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Supporting Information

Scalable Total Synthesis of *rac*-Jungermannenones B and C

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Supporting Information

Table of Contents	

a) General information

^{1}H NMR spectra were recorded on a Varian 400 MHz spectrometer at ambient temperature with $CDCl_3$ benzene-d^6 as the solvent unless otherwise stated. ^{13}C NMR spectra were recorded on a Varian 100 MHz spectrometer (with complete proton decoupling) at ambient temperature. Chemical shifts are reported in parts per million relative to chloroform (^{1}H, δ 7.26 for $CDCl_3$, δ 7.23 for benzene-d^6; ^{13}C, δ 77.00 for $CDCl_3$, δ 128.0 for benzene-d^6). Data for ^{1}H NMR are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet) and coupling constants. Infrared spectra were recorded on a Thermo Fisher FT-IR200 spectrophotometer. High-resolution mass spectra were obtained at Peking University Mass Spectrometry Laboratory using a Bruker APEX Flash chromatography. Chiral HPLC analysis was performed on an Agilent 1200 series. Analytical thin layer chromatography was performed using 0.25 mm silica gel 60-F plates, using 250nm UV light as the visualizing agent and a solution of phosphomolybdic acid and heat as developing agents. Flash chromatography was performed using 200-400 mesh silica gel. Yields refer to chromatographically and spectroscopically pure materials, unless otherwise stated. All reagents were used as supplied by Sigma-Aldrich, J&K, Alfa Aesar Chemicals, TCI and Beijing Ouhe Chemicals. Tetrahydrofuran and diethyl ether were distilled from sodium/ benzophenone ketyl prior to use; the other solvents were distilled from calcium hydride unless otherwise noted.

b) Comparison of natural and synthetic jungermannenones B and C

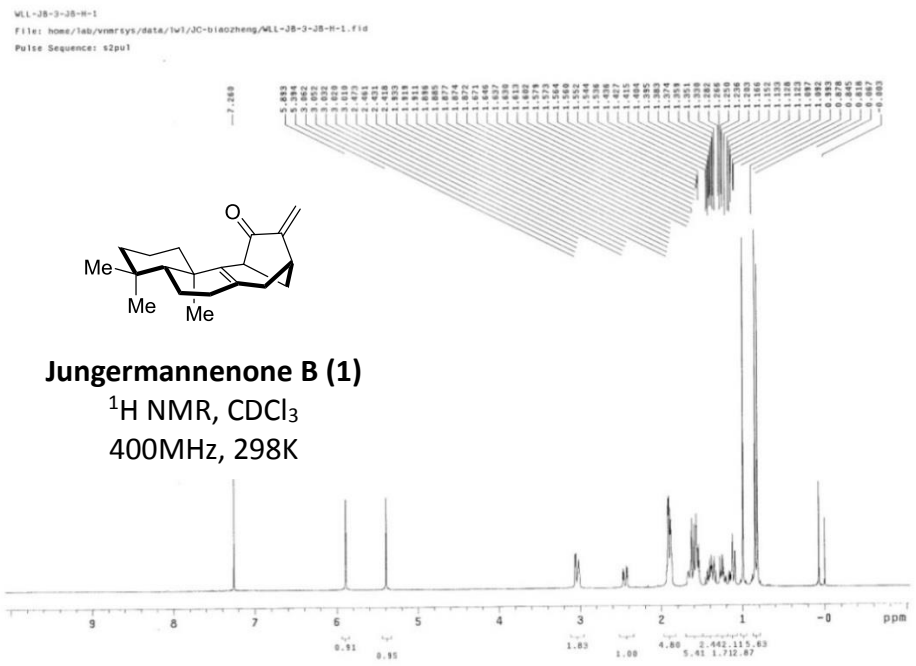
Table S1. Comparison of natural and synthetic Jungermannenone B (^{1}H NMR)

	Natural ^{1}H NMR (600 MHz, $CDCl_3$) δ [ppm, mult, *J* (Hz)]	**Synthetic** ^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm, mult, *J* (Hz)]	**Δδ** (Synthetic-Natural) (ppm)
1	1.88-1.93 m, α	1.87-1.93 m, α	-
	1.24 ddd (12.6, 12.6, 4.7), β	1.20-1.28 m, β	-
2	1.52-1.60 m, 2H	1.52-1.60 m, 2H	-
3	1.37 m, α	1.37 m, α	0
	1.13 ddd (12.6, 12.6, 4.9), β	1.10-1.17 m, β	-
5	1.11 dd (12.6, 1.9)	1.11 dd (12.4, 2.0)	0
6	1.41 m, α	1.41 m, α	0
	1.66 m, β	1.66 m, β	0
7	1.88-1.93 m, 2H	1.87-1.93 m, 2H	-
11	3.06 d (4.7)	3.06 d (4.4)	0
12	1.62 d (11.0), α	1.62 d (11.2), α	0
	1.88-1.93 m, β	1.87-1.93 m, β	-
13	3.03 br s	3.03 br s	0
14	2.45 dd (17.3, 4.9), α	2.45 dd (16.8, 4.4), α	0
	1.88-1.93 m, β	1.87-1.93 m, β	-
17	5.40 s	5.39 s	-0.01
	5.90 s	5.89 s	-0.01
18	0.85 s	0.85 s	0
19	0.82 s	0.82 s	0
20	1.00 s	0.99 s	-0.01

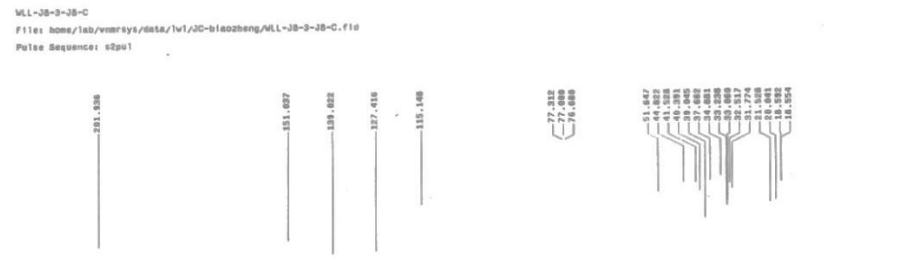
Table S2. Comparison of natural and synthetic Jungermannenone B (^{13}C NMR)

	Natural ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm)	**Synthetic** ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm)	**Δδ** (Synthetic-Natural) (ppm)
1	34.9	34.9	0
2	18.62	18.59	0
3	41.6	41.5	-0.1
4	33.3	33.2	-0.1
5	51.7	51.6	-0.1
6	18.58	18.55	0
7	31.8	31.8	0
8	127.4	127.4	0
9	139.1	139.0	-0.1
10	39.1	39.0	-0.1
11	44.9	44.8	-0.1
12	32.6	32.5	-0.1
13	37.7	37.7	0
14	40.4	40.4	0
15	201.9	201.9	0
16	151.1	151.0	-0.1
17	115.1	115.1	0
18	33.1	33.1	0
19	21.6	21.5	-0.1
20	20.1	20.0	-0.1

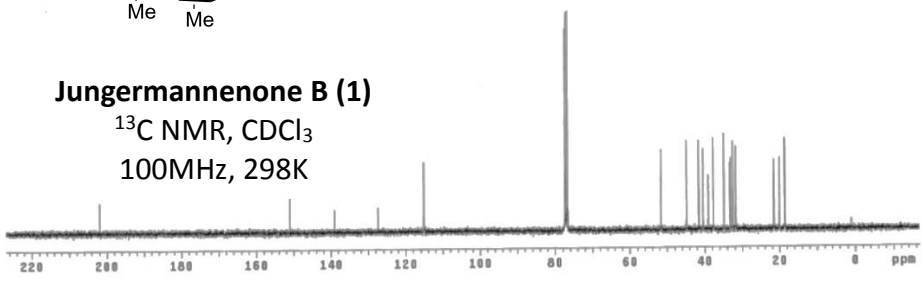
NMR spectra of synthetic Jungermannenone B:[1]



Jungermannenone B (1)
^{1}H NMR, $CDCl_3$
400MHz, 298K



Jungermannenone B (1)
^{13}C NMR, $CDCl_3$
100MHz, 298K



[1] Unfortunately, we have no access to the original NMR spectra for jungermannenones B and C, either from the original reference or any other resources. See: *Tetrahedron* **2005**, *61*, 4531–4544.

NMR Data comparison of natural and synthetic Jungermannenone C:

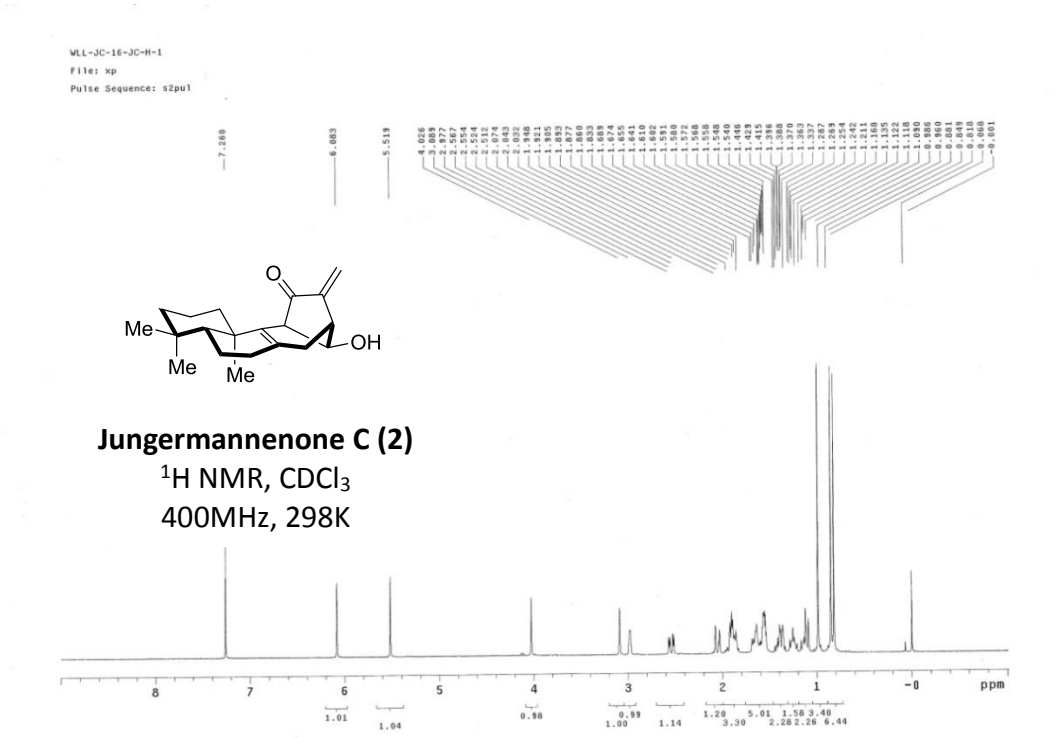
Table S3. Comparison of natural and synthetic Jungermannenone C (^{1}H NMR)

	Natural ^{1}H NMR (600 MHz, $CDCl_3$) δ [ppm, mult, *J* (Hz)]	**Synthetic** ^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm, mult, *J* (Hz)]	**Δδ** (Synthetic-Natural) (ppm)
1	1.84-1.90 m, α	1.83-1.90 m, α	-
	1.23 ddd (13.5, 13.5, 5.2), β	1.25 m, β	+0.02
2	1.56 m, α	1.56 m, α	0
	1.58 m, β	1.58 m, β	0
3	1.37 m, α	1.37 m, α	0
	1.13 ddd (13.5, 13.5, 5.8), β	1.13 m, β	0
5	1.10 dd (12.6, 1.9)	1.11 dd (12.8, 1.6)	+0.01
6	1.40 m, α	1.39 m, α	-0.01
	1.66 like dd (13.2, 6.9), β	1.65 m, β	0
7	1.92 ddd (11.0, 11.0, 6.9), α	1.91 m, α	-0.01
	1.84-1.90 m, β	1.84-1.90 m, β	-
11	3.09 s	3.09 s	0
12	4.01 s	4.03 s	+0.02
13	2.98 m	2.98 br s	0
14	2.53 dd (17.0, 4.9), α	2.54 dd (16.8, 4.4), α	+0.01
	2.05 like d (17.0), β	2.05 like d (16.8), β	0
17	5.51 s	5.52 s	+0.01
	6.06 s	6.08 s	+0.02
18	0.85 s	0.85 s	0
19	0.82 s	0.82 s	0
20	0.99 s	0.99 s	0
OH	2.21 br s	-	-

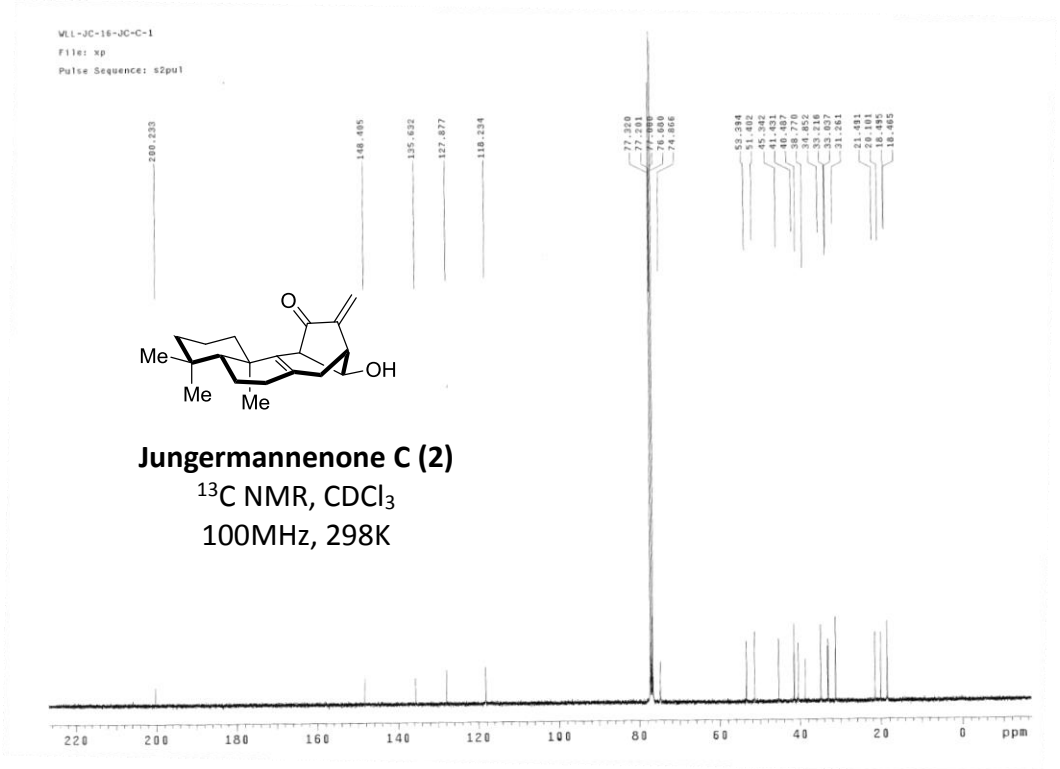
Table S4. Comparison of natural and synthetic Jungermannenone C (^{13}C NMR)

	Natural ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm)	**Synthetic** ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm)	**Δδ** (Synthetic-Natural) (ppm)
1	34.9	34.9	0
2	18.54	18.50	0
3	41.5	41.4	-0.1
4	33.2	33.2	0
5	51.5	51.4	-0.1
6	18.51	18.47	0
7	31.3	31.3	0
8	127.9	127.9	0
9	135.7	135.6	-0.1
10	38.8	38.8	0
11	53.4	53.4	0
12	74.8	74.9	+0.1
13	45.3	45.3	0
14	40.5	40.5	0
15	200.5	200.2	-0.3
16	148.5	148.4	-0.1
17	118.2	118.2	0
18	33.0	33.0	0
19	21.6	21.5	0
20	20.1	20.1	0

NMR spectra of synthetic Jungermanenone C:[1]

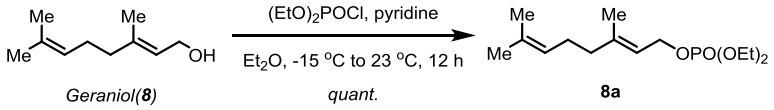


Jungermannenone C (2)
^{1}H NMR, $CDCl_3$
400MHz, 298K



Jungermannenone C (2)
^{13}C NMR, $CDCl_3$
100MHz, 298K

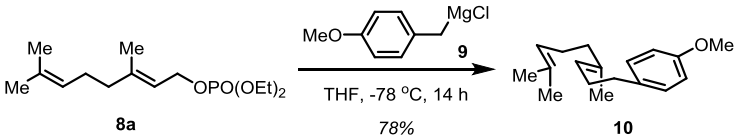
c) Experimental procedures for Scheme 2



*Geraniol(**8**)* *quant.* **8a**

To a stirred solution of geraniol **8** (69 mL, 400 mmol) and pyridine (96 mL, 1.2 mol) in Et_2O (240 mL) at -15 °C was added diethyl chlorophosphate (87 mL, 600 mmol) and the mixture was allowed to slowly warm to room temperature. The resulting reaction mixture was stirred at room temperature for 12 h by which time TLC analysis indicated that the reaction was completed. The reaction mixture was quenched with 1 M aqueous HCl solution (750 mL), extracted with ethyl acetate (3 × 500 mL), washed with *sat. aq.* $NaHCO_3$ (500 mL), brine (500 mL), dried over Na_2SO_4 and concentrated *in vacuo* to give geranyl diethyl phosphate **8a** (116 g, *quant.*) as a colorless oil which was used directly without purification.

The spectroscopic data of geranyl diethyl phosphate **8a** are in accordance with the literature values reported.[2]



8a *78%* **10**

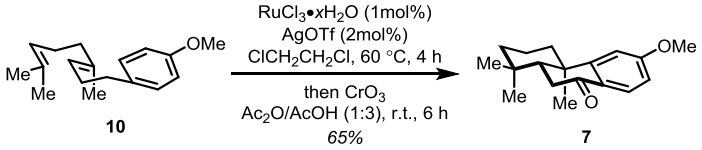
The Grignard reagent **9** was prepared as followed: To magnesium turnings (19 g, 795 mmol) stirred in dry THF (500 mL) was added a portion of 4-methoxybenzyl chloride (2 mL, 15 mmol), where the reaction could be started by gentle heating. Subsequently, a solution of 4-methoxybenzyl chloride (54 mL, 398 mmol) in THF (200 mL) was added dropwise over 2 h to maintain reflux. After complete addition, reflux was continued for another 2 h.

The reaction mixture containing **9** was cooled to -40 °C and a solution of geranyl diethyl

[2] D. C. Braddock, J. S. Marklew, K. M. Foote, A. J. White, *Chirality* **2013**, *25*, 692–700.

phosphate **8a** (57.6 g, 200 mmol) in THF (250 mL) was added dropwise via cannula at the same temperature. The reaction mixture was allowed to warm to room temperature and stirred for 14 h. When no starting material could be detected by TLC, the reaction was quenched with *sat. aq.* NH_4Cl (500 mL), extracted with Et_2O (2 × 500 mL), washed with *sat. aq.* $NaHCO_3$ (500 mL), brine (500 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude material was purified by flash chromatography (Petroleum ether/DCM = 1:0 ~ 3:1) to afford alkene **10** (40 g, 78%) as colorless oil.

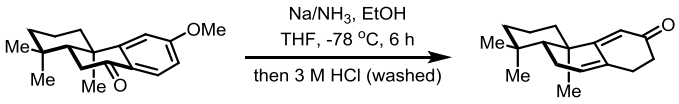
The spectroscopic data of alkene **10** are in accordance with the literature values reported.[2]



A mixture of $RuCl_3 \cdot xH_2O$ (412 mg, 1.99 mmol) and AgOTf (1.02 g, 3.97 mmol) in $ClCH_2CH_2Cl$ (350 mL) was stirred vigorously for 1 h. Then the cyclization precursor **10** (40 g, 155 mmol) in $ClCH_2CH_2Cl$ (650 mL) was added at room temperature. The resulting solution was heated to 60 °C and stirred for 4 h. TLC analysis indicated that the reaction was completed, the solvent was evaporated and the residue was used directly for the next step without further purification. The crude **11** from polyene cyclization was dissolved in Ac_2O (250 mL) and AcOH (750 mL), then CrO_3 (40 g, 0.4 mol) was added at room temperature and stirred for 6 h. After full conversion, silca gel (200 mL) was added. Then the solvent was evaporated and the resulting dry homogeneous mixture was directly purified by flash chromatography (Petroleum ether/Ethyl acetate = 30:1) to afford ketone **7** as a colorless oil (27.6 g, 65%).

Data of ketone **7**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.4 Hz, 1H), 6.83 (d, *J* = 2.4 Hz, 1H), 6.79 (dd, *J* = 8.4, 2.4 Hz, 1H), 3.85 (s, 3H), 2.63 (m, 2H), 2.27 (br d, *J* = 12.4 Hz, 1H), 1.85 (dd, *J* = 13.6, 4.4 Hz, 1H), 1.80-1.65 (m, 2H), 1.57-1.50 (m, 2H), 1.26 (td, *J* = 12.8, 4.0 Hz, 1H), 1.23 (s, 3H), 0.99 (s, 3H), 0.93 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.2, 164.1, 158.6, 129.9, 124.6, 111.2, 109.0, 55.3, 49.3, 41.3, 38.3, 37.8, 36.0, 33.3, 32.5,

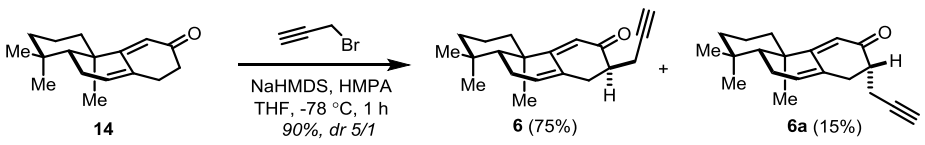
23.2, 21.4, 18.8 ppm; IR (film, cm^{-1}) 2927, 1673, 1596, 1273, 1242, 1216; HRMS(ESI) [M + Na]$^+$ calculated for $C_{18}H_{24}NaO_2$: 295.1669, found: 295.1670; TLC: Rf = 0.74 (Petroleum ether/Ethyl acetate = 3/1).



7 *54%* **14**

To a solution of ketone **7** (27.6 g, 101.6 mmol) and ethanol (177 mL, 3.04 mol) in THF (300 mL) at −78 °C was added liquid ammonia (about 1500 mL). Sodium (23.5 g, 1.02 mol) was added in small pieces until the dark blue coloration persisted, after which the solution was stirred at −78 °C for 6 h, by which time TLC analysis indicated that the reaction was completed. Solid ammonium chloride was added and the ammonia was allowed to evaporate. Then water (500 mL) was added and the aqueous phase was extracted with ethyl acetate (3 × 500 mL). The combined organic phases were washed with brine (3 × 200 mL) followed by 3M HCl (3 × 500 mL, the separation funnel was shook for at least 2 min each time to ensure the formation of dienone). Then the organic phase was dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude material was purified by flash chromatography (Petroleum ether/Ethyl acetate = 20:1) to afford dienone **14** as a white solid (13 g, 54%).

Data of dienone **14**: m.p. 53.5 - 55.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.02 (br s, 1H), 5.78 (s, 1H), 2.60 (m, 2H), 2.40 (m, 2H), 2.29 (like td, *J* = 19.2, 4.8 Hz, 1H), 2.11 (m, 1H), 1.82 (br d, *J* = 13.2 Hz, 1H), 1.66-1.56 (m, 2H), 1.46-1.32 (m, 3H), 1.17 (td, *J* = 13.2, 4.4 Hz, 1H), 1.03 (s, 3H), 0.95 (s, 3H), 0.89 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.9, 167.8, 130.3, 130.1, 118.8, 47.8, 41.7, 37.7, 37.4, 36.3, 33.6, 32.6, 30.8, 24.3, 22.1, 20.0, 18.6 ppm; IR (film, cm^{-1}) 2925, 1666, 1576, 1443, 1390, 1256, 1189; HRMS(ESI) [M + H]$^+$ calculated for $C_{17}H_{25}O$: 245.1900, found: 245.1902; TLC: Rf = 0.50 (Petroleum ether/Ethyl acetate = 5/1).

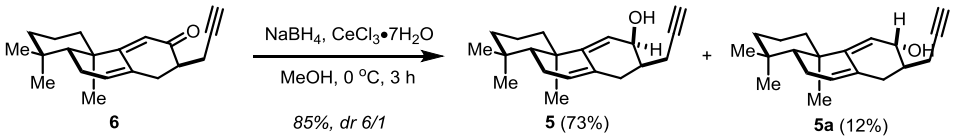


To a solution of dienone **14** (13 g, 53.3 mmol) in THF (250 mL) was added NaHMDS (1 M in THF, 64 mL, 64 mmol) dropwise at -78 °C and the reaction mixture was stirred at -78 °C for 15 min. The resulting yellow solution was treated with HMPA (27.7 mL, 160 mmol) and stirred for 15 min at -78 °C. Then propargyl bromide (13.8 mL, 160 mmol) was added over 2 min. The brown solution was stirred at -78 °C for 1 h by which time TLC analysis showed full conversion. The reaction was quenched by addition of saturated aqueous NH_4Cl (200 mL) and extracted with ethyl acetate (3 × 200 mL). The combined organic phases were washed with brine (2 × 200 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified on silica gel chromatography (Petroleum ether/Ethyl acetate = 30:1) to provide dienyne **6** as colorless oil (11.3 g, 75%) and its isomer dieneyne **6a** (2.25 g, 15%) as colorless oil. The ratio of dienyne **6** to its isomer **6a** was 5:1 as determined based on crude ^{1}H-NMR.

The configuration of dienyne **6** was confirmed by 2D NMR (see S46-S50).

Data of dienyne **6**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.15 (br d, *J* = 4.8 Hz, 1H, H_7), 5.74 (s, 1H, H_{11}), 2.82 (br d, *J* = 12 Hz, 1H, H_{14}), 2.66 (dd, *J* = 5.2, 14.8 Hz, 1H, H_{14}), 2.58-2.47 (m, 2H, H_{13}+H_{15}), 2.36-2.10 (m, 3H, H_6+H_{15}+H_6), 2.02 (t, *J* = 2.8 Hz, 1H, H_{17}), 1.85 (br d, *J* = 12.4 Hz, 1H, H_3), 1.71-1.58 (m, 2H, H_2×2), 1.46 (br d, *J* = 13.6, 1H, H_1), 1.39-1.31 (m, 2H, H_3+H_5), 1.18 (td, *J* = 4.4, 13.2 Hz, 1H, H_1), 1.05 (s, 3H, Me_{20}), 0.96 (s, 3H, Me_{19}), 0.90 (s, 3H, Me_{18}) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.0 (*C*O), 167.4 (C_9), 132.9 (C_7H), 128.4 (C_8), 117.3 (C_{11}H), 81.9 (C_{16}), 69.9 (C_{17}H), 48.3 (C_5H), 44.8 (C_{13}H), 41.6 (C_1H_2), 38.0 (C_{10}), 36.3 (C_3H_2), 34.3 ($C_{14}H_2$), 33.5 (C_4), 32.7 ($C_{18}H_3$), 24.4 (C_6H_2), 22.1 ($C_{19}H_3$), 20.5 ($C_{20}H_3$), 19.9 ($C_{15}H_2$), 18.6 (C_2H_2) ppm; IR (film, cm^{-1}) 3308, 2925, 2844, 1661, 1575, 1436, 1389, 1265, 1176; HRMS(ESI) $[M + Na]^+$ calculated for $C_{20}H_{26}NaO$: 305.1876, found: 305.1884; TLC: Rf = 0.61 (Petroleum ether/Ethyl acetate = 5/1).

Data of dienyne **6a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.09 (br s, 1H), 5.78 (s, 1H), 2.86-2.74 (m, 2H), 2.54-2.43 (m, 2H), 2.35-2.27 (m, 2H), 2.18-2.11 (m, 1H), 1.98 (t, *J* = 2.8 Hz, 1H), 1.82 (br d, *J* = 12.8 Hz, 1H), 1.70-1.56 (m, 2H), 1.48-1.33 (m, 3H), 1.27-1.11 (m, 1H), 1.04 (s, 3H), 0.96 (s, 3H), 0.89 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.0 (*C*O), 167.7 (*C*), 130.6 (*C*H), 130.2 (*C*), 118.3 (*C*H), 82.2 (*C*), 69.7 (*C*H), 47.8 (*C*H), 45.1 (*C*H), 41.8 (CH_2), 37.6 (*C*), 36.4 (CH_2), 36.2 (CH_2), 33.6 (*C*), 32.6 (CH_3), 24.4 (CH_2), 22.1 (CH_3), 19.9 (CH_3), 18.8 (CH_2), 18.6 (CH_2) ppm; IR (film, cm^{-1}) 3308, 2924, 1661, 1644, 1578, 1441, 1389, 1215, 1180, 632; HRMS(ESI) $[M + Na]^+$ calculated for $C_{20}H_{26}NaO$: 305.1876, found: 305.1883; TLC: Rf = 0.67 (Petroleum ether/Ethyl acetate = 5/1).



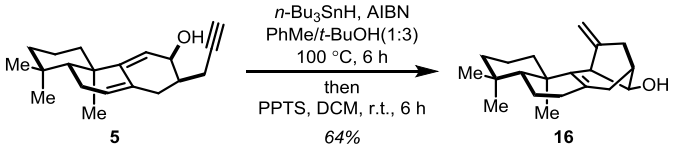
To a 500mL flask charged with magnetic stir bar was added dienyne **6** (10.1 g, 35.8 mmol) and MeOH (200 mL). Then Cerium chloride heptahydrate (23.2 g, 71.8 mmol) was added and the mixture was cooled to 0 °C. To this solution was added sodium borohydride (2.05 g, 53.8 mmol) portion wise. The reaction was stirred for 3 h at 0 °C until only alcohol was visible as indicated by TLC. The reaction was quenched at 0 °C by the addition of a saturated aqueous NH_4Cl (100 mL). The aqueous layer was extracted with ethyl acetate (3 × 100 mL) and the combined organic layers were washed with brine and dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified on silica gel chromatography (Petroleum ether/Ethyl acetate = 5:1) to provide alcohol **5** as colorless oil (7.43 g, 73%) with its isomer **5a** (1.22 g, 12%). The ratio of alcohol **5** to its isomer **5a** was 6:1 as determined based on crude ^{1}H-NMR.

The configuration of alcohol **5** was confirmed by 2D-NMR (see S52-S56).

Data of alcohol **5**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.65 (d, *J* = 5.6 Hz, 1H, H_7), 5.51 (d, *J* = 4.4 Hz, 1H, H_{11}), 4.42 (br d, *J* = 4 Hz, 1H, H_{12}), 2.42-2.31 (m, 3H, H_{15}+H_{14}×2), 2.18-2.12 (m, 2H, H_6+H_{15}), 2.05-1.94 (m, 3H, H_6+H_{13}+H_{17}), 1.86 (d, *J* = 12.8 Hz, 1H, H_1), 1.67-1.51 (m, 2H,

H$_2$×2), 1.43-1.40 (m, 1H, *H*$_3$), 1.33 (td, *J* = 12.8, 4.4 Hz, 1H, *H*$_1$), 1.24-1.12 (m, 2H, *H*$_5$+ *H*$_3$), 0.96 (s, 3H, *Me*$_{20}$), 0.91 (s, 3H, *Me*$_{19}$), 0.87 (s, 3H, *Me*$_{18}$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3 (*C*$_9$), 129.4 (*C*$_8$), 125.7 (*C*$_7$H), 118.0 (*C*$_{11}$H), 83.7 (*C*$_{16}$), 68.9 (*C*$_{17}$H), 67.9 (*C*$_{12}$H), 48.7 (*C*$_5$H), 42.0 (*C*$_3$H$_2$), 38.5 (*C*$_{13}$H), 37.02 (*C*$_{10}$), 36.96 (*C*$_1$H$_2$), 33.2 (*C*$_4$), 33.0 (*C*$_{18}$H$_3$), 32.1 (*C*$_{14}$H$_2$), 23.8 (*C*$_6$H$_2$), 22.1 (*C*$_{19}$H$_3$), 21.5 (*C*$_{20}$H$_3$), 18.8 (*C*$_2$H$_2$), 18.4 (*C*$_{15}$H$_2$) ppm; IR (film, cm^{-1}) 3308, 2922, 2843, 1458, 1372, 1045, 1006, 907, 732, 621; HRMS(ESI) $[M + Na]^+$ calculated for $C_{20}H_{28}NaO$: 307.2032, found: 307.2036; TLC: Rf = 0.42 (Petroleum ether/Ethyl acetate = 5/1).

Data of alcohol **5a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.62 (d, *J* = 5.6 Hz, 1H), 5.42 (br s, 1H), 4.12 (like d, *J* = 3.2 Hz, 1H), 2.52 (br d, *J* = 14.0 Hz, 1H), 2.29 (ddd, *J* = 16.8, 6.0, 2.8 Hz,1H), 2.21-2.13 (m, 3H), 2.04-1.98 (m, 2H), 1.87-1.75 (m, 2H), 1.67-1.51 (m, 2H), 1.42 (br d, *J* = 13.2 Hz, 1H), 1.32 (td, *J* = 13.2, 4.4 Hz, 1H), 1.26-1.12 (m, 2H), 0.98 (s, 3H), 0.92 (s, 3H), 0.87 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 129.5, 125.5, 118.6, 82.8, 69.9, 69.7, 49.0, 42.1, 40.3, 37.1, 37.0, 33.3, 33.0, 32.0, 23.9, 22.1, 21.4, 20.8, 18.9 ppm; IR (film, cm^{-1}) 3309, 2923, 2843, 1435, 1373, 1044, 993, 622; HRMS(ESI) $[M + Na]^+$ calculated for $C_{20}H_{28}NaO$: 307.2032, found: 307.2041; TLC: Rf = 0.39 (Petroleum ether/Ethyl acetate = 5/1).

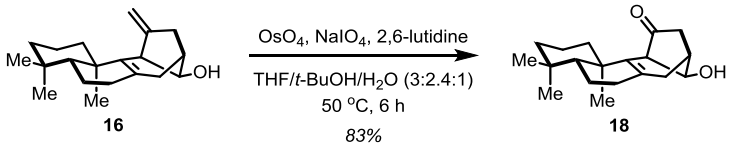


To a 500-mL sealed tube was added alcohol **5** (7.42 g, 26.1 mmol) and *t*-BuOH (300 mL), then the mixture was degassed following the freeze-pump-thaw technique and heated to 100 °C. A solution of the tri-*n*-butyl tin hydride (*n*-Bu$_3$SnH, 14.2 mL, 52.3 mmol) and 2,2'-azoisobutyronitrile (AIBN, 2.06 g, 13.1 mmol) in toluene (PhMe, 100 mL) was added dropwise via syringe using a syringe pump within 4 h at 100 °C followed by further 2 h of stirring at the same temperature. The TLC analysis showed full conversion. The solvent was removed and the mixture was dissolved in DCM (200 mL). Pyridinium *p*-toluenesulfonate (PPTS, 16.6 g, 65.5 mmol) was added at room temperature and the

resulting solution was stirred for 6 h. After full conversion, the reaction mixture was washed with water (100 mL), the water phase was extracted with DCM (3 × 100 mL), the combined organic layer was washed with brine (100 mL), dried over Na_2SO_4, filtered, concentrated *in vacuo* and purified on silica gel chromatography (Petroleum ether/Ethyl acetate = 20:1) to provide tetracycle **16** as waxy solid (4.78 g, 64%).

The structure of tetracycle **16** was determined by 2D-NMR (see S58-S62).

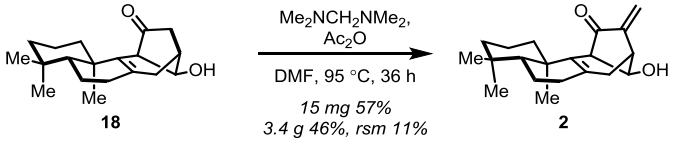
Data of tetracycle **16**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.98 (s, 1H, H_{17}), 4.87 (s, 1H, H_{17}), 3.84 (s, 1H, H_{12}), 2.91 (s, 1H, H_{11}), 2.57 (ddd, *J* = 16.8, 9.6, 2.0 Hz, 1H, H_{16}), 2.33 (dd, *J* = 18.0, 5.2 Hz, 1H, H_{14}), 2.22 (t, *J* = 6.0, Hz, 1H, H_{13}), 2.09 (d, *J* = 17.2 Hz, 1H, H_{16}), 1.91-1.79 (m, 4H, H_{14}+H_7×2+H_1), 1.67-1.46 (m, 3H, H_6+ H_2×2), 1.42-1.25 (m, 3H, H_6+H_3+H_1), 1.18-1.10 (m, 2H, H_3+H_5), 0.96 (s, 3H, Me_{20}), 0.86 (s, 3H, Me_{18}), 0.82 (s, 3H, Me_{19}) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8 (C_{15}), 140.6 (C_9), 123.8 (C_8), 107.1 ($C_{17}H_2$), 78.9 ($C_{12}H$), 51.6 (C_5H), 48.7 ($C_{11}H$), 41.6 (C_3H_2), 41.3 ($C_{14}H_2$), 40.0 ($C_{13}H$), 38.9 (C_{10}), 35.7 (C_1H_2), 35.2 ($C_{16}H_2$), 33.2 (C_4), 33.1 ($C_{18}H_3$), 31.0 (C_7H_2), 21.5 ($C_{19}H_3$), 20.0 ($C_{20}H_3$), 18.74 (C_2H_2), 18.70 (C_6H_2) ppm; IR (film, cm^{-1}) 3337, 2927, 1654, 1441, 1374, 1198, 1073, 1009, 873; HRMS(ESI) $[M + Na]^+$ calculated for $C_{20}H_{30}NaO$: 309.2189, found: 309.2195; TLC: Rf = 0.33 (Petroleum ether/Ethyl acetate = 5/1).



To a solution of alkene **16** (4.55 g, 16 mmol) in THF/water (3:1, 270 mL) were added 1, 4-diaza [2, 2, 2] bicyclooctane (DABCO, 9 g, 80 mmol), OsO_4 (0.00984M in *t*-BuOH, 162 mL, 1.6 mmol), and $NaIO_4$ (33.8 g, 160 mmol). The reaction was heated to 50 °C and stirred for 6 h. After the reaction was complete, 5% $Na_2S_2O_3$ (200 mL) and ethyl acetate (500 mL) were added. The organic layer was separated, and the water layer was extracted by ethyl acetate (3 × 200 mL). The combined organic layer was washed with brine and dried over Na_2SO_4. The solvent was removed and the residue was purified on silica gel

chromatography (Petroleum ether/Ethyl acetate = 3:1) to provide ketone **18** as white solid (3.8 g, 83%).

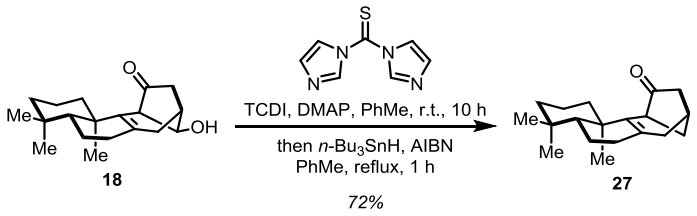
Data of ketone **18**: m.p. 154 - 157 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.99 (s, 1H), 2.90 (s, 1H), 2.56 (dd, *J* = 18.4, 8.0 Hz, 1H), 2.48-2.44 (m, 2H), 2.02-1.81 (m, 4H), 1.82 (d, *J* = 12.8 Hz,, 1H), 1.66-1.53 (m, 3H), 1.45-1.36 (m, 2H), 1.26-1.09 (m, 3H), 0.96 (s, 3H), 0.86 (s, 3H), 0.82 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.5, 134.8, 127.6, 76.4, 53.1, 51.5, 41.5, 40.3, 39.6, 38.6, 37.0, 34.9, 33.2, 33.1, 31.3, 21.5, 20.1, 18.53, 18.50 ppm; IR (film, cm^{-1}) 3438, 2926, 1731, 1439, 1143, 1073, 1007, 754; HRMS(ESI) $[M + Na]^+$ calculated for $C_{19}H_{28}NaO_2$: 311.1982, found: 311.1992; TLC: Rf = 0.26 (Petroleum ether/Ethyl acetate = 2/1).



A sealed tube with a magnetic stirring bar was charged with ketone **18** (3.4 g, 11.8 mmol), Ac_2O (30 mL), tetramethylmethanediamine (30 mL) and DMF (30 mL). The reaction mixture was heated to 100 °C and stirred for 24 h. Then additional Ac_2O (5 mL) and tetramethylmethanediamine (5 mL) were added. 12 h later, 1 M HCl (100 mL) and Et_2O (100 mL) were added. The organic layer was separated, and the water layer was extracted by Et_2O (3 × 100 mL). The combined organic layer was washed with brine (100 mL) and dried over Na_2SO_4. The solvent was removed and the residue was purified on silica gel chromatography (Petroleum ether/Ethyl acetate = 4:1) to provide jungermannenone C (**2**) as white solid (1.63 g, 46%) as well as recovered starting material (0.37g, 11%). Another run with 15 mg of ketone **18** using the same process gave 8.7 mg of jungermannenone C (56%) with full conversion in 12 h.

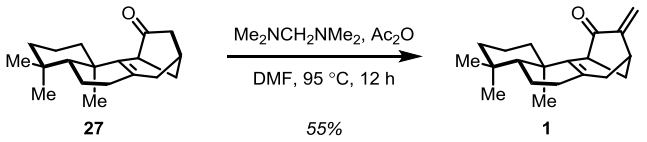
Data of **2**: m.p. 72 - 73 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.08 (s, 1H), 5.52 (s, 1H), 4.03 (s, 1H), 3.09 (s, 1H), 2.98 (br s, 1H), 2.54 (dd, *J* = 16.8, 4.4 Hz, 1H), 2.05 (like d, *J* = 16.8 Hz, 1H), 1.92-1.83 (m, 3H), 1.69-1.54 (m, 3H), 1.43-1.36 (m, 2H), 1.29-1.21 (m, 1H), 1.17-1.09 (m, 1H), 1.11 (dd, *J* = 16.8, 1.6 Hz, 1H), 0.99 (s, 3H), 0.85 (s, 3H), 0.82 (s, 3H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.2, 148.4, 135.6, 127.9, 118.2, 74.9, 53.4, 51.4, 45.3, 41.4, 40.5, 38.8, 34.9, 33.2, 33.0, 31.3, 21.5, 20.1, 18.50, 18.47 ppm; IR (film, cm^{-1}) 3441, 2934, 2897, 1730, 1651, 1457, 1251, 1157, 1074, 1007, 910, 731; HRMS(ESI) $[M + H]^+$ calculated for $C_{20}H_{29}O_2$: 301.2162, found: 301.2166; TLC: Rf = 0.32 (Petroleum ether/Ethyl acetate = 2/1).



To a stirred solution of **18** (10 mg, 0.035 mmol) in PhMe (1 mL) was added 1,1'-thiocarbonyldiimidazole (5 mg, 0.042 mmol) and DMAP (9.3 mg, 0.052 mmol) in a sealed tube. The mixture was stirred for 10 h by which time TLC analysis showed full conversion. The resulting ester was heated to 110 °C and a solution of the *n*-Bu_3SnH (46 µL, 0.17 mmol) and AIBN (11.4 mg, 0.069 mmol) in PhMe (1 mL) was added dropwise via syringe using a syringe pump within 1 h. The TLC analysis showed full conversion. The solvent was removed and the residue was purified on silica gel chromatography (Petroleum ether/Ethyl acetate = 30:1) to provide **27** as white solid (6.8 mg, 72%).

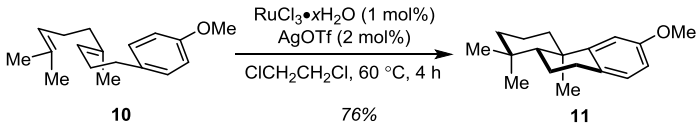
Data of **27**: m.p. 106.7 - 108.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.91 (d, *J* = 4.8 Hz, 1H), 2.52 (m, 1H), 2.37 (dd, *J* = 17.6, 4.8 Hz, 1H), 2.27 (dd, *J* = 18.4, 7.2 Hz, 1H), 2.03 (dd, *J* = 18.4, 3.2 Hz, 1H), 1.95-1.78 (m, 4H), 1.69-1.55 (m, 4H), 1.46-1.30 (m, 2H), 1.27-1.09 (m, 3H), 0.97 (s, 3H), 0.88 (m, 1H), 0.85 (s, 3H), 0.82 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.7, 138.1, 127.2, 51.7, 44.8, 44.3, 41.6, 39.3, 38.8, 34.9, 34.0, 33.2, 33.1, 31.8, 29.8, 21.5, 20.1, 18.7, 18.6 ppm; IR (film, cm^{-1}) 2938, 1738, 1457, 1162, 1131, 913, 744; HRMS(ESI) $[M + H]^+$ calculated for $C_{19}H_{29}O$: 273.2213, found: 273.2216; TLC: Rf = 0.89 (Petroleum ether/Ethyl acetate = 9/1).



A sealed tube with a magnetic stirring bar was charged with ketone **27** (10 mg, 0.037 mmol), Ac_2O (0.5 mL), tetramethylmethanediamine (0.5 mL) and DMF (0.5 mL). The reaction mixture was heated to 100 °C and stirred for 12 h. 1 M HCl (5 mL) and Et_2O (10 mL) were added. The organic layer was separated, and the water layer was extracted by Et_2O (3 × 10 mL). The combined organic layer was washed with brine (10 mL) and dried over Na_2SO_4. The solvent was removed and the residue was purified by silica gel chromatography (Petroleum ether/Ethyl acetate = 30:1) to provide jungermannenone B (**1**) as white solid (5.7 mg, 55%).

Data of **1**: m.p. 84 - 85 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.89 (s, 1H), 5.39 (s, 1H), 3.06 (d, *J* = 4.4 Hz, 1H), 3.03 (br s, 1H), 2.45 (dd, *J* = 16.8, 4.4 Hz, 1H), 1.93-1.87 (m, 5H), 1.67-1.54 (m, 3H), 1.62 (d, *J* = 4.4 Hz, 1H), 1.41 (m, 1H), 1.37 (m, 1H), 1.28-1.20 (m, 1H), 1.17-1.10 (m, 1H), 1.11 (dd, *J* = 12.4, 2.0 Hz, 1H), 0.99 (s, 3H), 0.85 (s, 3H), 0.82 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.9, 151.0, 139.0, 127.4, 115.1, 51.6, 44.8, 41.5, 40.4, 39.0, 37.7, 34.9, 33.2, 33.1, 32.5, 31.8, 21.5, 20.0, 18.59, 18.55 ppm; IR (film, cm^{-1}) 2935, 1730, 1457, 1389, 1259, 1200, 1161, 932, 630; HRMS(ESI) $[M + H]^+$ calculated for $C_{20}H_{29}O$: 285.2213, found: 285.2218; TLC: Rf = 0.63 (Petroleum ether/Ethyl acetate = 20/1).

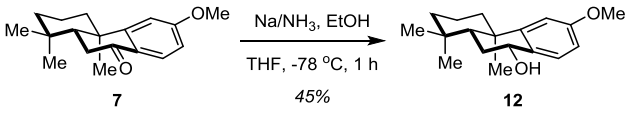
Synthesis of compounds 11, 12, 17



A mixture of $RuCl_3 \cdot xH_2O$ (2.1 mg, 0.01 mmol) and AgOTf (5.1 mg, 0.02 mmol) in $ClCH_2CH_2Cl$ (2 mL) was stirred vigorously for 1 h. Then the cyclization precursor **10** (258 mg, 1.0 mmol) in $ClCH_2CH_2Cl$ (3 mL) was added at room temperature. The resulting

solution was heated to 60 °C and stirred for 3 h. TLC analysis indicated that the reaction was completed, the solvent was evaporated and the residue was directly purified by flash chromatography (Petroleum ether/Acetone = 50:1) to afford ketone **11** as a white solid (196 mg, 76 %).[3]

Data of **11**: m.p. 29.5 - 30.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (d, *J* = 8.0 Hz, 1H), 6.82 (d, *J* = 2.4 Hz, 1H), 6.67 (dd, *J* = 8.0, 2.4 Hz, 1H), 3.78 (s, 3H), 2.84 (m, 2H), 2.25 (br d, J = 12.4 Hz, 1H), 1.87 (m, 1H), 1.81-1.60 (m, 3H), 1.48 (m, 1H), 1.41 (td, *J* = 12.8, 3.6 Hz, 1H), 1.33 (dd, *J* = 12.4, 2.4 Hz, 1H), 1.22 (td, J = 13.6, 3.6 Hz, 1H), 1.20 (s, 3H), 0.96 (s, 3H), 0.93 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 151.4, 129.7, 127.5, 110.6, 110.1, 55.2, 50.3, 41.6, 38.8, 38.0, 33.5, 33.3, 29.6, 24.7, 21.6, 19.3, 19.1 ppm; IR (film, cm^{-1}) 2954, 2925, 2830, 1710, 1611, 1501, 1281, 1261, 1252, 1049; HRMS(ESI) $[M + H]^+$ calculated for $C_{18}H_{27}O$: 259.2056, found: 259.2062; TLC: Rf = 0.34 (Petroleum ether/Ethyl acetate = 100/1).



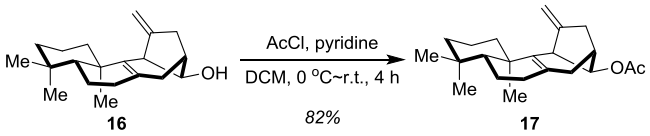
7 **12**

To a solution of the ketone **7** (52 mg, 0.19 mmol) and ethanol (0.2 mL, 3.4 mmol) in THF (3 mL) at −78 °C was added liquid ammonia (about 10 mL). Sodium (50 mg, 2.2 mmol) was added until the dark blue coloration persisted, after which the solution was stirred at −78 °C for 1 h, by which time TLC analysis indicated that new points were formed. Solid ammonium chloride was added and the ammonia was allowed to evaporate. Then water (20 mL) was added and the aqueous phase was extracted with ethyl acetate (3 × 20 mL). The combined organic phases were washed with brine (10 mL). The organic phase was dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude material was purified by flash chromatography (Petroleum ether/Ethyl acetate = 20:1) to afford alcohol **12** as a white solid (23 mg, 45%).

[3] S. W. Youn, S. J. Pastine, D. Sames, *Org. Lett.* **2004**, *6*, 581–584.

The configuration of alcohol **12** was confirmed by 2D NMR (see S65-S69).

Data of alcohol **12**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (td, *J* = 1.2, 7.6 Hz, 1H, H_{14}), 6.77-6.75 (m, 2H, H_{11}+H_{13}), 4.80-4.76 (m, 1H, H_7), 3.79 (s, 3H, *Me*O), 2.28-2.21 (m, 2H, H_6+H_1), 1.84 (br s, 1H, H_6), 1.77-1.59 (m, 4H, O*H*+H_6+H_2×2), 1.51-1.48 (m, 1H, H_3), 1.40-1.34 (m, 2H, H_1+H_5), 1.27 (s, 3H, Me_{17}), 1.25-1.33 (m, 1H, H_3), 0.96 (s, 3H, Me_{15}), 0.94 (s, 3H, Me_{16}) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9 (C_{12}), 151.6 (C_9), 130.6 (C_8), 128.6 (C_{14}H), 111.2 (C_{13}H), 109.9 (C_{11}H), 70.8 (C_7H), 55.2 (*Me*O), 49.3 (C_5H), 41.3 (C_3H_2), 38.8 (C_1H_2), 38.7 (C_{10}), 33.2 ($C_{15}H_3$), 33.1 (C_4), 30.3 (C_6H_2), 25.2 ($C_{17}H_3$), 21.6 ($C_{16}H_3$), 19.1 (C_2H_2) ppm; IR (film, cm^{-1}) 2927, 2360, 2341, 1609, 1574, 1500, 1462, 1244, 1070, 1038, 817; HRMS(ESI) $[M + Na]^+$ calculated for $C_{18}H_{26}NaO_2$: 297.1825, found: 297.1828; TLC: Rf = 0.53 (Petroleum ether/Ethyl acetate = 3/1).



To a solution of tetracycle **16** (41 mg, 0.15 mmol) and pyridine (36 μL, 0.45 mmol) in DCM (2 mL) was added acetyl chloride (23 μL, 0.30 mmol) at 0 °C. The resulting solution was slowly heated to room temperature and stirred for 4h until disappearance of the starting material. The mixture was quenched with a saturated aqueous $NaHCO_3$. The aqueous layer was extracted with ethyl acetate (3 × 20 mL) and the combined organic layers were washed with brine (30 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified on silica gel chromatography (Petroleum ether/Ethyl acetate = 30:1) to provide acetate **17** as white solid (35 mg, 82%).

Single crystals of acetate **17** suitable for X-ray crystallographic analysis were obtained by a single recrystallization at room temperature using *n*-hexanes/$CHCl_3$ as a solvent by slow evaporation. The configuration was determined by X-ray crystallographic analysis.

Data of acetate **17**: m.p. 145.2 - 146.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.88 (s, 1H), 4.78 (s, 1H), 4.73 (s, 1H), 3.07 (s, 1H), 2.61-2.54 (m, 1H), 2.42-2.31 (m, 2H), 2.11 (d, *J* = 16.8 Hz,

1H), 2.02 (s, 3H), 1.93-1.79 (m, 4H), 1.67-1.46 (m, 3H), 1.43-1.27 (m, 3H), 1.17-1.10 (m, 2H), 0.99 (s, 3H), 0.86 (s, 3H), 0.81 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 155.3, 140.8, 124.0, 105.6, 82.1, 51.6, 45.5, 41.7, 41.1, 39.0, 37.3, 36.3, 35.6, 33.2, 33.1, 31.0, 21.52, 21.46, 20.0, 18.70, 18.68 ppm; IR (film, cm^{-1}) 2931, 2900, 2872, 2832, 1738, 1444, 1374, 1240, 1037, 1018, 877; HRMS(ESI) $[M + Na]^+$ calculated for $C_{22}H_{32}NaO_2$: 351.2295, found: 351.2304; TLC: Rf = 0.36 (Petroleum ether/Ethyl acetate = 9/1).

Attempts at asymmetric polyene cyclization

Encouraged by the success of enantioselective polyene cyclization developed by Yamamoto [4] and Corey [5], we investigated the asymmetric polyene cyclization for the formation of enantiopure **11**. With precursor **10** in hand, we tested different conditions, but only no or low *ee* was obtained (see table S1). The stoichiometric use of a 1:1 complex of *o, o'*-dichloro-(*S*)-BINAL and $SbCl_5$ in DCM gave **11** with no *ee* (entries 1, 2). Excess ligand (entry 3), change of the solvent to toluene (entry 4) or addition of 3Å or 4Å molecular sieve (entries 5, 6) also gave racemic **11**. Though the stoichiometric use of weaker Lewis acid $SnCl_4$ gave 30% *ee*, the *ee* value was way too low for asymmetric total synthesis.

[4] a) K. Ishihara, H. Ishibashi, H. Yamamoto, *J. Am. Chem. Soc.* **2002**, *124*, 3647–3655; b) H. Ishibashi, K. Ishihara, H. Yamamoto, *J. Am. Chem. Soc.* **2004**, *126*, 11122–11123.

[5] a) K. Surendra, E. J. Corey, *J. Am. Chem. Soc.* **2012**, *134*, 11992–11994; b) K. Surendra, G. Rajendar, E. J. Corey, *J. Am. Chem. Soc.* **2014**, *136*, 642–645.

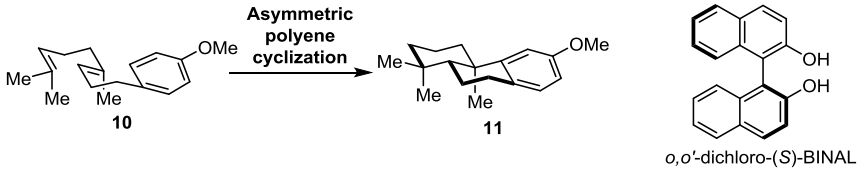


Table S5, entries for the asymmetric polyene cyclization

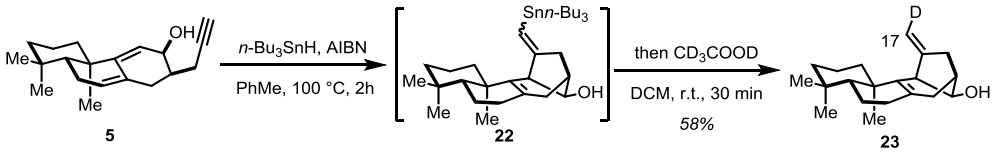
Entry	Lewis acid	*o, o'*-dichloro-(*S*)-BINAL	solvent	additive	Conversion (%)[a], ee[b] (%)	
1	$SbCl_5$(1.0 eq)	1.0 eq	DCM	no	>99,	0
2	$SbCl_5$(1.5 eq)	1.5 eq	DCM	no	>99,	0
3	$SbCl_5$(1.0 eq)	3.0 eq	DCM	no	>99,	0
4	$SbCl_5$(1.0 eq)	1.0 eq	PhMe	no	>99,	0
5	$SbCl_5$(1.0 eq)	1.0 eq	DCM	3Å MS	>99,	0
6	$SbCl_5$(1.0 eq)	1.0 eq	DCM	4Å MS	>99,	0
7	$SnCl_4$(1.5 eq)	1.5 eq	DCM	no	>99,	30

[a] Determined by GC analysis; [b] Determined by chiral HPLC analysis.

General procedure for asymmetric polyene cyclization:

To a solution of *o, o'*-dichloro-(*S*)-BINAL (1.0 – 3.0 eq, see table S1) in dry DCM or PhMe (0.2M) was cooled to -78 °C and then 1.0 M solution of $SbCl_5$ in DCM (1.0 – 1.5 eq, see table S1) was added and the mixture was stirred for 15 min at -78 °C. Then a precooled (−78 °C) solution of alkene (0.2 mmol, 1.0 eq) in dry DCM was added *via* cannula at -78 °C. The reaction mixture was stirred at -78 ℃ until the cyclization was complete as indicated by GC-MS (2-6 h). The reaction mixture was quenched with 5 mL of saturated $NaHCO_3$ solution, and aqueous layer was extracted with Et_2O (3 x 20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in *vacuo*. The crude material was purified by flash chromatography (Petroleum ether/Acetone = 50:1) to afford ketone **11** (65%-80%). Enantioselectivity was determined by using chiral HPLC analysis using Chiracel OD-H column (1% *i*-PrOH in hexanes; 1.0 ml/min; 254nm), retention times: 5.568 (major), 9.146 (minor).

d) Experimental procedures for Scheme 3b



To a 10-mL sealed tube was added alcohol **5** (19 mg, 0.067 mmol) and PhMe (1 mL), then the mixture was degassed following the freeze-pump-thaw technique and heated to 100 °C. A solution of the *n*-Bu_3SnH (36 µL, 0.13 mmol) and AIBN (5.5 mg, 0.033 mmol) in PhMe (1 mL) was added dropwise via syringe using a syringe pump within 1 h at 100 °C followed by further 1 h of stirring at the same temperature. The TLC analysis showed full conversion, a mixture of 1:1 E/Z isomer of **22** was obtained. [6] The solvent was removed and the mixture was dissolved in DCM (2 mL). CD_3COOD (10 µL, 0.16 mmol) was added at room temperature and the resulting solution was stirred for 30 min. After full conversion, the reaction mixture was concentrated *in vacuo* and purified on silica gel chromatography (Petroleum ether/Ethyl acetate = 20:1) to provide tetracycle **23** as waxy solid (11.1 mg, 58%).

Data of tetracycle **23**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.96 (s, 1H), 4.87 (s, 0.15 H), 3.84 (d, *J* = 5.2 Hz 1H), 2.91 (s, 1H), 2.57 (ddd, *J* = 16.8, 9.6, 2.0 Hz, 1H), 2.33 (dd, *J* = 18.0, 5.2 Hz, 1H), 2.22 (t, *J* = 6.0 Hz, 1H), 2.09 (d, *J* = 16.8 Hz, 1H), 1.89-1.80 (m, 4H), 1.67-1.48 (m, 3H), 1.42-1.26 (m, 3H), 1.18-1.11 (m, 2H), 0.96 (s, 3H), 0.87 (s, 3H), 0.82 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$)[7] δ 155.8, 140.6, 123.8, 78.9, 51.6, 48.7, 41.7, 41.4, 40.0, 39.0, 35.8, 35.2, 33.2, 33.1, 31.0, 21.5, 20.0, 18.76, 18.73 ppm; ^{2}H NMR δ 4.90 ppm; IR (film, cm^{-1}) 3339, 2925, 1637, 1457, 1374, 1206, 1072, 1008, 823, 718; HRMS(ESI) $[M + H]^+$ calculated for $C_{20}H_{30}DO$: 288.24322, found: 288.24387; TLC: Rf = 0.33 (Petroleum

[6] Due to the instability of organostannane intermediate, we performed detailed NMR spectroscopic studies based on the crude residue of compound **22** obtained after cyclization (S71-S76).

[7] The signal of C17 of compound **23** showed a mixture in the ^{13}C NMR result from the deuterium substitution.

ether/Ethyl acetate = 5/1).

^{1}H, ^{13}C NMR comparison of compounds 22 and 16

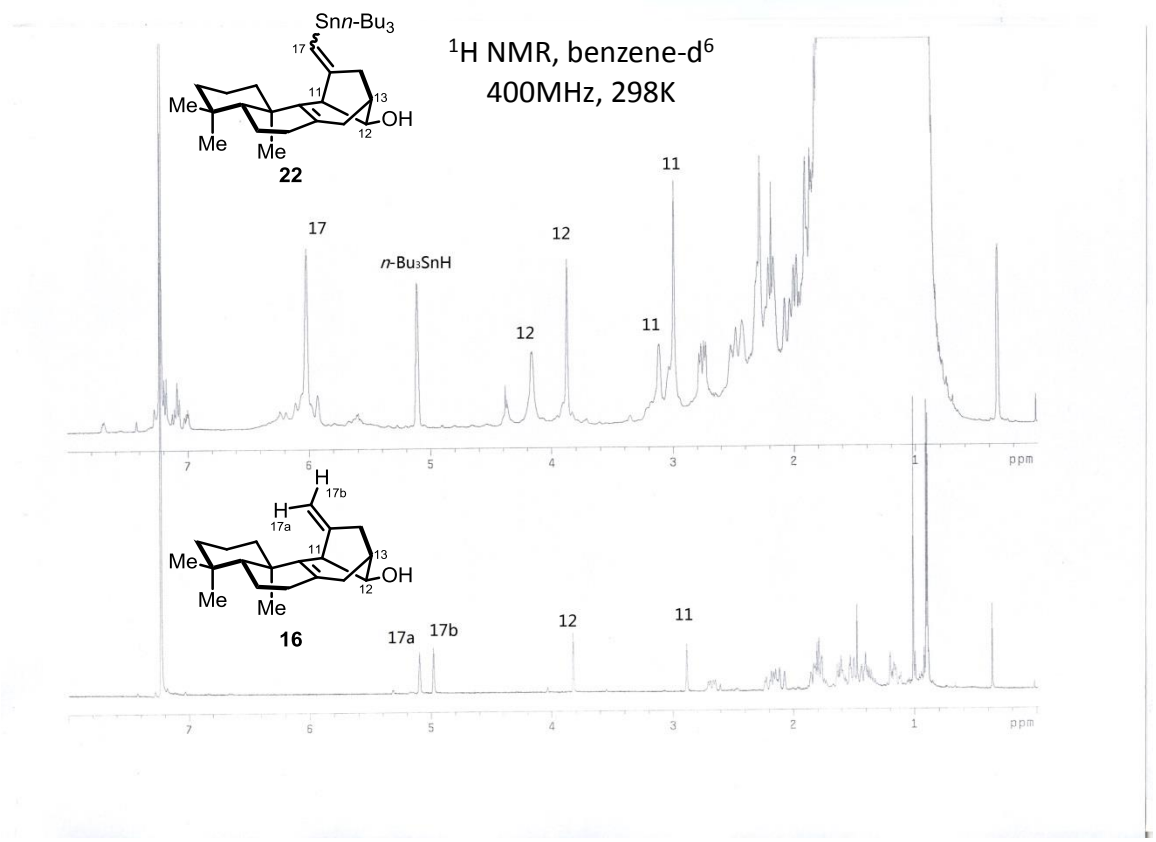


Tabela S6, ^{1}H NMR comparison of compounds 22 and 16

H	11	12	17a	17b
Compound 22	3.12 3.00	4.16 3.87	6.02	6.02
Compound 16	2.88	3.82	5.09	4.98

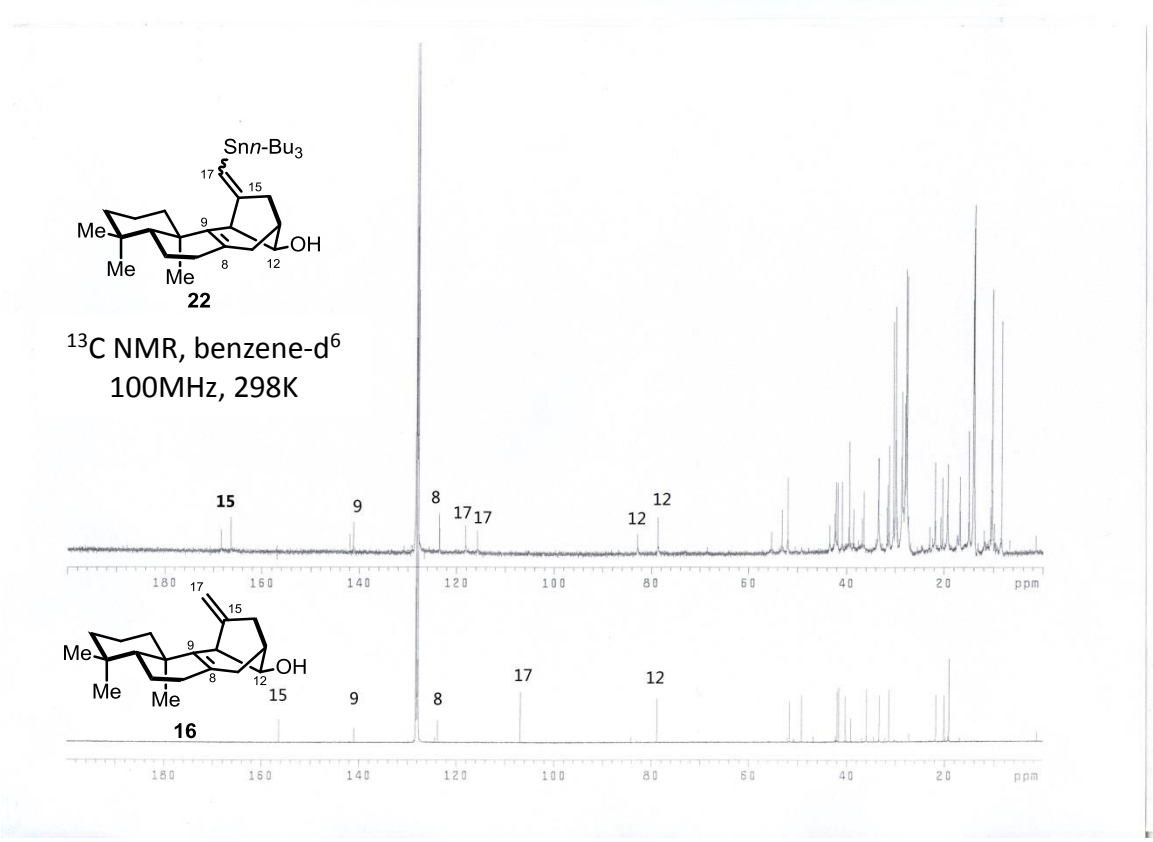
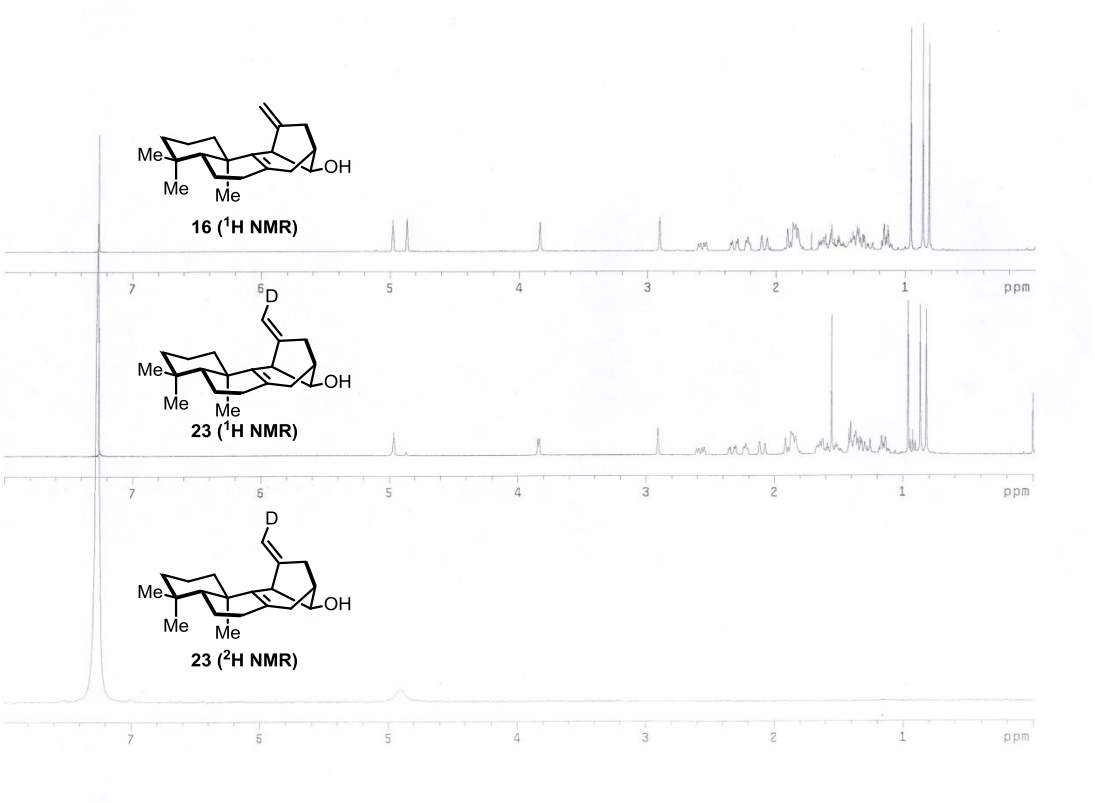


Tabela S7, ^{13}C NMR comparison of compounds 22 and 16

C	8	9	12	15	17
Compound 22	123.4 123.5	141.9 141.2	82.8 78.6	168.4 166.4	115.7 118.1
Compound 16	123.8	141.0	78.9	156.4	106.9

^{1}H, ^{2}D NMR comparison of compounds 16 and 23



e) Computational study

(1) Computational Methods

All DFT calculations were performed with the Gaussian 09 software package. [8] Geometry optimization and frequency calculations were carried out using the (U)B3LYP functional[9] with 6-31G(d) basis set (for C, H, O) and SDD psuedopotential and basis set (for Sn). Single point energy calculations using (U)B3LYP, (U)M06-2X, (U)BLYP-D3 functionals[10] have been performed based on the gas-phase (U)B3LYP-optimized structures, using 6-311+G(d,p) basis set (for C, H, O) and psuedopotential and basis set SDD (for Sn). Solvation energies in chloroform were evaluated by IEFPCM calculations with radii and non-electrostatic terms for SMD solvation model [11] using the gas-phase B3LYP-optimized structures. All discussed energies are based on (U)B3LYP calculations. All 3D structures in the Figures were prepared with CYLview.[12]

(2) Energy Profile of Dienynes Reductive Radical Cyclization of **S**

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[8] M.J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, 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, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford CT, **2013**.

[9] a) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785-789; b) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648-5652.

[10] a) Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215-241; b) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104; c) S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456-1465.

[11] A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* **2009**, *113*, 6378-6396.

[12] C. Y. Legault, CYLview, 1.0b; Université de Sherbrooke, **2009**. http://www.cylview.org.

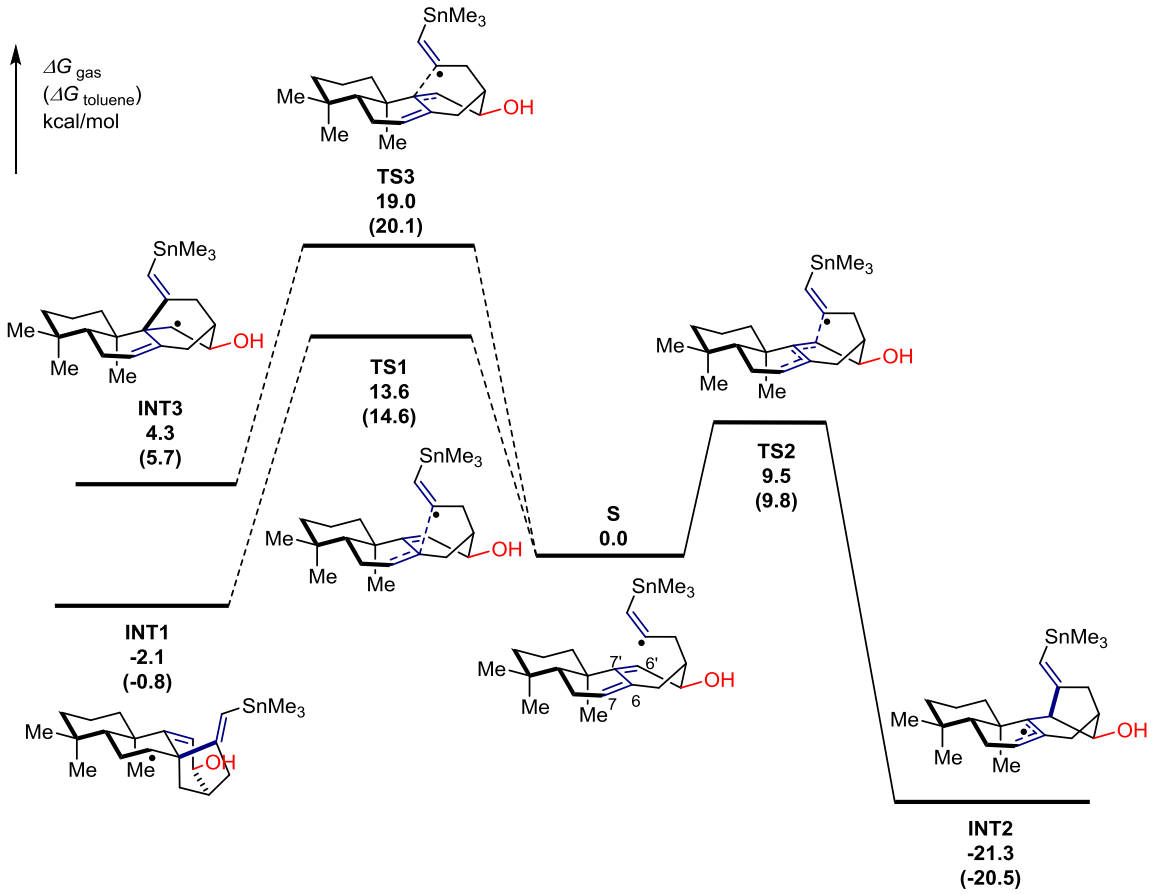

Figure S1. Energy Profile of Dienynes Reductive Radical Cyclization of S. Relative Gibbs free energies in kcal/mol in the gas phase at 298 K were computed at the UB3LYP/SDD-6-311+G(d,p)//UB3LYP/SDD-6-31G(d) level, relative Gibbs free energies in chloroform at 298K were computed at the SMD(UB3LYP/SDD-6-311+G(d,p))//UB3LYP/SDD-6-31G(d) level.

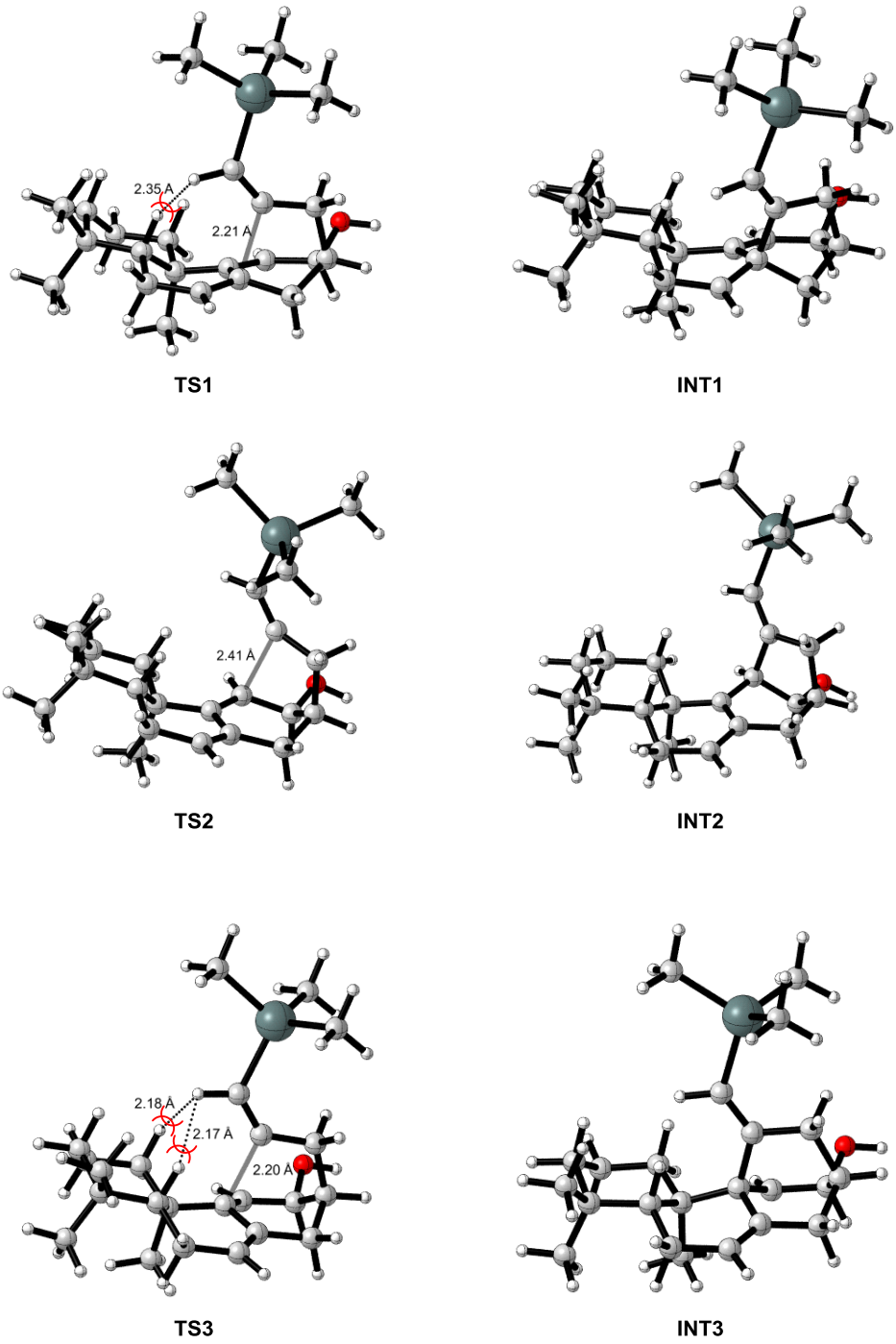

Figure S2. Computed Structures in Figure S1.

As shown in **Figure S1**, after the formation of the vinyl radical intermediate **S**, the subsequent competitive radical cyclization can occur at either C6, C7, C6' or C7' position. Radical attack to C7 atom is far away from the vinyl radical and such an addition is

impossible geometrically. Addition of vinyl radical to C6' via **TS2** only needs an activation free energy of 9.5 kcal/mol and this pathway is exergonic by 21.3 kcal/mol to furnish **INT2**. In contrast, radical additions to C6 (via **TS1**) and to C7' (via **TS3**) are both disfavored (by 4.1 kcal/mol and 9.5 kcal/mol respectively). The disfavors of **TS1** and **TS3** are partially contributed by the steric repulsions shown in **Figure S2**. Here we can see the H-H distance of 2.35 Å in **TS1** is larger than that corresponding H-H distance (2.17 Å) in **TS3**, and therefore reaction via **TS3** is much more difficult to occur. However, the most contribution of the observed selectivity comes from the orbitals of the diene moiety in the substrate (see discussion in part 3).

Table S8. Comparison of Relative Gibbs Free Energies of Species Shown in Figure S1 at 298 K. Calculated at UB3LYP/SDD-6-31G(d), DFT/SDD-6-311+G(d,p)//UB3LYP/SDD-6-31G(d), and SMD(toluene)//DFT/SDD-6-311+G(d,p)//UB3LYP/SDD-6-31G(d) level respectively.

	UB3LYP	UB3LYP//UB3LYP	UM06-2X//UB3LYP	SMD/UB3LYP	SMD/UM06-2X
S	0.0	0.0	0.0	0.0	0.0
TS1	12.4	13.6	10.6	14.6	11.4
INT1	-4.4	-2.1	-11.6	-0.8	-10.4
TS2	8.7	9.5	7.8	9.8	7.8
INT2	-23.8	-21.3	-26.8	-20.5	-26.2
TS3	17.8	19.0	14.5	20.1	15.3
INT3	2.2	4.3	-6.8	5.7	-5.6

We investigated how various DFT functionals affect the calculations. **Table S7** gives the free energies obtained by single point energy and solvation energy calculations with different functionals. In the gas phase, UM06-2X underestimates the selectivity in the reaction (**TS2** is only 2.8 kcal/mol lower than **TS1**). When solvation is considered with UM06-2X method, the selectivity of the reaction improved slightly (**TS2** is 3.6 kcal/mol lower than **TS1**). Also with UM06-2X functional, the reaction barriers are lower and the reaction becomes more exergonic. We can conclude that both UB3LYP and UM06-2X functionals give the same selectivity results of the present reaction, which agree with

the experimental results.

(3) Fukui Functions for Radical Additions and Energy Profile of Intermolecular Radical Addition Reactions Between **m1** and **m2**

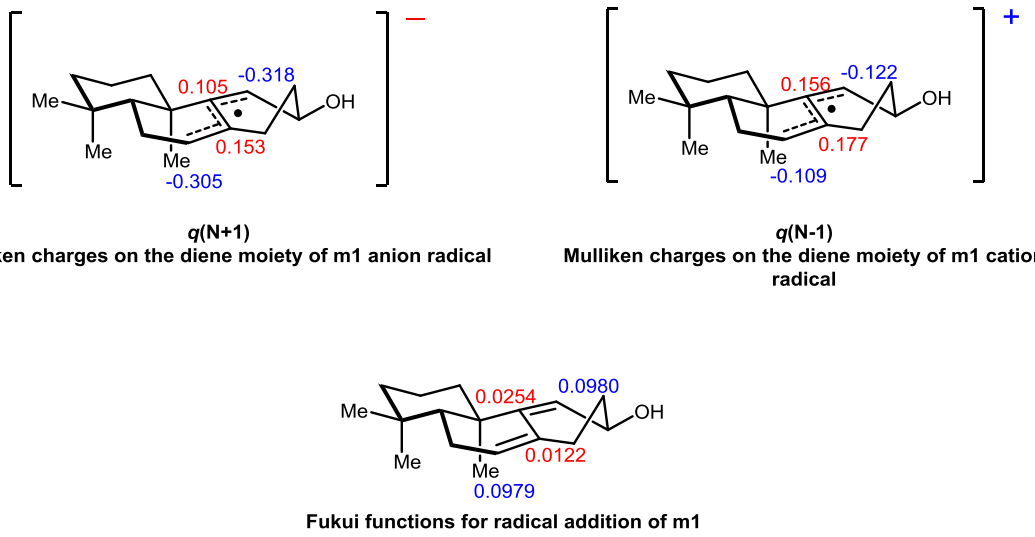

Figure S3. Computed Fukui Functions for Radical Additions. Mulliken charges were calculated at UB3LYP/ 6-31G(d) level based on the gas-phase optimized structures of **m1**.

For the molecule **m1** which will be attacked by radical, Fukui functions [13] for radical attack f^0 was widely used to estimate the relative reactivity of different reaction site in the molecule for radical addition reaction. Fukui functions for radical attack, f^0, can be approximated with the equation below:

$f^0=[q(\text{N-1})-q(\text{N+1})]/2$

Here we can see, after losing one electron, **m1** was transformed to the **m1** cation radical. The corresponding charges of the **m1** cation radical is q(N-1). Similarly, q(N+1) is the charges of the **m1** anion radical. With the equation above, we calculated the q(N+1) and

[13] a) R. G. Parr, W. Yang, *J. Am. Chem. Soc.* **1984**, *106*, 4049–4050; b) K. Fukui, *Science* **1987**, *218*, 747–754; c) P. W. Ayers, M. Levy, *Theo. Chem. Acc*. **2000**, 103, 353–360; c) P. W. Ayers, W. Yang, L. J. Bartolotti, in Chemical Reactivity Theory: A Density Functional View (Ed.:P. K. Chatteraj), CRC, Boca Raton, FL, **2009**, pp. 255 – 267.

q(N-1) respectively, and Fukui functions for radical attack f^0 were computed based on the above equation.

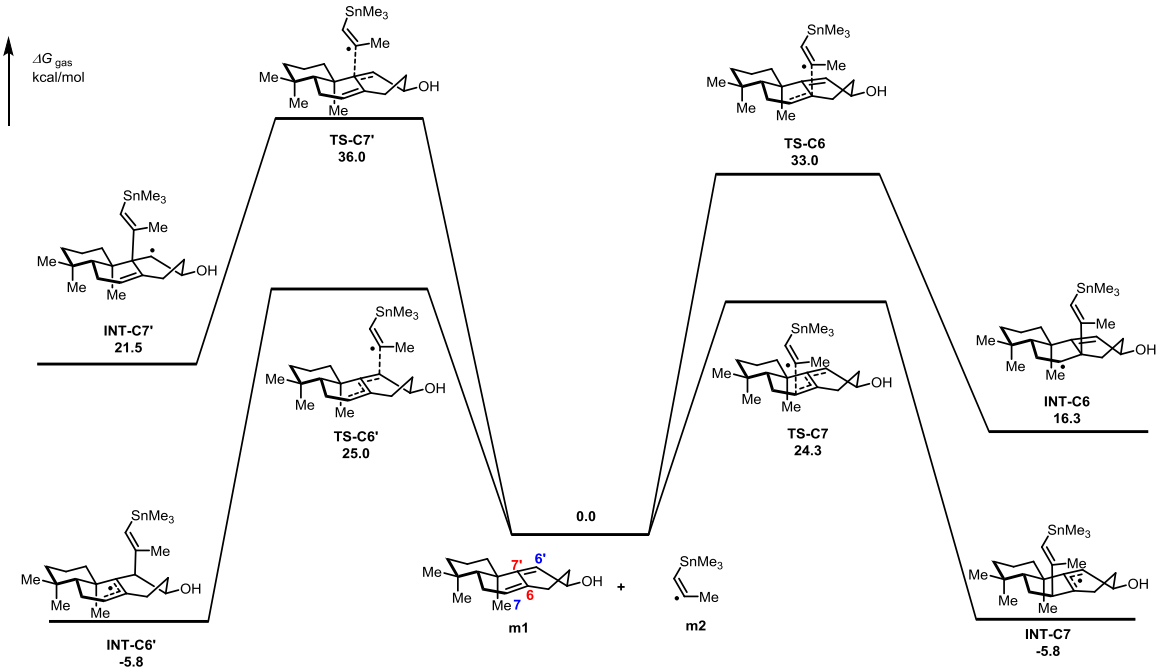

Figure S4. Computed Free Energy Profile of Intermolecular Radical Addition Reactions Between m1 and m2. Relative Gibbs free energies in gas phase at 298K. Calculated at (U)B3LYP/ 6-31G(d) level.

To rationalize the selectivity of the reaction, both HOMO and LUMO orbitals of the diene in **m1** need to be considered. Therefore, Fukui functions for radical attack were computed for model substrate **m1**, which showed that both C7 and C6' are more reactive than C6 and C7' (**Figure S3**). DFT calculations of the intermolecular additions of radical **m2** to the four possible positions are the same as that predicted by using the Fukui functions located at these positions. Calculations also indicated that radical additions to C7 and C6' have very close activation free energies (about 25 kcal/mol), while radical attack to C6 and C7' are both disfavored kinetically and thermodynamically (**Figure S4**). Therefore, intrinsically, both C7 and C6' in **S** should be favored, but C7 is not reachable geometrically by the radical in **S** and this product was not generated.

(4) Computed Energies of All Species

Table S9. Sum of electronic and thermal enthalpies *H*, sum of electronic and thermal free energies *G*, thermal correction to Gibbs free energy *TCG*, total free energy in toluene with non-electrostatic terms $E_{UB3LYP,sol}$, $E_{UM06\text{-}2X,sol}$, reported in Hartree.

	H	*G*	*TCG*	$E_{UB3LYP,sol}$	$E_{UM06\text{-}2X,sol}$
S	-976.622978	-976.718375	0.482689	-977.514075	-977.050059
TS1	-976.607286	-976.698613	0.484769	-977.492885	-977.033981
NIT1	-976.635107	-976.725337	0.487704	-977.520310	-977.071648
TS2	-976.612262	-976.704489	0.483843	-977.499673	-977.038753
INT2	-976.665843	-976.756228	0.488273	-977.552269	-977.097416
TS3	-976.598358	-976.689956	0.484117	-977.483529	-977.027109
INT3	-976.624227	-976.714868	0.487379	-977.509689	-977.063632
m1	-738.2518	-738.312276	0.357485		
m2	-239.5666	-239.622832	0.123550		
TS-C6'	-977.7992	-977.895263	0.502589		
INT-C6'	-977.85	-977.944402	0.507235		
TS-C7'	-977.7829	-977.877767	0.503331		
INT-C7'	-977.8077	-977.900856	0.507482		
TS-C6	-977.7854	-977.882475	0.501122		
INT-C6	-977.8153	-977.909116	0.506569		
TS-C7	-977.7987	-977.896387	0.500789		
INT-C7	-977.8505	-977.944397	0.507937		

(5). Computed Coordinates of All Species

S

C	6.80337200	0.66963800	0.17477800
C	6.20548800	-0.73809100	-0.06974700
C	4.66708600	-0.59255900	-0.35369500
C	3.82996500	0.31913000	0.61524700
C	4.57647800	1.66017000	0.82516400
C	6.04616000	1.48592800	1.22416000
C	3.94529400	-1.93329100	-0.57616600
C	2.51306000	-1.72466100	-0.97306900
C	1.84084400	-0.57533700	-0.77471000
C	2.44418000	0.54746400	-0.02997500
C	1.73958000	1.68600100	0.16153100
C	-1.82212600	0.74983600	-1.09598500
C	-2.74369700	1.47613000	-0.19980300
C	-3.90767500	1.38463700	0.39198800
C	6.89340100	-1.31604300	-1.32882200
C	3.54229800	-0.33037000	1.99661000
Sn	-5.29091700	-0.31966300	0.24572500
C	-4.20302000	-2.19687400	-0.01068900
C	-6.66570600	-0.04764100	-1.43020200
C	-6.42488800	-0.39511100	2.11085900
C	6.56143600	-1.67186600	1.10897600
H	7.86080300	0.56776100	0.45491600
H	6.78837600	1.22641100	-0.77437400
H	4.62069300	-0.06594200	-1.32037400
H	4.06262000	2.25750700	1.58759700
H	4.53257400	2.23953400	-0.10789900
H	6.51111200	2.47450200	1.33059900
H	6.12275600	1.01021100	2.21023100
H	4.44714600	-2.50858300	-1.36396200
H	4.00172800	-2.56361200	0.32434600
H	2.01534300	-2.54385800	-1.49206400
H	2.18395200	2.52510000	0.68820700
H	-2.24188300	-0.24248900	-1.34530400
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H	6.62619900	-2.36344700	-1.50705400
H	7.98370800	-1.27574500	-1.21470900
H	6.63222000	-0.74288100	-2.22702000
H	2.91122000	0.34346800	2.58625800
H	4.45260500	-0.52025700	2.56958600
H	3.00223300	-1.27677800	1.89788700
H	-3.41282500	-2.29065200	0.74040300
H	-4.88706600	-3.04454100	0.10310300
H	-3.74565800	-2.25980600	-1.00288300

H	-7.23447700	0.88013700	-1.31525200
H	-7.37315900	-0.88175000	-1.48502700
H	-6.11646300	0.00241400	-2.37530900
H	-7.15142900	-1.21389100	2.08644500
H	-5.75556600	-0.55488600	2.96183000
H	-6.96991200	0.54007400	2.27405500
H	6.24027500	-1.28656400	2.07951400
H	6.12277900	-2.66798500	0.98610400
H	7.64989500	-1.80105400	1.15688500
C	-0.41024500	0.56079100	-0.50032500
H	-0.51308500	0.12200500	0.50210600
C	0.45194400	-0.37592900	-1.35396200
H	0.53757000	0.06112200	-2.36229600
H	-0.03824000	-1.34774600	-1.48814900
C	0.32969900	1.90084800	-0.32681600
H	-0.22263500	2.51184300	0.39585100
O	0.31783400	2.68915800	-1.53379100
H	1.07572300	2.40000300	-2.06555800

TS1

C	-3.32909100	-2.33682900	1.49705100
C	-3.16745600	-2.27991000	-0.04200800
C	-2.42419100	-0.94888200	-0.42650000
C	-2.92866300	0.38417000	0.23838600
C	-3.12336600	0.15994700	1.75881400
C	-3.96219400	-1.07794500	2.09329700
C	-2.24937400	-0.75850300	-1.94546800
C	-1.49106600	0.49001300	-2.27991700
C	-2.28506100	-3.48115800	-0.45560500
C	-4.24722600	0.92898900	-0.37542600
C	-4.54394300	-2.47686200	-0.71629300
H	-3.91357200	-3.22790800	1.76503200
H	-2.33503400	-2.47195200	1.94954000
H	-1.41229600	-1.07930100	-0.01628700
H	-3.58640200	1.04615100	2.20943500
H	-2.13528300	0.05228300	2.22688900
H	-4.03718000	-1.18114300	3.18362200
H	-4.99126900	-0.95654900	1.73030400
H	-1.72843200	-1.62488900	-2.37643700
H	-3.23014000	-0.74086800	-2.44806600
H	-1.11807700	0.59834600	-3.29735800
H	-2.21540200	-3.59201600	-1.54327400
H	-2.70758600	-4.41367700	-0.06106400
H	-1.26666000	-3.38418300	-0.05945100
H	-4.50085300	1.88111900	0.10355600
H	-5.09160200	0.25003600	-0.23185700
H	-4.14843500	1.11980100	-1.44854300
H	-5.29026300	-1.74563800	-0.39691200
H	-4.47565500	-2.42587000	-1.80820100
H	-4.93516900	-3.47020900	-0.46297000
C	-1.62993200	2.47673200	0.83348500
C	1.34347200	2.29305100	-0.27151000
C	0.86333300	0.91677000	-0.59147600
C	1.35471200	-0.30378300	-0.57829000
Sn	3.34890700	-0.85130000	0.12429700
C	4.88218700	0.27321500	-0.95310500
C	3.55354400	-0.46747900	2.26417300
C	3.61639200	-2.98392400	-0.26251200
H	-2.15511400	2.54153800	1.78143800
H	2.24786100	2.50473600	-0.86104700
H	1.61676300	2.38160400	0.78820400
H	0.74122500	-1.13051000	-0.94454500
H	4.78969400	0.11301700	-2.03166900
H	5.88026700	-0.05187500	-0.64114500
H	4.79630600	1.34633400	-0.75643700
H	2.80163000	-1.02788000	2.82790400
H	4.54556200	-0.77297600	2.61293200
H	3.42333600	0.59609500	2.48598000
H	4.59703000	-3.31999000	0.08977600
H	3.54760700	-3.19489100	-1.33441600
H	2.84940700	-3.57122300	0.25237500
C	-0.58064500	2.78806000	-1.77032900
H	-1.39980000	3.48125700	-2.01109200
H	0.02630400	2.67264600	-2.67643800
C	-1.85984200	1.46545400	-0.02459500
C	-1.15157300	1.44369400	-1.34063400
C	0.26021700	3.34346200	-0.61169600
H	0.74116200	4.28933300	-0.89656900
C	-0.68612600	3.62089800	0.57479300
H	-1.28591400	4.51583500	0.32351900
O	0.01505200	3.87931000	1.79864600
H	0.50555900	4.70885400	1.68142600

INT1

C	-3.41911200	-2.19351500	1.52626100
C	-3.16322700	-2.21844900	-0.00053500
C	-2.33306500	-0.94371500	-0.40012700
C	-2.80551500	0.44343000	0.16908900
C	-3.10614400	0.30062800	1.68546800
C	-4.02281600	-0.87930500	2.02426600
C	-2.06585700	-0.83742800	-1.91444000
C	-1.21088200	0.33810300	-2.25847000
C	-2.31783200	-3.47863000	-0.30142000
C	-4.05696500	1.01562000	-0.55224000
C	-4.50475100	-2.38658700	-0.74967500
H	-4.06246100	-3.04214600	1.79672600
H	-2.46183500	-2.35361300	2.04516400
H	-1.35596000	-1.10662100	0.07601900
H	-3.55247900	1.22726100	2.06462200
H	-2.15474100	0.17311400	2.21925300
H	-4.16578900	-0.92507500	3.11172400
H	-5.02197500	-0.72832500	1.59535900
H	-1.58705600	-1.76040200	-2.27769400
H	-3.01799000	-0.78430900	-2.46753900
H	-0.82472300	0.42750200	-3.27202900
H	-2.18893700	-3.64780700	-1.37602700
H	-2.80937800	-4.36911100	0.10974600
H	-1.32160500	-3.41028700	0.15280100
H	-4.30482200	1.99262600	-0.12394300
H	-4.93490900	0.37308400	-0.44680900
H	-3.87706600	1.16578000	-1.62161300
H	-5.23410400	-1.60918800	-0.51029900
H	-4.36943400	-2.39173200	-1.83655800
H	-4.95641200	-3.34841000	-0.47622100
C	-1.57010500	2.57971200	0.70095600
C	1.36243200	2.16759300	-0.14823200

C	0.70359800	0.87896500	-0.63292400
C	1.25202100	-0.34301400	-0.63007200
Sn	3.19351800	-0.88667700	0.15332800
C	4.79693800	0.17931800	-0.88228600
C	3.33010700	-0.48023600	2.29399200
C	3.43557000	-3.02725000	-0.19176400
H	-2.24445300	2.75427900	1.53476600
H	2.36353800	2.26578800	-0.58606300
H	1.47726900	2.19457400	0.94128600
H	0.66781200	-1.15796500	-1.05934400
H	4.73911400	0.00608400	-1.96137400
H	5.77243400	-0.17173600	-0.53002300
H	4.73863500	1.25763300	-0.70452400
H	2.54105100	-1.01035600	2.83616900
H	4.29817300	-0.81189700	2.68351100
H	3.22519500	0.58943200	2.49931400
H	4.40157300	-3.37572600	0.18764800
H	3.38807500	-3.25513600	-1.26158000
H	2.64743800	-3.59518500	0.31319400
C	-0.33167500	2.67957400	-1.79854800
H	-1.22512800	3.24366600	-2.08982200
H	0.31114000	2.57435200	-2.68232500
C	-1.67423500	1.47434300	-0.05386100
C	-0.68667300	1.27789700	-1.23024000
C	0.43721500	3.31021300	-0.62513600
H	1.00561600	4.20182900	-0.92017500
C	-0.58506900	3.69302700	0.45943500
H	-1.14489800	4.58054000	0.11024800
O	0.02601000	4.00750100	1.71748600
H	0.57134300	4.79955500	1.58313900

TS2

C	2.90453700	-2.55427200	-1.28761700
C	3.19814600	-2.20925400	0.19355300
C	2.53702800	-0.82557400	0.53501500
C	2.75840600	0.35574200	-0.48076800
C	2.49243200	-0.14947700	-1.91969000
C	3.25759800	-1.43141200	-2.26596100
C	2.80491900	-0.34774500	1.97466700
C	2.06066600	0.91945100	2.28147600
C	2.53645900	-3.30751100	1.05859400
C	4.17794700	0.98510900	-0.41636900
C	4.71919800	-2.28018400	0.45684500
H	3.43561900	-3.47886800	-1.55345700
H	1.83127800	-2.77549300	-1.38937200
H	1.45421600	-1.01664500	0.48049100
H	2.74577700	0.63668800	-2.64203100
H	1.41770800	-0.34531200	-2.03379300
H	3.00472200	-1.73948600	-3.28883500
H	4.33968100	-1.24786800	-2.26610200
H	2.49888700	-1.11971500	2.69168600
H	3.88365000	-0.20557900	2.14472500
H	1.87815400	1.15085000	3.33067900
H	2.79013000	-3.21206000	2.12010400
H	2.87354300	-4.29946000	0.73251900
H	1.44342700	-3.28172400	0.96861000
H	4.22026600	1.84804600	-1.09096600
H	4.96452600	0.28995700	-0.72113400
H	4.41768500	1.34606800	0.58826100
H	5.30175900	-1.62238500	-0.19245400
H	4.96365300	-2.02328000	1.49309400
H	5.07348200	-3.30413500	0.28357400
C	1.09264200	2.22432500	-1.01794300
C	-1.42710500	2.34056800	0.45671600
C	-1.07100700	1.27449900	-0.52038500
C	-1.50927600	0.09225000	-0.88838200
Sn	-3.23602900	-0.93583500	-0.01819700
C	-3.07714700	-1.02668900	2.16015500
C	-5.09092600	0.08970700	-0.54991200
C	-3.27155500	-2.96425700	-0.82796300
H	1.20439500	2.03949700	-2.08062900
H	-1.72268400	1.90945800	1.42650000
H	-2.30218500	2.87554900	0.06448000
H	-1.01507100	-0.44871300	-1.69909700
H	-2.13783300	-1.50338200	2.45626400
H	-3.90615400	-1.60824500	2.57713500
H	-3.10714100	-0.02545300	2.60158000
H	-5.19194200	0.16098500	-1.63715100
H	-5.95622300	-0.45451300	-0.15718000
H	-5.10712500	1.10362500	-0.13808900
H	-4.12946700	-3.52121300	-0.43743400
H	-2.35971300	-3.50536500	-0.55629900
H	-3.34582900	-2.94441700	-1.91990600
C	0.76456000	2.97469000	1.71896200
H	1.43812000	3.83445300	1.85881400
H	0.28161200	2.80528200	2.68918100
C	1.78900000	1.48638800	-0.09182100
C	1.58107600	1.75144200	1.33064800
C	-0.28817500	3.37193900	0.66486900
H	-0.73279600	4.32861400	0.97443100
C	0.44185300	3.53823800	-0.67449900
H	1.22368600	4.31111700	-0.56484700
O	-0.42506300	3.89940300	-1.74771500
H	-0.75753000	4.79183100	-1.56295000

INT2

C	3.37363600	-2.70692500	-0.61430500
C	4.10434000	-1.72025700	0.33001600
C	3.16826500	-0.48423900	0.58474000
C	2.51981000	0.20366900	-0.67315300
C	1.87275000	-0.90166700	-1.54837800
C	2.82876600	-2.05310100	-1.88587800
C	3.76712600	0.56676600	1.53653100
C	2.78226800	1.65497000	1.83367300
C	4.33639700	-2.45763700	1.67020700
C	3.51434600	1.02720700	-1.53935500
C	5.49702400	-1.37455500	-0.24193800
H	4.05072300	-3.53487500	-0.86628700
H	2.53048200	-3.15376700	-0.06607000
H	2.30362600	-0.90724800	1.11946300
H	1.48826900	-0.46939400	-2.47960700
H	1.00682400	-1.31125200	-1.01292000
H	2.29405500	-2.80111400	-2.48561500
H	3.65268300	-1.69632200	-2.51688800
H	4.07769300	0.09274100	2.47607400
H	4.69004500	0.99603900	1.11235500

H	2.94124900	2.26421100	2.72186900
H	4.97265900	-1.88723500	2.35579000
H	4.83496900	-3.41804800	1.48911800
H	3.38908400	-2.66658400	2.18264400
H	2.96222100	1.56754400	-2.31803200
H	4.25616400	0.40333200	-2.04409000
H	4.04760900	1.77295700	-0.94200500
H	5.46332100	-1.00167800	-1.26813300
H	6.01259500	-0.62395000	0.36694900
H	6.12484800	-2.27450100	-0.24683600
C	0.26012600	1.56690700	-1.02693800
C	-1.48442400	2.00347800	0.64577300
C	-1.01521000	0.98302800	-0.39195500
C	-1.62068400	-0.16466300	-0.72365400
Sn	-3.43409300	-0.96916500	0.13341400
C	-3.32314400	-1.06915500	2.31401300
C	-5.16839200	0.23376300	-0.43281900
C	-3.67876800	-2.98896900	-0.65420200
H	0.37895500	1.25173900	-2.06519400
H	-1.50650200	1.58916100	1.66128500
H	-2.50273400	2.33053100	0.40513000
H	-1.17152500	-0.75446400	-1.52419500
H	-2.43533700	-1.62621100	2.62919800
H	-4.20688000	-1.57672000	2.71458900
H	-3.27526400	-0.06904500	2.75586600
H	-5.26080300	0.28192500	-1.52215100
H	-6.08654200	-0.20381900	-0.02733100
H	-5.07929500	1.25631300	-0.05309500
H	-4.60224400	-3.44214200	-0.27952000
H	-2.84076100	-3.62626200	-0.35387900
H	-3.72443500	-2.97847800	-1.74807400
C	0.73213400	3.03453800	1.44477300
H	1.29225600	3.98085800	1.45486800
H	0.40137400	2.87055400	2.47919300
C	1.47438200	1.21552300	-0.17691900
C	1.68400800	1.91317400	1.02242600
C	-0.49164500	3.18604300	0.52569700
H	-0.98010800	4.14848700	0.72771300
C	-0.00872900	3.07767100	-0.93279400
H	0.90088800	3.66948900	-1.11681200
O	-1.02035100	3.40099200	-1.88101100
H	-1.27899000	4.32411100	-1.73135500

TS3

C	2.65742400	-2.66441800	-1.15890500
C	3.16669500	-2.19088500	0.22482500
C	2.51582600	-0.79851000	0.55782100
C	2.51846200	0.29152800	-0.57484000
C	2.08910300	-0.32930300	-1.92972400
C	2.83402700	-1.62541900	-2.26841500
C	2.99650400	-0.18773900	1.88852700
C	2.28391900	1.09919200	2.19764900
C	2.68570500	-3.22491700	1.26989300
C	3.90782700	0.96678200	-0.75286600
C	4.71206000	-2.21520400	0.24643600
H	3.16332100	-3.60271400	-1.42560200
H	1.58675300	-2.90615000	-1.07571000
H	1.45472200	-1.02792000	0.71252300
H	2.24720400	0.39849400	-2.73455100
H	1.01292200	-0.53253500	-1.90916800
H	2.45119600	-2.02631700	-3.21599500
H	3.90002900	-1.42417200	-2.43573800
H	2.81758000	-0.89447500	2.70892000
H	4.08483100	-0.02282600	1.88048800
H	2.30291400	1.44297100	3.23216900
H	3.09661700	-3.03140500	2.26676300
H	3.00412100	-4.23359300	0.97848100
H	1.59182600	-3.23202500	1.35141800
H	3.84561800	1.73670400	-1.52885200
H	4.67733200	0.25258100	-1.05465900
H	4.24472100	1.45594600	0.16556100
H	5.16686500	-1.62631900	-0.55387200
H	5.11278900	-1.84790300	1.19724900
H	5.06225700	-3.24805300	0.12487400
C	1.22322800	2.41295400	-1.09235700
C	-1.21807300	2.10242100	0.53221900
C	-0.54155300	0.81745700	0.13386200
C	-1.04466900	-0.38072000	-0.10948100
Sn	-3.16621600	-0.90306100	0.01938400
C	-3.93375100	-0.57352800	2.03984400
C	-4.36067200	0.25828200	-1.39432100
C	-3.33038400	-3.02568600	-0.46686900
H	1.37506700	2.24451300	-2.15275700
H	-1.71379400	1.95890800	1.50365400
H	-2.00209500	2.33728800	-0.20040200
H	-0.39950200	-1.21239600	-0.39068600
H	-3.34453800	-1.13596300	2.77063400
H	-4.97474000	-0.90668600	2.10715600
H	-3.89632600	0.48614300	2.31148000
H	-3.98024600	0.13032400	-2.41207300
H	-5.40437400	-0.07240000	-1.37015700
H	-4.33260700	1.32471600	-1.15084000
H	-4.37855400	-3.34218300	-0.46196000
H	-2.78668300	-3.63526800	0.26190200
H	-2.91752700	-3.22898900	-1.46007700
C	0.84647400	3.07860600	1.65324300
H	1.51939400	3.95018600	1.65170900
H	0.44293000	2.99632700	2.66959200
C	1.55436500	1.43184000	-0.15120200
C	1.61172200	1.82123400	1.28762000
C	-0.27881200	3.32036700	0.63500300
H	-0.86956200	4.19643200	0.93676500
C	0.38392000	3.59721900	-0.72816200
H	1.00651900	4.50869900	-0.63429000
O	-0.56542800	3.79850700	-1.78214300
H	-1.00881900	4.64577400	-1.61477800

INT3

C	2.74233400	-2.57549300	-1.15511700
C	3.22424200	-2.04675200	0.21834300
C	2.43163500	-0.73322500	0.56623200
C	2.25756300	0.33813000	-0.57511800
C	1.93748700	-0.31705600	-1.94997900
C	2.81519700	-1.53312400	-2.27301400
C	2.91023100	-0.05370100	1.86663600
C	2.17940400	1.22728300	2.16009100

C	2.88492200	-3.12480700	1.27378900
C	3.54718800	1.18245600	-0.77143600
C	4.76267700	-1.89842300	0.20501100
H	3.32829200	-3.46601400	-1.42188900
H	1.69926700	-2.91407700	-1.05859600
H	1.41703100	-1.08554300	0.78054800
H	2.05973900	0.43282100	-2.74126200
H	0.89084700	-0.62584800	-1.99530200
H	2.47829900	-1.97759700	-3.21856900
H	3.85632400	-1.22893900	-2.43930800
H	2.77460100	-0.73972500	2.71327000
H	3.99066000	0.15133600	1.83238200
H	2.31076300	1.64527200	3.15979400
H	3.27059000	-2.86815000	2.26675800
H	3.32965600	-4.08734300	0.99138500
H	1.80125400	-3.27185600	1.36069800
H	3.36891300	1.98191800	-1.49769200
H	4.36741600	0.57398600	-1.15901400
H	3.88765300	1.65651400	0.15170000
H	5.12550400	-1.19497700	-0.54794100
H	5.14802700	-1.57085400	1.17627900
H	5.22122900	-2.87161200	-0.01149100
C	0.94477400	2.46589800	-1.11269400
C	-1.28125800	1.97645500	0.52463400
C	-0.37663400	0.83016200	0.03797200
C	-0.88404600	-0.39605500	-0.17981400
Sn	-2.94815000	-1.02065800	0.04034100
C	-3.64625100	-0.82649600	2.10307400
C	-4.28793400	0.09599600	-1.27558400
C	-2.99749100	-3.12819500	-0.52176700
H	1.14460000	2.30737300	-2.16666800
H	-1.71380200	1.71316900	1.49896500
H	-2.11120400	2.10711400	-0.17855200
H	-0.22296500	-1.19663600	-0.49743600
H	-2.97997000	-1.36255300	2.78610300
H	-4.65143300	-1.24952100	2.20149800
H	-3.68522500	0.22194600	2.41492200
H	-3.92927700	0.05755200	-2.30860800
H	-5.29392500	-0.33526400	-1.24290900
H	-4.35575800	1.14641300	-0.97698600
H	-4.01636200	-3.52388100	-0.45873600
H	-2.36049300	-3.72344500	0.14061700
H	-2.64317200	-3.26441400	-1.54871500
C	0.64686800	3.14690900	1.63493800
H	1.30342400	4.02903200	1.57511300
H	0.27704900	3.10251000	2.66664800
C	1.10931200	1.32996900	-0.12278100
C	1.40752600	1.88014500	1.28652200
C	-0.51753600	3.30454800	0.64177800
H	-1.19126900	4.11154700	0.95830800
C	0.08764700	3.62785900	-0.73692100
H	0.69329900	4.55228400	-0.65557500
O	-0.90168200	3.81416900	-1.75807000
H	-1.35576000	4.65213300	-1.57099000

m1

C	-2.91346700	-1.34078300	-0.78613000
C	-2.76296000	0.16739900	-0.46895700
C	-1.23510100	0.50591000	-0.32267000
C	-0.36005400	-0.45229100	0.56953600
C	-0.66775200	-1.92176600	0.19549900
C	-2.16417300	-2.25075500	0.18954700
C	-0.96223400	1.97862300	0.03561400
C	0.50620700	2.27978300	0.12045800
C	-3.33552400	0.95050300	-1.67323200
C	-0.56659100	-0.25702000	2.09581300
C	-3.62712100	0.53023800	0.75962900
H	-3.98127400	-1.59829900	-0.81258500
H	-2.52569200	-1.52586300	-1.79928600
H	-0.82782500	0.36363500	-1.33618000
H	-0.14416000	-2.59721000	0.88355600
H	-0.26384600	-2.12284200	-0.80631200
H	-2.30343500	-3.30005000	-0.10088000
H	-2.58436600	-2.15885100	1.19940400
H	-1.41696000	2.63802800	-0.71447200
H	-1.44732700	2.24592200	0.98703300
H	0.80008700	3.32910700	0.09144200
H	-3.37867100	2.02920600	-1.48678600
H	-4.35866700	0.61770200	-1.88772600
H	-2.73663600	0.78755100	-2.57766700
H	0.13925200	-0.89557700	2.63886800
H	-1.57376200	-0.52663400	2.42258200
H	-0.37744700	0.77472700	2.40668600
H	-3.37474100	-0.04646500	1.65254300
H	-3.54554500	1.59177100	1.01659000
H	-4.68259500	0.33321200	0.53407700
C	2.08248300	-1.02950700	0.16810200
H	1.85644900	-2.08921000	0.23346600
C	2.93067200	1.68531000	0.26208000
H	3.28778400	1.64564500	1.30338800
H	3.08788900	2.71317900	-0.08413600
C	1.11358100	-0.09978600	0.28695600
C	1.45802800	1.33585300	0.21750800
C	3.74883400	0.69426800	-0.57708300
H	4.81557800	0.95681100	-0.56083900
C	3.54103300	-0.72729800	-0.04965700
H	4.06639400	-0.82611000	0.91988700
O	4.04232600	-1.72131600	-0.95131600
H	4.99934000	-1.58112200	-1.02822300
H	3.41640000	0.72017600	-1.62197900

m2

C	2.52506800	0.92516000	-0.03418600
C	1.27332800	1.30778000	-0.04751800
Sn	-0.49037700	-0.00482800	-0.00028500
C	-1.57397300	0.18022200	-1.88850800
C	0.06935200	-2.09407600	0.30006700
C	-1.78022200	0.63778300	1.64126700
H	1.03065500	2.37402900	-0.08378500
H	-1.87769500	1.21683000	-2.06443000
H	-2.47377000	-0.44369800	-1.87473700
H	-0.94480100	-0.13917800	-2.72487900
H	0.64869000	-2.21855900	1.21996100
H	-0.83235200	-2.71063200	0.37951500
H	0.66377500	-2.46955400	-0.53853800
H	-2.70077100	0.04513300	1.66021800

H	-2.05390500	1.69190800	1.53230400
H	-1.26996700	0.51378700	2.60131100
C	3.39103400	-0.26646500	0.00540600
H	2.81260200	-1.20499600	0.03163900
H	4.04778100	-0.30461900	-0.87335700
H	4.04110200	-0.25149900	0.88984600

TS-C6'

C	2.44165400	-2.66503600	-1.32003400
C	2.96091700	-2.36148000	0.10731400
C	2.47643300	-0.92754900	0.52851700
C	2.67022500	0.24150900	-0.50870400
C	2.18298800	-0.22593500	-1.90124300
C	2.77270300	-1.57191200	-2.33896300
C	2.96670800	-0.49815000	1.92362000
C	2.45771900	0.85871500	2.31134000
C	2.32639600	-3.40280300	1.05879500
C	4.13626100	0.74224200	-0.62579300
C	4.49076400	-2.57259300	0.16207500
H	2.84087500	-3.63422900	-1.65012400
H	1.34799500	-2.77933500	-1.27794300
H	1.38319700	-1.02530900	0.60794800
H	2.41995300	0.53822400	-2.65266700
H	1.09034300	-0.31926300	-1.87603200
H	2.36201800	-1.84428100	-3.31997500
H	3.85869700	-1.49420300	-2.47850300
H	2.64598200	-1.22897200	2.67725700
H	4.06727600	-0.50235600	1.96842700
H	2.52503200	1.13208600	3.36423900
H	2.73214600	-3.34006100	2.07459200
H	2.52255400	-4.41847300	0.69297200
H	1.23844600	-3.27590500	1.12090600
H	4.16717100	1.61847600	-1.28387300
H	4.80569600	-0.00985900	-1.05119700
H	4.54258600	1.04807400	0.34276900
H	5.03942100	-1.95162500	-0.54976600
H	4.89428100	-2.36843800	1.15962100
H	4.72441500	-3.61879900	-0.07239900
C	1.10934700	2.24959100	-0.83024800
C	-1.01951700	1.07401400	-1.02070400
C	-1.38627000	0.40150400	0.04900100
Sn	-3.22003700	-0.78469000	0.22423900
C	-4.99356800	0.46576600	-0.02856400
C	-3.25030300	-2.38114600	-1.26757900
C	-3.23445100	-1.66400300	2.22269700
H	1.17922000	2.12765600	-1.90597700
H	-0.74729500	0.40618700	0.93520000
H	-5.00782100	1.26623100	0.71746500
H	-5.90352000	-0.13197200	0.08915300
H	-5.00942900	0.92419200	-1.02201700
H	-2.36668100	-3.01841300	-1.16368900
H	-4.14170300	-3.00514500	-1.14441000
H	-3.25706000	-1.96912600	-2.28137900
H	-4.13796900	-2.26390000	2.37293200
H	-3.21081900	-0.88402400	2.99034100
H	-2.36542000	-2.31358500	2.36762200
C	1.44584100	3.10300500	1.91197000
H	2.27213900	3.82576000	1.82115500
H	1.19211100	3.05891500	2.97739900
C	1.85531500	1.44798100	0.00395700
C	1.92869900	1.74344900	1.43448300
C	0.25683400	3.62033900	1.09316000
H	-0.00961100	4.63868000	1.41074900
C	0.61882400	3.61047500	-0.39089200
H	1.45399900	4.32081700	-0.54832100
O	-0.46925200	4.01051100	-1.22701500
H	-0.73244500	4.90084100	-0.94591600
H	-0.62400700	2.98497500	1.23564900
C	-1.54657600	1.31417400	-2.38291300
H	-2.51394000	0.81058800	-2.54847000
H	-1.67510300	2.38758200	-2.55096400
H	-0.84853100	0.94545900	-3.14634800

INT-C6'

C	3.06544700	-2.57092400	-1.00051000
C	3.74851400	-1.84912400	0.18667400
C	2.88230200	-0.59930800	0.58112200
C	2.41764900	0.36084600	-0.57660200
C	1.81798600	-0.50035000	-1.72163900
C	2.73412400	-1.64473300	-2.17216600
C	3.46410600	0.20856200	1.75539900
C	2.57147600	1.34536000	2.13809400
C	3.77074200	-2.83997100	1.37442600
C	3.55400300	1.24913800	-1.15932400
C	5.21913000	-1.53393100	-0.16688500
H	3.70276000	-3.40189600	-1.33335200
H	2.12894800	-3.02437200	-0.64208600
H	1.93967400	-1.03039200	0.95238600
H	1.58357200	0.13519600	-2.58434900
H	0.86808900	-0.93014100	-1.38230000
H	2.23223200	-2.21589900	-2.96403700
H	3.65467600	-1.25208500	-2.62298900
H	3.61509300	-0.44304800	2.62581100
H	4.46849000	0.58909900	1.50523900
H	2.71799200	1.80042200	3.11646700
H	4.34973600	-2.46003200	2.22333100
H	4.23009400	-3.78764800	1.06658400
H	2.75681300	-3.06246600	1.72937600
H	3.12834600	1.97910000	-1.85885100
H	4.30016700	0.67212600	-1.71129100
H	4.07059300	1.81239500	-0.37663900
H	5.32728900	-0.92905900	-1.07006600
H	5.73010700	-1.00834000	0.64696400
H	5.76352100	-2.47124700	-0.33779600
C	0.27689600	1.87920200	-0.88635700
C	-0.97507900	0.96846400	-0.94681200
C	-1.39193500	0.24564000	0.10960100
Sn	-3.14382800	-1.01568000	0.26799300
C	-4.97805200	0.14862000	0.03430300
C	-3.13250900	-2.62929600	-1.20567300
C	-3.10128700	-1.88470600	2.26855500
H	0.65789500	1.94912300	-1.91392000
H	-0.78167400	0.29699200	1.01247200
H	-5.03586600	0.92921200	0.79938000
H	-5.85780500	-0.49565300	0.13319000
H	-5.01266700	0.63091300	-0.94734900

H	-2.22997300	-3.23982500	-1.10237900
H	-4.00321400	-3.27806400	-1.06439500
H	-3.16205500	-2.23333100	-2.22541300
H	-3.98078700	-2.51461000	2.43674200
H	-3.09309100	-1.10150700	3.03365100
H	-2.20873700	-2.50378900	2.40545900
C	0.75190400	3.01269800	1.85496600
H	1.42440200	3.87893500	1.93862900
H	0.42881600	2.78812600	2.87893200
C	1.38753400	1.35133500	0.00646500
C	1.57280400	1.84508100	1.30629400
C	-0.45361400	3.40559600	0.99486400
H	-0.77567000	4.42518200	1.25180600
C	-0.08236000	3.33144700	-0.48082300
H	0.82294300	3.94077600	-0.64889400
O	-1.13001300	3.79732300	-1.32985900
H	-1.40097700	4.67014500	-1.00532200
H	-1.30715800	2.74302800	1.17353900
C	-1.67053300	0.97069600	-2.28826100
H	-2.57980300	0.36132700	-2.28752400
H	-1.93255300	1.99226900	-2.57944100
H	-1.00417100	0.57244100	-3.06659000

TS-C7'

C	2.90678400	-2.54564500	-1.44488700
C	2.93104400	-2.40367800	0.09709400
C	2.19658600	-1.06971800	0.49779900
C	2.57833100	0.23290700	-0.28999800
C	2.57163700	-0.07698100	-1.80645200
C	3.41008900	-1.30401600	-2.18511600
C	2.18645300	-0.81247100	2.01539200
C	1.53115200	0.48767400	2.38721000
C	2.13638100	-3.59624700	0.68024300
C	3.97096700	0.79619500	0.10700100
C	4.38374600	-2.54337000	0.60662700
H	3.48926000	-3.43134800	-1.73450400
H	1.87130300	-2.73990600	-1.76259700
H	1.15379100	-1.25007000	0.21235800
H	2.91856200	0.79478000	-2.37446400
H	1.53985700	-0.27004200	-2.11892400
H	3.34274700	-1.46708900	-3.26872300
H	4.47272200	-1.13179700	-1.97222100
H	1.67419600	-1.63541200	2.53079200
H	3.21028400	-0.81395800	2.42153500
H	1.32473200	0.64080500	3.44760100
H	2.20751900	-3.64911400	1.77235400
H	2.52771200	-4.54154700	0.28365200
H	1.07418100	-3.53747800	0.41265800
H	4.16371900	1.72612300	-0.43846500
H	4.78221300	0.10403000	-0.12720300
H	4.02447800	1.02642500	1.17522900
H	5.07681400	-1.83630700	0.14505300
H	4.45177000	-2.41371000	1.69186800
H	4.75289100	-3.55129900	0.37866600
C	1.60856500	2.56001000	-0.65782700
C	-0.46357500	0.65349300	-0.59392400
C	-1.18069900	-0.01552300	0.29080100
Sn	-3.22261100	-0.74687800	0.00765900
C	-4.59739900	0.88496400	-0.46297500
C	-3.29739900	-2.23337300	-1.59155200
C	-3.82415800	-1.67884100	1.88750300
H	2.05588400	2.58275600	-1.64679600
H	-0.74748500	-0.23969500	1.26837300
H	-4.60331500	1.62597200	0.34234100
H	-5.61546100	0.50035800	-0.58455200
H	-4.30760200	1.38904700	-1.38989400
H	-2.63963400	-3.07710100	-1.36102700
H	-4.31685500	-2.61445200	-1.71222900
H	-2.97747300	-1.80033800	-2.54425800
H	-4.84458300	-2.06900900	1.81531800
H	-3.79273500	-0.95471700	2.70781800
H	-3.15795600	-2.51026900	2.13890200
C	0.70079000	2.80676700	2.03610900
H	1.53558100	3.40532200	2.43389800
H	0.02309100	2.63211700	2.87977800
C	1.55467600	1.36357500	0.07453500
C	1.25249300	1.48213700	1.52759900
C	0.00083700	3.62152500	0.94417900
H	-0.33439300	4.58844400	1.34417400
C	0.95885200	3.84059000	-0.23014900
H	1.74776900	4.55090700	0.08893600
O	0.29711500	4.39383800	-1.38035100
H	-0.09353600	5.24058900	-1.10942600
H	-0.88344200	3.08859200	0.58010300
C	-0.79820900	1.18789800	-1.94604200
H	-1.82901500	0.92978700	-2.23089700
H	-0.69987000	2.27940700	-1.97222500
H	-0.13172700	0.79516800	-2.72212900

INT-C7'

C	2.82813300	-2.57570400	-1.36357200
C	2.99634700	-2.29472900	0.14946100
C	2.17375700	-1.00345800	0.53627600
C	2.29817500	0.25038900	-0.39846800
C	2.17017900	-0.21104200	-1.87152400
C	3.11543800	-1.35879400	-2.24514700
C	2.34651100	-0.60507600	2.01237300
C	1.65916100	0.68171800	2.36532900
C	2.39709000	-3.50048800	0.91166500
C	3.64576700	0.98827800	-0.21023000
C	4.50376100	-2.25501200	0.49273400
H	3.47054700	-3.42133500	-1.64560000
H	1.79293600	-2.89871900	-1.55060400
H	1.13003100	-1.32121400	0.42056400
H	2.32690500	0.63823000	-2.54903000
H	1.15042600	-0.57244300	-2.04471500
H	2.96460300	-1.62165200	-3.30031700
H	4.16521100	-1.05253200	-2.15680800
H	1.96944100	-1.40544800	2.66313400
H	3.41161200	-0.50537100	2.27016800
H	1.63983400	0.93526200	3.42745100
H	2.58301300	-3.44493800	1.98996400
H	2.84484700	-4.43589200	0.55331600
H	1.31300400	-3.57078000	0.75899500
H	3.72114700	1.84382100	-0.88851100
H	4.49602900	0.33767000	-0.42116400

H	3.76170100	1.36882000	0.80810100
H	5.06557100	-1.52617800	-0.09626500
H	4.68080300	-2.03458200	1.55026000
H	4.94598500	-3.23886700	0.29124100
C	1.33264800	2.60549600	-0.72542000
C	-0.31913100	0.74737500	-0.44459200
C	-1.07044000	-0.00761600	0.37960300
Sn	-3.02891400	-0.86695500	0.02724700
C	-4.52471600	0.66373900	-0.41266900
C	-2.97634900	-2.30990300	-1.61358600
C	-3.58158900	-1.89734500	1.86829700
H	1.78109800	2.62634900	-1.71364600
H	-0.66316300	-0.21768500	1.36837000
H	-4.59438900	1.38171300	0.41053400
H	-5.50909500	0.20509400	-0.55225100
H	-4.26829600	1.21197100	-1.32412600
H	-2.21240100	-3.07134800	-1.42788400
H	-3.94449200	-2.81137900	-1.71372800
H	-2.74483800	-1.81860700	-2.56370200
H	-4.56956800	-2.35922400	1.77319200
H	-3.61285800	-1.19802000	2.71012300
H	-2.85930000	-2.68495900	2.10625500
C	0.52624800	2.85465700	2.01194300
H	1.33585600	3.47081100	2.43136800
H	-0.15721500	2.64972300	2.84469900
C	1.11137100	1.28575000	-0.01999600
C	1.12388600	1.54544100	1.49535000
C	-0.19496600	3.67189400	0.93677800
H	-0.51927300	4.63772900	1.34739800
C	0.73553800	3.89305400	-0.25842200
H	1.55214800	4.57401900	0.05861400
O	0.05771100	4.49438300	-1.37551500
H	-0.25741200	5.36621900	-1.08535200
H	-1.09205600	3.14698200	0.59233600
C	-0.83186300	1.20134500	-1.80021700
H	-1.74009800	0.65922900	-2.08250100
H	-1.06451100	2.27320200	-1.79412600
H	-0.09950100	1.05720900	-2.59975200

TS-C6

C	2.84270700	-2.52403700	-1.34915700
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C	2.47561100	-0.77430500	0.45154200
C	2.61889700	0.39666300	-0.58605600
C	2.31843900	-0.14699300	-2.00708100
C	3.11504800	-1.40785100	-2.36007500
C	2.76386500	-0.26186400	1.87468200
C	1.98713100	0.98112500	2.18291300
C	2.59368000	-3.24105700	1.02425700
C	4.01946700	1.06824400	-0.57288900
C	4.71213500	-2.15260100	0.31670300
H	3.39797000	-3.43332200	-1.61848500
H	1.77549500	-2.78712300	-1.40395700
H	1.40381400	-1.01626300	0.43007100
H	2.51718800	0.62901600	-2.75541500
H	1.24644300	-0.37721900	-2.07440200
H	2.83417100	-1.74404700	-3.36671000
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H	2.51515400	-1.03759800	2.61329600
H	3.84138500	-0.07642200	2.01424100
H	1.91830700	1.29059400	3.22518700
H	2.89446600	-3.12032100	2.07090800
H	2.94642500	-4.22735400	0.69784300
H	1.49746700	-3.25076800	0.98590000
H	4.03441800	1.88939700	-1.29760000
H	4.82358300	0.37721200	-0.83654800
H	4.25290600	1.49663500	0.40710500
H	5.24933400	-1.51492900	-0.38921000
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H	5.08895300	-3.17403100	0.18003700
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C	-1.31286300	0.31122000	0.09677300
Sn	-3.17168300	-0.80968500	-0.19027900
C	-2.92432700	-2.88735500	0.44174200
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C	-3.64021200	-0.74195800	-2.31908100
H	1.51315200	2.34676600	-2.14670800
H	-0.90868300	0.76622600	-0.81100100
H	-2.08755100	-3.35141500	-0.08947200
H	-3.83037600	-3.46354500	0.22698600
H	-2.72464300	-2.95015400	1.51601300
H	-4.94842400	1.13700800	0.64195700
H	-5.73797800	-0.44717100	0.77688100
H	-4.58809400	0.08165600	2.02061400
H	-4.59053700	-1.24600600	-2.52270500
H	-2.85794000	-1.23666900	-2.90323800
H	-3.71964200	0.29403800	-2.66285700
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H	1.51172700	3.71968600	1.76410400
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C	0.39972800	3.65999100	-0.81077700
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O	-0.55192500	3.80692800	-1.87369700
H	-1.02579400	4.63993900	-1.72065500
H	-1.16912100	2.98742900	0.47586100
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H	-0.13627800	-0.62048500	2.99608800
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INT-C6

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C	2.49930800	0.42397800	-0.53220700
C	2.21325600	-0.08579600	-1.97103700
C	3.05190700	-1.30836200	-2.36129700
C	2.59313800	-0.30738800	1.90949300
C	1.78085800	0.90999200	2.20743300
C	2.56304500	-3.26090200	0.96400100
C	3.89600600	1.10015900	-0.48434200

C	4.65509600	-2.08919100	0.31801400
H	3.41072200	-3.34214400	-1.67703200
H	1.76225000	-2.76856600	-1.45751900
H	1.31115300	-1.07246800	0.39534400
H	2.37616900	0.72340900	-2.69218900
H	1.15004900	-0.35248600	-2.04086200
H	2.78265900	-1.62472000	-3.37754000
H	4.11750400	-1.04764300	-2.40001700
H	2.33838100	-1.11576700	2.61554700
H	3.65881800	-0.10114000	2.09745700
H	1.88072000	1.39412700	3.17654100
H	2.85484900	-3.16653300	2.01593100
H	2.94392300	-4.22608800	0.60755200
H	1.46758500	-3.29889000	0.91845800
H	3.92062800	1.94634000	-1.17828200
H	4.70479100	0.42193000	-0.76333900
H	4.11686500	1.49465900	0.51276800
H	5.18757100	-1.44938100	-0.38934400
H	4.91409300	-1.75563000	1.32870100
H	5.05674900	-3.10321100	0.19859400
C	1.27675800	2.58181400	-0.94671600
C	-0.50855400	0.51728300	1.17879800
C	-1.21254300	0.30758500	0.05183700
Sn	-3.02879200	-0.84135300	-0.22380400
C	-2.74731700	-2.92673500	0.36610400
C	-4.69212200	0.00496000	0.91404600
C	-3.49876100	-0.74898500	-2.34980400
H	1.80239300	2.64752600	-1.89761600
H	-0.82853200	0.76757800	-0.85883400
H	-1.90222200	-3.36715300	-0.17244300
H	-3.64295800	-3.51315100	0.13642300
H	-2.54959000	-3.00969000	1.43928600
H	-4.84285300	1.05505800	0.64495200
H	-5.61659700	-0.54081000	0.69876600
H	-4.50669700	-0.04833100	1.99127500
H	-4.43550200	-1.27318700	-2.56466800
H	-2.70459000	-1.21245500	-2.94381500
H	-3.60536200	0.29029200	-2.67665800
C	0.30515600	2.85130500	1.67590800
H	1.20004300	3.42497000	1.95469900
H	-0.30717300	2.76849600	2.58209700
C	1.46828100	1.52348700	-0.14428100
C	0.76574100	1.43262900	1.22332800
C	-0.45896100	3.59080100	0.57777300
H	-0.82257600	4.55964500	0.94725600
C	0.43698000	3.79301100	-0.64523400
H	1.13214100	4.63012200	-0.44130600
O	-0.31294300	4.09649200	-1.82840700
H	-0.78882100	4.92557100	-1.66103000
H	-1.33371000	3.00789900	0.27094600
C	-0.90686800	-0.06523400	2.51902700
H	-1.92180200	-0.47354000	2.49897100
H	-0.22880100	-0.87413300	2.82026200
H	-0.86670300	0.68576300	3.31756400

TS-C7

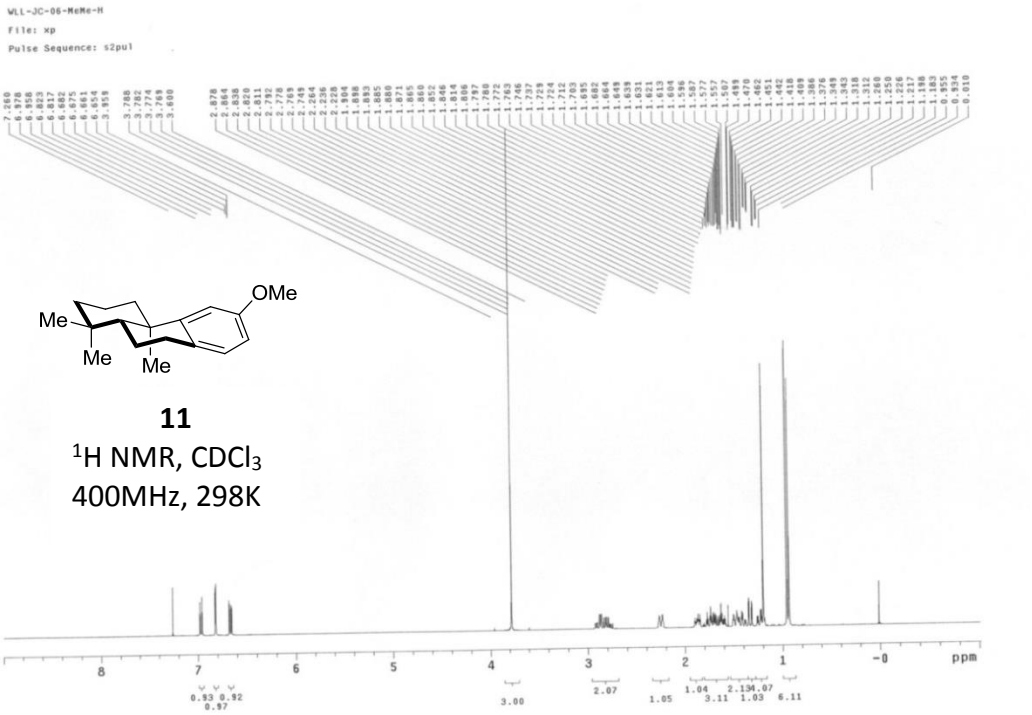
C	3.00394400	-2.48763500	-1.66914700
C	2.70267500	-2.50193400	-0.15014300
C	2.21064500	-1.07324700	0.28044500
C	3.05361900	0.16220400	-0.20633600
C	3.33900400	0.01350700	-1.72070400
C	3.92994000	-1.34847100	-2.10164600
C	1.89452400	-0.95336200	1.78052100
C	1.26773500	0.37723700	2.11011300
C	1.55688300	-3.51568000	0.08055400
C	4.39505400	0.35336300	0.55171400
C	3.93328000	-3.02571800	0.62401500
H	3.42558000	-3.45911700	-1.96251600
H	2.05262700	-2.38722200	-2.21320200
H	1.24531500	-0.95744800	-0.23375800
H	4.01760600	0.80888900	-2.05206100
H	2.39909700	0.15506100	-2.27235300
H	4.08043500	-1.38635800	-3.18839200
H	4.92540700	-1.47401200	-1.65603700
H	1.22537300	-1.76211400	2.09171500
H	2.80880200	-1.07877900	2.38086900
H	0.89044200	0.50666500	3.12262100
H	1.37194700	-3.70096100	1.14444400
H	1.81063400	-4.48039900	-0.37634400
H	0.61840500	-3.16835200	-0.36822600
H	4.88039300	1.26962200	0.19706800
H	5.09181600	-0.47338700	0.39422100
H	4.24203500	0.46406900	1.62960200
H	4.84923600	-2.47073800	0.40696300
H	3.77543300	-2.99447400	1.70756100
H	4.11833600	-4.07291300	0.35323600
C	2.24038200	2.51083200	-0.73923900
C	-1.03604300	-0.16445900	1.61547500
C	-1.45906100	0.10300900	0.39884800
Sn	-3.44444600	-0.37081700	-0.40257500
C	-3.86858200	-2.50521300	-0.20757400
C	-4.99453800	0.76298500	0.64038300
C	-3.42368300	0.18277400	-2.51235300
H	2.79900900	2.50038800	-1.66973900
H	-0.78767800	0.60338300	-0.30316500
H	-3.07842900	-3.09769400	-0.67891300
H	-4.81890400	-2.75002200	-0.69336500
H	-3.93610400	-2.80006100	0.84432200
H	-4.80003500	1.83722600	0.56566200
H	-5.97704500	0.55911800	0.20195700
H	-5.02955500	0.49414400	1.70072400
H	-4.40932600	0.02920500	-2.96352100
H	-2.69674500	-0.42209400	-3.06333600
H	-3.15195500	1.23621700	-2.63204100
C	0.95388700	2.84250900	1.78181600
H	1.75046400	3.42471000	2.27341100
H	0.16079700	2.70579700	2.52539700
C	2.22502100	1.43376000	0.08623000
C	1.49927600	1.49641500	1.35373300
C	0.42851200	3.63964500	0.57983100
H	0.04964800	4.62048400	0.89923700
C	1.53662600	3.81021500	-0.46139000
H	2.28069800	4.53192400	-0.07083400
O	1.03716100	4.29448800	-1.71347200
H	0.65781700	5.17266600	-1.55098700
H	-0.40187700	3.10077200	0.10910300

C	-1.59999400	-0.78586000	2.83728800
H	-2.61563700	-1.18248400	2.67291900
H	-0.97609100	-1.61747900	3.18997200
H	-1.65761100	-0.06054100	3.65971700

INT-C7

C	2.71504000	-2.75074600	-1.59592300
C	2.30113900	-2.72689800	-0.10254600
C	1.92662800	-1.25249800	0.28324200
C	2.94934700	-0.12733500	-0.09848100
C	3.28122700	-0.27952900	-1.60768800
C	3.75354600	-1.69219300	-1.97793100
C	1.45706000	-1.06549000	1.73200000
C	0.61921400	0.23186800	1.86269700
C	1.04228200	-3.61681400	0.02995200
C	4.27200700	-0.14188200	0.71411300
C	3.39920800	-3.36474200	0.77655500
H	3.07917600	-3.75475800	-1.85493000
H	1.81402200	-2.58451600	-2.20548400
H	1.04867900	-1.04028500	-0.34563700
H	4.04775100	0.44415300	-1.90651900
H	2.38231100	-0.03749200	-2.19197500
H	3.94320300	-1.73822200	-3.05826600
H	4.71566300	-1.91000200	-1.49666700
H	0.85689100	-1.91809100	2.06339300
H	2.31337700	-1.01260700	2.41384100
H	0.61881700	0.51945300	2.92881300
H	0.75886700	-3.78945600	1.07391900
H	1.23094900	-4.59975500	-0.41940100
H	0.18082300	-3.17287500	-0.48353000
H	4.86383700	0.74350900	0.45771500
H	4.88915300	-1.01836300	0.50678100
H	4.09319600	-0.10531800	1.79324600
H	4.39154100	-2.94286100	0.60366600
H	3.17344300	-3.25621700	1.84366900
H	3.46429600	-4.43946800	0.56480600
C	2.82239100	2.38561200	-0.42734500
C	-0.85731600	-0.04311300	1.50778600
C	-1.37953800	0.22248700	0.29679900
Sn	-3.39046800	-0.13085500	-0.42596700
C	-3.88960300	-2.25776600	-0.39380200
C	-4.86659000	0.96452600	0.75564300
C	-3.43820900	0.58766300	-2.48297400
H	3.66644300	2.31500600	-1.10468800
H	-0.70940600	0.69066200	-0.42707700
H	-3.15902700	-2.83235200	-0.97180900
H	-4.87974900	-2.42231500	-0.83119300
H	-3.89812600	-2.64800900	0.62866400
H	-4.64645400	2.03660300	0.74702300
H	-5.87013800	0.81704400	0.34338300
H	-4.87050400	0.62468800	1.79595900
H	-4.42881300	0.43895800	-2.92454400
H	-2.70756800	0.05243600	-3.09792100
H	-3.20267200	1.65587800	-2.52669900
C	0.66645400	2.74918600	1.40557300
H	1.15521000	3.14130000	2.31526400
H	-0.39801700	2.66235100	1.65267500
C	2.28766400	1.24759100	0.18455000
C	1.22899300	1.37895000	1.09358600
C	0.85660300	3.74624000	0.25708900
H	0.52164300	4.74961400	0.55404700
C	2.32416200	3.77474100	-0.17506800
H	2.92145800	4.22819200	0.64232800
O	2.52810800	4.52986300	-1.37291700
H	2.28208200	5.44828200	-1.17961200
H	0.25761500	3.43966800	-0.60920700
C	-1.64752300	-0.64824500	2.64657900
H	-2.64271400	-0.98107600	2.33730600
H	-1.12931100	-1.51123900	3.08516600
H	-1.77453100	0.08163300	3.45873200

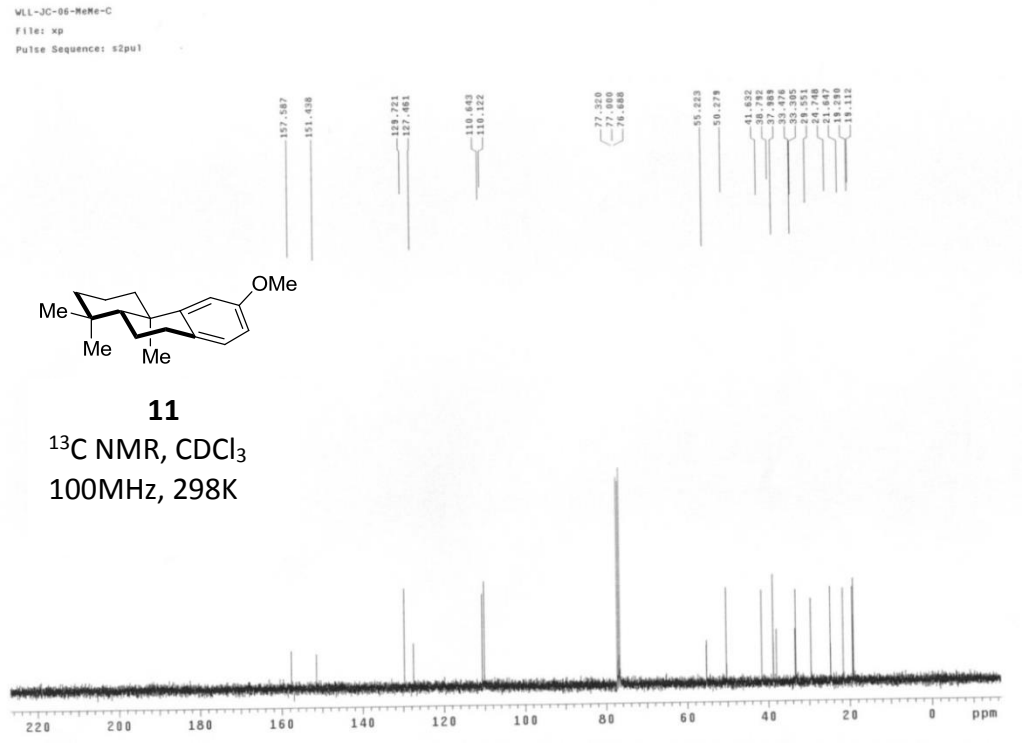
f) NMR spectra



11

^{1}H NMR, $CDCl_3$

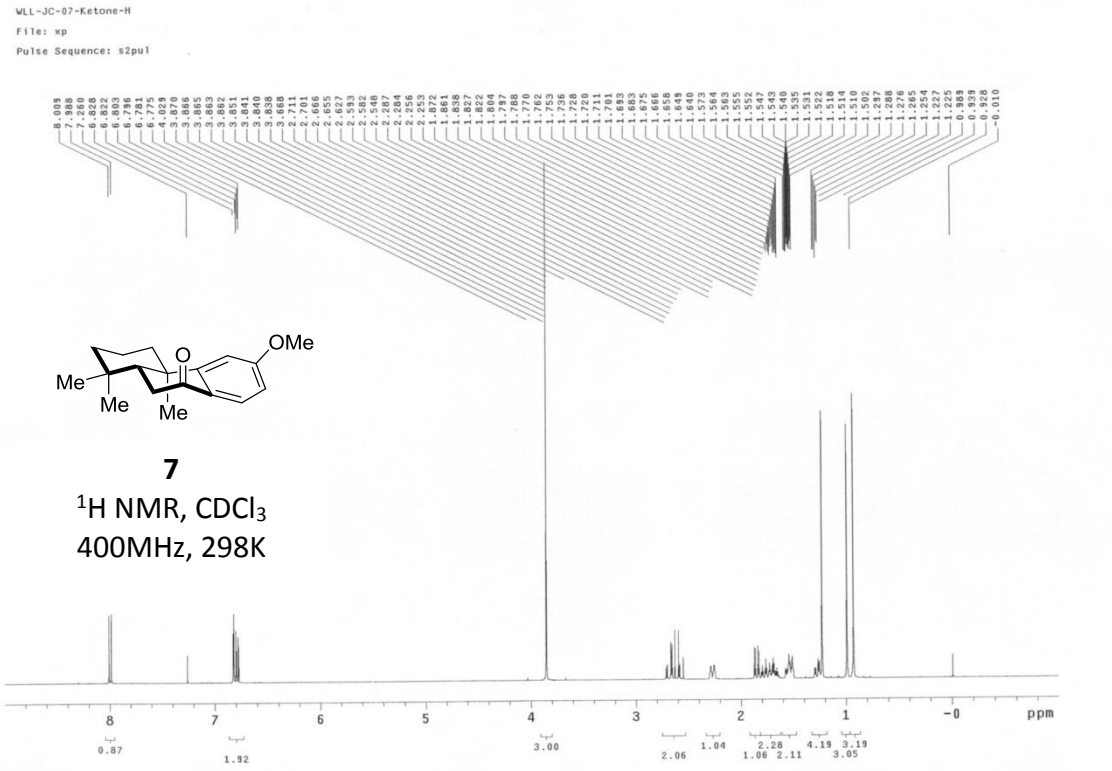
400MHz, 298K



11

^{13}C NMR, $CDCl_3$

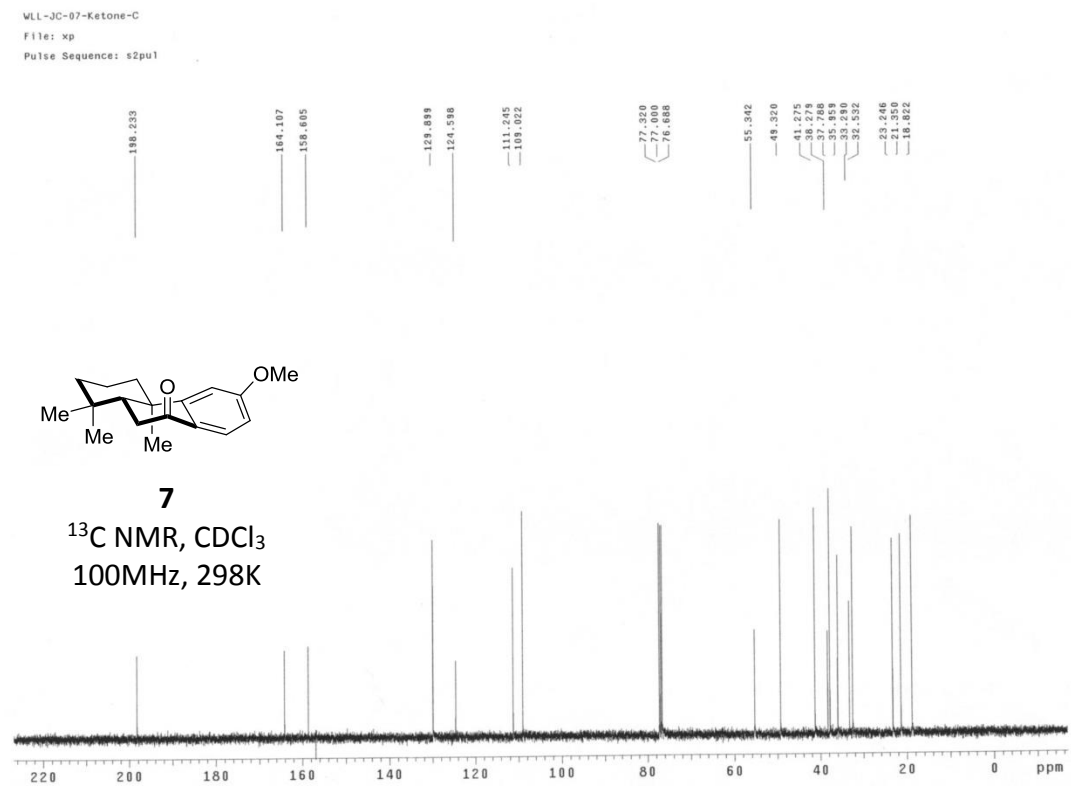
100MHz, 298K



7

^{1}H NMR, $CDCl_3$

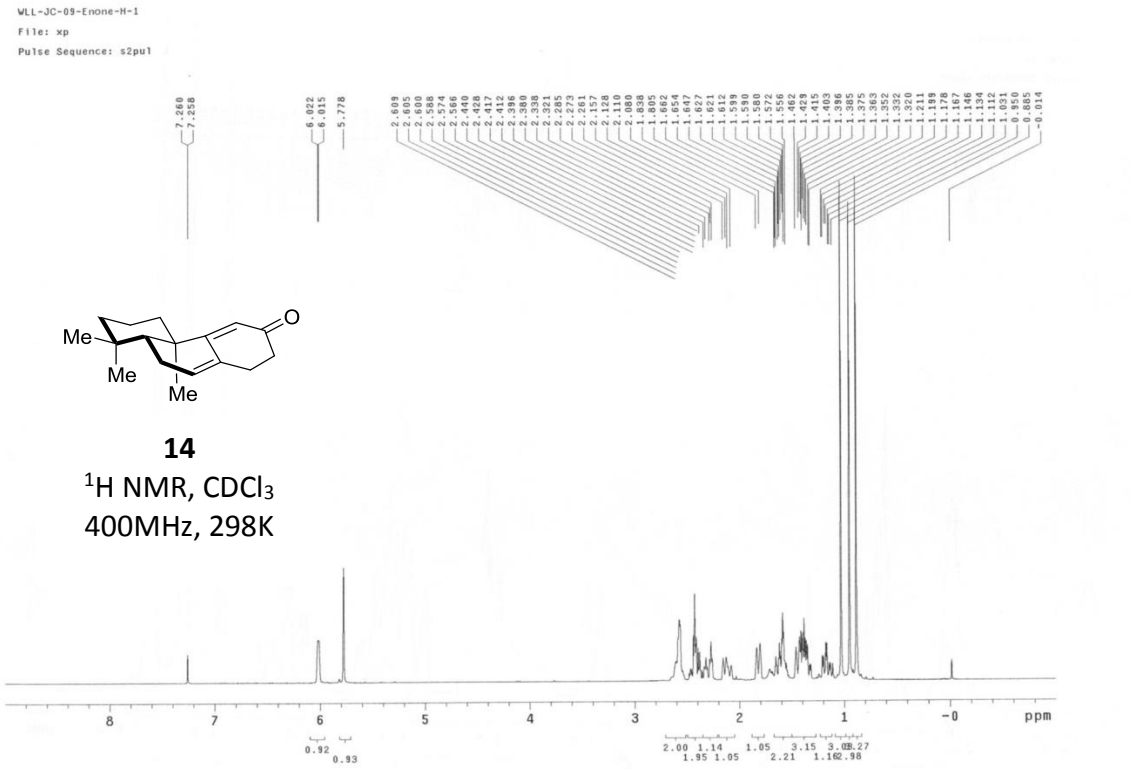
400MHz, 298K



7

^{13}C NMR, $CDCl_3$

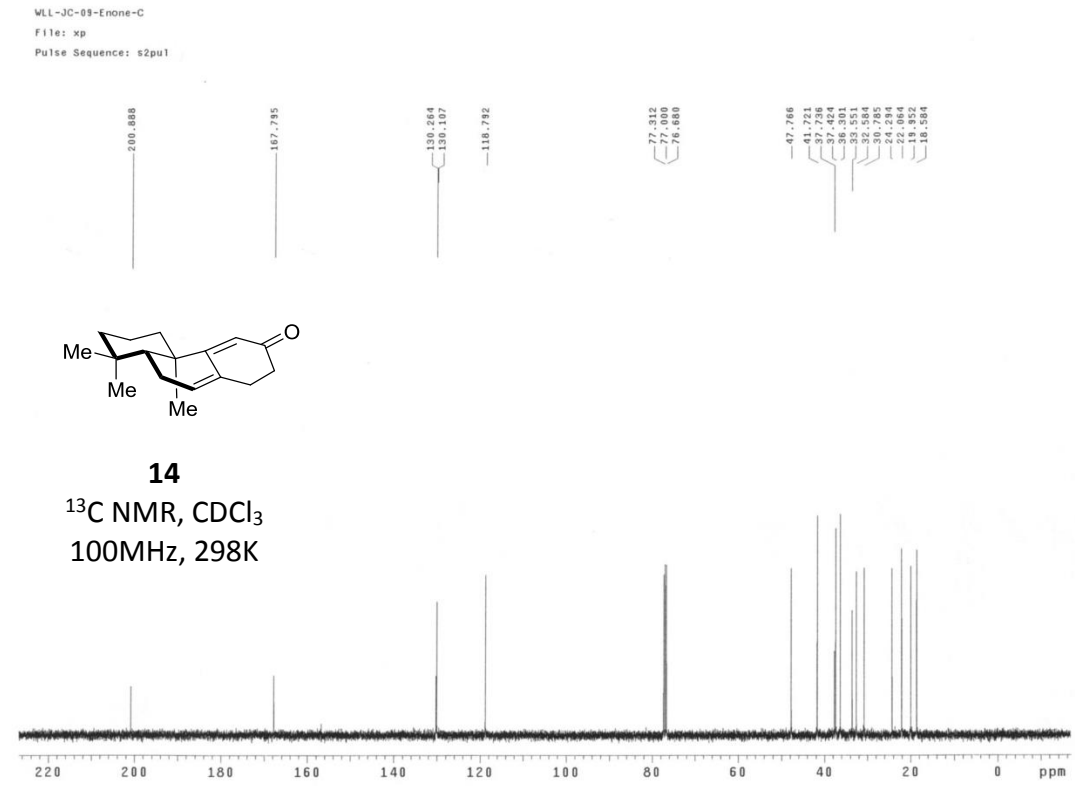
100MHz, 298K



14

^{1}H NMR, $CDCl_3$

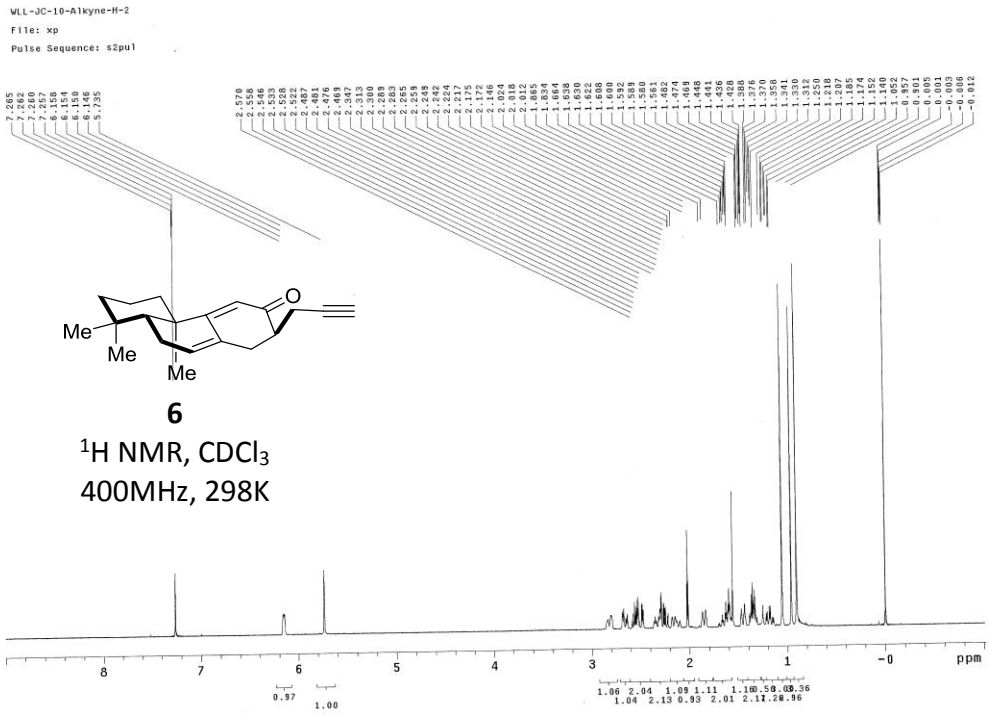
400MHz, 298K



14

^{13}C NMR, $CDCl_3$

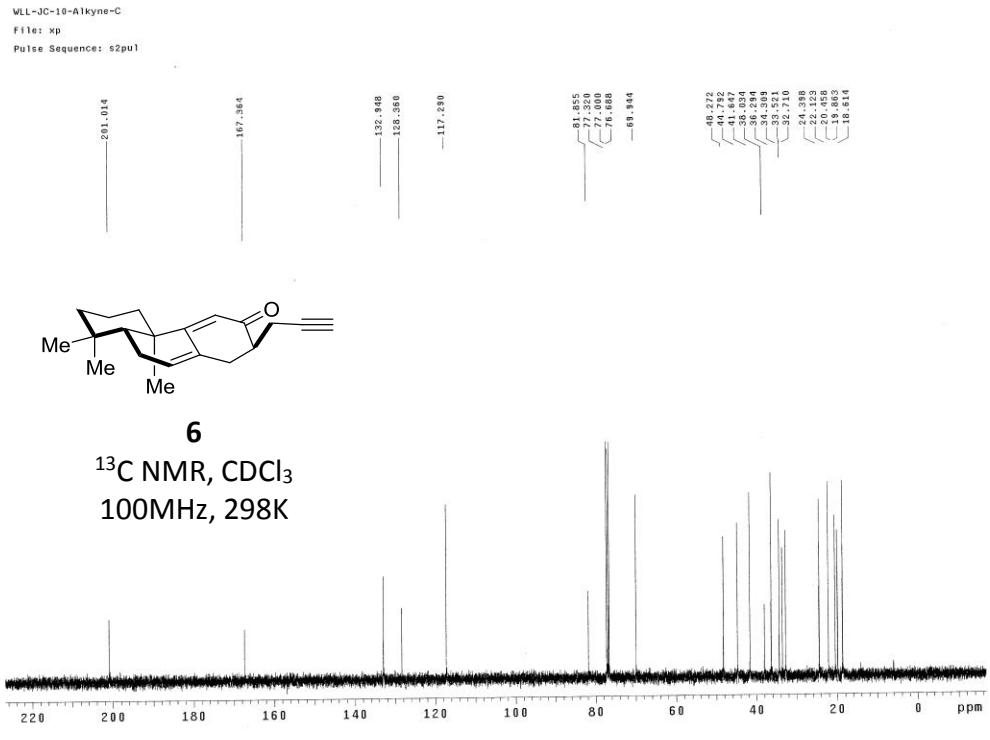
100MHz, 298K



6

^{1}H NMR, $CDCl_3$

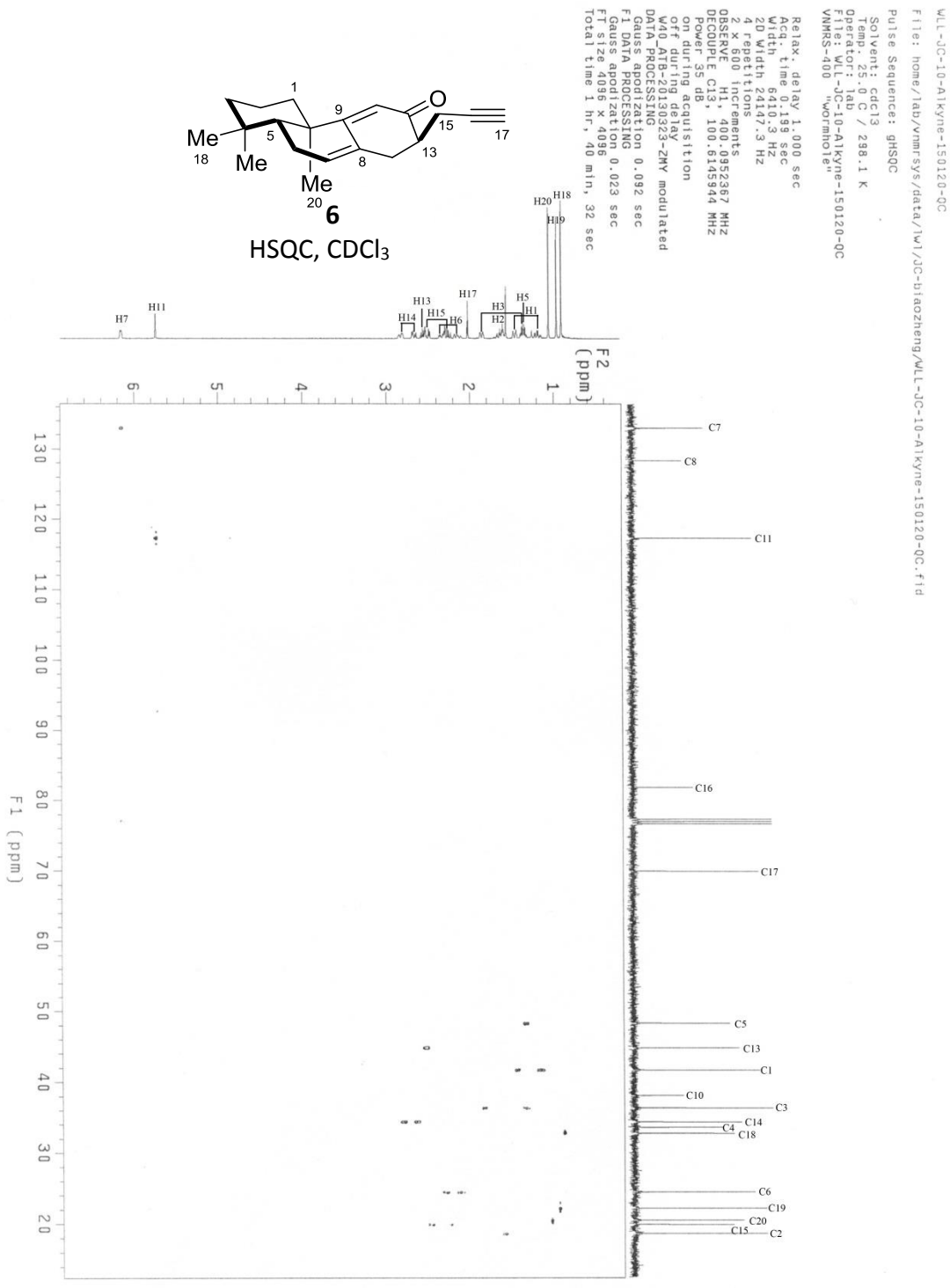
400MHz, 298K



6

^{13}C NMR, $CDCl_3$

100MHz, 298K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Operator: lab
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Acq. time 0.199 sec
Width 6410.3 Hz
2D width 24147.3 Hz
2 repetitions
256 increments
OBSERVE H1, 400.0852367 MHz
DECOUPLE C13, 100.6145944 MHz
Power 55 dB
continuously on during acquisition
off during delay
W40_ATB-20190323-ZMY modulated
DATA PROCESSING
Gauss apodization 0.092 sec
F1 DATA PROCESSING
Gauss apodization 0.023 sec
FT size 4096 x 4096
Total time 1 hr, 40 min, 32 sec
Me
Me
Me
O
1
5
8
9
13
15
17
18
20
6
HSQC, CDCl3
H7
H11
H14
H13
H15
H6
H17
H3
H2
H5
H1
H20
H18
H19
F2 (ppm)
F1 (ppm)
C7
C8
C11
C16
C17
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C13
C1
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C3
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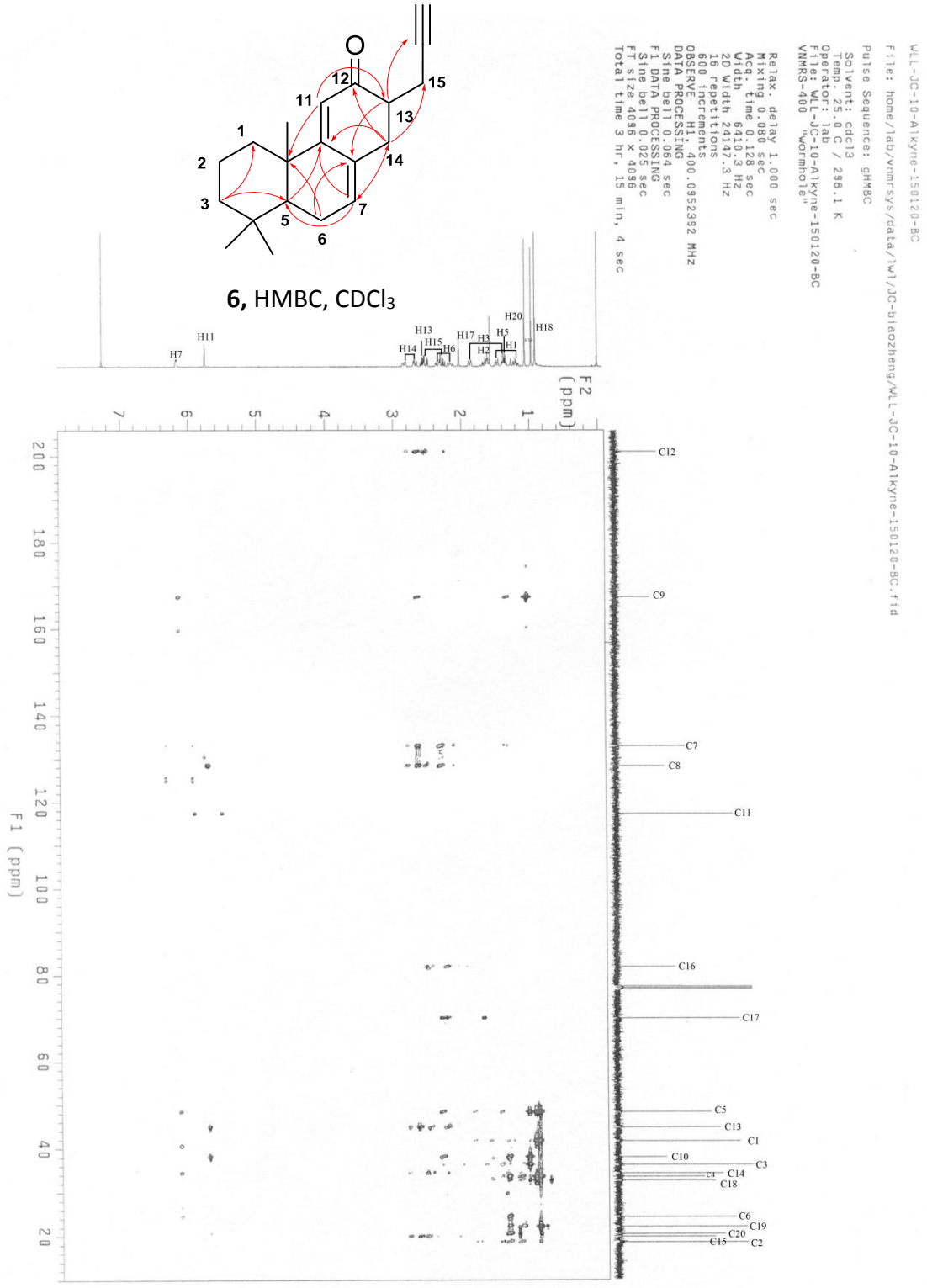
C19
C20
C15
C2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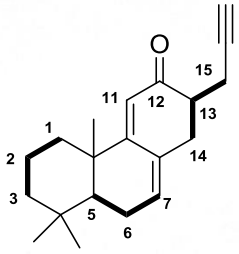
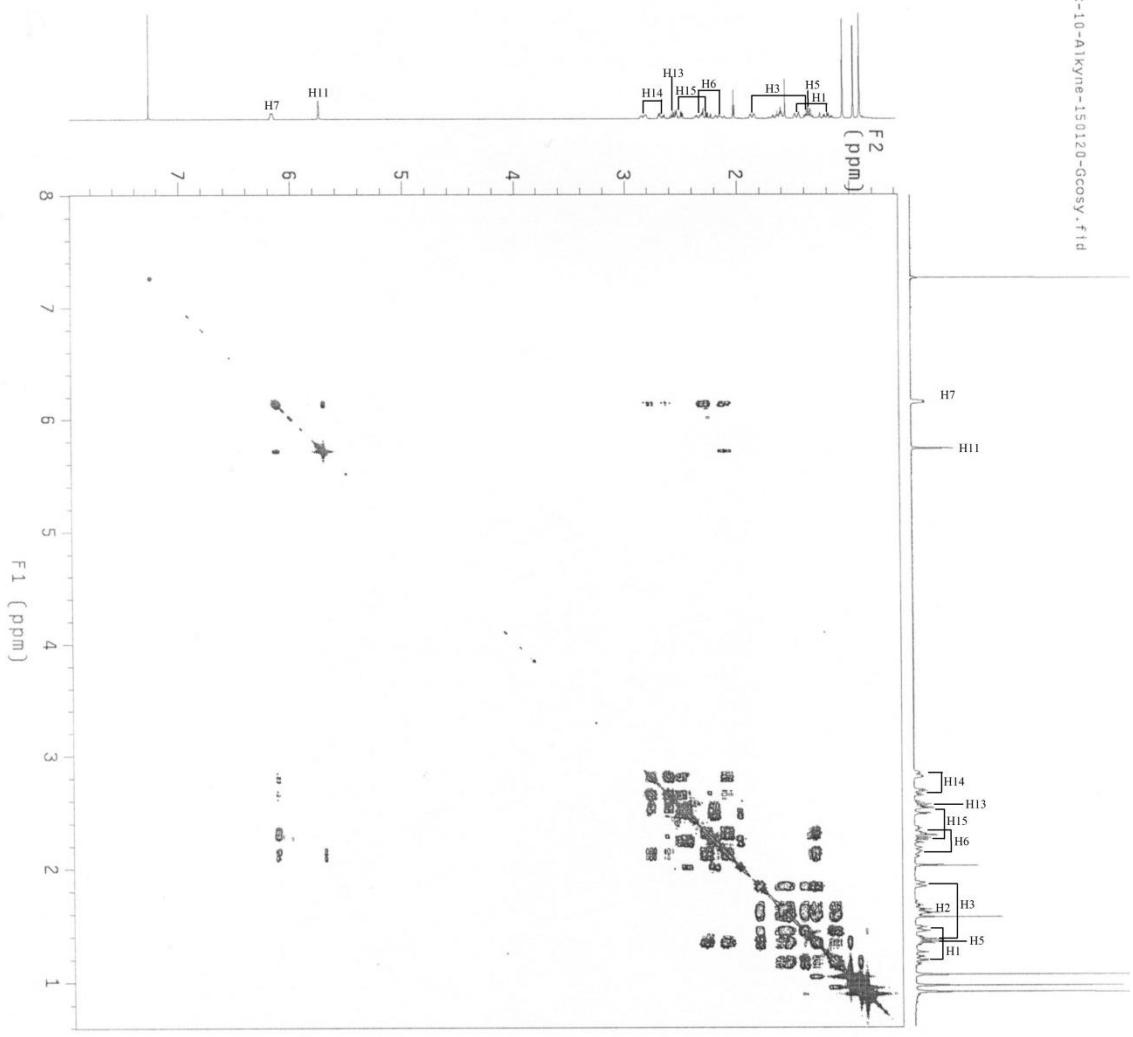
File: home/lab/vnmrsys/data/lwl/JC-biaozheng/WLL-JC-10-Alkyne-150120-BC.fid
Pulse Sequence: gHMBC
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: lab
File: WLL-JC-10-Alkyne-150120-BC
VNMRS-400 "wormhole"
Relax. delay 1.000 sec
Mixing 0.080 sec
Acq. time 0.128 sec
Width 6410.3 Hz
2D Width 24147.3 Hz
16 repetitions
600 increments
OBSERVE H1 400.0952392 MHz
DATA PROCESSING
FT size 16384 x 1024
Total time 3 hr, 15 min, 4 sec
F2 (ppm)
F1 (ppm)
O
1
2
3
5
6
7
11
12
13
14
15
H7
H11
H13
H14
H15
H6
H17
H3
H2
H5
H1
H20
H18
C12
C9
C7
C8
C11
C16
C17
C5
C13
C1
C10
C3
C4
C14
C18
C6
C19
C20
C15
C2

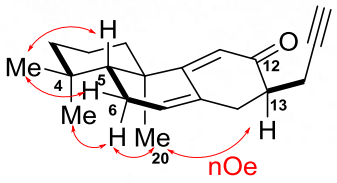
6, HMBC, $CDCl_3$



6

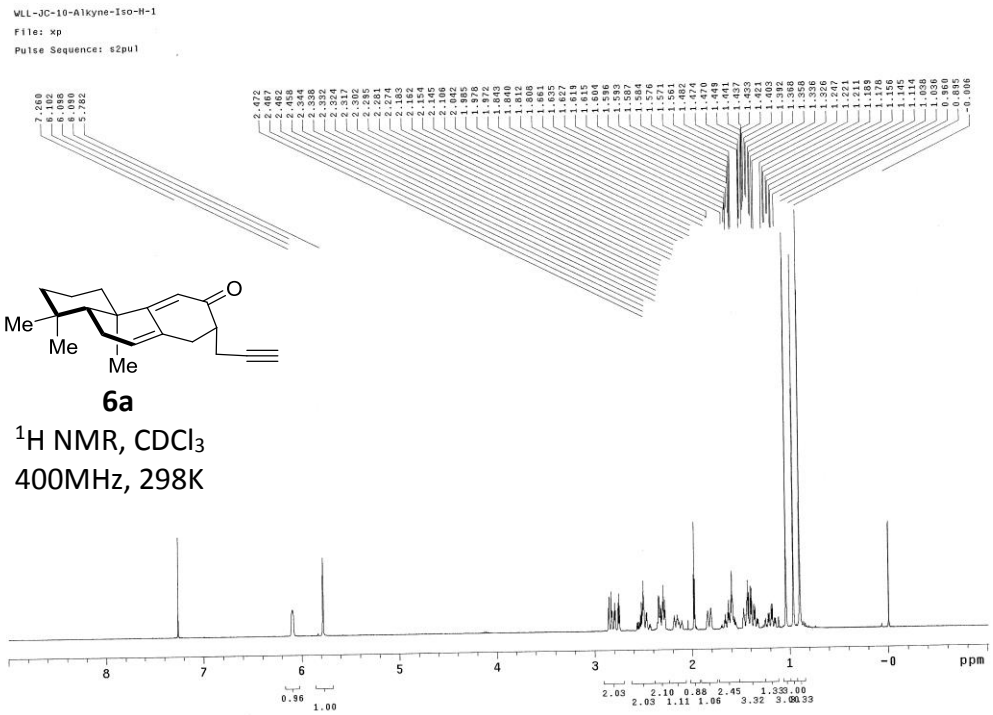
^{1}H-^{1}H COSY, $CDCl_3$





6

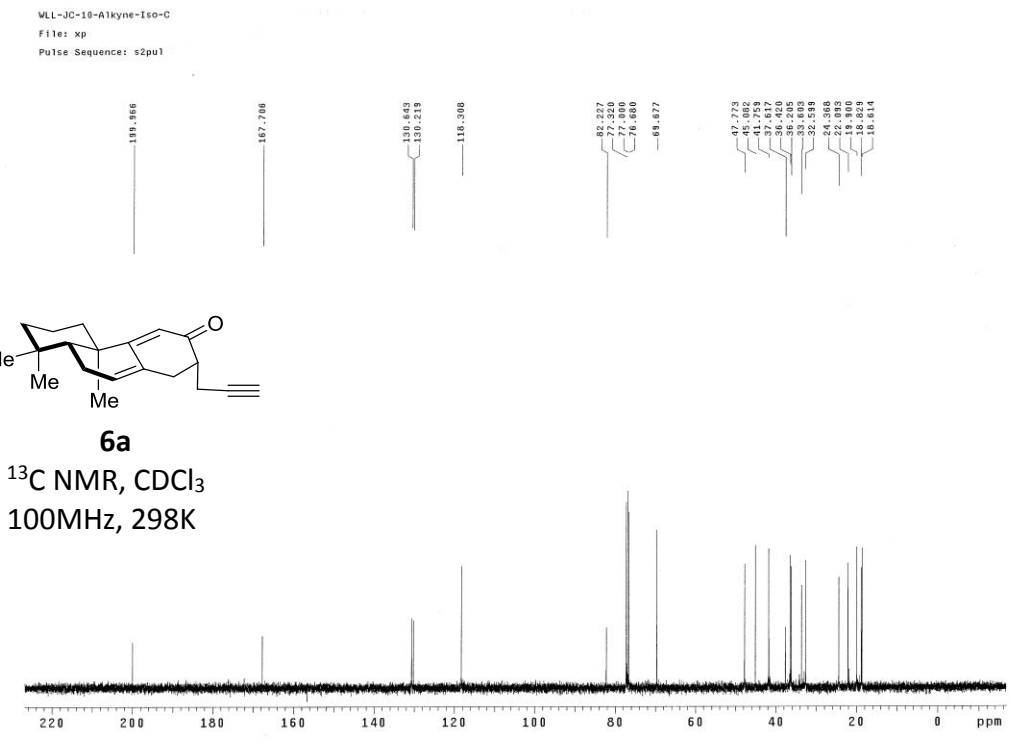
NOESY, $CDCl_3$



6a

^{1}H NMR, $CDCl_3$

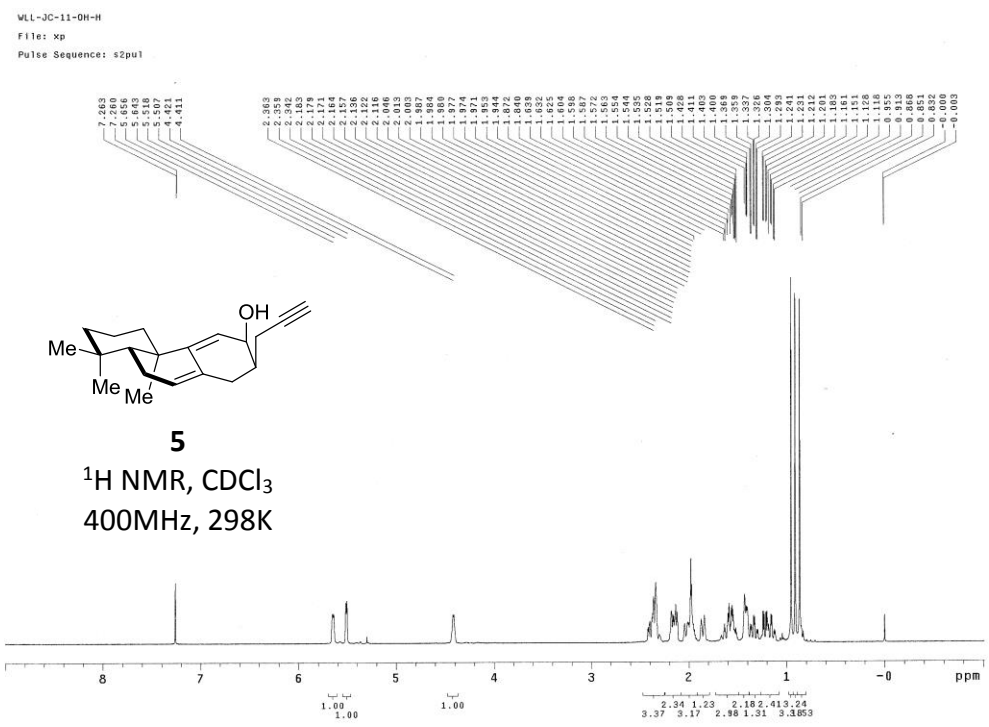
400MHz, 298K



6a

^{13}C NMR, $CDCl_3$

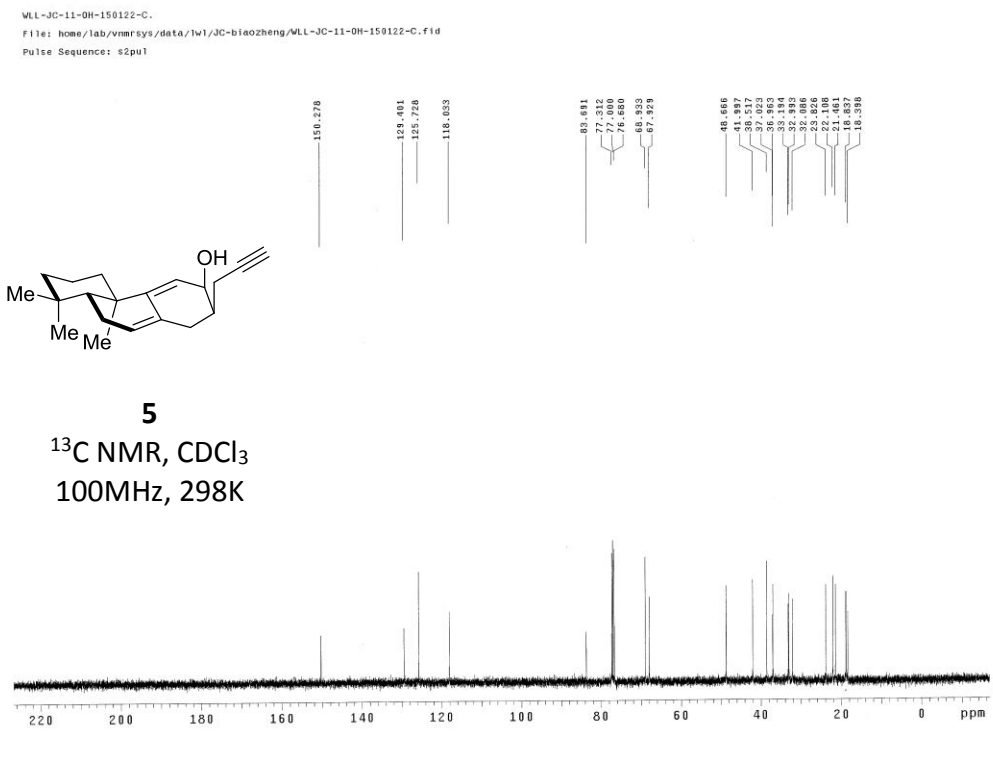
100MHz, 298K



5

^{1}H NMR, $CDCl_3$

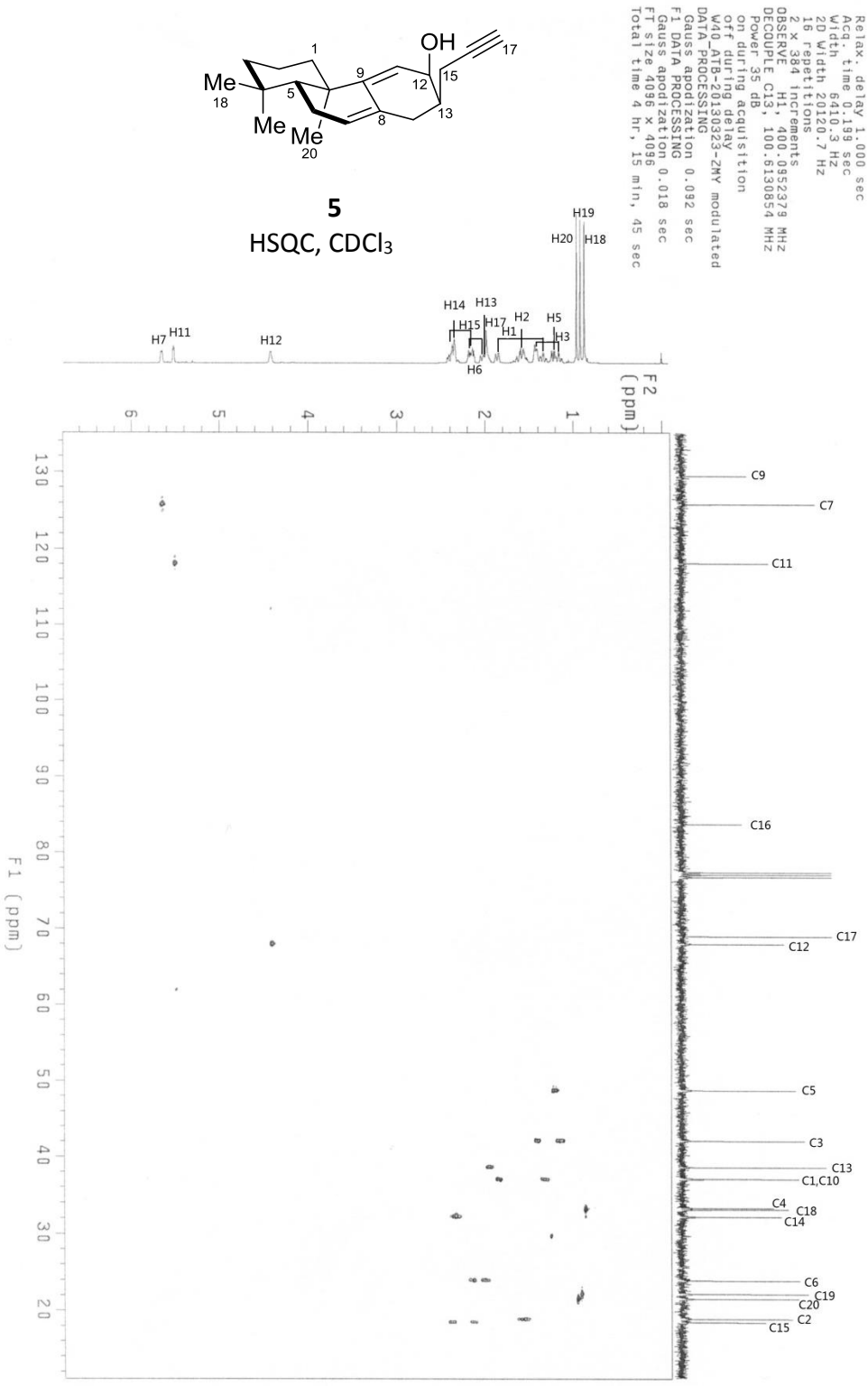
400MHz, 298K

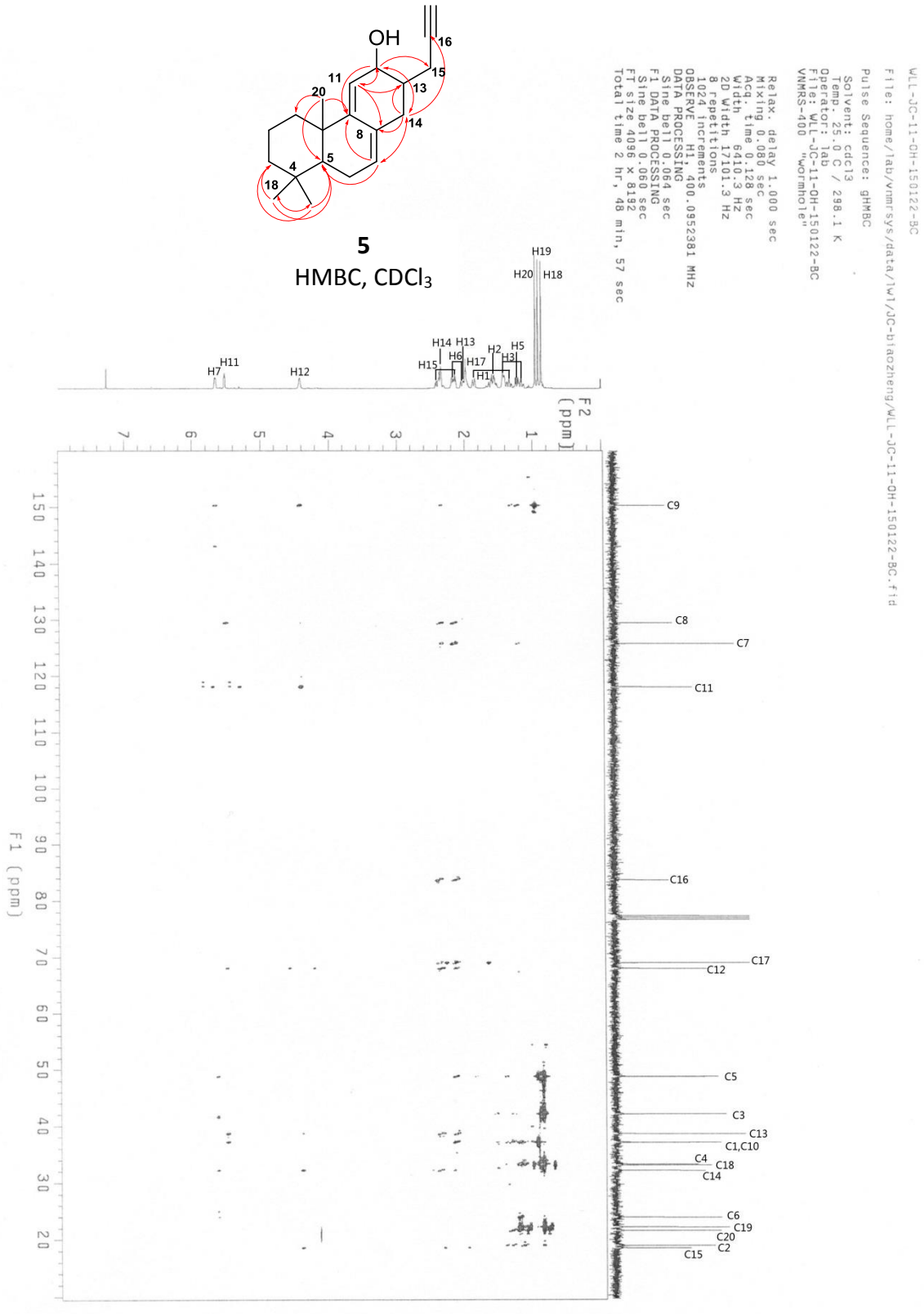


5

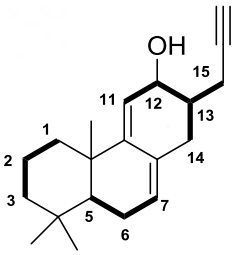
^{13}C NMR, $CDCl_3$

100MHz, 298K


OH
Me
Me
Me
1
5
8
9
12
13
15
17
18
20
5
HSQC, CDCl3
H19
H20
H18
H14
H13
H15
H17
H2
H5
H1
H3
H7
H11
H12
H6
F2 (ppm)
F1 (ppm)
C9
C7
C11
C16
C17
C12
C5
C3
C13
C1,C10
C4
C18
C14
C6
C19
C20
C2
C15

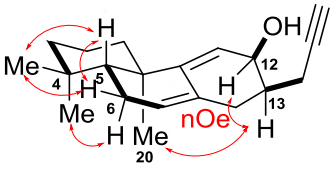

OH
16
15
13
14
11
20
8
5
4
18
5
HMBC, CDCl3
H19
H20
H18
H14 H13
H2
H5
H6
H17
H3
H15
H1
H7
H11
H12
F2 (ppm)
F1 (ppm)
C9
C8
C7
C11
C16
C17
C12
C5
C3
C13
C1,C10
C4
C18
C14
C6
C19
C20
C2
C15
WLL-JC-11-OH-150122-BC
File: home/lab/vnmrsys/data/lwl/JC-biaozheng/WLL-JC-11-OH-150122-BC.fid
Pulse Sequence: gHMBC
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: lab
Files: WLL-JC-11-OH-150122-BC
VNMRS-400 "wormhole"
Relax. delay 1.000 sec
Mixing 0.080 sec
Acq. time 0.128 sec
Width 6410.3 Hz
2D Width 17101.3 Hz
8 repetitions
1024 increments
OBSERVE H1, 400.0952381 MHz
DATA PROCESSING
Sine bell 0.064 sec
F1 DATA PROCESSING
Sine bell 0.060 sec
FT size 4096 x 8192
Total time 2 hr, 48 min, 57 sec

5



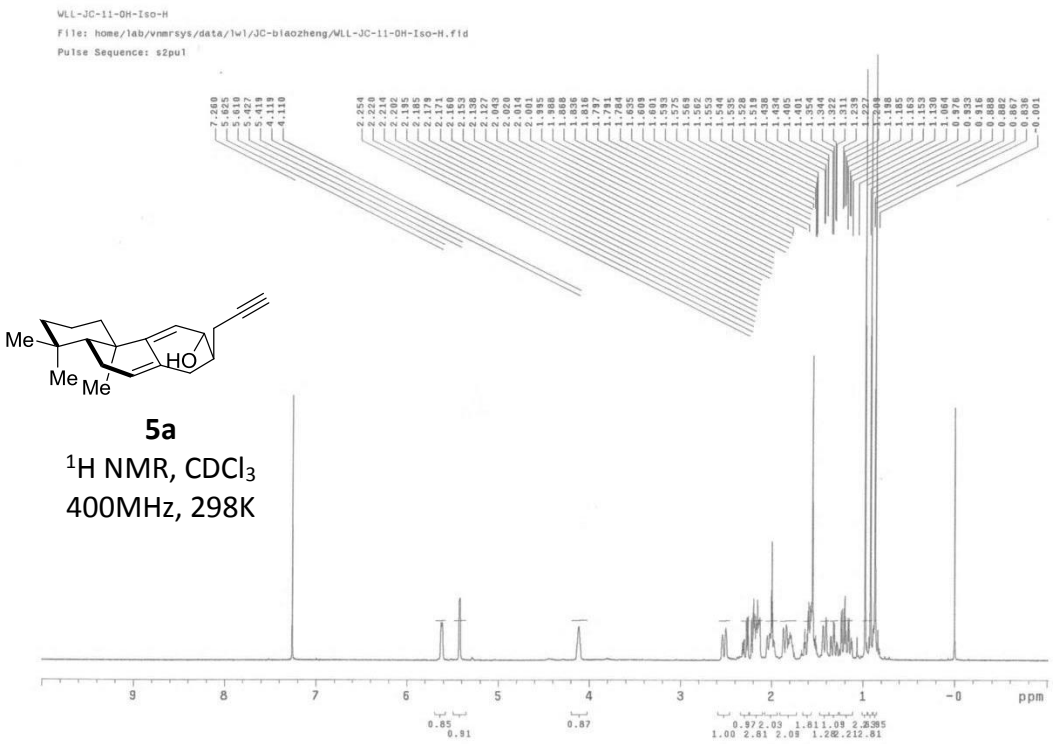
5

^{1}H-$^{1}HCOSY$, $CDCl_3$



5

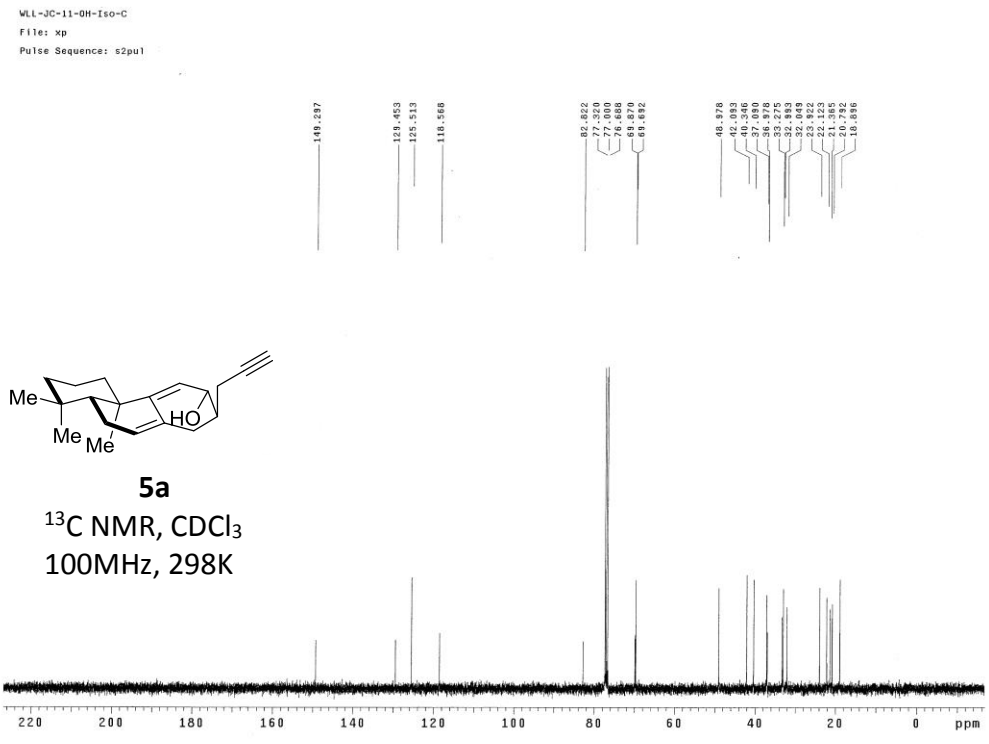
NOESY, $CDCl_3$



5a

^{1}H NMR, $CDCl_3$

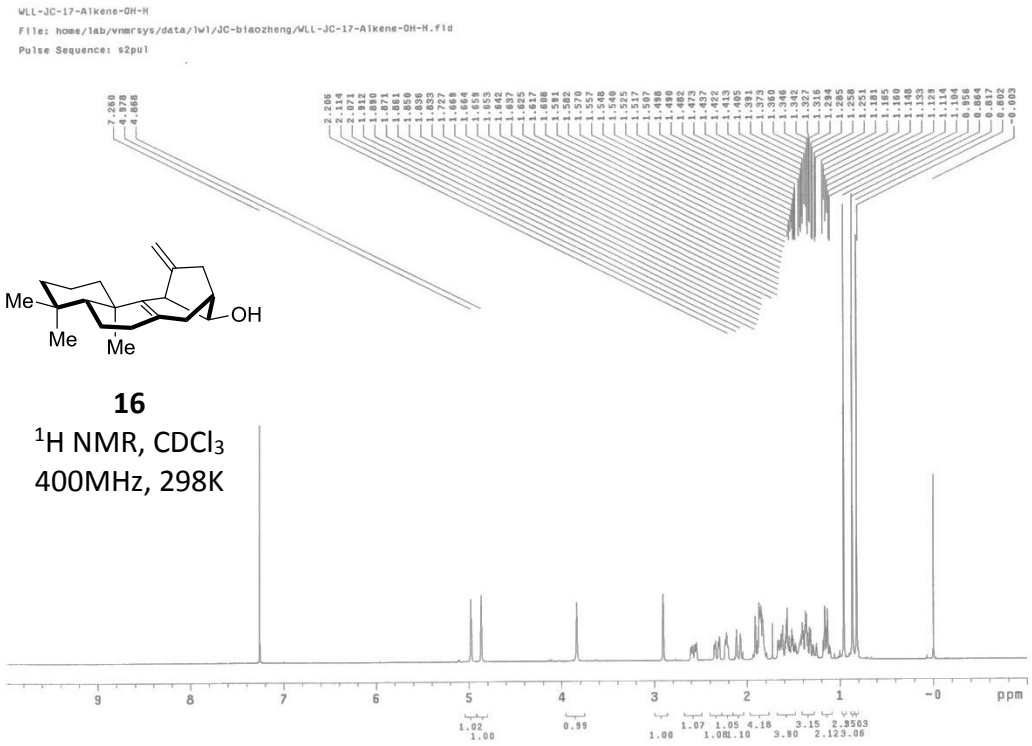
400MHz, 298K



5a

^{13}C NMR, $CDCl_3$

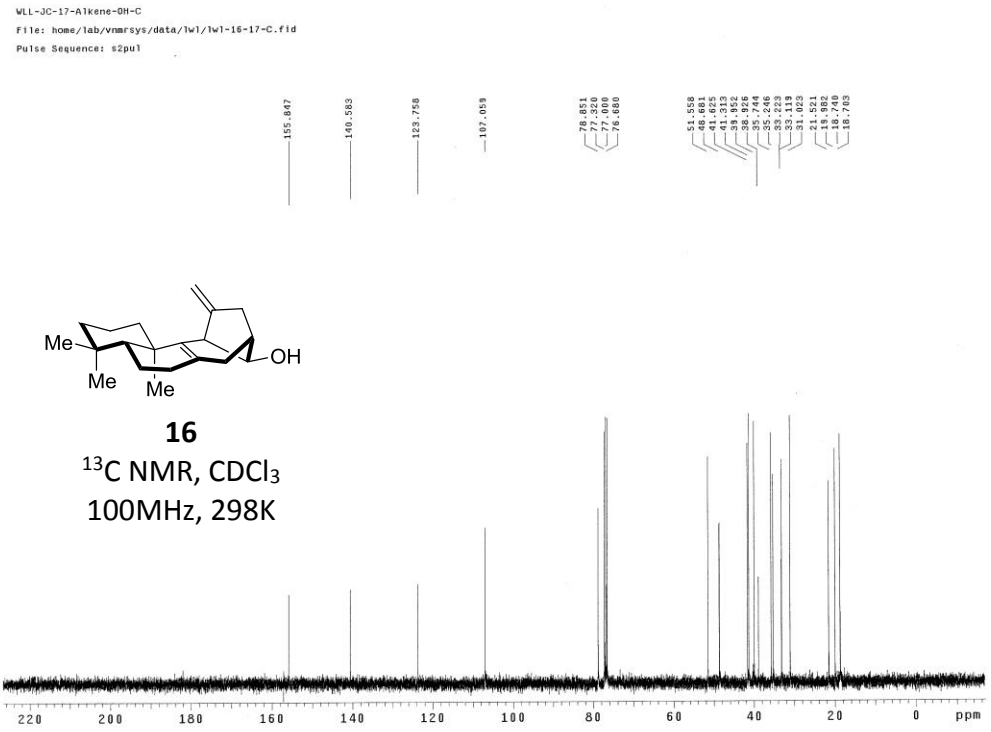
100MHz, 298K



16

^{1}H NMR, $CDCl_3$

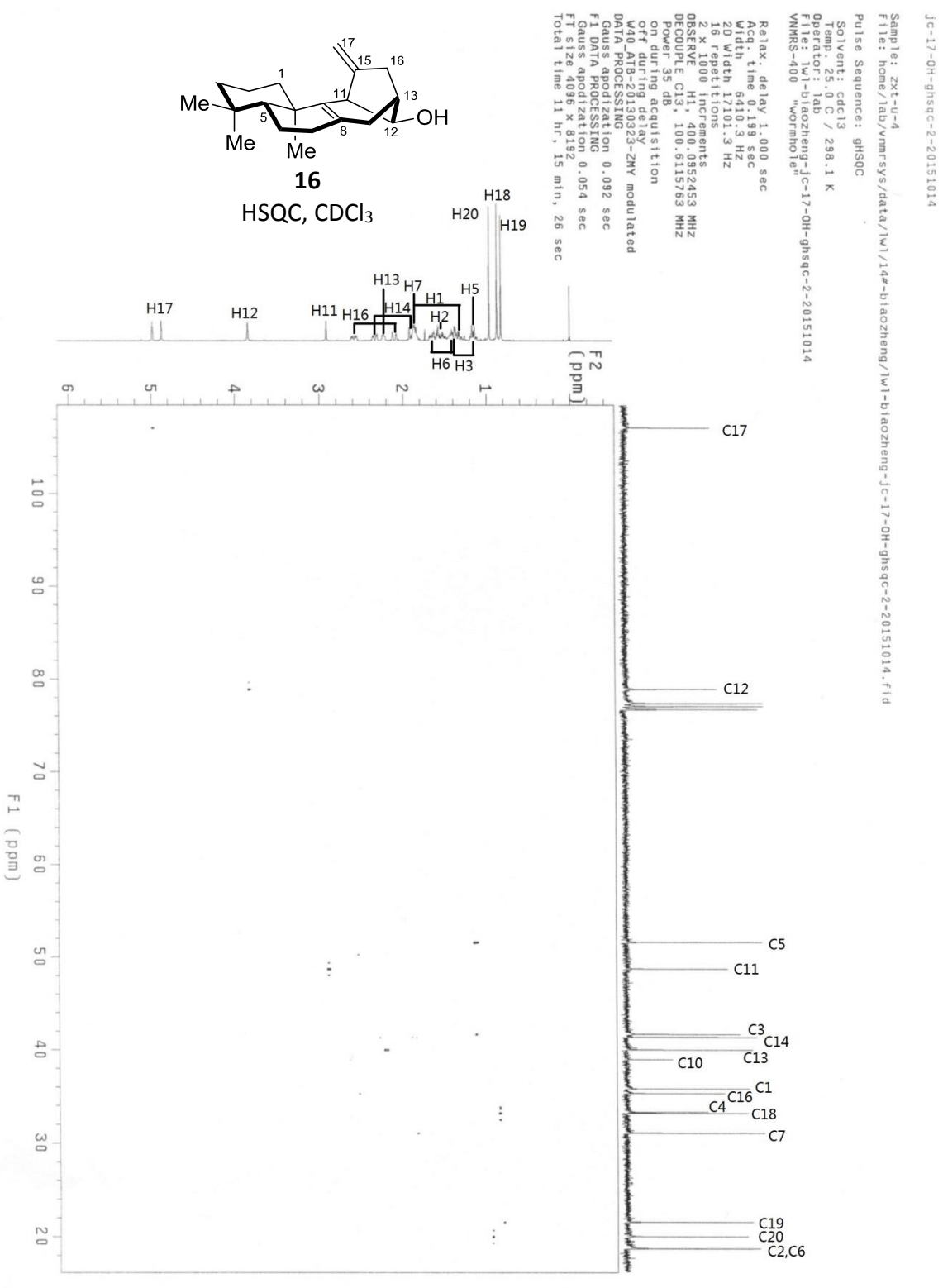
400MHz, 298K

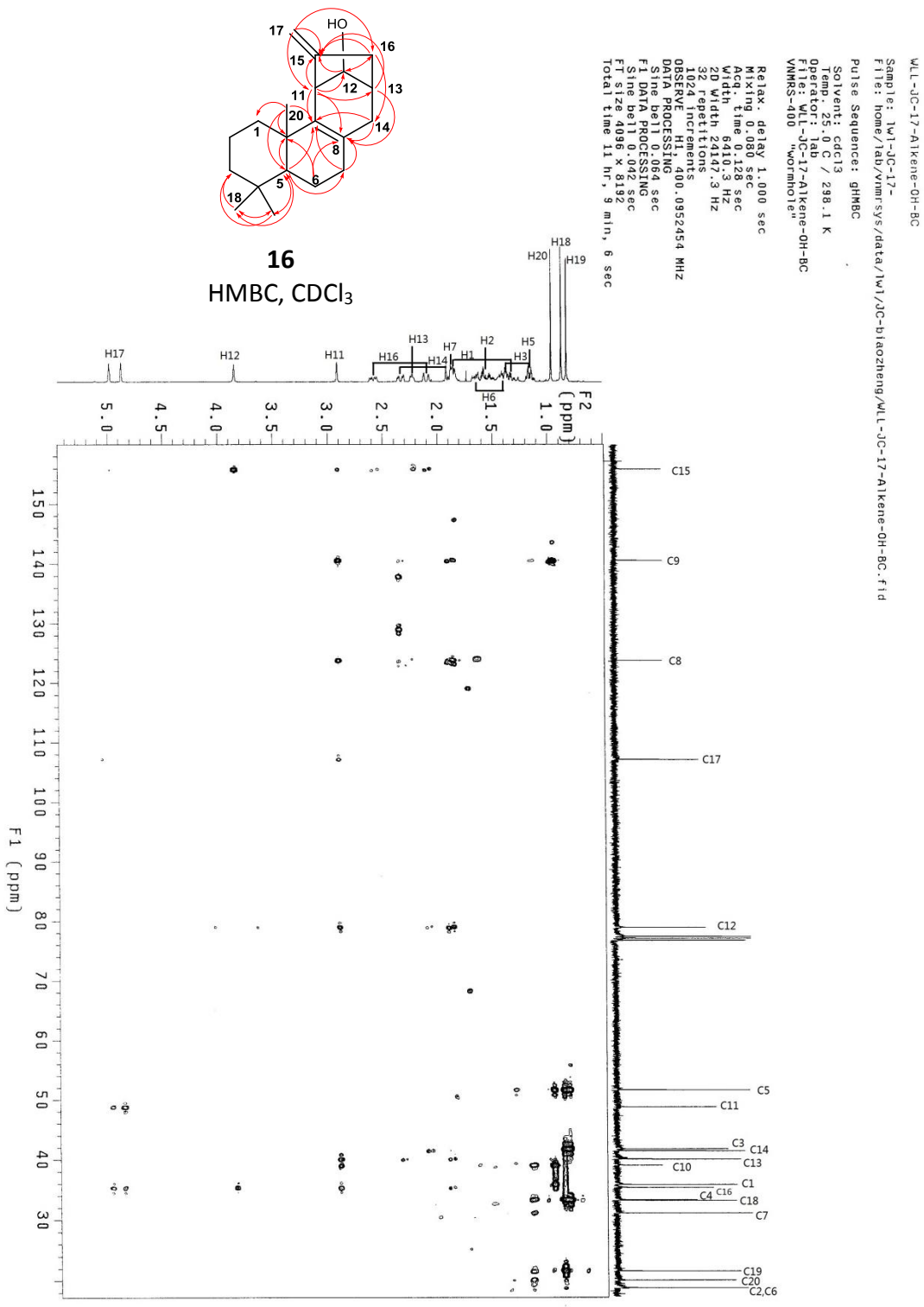


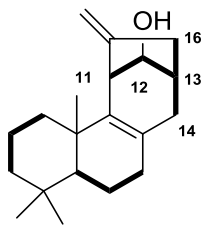
16

^{13}C NMR, $CDCl_3$

100MHz, 298K

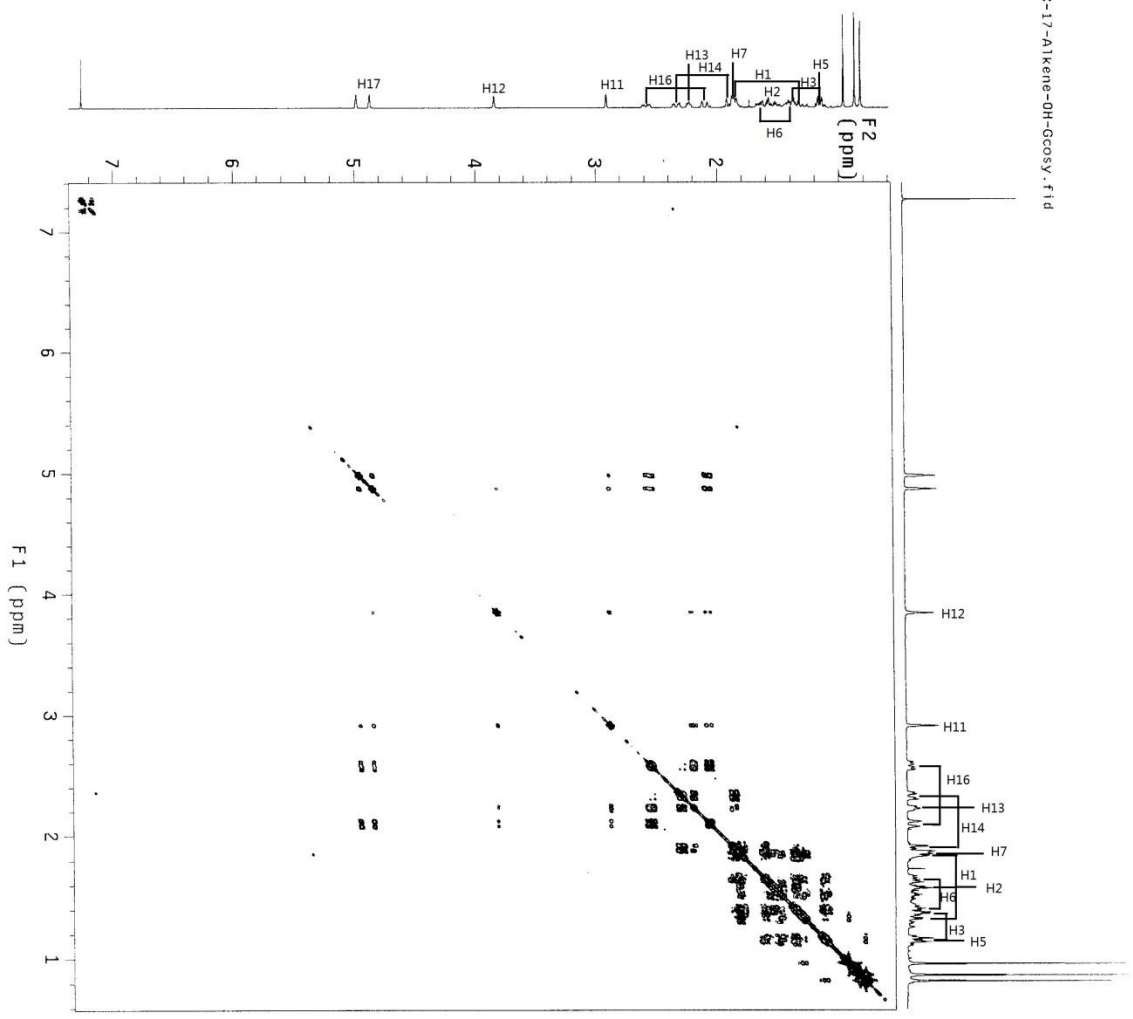

jc-17-OH-ghsqc-2-20151014
Sample: zxt-u-4
File: home/lab/vnmrsys/data/lwl/14#-biaozheng/lwl-biaozheng-jc-17-OH-ghsqc-2-20151014.fid
Pulse Sequence: gHSQC
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: lab
File: lwl-biaozheng-jc-17-OH-ghsqc-2-20151014
VNMRS-400 "wormhole"
Relax. delay 1.000 sec
Acq. time 0.193 sec
Width 6410.3 Hz
2D Width 17101.3 Hz
16 repetitions
2 x 1000 increments
OBSERVE H1, 400.0952453 MHz
DECOUPLE C13, 100.6115763 MHz
Power 35 dB
on during acquisition
off during delay
W40_ATB-20130323-2MY modulated
DATA PROCESSING
Gauss apodization 0.092 sec
F1 DATA PROCESSING
Gauss apodization 0.054 sec
FT size 4096 x 8192
Total time 11 hr, 15 min, 26 sec
Me
Me
Me
OH
16
HSQC, CDCl3
H18
H20
H19
H13
H7
H1
H5
H17
H12
H11
H16
H14
H2
H6
H3
F2 (ppm)
F1 (ppm)
C17
C12
C5
C11
C3
C14
C13
C10
C1
C16
C4
C18
C7
C19
C20
C2,C6

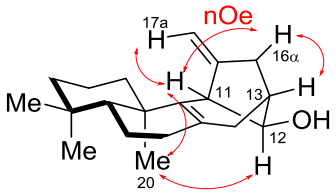

16
HMBC, CDCl3
WLL-JC-17-Alkene-OH-BC
Sample: lwl-JC-17-
File: home/lab/vnmrsys/data/lwl/JC-biaozheng/WLL-JC-17-Alkene-OH-BC.fid
Pulse Sequence: gHMBC
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: lab
File: WLL-JC-17-Alkene-OH-BC
VNMRS-400 "wormhole"
Relax. delay 1.000 sec
Mixing 0.080 sec
Acq. time 0.128 sec
Width 6410.3 Hz
2D Width 24147.3 Hz
32 repetitions
1024 increments
OBSERVE H1, 400.0952454 MHz
DATA PROCESSING
Sine bell 0.064 sec
F1 DATA PROCESSING
Sine bell 0.042 sec
FT size 4096 x 8192
Total time 11 hr, 9 min, 6 sec
F2 (ppm)
F1 (ppm)
H17
H12
H11
H16
H13
H14
H7
H1
H2
H3
H5
H6
H18
H20
H19
C15
C9
C8
C17
C12
C5
C11
C3
C14
C13
C10
C1
C4
C16
C18
C7
C19
C20
C2,C6



16

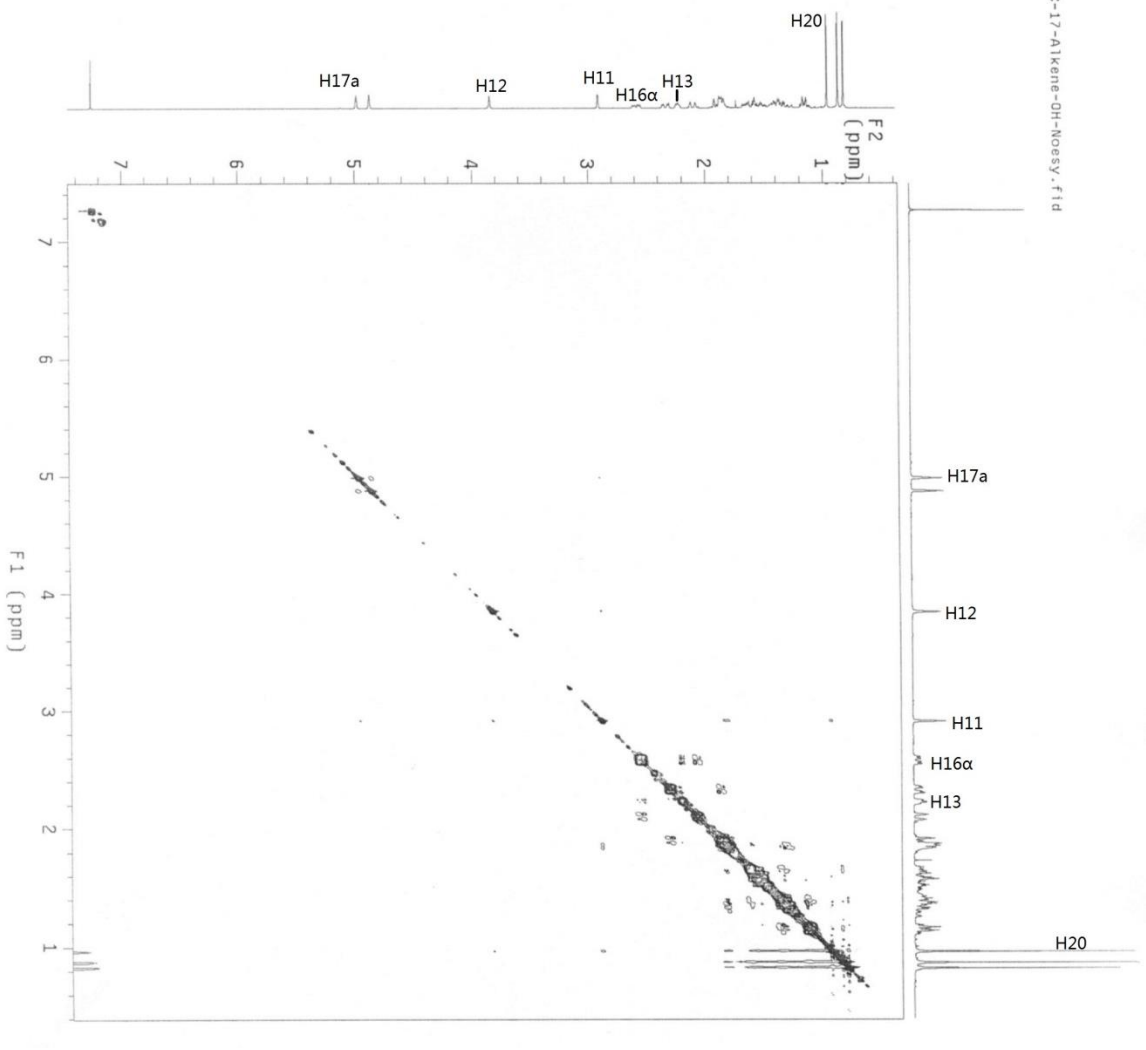
^{1}H-^{1}H COSY, $CDCl_3$

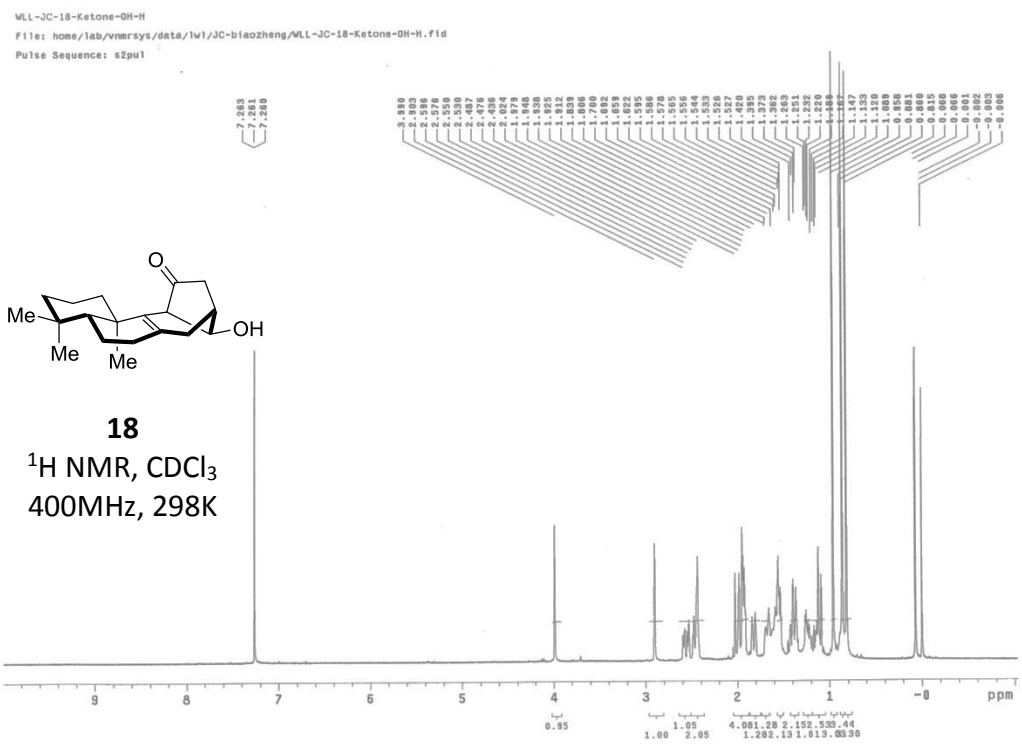




16

NOESY, $CDCl_3$

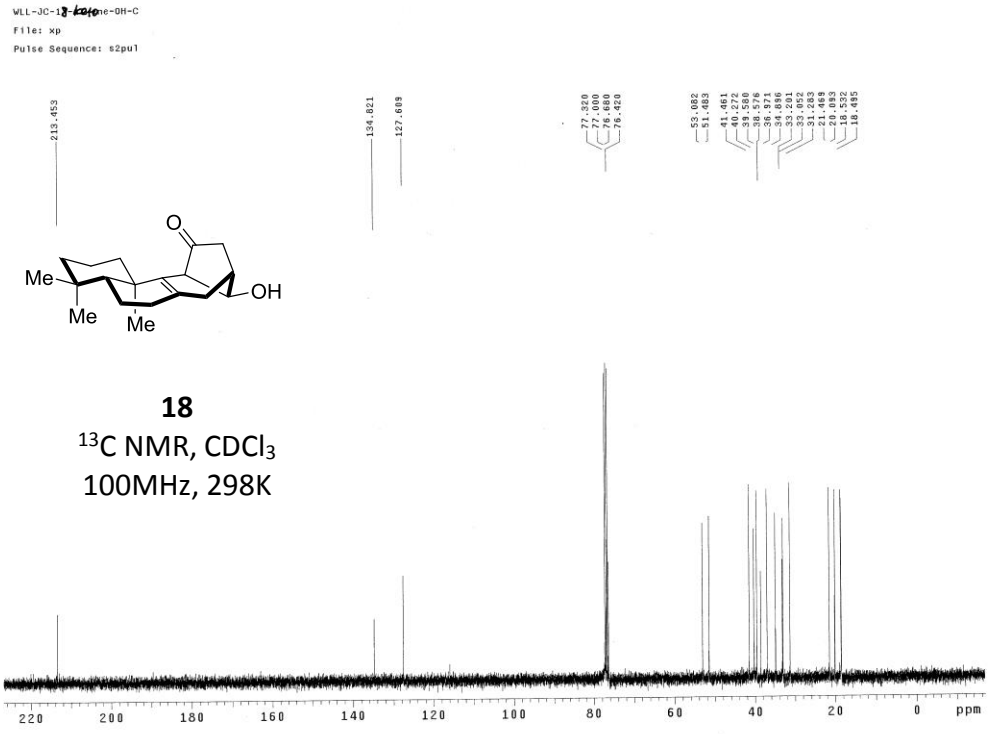




18

^{1}H NMR, $CDCl_3$

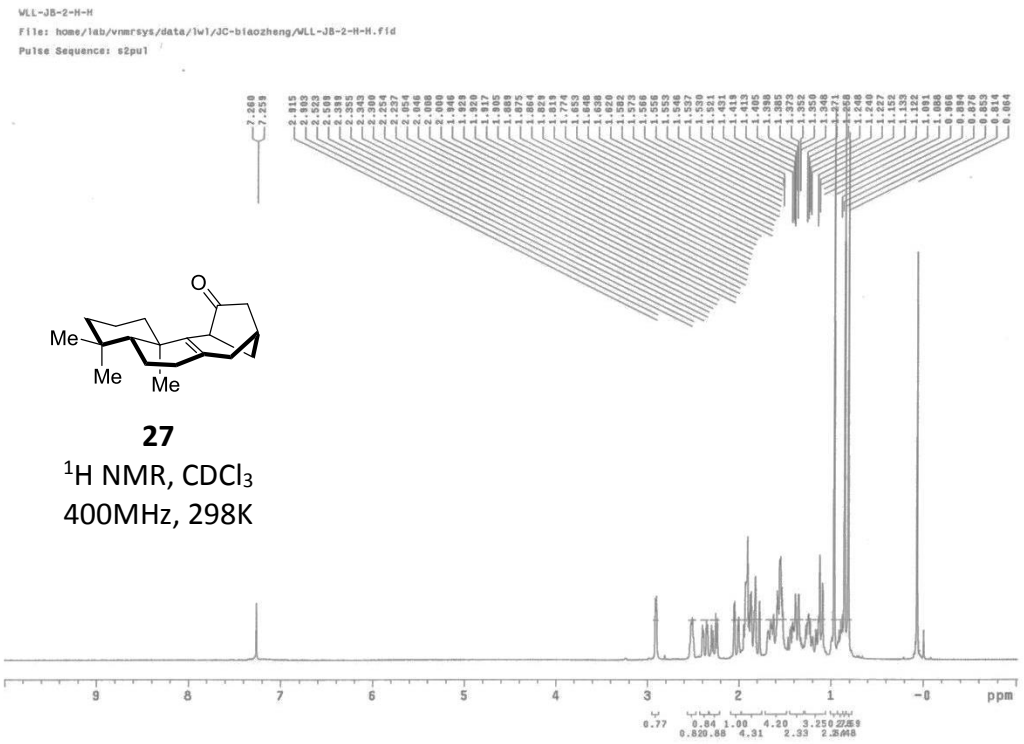
400MHz, 298K



18

^{13}C NMR, $CDCl_3$

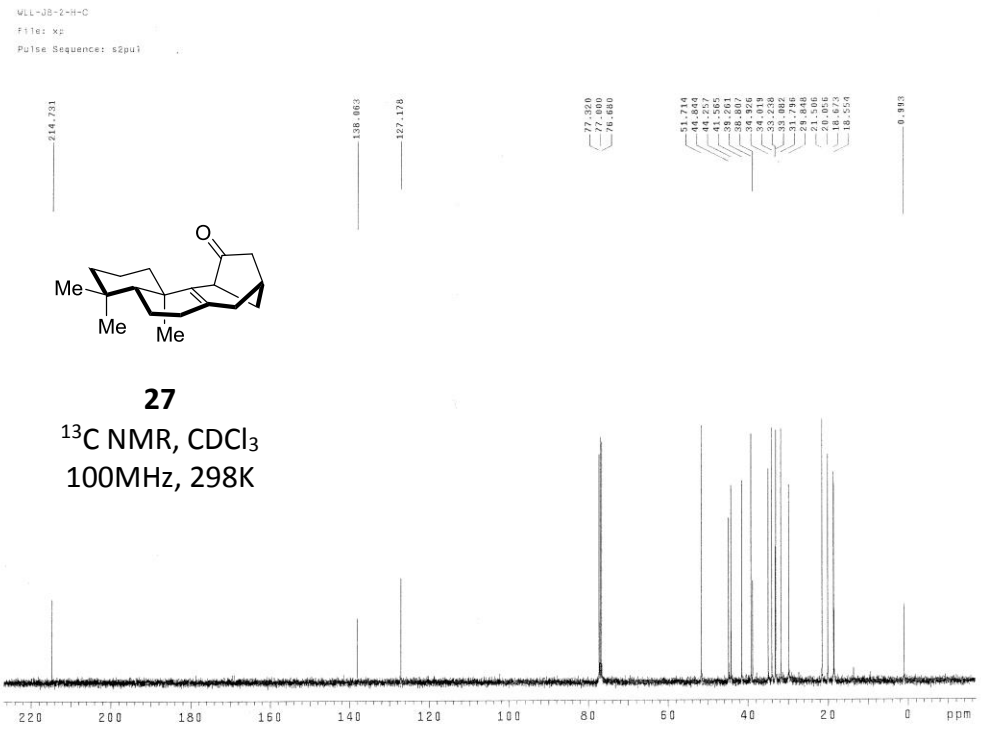
100MHz, 298K



27

^{1}H NMR, $CDCl_3$

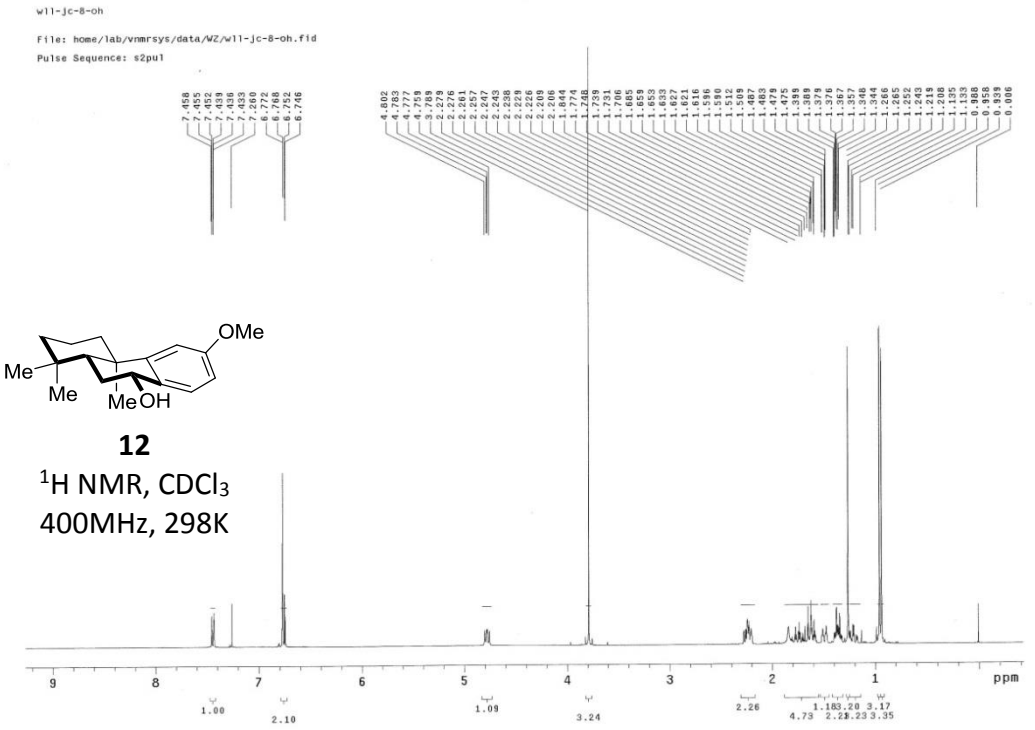
400MHz, 298K



27

^{13}C NMR, $CDCl_3$

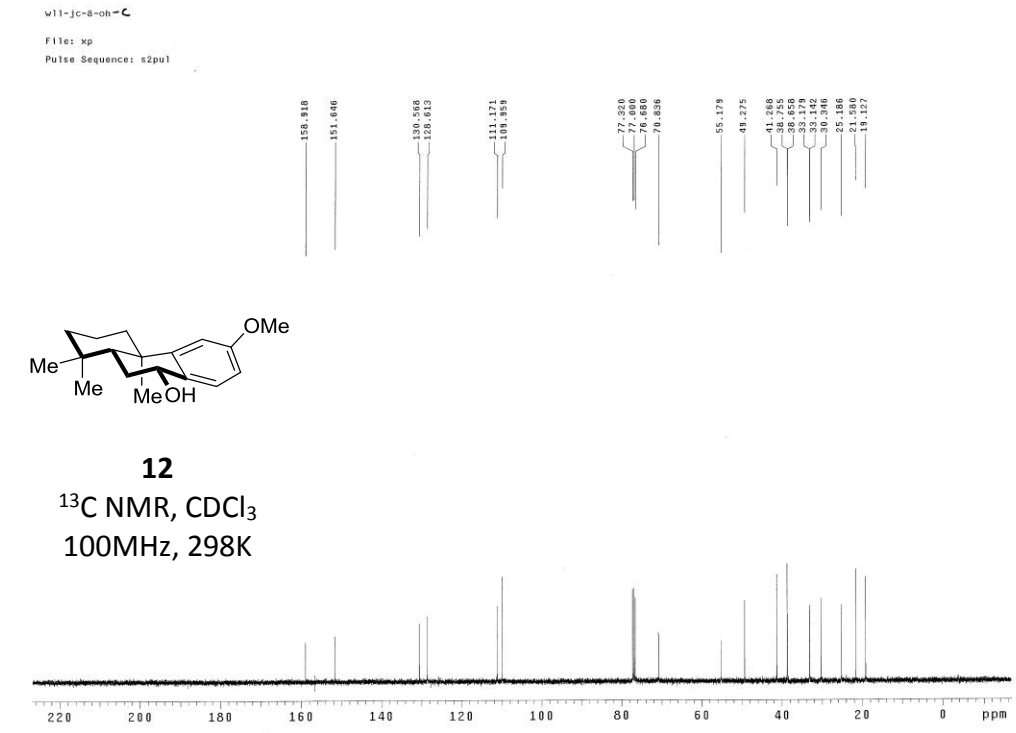
100MHz, 298K



12

^{1}H NMR, $CDCl_3$

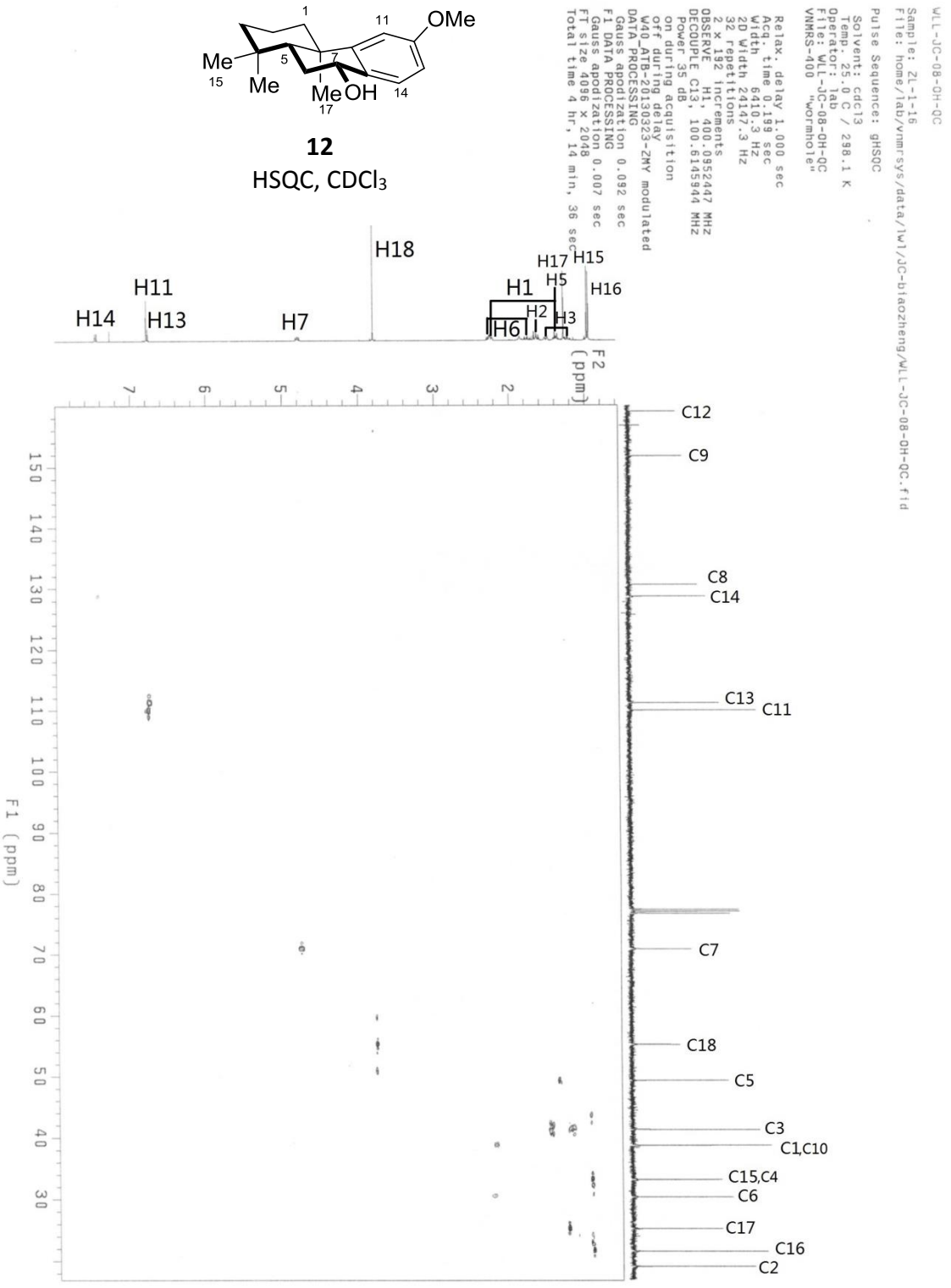
400MHz, 298K

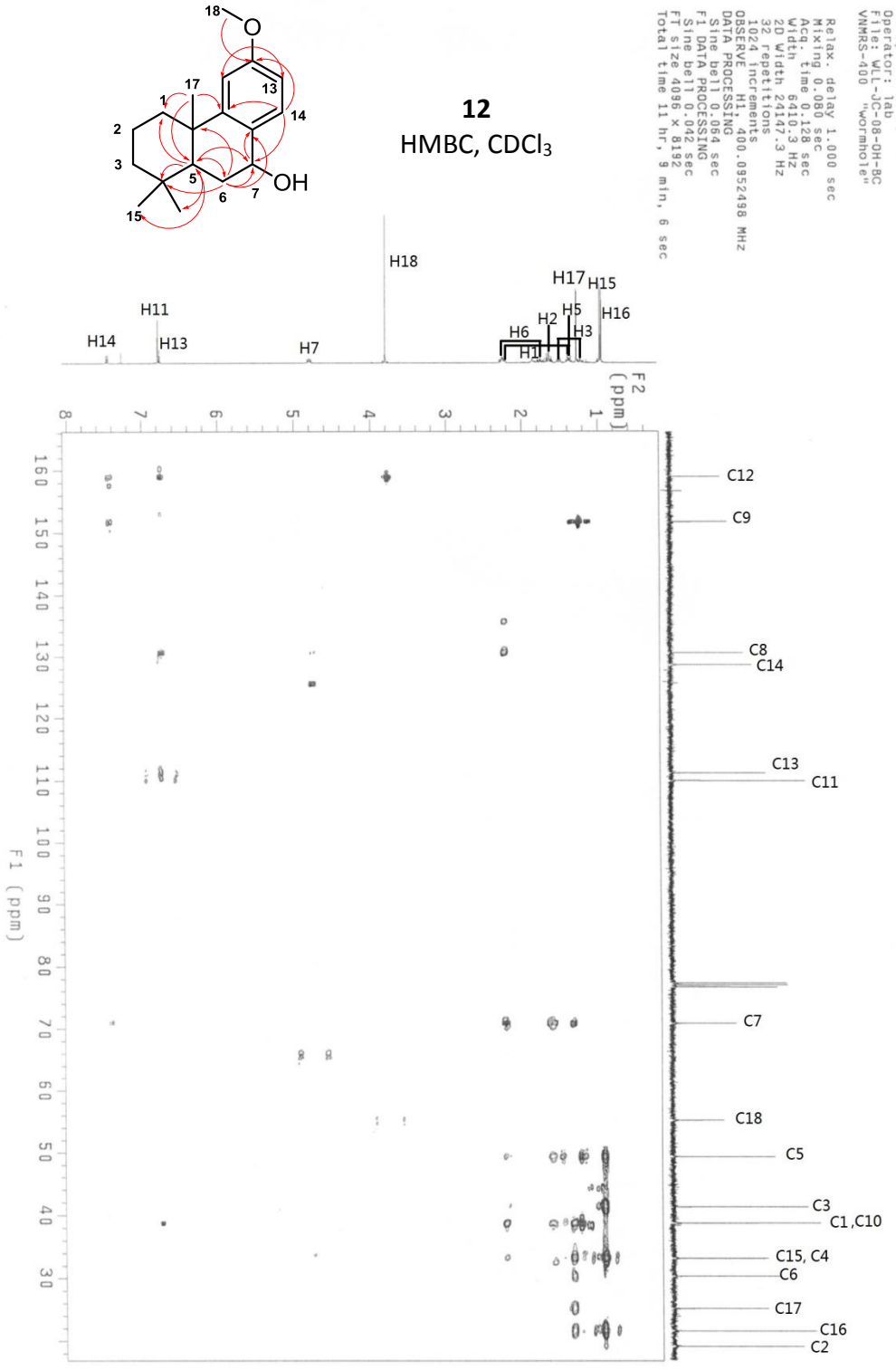


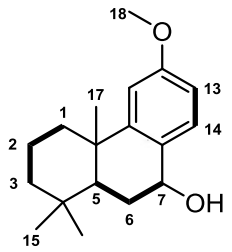
12

^{13}C NMR, $CDCl_3$

100MHz, 298K

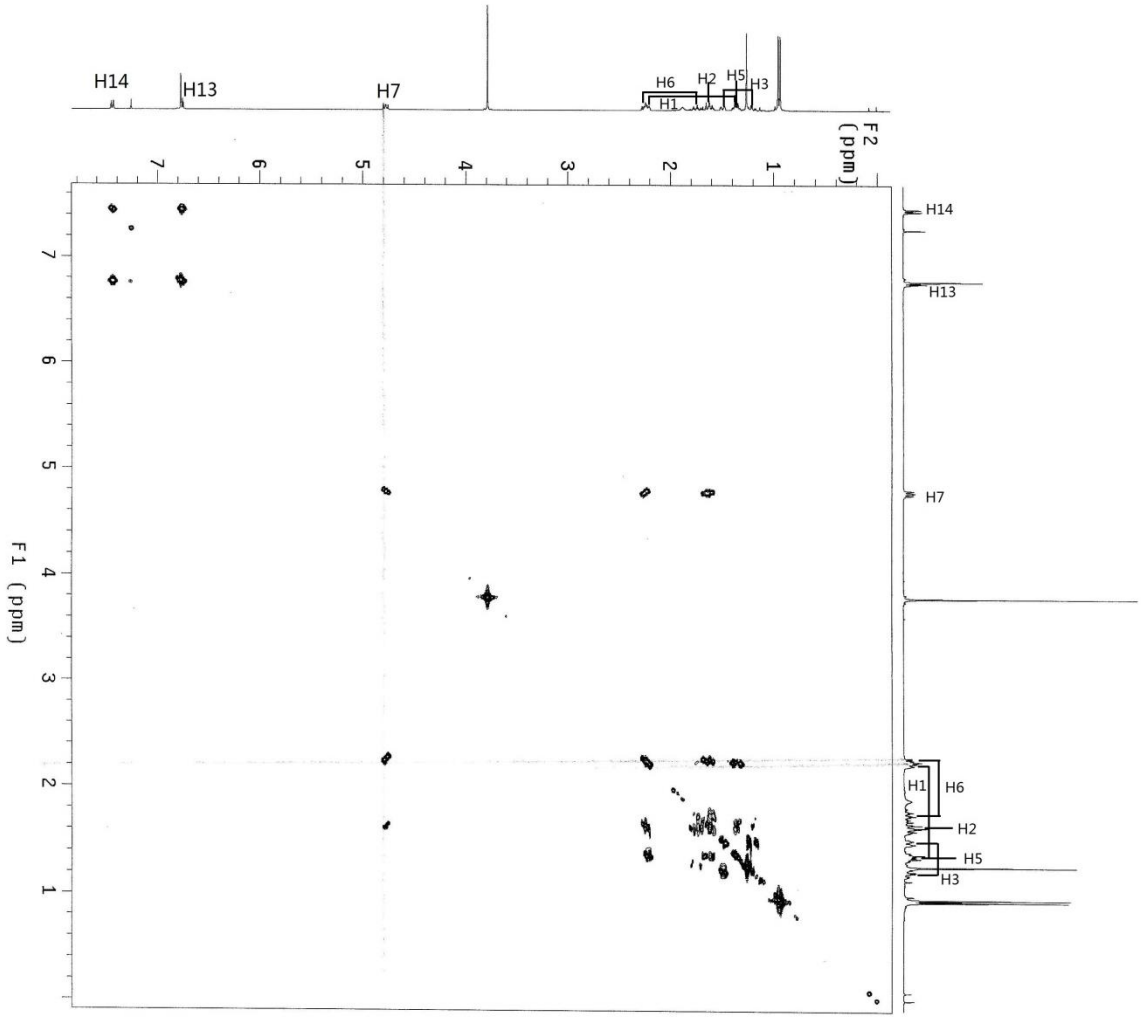

12
HSQC, CDCl3
H18
H11
H14
H13
H7
H17
H15
H5
H1
H16
H2
H3
H6
F2 (ppm)
F1 (ppm)
C12
C9
C8
C14
C13
C11
C7
C18
C5
C3
C1,C10
C15,C4
C6
C17
C16
C2
WLL-JC-08-OH-QC
Sample: ZL-1-15
File: home/lab/vnmrsys/data/lwl/JC-biaozheng/WLL-JC-08-OH-QC.fid
Pulse Sequence: gHSQC
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: lab
File: WLL-JC-08-OH-QC
VNMRS-400 "wormhole"
Relax. delay 1.000 sec
Acq. time 0.199 sec
Width 6410.3 Hz
2D Width 24147.3 Hz
32 repetitions
2 x 192 increments
OBSERVE H1, 400.0952447 MHz
DECOUPLE C13, 100.6145944 MHz
Power 35 dB
on during acquisition
off during delay
W40_ATB-20130323-ZMY modulated
DATA PROCESSING
Gauss apodization 0.092 sec
F1 DATA PROCESSING
Gauss apodization 0.007 sec
FT size 4096 x 2048
Total time 4 hr, 14 min, 36 sec

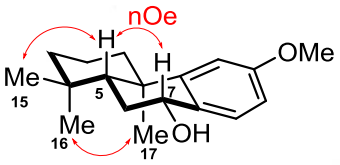

12
HMBC, CDCl3
OH
H18
H17
H15
H16
H11
H14
H13
H7
H6
H2
H5
H3
H1
F2 (ppm)
F1 (ppm)
C12
C9
C8
C14
C13
C11
C7
C18
C5
C3
C1,C10
C15, C4
C6
C17
C16
C2



12

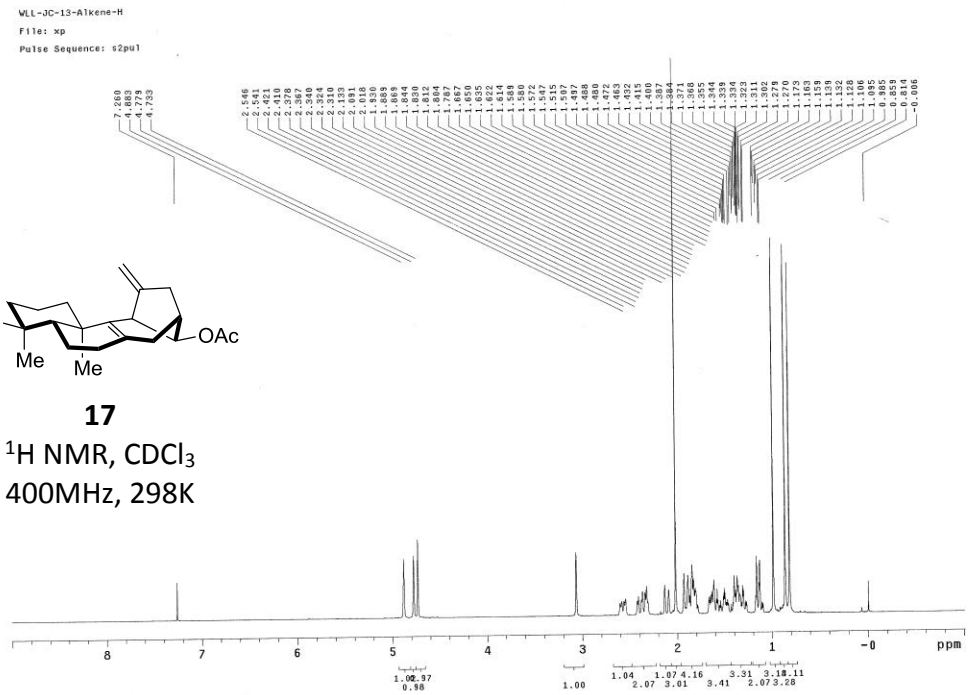
^{1}H-^{1}H COSY, $CDCl_3$





12

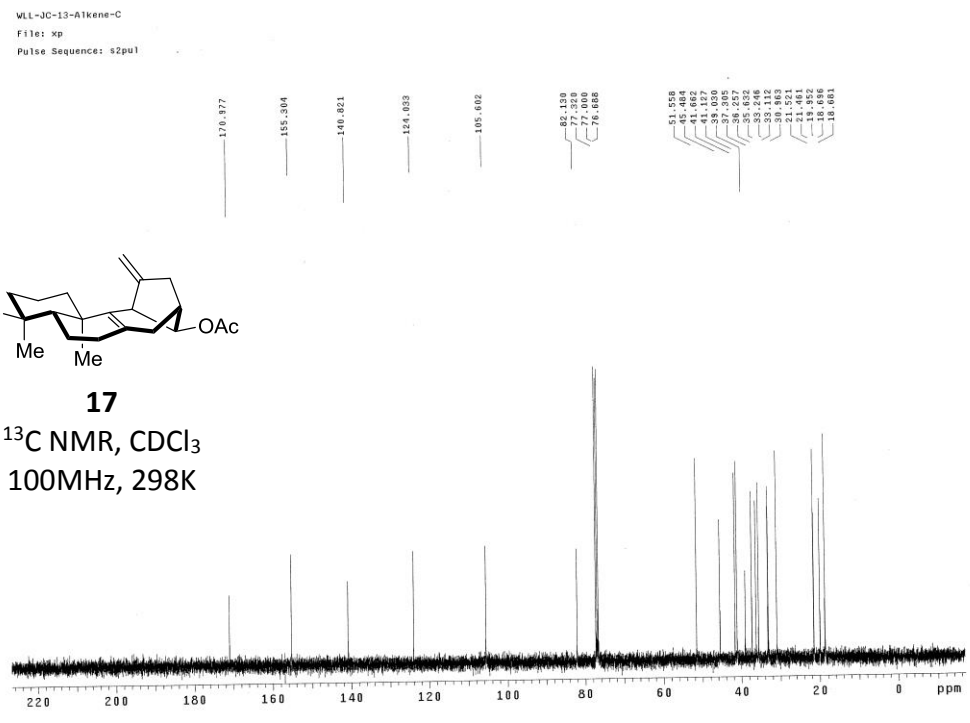
NOESY, $CDCl_3$



17

^{1}H NMR, $CDCl_3$

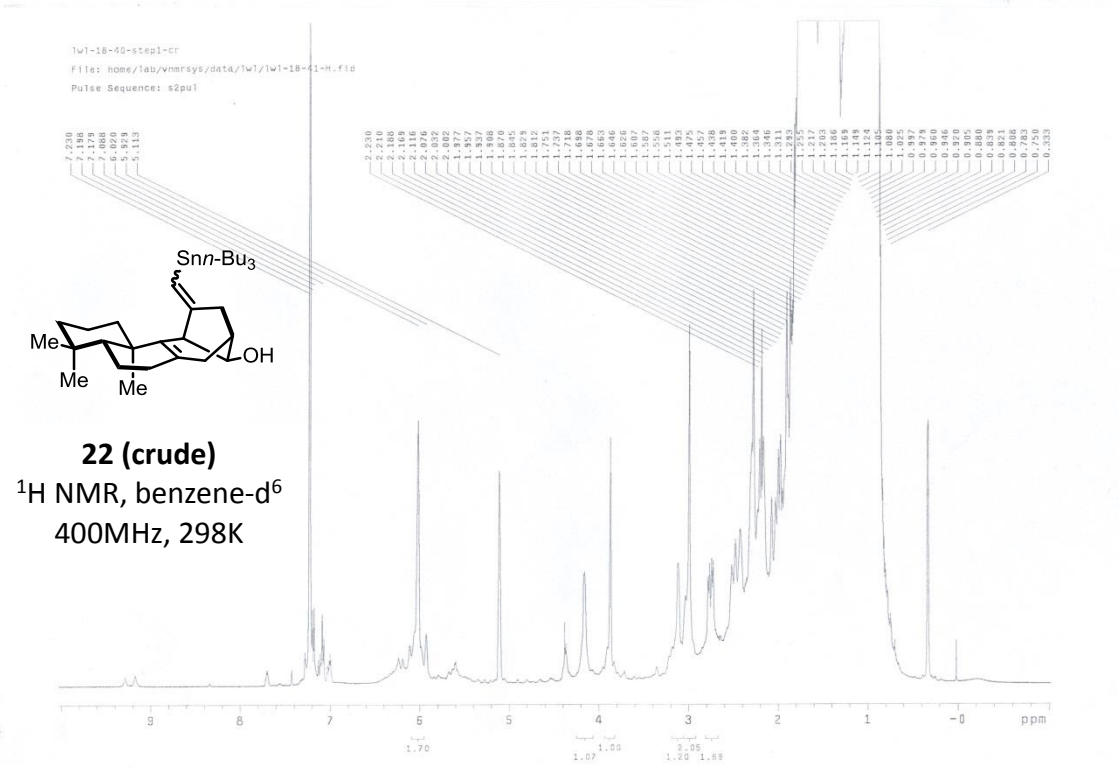
400MHz, 298K



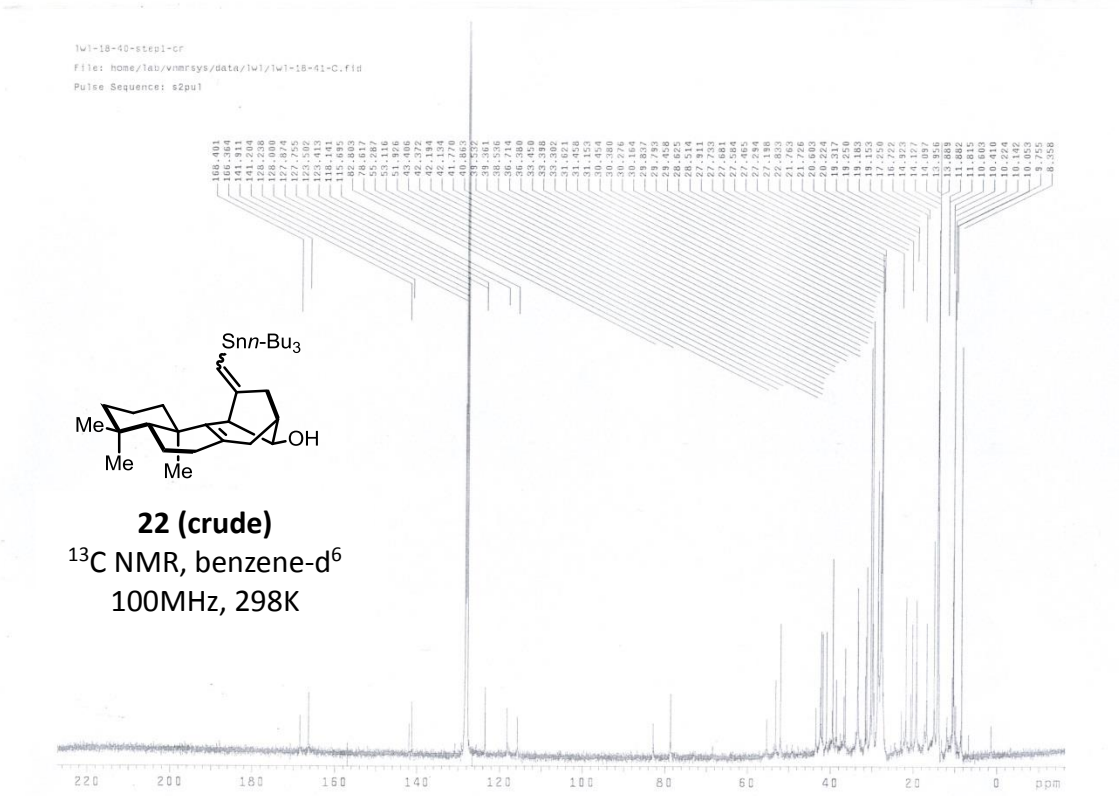
17

^{13}C NMR, $CDCl_3$

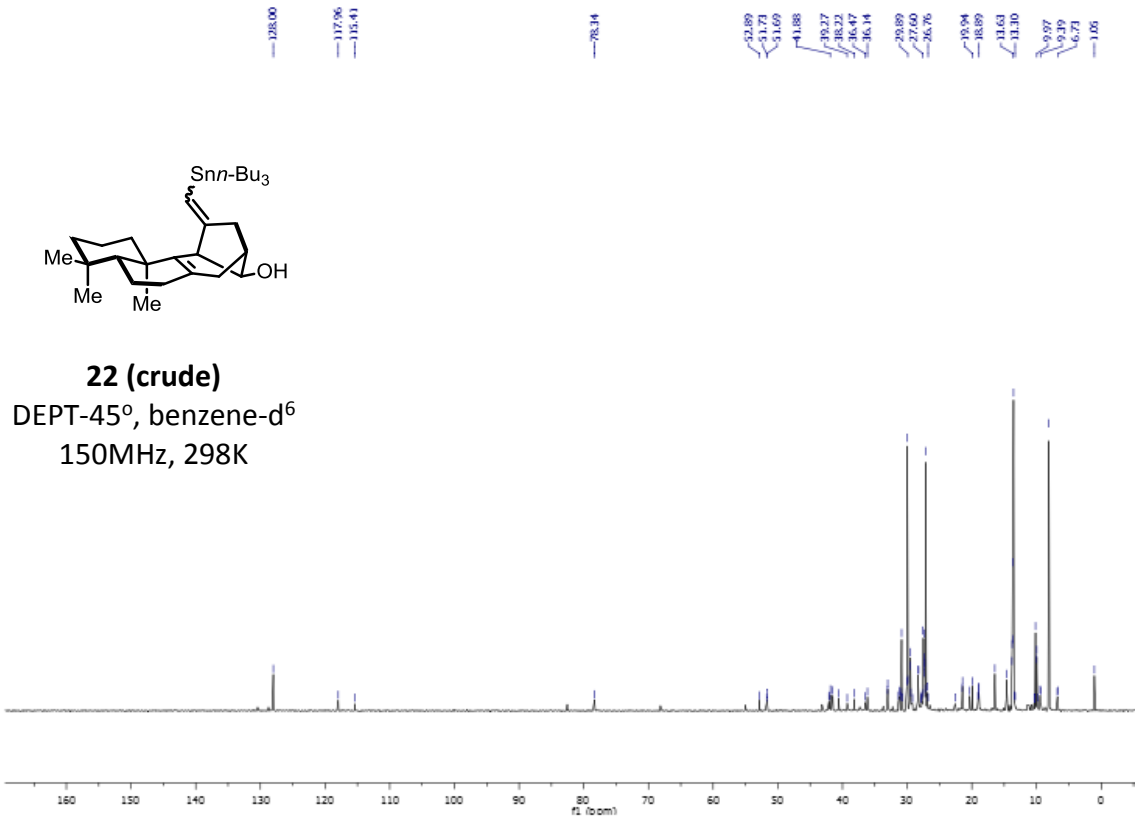
100MHz, 298K



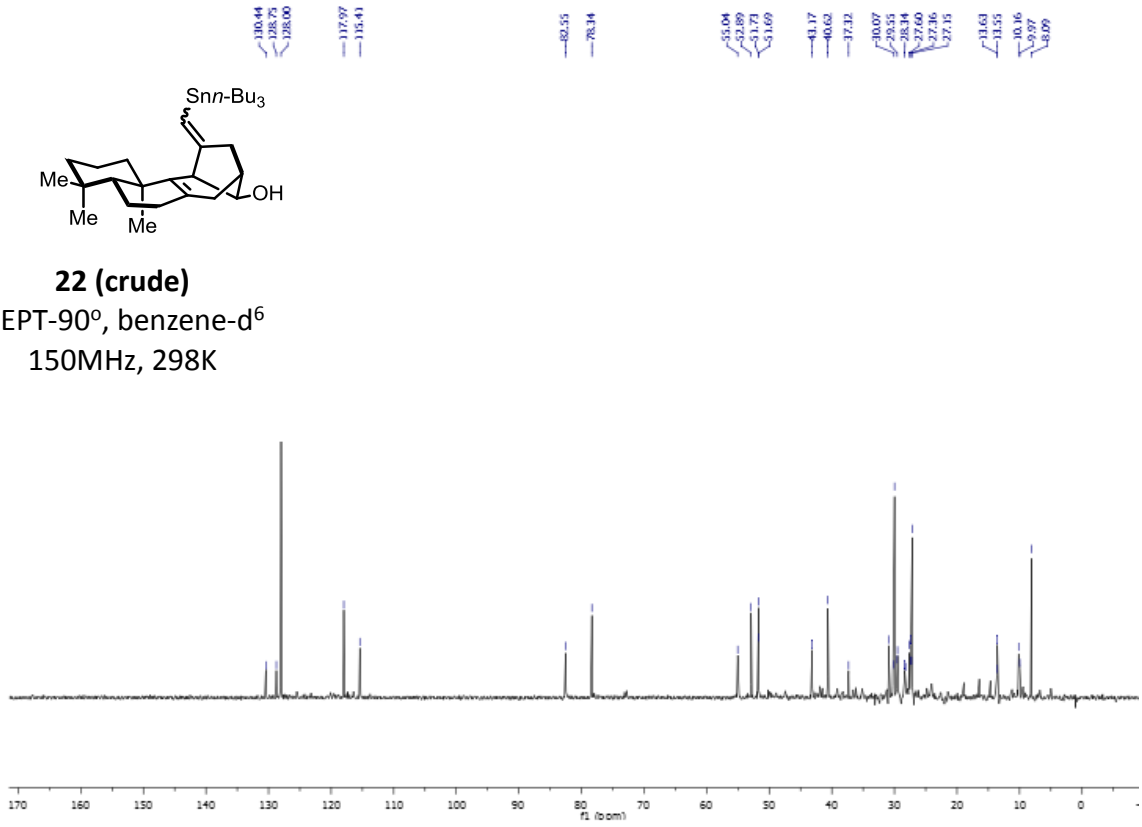
22 (crude)
^{1}H NMR, benzene-d^{6}
400MHz, 298K



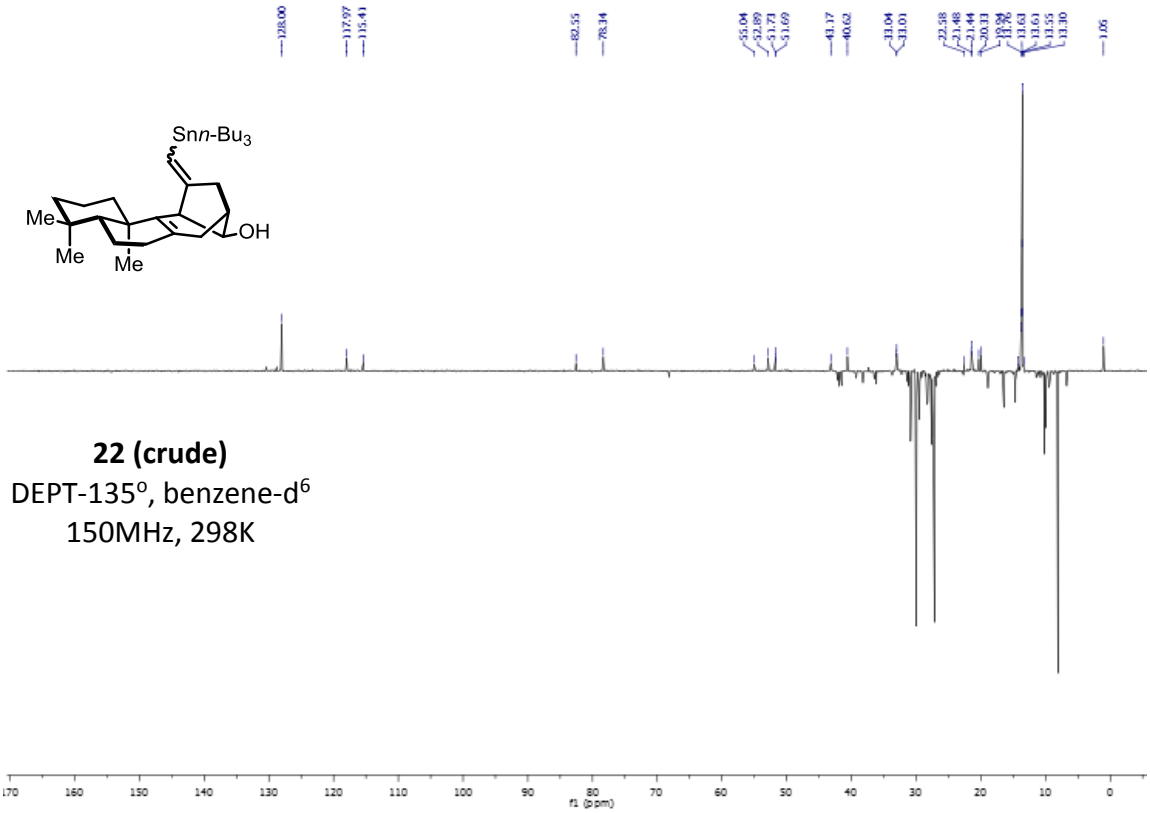
22 (crude)
^{13}C NMR, benzene-d^{6}
100MHz, 298K



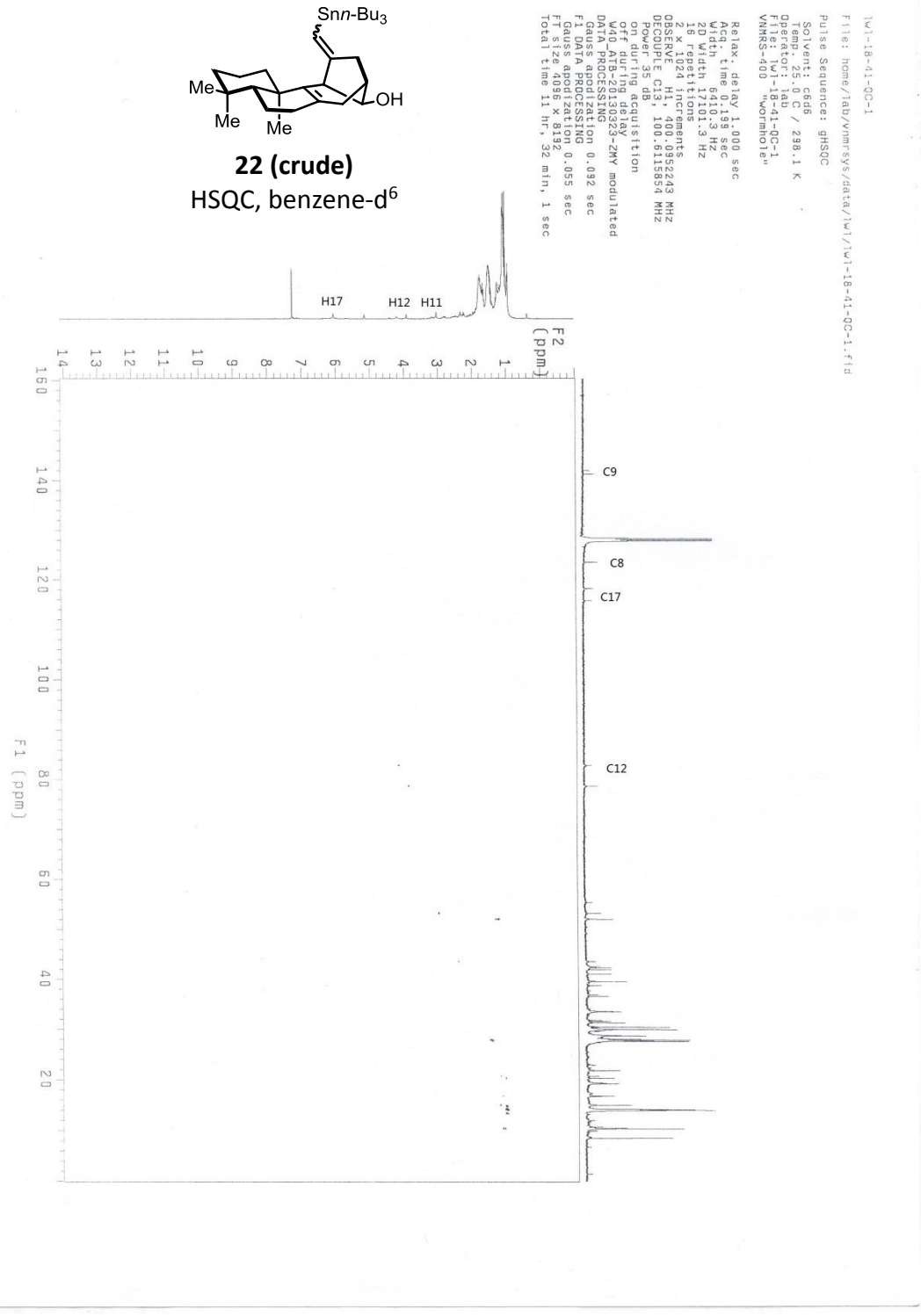
22 (crude)
DEPT-45°, benzene-d^6
150MHz, 298K

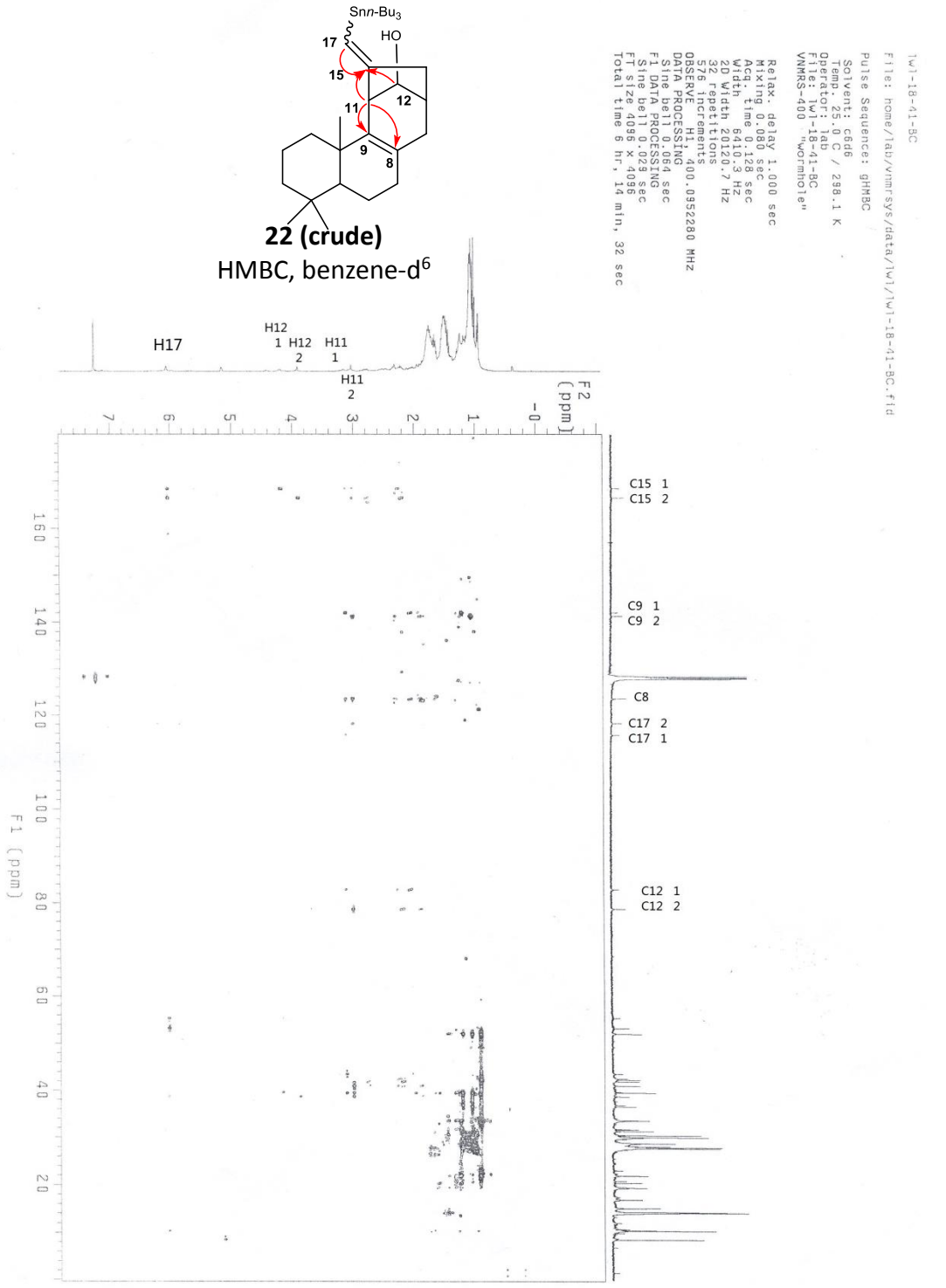


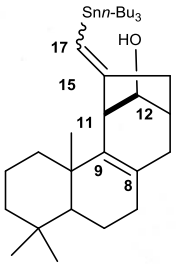
22 (crude)
DEPT-90°, benzene-d^6
150MHz, 298K



22 (crude)
DEPT-135°, benzene-d^6
150MHz, 298K

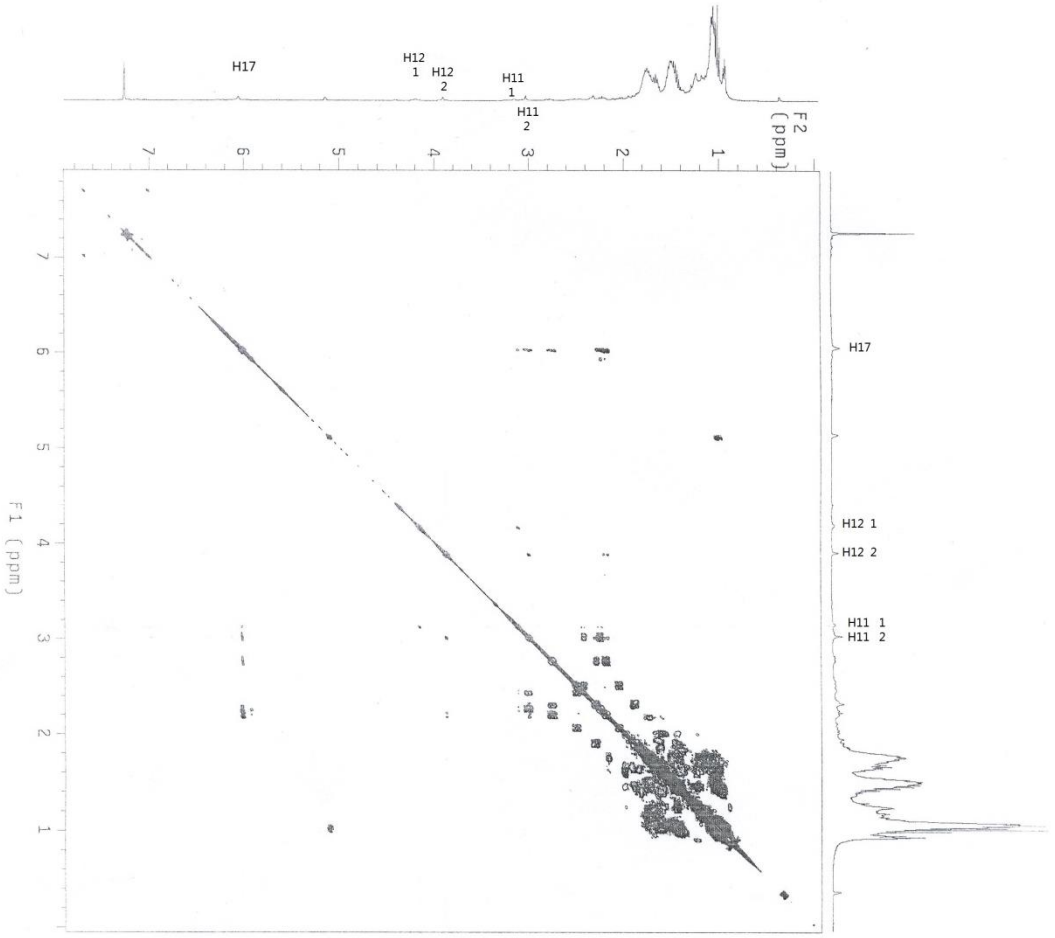

Sn*n*-Bu3
Me
Me
Me
OH
22 (crude)
HSQC, benzene-d6
H17
H12
H11
C9
C8
C17
C12
F2 (ppm)
F1 (ppm)

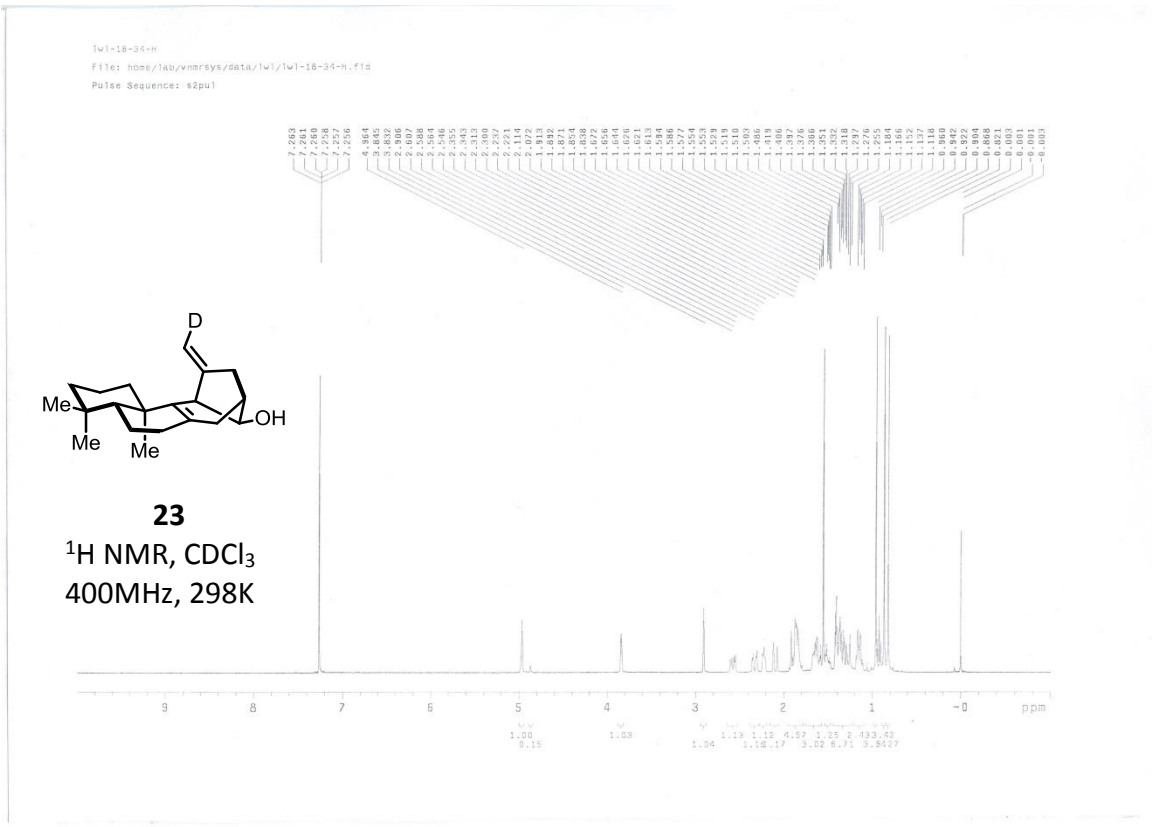

Sn*n*-Bu$_3$
HO
17
15
11
12
9
8
22 (crude)
HMBC, benzene-d^6
H17
H12
1 H12
2
H11
1
H11
2
F2 (ppm)
F1 (ppm)
C15 1
C15 2
C9 1
C9 2
C8
C17 2
C17 1
C12 1
C12 2
lwl-18-41-BC
File: home/lab/vnmrsys/data/lwl/lwl-18-41-BC.fid
Pulse Sequence: gHMBC
Solvent: c6d6
Temp. 25.0 C / 298.1 K
Operator: lab
File: lwl-18-41-BC
VNMRS-400 "wormhole"
Relax. delay 1.000 sec
Mixing 0.08000 sec
Acq. time 0.128 sec
Width 6410.3 Hz
2D Width 20120.7 Hz
32 repetitions
576 increments
OBSERVE H1 400.0352280 MHz
DATA PROCESSING
Sine bell 0.064 sec
F1 DATA PROCESSING
Sine bell 0.029 sec
FT size 4096 x 4096
Total time 6 hr, 14 min, 32 sec



22 (crude)

^{1}H-^{1}H COSY, benzene-d^6

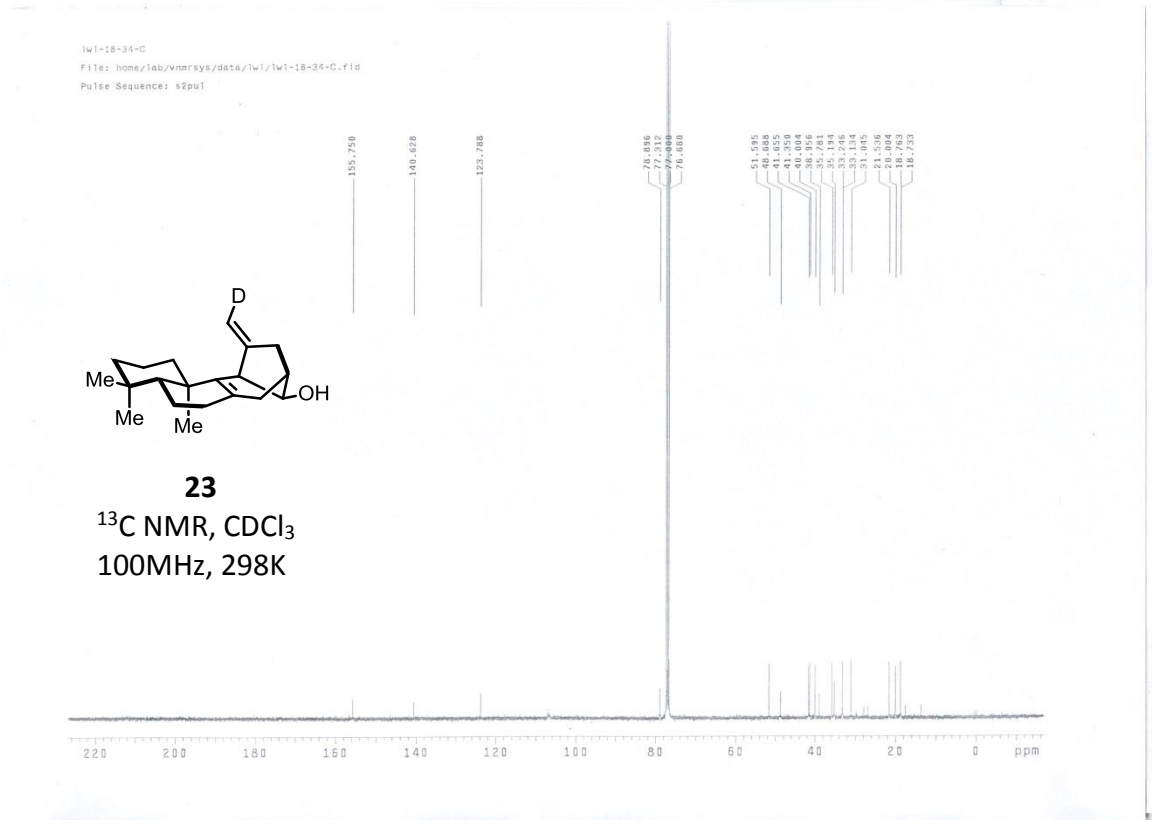




23

^{1}H NMR, $CDCl_3$

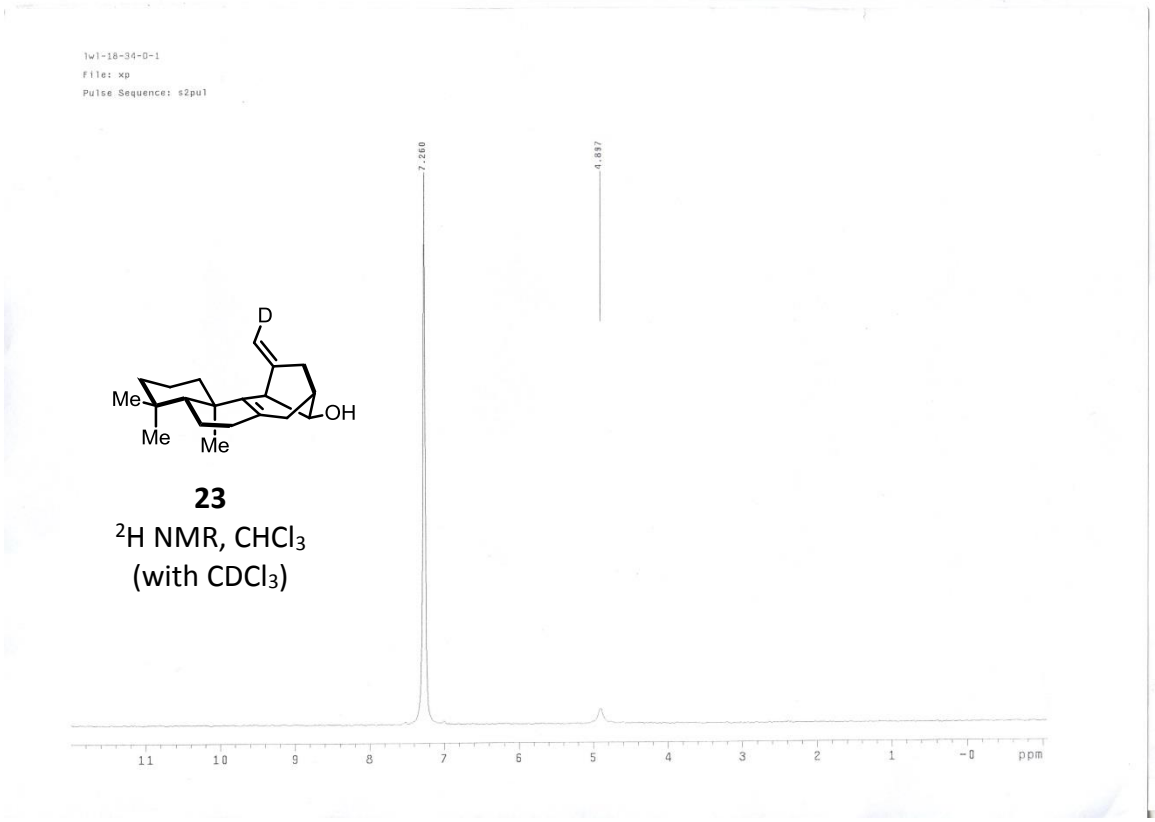
400MHz, 298K



23

^{13}C NMR, $CDCl_3$

100MHz, 298K



23

^{2}H NMR, $CHCl_3$
(with $CDCl_3$)

g) X-Ray crystallographic data of 17

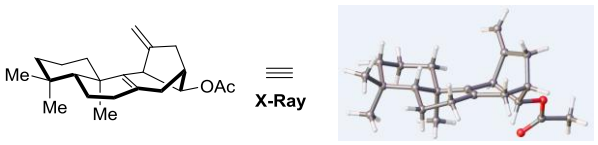


Table 1: Crystal data and structure refinement for compound 17

Identification code	CCDC 1435066
Empirical formula	$C_{22}H_{32}O_2$
Formula weight	328.48
Temperature / K	100.8
Crystal system	monoclinic
Space group	$P2_1$
a / Å, b / Å, c / Å	7.0843(6), 18.1527(6), 7.4623(4)
α/°, β/°, γ/°	90.00, 106.341(7), 90.00
Volume / Å^3	920.88(10)
Z	2
ρ_{calc} / mg mm^{-3}	1.185
μ / mm^{-1}	0.566
F(000)	360
Crystal size / mm^3	0.17 × 0.14 × 0.14
2Θ range for data collection	9.74 to 142.2°
Index ranges	-7 ≤ h ≤ 8, -21 ≤ k ≤ 21, -9 ≤ l ≤ 5
Reflections collected	5772
Independent reflections	3464[R(int) = 0.0244 (inf-0.9Å)]
Data/restraints/parameters	3464/1/221
Goodness-of-fit on F^2	1.036
Final R indexes [I>2σ (I) i.e. F_o>4σ (F_o)]	R_1 = 0.0387, wR_2 = 0.1016
Final R indexes [all data]	R_1 = 0.0404, wR_2 = 0.1039
Largest diff. peak/hole / e Å^{-3}	0.213/-0.226
Flack Parameters	0.1(2)
Completeness	0.982