Supporting Information

Formal Syntheses of (±)-Asterisca-3(15),6-diene and (±)-Pentalenene Using Rh(I)-Catalyzed [(5+2)+1] Cycloaddition

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1. General

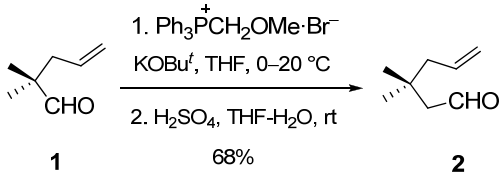
Air and moisture sensitive reactions were carried out in oven-dried glassware sealed with rubber septa under a positive pressure of dry argon. Similarly sensitive liquids and solutions were transferred via an oven-dried syringe. Reactions were stirred using Teflon-coated magnetic stir bars. Elevated temperatures were maintained using Thermostat-controlled silicone oil baths. Organic solutions were concentrated using a Büchi rotary evaporator with a desktop vacuum pump. Tetrahydrofuran, diethyl ether, and toluene were distilled from sodium and benzophenone prior to use. Dichloromethane was distilled from CaH_2 prior to use. Dioxane (extra dry, water < 50 ppm) was commercially available and used as received. Chemical reagents were used as received without further purification, unless otherwise indicated. Analytical TLC was performed with silica gel plates with a 254 nm fluorescent indicator. The TLC plates were visualized by ultraviolet light and treatment with phosphomolybdic acid stain followed by gentle heating. Purification of products was accomplished by flash chromatography on silica gel and the purified compounds show a single spot by analytical TLC.

NMR spectra were measured on Varian Mercury 200 (^{1}H at 200 MHz, ^{13}C at 50 MHz), Varian Mercury Plus 300 (^{1}H at 300 MHz, ^{13}C at 75 MHz), and Bruker ARX400 (^{1}H at 400 MHz, ^{13}C at 100 MHz) nuclear magnetic resonance spectrometers. Data for ^{1}H NMR spectra are reported as follows: chemical shift (ppm, referenced to TMS; s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, ddt = doublet of doublet of triplets, m = multiplet), coupling constant (Hz), and integration. Data for ^{13}C NMR are reported in terms of chemical shift (ppm) relative to residual solvent peak ($CDCl_3$: 77.0 ppm). Infrared spectra were recorded on an AVATAR 330 Fourier transform spectrometer (FT-IR) with an OMNI sampler and are reported in wavenumbers (cm^{-1}). Mass spectra (MS) and high-resolution mass spectra (HRMS) were recorded on VG-ZAB-HS (EI, 70 eV) and Bruker APEX IV (ESI) mass spectrometers.

Abbreviations:
THF = tetrehydrofuran
*m*CPBA = 3-chloroperoxybenzoic acid
PCC = pyridinium chlorochromate
PTSA = 4-methylbenzenesulfonic acid

2. Experimental Procedures and Characterization Data

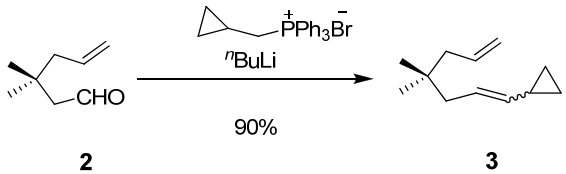
3,3-dimethylhex-5-enal (2)



1 68% **2**

To a stirred suspension of (methoxymethyl)triphenylphosphonium bromide (76.34 g, 223 mmol) in 350 mL of anhydrous THF was slowly added a solution of KOBu^t (26.09 g, 233 mmol) in THF (300 mL) at 0 °C via cannula under argon. The resulting cherry-red solution was stirred at 0 °C for another 1 h. A solution of 2,2-dimethylpent-4-enal (**1**, 14.01 g, 125 mmol) in THF (100 mL) was added dropwise within 20 min, and the resulting mixture was stirred at 20 °C for 2 h. The reaction was quenched by addition of water (10 mL) and the reaction mixture turned from light cherry-red to yellow. The reaction mixture was evaporated under reduced pressure in a water bath (35 °C) to a volume of ca. 300 mL, then aqueous 30% H_2SO_4 (60 mL) was added at room temperature under stirring. When GC indicated the disappearance of the enol ether, saturated $NaHCO_3$ (200 mL) was added. The reaction mixture was extracted with ether and the combined organic extract was washed with water, dried over $MgSO_4$, and concentrated to give a light yellow oil. Flash column chromatography on silica gel (eluted with pentane/ether 30:1) gave aldehyde **2** (10.66 g, 68%) as a colorless oil. Spectroscopic data of **2** was identical to that reported.[1]

(*E*)-(4,4-dimethylhepta-1,6-dienyl)cyclopropane (3)

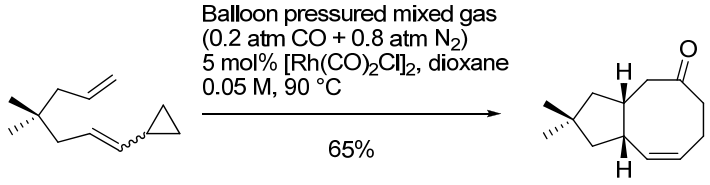


2 90% **3**

To a stirred suspension of (cyclopropylmethyl)triphenylphosphonium bromide (3.58 g, 9 mmol) in 40 mL of anhydrous THF was slowly added a solution of ^{n}BuLi (3.8 mL, 2.5 M，9.5mmol) at 0 °C via cannula under argon. The resulting cherry-red solution was stirred at 0 °C for another 30 min. A solution of 3,3-dimethylhex-5-enal (**2**, 990 mg, 6 mmol) in THF (10 mL) was added dropwise within 10 min, and the resulting mixture was stirred at 0 °C for 4 h. The reaction was quenched by addition of saturated aqueous solution of ammonium chloride (6 mL) and the reaction mixture turned from light cherry-red to light yellow. The reaction mixture was evaporated under reduced pressure in a water bath (15 °C) to a volume of ca. 10 ml. The mixture was diluted with ether, washed successively with brine, dried over $MgSO_4$, and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with pure petroleum ether 30-60 °C) to afford **3** (*Z*/*E* = 1:1.3, determined by ^{1}H NMR) as a colorless oil (1.16 g, 90%).

Z-isomer: ^{1}H NMR (200 MHz, $CDCl_3$): 0.28-0.34 (m, 2H), 0.67-0.76 (m, 2H), 0.90 (s, 6H), 1.47-1.68 (m, 1H), 1.99 (d, *J* = 6.8 Hz, 2H), 2.07 (d, *J* = 7.6 Hz, 2H), 4.83 (t, *J* = 10.2 Hz, 1H), 4.98-5.06 (m ,2H), 5.37 (dt, *J* = 10.5, 8.0 Hz, 1H), 5.86 (ddt, *J* = 7.5, 18.8, 7.6 Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): 135.9, 135.8, 124.5, 116.8, 46.3, 39.4, 34.2, 26.7, 9.7, 6.8. FT-IR: ν = 3078, 2959, 2927, 1639, 1468, 1384, 1045, 936, 912 cm^{-1}. MS (EI): m/z (%) = 164 (M^+, 5), 149 (10), 123 (10), 108 (12), 83 (65), 81 (70), 67(42), 55 (100), 41 (35). HRMS (EI): $C_{12}H_{20}$, calcd 164.1565, found 164.1566.

(±)-(1*R*, 8*R*)-10,10-dimethylbicyclo[6.3.0]undec-6-en-3-one (4)

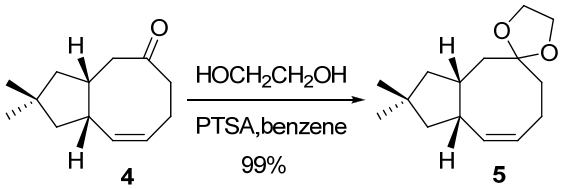


3 4

$[Rh(CO)_2Cl]_2$ (47 mg, 0.12 mmol) was charged in a base-washed, oven-dried Schlenk flask under an atmosphere of nitrogen, and then a solution of the *Z*/*E* mixture of ene-VCP substrate **3** (400 mg, 2.4 mmol) in degassed dioxane (50 mL) was added. The solution was bubbled with the mixed CO gas (0.2 atm CO + 0.8 atm N_2) for 5 min. The reaction mixture was then stirred at 90 °C under the same mixed CO gas for 120 h. After being cooled to room temperature, the mixture was concentrated and the residue was purified by flash column chromatography on silica gel (eluted with petroleum ether/ethyl acetate 80:1) to afford the cycloaddition product **4** (304 mg, 65%) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): 1.0 (s, 3H), 1.12 (s, 3H), 1.16-1.20 (m, 1H), 1.48-1.53 (m, 2H), 1.81 (dd, J = 7.9, 13.6 Hz, 1H), 2.17-2.34 (m, 4H), 2.42-2.55 (m, 3H), 2.74-2.82 (m, 1H), 5.47 (t, J = 9.5 Hz, 1H), 5.82-5.91 (m, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$): 214.2, 135.4, 128.2, 47.5, 47.4, 46.2, 43.9, 40.3, 39.6, 37.6, 31.6, 31.4, 23.5. FT-IR: ν = 2951, 2930, 2865, 1701, 1383, 1365 cm^{-1}. MS (EI): m/z (%) = 192 (M^+, 50), 177 (50), 151 (40), 135 (30), 107 (40), 93 (50), 83(100), 55 (65). HRMS (EI): $C_{13}H_{20}O$, calcd 192.1514, found 192.1516.

(±)-(*Z*)-(1*R*,8*R*)-10,10-dimethylbicyclo[6.3.0]undec-6-en-3-one ethylene glycol ketal (5)

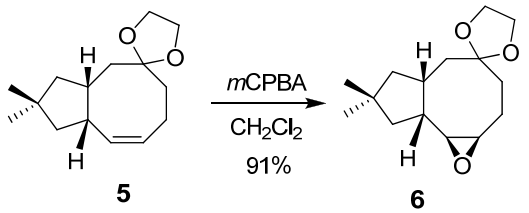


4 5

To a stirred solution of **4** (800 mg, 4.2 mmol) in 35 mL of benzene was added glycol (9.4 mL, 168 mmol) and PTSA·H_2O (160 mg, 0.84 mmol). The resulting mixture was refluxed for 20 h. Then the reaction was cooled to room temperature and diluted with Et_2O, quenched by addition of 5 mL aqueous $NaHCO_3$. The aqueous layer was separated and the organic phase was washed successively with saturated aqueous $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with petroleum ether/ethyl acetate 50:1) to afford **5** (968 mg, 99%) as a colorless oil.

^{1}H NMR (300 MHz, C_6D_6): 0.94 (s, 3H), 1.03 (s, 3H), 1.13 (t, J = 12.6 Hz, 1H), 1.38 (m, 2H), 1.65 (dd, J = 9.7, 11.5 Hz, 1H), 1.77 (m, 2H), 2.03 (dd, J = 11.8, 13.9 Hz, 1H), 2.12(m, 2H), 2.34(m, 1H), 2.57 (m, 1H), 3.25 (m, 1H), 3.52 (m, 4H), 5.28 (m, 1H), 5.58 (m, 1H). ^{13}C NMR (75.5 MHz, C_6D_6): 24.9, 30.9, 31.5, 36.9, 37.3, 39.5, 39.9, 40.5, 49.0, 49.5, 63.9, 64.6, 112.1, 130.2, 134.2. FT-IR: ν = 2951, 2865, 1737, 1463, 1366, 1111, 1055 cm^{-1}. HRMS (ESI): $[M+H]^+$ $C_{15}H_{25}O_2$, calcd 237.1849, found 237.1846.

(±)-(1*R*,6*R*,7*S*,8*R*)-10,10-dimethyl-6,7-epoxybicyclo[6.3.0]undecan-3-one ethylene glycol ketal (6)



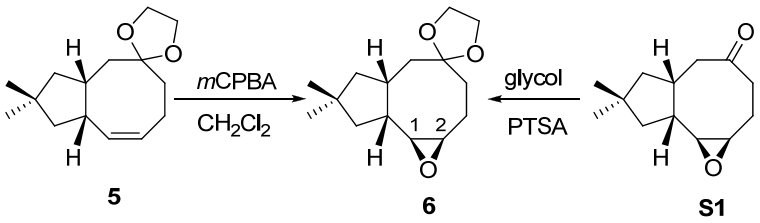
5 6

To a stirred solution of **5** (253 mg, 1.1 mmol) in 12 mL of CH_2Cl_2 was added $NaHCO_3$ (108 mg, 1.3 mmol)

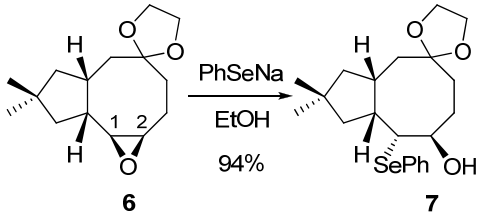
and *m*CPBA (317 mg, 70% wt, 1.3 mmol). The resulting mixture was stirred at room temperature for 3 h. The mixture was diluted with CH_2Cl_2, washed with saturated aqueous K_2CO_3, dried over Na_2SO_4, and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with petroleum ether/ ethyl acetate 10:1) to afford **6** (246 mg, 91%) as a colorless film.

^{1}H NMR (300 MHz, C_6D_6): 0.90 (s, 3H), 1.02 (s, 3H), 1.14 (t, J = 12.9 Hz, 1H), 1.33 (dd, J = 6.3, 12.2 Hz, 1H), 1.54 (m, 1H), 1.62-1.83 (m, 5H), 1.93 (m, 2H), 2.13 (m, 1H), 2.49 (m, 1H), 2.60 (dd, J = 4.2, 9.5 Hz, 1H), 2.69 (dt, J = 9.2, 4.0 Hz, 1H), 3.33-3.48 (m, 4H). ^{13}C NMR (75.5 MHz, C_6D_6): 23.8, 31.3, 31.7, 35.0, 37.2, 38.8, 40.8, 41.0, 46.2, 49.0, 55.9, 58.9, 63.6, 64.8, 110.6. FT-IR: ν = 2949, 2865, 1463, 1055, 1014, 947 cm^{-1}. HRMS (ESI): $[M+H]^+$ $C_{15}H_{25}O_3$, calcd 253.1798, found 253.1793.

The stereochemistry of **6** was assigned by the following transformations, where both **5** and **S1** led to the same compound **6**. The structure of compound **S1** was determined previously by X-ray analysis.[2]



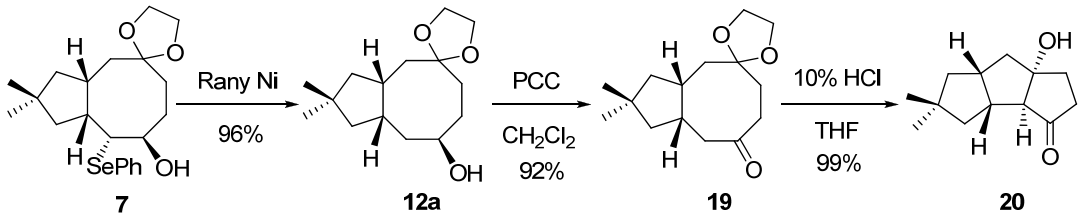
(±)-(1*R*,6*R*,7*R*,8*R*)-10,10-dimethyl-6-hydroxy-7-phenylselenylbicyclo[6.3.0]undecan-3-one ethylene glycol ketal (7)



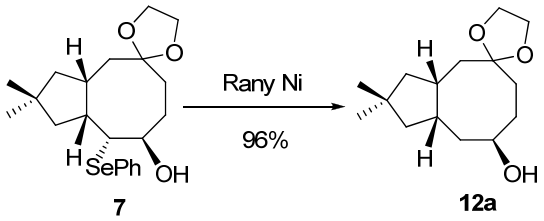
To a solution of diphenyldiselenide (660 mg, 2.1mmol) in absolute EtOH (15 mL) at 0 °C was added $NaBH_4$ (160 mg, 4.2 mmol) in portions. The originally yellow mixture turned to a clear, colorless solution upon complete addition of $NaBH_4$. The resulting sodium phenyl selenide solution was warmed to room temperature and stirred for 10 min. A solution of epoxide **6** (355 mg, 1.41 mmol) in absolute EtOH (5 mL) was added via cannula to the selenide solution, and the solution was heated to 70 °C for 24 h. To reduce any PhSeSePh formed during the course of the reaction, which usually causes yellowing of the reaction system, *ca*. 10 mg portions of $NaBH_4$ were added twice (2×10 mg). The reaction was then cooled to 0 °C, diluted with Et_2O and quenched with water. The aqueous layer was extracted twice with ether, and the combined organic layer was dried over $MgSO_4$, and concentrated. Purfication by flash column chromatography on silica gel (eluted with petroleum ether/ethyl acetate 5:1) afforded **7** (543 mg, 94%) as a light yellow solid.

^{1}H NMR (200 MHz, $CDCl_3$): 0.99 (t, J = 20.0 Hz, 3H), 1.11 (t, J = 20.0 Hz, 3H), 1.27-2.48 (m, 12H), 3.10 (m, 2H), 3.82-4.22 (m, 5H), 7.17-7.66 (m, 5H). ^{13}C NMR (50 MHz, $CDCl_3$): 25.1, 27.0, 27.6, 29.1, 35.9, 36.3, 36.7, 37.5, 50.0, 50.5, 60.2, 64.1, 64.4, 72.3, 112.4, 127.5, 129.2, 132.2, 133.7. FT-IR: ν =3480 ,2951, 2923, 2869, 1476, 1437 cm^{-1}. HRMS (ESI): $[M+H]^+$ $C_{21}H_{31}O_3Se$, calcd 411.1433, found 411.1431. m.p. 108-110 ℃.

In order to assign the regiochemistry of **7**, the following three transformations leading to the known compound **20**[1] were conducted, supporting the assignment of the structure of **7**.



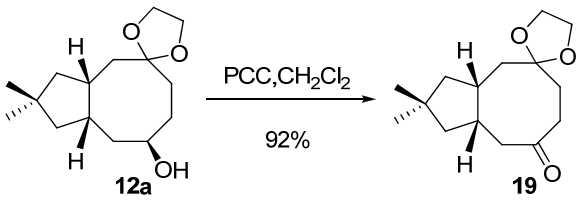
(±)-(1*R*,6*R*,8*S*)-10,10-dimethyl-6-hydroxybicyclo[6.3.0]undecan-3-one ethylene glycol ketal (12a)



To a round bottom flask, **7** (14 mg, 0.034 mmol) was added along with 2 mL of THF. Raney Ni (0.3 mL, 50% slurry in water/EtOH) was then added to this solution which was allowed to stir at room temperature for 24 h. Once completed, the mixture was filtered through a plug of celite and rinsed with EtOAc. The filtrate was then concentrated and purified by flash column chromatography on silica gel (eluted with petroleum ether/ethyl acetate 5:1) to yield **12a** (8.3 mg, 96%) as a white solid.

^{1}H NMR (400 MHz, C_6D_6): 0.92 (s, 3H), 0.97 (s, 3H), 1.05 (m, 2H), 1.42-1.74 (m, 8H), 1.85 (dt, J = 14.7, 8.9 Hz, 1H), 1.96 (dd, J = 11.3, 14.7 Hz, 1H), 2.08 (dd, J = 10.1, 14.6 Hz, 1H), 2.68 (m, 2H), 3.52 (m, 4H), 3.72 (m, 1H). ^{13}C NMR (100 MHz, C_6D_6): 27.5, 29.4, 30.0, 30.4, 31.9, 35.6, 36.6, 37.2, 39.4, 51.7, 51.9, 64.2, 64.4, 69.3, 111.8. FT-IR: v = 3426, 2947, 2927, 2868, 1463, 1365 cm^{-1}. HRMS (ESI): $[M+Na]^+$ $C_{15}H_{26}O_3Na$, calcd 277.1774, found 277.1772. m.p. 84-86 ℃.

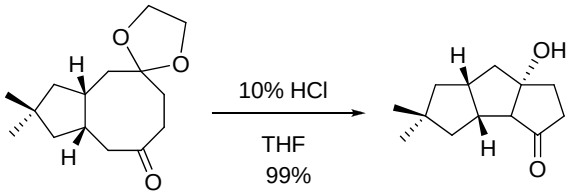
(±)-(1*R*,8*S*)-10,10-dimethyl-6-oxobicyclo[6.3.0]undecan-3-one ethylene glycol ketal (19)



A solution of 10 mL CH_2Cl_2 containing **12a** (190 mg, 0.75 mmol) and PCC (243 mg, 1.13 mmol) was stirred at room temperature for 3 h and quenched with 10 mL Et_2O. The suspension was filtered through an Al_2O_3 column and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with petroleum ether/ethyl acetate 15:1) to afford **19** (174 mg, 92%) as a colorless film.

^{1}H NMR (400 MHz, C_6D_6): 0.83 (s, 3H), 0.90 (s, 3H), 1.15 (m, 2H), 1.44 (dt, J = 6.5, 12.1 Hz, 2H), 1.58 (d, J = 14.9 Hz, 1H), 1.80 (m, 2H), 1.97 (ddd, J = 3.1, 9.8, 14.2 Hz, 1H), 2.12 (d, J = 10.4 Hz, 1H), 2.26-2.43 (m, 5H), 3.40-3.47 (m, 4H). ^{13}C NMR (100 MHz, C_6D_6): 31.0, 31.5, 34.2, 35.9, 38.1, 38.4, 39.7, 39.8, 44.6, 47.7, 50.0, 64.1, 64.5, 110.9, 211.6. FT-IR: v = 2950, 2932, 2864, 1698, 1462, 1364 cm^{-1}. HRMS (ESI): $[M+Na]^+$ $C_{15}H_{24}O_3Na$, calcd 275.1618, found 275.1611.

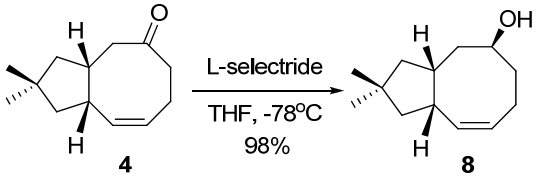
Compound 20[1]



19 20

To a stirred solution of **19** (48 mg, 0.2 mmol) in THF (6 mL) was added 10% HCl (5 mL). After stirred at room temperature for 30 h, the reaction was quenched with 3 M aqueous NaOH (6 mL) and diluted with Et_2O. After separation of the aqueous layer, the organic phase was washed successively with water and brine, dried over $MgSO_4$, and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with petroleum ether/ethyl acetate 5:1) to afford **20** (39 mg, 99%) as a colorless film.

(±)-(*Z*)-(1*R*,3*S*,8*R*)-10,10-dimethylbicyclo[6.3.0]undec-6-en-3-ol (8)

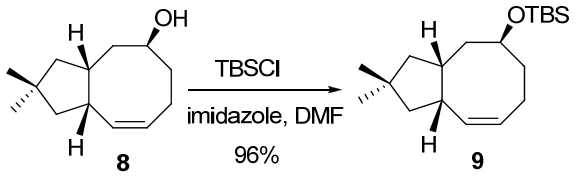


4 8

To a stirred solution of **4** (1.16 g, 6.04 mmol) in 45 mL anhydrous THF under argon was added L-selectride (9 mL, 1M in THF, 9 mmol) slowly at -78 °C. The resulting mixture was stirred at -78 °C for 2 h, then quenched by addition of saturated aqueous NH_4Cl slowly and diluted with 50 mL Et_2O. After separation of the organic phase, the aqueous layer was extracted with Et_2O twice. The combined organic layer was washed with saturated aqueous NH_4Cl and brine, dried over Na_2SO_4, and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with petroleum ether/ethyl acetate 20:1) to afford **8** (1.19 g, 98%) as a colorless oil .

^{1}H NMR (400 MHz, $CDCl_3$): 1.01 (s, 3H), 1.07 (s, 3H), 1.13 (t, J = 12.3 Hz, 1H), 1.41 (m, 2H), 1.67-1.74 (m, 4H), 1.88 (dd, J = 8.5, 13.3 Hz, 1H), 1.94 (m, 1H), 2.07 (m, 1H), 2.38 (m, 1H), 2.54 (m, 1H), 3.19 (m, 1H), 3.99 (dq, J = 8.4, 4.4 Hz, 1H), 5.20 (ddm, J = 6.1, 11.3 Hz, 1H), 5.53 (ddt, J = 2.3, 11.3, 5.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 25.3, 30.3, 31.1, 33.9, 35.8, 37.0, 38.0, 40.0, 49.0, 50.2, 71.3, 129.7, 133.7. FT-IR: ν = 3357, 3003, 2948, 2928, 2864, 1461 cm^{-1}. HRMS (ESI): $[M+Na]^+$ $C_{13}H_{22}Ona$, calcd 217.1563, found 217.1565.

(±)-(*Z*)-(1*R*,6*S*,8*R*)-10,10-dimethyl-6-(*tert*-butyldimethylsilyloxy)bicyclo[6.3.0]undec-2-ene (9)



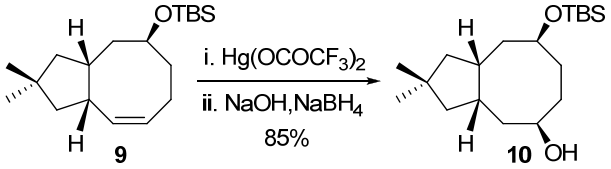
8 9

To a stirred solution of **8** (1.19 g, 6.13 mmol) in 12 mL DMF was added TBSCl (2.32 g, 15.3 mmol) and imidazole (1.2 g, 16.6 mmol) at room temperature. The resulting mixture was stirred overnight, and then diluted with 15 mL water and 20 mL Et_2O. The organic layer was separated, and the aqueous layer was extracted with Et_2O twice. The combined organic phase was washed with saturated aqueous NH_4Cl, dried over $MgSO_4$, and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with pure petroleum ether) to afford **9** (1.78 g, 96%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): 0.03 (s, 3H), 0.04 (s, 3H), 0.91 (s, 9H), 1.01 (s, 3H), 1.08 (s, 3H), 1.11 (m, 1H),

1.32 (dd, *J* = 6.2, 11.9 Hz, 1H), 1.41 (dd, *J* = 3.5, 13.1 Hz, 1H), 1.46-1.56 (m, 2H), 1.67 (ddd, *J* = 3.5, 7.1, 14.2 Hz, 1H), 1.75-1.95 (m, 3H), 2.43 (quintet, *J* = 8.6 Hz, 1H), 2.58 (m, 1H), 3.13 (m, 1H), 3.99 (m, 1H), 5.24 (ddd, *J* = 1.3, 7.1, 10.6 Hz, 1H), 5.59 (ddt, *J* = 2.2, 11.1, 6.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): -4.9, -4.8, 18.2, 23.4, 25.9, 30.8, 31.4, 36.0, 36.1, 37.1, 39.6, 39.8, 48.7, 49.4, 70.6, 130.3, 134.4. FT-IR: ν = 2952, 2856, 1472, 1462, 1252, 1080 cm^{-1}. HRMS (ESI): $[M+Na]^+$ $C_{19}H_{36}OsiNa$, calcd 331.2428, found 331.2428.

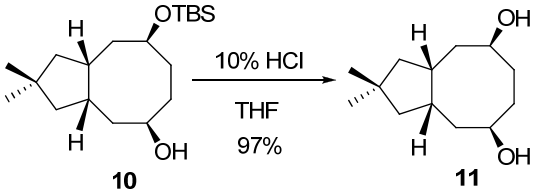
(±)-(1*S*,3*R*,6*S*,8*R*)-6-(*tert*-butyldimethylsilyloxy)-10,10-dimethylbicyclo[6.3.0]undecan-3-ol (10)



To a stirred solution of **9** (167 mg, 0.54 mmol) in 3 mL THF and 2 mL water was added $Hg(OOCCF_3)_2$ (578 mg, 1.35 mmol) at room temperature. The resulting mixture was stirred for 2.5 h, and then 1.8 mL 3 M aqueous NaOH and $NaBH_4$ (103 mg soluted in 0.5 mL 3 M aqueous NaOH) was added. The resulting mixture was stirred at room temperature for 30 min and diluted with 15 mL ethyl acetate. The organic layer was separated, the aqueous layer was extracted with ethyl acetate twice. The combined organic phase was washed with brine, dried over $MgSO_4$, and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with petroleum ether/ethyl acetate 20:1) to afford **10** (121 mg, 85%) as a colorless film.

^{1}H NMR (400 MHz, C_6D_6): 0.04 (s, 3H), 0.05 (s, 3H), 0.84 (s, H), 0.95 (s, 3H), 0.99 (s, 9H), 1.01 (s, 3H), 1.05 (m, 2H), 1.15 (s, 1H), 1.27 (m, 1H), 1.42 (m, 2H), 1.50-1.58 (m, 3H), 1.66 (ddd, *J* = 1.9, 7.6, 12.4 Hz, 1H), 1.75-1.88 (m, 2H), 2.61 (dq, *J* = 8.8, 9.7 Hz, 1H), 2.80 (quintet, *J* = 9.3 Hz, 1H), 3.65 (m, 1H), 3.77 (m, 1H). ^{13}C NMR (100 MHz, C_6D_6): -4.6, 18.4, 26.1, 27.5, 28.0, 29.8, 30.1, 32.16, 32.20, 36.6, 38.2, 51.7, 52.5, 70.0, 70.3. FT-IR: ν = 3369, 2927, 2907, 2856, 1471, 1250 cm^{-1}. HRMS (ESI): $[M+H]^+$ $C_{19}H_{39}O_2Si$, calcd 327.2714, found 327.2725.

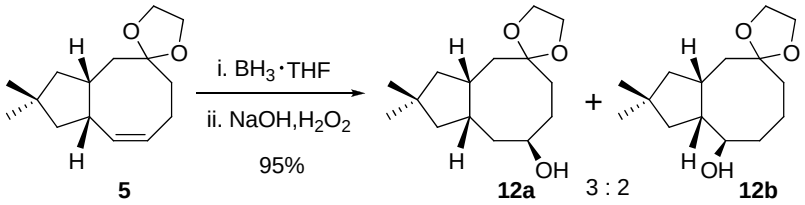
(±)-(1*S*,3*R*,6*S*,8*R*)-10,10-dimethylbicyclo[6.3.0]undecan-3,6-diol (11) [2]



To a stirred solution of **10** (33 mg, 0.10 mmol) in 4 mL THF was added 2.5 mL 10% HCl at 0 °C. The resulting mixture was stirred at room temperature for 3 h, and then the mixture was diluted with 10 mL ethyl acetate. After the organic layer was separated, the aqueous layer was extracted with ethyl acetate twice. The combined organic phase was washed with saturated aqueous $NaHCO_3$ and brine, dried over $MgSO_4$, and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with petroleum ether/ethyl acetate 3:1) to afford **11** (21 mg, 97%) as a white solid. Structure of **11** was determined by X-ray analysis.[2]

^{1}H NMR (200 MHz, $CDCl_3$): 0.97 (s, 3H), 1.00 (s, 3H), 1.03-1.14 (m, 2H), 1.38-1.48 (m, 2H), 1.50 (br s, 2H), 1.58-1.68 (m, 4H), 1.74-1.95 (m, 4H), 2.48-2.65 (m, 2H), 3.91-3.99 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): 69.8, 51.5, 36.5, 31.7, 29.6, 28.0, 27.1.

(±)-(1*R*,7*R*,8*R*)-10,10-dimethyl-7-hydroxybicyclo[6.3.0]undecan-3-one ethylene glycol ketal (12b)

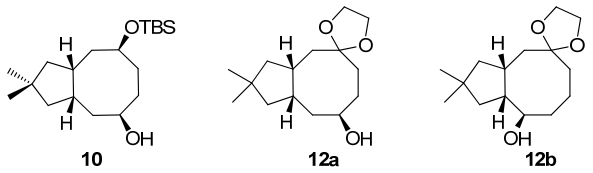


To a stirred solution of **5** (927 mg, 3.9 mmol) in 25 mL anhydrous THF under argon was added BH_3·THF (9.8 mL, 1 M in THF, 9.8 mmol) slowly at 0 °C. The resulting mixture was stirred at 0 °C for 2.5 h, then 3 M NaOH(7 mL) and 30% H_2O_2 (7 mL) were added very slowly. The resulting mixture was stirred at room temperature for 30 min and diluted with 100 mL ethyl acetate. After separation of the aqueous layer, the organic phase was washed with brine, dried over $MgSO_4$, and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with petroleum ether/ethyl acetate 8:1 to 3:1) to afford **12a** (566 mg) as a white solid and **12b** (377 mg) as a colorless film in 95% yield (ca **12a:12b** =3:2).

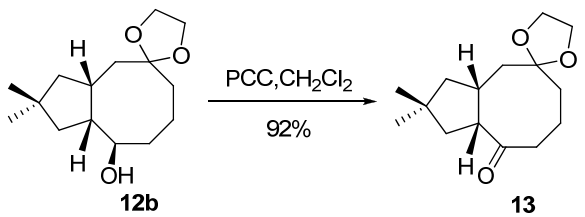
12b: ^{1}H NMR (400 MHz, C_6D_6): 0.91 (s, 3H), 0.92 (m, 1H), 1.02 (s, 3H), 1.13 (m, 2H), 1.35-1.49 (m, 3H), 1.56 (m, 1H), 1.64-1.87 (m, 6H), 1.97-2.08 (m, 2H), 2.60 (quintet, J = 9.2 Hz, 1H), 3.48-3.53 (m, 4H). ^{13}C NMR (100 MHz, C_6D_6): 19.2, 28.2, 30.3, 35.3, 36.0, 36.3, 40.1, 40.9, 46.5, 48.0, 52.8, 64.25, 64.32, 72.1, 111.6. FT-IR: ν = 3448, 2949, 2931, 2866, 1462, 1364 cm^{-1}. HRMS (ESI): $[M+Na]^+$ $C_{15}H_{26}O_3Na$, calcd 277.1774, found 277.1773.

A series of boron reagents (BH_3 • THF, 9-BBN, Evans' rhodium-catalyzed procedure with catecholborane) were tried with the ketal **5** and TBS ether **9.** The results are listed below.

	Substrate **5**	Substrate **9**
BH_3·THF	**12a/12b**= 3:2 95%	Inseparable mixture(88%), mainly compound **10**
9-BBN	**12a** 85%	**10** 77%
Catecholborane and Wilkinson' catalyst	messy	



(±)-(1*R*,8*R*)-10,10-dimethyl-7-oxobicyclo[6.3.0]undecan-3-one ethylene glycol ketal (13)

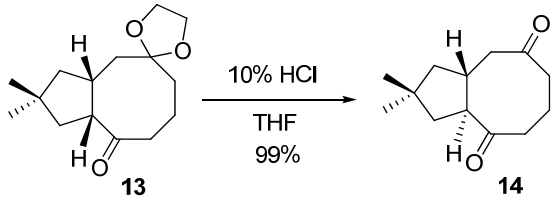


To a stirred solution of **12b** (190 mg, 0.75 mmol) in 10 mL CH_2Cl_2 was added PCC (323 mg, 1.5 mmol) at room temperature. The resulting mixture was stirred for 3 h, and then diluted with 10 mL Et_2O. The suspension was filtered through an Al_2O_3 column and concentrated. The crude product was purified by flash column

chromatography on silica gel (eluted with petroleum ether/ethyl acetate 100:1 to 80:1) to afford **13** (173 mg, 92%) as a colorless film**.**

^{1}H NMR (400 MHz, $CDCl_3$): 0.98 (s, 3H), 1.09 (s, 3H), 1.26 (t, J = 12.3 Hz, 1H), 1.43-1.58 (m, 4H), 1.73 (m, 2H), 1.91-2.07 (m, 3H), 2.31 (ddd, J = 4.1, 9.0, 12.6 Hz, 1H), 2.47 (ddd, J = 4.4, 9.7, 12.4 Hz, 1H), 2.72 (m, 1H), 3.44 (dt, J = 10.3, 8.0 Hz, 1H), 3.87-3.96 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): 19.4, 27.6, 28.6, 36.2, 37.6, 37.9, 39.0, 43.6, 47.3, 49.7, 50.8, 64.0, 64.5, 110.9, 216.3. FT-IR: ν = 2951, 2866, 1968, 1460, 1364, 1099 cm^{-1}. HRMS (ESI): $[M+Na]^+$ $C_{15}H_{24}O_3Na$, calcd 275.1618, found 275.1615.

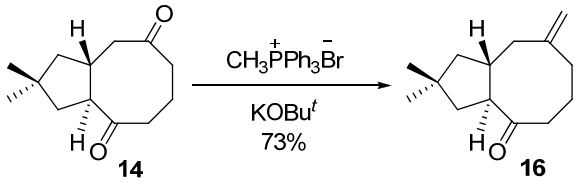
(±)-(1*S*,8*R*)-10,10-dimethylbicyclo[6.3.0]undecan-2,6-dione (14)



To a stirred solution of **13** (400 mg, 1.6 mmol) in 25 mL THF was added 21 mL 10% HCl at room temperature. The resulting mixture was stirred at room temperature for 36 h, then 22 mL 3 M aqueous NaOH was added and the resulting mixture was diluted with 120 mL Et_2O. After separation of the aqueous layer, the organic layer was washed with water and brine, dried over $MgSO_4$, and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with petroleum ether/ethyl acetate 3:1) to afford **14** (329 mg, 99%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): 1.07 (s, 3H), 1.10 (s, 3H), 1.30 (t, J = 11.9 Hz, 1H), 1.60 (dd, J = 7.6, 12.9 Hz, 1H), 1.81-1.87 (m, 2H), 2.07 (m, 1H), 2.28-2.59 (m, 8H), 2.91 (dt, J = 7.5, 11.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 21.5, 30.9, 31.4, 36.6, 42.6, 42.9, 43.4, 44.5, 46.8, 49.5, 56.2, 211.8, 213.7. FT-IR: ν = 2952, 2863, 1696, 1462, 1363, 1250 cm^{-1}. HRMS (ESI): $[M+Na]^+$ $C_{13}H_{20}O_2Na$, calcd 231.1356, found 231.1354. m.p. 95-97 ℃.

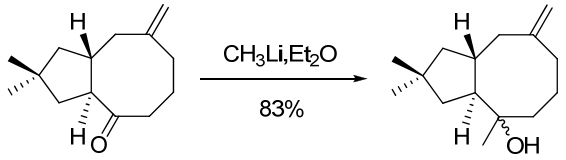
(±)-(1*S*,8*R*)-10,10-dimethyl-6-methylidenebicyclo[6.3.0]undecan-2-one (16)



To a stirred suspension of methyl triphenylphosphonium bromide (257 mg, 0.72 mmol) in 5 mL anhydrous benzene was added solid KOBu^t (65 mg, 0.58 mmol) under argon. The resulting mixture was stirred at 60 °C for 40 min, and then cooled to room temperature. A solution of **14** (100 mg, 0.48 mmol) in 4 mL benzene was added dropwise. The resulting mixture was stirred at 80 °C for 3.5 h, then cooled to room temperature, quenched by addition of 3 mL water, and diluted with 15 mL Et_2O. After separation of aqueous layer, the organic phase was washed with water and brine, dried over $MgSO_4$, and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with petroleum ether/ethyl acetate 50:1) to afford **16** (72 mg, 73%) as a white solid.

^{1}H NMR (400 MHz, C_6D_6): 0.93 (s, 3H), 0.97 (m, 1H), 1.01 (s, 3H), 1.42 (dd, J = 7.6, 13.0 Hz, 2H), 1.50 (dd, J = 7.0, 12.5 Hz, 2H), 1.80 (m, 2H), 1.91 (dd, J = 11.1, 12.9 Hz, 1H), 1.93-1.99 (m, 1H), 2.02-2.10 (m, 2H), 2.23 (m, 2H), 2.53 (dt, J = 7.4, 11.1 Hz, 1H), 4.78 (m, 1H), 4.80 (m, 1H). ^{13}C NMR (100 MHz, C_6D_6): 23.9, 31.3, 31.7, 36.5, 36.8, 39.7, 42.2, 44.6, 48.3, 49.5, 55.4, 115.6, 147.1, 212.2. FT-IR: ν = 3066, 2947, 2857, 1691, 1450, 1220 cm^{-1}. HRMS (ESI): $[M+H]^+$ $C_{14}H_{23}O$, calcd 207.1743, found 207.1744. m.p. 65-67 ℃.

(±)-(1*S*,8*R*)-6-methylidene-2,10,10-trimethylbicyclo[6.3.0]undecan-2-ol (17)

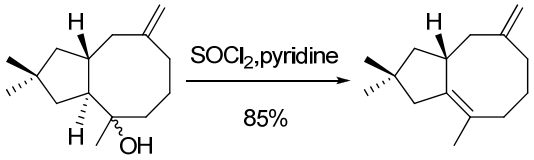


16 **17**

To a stirred solution of **16** (37 mg, 0.18 mmol) in 4 mL anhydrous Et_2O was added CH_3Li (0.17 ml, 1.6 M, 0.27 mmol) under argon at 0 °C. The resulting mixture was stirred at 0 °C for 4 h, then quenched by addition of 4 mL water and diluted with 15 mL Et_2O. After separation of the aqueous layer, the organic phase was washed with water and brine, dried over $MgSO_4$, and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with petroleum ether/ethyl acetate 30:1) to afford **17** (33 mg, 83%) as a colorless oil.

^{1}H NMR (400 MHz, C_6D_6): 0.98 (s, 3H), 0.99 (s, 3H), 1.06 (s, 3H), 1.13 (ddd, J = 1.7, 5.2, 12.9 Hz, 1H), 1.30-1.46 (m, 4H), 1.61-1.71 (m, 4H), 1.91-2.01 (m, 3H), 2.13 (m, 1H), 2.27 (m, 1H), 2.36 (dd, J = 5.4, 13.0 Hz, 1H), 4.76 (m, 1H), 4.86 (m, 1H). ^{13}C NMR (100 MHz, C_6D_6): 22.5, 29.1, 29.5, 29.9, 36.1, 37.7, 38.0, 39.6, 43.9, 46.6, 50.2, 51.0, 72.1, 114.1, 149.3. FT-IR: ν = 3472, 2932, 2865, 1446, 1364 cm^{-1}. HRMS (ESI): $[M+Na]^+$ $C_{15}H_{26}ONa$, calcd 245.1876, found 245.1875.

(±)-6-methylidene-2,10,10-trimethylbicyclo[6.3.0]undec-1-ene (18)

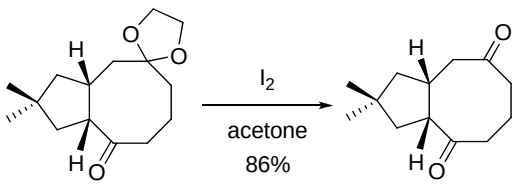


17 **18**

To a stirred solution of **17** (30 mg, 0.14 mmol) in 2 mL pyridine was added $SOCl_2$ (20 uL, 0.28 mmol) at 0 °C. The resulting mixture was stirred at 0 °C for 2.5 h, quenched by addition of 2 mL cold water, and diluted with 15 mL Et_2O. After separation of the aqueous layer, the organic phase was washed with saturated aqueous NH_4Cl and brine, dried over $MgSO_4$, and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with pentane) to afford **18** (23 mg, 85%) as a colorless oil .

^{1}H NMR (400 MHz, C_6D_6): 0.84 (s, 3H), 1.05 (s, 3H), 1.06 (m, 1H), 1.44-1.58 (m, 2H), 1.61 (m, 3H), 1.70-1.85 (m, 4H), 1.96 (d, J = 14.1 Hz, 1H), 2.10 (dd, J = 1.5, 14.1 Hz, 1H), 2.23 (dd, J = 5.3, 12.9 Hz, 1H), 2.34 (dd, J = 3.7, 12.3 Hz, 1H), 2.45 (dt, J = 5.3, 13.5 Hz, 1H), 2.64 (m, 1H), 4.82 (m, 1H), 4.95 (m, 1H). ^{13}C NMR (100 MHz, C_6D_6): 19.0, 27.3, 27.4, 28.9, 31.5, 32.2, 37.3, 41.8, 45.0, 49.1, 49.5, 111.9, 125.4, 139.9, 150.6.

(±)-(1*R*,8*R*)-10,10-dimethylbicyclo[6.3.0]undecan-2,6-dione (15)



13 **15**

To a stirred solution of **13** (31 mg, 0.12 mmol) in 4 mL acetone (≤0.5% H_2O) was added iodine (3 mg, 0.012 mmol) at room temperature. The resulting mixture was stirred for 13 h, and then diluted with 15 mL Et_2O. The mixture was washed successively with 5% aqueous $Na_2S_2O_3$, water and brine, dried over $MgSO_4$, and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with petroleum ether/ethyl acetate 5:1) to afford **15** (22 mg, 86%) as a white solid.

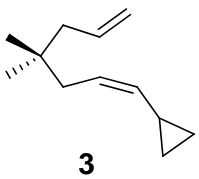
^{1}H NMR (400 MHz, C_6D_6): 0.99 (s, 3H), 1.13 (s, 3H), 1.34 (dd, *J* = 10.4, 12.3 Hz, 1H), 1.47 (dd, *J* = 7.9, 13.2 Hz, 1H), 1.62 (dd, *J* = 6.5, 12.3 Hz, 1H), 1.93 (dd, *J* = 7.4, 13.2 Hz, 1H), 2.10-2.16 (m, 2H), 2.25 (dd, *J* = 3.2, 13.4 Hz, 1H), 2.42-2.63 (m, 5H), 2.85-2.95 (m, 1H), 3.35 (q, *J* = 7.9 Hz, 1H). ^{13}C NMR (100 MHz, C_6D_6): 22.5, 29.3, 29.5, 37.6, 40.6, 42.0, 43.6, 44.2, 44.6, 47.9, 52.3, 213.6, 215.1. HRMS (ESI): $[M+H]^+$ $C_{13}H_{21}O_2$, calcd 209.15361, found 209.15415. m.p. 80-82 ℃.

References:

[1]. Jiao, L.; Yuan, C.; Yu, Z.-X. *J. Am. Chem. Soc.* **2008**, *130*, 4421.

[2]. Fan, X.; Tang, M.; Zhuo, L.; Tu, Y. Q.; Yu, Z.-X. *Tetrahedron Lett.* **2009**, *50*, 155.

3. ^{1}H and ^{13}C NMR Spectra for New Compounds



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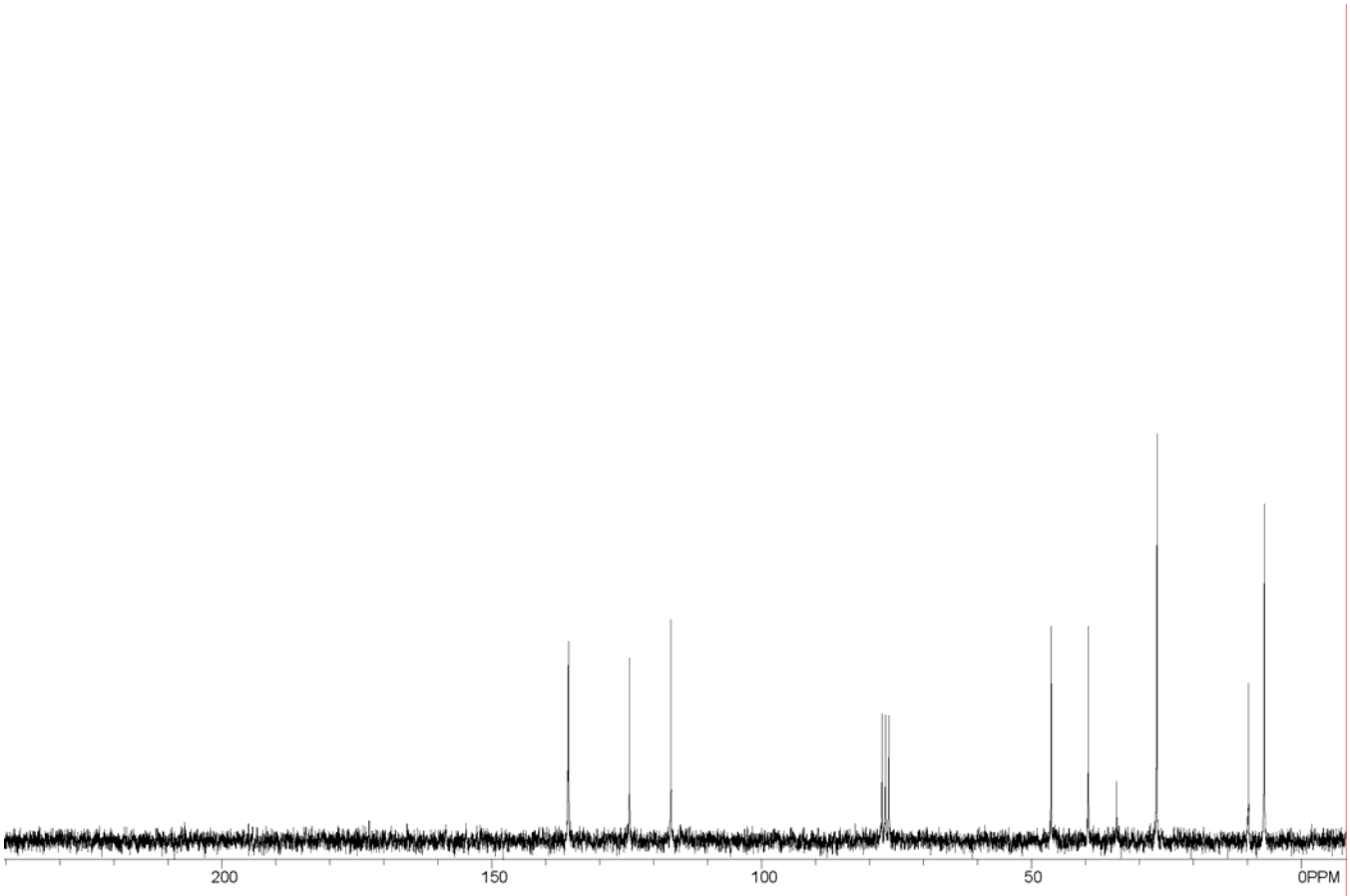

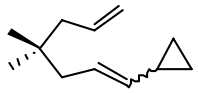

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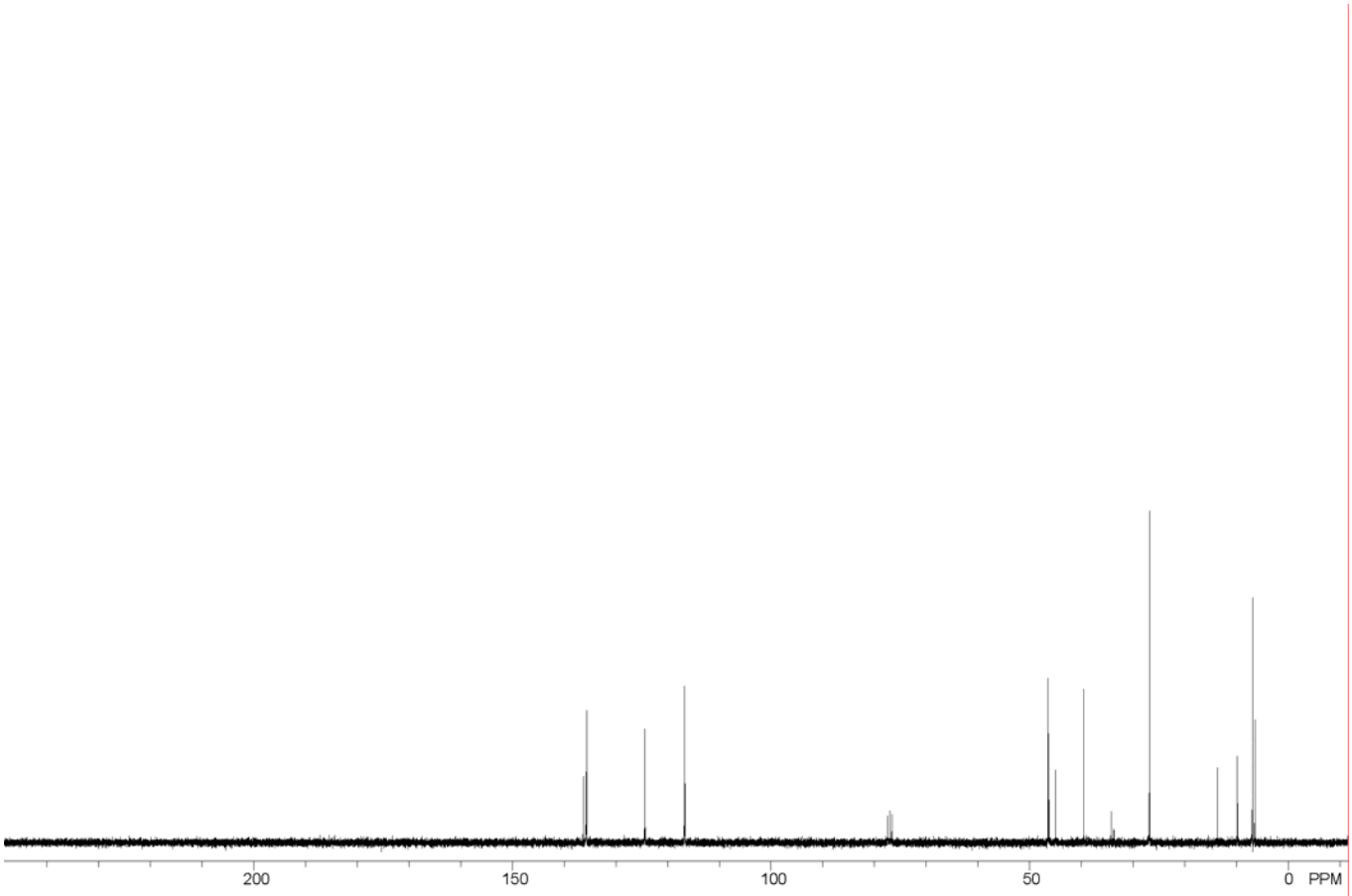

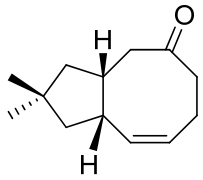

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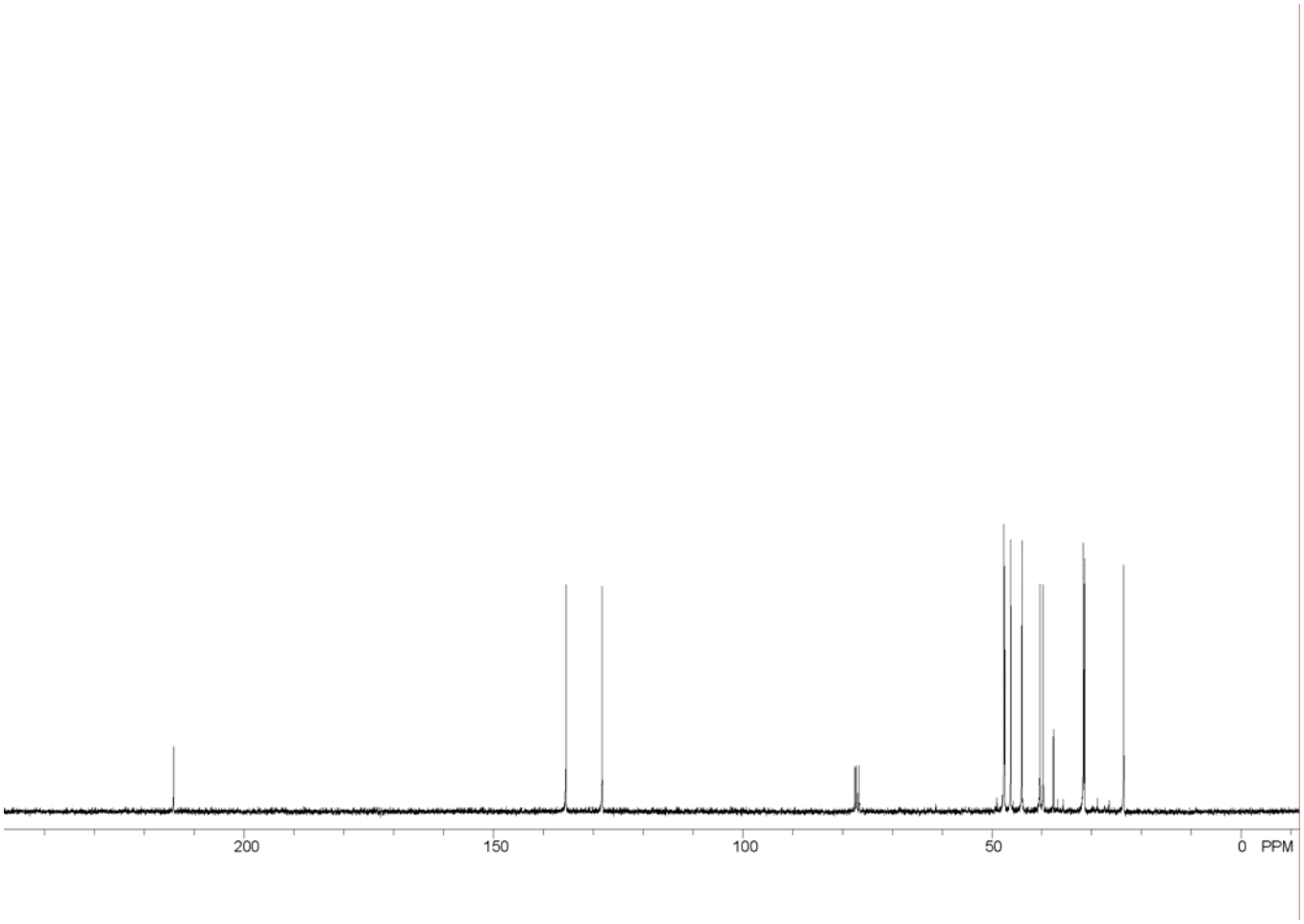

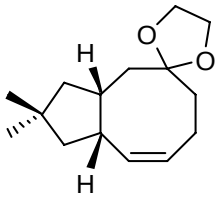

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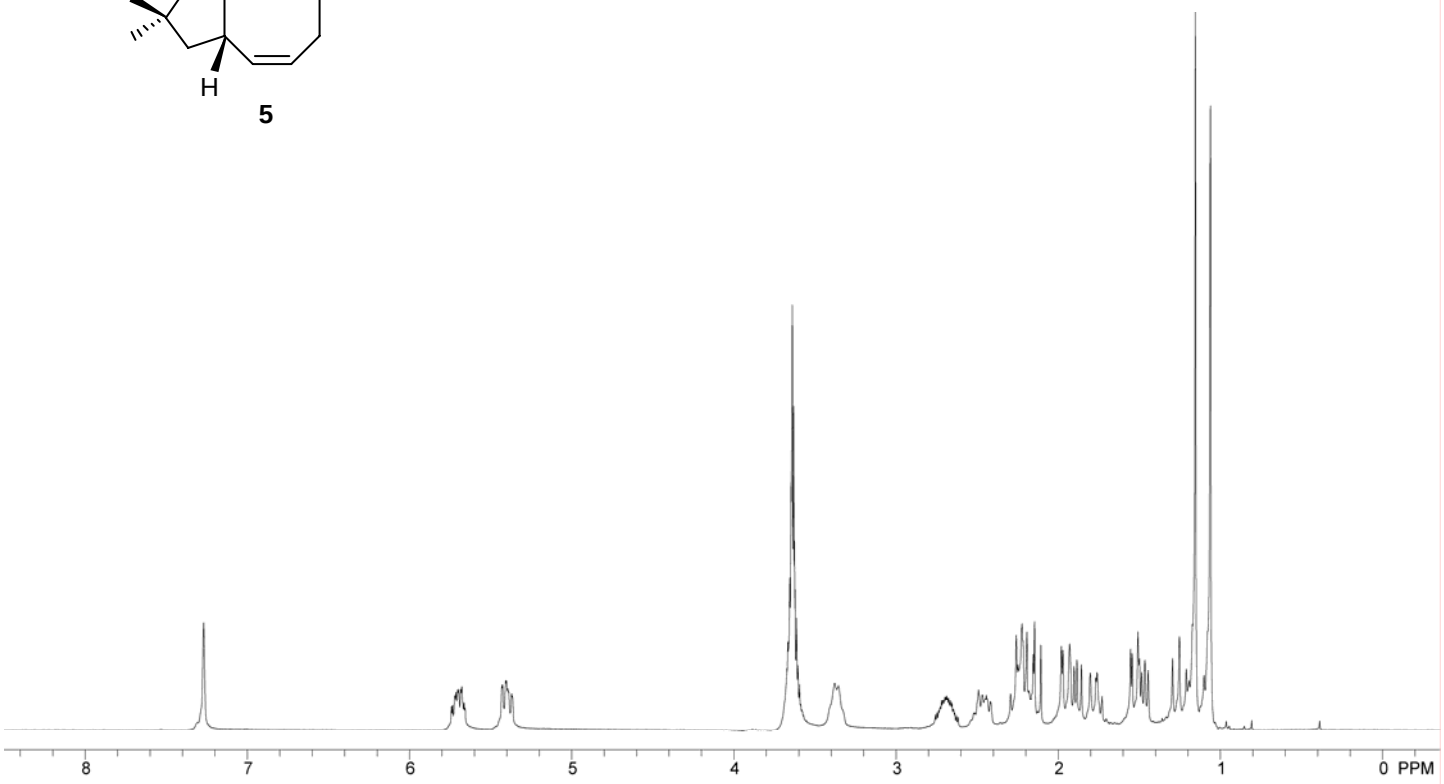

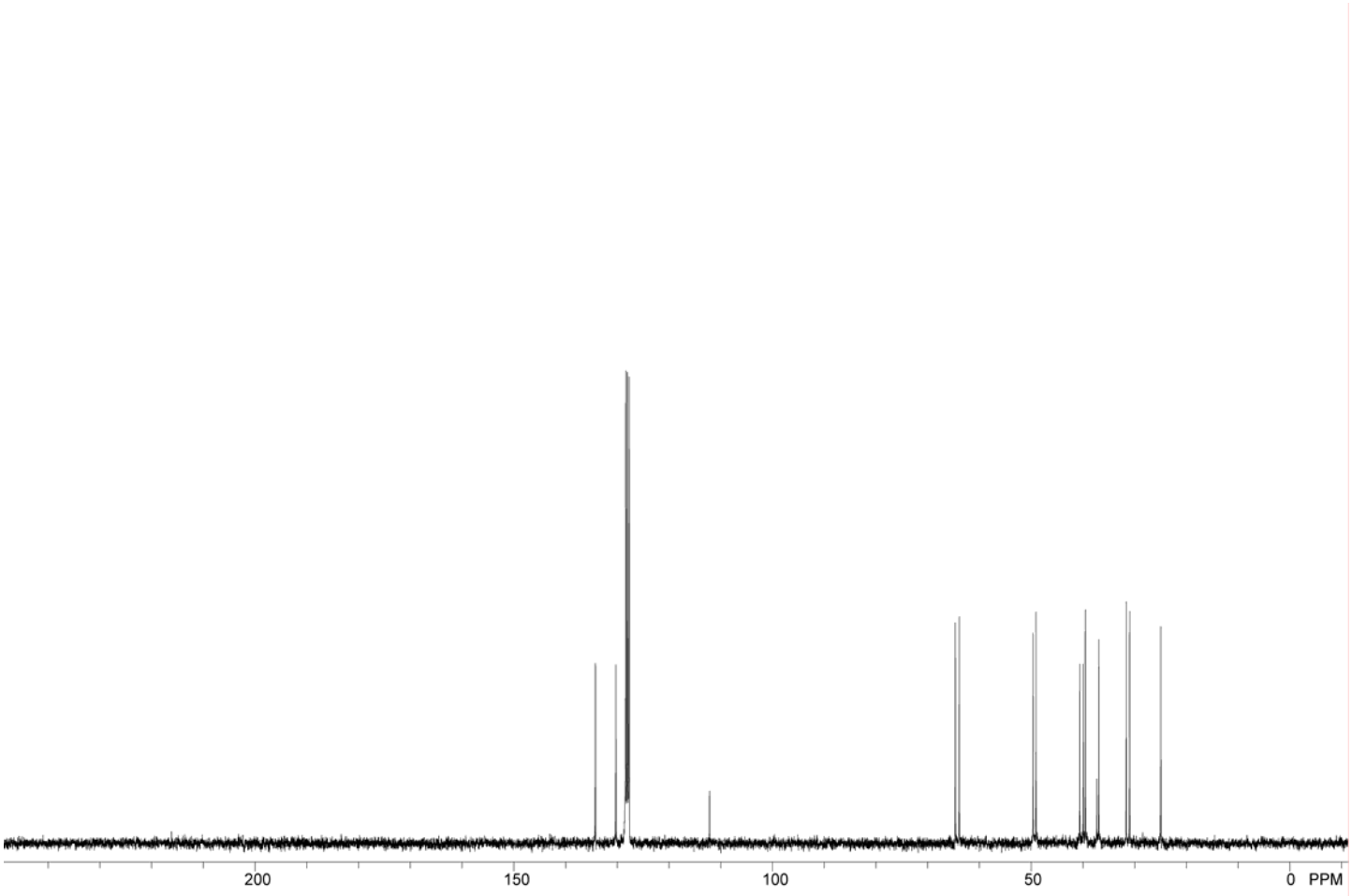

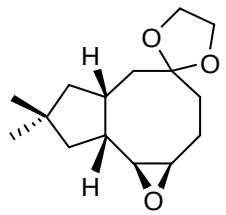

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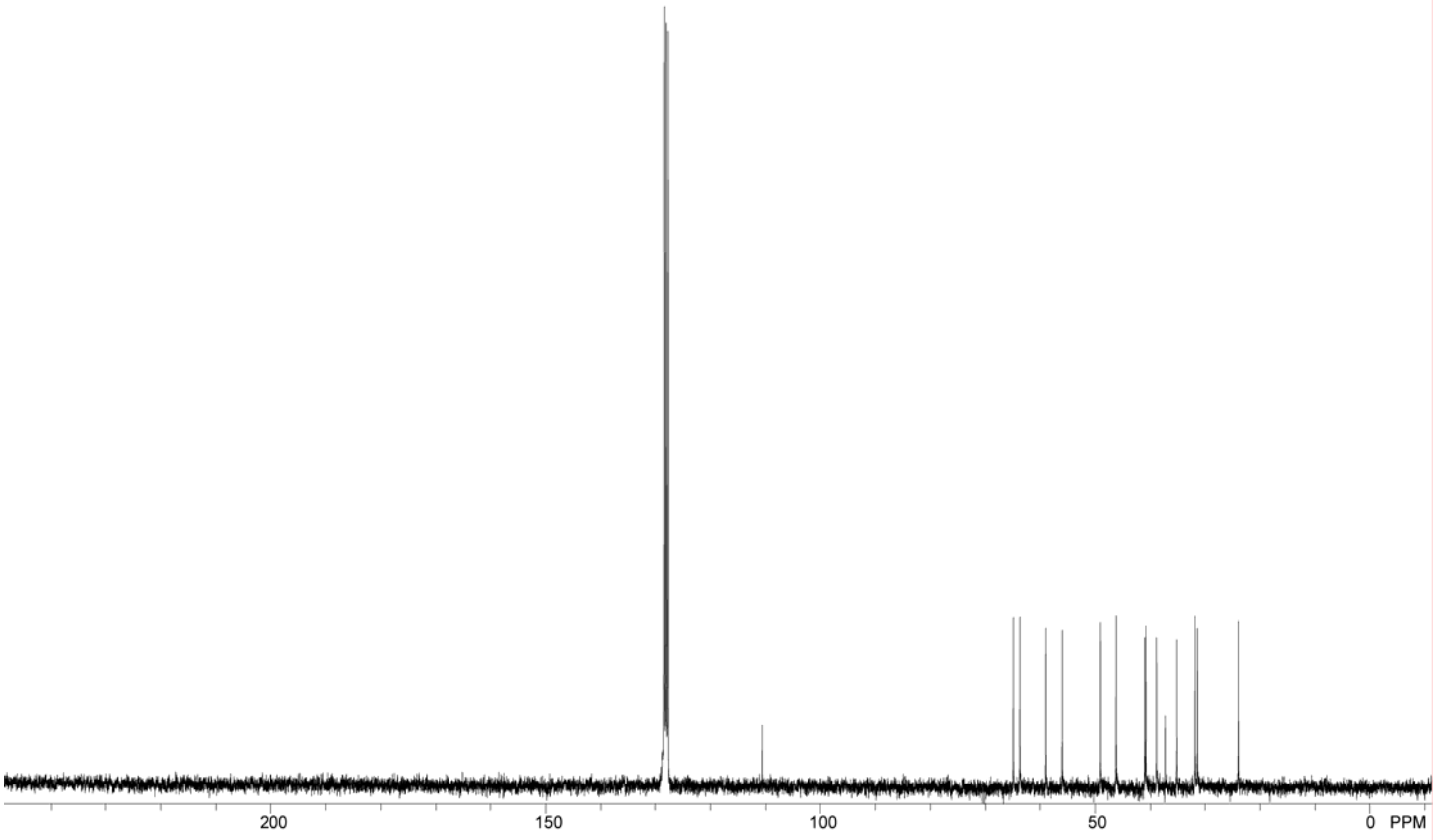

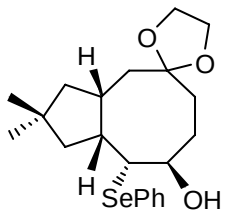

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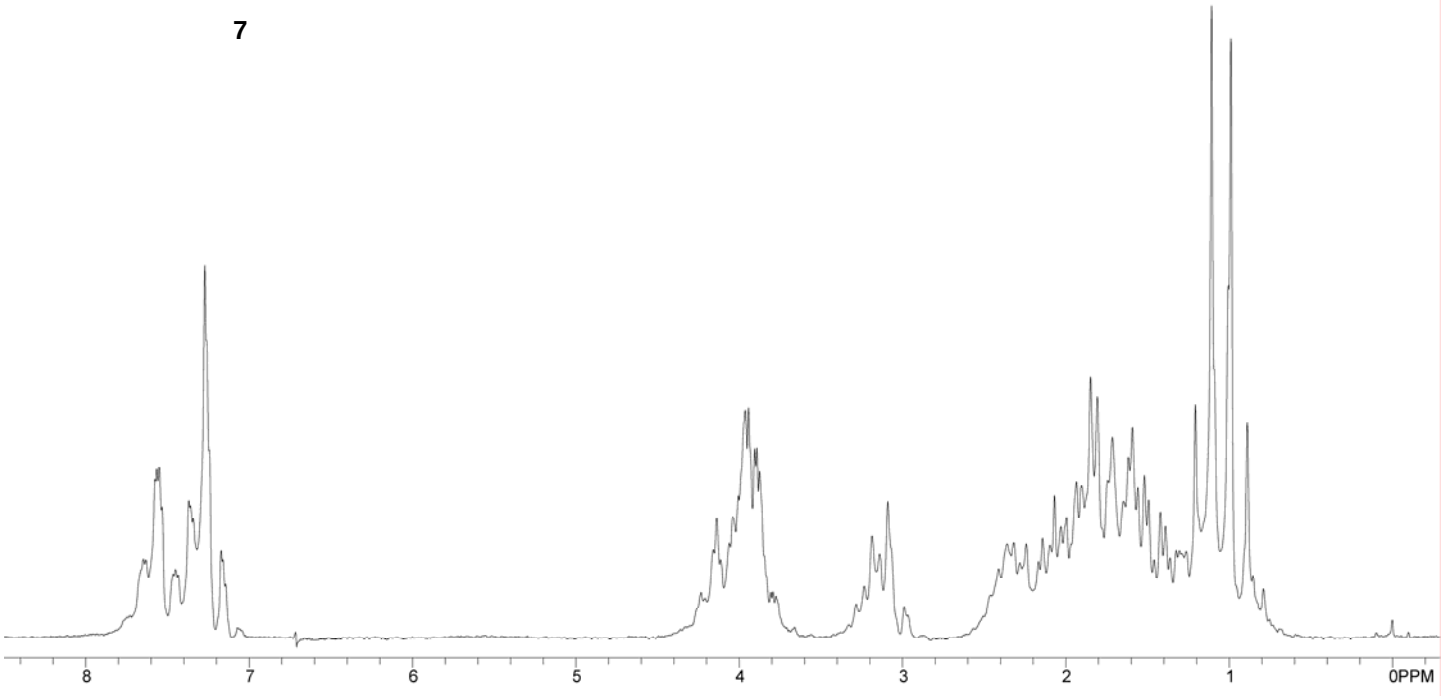

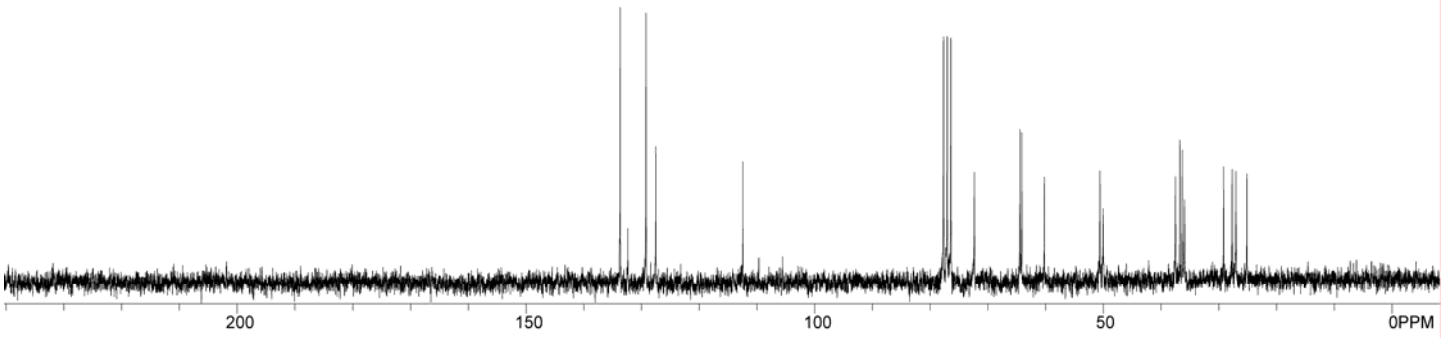

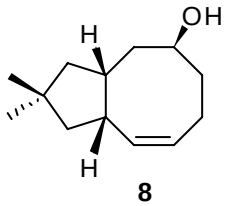

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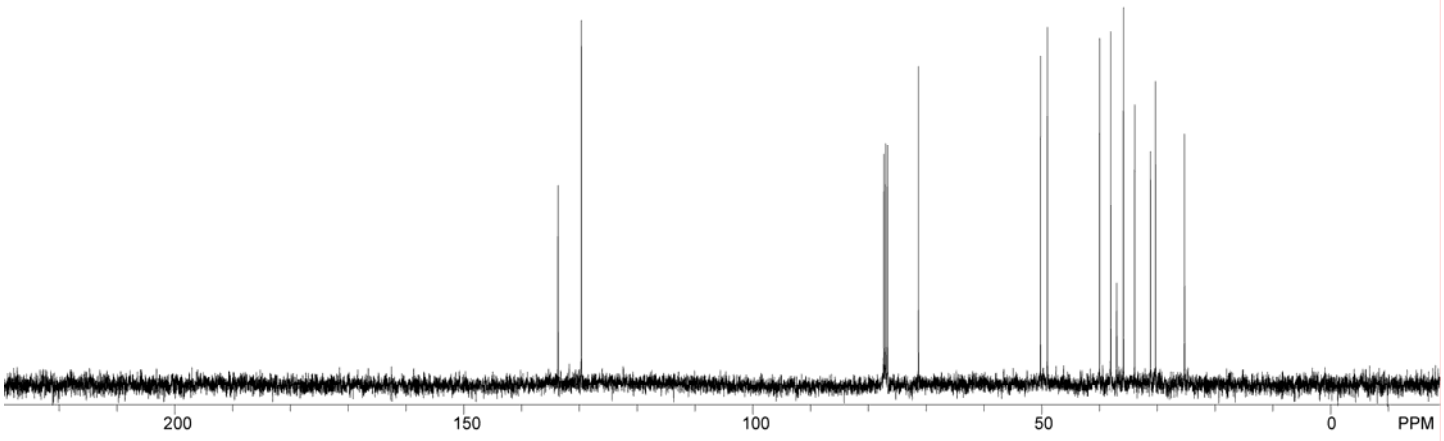

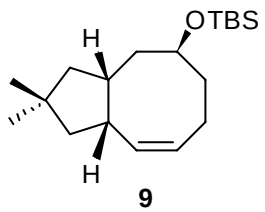

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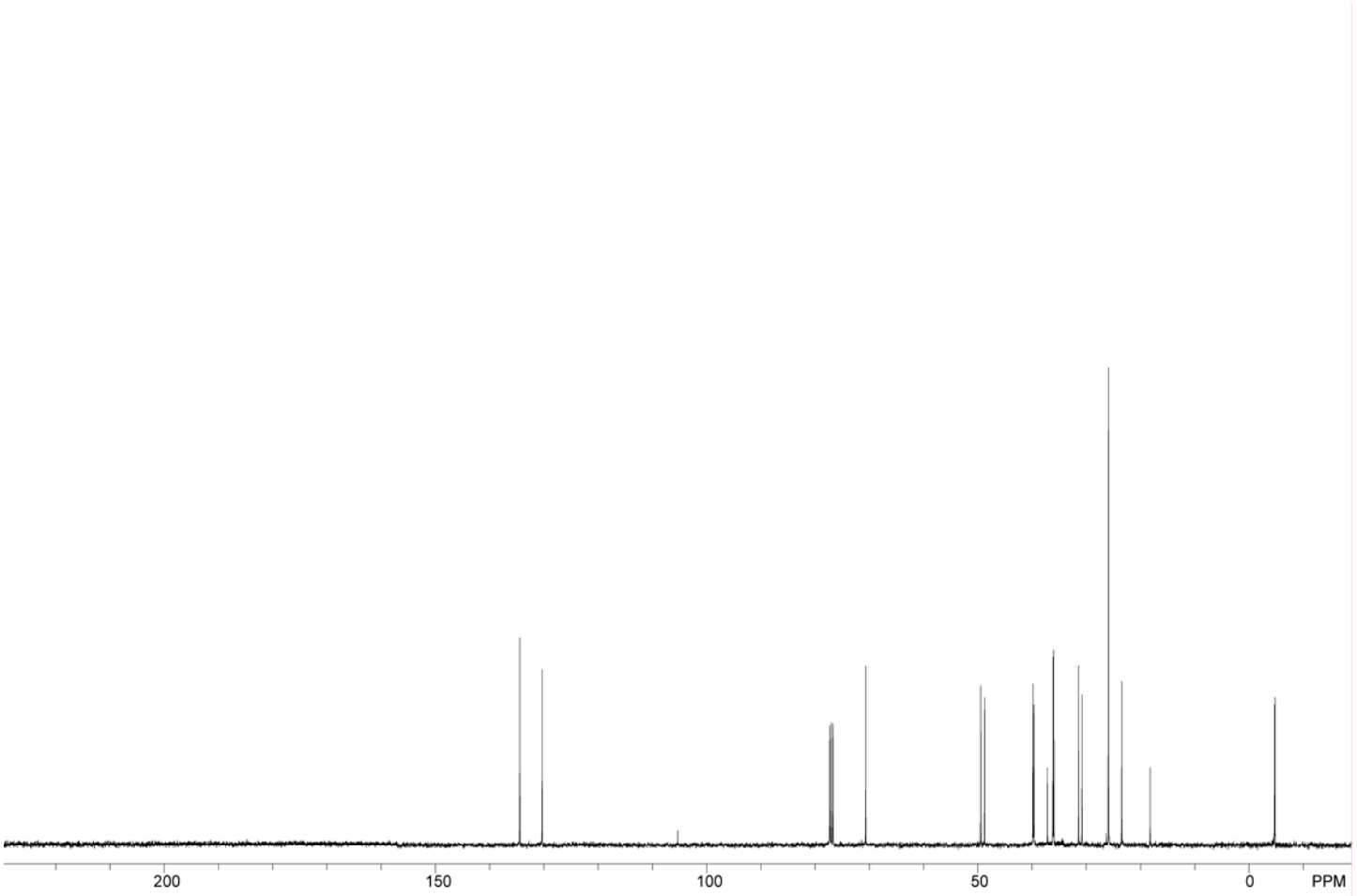

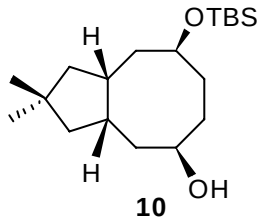

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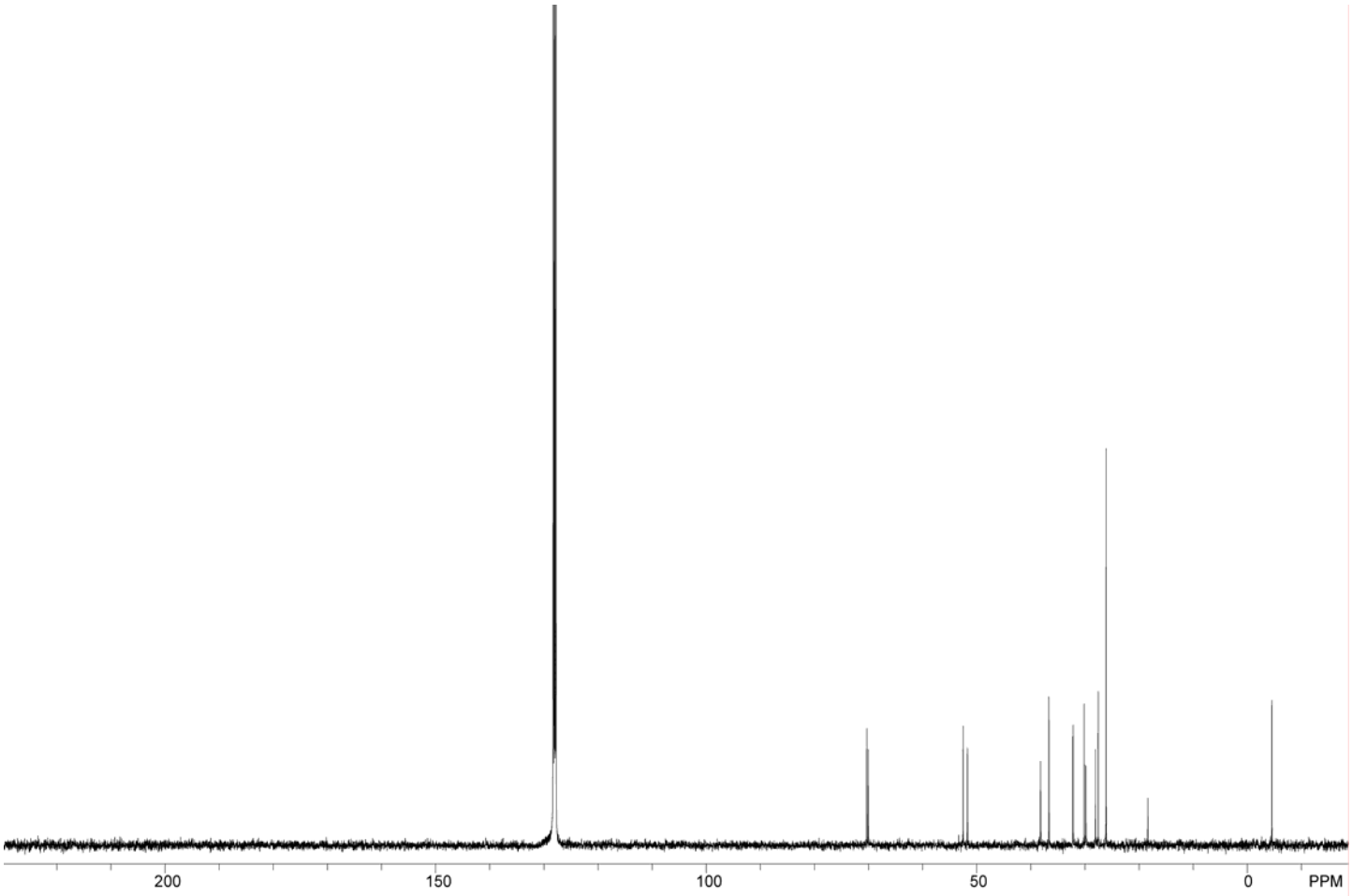

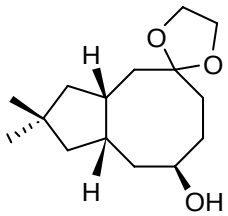

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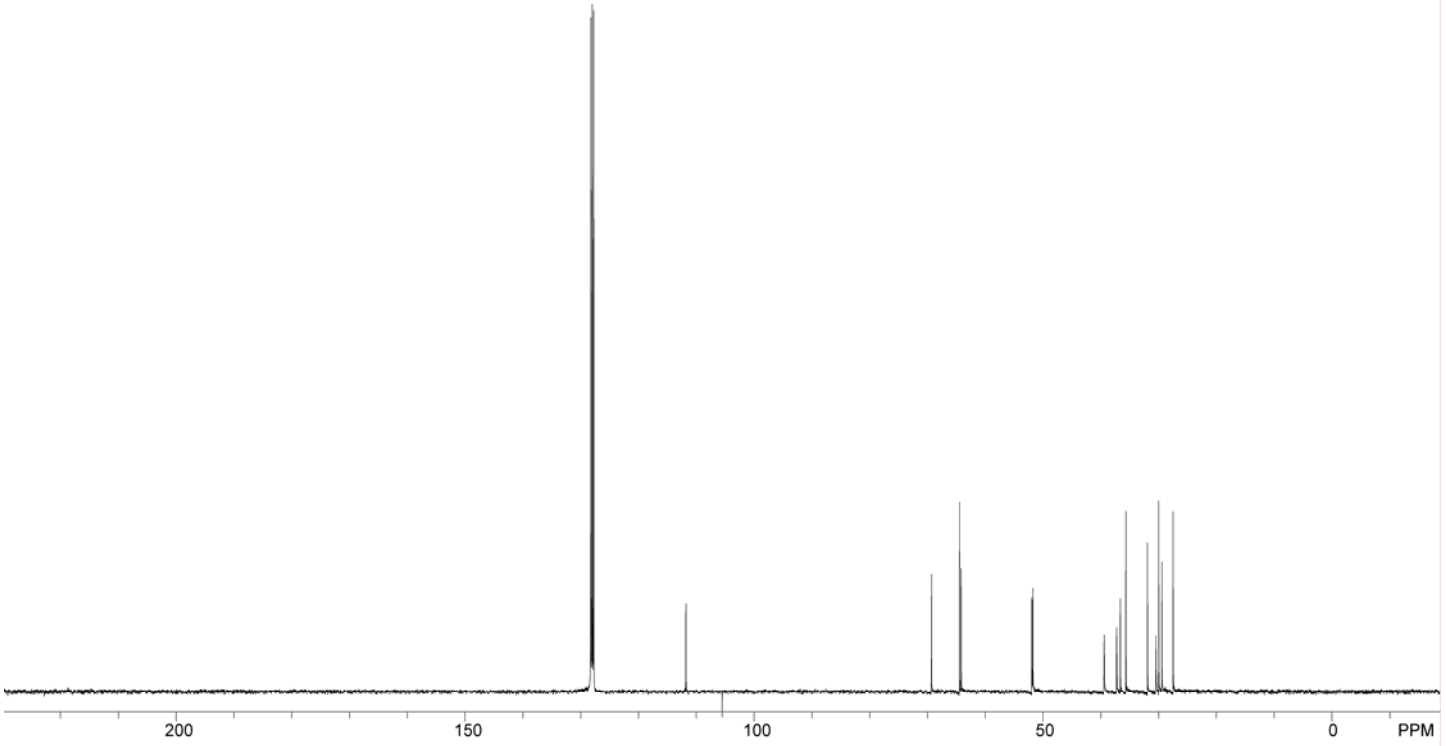

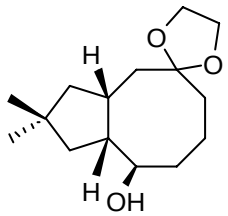

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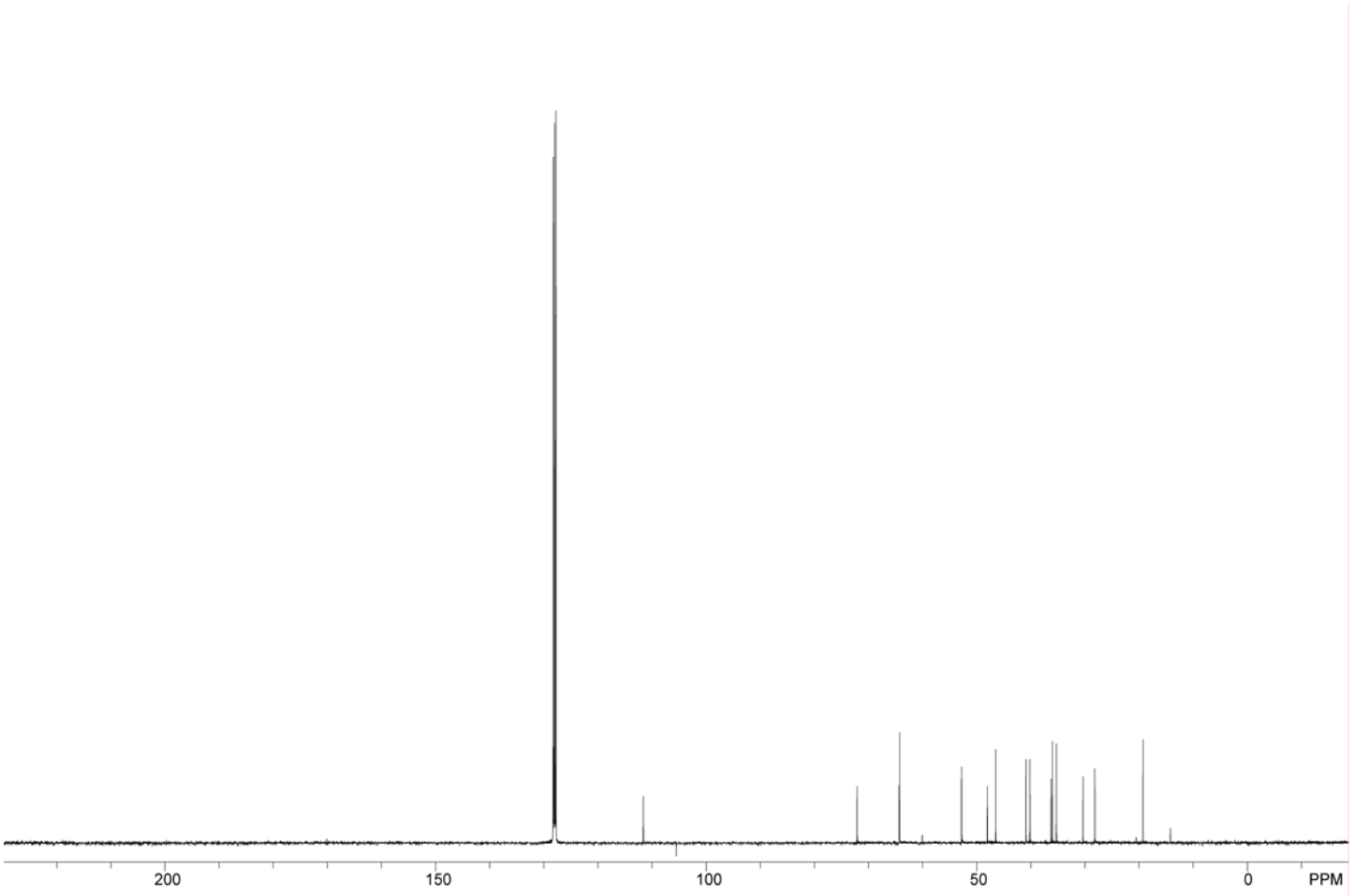

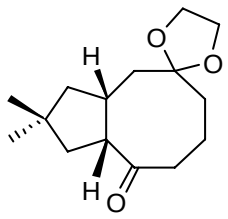

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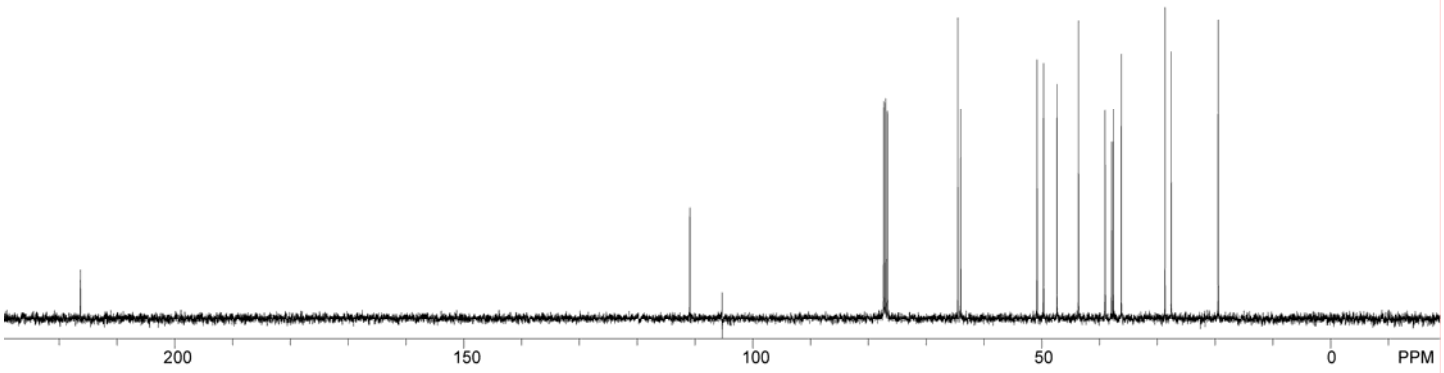

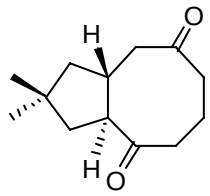

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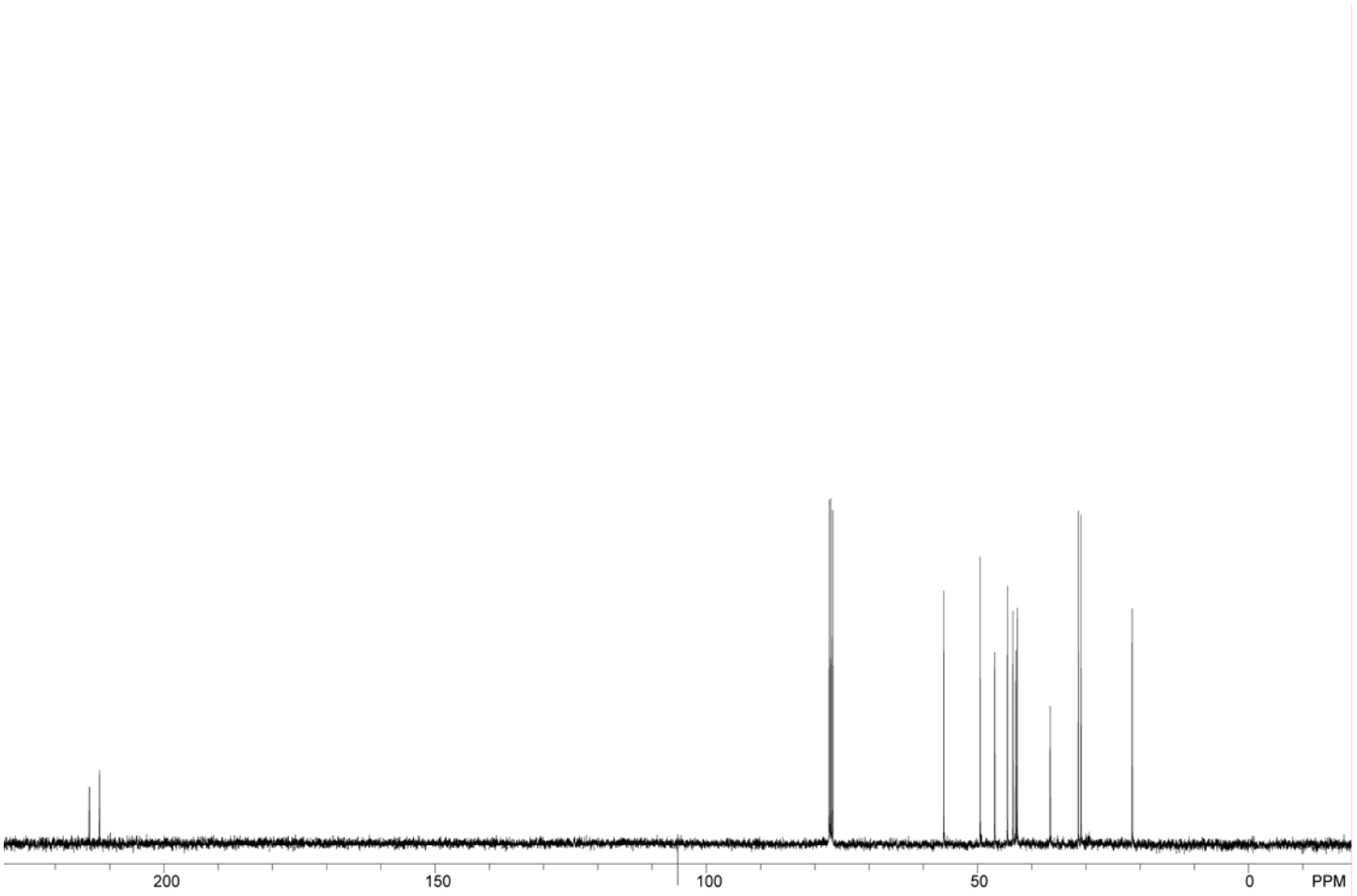

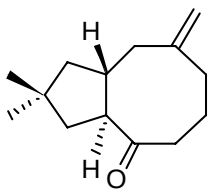

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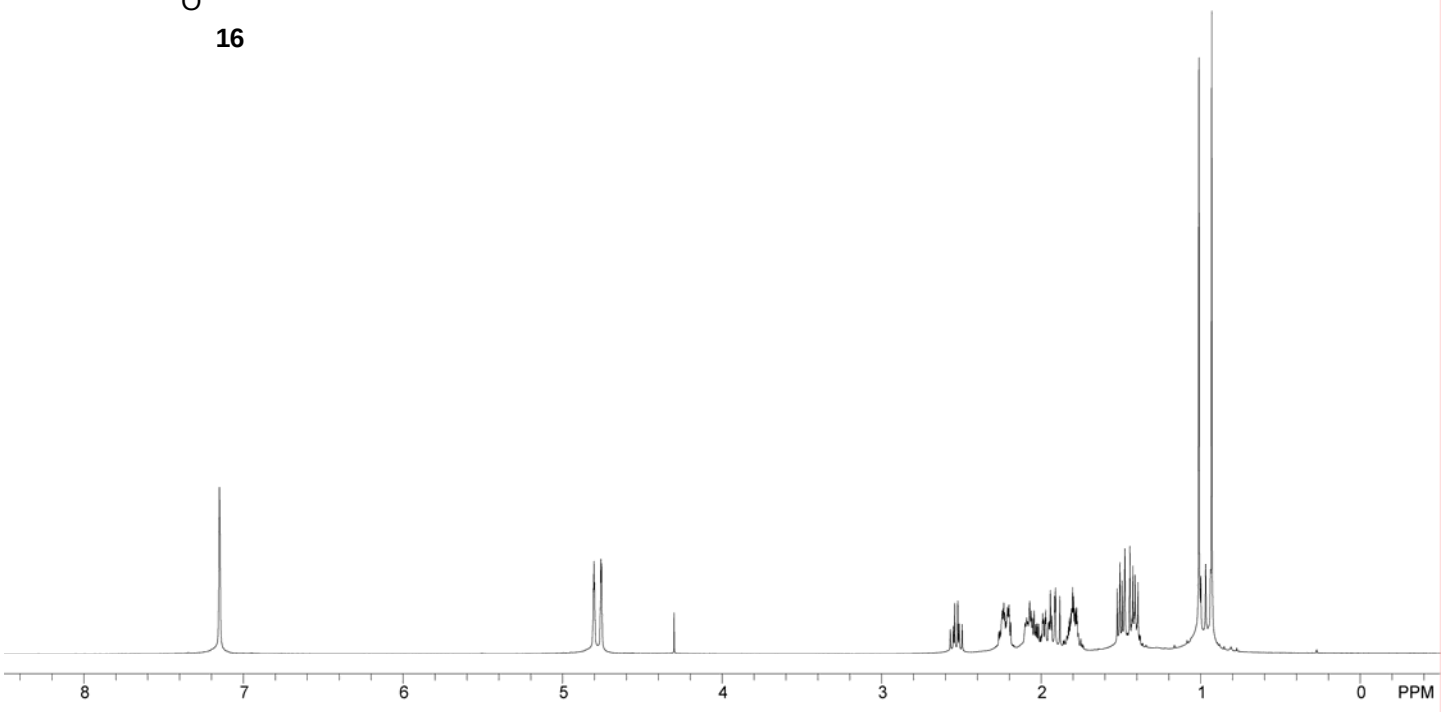

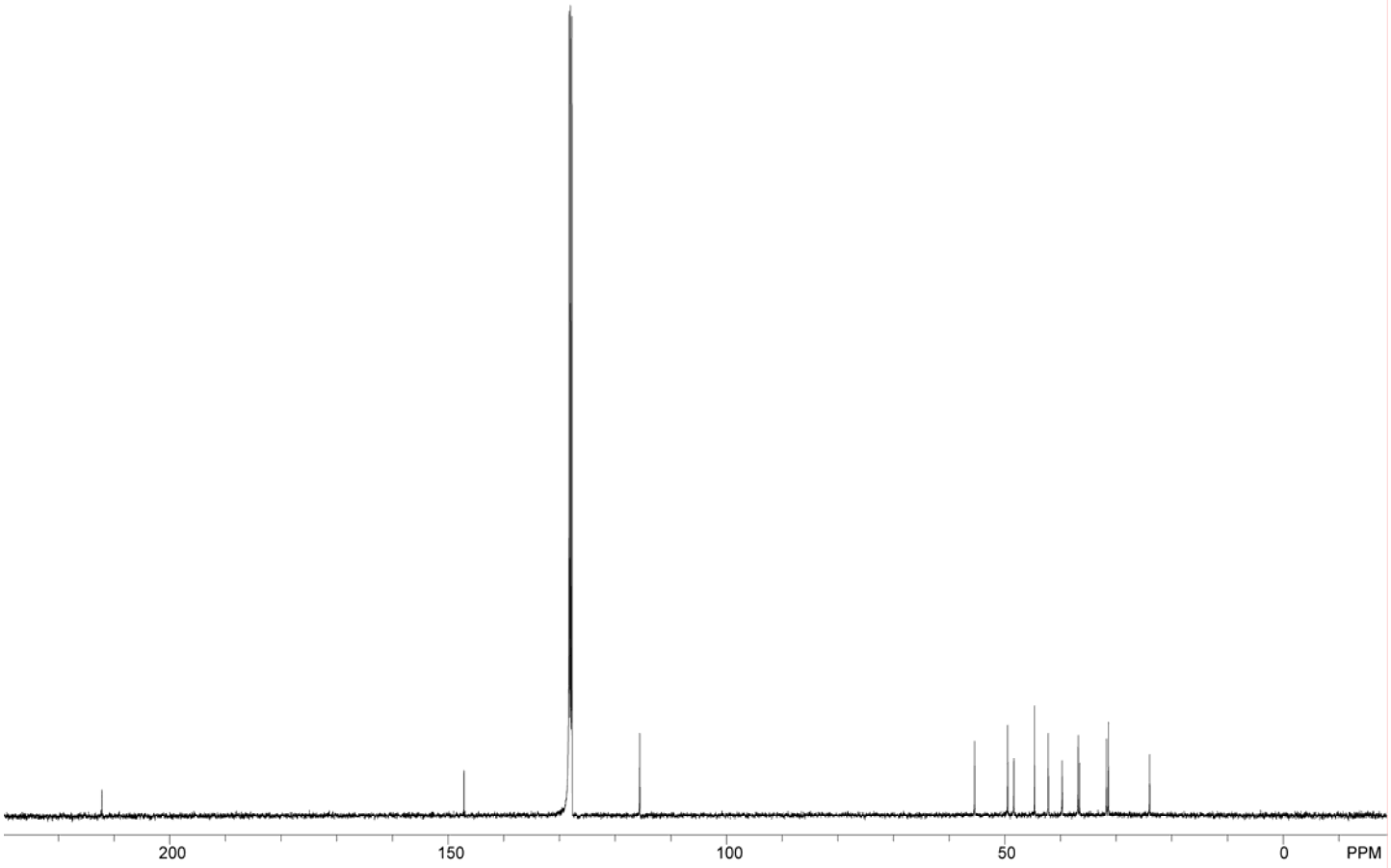

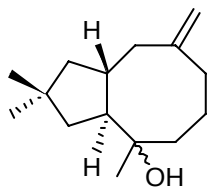

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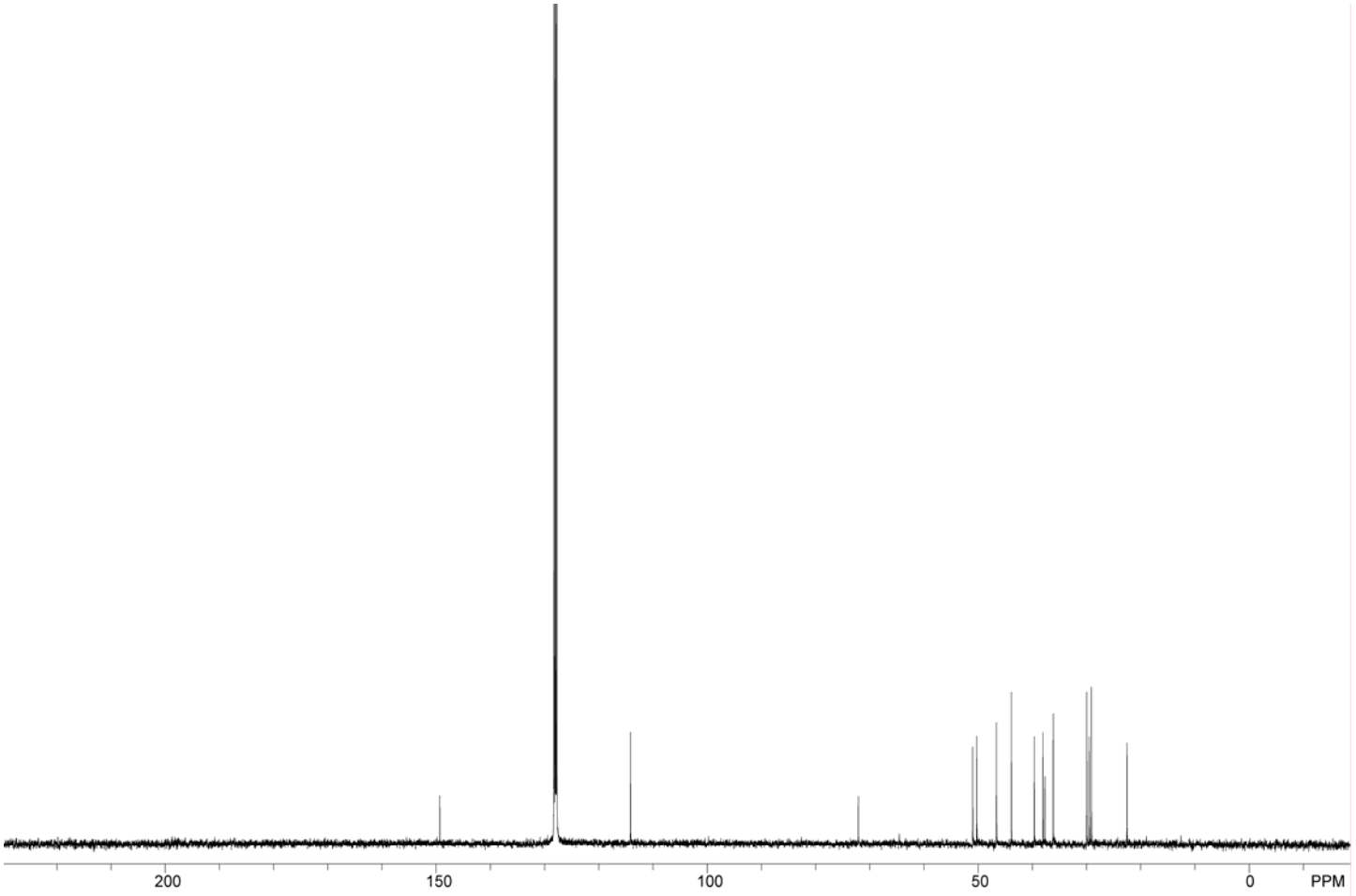

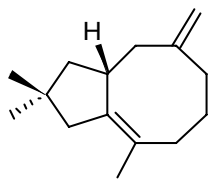

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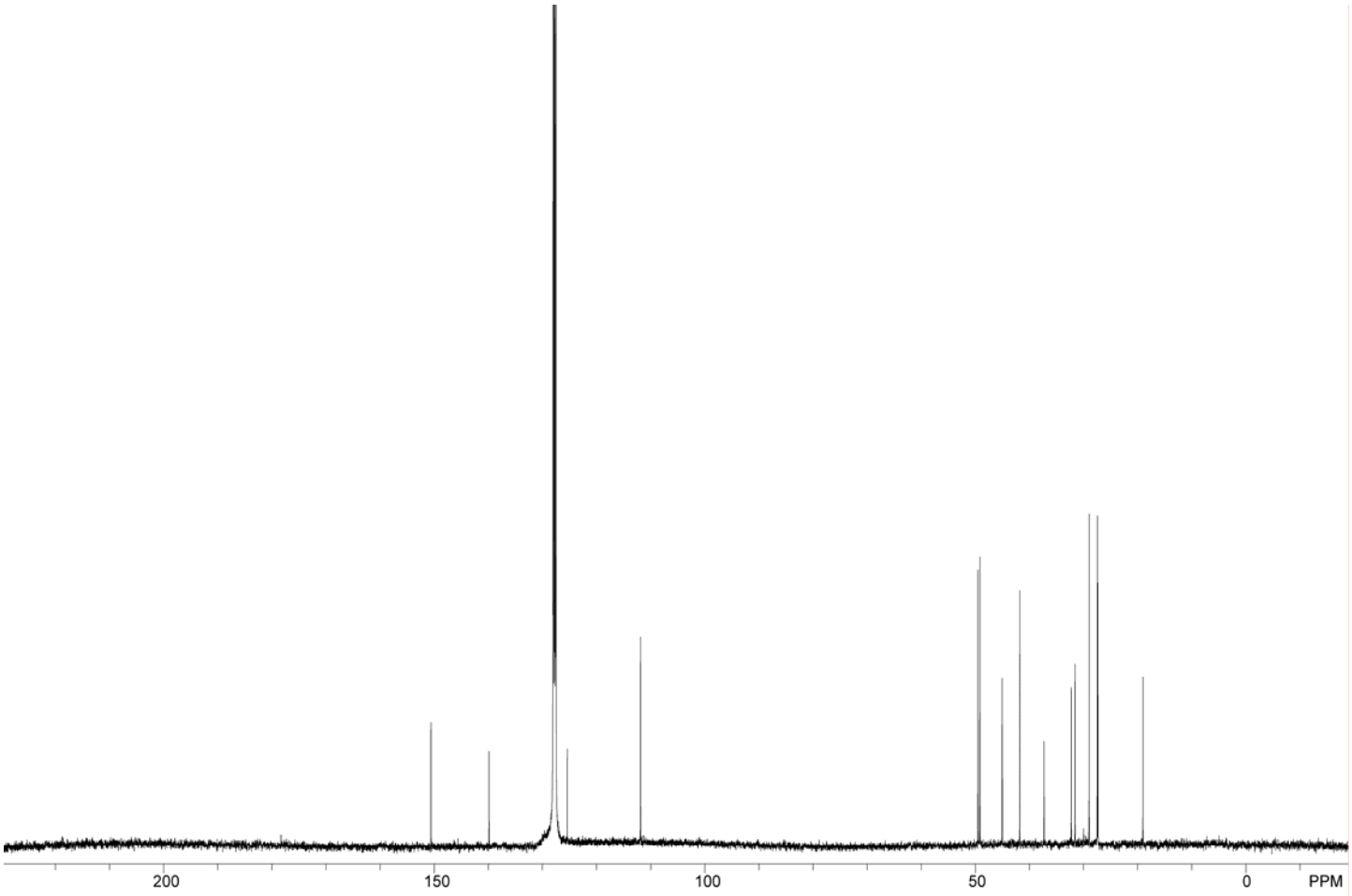

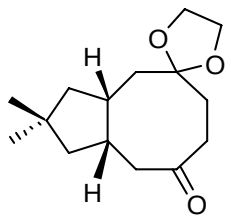

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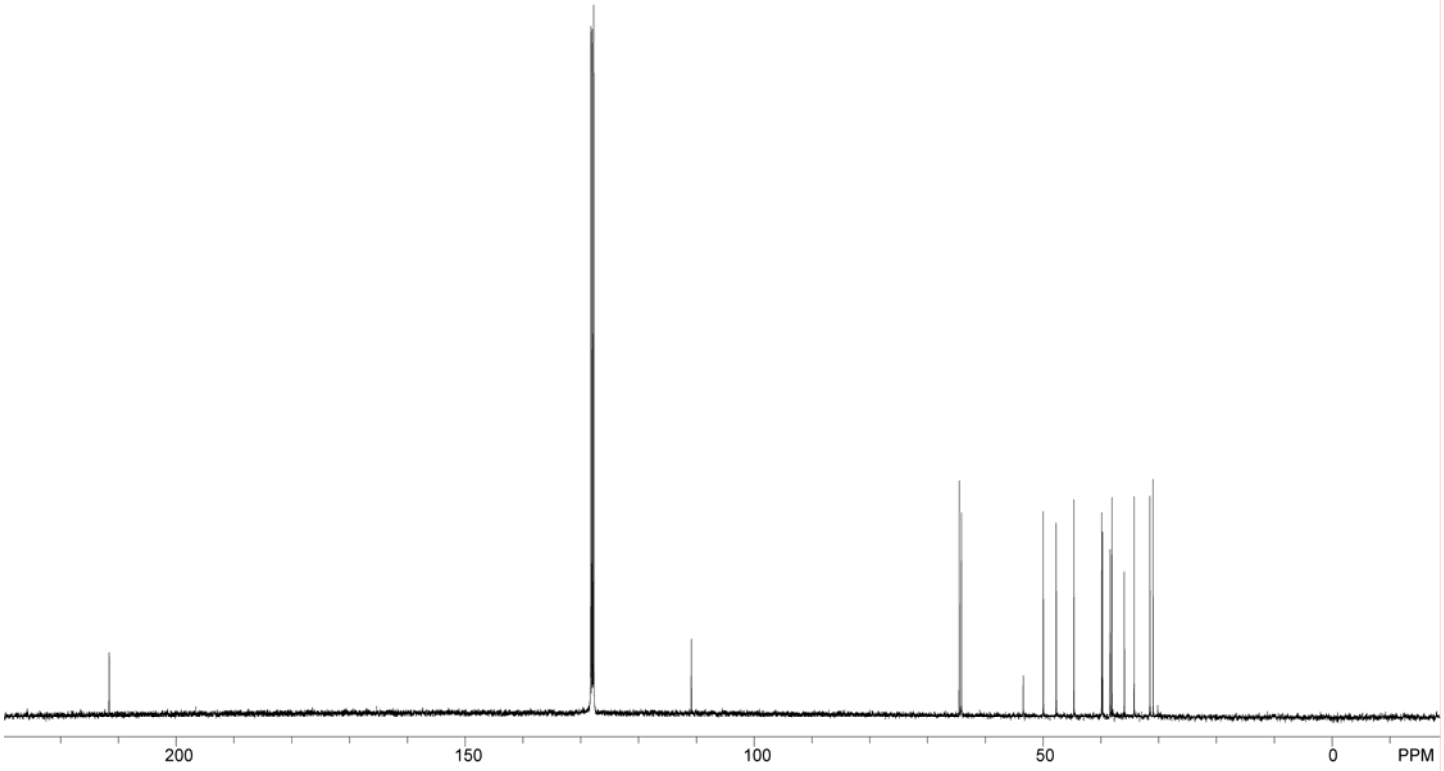

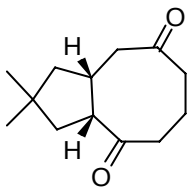

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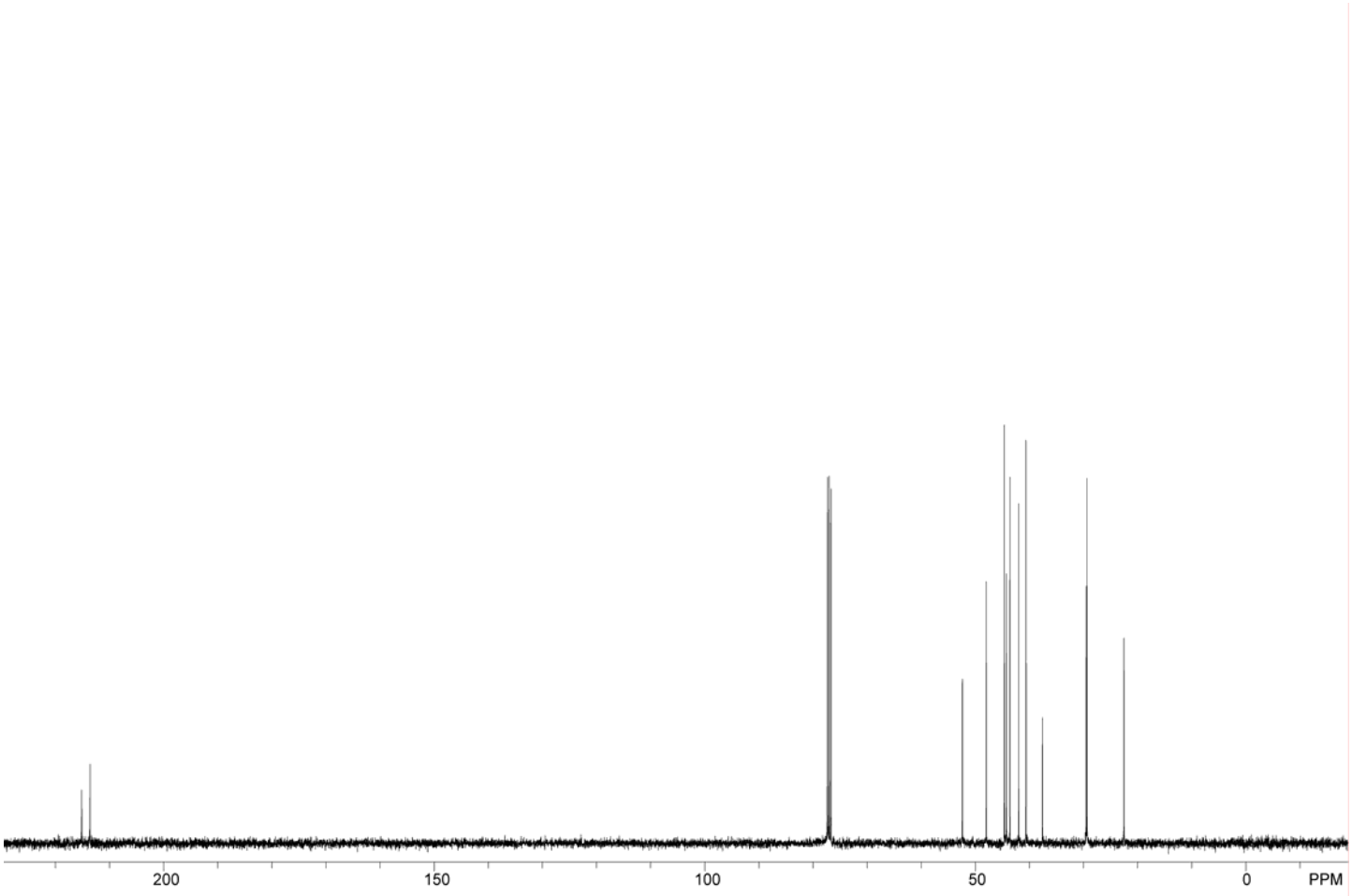
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