

Supporting Information

Regioselective Synthesis of Substituted Cyclopenta[1]phenanthrenes

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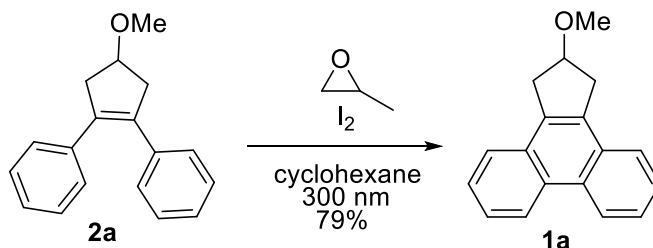
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General Experimental Methods: All reagents were purchased from Acros Organics, TCI America, or Alfa Aesar and were used as received unless otherwise noted. THF was distilled over sodium/benzophenone under argon atmosphere. All reactions were performed under argon atmosphere unless otherwise noted. Photoreactions were performed in a Rayonet RPR 100 photoreactor using 10 RPR300 bulbs in quartz glassware, with stirring and a cold finger (tap water as the cooling source). Column chromatography was performed using silica gel 40- 60 μm (230 x 400 mesh) purchased from Sorbent Technologies. TLC was performed on plastic-backed plates coated with silica gel and a fluorescent indicator (254 nm), purchased from J.T. Baker (IB-F). ^1H and ^{13}C NMR were performed on Varian Gemini 300, Varian Inova 400, Varian Inova 500, Bruker Nanobay 400 or Bruker Avance III (500 MHz), as noted. NMR experiments were performed in CDCl_3 or $(\text{CD}_3)_2\text{SO}$ as noted and were referenced to the residual solvent peak (7.26 ppm and 77.0 ppm for CDCl_3 and 2.50 ppm and 38.5 ppm for $(\text{CD}_3)_2\text{SO}$). Melting points were measured on a Thomas Hoover melting point apparatus. HRMS (EI) were obtained from the University of Illinois SCS Mass Spectroscopy Laboratory. HRMS (ESI) were obtained using an Agilent LC-UV-TOF at the Institute of Chemical Biology and Drug Discovery Analytical Laboratory at Stony Brook University. Compounds 2b and 2e showed no interpretable peaks in MS with either ESI or EI.

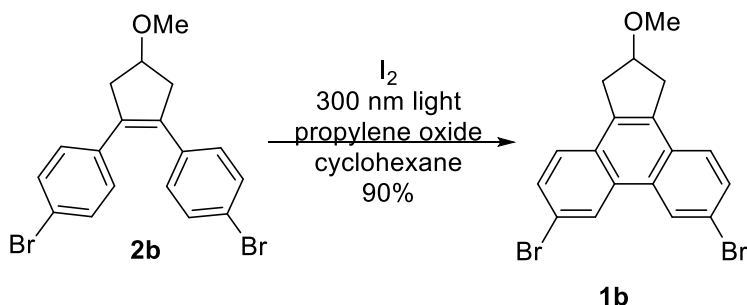
Safety Note: During the photooxidation reactions in the presence of air, cyclohexane reacts to form cyclohexane hydroperoxide. Although cyclohexane hydroperoxide is reported to be relatively stable,¹ we decomposed the hydroperoxide by washing the reaction mixture with 10% aq. sodium bisulfite solution before we concentrated the solutions.

2-Methoxy-2,3-dihydro-1H-cyclopenta[1]phenanthrene (1a)



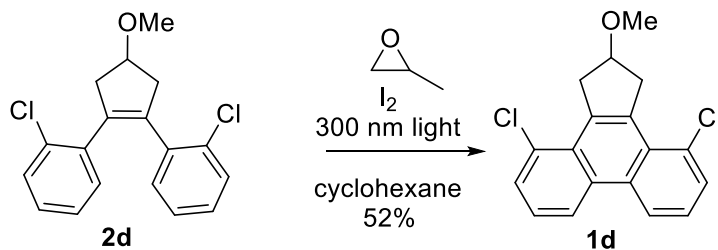
Stilbene **2a** (0.070 g, 0.28 mmol) was dissolved in 100 mL cyclohexane in a quartz photochemical reaction vessel. Iodine (0.071 g, 0.28 mmol) was added, and Ar was bubbled through the solution for 30 min. Propylene oxide (3.9 mL, 56 mmol) was added and the solution was put in the Rayonet photoreactor and irradiated with 300-nm light. After the disappearance of the iodine color (~48 h), the solution was transferred to a flask and the solvent was removed *in vacuo*. The resulting white solid was purified by column chromatography (SiO₂, 19:1 hexanes:ethyl acetate) to give **1a** (0.055 g, 79%) as white crystals. M.p. 131-133 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.68-8.74 (m, 2H), 7.82-7.88 (m, 2H), 7.60-7.66 (m, 4H), 4.52-4.60 (m, 1H), 3.57-3.62 (m, 2H), 3.51 (s, 3H), 3.37-3.41 (m, 2H) ¹³C NMR δ 134.5, 130.2, 129.7, 126.6, 125.7, 124.7, 123.1, 80.8, 56.6. 38.6. HRMS (EI) calculated for C₁₈H₁₆O 248.1201 found 248.1200.

6,9-Dibromo-2-methoxy-2,3-dihydro-1H-cyclopenta[1]phenanthrene (1b)



Stilbene **2b** (0.116 g, 0.32 mmol) was dissolved in 200 mL cyclohexane in a quartz photochemical reaction vessel. Iodine (0.080 g, 0.32 mmol) was added, and Ar was bubbled through the solution for 30 min. Propylene oxide (4.4 mL, 63.4 mmol) was added and the solution was put in the Rayonet, and irradiated with 300-nm light. After the disappearance of the iodine color (~48 h), the solution was transferred to a flask and the solvent was removed *in vacuo*. The resulting white solid was purified by column chromatography (SiO₂, 19:1 hexanes:ethyl acetate) to give **1b** (0.103 g, 90% yield) as orange crystals. M.p. 164-168 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.61(d, *J*=2.0 Hz, 2H), 7.68(dd, *J*= 8.8, 2.0 Hz, 2H), 7.62 (d, *J*= 8.8 Hz, 2H), 4.52 (m, 1H), 3.46-3.52 (m, 5H), 3.28-3.33 (m, 2H). ¹³C NMR (CDCl₃) δ 134.9, 130.6, 130.3, 128.5, 126.4, 125.9, 120.2, 80.6, 56.7, 38.6. HRMS (EI) calcd. for C₁₈H₁₄OBr₂ 403.9412 found 403.9409.

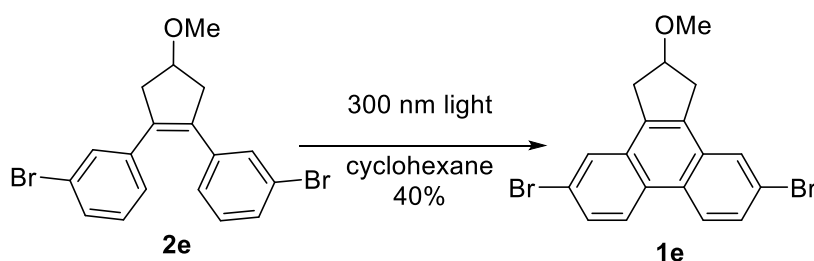
4,11-Dichloro-2-methoxy-2,3-dihydro-1H-cyclopenta[1]phenanthrene (1d)



Stilbene **2d** (0.400 g, 1.3 mmol) was dissolved in 500 mL cyclohexane in a quartz photochemical reaction vessel. Iodine (0.320 g, 1.3 mmol) was added, and Ar was bubbled through the solution

for 30 min. Propylene oxide (18 mL, 250 mmol) was added and the solution was put in the Rayonet and irradiated with 300-nm light. After the disappearance of the iodine color (~48 h), the solution was transferred to a flask and the solvent was removed *in vacuo*. The resulting white solid was purified by column chromatography (SiO₂, 19:1 hexanes:ethyl acetate) to give **1d** (0.210 g, 52% yield) as yellow crystals. M.p. 123-126 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.47 (d, *J*=8.8 Hz, 2H), 7.59-7.62 (m, 2H), 7.40 (t, *J*=8.0 Hz, 2H), 4.21-4.26 (m, 1H), 3.88-3.90 (m, 4H), 3.42 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 42.7, 56.3, 80.2, 122.6, 126.0, 128.3, 129.9, 131.6, 132.9, 136.2. HRMS (EI) expected 316.0422 found 316.0417.

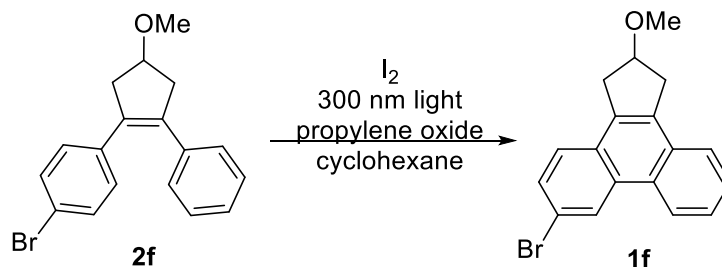
5,10-Dibromo-2-methoxy-2,3-dihydro-1H-cyclopenta[1]phenanthrene (**1e**)



Stilbene **2e** (0.055 g, 0.13 mmol) was dissolved in 135 mL cyclohexane in a quartz photochemical reaction vessel open to the air and the vessel was put in the Rayonet and irradiated with 300-nm bulbs. The reaction was monitored by removing aliquots, concentrating them *in vacuo* and subjecting them to proton NMR analysis. When the starting material had been consumed the solution was transferred to a flask and the solvent was removed *in vacuo*. The resulting yellow solid was purified by column chromatography (SiO₂, 19:1 hexanes:ethyl acetate) to give **1e** (0.021 g, 40% yield) as yellow crystals. M.p. 171-173 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.40 (d, *J*=8.9 Hz, 2H), 7.92 (d, *J*=1.8 Hz, 2H), 7.67 (dd, *J*= 8.9, 1.8 Hz, 2H), 4.50-4.53 (m, 1H), 3.48-3.53 (m, 2H), 3.48 (s, 3H), 3.30-3.34 (m, 2H). ¹³C NMR (125 MHz,

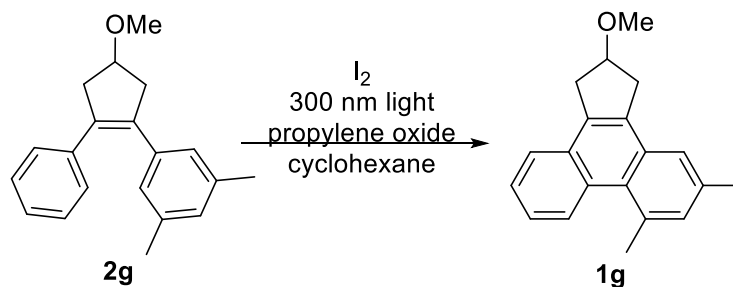
CDCl₃) δ 135.2, 131.0, 129.1, 128.4, 127.3, 124.7, 121.2, 80.4, 56.7, 38.6. HRMS (EI) calcd. for C₁₈H₁₄OBr₂ 403.9411 found 403.9408.

6-Bromo-2-methoxy-2,3-dihydro-1H-cyclopenta[*l*]phenanthrene (**1f**)



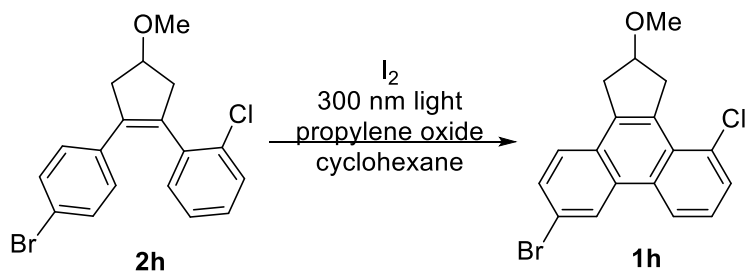
Stilbene **2f** (0.026 g, 0.07 mmol) was dissolved in 100 mL cyclohexane in a quartz photochemical reaction vessel. Iodine (0.018 g, 0.07 mmol) was added, and Ar was bubbled through the solution for 30 min. Propylene oxide (1.0 mL, 14 mmol) was added and the solution was put in the Rayonet and irradiated with 300-nm light. After the disappearance of the iodine color (~48 h), the solution was transferred to a flask and the solvent was removed *in vacuo*. The resulting yellow solid was purified by column chromatography (SiO₂, 19:1 hexanes:ethyl acetate) to give **1f** (0.020 g, 77% yield) as a yellow solid. M.p. 108-112 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.80 (s, 1H), 8.58-8.60 (m, 1H), 7.82-7.84 (m, 1H), 7.68 (m, 2H), 7.61-7.65 (m, 2H), 4.53-4.57 (m, 1H), 3.55-3.60 (m, 2H), 3.49 (s, 3H), 3.34-3.39 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 135.3, 134.2, 131.8, 130.0, 129.7, 129.2, 128.3, 127.3, 126.4, 126.07, 126.00, 124.9, 123.2, 120.0, 80.7, 56.7, 38.65, 38.58. HRMS (EI) calcd. for C₁₈H₁₅OBr 326.0306 found 326.0301.

2-Methoxy-5,7-dimethyl-2,3-dihydro-1H-cyclopenta[1]phenanthrene (**1g**)



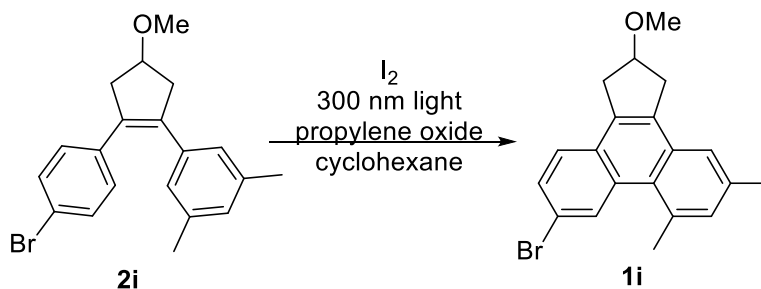
Stilbene **2g** (0.047 g, 0.17 mmol) was dissolved in 100 mL cyclohexane in a quartz photochemical reaction vessel. Iodine (0.043 g, 0.17 mmol) was added, and Ar was bubbled through the solution for 30 min. Propylene oxide (2.4 mL, 33.8 mmol) was added and the flask was placed in the Rayonet photoreactor and irradiated with 300-nm light. After the disappearance of the iodine color (~12 h), the solution was transferred to a flask and the solvent was removed *in vacuo*. The resulting brown solid was purified by column chromatography (SiO₂, 99:1 hexanes:ethyl acetate) to give **1g** (0.036 g, 76% yield) as a pale yellow solid. M.p. 74-77 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.87 (d, J= 8.5 Hz, 1H), 7.85-7.87 (m, 1H), 7.56-7.62 (m, 2 H), 7.53 (s, 1H), 7.32 (s, 1H), 4.53-4.57 (m, 1H), 3.57-3.64 (m, 2H), 3.51 (s, 3H), 3.35-3.40 (m, 2H), 3.12 (s, 3H), 2.55 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 136.3, 135.65, 135.63, 134.0, 133.0, 132.6, 131.7, 130.2, 129.1, 128.4, 126.9, 126.1, 123.2, 118.7, 80.5, 56.6, 39.2, 38.7, 27.2, 21.3. HRMS (EI) calcd. for C₂₀H₂₀O 276.1514 found 276.1513.

9-Bromo-4-chloro-2-methoxy-2,3-dihydro-1H-cyclopenta[1]phenanthrene (**1h**)



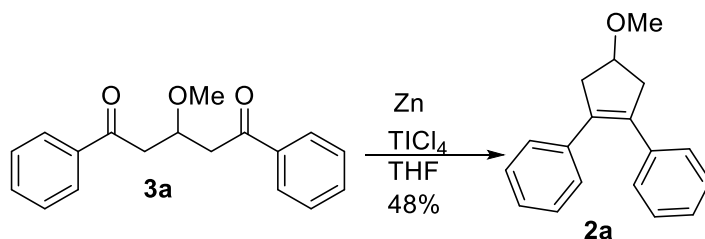
Stilbene **2h** (0.037 g, 0.10 mmol) was dissolved in 100 mL cyclohexane in a quartz photochemical reaction vessel. Iodine (0.026 g, 0.10 mmol) was added, and Ar was bubbled through the solution for 30 min. Propylene oxide (1.4 mL, 20 mmol) was added and the solution was placed in the Rayonet photoreactor and irradiated with 300-nm light. After the disappearance of the iodine color (~12 h), the solution was transferred to a flask and the solvent was removed *in vacuo*. The resulting brown solid was purified by column chromatography (SiO₂, 99:1 hexanes:ethyl acetate) to give **1h** (0.015 g, 42% yield) as pale yellow crystals. M.p. 157-159 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.74 (s, 1H), 8.52 (d, J= 8 Hz, 1H), 7.68-7.72 (m, 2H), 7.64 (dd, J= 7.6 Hz, 2H, 1H), 7.46 (t, J= 8 Hz), 4.39-4.43 (m, 1H), 4.04-4.10 (m, 1H), 3.94-4.00 (m, 1 H), 3.43-3.50 (m, 4H), 3.30-3.35 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 137.3, 134.0, 131.94, 131.87, 131.6, 130.4, 129.9, 128.5, 128.2, 126.4, 126.3, 125.8, 122.3, 120.6, 80.2, 56.5, 44.0, 37.8. HRMS (EI) calcd. for C₁₈H₁₄BrClO 359.9917 found 359.9915.

9-Bromo-2-methoxy-5,7-dimethyl-2,3-dihydro-1H-cyclopenta[1]phenanthrene (**1i**)



Stilbene **2i** (0.034 g, 0.09 mmol) was dissolved in 50 mL cyclohexane in a quartz photochemical reaction vessel. Iodine (0.024 g, 0.09 mmol) was added, and Ar was bubbled through the solution for 30 min. Propylene oxide (1.33 mL, 19 mmol) was added and the solution was placed in the Rayonet photoreactor and irradiated with 300-nm light. After the disappearance of the iodine color (~8 h), the solution was transferred to a flask and the solvent was removed *in vacuo*. The resulting brown solid was purified by column chromatography (SiO₂, 99:1 hexanes:ethyl acetate) to give **1i** (0.028 g, 83% yield) as a colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 8.98 (s, 1H), 7.65-7.69 (m, 2H), 7.50 (s, 1H), 7.31 (s, 1H), 4.50-4.54 (m, 1H), 3.51-3.57 (m, 2H), 3.49 (s, 3H), 3.31-3.35 (m, 2H), 3.07 (s, 3H), 2.54 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 136.3, 135.65, 135.63, 134.0, 133.0, 132.6, 131.7, 130.2, 129.1, 128.4, 126.9, 126.1, 123.2, 118.7, 80.5, 56.6, 39.2, 38.7, 27.2, 21.3. HRMS (EI) calcd. for C₂₀H₁₉OBr 354.0619 found 354.0615.

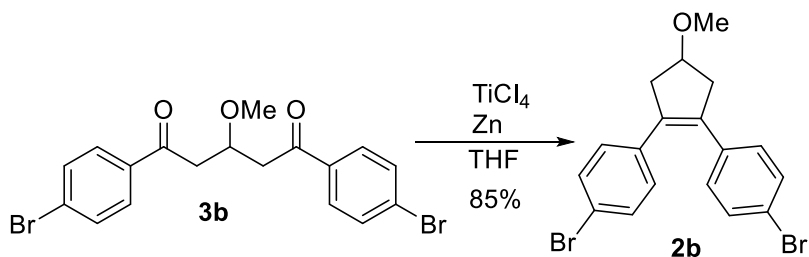
4-Methoxy-1,2-diphenylcyclopent-1-ene (**2a**)



In a flame-dried flask, dry THF (10 mL) was added to zinc dust (0.339 g, 5.22 mmol). The flask was cooled in an ice bath, and titanium tetrachloride (0.29 mL, 2.61 mmol) was added dropwise.

A yellow cloud formed and the solution became dark blue. After 15 min, a solution of **3a** (0.184 g, 0.65 mmol) in THF (2 mL) was added to the reaction mixture. The reaction mixture was then heated to reflux for 3 h. After cooling the reaction to ambient temperature, 10 mL water was added and gas evolution was seen. After the bubbling subsided, the mixture was extracted with ethyl acetate (3 x 35 mL). The organic layers were combined, dried over MgSO₄, filtered and the solvent was removed *in vacuo*. The resulting brown oil was purified by column chromatography (SiO₂, 9:1 hexanes:ethyl acetate) to give **2a** (0.078 g, 48 % yield) as a yellow oil. ¹H NMR (300 MHz, CDCl₃) δ 7.22-7.30 (m, 10 H), 4.27-4.31 (m, 1 H), 3.47 (s, 3 H), 3.22-3.26 (m, 2 H), 3.01-3.05 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 137.7, 134.7, 128.11, 128.02, 126.7, 78.5, 56.3, 44.9. HRMS (EI) calculated for C₁₈H₁₈O 250.1358 found 250.1356.

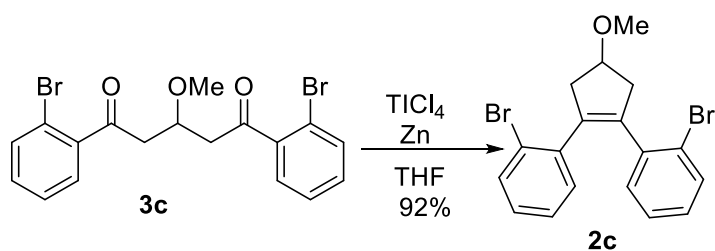
4,4'-(4-Methoxycyclopent-1-ene-1,2-diyl)bis(bromobenzene) (**2b**)



In a flame-dried flask, dry THF (30 mL) was added to zinc dust (2.20 g, 33.8 mmol). The flask was cooled in an ice bath, and titanium tetrachloride (1.9 mL, 17 mmol) was added dropwise. A yellow cloud formed and the solution became dark blue. After 15 min, a solution of **3b** (1.85 g, 4.2 mmol) in THF (5 mL) was added to the reaction mixture. The reaction mixture was then heated to reflux for 3 h. After cooling the reaction to ambient temperature, 20 mL water was added and gas evolution was seen. After the bubbling subsided, the reaction mixture was extracted with ethyl acetate (3 x 50 mL), the organic layers were combined, dried over MgSO₄, and filtered, and the solvent was removed *in vacuo* to give **2b** (1.16 g, 85%) as a colorless oil. ¹H

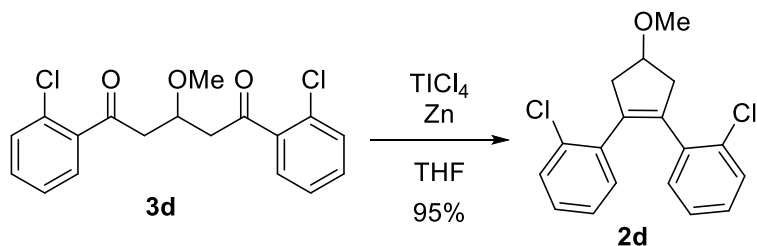
NMR (400 MHz, CDCl₃) δ 7.32-7.36(m, 4H), 7.01-7.05(m, 4H), 4.19(m, 1H), 3.38 (s, 3H), 3.09-3.14 (m, 2H), 2.87-2.92 (m, 2H) ¹³C NMR (CDCl₃) δ 136.2, 134.5, 131.4, 129.8, 120.9, 78.3, 56.4, 44.8.

2,2'-(4-Methoxycyclopent-1-ene-1,2-diyl)bis(bromobenzene) (2c)



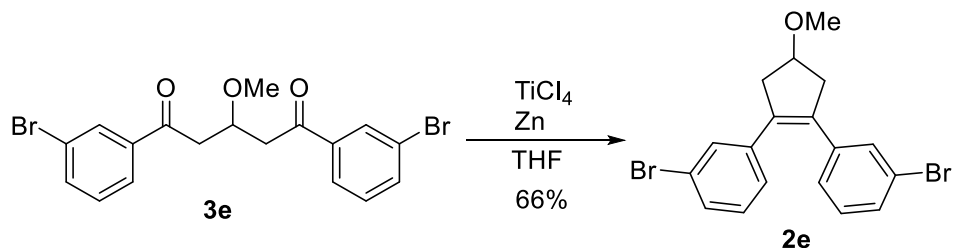
In a flame-dried flask, dry THF (10 mL) was added to zinc dust (0.289 g, 4.6 mmol). The flask was cooled in an ice bath, and titanium tetrachloride (0.25 mL, 2.3 mmol) was added dropwise. A yellow cloud formed and the solution became dark blue. After 15 min, a solution of **3c** (0.245 g, 0.57 mmol) in THF (5 mL) was added to the reaction mixture. The reaction mixture was then heated to reflux for 2 h. After cooling the reaction to ambient temperature, 20 mL water was added and gas evolution was seen. After the bubbling subsided, the reaction mixture was extracted with ether (3 x 50 mL). The organic layers were combined, dried over MgSO₄, filtered and the solvent was removed *in vacuo*. The resulting brown oil was purified by column chromatography (SiO₂, 9:1 hexanes:ethyl acetate) to give **2c** (0.208 g, 92 % yield) as a yellow oil. ¹H NMR (300 MHz, CDCl₃) δ 7.46 (m, 2H), 7.0-7.1 (m, 6H), 4.35 (m, 1H), 3.42 (s, 3 H), 3.14-3.22 (m, 2 H), 2.92-2.99 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 138.7, 132.4, 130.7, 128.5, 127.0, 122.8, 79.9, 56.5, 43.3.

2,2'-(4-Methoxycyclopent-1-ene-1,2-diyl)bis(chlorobenzene) (2d)



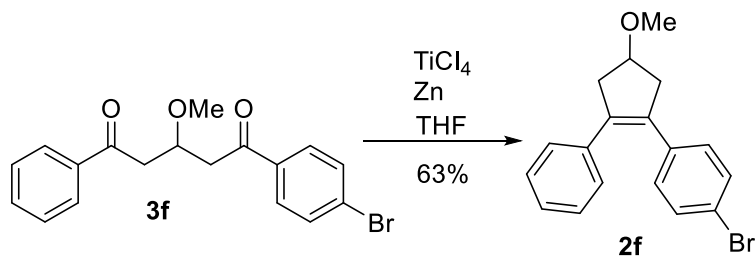
In a flame-dried flask equipped with a stir bar, 45 mL of dry THF was added to zinc dust (2.80 g, 43 mmol) under argon. The flask was cooled in an ice bath and titanium tetrachloride (2.4 mL, 21.5 mmol) was added dropwise. The solution was stirred for 30 min and became blue. A solution of **3d** (1.88 g, 5.4 mmol) in 8 mL THF was added to the reaction mixture via cannula. The reaction mixture was then heated to reflux for 2 h. Then, 20 mL water was added, and the mixture was extracted with ethyl acetate (3 x 50 mL). The organic layers were combined, dried over MgSO_4 , filtered and the solvent was removed *in vacuo*. The reaction mixture was purified by column chromatography (SiO_2 , 9:1 hexanes:ethyl acetate) to give **2d** (1.60 g, 92 % yield) as a yellow solid. M.p. 46-48 °C. ^1H NMR (300 MHz, CDCl_3) δ 7.28 (d, $J=8$ Hz, 2H), 7.0-7.1 (m, 4H), 4.35 (m, 1H), 3.42 (s, 3 H), 3.16-3.22 (m, 2 H), 2.94-2.99 (m, 2H) ^{13}C NMR (75 MHz, CDCl_3) δ 137.2, 136.7, 133.0, 130.7, 129.3, 126.4, 79.9, 56.4, 43.3. HRMS (EI) calcd. for $\text{C}_{18}\text{H}_{16}\text{OCl}_2$ 318.0578 found 318.0585.

3,3'-(4-Methoxycyclopent-1-ene-1,2-diyl)bis(bromobenzene) (2e)



In a flame-dried flask, dry THF (50 mL) was added to zinc dust (0.945 g, 14.5 mmol). The flask was cooled in an ice bath, and titanium tetrachloride (0.8 mL, 7.3 mmol) was added dropwise. A yellow cloud formed and the solution became dark blue. After 15 min, a solution of **3e** (0.800 g, 1.8 mmol) in THF (5 mL) was added to the reaction mixture. The reaction mixture was then heated to reflux for 3 h. After cooling the reaction to ambient temperature, 20 mL water was added and gas evolution was seen. After the bubbling subsided, the reaction mixture was extracted with ethyl acetate (3 x 50 mL), the organic layers were combined, dried over MgSO₄, and filtered, and the solvent was removed *in vacuo* to give **2e** (0.493 g, 66% yield) as a yellow orange solid. M.p. 72-73 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.31-7.34 (m, 4H), 7.04-7.09 (m, 4H), 4.17-4.22 (m, 1H), 3.39 (s, 3H), 3.10-3.15 (m, 2H), 2.89-2.93 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 136.2, 134.5, 131.4, 129.8, 120.9, 99.9, 78.3, 56.4, 44.8.

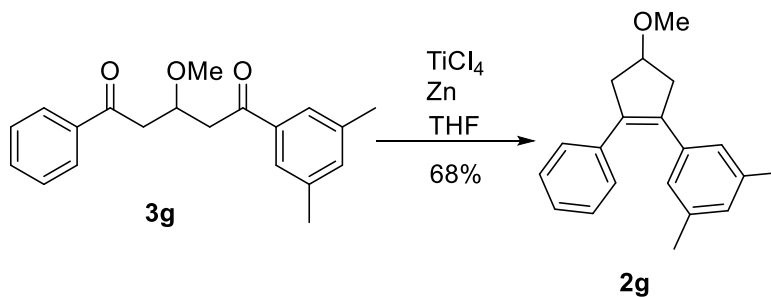
1-Bromo-4-(4-methoxy-2-phenylcyclopent-1-en-1-yl)benzene (2f)



To a flame-dried 2-necked flask under Ar, zinc dust (0.108 g, 1.67 mmol) was added. Then 10 mL dry THF was injected into the flask, and the mixture was stirred. The flask was cooled in an

ice water bath and TiCl_4 (0.09 mL, 0.83 mmol) was added dropwise. A yellow cloud formed, and the solution turned dark blue. The mixture was stirred for 15 min, then diketone **3f** (0.075 g, 0.21 mmol) in 1 mL dry THF was added dropwise. After the addition, the solution was heated to reflux for 3 h. The reaction was cooled and 25 mL water was added and the solution bubbled. After the bubbling subsided, the reaction mixture was extracted with ethyl acetate (3 x 25 mL), the organic layers were combined, dried over MgSO_4 , filtered, and the solvent was removed *in vacuo*. The resulting yellow oil was then purified by column chromatography (SiO_2 , 19:1 hexanes:ethyl acetate) to give **2f** (0.043 grams, 63%) as a colorless oil. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.31 (d, J = 8 Hz, 2H), 7.17-7.25 (m, 5H), 7.40 (d, J = 8 Hz, 2H), 4.19-4.23 (m, 1H), 3.39 (s, 3H), 3.11-3.16 (m, 2H), 2.88-2.95 (m, 2H), $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 137.4, 136.5, 135.9, 133.4, 131.2, 129.8, 128.2, 128.1, 127.1, 120.6, 78.4, 56.4, 45.1, 44.7. HRMS (EI) calculated for $\text{C}_{18}\text{H}_{17}\text{OBr}$ 328.0463 found 328.0462.

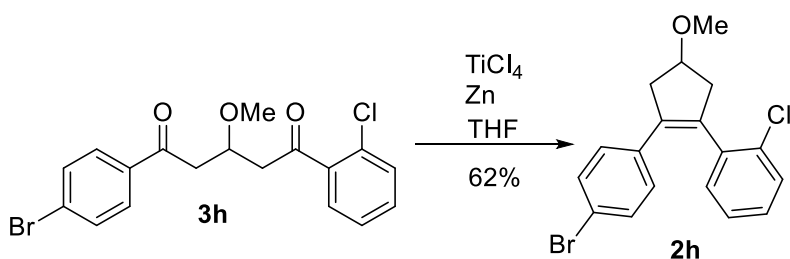
1-[2-(4-Bromophenyl)-4-methoxycyclopent-1-en-1-yl]-3,5-dimethylbenzene (**2g**)



To a flame-dried 2-necked flask under Ar, zinc dust (0.129 g, 2.0 mmol) was added. Then 5 mL dry THF was injected into the flask, and the mixture was stirred. The flask was cooled in an ice water bath and TiCl_4 (0.11 mL, 1.0 mmol) was added dropwise. A yellow cloud formed, and the solution turned dark blue. The mixture was stirred for 15 min, then diketone **3g** (0.077 g, 0.25 mmol) in 1 mL dry THF was added dropwise. After the addition, the solution was heated to reflux for 3 h. The reaction was cooled and 10 mL water was added and gas was evolved. After

the bubbling subsided, the reaction mixture was extracted with ethyl acetate (3 x 25 mL), the organic layers were combined, dried over MgSO₄, filtered, and the solvent was removed *in vacuo*. The resulting yellow oil was then purified by column chromatography (SiO₂, 19:1 hexanes:ethyl acetate) to give **2g** (0.047 grams, 63%) as a colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.18- 7.22 (m, 5H), 6.85 (s, 1H), 6.83 (s, 2H), 4.21-4.25 (m, 1H), 3.41 (s, 3H), 3.13-3.20 (m, 2H), 2.92-2.99 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 137.7, 137.4, 135.1, 134.1, 128.4, 128.1, 1287.9, 126.6, 125.9, 78.6, 56.3, 45.2, 44.7, 21.2. HRMS (EI) calculated for C₂₀H₂₂O 278.1671 found 278.1668.

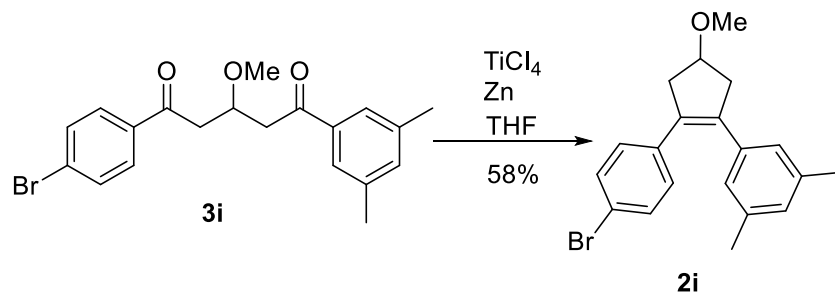
1-Bromo-4-[2-(2-chlorophenyl)-4-methoxycyclopent-1-en-1-yl]benzene (**2h**)



To a flame-dried 2-necked flask under Ar, zinc dust (0.042 g, 0.65 mmol) was added. Then 8 mL dry THF was injected into the flask, and the mixture was stirred. The flask was cooled in an ice water bath and TiCl₄ (0.04 mL, 0.32 mmol) was added dropwise. A yellow cloud formed, and the solution turned dark blue. The mixture was stirred for 15 min, then diketone **3h** (0.032 g, 0.08 mmol) in 2 mL dry THF was added dropwise. After the addition, the solution was heated to reflux for 3 h. The reaction was cooled and 5 mL water was added and gas was evolved. After the bubbling subsided, the reaction mixture was diluted with 25 mL of water and extracted with ethyl acetate (3 x 25 mL), the organic layers were combined, dried over MgSO₄, filtered, and the solvent was removed *in vacuo* to give **2h** (0.024 grams, 62%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) 7.39 (dd, J= 7.6 Hz, 1.6 Hz, 1H), 7.15-7.27 (m, 4H), 7.07 (dd, J= 7.6 Hz, 2 Hz,

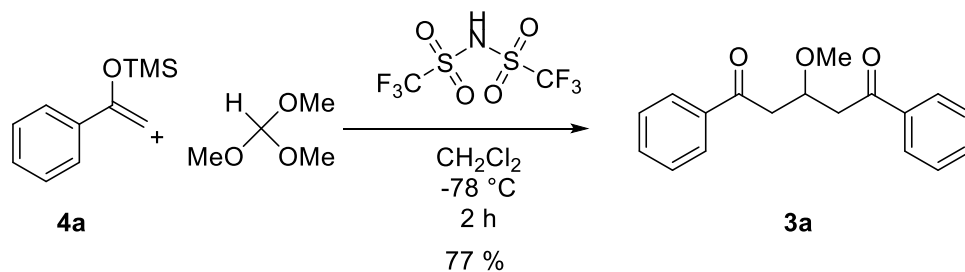
1H), 6.91-6.93 (m, 2H), 4.25-4.30 (m, 1H), 3.40 (s, 3H), 3.10-3.16 (m, 2H), 2.84-2.90 (m, 2H). ¹³C NMR (CDCl₃) δ 137.6, 135.4, 135.1, 135.0, 133.0, 131.0, 130.4, 129.8, 129.0, 128.6, 127.1, 120.7, 78.9, 56.4, 45.2, 42.7. HRMS (ESI) calculated for C₁₈H₁₆BrClO ([M+NH₄)⁺) 380.041 found 380.041.

1-[2-(4-Bromophenyl)-4-methoxycyclopent-1-en-1-yl]-3,5-dimethylbenzene (2i)



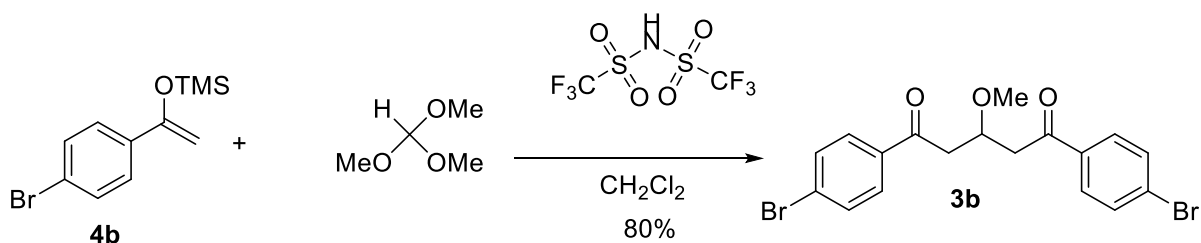
To a flame-dried 2-necked flask under Ar, zinc dust (0.135 g, 2.1 mmol) was added. Then 5 mL dry THF was injected into the flask, and the mixture was stirred. The flask was cooled in an ice water bath and TiCl₄ (0.11 mL, 1.0 mmol) was added dropwise. A yellow cloud formed, and the solution turned dark blue. The mixture was stirred for 15 min, then diketone **3i** (0.075 g, 0.19 mmol) in 1 mL dry THF was added dropwise. After the addition, the solution was heated to reflux for 3 h. The reaction was cooled and 10 mL water was added and gas was evolved. After the bubbling subsided, the reaction mixture was diluted with 25 mL water and extracted with ethyl acetate (3 x 25 mL), the organic layers were combined, dried over MgSO₄, filtered, and the solvent was removed *in vacuo* to give **2i** (0.40 grams, 58%) as a colorless oil. ¹H NMR (500 MHz, CDCl₃) 7.31 (d, J= 8.5 Hz, 2H), 7.06 (d, J= 8.5 Hz, 2H), 6.85 (s, 1H), 6.80 (s, 2H), 4.17-4.21 (m, 1H), 3.39 (s, 3H), 3.09-3.13 (m, 2H), 2.88-2.92 (m, 2H), 2.22 (s, 6H). ¹³C NMR (125 Mhz, CDCl₃) δ 137.7, 137.5, 136.5, 136.3, 132.7, 131.0, 129.7, 128.7, 125.8, 120.4, 78.4, 56.4, 45.5, 44.4, 21.2. HRMS (EI) calculated for C₂₀H₂₁BrO 356.0776 found 356.0773

3-Methoxy-1,5-diphenylpentane-1,5-dione (3a)



Silyl enol ether **4a** (0.470 g, 2.45 mmol) was dissolved in 7 mL dichloromethane in a 25-mL round-bottom flask. Trimethyl orthoformate (0.10 mL, 0.99 g, 0.94 mmol,) was added. The reaction flask was cooled to -78°C , and a solution of bis(trifluoromethane)sulfonimide (0.029 g, 0.10 mmol) in dichloromethane (1 mL) was added. The reaction mixture was stirred at -78°C for 2 h. The reaction mixture was then poured into saturated NaHCO_3 (aq). The mixture was extracted with ethyl acetate (3 x 50 mL), the organic layers were combined, dried over MgSO_4 , filtered, and the solvent was evaporated *in vacuo*. The resulting brown oil was purified by column chromatography (SiO_2 , 9:1 hexanes:ethyl acetate) to give **3a** (0.202 g, 77% yield) as a colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 8.06 (m, 2 H) 7.64 (m, 1 H), 7.54 (m, 2 H) 4.58 (m, 1 H) 3.45 (s, 3H), 3.40 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 198.2, 137.0, 133.2, 128.6, 128.2, 74.3, 57.6, 43.3. HRMS (EI) calculated for $\text{C}_{18}\text{H}_{18}\text{O}_3$ 282.1256 found 282.1256

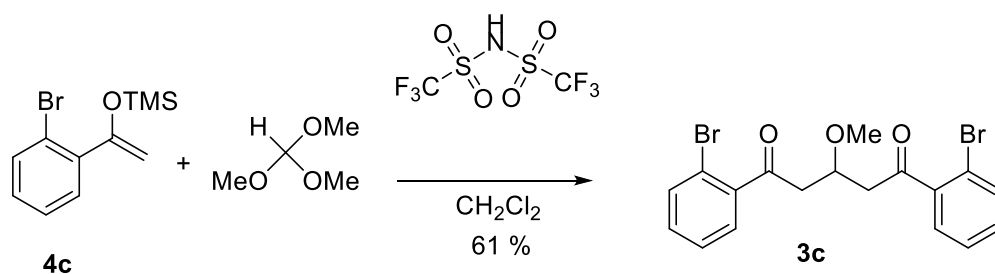
1,5-Bis(4-bromophenyl)-3-methoxypentane-1,5-dione (3b)



Silyl enol ether **4b** (2.72 g, 10 mmol) was dissolved in 30 mL dichloromethane in a 50-mL round-bottom flask. Trimethyl orthoformate (0.478 g, 4.5 mmol) was added. The reaction flask

was cooled to $-78\text{ }^{\circ}\text{C}$, and a solution of bis(trifluoromethane)sulfonimide (0.141 g, 0.5 mmol) in dichloromethane (5 mL) was added. The reaction mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 3 h, then poured into 50 mL NaHCO_3 (aq., sat.). The mixture was extracted with ethyl acetate (3 x 50 mL), the organic layers were combined, dried over MgSO_4 , filtered and the solvent was evaporated *in vacuo*. The reaction mixture was purified by column chromatography (SiO_2 , 9:1 hexanes:ethyl acetate) to give **3b** (1.32 g, 80% yield) as a pale yellow solid. M.p. $96\text{--}97\text{ }^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3) δ 7.82 (d, $J=9.2$ Hz, 4H), 7.59 (d, $J=9.2$ Hz, 4H), 4.41–4.47 (m, 1H), 3.34 (s, 3H), 3.26–3.32 (m, 2H), 3.15–3.20 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 197.1, 135.6, 131.8, 129.6, 128.4, 74.1, 57.6, 43.0. HRMS (EI) calcd. for $\text{C}_{18}\text{H}_{16}\text{O}_3\text{Br}_2$ 437.9467 found 437.9476.

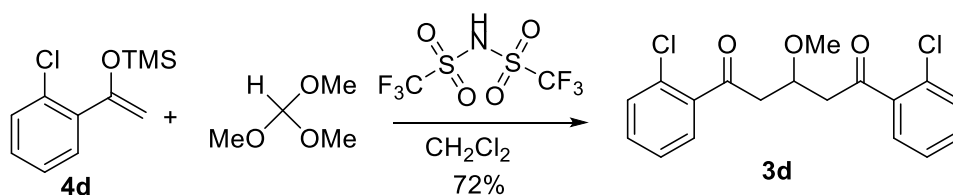
1,5-Bis(2-bromophenyl)-3-methoxypentane-1,5-dione (**3c**)



Silyl enol ether **4c** (1.0 g, 3.7 mmol) was dissolved in 5 mL dichloromethane in a 25-mL round-bottom flask. Trimethyl orthoformate (0.18 mL, 1.7 mmol) was added. The reaction flask was cooled to $-78\text{ }^{\circ}\text{C}$, and a solution of bis(trifluoromethane)sulfonimide (0.026 g, 0.09 mmol) in 3 mL dichloromethane was added. The reaction mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 3 h. The reaction mixture was then poured into 25 mL NaHCO_3 (aq., satd.). The mixture was then extracted with ether (3 x 25 mL). The organic layers were combined, dried over MgSO_4 , filtered and the solvent was evaporated *in vacuo*. The resulting brown oil was purified by column

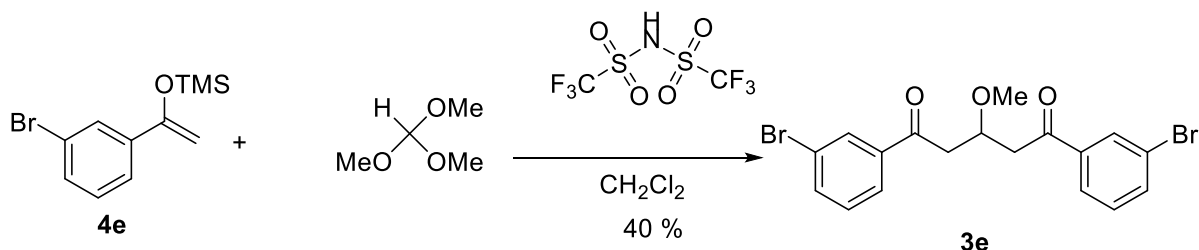
chromatography (SiO₂, 9:1 hexanes:ethyl acetate) to give **3c** (0.437 g, 61% yield) as a yellow oil. ¹H NMR (300 MHz, CDCl₃) δ 7.47-7.48 (m, 1H), 7.45 (m, 1H), 7.03-7.08 (m, 4H), 6.96-7.02 (m, 2H), 4.31-4.39 (m, 1H), 3.42 (s, 3H), 3.24-3.28 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 201.8, 141.7, 133.7, 131.7, 128.7, 127.5, 118.7, 74.0, 57.6, 47.0.

1,5-Bis(2-chlorophenyl)-3-methoxypentane-1,5-dione (**3d**)



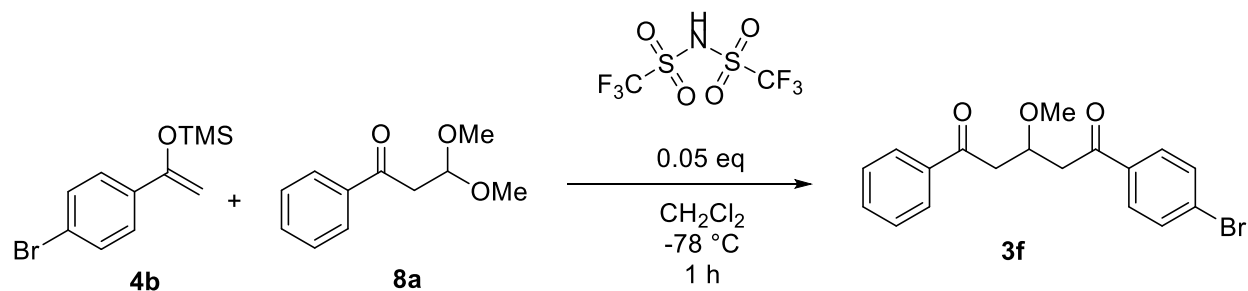
Silyl enol ether **4d** (2.3 g, 10.2 mmol) was dissolved in 50 mL dichloromethane in a 25-mL flask. Trimethyl orthoformate (0.5 mL, 4.6 mmol) was added. The reaction flask was cooled to -78 °C, and a solution of bis(trifluoromethane)sulfonimide (0.071 g, 0.09 mmol) in 3 mL dichloromethane was added. The reaction mixture was stirred at -78 °C for 3 h. The reaction mixture was then poured into 50 mL NaHCO₃ (aq, sat.) and the layers were separated. The aqueous layer was extracted with ethyl acetate (3 x 50 mL), the organic layers were combined, dried over MgSO₄, filtered and the solvent was removed *in vacuo*. The resulting brown oil was purified by column chromatography (SiO₂, 9:1 hexanes:ethyl acetate) to give **3d** (0.43 g, 72% yield) as a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.47-7.49 (m, 2H), 7.31-7.39 (m, 6H), 4.32 (m, 1H), 3.16-3.32 (m, 7H), ¹³C NMR (100 MHz, CDCl₃) δ 200.9, 139.1, 131.8, 130.8, 130.7, 129.0, 126.9, 74.0, 47.2. HRMS (EI) calcd. for C₁₈H₁₆O₃Cl₂ 350.0477 found 350.0474.

1,5-Bis(3-bromophenyl)-3-methoxypentane-1,5-dione (3e)



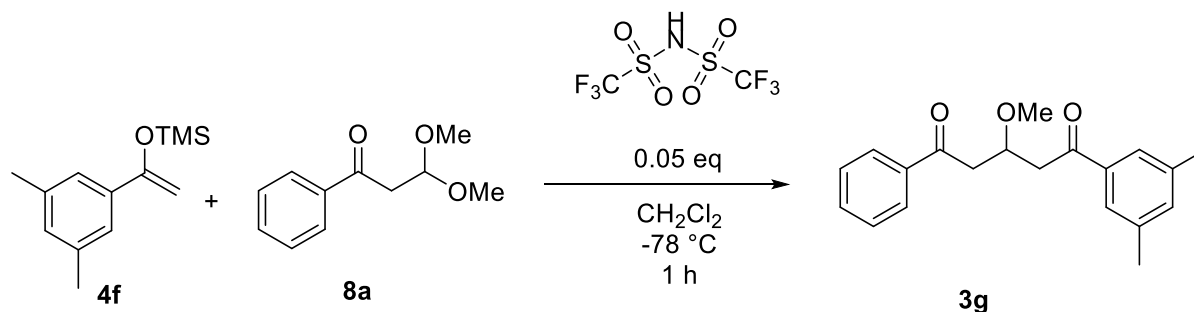
Silyl enol ether **4e** (5.23 g, 19.2 mmol) was dissolved in 150 mL dichloromethane in a 250-mL round-bottom flask. Trimethyl orthoformate (1.02 g, 9.6 mmol) was added. The reaction flask was cooled to -78 °C, and a solution of bis(trifluoromethane)sulfonimide (0.540 g, 1.9 mmol) in 10 mL dichloromethane was added. The reaction mixture was stirred at -78 °C for 2 h, then poured into 200 mL NaHCO₃ (aq., sat.). The mixture was extracted with dichloromethane (3 x 100 mL), the organic layers were combined, dried over MgSO₄, filtered and the solvent was evaporated *in vacuo*. The resulting red oil was purified by column chromatography (SiO₂, 9:1 hexanes:ethyl acetate) to give **3e** (1.70 g, 40% yield) as a yellow solid. M.p. 83-84 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.10-8.11 (m, 2H), 7.89-7.92 (m, 2H), 7.69-7.71 (m, 2H), 7.36 (t, J= 8 Hz, 2H), 4.44-4.50 (m, 1H), 3.37 (s, 3H), 3.29-3.35 (m, 2H), 3.17-3.22 (m, 2H) ¹³C NMR (125 MHz, CDCl₃) δ 196.8, 138.7, 136.1, 131.3, 130.2, 126.7, 123.1, 74.0, 57.8, 43.2. HRMS (EI) calcd. for C₁₈H₁₆O₃Br₂ 437.9467 found 437.9470.

1-(4-Bromophenyl)-3-methoxy-5-phenylpentane-1,5-dione (3f)



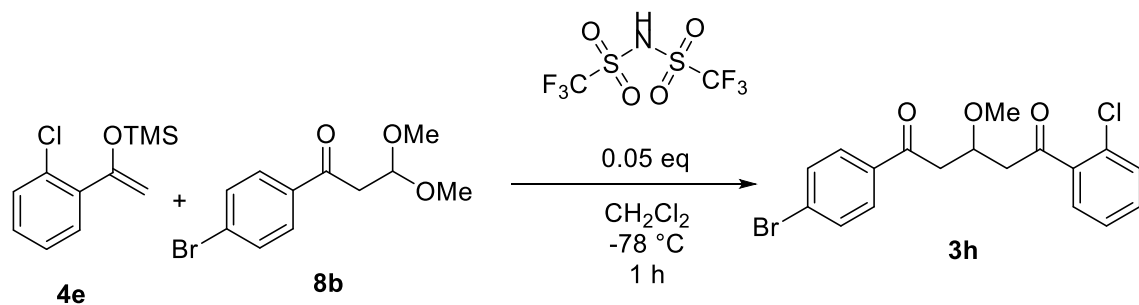
Silyl enol ether **4b** (0.195 g, 0.72 mmol) was dissolved in 5 mL dichloromethane in a 25-mL round-bottom flask. 3,3-Dimethoxy-1-phenylpropan-1-one **8a** (0.111 g, 0.60 mmol,) was added. The reaction flask was cooled to -78 °C and bis(trifluoromethane)sulfonimide (0.009 g, 0.03 mmol) was added in dichloromethane (1 mL). The reaction mixture was stirred at -78 °C for 1 h. The reaction mixture was then poured into 10 mL NaHCO₃ (aq., satd.). The mixture was extracted with ethyl acetate (3 x 15 mL), the organic layers were combined, dried over MgSO₄, filtered, and the solvent was evaporated *in vacuo*. The reaction mixture was purified by column chromatography (SiO₂, 9:1 hexanes:ethyl acetate) to give **3f** (0.120 g, 56% yield) as a yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.98 (d, J= 7.5 Hz, 2H), 7.85 (d, J= 8.5 Hz, 2H), 7.56-7.62 (m, 3H), 7.47 (t, J= 7.5 Hz, 2H), 4.45-4.50 (m, 1H), 3.34-3.40 (m, 4H), 3.27-3.31 (m, 1 H), 3.19-3.24 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 198.2, 197.3, 136.9, 135.7, 133.3, 131.9, 129.7, 128.6, 128.4, 128.1, 74.2, 57.7, 43.4, 43.0. HRMS (EI) calculated for C₁₈H₁₇BrO₃ 360.0361 found 360.0352.

1-(3,5-Dimethylphenyl)-3-methoxy-5-phenylpentane-1,5-dione (3g)



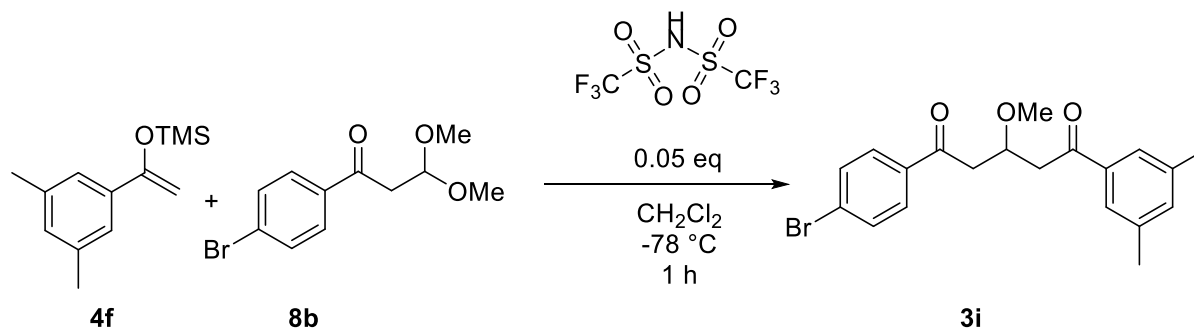
Silyl enol ether **4f** (0.210 g, 0.83 mmol) was dissolved in 5 mL dichloromethane in a 25-mL round-bottom flask. 3,3-Dimethoxy-1-phenylpropan-1-one **8a** (0.129 g, 0.69 mmol) was added. The reaction flask was cooled to -78 °C and bis(trifluoromethane)sulfonimide (0.010 g, 0.03 mmol) was added in dichloromethane (1 mL). The reaction mixture was stirred at -78 °C for 1 h. The reaction mixture was then poured into 15 mL NaHCO₃ (aq., satd.). The mixture was extracted with ethyl acetate (3 x 15 mL), the organic layers were combined, dried over MgSO₄, filtered, and the solvent was evaporated *in vacuo*. The reaction mixture was purified by column chromatography (SiO₂, 9:1 hexanes:ethyl acetate) to give **3g** (0.077 g, 36% yield) as a yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.99 (d, J= 7 Hz, 2H), 7.59 (s, 2H), 7.54 (t, J= 7 Hz, 1H), 7.46 (t, J= 7 Hz, 2H), 7.19 (s, 1H), 4.48-4.53 (m, 1H), 3.37 (s, 3H), 3.31-3.36 (m, 2H), 3.17-3.25 (m, 2H), 2.36 (s, 6H) ¹³C NMR (125 MHz, CDCl₃) δ 198.6, 198.2, 138.2, 137.0, 136.9, 134.8, 133.1, 128.5, 128.1, 125.9, 74.2, 57.6, 43.3, 43.2, 21.1. HRMS (EI) calculated for C₂₀H₂₂O₃ 310.1569 found 310.1565.

1-(2-Chlorophenyl)-3-methoxy-5-(4-bromophenyl)-pentane-1,5-dione (**3h**)



Silyl enol ether **4e** (0.133 g, 0.51 mmol) was dissolved in 5 mL dichloromethane in a 25-mL round-bottom flask. 1-(4-Bromophenyl)-3,3-dimethoxypropan-1-one **8b** (0.124 g, 0.46 mmol,) was added. The reaction flask was cooled to -78°C and bis(trifluoromethane)sulfonimide (0.007 g, 0.02 mmol) was added in dichloromethane (1 mL). The reaction mixture was stirred at -78°C for 1 h. The reaction mixture was then poured into 15 mL NaHCO_3 (aq., satd.). The layers were separated and then the aqueous layer was extracted with dichloromethane (3 x 25 mL), the organic layers were combined, dried over MgSO_4 , filtered, and the solvent was evaporated *in vacuo*. The reaction mixture was purified by column chromatography (SiO_2 , 9:1 hexanes:ethyl acetate) to give **3h** (0.169 g, 92% yield) as an orange solid. M.p. $73\text{--}75^\circ\text{C}$ $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.83 (d, $J = 8.5$ Hz, 2H), 7.61 (d, $J = 8.5$ Hz, 2H), 7.51 (dd, $J = 7.5, 1.5$ Hz, 1H), 7.37-7.43 (m, 2H), 7.32-7.35 (m, 1H), 4.38-4.43 (m, 1H), 3.22-3.33 (m, 6H), 3.14-3.18 (m, 1H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 201.1, 197.1, 139.2, 135.7, 131.93, 131.88, 130.9, 130.6, 129.7, 129.1, 128.5, 127.0, 74.1, 57.6, 47.3, 43.0. HRMS (ESI) calculated for $\text{C}_{18}\text{H}_{16}\text{O}_3\text{BrCl}$ ($[\text{M}+\text{Na}]^+$) 418.9869 found 418.9870.

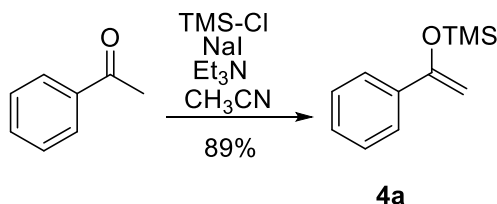
1-(3,5-Dimethylphenyl)-3-methoxy-5-(4-bromophenyl)-pentane-1,5-dione (**3i**)



Silyl enol ether **4f** (0.210 g, 0.83 mmol) was dissolved in 5 mL dichloromethane in a 10-mL round-bottom flask. 1-(4-Bromophenyl)-3,3-dimethoxypropan-1-one **8b** (0.184 g, 0.70 mmol) was added. The reaction flask was cooled to -78°C and bis(trifluoromethyl)sulfonamide (0.010 g, 0.03 mmol) was added in dichloromethane (1 mL). The reaction mixture was stirred at -78°C for 1 h. The reaction mixture was then poured into 15 mL NaHCO_3 (aq., satd.). The layers were separated and then the aqueous layer was extracted with dichloromethane (3 x 25 mL), the organic layers were combined, dried over MgSO_4 , filtered, and the solvent was evaporated *in vacuo*. The reaction mixture was purified by column chromatography (SiO_2 , 9:1 hexanes:ethyl acetate) to give **3i** (0.075 g, 28% yield) as a yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 7.85 (d, $J = 8.5$ Hz, 2H), 7.60 (d, $J = 8.5$ Hz, 2H), 7.57 (s, 2H), 7.20 (s, 1H), 4.44-4.49 (m, 1H), 3.33-3.40 (m, 4H), 3.15-3.28 (m, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 198.6, 197.3, 138.2, 137.0, 135.7, 134.9, 131.9, 129.7, 128.3, 125.9, 74.2, 57.6, 43.4, 43.0, 21.2. HRMS (EI) calculated for $\text{C}_{20}\text{H}_{21}\text{BrO}_3$ 388.0674 found 388.0671.

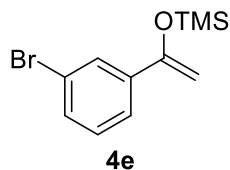
General Procedure for the synthesis of silyl enol ethers.

Trimethyl((1-phenylvinyl)oxy)silane (**4a**)²



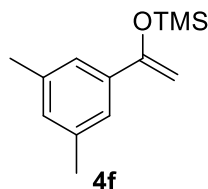
Acetophenone (0.19 mL, 0.20 g, 1.7 mmol), chlorotrimethylsilane (0.46 mL, 0.34 g, 3.3 mmol), and triethylamine (0.32 mL, 0.27 g, 2.5 mmol) were placed in a round-bottom flask with 8 mL acetonitrile. Sodium iodide (0.375 g, 2.5 mmol) in 2 mL acetonitrile was added dropwise, and the reaction mixture was stirred for 2 h. The solvent was removed *in vacuo*. The resulting brown slurry was purified by column chromatography (SiO₂, hexanes) to give silyl enol ether **4a** (0.285 g, 89% yield) as a colorless liquid. ¹H NMR matches the reported spectrum.² The material was then used immediately in the next step. Compounds **4b**³, **4c**⁴, and **4d**⁵ all match the reported ¹H NMR spectra.

((1-(3-Bromophenyl)vinyl)oxy)trimethylsilane (**4e**)⁶



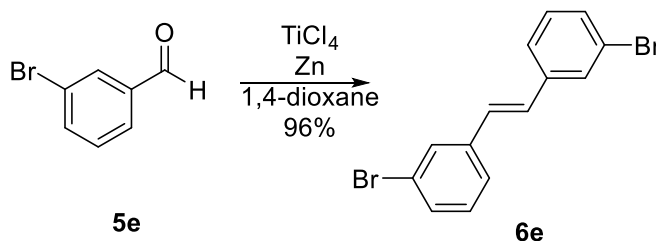
¹H NMR (400 MHz, CDCl₃) δ 7.73 (t, J=1.8 Hz, 1H), 7.50-7.53 (m, 1H), 7.40-7.43 (m, 1H), 7.19 (t, J=7.9 Hz, 1H), 4.91 (d, J=2 Hz, 1H), 4.46 (d, J=2 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 154.2, 139.7, 131.1, 129.6, 128.3, 123.8, 122.3, 92.0, 0.0.

((1-(3,5-Dimethylphenyl)vinyl)oxy)trimethylsilane (**4f**)⁷



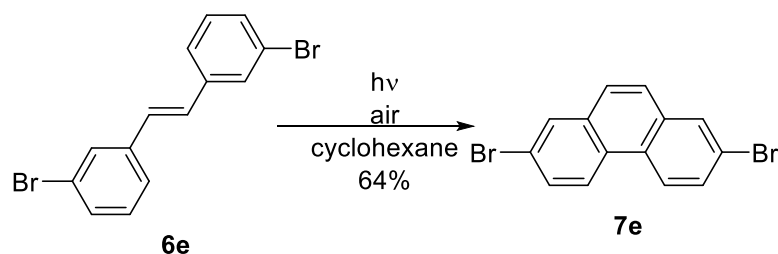
¹H NMR (400 MHz, CDCl₃) δ 7.21 (s, 2H), 6.94 (s, 1H), 4.88 (d, J=1.4 Hz, 1H), 4.40 (d, J=1.4 Hz, 1H), 2.33 (s, 6H), 0.27 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 155.9, 137.46, 137.45, 129.9, 123.1, 90.9, 21.4, 0.1.

1,2-Bis(3-bromophenyl)ethene (**6e**)



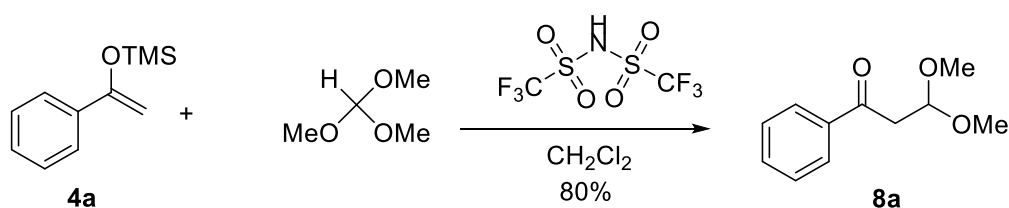
In an oven dried flask equipped with a stir bar was placed Zn dust (1.40 g, 21.6 mmol) and 1,4-dioxane (50 mL). The mixture was stirred under Ar and cooled in an ice bath. TiCl₄ (1.19 mL, 10.8 mmol) was added dropwise and yellow smoke was seen. The solution was stirred for five min and darkened to a deep blue color. 3-bromobenzaldehyde (0.63 mL, 5.4 mmol) was added dropwise and the mixture turned purple. The ice bath was removed and the reaction was allowed to warm to ambient temperature for 10 min. A reflux condenser was attached and the reaction was heated to reflux with an oil bath. After 4 h the reaction was cooled to r.t. and Na₂CO₃ (10 mL, satd., aq.) and water (50 mL) was added. The dark blue mixture was then transferred to a separatory funnel and extracted with ether (3 x 75 mL). The organic layers were combined, dried with MgSO₄, filtered and the solvent was removed *in vacuo* giving **6e** (0.872 g, 95 % yield) as a pale yellow solid. ¹H NMR matches the reported spectrum.⁸

2,7-Dibromophenanthrene (7e)



Stilbene **6e** (0.102 g, 0.30 mmol) was dissolved in 330 mL cyclohexane in a quartz photochemical reaction vessel open to the air and the vessel was put in the Rayonet and irradiated with 300-nm bulbs. The reaction was monitored by removing aliquots, washing them with sodium bisulfite (10%, aq) concentrating them *in vacuo* and subjecting them to proton NMR analysis. After 12 h of irradiation the starting material had been consumed and the solution was transferred to a separatory funnel washed with sodium bisulfite (100 mL, 10%, aq.), NaCl (satd., aq.), dried with MgSO₄, filtered and the solvent was removed *in vacuo*. The resulting yellow solid was purified by column chromatography (SiO₂, hexanes) to give **7e** (0.065 g, 64% yield) as a white solid. M.p. 200-201 °C (lit. M.p. 197-201 °C)⁹ ¹H NMR matches the reported spectrum.¹⁰

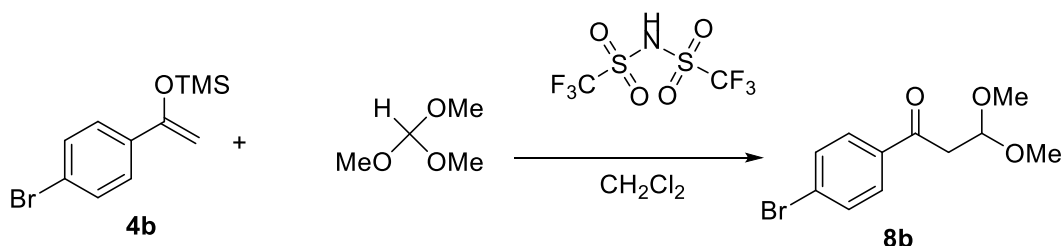
3,3-Dimethoxy-1-phenylpropan-1-one (8a)¹¹



Silyl enol ether **4a** (2.35 g, 10.4 mmol) was dissolved in 40 mL dichloromethane in a 100-mL round-bottom flask. Trimethyl orthoformate (1.14 mL, 10.4 mmol) was added. The reaction flask was cooled to -78 °C and a solution of bis(trifluoromethane)sulfonimide (0.146 g, 0.52 mmol) in 5 mL dichloromethane was added. The reaction mixture was stirred at -78 °C for 1 h,

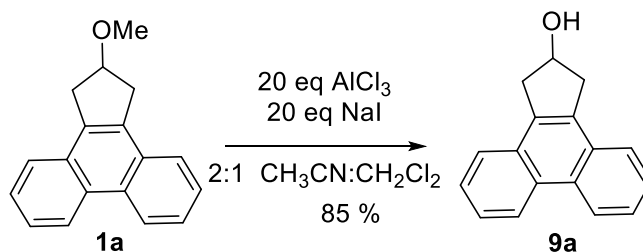
then poured into 50 mL NaHCO₃ (aq., sat.). The mixture was extracted with ethyl acetate (3 x 50 mL), the organic layers were combined, dried over MgSO₄, filtered and the solvent was evaporated *in vacuo*. The reaction mixture was purified by column chromatography (SiO₂, 9:1 hexanes:ethyl acetate) to give **8a** (2.08 g, 83% yield) as a yellow liquid. ¹H and ¹³C NMR match the reported spectra.¹¹

1-(4-Bromophenyl)-3,3-dimethoxypropan-1-one (**8b**)



Silyl enol ether **4b** (6.83 g, 25 mmol) was dissolved in 150 mL dichloromethane in a 250-mL round-bottom flask. Trimethyl orthoformate (2.75 mL, 25 mmol) was added. The reaction flask was cooled to -78 °C and a solution of bis(trifluoromethane)sulfonimide (0.352 g, 1.26 mmol) in 10 mL dichloromethane was added. The reaction mixture was stirred at -78 °C for 1 h, then poured into 200 mL NaHCO₃ (aq., sat.). The mixture was extracted with ethyl acetate (3 x 100 mL), the organic layers were combined, dried over MgSO₄, filtered and the solvent was evaporated *in vacuo*. The reaction mixture was purified by column chromatography (SiO₂, 9:1 hexanes:ethyl acetate) to give **8b** (6.86 g, 83% yield) as a yellow liquid. ¹H NMR matches the reported spectrum.¹² HRMS (EI) calculated for C₁₁H₁₃O₃Br 272.0048 found 272.0047.

2,3-Dihydro-1H-cyclopenta[1]phenanthren-2-ol (**9a**)

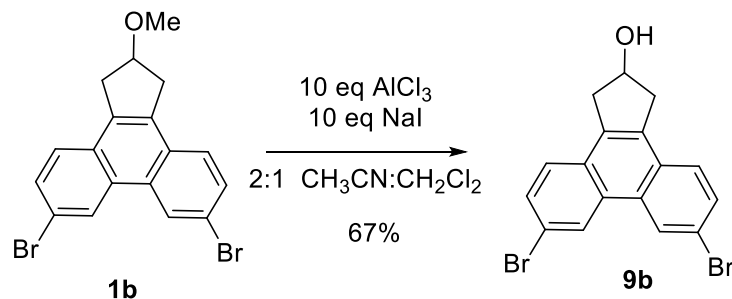


Methyl ether **1a** (0.021 g, 0.08 mmol) was dissolved in 1 mL CH_2Cl_2 and 2 mL acetonitrile in a flask. Sodium iodide (0.127 g, 0.8 mmol) was added and the solution was cooled to 0 °C.

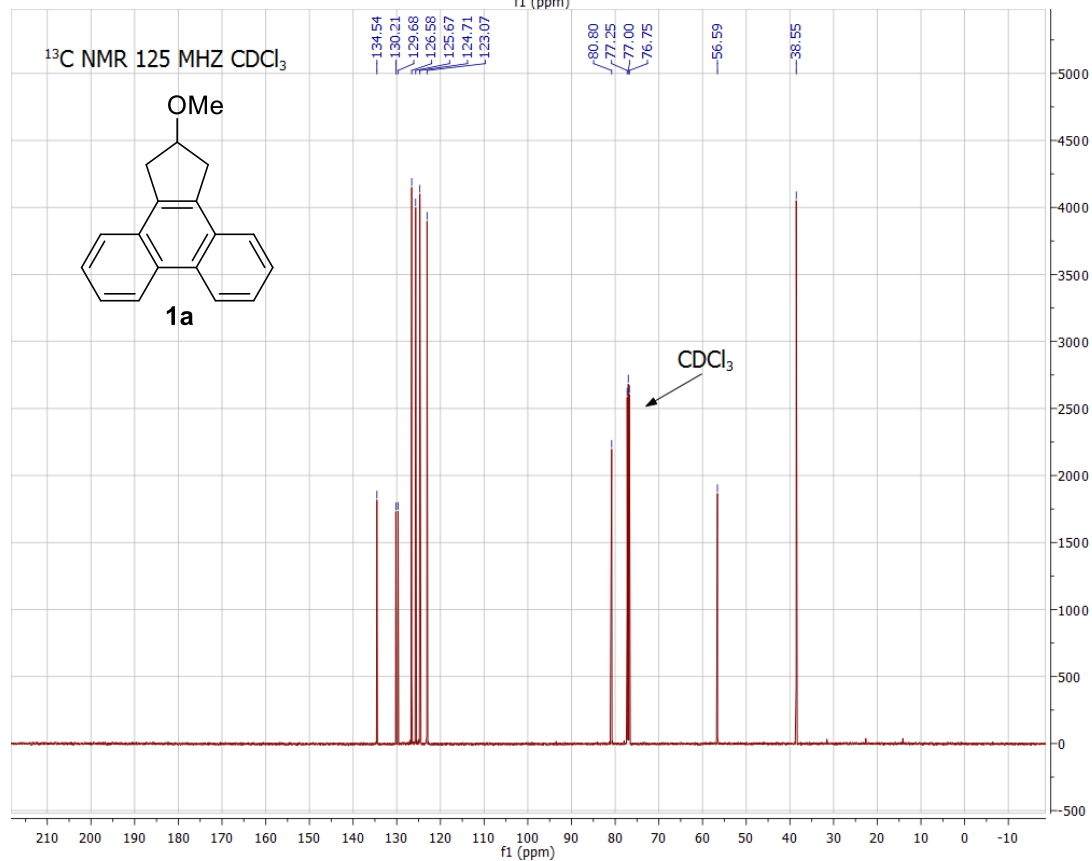
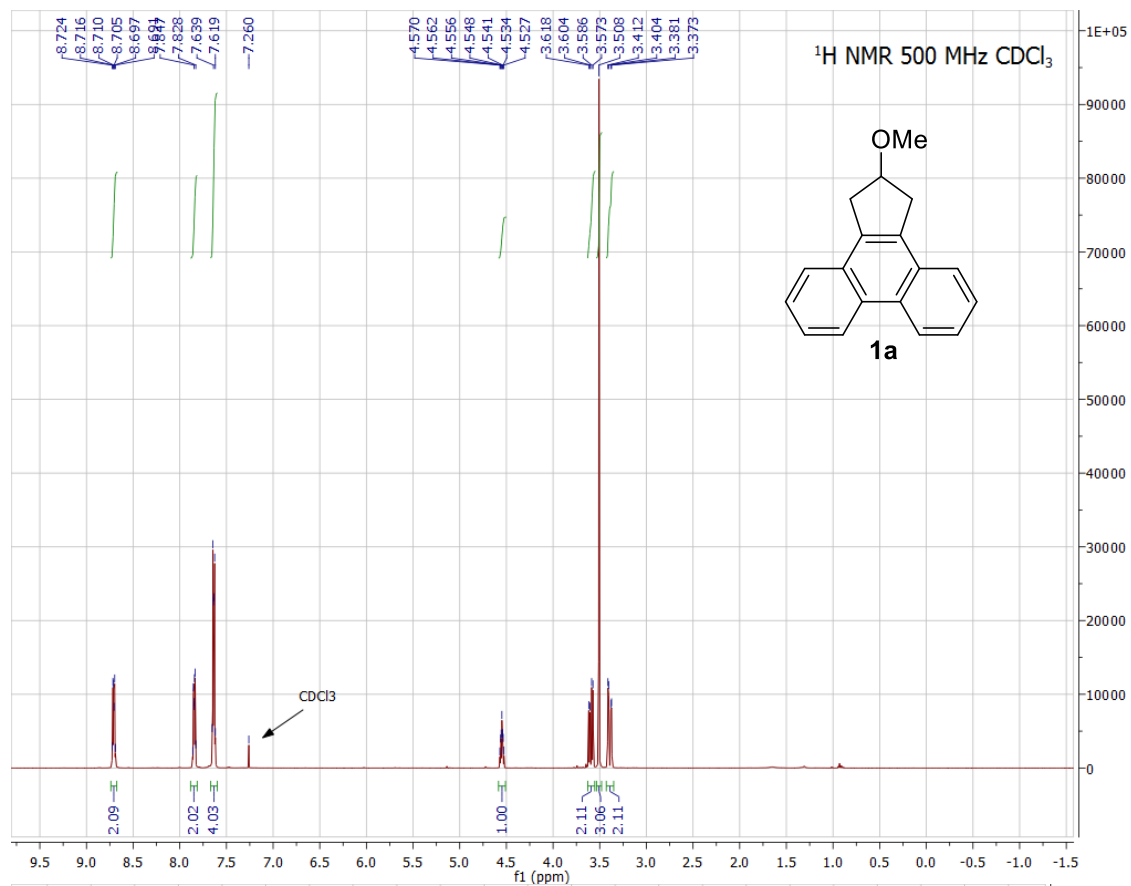
Aluminum trichloride (0.113 g, 0.8 mmol) was added, the solution darkened, and was stirred at 0 °C for 6 h. The reaction was then warmed to r.t. and stirred for a further 16 h. The reaction mixture was then poured into 50 mL water and extracted with CH_2Cl_2 (3 x 30 mL). The organic layers were combined and washed with 50 mL sodium thiosulfate (5 %, aq.). The organic layer was then dried over MgSO_4 , filtered, and the solvent removed *in vacuo* to give a white solid.

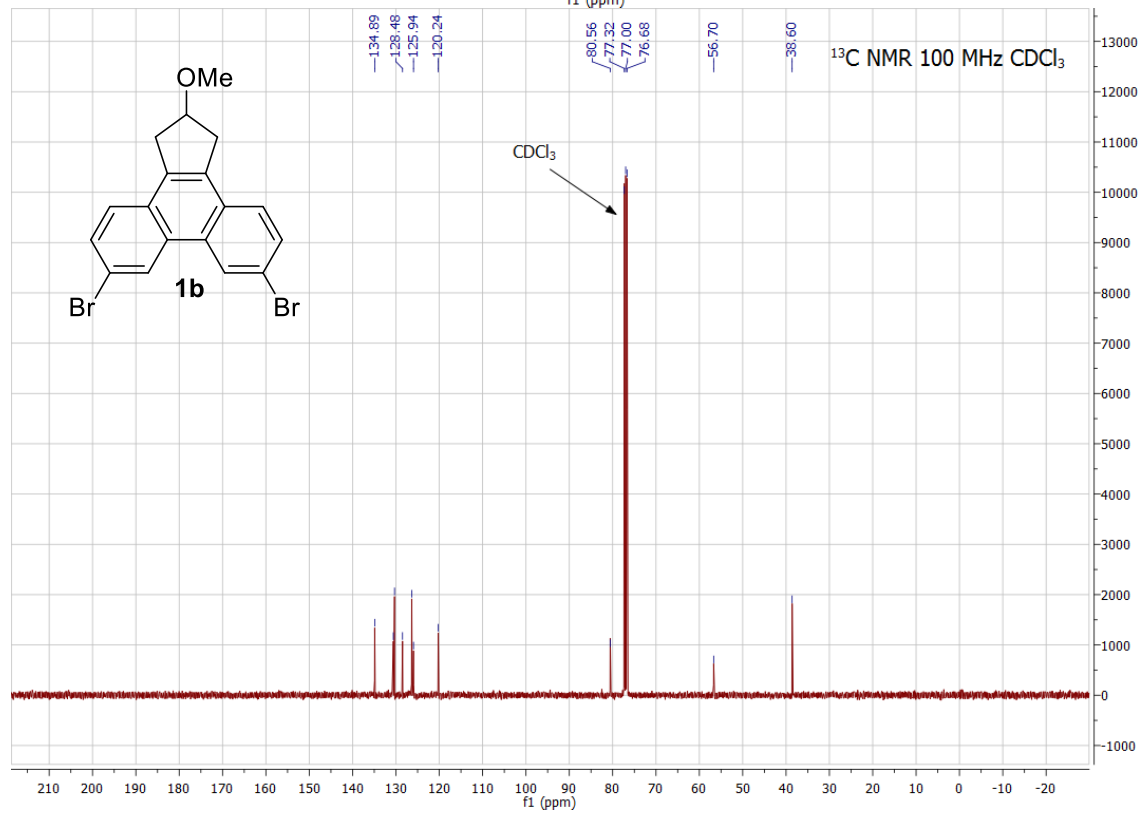
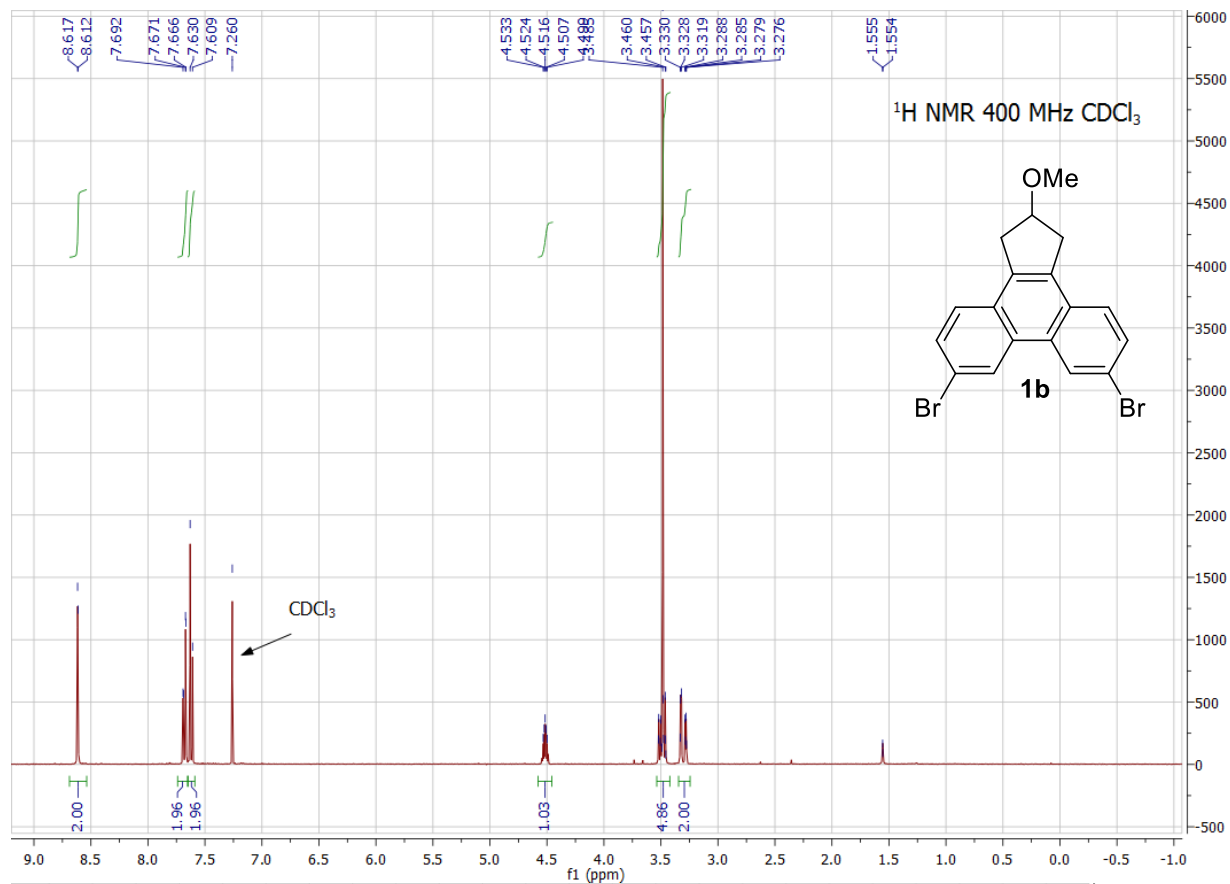
The solid was purified by column chromatography (SiO_2 , 3:1 hexanes:ethyl acetate) to give **9a** (0.017 g, 85% yield) as a white solid. M.p. 185-186 °C (lit. 187-188 °C^{13,14}, 185-186 °C¹⁵) ¹H NMR (400 MHz, CDCl_3) 8.70-8.72 (m, 2H), 7.88-7.85 (m, 2H), 7.62-7.64 (m, 4H), 5.00 (bs, 1H), 3.62-3.68 (m, 2H), 3.33-3.37 (m, 2H), 1.85 (bs, 1H). ¹³C NMR (100 MHz, CDCl_3) δ 134.5, 130.3, 129.8, 126.7, 125.8, 124.8, 123.2, 72.1, 42.4. ¹H NMR is consistent with the reported spectrum.¹⁶

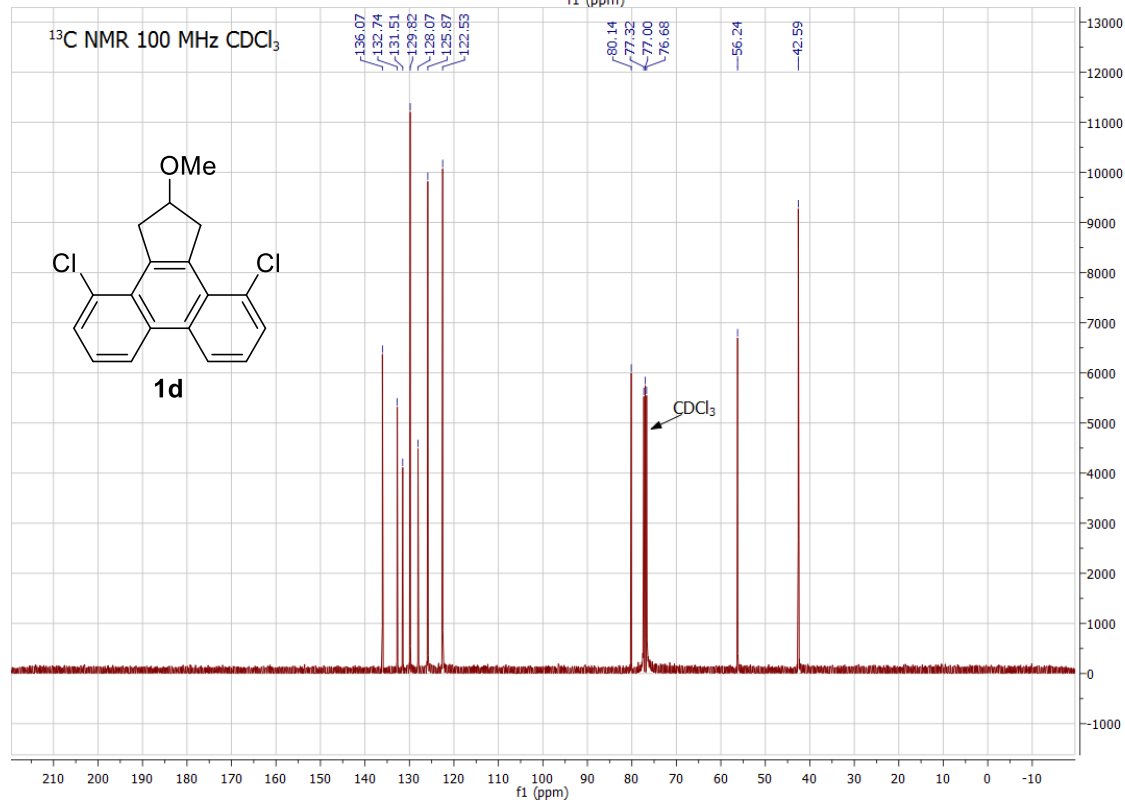
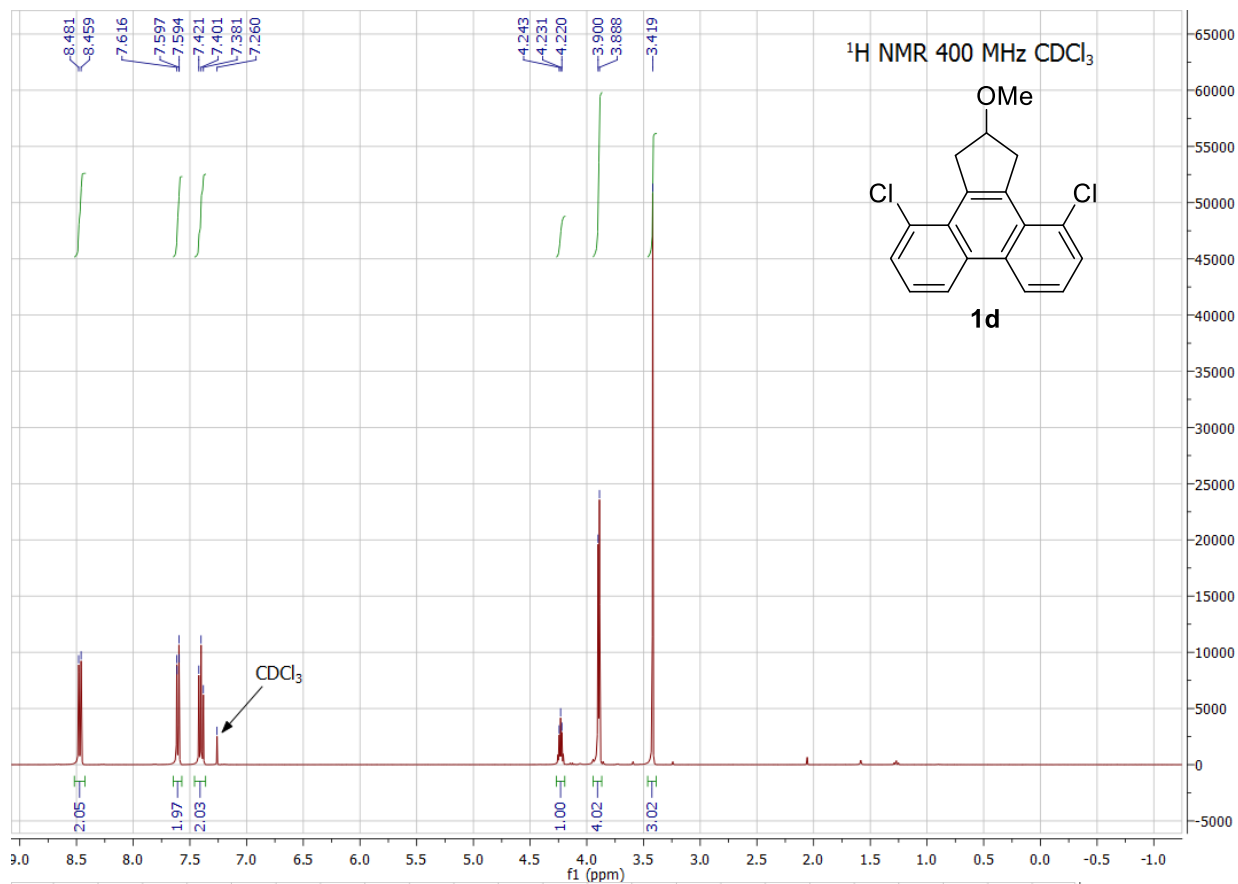
6,9-Dibromo-2,3-dihydro-1H-cyclopenta[1]phenanthren-2-ol (**9b**)

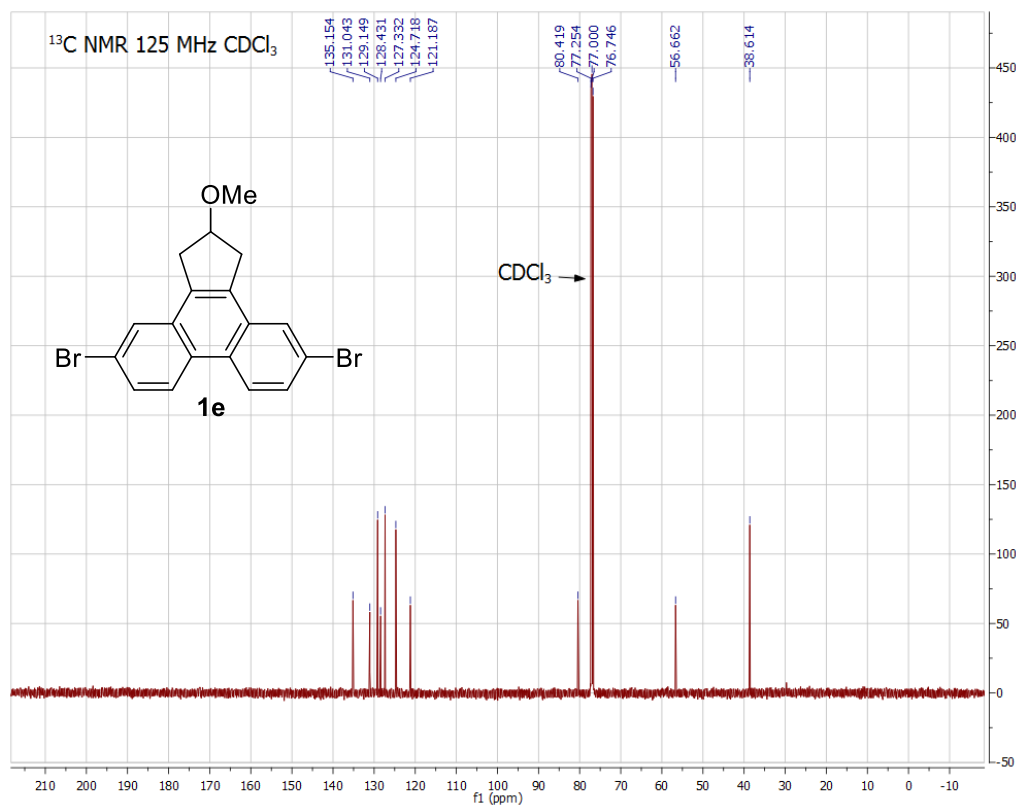
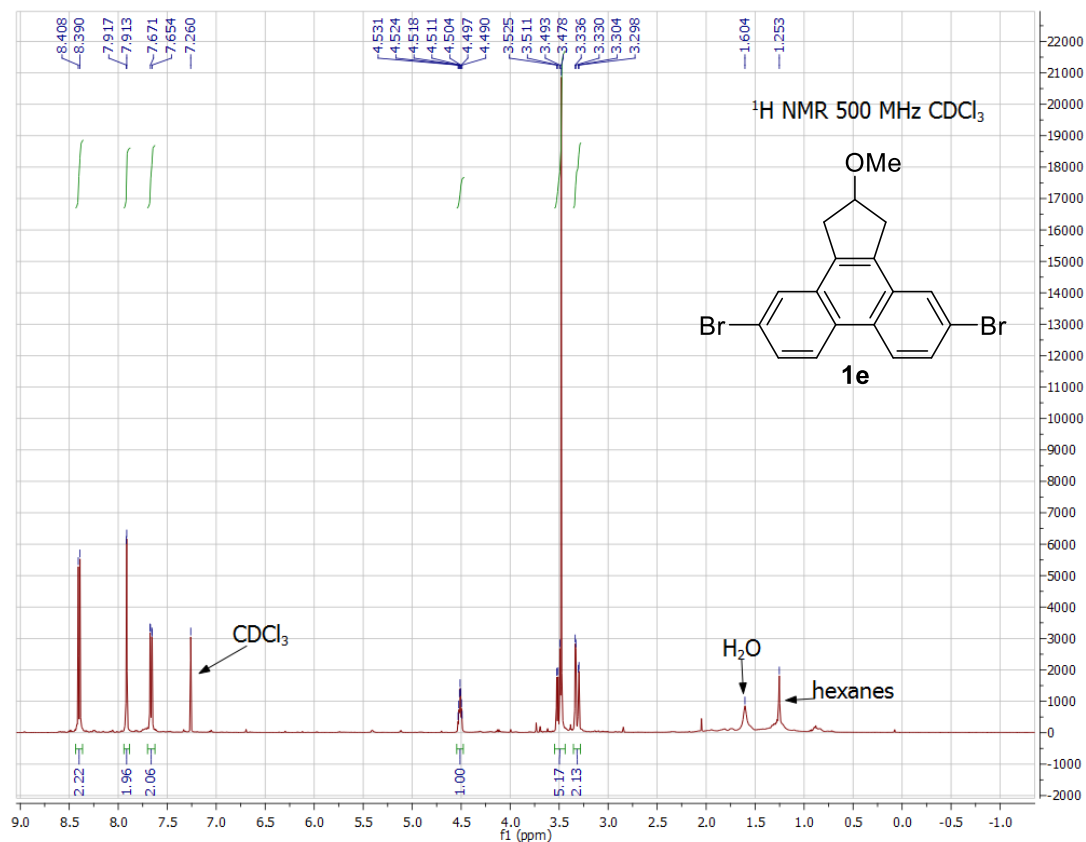


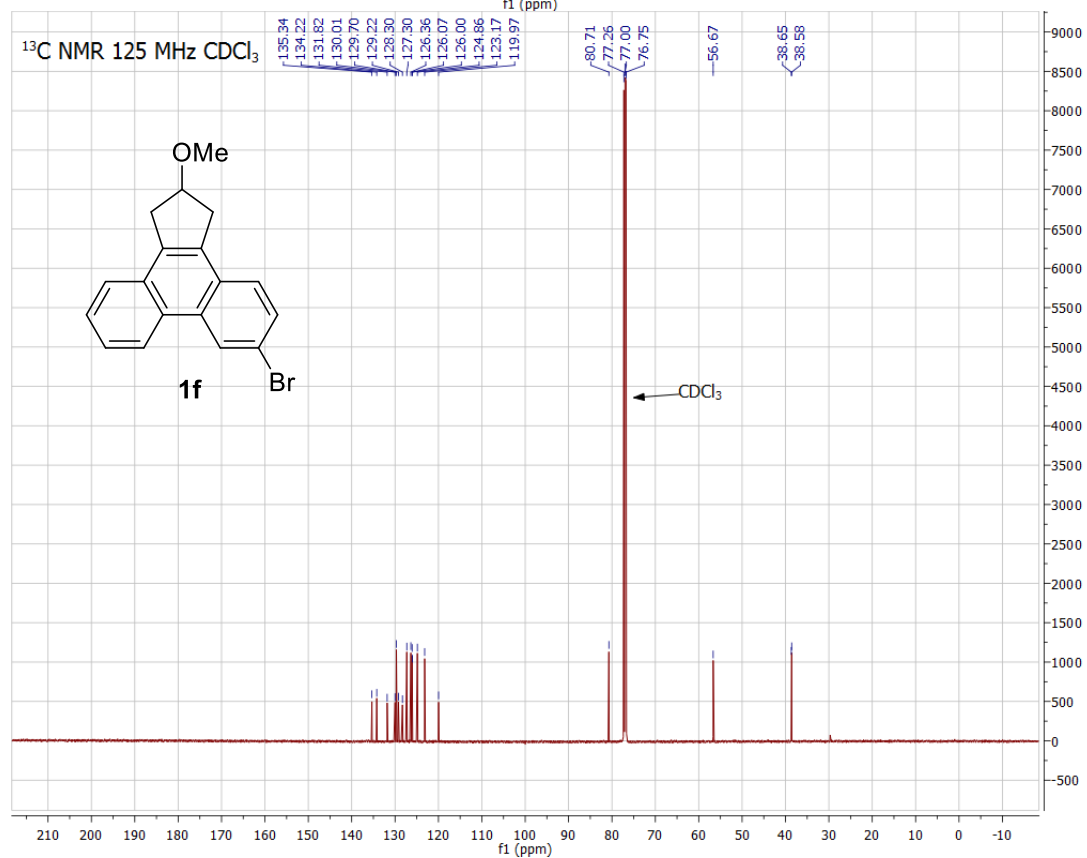
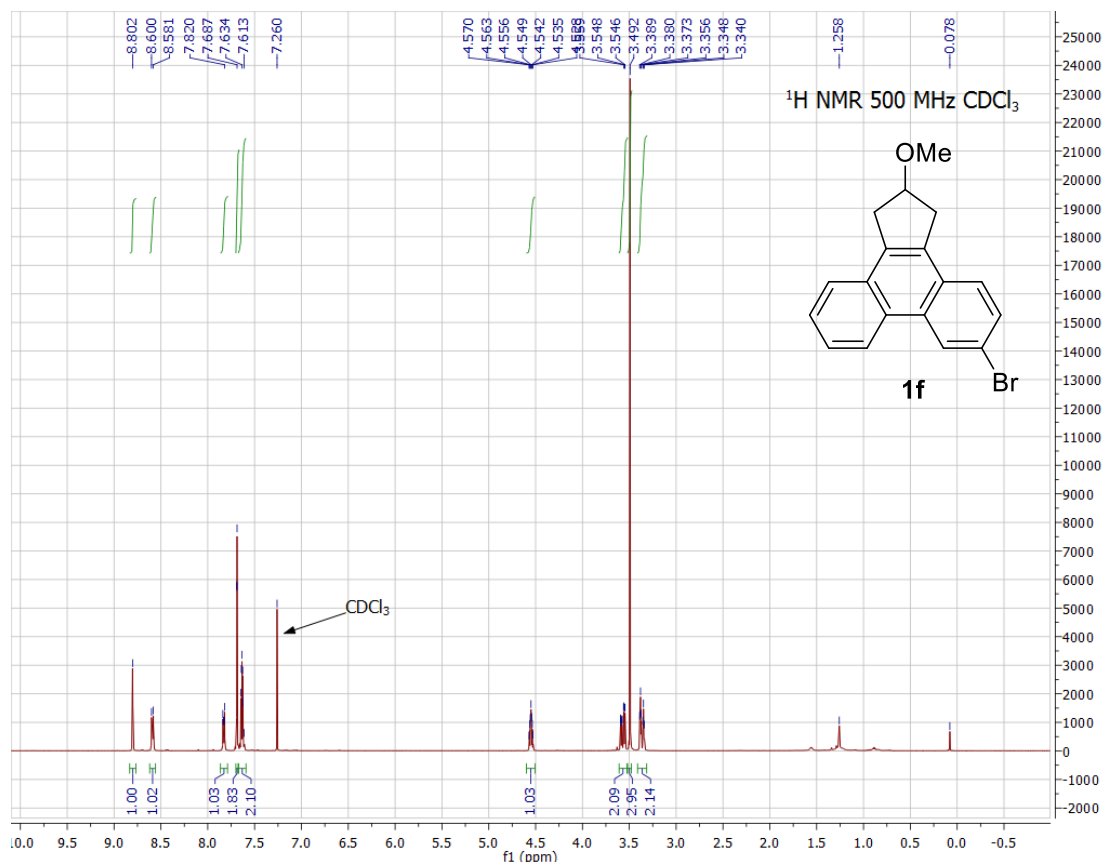
Methyl ether **1b** (0.048 g, 0.12 mmol) was dissolved in 3 mL CH_2Cl_2 and 6 mL acetonitrile in a flask. Sodium iodide (0.177 g, 1.2 mmol) was added and the solution was cooled to 0 °C. Aluminum trichloride (0.157 g, 1.2 mmol) was added, the solution darkened, and was stirred at 0 °C for 2 h. Then the reaction was warmed to room temperature and stirred for 16 h. The reaction mixture was then poured into 50 mL water and diluted with 50 mL CH_2Cl_2 . The layers were separated and the aqueous layer was extracted with 50 mL CH_2Cl_2 . The organic layers were combined and washed with 30 mL sodium thiosulfate (5 %, aq.). The organic layer was then dried over MgSO_4 , filtered, and the solvent removed *in vacuo* to give a yellow solid. The solid was purified by column chromatography (SiO_2 , 3:1 hexanes:ethyl acetate) to give **9b** (0.031 g, 67% yield) as a white solid. M.p. >200 °C ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{SO}$) δ 9.02 (s, 2H), 7.77-7.82 (m, 4H), 5.0 (bs, 1H), 4.76-4.84 (m, 1H), 3.47 (dd, $J=16$ Hz, 6.4 Hz, 2H), 3.15 (dd, $J=16$ Hz, 2.8 Hz, 2H). ^{13}C NMR (100 MHz, $(\text{CD}_3)_2\text{SO}$) δ 135.5, 130.24, 130.15, 128.3, 126.7, 126.0, 119.6, 99.3, 69.8, 41.6. HRMS (EI) calcd. for $\text{C}_{17}\text{H}_{12}\text{OBr}_2$ 389.9255 found 389.9254.

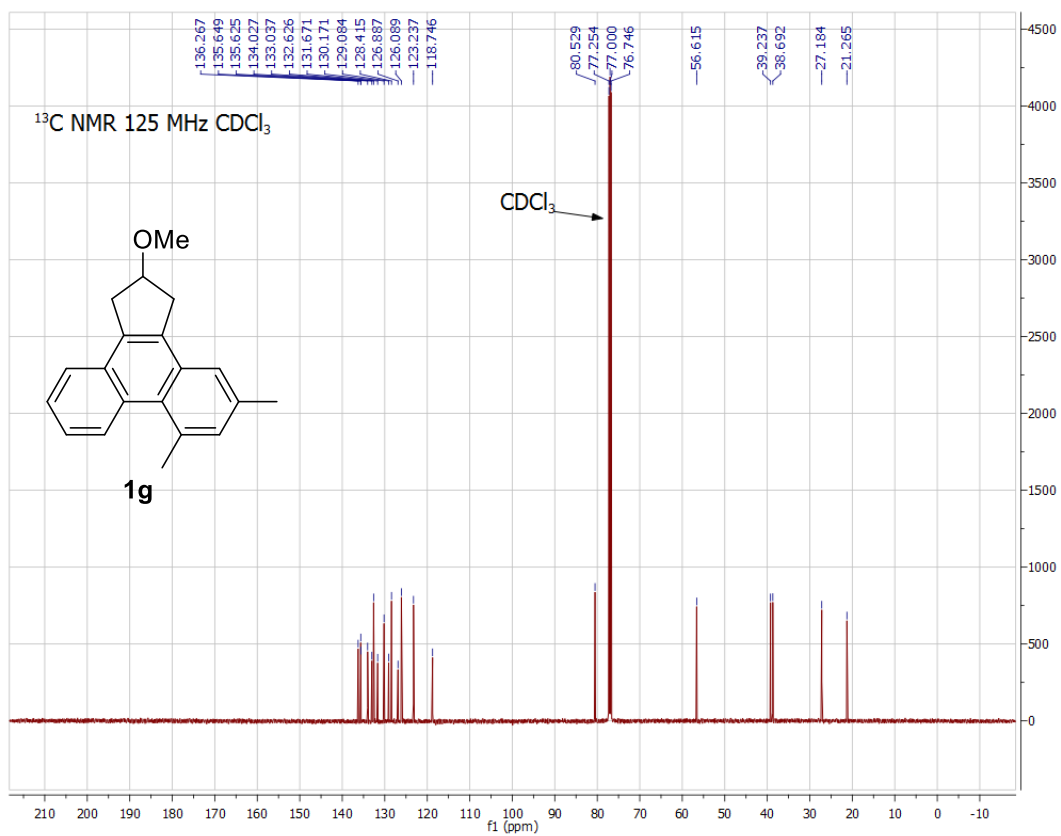
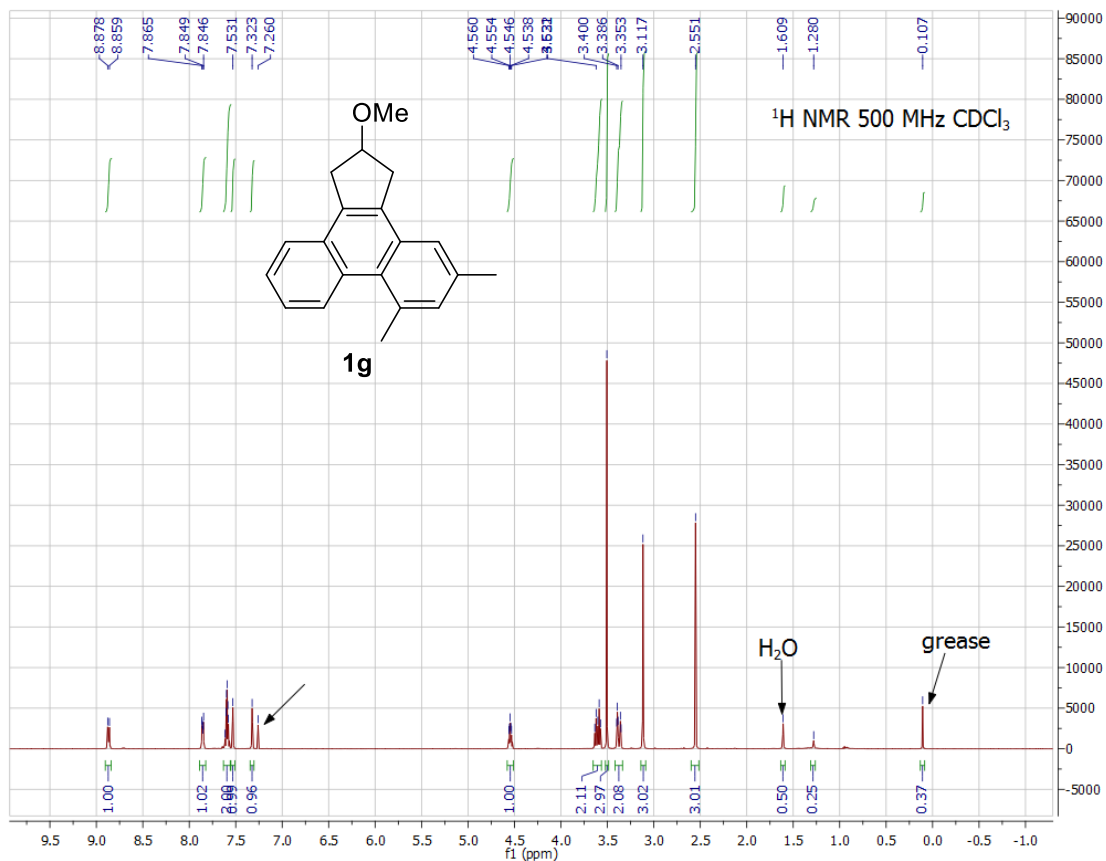


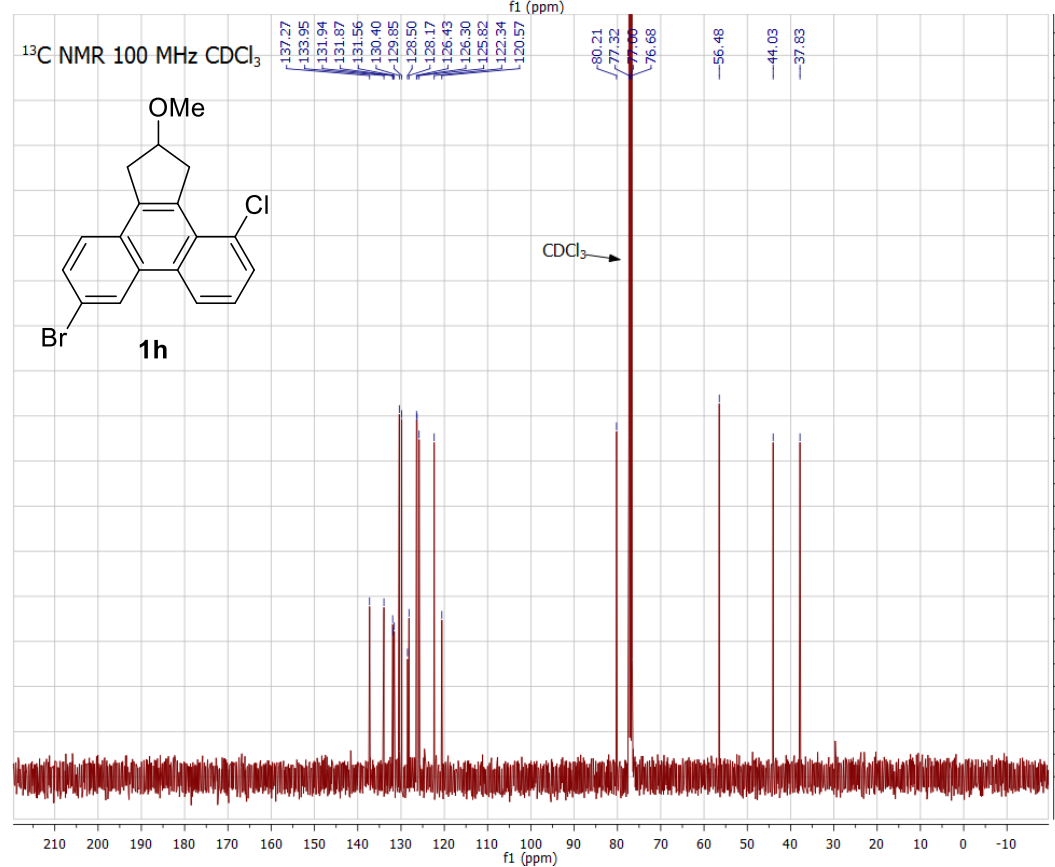
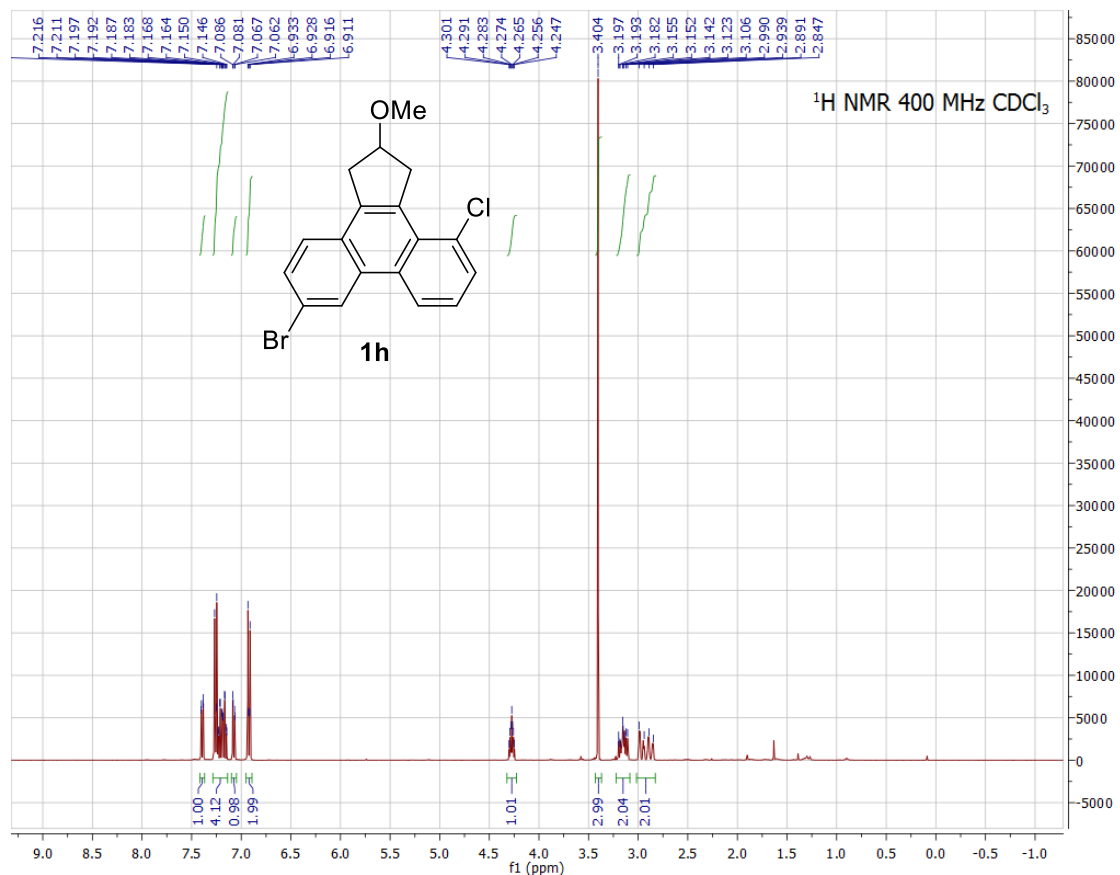


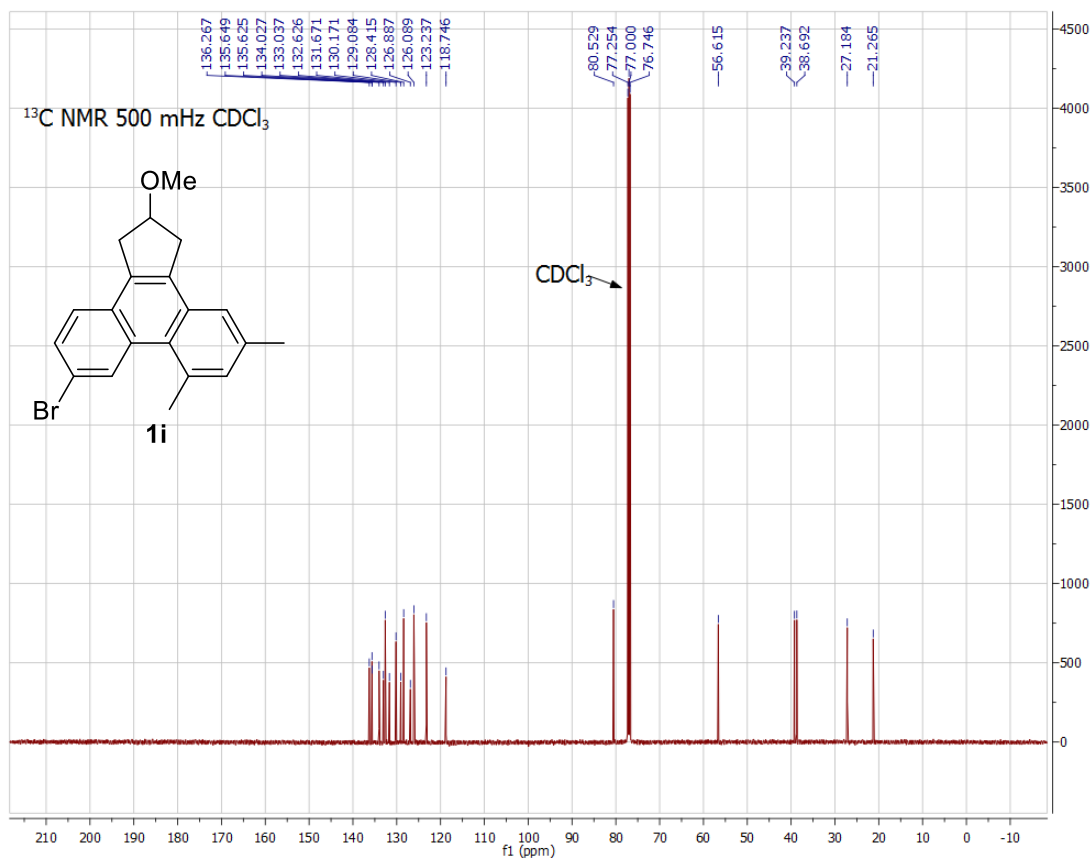
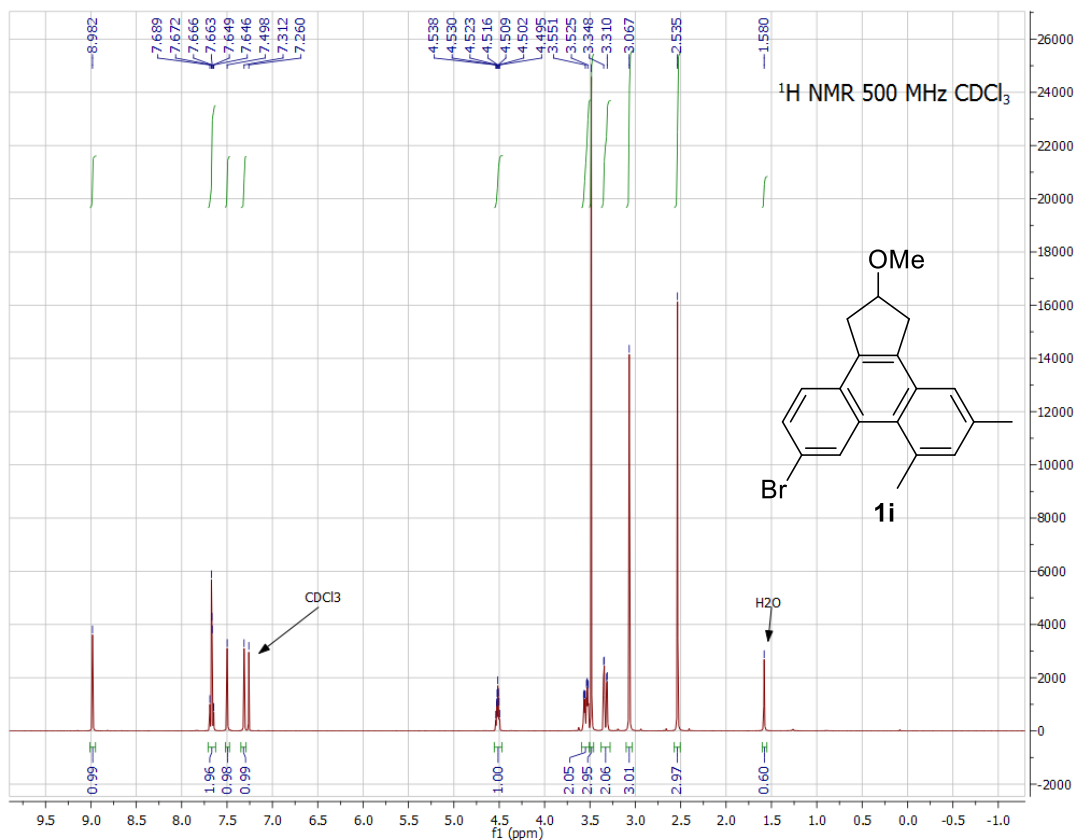


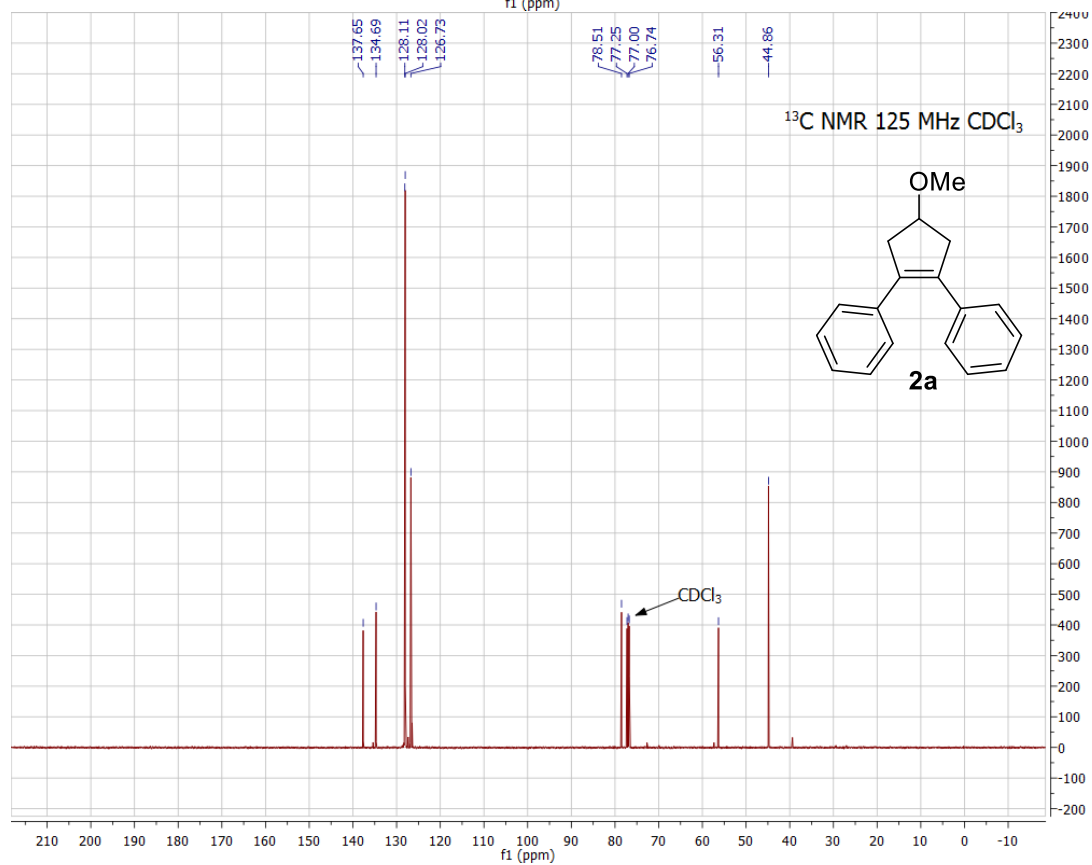
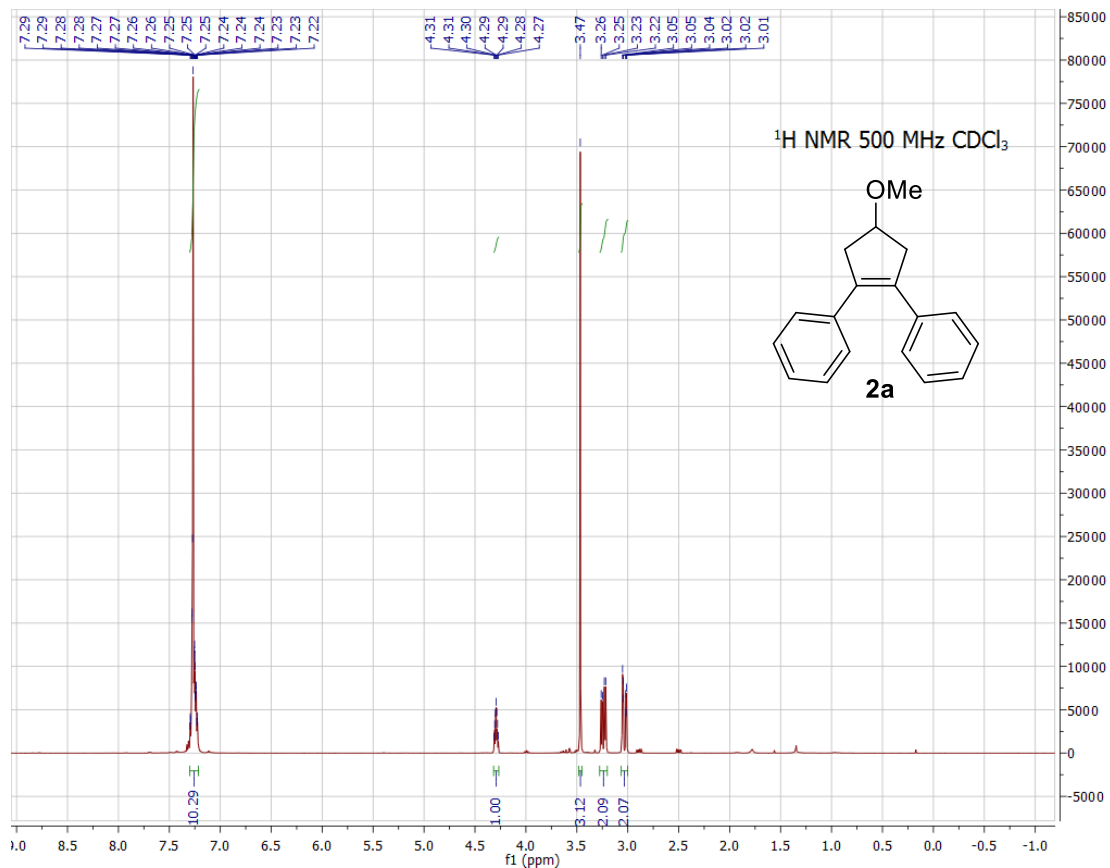


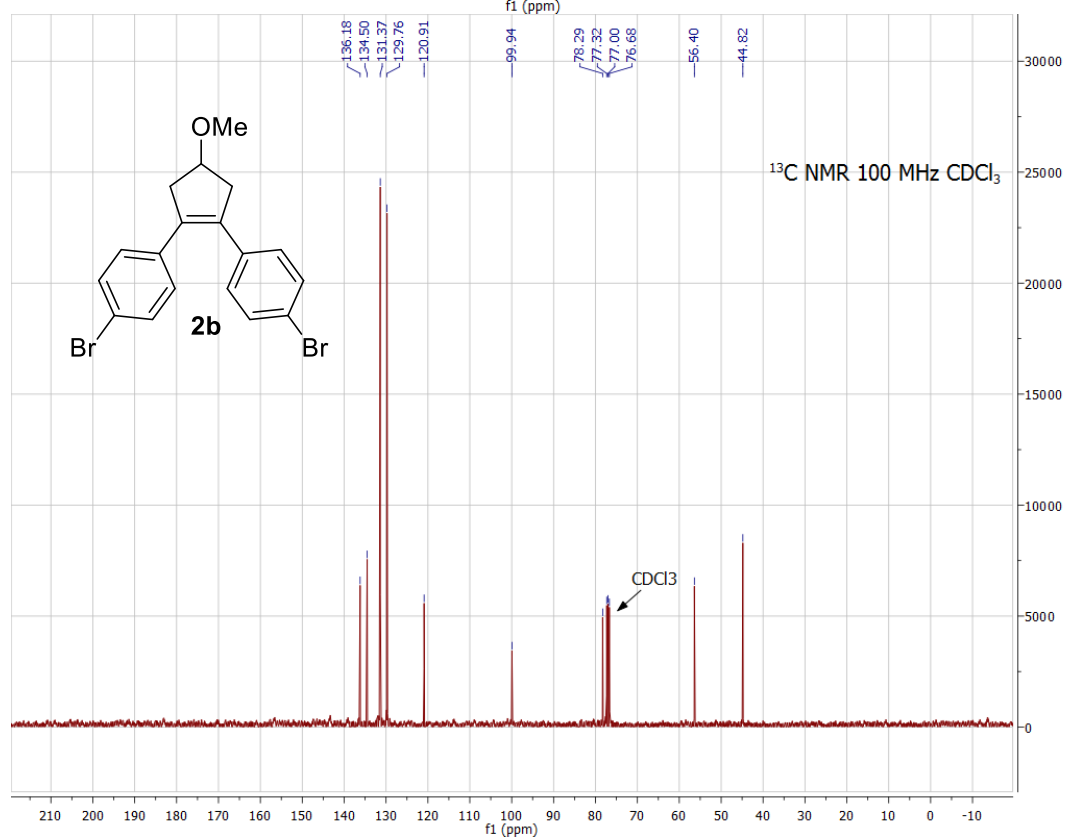
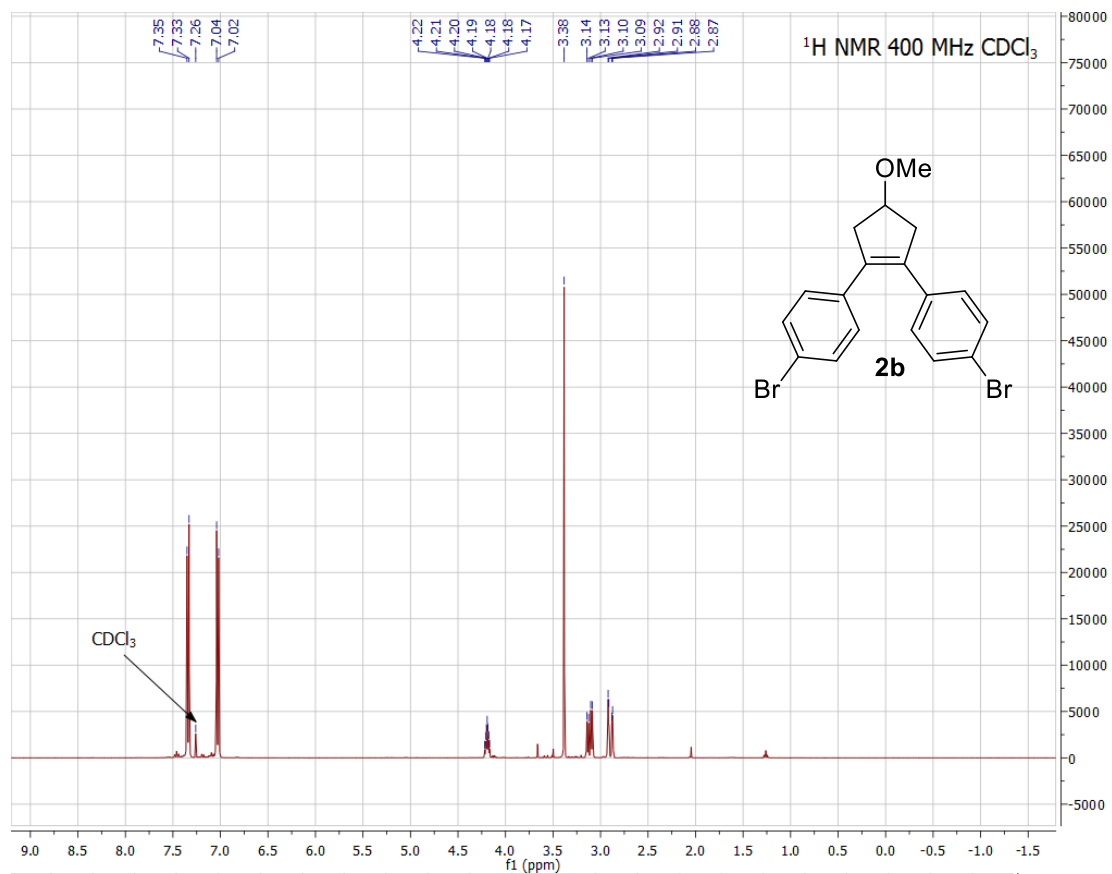


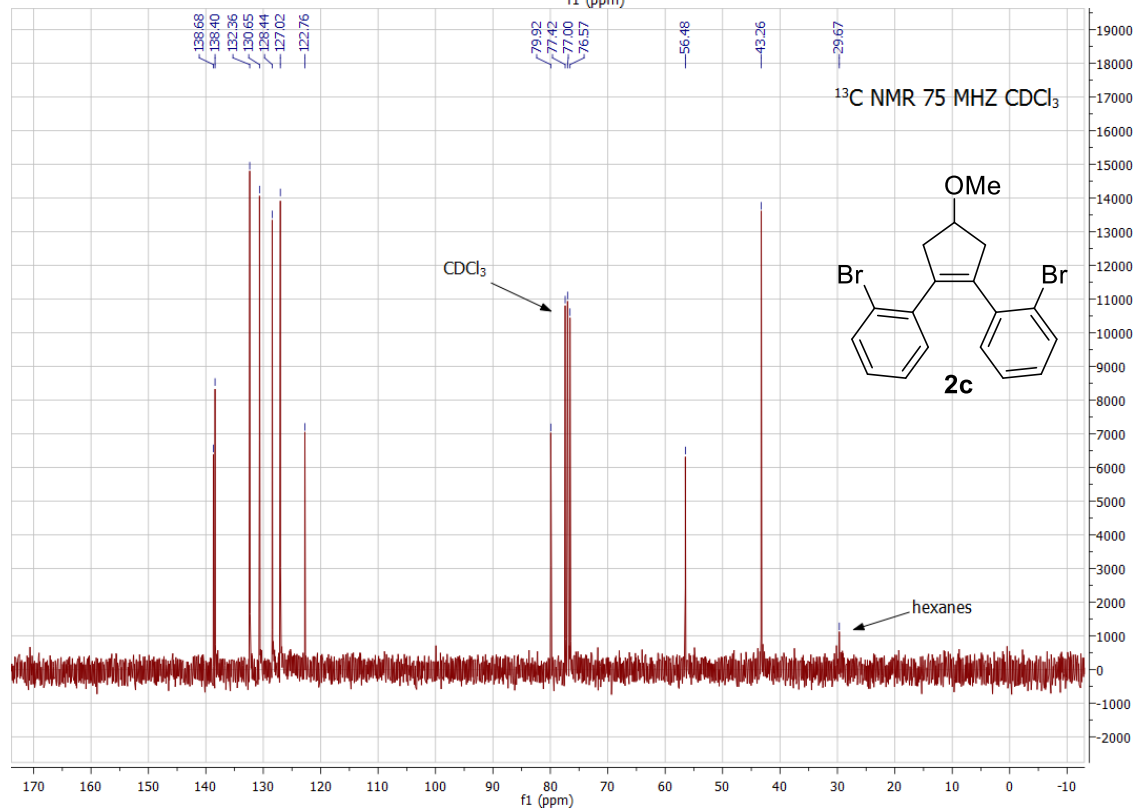
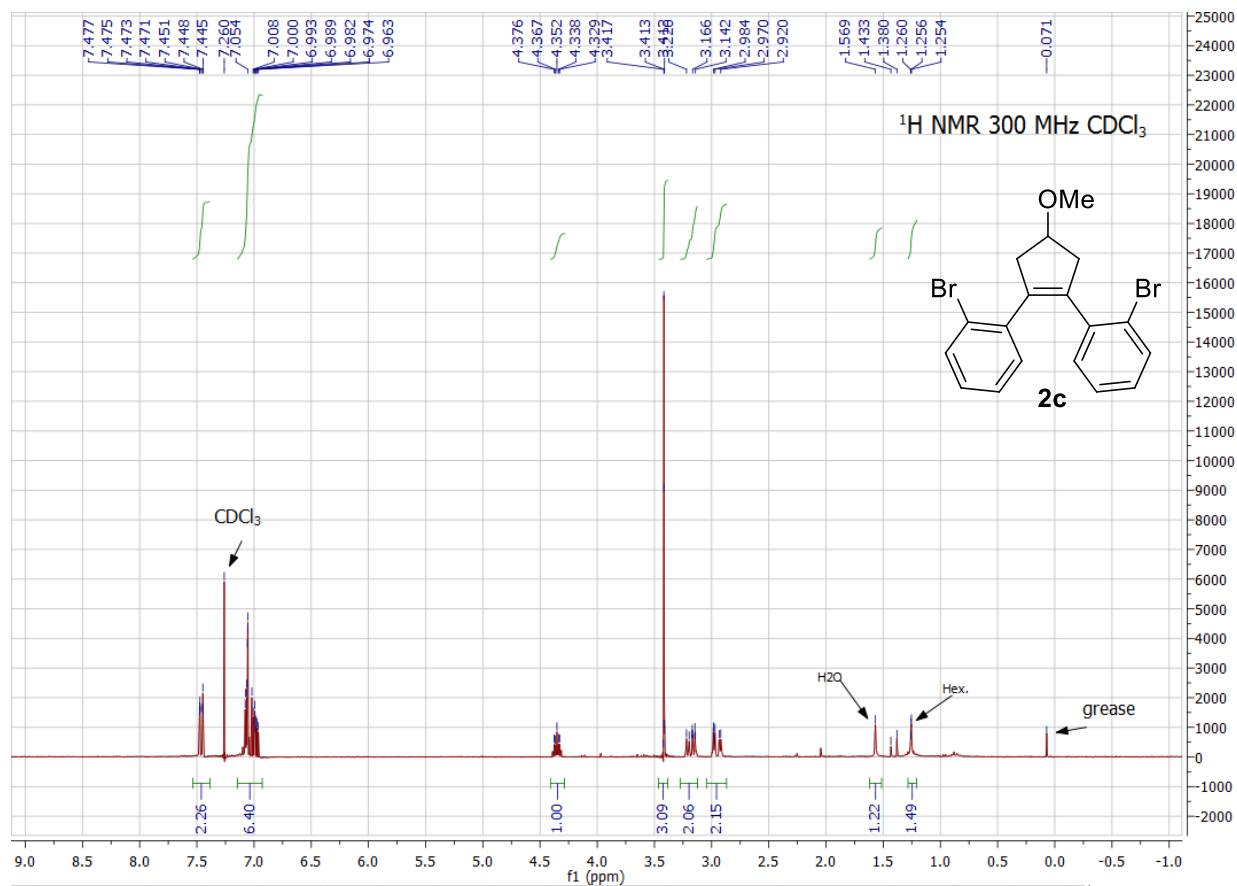


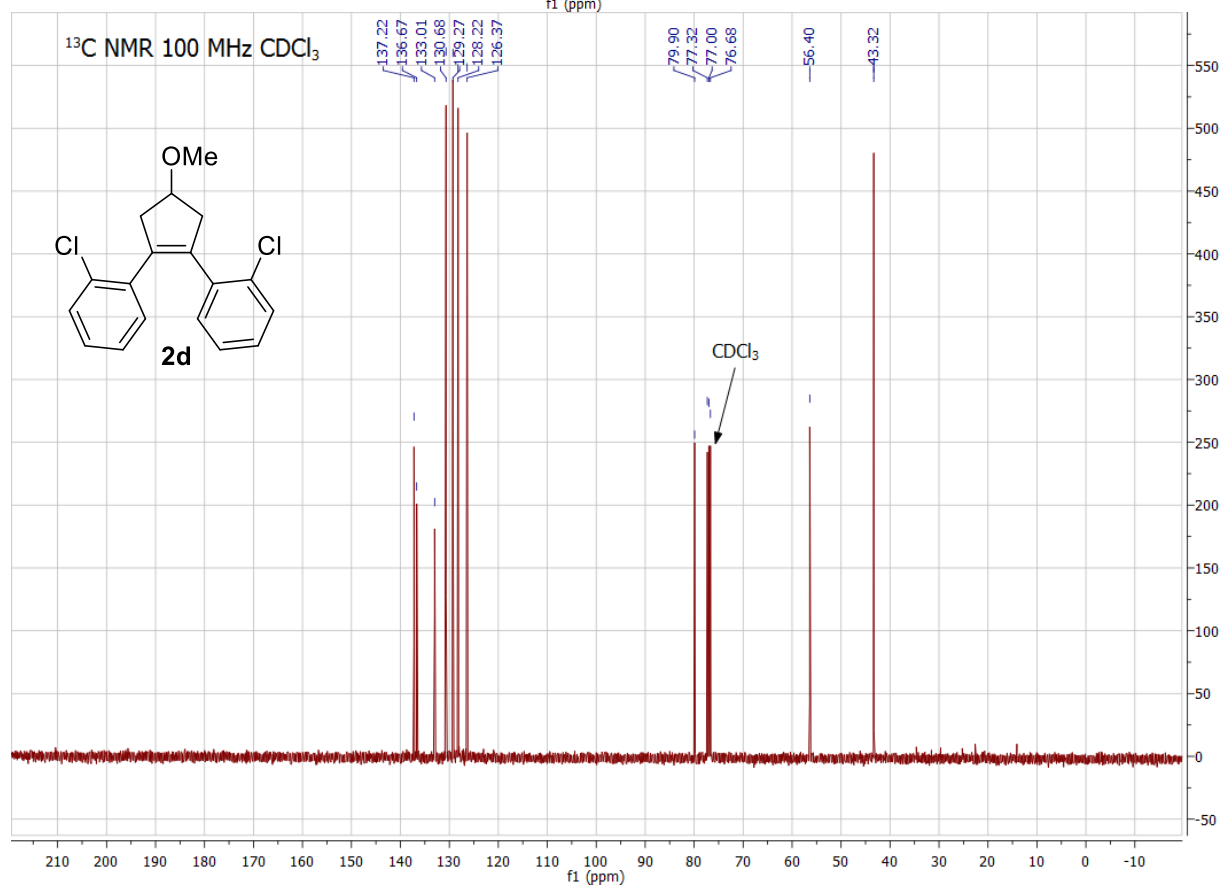
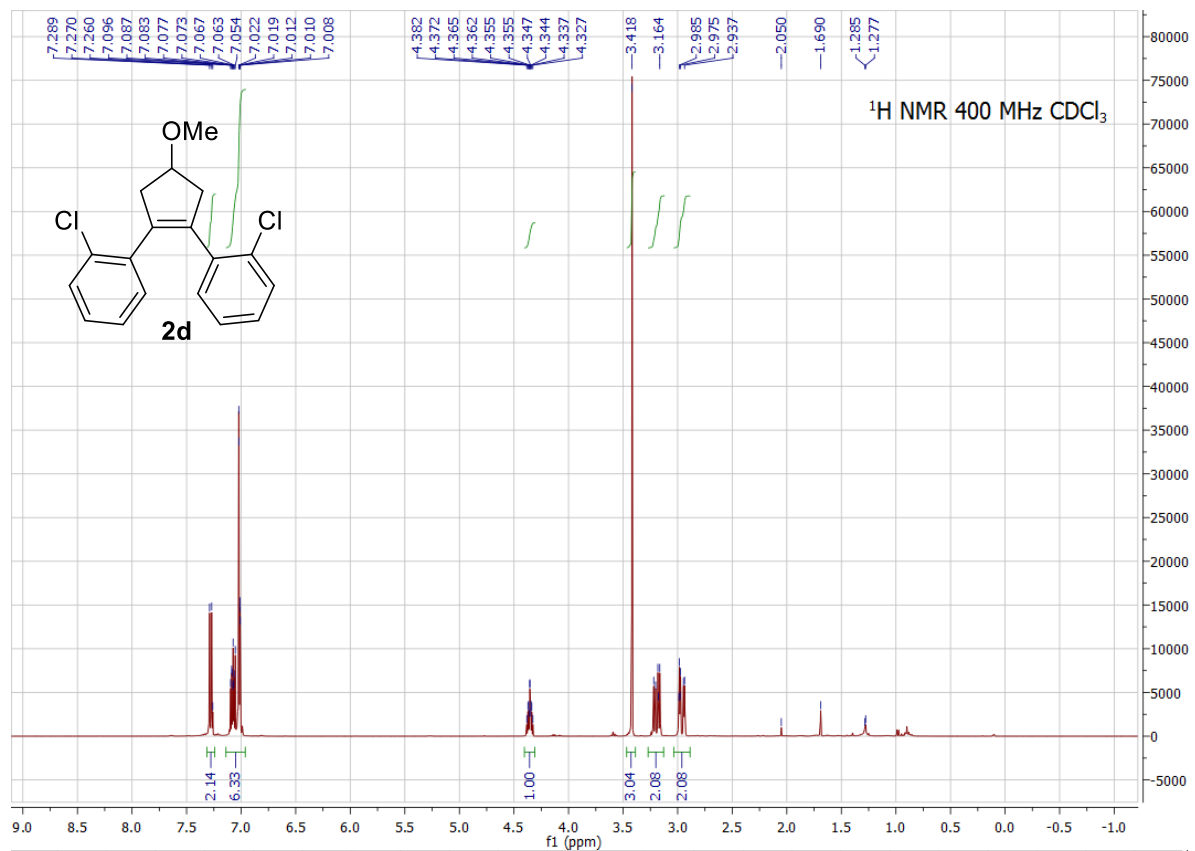


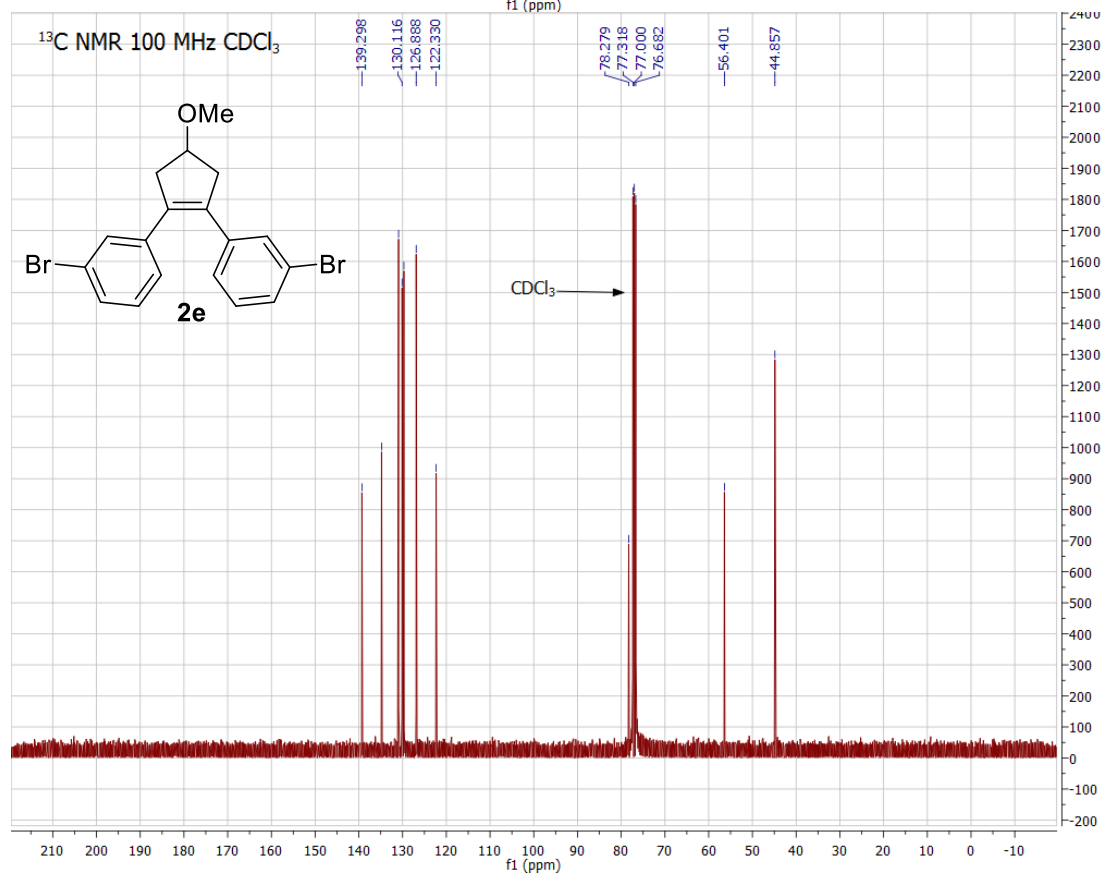
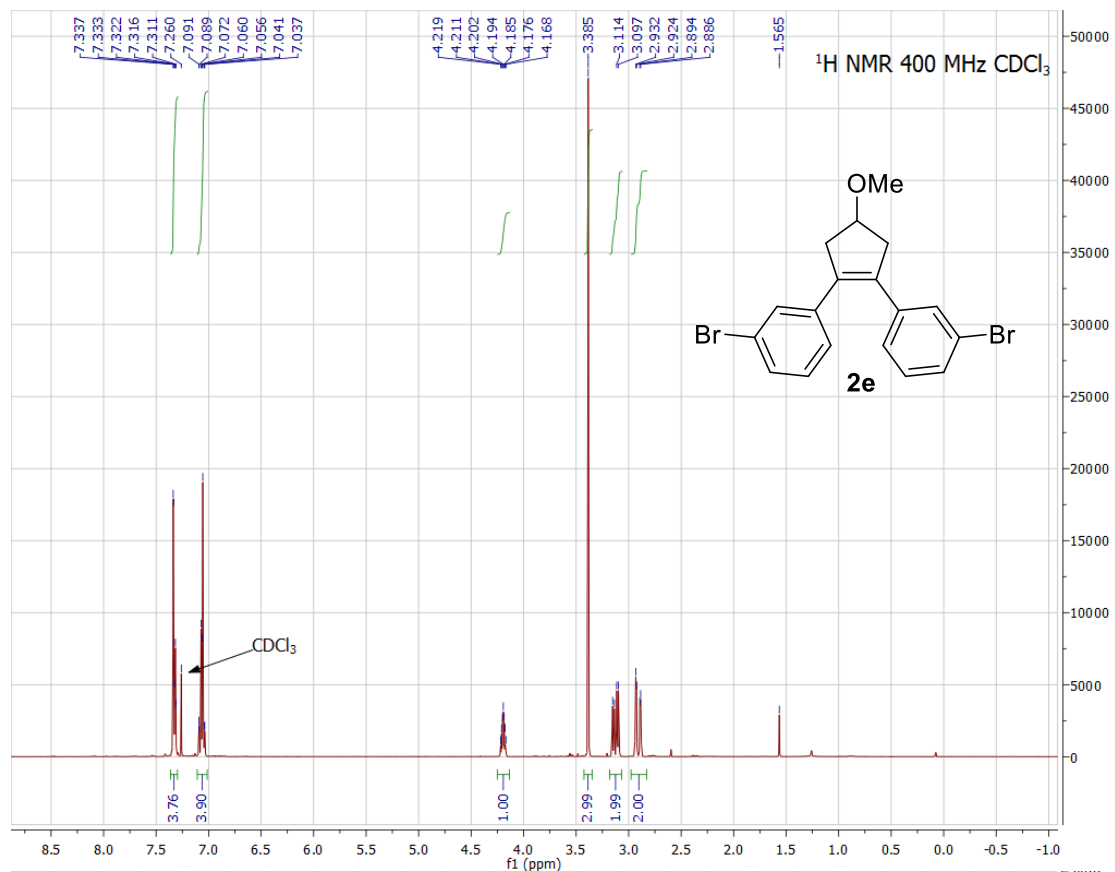


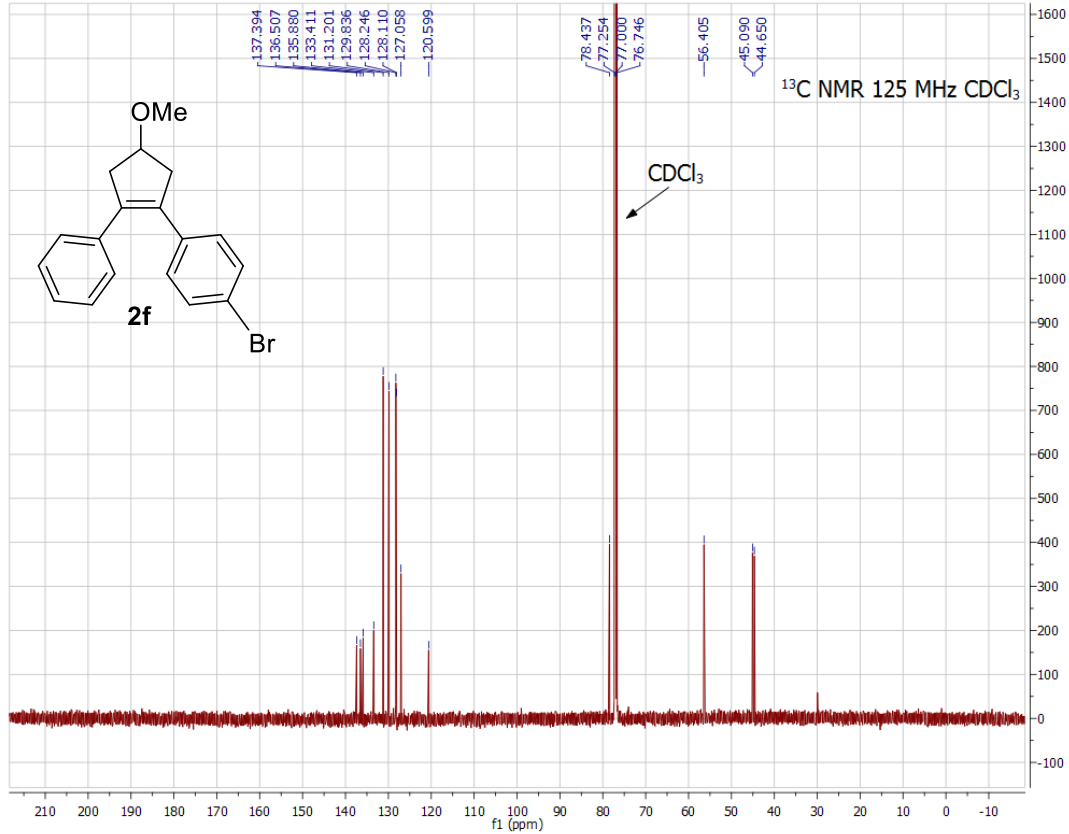
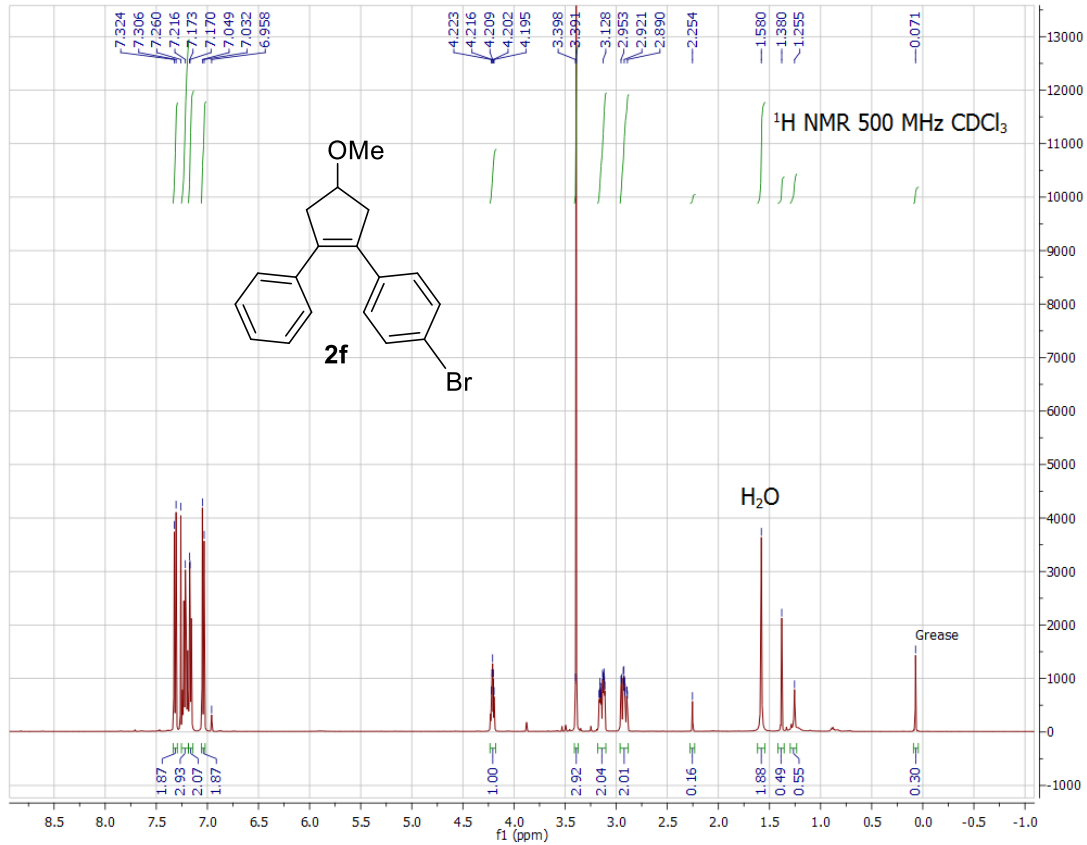


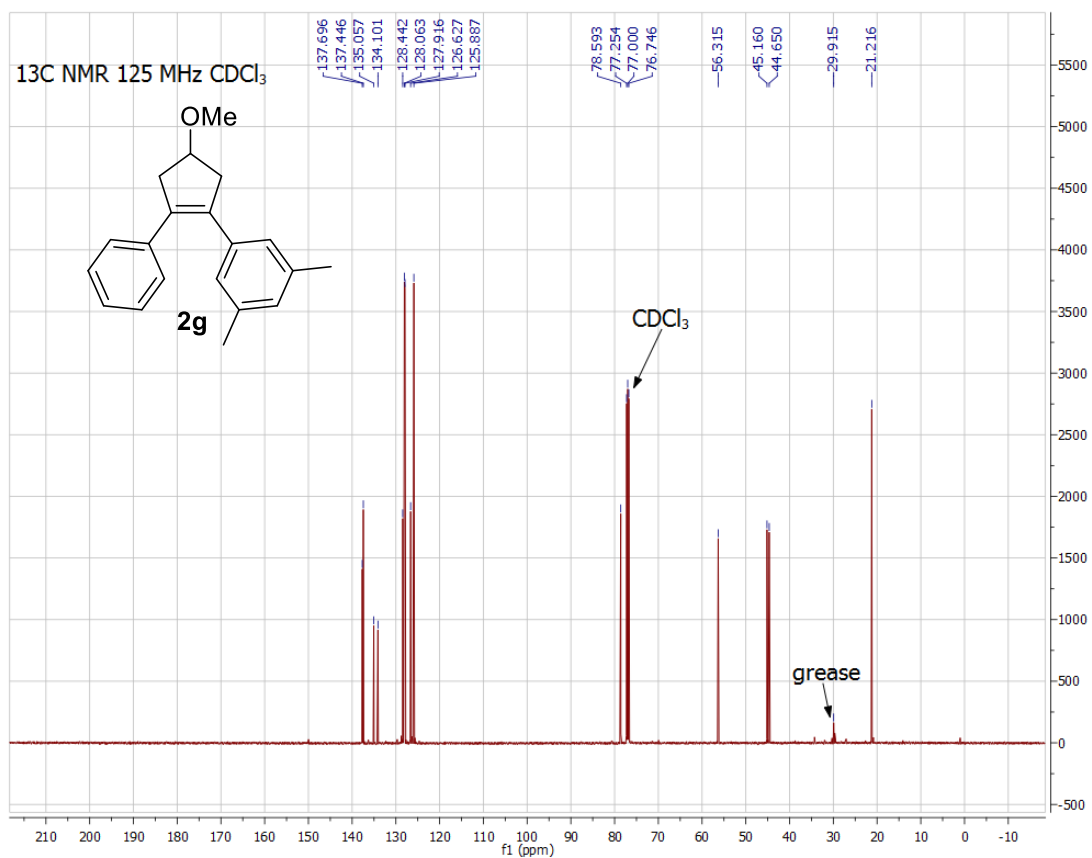
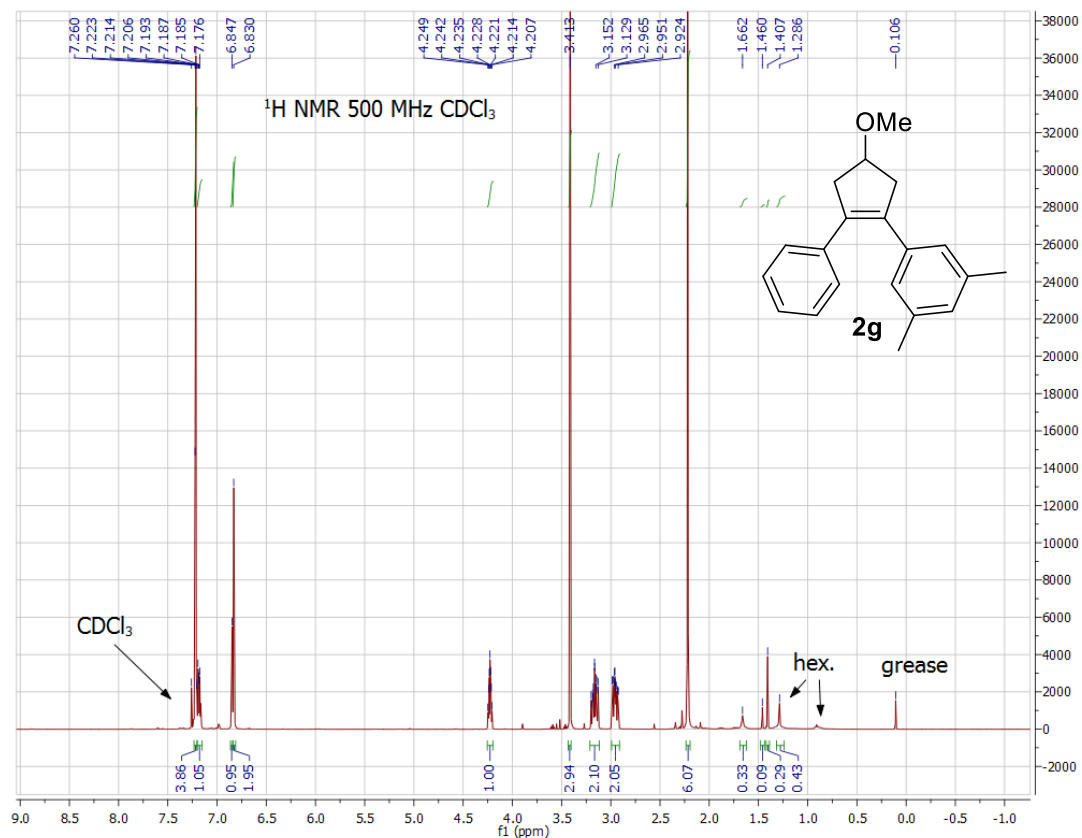


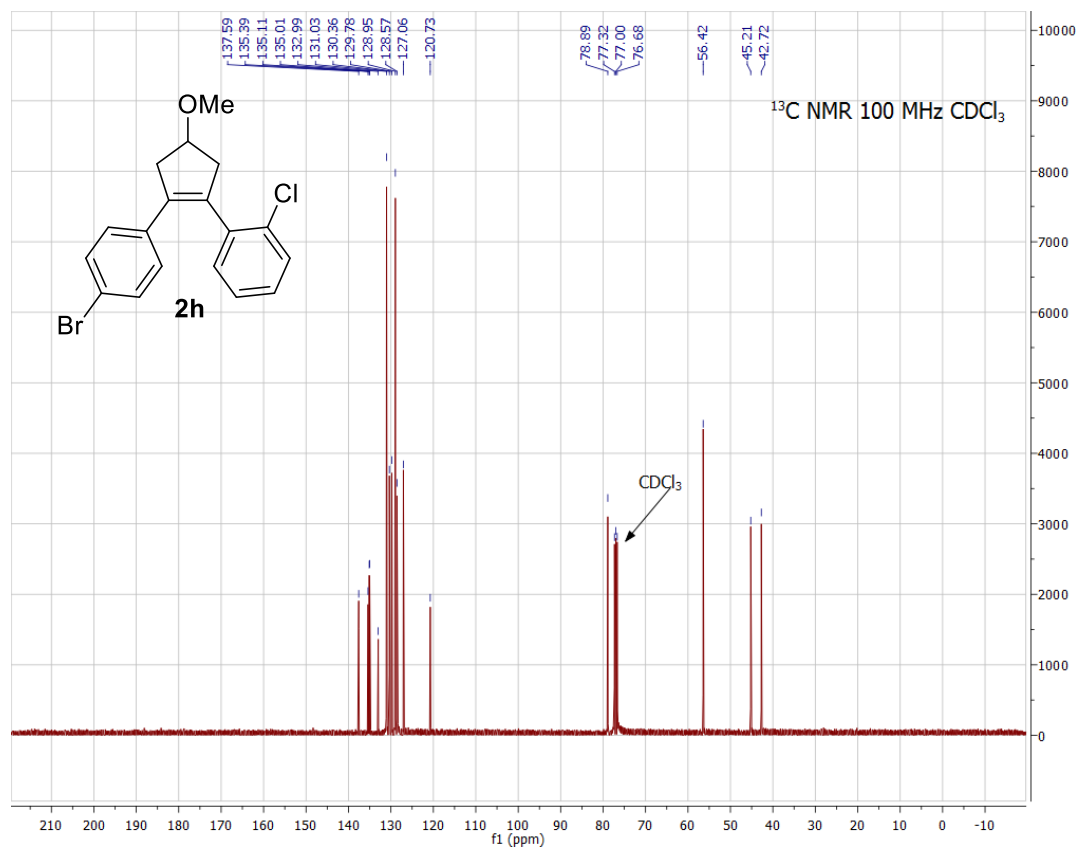
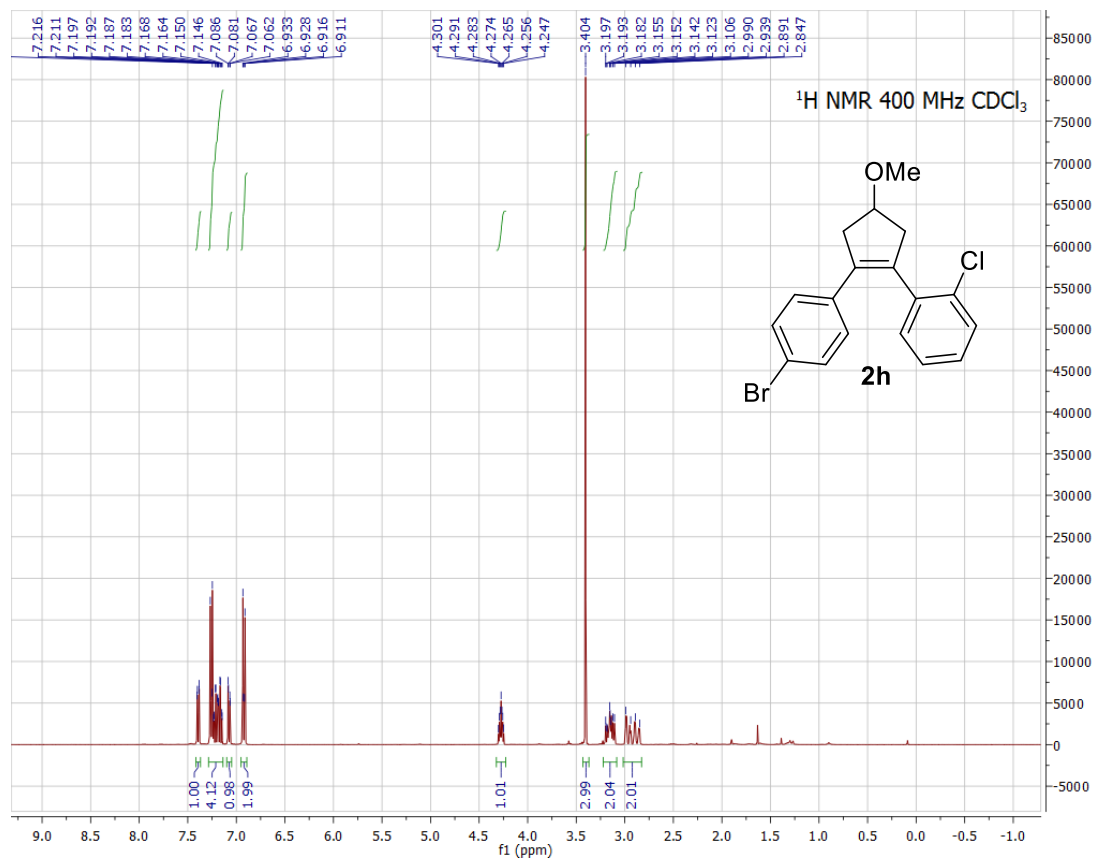


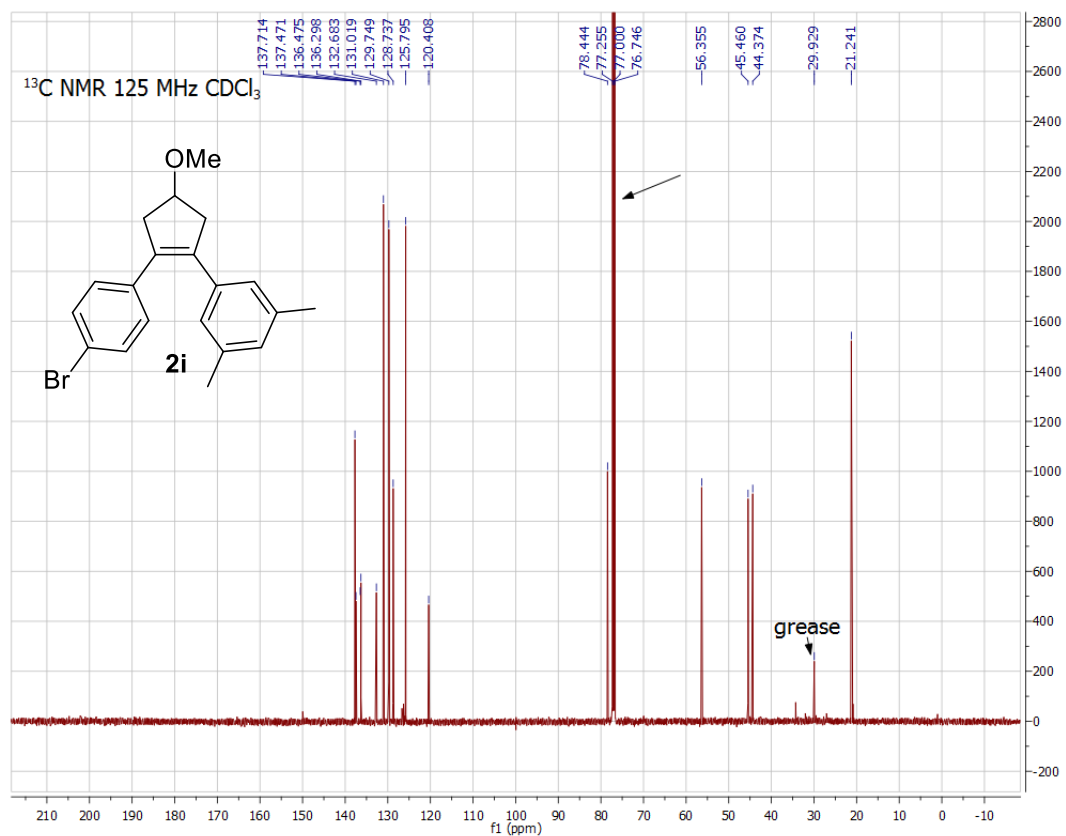
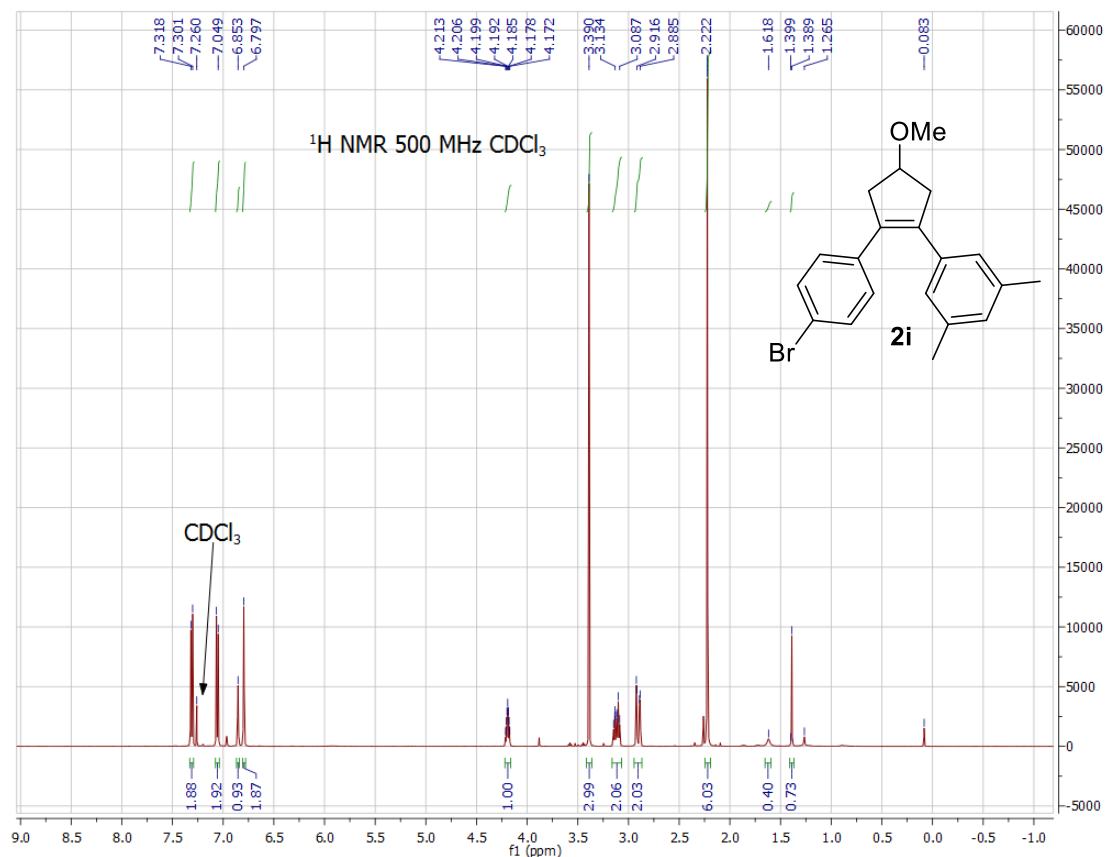


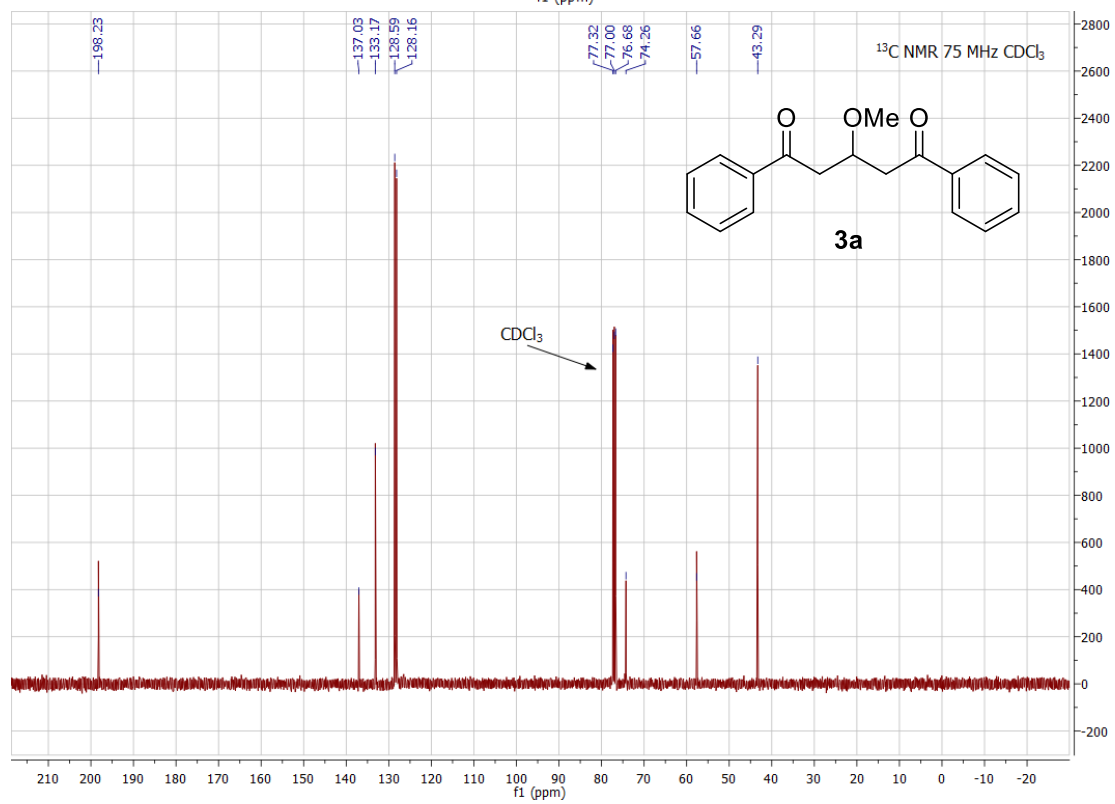
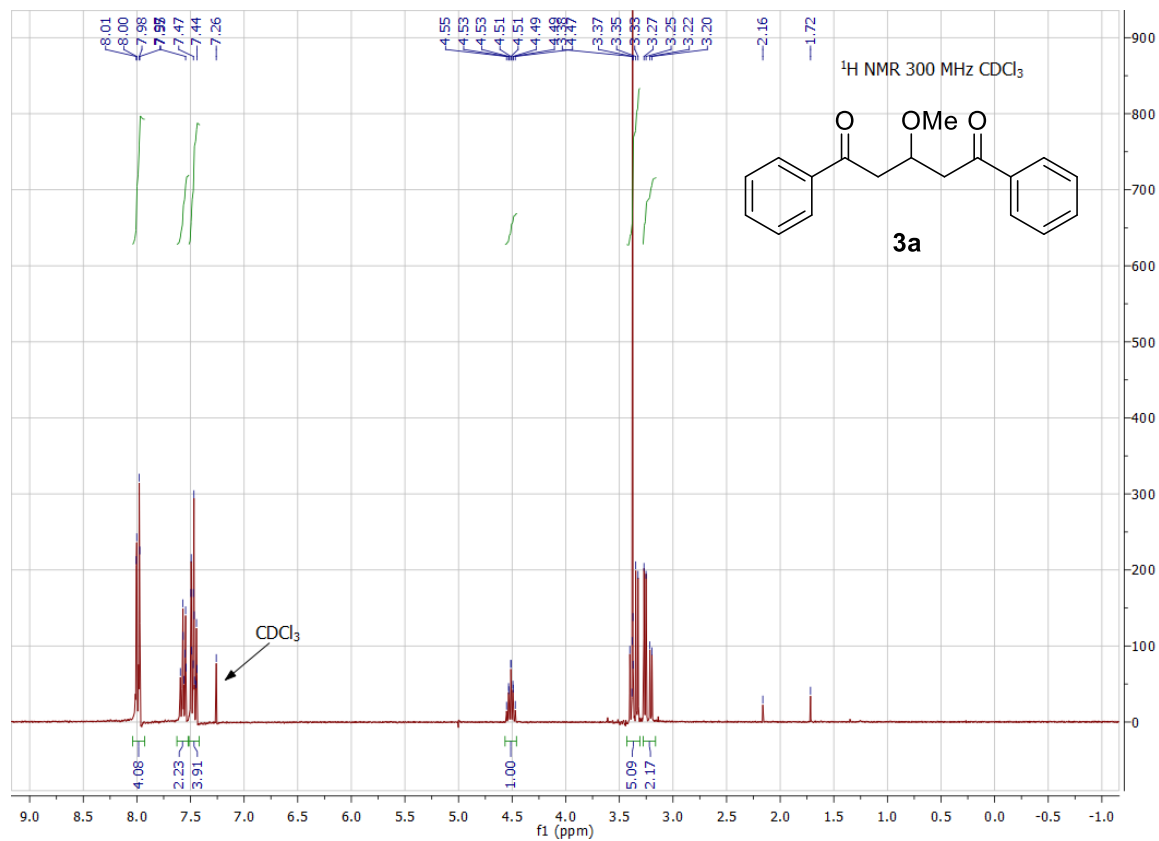


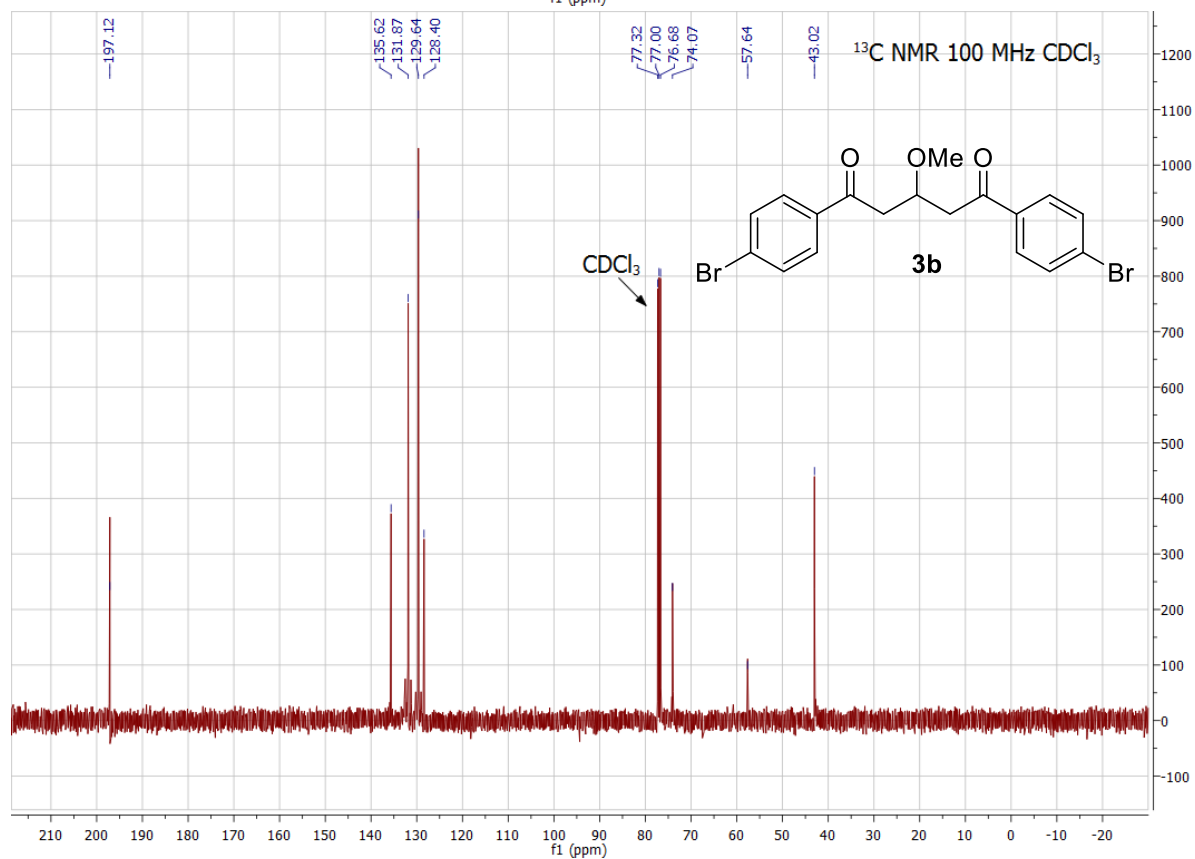
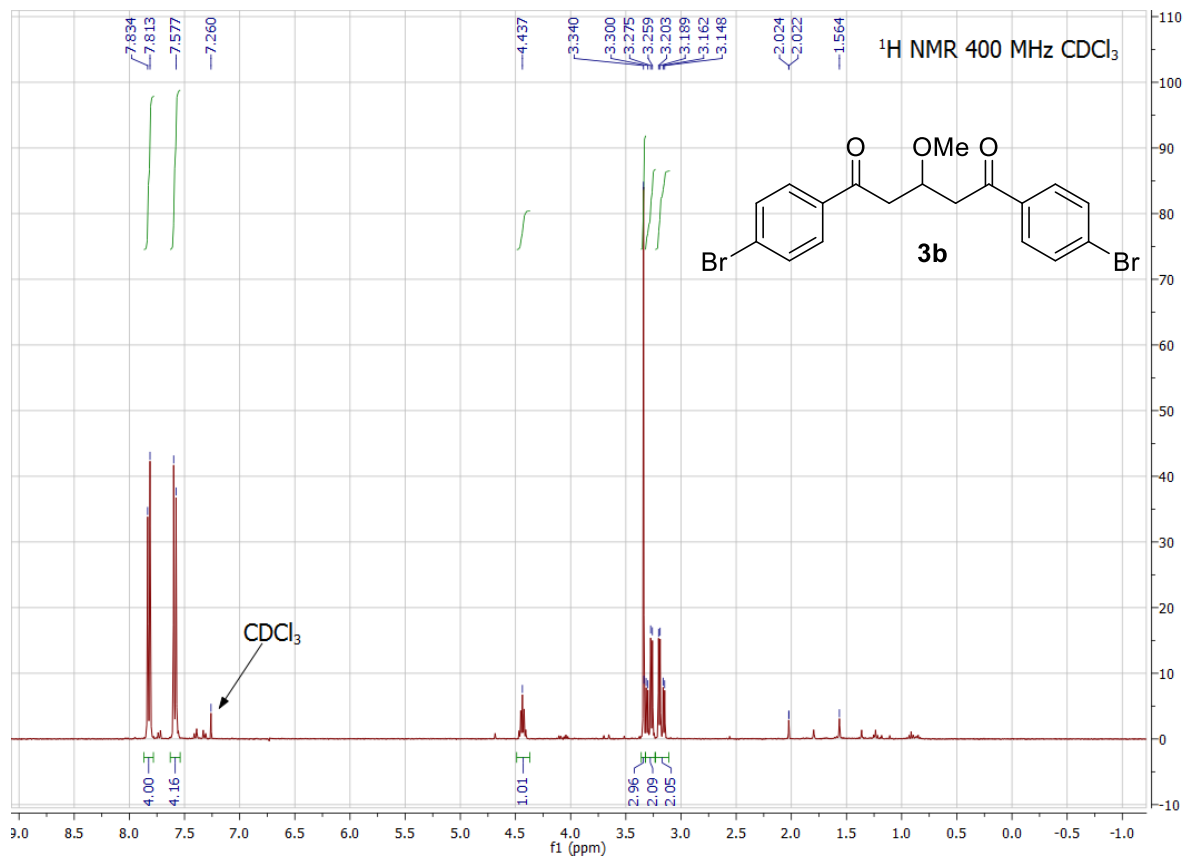


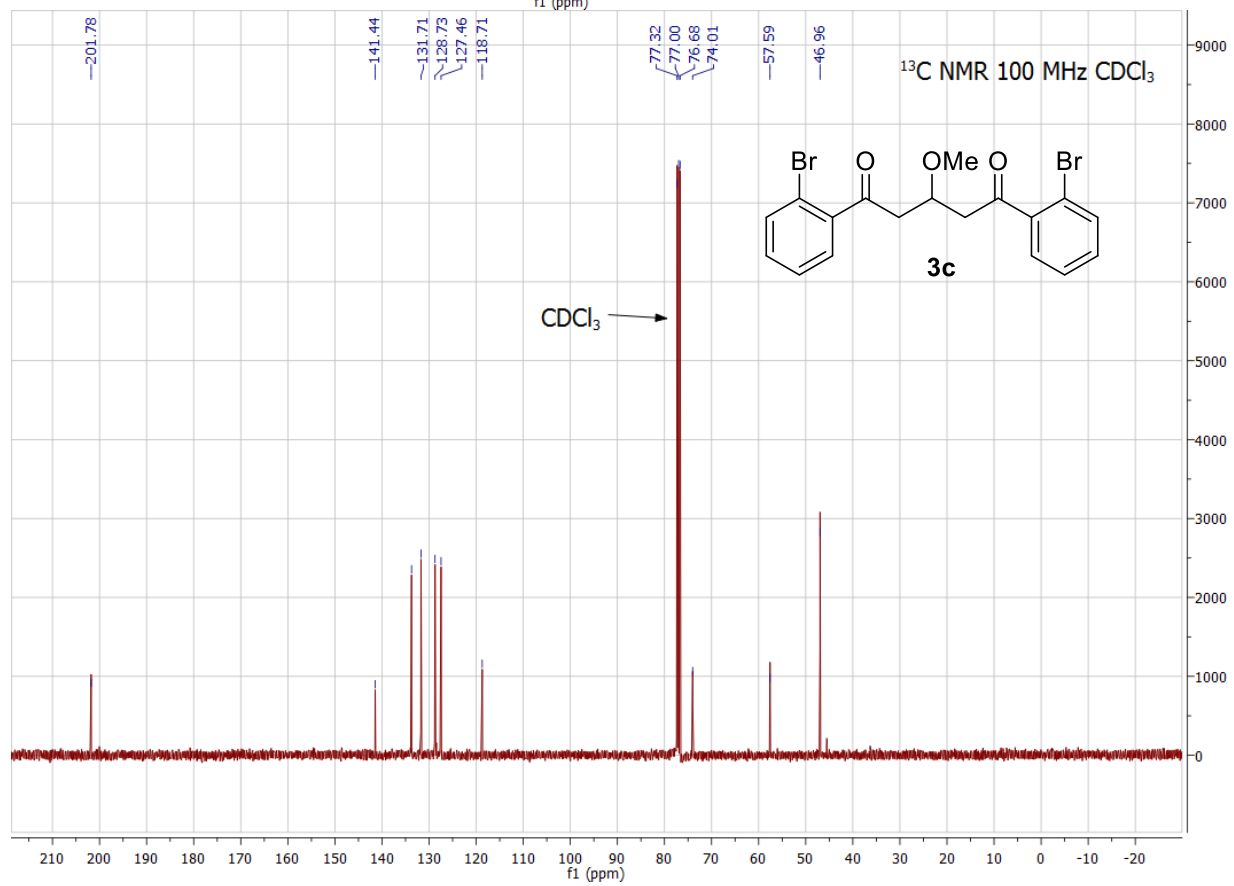
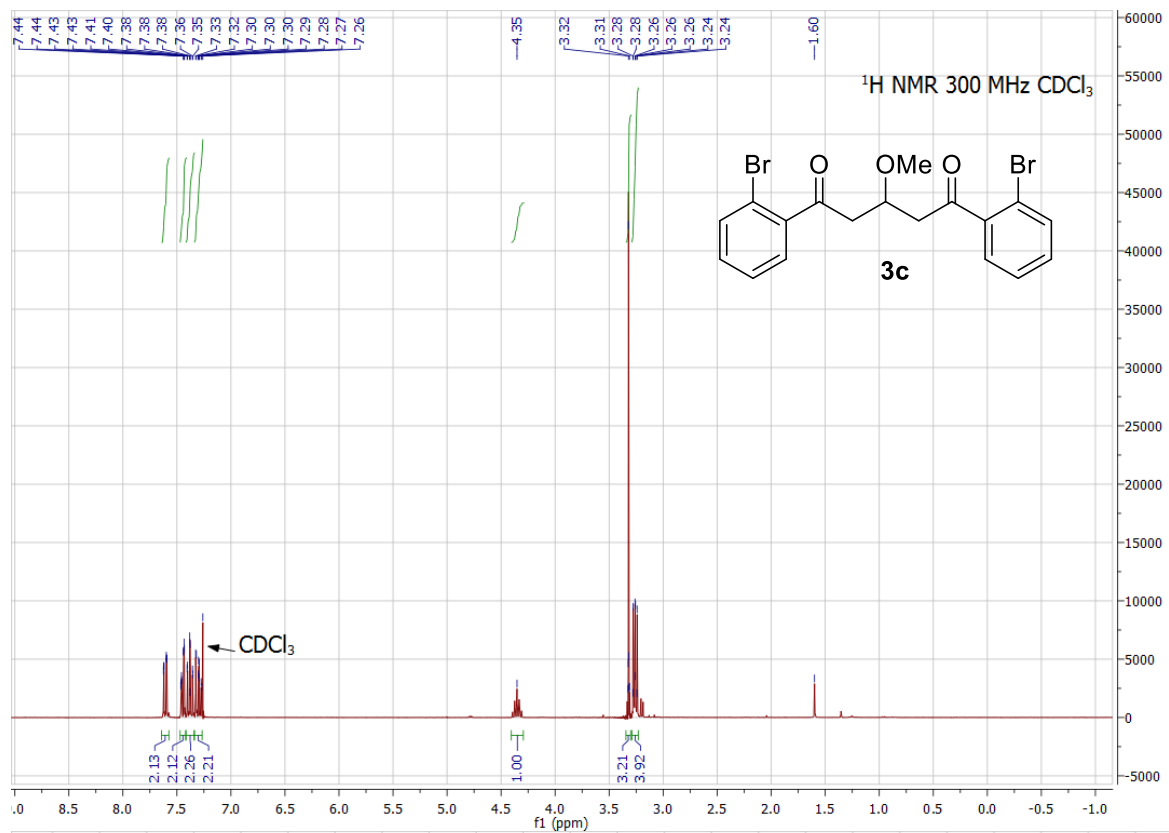


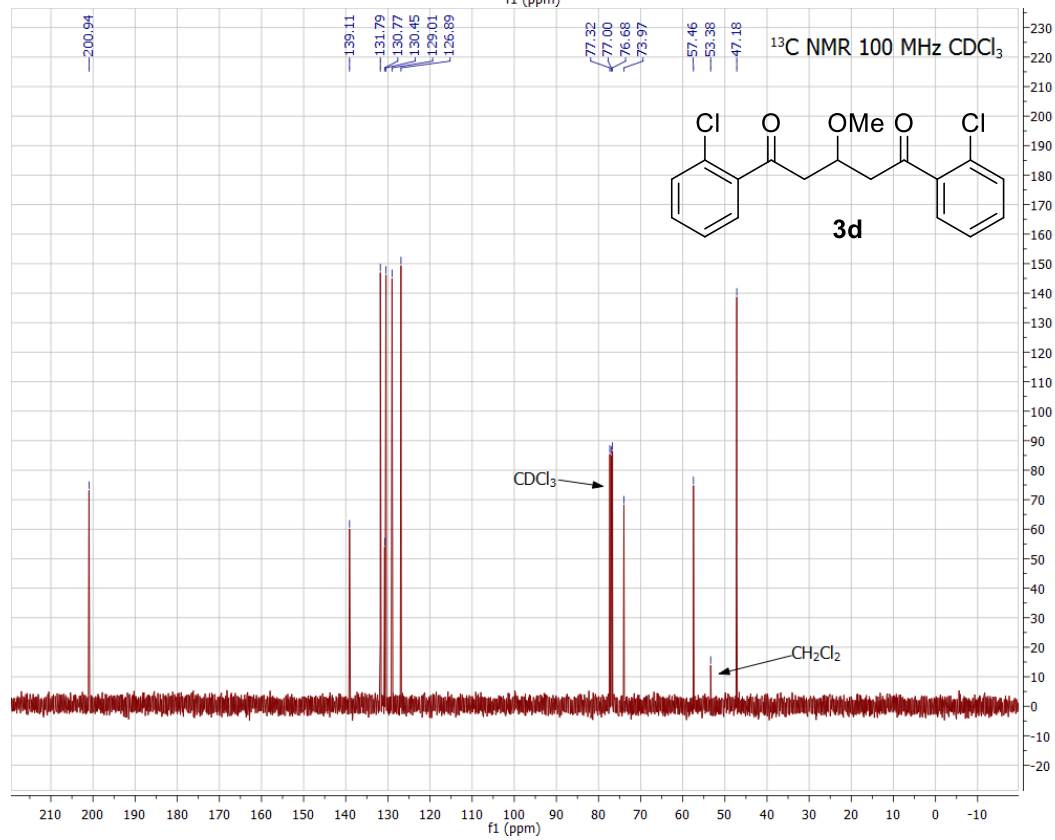
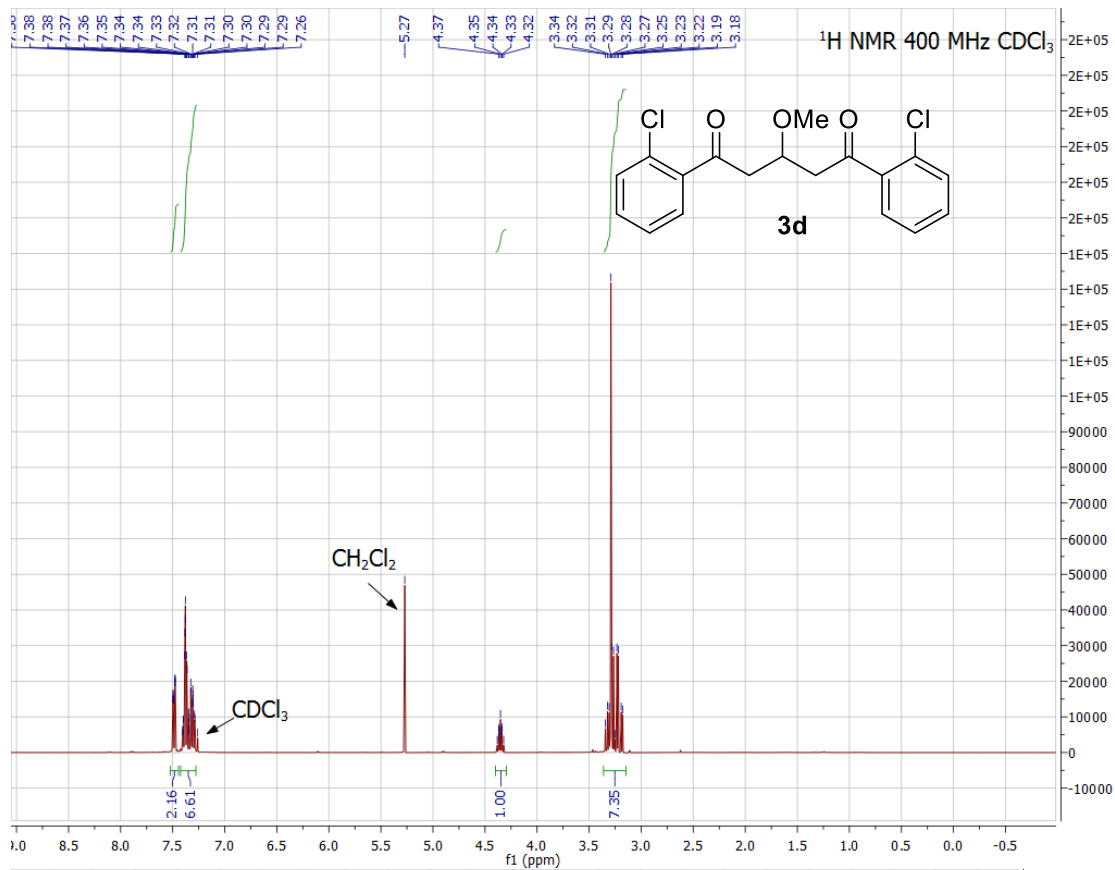


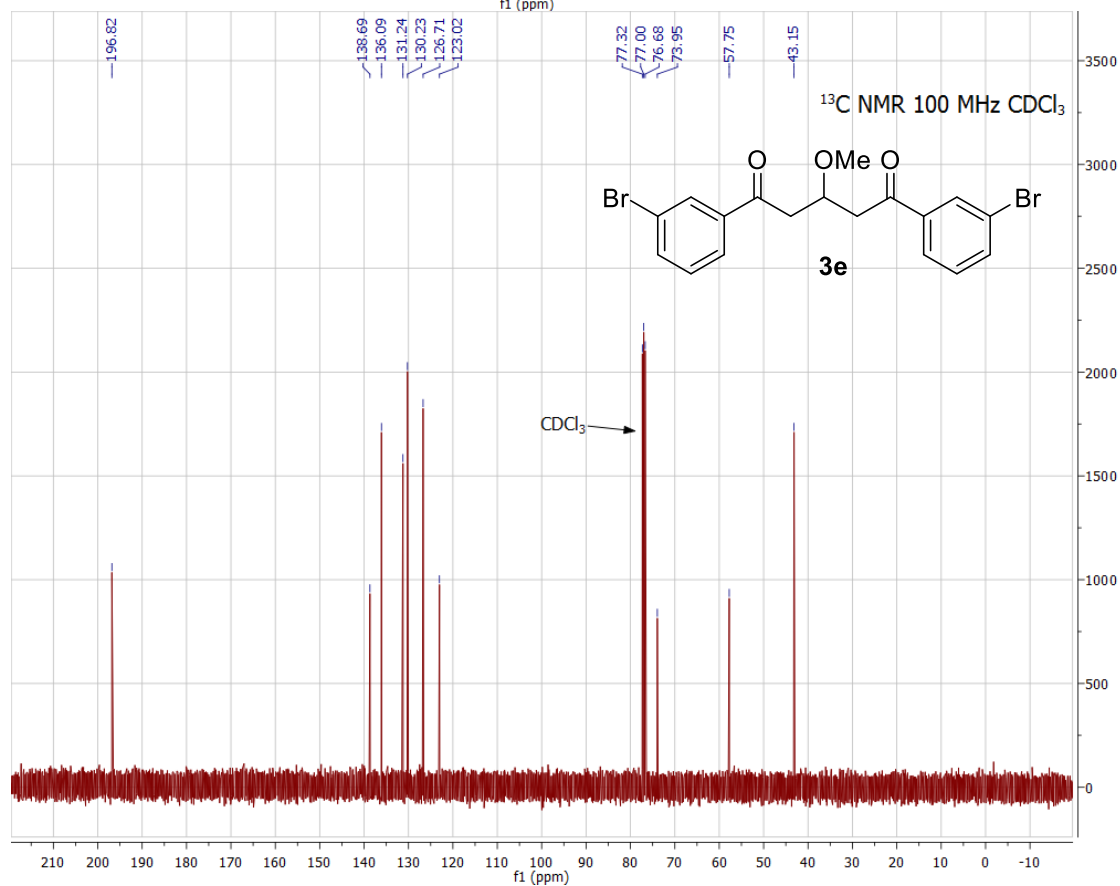
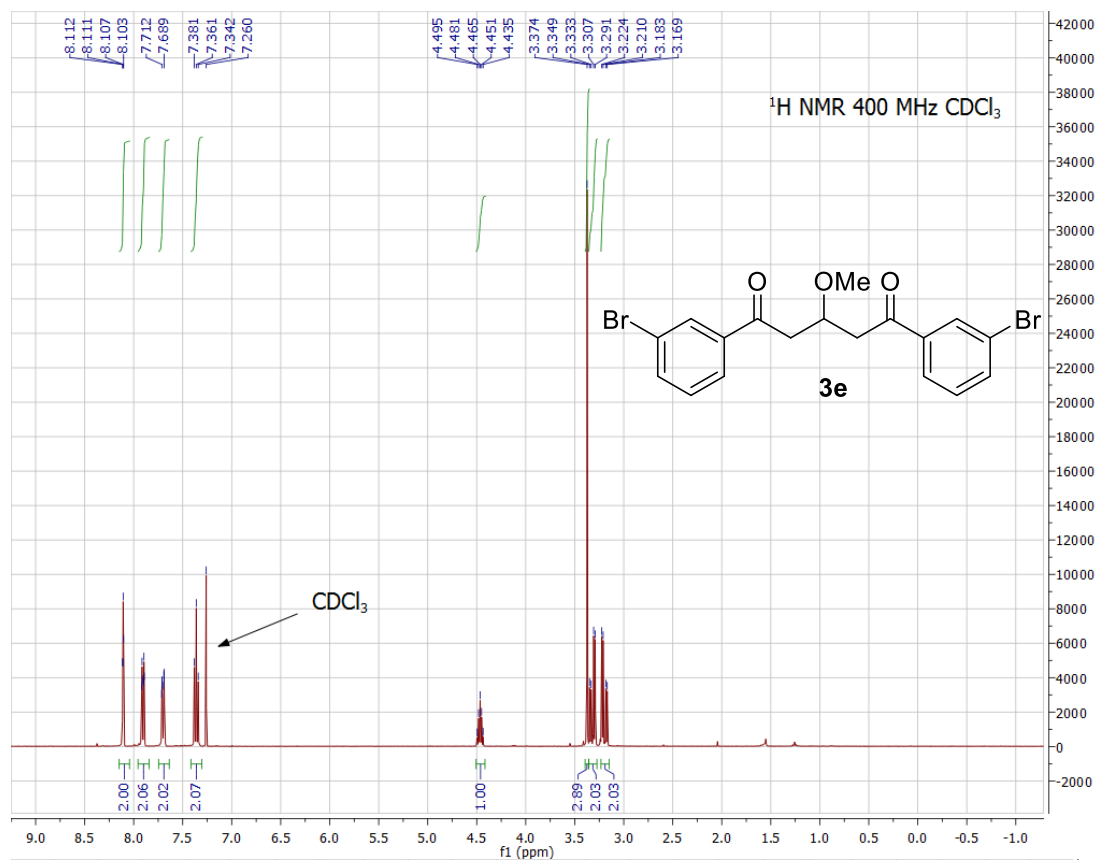


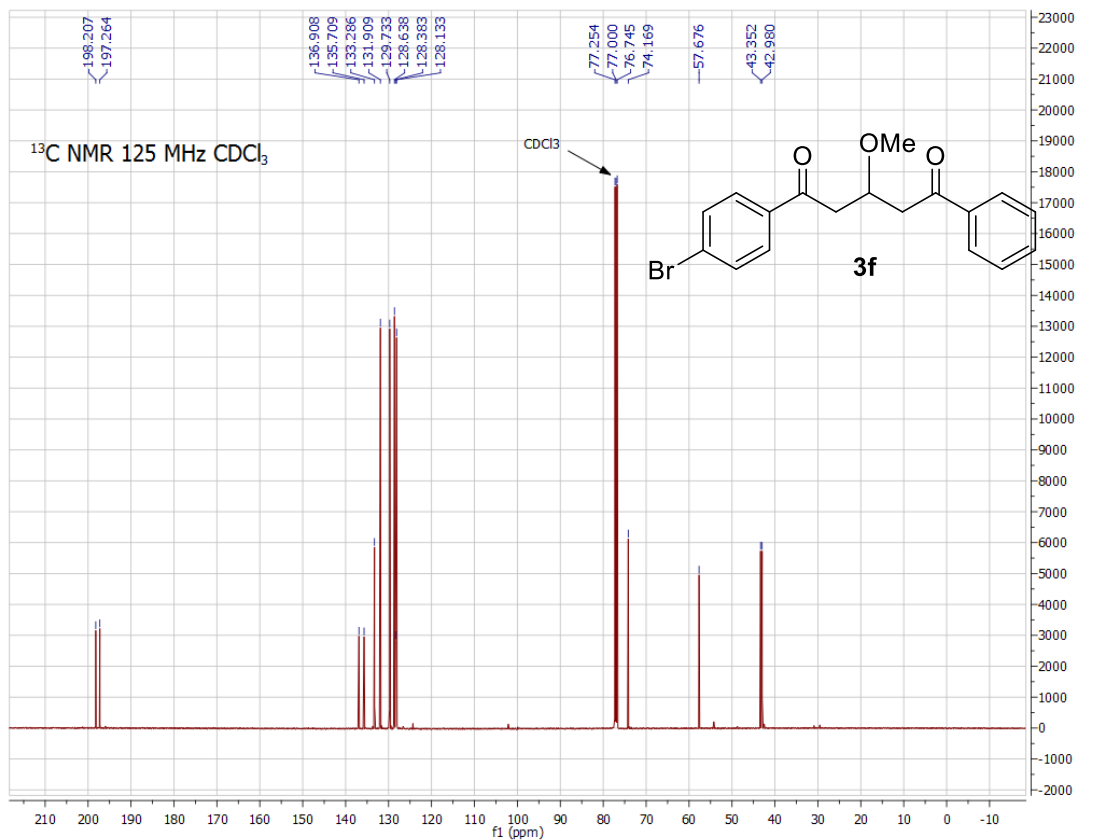
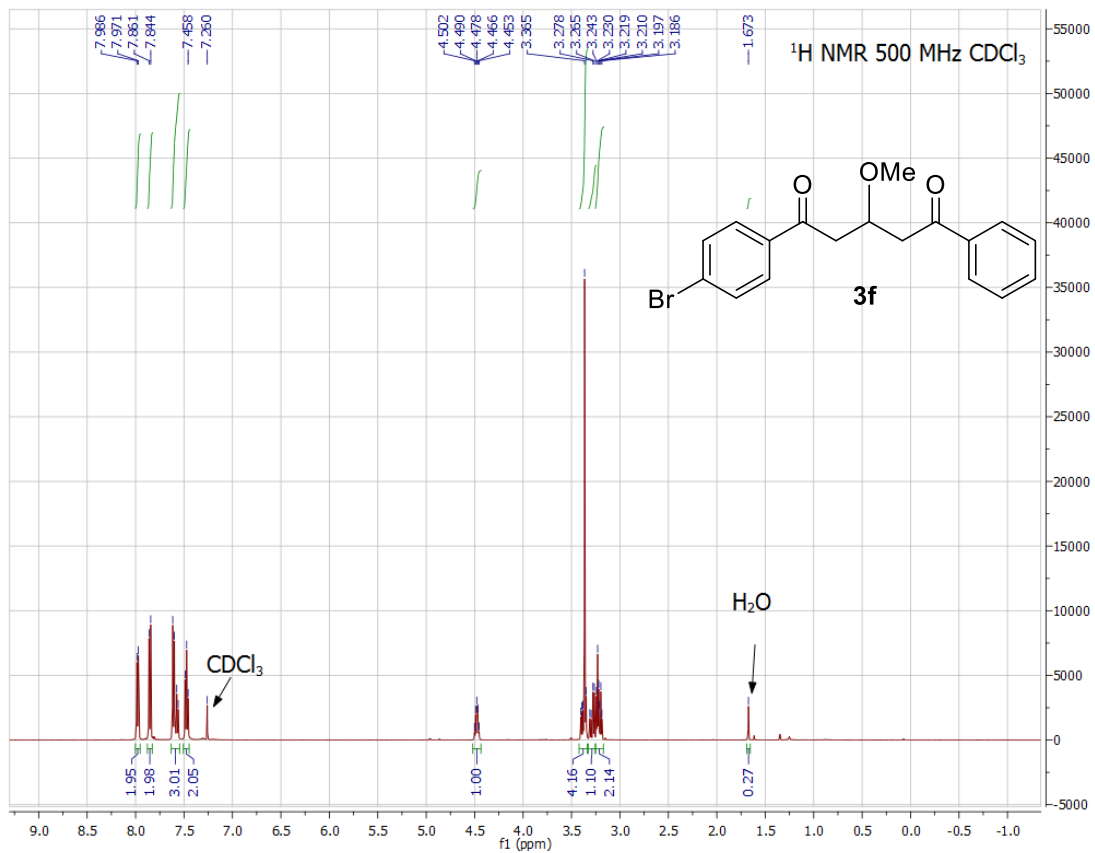


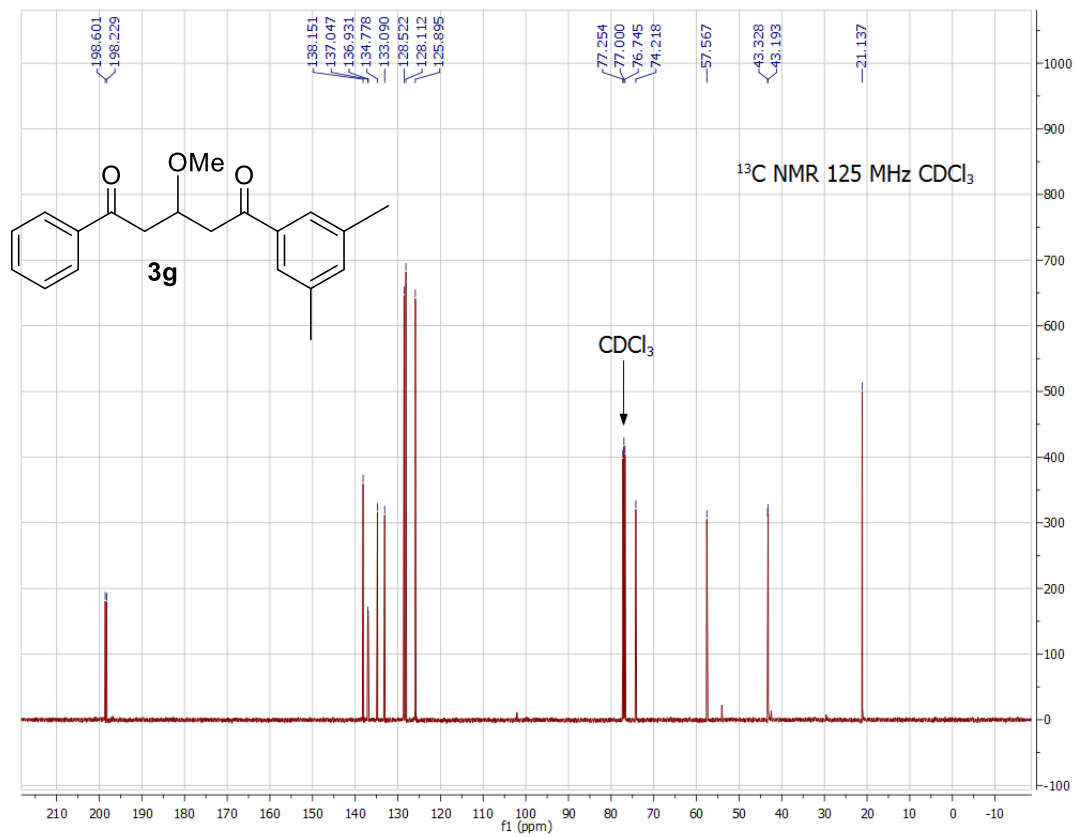
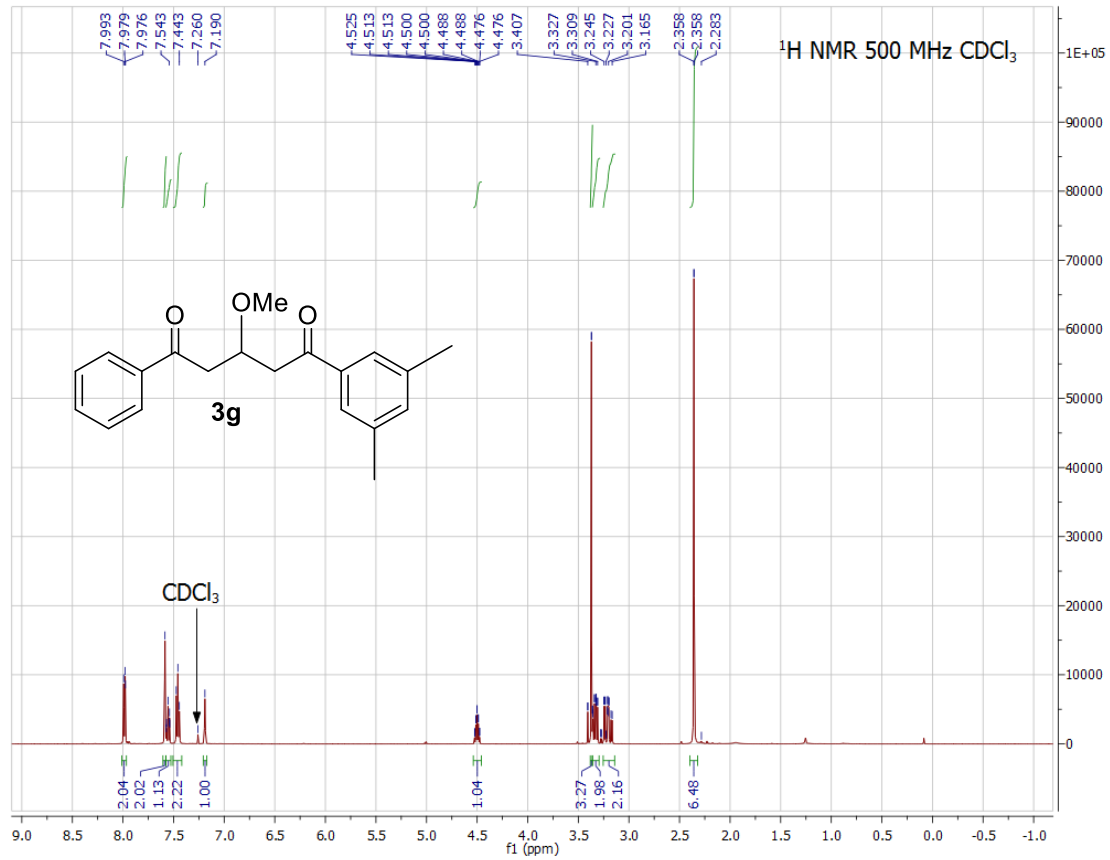


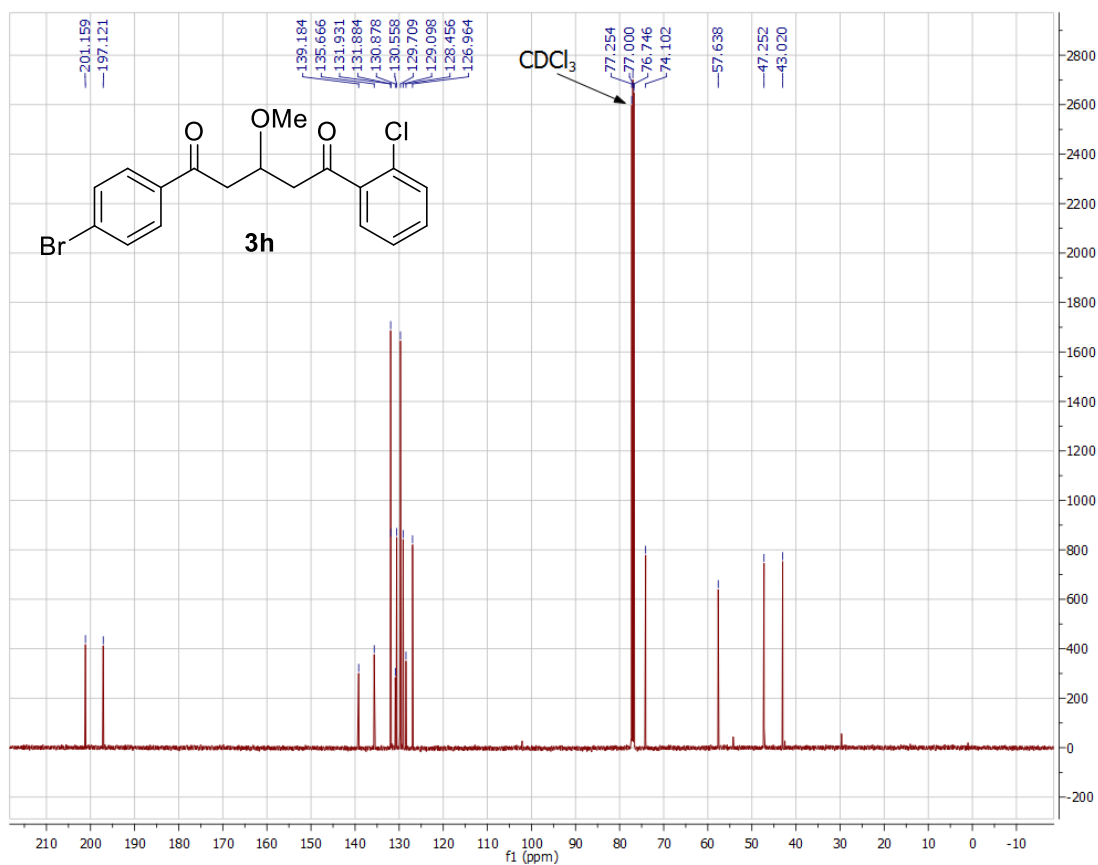
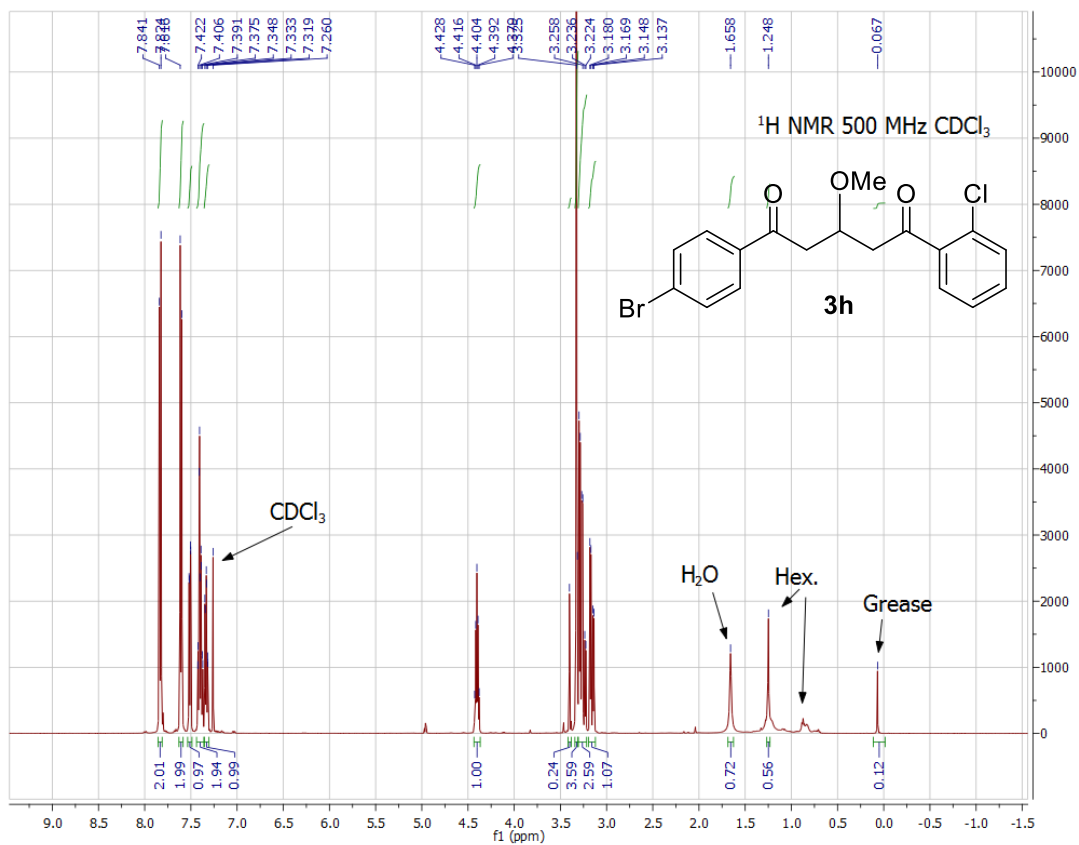


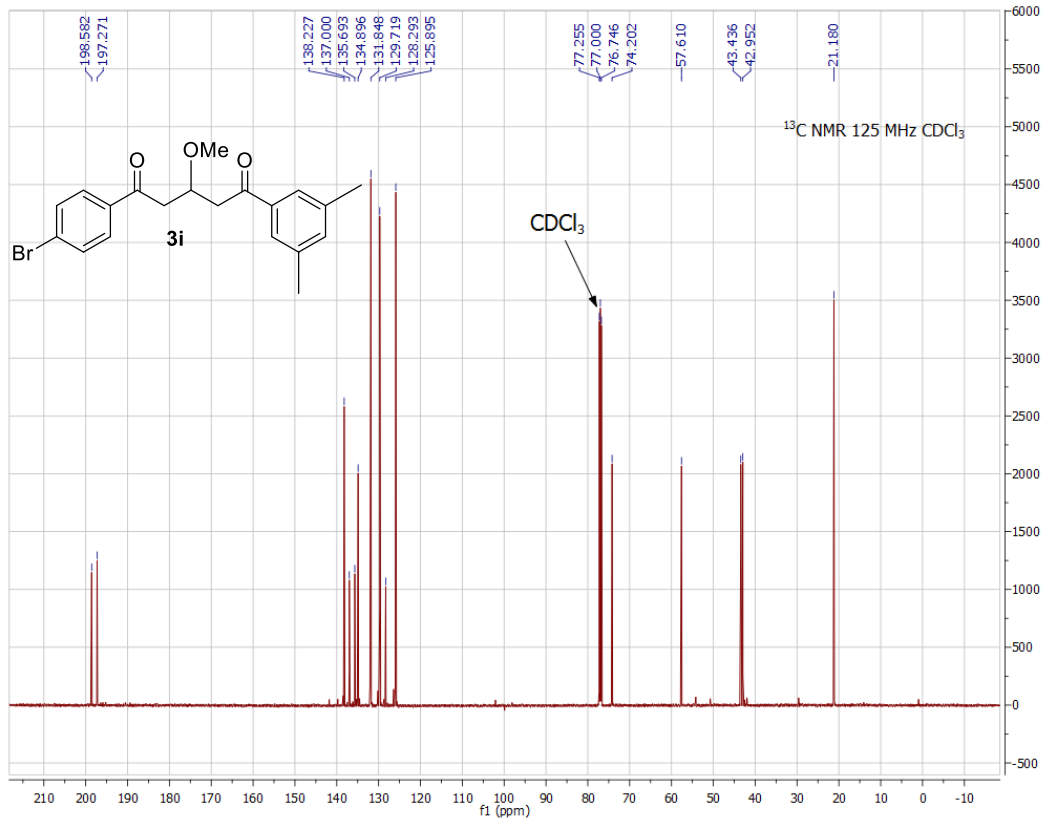
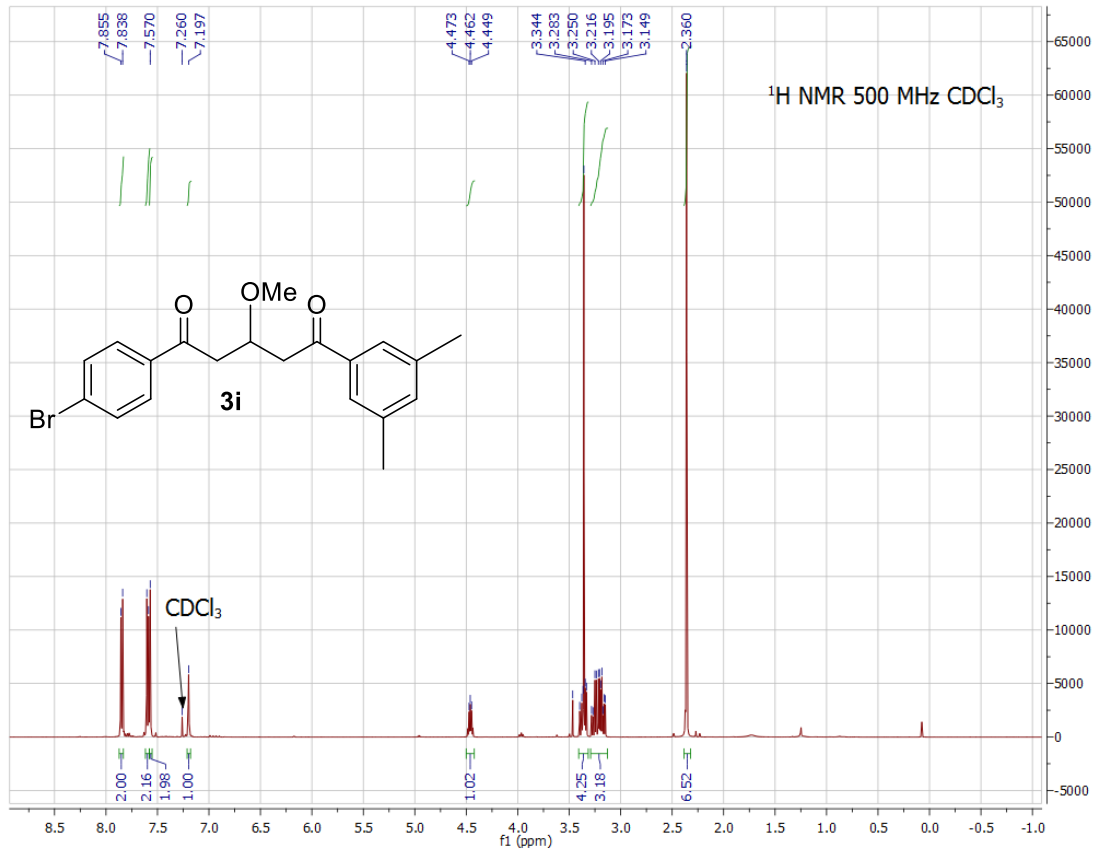


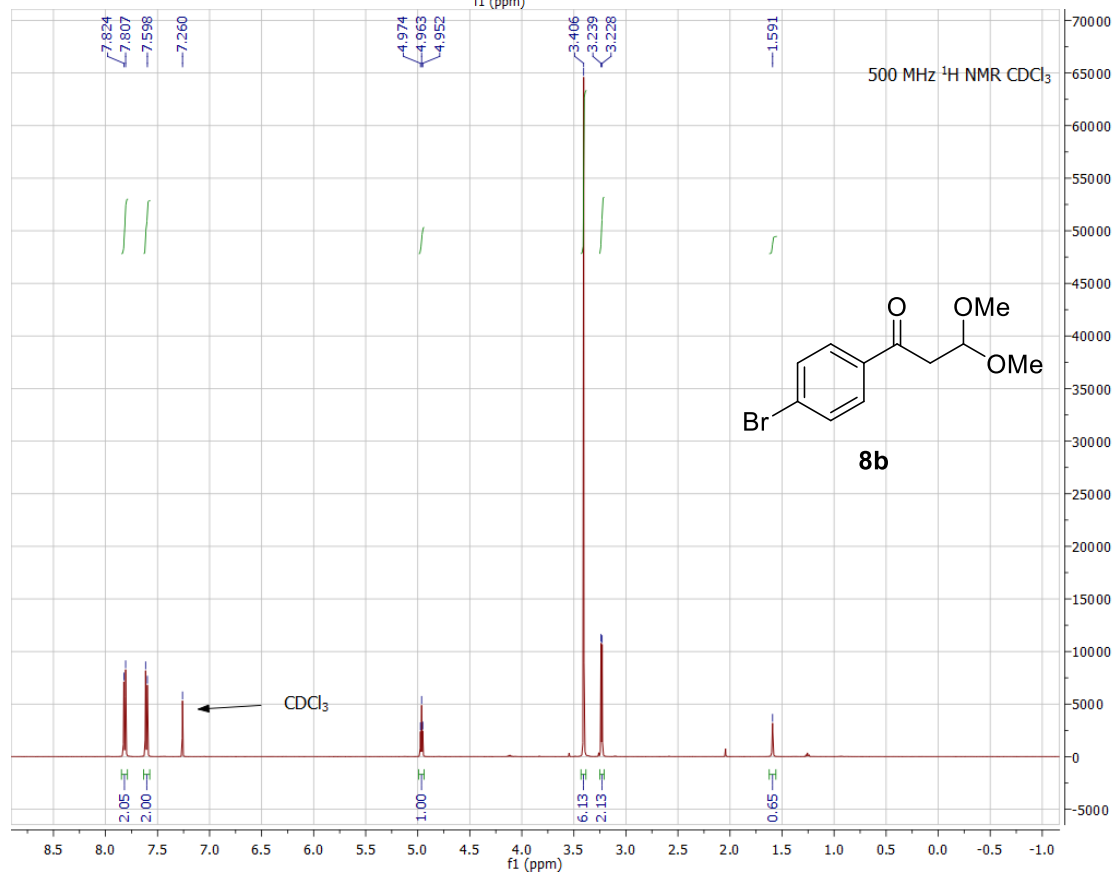
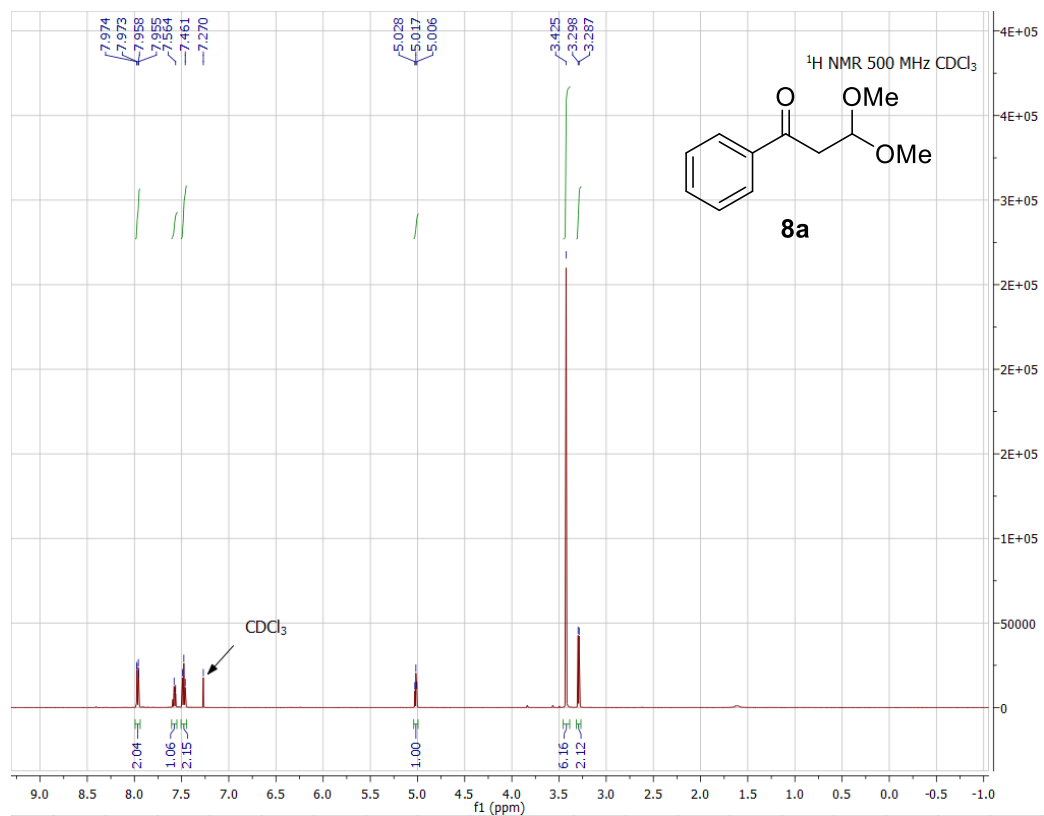


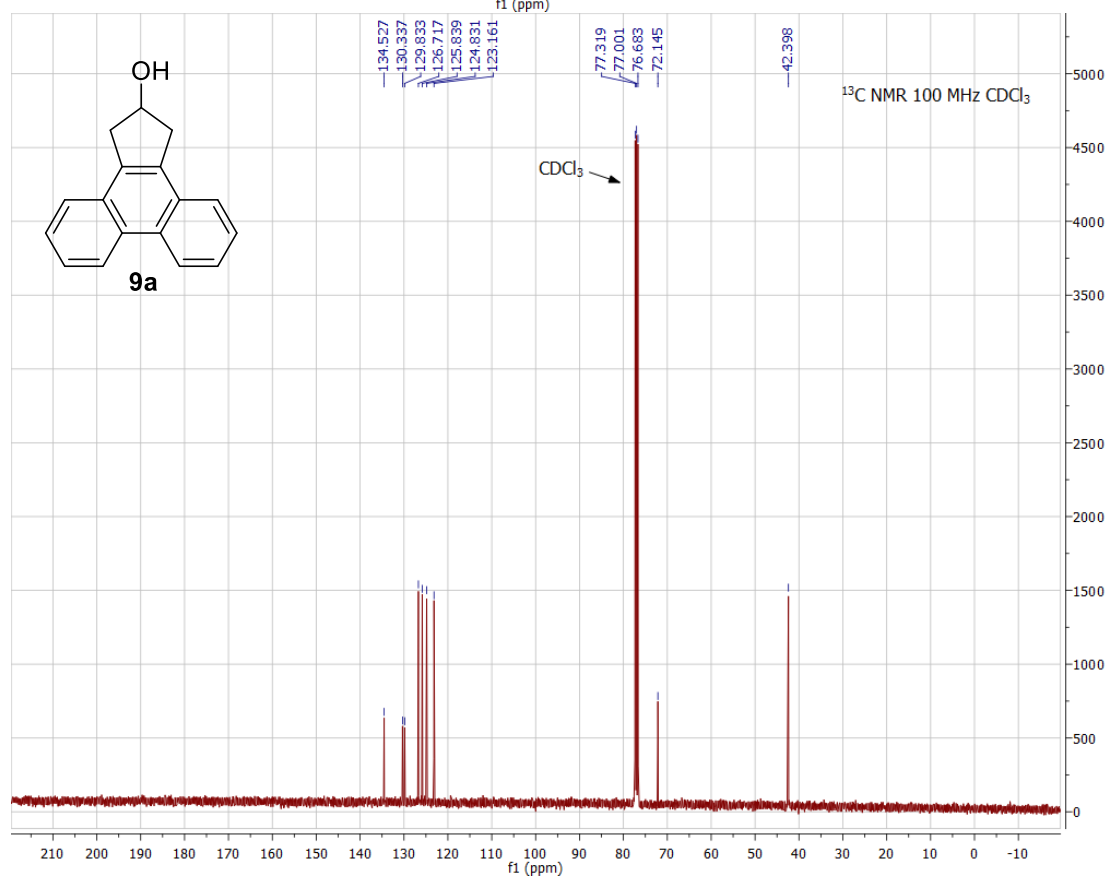
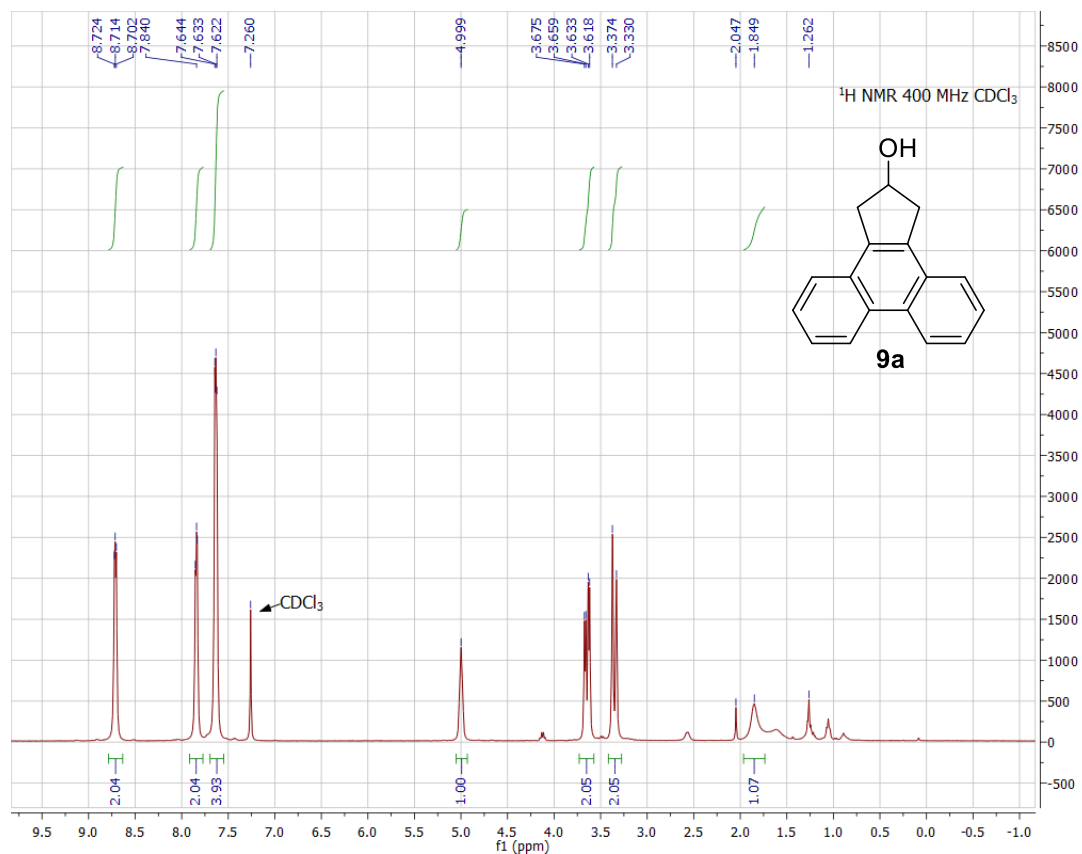


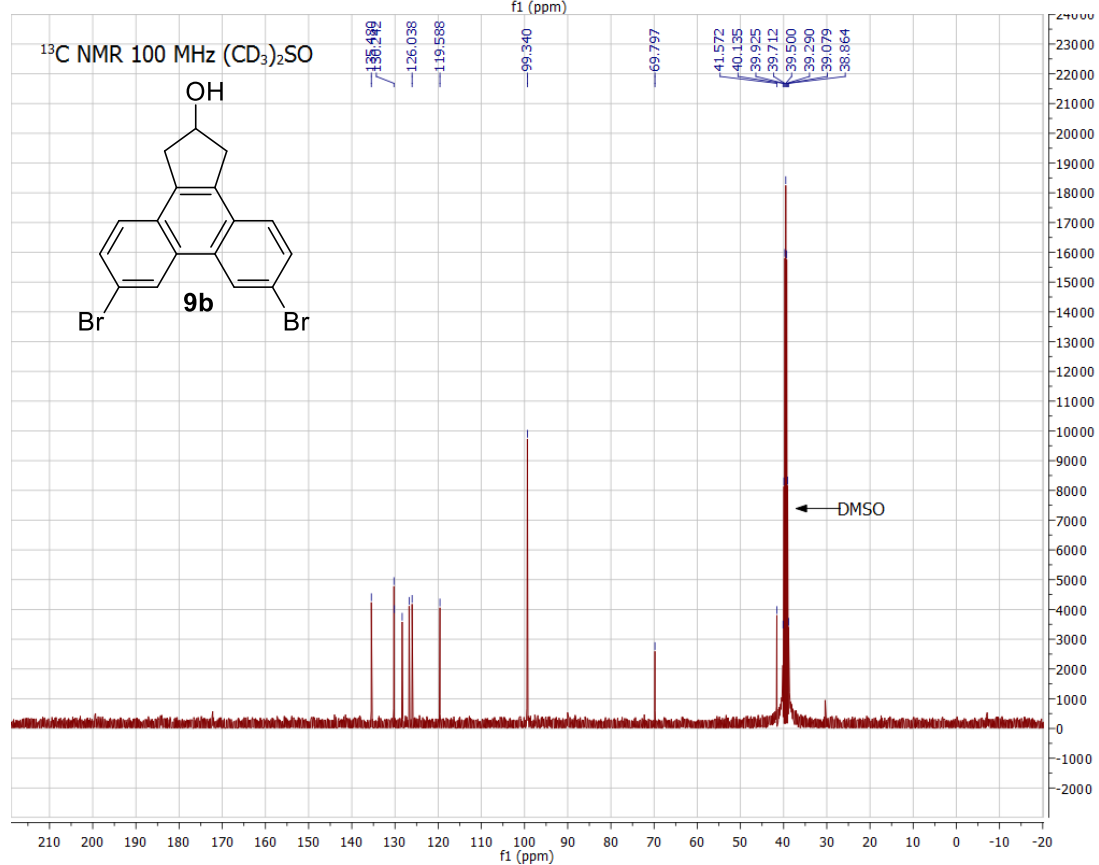
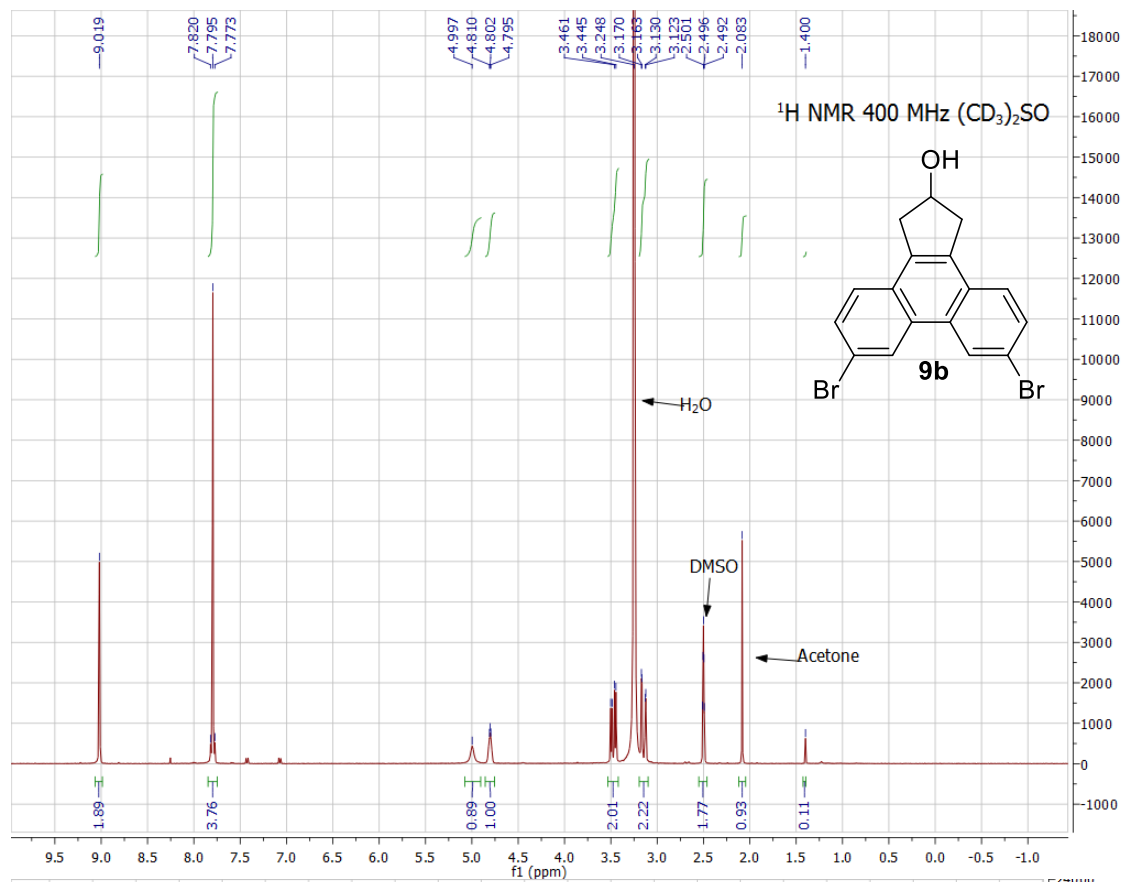












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