Supporting Information to Accompany:

Synthesis of Substituted Chromanones:

An Organocatalytic Aldol/oxa-Michael Reaction

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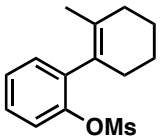
I. General Methods, Materials, and Abbreviations

General Procedures. All chemicals were purchased from commercial suppliers and used without further purification. Analytical thin layer chromatography was carried out on pre-coated plates (silica gel 60 F_{254}, 250 μm thickness) and visualized with UV light. Flash chromatography was performed using 60 Å, 32-63 μm silica gel (Scientific Adsorbents). Concentration *in vacuo* refers to rotary evaporation under reduced pressure. ^{1}H NMR spectra were recorded at 300 MHz, 400 MHz, or 600 MHz at ambient temperature with Acetone-d_6, DMSO-d_6, $CDCl_3$, CD_3CN, or CD_3OD as solvents. ^{13}C NMR spectra were recorded at 75 MHz, 100 MHz, or 150 MHz at ambient temperature with Acetone-d_6, DMSO-d_6, $CDCl_3$, CD_3CN, or CD_3OD as solvents. Chemical shifts are reported in parts per million (ppm) relative to the residual solvent peak. Infrared spectra were recorded on an ATI-FTIR spectrometer. The specifications of the LC/MS are as follows: electrospray (+) ionization, mass range 150 - 1500 Da, 20 V cone voltage, and Xterra® MS C_{18} column (2.1 mm x 50 mm x 3.5 μm). Preparative HPLC specifications are as follows: 15 mL/min flow rate, Xterra Prep MS C_{18} OBD column (19 mm x 100 mm) and dual wavelength absorbance detector.

II. Preparation of 2-(2-methylcyclohex-1-enyl)phenyl methanesulfonates

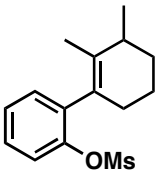


2-(2-methylcyclohex-1-enyl)phenyl methanesulfonate (7a). To a solution of 2-bromophenol (3.0 mL, 27.6 mmol) in diethyl ether (100 mL) cooled to 0 °C was added *n*-butyllithium (2.5 M in hexanes, 22 mL). After stirring for 3h, the solution was cooled to -78 °C and 2-methylcyclohexanone (3.7 mL, 30.4 mmol) was added. The reaction was slowly warmed to 23 °C over 12 h. The mixture was cooled to 0 °C and concentrated hydrochloric acid (12 mL) was added. After stirring for 1 hour, water (10 mL) was added. The layers were separated and the organic layer washed with water, 1N aqueous sodium hydroxide, saturated aqueous ammonium chloride, brine, dried over sodium sulfate, filtered, and concentrated *in vacuo* yielding the mixture of **1a:1b** isomers, a clear oil (4.6 g, 88%).

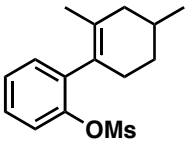
To mesyl protect, the mixture of isomers (**1a/b**, 4.6 g, 24.5 mmol) and Et_3N (7.1 mL, 51.4 mmol) were dissolved in DCM (50 mL) and cooled to 0 °C. Mesyl chloride (3.8 mL, 49.0 mmol) was slowly added over 5 min. Upon complete addition, the ice bath was removed and stirred at 20 °C for 2 h under TLC control. After the phenolic starting material was consumed, water (15 mL) was added. The layers were separated and the aqueous layer extracted with additional DCM. The combined organics were washed with brine, dried over sodium sulfate and concentrated *in vacuo*. The residue was purified by a plug flash chromatography (10-15% ethyl acetate in hexanes) yielding the inseparable mixture of **7a:7b**, a clear oil (6.4 g, 98%). Crude ^{1}H-NMR spectra before and after isomerization with diagnostic peak assignment of **7a** and **7b** can be found at the end of NMR Section (**X**).

To isomerize this mixture, **7a/b** (3.75 g, 14.2 mmol) was dissolved in DCE (30 mL). $PdCl_2$ (250 mg, 1.42 mmol) and $FeCl_3$ (230 mg, 1.42 mmol) were added and the mixture warmed to 60 °C. While the isomerization was complete in most cases within 8 h, the mixture was often stirred overnight (12-18 h). The mixture was concentrated *in vacuo* and purified by flash chromatography (12% ethyl acetate in hexanes) yielding only **7a**, a clear oil (3.48 g, 92%). IR (neat) ν_{max} 2928, 1482, 1442, 1360, 1189, 1153, 1097, 966, 864, 765, 709 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32-7.31 (m, 1H),

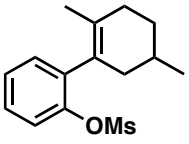
7.26-7.24 (m, 2H), 7.17-7.15 (m, 1H), 3.04 (s, 3H), 2.34-2.03 (br m, 1H), 2.14-2.08 (br m, 3H), 1.69 (br s, 4H), 1.48 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.9, 137.4, 132.3, 131.4, 128.1, 128.1, 127.4, 123.0, 38.4, 31.6, 31.1, 23.5, 23.2, 21.1; ESI MS calc'd. for $[C_{14}H_{19}O_3S + H]^+$: 267.1, found: 267.1. Purity was determined to be 89% by HPLC trace.



2-(2,3-dimethylcyclohex-1-enyl)phenyl methanesulfonate (8a). Following the procedure for the preparation of isomerically pure **7a** the target was synthesized yielding only **8a**, a clear oil (3.2 g, 81%). IR (neat) ν_{max} 2932, 1484, 1445, 1354, 1184, 1152, 968, 868, 766, 707 cm^{-1}; at 25 °C **8a** exists as a mixture of rotational isomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35-7.05 (m, 4H), 2.99 (s, 3H), 2.22-2.04 (m, 3H), 1.75-1.66 (m, 2H), 1.60-1.55 (m, 1H), 1.42 (s, 3H), 1.04 (d, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.9, 136.3, 131.9, 128.3, 128.1, 127.9, 127.2, 122.8, 38.5, 34.6, 31.7, 29.8, 28.5, 20.2, 19.0; ESI MS calc'd. for $[C_{15}H_{21}O_3S + H]^+$: 281.1, found: 281.1. Purity was determined to be 91% by HPLC trace.

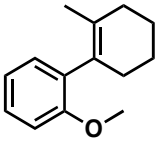


2-(2,4-dimethylcyclohex-1-enyl)phenyl methanesulfonate (9a). Following the procedure for the preparation of isomerically pure **7a** the target was synthesized yielding only **9a**, a clear oil (3.4 g, 85%). IR (neat) ν_{max} 2918, 1484, 1442, 1357, 1188, 1152, 1098, 967, 857, 766 cm^{-1}; at 25 °C **9a** exists as a mixture of rotational isomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33-7.16 (m, 4H), 3.18-3.06 (br m, 3H), 2.50-2.14 (m, 3H), 1.84-1.72 (br m, 3H), 1.50 (s, 3H), 1.32-1.28 (m, 1H), 1.03 (br s, *3H*); ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.1, 137.3, 131.7, 131.3, 128.0, 127.2, 122.8, 122.8, 40.3, 38.4, 31.7, 31.2, 29.2, 21.8, 20.9; ESI MS calc'd. for $[C_{15}H_{21}O_3S + H]^+$: 281.1, found: 281.1. Purity was determined to be 96% by HPLC trace.



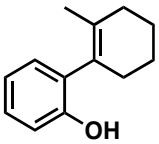
2-(2,5-dimethylcyclohex-1-enyl)phenyl methanesulfonate (10a). Following the procedure for the preparation of isomerically pure **7a** the target was synthesized yielding only **10a**, a clear oil (3.5 g, 89%). IR (neat) ν_{max} 2918, 1698, 1483, 1442, 1356, 1188, 1152, 1096, 967, 868, 820, 785, 766 cm^{-1}; at 25 °C appears as a mixture of rotational isomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33-7.31 (m, 1H), 7.27-7.25 (m, 2H), 7.17-7.15 (m, 1H), 3.03 (s, 3H), 2.29-2.26 (m, 1H), 2.19-2.09 (m, 3H), 1.80-1.73 (m, 3H), 1.49 (s, 3H), 0.99 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.8, 137.1, 131.7, 131.2, 127.9, 127.6, 127.2, 127.8, 39.5, 38.2, 31.6, 31.4, 29.3, 21.7, 20.7; ESI MS calc'd. for $[C_{15}H_{21}O_3S + H]^+$: 281.1, found: 281.1. Purity was determined to be 93% by HPLC trace.

III. Preparation of 1-methoxy-2-(2-methylcyclohex-1-enyl)benzene

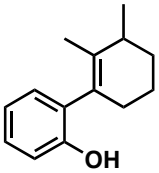


1-methoxy-2-(2-methylcyclohex-1-enyl)benzene (6a). Following the general synthesis of **7a** omitting the mesyl protection, the target was synthesized yielding a clear oil (2.5 g, 86%). IR (neat) ν_{max} 2927, 1673, 1597, 1578, 1488, 1434, 1291, 1241, 1027, 750 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.24 (ddd, J = 8.0, 7.8, 1.7 Hz, 1H), 7.05 (dd, J = 7.5, 1,7 Hz 1H), 6.96-6.91 (m, 2H), 3.22 (s, 3H), 2.39 (br d, J = 14.3 Hz, 1H), 2.20-2.04 (m, 4H), 1.74 (br s, 3H), 1.50 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.8, 133.3, 130.6, 129.7, 129.5, 127.5, 120.5, 111.2, 55.7, 31.4, 30.8, 23.5, 23.4, 20.8; ESI MS calc'd. for $[C_{14}H_{19}O + H]^+$: 203.1, found: 203.1. Purity was determined to be 95% by HPLC trace.

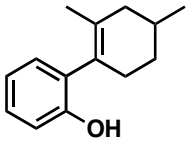
IV. Preparation of 2-(2-methylcyclohex-1-enyl)phenols



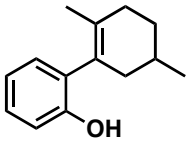
2-(2-methylcyclohex-1-enyl)phenol (1a). 7a (3.0 g, 11.3 mmol) was dissolved in 50 mL of 1:1 dioxane and MeOH. 3N aqueous NaOH (30 mL) was added, and the solution was warmed to 50 °C for 12 h. The solution was concentrated *in vacuo* and dissolved in ethyl acetate. The organic layer was washed with aqueous citric acid, water, brine, dried over sodium sulfate, and concentrated *in vacuo.* The resulting residue was purified by flash chromatography (6% ethyl acetate in hexanes) yielding a clear oil (2.1 g, 99%). IR (neat) ν_{max} 3504, 2927, 1578, 1485, 1445, 1281, 1201, 1034, 749 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.18 (t, J = 8.4 Hz, 1H), 7.04 (d, J = 7.6 Hz, 1H), 6.96-6.90 (m, 2H), 5.32 (br s, 1H), 2.29-2.07 (br m, 4H), 1.79-1.71 (br m, 4H), 1.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.0, 134.4, 129.8, 128.9, 128.5, 127.0, 120.6, 114.8, 31.7, 31.5, 23.6, 23.3, 20.7; ESI MS calc'd. for $[C_{13}H_{17}O + H]^+$: 189.1, found: 189.1. Purity was determined to be 92% by HPLC trace.



2-(2,3-dimethylcyclohex-1-enyl)phenol (2a). Following the general synthesis of **1a** the target was synthesized yielding a clear oil (2.2 g, 95%). IR (neat) ν_{max} 3507, 2926, 1578, 1484, 1451, 1339, 1174, 1033, 828, 750 cm^{-1}; at 25 °C **2a** exists as a mixture of rotational isomers. ^1H NMR (600 MHz, $CDCl_3$) δ 7.15 (ddd, J = 8.4, 7.8, 1.5 Hz 1H), 7.02-6.99 (m, 1H), 6.92-6.88 (m, 2H), 5.21-5.16 (br m, 1H), 2.28-2.07 (m, 3H), 1.89-1.76 (m, 2H), 1.82-1.65 (m, 1H), 1.59-1.42 (m, 4H), 1.16-1.12 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.7, 138.8, 130.0, 129.1, 128.3, 127.1 120.5, 114.6, 34.5, 32.1, 31.4, 20.6, 19.6, 18.5; ESI MS calc'd. for $[C_{14}H_{19}O + H]^+$: 203.1, found: 203.1. Purity was determined to be 87% by HPLC trace.

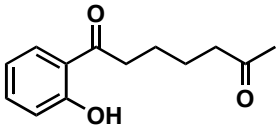


2-(2,4-dimethylcyclohex-1-enyl)phenol (3a). Following the general synthesis of **1a** the target was synthesized yielding a clear oil (2.2 g, 98%). IR (neat) ν_{max} 3505, 2913, 1578, 1484, 1452, 1223, 1172, 819, 750 cm^{-1}; at 25 °C **3a** exists as a mixture of rotational isomers. ^1H NMR (300 MHz, $CDCl_3$) δ 7.22-7.17 (m, 1H), 7.08-7.01 (m, 1H), 6.98-6.91 (m, 2H), 5.36-5.20 (br m, 1H), 2.42-2.09 (m, 3H), 1.86-1.79 (m, 3H), 1.57 (s, 3H), 1.47-1.30 (m, 1H), 1.08 (d, J = 4.8 Hz, 3H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 152.0, 133.9, 129.2, 128.8, 128.4, 126.6, 120.6, 114.8, 40.2, 32.1, 31.6, 29.3, 22.1, 20.6; ESI MS calc'd. for $[C_{14}H_{19}O + H]^+$: 203.1, found: 203.1. Purity was determined to be 89% by HPLC trace.

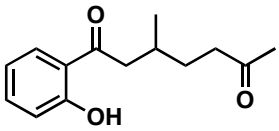


2-(2,5-dimethylcyclohex-1-enyl)phenol (4a). Following the general synthesis of **1a** the target was synthesized yielding a clear oil (2.2 g, 96%). IR (neat) ν_{max} 3506, 2909, 1578, 1484, 1452, 1282, 1200, 1034, 841, 749 cm^{-1}; at 25 °C **4a** exists as a mixture of rotational isomers. ^1H NMR (600 MHz, $CDCl_3$) δ 7.19-7.16, (m, 1H), 7.06-7.00 (m, 1H), 6.96-6.91 (m, 2H), 5.31-5.18 (br m, 1H), 2.31-2.13 (m, 3H), 1.95-1.82 (m, 3H), 1.55 (s, 3H), 1.42-1.31 (m, 1H), 1.03 (d, J = 6.0 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.9, 133.8, 129.6, 128.8, 128.2, 126.4, 120.4, 114.6, 40.1, 31.5, 31.2, 29.4, 21.7, 20.7; ESI MS calc'd. for $[C_{14}H_{19}O + H]^+$: 203.1, found: 203.1. Purity was determined to be 91% by HPLC trace.

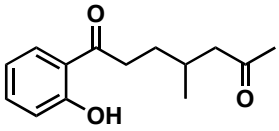
V. Preparation of 1-(2-hydroxyphenyl)heptane-1,6-diones



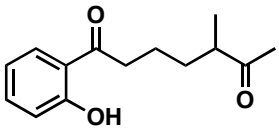
1-(2-hydroxyphenyl)heptane-1,6-dione (11). 1a (1.0 g, 5.3 mmol) dissolved in DCM (30 mL) was added to a gas apparatus equipped with glass gas inlet and outlet tubes. The vessel was cooled to -78 °C, and bubbled with excess O_3 until the solution was noticeable blue. The system was purged by bubbling dry N_2 for 1-2 min and dimethyl sulfide (0.5 mL, 6.9 mmol) added. The mixture was stirred for 8 h while warming to 20 °C. The mixture was concentrated *in vacuo* and the residue purified by flash chromatography (15% ethyl acetate in hexanes) yielding an amorphous white solid (1.0 g, 89%). IR (neat) ν_{max} 2939, 1707, 1636, 1615, 1490, 1444, 1361, 1279, 1156, 980, 762 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 12.31 (s, 1H), 7.73 (d, J = 7.2 Hz, 1H), 7.44 (t, J = 8.4 Hz, 1H), 6.96 (d, J = 8.4 Hz, 1H), 6.88 (t, J = 7.6 Hz, 1H), 3.00 (t, J = 6.8 Hz, 2H), 2.49 (t, J = 7.2 Hz, 2H), 2.14 (s, 3H), 1.75-1.63 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.0, 206.5, 162.7, 136.6, 130.1, 119.5, 119.2, 118.8, 43.6, 38.2, 30.2, 23.9, 23.5; ESI MS calc'd. for $[C_{13}H_{17}O_3 + H]^+$: 221.1, found: 221.1. Purity was determined to be 99% by HPLC trace.



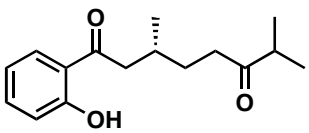
1-(2-hydroxyphenyl)-3-methylheptane-1,6-dione (12). Following the general synthesis of **11** the target was synthesized yielding a clear oil (1.0 g, 81%). IR (neat) v_{max} 2945, 1708, 1636, 1613, 1580, 1487, 1446, 1354, 1279, 1243, 1155, 978, 753 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 12.33 (s, 1H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.37 (t, *J* = 8.4 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.80 (t, *J* = 8.1 Hz, 1H), 2.88 (dd, *J* = 15.9, 5.7 Hz, 1H), 2.72 (dd, *J* = 15.9, 7.5 Hz, 1H), 2.45-2.37 (m, 2H), 2.06 (s, 3H), 1.69-1.58 (m, 1H), 1.49-1.37 (m, 1H), 0.89 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.8, 206.4, 162.7, 136.5, 130.3, 119.7, 119.1, 118.7, 45.5, 41.4, 30.8, 30.1, 29.5, 19.9; ESI MS calc'd. for $[C_{14}H_{19}O_3 + H]^+$: 235.1, found: 235.1. Purity was determined to be 97% by HPLC trace.



1-(2-hydroxyphenyl)-4-methylheptane-1,6-dione (13). Following the general synthesis of **11** the target was synthesized yielding a clear oil (0.97 g, 78%). IR (neat) v_{max} 2958, 2927, 1710, 1636, 1613, 1581, 1487, 1446, 1355, 1249, 1199, 1155, 753 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 12.30 (s, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.44 (t, *J* = 7.2 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 6.87 (t, *J* = 7.2 Hz, 1H), 3.03-2.93 (m, 2H), 2.45 (dd, *J* = 16.2, 6.0 Hz, 1H), 2.32 (dd, *J* = 16.8, 7.8 Hz, 1H), 2.12 (s, 3H), 2.12-2.06 (m, 1H), 1.78-1.72 (m, 1H), 1.59-1.53 (m, 1H), 0.95 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 206.7, 204.8, 160.7, 134.6, 128.2, 117.5, 117.2, 116.8, 49.1, 34.2, 29.3, 28.8, 27.0, 18.0; ESI MS calc'd. for $[C_{14}H_{19}O_3 + H]^+$: 235.1, found: 235.1. Purity was determined to be 96% by HPLC trace.

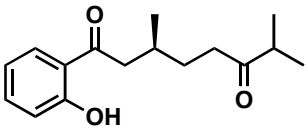


1-(2-hydroxyphenyl)-5-methylheptane-1,6-dione (14). Following the general synthesis of **11** the target was synthesized yielding a clear oil (1.1 g, 88%). IR (neat) v_{max} 2945, 1708, 1636, 1613, 1487, 1446, 1279, 1198, 1034, 754, 726 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 12.29 (s, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.43 (t, *J* = 8.4 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 6.87 (t, *J* = 7.8 Hz, 1H), 2.99-2.96 (m, 2H), 2.55-2.52 (m, 1H), 2.13 (s, 3H), 1.74-1.64 (m, 3H), 1.43-1.39 (m, 1H), 1.08 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 212.6, 206.4, 162.7, 136.5, 130.1, 119.5, 119.1, 118.7, 47.2, 38.3, 32.4, 28.3, 22.1, 16.6; ESI MS calc'd. for $[C_{14}H_{19}O_3 + H]^+$: 235.1, found: 235.1. Purity was determined to be 95% by HPLC trace.



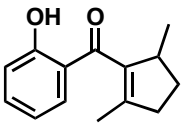
(*R*)-1-(2-hydroxyphenyl)-3,7-dimethyloctane-1,6-dione (19). To a solution of 2-bromophenol (1.0 mL, 9.2 mmol) in diethyl ether (30 mL) cooled to 0 °C was added *n*-butyllithium (2.5 M in hexanes, 7.5 mL). After stirring for 3h, the solution was cooled to -78 °C and slowly canulated into a flask containing (4*R*)-7-isopropyl-4-methyloxepan-2-one (7.8 g, 46.0 mmol) dissolved in diethyl ether at -78 °C while stirring vigorously. The reaction was slowly warmed to 23 °C over 12 h. The mixture was concentrated *in vacuo* yielding and the residue dissolved in DCM (25 mL). To the mixture was added PDC (5.2 g, 13.8 mmol). This orange solution was stirred for 8 h and concentrated *in vacuo* . The resulting residue was purified by flash chromatography (15% ethyl acetate in hexanes) yielding a white amorphous solid (75 mg, 31%). $[\alpha]^{23}_D$ +5.13° (*c* 1.00, MeOH);IR (neat) v_{max} 2964, 1708, 1637, 1614, 1488, 1369, 1307, 1250, 1205, 1156, 1006, 751 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 12.34 (s, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.82 (t, *J* = 7.8 Hz, 1H),

2.90 (dd, *J* = 15.6, 6.0 Hz, 1H), 2.74 (dd, *J* = 15.6, 8.1 Hz, 1H), 2.57-2.28 (m, 2H), 2.12-2.06 (m 1H), 1.67-1.63 (m, 1H), 1.05-1.43 (m, 2H), 1.02 (d, *J* = 6.9 Hz, 6H) 0.91 (d, *J* = 6.6 Hz, 3H), 0.84-0.81 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 214.7, 206.5, 162.8, 136.6, 130.3, 119.8, 119.1, 118.8, 45.7, 41.1, 38.2, 31.0, 29.8, 20.0, 18.6; ESI MS calc'd. for $[C_{16}H_{23}O_3 + H]^+$: 263.2, found: 263.2. Purity was determined to be 96% by HPLC trace.



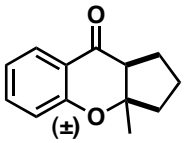
(*S*)-1-(2-hydroxyphenyl)-3,7-dimethyloctane-1,6-dione (20). Following the same synthesis of **19** the target was synthesized yielding a white amorphous solid (70 mg, 29%). $[\alpha]^{23}_D$ -5.29° (*c* 1.00, MeOH); ESI MS calc'd. for $[C_{16}H_{23}O_3 + H]^+$: 263.2, found: 263.2. Purity was determined to be 98% by HPLC trace.

VI. Preparation of (2-hydroxyphenyl)(2,5-dimethylcyclopent-1-enyl)methanone

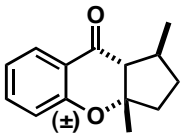


(2-hydroxyphenyl)(2,5-dimethylcyclopent-1-enyl)methanone (26). The mixture of **16a/b** (50 mg, 0.23 mmol) dissolved in MeOH was added to a round bottom flask. KOH (65 mg, 1.2 mmol) was added and the mixture was stirred at 50 °C for 12h. The mixture was concentrated *in vacuo*. To the residue was added 1N aqueous HCl. The cloudy mixture was extracted with diethyl ether, and the combined organics were washed with brine, dried over sodium sulfate, and concentrated *in vacuo* yielding a light yellow oil (49 mg, 99%). IR (neat) ν_{max} 2955, 1620, 1596, 1481, 1444, 1348, 1298, 1245, 1213, 1157, 1031, 910, 811, 755 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.27 (s, 1H), 7.56 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.40 (dt, *J* = 7.8, 1.8 Hz, 1H), 6.93 (dd, *J* = 8.4, 0.6 Hz, 1H), 6.81 (dt, *J* = 8.4, 0.6 Hz, 1H), 3.25-3.21 (m, 1H), 2.47-2.37 (m, 2H), 2.19-2.14 (m, 1H), 1.59 (s, 3H), 1.46-1.40 (m, 1H), 0.99 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 204.0, 162.8, 145.4, 140.1, 136.6, 133.1, 120.8, 119.1, 118.4, 44.1, 38.6, 32.0, 19.9, 16.6; ESI MS calc'd. for $[C_{14}H_{17}O_2 + H]^+$: 217.1, found: 217.1. Purity was determined to be 96% by HPLC trace.

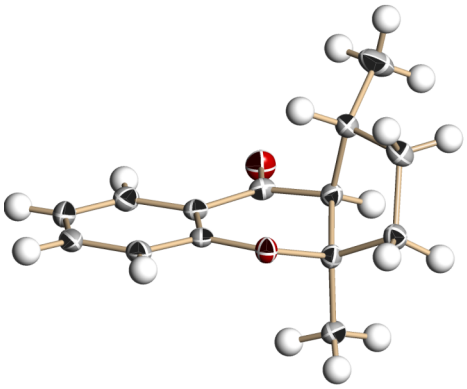
VII. Preparation of various substituted 1,2,3,3a-tetrahydro-3a-methylcyclopenta[*b*]chromen-9(9aH)-ones

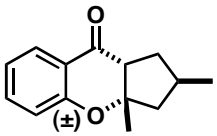


1,2,3,3a-tetrahydro-3a-methylcyclopenta[*b*]chromen-9(9a*H*)-one (15). 11 (100 mg, 0.45 mmol) dissolved in MeOH (5 mL) was added to a round bottom flask. Pyrrolidine (5.5 μL, 15 mol%, 0.07 mmol) was added, and the mixture was warmed to 50 °C. The mixture was stirred at 50 °C for 48 h under TLC control, monitoring the disappearance of all other spots except the chromanone characteristic purple spot under 254 nm light. The reaction was concentrated *in vacuo* and then diluted with diethyl ether. The organics were washed with saturated aqueous ammonium chloride, water, brine, dried over sodium sulfate, and concentrated *in vacuo*. The residue was purified by flash chromatography (10% ethyl acetate in hexanes) yielding **15**, an amorphous white solid as a single diastereomer (79 mg, 87%). IR (neat) ν_{max} 2920, 2850, 1710, 1684, 1462, 1254, 1170, 1027, 935, 757, 702 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (dd, J = 7.8, 1.8 Hz, 1H), 7.39 (dt, J = 7.8, 1.8 Hz, 1H), 6.90 (dt, J = 7.8, 1.2 Hz, 1H), 6.83 (dd, J = 7.8, 0.6 Hz, 1H), 2.54 (t, J = 10.2 Hz, 1H), 2.16-2.06 (m, 2H), 1.94-1.84 (m, 2H), 1.79-1.73 (m, 2H), 1.36 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.3, 159.7, 136.3, 127.2, 121.0, 118.7, 118.3, 90.6, 55.9, 40.0, 29.6, 22.6, 22.1; ESI MS calc'd. for $[C_{13}H_{15}O_2 + H]^+$: 203.1, found: 203.1. Purity was determined to be 98% by HPLC trace.

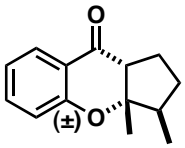


1,2,3,3a-tetrahydro-1,3a-dimethylcyclopenta[*b*]chromen-9(9a*H*)-one (16a). Following the general synthesis of **15** the target was synthesized yielding a 9:1 ratio of **16a:16b**, a white solid (86 mg, 88%). Analytical data for **16a** is as follows: mp 73.8 – 75.5 °C; IR (neat) ν_{max} 2929, 1681, 1605, 1461, 1309, 1237, 1144, 1028, 883, 748 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (dd, J = 8.4, 1.8 Hz, 1H), 7.38 (dt, J = 7.2, 1.8 Hz, 1H), 6.90 (dt, J = 7.2, 0.6 Hz, 1H), 6.82 (dd, J = 8.4, 0.6 Hz, 1H), 2.33-2.28 (m, 1H), 2.17-2.07 (m, 3H), 1.86-1.80 (m, 1H), 1.39-1.34 (m, 1H), 1.33 (s, 3H), 1.04 (d, J = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 194.7, 159.6, 136.3, 127.1, 121.0, 118.7, 118.5, 91.4, 63.5, 39.1, 38.5, 32.0, 22.4, 19.4; ESI MS calc'd. for $[C_{14}H_{17}O_2 + H]^+$: 217.1, found: 217.1. Purity was determined to be 99% by HPLC trace. The absolute structure was solved by X-ray crystallography that is represent by the structure below.

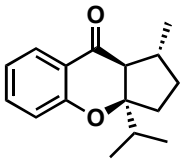




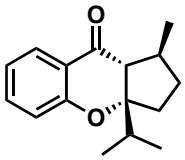
1,2,3,3a-tetrahydro-2,3a-dimethylcyclopenta[*b*]chromen-9(9a*H*)-one (17a). Following the general synthesis of **15** the target was synthesized yielding a 2:1 ratio of **17a:17b**, a white amorphous solid (80 mg, 82%). Analytical data for **17a** is as follows: IR (neat) ν_{max} 2928, 1680, 1606, 1461, 1309, 1237, 1145, 1028, 883, 750 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.45 (dt, *J* = 8.4, 1.8 Hz, 1H), 6.96 (dt, *J* = 7.8, 0.6 Hz, 1H), 6.89 (dd, *J* = 8.4, 0.6 Hz, 1H), 2.76 (t, *J* = 10.2 Hz, 1H), 2.39 (dd, *J* = 13.8, 7.8 Hz, 1H), 2.18-2.12 (m, 1H), 1.78-1.74 (m, 1H), 1.43-1.39 (m, 1H) 1.41 (s, 3H), 1.07 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.3, 160.0, 136.3, 127.3, 121.1, 118.7, 118.3, 91.0, 54.7, 49.2, 37.8, 31.4, 22.3, 22.3; ESI MS calc'd. for $[C_{14}H_{17}O_2 + H]^+$: 217.1, found: 217.1. Purity was determined to be 93% by HPLC trace.



1,2,3,3a-tetrahydro-3,3a-dimethylcyclopenta[*b*]chromen-9(9a*H*)-one (18a). Following the general synthesis of **15** the target was synthesized yielding a 5:1 ratio of **18a:18b**, an amorphous white solid (85 mg, 87%). Analytical data for **18a** is as follows: IR (neat) ν_{max} 2964, 1682, 1605, 1461, 1381, 1307, 1237, 1145, 1123, 1047, 924, 751 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.45 (dt, *J* = 8.4, 1.8 Hz, 1H), 6.96 (dt, *J* = 7.8, 0.6 Hz, 1H), 6.91 (dd, *J* = 8.4, 0.6 Hz, 1H), 2.68 (t, *J* = 10.2 Hz, 1H), 2.14-2.07 (m, 1H), 2.05-1.99 (m, 1H), 1.98-1.91 (m, 1H), 1.80-1.74 (m, 1H) 1.68-1.61 (M, 1H), 1.32 (s, 3H), 1.16 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.8, 159.9, 136.2, 127.3, 121.0, 118.7, 118.4, 90.1, 56.3, 45.4, 31.5, 27.1, 19.6, 12.2; ESI MS calc'd. for $[C_{14}H_{17}O_2 + H]^+$: 217.1, found: 217.1. Purity was determined to be 98% by HPLC trace.

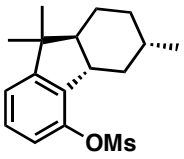


(1*R*,3a*S*,9a*S*)-1,2,3,3a-tetrahydro-3a-isopropyl-1-methylcyclopenta[*b*]chromen-9(9a*H*)-one (24). Following the general synthesis of **15** the target was synthesized yielding **24**, an amorphous white solid as a single stereoisomer (94 mg, 86%). $[\alpha]^{25}_D$ -93.94° (*c* 1.00, MeOH); IR (neat) ν_{max} 2960, 1681, 1606, 1461, 1310, 1239, 1144, 983, 768, 753 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.38 (dt, *J* = 7.2, 1.8 Hz, 1H), 6.88 (dt, *J* = 8.4, 1.2 Hz, 1H), 6.83 (dd, *J* = 8.4, 0.6 Hz, 1H), 2.32-2.26 (m, 2H), 2.12-2.07 (m, 1H), 2.01-1.86 (m, 3H), 1.32-1.26 (m, 1H), 1.04 (d, *J* = 6.6 Hz, 3H), 0.86 (d, *J* = 6.6 Hz, 3H), 0.85 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 194.8, 159.8, 136.3, 127.0, 120.7, 119.1, 118.3, 97.4, 60.3, 38.6, 32.6, 32.5, 31.8, 19.2, 18.1, 17.8; ESI MS calc'd. for $[C_{16}H_{21}O_2 + H]^+$: 245.1, found: 245.1. Purity was determined to be 99% by HPLC trace.

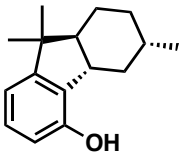


(1*S*,3a*R*,9aR)-1,2,3,3a-tetrahydro-3a-isopropyl-1-methylcyclopenta[*b*]chromen-9(9a*H*)-one (25). Following the general synthesis of **15** the target was synthesized yielding **25**, an amorphous white solid as a single stereoisomer (93 mg, 85%). $[\alpha]^{25}_D$ +94.03° (*c* 1.00, MeOH); ESI MS calc'd. for $[C_{14}H_{17}O_2 + H]^+$: 217.1, found: 217.1. Purity was determined to be 99% by HPLC trace.

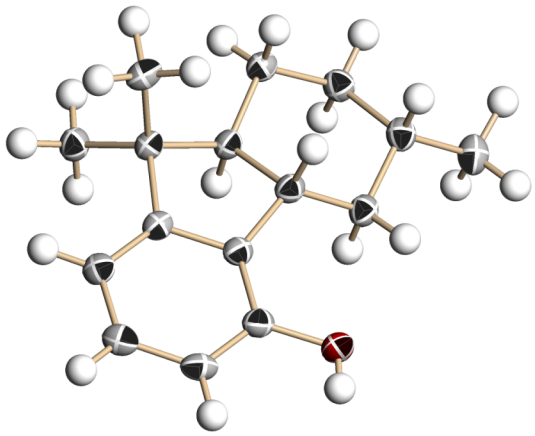
VIII. Preparation of methyl substituted 2,3,4,4a,9,9a-hexahydro-3,9,9-trimethyl-1H-fluorene



(3*R*,4a*S*,9a*R*)-2,3,4,4a,9,9a-hexahydro-3,9,9-trimethyl-1*H*-fluoren-5-yl methanesulfonate. Following the general synthesis of **1a** on 50% scale the target was synthesized yielding a clear oil (1.7 g, 76%). IR (neat) ν_{max} 2954, 1457, 1364, 1161, 957, 918, 828, 808, 750 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.19 (t, *J* = 7.8 Hz, 1H), 7.11 (d, *J* = 7.8 Hz, 1H), 7.08 (d, *J* = 7.8 Hz, 1H), 3.12 (s, 3H), 2.88-2.84 (m, 1H), 2.68-2.66 (m, 1H), 1.90-1.87 (m, 1H), 1.79-1.76 (m, 1H), 1.68-1.57 (m, 2H), 1.49-1.45 (m, 2H), 1.31 (s, 3H), 1.20-1.07 (m, 2H), 1.02 (d, *J* = 6.6, 3H), 0.97 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.7, 146.1, 137.0, 128.2, 121.4, 119.8, 59.2, 46.6, 44.1, 38.5, 37.9, 35.5, 33.6, 26.2, 25.1, 22.8, 22.3; ESI MS calc'd. for $[C_{17}H_{25}O_3S + H]^+$: 309.1, found: 309.1. Purity was determined to be 92% by HPLC trace.



(4b*S*,6*R*,8a*R*)-5,6,7,8,8a,9-hexahydro-6,9,9-trimethyl-4b*H*-fluoren-4-ol (21). Following the general synthesis of **1a** on 50% scale the target was synthesized yielding slightly yellow solid (1.2 g, 95%). $[\alpha]^{23}_{D}$ +3.43° (*c* 1.00, MeOH); mp 70.1 – 73.0 °C; IR (neat) ν_{max} 568, 2949, 2920, 2858, 1581, 1456, 1275, 960, 919, 786, 737, 693 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.07 (t, *J* = 7.8 Hz, 1H), 6.79 (d, *J* = 7.8 Hz, 1H), 6.58 (d, *J* = 7.8 Hz, 1H), 6.74 (s, 1H), 2.81-2.77 (m, 1H), 2.63-2.61 (m, 1H), 1.91-1.89 (m, 1H), 1.79-1.76 (m, 1H), 1.68-1.57 (m, 2H), 1.49-1.45 (m, 2H), 1.41-1.34 (m, 1H), 1.30 (s, 3H), 1.03 (d, *J* = 6.6, 3H), 0.96 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.6, 152.7, 129.4, 128.0, 115.0, 114.0, 59.4, 46.0, 43.9, 39.5, 35.7, 33.8, 26.3, 25.1, 22.8, 22.3; ESI MS calc'd. for $[C_{17}H_{23}O + H]^+$: 231.2, found: 231.2. Purity was determined to be 99% by HPLC trace. The absolute structure was solved by X-ray crystallography, which is represent by the structure below.



IX. Computational Details

All calculations were performed with *GAUSSIAN03*. Structures were optimized without symmetry constraints using the B3LYP/6-31+G(d,p) level of theory. Frequency analyses at the same level were used to confirm each structure as a minimum. Reported energies are computed free energies including unscaled zero-point energy corrections. Structural drawings were produced using *Ball&Stick*.

Gaussian03 Full Reference

M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria,
M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven,
K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi,
V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega,
G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota,
R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao,
H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross,
V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann,
O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski,
P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg,
V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain,
O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari,
J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford,
J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz,
I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham,
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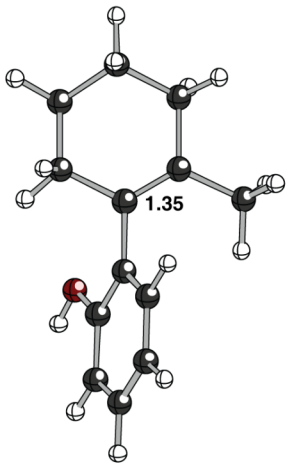
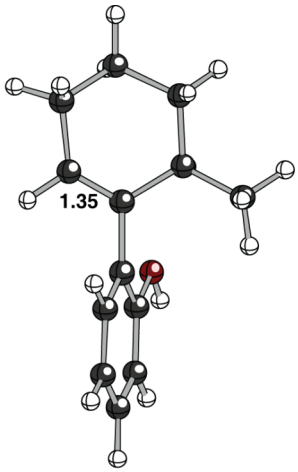
Ball&Stick Reference: Müller, N.; Falk, A. Ball & Stick 4.0a12, molecular graphics software for MacOS, Johannes Kepler University Linz, 2000.

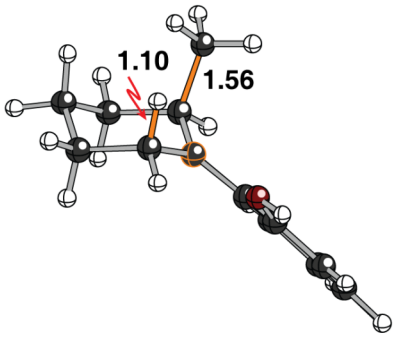
Computed Structure Images



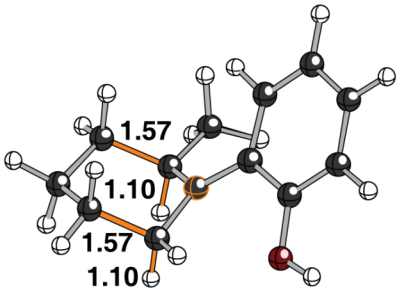
alkene 1a
"0" kcal/mol



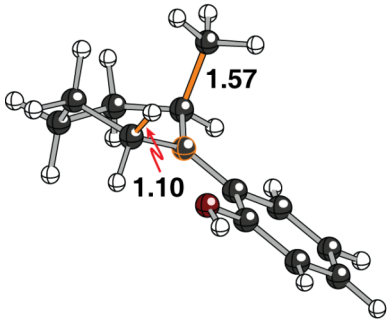
alkene 1b
2.27



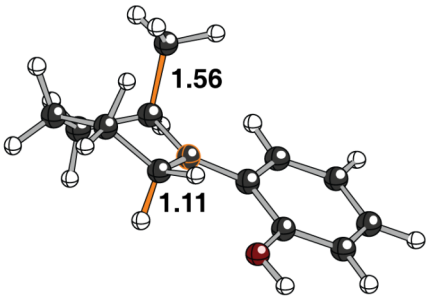
cat1.1
"0" kcal/mol



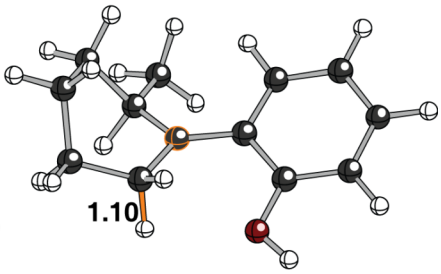
cat1.2
3.62



cat1.3
2.00



cat1.4
2.22



cat1.5
5.03

Computed energy and coordinates for alkene 1a

HF = -580.283528 hartrees (-364133.71665528 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.258763 (Hartree/Particle)
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies = -580.063926 hartrees (-363995.91420426 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.644576	-0.007665	-0.148763
2	6	1.412519	0.920630	0.458693
3	6	1.232736	-1.206380	-0.880621
4	1	0.641412	-2.095599	-0.634387
5	1	1.105754	-1.052145	-1.964065
6	6	2.928707	0.850328	0.428986
7	1	3.284980	0.579800	1.436063
8	6	2.711022	-1.450971	-0.558334
9	1	3.132392	-2.180575	-1.260409
10	1	2.796413	-1.888308	0.445949
11	6	3.490606	-0.133980	-0.603555
12	1	4.559074	-0.301096	-0.421674
13	1	3.404575	0.301352	-1.609045
14	1	3.326043	1.858647	0.243807
15	6	0.865437	2.083914	1.250453
16	1	-0.218750	2.044517	1.368653
17	1	1.318086	2.104564	2.251278
18	1	1.122824	3.040455	0.774914
19	6	-0.847207	0.083010	-0.192237
20	6	-1.658554	-0.824207	0.518005
21	6	-1.494815	1.044415	-0.982242
22	6	-3.053605	-0.759929	0.440700
23	6	-2.887814	1.120480	-1.067545
24	1	-0.880071	1.744893	-1.540820
25	6	-3.668491	0.211412	-0.351853
26	1	-3.657297	-1.467729	1.005915
27	1	-3.355334	1.878328	-1.688591
28	1	-4.752484	0.252836	-0.405227
29	8	-1.024554	-1.760378	1.299805
30	1	-1.681891	-2.323260	1.729071

Computed energy and coordinates for alkene 1b

HF = -580.2805911 hartrees (-364131.873721161 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.259101 (Hartree/Particle)
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies = -580.060306 hartrees (-363993.64261806 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.273303	1.402588	-0.504524
2	1	0.672694	2.257066	-0.813838
3	6	0.640054	0.300217	-0.059822
4	6	2.767350	1.541871	-0.649116
5	1	2.995224	2.040575	-1.600633
6	1	3.149741	2.215237	0.134732
7	6	1.404846	-0.945046	0.398356
8	1	1.304424	-1.699544	-0.394038
9	6	3.478314	0.185031	-0.567315
10	1	4.558691	0.326458	-0.443968
11	1	3.333801	-0.358534	-1.510873
12	6	2.903473	-0.640826	0.586737
13	1	3.449548	-1.586070	0.697242
14	1	3.041473	-0.087454	1.527593
15	6	-0.852769	0.304142	0.004838
16	6	-1.535039	1.304909	0.715294
17	6	-1.637747	-0.663971	-0.654433
18	6	-2.929906	1.358184	0.775797
19	1	-0.944114	2.049496	1.240486
20	6	-3.034088	-0.624552	-0.597070
21	6	-3.682212	0.385004	0.117325
22	1	-3.420269	2.146161	1.339011
23	1	-3.613630	-1.381828	-1.122021
24	1	-4.767387	0.404737	0.155207
25	6	0.819185	-1.553802	1.685297
26	1	0.850083	-0.832786	2.511047
27	1	-0.219814	-1.868496	1.554178
28	1	1.401351	-2.432994	1.984635
29	8	-0.981657	-1.636234	-1.372701
30	1	-1.627148	-2.224641	-1.785343

Computed energy and coordinates for cation cat1.1

Values come from Link 3:
HF = -580.6369671 hartrees (-364355.503224921 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.272326 (Hartree/Particle)
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies = -580.403976 hartrees (-364209.29897976 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.182417	1.380854	-0.062626
2	6	2.396320	1.312511	-1.036450
3	6	3.394929	0.222323	-0.651135
4	6	2.686338	-1.130032	-0.547591
5	6	1.451419	-1.096676	0.393791
6	6	0.524739	0.048582	0.101986
7	1	4.190914	0.163292	-1.400949
8	1	2.019229	1.136133	-2.051686
9	1	2.864536	2.301326	-1.043356
10	1	1.549864	1.697188	0.926413
11	1	0.481520	2.143920	-0.388276
12	1	2.353341	-1.444040	-1.545079
13	1	3.364841	-1.909324	-0.185023
14	1	0.924852	-2.047445	0.308513
15	1	3.883550	0.476463	0.297182
16	6	1.865278	-0.985009	1.898585
17	1	0.992278	-0.954065	2.556500
18	1	2.447479	-1.876053	2.149522
19	1	2.481186	-0.105520	2.095157
20	6	-0.879344	-0.144634	-0.000625
21	6	-1.850052	0.909630	0.200909
22	6	-1.407274	-1.434327	-0.358739
23	6	-3.214390	0.668884	0.006787
24	6	-2.750196	-1.649998	-0.563697
25	1	-0.720333	-2.249154	-0.543277
26	6	-3.658362	-0.588969	-0.377121
27	1	-3.926067	1.473293	0.172388
28	1	-3.106754	-2.625399	-0.874612
29	1	-4.721001	-0.752986	-0.528715
30	8	-1.421186	2.098218	0.653533
31	1	-2.160879	2.707790	0.802591

Computed energy and coordinates for cation cat1.2

HF = -580.6318352 hartrees (-364352.282906352 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.272303 (Hartree/Particle)
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies = -580.398214 hartrees (-364205.68326714 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.208749	-1.505067	-0.982718
2	6	3.296515	-0.462083	-0.736318
3	6	2.692399	0.905471	-0.417266
4	6	1.634756	0.814136	0.744487
5	6	0.598985	-0.214876	0.382685
6	6	1.181223	-1.578685	0.205669
7	1	3.461179	1.616382	-0.098911
8	1	3.938518	-0.783460	0.093684
9	1	3.940288	-0.384294	-1.619839
10	1	1.662830	-1.280307	-1.907122
11	1	2.630188	-2.508251	-1.098879
12	1	2.174656	0.317744	1.565916
13	1	1.727490	-1.875922	1.109332
14	1	0.433808	-2.336402	-0.006849
15	1	2.206025	1.334278	-1.302662
16	6	1.221925	2.201823	1.260017
17	1	0.324849	2.166872	1.884451
18	1	2.037102	2.594868	1.873854
19	1	1.060358	2.926249	0.457734
20	6	-0.769076	0.058832	0.114212
21	6	-1.822029	-0.912036	0.307536
22	6	-1.155954	1.324754	-0.440238
23	6	-3.135158	-0.618467	-0.072993
24	6	-2.446253	1.584520	-0.844072
25	1	-0.392594	2.067606	-0.617247
26	6	-3.441449	0.606979	-0.650944
27	1	-3.916762	-1.354342	0.096010
28	1	-2.694389	2.532966	-1.306822
29	1	-4.465730	0.811833	-0.947441
30	8	-1.524950	-2.059297	0.940917
31	1	-2.316008	-2.603250	1.077104

Computed energy and coordinates for cation cat1.3

HF = -580.6334557 hartrees (-364353.299786307 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.272176 (Hartree/Particle)
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies = -580.400783 hartrees (-364207.29534033 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.199898	1.350413	0.131646
2	1	0.729049	1.994122	-0.621934
3	6	0.536025	0.009675	0.066396
4	6	2.725299	1.355017	-0.050693
5	1	3.031549	2.368167	-0.327202
6	1	3.239538	1.124969	0.888904
7	6	1.445370	-1.173489	0.188350
8	1	0.931473	-2.094051	-0.078962
9	6	3.116305	0.341246	-1.127607
10	1	4.186378	0.393938	-1.347152
11	1	2.594287	0.594585	-2.060449
12	6	2.744712	-1.080658	-0.680424
13	1	2.618182	-1.725822	-1.555414
14	1	3.561808	-1.510495	-0.092312
15	6	-0.877278	-0.140811	-0.038540
16	6	-1.461927	-1.431332	-0.291763
17	6	-1.812483	0.956399	0.093595
18	6	-2.817932	-1.623965	-0.410141
19	1	-0.814847	-2.286673	-0.424258
20	6	-3.191768	0.743444	-0.018216
21	6	-3.689720	-0.525912	-0.268454
22	1	-3.213646	-2.611551	-0.618201
23	1	-3.869738	1.585508	0.093273
24	1	-4.762346	-0.668902	-0.358037
25	6	1.764174	-1.312461	1.718838
26	1	2.312208	-0.453953	2.110928
27	1	0.851297	-1.446147	2.305778
28	1	2.386787	-2.202233	1.845911
29	8	-1.338601	2.184934	0.354192
30	1	-2.060371	2.826701	0.448341
31	1	0.903147	1.826973	1.079331

Computed energy and coordinates for cation cat1.4

HF = -580.6337621 hartrees (-364353.492055371 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.272178 (Hartree/Particle)
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies = -580.400442 hartrees (-364207.08135942 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.663882	-0.661075	-1.068456
2	6	1.412095	-1.130246	-0.283638
3	6	0.499643	0.042255	-0.037626
4	6	1.179246	1.352349	0.193923
5	6	2.660337	1.283222	0.594740
6	6	3.518330	0.377995	-0.318858
7	1	0.895887	-1.861681	-0.909491
8	1	4.281439	-0.121140	0.285390
9	1	2.326543	-0.251869	-2.028234
10	1	1.064587	1.905639	-0.757500
11	1	0.613062	1.960549	0.904139
12	1	2.717032	0.938492	1.632270
13	1	3.051072	2.304425	0.602807
14	1	4.060309	0.982318	-1.052407
15	1	3.257103	-1.548749	-1.310533
16	6	1.779838	-1.849246	1.049111
17	1	0.892292	-2.246255	1.548690
18	1	2.444332	-2.685082	0.811922
19	1	2.297946	-1.194724	1.751597
20	6	-0.913127	-0.107414	-0.068005
21	6	-1.495385	-1.423199	-0.114571
22	6	-1.846876	0.996828	-0.022034
23	6	-2.852462	-1.634268	-0.072170
24	1	-0.843122	-2.284767	-0.154129
25	6	-3.227885	0.766902	0.008673
26	6	-3.724427	-0.527364	-0.010316
27	1	-3.251267	-2.642172	-0.087941
28	1	-3.907766	1.614174	0.039742
29	1	-4.798515	-0.684628	0.015378
30	8	-1.366914	2.249129	-0.045284
31	1	-2.084863	2.902014	-0.034054

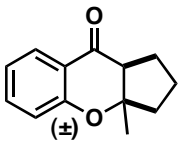
Computed energy and coordinates for cation cat1.5

HF = -580.629373 hartrees (-364350.73785123 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.271999 (Hartree/Particle)
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies = -580.395968 hartrees (-364204.27387968 kcal/mol)

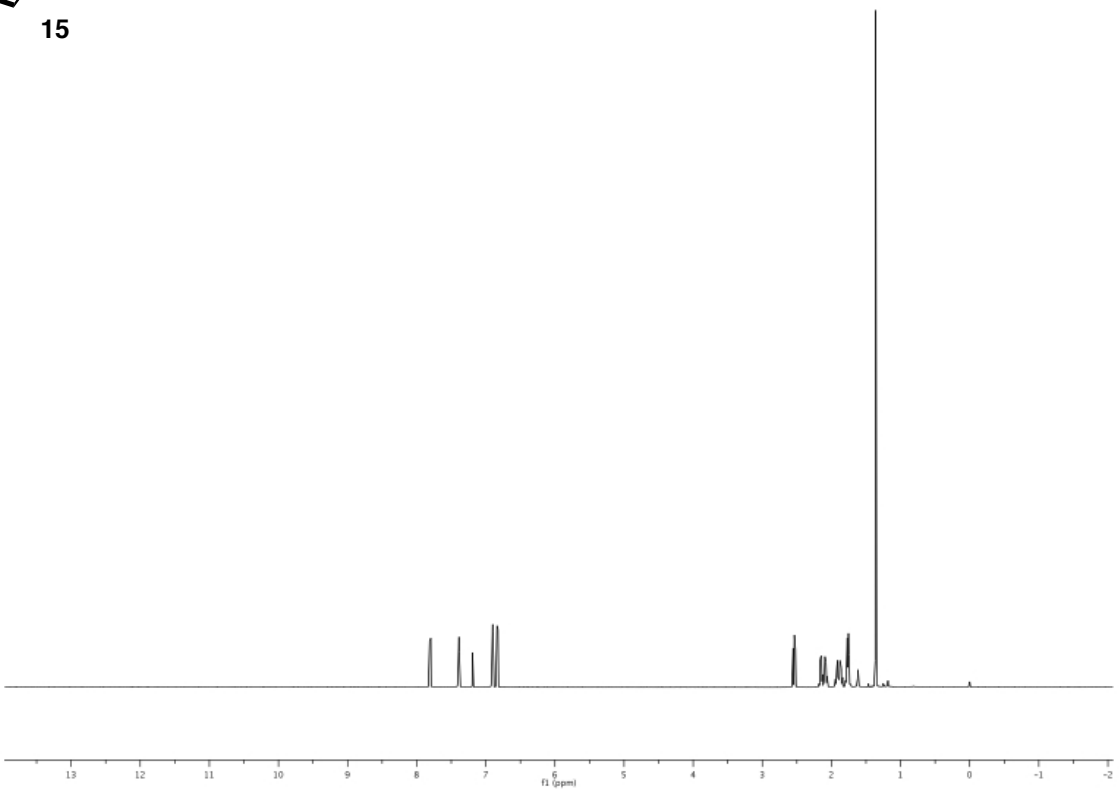
Coordinates (from last standard orientation):

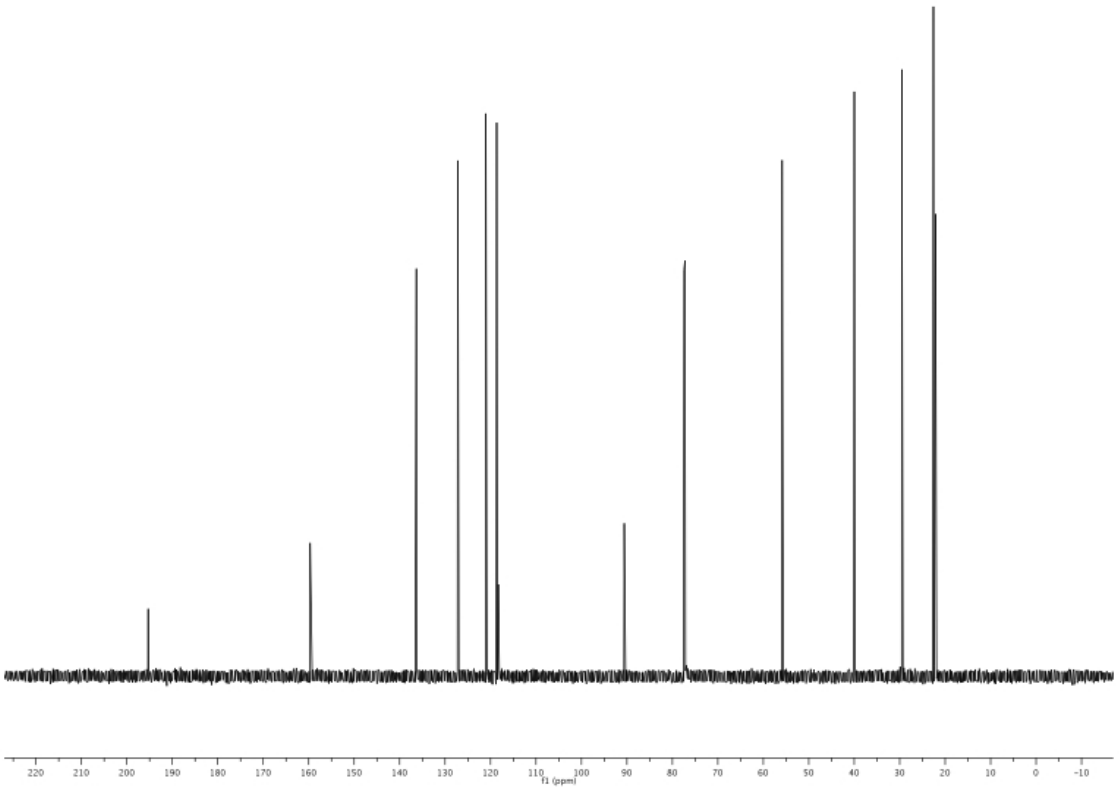
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.722550	-1.509995	-0.083085
2	6	3.058347	-0.415913	-1.105299
3	6	2.676467	0.971336	-0.553381
4	6	1.601853	0.903442	0.597642
5	6	0.585293	-0.150702	0.280829
6	6	1.205519	-1.515764	0.189409
7	1	3.545638	1.476407	-0.120948
8	1	4.120550	-0.441050	-1.364073
9	1	2.506167	-0.619039	-2.031679
10	1	0.678965	-2.103609	-0.568692
11	1	3.294078	-1.355265	0.840009
12	1	2.138764	0.413512	1.427782
13	1	0.983941	-2.038658	1.134513
14	1	3.005566	-2.499912	-0.452184
15	1	2.289949	1.621731	-1.344991
16	6	1.227051	2.301921	1.106693
17	1	0.379747	2.285932	1.797813
18	1	2.086721	2.703746	1.650924
19	1	1.014338	3.010802	0.302102
20	6	-0.805549	0.059080	0.079210
21	6	-1.300256	1.354225	-0.294709
22	6	-1.788565	-0.997538	0.172125
23	6	-2.626928	1.583554	-0.579783
24	1	-0.596693	2.162449	-0.414549
25	6	-3.139917	-0.739587	-0.079630
26	6	-3.553808	0.530574	-0.457175
27	1	-2.956171	2.567080	-0.895233
28	1	-3.863097	-1.544923	0.017765
29	1	-4.605692	0.707698	-0.660096
30	8	-1.382835	-2.220443	0.551802
31	1	-2.132436	-2.831157	0.630045

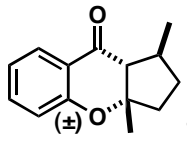
X. ^{1}H and ^{13}C NMR Spectra



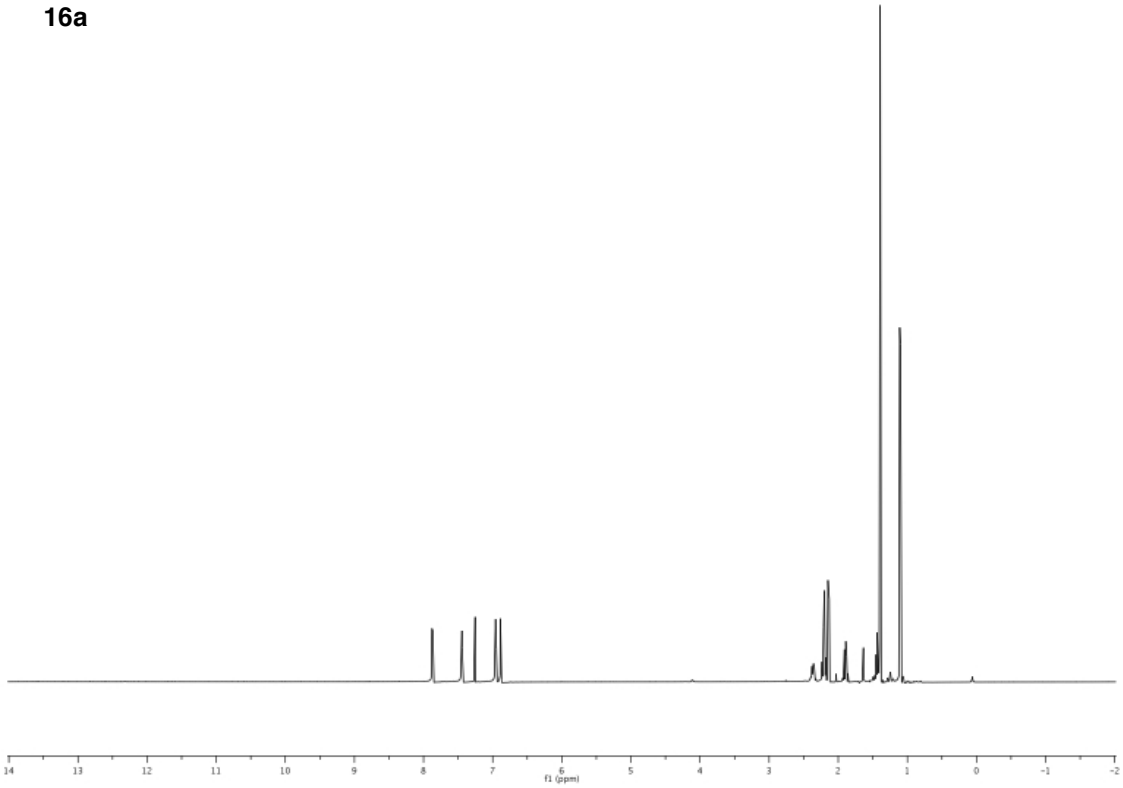
15

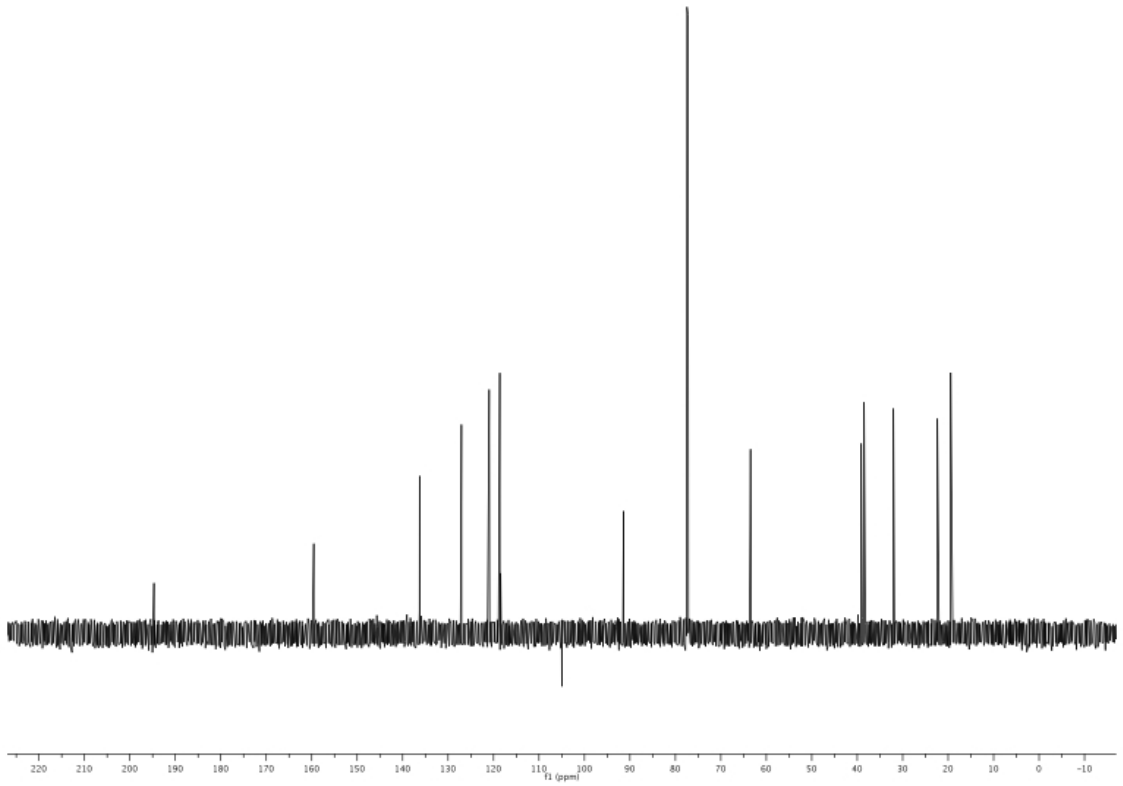


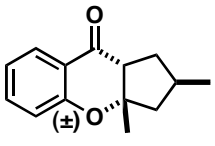



O
(±) O

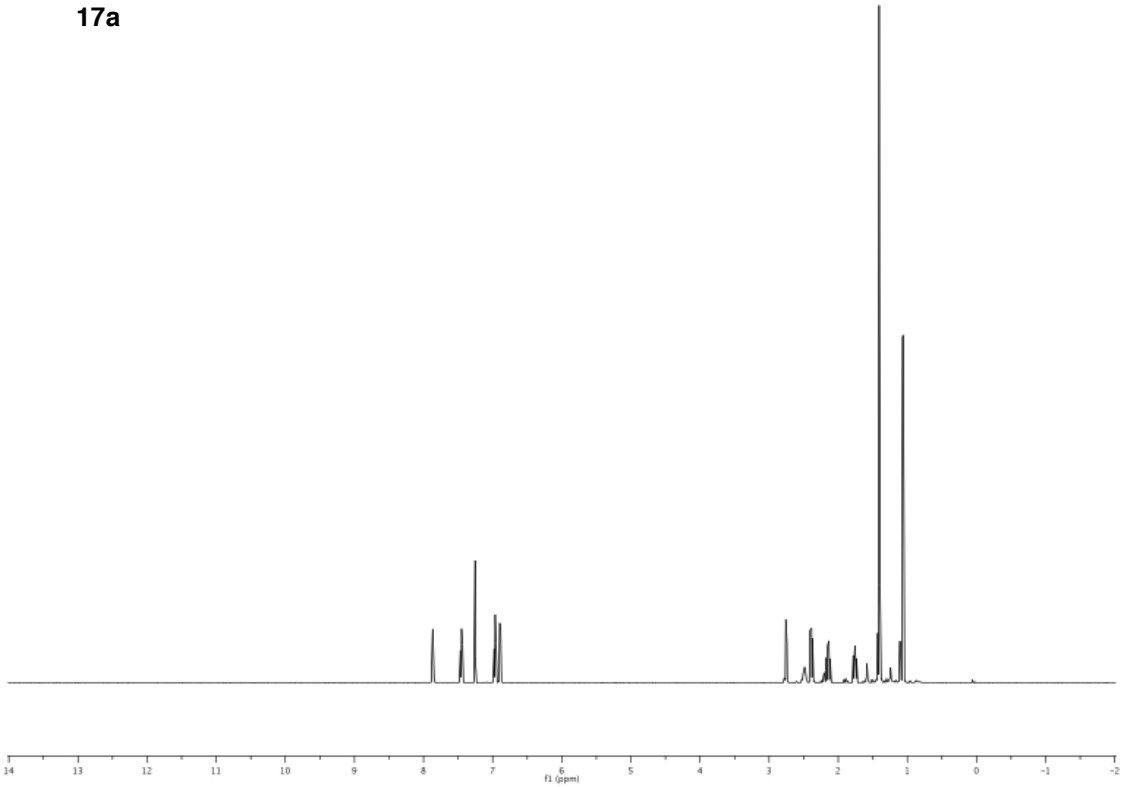
16a

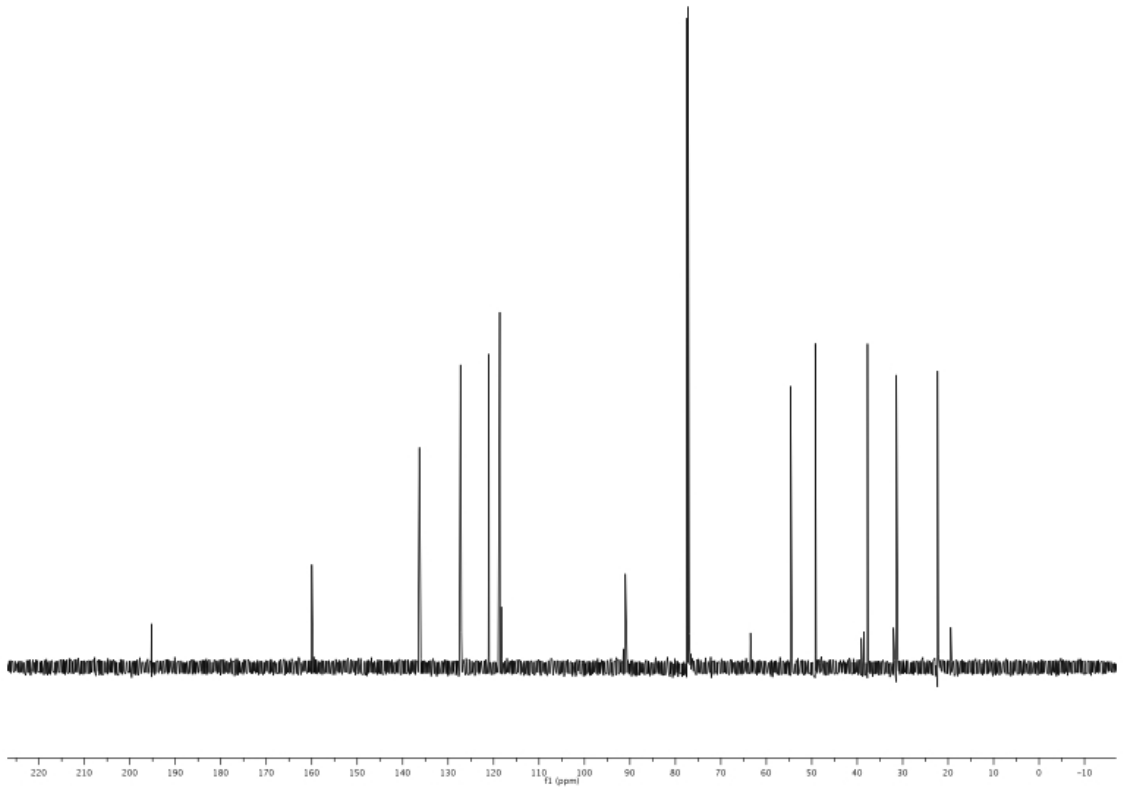

14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2
f1 (ppm)


220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


O
(±) O

17a


14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2
f1 (ppm)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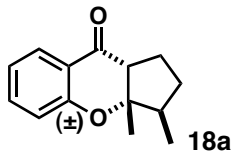
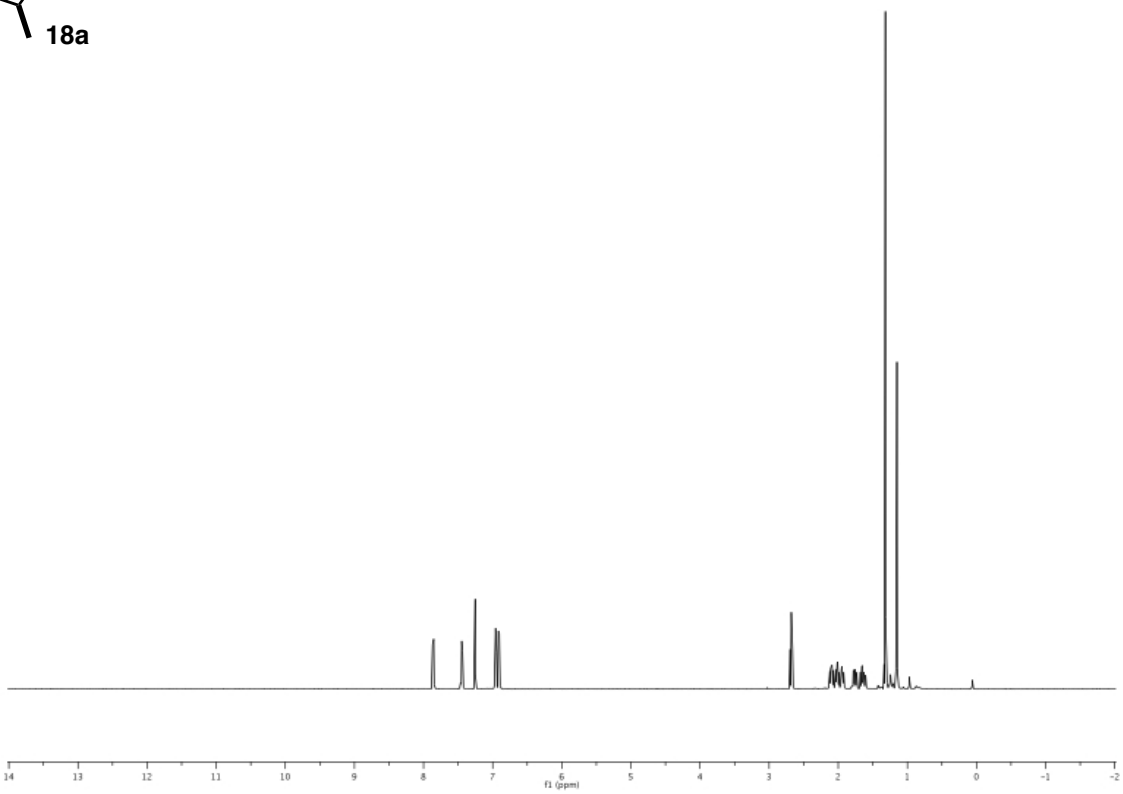
f1 (ppm)


O
(±) O

18a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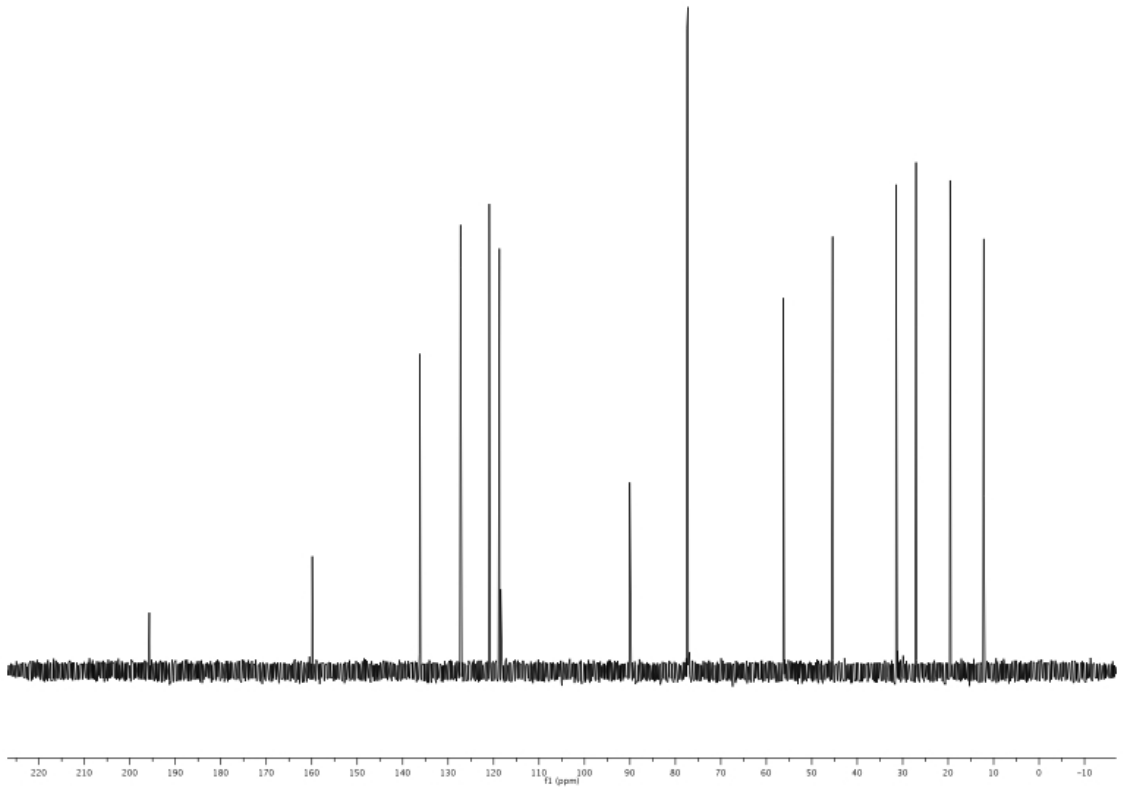
f1 (ppm)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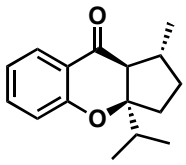
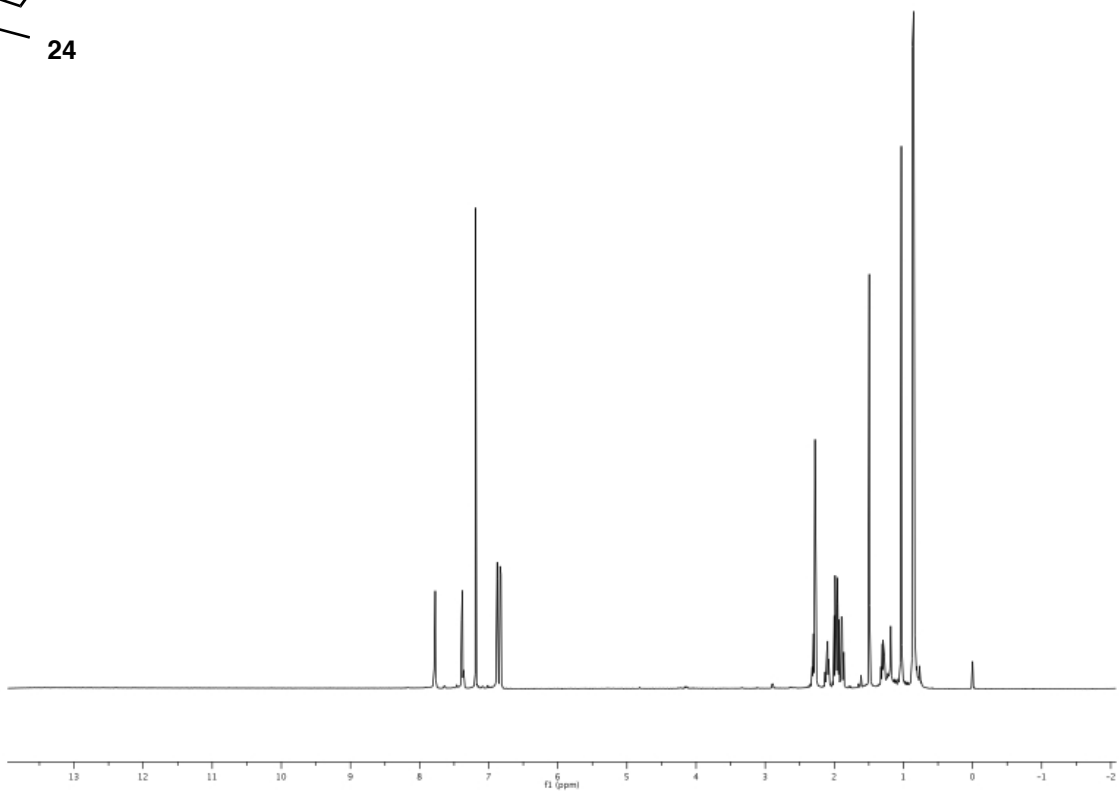
f1 (ppm)



24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4
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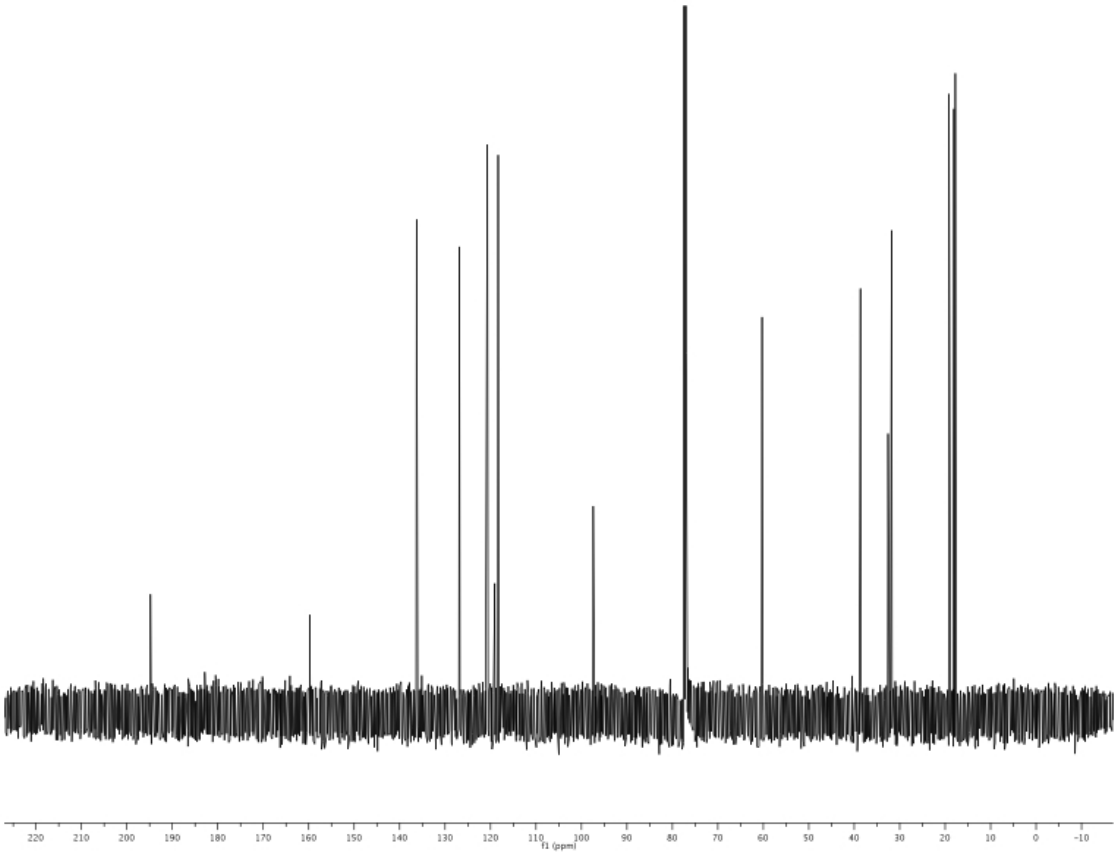
1
0
−1
−2
f1 (ppm)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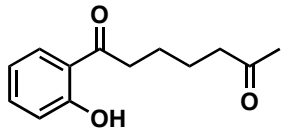
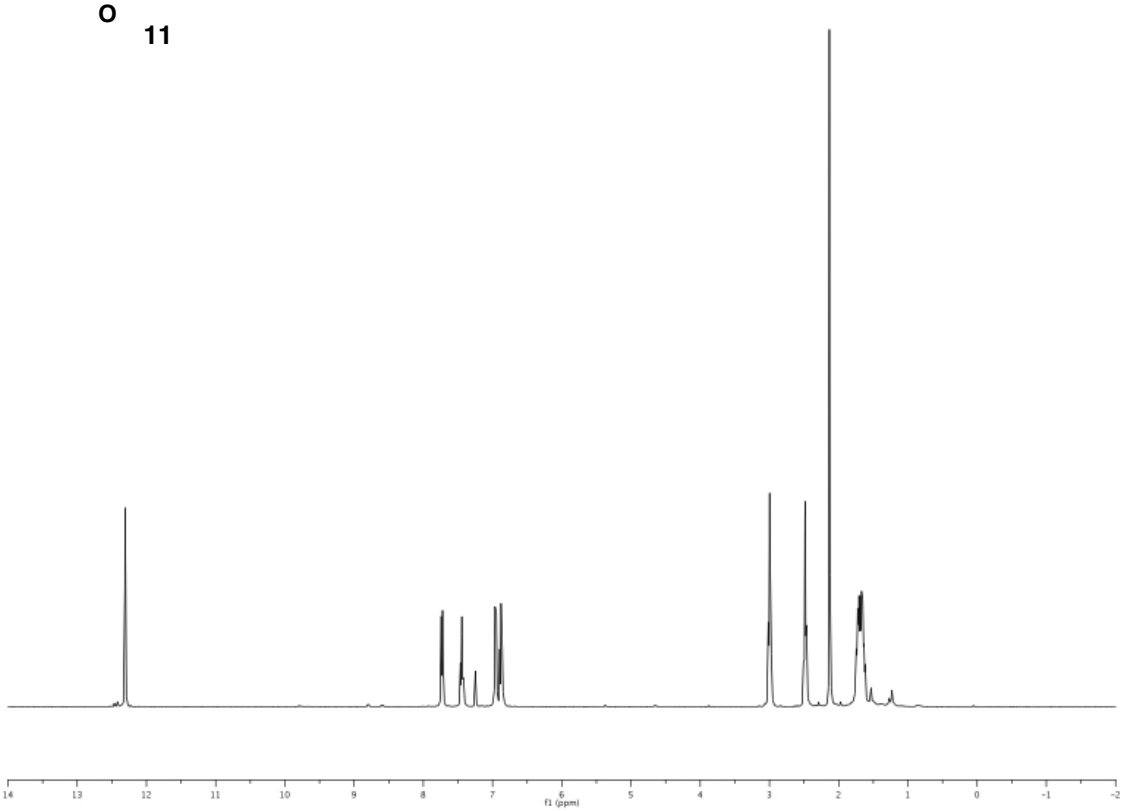
f1 (ppm)


O
OH
O

11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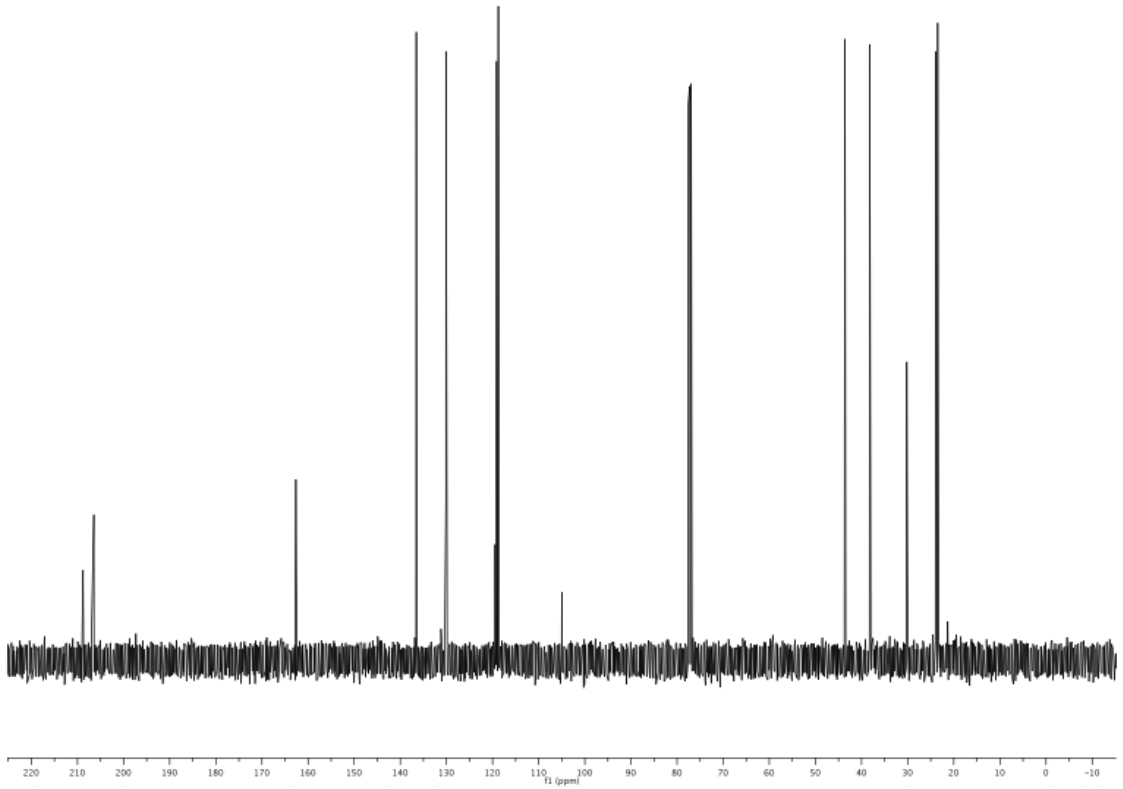
f1 (ppm)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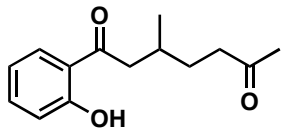
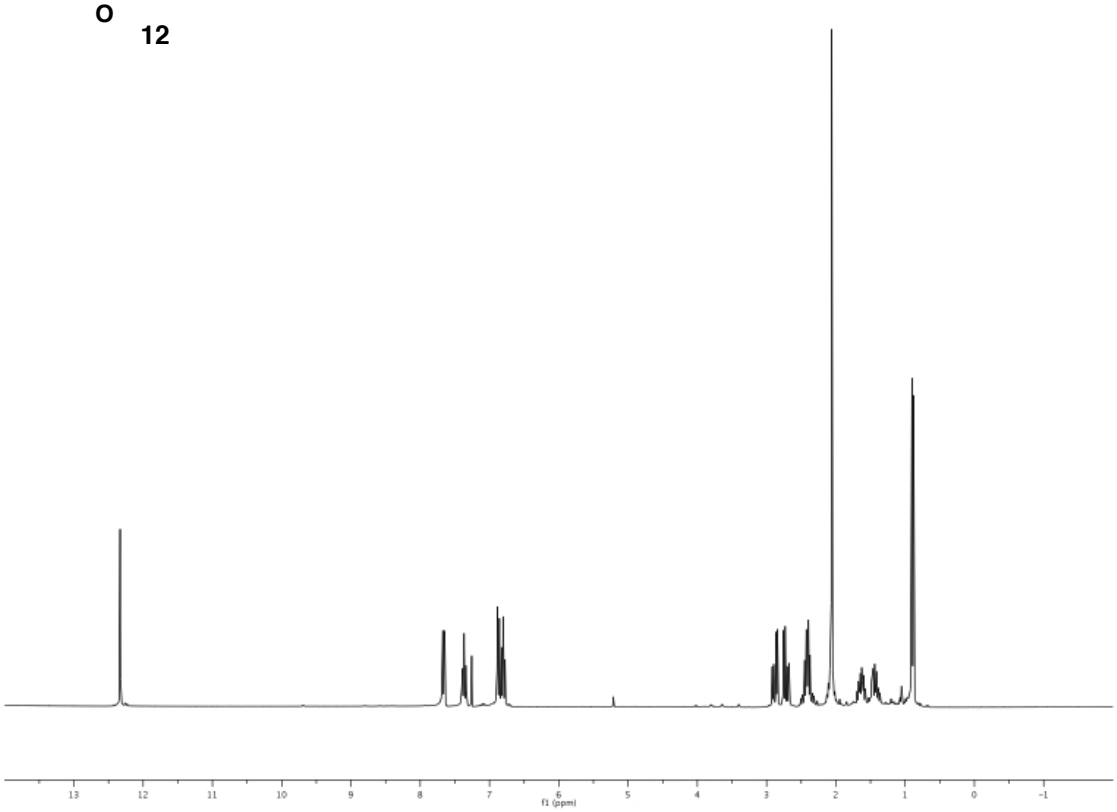
f1 (ppm)


O
OH
O

12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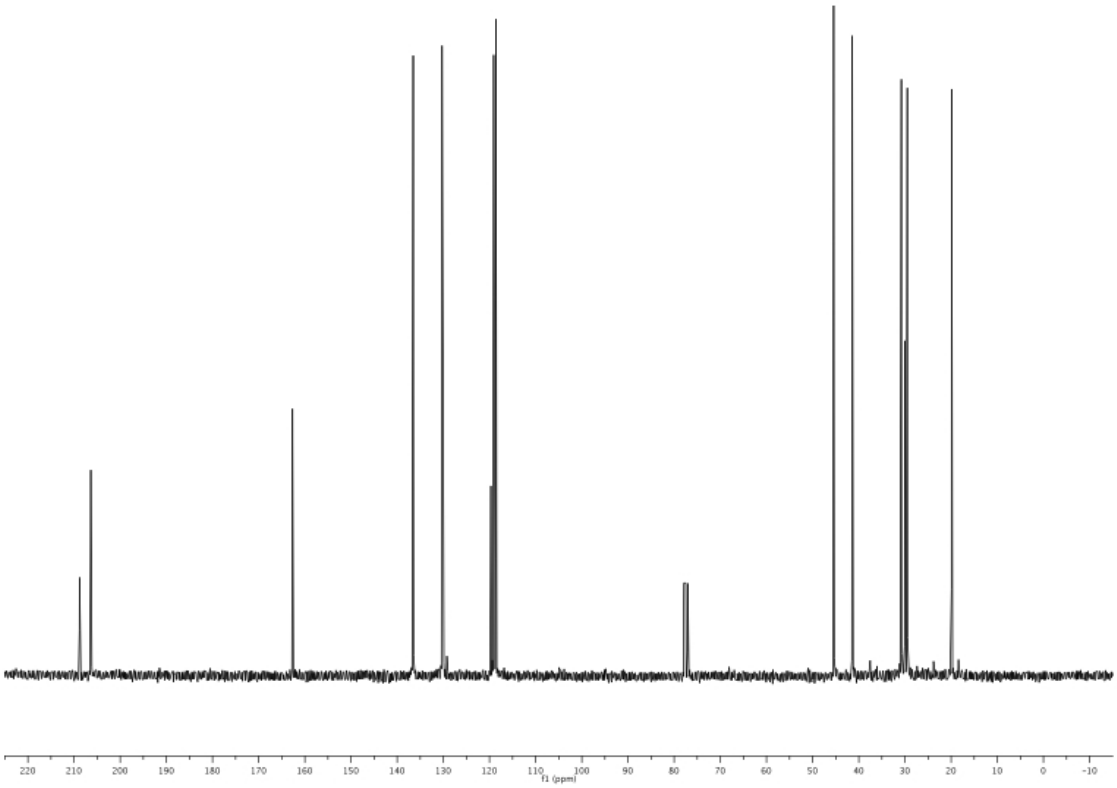
f1 (ppm)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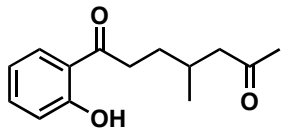
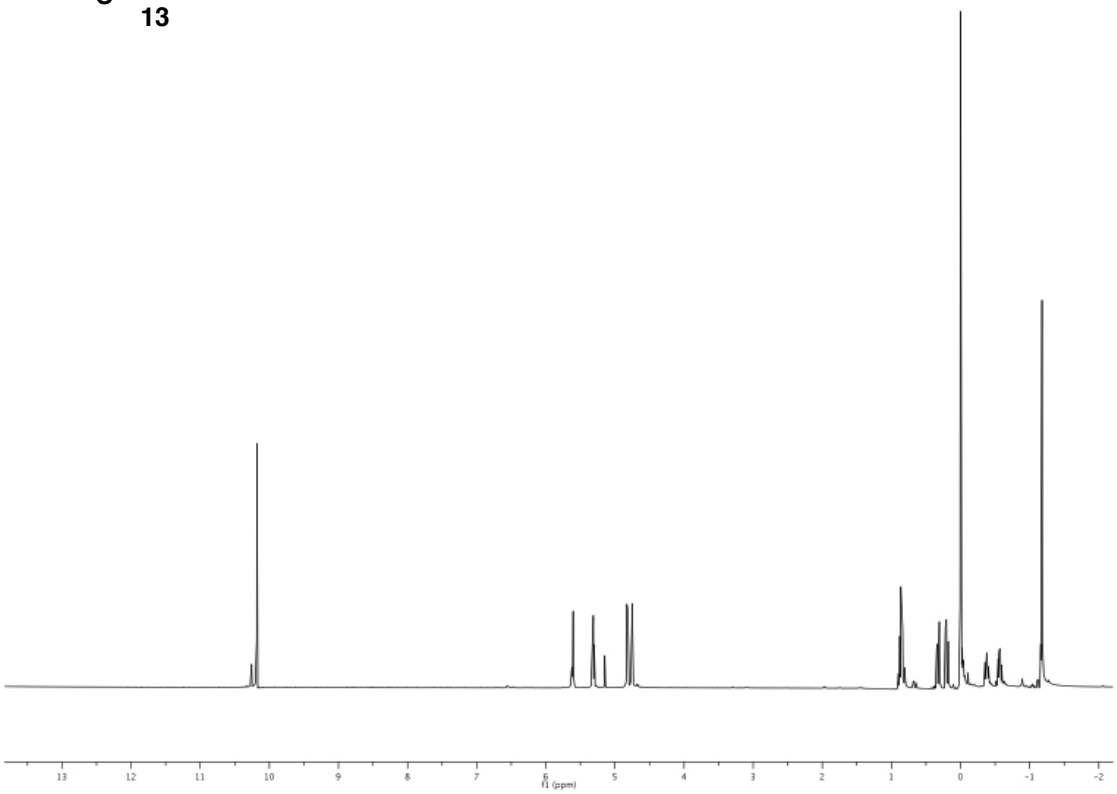
-10
f1 (ppm)


O
OH
O

13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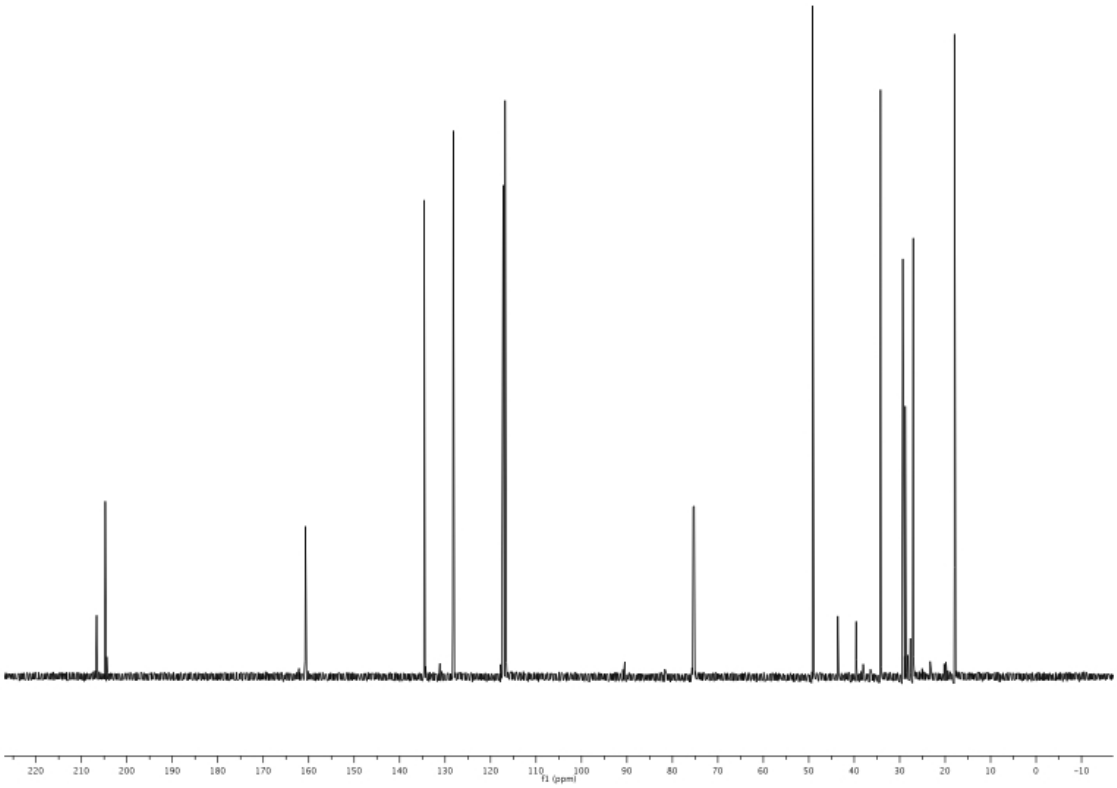
f1 (ppm)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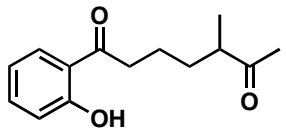
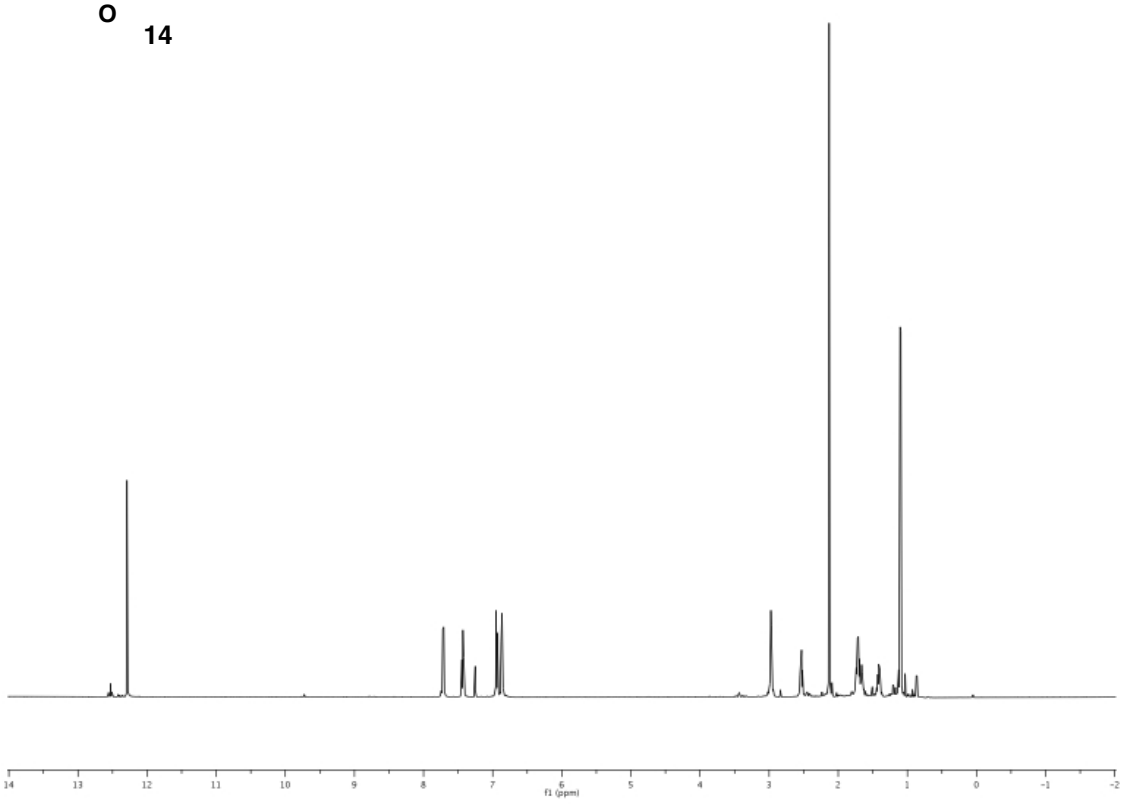
f1 (ppm)


O
OH
O

14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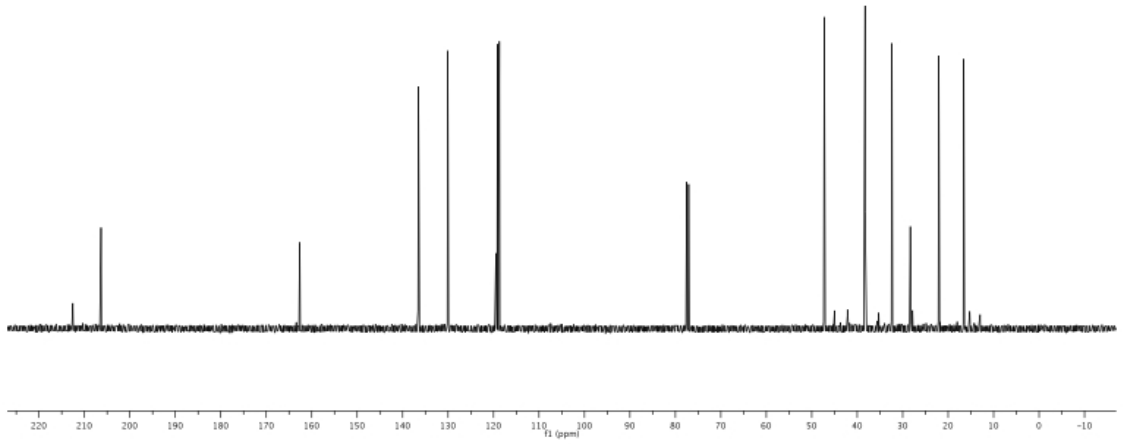
f1 (ppm)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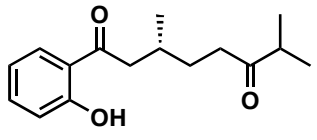
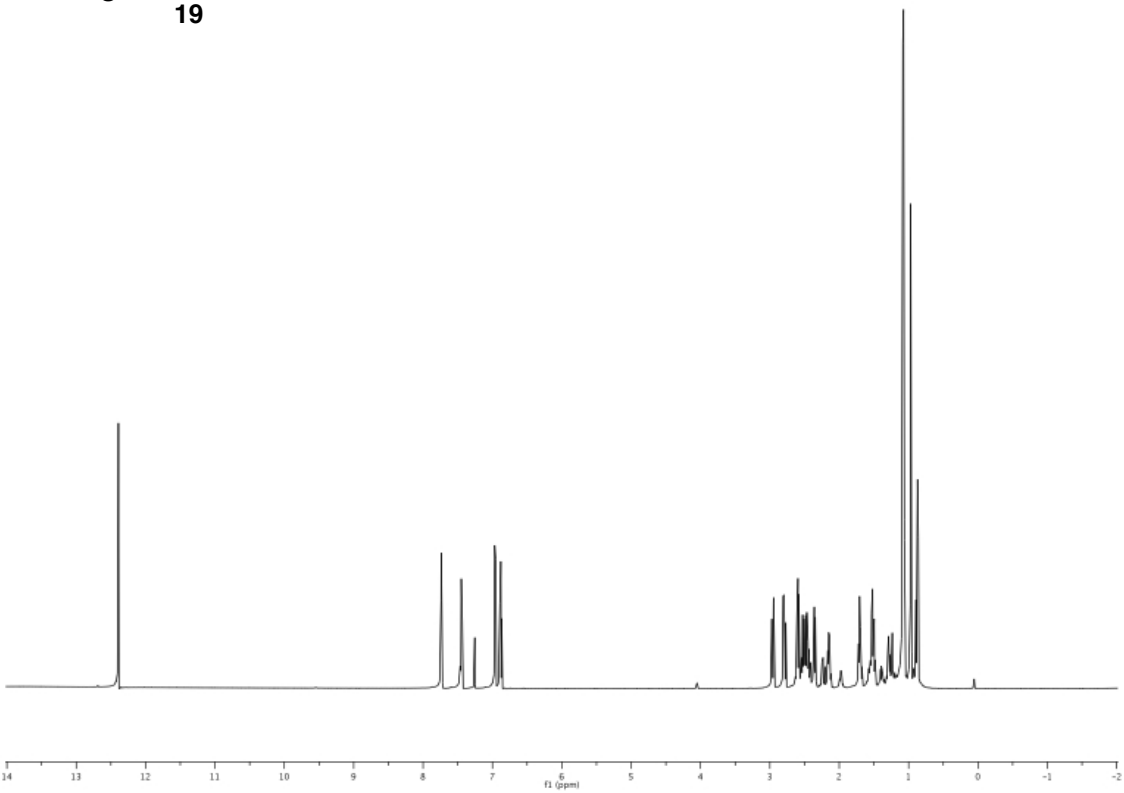
f1 (ppm)


O
OH
O

19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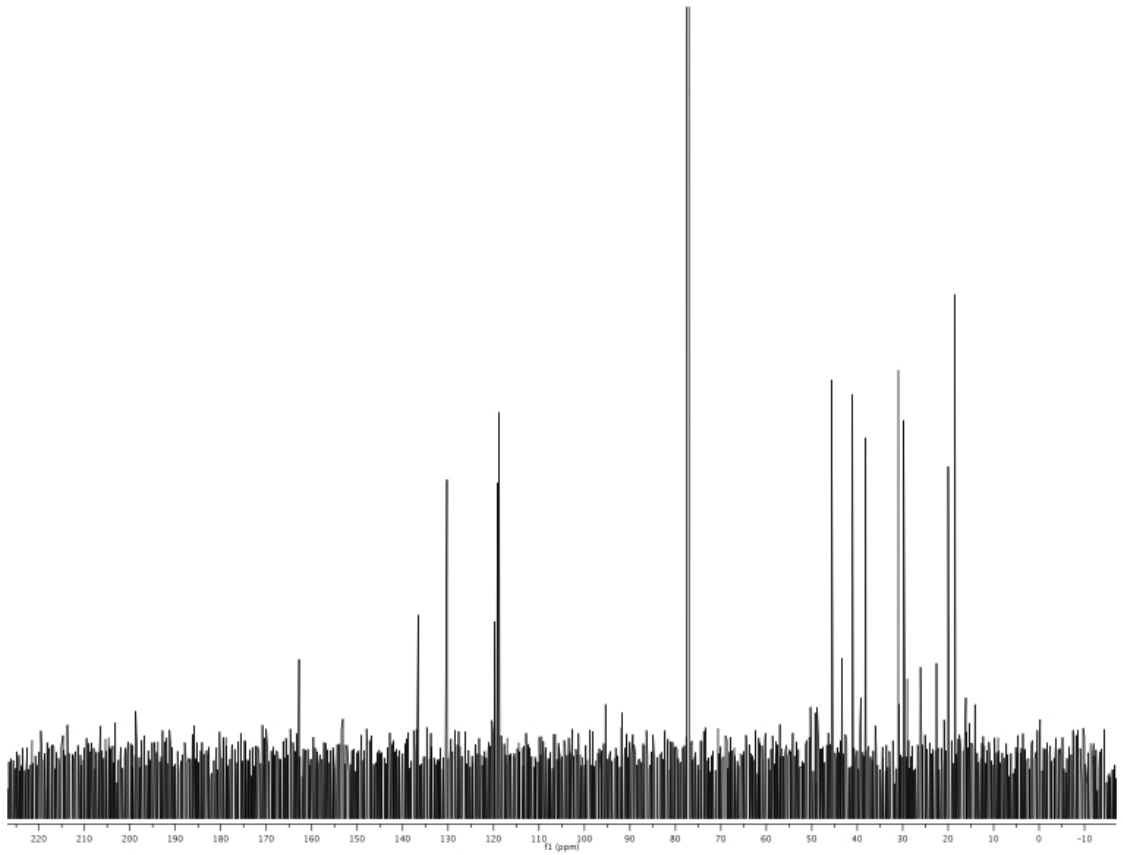
f1 (ppm)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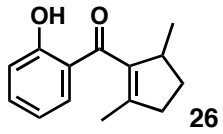
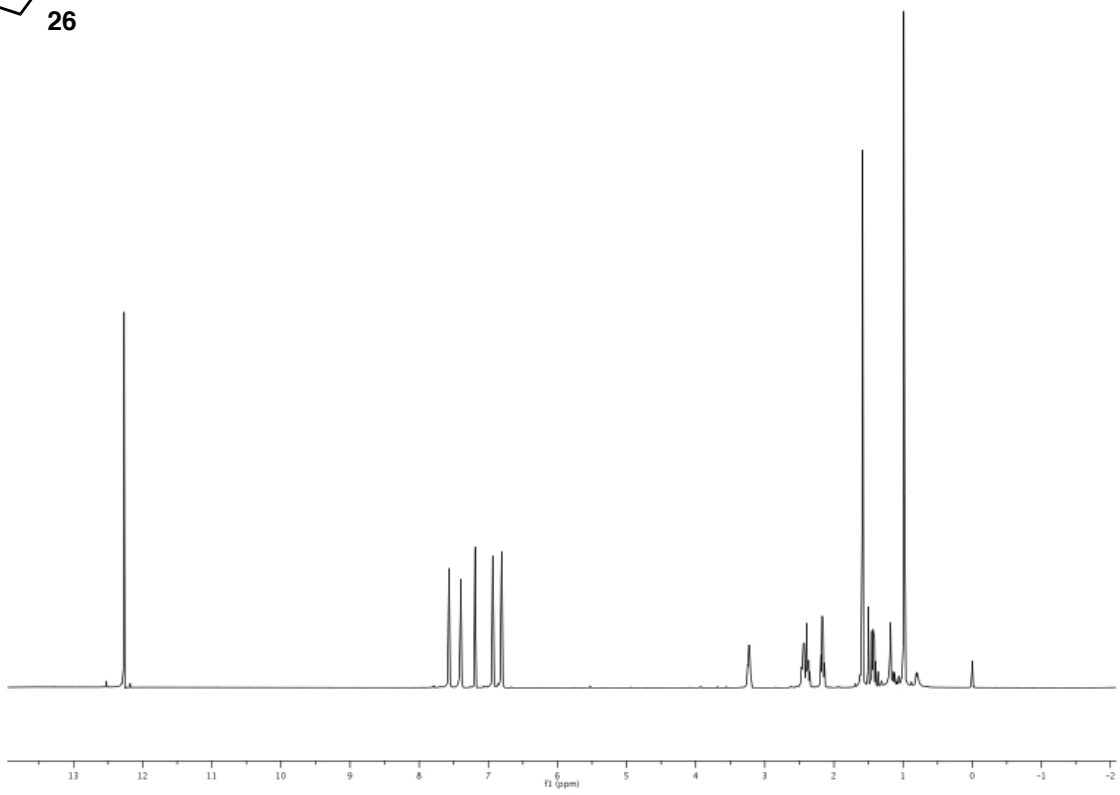
-10
f1 (ppm)


OH
O

26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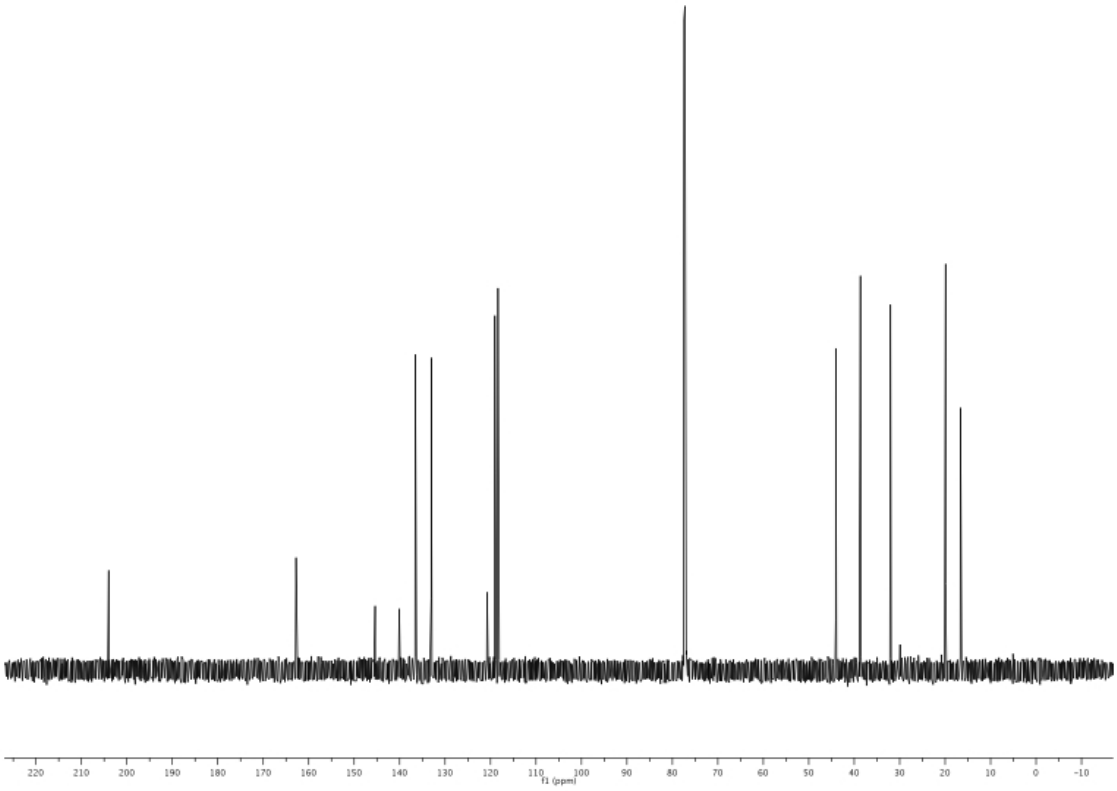
f1 (ppm)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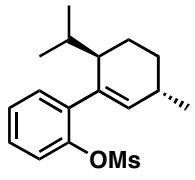
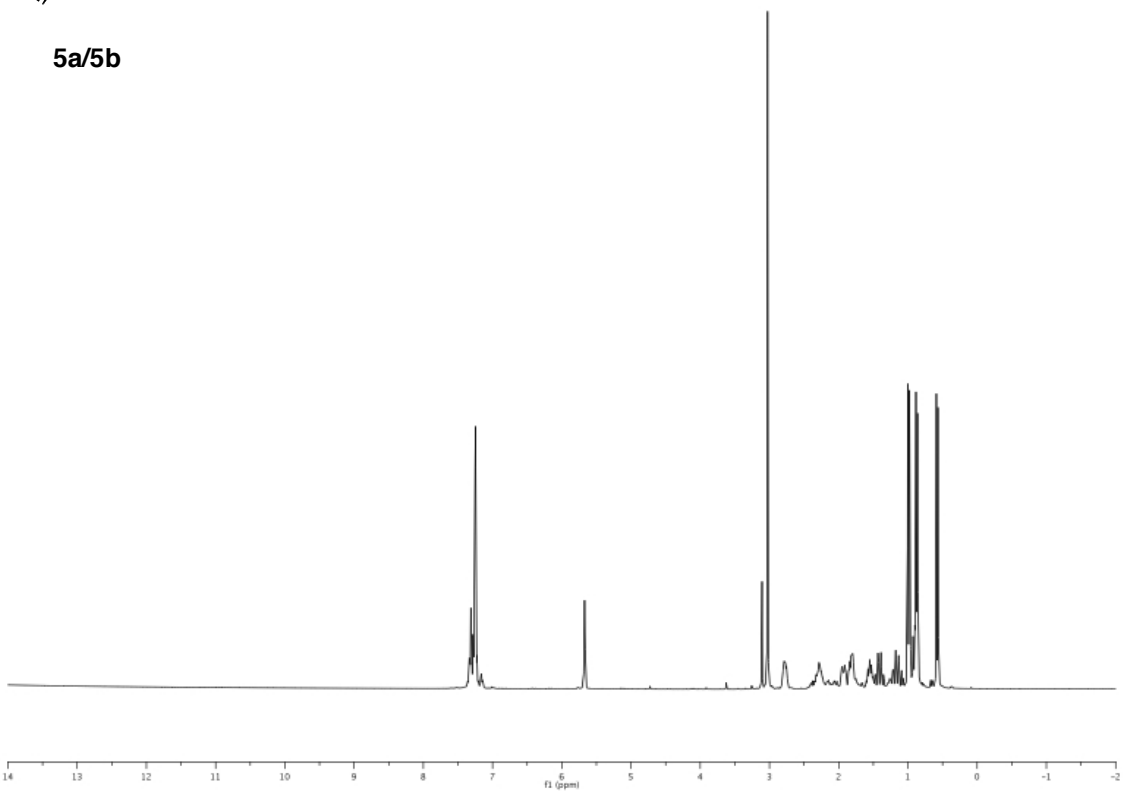
f1 (ppm)


OMs

5a/5b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f1 (ppm)
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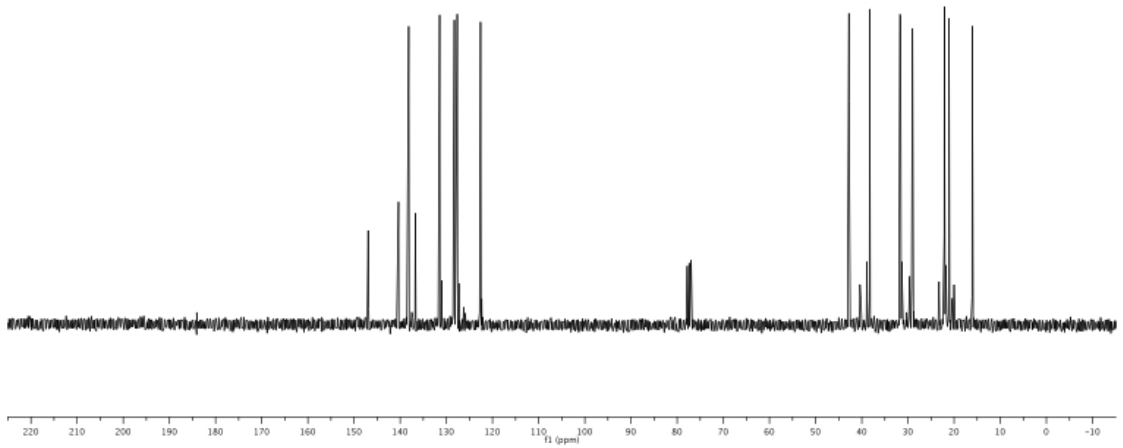
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f1 (ppm)
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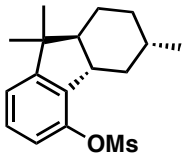
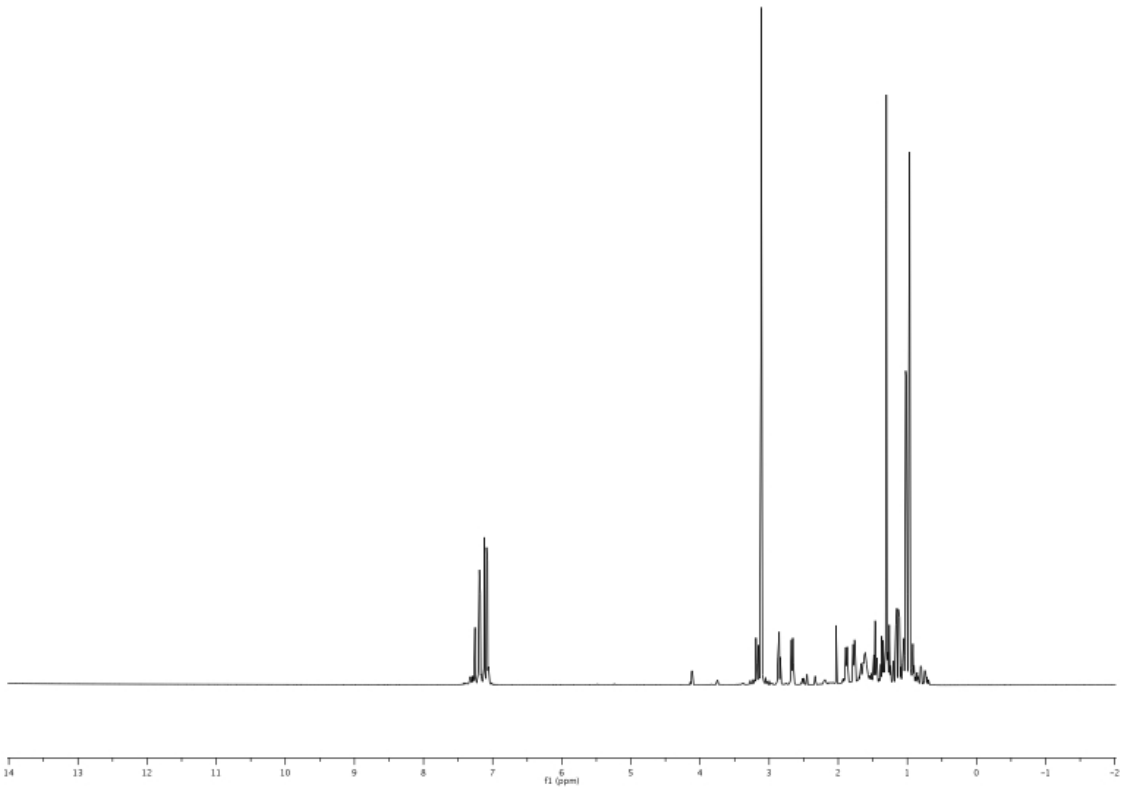

OMs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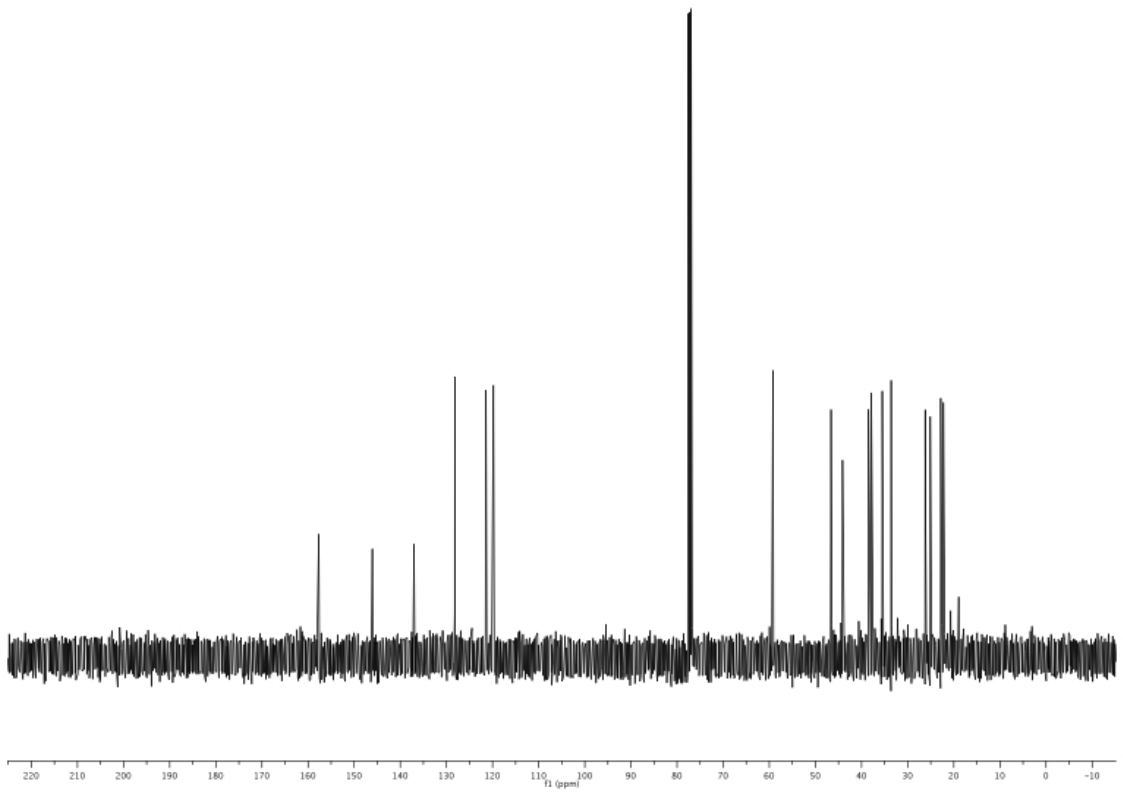
f1 (ppm)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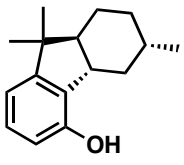
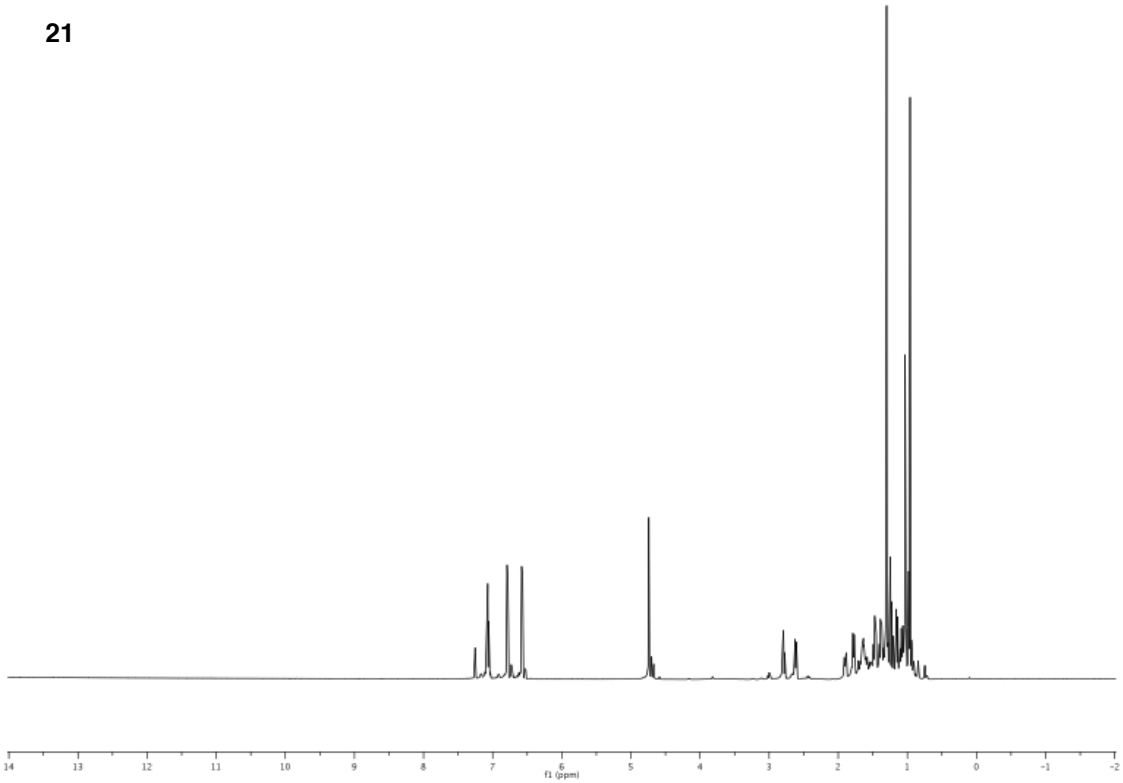
f1 (ppm)


OH

21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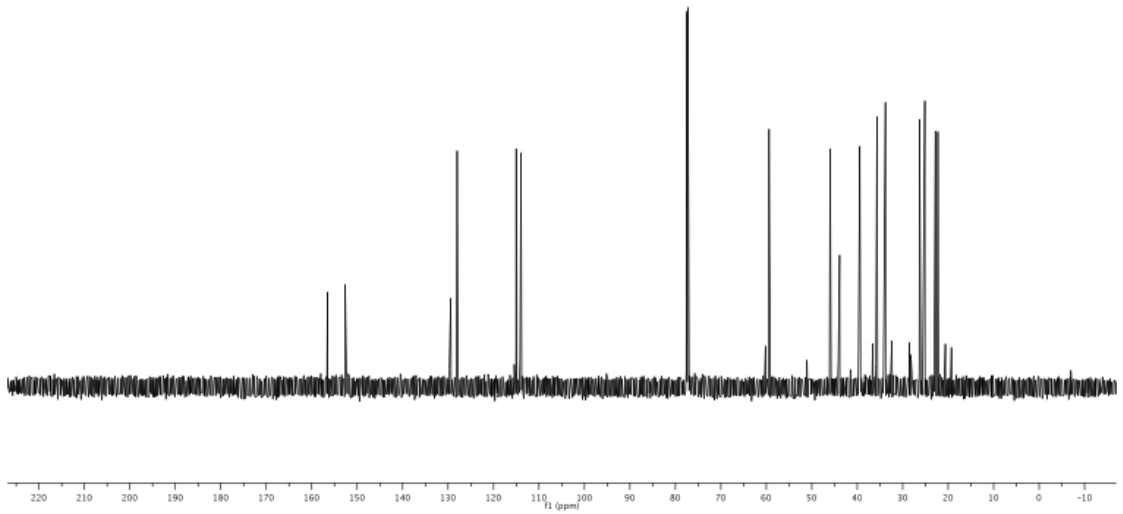
f1 (ppm)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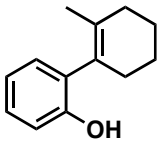
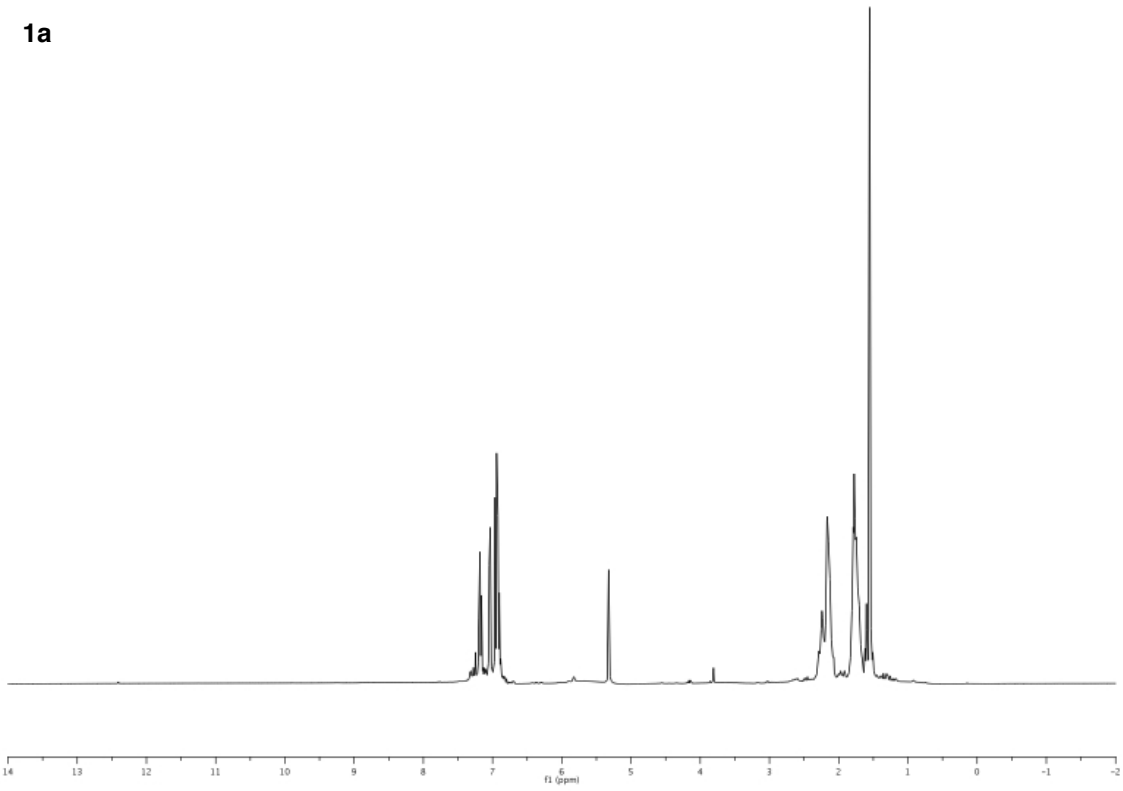
−10
f1 (ppm)


OH

1a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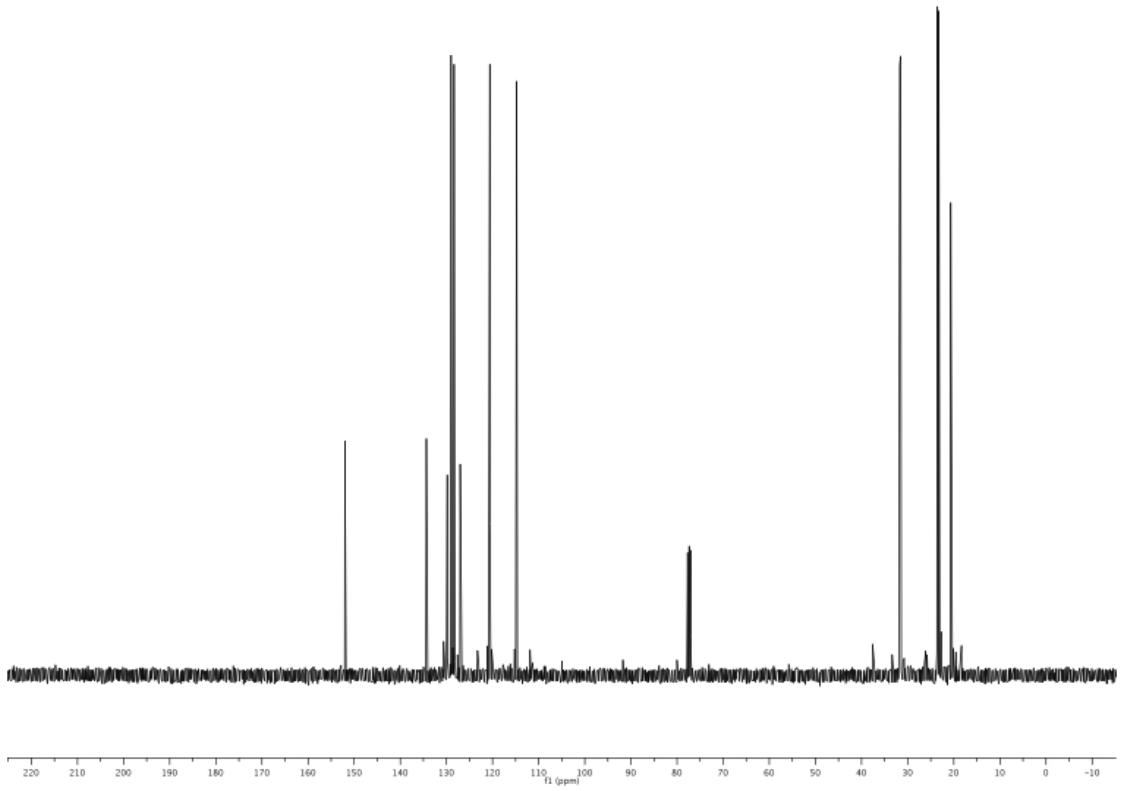
-2
f1 (ppm)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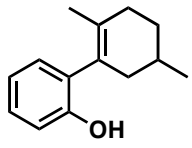
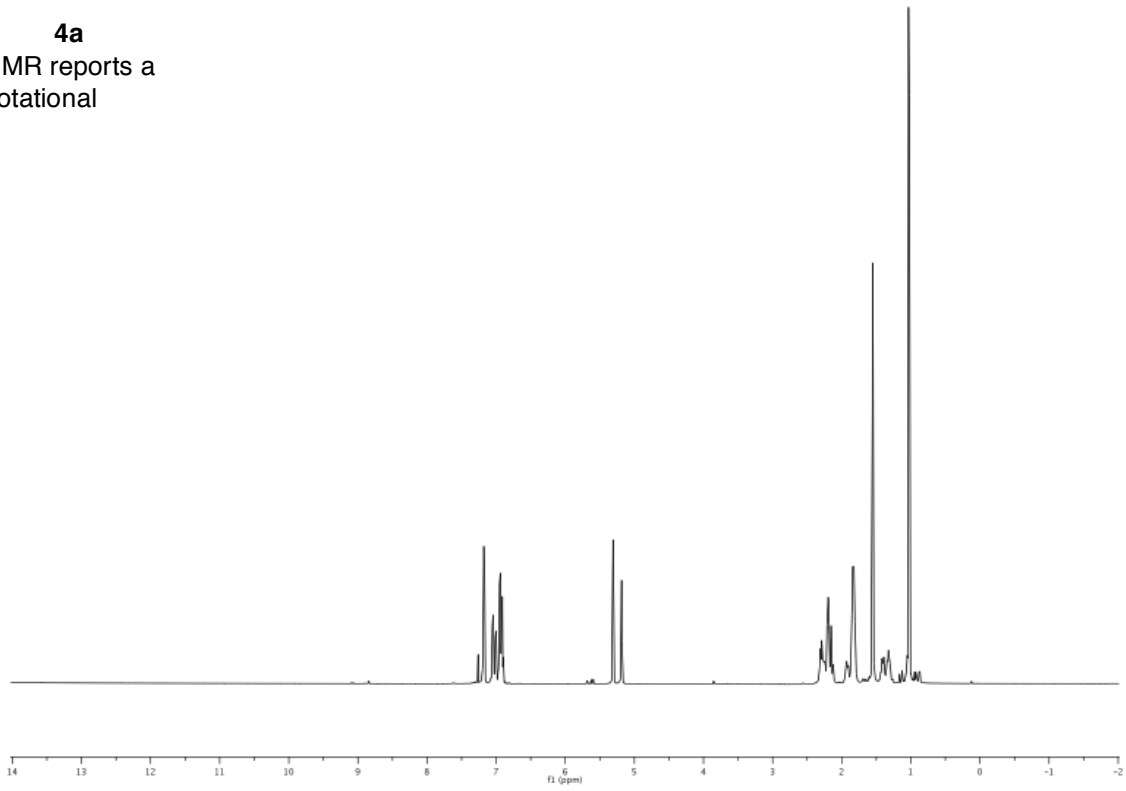
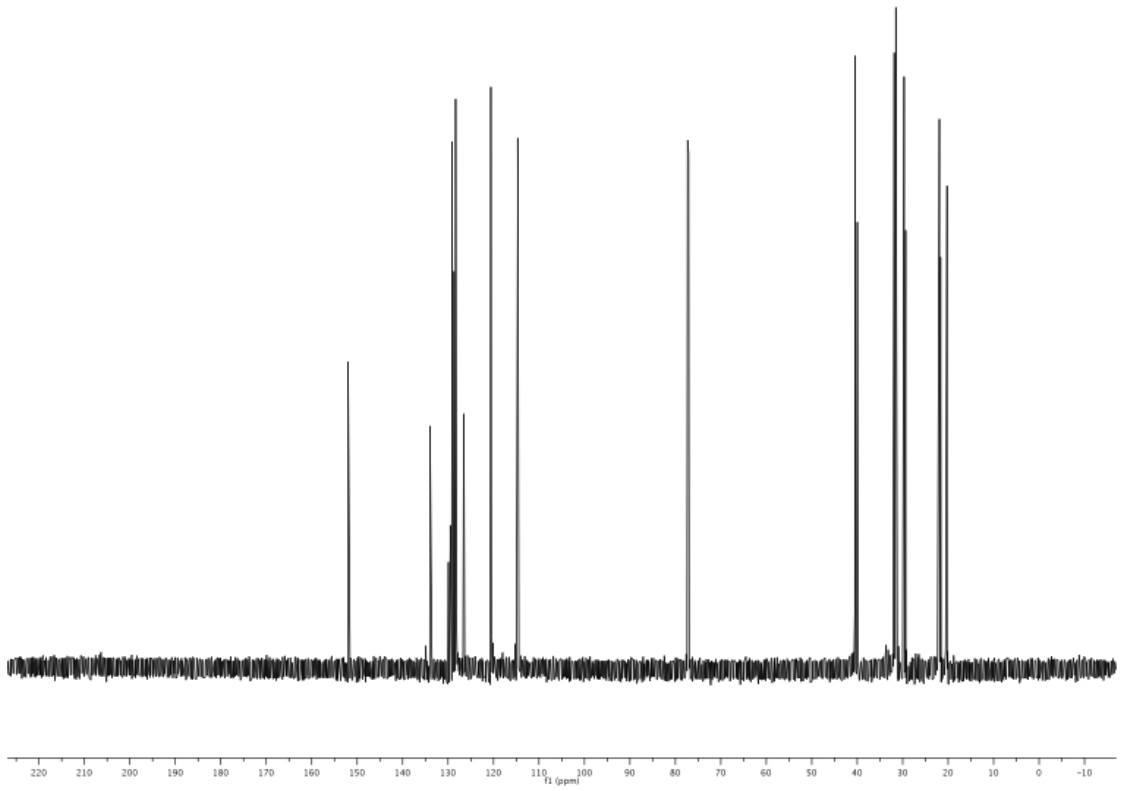
0
-10
f1 (ppm)

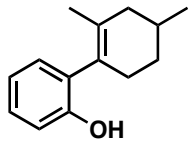


4a

[at 25 °C, NMR reports a mixture of rotational isomers]

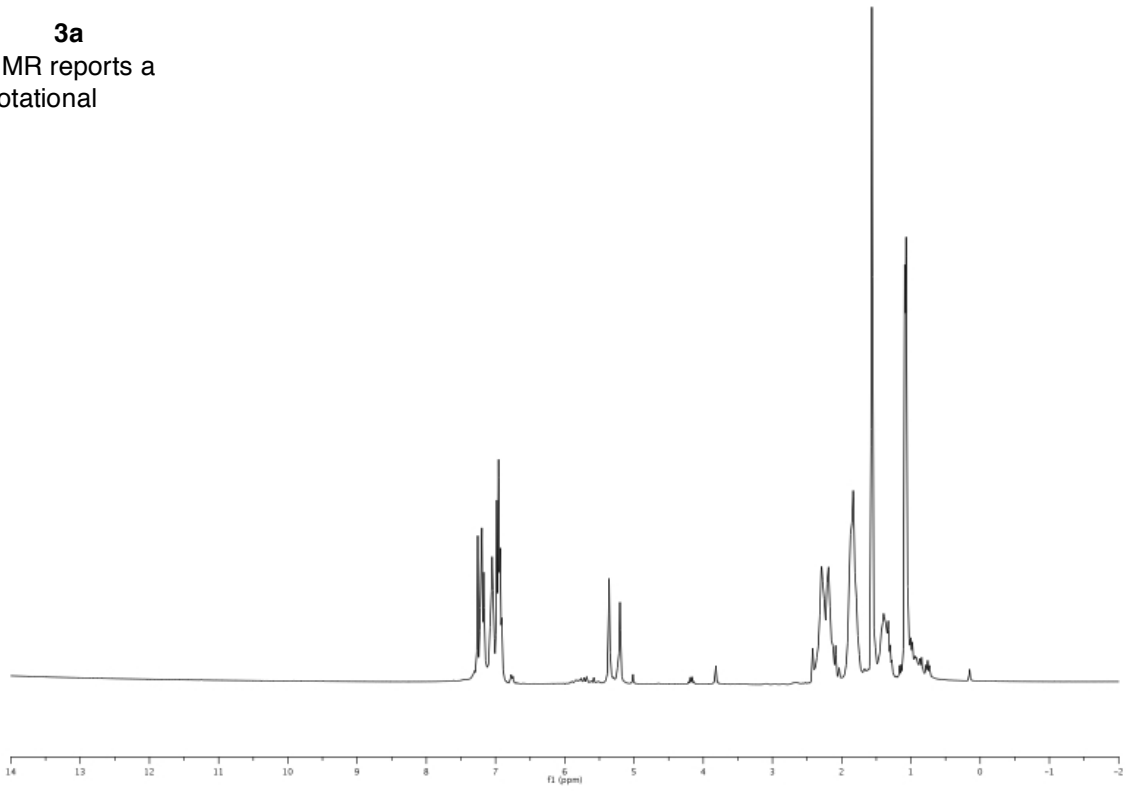


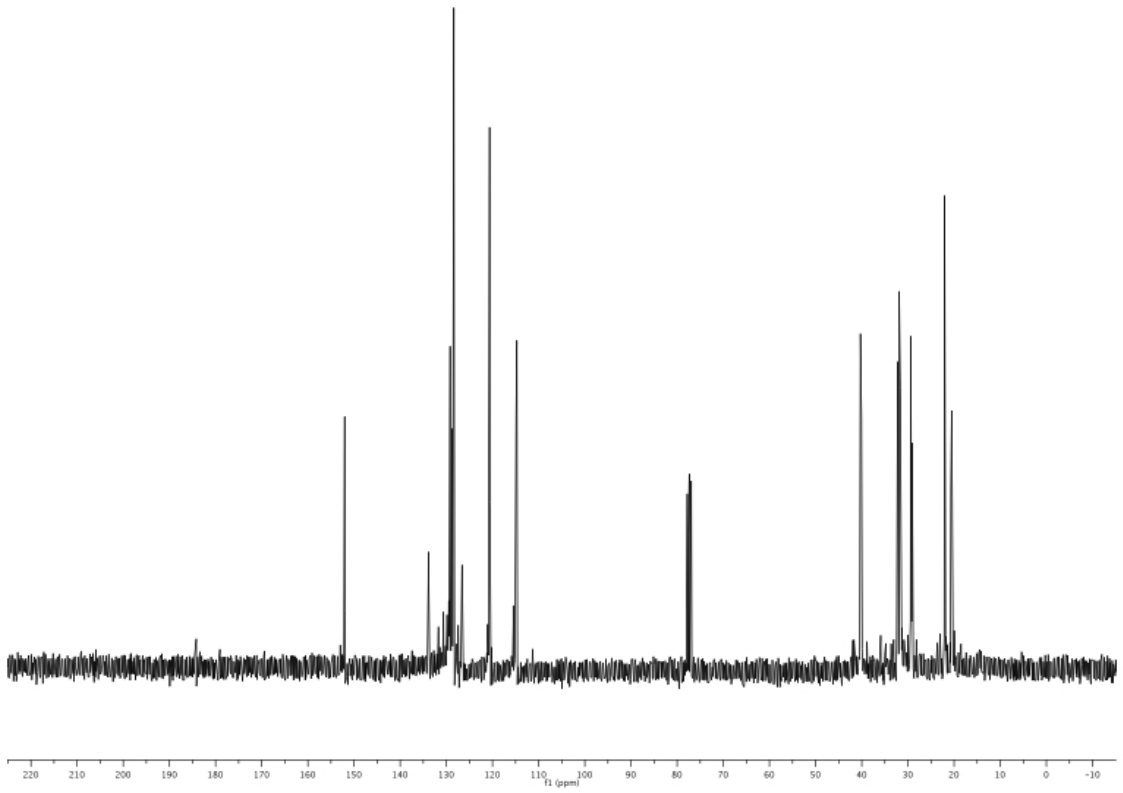


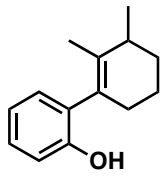


3a

[at 25 °C, NMR reports a mixture of rotational isomers]

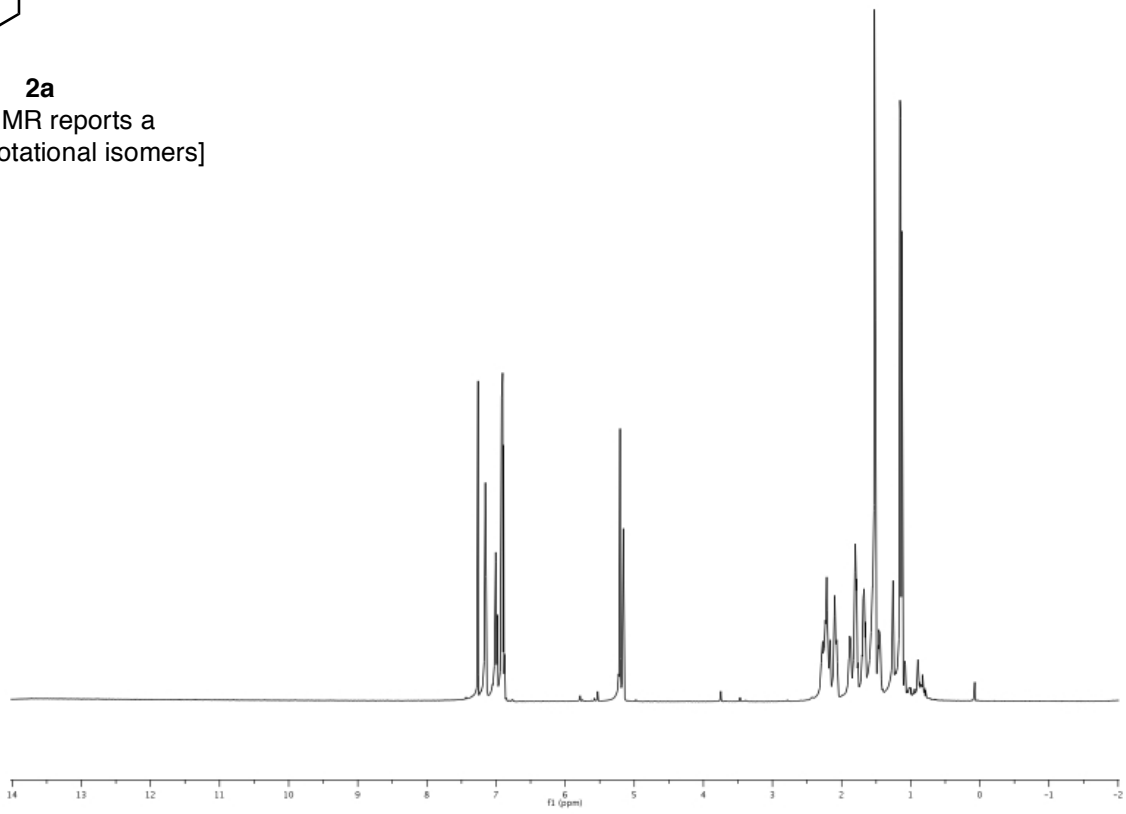


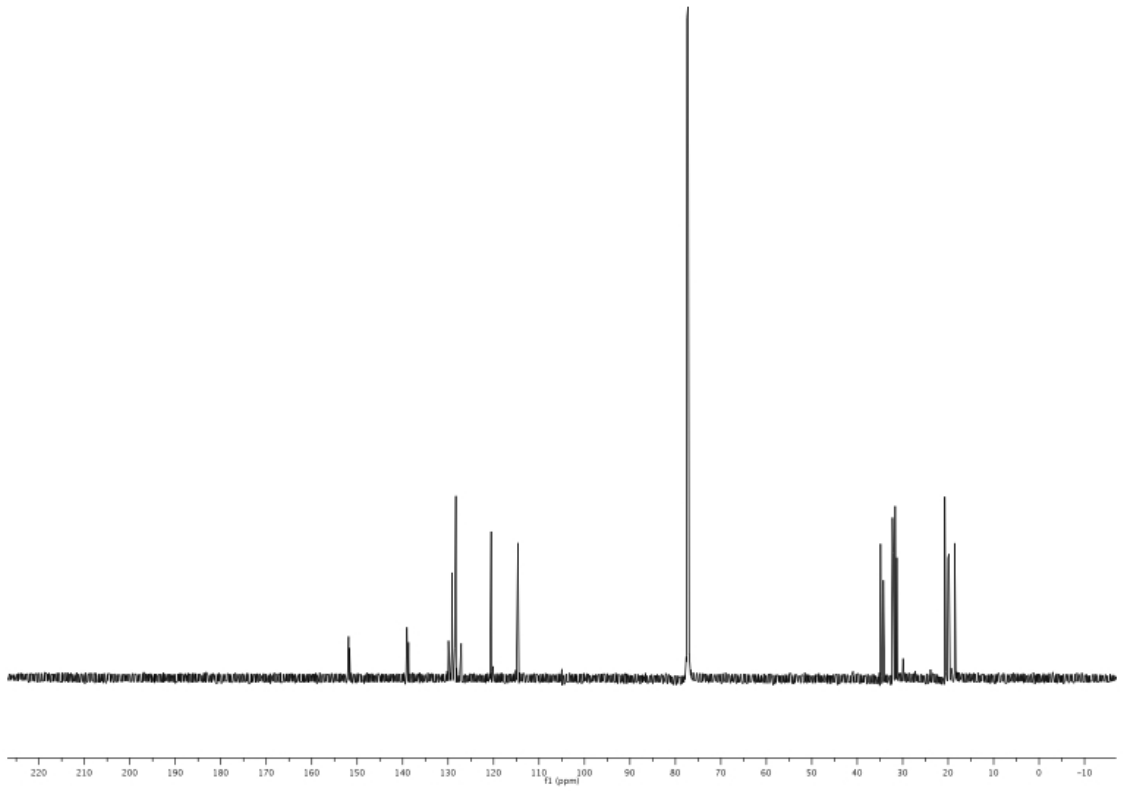


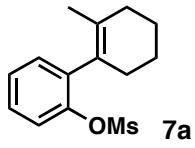


2a

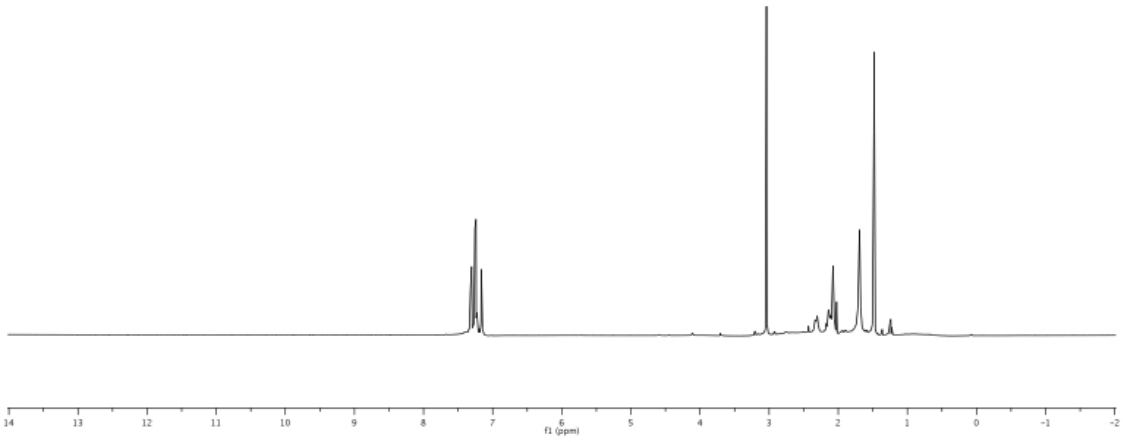
[at 25 °C, NMR reports a mixture of rotational isomers]

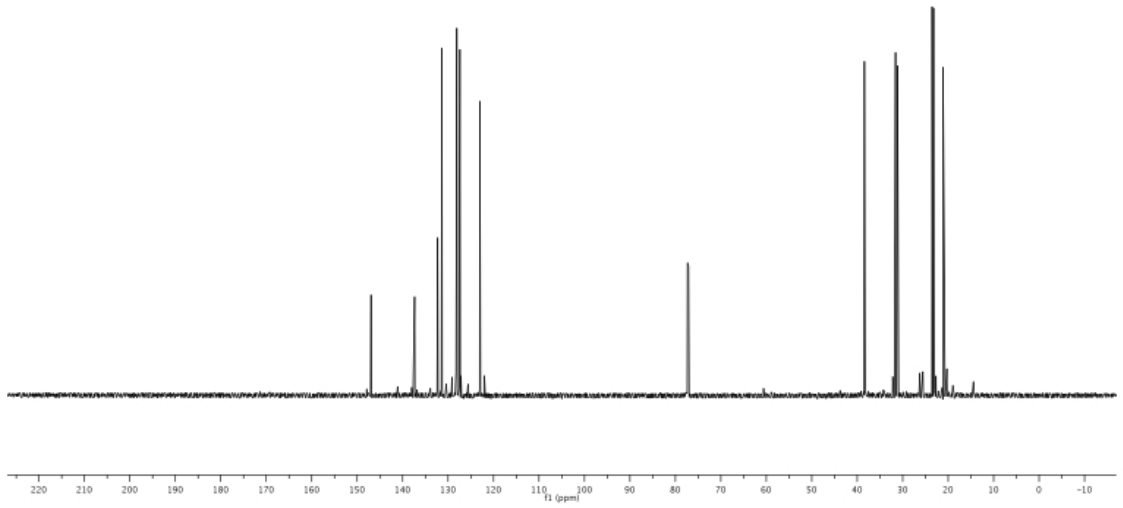


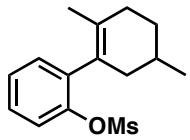



OMs

7a

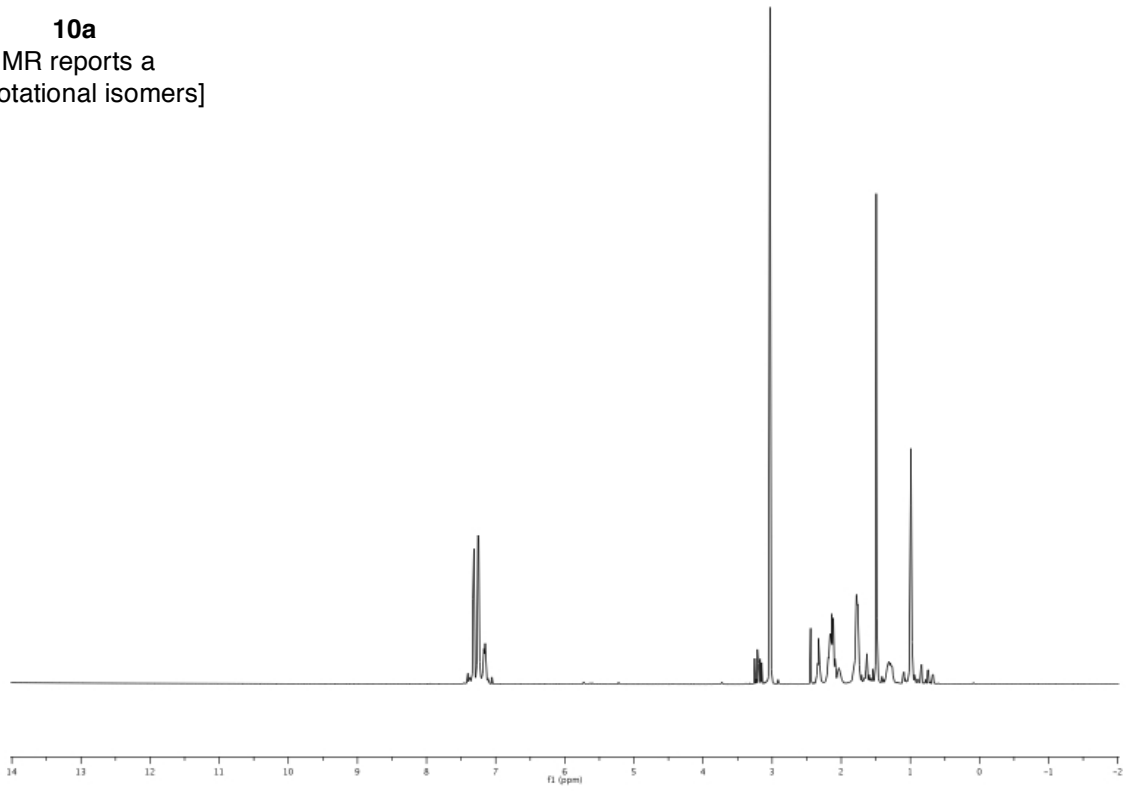

14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)

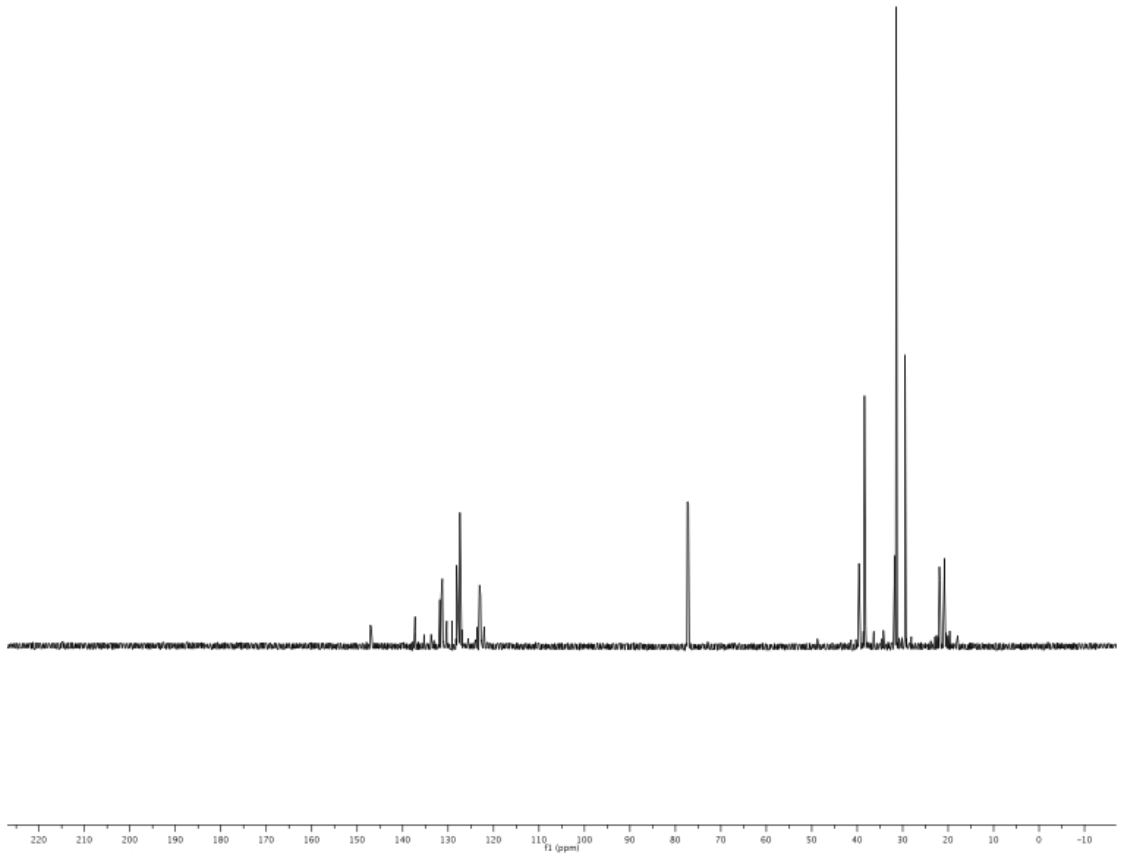

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

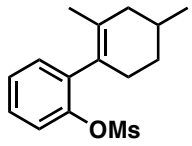


10a

[at 25 °C, NMR reports a mixture of rotational isomers]

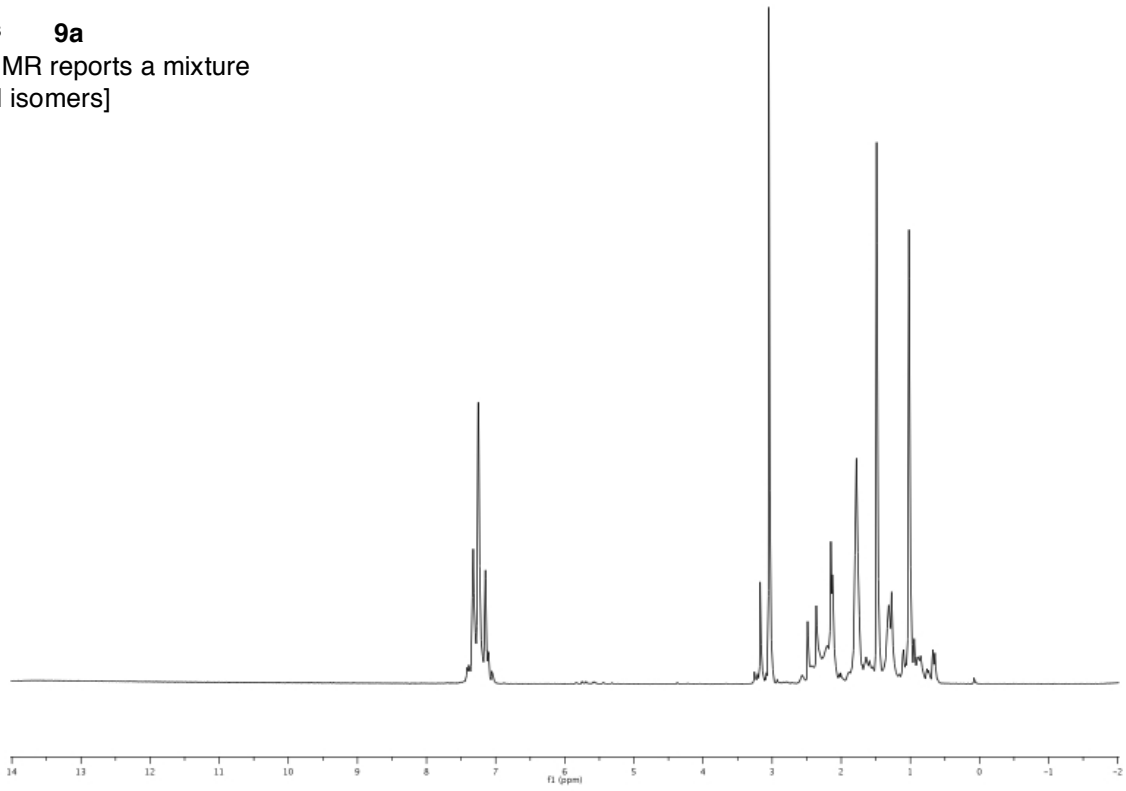


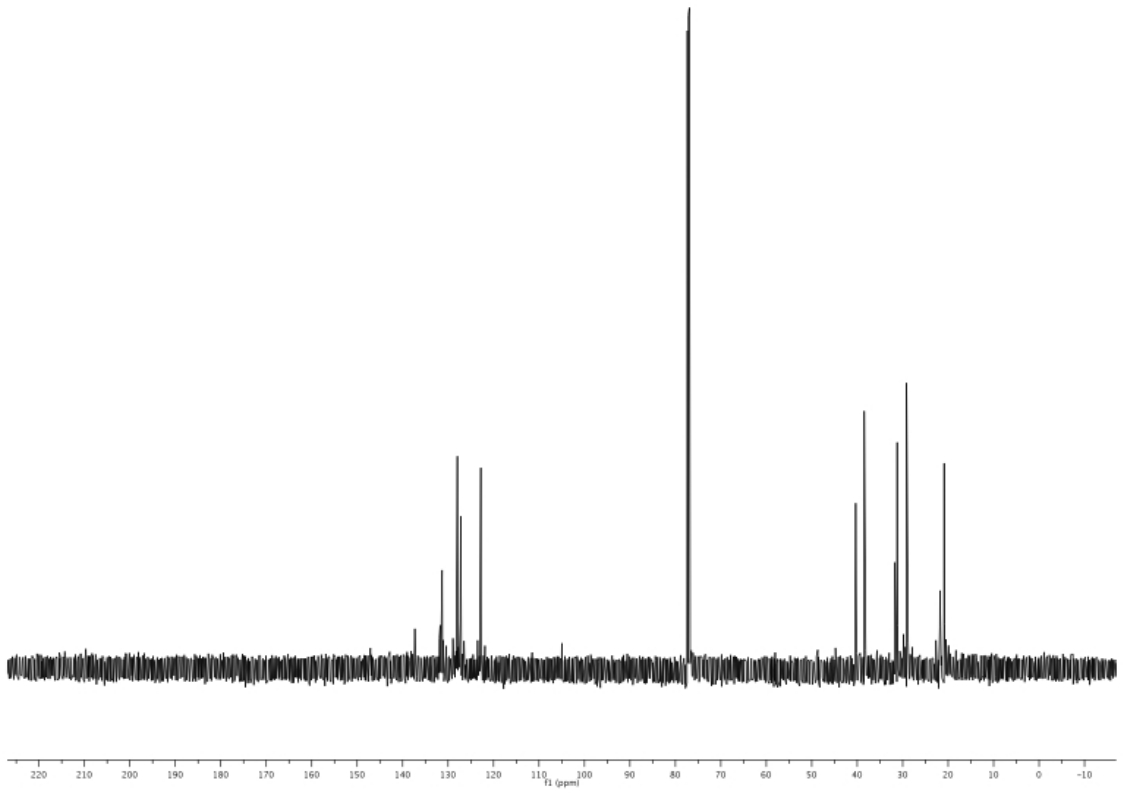


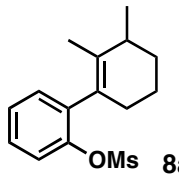


9a

[at 25 °C, NMR reports a mixture of rotational isomers]

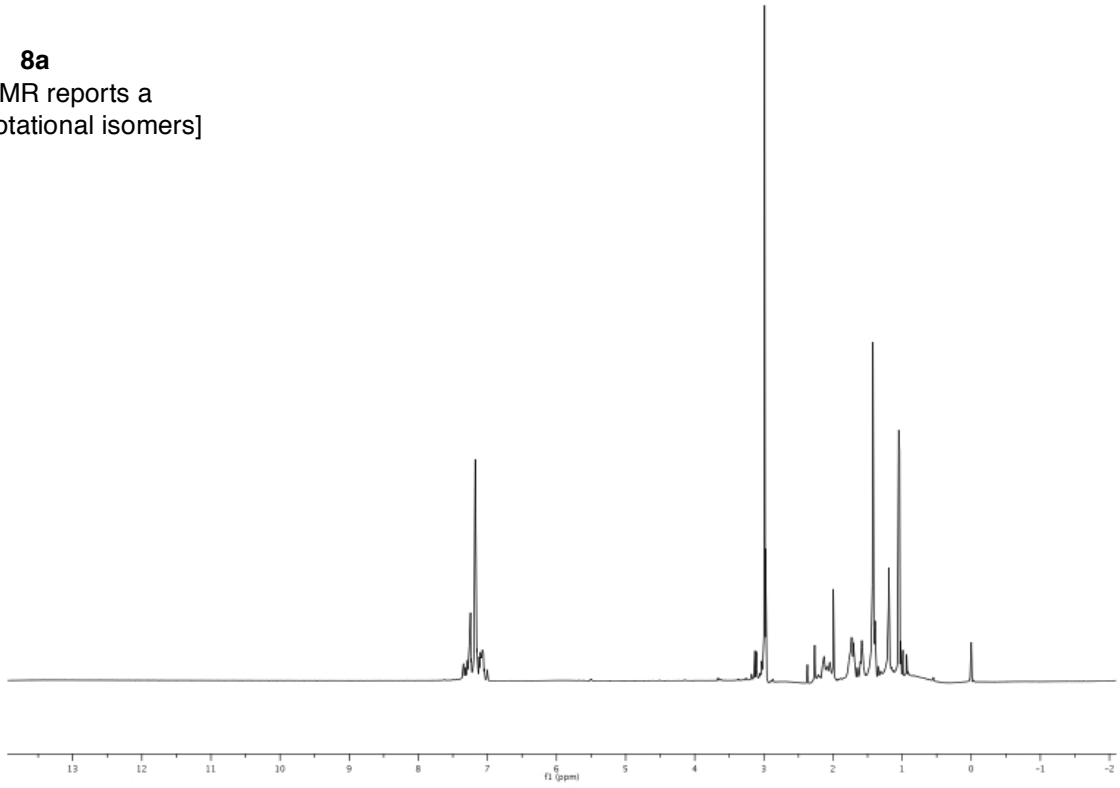


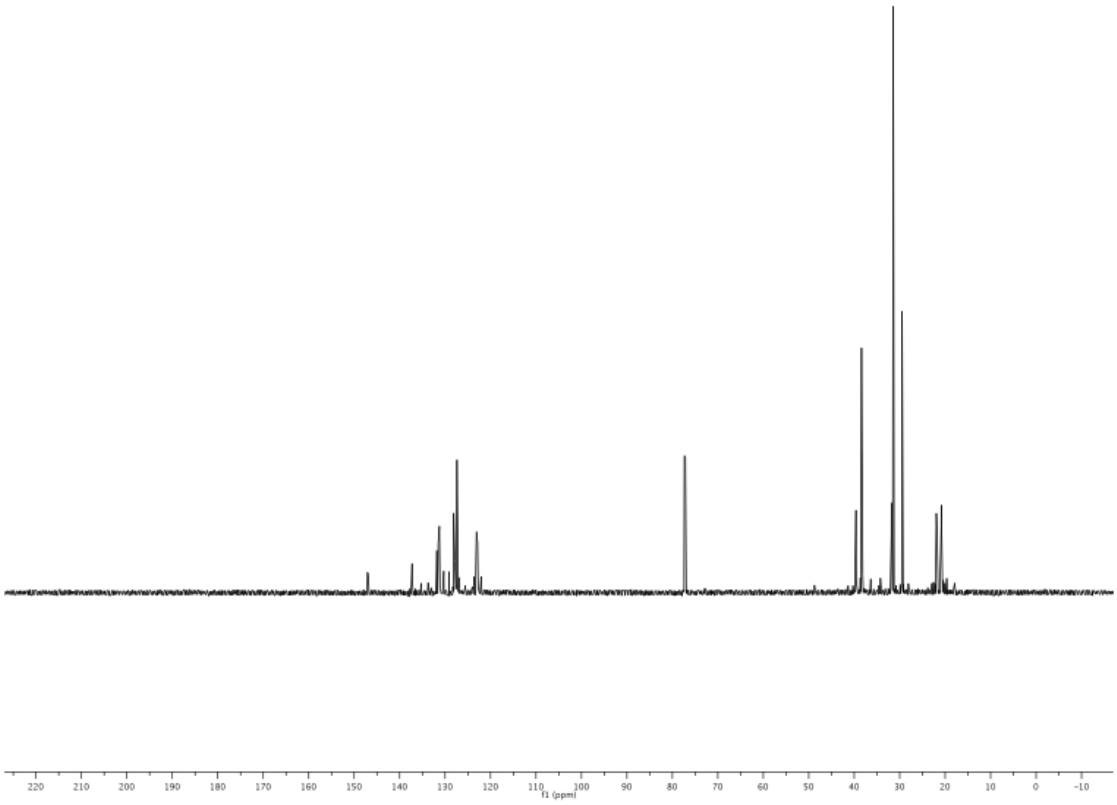


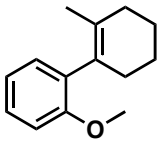


8a

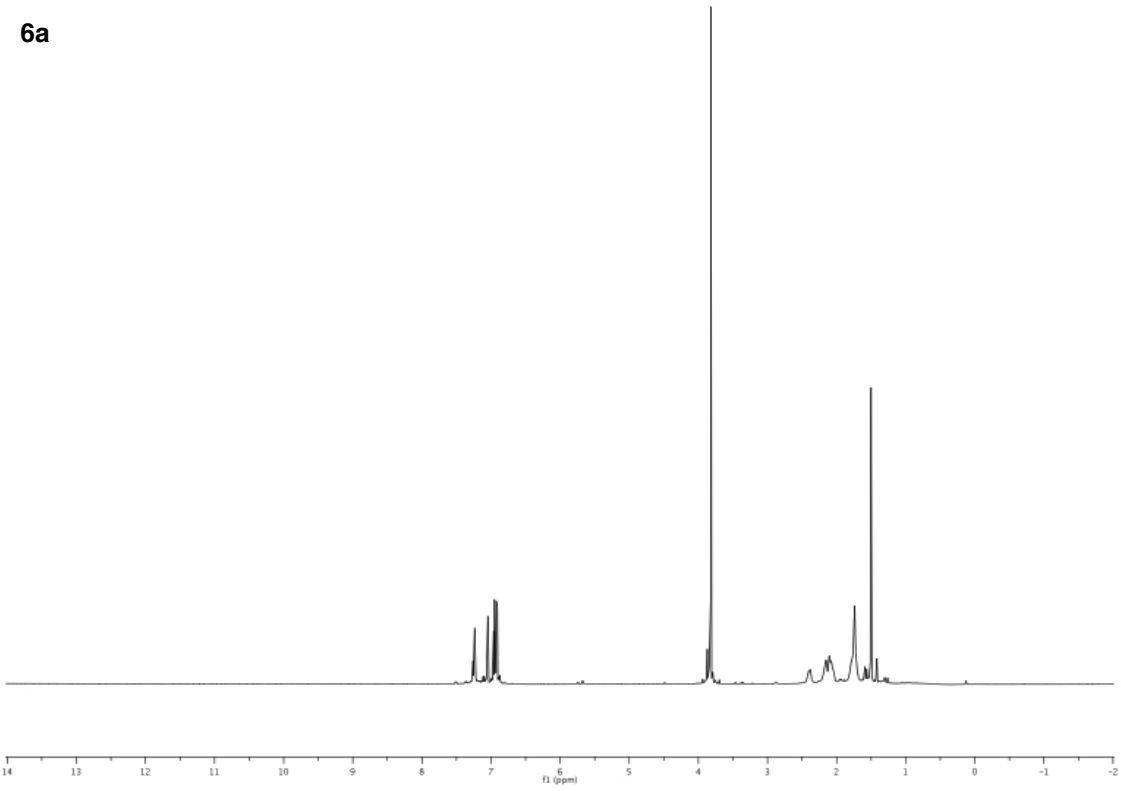
[at 25 °C, NMR reports a mixture of rotational isomers]

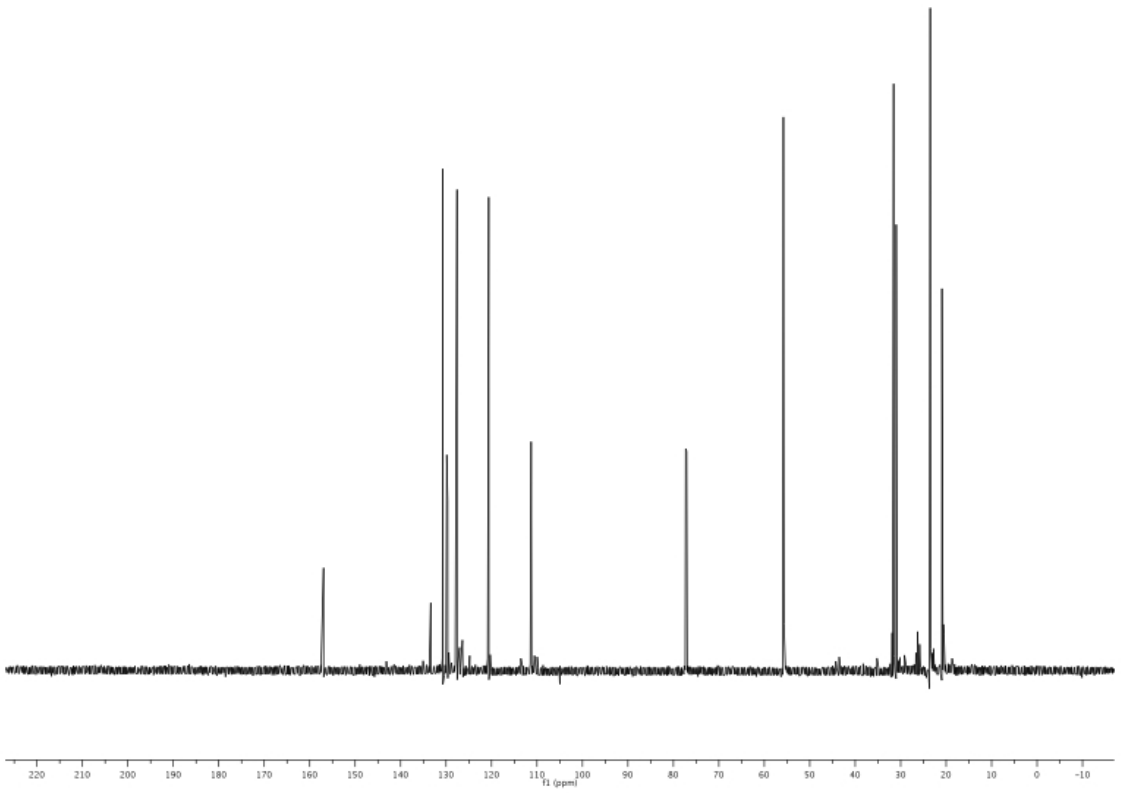


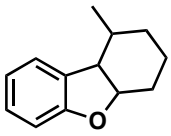


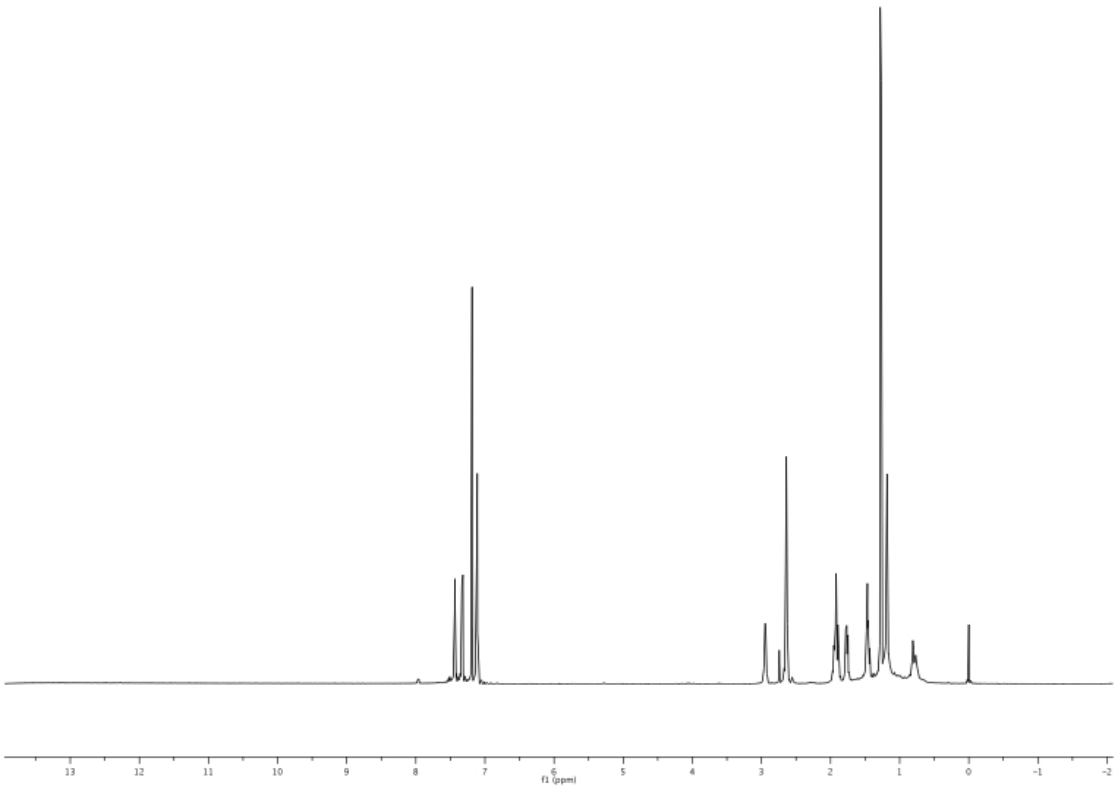


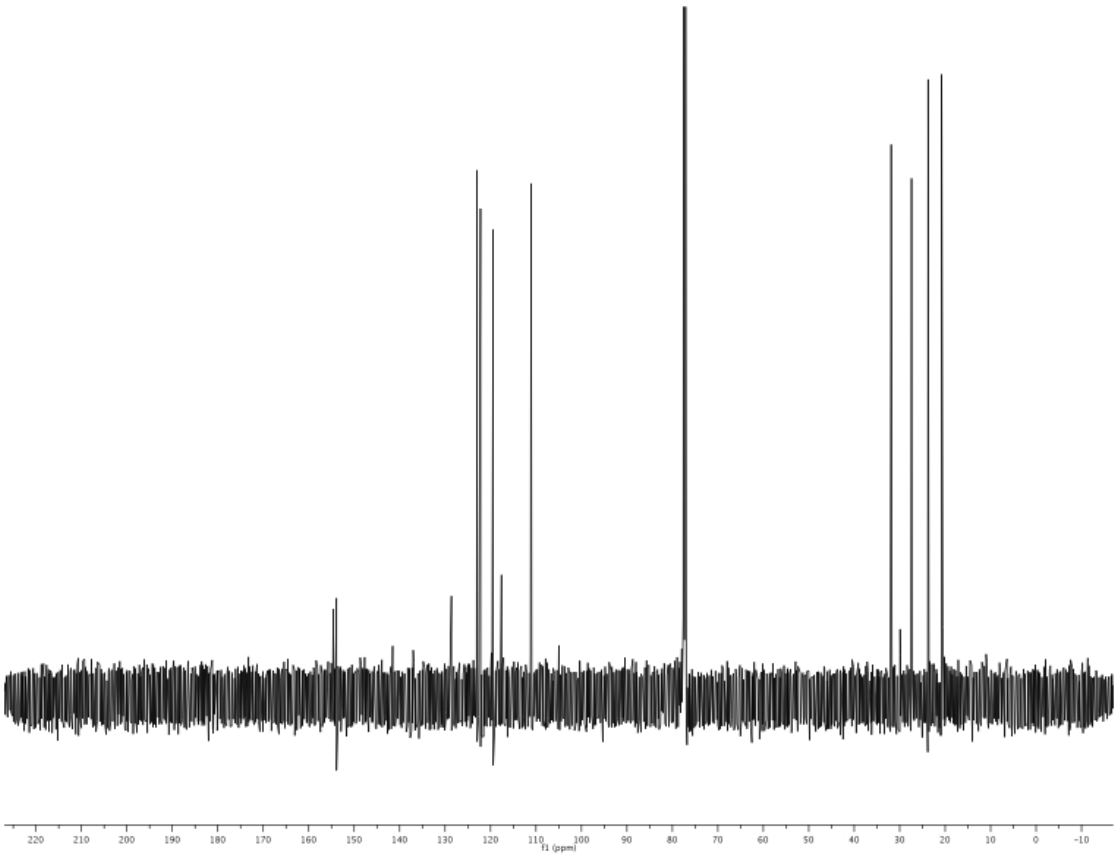
6a


14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)

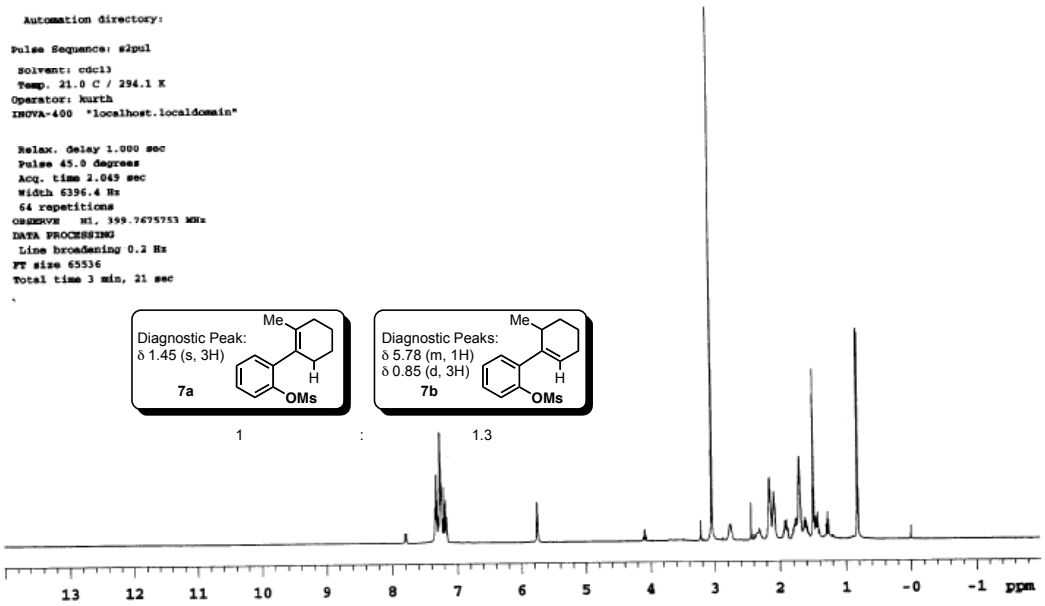

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

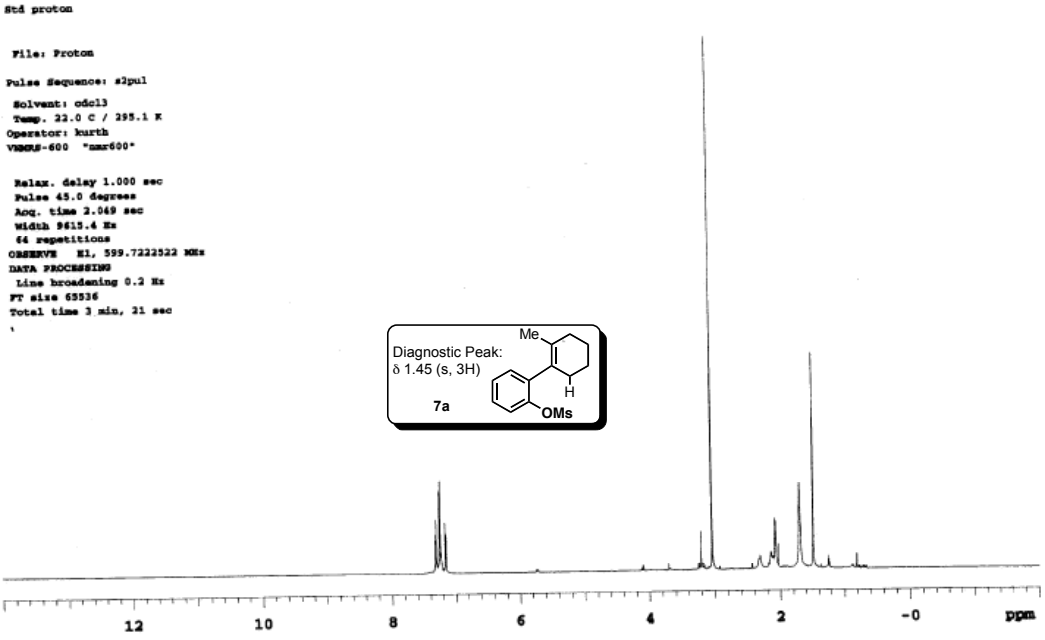


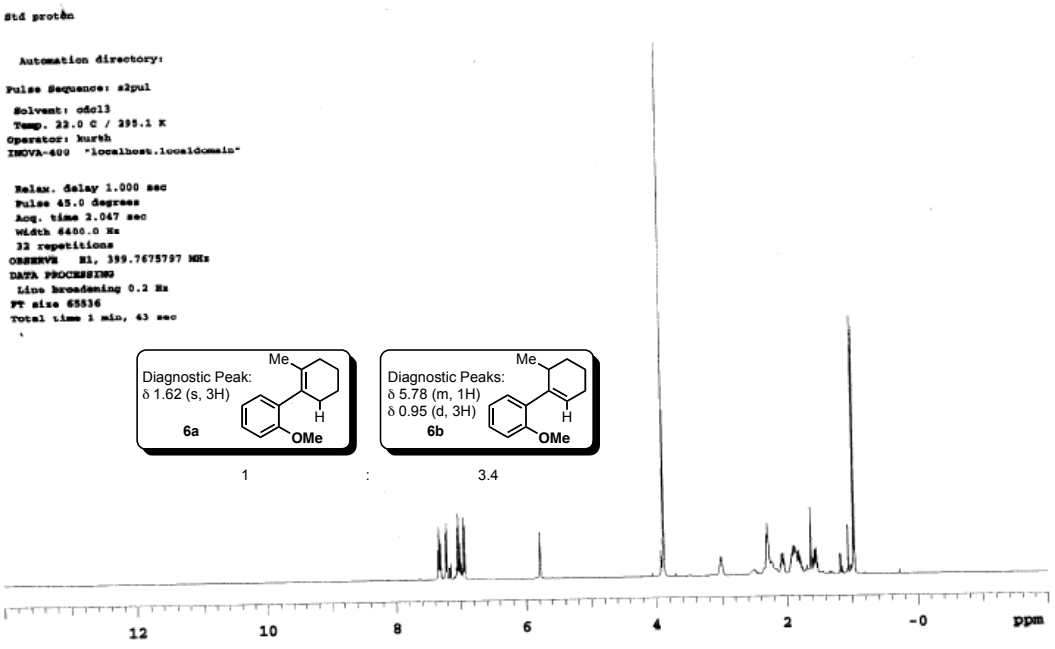

13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
f1 (ppm)


220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

Crude ^{1}H NMR of dehydration mixtures, diagnostic assignments, and isomerization






Std proton
Automation directory:
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 22.0 C / 295.1 K
Operator: kurth
INOVA-400 "localhost.localdomain"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.047 sec
Width 6400.0 Hz
32 repetitions
OBSERVE H1, 399.7675797 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 43 sec
Diagnostic Peak:
δ 1.62 (s, 3H)
Me
H
OMe
6a
Diagnostic Peaks:
δ 5.78 (m, 1H)
δ 0.95 (d, 3H)
Me
H
OMe
6b
1 : 3.4
12
10
8
6
4
2
-0
ppm