

Total Synthesis of (\pm)-Antroquinonol

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Supporting Information

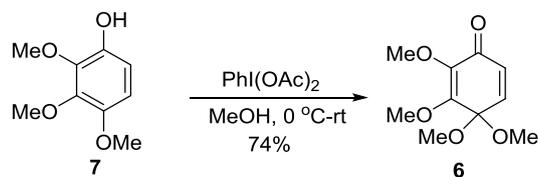
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D) General Information

^1H NMR spectra were recorded on a Varian 400 MHz spectrometer at ambient temperature with CDCl_3 as the solvent unless otherwise stated. ^{13}C NMR spectra were recorded on a Varian 100 MHz spectrometer (with complete proton decoupling) at ambient temperature. Chemical shifts are reported in parts per million relative to chloroform (^1H , δ 7.26 ppm; ^{13}C , δ 77.00 ppm). Data for ^1H NMR are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet) and coupling constants. Infrared spectra were recorded on a Thermo Fisher FT-IR200 spectrophotometer. High-resolution mass spectra were obtained at Peking University Mass Spectrometry Laboratory using a Bruker APEX Flash chromatography. The samples were analyzed by HPLC/MS on a Waters Auto Purification LC/MS system (3100 Mass Detector, 2545 Binary Gradient Module, 2767 Sample Manager, and 2998 Photodiode Array (PDA) Detector). The system was equipped with a Waters C18 5 m SunFire separation column (150*4.6 mm), equilibrated with HPLC grade water (solvent A) and HPLC grade methanol (solvent B) with a flow rate of 1.0 mL/min at room temperature. Analytical thin layer chromatography was performed using 0.25 mm silica gel 60-F plates. Flash chromatography was performed using 200-400 mesh silica gel. Yields refer to chromatographically and spectroscopically pure materials, unless otherwise stated. All reagents were used as supplied by Sigma-Aldrich, J&K and Alfa Aesar Chemicals. Methylene chloride, toluene, 1,2-dichloroethane were distilled from calcium hydride; tetrahydrofuran were distilled from sodium/benzophenone ketyl prior to use. All reactions were carried out in oven-dried glassware under an argon atmosphere unless otherwise noted.

II) Detailed experimental procedures



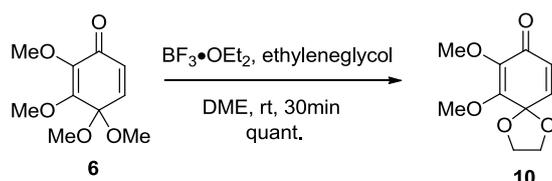
Dienone 7. 2,3,4-Trimethoxyphenol (4.5 g, 24.5 mmol) was dissolved in MeOH (30 mL) and cooled to $0\text{ }^\circ\text{C}$. To this solution, diacetoxyiodobenzene (8.7 g, 26.9 mmol) was added as solution in MeOH (60 mL) dropwise over the course of 1 h. The affording mixture was stirred at RT for an additional 2 hour. The reaction was quenched with sat. aq. NaHCO_3 (100 mL) and was allowed to stir until gas evolution subsided. The reaction mixture was extracted with DCM (3x200 mL). The combined organic layers was washed with 2M KOH (200 mL) and were then subsequently washed with brine (300 mL), dried (Na_2SO_4), and concentrated in vacuo. The crude oil was purified by column chromatography on silica gel (PE/EtOAc=8/1 to 5/1) to afford the dienone **6** (3.9 g, 74%) as a yellow oil.

^1H NMR (400 MHz, CDCl_3) δ 6.49 (d, $J = 10.4$ Hz, 1H), 6.26 (d, $J = 10$ Hz, 1H), 4.17 (s, 3H), 3.75 (s, 3H), 3.31 (m, 6H);

^{13}C NMR (100 MHz, CDCl_3) δ 183.2, 155.3, 140.2, 138.7, 130.2, 97.1, 61.2, 60.5, 51.4;

IR (neat) ν_{max} 2946, 2833, 1670, 1645, 1452, 1310, 1293, 1205, 1066, 971, 830, 635 cm^{-1} ;

HRMS (ESI) $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{10}\text{H}_{15}\text{O}_5$: 215.00914, found: 215.0911.



Dienone 10. To a stirred and cooled ($0\text{ }^\circ\text{C}$) solution of dienone **6** (3.9 g, 18.2 mmol) and ethyleneglycol (10 mL) in DME 20 mL, was added dropwise of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (460 μL , 3.6 mmol) and the resulting mixture was stirred at RT for 30 min. The mixture was recooled to $0\text{ }^\circ\text{C}$ and slowly quenched with sat. aq. NaHCO_3 , extracted with EtOAc. The combined organic layers was washed with brine, dried (Na_2SO_4), and concentrated in vacuo. Purification of the crude product on silica gel (PE/EtOAc=4/1) afforded the dienone **10** (3.86 g, quant.) as a brown oil.

^1H NMR (400 MHz, CDCl_3) δ 6.33 (d, $J = 10$ Hz, 1H), 6.01 (d, $J = 10$ Hz, 1H), 4.26-4.23 (m, 2H),

4.12-4.09 (m, 2H), 4.07 (s, 3H), 3.70 (m, 3H);

^{13}C NMR (100 MHz, CDCl_3) δ 183.7, 157.2, 140.6, 136.4, 127.2, 101.1, 67.0, 60.9, 60.8;

IR (neat) ν_{max} 2952, 2899, 1673, 1608, 1305, 1204, 1133, 1055, 971, 825, 630 cm^{-1} ;

HRMS (ESI) $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{10}\text{H}_{13}\text{O}_5$: 213.0758, found: 213.0752.



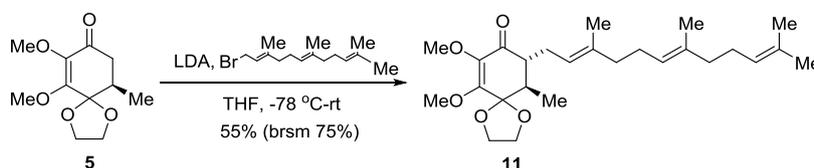
Enone 5. To a solution of BHT (848 mg, 4.0 mmol) in toluene (5 mL) at 25 °C under Argon was added AlMe_3 (1.0 M, 2 mL, 2 mmol). When gas evolution was complete the reagent MAD was ready to use, cooled to -78 °C. Dienone **10** was dissolved in toluene (1 mL), the afforded mixture was added to above MAD solution. The mixture turn to deep red solution. MeLi (3.0 M, 733 μL , 2.2 mmol) was added dropwise via syringe over 5 min and water (0.1 mL) was added at -78 °C. The mixture was stirred vigorously at RT for 1 h. The mixture was filtered through celite washed with Et_2O (20 mLx3). The combined components were dried (Na_2SO_4), and concentrated in vacuo. Purification of the crude product on silica gel (PE/ EtOAc =10/1 to 4/1) afforded the enone **5** (456 mg, 50%) as a light yellow oil.

^1H NMR (400 MHz, CDCl_3) δ 4.23-4.14 (m, 2H), 4.10-4.07 (m, 1H), 4.05 (s, 3H), 4.03-3.98 (m, 1H), 3.67 (m, 3H), 2.52-2.27 (m, 4H), 0.98 (d, $J = 6.4$ Hz, 3H);

^{13}C NMR (100 MHz, CDCl_3) δ 194.4, 161.2, 137.5, 108.1, 67.1, 66.8, 60.8, 60.6, 42.0, 36.7, 13.5;

IR (neat) ν_{max} 2953, 2898, 1670, 1608, 1450, 1268, 1181, 1115, 1096, 940, 641 cm^{-1} ;

HRMS (ESI) $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{11}\text{H}_{17}\text{O}_5$: 229.1071, found: 229.1067.



Compound 11. To a stirred solution of diisopropylamine (409 μL , 2.91 mmol) in THF (4 mL) was added $n\text{-BuLi}$ (1.7 mL, 2.72 mmol) at 0 °C, and kept stirring at this temperature for 30 min then cooled to -78 °C. A solution of enone **5** (443 mg, 1.94 mmol) in THF (4 mL) was added to above mixture and stirred at this temperature for 30 min. A solution of alkyl bromide (662 mg, 2.33 mmol)

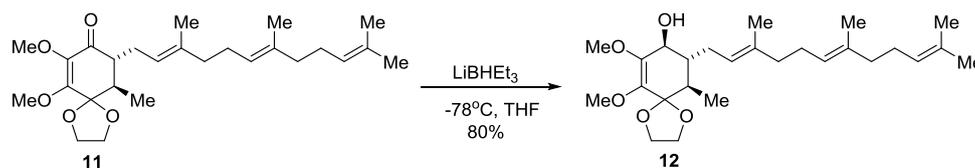
in THF (1 mL) was added and quickly warmed to RT and stirred at RT for 3 h. The reaction mixture was quenched with water at RT slowly and extracted with EtOAc, dried (Na₂SO₄), and concentrated in vacuo. Purification of the crude product on silica gel (PE/EtOAc=20/1) afforded the compound **11** (587 mg, 55%) as a light yellow oil

¹H NMR (400 MHz, CDCl₃) δ 5.11-5.05 (m, 2H), 4.98 (t, *J* = 6.0 Hz, 1H), 4.25-4.22 (m, 1H), 4.17-4.13 (m, 1H), 4.10-3.99 (m, 5H), 3.66 (s, 3H), 2.73-2.67 (m, 1H), 2.41-2.33 (m, 1H), 2.32-2.27 (m, 1H), 2.20-2.16 (m, 1H), 2.05-2.00 (m, 5H), 2.00-1.94 (m, 4H), 1.68 (s, 3H), 1.64 (s, 3H), 1.60 (s, 3H), 1.57 (s, 6H), 0.98 (d, *J* = 3.6 Hz, 3H);

¹³C NMR (100 MHz, CDCl₃) δ 196.0, 160.2, 137.4, 137.0, 135.0, 131.2, 124.4, 124.1, 120.3, 108.2, 67.2, 66.7, 60.7, 60.5, 49.3, 39.8, 39.7, 39.2, 26.7, 26.6, 25.7, 25.6, 17.7, 16.3, 16.0, 12.2, 10.3;

IR (neat) ν_{\max} 2913, 1672, 1620, 1449, 1275, 1189, 1070, 946 cm⁻¹;

HRMS (ESI) [M + H]⁺ calculated for C₂₆H₄₁O₅: 433.2949, found: 433.2945.



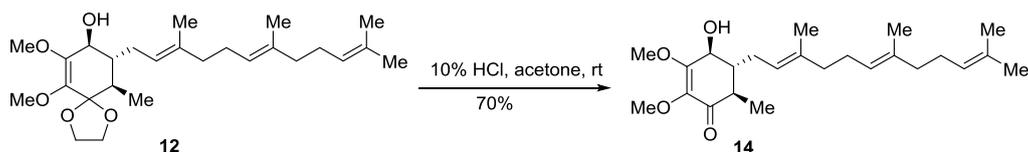
Compound 12. To a stirred solution of compound **11** (331 mg, 0.766 mmol) in THF (20 mL) under Argon was added LiBHET₃ (1 M, 1.15 mL, 1.15 mmol) at -78 °C, and kept stirring at this temperature for 1 h. The reaction mixture was quenched with sat. aq. NH₄Cl at -78 °C, slowly warmed to RT, extracted with EtOAc, dried (Na₂SO₄), filtered and concentrated in vacuo. Purification of the crude residue on silica gel (PE/EtOAc=20/1) afforded the compound **12** (266 mg, 80%) as a white solid. Mp 43-44 °C;

¹H NMR (400 MHz, CDCl₃) δ 5.13-5.07 (m, 3H), 4.21-4.15 (m, 2H), 4.11-4.08 (m, 1H), 4.10-3.99 (m, 1H), 4.00 (dd, *J* = 8.4, 3.2 Hz, 1H) 3.99-3.91 (m, 1H), 3.76 (s, 3H), 3.72 (s, 3H), 2.57-2.50 (m, 1H), 2.17-1.94 (m, 9H), 1.82-1.69 (m, 2H), 1.67 (s, 6H), 1.59 (s, 6H), 0.91 (d, *J* = 4.0 Hz, 3H);

¹³C NMR (100 MHz, CDCl₃) δ 144.4, 141.4, 137.9, 135.1, 131.2, 124.4, 124.1, 120.0, 109.9, 68.2, 67.0, 66.6, 60.8, 58.9, 43.9, 40.0, 39.7, 38.9, 26.7, 26.6, 25.7, 25.5, 17.7, 16.3, 16.0, 10.4;

IR (neat) ν_{\max} 2973, 2915, 1680, 1444, 1275, 1235, 1062, 937 cm⁻¹;

HRMS (ESI) [M + H]⁺ calculated for C₂₆H₄₃O₅: 457.2925, found: 457.2926.



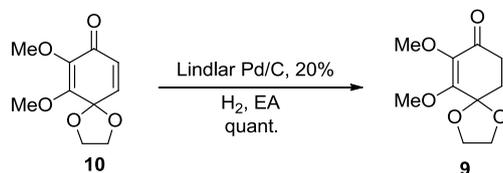
Compound 14. To a stirred solution of compound **12** (15 mg, 0.035 mmol) in THF (1 mL) under Argon was added 10% HCl (0.1 mL) at 0 °C, and kept stirring at this temperature for 20 min. The reaction mixture was quenched with brine at 0 °C, extracted with CH₂Cl₂, dried (Na₂SO₄), filtered and concentrated in vacuo. Purification of the crude residue on silica gel (PE/EtOAc=5/1) afforded the compound **14** (11.8 mg, 70%) as a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 5.13 (t, *J* = 7.2 Hz, 1H), 5.07 (t, *J* = 6.4 Hz, 1H), 4.27 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.12 (s, 3H), 3.66 (s, 3H), 2.62 (d, *J* = 2.0 Hz, 1H) 2.60-2.54 (m, 1H), 2.24-2.02 (m, 6H), 1.96-1.93 (m, 2H), 1.86-1.80 (m, 1H), 1.67 (s, 6H), 1.59 (s, 6H), 1.57 (s, 3H), 1.21(d, *J* = 7.2 Hz, 3H);

¹³C NMR (100 MHz, CDCl₃) δ 197.1, 160.3, 138.8, 135.2, 135.1, 131.4, 124.2, 124.0, 118.8, 69.1, 60.7, 60.3, 45.8, 42.0, 40.0, 39.7, 26.7, 26.4, 26.2, 25.7, 17.7, 16.3, 16.0, 13.1;

IR (neat) ν_{\max} 3443, 2967, 2919, 2851, 1666, 1616, 1450, 1280, 1248, 1071, 1035 cm⁻¹;

HRMS (ESI) [M + H]⁺ calculated for C₂₄H₃₉O₄: 391.2843, found: 391.2836.



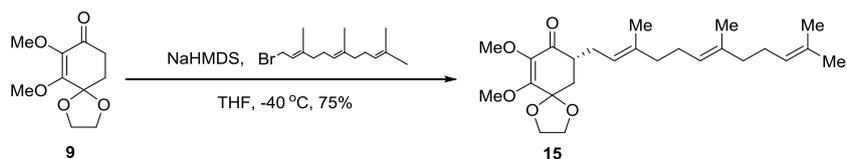
Compound 9. To a stirred solution of dienone **10** (2.54 g, 11.97 mmol) in EtOAc (20 mL) was added Lindlar Pd/C (500 mg, 20 wt%) at RT, and the mixture was kept stirring at this temperature under a balloon pressure of hydrogen for 3 h. The reaction mixture was filtered through a short silica gel pad and the filtrate was concentrated in vacuo to afford the compound **9** (2.56 g, quant.) as a light yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 4.18-4.14 (m, 2H), 4.07 (s, 3H), 4.05-3.68 (m, 2H), 3.68 (s, 3H), 2.56 (t, *J* = 6.4 Hz, 2H), 2.07 (t, *J* = 6.4 Hz, 2H);

¹³C NMR (100 MHz, CDCl₃) δ 194.6, 160.4, 138.0, 106.3, 66.3, 60.8, 60.6, 34.1, 32.0;

IR (neat) ν_{\max} 2953, 2898, 1670, 1606, 1448, 1295, 1193, 1170, 1081, 1046, 996, 916 cm⁻¹;

HRMS (ESI) [M + H]⁺ calculated for C₁₀H₁₅O₅: 215.0914, found: 215.0910.



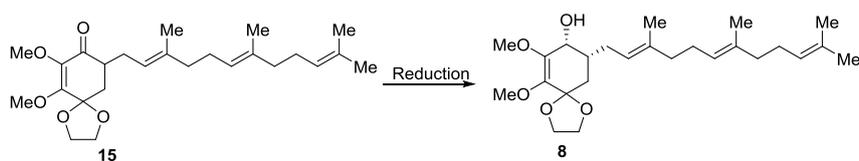
Compound 15. To a stirred solution of enone **9** (2.14 g, 10 mmol) in THF (20 mL) was added NaHMDS (1.0 M in THF, 15 mL, 15 mmol) at -40 °C, and the mixture was kept stirring at this temperature for 45 min. A solution of alkyl bromide (4.16 g, 15 mmol) in THF was added at -40 °C. The temperature was slowly warmed to -10 °C in 2 h. The reaction mixture was quenched with sat. aq. NaHCO₃ at -10 °C, slowly warmed to RT. The reaction mixture was extracted with EtOAc, dried (Na₂SO₄), filtered and concentrated in vacuo. Purification of the crude residue on silica gel (PE/EtOAc=15/1) afforded the compound **15** (3.14 g, 75%) as a yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 5.10-5.06 (m, 3H), 4.16-4.12 (m, 2H), 4.08-4.04 (m, 4H), 3.97-3.94 (m, 1H), 3.67 (s, 3H), 2.58-2.54 (m, 2H), 2.53-2.18 (m, 2H), 2.08-1.84 (m, 9H), 1.67 (s, 3H), 1.60 (s, 9H);

¹³C NMR (100 MHz, CDCl₃) δ 196.1, 159.6, 137.9, 137.5, 135.0, 131.3, 124.3, 124.0, 106.0, 66.9, 65.8, 60.8, 60.6, 43.4, 39.8, 39.7, 37.0, 27.7, 26.7, 26.5, 25.7, 17.7, 16.1, 16.0;

IR (neat) ν_{\max} 2916, 1673, 1615, 1448, 1298, 1192, 1063, 949, 838 cm⁻¹;

HRMS (ESI) [M + H]⁺ calculated for C₂₅H₃₉O₅: 419.2792, found: 419.2803.



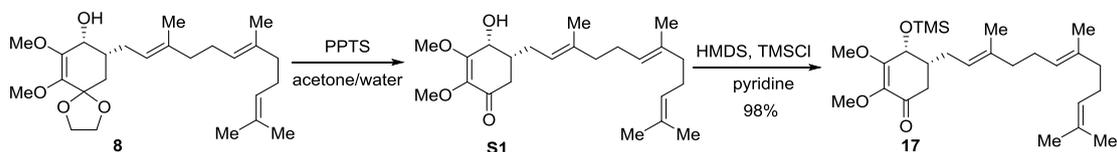
Compound 8. To a stirred solution of compound **15** (120 mg, 0.288 mmol) in THF (5 mL) was added L-selectride (1 M, 574 μ L, 0.574 mmol) dropwise at -78 °C, and kept stirring at this temperature for 3 h. The reaction mixture was quenched with sat. aq. NH₄HCO₃ at -78 °C, slowly warmed to RT, extracted with EtOAc, dried (Na₂SO₄), filtered and concentrated in vacuo. Purification of the crude residue on silica gel (PE/EtOAc=10/1) afforded the compound **8** (109 mg, 90%) as a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 5.16 (t, *J* = 5.8 Hz, 1H), 5.11-5.07 (m, 2H), 4.16-4.01 (m, 5H), 3.89-3.87 (m, 1H), 3.77 (s, 3H), 3.72 (s, 3H), 2.17-2.15 (m, 1H), 2.09-1.95 (m, 10H), 1.89-1.86 (m, 2H), 1.67 (s, 3H), 1.63 (s, 3H), 1.60 (s, 6H);

^{13}C NMR (100 MHz, CDCl_3) δ 145.9, 140.4, 137.2, 135.1, 131.3, 124.3, 124.0, 121.6, 108.0, 67.8, 66.3, 65.1, 60.9, 58.1, 39.8, 39.7, 36.6, 35.2, 29.5, 26.7, 26.6, 25.7, 17.7, 16.2, 16.0;

IR (neat) ν_{max} 3471, 2925, 1671, 1446, 1315, 1161, 1052, 961 cm^{-1} ;

HRMS (ESI) $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{25}\text{H}_{41}\text{O}_5$: 421.2949, found: 421.2950.



Compound S1. To a stirred solution of compound **8** (200 mg, 0.476 mmol) in water (0.4 mL) and acetone (4 mL), was added PPTS (24 mg, 0.095 mmol) at RT, and kept stirring at this temperature for 2 h. The reaction mixture was concentrated to remove acetone and diluted with water, extracted with EtOAc, dried (Na_2SO_4), filtered and concentrated in vacuo to afford the compound **S1** which was used directly in the next step.

^1H NMR (400 MHz, CDCl_3) δ 5.13-5.06 (m, 3H), 4.34 (d, $J = 4.8$ Hz, 1H), 4.07 (s, 3H), 3.66 (s, 3H), 2.49 (dd, $J = 16.8, 12$ Hz, 1H), 2.33 (t, $J = 3.2$ Hz, 1H), 2.30-2.21 (m, 2H), 2.11-1.94 (m, 10H), 1.67 (s, 3H), 1.63 (s, 3H), 1.59 (s, 6H);

^{13}C NMR (100 MHz, CDCl_3) δ 195.2, 162.2, 138.0, 136.5, 135.2, 131.3, 124.3, 123.9, 120.6, 68.7, 60.6, 59.0, 39.8, 39.7, 37.8, 37.6, 29.1, 26.7, 26.5, 25.7, 17.8, 16.2, 16.0;

IR (neat) ν_{max} 3395, 2914, 2851, 1652, 1448, 1322, 1231, 1131, 986, 948, 763 cm^{-1} ;

HRMS (ESI) $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{23}\text{H}_{37}\text{O}_4$: 377.2686, found: 377.2686.

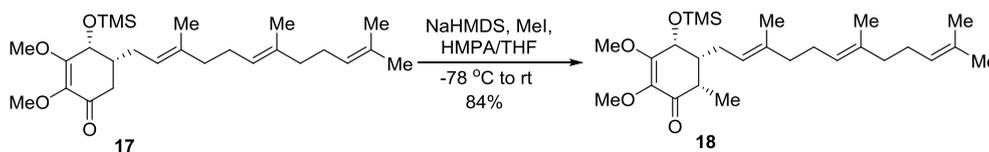
Compound 17. The crude compound **S1** was dissolved in pyridine (3 mL), HMDS (397 μL , 1.904 mmol) and TMSCl (126 μL , 1.428 mmol) was added at RT. The mixture was stirred at RT for 4 h. The reaction mixture was diluted with EtOAc and quenched with sat. aq. NaHCO_3 at -78 $^\circ\text{C}$, slowly warmed to RT, and extracted with EtOAc, dried (Na_2SO_4), filtered and concentrated in vacuo. Purification of the crude residue on silica gel (PE/EtOAc=10/1) afforded the compound **17** (209 mg, 98%) as a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 5.09-5.06 (m, 3H), 4.15 (d, $J = 2.0$ Hz, 1H), 4.05 (s, 3H), 3.63 (s, 3H), 2.49 (dd, $J = 16.8, 12$ Hz, 1H), 2.28-2.23 (m, 1H), 2.08-1.94 (m, 11H), 1.66 (s, 3H), 1.58 (s, 9H), 0.12 (s, 9H);

^{13}C NMR (100 MHz, CDCl_3) δ 196.2, 162.8, 137.5, 136.0, 135.1, 131.3, 124.3, 124.0, 121.0, 77.3, 77.00, 76.7, 71.4, 60.8, 60.0, 39.8, 39.7, 38.7, 38.1, 29.7, 29.4, 26.7, 26.5, 25.7, 17.7, 16.3, 16.0, 0.2;

IR (neat) ν_{max} 2954, 2918, 2852, 1675, 1623, 1451, 1318, 1230, 1130, 1045, 865, 841, 750 cm^{-1} ;

HRMS (ESI) $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{26}\text{H}_{45}\text{O}_4\text{Si}$: 449.3082, found: 449.3082.



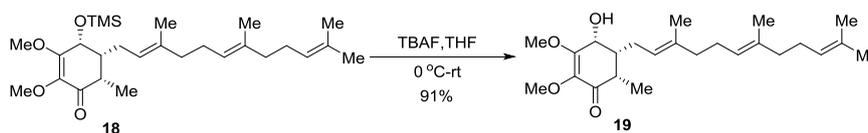
Compound 18. To a stirred solution of enone **17** (46.3 mg, 0.103 mmol) in THF (2.5 mL) and HMPA (0.5 mL) was added NaHMDS (1.0 M in THF, 0.53 mL, 0.53 mmol) at -78 °C, and the mixture was kept stirring at this temperature for 45 min. Methyl iodide (64.3 μL , 1.0 mmol) was added dropwise at -78 °C. The resulting mixture was stirred at -78 °C for 1.5 h. The reaction mixture was quenched with sat. aq. NH_4Cl at -78 °C, and slowly warmed to RT. The reaction mixture was extracted with EtOAc, dried (Na_2SO_4), filtered and concentrated in vacuo. Purification of the crude residue on silica gel (PE/EtOAc=15/1) afforded the compound **18** (40 mg, 84%) as a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 5.09 (t, $J = 7.2$ Hz, 3H), 4.24 (d, $J = 3.6$ Hz, 1H), 4.07 (s, 3H), 3.65 (s, 3H), 2.47-2.44 (m, 1H), 2.17-1.96 (m, 10H), 1.67 (s, 3H), 1.63 (s, 3H), 1.59 (s, 6H), 1.21 (d, $J = 7.2$ Hz, 3H), 0.13 (s, 9H);

^{13}C NMR (100 MHz, CDCl_3) δ 200.4, 161.9, 137.1, 135.1, 135.0, 131.3, 124.3, 124.0, 121.4, 117.2, 71.7, 60.7, 60.1, 43.8, 39.8, 39.7, 26.7, 26.6, 25.7, 17.7, 16.3, 16.0, 14.8, 0.22;

IR (neat) ν_{max} 2918, 2852, 1670, 1624, 1450, 1317, 1249, 1227, 1137, 1052, 872, 842, 751 cm^{-1} ;

HRMS (ESI) $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{27}\text{H}_{47}\text{O}_4\text{Si}$: 463.3238, found: 463.3239.



Compound 19. TBAF (422 μL , 0.422 mmol) was added to a stirred solution of compound **18** (39 mg, 0.084 mmol) in THF (2 mL) at 0 °C, and the mixture was kept stirring while the temperature was allowed to rise to RT in 2 h. The reaction mixture was concentrated in vacuo. Purification of the crude residue on silica gel (PE/EtOAc=5/1) afforded the compound **19** (30 mg, 91%) as a

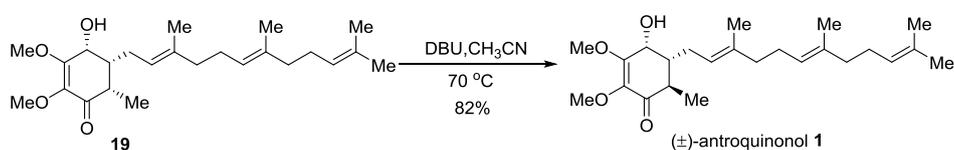
colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 5.15-5.07 (m, 3H), 4.22 (t, $J = 4.0$ Hz, 1H), 4.10 (s, 3H), 3.68 (s, 3H), 2.50-2.47 (m, 1H), 2.36-2.34 (m, 1H), 2.14-1.95 (m, 11H), 1.67 (s, 3H), 1.65 (s, 3H), 1.58 (s, 6H), 1.24 (d, $J = 7.2$ Hz, 3H);

^{13}C NMR (100 MHz, CDCl_3) δ 199.3, 160.6, 137.4, 135.2, 131.3, 124.3, 123.9, 121.5, 69.7, 60.6, 59.6, 44.0, 40.2, 39.8, 39.7, 26.7, 26.5, 25.7, 25.6, 17.7, 16.2, 16.0, 14.8;

IR (neat) ν_{max} 3429, 2917, 1653, 1611, 1450, 1322, 1231, 1137, 1012, 907, 649 cm^{-1} ;

HRMS (ESI) $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{24}\text{H}_{38}\text{O}_4$: 391.2843, found: 391.2845.



(\pm) -**Antroquinonol 1**. A mixture of Compound **19** (7.0 mg, 0.018 mmol) and DBU (41 μL , 0.27 mmol) in CH_3CN (0.5 mL) was stirred at 70°C for 12 h. The reaction mixture was concentrated in vacuo. Purification of the crude residue on silica gel (PE/EtOAc=5/1) afforded (\pm) -antroquinonol **1** (5.7 mg, 82%) as a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 5.16 (t, $J = 7.2$ Hz, 1H), 5.09 (t, $J = 6.8$ Hz, 1H), 4.35 (d, $J = 3.6$, 3H), 4.07 (s, 3H), 3.67 (s, 3H), 2.53 (dp, $J = 11.2, 6.8$ Hz 1H), 2.24 (t, $J = 7.6$ Hz, 2H), 2.09-1.96 (m, 10H), 1.76 (m, 1H), 1.68 (s, 3H), 1.66 (s, 3H), 1.60 (s, 6H), 1.17 (d, $J = 7.2$ Hz, 3H);

^{13}C NMR (100 MHz, CDCl_3) δ 197.1, 160.4, 138.1, 135.9, 135.4, 131.3, 124.3, 123.8, 120.9, 68.0, 60.6, 59.2, 43.3, 40.3, 39.8, 39.7, 27.0, 26.7, 26.4, 25.7, 17.7, 16.1, 16.0, 12.3;

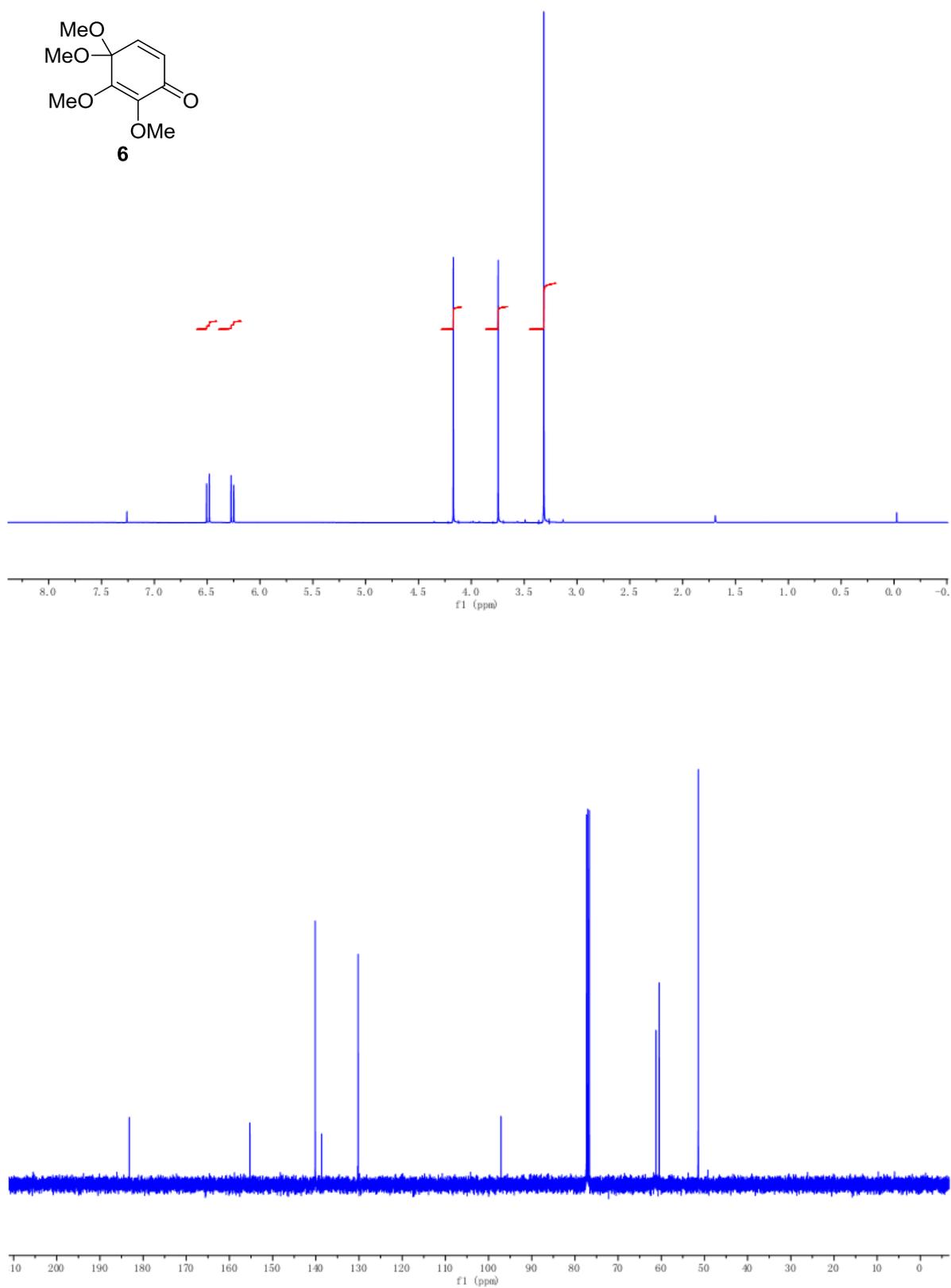
IR (neat) ν_{max} 2994, 1769, 1758, 1611, 1374, 1243, 1058, 907, 668 cm^{-1} ;

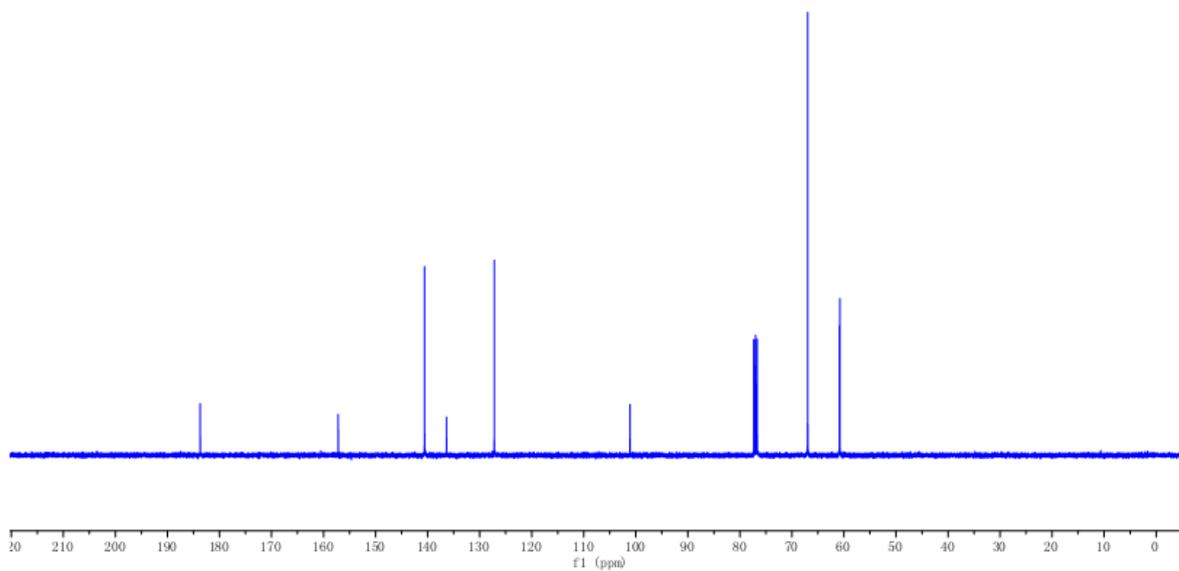
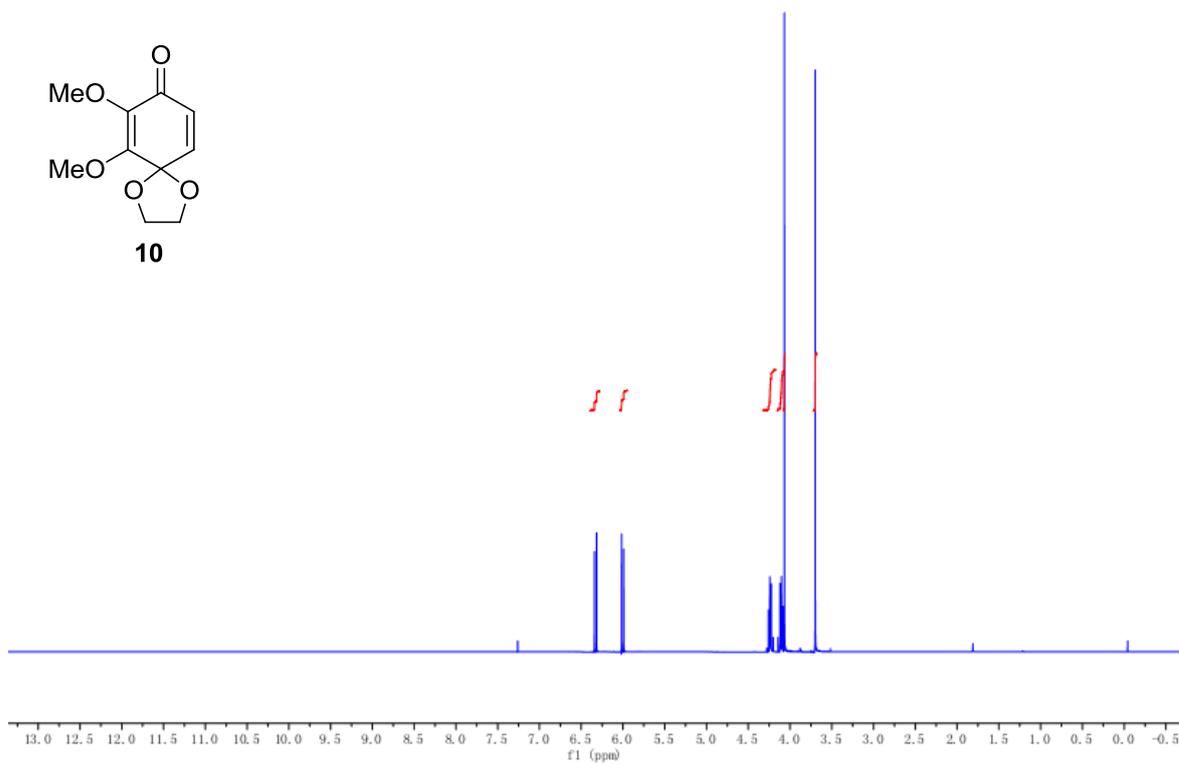
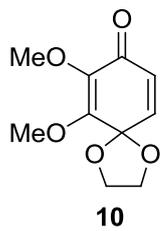
HRMS (ESI) $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{24}\text{H}_{38}\text{O}_4$: 391.2843, found: 391.2845.

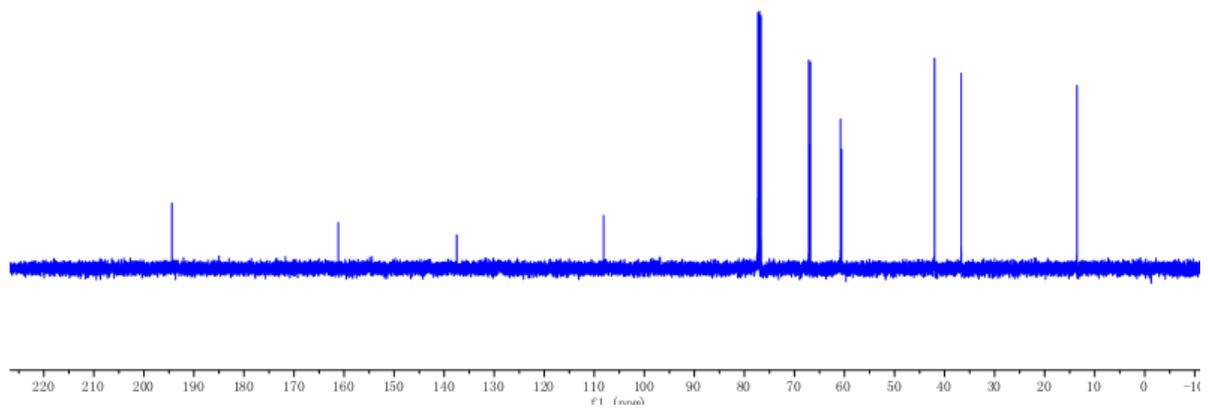
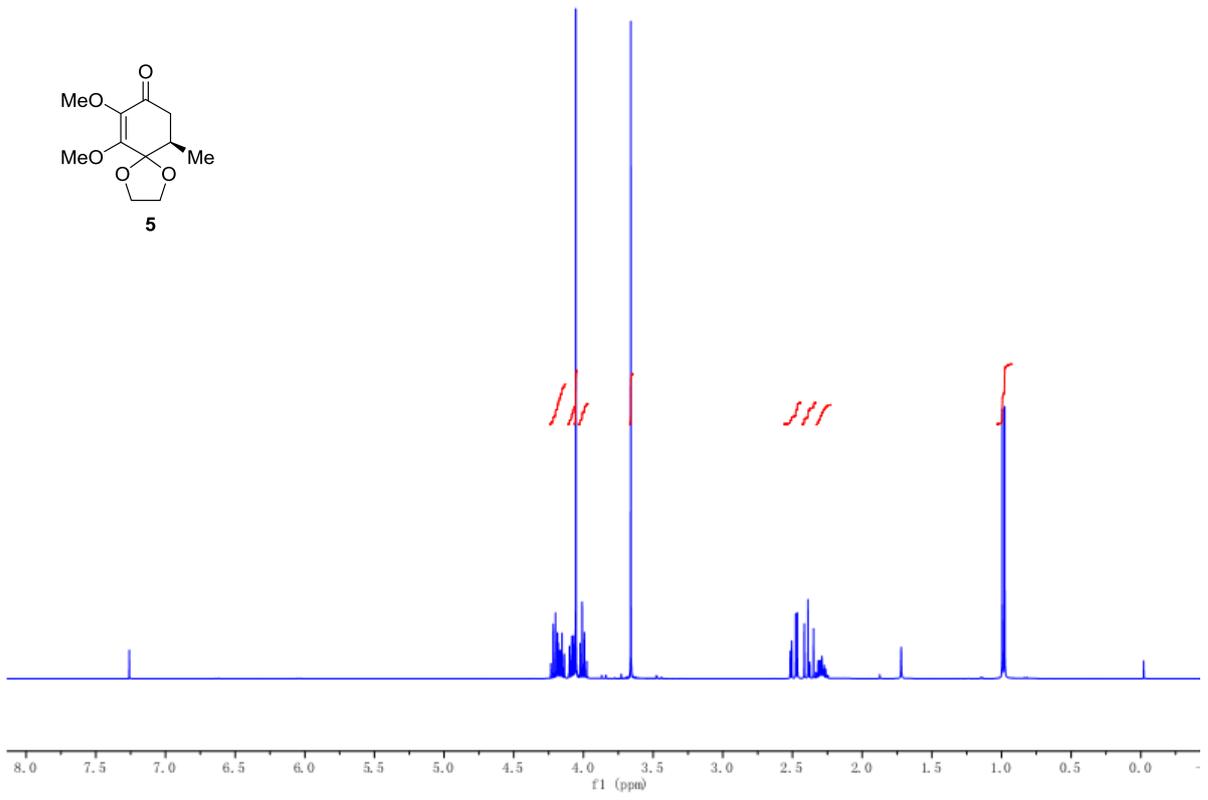
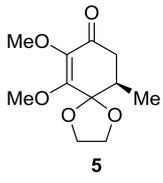
III) Comparison of Natural and Synthetic (\pm)-Antroquinonol

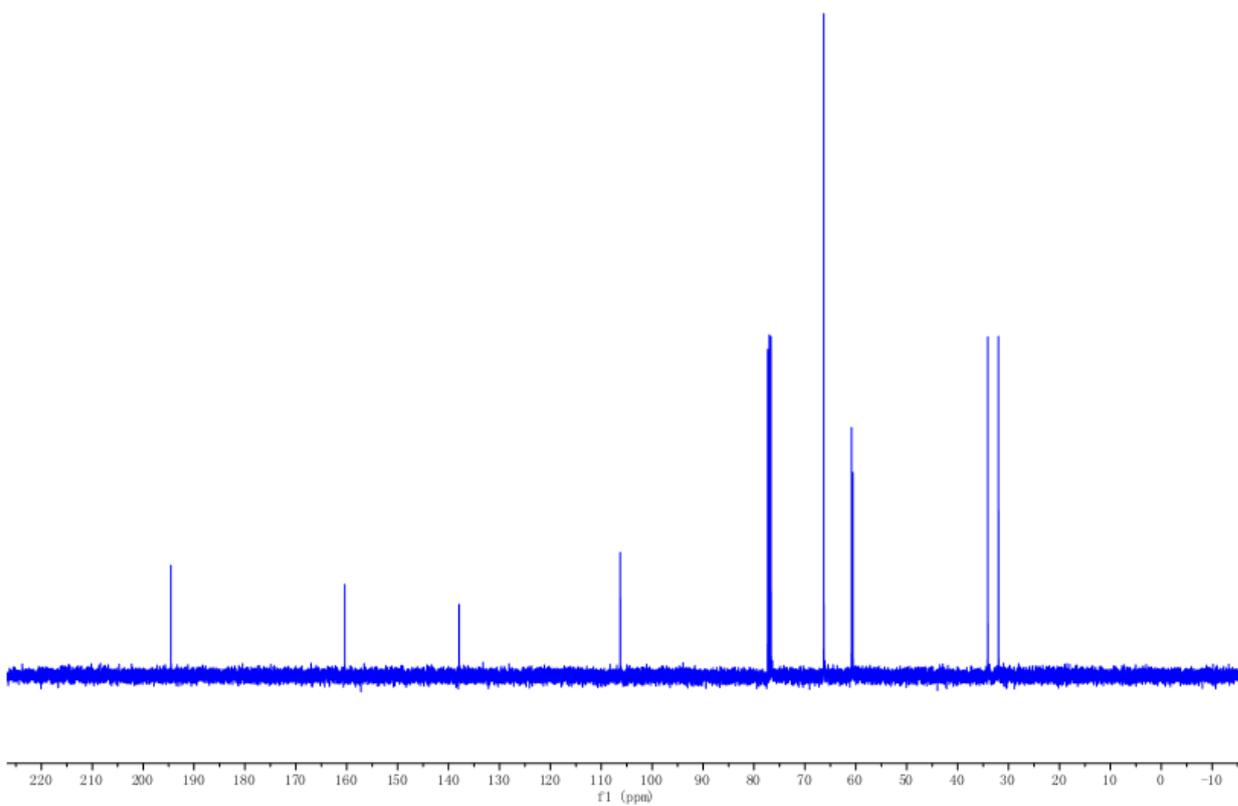
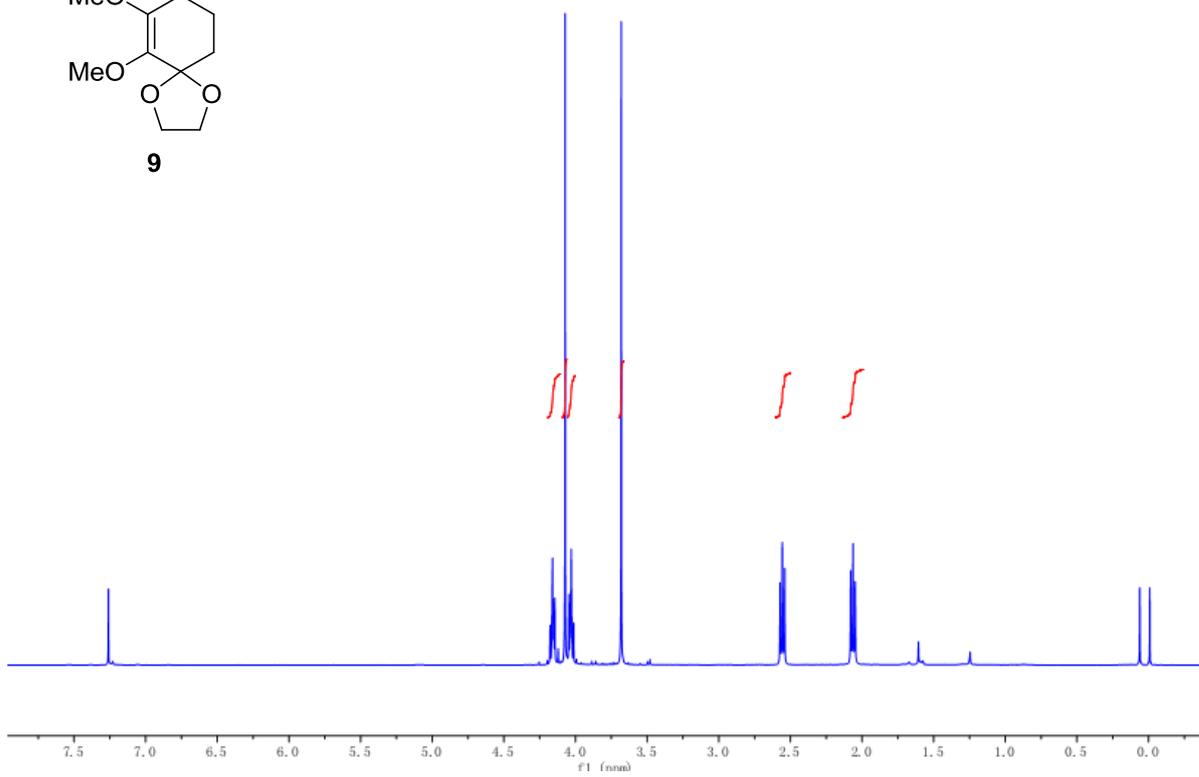
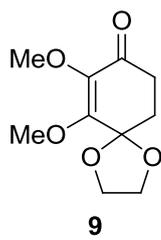
^1H NMR (Hz)		^{13}C NMR (Hz)	
Natural (500 MHz, δ CDCl_3 , 7.24 ppm)	Synthetic (400 MHz, δ CDCl_3 , 7.26 ppm)	Natural (125 MHz, δ CDCl_3 , 77.0 ppm)	Synthetic (100 MHz, δ CDCl_3 , 77.0 ppm)
5.14 (t, 7.4, 1H)	5.16 (t, 7.2, 1H)	197.1	197.1
5.07 (t, 6.9, 2H)	5.09 (t, 6.8, 2H)	160.5	160.5
4.33 (d, 3.4, 1H)	4.35 (d, 3.6, 1H)	138.1	138.1
4.05 (s, 3H)	4.07 (s, 3H)	135.9	135.9
3.65 (s, 3H)	3.67 (s, 3H)	135.4	135.4
2.53 (dp, 11.2, 6.9, 1H)	2.55 (dp, 11.2, 6.8, 1H)	131.3	131.3
2.22 (dd, 7.4, 7.4, 2H)	2.24 (t, 7.6, 2H)	124.3	124.3
2.07-2.03 (m, 4H)	2.09-2.05 (m, 4H)	123.8	123.8
2.03-1.95 (m, 4H)	2.05-1.96 (m, 4H)	121.0	120.9
1.74 (m, 1H)	1.76 (m, 1H)	68.0	68.0
1.65 (s, 3H)	1.68 (s, 3H)	60.6	60.6
1.64 (s, 3H)	1.66 (s, 3H)	59.2	59.2
1.58 (s, 6H)	1.60 (s, 6H)	43.4	43.3
1.15 (d, 6.9, 3H)	1.17 (d, 7.2, 3H)	40.3	40.3
		39.8	39.8
		39.7	39.7
		27.0	27.0
		26.7	26.7
		26.4	26.4
		25.7	25.7
		17.7	17.7
		16.1	16.1
		16.0	16.0
		12.3	12.3

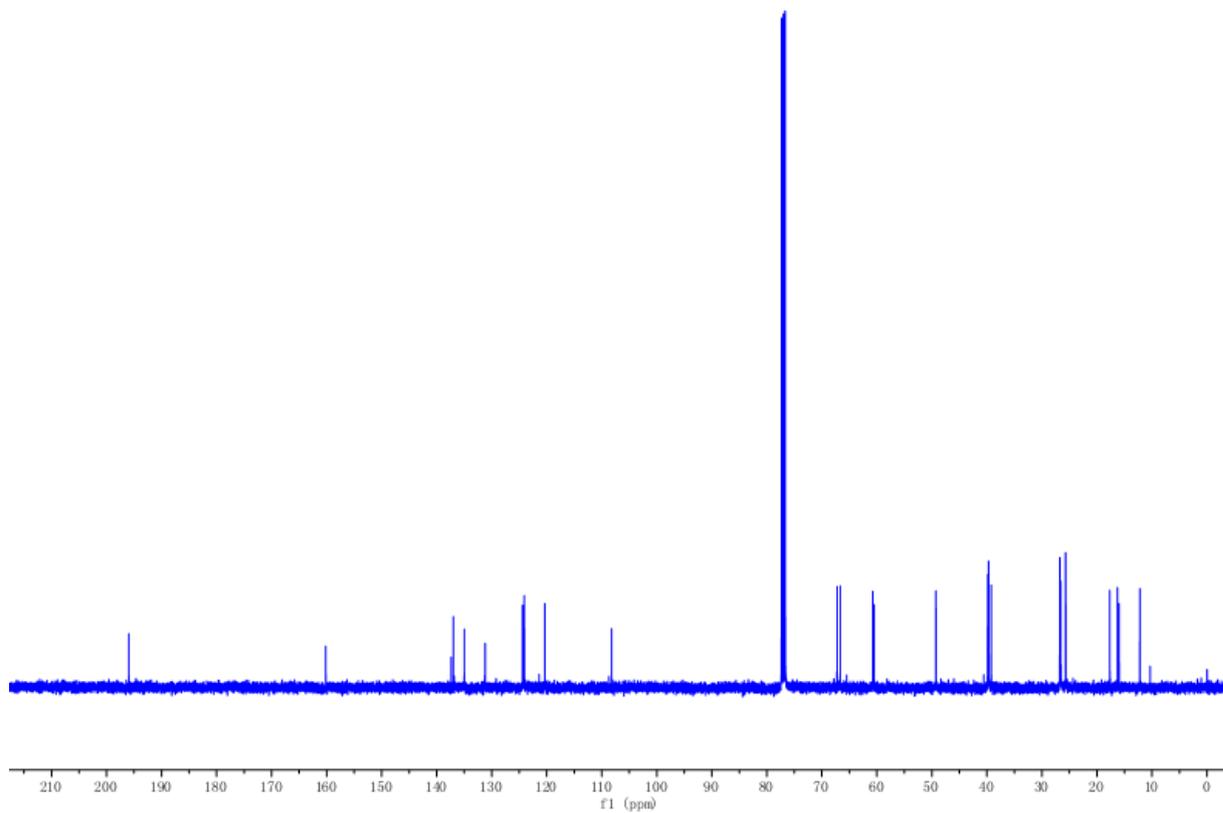
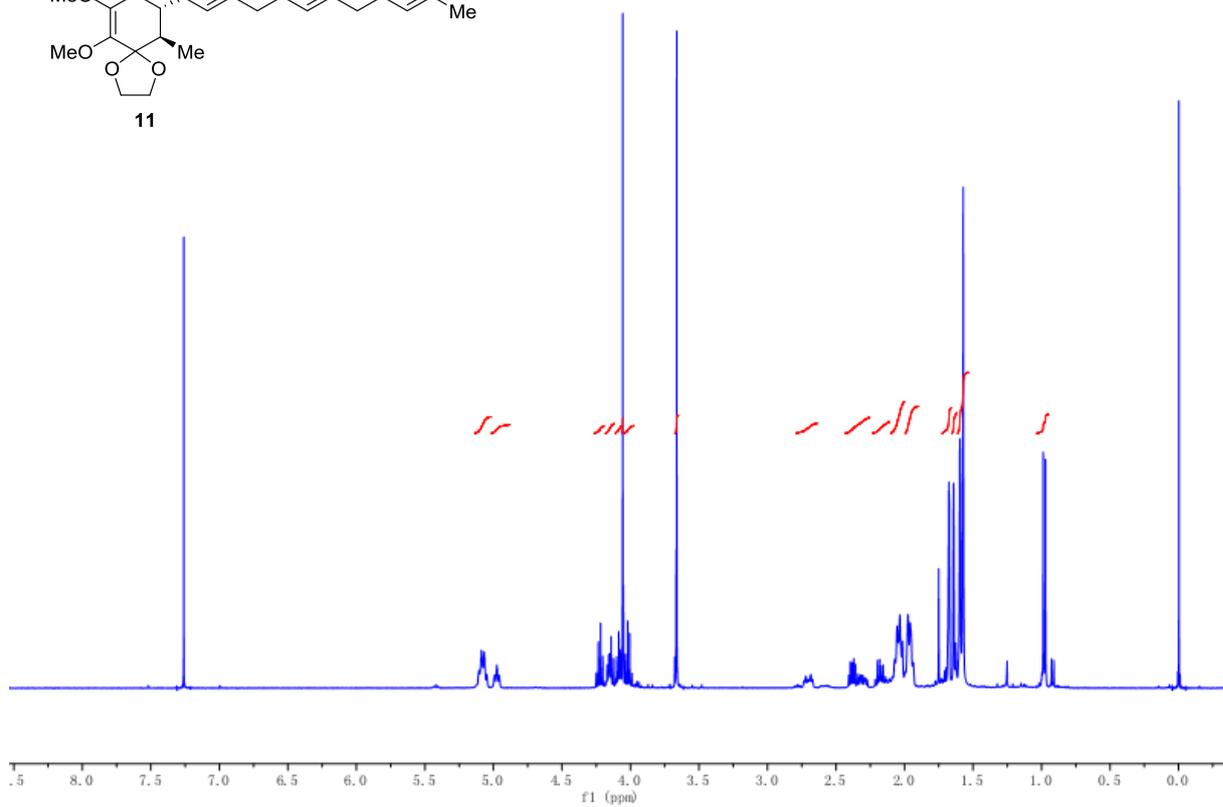
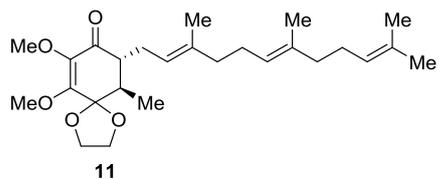
IV) NMR spectra

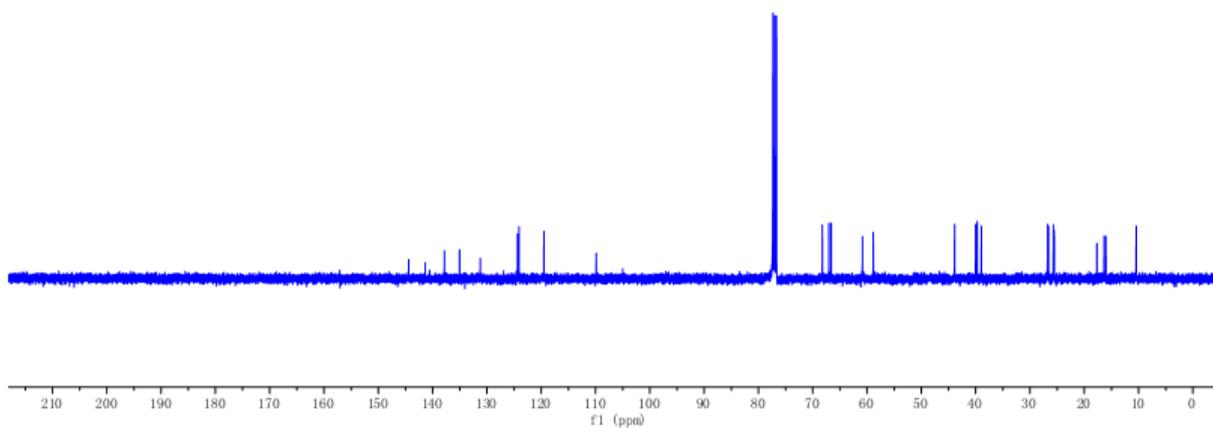
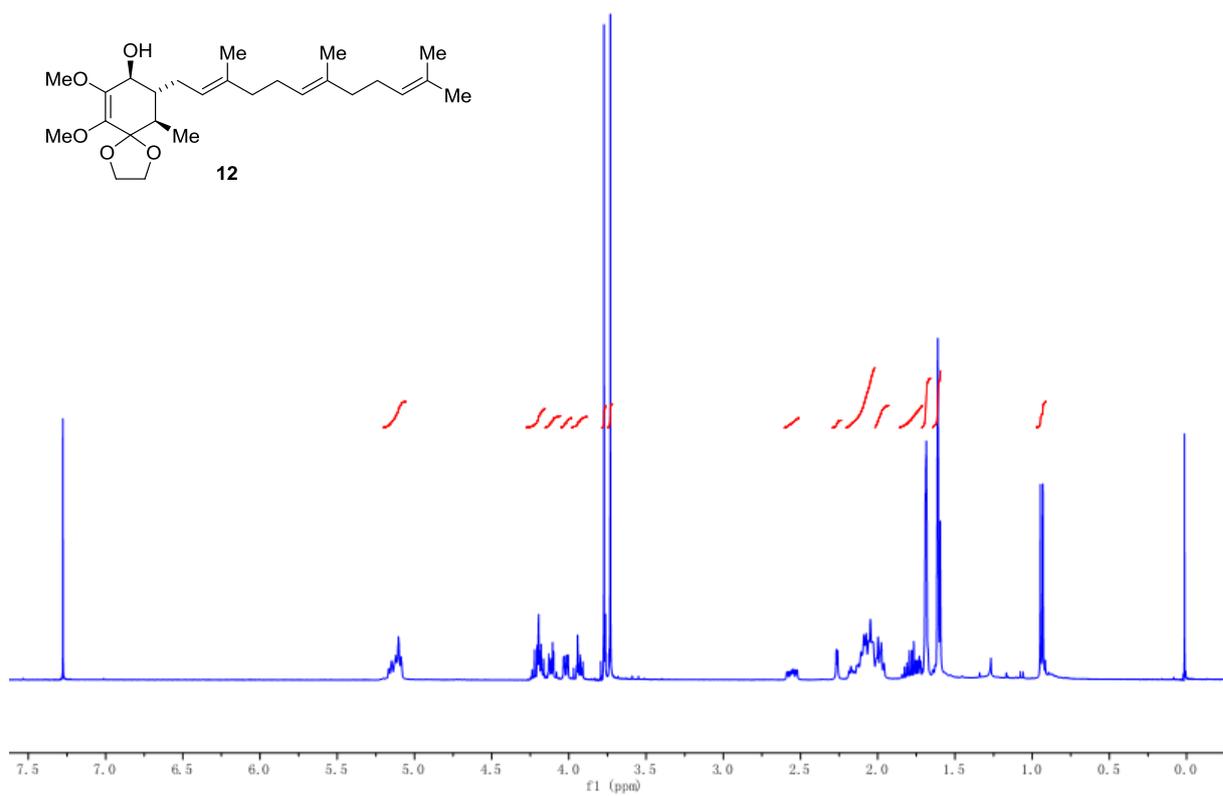
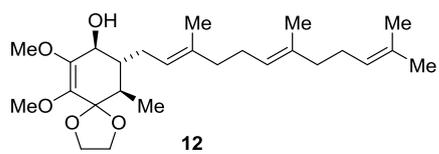


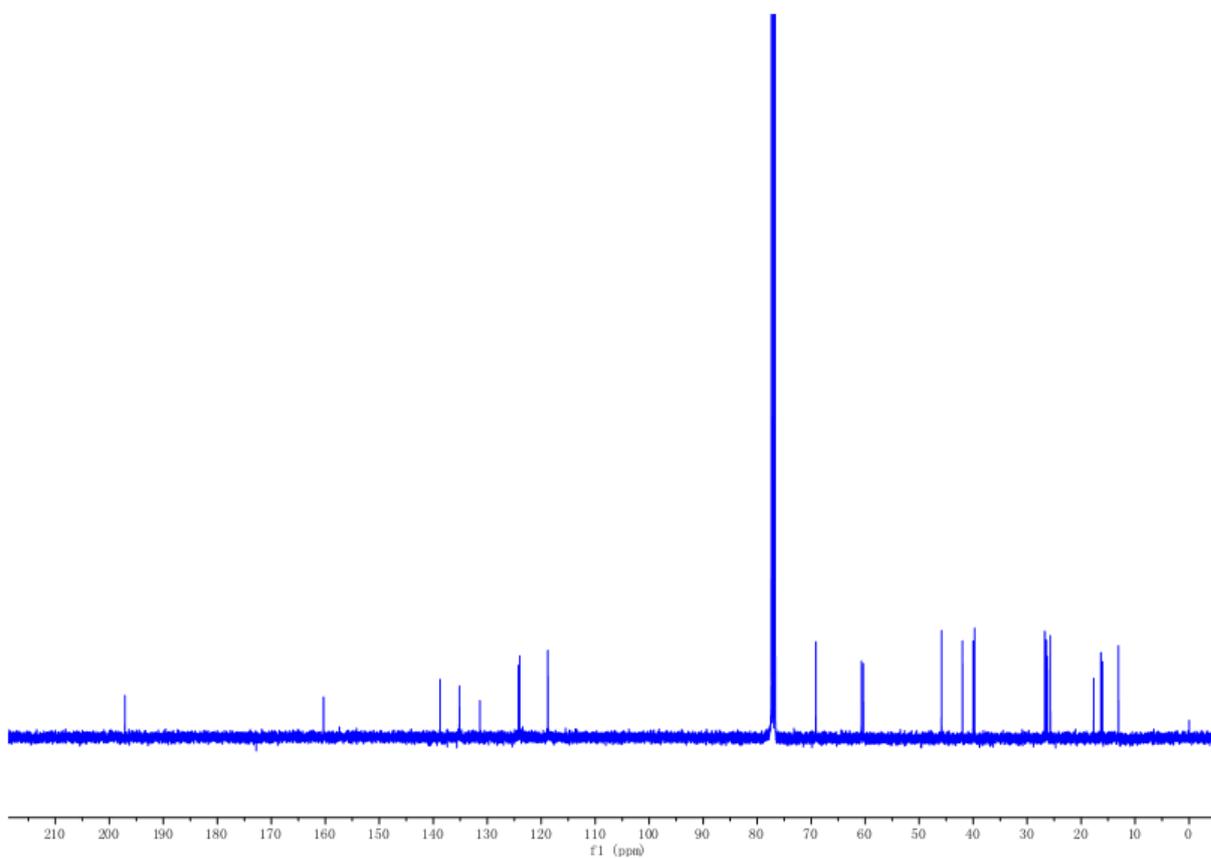
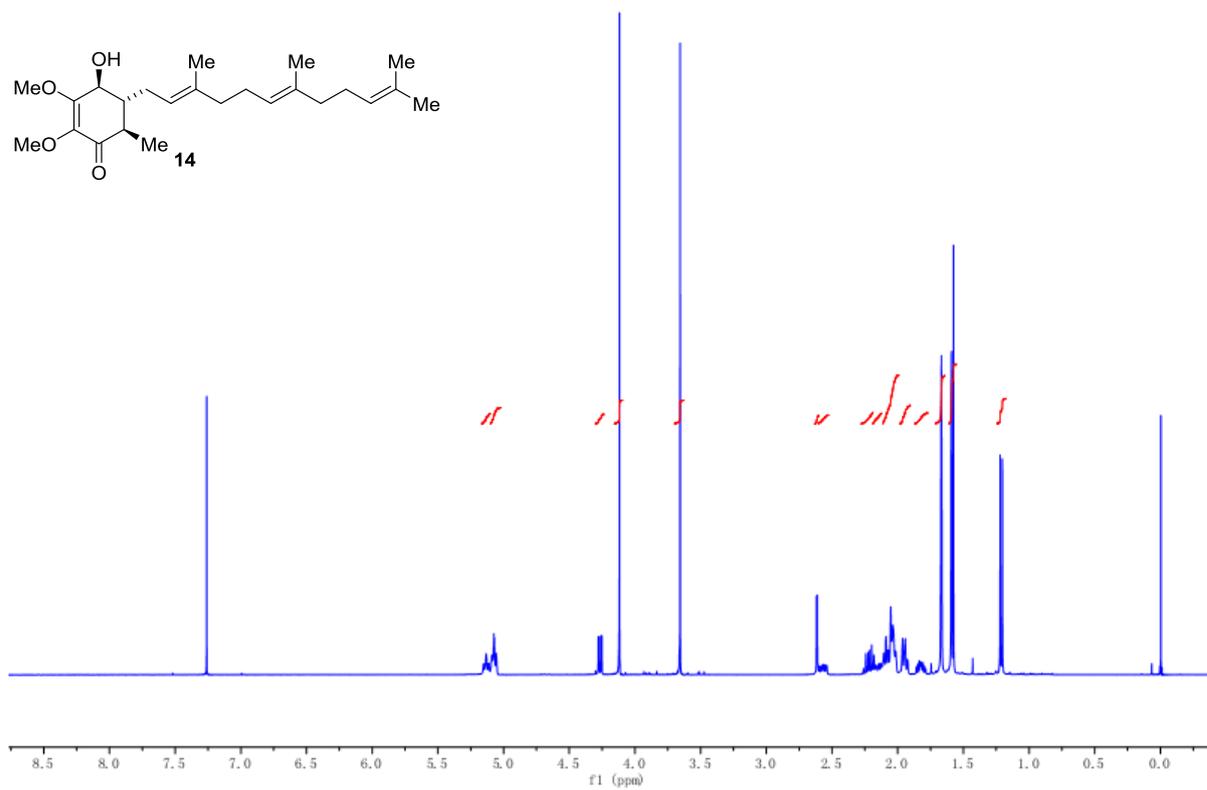
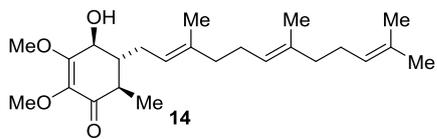






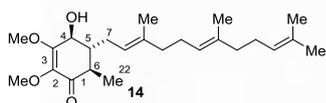
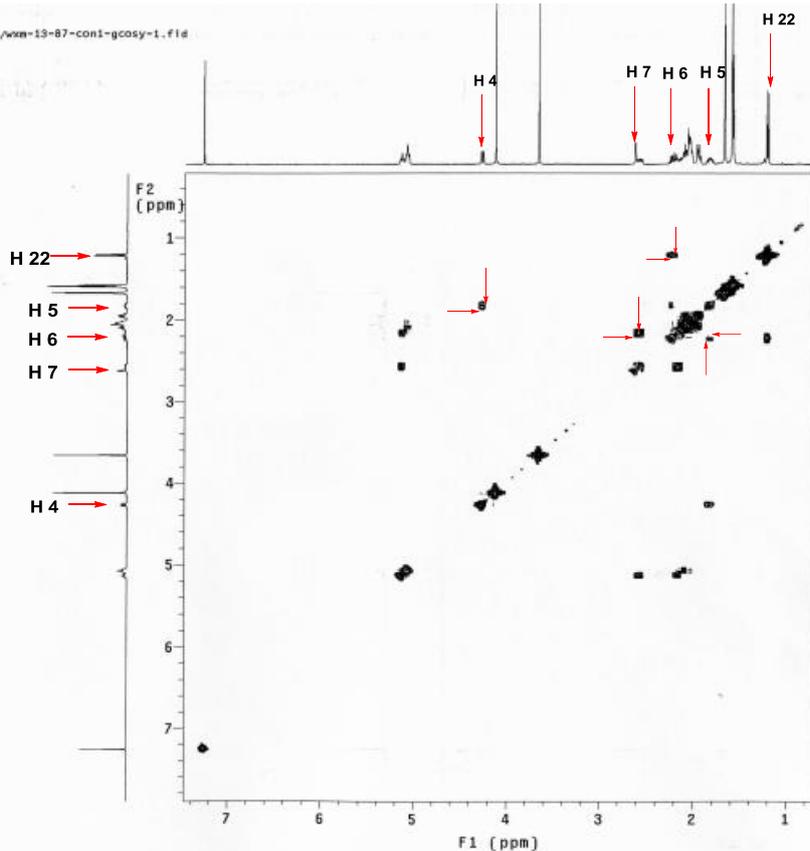




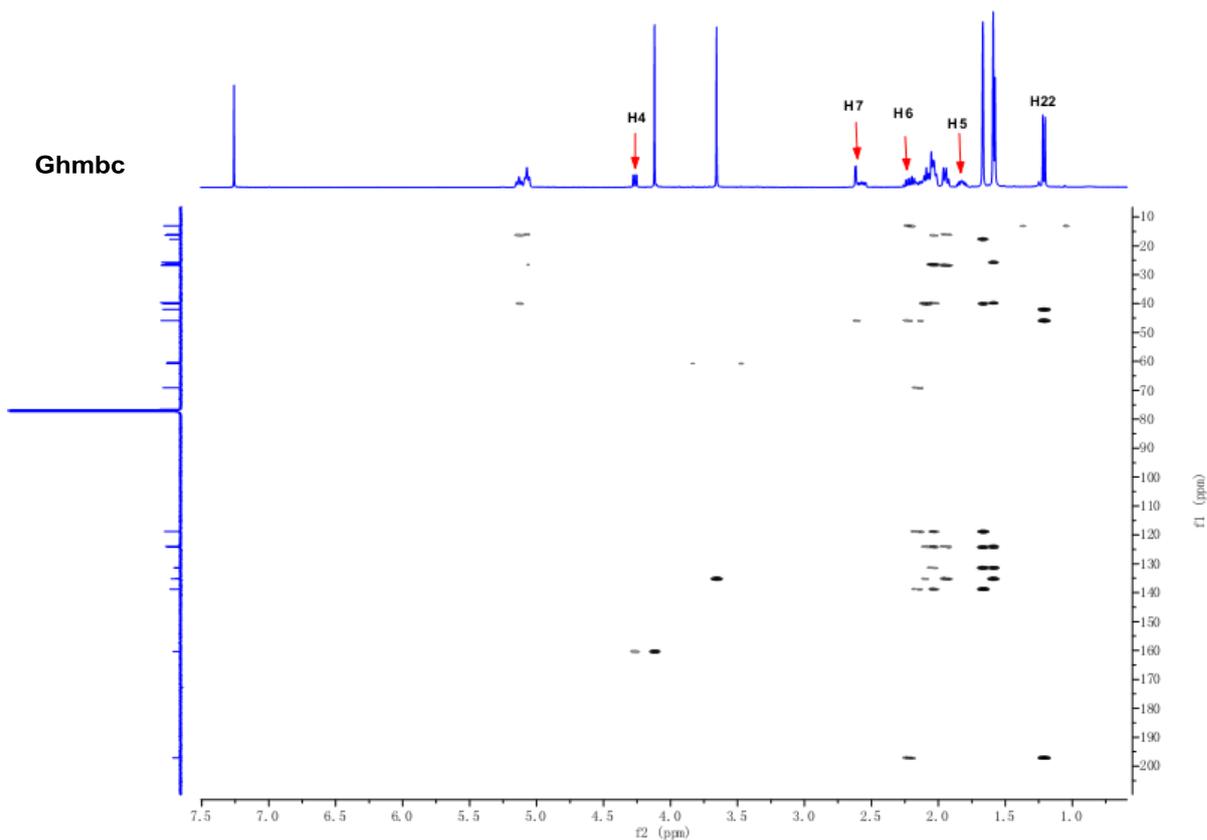


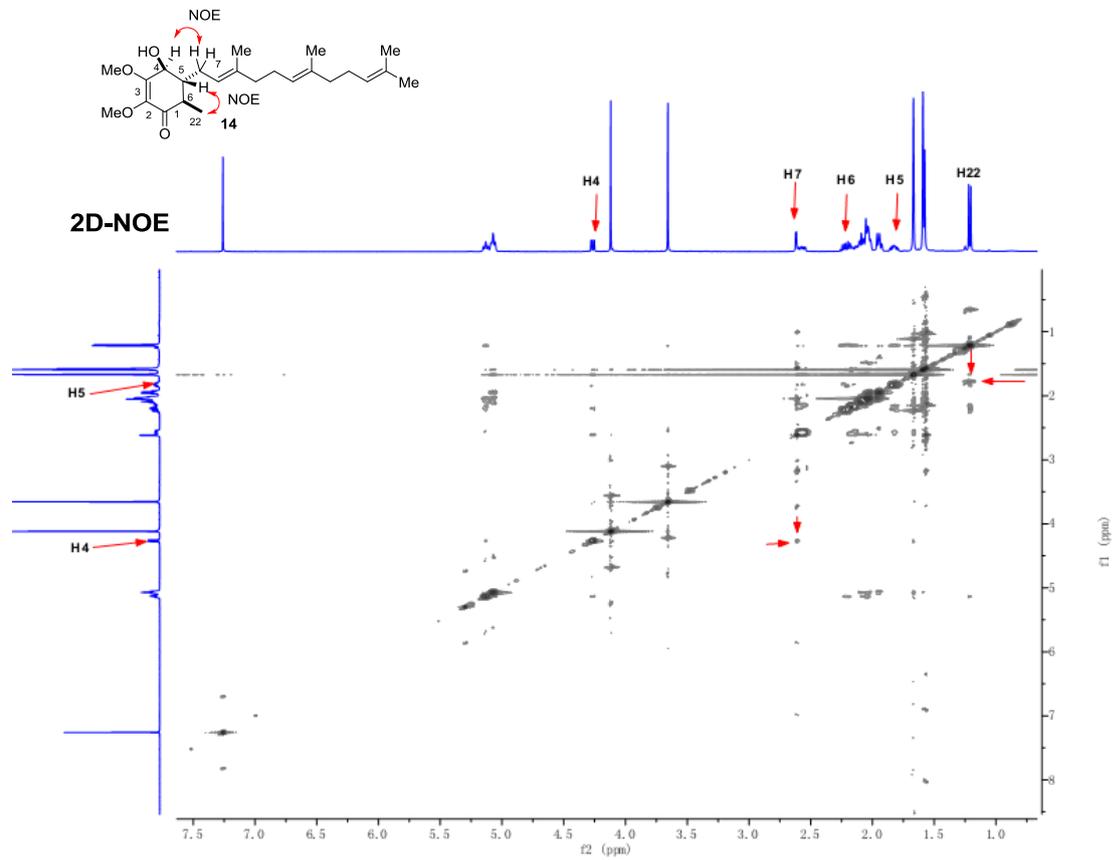
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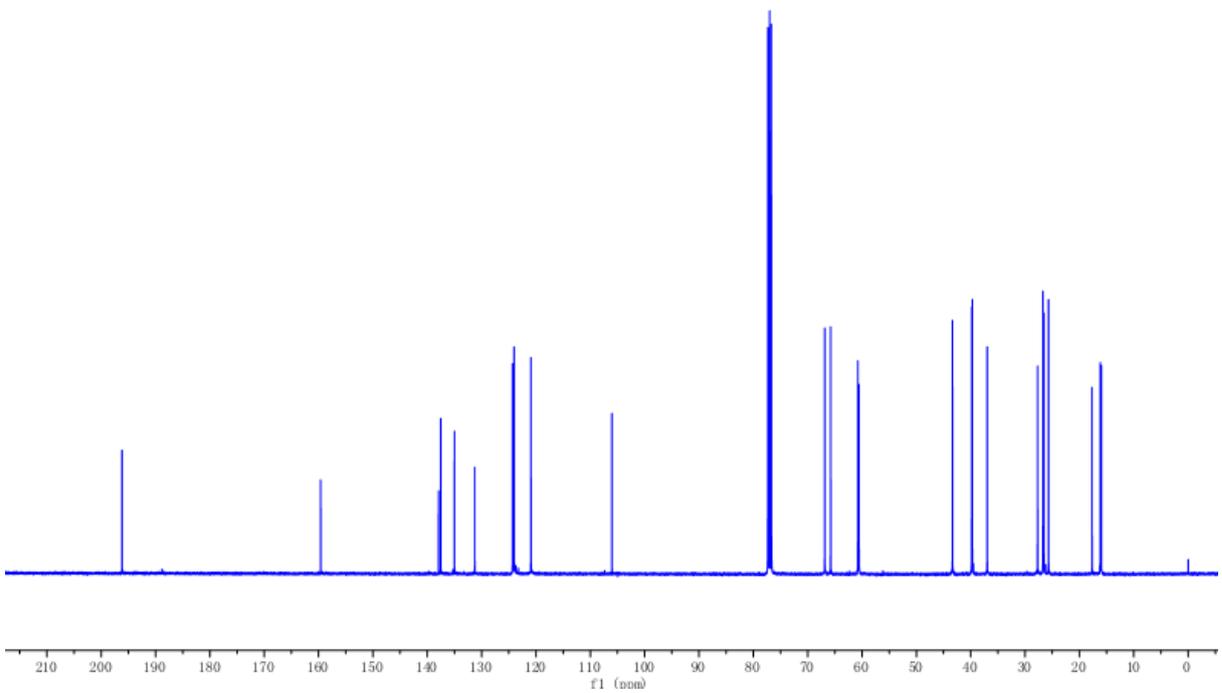
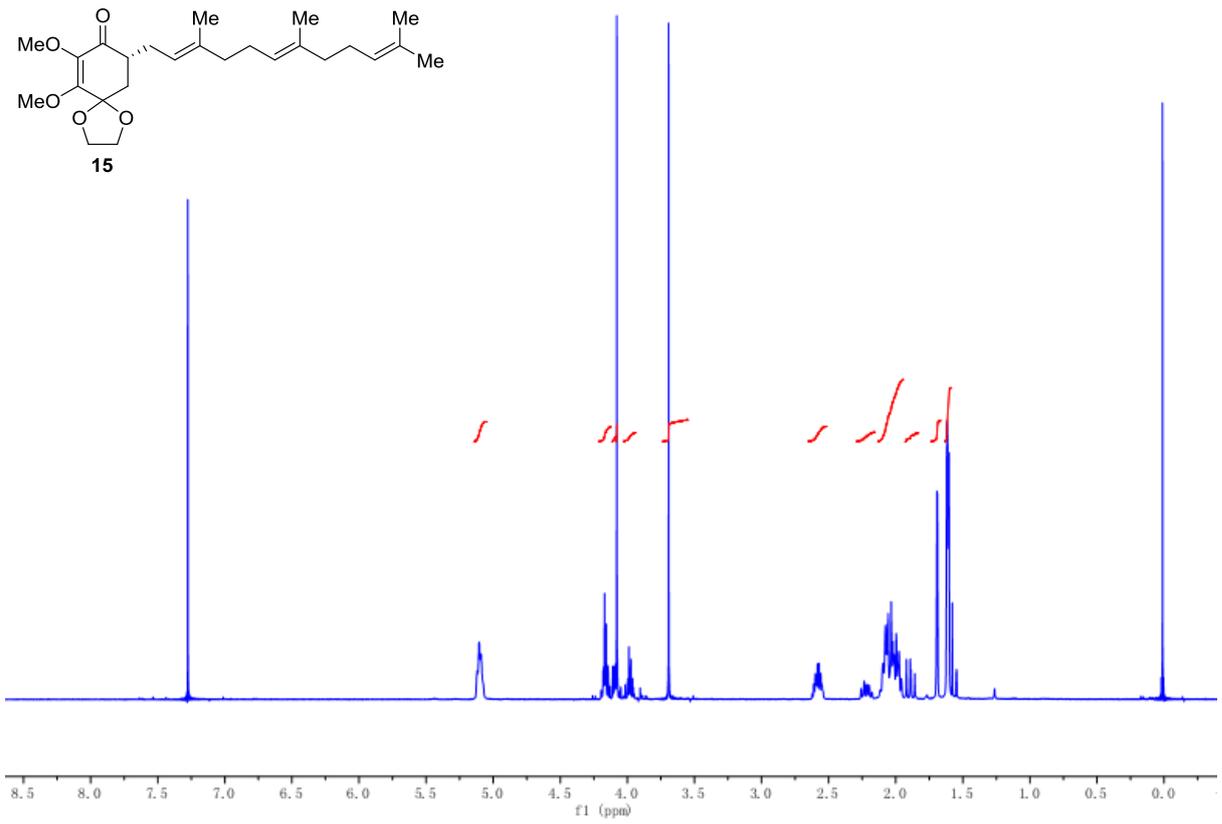
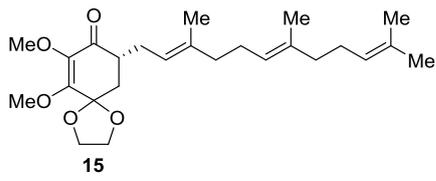
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 Solvent: cdc13
 Temp: 25.0 C / 298.1 K
 Operator: lab
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 Acq. time 0.180 sec
 Width 4095.4 Hz
 2D Width 4095.4 Hz
 4 repetitions
 512 increments
 OBSERVE H1, 400.0952476 MHz
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 Sine bell 0.080 sec
 F1 DATA PROCESSING
 Sine bell 0.038 sec
 FT size 4095 x 4095
 Total time 42 min, 13 sec

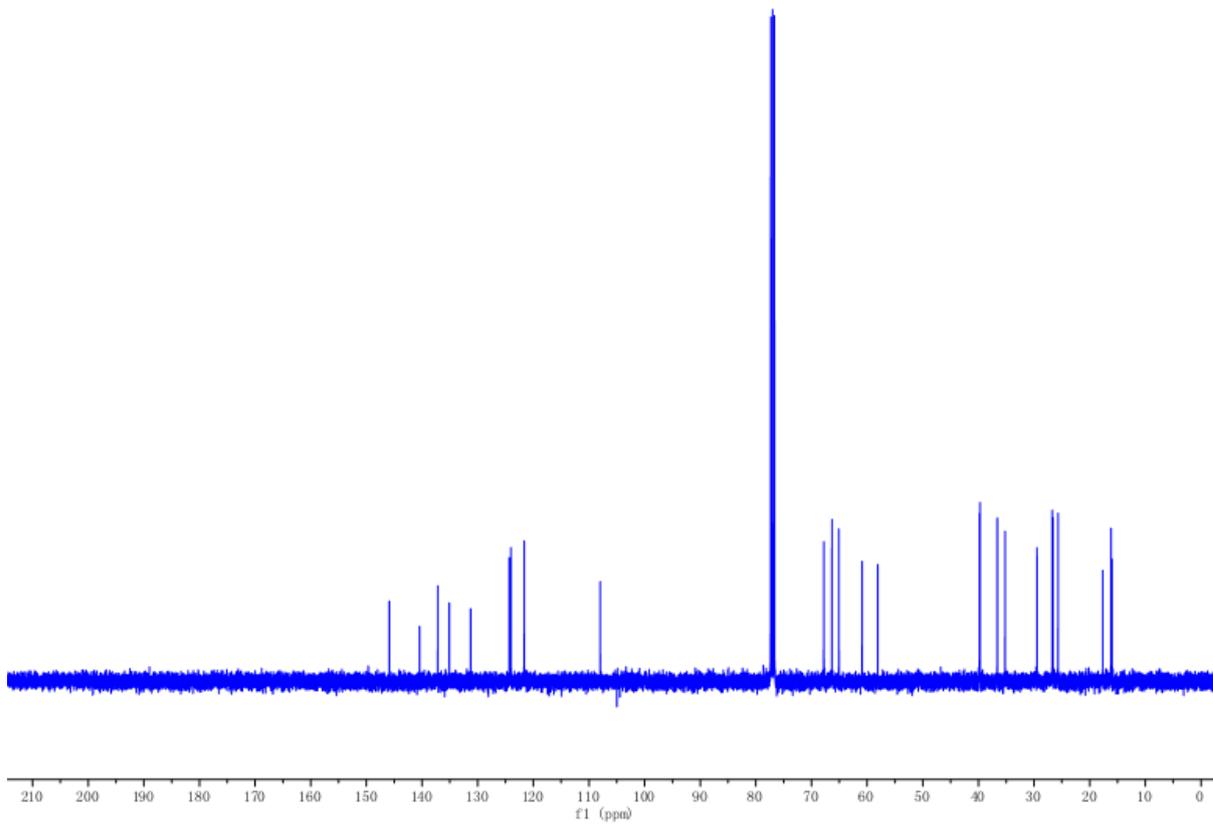
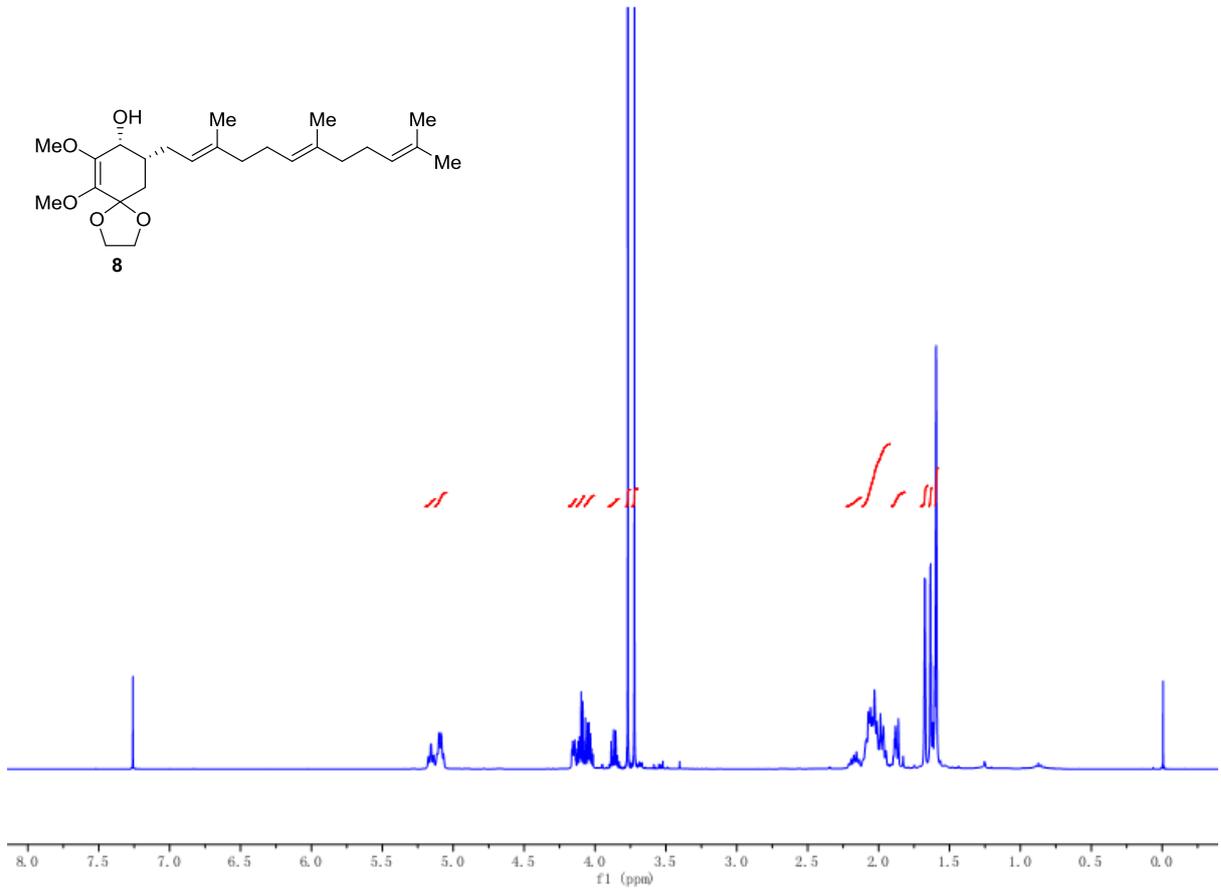
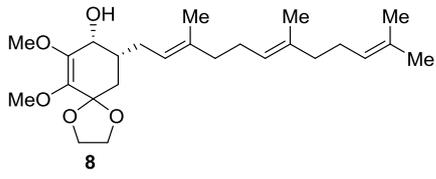


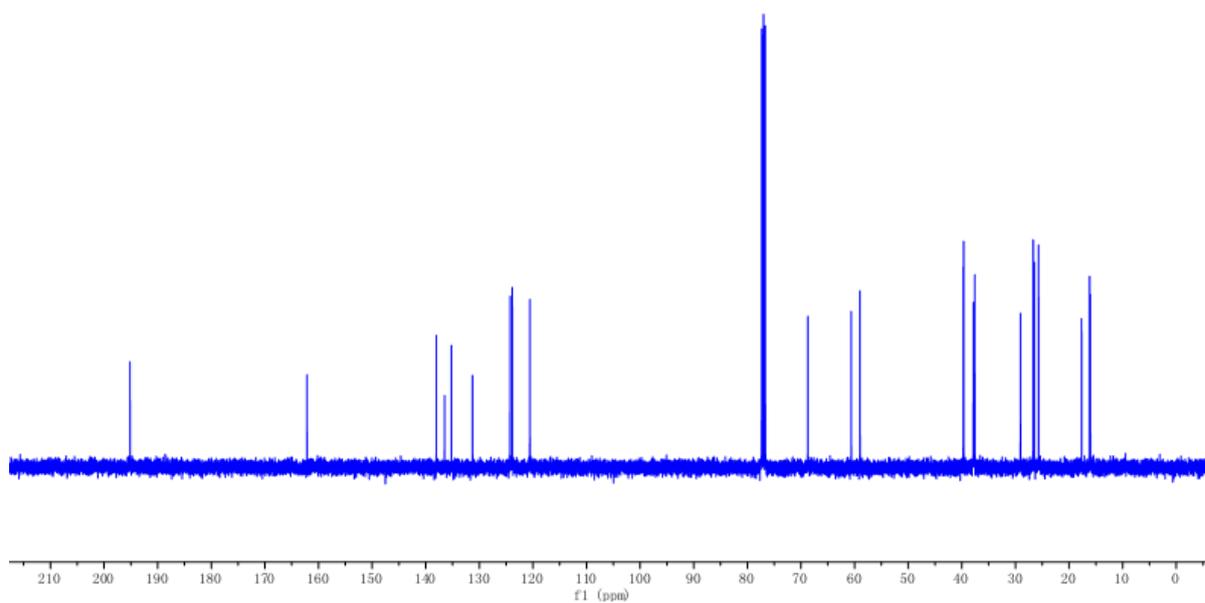
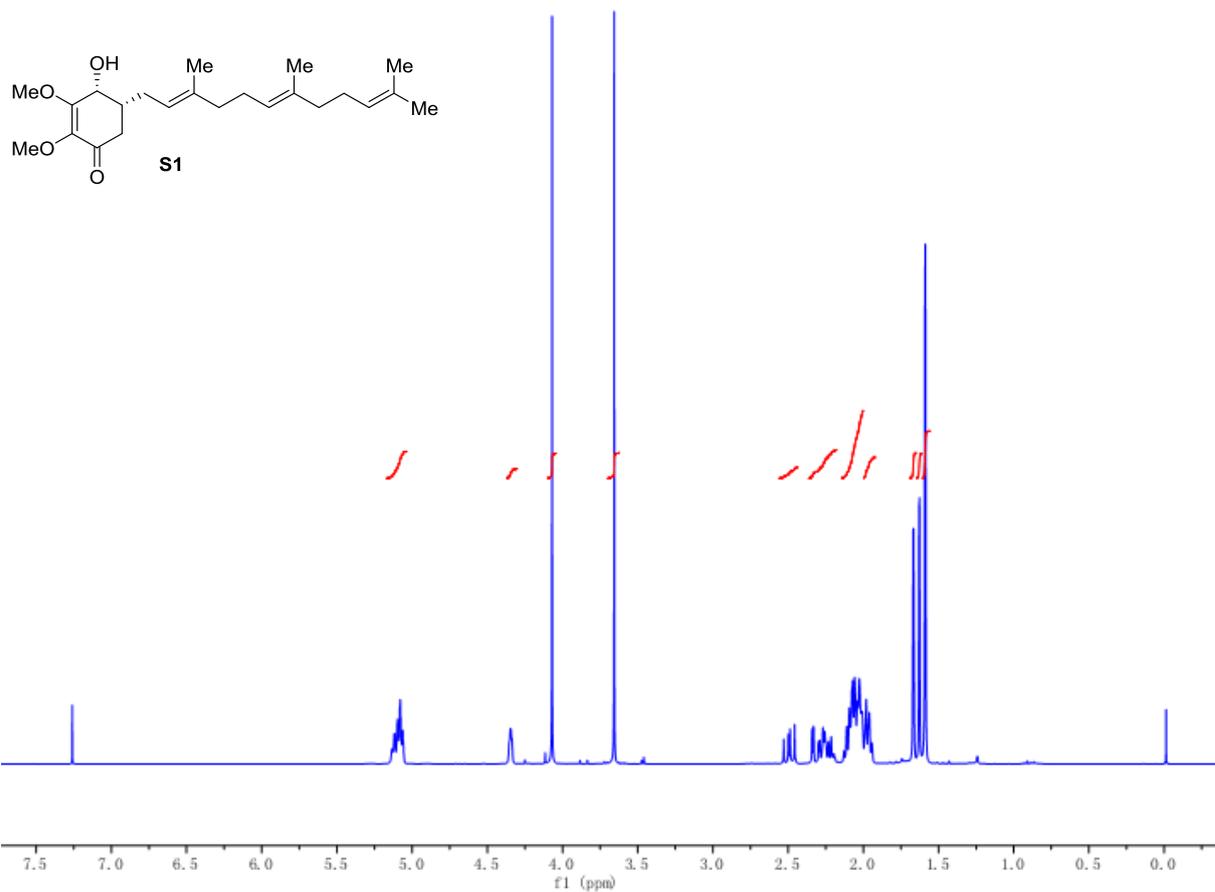
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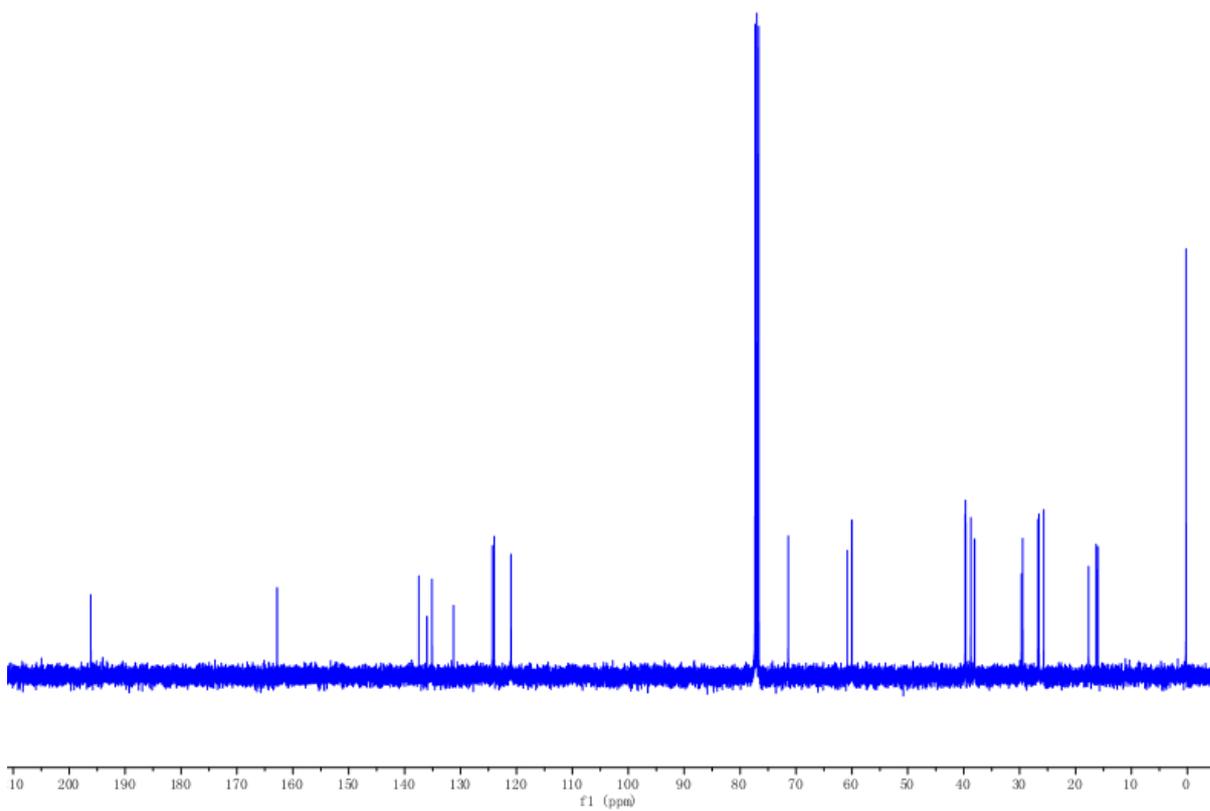
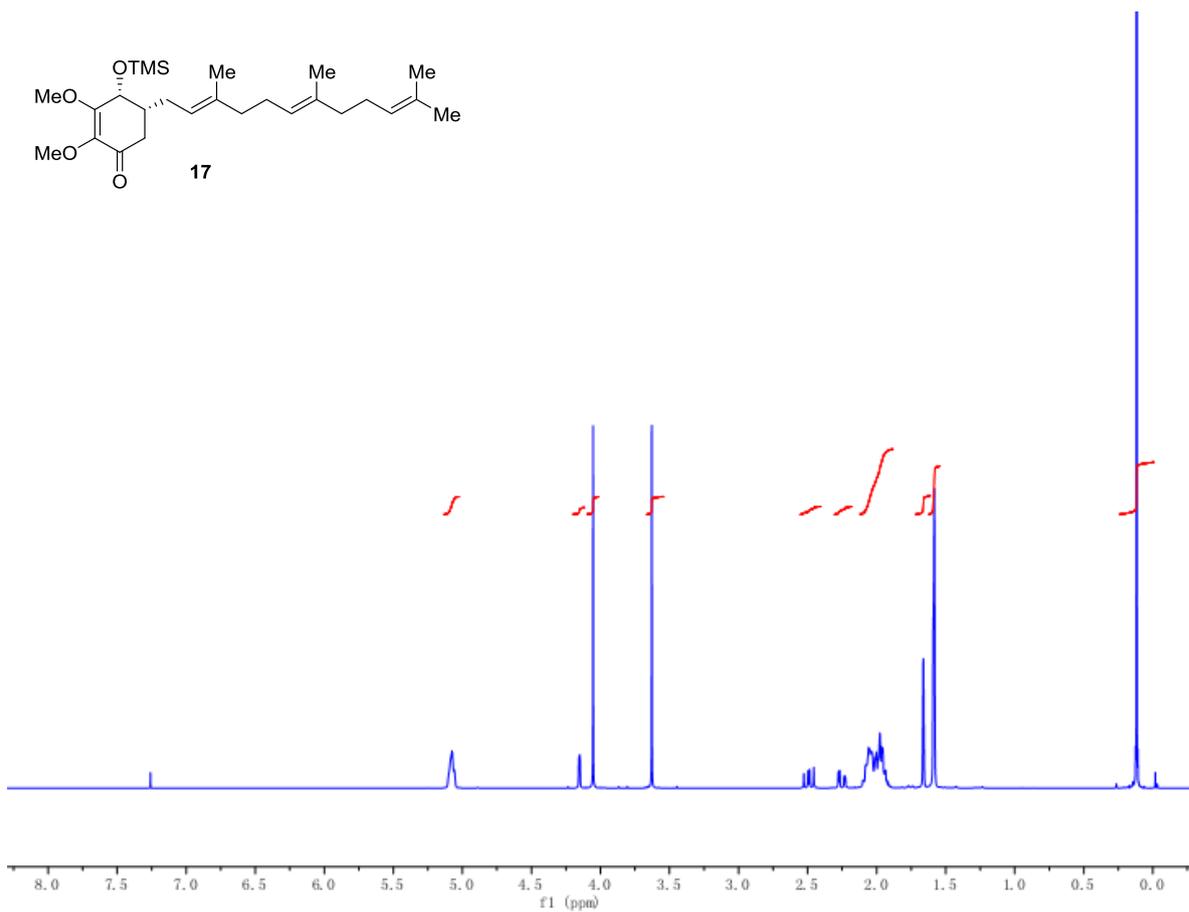
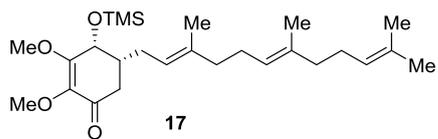


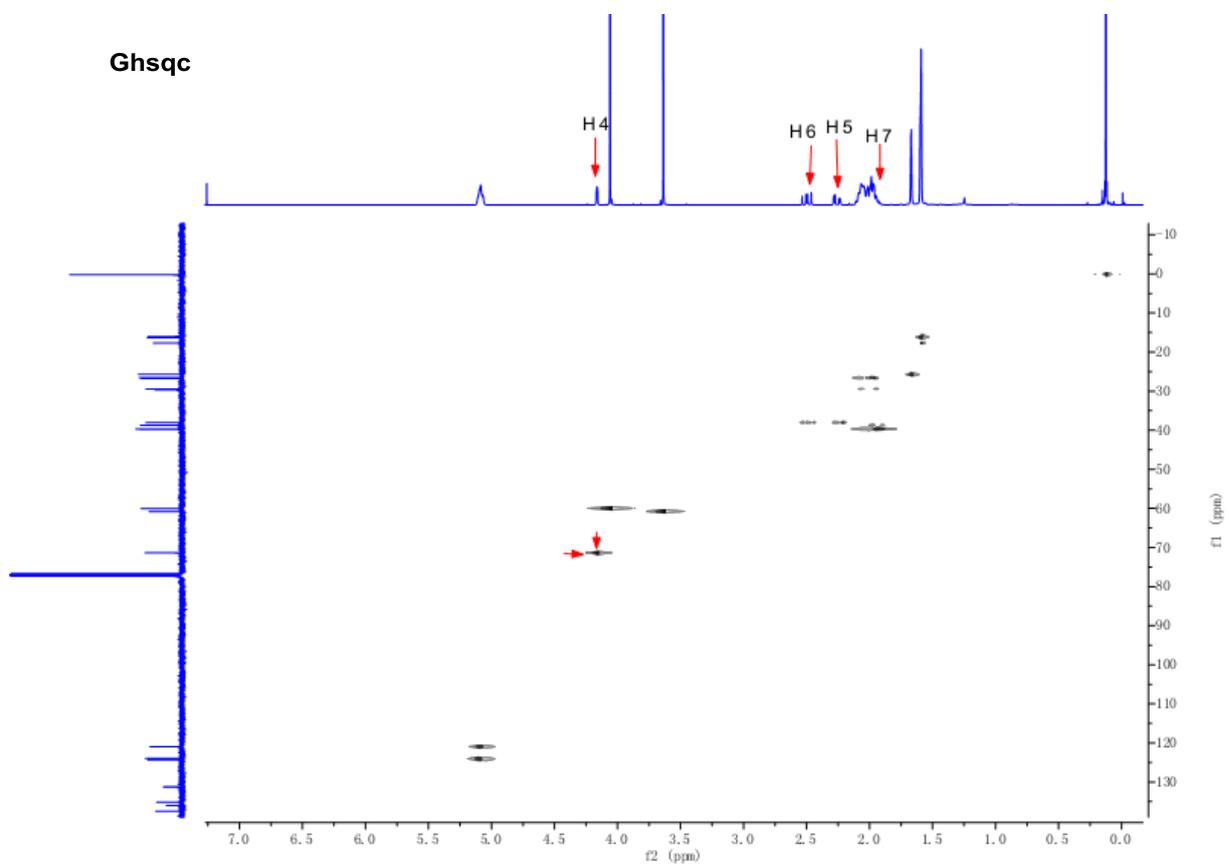
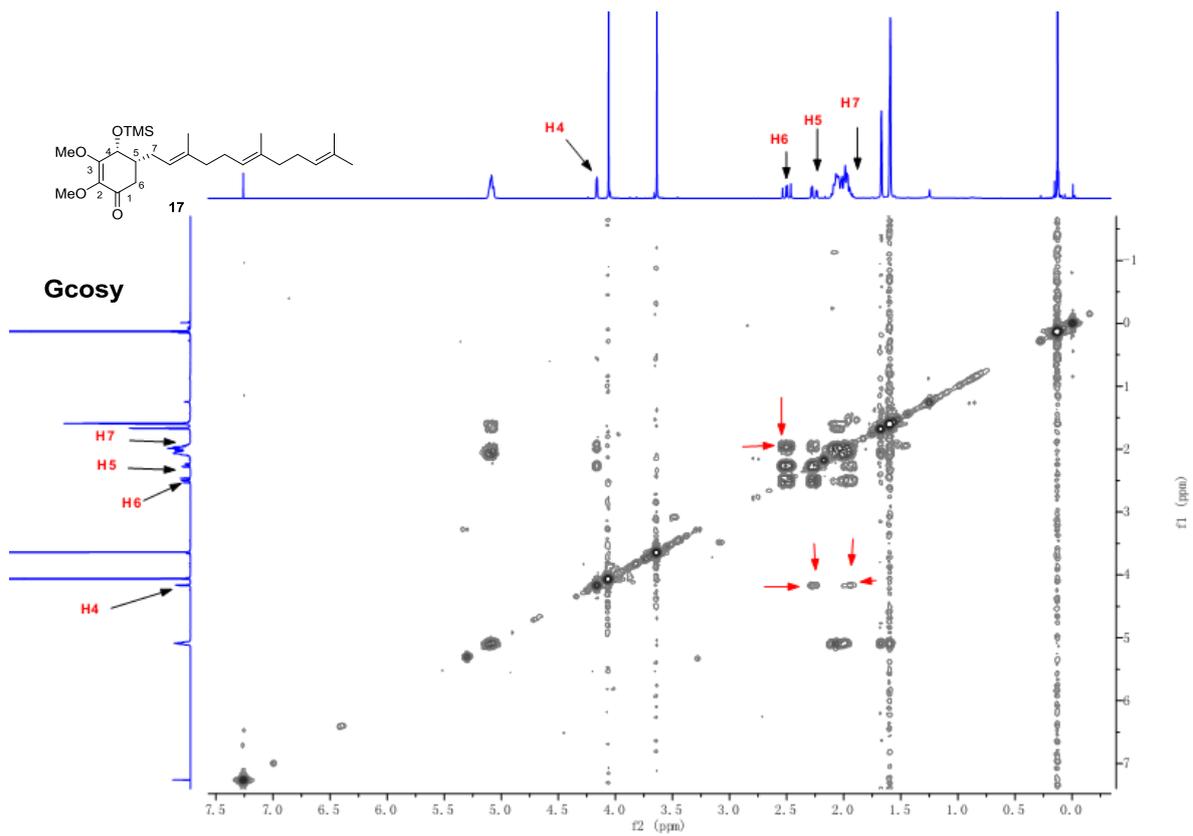


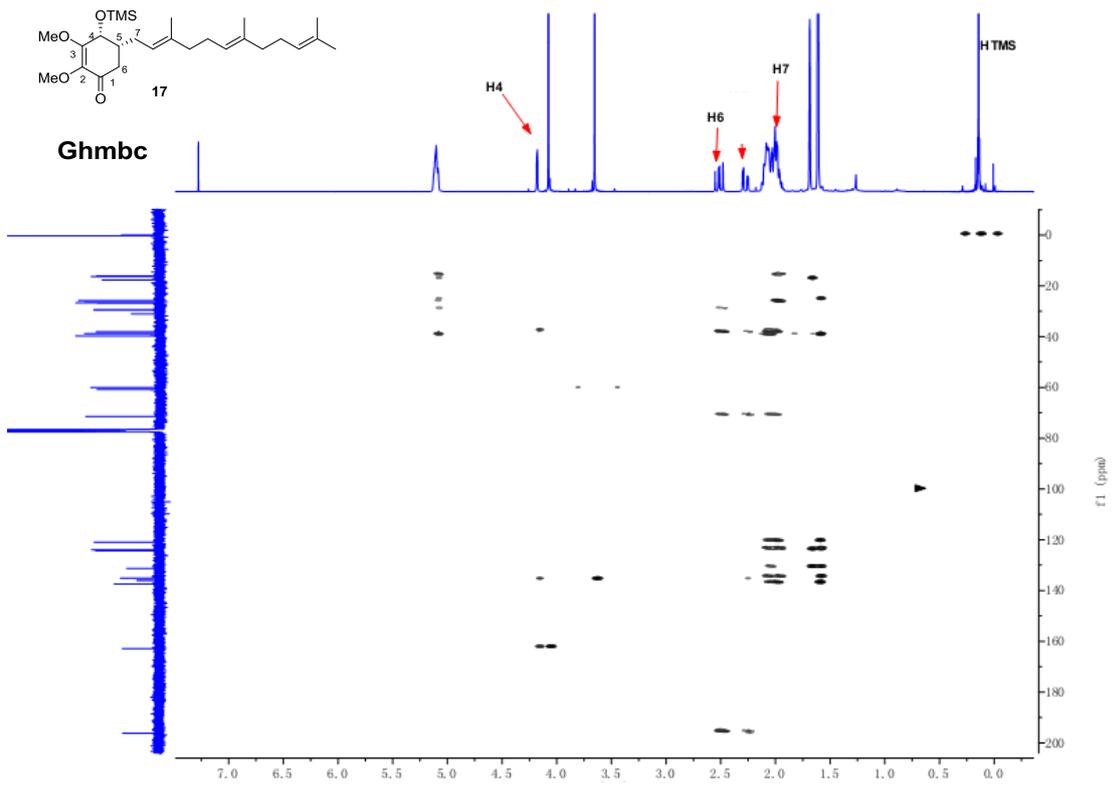






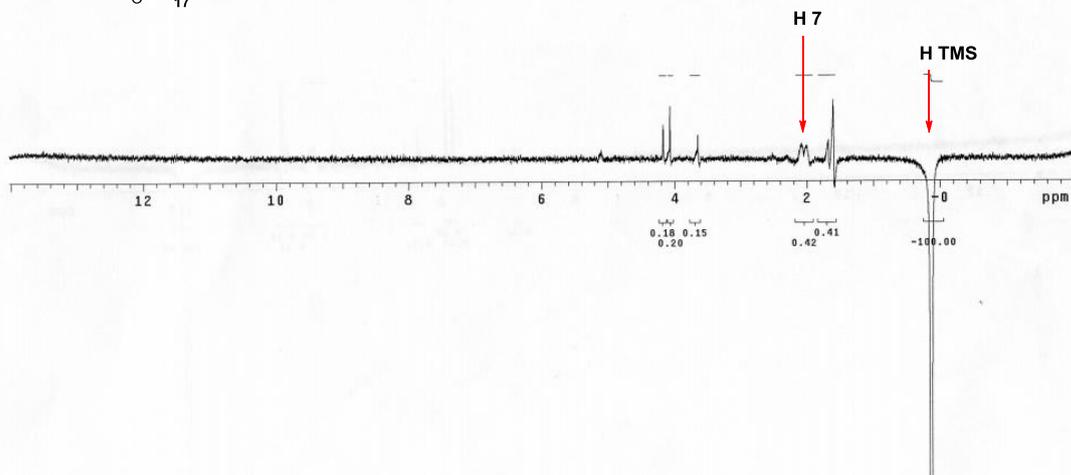
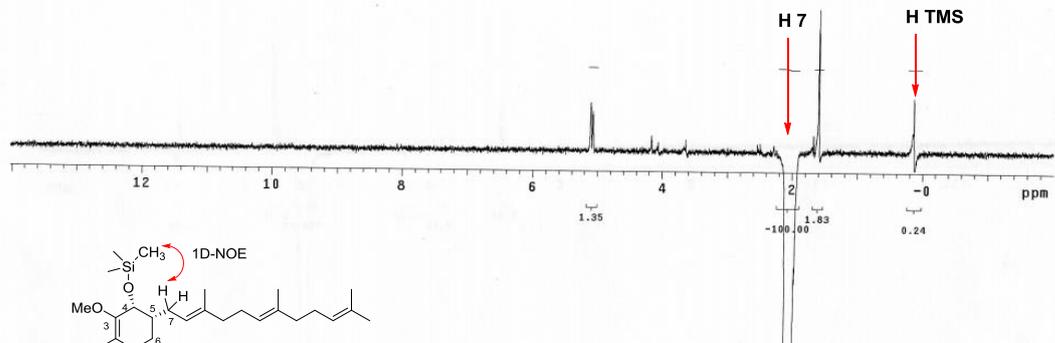


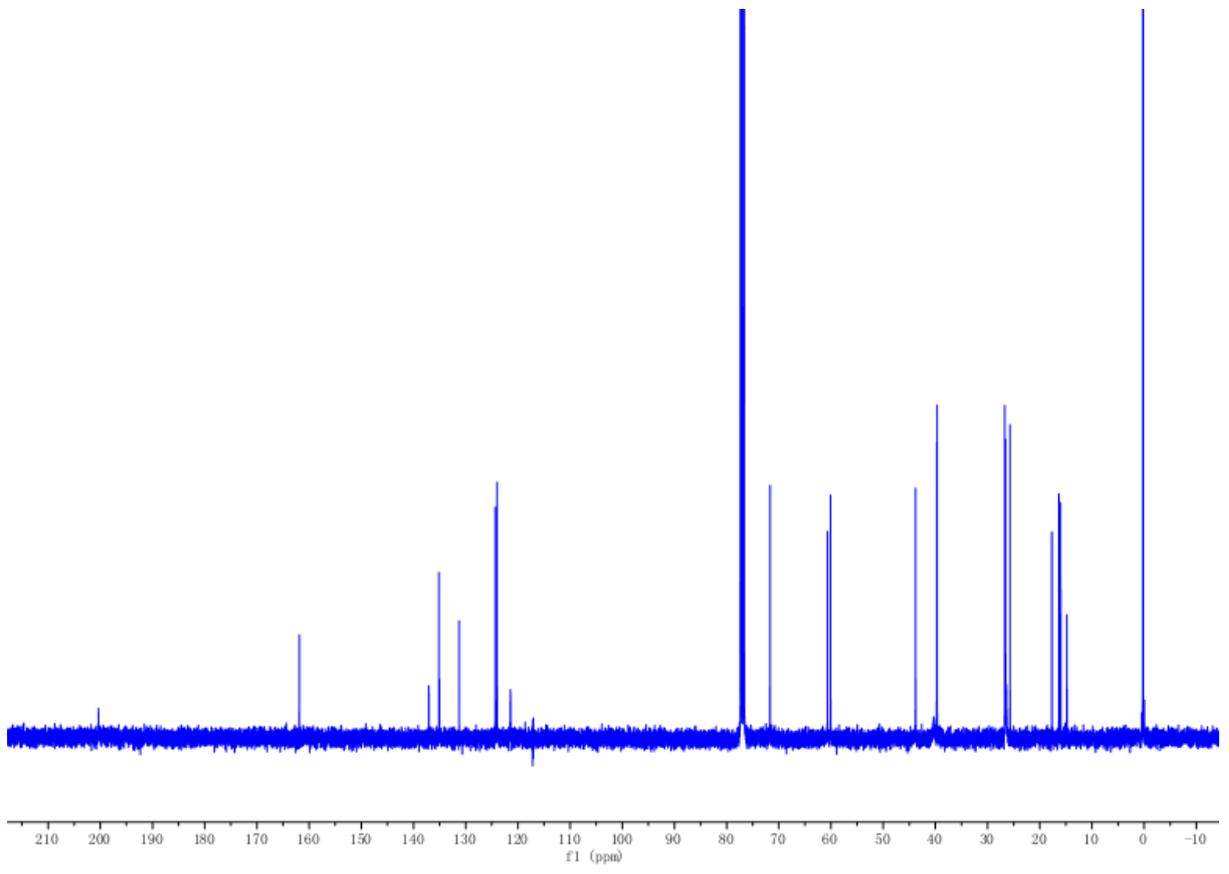
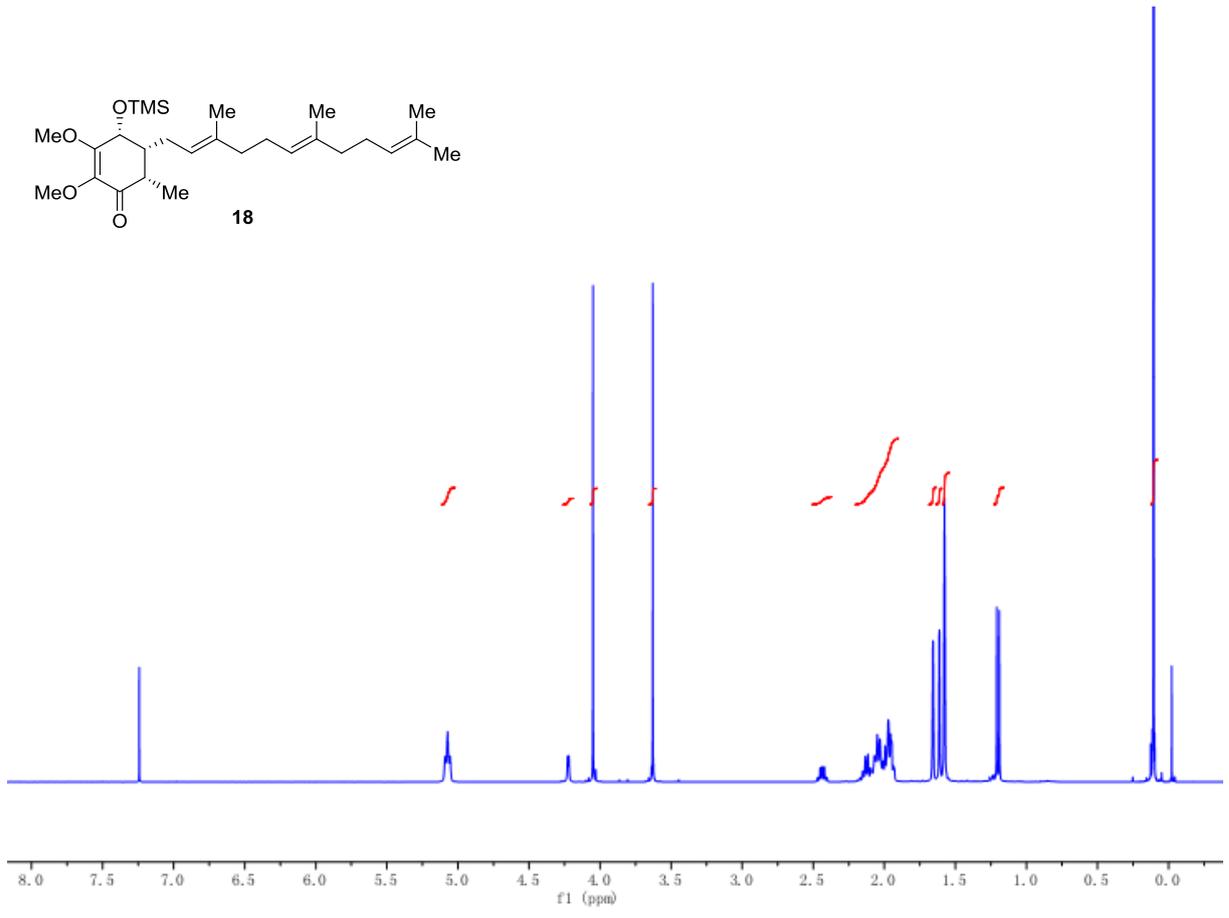
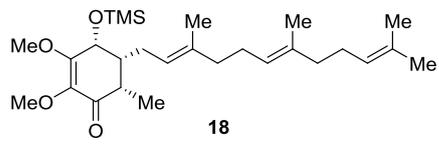


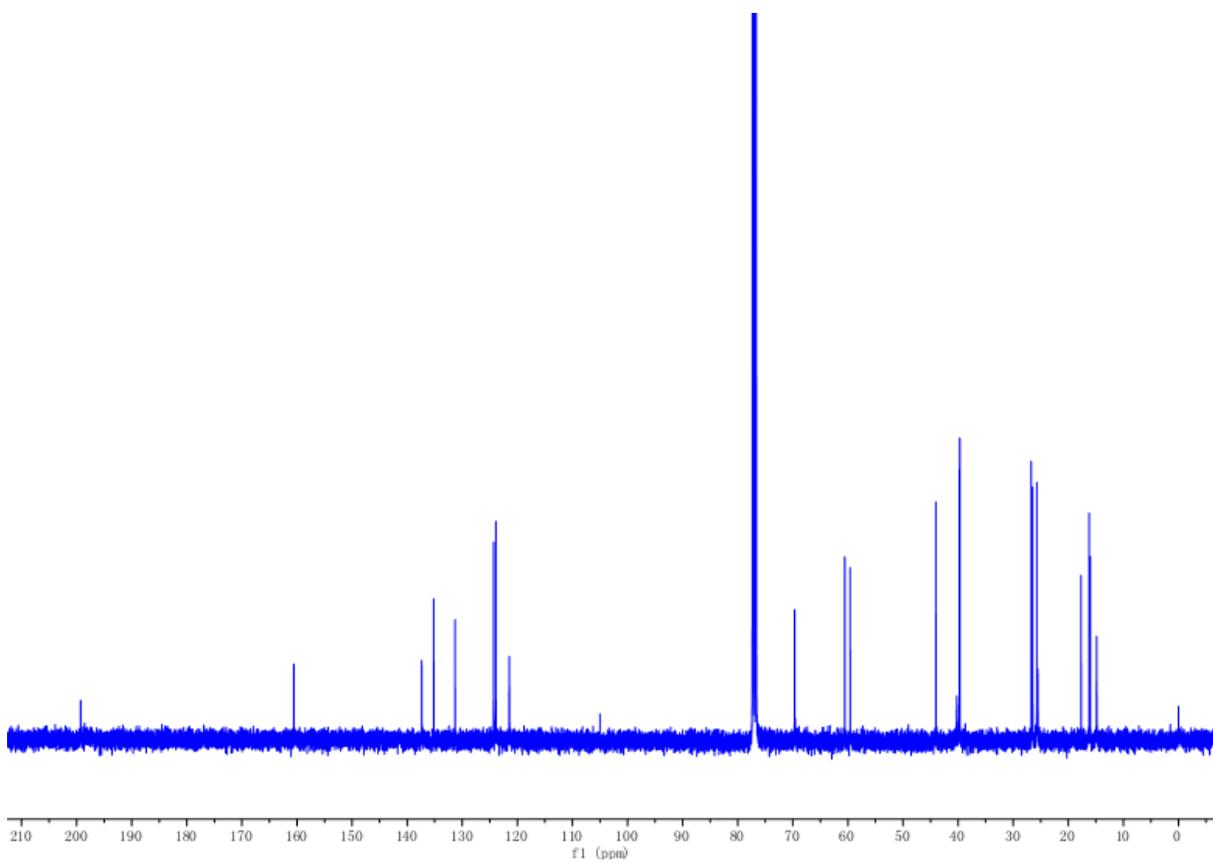
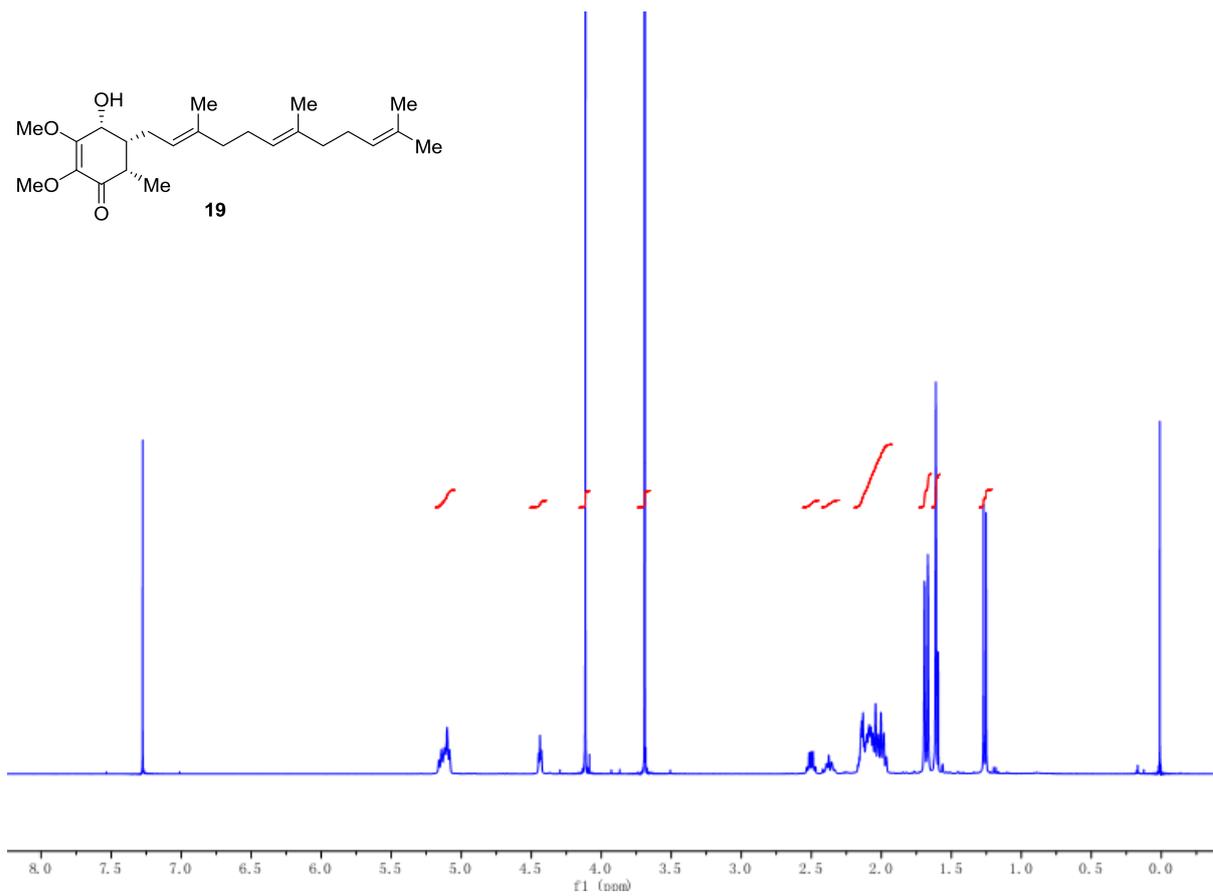
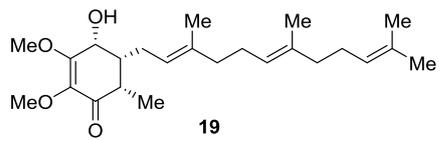


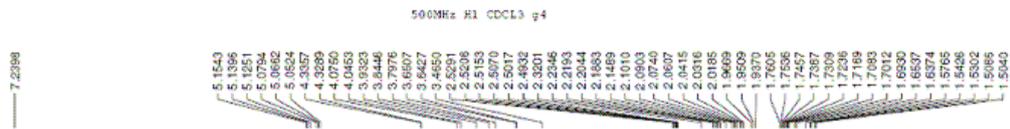
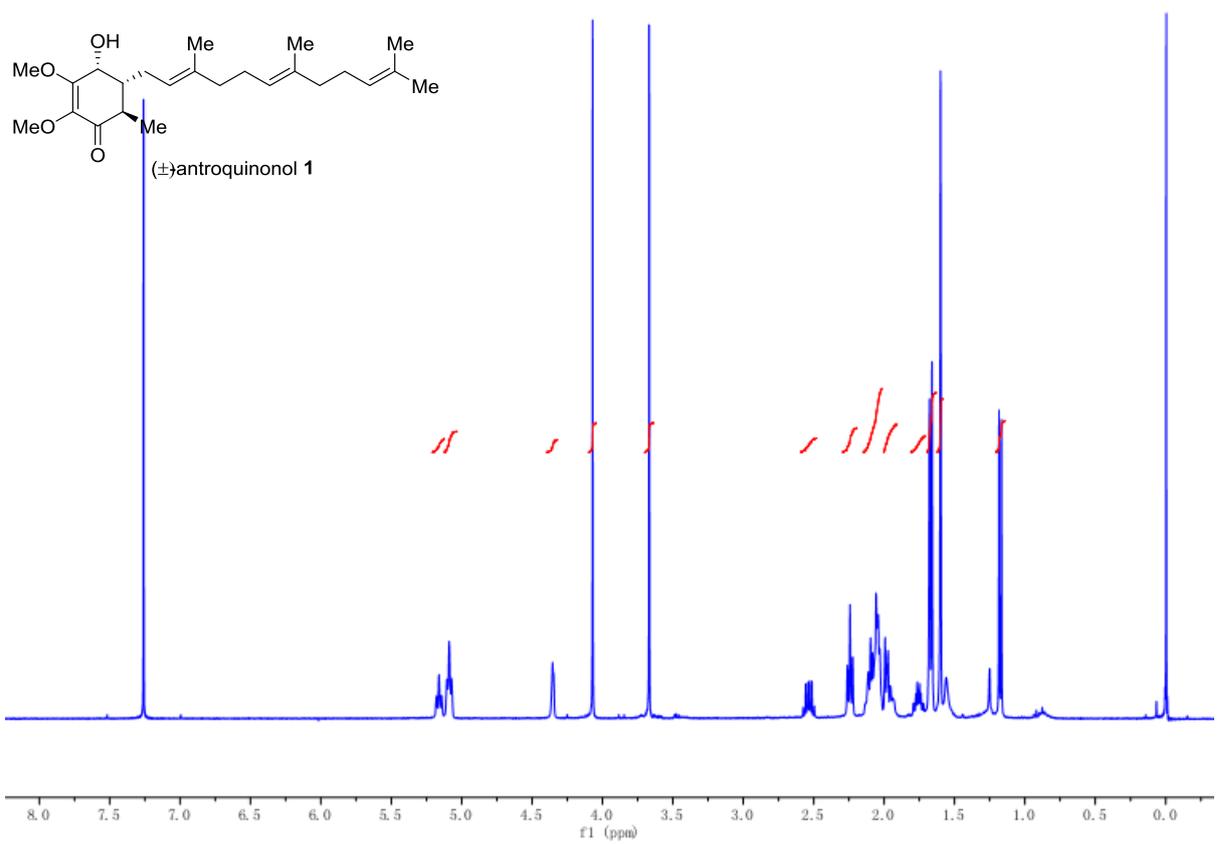
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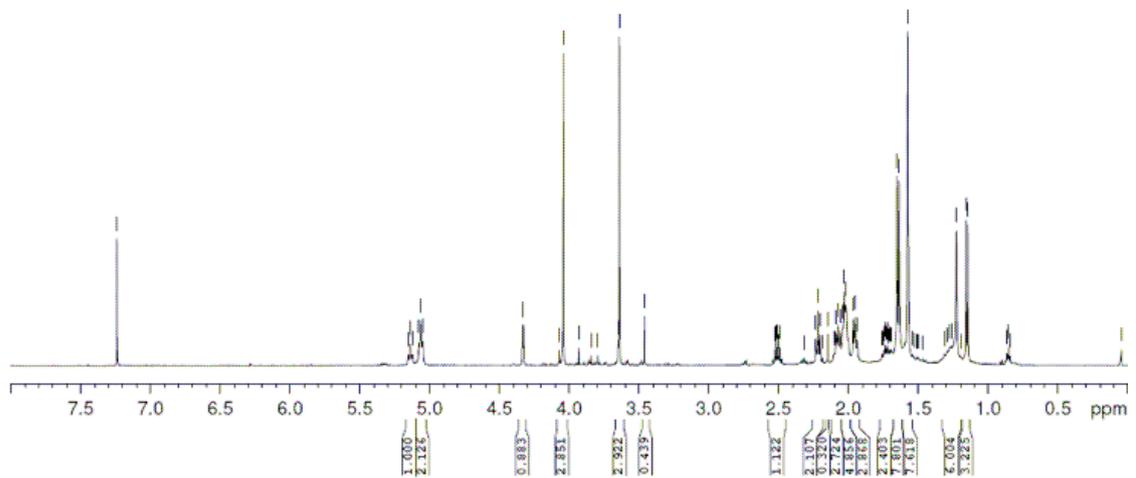


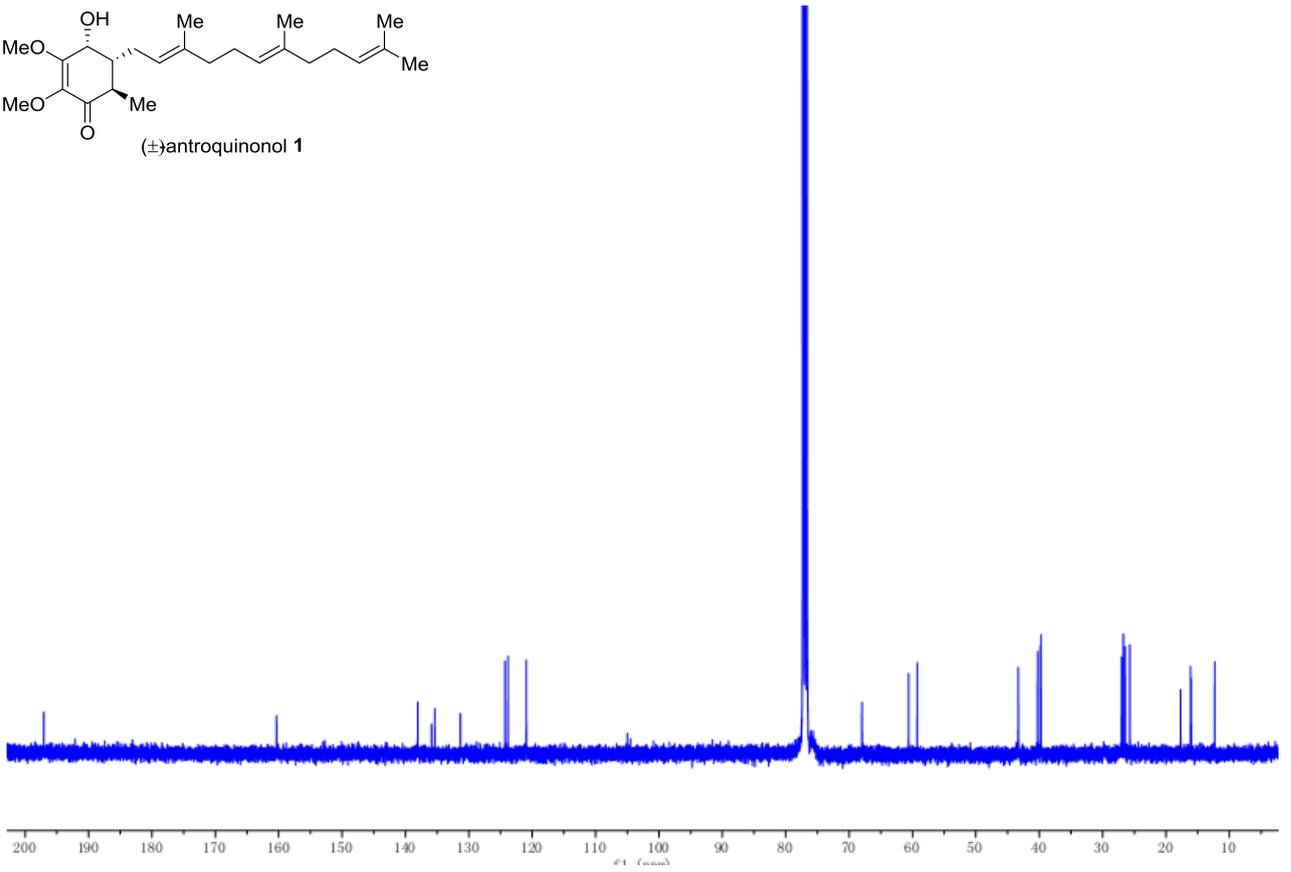
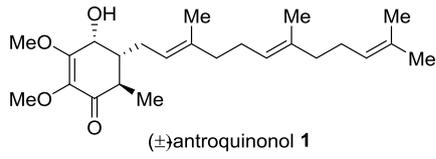






Natural product





Natural product

