

## ***Supporting Information***

# **Photocatalytic Synthesis of *para*-Peroxyquinols: Total Synthesis of ( $\pm$ )-Stemenone B and ( $\pm$ )-Parvistilbene B**

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## **1. General Considerations**

Reactions requiring heating were performed either in (a) round-bottom flasks using a silicone oil bath heated with an IKA C-MAG HS7 heat/stir plate or in (b) Chemglass 8 mL scintillation vials with a rubber septum (c) Chemglass 20 mL scintillation vials with a rubber septum using a Chemglass OptiChem block heated with an IKA C-MAG HS7 heat/stir plate. When necessary, solvents were dried and purified before use via a solvent purification system ( $\text{CH}_2\text{Cl}_2$ , THF,  $\text{Et}_2\text{O}$ ) or used from Sure/Seal<sup>TM</sup> bottle (DMF, MeCN). Other commercial reagents were used without additional purification. For light irradiation, a Kessil PR160L blue LED lamp ( $\lambda_{\text{max}} = 440$  nm, 100% intensity, max 45W, 7 cm from wall of flask) was employed with a commercial blade fan for cooling.

Analytical thin layer chromatography (TLC) was performed on EM Reagents 0.25 mm silica-gel 254-F plates. Visualization was accomplished with UV light. Automated flash chromatography was performed using a Teledyne ISCO CombiFlash<sup>®</sup> (254 nm & 280 nm UV detector) with RediSep R<sub>f</sub> Gold<sup>®</sup> disposable columns (60 Å porosity, 20–40  $\mu\text{m}$ ) or flash chromatography with forced flow of the indicated solvent system on Silica-P flash silica gel (50-63  $\mu\text{m}$  mesh particle size). NMR spectra ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$ ) were recorded on a Fourier transform (Bruker NEO) NMR spectrometer equipped with SampleCase at 298 K at 400/600 MHz, 151 MHz, and 376 MHz, respectively. Chemical shifts are reported relative to the solvent resonance peak  $\delta$  7.26 ( $\text{CDCl}_3$ ) and  $\delta$  2.50 ( $\text{DMSO}-d^6$ ) for  $^1\text{H}$  NMR spectra and  $\delta$  77.16 ( $\text{CDCl}_3$ ) for  $^{13}\text{C}$  NMR spectra. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, b = broad singlet, m = multiplet), coupling constants, and number of protons. Accurate mass measurement analyses were acquired on Waters instruments. These measurements were conducted on either a GCMS with electron ionization (EI) or an LCMS with electrospray ionization (ESI). The signals were mass measured (TOF) against an internal lock mass reference of perfluorotributylamine (PFTBA) for EI-GCMS, and leucine enkephalin for ESI-LCMS. Waters software calibrates the instruments, and reports measurements, by use of neutral atomic masses; the mass of the electron is not subtracted (positive ions) or added (negative ions). Unless otherwise noted, yields refer to isolated material based on product purity ( $\geq 95\%$ ) determined by  $^1\text{H}$ -NMR spectroscopy following silica gel chromatography.

## **2. General Procedures**

[**WARNING:** Reactions run under an atmosphere of pure dioxygen are inherently dangerous given the flammability of oxygen. Special care should be taken when charging reaction flasks with a positive pressure of dioxygen.]

### ***General procedure A: for optimization (Table 1)***

An 8 mL scintillation vial equipped with a stirbar was charged with 3,4,5-trimethylphenol (0.25 mmol, 1.0 equiv), Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (0.005 mmol, 2 mol%), pyridine (0.625 mmol, 2.50 equiv), and MeCN (2.5 mL, 0.10 M). The vial was capped with a rubber septum and evacuated/backfilled, using house vacuum, with oxygen (3x). A needle attached to an oxygen balloon was placed below the solvent level and the headspace was attached to an outlet to allow a slow active sparge of the solution during the reaction. This vial was then irradiated with 440 nm light (blue Kessil lamp, 100% power, 7 cm from wall of flask) for 1.5 h. The reaction was then quenched with water and extracted with EtOAc (3x, added 0.5 M HCl if emulsion formed). The combined organic layers were washed with 0.5 M HCl (2x) and brine (1x), dried over anhydrous sodium sulfate, and concentrated *in vacuo*. The resultant material was analyzed by <sup>1</sup>H-NMR spectroscopy with CH<sub>2</sub>Br<sub>2</sub> (17 µL, 0.25 mmol) as internal standard.

\*NOTE: the catalyst Tris(2,2'-bipyridine) ruthenium(II) hexafluorophosphate will be abbreviated "Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub>" hereafter.

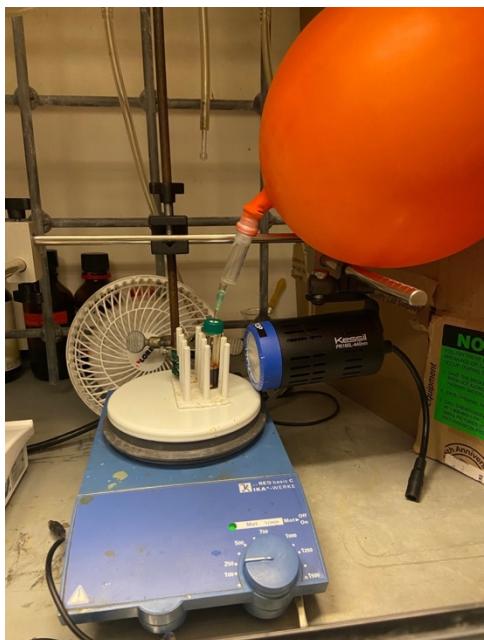
### ***General procedure B: for scope (Scheme 2)***

An 8 mL scintillation vial equipped with a stirbar was charged with phenol (0.25 mmol, 1.0 equiv), Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (0.005 mmol, 2 mol%), pyridine (0.625 mmol, 2.50 equiv), and MeCN (2.5 mL, 0.10 M). The vial was capped with a rubber septum and evacuated/backfilled, using house vacuum, with oxygen (3x). A needle attached to an oxygen balloon was placed below the solvent level and the headspace was attached to an outlet to allow a slow active sparge of the solution during the reaction. This vial was then irradiated with 440 nm light (blue Kessil lamp, 100% power, 7 cm from wall of flask) for 1.5 h. The reaction was then quenched with water and extracted with EtOAc (3x, added 0.5 M HCl if emulsion formed). The combined organic layers were washed with 0.5 M HCl (2x) and brine (1x), dried over anhydrous sodium sulfate, and concentrated *in vacuo*. The resultant material was purified by silica gel column chromatography using EtOAc/n-hexanes as an eluent to afford pure product as determined by <sup>1</sup>H- and <sup>13</sup>C-NMR spectroscopy.

### ***General procedure C: for 1 mmol scale reaction (Scheme 2)***

A 20 mL scintillation vial equipped with a stirbar was charged with 3,5-dimethoxy-4-methylphenol (1.0 mmol, 1.0 equiv), Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (0.02 mmol, 2 mol%), pyridine (2.5 mmol, 2.5 equiv), and MeCN (10 mL, 0.10 M). The vial was capped with a rubber septum and evacuated/backfilled, using house vacuum, with oxygen (3x). A needle attached to an oxygen balloon was placed below the solvent level and the headspace was

attached to an outlet to allow a slow active sparge of the solution during the reaction. This vial was then irradiated with 440 nm light (blue Kessil lamp, 100% power, 7 cm from wall of flask) until complete consumption of starting phenol was observed via TLC. The reaction was then quenched with water and extracted with EtOAc (3x, added 0.5 M HCl if emulsion formed). The combined organic layers were washed with 0.5 M HCl (2x) and brine (1x), dried over anhydrous sodium sulfate, and concentrated *in vacuo*. The resultant material was purified by silica gel column chromatography using 50% EtOAc/n-hexanes as eluent to afford **7a** (187 mg, 93% yield) as an amorphous white solid.

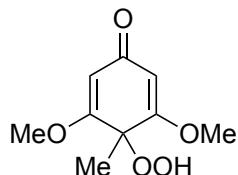


**Figure S1.** Example setup for 0.25 mmol scale reaction.

### **3. Characterization for Substrate Scope (Scheme 2)**

\*(see S14 for Scheme S1)

Compounds 6a–t were obtained from commercially available sources.



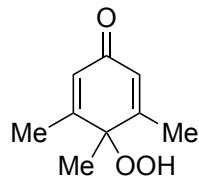
**4-Hydroperoxy-3,5-dimethoxy-4-methylcyclohexa-2,5-dien-1-one (7a)** General procedure C was followed using 3,5-dimethoxy-4-methylphenol (168 mg, 1.00 mmol), Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (17 mg, 2.0 mol%), pyridine (202 μL, 2.50 equiv) in MeCN (10 mL, 0.10 M) for 30 min. Flash chromatography (50% EtOAc/n-hexanes) afforded an amorphous white solid (187 mg, 0.934 mmol) in 93% yield.

$R_f$  = 0.10 (50% EtOAc/n-hexanes, brown with cerium ammonium molybdate).

**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)** δ 8.69 (s, 1H), 5.52 (s, 2H), 3.81 (s, 6H), 1.54 (s, 3H).

**<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)** δ 187.4, 170.5, 102.2, 81.0, 56.5, 21.6.

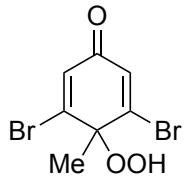
**HRMS (ESI-TOF)**  $m/z$  = 201.0765 calcd for C<sub>9</sub>H<sub>13</sub>O<sub>5</sub> [M+H]<sup>+</sup>, found 201.0763.



**4-Hydroperoxy-3,4,5-trimethylcyclohexa-2,5-dien-1-one (7b)** General procedure B was followed using 3,4,5-trimethylphenol (34 mg, 0.25 mmol), Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (4 mg, 2 mol%), pyridine (51 μL, 2.5 equiv) in MeCN (2.5 mL, 0.10 M) for 1.5 h. Flash chromatography (50% EtOAc/n-hexanes) afforded an amorphous white solid (34 mg, 0.20 mmol) in 81% yield.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.91 (s, 1H), 6.14 (s, 2H), 2.11 (s, 6H), 1.37 (s, 3H).

Spectral data were in agreement with those reported [*Angew. Chem. Int. Ed.* **2006**, *45* (17), 2737].



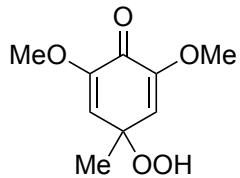
**3,5-Dibromo-4-hydroperoxy-4-methylcyclohexa-2,5-dien-1-one (7c)** General procedure B was followed using 3,5-dibromo-4-methylphenol (66 mg, 0.25 mmol), Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (4 mg, 2 mol%), pyridine (51 µL, 2.5 equiv) in MeCN (2.5 mL, 0.10 M) for 14 h. Flash chromatography (50% EtOAc/n-hexanes) afforded an amorphous white solid (20 mg, 0.067 mmol) in 27% yield.

$R_f$  = 0.60 (50% EtOAc/n-hexanes).

**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)** δ 8.43 (s, 1H), 6.82 (s, 2H), 1.63 (s, 3H).

**<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)** δ 181.1, 148.5, 133.9, 83.7, 24.7.

**HRMS (ESI-TOF)** *m/z* = 263.8785 calcd for C<sub>7</sub>H<sub>6</sub>Br<sub>2</sub>O [M-O<sub>2</sub>]<sup>+</sup>, found 263.8781.



**4-Hydroperoxy-2,6-dimethoxy-4-methylcyclohexa-2,5-dien-1-one (7d)** General procedure B was followed using 2,6-dimethoxy-4-methylphenol (42 mg, 0.25 mmol), Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (4.3 mg, 2 mol%), pyridine (51 µL, 2.5 equiv) in MeCN (2.5 mL, 0.1 M) for 3 h. Flash chromatography (50% EtOAc/n-hexanes) afforded a colorless oil (14 mg, 0.070 mmol) in 28% yield.

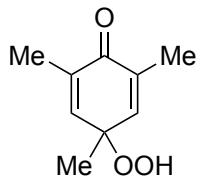
$R_f$  = 0.30 (50% EtOAc/n-hexanes).

**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)** δ 7.83 (s, 1H), 5.75 (s, 2H), 3.72 (s, 6H), 1.54 (s, 3H).

**<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)** δ 176.5, 151.5, 115.7, 79.6, 55.6, 25.3.

**HRMS (ESI-TOF)** *m/z* = 223.0582 calcd for C<sub>9</sub>H<sub>12</sub>O<sub>5</sub>Na [M+Na]<sup>+</sup>, found 223.0566.

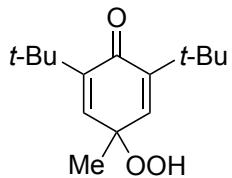
**(EI-TOF)** *m/z* = 168.0786 calcd for C<sub>9</sub>H<sub>12</sub>O<sub>3</sub> [M-O<sub>2</sub>]<sup>+</sup>, found 168.0788.



**4-Hydroperoxy-2,4,6-trimethylcyclohexa-2,5-dien-1-one (7e)** General procedure B was followed using 2,4,6-trimethylphenol (34 mg, 0.25 mmol), Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (4 mg, 2 mol%), pyridine (51 µL, 2.5 equiv) in MeCN (2.5 mL, 0.10 M) for 1 h. Flash chromatography (25% EtOAc/n-hexanes) afforded an amorphous white solid (42 mg, 0.25 mmol) in 99% yield.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.70 (s, 1H), 6.62 (s, 2H), 1.93 (s, 6H), 1.37 (s, 3H).

Spectral data were in agreement with those reported [Angew. Chem. Int. Ed. **2006**, 45 (17), 2737].



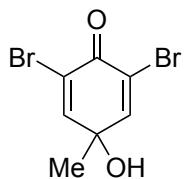
**2,6-Di-tert-butyl-4-hydroperoxy-4-methylcyclohexa-2,5-dien-1-one (7f)** General procedure B was followed using 2,6-di-tert-butyl-4-methylphenol (55 mg, 0.25 mmol), Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (4 mg, 2 mol%), pyridine (51 µL, 2.5 equiv) in MeCN (2.5 mL, 0.10 M) for 45 min. Flash chromatography (10% EtOAc/n-hexanes) afforded a white amorphous solid (40 mg, 0.16 mmol) in 63% yield.

R<sub>f</sub> = 0.35 (10% EtOAc/n-hexanes, brown with cerium ammonium molybdate).

**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)** δ 7.63 (s, 1H), 6.56 (s, 2H), 1.37 (s, 3H), 1.24 (s, 18H).

**<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)** δ 186.4, 149.0, 140.1, 78.9, 35.0, 29.6, 24.0.

**HRMS (EI-TOF)** m/z = 220.1827 calcd for C<sub>15</sub>H<sub>24</sub>O [M-O<sub>2</sub>]<sup>+</sup>, found 220.1841.

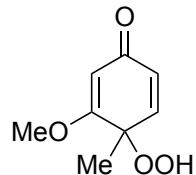


**2,6-Dibromo-4-hydroxy-4-methylcyclohexa-2,5-dien-1-one (7g)** General procedure B was followed using 2,6-dibromo-4-methylphenol (66 mg, 0.25 mmol), Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (4 mg, 2 mol%), pyridine (51 µL,

2.5 equiv) in MeCN (2.5 mL, 0.10 M) for 5 h. Utilizing a literature procedure [Angew. Chem. Int. Ed. **2006**, *45* (17), 2737]: the reaction was diluted with water (6 mL) and an excess of anhydrous sodium thiosulfate (1.1 mmol, 25 equiv) was added before capping the vial. Upon completion (monitored by TLC and LC-MS), the mixture was diluted with water (10 mL) and extracted with EtOAc (3x). The combined organic layers were washed with 0.5 M HCl (2x), brine (1x), dried over anhydrous sodium sulfate, and concentrated *in vacuo*. Flash chromatography (25% EtOAc/n-hexanes) afforded an amorphous white solid (24 mg, 0.085 mmol) in 34% yield.

**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)** δ 7.34 (s, 2H), 2.17 (s, 1H), 1.56 (s, 3H).

Spectral data were in agreement with those reported [Chem. Asian J. **2020**, *15* (7), 1022].



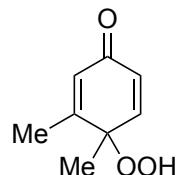
**4-Hydroperoxy-3-methoxy-4-methylcyclohexa-2,5-dien-1-one (7h)** General procedure B was followed using 3-methoxy-4-methylphenol (35 mg, 0.25 mmol), Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (4 mg, 2 mol%), pyridine (51 μL, 2.5 equiv) in MeCN (2.5 mL, 0.10 M) for 4 h. Flash chromatography (50% EtOAc/n-hexanes) afforded a colorless oil (26 mg, 0.15 mmol) in 61% yield.

R<sub>f</sub> = 0.35 (10% EtOAc/n-hexanes, brown with cerium ammonium molybdate).

**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)** δ 9.60 (s, 1H), 6.70 (d, J = 10.0 Hz, 1H), 6.19 (d, J = 10.0 Hz, 1H), 5.56 (s, 1H), 3.80 (s, 3H), 1.44 (s, 3H).

**<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)** δ 188.1, 174.2, 146.9, 129.4, 103.1, 79.6, 56.3, 22.1.

**HRMS (ESI-TOF)** *m/z* = 171.0657 calcd for C<sub>8</sub>H<sub>11</sub>O<sub>4</sub> [M+H]<sup>+</sup>, found 171.0655.

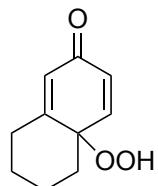


**4-Hydroperoxy-3,4-dimethylcyclohexa-2,5-dien-1-one (7i)** General procedure B was followed using 3,4-dimethylphenol (31 mg, 0.25 mmol), Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (4 mg, 2 mol%), pyridine (51 μL, 2.5 equiv) in MeCN

(2.5 mL, 0.10 M) for 1.5 h. Flash chromatography (50% EtOAc/n-hexanes) afforded an amorphous white solid (37 mg, 0.24 mmol) in 96% yield.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.20 (s, 1H), 6.90 (d, J = 10.0 Hz, 1H), 6.27 (dd, J = 10.0, 2.0 Hz, 1H), 6.22 – 6.11 (m, 1H), 2.09 (d, J = 1.4 Hz, 3H), 1.38 (s, 3H).

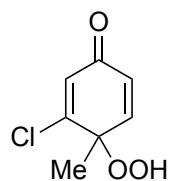
Spectral data were in agreement with those reported [Angew. Chem. Int. Ed. 2006, 45 (17), 2737].



**4a-Hydroperoxy-5,6,7,8-tetrahydronaphthalen-2(4aH)-one (7j)** General procedure B was followed using 5,6,7,8-tetrahydronaphthalen-2-ol (37 mg, 0.25 mmol), Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (4 mg, 2 mol%), pyridine (51 μL, 2.5 equiv) in MeCN (2.5 mL, 0.10 M) for 4.5 h. Flash chromatography (25% EtOAc/n-hexanes) afforded an amorphous white solid (27 mg, 0.15 mmol) in 60% yield.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.05 (s, 1H), 6.81 (d, J = 10.0 Hz, 1H), 6.30 (dd, J = 10.1, 1.9 Hz, 1H), 6.18 (t, J = 1.9 Hz, 1H), 2.65 (tdd, J = 13.2, 5.1, 1.7 Hz, 1H), 2.41 (ddt, J = 12.8, 4.0, 1.9 Hz, 1H), 2.18 (ddt, J = 14.2, 4.2, 2.2 Hz, 1H), 2.10 – 2.00 (m, 1H), 1.81 (quartet of triplets, J = 13.6, 4.1 Hz, 1H), 1.68– 1.57 (m, 1H), 1.51 – 1.32 (m, 2H).

Spectral data were in agreement with those reported [Angew. Chem. Int. Ed. 2006, 45 (17), 2737].



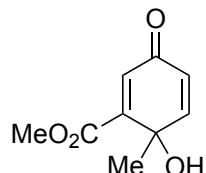
**3-Chloro-4-hydroperoxy-4-methylcyclohexa-2,5-dien-1-one (7k)** General procedure B was followed using 3-chloro-4-methylphenol (36 mg, 0.25 mmol), Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (4 mg, 2 mol%), pyridine (51 μL, 2.5 equiv) in MeCN (2.5 mL, 0.10 M) for 3 h. Flash chromatography (50% EtOAc/n-hexanes) afforded an amorphous white solid (19 mg, 0.11 mmol) in 44% yield.

R<sub>f</sub> = 0.65 (50% EtOAc/n-hexanes, brown with cerium ammonium molybdate).

**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)** δ 8.17 (s, 1H), 6.96 (dd, J = 10.0, 1.0 Hz, 1H), 6.56 – 6.52 (m, 1H), 6.33 (dt, J = 10.0, 1.5 Hz, 1H), 1.51 (s, 3H).

**<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)** δ 184.1, 156.1, 149.2, 130.4, 129.6, 80.8, 22.5.

**HRMS (EI-TOF)** m/z = 142.0185 calcd for C<sub>7</sub>H<sub>7</sub>ClO [M-O<sub>2</sub>]<sup>+</sup>, found 142.0195.



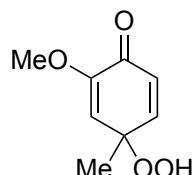
**Methyl 6-hydroxy-6-methyl-3-oxocyclohexa-1,4-diene-1-carboxylate (7l)** General procedure B was followed using methyl 5-hydroxy-2-methylbenzoate (42 mg, 0.25 mmol), Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (4 mg, 2 mol%), pyridine (51 μL, 2.5 equiv) in MeCN (2.5 mL, 0.10 M) for 5 h. Utilizing a literature procedure [*Angew. Chem. Int. Ed.* **2006**, 45 (17), 2737]: the reaction was diluted with water (6 mL) and an excess of anhydrous sodium thiosulfate (1.1 mmol, 25 equiv) was added before capping the vial. Upon completion (monitored by TLC and LC-MS), the mixture was diluted with water (10 mL) and extracted with EtOAc (3x). The combined organic layers were washed with 0.5 M HCl (2x), brine (1x), dried over anhydrous sodium sulfate, and concentrated *in vacuo*. Flash chromatography (50% EtOAc/n-hexanes) afforded a colorless oil (17 mg, 0.093 mmol) in 37% yield.

R<sub>f</sub> = 0.45 (50% EtOAc/n-hexanes)

**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)** δ 6.94 (d, J = 10.1, 1H), 6.88 (s, 1H), 6.22 (d, J = 10.2, 1H), 4.18 (s, 1H), 3.90 (s, 3H), 1.63 (s, 3H).

**<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)** δ 186.0, 166.7, 153.2, 147.6, 132.5, 126.6, 68.6, 53.0, 28.7.

**HRMS (EI-TOF)** m/z = 167.0344 calcd for C<sub>8</sub>H<sub>7</sub>O<sub>4</sub> [M-CH<sub>3</sub>]<sup>+</sup>, found 167.0351.

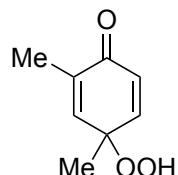


**4-Hydroperoxy-2-methoxy-4-methylcyclohexa-2,5-dien-1-one (7m)** General procedure B was followed 2-methoxy-4-methylphenol (35 mg, 0.25 mmol), Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (4 mg, 2 mol%), pyridine (51 μL, 2.5 equiv)

in MeCN (2.5 mL, 0.10 M) for 3 h. Flash chromatography (50% EtOAc/n-hexanes) afforded an amorphous white solid (15 mg, 0.088 mmol) in 35% yield.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.38 (s, 1H), 6.90 (dd, *J* = 10.0, 2.7 Hz, 1H), 6.28 (d, *J* = 10.0 Hz, 1H), 5.73 (d, *J* = 2.7 Hz, 1H), 3.69 (s, 3H), 1.47 (s, 3H).

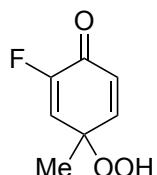
Spectral data were in agreement with those reported [Angew. Chem. Int. Ed. **2006**, *45* (17), 2737].



**4-Hydroperoxy-2,4-dimethylcyclohexa-2,5-dien-1-one (7n)** General procedure B was followed 2,4-dimethylphenol (31 mg, 0.25 mmol), Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (4 mg, 2 mol%), pyridine (51 μL, 2.5 equiv) in MeCN (2.5 mL, 0.10 M) for 1.5 h. Flash chromatography (50% EtOAc/n-hexanes) afforded a colorless oil (26 mg, 0.17 mmol) in 67% yield.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.44 (s, 1H), 6.87 (dd, *J* = 10.0, 3.1 Hz, 1H), 6.70 – 6.64 (m, 1H), 6.27 (d, *J* = 10.0 Hz, 1H), 1.91 (d, *J* = 1.6 Hz, 3H), 1.39 (s, 3H).

Spectral data were in agreement with those reported [Angew. Chem. Int. Ed. **2006**, *45* (17), 2737].



**2-Fluoro-4-hydroperoxy-4-methylcyclohexa-2,5-dien-1-one (7o)** General procedure B was followed using 2-fluoro-4-methylphenol (32 mg, 0.25 mmol), Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (4 mg, 2 mol%), pyridine (51 μL, 2.5 equiv) in MeCN (2.5 mL, 0.10 M) for 6 h. Flash chromatography (50% EtOAc/n-hexanes) afforded an amorphous white solid (17 mg, 0.11 mmol) in 44% yield.

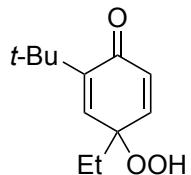
R<sub>f</sub> = 0.45 (50% EtOAc/n-hexanes, brown with cerium ammonium molybdate).

**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)** δ 8.39 (s, 1H), 6.91 (dd, *J* = 10.1, 2.8 Hz, 1H), 6.42 (dd, *J* = 12.0, 2.8 Hz, 1H), 6.31 (dd, *J* = 10.1, 7.1 Hz, 1H), 1.49 (d, *J* = 1.1 Hz, 3H).

**<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)** δ 178.55 (d, *J* = 22.8 Hz), 154.22 (d, *J* = 269.1 Hz), 150.60 (d, *J* = 3.0 Hz), 128.98 (d, *J* = 4.3 Hz), 124.87 (d, *J* = 12.0 Hz), 80.70 (d, *J* = 8.7 Hz), 23.15 (d, *J* = 2.3 Hz).

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -127.17.

**HRMS (EI-TOF)** *m/z* = 126.0481 calcd C<sub>7</sub>H<sub>7</sub>FO [M-O<sub>2</sub>]<sup>+</sup>, found 126.0503.



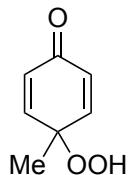
**2-(tert-butyl)-4-ethyl-4-hydroperoxycyclohexa-2,5-dien-1-one (7p)** General procedure B was followed using 2-(tert-butyl)-4-ethylphenol (45 mg, 0.25 mmol), Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (4 mg, 2 mol%), pyridine (51 μL, 2.5 equiv) in MeCN (2.5 mL, 0.10 M) for 1.5 h. Flash chromatography (25% EtOAc/n-hexanes) afforded a colorless oil (39 mg, 0.19 mmol) in 74% yield.

R<sub>f</sub> = 0.25 (50% EtOAc/n-hexanes, brown/blue with cerium ammonium molybdate).

**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)** δ 8.96 (s, 1H), 6.74 (dd, *J* = 10.0, 3.0 Hz, 1H), 6.61 (s, 1H), 6.22 (d, *J* = 10.0 Hz, 1H), 1.70 (qd, *J* = 7.6, 1.2 Hz, 2H), 1.23 (s, 9H), 0.79 (t, *J* = 7.6 Hz, 3H).

**<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)** δ 186.5, 148.9, 146.9, 142.8, 132.9, 82.9, 34.9, 29.3, 29.2, 7.9.

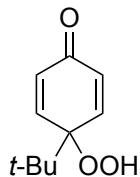
**HRMS (EI-TOF)** *m/z* = 178.1358 calcd C<sub>12</sub>H<sub>18</sub>O [M-O<sub>2</sub>]<sup>+</sup>, found 178.1359.



**4-Hydroperoxy-4-methylcyclohexa-2,5-dien-1-one (7q)** General procedure B was followed *p*-cresol (27 mg, 0.25 mmol), Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (4 mg, 2 mol%), pyridine (51 μL, 2.5 equiv) in MeCN (2.5 mL, 0.10 M) for 3.5 h. Flash chromatography (50% EtOAc/n-hexanes) afforded an amorphous white solid (23 mg, 0.17 mmol) in 65% yield.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.82 (s, 1H), 6.91 (d, *J* = 10.1 Hz, 2H), 6.28 (d, *J* = 10.1 Hz, 2H), 1.41 (s, 3H).

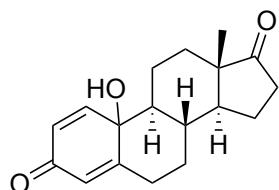
Spectral data were in agreement with those reported [Angew. Chem. Int. Ed. **2006**, 45 (17), 2737].



**4-(tert-Butyl)-4-hydroperoxycyclohexa-2,5-dien-1-one (7r)** General procedure B was followed 4-(tert-butyl)phenol (38 mg, 0.25 mmol), Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (4 mg, 2 mol%), pyridine (51 µL, 2.5 equiv) in MeCN (2.5 mL, 0.01 M) for 15 h. Flash chromatography (60% EtOAc/n-hexanes) afforded an amorphous white solid (19 mg, 0.10 mmol) in 42% yield.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.26 (s, 1H), 7.06 (d, *J* = 10.3 Hz, 2H), 6.38 (d, *J* = 10.3 Hz, 2H), 1.03 (s, 9H).

Spectral data were in agreement with those reported [Org. Process Res. Dev. **2021**, 25 (8), 1873].

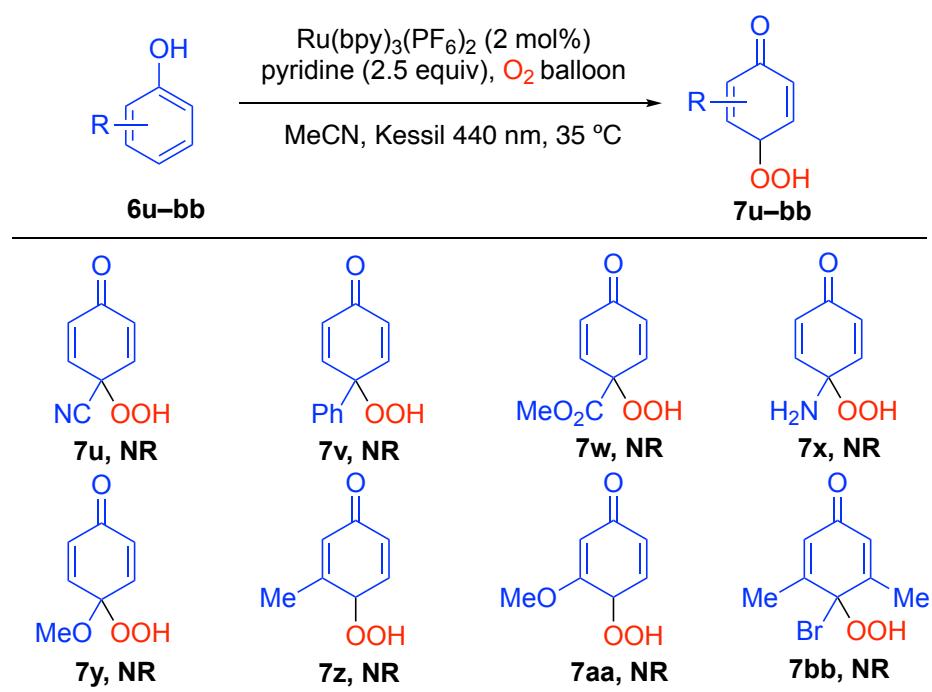


**(8S,9S,13S,14S)-10-Hydroxy-13-methyl-7,8,9,10,11,12,13,14,15,16-decahydro-3H-cyclopenta[a]phenanthrene-3,17(6H)-dione (7s)** General procedure B was followed using estrone (68 mg, 0.25 mmol), Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (4 mg, 2 mol%), pyridine (51 µL, 2.5 equiv) in MeCN (2.5 mL, 0.10 M) for 5 h. Utilizing a literature procedure [Angew. Chem. Int. Ed. **2006**, 45 (17), 2737]: the reaction was diluted with water (6 mL) and an excess of anhydrous sodium thiosulfate (1.1 mmol, 25 equiv) was added before capping the vial. Upon completion (monitored by TLC and LC-MS), the mixture was diluted with water (10 mL) and extracted with EtOAc (3x). The combined organic layers were washed with 0.5 M HCl (2x), brine (1x), dried over anhydrous sodium sulfate, and concentrated *in vacuo*. Flash chromatography (50% EtOAc/n-hexanes) afforded an amorphous slight yellow solid (42 mg, 0.15 mmol) in 59% yield.

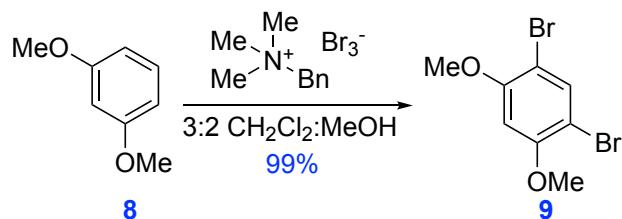
**<sup>1</sup>H NMR (600 MHz, DMSO-d<sup>6</sup>)** δ 7.12 (d, *J* = 10.2 Hz, 1H), 6.05 (dd, *J* = 10.2, 2.0 Hz, 1H), 5.94 – 5.91 (m, 1H), 5.65 (s, 1H), 2.70 – 2.63 (m, 1H), 2.42 – 2.36 (m, 1H), 2.34 – 2.29 (m, 1H), 2.02 – 1.96 (m, 3H), 1.91 – 1.82 (m, 2H), 1.70 – 1.61 (m, 2H), 1.56 – 1.50 (m, 1H), 1.29 – 1.22 (m, 1H), 1.18 – 1.02 (m, 3H), 0.84 (s, 3H).

Spectral data were in agreement with those reported [Chem. Asian J. **2020**, 15 (7), 1022].

**Scheme S1.** Non-reactive substrates



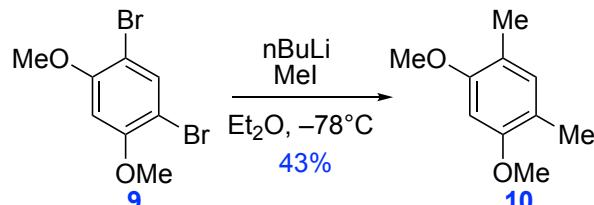
#### 4. Preparation of ( $\pm$ )-Stemen7one B and ( $\pm$ )-Parvistilbene B



**1,5-Dibromo-2,4-dimethoxybenzene (9)** was prepared using a literature procedure [Bull. Chem. Soc. Jpn. **1987**, *60* (1), 55]: To a solution of 1,3-dimethoxybenzene (2.00 g, 14.5 mmol) in 3:2 CH<sub>2</sub>Cl<sub>2</sub>:MeOH (280 mL) was added benzyltrimethylammonium tribromide (29 mmol, 2.0 equiv) dropwise (in 50 mL CH<sub>2</sub>Cl<sub>2</sub>) under stirring at room temperature. The mixture was stirred for 30 min until a discoloration of the orange solution occurred. The sample was concentrated *in vacuo* and then 30 mL H<sub>2</sub>O was added and extracted with EtOAc (3x), sodium thiosulfate (2x), brine (1x) then dried with anhydrous sodium sulfate to afford an amorphous white solid (4.27 g, 14.4 mmol) in 99% yield without need for further purification.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.66 (s, 1H), 6.50 (s, 1H), 3.91 (s, 6H).

Spectral data were in agreement with those reported [Bull. Chem. Soc. Jpn. **1987**, *60* (1), 55].

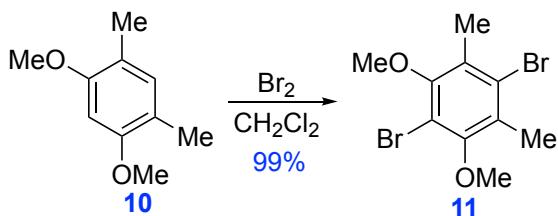


[**WARNING:** n-BuLi is an extremely strong base that is pyrophoric so special care should be taken in handling. Excess reagent should be destroyed according to known protocols before handling the reaction mixture during workup.]

**1,5-Dimethoxy-2,4-dimethylbenzene (10)** was prepared using a literature procedure [Organometallics **2008**, *27* (17), 4357]: Add *n*-BuLi (23 mmol, 1.1 equiv, 2.5 M in *n*-hexanes) to a solution of 1,5-dibromo-2,4-dimethoxybenzene (21 mmol, 1.0 equiv) in 96 mL (0.22 M) of dry ether at  $-78^\circ\text{C}$  under argon and stirred for 30 min. Iodomethane (47 mmol, 2.2 equiv) was added slowly at  $-78^\circ\text{C}$  under argon and the mixture was warmed to room temperature and stirred for 1 h. A second portion of *n*-BuLi (23 mmol, 1.1 equiv, 2.5 M in *n*-hexanes) solution slowly added at  $-78^\circ\text{C}$  and mixture was allowed to warm up to room temperature and stirred for 1 h. Mixture was diluted with ether and quenched by addition of NH<sub>4</sub>Cl and washed with aqueous NaOH (1x), water (1x), and brine (1x). The mixture was dried with anhydrous sodium sulfate and concentrated *in vacuo*. Chromatography (5% EtOAc/*n*-hexanes afforded an amorphous white solid (1.5 g, 9.0 mmol) in 43% yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.88 (s, 1H), 6.42 (s, 1H), 3.82 (s, 6H), 2.13 (s, 6H).

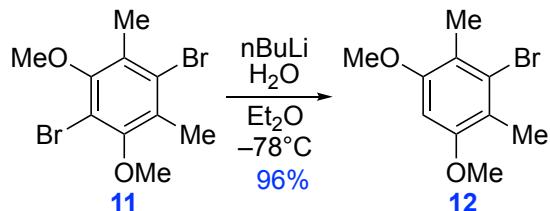
Spectral data were in agreement with those reported [Organometallics **2008**, 27 (17), 4357].



**1,4-Dibromo-2,6-dimethoxy-3,5-dimethylbenzene (11)** was prepared using a literature procedure [Organometallics **2008**, 27 (17), 4357]: To a stirred solution of 1,5-dimethoxy-2,4-dimethylbenzene (0.60 mmol, 1.0 equiv) in 3 mL CH<sub>2</sub>Cl<sub>2</sub> was added Br<sub>2</sub> (2.1 mmol, 3.5 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) at 0 °C via a cannula over 2 min under argon. The reaction was stirred for 16 h at room temperature and progress was analyzed by TLC. The product was washed with sodium thiosulfate (until organic is colorless), dried with anhydrous sodium sulfate, and solvent removed under reduced pressure to afford a white solid (194 mg, 0.599 mmol) in 99% yield without need for further purification.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 3.77 (s, 6H), 2.39 (s, 6H).

Spectral data were in agreement with those reported [Organometallics **2008**, 27 (17), 4357].

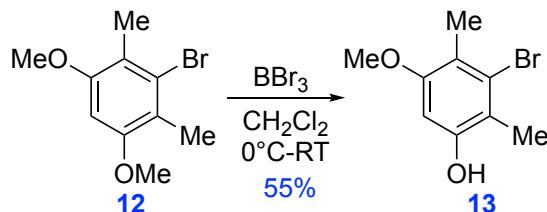


[WARNING: See safety note above regarding the use of *n*-BuLi].

**3-Bromo-1,5-dimethoxy-2,4-dimethylbenzene (12)** was prepared using a literature procedure [Organometallics **2008**, 27 (17), 4357]: A *n*-BuLi (0.91 mmol, 1.0 equiv, 2.5 M in *n*-hexanes) solution was added to a solution of 1,4-dibromo-2,6-dimethoxy-3,5-dimethylbenzene (0.91 mmol, 1.0 equiv) in 7.5 mL of dry ether at -78 °C under argon, and the colorless solution was stirred at -78 °C for 1 h. H<sub>2</sub>O (1.8 mmol, 2.0 equiv) in 1.5 mL of THF was added slowly at -78 °C under argon. The mixture was allowed to warm to room temperature and stirred for 1 h. The mixture was quenched with saturated NH<sub>4</sub>Cl, washed with NH<sub>4</sub>OH (1x), water (1x), and brine (1x), dried with anhydrous sodium sulfate, and concentrated under reduced pressure to give pure product as an amorphous white solid (214 mg, 0.873 mmol) in 96% yield without need for further purification.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.43 (s, 1H), 3.82 (s, 6H), 2.27 (s, 6H).

Spectral data were in agreement with those reported [Organometallics **2008**, 27 (17), 4357].



[**WARNING:** BBr<sub>3</sub> is a water-sensitive Lewis acid reagent. When syringing the reagent from a Sure/Seal™ bottle, the reagent may smoke, and should be used in a well-ventilated fume hood. Carefully quench all excess reagent with large quantities of water.]

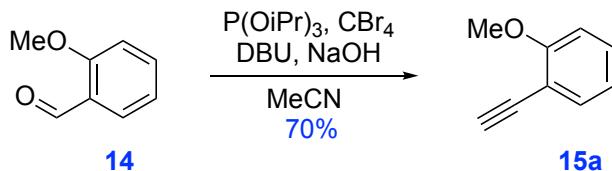
**3-Bromo-5-methoxy-2,4-dimethylphenol (13)** A solution of 3-bromo-1,5-dimethoxy-2,4-dimethylbenzene (0.20 mmol, 1.0 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) under argon was cooled to 0 °C and BBr<sub>3</sub> (0.070 mmol, 0.35 equiv, 1.0 M in CH<sub>2</sub>Cl<sub>2</sub>) was added with the aid of a syringe. The resulting mixture was allowed to stir under argon for 10 min at 0 °C. Then, the cold bath was removed, and the mixture was stirred for 10 h at room temperature and cooled again to 0 °C. To this reaction mixture was added MeOH (2 mL) dropwise and then the solvent was removed under vacuum. This mixture was extracted with EtOAc (3x) and the combined organic layers were dried over anhydrous sodium sulfate and concentrated under reduced pressure. Chromatography (50% EtOAc/n-hexanes) afforded an amorphous brown solid (25 mg, 0.11 mmol) in 55% yield.

R<sub>f</sub> = 0.60 (50% EtOAc/n-hexanes).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.36 (s, 1H), 4.63 (s, 1H), 3.77 (s, 3H), 2.30 (s, 3H), 2.26 (s, 3H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 156.5, 152.1, 129.3, 119.6, 115.7, 98.3, 56.0, 16.1, 15.8.

HRMS (EI-TOF) m/z = 229.9942 calcd for C<sub>9</sub>H<sub>11</sub>BrO<sub>2</sub> [M]<sup>+</sup>, found 229.9946.

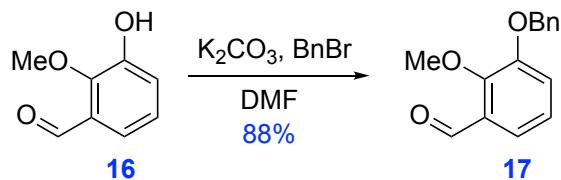


[**WARNING:** P(OiPr)<sub>3</sub> is an acutely toxic reagent that must be used in a well-ventilated fume hood. Appropriate care must be taken to avoid environmental contamination.]

**1-Ethynyl-2-methoxybenzene (15a)** was prepared using a literature procedure [Adv. Synth. Catal. **2019**, 361 (3), 611]: To a stirred solution of 2-methoxybenzaldehyde (3.8 mmol, 1.0 equiv) and tetrabromomethane (5.6 mmol, 1.5 equiv) in 7.5 mL dry MeCN, triisopropyl phosphite (7.5 mmol, 2.0 equiv) was added drop wise over a period of 5 min at 0 °C. After 10 min, DBU (15 mmol, 4.0 equiv) was added to the reaction mixture drop wise over a period of 5 min at 0 °C. The reaction mixture was then allowed to reach ambient temperature over 30 min under stirring. Powdered sodium hydroxide (19 mmol, 5.0 equiv) was added to the reaction mixture and allowed to stir for 4 h at room temperature. After completion of the reaction (monitored by TLC), the reaction mixture was quenched with 10 mL of water. The reaction mixture was extracted with EtOAc (3x) and the organic layers were washed with brine (1x). The organic layers were dried over anhydrous sodium sulfate, and the solvent was evaporated under reduced pressure to afford a crude residue. Chromatography (10% EtOAc/n-hexanes) afforded a yellow oil (347 mg, 2.63 mmol) in 70% yield.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.47 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.32 (ddd, *J* = 8.3, 7.4, 1.7 Hz, 1H), 6.95 – 6.86 (m, 2H), 3.91 (s, 3H), 3.31 (s, 1H).

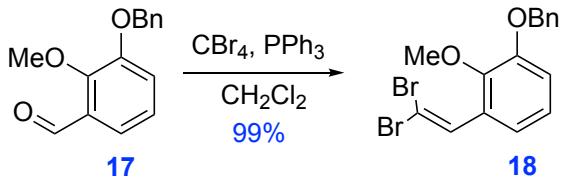
Spectral data were in agreement with those reported [Adv. Synth. Catal. **2019**, 361 (3), 611].



**3-(Benzyl oxy)-2-methoxybenzaldehyde (17)** was prepared using a literature procedure [Tetrahedron **2007**, 63 (50), 12379]: Add benzyl bromide (1.0 mmol, 1.3 equiv) to a mixture of 3-hydroxy-2-methoxybenzaldehyde (0.78 mmol, 1.0 equiv) and potassium carbonate (1.2 mmol, 1.5 equiv) in 6 mL dry DMF. The mixture was heated at 50 °C for 1.5 h and then cooled to room temperature before adding 10 mL EtOAc and 10 mL H<sub>2</sub>O. The aqueous phase was extracted with EtOAc (2x), then the combined organic layers were washed H<sub>2</sub>O (1x), brine (1x), dried over anhydrous sodium sulfate, and the solvent was evaporated under reduced pressure to afford a crude residue. Chromatography (25% EtOAc/n-hexanes) afforded an amorphous white solid (167 mg, 0.689 mmol) in 88% yield.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 10.45 (d, *J* = 0.9 Hz, 1H), 7.48 – 7.32 (m, 6H), 7.20 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.10 (td, *J* = 8.0, 0.9 Hz, 1H), 5.16 (s, 2H), 4.03 (s, 3H).

Spectral data were in agreement with those reported [Tetrahedron **2007**, 63 (50), 12379].



[**WARNING:** Pyrrolidine is a highly flammable reagent with an unpleasant odor. When syringing the reagent from a Sure/Seal™ bottle, the reagent may smoke, and should be used in a well-ventilated fume hood. Carefully quench all excess reagent with large quantities of water.]

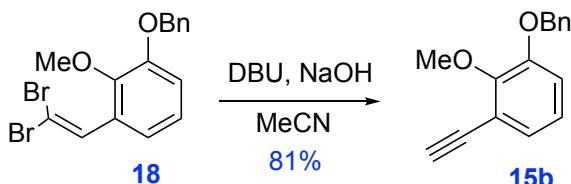
**1-(BenzylOxy)-3-(2,2-dibromovinyl)-2-methoxybenzene (18)** was prepared using a literature procedure [*Tetrahedron* **2002**, 58 (50), 9925]: To an ice cold stirred solution of 3-(benzyloxy)-2-methoxybenzaldehyde (2.0 mmol, 1.0 equiv) and tetrabromomethane (3.1 mmol, 1.5 equiv) in 16 mL CH<sub>2</sub>Cl<sub>2</sub> was added PPh<sub>3</sub> (6.1 mmol, 3.0 equiv) in 15 mL CH<sub>2</sub>Cl<sub>2</sub> with an addition funnel for 10 min. After consumption of starting material by TLC, the reaction mixture was concentrated under reduced pressure and then 20 mL CHCl<sub>3</sub> was added to the residue. The suspended mixture was filtered to remove triphenylphosphine oxide that was washed with CHCl<sub>3</sub> (2x). The combined filtrates were concentrated under reduced pressure and the crude product was purified with column chromatography (15% EtOAc/n-hexanes) afforded an amorphous white solid (812 mg, 2.04 mmol) in 99% yield.

R<sub>f</sub> = 0.61 (15% EtOAc/n-hexanes, yellow with KMnO<sub>4</sub>)

**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)** δ 7.64 (s, 1H), 7.45 (d, J = 7.2 Hz, 2H), 7.39 (t, J = 7.6 Hz, 2H), 7.37 – 7.31 (m, 2H), 7.03 (t, J = 8.0 Hz, 1H), 6.97 (dd, J = 8.2, 1.5 Hz, 1H), 5.13 (s, 2H), 3.87 (s, 3H).

**<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)** δ 151.9, 147.4, 136.9, 132.9, 130.1, 128.8, 128.2, 127.4, 123.8, 121.5, 114.9, 90.6, 71.0, 61.3.

**HRMS (EI-TOF)** m/z = 395.9361 calcd for C<sub>16</sub>H<sub>14</sub>Br<sub>2</sub>O<sub>2</sub> [M]<sup>+</sup>, found 395.9373.



**1-(BenzylOxy)-3-ethynyl-2-methoxybenzene (15b)** was prepared using a literature procedure [*Adv. Synth. Catal.* **2019**, 361 (3), 611]: DBU (2.2 mmol, 4.0 equiv) was added to 1-(benzyloxy)-3-(2,2-dibromovinyl)-2-methoxybenzene (0.56 mmol, 1.0 equiv) in 1.5 mL dry MeCN drop wise over a period of 5 min at 0 °C under argon. The mixture was allowed to reach room temperature over 30 min and then powdered sodium hydroxide (3.9 mmol, 7.0 equiv) was added and stirred for 4 h. After completion of

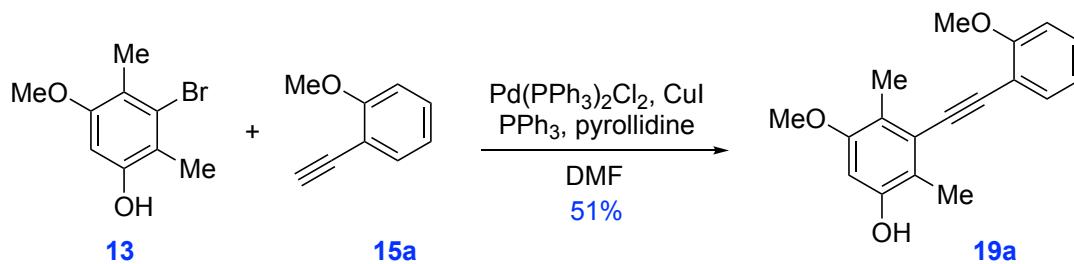
reaction (monitored by TLC), 10 mL water was added to quench and then extracted EtOAc (3x). The combined organic layers were washed brine (1x), dried over anhydrous sodium sulfate, and concentrated *in vacuo*. Chromatography (5% EtOAc/*n*-hexanes) afforded a white amorphous solid (107 mg, 0.449 mmol) in 81% yield.

$R_f$  = 0.60 (5% EtOAc/*n*-hexanes, yellow with KMnO<sub>4</sub>).

**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)** δ 7.46 – 7.43 (m, 2H), 7.41 – 7.37 (m, 2H), 7.35 – 7.31 (m, 1H), 7.08 (dd, *J* = 6.6, 2.7 Hz, 1H), 6.97 – 6.93 (m, 2H), 5.13 (s, 2H), 3.98 (s, 3H), 3.27 (s, 1H).

**<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)** δ 151.9, 151.8, 136.9, 128.7, 128.1, 127.4, 126.2, 123.9, 117.2, 116.0, 81.2, 79.8, 71.2, 61.2.

**HRMS (EI-TOF)** *m/z* = 238.0994 calcd for C<sub>16</sub>H<sub>14</sub>O<sub>2</sub> [M]<sup>+</sup>, found 238.0999.



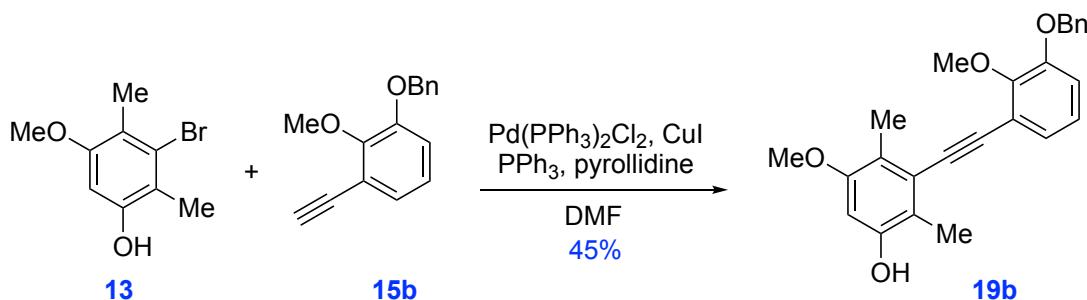
**5-Methoxy-3-((2-methoxyphenyl)ethynyl)-2,4-dimethylphenol (19a)** An 8 mL flame dried scintillation vial equipped with stirring was charged with 3-bromo-5-methoxy-2,4-dimethylphenol (0.22 mmol, 1.0 equiv), 1-ethynyl-2-methoxybenzene (0.270 mmol, 1.25 equiv), PPh<sub>3</sub> (0.022 mmol, 10 mol%), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.022 mmol, 10 mol%), cuprous iodide (0.01 mmol, 5 mol%, 0.05 M in DMF), and pyrrolidine (0.61 mmol, 14 equiv) in dry DMF (1.1 mL, 0.20 M) and sealed under argon. The reaction mixture was heated at 90 °C for 24 h. NH<sub>4</sub>Cl was added to quench the reaction and then was extracted with EtOAc (3x). The combined organic layers were washed brine (1x), dried over anhydrous sodium sulfate, and purified by column chromatography (25% EtOAc/*n*-hexanes) to afford a yellow amorphous solid (31 mg, 0.11 mmol) in 51% yield.

$R_f$  = 0.20 (25% EtOAc/*n*-hexanes).

**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)** <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.51 (d, *J* = 7.5 Hz, 1H), 7.34 – 7.27 (m, 1H), 6.99 – 6.87 (m, 2H), 6.41 (s, 1H), 3.92 (s, 3H), 3.78 (s, 3H), 2.41 (s, 3H), 2.38 (s, 3H).

**<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)** δ 160.1, 156.3, 151.9, 133.2, 129.7, 125.2, 121.4, 120.6, 116.7, 113.2, 110.9, 99.6, 93.7, 91.7, 55.9, 55.8, 13.8, 13.3.

**HRMS (EI-TOF)**  $m/z$  = 282.1256 calcd for  $C_{18}H_{18}O_3$  [M]<sup>+</sup>, found 282.1254.



[WARNING: See safety note above regarding the use of pyrrolidine].

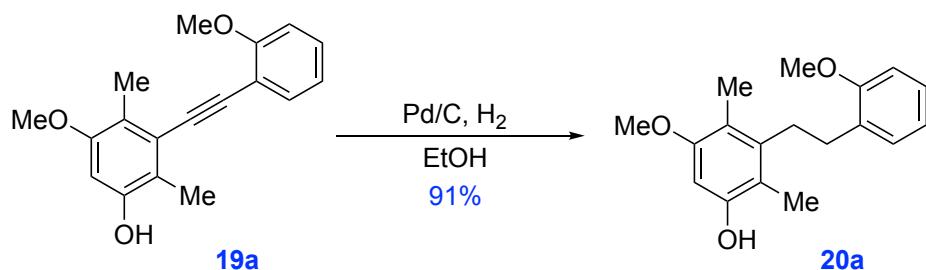
**3-((3-(Benzyl oxy)-2-methoxyphenyl)ethynyl)-5-methoxy-2,4-dimethylphenol (19b)** An 8 mL flame dried scintillation vial equipped with stirring was charged with 3-bromo-5-methoxy-2,4-dimethylphenol (0.22 mmol, 1.0 equiv), 1-(benzyloxy)-3-ethynyl-2-methoxybenzene (0.270 mmol, 1.25 equiv), PPh<sub>3</sub> (0.022 mmol, 10 mol%), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.022 mmol, 10 mol%), cuprous iodide (0.01 mmol, 5 mol%, 0.05 M in DMF), and pyrrolidine (0.61 mmol, 14 equiv) in dry DMF (1.1 mL, 0.20 M) and sealed under argon. The reaction mixture was heated at 90 °C for 24 h. NH<sub>4</sub>Cl was added to quench the reaction and then was extracted with EtOAc (3x). The combined organic layers were washed brine (1x), dried over anhydrous sodium sulfate, and purified by column chromatography (50% EtOAc/n-hexanes) to afford a yellow amorphous solid (38 mg, 0.098 mmol) in 45% yield.

$R_f$  = 0.50 (50% EtOAc/n-hexanes).

**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)** δ 7.46 (d,  $J$  = 7.5 Hz, 2H), 7.40 (t,  $J$  = 7.5 Hz, 2H), 7.33 (t,  $J$  = 7.4 Hz, 1H), 7.15 (dd,  $J$  = 7.7, 1.6 Hz, 1H), 7.00 (t,  $J$  = 7.9 Hz, 1H), 6.95 (dd,  $J$  = 8.2, 1.6 Hz, 1H), 6.41 (s, 1H), 5.15 (s, 2H), 4.98 (s, 1H), 4.02 (s, 3H), 3.76 (s, 3H), 2.42 (s, 3H), 2.39 (s, 3H).

**<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)** δ 156.2, 152.1 (2C), 150.7, 137.0, 128.7, 128.1, 127.4, 125.5, 124.9, 124.1, 121.4, 118.9, 116.9, 115.2, 99.8, 93.3, 91.5, 71.1, 61.2, 55.8, 13.7, 13.3.

**HRMS (EI-TOF)**  $m/z$  = 388.1675 calcd for  $C_{25}H_{24}O_4$  [M]<sup>+</sup>, found 388.1667.



**[WARNING:** The combination of dry Pd/C, flammable solvent, and hydrogen or dioxygen gas can result in a fire. Prior to filtration, the flask must be backfilled with Ar. During filtration, the Pd/C on celite should remain saturated with solvent. Once the filtration is complete, quickly transfer the saturated Pd/C and celite to a segregated waste contained filled with water.]

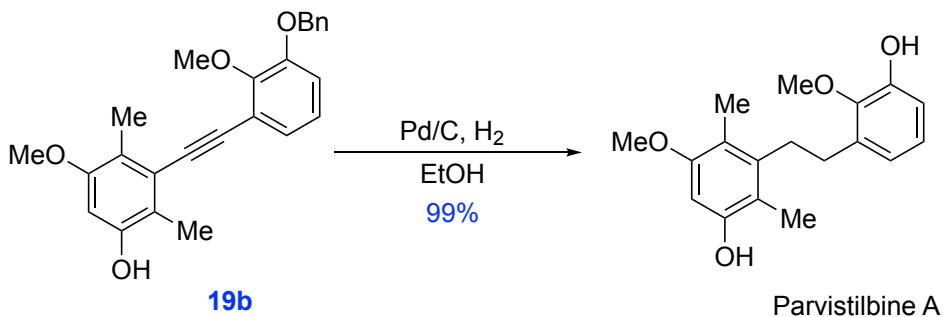
**5-Methoxy-3-(2-methoxyphenethyl)-2,4-dimethylphenol (20a)** An 8 mL flame dried scintillation vial equipped with stirring was charged with 5-methoxy-3-((2-methoxyphenyl)ethynyl)-2,4-dimethylphenol (0.070 mmol, 1.0 equiv), Pd/C (13 mg, 10% w/w), EtOH (1 mL, 0.06 M), and sealed with a rubber septa. The vial was evacuated/backfilled, using house vacuum, with (3x) hydrogen. A needle connected to a hydrogen balloon was attached to the vial and the reaction was stirred for 24 h at room temperature. Then, argon was backfilled, and the suspension was then filtered through celite with multiple EtOH washes and concentrated *in vacuo* to afford a white amorphous solid (16 mg, 0.060 mmol) in 91% yield without need for further purification.

$R_f$  = 0.62 (25% EtOAc/*n*-hexanes).

**$^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )**  $\delta$  7.22 (t,  $J$  = 7.7 Hz, 1H), 7.19 (d,  $J$  = 7.3 Hz, 1H), 6.95 – 6.87 (m, 2H), 6.32 (s, 1H), 3.88 (s, 3H), 3.78 (s, 3H), 2.93 – 2.86 (m, 2H), 2.76 – 2.68 (m, 2H), 2.24 (s, 3H), 2.22 (s, 3H).

**$^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ )**  $\delta$  157.7, 156.3, 152.1, 141.3, 130.7, 129.9, 127.4, 120.6, 117.2, 113.6, 110.4, 97.0, 55.7, 55.4, 30.9, 30.7, 11.1, 10.9.

**HRMS (EI-TOF)**  $m/z$  = 286.1569 calcd for  $\text{C}_{18}\text{H}_{22}\text{O}_3$  [M] $^+$ , found 286.1555.



**[WARNING:** See safety note above regarding the use of Pd/C].

**3-(3-Hydroxy-2-methoxyphenethyl)-5-methoxy-2,4-dimethylphenol; Parvistilbene A (20b)** An 8 mL flame dried scintillation vial equipped with stirring was charged with 3-((3-(benzyloxy)-2-methoxyphenyl)ethynyl)-5-methoxy-2,4-dimethylphenol (0.062 mmol, 1.0 equiv), Pd/C (13 mg, 10% w/w), EtOH (1.2 mL, 0.050 M), and sealed with a rubber septa. The vial was evacuated/backfilled, using house vacuum, with hydrogen (3x). A needle connected to a hydrogen balloon was attached to the vial and the reaction was stirred for 24 h at room temperature. Then, argon was backfilled, and the suspension was

then filtered through celite with multiple EtOH washes and concentrated *in vacuo* to afford a white amorphous solid (19 mg, 0.062 mmol) in 99% yield without need for further purification.

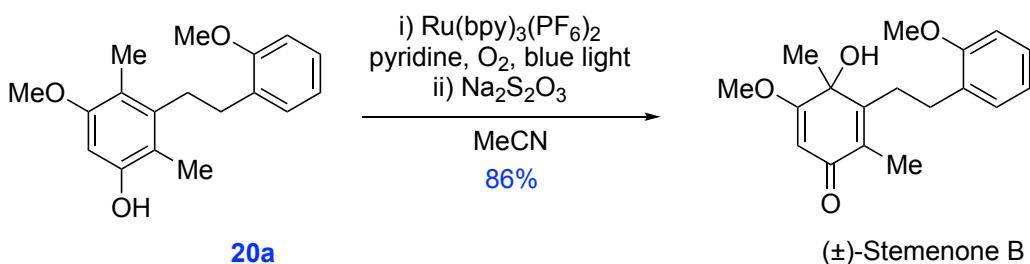
$R_f = 0.35$  (25% EtOAc/*n*-hexanes, orange with cerium ammonium molybdate).

**$^1\text{H NMR}$  (600 MHz, CDCl<sub>3</sub>)**  $\delta$  6.99 (t,  $J = 7.8$  Hz, 1H), 6.85 (d,  $J = 8.0$  Hz, 1H), 6.81 (d,  $J = 7.6$  Hz, 1H), 6.33 (s, 1H), 3.81 (s, 3H), 3.78 (s, 3H), 2.95 – 2.87 (m, 2H), 2.77 – 2.68 (m, 2H), 2.23 (s, 3H), 2.21 (s, 3H).

**$^{13}\text{C NMR}$  (151 MHz, CDCl<sub>3</sub>)**  $\delta$  156.4, 152.2, 149.2, 145.4, 140.8, 135.3, 125.2, 121.5, 116.9, 113.9, 113.5, 97.2, 61.5, 55.7, 31.6, 29.9, 11.2, 11.1.

**HRMS (ESI-TOF)**  $m/z = 303.1596$  calcd for C<sub>18</sub>H<sub>23</sub>O<sub>4</sub> [M+H]<sup>+</sup>, found 303.1597.

Spectral data were in agreement with those reported [*Phytochemistry* **2019**, *159*, 208].



[WARNING: See safety note above regarding the use of dioxygen].

**4-Hydroxy-5-methoxy-3-(2-methoxyphenethyl)-2,4-dimethylcyclohexa-2,5-dien-1-one;**

**(±)-Stemenone B (4)** General procedure B was followed using 5-methoxy-3-(2-methoxyphenethyl)-2,4-dimethylphenol (13 mg, 0.044 mmol), Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (0.001 mmol, 2 mol%), pyridine (0.11 mmol, 2.5 equiv) in MeCN (0.5 mL, 0.09 M) for 30 min. The vial was removed from light and argon was backfilled before removing the cap. Utilizing a literature procedure [*Angew. Chem. Int. Ed.* **2006**, *45* (17), 2737]: the reaction was diluted with water (6 mL) and an excess of anhydrous sodium thiosulfate (1.1 mmol, 25 equiv) was added before capping the vial. Upon completion (monitored by TLC and LC-MS), the mixture was diluted with water (10 mL) and extracted with EtOAc (3x). The combined organic layers were washed with 0.5 M HCl (2x), brine (1x), dried over anhydrous sodium sulfate, and concentrated *in vacuo*. Flash chromatography (50% EtOAc/*n*-hexanes) afforded an amorphous white solid (12 mg, 0.038 mmol) in 86% yield to complete the total synthesis of (±)-stemenone B in 9 total steps with a 6% overall yield.

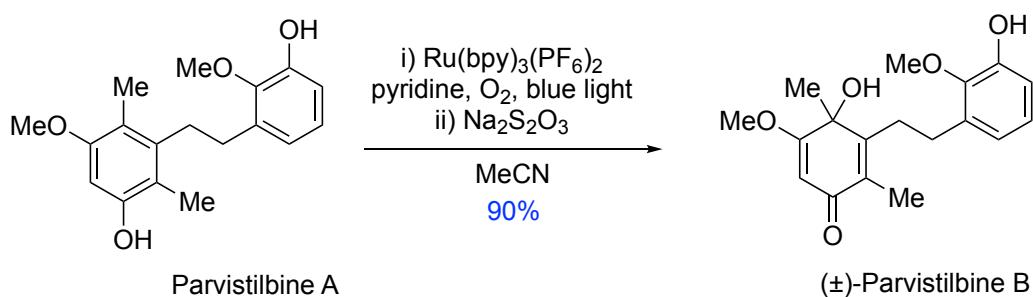
$R_f = 0.30$  (50% EtOAc/*n*-hexanes, orange with cerium ammonium molybdate).

**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)** δ 7.23 – 7.16 (m, 2H), 6.91 (td, J = 7.4, 1.1 Hz, 1H), 6.86 (d, J = 8.2 Hz, 1H), 5.49 (s, 1H), 3.84 (s, 3H), 3.80 (s, 3H), 2.88 – 2.83 (m, 2H), 2.81 – 2.74 (m, 1H), 2.66 – 2.58 (m, 1H), 2.50 (s, 1H), 1.89 (s, 3H), 1.56 (s, 3H).

**<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)** δ 187.3, 175.6, 157.5, 153.4, 130.8, 130.2, 130.0, 127.8, 120.8, 110.5, 99.7, 71.8, 56.1, 55.4, 30.3, 29.4, 27.6, 11.3.

**HRMS (ESI-TOF)** m/z = 303.1596 calcd for C<sub>18</sub>H<sub>23</sub>O<sub>4</sub> [M+H]<sup>+</sup>, found 303.1601.

Spectral data were in agreement with those reported [*Fitoterapia* **2018**, 129, 150].



[WARNING: See safety note above regarding the use of dioxygen].

**4-hydroxy-3-(3-hydroxy-2-methoxyphenethyl)-5-methoxy-2,4-dimethylcyclohexa-2,5-dien-1-one;**

**(±)-Parvistilbene B (5)** General procedure B was followed using parvistilbene A (14 mg, 0.045 mmol), Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (0.001 mmol, 2 mol%), pyridine (0.11 mmol, 2.5 equiv) in MeCN (1 mL, 0.04 M) for 40 min. The vial was removed from light and argon was backfilled before removing the cap. Utilizing a literature procedure [*Angew. Chem. Int. Ed.* **2006**, 45 (17), 2737]: the reaction was diluted with water (6 mL) and an excess of anhydrous sodium thiosulfate (1.1 mmol, 25 equiv) was added before capping the vial. Upon completion (monitored by TLC and LC-MS), the mixture was diluted with water (10 mL) and extracted with EtOAc (3x). The combined organic layers were washed with 0.5 M HCl (2x), brine (1x), dried over anhydrous sodium sulfate, and concentrated *in vacuo*. Flash chromatography (50% EtOAc/n-hexanes) afforded an amorphous white solid (13 mg, 0.041 mmol) in 90% yield to complete the total synthesis of (±)-parvistilbene B in 11 total steps with a 6% overall yield.

R<sub>f</sub> = 0.22 (50% EtOAc/n-hexanes, brown/orange with cerium ammonium molybdate).

**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)** δ 6.98 (t, J = 7.8 Hz, 1H), 6.84 (dd, J = 8.0, 1.6 Hz, 1H), 6.80 (dd, J = 7.6, 1.6 Hz, 1H), 5.59 (s, 1H), 5.51 (s, 1H), 3.83 (s, 3H), 3.80 (s, 3H), 2.94 (ddd, J = 13.8, 11.7, 5.0 Hz, 1H), 2.80 – 2.70 (m, 2H), 2.70 – 2.64 (m, 1H), 2.46 (s, 1H), 1.97 (s, 3H), 1.56 (s, 3H).

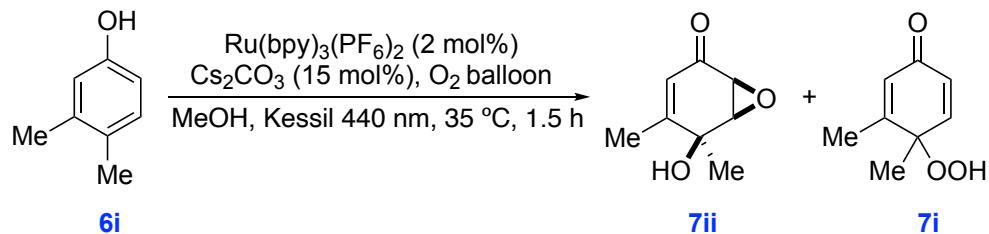
**$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )**  $\delta$  187.1, 175.4, 153.1, 149.2, 145.4, 134.9, 130.8, 125.2, 121.6, 114.2, 99.7, 71.8, 61.5, 56.2, 30.1, 29.4, 28.0, 11.3.

**HRMS (ESI-TOF)**  $m/z$  = 319.1545 calcd for  $\text{C}_{18}\text{H}_{23}\text{O}_5$   $[\text{M}+\text{H}]^+$ , found 319.1540.

Spectral data were in agreement with those reported [*Phytochemistry* **2019**, *159*, 208].

## **5. Additional Mechanistic Experiments**

### **Solvent and base dependency**



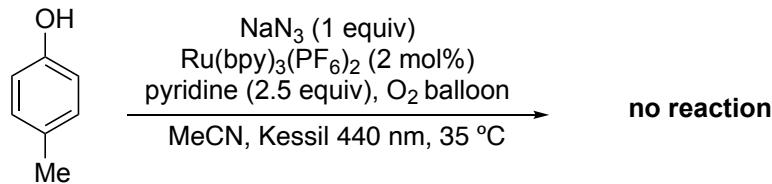
A 20 mL scintillation vial equipped with a stirbar was charged with 3,4-dimethylphenol (0.25 mmol, 1.0 equiv), Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (0.005 mmol, 2 mol%), cesium carbonate (0.038 mmol, 15 mol%), and MeCN (10 mL, 25 mM). The vial was capped with a rubber septum and evacuated/backfilled, using house vacuum, with oxygen (3x). A needle attached to an oxygen balloon was placed below the solvent level and the headspace was attached to an outlet to allow a slow active sparge of the solution during the reaction. This vial was then irradiated with 440 nm light (blue Kessil lamp, 100% power, 7 cm from wall of flask) until complete consumption of starting phenol was observed via TLC. The reaction was then quenched with water and extracted with EtOAc (3x, added 0.5 M HCl if emulsion formed). The combined organic layers were washed with 0.5 M HCl (2x) and brine (1x), dried over anhydrous sodium sulfate, and concentrated *in vacuo*. Flash chromatography (50% EtOAc/n-hexanes) afforded **7ii** as a white amorphous solid (21 mg, 0.14 mmol) in 54% yield and **7i** as a white amorphous solid (11 mg, 0.07 mmol) in 29% yield.

**7ii:** <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 5.75 – 5.70 (m, 1H), 3.65 (d, J = 3.9 Hz, 1H), 3.51 (dd, J = 4.0, 2.1 Hz, 1H), 2.01 (d, J = 1.4 Hz, 3H), 1.47 (s, 3H).

Spectral data were in agreement with those reported [*J. Org. Chem.* **2021**, 86 (24), 18192].

**7i:** previously characterized (see S8–9).

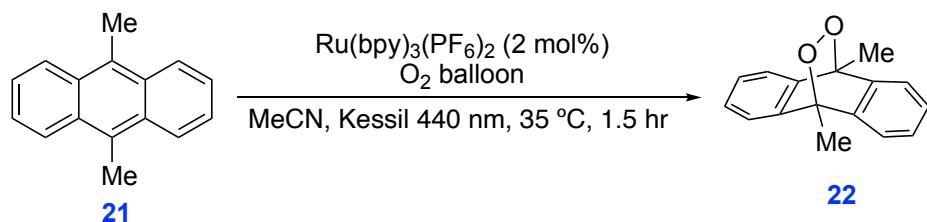
### **Singlet oxygen inhibition experiment**



[**WARNING:** Sodium azide is highly toxic, thermally unstable, and reacts explosively with various metals. A stainless-steel spatula should be used for handling and its waste streams should be properly segregated as according to OSHA Lab Standard].

General procedure B was followed using *para*-cresol (27 mg, 1.0 equiv), Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (4 mg, 2 mol%), pyridine (51 µL, 2.5 equiv), sodium azide (16 mg, 1.0 equiv) in MeCN (2.5 mL, 0.10 M). After 4 h, no product formation/starting material consumption was observed by TLC or LC-MS. Sodium azide is known to be a singlet oxygen quencher [J. Org. Chem. **2021**, 86 (24), 18192], so singlet oxygen is a reactive species in this chemistry.

**[4+2] cycloaddition isolable intermediate**



General procedure B was followed using 9,10-dimethylanthracene (0.25 mmol, 1.0 equiv), Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (0.005 mmol, 2 mol%) in MeCN (2.5 mL, 0.10 M) for 1.5 h. Flash chromatography (25% EtOAc/*n*-hexanes) afforded **22** as an amorphous white solid (54 mg, 0.23 mmol) in 91% yield.

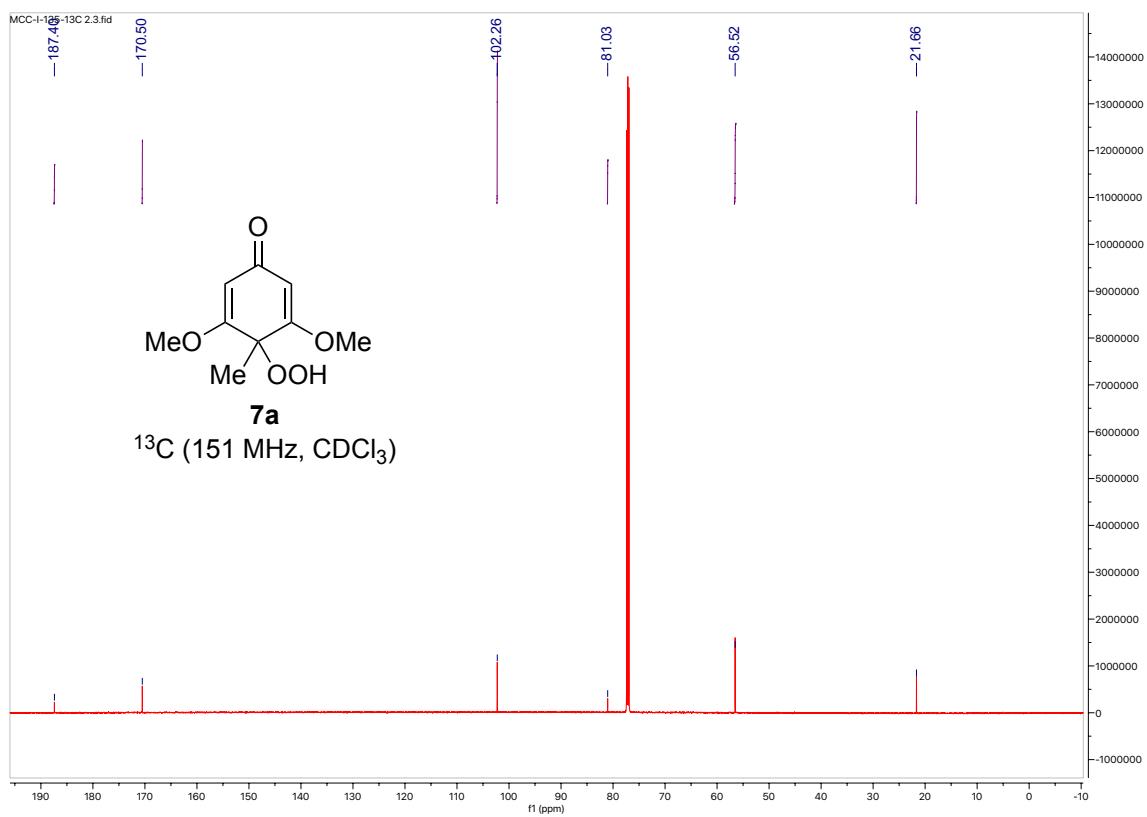
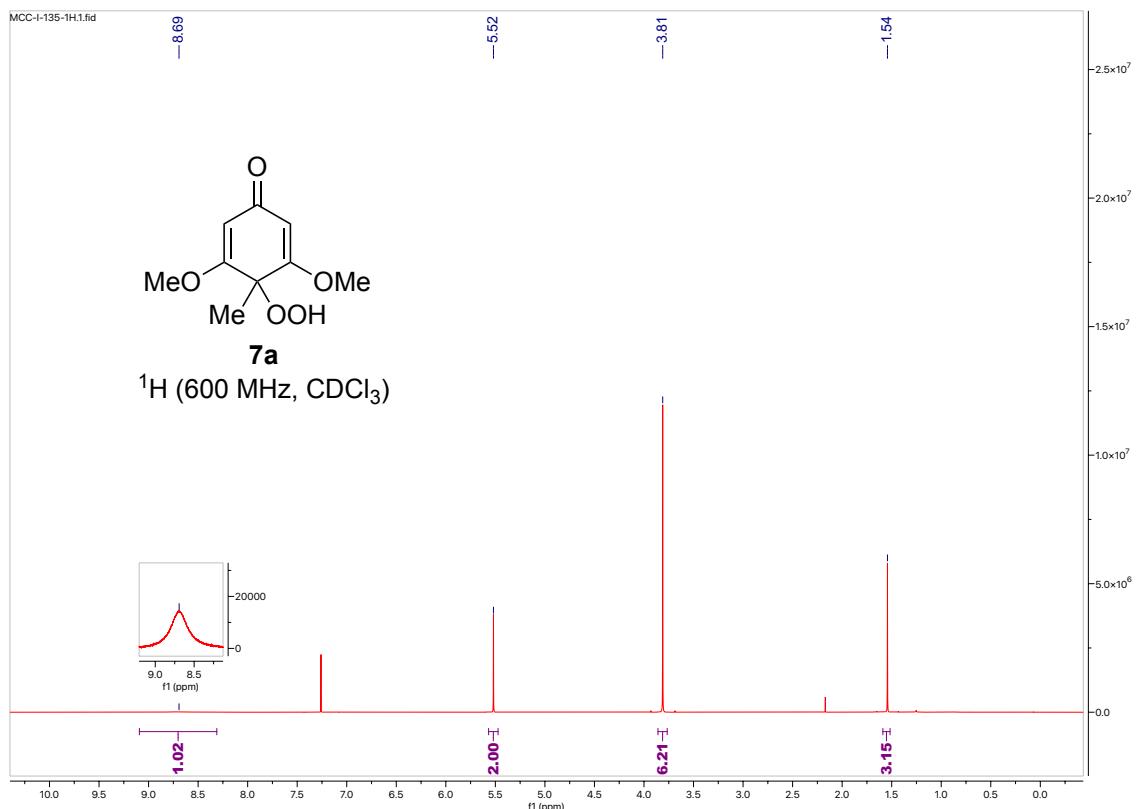
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.42 – 7.37 (m, 4H), 7.31 – 7.27 (m, 4H), 2.15 (s, 6H).

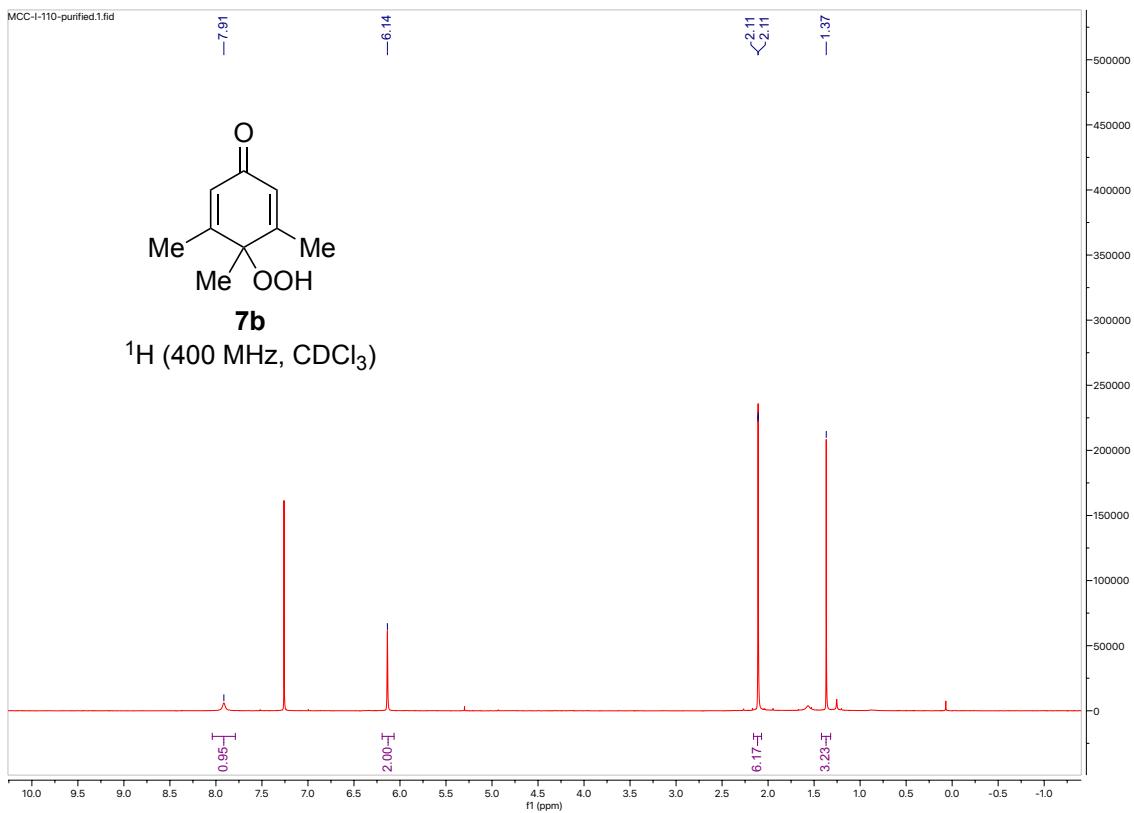
Spectral data were in agreement with those reported [Angew. Chem. Int. Ed. **2006**, 45 (17), 2737].

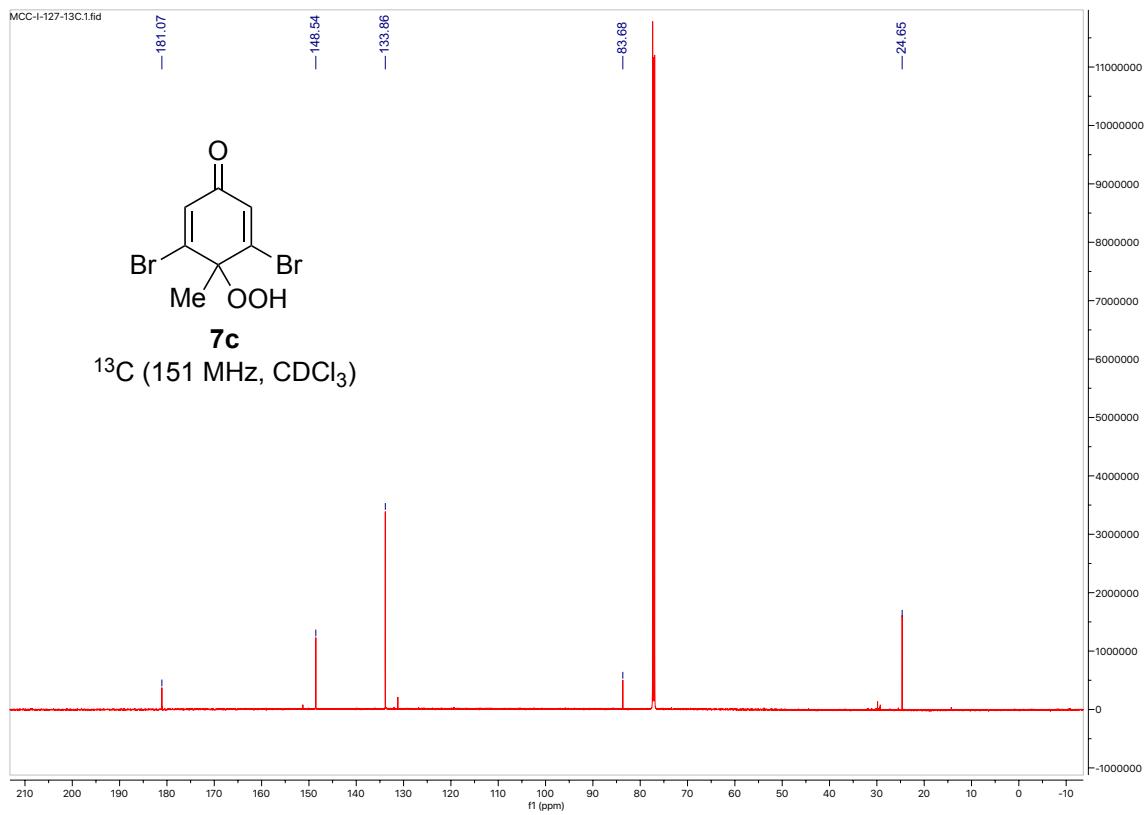
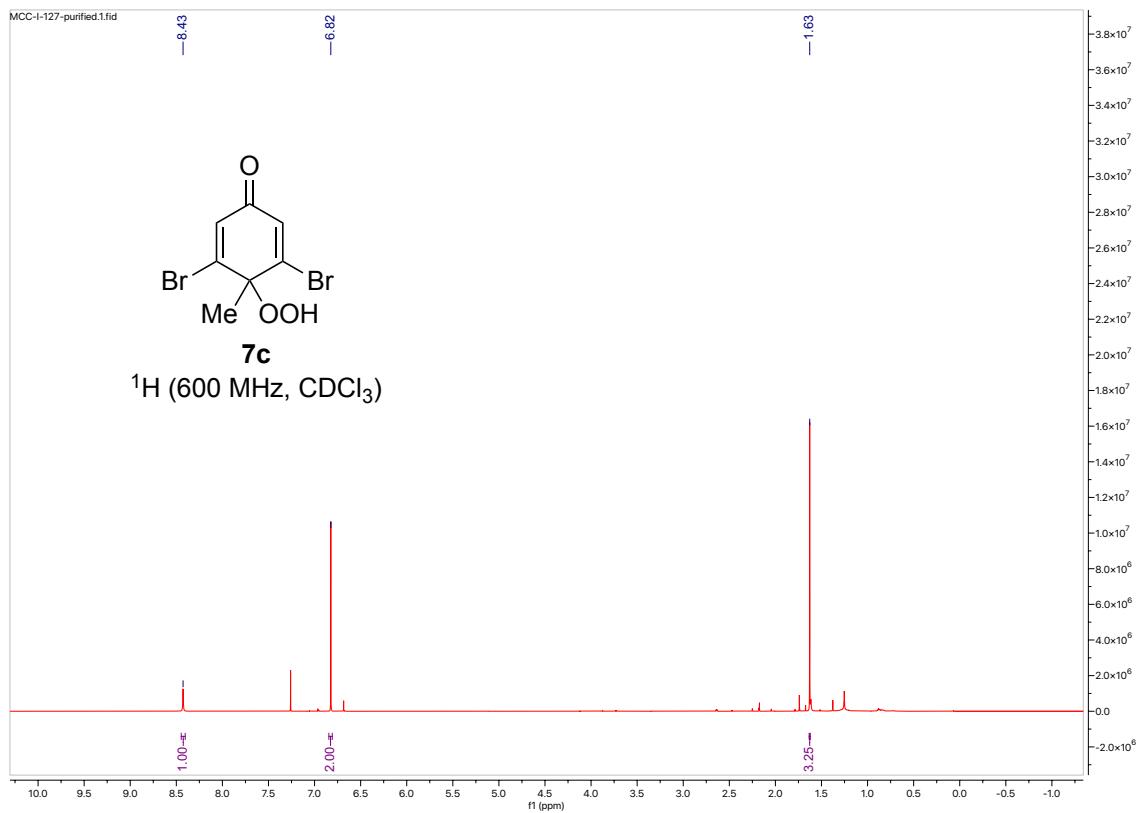
## **6. References**

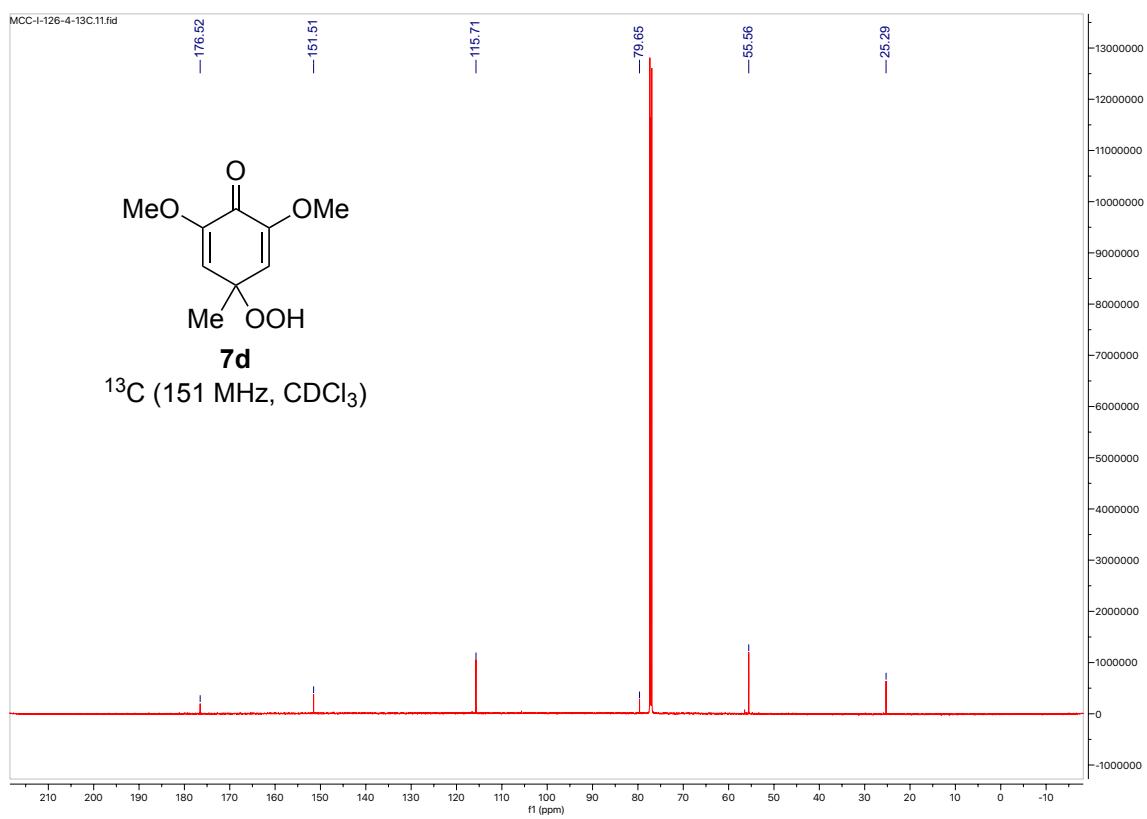
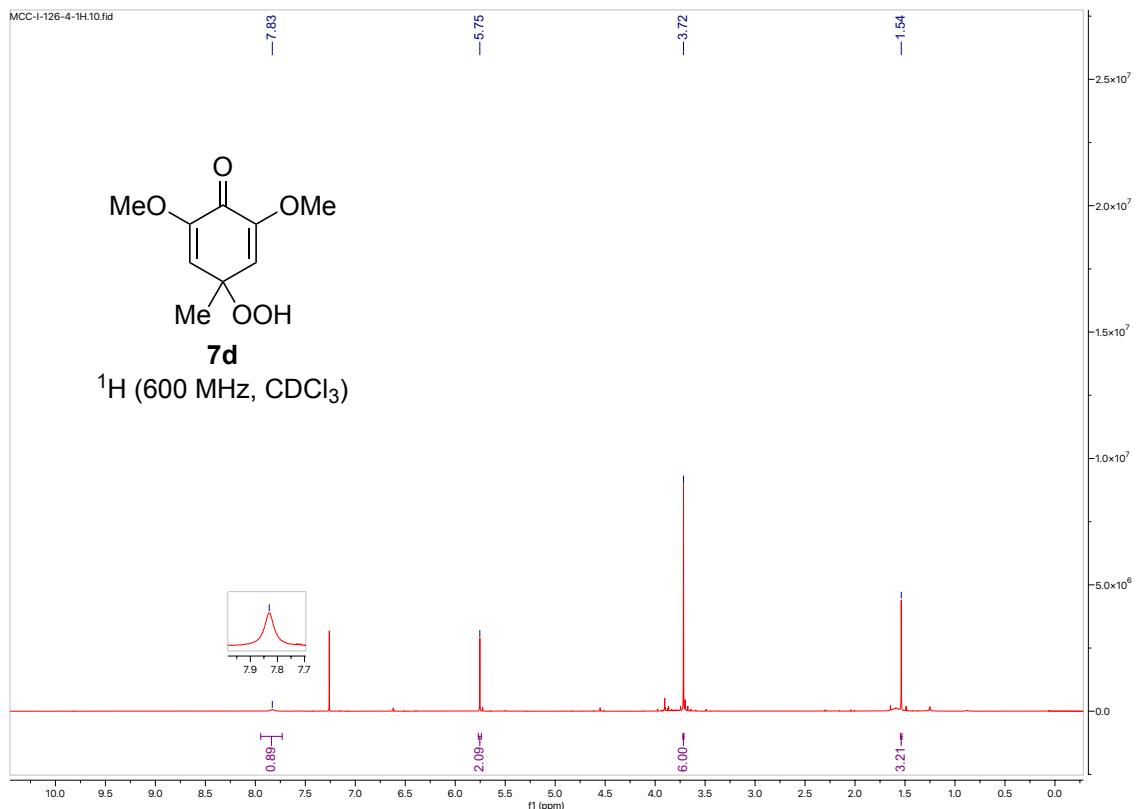
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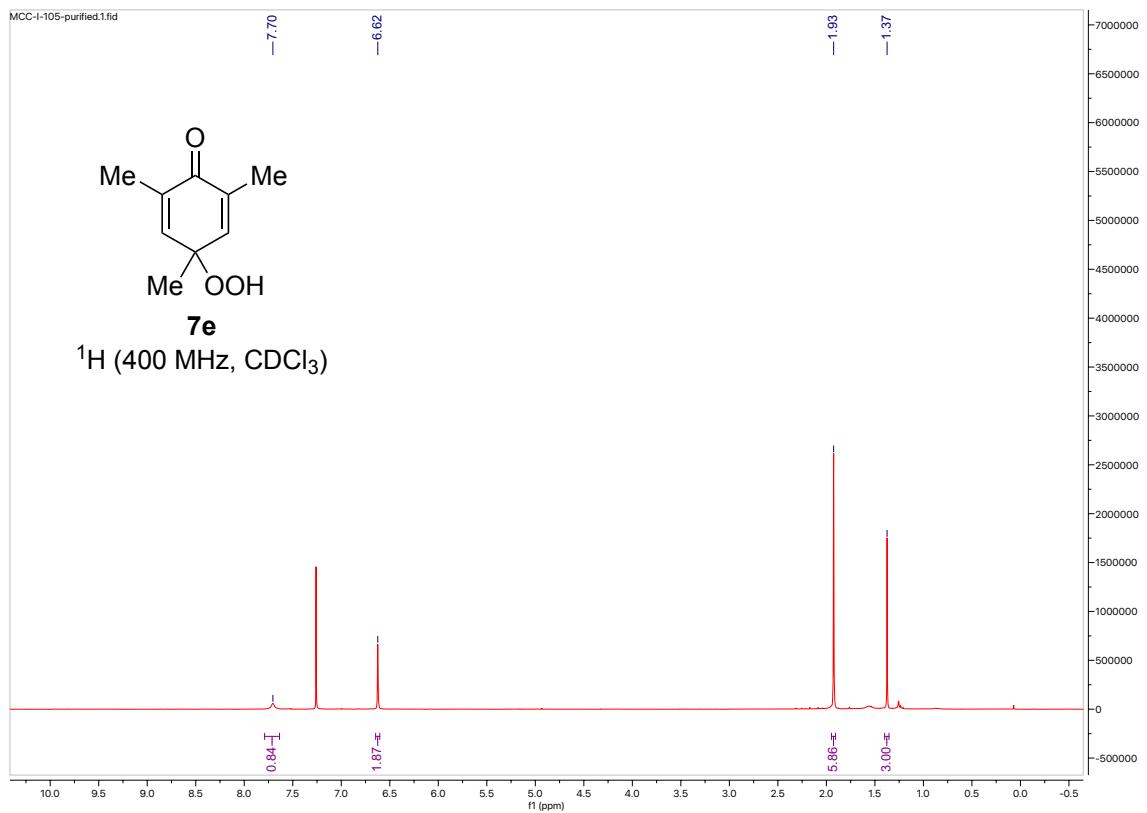
## 7. NMR Spectra

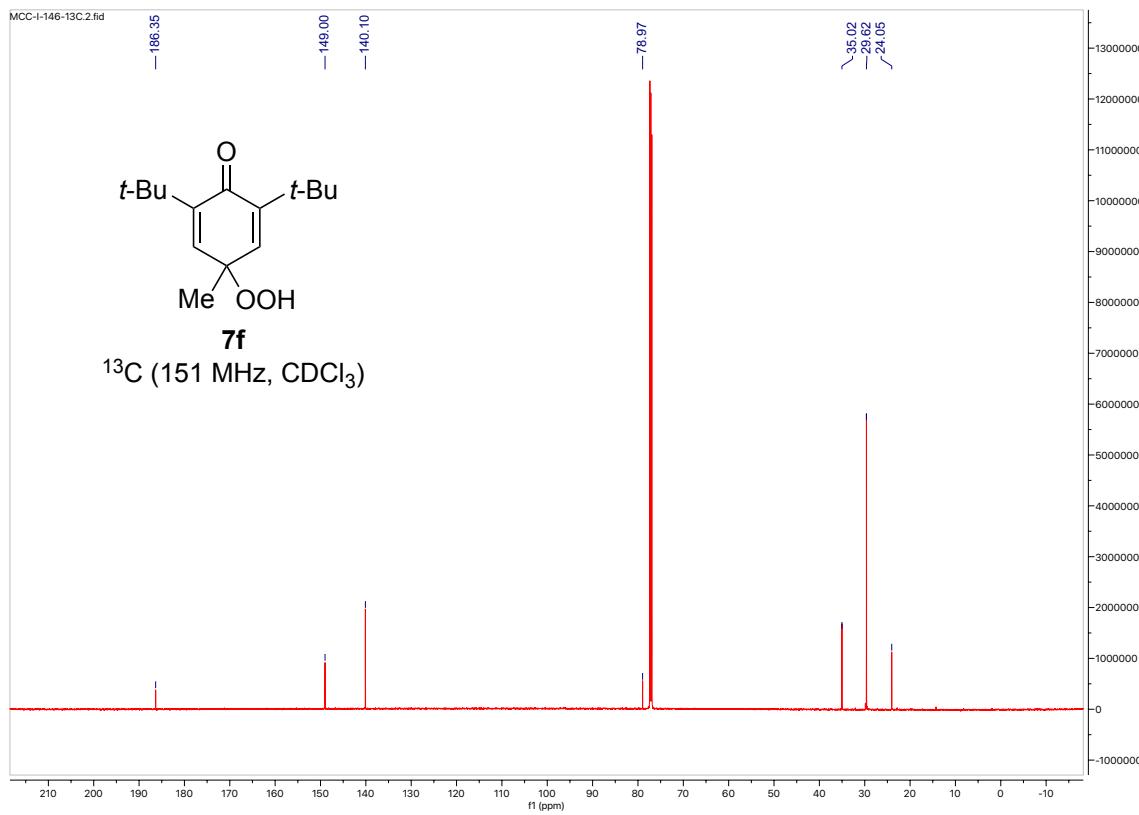
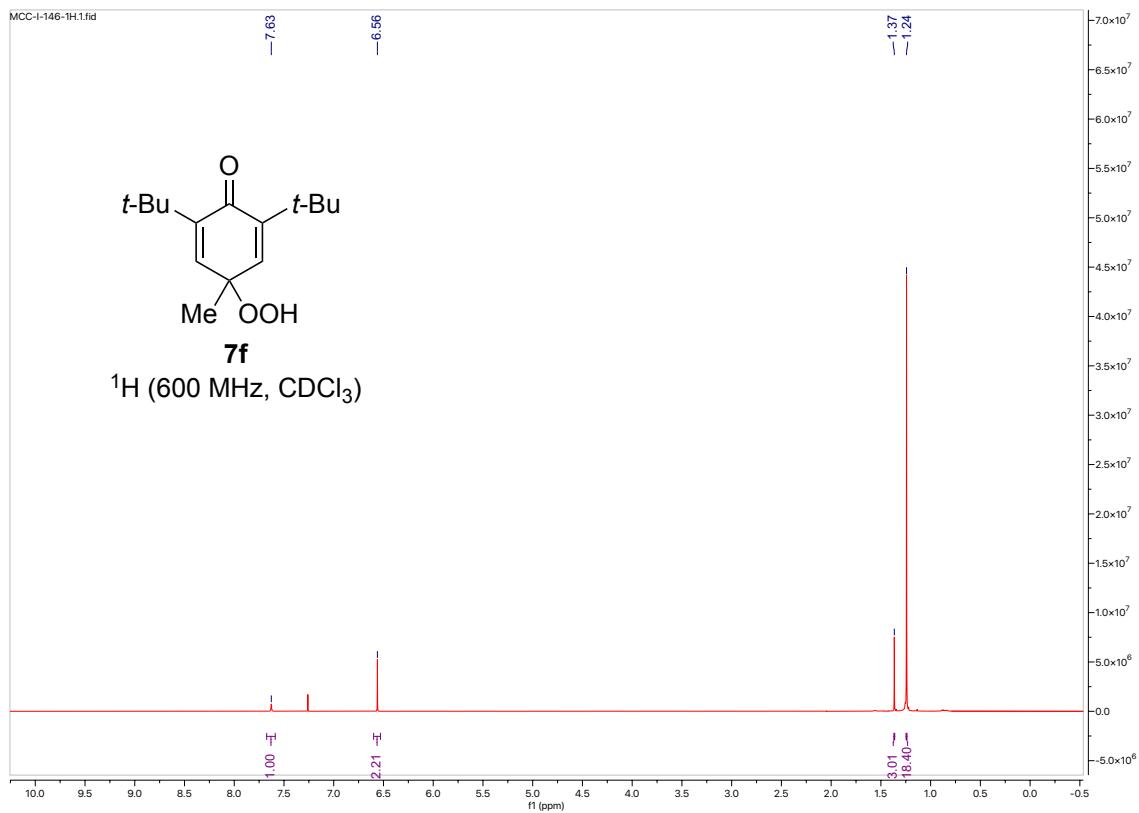


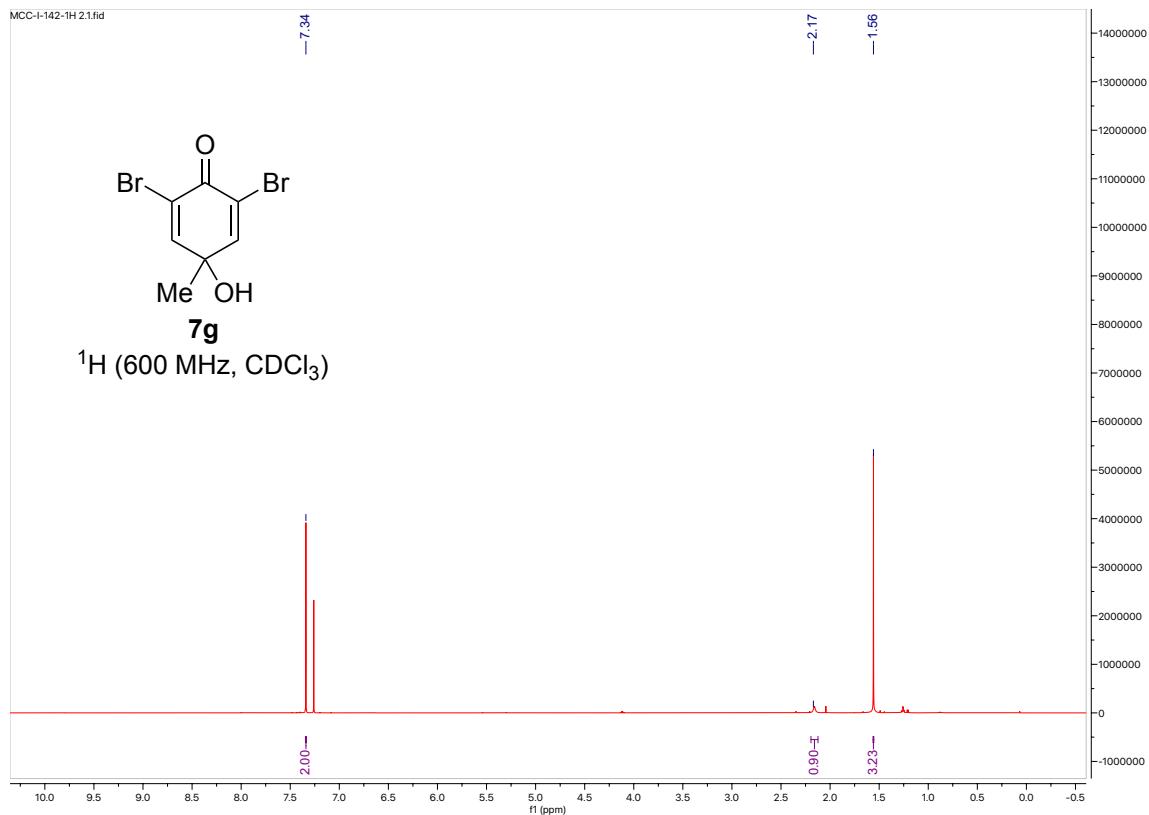


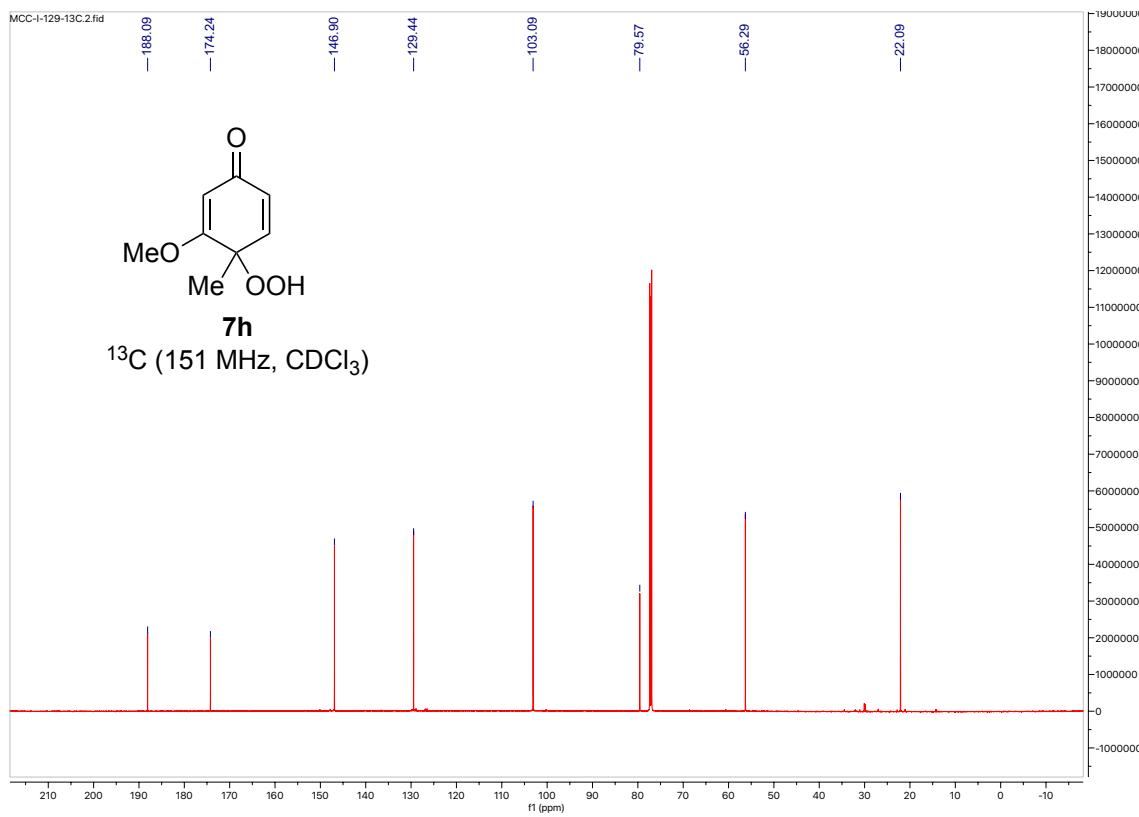
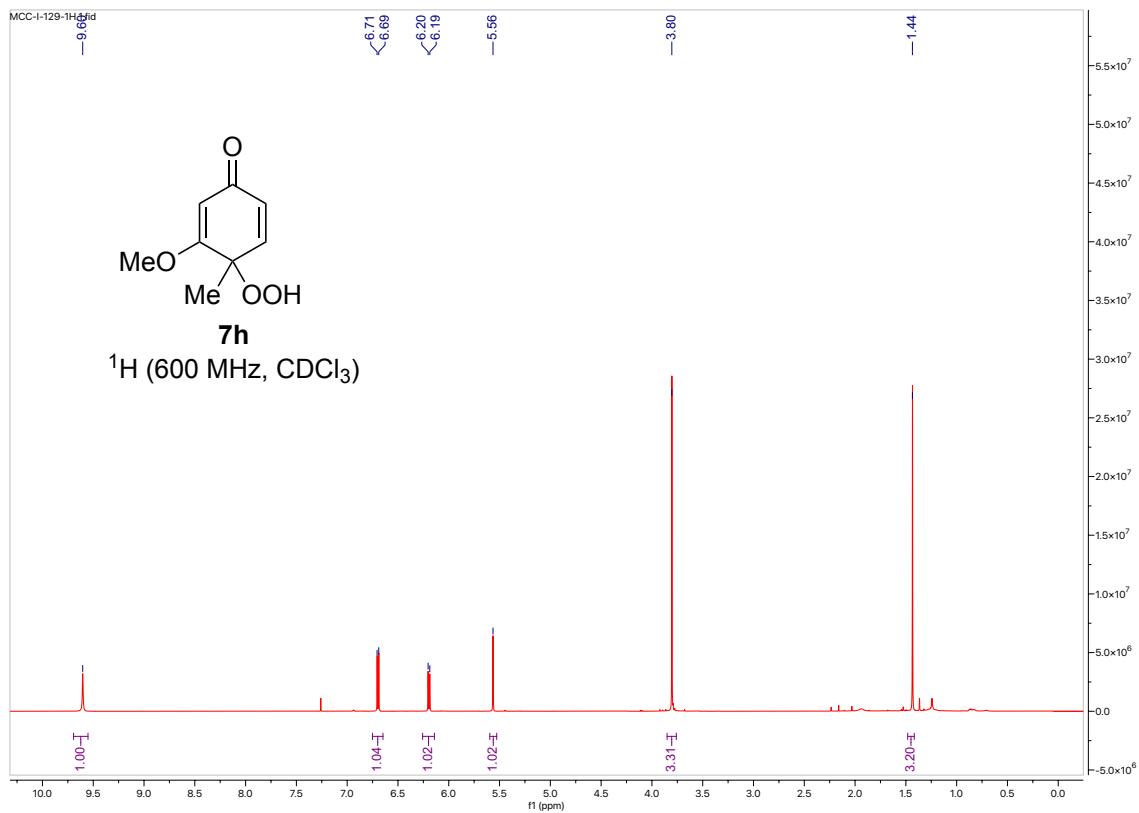


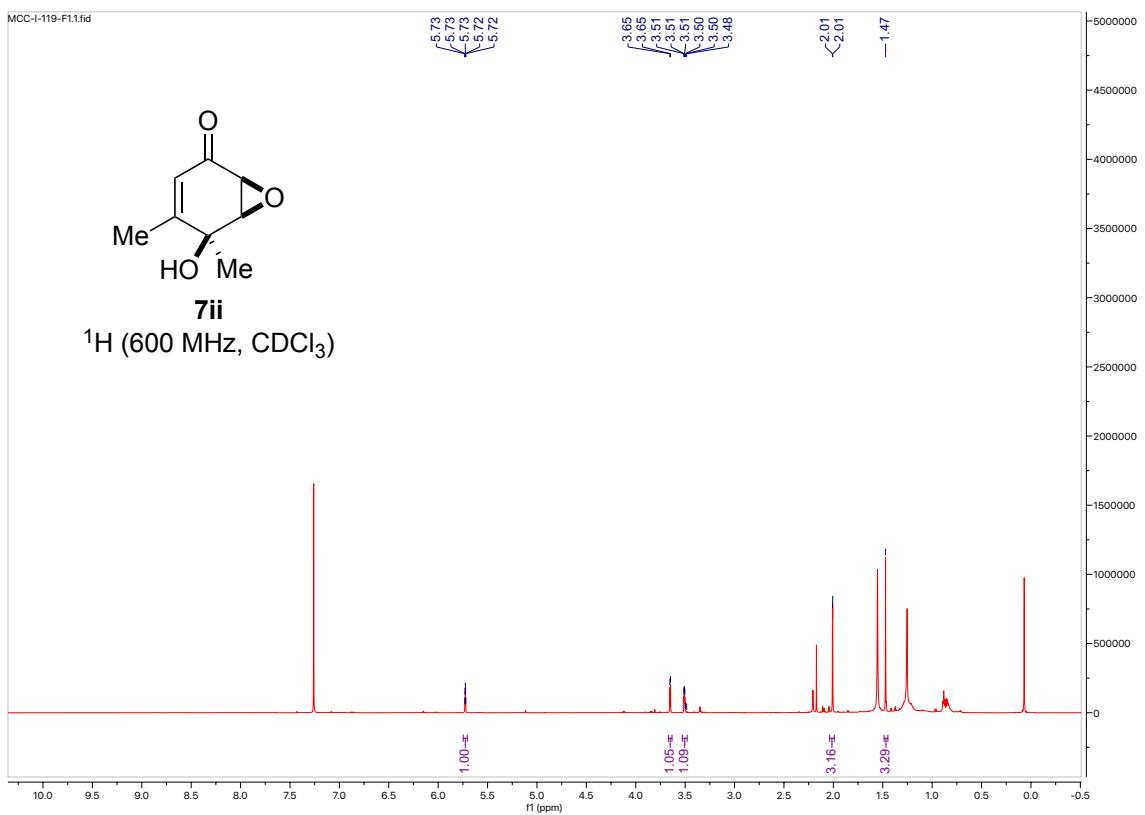
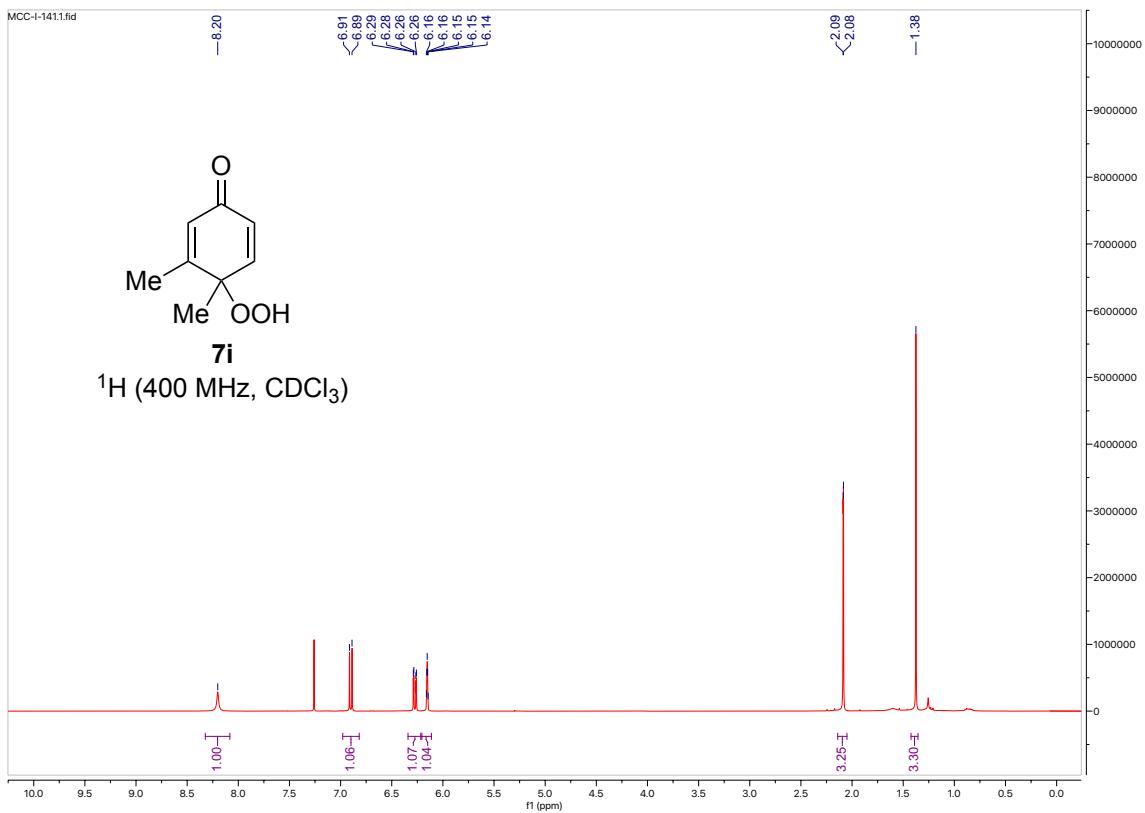


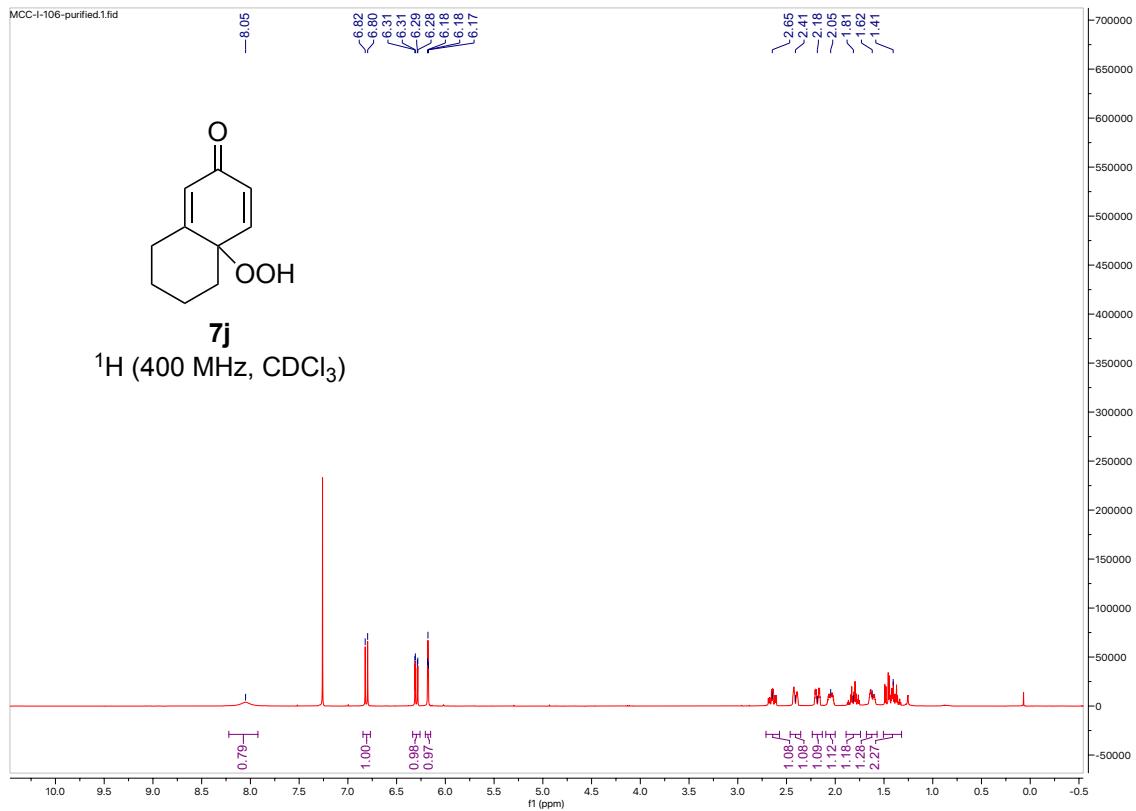


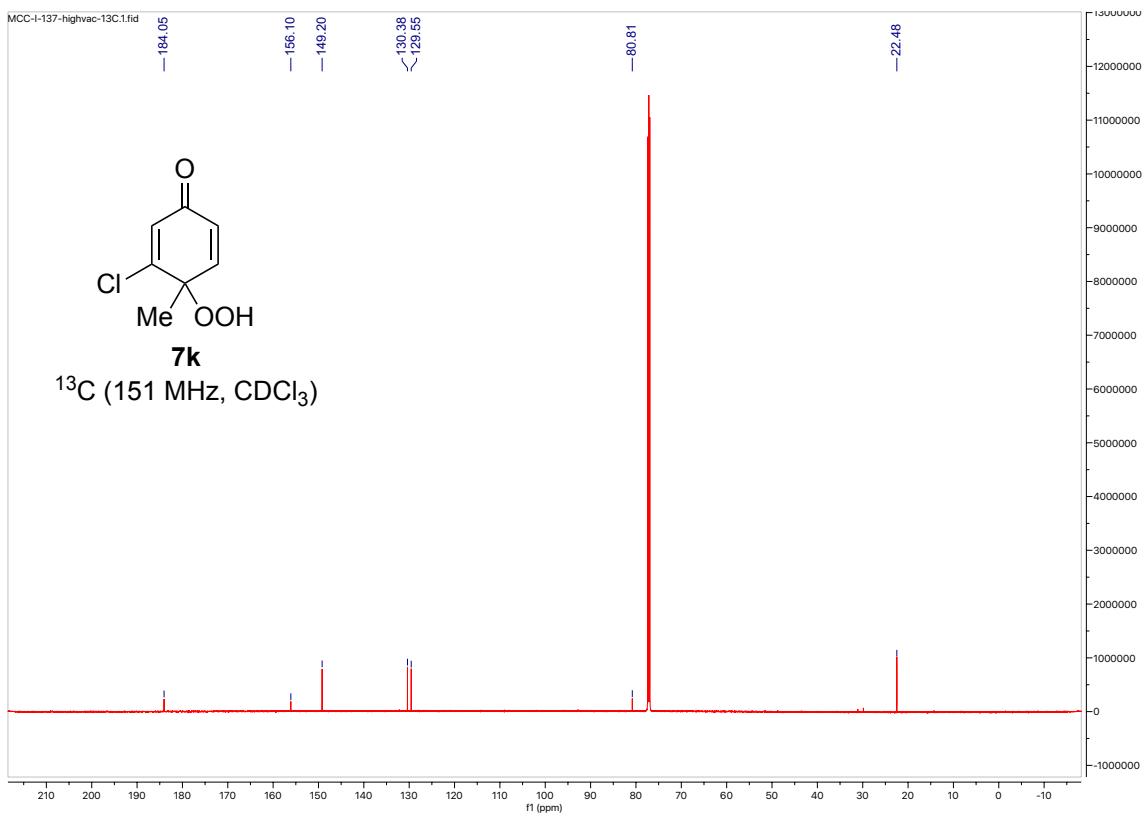
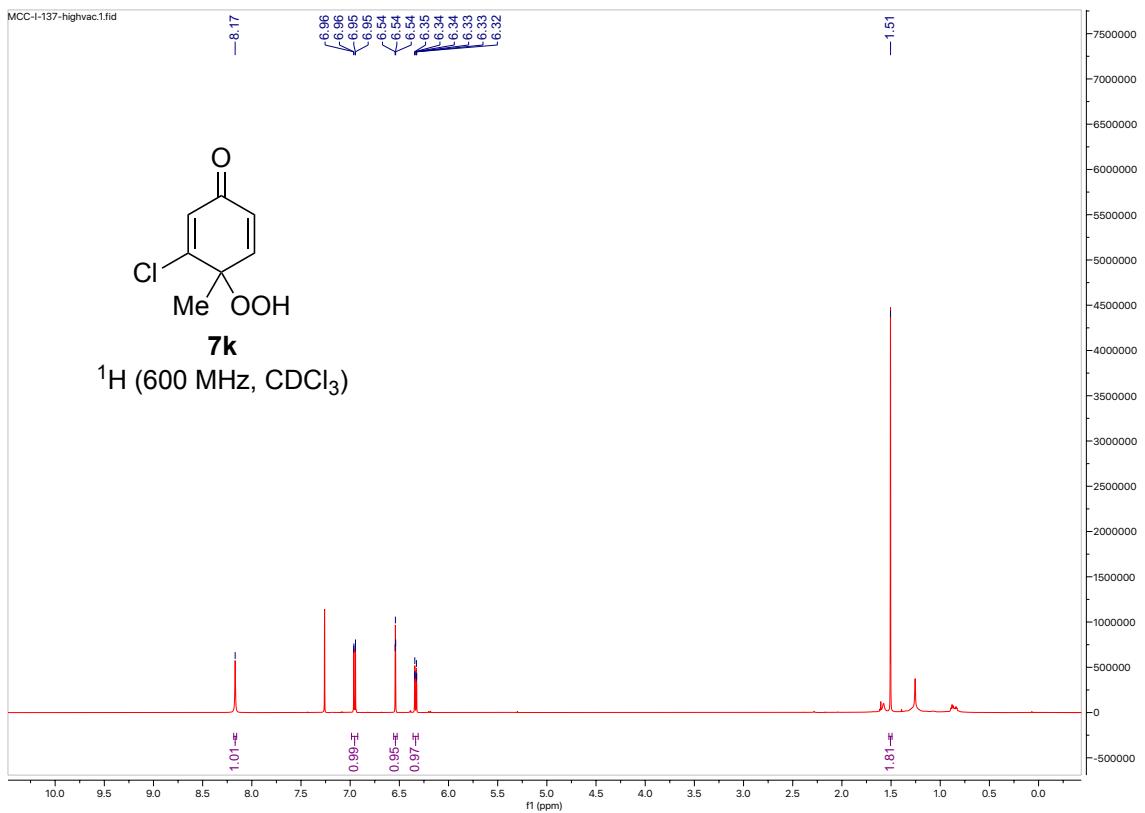


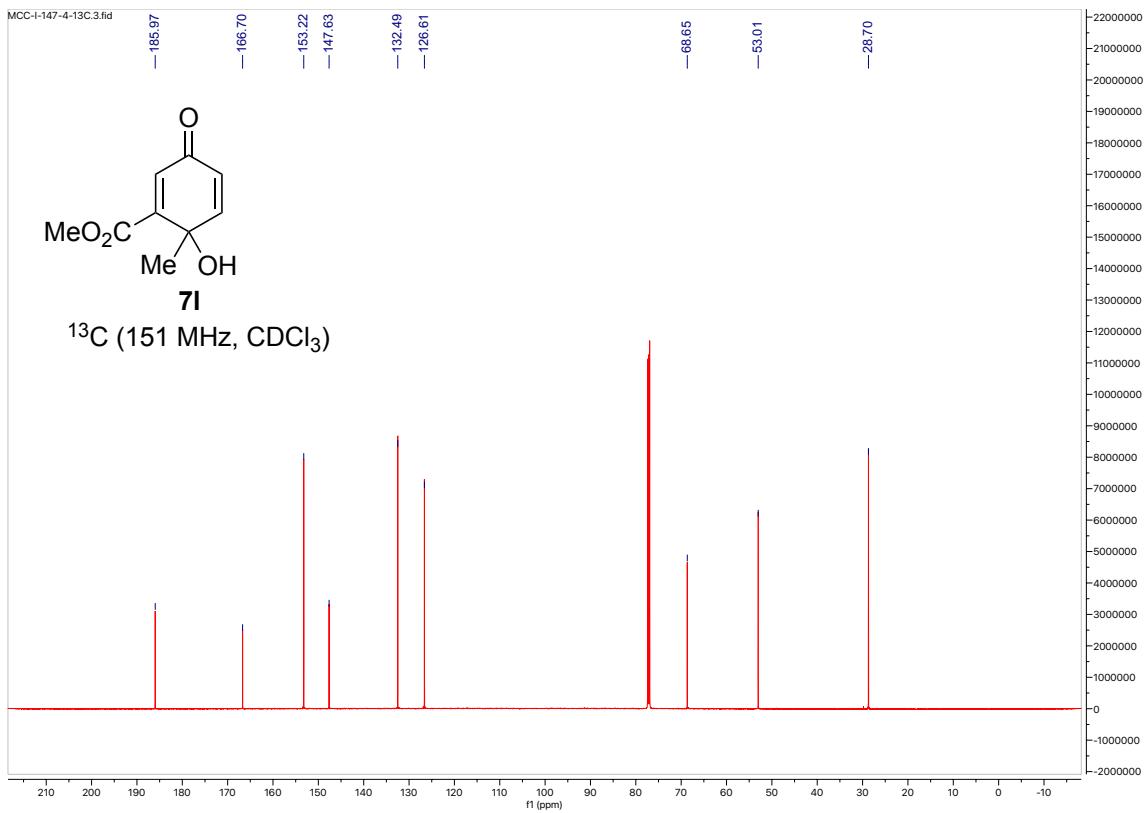
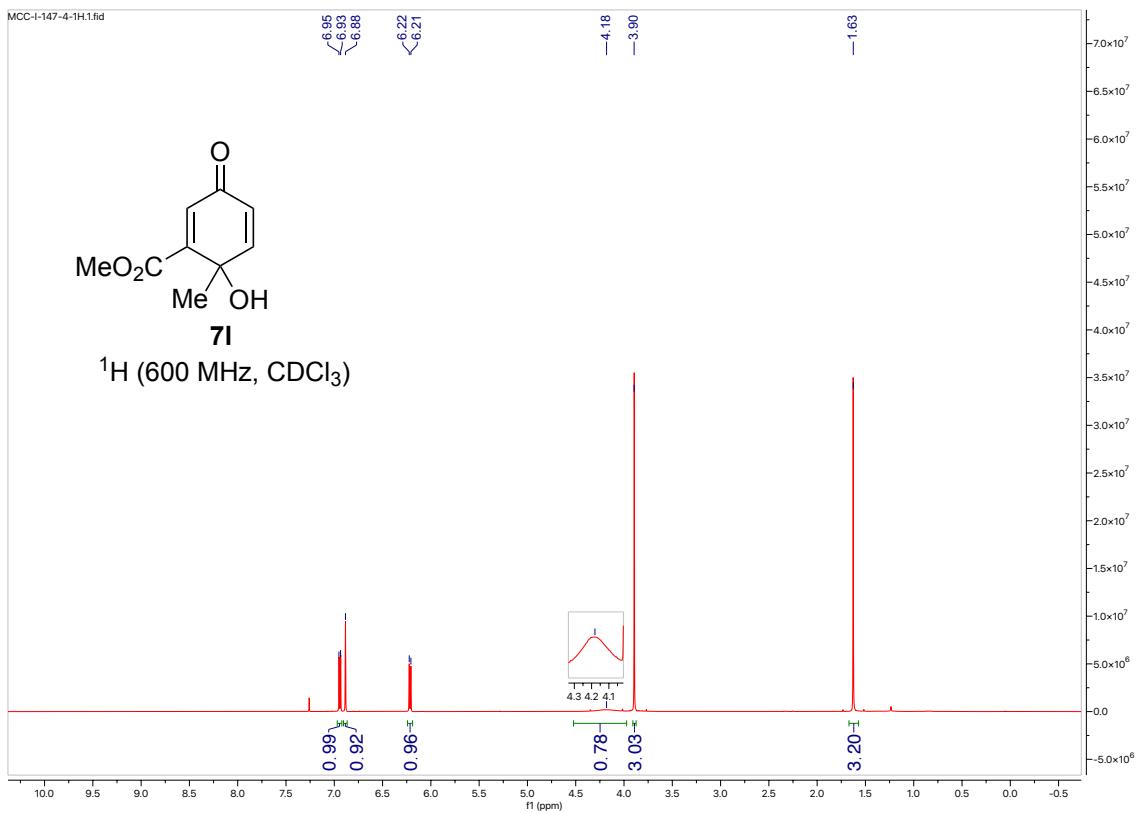


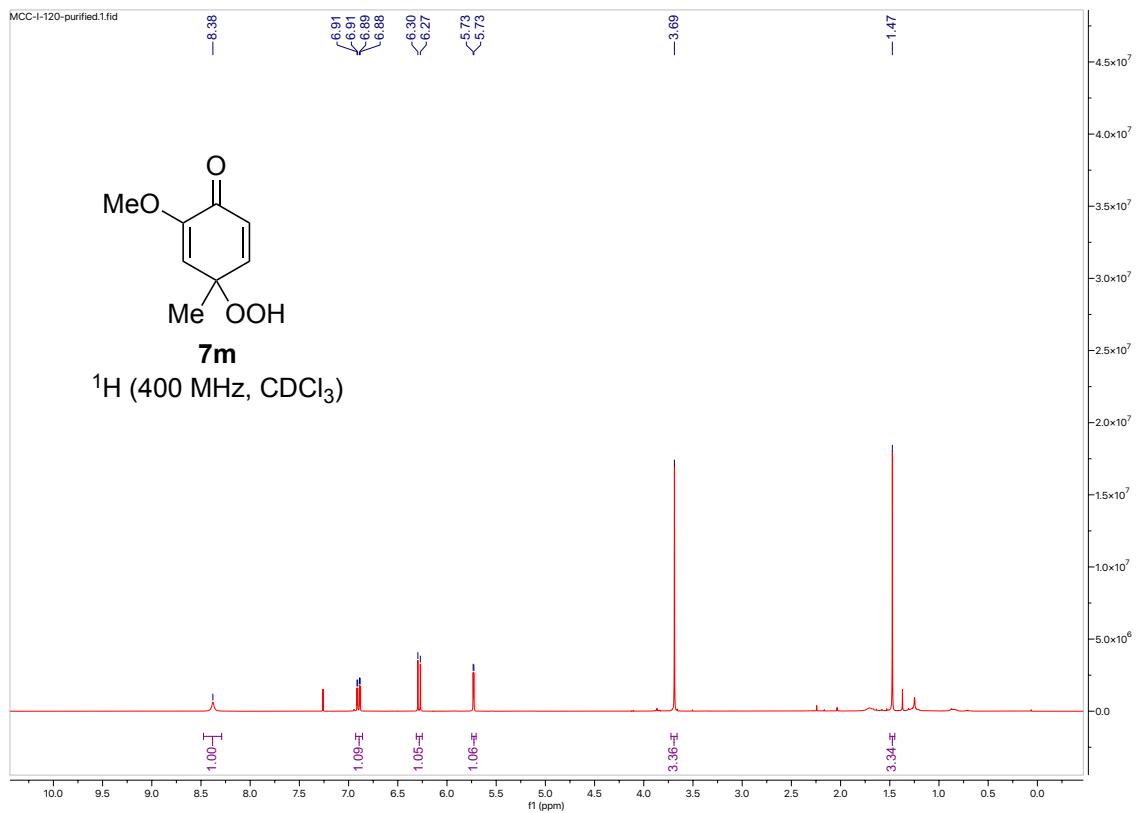


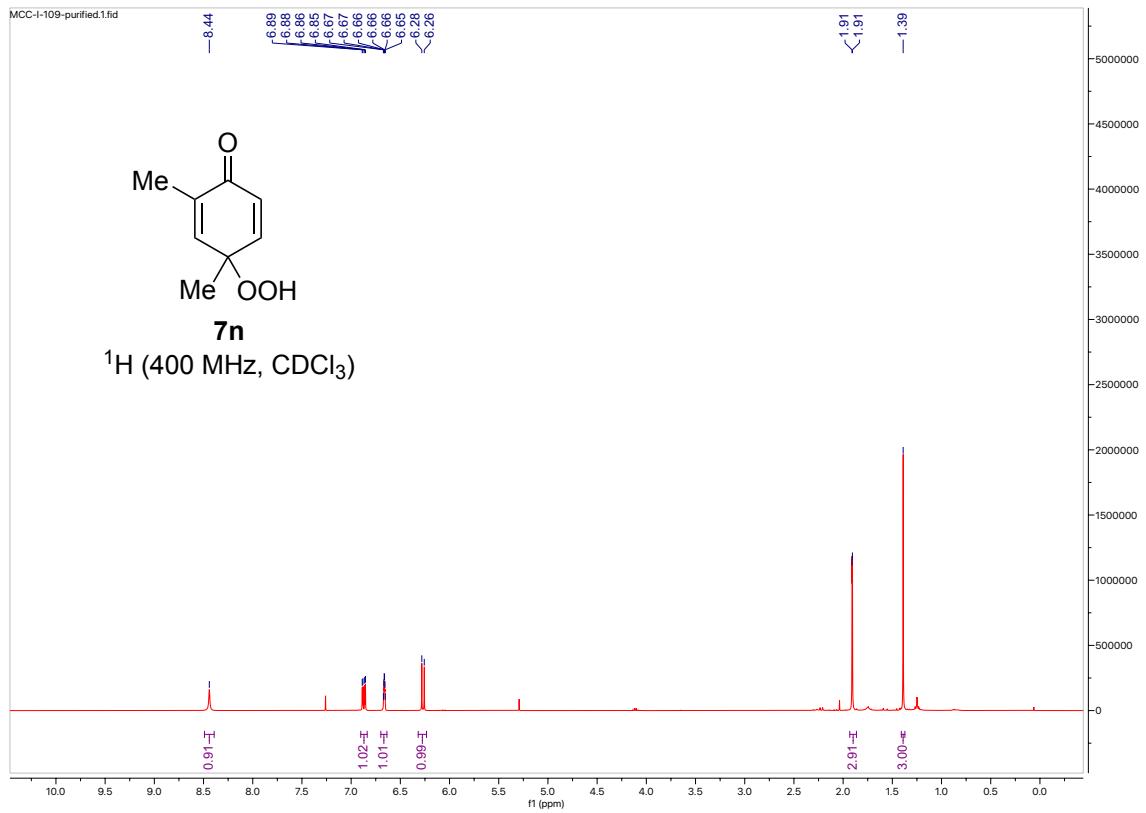


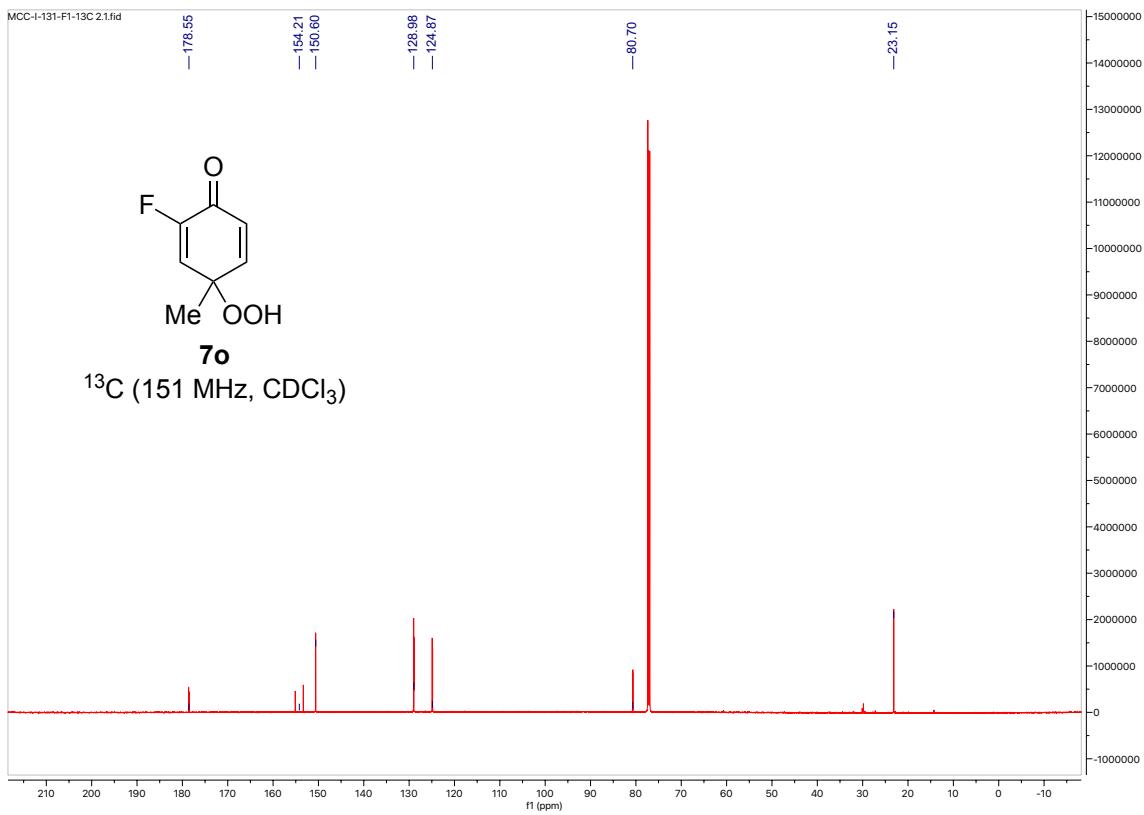
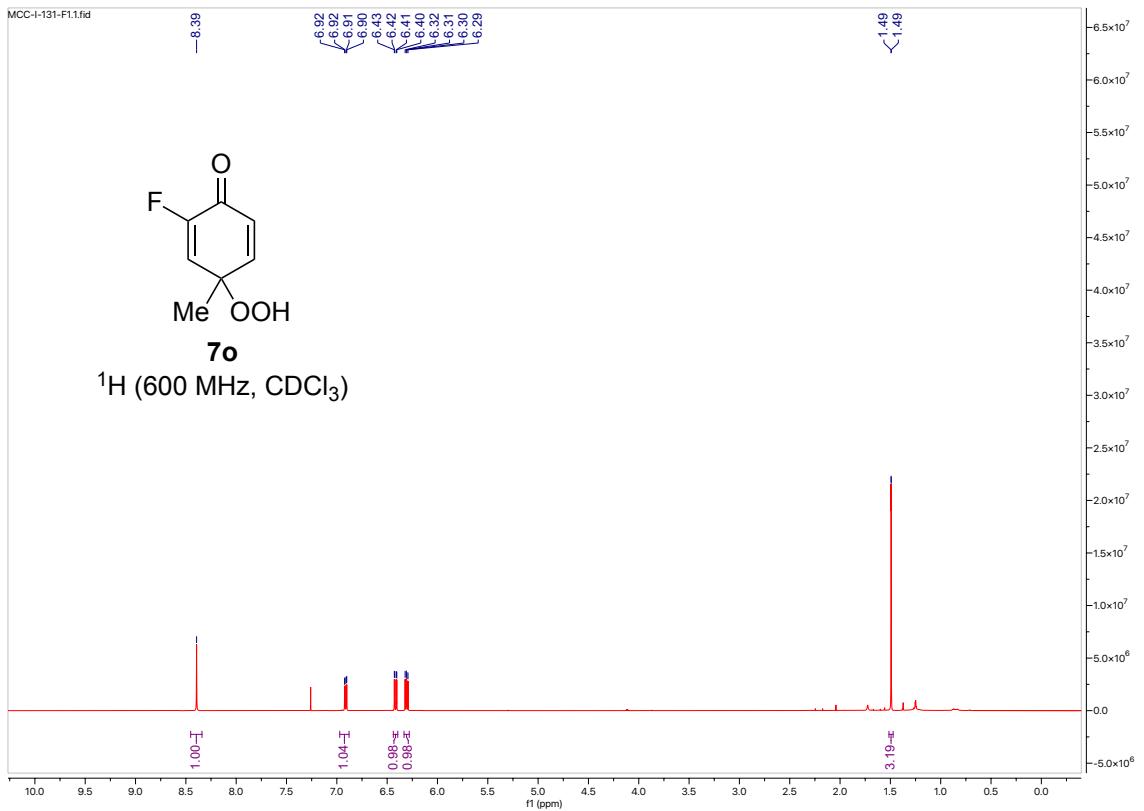


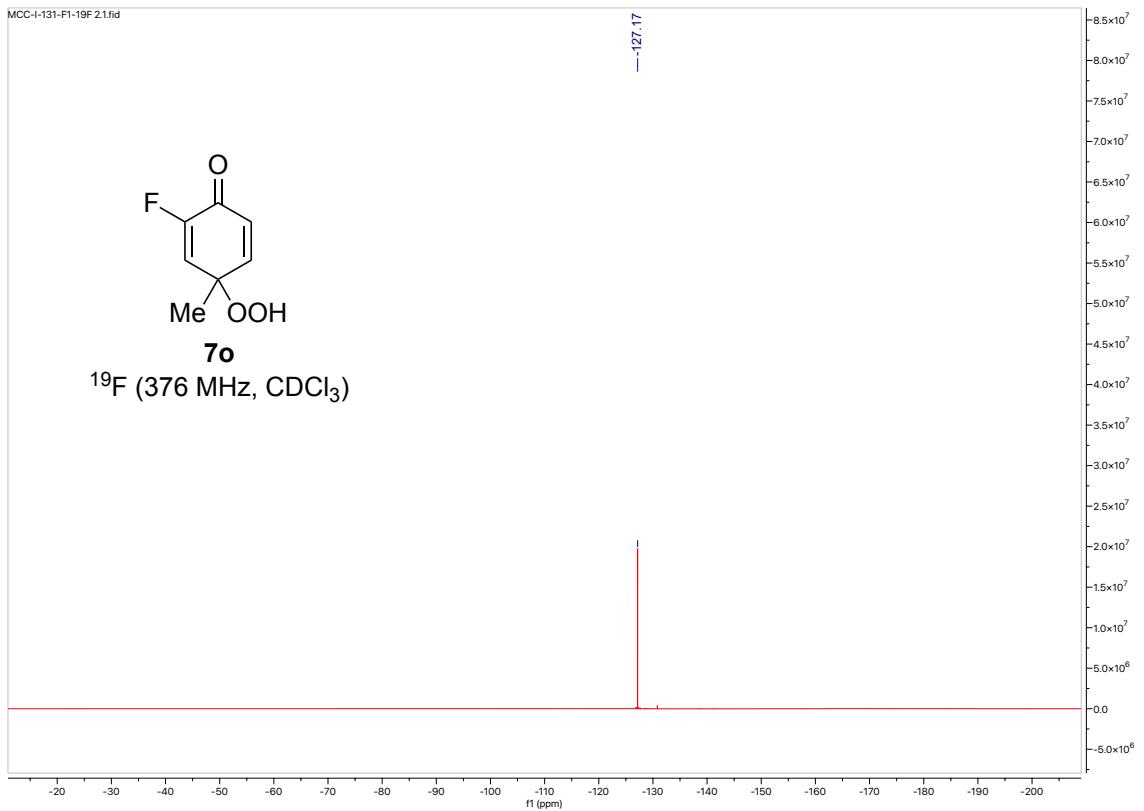


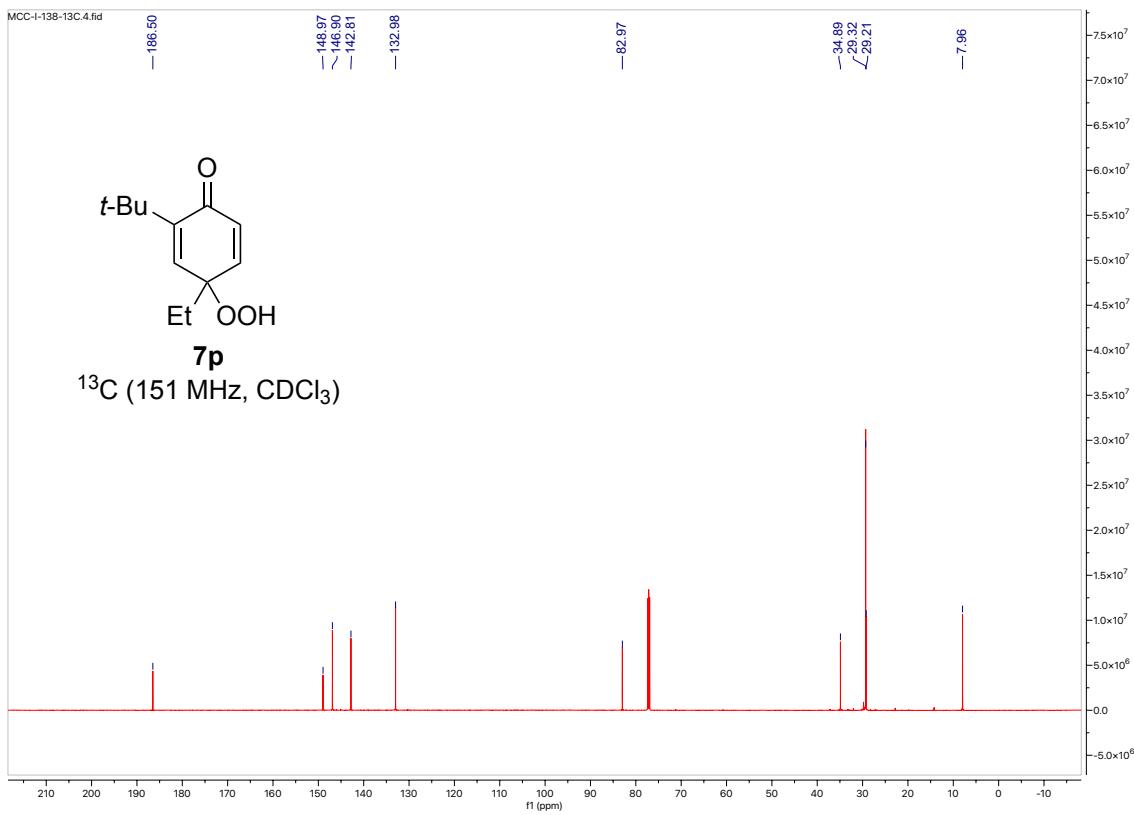
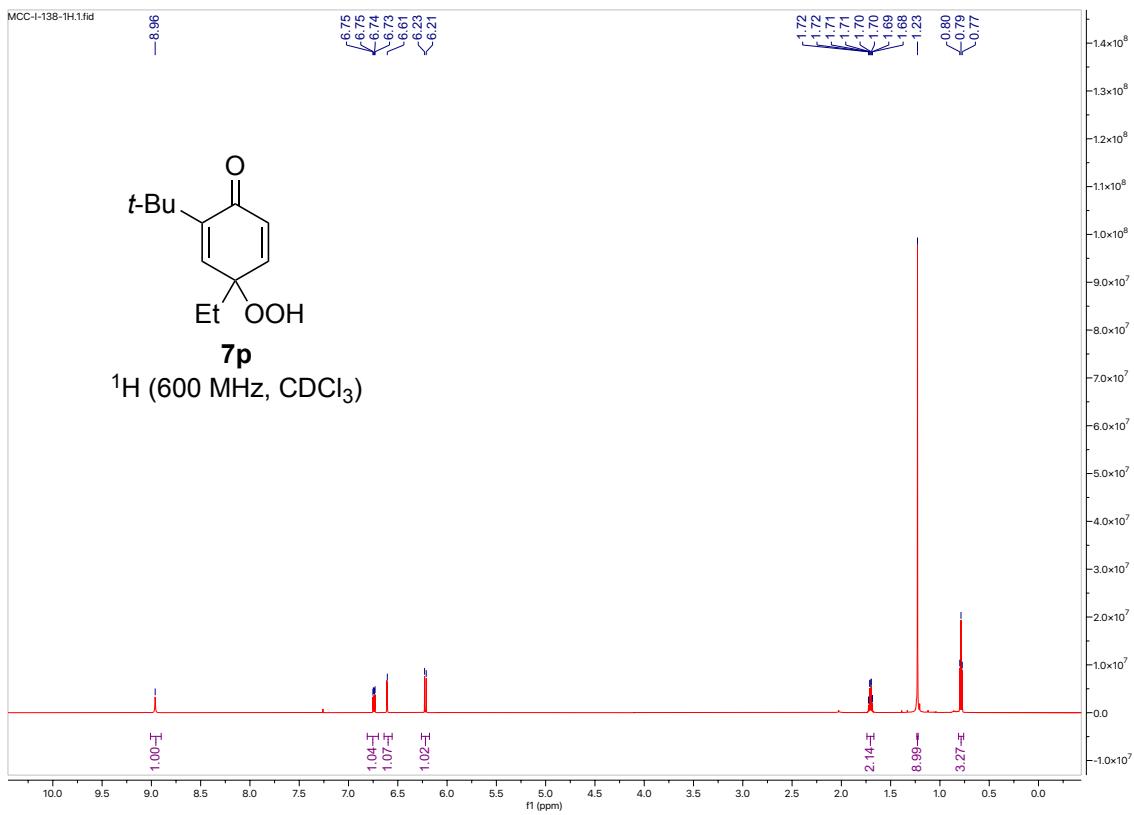


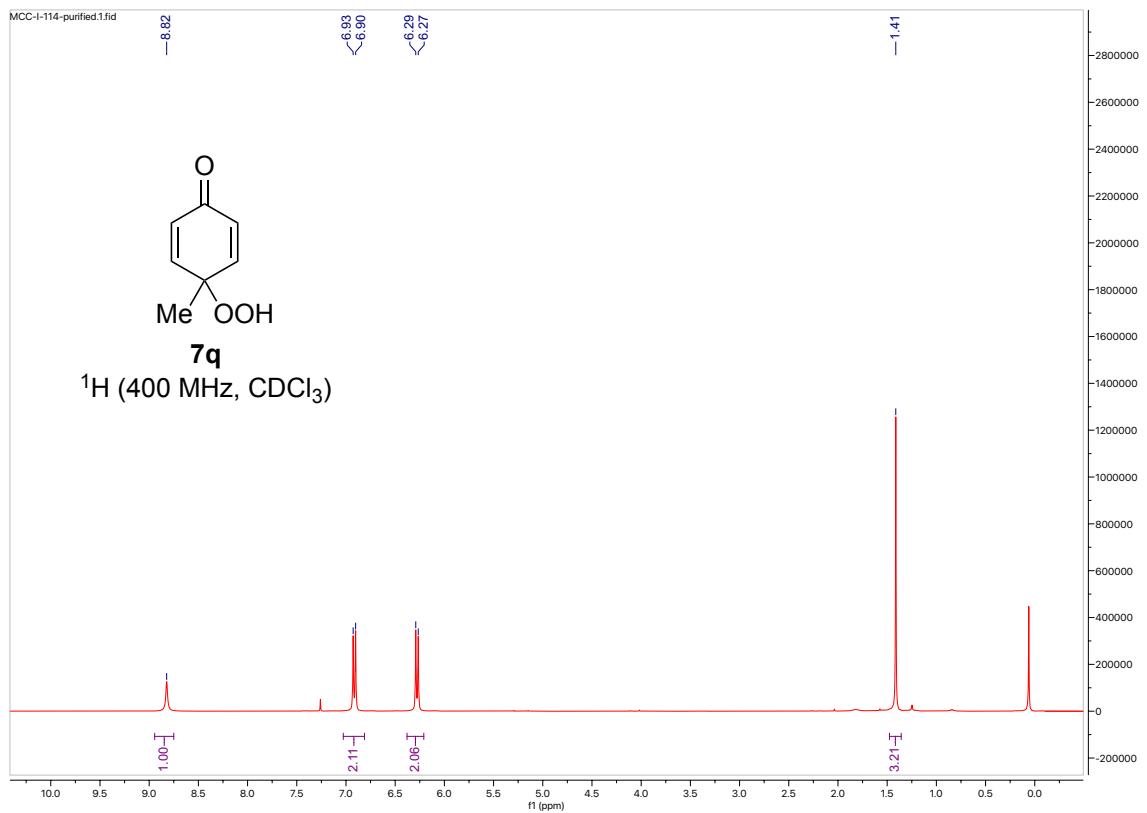


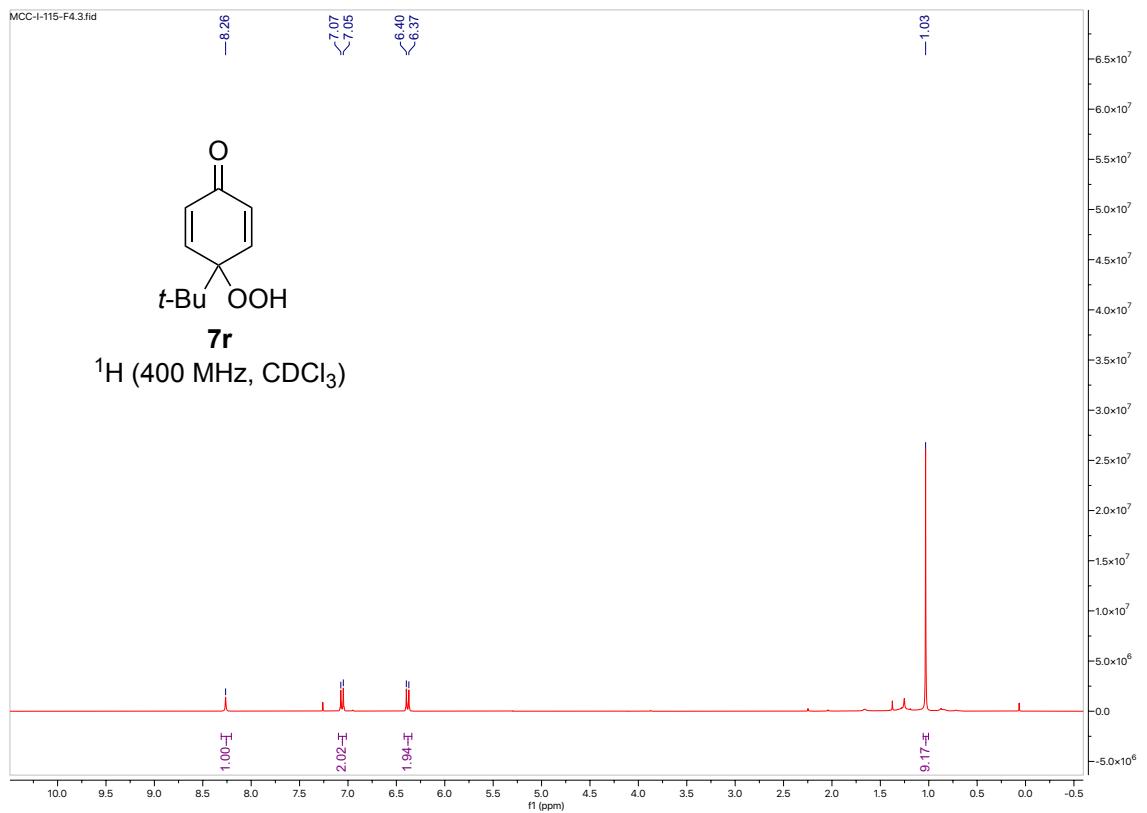


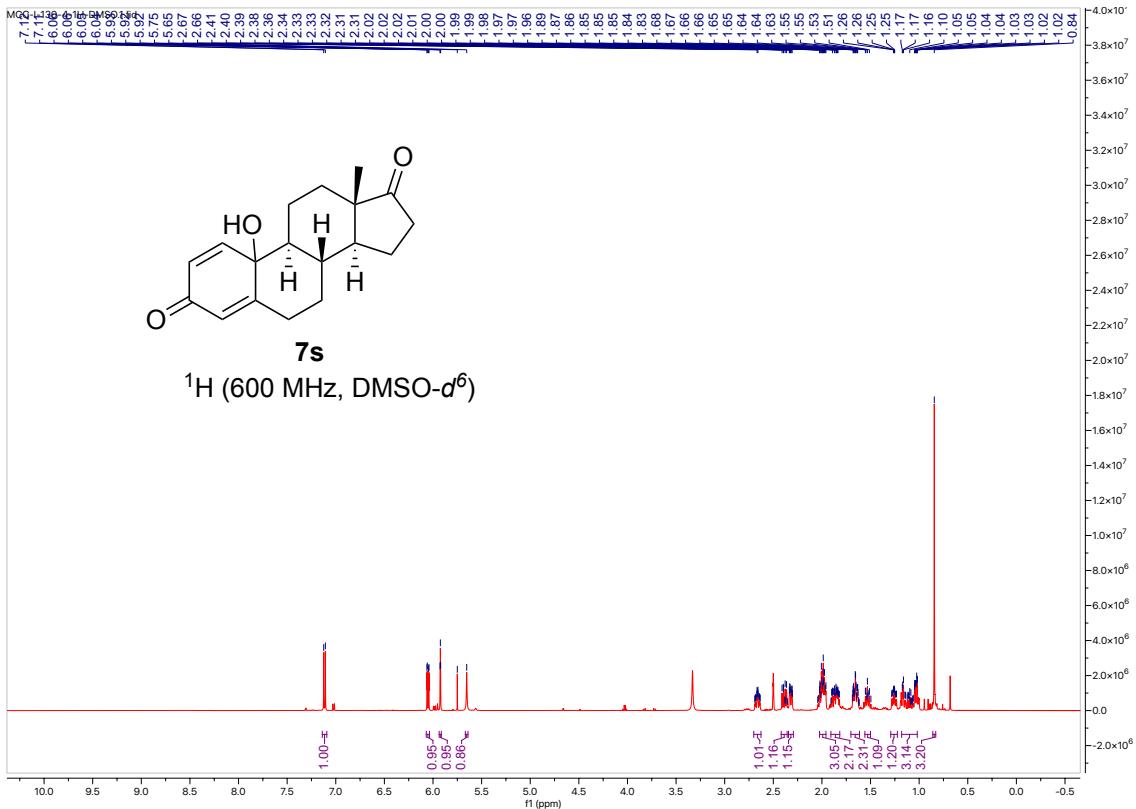


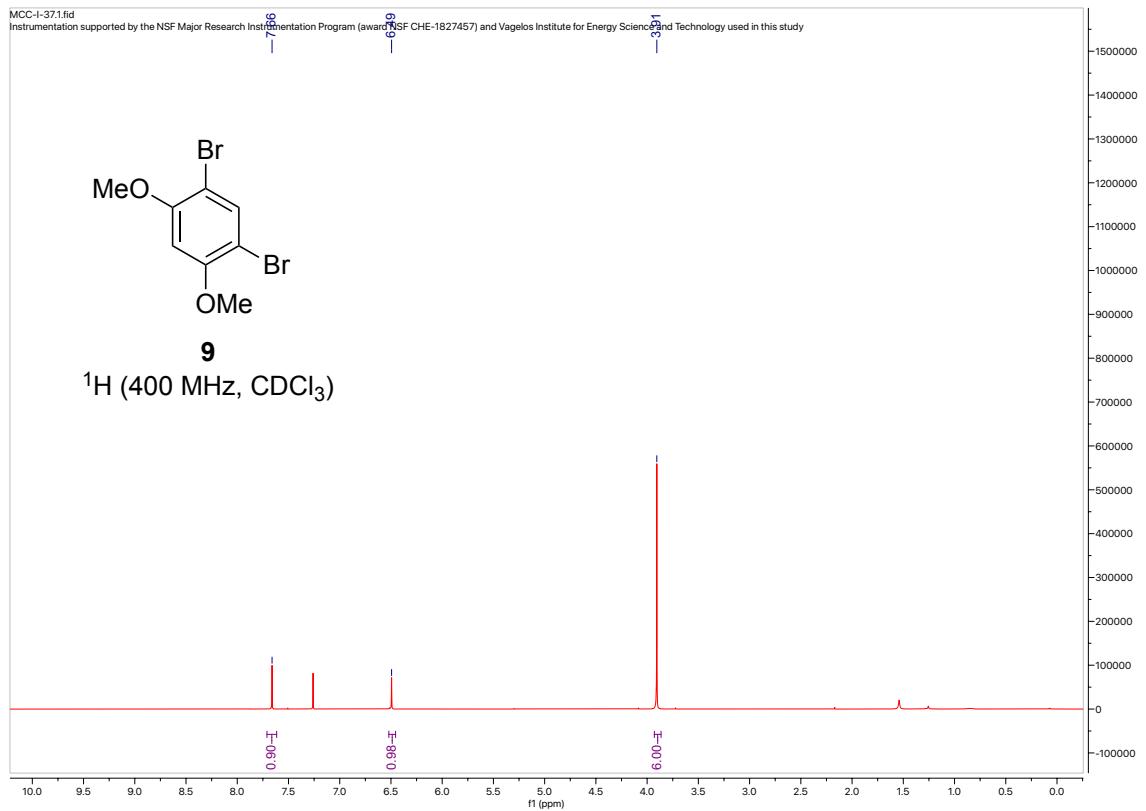


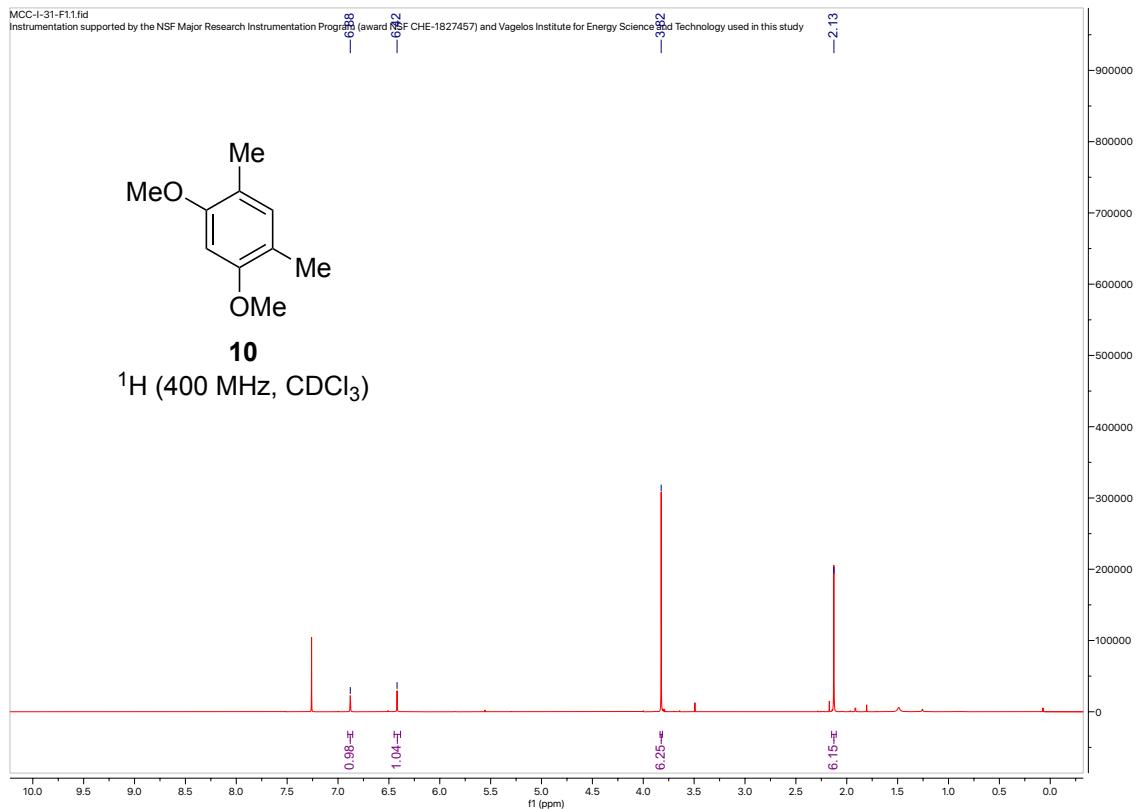


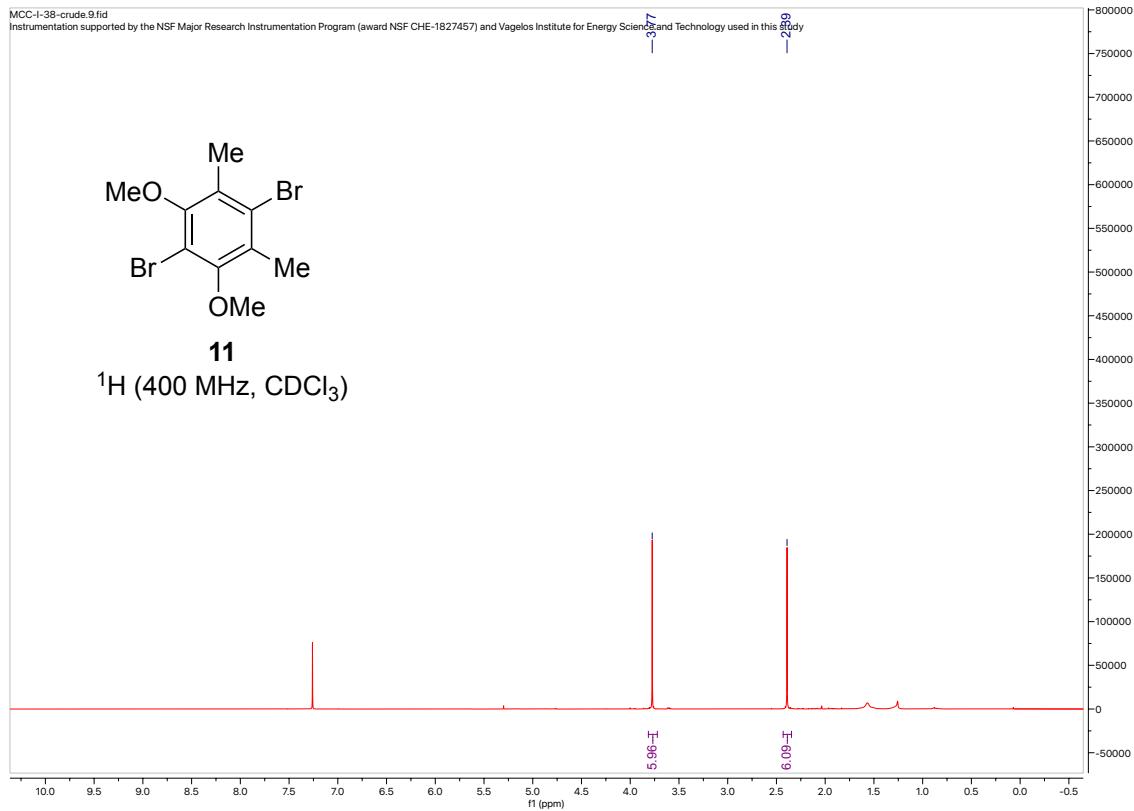


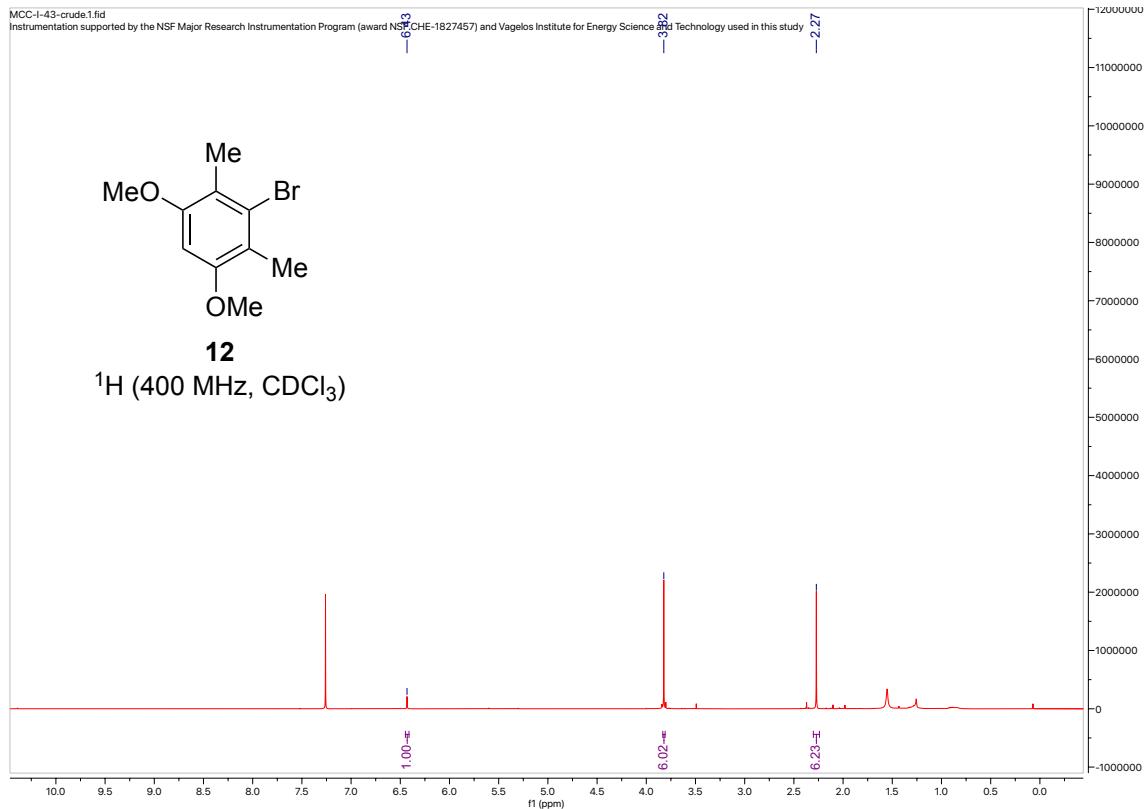


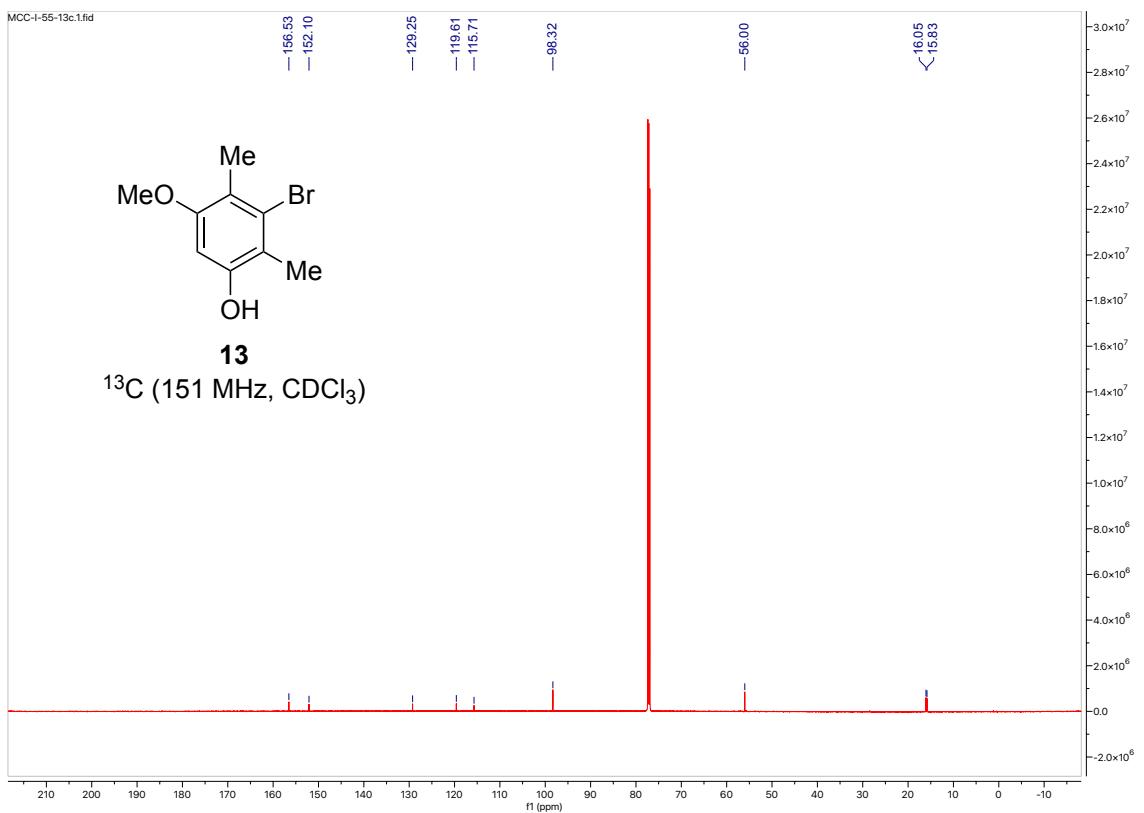
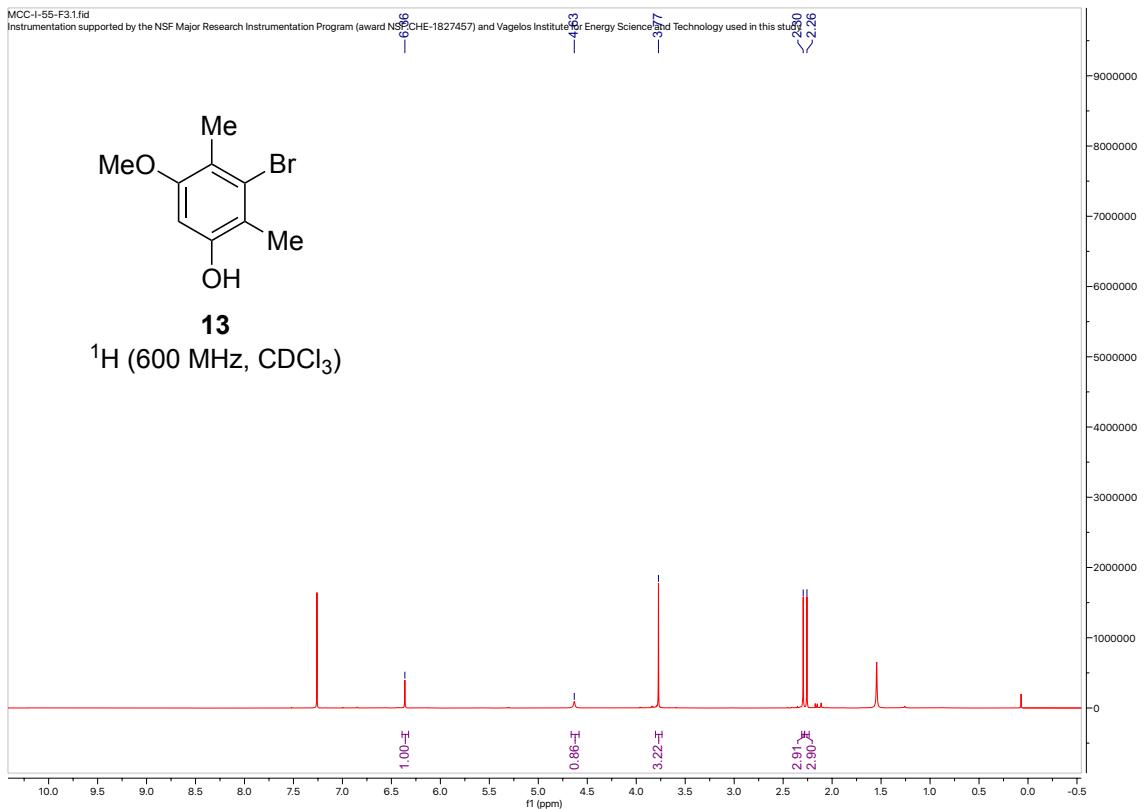


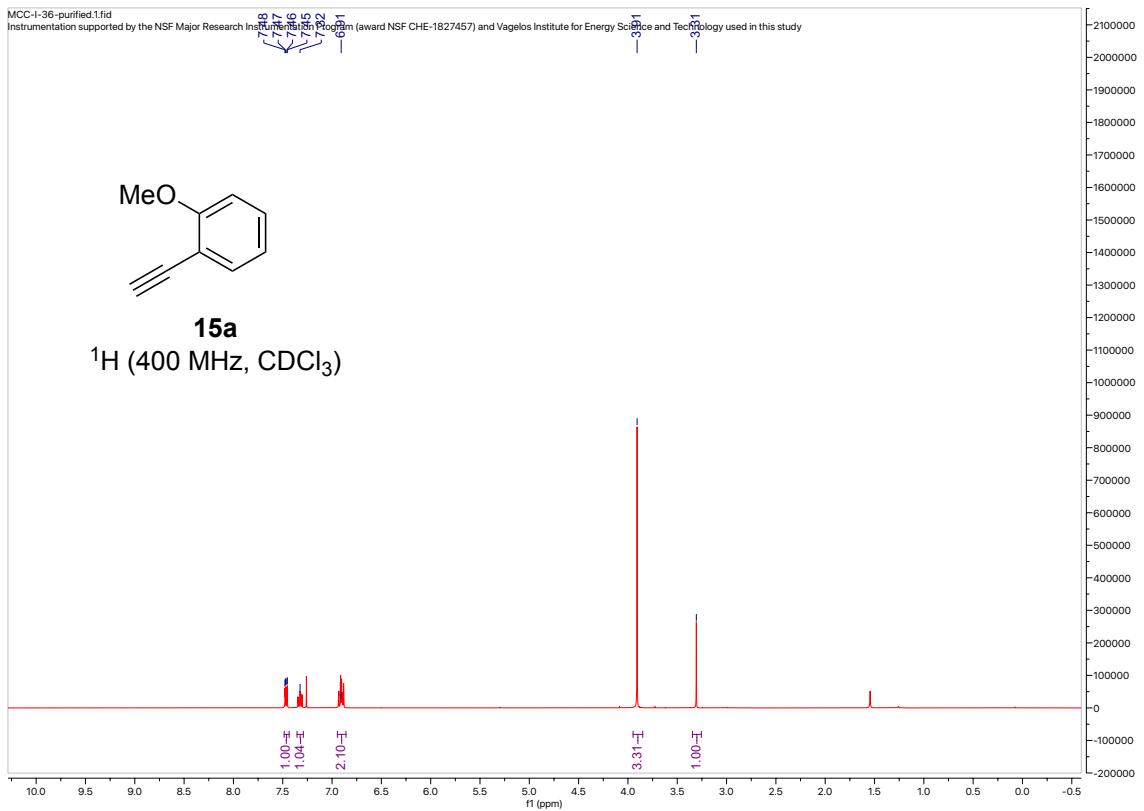


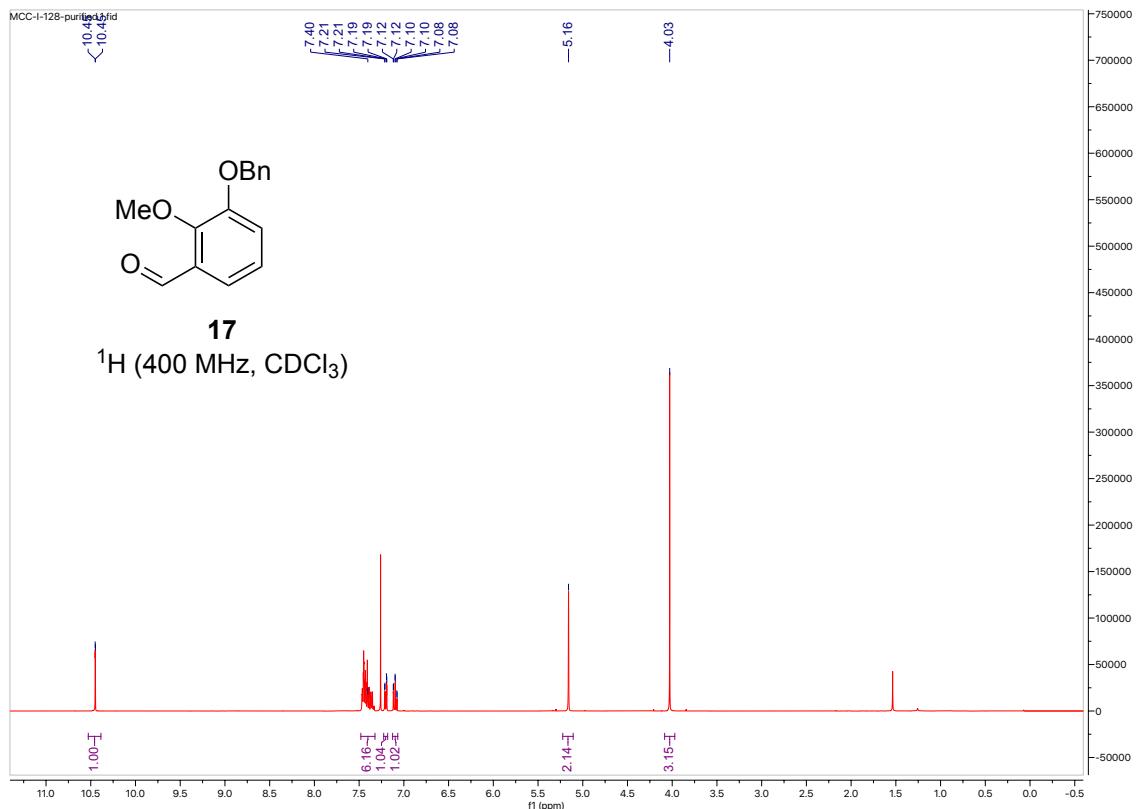


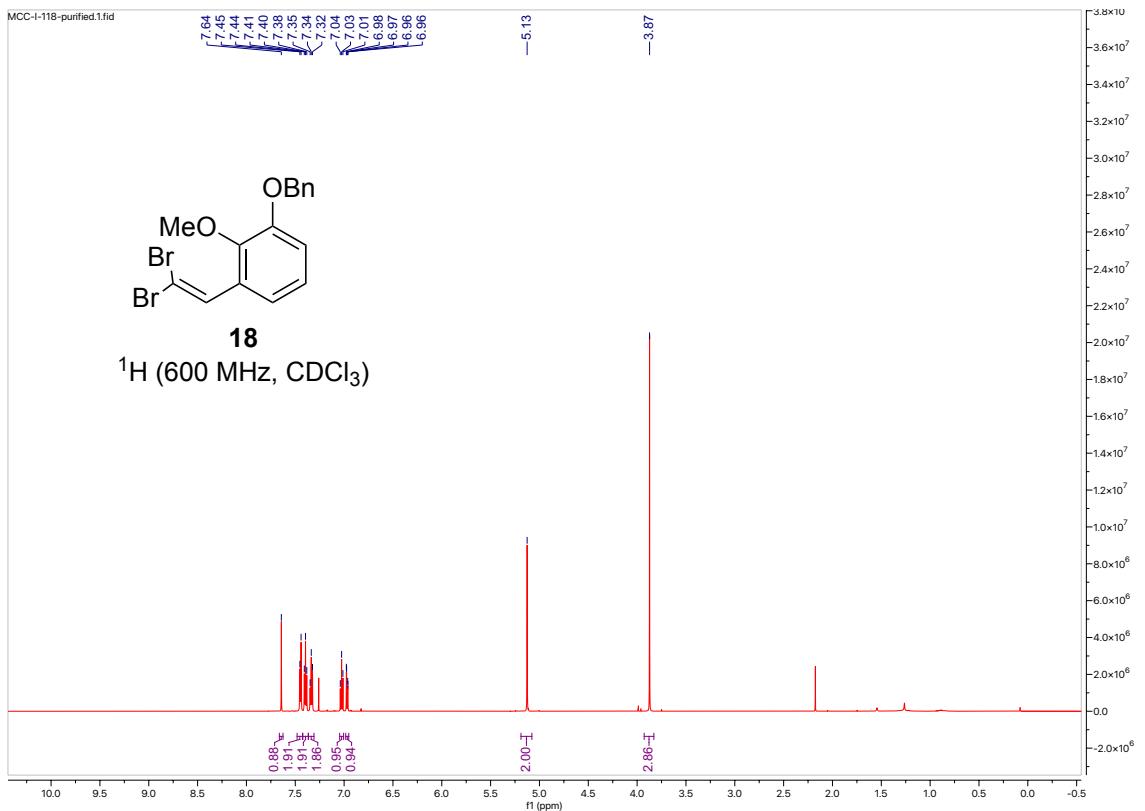


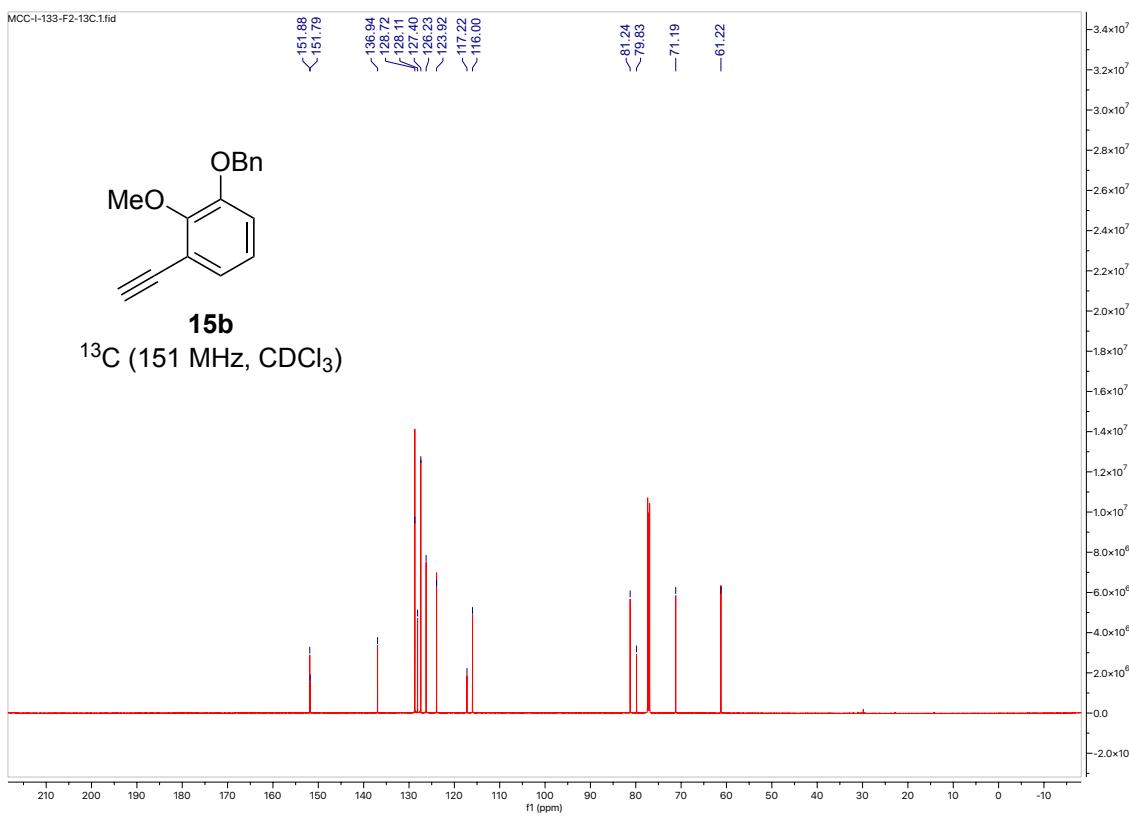
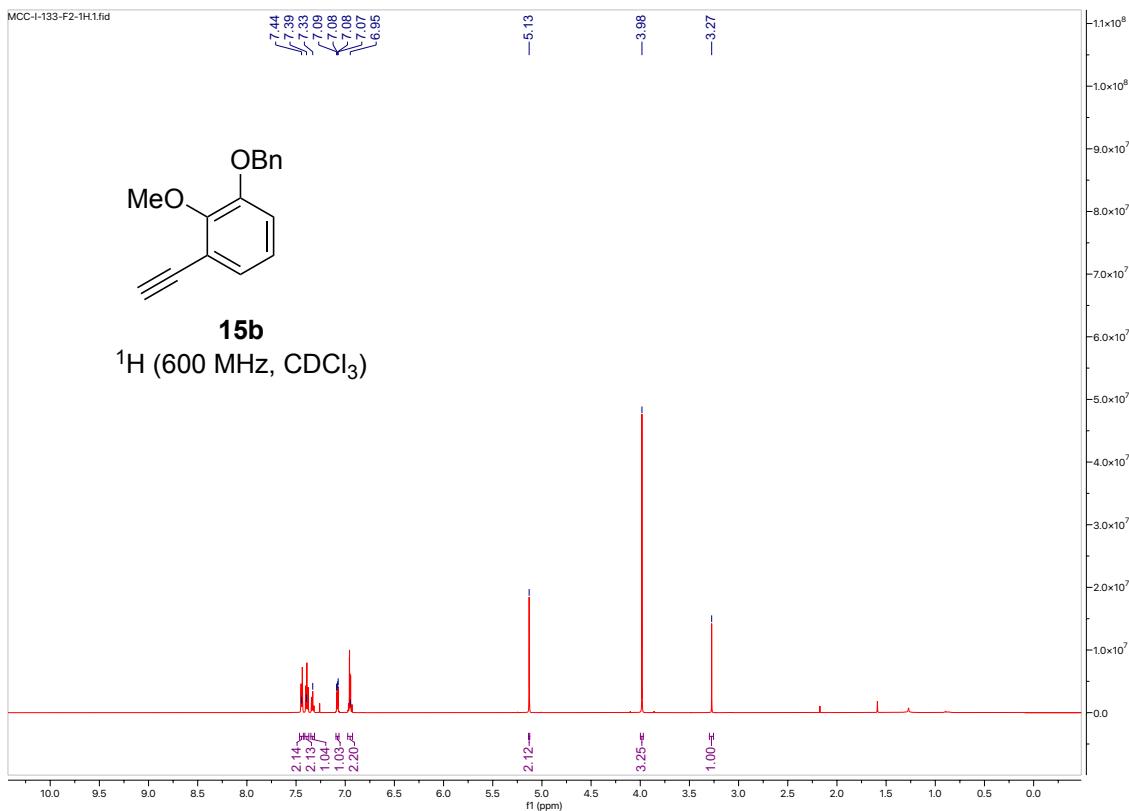


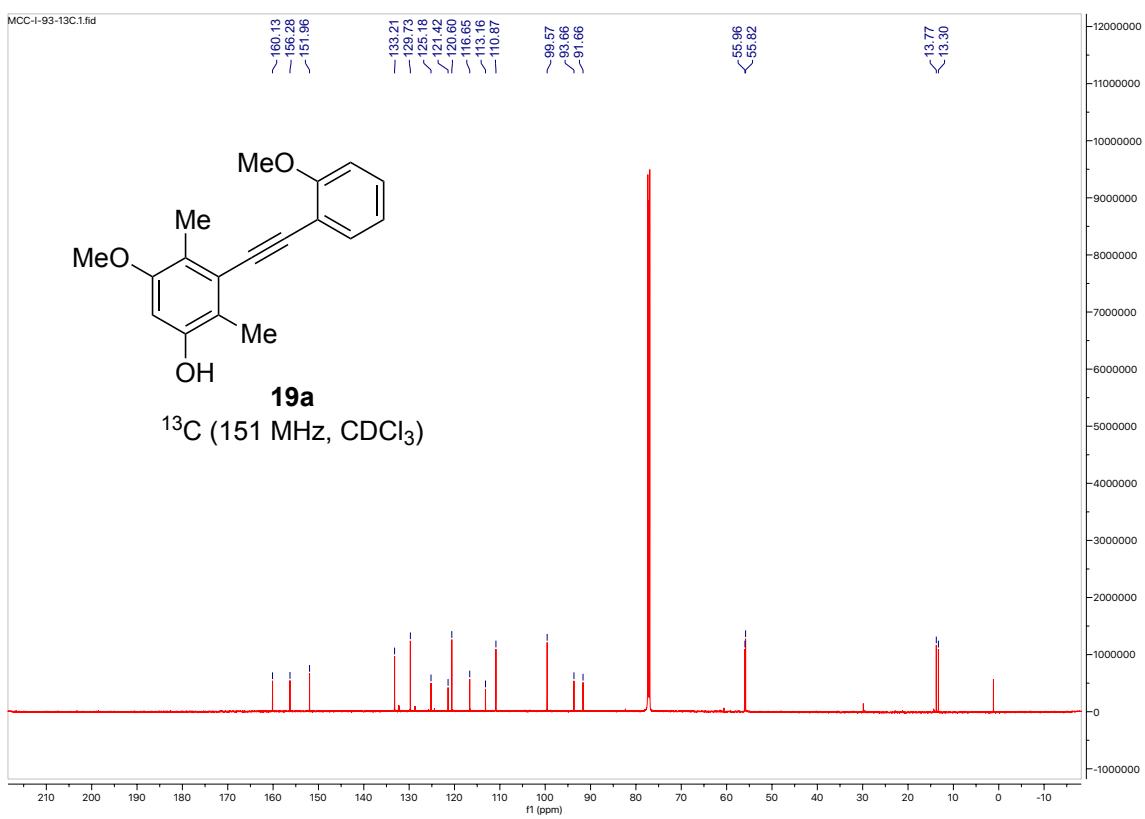
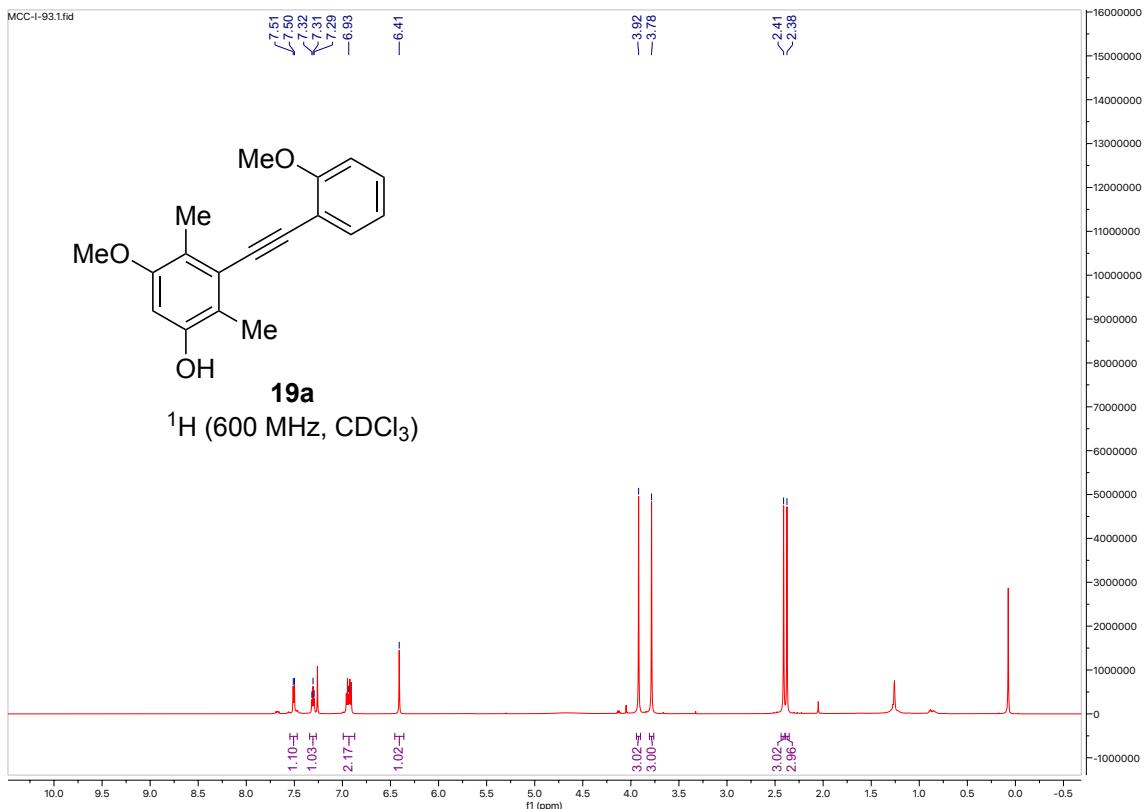


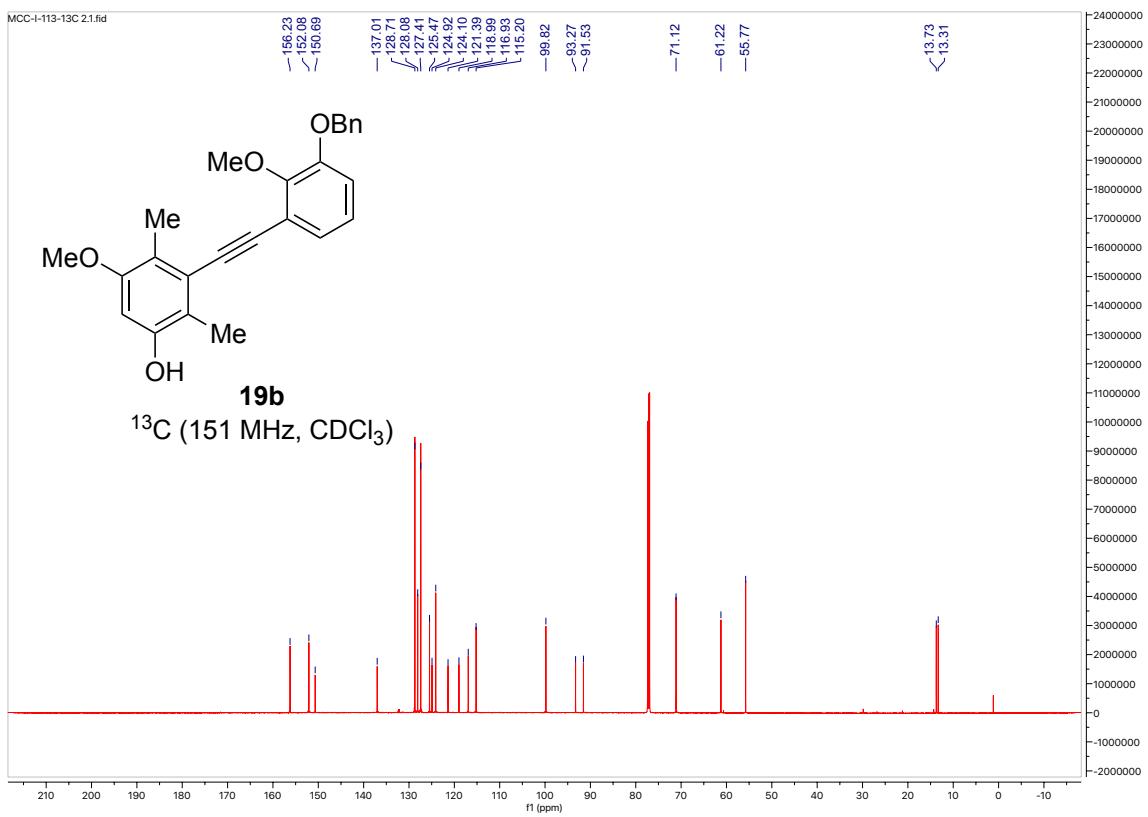
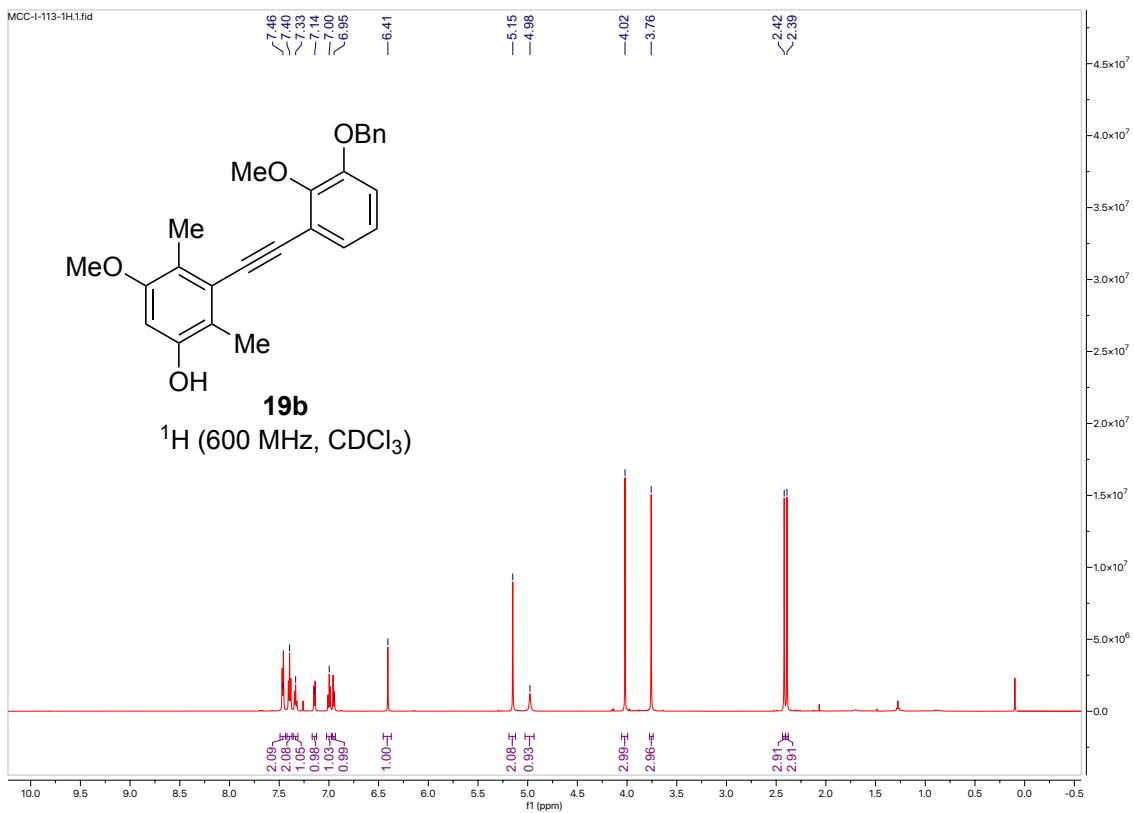


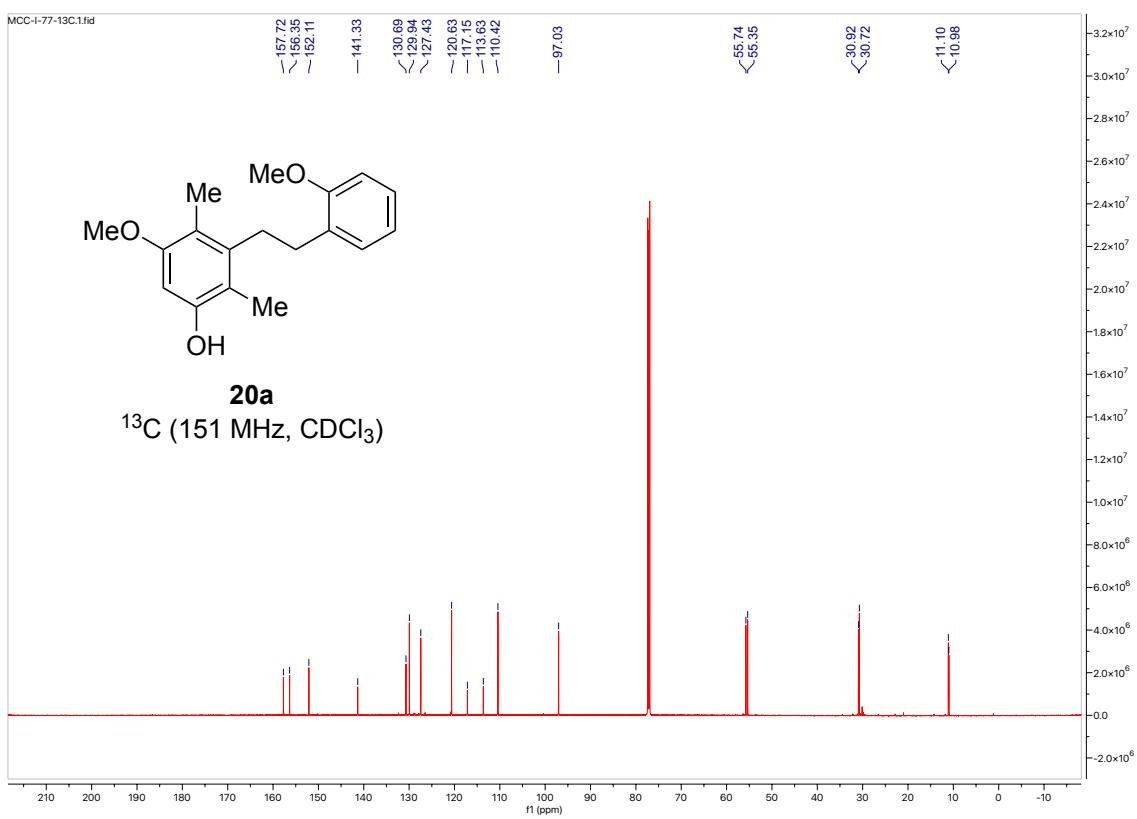
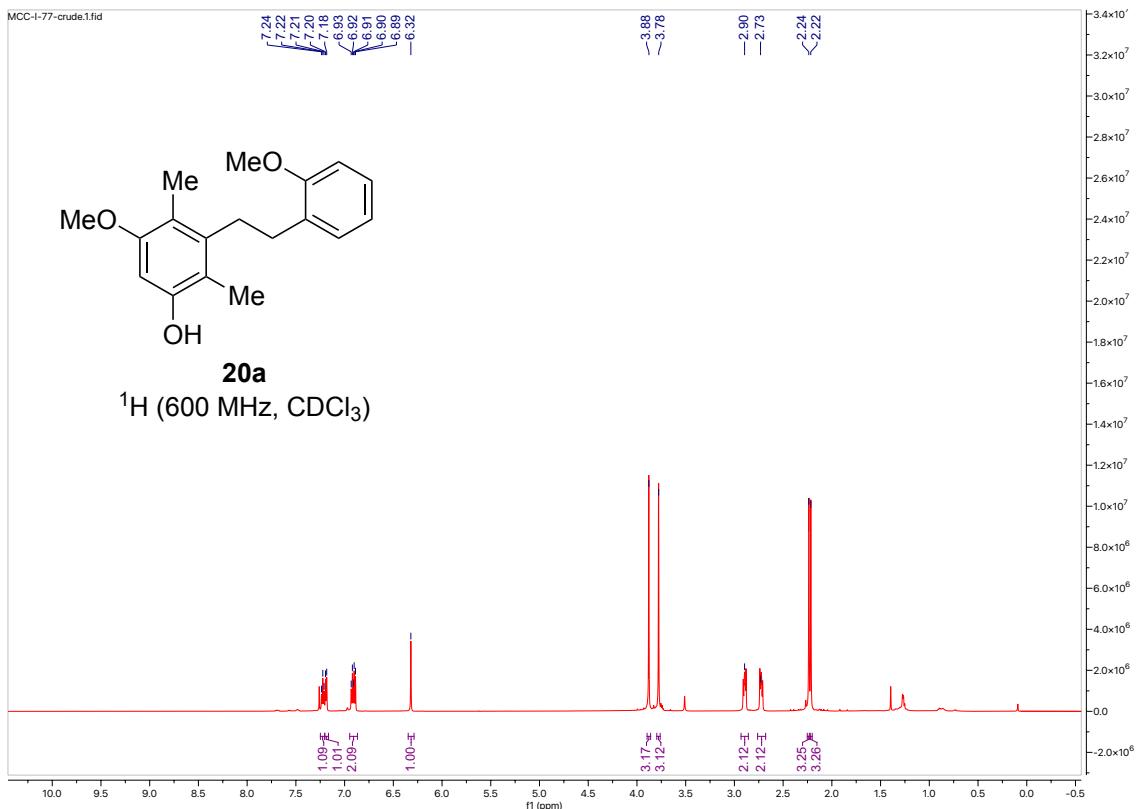


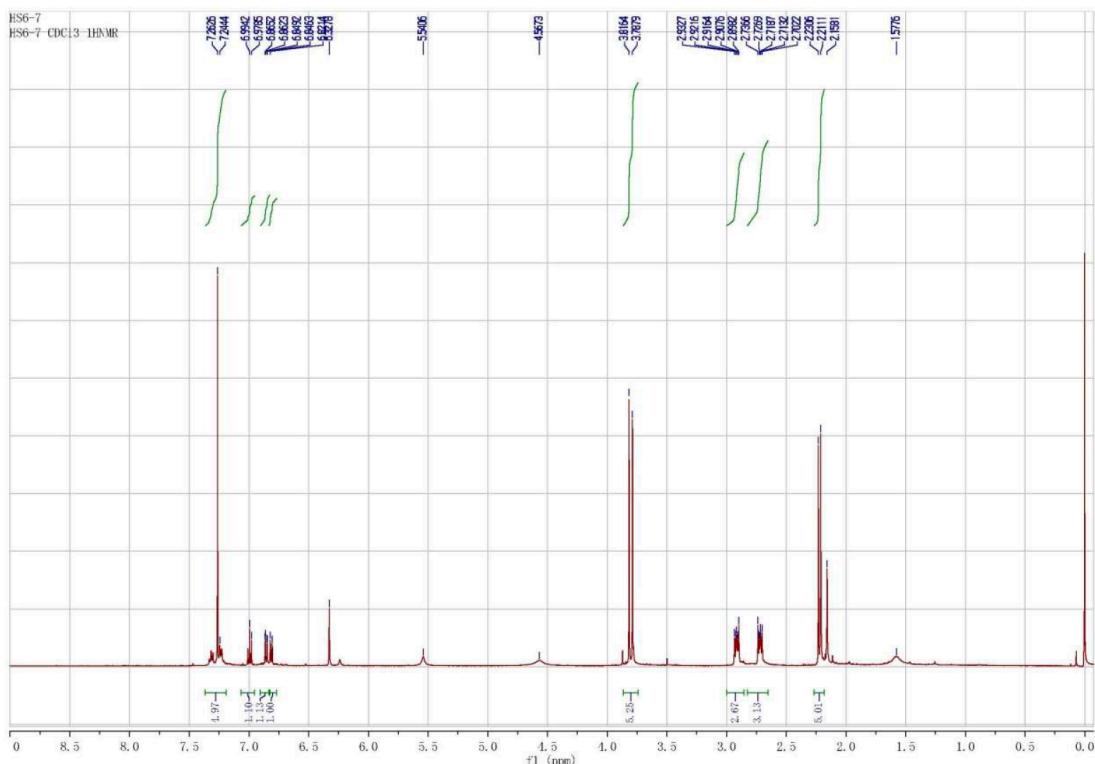
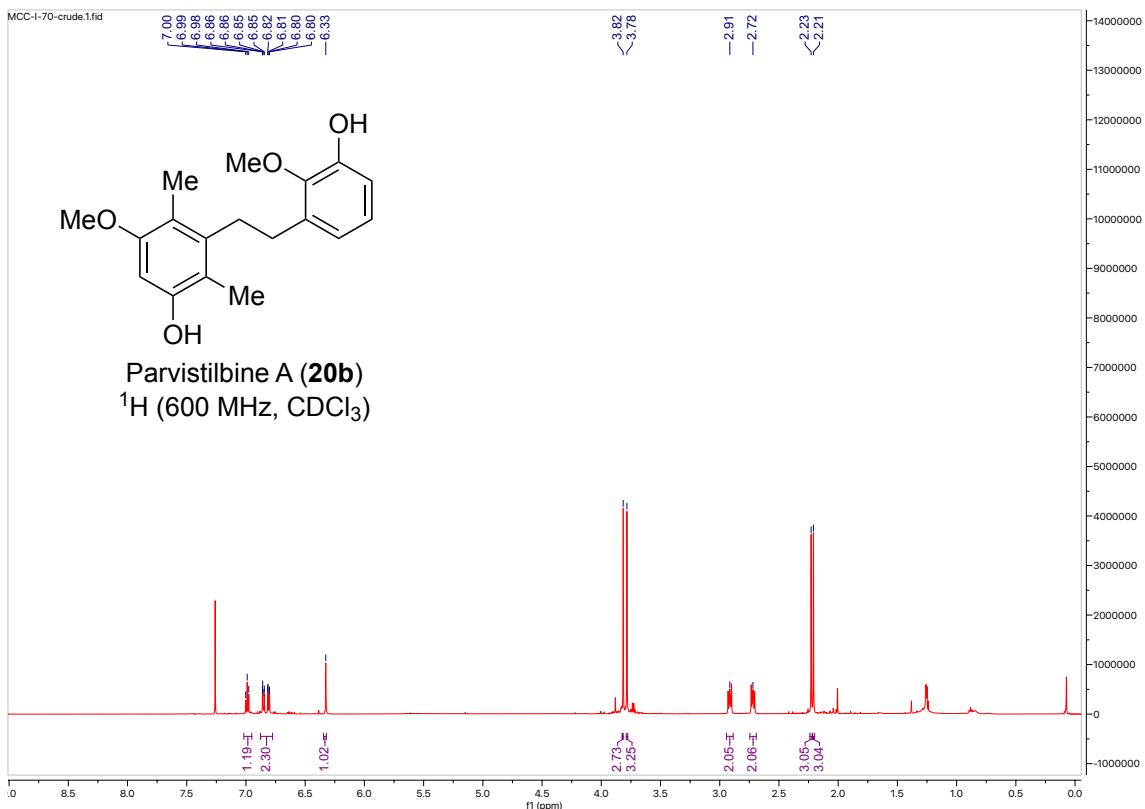




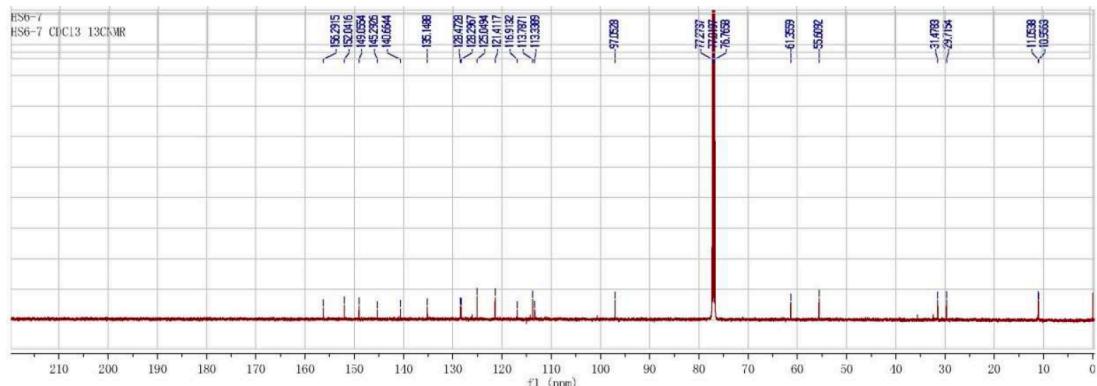
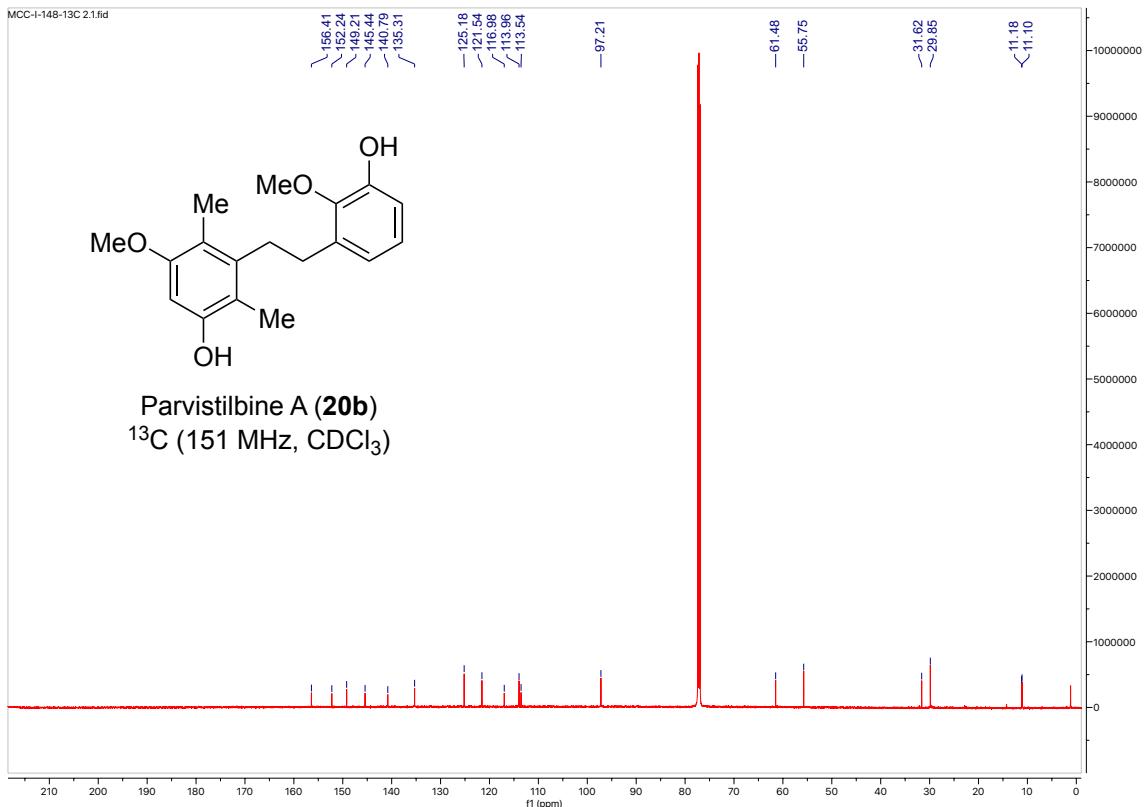




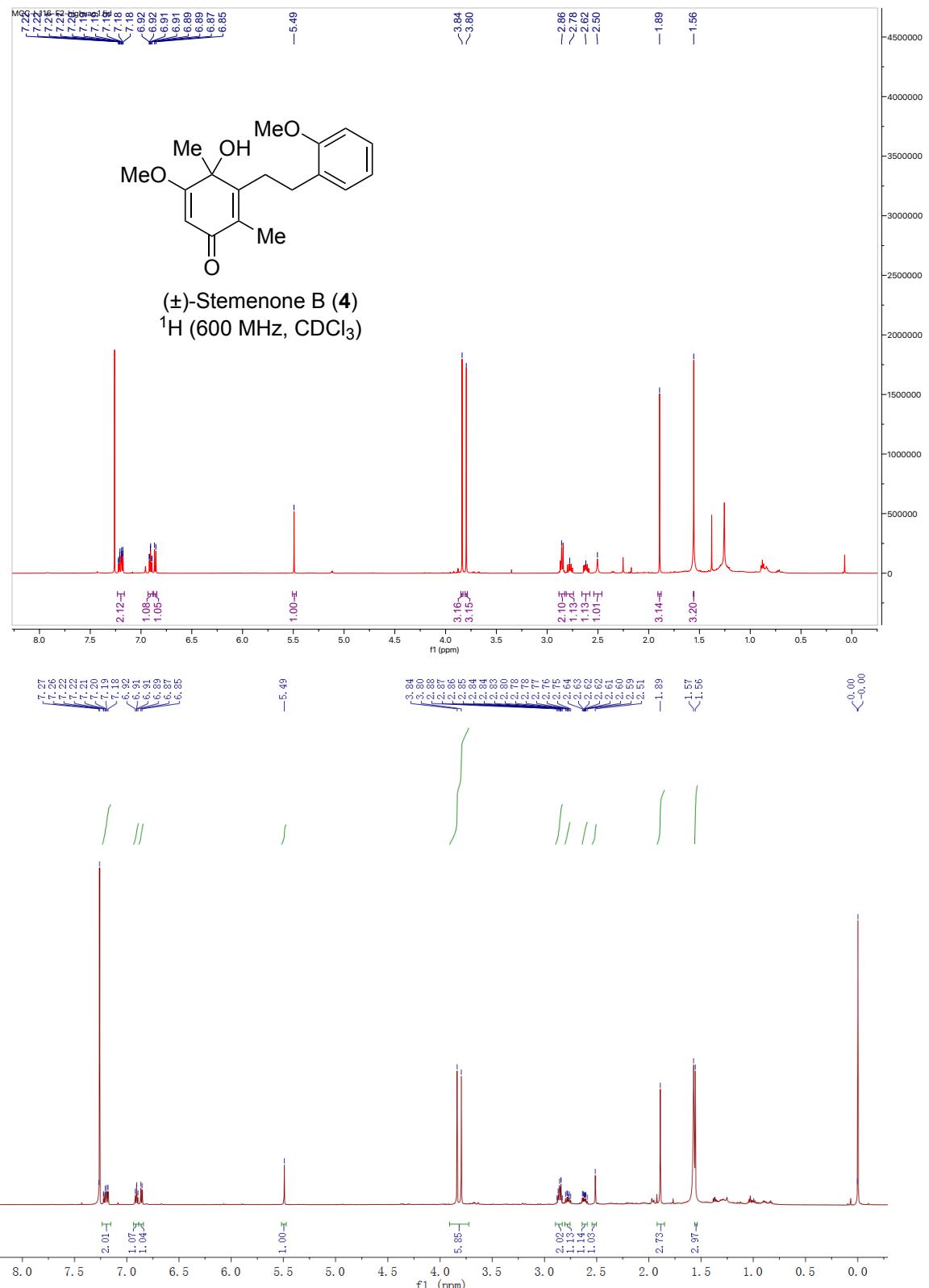




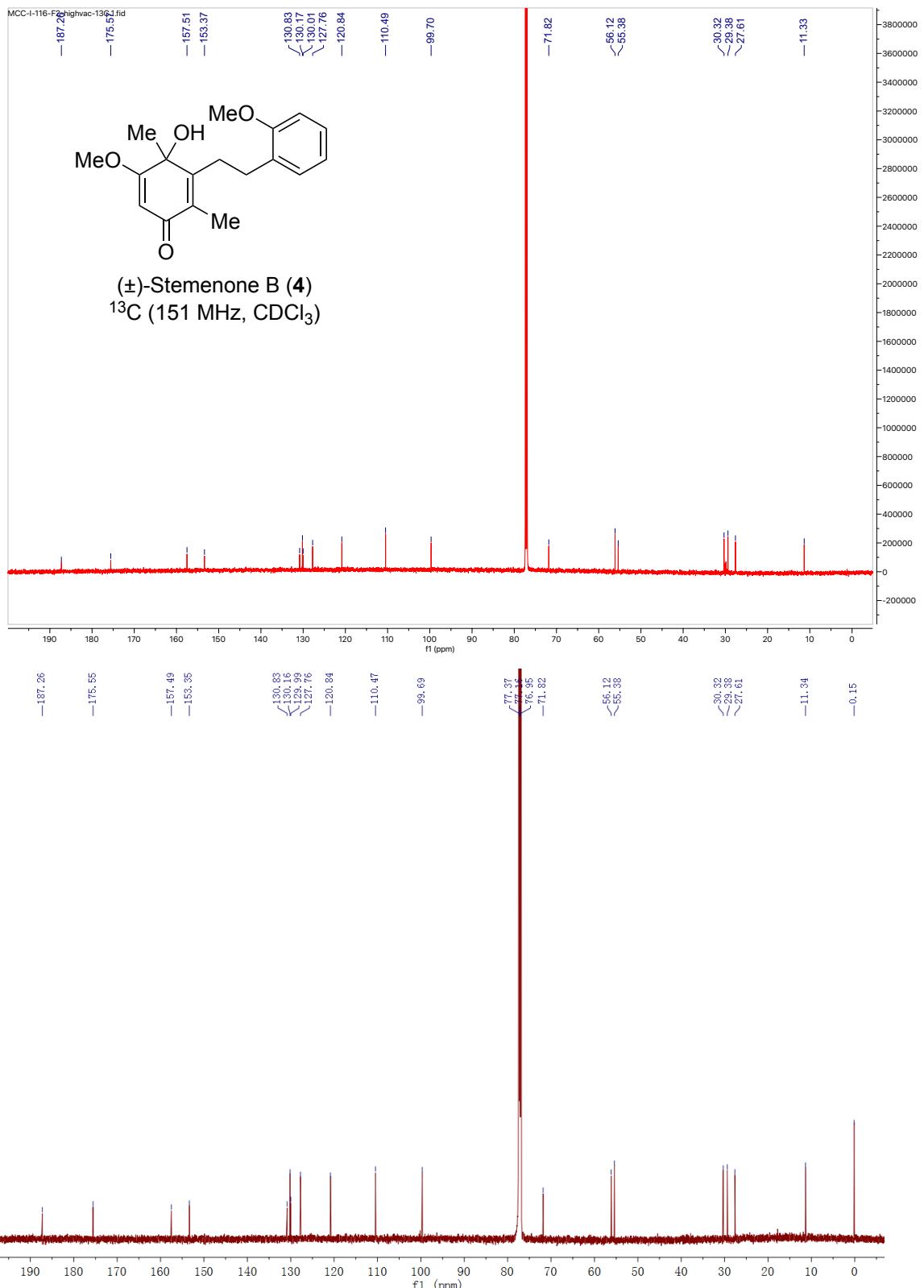
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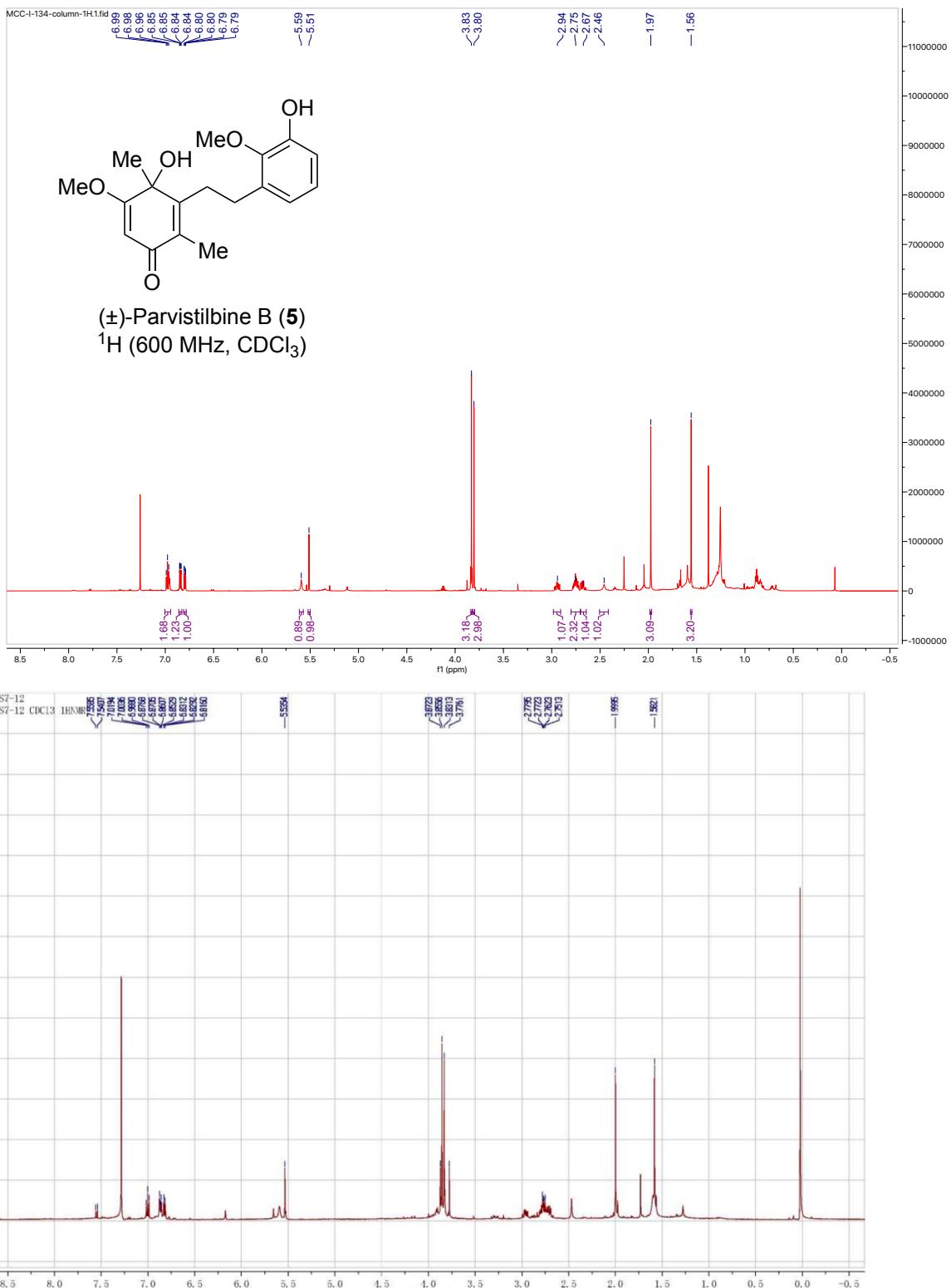


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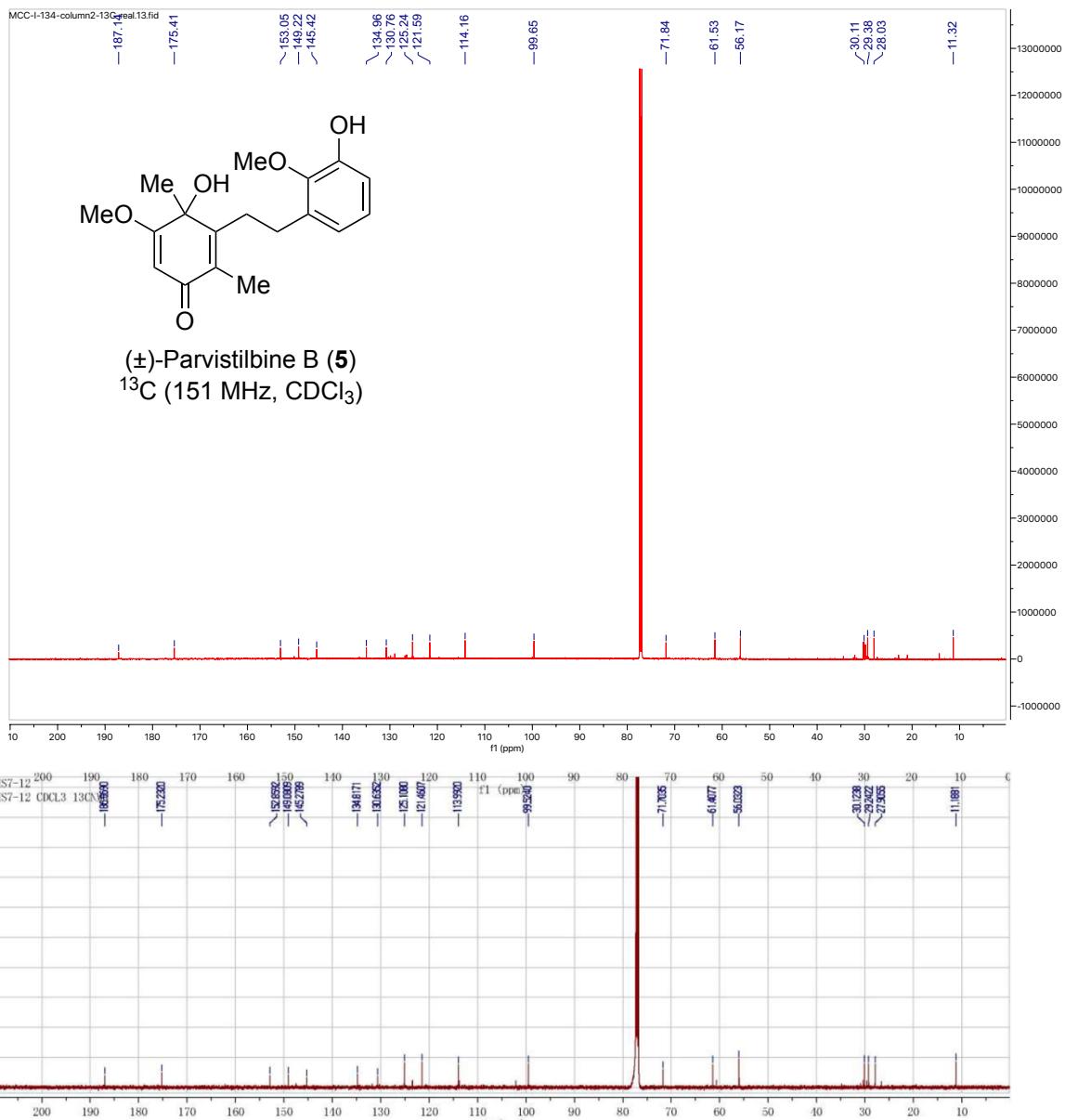


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