Supporting Information for

LiOO*t*-Bu as a Terminal Oxidant in a Titanium Alkoxide-Mediated [2+2+2] Reaction Cascade

Wan Shin Kim, Claudio Aquino, Haruki Mizoguchi, and Glenn C. Micalizio*

Department of Chemistry, Dartmouth College, Hanover, NH 03755

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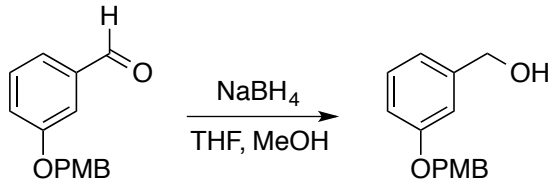
1. Materials and Methods:

All reactions were conducted in flame-dried glassware under a nitrogen atmosphere with dry solvents, unless otherwise noted. All reagents and starting materials were purchased from commercial sources and used as supplied, unless otherwise noted. Anhydrous toluene (PhMe) was obtained by distillatioin over sodium and bezophenone. Titanium isopropoxide (Ti(O*i*-Pr)$_4$) was distilled before use. A solution of *n*-BuLi was purchased from Aldrich and titrated against *N*-benzylbenzamide. Yields refer to chromatographically purified materials, unless otherwise stated. Flash chromatography was performed on the Biotage® Automated Liquid Chromatography System Isolera One® using Biotage® SNAP KP-Sil 10-100 g silica gel cartridges. TLC analyses were conducted on EMD TLC Silica gel 60 F_{254} Glass Plates and the spots were visualized by UV-light (254 nm) or an aqueous solution of phosphomolybdic acid, ceric sulfate, and sulfuric acid. ^{1}H NMR data were recorded on a Bruker Avance III 500 MHz spectrometer (TBI probe) and a Bruker Avance III 600 MHz spectrometer (BBFO probe) with calibration of spectra to $CDCl_3$ (7.26 ppm). ^{13}C NMR data were recorded at 125 MHz on a Bruker Avance III 500 MHz spectrometer (TBI probe) and at 150 MHz on a Bruker Avance III 600 MHz spectrometer (BBFO probe) with calibration to the central line of $CDCl_3$ (77.0 ppm). Infrared spectra were recorded on a JASCO FT/IR-4100 Fourier Transform Infrared Spectrometer. HRMS (ESI-TOF) analyses were performed at the Mass Spectrometry Laboratory of the University of Illinois at Urbana-Champaign. All compounds purified by chromatography were sufficiently pure for use in further experiments, unless indicated otherwise.

Note: While the compound numbers for the hydrindane products reported in this supporting information remain the same as the numbers reported in the manuscript, distinction between *cis*- and *trans*-fused isomers here has been accomplished by a subclassification in the style of "**compound #**" for the *cis*-isomer and "**compound #a**" for the *trans*-isomer.

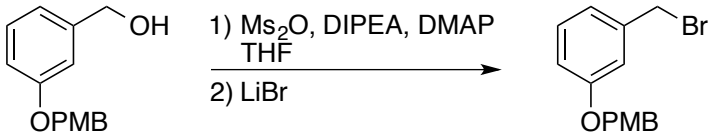
2. Experimental Procedures

A. Synthesis of Alkyne 17



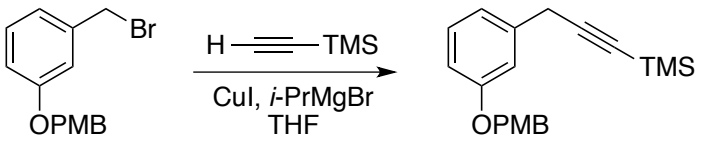
S1 **S2**

Benzyl Alcohol S2: To a 0 °C solution of **S1**[1] (2.0 g, 8.25 mmol) in THF/MeOH (1:1, 20.0 mL) was added $NaBH_4$ (624 mg, 16.5 mmol) in small portions. The reaction mixture was then allowed to slowly warm to rt and stirred for 4 h. Subsequently the mixture was diluted with ethyl acetate (40 mL), washed with brine (20 mL, three times), dried over $MgSO_4$ and concentrated *in vacuo* to give a crude oil (1.5 g) which was used in the next step without further purification.



S2 **S3**

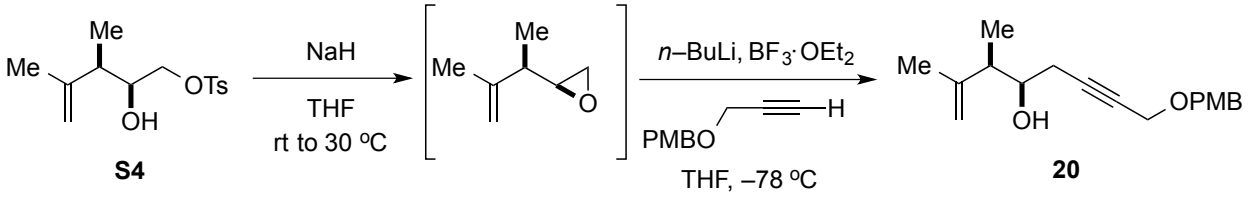
Benzyl Bromide S3: To a 0 °C solution of **S2** (1.5 g, 6.18 mmol) in THF (10.0 mL) were added DIPEA (3.2 mL, 18.5 mmol) and DMAP (73 mg, 0.6 mmol). Methanesulfonic anhydride (2.15 g, 12.36 mmol) dissolved in THF (10 mL) was then added dropwise and the reaction mixture was stirred at rt for 3 h. After this period, LiBr (2.15 g, 24.7 mmol) dissolved in THF (15.0 mL) was added and the reaction mixture was stirred overnight at rt. Subsequently $NaHCO_3$ (25 mL, aq. sat.) was added and the resulting heterogeneous mixture was then diluted with EtOAc (100 mL), washed with brine, filtered through $MgSO_4$, and concentrated *in vacuo* to give the crude bromide **S3** (1.6 g) as a white solid which was used in the next step without further purification.



S3 **17**

Alkyne 17: To a flask charged with ethynyltrimethylsilane (3.0 mL, 20.8 mmol) and THF (20 mL) was added isopropylmagnesium bromide (2.0 M in Et_2O, 10 mL, 20.4 mmol) dropwise at 0°C. After the addition was complete, the ice bath was removed and the reaction mixture was stirred at rt for 45 min before CuI (3.8 g, 2.0 mmol) was added in one portion. After 5 min, a solution of benzyl bromide **S3** (1.6 g, 5.2 mmol) in THF (20 mL) was added, the reaction vessel was equipped with a reflux condenser, and refluxed overnight. After completion of the reaction, the heating bath was removed and the mixture was allowed to cool to rt. Subsequently, the reaction vessel was placed into an ice bath and saturated aqueous NH_4Cl was added. The resulting heterogeneous mixture was then diluted with EtOAc, washed with brine, filtered through $MgSO_4$, and concentrated *in vacuo*. The crude residue from evaporation was purified via flash chromatography to afford **17** (1.6 g, 60% over three steps) as an amorphous white solid. Spectral data for **17**: 1H NMR ($CDCl_3$, 600 MHz): δ (ppm) 7.37 (d, J=8.4 Hz, 2H), 7.24 (t, J=7.9 Hz, 1H), 7.00 (br. s, 1H), 6.94 – 6.92 (m, 3H), 6.85 – 6.84 (m, 1H), 4.99 (s, 2H), 3.82 (s, 3H), 3.64 (s, 2H), 0.19 (s, 9H); 13C NMR ($CDCl_3$, 150 MHz): δ (ppm) 159.4, 159.0, 137.9, 129.4, 129.2, 129.0, 120.4, 114.4, 114.0, 113.1, 104.1, 87.0, 69.7, 55.3, 26.2, 0.1; IR (thin film): 2957.3, 2176.27, 1611.23, 1514.81, 1248.68, 1031.73, 843.704 cm^{-1}; HRMS (ESI-TOF) calculated for $C_{20}H_{24}O_2Si$ [M] 324.1546, found 324.1543

B. Synthesis of Enyne 20

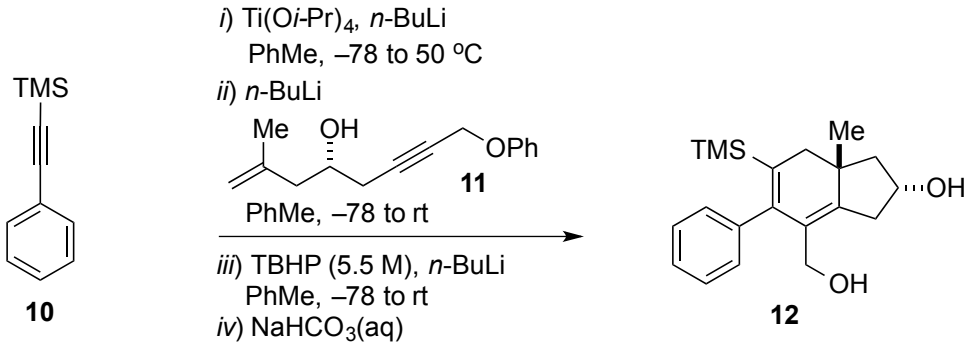


S4 **20**

Enyne 20: A solution of tosylate **S4**[2] (1.00 g, 3.52 mmol, 1.0 equiv) in THF (18.0 mL) was added NaH (60% dispersion in mineral oil, 352 mg, 8.8 mmol, 2.5 equiv) at 0 °C and stirred at rt for 20 min and 35 °C for 2 h. Additional NaH (60% dispersion in mineral oil, 300 mg, 7.50 mmol, 2.1 equiv) was then added and the resulting mixture was stirred at 35 °C for 3 h to form the intermediate epoxide. In the meantime, 1-methoxy-4-((prop-2-yn-1-yloxy)methyl)benzene (1.24 g, 7.04 mmol, 2.0 equiv) was dissolved in THF (12 mL) and treated with *n*-BuLi (2.49 M in hexane, 2.40 mL, 5.98 mmol, 1.7 equiv) at –78 °C and stirred at this temperature for 30 min. The resulting lithium acetylide solution was added dropwise to the epoxide mixture at –78 °C. After 15 min, $BF_3{\cdot}OEt_2$ (0.78 mL, 6.32 mmol, 1.8 equiv) was added dropwise by syringe. After stirring for an additional 45 min at –78 °C, saturated aqueous sodium bicarbonate was added. The

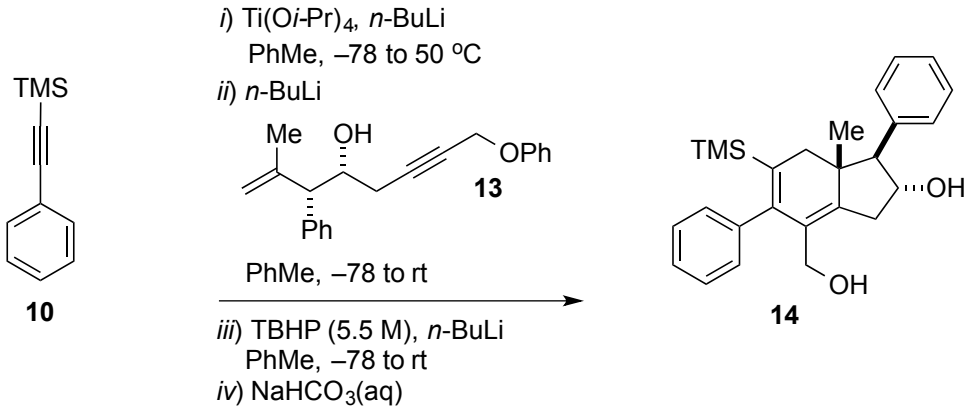
flask was warmed to rt, and the layer was then separated. The aqueous layer was extracted with diethyl ether. The combined organic extracts were washed with a saturated aqueous sodium bicarbonate and brine, and dried over Na_2SO_4. The solvent was removed *in vacuo*, and the resulting crude mixture was purified via flash chromatography to afford the title compound as a colorless oil (692 mg, 2.40 mmol, 68%). Spectral data for **20**: ^{1}H NMR ($CDCl_3$, 600 MHz): δ (ppm) 7.31 - 7.28 (d, 2H), 6.91 – 6.87 (d, 2H), 4.86 – 4.83 (m, 1H), 4.81 – 4.79 (m, 1H), 4.53 (s, 2H), 4.16 (app. t, *J*=2.0 Hz, 2H), 3.82 (s, 3H), 3.72 – 3.68 (m, 1H), 2.53 – 2.38 (m, 2H), 2.35 (dq, *J*=6.9 Hz, 1H), 1.87 (d, *J*=4.4 Hz, 1H), 1.73 (s, 3H), 1.12 (d, *J*=7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ (ppm) 160, 147.49, 129.84, 129.68, 113.94, 112.10, 83.52, 78.56, 71.53, 71.32, 57.41, 55.35, 45.96, 25.67, 20.59, 14.43; IR (thin film): 3434.6, 2935.13, 1612.2, 1513.85, 1249.65, 1174.44, 1069.33, 1035.59, 893.844, 820.563 cm^{-1}; HRMS (ESI-TOF) Calculated for $C_{18}H_{25}O_3$ [M+H$^+$] 289.1798, found 289.1804.

C. Synthesis of Hydrindanes 12, 14, 16, 18, and 21 via the Ti(O*i*-Pr)$_4$/*n*-BuLi-mediated Coupling Process.



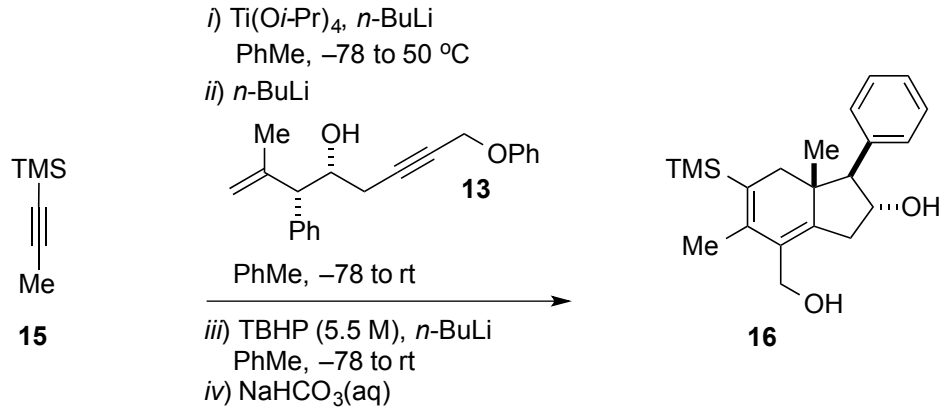
Hydrindane 12: To a solution of alkyne **10** (174 mg, 1.0 mmol) in PhMe (6.0 mL) was added Ti(O*i*-Pr)$_4$ (0.30 mL, 1.0 mmol) at rt. The mixture was cooled to –78 °C and *n*-BuLi (2.49 M in hexanes, 0.80 mL, 2.0 mmol) was added dropwise (by syringe) over the course of 5 min. After this period, the flask was taken out of the cooling bath and allowed to warm to rt (approx. 20 min). The reaction mixture was then heated to 50 °C (no reflux condenser required) for 1 h and allowed to cool to rt before it was placed into a –78 °C bath. In the meantime, enyne **11**[2] (69 mg, 0.30 mmol) was dissolved in PhMe (4.0 mL), treated with *n*-BuLi (2.49 M in hexane, 0.33 mmol, 0.13 mL) at –78 °C, and the resulting alkoxide solution was allowed to warm to rt before it was added dropwise (by syringe) to the black Ti-alkyne complex solution at –78 °C. The reaction mixture was then allowed to warm to rt overnight (approx. 15 h). A separate flame-dried round bottom flask was charged with *t*-butylhydroperoxide (2.0 mmol, 0.36 mL, 5.5 M in decane), diluted with toluene (2 mL), and cooled to –78 °C. To this *t*-butylhydroperoxide solution in toluene was added *n*-BuLi (2.49 M in hexane, 0.80 mL, 2.0 mmol) at –78 °C under N_2. The mixture was stirred for 10 min at –78 °C, warmed to rt, and stirred for an additional 5 min. In the mean time, the black Ti-alkyne complex solution was cooled to –78 °C. The resulting lithium *t*-butylperoxide solution in toluene was cannula transferred (teflon cannula was used) to the Ti-alkyne complex solution at –78 °C. The resulting mixture was slowly warmed to rt, stirred for 30 min, and quenched with 20 mL of saturated $NaHCO_3$ (aq). The organic layer was separated, and the aqueous layer was extracted with ethyl

acetate (30 mL X 2). The organic layers were combined, dried over Na_2SO_4, and concentrated *in vacuo*. Purification of the crude product by flash chromatography afforded hydrindane **12** (49.3 mg, 50%, amorphous white solid). Spectral data for **12**: ^{1}H NMR ($CDCl_3$, 600 MHz): δ (ppm) 7.43 – 7.28 (m, 4H), 7.05 (br. s, 1H), 4.58 – 4.54 (app. quint, 1H), 3.99, 3.77 (ABq, *J*=11.7 Hz, 2H), 2.94 (dd, *J*=18.0, 7.3 Hz, 1H), 2.54 (dd, *J*=18.0, 5.9 Hz, 1H), 2.39, 2.26 (ABq, *J*=15.8 Hz, 2H), 2.16 (dd, *J*=12.7, 6.1 Hz, 1H), 1.76 (br. S, 2H), 1.61 (dd, *J*=12.5, 7.3 Hz, 1H), 1.01 (s, 3H), -0.25 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ (ppm) 148.5, 146.2, 141.8, 132.4, 128.7, 128.0, 127.0, 71.9, 59.8, 50.5, 40.7, 39.6, 38.0, 21.2, -0.9; IR (thin film): 3317.93, 2950.55, 1246.75, 1005.7, 834.062 cm^{-1}; HRMS (ESI-TOF) calculated for $C_{20}H_{28}O_2SiNa^+$ [M+Na$^+$] 351.1756, found 351.1758.

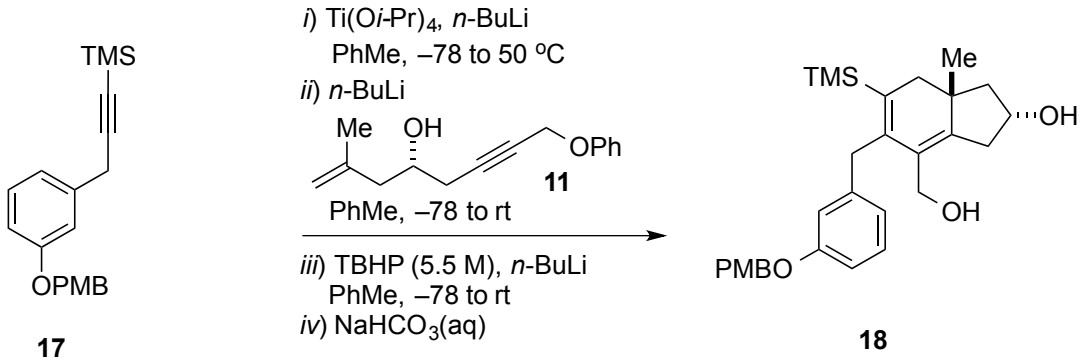


Hydrindane 14: To a solution of alkyne **10** (174 mg, 1.0 mmol) in PhMe (6.0 mL) was added Ti(O*i*-Pr)$_4$ (0.30 ml, 1.0 mmol) at rt. The mixture was cooled to –78 °C and *n*-BuLi (2.49 M in hexanes, 0.80 mL, 2.0 mmol) was added dropwise (by syringe) over the course of 5 min. After this period, the flask was taken out of the cooling bath and allowed to warm to rt (approx. 20 min). The reaction mixture was then heated to 50 °C (no reflux condenser required) for 1 h and allowed to cool to rt before it was placed into a –78 °C bath. In the meantime, enyne **13**[2] (92 mg, 0.30 mmol) was dissolved in PhMe (4.0 mL), treated with *n*-BuLi (2.49 M in hexane, 0.13 ml, 0.33 mmol) at –78 °C, and the resulting alkoxide solution was allowed to warm to rt before it was added dropwise (by syringe) to the black Ti-alkyne complex solution at –78 °C. The reaction mixture was then allowed to warm to rt overnight (approx. 15 h). A separate flame-dried round bottom flask was charged with *t*-butylhydroperoxide (2.0 mmol, 0.36 mL, 5.5 M in decane), diluted with toluene (2 mL), and cooled to –78 °C. To this *t*-butylhydroperoxide solution in toluene was added *n*-BuLi (2.49 M in hexane, 0.80 mL, 2.0 mmol) at –78 °C under N_2. The mixture was stirred for 10 min at –78 °C, warmed to rt, and stirred for an additional 5 min. In the mean time, the black Ti-alkyne complex solution was cooled to –78 °C. The resulting lithium *t*-butylperoxide solution in toluene was cannula transferred (teflon cannula was used) to the Ti-alkyne complex solution at –78 °C. The resulting mixture was slowly warmed to rt, stirred for 30 min, and quenched with 20 mL of saturated $NaHCO_3$ (aq). The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (30 ml X 2). The organic layers were combined, dried over Na_2SO_4, and concentrated *in vacuo*. Purification of the crude product by flash chromatography afforded hydrindane **14** (52.2 mg, 43%, amorphous white solid). Spectral data for **14**: ^{1}H NMR ($CDCl_3$, 600 MHz): δ (ppm) 7.42 – 7.37 (m, 2H), 7.36 – 7.27 (m, 7H), 7.04 (br. s, 1H), 4.95 – 4.87 (m, 1H), 4.03 (dd, *J*=11.7, 4.7 Hz, 1H), 3.86 – 3.81 (m, 1H), 3.21 (dd, *J*=18.7, 8.4 Hz, 1H), 2.96 (d, *J*=10.3 Hz, 1H), 2.62 (dd, *J*=18.7, 8.1 Hz, 1H), 2.17, 2.07 (ABq,

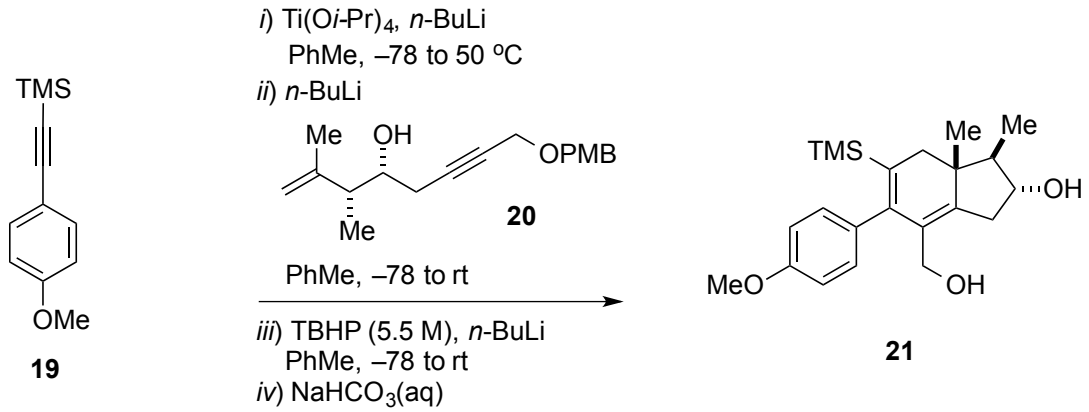
J=15.4 Hz, 2H), 1.72 (d, *J*=3.7 Hz, 1H), 0.92 (t, *J*=5.7 Hz, 1H), 0.74 (s, 3H), -0.33 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ (ppm) 146.9, 146.3, 141.6, 137.3, 131.9, 129.9, 129.2, 129.0, 128.5, 128.1, 127.1, 127.1, 73.0, 65.2, 59.7, 43.5, 39.7, 35.7, 15.8, -1.0; IR (thin film): 3314.07, 2956.34, 1245.79, 1073.19, 874.56, 852.382, 834.062, 700.998 cm^{-1}; HRMS (ESI-TOF) calculated for $C_{26}H_{32}O_2SiNa^+$ [M+Na$^+$] 427.2069, found 427.2068.



Hydrindane 16: To a solution of alkyne **15** (112 mg, 1.0 mmol) in PhMe (6.0 mL) was added Ti(O*i*-Pr)$_4$ (0.30 mL, 1.0 mmol) at rt. The mixture was cooled to –78 °C and *n*-BuLi (2.49 M in hexanes, 0.80 mL, 2.0 mmol) was added dropwise (by syringe) over the course of 5 min. After this period, the flask was taken out of the cooling bath and allowed to warm to rt (approx. 20 min). The reaction mixture was then heated to 50 °C (no reflux condenser required) for 1 h and allowed to cool to rt before it was placed into a –78 °C bath. In the meantime, enyne **13**[2] (92 mg, 0.30 mmol) was dissolved in PhMe (4.0 mL), treated with *n*-BuLi (2.49 M in hexane, 0.33 mmol, 0.13 mL) at –78 °C, and the resulting alkoxide solution was allowed to warm to rt before it was added dropwise (by syringe) to the black Ti-alkyne complex solution at –78 °C. The reaction mixture was then allowed to warm to rt overnight (approx. 15 h). A separate flame-dried round bottom flask was charged with *t*-butylhydroperoxide (2.0 mmol, 0.36 mL, 5.5 M in decane), diluted with toluene (2 mL), and cooled to –78 °C. To this *t*-butylhydroperoxide solution in toluene was added *n*-BuLi (2.49 M in hexane, 0.80 mL, 2.0 mmol) at –78 °C under N_2. The mixture was stirred for 10 min at –78 °C, warmed to rt, and stirred for an additional 5 min. In the mean time, the black Ti-alkyne complex solution was cooled to –78 °C. The resulting lithium *t*-butylperoxide solution in toluene was cannula transferred (teflon cannula was used) to the Ti-alkyne complex solution at –78 °C. The resulting mixture was slowly warmed to rt, stirred for 30 min, and quenched with 20 mL of saturated $NaHCO_3$ (aq). The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (30 ml X 2). The organic layers were combined, dried over Na_2SO_4, and concentrated *in vacuo*. Purification of the crude product by flash chromatography afforded hydrindane **16** (41.1 mg, 40%, amorphous white solid). Spectral data for **16**: ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.37 (t, 2H), 7.31 – 7.23 (m, 3H), 4.92 – 4.82 (m, 1H), 4.28 (app. d, *J*=5.2 Hz, 2H), 3.15 (dd, *J*=18.6, 8.5 Hz, 1H), 2.89 (d, *J*=10.1 Hz, 1H), 2.59 (dd, *J*=18.5, 8.1 Hz, 1H), 2.17, 2.07 (ABq, *J*=16.2 Hz, 2H), 2.02 (app. d, *J*=2.4 Hz, 3H), 1.70 (app. d, *J*=4.0 Hz, 1H), 1.13 (app. t, *J*=5.2 Hz, 1H), 0.58 (s, 3H), 0.10 (s, 9H); ^{13}C NMR ($CDCl_3$,150 MHz): δ (ppm) 146.8, 140.2, 137.4, 129.9, 128.9, 128.4, 128.3, 127.0, 73.1, 65.2, 59.9, 43.5, 40.0, 35.6, 18.6, 15.6, -0.2; IR (thin film): 3346.85, 2955.38, 1453.10, 1247.72, 1073.19, 835.026, 700.034 cm^{-1}; HRMS (ESI-TOF) calculated for $C_{21}H_{30}O_2SiNa^+$ [M+Na$^+$] 365.1913, found 365.1915.

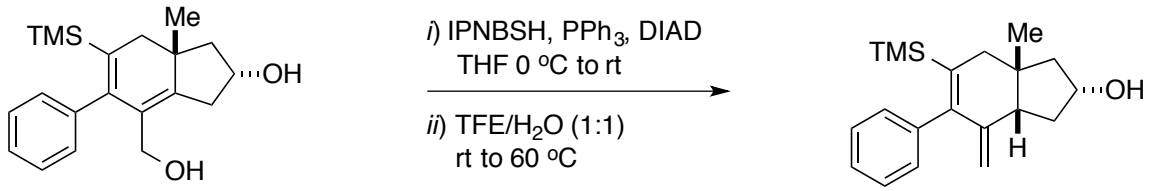


Hydrindane 18: To a solution of alkyne **17** (325 mg, 1.0 mmol) in PhMe (6.0 mL) was added Ti(O*i*-Pr)$_4$ (0.30 mL, 1.0 mmol) at rt. The mixture was cooled to –78 °C and *n*-BuLi (2.49 M in hexanes, 0.80 mL, 2.0 mmol) was added dropwise (by syringe) over the course of 5 min. After this period, the flask was taken out of the cooling bath and allowed to warm to rt (approx. 20 min). The reaction mixture was then heated to 50 °C (no reflux condenser required) for 1 h and allowed to cool to rt before it was placed into a –78 °C bath. In the meantime, enyne **11**[2] (69 mg, 0.30 mmol) was dissolved in PhMe (4.0 mL), treated with *n*-BuLi (2.49 M in hexane, 0.33 mmol, 0.13 mL) at –78 °C, and the resulting alkoxide solution was allowed to warm to rt before it was added dropwise (by syringe) to the black Ti-alkyne complex solution at –78 °C. The reaction mixture was then allowed to warm to rt overnight (approx. 15 h). A separate flame-dried round bottom flask was charged with *t*-butylhydroperoxide (2.0 mmol, 0.36 mL, 5.5 M in decane), diluted with toluene (2 mL), and cooled to –78 °C. To this *t*-butylhydroperoxide solution in toluene was added *n*-BuLi (2.49 M in hexane, 0.80 mL, 2.0 mmol) at –78 °C under N_2.The mixture was stirred for 10 min at –78 °C, warmed to rt, and stirred for an additional 5 min. In the mean time, the black Ti-alkyne complex solution was cooled to –78 °C. The resulting lithium *t*-butylperoxide solution in toluene was cannula transferred (teflon cannula was used) to the Ti-alkyne complex solution at –78 °C. The resulting mixture was slowly warmed to rt, stirred for 30 min, and quenched with 20 mL of saturated $NaHCO_3$ (aq). The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (30 ml X 2). The organic layers were combined, dried over Na_2SO_4, and concentrated *in vacuo*. Purification of the crude product by flash chromatography afforded hydrindane **18** (57.4 mg, 40%, colorless oil). Spectral data for **18**: ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.32 (d, 2H), 7.18 (t, 1H), 6.91 (d, 2H), 6.86 – 6.77 (m, 3H), 4.94 (s, 2H), 4.54 – 4.45 (m, 1H), 4.04, 3.92 (ABq, *J*=11.9 Hz, 2H), 3.84, 3.79 (ABq, 2H), 3.81 (s, 3H), 2.80 (dd, *J*=17.9, 7.2 Hz, 1H), 2.47 (dd, *J*=17.7, 5.5 Hz, 1H), 2.34, 2.20 (ABq, *J*=16.2 Hz, 2H), 2.11 (dd, *J*=12.7, 6.0 Hz, 1H), 1.90 (br. s, 1H), 1.57 (dd, *J*=12.7, 6.9 Hz, 1H), 1.27 (s, 1H), 0.97 (s, 3H), 0.17 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ (ppm) 159.4, 159.0, 149.8, 142.6, 141.8, 132.1, 129.4, 129.1, 128.9, 120.8, 114.4, 114.0, 112.9, 71.9, 69.6, 59.7, 55.3, 50.7, 41.4, 39.3, 38.1, 21.3, 0.2; IR (thin film) 3583.09, 3388.32, 2918.73, 1583.27, 1441.53, 1247.72, 1063.55 cm^{-1}; HRMS (ESI-TOF) calculated for $C_{29}H_{38}O_4SiNa^+$ [M+Na$^+$] 501.2437, found 501.2437.



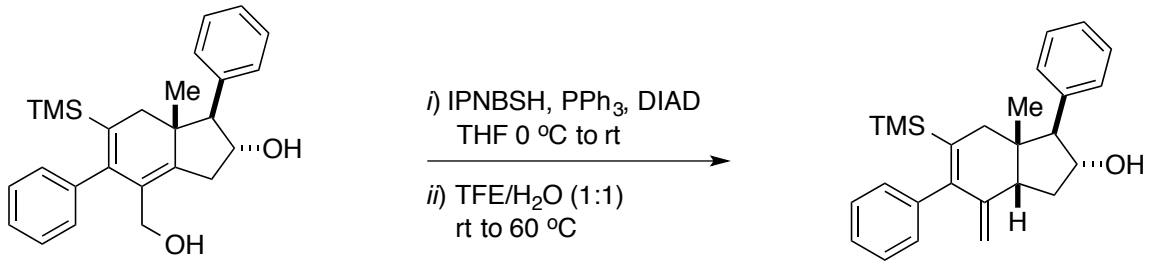
Hydrindane 21: To a solution of alkyne **19** (204 mg, 1.0 mmol) in PhMe (6.0 mL) was added Ti(O*i*-Pr)$_4$ (0.30 mL, 1.0 mmol) at rt. The mixture was cooled to –78 °C and *n*-BuLi (2.49 M in hexanes, 0.80 mL, 2.0 mmol) was added dropwise (by syringe) over the course of 5 min. After this period, the flask was taken out of the cooling bath and allowed to warm to rt (approx. 20 min). The reaction mixture was then heated to 50 °C (no reflux condenser required) for 1 h and allowed to cool to rt before it was placed into a –78 °C bath. In the meantime, enyne **20** (87 mg, 0.30 mmol) was dissolved in PhMe (4.0 mL), treated with *n*-BuLi (2.49 M in hexane, 0.33 mmol, 0.13 mL) at –78 °C, and the resulting alkoxide solution was allowed to warm to rt before it was added dropwise (by syringe) to the black Ti-alkyne complex solution at –78 °C. The reaction mixture was then allowed to warm to rt overnight (approx. 15 h). A separate flame-dried round bottom flask was charged with *t*-butylhydroperoxide (2.0 mmol, 0.36 mL, 5.5 M in decane), diluted with toluene (2 mL), and cooled to –78 °C. To this *t*-butylhydroperoxide solution in toluene was added *n*-BuLi (2.49 M in hexane, 0.80 mL, 2.0 mmol) at –78 °C under N_2. The mixture was stirred for 10 min at –78 °C, warmed to rt, and stirred for an additional 5 min. In the mean time, the black Ti-alkyne complex solution was cooled to –78 °C. The resulting lithium *t*-butylperoxide solution in toluene was cannula transferred (teflon cannula was used) to the Ti-alkyne complex solution at –78 °C. The resulting mixture was slowly warmed to rt, stirred for 30 min, and quenched with 20 mL of saturated $NaHCO_3$ (aq). The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (30 ml X 2). The organic layers were combined, dried over Na_2SO_4, and concentrated *in vacuo*. Purification of the crude product by flash chromatography afforded hydrindane **21** (60.4 mg, 54%, amorphous white solid). Spectral data for **21**: ^{1}H NMR ($CDCl_3$, 600 MHz): δ (ppm) 7.16 (br. s, 1H), 6.97 (br. s, 1H), 6.86 (br. s, 2H), 4.04 – 3.95 (m, 2H), 3.84 – 3.78 (m, 4H), 3.04 (dd, *J*=18.9, 8.6 Hz, 1H), 2.41 (dd, *J*=18.7, 8.1 Hz, 1H), 2.34, 2.07 (ABq, *J*=15.8 Hz, 2H), 1.77 (br. s, 1H), 1.65 (dq, *J*=9.5, 6.8 Hz, 1H), 1.07 (d, *J*=7.0 Hz, 3H), 0.99 (br. s, 1H), 0.82 (s, 3H), -0.23 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ (ppm) 158.7, 147.7, 145.7, 134.0, 132.1, 131.0, 130.2, 128.8, 113.5, 113.3, 77.0, 59.8, 55.2, 53.5, 41.5, 39.5, 36.7, 14.9, 11.1, -0.8; IR (thin film): 3335.28, 2955.38, 1506.13, 1244.83, 1034.62, 868.774, 834.062 cm^{-1}; HRMS (ESI-TOF) Calculated for $C_{22}H_{33}O_3Si$ $[M + H]^+$ 373.2193, found 373.2196.

D. Synthesis of Hydrindanes 25, 26, and 27 via IPNBSH-mediated Allylic Diazene Rearrangement.



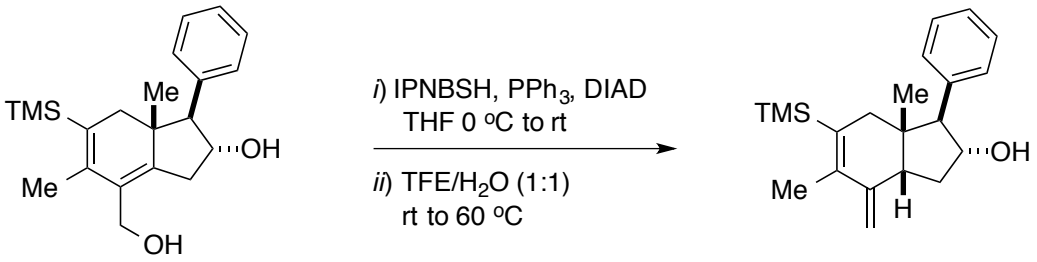
12 **25**

Hydrindane 25: To a solution of hydrindane **12** (50.0 mg, 0.15 mmol), PPh_3 (60 mg, 0.23 mmol), and IPNBSH (59.0 mg, 0.23 mmol) in THF (1.5 mL) was added DIAD (46.2 mg, 0.23 mmol) dropwise (by syringe) at 0 °C. The reaction mixture was warmed to rt, The mixture was stirred for 2 h at rt, and 1 mL of a TFE/H_2O mixture (1:1) was added. The reaction mixture was stirred for 2 h at rt, warmed to 60 °C, and stirred until all of the starting material was converted to **25** via TLC analysis. The reaction mixture was diluted with 20 mL of ethyl acetate and washed with brine (10 mL). The organic layer was separated, and the aqueous layer was extracted with 60 mL ethyl acetate (20 mL X 3). The organic layers were combined, dried over Na_2SO_4, and concentrated *in vacuo*. Purification of the crude product by flash chromatography afforded *cis*-hydrindane **25**[2] (29.5 mg, 63%, colorless oil). The spectral properties matched literature values.

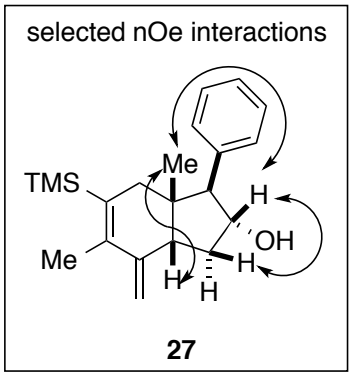


14 **26**

Hydrindane 26: To a solution of hydrindane **14** (22.0 mg, 0.054 mmol), PPh_3 (21.4 mg, 0.081 mmol), and IPNBSH (20.9 mg, 0.81 mmol) in THF (0.5 mL) was added DIAD (16.5 mg, 0.081 mmol) dropwise (by syringe) at 0 °C. The reaction mixture was warmed to rt, The mixture was stirred for 2 h at rt, and 1 mL of a TFE/H_2O mixture (1:1) was added. The reaction mixture was stirred for 2 h at rt, warmed to 60 °C, and stirred until all of the starting material was converted to **26** via TLC analysis. The reaction mixture was diluted with 20 mL of ethyl acetate and washed with brine (10 mL). The organic layer was separated, and the aqueous layer was extracted with 60 mL ethyl acetate (20 mL X 3). The organic layers were combined, dried over Na_2SO_4, and concentrated *in vacuo*. Purification of the crude product by flash chromatography afforded *cis*-hydrindane **26**[2] (11.9 mg, 57%, colorless oil). The spectral properties matched the literature values**.**



16 **27**



27

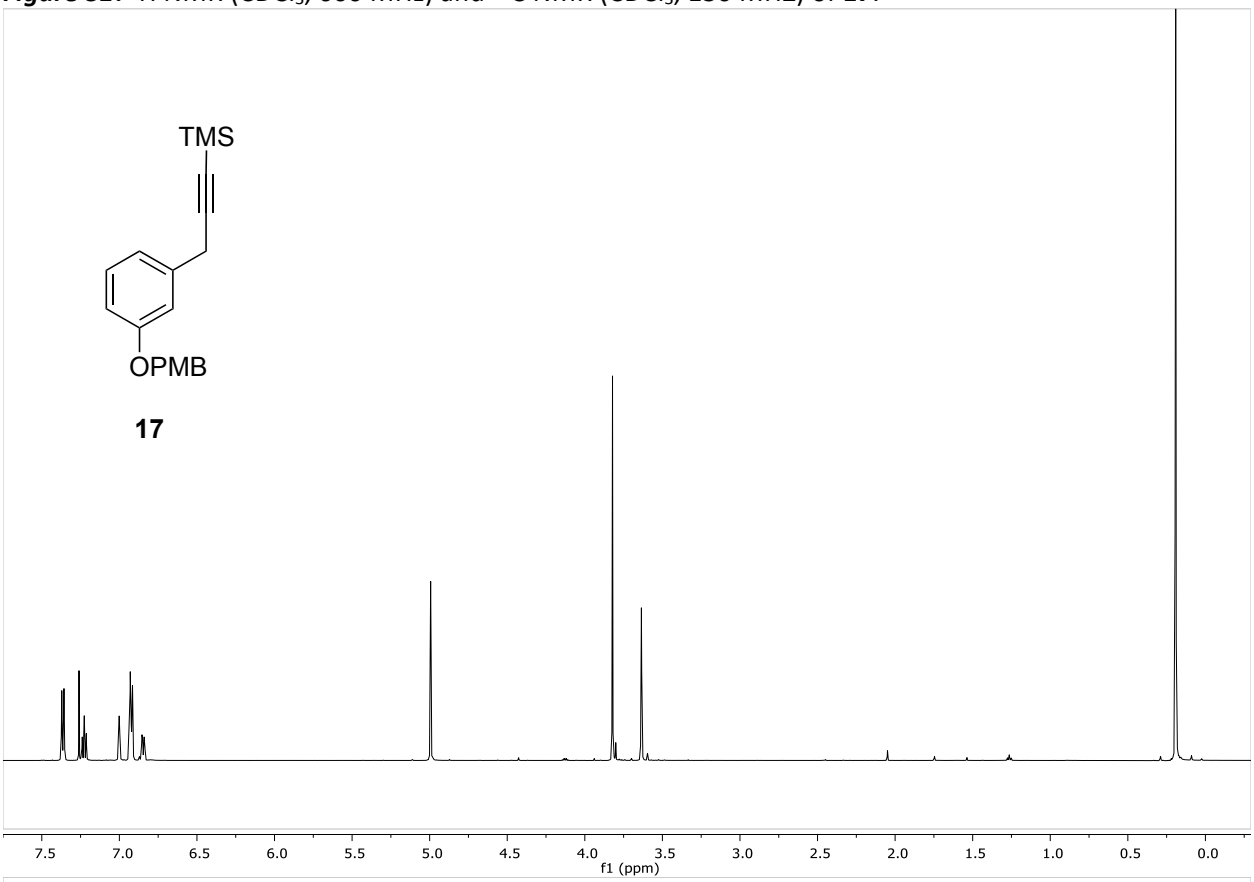
Hydrindane 27: To a solution of hydrindane **16** (16 mg, 0.047 mmol), PPh_3 (18.4 mg, 0.071 mmol), and IPNBSH (18 mg, 0.071 mmol) in THF (0.5 mL) was added DIAD (14.2 mg, 0.071 mmol) dropwise (by syringe) at 0 °C. The reaction mixture was warmed to rt, The mixture was stirred for 2 h at rt, and 1 mL of a TFE/H_2O mixture (1:1) was added. The reaction mixture was stirred for 2 h at rt, warmed to 60 °C, and stirred until all of the starting material was converted to **27** via TLC analysis. The reaction mixture was diluted with 20 mL of ethyl acetate and washed with brine (10 mL). The organic layer was separated, and the aqueous layer was extracted with 60 mL ethyl acetate (20 mL X 3). The organic layers were combined, dried over Na_2SO_4, and concentrated *in vacuo*. Purification of the crude product by flash chromatography afforded *cis*-hydrindane **27** (9.2 mg, 60%, colorless oil). Spectral data for **27**: ^{1}H NMR ($CDCl_3$, 600 MHz): δ (ppm) 7.33 (t, 2H), 7.25 (t, 1H), 7.17 (d, *J*=7.0 Hz, 2H), 5.07 (s, 1H), 4.87 (s, 1H), 4.66 - 4.58 (m, 1H), 2.73 (d, *J*=7.3 Hz, 1H), 2.56 (dd, *J*=10.5, 7.9 Hz, 1H), 2.45 (dt, *J*=12.8, 7.3 Hz, 1H), 2.34, 1.86 (ABq, *J*=16.5 Hz, 2H), 2.02 (s, 3H), 1.70 - 1.63 (m, 2H), 0.55 (s, 3H), 0.21 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ (ppm) 148.0, 141.1, 140.9, 134.4, 129.1, 128.2, 126.5, 109.6, 76.7, 63.7, 49.9, 43.2, 41.7, 40.3, 24.7, 20.2, 0.3; IR (thin film): 3365.17, 2952.48, 2922.59, 1453.10, 1248.68, 1055.84, 880.345, 834.062 cm^{-1}; HRMS (ESI-TOF) calculated for $C_{21}H_{31}OSi^+$ [M+H$^+$] 327.2144, found 327.2143

Notes:

1. Lee, Y. S.; Kim, H. Y.; Kim, Y.; Seo, J. H.; Roh, E. J.; Han, H.; Shin, K. J. Bioorg. Med. Chem. **2012,** *20* 4921–4935
2. Jeso, V.; Aquino, C.; Cheng, X.; Mizoguchi, H.; Nakashige, M.; Micalizio, G. C. *J. Am. Chem. Soc*. **2014**, *136*, 8209-8212

4. Spectral Data

***Figure S1*:** ^{1}H NMR ($CDCl_3$, 600 MHz) and ^{13}C NMR ($CDCl_3$, 150 MHZ) of **17**.



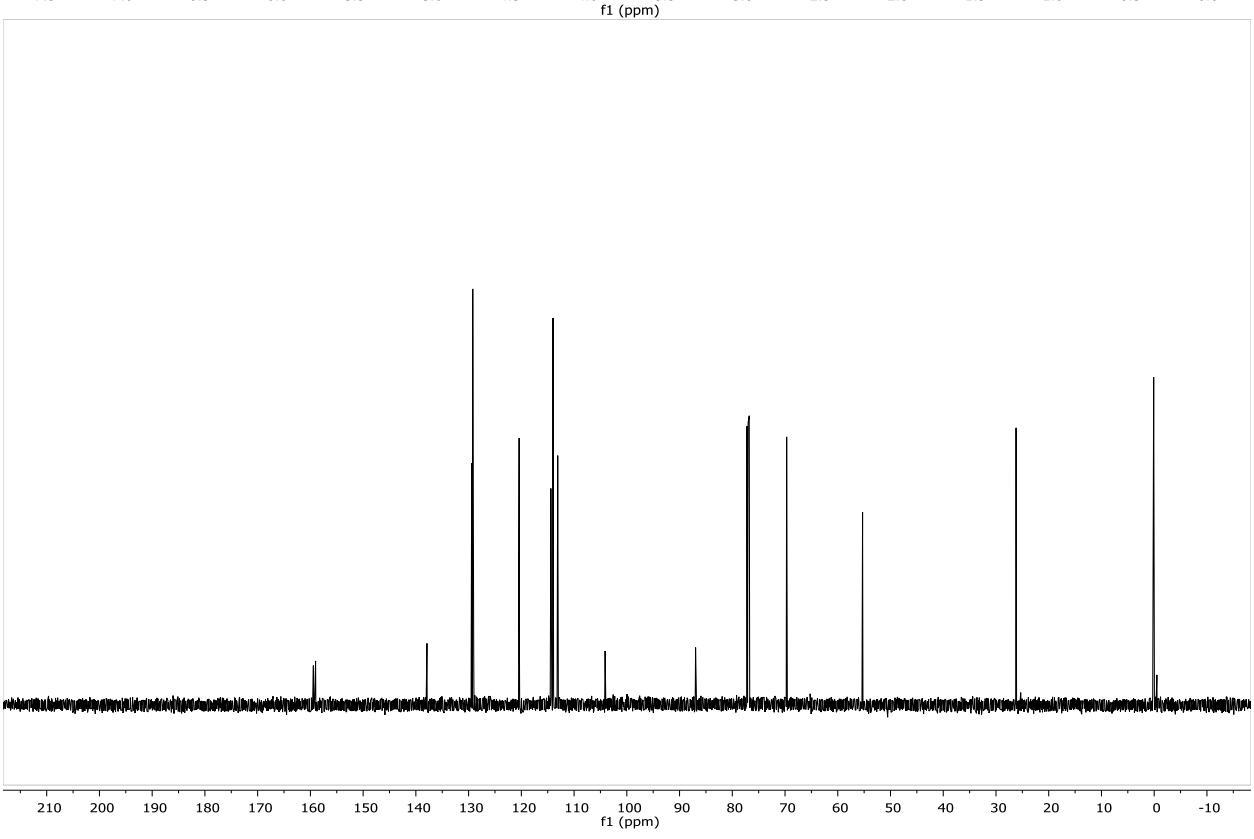


Figure S2: ^{1}H NMR ($CDCl_3$, 600 MHz) and ^{13}C NMR ($CDCl_3$, 150 MHZ) of **20**.

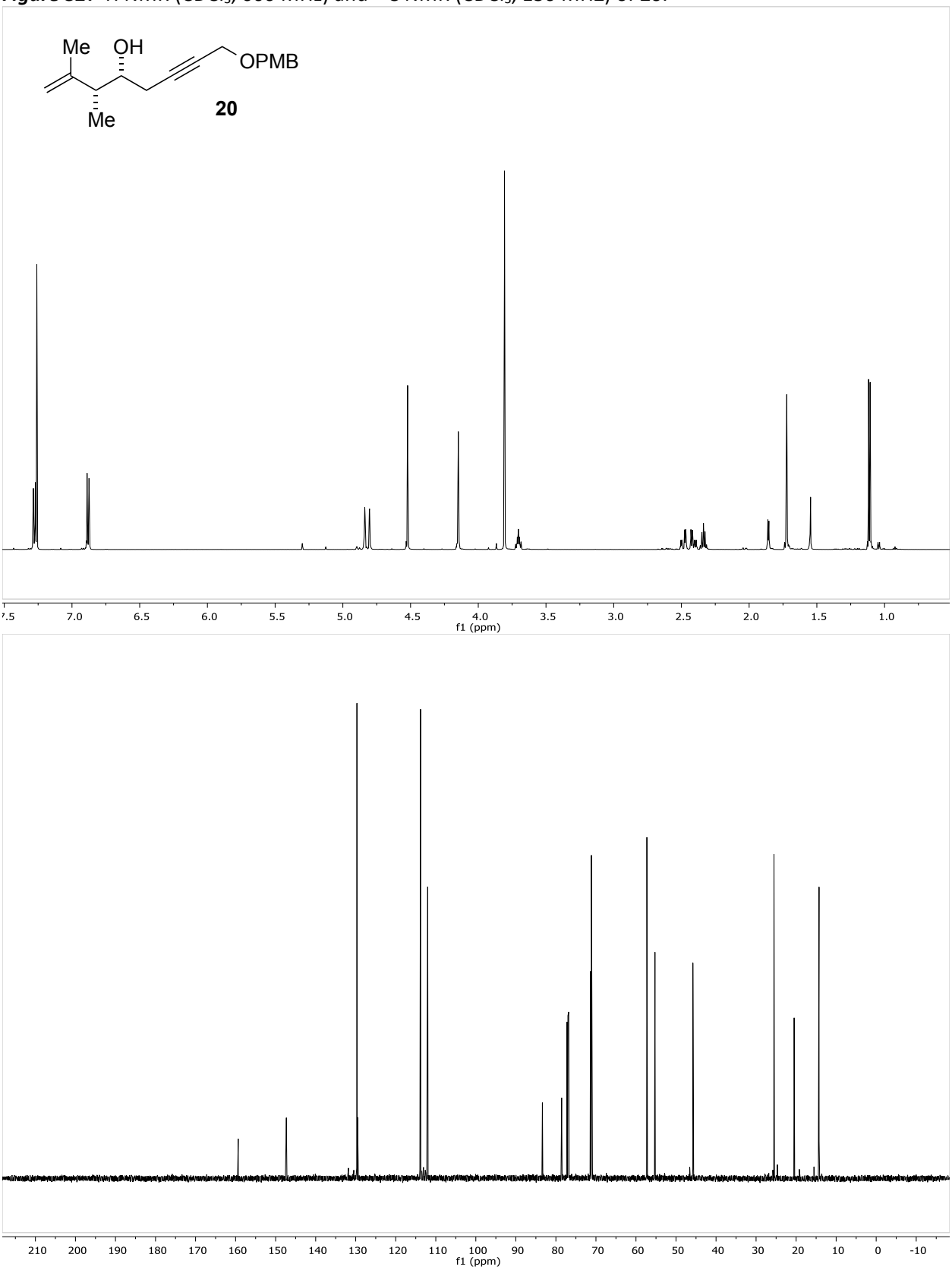


Figure S3: ^{1}H NMR ($CDCl_3$, 600 MHz) and ^{13}C NMR ($CDCl_3$, 150 MHZ) of **12**.

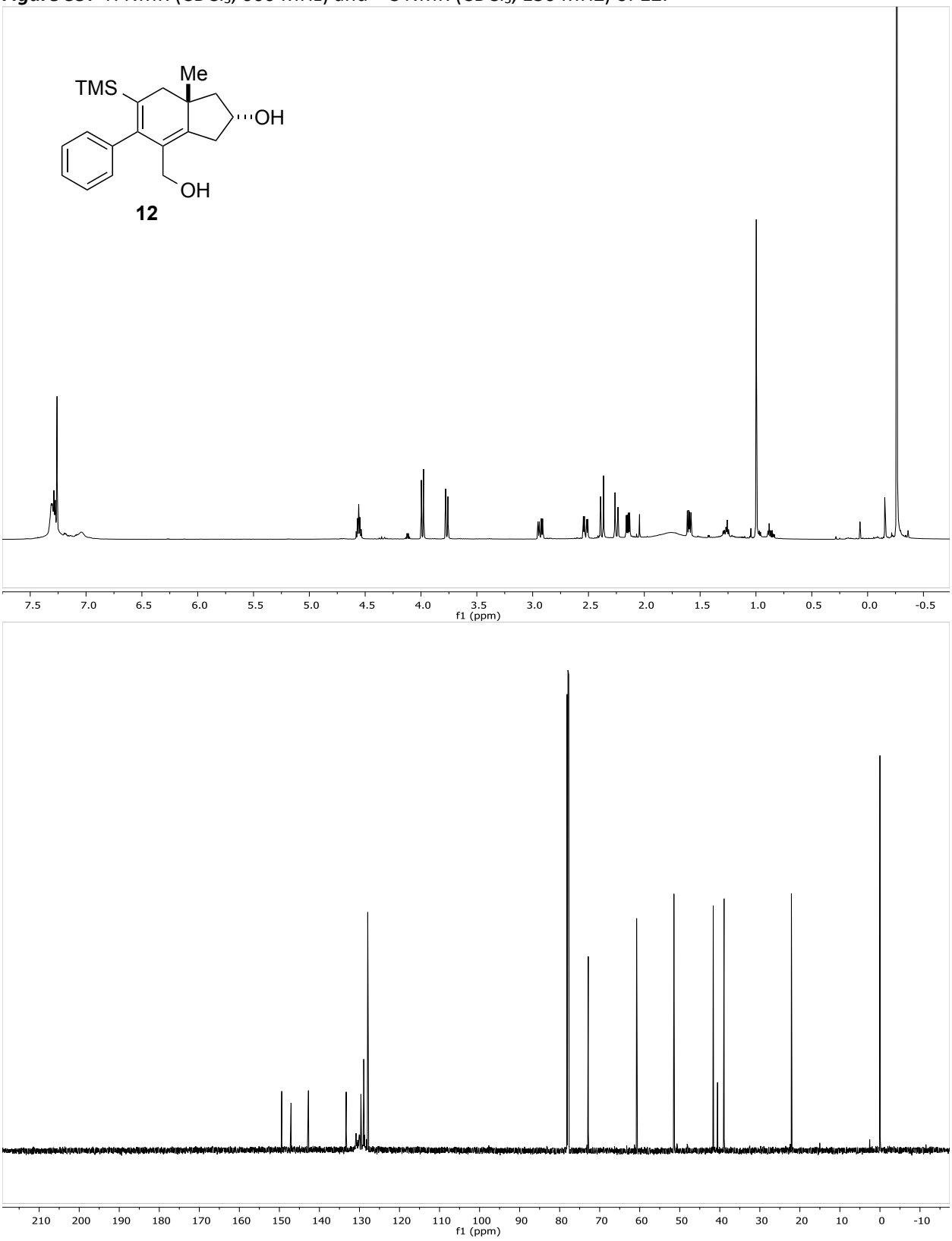


Figure S4: ^{1}H NMR ($CDCl_3$, 600 MHz) and ^{13}C NMR ($CDCl_3$, 150 MHZ) of **14**.

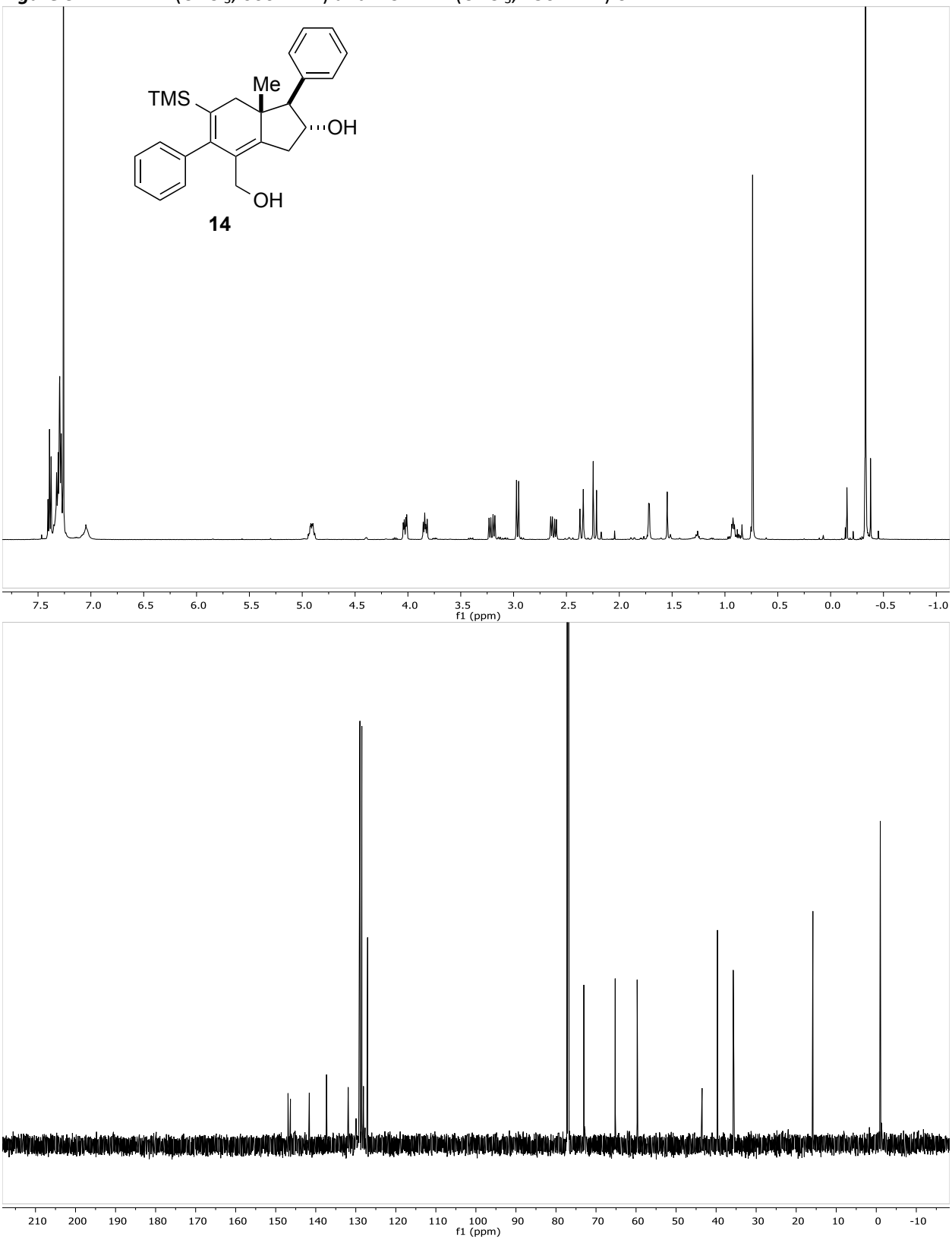


***Figure S5*:** ^{1}H NMR ($CDCl_3$, 600 MHz) and integral comparison of **14** and **S5**.

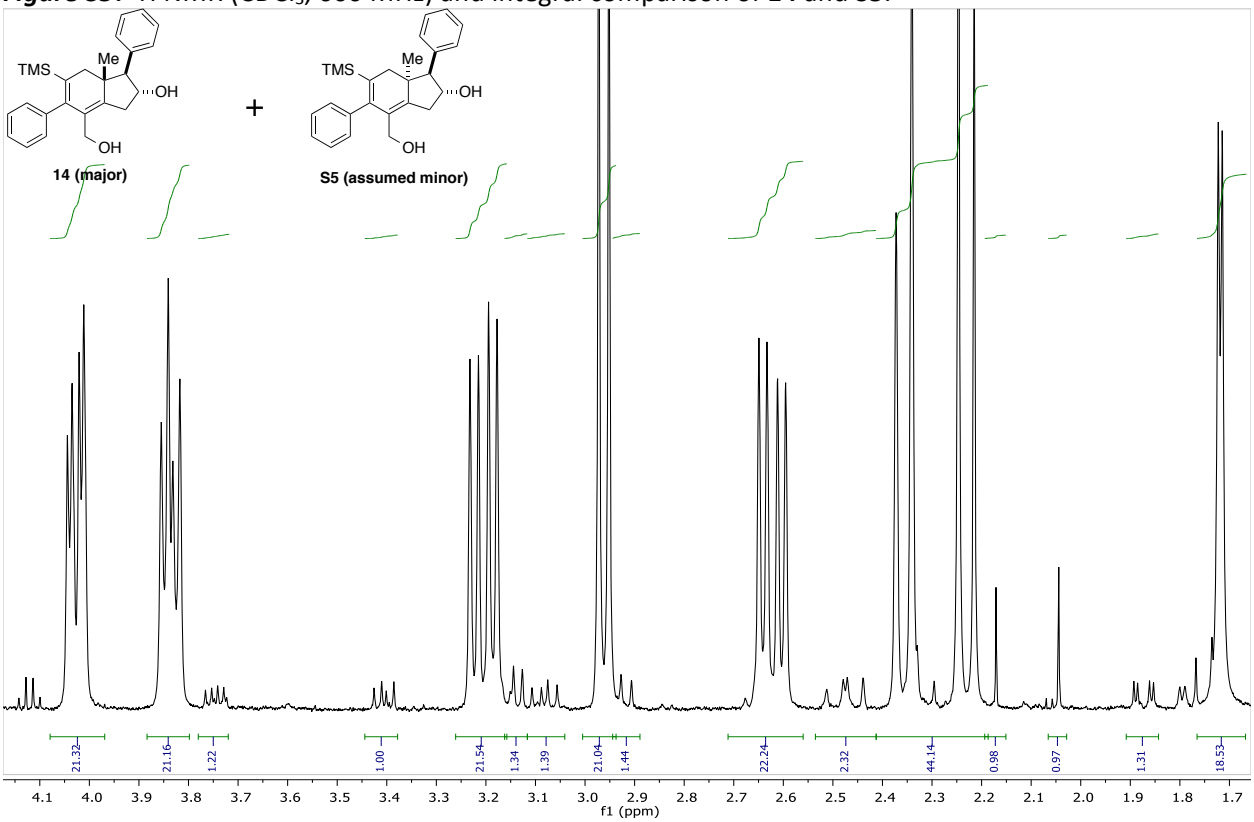


Figure S6: ^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 150 MHZ) of **16**

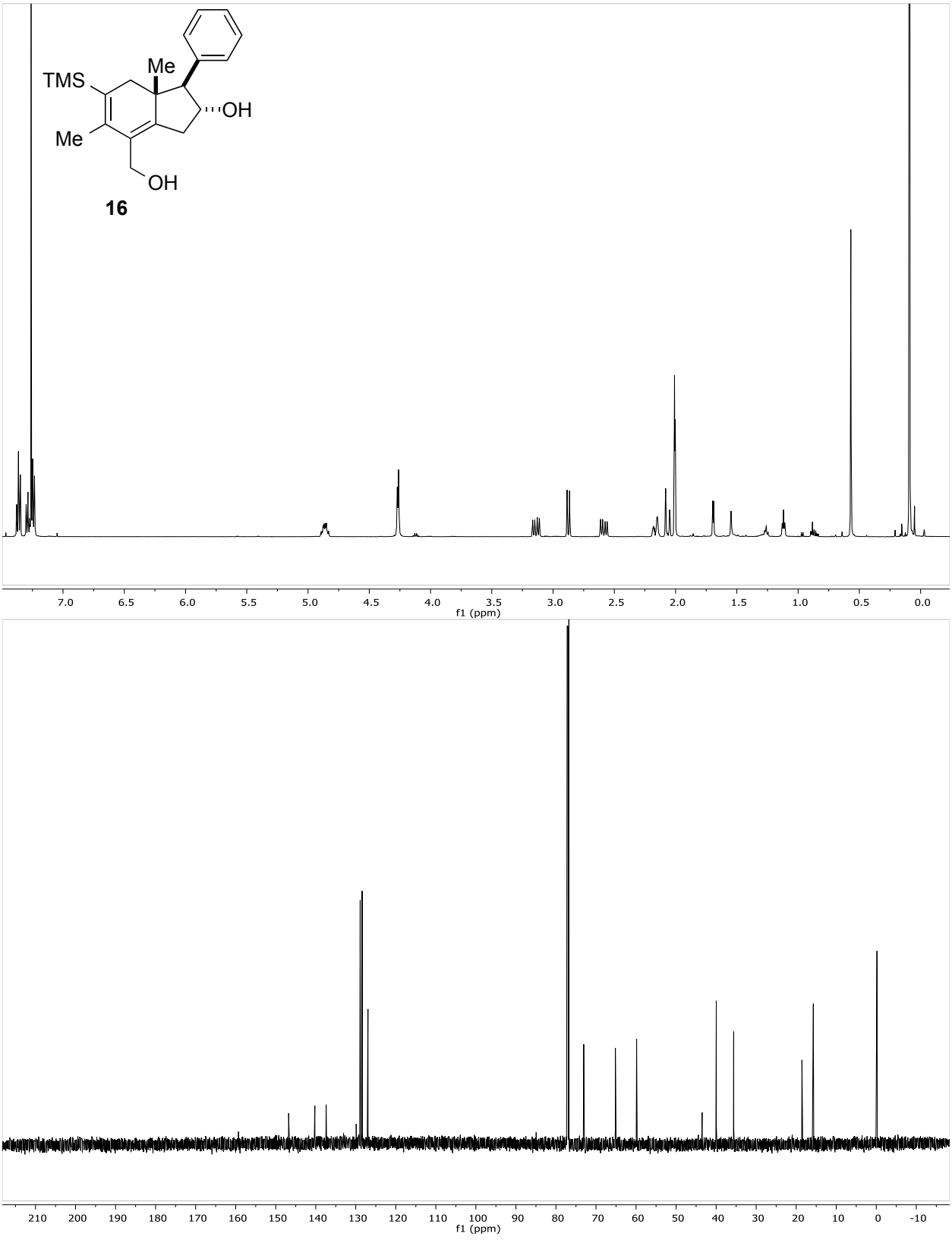


***Figure S7*:** ^{1}H NMR ($CDCl_3$, 600 MHz) and ^{13}C NMR ($CDCl_3$, 150 MHZ) of **18**.

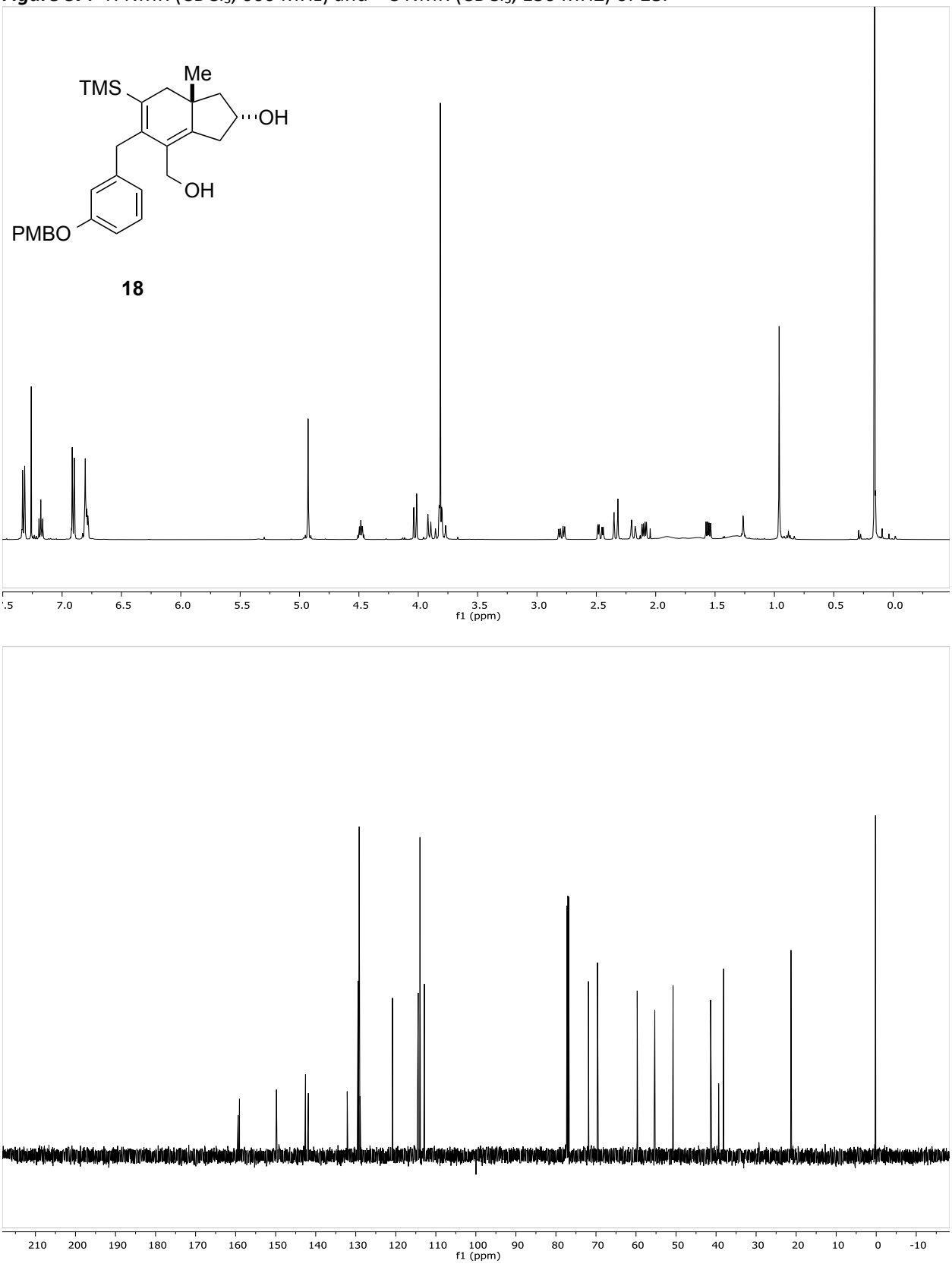
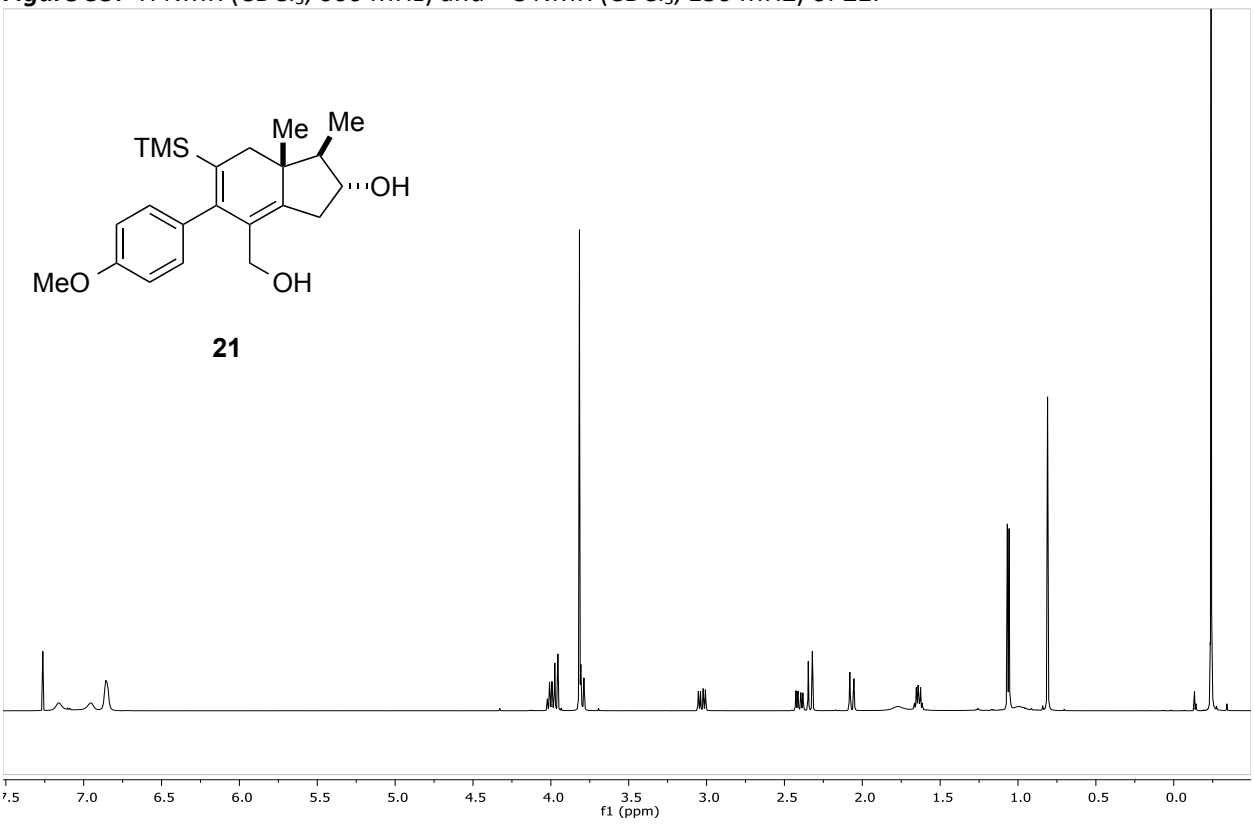


Figure S8: ^{1}H NMR ($CDCl_3$, 600 MHz) and ^{13}C NMR ($CDCl_3$, 150 MHZ) of **21**.



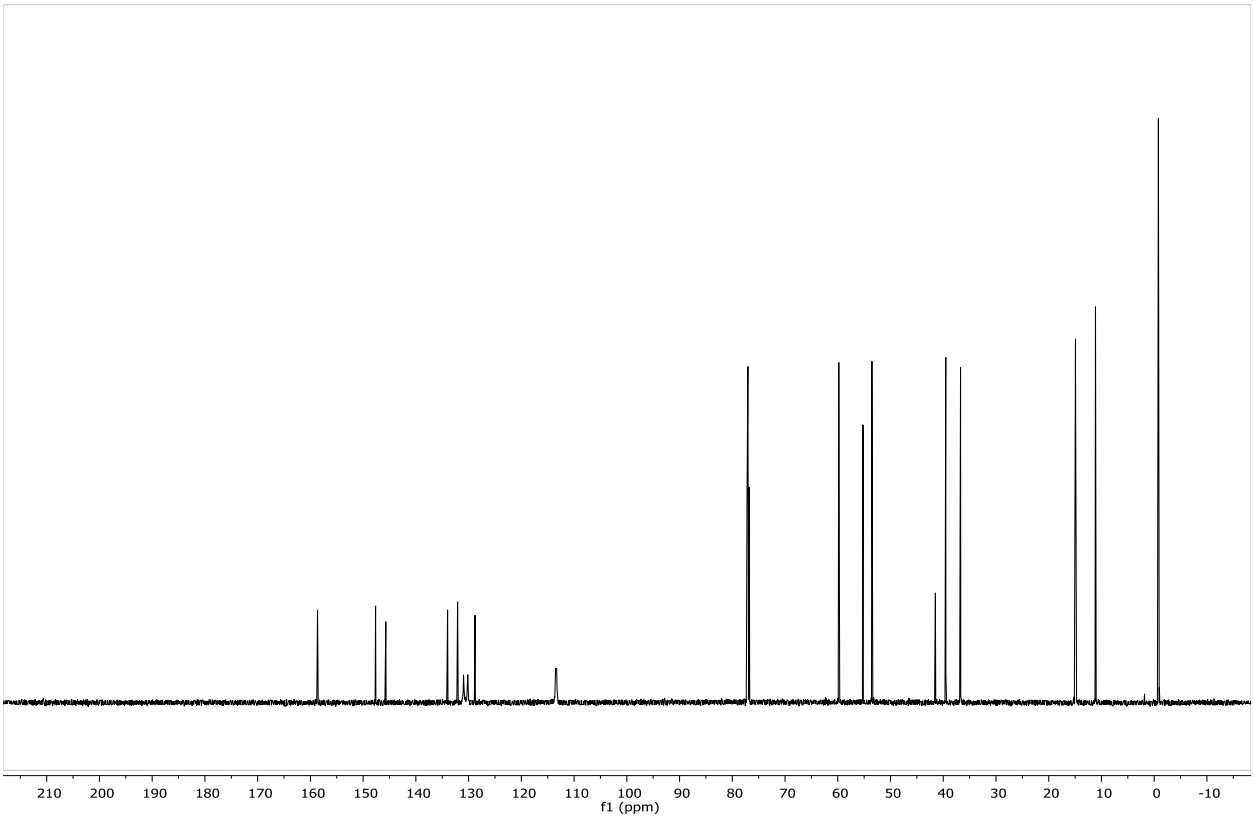


Figure S9: ^{1}H NMR ($CDCl_3$, 600 MHz) and ^{13}C NMR ($CDCl_3$, 150 MHZ) of **25**.

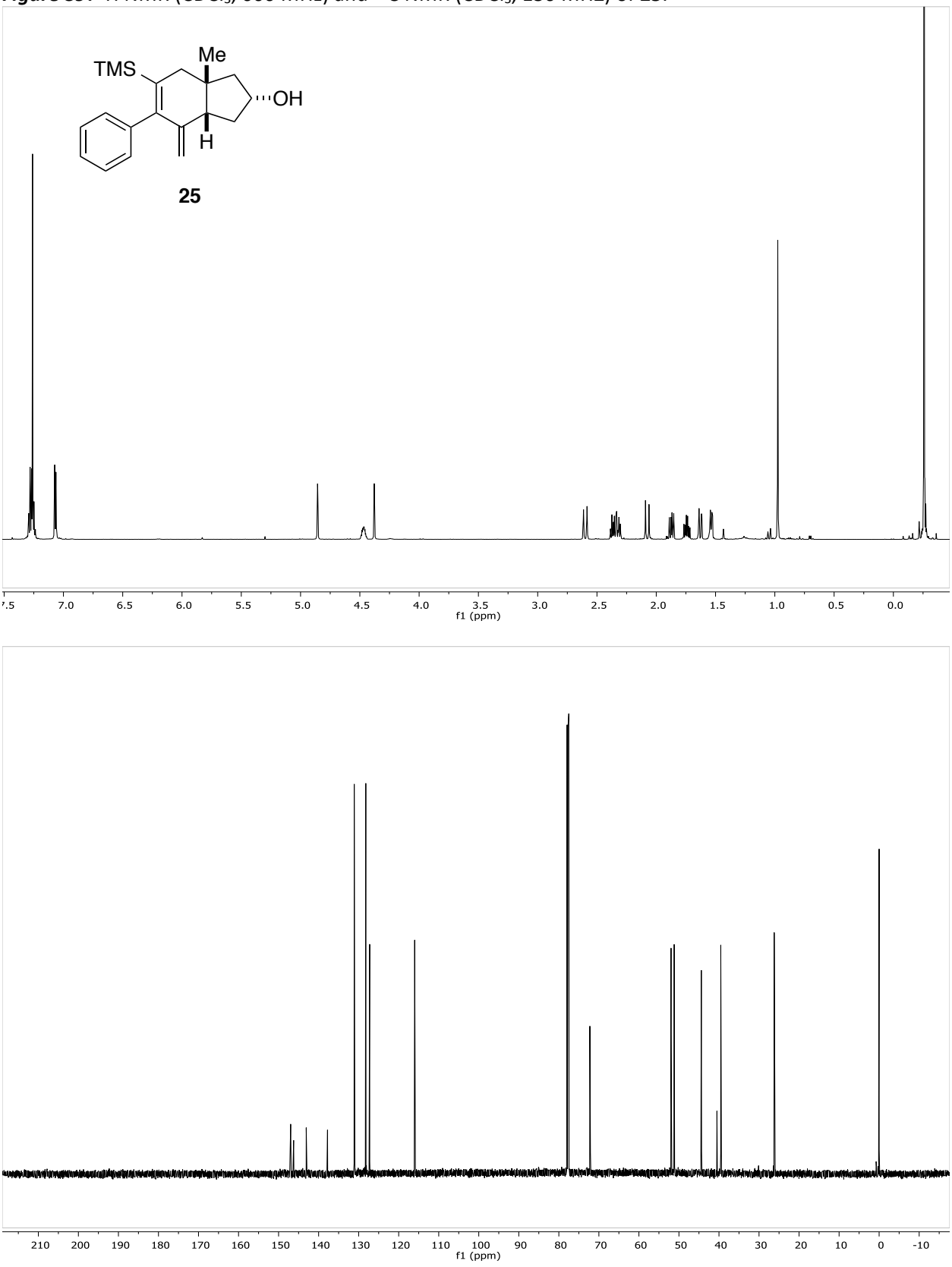


Figure S10: ^{1}H NMR ($CDCl_3$, 600 MHz) of crude **25**.

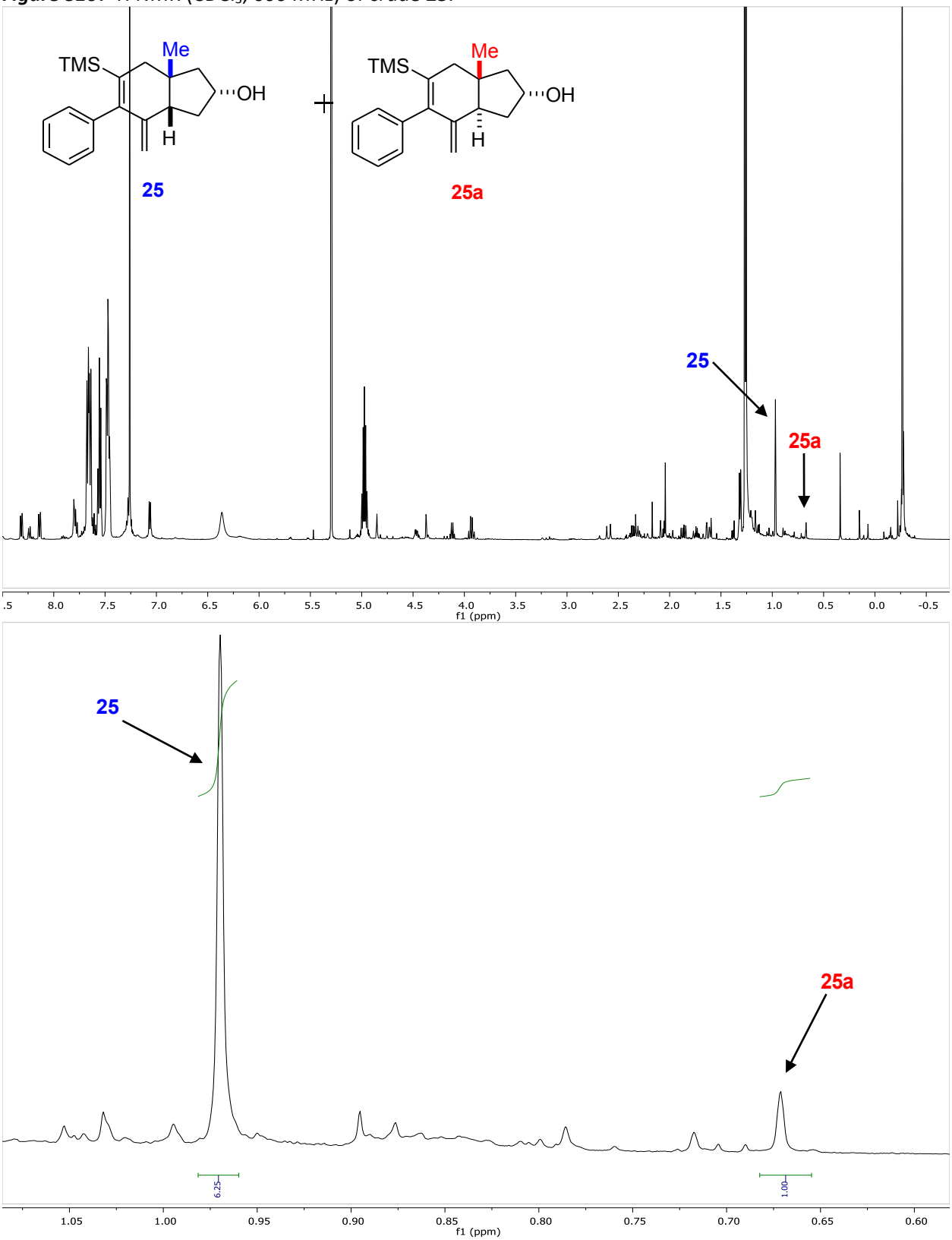
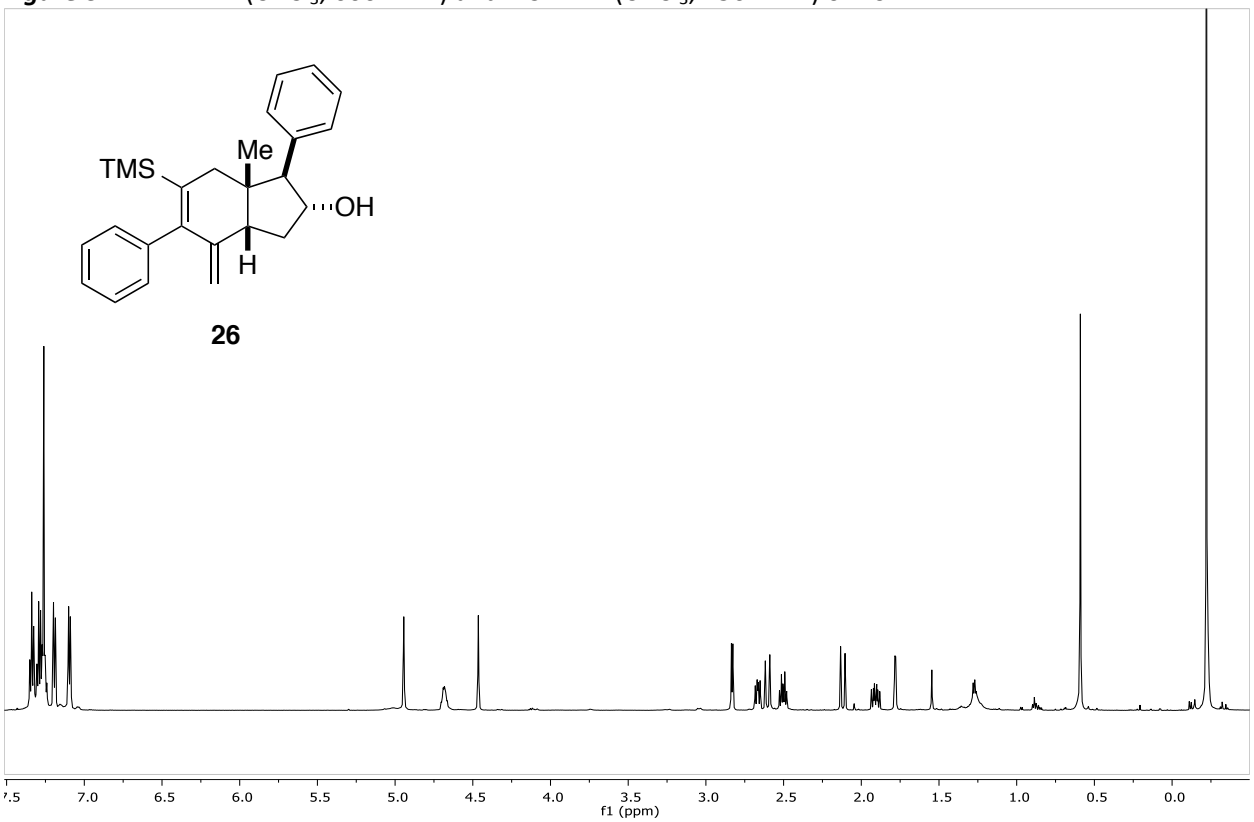


***Figure S11*:** ^{1}H NMR ($CDCl_3$, 600 MHz) and ^{13}C NMR ($CDCl_3$, 150 MHZ) of **26**.



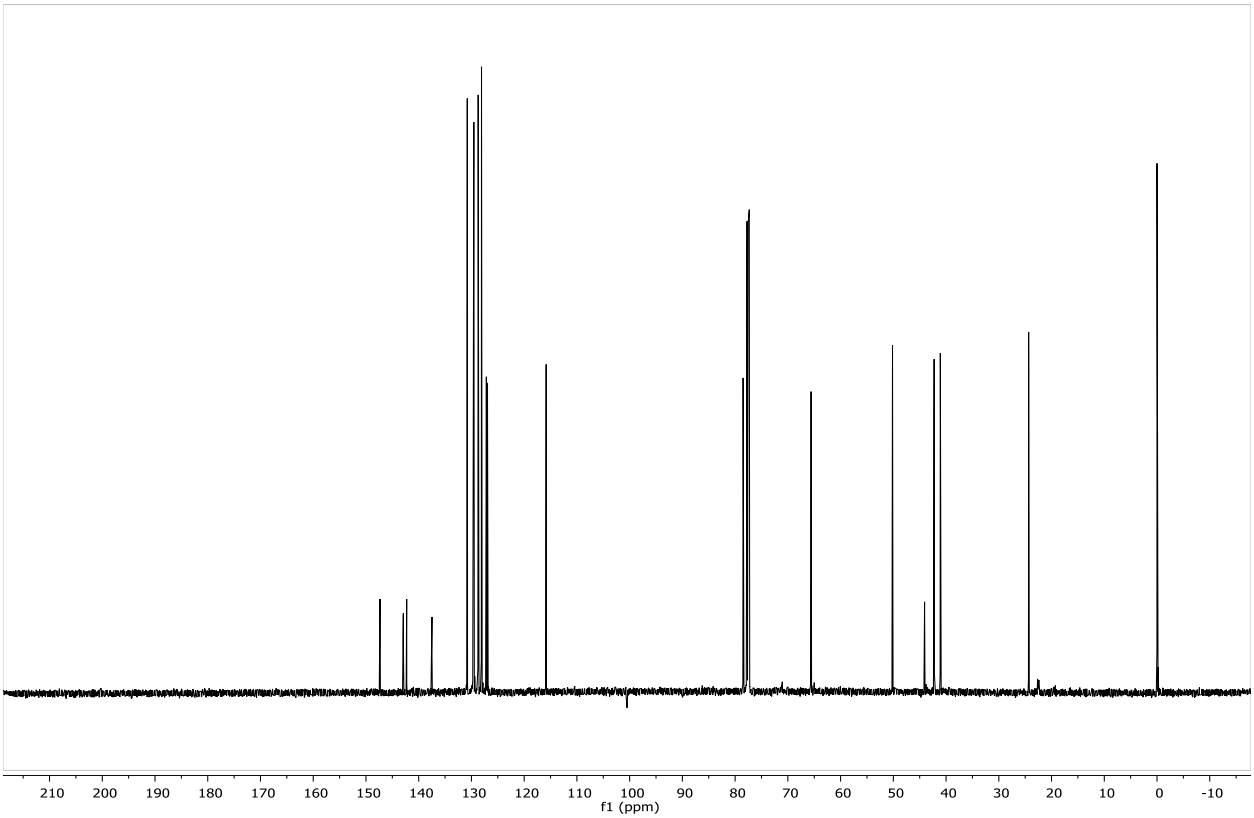


Figure S12: ^{1}H NMR ($CDCl_3$, 600 MHz) of crude **26**.

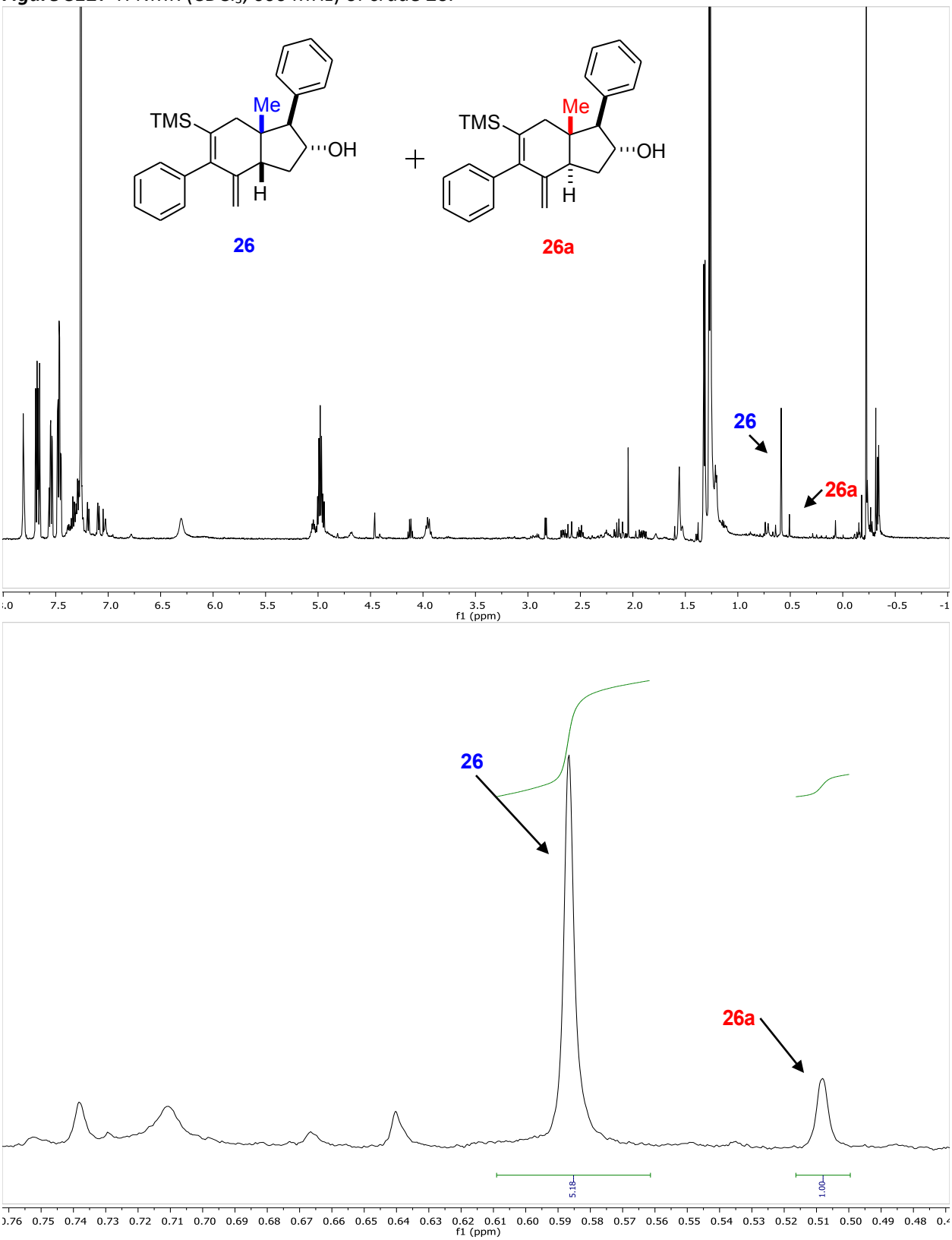


Figure S13: ^{1}H NMR ($CDCl_3$, 600 MHz) and ^{13}C NMR ($CDCl_3$, 150 MHZ) of **27**.

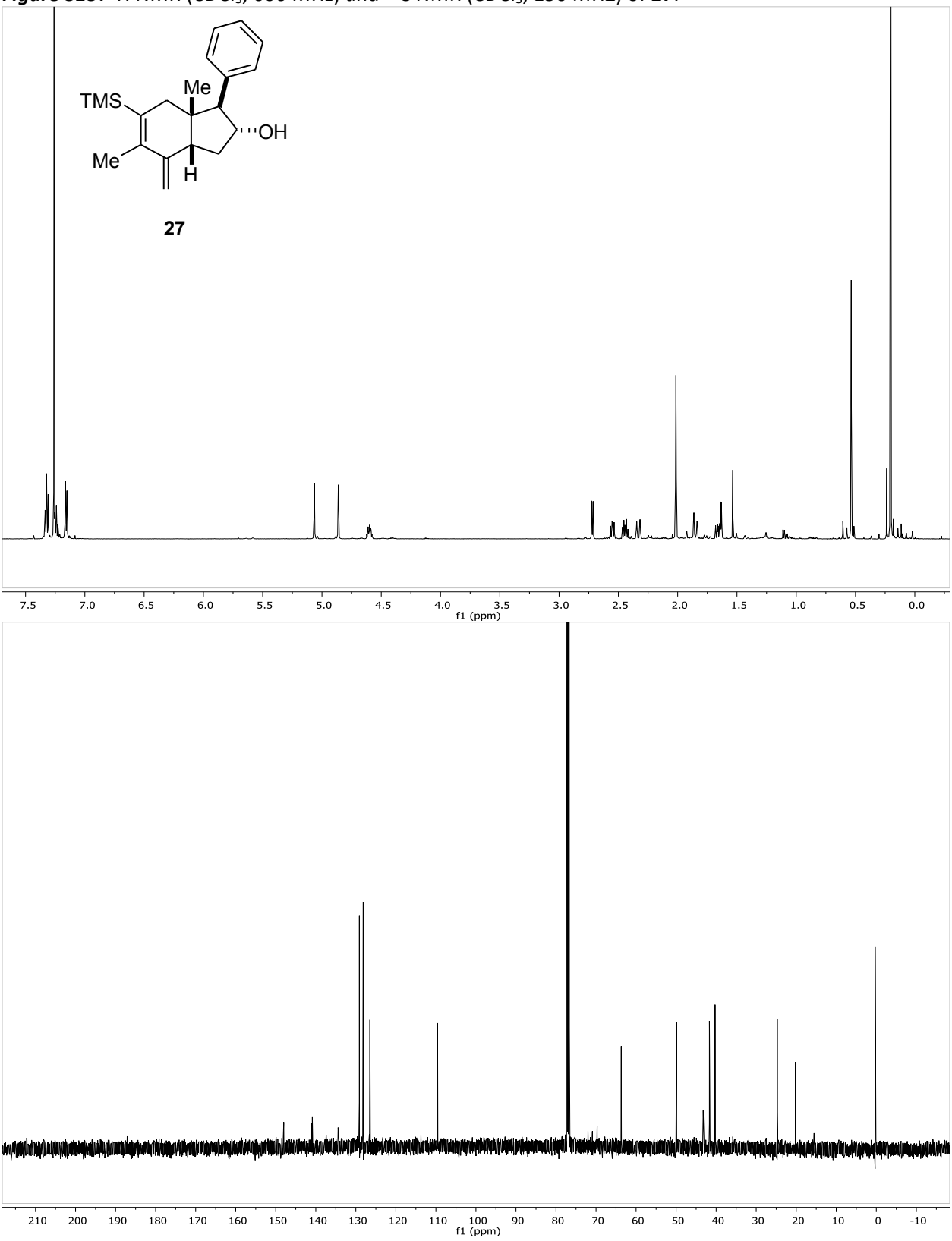


Figure S14: ^{1}H NMR ($CDCl_3$, 600 MHz) of crude **27**