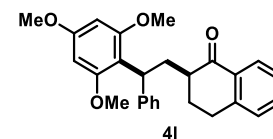
#### 2-(2-Phenyl-2-(2,4,6-trimethoxyphenyl)ethyl)-3,4-dihydronaphthalen-1(2H)-one (4l):

**Yield:** 76% yield (63 mg)

**Nature:** White solid.

**Mp:** 116-118 °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 the mixture) 8.04 – 8.01 (m, 1H), 7.45 – 7.39 (m, 3H), 7.30 – 7.28 (m, 1H), 7.25 – 7.18 (m, 3H), 7.15 – 7.10 (m, 1H), 6.13 – 6.12 (m, 2H), 4.92 – 4.80 (m, 1H), 3.79 – 3.75 (m, 9H), 3.34 – 3.12 (m, 1H), 3.04 – 2.83 (m, 2H), 2.51 – 2.38 (m, 1H), 2.31 – 2.17 (m, 1H), 2.09 – 1.84 (m, 2H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** (for the mixture) 201.0, 200.8, 159.8, 159.6, 159.5, 159.3, 145.6, 144.8, 144.1, 144.0, 133.0, 132.9, 132.8, 128.70, 128.66, 128.3, 128.0, 127.7, 127.4, 126.5, 125.3, 114.2, 112.30, 91.30, 91.28, 55.8, 55.3, 46.4, 46.3, 37.3, 36.2, 31.9, 30.9, 29.0, 28.6, 28.5, 27.8.

**HRMS (ESI):** *m/z* calculated for C<sub>27</sub>H<sub>28</sub>NaO<sub>4</sub> [M+Na]<sup>+</sup>: 439.1885; found: 439.1878.

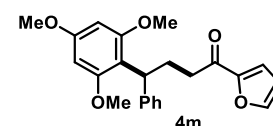
#### 1-(Furan-2-yl)-4-phenyl-4-(2,4,6-trimethoxyphenyl)butan-1-one (4m):

**Yield:** 72% yield (55 mg)

**Nature:** Light-yellow solid.

**Mp:** 79-81 °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):** 7.52 (d, *J* = 1.2 Hz, 1H), 7.32 (d, *J* = 7.5 Hz, 2H), 7.21 (t, *J* = 7.6 Hz, 2H), 7.10 (t, *J* = 7.3 Hz, 1H), 7.02 (d, *J* = 3.4 Hz, 1H), 6.46 (dd, *J* = 3.5, 1.6 Hz, 1H), 6.09 (s, 2H), 4.63 (dd, *J* = 9.5, 6.3 Hz, 1H), 3.78 (s, 3H), 3.68 (s, 6H), 2.83 – 2.75 (m, 1H), 2.71 – 2.62 (m, 2H), 2.61 – 2.54 (m, 1H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 190.1, 159.9, 159.4, 153.0, 146.1, 145.2, 128.0, 127.7, 125.4, 116.8, 112.9, 112.0, 91.3, 55.7, 55.3, 39.0, 37.6, 26.7.

**HRMS (ESI):** *m/z* calculated for C<sub>23</sub>H<sub>24</sub>NaO<sub>5</sub> [M+Na]<sup>+</sup>: 403.1521; found: 403.1524.

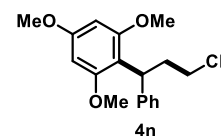
#### 4-Phenyl-4-(2,4,6-trimethoxyphenyl)butanenitrile (4n):

**Yield:** 67% yield (42 mg)

**Nature:** White Solid.

**Mp:** 88-90 °C.

**R<sub>f</sub> value** = 0.3 [EtOAc/petroleum ether = 2:8 (v/v)]



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 7.30 (d, *J* = 7.4 Hz, 2H), 7.24 (t, *J* = 7.5 Hz, 2H), 7.14 (t, *J* = 7.2 Hz, 1H), 6.13 (s, 2H), 4.69 (dd, *J* = 10.1, 6.3 Hz, 1H), 3.80 (s, 3H), 3.75 (s, 6H), 2.70 – 2.61 (m, 1H), 2.53 – 2.44 (m, 1H), 2.26 – 2.22 (m, 2H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 160.2, 159.4, 144.0, 128.0, 127.8, 125.8, 120.4, 111.0, 91.2, 55.7, 55.4, 38.8, 28.2, 16.1.

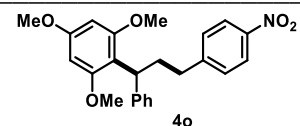
**HRMS (ESI):** *m/z* calculated for C<sub>19</sub>H<sub>22</sub>NO<sub>3</sub> [M+H]<sup>+</sup>: 312.1600; found: 312.1614.

#### 1,3,5-Trimethoxy-2-(3-(4-nitrophenyl)-1-phenylpropyl)benzene (4o):

**Yield:** 60% yield (49 mg)

**Nature:** Colourless liquid.

**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):** 8.10 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 7.6 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 7.22 (t, *J* = 7.6 Hz, 2H), 7.12 (t, *J* = 7.3 Hz, 1H), 6.13 (s, 2H), 4.59 (t, *J* = 7.6 Hz, 1H), 3.80 (s, 3H), 3.72 (s, 6H), 2.70 – 2.62 (m, 3H), 2.46 – 2.39 (m, 1H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 159.9, 159.4, 151.4, 146.2, 145.2, 129.4, 127.94, 127.88, 125.5, 123.5, 112.7, 91.2, 55.7, 55.4, 39.1, 34.8, 33.6.

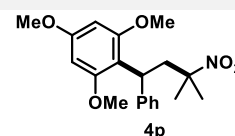
**HRMS (ESI):** *m/z* calculated for C<sub>24</sub>H<sub>26</sub>NO<sub>5</sub> [M+H]<sup>+</sup>: 408.1811; found: 408.1805.

#### 1,3,5-Trimethoxy-2-(3-methyl-3-nitro-1-phenylbutyl)benzene (4p):

**Yield:** 74% yield (53 mg)

**Nature:** Colourless liquid.

**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):** 7.32 (d, *J* = 7.6 Hz, 2H), 7.21 (t, *J* = 7.6 Hz, 2H), 7.11 (t, *J* = 7.3 Hz, 1H), 6.09 (s, 2H), 4.70 (dd, *J* = 9.5, 4.4 Hz, 1H), 3.78 (s, 9H), 3.19 (dd, *J* = 14.4, 9.6 Hz, 1H), 2.69 (dd, *J* = 14.4, 4.4 Hz, 1H), 1.51 (s, 3H), 1.48 (s, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 160.1, 145.0, 127.9, 127.8, 125.7, 112.5, 91.2, 89.2, 55.7, 55.3, 42.6, 35.2, 26.4, 26.0.

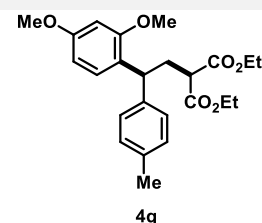
**HRMS (ESI):** *m/z* calculated for C<sub>20</sub>H<sub>26</sub>NO<sub>5</sub> [M+H]<sup>+</sup>: 360.1811; found: 360.1804.

#### Diethyl 2-(2-(2,4-dimethoxyphenyl)-2-(*p*-tolyl)ethyl)malonate (4q):

**Yield:** 71% yield (59 mg)

**Nature:** Colourless liquid.

**R<sub>f</sub> value** = 0.3 [EtOAc/petroleum ether = 2:8 (v/v)]



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 7.16 – 7.06 (m, 5H), 6.45 (dd, *J* = 8.4, 2.3 Hz, 1H), 6.41 (d, *J* = 2.3 Hz, 1H), 4.32 (t, *J* = 8.1 Hz, 1H), 4.20 – 4.11 (m, 4H), 3.77 (s, 3H), 3.74 (s, 3H), 3.26 (t, *J* = 7.4 Hz, 1H), 2.65 – 2.53 (m, 2H), 2.29 (s, 3H), 1.25 (dd, *J* = 13.0, 7.0 Hz, 6H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 169.7, 169.6, 159.4, 158.1, 140.9, 135.6, 129.1, 128.3, 128.0, 124.6, 104.3, 98.8, 61.36, 61.32, 55.45, 55.37, 50.6, 40.2, 34.0, 21.1, 14.1.

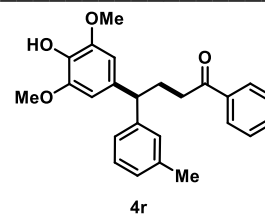
**HRMS (ESI):** *m/z* calculated for C<sub>24</sub>H<sub>30</sub>NaO<sub>6</sub> [M+Na]<sup>+</sup>: 437.1940; found: 437.1931.

#### Diethyl 2-(2-(2,4-dimethoxyphenyl)-2-(*p*-tolyl)ethyl)malonate (4r):

**Yield:** 46% yield (36 mg)

**Nature:** Colourless liquid.

**R<sub>f</sub> value** = 0.2 [EtOAc/petroleum ether = 2:8 (v/v)]



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 7.87 – 7.85 (m, 2H), 7.55 – 7.51 (m, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 7.7 Hz, 1H), 7.07 (d, *J* = 7.7 Hz, 2H), 7.01 (d, *J* = 7.3 Hz, 1H), 6.48 (s, 2H), 5.39 (s, 1H), 3.89 (t, *J* = 8.0 Hz, 1H), 3.84 (s, 6H), 2.93 (t, *J* = 7.4 Hz, 2H), 2.49 – 2.42 (m, 2H), 2.31 (s, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 200.3, 147.1, 144.6, 138.2, 137.1, 135.7, 133.4, 133.1, 128.7, 128.5, 128.1, 127.3, 124.7, 104.8, 56.4, 50.6, 37.0, 30.2, 21.6.

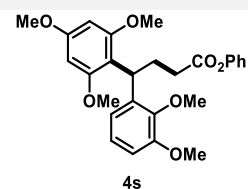
**HRMS (ESI): *m/z*** calculated for C<sub>25</sub>H<sub>26</sub>NaO<sub>4</sub> [M+Na]<sup>+</sup>: 413.1729; found: 413.1724.

#### Phenyl 4-(2,3-dimethoxyphenyl)-4-(2,4,6-trimethoxyphenyl)butanoate (4s):

**Yield:** 80% yield (75 mg)

**Nature:** Colourless liquid.

**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):** 7.38 – 7.33 (m, 2H), 7.23 – 7.18 (m, 1H), 7.07 – 7.02 (m, 2H), 6.96 (d, *J* = 1.9 Hz, 1H), 6.89 (dd, *J* = 8.3, 1.8 Hz, 1H), 6.75 (d, *J* = 8.3 Hz, 1H), 6.14 (s, 2H), 4.63 (dd, *J* = 9.9, 6.3 Hz, 1H), 3.84 (s, 3H), 3.83 (s, 3H), 3.80 (s, 3H), 3.75 (s, 6H), 2.71 – 2.63 (m, 1H), 2.59 – 2.53 (m, 1H), 2.52 – 2.46 (m, 2H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 172.6, 159.9, 159.4, 151.0, 148.4, 147.0, 137.8, 129.4, 125.7, 121.7, 120.0, 112.5, 111.7, 110.8, 91.4, 56.0, 55.9, 55.8, 55.4, 38.7, 33.5, 27.7.

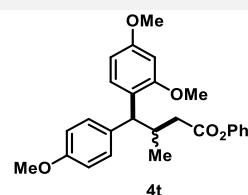
**HRMS (ESI): *m/z*** calculated for C<sub>27</sub>H<sub>30</sub>NaO<sub>7</sub> [M+Na]<sup>+</sup>: 489.1889; found: 489.1885.

#### Phenyl 4-(2,4-dimethoxyphenyl)-4-(4-methoxyphenyl)-3-methylbutanoate (4t):

**Yield:** 73% yield (61 mg)

**Nature:** Colourless liquid.

**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 the mixture) 7.36 (t, *J* = 7.8 Hz, 2H), 7.29 – 7.25 (m, 3H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.03 (d, *J* = 7.8 Hz, 2H), 6.81 (dd, *J* = 8.7, 2.2 Hz, 2H), 6.48 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.42 (t, *J* = 2.2 Hz, 1H), 4.09 (t, *J* = 11.1 Hz, 1H), 3.79 (d, *J* = 4.5 Hz, 3H), 3.77 (d, *J* = 4.1 Hz, 6H), 3.02 – 2.89 (m, 1H), 2.66 (td, *J* = 15.6, 3.4 Hz, 1H), 2.30 – 2.22 (m, 1H), 1.03 (t, *J* = 6.0 Hz, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** (for the mixture) 172.2, 172.1, 159.2, 159.0, 158.15, 158.09, 157.9, 157.8, 150.9, 136.24, 136.21, 129.5, 129.4, 129.3, 128.2, 128.1, 125.8, 125.0, 121.7, 114.0, 113.8, 104.8, 104.6, 98.92, 98.87, 55.6, 55.4, 55.3, 48.5, 48.4, 40.8, 40.4, 34.1, 34.0, 19.2, 18.6.

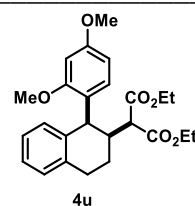
**HRMS (ESI): *m/z*** calculated for C<sub>26</sub>H<sub>28</sub>NaO<sub>5</sub> [M+Na]<sup>+</sup>: 443.1834; found: 443.1823.

#### Diethyl 2-(1-(2,4-dimethoxyphenyl)-1,2,3,4-tetrahydronaphthalen-2-yl)malonate (4u)

**Yield:** 78% yield (66 mg)

**Nature:** Colourless oil.

**R<sub>f</sub> value** = 0.3 [EtOAc/petroleum ether = 2:8 (v/v)]



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 7.12 – 7.06 (m, 2H), 7.04 – 6.96 (m, 1H), 6.75 (d, *J* = 8.3 Hz, 2H), 6.47 (d, *J* = 2.3 Hz, 1H), 6.39 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.38 (d, *J* = 8.1 Hz, 1H), 4.25 – 4.09 (m, 4H), 3.79 (s, 3H), 3.74 (s, 3H), 3.41 (d, *J* = 6.5 Hz, 1H), 2.99 – 2.84 (m, 2H), 2.83 – 2.76 (m, 1H), 2.11 – 2.03 (m, 1H), 1.90 – 1.81 (m, 1H), 1.26 (dt, *J* = 15.7, 7.1 Hz, 6H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 169.5, 168.8, 159.6, 158.5, 139.1, 136.7, 131.3, 130.0, 128.5, 125.9, 125.7, 125.6, 104.3, 98.7, 61.2, 61.0, 55.43, 55.36, 53.8, 42.0, 40.2, 28.3, 23.9, 14.23, 14.16.

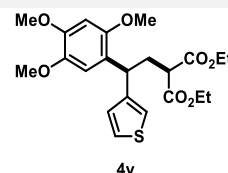
**HRMS (ESI): *m/z*** calculated for C<sub>25</sub>H<sub>30</sub>NaO<sub>6</sub> [M+Na]<sup>+</sup>: 449.1940; found: 449.1930.

**Diethyl 2-(2-(thiophen-3-yl)-2-(2,4,5-trimethoxyphenyl)ethyl)malonate (4v):**

**Yield:** 74% yield (65 mg)

**Nature:** Colourless liquid.

**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):** 7.21 (dd, *J* = 4.9, 3.0 Hz, 1H), 7.01 (d, *J* = 2.6 Hz, 1H), 6.92 (dd, *J* = 4.8, 0.6 Hz, 1H), 6.65 (s, 1H), 6.50 (s, 1H), 4.47 (dd, *J* = 8.9, 7.1 Hz, 1H), 4.22 – 4.10 (m, 4H), 3.86 (s, 3H), 3.76 (s, 3H), 3.75 (s, 3H), 3.24 (dd, *J* = 8.1, 6.3 Hz, 1H), 2.71 – 2.64 (m, 1H), 2.53 – 2.45 (m, 1H), 1.24 (dt, *J* = 9.4, 7.1 Hz, 6H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 169.7, 169.5, 151.5, 148.4, 144.9, 143.3, 128.0, 125.4, 122.8, 120.4, 112.4, 97.9, 61.5, 61.4, 56.8, 56.6, 56.2, 50.4, 36.7, 34.2, 14.18, 14.15.

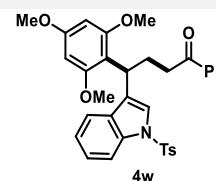
**HRMS (ESI): *m/z*** calculated for C<sub>22</sub>H<sub>28</sub>NaO<sub>7</sub>S [M+Na]<sup>+</sup>: 459.1453; found: 459.1475.

**1-Phenyl-4-(1-(tosyl-1*H*-indol-3-yl)-4-(2,4,6-trimethoxyphenyl)butan-1-one (4w):**

**Yield:** 53% yield (62 mg)

**Nature:** Colourless liquid.

**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):** 7.92 (d, *J* = 8.3 Hz, 1H), 7.87 – 7.83 (m, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.54 – 7.49 (m, 1H), 7.48 (d, *J* = 1.0 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.34 (d, *J* = 7.8 Hz, 1H), 7.21 – 7.17 (m, 1H), 7.15 (d, *J* = 8.2 Hz, 2H), 7.10 – 7.05 (m, 1H), 6.05 (s, 2H), 4.77 – 4.72 (m, 1H), 3.76 (s, 3H), 3.64 (s, 6H), 3.00 – 2.92 (m, 1H), 2.86 – 2.79 (m, 1H), 2.71 – 2.54 (m, 2H), 2.30 (s, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 200.7, 160.1, 159.48, 159.46, 144.6, 137.3, 135.8, 135.2, 132.9, 131.6, 129.8, 128.5, 128.2, 126.8, 126.4, 124.1, 123.3, 122.9, 120.2, 113.6, 110.5, 91.1, 55.5, 55.3, 37.0, 30.5, 26.4, 21.6.

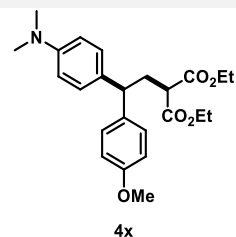
**HRMS (ESI): *m/z*** calculated for C<sub>34</sub>H<sub>33</sub>NNaO<sub>6</sub>S [M+Na]<sup>+</sup>: 606.1926; found: 606.1921.

**Diethyl 2-(2-(4-(dimethylamino)phenyl)-2-(4-methoxyphenyl)ethyl)malonate (4x):**

**Yield:** 65% yield (54 mg)

**Nature:** Colourless oil.

**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):** 7.15 (d, *J* = 8.6 Hz, 2H), 7.09 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 6.68 (d, *J* = 8.7 Hz, 2H), 4.17 (q, *J* = 7.1 Hz, 4H), 3.83 (t, *J* = 8.1 Hz, 1H), 3.77 (s, 3H), 3.26 (t, *J* = 7.4 Hz, 1H), 2.91 (s, 6H), 2.59 (t, *J* = 7.8 Hz, 2H), 1.25 (td, *J* = 7.0, 0.8 Hz, 6H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 169.6, 158.1, 149.4, 136.5, 131.8, 128.9, 128.5, 114.0, 112.9, 61.4, 55.3, 50.5, 46.9, 40.8, 35.0, 14.2.

**HRMS (ESI): *m/z*** calculated for C<sub>24</sub>H<sub>32</sub>NO<sub>5</sub> [M+H]<sup>+</sup>: 414.2280; found: 414.2281.

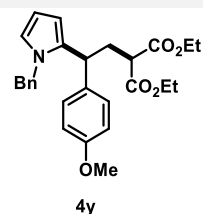
**Diethyl 2-(2-(1-benzyl-1*H*-pyrrol-2-yl)-2-(4-methoxyphenyl)ethyl)malonate (4y):**

**Yield:** 77% yield (69 mg)

**Nature:** Grey solid.

**Mp:** 88-90 °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):** 7.27 – 7.20 (m, 3H), 6.99 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 6.6 Hz, 2H), 6.79 (d, *J* = 8.7 Hz, 2H), 6.63 – 6.61 (m, 1H), 6.24 (dd, *J* = 3.4, 1.4 Hz, 1H), 6.21 – 6.19 (m, 1H), 4.84 (d, *J* = 16.3 Hz, 1H), 4.73 (d, *J* = 16.3 Hz, 1H), 4.15 – 3.96 (m, 4H), 3.77 (s, 3H), 3.70 (t, *J* = 7.6 Hz, 1H), 3.36 (t, *J* = 7.3 Hz, 1H), 2.58 – 2.51 (m, 1H), 2.44 – 2.37 (m, 1H), 1.19 (dd, *J* = 13.7, 6.9 Hz, 6H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 169.5, 169.3, 158.4, 138.4, 134.8, 134.1, 128.9, 128.7, 127.2, 126.3, 122.1, 114.1, 107.1, 106.5, 61.42, 61.36, 55.3, 50.3, 50.2, 40.1, 35.5, 14.1, 14.0.

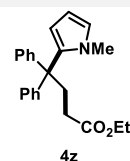
**HRMS (ESI): *m/z*** calculated for C<sub>27</sub>H<sub>31</sub>NNaO<sub>5</sub> [M+Na]<sup>+</sup>: 472.2100 ; found: 472.2105.

**Ethyl 4-(1-methyl-1*H*-pyrrol-2-yl)-4,4-diphenylbutanoate (4z):**

**Yield:** 74% yield (51 mg)

**Nature:** Colourless liquid.

**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):** 7.32 – 7.26 (m, 8H), 7.32 – 7.19 (m, 2H), 6.54 (s, 1H), 6.18 – 6.16 (m, 1H), 6.13 – 6.11 (m, 1H), 4.06 (q, *J* = 7.1 Hz, 2H), 2.95 (s, 3H), 2.85 – 2.81 (m, 2H), 2.15 – 2.11 (m, 2H), 1.20 (t, *J* = 7.1 Hz, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 173.8, 144.3, 136.4, 128.9, 128.2, 126.4, 123.8, 109.4, 106.2, 60.5, 52.4, 38.0, 36.5, 31.8, 14.3.

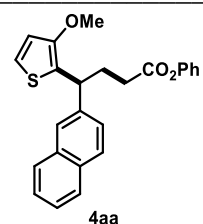
**HRMS (ESI): *m/z*** calculated for C<sub>23</sub>H<sub>26</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 348.1964; found: 348.1952.

**Phenyl 4-(3-methoxythiophen-2-yl)-4-(naphthalen-2-yl)butanoate (4aa):**

**Yield:** 69% yield (55 mg)

**Nature:** Colourless liquid.

**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):** 7.83 – 7.79 (m, 4H), 7.51 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.49 – 7.41 (m, 2H), 7.38 – 7.35 (m, 2H), 7.24 – 7.20 (m, 1H), 7.08 (d, *J* = 5.5 Hz, 1H), 7.06 – 7.03 (m, 2H), 6.83 (d, *J* = 5.5 Hz, 1H), 4.59 (t, *J* = 7.6 Hz, 1H), 3.82 (s, 3H), 2.64 – 2.54 (m, 4H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 172.0, 153.9, 150.9, 141.3, 133.7, 132.5, 129.5, 128.4, 128.0, 127.7, 126.5, 126.2, 126.0, 125.9, 125.7, 124.2, 121.71, 121.69, 116.8, 59.0, 42.0, 33.0, 31.5.

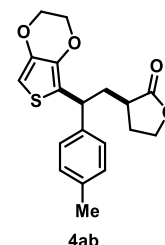
**HRMS (ESI):** *m/z* calculated for C<sub>25</sub>H<sub>22</sub>NaO<sub>3</sub>S [M+Na]<sup>+</sup>: 425.1187; found: 425.1173.

### 3-(2-(2,3-Dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-2-(*p*-tolylethyl)dihydrofuran-2(3*H*)-one (4ab):

**Yield:** 65% yield (45 mg)

**Nature:** Colourless liquid.

**R<sub>f</sub> value** = 0.3 [EtOAc/petroleum ether = 3:7 (v/v)]



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** (for the mixture) 7.25 (d, *J* = 8.2 Hz, 2H), 7.14 – 7.11 (m, 2H), 6.16 – 6.14 (m, 1H), 4.34 – 4.22 (m, 2H), 4.19 – 4.14 (m, 4H), 4.11 – 4.05 (m, 1H), 2.76 – 2.38 (m, 2H), 2.32 (m, 3H), 2.14 – 1.89 (m, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** (for the mixture) 179.42, 179.38, 141.8, 141.7, 140.3, 138.9, 138.0, 137.6, 136.7, 136.5, 129.6, 129.4, 127.7, 127.6, 121.0, 120.0, 64.8, 64.75, 64.73, 41.1, 40.8, 37.9, 37.8, 36.9, 36.5, 29.3, 28.9.

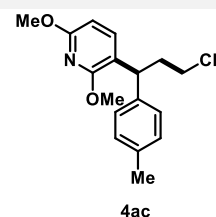
**HRMS (ESI):** *m/z* calculated for C<sub>19</sub>H<sub>20</sub>NaO<sub>4</sub>S [M+Na]<sup>+</sup>: 367.0980; found: 367.0989.

### 4-(2,6-Dimethoxypyridin-3-yl)-4-(*p*-tolyl)butanenitrile (4ac):

**Yield:** 57% yield (34 mg)

**Nature:** Colourless liquid.

**R<sub>f</sub> value** = 0.3 [EtOAc/petroleum ether = 2:8 (v/v)]



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 7.31 (d, *J* = 8.1 Hz, 1H), 7.15 – 7.10 (m, 4H), 6.25 (d, *J* = 8.1 Hz, 1H), 4.24 (dd, *J* = 9.3, 6.0 Hz, 1H), 3.94 (s, 3H), 3.89 (s, 3H), 2.36 – 2.33 (m, 1H), 2.32 (s, 3H), 2.30 – 2.24 (m, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 161.7, 160.0, 139.1, 138.9, 136.4, 129.4, 127.8, 119.7, 116.5, 100.7, 53.6, 53.5, 42.1, 30.3, 21.1, 15.9.

**HRMS (ESI):** *m/z* calculated for C<sub>18</sub>H<sub>21</sub>N<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 297.1603; found: 297.1610.

### Ethyl 4-(1*H*-indol-3-yl)-4-(4-methoxyphenyl)-2-methylbutanoate (4ad):

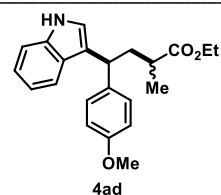


**Yield:** 74% yield (52 mg)

**Nature:** White crystalline solid.

**Mp:** 150-152 °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 the mixture) 8.09 (d, *J* = 7.4 Hz, 1H), 7.49 (dd, *J* = 23.0, 7.9 Hz, 1H), 7.32 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.26 – 7.21 (m, 2H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.05 (td, *J* = 7.4, 5.1 Hz, 1H), 6.98 (dd, *J* = 7.6, 1.9 Hz, 1H), 6.84 (dd, *J* = 8.4, 5.8 Hz, 2H), 4.26 – 4.20 (m, 1H), 4.18 – 4.14 (m, 1H), 4.13 – 4.04 (m, 1H), 3.78 (d, *J* = 4.4 Hz, 3H), 2.69 – 2.42 (m, 2H), 2.26 – 1.96 (m, 1H), 1.30 – 1.19 (m, 6H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** (for the mixture) 177.0, 158.05, 158.02, 136.74, 136.71, 136.67, 136.5, 129.0, 128.9, 127.0, 126.9, 122.1, 121.22, 121.17, 120.01, 119.98, 119.60, 119.55, 119.36, 119.31, 113.9, 111.24, 111.16, 60.39, 60.36, 55.3, 40.5, 40.1, 39.8, 39.7, 37.9, 37.8, 17.9, 17.3, 14.4, 14.3.

**HRMS (ESI):** *m/z* calculated for C<sub>22</sub>H<sub>25</sub>NNaO<sub>3</sub> [M+Na]<sup>+</sup>: 374.1732; found: 374.1708.

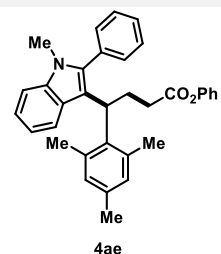
#### Phenyl 4-mesityl-4-(1-methyl-2-phenyl-1H-indol-3-yl)butanoate (4ae):

**Yield:** 78% yield (76 mg)

**Nature:** White crystalline solid.

**Mp:** 150-152 °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):** 7.67 (d, *J* = 8.2 Hz, 1H), 7.41 – 7.29 (m, 6H), 7.26 – 7.10 (m, 5H), 6.99 – 6.96 (m, 2H), 6.70 (s, 2H), 4.66 (t, *J* = 8.2 Hz, 1H), 3.41 (s, 3H), 2.92 – 2.83 (m, 1H), 2.70 – 2.62 (m, 1H), 2.54 – 2.38 (m, 2H), 2.25 (s, 3H), 2.01 (s, 6H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 172.3, 150.8, 139.2, 139.0, 137.0, 136.6, 135.2, 133.1, 130.0, 129.4, 128.4, 128.1, 127.7, 125.7, 121.7, 121.05, 121.01, 119.5, 113.4, 109.5, 38.7, 33.1, 30.5, 28.0, 21.4, 20.8.

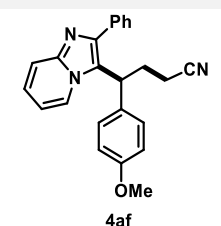
**HRMS (ESI):** *m/z* calculated for C<sub>34</sub>H<sub>33</sub>NNaO<sub>2</sub> [M+Na]<sup>+</sup>: 510.2409; found: 510.2403.

#### 4-(4-Methoxyphenyl)-4-(2-phenylimidazo[1,2-*a*]pyridin-3-yl)butanenitrile (4af):

**Yield:** 62% yield (46 mg)

**Nature:** Colourless liquid.

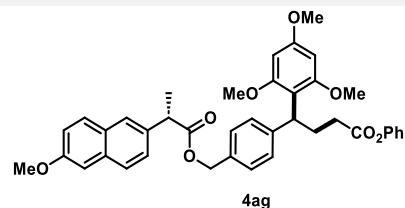
**R<sub>f</sub> value** = 0.2 [EtOAc/petroleum ether = 3:7 (v/v)]



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 7.80 (d, *J* = 9.0 Hz, 1H), 7.71 (d, *J* = 7.0 Hz, 1H), 7.68 (d, *J* = 6.8 Hz, 2H), 7.48 – 7.40 (m, 3H), 7.29 – 7.25 (m, 1H), 7.21 (d, *J* = 8.5 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 6.76 (t, *J* = 6.8 Hz, 1H), 4.78 (dd, *J* = 10.1, 6.2 Hz, 1H), 3.81 (s, 3H), 2.54 – 2.39 (m, 2H), 2.12 – 1.96 (m, 2H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 159.0, 145.2, 145.2, 134.3, 130.8, 129.3, 128.8, 128.5, 128.2, 125.0, 124.2, 118.9, 118.0, 114.8, 112.8, 55.4, 39.0, 27.4, 15.7.

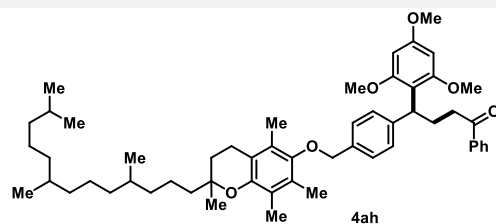
**HRMS (ESI):** *m/z* calculated for C<sub>24</sub>H<sub>22</sub>N<sub>3</sub>O [M+H]<sup>+</sup>: 368.1763; found: 368.1758.

**Compound 4ag:****Yield:** 70% yield (91 mg)**Nature:** Colourless liquid.**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 – 7.66 (m, 3H), 7.44 – 7.41 (m, 1H), 7.38 (t, *J* = 7.9 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.19 – 7.12 (m, 4H), 7.08 (d, *J* = 7.6 Hz, 2H), 6.16 (s, 2H), 5.14 (d, *J* = 12.3 Hz, 1H), 5.06 (d, *J* = 12.3 Hz, 1H), 4.71 (dd, *J* = 9.9, 6.0 Hz, 1H), 3.94 – 3.89 (m, 4H), 3.81 (s, 3H), 3.73 (s, 6H), 2.77 – 2.57 (m, 2H), 2.56 – 2.47 (m, 2H), 1.61 (d, *J* = 7.2 Hz, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 174.6, 172.5, 160.0, 159.3, 157.7, 150.9, 145.0, 135.7, 133.7, 132.9, 129.4, 129.0, 128.0, 127.7, 127.2, 126.4, 126.0, 125.7, 121.7, 119.0, 112.1, 105.6, 91.3, 66.6, 55.7, 55.35, 55.30, 45.5, 38.6, 33.4, 27.1, 27.0, 18.7.

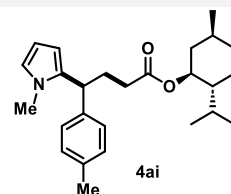
**HRMS (ESI): *m/z*** calculated for C<sub>40</sub>H<sub>44</sub>NO<sub>8</sub> [M+NH<sub>4</sub>]<sup>+</sup>: 666.3067; found: 666.3060.

**Compound 4ah:****Yield:** 73% yield (122 mg)**Nature:** Colourless liquid.**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):** 7.88 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.55 – 7.50 (m, 1H), 7.44 – 7.34 (m, 6H), 6.12 (s, 2H), 4.70 (dd, *J* = 9.7, 6.5 Hz, 1H), 4.64 (s, 2H), 3.80 (s, 3H), 3.71 (s, 6H), 3.01 – 2.93 (m, 1H), 2.89 – 2.81 (m, 1H), 2.75 – 2.62 (m, 1H), 2.59 (t, *J* = 6.8 Hz, 1H), 2.22 (s, 3H), 2.17 (s, 3H), 2.11 (s, 3H), 1.86 – 1.75 (m, 2H), 1.59 – 1.50 (m, 3H), 1.46 – 1.37 (m, 4H), 1.31 – 1.23 (m, 10H), 1.18 – 1.13 (m, 3H), 1.12 – 1.07 (m, 3H), 0.90 – 0.86 (m, 13H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 201.0, 159.9, 159.4, 148.4, 148.0, 145.0, 137.4, 134.9, 132.8, 128.5, 128.2, 128.1, 127.5, 126.1, 122.9, 117.6, 112.9, 91.2, 77.5, 76.8, 74.95, 74.91, 55.7, 55.4, 40.2, 39.5, 38.8, 37.7, 37.6, 37.5, 37.4, 32.9, 32.8, 31.5, 31.4, 28.1, 26.8, 24.9, 24.6, 24.0, 22.9, 22.8, 21.2, 20.8, 19.9, 19.8, 19.7, 13.0, 12.1, 11.9.

**HRMS (ESI): *m/z*** calculated for C<sub>55</sub>H<sub>76</sub>NaO<sub>6</sub> [M+Na]<sup>+</sup>: 855.5540; found: 855.5543.

**Compound 4ai:****Yield:** 68% yield (54 mg)**Nature:** Colourless liquid.**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 the mixture) 7.08 (d, *J* = 7.5 Hz, 2H), 7.00 (d, *J* = 7.9 Hz, 2H), 6.52 (t, *J* = 1.8 Hz, 1H), 6.14 – 6.10 (m, 2H), 4.73 – 4.65 (m, 1H), 3.88 (t, *J* = 7.2 Hz, 1H), 3.29 (d, *J* = 3.6 Hz, 3H), 2.43 – 2.32

(m, 2H), 2.30 (s, 3H), 2.19 – 2.12 (m, 1H), 2.02 – 1.93 (m, 1H), 1.89 – 1.79 (m, 1H), 1.70 – 1.44 (m, 4H), 1.39 – 1.32 (m, 1H), 1.11 – 0.94 (m, 2H), 0.92 – 0.85 (m, 7H), 0.76 (dd,  $J = 13.2, 6.9$  Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): (for the mixture) 173.22, 173.18, 140.3, 140.2, 136.0, 135.0, 134.9, 129.4, 127.95, 127.92, 121.8, 106.4, 105.73, 105.67, 74.1, 47.1, 42.35, 42.28, 41.1, 34.4, 33.9, 33.0, 32.8, 31.6, 31.5, 31.4, 26.3, 23.5, 22.1, 21.1, 20.9, 16.4.

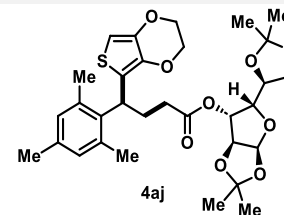
HRMS (ESI):  $m/z$  calculated for  $\text{C}_{26}\text{H}_{38}\text{NO}_2$   $[\text{M}+\text{H}]^+$ : 396.2903; found: 396.2902.

#### Compound 4aj:

**Yield:** 65% yield (76 mg)

**Nature:** yellowish liquid.

**R<sub>f</sub> value** = 0.3 [EtOAc/petroleum ether = 2:8 (v/v)]



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): (for the mixture) 6.80 (s, 2H), 6.22 – 5.84 (m, 2H), 5.25 – 4.48 (m, 4H), 4.24 – 4.18 (m, 2H), 4.18 – 4.15 (m, 2H), 4.08 – 3.95 (m, 3H), 3.67 (d,  $J = 1.0$  Hz, 1H), 2.57 – 2.43 (m, 2H), 2.38 (s, 6H), 2.23 (s, 3H), 2.02 – 1.92 (m, 1H), 1.50 (s, 3H), 1.39 (s, 3H), 1.30 – 1.26 (m, 6H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): (for the mixture) 172.6, 172.5, 169.0, 141.3, 139.4, 136.74, 136.71, 136.36, 136.33, 135.9, 130.2, 112.4, 112.3, 109.48, 109.45, 109.3, 107.6, 105.1, 105.1, 98.0, 83.4, 83.3, 83.2, 79.8, 77.4, 76.8, 76.3, 76.2, 72.6, 72.54, 72.47, 70.7, 70.1, 67.3, 67.1, 31.7, 31.5, 31.3, 30.64, 30.58, 26.95, 26.83, 26.79, 26.3, 25.3, 25.2, 20.8, 20.7, 20.6.

HRMS (ESI):  $m/z$  calculated for  $\text{C}_{31}\text{H}_{40}\text{KO}_9\text{S}$   $[\text{M}+\text{K}]^+$ : 627.2030; found: 627.2018.

## 5. Procedures for synthesis of lignans Pachypostaudin-A & B:

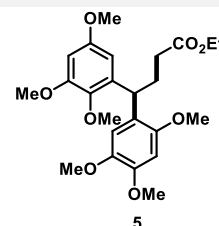
**Step-1: Synthesis of the ester derivative 5:** An oven-dried 100 mL Schlenk tube equipped with a magnetic stir bar was successively charged with the photocatalyst PTH (22 mg, 2 mol%), 1,2,5-trimethoxy-3-vinylbenzene (1.55 gm, 8 mmol), ethyl bromoacetate (668 mg, 443  $\mu\text{L}$ , 4.0 mmol), 1,2,4-trimethoxybenzene (673 mg, 597  $\mu\text{L}$ , 4.0 mmol), and  $\text{Zn}(\text{OAc})_2$  (1.76 gm, 8.0 mmol) in dry DCE (40 mL). Then the tube was evacuated and backfilled with argon and placed under purple LEDs at an approximate distance of 5 cm and irradiated for 6 h. A high-speed fan was also applied to maintain the temperature. After completion of the reaction (checked by TLC), 100 mL of distilled water was added to the reaction mixture and the organic part was extracted with DCM (2 x 30 mL). Combined organic layers were washed with brine (30 mL), dried over  $\text{Na}_2\text{SO}_4$  and concentrated. Finally, the crude residue was purified by flash column chromatography to get the corresponding alkylated product, the ester derivative 5.

#### Ethyl 4-(2,3,5-trimethoxyphenyl)-4-(2,4,5-trimethoxyphenyl)butanoate (5):

**Yield:** 72% yield (1.3 g)

**Nature:** Colourless liquid.

**R<sub>f</sub> value** = 0.2 [EtOAc/petroleum ether = 2:8 (v/v)]



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 6.81 (s, 1H), 6.48 (s, 1H), 6.37 (d, *J* = 2.9 Hz, 1H), 6.35 (d, *J* = 2.9 Hz, 1H), 4.69 (t, *J* = 7.7 Hz, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 3.85 (s, 3H), 3.81 (s, 3H), 3.80 (s, 3H), 3.75 (s, 3H), 3.73 (s, 3H), 3.62 (s, 3H), 2.32 – 2.28 (m, 2H), 2.25 – 2.17 (m, 2H), 1.21 (t, *J* = 7.1 Hz, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 173.9, 155.9, 153.4, 151.7, 148.1, 143.1, 141.2, 138.6, 124.1, 113.0, 104.0, 98.1, 97.9, 60.5, 60.3, 57.0, 56.5, 56.2, 55.8, 55.6, 36.2, 33.0, 30.3, 14.3.

**HRMS (ESI):** *m/z* calculated for C<sub>24</sub>H<sub>32</sub>NaO<sub>8</sub> [M+Na]<sup>+</sup>: 471.1995; found: 471.1985.

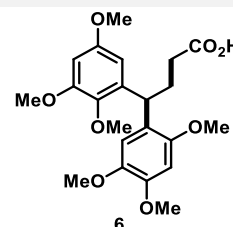
**Step-2: Synthesis of the acid derivative 6:** An oven-dried 100 mL round bottom flask equipped with magnetic stir bar was charged with the ester derivative **5** (538 mg, 1.2 mmol) in 40 mL (1:1) solution of EtOH/H<sub>2</sub>O and NaOH (96 mg, 2.4 mmol) was added to it and stirred for 10 hours at room temperature. After the full consumption of ester **5** (checked by TLC), ethanol was removed off under reduced pressure, aqueous phase was neutralized by adding 2(N) HCl solution and the mixture was extracted with ethyl acetate (3 x 10 mL). Combined organic layers were washed brine solution (15 mL), passed over dried Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. Finally, the crude reaction mixture was purified *via* flash column chromatography to afford the corresponding acid derivative **6**.

**4-(2,3,5-Trimethoxyphenyl)-4-(2,4,5-trimethoxyphenyl)butanoic acid (6):**

**Yield:** 87% yield (439 mg)

**Nature:** Gummy liquid.

**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):** 6.80 (s, 1H), 6.49 (s, 1H), 6.35 (s, 2H), 4.71 (t, *J* = 7.8 Hz, 1H), 3.85 (s, 3H), 3.81 (s, 3H), 3.79 (s, 3H), 3.75 (s, 3H), 3.73 (s, 3H), 3.62 (s, 3H), 2.39 – 2.31 (m, 2H), 2.25 – 2.17 (m, 2H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 179.7, 155.9, 153.4, 151.7, 148.2, 143.0, 141.2, 138.4, 123.9, 113.0, 103.9, 98.1, 97.9, 60.4, 57.0, 56.5, 56.2, 55.8, 55.6, 36.0, 32.5, 30.0.

**HRMS (ESI):** *m/z* calculated for C<sub>22</sub>H<sub>28</sub>NaO<sub>8</sub> [M+Na]<sup>+</sup>: 443.1682; found: 443.1688.

**Step-3: Synthesis of the tetralone derivative 7:** An oven-dried 25 mL round bottom flask was charged with the acid derivative **6** (252 mg, 0.6 mmol) in trifluoroacetic acid (4 mL), allowed to cool to 0 °C in an ice-water bath. Trifluoroacetic anhydride (167 μL, 1.2 mmol) was then added dropwise and the reaction was stirred at 0 °C for 5 hours. After completion of the reaction (checked by TLC), saturated aqueous Na<sub>2</sub>CO<sub>3</sub> was added dropwise to the reaction mixture until the aqueous phase turns into basic. Organic part was extracted then with ethyl acetate (3 x 5 mL), combined organic layers were washed with brine (10 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. Finally, the crude reaction mixture was purified *via* flash column chromatography to afford the corresponding tetralone derivative **7**.

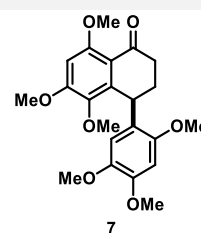
**5,6,8-Trimethoxy-4-(2,4,5-trimethoxyphenyl)-3,4-dihydronaphthalen-1(2H)-one (7):**

**Yield:** 53% yield (128 mg)

**Nature:** White solid.

**Mp:** 138-140 °C.

**R<sub>f</sub> value** = 0.2 [EtOAc/petroleum ether = 4:6 (v/v)]



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 6.57 (s, 1H), 6.48 (s, 1H), 6.19 (s, 1H), 5.03 (dd, *J* = 3.9, 2.7 Hz, 1H), 3.95 (s, 3H), 3.92 (s, 3H), 3.90 (s, 3H), 3.86 (s, 3H), 3.56 (s, 3H), 3.36 (s, 3H), 2.53 – 2.37 (m, 2H), 2.27 – 2.11 (m, 2H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 197.6, 158.5, 157.7, 151.6, 148.4, 142.6, 142.0, 139.2, 123.0, 116.4, 114.2, 98.2, 95.7, 60.6, 57.2, 56.7, 56.5, 56.3, 55.8, 35.8, 32.4, 27.5.

**HRMS (ESI): *m/z*** calculated for C<sub>22</sub>H<sub>27</sub>O<sub>7</sub> [M+H]<sup>+</sup>: 403.1757; found: 403.1749.

**Step-4: Synthesis of 1,2-Dihydronaphthalene derivative 8 (Pachypostaudin-B):** An oven-dried 25 mL round bottom flask was charged with the tetralone derivative **7** (121 mg, 0.3 mmol) in dry MeOH (5 mL) under argon atmosphere, allowed to cool to 0 °C in an ice-water bath. Sodium borohydride (34 mg, 0.9 mmol) was then added in portion and the reaction was stirred at 0 °C for 1 hours. After completion of the reaction (checked by TLC), it was quenched by adding saturated aqueous NH<sub>4</sub>Cl (2 mL), MeOH was removed off under reduced pressure and the organic part was extracted with DCM (3 x 5 mL). The combined organic layers were washed with brine (10 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, concentrated under reduced pressure and used for the next step without purification. This crude was dissolved in 5 mL (1:1) solution of Toluene/THF, then 4 Å molecular sieves (50 mg) and *p*-TSA (52 mg, 0.3 mmol) was successively added to the reaction mixture and reflux for 1 hour at 110 °C. After completion of reaction (checked by TLC), the crude reaction mixture was passed through a short pad of celite, washed with dichloromethane and concentrated under reduced pressure. Finally, the crude reaction mixture was purified *via* flash column chromatography to afford the corresponding 1,2-Dihydronaphthalene derivative **8** (Pachypostaudin-B).

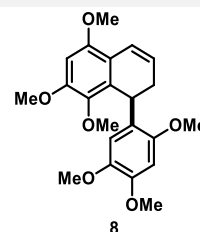
**5,7,8-Trimethoxy-1-(2,4,5-trimethoxyphenyl)-1,2-dihydronaphthalene (8):<sup>11</sup>**

**Yield:** 78% yield (90 mg) (over 2 steps)

**Nature:** White crystalline solid.

**Mp:** 156-158 °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):** 6.81 (dd, *J* = 9.8, 3.1 Hz, 1H), 6.52 (s, 1H), 6.43 (s, 1H), 6.29 (s, 1H), 5.69 – 5.64 (m, 1H), 4.88 (d, *J* = 8.0 Hz, 1H), 3.90 (s, 3H), 3.86 (s, 3H), 3.86 (s, 3H), 3.84 (s, 3H), 3.57 (s, 3H), 3.38 (s, 3H), 2.70 – 2.62 (m, 1H), 2.42 (dd, *J* = 17.2, 6.5 Hz, 1H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 152.6, 151.7, 150.8, 148.1, 142.6, 140.5, 132.4, 124.7, 123.6, 121.2, 117.1, 114.5, 98.1, 96.2, 60.5, 57.0, 56.8, 56.4, 56.2, 56.1, 29.9, 28.4.

**Synthesis of 1,2,3,4-Tetrahydronaphthalene derivative 9 (Pachypostaudin-A):** In a 25 mL round bottom flask compound **8** (Pachypostaudin-B) (39 mg, 0.1 mmol) was dissolved in dry EtOAc (6 mL) and then 10% Pd/C (8 mg) was added to it. Then the resultant mixture was allowed to stirring for 10 hours under H<sub>2</sub> balloon pressure at room temperature. After completion of the reaction (checked by TLC), the crude reaction mixture was filtered through celite-pad and washed with ethyl acetate and concentrated under reduced pressure. Finally, the crude reaction mixture was purified *via* flash column chromatography to afford the corresponding 1,2,3,4-tetrahydronaphthalene derivative **9** (Pachypostaudin-A).

**5,7,8-Trimethoxy-1-(2,4,5-trimethoxyphenyl)-1,2,3,4-tetrahydronaphthalene (9):<sup>12</sup>**

<sup>11</sup> I.G.A.A. Kartika, I.J. Bang, C. Riani, M. Insanu, J.H. Kwak, K.H. Chung and I.K. Adnyana, *Molecules*, 2020, **25**, 4914.

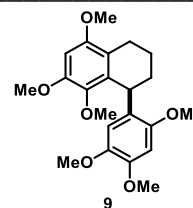
<sup>12</sup> D. Kumar, A. Salam, T. K. Sahu, S. S. Sahoo and T. Khan, *J. Org. Chem.*, 2021, **86**, 15096–15116.

**Yield:** 85% yield (33 mg)

**Nature:** White solid.

**Mp:** 123-125 °C.

**R<sub>f</sub> value** = 0.2 [EtOAc/petroleum ether = 2:8 (v/v)]



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 6.56 (s, 1H), 6.43 (s, 1H), 6.19 (s, 1H), 4.77 – 4.71 (m, 1H), 3.89 (s, 3H), 3.86 (s, 3H), 3.84 (s, 3H), 3.82 (s, 3H), 3.59 (s, 3H), 3.28 (s, 3H), 2.85 – 2.78 (m, 1H), 2.51 – 2.42 (m, 1H), 1.88 – 1.78 (m, 2H), 1.68 – 1.55 (m, 2H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 153.3, 151.1, 150.7, 147.8, 142.4, 140.9, 134.4, 128.2, 119.7, 115.5, 98.3, 95.8, 60.1, 57.3, 57.0, 56.5, 56.2, 55.7, 32.0, 29.2, 23.0, 17.6.

## 6. Procedure for synthesis of lignan derivative 11:

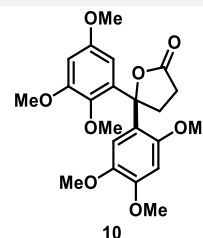
**Step-1: Synthesis of lactone derivative 10:** An oven-dried 25 mL round bottom flask equipped with a magnetic stir bar was successively charged with the photocatalyst 4CzIPN (6 mg, 2 mol%), 4-(2,3,5-Trimethoxyphenyl)-4-(2,4,5-trimethoxyphenyl)butanoic acid **6** (168 mg, 0.4 mmol) and K<sub>2</sub>CO<sub>3</sub> (110 mg, 0.8 mmol) in dry CH<sub>3</sub>CN (8 mL) under argon atmosphere. Then the tube was evacuated and backfilled with argon and placed under blue LEDs at an approximate distance of 5 cm and irradiated for 10 h. A high-speed fan was also applied to maintain the temperature. After completion of the reaction (checked by TLC), solvent was removed off under reduced pressure and 10 mL of distilled water was added to the reaction mixture and the organic part was extracted with ethyl acetate (2 x 5 mL). Combined organic layers were washed with brine (5 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. Finally, the crude residue was purified by flash column chromatography to afford the lactone derivative **10**.

### 5-(2,3,5-Trimethoxyphenyl)-5-(2,4,5-trimethoxyphenyl)dihydrofuran-2(3H)-one (**10**):

**Yield:** 62% yield (104 mg)

**Nature:** Colourless liquid.

**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):** 6.95 (s, 1H), 6.54 (s, 1H), 6.48 (d, *J* = 2.9 Hz, 1H), 6.39 (d, *J* = 2.8 Hz, 1H), 3.89 (s, 3H), 3.83 (s, 3H), 3.79 (s, 3H), 3.71 (s, 3H), 3.69 (s, 3H), 3.56 (s, 3H), 3.07 – 2.99 (m, 1H), 2.94 – 2.87 (m, 1H), 2.66 – 2.55 (m, 2H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 177.6, 155.1, 153.8, 151.2, 149.8, 142.6, 140.6, 136.9, 122.7, 112.1, 103.6, 100.1, 98.5, 88.6, 60.5, 56.8, 56.5, 56.2, 55.9, 55.7, 34.7, 29.4.

**HRMS (ESI): *m/z*** calculated for C<sub>22</sub>H<sub>27</sub>O<sub>8</sub> [M+H]<sup>+</sup>: 419.1706; found: 419.1707.

**Step-2: Synthesis of Tetrahydrofuran derivative 11:** The stirred solution of **10** (21 mg, 0.05 mmol) in dry THF (2 mL) was allowed to cool at 0 °C in an ice-water bath. Then, LiAlH<sub>4</sub> (6 mg, 0.15 mmol) was added to the solution in two portions under argon atmosphere and the resultant mixture was allowed to stir for 30 minutes at room temperature. After completion of the reaction (checked by TLC), it was quenched with 5 mL of saturated NH<sub>4</sub>Cl solution and organic part was extracted with DCM (3 x 10 mL). Combined organic layers were washed with brine solution (15 mL), passes over dried Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure and used for the next step without purification. The crude product was dissolved in dry DCM (2 mL), allowed to cool to 0 °C in an ice-water bath and then TFA (8 μL, 0.1 mmol)

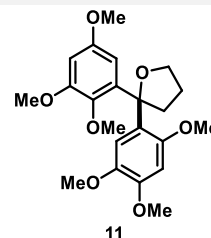
was added in one portion. After stirring for 10 minutes, the reaction was quenched with a saturated aqueous NaHCO<sub>3</sub> solution (5 mL) and extracted with DCM (2 x 5 mL). The combined organic layers were washed with brine (5 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. Finally, the crude reaction mixture was purified *via* flash column chromatography to afford the corresponding compound tetrahydrofuran derivative **11**.

**2-(2,3,5-Trimethoxyphenyl)-2-(2,4,5-trimethoxyphenyl)tetrahydrofuran (11):**

**Yield:** 83% yield (17 mg) (over 2 steps)

**Nature:** Colourless liquid.

**R<sub>f</sub> value** = 0.3 [EtOAc/petroleum ether = 2:8 (v/v)]



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):** 7.17 (s, 1H), 6.72 (d, *J* = 2.9 Hz, 1H), 6.47 (s, 1H), 6.40 (d, *J* = 2.9 Hz, 1H), 4.09 – 3.95 (m, 2H), 3.88 (s, 3H), 3.84 (s, 3H), 3.79 (s, 3H), 3.78 (s, 3H), 3.49 (s, 3H), 3.20 (s, 3H), 2.72 – 2.56 (m, 2H), 1.95 – 1.88 (m, 2H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 154.9, 153.7, 151.6, 148.7, 142.7, 140.4, 140.3, 129.8, 126.4, 112.2, 103.8, 99.7, 99.1, 86.1, 68.0, 60.0, 57.2, 56.8, 56.1, 55.9, 55.8, 37.0, 25.7.

**HRMS (ESI): *m/z*** calculated for C<sub>22</sub>H<sub>28</sub>NaO<sub>7</sub> [M+Na]<sup>+</sup>: 427.1733; found: 427.1718.

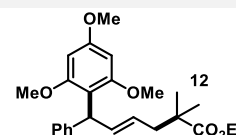
**7. Procedure for four-carbon homologated alkylation with conjugated olefins:** An oven-dried culture tube equipped with a magnetic stir bar was successively charged with the photocatalyst PTH (1 mg, 2 mol%), (*E*)-Buta-1,3-dien-1-ylbenzene (0.4 mmol, 2.0 equiv.), ethyl-2-bromoisobutyrate (29 μL, 0.2 mmol), 1,3,5-trimethoxybenzene **3a** (34 mg, 0.2 mmol), and Zn(OAc)<sub>2</sub> (88 mg, 0.4 mmol) in dry DCE (2 mL). Then the tube was sealed with a rubber screw cap, evacuated and backfilled with argon, placed under purple LEDs at an approximate distance of 5 cm and irradiated for 6 h. A high-speed fan was also applied to maintain the temperature. After completion of the reaction (checked by TLC), 5 mL of distilled water was added to the reaction mixture and the organic part was extracted with DCM (2 x 3 mL). Combined organic layers were washed with brine (3 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. Finally, the crude residue was purified by flash column chromatography to get the corresponding 1,2- and 1,4-alkylated products **12** and **13** in equal amount.

**Ethyl (*E*)-2,2-dimethyl-6-phenyl-6-(2,4,6-trimethoxyphenyl)hex-4-enoate (12):**

**Yield:** 37% yield (30 mg)

**Nature:** Colourless liquid.

**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):** 7.23 – 7.16 (m, 4H), 7.11 (t, *J* = 6.8 Hz, 1H), 6.19 (dd, *J* = 15.2, 8.5 Hz, 1H), 6.15 (s, 2H), 5.50 (dt, *J* = 15.0, 7.4 Hz, 1H), 5.25 (d, *J* = 8.5 Hz, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 3H), 3.68 (s, 6H), 2.30 (d, *J* = 7.5 Hz, 2H), 1.21 – 1.18 (m, 9H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 177.9, 159.8, 158.8, 144.9, 134.9, 127.7, 127.4, 126.8, 125.2, 113.3, 91.5, 60.3, 55.8, 55.3, 43.7, 42.9, 42.7, 25.1, 25.0, 14.2.

**HRMS (ESI): *m/z*** calculated for C<sub>25</sub>H<sub>33</sub>O<sub>5</sub> [M+H]<sup>+</sup>: 413.2328; found: 413.2328.

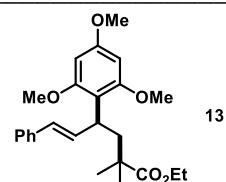
**Ethyl (*E*)-2,2-dimethyl-6-phenyl-4-(2,4,6-trimethoxyphenyl)hex-5-enoate (13):**

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**Yield:** 39% yield (32 mg)

**Nature:** Colourless liquid.

**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):** 7.30 (d, *J* = 7.4 Hz, 2H), 7.23 (t, *J* = 7.5 Hz, 2H), 7.12 (t, *J* = 7.2 Hz, 1H), 6.62 (dd, *J* = 15.9, 8.5 Hz, 1H), 6.30 (d, *J* = 15.9 Hz, 1H), 6.10 (s, 2H), 4.17 (dd, *J* = 14.9, 6.9 Hz, 1H), 3.87 – 3.83 (m, 1H), 3.82 (s, 6H), 3.77 (s, 3H), 3.75 – 3.71 (m, 1H), 2.16 (dd, *J* = 6.7, 3.2 Hz, 2H), 1.18 (s, 3H), 1.15 (s, 3H), 1.10 (t, *J* = 7.1 Hz, 3H).

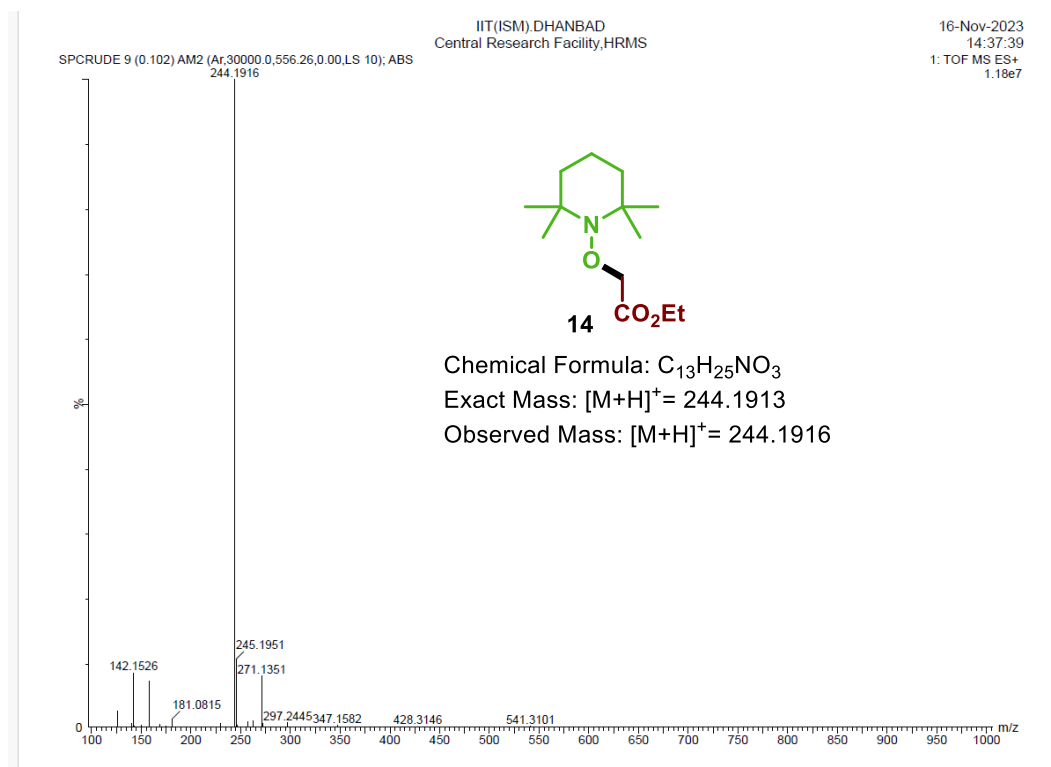
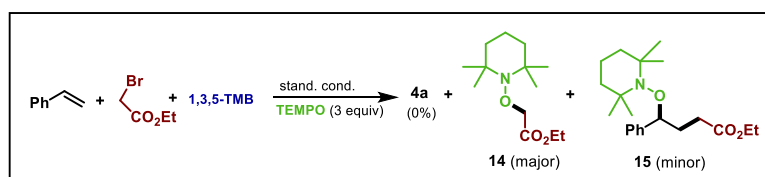
**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):** 178.0, 159.5, 138.4, 134.5, 128.5, 128.4, 126.6, 126.1, 113.6, 91.1, 60.1, 55.8, 55.4, 44.7, 42.2, 35.4, 26.0, 25.7, 14.1.

**HRMS (ESI): *m/z*** calculated for C<sub>25</sub>H<sub>32</sub>NaO<sub>5</sub> [M+Na]<sup>+</sup>: 435.2147; found: 435.2148.

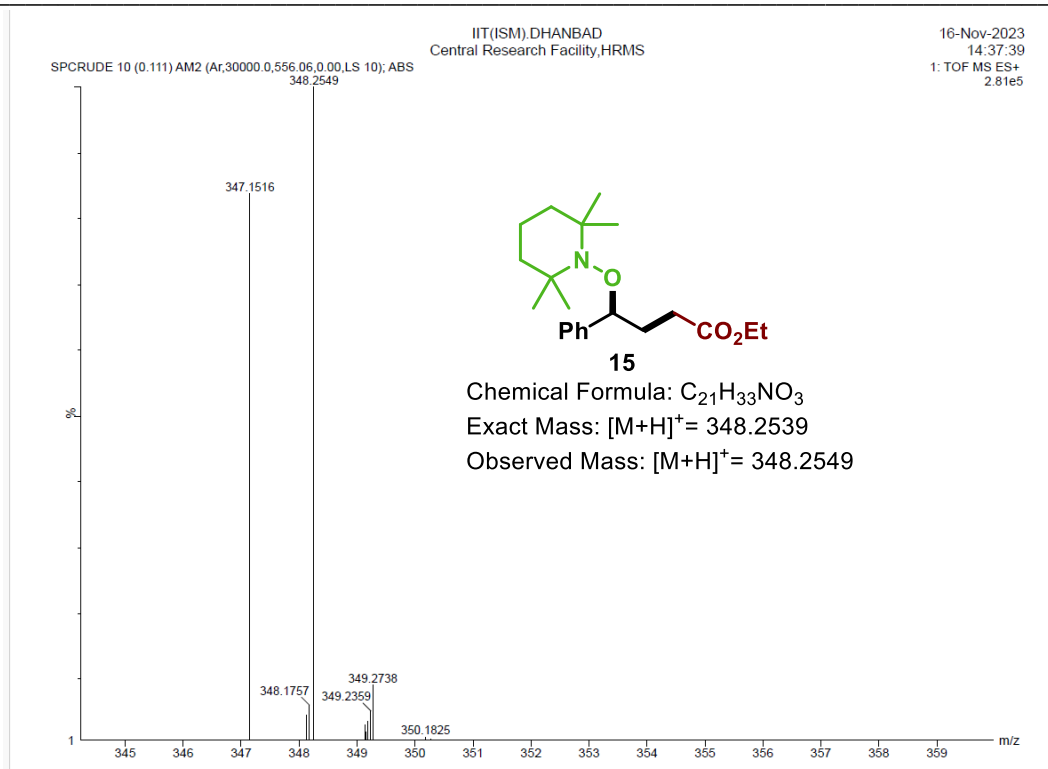


## 8. Mechanistic Studies and Control Experiments:

**8.1. Radical Trapping with TEMPO:** An oven-dried culture tube equipped with a magnetic stir bar was successively charged with the photocatalyst PTH (1 mg, 2 mol%), styrene **1a** (47  $\mu$ L, 0.4 mmol), ethyl bromoacetate **2a** (22  $\mu$ L, 0.2 mmol), 1,3,5-trimethoxy benzene **3a** (34 mg, 0.2 mmol), Zn(OAc)<sub>2</sub> (88 mg, 0.4 mmol) and the radical quencher TEMPO (94 mg, 0.6 mmol) in dry DCE (2 mL). Then, the tube was sealed with a rubber screw cap, evacuated and backfilled with argon and placed under purple LEDs at an approximate distance of 5 cm and irradiated for 6 h. A high-speed fan was also applied to maintain the temperature. After the reaction, the crude reaction mixture was concentrated and sent for high-resolution mass spectroscopy (HRMS) analysis. The HRMS analysis results show that in the presence of TEMPO, the formation of carbo-arylated product gets hampered, and two TEMPO adducts, **14** and **15**, were formed, indicating the radical involvements in the reaction course.



**Figure S1.** HRMS data of crude reaction mixture (compound **14**)



**Figure S2.** HRMS data of crude reaction mixture (compound **15**)

**8.2. Cation Trapping with MeOH as nucleophile:** An oven-dried culture tube equipped with a magnetic stir bar was successively charged with the photocatalyst PTH (1 mg, 2 mol%), styrene **1a** (47  $\mu$ L, 0.4 mmol), bromo-acetonitrile **2n** (14  $\mu$ L, 0.2 mmol), Zn(OAc)<sub>2</sub> (88 mg, 0.4 mmol) in the solvent system, DCE: MeOH (1:1). Then, the tube was sealed with a rubber screw cap, evacuated, backfilled with argon, placed under purple LEDs at an approximate distance of 5 cm and irradiated for 6 h. A high-speed fan was also applied to maintain the temperature. After completion of the reaction (checked by TLC), the crude reaction mixture was concentrated under reduced pressure, 5 mL of distilled water was added, and the organic part was extracted with DCM (2 x 3 mL). Combined organic layers were washed with brine (3 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. Finally, the crude residue was purified by flash column chromatography to get the corresponding product **16**.

#### 4-Methoxy-4-phenylbutanenitrile (**16**):<sup>13</sup>

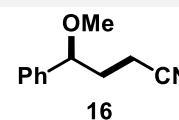
**Yield:** 75% yield (26 mg)

**Nature:** Colourless 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>)  $\delta$  (ppm):** 7.41 – 7.27 (m, 5H), 4.25 (dd, *J* = 8.7, 4.7 Hz, 1H), 3.24 (s, 3H), 2.58 – 2.49 (m, 1H), 2.58 – 2.49 (m, 1H), 2.10 – 1.91 (m, 2H).

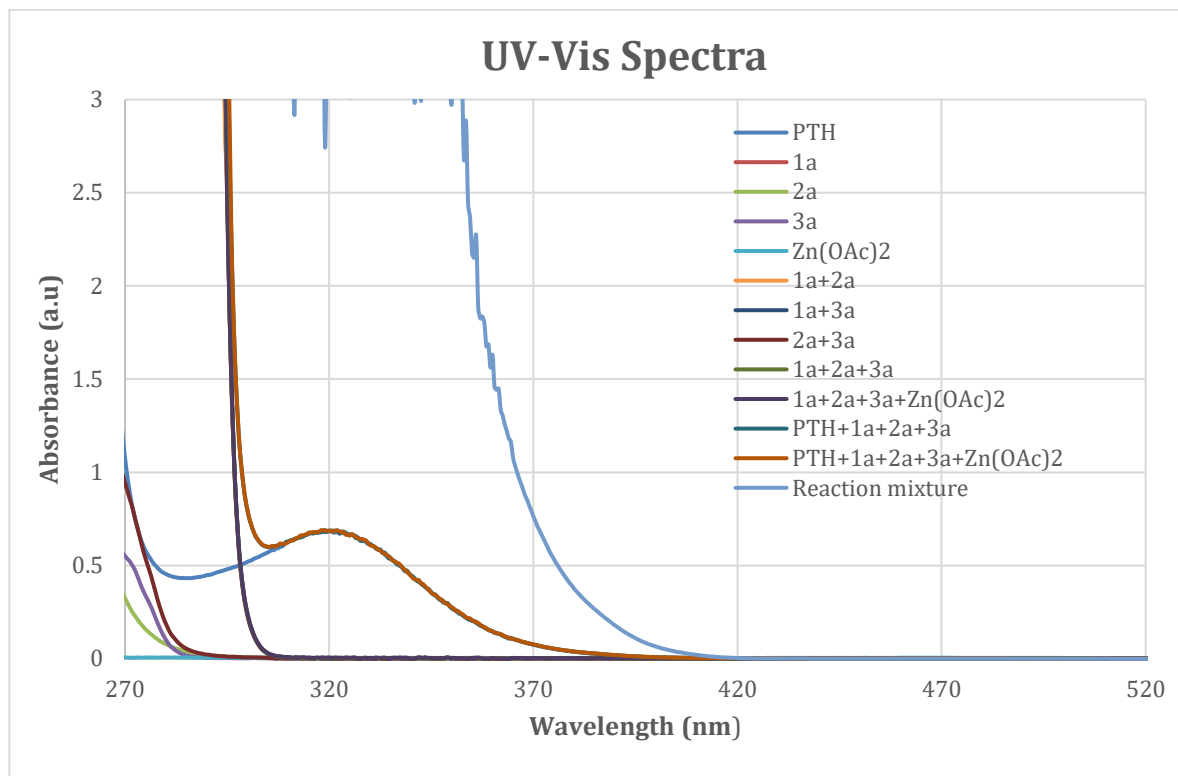
**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm):** 140.4, 128.8, 128.3, 126.5, 119.6, 81.5, 56.9, 33.7, 13.9.



**8.3. UV-Visible Study:** UV-Vis absorption spectra were recorded by using Shimadzu UV-1800 Spectrophotometer. At first, 0.2 mM solution of PTH, 0.02 M solution of **1a**, **2a**, **3a** and Zn(OAc)<sub>2</sub> in dry DCE was prepared, and then absorbance of individual reacting components as well as several combinations of them were measured with the

<sup>13</sup> W. Ai, Y. Liu, Q. Wang, Z. Lu and Q. Liu, *Org. Lett.*, 2018, **20**, 409–412.

wavelength range from 200 to 600 nm using quartz cuvette (path length= 1.0 cm). Absorption spectra of the reaction mixture (before irradiation) is also included here (Figure-S4).



**Figure S3.** UV-Vis Spectra of PTH, individual reactants [1a, 2a, 3a and Zn(OAc)<sub>2</sub>] and their combined mixtures.

**Comments:** These spectrums clearly indicates that the photocatalyst (PTH) shows absorption exclusively at  $\lambda_{\text{max}} = 320$  nm. And there is no new peak in the absorption spectra of different combined solutions of the reactants. Hence, the formation of any electron donor-acceptor (EDA) complex is being ruled out.

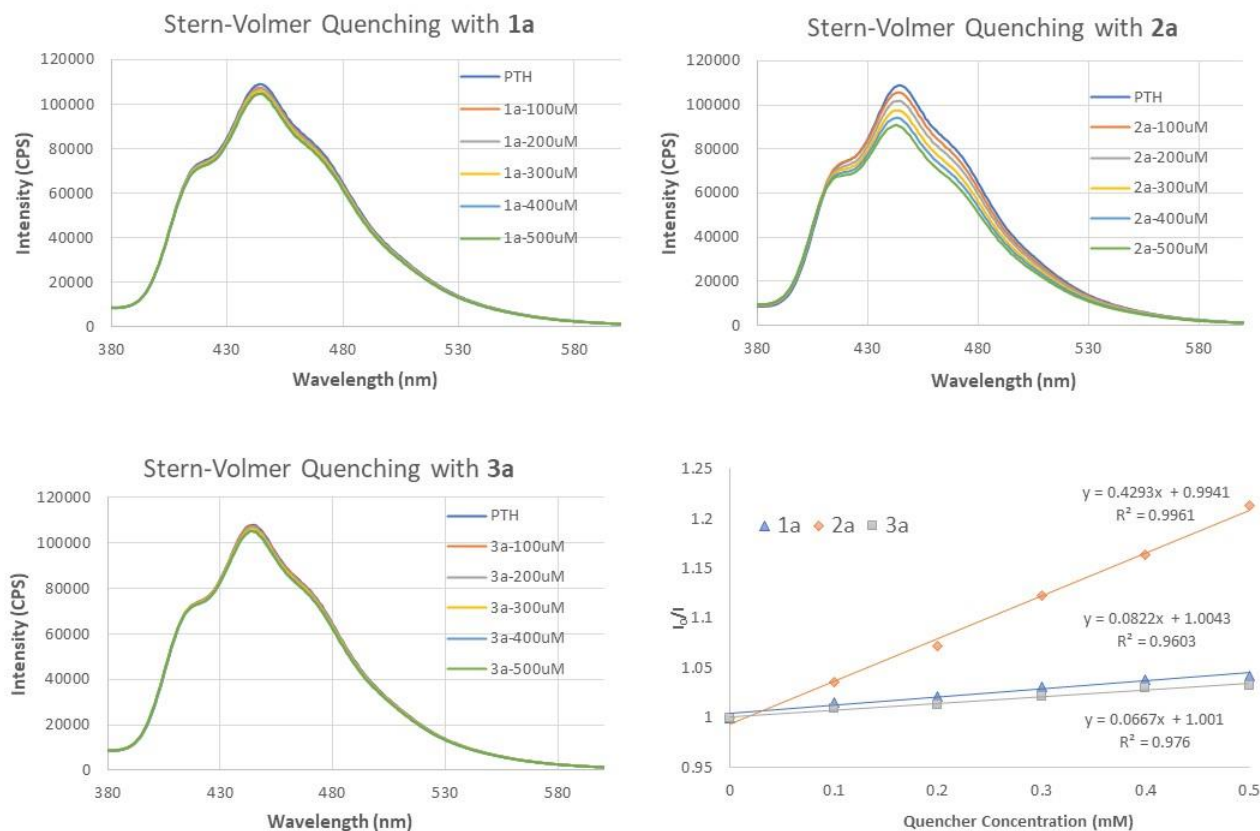
#### 8.4. Stern-Volmer Quenching Study:

All emission spectra were recorded using a Shimadzu RF-6000 Spectrophotometer. Photocatalyst PTH and different concentrations of added quenchers were prepared in dry DCE in quartz cuvettes. For the quenching experiments, the concentration of PTH was  $4.0 \times 10^{-5}$  M. The solutions were excited at 320 nm, and the emission intensity was measured at 445 nm for PTH. Plots were derived according to the Stern–Volmer equation, and  $K_{\text{sv}}$  was calculated.

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

Where  $I_0$  is the luminescence intensity of the photocatalyst in the absence of a quencher,  $I$  is the intensity of the photocatalyst in the presence of quenchers,  $[Q]$  is the concentration of added quencher, and  $K_{\text{sv}}$  is the Stern–Volmer quenching constant. All emission spectra were recorded after each addition of the quencher. The obtained spectra (Figure-S5) show that Ethyl bromoacetate **2a** is the prominent quencher here and suggested a mechanism started with the radical engagement from **2a** (calculated  $K_{\text{sv}}$  value of styrene, ethyl bromoacetate and 1,3,5-trimethoxybenzene are  $0.08 \text{ mM}^{-1}$ ,  $0.43 \text{ mM}^{-1}$  and  $0.07 \text{ mM}^{-1}$  respectively).

## Luminescence Quenching Study

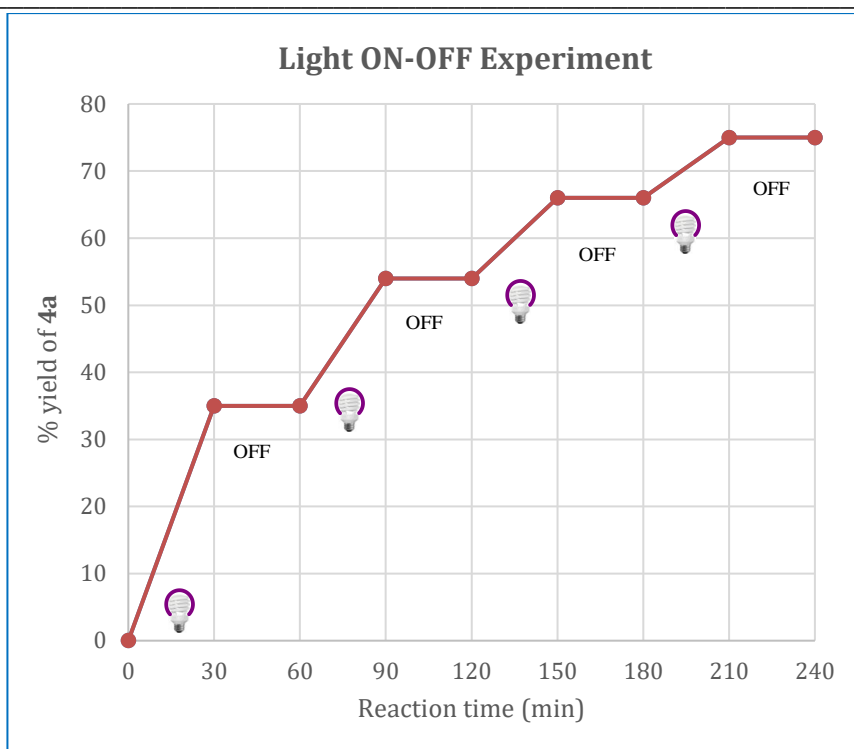


**Figure S4.** Emission spectra and Stern-Volmer plot of PTH, quenching with different concentrations of added quenchers- Styrene (**1a**), Ethyl bromoacetate (**2a**) and 1,3,5-Trimrthoxybenzene (**3a**).

### 8.5. Light ON-OFF Experiment:

Eight standard reactions were setup in 0.2 mmol scale. Then resulting mixtures were placed in light and dark in every alternative 30 minutes. Like this way alternative switch on-off of the light source was continue for 240 min. From the crude reaction mixture, the  $^1\text{H}$  NMR yields were measured using 1,1,2,2-tetrachloroethane as internal standard.

Entry	Time (min)	Light source	% Yield of <b>4a</b>
1	30	ON	35
2	60	OFF	35
3	90	ON	54
4	120	OFF	54
5	150	ON	66
6	180	OFF	66
7	210	ON	75
8	240	OFF	75



**Figure S5.** Light ON-OFF Experiment

**Comments:** The result of light ON-OFF experiment clearly indicates that the reaction progresses only when the light source is on, which discards the possibility of radical chain process in the reaction course.

## 9. X-ray Crystal Structures and Data:

### 9.1. X-ray Crystal Structures and Data of compound 4ae:

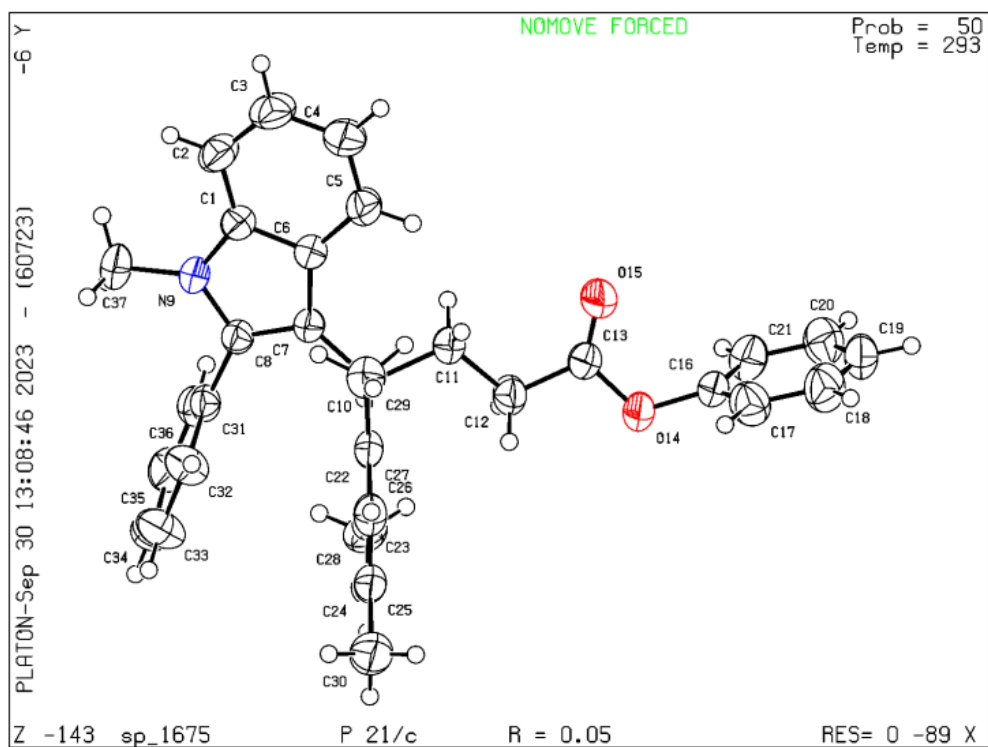
**Crystal growth process for compound 4ae:** Recrystallization of compound 4ae was performed in a 5 mL glass vial by dissolving 18 mg of the compound 4ae in acetonitrile (0.2 mL) and ethyl ether (3 mL) was slowly added on the top and then the vial was capped and stored at room temperature for the growth of the crystals. After 4 days crystal was formed and was send for the SC-XRD analysis.

**Crystal data for compound 4ae:** X-ray single crystal data were collected using MoK $\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) 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: **2256316**) contains the supplementary crystallographic data of compound 4ae. 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 S3: Crystal data and structure refinement for compound 4ae**

Identification code	CCDC: 2256316
Empirical formula	C <sub>34</sub> H <sub>33</sub> NO <sub>2</sub>
Formula weight	487.61

Temperature/K	293(2)
Crystal system	monoclinic
Space group	P 21/c
a/Å	21.9010(16)
b/Å	11.9356(11)
c/Å	10.1958(8)
$\alpha$ /°	90
$\beta$ /°	95.864(7)
$\gamma$ /°	90
Volume/Å <sup>3</sup>	2651.2(4)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.222
$\mu/\text{mm}^{-1}$	0.075
F(000)	1040
Radiation	MoK $\alpha$ ( $\lambda$ = 0.71073)
Theta (min)	1.869
Theta (max)	29.197
h, k, l (max)	29, 16, 13
R (reflections)	0.0544 (3535)
wR2 (reflections)	0.1538 (6075)



**Figure S6.** ORTEP plot of compound **4ae** with 50% ellipsoid probability.

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## 9.2. X-ray Crystal Structures and Data of compound 8:

**Crystal growth process for compound 8:** Recrystallization of compound 8 was performed in a 5 mL glass vial by dissolving 20 mg of the compound 8 in ethyl acetate (0.3 mL) and chloroform (3 mL) was slowly added on the top and then the vial was capped and stored at room temperature for the growth of the crystals. After 5 days crystal was formed and was send for the SC-XRD analysis.

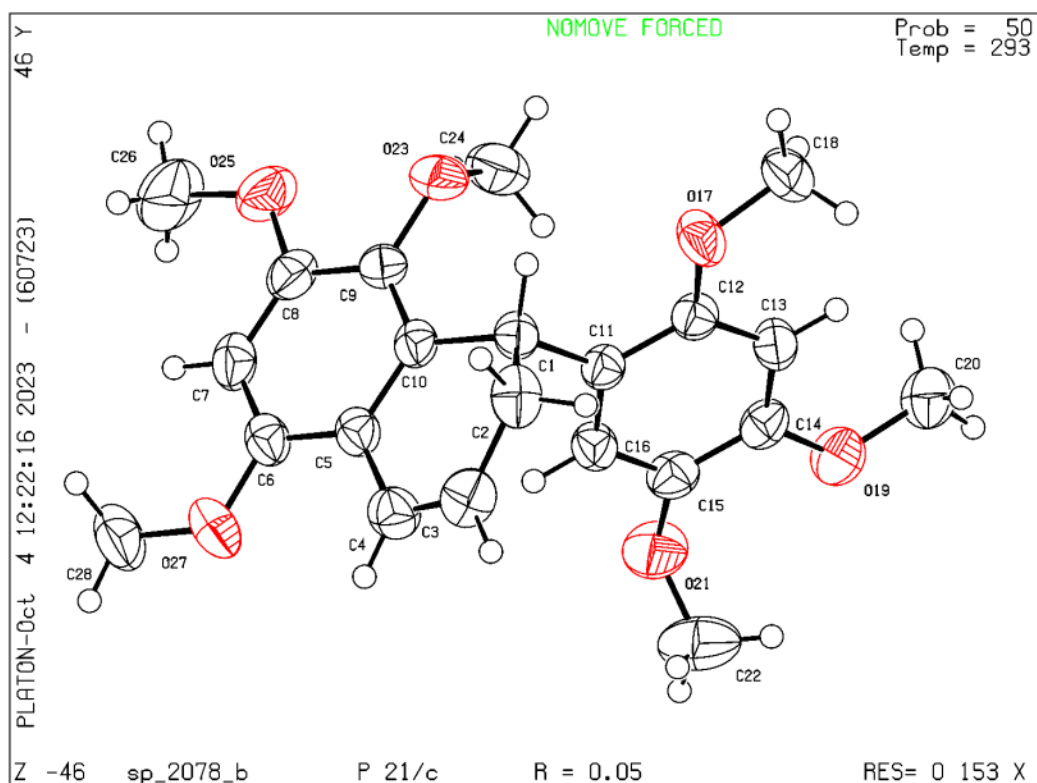
**Crystal data for compound 8:** X-ray single crystal data were collected using MoK $\alpha$  ( $\lambda = 0.71073$  Å) radiation on a Rigaku SuperNova diffractometer equipped with an Eos S2 detector. Structure solution/refinement were carried out using Shelx-2013. The structure was solved by direct method and refined in a routine manner. Non-hydrogen atoms were treated anisotropically. All hydrogen atoms were geometrically fixed. CCDC (CCDC No: **2299215**) contains the supplementary crystallographic data of compound 8. 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 S4: Crystal data and structure refinement for compound 8**

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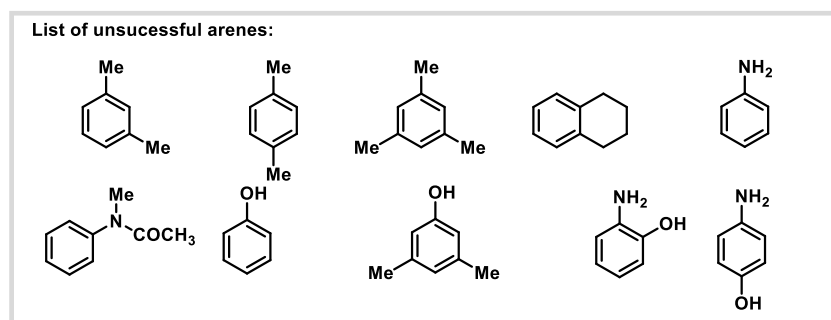
Identification code	CCDC: 2299215
Empirical formula	C <sub>22</sub> H <sub>26</sub> O <sub>6</sub>
Formula weight	386.43
Temperature/K	293(2)
Crystal system	monoclinic
Space group	P 21/c
a/Å	13.0879(16)
b/Å	11.0775(10)
c/Å	14.0938(12)
$\alpha$ /°	90
$\beta$ /°	102.597(10)
$\gamma$ /°	90
Volume/Å <sup>3</sup>	1994.2(4)
Z	4
$\rho_{\text{calc}}$ /cm <sup>3</sup>	1.287
$\mu$ /mm <sup>-1</sup>	0.093
F(000)	824
Radiation	MoK $\alpha$ ( $\lambda = 0.71073$ )
Theta (min)	2.361
Theta (max)	29.202
h, k, l (max)	16, 14, 18
R (reflections)	0.0482 (2950)
wR2 (reflections)	0.1268 (4529)

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**Figure S7.** ORTEP plot of compound **8** with 50% ellipsoid probability.

#### 10. List of Unsuccessful arenes:

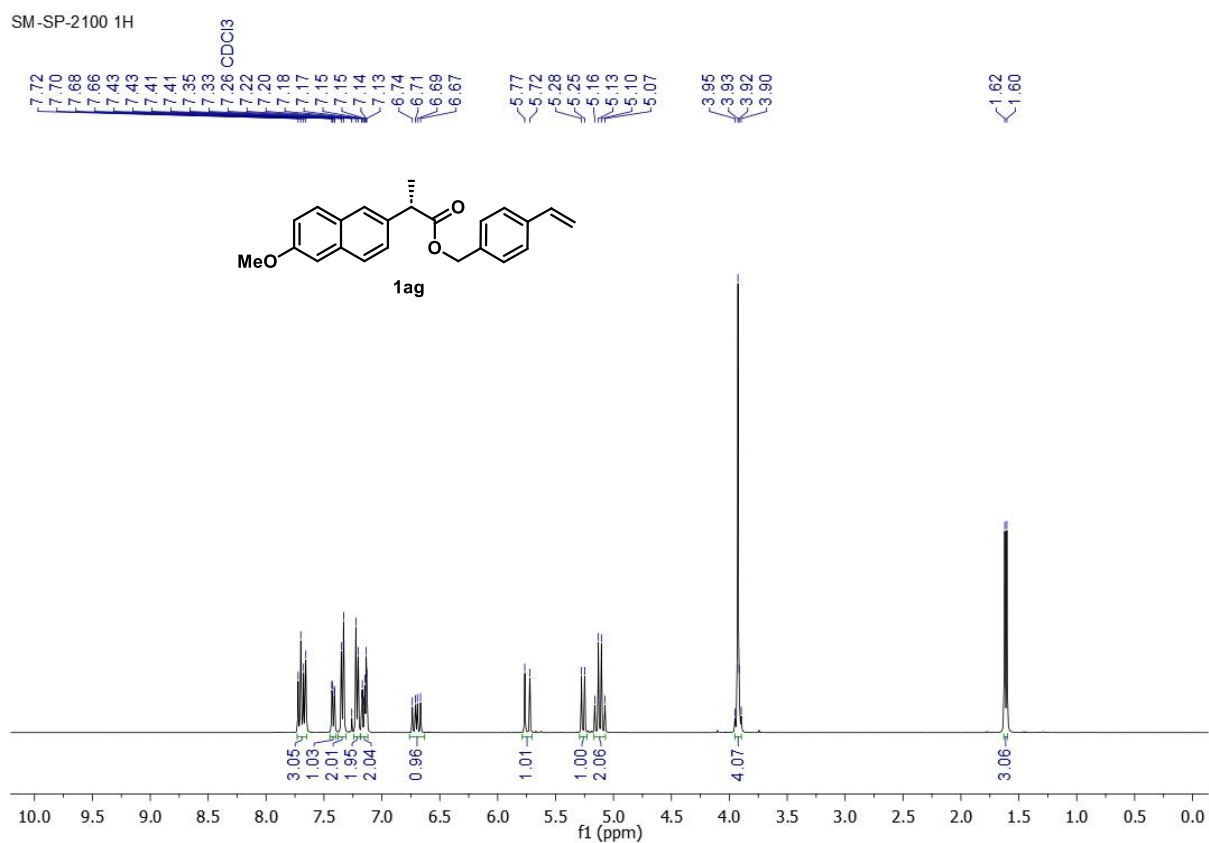


**Figure S8.** List of Unsuccessful arenes.

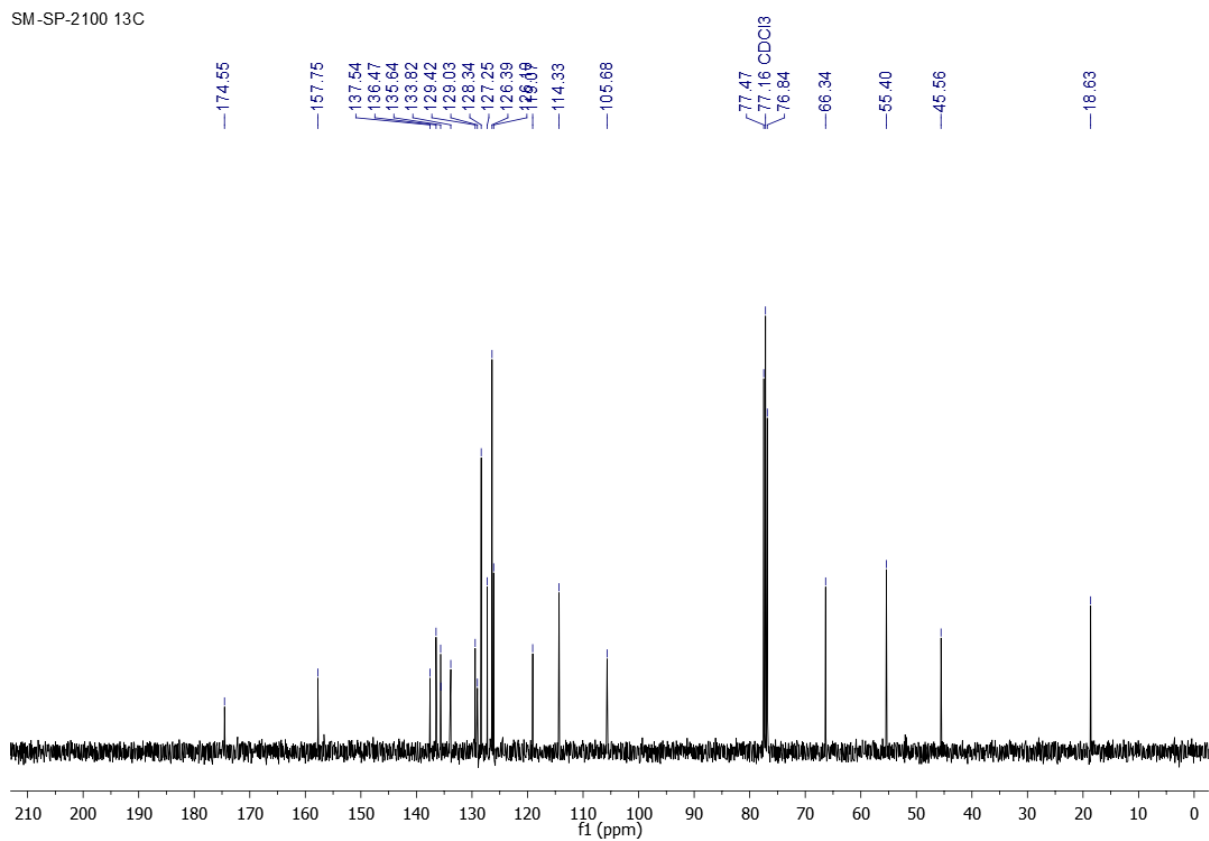


## 11. NMR Spectra:

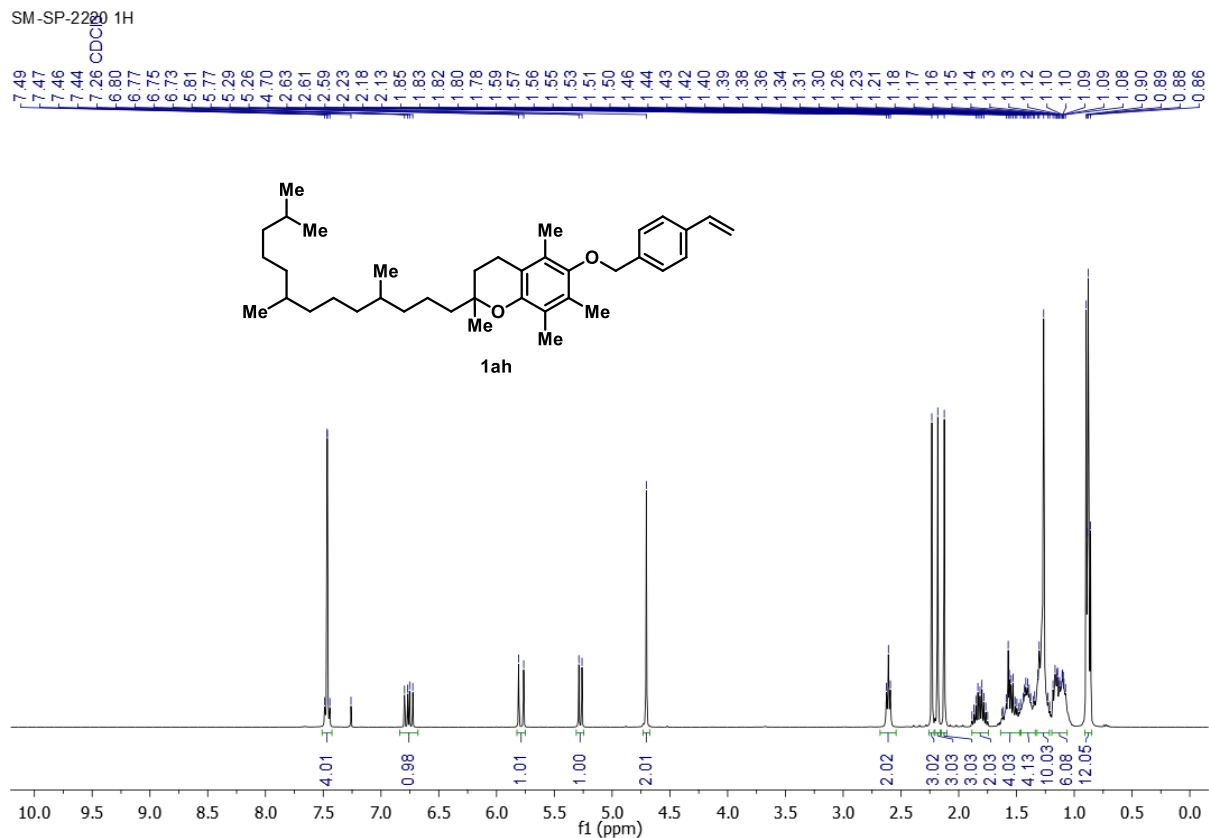
$^1\text{H}$  NMR of **1ag** (400 MHz,  $\text{CDCl}_3$ ):



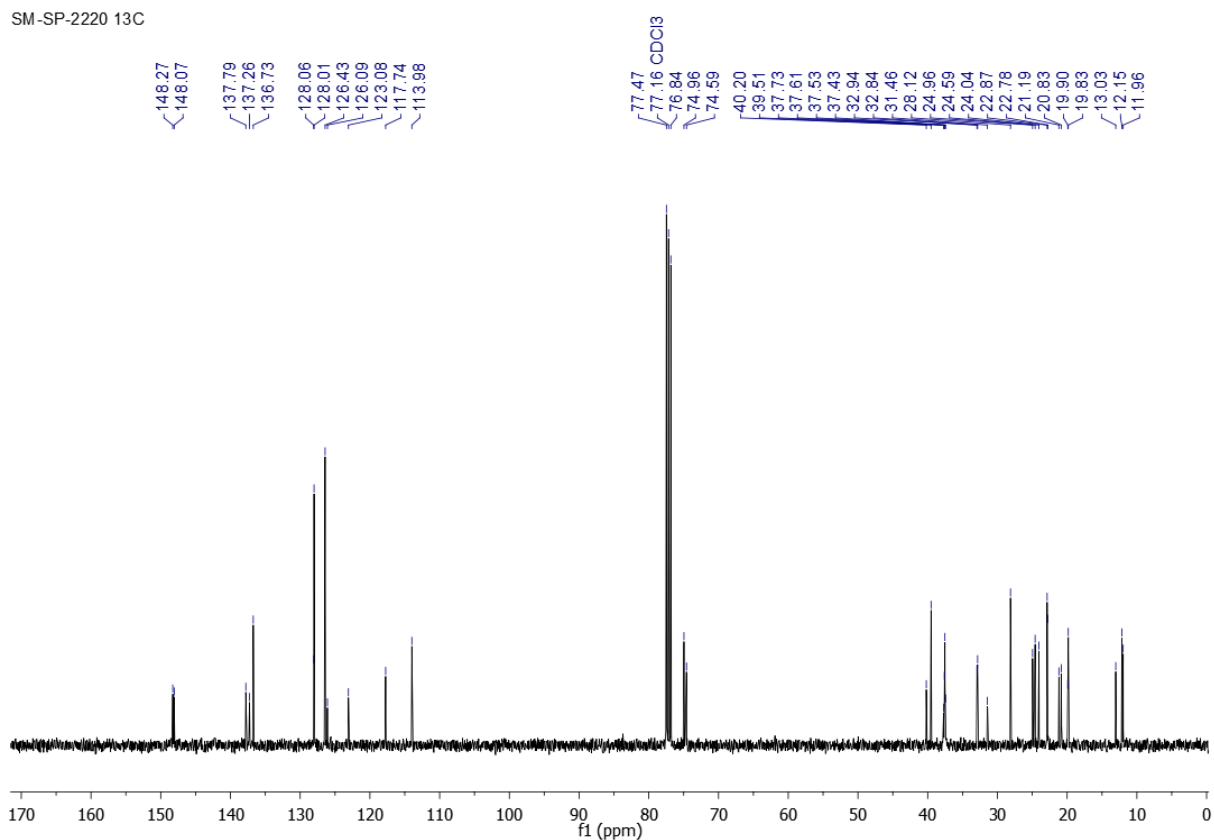
$^{13}\text{C}\{^1\text{H}\}$  NMR of **1ag** (101 MHz,  $\text{CDCl}_3$ ):



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

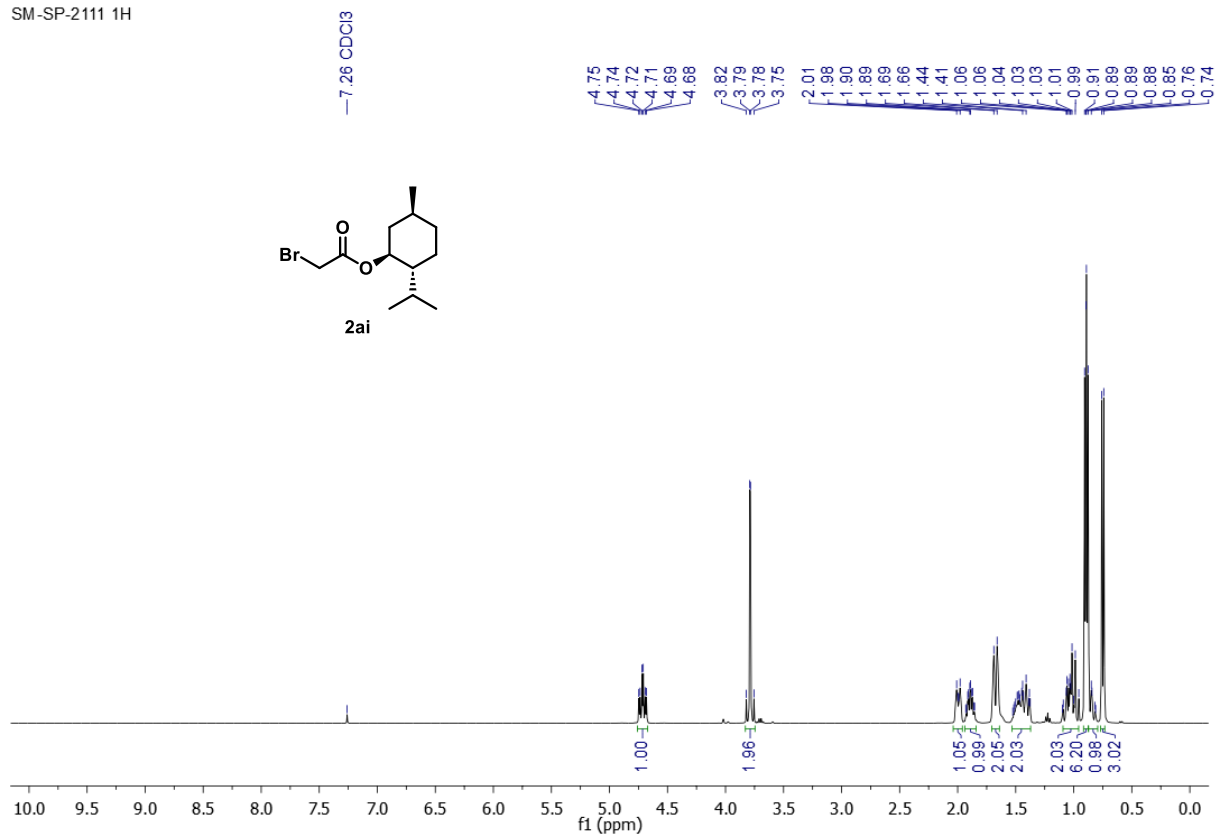


<sup>13</sup>C{<sup>1</sup>H} NMR of **1ah** (101 MHz, CDCl<sub>3</sub>):



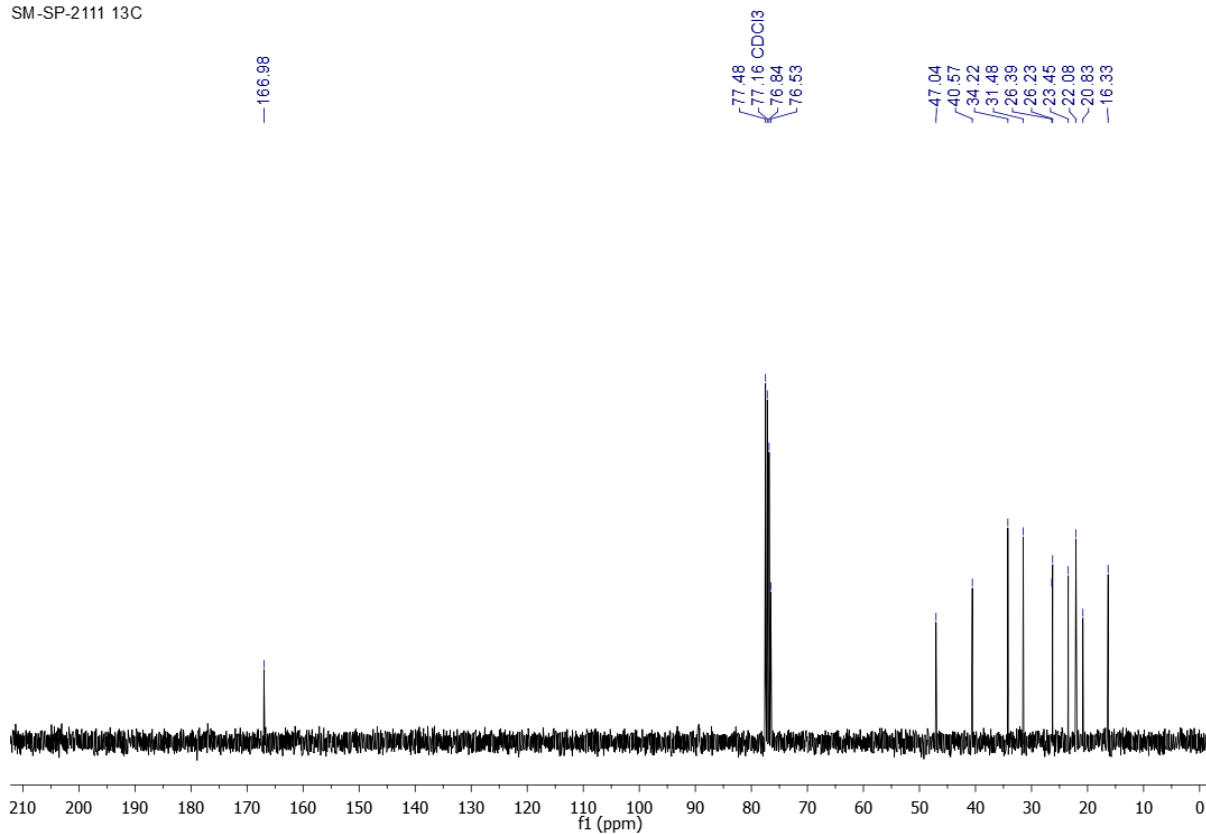
<sup>1</sup>H NMR of **2ai** (400 MHz, CDCl<sub>3</sub>):

SM-SP-2111 1H



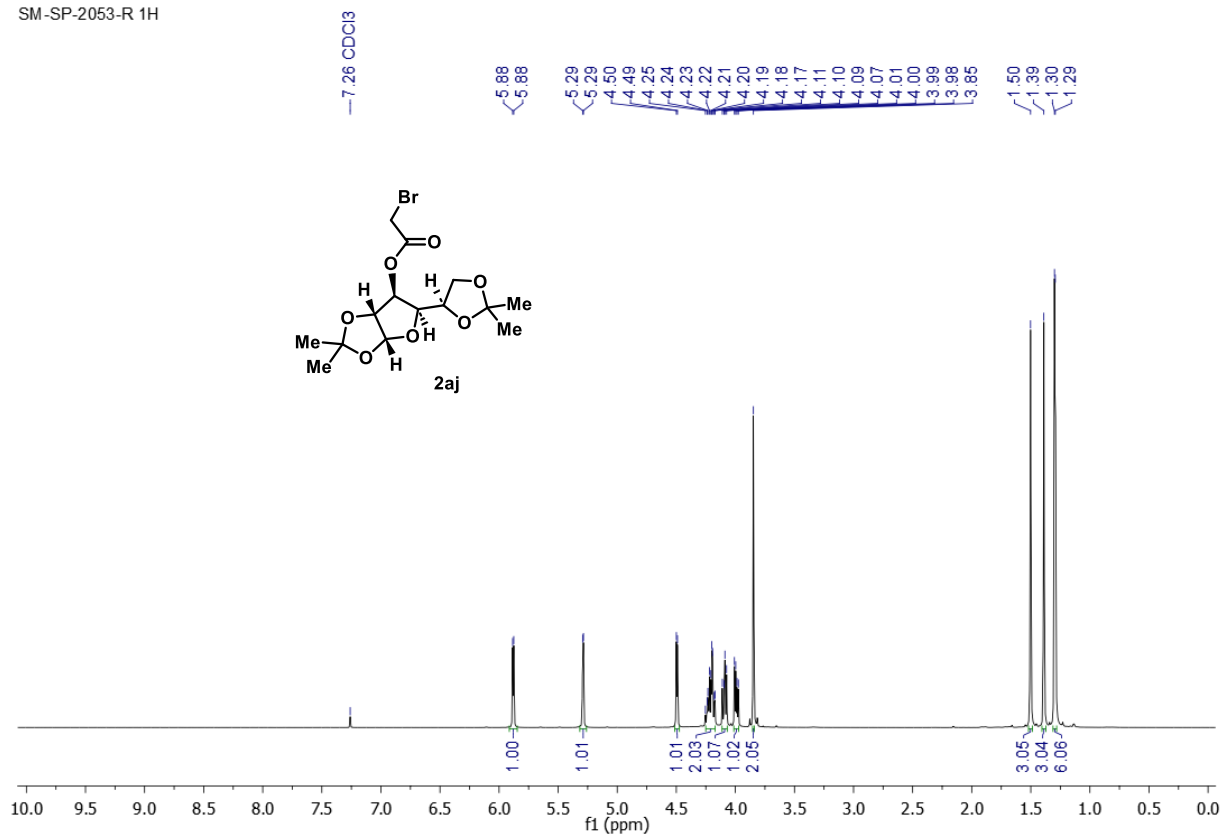
<sup>13</sup>C{<sup>1</sup>H} NMR of **2ai** (101 MHz, CDCl<sub>3</sub>):

SM-SP-2111 13C



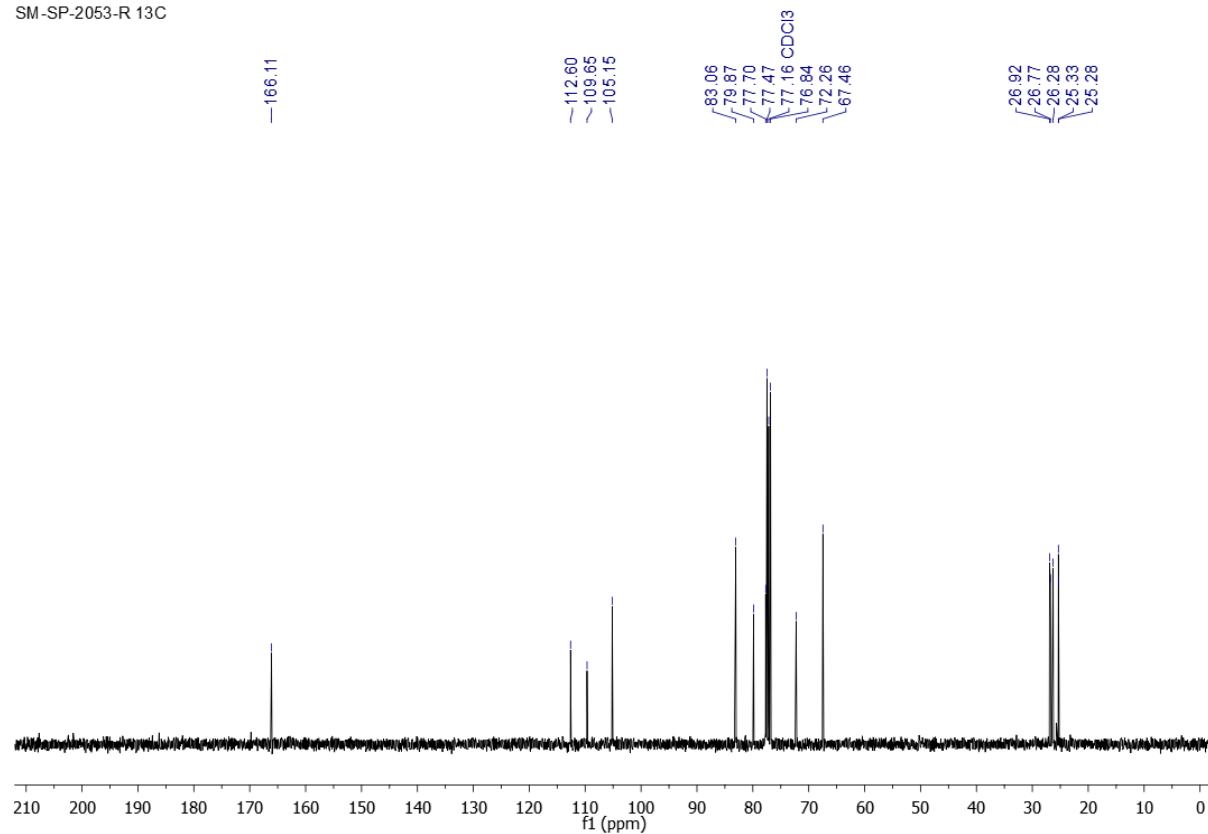
<sup>1</sup>H NMR of **2aj** (400 MHz, CDCl<sub>3</sub>):

SM-SP-2053-R 1H



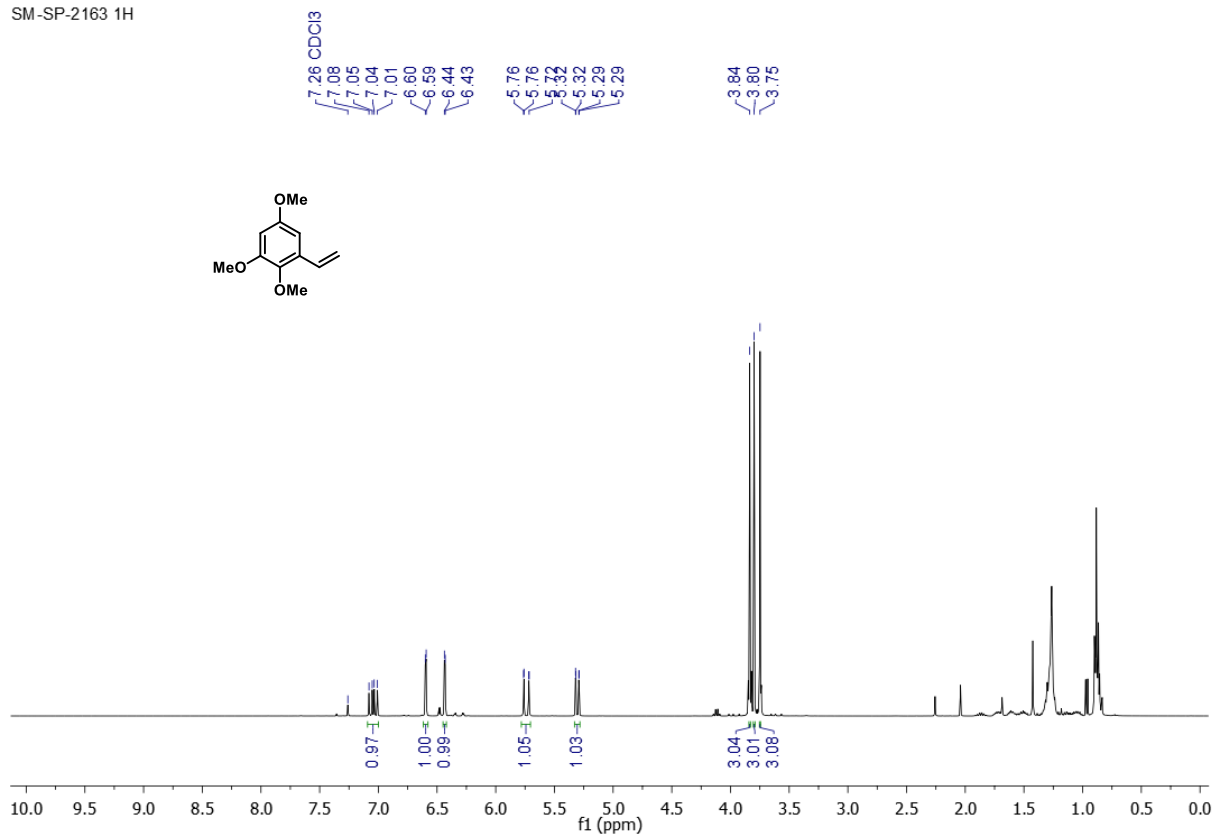
<sup>13</sup>C{<sup>1</sup>H} NMR of **2aj** (101 MHz, CDCl<sub>3</sub>):

SM-SP-2053-R 13C



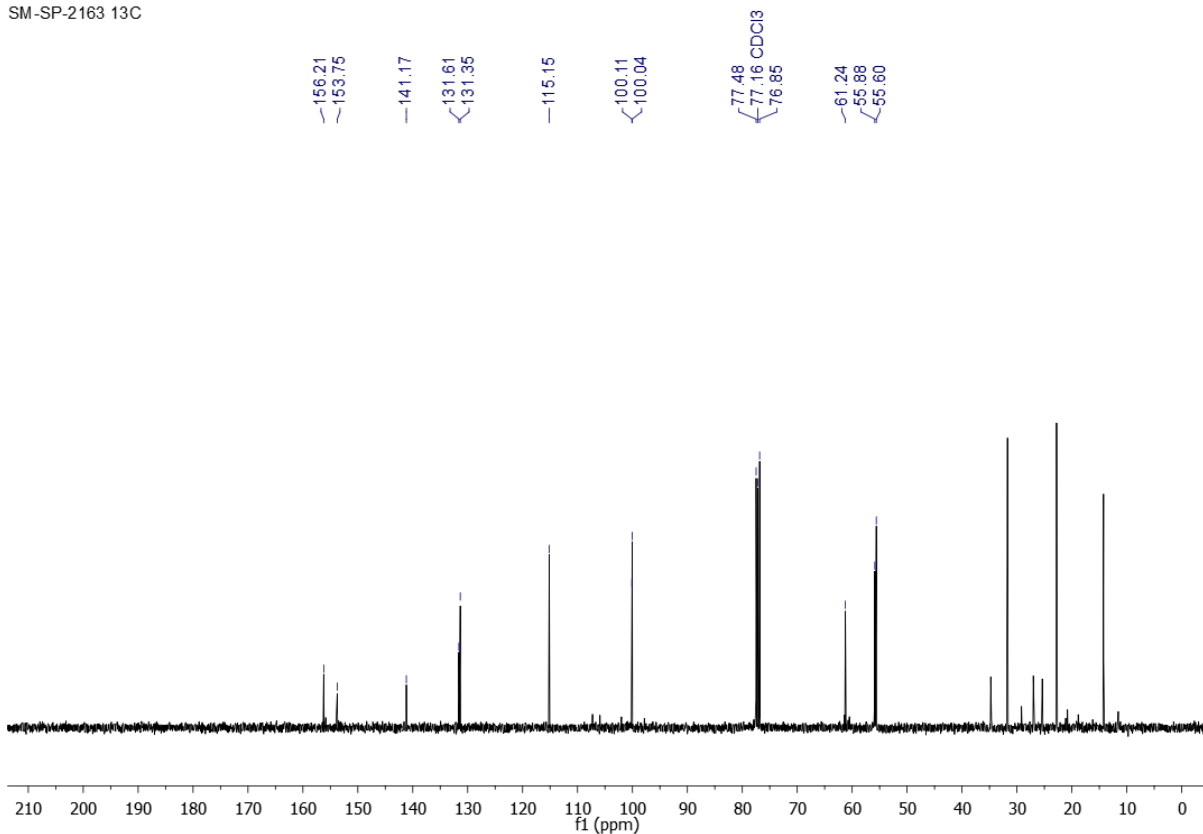
<sup>1</sup>H NMR of **1,2,5-Trimethoxy-3-vinylbenzene** (400 MHz, CDCl<sub>3</sub>):

SM-SP-2163 1H



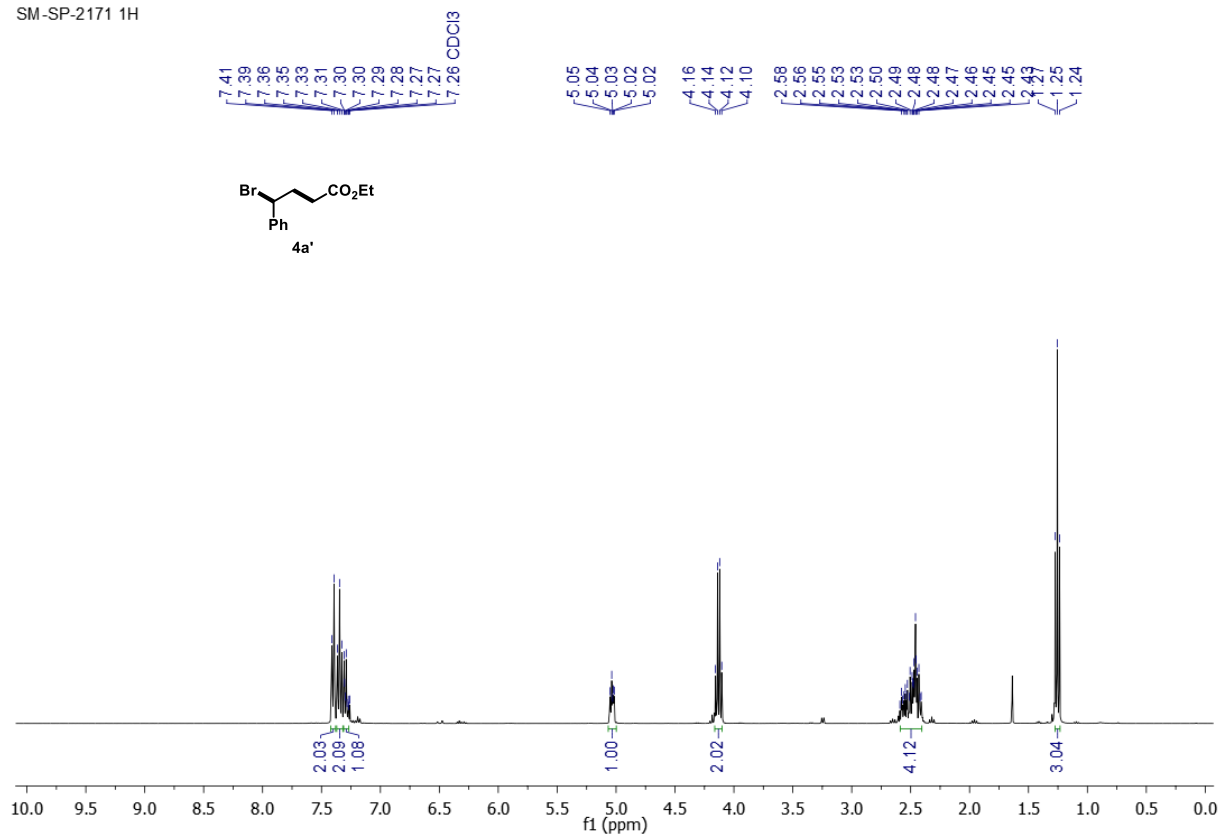
<sup>13</sup>C{<sup>1</sup>H} NMR of **1,2,5-Trimethoxy-3-vinylbenzene** (101 MHz, CDCl<sub>3</sub>):

SM-SP-2163 13C



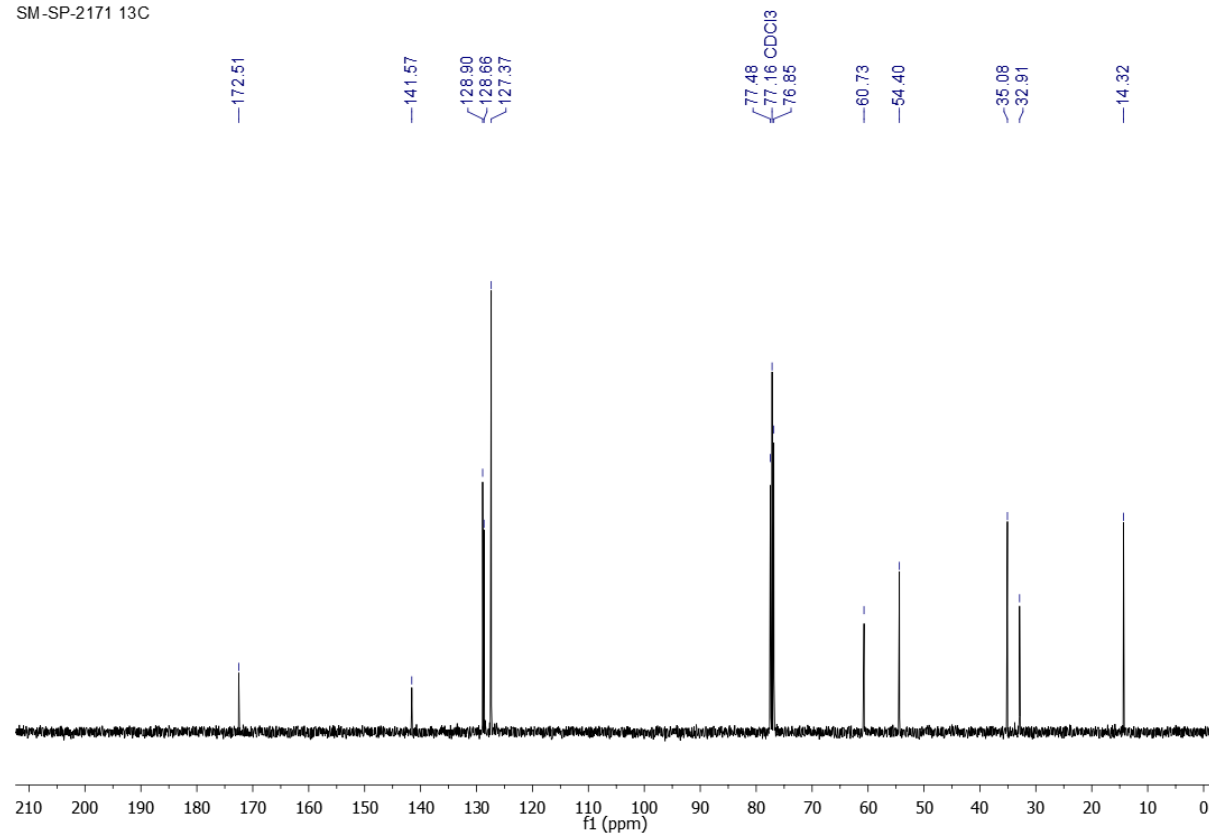
<sup>1</sup>H NMR of **4a'** (400 MHz, CDCl<sub>3</sub>):

SM-SP-2171 1H



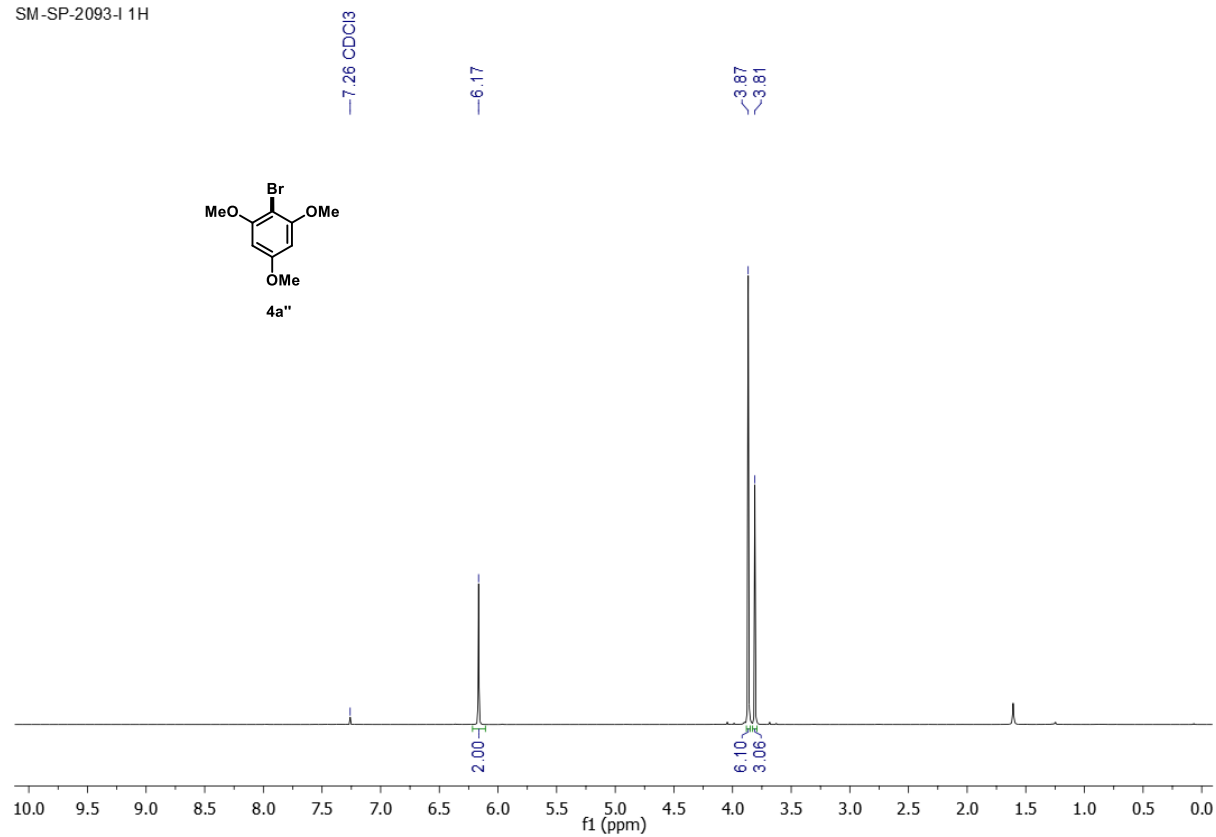
<sup>13</sup>C{<sup>1</sup>H} NMR of **4a'** (101 MHz, CDCl<sub>3</sub>):

SM-SP-2171 13C



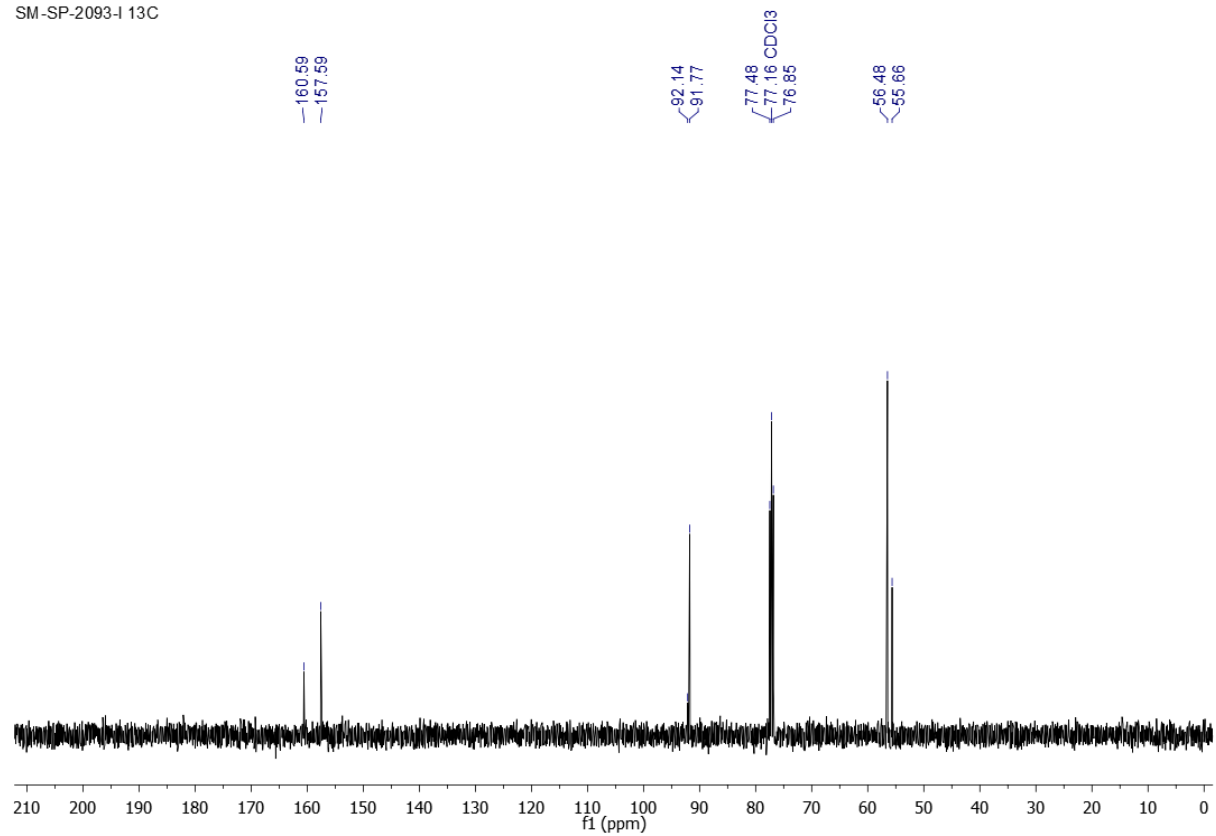
<sup>1</sup>H NMR of **4a''** (400 MHz, CDCl<sub>3</sub>):

SM-SP-2093-I 1H



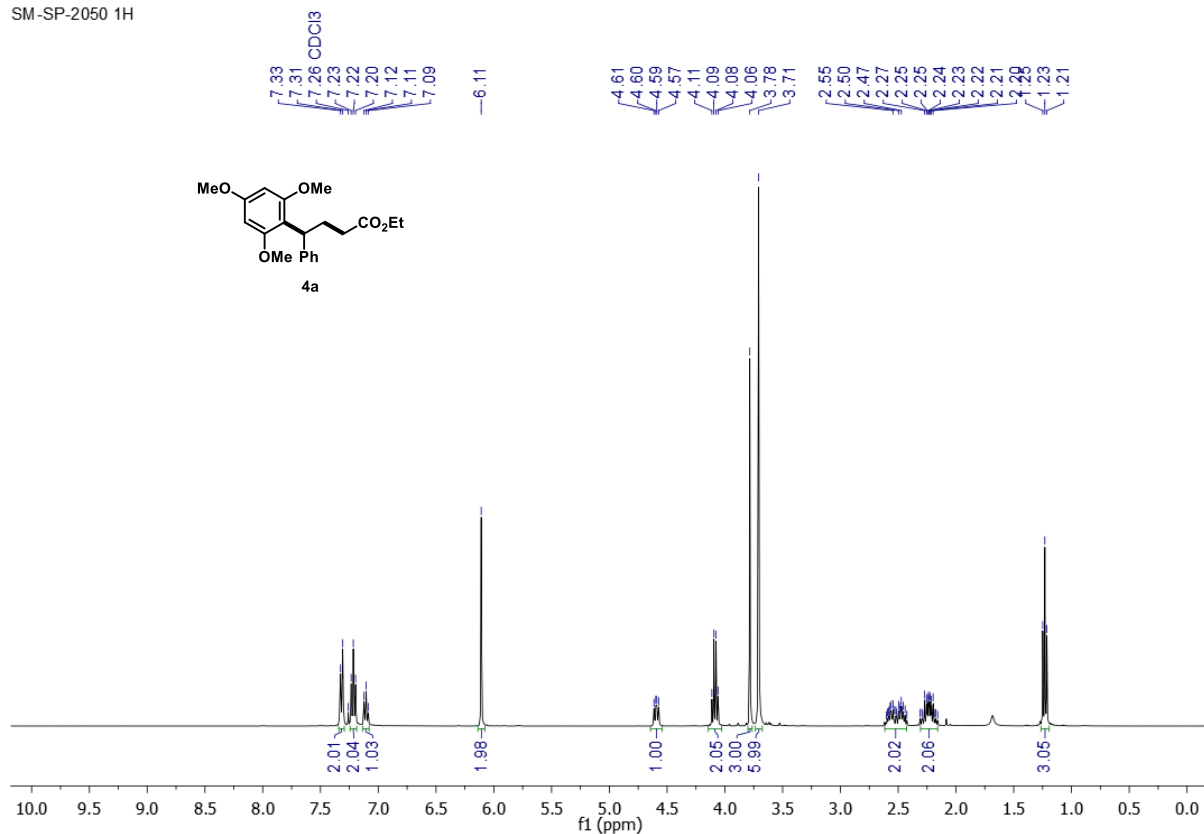
<sup>13</sup>C{<sup>1</sup>H} NMR of **4a''** (101 MHz, CDCl<sub>3</sub>):

SM-SP-2093-I 13C



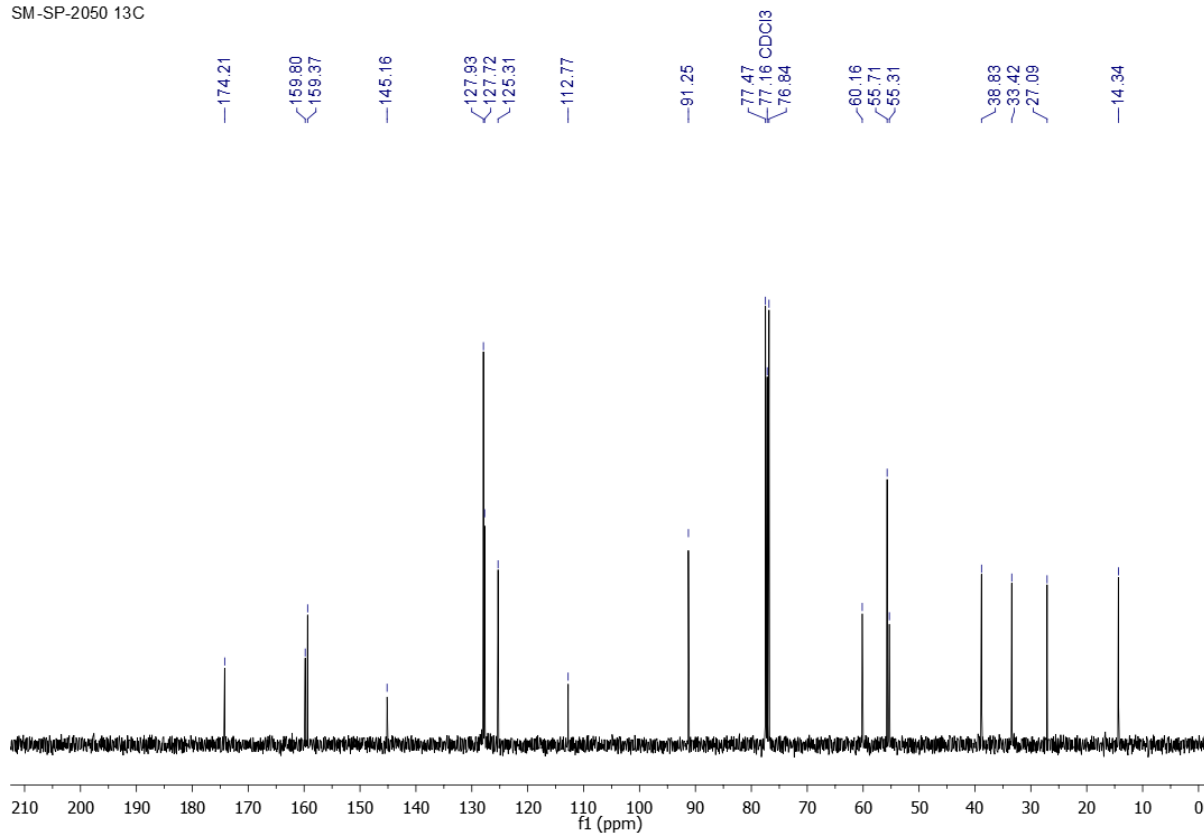
<sup>1</sup>H NMR of **4a** (400 MHz, CDCl<sub>3</sub>):

SM-SP-2050 1H



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

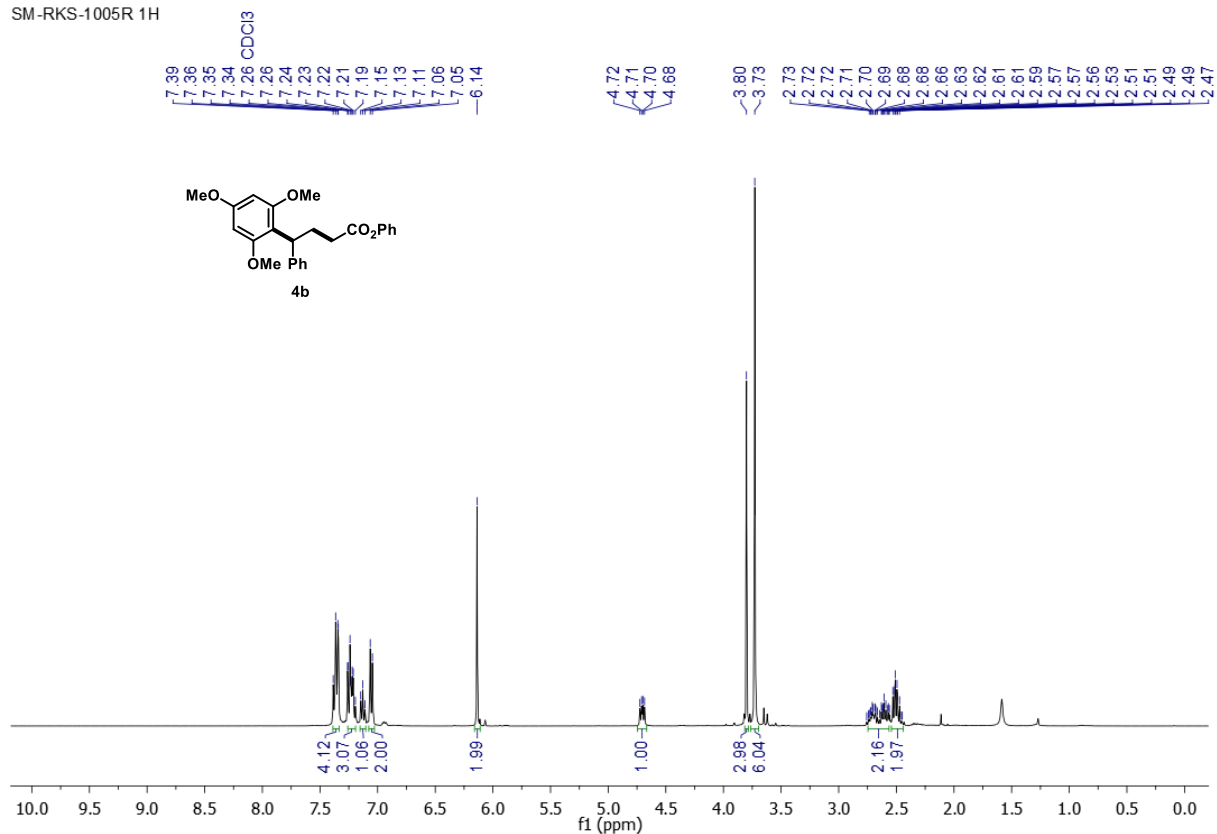
SM-SP-2050 13C





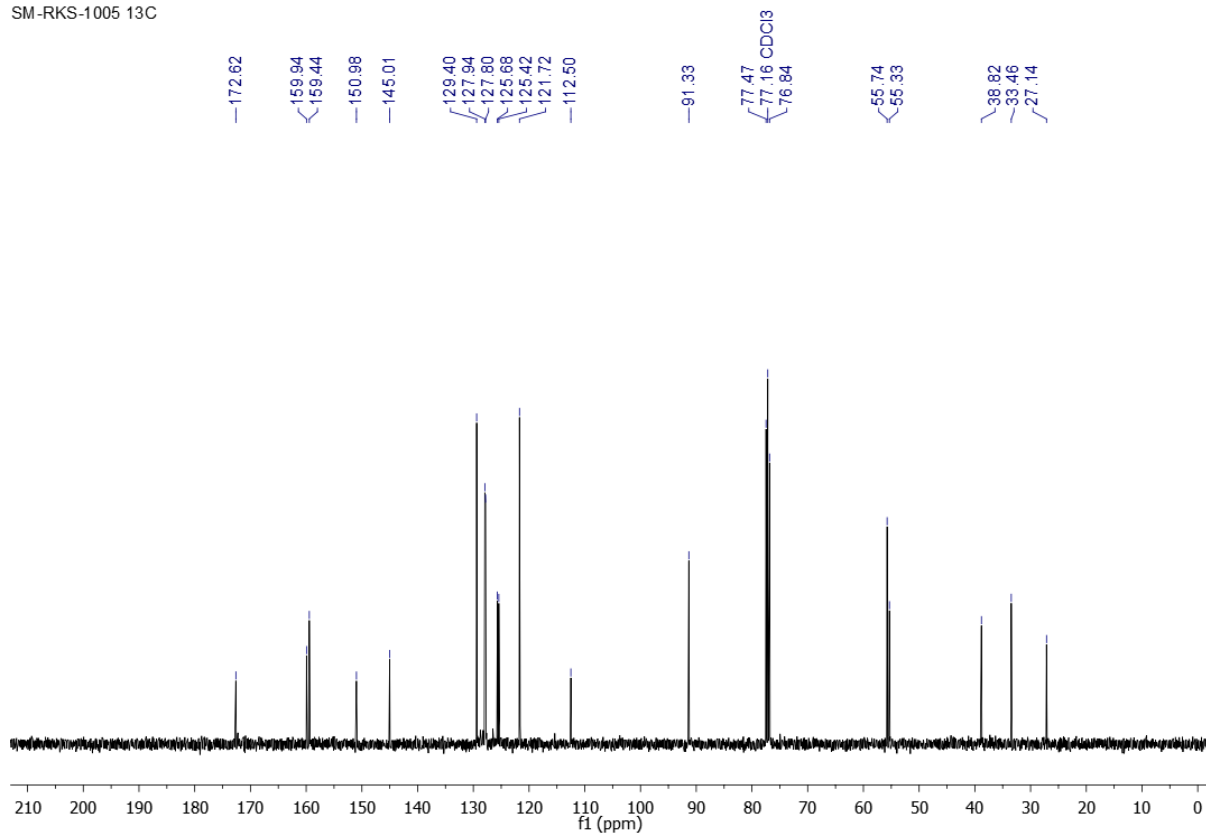
<sup>1</sup>H NMR of **4b** (400 MHz, CDCl<sub>3</sub>):

SM-RKS-1005R 1H

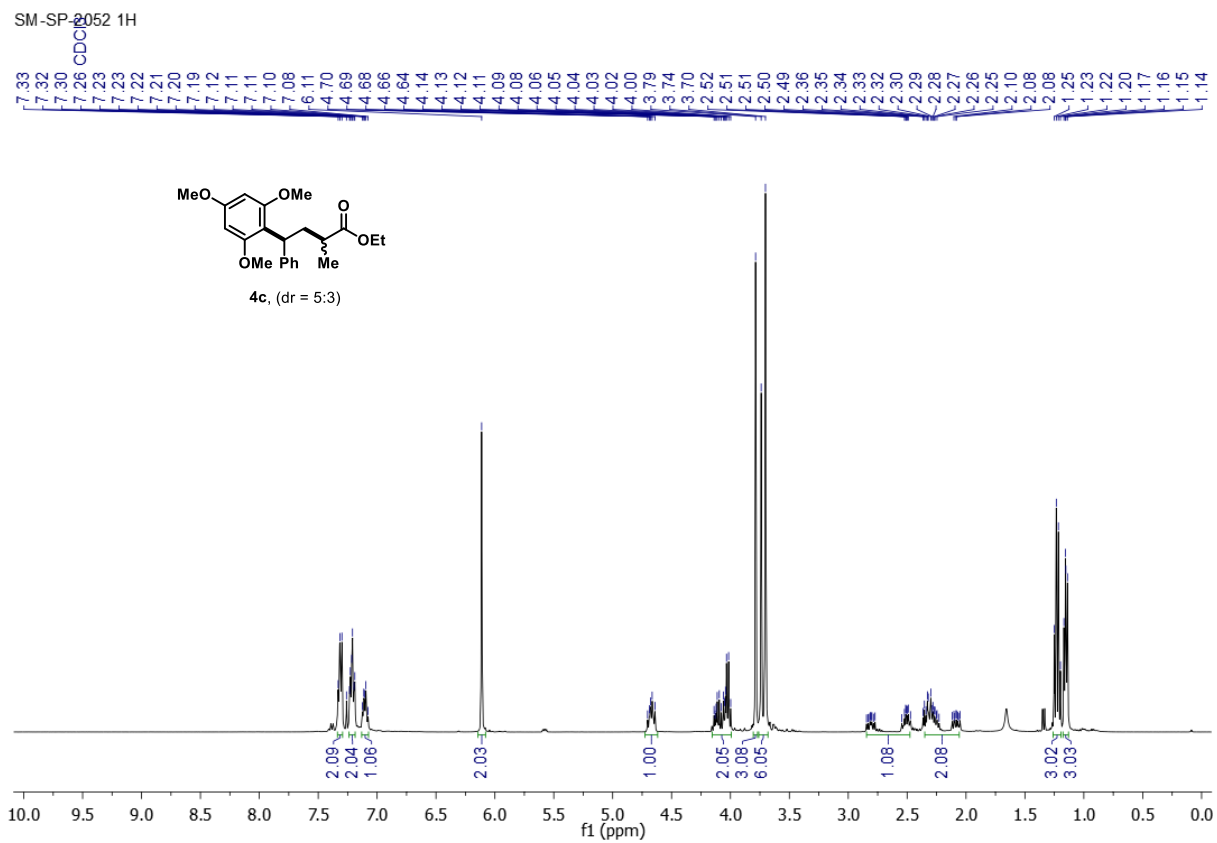


<sup>13</sup>C{<sup>1</sup>H} NMR of **4b** (101 MHz, CDCl<sub>3</sub>):

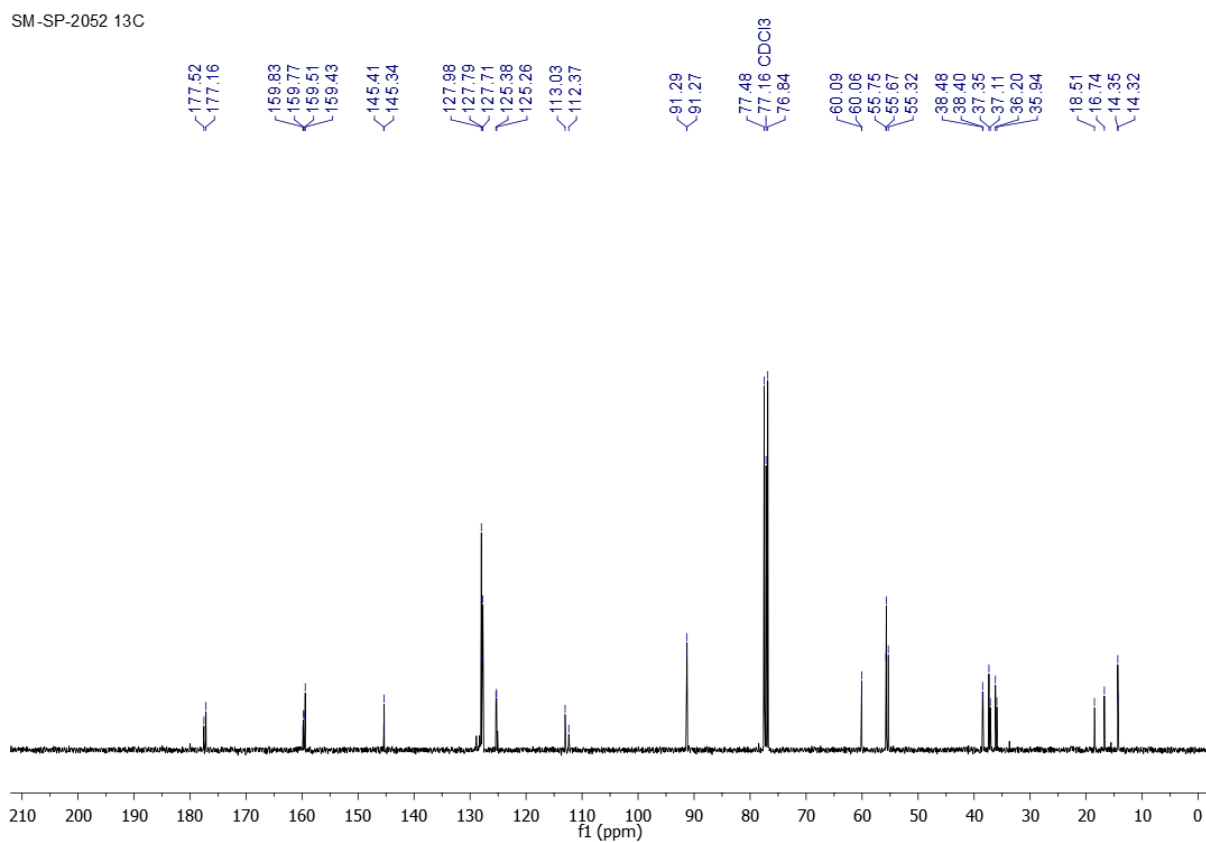
SM-RKS-1005 13C



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

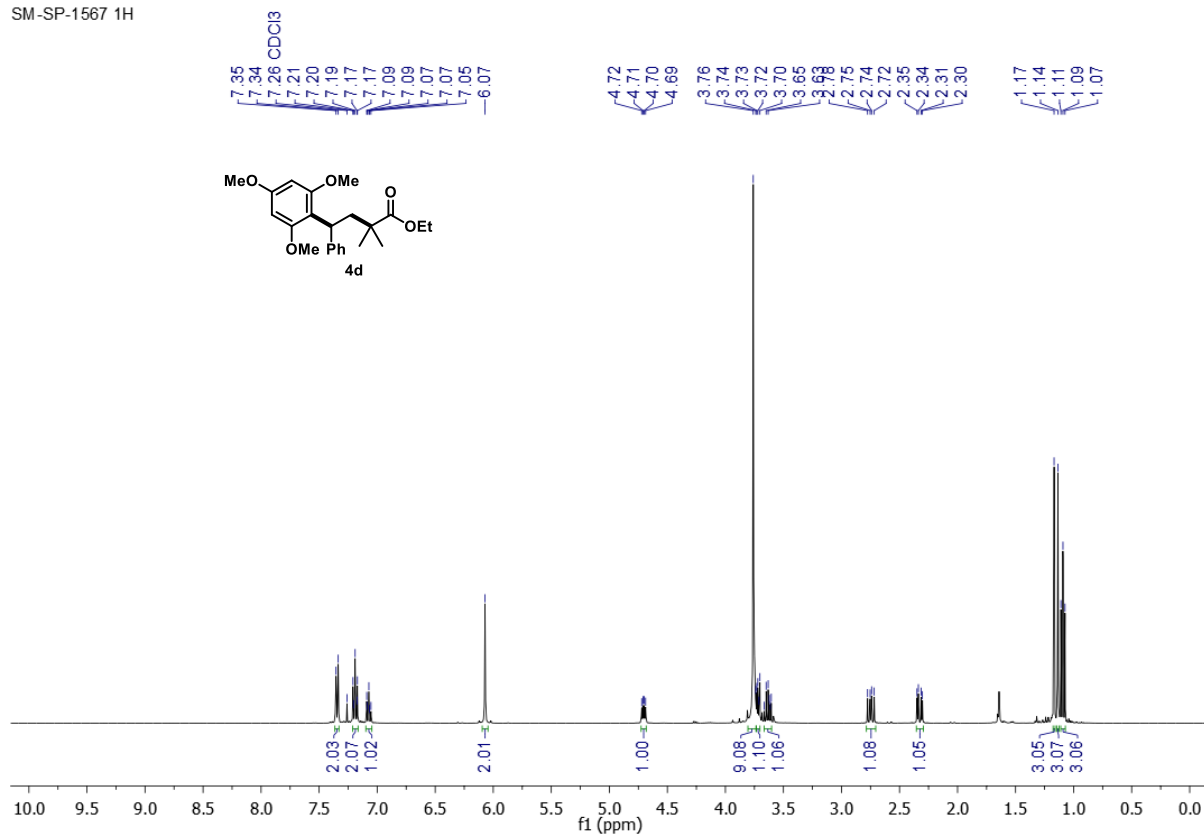


<sup>13</sup>C{<sup>1</sup>H} NMR of **4c** (101 MHz, CDCl<sub>3</sub>):



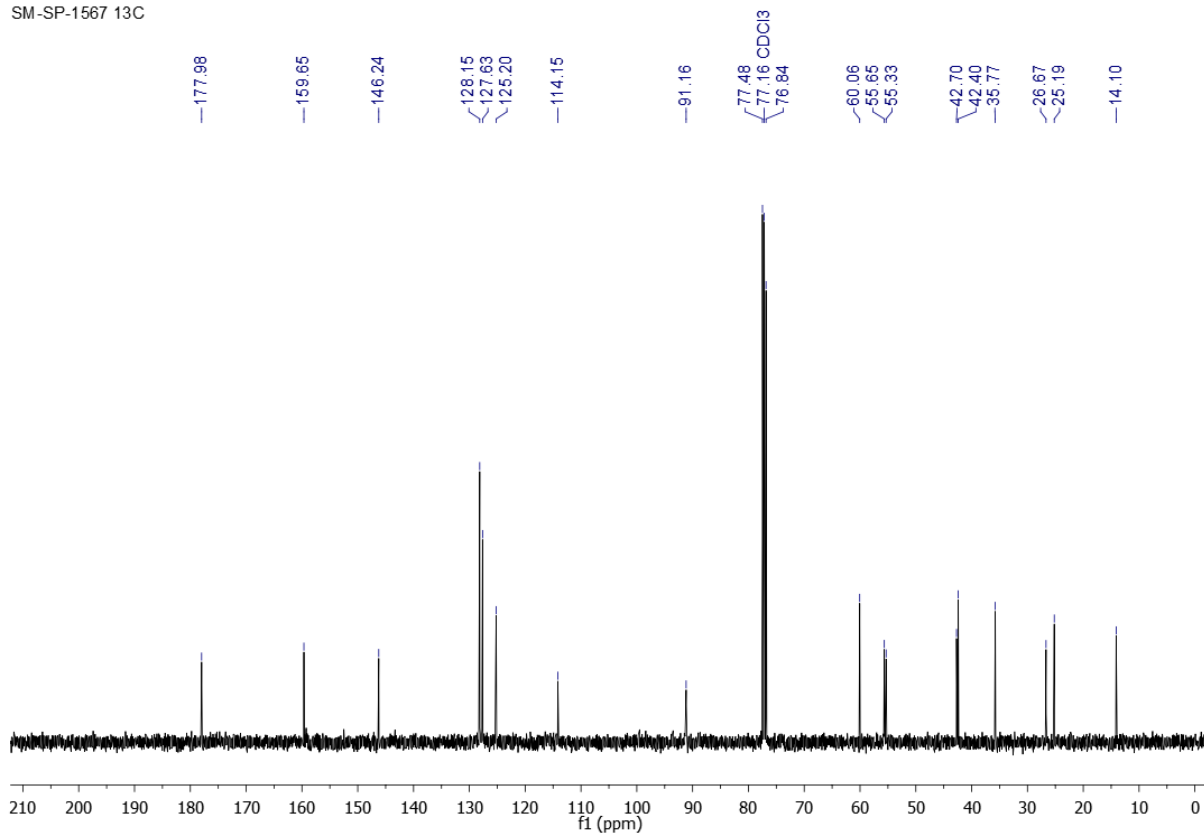
<sup>1</sup>H NMR of **4d** (400 MHz, CDCl<sub>3</sub>):

SM-SP-1567 1H



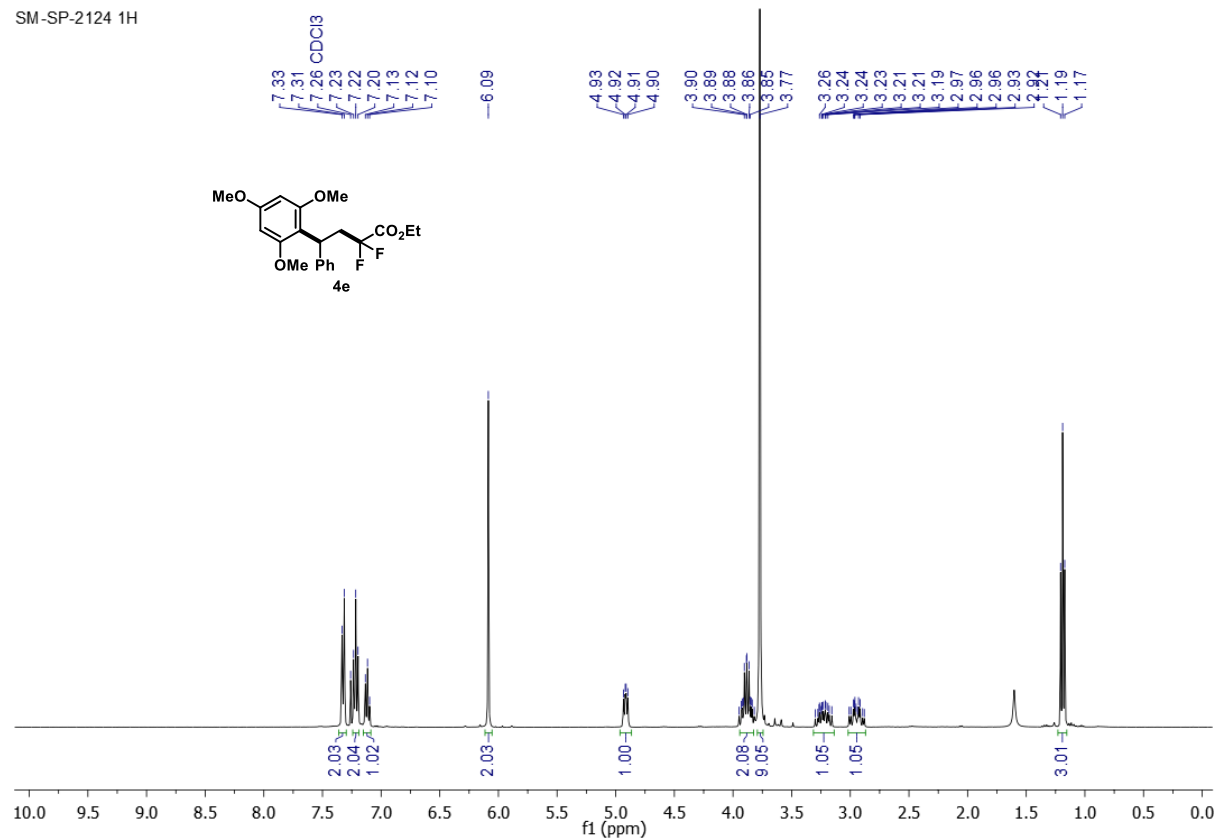
<sup>13</sup>C{<sup>1</sup>H} NMR of **4d** (101 MHz, CDCl<sub>3</sub>):

SM-SP-1567 13C



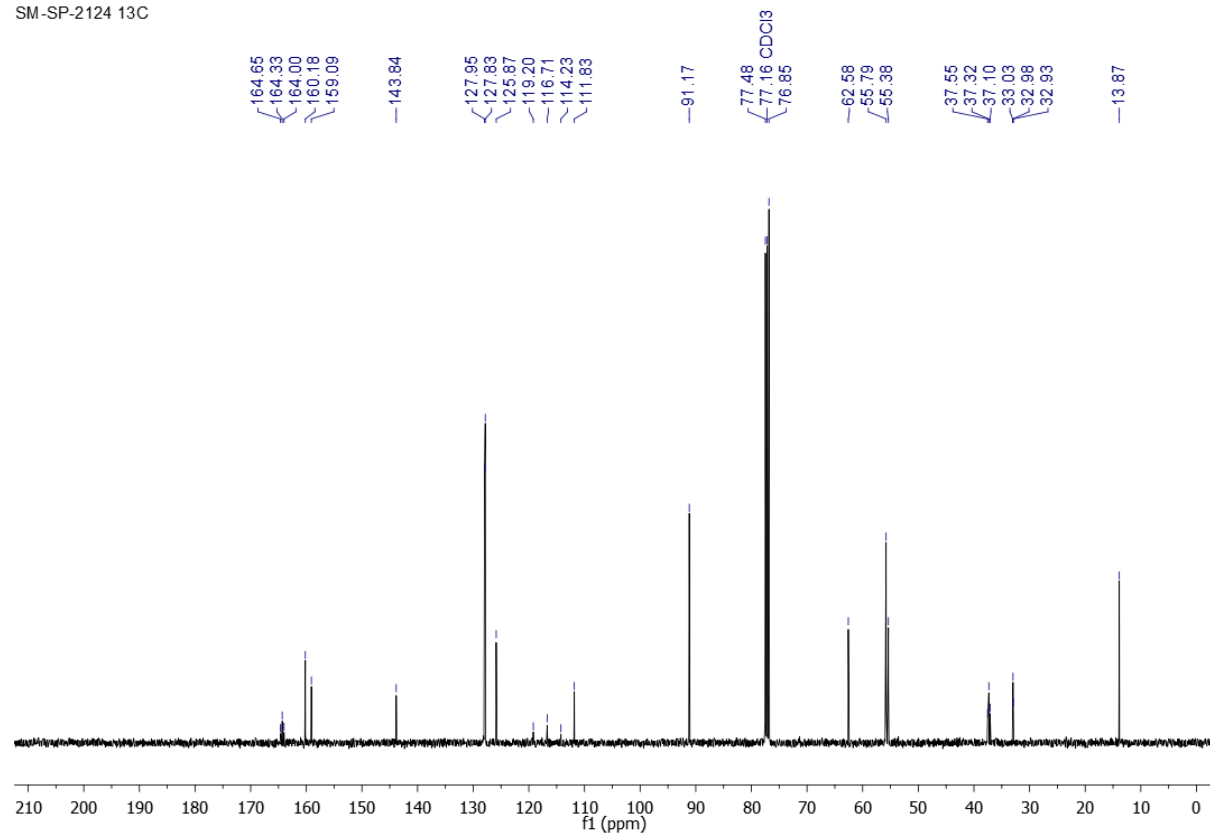
$^1\text{H}$  NMR of **4e** (400 MHz,  $\text{CDCl}_3$ ):

SM-SP-2124 1H



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

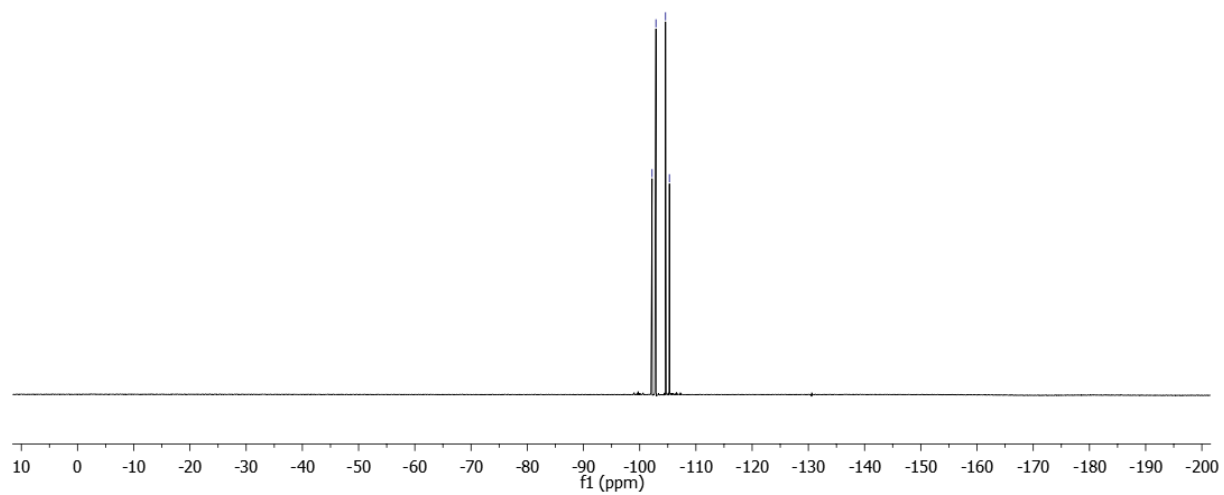
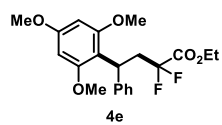
SM-SP-2124 13C



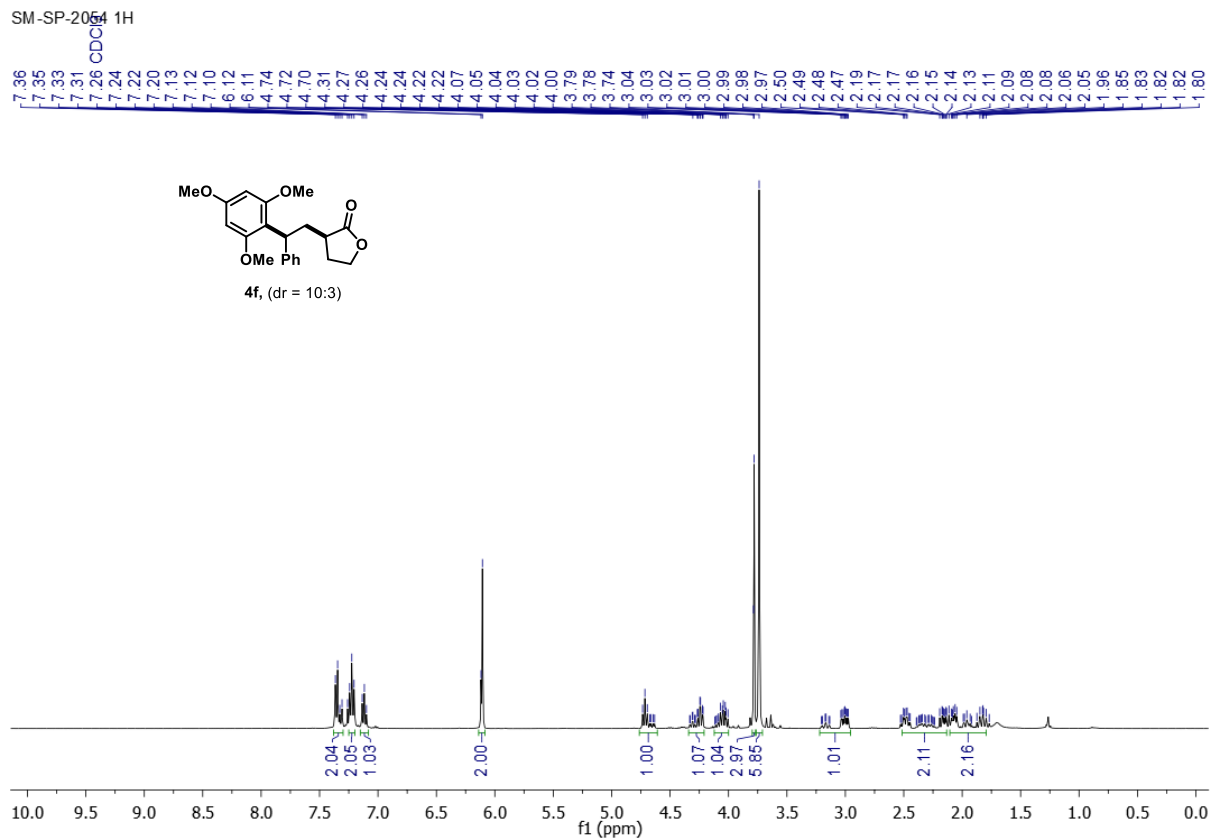
<sup>19</sup>F NMR of **4e** (377 MHz, CDCl<sub>3</sub>):

SM-SP-2124 19F

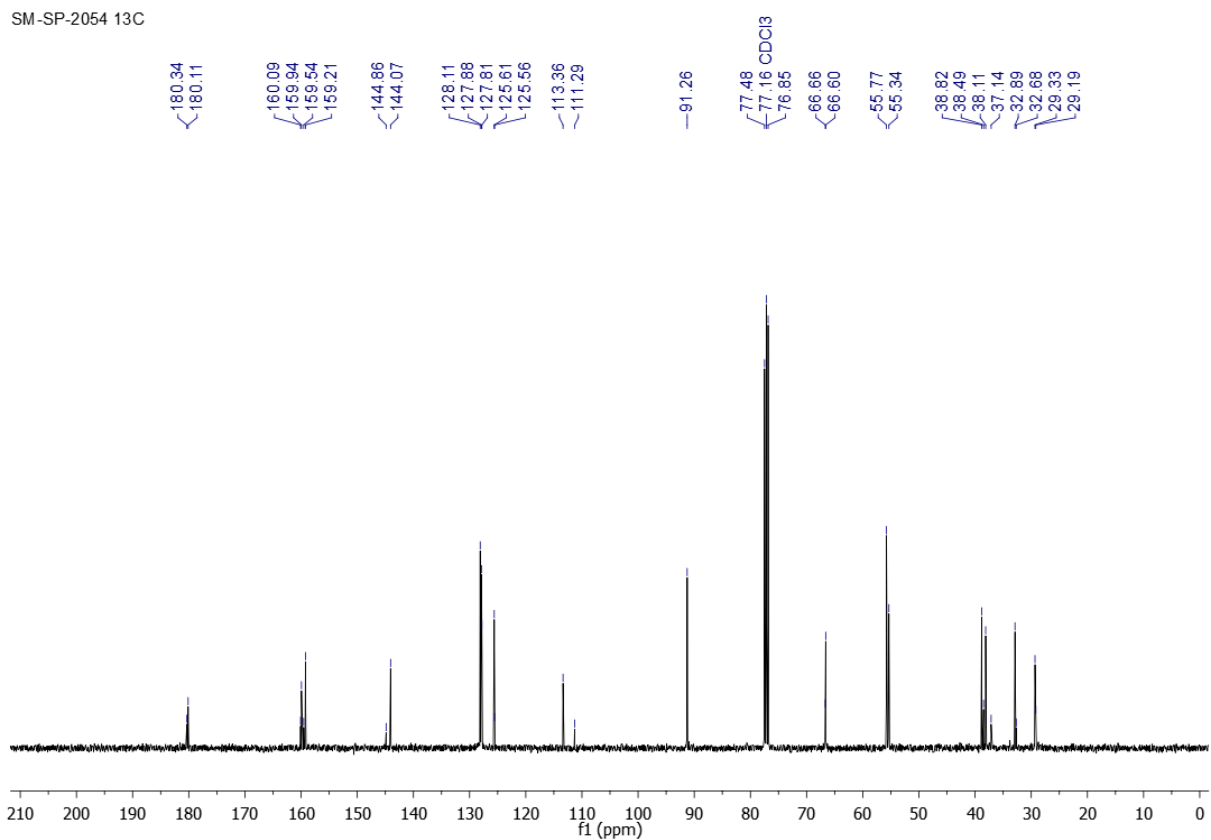
102.21  
102.89  
104.60  
105.28



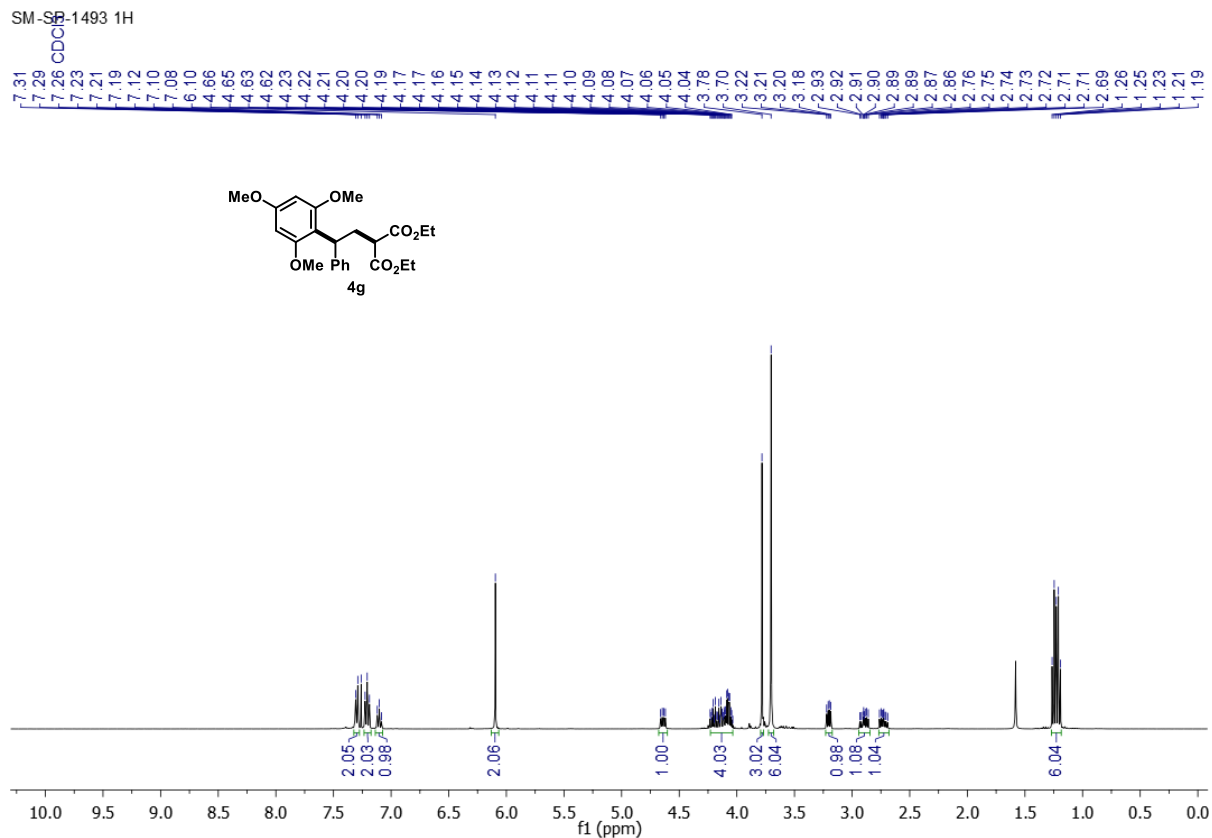
<sup>1</sup>H NMR of **4f** (400 MHz, CDCl<sub>3</sub>):



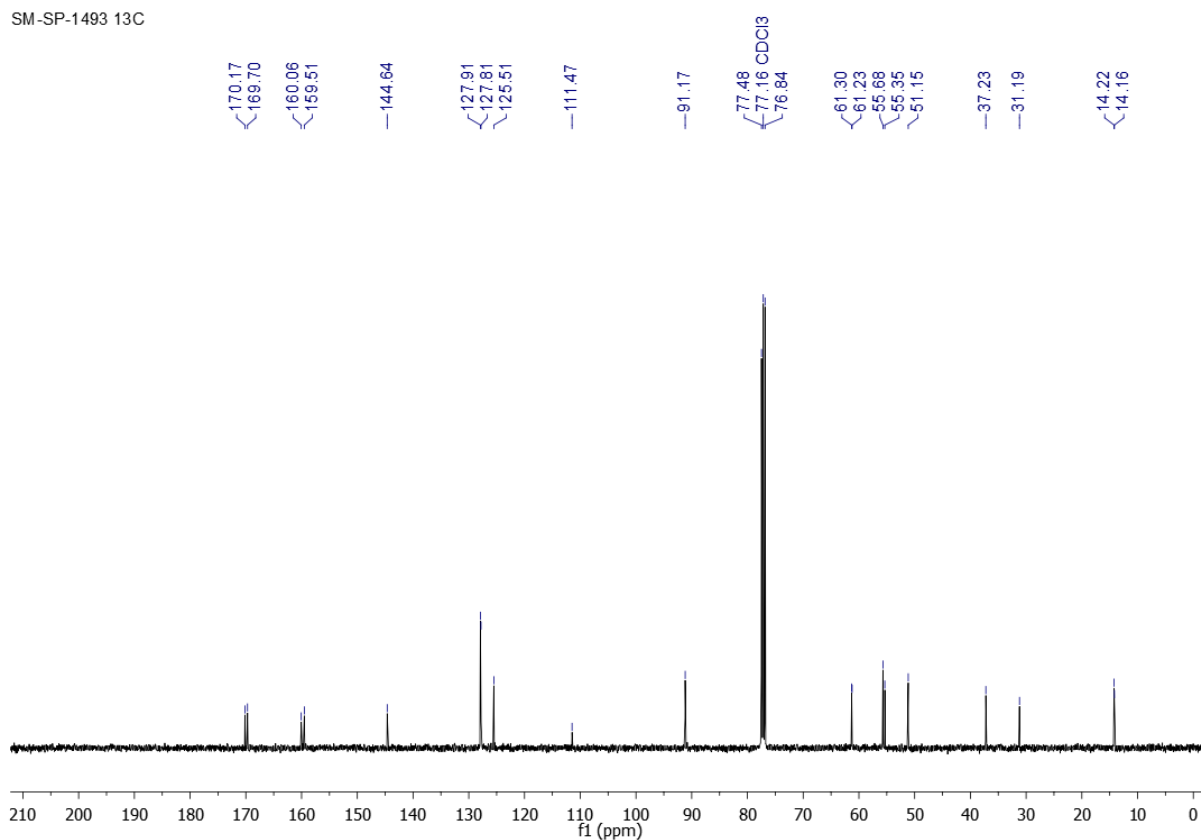
<sup>13</sup>C{<sup>1</sup>H} NMR of **4f** (101 MHz, CDCl<sub>3</sub>):



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

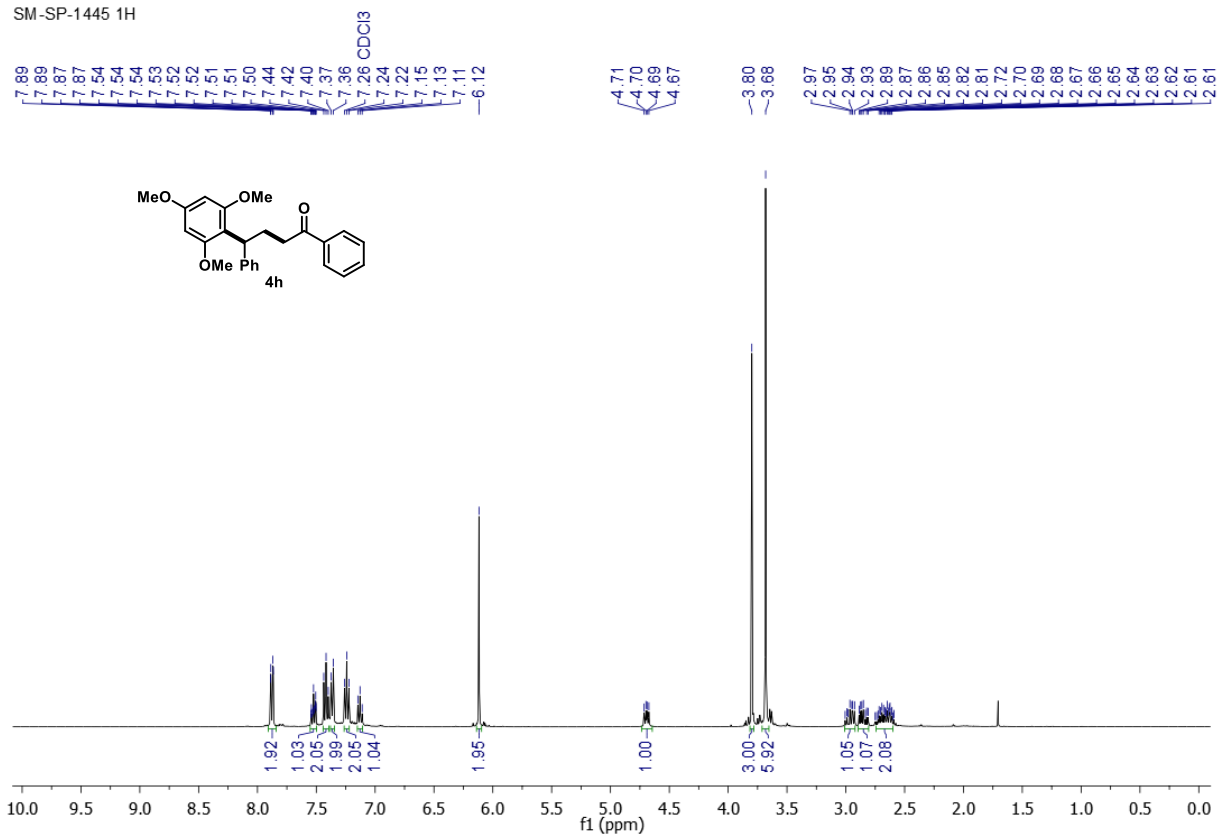


<sup>13</sup>C{<sup>1</sup>H} NMR of **4g** (101 MHz, CDCl<sub>3</sub>):



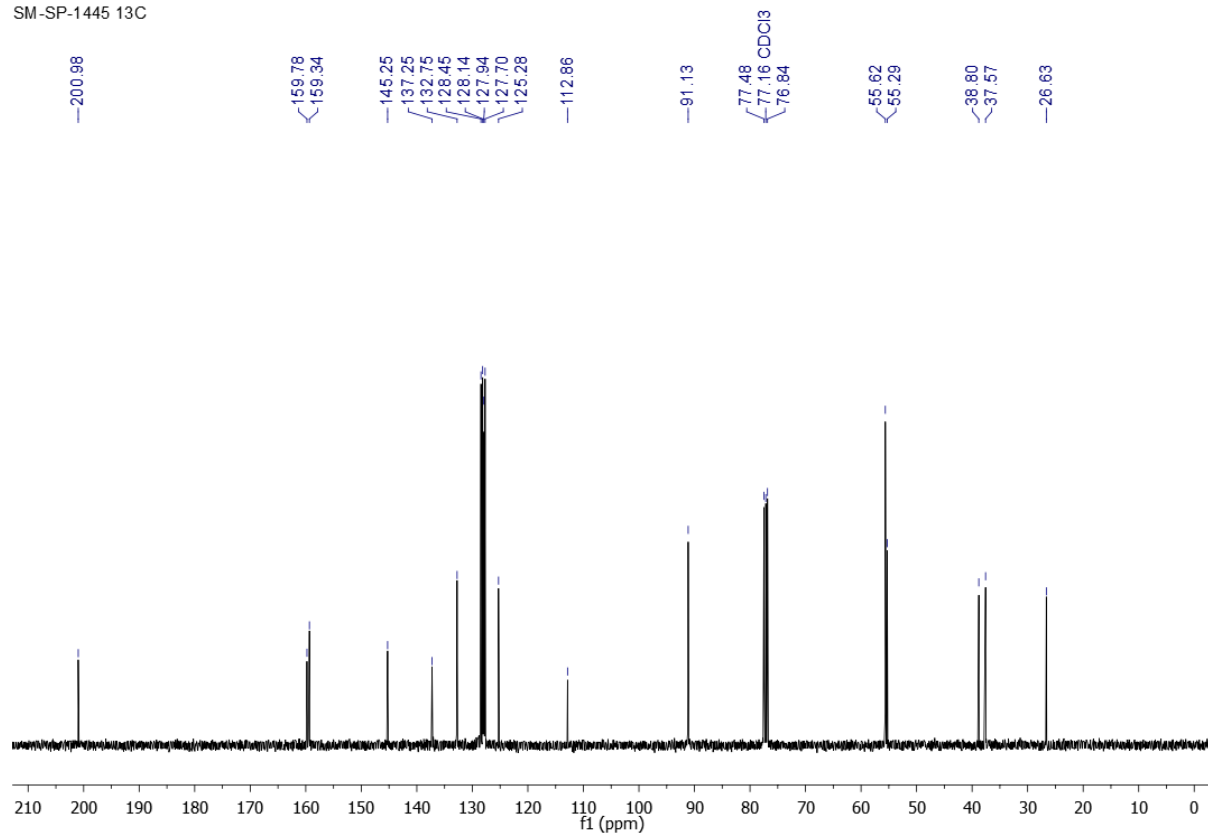
$^1\text{H}$  NMR of **4h** (400 MHz,  $\text{CDCl}_3$ ):

SM-SP-1445 1H



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

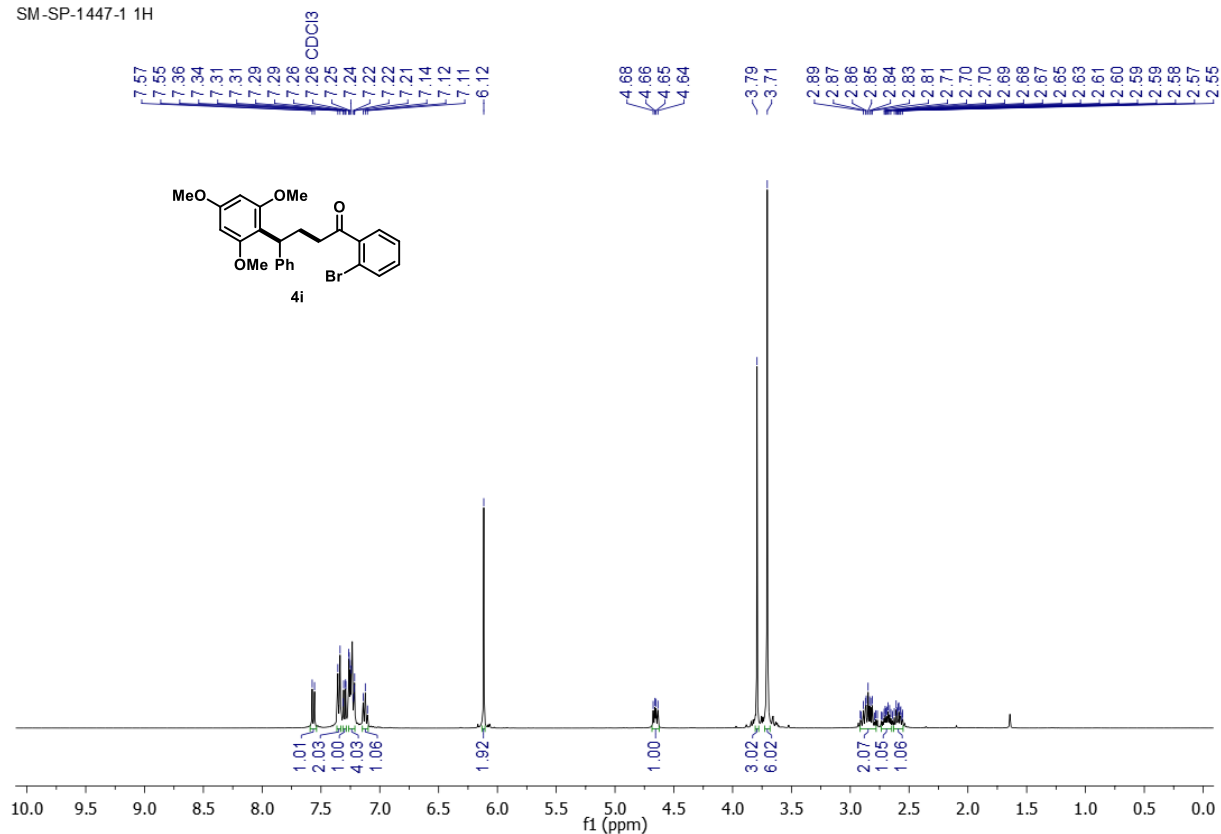
SM-SP-1445 13C





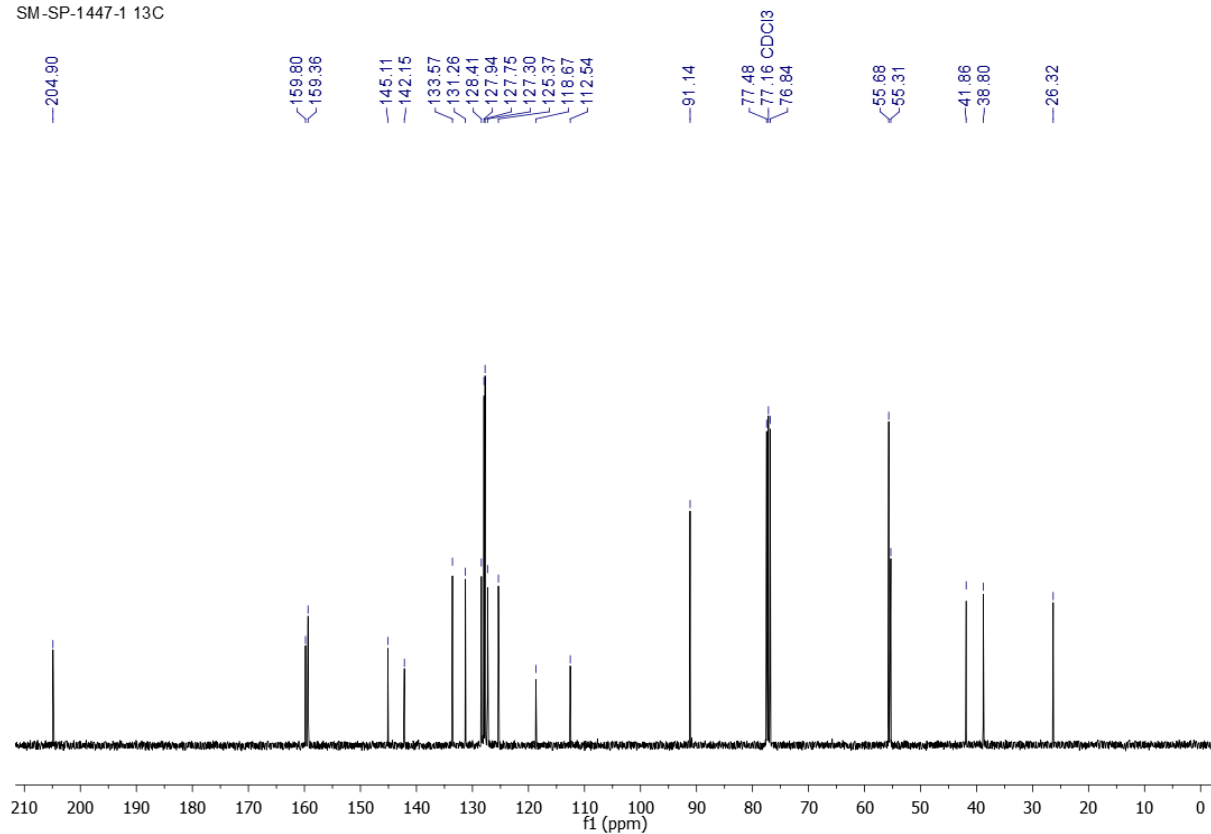
$^1\text{H}$  NMR of **4i** (400 MHz,  $\text{CDCl}_3$ ):

SM-SP-1447-1 1H



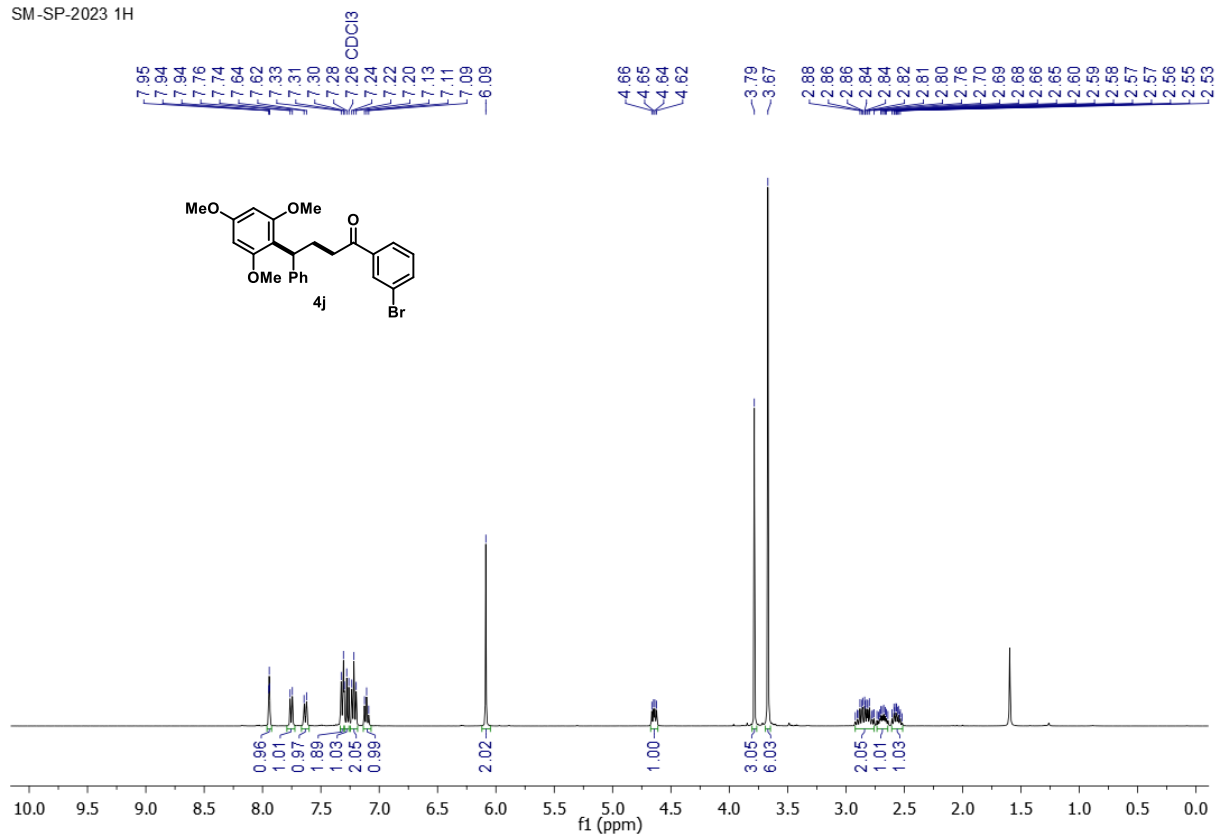
$^{13}\text{C}\{^1\text{H}\}$  NMR of **4i** (101 MHz,  $\text{CDCl}_3$ ):

SM-SP-1447-1 13C



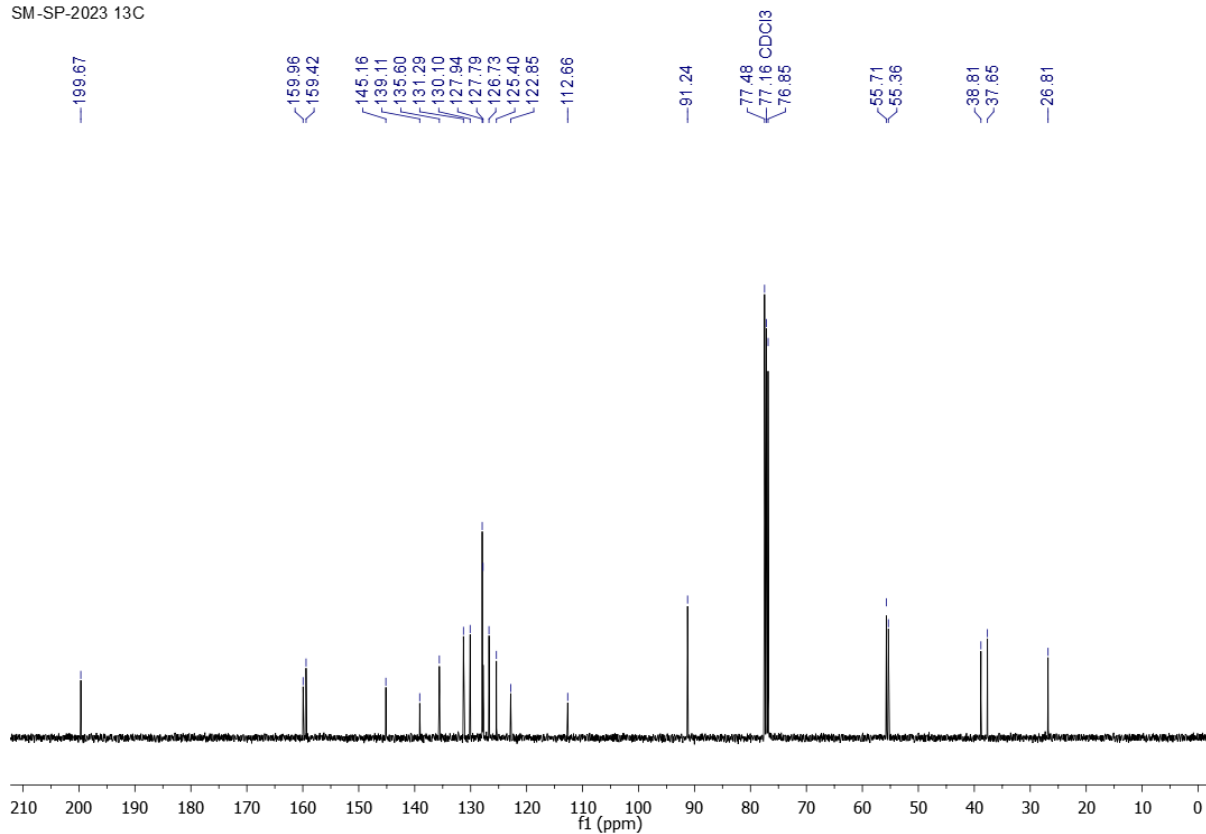
$^1\text{H}$  NMR of **4j** (400 MHz,  $\text{CDCl}_3$ ):

SM-SP-2023 1H



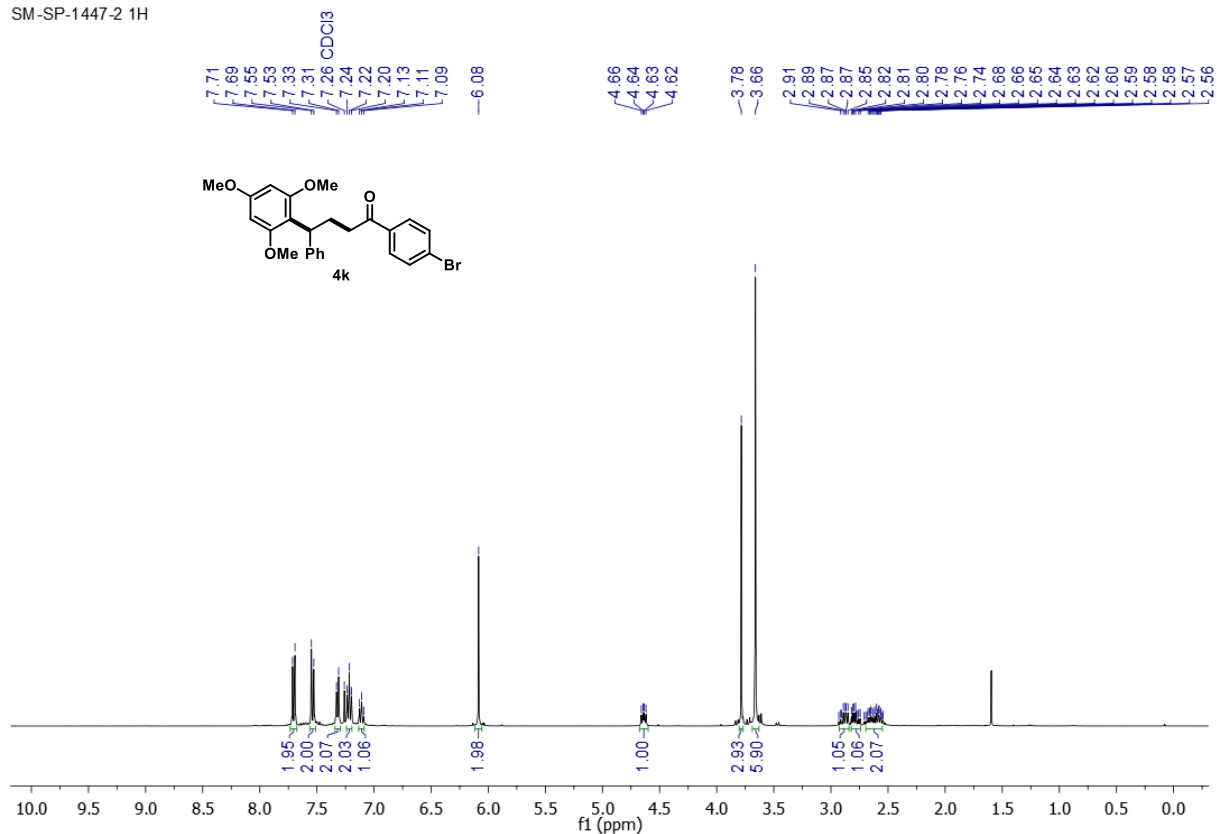
$^{13}\text{C}\{^1\text{H}\}$  NMR of **4j** (101 MHz,  $\text{CDCl}_3$ ):

SM-SP-2023 13C



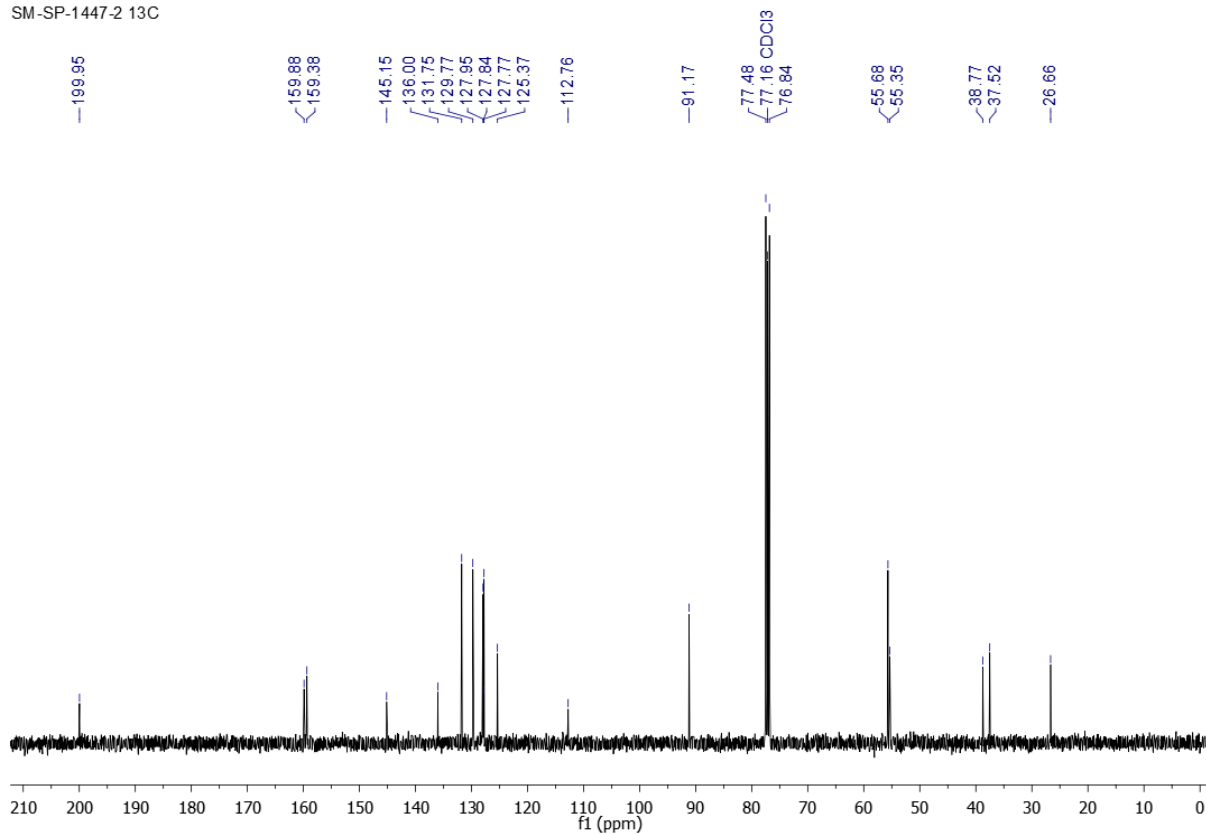
<sup>1</sup>H NMR of **4k** (400 MHz, CDCl<sub>3</sub>):

SM-SP-1447-2 1H



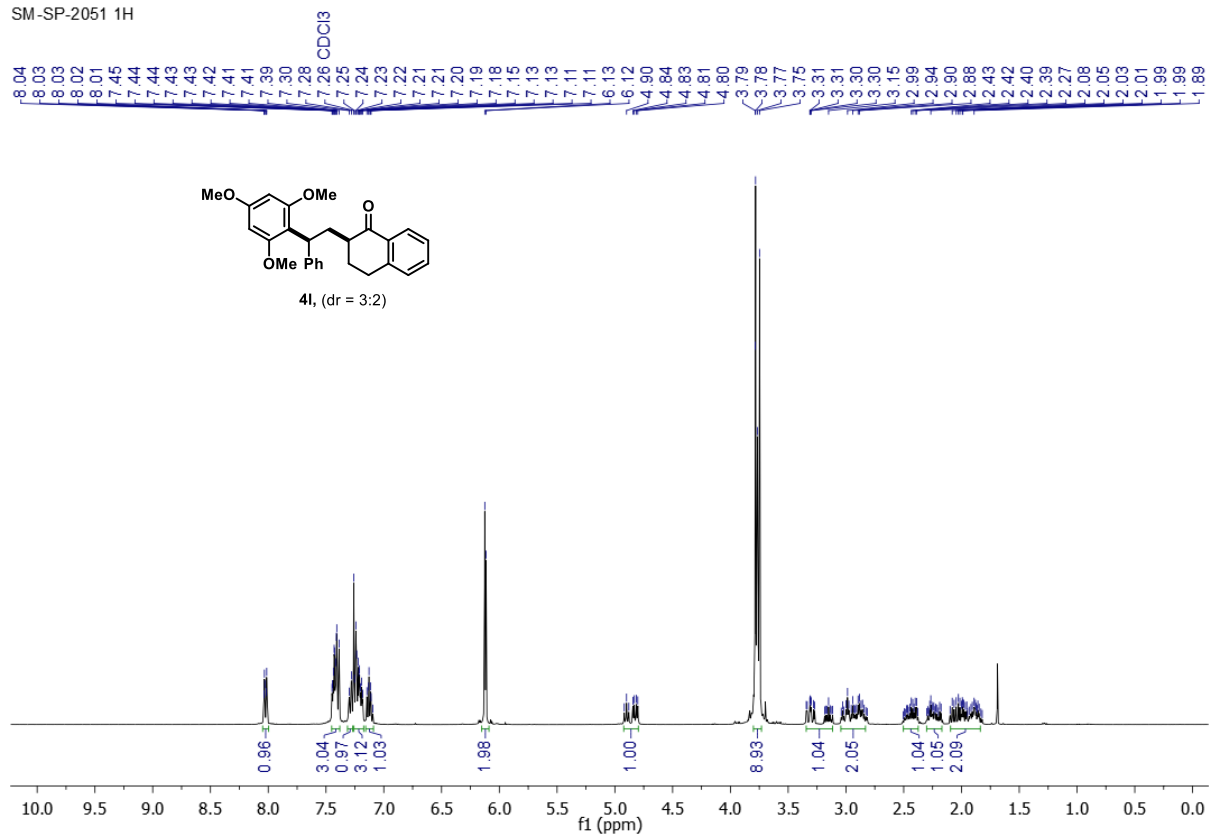
<sup>13</sup>C{<sup>1</sup>H} NMR of **4k** (101 MHz, CDCl<sub>3</sub>):

SM-SP-1447-2 13C



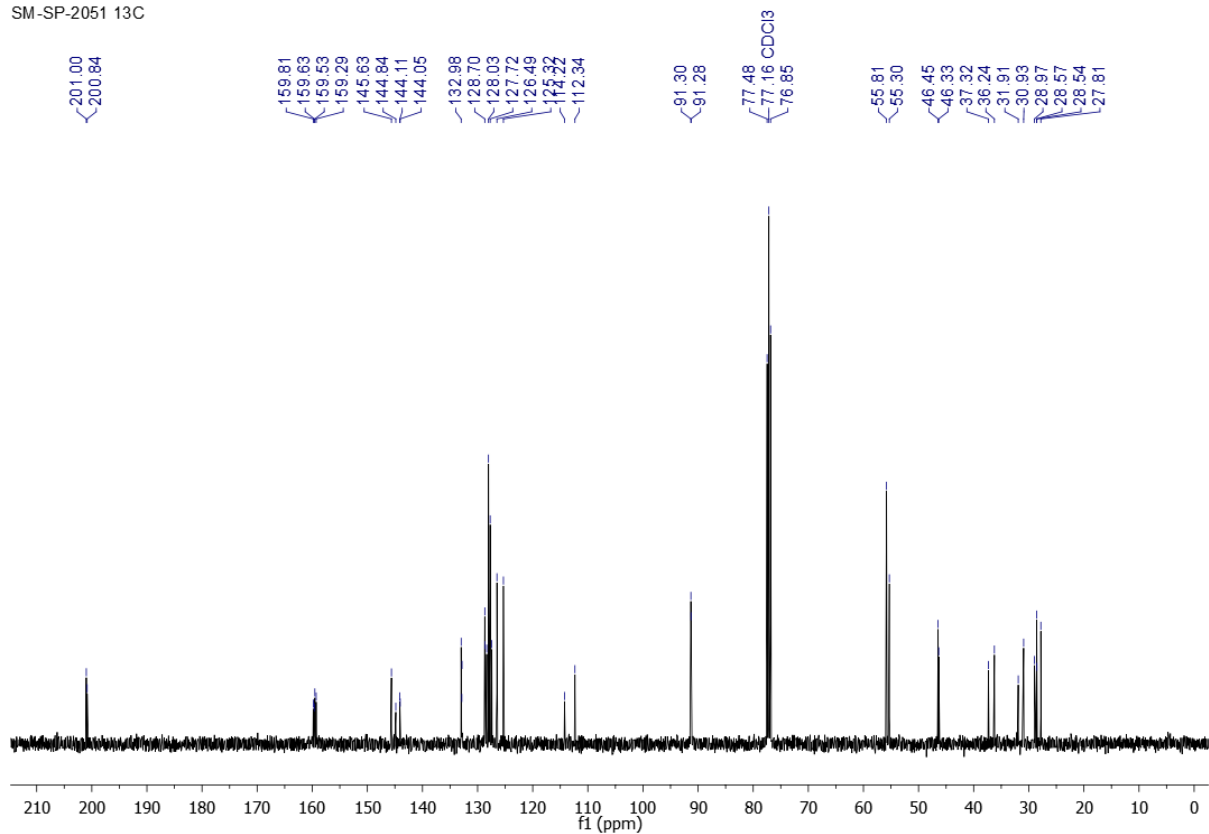
$^1\text{H}$  NMR of **4I** (400 MHz,  $\text{CDCl}_3$ ):

SM-SP-2051 1H



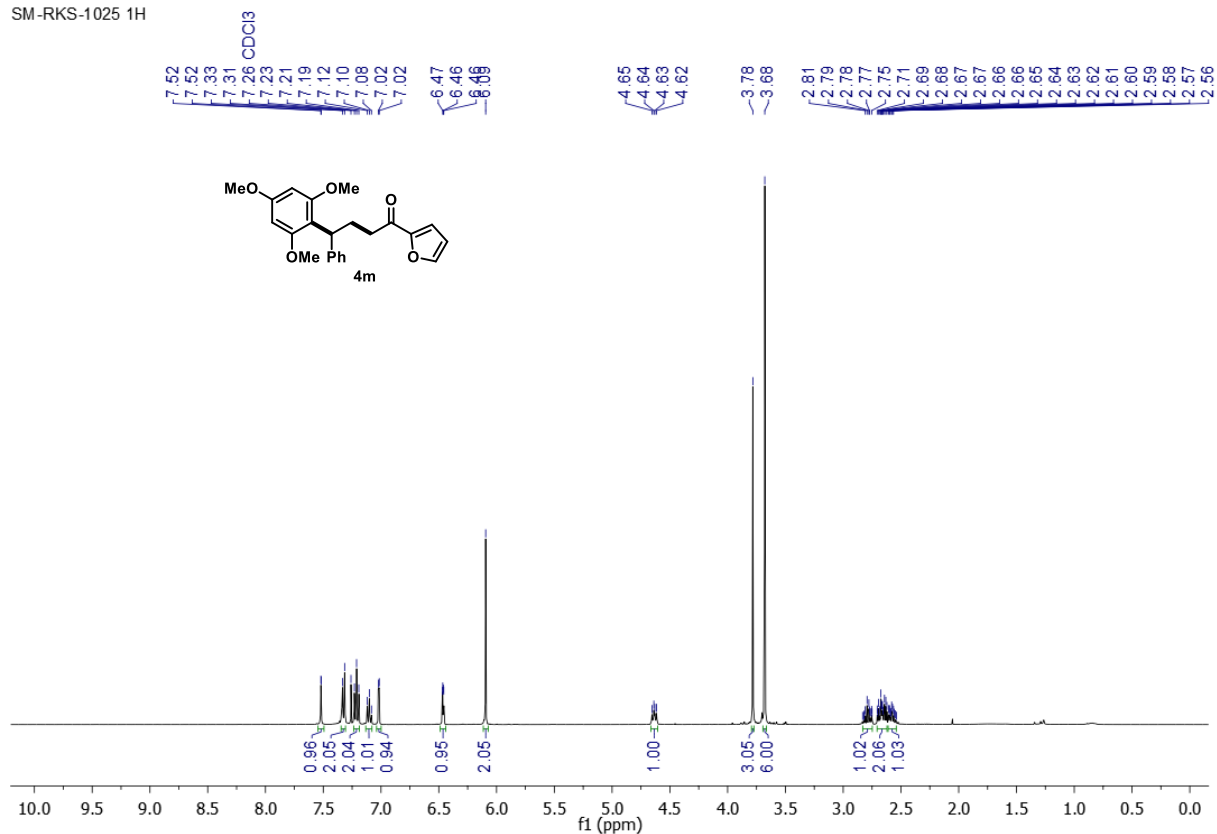
$^{13}\text{C}\{^1\text{H}\}$  NMR of **4I** (101 MHz,  $\text{CDCl}_3$ ):

SM-SP-2051 13C



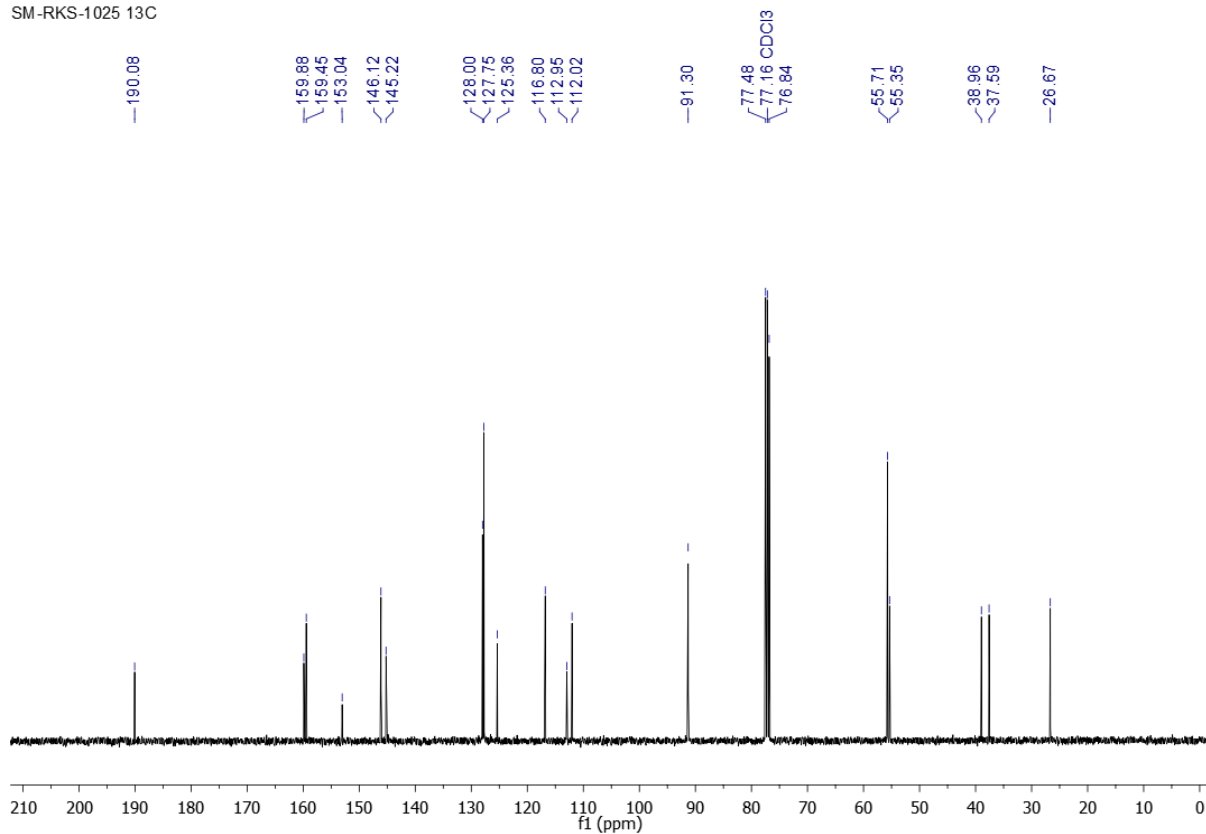
<sup>1</sup>H NMR of **4m** (400 MHz, CDCl<sub>3</sub>):

SM-RKS-1025 1H



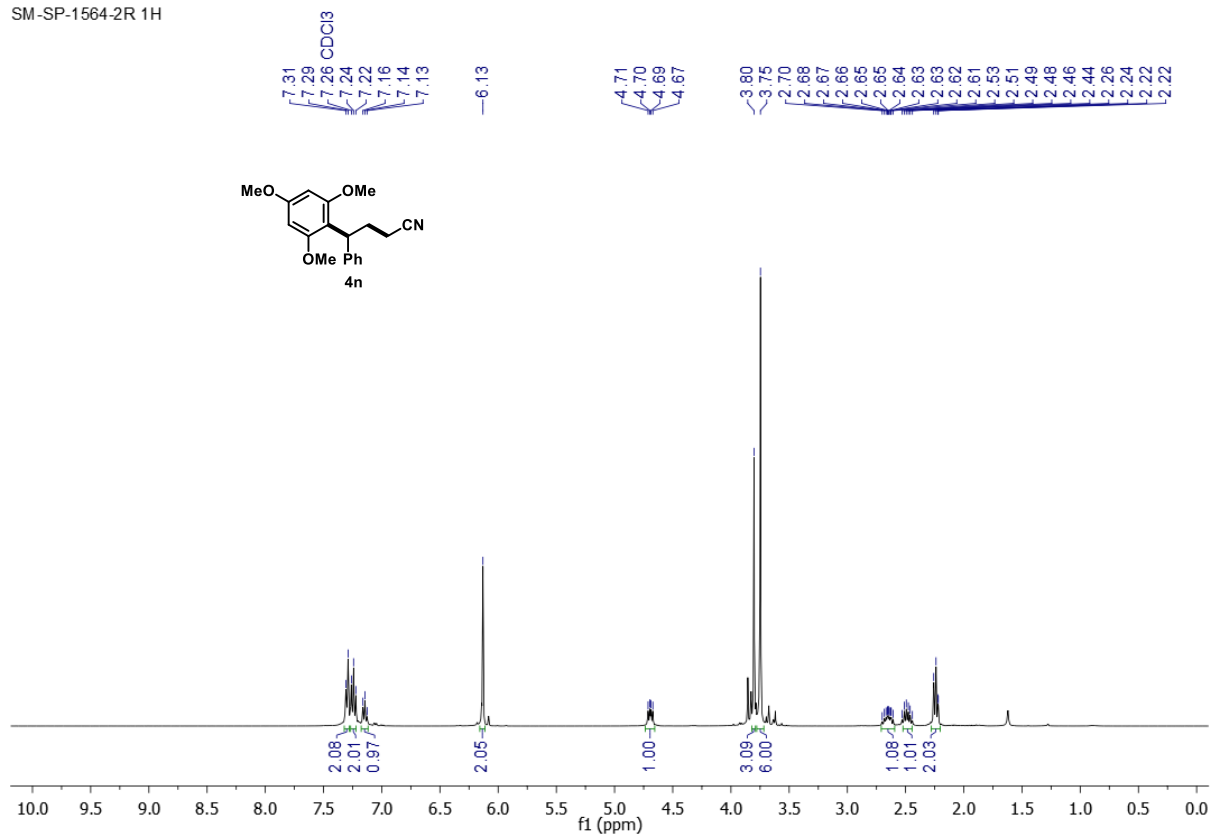
<sup>13</sup>C{<sup>1</sup>H} NMR of **4m** (101 MHz, CDCl<sub>3</sub>):

SM-RKS-1025 13C



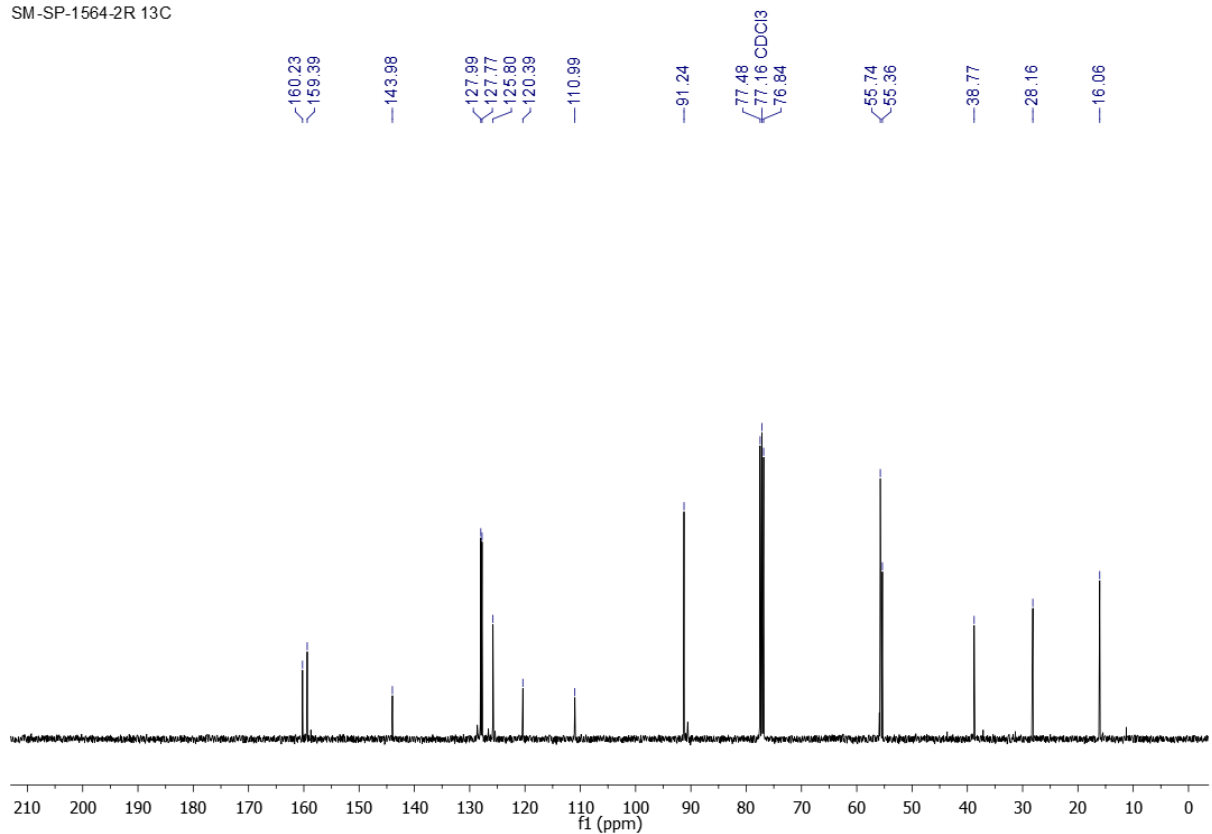
$^1\text{H}$  NMR of **4n** (400 MHz,  $\text{CDCl}_3$ ):

SM-SP-1564-2R 1H



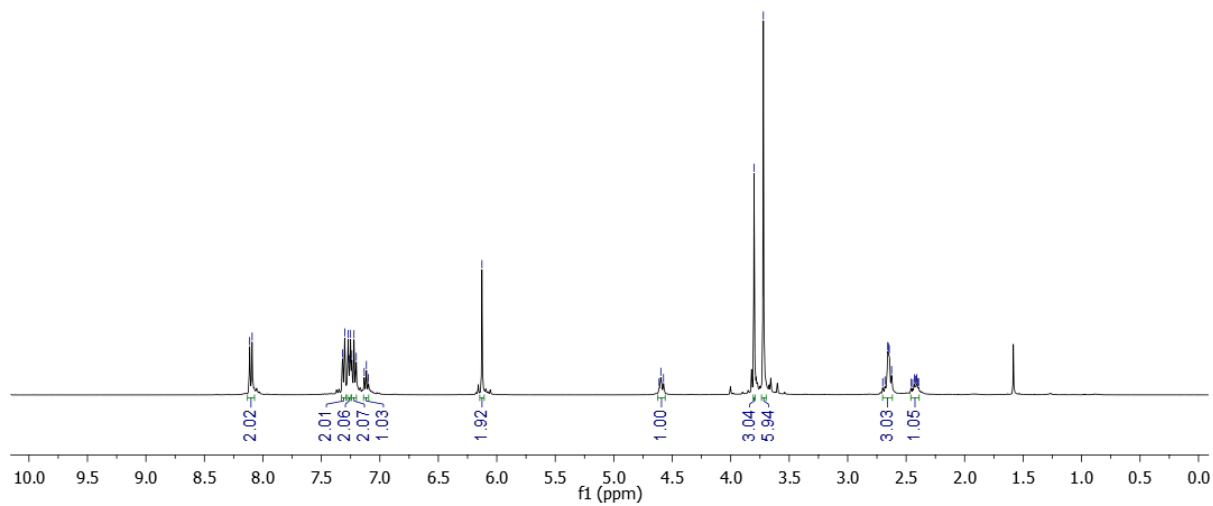
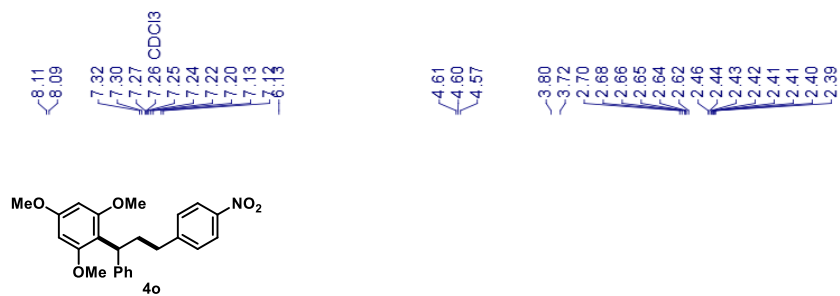
$^{13}\text{C}\{^1\text{H}\}$  NMR of **4n** (101 MHz,  $\text{CDCl}_3$ ):

SM-SP-1564-2R 13C



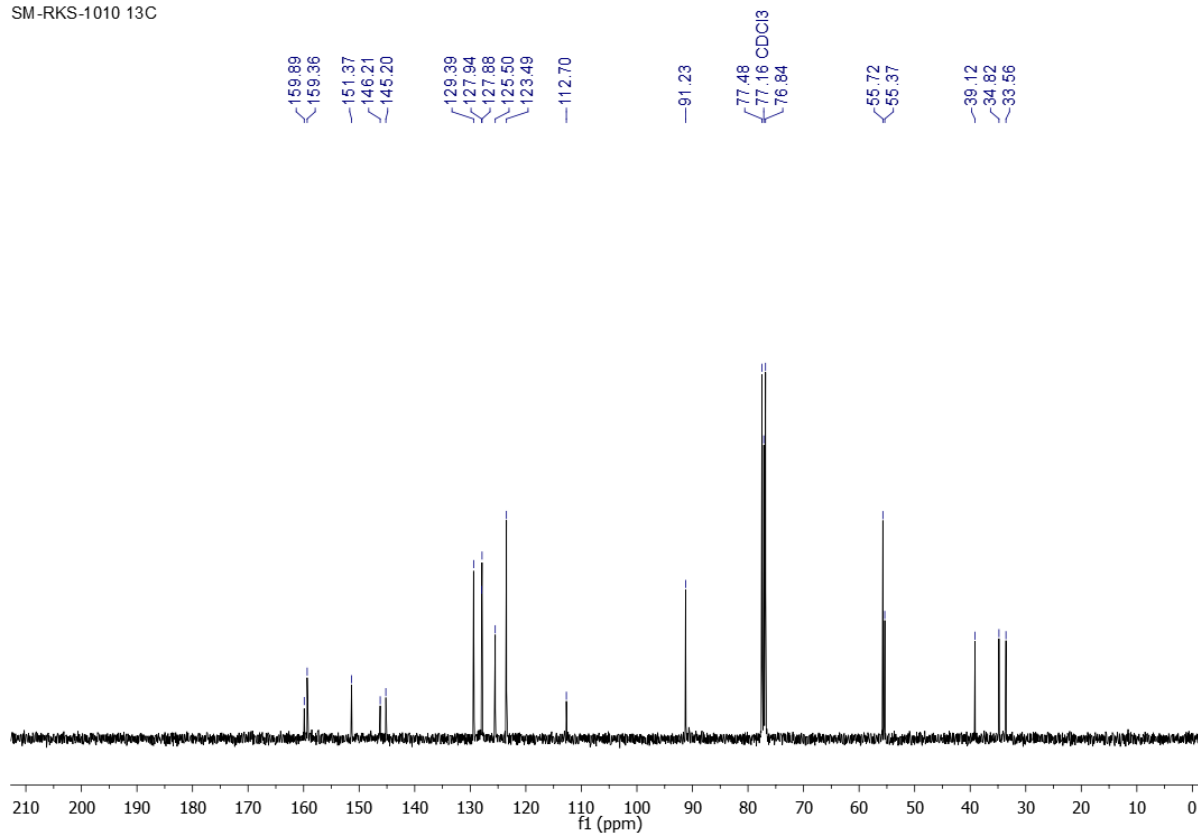
<sup>1</sup>H NMR of **4o** (400 MHz, CDCl<sub>3</sub>):

SM-RKS-1010 1H



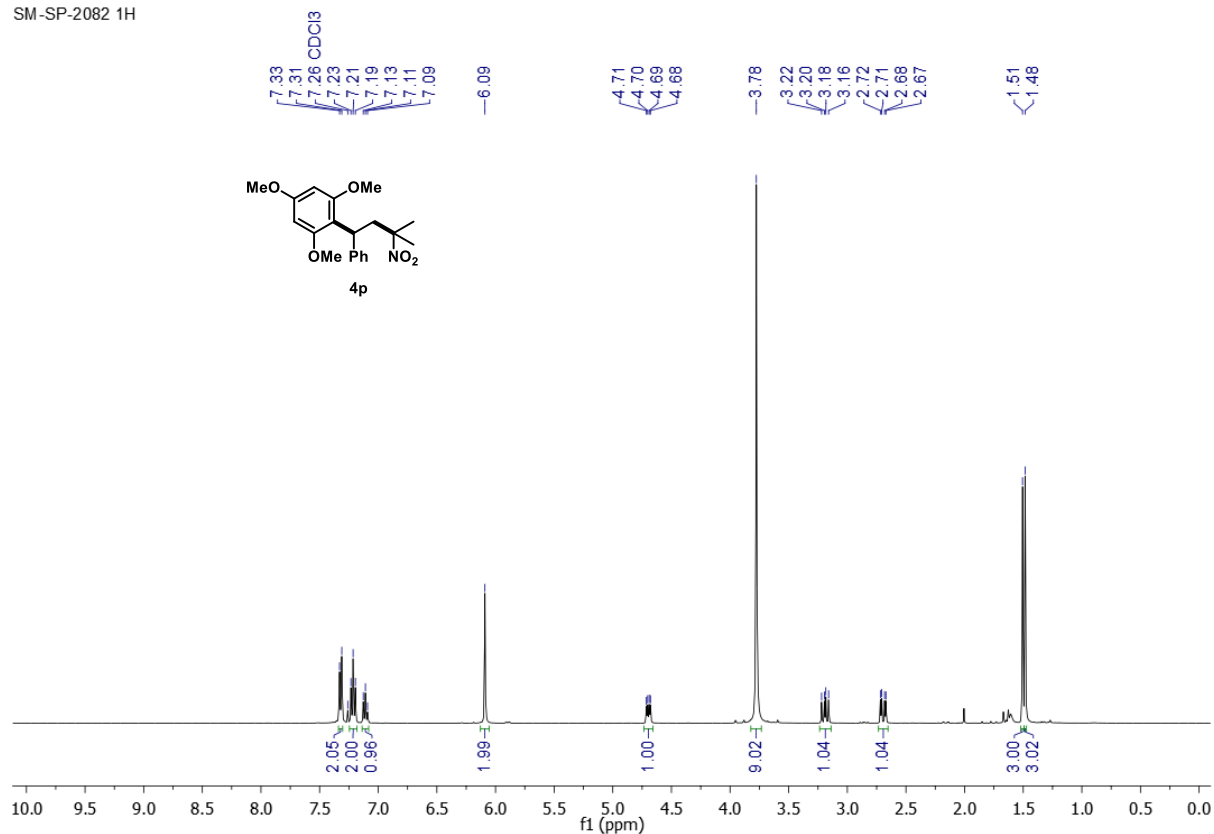
<sup>13</sup>C{<sup>1</sup>H} NMR of **4o** (101 MHz, CDCl<sub>3</sub>):

SM-RKS-1010 13C



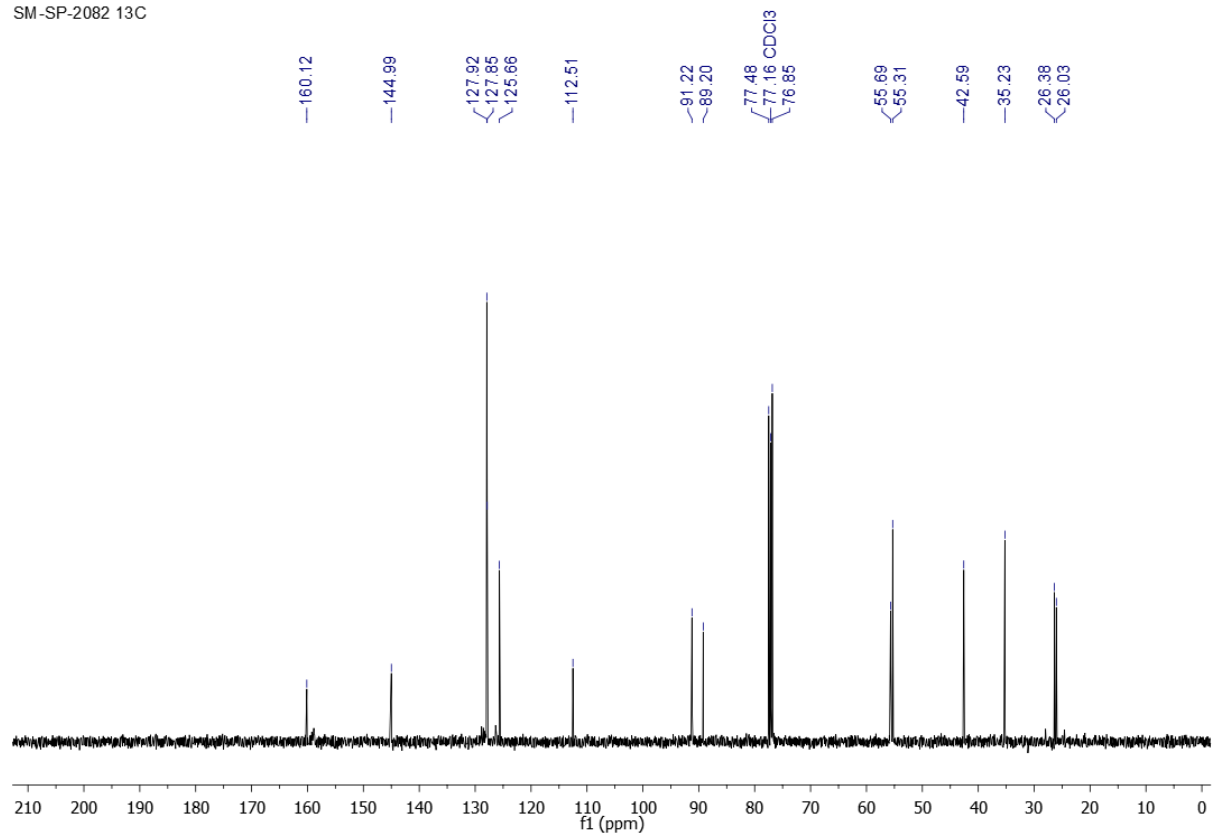
$^1\text{H}$  NMR of **4p** (400 MHz,  $\text{CDCl}_3$ ):

SM-SP-2082 1H



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

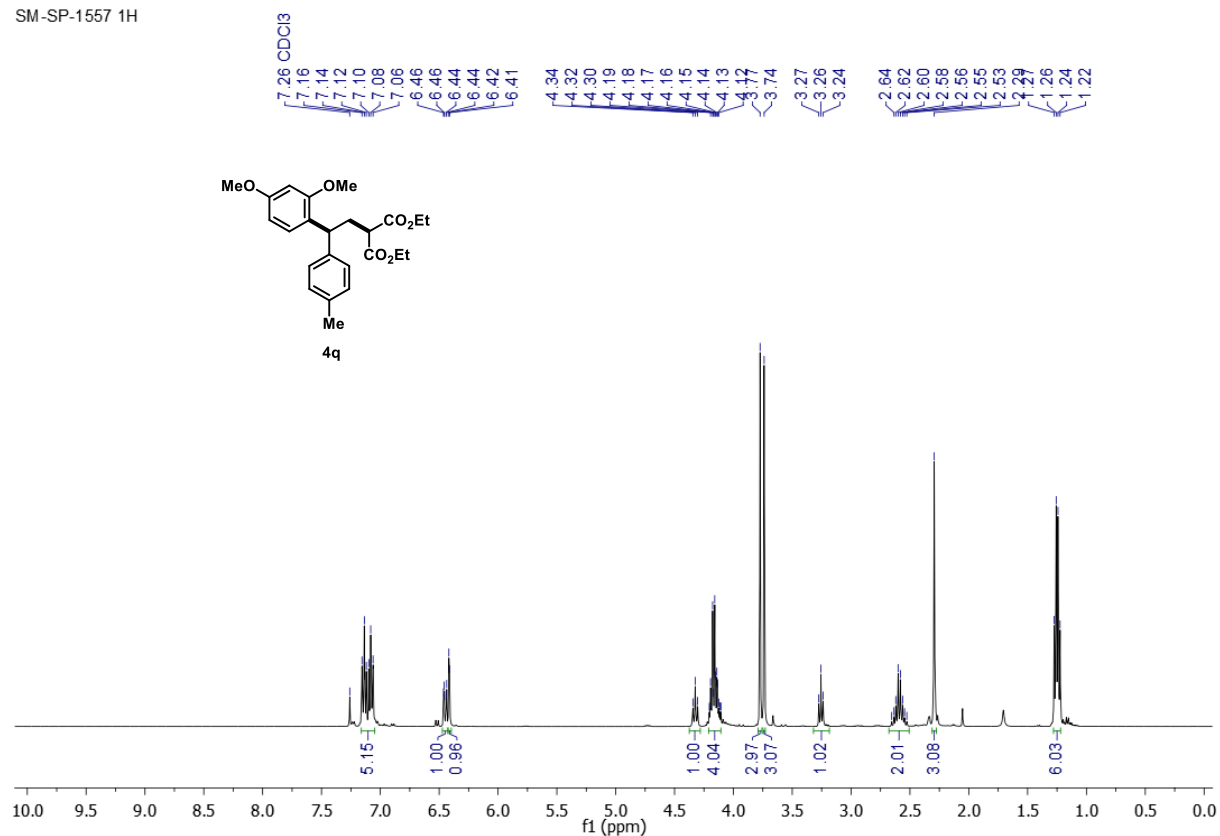
SM-SP-2082 13C





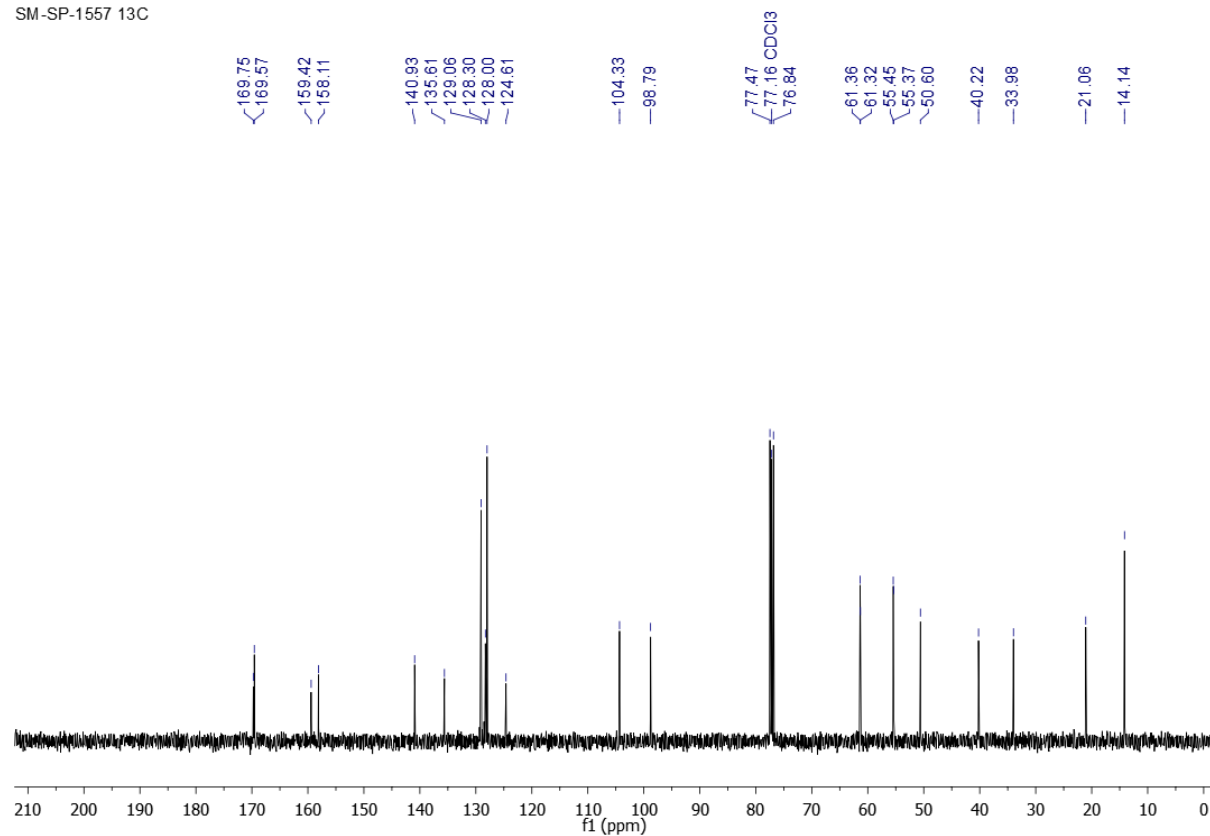
<sup>1</sup>H NMR of **4q** (400 MHz, CDCl<sub>3</sub>):

SM-SP-1557 1H



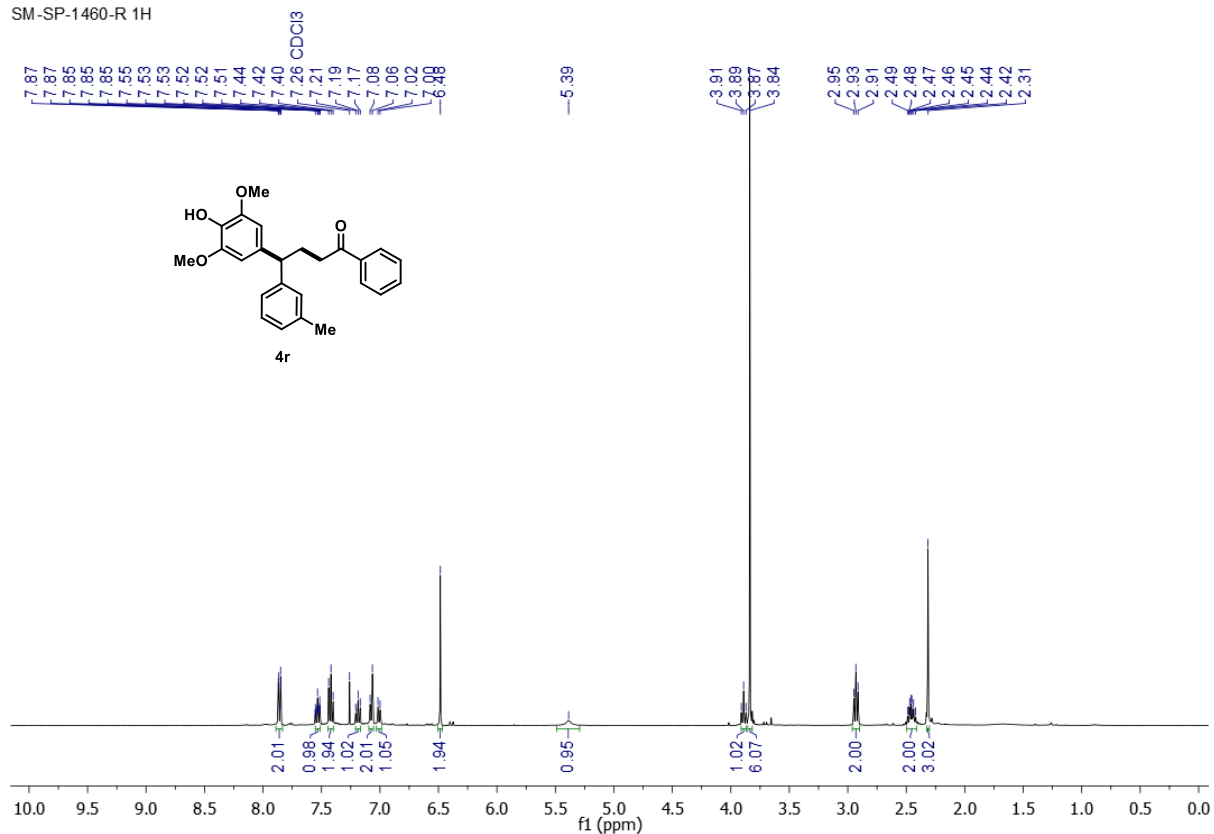
<sup>13</sup>C{<sup>1</sup>H} NMR of **4q** (101 MHz, CDCl<sub>3</sub>):

SM-SP-1557 13C



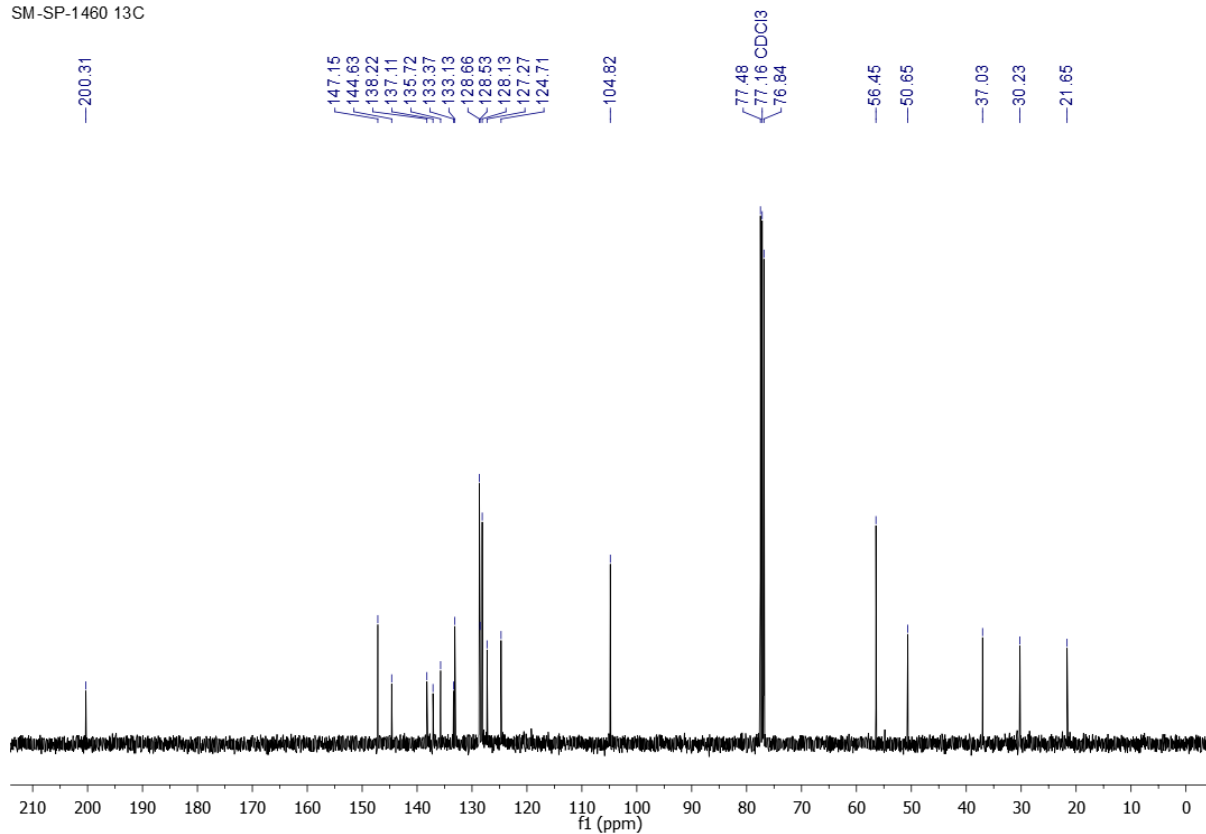
$^1\text{H}$  NMR of **4r** (400 MHz,  $\text{CDCl}_3$ ):

SM-SP-1460-R 1H

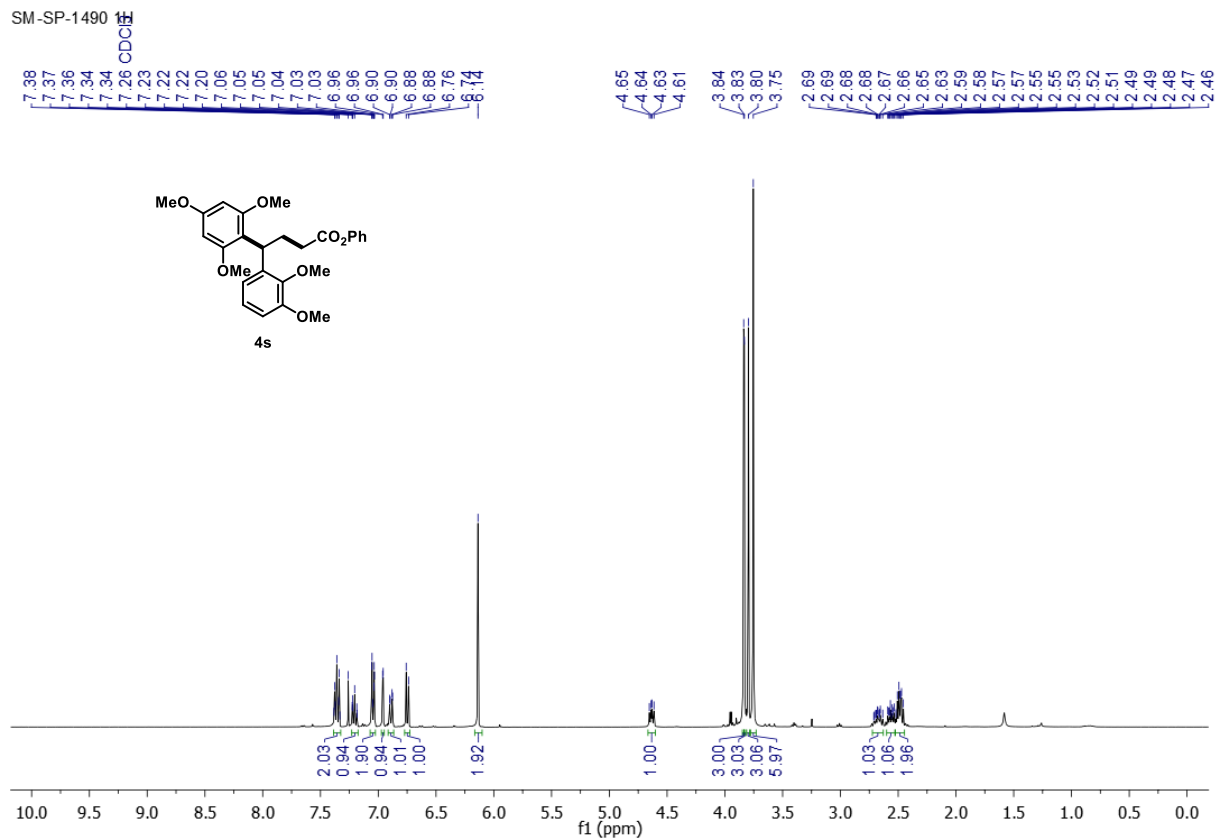


$^{13}\text{C}\{^1\text{H}\}$  NMR of **4r** (101 MHz,  $\text{CDCl}_3$ ):

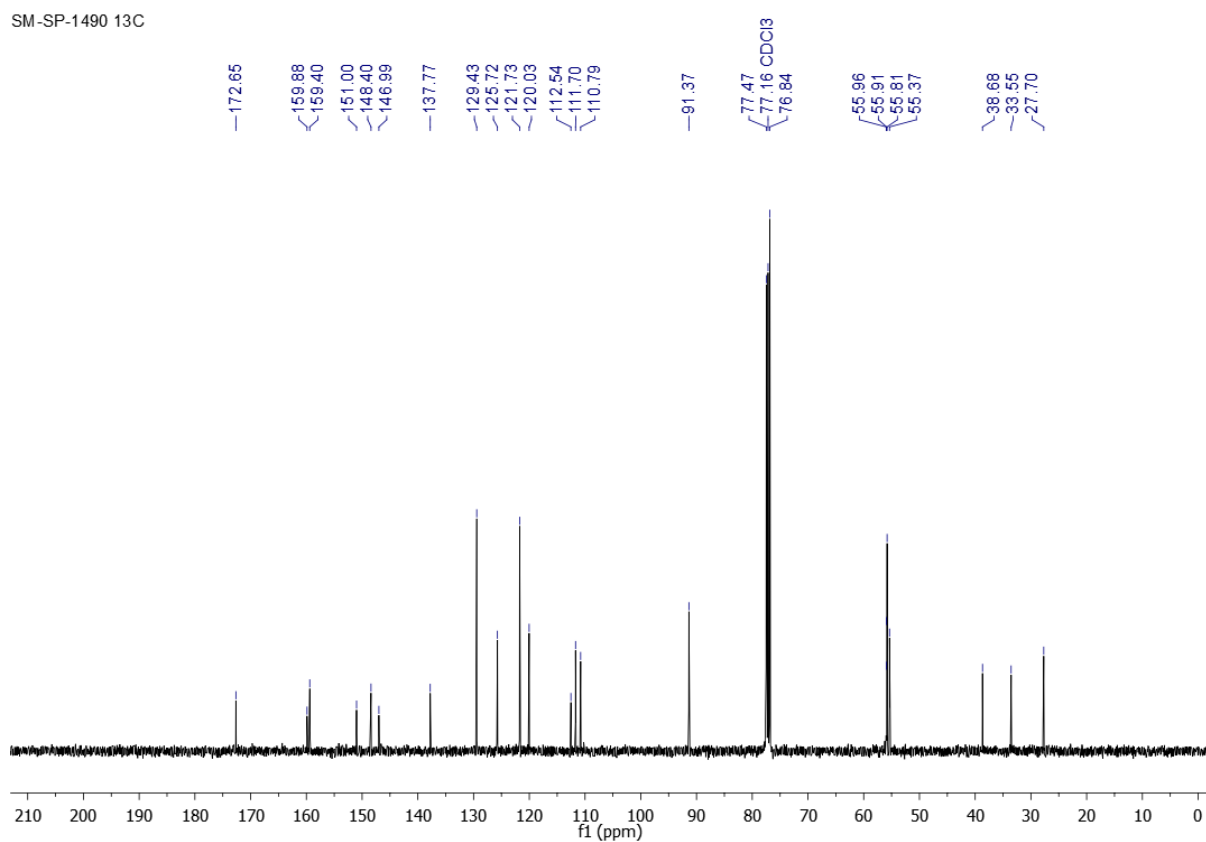
SM-SP-1460 13C



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

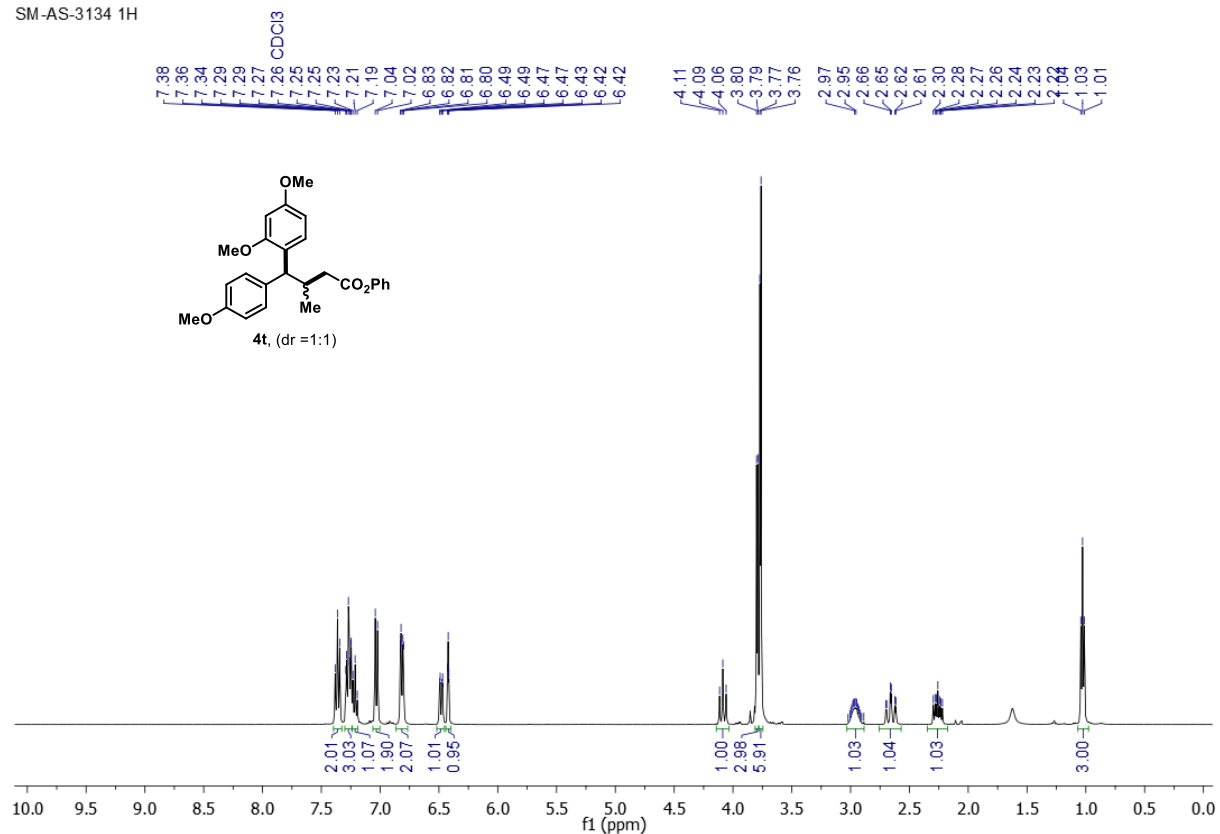


$^{13}\text{C}\{^1\text{H}\}$  NMR of **4s** (101 MHz,  $\text{CDCl}_3$ ):



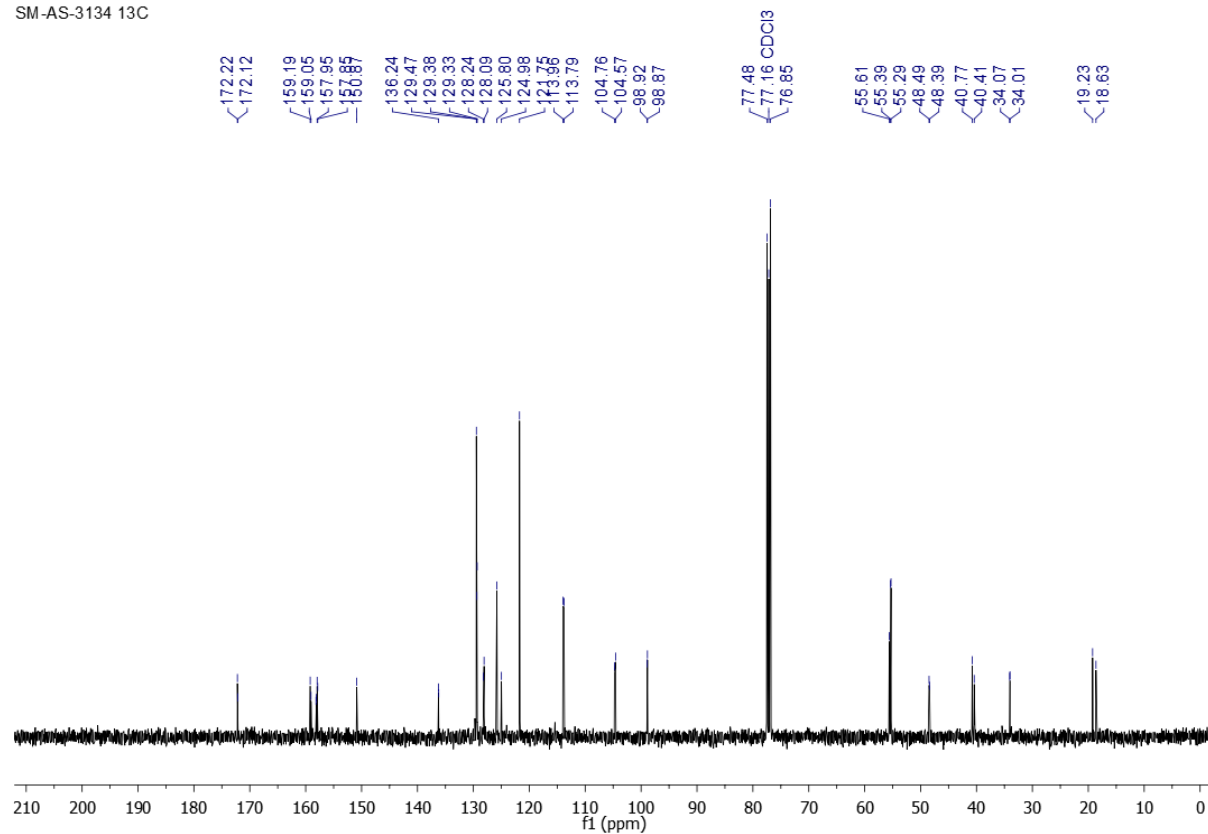
$^1\text{H}$  NMR of **4t** (400 MHz,  $\text{CDCl}_3$ ):

SM-AS-3134 1H

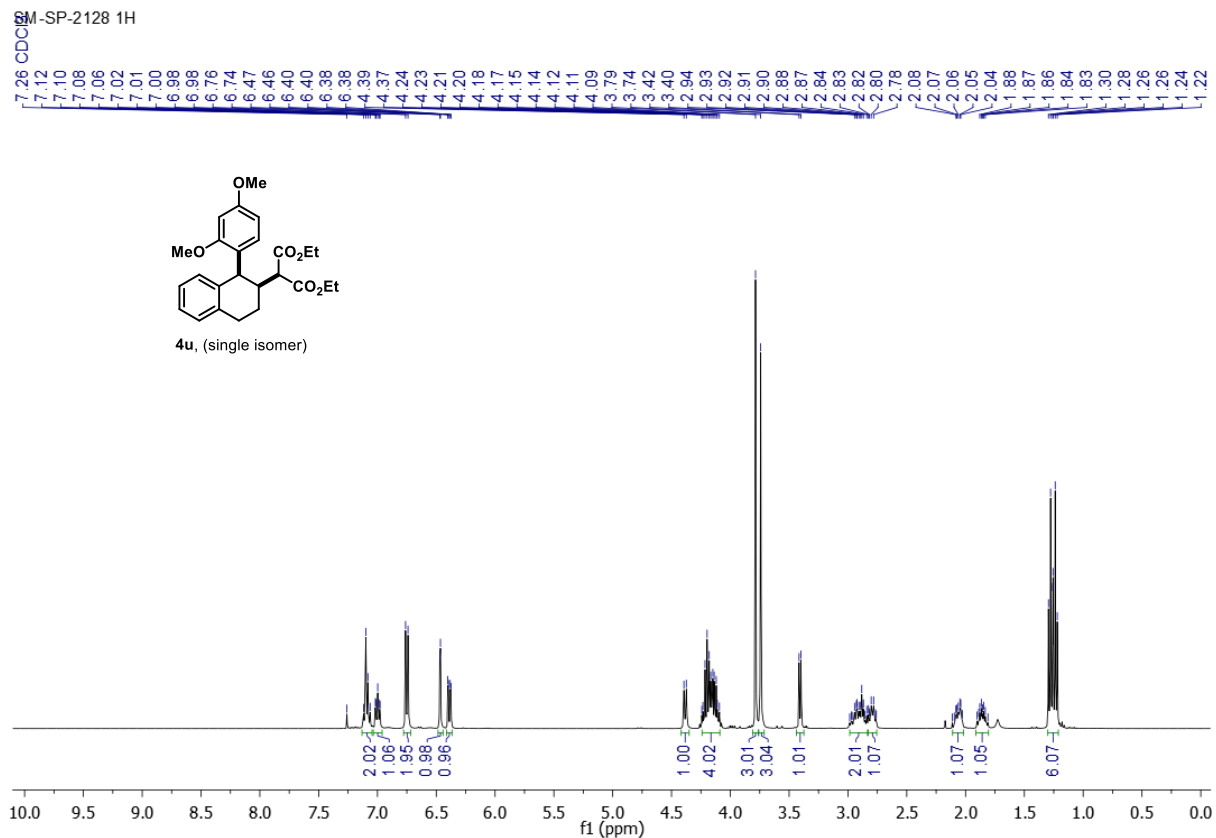


$^{13}\text{C}\{^1\text{H}\}$  NMR of **4t** (101 MHz,  $\text{CDCl}_3$ ):

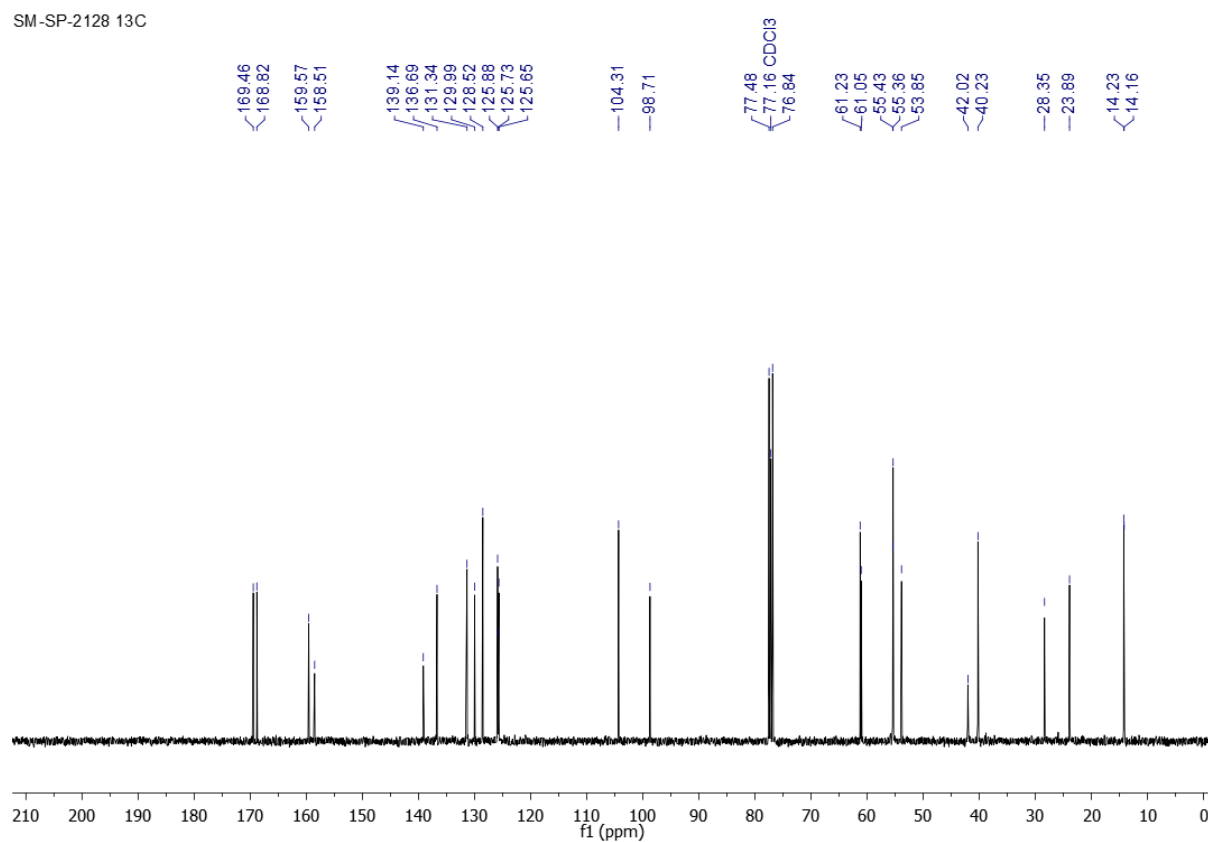
SM-AS-3134 13C



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

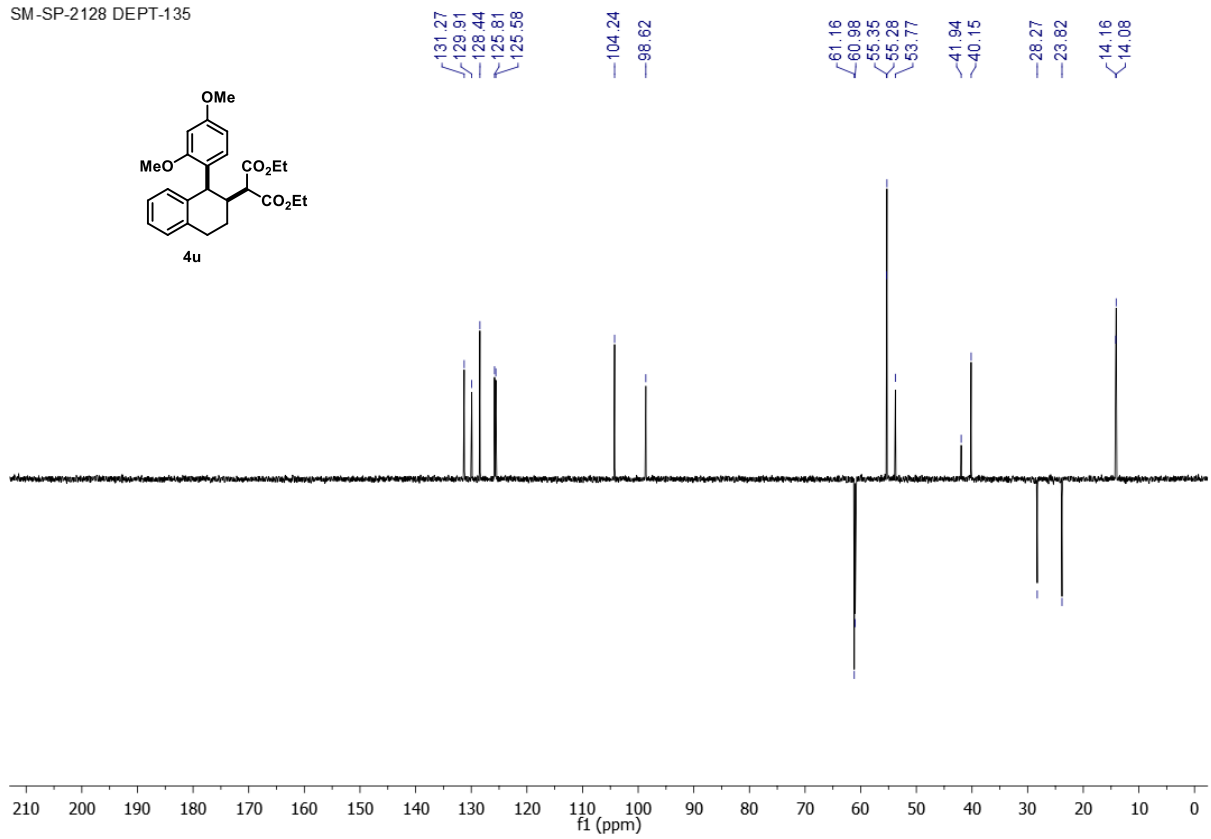


<sup>13</sup>C{<sup>1</sup>H} NMR of **4u** (101 MHz, CDCl<sub>3</sub>):

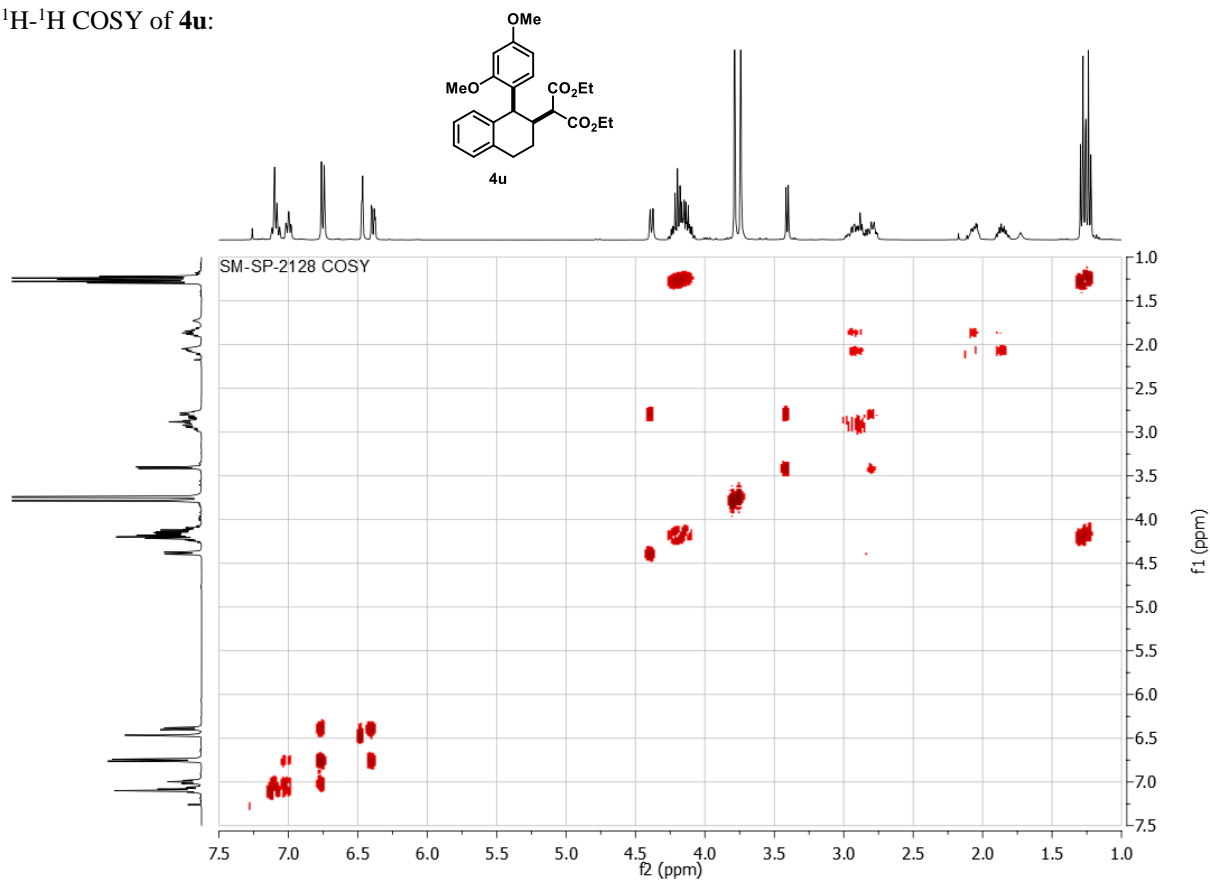


$^{13}\text{C}\{^1\text{H}\}$  DEPT-135 NMR of **4u** (101 MHz,  $\text{CDCl}_3$ ):

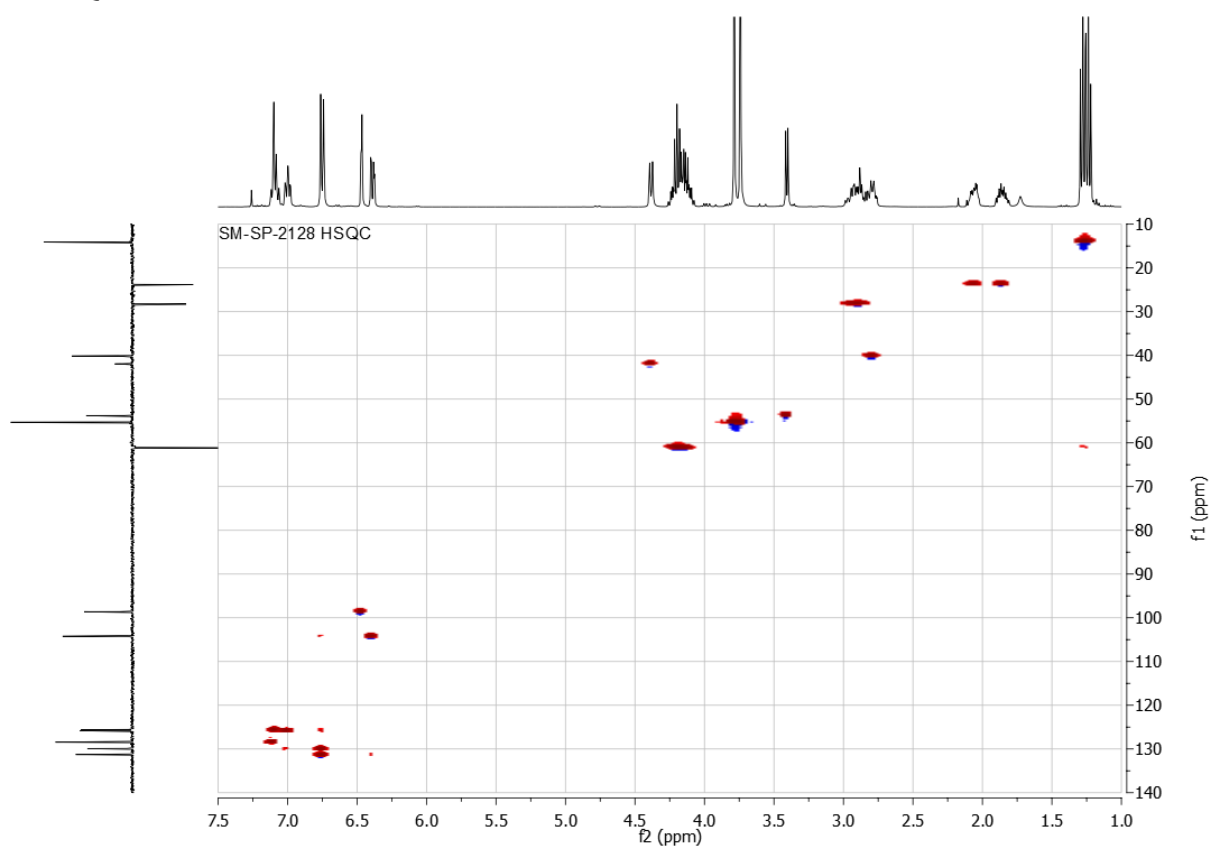
SM-SP-2128 DEPT-135



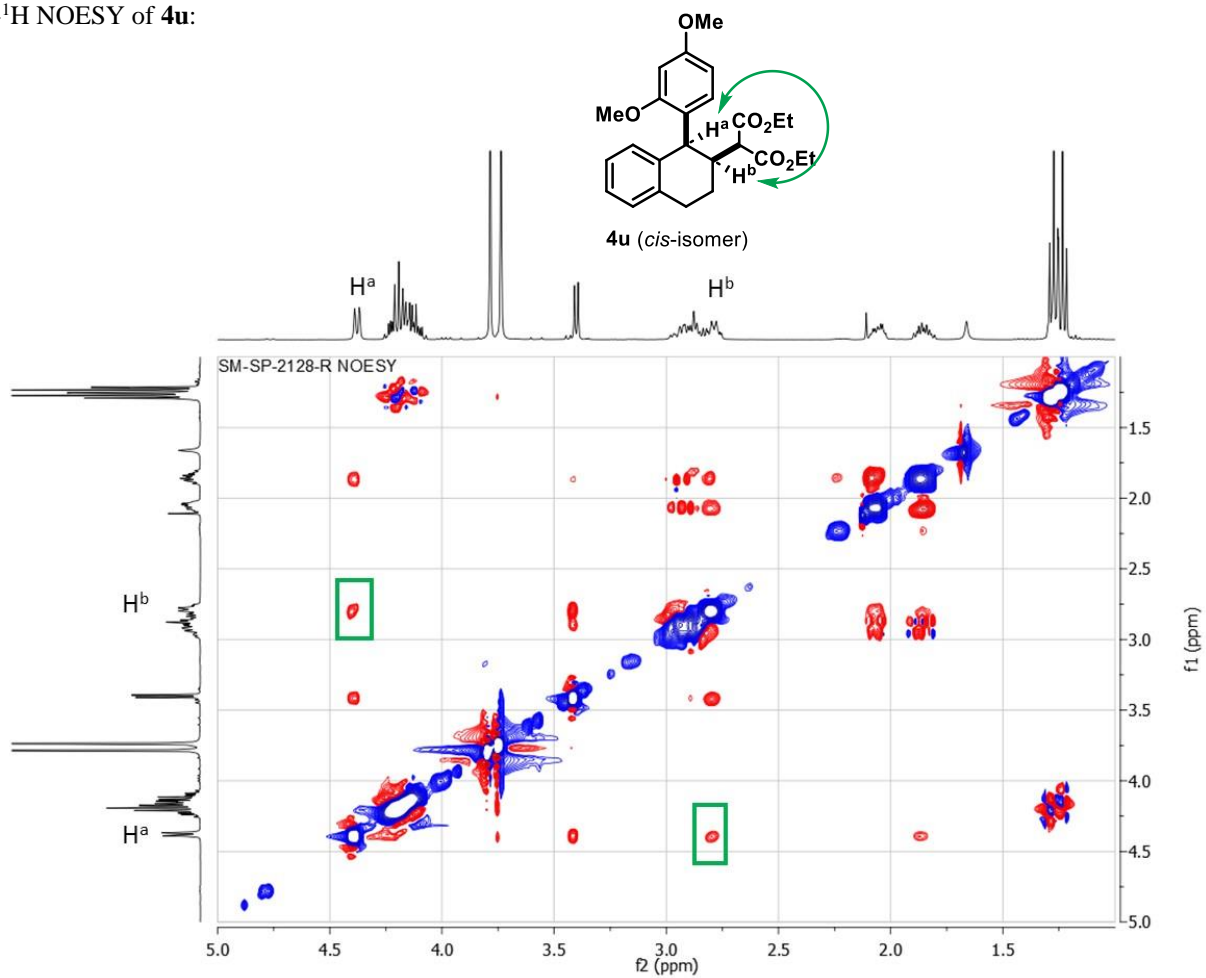
$^1\text{H}$ - $^1\text{H}$  COSY of **4u**:



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



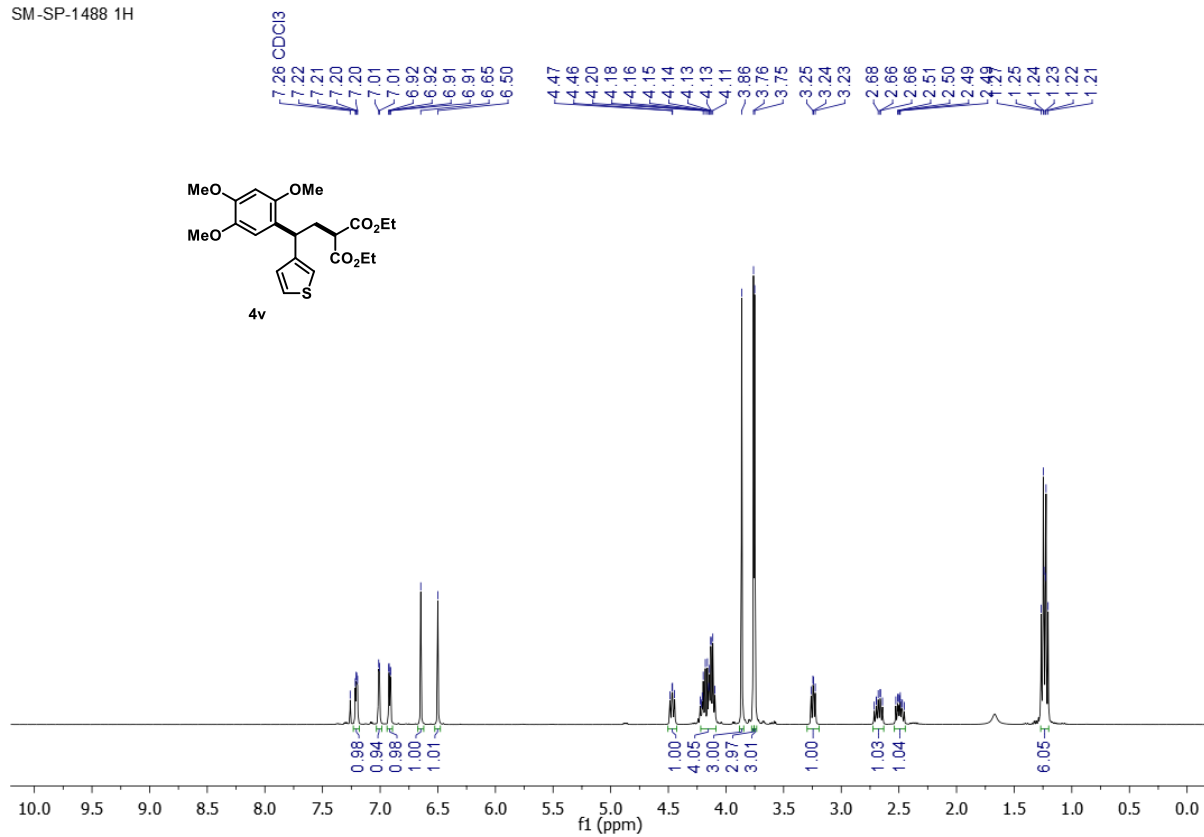
$^1\text{H}$ - $^1\text{H}$  NOESY of **4u**:





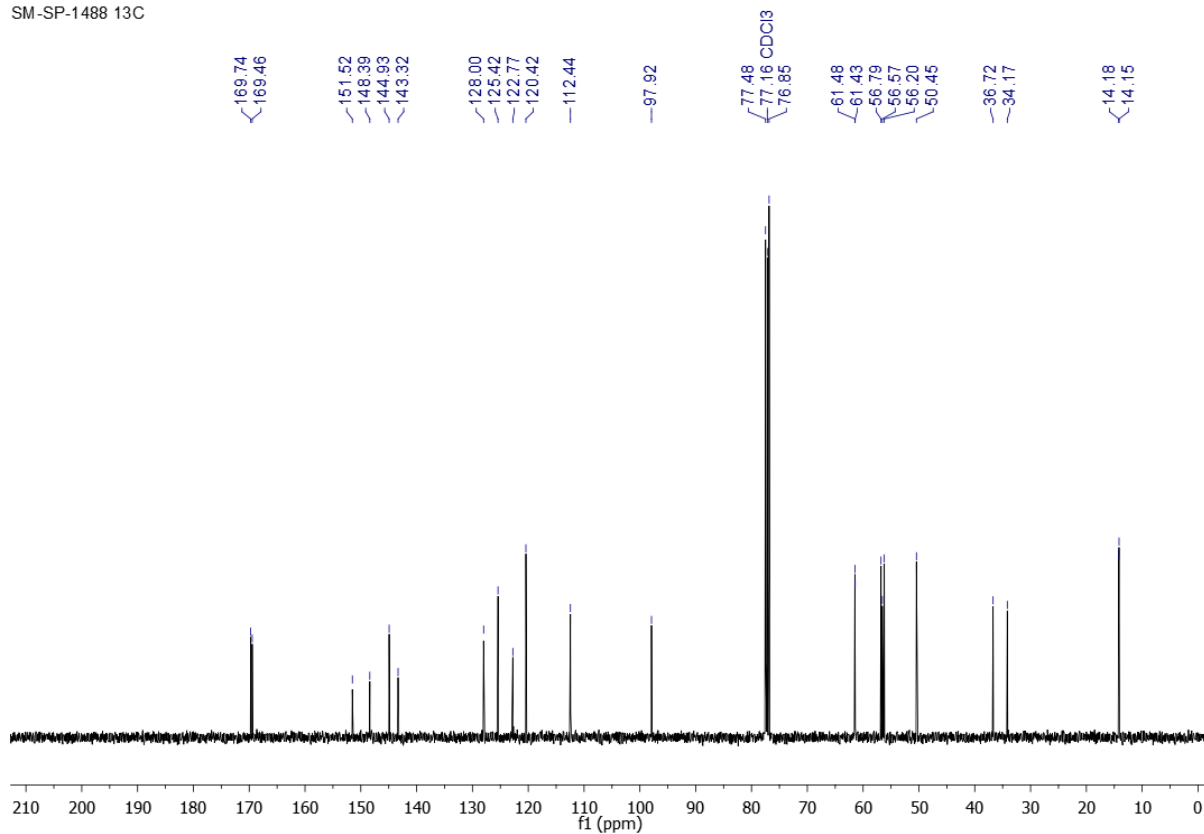
<sup>1</sup>H NMR of **4v** (400 MHz, CDCl<sub>3</sub>):

SM-SP-1488 1H



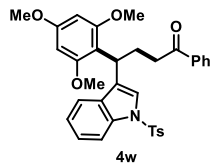
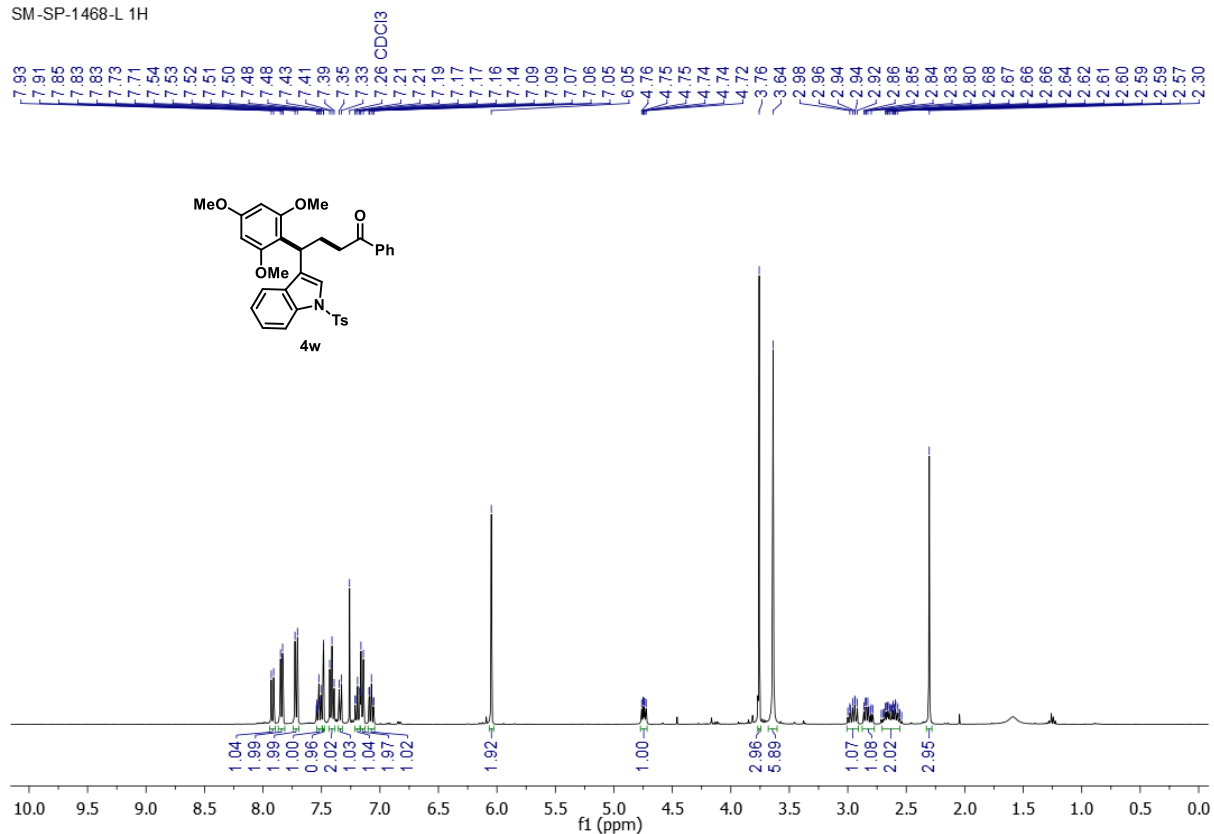
<sup>13</sup>C{<sup>1</sup>H} NMR of **4v** (101 MHz, CDCl<sub>3</sub>):

SM-SP-1488 13C



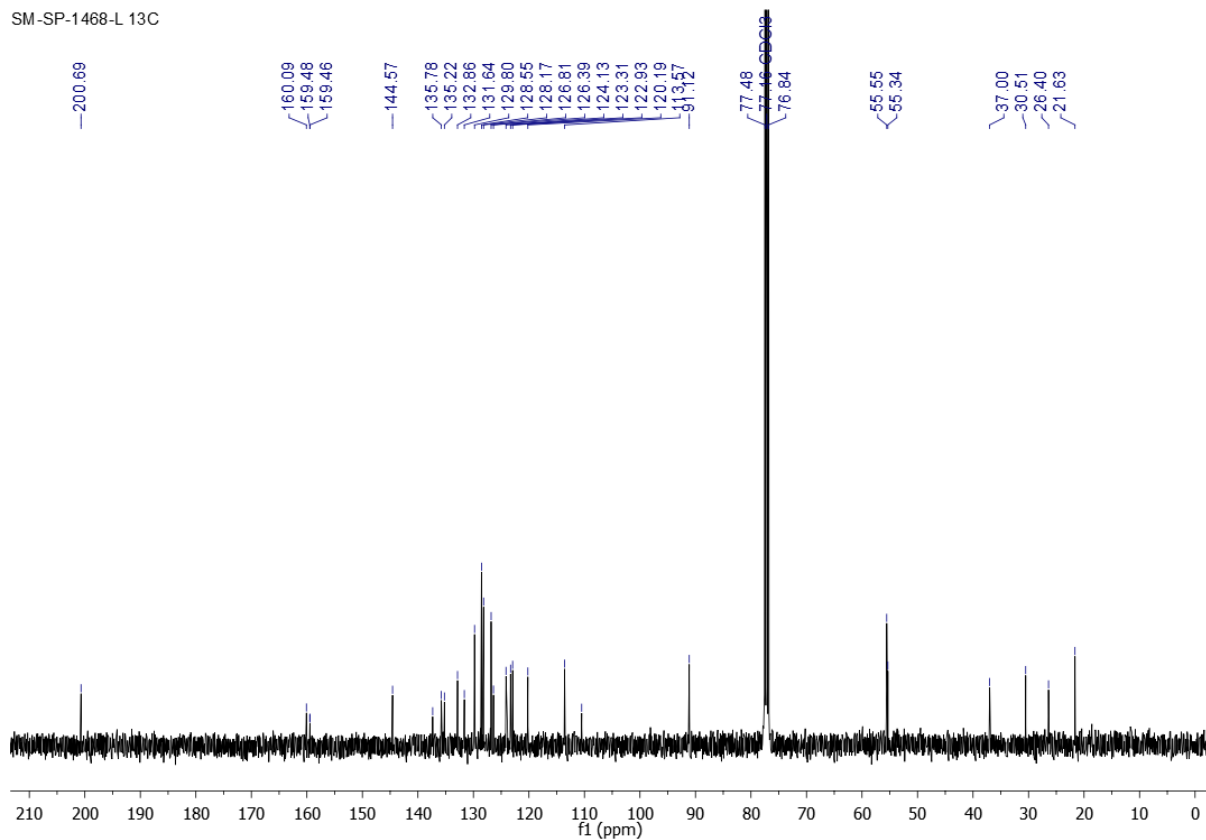
$^1\text{H}$  NMR of **4w** (400 MHz,  $\text{CDCl}_3$ ):

SM-SP-1468-L 1H



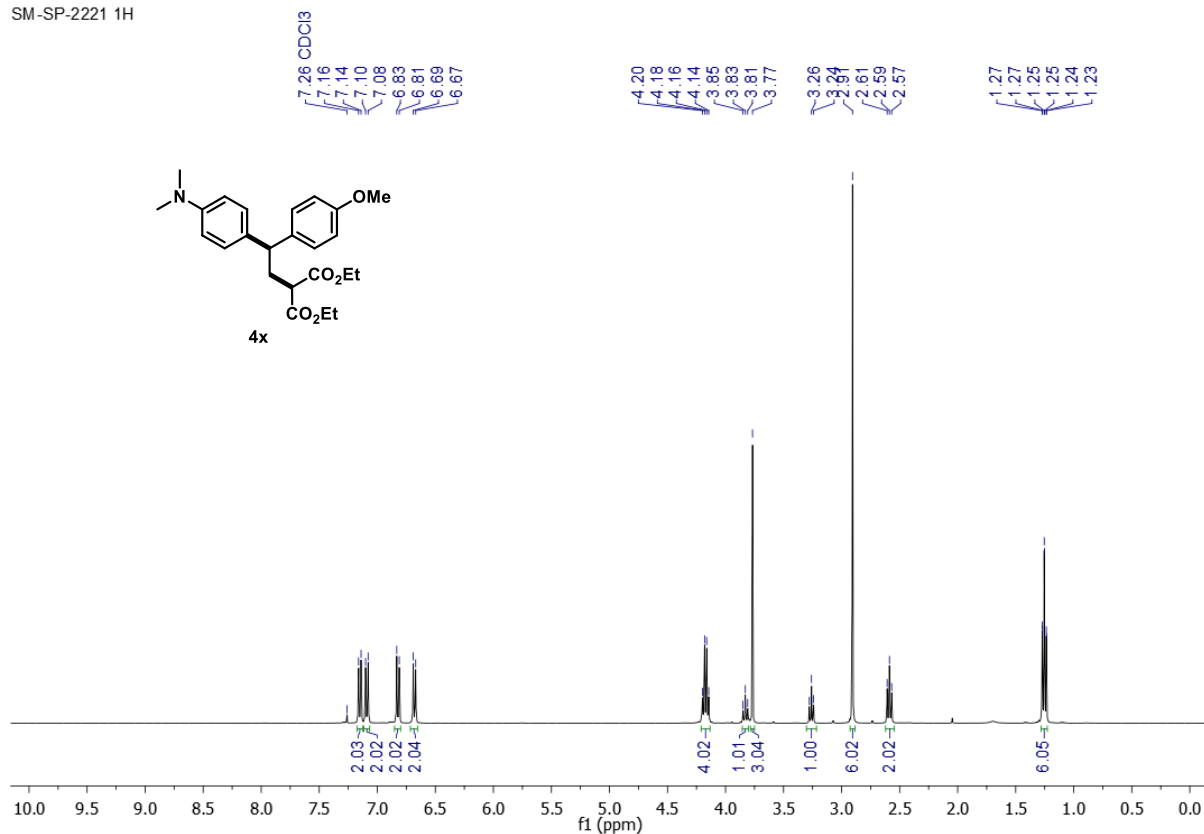
$^{13}\text{C}\{^1\text{H}\}$  NMR of **4w** (101 MHz,  $\text{CDCl}_3$ ):

SM-SP-1468-L 13C



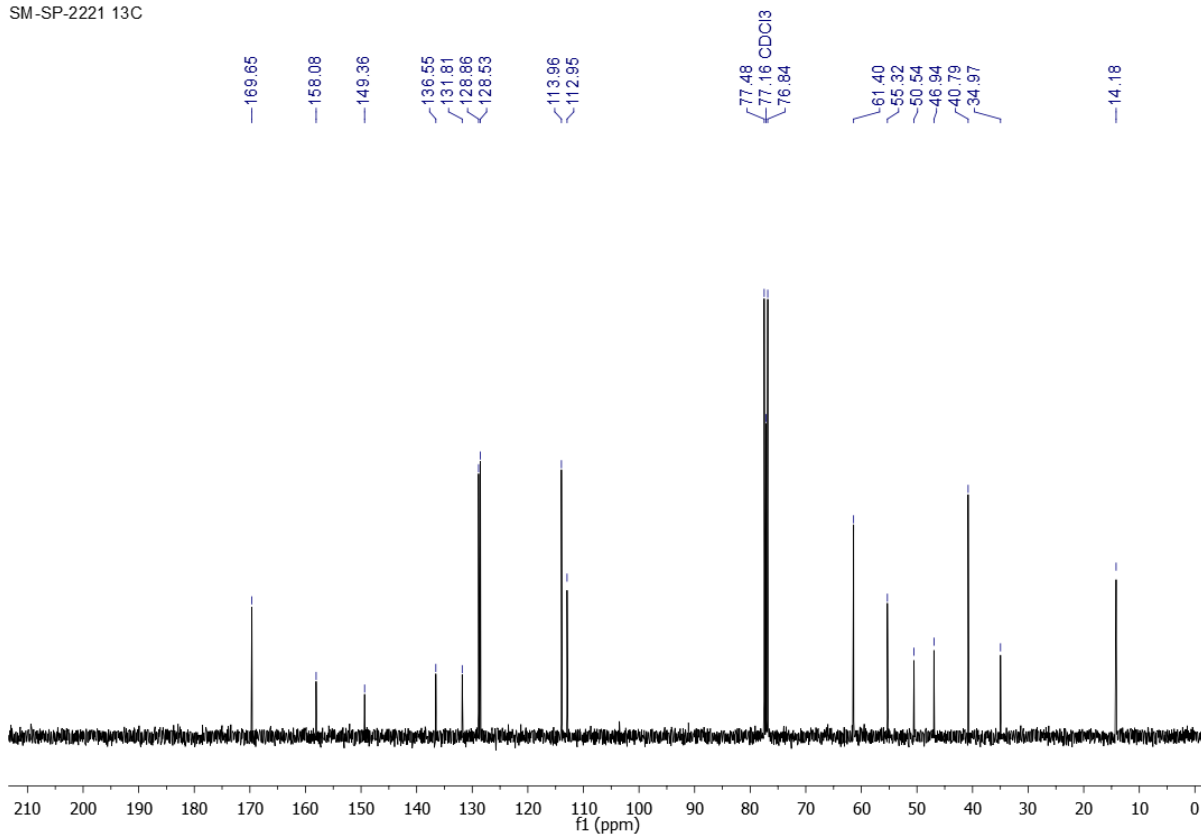
<sup>1</sup>H NMR of **4x** (400 MHz, CDCl<sub>3</sub>):

SM-SP-2221 1H

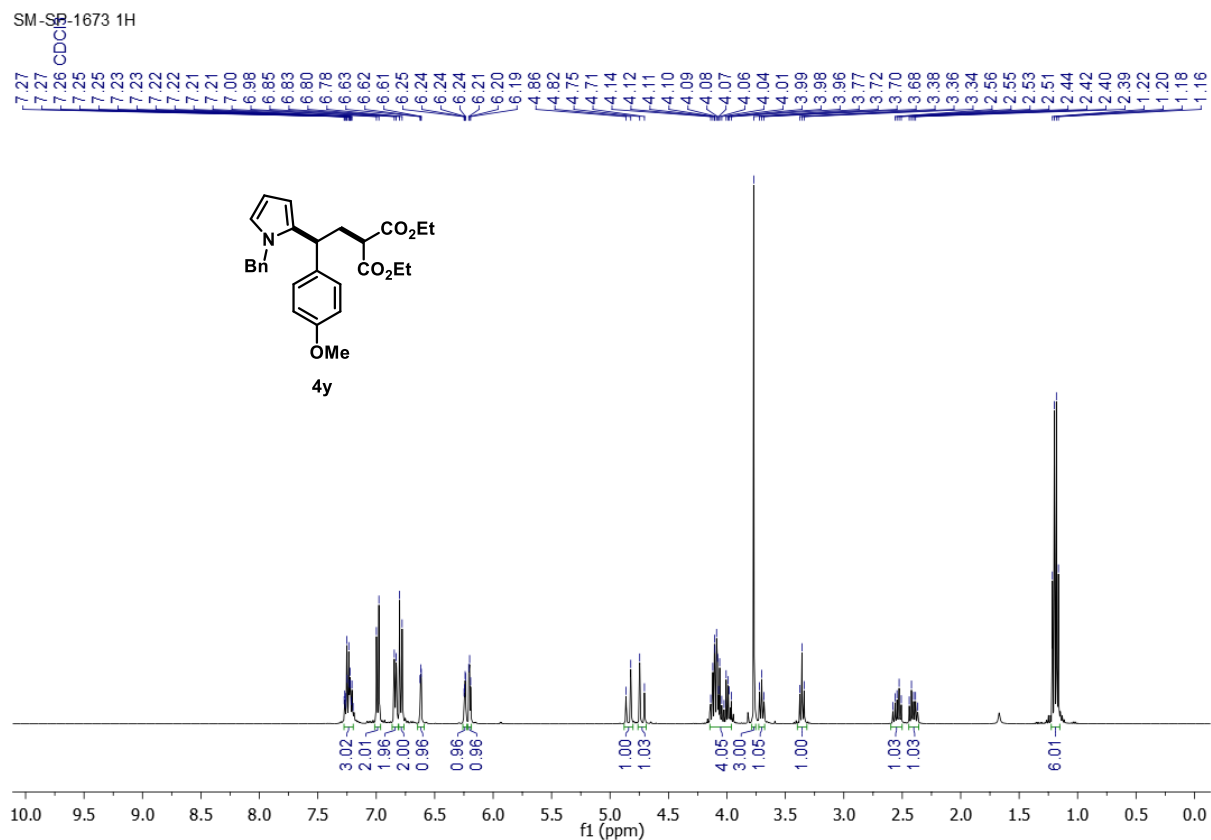


<sup>13</sup>C{<sup>1</sup>H} NMR of **4x** (101 MHz, CDCl<sub>3</sub>):

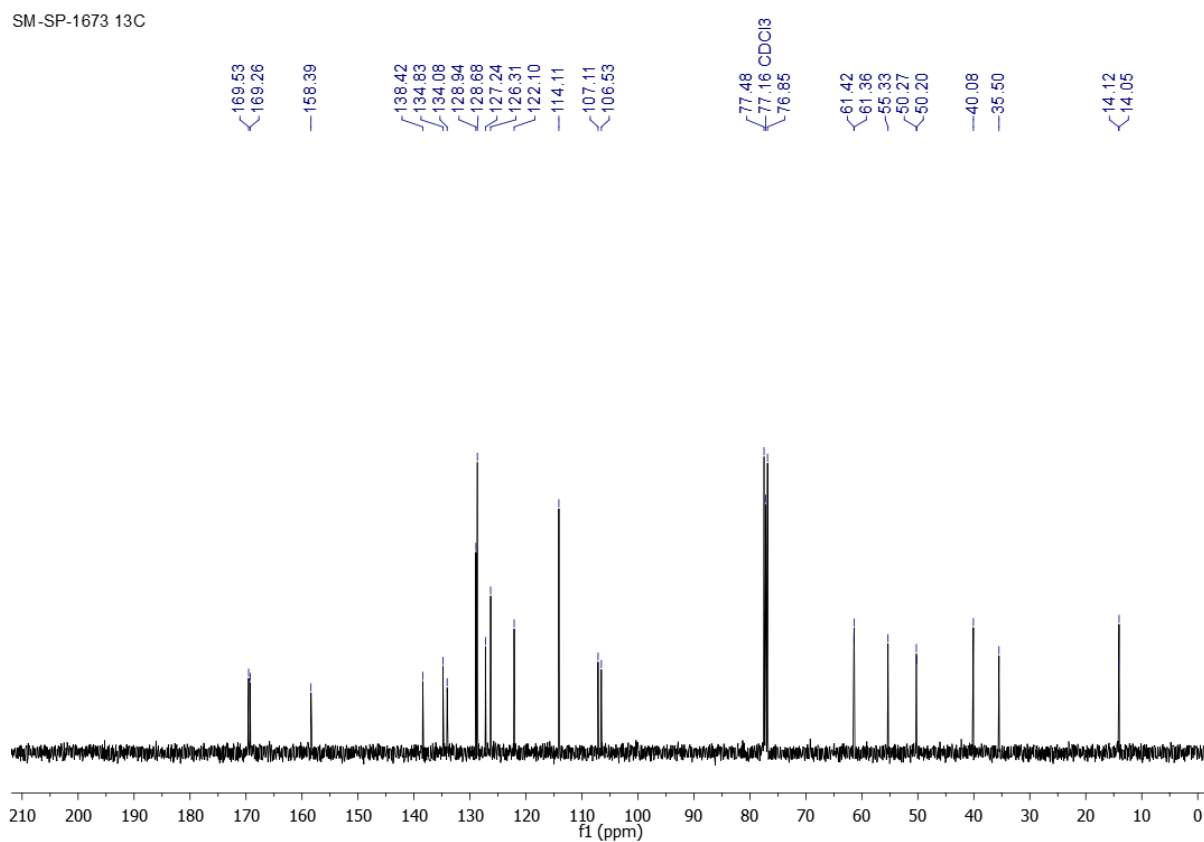
SM-SP-2221 13C



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

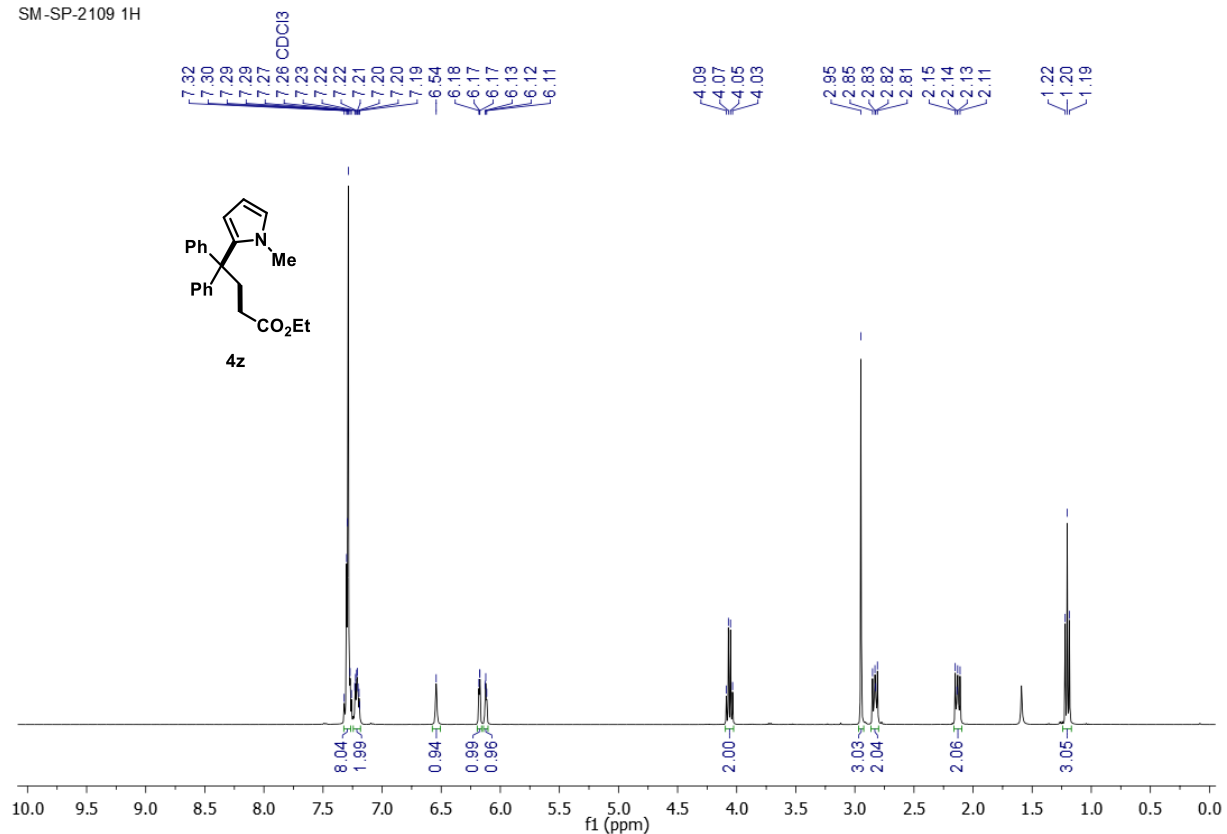


<sup>13</sup>C{<sup>1</sup>H} NMR of **4y** (101 MHz, CDCl<sub>3</sub>):



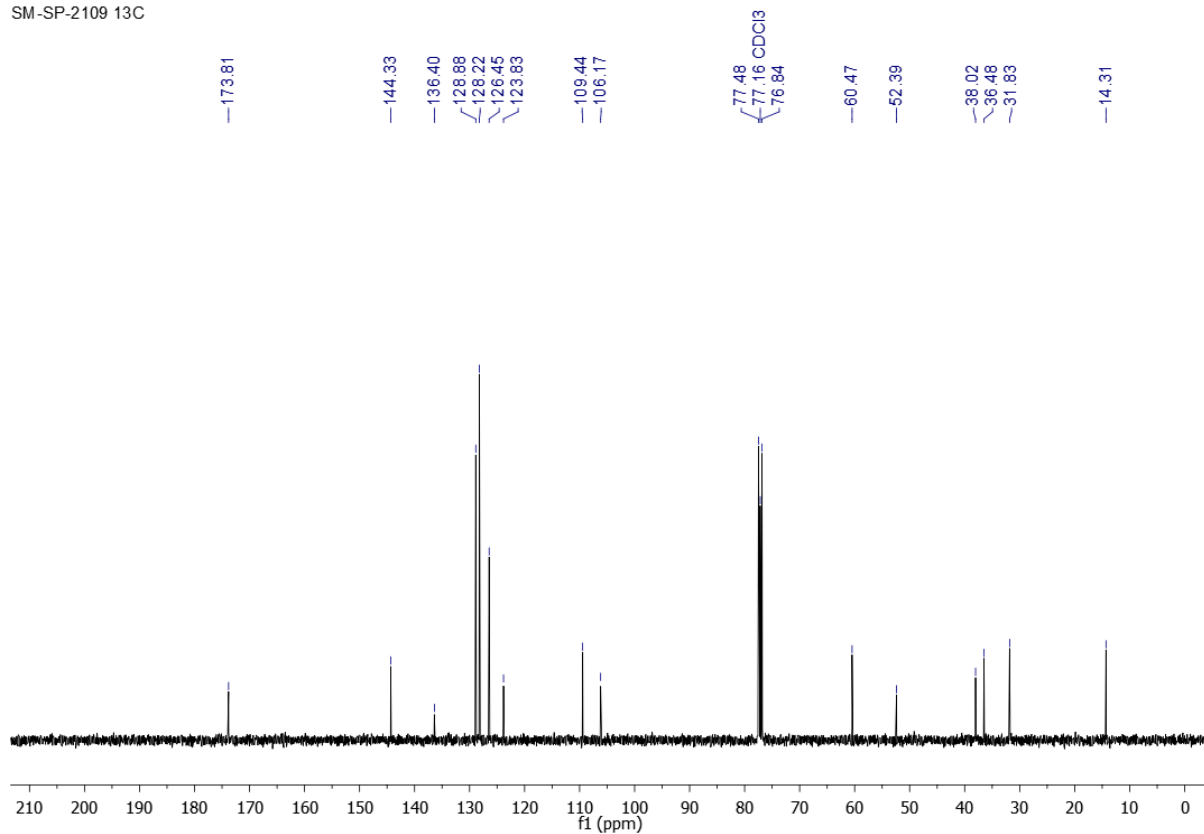
$^1\text{H}$  NMR of **4z** (400 MHz,  $\text{CDCl}_3$ ):

SM-SP-2109 1H



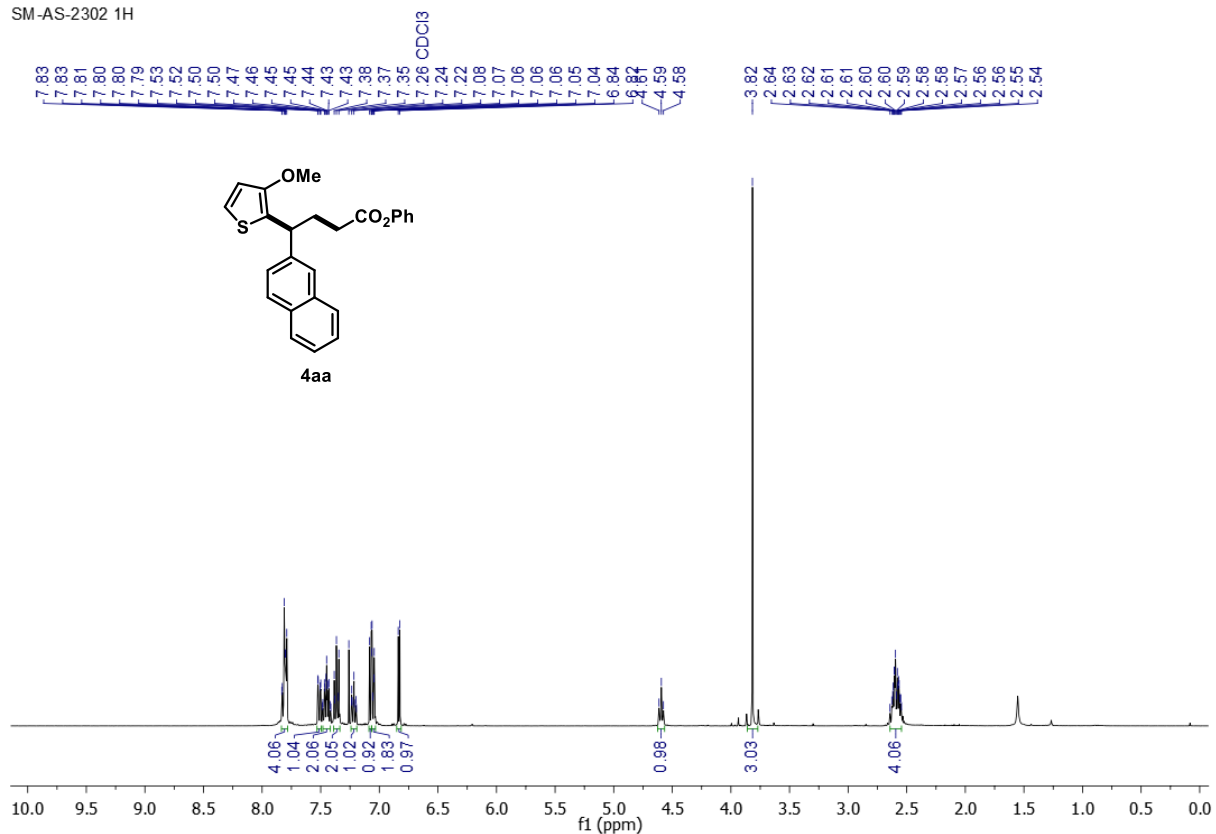
$^{13}\text{C}\{^1\text{H}\}$  NMR of **4z** (101 MHz,  $\text{CDCl}_3$ ):

SM-SP-2109 13C



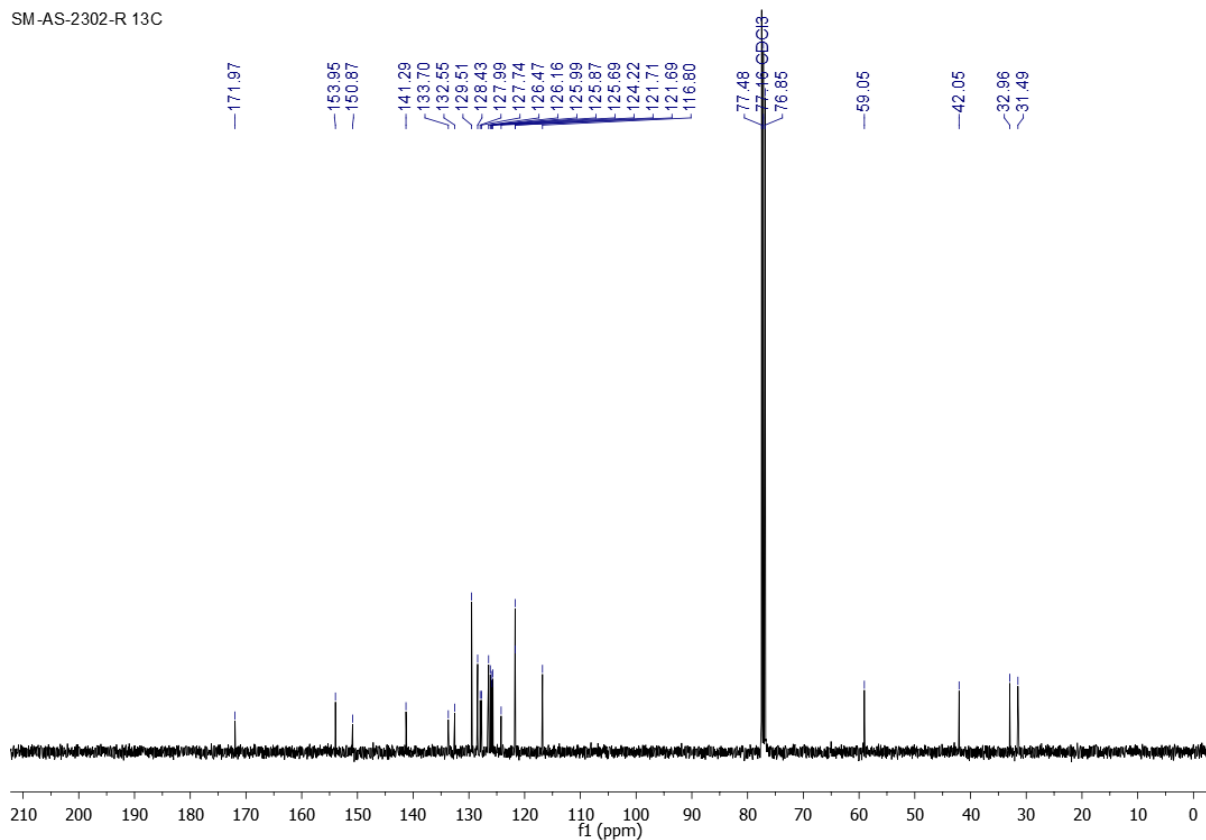
<sup>1</sup>H NMR of **4aa** (400 MHz, CDCl<sub>3</sub>):

SM-AS-2302 1H

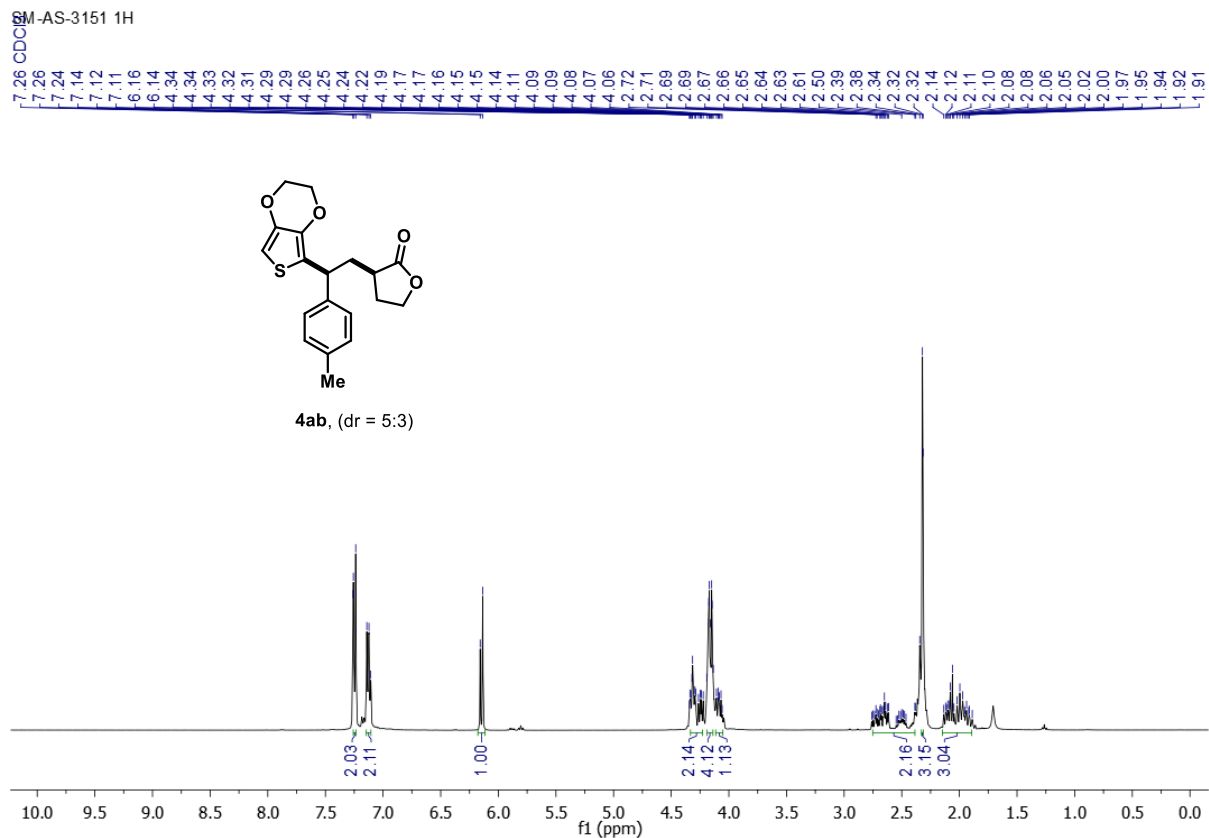


<sup>13</sup>C{<sup>1</sup>H} NMR of **4aa** (101 MHz, CDCl<sub>3</sub>):

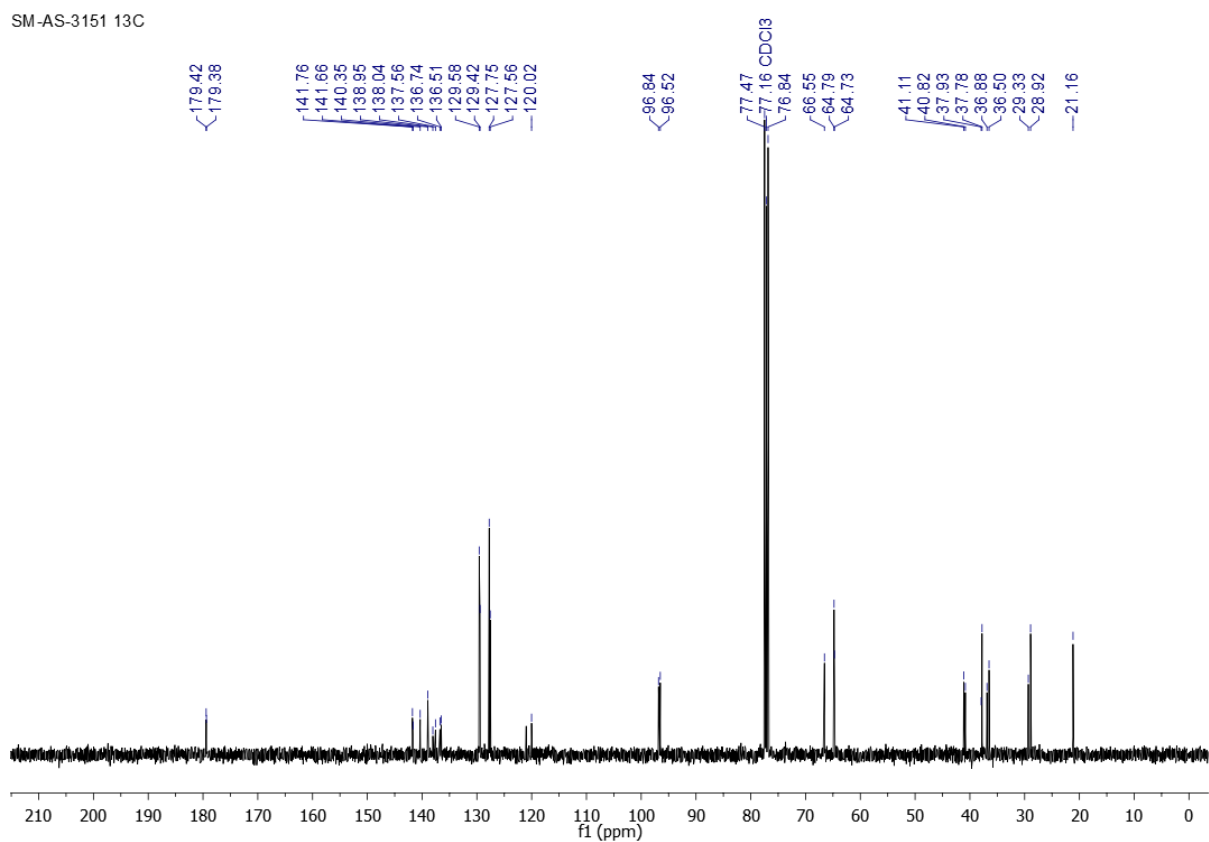
SM-AS-2302-R 13C



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

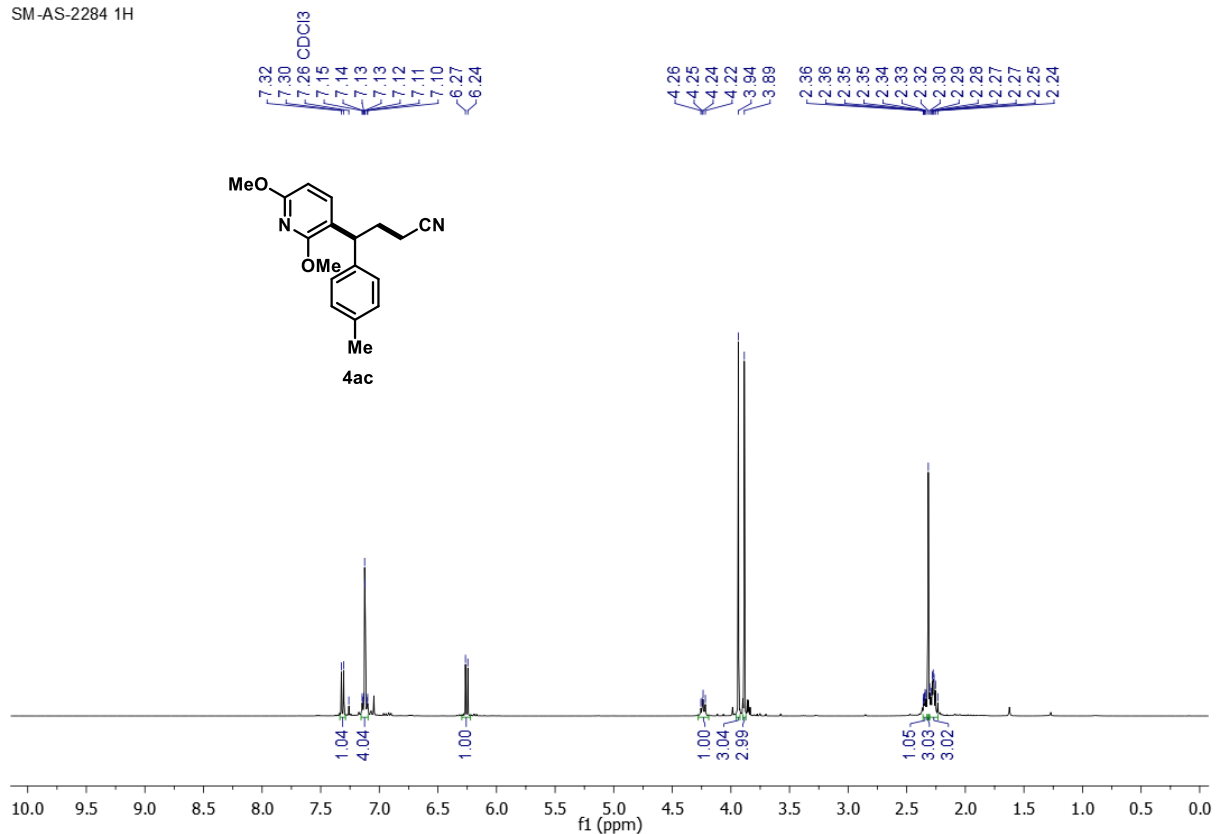


<sup>13</sup>C{<sup>1</sup>H} NMR of **4ab** (101 MHz, CDCl<sub>3</sub>):



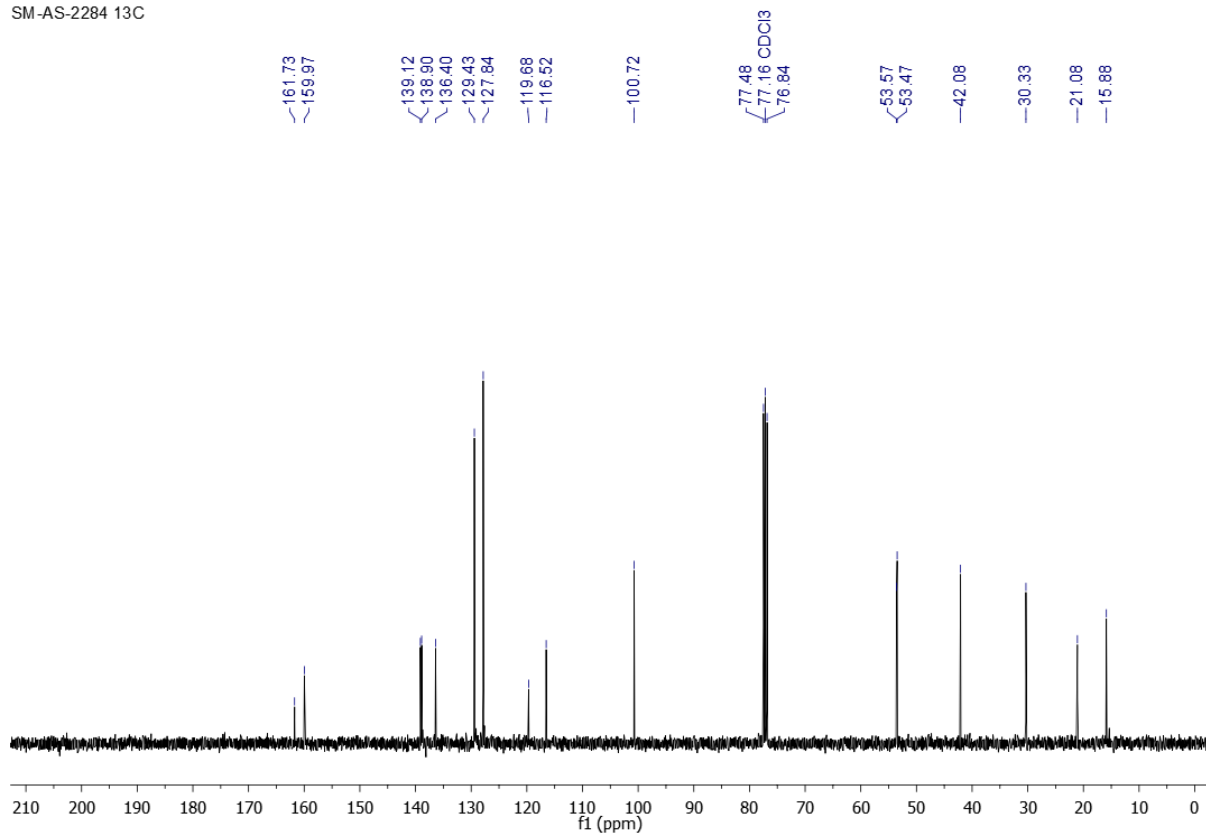
$^1\text{H}$  NMR of **4ac** (400 MHz,  $\text{CDCl}_3$ ):

SM-AS-2284 1H



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

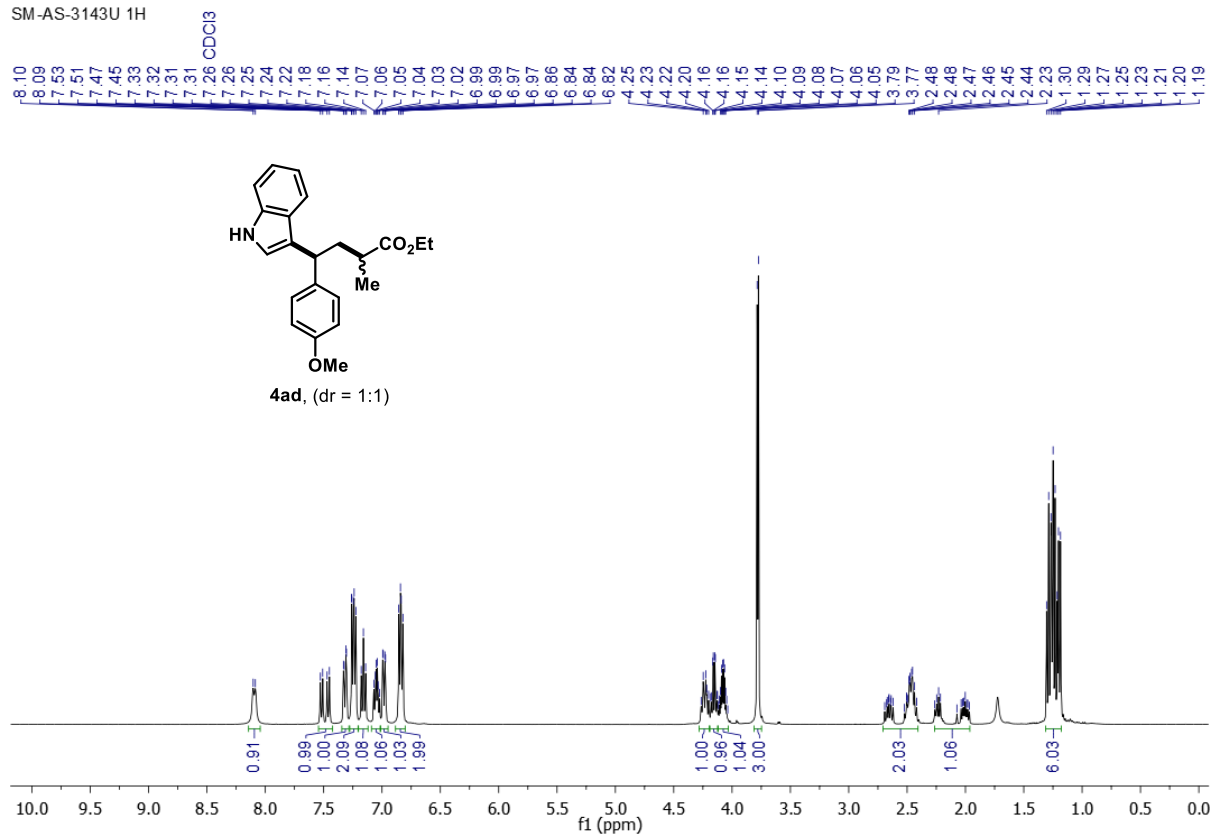
SM-AS-2284 13C





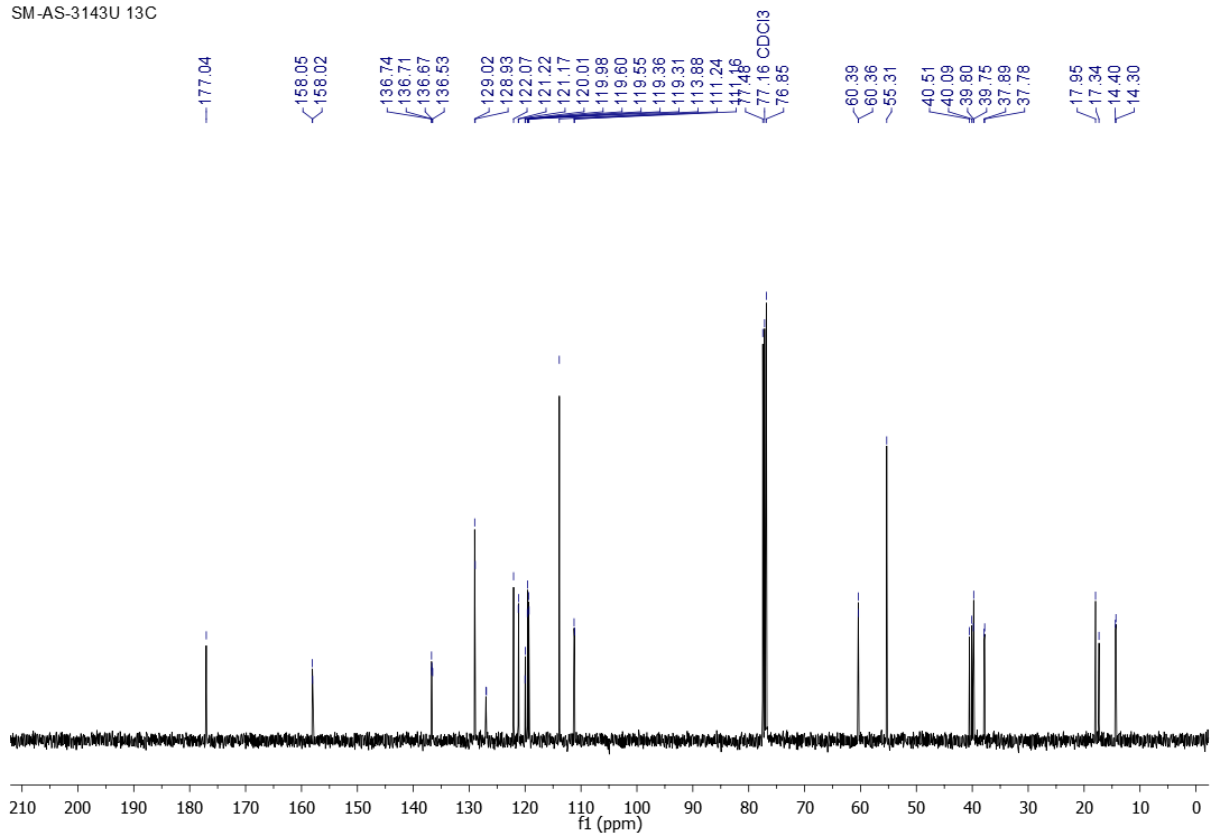
<sup>1</sup>H NMR of **4ad** (400 MHz, CDCl<sub>3</sub>):

SM-AS-3143U 1H



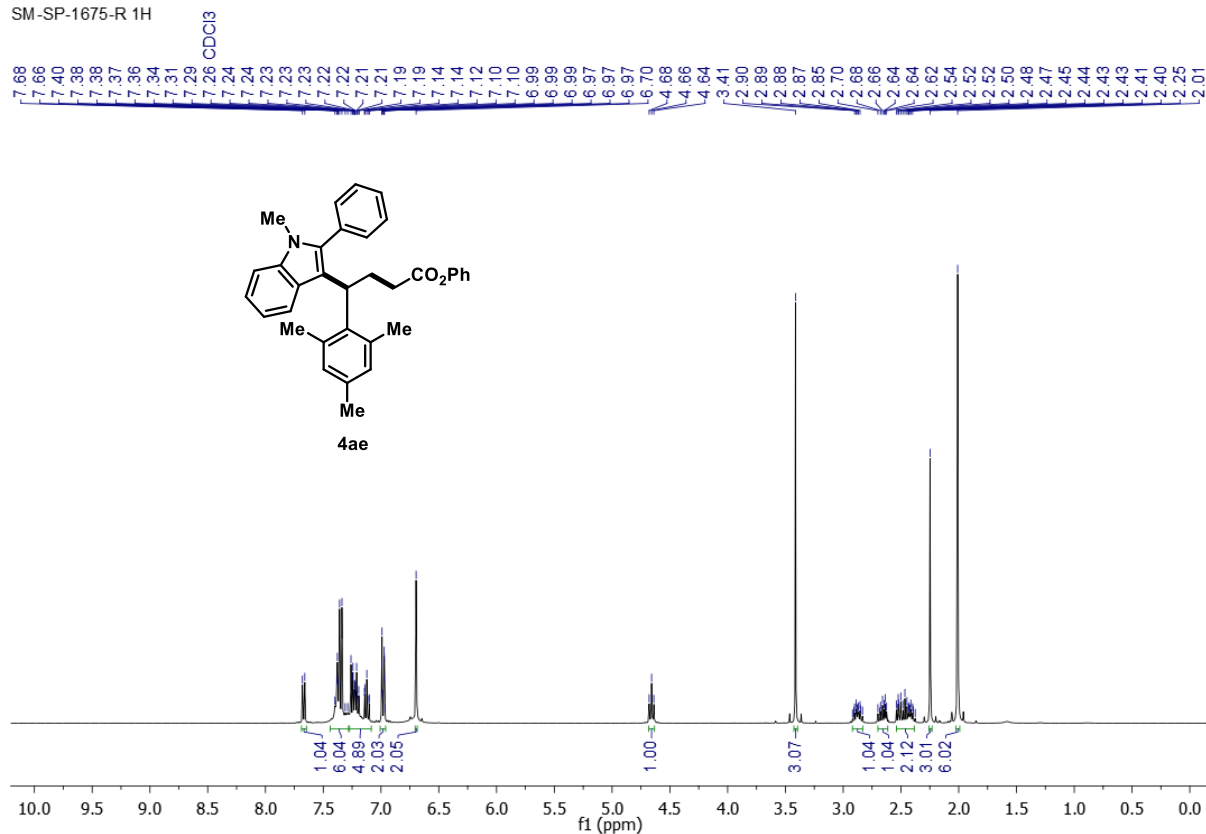
<sup>13</sup>C{<sup>1</sup>H} NMR of **4ad** (101 MHz, CDCl<sub>3</sub>):

SM-AS-3143U 13C



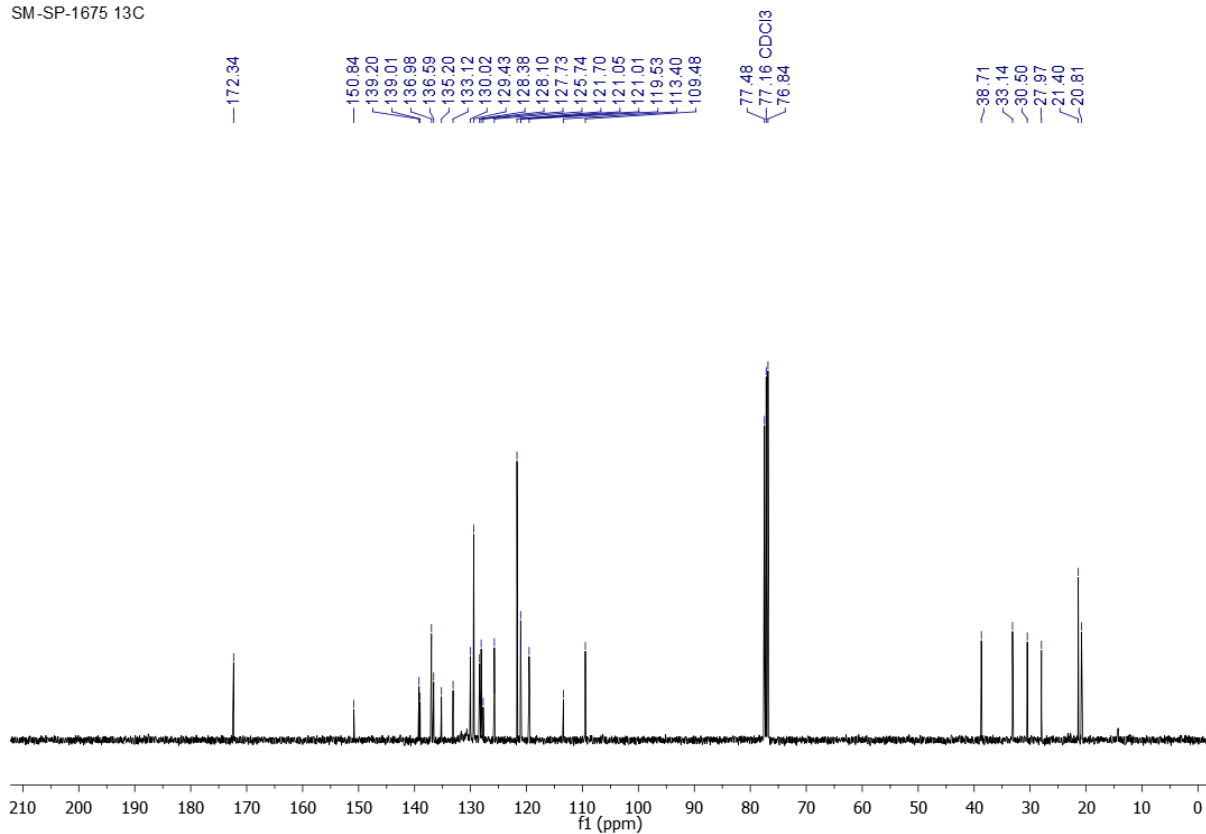
<sup>1</sup>H NMR of **4ae** (400 MHz, CDCl<sub>3</sub>):

SM-SP-1675-R 1H



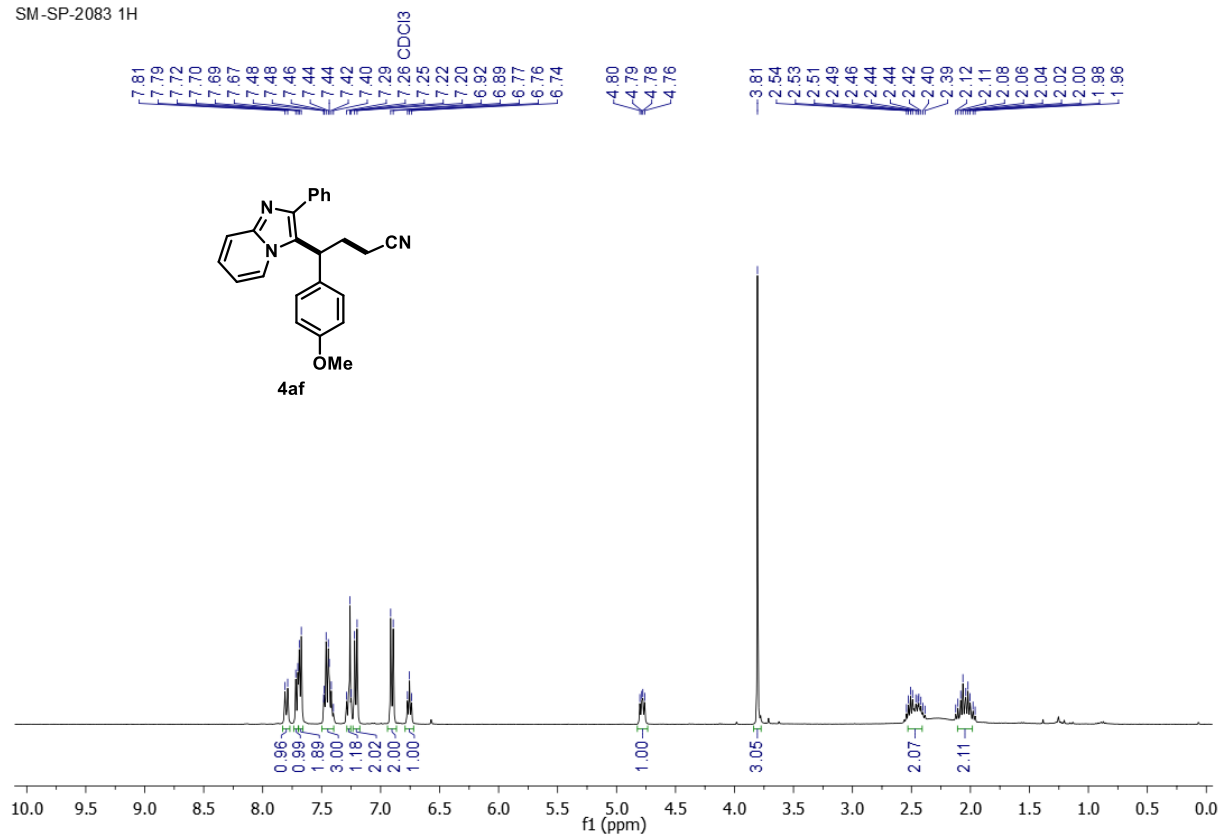
<sup>13</sup>C{<sup>1</sup>H} NMR of **4ae** (101 MHz, CDCl<sub>3</sub>):

SM-SP-1675 13C



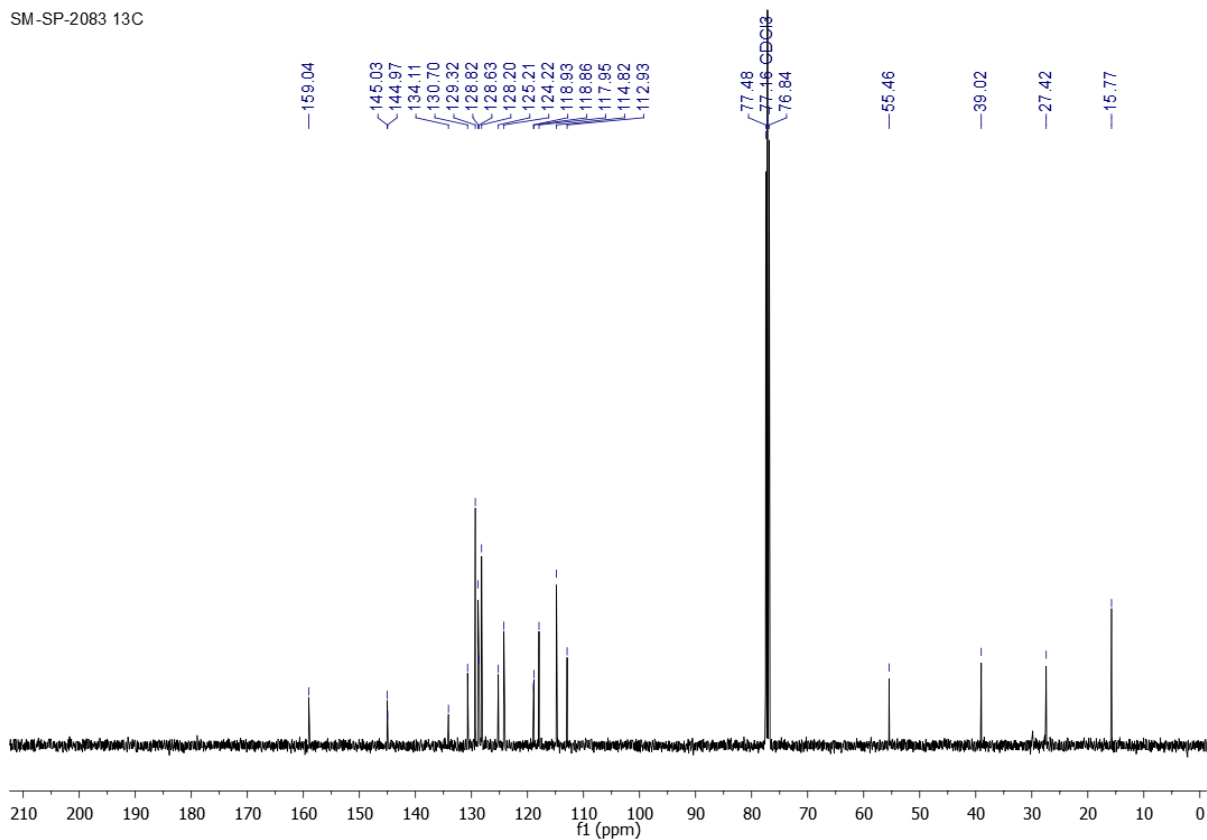
$^1\text{H}$  NMR of **4af** (400 MHz,  $\text{CDCl}_3$ ):

SM-SP-2083 1H



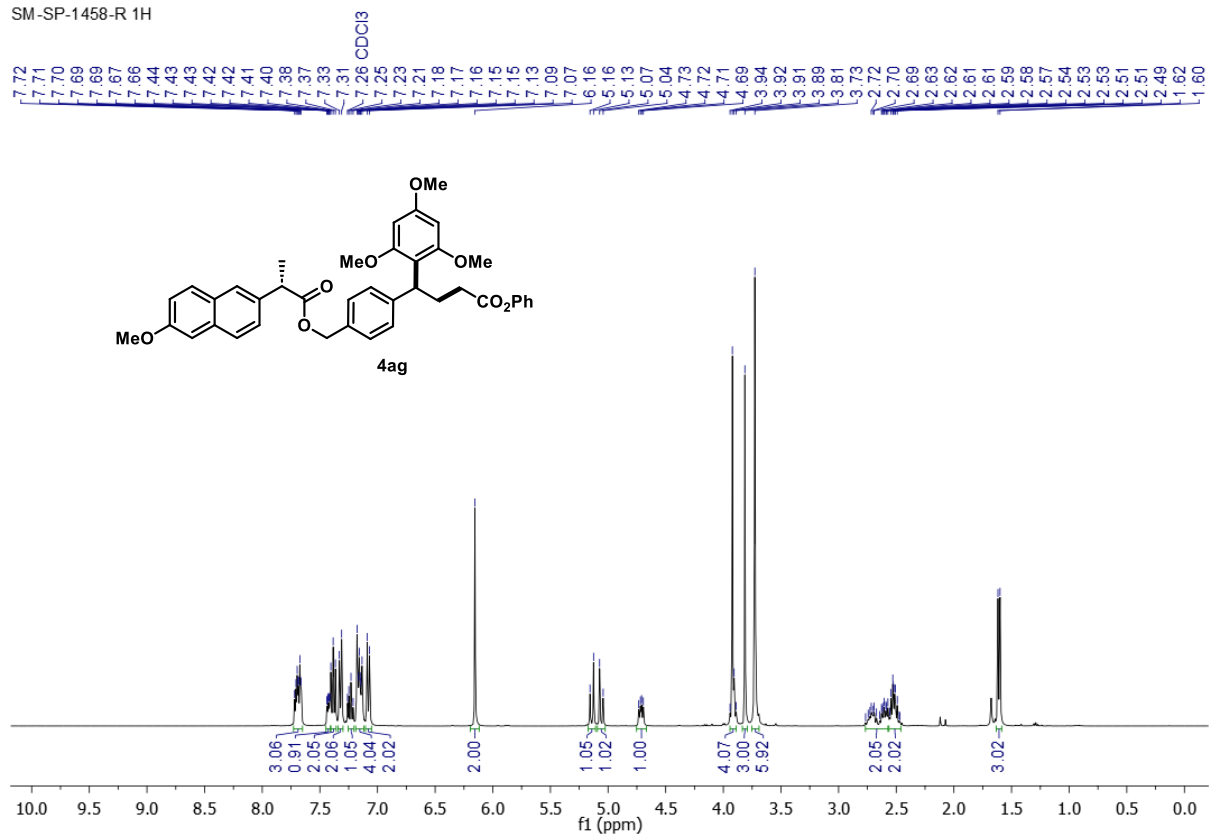
$^{13}\text{C}\{^1\text{H}\}$  NMR of **4af** (101 MHz,  $\text{CDCl}_3$ ):

SM-SP-2083 13C



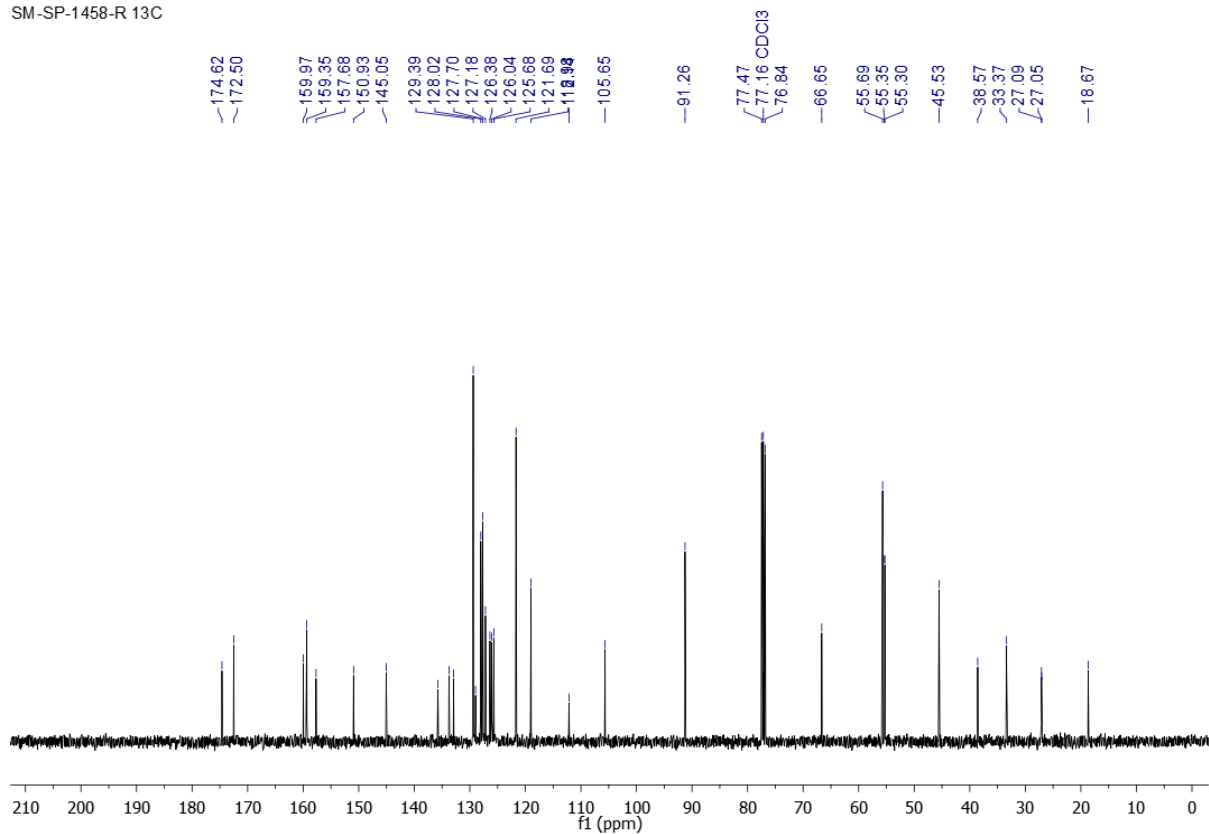
<sup>1</sup>H NMR of **4ag** (400 MHz, CDCl<sub>3</sub>):

SM-SP-1458-R 1H



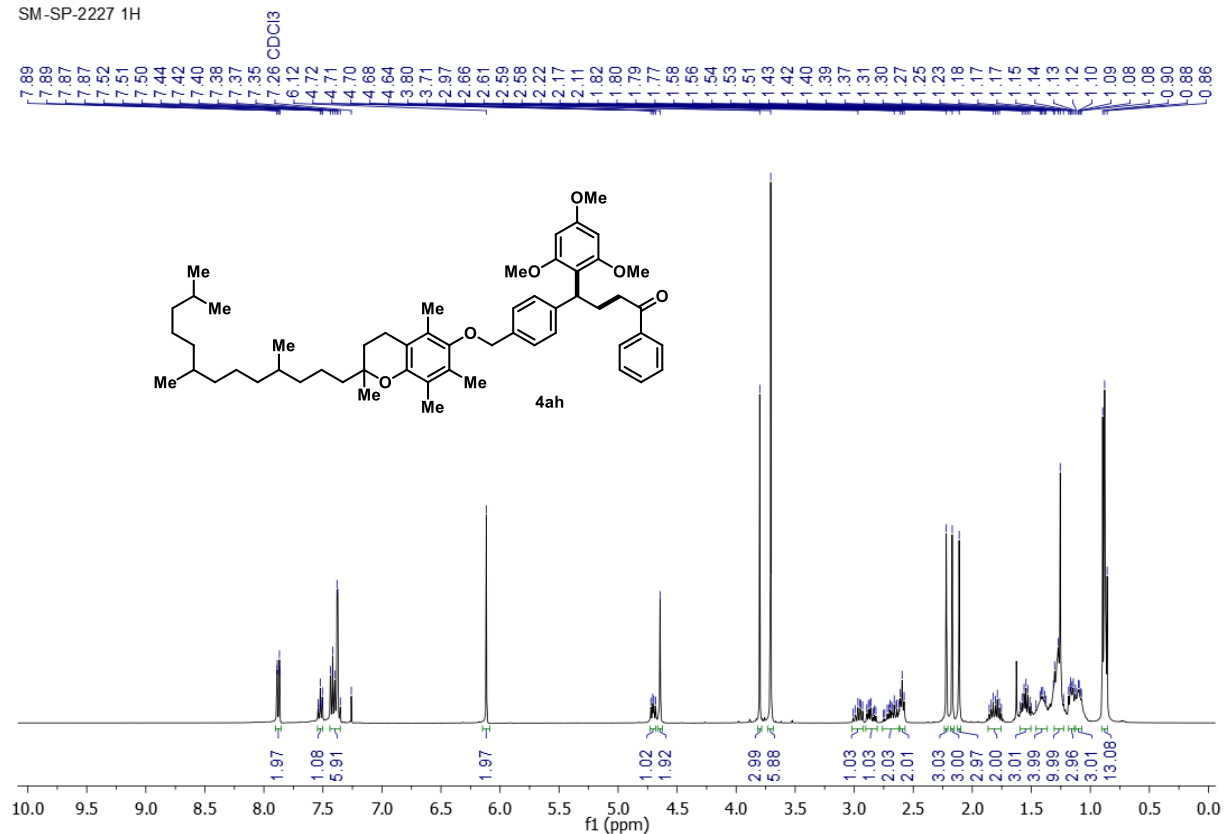
<sup>13</sup>C{<sup>1</sup>H} NMR of **4ag** (101 MHz, CDCl<sub>3</sub>):

SM-SP-1458-R 13C



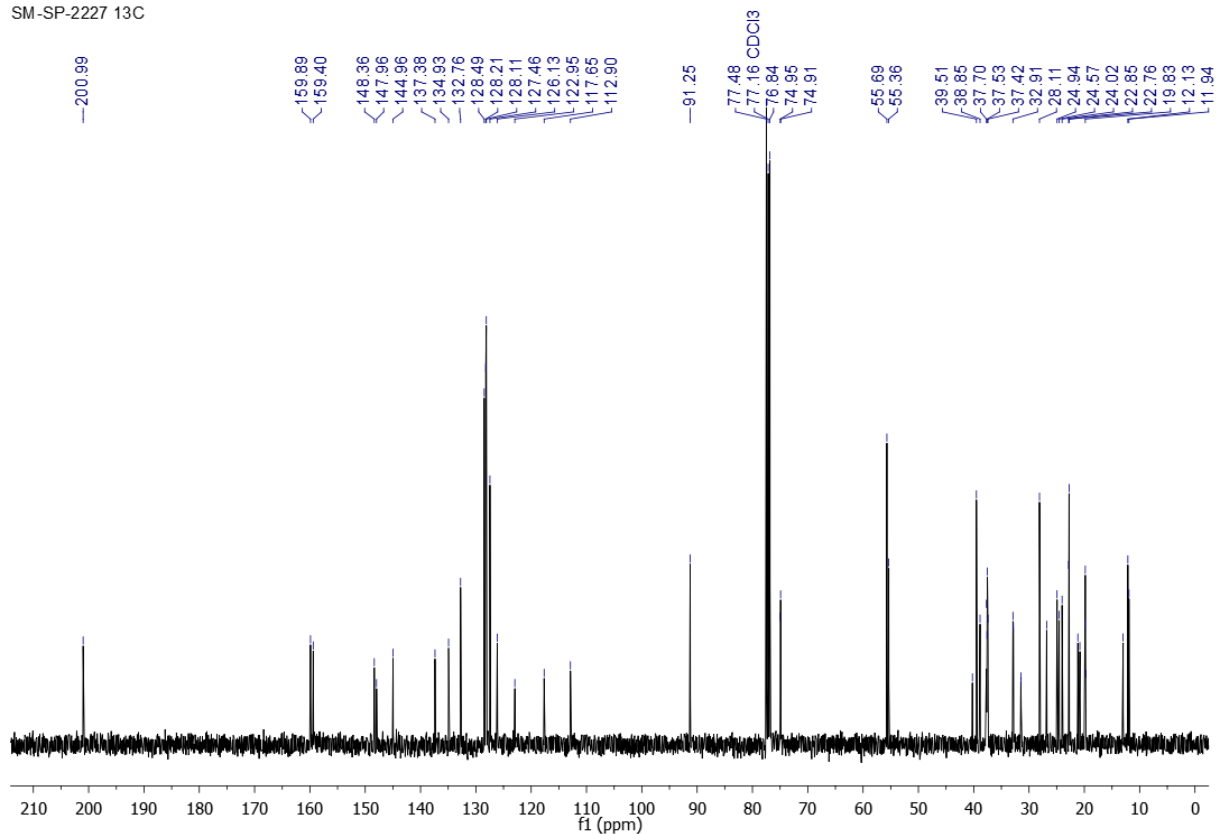
$^1\text{H}$  NMR of **4ah** (400 MHz,  $\text{CDCl}_3$ ):

SM-SP-2227 1H

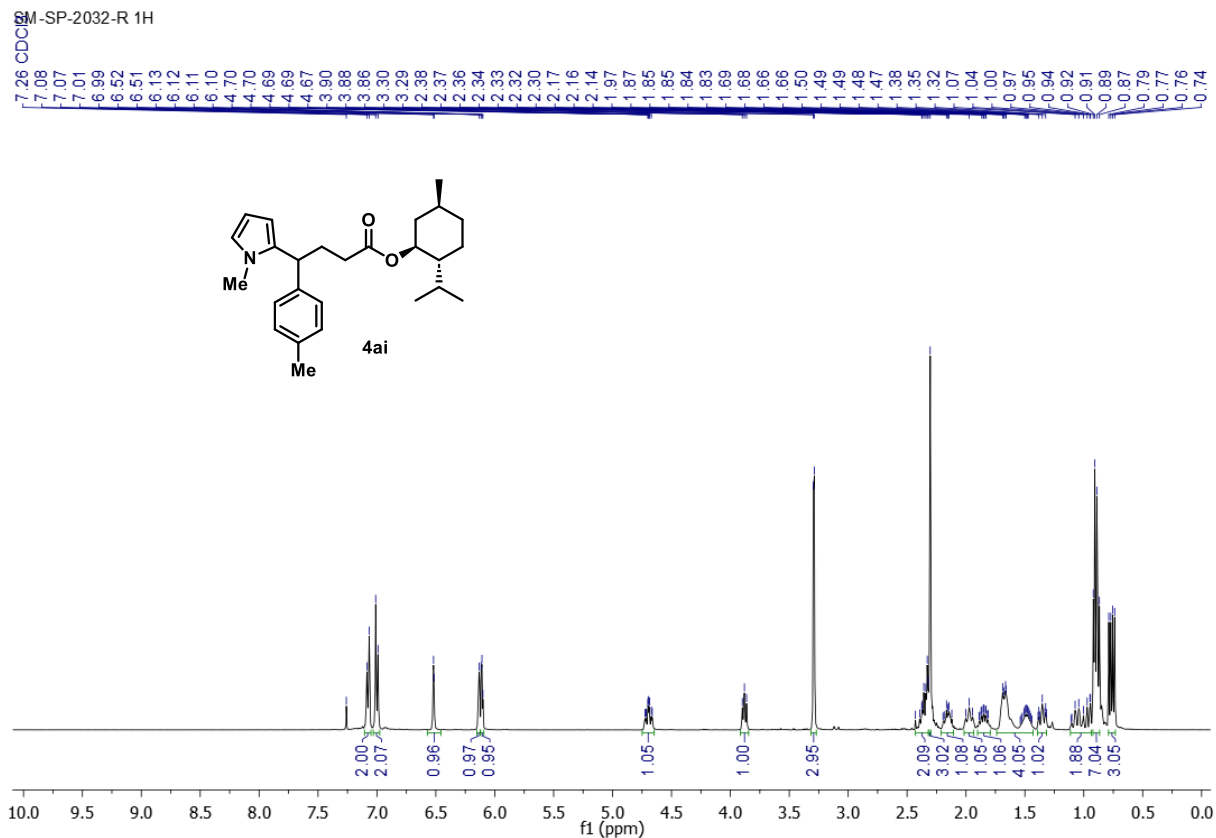


$^{13}\text{C}\{^1\text{H}\}$  NMR of **4ah** (101 MHz,  $\text{CDCl}_3$ ):

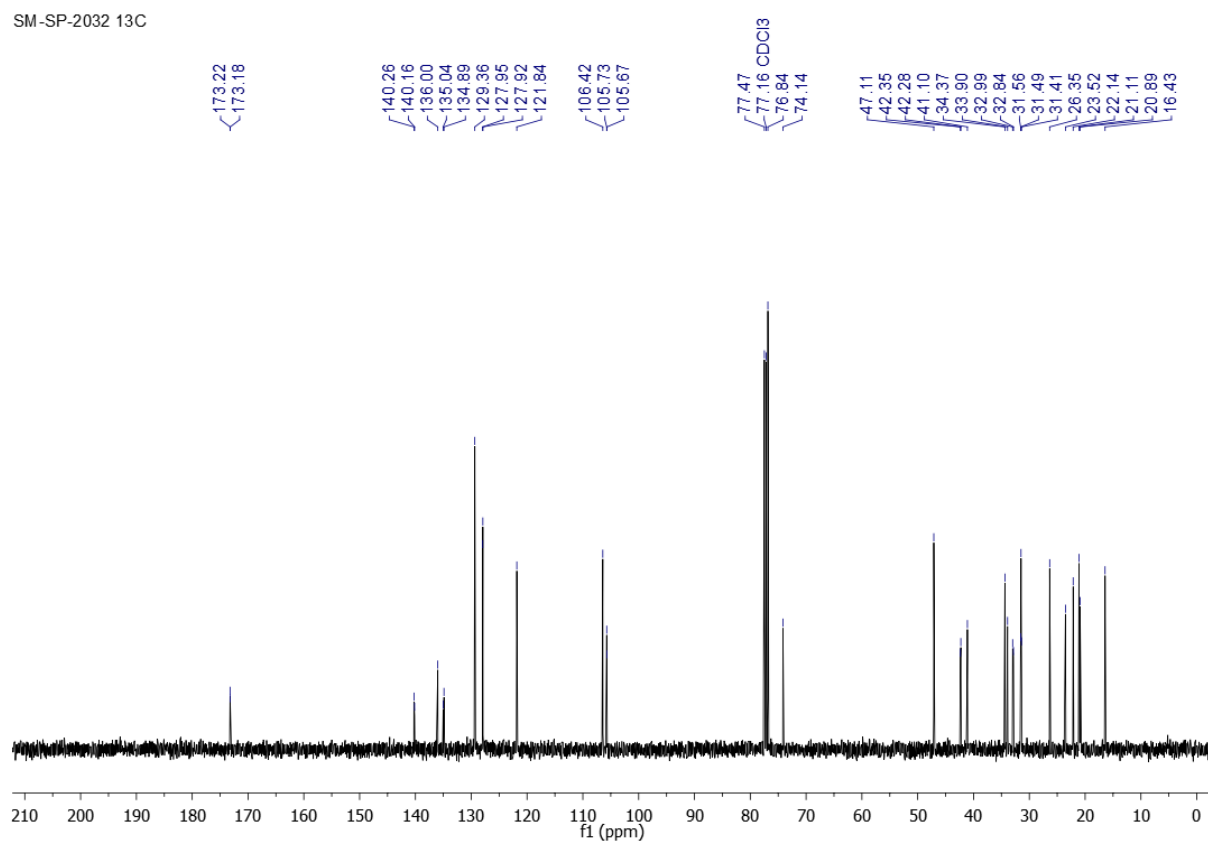
SM-SP-2227 13C



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

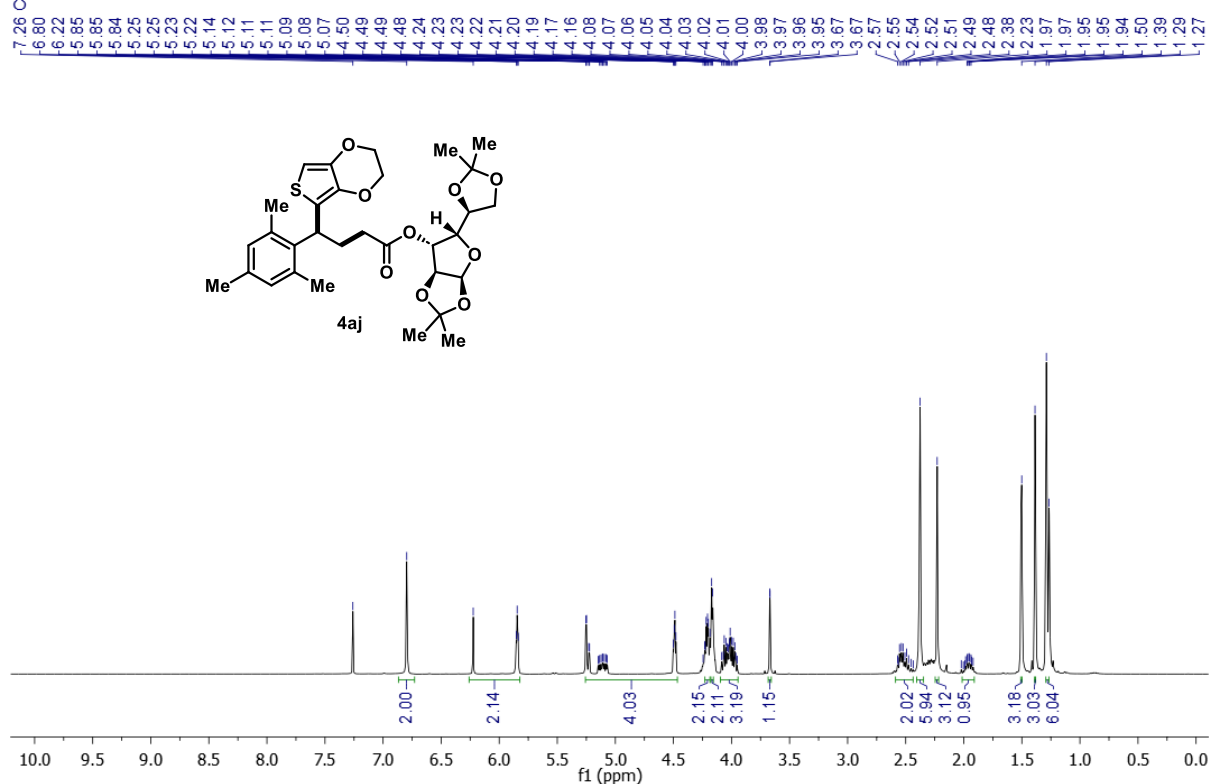


<sup>13</sup>C{<sup>1</sup>H} NMR of **4ai** (101 MHz, CDCl<sub>3</sub>):



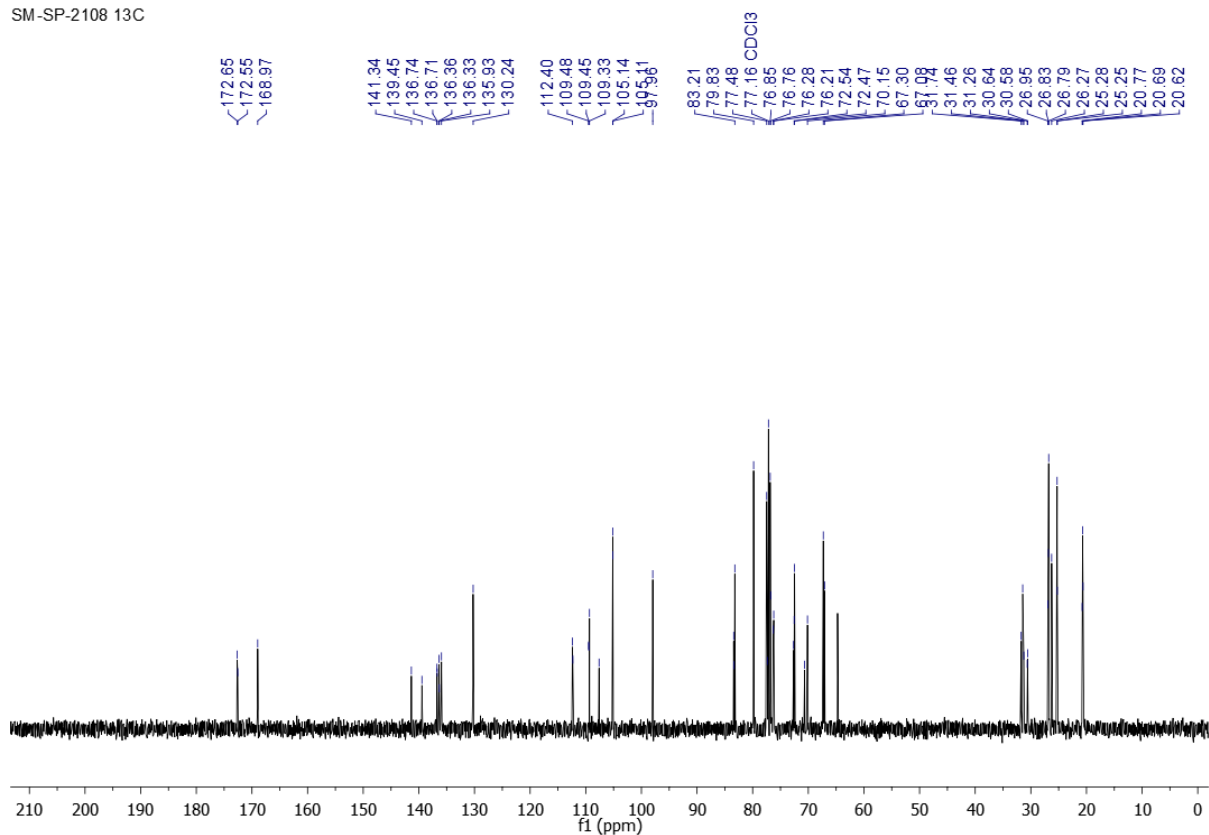
<sup>1</sup>H NMR of **4aj** (400 MHz, CDCl<sub>3</sub>):

SM-SP-2108 1H



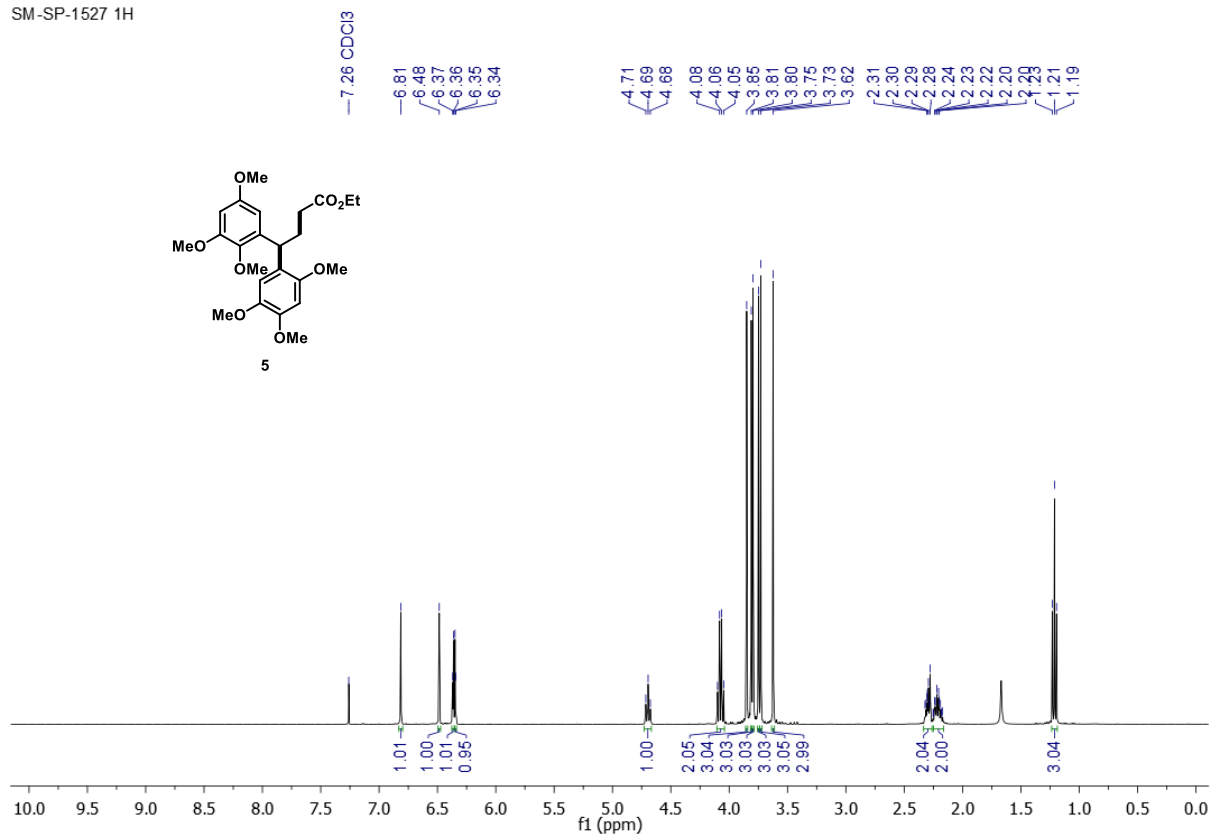
<sup>13</sup>C{<sup>1</sup>H} NMR of 4aj (101 MHz, CDCl<sub>3</sub>):

SM-SP-2108 13C



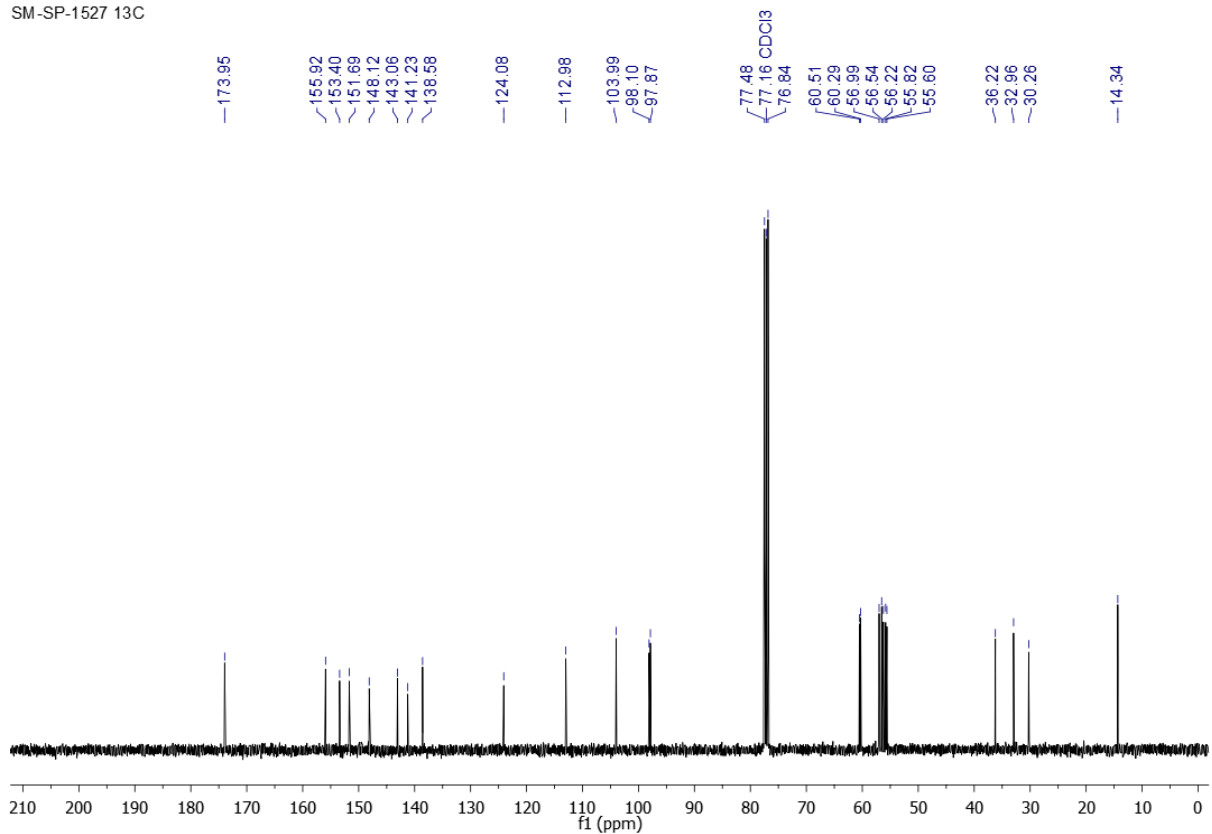
<sup>1</sup>H NMR of **5** (400 MHz, CDCl<sub>3</sub>):

SM-SP-1527 1H



<sup>13</sup>C{<sup>1</sup>H} NMR of **5** (101 MHz, CDCl<sub>3</sub>):

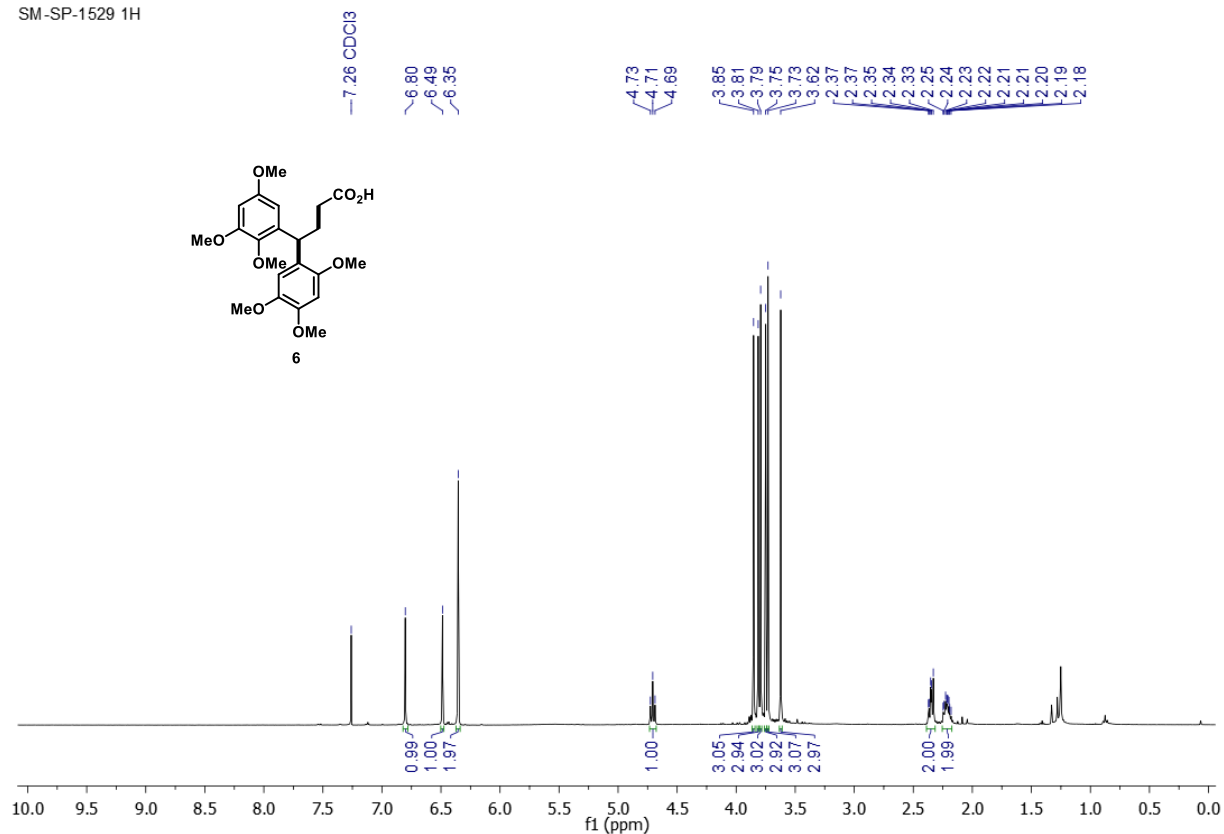
SM-SP-1527 13C





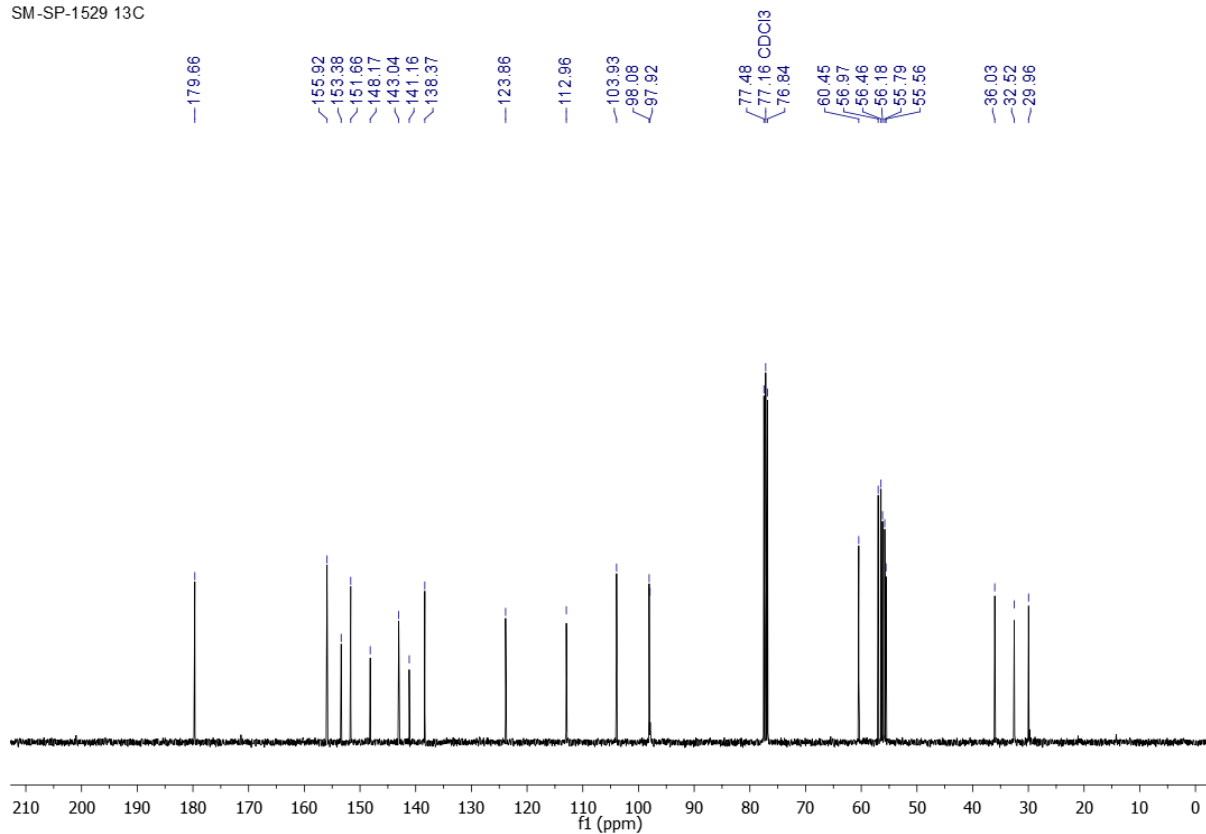
<sup>1</sup>H NMR of **6** (400 MHz, CDCl<sub>3</sub>):

SM-SP-1529 1H



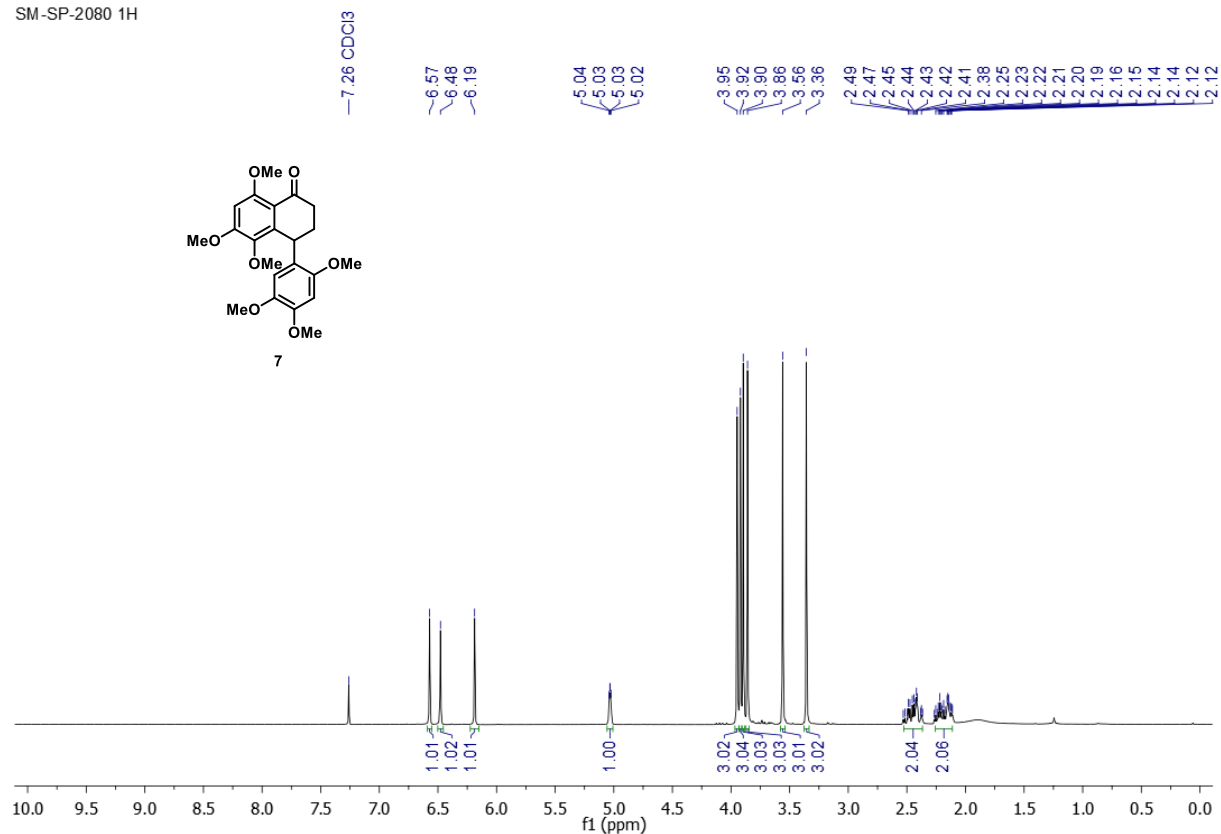
<sup>13</sup>C{<sup>1</sup>H} NMR of **6** (101 MHz, CDCl<sub>3</sub>):

SM-SP-1529 13C



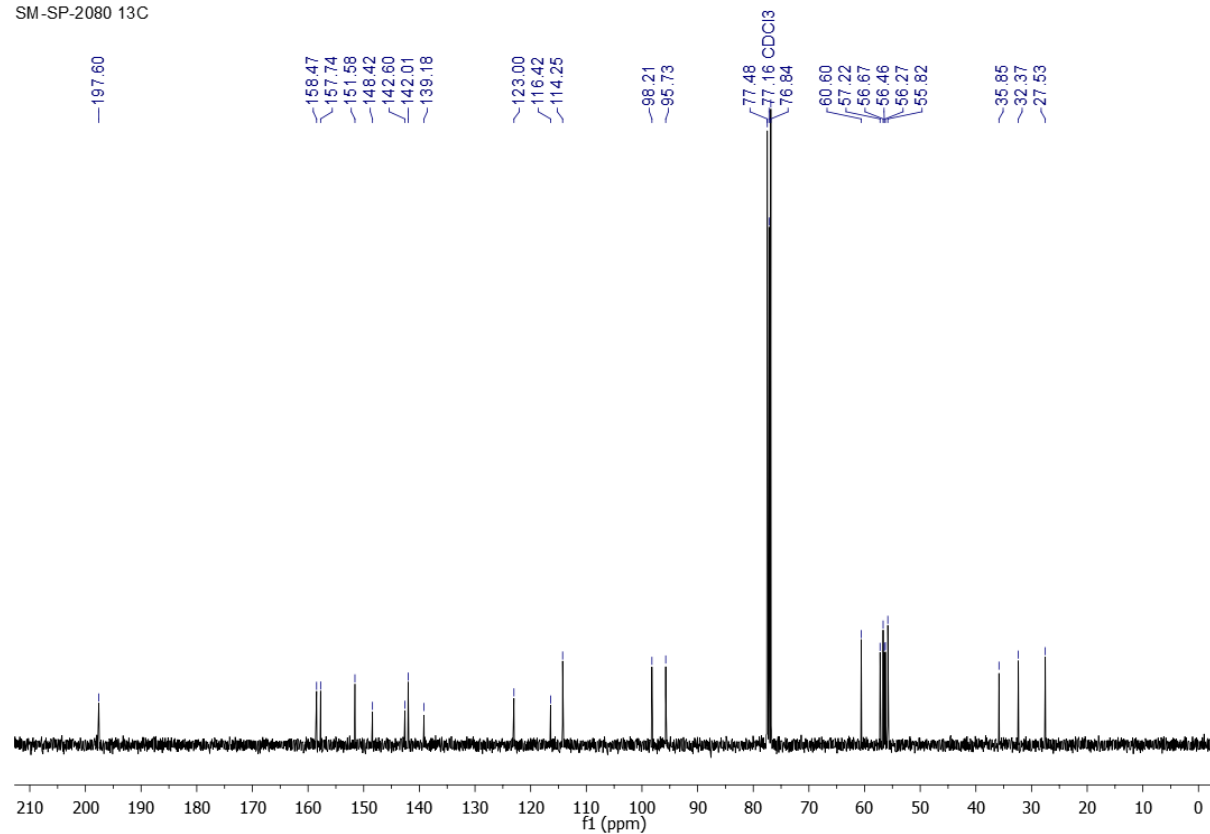
<sup>1</sup>H NMR of **7** (400 MHz, CDCl<sub>3</sub>):

SM-SP-2080 1H



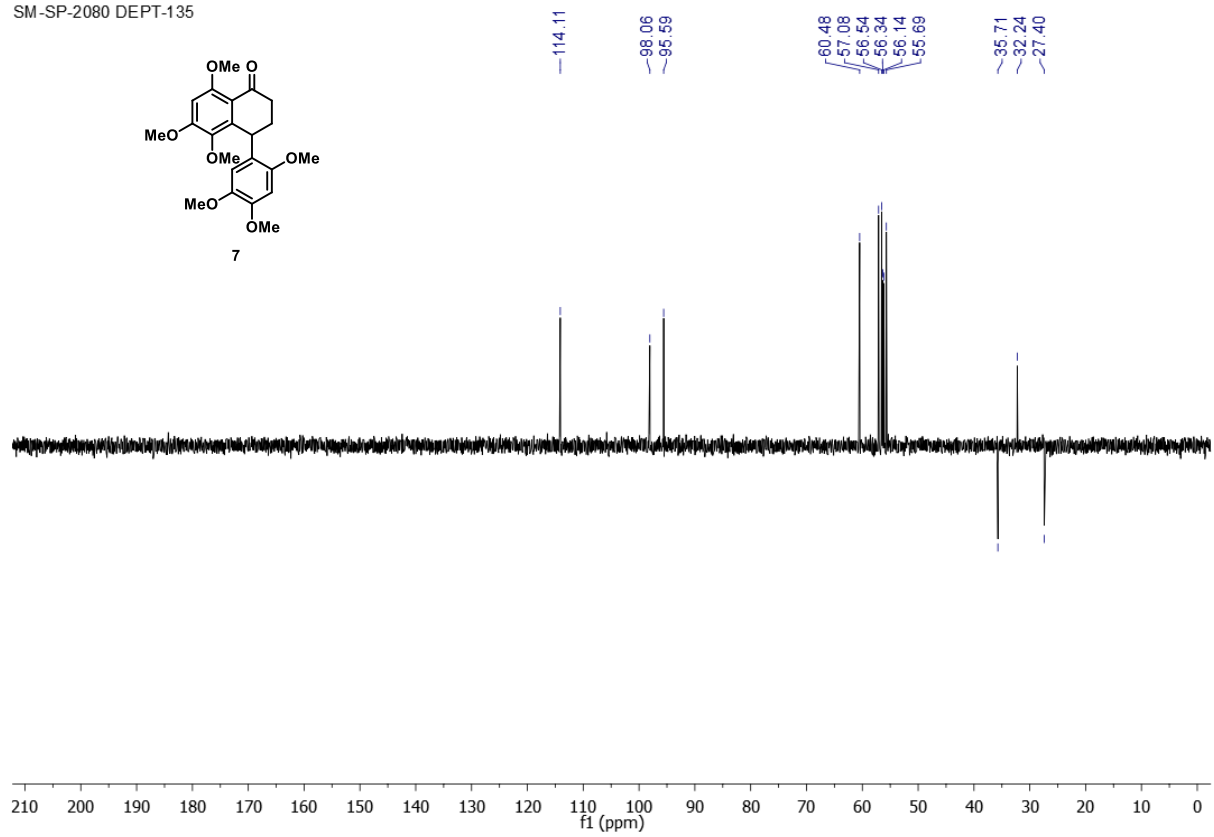
<sup>13</sup>C{<sup>1</sup>H} NMR of **7** (101 MHz, CDCl<sub>3</sub>):

SM-SP-2080 13C



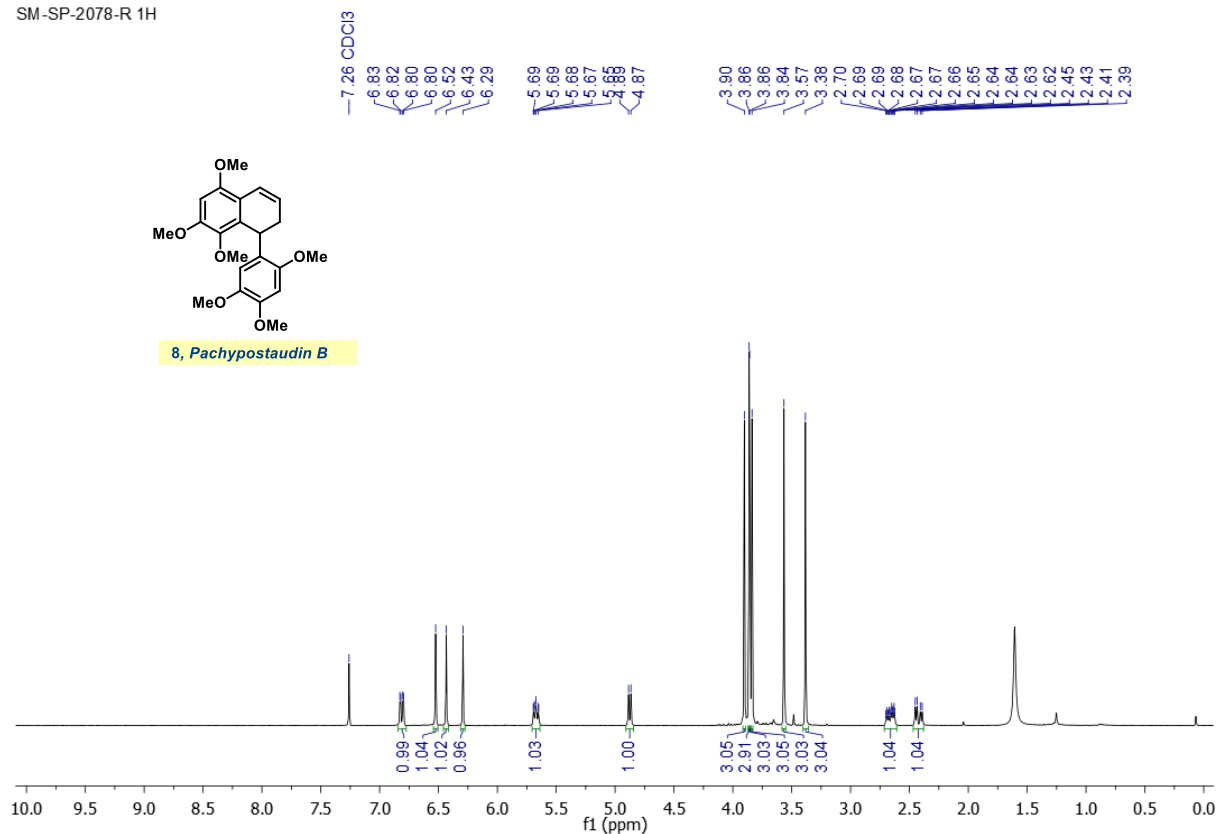
$^{13}\text{C}\{^1\text{H}\}$  DEPT-135 NMR of **7** (101 MHz,  $\text{CDCl}_3$ ):

SM-SP-2080 DEPT-135



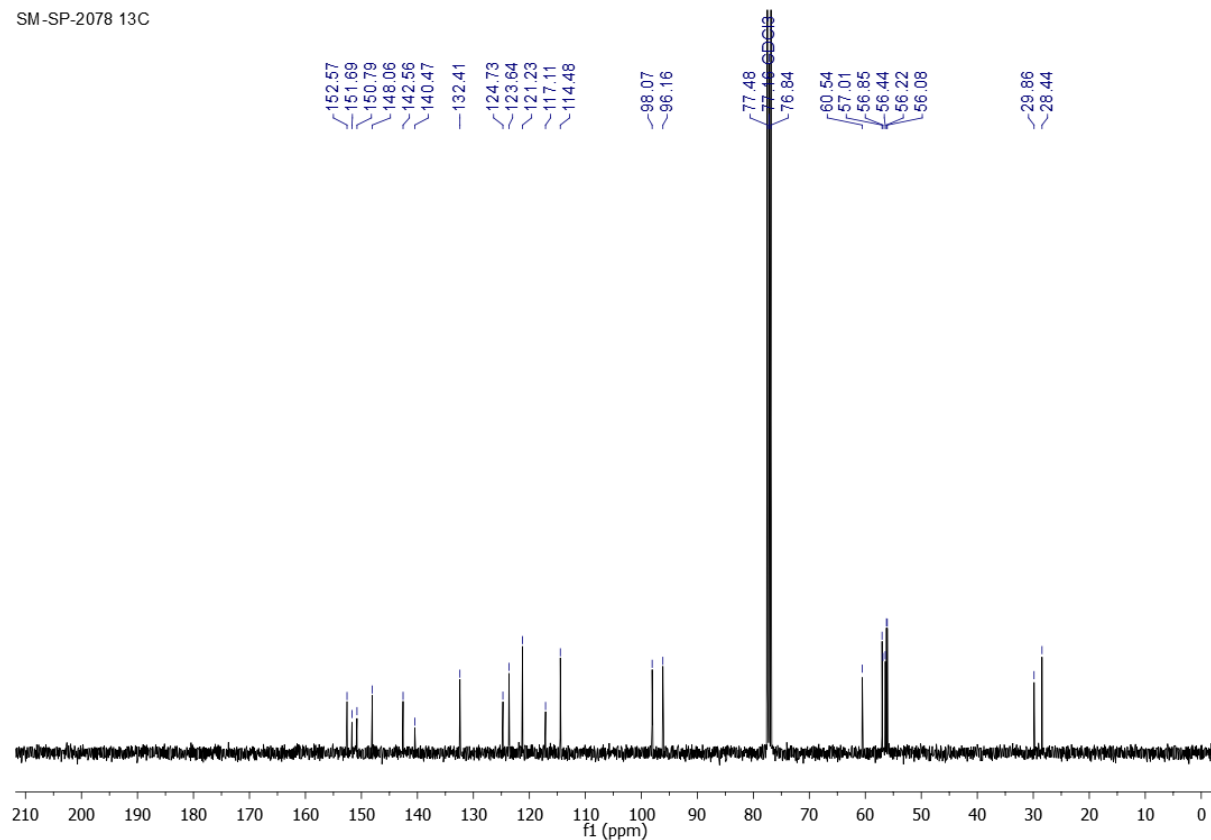
$^1\text{H}$  NMR of **8** (400 MHz,  $\text{CDCl}_3$ ):

SM-SP-2078-R 1H



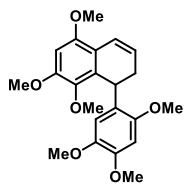
$^{13}\text{C}\{^1\text{H}\}$  NMR of **8** (101 MHz,  $\text{CDCl}_3$ ):

SM-SP-2078 13C

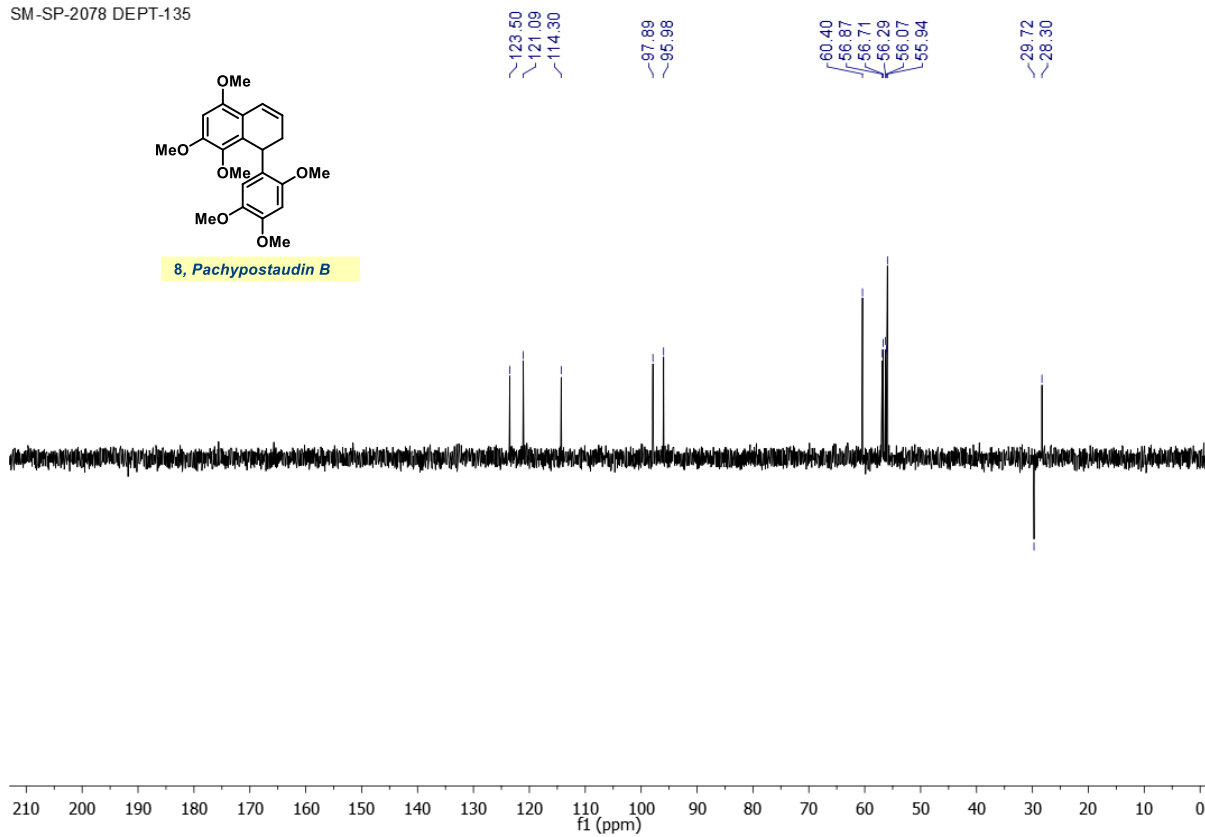


$^{13}\text{C}\{^1\text{H}\}$  DEPT-135 NMR of **8** (101 MHz,  $\text{CDCl}_3$ ):

SM-SP-2078 DEPT-135

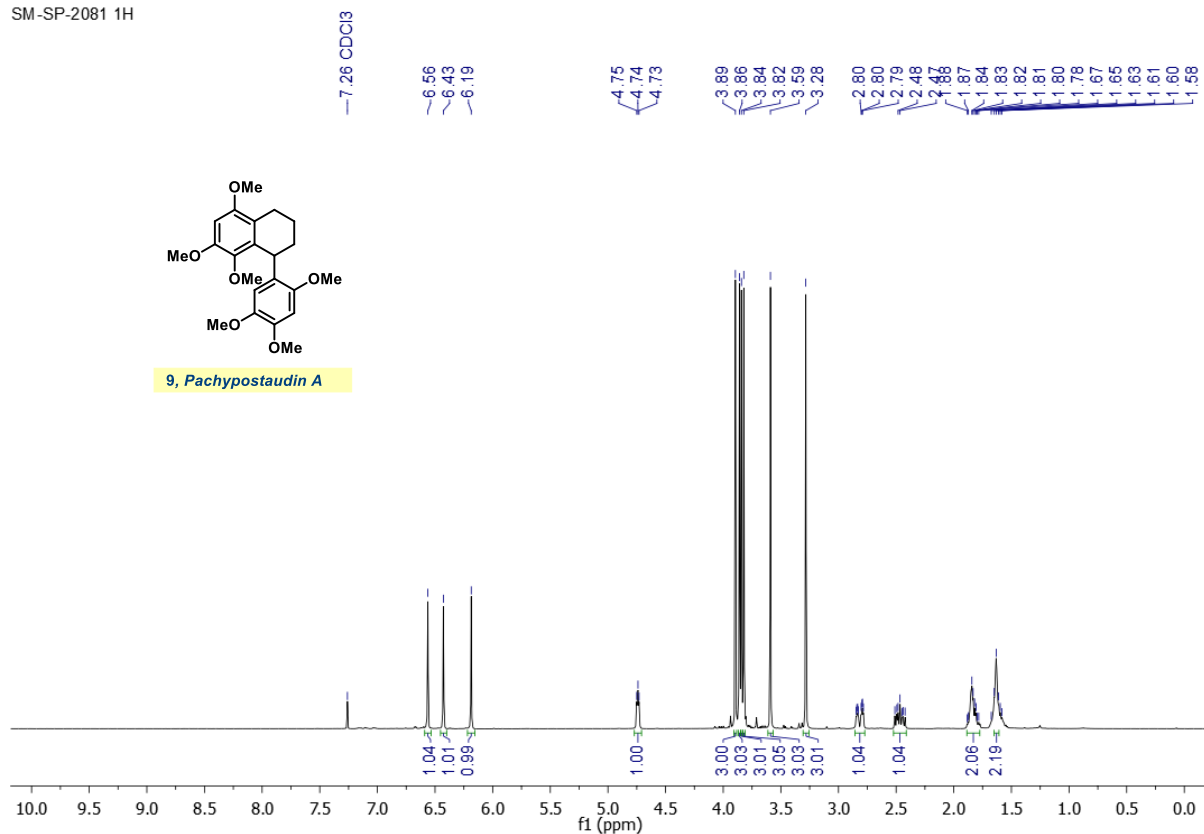


**8, Pachypostaudin B**



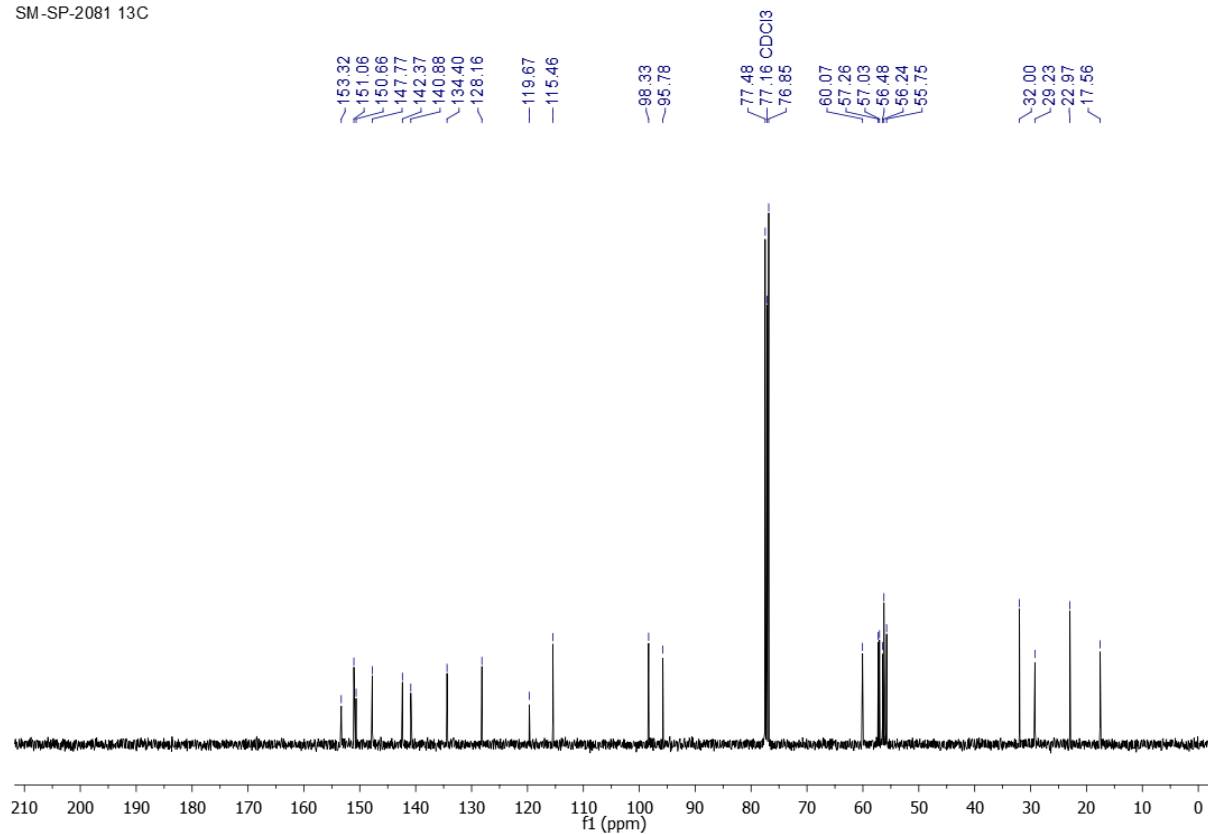
<sup>1</sup>H NMR of **9** (400 MHz, CDCl<sub>3</sub>):

SM-SP-2081 1H

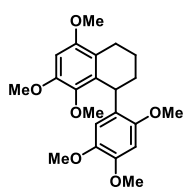


<sup>13</sup>C{<sup>1</sup>H} NMR of **9** (101 MHz, CDCl<sub>3</sub>):

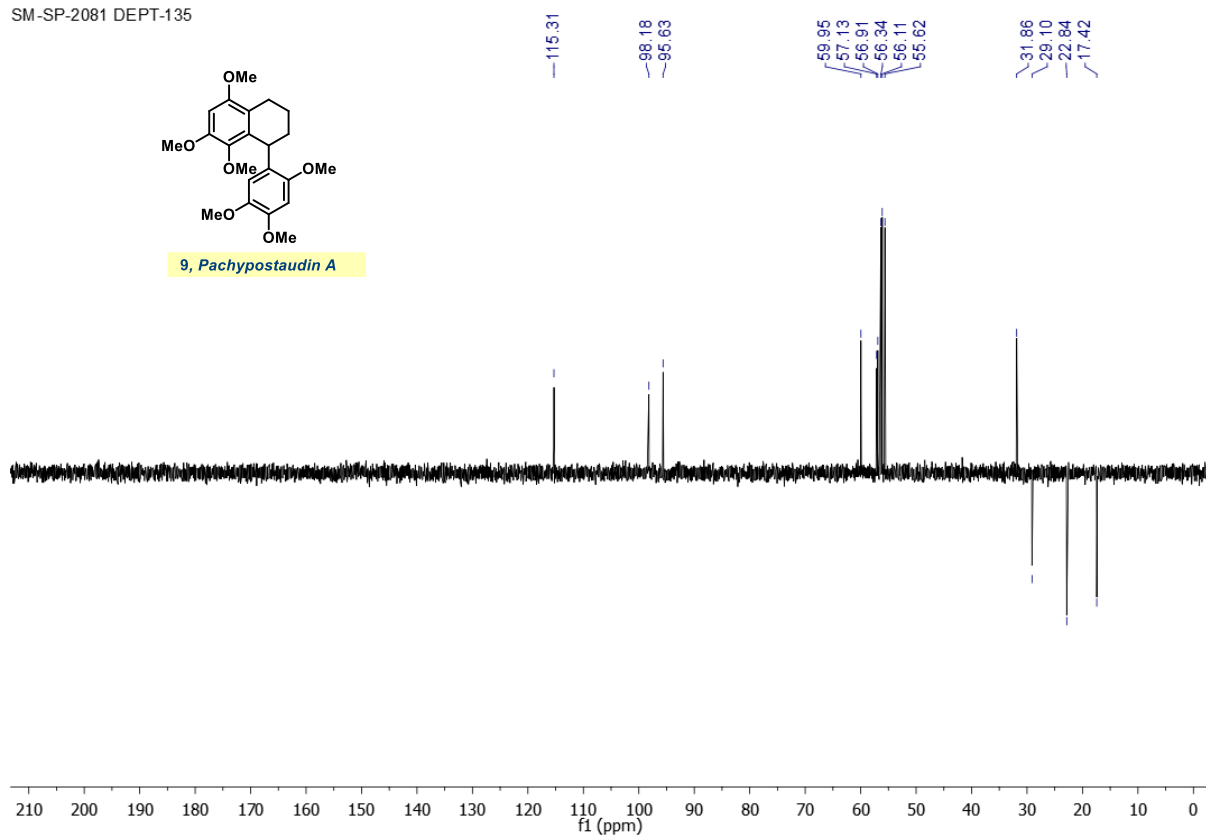
SM-SP-2081 13C



<sup>13</sup>C{<sup>1</sup>H} DEPT-135 NMR of **9** (101 MHz, CDCl<sub>3</sub>):

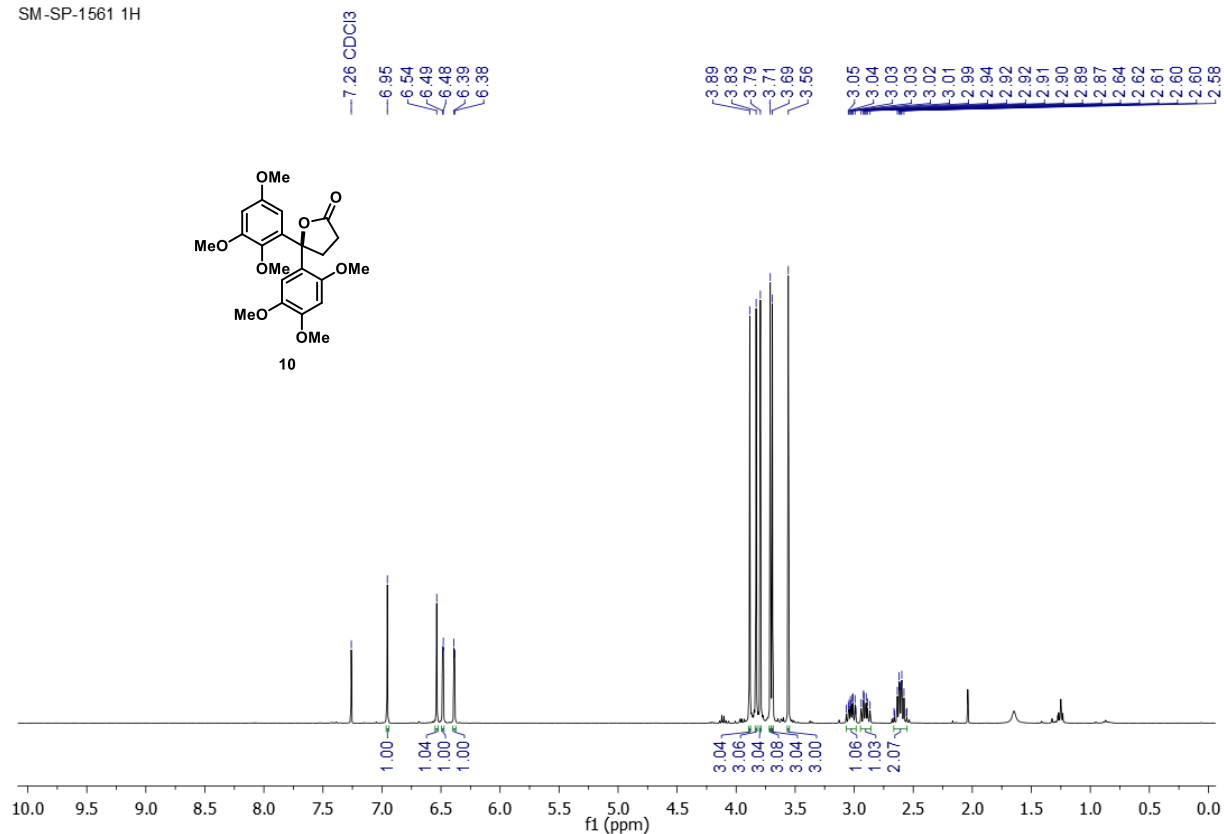


9, *Pachypostaudin A*



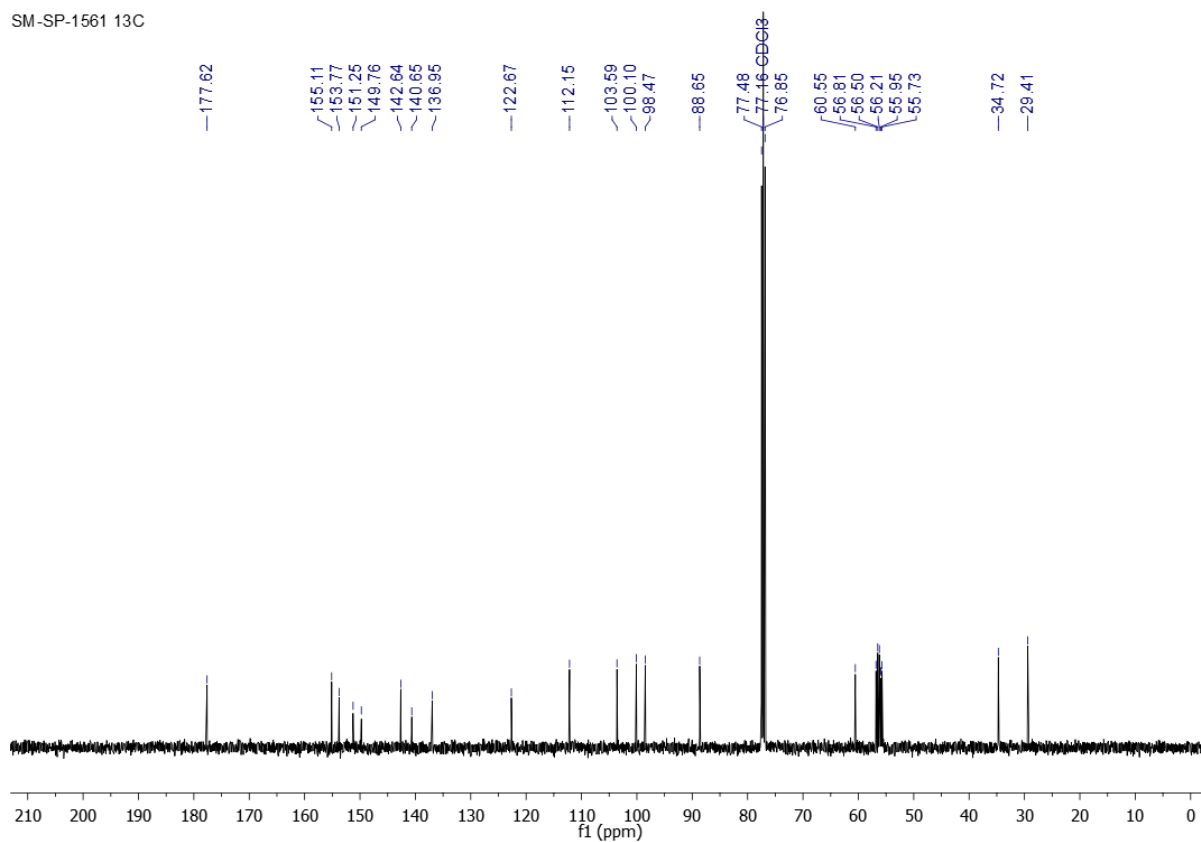
<sup>1</sup>H NMR of **10** (400 MHz, CDCl<sub>3</sub>):

SM-SP-1561 1H



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

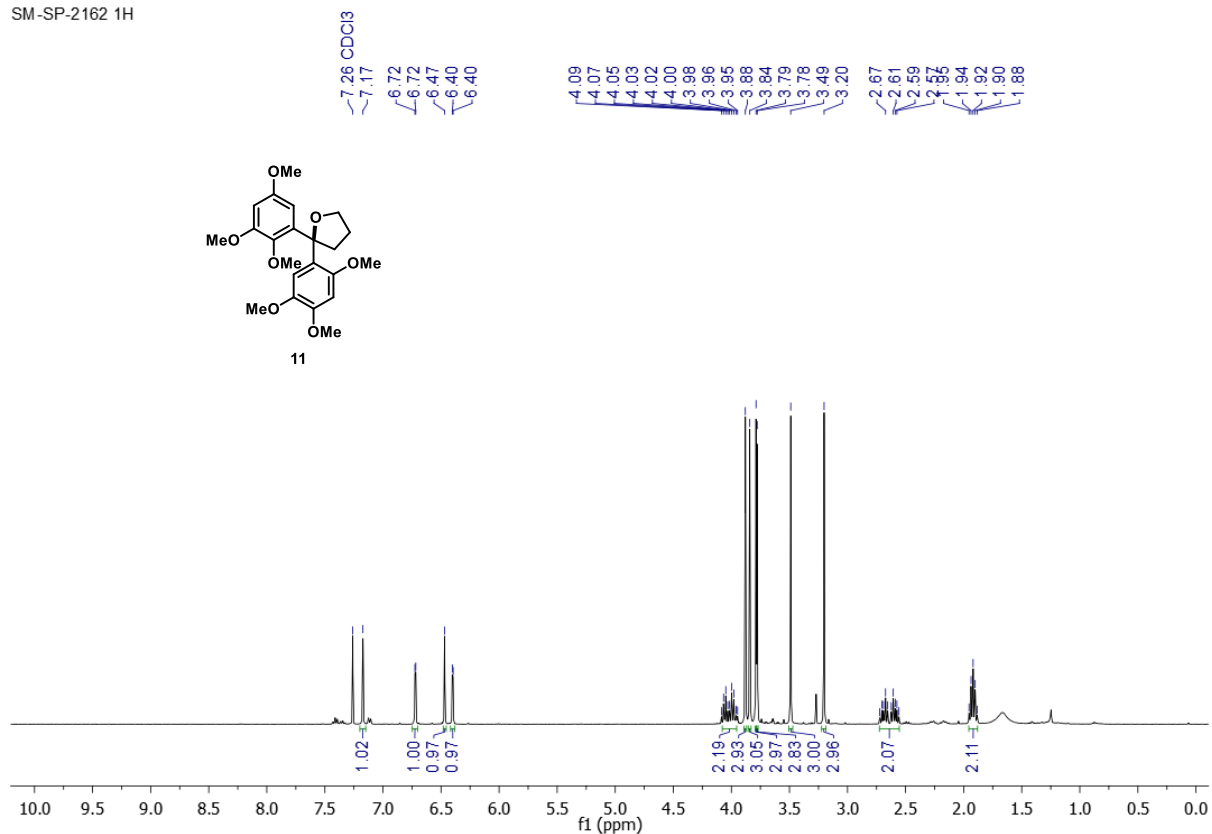
SM-SP-1561 13C





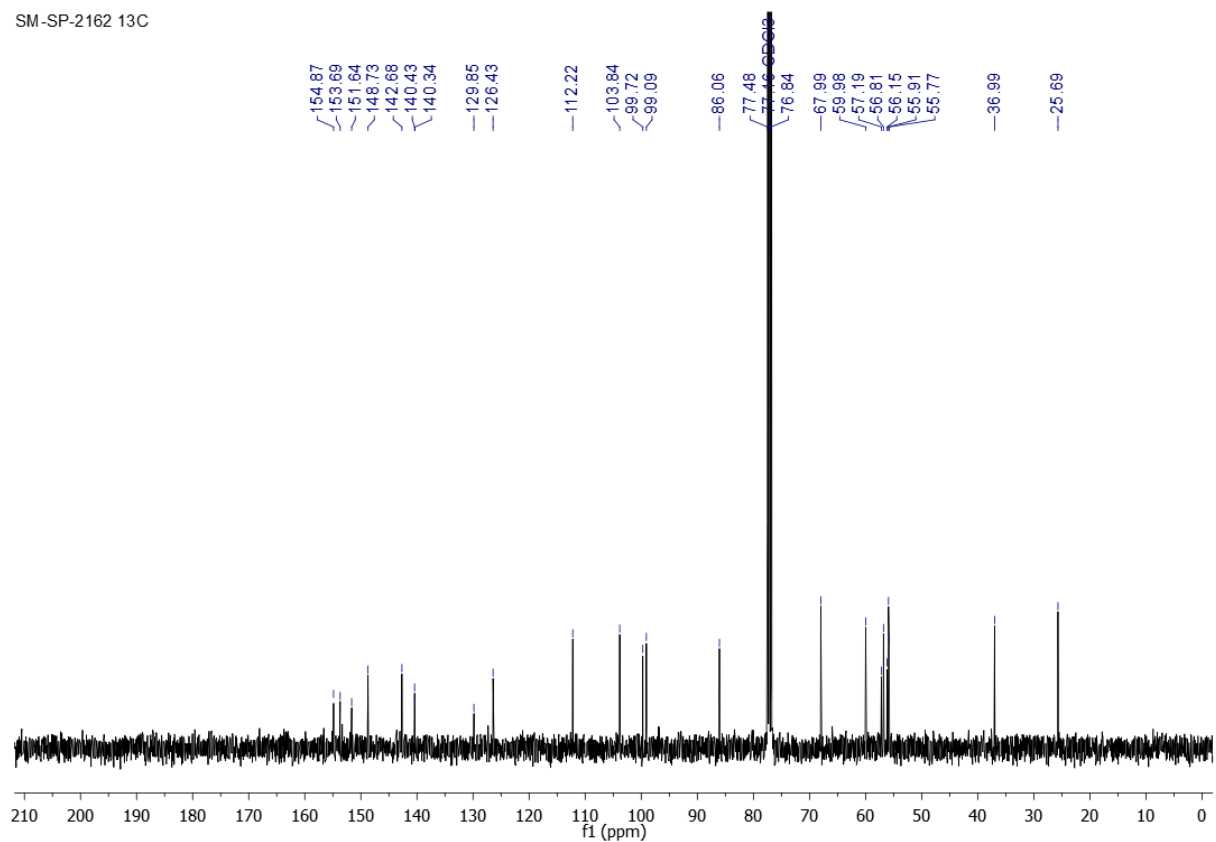
<sup>1</sup>H NMR of **11** (400 MHz, CDCl<sub>3</sub>):

SM-SP-2162 1H



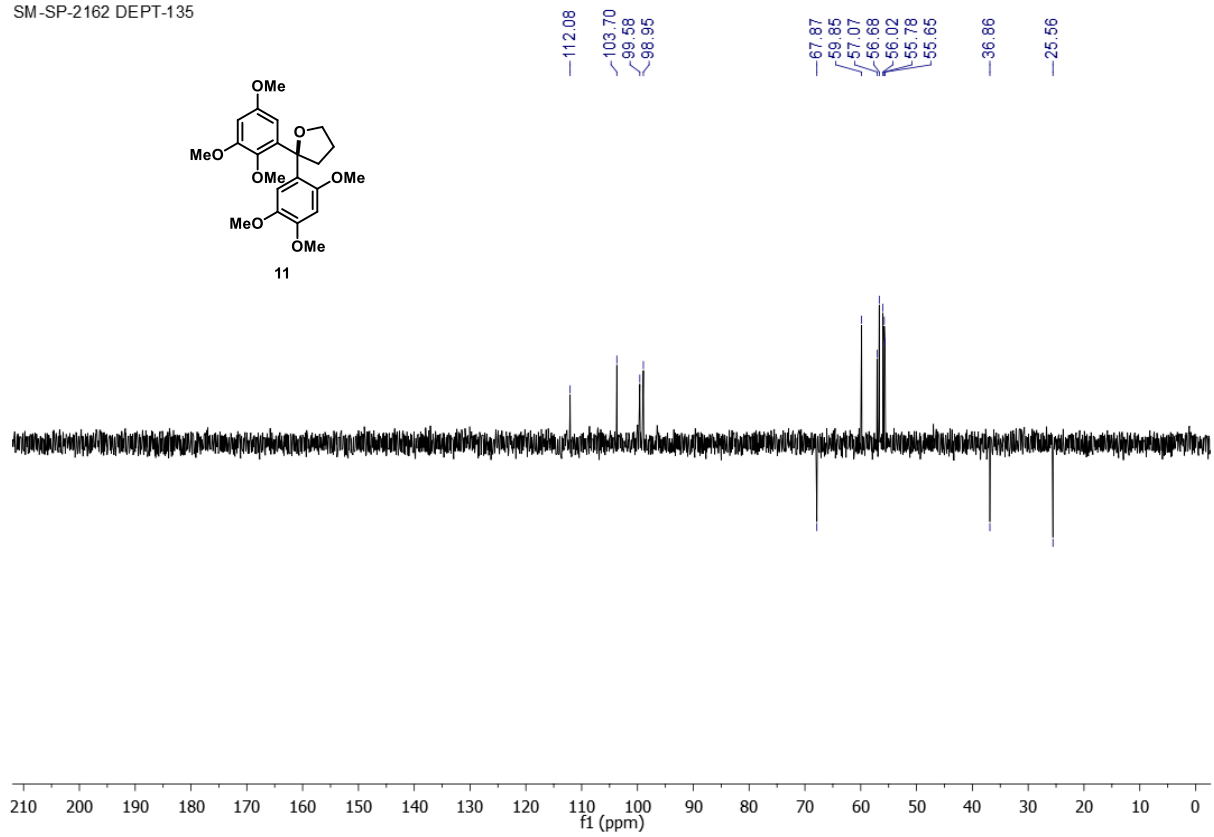
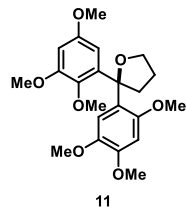
<sup>13</sup>C{<sup>1</sup>H} NMR of **11** (101 MHz, CDCl<sub>3</sub>):

SM-SP-2162 13C



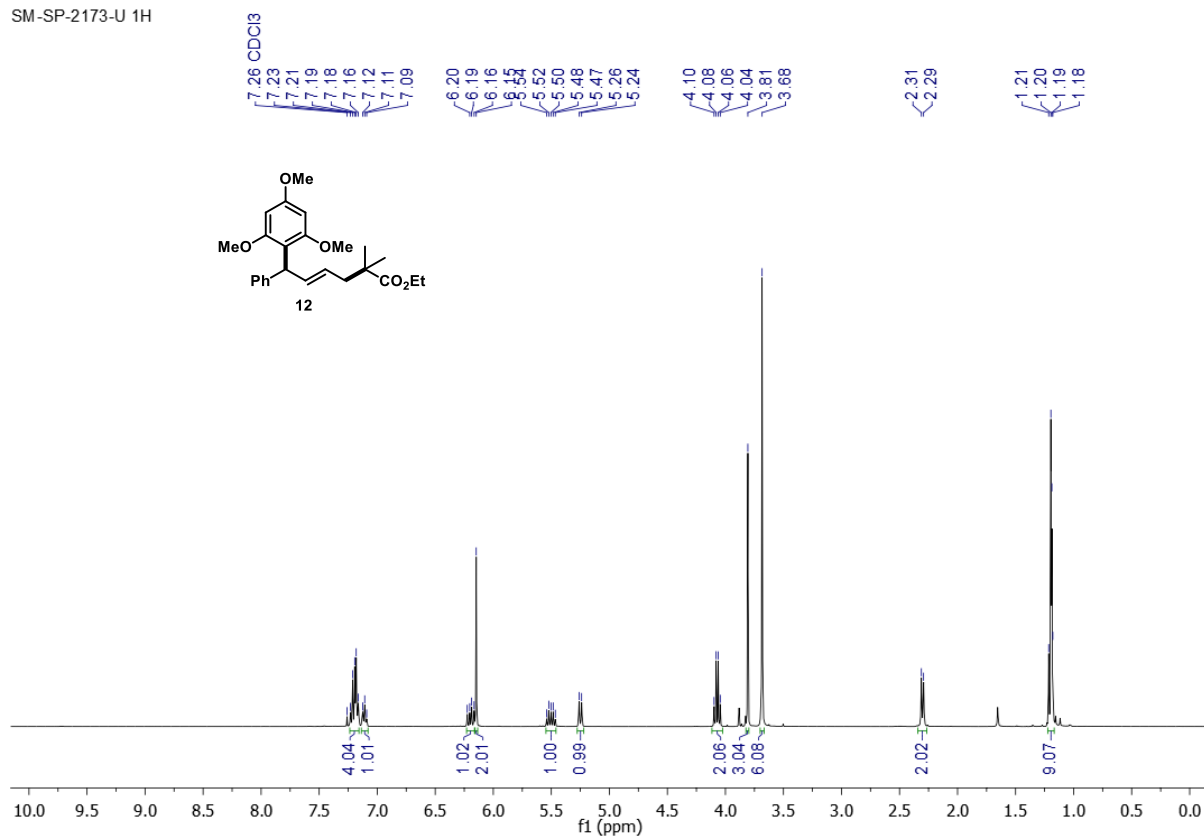
$^{13}\text{C}\{^1\text{H}\}$  DEPT-135 NMR of **11** (101 MHz,  $\text{CDCl}_3$ ):

SM-SP-2162 DEPT-135



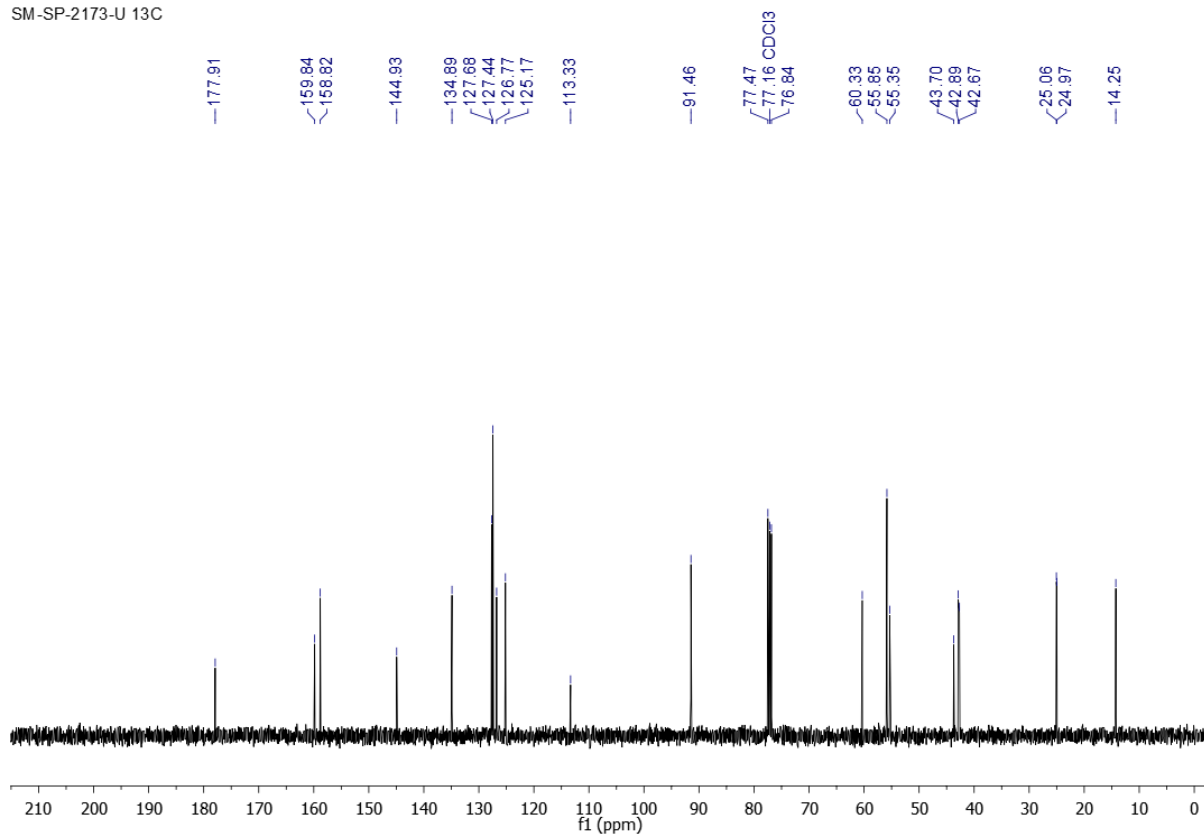
$^1\text{H}$  NMR of **12** (400 MHz,  $\text{CDCl}_3$ ):

SM-SP-2173-U 1H



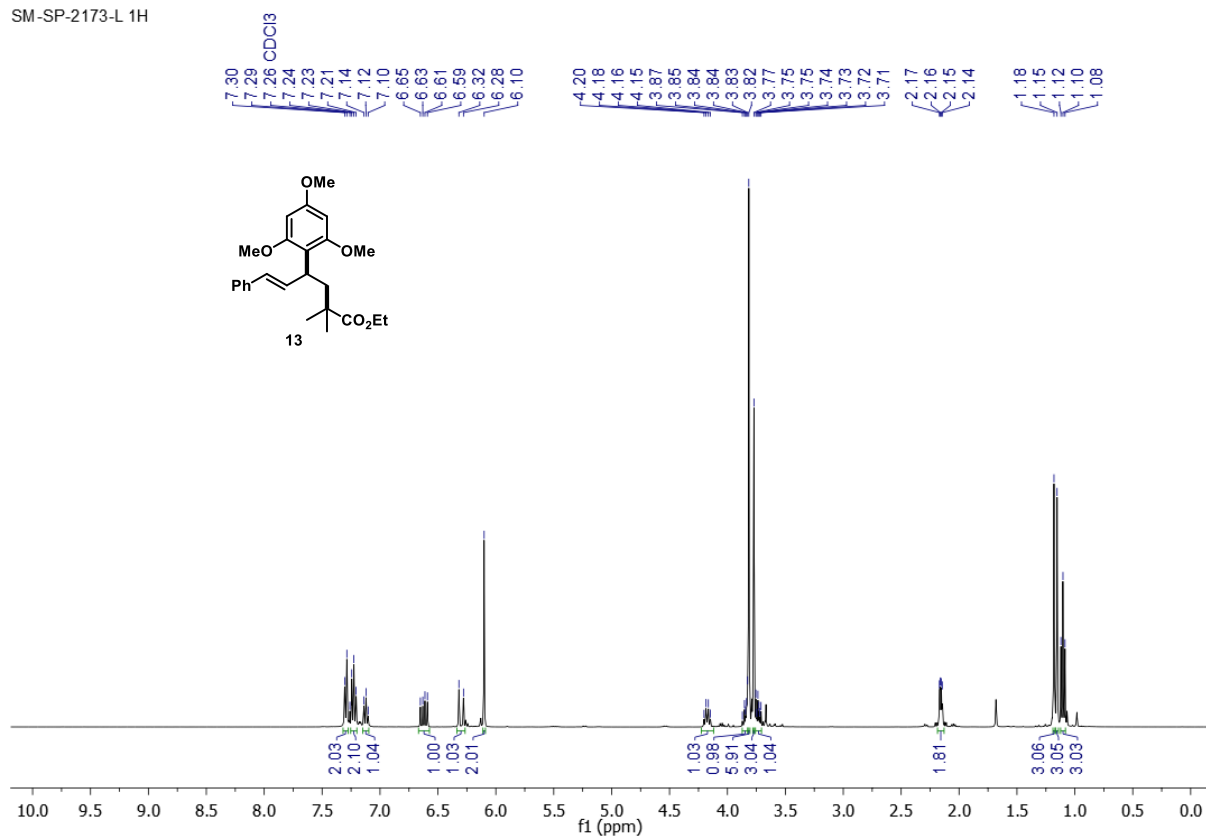
$^{13}\text{C}\{^1\text{H}\}$  NMR of **12** (101 MHz,  $\text{CDCl}_3$ ):

SM-SP-2173-U 13C



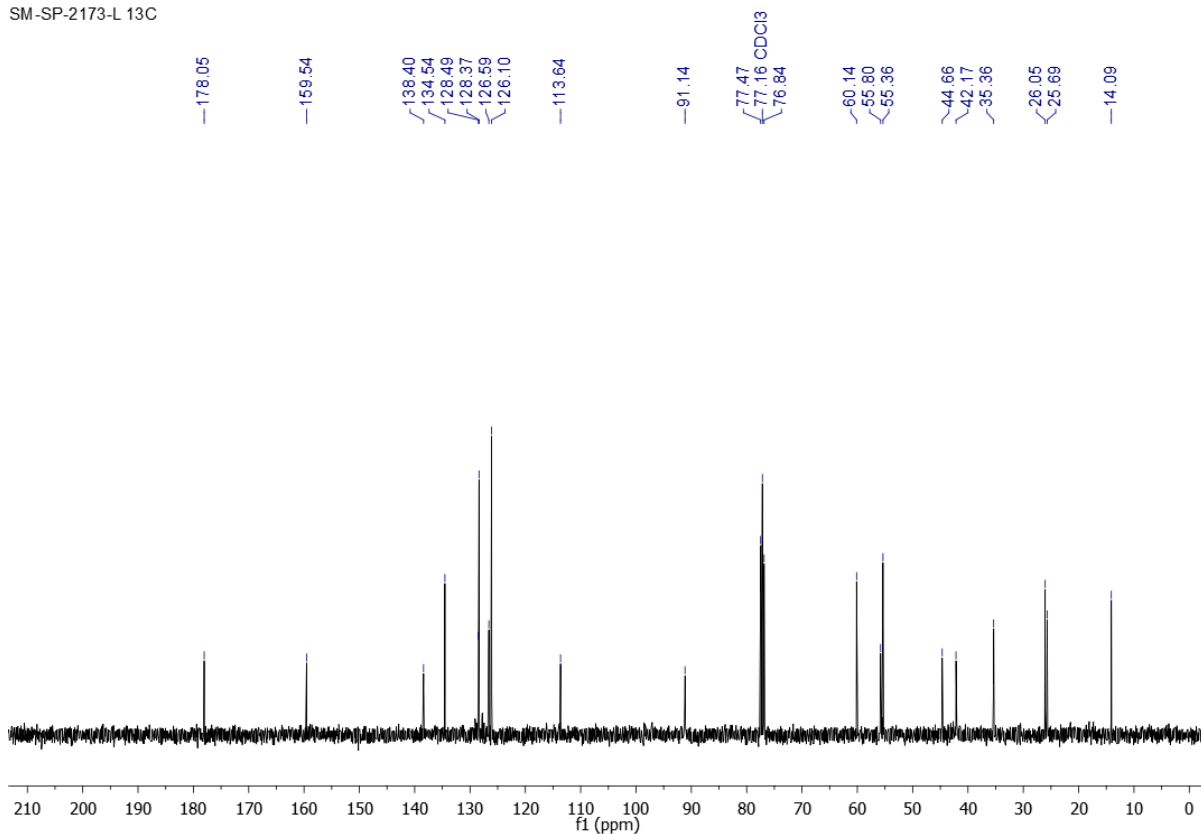
<sup>1</sup>H NMR of **13** (400 MHz, CDCl<sub>3</sub>):

SM-SP-2173-L 1H



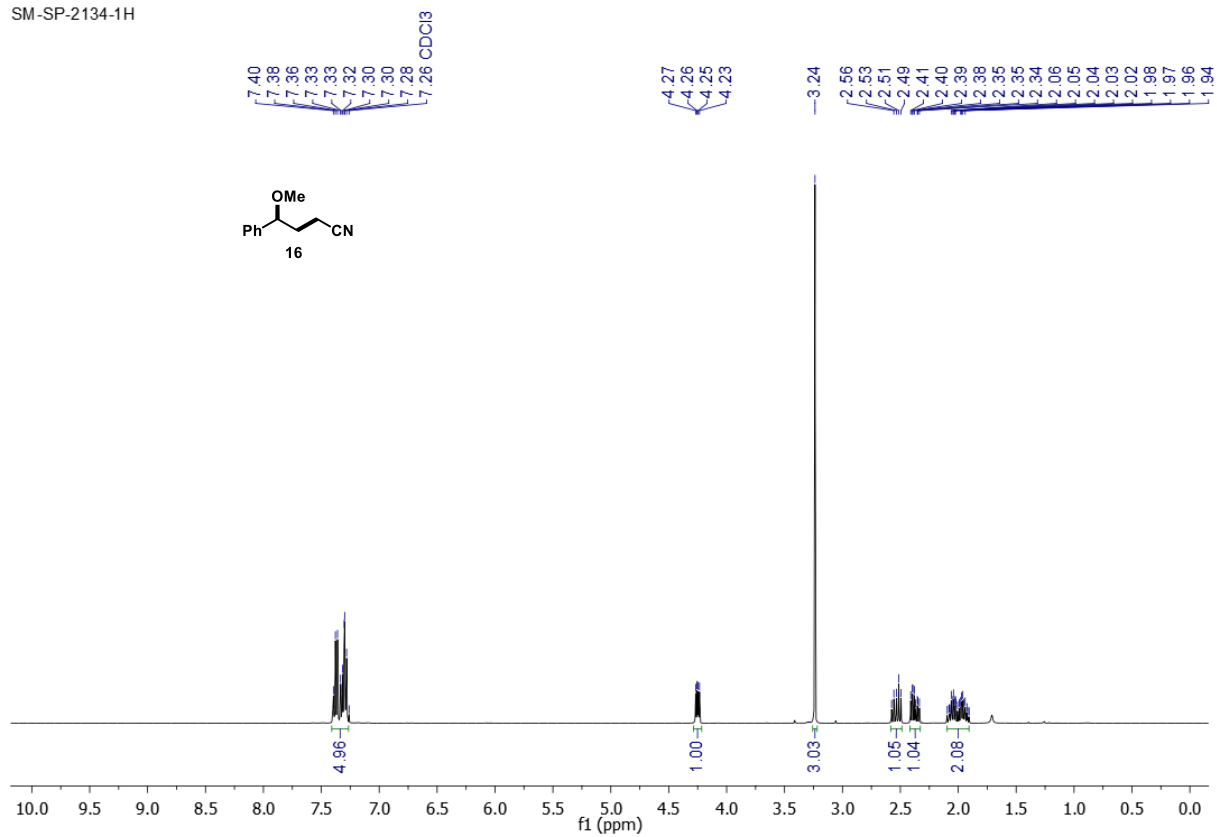
<sup>13</sup>C{<sup>1</sup>H} NMR of **13** (101 MHz, CDCl<sub>3</sub>):

SM-SP-2173-L 13C



<sup>1</sup>H NMR of **16** (400 MHz, CDCl<sub>3</sub>):

SM-SP-2134-1H



<sup>13</sup>C{<sup>1</sup>H} NMR of **16** (101 MHz, CDCl<sub>3</sub>):

SM-SP-2134-13C

