Supplementary Information (SI) for Organic & Biomolecular Chemistry.

Supplementary information

Synthesis of the Tricyclic Skeleton of Aberrarone

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1. General Information

Unless otherwise stated, all reactions were performed with magnetic stirring under a positive pressure of nitrogen or argon gas. Oven-dried glassware (over temperature of 70 ºC) was further dried with a heat-gun at 650 ºC under vacuum, followed by back-filling with inert gas, three times and fitted with rubber septa prior to use. Solids were added under inert gas counter flow or were dissolved and transferred in the appropriate solvent. Solutions and liquids reagents were transferred to reaction vessels by oven-dried stainless-steel cannulas or nitrogen flushed syringes. Low temperature reactions were carried out in a Dewar vessel filled with acetone/dry ice (–78 ºC) or distilled water/ice (0 ºC). High temperature reactions were conducted using a heated silicon oil bath in reaction vessels equipped with a reflux condenser.

Dry Tetrahydrofuran (THF), diethyl ether (Et_2O), Dicholormethane (CH_2Cl_2), triethylamine (Et_3N) and *N,N*-dimethylformamide (DMF), toluene (PhMe), dioxane and methanol (MeOH) were purchased from Adamas Chemical as extra dry regents under inert gas atmosphere and stored over molecular sieves. Ethyl acetate (EtOAc), Et_2O, CH_2Cl_2 (DCM) and MeOH used specifically for extraction and flash column chromatography were purchased at technical grade from commercial sources and distilled under reduced pressure. All other solvents and regents were used as received from commercial sources (Sigma Aldrich, Energy chemical, 3A, Innochem, and Adamas).

Reactions were monitored by thin-layer chromatography (TLC) using silica gel F254 pre-coated glass plates (*Merck*) and visualized by exposure to ultraviolet light (254 nm) or by staining with aqueous potassium permanganate ($KMnO_4$) solution (7.5 g $KMnO_4$, 50 g K_2CO_3, 6.25 mL aqueous 10% NaOH, 1000 mL distilled H_2O), Phosphomolybdic acid hydrate (PMA) solution (10.0 g PMA, 100 mL EtOH) followed by heating with a heat gun (150-600 ºC). Flash column chromatography was performed using silica gel (60 Å, 40-63 µm, *Merck*) and a forced flow of eluent.

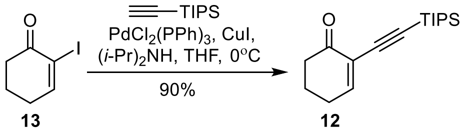
Proton (^1H) and carbon (^{13}C) nuclear magnetic resonance spectra were recorded on a Brucker Avance III HD 500 MHz spectrometer equipped with a CroProbeTM. Proton chemical shifts are expressed in parts per million (ppm, δ scale) and referenced to residual undeuterated solvent signals ($CDCl_3$: 7.26 ppm; C_6D_6: 7.16 ppm). Carbon chemical shifts are expressed in parts per million (ppm, δ scale) and referenced to the central carbon resonance of the solvent ($CDCl_3$: 77.16 ppm; C_6D_6: 128.06 ppm). The reported data is represented as follows: chemical shift in parts per million (ppm, δ scale) (multiplicity, coupling constants *J* in Hz, integration intensity, proton assignment).

Abbreviations used for analysis of multiplets are as follows: s (singlet), br s (broad singlet), d (doublet), t (triplet), q (quartet), quin (quintet), h (hextet), and m (multiplet). Variable temperature NMR spectroscopy was performed at the Northwest A&F University NMR facility.

Mass spectroscopy (MS) experiments were performed in high resolution with an AB SCIEX Triple TOF 5600+ spectrometer (AB SCIEX, Boston, MA, USA) at the Northwest A&F University.

2. Experimental Procedures and Characterization Data

2.1 Synthesis of Cyclization Precursor **23**

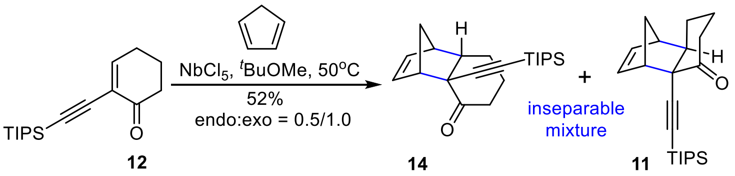


To a stirred solution of 2-iodocyclohexenone **13** (10 g, 45.06 mmol) in dry THF (150 mL) at 0°C was added $PdCl_2(PPh_3)_2$ (1.58 g, 2.25 mmol) and CuI (1.29 g, 6.76 mmol). The reaction mixture was stirred at 0°C for 10 min, then triisopropylsilylacetylene (12.2 mL, 54.07 mmol) and $(i\text{-Pr})_2NH$ (19.1 mL, 135.18 mmol) were added and stirred at 0°C for 4 h. The reaction mixture was quenched by 0.5M HCl (5 mL). After extracted with CH_2Cl_2 (2×150 mL), the combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. Filtered and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (PE : EtOAc = 40 : 1) to afford alkyne **12** (11.2 g, 40.55 mmol, 90% yield) as a tawny oil.

^{1}H-NMR (500 MHz, CDCl$_3$) δ: 7.29 (t, J = 4.7 Hz, 1H), 2.47 – 2.43 (m, 4H), 2.04 – 1.99 (m, 2H), 1.09 (s, 21H).

^{13}C-NMR (125 MHz, CDCl$_3$) δ: 195.1, 154.4, 125.6, 101.3, 93.7, 38.1, 26.3, 22.4, 18.6, 11.3.

HRMS (ESI) calcd for $C_{17}H_{29}SiO$ $[M+H]^+$: 277.1982, found 277.1984.

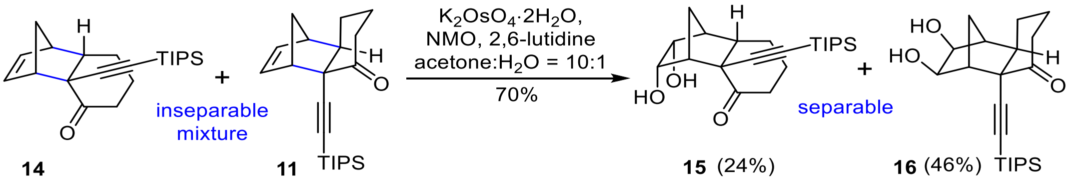


To a stirred solution of alkyne **12** (10 g, 36.2 mmol) in dry *t*-BuOMe (75 mL) was added $NbCl_5$ (6.85 g, 25.34 mmol) and cyclopentadiene (15 mL, 181.0 mmol). The reaction mixture was stirred at 50 °C under argon atmosphere for 12 h. Then, 5% citric acid aqueous solution (5 mL) was added to the reaction mixture, and the mixture was extracted with *t*-BuOMe (2×80 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. Purification by flash chromatography (PE : EtOAc = 100 : 1) afforded inseparable mixtures for **14** and **11** (6.43 g, 18.8 mmol, 52% yield) as a tawny oil.

^{1}H-NMR (500 MHz, CDCl$_3$) δ: 6.29 (dd, J = 5.7, 3.0 Hz, 0.5H), 6.15–6.08 (m, 1.5H), 5.93 (dd, *J* = 5.7, 3.0 Hz, 1.0H), 3.40 (s, 0.5H), 3.21 (s, 1.0H), 2.88 (dd, *J* = 17.7, 8.5 Hz, 0.5H), 2.81 (s, 1.0H), 2.79–2.73 (m, 1.0H), 2.68–2.60 (m, 1.0H), 2.52 (s, 0.5H), 2.26–2.17 (m, 0.5H), 2.12–2.07 (m, 0.5H), 2.06–1.94 (m, 3.5H), 1.94–1.89 (m, 1.0H), 1.84–1.78 (m, 1.0H), 1.75 (d, *J* = 8.7 Hz, 1.0H), 1.54–1.50 (m, 1.0H), 1.34 (dd, *J* = 9.4, 2.0 Hz, 0.5H), 1.17 (d, *J* = 9.4 Hz, 0.5H), 1.03–0.99 (m, 20H), 0.99–0.96 (m, 11H), 0.89–0.79 (m, 1.0H), 0.65–0.56 (m, 1.0H).

^{13}C-NMR (125 MHz, $CDCl_3$) δ: 209.9, 209.2, 138.7, 138.0, 134.6, 134.5, 111.0, 109.9, 83.3, 82.0, 54.5, 54.3, 54.0, 52.0, 51.9, 48.4, 47.3, 47.2, 46.3, 45.2, 36.9, 36.8, 29.6, 28.4, 21.2, 21.1, 18.61, 18.58, 18.57, 11.2.

HRMS (ESI) calcd for $C_{22}H_{35}SiO$ [M+H]$^+$: 343.2452, found 343.2455.



To a stirred solution of **14** and **11** (6.5 g, 19.0 mmol) in acetone/H_2O (v/v 10:1, 66 mL) at r.t was added $K_2OsO_4.2H_2O$ (140 mg, 0.38 mmol), NMO (3.34 g, 28.5 mmol) and 2,6-lutidine (3.54 mL, 30.4 mmol). After stirred overnight, the reaction mixture was quenched by saturated aqueous solution of Na_2SO_3 (5 mL), and then extracted with *t*-BuOMe (2×50 mL). The combined organic layers were washed with brine and dried over Na_2SO_4. Filtered and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (PE : EtOAc = 6 : 1) to afford the separable vicinal diols **15** (1.71 g, 4.55 mmol, 24% yield) and **16** (3.29 g, 8.75 mmol, 46% yield) as white flake solid.

Data for vicinal diol **15**:

^{1}H-NMR (500 MHz, $CDCl_3$) δ: 3.91 – 3.88 (m, 2H), 3.03 (s, 2H), 2.79 – 2.75 (m, 1H), 2.58 (s, 1H), 2.57 – 2.52 (m, 1H), 2.29 (d, *J* = 3.3 Hz, 1H), 2.14 – 2.04 (m, 1H), 1.95 – 1.86 (m, 4H), 1.68 (d, *J* = 10.7 Hz, 1H), 1.02 (s, 21H).

^{13}C-NMR (125 MHz, $CDCl_3$) δ: 209.1, 109.9, 84.6, 69.3, 68.5, 53.1, 51.8, 50.8, 47.4, 37.8, 30.9, 24.5, 21.3, 18.6, 11.2.

HRMS (ESI) calcd for $C_{22}H_{37}SiO_3$ [M+H]$^+$: 377.2507, found 377.2506.

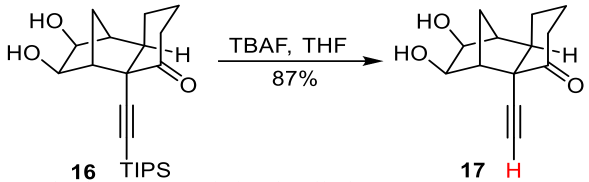
Data for vicinal diol **16**:

^{1}H-NMR (500 MHz, $CDCl_3$) δ: 4.41 (d, *J* = 5.7 Hz, 1H), 3.86 (d, *J* = 5.8 Hz, 1H), 2.85 (dd, *J* = 18.0, 7.9 Hz, 1H), 2.72 (s, 1H), 2.25 – 2.17 (m, 1H), 2.11 – 2.02 (m, 2H), 1.97

– 1.87 (m, 3H), 1.74 (dd, *J* = 11.5, 1.6 Hz, 1H), 1.13 (d, *J* = 11.8 Hz, 1H), 1.04 (s, 21H).

^{13}C-NMR (125 MHz, CDCl$_3$) δ: 207.5, 106.9, 86.7, 74.2, 71.1, 52.8, 52.1, 49.4, 49.1, 36.3, 29.9, 27.6, 20.6, 18.67, 18.66, 11.2.

HRMS (ESI) calcd for $C_{22}H_{37}SiO_3$ $[M+H]^+$: 377.2507, found 377.2504.

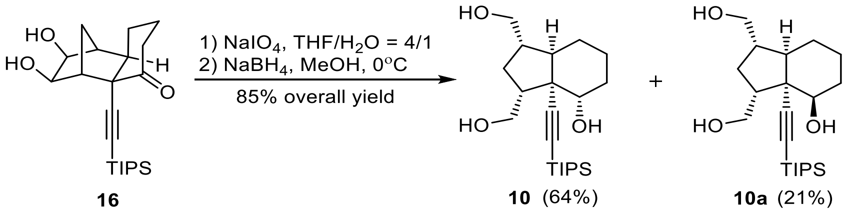


To a stirred solution of vicinal diol **16** (200 mg, 0.53 mmol) in THF (5 mL) was added TBAF (1.06 mL, 1.06 mmol, 1.0 M in THF). The reaction mixture was stirred at r.t for 4 h, then diluted with water (5 mL) and extracted with EtOAc (2×10 mL). Then combined organic layers were washed with brine and dried over Na_2SO_4. Filtered and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (PE : EtOAc = 1 : 1) to afford alkyne **17** (101 mg, 0.46 mmol, 87% yield) as a white solid. The solid was dissolved in EtOAc, slowly volatilized at r.t to obtain colorless crystal.

^{1}H-NMR (500 MHz, CDCl$_3$) δ: 4.39 (d, *J* = 6.0 Hz, 1H), 3.87 (d, *J* = 5.9 Hz, 1H), 2.84 (dd, *J* = 18.4, 7.7 Hz, 1H), 2.72 (s, 1H), 2.32 (s, 1H), 2.26–2.18 (m, 1H), 2.09–2.01 (m, 2H), 2.00–1.94 (m, 2H), 1.91–1.86 (m, 1H), 1.76 (dd, *J* = 11.5, 1.2 Hz, 1H), 1.13 (d, *J* = 11.5 Hz, 1H), 0.99–0.90 (m, 1H).

^{13}C-NMR (125 MHz, CDCl$_3$) δ: 207.4, 83.3, 74.0, 73.4, 70.9, 51.5, 50.6, 49.4, 49.2, 36.4, 29.9, 27.6, 20.4.

HRMS (ESI) calcd for $C_{13}H_{16}O_3$ $[M+H]^+$: 221.1172, found 221.1183.



To a stirred solution of **16** (2.5 g, 6.64 mmol) in THF/H_2O (v/v, 4:1, 50 mL) at r.t was added $NaIO_4$ (5.68 g, 26.56 mmol) and stirred for 5 h. Then the reaction mixture was diluted by H_2O (20 mL) and extracted with EtOAc (2×50 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure to afford crude dialdehyde which was directly used for next step.

To a stirred solution of the above crude dialdehyde in MeOH (30 ml) was added

NaBH$_4$ (1.26 g, 33.20 mmol) carefully. After 1h, the reaction mixture was evaporated under reduced pressure to remove MeOH and thendiluted with water (30 mL) and extracted with EtOAc (2×30 mL). Then combined organic layers were washed with brine and dried over Na$_2$SO$_4$. Filtered and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (PE : EtOAc = 1 : 1) to afford triols **10** (1.61 g, 4.23 mmol, 64% yield) and **10a** (0.54 g, 1.41 mmol, 21% yield) as white powdery solid.

Data for triol **10**:

^{1}H-NMR (500 MHz, CD$_3$OD) δ: 3.97 (dd, J = 10.7, 6.0 Hz, 1H), 3.57 (dd, J = 10.7, 4.3 Hz, 1H), 3.45–3.39 (m, 3H), 2.40–2.34 (m, 1H), 2.14–2.01 (m, 3H), 1.79–1.72 (m, 3H), 1.63–1.48 (m, 4H), 1.12–1.05 (m, 21H).

^{13}C-NMR (125 MHz, CD$_3$OD) δ: 109.8, 84.9, 71.3, 65.0, 64.9, 52.2, 49.3, 45.7, 41.4, 30.7, 30.6, 22.6, 20.0, 17.8, 11.2.

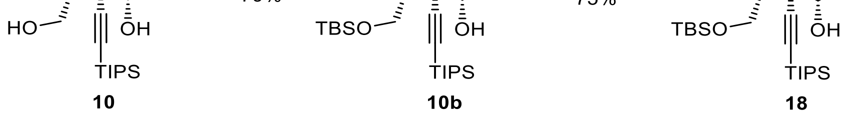
HRMS (ESI) calcd for C$_{22}$H$_{41}$SiO$_3$ [M+H]$^+$: 381.2820, found 381.2814.

Data for triol **10a**:

^{1}H-NMR (500 MHz, CD$_3$OD) δ: 3.87 (dd, J = 11.0, 9.0 Hz, 1H), 3.82 (dd, J = 10.9, 4.1 Hz, 1H), 3.76 (dd, J = 10.5, 7.9 Hz, 2H), 3.57 (dd, J = 10.4, 7.3 Hz, 1H), 3.50 (dd, J = 11.0, 4.1 Hz, 1H), 2.52–2.45 (m, 1H), 2.12–2.08 (m, 1H), 2.06–2.01 (m, 1H), 1.90–1.83 (m, 1H), 1.79–1.71 (m, 2H), 1.67–1.63 (m, 1H), 1.53–1.45 (m, 1H), 1.40–1.32 (m, 1H), 1.31–1.23 (m, 2H), 1.13–1.07 (m, 21H).

^{13}C-NMR (125 MHz, CD$_3$OD) δ: 113.1, 84.0, 74.2, 66.8, 62.5, 51.7, 50.1, 45.6, 43.3, 30.6, 30.1, 22.3, 17.8, 11.2.

HRMS (ESI) calcd for C$_{22}$H$_{41}$SiO$_3$ [M+H]$^+$: 381.2820, found 381.2813.



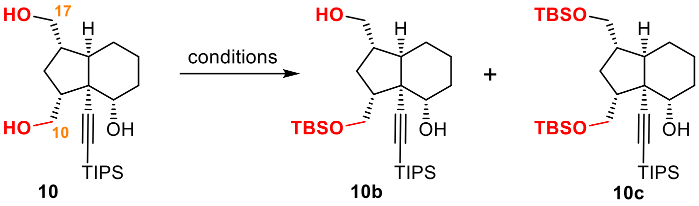
To a stirred solution of compound **10** (2.0 g, 5.26 mmol) in dry THF (25 mL) at r.t was added NaH (0.84 g, 21.04 mmol, 60% in mineral oil), after 40 min, a solution of TBSCl (1.43 g, 9.47 mmol) in dry THF (5 mL) was dropwise. The reaction mixture stirred at r.t for 3h and quenched by saturated aqueous solution of NH$_4$Cl (3 mL). After extracted with EtOAc (2×30 mL), the combined organic layers were washed with brine and dried over Na_2SO_4. Filtered and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (PE : EtOAc = 5 : 1) to afford **10b** (2.05 g, 4.15 mmol, 79% yield) as a colorless oil.

^{1}H-NMR (500 MHz, $CDCl_3$) δ: 3.90 (dd, J = 9.8, 5.4 Hz, 1H), 3.63 (dd, J = 10.6, 4.2 Hz, 1H), 3.53–3.47 (m, 2H), 3.33 (d, J = 8.6 Hz, 1H), 2.39–2.34 (m, 1H), 2.13–2.09 (m, 1H), 2.08–2.01 (m, 3H), 1.79–1.76 (m, 1H), 1.68–1.63 (m, 1H), 1.60–1.50 (m, 4H), 1.06–1.04 (m, 21H), 0.87 (s, 9H), 0.02 (s, 6H).

^{13}C-NMR (125 MHz, $CDCl_3$) δ: 108.3, 86.7, 71.4, 66.2, 66.0, 53.1, 48.3, 45.8, 41.7, 31.3, 30.3, 26.0, 23.6, 20.1, 18.7, 18.3, 11.3, -5.3, -5.4.

HRMS (ESI) calcd for $C_{28}H_{55}Si_2O_3$ $[M+H]^+$: 495.3684, found 495.3679.

Table S1. Conditions for TBS protection



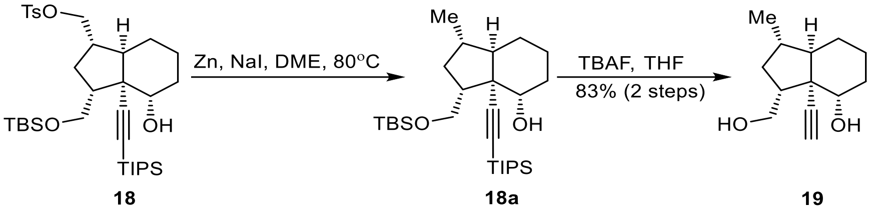
Entry	Reaction conditions	Yield (**10b**)	ratio (**10b:10c**)
1	TBSCl, imidazole, DMAP, DCM, 0°C	25%	1.0 : 2.0
2	TBSCl, imidazole, DMAP, DCM, –35°C	32%	1.0 : 1.0
3	TBSCl solution, imidazole, DCM/DMF = 4/1, –45°C	29%	1.0 : 0.9
4	TBSCl, NaH, THF, rt	79%	20 : 1

To a stirred solution of compound **10b** (2.05 g, 4.15 mmol) in dry DCM (20 mL) was added triethylamine (2.20 mL, 15.78 mmol), DMAP (128 mg, 1.05 mmol) and *p*-TsCl (2.0 g, 10.52 mmol). The reaction mixture was stirred at r.t for 2h and then directly concentrated and purified by flash chromatography on silica gel (PE : EtOAc = 8 : 1) to afford compound **18** (2.02 g, 3.11 mmol, 75% yield) as a colorless oil.

^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.77 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.1, 2H), 4.00 (dd, J = 9.5, 5.6 Hz, 1H), 3.91 (dd, J = 9.4, 6.5 Hz, 1H), 3.83 (dd, J = 9.8, 5.0 Hz, 1H), 3.47 (dd, J = 9.7, 8.1 Hz, 1H), 3.29 – 3.24 (m, 1H), 2.44 (s, 3H), 2.38 – 2.32 (m, 1H), 2.21 – 2.13 (m, 1H), 2.08 – 2.03 (m, 2H), 2.00 (d, J = 9.9, 1H), 1.79 – 1.75 (m, 1H), 1.59 – 1.54 (m, 2H), 1.46 – 1.37 (m, 3H), 1.06 – 1.05 (m, 21H), 0.85 (s, 9H), 0.00 (d, J = 3.9, 6H).

^{13}C-NMR (125 MHz, $CDCl_3$) δ: 144.7, 133.1, 129.9, 127.9, 107.7, 87.2, 73.7, 71.3, 65.7, 53.0, 48.6, 45.6, 38.6, 31.1, 30.4, 26.0, 23.3, 21.7, 19.9, 18.7, 18.3, 11.2. -5.38, -5.42.

HRMS (ESI) calcd for $C_{35}H_{61}Si_2SO_5$ $[M+H]^+$: 649.3773, found 649.3770.



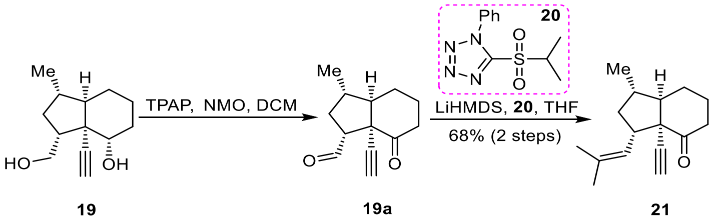
To a stirred solution of compound **18** (2.0 g, 3.08 mmol) in dry DME (30 mL) at r.t was added activated zinc powder (3.02 g, 46.20 mmol) and NaI (6.92 g, 46.20 mmol), then the reaction mixture heated at 80 ℃ and stirred overnight, and then directly concentrated and purified by flash chromatography on silica gel (PE : EtOAc = 50 : 1) to afford compound **18a** as a colorless oil.

To a stirred solution of above crude compound **18a** in THF (20 ml) at r.t was added TBAF (9.24 mL, 9.24 mmol, 1.0 M solution in THF). After 4h, the reaction mixture was quenched by water (20 mL) and extracted with EtOAc (2×30 mL). Then combined organic layers were washed with brine and dried over Na_2SO_4. Filtered and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (PE : EtOAc = 2 : 1) to afford alkynyl diol **19** (530 mg, 2.55 mmol, 83% yield) as a colorless oil.

^{1}H-NMR (500 MHz, $CDCl_3$) *δ*: 3.72 (dd, *J* = 11.7, 7.9 Hz, 1H), 3.58 (dd, *J* = 11.3, 4.1 Hz, 1H), 3.32 (dd, *J* = 11.7, 4.0 Hz, 1H), 2.38 – 2.32 (m, 2H), 2.12 – 2.06 (m, 2H), 1.89 – 1.79 (m, 2H), 1.75 – 1.72 (m, 1H), 1.70 – 1.63 (m, 1H), 1.61 – 1.51 (m, 2H), 1.44 – 1.34 (m, 1H), 1.07 – 1.01 (m, 1H), 0.92 (d, *J* = 6.7 Hz, 3H).

^{13}C-NMR (125 MHz, $CDCl_3$) *δ*: 85.7, 73.9, 73.2, 65.5, 54.3, 51.2, 48.0, 36.6, 33.8, 31.6, 21.8, 20.3, 18.6.

HRMS (ESI) calcd for $C_{13}H_{21}O_2$ $[M+H]^+$: 209.1536, found 209.1534.



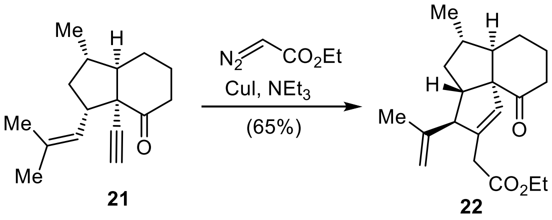
To a stirred solution of compound **19** (500 mg, 2.40 mmol) in dry CH_2Cl_2 (20 mL) at r.t was added TPAP (211 mg, 0.60 mmol) and NMO (1.12 g, 9.60 mmol). After 2h the reaction mixture was directly concentrated and purified by flash chromatography on silica gel (PE : EtOAc = 10 : 1) to afford aldehyde **19a** as a colorless oil which was directly used for next step.

To a stirred solution of reagent **20** (1.45 g, 5.76 mmol) in dry THF (25 mL) at −78°C was added LiHMDS (5.76 mL, 5.76 mmol, 1.0 M solution in THF) dropwise, after stirred at −78°C for 40 min, then a solution of above aldehyde **19a** in dry THF (3 ml) was added dropwise and stirred at −78°C for 10 min and warmed to 0°C and stirred for 2h. The reaction mixture was quenched by saturated aqueous solution of NH_4Cl (3 mL) and extracted with EtOAc (2×30 mL). Then combined organic layers were washed with brine and dried over Na_2SO_4. Filtered and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (PE : EtOAc = 50 : 1) to afford 1,5-enyne **21** (375 mg, 1.63 mmol, 68% overall yield) as a colorless oil.

^{1}H-NMR (500 MHz, CDCl$_3$) *δ*: 5.18 (d, *J* = 9.7 Hz, 1H), 3.59 – 3.54 (m, 1H), 2.91 – 2.85 (m, 1H), 2.35 (s, 1H), 2.33 – 2.28 (m, 1H), 2.14 – 2.08 (m, 3H), 1.96–1.89 (m, 1H), 1.87 – 1.76 (m, 1H), 1.71 (s, 3H), 1.65 (d, *J* = 1.2 Hz, 3H), 1.63 – 1.57 (m, 2H), 1.09 – 1.03 (m, 1H), 0.98 (d, *J* = 6.5 Hz, 3H), 0.90 – 0.83 (m, 1H).

^{13}C-NMR (125 MHz, CDCl$_3$) *δ*: 207.7, 132.4, 126.6, 84.2, 74.2, 59.2. 57.4, 40.5, 39.8, 38.4, 35.4, 25.9, 24.1, 23.1, 19.0, 18.3.

HRMS (ESI) calcd for $C_{16}H_{23}O$ $[M+H]^+$: 231.1743, found 231.1740.



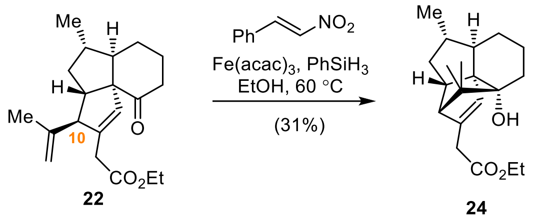
To a stirred solution of **21** (200 mg, 0.87 mmol) in dry MeCN (10 mL) at r.t was added CuI (84 mg, 0.44 mmol) and ethyl diazoacetate (0.14 mL, 1.31 mmol). After stirred at r.t for 5 h, NEt_3 (0.36 mL, 2.61 mmol) was added, and stirred at r.t for 4h. The reaction mixture was directly concentrated and purified by flash chromatography on silica gel (PE : EtOAc = 20 : 1) to afford tricyclic ester **22** (180 mg, 0.57 mmol, 65% yield) as a colorless oil.

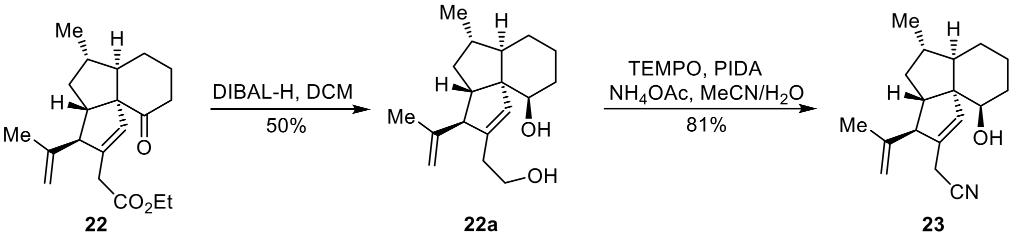
^{1}H-NMR (500 MHz, CDCl$_3$) *δ*: 5.77 (s, 1H), 4.76 (s, 1H), 4.69 (s, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.11 (td, *J* = 9.0, 4.1 Hz, 1H), 2.98 (d, *J* = 17.5 Hz, 2H), 2.85 (d, *J* = 16.4 Hz, 1H), 2.52–2.45 (m, 1H), 2.36 – 2.32 (m, 1H), 2.23 – 2.18 (m, 1H), 1.97 – 1.93 (m, 2H), 1.81 – 1.76 (m, 1H), 1.66 – 1.60 (m, 4H), 1.54 – 1.48 (m, 1H), 1.45 – 1.37 (m, 1H), 1.25 (t, *J* = 7.3 Hz, 3H), 0.98 – 0.93 (m, 1H), 0.90 (d, *J* = 6.3 Hz, 3H).

^{13}C-NMR (125 MHz, CDCl$_3$) *δ*: 211.8, 171.0, 146.6, 138.0, 130.8, 112.2, 74.1, 64.0, 60.5, 57.0, 46.0, 42.4, 40.0, 38.1, 34.8, 24.7, 22.5, 19.4, 17.2, 14.2.

HRMS (ESI) calcd for $C_{20}H_{29}O_3$ $[M+H]^+$: 317.2038, found 317.2040.

When compound **22** was submitted to Fe-catalyzed reductive coupling with β-Nitroalkenes, compound **24** was isolated, which confirmed the stereochemistry of C10.





To a stirred solution of tricyclic ester **22** (100 mg, 0.30 mmol) in dry DCM (5 mL) at 0℃ was added DIBAL-H (1.20 mL, 1.0 M in toluene) dropwise and stirred for 2h. The reaction mixture was diluted with Et_2O (4 mL) and quenched by saturated aqueous solution of Rochelle salt (4 mL). The reaction mixture was stirred until the organic layers became completely clear and then extracted with EtOAc (2×10 mL). The combined organic layers were washed with brine and dried over Na_2SO_4. Filtered and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (PE : EtOAc = 1 : 1) to afford diol **22a** (41 mg, 0.15 mmol, 50% yield) as a colorless solid.

^{1}H-NMR (500 MHz, $CDCl_3$) δ: 5.70 (s, 1H), 4.78–4.75 (m, 1H), 4.73–4.70 (m, 1H), 3.76–3.64 (m, 2H), 3.38 (dd, J = 14.6, 5.6 Hz, 1H), 2.89 (d, J = 4.4 Hz, 1H), 2.39–2.29 (m, 3H), 2.21–2.13 (m, 1H), 1.93–1.82 (m, 2H), 1.70 (s, 3H), 1.64–1.58 (m, 2H), 1.38–1.34 (m, 1H), 1.33–1.24 (m, 3H), 1.08–1.02 (m, 1H), 0.89 (d, J = 7.9 Hz, 3H).

^{13}C-NMR (125 MHz, $CDCl_3$) δ: 146.6, 142.9, 127.7, 110.3, 72.5, 64.8, 63.6, 59.7, 54.1, 50.4, 41.8, 35.5, 32.2, 32.0, 22.1, 19.9, 18.9, 17.1.

HRMS (ESI) calcd for $C_{18}H_{28}O_2Na$ $[M+Na]^+$: 299.1981, found 299.1983.

To a stirred solution of **22a** (25 mg, 0.09 mmol) in MeCN/H_2O (v/v, 10:1, 5.5 at 0℃ was added TEMPO (2.8 mg, 0.018 mmol), $PhI(OAc)_2$ (87 mg, 0.27 mmol) and NH_4OAc (42 mg, 0.54 mmol) and stirred at r.t overnight. The reaction mixture was directly concentrated and purified by flash chromatography on silica gel (PE : EtOAc = 5 : 1) to afford cyano-diene **23** (19 mg, 0.07 mmol, 81% yield) as a colorless oil.

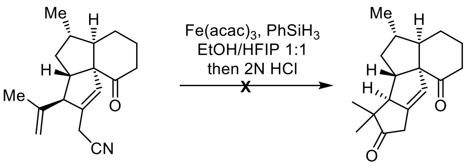
^{1}H-NMR (500 MHz, CDCl$_3$) δ: 6.03 (s, 1H), 4.81(s, 1H), 4.72 (s, 1H), 3.44 – 3.36 (m, 1H), 3.08 (d, J = 24.2 Hz, 1H), 2.93 – 2.86 (m, 2H), 2.44 – 2.32 (m, 2H), 1.92 –1.82(m, 2H), 1.70 (s, 3H), 1.68 – 1.59 (m, 3H), 1.39 – 1.29 (m, 3H), 1.11 – 1.03 (m, 1H), 0.90 (d, J = 7.9 Hz, 3H).

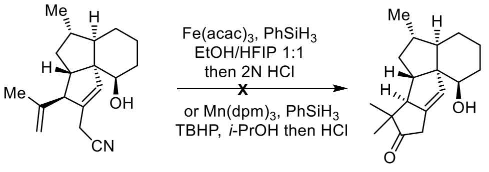
^{13}C-NMR (125 MHz, CDCl$_3$) δ: 145.3, 133.7, 131.2, 116.5, 111.0, 72.4, 65.0, 63.1, 53.3, 50.8, 41.7, 35.4, 32.1, 22.0, 19.9, 19.0, 17.7, 17.0.

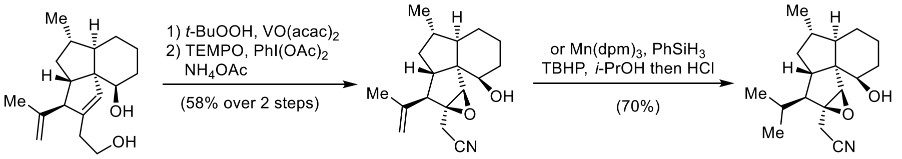
HRMS (ESI) calcd for $C_{18}H_{25}NONa$ $[M+Na]^+$: 294.1828, found 294.1832.

Several methodologies were tried for ring construction.

(a) HAT cyclization.

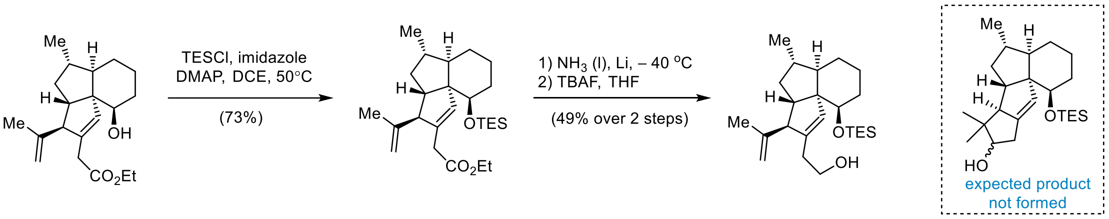




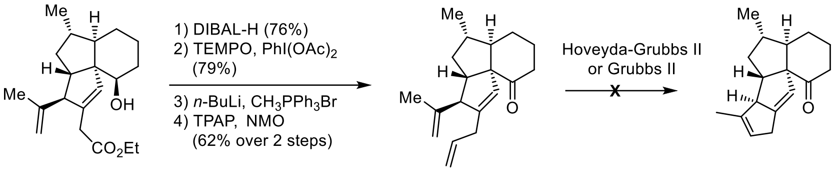


(b) Reductive cyclization

The cyclization methodology developed by Srikrishna group (*Tetrahedron Lett*. **2004**, *45*, 379-382; *Tetrahedron Lett*. **2004**, *45*, 383-386; *Tetrahedron* **2010**, *66*, 852-861) was tried, only the ester reduction product was obtained.

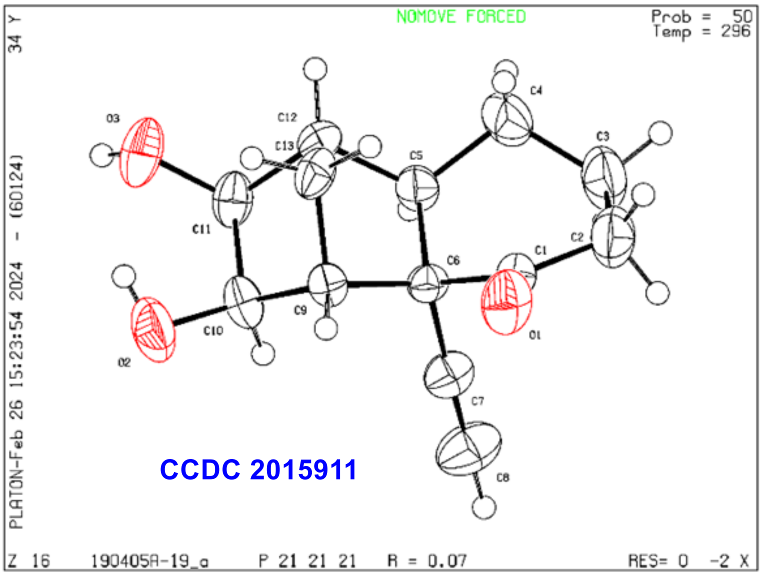


(c) Ring-closure metathesis

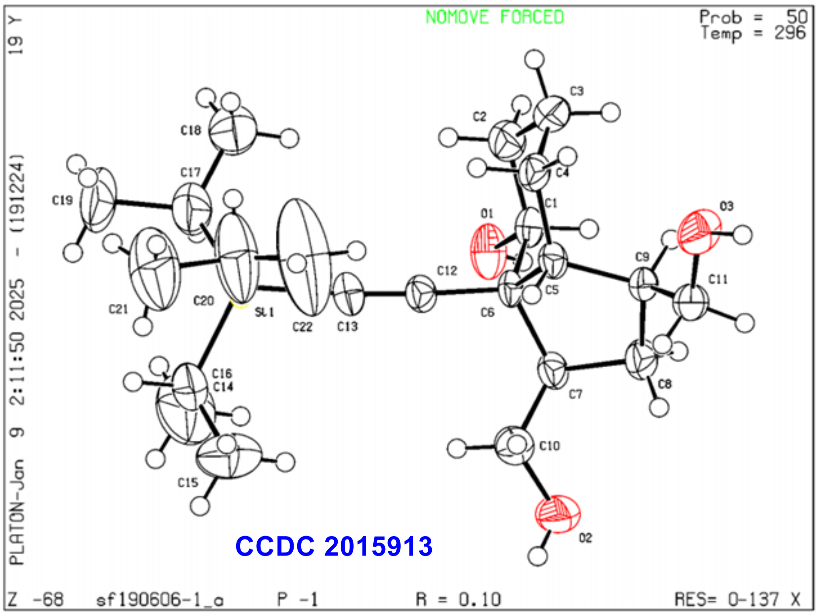


We also tried RCM, not no expected product was isolated.

3. X-ray Crystallographic Data

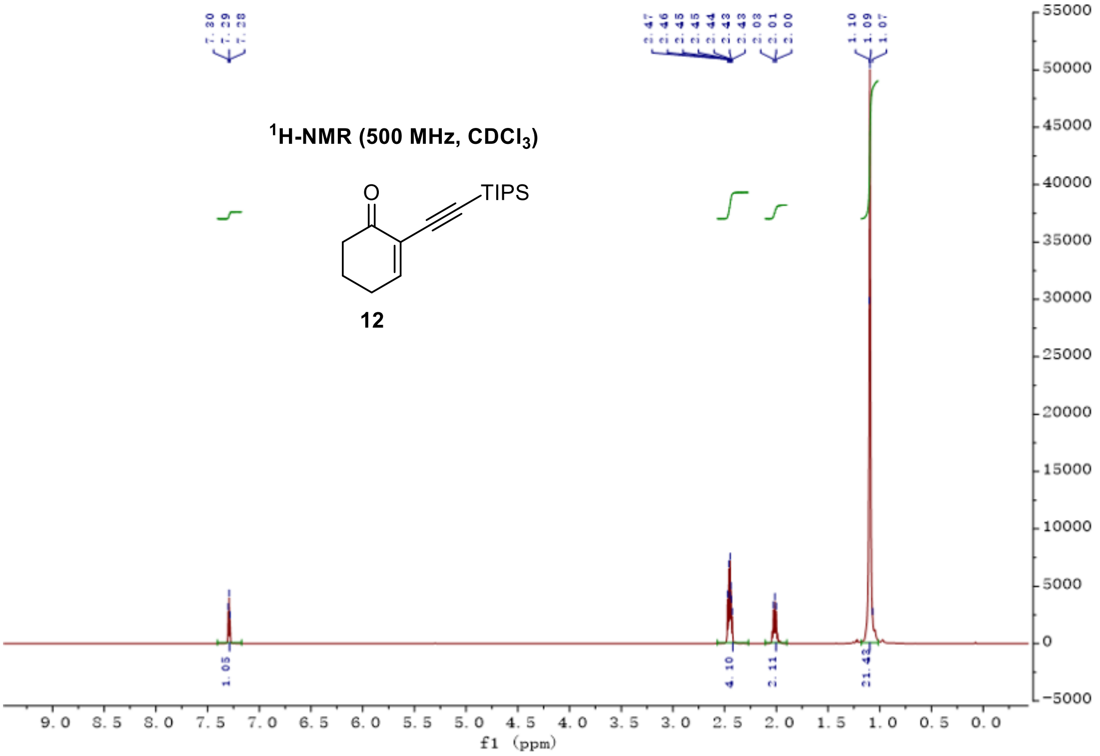


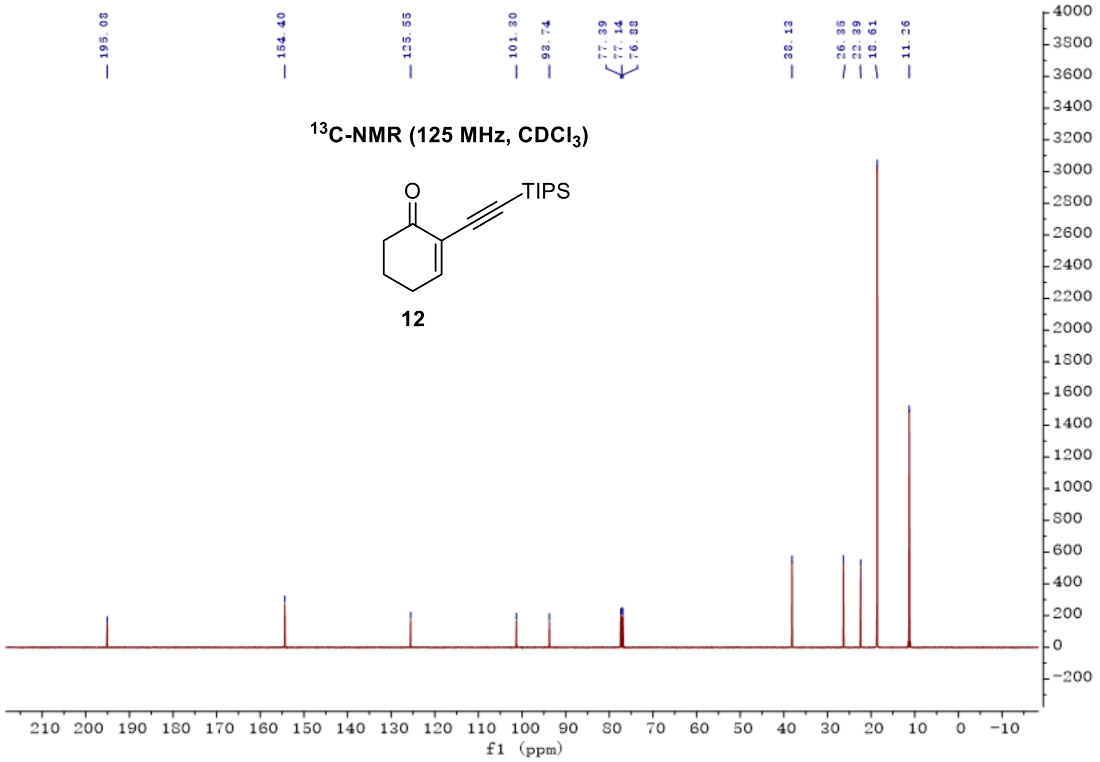
```
Bond precision:   C-C = 0.0058 A            Wavelength=0.71073

Cell:               a=8.4757(17)       b=11.538(3)       c=11.708(2)
                    alpha=90           beta=90           gamma=90
Temperature:        296 K

                 Calculated                  Reported
Volume           1145.0(4)                   1144.9(4)
Space group      P 21 21 21                  P 21 21 21
Hall group       P 2ac 2ab                   P 2ac 2ab
Moiety formula   C13 H16 O3                  C13 H16 O3
Sum formula      C13 H16 O3                  C13 H16 O3
Mr               220.26                      220.26
Dx,g cm-3        1.278                       1.278
Z                4                           4
Mu (mm-1)        0.090                       0.090
F000             472.0                       472.0
F000'            472.25
h,k,lmax         10,14,14                    10,14,14
Nref             2346[ 1367]                 2345
Tmin,Tmax        0.973,0.975                 0.681,0.745
Tmin'            0.973

Correction method= # Reported T Limits: Tmin=0.681 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness= 1.72/1.00        Theta(max)= 26.373

                                                      wR2(reflections)=
R(reflections)= 0.0668( 1182)                         0.1059( 2345)

S = 1.009                  Npar= 145
```

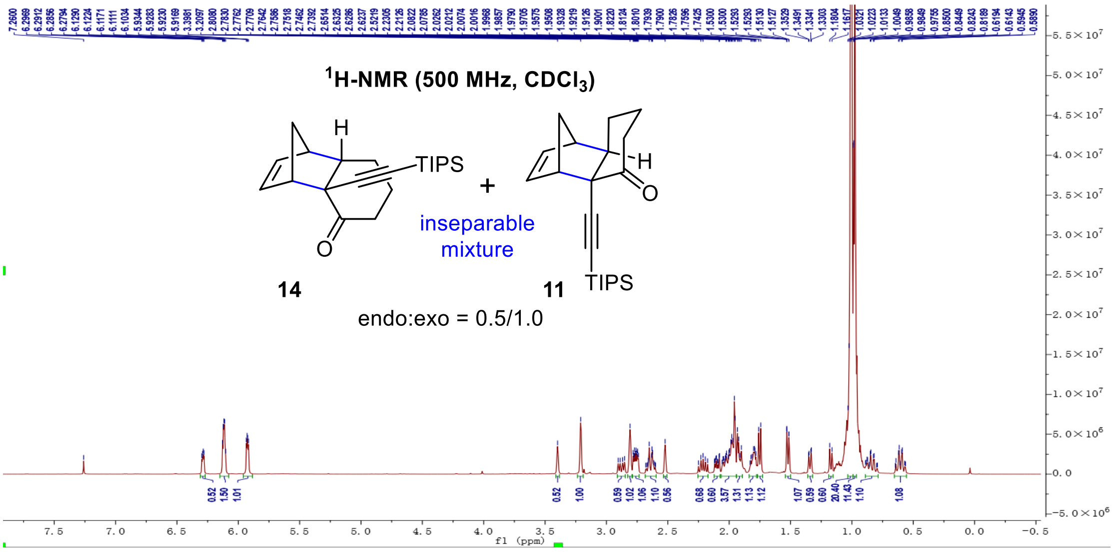


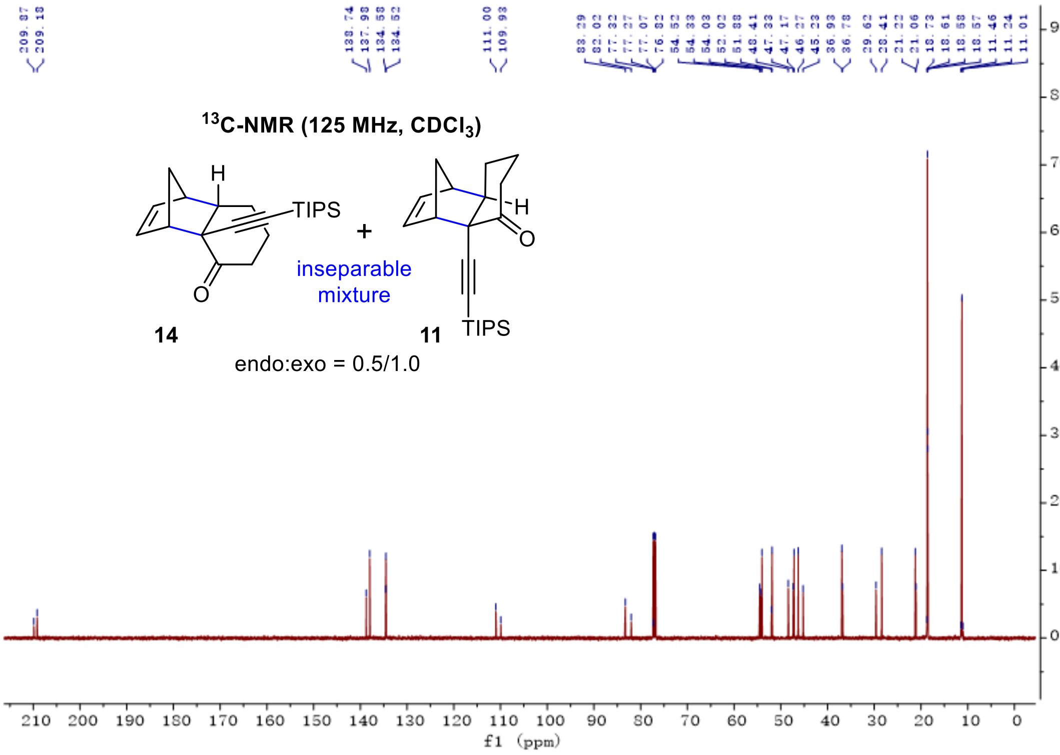
```
Bond precision:    C-C = 0.0062 A            Wavelength=0.71073

Cell:              a=8.2115(14)      b=8.6473(15)      c=18.221(3)
                   alpha=92.225(4)   beta=95.522(4)    gamma=117.574(4)
Temperature:       296 K

                    Calculated                   Reported
Volume              1136.4(3)                    1136.4(3)
Space group         P -1                         P -1
Hall group          -P 1                         -P 1
Moiety formula      C22 H39 O3 Si                ?
Sum formula         C22 H39 O3 Si                C22 H39 O3 Si
Mr                  379.62                       379.62
Dx,g cm-3           1.109                        1.109
Z                   2                            2
Mu (mm-1)           0.121                        0.121
F000                418.0                        418.0
F000'               418.32
h,k,lmax            11,11,24                     11,11,24
Nref                5837                         5819
Tmin,Tmax           0.962,0.964                  0.664,0.746
Tmin'               0.962

Correction method= # Reported T Limits: Tmin=0.664 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.997            Theta(max)= 28.610

                                                         wR2(reflections)=
R(reflections)= 0.0953( 2320)                            0.2144( 5819)

S = 1.007                    Npar= 243
```

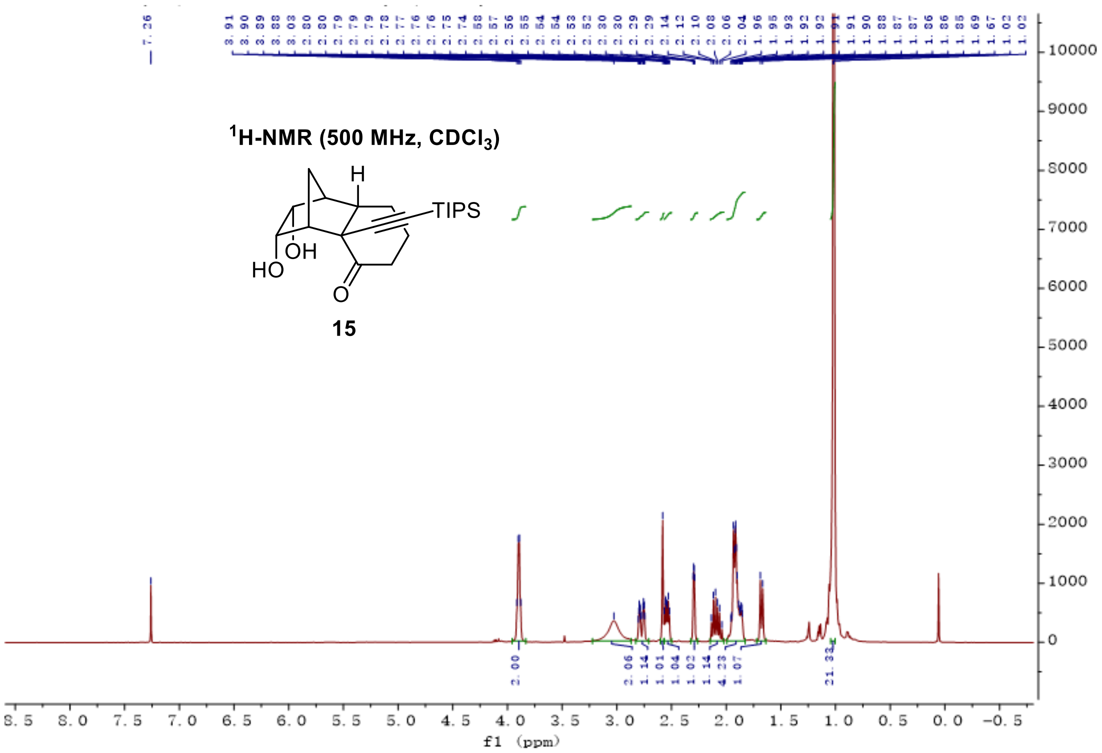
4. NMR Spectra

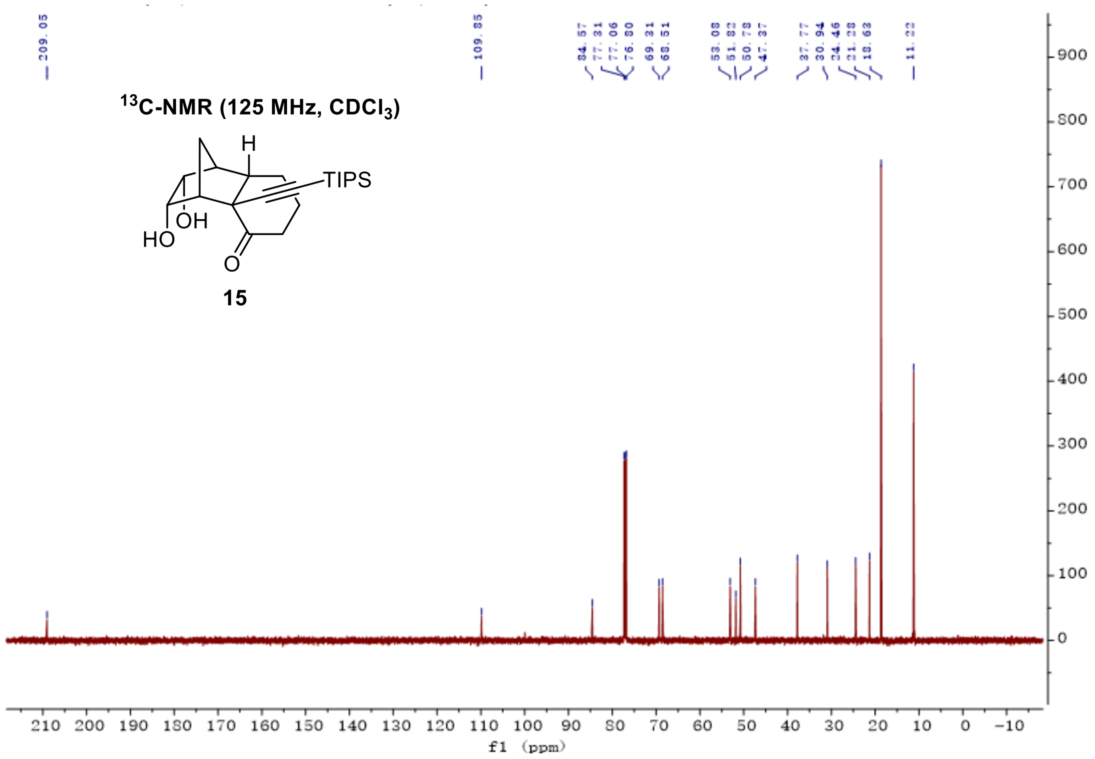


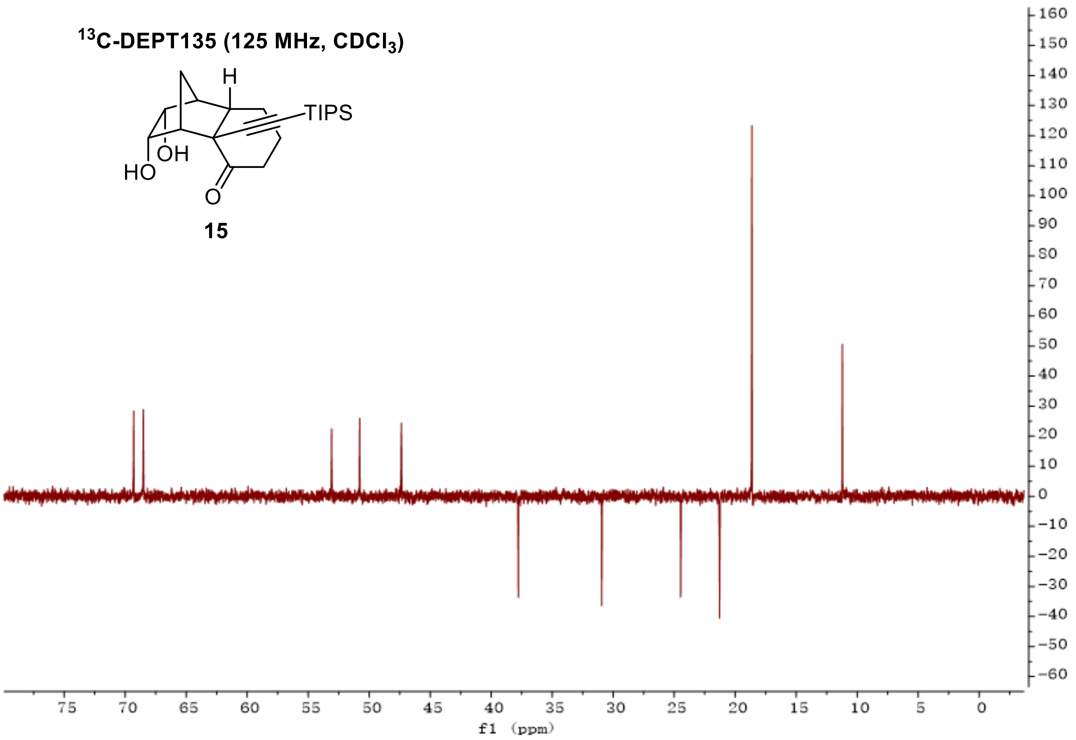


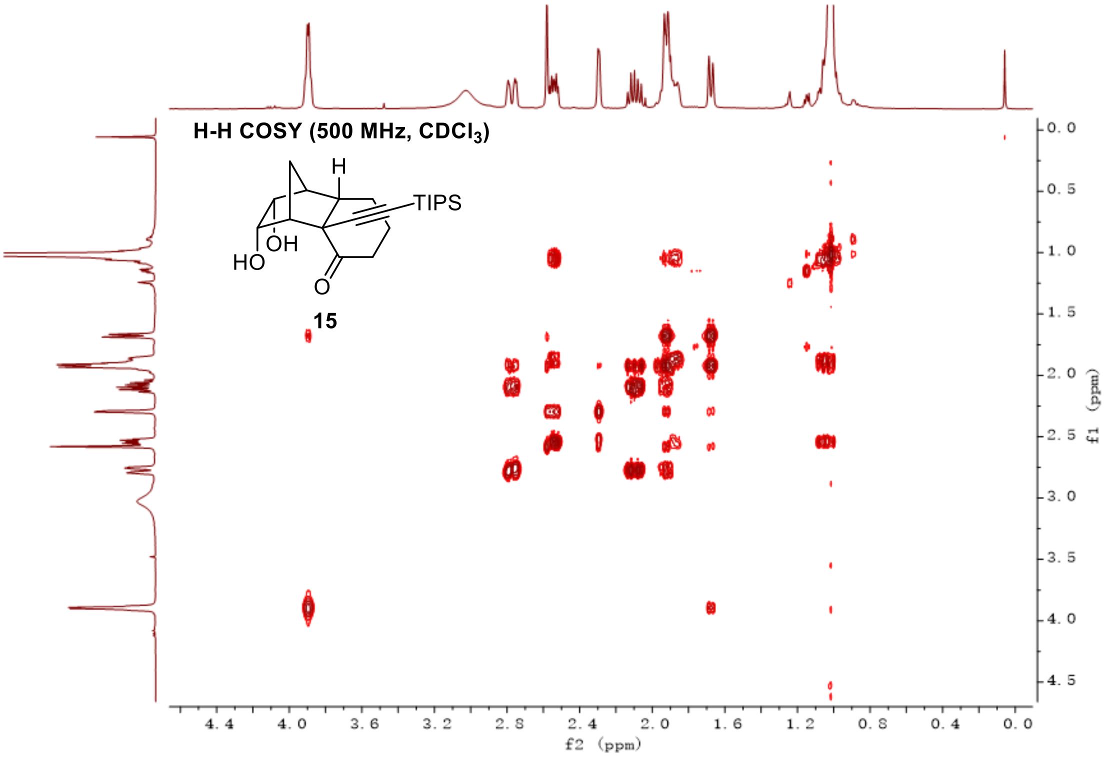

7.2600 6.2969 6.2912 6.2856 6.2794 6.1290 6.1224 6.1171 6.1111 6.1034 5.9344 5.9283 5.9230 5.9169 3.3981 3.2097 2.8080 2.7830 2.7762 2.7709 2.7642 2.7586 2.7518 2.7462 2.7392 2.6514 2.6325 2.6286 2.6237 2.5219 2.2305 2.2126 2.0822 2.0785 2.0262 2.0212 2.0074 2.0016 1.9968 1.9857 1.9790 1.9705 1.9575 1.9508 1.9328 1.9219 1.9126 1.9001 1.8220 1.8124 1.8010 1.7939 1.7900 1.7826 1.7596 1.7425 1.5300 1.5300 1.5293 1.5293 1.5130 1.5127 1.3529 1.3491 1.3341 1.3303 1.1804 1.1617 1.0321 1.0223 1.0133 1.0049 0.9858 0.9849 0.9755 0.8500 0.8449 0.8243 0.8189 0.6194 0.6143 0.5945 0.5890
^{1}H-NMR (500 MHz, CDCl$_3$)
H
TIPS
+
inseparable
mixture
H
O
O
TIPS
14
11
endo:exo = 0.5/1.0
0.52 1.50 1.01
0.52 1.00
0.59 1.02 1.06 1.10 0.56
0.68 0.60 3.57 1.31 1.13 1.12
1.07 0.59 0.60 20.40 11.43 1.10
1.08
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
-5.5×10⁷
-5.0×10⁷
-4.5×10⁷
-4.0×10⁷
-3.5×10⁷
-3.0×10⁷
-2.5×10⁷
-2.0×10⁷
-1.5×10⁷
-1.0×10⁷
-5.0×10⁶
-0.0
-−5.0×10⁶

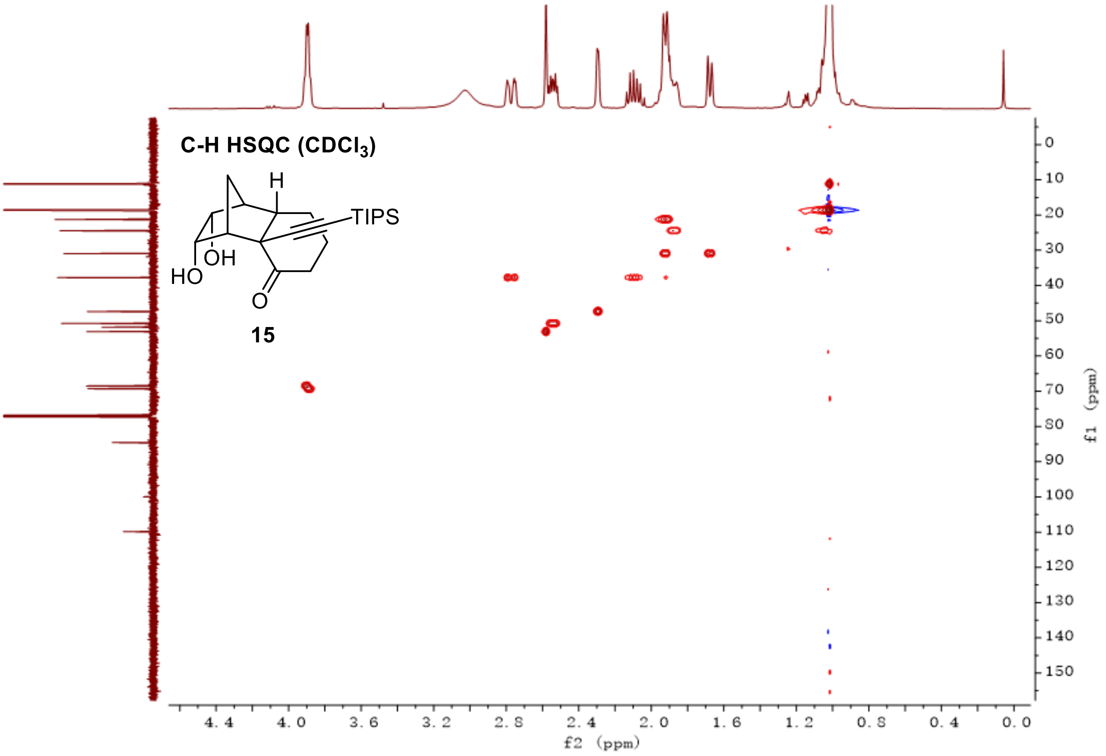

209.87 209.18
138.74 137.98 134.58 134.52
111.00 109.93
83.29 82.02 77.32 77.27 77.07 76.82 54.52 54.33 54.03 52.02 51.88 48.41 47.33 47.17 46.27 45.23 36.93 36.78 29.62 28.41 21.23 21.06 18.73 18.61 18.58 18.57 11.46 11.24 11.01
^{13}C-NMR (125 MHz, CDCl$_3$)
H
TIPS
+
inseparable
mixture
H
O
O
TIPS
14
11
endo:exo = 0.5/1.0
900
800
700
600
500
400
300
200
100
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

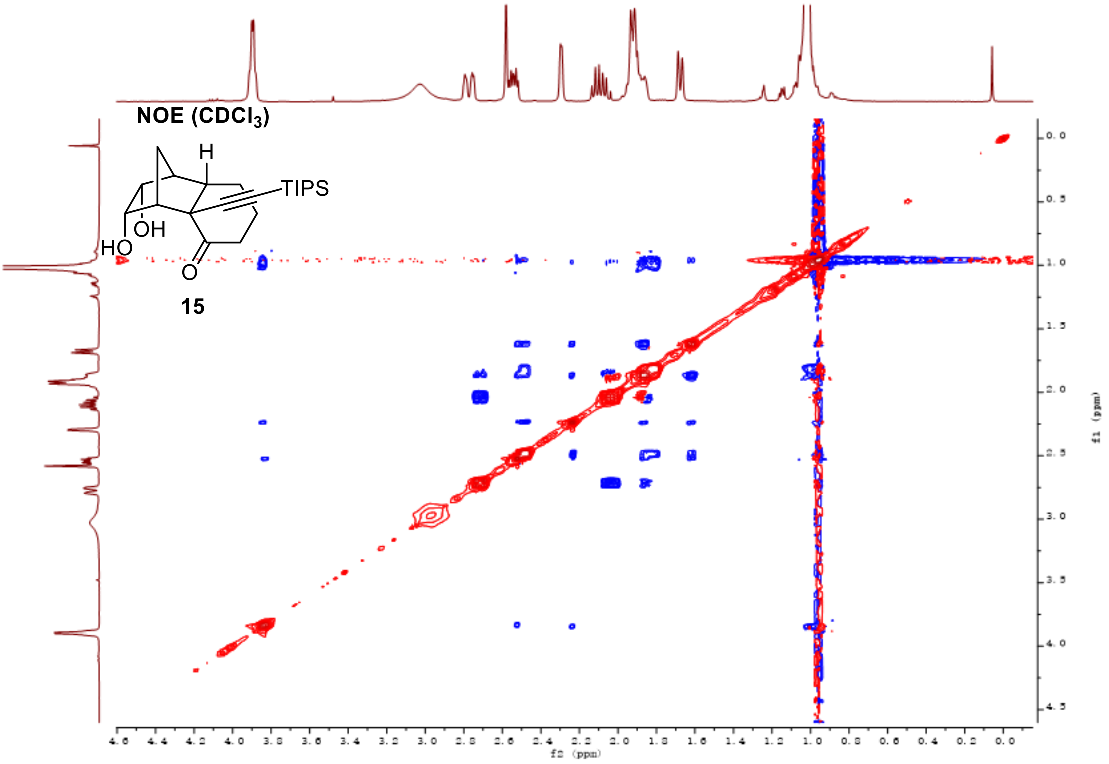

7.26
3.91
3.90
3.89
3.88
3.03
2.80
2.79
2.79
2.79
2.78
2.77
2.76
2.76
2.75
2.74
2.58
2.57
2.56
2.55
2.54
2.54
2.53
2.52
2.30
2.30
2.29
2.29
2.14
2.12
2.10
2.08
2.06
2.04
1.96
1.93
1.93
1.92
1.92
1.91
1.91
1.90
1.88
1.87
1.87
1.86
1.86
1.85
1.69
1.67
1.02
1.02
^{1}H-NMR (500 MHz, CDCl$_3$)
H
TIPS
OH
HO
O
15
2.00
2.06
1.14
1.01
1.04
1.02
1.14
4.23
1.07
21.33
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

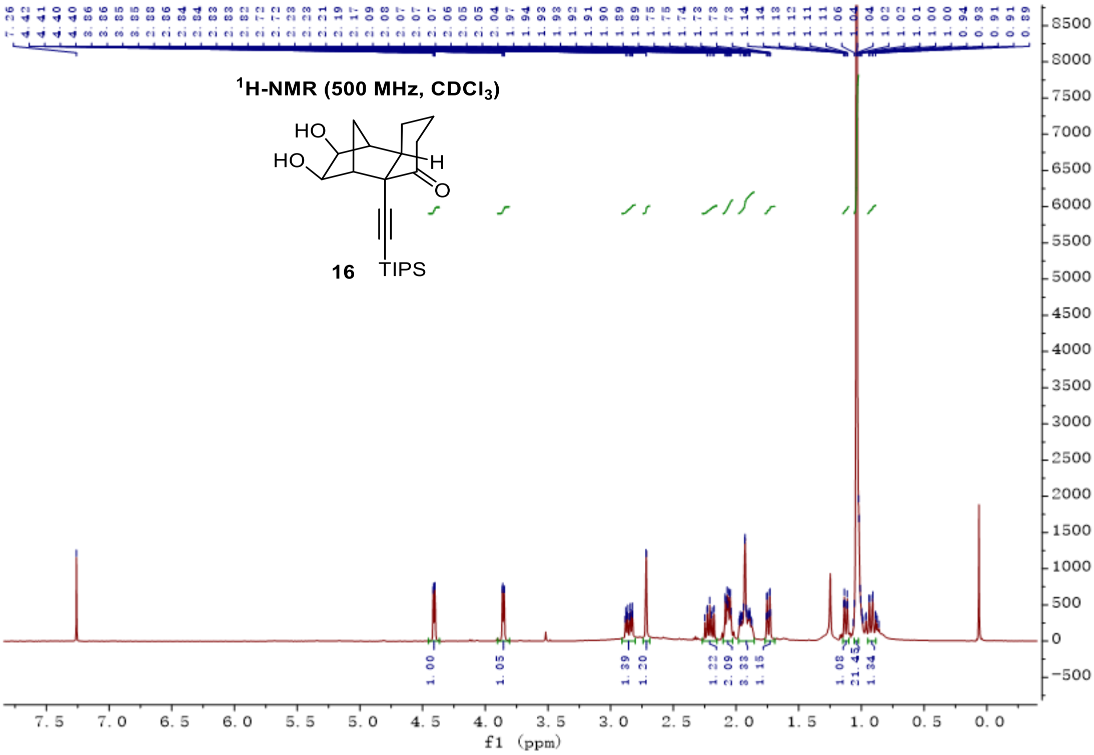

209.05
109.85
84.57
77.31
77.06
76.80
69.31
68.51
53.08
51.82
50.78
47.37
37.77
30.94
24.46
21.28
18.63
11.22
^{13}C-NMR (125 MHz, CDCl$_3$)
H
TIPS
OH
HO
O
15
900
800
700
600
500
400
300
200
100
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


^{13}C-DEPT135 (125 MHz, CDCl$_3$)
H
TIPS
OH
HO
O
15
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)


H-H COSY (500 MHz, CDCl$_3$)
H
TIPS
OH
HO
O
15
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
f1 (ppm)
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.0
f2 (ppm)


C-H HSQC (CDCl$_3$)
H
TIPS
OH
HO
O
15
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.0
f2 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)


NOE (CDCl$_3$)
H
TIPS
OH
HO
O
15
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
f2 (ppm)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
f1 (ppm)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4.42
4.41
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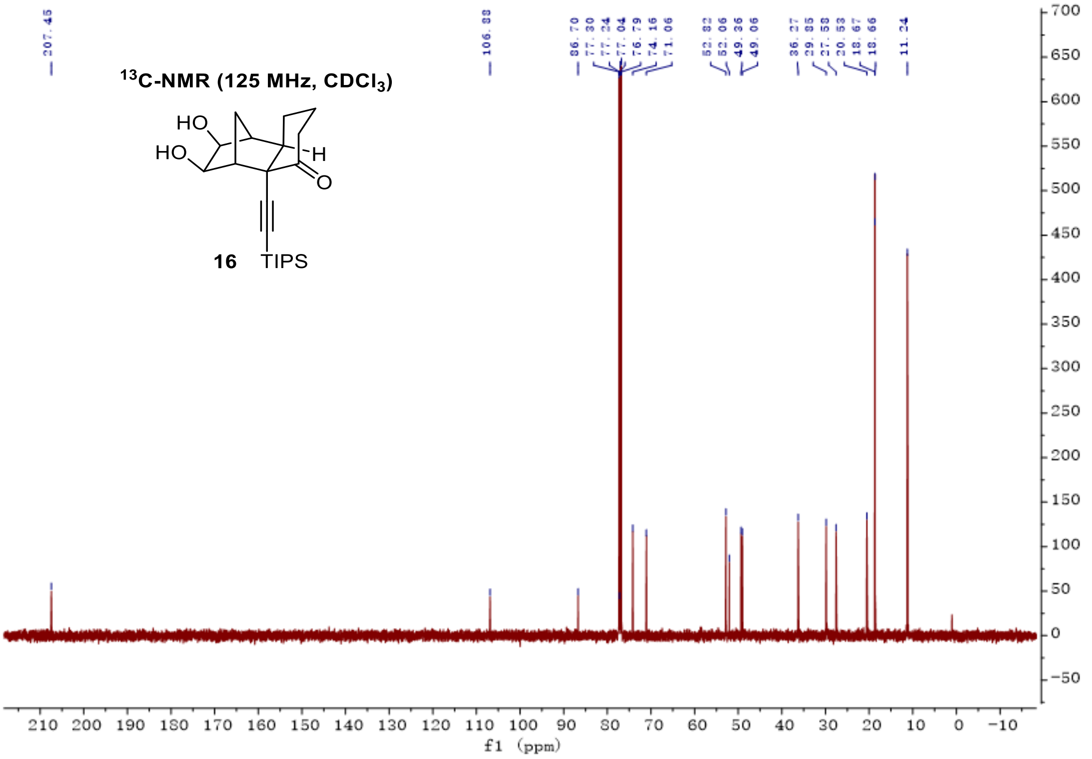
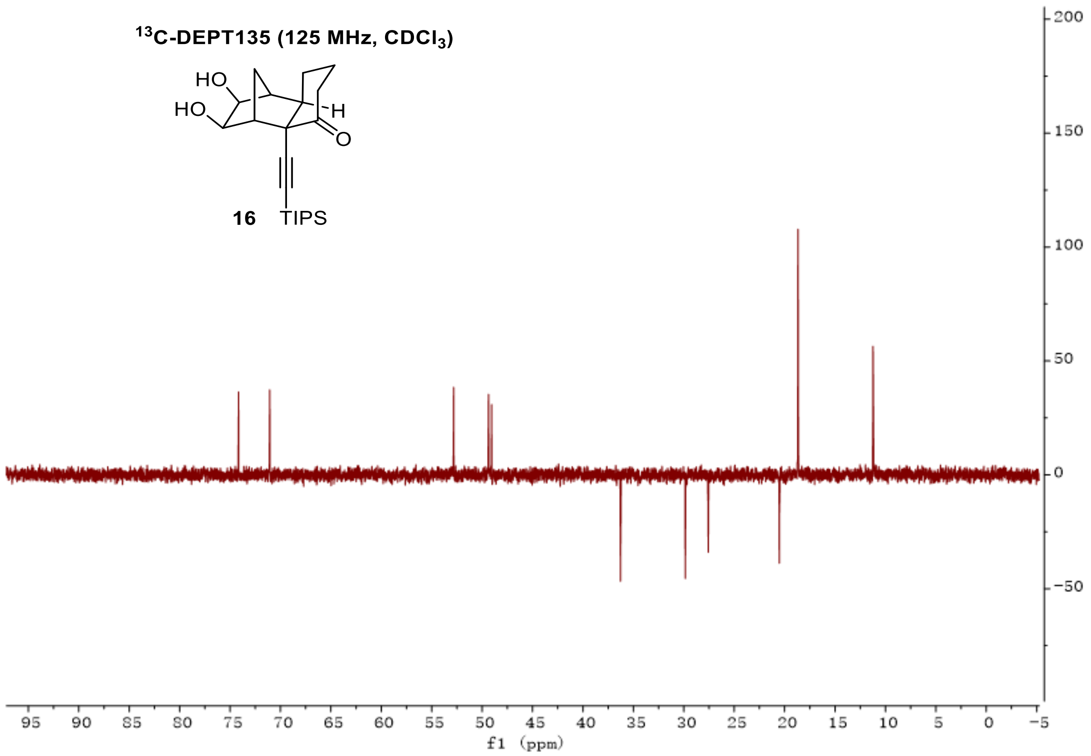
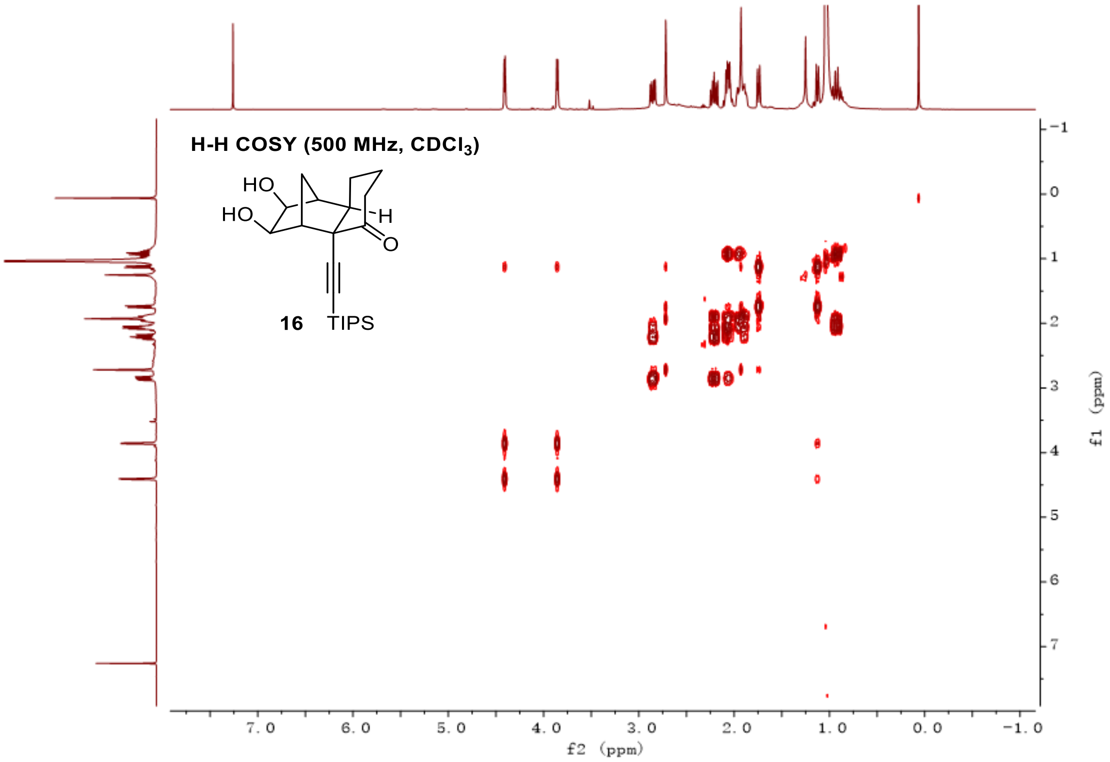
4.40
3.86
3.86
3.85
3.85
2.88
2.86
2.84
2.84
2.83
2.83
2.82
2.72
2.72
2.23
2.23
2.21
2.19
2.17
2.09
2.08
2.07
2.07
2.07
2.06
2.05
2.05
2.04
1.97
1.94
1.93
1.93
1.92
1.91
1.90
1.89
1.89
1.75
1.75
1.74
1.73
1.73
1.73
1.14
1.14
1.13
1.12
1.11
1.11
1.06
1.04
1.04
1.02
1.02
1.01
1.00
1.00
0.94
0.93
0.91
0.91
0.89
¹H-NMR (500 MHz, CDCl₃)
HO
HO
H
O
16
TIPS
1.00
1.05
1.39
1.20
1.22
2.09
3.33
1.15
1.08
21.45
1.34
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


207.45
106.88
86.70
77.30
77.24
77.04
76.79
74.16
71.06
52.82
52.06
49.36
49.06
36.27
29.85
27.58
20.53
18.67
18.66
11.24
¹³C-NMR (125 MHz, CDCl₃)
HO
HO
H
O
16
TIPS
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



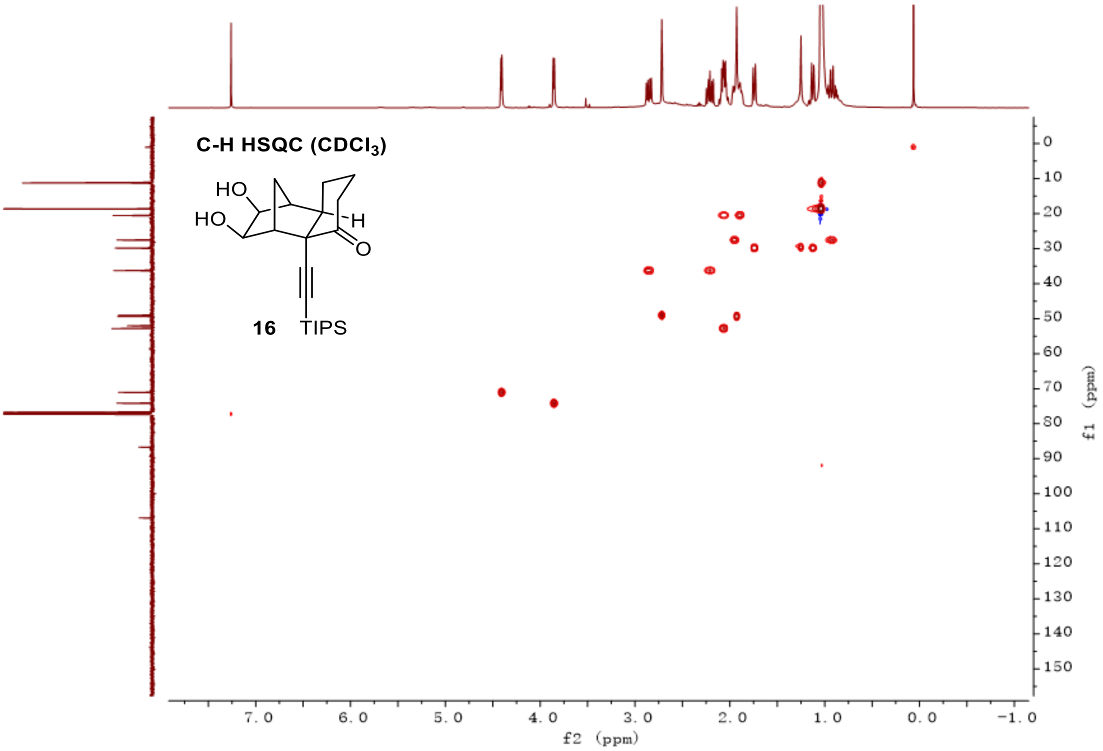
^{13}C-DEPT135 (125 MHz, CDCl$_3$)

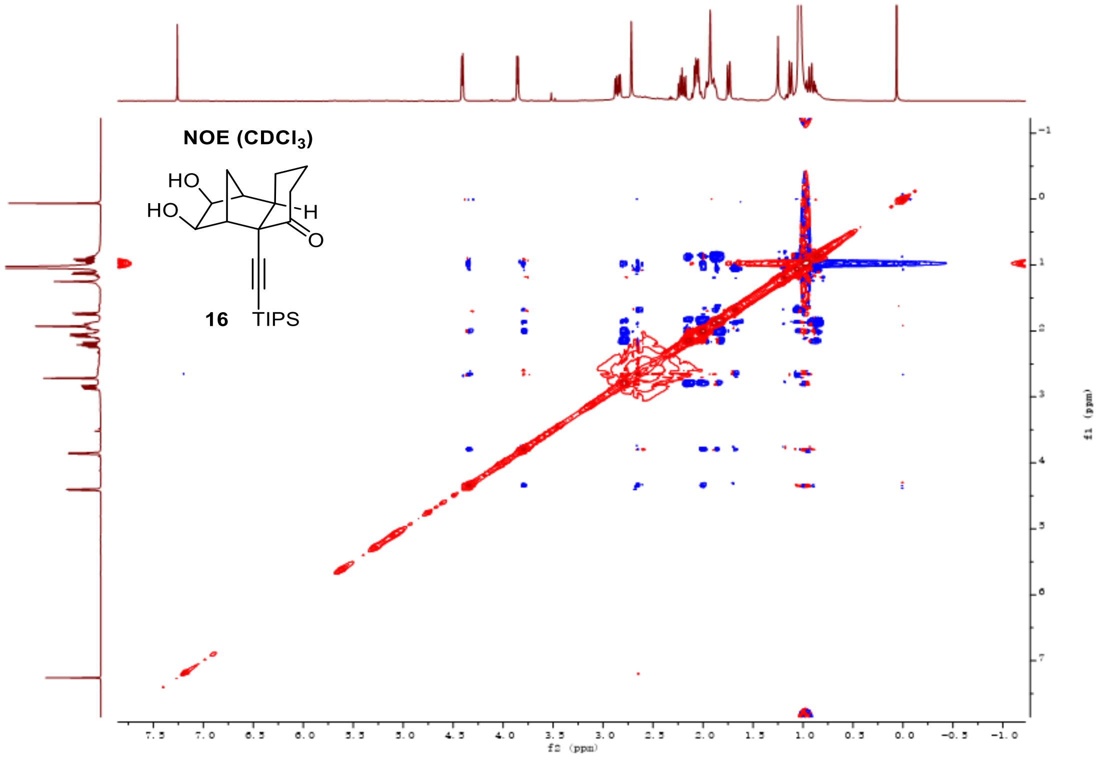
16

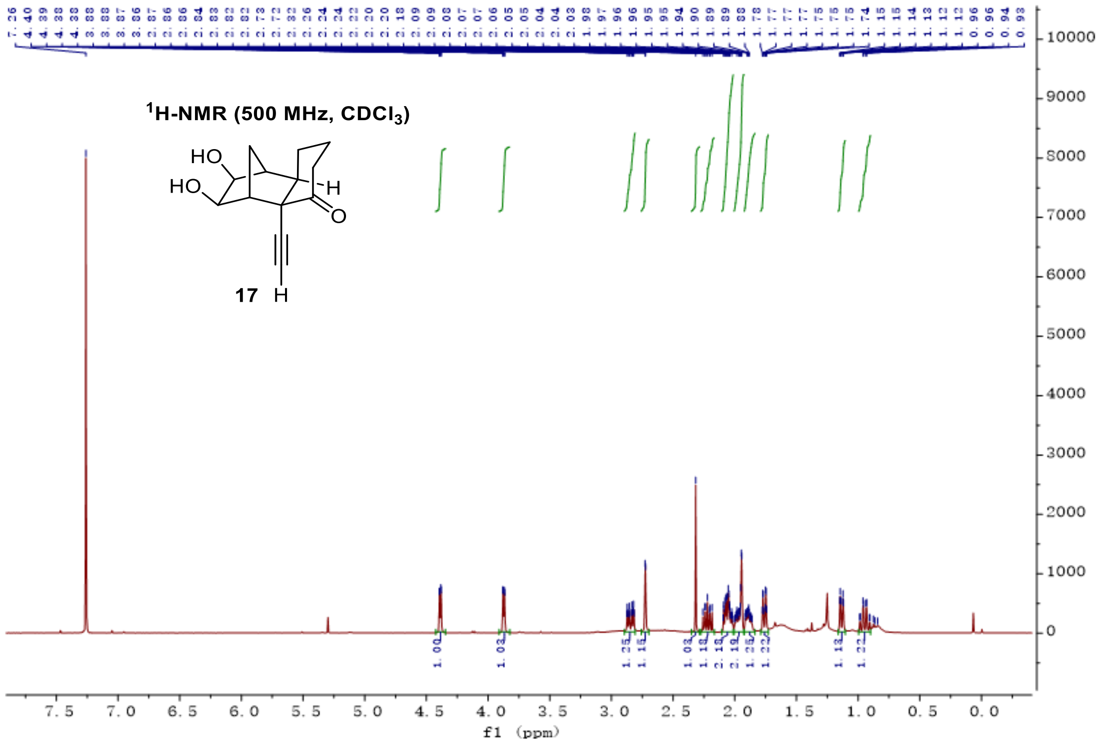


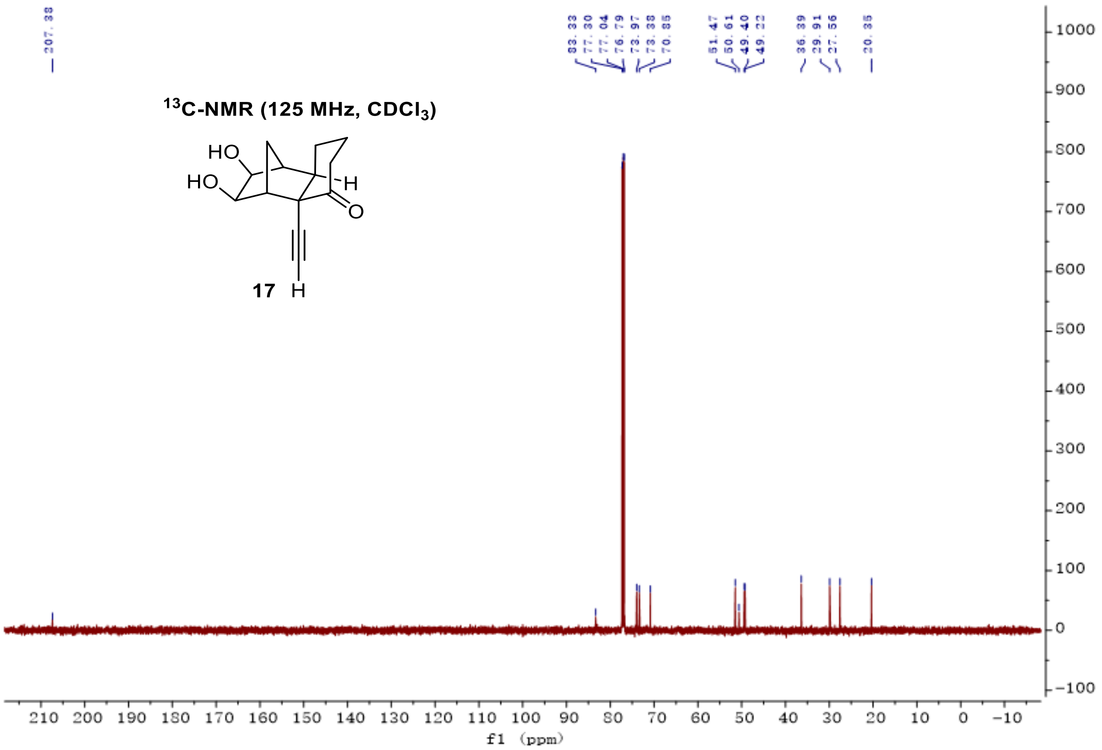
H-H COSY (500 MHz, CDCl$_3$)

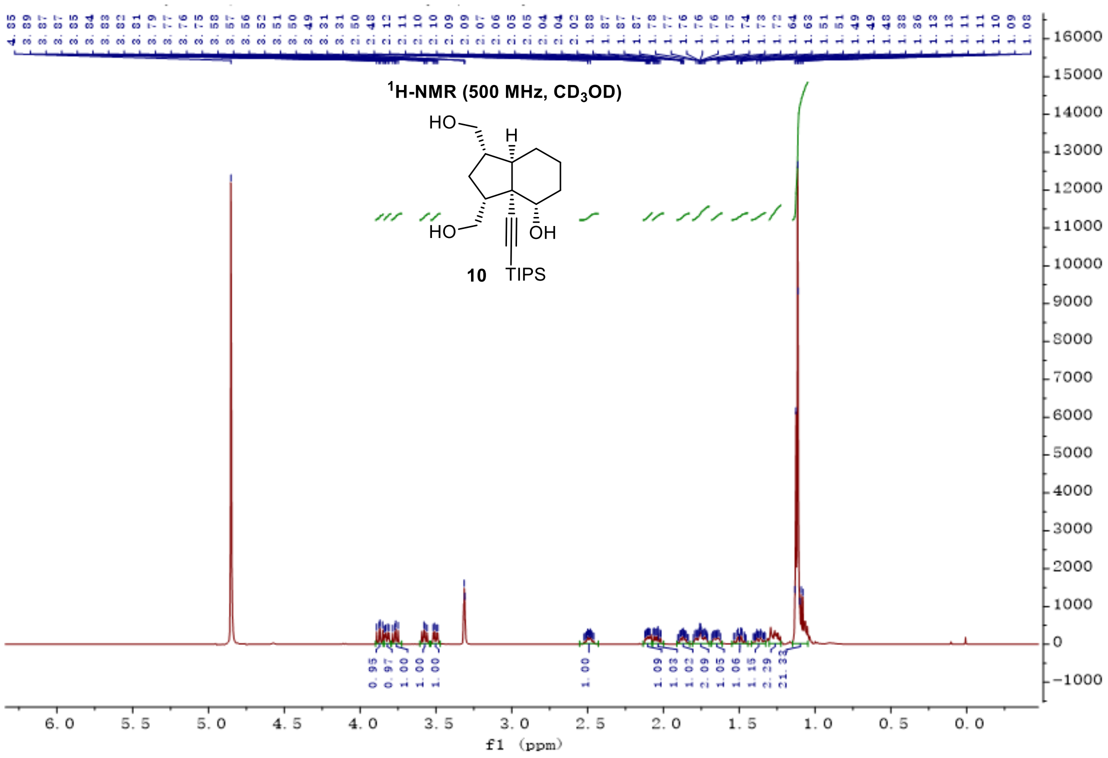
16

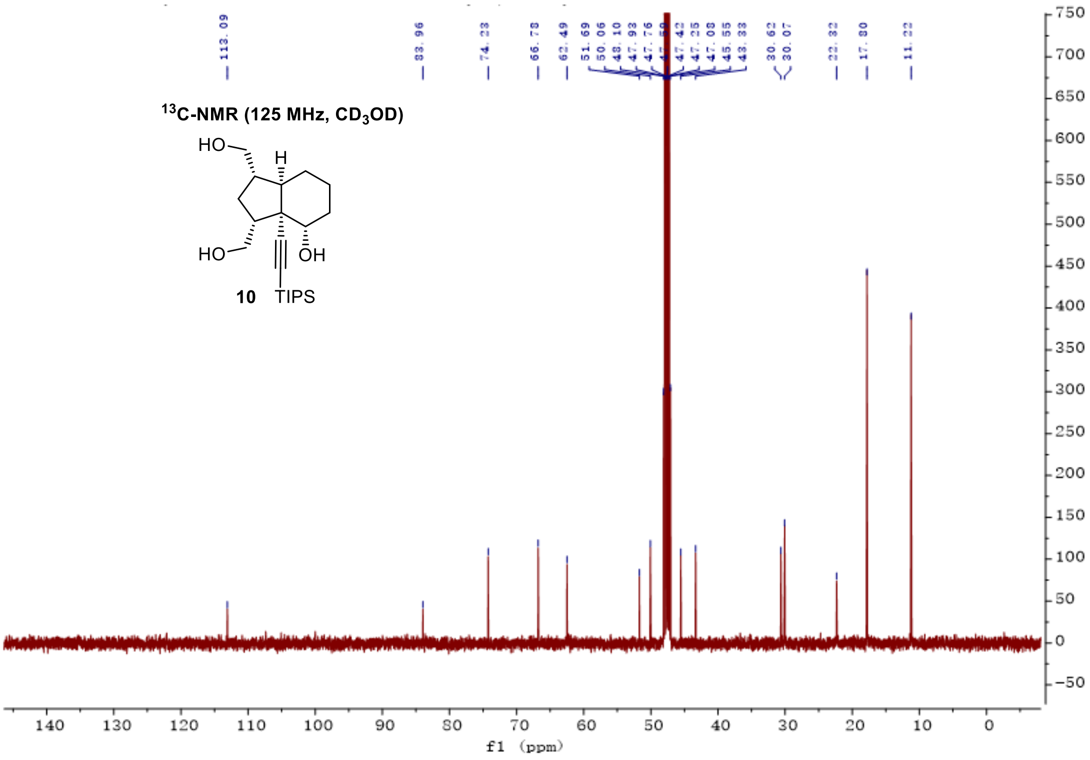

C-H HSQC (CDCl$_3$)
HO
HO
H
O
16
TIPS
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f2 (ppm)

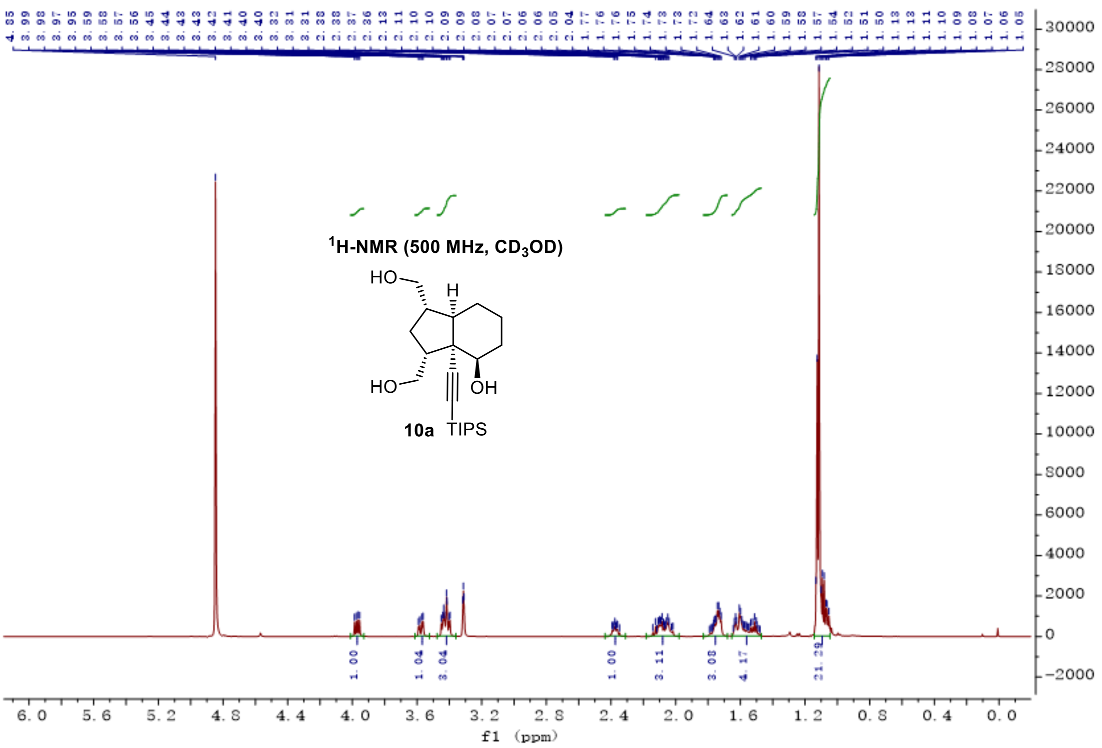

NOE (CDCl$_3$)
HO
HO
H
O
16
TIPS
-1
0
1
2
3
4
5
6
7
f1 (ppm)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f2 (ppm)

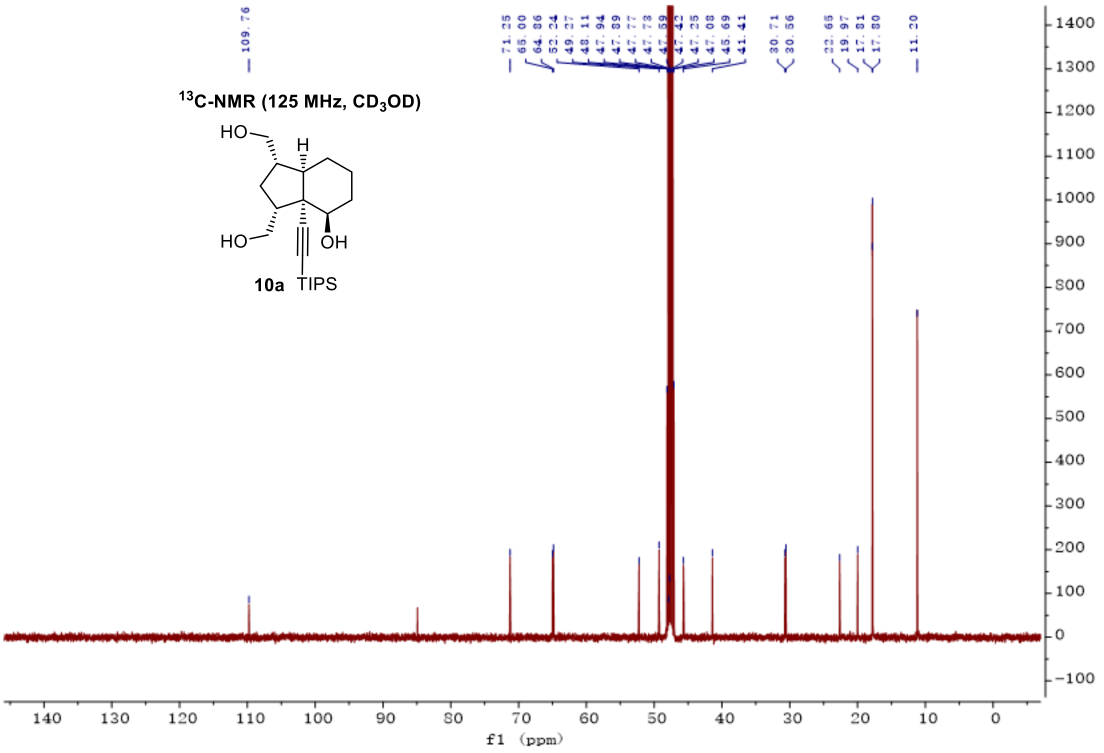

7.26
4.40
4.39
4.38
4.38
3.88
3.88
3.87
3.86
2.87
2.86
2.86
2.84
2.83
2.82
2.82
2.73
2.72
2.32
2.26
2.24
2.24
2.22
2.20
2.20
2.18
2.09
2.09
2.08
2.07
2.07
2.06
2.05
2.05
2.04
2.04
2.03
1.98
1.97
1.96
1.96
1.95
1.95
1.94
1.90
1.89
1.89
1.88
1.78
1.77
1.77
1.77
1.75
1.75
1.75
1.74
1.15
1.15
1.14
1.13
1.12
1.12
0.96
0.96
0.94
0.93
^{1}H-NMR (500 MHz, CDCl$_3$)
HO
HO
H
O
17
H
1.00
1.03
1.25
1.16
1.03
1.18
2.18
2.19
1.25
1.22
1.13
1.22
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

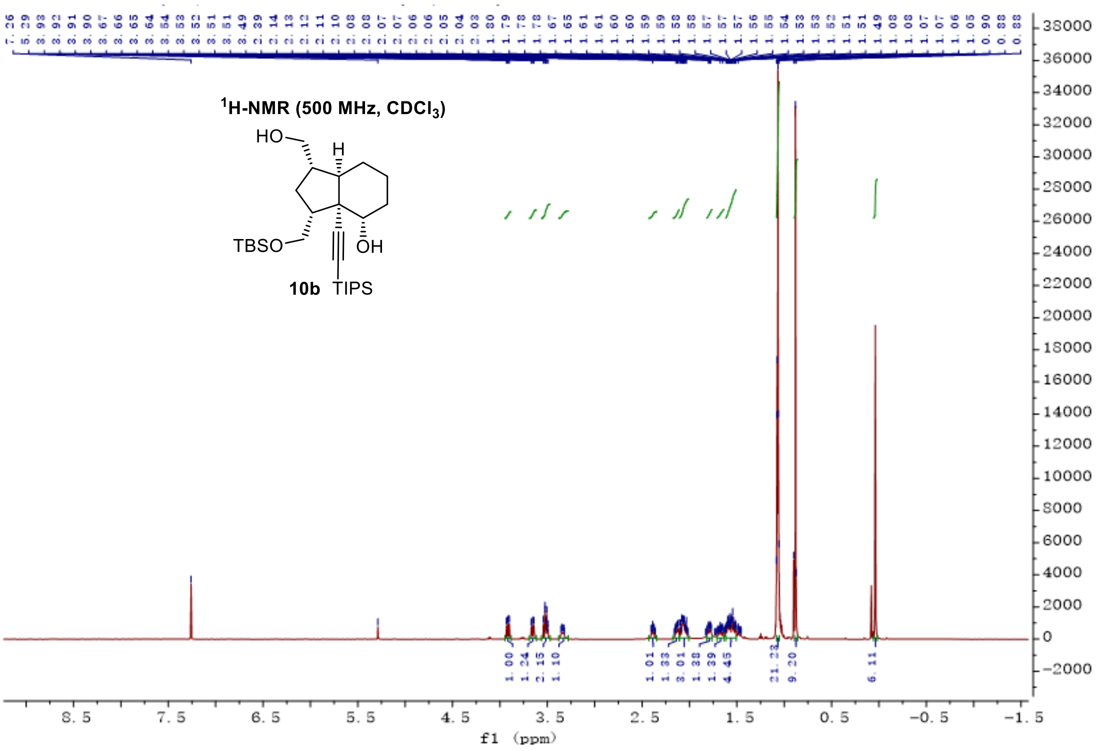

207.38
83.33
77.30
77.04
76.79
73.97
73.38
70.85
51.47
50.61
49.40
49.22
36.39
29.91
27.56
20.36
^{13}C-NMR (125 MHz, CDCl$_3$)
HO
HO
H
O
17
H
1000
900
800
700
600
500
400
300
200
100
0
−100
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

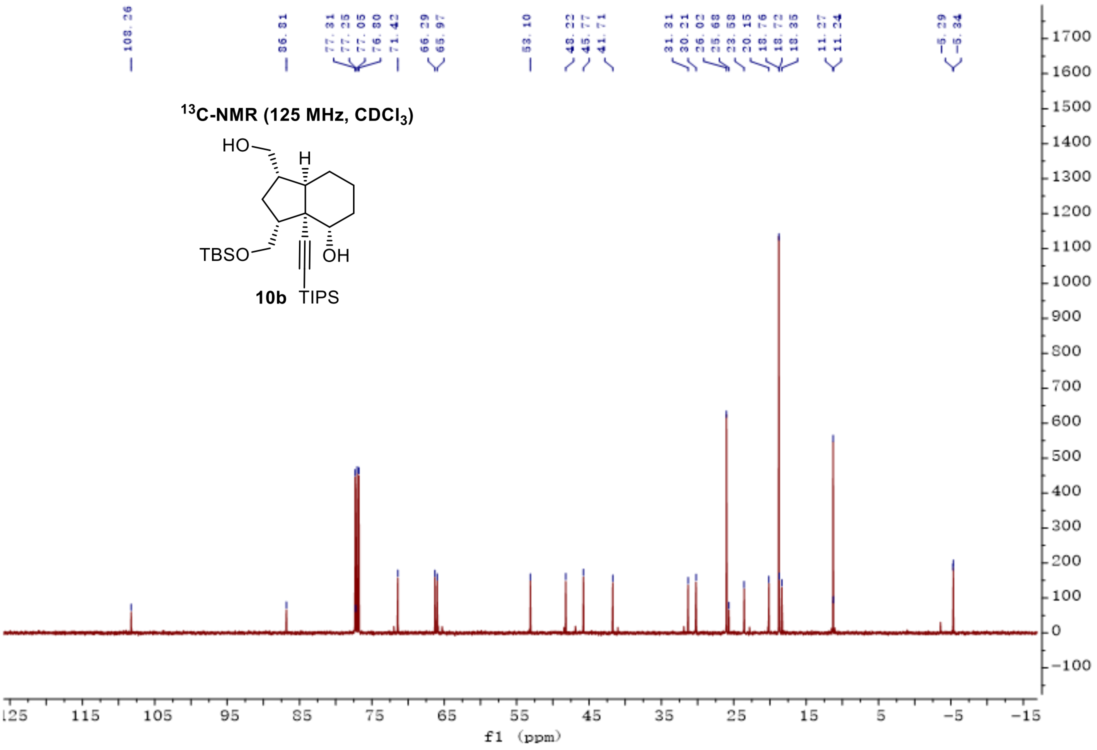

4.85
3.89
3.87
3.87
3.85
3.84
3.83
3.82
3.81
3.79
3.77
3.76
3.75
3.58
3.57
3.56
3.52
3.51
3.50
3.49
3.31
3.31
2.50
2.48
2.12
2.11
2.10
2.10
2.09
2.09
2.07
2.06
2.05
2.05
2.04
2.04
2.02
1.88
1.87
1.87
1.87
1.78
1.77
1.76
1.76
1.76
1.75
1.74
1.73
1.72
1.64
1.63
1.51
1.51
1.49
1.49
1.48
1.38
1.36
1.13
1.13
1.11
1.11
1.10
1.09
1.08
^{1}H-NMR (500 MHz, CD$_3$OD)
HO
H
HO
OH
10
TIPS
0.95
0.97
1.00
1.00
1.00
1.00
1.09
1.03
1.02
2.09
1.05
1.06
1.15
2.29
21.33
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000

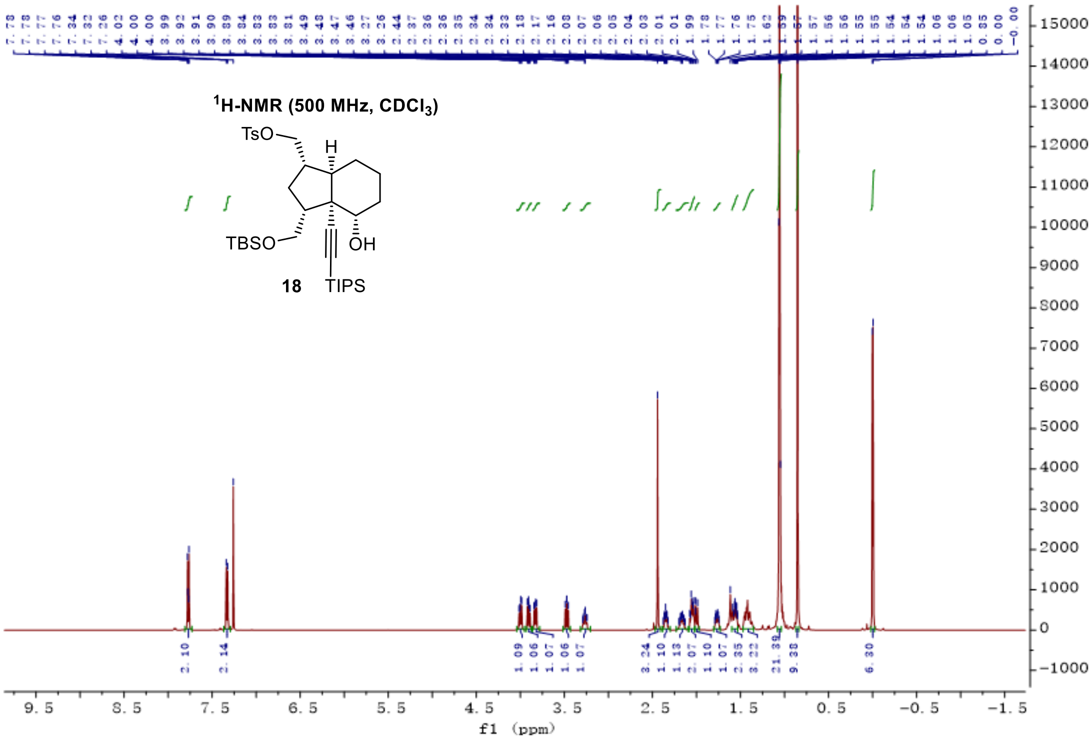

113.09
83.96
74.23
66.78
62.49
51.69
50.06
48.10
47.93
47.76
47.59
47.42
47.25
47.08
45.55
43.33
30.62
30.07
22.32
17.80
11.22
^{13}C-NMR (125 MHz, CD$_3$OD)
HO
H
HO
OH
10
TIPS
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
−50

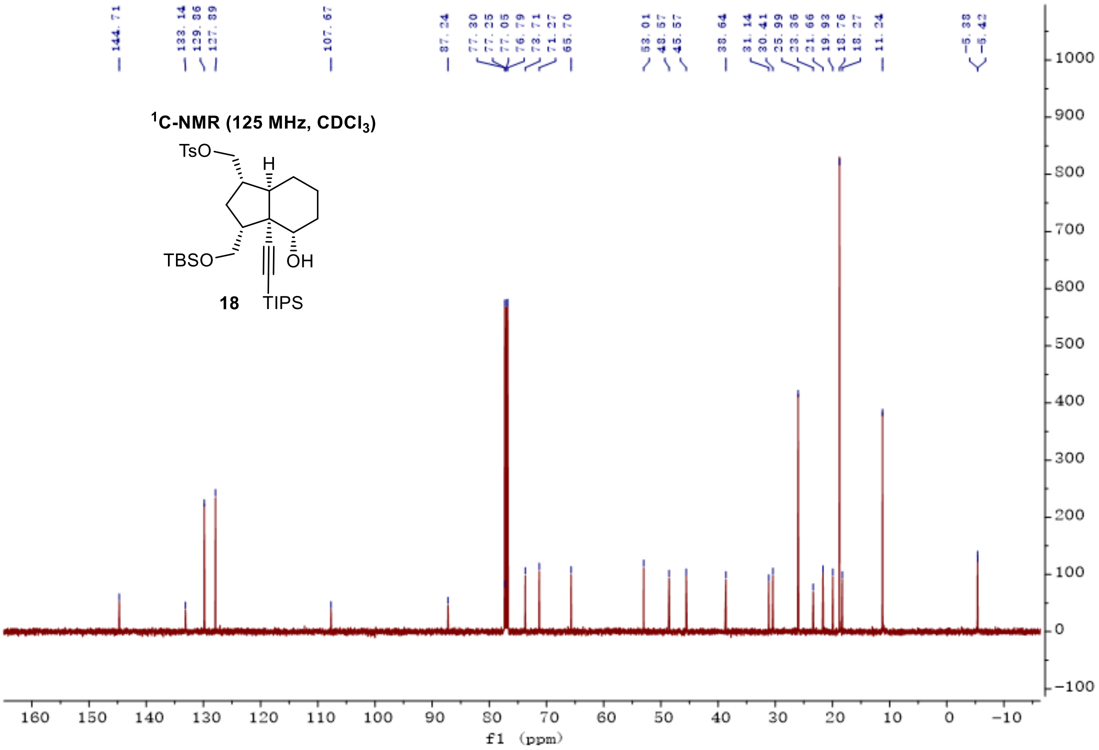

4.85 3.99 3.98 3.97 3.95 3.59 3.58 3.57 3.56 3.45 3.44 3.43 3.43 3.42 3.41 3.40 3.40 3.32 3.31 3.31 2.38 2.38 2.37 2.36 2.13 2.11 2.10 2.09 2.09 2.08 2.07 2.07 2.06 2.06 2.05 2.04 1.77 1.76 1.76 1.75 1.74 1.73 1.73 1.72 1.64 1.63 1.62 1.61 1.60 1.59 1.58 1.57 1.54 1.52 1.51 1.50 1.13 1.13 1.11 1.10 1.09 1.08 1.07 1.06 1.05
^{1}H-NMR (500 MHz, CD$_3$OD)
HO
H
HO
OH
10a
TIPS
1.00
1.04
3.04
1.00
3.11
3.08
4.17
21.29
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
−2000
6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2 0.8 0.4 0.0
f1 (ppm)

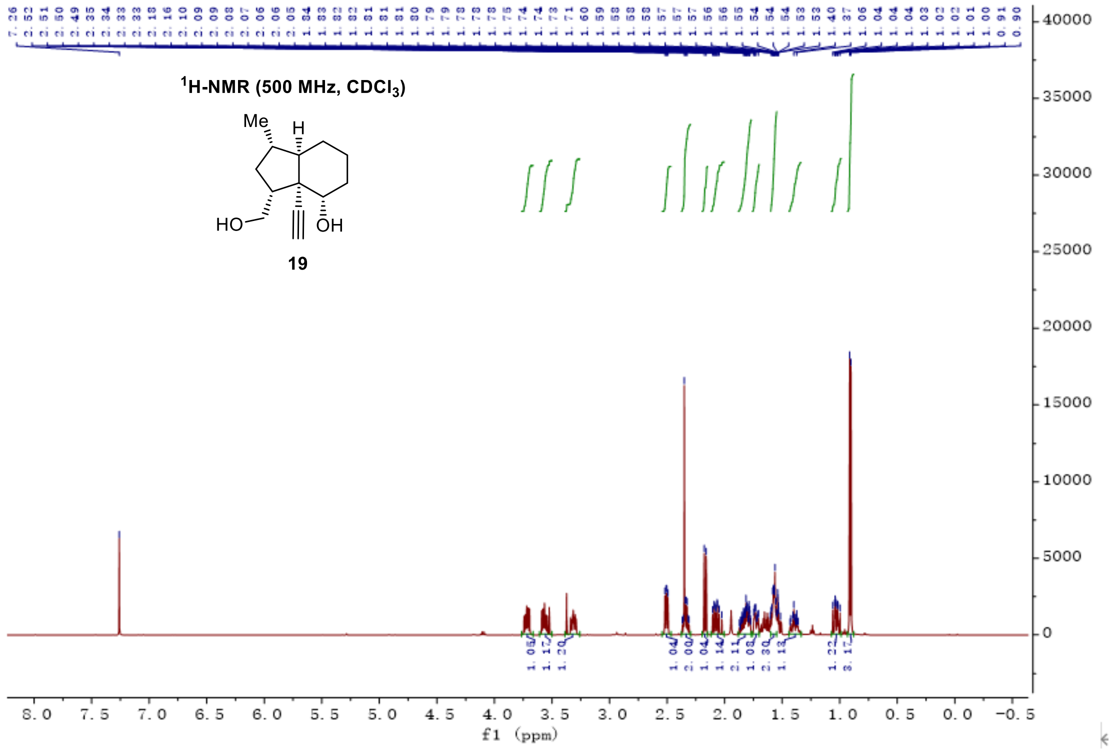

109.76
71.25 65.00 64.86 52.24 49.27 48.11 47.94 47.89 47.77 47.73 47.59 47.42 47.25 47.08 45.69 41.41
30.71 30.56
22.65 19.97 17.81 17.80
11.20
^{13}C-NMR (125 MHz, CD$_3$OD)
HO
H
HO
OH
10a
TIPS
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

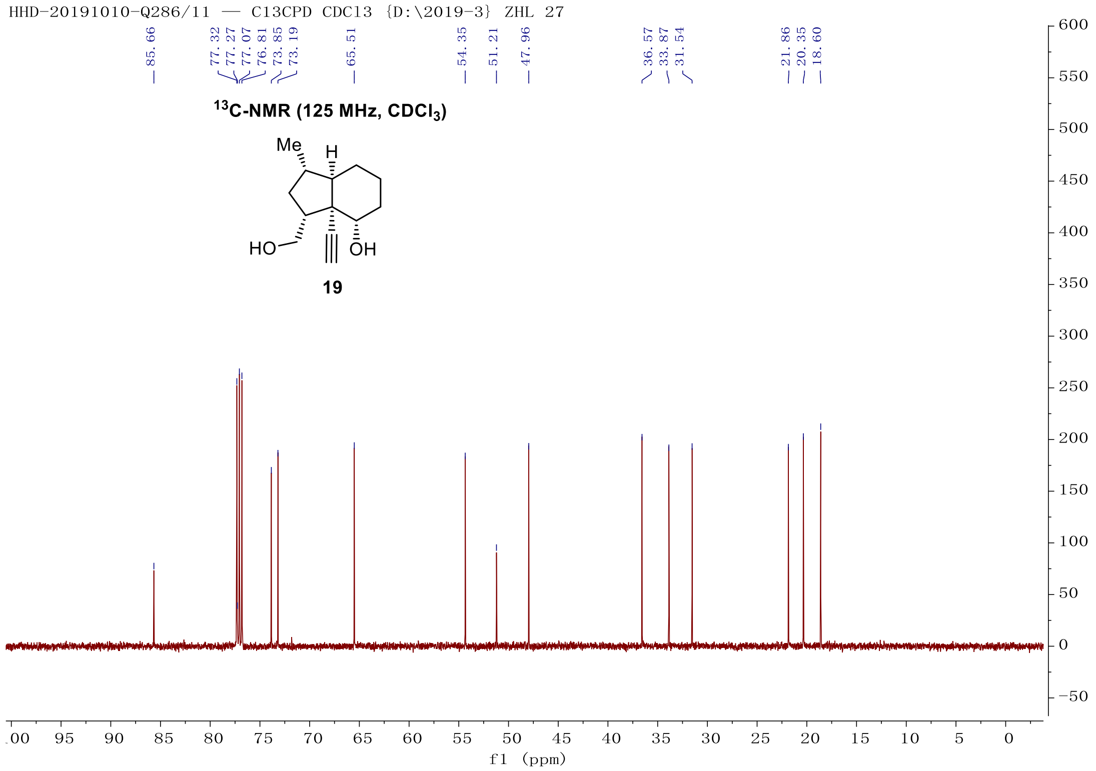

7.26
5.29
3.93
3.92
3.91
3.90
3.67
3.66
3.65
3.64
3.54
3.53
3.52
3.51
3.51
3.49
2.39
2.14
2.13
2.12
2.11
2.10
2.08
2.08
2.07
2.07
2.06
2.06
2.05
2.04
2.03
1.80
1.79
1.78
1.78
1.67
1.65
1.61
1.61
1.60
1.60
1.59
1.59
1.58
1.58
1.57
1.57
1.57
1.56
1.55
1.54
1.53
1.53
1.52
1.51
1.51
1.49
1.08
1.08
1.07
1.07
1.06
1.05
0.90
0.88
0.88
¹H-NMR (500 MHz, CDCl₃)
HO
H
TBSO
OH
10b
TIPS
1.00
1.24
2.15
1.10
1.01
1.33
3.01
1.38
1.39
4.45
21.23
9.20
6.11
38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5
f1 (ppm)

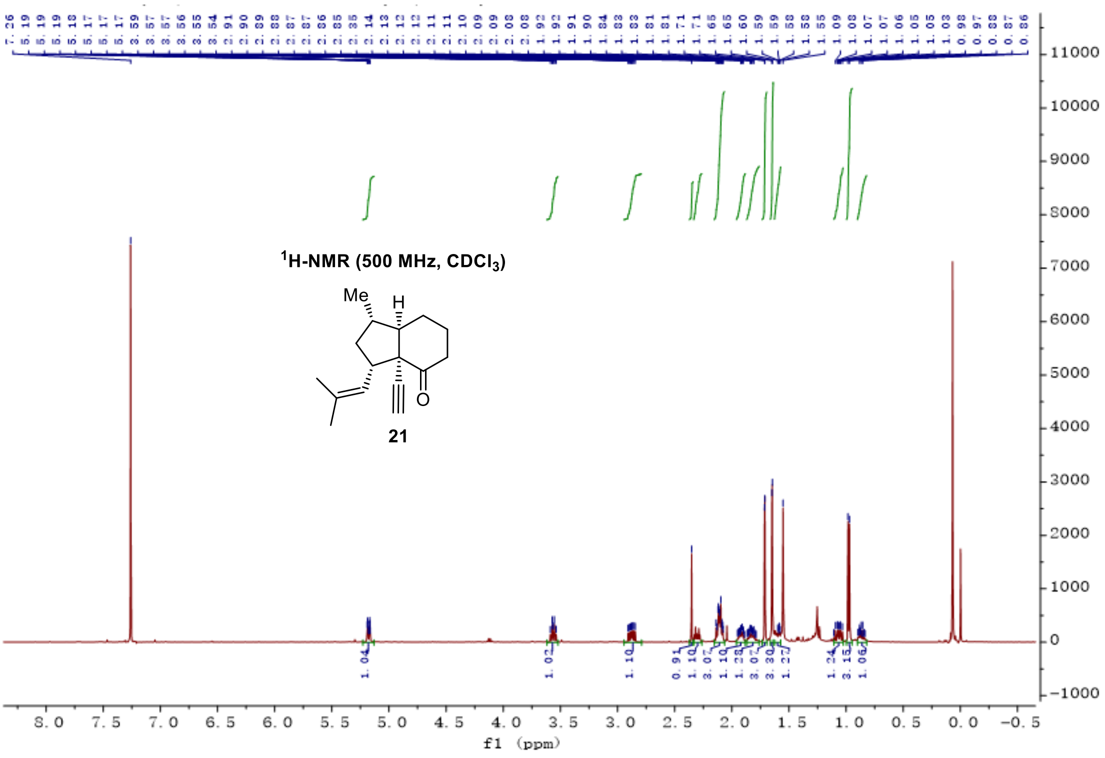

108.26
86.81
77.31
77.25
77.05
76.80
71.42
66.29
65.97
53.10
48.22
45.77
41.71
31.31
30.21
26.02
25.68
23.58
20.15
18.76
18.72
18.35
11.27
11.24
-5.29
-5.34
¹³C-NMR (125 MHz, CDCl₃)
HO
H
TBSO
OH
10b
TIPS
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
125
115
105
95
85
75
65
55
45
35
25
15
5
-5
-15
f1 (ppm)

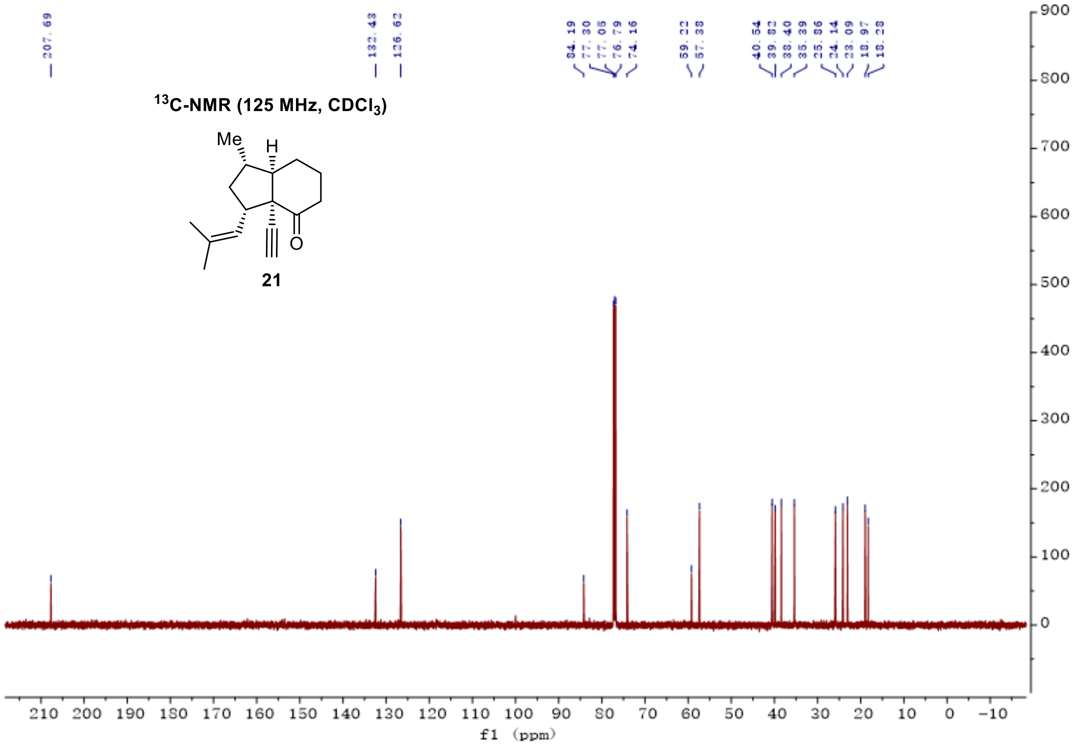

7.78
7.78
7.77
7.76
7.34
7.32
7.26
4.02
4.00
4.00
3.99
3.92
3.91
3.90
3.89
3.84
3.83
3.83
3.81
3.49
3.48
3.47
3.46
3.27
3.26
2.44
2.37
2.36
2.36
2.35
2.34
2.34
2.33
2.18
2.17
2.16
2.08
2.07
2.06
2.05
2.04
2.03
2.01
2.01
1.99
1.78
1.77
1.76
1.75
1.62
1.59
1.57
1.57
1.56
1.56
1.55
1.55
1.54
1.54
1.54
1.06
1.06
1.05
0.85
0.00
-0.00
^{1}H-NMR (500 MHz, CDCl$_3$)
TsO
H
TBSO
OH
18
TIPS
2.10
2.14
1.09
1.06
1.07
1.06
1.07
3.24
1.10
1.13
2.07
1.10
1.07
2.35
3.22
21.38
9.38
6.30
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5
f1 (ppm)

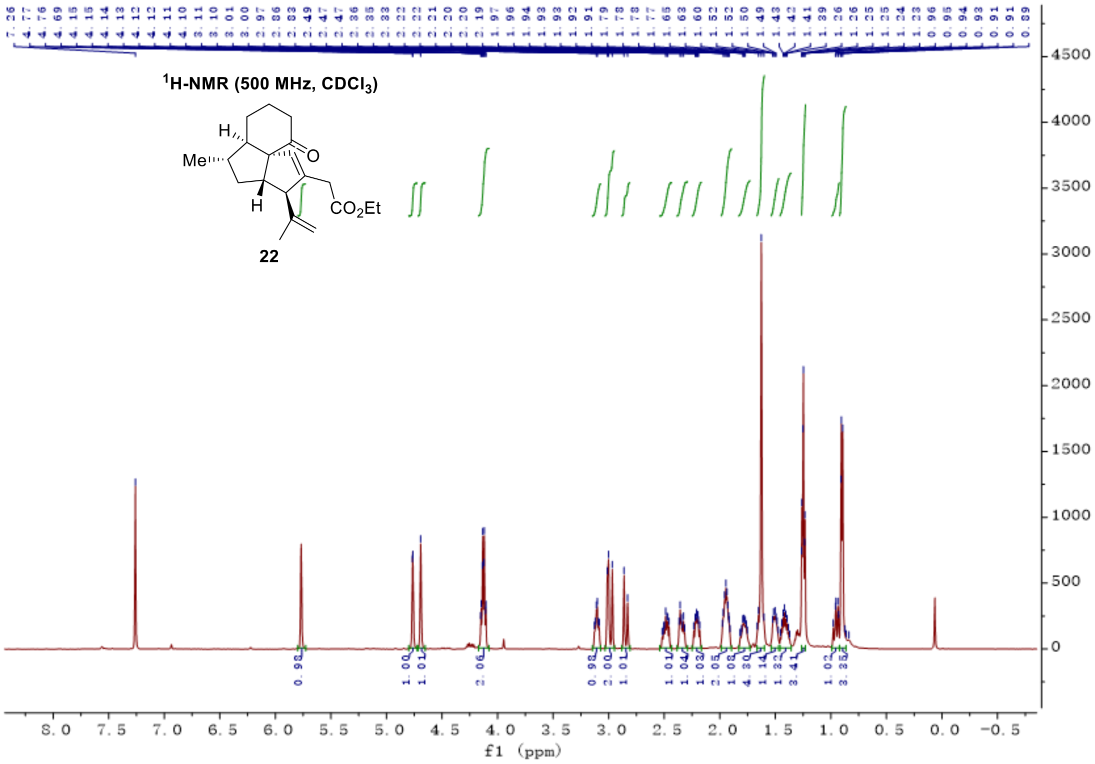

144.71
133.14
129.86
127.89
107.67
87.24
77.30
77.25
77.05
76.79
73.71
71.27
65.70
53.01
48.57
45.57
38.64
31.14
30.41
25.99
23.36
21.66
19.93
18.76
18.27
11.24
-5.38
-5.42
^{1}C-NMR (125 MHz, CDCl$_3$)
TsO
H
TBSO
OH
18
TIPS
1000
900
800
700
600
500
400
300
200
100
0
-100
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

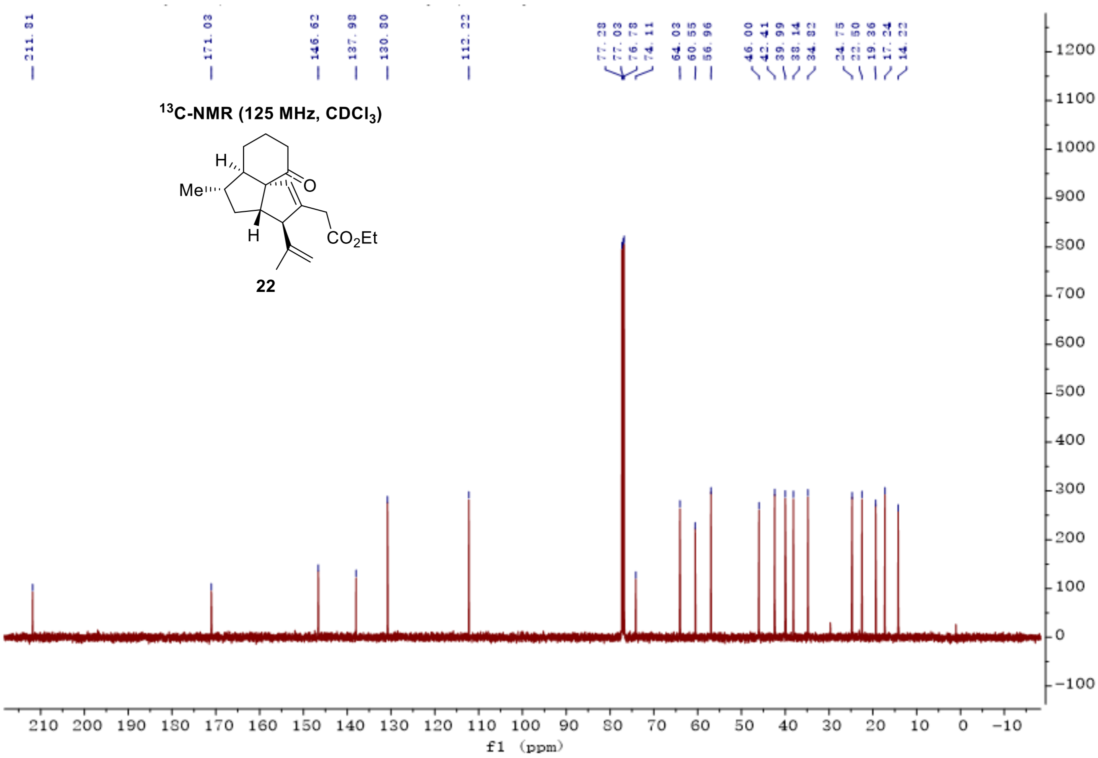

7.26
2.52
2.51
2.50
2.49
2.35
2.34
2.33
2.33
2.18
2.16
2.10
2.09
2.09
2.08
2.07
2.06
2.06
2.05
1.84
1.83
1.82
1.82
1.81
1.81
1.81
1.80
1.79
1.79
1.78
1.78
1.78
1.75
1.74
1.74
1.73
1.71
1.60
1.59
1.58
1.58
1.58
1.57
1.57
1.57
1.56
1.56
1.55
1.54
1.54
1.54
1.53
1.53
1.40
1.37
1.06
1.04
1.04
1.04
1.03
1.02
1.02
1.01
1.00
0.91
0.90
¹H-NMR (500 MHz, CDCl₃)
Me
H
HO
OH
19
1.05
1.17
1.20
1.04
2.00
1.04
1.14
2.11
1.08
2.30
1.13
1.22
3.17
40000
35000
30000
25000
20000
15000
10000
5000
0
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

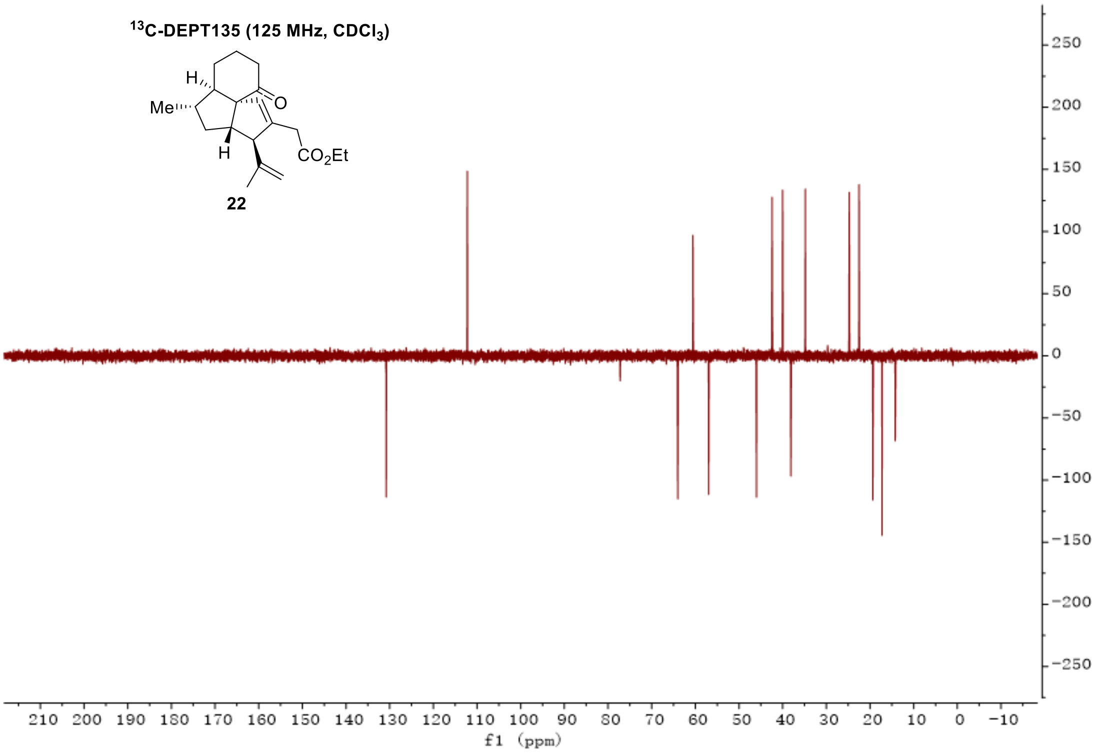

HHD-20191010-Q286/11 — C13CPD CDC13 {D:\2019-3} ZHL 27
85.66
77.32
77.27
77.07
76.81
73.85
73.19
65.51
54.35
51.21
47.96
36.57
33.87
31.54
21.86
20.35
18.60
¹³C-NMR (125 MHz, CDCl₃)
Me
H
HO
OH
19
600
550
500
450
400
350
300
250
200
150
100
50
0
−50
.00
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)


7.26 5.19 5.19 5.18 5.17 5.17 5.17 3.59 3.57 3.57 3.56 3.55 3.54 2.91 2.90 2.89 2.87 2.87 2.86 2.85 2.85 2.14 2.13 2.12 2.12 2.11 2.11 2.10 2.09 2.09 2.08 2.08 1.92 1.92 1.91 1.90 1.84 1.83 1.83 1.81 1.81 1.71 1.65 1.65 1.60 1.59 1.59 1.58 1.58 1.55 1.09 1.08 1.07 1.07 1.06 1.05 1.05 1.03 0.98 0.97 0.88 0.87 0.86
^{1}H-NMR (500 MHz, CDCl$_3$)
Me
H
O
21
1.04
1.02
1.10
0.91
1.10
3.07
1.10
1.28
3.07
3.30
1.27
1.24
3.15
1.06
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


207.69
132.43
126.62
84.19
77.30
77.05
76.79
74.16
59.22
57.38
40.54
39.82
38.40
35.39
25.86
24.14
23.09
18.97
18.28
^{13}C-NMR (125 MHz, CDCl$_3$)
Me
H
O
21
900
800
700
600
500
400
300
200
100
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

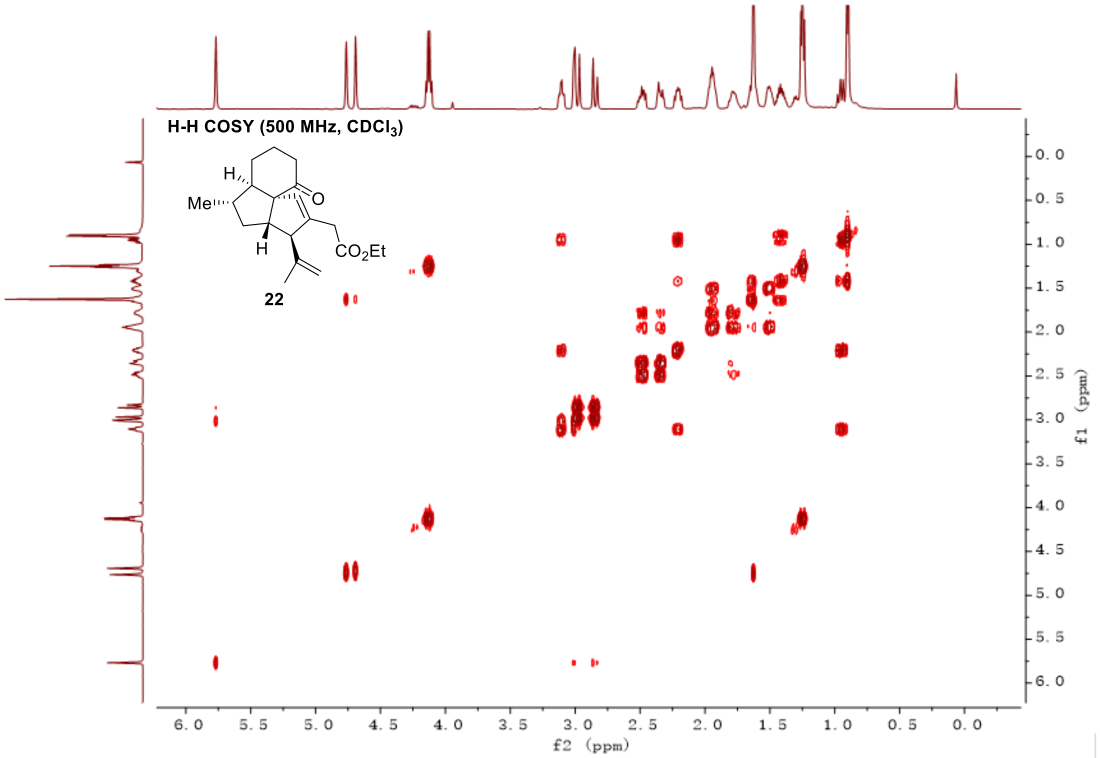

7.26 4.77 4.76 4.69 4.15 4.15 4.14 4.13 4.12 4.12 4.11 4.10 3.11 3.10 3.01 3.00 2.97 2.86 2.83 2.49 2.47 2.47 2.36 2.35 2.33 2.22 2.22 2.21 2.20 2.20 2.19 1.97 1.96 1.94 1.93 1.93 1.92 1.91 1.79 1.78 1.78 1.77 1.65 1.63 1.60 1.52 1.52 1.50 1.49 1.43 1.42 1.41 1.39 1.26 1.26 1.25 1.25 1.24 1.23 0.96 0.95 0.94 0.93 0.91 0.91 0.89
^{1}H-NMR (500 MHz, CDCl$_3$)
H
Me
O
H
CO$_2$Et
22
0.98
1.00
1.01
2.06
0.98
2.00
1.01
1.01
1.04
1.03
2.05
1.08
4.30
1.14
1.32
3.41
1.02
3.35
4500
4000
3500
3000
2500
2000
1500
1000
500
0
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


211.81
171.03
146.62
137.98
130.80
112.22
77.28 77.03 76.78 74.11
64.03 60.55 56.96
46.00 42.41 39.99 38.14 34.82
24.75 22.50 19.36 17.24 14.22
^{13}C-NMR (125 MHz, CDCl$_3$)
H
Me
O
H
CO$_2$Et
22
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



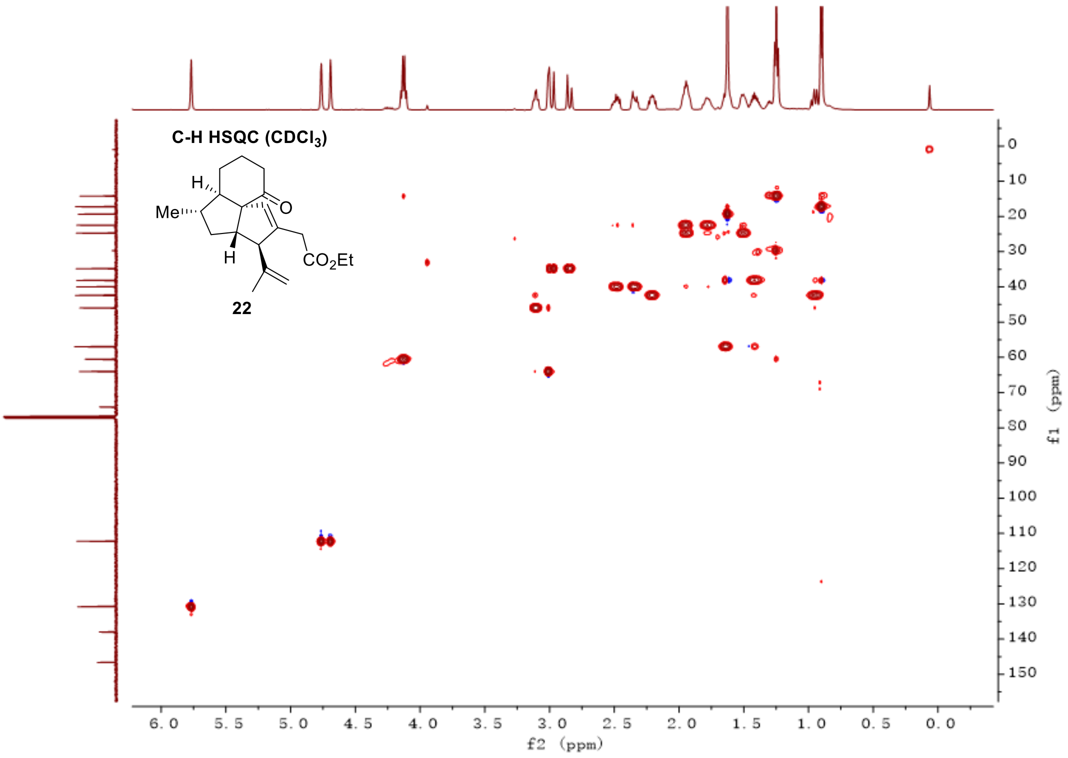
^{13}C-DEPT135 (125 MHz, $CDCl_3$)

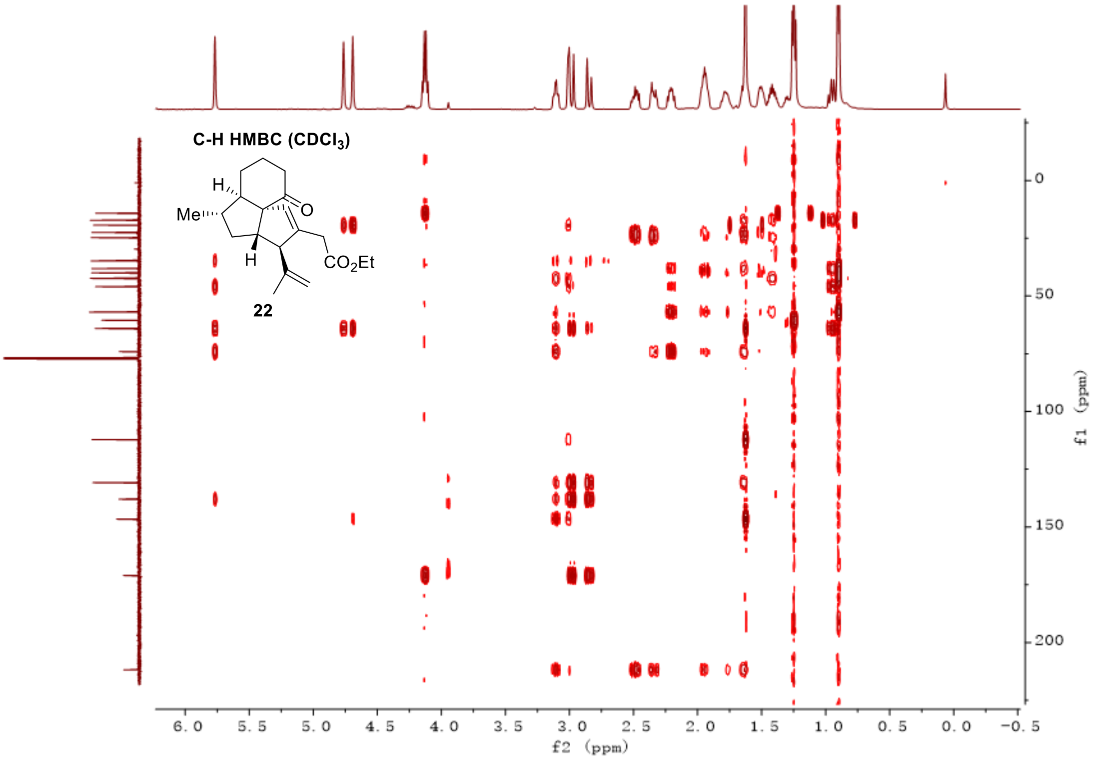
22

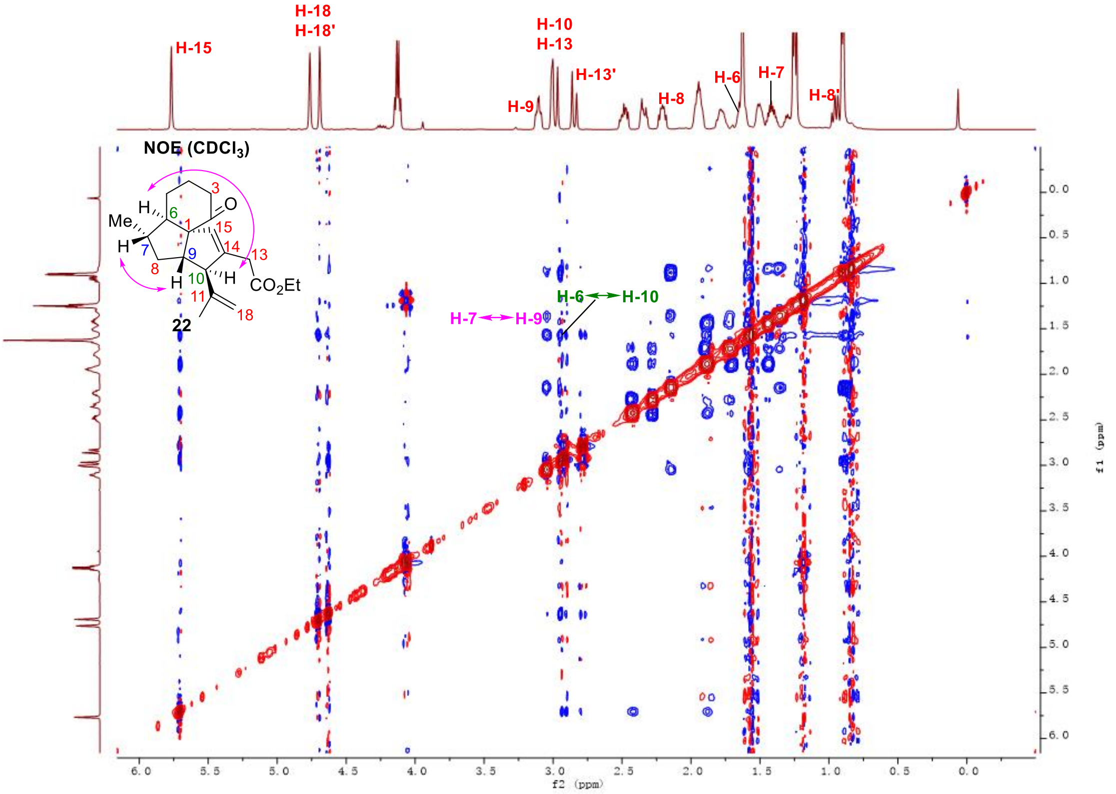


H-H COSY (500 MHz, $CDCl_3$)

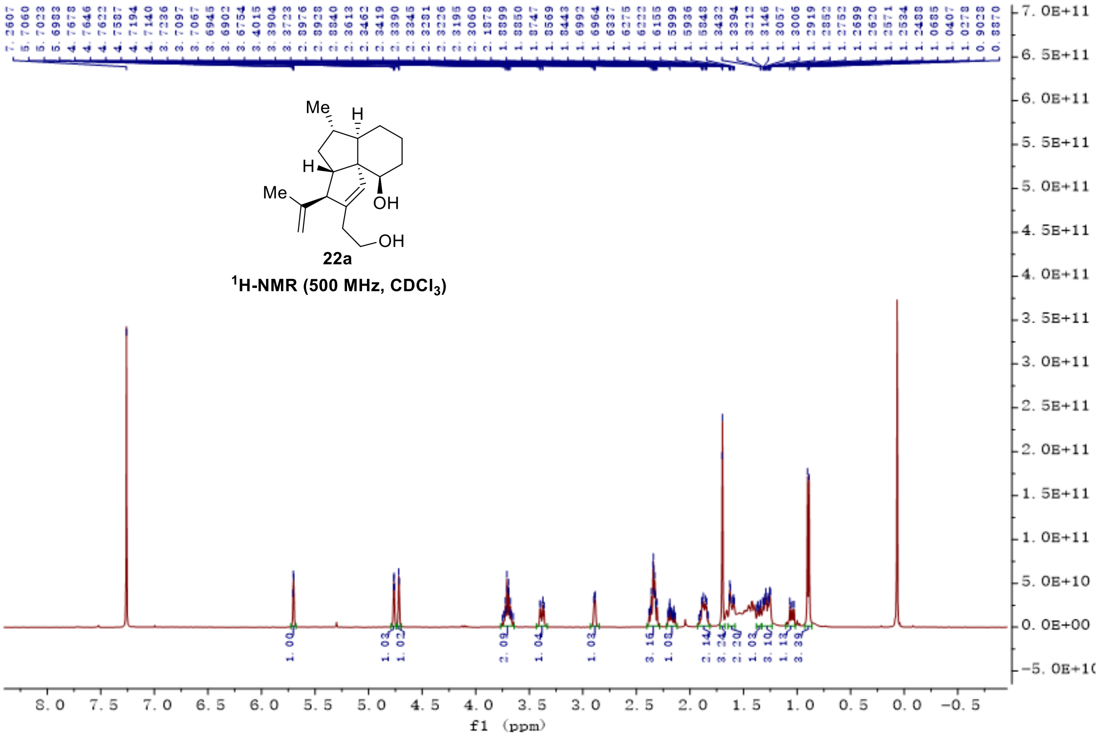
22


C-H HSQC (CDCl$_3$)
H
Me
O
H
CO$_2$Et
22
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)

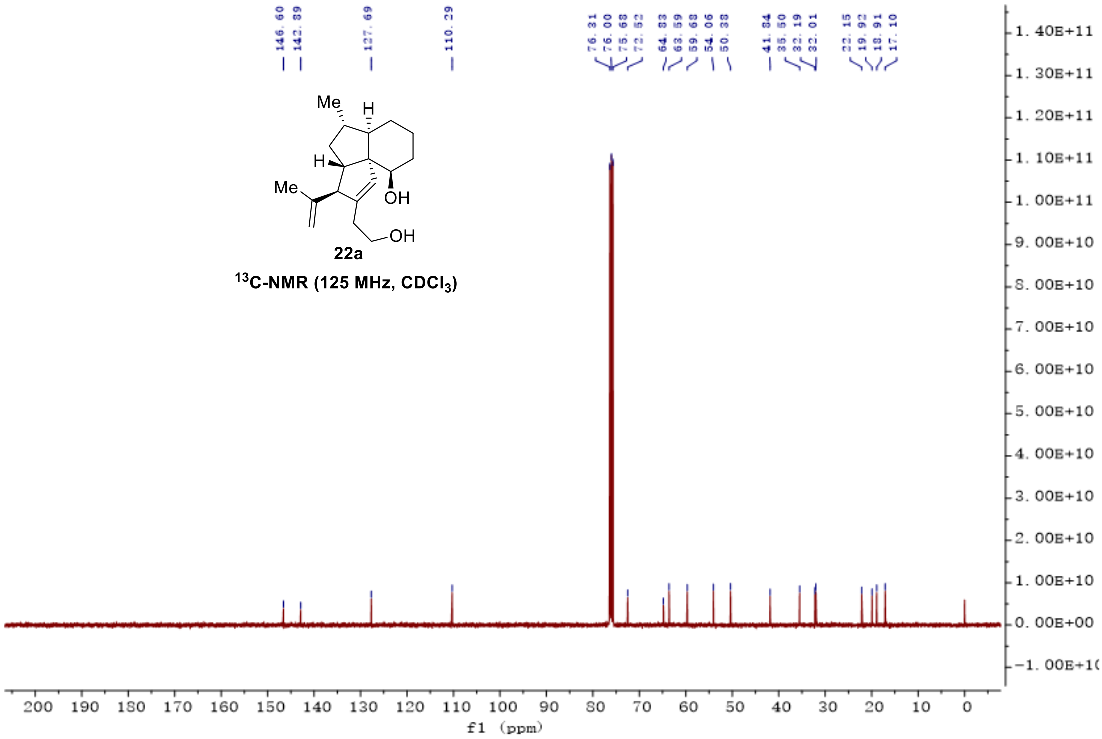

C-H HMBC (CDCl$_3$)
H
Me
O
H
CO$_2$Et
22
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f2 (ppm)
0
50
100
150
200
f1 (ppm)



H-15
H-18
H-18'
H-10
H-13
H-13'
H-9
H-8
H-6
H-7
H-8'
NOE (CDCl$_3$)
3
O
H
6
Me
1
15
14
13
7
H
9
8
10
H
H
CO$_2$Et
11
18
22
H-7 ↔ H-9
H-6 ↔ H-10
6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f2 (ppm)
0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0
f1 (ppm)

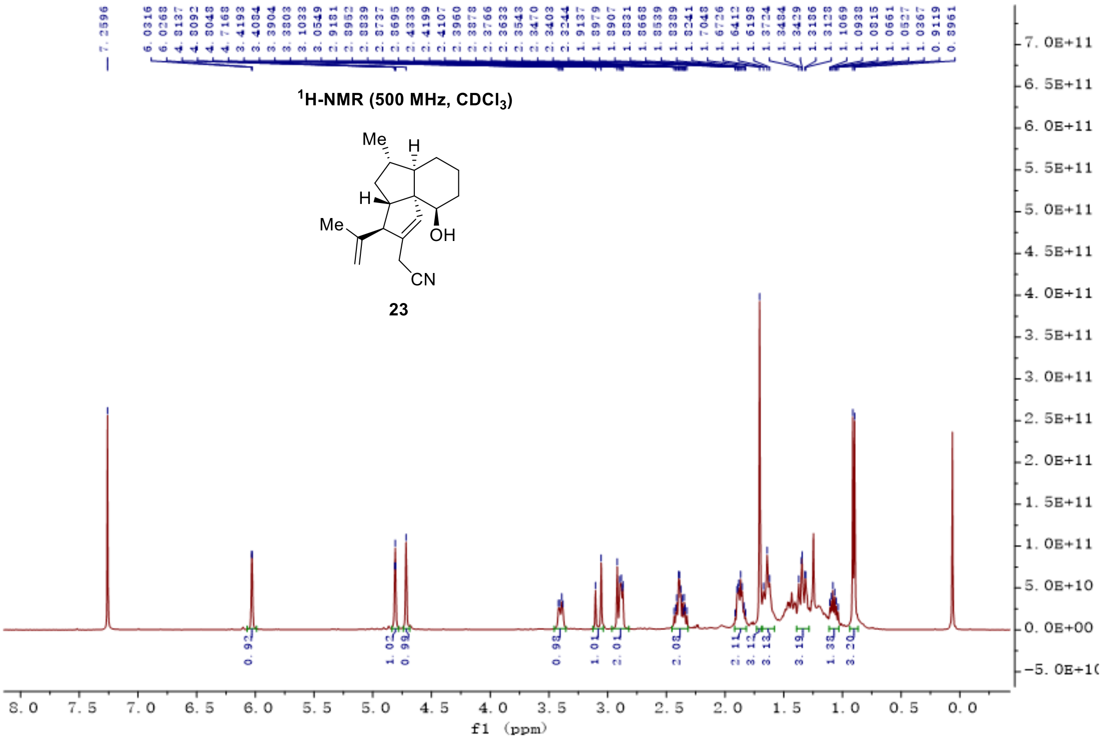


7.2607 5.7060 5.7023 5.6983 4.7678 4.7646 4.7622 4.7587 4.7194 4.7140 3.7236 3.7097 3.7067 3.6945 3.6902 3.6754 3.4015 3.3904 3.3723 2.8976 2.8928 2.8840 2.3613 2.3462 2.3419 2.3390 2.3345 2.3281 2.3226 2.3195 2.3060 2.1878 1.8899 1.8850 1.8747 1.8569 1.8443 1.6992 1.6964 1.6337 1.6275 1.6222 1.6155 1.5999 1.5936 1.5848 1.3432 1.3394 1.3212 1.3146 1.3057 1.3006 1.2919 1.2852 1.2752 1.2699 1.2620 1.2571 1.2534 1.2488 1.0685 1.0407 1.0278 0.9028 0.8870
Me
H
H
Me
OH
OH
22a
^{1}H-NMR (500 MHz, CDCl$_3$)
1.00
1.03
1.03
2.09
1.04
1.03
3.16
1.08
2.14
3.24
2.20
1.03
3.10
1.13
3.39
7.0E+11 6.5E+11 6.0E+11 5.5E+11 5.0E+11 4.5E+11 4.0E+11 3.5E+11 3.0E+11 2.5E+11 2.0E+11 1.5E+11 1.0E+11 5.0E+10 0.0E+00 −5.0E+10
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)



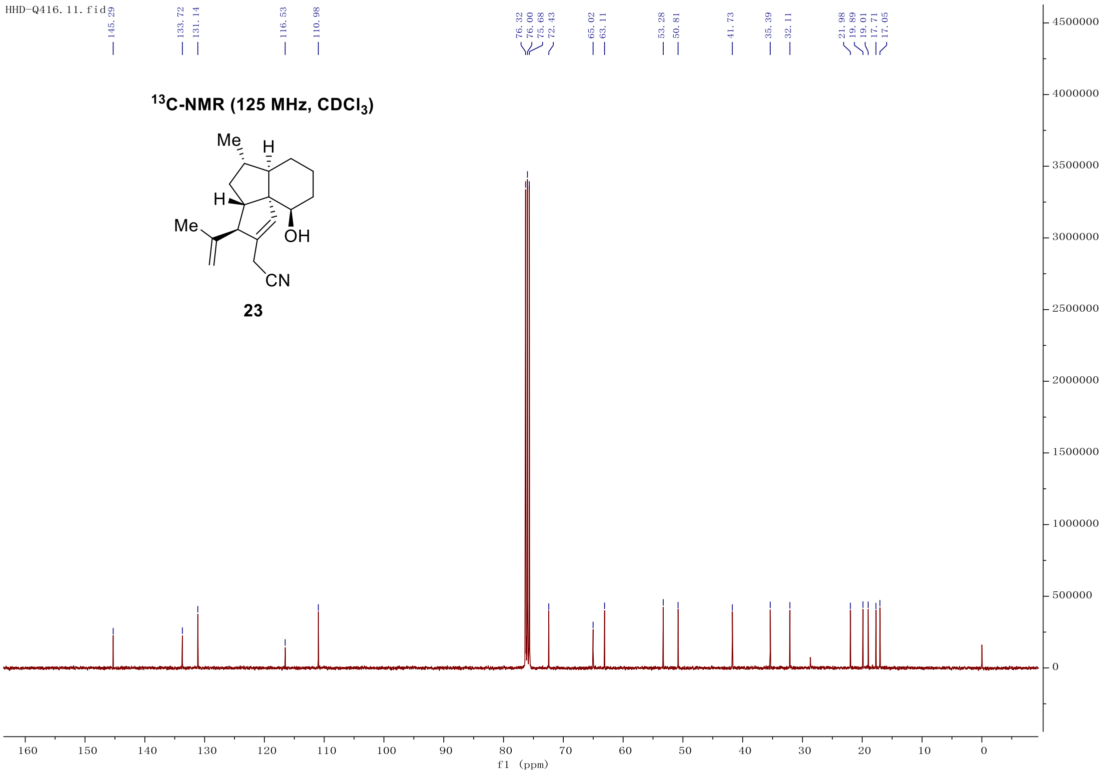
22a

^{13}C-NMR (125 MHz, CDCl$_3$)



^{1}H-NMR (500 MHz, CDCl$_3$)

23


^{13}C-NMR (125 MHz, $CDCl_3$)

23