Supplementary Information

Enantioselective total synthesis of (+)-asteriscanolide via Rh(I)-catalyzed [(5+2)+1] reaction

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Contents

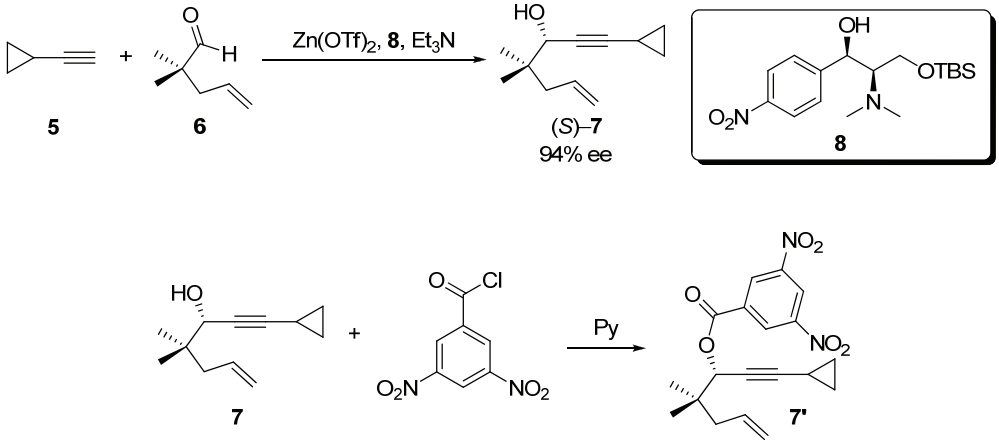
1. General methods

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 syringe. Reactions were stirred using Teflon-coated magnetic stir bars. Elevated temperatures were maintained using Thermostat-controlled silicone oil baths. Organic solutions were concentrated under reduced pressure using a Büchi rotary evaporator with a desktop vacuum pump. Tetrahydrofuran, benzene, and toluene were distilled from sodium and benzophenone prior to use. Dichloromethane was distilled from CaH_2 prior to use. Synthetic reagents were purchased from Acros, Aldrich, and Alfa Aesar and used without further purification, unless otherwise indicated. Analytical TLC was performed with 0.25 mm silica gel G 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 showed a single spot by analytical TLC. The diastereomeric ratio and the regioisomeric ratio were determined by ^{1}H NMR of crude reaction mixtures.

NMR spectra were measured on Bruker ARX 400 (^{1}H at 400 MHz, ^{13}C at 101 MHz) and Bruker AVANCE 600 (^{1}H at 600 MHz, ^{13}C at 150 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, m = multiplet), coupling constant (Hz), and integration. Data for ^{13}C-NMR spectra are reported in terms of chemical shift (ppm) relative to residual solvent peak ($CDCl_3$: 77.0 ppm). Infrared spectra were recorded on Mettler-Toledo ReactIR iC10 system with an SiComp probe and are reported in wavenumbers (cm^{-1}). High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer (ESI).

Abbreviations:
acac = acetylacetonyl
AIBN = 2,2'-azo *bis*isobutyronitrile
brsm = based on recovered starting material
DIBAl-H = diisobutylaluminum hydride
DMAP = *N,N*-4-dimethylaminopyridine
DMF = *N,N*-dimethylformamide
DMP = Dess-Martin periodinane
*m*CPBA = *m*-chloroperbenzoic acid
PE = petroleum ether
PMB = *p*-methoxybenzyl
Py = pyridine
Red-Al = sodium *bis*(2-methoxyethoxy) aluminum hydride
TBAF = tetrabutylammonium fluoride
TBS = *tert*-butyldimethylsilyl
Tf = trifluoromethanesulfonyl
THF = tetrahydrofuran
TMS = trimethylsilyl

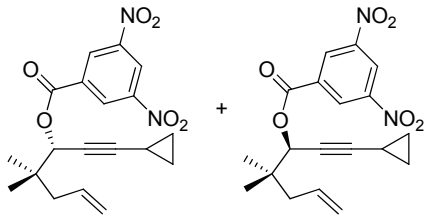
2. Experimental procedures and characterization data



A mixture of $Zn(OTf)_2$ (326 mg, 0.90 mmol), triethylamine (331 mg, 3.28 mmol), and the chiral ligand **8**[1] (402 mg, 1.13 mmol) in 30 mL anhydrous toluene was stirred under argon at 55 ºC until a clear solution was formed, and alkyne **5** (594 mg, 8.99 mmol) was added subsequently. After stirred for 30 min, aldehyde **6** (561 mg, 5.00 mmol) was added. The reaction was completed after stirred for 46 h at 55 ºC. The reaction mixture was diluted with diethyl ether, and then the organic phase was washed with 1M HCl and sat aq NaCl, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel to afford alcohol **7** (804 mg, 90%). 94% ee was determined by HPLC analysis of the 3,5-dinitrobenzoate ester **7'**[2] (Chiralcel OD-H, hexane:isopropanol = 90:10, 1.0 mL/min, 254 nm).

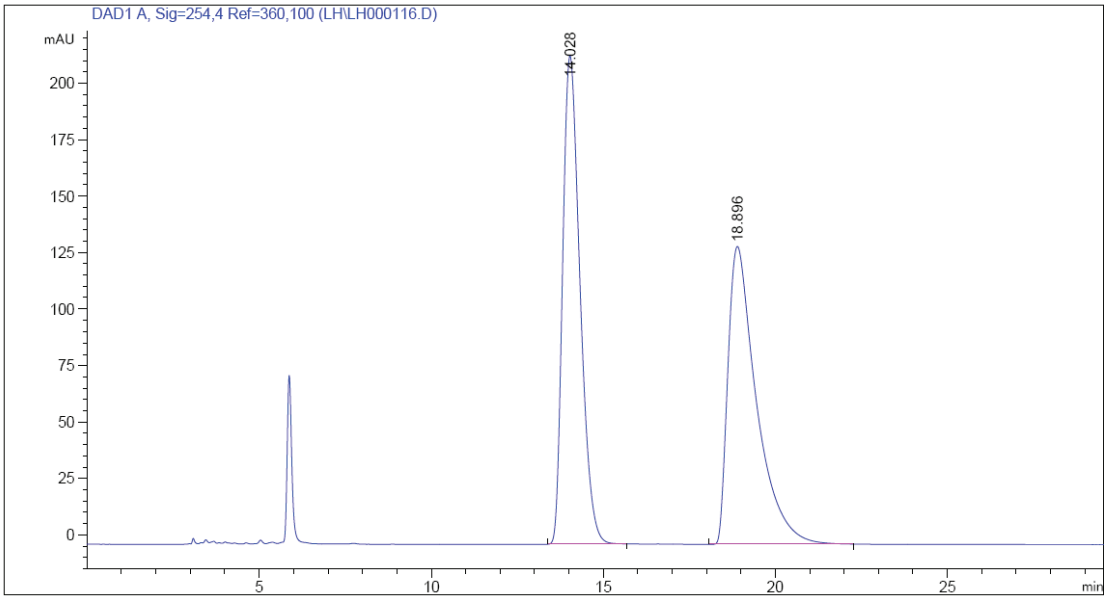
7: colorless oil; R_f = 0.31 (PE/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.65−0.70 (m, 2H), 0.75−0.80 (m, 2H), 0.93 (s, 3H), 0.94 (s, 3H), 1.22−1.31 (m, 1H), 1.74−1.79 (m, 1H), 2.07 (dd, J = 13.5, 7.5 Hz, 1H), 2.14 (dd, J = 13.5, 7.5 Hz, 1H), 4.02 (dd, J = 6.2, 1.7 Hz, 1H), 5.04 (s, 1H), 5.08 (d, J = 4.9 Hz, 1H), 5.78−5.90 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ −0.6, 8.2, 22.5, 22.6, 38.7, 42.7, 70.4, 74.6, 89.8, 117.4, 135.1. IR ν (cm^{-1}): 1371, 1386, 1475, 1643, 2242, 2972, 3389. HRMS (ESI): calcd for $C_{12}H_{18}NaO$: 201.1250; found: 201.1250. $[\alpha]^{20}_D$: +15.7 (c 1.53, $CHCl_3$).

[1] B. Jiang, Z. Chen and X. Tang, *Org. Lett.*, 2002, **4**, 3451.
[2] Propargylic alcohol **7** was treated with 3,5-dinitrobenzoyl chloride and pyridine in CH_2Cl_2 at room temperature to give 3,5-dinitrobenzoate ester **7'** quantitatively. **7'**: pale yellow oil; R_f = 0.44 (PE/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.69−0.74 (m, 2H), 0.79−0.85 (m, 2H), 1.10 (s, 3H), 1.11 (s, 3H), 1.25−1.34 (m, 1H), 2.22 (d, J = 7.4 Hz, 2H), 5.03−5.15 (m, 2H), 5.42 (d, J = 1.9 Hz, 1H), 5.80−5.92 (m, 1H), 9.16 (d, J = 2.0 Hz, 2H), 9.24 (t, J = 2.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ -0.6, 8.3, 23.07, 23.14, 38.4, 43.1, 69.9, 74.1, 91.7, 118.2, 122.3, 129.4, 133.7, 133.9, 148.6, 161.5. IR ν (cm^{-1}): 1266, 1348, 1549, 1631, 1736, 2246, 2980. HRMS (ESI): calcd for $C_{19}H_{20}N_2NaO_6$: 395.1214; found: 395.1213.



(*S*)–**7'** : (*R*)–**7'**

50 : **50**



Peak RetTime Type Width Area Height Area%

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
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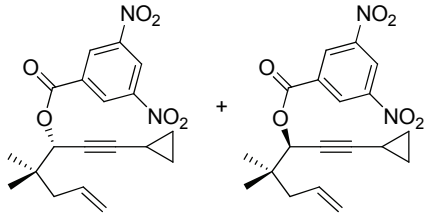
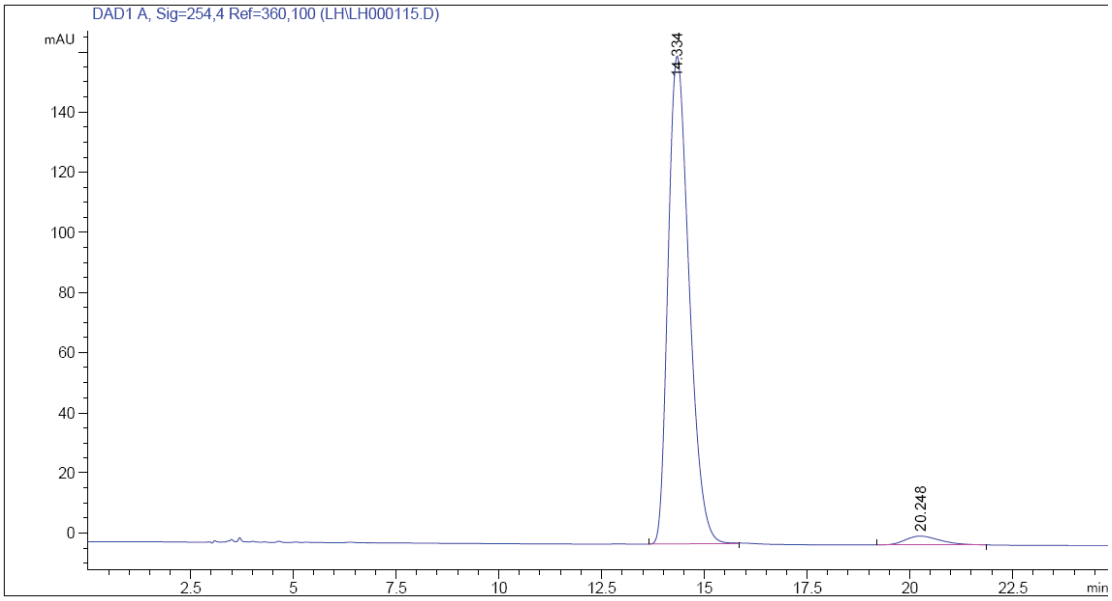
2	18.896	BB	0.8467	7583.31885	131.91266	50.0385



(*S*)–**7'** : (*R*)–**7'**

97 : **3**



Peak RetTime Type Width Area Height Area%

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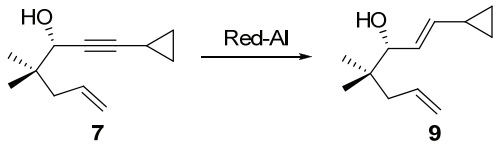
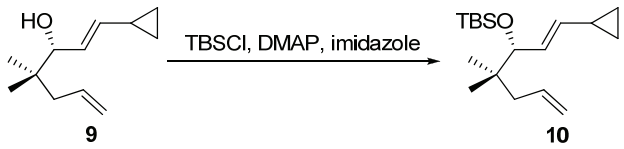
1	14.334	BB	0.5521	5785.60596	162.22356	96.9810
2	20.248	BB	0.9326	180.10561	2.96553	3.0190



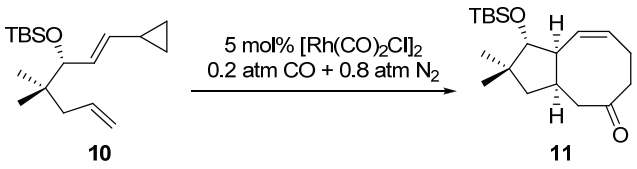
To a solution of propargylic alcohol **7** (930 mg, 5.22 mmol) in anhydrous THF (10 mL) at −78 ºC was slowly added Red-Al (3.5 M in toluene, 3.6 mL, 12.6 mmol). Then the reaction mixture was allowed to warm up to room temperature. After stirred at 40 ºC for 20 h, the reaction mixture was cooled to 0 ºC and quenched by sat aq potassium sodium tartrate. After stirred overnight at room temperature, the reaction mixture was diluted with diethyl ether and separated. The aqueous layer was extracted with diethyl ether. The combined organic phase was washed with sat aq NaCl, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel to afford allylic alcohol **9** (860 mg, 92%).

9: colorless oil; R_f = 0.33 (PE/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.35−0.39 (m, 2H), 0.69−0.74 (m, 2H), 0.85 (s, 3H), 0.89 (s, 3H), 1.35−1.45 (m, 1H), 1.49 (br, 1H), 1.98 (dd, J = 13.5, 7.5 Hz, 1H), 2.10 (dd, J = 13.5, 7.5 Hz, 1H), 3.74 (dd, J = 7.7, 3.7 Hz, 1H), 5.00−5.07 (m, 2H), 5.16 (dd, J = 15.5, 8.8 Hz, 1H), 5.60 (dd, J = 15.5, 7.7 Hz, 1H), 5.79−5.91 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 6.69, 6.74, 13.5, 22.6, 22.9, 37.7, 43.4, 79.6, 117.1, 126.8, 135.5, 137.6. IR ν (cm^{-1}): 1371, 1389, 1475, 1643, 1669, 2969, 3393. HRMS (ESI): calcd for $C_{12}H_{20}NaO$: 203.1406; found: 203.1405. $[\alpha]^{20}_D$: +30.1 (c 0.98, $CHCl_3$).



To a solution of allylic alcohol **9** (1.80 g, 10.0 mmol) in 40 mL anhydrous DMF was added imidazole (1.20 g, 17.6 mmol), DMAP (0.35 g, 2.9 mmol), and TBSCl (2.17 g, 14.4 mmol). After stirred at 40 ºC for 48 h, the reaction mixture was poured into 150 mL water and extracted with diethyl ether. The combined organic extracts were washed with sat aq NaCl and dried over $MgSO_4$. The filtrate was evaporated and purified by flash column chromatography on silica gel to afford compound **10** (2.83 g, 96%).

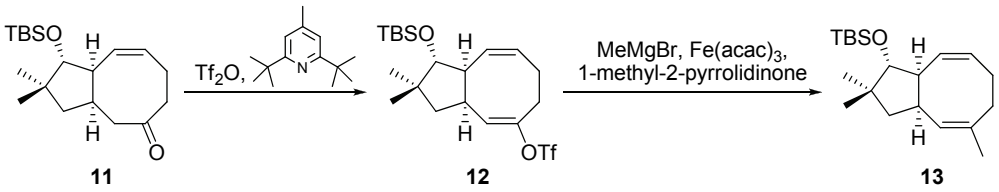
10: colorless oil; R_f = 0.61 (PE). ^{1}H NMR (400 MHz, $CDCl_3$): δ −0.01 (s, 3H), 0.01 (s, 3H), 0.30−0.38 (m, 2H), 0.65−0.72 (m, 2H), 0.79 (s, 3H), 0.83 (s, 3H), 0.89 (s, 9H), 1.32−1.42 (m, 1H), 1.94 (dd, J = 13.5, 7.7 Hz, 1H), 2.06 (dd, J = 13.5, 7.7 Hz, 1H), 3.66 (d, J = 8.0 Hz, 1H), 4.96−5.09 (m, 3H), 5.46 (dd, J = 15.4, 8.0 Hz, 1H), 5.77−5.89 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ −4.9, −3.5, 6.3, 6.4, 13.2, 18.2, 22.92, 22.94, 26.0, 38.5, 43.2, 80.8, 116.6, 127.9, 135.9, 136.2. IR ν (cm^{-1}): 1255, 1367, 1389, 1475, 1643, 1669, 2961. HRMS (ESI): calcd for $C_{18}H_{34}NaOSi$: 317.2271; found: 317.2278. $[\alpha]^{20}_D$: +10.6 (c 1.78, $CHCl_3$).



10 **11**

A solution of substrate **10** (1.50 g, 5.1 mmol) and $[Rh(CO)_2Cl]_2$ (100 mg, 0.26 mmol) in 310 mL anhydrous toluene was degassed by bubbling CO/N_2 (balloon pressured mixed gas of CO and N_2, 1:4 V/V) for 5 min. Then the reaction mixture was immersed in a 90 ºC oil bath and stirred under the above atmosphere for 50 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. The crude mixture was submitted to flash column chromatography on silica gel to afford the [(5+2)+1] cycloadduct **11** (1.15 g, 70%).

11: pale yellow oil; R_f = 0.19 (PE/AcOEt = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ −0.02 (s, 3H), 0.02 (s, 3H), 0.86 (s, 9H), 0.93 (s, 3H), 1.01 (s, 3H), 1.10 (t, J = 12.4 Hz, 1H), 1.54−1.63 (m, 1H), 2.01−2.30 (m, 3H), 2.34−2.56 (m, 4H), 2.61−2.70 (m, 1H), 3.63 (d, J = 4.4 Hz, 1H), 5.44−5.51 (m, 1H), 5.87−5.96 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ −4.9, −4.2, 18.0, 22.0, 23.8, 25.8, 28.4, 36.9, 41.7, 44.6, 44.7, 46.7, 47.8, 89.2, 130.0, 133.9, 213.9. IR ν (cm^{-1}): 1255, 1367, 1464, 1706, 2957. HRMS (ESI): calcd for $C_{19}H_{34}NaO_2Si$: 345.2220; found: 345.2221. $[\alpha]^{20}_D$: −45.3 (c 1.18, $CHCl_3$).



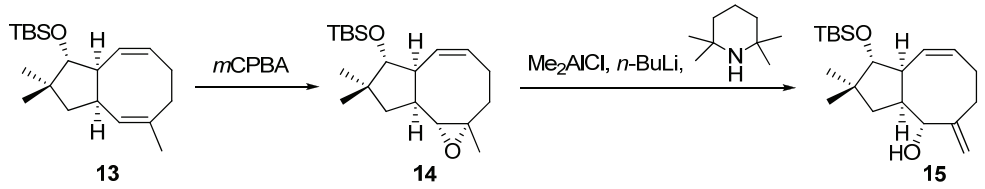
11 **12** **13**

To a solution of 2,6-di-*tert*-butyl-4-methylpyridine (1.16 g, 5.67 mmol) in 30 mL anhydrous CH_2Cl_2 was added sequentially trifluoromethanesulfonic anhydride (1.32 g, 4.68 mmol) and a solution of ketone **11** (890 mg, 2.76 mmol) in 30 mL anhydrous CH_2Cl_2. The reaction mixture was stirred at 25 ºC for 12 h. After the solvent was removed by evaporation, the residue was dissolved in 150 mL diethyl ether, washed with 1M HCl solution and sat aq NaCl, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting brown oil was filtered through a pad of silica gel, and the filtrate was concentrated under reduced pressure to give the crude enol triflate **12**, which was used in the next step without further purification.

A solution of the crude enol triflate **12** in 35 mL THF was added to a mixture of $Fe(acac)_3$ (199 mg, 0.56 mmol) and 1-methyl-2-pyrrolidinone (3 mL), and the resulting mixture was cooled to −10 ºC. After MeMgBr (3.0 M in ether, 3.5 mL, 10.5 mmol) was added dropwise, the reaction mixture was allowed to warm up to room temperature and stirred overnight. Then, to the reaction mixture was added sat aq NH_4Cl and diethyl ether, and the aqueous layer was extracted with diethyl ether. The combined organic

phase was washed with sat aq NaCl, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give compound **13** (515 mg, 58% over two steps).

13: colorless oil; R_f = 0.39 (PE). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.04 (s, 3H), 0.05 (s, 3H), 0.89 (s, 9H), 0.92 (s, 3H), 0.98 (s, 3H), 1.24 (t, J = 12.4 Hz, 1H), 1.66 (s, 3H), 1.73 (dd, J = 12.4, 7.6 Hz, 1H), 1.79 (dt, J = 14.1, 6.8 Hz, 1H), 2.02–2.12 (m, 1H), 2.39–2.48 (m, 1H), 2.58–2.66 (m, 1H), 2.84–2.92 (m, 1H), 3.14–3.24 (m, 1H), 3.46 (d, J = 7.7 Hz, 1H), 5.09 (d, J = 4.6 Hz, 1H), 5.41 (ddd, J = 11.0, 5.5, 2.4 Hz, 1H), 5.50–5.57 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ −4.5, −3.8, 18.2, 21.2, 23.8, 26.0, 26.6, 27.8, 32.0, 38.3, 40.7, 46.0, 50.5, 88.7, 128.6, 128.7, 133.7, 136.4. IR ν (cm^{-1}): 1255, 1363, 1468, 2935. HRMS (ESI): calcd for $C_{20}H_{36}NaOSi$: 343.2428; found: 343.2431. $[\alpha]^{20}_D$: +13.8 (c 1.00, $CHCl_3$).



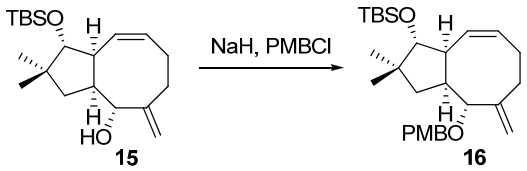
13 **14** **15**

To a solution of compound **13** (200 mg, 0.63 mmol) in 6 mL ethyl acetate at 0 ºC was added *m*CPBA (70 wt%, 195 mg, 0.79 mmol). After stirred at 0 ºC for 2 h, sat aq $NaHCO_3$ was added, and the mixture was extracted with diethyl ether. The combined organic phase was washed with sat aq NaCl, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give the crude epoxide **14**, which was used in the next step without further purification.

To a solution of 2,2,6,6-tetramethylpiperidine (520 mg, 3.69 mmol) in 20 mL anhydrous benzene was added *n*-BuLi (1.6 M in hexane, 2.2 mL, 3.5 mmol). To the resulting mixture at 0 ºC was added Me_2AlCl (0.9 M in heptane, 4.0 mL, 3.6 mmol), and the reaction mixture was stirred at 0 ºC for 25 min before a solution of the crude epoxide **14** in 15 mL anhydrous benzene was added. After stirred at 0 ºC for 2 h, the reaction mixture was quenched with 1M HCl and extracted with diethyl ether. The combined organic extracts were washed with water and sat aq NaCl, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography to give alcohol **15** (180 mg, 86% over two steps).

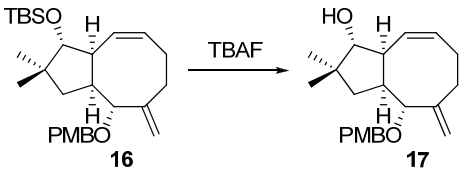
15: colorless oil; R_f = 0.24 (PE/AcOEt = 10:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ −0.03 (s, 3H), 0.00 (s, 3H), 0.86 (s, 9H), 0.98 (s, 3H), 1.11 (s, 3H), 1.32 (t, J = 12.7 Hz, 1H), 1.39 (d, J = 3.0 Hz, 1H), 1.76–1.80 (m, 1H), 2.00–2.07 (m, 2H), 2.16–2.29 (m, 2H), 2.40–2.46 (m, 1H), 2.60 (t, J = 8.4 Hz, 1H), 3.62 (s, 1H), 3.84 (dd, J = 9.7, 2.4 Hz, 1H), 4.98 (s, 1H), 5.24 (s, 1H), 5.42 (t, J = 9.7 Hz, 1H), 5.71–5.76 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ −5.1, −4.6, 18.1, 24.3, 25.8, 28.3, 30.2, 37.0, 42.6, 44.7, 49.0, 50.7, 75.7, 88.1, 111.6, 130.1, 132.2, 157.2. IR ν (cm^{-1}): 1255, 1367, 1468, 1643, 2935, 3360.

HRMS (ESI): calcd for $C_{20}H_{36}NaO_2Si$: 359.2377; found: 359.2377. $[\alpha]^{20}_D$: −7.1 (*c* 1.07, $CHCl_3$).



To a solution of alcohol **15** (393 mg, 1.17 mmol) in 6 mL anhydrous DMF was added NaH (206 mg, 8.57 mmol). After stirred at 50 ºC for 50 min, freshly distilled PMBCl (658 mg, 4.21 mmol) was added, and the reaction mixture was stirred at 50 ºC for 5 h before 30 mL water was added. The resulting mixture was extracted with diethyl ether and petroleum ether, and the combined organic extracts were washed with sat aq NaCl, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude mixture was submitted to flash column chromatography on silica gel to afford compound **16** (440 mg, 82%).

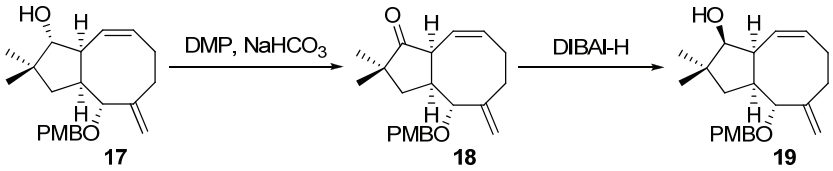
16: colorless oil; R_f = 0.31 (PE/AcOEt = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ −0.04 (s, 3H), −0.02 (s, 3H), 0.85 (s, 9H), 0.95 (s, 3H), 1.09 (s, 3H), 1.23 (t, *J* = 12.7 Hz, 1H), 1.84−1.92 (m, 2H), 1.96−2.08 (m, 1H), 2.12−2.22 (m, 1H), 2.29−2.41 (m, 1H), 2.49 (ddd, *J* = 12.5, 5.6, 1.9 Hz, 1H), 2.58 (t, *J* = 8.4 Hz, 1H), 3.45 (d, *J* = 9.9 Hz, 1H), 3.60 (d, *J* = 1.5 Hz, 1H), 3.80 (s, 3H), 4.07 (d, *J* = 11.3 Hz, 1H), 4.41 (d, *J* = 11.3 Hz, 1H), 5.07 (s, 1H), 5.28 (d, *J* = 1.7 Hz, 1H), 5.37−5.43 (m, 1H), 5.66−5.74 (m, 1H), 6.85 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ −5.1, −4.7, 18.1, 24.7, 25.8, 28.4, 30.5, 37.8, 42.5, 45.0, 49.0, 50.0, 55.2, 69.5, 82.7, 87.7, 112.5, 113.6, 129.2, 129.8, 131.3, 132.3, 152.9, 158.9. IR *v* (cm^{-1}): 1255, 1468, 1520, 1620, 2935. HRMS (ESI): calcd for $C_{28}H_{44}NaO_3Si$: 479.2952; found: 479.2954. $[\alpha]^{20}_D$: +39.7 (*c* 2.20, $CHCl_3$).



To a solution of compound **16** (395 mg, 0.87 mmol) in 7 mL anhydrous THF was added TBAF (850 mg, 3.25 mmol). After stirred at 40 ºC for 21 h, the reaction mixture was quenched with 50 mL sat aq NH_4Cl and extracted with diethyl ether. The combined organic extracts were washed with sat aq NaCl, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column

chromatography to give alcohol **17** (266 mg, 90%).

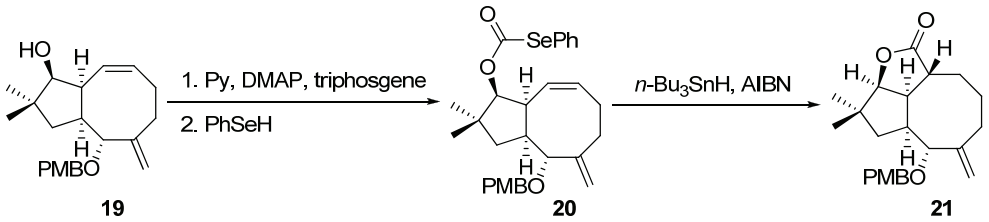
17: colorless oil; R_f = 0.22 (PE/AcOEt = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.03 (s, 3H), 1.15 (s, 3H), 1.32 (t, J = 12.6 Hz, 1H), 1.50 (d, J = 4.4 Hz, 1H), 1.87−1.95 (m, 2H), 2.06−2.13 (m, 1H), 2.15−2.21 (m, 1H), 2.32−2.39 (m, 1H), 2.50 (ddd, J = 12.8, 5.5, 2.4 Hz, 1H), 2.68 (t, J = 8.1 Hz, 1H), 3.47 (d, J = 9.7 Hz, 1H), 3.69 (d, J = 2.4 Hz, 1H), 3.80 (s, 3H), 4.07 (d, J = 11.4 Hz, 1H), 4.41 (d, J = 11.4 Hz, 1H), 5.07 (s, 1H), 5.28 (d, J = 1.7 Hz, 1H), 5.41−5.46 (m, 1H), 5.69−5.75 (m, 1H), 6.86 (d, J = 9.0 Hz, 2H), 7.20 (d, J = 9.0 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 23.7, 28.2, 30.5, 37.5, 41.7, 45.3, 48.6, 49.8, 55.2, 69.5, 82.6, 87.3, 112.9, 113.6, 129.2, 130.3, 131.1, 131.5, 152.4, 158.9. IR ν (cm^{-1}): 1248, 1520, 1620, 2935, 3430. HRMS (ESI): calcd for $C_{22}H_{30}NaO_3$: 365.2087; found: 365.2088. $[\alpha]^{20}_D$: +91.8 (c 1.20, $CHCl_3$).



To a mixture of alcohol **17** (106 mg, 0.31 mmol) and $NaHCO_3$ (200 mg, 2.38 mmol) in 7 mL anhydrous CH_2Cl_2 was added Dess-Martin periodinane (425 mg, 1.00 mmol). After stirred for 90 min, the reaction mixture was quenched with 20 mL sat aq $NaHCO_3$ and 20 mL sat aq $Na_2S_2O_3$ and then extracted with CH_2Cl_2. The combined organic extracts were washed with sat aq NaCl, dried over $MgSO_4$ twice, filtered, and used directly in the next step.

To the solution of ketone **18** at −78 ºC was added DIBAl-H (1.0 M in hexane, 8.0 mL, 8.0 mmol). After stirred at −78 ºC for 2 h, the reaction mixture was allowed to warm up to 0 ºC and quenched with sat aq potassium sodium tartrate. The aqueous layer was separated and extracted with CH_2Cl_2. The combined organic phase was washed with sat aq NaCl, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel to afford alcohol **19** (89 mg, 84% over two steps).

19: white solid, mp 113−114 °C; R_f = 0.26 (PE/AcOEt = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.07 (s, 3H), 1.08 (s, 3H), 1.33−1.40 (m, 1H), 1.51 (d, J = 5.0 Hz, 1H), 1.87−1.97 (m, 3H), 2.08−2.16 (m, 1H), 2.18−2.40 (m, 1H), 2.52 (ddd, J = 12.8, 5.4, 2.4 Hz, 1H), 3.02−3.08 (m, 1H), 3.40−3.44 (m, 1H), 3.80 (s, 3H), 3.86 (t, J = 5.5 Hz, 1H), 4.07 (d, J = 11.3 Hz, 1H), 4.40 (d, J = 11.3 Hz, 1H), 5.10 (s, 1H), 5.27 (d, J = 1.7 Hz, 1H), 5.67−5.71 (m, 1H), 5.84−5.90 (m, 1H), 6.85 (d, J = 8.8 Hz, 2H), 7.19 (d, J = 8.8 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 25.8, 28.2, 31.9, 38.1, 39.5, 44.7, 45.2, 46.8, 55.2, 69.6, 81.8, 83.5, 112.6, 113.7, 127.3, 129.3, 131.0, 132.3, 152.3, 159.0. IR ν (cm^{-1}): 1251, 1520, 1616, 2928, 3423. HRMS (ESI): calcd for $C_{22}H_{30}NaO_3$: 365.2087; found: 365.2092. $[\alpha]^{20}_D$: +111.5 (c 0.96, $CHCl_3$).

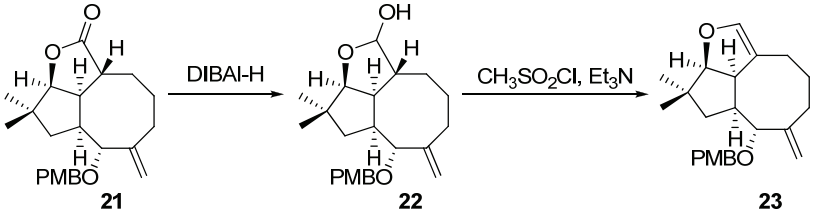


19 **20** **21**

To a mixture of alcohol **19** (101 mg, 0.29 mmol), DMAP (27 mg, 0.22 mmol), and pyridine (0.88 g, 11.1 mmol) in 8 mL anhydrous THF was added a solution of triphosgene (145 mg, 0.49 mmol) in 8 mL anhydrous benzene. After stirred at 30 ºC for 3 h, freshly distilled PhSeH (387 mg, 2.46 mmol) was added, and the reaction mixture was stirred at 30 ºC for 16 h before 100 mL water and 100 mL diethyl ether were added. The aqueous layer was separated and extracted with diethyl ether. The combined organic phase was washed sequentially with 1M HCl, water, and sat aq $NaHCO_3$, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting yellow oil was filtered through a pad of silica gel, and the filtrate was concentrated under reduced pressure to give the crude selenocarbonate **20**, which was used in the next step without further purification.

To a solution of the crude selenocarbonate **20** and AIBN (21 mg, 0.13 mmol) in 60 mL anhydrous benzene was added *n*-Bu_3SnH (360 mg, 1.20 mmol). The resulting mixture was heated in a 90 °C oil bath to reflux for 3.5 h. The solvent was removed by evaporation, and the residue was submitted to flash column chromatography on silica gel to afford the tricyclic compound **21** (104 mg, 95% over two steps).

21: colorless oil; R_f = 0.35 (PE/AcOEt = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.01 (s, 3H), 1.05 (s, 3H), 1.34−1.45 (m, 2H), 1.69−1.82 (m, 2H), 1.89−2.02 (m, 1H), 2.08−2.25 (m, 2H), 2.39 (dq, J = 12.8, 6.4 Hz, 1H), 2.50−2.63 (m, 2H), 2.77 (dd, J = 15.4, 7.8 Hz, 1H), 3.78 (d, J = 6.9 Hz, 1H), 3.81 (s, 3H), 4.20 (d, J = 11.3 Hz, 1H), 4.30 (d, J = 7.7 Hz, 1H), 4.50 (d, J = 11.3 Hz, 1H), 5.10 (s, 1H), 5.13 (s, 1H), 6.88 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 24.4, 25.2, 28.8, 29.9, 34.5, 38.1, 40.4, 43.1, 46.0, 46.3, 55.2, 70.4, 81.7, 89.8, 113.8, 113.9, 129.3, 130.3, 148.8, 159.2, 180.0. IR ν (cm^{-1}): 1251, 1520, 1620, 1769, 2939. HRMS (ESI): calcd for $C_{23}H_{30}NaO_4$: 393.2036; found: 393.2035. $[\alpha]^{20}_D$: +36.0 (c 0.87, $CHCl_3$).



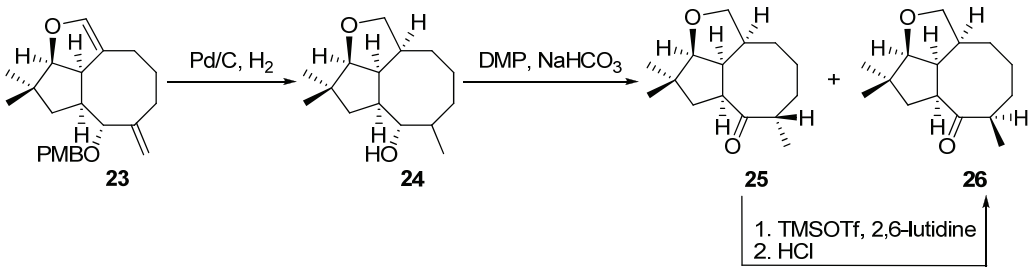
21 **22** **23**

To a solution of compound **21** (104 mg, 0.28 mmol) in 2.5 mL anhydrous CH_2Cl_2 at −78 ºC was added DIBAl-H (1.0 M in hexane, 0.9 mL, 0.9 mmol). After stirred at −78

ºC for 3 h, the reaction mixture was diluted with 30 mL diethyl ether and quenched with 30 mL sat aq potassium sodium tartrate. The aqueous layer was separated and extracted with diethyl ether. The combined organic extracts were washed with sat aq NaCl, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give the crude hemiacetal **22**, which was used in the next step without further purification.

To a solution of the crude hemiacetal **22** and triethylamine (291 mg, 2.88 mmol) in 8 mL anhydrous CH_2Cl_2 was added methanesulfonyl chloride (85 mg, 0.74 mmol). The resulting mixture was stirred at 25 ºC for 2 h before it was diluted with diethyl ether and washed with sat aq $NaHCO_3$ and sat aq NaCl. The organic phase was dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give a residue, which was purified by flash column chromatography to give enol ether **23** (85 mg, 85% over two steps).

23: colorless oil; R_f = 0.10 (PE/AcOEt = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.96 (s, 3H), 1.07 (s, 3H), 1.40 (t, J = 12.4 Hz, 1H), 1.57−1.74 (m, 2H), 1.85 (dd, J = 12.4, 5.6 Hz, 1H), 1.95−2.04 (m, 1H), 2.21−2.31 (m, 2H), 2.34−2.52 (m, 2H), 3.17 (t, J = 8.3 Hz, 1H), 3.66 (d, J = 10.2 Hz, 1H), 3.80 (s, 3H), 4.19 (d, J = 11.2 Hz, 1H), 4.37 (d, J = 8.2 Hz, 1H), 4.46 (d, J = 11.2 Hz, 1H), 5.13 (s, 1H), 5.28 (s, 1H), 6.06 (s, 1H), 6.86 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 23.8, 25.4, 26.8, 27.2, 38.9, 42.3, 42.6, 50.1, 50.3, 55.2, 69.8, 79.3, 96.0, 113.2, 113.7, 114.4, 129.2, 131.0, 142.9, 151.0, 159.0. IR ν (cm^{-1}): 1251, 1516, 1616, 1654, 2928. HRMS (ESI): calcd for $C_{23}H_{31}O_3$: 355.2268; found: 355.2264. $[\alpha]^{20}_D$: +38.6 (c 0.76, $CHCl_3$).



To a solution of enol ether **23** (100 mg, 0.28 mmol) in 10 mL ethanol under argon was added Pd/C (10 wt%, 30 mg, 0.028 mmol). Then the argon atmosphere was replaced by hydrogen (1 atm) atmosphere. After stirred at 60 ºC for 20 h, the reaction mixture was filtered through a pad of silica gel to remove Pd/C, and the filtrate was concentrated under reduced pressure to give the crude alcohol **24**, which was used in the next step without further purification.

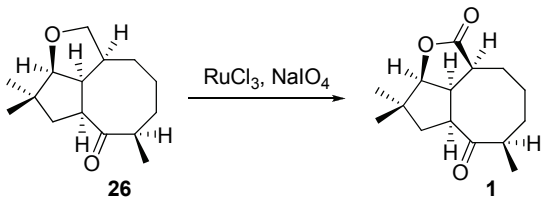
To a mixture of the crude alcohol **24** and $NaHCO_3$ (177 mg, 2.10 mmol) in 5 mL anhydrous CH_2Cl_2 was added Dess-Martin periodinane (447 mg, 1.06 mmol). After stirred at 25 ºC for 40 min, the reaction mixture was quenched with 25 mL sat aq $NaHCO_3$ and 25 mL sat aq $Na_2S_2O_3$ and then extracted with CH_2Cl_2. The combined organic extracts were washed with sat aq NaCl, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude mixture was purified by flash column

chromatography on silica gel to afford compounds **25** (31 mg, 46%) and **26** (16 mg, 24%).

To a solution of compound **25** (14.1 mg, 0.060 mmol) and 2,6-lutidine (57 mg, 0.53 mmol) in 1 mL anhydrous CH_2Cl_2 at 0 ºC was added TMSOTf (96 mg, 0.43 mmol). After stirred at 0 ºC for 2 h and at 25 ºC for 20 h, 2 mL diethyl ether and 1 mL 1M HCl were added, and the resulting mixture was stirred at 25 ºC for 2 h. Then it was diluted with diethyl ether, washed with sat aq NaCl, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was submitted to flash column chromatography on silica gel to get the recovered compound **25** (6.4 mg, 45%) and the desired compound **26** (3.7 mg, 48% brsm).

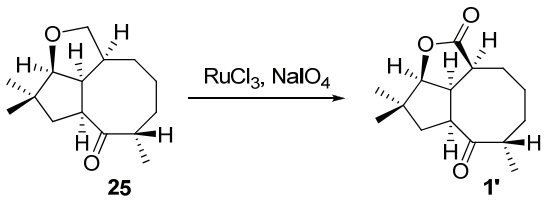
25: white solid, mp 70−71 °C; R_f = 0.22 (PE/AcOEt = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.91 (s, 3H), 1.11 (s, 3H), 1.16 (d, J = 7.2 Hz, 3H), 1.24−1.34 (m, 2H), 1.55 (ddd, J = 15.4, 8.5, 4.2 Hz, 1H), 1.62−1.76 (m, 3H), 2.01 (t, J = 12.7 Hz, 1H), 2.12−2.25 (m, 1H), 2.26−2.38 (m, 1H), 2.45−2.56 (m, 1H), 3.15−3.24 (m, 2H), 3.35 (ddd, J = 11.1, 7.4, 5.5 Hz, 1H), 3.88 (t, J = 7.8 Hz, 1H), 3.97 (dd, J = 5.4, 1.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 20.7, 22.8, 23.1, 25.9, 26.1, 30.5, 40.5, 41.5, 44.0, 46.3, 48.8, 49.2, 74.8, 94.5, 217.9. IR ν (cm^{-1}): 1266, 1371, 1468, 1698, 2935. HRMS (ESI): calcd for $C_{15}H_{24}NaO_2$: 259.1668; found: 259.1667. $[\alpha]^{20}_D$: +39.1 (c 1.14, $CHCl_3$).

26: white solid, mp 85−86 °C; R_f = 0.26 (PE/AcOEt = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.90 (s, 3H), 1.03−1.11 (m, 1H), 1.12 (s, 3H), 1.13 (d, J = 6.7 Hz, 3H), 1.33 (dd, J = 13.1, 6.6 Hz, 1H), 1.47−1.54 (m, 1H), 1.55−1.66 (m, 1H), 1.75−1.88 (m, 2H), 2.03 (t, J = 12.9 Hz, 1H), 2.28−2.36 (m, 1H), 2.48−2.56 (m, 2H), 3.15 (ddd, J = 12.3, 11.1, 6.6 Hz, 1H), 3.19 (dd, J = 11.5, 7.7 Hz, 1H), 3.39 (ddd, J = 11.0, 7.5, 5.5 Hz, 1H), 3.86 (t, J = 7.9 Hz, 1H), 3.98 (d, J = 5.3 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 13.6, 22.3, 23.1, 23.2, 25.9, 28.6, 40.5, 41.8, 44.2, 45.8, 48.7, 50.7, 74.9, 94.4, 215.6. IR ν (cm^{-1}): 1266, 1371, 1468, 1702, 2939. HRMS (ESI): calcd for $C_{15}H_{24}NaO_2$: 259.1668; found: 259.1665. $[\alpha]^{20}_D$: +10.1 (c 0.55, $CHCl_3$).



To a mixture of compound **26** (10.5 mg, 0.044 mmol) and sodium periodate (47.0 mg, 0.22 mmol) in 3 mL $CH_3CN/CCl_4/H_2O$ (1:1:1, V/V/V) was added ruthenium trichloride (4.7 mg, 0.023 mmol). After stirred at 25 ºC for 9 h, the reaction mixture was diluted with CH_2Cl_2, washed with water, dried over $MgSO_4$, and filtered. After solvent evaporation, the residue was subjected to flash column chromatography on silica gel to give natural product **1** (6.6 mg, 59%).

1: white solid, mp 155−156 °C (lit mp 178 °C[3], 156-158 °C[4], 163-165 °C[5], 142-143 °C[6]); R_f = 0.16 (PE/AcOEt = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.00 (s, 3H), 1.13 (d, J = 6.3 Hz, 3H), 1.20 (s, 3H), 1.31−1.44 (m, 2H), 1.51-1.62 (m, 1H), 1.76−1.85 (m, 1H), 1.88−2.01 (m, 2H), 2.19 (t, J = 13.4 Hz, 1H), 2.36−2.57 (m, 2H), 2.72 (ddd, J = 12.3, 9.6, 6.3 Hz, 1H), 3.21 (dt, J = 11.9, 6.8 Hz, 1H), 3.73 (dt, J = 10.5, 5.3 Hz, 1H), 4.27 (d, J = 5.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 13.2, 22.4, 23.0 (2 C), 24.5, 28.0, 38.4, 40.7, 43.2, 45.66, 45.72, 50.2, 90.9, 177.8, 213.6. IR ν (cm^{-1}): 1274, 1475, 1698, 1769, 2928. HRMS (ESI): calcd for $C_{15}H_{22}NaO_3$: 273.1461; found: 273.1463. $[\alpha]^{20}_D$: +11.8 (c 0.28, $CHCl_3$; lit value +12.1[3], +8.5[4], +16.6[5]).



To a mixture of compound **25** (11.4 mg, 0.048 mmol) and sodium periodate (50.4 mg, 0.24 mmol) in 3 mL $CH_3CN/CCl_4/H_2O$ (1:1:1, V/V/V) was added ruthenium trichloride (5.4 mg, 0.026 mmol). After stirred at room temperature for 23 h, the reaction mixture was diluted with CH_2Cl_2, washed with water, dried over $MgSO_4$, and filtered. After solvent evaporation, the residue was subjected to flash column chromatography on silica gel to give **1'** (6.0 mg, 50%).

1': white solid, mp 165−166 °C; R_f = 0.14 (PE/AcOEt = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.01 (s, 3H), 1.16 (d, J = 7.3 Hz, 3H), 1.20 (s, 3H), 1.38 (dd, J = 13.3, 6.9 Hz, 1H), 1.53−1.85 (m, 4H), 1.99−2.08 (m, 2H), 2.15 (t, J = 13.3 Hz, 1H), 2.48−2.57 (m, 1H), 2.71 (ddd, J = 12.5, 9.7, 4.8 Hz, 1H), 3.26 (dt, J = 12.1, 6.9 Hz, 1H), 3.70 (dt, J = 10.5, 5.3 Hz, 1H), 4.27 (d, J = 5.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 20.6, 22.8, 23.0, 24.6, 26.1, 30.0, 38.4, 40.5, 43.0, 45.4, 45.9, 49.1, 91.0, 177.7, 215.9. IR ν (cm^{-1}): 1274, 1359, 1468, 1698, 1765, 2935. HRMS (ESI): calcd for $C_{15}H_{22}NaO_3$: 273.1461; found: 273.1458. $[\alpha]^{20}_D$: +41.8 (c 0.30, $CHCl_3$).

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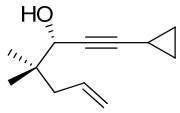
3. ^{1}H- and ^{13}C-NMR spectra



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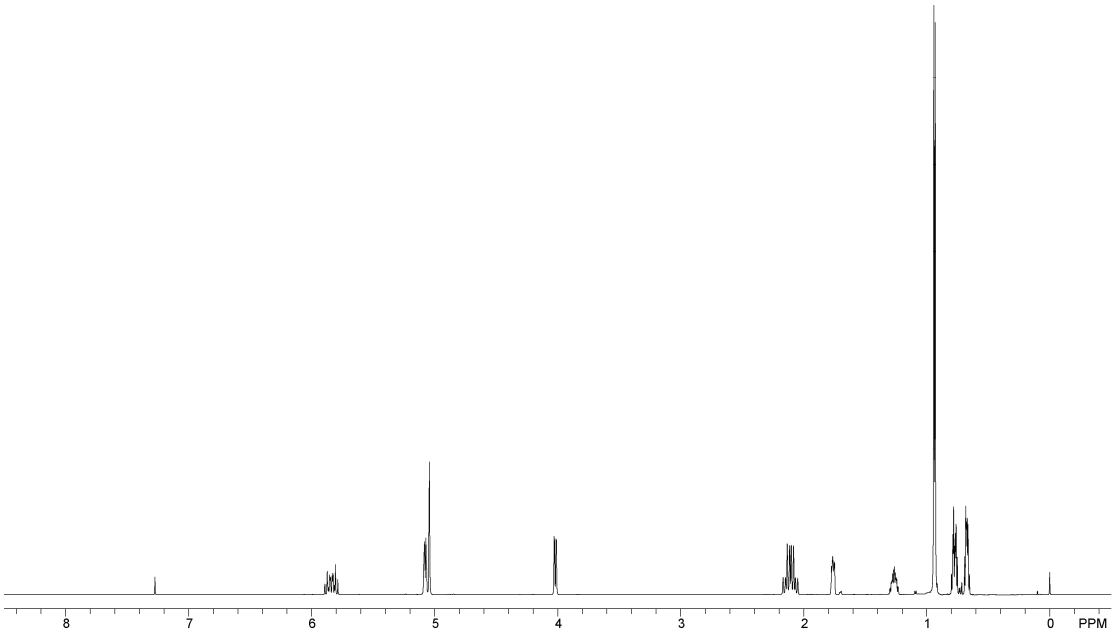

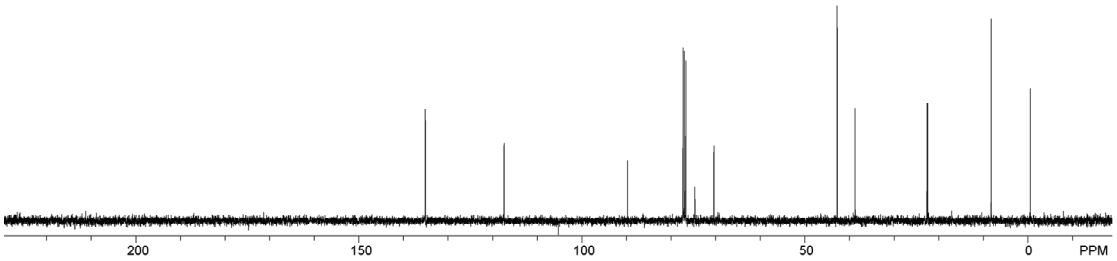

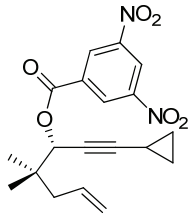

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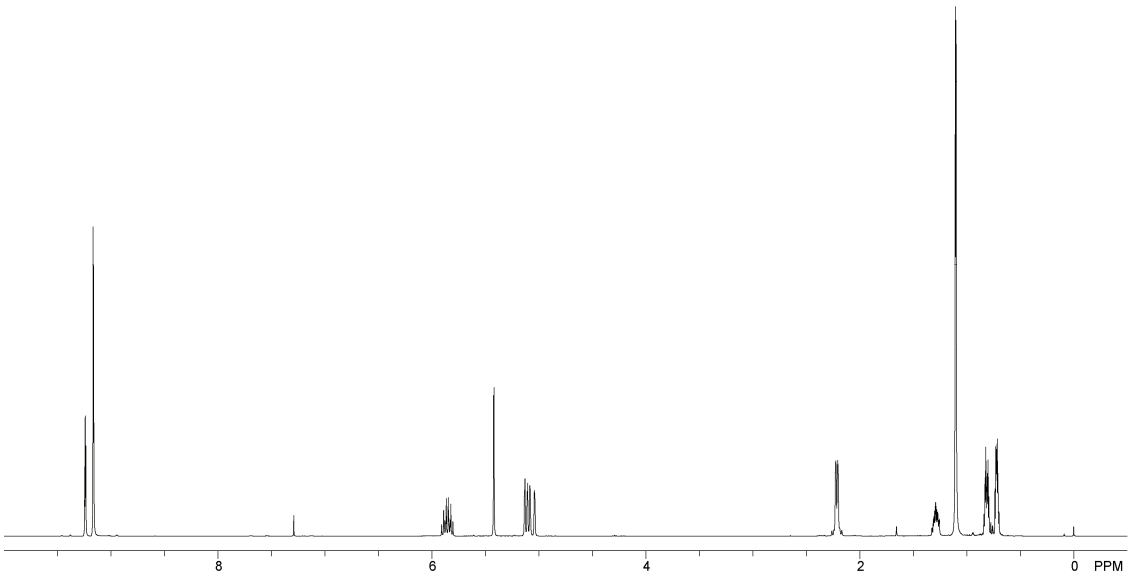

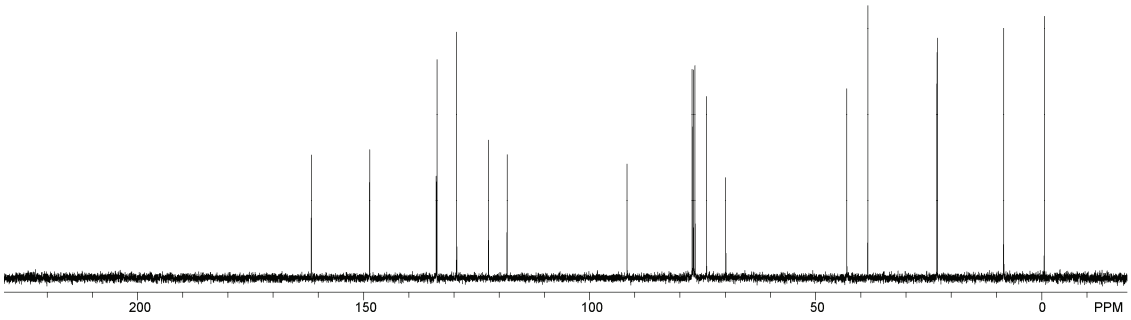

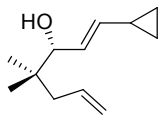

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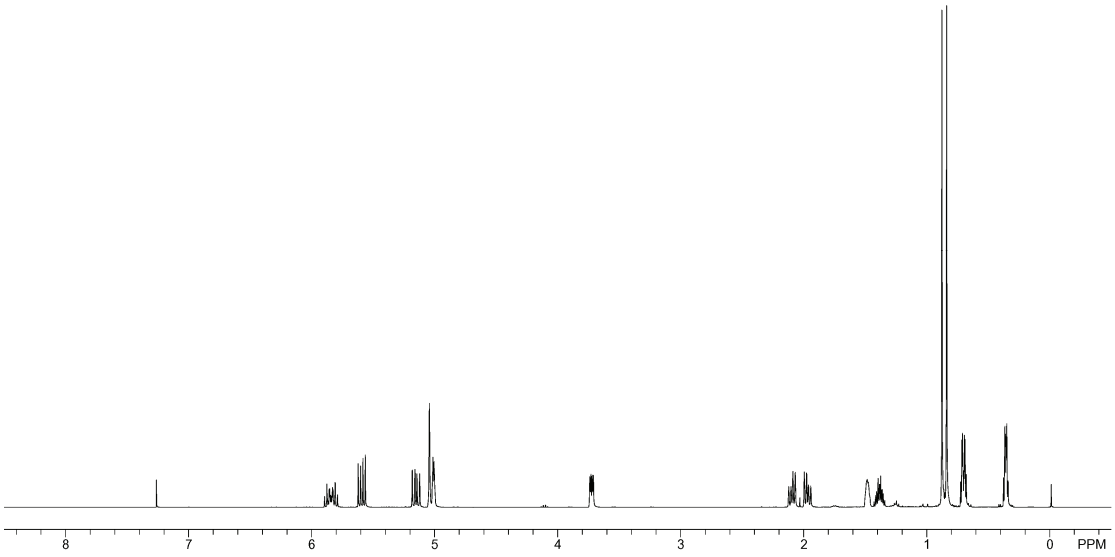

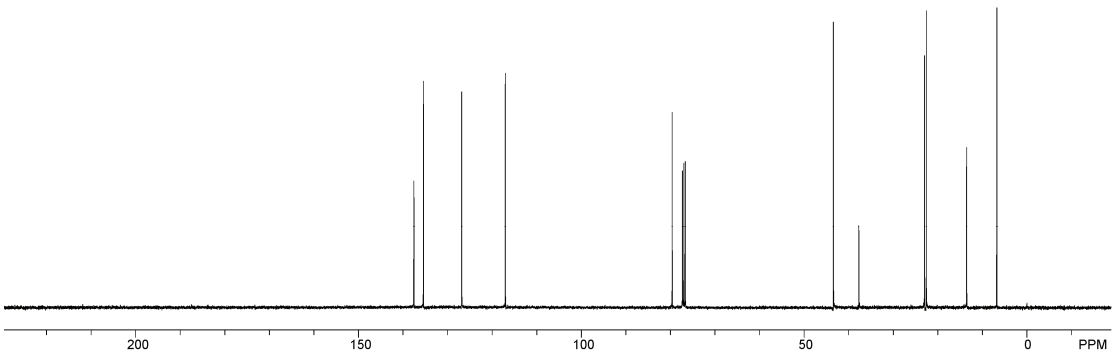

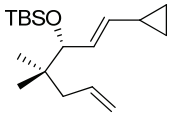

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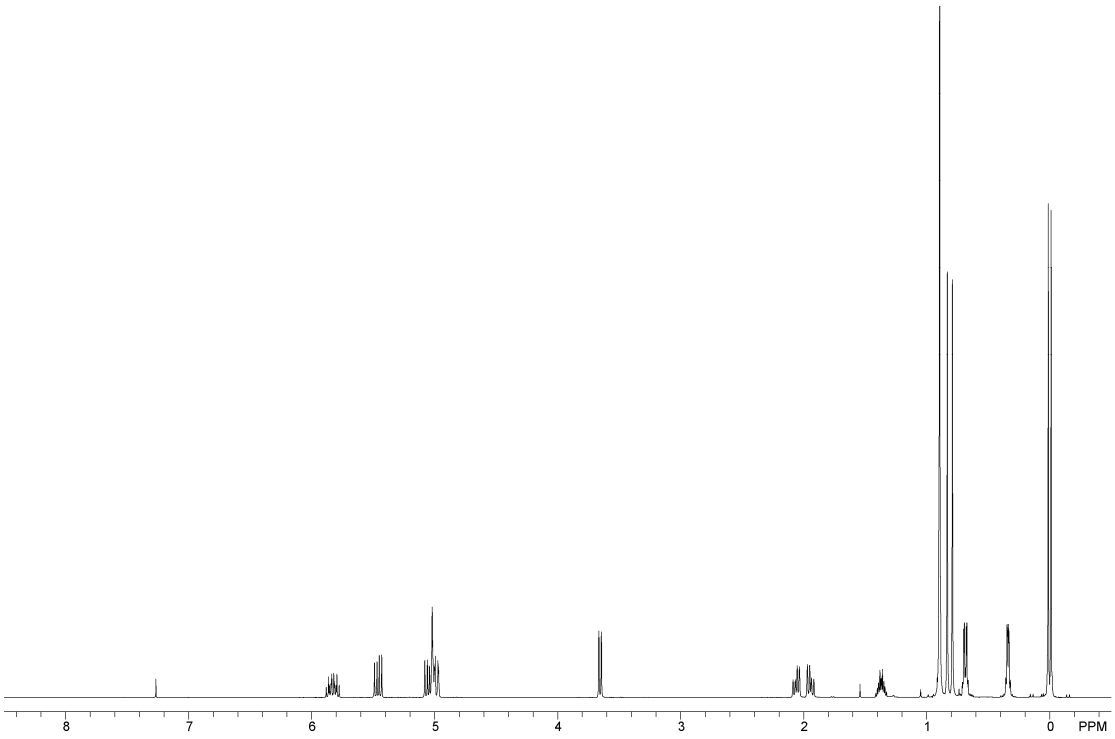

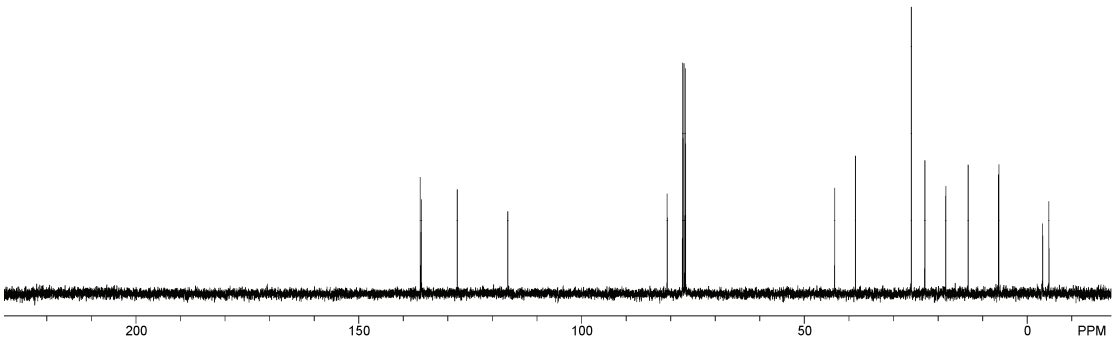

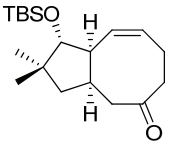

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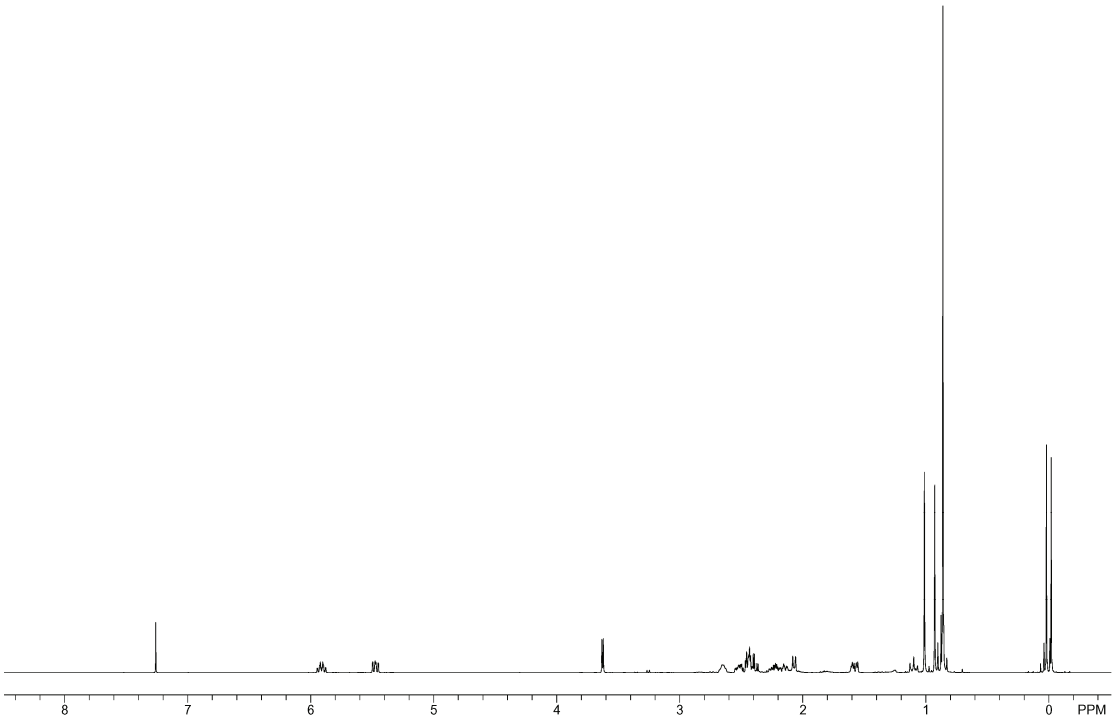

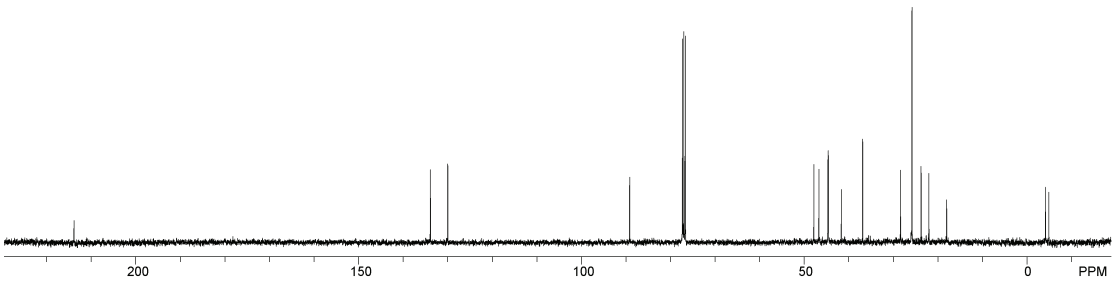

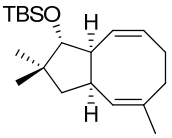

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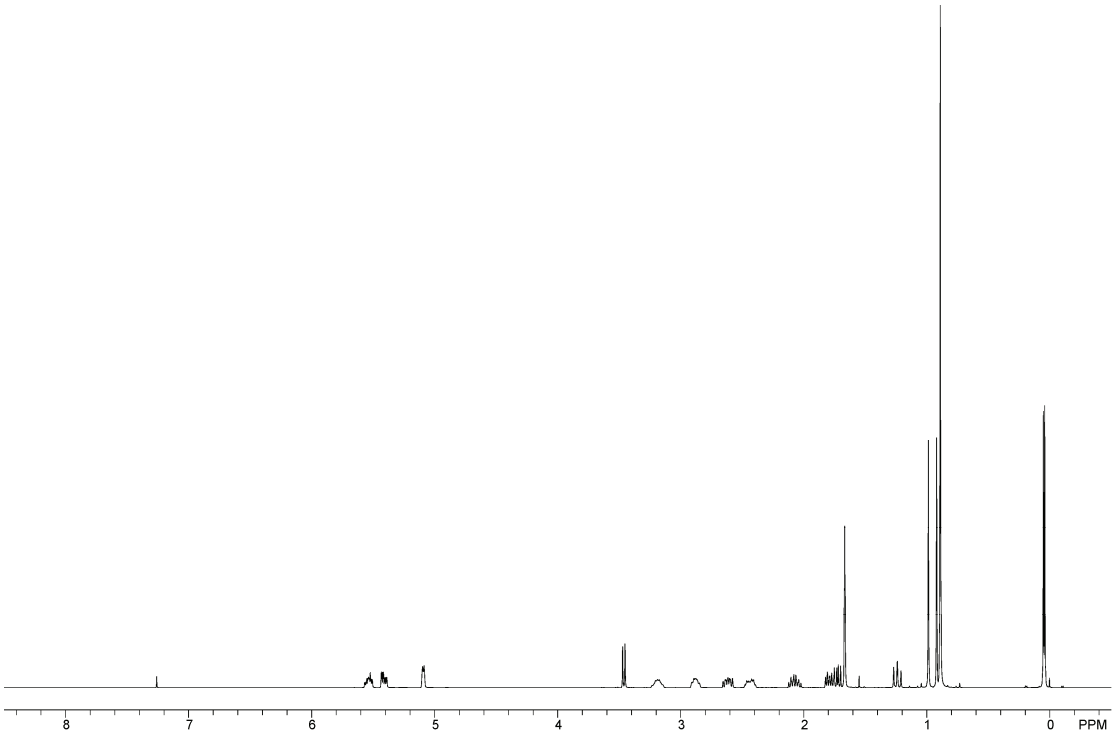

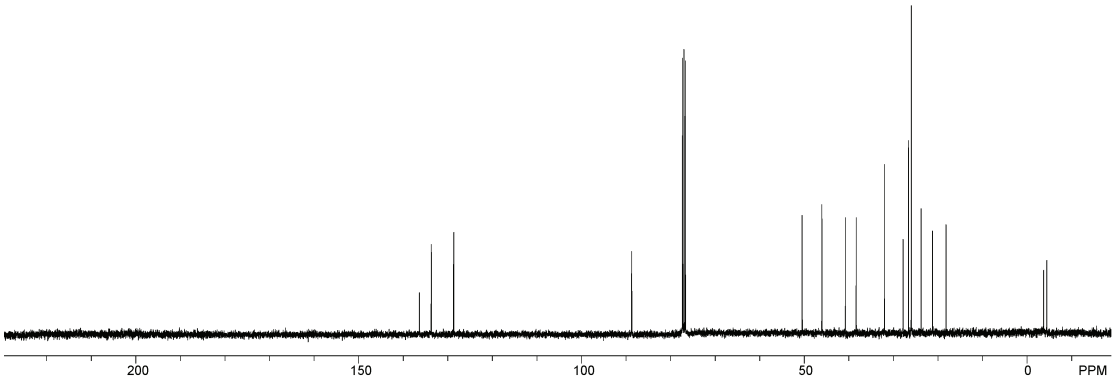

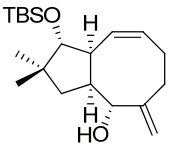

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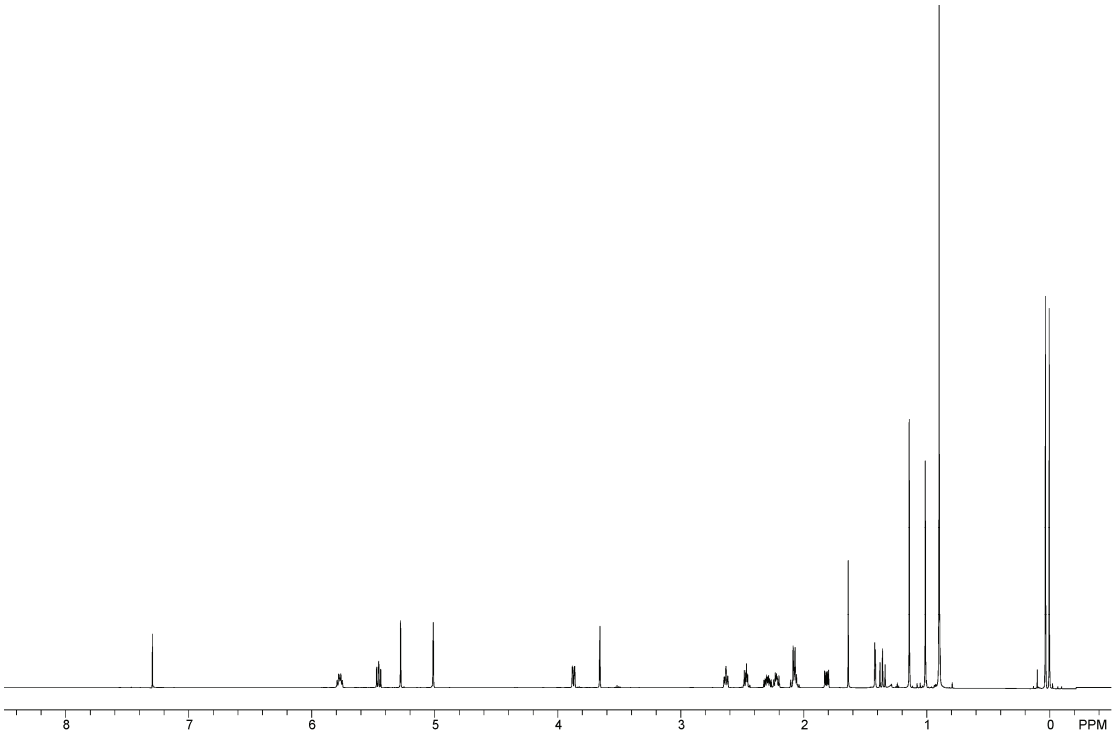

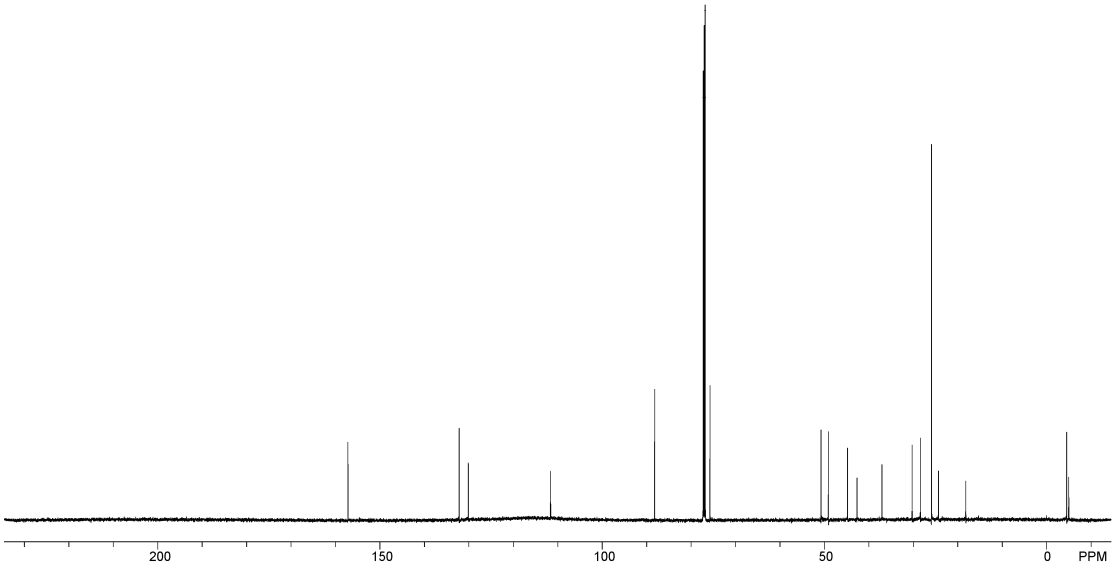

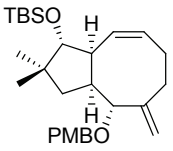

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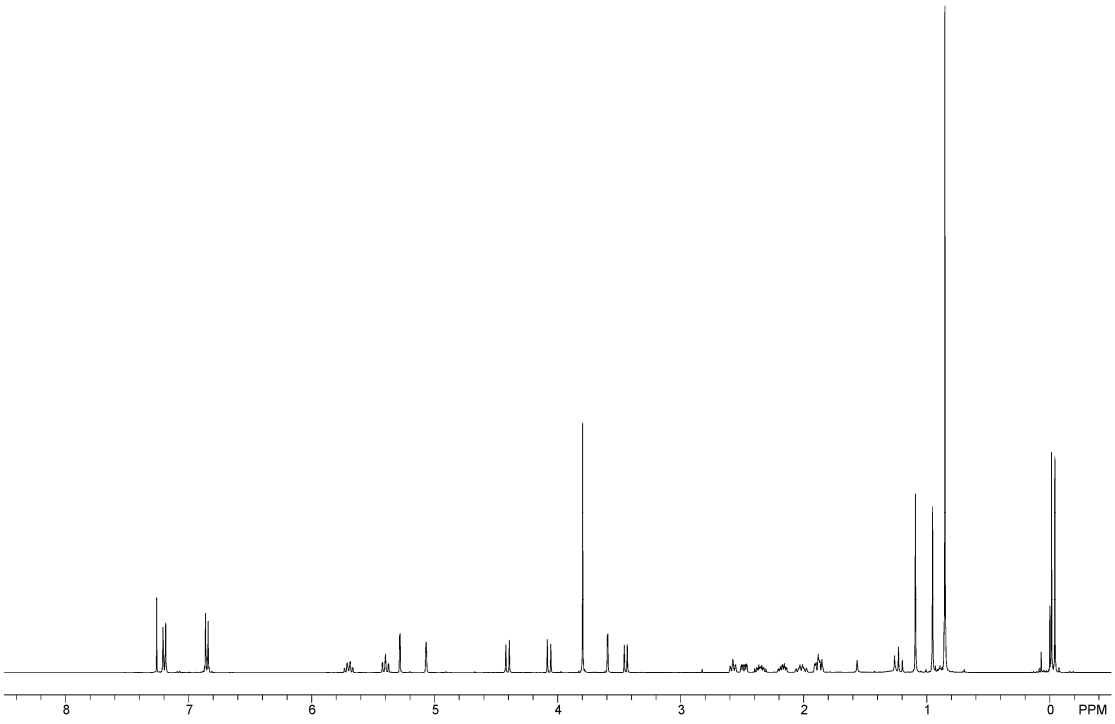

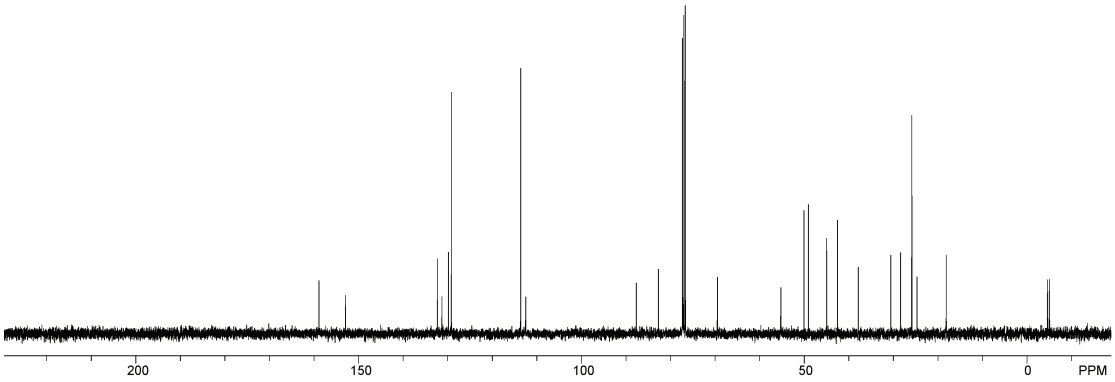

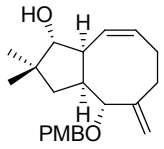

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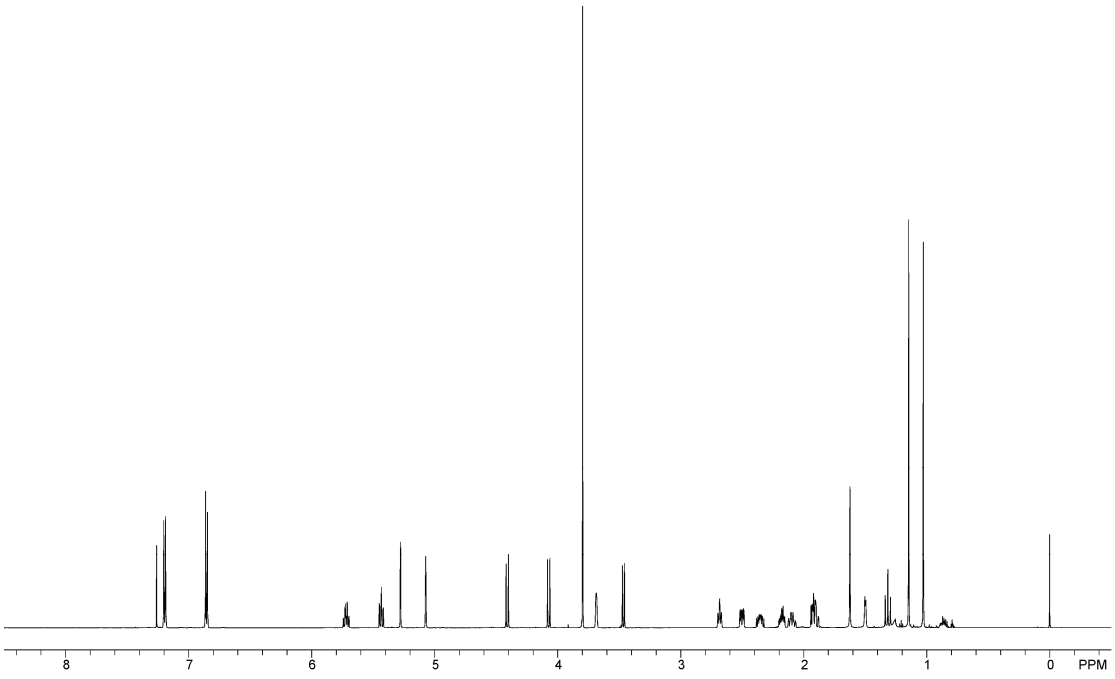

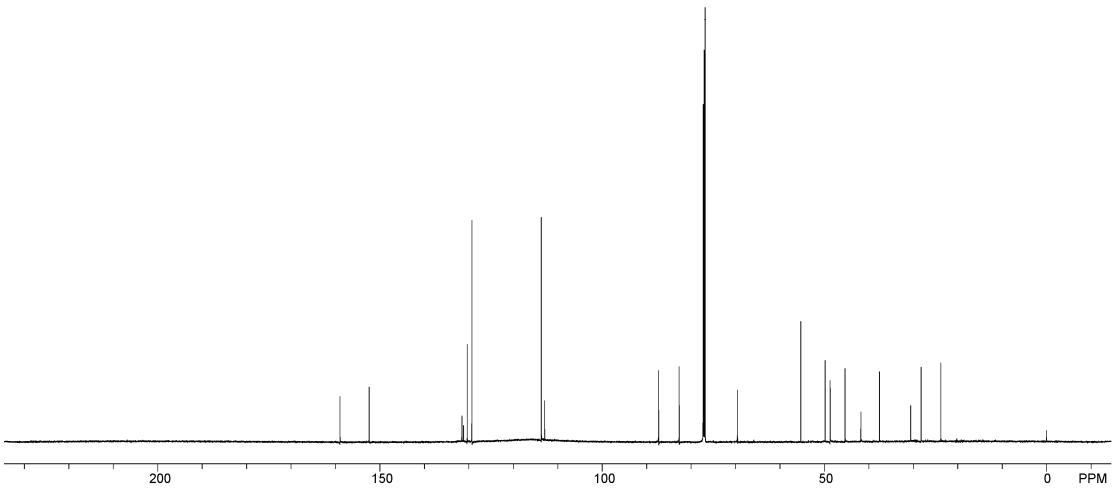

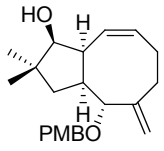

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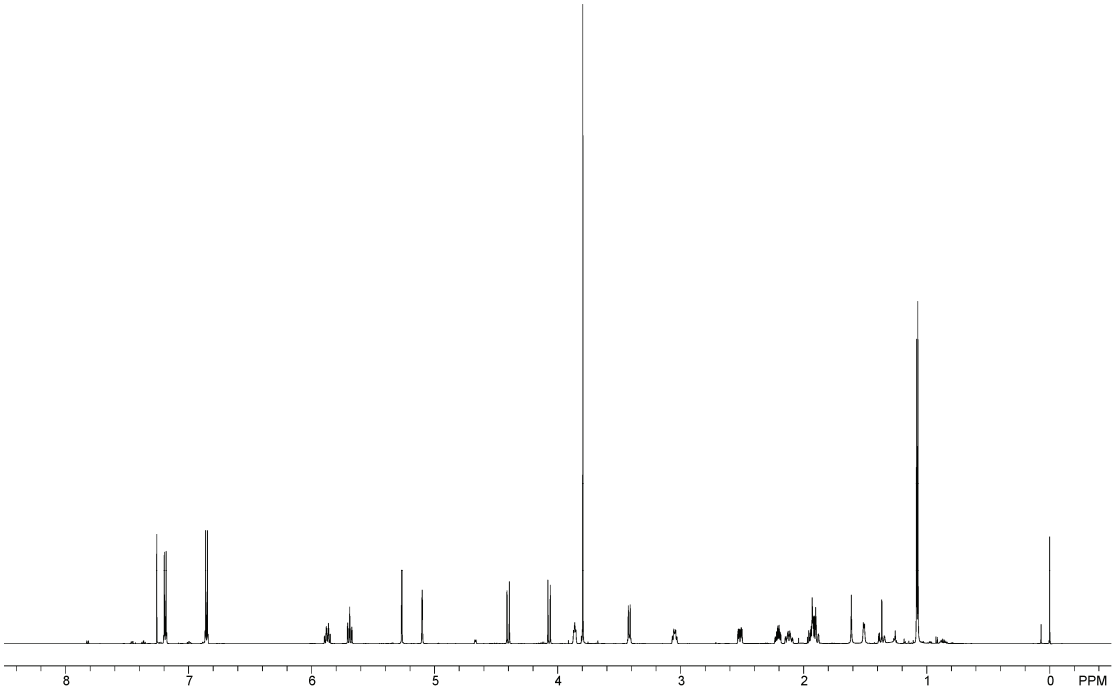

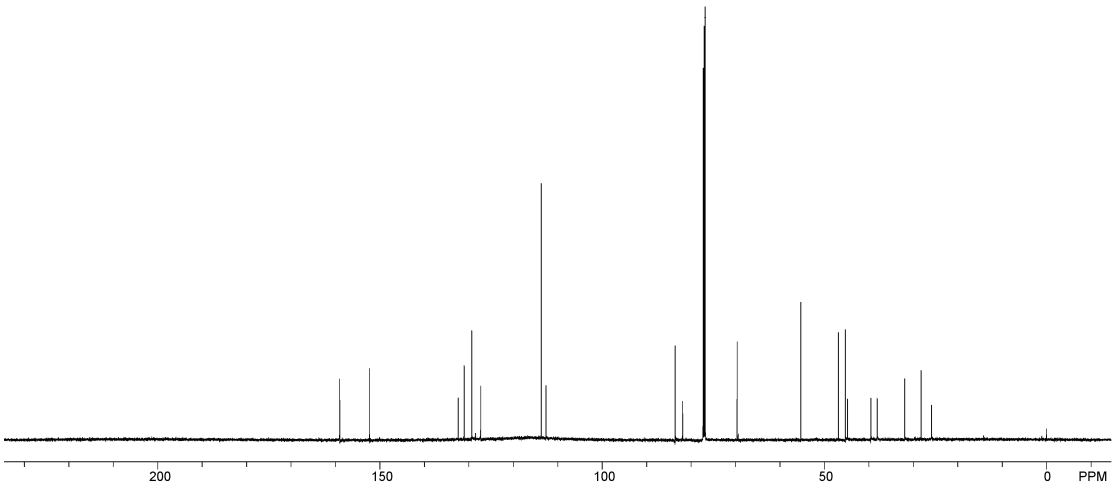

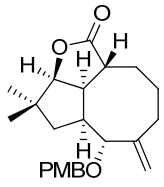

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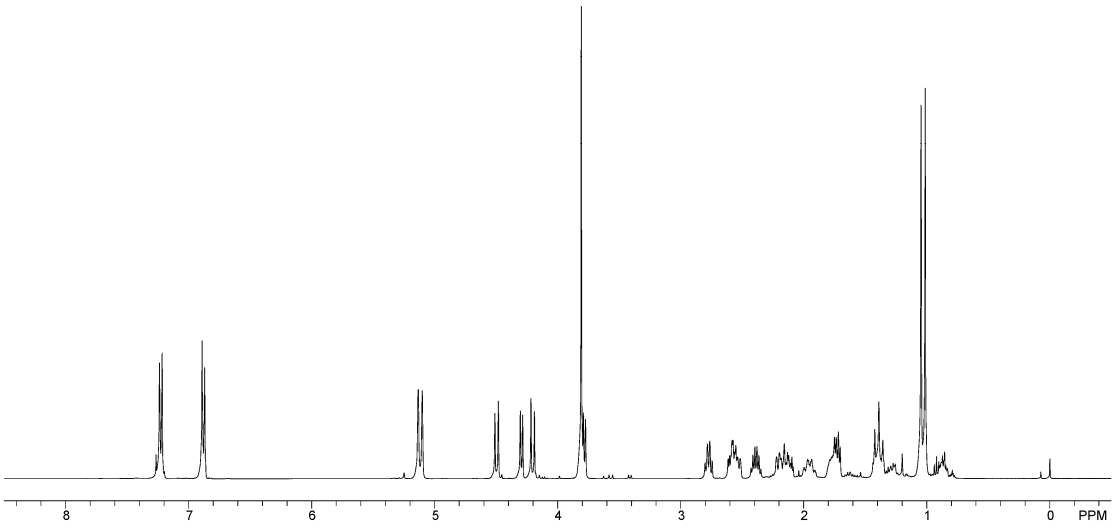

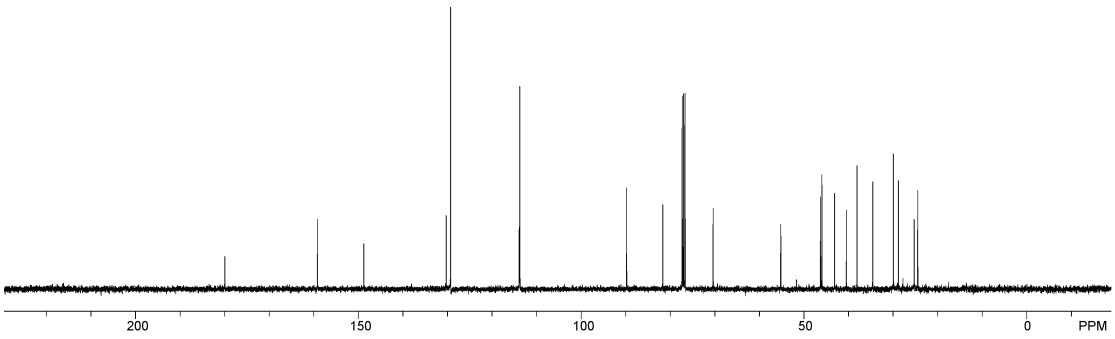

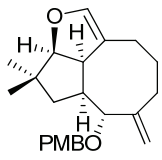

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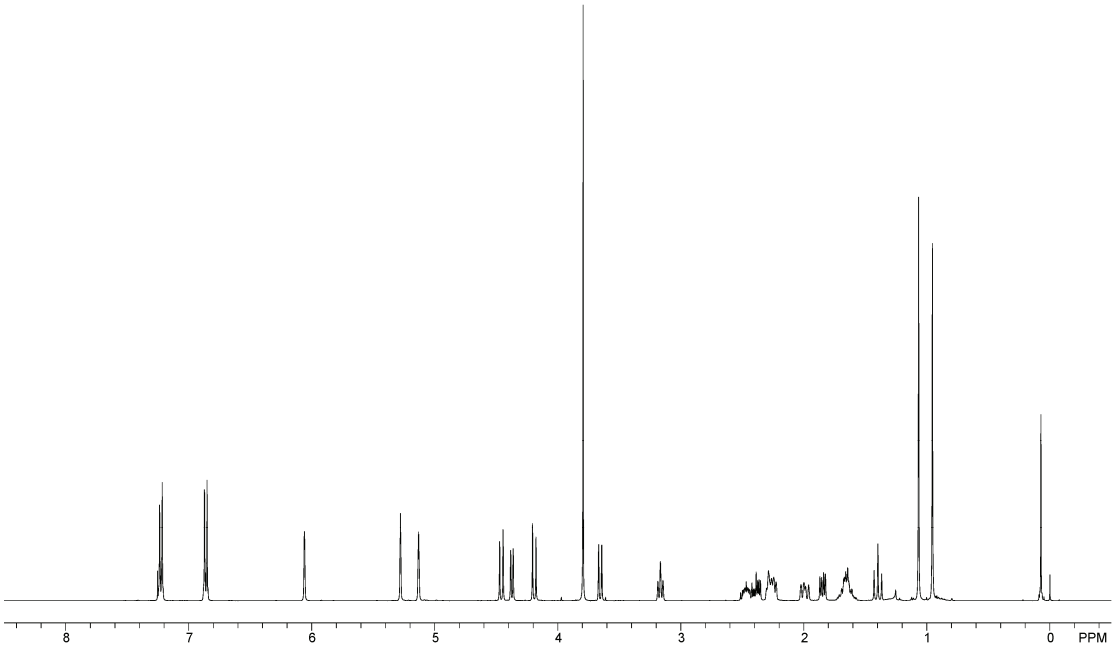

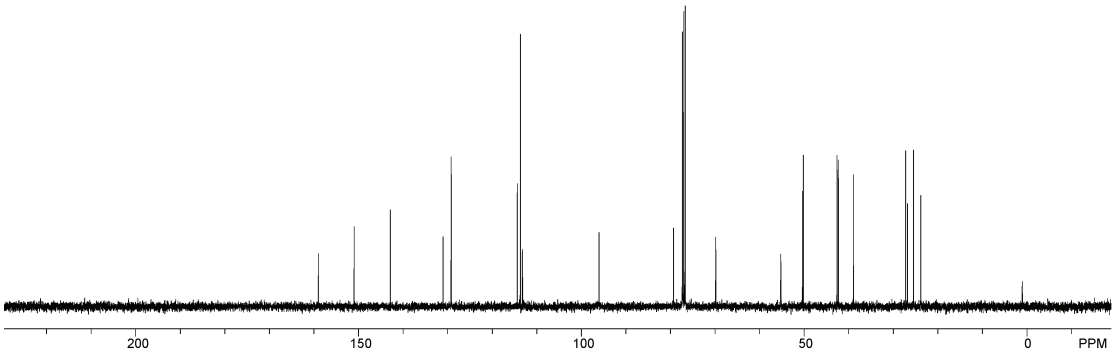

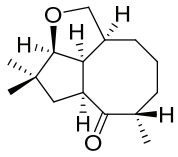

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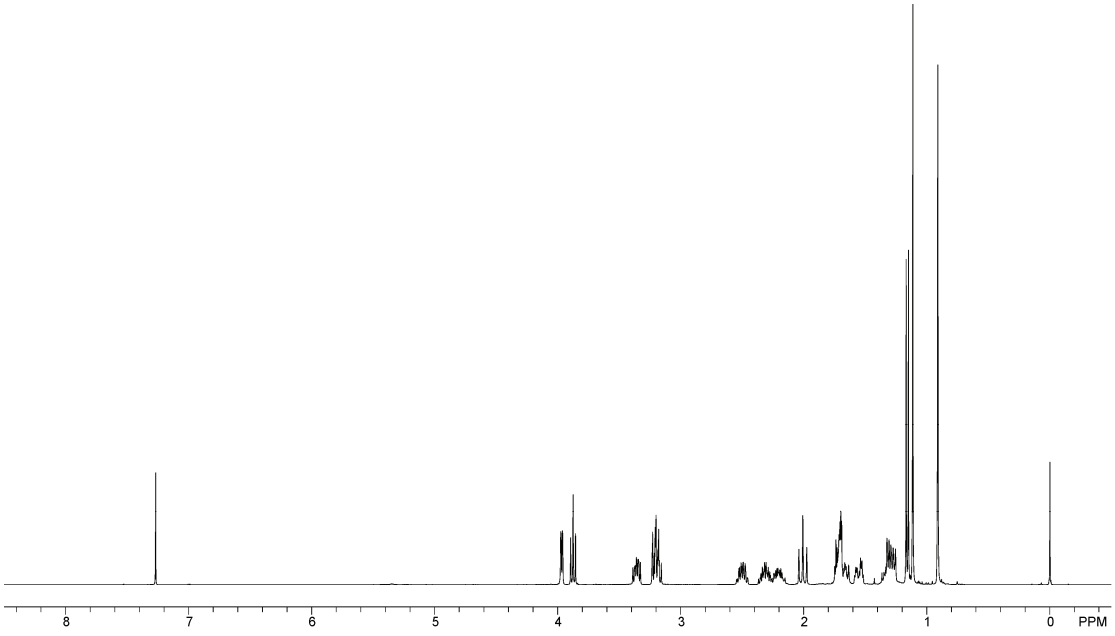

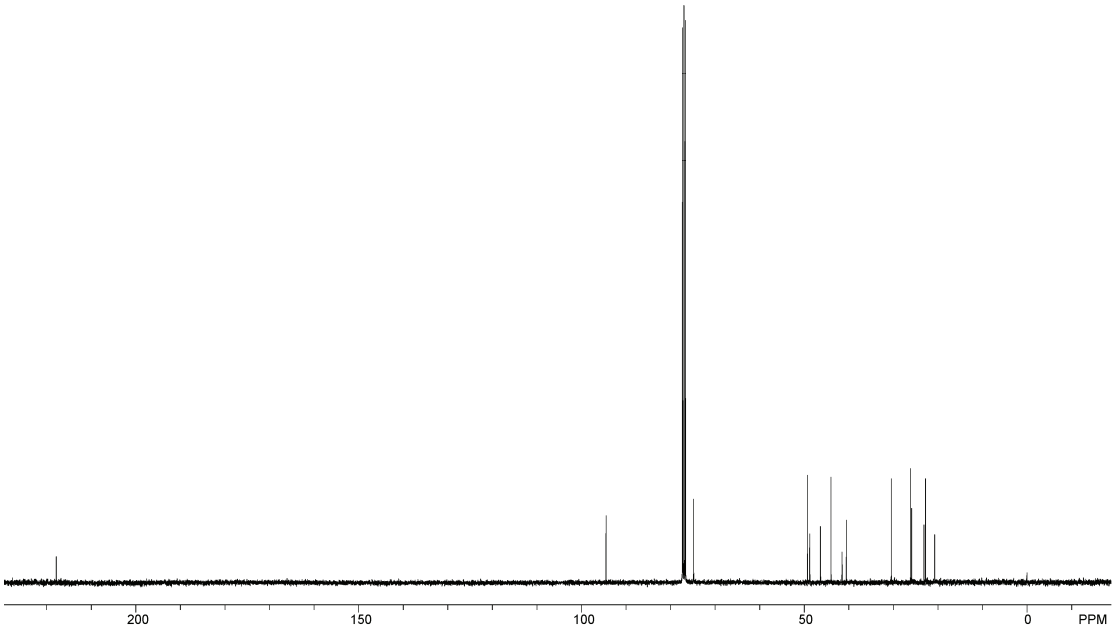

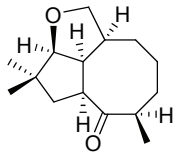

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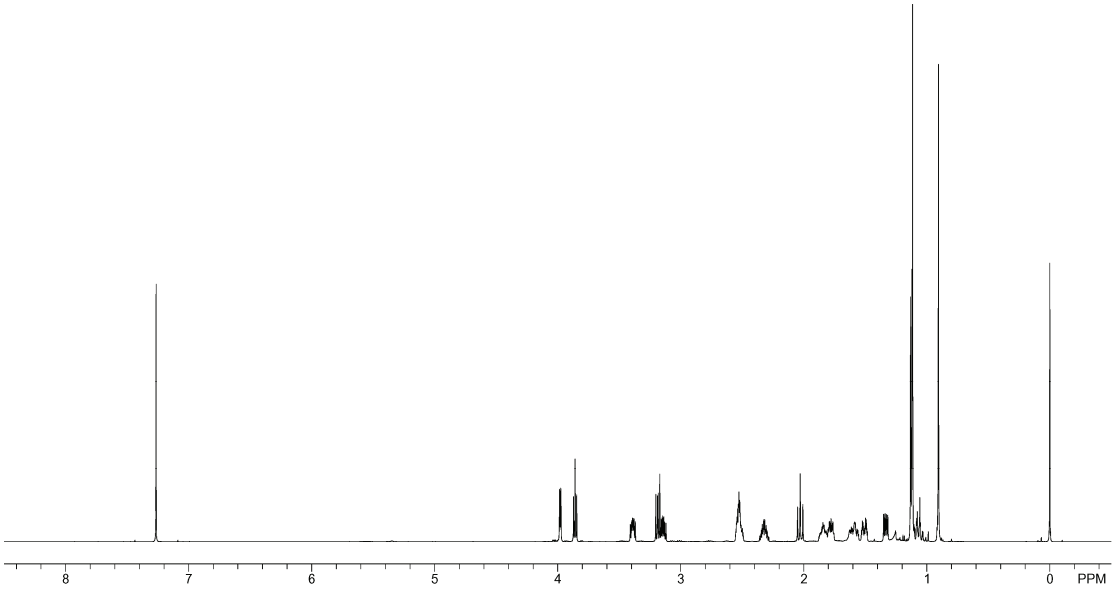

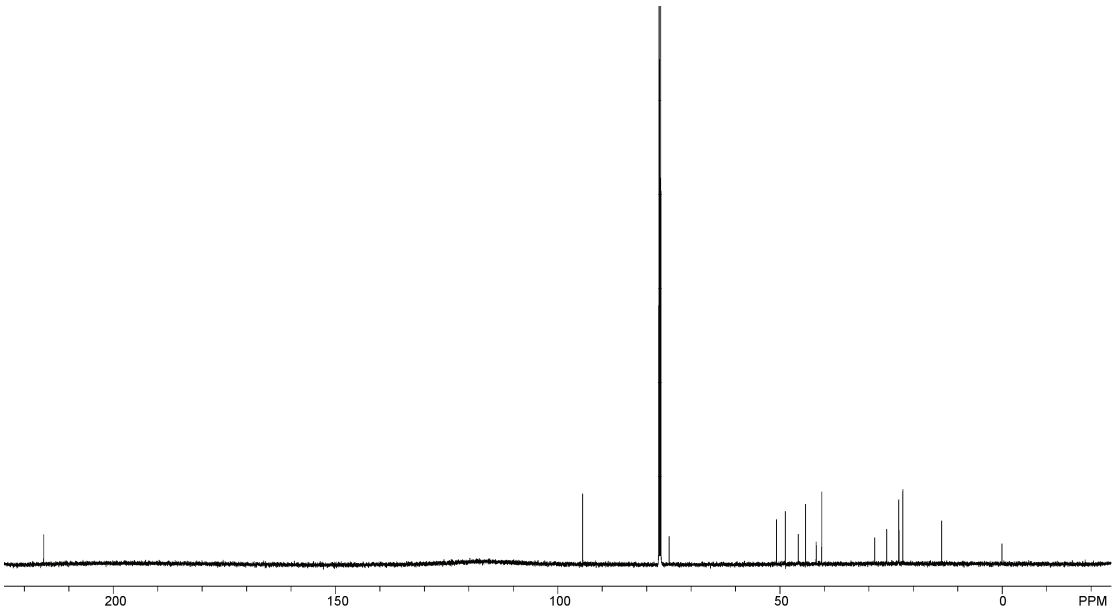

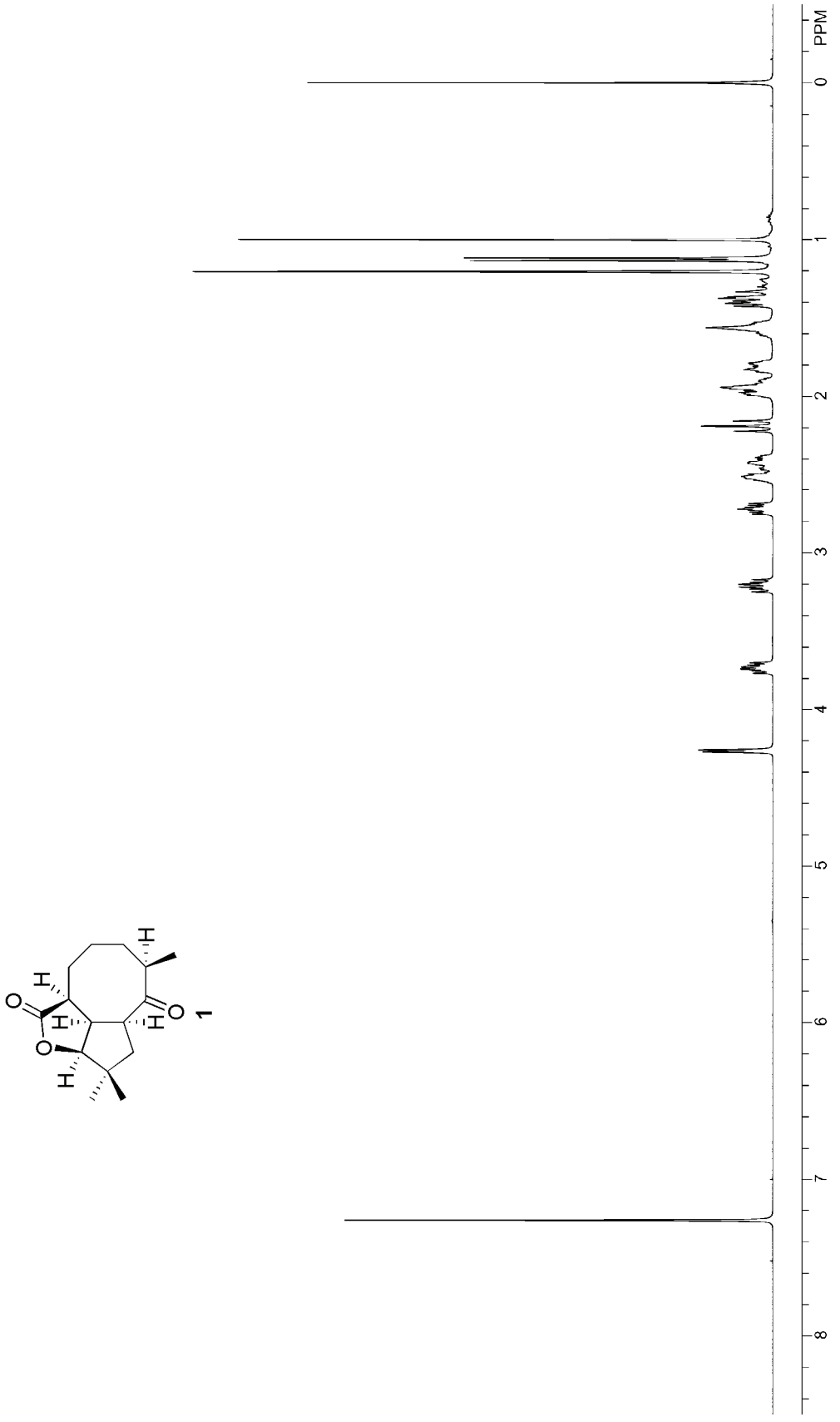
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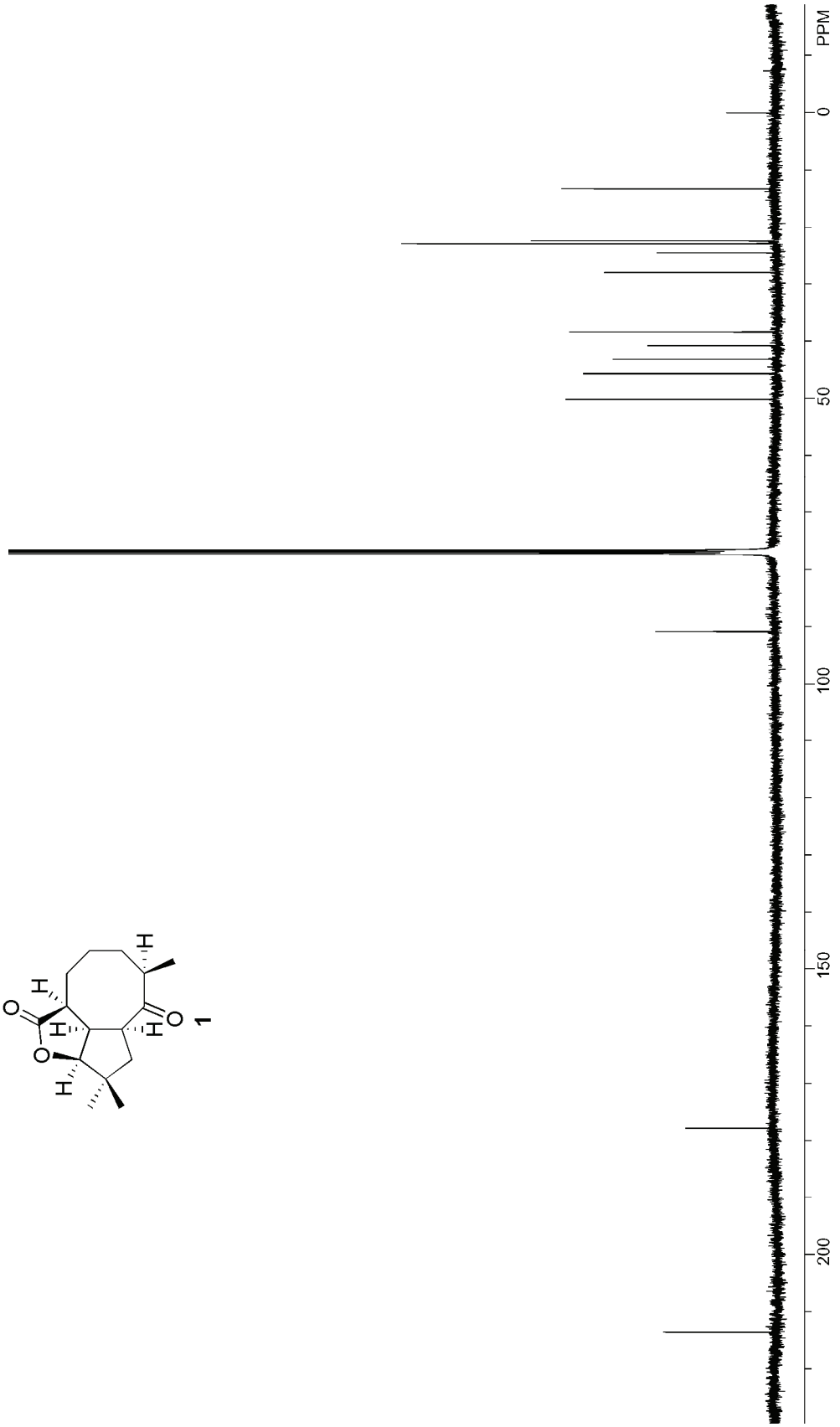

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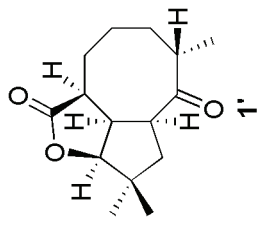
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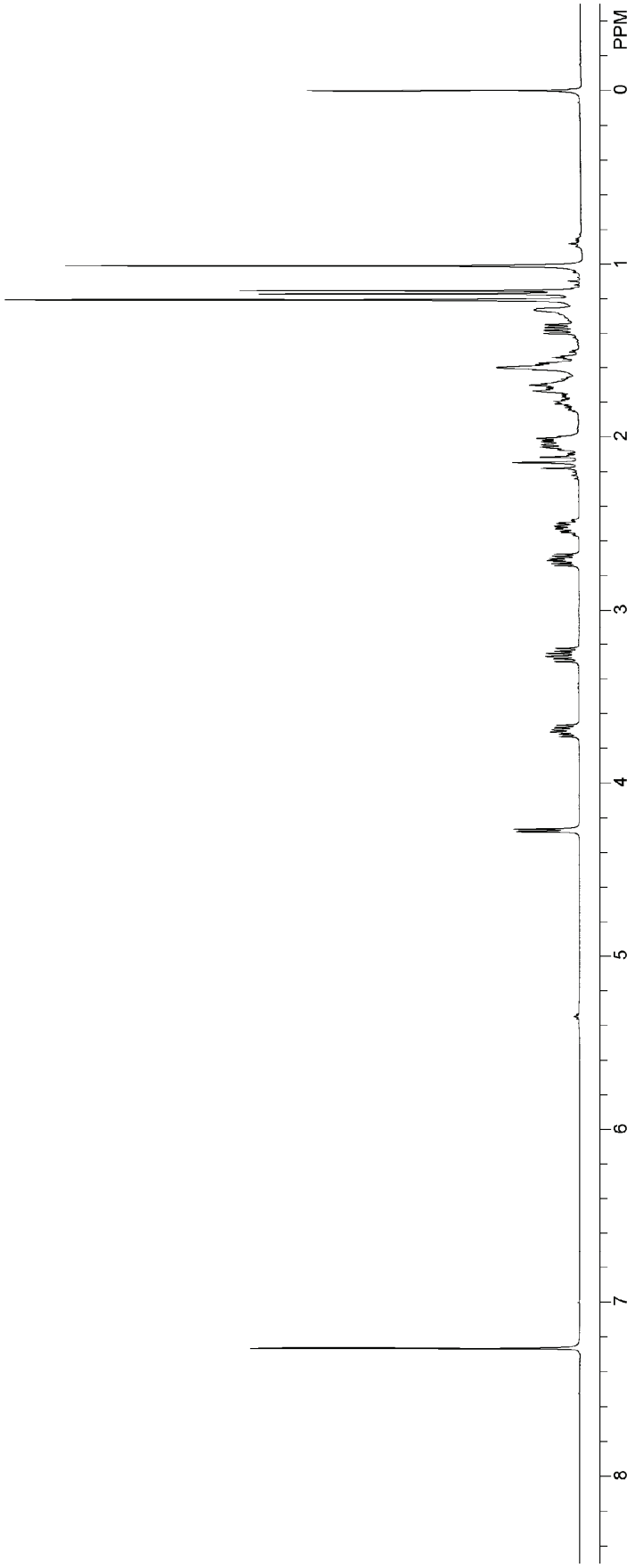
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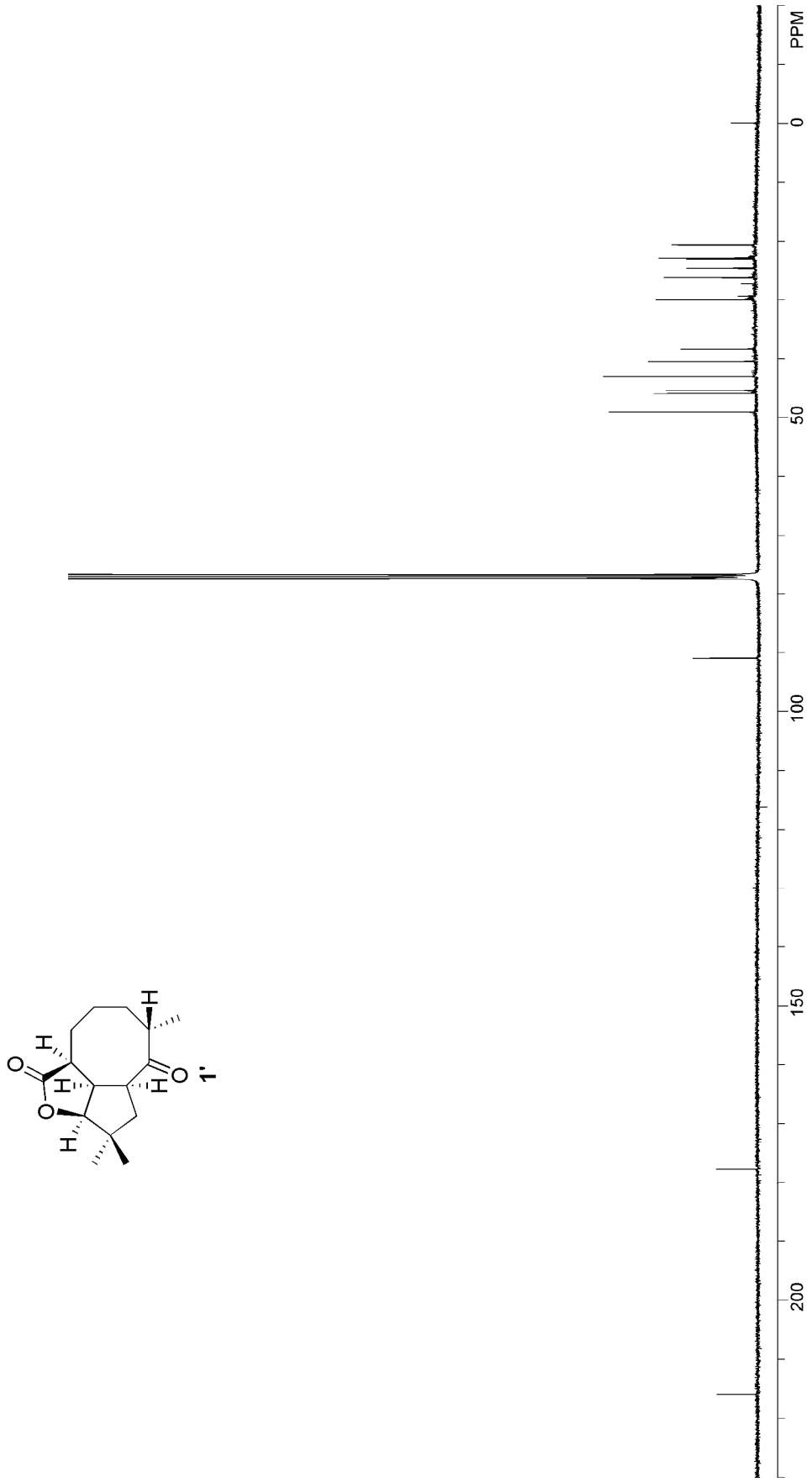


1'

4. DFT-computed 3D picture of lactone 21

To better understand the inside-outside stereochemical feature of lactone **21**, the 3D structure of **21** was optimized by DFT calculations at the B3LYP/6-31G(d) level in Gaussian 03.[7,8,9] It was found that, the "inside" hydrogen at C3 (shown in a blue circle, Figure S1) of the tricyclic compound **21** was on the concave face of the bowl like molecule. Therefore, the deprotonation of this "inside" hydrogen was very difficult to achieve due to the steric congestion in converting inside-outside stereochemistry to outside-outside.

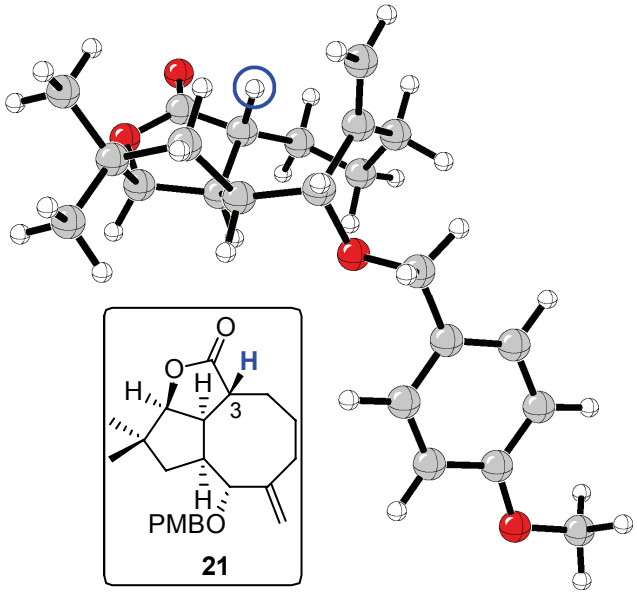
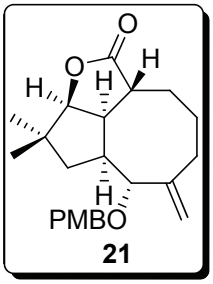


Figure S1 DFT-computed structure of lactone **21** (carbon, gray; hydrogen, white; oxygen, red).

[7] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *Gaussian 03*, Revision C.02, Gaussian Inc.: Wallingford CT, 2004.
[8] (*a*) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; (*b*) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.
[9] W. J. Hehre, L. Radom, P. v. R. Schleyer and J. A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley: New York, 1986.



21

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.953486	-1.069295	-1.504095
2	6	0	2.637532	-1.189180	-0.744757
3	6	0	2.024468	0.223511	-0.806601
4	6	0	3.250548	1.118444	-1.159168
5	8	0	4.270459	0.243765	-1.683316
6	6	0	1.493677	0.819571	0.517000
7	6	0	2.780959	1.242191	1.247963
8	6	0	3.680673	1.873611	0.149468
9	6	0	3.348822	3.370880	-0.014963
10	6	0	5.174268	1.719917	0.469016
11	6	0	0.477475	0.040308	1.388657
12	6	0	0.813905	-1.413759	1.723924
13	6	0	1.500771	-1.688291	2.840411
14	6	0	1.765433	-2.327950	-1.292245
15	6	0	0.357429	-2.374394	-0.688417
16	6	0	0.281140	-2.534684	0.841748
17	8	0	4.660286	-1.959974	-1.902453
18	1	0	3.040664	1.831854	-1.961058
19	1	0	2.583890	1.940444	2.070435
20	1	0	3.275696	0.365552	1.686206
21	1	0	0.944465	1.733378	0.253808
22	1	0	1.268087	0.262212	-1.597599
23	1	0	0.435201	0.593851	2.341534
24	1	0	-0.782254	-2.667398	1.088834
25	1	0	0.775431	-3.468153	1.141706
26	1	0	-0.204063	-1.479470	-0.973848
27	1	0	-0.176849	-3.223490	-1.134410
28	1	0	2.293171	-3.274842	-1.125283
29	1	0	2.915272	-1.430669	0.288408
30	1	0	1.780992	-2.704891	3.105710
31	1	0	1.807581	-0.908477	3.533975
32	1	0	3.583819	3.923113	0.902327

33	1	0	2.288424	3.536805	-0.240700
34	1	0	3.933330	3.811459	-0.831512
35	1	0	5.412977	2.250420	1.398830
36	1	0	5.799301	2.135695	-0.328543
37	1	0	5.458347	0.671042	0.596123
38	1	0	1.676090	-2.217449	-2.381428
39	8	0	-0.795372	0.158047	0.747396
40	6	0	-1.907900	0.052076	1.636549
41	1	0	-1.807717	0.822763	2.420426
42	1	0	-1.915158	-0.923027	2.145487
43	6	0	-3.183031	0.242028	0.856996
44	6	0	-4.194262	-0.717317	0.874379
45	6	0	-3.385872	1.405725	0.096488
46	6	0	-5.388231	-0.537573	0.167386
47	1	0	-4.058635	-1.630015	1.450599
48	6	0	-4.559080	1.599186	-0.616531
49	1	0	-2.604055	2.159308	0.058274
50	6	0	-5.572290	0.626727	-0.584431
51	1	0	-6.151725	-1.306057	0.206026
52	1	0	-4.720708	2.494763	-1.208484
53	8	0	-6.687427	0.912706	-1.317652
54	6	0	-7.741856	-0.035931	-1.333165
55	1	0	-8.518192	0.389405	-1.971775
56	1	0	-7.414463	-0.996897	-1.751867
57	1	0	-8.150867	-0.202369	-0.327662