# A Concise Ring Expansion Route to the Compact Core of Platensimycin

Nicholas A. McGrath, Emily S. Bartlett, Satapanawat Sittihan and Jon T. Njardarson*

*Department of Chemistry and Chemical Biology, Baker Laboratory, Cornell University*

*Ithaca, New York 14853-1301*

**Supporting Information**

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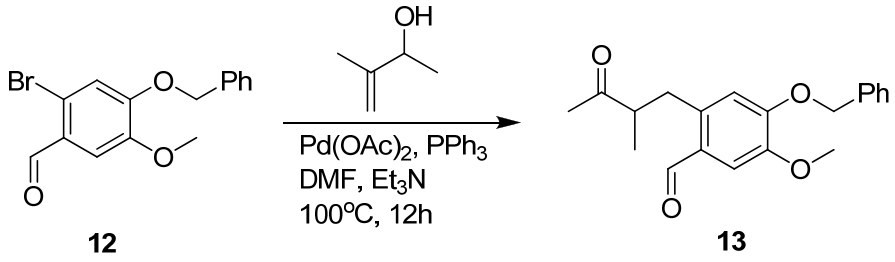
**General Information:** Commercial reagents were purchased and used without further purification. All glassware was flame dried and reactions were performed under a nitrogen atmosphere, unless otherwise stated. Toluene, dichloromethane, diethyl ether, and THF were dried over a column of alumina. Flash chromatography was done with MP Silitech 32-63D 60Å silica, and thin layer chromatography (TLC) was performed with EMD 250 μm silica gel 60-$F_{254}$ plates. $^{1}H$ and $^{13}C$ NMR data was acquired on a Varian Inova 400, 500, or 600 (400, 500 or 600 MHz) spectrometer and referenced to residual protic solvent or TMS. IR spectroscopy was done on a Mattson RS-10500 FTIR spectrometer. High-resolution mass spectrometry was performed at the University of Illinois at Urbana-Champaign facility.




**12** **13**

The known bromoaldehyde **12** (10 g, 31.14 mmol), was added to a flame-dried round bottom flask and dissolved in dry DMF (311.4 mL). Triethyl amine (5.4 mL, 38.9 mmol) was added followed by palladium acetate (0.35 g, 1.6 mmol) and triphenylphosphine (0.82 g, 3.2 mmol). Then the allylic alcohol (13.4 g, 156 mmol) was added and the reaction was heated at 100°C for 12 hours. Upon completion, the reaction mixture was quenched with one molar hydrochloric acid (100 mL) and extracted with ether. The combined ether extracts were subsequently washed with distilled water and dried with sodium sulfate. The ethereal solution was concentrated and purified by column chromatography (70% hexanes, 30% ethyl acetate) to yield **13** (7.9 g, 78%).

**FTIR (thin film/NaCl)** 2958, 2930, 1708, 1677, 1597, 1511, 1354, 1270, 1108 $cm^{-1}$; **$^1$H NMR (400 MHz, $C_6D_6$)** δ = 10.02 (s, 1H), 7.27-7.21 (m, 3H), 7.14-7.01 (m, 3H), 6.63 (s, 1H), 4.82-4.70 (m, 2H), 3.32 (s, 3H), 3.28 (dd, *J*=7.1, 13.2, 1H), 2.76 (dd, *J*=7.1, 13.2, 1H), 2.61-2.58 (m, 1H), 1.68 (s, 3H), 0.86 (d, *J*=7.1, 3H); **$^{13}$C NMR (126 MHz, $C_6D_6$)** δ = 210.2, 190.2, 153.3, 149.3, 137.7, 137.1, 129.1, 128.7, 128.1, 127.9, 117.0, 115.0, 71.0, 55.8, 49.3, 35.4, 29.1, 16.8; **HRMS** (EI) *m/z* 349.1408 [calc'd for $C_{20}H_{22}O_4Na$ (M+Na) 349.1416].

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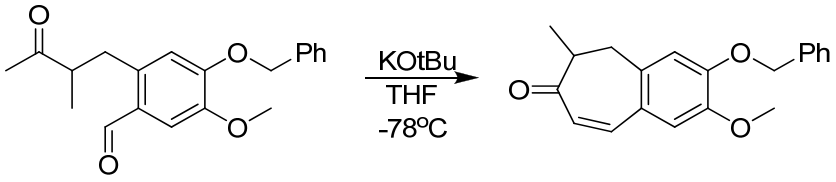
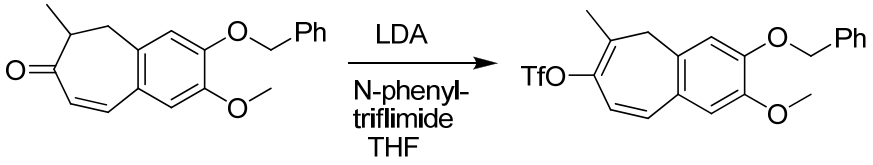



**13** **14**

Potassium tert-butoxide (2.02 g, 17.1 mmol) was added to a flame-dried round bottom flask and dry THF (300 mL) was added under a nitrogen atmosphere at -78°C. The starting material **13** (5.07 g, 15.6 mmol) was dissolved in dry THF (11 mL) and added drop-wise to the butoxide slurry. Upon complete addition, the reaction was allowed to stir for an additional 30 minutes at -78°C at which time the bath was removed and the reaction allowed to warm to room temperature. The reaction was neutralized with saturated sodium bicarbonate and extracted with ether. The combined extracts were dried over sodium sulfate, concentrated, and purified by column chromatography (70% hexanes, 30% ethyl acetate) to yield **14** (4.31 g, 90%).

**FTIR (thin film/NaCl)** 2964, 2933, 1651, 1567, 1519, 1455, 1354, 1268, 1164, 1098 $cm^{-1}$; **$^1$H NMR (400 MHz, $CDCl_3$)** δ = 7.41-7.30 (m, 5H), 6.95 (d, *J*=12.6, 1H), 6.84 (s, 1H), 6.76 (s, 1H), 6.04 (d, *J*=12.6, 1H), 5.18 (s, 2H), 3.88 (s, 3H), 2.89-2.72 (m, 2H), 2.66 (m, 1H), 1.07 (d, *J*=7.1, 3H); **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ = 203.5, 149.4, 148.2, 142.0, 136.6, 134.2, 128.8, 128.2, 127.5, 127.4, 127.4, 115.9, 115.3, 71.1, 56.4, 44.7, 37.0, 15.7; **HRMS** (EI) *m/z* 309.1483 [calc'd for $C_{20}H_{21}O_3$ (M+H) 309.1491].




**14** **15**

Freshly distilled diisopropyl amine (2.50 mL, 17.8 mmol) was added to a flame-dried flask and diluted with dry THF (60 mL) and cooled to -78°C under nitrogen. Butyl lithium (2.5M, 6.5 mL, 16.2 mmol) was then added and allowed to react for 30 minutes. Starting material **14** (2.5 g, 8.11 mmol) was then dissolved in THF (10 mL) and added drop-wise to the LDA solution over 1 minute and allowed to stir for an additional 15 minutes. A stock solution of N-phenyl triflimide (3.19 g, 8.9 mmol) was then added and the bath removed as the reaction warmed to room temperature. After 1 hour the reaction was diluted with ether (500 mL) and washed with NaOH solution (0.1M, 200 mL). The ethereal solution was then dried over sodium sulfate, concentrated, and purified with column chromatography (70% hexanes, 30% ethyl acetate) to yield **15** (3.10 g, 87%).

**FTIR (thin film/NaCl)** 3033, 2963, 2840, 1736, 1657, 1603, 1561, 1512, 1413, 1211, 1141, 1029 $cm^{-1}$; **$^1$H NMR (400 MHz, $CDCl_3$)** δ = 7.48-7.30 (m, 5H), 7.04 (d, *J*=11.8, 1H), 6.84 (s, 1H), 6.68 (s, 1H), 6.26 (d, *J*=11.8, 1H), 5.18 (s, 2H), 3.88 (s, 3H), 2.97 (s, 2H), 2.03 (s, 3H); **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ = 150.2, 148.4, 140.5, 136.9, 134.7, 128.8, 128.5, 128.3, 128.2, 127.6, 127.4, 121.1, 116.5, 113.1, 111.5, 71.3, 56.3, 38.1, 18.8; **HRMS** (EI) *m/z* 440.0901 [calc'd for $C_{21}H_{19}F_3O_5S$ (M+) 440.0905].

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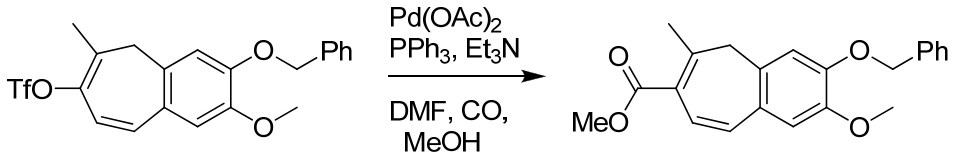
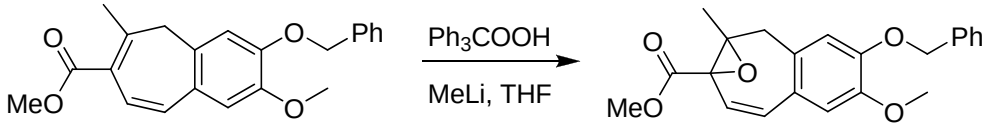



**15** **16**

Palladium acetate (0.087 g, 0.39 mmol) and triphenylphosphine (0.203 g, 0.78 mmol) were added to a flame-dried flask at room temperature under nitrogen. Dry DMF (30 mL) was added followed by triethylamine (0.54 mL, 3.86 mmol) and methanol (6.2 mL, 154 mmol). Starting triflate **15** (1.70 g, 3.86 mmol) was dissolved in dry DMF (9 mL) and added to the reaction and a balloon of carbon monoxide was attached *via* needle through a septum. The reaction was heated at 80°C for 3 hours until the starting material was consumed. The reaction was then diluted with ethyl acetate (300 mL) and washed with distilled water (3 x 50 mL). The organics were then dried over sodium sulfate and purified with silica gel chromatography (70% hexanes, 30% ethyl acetate) to yield **16** (1.11 g, 82%).

**FTIR (thin film/NaCl)** 3029, 2936, 1713, 1602, 1509, 1453, 1222 $cm^{-1}$; **$^1$H NMR (400 MHz, $CDCl_3$)** δ = 7.47-7.30 (m, 5H), 7.02 (d, *J*=11.6, 1H), 6.83 (s, 1H), 6.80 (d, *J*=11.6, 1H), 6.70 (s, 1H), 5.17 (s, 2H), 3.87 (s, 3H), 3.74 (s, 3H), 2.94 (s, 2H), 2.31 (s, 3H); **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ = 168.2, 149.6, 148.3, 146.9, 137.1, 131.6, 128.9, 128.7, 128.1, 127.8, 127.6, 127.2, 124.0, 112.7, 110.8, 71.3, 56.3, 51.7, 43.2, 22.8; **HRMS** (EI) *m/z* 351.1584 [calc'd for $C_{22}H_{23}O_4$ (M+H) 351.1596].




**16** **17**

Triphenylmethyl hydroperoxide (0.166 g, 0.60 mmol) was added to a flame-dried flask and dissolved in dry THF (7 mL) under nitrogen and then cooled to -78°C. Methyl lithium (1.6M, 0.33 mL, 0.52 mmol) was added and the reaction was stirred for 10 minutes. Starting diene **16** (0.140 g, 0.40 mmol) was then dissolved in dry THF (1 mL), added to the reaction, and allowed to stir at -78°C for 1 hour. The reaction was then warmed to room temperature and quenched with saturated ammonium chloride (50 mL) and extracted with ethyl acetate (3 x 100 mL). The organics were then dried over sodium sulfate, concentrated, and purified by silica gel chromatography (80% hexanes, 20% ethyl acetate) to yield **17** (0.129 g, 89%).

**FTIR (thin film/NaCl)** 2953, 2935, 1747, 1604, 1518, 1267, 1099, 1064, 1454 $cm^{-1}$; **$^1$H NMR (300 MHz, $CDCl_3$)** δ = 7.51-7.28 (m, 5H), 6.81 (s, 1H), 6.74 (s, 1H), 6.68 (d, *J*=11.4, 1H), 6.16 (d, *J*=11.4, 1H), 5.17 (s, 2H), 3.89 (s, 3H), 3.72 (s, 3H), 2.97 (d, *J*=13.6, 1H), 2.78 (d, *J*=13.6, 1H), 1.36 (s, 3H); **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ = 169.6, 148.8, 147.9, 137.1, 134.1, 128.9, 128.8, 128.5, 128.2, 127.6, 124.2, 115.7, 113.6, 71.6, 71.4, 62.9, 56.4, 52.9, 43.4, 18.7; **HRMS** (EI) *m/z* 367.1541 [calc'd for $C_{22}H_{23}O_5$ (M+H) 367.1545].

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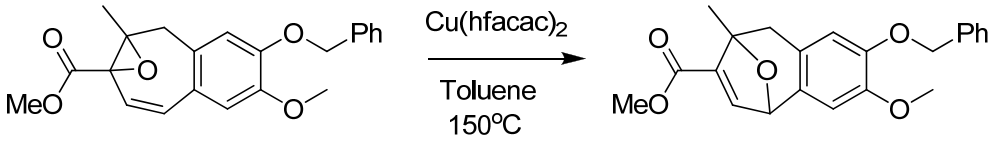
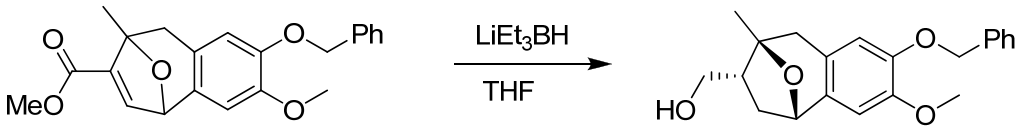



**17** **18**

Starting epoxide **17** (0.120 g, 0.33 mmol) was dissolved in dry toluene (0.33 mL) and dry $Cu(hfacac)_2$ (8 mg, 0.017 mmol, dried on vacuum pump for 2 hours prior to use) was added at room temperature. The vial was sealed well and the reaction heated at 100°C for 12 hours. After allowing the reaction to cool to room temperature, it was filtered through neutral alumina (activity grade 1), concentrated and purified with silica gel chromatography (80% hexanes, 20% ethyl acetate) to give **18** (0.118 g, 99%).

**FTIR (thin film/NaCl)** 2952, 2935, 1714, 1611, 1506, 1452, 1307, 1261, 1100, 1070, $cm^{-1}$; **$^1$H NMR (600 MHz, $CDCl_3$)** δ = 7.44-7.28 (m, 5H), 7.21 (s, 1H), 6.63 (s, 1H), 6.61 (s, 1H), 5.27 (d, *J*=2.0, 1H), 5.08 (s, 2H), 3.85 (s, 3H), 3.71 (s, 3H), 2.85 (d, *J*=17.1, 1H), 2.70 (d, *J*=17.1, 1H), 1.70 (s, 3H); **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ = 164.2, 148.3, 147.8, 147.6, 137.3, 135.2, 128.8, 128.8, 128.1, 127.5, 126.3, 116.4, 108.4, 84.2, 79.7, 71.4, 56.5, 51.7, 34.7, 23.6; **HRMS** (EI) *m/z* 367.1531 [calc'd for $C_{22}H_{23}O_5$ (M+H) 367.1545].




**18** **19**

Methyl enoate **18** (80 mg, 0.219 mmol) was dissolved in dry THF (4.4 mL) and the solution cooled to -78°C under nitrogen. Lithium triethylborohydride (1M, 0.88 mL, 0.88 mmol) was added drop-wise and the reaction stirred for 90 minutes. The bath was then removed and when the reaction had come to room temperature it was quenched with saturated ammonium chloride and extracted with DCM. The organics were dried over sodium sulfate, concentrated, and chromatographed (50% hexanes, 50% ethyl acetate) to give **19** (65 mg, 88%).

**FTIR (thin film/NaCl)** 2922, 2939, 1509, 1454, 1333, 1257, 1223, 1117, 1073, 1015 $cm^{-1}$; **$^1$H NMR (400 MHz, $CDCl_3$)** δ = 7.46-7.28 (m, 5H), 6.59 (s, 1H), 6.51 (s, 1H), 5.09 (s, 2H), 4.93 (d, *J*=6.9, 1H), 3.84 (s, 3H), 3.62-3.56 (m, 1H), 3.49-3.42 (m, 1H), 2.89 (d, *J*=17.0, 1H), 2.75 (d, *J*=17.0, 1H), 2.58-2.44 (m, 1H), 2.38-2.20 (m, 1H), 1.52 (s, 3H), 1.51-1.46 (m, 1H); **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ = 148.1, 147.4, 137.4, 134.4, 128.7, 128.0, 127.5, 124.4, 114.6, 107.9, 81.8, 77.3, 71.5, 64.9, 56.3, 49.8, 40.1, 36.5, 28.4; **HRMS** (EI) *m/z* 341.1758 [calc'd for $C_{21}H_{25}O_4$(M+H) 341.1753].

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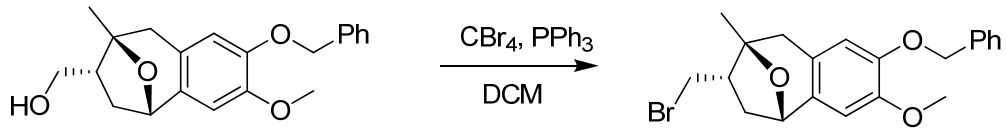
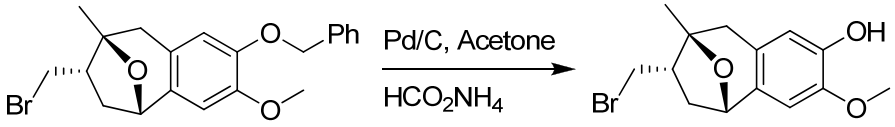



**19** **20**

Primary alcohol **19** (10 mg, 0.03 mmol) was dissolved in dry DCM (0.6 mL) at room temperature. Triphenyl phosphine (11.6 mg, 0.045 mmol) was then added followed by carbon tetrabromide (15 mg, 0.045 mmol) and the reaction was stirred for 4 hours until the starting material was consumed. The crude reaction mixture was concentrated and directly purified by silica gel chromatography (30% ethyl acetate, 70% hexanes) to give bromide **20** (10 mg, 84%).

**FTIR (thin film/NaCl)** 2953, 2917, 1653, 1507, 1457, 1338, 1257, 1225, 1012 $cm^{-1}$; **$^1$H NMR (600 MHz, $CDCl_3$)** δ = 7.45-7.29 (m, 5H), 6.60 (s, 1H), 6.51 (s, 1H), 5.14-5.06 (m, 2H), 4.91 (d, *J*=6.7, 1H), 3.85 (s, 3H), 3.31-3.22 (m, 2H), 2.88 (d, *J*=17.1, 1H), 2.77 (d, *J*=17.1, 1H), 2.68-2.60 (m, 1H), 2.56-2.48 (m, 1H), 1.62 (dd, *J*=3.8, 12.3, 1H), 1.55 (s, 3H); **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ = 148.4, 147.6, 137.3, 134.0, 128.8, 128.1, 127.6, 123.8, 114.6, 108.0, 82.2, 76.6, 71.5, 56.4, 50.2, 43.3, 36.1, 35.1, 28.1; **HRMS** (EI) *m/z* 403.0908 [calc'd for $C_{21}H_{24}O_3Br$ (M+H) 403.0909].




**20** **21**

Benzyl-protected phenol **20** (11 mg, 0.027 mmol) was dissolved in dry acetone (2.7 mL) at room temperature. 10% Pd/C (20 mg) was added followed by ammonium formate (8.6 mg, 0.135 mmol). The reaction was sealed in a vial and heated at 60°C for 4 hours. The reaction was filtered through Celite and concentrated to yield pure phenol **21** (8 mg, 94%).

**FTIR (thin film/NaCl)** 2967, 2880, 1591, 1451, 1247, 1099, 1070, 1024 $cm^{-1}$; **$^1$H NMR (400 MHz, $CDCl_3$)** δ = 6.64 (s, 1H), 6.47 (s, 1H), 4.90 (d, *J*=6.6, 1H), 3.86 (s, 3H), 3.32-3.26 (m, 2H), 2.91 (d, *J*=17.2, 1H), 2.80 (d, *J*=17.2, 1H), 2.69-2.59 (m, 1H), 2.58-2.49 (m, 1H), 1.64-1.58 (m, 1H), 1.55 (s, 3H); **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ = 145.1, 144.9, 132.8, 124.6, 114.4, 106.7, 82.2, 76.7, 56.2, 50.2, 43.4, 36.0, 35.1, 28.1; **HRMS** (EI) *m/z* 312.0356 [calc'd for $C_{14}H_{17}O_3Br$ (M+) 312.0361].

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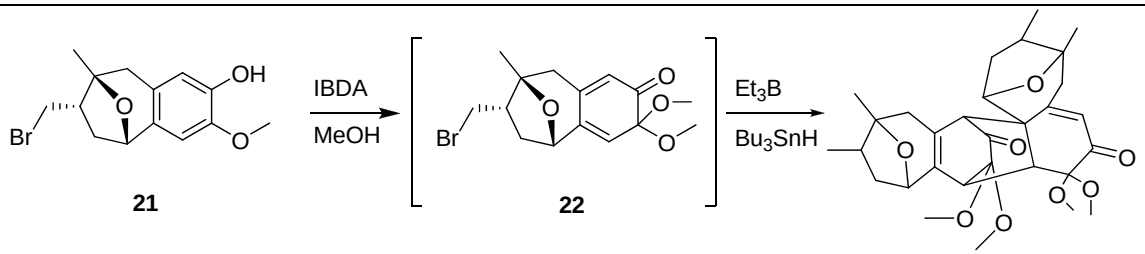
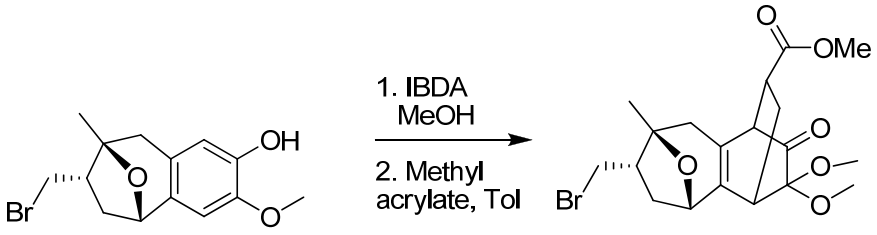



**21** **22**

Starting phenol **21** (5 mg, 0.016 mmol) was dissolved in anhydrous methanol (2 mL) and stirred at room temperature. Iodobenzene diacetate (6 mg, 0.018 mmol) was added to the reaction and after a few seconds, the reaction turned a bright yellow. The reaction was stirred for 10 minutes before being concentrated and directly purified using silica gel chromatography (30% ethyl acetate, 70% hexanes) to give dearomatized product **22** (5 mg, 91%). This *ortho*-quinone *mono*-ketal was dissolved in dry toluene (2 mL) and tributyltin hydride (0.01 mL, 0.032 mmol) was added at -78°C, followed by active triethylborane (1M, 0.01 mL, 0.01 mmol). The reaction was warmed to room temperature and was diluted with ethyl acetate and washed with brine, dried over sodium sulfate, and the organics were concentrated. The product was purified using silica gel chromatography to give the quenched, dimerized product (3 mg, 55%).

**<u>Monomer:</u>** **$^1$H NMR (400 MHz, $CDCl_3$)** δ = 5.97 (s, 1H), 5.87 (s, 1H), 4.74 (d, *J*=7.8, 1H), 3.38 (s, 3H), 3.37-3.33 (m, 2H), 3.30 (s, 3H), 2.80-2.68 (m, 3H), 2.51-2.40 (m, 1H), 1.52-1.48 (m, 1H), 1.47 (s, 3H).

**<u>Dimer:</u>** **$^1$H NMR (600 MHz, $C_6D_6$)** δ = 5.78-5.75 (m, 1H), 4.50 (d, *J*=6.5, 1H), 4.31 (d, *J*=7.5, 1H), 3.78 (s, 1H), 3.14 (s, 3H), 3.13 (s, 3H), 3.13 (s, 3H), 2.98-2.95 (m, 1H), 2.88 (s, 3H), 2.61-2.57 (m, 1H), 2.39-2.35 (m, 1H), 2.28-2.22 (m, 1H), 2.15-2.06 (m, 2H), 1.92-1.88 (m, 1H), 1.88-1.82 (m, 1H), 1.80-1.65 (m, 2H), 1.24 (s, 3H), 1.17 (s, 3H), 0.94-0.82 (m, 2H), 0.83 (d, *J*=7.3, 3H), 0.70 (d, *J*=7.1, 3H); **HRMS** (EI) *m/z* 513.24973 [calc'd for $C_{29}H_{37}O_8$ (M $(-CH_3)$ +) 513.24883].




**21** **24**

Phenol **21** (4 mg, 0.013 mmol) was dissolved in dry methanol (0.2 mL) at room temperature. Solid iodobenzene diacetate (4.5 mg, 0.014 mmol) was added and the reaction turned a bright yellow over the course of five minutes. The reaction was concentrated and filtered through a plug of silica to give the crude oxidation product. This product was next dissolved in dry toluene (0.2 mL) and methyl acrylate (0.01 mL, 0.13 mmol) was added. The reaction was stirred at 50°C for five hours at which time the solvent was evacuated and the crude oil subjected to silica gel chromatography to give **24** (5 mg, 91%).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ = 4.36 (d, *J*=6.5, 1H), 3.69 (s, 3H), 3.36 (s, 3H), 3.30 (s, 3H), 3.18-3.12 (m, 1H), 3.06-3.00 (m, 1H), 2.94-2.85 (m, 1H), 2.53-2.28 (m, 6H), 2.18 (d, *J*=18.0, 1H), 2.00 (d, *J*=11.9, 1H), 1.80-1.71 (m, 1H), 1.47 (s, 3H); **HRMS** (EI) *m/z* 429.0896 [calc'd for $C_{19}H_{26}O_6Br$ (M+H) 429.0913].

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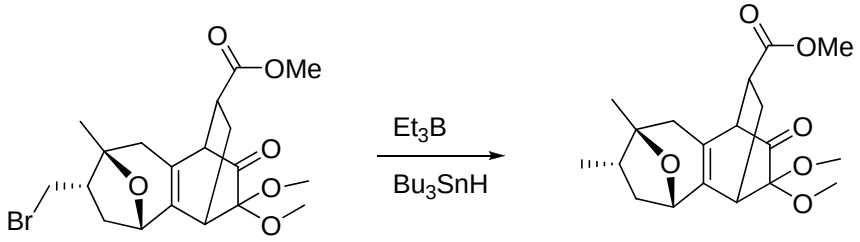
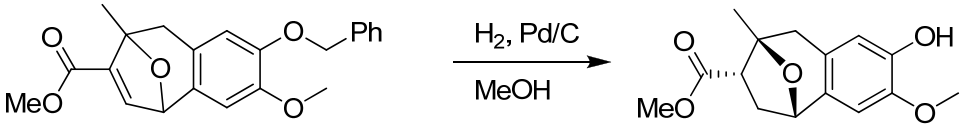



**24**

A solution of Diels-Alder product **24** (0.010g, 0.023 mmol) and dry toluene (2.3 mL) was purged with nitrogen and cooled to -78°C. To this was added tributyltin hydride (10% in toluene, 0.07 mL, 0.025 mmol) followed by triethyl borane (1M, 0.023 mL) that had been activated by addition of dry air. The reaction was allowed to stir for 10 minutes and the bath was removed. After 30 minutes, the reaction was concentrated and purified using silica gel chromatography to give quenched product (0.007g, 86%).

**FTIR (thin film/NaCl)** 2966, 2950, 1734, 1456, 1437, 1202, 1135, 1096, 1055, 750 $cm^{-1}$; **$^1$H NMR (600 MHz, $CDCl_3$)** δ = 4.35-4.28 (m, 1H), 3.68 (s, 3H), 3.34 (s, 3H), 3.30 (s, 3H), 3.04-2.99 (m, 1H), 2.94-2.88 (m, 1H), 2.42-2.31 (m, 1H), 2.29-2.23 (m, 1H), 2.17 (s, 1H), 2.10-2.02 (m, 1H), 1.80-1.75 (m, 1H), 1.75-1.69 (m, 1H), 1.64-1.56 (m, 2H), 1.34 (s, 3H), 0.94-0.88 (m, 3H); **HRMS** (EI) *m/z* 351.1813 [calc'd for $C_{19}H_{27}O_6$ (M+H) 351.1808].




**18** **26**

Starting material **18** (0.035 g, 0.096 mmol) was dissolved in dry methanol (1.9 mL) at room temperature under nitrogen. Palladium on carbon (10%, 30 mg) was added to the reaction and the nitrogen was replaced by a balloon of hydrogen gas. The reaction was heated at 50°C for 12 hours and then filtered through a plug of Celite. The reaction was concentrated and loaded directly onto a silica gel column for purification yielding **26** (0.024 g, 90%).

**FTIR (thin film/NaCl)** 2973, 2939, 1736, 1509, 1343, 1284, 1199, 1108 $cm^{-1}$; **$^1$H NMR (400 MHz, $CDCl_3$)** δ = 6.55 (s, 1H), 6.49 (s, 1H), 5.48 (bs, 1H), 4.98 (d, *J*=6.8, 1H), 3.85 (s, 3H), 3.64 (s, 3H), 3.02-2.86 (m, 1H), 2.90 (d, *J*=17.0, 1H), 2.56 (d, *J*=17.0, 1H), 2.52-2.43 (m, 1H), 2.42-2.34 (m, 1H), 1.64 (s, 3H); **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ = 172.9, 144.9, 144.8, 132.0, 124.4, 114.3, 106.5, 82.4, 77.7, 56.1, 53.6, 52.1, 38.9, 37.6, 28.0; **HRMS** (EI) *m/z* 278.1154 [calc'd for $C_{15}H_{18}O_5$ (M+) 278.1154].

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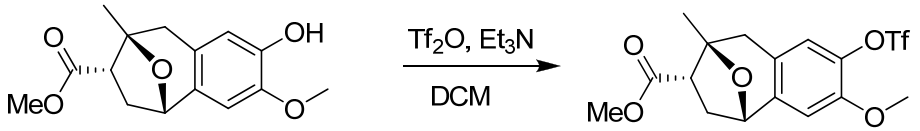
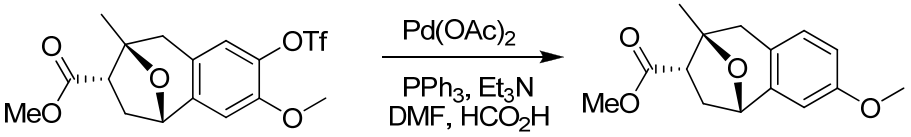



**26**

Starting phenol **26** (0.034 g, 0.122 mmol) was dissolved in dry DCM (2.5 mL) at 0°C under nitrogen. To this was added freshly distilled triethylamine (0.04 mL, 0.244 mmol) and then triflic anhydride (0.02 mL, 0.139 mmol). The reaction was stirred for 10 minutes until the reaction was complete. The solvent was partially removed and the residue purified by silica gel chromatography to yield the triflate (0.044 g, 88%).

**FTIR (thin film/NaCl)** 2982, 2957, 1737, 1614, 1508, 1421, 1206, 1141, 1082 $cm^{-1}$; **$^1$H NMR (600 MHz, $CDCl_3$)** δ = 6.85 (s, 1H), 6.67 (s, 1H), 5.04 (d, *J*=7.1, 1H), 3.88 (s, 3H), 3.63 (s, 3H), 3.03-3.00 (m, 1H), 2.93 (d, *J*=17.2, 1H), 2.62 (d, *J*=17.2, 1H), 2.55-2.48 (m, 1H), 2.40 (dd, *J*=4.1, 12.5, 1H), 1.65 (s, 3H); **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ = 172.6, 157.8, 149.6, 141.3, 137.7, 124.7, 122.2, 108.8, 82.4, 56.4, 54.8, 53.7, 52.2, 38.7, 37.2, 27.8.; **HRMS** (EI) *m/z* 410.06474 [calc'd for $C_{16}H_{17}F_3O_7S$ (M+) 410.06471].




**27**

Starting triflate (0.026 g, 0.063 mmol) was dissolved in anhydrous DMF (1.3 mL) at room temperature. To this was added freshly distilled triethylamine (0.09 mL, 6.3 mmol), palladium acetate (0.001 g, 0.006 mmol), and triphenylphosphine (0.003 g, 0.012 mmol). Upon addition of formic acid (0.02 mL, 0.63 mmol), a white smoke was observed and the reaction was sealed and heated at 100°C for 15 hours. After cooling to room temperature the reaction was quenched with saturated sodium bicarbonate (10 mL) and extracted with ethyl acetate (3 x 50 mL). The extracts were dried over anhydrous sodium sulfate, concentrated to an oil and purified with silica gel chromatography to give the deoxygenated product **27** (0.015 g, 90%).

**FTIR (thin film/NaCl)** 2950, 2902, 1736, 1613, 1503, 1433, 1251, 1198, 1164, 1035 $cm^{-1}$; **$^1$H NMR (400 MHz, $CDCl_3$)** δ = 6.90 (d, *J*=8.5, 1H), 6.70 (dd, *J*=2.6, 8.5, 1H), 6.55 (d, *J*=2.6, 1H), 5.01 (d, *J*=6.9, 1H), 3.77 (s, 3H), 3.63 (s, 3H), 3.02-2.97 (m, 1H), 2.93 (d, *J*=17.0, 1H), 2.62 (d, *J*=17.0, 1H), 2.55-2.46 (m, 1H), 2.42-2.37 (m, 1H), 1.65 (s, 3H); **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ = 172.9, 157.9, 141.3, 129.3, 123.7, 113.0, 109.1, 82.6, 78.0, 55.4, 53.7, 52.1, 38.7, 37.4, 28.0; **HRMS** (EI) *m/z* 262.12055 [calc'd for $C_{15}H_{18}O_4$ (M+) 262.12051].

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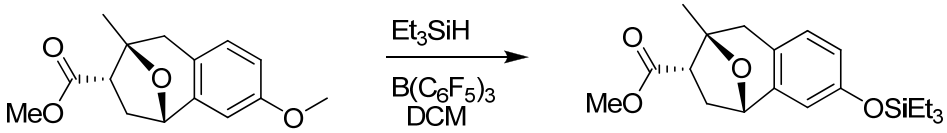
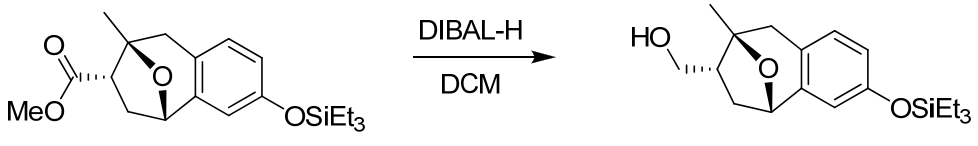



**27** **28**

Starting material **27** (9 mg, 0.031 mmol) was dissolved in DCM (0.62 mL) at room temperature. The tris(pentafluorophenyl)borane (2 mg, 0.003 mmol) was then added followed by a 10% stock solution of triethylsilane (0.06 mL, 0.034 mmol) and the reaction was allowed to stir at room temperature for 1 hour. After starting material was consumed, the reaction was quenched with 3 drops of triethyl amine and filtered through a Celite plug before being purified by silica gel chromatography (80% hexanes, 20% ethyl acetate) to give pure **28** (11 mg, 88%).

**FTIR (thin film/NaCl)** 3014, 2993, 1770, 1374, 1241, 1057, 914 $cm^{-1}$; **$^1$H NMR (400 MHz, $CDCl_3$)** δ = 6.83 (d, *J*=8.2, 1H), 6.64 (dd, *J*=8.2, 2.3, 1H), 6.50 (d, *J*=2.3, 1H), 4.97 (d, *J*=7.0, 1H), 3.61 (s, 3H), 3.05-2.95 (m, 1H), 2.92 (d, *J*=17.1, 1H), 2.62 (d, *J*=17.1, 1H), 2.55-2.43 (m, 1H), 2.41-2.32 (m, 1H), 1.65 (s, 3H), 0.98 (t, *J*=7.9, 9H), 0.72 (q, *J*=7.9, 6H); **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ = 172.8, 153.7, 141.3, 129.2, 124.3, 118.9, 115.2, 82.6, 77.8, 53.7, 52.0, 38.7, 37.4, 28.0, 6.9, 5.2; **HRMS** (EI) *m/z* 362.1911 [calc'd for $C_{20}H_{30}O_4Si$ (M+) 362.1913].




**28** **29**

Starting ester **28** (6 mg, 0.018 mmol) was dissolved dry DCM (0.9 mL) under nitrogen at -78°C. To this was added 20% by weight DIBAL-H in THF (0.04 mL, 0.054 mmol) drop-wise and the reaction was then maintained at -78°C for 30 minutes. The bath was removed and when the reaction reached room temperature, saturated sodium potassium tartrate (0.2 mL) was added followed by ethyl acetate (0.2 mL) to quench remaining DIBAL-H. The reaction was extracted with ethyl acetate, dried over sodium sulfate, concentrated, and purified with silica gel chromatography to give **29** (5 mg, 90%).

**FTIR (thin film/NaCl)** 2958, 2922, 2875, 1499, 1279, 1264, 1015, 974, 905 $cm^{-1}$; **$^1$H NMR (300 MHz, $CDCl_3$)** δ = 6.90 (d, *J*=8.3, 1H), 6.64 (dd, *J*=8.3, 2.7, 1H), 6.47 (d, *J*=2.7, 1H), 4.91 (d, *J*=7.2, 1H), 3.65-3.42 (m, 2H), 2.90 (d, *J*=17.0, 1H), 2.85 (d, *J*=17.0, 1H), 2.60-2.44 (m, 1H), 2.37-2.18 (m, 1H), 1.54 (s, 3H), 1.50-1.43 (m, 1H), 0.98 (t, *J*=7.8, 9H), 0.72 (q, *J*=7.8, 6H); **$^{13}$C NMR (600 MHz HSQCAD/gHMBCAD, $CDCl_3$)** δ = 152.4, 141.3, 128.5, 123.4, 113.0, 109.4, 80.7, 75.9, 63.7, 48.4, 38.8, 34.9, 27.2, 5.6, 3.9; **HRMS** (EI) *m/z* 334.1964 [calc'd for $C_{19}H_{30}O_3Si$ (M+) 334.1964].

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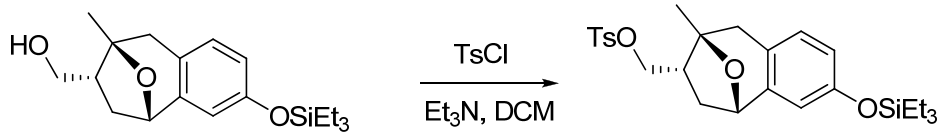
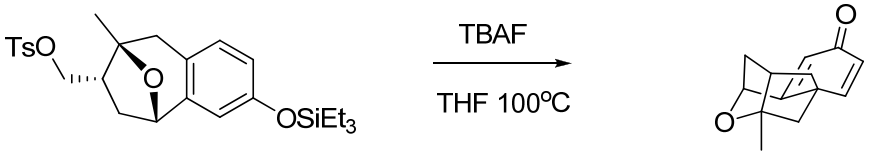



**29** **30**

Starting alcohol **29** (2 mg, 0.007 mmol) was dissolved in dry DCM (0.3 mL) at 0°C under nitrogen. Freshly distilled triethylamine (0.01 mL, 0.07 mmol) was added followed by *p*-toluenesulfonyl chloride (6 mg, 0.032 mmol). The bath was removed and the reaction stirred for 16 hours. The reaction was quenched with water (1 mL) and extracted with DCM (3 x 5 mL). The organics were dried with sodium sulfate, concentrated and purified with silica gel chromatography to give tosylate **30** (2 mg, 67%).

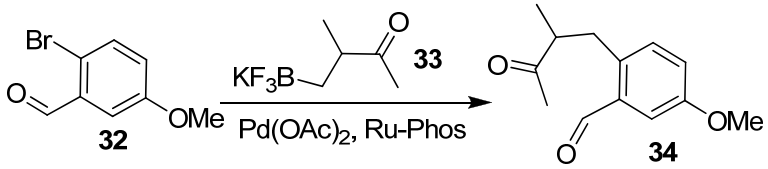
**FTIR (thin film/NaCl)** 2954, 2915, 1674, 1622, 1497, 1457, 1372, 1243, 1177, 1156, 1124, 1062, 1011 $cm^{-1}$; **$^1$H NMR (600 MHz, $CDCl_3$)** δ = 7.72 (d, *J*=8.0, 1H), 7.33 (d, *J*=8.0, 1H), 6.69 (d, *J*=8.2, 1H), 6.59 (dd, *J*=2.5, 8.2, 1H), 6.38 (d, *J*=2.5, 1H), 4.85 (d, *J*=6.9, 1H), 4.01-3.94 (m, 1H), 3.79-3.73 (m, 1H), 2.86 (d, *J*=17.1, 1H), 2.54 (d, *J*=17.1, 1H), 2.51-2.45 (m, 1H), 2.47 (s, 3H), 2.40-2.35 (m, 1H), 1.47 (s, 3H), 1.31 (dd, *J*=3.9, 12.3, 1H), 0.97 (t, *J*=7.8, 9H), 0.71 (q, *J*=7.8, 6H); **$^{13}$C NMR (600 MHz HSQCAD/gHMBCAD, $CDCl_3$)** 153.7, 144.9, 141.6, 130.8, 129.9, 129.1, 128.0, 124.0, 118.8, 115.1, 81.8, 76.8, 71.4, 46.0, 39.7, 35.9, 27.9, 21.5, 6.7, 4.8; **HRMS** (EI) *m/z* 489.2151 [calc'd for $C_{26}H_{37}O_5SiS$ (M+H) 489.2131].




**30** **31**

Starting tosylate **30** (16 mg, 0.033 mmol) was dissolved in dry THF (2.0 mL) at room temperature. A 10% stock solution of TBAF (0.4 mL, 0.04 mmol) was added and the reaction allowed to stir for 1 hour at 100°C. The reaction was then concentrated and purified with silica gel to yield known dienone **31** (6 mg, 91%).

**FTIR (thin film/NaCl)** 2963, 2942, 1659, 1626, 1149 $cm^{-1}$; **$^{1}$H NMR (600 MHz, $CDCl_3$)** δ = 6.66 (d, *J*=10.0, 1H), 6.32 (dd, *J*=1.6, 10.0, 1H), 6.12 (d, *J*=1.6, 1H), 4.71 (d, *J*=4.3, 1H), 2.59 (t, *J*=6.2, 1H), 2.27-2.21 (m, 1H), 2.20-2.15 (m, 1H), 2.01-1.92 (m, 2H), 1.78 (d, *J*=11.4, 1H), 1.56-1.50 (m, 1H), 1.51 (s, 3H); **$^{13}$C NMR (600 MHz HSQCAD/gHMBC, $CDCl_3$)** 187.1, 160.4, 150.9, 130.1, 121.9, 87.1, 80.0, 54.9, 49.9, 48.7, 44.4, 42.6, 22.2; **HRMS** (EI) *m/z* 202.0993 [calc'd for $C_{13}H_{14}O_2$ (M+) 202.0994].



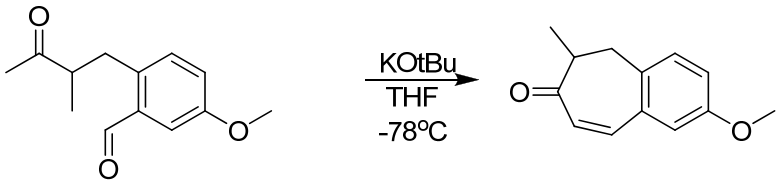

Starting bromide **32** (1.0 g, 4.65 mmol) was mixed with keto-boronate **33** (1.79 g, 9.3 mmol), $K_2CO_3$ (1.93 g, 13.95 mmol), palladium acetate (26.1 mg, 0.12 mmol), and RuPhos (2-dicyclohexylphosphino-2',6'-diisopropoxybiphenyl) (108 mg, 0.23 mmol) under an atmosphere of nitrogen. Freshly degassed dry toluene (18.6 mL) and freshly degassed distilled water (4.7 mL) were sequentially added and the reaction was heated at 85°C for 16 hours. The reaction was then quenched with pH 7.5 phosphate buffer and extracted with ethyl acetate. The organics were dried over sodium sulfate, concentrated and purified with silica gel chromatography to give **34** (725 mg, 71%).

**FTIR (thin film/NaCl)** 2970, 2935, 1706, 1608, 1572, 1499, 1263, 1164, 1037 $cm^{-1}$; **$^1$H NMR (400 MHz, $CDCl_3$)** δ = 10.20 (s, 1H), 7.34 (d, *J*=2.9, 1H), 7.17 (d, *J*=8.4, 1H), 7.05 (dd, *J*=2.9, 8.4, 1H), 3.86 (s, 3H), 3.42-3.30 (m, 1H), 2.90-2.77 (m, 2H), 2.11 (s, 3H), 1.11-1.08 (m, 3H); **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ = 212.3, 192.5, 158.7, 134.8, 134.7, 133.6, 120.3, 116.9, 55.7, 48.9, 34.8, 29.3, 16.5; **HRMS** (EI) *m/z* 220.1099 [calc'd for $C_{13}H_{16}O_3$ (M+) 220.1100].

Synthesis of 33:

Copper chloride (35 mg, 0.36 mmol), sodium tert-butoxide (103 mg, 1.07 mmol), and DPEPhos (192 mg, 0.36 mmol) were mixed under nitrogen. THF (15 mL) was added at room temperature and the mixture was stirred for 30 minutes. Bispinacolato diboron (3.17 g, 12.50 mmol) in THF (9 mL) was added and the reaction was stirred for 15 minutes. 3-methyl-3-butene-2-one (1.0 g, 11.89 mmol) was then added followed by anhydrous methanol (0.9 mL) and the reaction was stirred for 2 hours. This mixture was then filtered through Celite, concentrated to an oil, and subsequently dissolved in acetonitrile (60 mL) and cooled to 0°C. Saturated $KHF_2$ (3.71 g, 47.6 mmol, 10 mL $H_2O$) was added drop-wise and the reaction was stirred 2 hours. The solvent was then removed. The solids were triturated with hot acetone and the acetone washings combined and concentrated to 10% of the original volume. The product was precipitated by adding diethyl ether and recrystallized with acetone to give **33** (1.95 g, 85%, mp=110-112°C).

**$^1$H NMR (400 MHz, $(CD_3)_2CO$)** δ = 2.49-2.40 (m, 1H), 2.03-1.98 (m, 2H), 1.95 (s, 3H), 0.94 (d, *J*=6.8, 3H); **$^{13}$C NMR (75 MHz, $(CD_3)_2CO$)** δ = 205.6, 44.9, 29.2, 26.1, 18.3.




**34**

Potassium tert-butoxide (3.24 g, 27.3 mmol) was added to a flame-dried round bottom flask and dry THF (360 mL) was added under a nitrogen atmosphere at -78°C. The starting material **34** (4.01 g, 18.2 mmol) was dissolved in dry THF (10 mL) and added drop-wise to the butoxide slurry. Upon complete addition, the reaction was allowed to stir for an additional 30 minutes at -78°C at which time the bath was removed and the reaction allowed warming to room temperature. The reaction was neutralized with saturated sodium bicarbonate and extracted with ether. The combined extracts were dried over sodium sulfate, concentrated, and purified by column chromatography (70% hexanes, 30% ethyl acetate) to yield enone (3.42 g, 93%).

**FTIR (thin film/NaCl)** 2970, 2935, 1657, 1600, 1569, 1504, 1275, 1175, 1327 $cm^{-1}$; **$^1$H NMR (400 MHz, $CDCl_3$)** δ = 7.20 (d, *J*=7.2, 1H), 7.02 (d, *J*=12.8, 1H), 6.90-6.84 (m, 2H), 6.15 (d, *J*=12.8, 1H), 3.83 (s, 3H), 2.96-2.84 (m, 2H), 2.75-2.62 (m, 1H), 1.12 (d, *J*= 7.1, 3H); **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ = 203.7, 158.7, 142.0, 135.3, 132.7, 131.1, 129.4, 117.5, 115.5, 55.7, 45.3, 36.5, 15.9; **HRMS** (EI) *m/z* 202.0993 [calc'd for $C_{13}H_{14}O_2$ (M+) 202.0994].

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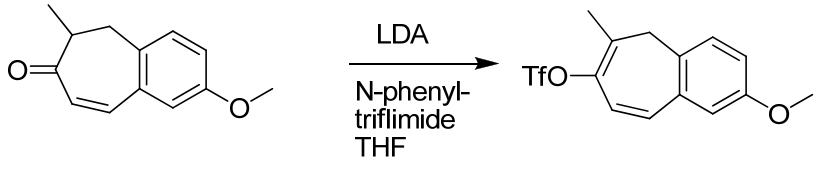
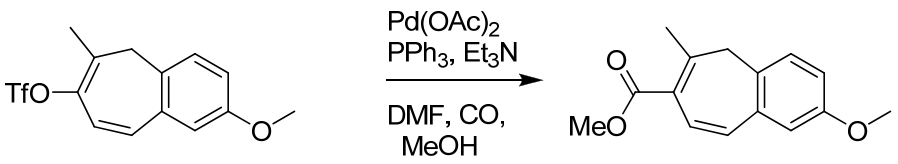



**35**

Freshly distilled diisopropyl amine (5.2 mL, 37 mmol) was added to a flame-dried flask and diluted with dry THF (160 mL) and cooled to -78°C under nitrogen. Butyl lithium (1.6M, 21 mL, 33.6 mmol) was then added and allowed to react for 30 minutes. Starting enone (3.4 g, 16.8 mmol) was then dissolved in THF (8 mL) and added drop-wise to the LDA solution over 1 minute and allowed to stir for an additional 15 minutes. A stock solution of N-phenyl triflimide (6.61 g, 18.5 mmol) was then added and the bath removed as the reaction warmed to room temperature. After 1 hour the reaction was diluted with ether (250 mL) and washed with NaOH solution (0.1M, 100 mL). The ethereal solution was then dried over sodium sulfate, concentrated, and purified with column chromatography (70% hexanes, 30% ethyl acetate) to yield **35** (3.24 g, 58%).

**FTIR (thin film/NaCl)** 2945, 2838, 1498, 1414, 1206, 1139, 1032 $cm^{-1}$; **$^1$H NMR (400 MHz, $CDCl_3$)** δ = 7.10-7.02 (m, 2H), 6.93 (dd, *J*=2.6, 8.3, 1H), 6.83 (d, *J*=2.6, 1H), 6.32 (d, *J*=11.9, 1H), 3.79 (s, 3H), 3.05 (s, 2H), 2.07 (s, 3H); **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ = 158.5, 140.3, 135.8, 135.0, 129.5, 128.9, 128.5, 122.9, 120.8, 116.3, 112.8, 55.6, 37.8, 18.9; **HRMS** (EI) *m/z* 335.0558 [calc'd for $C_{14}H_{14}O_4F_3S$ (M+H) 335.0565].




**35** **36**

Palladium acetate (46 mg, 0.21 mmol) and triphenylphosphine (108 mg, 0.42 mmol) were added to a flame-dried flask at room temperature under nitrogen. Dry DMF (21 mL) was added followed by triethylamine (0.8 mL, 6.2 mmol) and methanol (3.4 mL, 83 mmol). Starting triflate **35** (690 mg, 2.07 mmol) was dissolved in dry DMF (3 mL) and added to the reaction and a balloon of carbon monoxide was attached *via* needle through a septum. The reaction was heated at 80°C for 3 hours until the starting material was consumed. The reaction was then diluted with ethyl acetate (250 mL) and washed with distilled water (3 x 50 mL). The organics were then dried over sodium sulfate and purified with silica gel chromatography (70% hexanes, 30% ethyl acetate) to yield **36** (485 mg, 96%).

**FTIR (thin film/NaCl)** 2952, 1716, 1604, 1495, 1434, 1257, 1221 $cm^{-1}$; **$^1$H NMR (400 MHz, $CDCl_3$)** δ = 7.09 (d, *J*=8.4, 1H), 7.03 (d, *J*=11.8, 1H), 6.90 (dd, *J*=2.7, 8.4, 1H), 6.86 (d, *J*=11.8, 1H), 6.82 (d, *J*=2.7, 1H), 3.78 (s, 3H), 3.72 (s, 3H), 3.03 (s, 2H), 2.36 (s, 3H); **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ = 168.1, 158.2, 148.9, 136.4, 131.9, 128.8, 128.3, 128.2, 124.0, 115.6, 111.7, 55.6, 51.7, 42.9, 22.9; **HRMS** (EI) *m/z* 244.1097 [calc'd for $C_{15}H_{16}O_3$ (M+) 244.1100].

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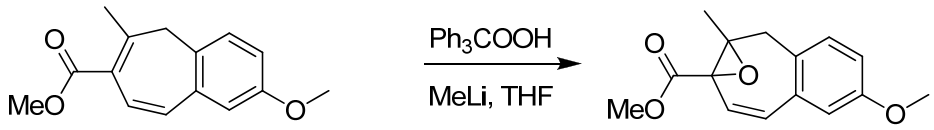
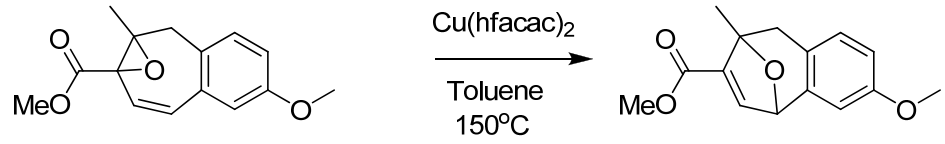



**36** **37**

Triphenylmethyl hydroperoxide (0.153 g, 0.554 mmol) was added to a flame-dried flask and dissolved in dry THF (7 mL) under nitrogen and then cooled to -78°C. Methyl lithium (1.6M, 0.3 mL, 0.480 mmol) was added and the reaction was stirred for 10 minutes. Starting diene **36** (0.090 g, 0.368 mmol) was then dissolved in dry THF (0.4 mL), added to the reaction, and allowed to stir at -78°C for 1 hour. The reaction was then warmed to room temperature and quenched with saturated ammonium chloride (5 mL) and extracted with ethyl acetate (3 x 50 mL). The organics were then dried over sodium sulfate, concentrated, and purified by silica gel chromatography (80% hexanes, 20% ethyl acetate) to yield **37** (0.086 g, 90%).

**FTIR (thin film/NaCl)** 2957, 1749, 1605, 1572, 1503, 1435, 1266, 1045 $cm^{-1}$; **$^1$H NMR (400 MHz, $CDCl_3$)** δ = 7.01-6.96 (m, 2H), 6.77 (dd, *J*=2.7, 8.3, 1H), 4.23 (d, *J*=4.3, 1H), 4.18 (d, *J*=4.3, 1H), 3.96 (d, *J*=13.6, 1H), 3.80 (s, 3H), 3.75 (s, 3H), 3.26 (d, *J*=13.6, 1H), 2.24 (s, 3H); **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ = 169.5, 158.9, 136.9, 134.2, 130.6, 127.9, 125.7, 115.1, 113.6, 71.6, 62.7, 55.5, 52.9, 42.8, 18.6; **HRMS** (EI) *m/z* 260.1050 [calc'd for $C_{15}H_{16}O_4$ (M+) 260.1049].




**37** **38**

Starting epoxide **37** (0.062 g, 0.238 mmol) was dissolved in dry toluene (0.5 mL) and dry $Cu(hfacac)_2$ (35 mg, 0.071 mmol, dried on vacuum pump for 2 hours prior to use) was added at room temperature. The vial was sealed well and the reaction heated at 150°C for 30 minutes. After allowing the reaction to cool to room temperature, it was filtered through neutral alumina (activity grade 1), concentrated and purified with silica gel chromatography (80% hexanes, 20% ethyl acetate) to give **38** (0.050 g, 81%).

**FTIR (thin film/NaCl)** 2947, 2933, 1714, 1598, 1494, 1437, 1253 $cm^{-1}$; **$^1$H NMR (300 MHz, $CDCl_3$)** δ = 6.98 (d, *J*=8.5, 1H), 6.76 (dd, *J*=8.5, 2.6, 1H), 6.63 (d, *J*=2.6, 1H), 5.30 (d, *J*=1.8, 1H), 3.77 (s, 3H), 3.71 (s, 3H), 2.92 (d, *J*=17.0, 1H), 2.78 (d, *J*=17.0, 1H), 1.72 (s, 3H); **$^{13}$C NMR (151 MHz, $CDCl_3$)** δ = 164.1, 157.6, 147.4, 137.0, 135.7, 131.3, 126.1, 113.4, 110.0, 84.5, 80.2, 55.6, 51.7, 34.6, 23.6; **HRMS** (EI) *m/z* 261.1129 [calc'd for $C_{15}H_{17}O_4$ (M+H) 261.1127].

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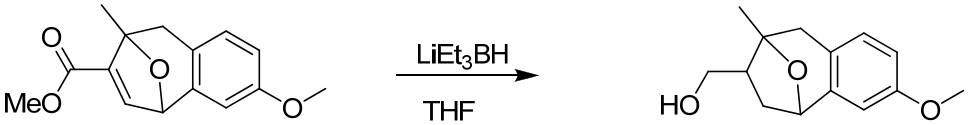
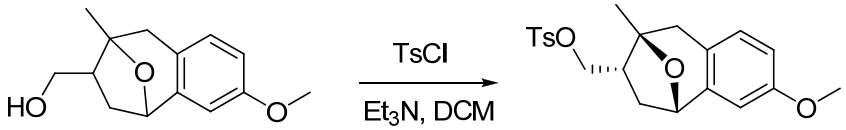



**38** **39**

Methyl enoate **38** (135 mg, 0.52 mmol) was dissolved in dry THF (26 mL) and the solution cooled to -78°C under nitrogen. Lithium triethylborohydride (1M, 2.1 mL, 2.08 mmol) was added drop-wise and the reaction stirred for 90 minutes. The bath was then removed and when the reaction had come to room temperature it was quenched with saturated ammonium chloride and extracted with DCM. The organics were dried over sodium sulfate, concentrated, and chromatographed (50% hexanes, 50% ethyl acetate) to give **39** (118 mg, 97%).

**FTIR (thin film/NaCl)** 2953, 2922, 1610, 1502, 1451, 1382, 1258, 1155, 1034 $cm^{-1}$; **$^1$H NMR (400 MHz, $CDCl_3$)** δ = 6.97 (d, *J*=8.1, 1H), 6.70 (dd, *J*=2.5, 8.1, 1H), 6.51 (d, *J*=2.5, 1H), 4.95 (d, *J*=7.2, 1H), 3.77 (s, 3H), 3.64-3.55 (m, 1H), 3.54-3.44 (m, 1H), 2.94 (d, *J*=17.0, 1H), 2.83 (d, *J*=17.0, 1H), 2.60-2.50 (m, 1H), 2.33-2.24 (m, 1H), 1.54 (s, 3H), 1.50 (dd, *J*=4.2, 12.2, 1H); **$^{13}$C NMR (600 MHz HSQCAD/gHMBC, $CDCl_3$)** δ =157.7, 142.3, 129.3, 124.3, 112.7, 109.0, 81.8, 77.1, 64.8, 55.4, 49.5, 40.0, 36.2, 28.3; **HRMS** (EI) *m/z* 234.1259 [calc'd for $C_{14}H_{18}O_3$ (M+) 234.1256]..




**39**

Starting alcohol **39** (49 mg, 0.210 mmol) was dissolved in dry DCM (4.2 mL) at 0°C under nitrogen. Freshly distilled triethylamine (0.3 mL, 2.10 mmol) was added followed by *p*-toluenesulfonyl chloride (60 mg, 0.315 mmol). The bath was removed and the reaction stirred for 10 hours. The reaction was quenched with water (2 mL) and extracted with DCM (3 x 5 mL). The organics were dried with sodium sulfate, concentrated and purified with silica gel chromatography to give the tosylate (78 mg, 96%).

**FTIR (thin film/NaCl)** 2970, 2929, 1612, 1503, 1452, 1360, 1253, 1176, 1096, 1017, 950 $cm^{-1}$ ; **$^1$H NMR (400 MHz, $CDCl_3$)** δ = 7.73 (d, *J*=8.2, 2H), 7.33 (d, *J*=8.2, 2H), 6.77 (d, *J*=8.3, 1H), 6.66 (dd, *J*=2.6, 8.3, 1H), 6.43 (d, *J*=2.6, 1H), 4.90 (d, *J*=6.8, 1H), 4.00-3.94 (m, 1H), 3.82-3.76 (m, 1H), 3.76 (s, 3H), 2.87 (d, *J*=17.0, 1H), 2.56 (d, *J*=17.0, 1H), 2.53-2.35 (m, 2H), 2.47 (s, 3H), 1.48 (s, 3H), 1.34 (dd, *J*=3.7, 12.1, 1H); **$^{13}$C NMR (600 MHz HSQCAD/gHMBC, $CDCl_3$)** δ =157.8, 144.9, 141.7, 132.7, 129.7, 129.0, 127.6, 123.1, 112.6, 108.7, 81.5, 76.5, 71.2, 55.0, 45.7, 39.4, 35.6, 27.6, 21.3; **HRMS** (EI) *m/z* 389.1417 [calc'd for $C_{21}H_{25}O_5S$ (M+H) 389.1423].

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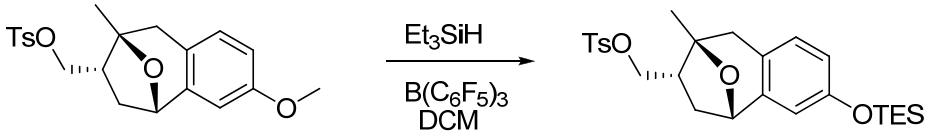
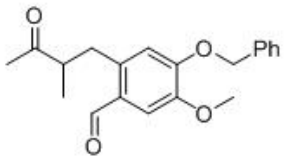



**30**

Starting tosylate (34 mg, 0.088 mmol) was dissolved in DCM (1.8 mL) at room temperature. The tris(pentafluorophenyl)borane (4.5 mg, 0.009 mmol) was then added followed by a 10% stock solution of triethylsilane (0.15 mL, 0.097 mmol) and the reaction was allowed to stir at room temperature for 1 hour. After the starting material was consumed, the reaction was purified by silica gel chromatography (80% hexanes, 20% ethyl acetate) to give pure **30** (36 mg, 84%).

**FTIR (thin film/NaCl)** 2954, 2915, 1674, 1622, 1497, 1457, 1372, 1243, 1177, 1156, 1124, 1062, 1011 $cm^{-1}$; **$^1$H NMR (600 MHz, $CDCl_3$)** δ = 7.72 (d, *J*=8.0, 1H), 7.33 (d, *J*=8.0, 1H), 6.69 (d, *J*=8.2, 1H), 6.59 (dd, *J*=2.5, 8.2, 1H), 6.38 (d, *J*=2.5, 1H), 4.85 (d, *J*=6.9, 1H), 4.01-3.94 (m, 1H), 3.79-3.73 (m, 1H), 2.86 (d, *J*=17.1, 1H), 2.54 (d, *J*=17.1, 1H), 2.51-2.45 (m, 1H), 2.47 (s, 3H), 2.40-2.35 (m, 1H), 1.47 (s, 3H), 1.31 (dd, *J*=3.9, 12.3, 1H), 0.97 (t, *J*=7.8, 9H), 0.71 (q, *J*=7.8, 6H); **$^{13}$C NMR (600 MHz HSQCAD/gHMBCAD, $CDCl_3$)** 153.7, 144.9, 141.6, 130.8, 129.9, 129.1, 128.0, 124.0, 118.8, 115.1, 81.8, 76.8, 71.4, 46.0, 39.7, 35.9, 27.9, 21.5, 6.7, 4.8; **HRMS** (EI) *m/z* 489.2151 [calc'd for $C_{26}H_{37}O_5SiS$ (M+H) 489.2131].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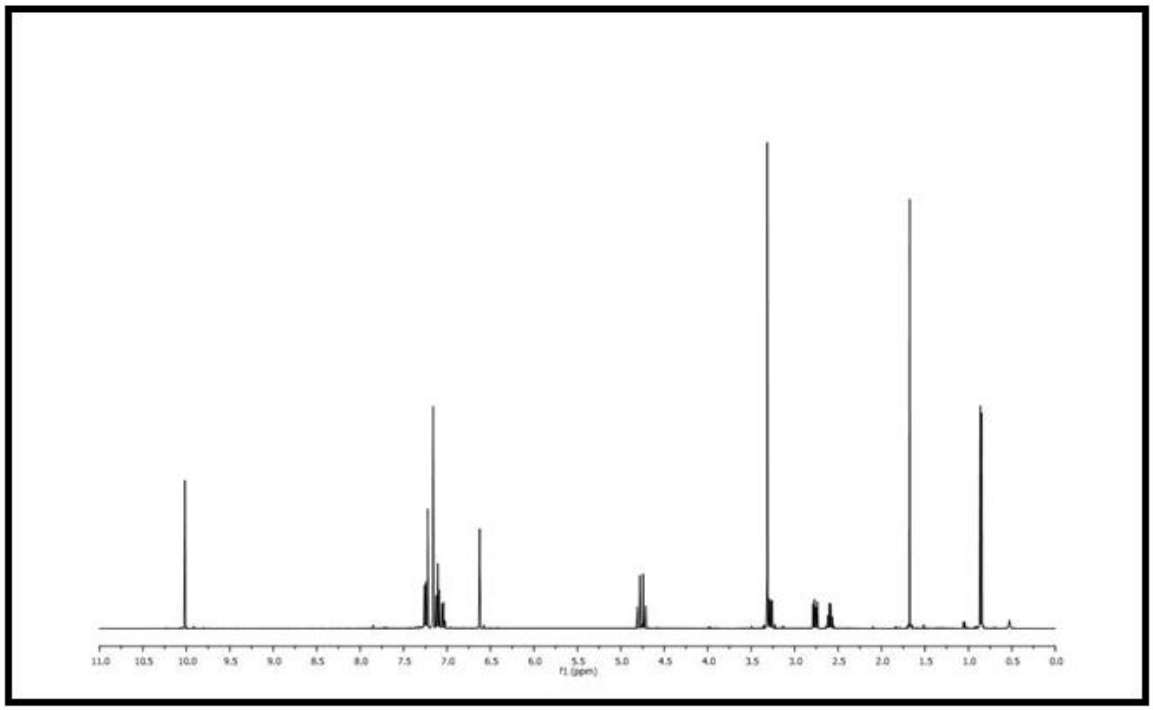
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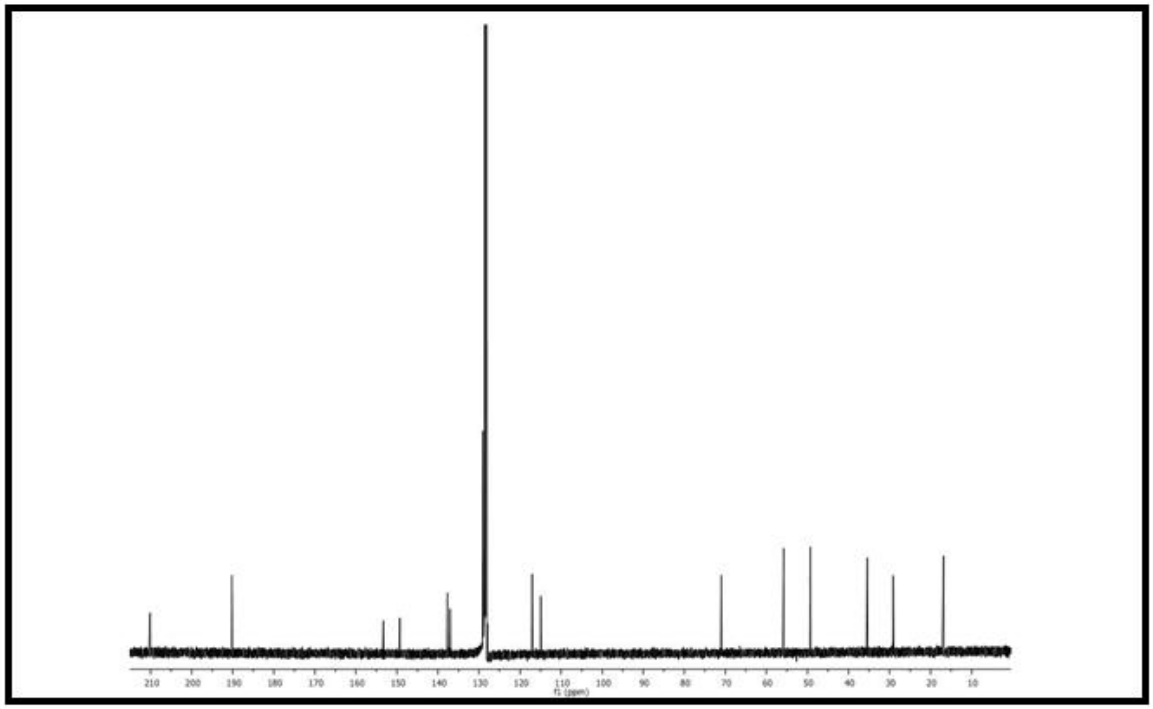
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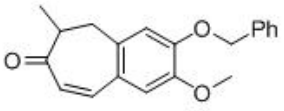
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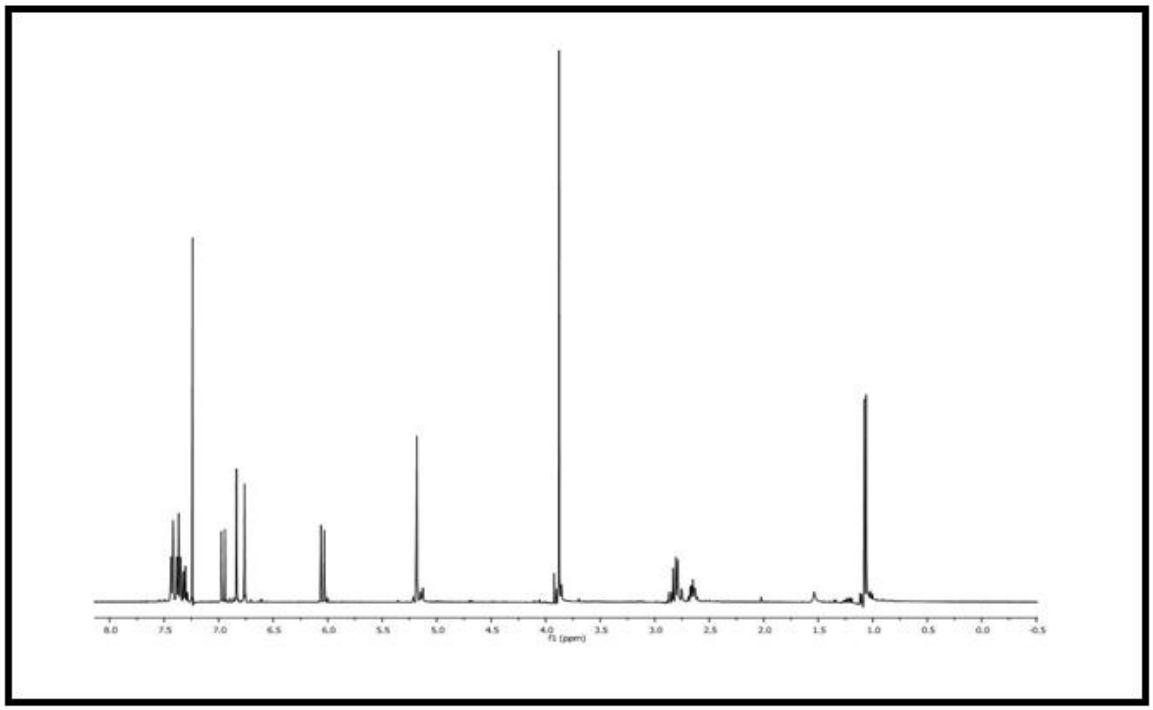
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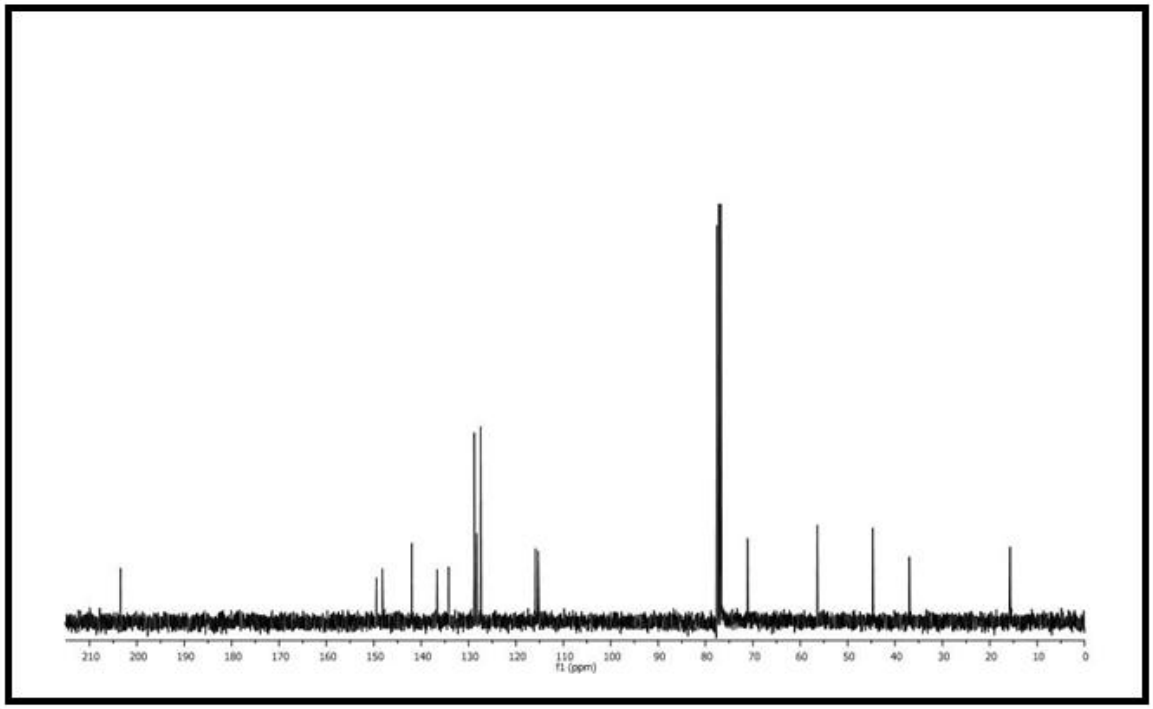
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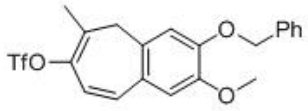
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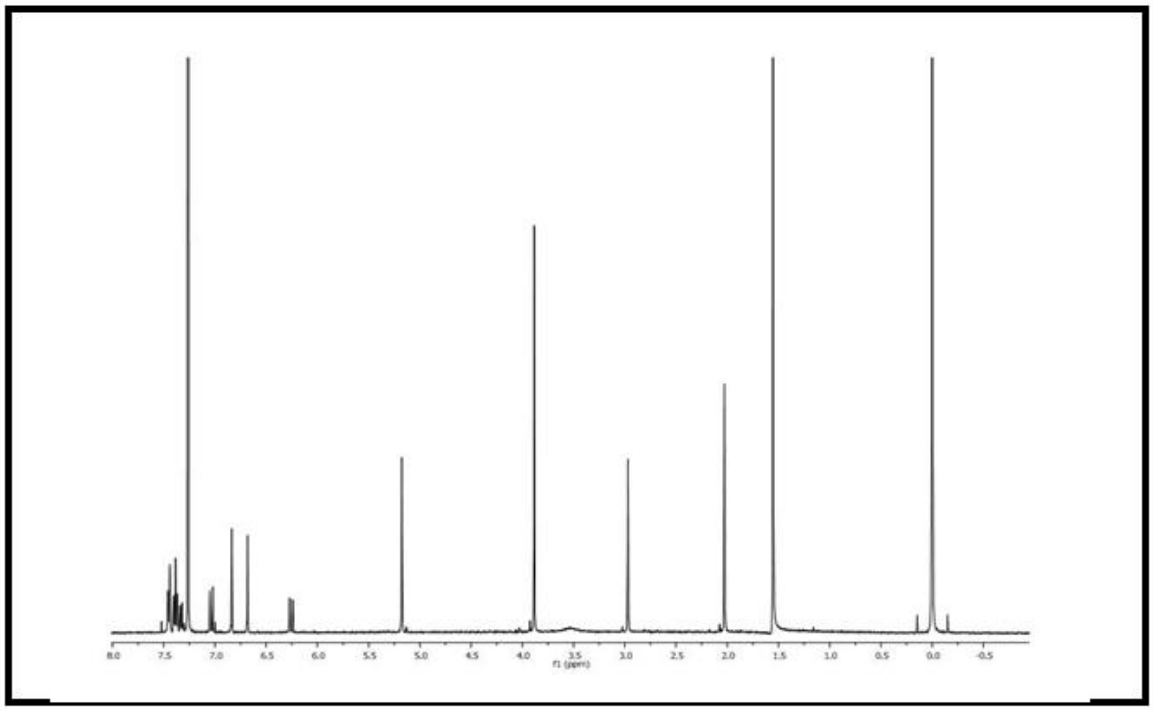
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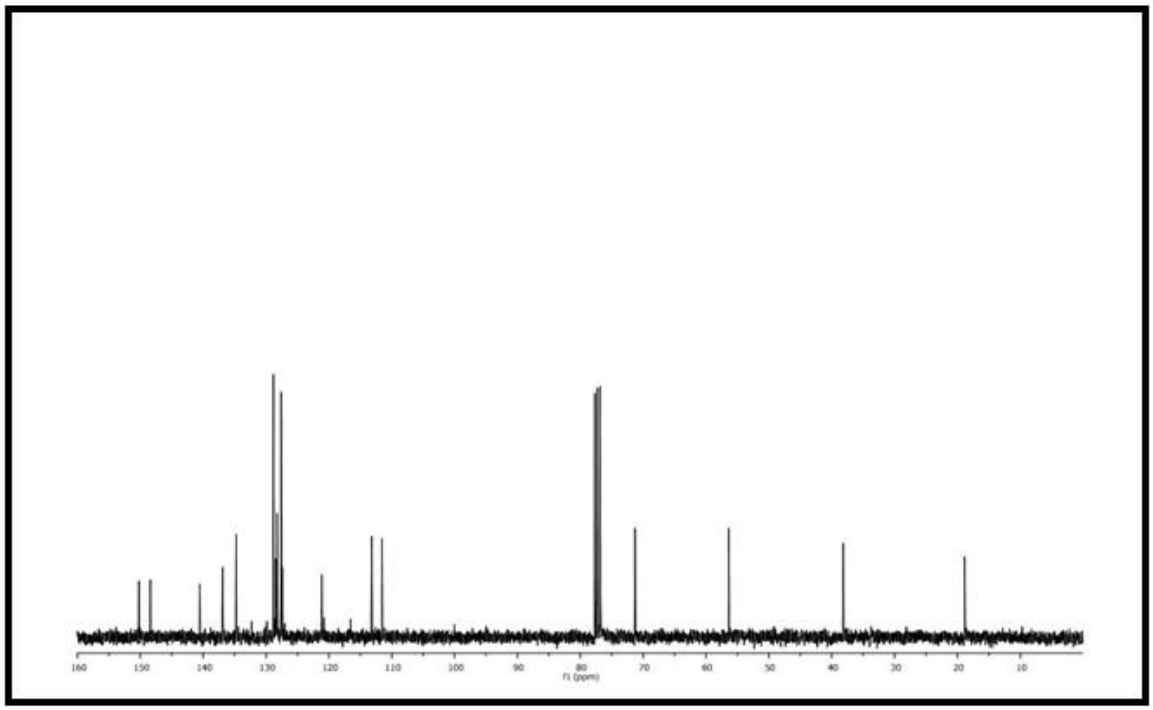
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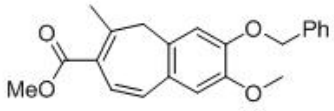
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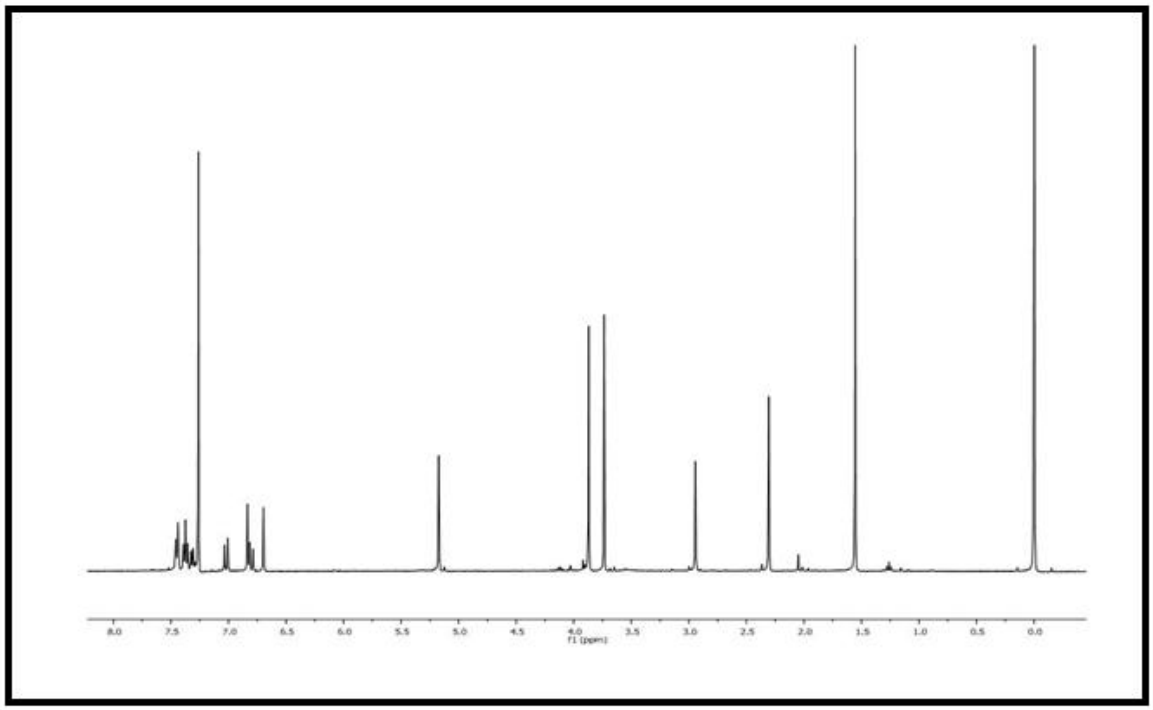
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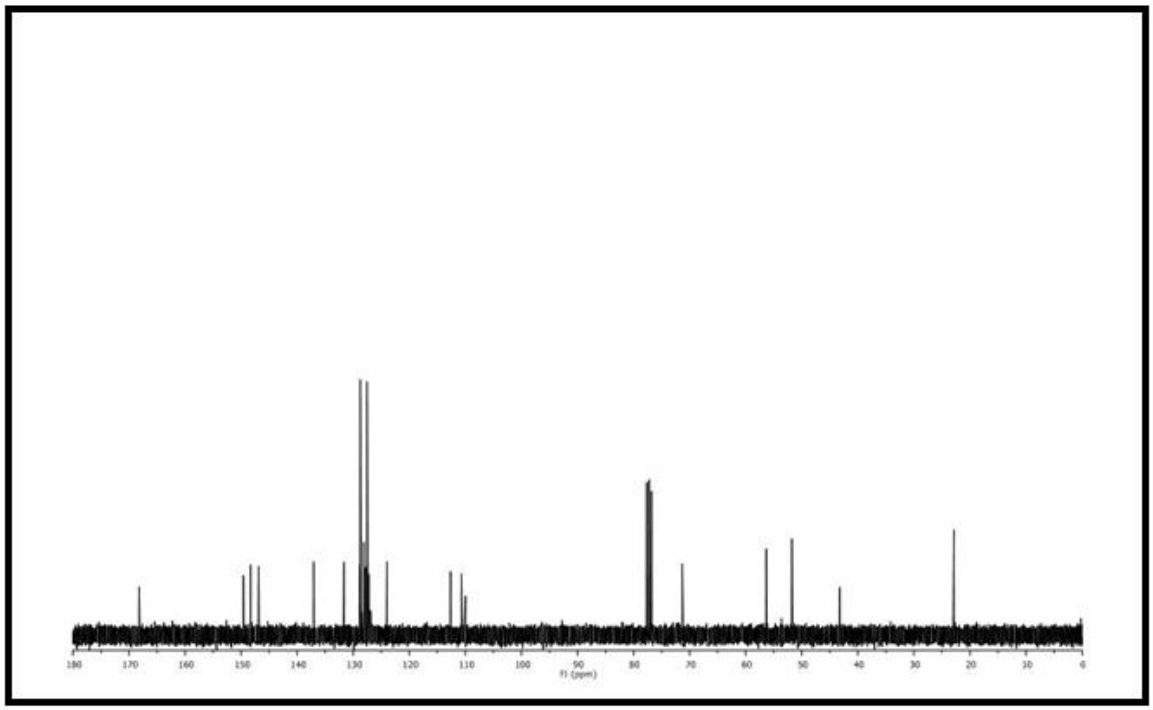
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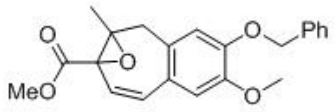
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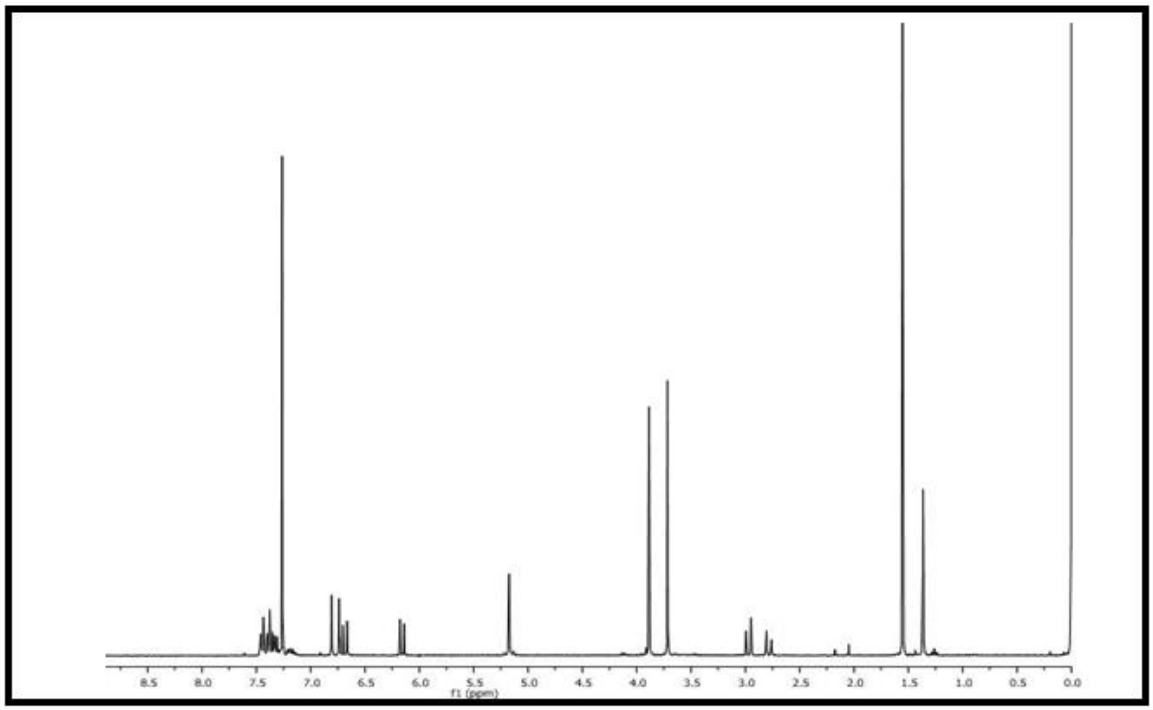
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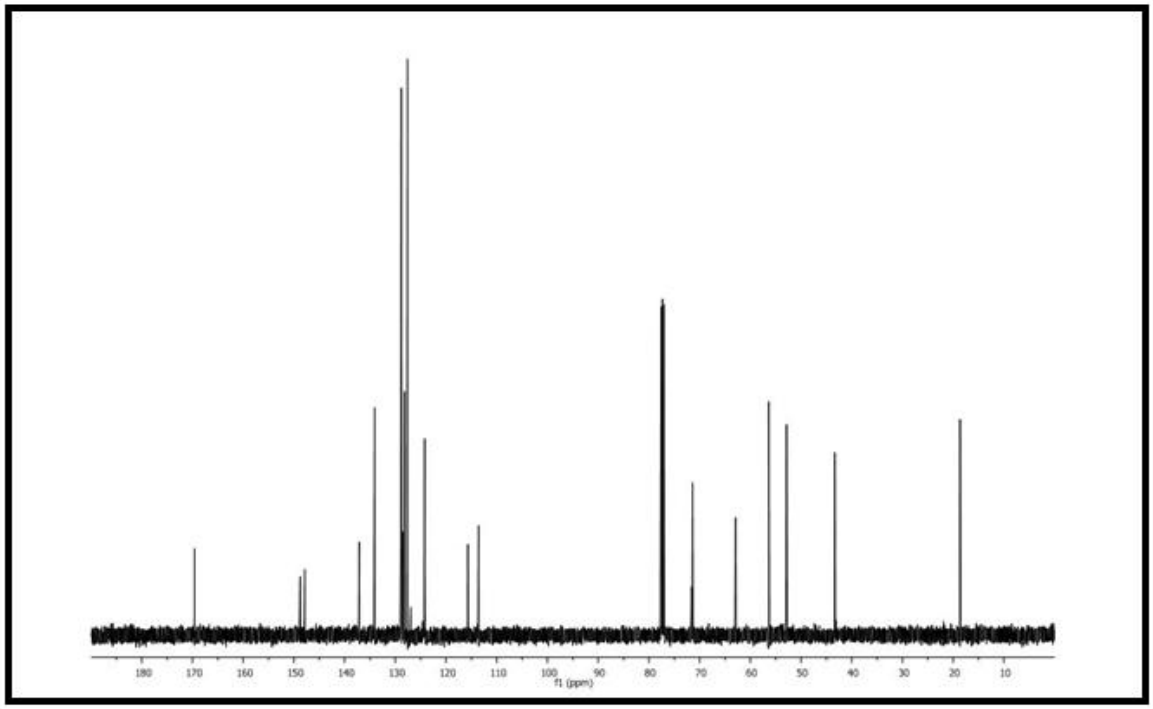
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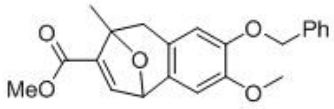
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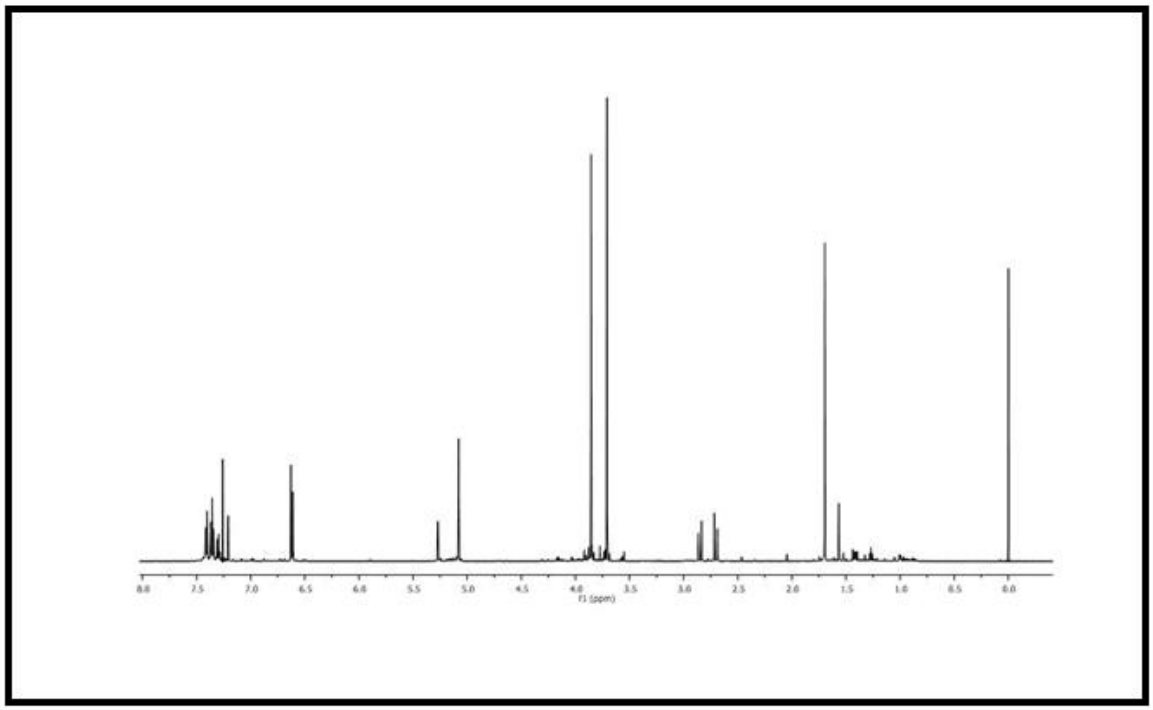
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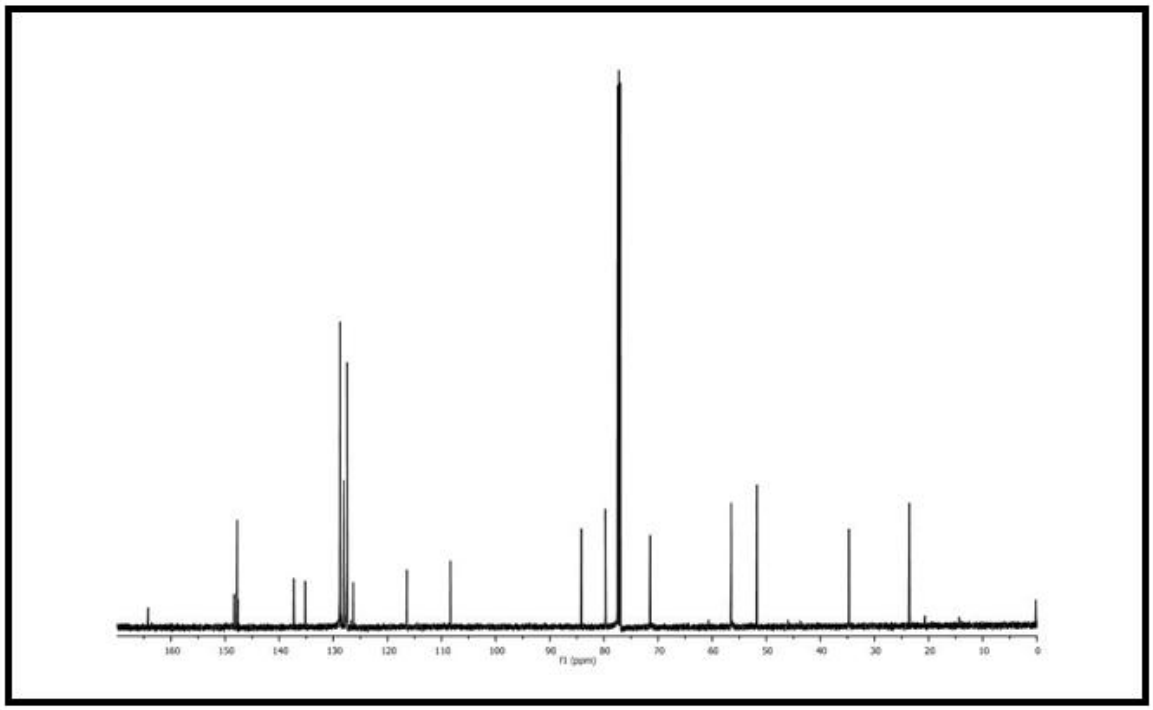
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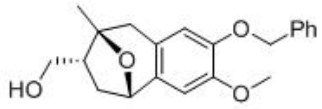
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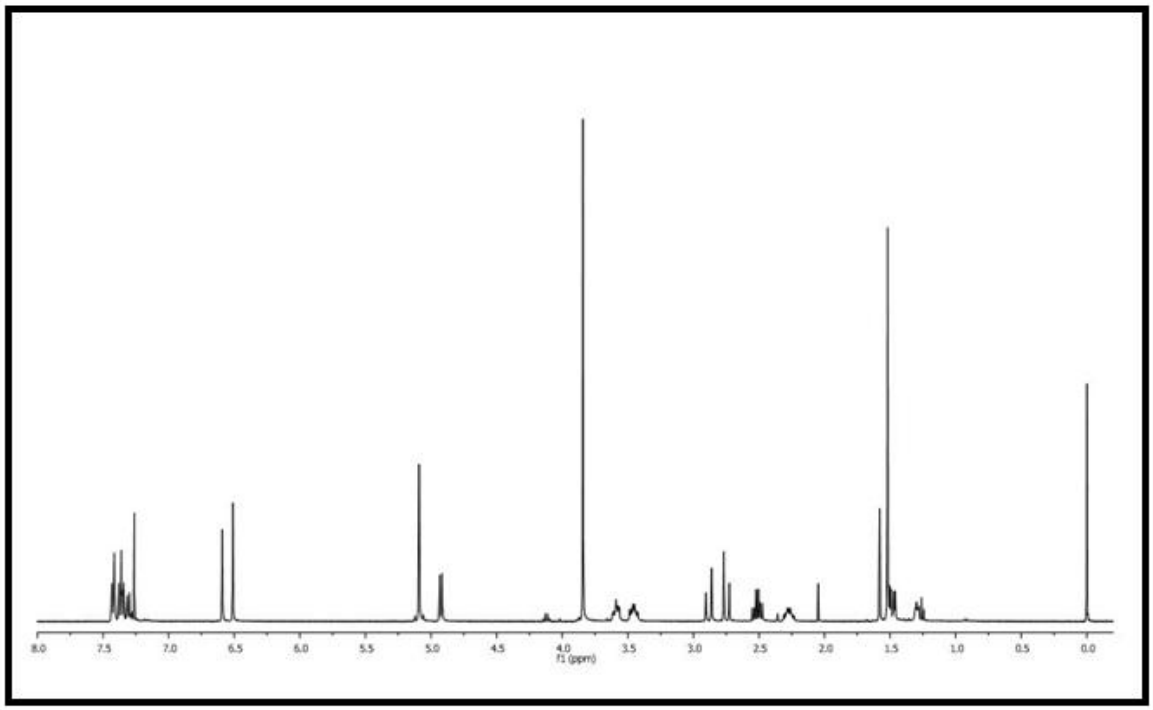
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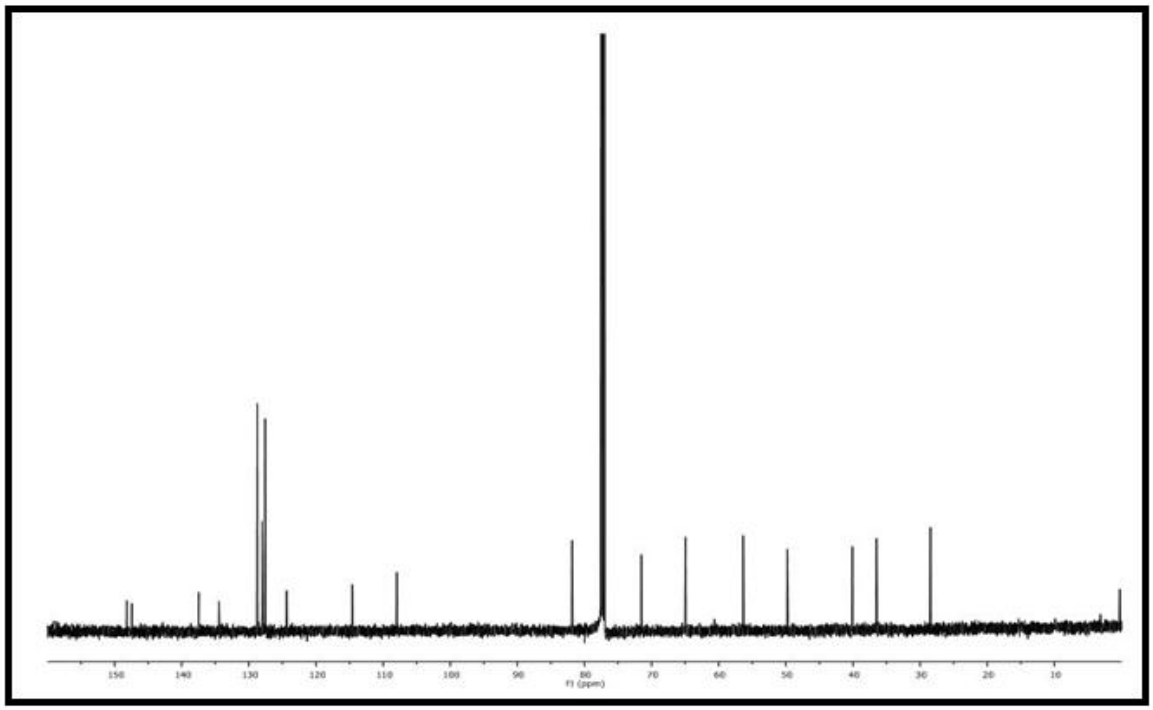
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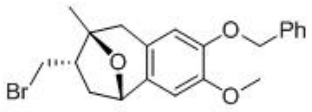
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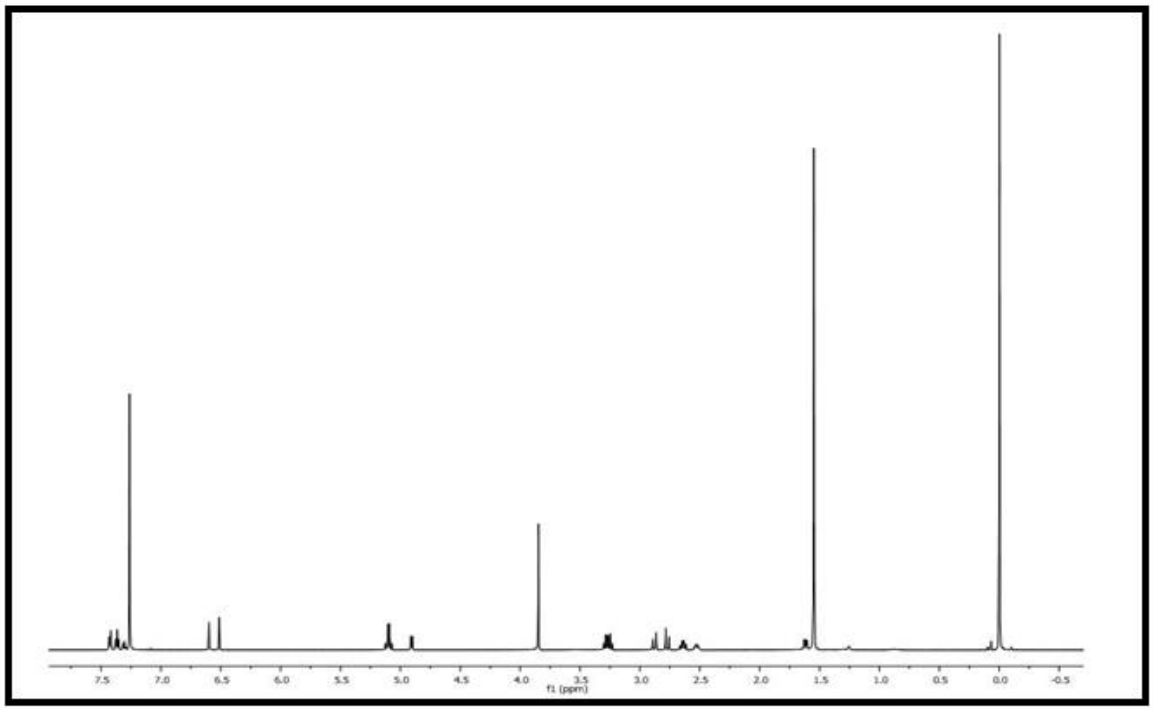
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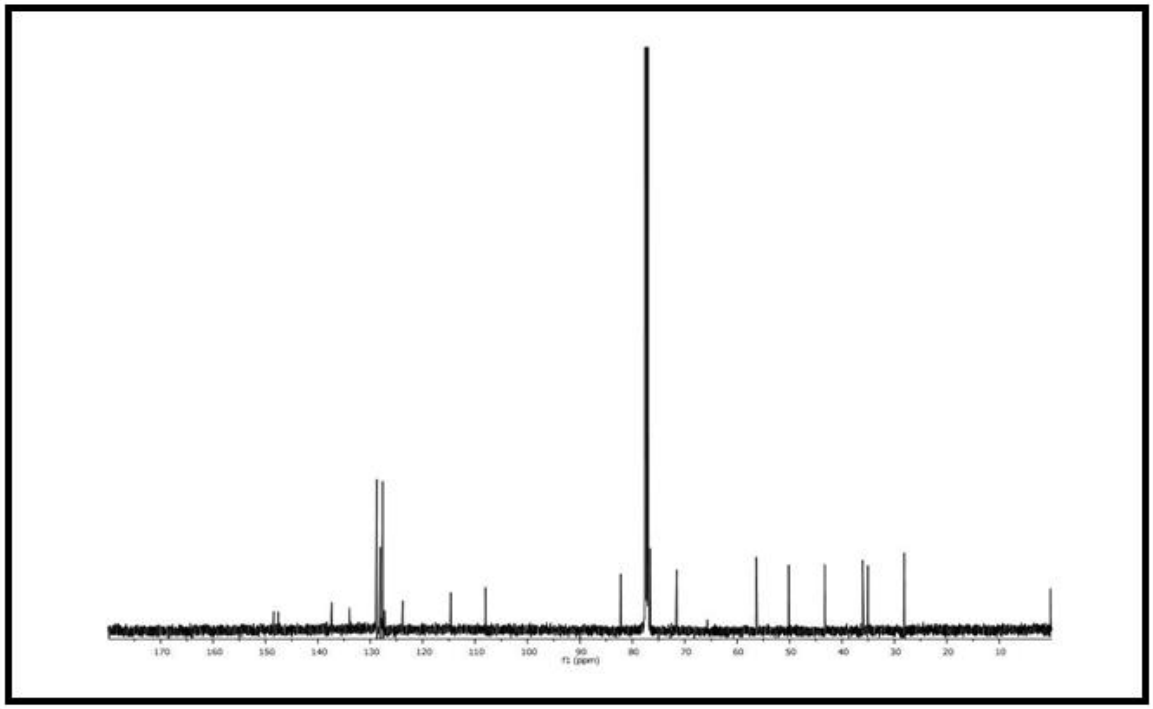
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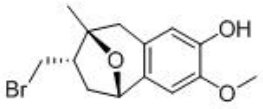
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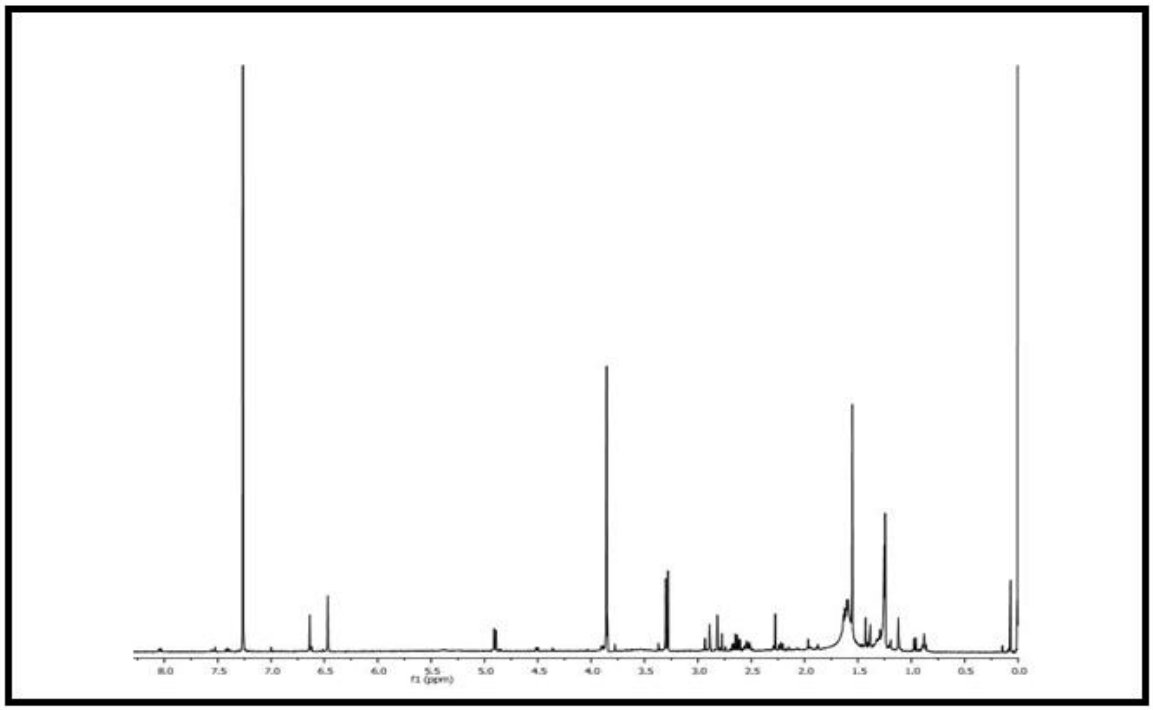
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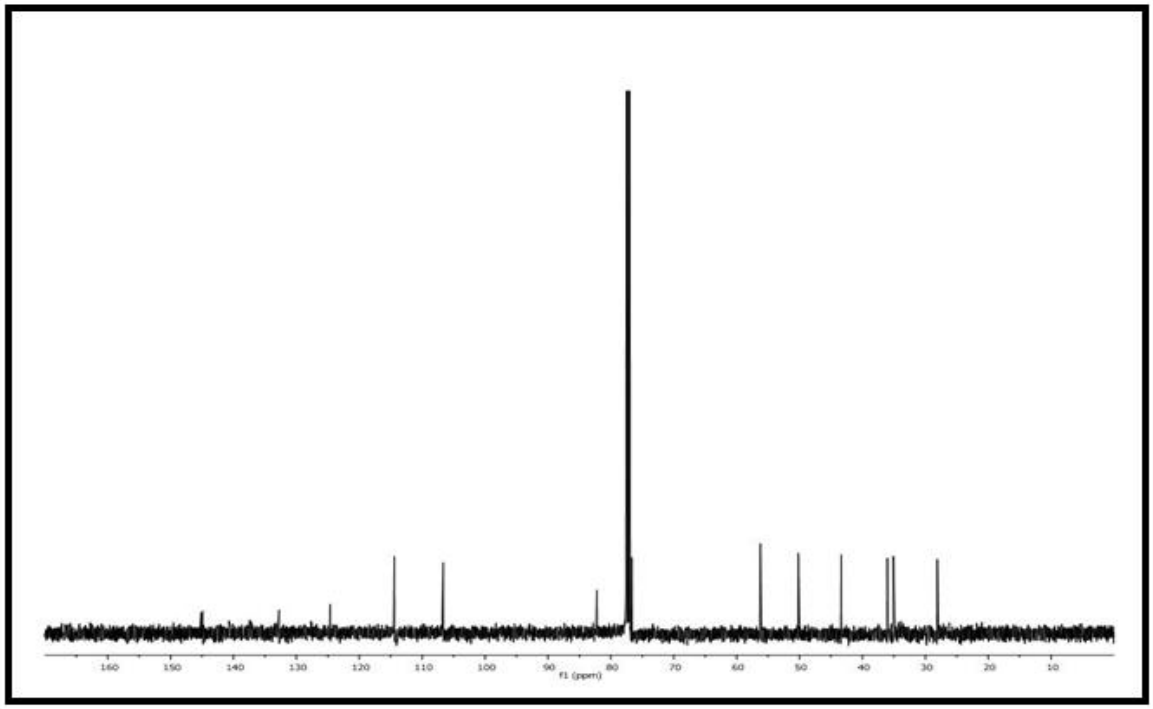
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80
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60
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20
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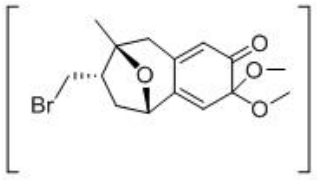
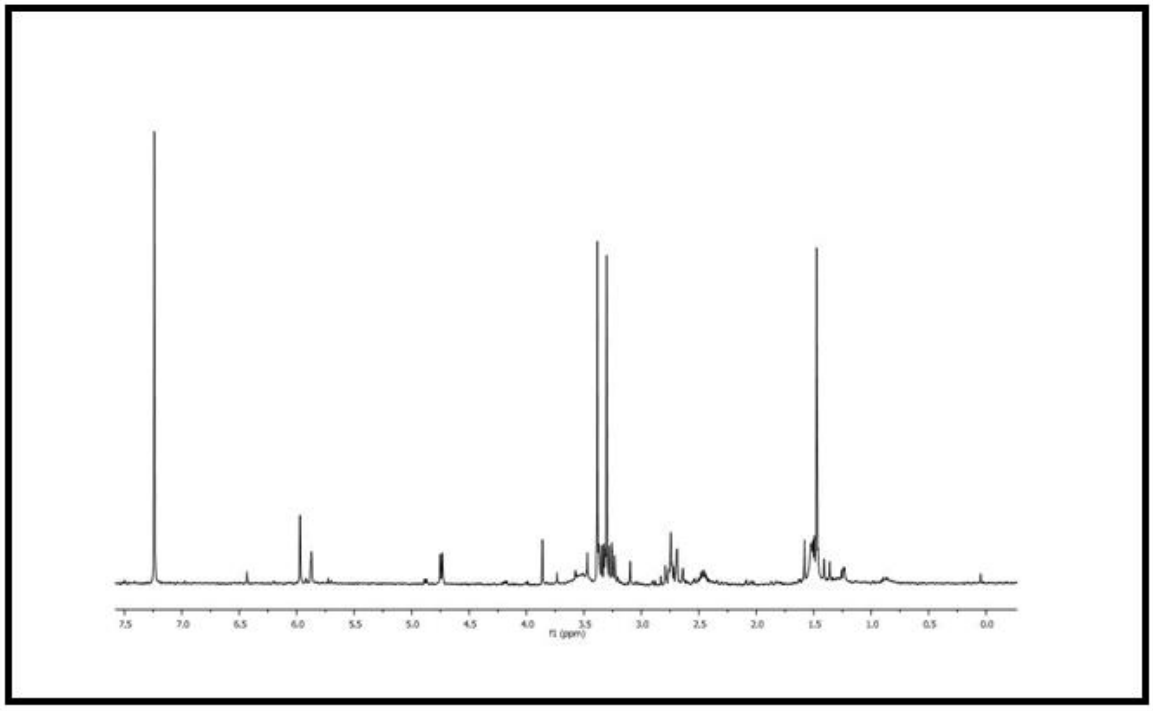
f1 (ppm)


Br
O
O
O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7.0
6.5
6.0
5.5
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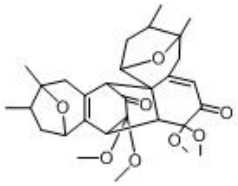
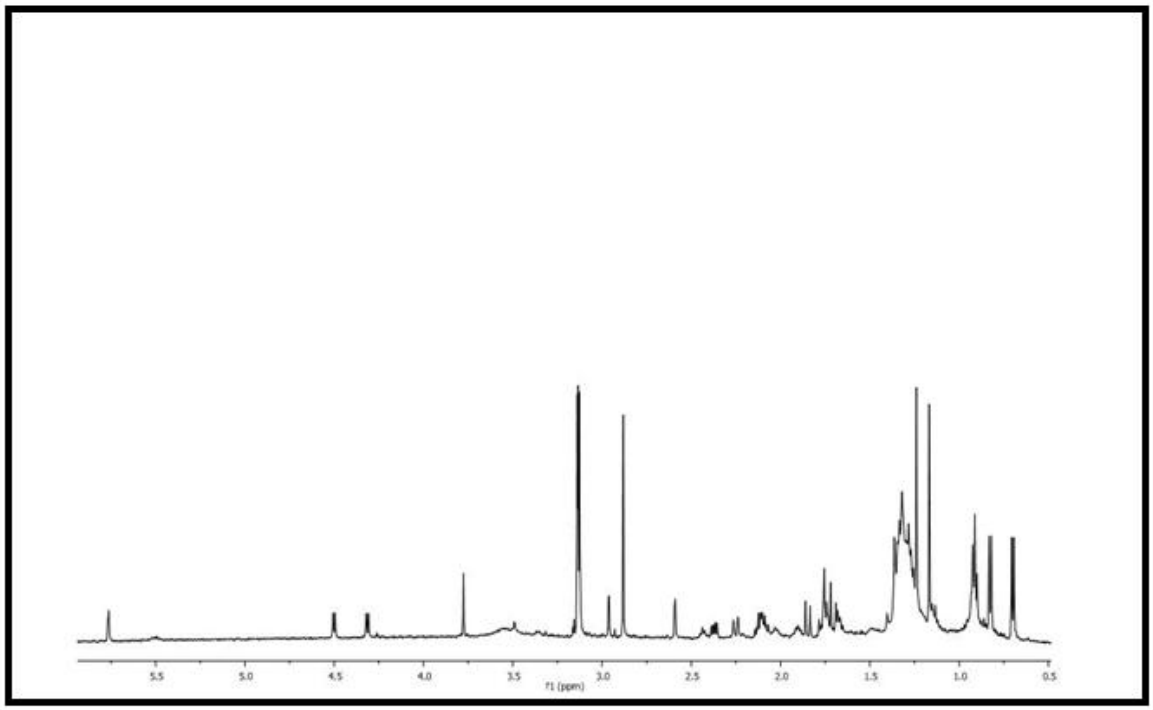
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

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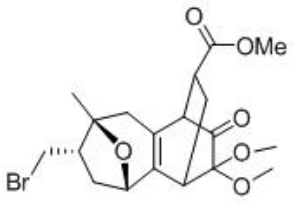
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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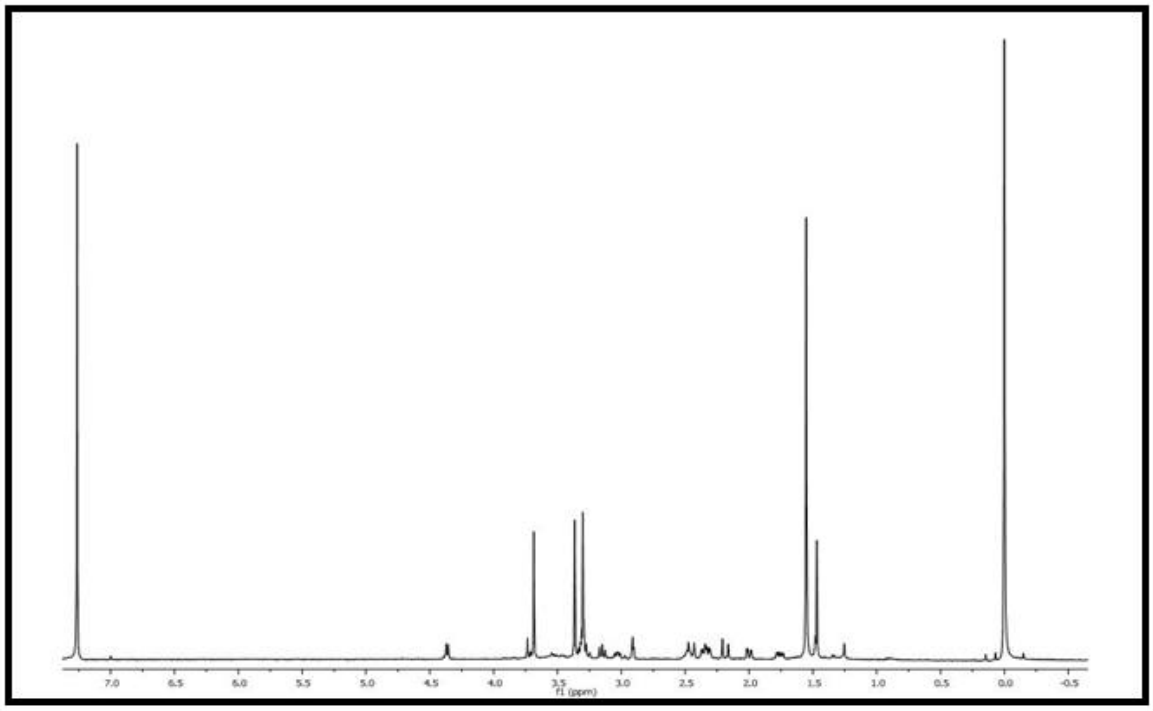
OMe
O
O
O
Br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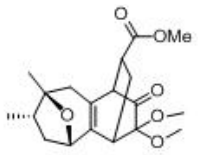
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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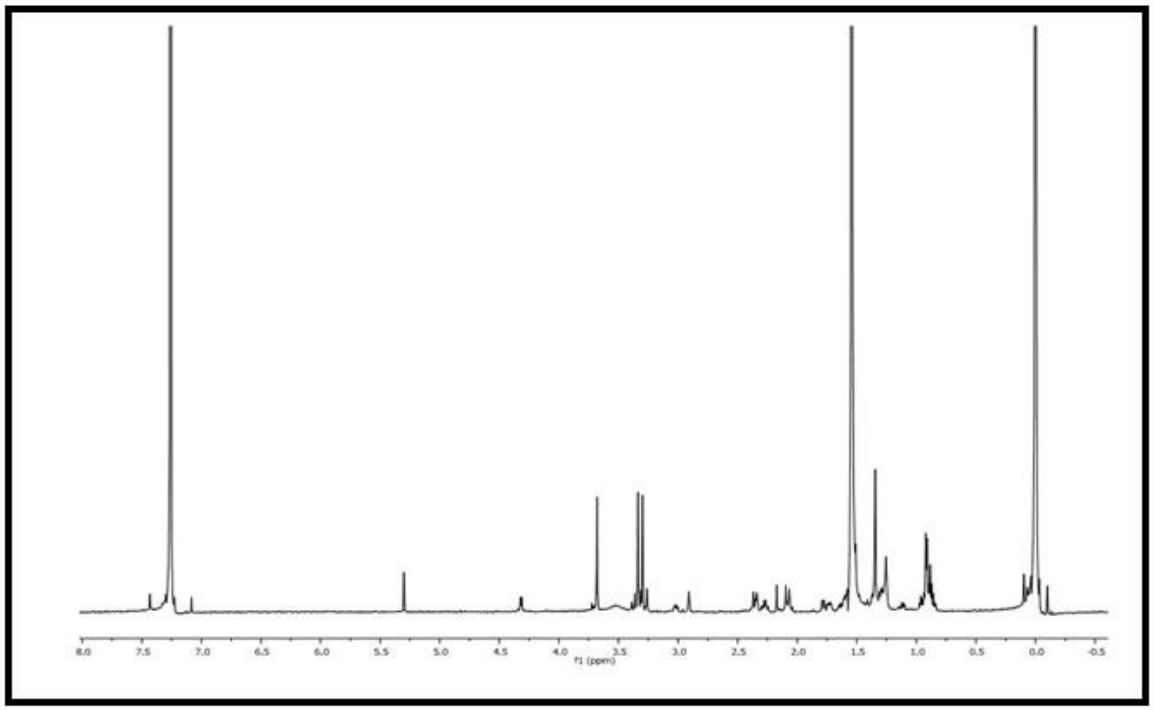
O
O
O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5.0
4.5
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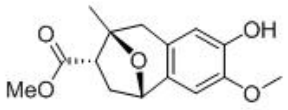
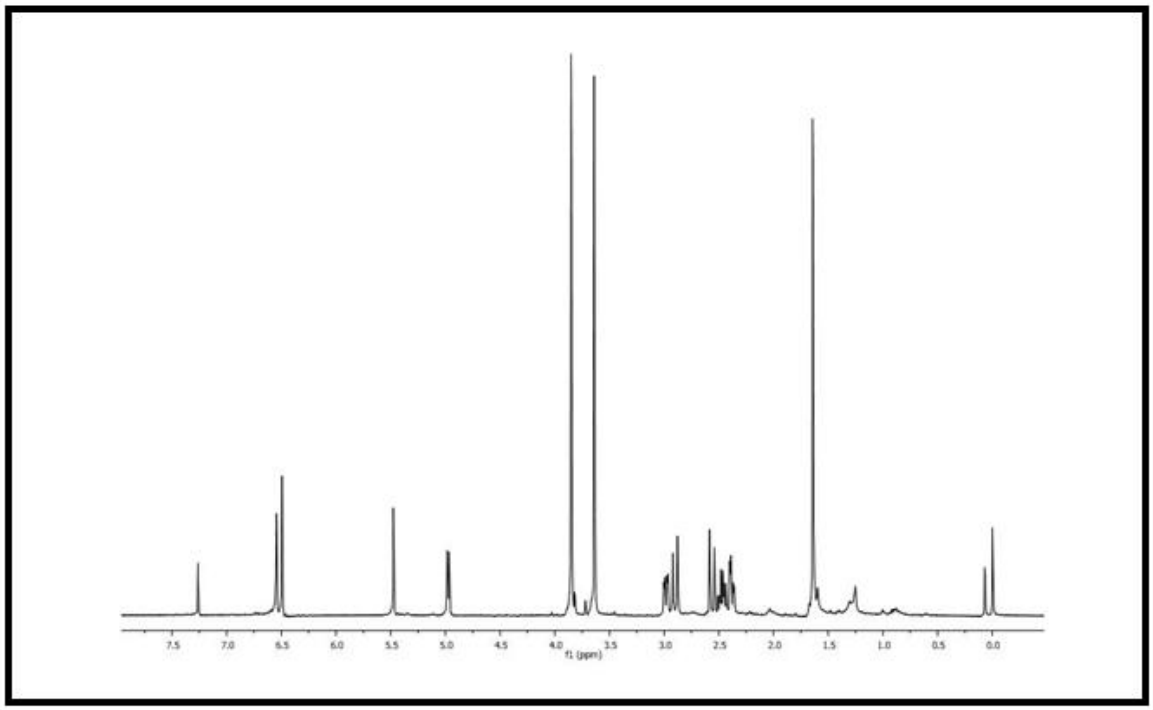
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


O
MeO
O
OH
O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2.0
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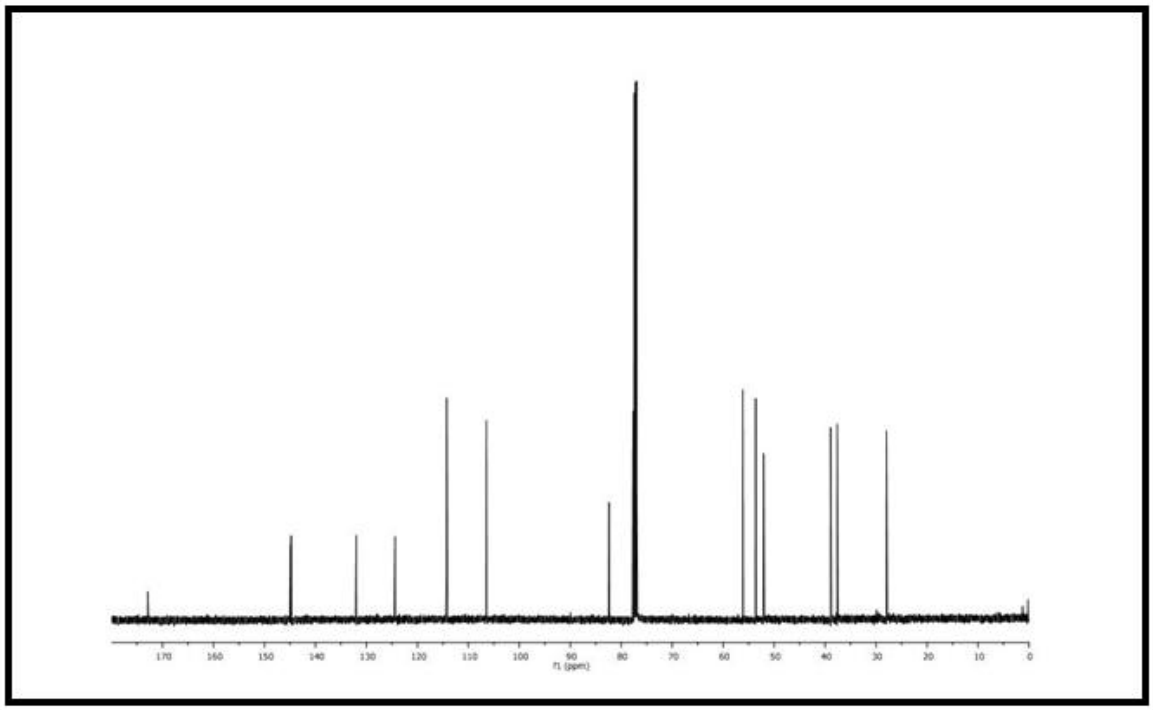
0.0
f1 (ppm)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90
80
70
60
50
40
30
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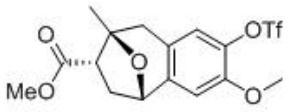
10
0
f1 (ppm)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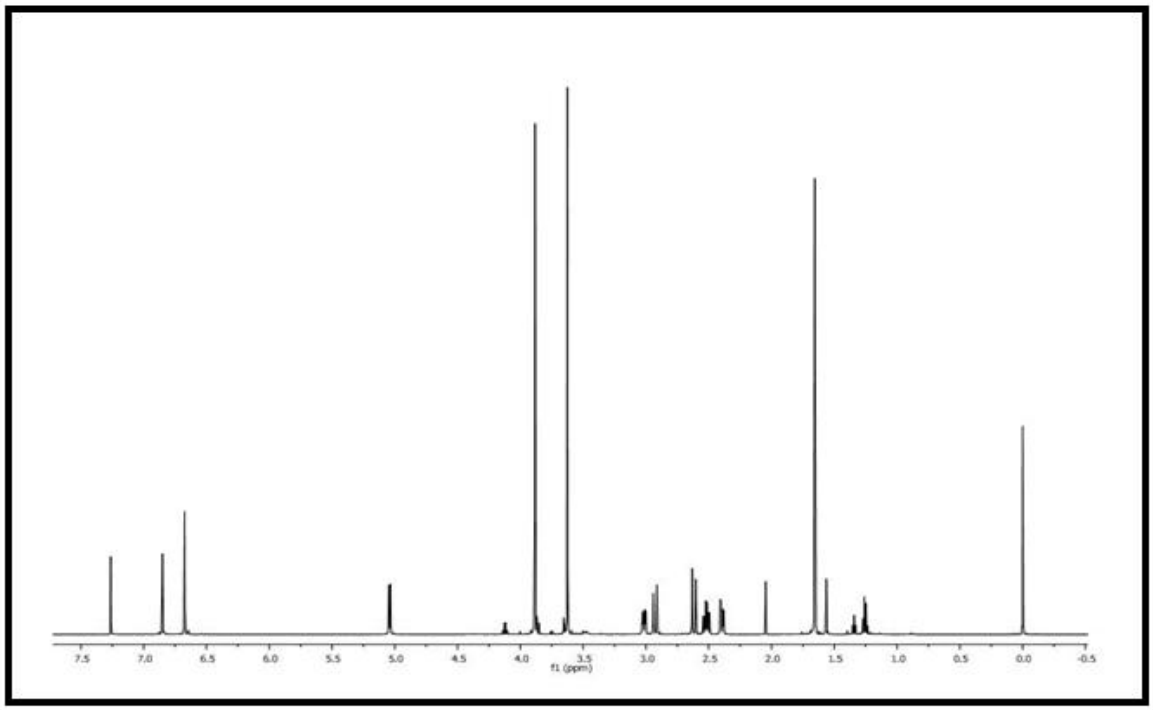
MeO
O
OTf
O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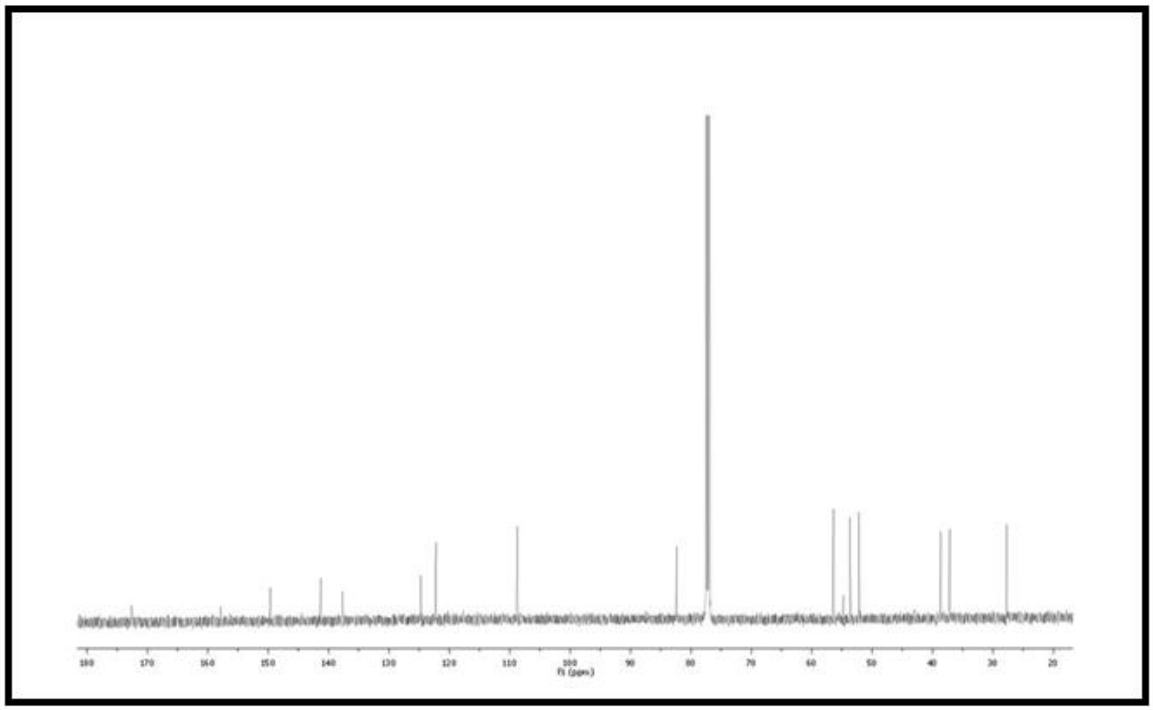
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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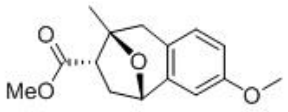
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)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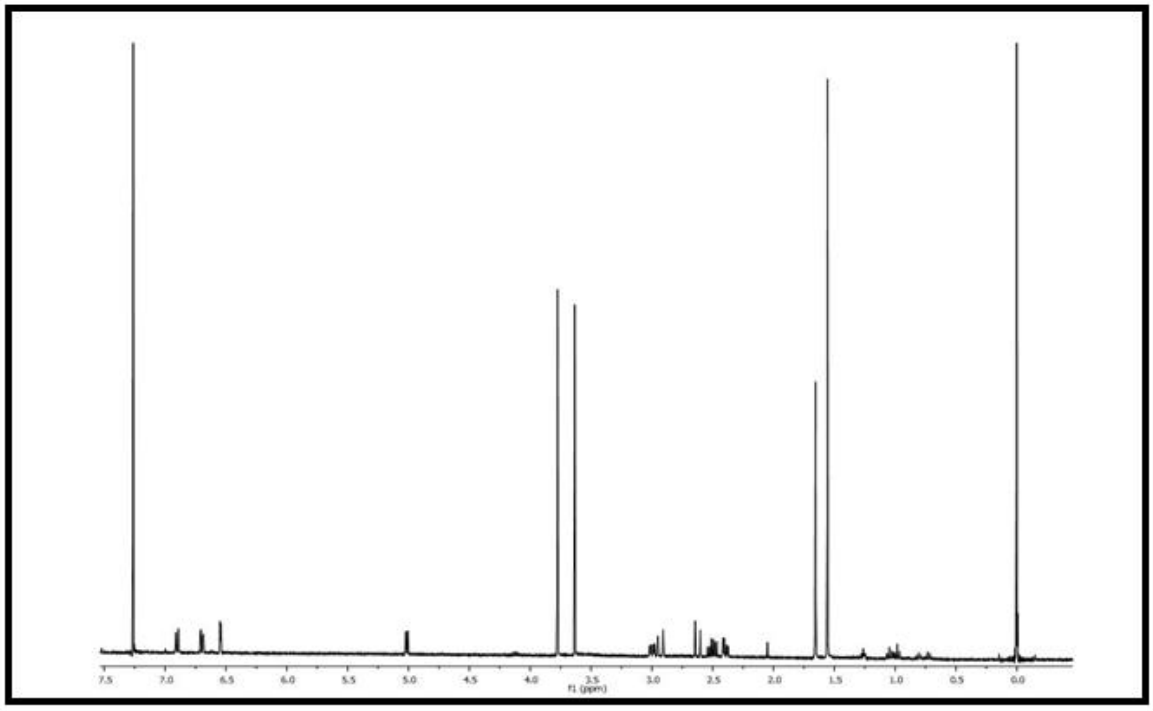
MeO
O
O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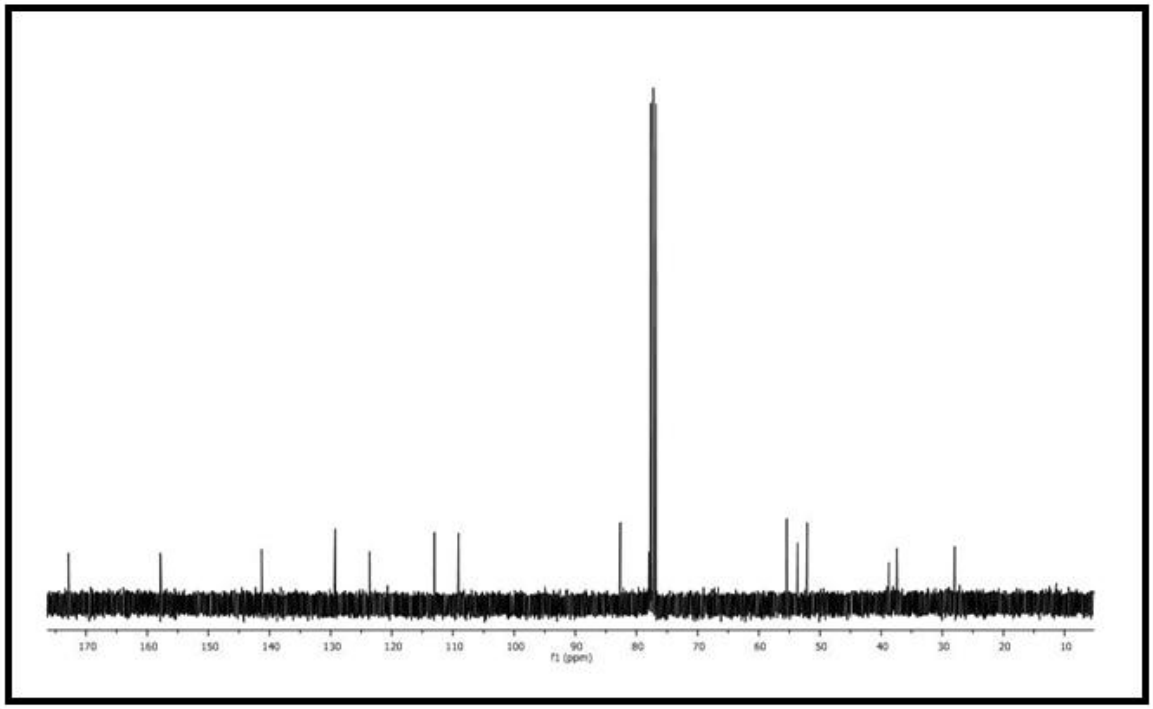
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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50
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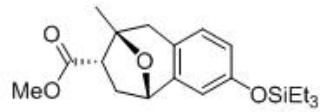
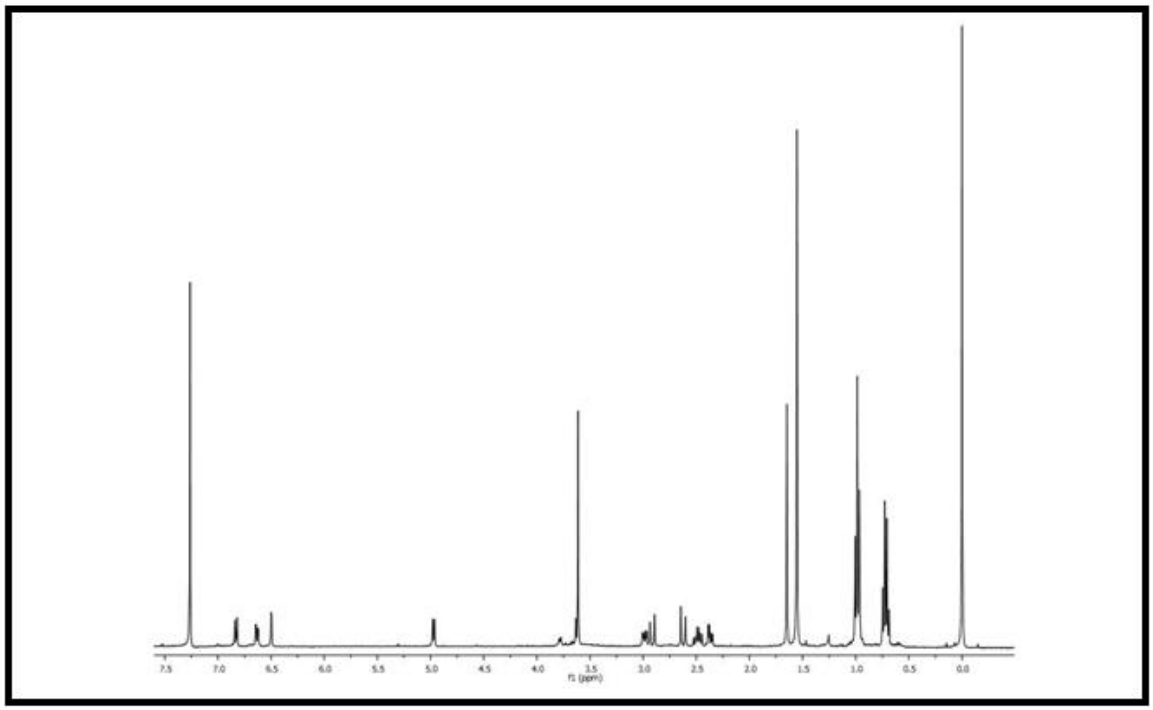
f1 (ppm)


O
MeO
O
OSiEt3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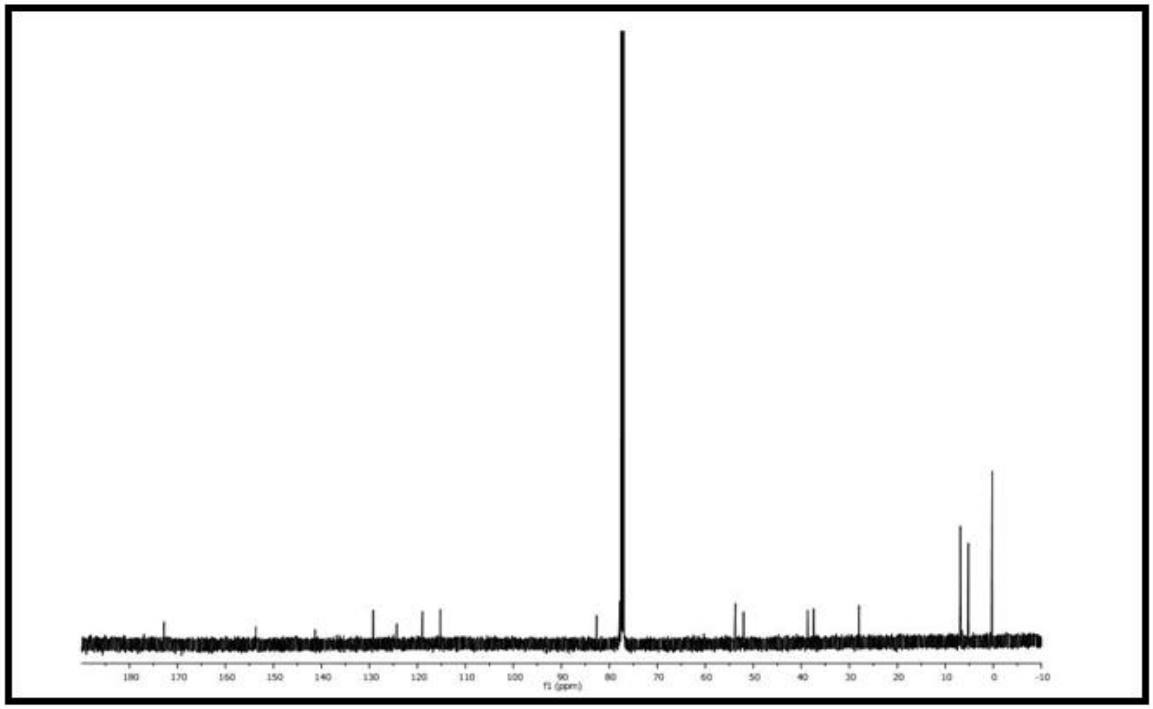
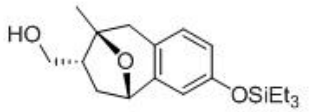
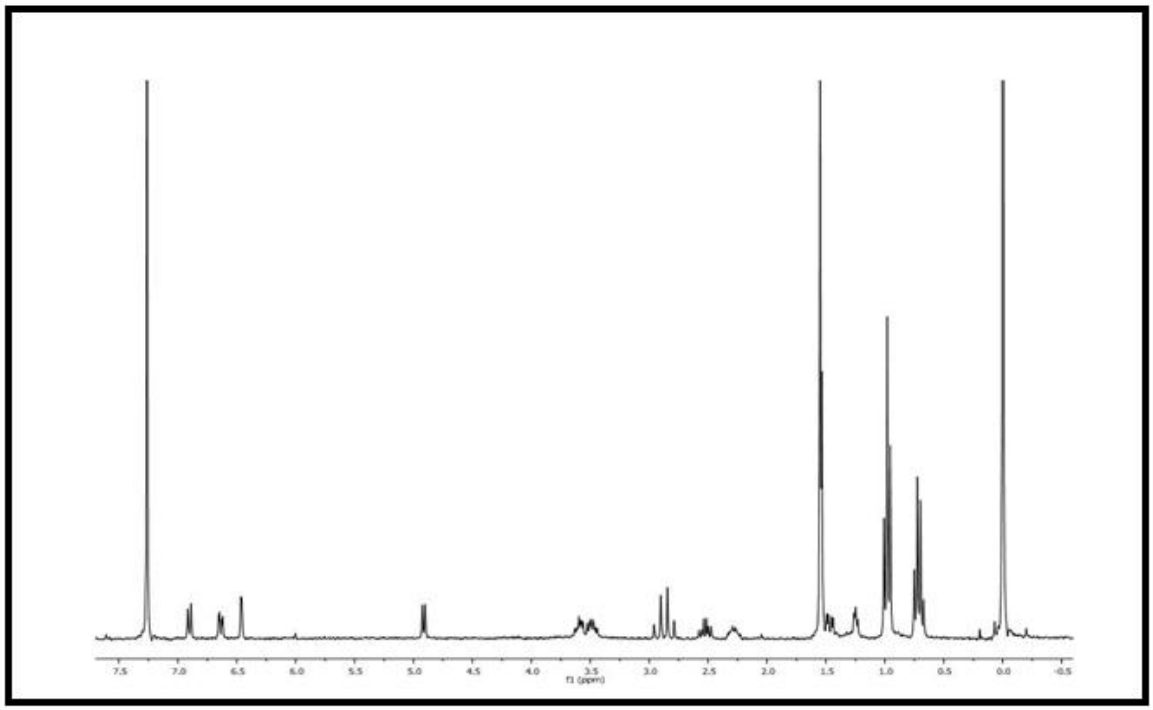
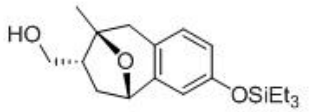
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
f1 (ppm)
3.0
2.5
2.0
1.5
1.0
0.5
0.0


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


HO
O
OSiEt3


7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


HO
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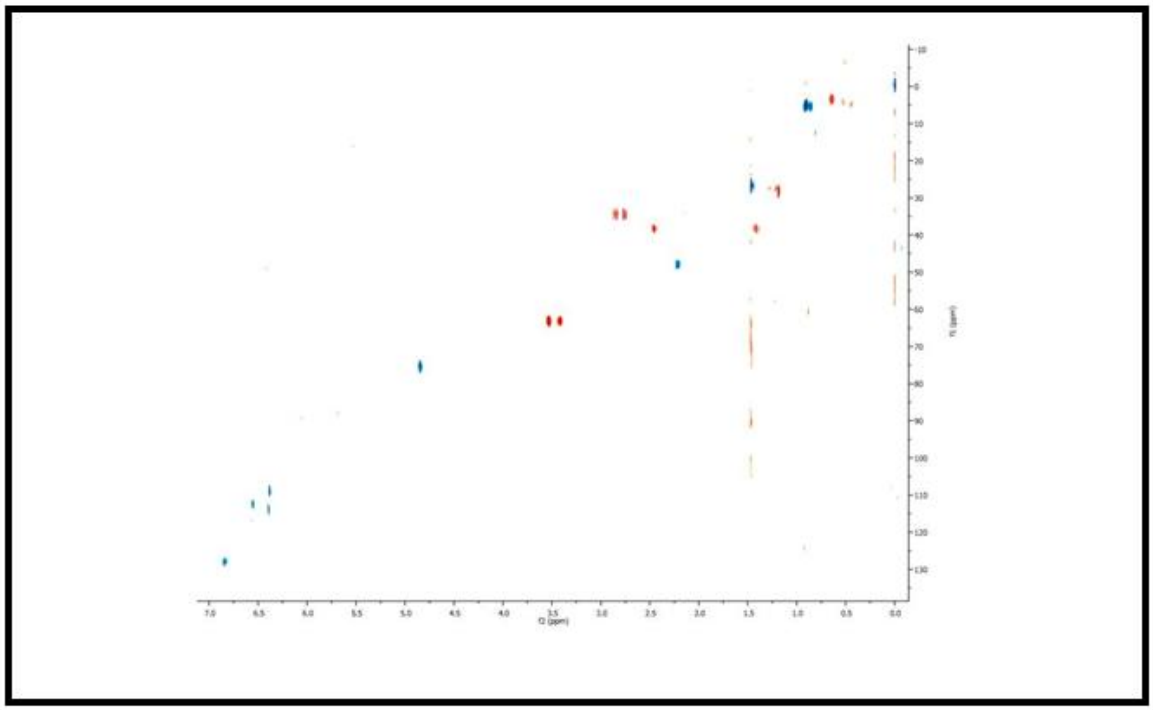
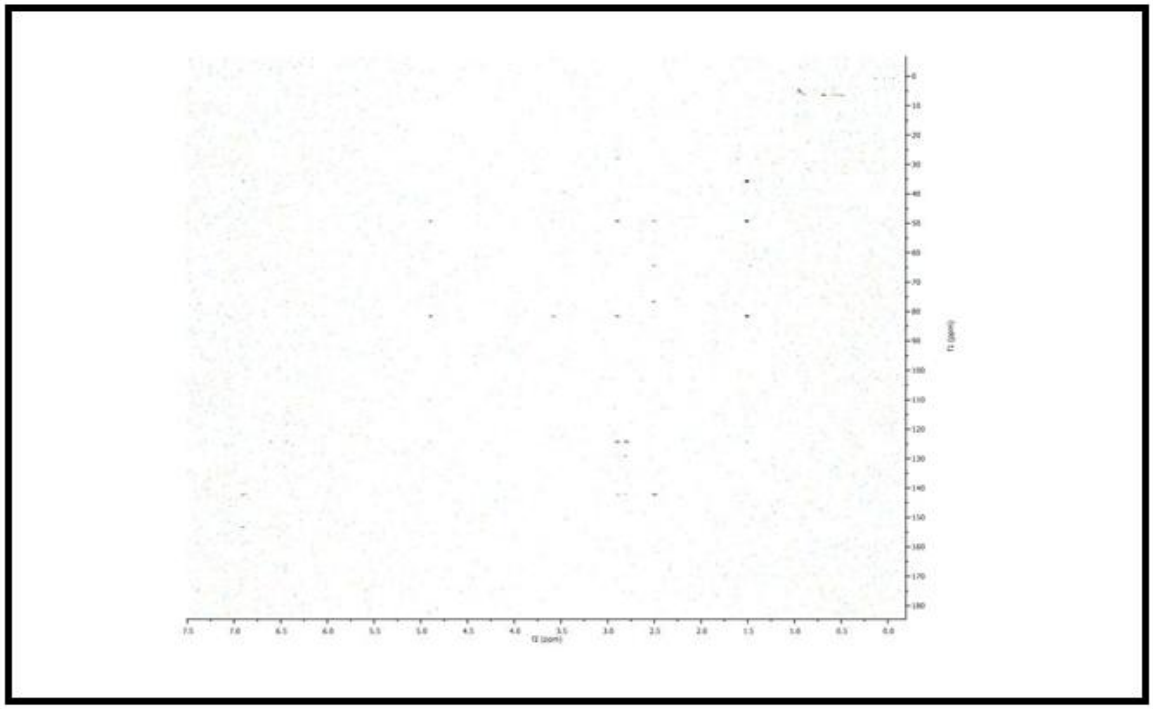
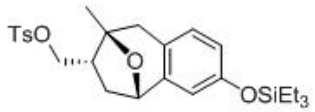
OSiEt3






TsO
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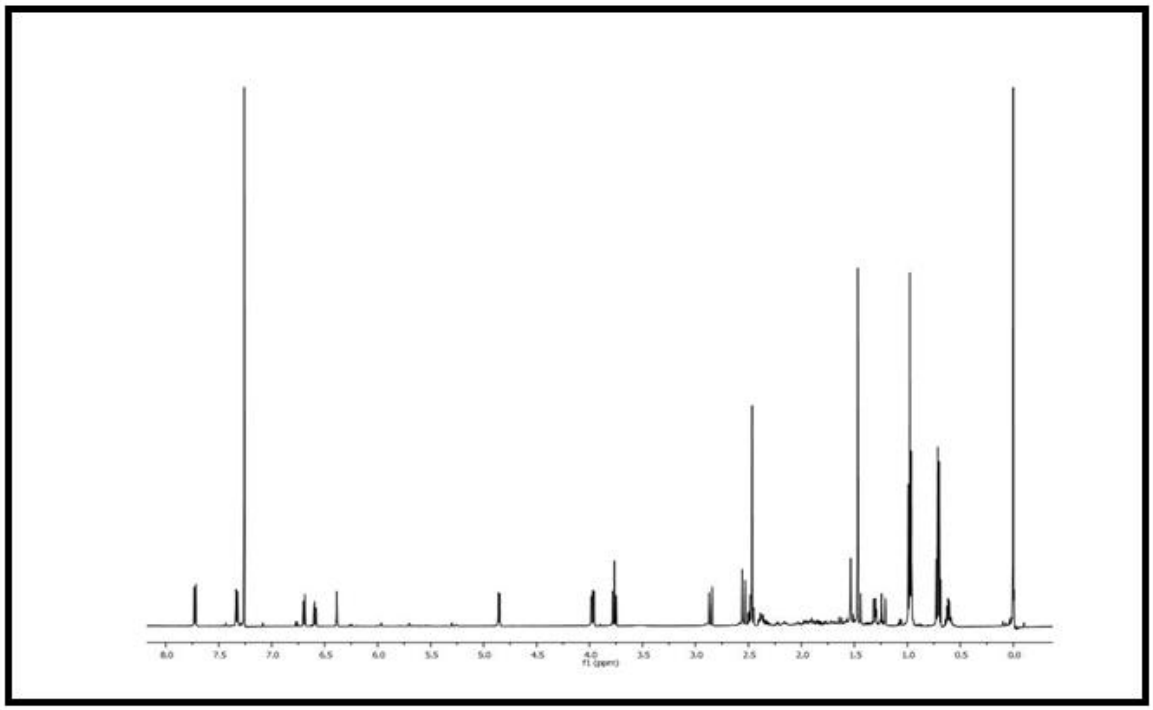
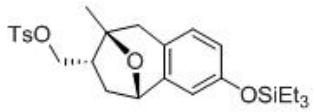
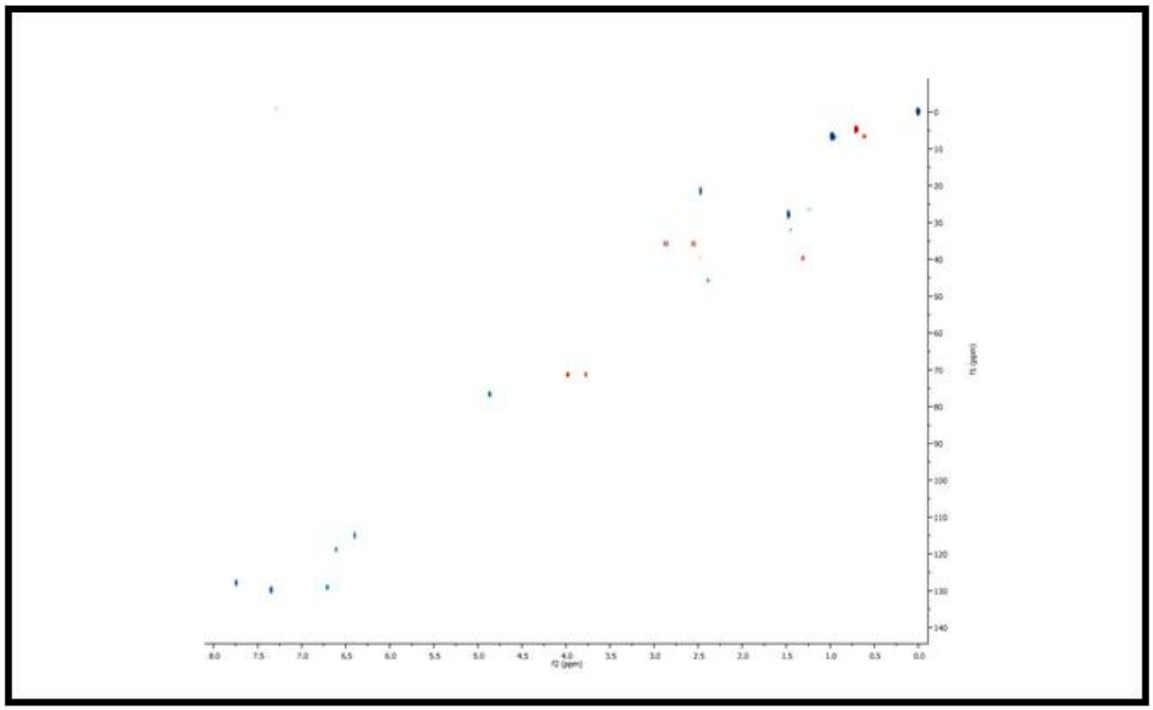
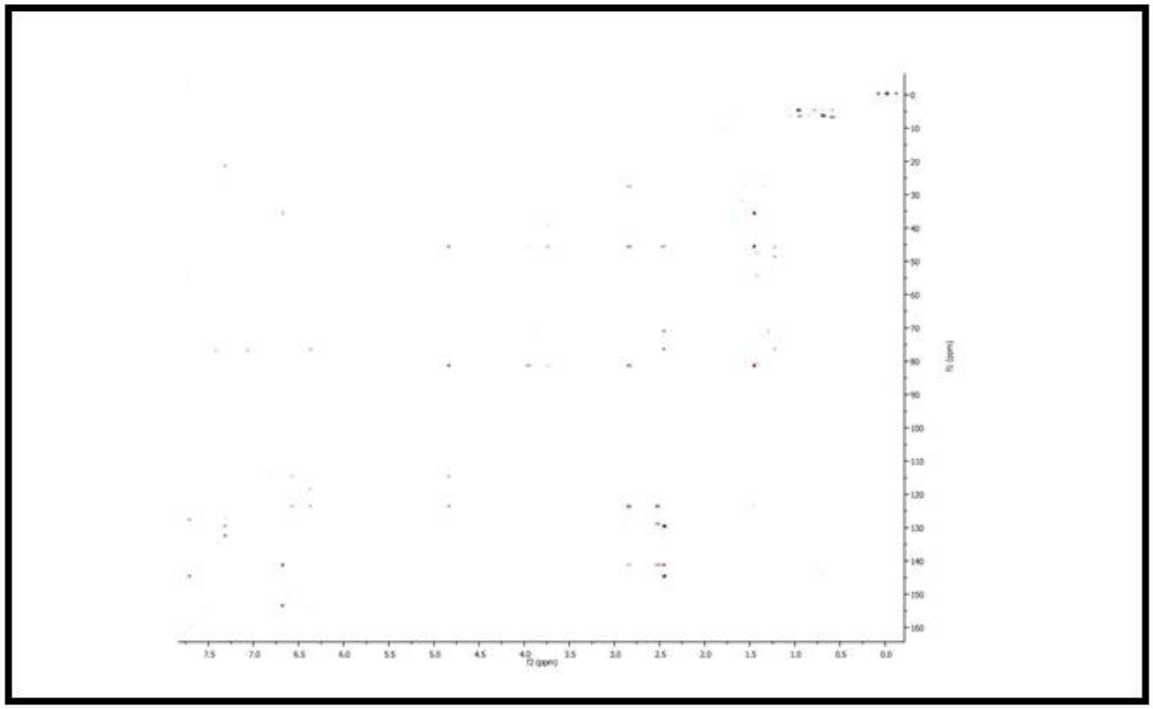
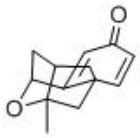
OSiEt3

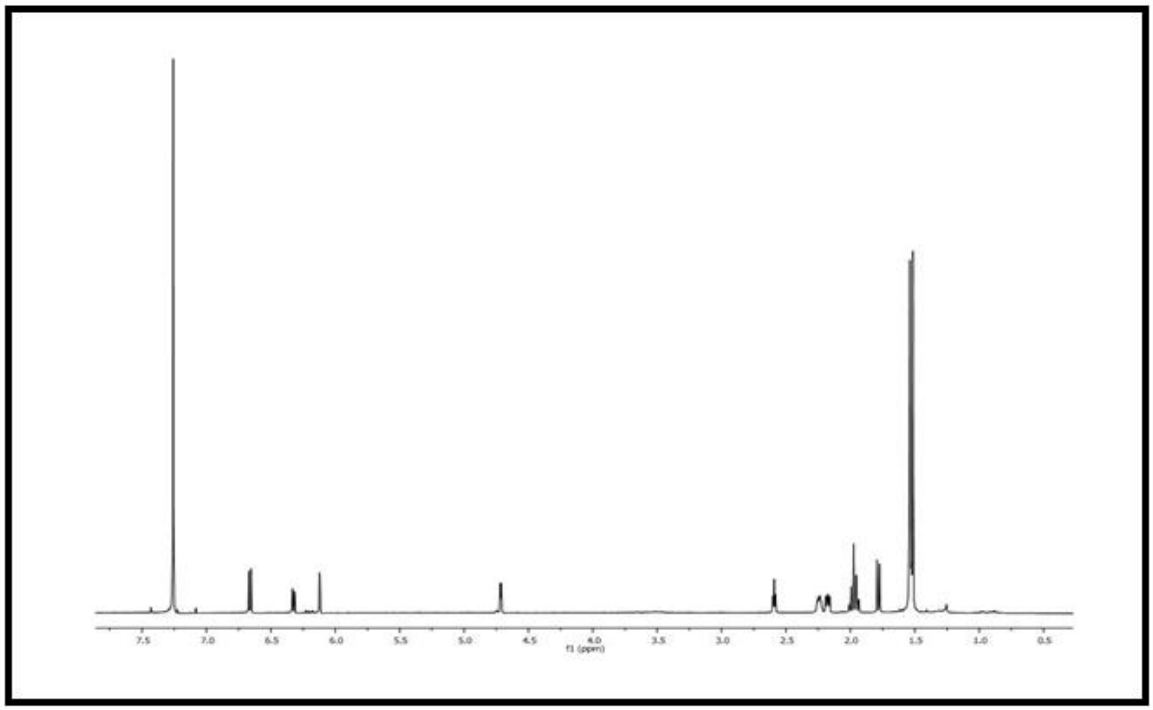


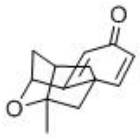

TsO
O
OSiEt3

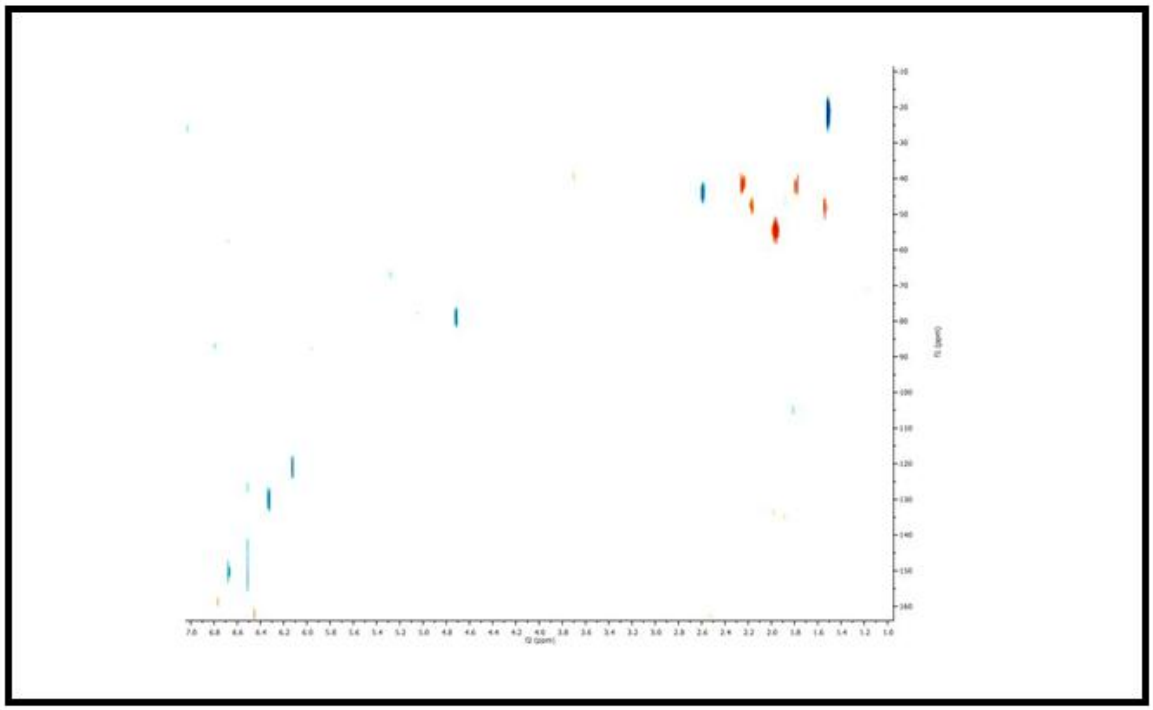


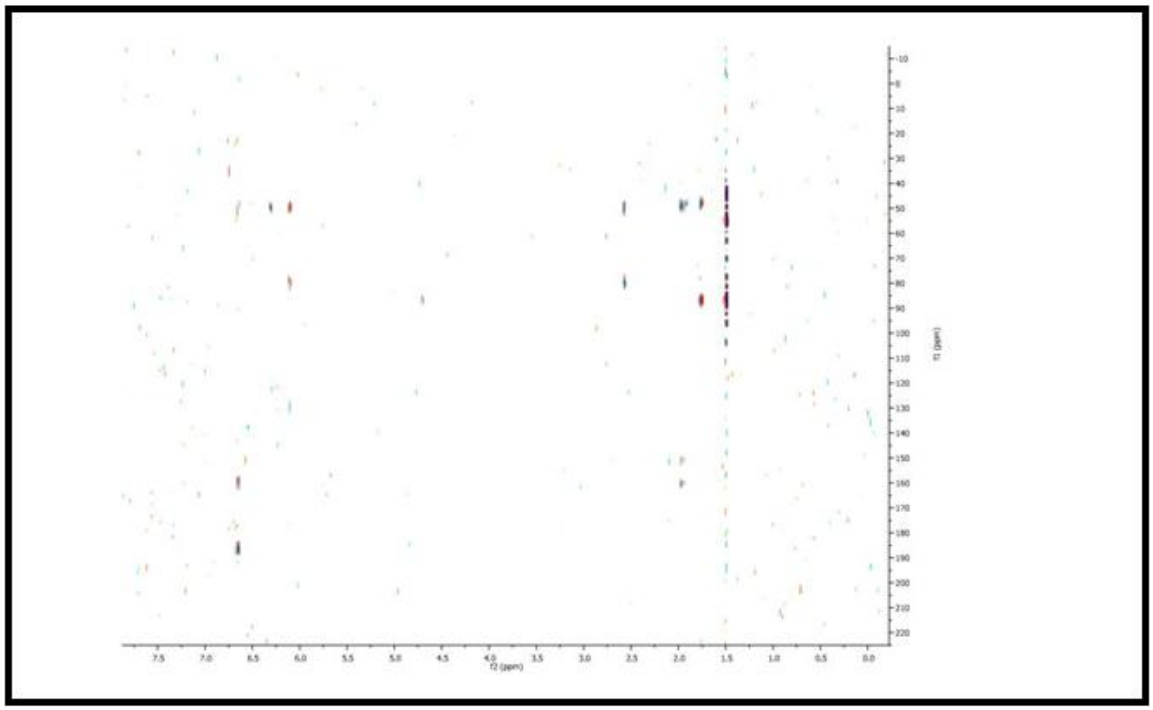


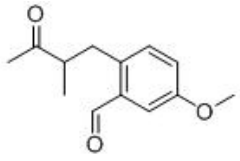


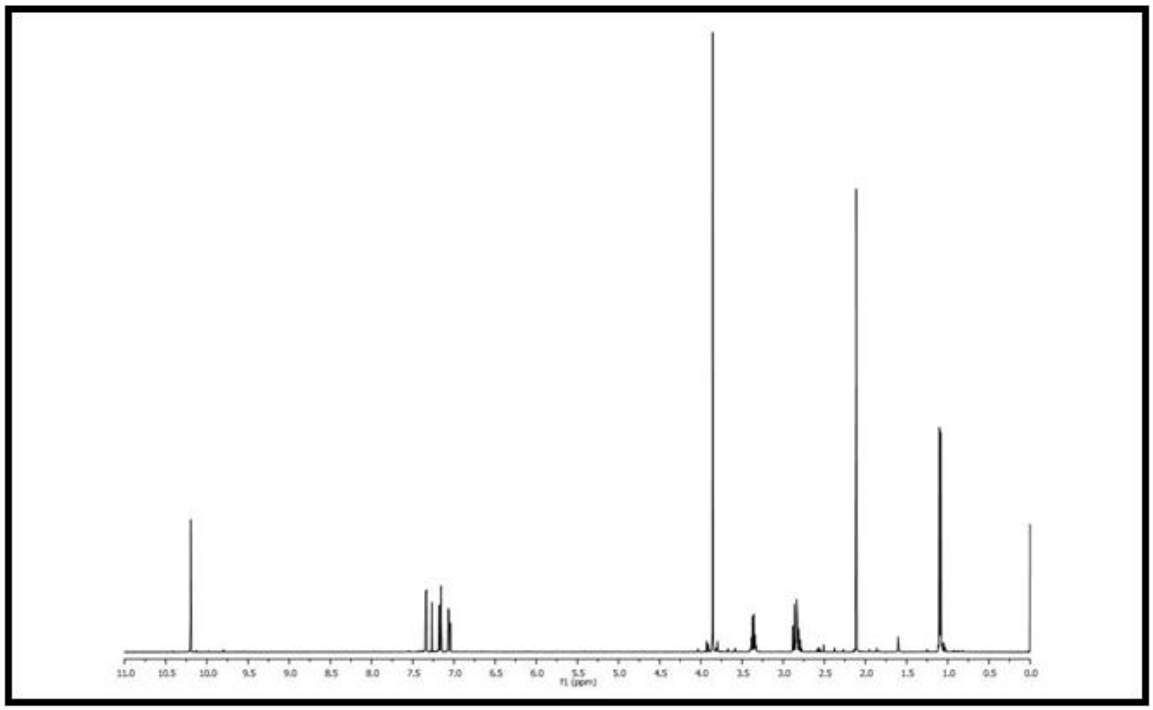

7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
f1 (ppm)
3.5
3.0
2.5
2.0
1.5
1.0
0.5

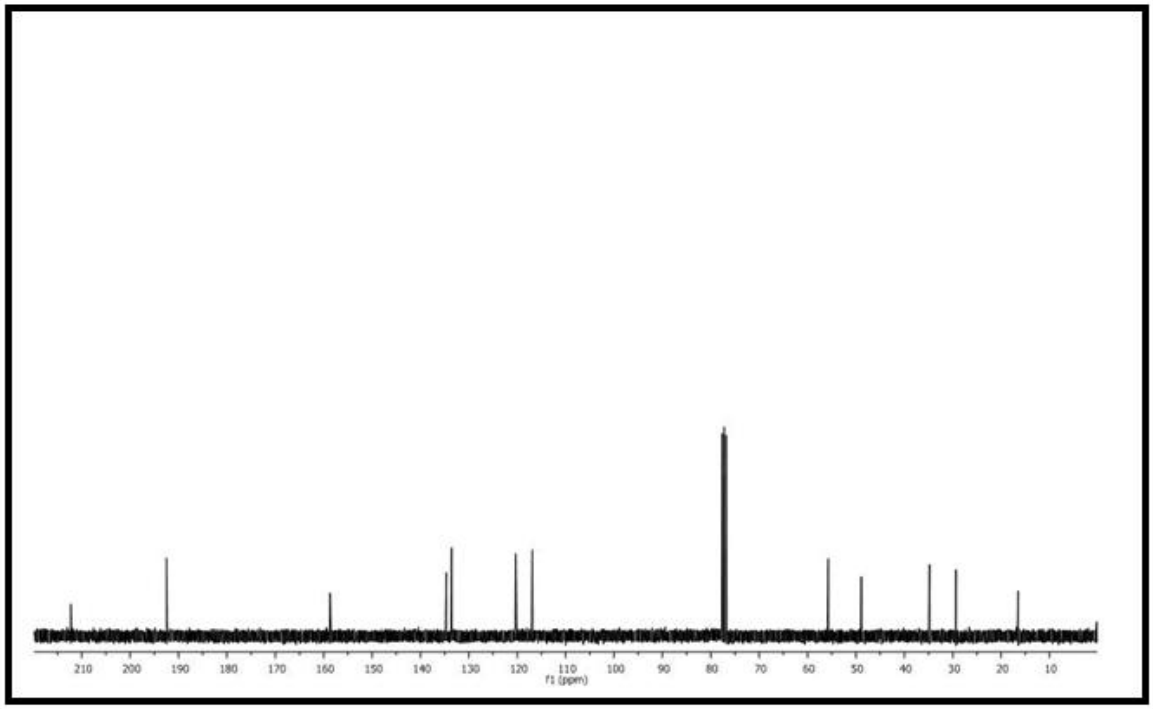


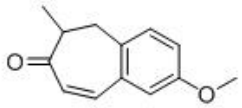


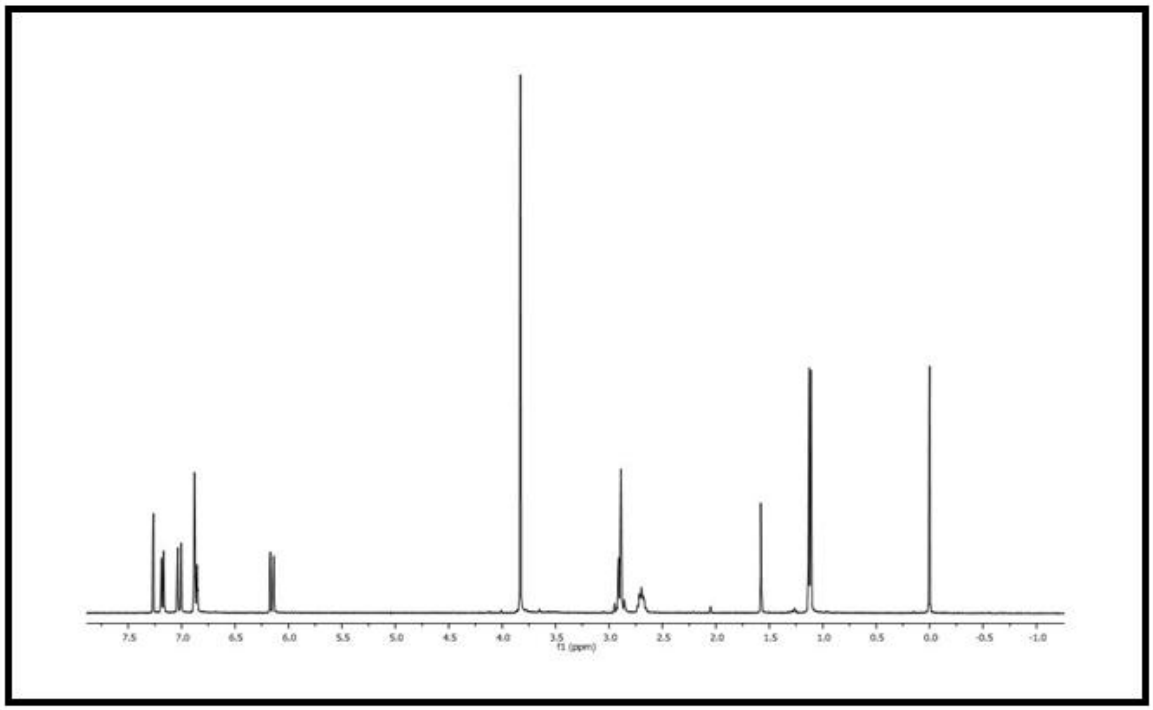


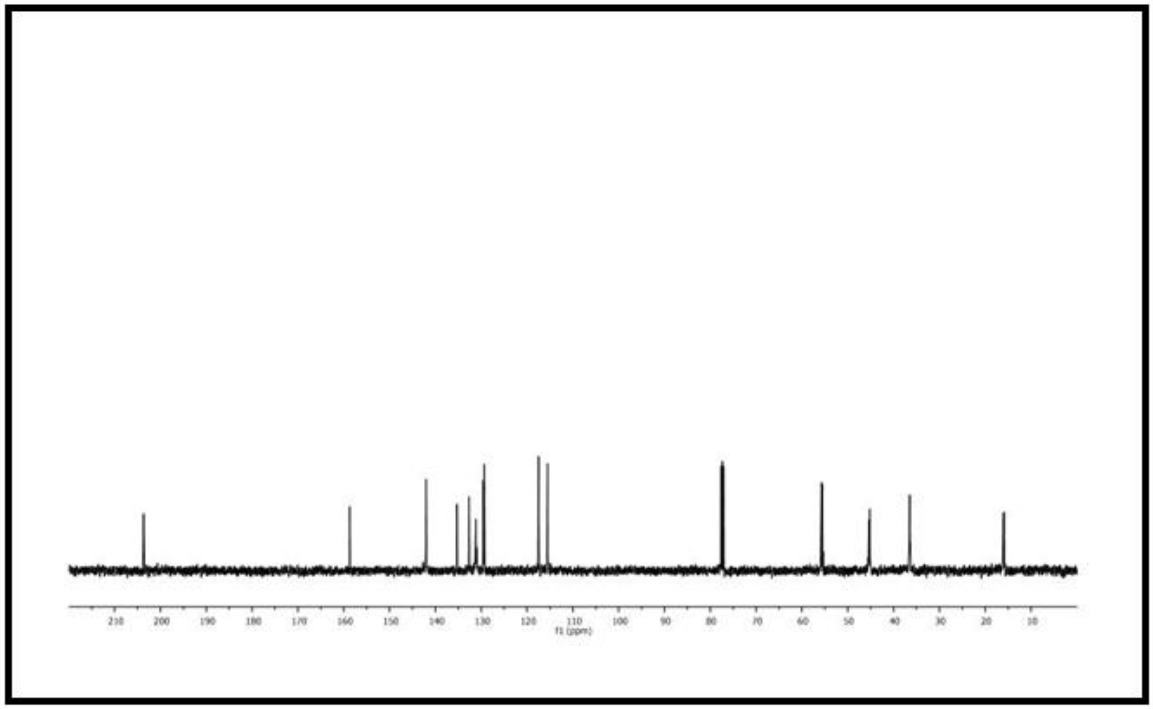



11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


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




7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


210
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100
90
80
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60
50
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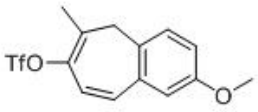
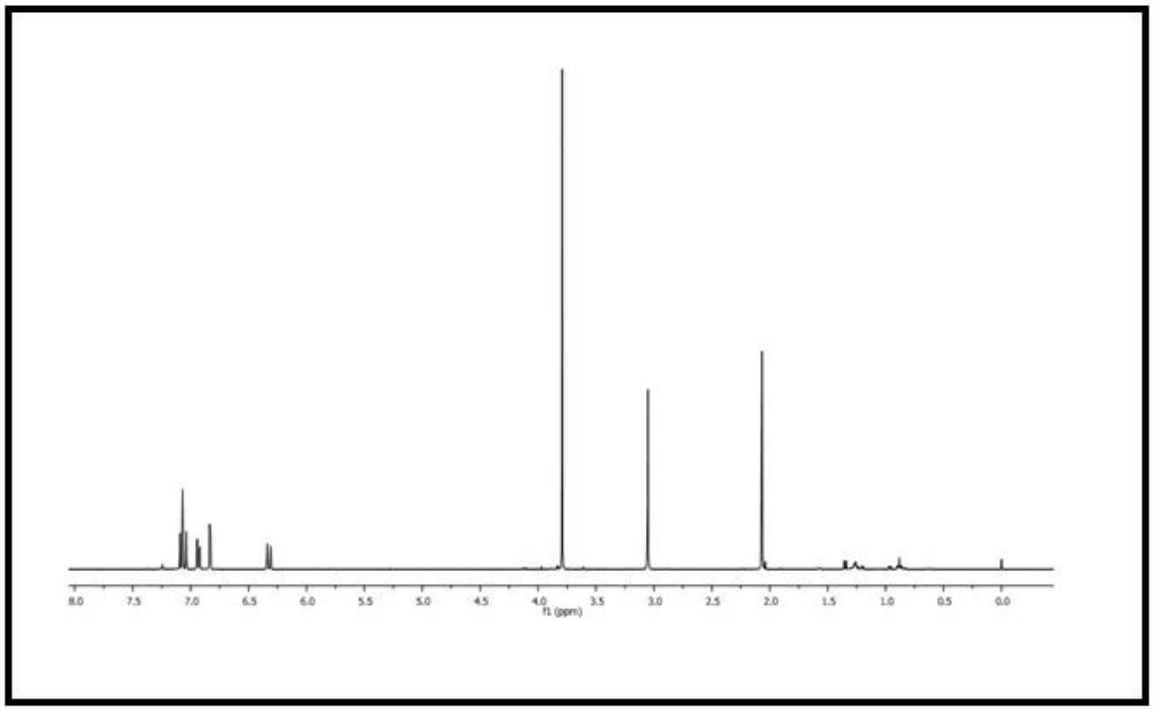
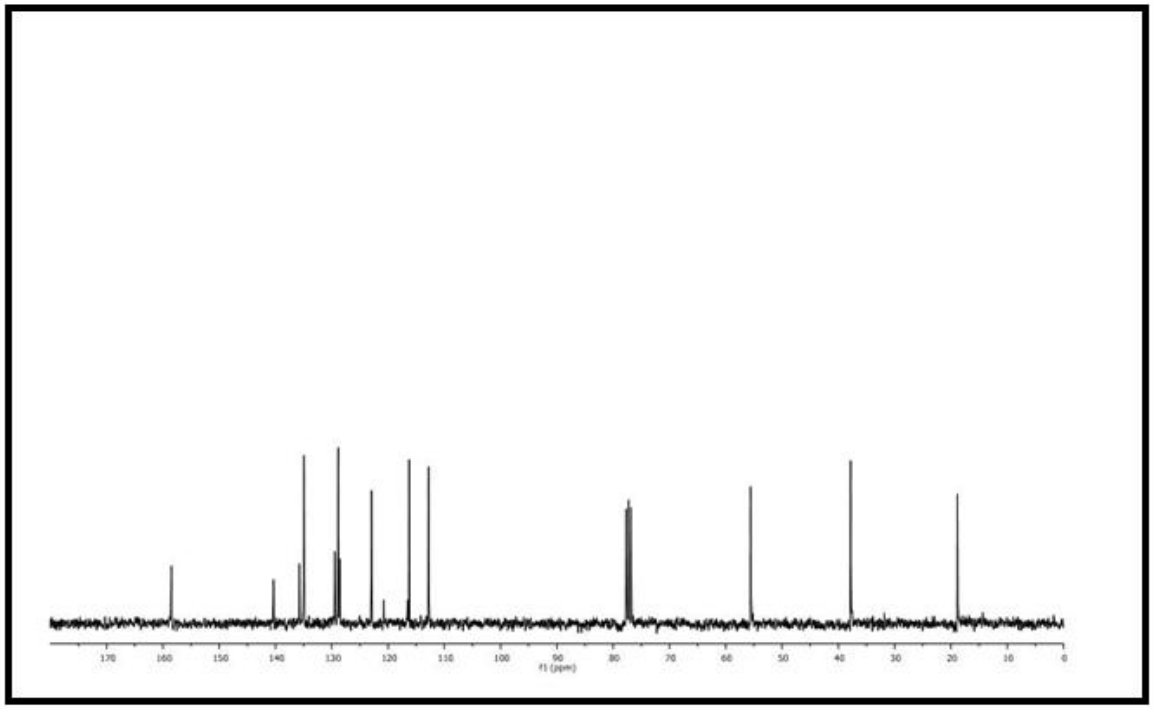
30
20
10
f1 (ppm)


TfO
O


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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120
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90
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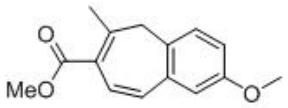
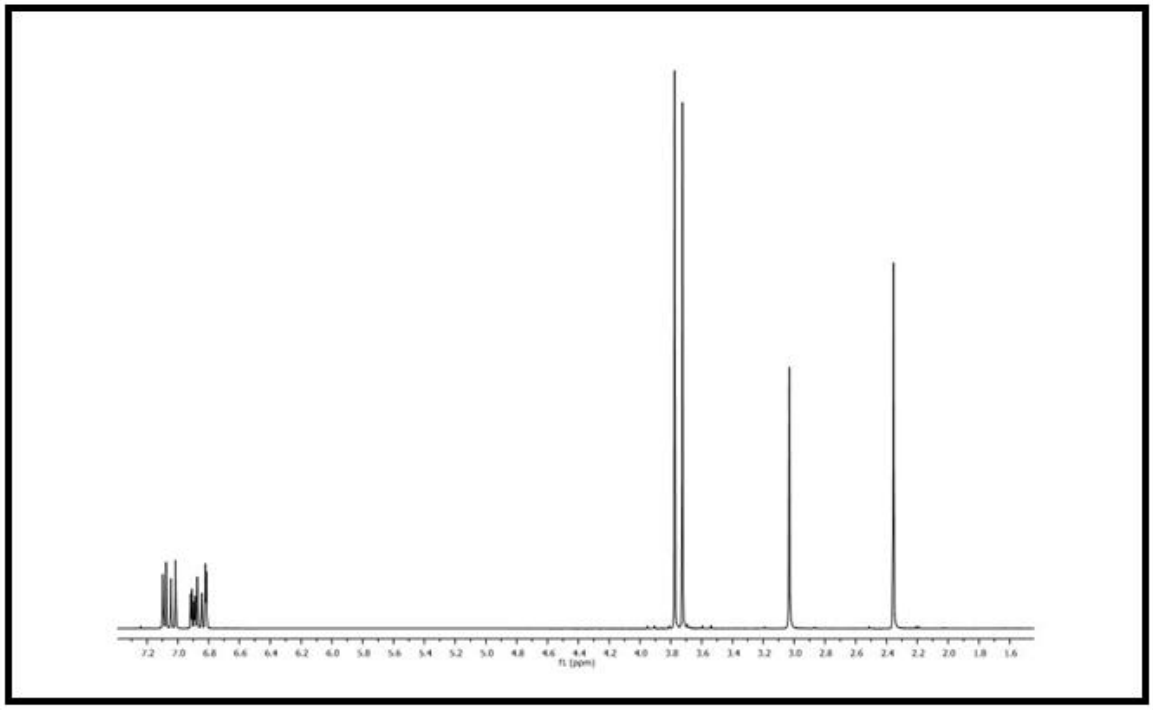
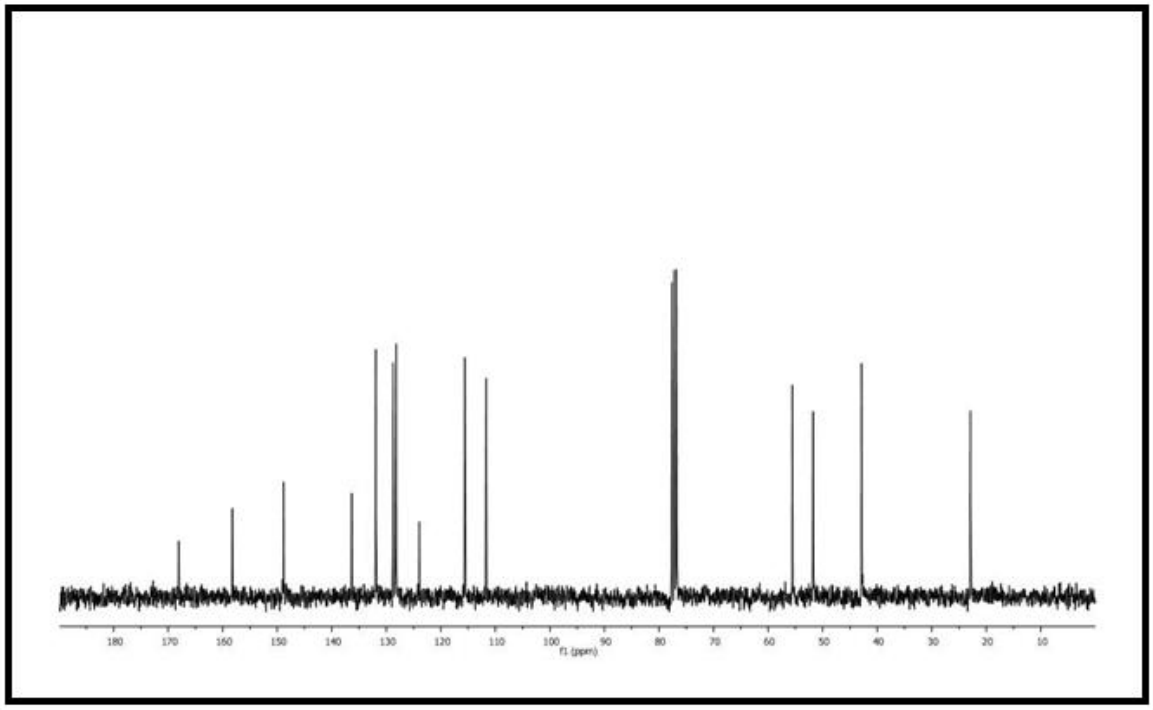
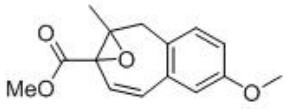
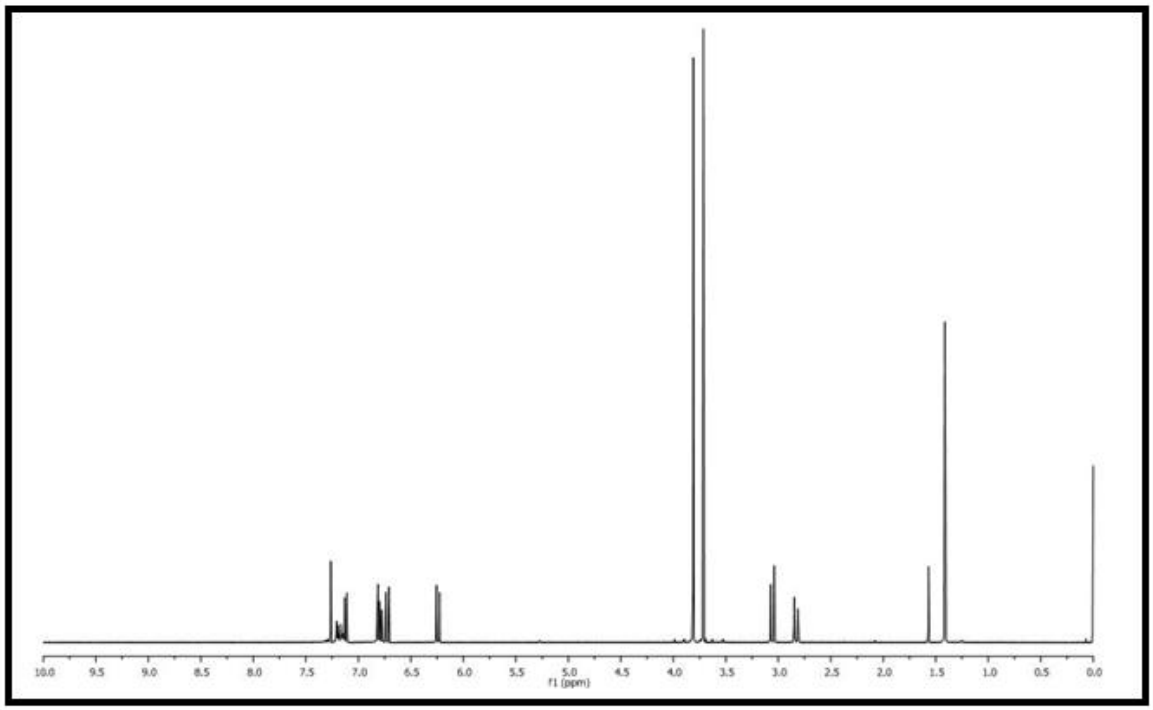
50
40
30
20
10
0
f1 (ppm)

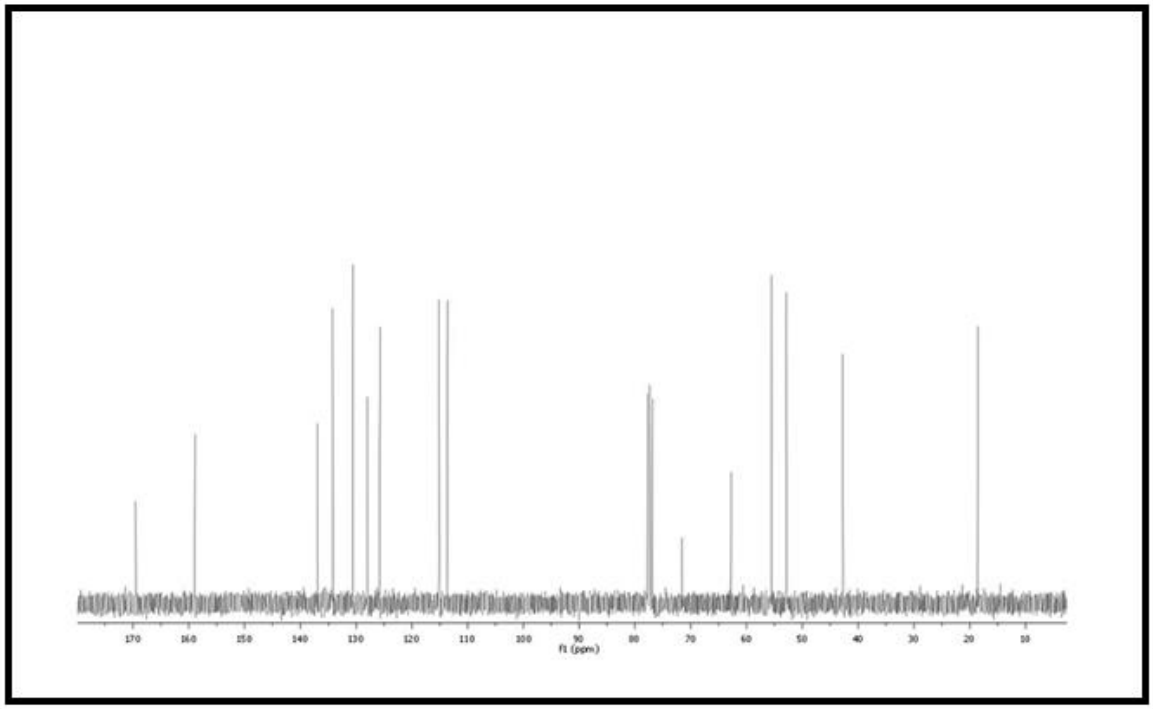

O
MeO
O

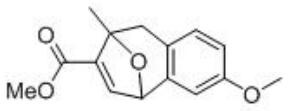

7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6
f1 (ppm)

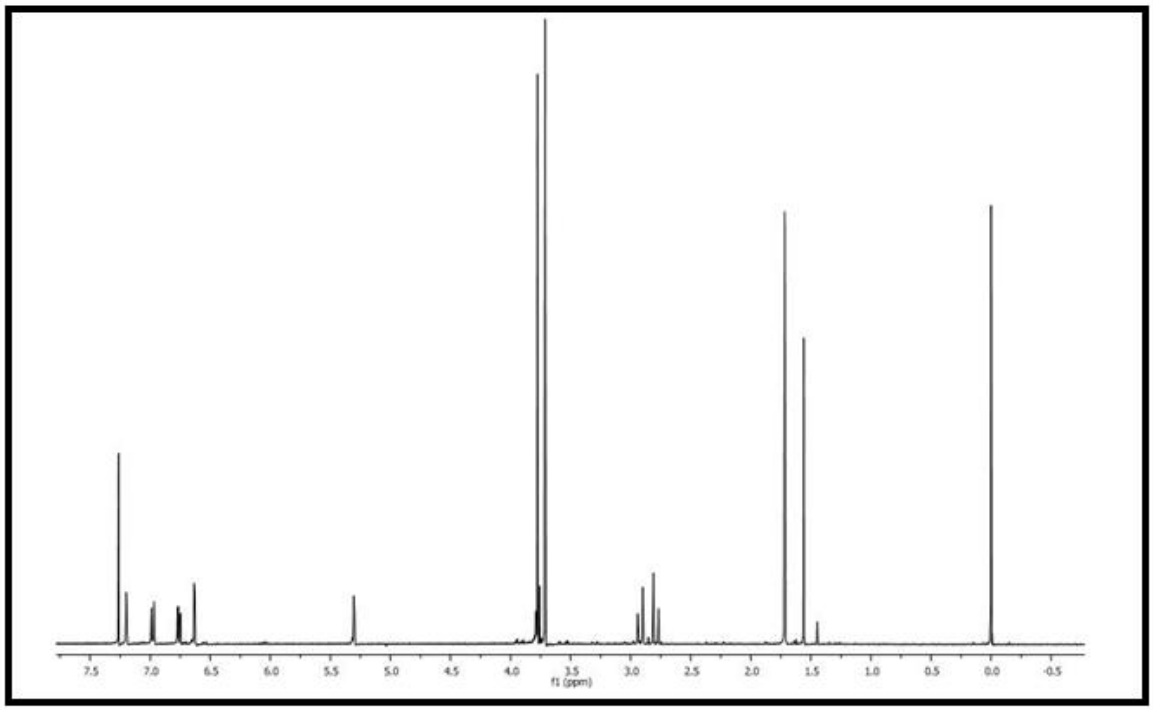

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

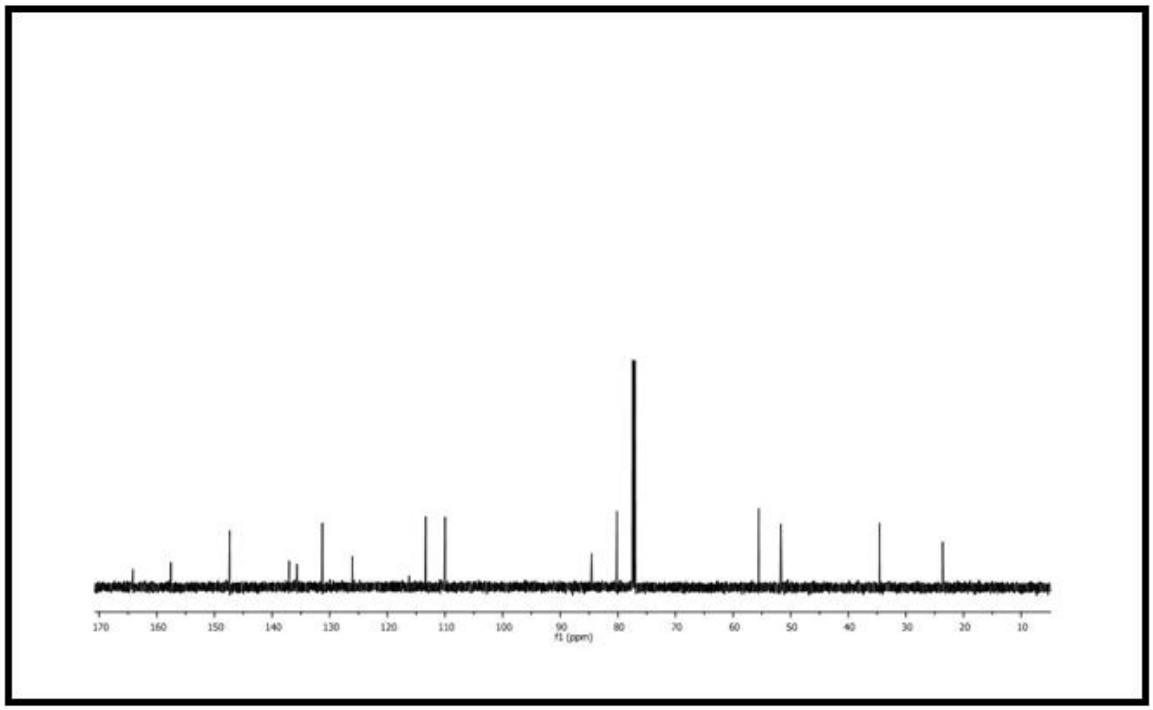

O
MeO
O
O

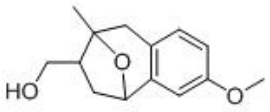

10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

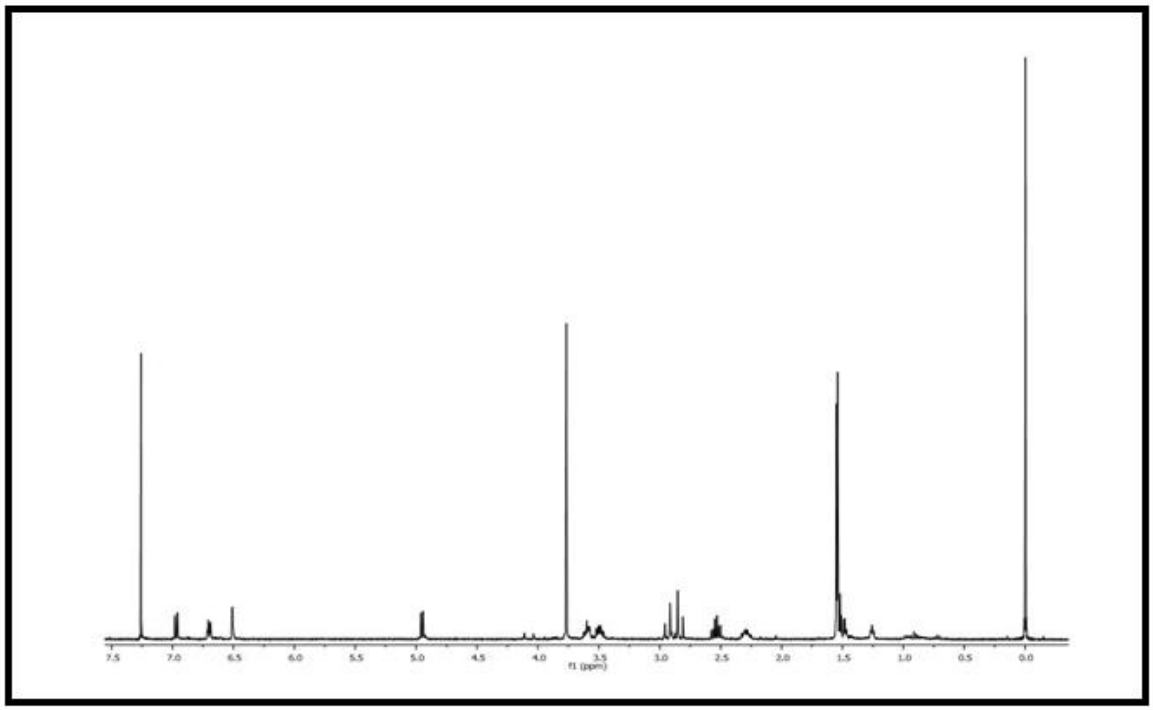

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

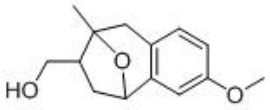

O
MeO
O
O

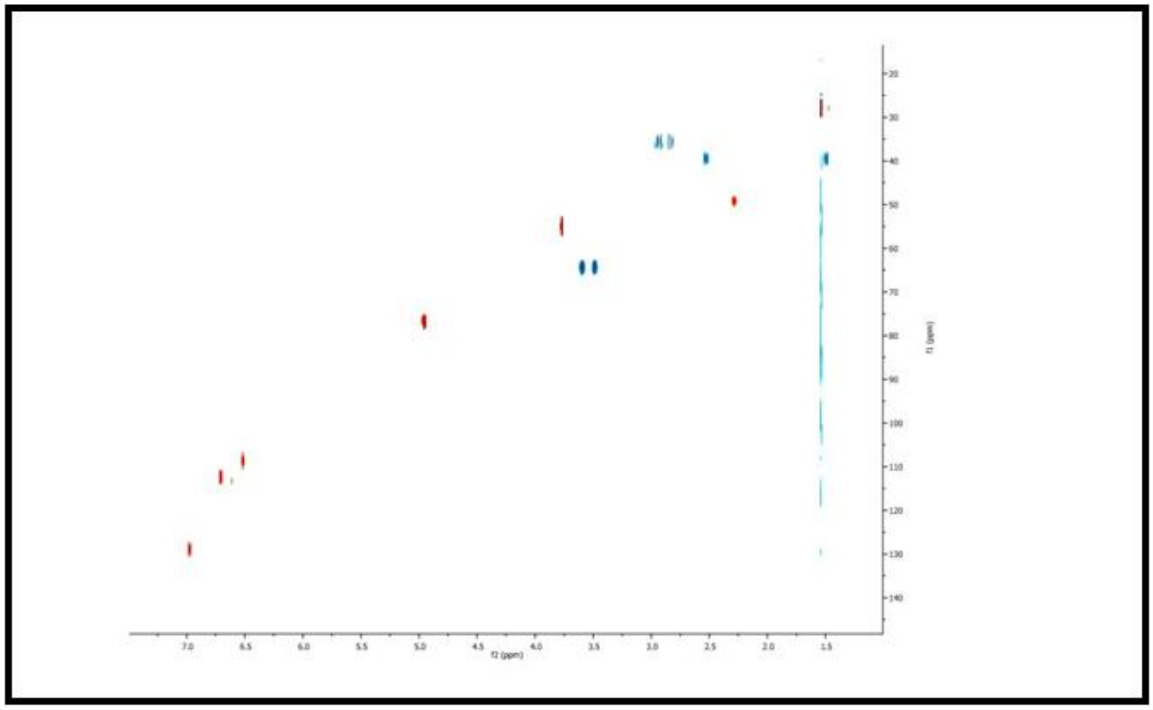

7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
f1 (ppm)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

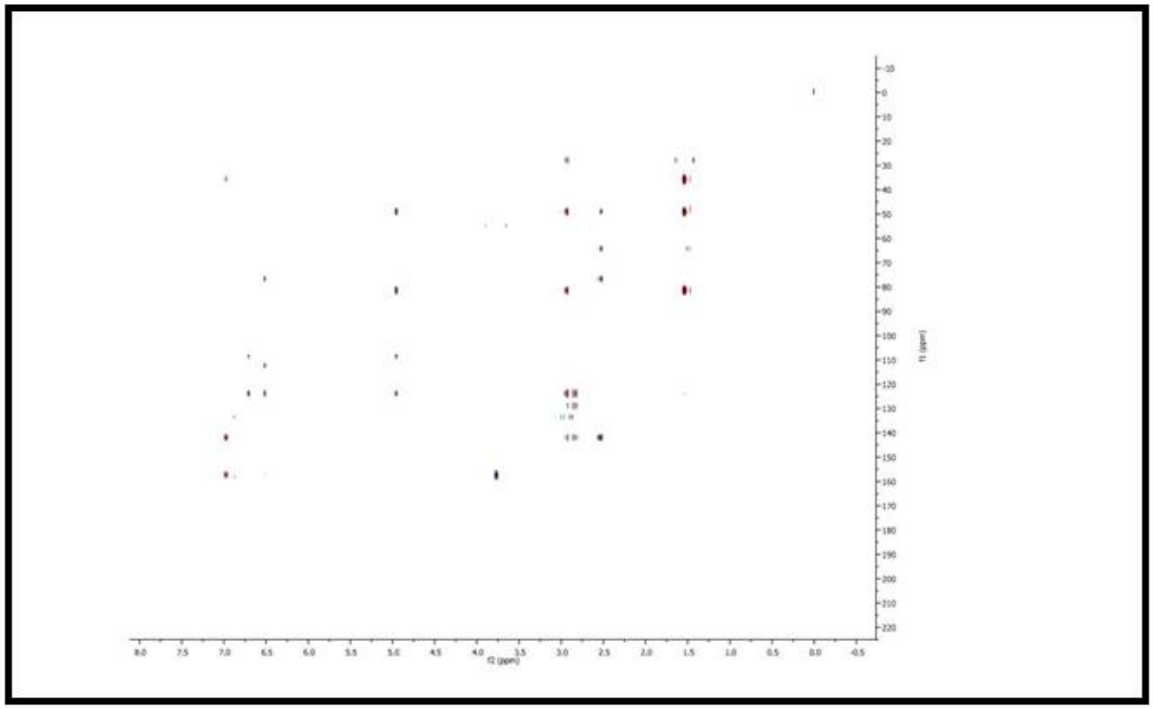

170
160
150
140
130
120
110
100
90
f1 (ppm)
80
70
60
50
40
30
20
10

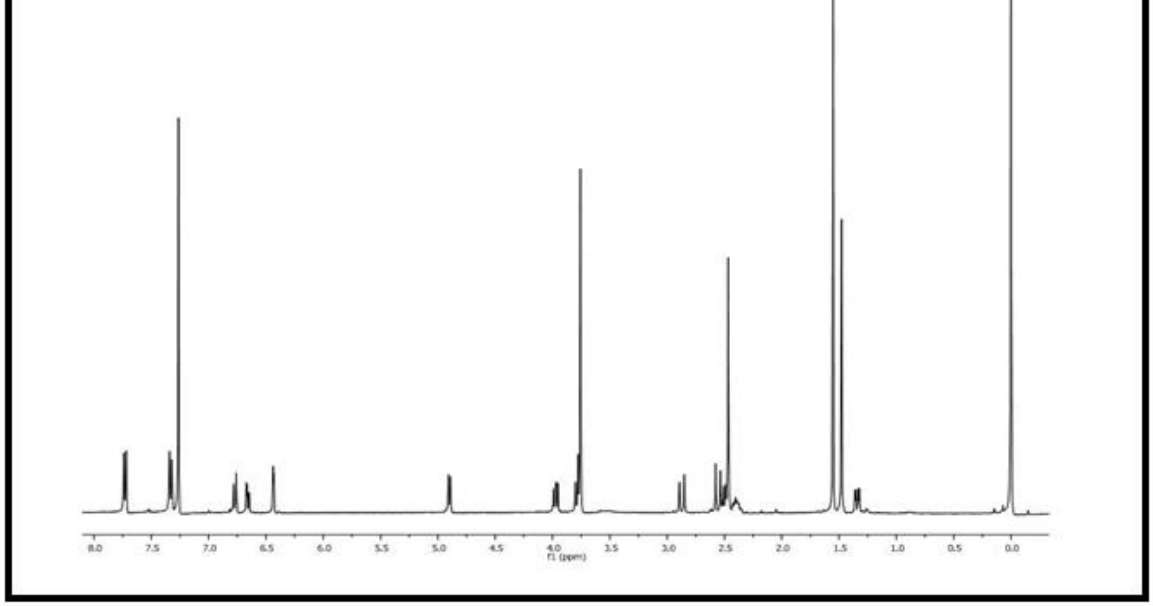

HO
O
O

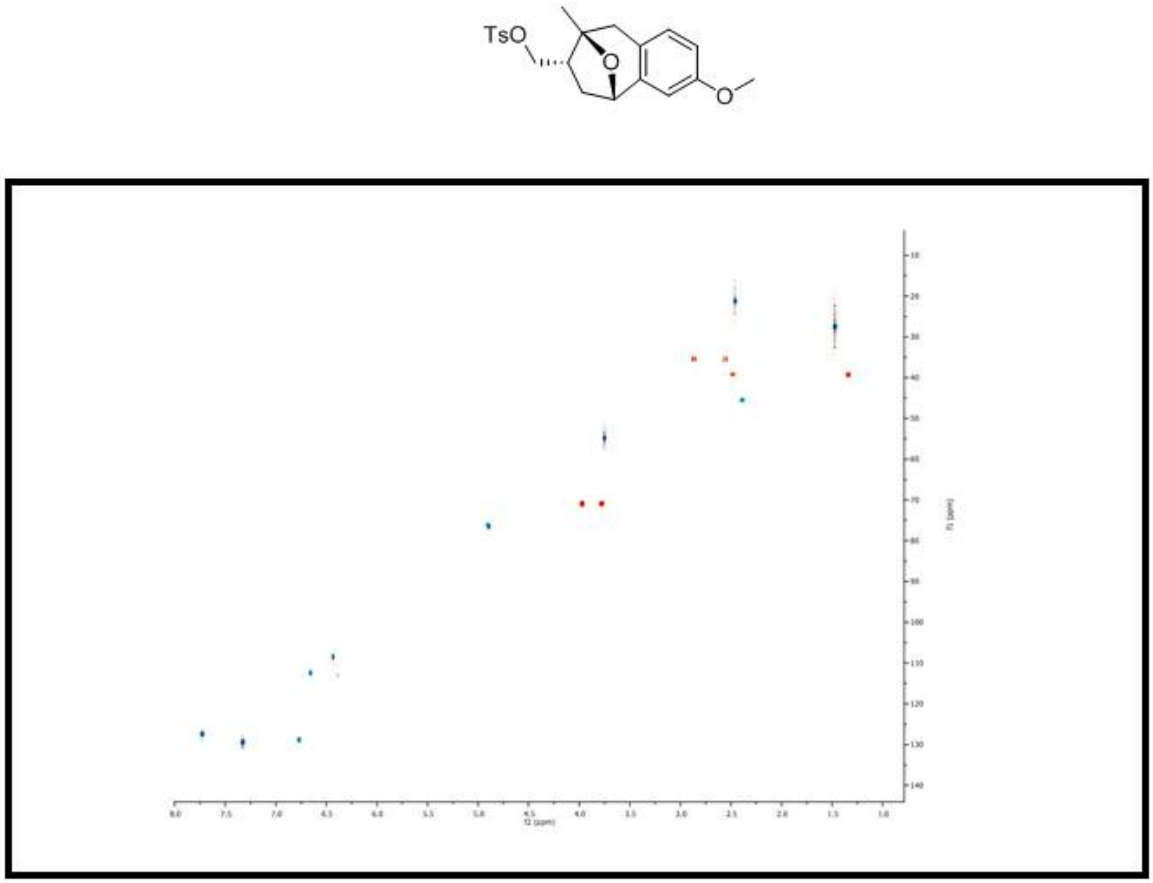

7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


HO
O
O






8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


TsO
O
O