

CHEMISTRY

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Supporting Information

Conformational Bias by a Removable Silyl Group: Construction of Bicyclo[*n*.3.1]alkenes by Ring Closing Metathesis

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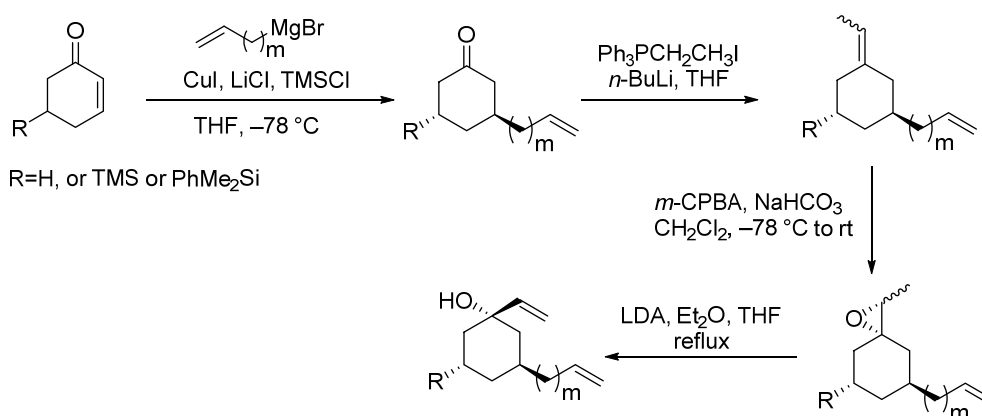
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1. General Information

All reactions were carried out under an argon atmosphere with dry solvents under anhydrous conditions, unless otherwise stated. All the chemicals were purchased commercially and used without further purification, unless otherwise stated. The boiling point of petroleum ether (PE) is between 60-90 °C. Tetrahydrofuran (THF) was distilled from sodium-benzophenone; Dichloromethane (CH_2Cl_2) was distilled from calcium hydride. Toluene was distilled from sodium under argon atmosphere. Reactions were monitored by thin layer chromatography (TLC) carried out on 0.25mm Qingdao silica gel plates (60F-254) using UV lights as the visualizing agent and KMnO_4 . Flash column chromatography was performed over Qingdao silica gel (200-300 mesh). Infrared spectra were recorded on a Nicolet AVATER FTIR330 spectrometer as thin film and are reported in reciprocal centimeter (cm^{-1}). High resolution mass spectra (HRMS) was recorded on a Micromass QTOF2 Quadrupole/Time-of-Flight Tandem mass spectrometer using electron spray ionization. Mass spectra was recorded on a Bruker Esquire 3000 Plus using electron spray ionization or a Shimadzu GCMS-QP2010 Plus using electron ionization. NMR spectra were recorded on Bruker AV-400 and Bruker AV-500 instruments and were calibrated using residual undeuterated solvents (CHCl_3 , $\delta_{\text{H}} = 7.26$ ppm; CH_3OH , $\delta_{\text{H}} = 3.31$ ppm) and deuterated solvents (CDCl_3 , $\delta_{\text{C}} = 77.0$ ppm; CD_3OD , $\delta_{\text{C}} = 49.0$ ppm) as internal references. The data for ^1H NMR are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, brs = broad singlet), coupling constants (Hz) and integration.

2. General Procedures for the Synthesis of Substrates

2.1) Method A:



To a stirred mixture of CuI (1.0 equiv) and LiCl (1.0 equiv) in THF (0.25 M) at -78°C was added the Grignard reagent (3.0 equiv, 1M in THF) dropwise. After 30 mins, TMSCl (1.0

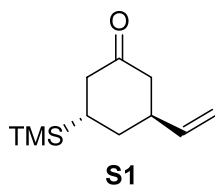
equiv) was added dropwise followed immediately by addition of the enone in THF.^[1] The solution was stirred for 2 h and then quenched with 1N aqueous HCl (10 equiv) and saturated aqueous NH₄Cl at -78 °C. The mixture was extracted with Et₂O and the combined organic layers was dried over MgSO₄ and concentrated *in vacuo*. Purification of the residue by flash chromatography (PE/EtOAc = 100:1) afforded the corresponding ketone.

To a stirred suspension of ethyltriphenylphosphonium iodide or methyltriphenylphosphonium bromide (2.5 equiv) in THF was added *n*-BuLi (2.0 equiv). The reaction mixture was stirred at 0 °C for 0.5 h before the addition of a solution of the ketone (1.0 equiv) in THF. The reaction mixture was stirred for another 3 h before being quenched with saturated aqueous NH₄Cl solution and extracted with Et₂O. The combined organic extract was washed with brine, dried over MgSO₄ and concentrated *in vacuo*. Purification of the residue by flash chromatography (pure PE) afforded the corresponding diene.

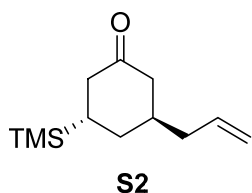
To the diene (1.0 equiv) in CH₂Cl₂ at -78 °C were added *m*-CPBA (1.05 equiv) and NaHCO₃ (3.0 equiv). The reaction mixture was stirred and slowly warmed to rt in 6 h and then quenched with a saturated solution of Na₂SO₃ and NaHCO₃ and extracted with CH₂Cl₂. The combined organic extract was washed with brine, dried over MgSO₄ and concentrated *in vacuo*. Purification of the residue by flash chromatography (PE/toluene = 4:1) afforded the corresponding epoxide.

To LDA (3.0 equiv) in Et₂O (0.1 M) was added epoxide (1.0 equiv) in Et₂O dropwise. The resulting mixture was heated to reflux for 3 h and then quenched with water at rt. The mixture was extracted with Et₂O. The combined organic extract was washed with brine, dried over MgSO₄ and concentrated *in vacuo*. Purification of the residue by flash chromatography (PE/EtOAc = 100:1) to give the corresponding diene alcohol.

Dienols **1a**, **1e**, **1h**, **1i**, **1k** and **1g** were prepared via method A:

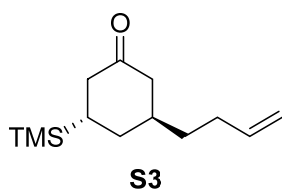


***rac*-(3*S*,5*R*)-3-(trimethylsilyl)-5-vinylcyclohexan-1-one (S1):** Colorless oil, 84% yield. ¹H NMR (400 MHz, CDCl₃) δ 5.77 (ddd, *J* = 17.3, 10.7, 5.5 Hz, 1H), 5.10 (dt, *J* = 10.7, 1.3 Hz, 1H), 5.04 (ddd, *J* = 17.3, 1.7, 0.5 Hz, 1H), 3.01 – 2.94 (m, 1H), 2.54 – 2.42 (m, 2H), 2.30 – 2.22 (m, 1H), 2.16 – 2.03 (m, 1H), 1.83 – 1.70 (m, 2H), 1.28 (ddt, *J* = 13.1, 11.8, 4.1 Hz, 1H), -0.01 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 212.0, 140.4, 115.6, 44.8, 42.1, 40.8, 30.6, 21.5, -3.6. IR (KBr, cm⁻¹): 2956, 1713, 1248, 919, 856. HRMS (ESI) *m/z* calc'd for C₁₁H₂₀OSi [M+Na]⁺: 219.1176, found: 219.1179.



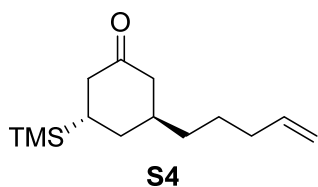
***rac*-(3*R*,5*S*)-3-allyl-5-(trimethylsilyl)cyclohexan-1-one (S2):** Colorless oil, 70% yield. ^1H NMR (400 MHz, CDCl_3) δ 5.71 (ddt, J = 17.4, 10.6, 7.1 Hz, 1H), 5.07 – 4.98 (m, 2H), 2.48 (ddd, J = 13.5, 8, 0.6 Hz, 1H), 2.34 – 2.20 (m, 3H), 2.19 – 2.00 (m, 3H), 1.73 – 1.66 (m, 2H), 1.35 – 1.26 (m, 1H), 0.00 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 212.7, 136.2, 116.6, 46.2, 42.0, 37.5, 37.4, 29.3, 21.3, -3.6.

IR (KBr, cm^{-1}): 2956, 1710, 1636, 992, 845. HRMS (ESI) m/z calc'd for $\text{C}_{12}\text{H}_{22}\text{OSi}$ $[\text{M}+\text{Na}]^+$: 233.1332, found: 233.1337.



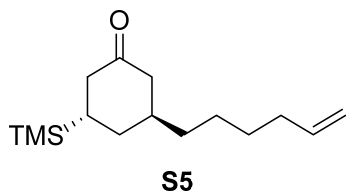
***rac*-(3*R*,5*S*)-3-(but-3-en-1-yl)-5-(trimethylsilyl)cyclohexan-1-one (S3):** Colorless oil, 89% yield. ^1H NMR (500 MHz, CDCl_3) δ 5.76 (ddt, J = 17.0, 10.2, 6.6 Hz, 1H), 5.00 (ddd, J = 17.0, 3.4, 1.6 Hz, 1H), 4.97 – 4.92 (m, 1H), 2.46 (m, 1H), 2.29 – 2.24 (m, 1H), 2.23 – 2.16 (m, 2H), 2.12 (m, 1H), 2.08 – 1.98 (m, 2H), 1.74 –

1.61 (m, 2H), 1.47 – 1.32 (m, 2H), 1.30 – 1.22 (m, 1H), -0.01 (s, 9H). ^{13}C NMR (125 MHz, CDCl_3) δ 212.7, 138.2, 114.8, 46.6, 42.0, 37.0, 32.2, 31.3, 29.8, 21.5, -3.6. IR (KBr, cm^{-1}): 2946, 1703, 1639, 1248, 838. HRMS (ESI) m/z calc'd for $\text{C}_{13}\text{H}_{24}\text{OSi}$ $[\text{M}+\text{Na}]^+$: 247.1489, found: 247.1492.



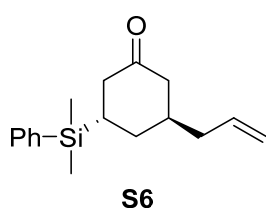
***rac*-(3*R*,5*S*)-3-(pent-4-en-1-yl)-5-(trimethylsilyl)cyclohexan-1-one (S4):** Colorless oil, 80% yield. ^1H NMR (400 MHz, CDCl_3) δ 5.77 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H), 5.02 – 4.89 (m, 2H), 2.50 – 2.41 (m, 1H), 2.28 – 2.09 (m, 4H), 2.05 – 1.99 (m, 2H), 1.73 – 1.60 (m, 2H), 1.40 – 1.23 (m, 5H), 0.00 –

-0.03 (m, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 212.9, 138.5, 114.6, 46.7, 42.0, 37.7, 33.6, 32.4, 29.9, 26.5, 21.5, -3.6. IR (KBr, cm^{-1}): 2946, 1707, 1643, 1246, 912. HRMS (ESI) m/z calc'd for $\text{C}_{14}\text{H}_{26}\text{OSi}$ $[\text{M}+\text{Na}]^+$: 261.1645, found: 261.1652.

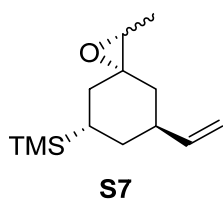


***rac*-(3*R*,5*S*)-3-(hex-5-en-1-yl)-5-(trimethylsilyl)cyclohexan-1-one (S5):** Colorless oil, 80% yield. ^1H NMR (400 MHz, CDCl_3) δ 5.78 (ddt, J = 16.9, 10.2, 6.6 Hz, 1H), 5.02 – 4.90 (m, 2H), 2.46 (dd, J = 14.8, 6.6 Hz, 1H), 2.29 – 2.22 (m, 1H), 2.22 – 2.15 (m, 2H), 2.15 – 2.07 (m, 1H), 2.06 – 2.01

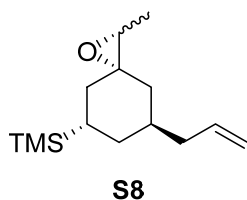
(m, 2H), 1.73 – 1.63 (m, 2H), 1.40 – 1.26 (m, 7H), 0.00 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 213.0, 138.8, 114.4, 46.8, 42.1, 37.7, 33.6, 32.7, 29.9, 28.8, 26.6, 21.5, -3.6. IR (KBr, cm^{-1}): 2946, 1707, 1640, 1245, 835. HRMS (ESI) m/z calc'd for $\text{C}_{15}\text{H}_{28}\text{OSi}$ $[\text{M}+\text{Na}]^+$: 275.1796, found: 275.1801.



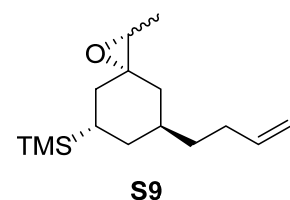
***rac*-(3*R*,5*S*)-3-allyl-5-(dimethyl(phenyl)silyl)cyclohexan-1-one (S6):** Colorless oil, 69% yield. ^1H NMR (500 MHz, CDCl_3) δ 7.48 – 7.45 (m, 2H), 7.39 – 7.33 (m, 3H), 5.70 – 5.59 (m, 1H), 5.02 – 4.95 (m, 2H), 2.42 (ddd, $J = 13.6, 5.5, 0.8$ Hz, 1H), 2.30 – 2.17 (m, 3H), 2.16 – 1.99 (m, 3H), 1.70 – 1.64 (m, 2H), 1.53 – 1.45 (m, 1H), 0.31 (s, 3H), 0.29 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 212.4, 136.6, 136.1, 133.9, 129.3, 127.8, 116.6, 46.1, 42.0, 37.3, 37.3, 29.3, 21.0, -5.2, -5.3. IR (KBr, cm^{-1}): 3071, 2959, 1703, 1636, 1428, 1242, 1104, 909, 832, 768, 736, 694. HRMS (ESI) m/z calc'd for $\text{C}_{17}\text{H}_{24}\text{OSi}$ $[\text{M}+\text{Na}]^+$: 295.1489, found: 295.1493.



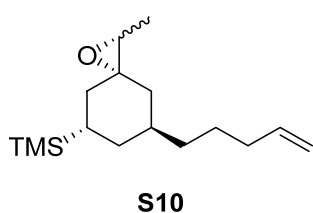
***rac*-trimethyl((3*R*,5*S*,7*R*)-2-methyl-7-vinyl-1-oxaspiro[2.5]octan-5-yl)silane (S7):** Colorless oil, 44% yield over two steps from ketone **S1**, $dr = 6.1:1$. ^1H NMR (500 MHz, CDCl_3) δ 5.99 – 5.90 (m, 1H), 5.07 – 5.04 (m, 1H), 5.04 – 5.00 (m, 1H), 2.90 – 2.82 (m, 1H), 2.77 – 2.67 (m, 1H), 2.07 (td, $J = 12.7, 5.2$ Hz, 1H), 1.74 – 1.64 (m, 2H), 1.58 – 1.42 (m, 3H), 1.36 – 1.29 (m, 3H), 1.13 – 0.93 (m, 1H), 0.00 (s, 9H). IR (KBr, cm^{-1}): 2956, 2853, 1636, 1242, 909, 832. MS (ESI) m/z calc'd for $\text{C}_{13}\text{H}_{24}\text{OSi}$ $[\text{M}+\text{Na}]^+$: 247, found: 247.



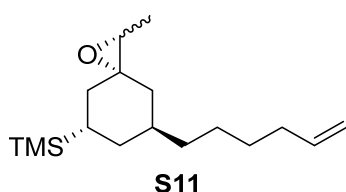
***rac*-((3*R*,5*S*,7*R*)-7-allyl-2-methyl-1-oxaspiro[2.5]octan-5-yl)trimethylsilane (S8):** Colorless oil, 67% yield over two steps from ketone **S2**, $dr = 6.7:1$. ^1H NMR (500 MHz, CDCl_3) δ 5.79 – 5.65 (m, 1H), 5.02 – 4.92 (m, 2H), 2.86 – 2.80 (m, 1H), 2.16 – 2.00 (m, 3H), 1.99 – 1.80 (m, 1H), 1.62 – 1.54 (m, 1H), 1.49 – 1.39 (m, 2H), 1.38 – 1.31 (m, 1H), 1.29 – 1.18 (m, 4H), 0.96 – 0.78 (m, 1H), -0.03 – -0.07 (m, 9H). IR (KBr, cm^{-1}): 2955, 1635, 1242, 919, 829. MS (ESI) m/z calc'd for $\text{C}_{14}\text{H}_{26}\text{OSi}$ $[\text{M}+\text{Na}]^+$: 261, found: 261.



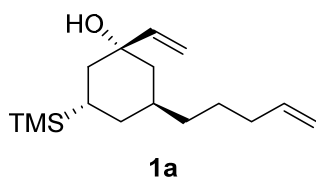
***rac*-((3*R*,5*S*,7*R*)-7-(but-3-en-1-yl)-2-methyl-1-oxaspiro[2.5]octan-5-yl)trimethylsilane (S9):** Colorless oil, 88% yield over two steps from ketone **S3**, $dr = 4.2:1$. ^1H NMR (500 MHz, CDCl_3) δ 5.86 – 5.74 (m, 1H), 5.03 – 4.97 (m, 1H), 4.97 – 4.93 (m, 1H), 2.86 – 2.80 (m, 1H), 2.11 – 1.92 (m, 4H), 1.60 – 1.52 (m, 1H), 1.49 – 1.32 (m, 5H), 1.29 – 1.16 (m, 4H), 0.98 – 0.77 (m, 1H), -0.02 – -0.07 (m, 9H). IR (KBr, cm^{-1}): 2949, 1636, 1245, 906, 832. MS (ESI) m/z calc'd for $\text{C}_{15}\text{H}_{28}\text{OSi}$ $[\text{M}+\text{Na}]^+$: 275, found: 275.



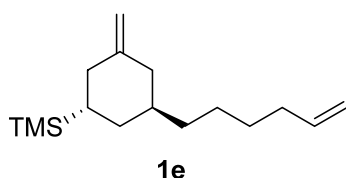
***rac*-trimethyl((3*R*,5*S*,7*R*)-2-methyl-7-(pent-4-en-1-yl)-1-oxaspiro[2.5]octan-5-yl)silane (S10):** Colorless oil, 79% yield over two steps from ketone **S4**, *dr* = 4.5:1. ¹H NMR (400 MHz, CDCl₃) δ 5.80 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.07 – 4.90 (m, 2H), 2.88 – 2.76 (m, 1H), 2.11 – 1.89 (m, 4H), 1.60 – 1.51 (m, 1H), 1.48 – 1.41 (m, 2H), 1.39 – 1.31 (m, 5H), 1.30 – 1.25 (m, 4H), 0.89 – 0.78 (m, 1H), -0.01 – -0.06 (m, 9H). IR (KBr, cm⁻¹): 2949, 1636, 1460, 1248, 902, 835. MS (ESI) *m/z* calc'd for C₁₆H₃₀OSi [M+Na]⁺: 289, found: 289.



***rac*-((3*R*,5*S*,7*R*)-7-(hex-5-en-1-yl)-2-methyl-1-oxaspiro[2.5]octan-5-yl)trimethylsilane (S11):** Colorless oil, 66% yield over two steps from ketone **S5**, *dr* = 6.7:1. ¹H NMR (400 MHz, CDCl₃) δ 5.79 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.02 – 4.91 (m, 2H), 2.86 – 2.78 (m, 1H), 2.08 – 2.00 (m, 2H), 1.98 – 1.90 (m, 2H), 1.58 – 1.50 (m, 1H), 1.47 – 1.42 (m, 2H), 1.40 – 1.26 (m, 10H), 1.22 – 1.13 (m, 1H), 0.87 – 0.77 (m, 1H), -0.02 – -0.06 (m, 9H). IR (KBr, cm⁻¹): 2955, 1639, 1245, 906, 829. MS (ESI) *m/z* calc'd for C₁₇H₃₂OSi [M+Na]⁺: 303, found: 303.

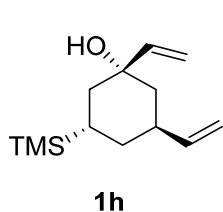


***rac*-(1*R*,3*R*,5*S*)-3-(pent-4-en-1-yl)-5-(trimethylsilyl)-1-vinylcyclohexan-1-ol (1a):** Colorless oil, 88% yield from **S10**. ¹H NMR (500 MHz, CDCl₃) δ 6.03 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.80 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.23 (dd, *J* = 17.4, 1.2 Hz, 1H), 5.05 – 4.96 (m, 2H), 4.93 (ddt, *J* = 10.2, 2.2, 1.2 Hz, 1H), 2.06 – 1.98 (m, 2H), 1.83 – 1.71 (m, 2H), 1.63 – 1.55 (m, 2H), 1.52 – 1.42 (m, 2H), 1.41 – 1.34 (m, 2H), 1.34 – 1.22 (m, 4H), 0.96 – 0.86 (m, 1H), 0.01 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 146.2, 139.1, 114.2, 111.5, 72.0, 43.6, 38.2, 34.7, 33.9, 32.1, 31.2, 26.9, 19.4, -2.3. IR (KBr, cm⁻¹): 3459, 2993, 1636, 1248, 909, 835. HRMS (ESI) *m/z* calc'd for C₁₆H₃₀OSi [M+Na]⁺: 289.1958, found: 289.1959.

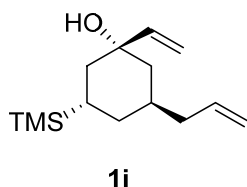


***rac*-((1*S*,3*R*)-3-(hex-5-en-1-yl)-5-methylenecyclohexyl)trimethylsilane (1e):** Colorless oil, 89% yield from ketone **S5**. ¹H NMR (400 MHz, CDCl₃) δ 5.81 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.03 – 4.96 (m, 1H), 4.93 (ddt, *J* = 10.2, 2.3, 1.2 Hz, 1H), 4.63 (s, 1H), 4.54 (s, 1H), 2.25 – 2.16 (m, 2H), 2.09 – 2.02 (m, 3H), 1.87 (t, *J* = 12.6 Hz, 1H), 1.76 (dd, *J* = 7.4, 3.4 Hz, 1H), 1.53 – 1.35 (m, 4H), 1.30 – 1.24 (m, 4H), 0.93 – 0.85 (m, 1H), -0.04 (s, 9H). ¹³C NMR (100 MHz,

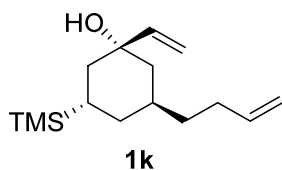
CDCl₃) δ 148.0, 139.2, 114.1, 107.5, 39.9, 35.8, 35.4, 33.8, 31.6, 31.0, 29.1, 26.8, 21.6, -3.3. IR (KBr, cm⁻¹): 2917, 1633, 1460, 1079, 835. MS (EI) m/z calc'd for C₁₆H₃₀Si [M]⁺: 250, found: 250.



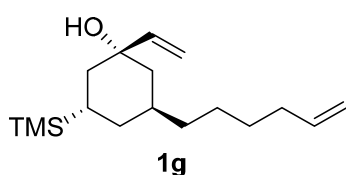
***rac*-(1*R*,3*S*,5*R*)-3-(trimethylsilyl)-1,5-divinylcyclohexan-1-ol (1h):** Colorless oil, 62% yield from **S7**. ¹H NMR (500 MHz, CDCl₃) δ 6.09 (dd, J = 17.4, 10.8 Hz, 1H), 5.85 (ddd, J = 17.0, 10.8, 6.3 Hz, 1H), 5.23 (dd, J = 17.4, 1.2 Hz, 1H), 5.03 (dd, J = 10.8, 1.2 Hz, 1H), 4.99 – 4.92 (m, 2H), 2.61 – 2.53 (m, 1H), 1.73 (td, J = 13.5, 4.4 Hz, 2H), 1.66 – 1.60 (m, 1H), 1.59 – 1.55 (m, 2H), 1.52 – 1.46 (m, 1H), 1.30 – 1.25 (m, 1H), 1.03 – 0.96 (m, 1H), 0.01 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 145.7, 143.3, 112.6, 111.6, 71.9, 43.9, 38.4, 36.3, 30.0, 19.0, -2.6. IR (KBr, cm⁻¹): 3446, 2949, 1636, 1245, 915, 829. HRMS (ESI) m/z calc'd for C₁₃H₂₄OSi [M+Na]⁺: 247.1489, found: 247.1496.



***rac*-(1*R*,3*R*,5*S*)-3-allyl-5-(trimethylsilyl)-1-vinylcyclohexan-1-ol (1i):** Colorless oil, 83% yield from **S8**. ¹H NMR (500 MHz, CDCl₃) δ 6.03 (dd, J = 17.4, 10.8 Hz, 1H), 5.74 (ddt, J = 16.4, 10.8, 7.1 Hz, 1H), 5.26 – 5.20 (dd, J = 17.4, 1.1 Hz, 1H), 5.04 (dd, J = 10.8, 1.1 Hz, 1H), 4.99 – 4.94 (m, 2H), 2.06 – 1.95 (m, 2H), 1.93 – 1.84 (m, 1H), 1.78 (dd, J = 13.5, 4.7 Hz, 1H), 1.63 (dd, J = 13.5, 4.7 Hz, 1H), 1.55 (ddd, J = 13.0, 8.2, 4.4 Hz, 1H), 1.52 – 1.45 (m, 2H), 1.37 – 1.28 (m, 2H), 0.94 – 0.85 (m, 1H), 0.00 (s, 9H). ¹³C NMR (125 MHz, CDCl₃) δ 146.1, 137.7, 115.6, 111.8, 71.9, 43.2, 39.6, 38.0, 32.3, 30.6, 19.2, -2.4. IR (KBr, cm⁻¹): 3446, 2953, 1639, 1242, 906, 829. HRMS (ESI) m/z calc'd for C₁₄H₂₆OSi [M+Na]⁺: 261.1645, found: 261.1648.



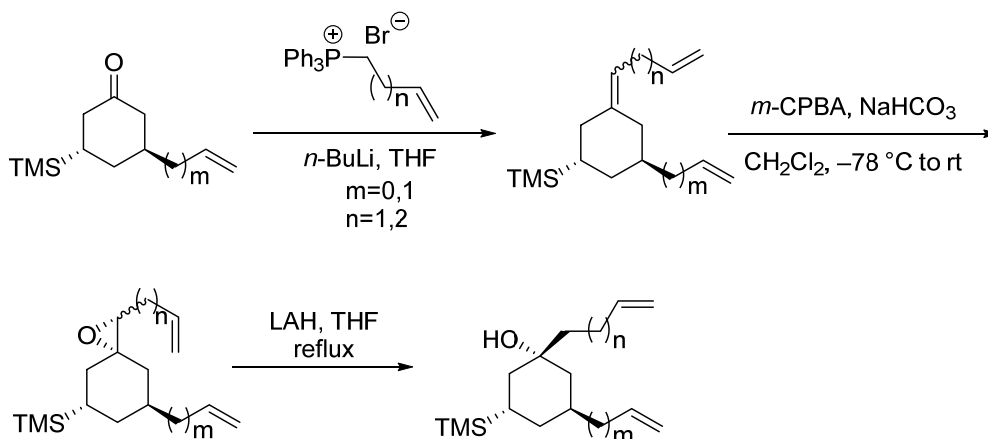
***rac*-(1*R*,3*R*,5*S*)-3-(but-3-en-1-yl)-5-(trimethylsilyl)-1-vinylcyclohexan-1-ol (1k):** Colorless oil, 96% yield from **S8**. ¹H NMR (500 MHz, CDCl₃) δ 6.04 (dd, J = 17.4, 10.8 Hz, 1H), 5.80 (ddt, J = 17.0, 10.2, 6.7 Hz, 1H), 5.24 (dd, J = 17.4, 1.1 Hz, 1H), 5.06 – 4.96 (m, 2H), 4.93 (ddt, J = 10.2, 2.1, 1.1 Hz, 1H), 2.10 – 1.98 (m, 2H), 1.86 – 1.79 (m, 1H), 1.76 (dd, J = 13.4, 4.7 Hz, 1H), 1.66 – 1.53 (m, 3H), 1.53 – 1.42 (m, 2H), 1.38 – 1.29 (m, 3H), 0.97 – 0.88 (m, 1H), 0.01 (s, 9H). ¹³C NMR (125 MHz, CDCl₃) δ 146.1, 139.1, 114.3, 111.6, 72.0, 43.6, 38.2, 34.5, 31.7, 31.0, 19.4, -2.3. IR (KBr, cm⁻¹): 3445, 2949, 1640, 1246, 906, 826. HRMS (ESI) m/z calc'd for C₁₅H₂₈OSi [M+Na]⁺: 275.1802, found: 275.1801.



***rac*-(1*R*,3*R*,5*S*)-3-(hex-5-en-1-yl)-5-(trimethylsilyl)-1-vinylcyclohexan-1-ol (1g):** Colorless oil, 93% yield from S11.

¹H NMR (400 MHz, CDCl₃) δ 6.02 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.79 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.22 (dd, *J* = 17.4, 1.2 Hz, 1H), 5.03 – 4.94 (m, 2H), 4.92 (ddt, *J* = 10.2, 2.2, 1.2 Hz, 1H), 2.06 – 1.98 (m, 2H), 1.81 – 1.71 (m, 2H), 1.63 – 1.40 (m, 5H), 1.37 – 1.24 (m, 7H), 0.96 – 0.85 (m, 1H), 0.01 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 146.1, 139.0, 114.2, 111.5, 71.9, 43.6, 38.2, 34.9, 33.7, 32.2, 31.1, 29.0, 26.9, 19.3, -2.4. IR (KBr, cm⁻¹): 3455, 2920, 1642, 1242, 915, 835. HRMS (ESI) *m/z* calc'd for C₁₇H₃₂OSi [M+Na]⁺: 303.2115, found: 303.2116.

2.2) Method B:

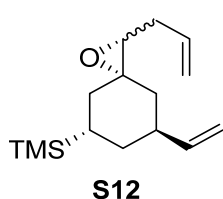


To a stirred suspension of Wittig reagent (2.5 equiv) in THF was added *n*-BuLi (2.0 equiv) and the mixture was stirred at 0 °C for 0.5 h. Then a solution of the ketone (1.0 equiv) in THF was added slowly and the resulting mixture was stirred for another 2 h. The reaction was quenched with saturated aqueous NH₄Cl solution and extracted with Et₂O. The combined organic extract was washed with brine, dried over MgSO₄ and concentrated *in vacuo*. Purification of the residue by flash chromatography (pure PE) afforded the corresponding diene.

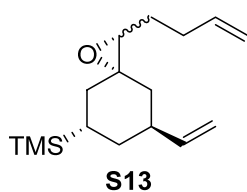
To the diene (1.0 equiv) in DCM were added *m*-CPBA (1.05 equiv) and NaHCO₃ (3.0 equiv) at -78 °C. The reaction mixture was stirred and slowly warmed to rt in a time period of 3~5 h and then quenched with a saturated solution of Na₂SO₃ and NaHCO₃ and extracted with CH₂Cl₂. The combined organic extract was washed with brine, dried over MgSO₄ and concentrated *in vacuo*. Purification of the residue by flash chromatography (PE/EtOAc = 100:1) afforded the corresponding epoxide.

To a stirred slurry of lithium aluminum hydride (3.0 equiv) in THF (0.1 M) was added the epoxide (1.0 equiv) in THF dropwise.^[2] The solution was heated to reflux and stirred overnight before being quenched with water at rt. The mixture was extracted with Et₂O. The combined organic extract was washed with brine, dried over MgSO₄ and concentrated *in vacuo*. Purification of the residue by flash chromatography (PE/EtOAc = 100:1) afforded the corresponding diene alcohol.

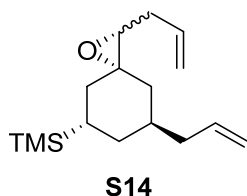
Dienols **1c**, **1d**, **1f** and **1m** were prepared via method B:



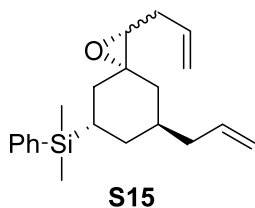
***rac*-((3*R*,5*S*,7*R*)-2-allyl-7-vinyl-1-oxaspiro[2.5]octan-5-yl)trimethylsilane (S12):** Colorless oil, 55% yield over two steps from ketone **S1**, *dr* = 6.3:1. ¹H NMR (400 MHz, CDCl₃) δ 5.99 – 5.81 (m, 2H), 5.20 – 5.09 (m, 2H), 5.06 – 4.99 (m, 2H), 2.81 (t, *J* = 6.4 Hz, 1H), 2.76 – 2.68 (m, 1H), 2.42 – 2.33 (m, 1H), 2.28 – 2.19 (m, 1H), 2.06 (dd, *J* = 12.9, 5.0 Hz, 1H), 1.72 – 1.64 (m, 1H), 1.55 – 1.41 (m, 3H), 1.36 – 1.30 (m, 1H), 1.03 – 0.94 (m, 1H), 0.00 – -0.03 (m, 9H). IR (KBr, cm⁻¹): 2949, 1642, 1248, 909, 829. MS (ESI) *m/z* calc'd for C₁₅H₂₆OSi [M+Na]⁺: 273, found: 273.



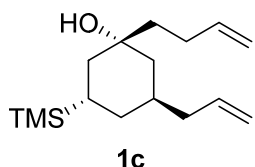
***rac*-((3*R*,5*S*,7*R*)-2-(but-3-en-1-yl)-7-vinyl-1-oxaspiro[2.5]octan-5-yl)trimethylsilane (S13):** Colorless oil, 74% yield over two steps from ketone **S1**, *dr* = 7:1. ¹H NMR (400 MHz, CDCl₃) δ 6.00 – 5.80 (m, 2H), 5.12 – 4.97 (m, 4H), 2.79 – 2.69 (m, 2H), 2.31 – 2.14 (m, 2H), 2.05 (dd, *J* = 12.9, 5.1 Hz, 1H), 1.73 – 1.66 (m, 1H), 1.66 – 1.58 (m, 2H), 1.52 – 1.45 (m, 2H), 1.36 – 1.30 (m, 2H), 1.03 – 0.92 (m, 1H), 0.01 – -0.03 (m, 9H). IR (KBr, cm⁻¹): 2952, 1639, 1245, 906, 832. MS (ESI) *m/z* calc'd for C₁₅H₂₈OSi [M+Na]⁺: 287, found: 287.



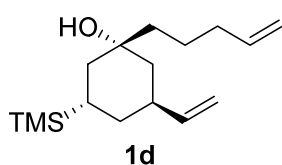
***rac*-((3*R*,5*S*,7*R*)-2,7-diallyl-1-oxaspiro[2.5]octan-5-yl)trimethylsilane (S14):** Colorless oil, 78% yield over two steps from ketone **S2**, *dr* = 6.5:1. ¹H NMR (500 MHz, CDCl₃) δ 5.95 – 5.85 (m, 1H), 5.72 (ddt, *J* = 17.1, 10.3, 6.9 Hz, 1H), 5.21 – 5.12 (m, 2H), 5.02 – 4.95 (m, 2H), 2.80 (t, *J* = 6.4 Hz, 1H), 2.46 – 2.37 (m, 1H), 2.28 – 2.21 (m, 1H), 2.17 – 2.03 (m, 3H), 1.96 (dd, *J* = 13.0, 4.7 Hz, 1H), 1.61 – 1.55 (m, 2H), 1.52 – 1.46 (m, 2H), 1.39 – 1.33 (m, 1H), 0.94 – 0.81 (m, 1H), -0.02 – -0.04 (m, 9H). IR (KBr, cm⁻¹): 2952, 1639, 1248, 915, 835. MS (ESI) *m/z* calc'd for C₁₆H₂₆OSi [M+Na]⁺: 287, found: 287.



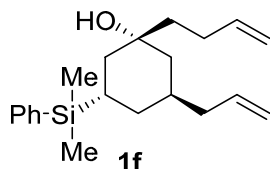
***rac*-((3*R*,5*S*,7*R*)-2,7-diallyl-1-oxaspiro[2.5]octan-5-yl)dimethyl(phenyl)silane (S15):** Colorless oil, 66% yield over two steps from ketone **S6**, *dr* = 10:1. ¹H NMR (500 MHz, CDCl₃) δ 7.48 – 7.44 (m, 2H), 7.36 – 7.31 (m, 3H), 5.91 – 5.81 (m, 1H), 5.67 (ddt, *J* = 17.4, 10.4, 7.0 Hz, 1H), 5.14 – 5.05 (m, 2H), 5.00 – 4.93 (m, 2H), 2.77 (t, *J* = 6.6 Hz, 1H), 2.39 – 2.30 (m, 1H), 2.16 – 2.06 (m, 3H), 2.05 – 1.98 (m, 1H), 1.92 (dd, *J* = 13.0, 4.8 Hz, 1H), 1.61 – 1.56 (m, 1H), 1.51 – 1.45 (m, 2H), 1.39 – 1.32 (m, 1H), 1.24 – 1.18 (m, 1H), 1.15 – 1.07 (m, 1H), 0.28 (overlapped, 3H), 0.28 (overlapped, 3H). IR (KBr, cm⁻¹): 2920, 2847, 1636, 1424, 1245, 1111, 912, 835, 698. MS (ESI) *m/z* calc'd for C₂₁H₃₀OSi [M+Na]⁺: 349, found: 349.



***rac*-(1*R*,3*R*,5*S*)-3-allyl-1-(but-3-en-1-yl)-5-(trimethylsilyl)cyclohexan-1-ol (1c):** Colorless oil, 72% yield from **S14**. ¹H NMR (400 MHz, CDCl₃) δ 5.92 – 5.70 (m, 2H), 5.08 – 4.93 (m, 4H), 2.20 – 2.10 (m, 2H), 2.00 (t, *J* = 7.1 Hz, 2H), 1.89 – 1.76 (m, 1H), 1.66 – 1.48 (m, 6H), 1.31 – 1.22 (m, 2H), 1.14 – 1.06 (m, 1H), 0.92 – 0.83 (m, 1H), 0.02 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 139.3, 137.6, 115.6, 114.4, 72.1, 43.0, 42.0, 40.5, 38.4, 31.6, 31.1, 27.8, 19.8, -2.0. IR (KBr, cm⁻¹): 3461, 2914, 1639, 1245, 906, 835. HRMS (ESI) *m/z* calc'd for C₁₆H₃₀OSi [M+Na]⁺: 289.1958, found: 289.1964.

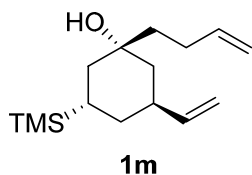


***rac*-(1*R*,3*S*,5*R*)-1-(pent-4-en-1-yl)-3-(trimethylsilyl)-5-vinylcyclohexan-1-ol (1d):** Colorless oil, 66% yield from **S13**. ¹H NMR (500 MHz, CDCl₃) δ 5.88 – 5.75 (m, 2H), 5.03 – 4.93 (m, 4H), 2.55 – 2.47 (m, 1H), 2.07 – 2.01 (m, 2H), 1.63 – 1.37 (m, 11H), 0.94 – 0.86 (m, 1H), 0.00 (s, 9H). ¹³C NMR (125 MHz, CDCl₃) δ 143.4, 138.8, 114.5, 112.5, 71.9, 42.8, 40.9, 38.8, 36.0, 34.1, 30.0, 22.5, 19.2, -2.6. IR (KBr, cm⁻¹): 3423, 2917, 1636, 1248, 906, 835. HRMS (ESI) *m/z* calc'd for C₁₆H₃₀OSi [M+Na]⁺: 289.1958, found: 289.1955.



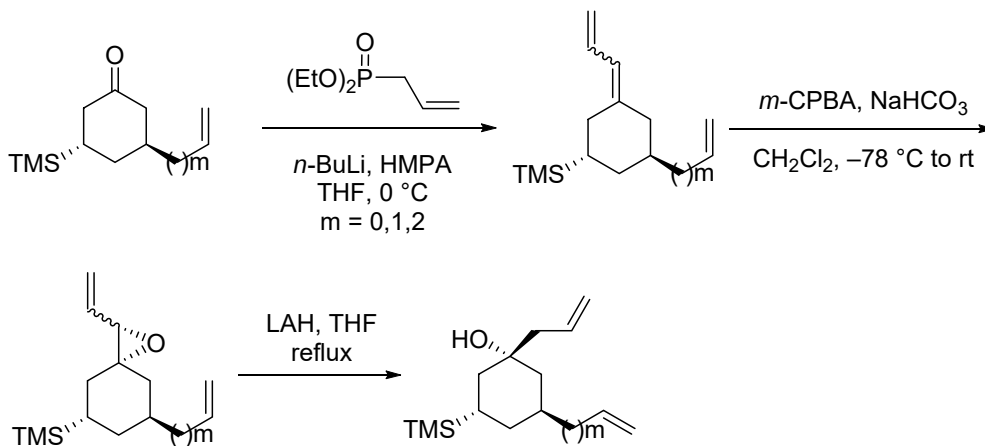
***rac*-(1*R*,3*R*,5*S*)-3-allyl-1-(but-3-en-1-yl)-5-(dimethyl(phenyl)silyl)cyclohexan-1-ol (1f):** Colorless oil, 75% yield from **S15**. ¹H NMR (500 MHz, CDCl₃) δ 7.54 – 7.49 (m, 2H), 7.37 – 7.33 (m, 3H), 5.82 (ddt, *J* = 16.9, 10.3, 6.6 Hz, 1H), 5.72 (ddt, *J* = 17.4, 10.3, 7.1 Hz, 1H), 5.02 – 4.90 (m, 4H), 2.12 – 2.05 (m, 2H), 1.98 – 1.92 (m, 2H), 1.77 – 1.68 (m, 2H), 1.57 – 1.49 (m, 5H), 1.29 – 1.25 (m, 1H), 1.21 – 1.15 (m, 2H), 1.00 (s, 1H), 0.32 (overlapped, 3H), 0.32 (overlapped, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 139.4, 139.2, 137.4, 134.0, 128.8, 127.7, 115.7, 114.4, 72.0, 43.0, 42.1, 40.6,

38.2, 31.4, 27.7, 19.8, -3.4. IR (KBr, cm^{-1}): 3465, 2920, 1636, 1424, 1245, 1111, 906, 813, 733, 694. HRMS (ESI) m/z calc'd for $\text{C}_{21}\text{H}_{32}\text{OSi}$ $[\text{M}+\text{Na}]^+$: 351.2115, found: 351.2109.



***rac*-(1*R*,3*S*,5*R*)-1-(but-3-en-1-yl)-3-(trimethylsilyl)-5-vinylcyclohexan-1-ol (1m)**: Colorless oil, 99% yield from **S12**. ^1H NMR (500 MHz, CDCl_3) δ 5.89 – 5.80 (m, 2H), 5.03 (ddd, $J = 17.2, 3.4, 1.6$ Hz, 1H), 5.00 – 4.92 (m, 3H), 2.56 – 2.49 (m, 1H), 2.17 – 2.08 (m, 2H), 1.66 – 1.48 (m, 8H), 1.40 (dd, $J = 13.2, 9.5$ Hz, 1H), 0.96 – 0.87 (m, 1H), 0.00 (s, 9H). ^{13}C NMR (125 MHz, CDCl_3) δ 143.3, 139.2, 114.4, 112.6, 71.9, 42.8, 40.4, 38.8, 36.0, 29.9, 27.7, 19.1, -2.6. IR (KBr, cm^{-1}): 3413, 2923, 1639, 1245, 906, 835. HRMS (ESI) m/z calc'd for $\text{C}_{15}\text{H}_{28}\text{OSi}$ $[\text{M}+\text{Na}]^+$: 275.1802, found: 275.1803.

2.3) Method C:



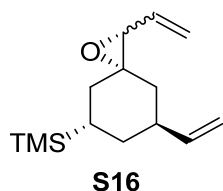
To a stirred suspension of Horner reagent (2.0 equiv) in THF was added *n*-BuLi (1.8 equiv) and the mixture was stirred at 0 °C for 0.5 h before sequential addition of HMPA (4.0 equiv) and a solution of the ketone (1.0 equiv) in THF. The reaction mixture was stirred for another 2 h and then quenched with saturated aqueous NH_4Cl solution and extracted with Et_2O . The combined organic extract was washed with brine, dried over MgSO_4 and concentrated *in vacuo*. Purification of the residue by flash chromatography (pure PE) afforded the corresponding diene.

To the diene (1.0 equiv) in CH_2Cl_2 were added *m*-CPBA (1.05 equiv) and NaHCO_3 (3.0 equiv) at -78 °C. The reaction mixture was stirred and slowly warmed to rt in a time period of 3~5 h before being quenched with saturated solution of Na_2SO_3 and NaHCO_3 and extracted with CH_2Cl_2 . The combined organic extract was washed with brine, dried over MgSO_4 and concentrated *in vacuo*. Purification of the residue by flash chromatography

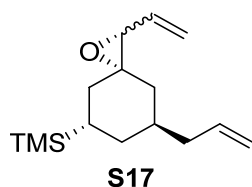
(PE/toluene = 4:1) afforded the corresponding epoxide.

To a stirred slurry of lithium aluminum hydride (3.0 equiv) in THF (0.1 M) was added the epoxide (1.0 equiv) in THF dropwise.^[2] The reaction mixture was heated to reflux and stirred overnight. Then the reaction mixture was quenched with water and extracted with Et₂O. The combined organic extract was washed with brine, dried over MgSO₄ and concentrated *in vacuo*. Purification of the residue by flash chromatography (PE/EtOAc = 100:1) afforded the corresponding diene alcohol.

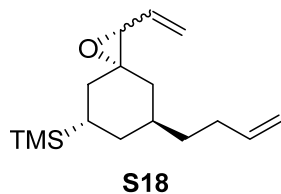
Dienols **1b**, **1j** and **1l** were prepared via method C:



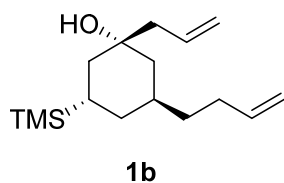
***rac*-((3*R*,5*S*,7*R*)-2,7-divinyl-1-oxaspiro[2.5]octan-5-yl)trimethylsilane (S16):** Colorless oil, 30% yield over two steps from ketone **S1**, *dr* = 7.5:1, ¹H NMR (400 MHz, CDCl₃) δ 6.01 – 5.90 (m, 1H), 5.72 (ddd, *J* = 17.4, 10.5, 7.0 Hz, 1H), 5.44 (d, *J* = 17.1 Hz, 1H), 5.33 (d, *J* = 10.5 Hz, 1H), 5.09 – 4.92 (m, 2H), 3.20 (d, *J* = 7.1 Hz, 1H), 2.71 (brs, 1H), 2.08 (dd, *J* = 12.9, 5.0 Hz, 1H), 1.72 – 1.62 (m, 1H), 1.53 – 1.47 (m, 2H), 1.47 – 1.40 (m, 1H), 1.40 – 1.34 (m, 1H), 0.96 – 0.85 (m, 1H), -0.02 – -0.06 (m, 9H). IR (KBr, cm⁻¹): 2949, 1636, 1245, 909, 832. MS (ESI) *m/z* calc'd for C₁₄H₂₄OSi [M+Na]⁺: 259, found: 259.



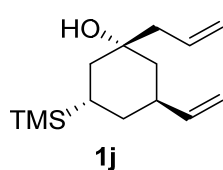
***rac*-((3*R*,5*S*,7*R*)-7-allyl-2-vinyl-1-oxaspiro[2.5]octan-5-yl)trimethylsilane (S17):** Colorless oil, 33% yield over two steps from ketone **S2**, *dr* = 6.5:1. ¹H NMR (400 MHz, CDCl₃) δ 5.80 – 5.65 (m, 2H), 5.51 – 5.41 (m, 1H), 5.38 – 5.30 (m, 1H), 5.05 – 4.93 (m, 2H), 3.21 – 3.16 (m, 1H), 2.20 – 1.94 (m, 4H), 1.70 – 1.51 (m, 2H), 1.39 – 1.23 (m, 3H), 1.01 – 0.74 (m, 1H), 0.00 – -0.07 (m, 9H). IR (thin film) 2949, 1629, 1252, 915, 829. MS (ESI) *m/z* calc'd for C₁₅H₂₆OSi [M+Na]⁺: 273, found: 273.



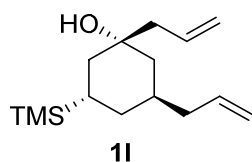
***rac*-((3*R*,5*S*,7*R*)-7-(but-3-en-1-yl)-2-vinyl-1-oxaspiro[2.5]octan-5-yl)trimethylsilane (S18):** Colorless oil, 32% yield over two steps from ketone **S3**, *dr* = 8.1:1. ¹H NMR (400 MHz, CDCl₃) δ 5.86 – 5.67 (m, 2H), 5.48 – 5.40 (m, 1H), 5.37 – 5.29 (m, 1H), 5.05 – 4.93 (m, 2H), 3.17 (d, *J* = 7.2 Hz, 1H), 2.12 – 1.90 (m, 4H), 1.58 – 1.51 (m, 1H), 1.52 – 1.42 (m, 4H), 1.39 – 1.27 (m, 2H), 0.90 – 0.75 (m, 1H), -0.02 – -0.06 (m, 9H). IR (KBr, cm⁻¹): 2920, 1636, 1242, 909, 838. MS (ESI) *m/z* calc'd for C₁₆H₂₈OSi [M+Na]⁺: 287, found: 287.



***rac*-(1*R*,3*R*,5*S*)-1-allyl-3-(but-3-en-1-yl)-5-(trimethylsilyl)cyclohexan-1-ol (1b):** Colorless oil, 63% yield from **S18**. ^1H NMR (400 MHz, CDCl_3) δ 5.95 – 5.74 (m, 2H), 5.19 – 5.07 (m, 2H), 5.00 (ddd, J = 17.1, 3.4, 1.6 Hz, 1H), 4.96 – 4.90 (m, 1H), 2.24 (d, J = 7.5 Hz, 2H), 2.12 – 1.99 (m, 2H), 1.80 – 1.69 (m, 1H), 1.68 – 1.62 (m, 1H), 1.62 – 1.53 (m, 2H), 1.52 – 1.46 (m, 1H), 1.36 – 1.19 (m, 5H), 0.92 – 0.84 (m, 1H), 0.00 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 139.1, 133.9, 118.9, 114.3, 71.5, 47.2, 43.3, 38.2, 35.4, 31.8, 31.3, 31.2, 19.8, -2.1. IR (KBr, cm^{-1}): 3465, 2920, 1636, 1242, 906, 832. HRMS (ESI) m/z calc'd for $\text{C}_{16}\text{H}_{30}\text{OSi}$ $[\text{M}+\text{Na}]^+$: 289.1958, found: 289.1965.



***rac*-(1*R*,3*S*,5*R*)-1-allyl-3-(trimethylsilyl)-5-vinylcyclohexan-1-ol (1j):** Colorless oil, 61% yield from **S16**. ^1H NMR (500 MHz, CDCl_3) δ 5.91 – 5.81 (m, 2H), 5.19 – 5.15 (m, 1H), 5.14 – 5.08 (m, 1H), 4.99 (dt, J = 7.1, 1.7 Hz, 1H), 4.97 (d, J = 1.8 Hz, 1H), 2.59 – 2.51 (m, 1H), 2.26 (d, J = 7.5 Hz, 2H), 1.66 – 1.60 (m, 3H), 1.60 – 1.56 (m, 1H), 1.56 – 1.49 (m, 2H), 1.40 (dd, J = 13.2, 9.6 Hz, 1H), 0.95 – 0.88 (m, 1H), 0.01 (s, 9H). ^{13}C NMR (125 MHz, CDCl_3) δ 143.4, 133.9, 119.1, 112.6, 71.3, 45.6, 42.8, 38.4, 35.9, 29.7, 19.0, -2.7. IR (KBr, cm^{-1}): 3385, 2917, 1642, 1248, 861, 829. HRMS (ESI) m/z calc'd for $\text{C}_{14}\text{H}_{26}\text{OSi}$ $[\text{M}+\text{Na}]^+$: 261.1645, found: 261.1649.

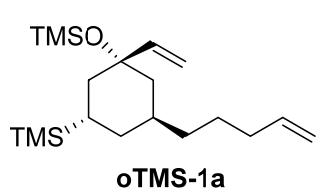


***rac*-(1*R*,3*R*,5*S*)-1,3-diallyl-5-(trimethylsilyl)cyclohexan-1-ol (1l):** Colorless oil, 54% yield from **S17**. ^1H NMR (400 MHz, CDCl_3) δ 5.96 – 5.69 (m, 2H), 5.20 – 5.06 (m, 2H), 5.02 – 4.94 (m, 2H), 2.24 (d, J = 7.5 Hz, 2H), 2.06 – 1.95 (m, 2H), 1.88 – 1.77 (m, 1H), 1.65 – 1.42 (m, 5H), 1.31 – 1.23 (m, 2H), 0.91 – 0.83 (m, 1H), -0.01 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 137.6, 133.8, 119.0, 115.6, 71.4, 47.3, 43.0, 40.6, 38.0, 31.6, 31.0, 19.8, -2.1. IR (KBr, cm^{-1}): 3385, 2920, 1636, 1434, 1242, 835. HRMS (ESI) m/z calc'd for $\text{C}_{15}\text{H}_{28}\text{OSi}$ $[\text{M}+\text{Na}]^+$: 275.1802, found: 275.1807.

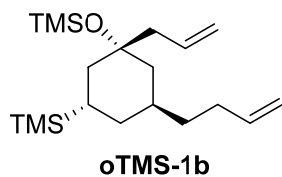
2.3) Method D:

To alcohol **1a** (1.0 equiv) in CH_2Cl_2 (0.3 M) at 0 °C was added imidazole (2.0 equiv), 4-(dimethylamino)pyridine (0.1 equiv) and chlorotrimethylsilane (1.8 equiv) in sequence. The reaction mixture was stirred for 0.5 h and then quenched with H_2O (5 mL), extracted with CH_2Cl_2 . The combined organic extract was washed with brine, dried over MgSO_4 and concentrated *in vacuo*. Purification of the residue by flash chromatography (PE) afforded TMS-diene as a colorless oil.

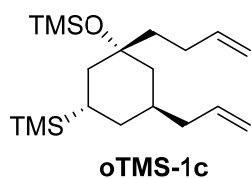
oTMS-dienes **oTMS-1a**, **oTMS-1b**, **oTMS-1c** and **oTMS-1d** were prepared via method D:



rac-trimethyl((1*S*,3*R*,5*R*)-5-(pent-4-en-1-yl)-3-((trimethylsilyloxy)-3-vinylcyclohexyl)silane (oTMS-1a**):** Colorless oil, 92% yield from dienol **1a**. ^1H NMR (400 MHz, CDCl_3) δ 5.99 (dd, $J = 17.6, 10.8$ Hz, 1H), 5.81 (ddt, $J = 16.9, 10.2, 6.7$ Hz, 1H), 5.14 (dd, $J = 17.6, 1.3$ Hz, 1H), 5.05 – 4.96 (m, 2H), 4.94 (ddt, $J = 10.2, 2.2, 1.2$ Hz, 1H), 2.06 – 1.98 (m, 2H), 1.82 – 1.74 (m, 2H), 1.71 (dd, $J = 13.2, 4.7$ Hz, 1H), 1.59 – 1.53 (m, 1H), 1.52 – 1.43 (m, 2H), 1.40 – 1.20 (m, 5H), 0.85 (ddd, $J = 14.1, 9.5, 4.4$ Hz, 1H), 0.09 (s, 9H), -0.01 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 145.6, 139.2, 114.2, 112.3, 74.8, 43.5, 39.0, 34.2, 34.0, 32.6, 30.9, 27.1, 18.7, 3.0, -2.7. IR (KBr, cm^{-1}): 2923, 1245, 1047, 906, 835. HRMS (ESI) m/z calc'd for $\text{C}_{19}\text{H}_{38}\text{OSi}_2$ $[\text{M}+\text{Na}]^+$: 361.2353, found: 361.2354.



rac-(((1*R*,3*R*,5*S*)-1-allyl-3-(but-3-en-1-yl)-5-(trimethylsilyl)cyclohexyl)oxy)trimethylsilane (oTMS-1b**):** Colorless oil, 81% yield from dienol **1b**. ^1H NMR (400 MHz, CDCl_3) δ 5.96 – 5.74 (m, 2H), 5.09 – 4.88 (m, 4H), 2.37 – 2.23 (m, 2H), 2.13 – 1.96 (m, 2H), 1.82 – 1.73 (m, 1H), 1.69 – 1.57 (m, 2H), 1.53 – 1.27 (m, 6H), 0.77 – 0.68 (m, 1H), 0.12 (s, 9H), -0.03 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 139.1, 135.5, 116.8, 114.2, 76.1, 46.2, 43.2, 38.7, 34.5, 32.3, 32.1, 30.3, 18.2, 3.0, -3.0. IR (KBr, cm^{-1}): 2953, 1248, 1070, 836, 751. HRMS (ESI) m/z calc'd for $\text{C}_{19}\text{H}_{38}\text{OSi}_2$ $[\text{M}+\text{Na}]^+$: 361.2353, found: 361.2358.

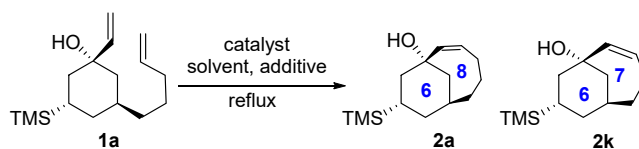


rac-(((1*R*,3*R*,5*S*)-3-allyl-1-(but-3-en-1-yl)-5-(trimethylsilyl)cyclohexyl)oxy)trimethylsilane (oTMS-1c**):** Colorless oil, 86% yield from dienol **1c**. ^1H NMR (400 MHz, CDCl_3) δ 5.90 – 5.68 (m, 2H), 5.05 – 4.88 (m, 4H), 2.16 – 2.08 (m, 2H), 2.07 – 2.01 (m, 2H), 1.88 – 1.81 (m, 1H), 1.66 – 1.59 (m, 3H), 1.58 – 1.31 (m, 5H), 0.74 (ddd, $J = 14.9, 9.6, 4.4$ Hz, 1H), 0.10 (s, 9H), -0.03 (s, 9H). ^{13}C NMR (125 MHz, CDCl_3) δ 139.5, 138.1, 115.5, 113.9, 76.0, 43.1, 40.8, 39.6, 39.0, 32.5, 30.0, 28.1, 18.3, 2.9, -3.0. IR (KBr, cm^{-1}): 2951, 1249, 1064, 837, 752. HRMS (ESI) m/z calc'd for $\text{C}_{19}\text{H}_{38}\text{OSi}_2$ $[\text{M}+\text{Na}]^+$: 361.2353, found: 361.2358.

rac-trimethyl((1S,3R,5R)-3-(pent-4-en-1-yl)-3-((trimethylsilyl)oxy)-5-vinylcyclohexyl)silane (oTMS-1d): Colorless oil, 84% yield from dienol **1d**. ¹H NMR (500 MHz, CDCl₃) δ 5.91 – 5.76 (m, 2H), 5.04 – 4.91 (m, 4H), 2.58 – 2.49 (m, 1H), 2.01 (dd, *J* = 13.7, 6.9 Hz, 2H), 1.78 – 1.71 (m, 1H), 1.69 – 1.60 (m, 3H), 1.52 – 1.32 (m, 6H), 0.82 (tt, *J* = 11.9, 3.6 Hz, 1H), 0.09 (s, 9H), -0.03 (s, 9H). ¹³C NMR (125 MHz, CDCl₃) δ 143.3, 139.2, 114.2, 112.4, 76.1, 43.5, 39.7, 39.5, 36.6, 34.2, 29.0, 22.8, 18.2, 2.9, -3.3. IR (KBr, cm⁻¹): 2951, 1248, 1079, 835, 750. HRMS (ESI) *m/z* calc'd for C₁₉H₃₈OSi₂ [M+Na]⁺: 361.2353, found: 361.2359.

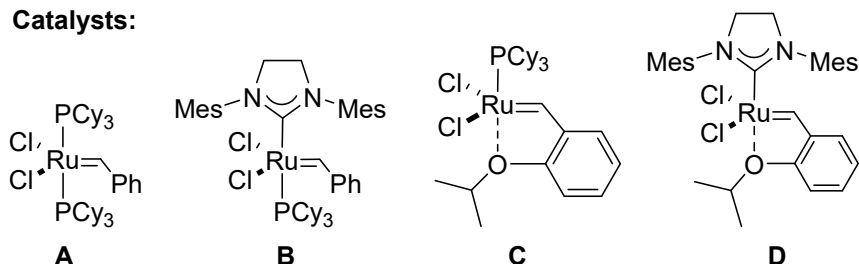
3. Condition Screening of RCM

3.1) Table S1: Optimization of RCM Reaction Conditions.^[a]



Entry	Catalyst [mol%]	Solvent	Time [h]	Additive	Yield [%] ^[b] (2a:2k)
1	A (10)	CH ₂ Cl ₂	12	—	22:16
2	B (10)	CH ₂ Cl ₂	12	—	20:13
3	C (10)	CH ₂ Cl ₂	12	—	17:trace
4	D (10)	CH ₂ Cl ₂	4	—	45:26
5	D (10)	CH ₂ Cl ₂	4	Ti(OiPr) ₄	61 ^[c]
6	D (10)	Toluene	4	Ti(OiPr) ₄	0:15
7	D (5)	CH ₂ Cl ₂	4	Ti(OiPr) ₄	60 ^[c]
8	D (5)	CH ₂ Cl ₂	4	BQ ^[d]	53:29

Catalysts:

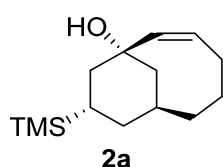


[a] Reactions were performed with 0.375 mmol of **1a**, 5–10 mol% of catalyst, and 0 or 1.0 equiv of Ti(OiPr)₄ in specified solvent (0.005 M). [b] NMR yield with anthracene as an internal standard. [c] Isolated yield of **2a**. [d] 1.0 equiv of 1,4-benzoquinone (BQ) as additive.

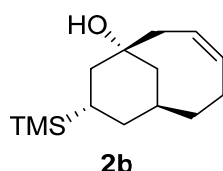
3.2) Typical Procedure for RCM Reaction

To the dienol (1.0 equiv) in freshly distilled and degassed CH₂Cl₂ (0.005 M) under argon atmosphere was added Ti(Oi-Pr)₄ (1.0 equiv) via syringe or without Ti(Oi-Pr)₄. The reaction mixture was stirred for 5 mins at rt before the addition of H-G-II catalyst (5 mol%) in CH₂Cl₂. The reaction mixture was heated to reflux for 4 h and then concentrated *in vacuo*. Purification of the residue by flash chromatography (PE/EtOAc = 40:1 → 20:1) afforded the corresponding bicyclo[n.3.1]alkene.

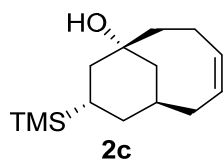
4. Characterization of Bicyclo[n.3.1]alkenes 2a - 2m and oTMS-2b - oTMS-2d



rac-(1R,7R,9S,Z)-9-(trimethylsilyl)bicyclo[5.3.1]undec-2-en-1-ol (2a): Following the typical procedure, **2a** (59 mg, 0.22 mmol) was obtained from dienol **1a** (100 mg, 0.37 mmol) as a white solid in 60% yield. m.p. 97 – 99 °C. ¹H NMR (500 MHz, CDCl₃) δ 5.62 – 5.51 (m, 2H), 2.86 – 2.76 (m, 1H), 2.70 – 2.61 (m, 1H), 2.15 – 2.07 (m, 1H), 2.03 – 1.94 (m, 1H), 1.77 – 1.68 (m, 2H), 1.64 – 1.56 (m, 2H), 1.55 – 1.50 (m, 1H), 1.34 – 1.26 (m, 5H), 1.07 – 0.99 (m, 1H), -0.04 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 139.0, 128.1, 72.4, 43.4, 40.6, 34.6, 32.1, 27.1, 24.4, 21.5, 18.4, -3.6. IR (KBr, cm⁻¹): 3298, 2911, 1431, 1239, 1018, 826. HRMS (ESI) *m/z* calc'd for C₁₄H₂₆OSi [M+Na]⁺: 261.1645, found: 261.1650.

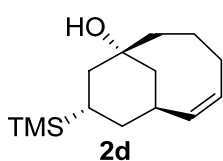


rac-(1S,7R,9S,Z)-9-(trimethylsilyl)bicyclo[5.3.1]undec-3-en-1-ol (2b): Following the typical procedure, **2b** (21 mg, 0.09 mmol) was obtained from dienol **1b** (48 mg, 0.18 mmol) as a white solid in 49% yield. m.p. 89 – 91 °C. ¹H NMR (400 MHz, CDCl₃) δ 5.74 – 5.67 (m, 1H), 5.61 – 5.51 (m, 1H), 3.01 – 2.92 (m, 1H), 2.51 – 5.40 (m, 1H), 2.18 – 2.07 (m, 2H), 2.06 – 1.96 (m, 2H), 1.85 (dd, *J* = 14.0, 9.0 Hz, 1H), 1.65 – 1.58 (m, 1H), 1.47 – 1.39 (m, 1H), 1.38 – 1.31 (m, 3H), 1.28 – 1.23 (m, 2H), 0.99 (tt, *J* = 13.3, 4.0 Hz, 1H), -0.03 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 133.7, 123.0, 73.2, 41.0, 38.6, 36.9, 34.5, 31.4, 30.9, 27.3, 18.2, -3.5. IR (KBr, cm⁻¹): 3330, 2920, 1434, 1242, 1059, 822. HRMS (ESI) *m/z* calc'd for C₁₄H₂₆OSi [M+Na]⁺: 261.1645, found: 261.1648.

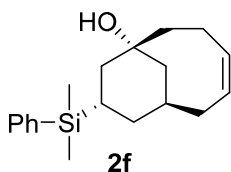


rac-(1R,7R,9S,Z)-9-(trimethylsilyl)bicyclo[5.3.1]undec-4-en-1-ol (2c): Following the typical procedure, **2c** (162 mg, 0.68 mmol) was obtained from dienol **1c** (274 mg, 1.03 mmol) as a white solid in 66% yield. m.p. 128 – 130 °C. ¹H NMR (500 MHz, CDCl₃) δ 5.65 – 5.59

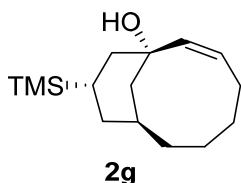
(m, 1H), 5.57 – 5.49 (m, 1H), 2.55 – 2.46 (m, 1H), 2.46 – 2.41 (m, 1H), 2.40 – 2.34 (m, 1H), 2.33 – 2.24 (m, 1H), 2.11 (ddd, $J = 12.9, 4.8, 2.9$ Hz, 1H), 2.06 – 1.97 (m, 1H), 1.82 – 1.73 (m, 1H), 1.64 – 1.58 (m, 1H), 1.41 – 1.31 (m, 4H), 1.25 – 1.19 (m, 2H), 1.03 (tt, $J = 13.6, 3.7$ Hz, 1H), -0.03 (s, 9H). ^{13}C NMR (125 MHz, CDCl_3) δ 132.1, 125.4, 72.8, 41.8, 38.0, 35.6, 33.3, 30.7, 28.5, 27.5, 17.9, -3.5. IR (KBr, cm^{-1}): 3362, 2923, 1431, 1242, 829. HRMS (ESI) m/z calc'd for $\text{C}_{14}\text{H}_{26}\text{OSi}$ $[\text{M}+\text{Na}]^+$: 261.1645, found: 261.1645.



***rac*-(1*R*,7*R*,9*S*,*Z*)-9-(trimethylsilyl)bicyclo[5.3.1]undec-5-en-1-ol (2d):** Following the typical procedure, **2d** (42 mg, 0.18 mmol) was obtained from dienol **1d** (91 mg, 0.34 mmol) as a white solid in 53% yield. m.p. 106 – 108 °C. ^1H NMR (500 MHz, CDCl_3) δ 5.49 – 5.38 (m, 2H), 2.73 – 2.62 (m, 2H), 2.59 (ddd, $J = 13.5, 5.1, 2.7$ Hz, 1H), 2.22 – 2.13 (m, 1H), 2.11 – 2.02 (m, 1H), 1.92 – 1.82 (m, 1H), 1.62 – 1.45 (m, 4H), 1.43 – 1.37 (m, 1H), 1.27 – 1.21 (m, 2H), 1.20 – 1.13 (m, 1H), 1.08 (tt, $J = 13.7, 3.2$ Hz, 1H), -0.04 (s, 9H). ^{13}C NMR (125 MHz, CDCl_3) δ 137.3, 125.5, 74.0, 42.7, 39.9, 37.0, 34.9, 34.1, 24.1, 20.0, 19.4, -3.6. IR (KBr, cm^{-1}): 3362, 2907, 1453, 1245, 874, 829. HRMS (ESI) m/z calc'd for $\text{C}_{14}\text{H}_{26}\text{OSi}$ $[\text{M}+\text{Na}]^+$: 261.1645, found: 261.1644.

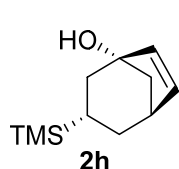


***rac*-(1*R*,7*R*,9*S*,*Z*)-9-(dimethyl(phenyl)silyl)bicyclo[5.3.1]undec-4-en-1-ol (2f):** Following the typical procedure, **2f** (388 mg, 1.29 mmol) was obtained from dienol **1f** (700 mg, 2.13 mmol) as a white solid in 61% yield. m.p. 83 – 85 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.50 – 7.47 (m, 2H), 7.37 – 7.33 (m, 3H), 5.63 – 5.58 (m, 1H), 5.55 – 5.48 (m, 1H), 2.54 – 2.40 (m, 2H), 2.39 – 2.32 (m, 1H), 2.31 – 2.24 (m, 1H), 2.09 (ddd, $J = 12.9, 4.6, 2.8$ Hz, 1H), 2.03 – 1.94 (m, 1H), 1.79 – 1.72 (m, 1H), 1.65 – 1.60 (m, 1H), 1.45 – 1.31 (m, 4H), 1.30 – 1.27 (m, 2H), 1.20 – 1.15 (m, 1H), 0.28 (s, 6H). ^{13}C NMR (125 MHz, CDCl_3) δ 137.8, 134.0, 132.2, 129.0, 127.7, 125.3, 72.8, 41.8, 37.9, 35.6, 33.3, 30.8, 28.4, 27.4, 17.5, -5.1. IR (KBr, cm^{-1}): 3365, 2914, 1424, 1245, 1114, 1053, 944, 829, 733, 701. HRMS (ESI) m/z calc'd for $\text{C}_{19}\text{H}_{28}\text{OSi}$ $[\text{M}+\text{Na}]^+$: 323.1802, found: 323.1800.

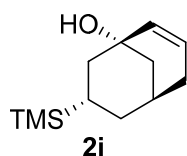


***rac*-(1*R*,8*S*,10*R*,*Z*)-10-(trimethylsilyl)bicyclo[6.3.1]dodec-2-en-1-ol (2g):** Following the typical procedure, **2g** (22 mg, 0.09 mmol) was obtained from dienol **1g** (106 mg, 0.38 mmol) as a white solid in 24% yield. m.p. 171 – 173 °C. ^1H NMR (500 MHz, CDCl_3) δ 5.68 – 5.58 (m, 2H), 2.18 – 2.09 (m, 1H), 2.00 – 1.91 (m, 1H), 1.84 (dd, $J = 13.2, 3.5$ Hz, 1H), 1.81 – 1.75 (m, 1H), 1.63 – 1.58 (m, 2H), 1.44 – 1.27 (m, 9H), 1.18 – 1.10 (m, 1H), 0.92 – 0.84 (m, 1H), 0.00 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 137.8, 127.9, 71.3,

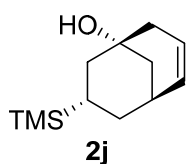
43.1, 38.8, 34.3, 33.4, 32.0, 31.9, 29.5, 26.2, 18.9, -2.8. IR (KBr, cm^{-1}): 3385, 2920, 1460, 1242, 973, 832. HRMS (ESI) m/z calc'd for $\text{C}_{15}\text{H}_{28}\text{OSi}$ $[\text{M}+\text{Na}]^+$: 275.1802, found: 275.1795.



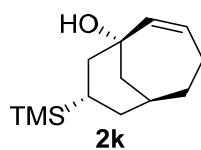
***rac*-(1*R*,3*S*,5*R*)-3-(trimethylsilyl)bicyclo[3.2.1]oct-6-en-1-ol (2h):** Following the typical procedure, **2h** (30 mg, 0.15 mmol) was obtained from dienol **1h** (50 mg, 0.22 mmol) as a white solid in 69% yield. m.p. 61 – 64 °C. ^1H NMR (400 MHz, CDCl_3) δ 5.79 (dd, $J = 5.7, 3.0$ Hz, 1H), 5.72 (d, $J = 5.7$ Hz, 1H), 2.75 (td, $J = 5.6, 2.9$ Hz, 1H), 2.06 – 1.98 (m, 1H), 1.82 (brs, 1H), 1.47 (ddd, $J = 12.2, 6.1, 3.0$ Hz, 1H), 1.38 – 1.34 (m, 1H), 1.33 – 1.27 (m, 1H), 1.22 – 1.12 (m, 2H), 1.03 – 0.92 (m, 1H), -0.05 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 136.4, 132.8, 82.6, 52.7, 41.5, 33.5, 25.1, 19.1, -3.4. IR (KBr, cm^{-1}): 3333, 2917, 1456, 1242, 1149, 838. HRMS (ESI) m/z calc'd for $\text{C}_{11}\text{H}_{20}\text{OSi}$ $[\text{M}+\text{Na}]^+$: 219.1176, found: 219.1177.



***rac*-(1*R*,5*R*,7*S*)-7-(trimethylsilyl)bicyclo[3.3.1]non-2-en-1-ol (2i):** Following the typical procedure, **2i** (108 mg, 0.51 mmol) was obtained from dienol **1i** (124 mg, 0.52 mmol) as a white solid in 99% yield. m.p. 104 – 106 °C. ^1H NMR (400 MHz, CDCl_3) δ 5.82 – 5.75 (m, 1H), 5.54 – 5.49 (m, 1H), 2.36 – 2.20 (m, 2H), 1.78 – 1.63 (m, 3H), 1.61 – 1.54 (m, 1H), 1.52 – 1.42 (m, 2H), 1.31 – 1.22 (m, 2H), 0.92 (tt, $J = 13.5, 4.0$ Hz, 1H), -0.06 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 134.1, 129.2, 70.7, 40.5, 38.4, 33.7, 31.7, 30.7, 19.6, -3.5. IR (KBr, cm^{-1}): 3269, 2914, 1434, 1239, 1059, 826. HRMS (ESI) m/z calc'd for $\text{C}_{12}\text{H}_{22}\text{OSi}$ $[\text{M}+\text{Na}]^+$: 233.1332, found: 233.1334.

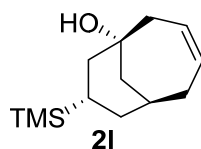


***rac*-(1*R*,5*R*,7*S*)-7-(trimethylsilyl)bicyclo[3.3.1]non-3-en-1-ol (2j):** Following the typical procedure, **2j** (61 mg, 0.29 mmol) was obtained from dienol **1j** (88 mg, 0.37 mmol) as a white solid in 79% yield. m.p. 93 – 95 °C. ^1H NMR (400 MHz, CDCl_3) δ 5.74 (dt, $J = 9.6, 3.5$ Hz, 1H), 5.58 – 5.48 (m, 1H), 2.68 – 2.61 (m, 1H), 2.27 – 2.09 (m, 2H), 1.85 – 1.78 (m, 1H), 1.69 – 1.45 (m, 3H), 1.35 – 1.20 (m, 3H), 1.11 – 1.00 (m, 1H), -0.07 (s, 9H). ^{13}C NMR (125 MHz, CDCl_3) δ 129.4, 127.6, 69.4, 42.6, 41.4, 40.5, 34.9, 29.0, 17.6, -3.6. IR (KBr, cm^{-1}): 3308, 2911, 1434, 1242, 1053, 826. HRMS (ESI) m/z calc'd for $\text{C}_{12}\text{H}_{22}\text{OSi}$ $[\text{M}+\text{Na}]^+$: 233.1332, found: 233.1339.



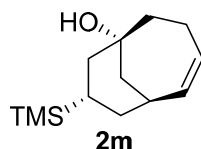
***rac*-(1*R*,6*R*,8*S*)-8-(trimethylsilyl)bicyclo[4.3.1]dec-2-en-1-ol (2k):**

Following the typical procedure, **2k** (66 mg, 0.30 mmol) was obtained from dienol **1k** (81 mg, 0.32 mmol) as a white solid in 94% yield. m.p. 95 – 96 °C. ¹H NMR (400 MHz, CDCl₃) δ 5.83 (ddd, *J* = 11.6, 8.0, 4.0 Hz, 1H), 5.33 (dt, *J* = 11.6, 2.5 Hz, 1H), 2.33 – 2.22 (m, 2H), 2.17 – 2.12 (m, 1H), 2.12 – 2.03 (m, 1H), 1.92 – 1.82 (m, 1H), 1.64 – 1.59 (m, 2H), 1.53 (ddd, *J* = 12.9, 4.8, 2.5 Hz, 1H), 1.39 – 1.21 (m, 4H), 0.95 – 0.84 (m, 1H), -0.05 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 136.7, 130.9, 74.6, 40.5, 40.1, 31.9, 31.3, 30.2, 25.4, 17.9, -3.5. IR (KBr, cm⁻¹): 3308, 2917, 1444, 1239, 1027, 835. HRMS (ESI) *m/z* calc'd for C₁₂H₂₄OSi [M+Na]⁺: 247.1489, found: 247.1489.



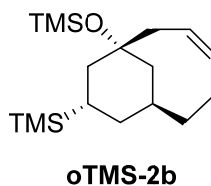
***rac*-(1*S*,6*R*,8*S*)-8-(trimethylsilyl)bicyclo[4.3.1]dec-3-en-1-ol (2l):**

Following the typical procedure, **2l** (45 mg, 0.20 mmol) was obtained from dienol **1l** (66 mg, 0.26 mmol) as a white solid in 77% yield. m.p. 98 – 100 °C. ¹H NMR (500 MHz, CDCl₃) δ 5.71 – 5.64 (m, 1H), 5.54 – 5.46 (m, 1H), 2.46 – 2.36 (m, 3H), 2.27 – 2.20 (m, 1H), 2.19 – 2.15 (m, 1H), 2.08 (ddd, *J* = 12.8, 4.0, 2.2 Hz, 1H), 1.89 – 1.79 (m, 2H), 1.59 – 1.50 (m, 2H), 1.45 – 1.33 (m, 3H), -0.08 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 130.5, 125.1, 70.6, 45.4, 44.7, 42.7, 36.3, 32.9, 30.7, 21.2, -3.8. IR (KBr, cm⁻¹): 3317, 2914, 1437, 1242, 1024, 832. HRMS (ESI) *m/z* calc'd for C₁₃H₂₄OSi [M+Na]⁺: 247.1489, found: 247.1488.



***rac*-(1*R*,6*R*,8*S*)-8-(trimethylsilyl)bicyclo[4.3.1]dec-4-en-1-ol (2m):**

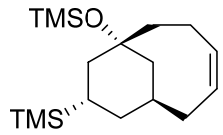
Following the typical procedure, **2m** (58 mg, 0.26 mmol) was obtained from dienol **1m** (89 mg, 0.35 mmol) as a white solid in 74% yield. m.p. 103 – 104 °C. ¹H NMR (400 MHz, CDCl₃) δ 5.80 – 5.71 (m, 1H), 5.45 – 5.38 (m, 1H), 2.65 (brs, 1H), 2.50 – 2.40 (m, 1H), 2.39 – 2.32 (m, 1H), 2.08 – 1.97 (m, 2H), 1.80 – 1.66 (m, 2H), 1.51 – 1.43 (m, 2H), 1.35 – 1.29 (m, 1H), 1.25 – 1.18 (m, 2H), 1.02 (tt, *J* = 13.6, 3.2 Hz, 1H), -0.05 (s, 9H). ¹³C NMR (125 MHz, CDCl₃) δ 133.8, 130.4, 72.3, 42.1, 41.7, 41.4, 36.6, 30.9, 23.7, 18.9, -3.6. IR (KBr, cm⁻¹): 3308, 2927, 1450, 1242, 1053, 829. HRMS (ESI) *m/z* calc'd for C₁₃H₂₄OSi [M+Na]⁺: 247.1489, found: 247.1497.

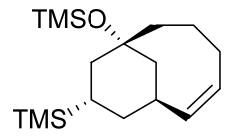


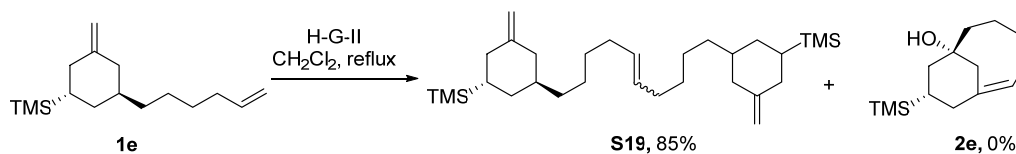
***rac*-trimethyl(((1*S*,7*R*,9*S*,*Z*)-9-(trimethylsilyl)bicyclo[5.3.1]undec-3-en-1-yl)oxy)silane (oTMS-2b):**

Following the typical procedure, **oTMS-2b** (76 mg, 0.23 mmol) was obtained from **oTMS-1b** (100 mg, 0.30 mmol) as a colorless oil in 76% yield. ¹H NMR (400 MHz, CDCl₃) δ 5.65 (dd, *J* = 11.9, 1.7 Hz, 1H), 5.59 – 5.50 (m, 1H), 2.94 – 2.83 (m,

1H), 2.49 – 2.37 (m, 1H), 2.20 – 2.06 (m, 2H), 2.02 – 1.94 (m, 2H), 1.92 – 1.85 (m, 1H), 1.63 (dt, $J = 12.7, 2.6$ Hz, 1H), 1.44 – 1.28 (m, 5H), 1.01 – 0.91 (m, 1H), 0.09 (s, 9H), -0.03 (s, 9H). ^{13}C NMR (125 MHz, CDCl_3) δ 132.4, 124.3, 76.6, 41.8, 38.7, 37.2, 34.5, 31.3, 31.0, 27.6, 18.4, 3.0, -3.5. IR (KBr, cm^{-1}): 2954, 1248, 1076, 835, 748. HRMS (ESI) m/z calc'd for $\text{C}_{17}\text{H}_{34}\text{OSi}_2$ $[\text{M}+\text{Na}]^+$: 333.2040, found: 333.2048.

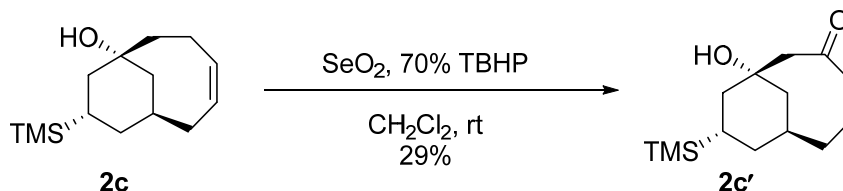

oTMS-2c *rac*-trimethyl(((1*R*,7*R*,9*S*,*Z*)-9-(trimethylsilyl)bicyclo[5.3.1]undec-4-en-1-yl)oxy)silane (**oTMS-2c**): Following the typical procedure, **oTMS-2c** (113 mg, 0.36 mmol) was obtained from **oTMS-1c** (150 mg, 0.44 mmol) as a colorless oil in 82% yield. ^1H NMR (500 MHz, CDCl_3) δ 5.67 – 5.60 (m, 1H), 5.58 – 5.48 (m, 1H), 2.54 – 2.45 (m, 1H), 2.44 – 2.32 (m, 2H), 2.26 – 2.16 (m, 1H), 2.13 – 2.06 (m, 1H), 2.02 – 1.93 (m, 1H), 1.81 – 1.71 (m, 1H), 1.66 – 1.59 (m, 1H), 1.44 – 1.23 (m, 6H), 1.00 (dtd, $J = 16.5, 6.9, 3.4$ Hz, 1H), 0.10 (s, 9H), -0.03 (s, 9H). ^{13}C NMR (125 MHz, CDCl_3) δ 132.6, 125.1, 76.7, 41.6, 38.5, 36.0, 33.4, 30.7, 28.7, 27.6, 18.1, 3.0, -3.5. IR (KBr, cm^{-1}): 2954, 1475, 1248, 1075, 874, 734. HRMS (ESI) m/z calc'd for $\text{C}_{17}\text{H}_{34}\text{OSi}_2$ $[\text{M}+\text{Na}]^+$: 333.2040, found: 333.2046.


oTMS-2d *rac*-trimethyl(((1*R*,7*R*,9*S*,*Z*)-9-(trimethylsilyl)bicyclo[5.3.1]undec-5-en-1-yl)oxy)silane (**oTMS-2d**): Following the typical procedure, **oTMS-2d** (34 mg, 0.11 mmol) was obtained from **oTMS-1d** (60 mg, 0.18 mmol) as a colorless oil in 62% yield. ^1H NMR (500 MHz, CDCl_3) δ 5.54 – 5.30 (m, 2H), 2.68 – 2.62 (m, 1H), 2.58 (dd, $J = 13.6, 2.4$ Hz, 1H), 2.14 – 2.01 (m, 2H), 1.93 – 1.82 (m, 1H), 1.65 – 1.52 (m, 3H), 1.48 – 1.40 (m, 2H), 1.32 – 1.27 (m, 1H), 1.25 – 1.17 (m, 2H), 0.99 – 0.91 (m, 1H), 0.11 (s, 9H), -0.05 (s, 9H). ^{13}C NMR (125 MHz, CDCl_3) δ 137.5, 125.6, 77.8, 42.7, 40.7, 37.3, 35.0, 34.0, 24.3, 20.2, 19.5, 3.1, -3.6. IR (KBr, cm^{-1}): 2953, 1249, 1088, 836, 751. HRMS (ESI) m/z calc'd for $\text{C}_{17}\text{H}_{34}\text{OSi}_2$ $[\text{M}+\text{Na}]^+$: 333.2040, found: 333.2051.



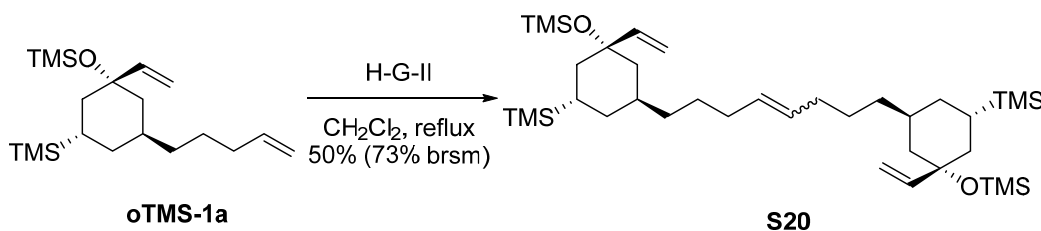
***rac*-1-((1*R*,5*S*)-3-methylene-5-(trimethylsilyl)cyclohexyl)-10-(3-methylene-5-(trimethylsilyl)cyclohexyl)dec-5-ene (S19)**: To the diene **1e** (100 mg, 0.40 mmol) in CH_2Cl_2 (80 mL) was added H-G-II catalyst (13 mg, 0.02 mmol) in CH_2Cl_2 . The reaction mixture was heated to reflux for 6 h and then concentrated *in vacuo*. Purification of the residue by flash chromatography (pure PE) afforded the dimer **S19** (81 mg, 85% yield) as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 5.44 – 5.32 (m, 1H), 4.62 (s, 1H), 4.54 (s, 1H), 2.23 – 2.15

(m, 2H), 2.07 – 2.02 (m, 1H), 2.01 – 1.94 (m, 2H), 1.92 – 1.83 (m, 1H), 1.79 – 1.72 (m, 1H), 1.54 – 1.44 (m, 2H), 1.36 – 1.22 (m, 6H), 0.93 – 0.83 (m, 1H), -0.04 (s, 9H). ¹³C NMR (125 MHz, CDCl₃) δ 148.0, 130.3, 107.5, 40.0, 35.9, 35.4, 32.6, 31.6, 31.0, 29.8, 26.9, 21.6, -3.3. IR (KBr, cm⁻¹): 2927, 1639, 1242, 877, 829. MS (EI) *m/z* calc'd for C₃₀H₅₆Si₂ [M]⁺: 473, found: 473.



***rac*-(1*S*,7*R*,9*S*,*Z*)-1-hydroxy-9-(trimethylsilyl)bicyclo[5.3.1]undec-4-en-3-one (2c'):**

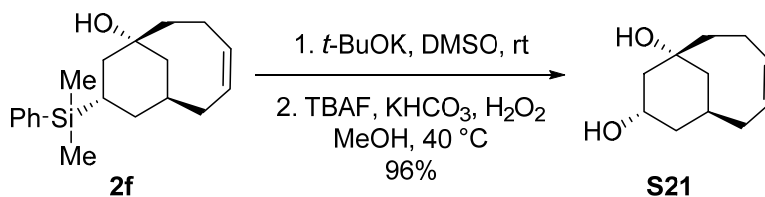
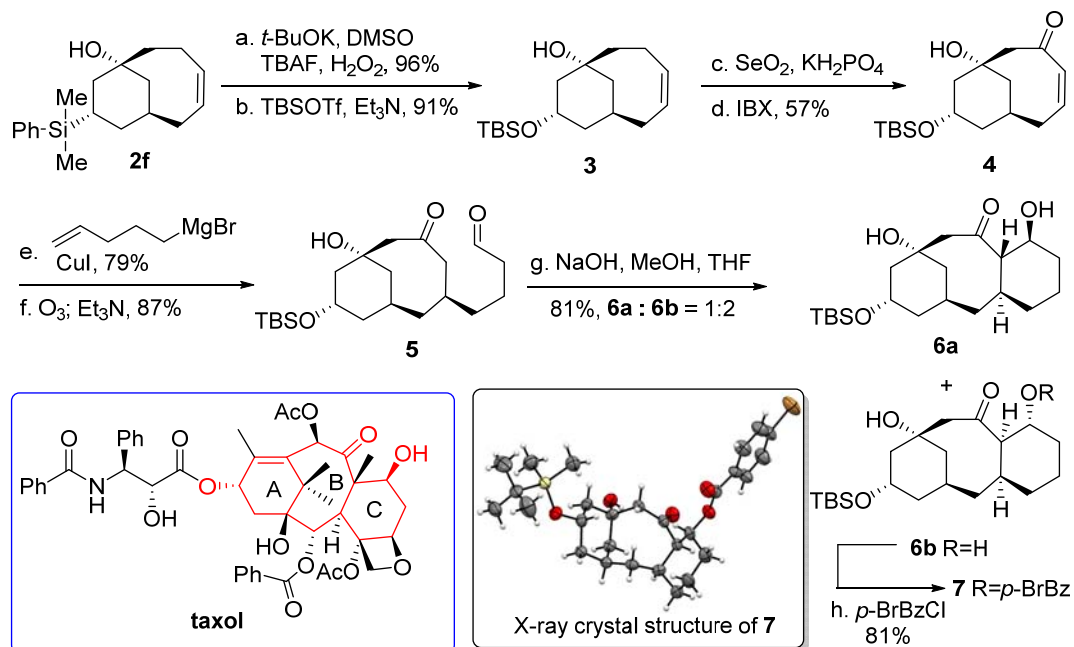
To a solution of **2c** (181 mg, 0.76 mmol) in CH₂Cl₂ (10 mL) was added selenium dioxide (25 mg, 0.23 mmol) and *tert*-butyl hydroperoxide (0.16 mL, 70% aqueous solution). The reaction mixture was stirred at rt for 20 h before being quenched with saturated Na₂SO₃ and 1N NaOH solution and extracted with CH₂Cl₂.^[3] The combined organic extract was washed with brine, dried over MgSO₄ and concentrated *in vacuo*. Purification of the residue by flash chromatography (PE/EtOAc = 4:1) afforded enone **2c'** (56 mg, 0.22 mmol, 29% yield) as a white solid. m.p. 132 – 134 °C. ¹H NMR (500 MHz, CDCl₃) δ 6.58 (ddd, *J* = 12.1, 9.9, 7.3 Hz, 1H), 6.24 (dt, *J* = 12.1, 2.1 Hz, 1H), 3.49 (d, *J* = 12.9 Hz, 1H), 2.89 – 2.80 (m, 1H), 2.34 (d, *J* = 12.9 Hz, 1H), 2.27 (ddd, *J* = 14.3, 9.8, 7.6 Hz, 1H), 2.16 – 1.99 (m, 2H), 1.86 (ddd, *J* = 13.8, 4.9, 2.9 Hz, 1H), 1.70 – 1.65 (m, 1H), 1.55 – 1.40 (m, 3H), 1.37 – 1.31 (m, 1H), 1.12 (tt, *J* = 13.6, 3.8 Hz, 1H), 0.00 (s, 9H). ¹³C NMR (125 MHz, CDCl₃) δ 200.8, 143.9, 136.4, 69.4, 53.0, 40.3, 38.5, 30.6, 30.5, 30.2, 17.8, -3.6. IR (KBr, cm⁻¹): 3391, 2911, 1633, 1248, 742. HRMS (ESI) *m/z* calc'd for C₁₄H₂₄O₂Si [M+Na]⁺: 275.1438, found: 275.1436.



***rac*-1-((1*R*,3*R*,5*S*)-5-(trimethylsilyl)-3-((trimethylsilyl)oxy)-3-vinylcyclohexyl)-8-(5-(trimethylsilyl)-3-((trimethylsilyl)oxy)-3-vinylcyclohexyl)oct-4-ene (S20):** To compound **oTMS-1a** (100 mg, 0.30 mmol) in CH₂Cl₂ (55 mL) was added H-G-II catalyst (10 mg, 0.016 mmol) in CH₂Cl₂ (5 mL) via syringe. The reaction mixture was heated to reflux for 12 hours and concentrated *in vacuo*. Purification of the residue by flash chromatography

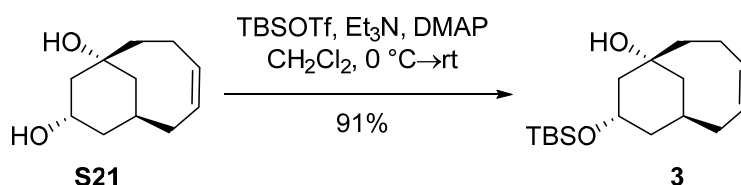
(pure PE) afforded dimer **S20** (48 mg, 0.083 mmol, 50% yield, 73% yield brsm) as a colorless oil. ^1H NMR (500 MHz, CDCl_3) δ 5.99 (dd, $J = 17.6, 10.8$ Hz, 1H), 5.41 – 5.34 (m, 1H), 5.16 – 5.11 (m, 1H), 5.05 – 5.00 (m, 1H), 2.01 – 1.93 (m, 2H), 1.82 – 1.75 (m, 2H), 1.73 – 1.67 (m, 1H), 1.59 – 1.53 (m, 1H), 1.52 – 1.44 (m, 2H), 1.33 – 1.22 (m, 5H), 0.89 – 0.80 (m, 1H), 0.09 (s, 9H), -0.01 (s, 9H). ^{13}C NMR (125 MHz, CDCl_3) δ 145.7, 130.4, 112.3, 74.9, 43.6, 39.0, 34.3, 32.8, 32.6, 30.9, 27.8, 18.7, 3.0, -2.7. IR (KBr, cm^{-1}): 2920, 1453, 1245, 1043, 918, 835. HRMS (ESI) m/z calc'd for $\text{C}_{36}\text{H}_{72}\text{O}_2\text{Si}_4$ $[\text{M}+\text{Na}]^+$: 671.4502, found: 671.4495.

5. Synthesis of A-B-C Ring Skeleton of Taxol

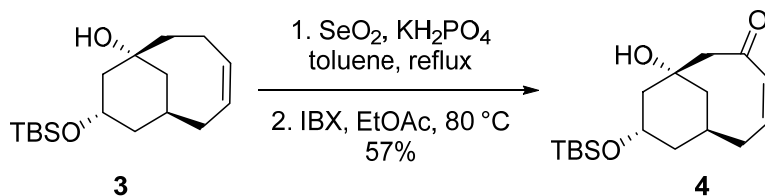


rac-(1R,7S,9S,Z)-bicyclo[5.3.1]undec-4-ene-1,9-diol (S21): To a solution of **2f** (250 mg, 0.83 mmol) in DMSO (15 mL) was added potassium *t*-butoxide (205 mg, 1.83 mmol).^[4] The reaction mixture was stirred for 3 h at rt and then diluted with Et₂O (40 mL) and phosphate buffer solution (pH $\approx$ 7, 40 mL) and extracted with Et₂O. The combined organic extract was concentrated *in vacuo*. The residue was redissolved in MeOH (15 mL) and then

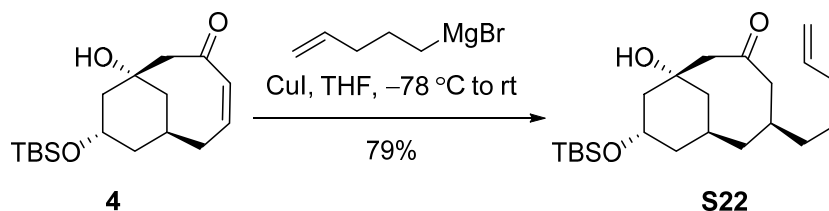
KHCO₃ (210 mg, 2.50 mmol), TBAF (1.0 M in THF, 3.74 mL, 3.74 mmol) and H₂O₂ (30% in water, 1.27 mL, 12.48 mmol) were added in sequence to the resulting solution. The reaction mixture was heated at 40 °C for 6 h and then poured into a saturated solution of Na₂SO₃ and extracted with CHCl₃. The combined organic layers were dried over MgSO₄, and concentrated under reduced pressure. Purification of the residue by flash chromatography (PE/EtOAc = 1:1 → 1:3) afforded the diol **S21** (146 mg, 0.80 mmol, 96% yield over two steps) as a white solid. m.p. 152 – 154 °C. ¹H NMR (500 MHz, CD₃OD) δ 5.69 – 5.61 (m, 1H), 5.57 – 5.49 (m, 1H), 4.01 – 3.91 (m, 1H), 2.54 – 2.43 (m, 2H), 2.36 – 2.24 (m, 2H), 2.18 (ddd, *J* = 13.2, 4.7, 2.7 Hz, 1H), 2.13 – 2.04 (m, 2H), 2.02 – 1.92 (m, 1H), 1.87 – 1.81 (m, 1H), 1.58 – 1.51 (m, 1H), 1.51 – 1.45 (m, 1H), 1.41 (t, *J* = 11.7 Hz, 1H), 1.34 – 1.28 (m, 1H). ¹³C NMR (125 MHz, CD₃OD) δ 133.6, 125.8, 74.2, 66.3, 50.9, 40.2, 37.6, 37.5, 33.0, 30.4, 28.2. IR (KBr, cm⁻¹): 3340, 2930, 1469, 1027, 1011. HRMS (ESI) *m/z* calc'd for C₁₁H₁₈O₂ [M+Na]⁺: 205.1199, found: 205.1203.



***rac*-(1*R*,7*S*,9*S*,*Z*)-9-((*tert*-butyldimethylsilyl)oxy)bicyclo[5.3.1]undec-4-en-1-ol (**3**):** To a solution of diol **S21** (147 mg, 0.81 mmol) in CH₂Cl₂ (20 mL) at 0 °C was added Et₃N (0.28 mL, 204 mg, 2.02 mmol), 4-(dimethylamino)pyridine (30 mg, 0.24 mmol) and *t*-Butyldimethylsilyl triflate (0.28 mL, 320 mg, 1.21 mmol) in sequence. The reaction mixture was stirred for 3 h and then poured into H₂O (5 mL) and extracted with CH₂Cl₂. The combined organic layers were washed with brine, dried over MgSO₄ and concentrated *in vacuo*. Purification of the residue by flash chromatography (PE/EtOAc = 10:1) afforded **3** (200 mg, 0.68 mmol, 84% yield) as a white solid. m.p. 92 – 93 °C. ¹H NMR (400 MHz, CDCl₃) δ 5.67 – 5.59 (m, 1H), 5.54 – 5.44 (m, 1H), 4.03 – 3.93 (m, 1H), 2.46 – 2.31 (m, 2H), 2.31 – 2.20 (m, 2H), 2.14 (dd, *J* = 13.1, 2.0 Hz, 1H), 2.10 – 1.89 (m, 3H), 1.75 – 1.68 (m, 1H), 1.55 – 1.43 (m, 4H), 1.29 – 1.22 (m, 1H), 0.89 (s, 9H), 0.07 (s, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 132.5, 124.9, 73.5, 66.6, 50.5, 39.7, 37.3, 36.8, 31.6, 29.5, 27.0, 25.9, 18.2, -4.6, -4.6. IR (KBr, cm⁻¹): 3308, 2927, 1469, 1248, 1085, 832. HRMS (ESI) *m/z* calc'd for C₁₇H₃₂O₂Si [M+Na]⁺: 319.2064, found: 319.2060.

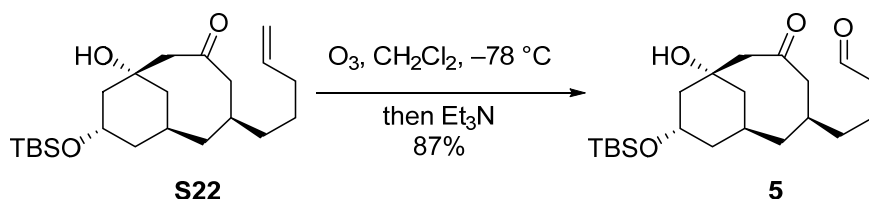


***rac*-(1*R*,7*S*,9*S*,*Z*)-9-((*tert*-butyldimethylsilyl)oxy)-1-hydroxybicyclo[5.3.1]undec-4-en-3-one (4):** A mixture of olefin **3** (167 mg, 0.56 mmol), potassium dihydrogen phosphate (230 mg, 1.69 mmol), and selenium dioxide (125 mg, 1.13 mmol) in toluene (20 mL) was refluxed for 2 h and then cooled to rt.^[3] The reaction mixture was diluted with Et₂O, washed with saturated NaHCO₃ solution and brine, dried over MgSO₄ and concentrated *in vacuo*. The residue was redissolved in ethyl acetate (20 mL), and IBX (392 mg, 1.41 mmol) was added. The resulting suspension was immersed in an oil bath set to 80 °C and stirred vigorously open to the atmosphere for 3.5 h. The reaction mixture was cooled to rt and filtered. The filter cake was washed with 3 × 10 mL of EtOAc, and the combined filtrates were concentrated. Purification of the residue by flash chromatography (PE/EtOAc = 4:1) afforded enone **4** (100 mg, 0.32 mmol, 57% overall yield) as a white solid. m.p. 159 – 161 °C. ¹H NMR (500 MHz, CDCl₃) δ 6.53 (ddd, *J* = 12.1, 9.9, 7.2 Hz, 1H), 6.25 (dt, *J* = 12.1, 2.0 Hz, 1H), 4.09 – 4.01 (m, 1H), 3.17 (d, *J* = 13.0 Hz, 1H), 2.65 – 2.56 (m, 1H), 2.50 (d, *J* = 13.0 Hz, 1H), 2.42 (ddd, *J* = 14.5, 9.8, 7.9 Hz, 1H), 2.15 – 2.04 (m, 3H), 1.87 – 1.78 (m, 2H), 1.62 – 1.55 (m, 1H), 1.56 – 1.50 (m, 1H), 1.50 – 1.45 (m, 1H), 0.88 (s, 9H), 0.06 (s, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 199.7, 143.1, 136.9, 69.8, 66.0, 54.0, 49.4, 39.5, 37.7, 31.4, 29.0, 25.8, 18.2, -4.6, -4.6. IR (KBr, cm⁻¹): 3397, 2923, 1636, 1476, 1091, 835. HRMS (ESI) *m/z* calc'd for C₁₇H₃₀O₃Si [M+Na]⁺: 333.1856, found: 333.1857.

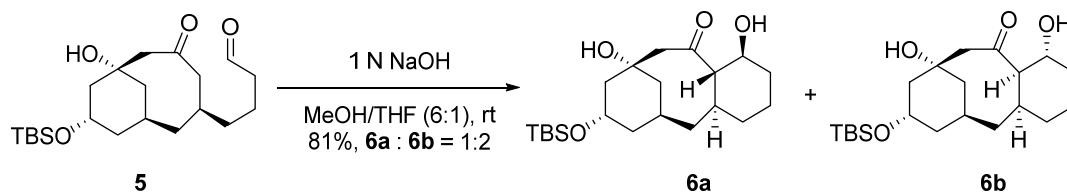


***rac*-(1*R*,5*S*,7*S*,9*S*)-9-((*tert*-butyldimethylsilyl)oxy)-1-hydroxy-5-(pent-4-en-1-yl)bicyclo[5.3.1]undecan-3-one (S22):** To a stirred mixture of CuI (120 mg, 0.63 mmol) in THF (2 mL) at -78 °C was added pent-4-en-1-ylmagnesium bromide (2.52 mmol, 1M in THF) dropwise. The dry ice-acetone bath was removed and the reaction mixture was stirred for 20 mins before cooling to -78 °C again. To the resulting mixture was added the enone **4** (196 mg, 0.63 mmol) in THF (2 mL). The reaction mixture was stirred for 1h at this temperature before being quenched with saturated aqueous NH₄Cl and extracted with Et₂O. The combined organic extract was washed with brine, dried over MgSO₄ and concentrated

in vacuo. Purification of the residue by flash chromatography (PE/EtOAc = 10:1) afforded the ketone **S22** (190 mg, 0.50 mmol, 79% yield) as a white solid. m.p. 149 – 151 °C. ¹H NMR (400 MHz, CDCl₃) δ 5.77 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.03 – 4.92 (m, 2H), 4.01 – 3.90 (m, 1H), 3.02 (t, *J* = 6.5 Hz, 2H), 2.42 (d, *J* = 11.6 Hz, 1H), 2.34 (d, *J* = 13.0 Hz, 1H), 2.18 (t, *J* = 11.2 Hz, 1H), 2.07 – 1.93 (m, 4H), 1.79 – 1.70 (m, 2H), 1.64 – 1.53 (m, 3H), 1.48 – 1.30 (m, 7H), 0.88 (s, 9H), 0.05 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 214.6, 138.4, 114.8, 72.4, 66.0, 54.0, 52.1, 47.4, 40.0, 38.3, 38.2, 37.3, 34.2, 33.7, 31.2, 26.0, 25.8, 18.2, -4.6. IR (KBr, cm⁻¹): 3529, 2927, 1687, 1469, 1098, 835. HRMS (ESI) *m/z* calc'd for C₂₂H₄₀O₃Si [M+Na]⁺: 403.2639, found: 403.2642.

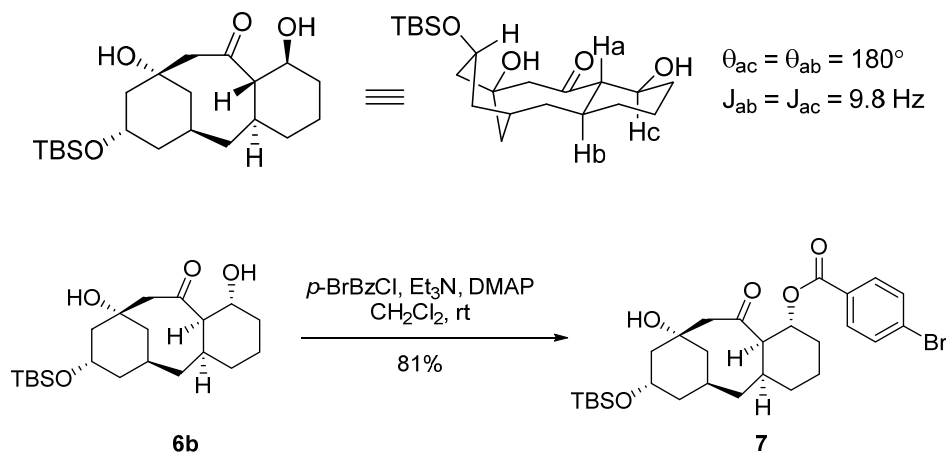


***rac*-4-((1*S*,3*S*,7*R*,9*S*)-9-((*tert*-butyldimethylsilyl)oxy)-7-hydroxy-5-oxobicyclo[5.3.1]undecan-3-yl)butanal (5)**: Ozone was bubbled through a solution of olefin **S22** (55 mg, 0.15 mmol) in CH₂Cl₂ (5 mL) at -78 °C. When TLC indicated the consumption of the starting material, Et₃N (0.06 mL, 44 mg, 0.44 mmol) was added and the reaction mixture was stirred overnight. The solvent was removed *in vacuo*. Purification of the residue by flash chromatography (PE/EtOAc = 4:1) provided aldehyde **5** (48 mg, 0.13 mmol, 87% yield) as a colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 9.76 (t, *J* = 1.4 Hz, 1H), 4.00 – 3.92 (m, 1H), 3.04 – 2.95 (m, 2H), 2.46 – 2.39 (m, 3H), 2.34 (d, *J* = 13.0 Hz, 1H), 2.21 (t, *J* = 11.2 Hz, 1H), 2.06 – 1.94 (m, 2H), 1.79 – 1.72 (m, 2H), 1.70 – 1.57 (m, 5H), 1.51 – 1.40 (m, 3H), 1.39 – 1.31 (m, 2H), 0.88 (s, 9H), 0.07 (s, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 214.2, 201.8, 72.3, 66.0, 53.8, 52.1, 47.4, 43.7, 40.0, 38.2, 38.1, 37.1, 34.2, 31.2, 25.8, 19.1, 18.1, -4.6. IR (KBr, cm⁻¹): 3532, 2930, 1722, 1466, 1098, 838. HRMS (ESI) *m/z* calc'd for C₂₁H₃₈O₄Si [M+Na]⁺: 405.2432, found: 405.2433.



***rac*-(1*S*,4*aS*,6*S*,8*S*,10*R*,12*aS*)-8-((*tert*-butyldimethylsilyl)oxy)-1,10-dihydroxydodecahydro-6,10-methanobenzo[10]annulen-12(2H)-one (6a)** and ***rac*-(1*R*,4*aS*,6*S*,8*S*,10*R*,12*aR*)-8-((*tert*-butyldimethylsilyl)oxy)-1,10-dihydroxydodecahydro-6,10-methanobenzo[10]annulen-12(2H)-one (6b)**: To a solution of **5** (62 mg, 0.16 mmol) in methanol (4.2 mL) were added THF (0.7 mL) and aqueous NaOH solution (1N,

0.89 mL). The resulting solution was stirred 6h and then quenched with saturated NH_4Cl solution and extracted with Et_2O . The combined organic extract was washed with brine, dried over MgSO_4 and concentrated *in vacuo*. Purification of the residue by flash chromatography ($\text{CH}_2\text{Cl}_2/\text{MeOH} = 20:1$) afforded **6a** and **6b** as a mixture (50 mg, 0.13 mmol, 81% yield, **6a** : **6b** = 1:2). Analytic sample of **6a** and **6b** were obtained by careful flash column chromatography ($\text{CH}_2\text{Cl}_2/\text{MeOH} = 100:1$). **6a**: m.p. 129 – 130 °C. ^1H NMR (400 MHz, CDCl_3) δ 4.01 – 3.90 (m, 2H), 3.23 – 3.10 (m, 1H), 3.05 (d, $J = 13.4$ Hz, 1H), 2.42 (dd, $J = 13.5, 1.6$ Hz, 1H), 2.17 (t, $J = 9.8$ Hz, 1H), 2.10 – 1.95 (m, 3H), 1.81 – 1.55 (m, 7H), 1.48 – 1.39 (m, 3H), 1.34 – 1.25 (m, 4H), 0.89 (s, 9H), 0.07 (s, 6H). ^{13}C NMR (125 MHz, CDCl_3) δ 217.4, 72.4, 69.3, 67.8, 65.9, 53.2, 47.1, 39.9, 38.7, 38.1, 37.0, 36.7, 32.2, 30.7, 25.8, 23.8, 18.2, -4.6. IR (KBr, cm^{-1}): 3362, 2930, 1697, 1085, 835. HRMS (ESI) m/z calc'd for $\text{C}_{21}\text{H}_{38}\text{O}_4\text{Si}$ $[\text{M}+\text{Na}]^+$: 405.2432, found: 405.2430. **6b**: m.p. 133 – 135 °C. ^1H NMR (500 MHz, CDCl_3) δ 4.06 – 3.93 (m, 2H), 3.23 – 3.12 (m, 2H), 2.32 (dd, $J = 10.9, 4.0$ Hz, 1H), 2.24 (d, $J = 13.2$ Hz, 1H), 2.13 – 1.98 (m, 4H), 1.92 – 1.81 (m, 1H), 1.77 – 1.71 (m, 1H), 1.70 – 1.55 (m, 4H), 1.50 – 1.38 (m, 6H), 1.28 – 1.23 (m, 1H), 0.89 (s, 9H), 0.08 (s, 6H). ^{13}C NMR (125 MHz, CDCl_3) δ 216.2, 72.1, 68.7, 66.0, 64.6, 47.4, 47.4, 40.0, 38.0, 35.8, 34.4, 34.1, 32.9, 31.2, 25.8, 20.3, 18.1, -4.5, -4.5. IR (KBr, cm^{-1}): 3413, 2930, 1687, 1091, 835. HRMS (ESI) m/z calc'd for $\text{C}_{21}\text{H}_{38}\text{O}_4\text{Si}$ $[\text{M}+\text{Na}]^+$: 405.2432, found: 405.2435.

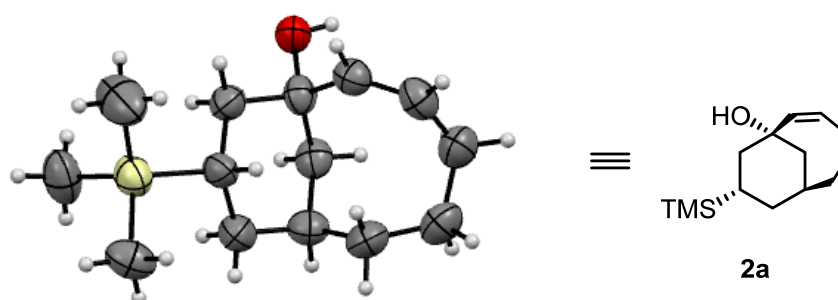


***rac*-(1*R*,4*aS*,6*S*,8*S*,10*R*,12*aR*)-8-((tert-butyldimethylsilyl)oxy)-10-hydroxy-12-oxo-tetradecahydro-6,10-methanobenzo[10]annulen-1-yl 4-bromobenzoate (**7**):** To a stirred solution of alcohol **6b** (21 mg, 0.055 mmol) in CH_2Cl_2 (4 mL) at rt was added Et_3N (0.025 mL, 17 mg, 0.165 mmol), DMAP (7 mg, 0.055 mmol) and 4-bromobenzoyl chloride (24 mg, 0.110 mmol) in sequence. After stirring overnight, the reaction mixture was quenched with saturated NaHCO_3 aqueous solution and extracted with CH_2Cl_2 . The combined organic extract was washed with brine, dried over MgSO_4 and concentrated *in vacuo*. Purification of the residue by flash chromatography ($\text{PE}/\text{EtOAc} = 8:1 \rightarrow 5:1$) afforded 4-

bromobenzoate **7** (25 mg, 81%) as a white solid. m.p. 138 – 140 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.82 – 7.76 (m, 2H), 7.58 – 7.52 (m, 2H), 5.44 (td, J = 11.2, 4.6 Hz, 1H), 4.06 – 3.97 (m, 1H), 3.14 (d, J = 13.3 Hz, 1H), 3.06 – 2.99 (m, 1H), 2.76 (dd, J = 11.6, 4.0 Hz, 1H), 2.34 – 2.28 (m, 1H), 2.20 – 2.15 (m, 1H), 2.08 – 1.94 (m, 4H), 1.81 – 1.70 (m, 2H), 1.68 – 1.59 (m, 3H), 1.52 – 1.32 (m, 6H), 0.99 (s, 9H), 0.10 (overlapped, 3H), 0.10 (overlapped, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 214.6, 165.0, 131.8, 131.1, 128.5, 72.2, 71.7, 65.9, 61.4, 47.4, 47.3, 39.9, 38.0, 34.3, 34.2, 32.8, 31.5, 31.2, 25.8, 19.9, 18.1, -4.4. IR (KBr, cm^{-1}): 3420, 2933, 1719, 1264, 1095, 752. HRMS (ESI) m/z calc'd for $\text{C}_{28}\text{H}_{41}\text{BrO}_5\text{Si}$ $[\text{M}+\text{Na}]^+$: 587.1799, found: 587.1795.

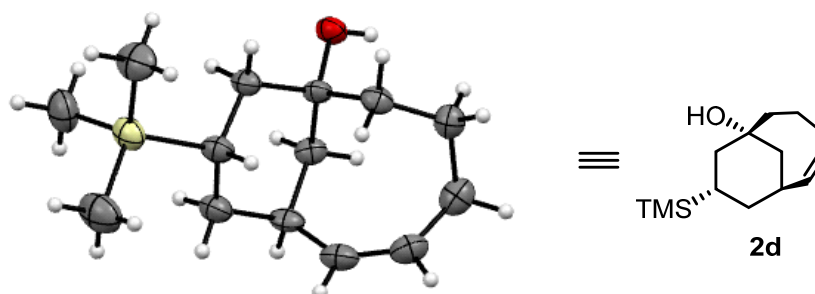
6. X-Ray Crystallographic Data

1) X-ray crystal structure of compound **2a**



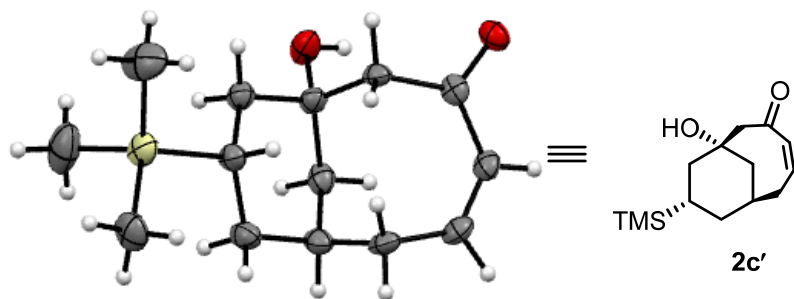
Perspective view of the molecular structure of **2a** ($\text{C}_{14}\text{H}_{26}\text{OSi}$) with the atom labeling scheme. CCDC number: 1578169.

2) X-ray crystal structure of compound **2d**



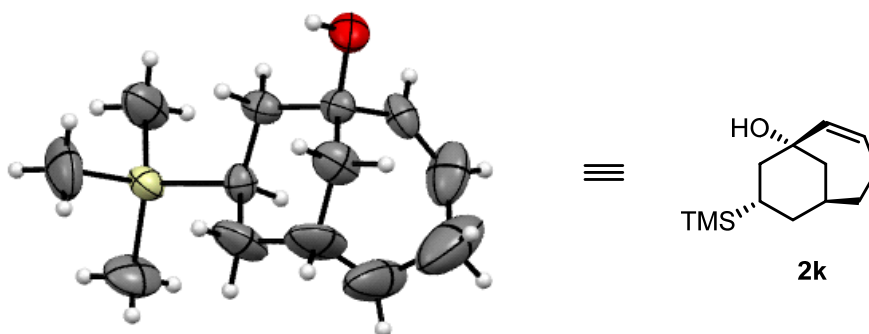
Perspective view of the molecular structure of **2d** ($\text{C}_{14}\text{H}_{26}\text{OSi}$) with the atom labeling scheme. CCDC number: 1578171.

3) X-ray crystal structure of compound **2c'**



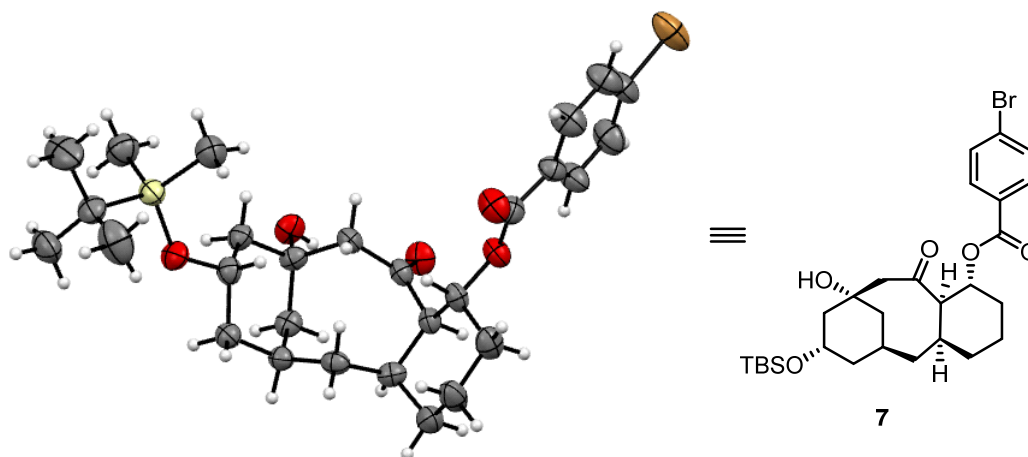
Perspective view of the molecular structure of **2c'** ($C_{14}H_{24}O_2Si$) with the atom labeling scheme. CCDC number: 1578167.

4) X-ray crystal structure of compound **2k**



Perspective view of the molecular structure of **2k** ($C_{13}H_{24}OSi$) with the atom labeling scheme. CCDC number: 1578170.

5) X-ray crystal structure of compound **7**



Perspective view of the molecular structure of **7** (C₂₈H₄₁BrO₅Si) with the atom labeling scheme. CCDC number: 1578168.

7. Computational Studies

7.1) Computational Methods

All calculations were performed with the Gaussian 09 software package.^[5] Geometry optimization and frequency calculations were carried out using the B3LYP functional^[6] with 6-31G(d) basis set. The keyword “5D” was used to specify that five d-type orbitals were used for all elements in the calculations. Single point energies were calculated with B3LYP, M06-2X^[7] functionals and 6-311+G(d,p) basis set, based on the gas-phase optimized structures. Solvation energies in dichloromethane using the B3LYP, M06-2X functionals with 6-311+G(d, p) basis set were evaluated by IEFPCM calculations with radii and non-electrostatic terms for SMD solvation model,^[8] also using the gas-phase optimized structures.

The relative free energies (in both the gas phase and solution) calculated with B3LYP and M06-2X functionals were presented in Scheme S1. These data gave the relative pref-

erence of the diax and dieq conformers and also gave the trends of the CM and RCM reactions. We found that M06-2X and B3LYP calculations predicted the same trends, suggesting that substrates in column III are better, compared to substrates in columns I and II, for RCM reactions (because the population of diax conformers increased with respect to the population of dieq conformers for substrates in column III). In both the gas phase and solution, the relative free energies of diax and dieq conformers in columns I and II are similar for both B3LYP and M06-2X calculations, while the relative free energies of diax conformers were overestimated in column III using B3LYP calculations, compared with those using M06-2X calculations. This means that, for substrates in column III, B3LYP calculations suggested that diax conformers are the dominant ones while M06-2X predicted that both diax and dieq conformers have similar populations. Since M06-2X has a good approximation of dispersion energy, we therefore chose M06-2X calculations to discuss the reaction trends in the present paper. We are also studying the detailed mechanisms of the CM and RCM reactions for substrates in column I & II of Scheme S1, finding that M06-2X is a good functional to explain the experimentally observed reaction selectivities (CM vs. RCM).

7.2) Conformational Analysis

Scheme S1. DFT computed energy differences between the diax and dieq conformers (Gas phase free energies in the first row were calculated at B3LYP/6-311+G(d, p)//B3LYP/6-31G(d) level, and solvation free energies in italics were calculated at the SMD(CH₂Cl₂)/B3LYP/6-311+G(d, p)//B3LYP/6-31G(d) level. Gas phase free energies in the parentheses were calculated at M06-2X/6-311+G(d, p)//B3LYP/6-31G(d) level, while solvation free energies in square brackets were calculated at the SMD(CH₂Cl₂)/M06-2X/6-311+G(d, p)//B3LYP/6-31G(d) level.)

ΔG diax-dieq (kcal/mol)		ΔG diax-dieq (kcal/mol)		ΔG diax-dieq (kcal/mol)	
 deTMS-1a (dieq) deTMS-1a (diax)		 1a (dieq) 1a (diax)		 oTMS-1a (dieq) oTMS-1a (diax)	
5.1 4.8 (4.2) [4.1]		0.3 -0.7 (1.9) [1.0]		-1.3 -2.3 (0.9) [-0.1]	
 deTMS-1b (dieq) deTMS-1b (diax)		 1b (dieq) 1b (diax)		 oTMS-1b (dieq) oTMS-1b (diax)	
5.2 4.7 (4.7) [4.3]		0.7 -0.7 (2.4) [1.1]		-2.3 -3.1 (1.3) [0.5]	
 deTMS-1c (dieq) deTMS-1c (diax)		 1c (dieq) 1c (diax)		 oTMS-1c (dieq) oTMS-1c (diax)	
5.2 4.9 (4.2) [4.0]		1.0 -0.3 (2.4) [1.1]		-3.4 -4.6 (1.0) [-0.2]	
 deTMS-1d (dieq) deTMS-1d (diax)		 1d (dieq) 1d (diax)		 oTMS-1d (dieq) oTMS-1d (diax)	
5.3 5.0 (4.7) [4.5]		0.5 -0.7 (2.1) [1.0]		-4.0 -5.1 (0.4) [-0.7]	
 deTMS-1n (dieq) deTMS-1n (diax)		 1n (dieq) 1n (diax)		 oTMS-1n (dieq) oTMS-1n (diax)	
5.0 4.6 (4.6) [4.3]		0.5 -0.8 (2.4) [1.2]		-1.6 -2.5 (2.1) [1.2]	

7.3) Computed Energy of All Species

Table S2. Sum of electronic and thermal enthalpies H , sum of electronic and thermal free energies G , thermal correction to enthalpy TCH , thermal correction to Gibbs free energy TCG , total free energy in dichloromethane with non-electrostatic terms $E_{B3LYP,sol}$, $E_{M06-2X,sol}$ respectively, reported in Hartree.

	H	G	TCH	TCG	$E_{B3LYP,sol}$	$E_{M06-2X,sol}$
oTMS-1a (di-ax)	-1400.611842	-1400.707077	0.562952	0.467717	-1401.499877	-1401.021663
oTMS-1a (dieq)	-1400.611451	-1400.705165	0.562804	0.469089	-1401.497624	-1401.022944
1a (di-ax)	-992.010085	-992.087781	0.452668	0.374972	-992.732364	-992.354835
1a (dieq)	-992.013773	-992.089763	0.452733	0.376743	-992.732997	-992.358192
deTMS-1a (di-ax)	-583.45473	-583.513761	0.343477	0.284446	-583.998945	-583.723259
deTMS-1a (dieq)	-583.462478	-583.521917	0.343224	0.283785	-584.00601	-583.729094
oTMS-1b (di-ax)	-1400.610842	-1400.706097	0.562838	0.467582	-1401.500245	-1401.022547
oTMS-1b (dieq)	-1400.610099	-1400.702868	0.562685	0.469915	-1401.497663	-1401.025697
1b (di-ax)	-992.010376	-992.087698	0.452849	0.375527	-992.733277	-992.35685
1b (dieq)	-992.015002	-992.090847	0.452749	0.376905	-992.733492	-992.359944
deTMS-1b (di-ax)	-583.455291	-583.514224	0.343467	0.284533	-583.999824	-583.72489
deTMS-1b (dieq)	-583.46359	-583.522934	0.343165	0.283821	-584.006672	-583.73105
oTMS-1c (di-ax)	-1400.610366	-1400.706752	0.562676	0.46629	-1401.499845	-1401.022436
oTMS-1c (dieq)	-1400.610184	-1400.702585	0.562916	0.470515	-1401.496684	-1401.02636
1c (di-ax)	-992.009594	-992.086914	0.452519	0.375199	-992.732999	-992.356889
1c (dieq)	-992.013881	-992.090283	0.452418	0.376015	-992.733391	-992.359522
deTMS-1c (di-ax)	-583.454394	-583.513471	0.343174	0.284098	-583.999511	-583.724963
deTMS-1c (dieq)	-583.462714	-583.52208	0.342898	0.283533	-584.006785	-583.730816
oTMS-1d (di-ax)	-1400.610628	-1400.708002	0.562606	0.465232	-1401.500741	-1401.02176
oTMS-1d (dieq)	-1400.61035	-1400.702486	0.563018	0.470881	-1401.49828	-1401.026261
1d (di-ax)	-992.009344	-992.08803	0.452663	0.373978	-992.733151	-992.355495
1d (dieq)	-992.013868	-992.090381	0.45266	0.376147	-992.734211	-992.359293
deTMS-1d (di-ax)	-583.454197	-583.513833	0.343329	0.283693	-583.999821	-583.723593
deTMS-1d (dieq)	-583.462442	-583.522368	0.343065	0.283139	-584.00726	-583.730231
oTMS-1n (di-ax)	-1206.623626	-1206.704041	0.461476	0.38106	-1207.347948	-1206.957221
oTMS-1n (dieq)	-1206.623731	-1206.70224	0.461309	0.3828	-1207.345628	-1206.96081
1n (di-ax)	-798.021527	-798.083771	0.351268	0.289024	-798.580109	-798.291819
1n (dieq)	-798.025961	-798.08647	0.35123	0.29072	-798.580535	-798.29539
deTMS-1n (di-ax)	-389.466357	-389.510262	0.241973	0.198068	-389.846829	-389.660276
deTMS-1n (dieq)	-389.474635	-389.51872	0.241601	0.197516	-389.853577	-389.666529

7.4) Computed Coordinates of All Species

1a (diat)

C	0.36539300	3.79003600	-1.62309000
H	0.68100200	4.65407500	-1.04480000
H	-0.06462400	3.97989000	-2.60272800
C	-0.75941400	0.66628400	1.24761100
C	0.03683100	1.98751000	1.31125400
C	1.09436600	2.20508200	0.20518900
C	1.99801500	0.94906700	0.09604500
C	1.22380700	-0.38051300	-0.04586800
C	0.21703800	-0.52797100	1.11788300
C	-1.88533000	0.65297000	0.18760100
H	-1.25997600	0.57263300	2.22326800
H	-0.64034000	2.84949700	1.32450000
H	0.59532800	2.00919100	2.25657800
O	1.87473900	3.30915200	0.68652300
H	2.69716300	1.08762900	-0.74088700
H	2.60220300	0.92834500	1.01308200
Si	2.38342900	-1.89524100	-0.21973100
H	0.65653000	-0.35396100	-0.99081300
H	-0.35215100	-1.46021500	1.01552400
H	0.77689600	-0.61465200	2.06062800
C	3.41780300	-2.13707300	1.35260800
C	1.34213000	-3.45146400	-0.52935700
C	3.54284600	-1.63448800	-1.69927300
H	-2.34740400	1.64915300	0.14639200
H	2.51031600	3.53129500	-0.01434300
H	4.08910300	-2.99816900	1.24572600
H	2.78687800	-2.32088900	2.23048300
H	4.04078200	-1.26115600	1.57016700
H	1.98563800	-4.32463800	-0.69382300

H	0.70718900	-3.34059300	-1.41722000
H	0.68770100	-3.68318300	0.31930800
H	4.17001500	-2.51965200	-1.86250700
H	4.21457800	-0.78121900	-1.54857700
H	2.98174500	-1.45517900	-2.62487700
H	-1.47333500	0.47498000	-0.81435800
C	0.48447000	2.55086000	-1.14225200
H	0.14808800	1.71313400	-1.75007800
C	-2.98161300	-0.38655300	0.46375000
H	-2.54354100	-1.39306300	0.51826100
H	-3.43054200	-0.19531900	1.44821200
C	-4.09386000	-0.38315200	-0.60364700
H	-4.55652400	0.61165900	-0.65294400
H	-3.63356100	-0.56254100	-1.58812500
C	-5.15286200	-1.42218700	-0.35259700
H	-4.80487400	-2.45695500	-0.32759800
C	-6.44715200	-1.17120500	-0.14993400
H	-6.84045700	-0.15630600	-0.16345000
H	-7.16454700	-1.96685200	0.03351900

1a (dieq)

C	3.73908400	-3.13909100	-0.68030300
H	4.34711400	-4.02656600	-0.52905400
H	3.97422800	-2.51887100	-1.54072300
C	-0.59818400	-0.83227300	0.18187100
C	0.38309400	-2.01773400	0.17908700
C	1.86338100	-1.59510400	0.02842100
C	2.22474500	-0.55264600	1.10525100
C	1.26765100	0.65929600	1.16747900
C	-0.19876800	0.17506900	1.27832000
C	-2.04671900	-1.33610600	0.33608400

H	-0.51603900	-0.33467400	-0.79245000	H	-4.69099700	-1.61158800	-0.56437000
H	0.27348400	-2.58262500	1.11674700	C	-5.62208400	0.21325900	0.05715900
H	0.12892300	-2.71941100	-0.62979400	H	-5.61297100	1.00502400	0.80904000
O	2.06963800	-0.94855000	-1.23534100	C	-6.53655500	0.25406000	-0.91303100
H	2.20617400	-1.07262200	2.07484600	H	-6.58296500	-0.51134900	-1.68565900
H	3.26116600	-0.23881700	0.94153000	H	-7.27536400	1.04900700	-0.97276500
Si	1.56226000	2.08951000	-0.09549800	1b (diac)			
H	1.50040700	1.17045300	2.11610300	C	-1.33767700	0.31977700	1.41467500
H	-0.34436800	-0.31595500	2.25575800	C	-0.46491600	1.56959600	1.67763400
H	-0.88145200	1.03413400	1.26957100	C	0.68563500	1.84005000	0.68921400
C	3.40842400	2.21857800	-0.50545100	C	1.50134900	0.54259600	0.47764600
C	0.56564600	1.99868300	-1.70675600	C	0.64722300	-0.68556300	0.09153700
C	1.02447500	3.67684500	0.80678700	C	-0.43882900	-0.91637200	1.16736300
H	-2.21408900	-2.14663500	-0.38918400	C	-2.41711600	0.50956100	0.32404800
H	1.82712800	-1.58364300	-1.92942100	Si	1.70495600	-2.24547200	-0.24656100
H	3.61186600	3.11414300	-1.10584200	C	2.63539000	-2.78393600	1.31634400
H	3.74097100	1.34537900	-1.07698700	C	0.57955200	-3.65891600	-0.82801900
H	4.02443200	2.28497100	0.40019300	C	2.95891300	-1.86742500	-1.62108400
H	0.76369500	2.88905200	-2.31764600	C	-3.60783500	-0.46286400	0.46210500
H	-0.51508100	1.96490300	-1.52359600	C	-4.67496700	-0.22340000	-0.57140100
H	0.84313700	1.11659400	-2.29039300	C	-5.08794700	-1.11260000	-1.47591500
H	1.13884800	4.55651000	0.16118100	C	0.18613400	2.46768500	-0.64777100
H	1.62267700	3.85082800	1.71002100	C	1.30637700	2.90016200	-1.55835500
H	-0.02856100	3.63297400	1.11329500	C	1.74243300	4.15813500	-1.68193200
H	-2.16839700	-1.79170500	1.33116900	H	-1.88722600	0.13998300	2.35130900
C	2.76088100	-2.81076000	0.16385400	H	-1.09233000	2.46709800	1.75509000
H	2.56071900	-3.44060100	1.03115700	H	0.01703500	1.44967400	2.65684100
C	-3.13018600	-0.26736200	0.13101900	H	2.29112300	0.72547700	-0.26273100
H	-3.02634400	0.52568300	0.88329600	H	2.01495900	0.34720500	1.42892600
H	-2.99173000	0.21593800	-0.84618200	H	0.14534900	-0.47463500	-0.86781000
C	-4.55900700	-0.84114200	0.20717400	H	-1.06484500	-1.77867700	0.90528800
H	-4.68061900	-1.34671900	1.17807600	H	0.05517000	-1.17562200	2.11526400

H	-2.80072800	1.53837600	0.37273700	C	-3.95465200	-0.06501800	-0.59502100
H	-1.99158900	0.39183500	-0.67993200	C	-1.65025300	-1.63761500	-1.93857600
H	3.25795700	-3.66417100	1.11331700	C	-3.31055700	-2.96143000	0.25887700
H	1.94883600	-3.04921200	2.12923800	C	3.42724900	-0.93476900	-0.56963700
H	3.29789600	-1.99251800	1.68677400	C	4.68759300	-1.75332400	-0.48816800
H	1.17026900	-4.54727100	-1.08395300	C	5.90232100	-1.27740200	-0.21045500
H	0.00874100	-3.37611300	-1.72131000	C	-0.23455400	3.01236700	0.87897300
H	-0.13977600	-3.95630300	-0.05575800	C	0.65133300	3.81454400	-0.03731700
H	3.53455200	-2.76468300	-1.88025100	C	0.20823400	4.56380200	-1.05255600
H	3.67692100	-1.09450500	-1.32195500	H	0.65750200	-0.83134800	-0.72819600
H	2.46141700	-1.52268500	-2.53637100	H	1.46586000	0.97992800	1.59270700
H	-3.26262800	-1.50240800	0.39508500	H	1.74505300	1.29463700	-0.11869300
H	-4.04043700	-0.34047200	1.46753700	H	-1.00367200	0.97077400	2.44361600
H	-5.12392600	0.77200200	-0.56556100	H	-2.30587900	1.29128500	1.30096300
H	-4.66982800	-2.11664400	-1.52216900	H	-2.01777600	-1.11711300	2.02654800
H	-5.86150200	-0.87591700	-2.20181700	H	0.33205300	-1.30347200	2.27045000
H	-0.45773100	1.75898300	-1.17835200	H	-0.09944200	-2.44256100	1.00505200
H	-0.42948100	3.33697800	-0.38797500	H	2.75318500	-1.22421700	1.46969500
H	1.80394900	2.11665700	-2.13082500	H	2.22222500	-2.47006500	0.35187800
H	2.56657100	4.41815900	-2.34137800	H	-4.66384000	-0.44304800	-1.34203000
H	1.27244600	4.97871400	-1.14294700	H	-3.55029200	0.88520800	-0.95898400
O	1.50334700	2.81043700	1.35584300	H	-4.52188900	0.13557200	0.32276800
H	2.12037200	3.16490200	0.69226200	H	-2.36286300	-2.00446200	-2.68875800
1b (dieq)				H	-0.87143500	-2.40239700	-1.83082400
C	0.99027600	-0.70107900	0.30908500	H	-1.18686200	-0.72506800	-2.32376200
C	1.05451800	0.81271100	0.58493300	H	-3.94583700	-3.39267800	-0.52492100
C	-0.32250700	1.50634900	0.49166700	H	-3.93111600	-2.83958400	1.15565300
C	-1.33192800	0.79903000	1.40672100	H	-2.53607000	-3.70284600	0.49409700
C	-1.44872400	-0.72395600	1.16831200	H	2.99829800	-1.02775600	-1.57997200
C	-0.04435000	-1.36944700	1.23566100	H	3.67391800	0.12468700	-0.42957400
C	2.36386400	-1.38402100	0.45374600	H	4.56734700	-2.82453100	-0.66289700
Si	-2.55319900	-1.30732100	-0.30354200	H	6.07268300	-0.21811100	-0.02610200

H	6.77428900	-1.92427000	-0.15947000	H	-4.03269100	-0.49949900	1.70725400
H	-1.25365600	3.41678600	0.85116800	H	-3.56726500	-2.15460800	1.28849800
H	0.12433000	3.09285400	1.91324600	H	-4.76509100	0.81524200	-1.61774100
H	1.72637500	3.74057500	0.12823900	H	-3.17448200	1.44935000	-2.06078300
H	0.88753200	5.10611400	-1.70525200	H	-3.84924100	1.79013500	-0.46191000
H	-0.85557100	4.68218400	-1.25045500	H	-3.93649100	-2.04936100	-2.33319800
O	-0.84321600	1.40624500	-0.84109700	H	-2.52358400	-2.82320400	-1.60833800
H	-0.33110300	2.02100900	-1.39528900	H	-2.31151300	-1.53219800	-2.80060300
1c (diac)				H	1.81954700	-2.02536400	-0.92904800
C	0.36421700	1.27320900	1.47469500	H	1.57503100	-0.29844700	-1.03942700
C	1.13869800	-0.00476400	1.87016200	C	0.52314700	3.55421400	0.34919300
C	1.05680700	-1.19502400	0.89290100	H	0.50375400	4.11584300	1.28580500
C	-0.42010800	-1.44142200	0.50541100	C	0.05304400	4.13175200	-0.75809800
C	-1.16156200	-0.18837600	-0.01124200	H	0.05197000	3.61456800	-1.71591900
C	-1.08256800	0.92881700	1.05360400	H	-0.34065200	5.14485700	-0.75423300
C	1.09497400	2.16437600	0.43607800	C	3.44580600	-0.86610500	-0.10297100
Si	-2.95456500	-0.56444300	-0.56809200	H	3.75711500	-1.57913900	0.67270300
C	-3.98247200	-1.22328200	0.88492300	H	3.62126100	0.13874200	0.29889400
C	-3.75691700	1.01975900	-1.23633300	C	4.27875200	-1.05870900	-1.34101000
C	-2.92456500	-1.86253700	-1.95278400	H	4.22685700	-2.04976800	-1.79735900
C	1.94358500	-1.08320500	-0.37046500	C	5.04542100	-0.12762300	-1.91095300
H	0.30066400	1.88004600	2.39082100	H	5.12914700	0.87547600	-1.49666600
H	2.18734300	0.23361500	2.08375800	H	5.62284800	-0.33088200	-2.80906900
H	0.71752000	-0.37835100	2.81223500	O	1.52724300	-2.31323600	1.67288500
H	-0.45789500	-2.25476600	-0.23484600	H	1.45371000	-3.10438900	1.11359400
H	-0.92201800	-1.81561900	1.40853800	1c (dieq)			
H	-0.65178300	0.16597700	-0.92205800	C	1.32473000	1.43681200	0.22301700
H	-1.57830300	1.83952700	0.69713700	C	-0.19364100	1.64271700	0.34091000
H	-1.63164000	0.60276000	1.94919500	C	-1.00753000	0.33791600	0.21155100
H	2.15202000	2.23518500	0.73516000	C	-0.48718500	-0.70349100	1.21452000
H	1.08439600	1.70880600	-0.56039900	C	1.03896900	-0.95117000	1.15090800
H	-5.01211100	-1.43291900	0.56954500	C	1.80088400	0.39192900	1.24825500

C	2.09506700	2.76789000	0.38834200	C	-3.46231600	-0.55008400	0.23034800
Si	1.68515400	-2.15571000	-0.21145800	H	-3.25678500	-1.03228100	-0.73175700
C	0.37488900	-3.46812700	-0.60197900	H	-3.25827400	-1.29785700	1.00978100
C	2.27130600	-1.35147300	-1.82655700	C	-4.90939500	-0.14352600	0.30782800
C	3.19912800	-3.01667200	0.55791100	H	-5.22738400	0.31006800	1.24899900
C	-2.50923500	0.64729400	0.41253700	C	-5.80173200	-0.28459700	-0.67370300
H	1.53406000	1.05176000	-0.78267200	H	-6.83485300	0.03366400	-0.56056800
H	-0.41956900	2.09960900	1.31618400	H	-5.53281600	-0.73075600	-1.62949800
H	-0.53777300	2.36232200	-0.41586700	O	-0.81035600	-0.23958300	-1.09574900
H	-0.74648200	-0.33592000	2.21924300	H	-1.05632100	0.43104100	-1.75386300
H	-1.03235100	-1.64289000	1.07620100	1d (diac)			
H	1.28425100	-1.51857100	2.06345200	C	1.18366400	2.44239600	0.08774600
H	1.66094300	0.81540600	2.25715500	C	0.17671800	2.33935900	-1.09175600
H	2.88301200	0.23472800	1.13663000	C	-0.60421800	1.01245200	-1.24019100
H	1.84918400	3.21951300	1.35967500	C	0.37980100	-0.17069500	-1.16877300
H	3.17111800	2.53545200	0.41454400	C	1.29402700	-0.14501800	0.07512100
H	0.78296100	-4.23843900	-1.26837900	C	2.08530000	1.18192800	0.11841300
H	-0.49044900	-3.01544600	-1.09737500	Si	2.43036900	-1.68380900	0.18551500
H	0.02015900	-3.97527400	0.30417600	C	3.66528800	-1.70928900	-1.25511900
H	2.68580600	-2.11868000	-2.49329800	C	3.37920900	-1.64210800	1.82845600
H	3.06160200	-0.61026100	-1.65598000	C	1.37283800	-3.25789000	0.12999100
H	1.44475600	-0.85965800	-2.34722800	C	-1.77716600	0.90779900	-0.23605000
H	3.66087600	-3.71616300	-0.15013700	H	1.82313500	3.30750900	-0.13651600
H	2.92789100	-3.58734700	1.45502600	H	-0.52828600	3.18190900	-1.04771700
H	3.97149300	-2.29366400	0.85057700	H	0.74837400	2.45209500	-2.02245600
H	-2.65235600	1.08818800	1.40878200	H	-0.18165800	-1.10881000	-1.23412300
H	-2.79269400	1.43115400	-0.30634400	H	0.99453500	-0.11895100	-2.07784700
C	1.83973100	3.76059300	-0.71375200	H	0.65796900	-0.19921600	0.97440500
H	2.09836400	3.42364000	-1.72006700	H	2.72890700	1.22485100	1.00611800
C	1.33456600	4.98547000	-0.55526800	H	2.75414200	1.22312500	-0.75361800
H	1.06227400	5.36828100	0.42657700	H	4.30728300	-2.59720000	-1.20000000
H	1.18064200	5.65610200	-1.39677700	H	4.32102600	-0.83033600	-1.24721100

H	3.15528900	-1.73369800	-2.22568300	C	1.29857900	-0.58502900	1.15711000
H	4.01463200	-2.53010200	1.93483800	Si	1.91167800	-1.93689100	-0.07619400
H	2.69570500	-1.62358500	2.68645800	C	0.50631100	-3.14784200	-0.46455100
H	4.03008800	-0.76312900	1.90517400	C	2.67293000	-1.31212600	-1.69745700
H	1.99529400	-4.14938500	0.27647000	C	3.28397700	-2.87688000	0.85016200
H	0.85848100	-3.37242600	-0.83128800	C	-2.01822200	1.27893600	0.05722000
H	0.60854800	-3.25905800	0.91717500	H	2.12747200	1.22976300	-0.86232700
H	-1.39985900	0.93552400	0.79197500	H	0.13376400	2.60198700	1.00785900
H	-2.38561500	1.81987100	-0.34678600	H	0.16835200	2.73522000	-0.74433100
C	-2.68483900	-0.31842500	-0.41014400	H	-0.48473800	0.27090000	2.05024800
H	-2.97638800	-0.40339000	-1.46380400	H	-0.82276700	-1.08047800	0.97594100
H	-2.13586300	-1.23651800	-0.16606200	H	1.42593400	-1.10795000	2.11889800
C	-3.94313800	-0.25098200	0.47755900	H	0.87582000	-3.99514500	-1.05572700
H	-3.65250500	-0.16452100	1.53340000	H	-0.28430200	-2.65357100	-1.03878300
H	-4.49821300	0.66813100	0.23135600	H	0.05677400	-3.55765800	0.44872000
C	0.55519200	2.72087700	1.43428000	H	3.04554200	-2.16381300	-2.28129400
H	0.09588500	1.88008200	1.95335000	H	3.52324700	-0.64190200	-1.52297700
C	0.55116900	3.91264100	2.03486700	H	1.93423900	-0.78125400	-2.30439700
H	1.00637800	4.78778700	1.57389400	H	3.71829900	-3.66465100	0.22194500
H	0.09310200	4.06277100	3.00913100	H	2.90389400	-3.35515400	1.76168400
C	-4.84603500	-1.44140600	0.29790900	H	4.10320600	-2.20951300	1.14706200
H	-5.22578000	-1.59826600	-0.71370100	H	-2.18024600	1.81200900	1.00446200
C	-5.18880800	-2.30205300	1.25757800	H	-2.17039800	2.02843000	-0.73675300
H	-5.83975300	-3.15033400	1.06241400	C	-3.06801000	0.17115800	-0.10008100
H	-4.83256400	-2.18878400	2.27997000	H	-2.83289900	-0.42007400	-0.99384400
O	-1.13940800	0.95776900	-2.57811100	H	-3.02317000	-0.51985700	0.75050100
H	-1.73620800	1.71770900	-2.68094200	C	-4.50183700	0.72727900	-0.20601500
1d (dieq)				H	-4.73842600	1.32215400	0.68663400
C	1.88452200	1.69582400	0.09887200	H	-4.54805600	1.41857100	-1.06247800
C	0.38251300	2.05009500	0.08956400	C	-5.53435300	-0.35346400	-0.38077000
C	-0.54309000	0.81937100	-0.01165600	H	-5.41782300	-0.98071400	-1.26679000
C	-0.19616700	-0.19054100	1.09333100	C	-6.54107100	-0.59998200	0.45880900

H	-6.69449400	-0.00307900	1.35611000	H	0.07588200	1.13117500	-1.74636600
H	-7.25204200	-1.40305600	0.28306200	H	-3.07695500	2.53824900	0.84117800
C	2.72470900	2.93770500	0.24880700	H	-1.64917600	1.87276100	1.64210500
H	2.58332300	3.49333800	1.17914000	H	3.82648200	-0.70877900	-1.78186400
C	3.60317200	3.38981400	-0.64770900	H	2.49080100	0.25726600	-2.42065300
H	3.77943400	2.86981800	-1.58767800	H	2.25201000	-1.46045000	-2.06748700
H	4.18205300	4.29422100	-0.47886000	H	4.22525600	1.31181200	0.60097200
C	2.18049900	0.68390800	1.22908900	H	2.85221000	1.76409200	1.61907600
H	2.00719700	1.19118600	2.19291300	H	2.92715900	2.31089300	-0.06256700
H	3.24764300	0.42629200	1.21324900	H	3.82693000	-1.65309700	1.23027600
O	-0.31213400	0.13228700	-1.25834000	H	2.30237300	-2.48635600	0.90569900
H	-0.44002300	0.77280800	-1.97710300	H	2.41551600	-1.33906400	2.24842600
1n (diac)				H	-1.91483600	-0.17737800	2.05935300
C	-1.65362100	1.63967500	-0.55480800	H	-3.49626800	-0.77939900	1.55521400
C	-2.45911400	0.33817100	-0.78176600	O	-2.55810400	-2.08080200	-0.65647600
C	-1.98972500	-0.92144700	-0.01630500	H	-3.52286500	-2.01857100	-0.56260400
C	-0.46821500	-1.09767100	-0.17691800	H	-1.52383900	3.38257600	0.74031400
C	0.34373400	0.16828200	0.17398700	H	-2.17888900	-1.92317000	1.88857200
C	-0.13994400	1.35493600	-0.69108300	1n (dieq)			
C	-1.99448000	2.39181000	0.74275300	C	-1.40124300	1.44915800	-0.22715100
Si	2.23434200	-0.11220200	0.05880400	C	-2.34173400	0.23929500	-0.09863000
C	2.74365700	-0.54500300	-1.71700000	C	-1.59869300	-1.10630400	0.02004100
C	3.13895800	1.46569600	0.60294200	C	-0.58091700	-1.04582300	1.16942200
C	2.73693700	-1.52915100	1.21676300	C	0.39820500	0.14930900	1.09771200
C	-2.41438200	-0.94315000	1.45980200	C	-0.39627100	1.46887700	0.94031700
H	-1.93281200	2.31542200	-1.37652800	C	-2.19255400	2.76063000	-0.30676300
H	-3.52583600	0.51617500	-0.57560000	Si	1.93075700	-0.02972500	-0.06009900
H	-2.38786200	0.07707100	-1.84570500	C	2.45154900	-1.84864800	-0.17726000
H	-0.15289700	-1.95753200	0.42732000	C	1.73966000	0.68611900	-1.80584900
H	-0.29021000	-1.37231000	-1.22576800	C	3.32423300	0.94802700	0.79359800
H	0.15884200	0.41537500	1.23261300	C	-2.58622700	-2.26282600	0.22332200
H	0.42019000	2.26758300	-0.44763200	H	-0.83973200	1.33226800	-1.16161800

H	-2.97973600	0.36678500	0.78881200	C	-1.43094100	-1.73045400	1.16146000
H	-3.02542900	0.19962500	-0.96148200	C	-0.48403000	-2.04495700	-0.00732000
H	-1.15775100	-0.97689600	2.10418900	C	0.88330500	0.13854000	-0.19336700
H	-0.03997000	-1.99871500	1.20777900	H	0.31891000	-1.15499700	-1.79064100
H	0.88645600	0.19300400	2.08492300	H	-1.23542400	0.83139300	-1.83416700
H	-0.96091700	1.66115600	1.86839600	H	-1.98575700	-0.75365900	-1.99638000
H	0.28467200	2.32360000	0.82272100	O	-3.67435000	0.55969200	-0.88143800
H	-2.77401000	2.92884100	0.60944300	H	-3.38498500	-0.82648600	1.51221200
H	-1.52376900	3.62006800	-0.43750000	H	-3.26970300	-1.76278400	0.01993800
H	3.39508500	-1.94880600	-0.72838700	H	-0.92685300	-1.08577400	1.89399900
H	1.68890200	-2.43556700	-0.70011100	H	0.43583000	-2.51058400	0.36784000
H	2.60358000	-2.29527000	0.81356400	H	-0.96574500	-2.79279900	-0.65340200
H	2.68316900	0.58271400	-2.35735700	H	0.83484600	1.12372600	-0.67751600
H	1.48964200	1.75396500	-1.78902300	H	-4.32969900	0.82534900	-0.21477200
H	0.95946100	0.15903300	-2.36193700	H	0.62805400	0.31244400	0.86013900
H	4.24498500	0.92977900	0.19720600	C	-2.04615000	1.36954100	0.71605500
H	3.56336100	0.53305300	1.78091900	H	-1.34195300	1.13111700	1.51072600
H	3.05070200	2.00123500	0.93813700	C	2.32811300	-0.37714300	-0.27103800
H	-3.16662300	-2.14030700	1.14487500	H	2.40172500	-1.36789100	0.19917000
H	-3.29767900	-2.31621100	-0.61189900	H	2.61311900	-0.51645300	-1.32297400
O	-0.82816200	-1.35757300	-1.17275800	C	3.33920900	0.57300400	0.40033900
H	-1.44141400	-1.36093100	-1.92539800	H	3.29163400	1.56062900	-0.07751300
H	-2.04882300	-3.21581700	0.27378900	H	3.03801700	0.71887200	1.44970400
H	-2.89551200	2.75322900	-1.14914000	C	4.75173100	0.05623700	0.35524200
deTMS-1a (diac)				H	4.92035100	-0.90521000	0.84482900
C	-2.49061700	2.62208700	0.59716300	C	5.77856700	0.66753900	-0.23730900
H	-3.18628900	2.90346100	-0.18855900	H	5.65971600	1.62581700	-0.73981100
H	-2.16123500	3.40751700	1.27184400	H	6.77726900	0.23867100	-0.24143900
C	-0.14948300	-0.79982100	-0.86077800	H	-1.67890900	-2.65519400	1.69754500
C	-1.45595000	-0.09656200	-1.29400400	deTMS-1a (dieq)			
C	-2.47630400	0.21441900	-0.17285100	C	4.69334200	-1.54345800	-0.09621600
C	-2.72380300	-1.06321300	0.66652800	H	5.48506200	-2.08669900	0.41210200

H	4.75727900	-1.47171700	-1.17847500	H	-6.94712700	-0.14085900	-1.11319200
C	-0.00884300	0.10957800	0.00673600	H	1.48446500	2.07644300	-1.37208500
C	1.20333000	-0.69037000	0.51940400	deTMS-1b (diiax)			
C	2.55476900	-0.19437700	-0.05234300	C	-0.85414700	-1.12631500	0.69299900
C	2.72028900	1.31549100	0.22173900	C	0.55139800	-0.90302700	1.30387400
C	1.51903300	2.12964900	-0.27748100	C	1.66459500	-0.40974700	0.35606000
C	0.19562900	1.60774500	0.30175500	C	1.67031700	-1.27118400	-0.92608400
C	-1.31643700	-0.45184000	0.59637300	C	0.28984400	-1.39146100	-1.58939700
H	-0.04454600	-0.01522300	-1.08543500	C	-0.74323900	-1.95958400	-0.60428900
H	1.24037800	-0.63362400	1.61753600	C	-1.68624400	0.16515500	0.51408500
H	1.08555300	-1.75655400	0.27367600	C	-3.20701100	-0.08739100	0.44187100
O	2.56370200	-0.32788600	-1.47921900	C	-3.99992000	1.18642700	0.32502500
H	2.84551700	1.45888200	1.30386700	C	-4.80395000	1.50548100	-0.69039600
H	3.64695400	1.65048000	-0.25755400	C	1.55706400	1.11808000	0.06143700
H	1.65555400	3.18611500	-0.01311900	C	2.72593300	1.65725100	-0.72238000
H	0.18609500	1.75948500	1.39329900	C	3.76598400	2.30428500	-0.18606200
H	-0.63852200	2.19472300	-0.10116900	H	-1.40169000	-1.73495000	1.42828500
H	-1.32158200	-1.54381400	0.46036500	H	0.48965500	-0.22786600	2.16720600
H	2.43862500	-1.27035400	-1.67916100	H	0.90956600	-1.86470900	1.69381200
H	-1.32500500	-0.28380400	1.68456200	H	2.41296000	-0.88665400	-1.63734600
C	3.69638400	-0.96889300	0.57700500	H	2.01592100	-2.27038200	-0.63000400
H	3.66758700	-1.03775000	1.66514200	H	-0.04077100	-0.41308600	-1.96525900
C	-2.60257100	0.12115300	-0.01623900	H	-1.72374300	-2.04520200	-1.08917000
H	-2.65379100	1.20442800	0.15638300	H	-0.44132900	-2.98293000	-0.33909100
H	-2.58444100	-0.01553600	-1.10641700	H	-1.48477200	0.84031700	1.35753200
C	-3.87726400	-0.53596000	0.54934300	H	-1.38566400	0.71008600	-0.38890200
H	-3.87808900	-0.41155300	1.64365700	H	-3.44560900	-0.74416000	-0.40411500
H	-3.85210500	-1.61726500	0.35855900	H	-3.51306400	-0.62542700	1.35273000
C	-5.14128600	0.04921900	-0.01993700	H	-3.87876500	1.89622100	1.14598900
H	-5.29134500	1.11607500	0.15804400	H	-4.95557000	0.83239500	-1.53242200
C	-6.05586100	-0.62324000	-0.72036100	H	-5.34526300	2.44753700	-0.71977900
H	-5.94921400	-1.68696900	-0.92551100	H	0.62922900	1.33354200	-0.47812800

H	1.49925700	1.63089400	1.02872200	H	-3.25070600	-0.17167000	-1.31975500
H	2.72235200	1.47629500	-1.79767900	H	-4.77665400	-0.49710800	1.35389800
H	4.59563600	2.65954600	-0.79199000	H	-5.15001000	-1.73191800	-1.43886300
H	3.81261900	2.52263100	0.87926200	H	-6.18445900	-2.01427000	0.06847300
O	2.87534500	-0.63489400	1.08866400	H	3.92358200	0.25119000	0.36392500
H	3.58296500	-0.15930800	0.61992800	H	2.97676700	-0.09479400	1.81921300
H	0.35957100	-2.04345800	-2.46935800	H	2.59233300	-2.43376600	1.08464800
deTMS-1b (dieq)				H	4.07546400	-3.35525900	-0.61289800
C	-0.77858300	0.33854300	-0.06226000	H	4.65264800	-1.65471400	-1.06044600
C	0.48026400	-0.29439600	0.56199600	O	1.90962500	0.13267300	-1.37371800
C	1.79537800	0.32806600	0.04078600	H	2.11280100	-0.80871300	-1.51259200
C	1.77343500	1.85036200	0.25367100	H	0.57625900	2.39340400	-1.45400700
C	0.52940800	2.50306200	-0.36390400	deTMS-1c (diac)			
C	-0.76488900	1.86250400	0.15968400	C	-1.57250600	-0.29402400	0.88188600
C	-2.04844400	-0.34269300	0.48144400	C	-0.24226300	-0.97804600	1.27924400
C	-3.35241500	0.04191800	-0.24719500	C	0.68547800	-1.42214100	0.12746100
C	-4.55384800	-0.68021100	0.30063500	C	-0.13637100	-2.20529800	-0.91951100
C	-5.33279600	-1.51621100	-0.38766200	C	-1.39794700	-1.46572200	-1.39069900
C	3.04375600	-0.28510700	0.73988100	C	-2.30348500	-1.11717400	-0.20009700
C	3.20646900	-1.76054400	0.48609700	C	-1.42760300	1.20342100	0.50176000
C	4.01049500	-2.28308200	-0.44600900	C	1.49784200	-0.29039100	-0.54772900
H	-0.72701900	0.15621700	-1.14547600	H	-2.19878600	-0.31052100	1.78640200
H	0.44087100	-0.18153900	1.65662300	H	0.31470800	-0.35083600	1.98490600
H	0.48260800	-1.37436800	0.35985300	H	-0.48538000	-1.89990800	1.82255300
H	1.79920600	2.05127300	1.33414300	H	0.50577400	-2.45817500	-1.77643200
H	2.68569300	2.27842400	-0.17939800	H	-0.42934500	-3.15511500	-0.45200900
H	0.53125700	3.57963400	-0.15022200	H	-1.12272100	-0.55455100	-1.93854000
H	-0.86618500	2.06654400	1.23798500	H	-3.19304800	-0.57487000	-0.54169800
H	-1.62899100	2.33050800	-0.32767600	H	-2.65867500	-2.05414200	0.25240300
H	-1.92618800	-1.43263800	0.41167800	H	-0.76915300	1.67919800	1.24464800
H	-2.15134200	-0.11669000	1.55407300	H	-0.93633900	1.32336600	-0.47007800
H	-3.51431100	1.12560600	-0.15644400	H	2.14883000	-0.77190100	-1.29557100

H	0.84264300	0.37546600	-1.11929300	H	-2.13929100	0.84192900	1.60962900
C	-2.74339100	1.93466900	0.48342300	H	-3.16930300	1.26624900	0.24775900
H	-3.30843100	1.91227500	1.41789000	H	-1.98862700	-2.29218900	-0.43646800
C	-3.25357700	2.58682300	-0.56297400	H	-2.49000000	-1.64339700	1.12485400
H	-2.72911100	2.63807700	-1.51545500	H	2.80815300	1.42474400	0.16639800
H	-4.20957200	3.10106600	-0.50799300	H	2.24777100	0.34102600	1.42750700
C	2.37817500	0.54539600	0.40187800	C	-3.88635600	-1.32023200	-0.46749400
H	2.91736000	-0.14970800	1.05979700	H	-3.98322100	-1.13486100	-1.53939200
H	1.75443300	1.17633800	1.04587800	C	-4.99263200	-1.42907800	0.27040000
C	3.35739800	1.41054900	-0.34422200	H	-4.94844300	-1.61293800	1.34230800
H	4.07326100	0.87924800	-0.97541700	H	-5.98437100	-1.34479800	-0.16650000
C	3.40303900	2.74304900	-0.30105900	C	2.93780400	-0.66874500	-0.36699000
H	2.71004900	3.31902100	0.30952700	H	2.78133000	-0.55320700	-1.44837100
H	4.13565200	3.31059400	-0.86896700	H	2.47789600	-1.62164800	-0.07941400
O	1.61496500	-2.32197500	0.76448700	C	4.41056400	-0.71541500	-0.06306700
H	2.19640500	-2.67301900	0.06969800	H	4.98458200	0.16449700	-0.36192500
H	-1.94702100	-2.09276600	-2.10431000	C	5.04390400	-1.72277000	0.53991200
deTMS-1c (dieq)				H	4.51593200	-2.61965800	0.85892000
C	-1.61445100	-0.17668900	-0.22536900	H	6.11289600	-1.69453600	0.73425000
C	-0.13846800	-0.44598900	0.12284200	O	0.74941400	0.99289400	-1.53776900
C	0.77788600	0.76819600	-0.11461900	H	1.25085900	1.80583600	-1.71391100
C	0.21694500	2.00495100	0.62103300	H	-1.31356000	2.55963800	-0.79623900
C	-1.24839900	2.28798100	0.26503200	deTMS-1d (diax)			
C	-2.12996600	1.06015700	0.52941900	C	-2.74748800	0.31433800	0.09280900
C	-2.47606000	-1.43062400	0.04637700	C	-1.85788900	-0.50436100	1.07237800
C	2.23055400	0.50285500	0.34170100	C	-0.48869600	-1.00242800	0.54689700
H	-1.66044700	0.04052500	-1.30188400	C	-0.68483500	-1.68325100	-0.81897100
H	-0.05827200	-0.73703700	1.18060200	C	-1.45837000	-0.81259900	-1.81957800
H	0.22813500	-1.29125000	-0.47121900	C	-2.83713900	-0.41932700	-1.26738100
H	0.30909300	1.84296200	1.70445800	C	0.57712500	0.11994900	0.53652600
H	0.84659000	2.87697700	0.38707500	H	-3.75180300	0.32695000	0.53773600
H	-1.61096800	3.15039200	0.83865800	H	-1.71137200	0.06879800	1.99887100

H	-2.41625200	-1.40967800	1.34421400	C	2.56310600	-1.94326800	-0.18045600
H	0.28439300	-1.98677200	-1.22890600	C	3.22764100	-0.64829300	0.30592000
H	-1.24623400	-2.60873600	-0.63492300	C	-1.16242200	-0.96625700	0.49664600
H	-0.87893400	0.08700900	-2.06951100	H	2.39556400	0.64664500	-1.20365900
H	-3.37918200	0.20338000	-1.98985000	H	0.92659400	0.50603100	1.47719200
H	-3.43170000	-1.33388500	-1.13065400	H	0.38152300	1.33563500	0.01746300
H	0.26475700	0.93463600	-0.12590800	H	1.10922000	-2.13761600	1.41497100
H	0.59870000	0.55917900	1.54702100	H	0.64046900	-2.95975700	-0.06772100
C	1.99649300	-0.32686700	0.15904900	H	3.13779200	-2.81533800	0.15641500
H	2.26009400	-1.21607700	0.74400000	H	3.31675900	-0.67238500	1.40352900
H	2.03361500	-0.62798400	-0.89531700	H	4.24846000	-0.56907600	-0.08781000
C	3.04418300	0.78036000	0.38889300	H	-1.56714900	-1.93086400	0.14878700
H	2.78393900	1.67095200	-0.19933100	H	-1.09502300	-1.04917600	1.59083600
H	3.00707800	1.08450600	1.44704200	C	-2.14721700	0.14821900	0.11938300
C	-2.33976800	1.76133700	-0.07091000	H	-2.12885700	0.29568000	-0.96647700
H	-1.48936200	1.96928300	-0.71973000	H	-1.82743900	1.09870800	0.56648600
C	-2.96503100	2.79177500	0.50168500	C	-3.58749100	-0.15852300	0.57493300
H	-3.82962400	2.64937100	1.14805900	H	-3.58251200	-0.33694500	1.66195100
H	-2.63972900	3.81752400	0.34848200	H	-3.93446900	-1.09077500	0.10875200
C	4.44161300	0.33949200	0.04649700	C	3.04346300	1.86079700	0.42025500
H	4.81685000	-0.51930600	0.60666400	H	3.12782100	1.92572800	1.50806000
C	5.22212400	0.89909300	-0.87914300	C	3.49130100	2.87265100	-0.32469200
H	6.22267200	0.52878400	-1.08683900	H	3.42786100	2.85322500	-1.41108900
H	4.88989300	1.75481900	-1.46427500	H	3.93718700	3.75900600	0.11946000
O	-0.03575600	-2.05762200	1.41828700	C	-4.55101200	0.95306500	0.25751500
H	0.06584200	-1.67529400	2.30582700	H	-4.32499700	1.91987900	0.71180100
H	-1.58152200	-1.36155100	-2.76146900	C	-5.62166000	0.84423700	-0.53045600
deTMS-1d (dieq)				H	-5.88560800	-0.09771200	-1.00800700
C	2.41440300	0.59762500	-0.10764300	H	-6.27725000	1.68829800	-0.72810000
C	0.95182200	0.47336000	0.37813100	O	0.19825600	-0.72862600	-1.51972500
C	0.26271600	-0.82400600	-0.08365900	H	-0.18566000	-1.55764000	-1.84932500
C	1.11667000	-2.04628600	0.31940700	H	2.56573700	-1.96246000	-1.27742400

deTMS-1n (diac)				C	-1.48365800	1.11514900	0.22758100
C	1.42710300	-0.48824700	0.63774100	C	-2.68149900	-1.12211100	0.05581900
C	-0.06072300	-0.76004100	0.97183400	C	2.34598700	-0.98334600	0.65360800
C	-1.12365000	-0.11905800	0.04528500	H	-1.29587300	-0.30605400	-1.37034600
C	-0.80145300	1.36954400	-0.16805300	H	-0.26574200	-1.14401400	1.37892900
C	0.64915300	1.61479000	-0.60801300	H	-0.07110200	-2.04651000	-0.12709300
C	1.64477800	1.02245200	0.40144500	H	0.98421100	1.18478600	1.59433900
C	1.99976700	-1.34884400	-0.50179900	H	1.95353900	1.72684000	0.22937200
C	-1.31068400	-0.86129200	-1.28723400	H	-0.26243900	2.91445000	0.32311800
H	1.99364400	-0.76484500	1.53855600	H	-1.65655200	1.10803400	1.31586400
H	-0.23747300	-1.84461500	1.03497200	H	-2.34933500	1.62145000	-0.22025000
H	-0.26202400	-0.35346900	1.97141000	H	-2.63008900	-2.14812100	-0.32872800
H	-1.51000900	1.79352600	-0.89038900	H	-2.83698800	-1.18114600	1.14147900
H	-0.98305200	1.88025400	0.78706600	H	3.28117300	-0.45461000	0.42393500
H	0.82136400	1.18687600	-1.60488300	H	2.24814900	-1.02358600	1.74477000
H	2.67664600	1.20406000	0.07273100	O	1.30024700	-0.30281600	-1.42657400
H	1.52449500	1.55116300	1.35813700	H	2.11057700	0.18658000	-1.64231400
H	1.78713200	-2.41240700	-0.33858700	H	-0.08063700	1.98720400	-1.16661300
H	1.59965900	-1.08019400	-1.48427400	H	2.43244400	-2.00687000	0.27345900
H	-2.17059200	-0.43837800	-1.81757400	H	-3.56777000	-0.64542900	-0.38058500
H	-0.43772500	-0.79488800	-1.94238900	oTMS-1a (diac)			
O	-2.38874400	-0.12320100	0.73435000	C	1.31325100	-0.72046700	1.33746500
H	-2.64128700	-1.05129500	0.86901600	C	-0.13938500	-1.24220600	1.39561900
H	0.82206300	2.69352100	-0.70970400	C	-1.09688200	-0.74439900	0.28595100
H	-1.50772900	-1.92761000	-1.11275300	C	-1.00969000	0.79294700	0.18598500
H	3.08908700	-1.23192100	-0.55337700	C	0.43127400	1.33871600	0.05046300
deTMS-1n (dieq)				C	1.30236100	0.82165900	1.21716600
C	-1.40784900	-0.33682700	-0.27809700	C	2.18207200	-1.42859100	0.27439100
C	-0.15842100	-1.03475800	0.28961900	O	-2.40834300	-1.10747700	0.76712700
C	1.14940900	-0.27548700	0.00552700	Si	0.47827800	3.24487600	-0.12626300
C	1.03433100	1.18341600	0.49594700	C	-0.24314500	4.08585300	1.41430800
C	-0.19755600	1.89555100	-0.07946100	C	2.27360000	3.81073400	-0.36901600

C	-0.53062300	3.76156500	-1.64982400	H	-4.84936200	-2.14760900	2.19844900
C	3.69023200	-1.18159700	0.42579200	H	-5.04514400	-3.13898500	-1.22657300
Si	-3.90748300	-1.31339500	0.04093900	H	-3.72344300	-3.79498600	-0.24926900
C	-4.36506500	0.10037100	-1.13101600	H	-3.37101400	-2.96755900	-1.77631300
C	-5.10259700	-1.34355000	1.49778000	C	-0.85593400	-1.47691800	-1.02324500
C	-4.01595500	-2.95537100	-0.89132800	H	-0.78870300	-2.55954600	-0.90773800
H	1.76341000	-0.96720300	2.31145700	C	-0.77112100	-0.95845000	-2.25065800
H	-0.15608800	-2.34004500	1.41260700	H	-0.82727400	0.10895700	-2.44413100
H	-0.59208500	-0.91291300	2.33932100	H	-0.63358300	-1.59605600	-3.12026400
H	-1.64627600	1.14324700	-0.63478800	C	4.53369500	-2.00923800	-0.56437700
H	-1.45964300	1.17968100	1.10990700	H	4.34391700	-3.07934200	-0.40646800
H	0.85935100	0.95520300	-0.88858800	H	4.19751500	-1.77961100	-1.58770000
H	2.32946900	1.19465200	1.12526500	C	6.00859900	-1.73387300	-0.45045500
H	0.91353700	1.23250700	2.16067900	H	6.31411500	-0.70335100	-0.64342500
H	1.99926100	-2.51074400	0.35101700	C	6.93906400	-2.63154800	-0.12220700
H	1.86589000	-1.14528000	-0.73676600	H	6.68393200	-3.66985600	0.08215000
H	-0.20943400	5.17776400	1.31366100	H	7.99071400	-2.36723900	-0.04742100
H	0.31557700	3.82281600	2.32057000	oTMS-1a (dieq)			
H	-1.29025100	3.80387900	1.57752500	C	-0.89437000	-1.12220100	-0.58218500
H	2.32062800	4.89172100	-0.55033200	C	-0.73520400	0.21344600	-1.32991800
H	2.73803500	3.31308500	-1.22945400	C	0.70726000	0.75459400	-1.30732100
H	2.89316500	3.59911800	0.51039600	C	1.68010300	-0.32839500	-1.82841200
H	-0.47160400	4.84583500	-1.80666200	C	1.54269700	-1.72736000	-1.18308900
H	-1.59137600	3.50380800	-1.54752500	C	0.06003800	-2.17119300	-1.18400800
H	-0.15797600	3.27915200	-2.56232000	C	-2.34838000	-1.63354400	-0.60520300
H	3.91831000	-0.11668500	0.28077500	O	1.08640200	1.06124600	0.05395600
H	4.00467700	-1.42467200	1.45051300	Si	2.47841900	-2.07210500	0.46613200
H	-5.38640700	-0.04029300	-1.50865000	C	4.02359100	-0.98166800	0.60240100
H	-3.69746600	0.14716300	-1.99858800	C	1.42679800	-1.90481000	2.03475000
H	-4.33221500	1.07270900	-0.62534200	C	3.03576100	-3.88916200	0.36337900
H	-6.13451200	-1.50512200	1.16163600	C	-3.35327300	-0.78381400	0.18635700
H	-5.07453800	-0.39893100	2.05313700	Si	0.90385100	2.47143400	0.95994200

C	2.12945100	3.81456800	0.43494000	H	0.57982000	1.23952900	3.12209200
C	-0.85552700	3.16242100	0.89963000	C	0.90080000	1.98606500	-2.17548400
C	1.31068500	1.95413900	2.72711900	H	1.92757700	2.35391300	-2.17995700
H	-0.61158700	-0.95851800	0.46498300	C	-0.01186700	2.61660100	-2.91713000
H	-1.03242400	0.06233500	-2.37755400	H	-1.04985400	2.30066500	-2.96761400
H	-1.40626400	0.97266500	-0.91527300	H	0.25444600	3.48550800	-3.51355000
H	1.48429000	-0.42254000	-2.90720400	C	-4.76758000	-1.39700800	0.20875000
H	2.70410300	0.05099300	-1.73110100	H	-5.14466100	-1.49548200	-0.81806200
H	2.07468400	-2.41075900	-1.86499200	H	-4.69906700	-2.41792100	0.61602400
H	-0.25971200	-2.36588500	-2.22140900	C	-5.74107000	-0.59647000	1.03077800
H	-0.05940100	-3.12469200	-0.65066200	H	-5.48625500	-0.48081500	2.08630900
H	-2.68666700	-1.72256500	-1.64928100	C	-6.85261900	-0.02202900	0.56840400
H	-2.36171200	-2.65497800	-0.19651000	H	-7.14737000	-0.10767000	-0.47599400
H	4.61522400	-1.25454400	1.48521200	H	-7.51319200	0.55204000	1.21300400
H	3.75275600	0.07592000	0.68942000	oTMS-1b (diox)			
H	4.67488100	-1.09096200	-0.27392300	C	1.31345400	-1.26773200	1.23644400
H	2.02581600	-2.16010400	2.91834500	C	-0.14954000	-1.66229600	0.91095100
H	0.56732200	-2.58581400	2.01669700	C	-0.83253300	-0.93990000	-0.27440900
H	1.05238000	-0.88597500	2.16359100	C	-0.60951800	0.58359800	-0.15534100
H	3.55533100	-4.19752800	1.27922300	C	0.87176200	0.98095400	0.03690200
H	3.72223800	-4.05471300	-0.47651300	C	1.44581900	0.27334700	1.28504800
H	2.18307600	-4.56706900	0.22867500	C	2.38390500	-1.93557300	0.34217200
H	-2.99371300	-0.66781400	1.21959900	O	-2.23109900	-1.27014900	-0.23344700
H	-3.41845000	0.22884800	-0.23120300	Si	1.11268900	2.88065500	0.08488600
H	3.15139400	3.42008000	0.37991500	C	0.23296900	3.62093200	1.59598300
H	2.13078900	4.62875900	1.17145000	C	2.96614100	3.27687200	0.17923900
H	1.88254500	4.25015300	-0.53861600	C	0.39820900	3.64990400	-1.49516200
H	-0.94196000	4.02072300	1.57886200	C	3.77212900	-2.01850400	1.01160200
H	-1.59352600	2.41647700	1.21777500	C	4.79657400	-2.69581400	0.14185300
H	-1.13069700	3.50613600	-0.10330900	C	5.92374600	-2.13634500	-0.30076000
H	1.31071200	2.82827600	3.39060200	C	-0.34853100	-1.49494500	-1.64110400
H	2.30037700	1.48766300	2.79172100	C	-1.02758000	-0.88471500	-2.83649600

C	-0.39687400	-0.30455600	-3.85999200	H	-0.93842500	0.10539000	-4.70881800
Si	-3.60440100	-0.68289900	0.51644400	H	0.68854200	-0.22594200	-3.89561200
C	-4.18579600	0.94157600	-0.26022600	H	-5.16218700	1.23351700	0.14794300
C	-3.38991900	-0.43549400	2.38238600	H	-4.29862200	0.84189100	-1.34640400
C	-4.89667000	-2.02074700	0.21241200	H	-3.49033100	1.76751400	-0.07368700
H	1.49880400	-1.64370800	2.25429300	H	-4.34404600	-0.12645700	2.82926600
H	-0.22913000	-2.74690800	0.76015500	H	-2.65176100	0.33694200	2.62801500
H	-0.75520400	-1.43181100	1.79642600	H	-3.08059300	-1.36306900	2.87859400
H	-1.03659800	1.07405700	-1.03708900	H	-5.86742200	-1.74112600	0.64045700
H	-1.17681800	0.93814200	0.71674700	H	-4.59285400	-2.97245700	0.66348500
H	1.43735000	0.64401600	-0.84660800	H	-5.04160400	-2.19398600	-0.86020800
H	2.49772000	0.54840000	1.43366200	oTMS-1b (dieq)			
H	0.90888700	0.63633300	2.17399400	C	-1.51720100	-0.33652100	0.77943900
H	2.05829500	-2.95333200	0.08548200	C	-0.33110400	-1.13146100	1.35451500
H	2.49257900	-1.40238700	-0.60983800	C	1.04372800	-0.48058700	1.10273300
H	0.34522800	4.71200000	1.61700600	C	1.02112000	0.98063500	1.59260500
H	0.64055100	3.23158700	2.53685100	C	-0.17200900	1.84089200	1.11519000
H	-0.84234800	3.40378300	1.58583800	C	-1.50757500	1.09386000	1.35267700
H	3.13548100	4.36052900	0.15384800	C	-2.83777700	-1.08114100	1.05743700
H	3.51303600	2.83971200	-0.66541800	O	1.35152500	-0.46298300	-0.30295600
H	3.42115700	2.89618700	1.10132100	Si	-0.02679200	2.73505800	-0.58390400
H	0.62204600	4.72286600	-1.54331800	C	1.78716300	3.14021300	-0.95628300
H	-0.69121000	3.53913200	-1.54690400	C	-0.79485100	1.83522400	-2.06705500
H	0.81848400	3.18358300	-2.39460800	C	-0.98500000	4.36733500	-0.38559900
H	4.12762500	-1.01496100	1.27778200	C	-4.07153900	-0.51294600	0.32651100
H	3.66936000	-2.57524400	1.95621400	C	-5.32342900	-1.29685600	0.61540600
H	4.56837900	-3.72412200	-0.14597500	C	-6.05189700	-1.95034700	-0.29103900
H	6.19341000	-1.11375800	-0.04255800	C	2.13807100	-1.26595400	1.87715000
H	6.62273200	-2.67661500	-0.93388300	C	3.53361300	-0.72526900	1.71984000
H	0.73386800	-1.37705500	-1.73731800	C	4.35723100	-0.43184600	2.72786600
H	-0.55351200	-2.57476900	-1.62377000	Si	1.54417700	-1.61509900	-1.50874100
H	-2.11458900	-0.94862900	-2.84540600	C	2.57525200	-3.11739700	-0.98926000

C	-0.11071100	-2.25436900	-2.16959400	H	2.05298200	-3.77116000	-0.28108200
C	2.45886500	-0.69465600	-2.87693600	H	3.53280000	-2.83122700	-0.54024300
H	-1.38599000	-0.27626700	-0.30815600	H	0.06647100	-2.93732300	-3.01088100
H	-0.46826000	-1.23037400	2.44167500	H	-0.75011000	-1.44257700	-2.53379600
H	-0.32773300	-2.15424300	0.95300300	H	-0.67638800	-2.81024900	-1.41287200
H	0.99317800	0.93533200	2.69213300	H	2.61700300	-1.34161100	-3.74893700
H	1.97597300	1.44988800	1.33489600	H	3.44249900	-0.35363800	-2.53285400
H	-0.18332600	2.71399800	1.78853000	H	1.90341700	0.18808400	-3.21302500
H	-1.69387200	1.02167600	2.43755700	oTMS-1c (diax)			
H	-2.34512500	1.67320300	0.94319500	C	-0.95267900	1.86334300	1.02481100
H	-2.72249800	-2.13382600	0.76349800	C	0.45680300	1.22510700	1.10113800
H	-3.02865300	-1.08819800	2.14157400	C	0.74060300	0.01646600	0.17583600
H	1.87207600	3.74929600	-1.86495800	C	-0.41824800	-0.99644100	0.31395100
H	2.37339400	2.22707800	-1.10514800	C	-1.81708100	-0.38464100	0.08481200
H	2.25061800	3.70592500	-0.13827300	C	-2.04735100	0.77336600	1.08215900
H	-0.71047900	2.46155800	-2.96458900	C	-1.15937400	2.85300100	-0.15271900
H	-1.86138200	1.63113300	-1.91384400	O	1.90804400	-0.68153500	0.64195500
H	-0.29435900	0.88554700	-2.27290100	Si	-3.21315000	-1.69504300	0.14256300
H	-0.97670400	4.94712100	-1.31694300	C	-3.32133700	-2.48348100	1.86518700
H	-0.55073400	4.99870500	0.39965700	C	-4.86861200	-0.86732100	-0.27681000
H	-2.03550500	4.19071300	-0.12109500	C	-2.86208400	-3.04550900	-1.14378400
H	-4.22615200	0.53244300	0.62998800	C	0.98868200	0.45054200	-1.28915600
H	-3.88479200	-0.50258600	-0.75584500	Si	3.43971500	-0.25761100	1.16303900
H	-5.63111800	-1.32788100	1.66267600	C	4.24712100	1.09408500	0.11029300
H	-5.78439700	-1.95064000	-1.34621900	C	4.42910600	-1.85556300	1.01617900
H	-6.94446600	-2.50678400	-0.01702100	C	3.42445000	0.30170900	2.97086900
H	1.87085200	-1.28029800	2.94104700	H	-1.04875000	2.47092200	1.93753600
H	2.10856200	-2.31032000	1.53773900	H	1.22351200	1.99748700	0.94617100
H	3.87641300	-0.57579600	0.69666000	H	0.58934100	0.85359800	2.12523800
H	5.36273100	-0.05684100	2.55510200	H	-0.23241800	-1.84265200	-0.35653600
H	4.05955100	-0.55858200	3.76727100	H	-0.35833700	-1.39842100	1.33447000
H	2.79624700	-3.71969100	-1.88046100	H	-1.85758900	0.02428800	-0.93860100

H	-3.02527000	1.24222800	0.91843100	C	1.78196000	-0.15321600	-3.61063400
H	-2.06642900	0.35999700	2.10126700	H	1.00994100	0.40591600	-4.14371600
H	-0.23897200	3.44453600	-0.27328400	C	2.97736000	-0.30576000	-4.18345900
H	-1.31380000	2.32180300	-1.09831000	H	3.77886400	-0.85557000	-3.69312300
H	-4.11554600	-3.23958400	1.89840600	H	3.20098300	0.10518300	-5.16457000
H	-3.54478100	-1.73985900	2.63959900	oTMS-1c (dieq)			
H	-2.38393400	-2.98018800	2.14294600	C	1.55271900	1.46001200	0.73840600
H	-5.68337200	-1.60197500	-0.28321600	C	0.06176800	1.44104200	1.11413000
H	-4.84215800	-0.39826700	-1.26825000	C	-0.61972200	0.06696500	0.93418800
H	-5.13321800	-0.08936400	0.44896200	C	0.20204500	-1.01625100	1.66469800
H	-3.68502200	-3.76994300	-1.18474200	C	1.72459600	-1.02915800	1.38701600
H	-1.94674600	-3.60312900	-0.91313700	C	2.31189500	0.39280000	1.54664800
H	-2.74790600	-2.62263400	-2.14981000	C	2.17642800	2.85874000	0.96458600
H	0.09341500	0.94291400	-1.68267800	O	-0.67283900	-0.29901000	-0.45672300
H	1.77729400	1.21244200	-1.28867500	Si	2.36141800	-2.01153200	-0.14246600
H	5.28137600	1.25323900	0.44304500	C	1.20151500	-3.45830500	-0.53268300
H	3.72899300	2.05697800	0.19384700	C	2.65255300	-0.99588500	-1.71809000
H	4.28063100	0.82424100	-0.95173600	C	4.05487200	-2.71201900	0.37135400
H	5.45823500	-1.72431000	1.37303300	C	-2.04990200	0.13358300	1.52738400
H	4.47690700	-2.19897500	-0.02386800	Si	-1.37220900	0.33666300	-1.84516100
H	3.96934800	-2.65586200	1.60759200	C	-3.11696700	1.03463200	-1.60788700
H	4.44934500	0.42393700	3.34474800	C	-0.32300900	1.71234300	-2.61220200
H	2.92668400	-0.43902800	3.60816500	C	-1.44855500	-1.13328500	-3.02473500
H	2.90857000	1.25904300	3.10733700	H	1.64376000	1.21716100	-0.32771900
C	-2.31502200	3.79085400	0.07572100	H	-0.03091900	1.72765700	2.17251000
H	-2.25013300	4.41032800	0.97294900	H	-0.48804800	2.20130100	0.54553400
C	-3.38311000	3.91213900	-0.71483400	H	0.05438500	-0.84117800	2.74171100
H	-4.18361000	4.61352100	-0.49433100	H	-0.23467000	-1.99630800	1.44863600
H	-3.49466600	3.31763800	-1.61974900	H	2.15770600	-1.63654500	2.19888000
C	1.39587300	-0.68139400	-2.25504100	H	2.27357400	0.68245400	2.61018600
H	2.22519900	-1.25362400	-1.82716600	H	3.37595000	0.40949200	1.27111100
H	0.55537500	-1.38112400	-2.36941400	H	2.02160100	3.16382800	2.00907000

H	3.26484000	2.77102700	0.82299900	H	-6.37966400	-1.09227600	1.56969700
H	1.61806900	-4.08252300	-1.33312000	H	-5.30276400	-1.66970700	0.18117000
H	0.22103800	-3.09756900	-0.86105700	oTMS-1d (diox)			
H	1.04749100	-4.10549400	0.33985700	C	0.93238400	-1.83753800	-1.76097600
H	3.09198600	-1.63583200	-2.49409800	C	-0.38118800	-1.72271000	-0.93424100
H	3.35026300	-0.16709400	-1.54776900	C	-0.54737700	-0.46432600	-0.05028200
H	1.72256300	-0.57989300	-2.11447200	C	0.73737100	-0.27251900	0.78850000
H	4.51183000	-3.28288700	-0.44664000	C	2.03556500	-0.24486600	-0.04638000
H	3.97051200	-3.38363000	1.23490200	C	2.15835500	-1.55498000	-0.85689800
H	4.75778800	-1.91416000	0.64347700	O	-1.59223400	-0.68201400	0.91382000
H	-1.96844700	0.44524900	2.57767100	Si	3.59126800	0.11905900	1.01101400
H	-2.60249200	0.93134200	1.01866600	C	3.89275500	-1.27200000	2.26559500
H	-3.54395200	1.25078600	-2.59653100	C	5.09914300	0.27672200	-0.13104800
H	-3.12181500	1.97488700	-1.04429100	C	3.35418900	1.75704100	1.93874100
H	-3.79436200	0.33872000	-1.10166300	C	-0.91654500	0.78425600	-0.88684400
H	-0.78001800	2.04114900	-3.55494600	Si	-3.11476800	-1.37066300	0.92457700
H	0.69688500	1.38218000	-2.83919600	C	-4.20028100	-0.80610300	-0.52083000
H	-0.25346500	2.58889900	-1.95829500	C	-3.86691100	-0.78206500	2.54959000
H	-1.84676400	-0.83527700	-4.00273200	C	-3.03680900	-3.26175400	0.92496000
H	-2.09522000	-1.92528000	-2.62867200	H	0.98704700	-2.88766100	-2.08055700
H	-0.45609400	-1.56867700	-3.18716300	H	-1.24224200	-1.82607800	-1.60738700
C	1.65462800	3.92545100	0.04022100	H	-0.40238600	-2.58139700	-0.25119400
H	1.83880300	3.75923700	-1.02281100	H	0.63020800	0.63177500	1.39690000
C	1.00350000	5.02854300	0.41555300	H	0.77537900	-1.11275200	1.49514600
H	0.79781900	5.24216200	1.46288400	H	1.97678000	0.59819000	-0.75477300
H	0.65864800	5.76469600	-0.30605200	H	3.06437400	-1.55138700	-1.47595700
C	-2.86814800	-1.17138500	1.45609900	H	2.26379500	-2.39554200	-0.15561600
H	-2.85342600	-1.56940600	0.43535500	H	4.77466500	-1.05500200	2.88105800
H	-2.39312300	-1.92920700	2.09492200	H	4.06690900	-2.23633300	1.77341100
C	-4.29045500	-0.97657600	1.90890600	H	3.04121400	-1.39500200	2.94557700
H	-4.41746200	-0.56729500	2.91340000	H	5.99872900	0.53123100	0.44307400
C	-5.37626300	-1.25653900	1.18560000	H	4.95402500	1.06559000	-0.87957800

H	5.30695100	-0.65566900	-0.66914900	C	-1.93711500	-0.91234300	1.50536700
H	4.26168900	2.02559800	2.49374500	C	-0.42120200	-1.12900000	1.69695100
H	2.53229400	1.70259200	2.66219000	C	0.46012500	-0.16173900	0.87752400
H	3.13491600	2.58244200	1.24995100	C	0.01797400	1.29307800	1.14271100
H	-0.13686900	0.96874800	-1.63296500	C	-1.49904200	1.58487200	1.04277500
H	-1.82180400	0.54237900	-1.45960400	O	0.30458800	-0.40740100	-0.53160200
H	-5.20943400	-1.22572900	-0.41595200	Si	-2.23451900	2.00758100	-0.68656300
H	-3.81175700	-1.13388300	-1.49227000	C	-0.92232800	2.83706700	-1.77393600
H	-4.29977500	0.28540100	-0.55112900	C	-3.02078100	0.56145000	-1.62893900
H	-4.87438800	-1.19130700	2.69555100	C	-3.62846100	3.26093400	-0.35890400
H	-3.94201700	0.31120000	2.57951300	C	1.94025000	-0.34740600	1.29701800
H	-3.25207600	-1.09436700	3.40167700	Si	0.53541700	-1.71456700	-1.55849200
H	-4.03521200	-3.68416400	1.09844100	C	2.12920900	-2.68782600	-1.23884100
H	-2.37952500	-3.63130500	1.72120000	C	-0.90291600	-2.94463500	-1.50057400
H	-2.67023500	-3.66607000	-0.02525500	C	0.62909000	-0.93841500	-3.27477500
C	-1.15569200	2.07682700	-0.09368400	H	-2.18169100	-1.09176600	0.45299900
H	-1.85606500	1.88234400	0.72727900	H	-0.17941100	-0.99579500	2.76165100
H	-0.22228100	2.41955200	0.37040200	H	-0.15452400	-2.16450300	1.44930900
C	-1.70407100	3.21029000	-0.98409600	H	0.34470000	1.53284200	2.16632600
H	-1.00760500	3.40592000	-1.81082500	H	0.57868800	1.95643600	0.47709400
H	-2.64497700	2.86921700	-1.44417200	H	-1.63772400	2.55268700	1.55249500
C	0.96340800	-1.01320000	-3.02870400	H	-1.36160500	3.18187500	-2.71840900
H	1.22860500	0.03925900	-2.93260200	H	-0.11011500	2.14221100	-2.01299900
C	0.72032500	-1.49513900	-4.24915800	H	-0.48196800	3.71232200	-1.28011400
H	0.46664500	-2.54147100	-4.41204300	H	-3.50459700	0.93421300	-2.54093900
H	0.76359800	-0.86527100	-5.13394200	H	-3.79265800	0.05836000	-1.03408300
C	-1.95430400	4.48364100	-0.22267400	H	-2.28118300	-0.18683300	-1.92598500
H	-2.66590600	4.40960100	0.60217100	H	-4.12717000	3.54834300	-1.29303700
C	-1.37102100	5.65767900	-0.46915100	H	-3.24752100	4.17847200	0.10684400
H	-1.58855200	6.54269100	0.12316400	H	-4.39789800	2.84969700	0.30692600
H	-0.65363200	5.77969700	-1.27882200	H	2.01020300	-0.16509200	2.37831600
oTMS-1d (dieq)				H	2.21127600	-1.40098000	1.15309700

H	2.27039700	-3.41369400	-2.05062800	C	0.53410700	-0.59124600	0.20157200
H	2.10156100	-3.25492100	-0.30129400	C	1.81728600	0.26763700	0.19338600
H	3.01504900	-2.04326200	-1.21830500	C	1.69502500	1.37441700	-0.87874900
H	-0.72775900	-3.75058800	-2.22555700	C	0.61910900	3.31493000	0.40721000
H	-1.85728700	-2.47267000	-1.75972900	O	-1.83116100	-0.71283300	0.16136600
H	-1.02050700	-3.41083700	-0.51559900	Si	3.40803700	-0.77952300	-0.00763200
H	0.74021500	-1.70814100	-4.04878700	C	3.44379200	-1.62780400	-1.70475800
H	1.48527600	-0.25827400	-3.35563000	C	4.92432200	0.35010200	0.16094300
H	-0.27345900	-0.36150500	-3.50577900	C	3.47536800	-2.10061400	1.35289100
C	2.96428800	0.53956800	0.57535500	C	-0.89246900	0.65587000	1.89507300
H	2.83413400	0.44729900	-0.51021300	Si	-3.47098200	-0.61251900	-0.14079200
H	2.79171800	1.59512200	0.81675900	C	-4.37184300	0.59195700	1.00973900
C	4.41652500	0.18259700	0.95167700	C	-4.10088100	-2.36347300	0.15995700
H	4.55272300	0.27616200	2.03760300	C	-3.82151600	-0.12051500	-1.93405900
H	4.59333100	-0.87630000	0.70551700	H	0.31963500	2.83601600	-1.63665000
C	5.43020600	1.03720500	0.23979400	H	-1.69499200	2.02103500	-0.35880400
H	5.41398700	0.98193000	-0.85062100	H	-1.00745200	0.93298000	-1.56210400
C	6.30909600	1.84686600	0.83234000	H	0.58370700	-1.38003200	0.96249500
H	6.36117600	1.93770100	1.91585100	H	0.42550800	-1.09967700	-0.76631200
H	7.01227300	2.44743400	0.26119900	H	1.92051700	0.75066600	1.17889600
C	-2.72071200	-1.88598900	2.34760800	H	2.59039400	2.01034600	-0.88701300
H	-2.56965900	-1.80237400	3.42676100	H	1.64362400	0.89952100	-1.86967500
C	-3.56029500	-2.81284200	1.88230700	H	-0.30175900	3.89233100	0.55365700
H	-3.74390300	-2.93486000	0.81647800	H	0.89053800	2.87737700	1.37257200
H	-4.09718000	-3.48541000	2.54643200	H	4.35193300	-2.23288200	-1.81773100
C	-2.30464100	0.54594900	1.85786300	H	3.43150000	-0.89979000	-2.52479600
H	-2.10867900	0.69468100	2.93264600	H	2.58543000	-2.29640500	-1.84197900
H	-3.38510700	0.69068200	1.72705200	H	5.85358600	-0.22847100	0.08819200
oTMS-1n (diax)				H	4.93421600	0.86595900	1.12919700
C	0.44397700	2.26577300	-0.70426000	H	4.95366000	1.11654400	-0.62259500
C	-0.82468100	1.38698700	-0.57966800	H	4.41386900	-2.66649200	1.30150300
C	-0.76518000	0.21545800	0.42834900	H	2.65320300	-2.82023200	1.26333700

H	3.41619500	-1.65302600	2.35282100	C	1.71250200	1.11299100	-2.33160500
H	-0.00773200	1.19408700	2.24486100	Si	2.35498300	-0.84809700	0.39237300
H	-1.76019000	1.30762900	2.04001900	C	4.01968700	-0.52602400	-0.45191800
H	-5.45283400	0.55006800	0.82232500	C	2.42637000	-0.09428700	2.12754900
H	-4.05666600	1.63138400	0.85958600	C	2.09714300	-2.71185000	0.52201800
H	-4.21027300	0.34179200	2.06467600	H	-0.30294800	1.18208200	1.41512500
H	-5.17697200	-2.44263700	-0.03902700	H	0.49968800	3.00928700	-0.89241500
H	-3.92812300	-2.67144300	1.19775800	H	1.61612100	2.23283100	0.22159200
H	-3.58699700	-3.08286200	-0.48818000	H	-0.86280500	1.48147300	-2.54409400
H	-4.89472200	-0.19963900	-2.15133700	H	-0.66121300	-0.26149300	-2.43035800
H	-3.29379500	-0.77900200	-2.63442200	H	-2.79136900	0.75782400	-1.48278000
H	-3.51700900	0.90965200	-2.15170300	H	-2.04282200	2.77757800	-0.51643500
H	-1.01998000	-0.23100400	2.52494300	H	-2.64099100	1.82719900	0.83345700
H	1.41401200	4.02058100	0.13675000	H	-0.64998400	4.21218100	1.06954900
oTMS-1n (dieq)				H	-1.25763000	3.25388800	2.42965900
C	-0.48332300	2.05417400	0.77580200	H	-2.17195000	-3.44190200	-0.60918200
C	0.64133700	2.11209100	-0.27092400	H	-0.73926500	-2.55568500	-1.16369900
C	0.69023800	0.88691200	-1.20699800	H	-2.26512700	-2.43122800	-2.05624200
C	-0.70136400	0.65696300	-1.83312600	H	-1.99015500	-2.17255700	2.21607700
C	-1.89683500	0.63316700	-0.85043200	H	-1.94401700	-0.42124600	2.44091900
C	-1.84333200	1.87049100	0.07855000	H	-0.53371100	-1.26466200	1.77845000
C	-0.47457400	3.30522100	1.66333000	H	-4.57302300	-1.93650300	0.71473200
O	1.02538700	-0.30649100	-0.47393600	H	-4.72135100	-0.99735000	-0.77718400
Si	-2.33010400	-1.02475400	0.02738200	H	-4.58516200	-0.17077000	0.78075600
C	-1.82707300	-2.49929000	-1.05242100				
C	-1.62659200	-1.23447900	1.77696800				
C	-4.22599200	-1.03101100	0.20134600				

H	1.40507500	1.94759300	-2.97142500	H	2.60195400	0.98762400	2.10464200
H	2.70321400	1.34837100	-1.93175000	H	2.91178300	-3.18281800	1.08646100
H	4.80499700	-1.06948900	0.09002900	H	2.07002700	-3.17298300	-0.47230900
H	4.30150500	0.53315900	-0.45188200	H	1.15622200	-2.95875800	1.02624600
H	4.03107000	-0.87825000	-1.48936400	H	1.79590500	0.21619400	-2.95539600
H	3.24738700	-0.54626300	2.69953500	H	0.48769400	3.42494800	2.17639300
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8. References

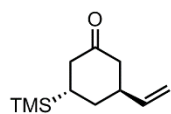
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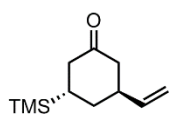
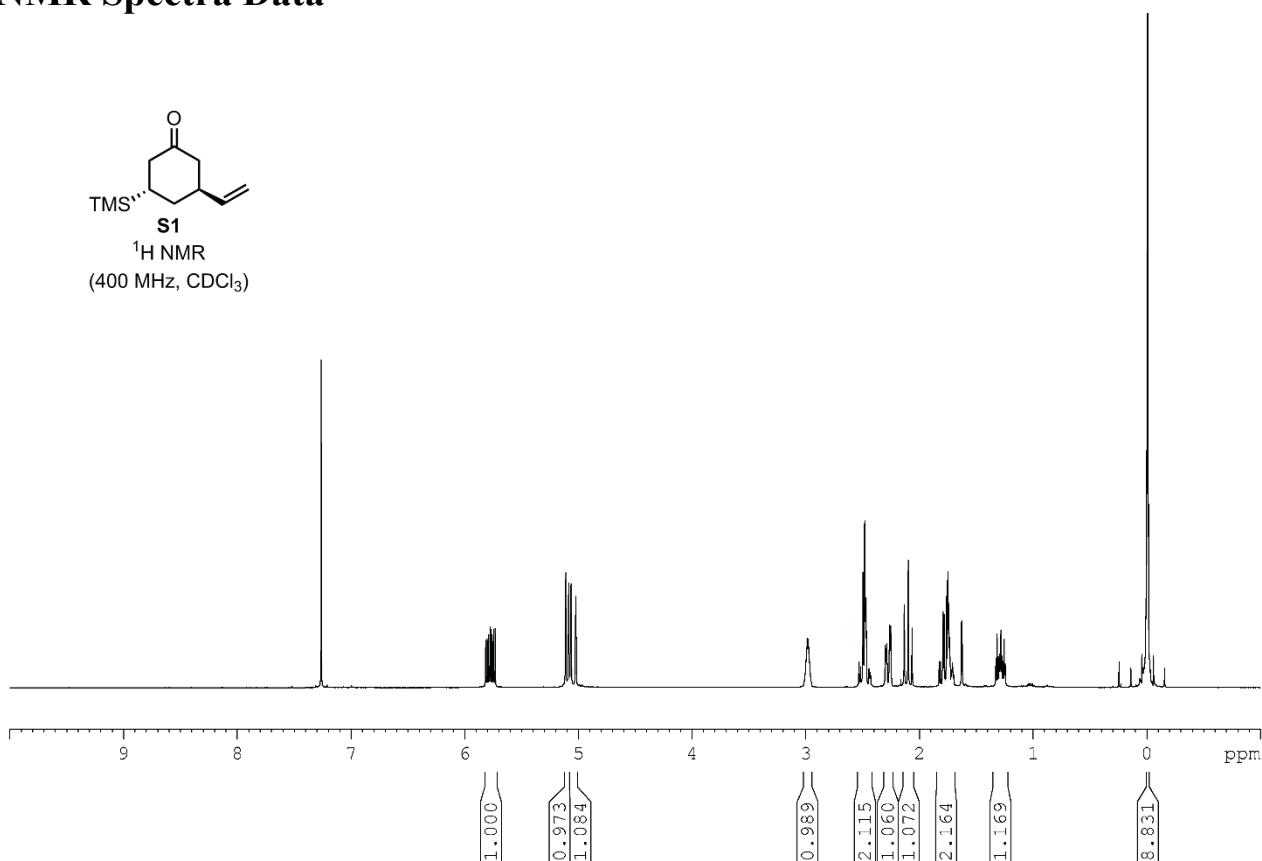
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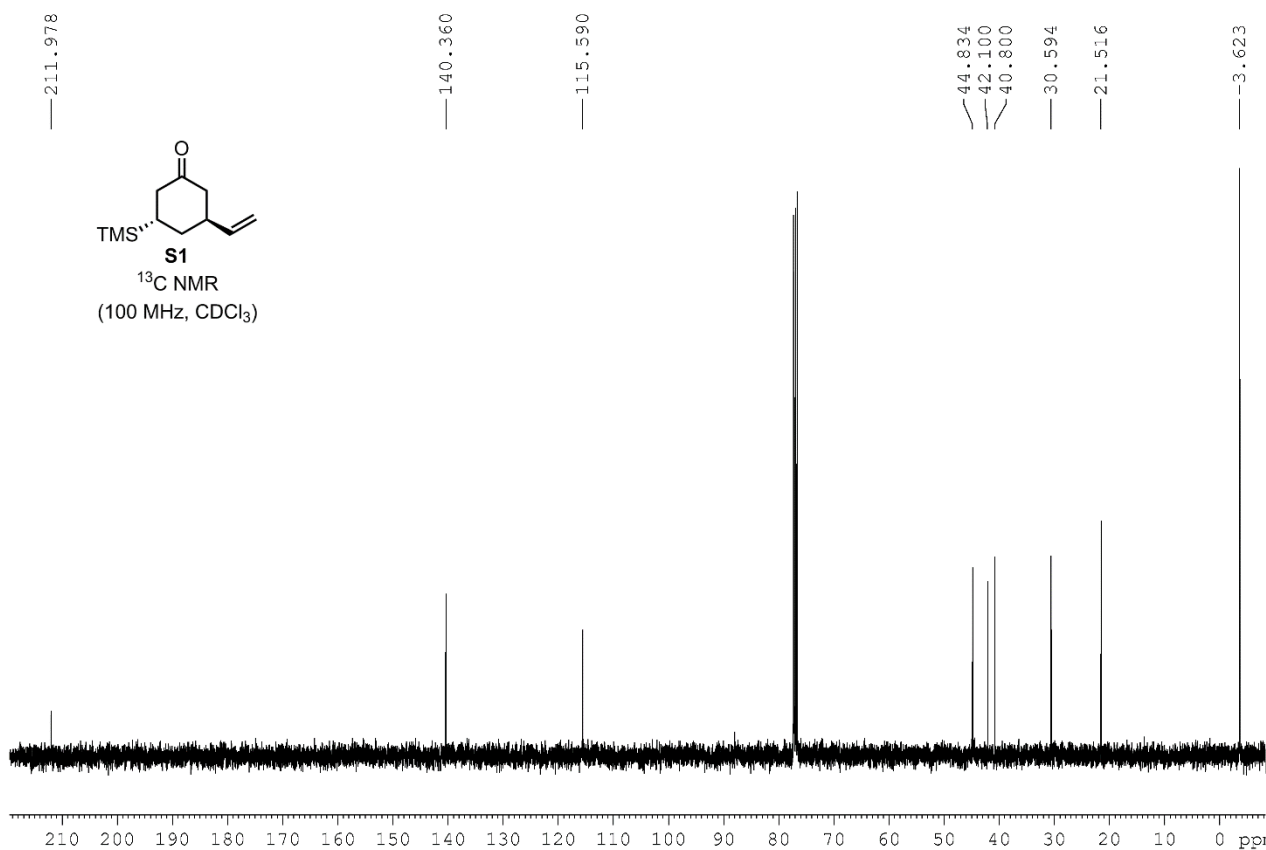
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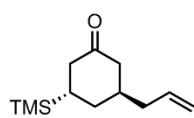


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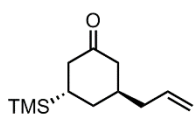
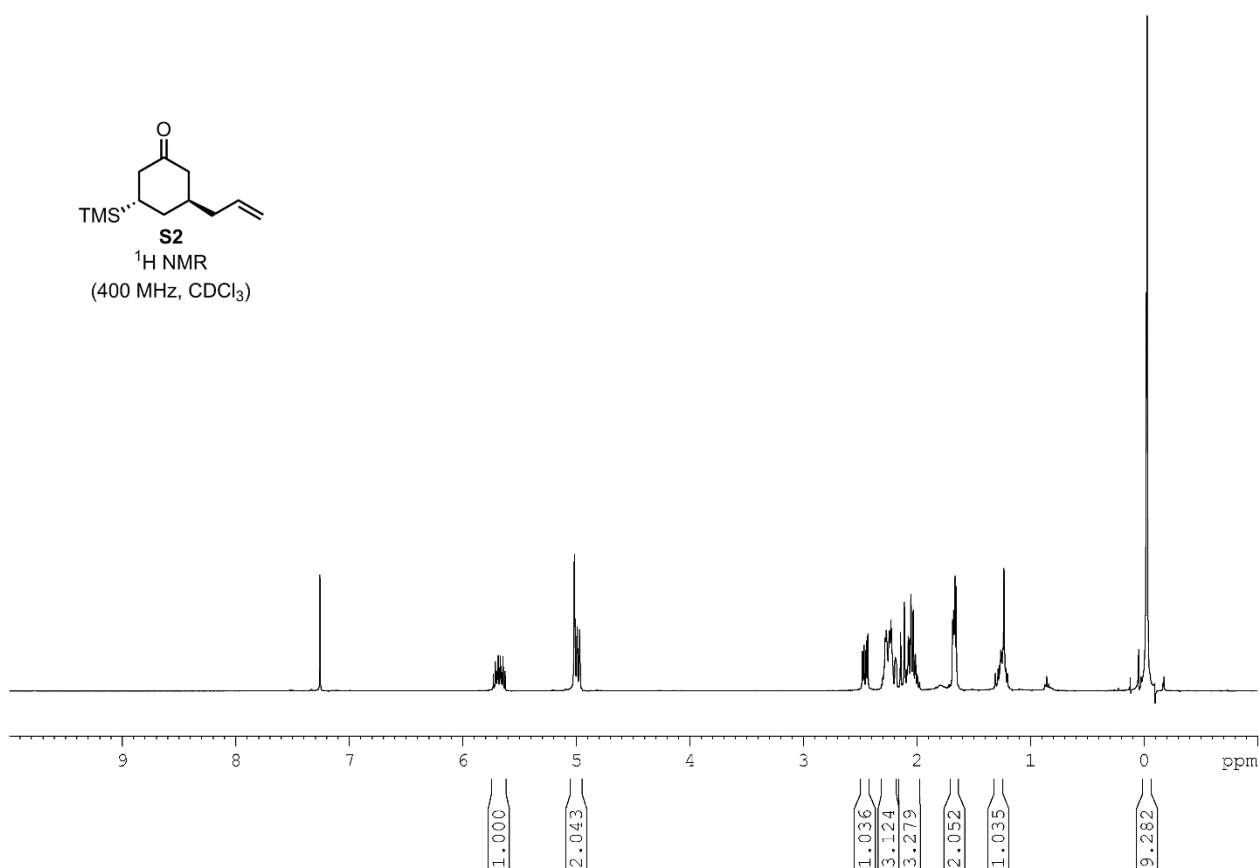


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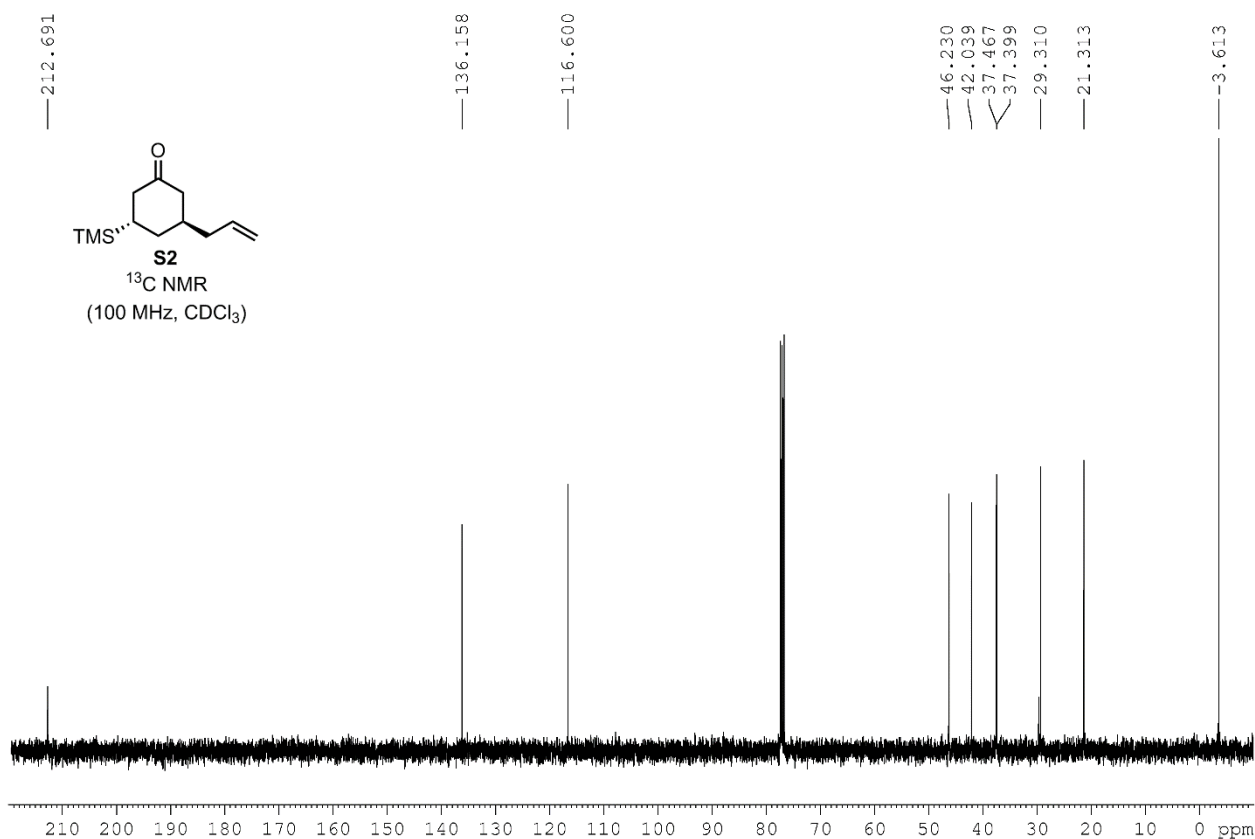


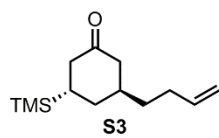


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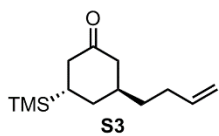
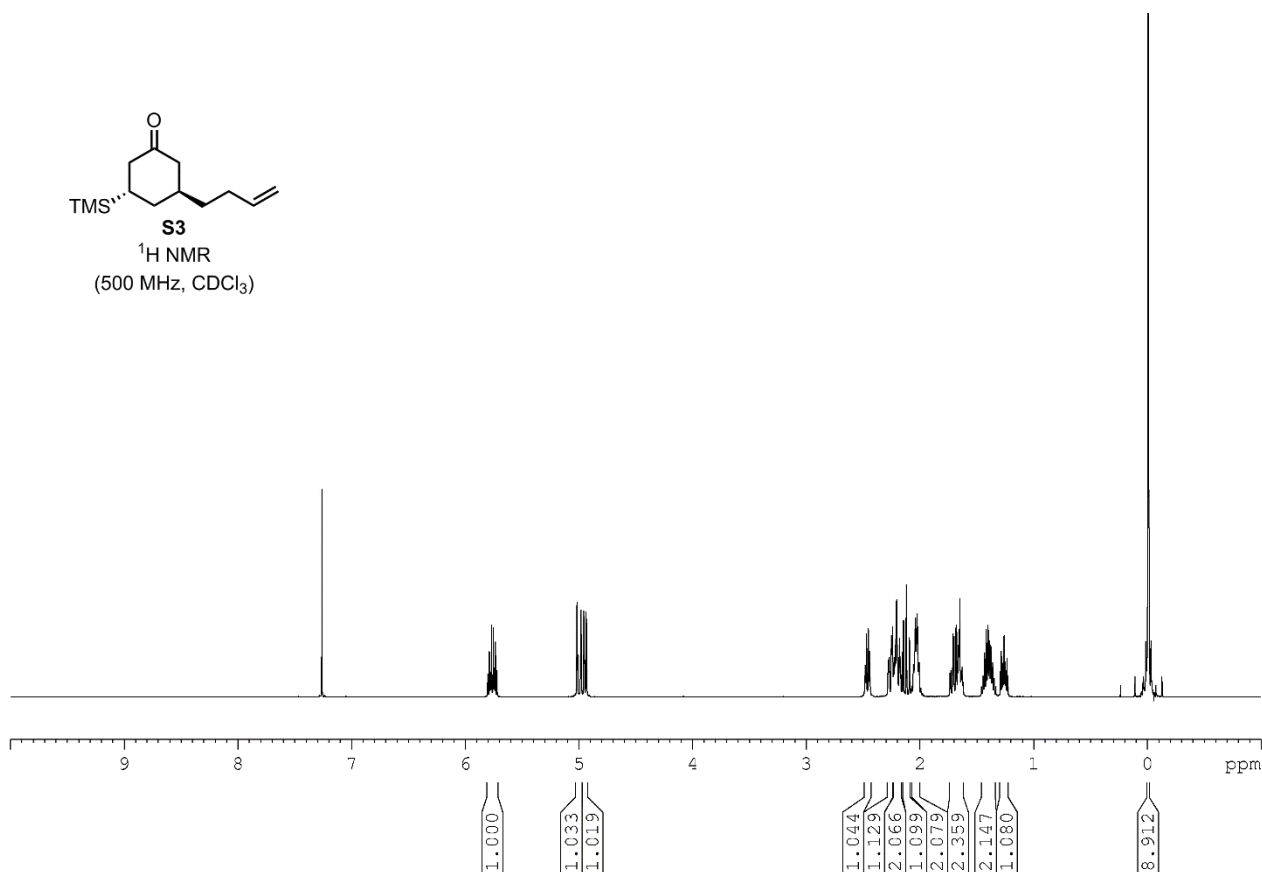


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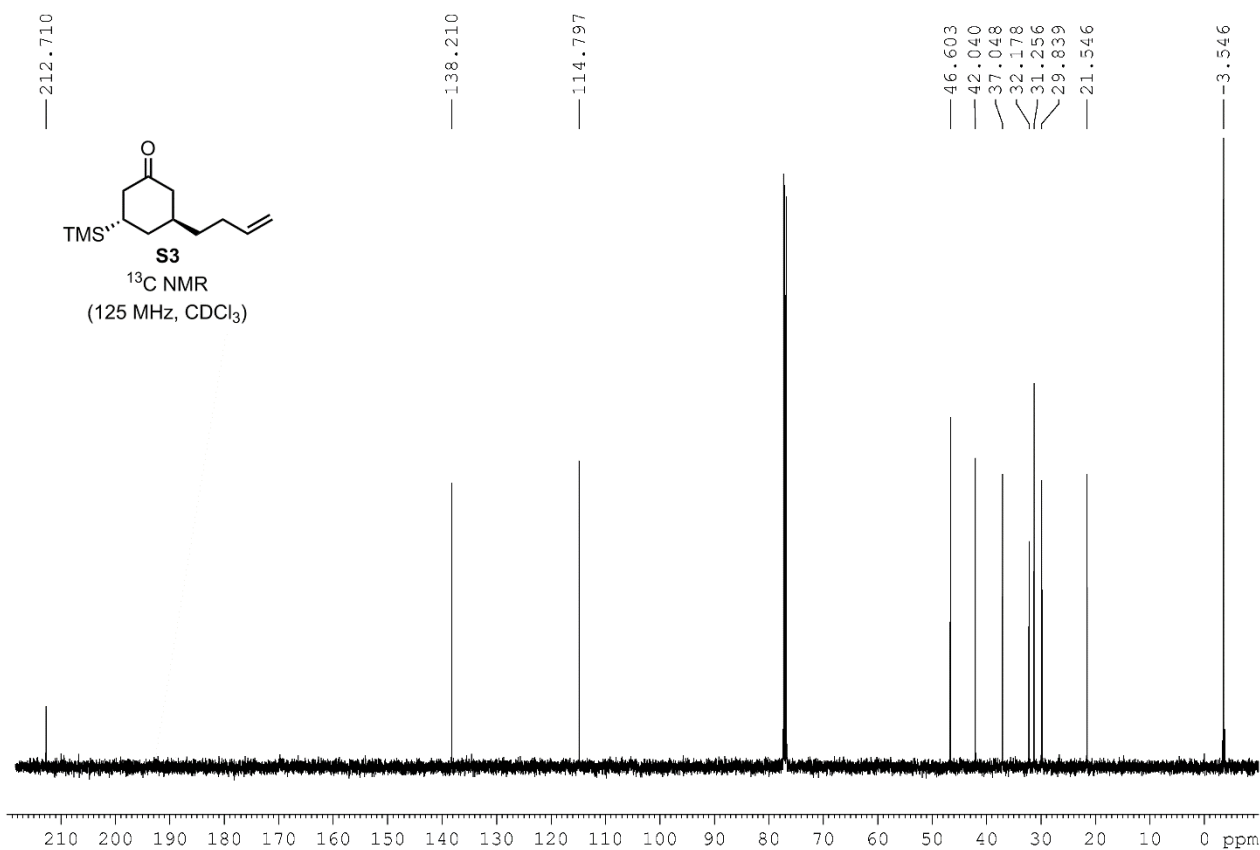


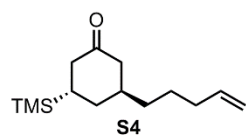


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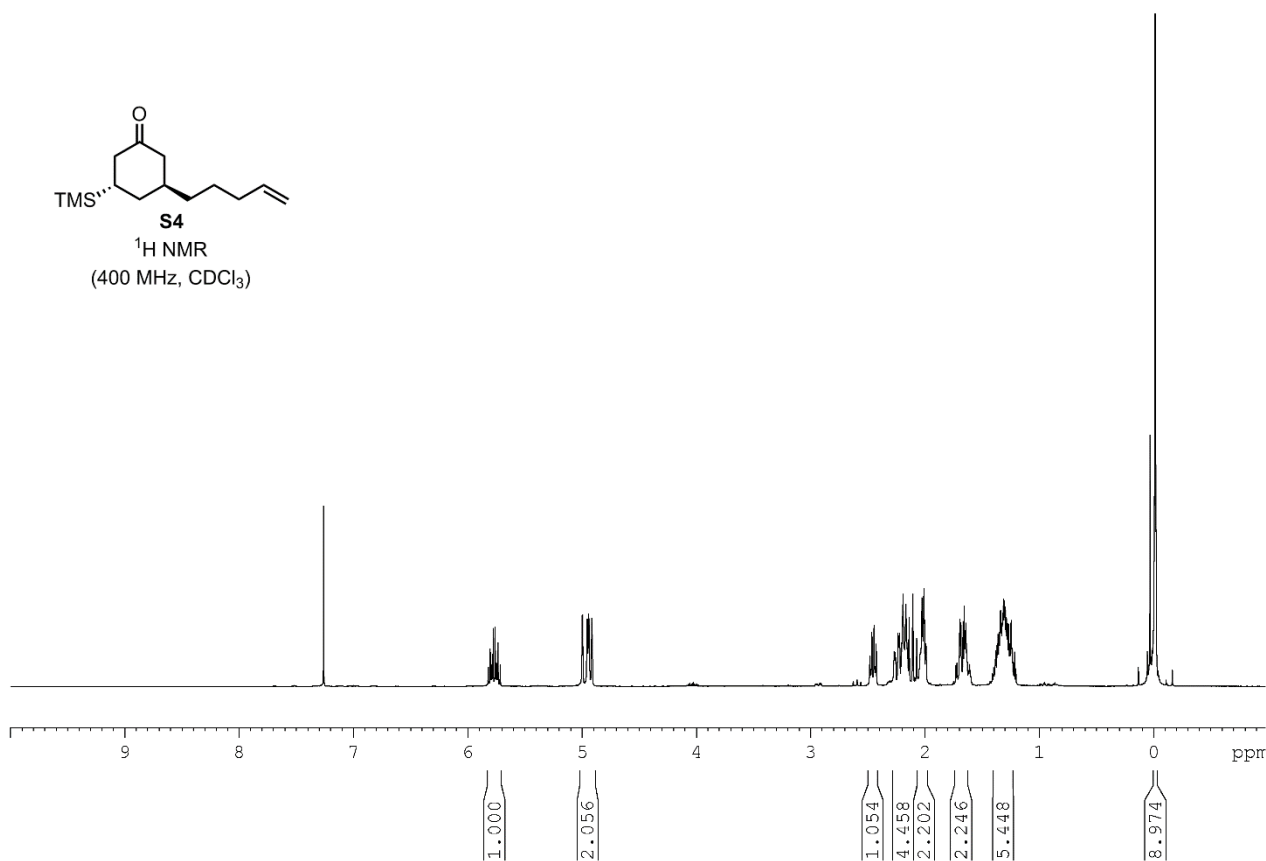


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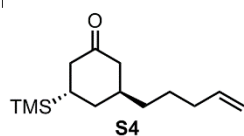




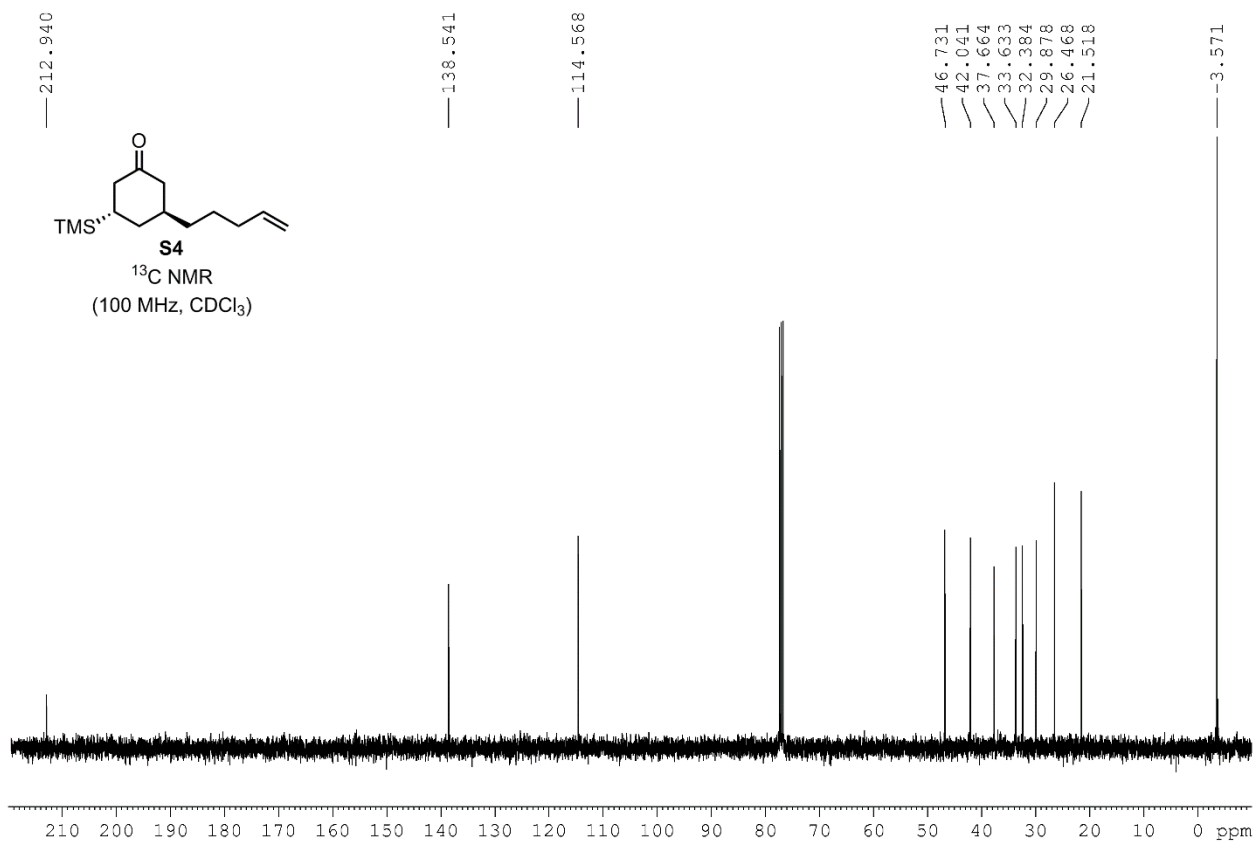
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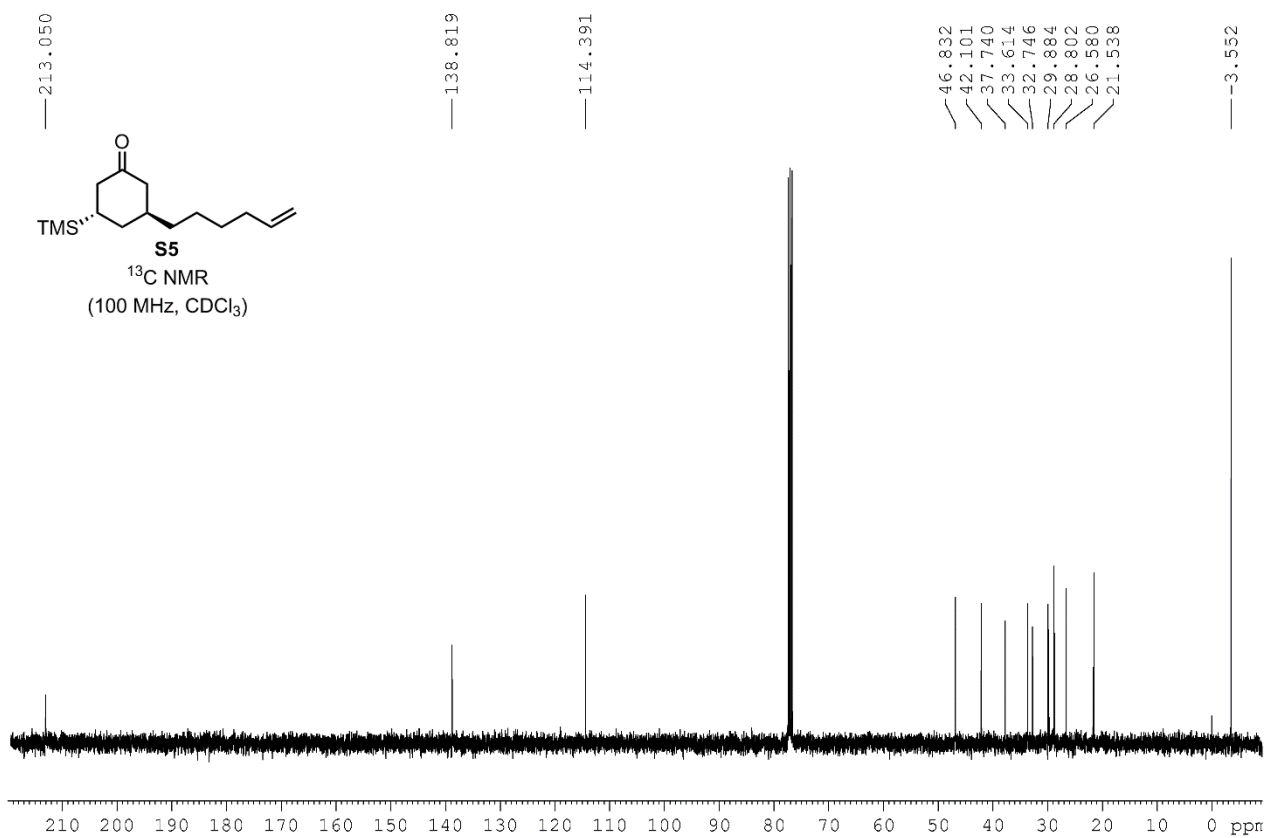
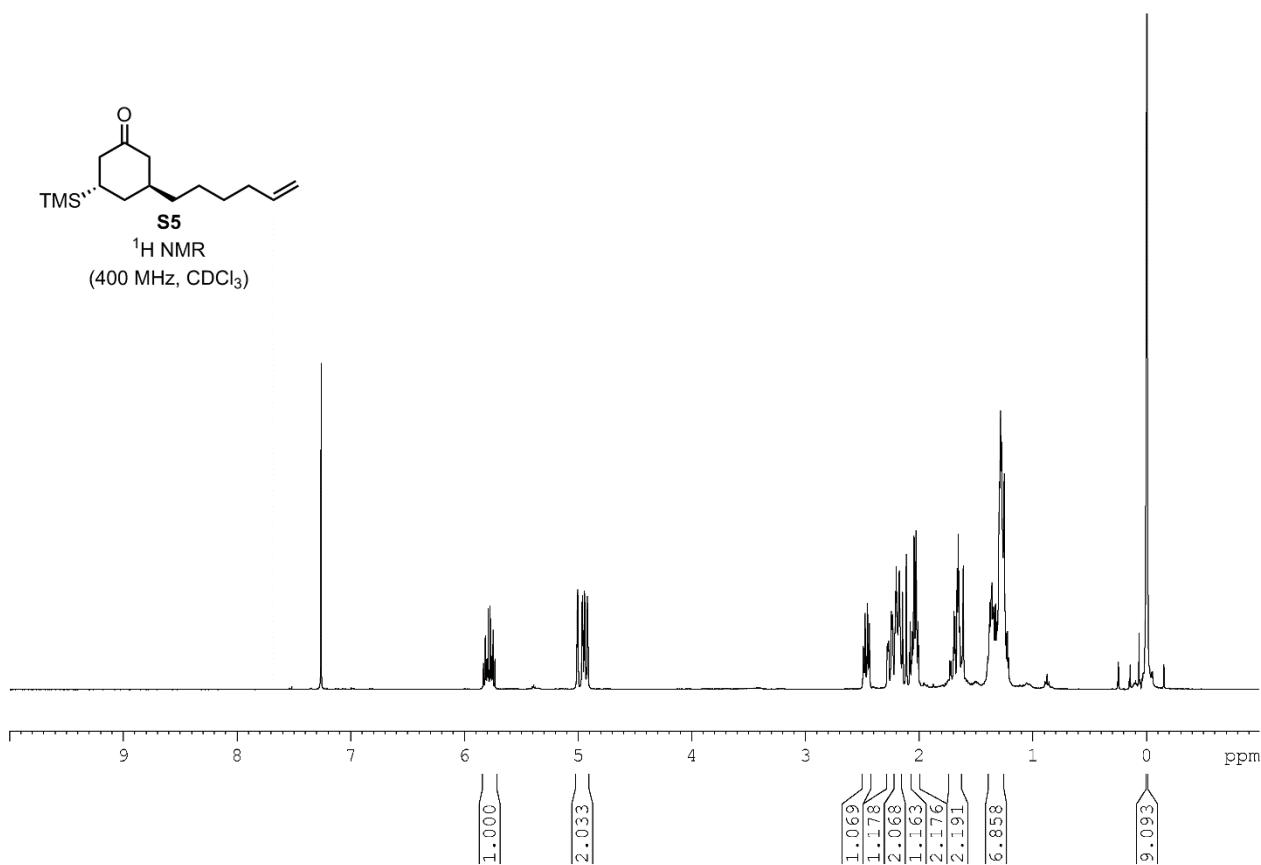


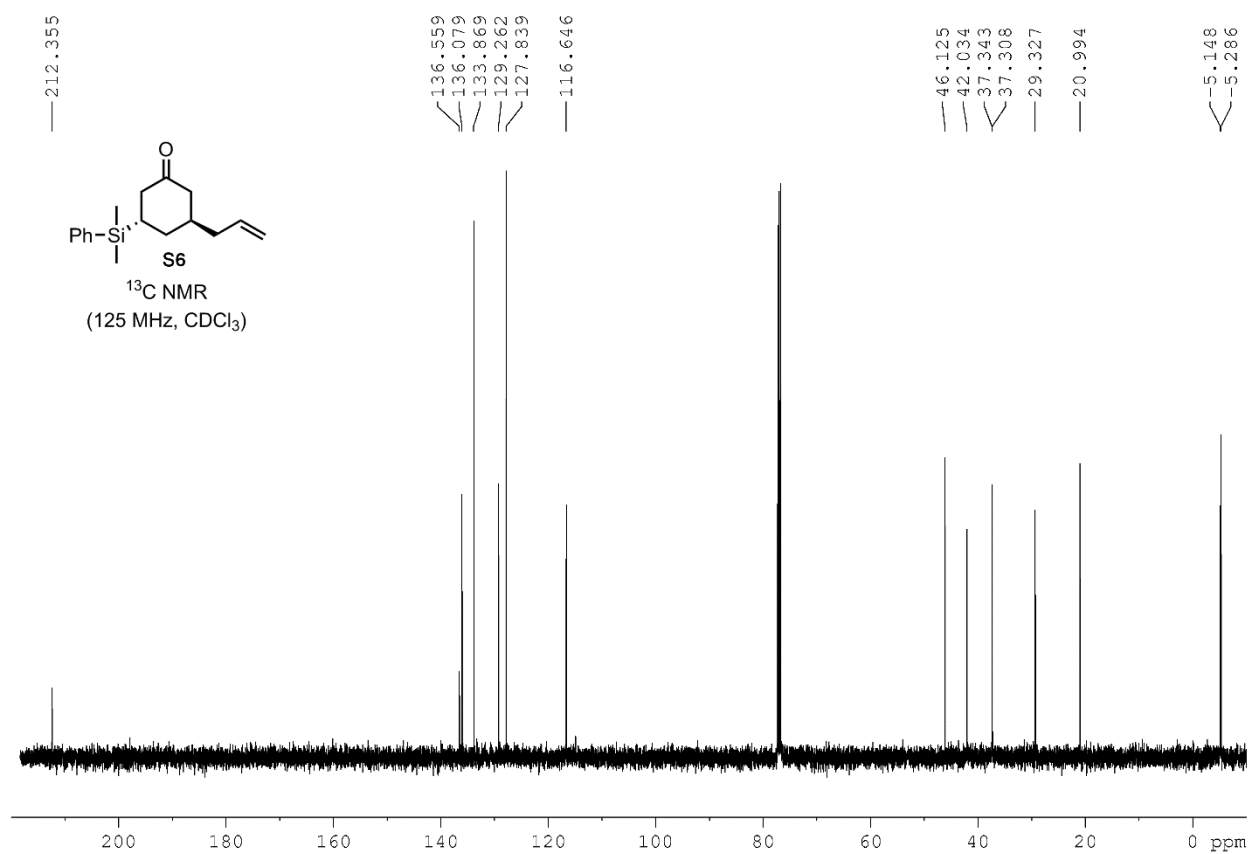
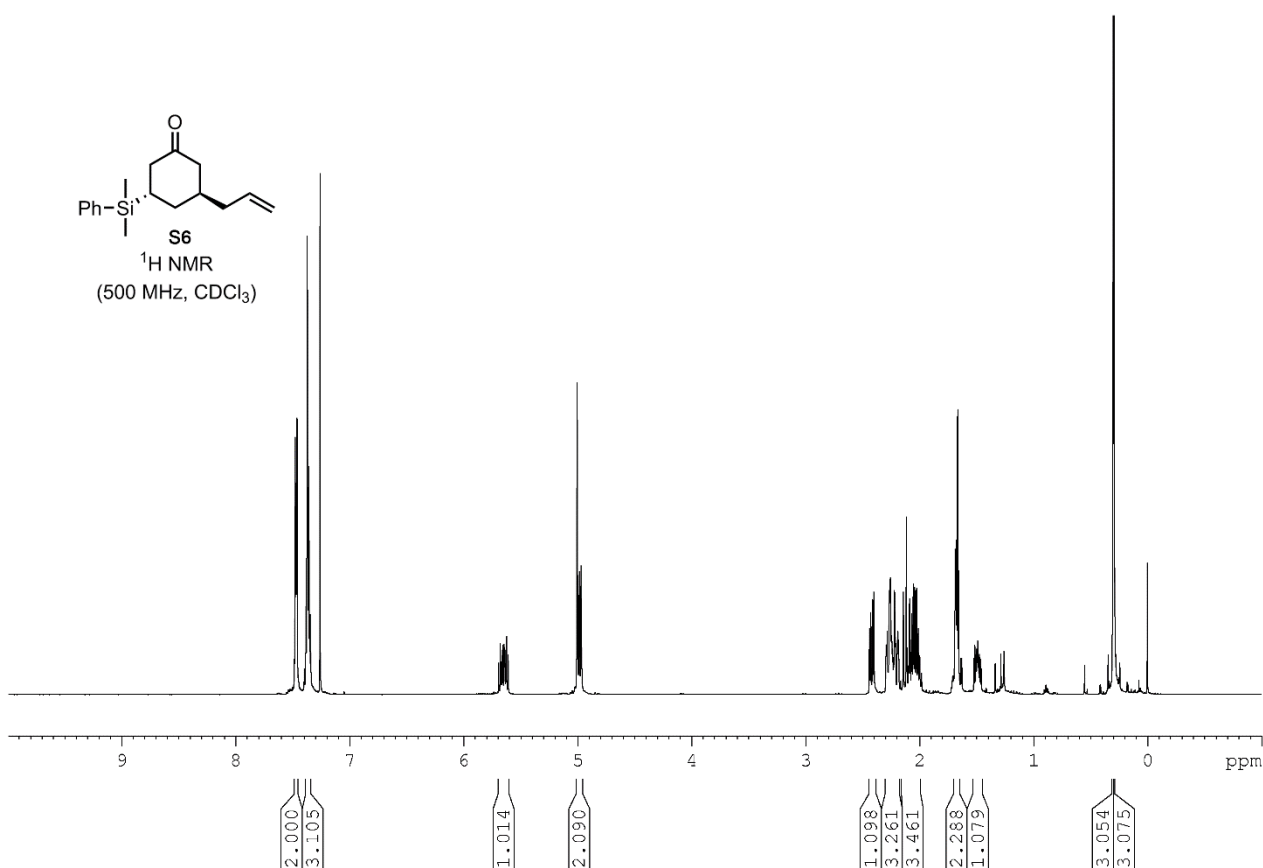
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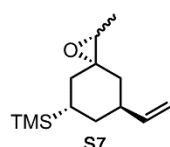


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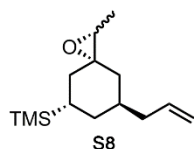
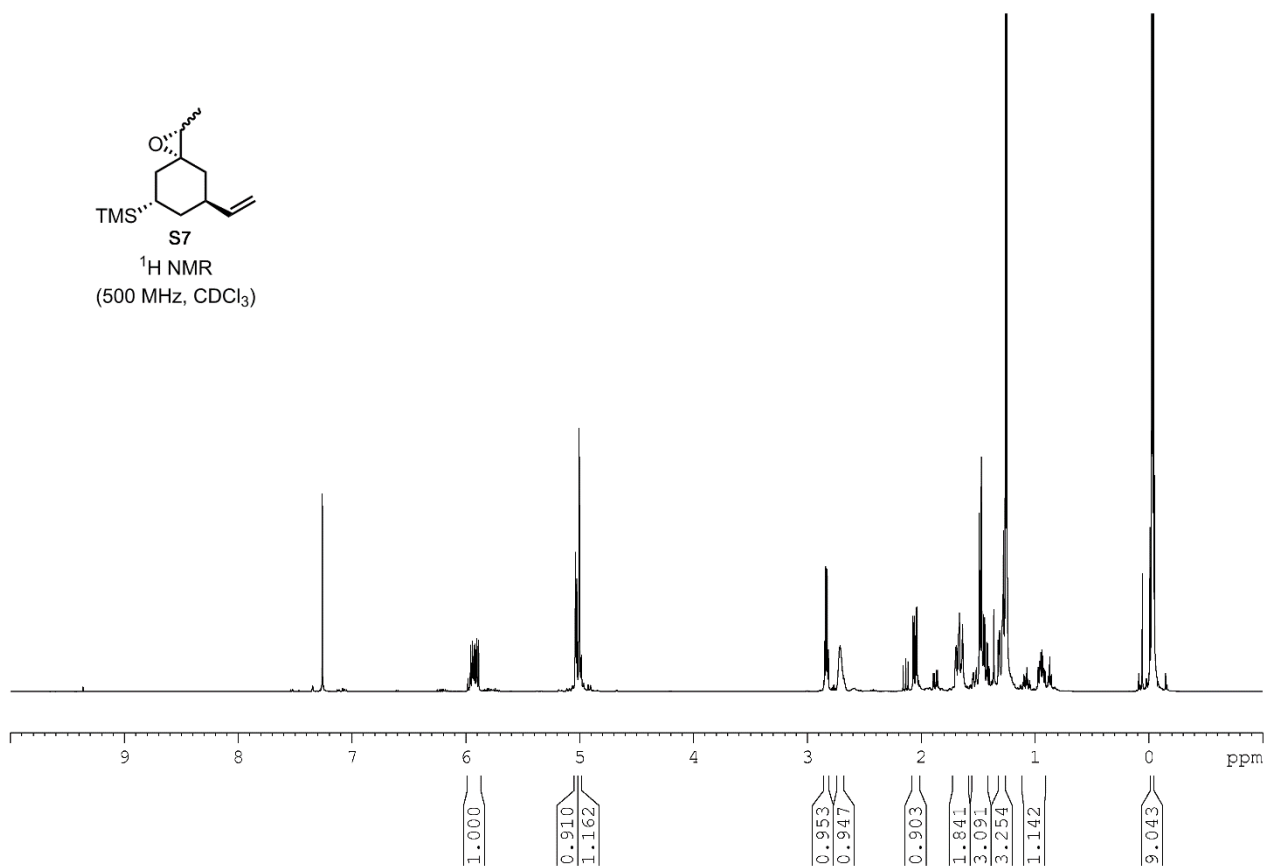




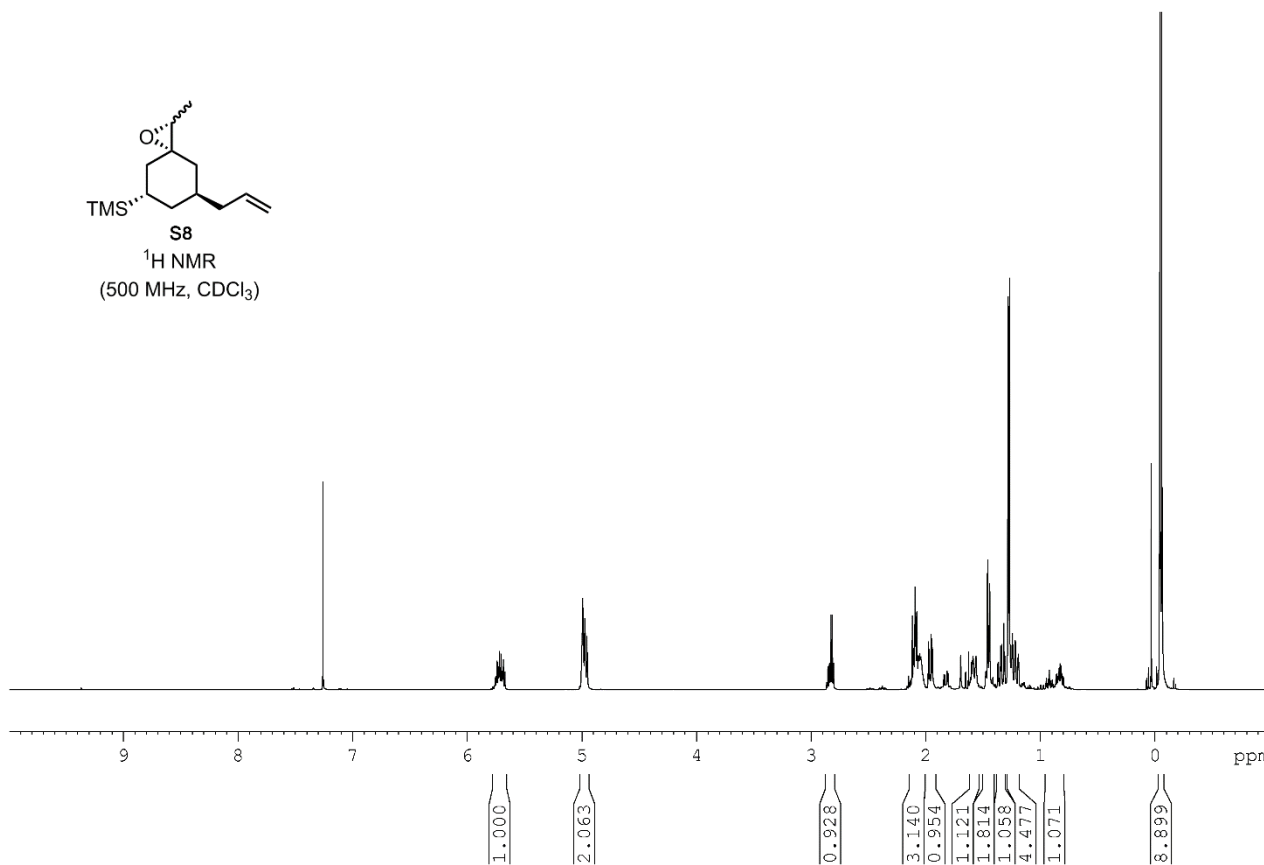


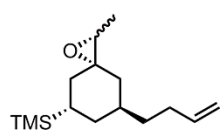


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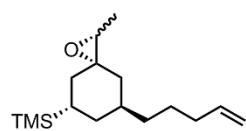
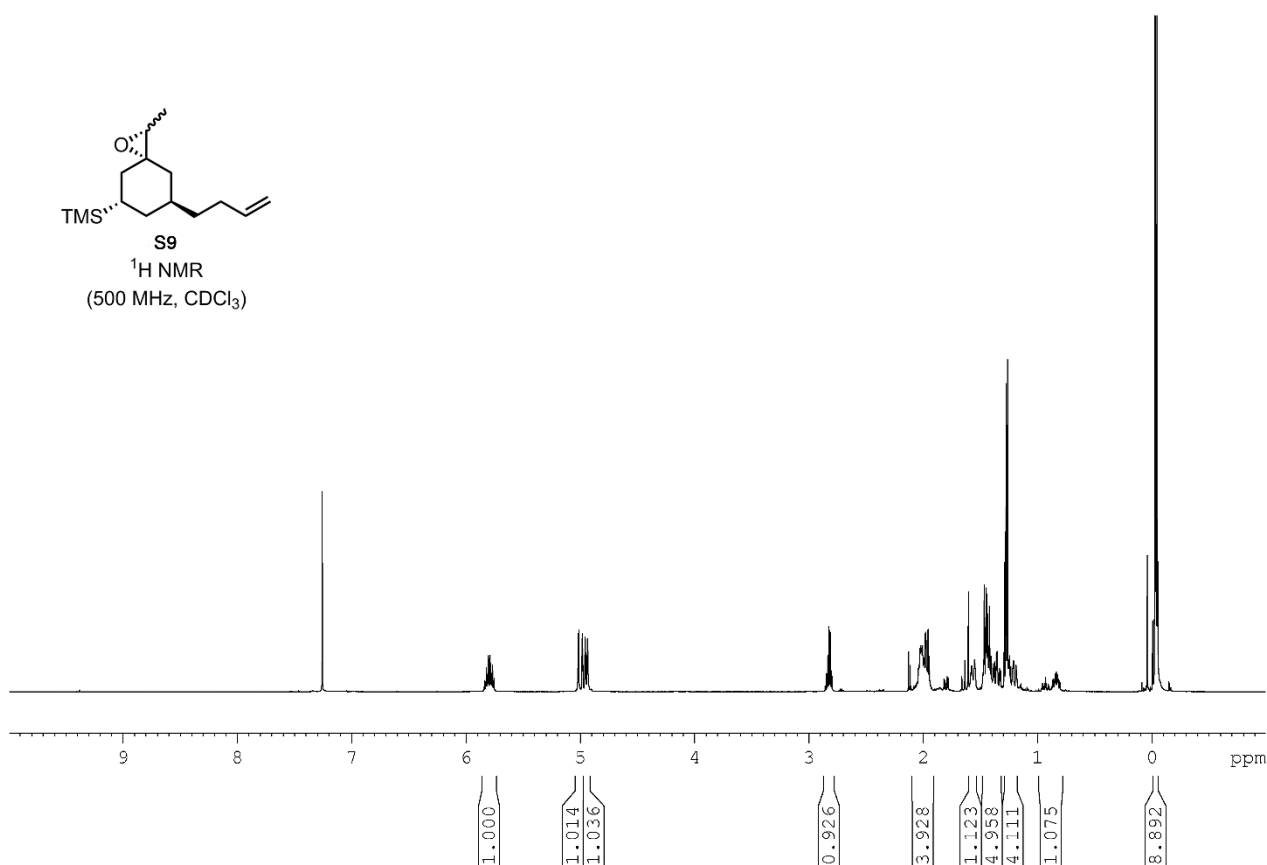


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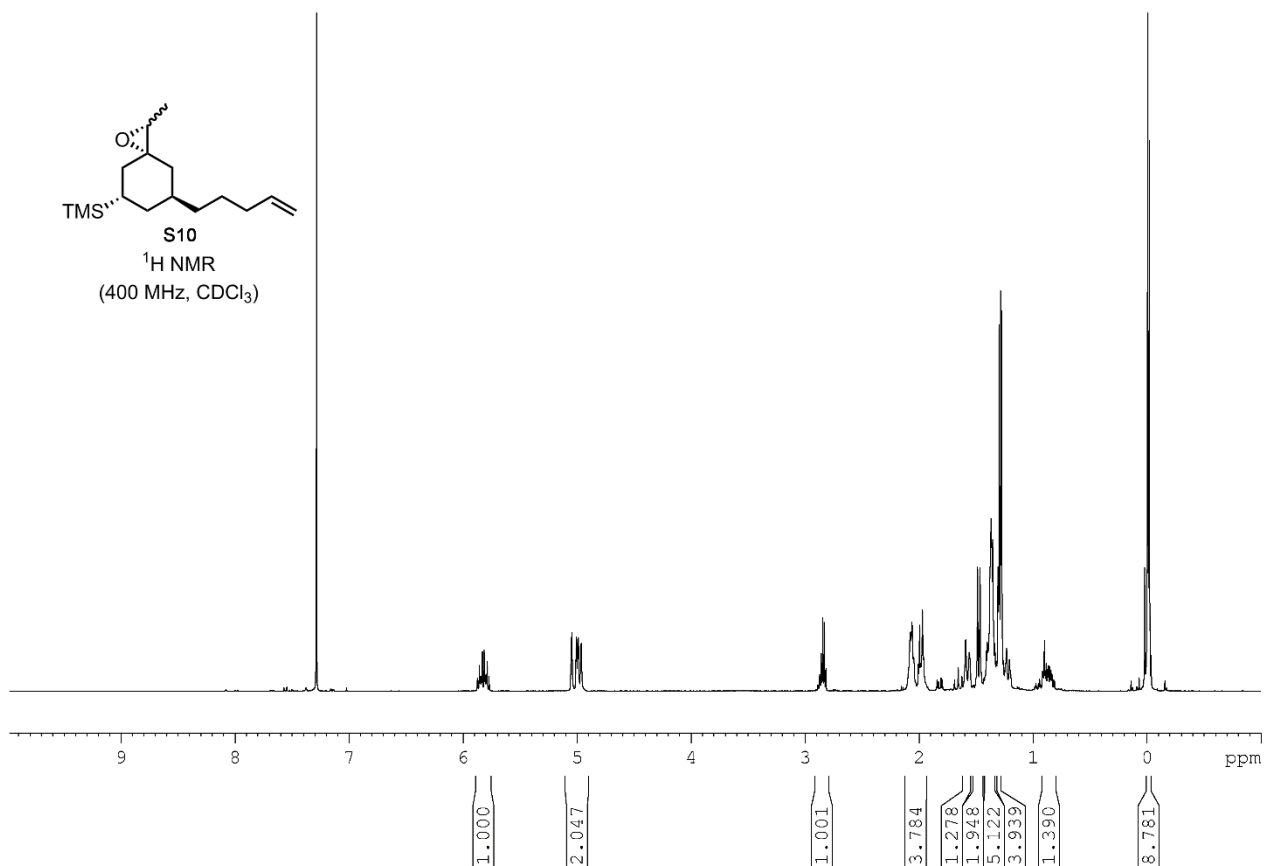


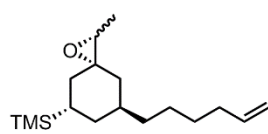


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¹H NMR
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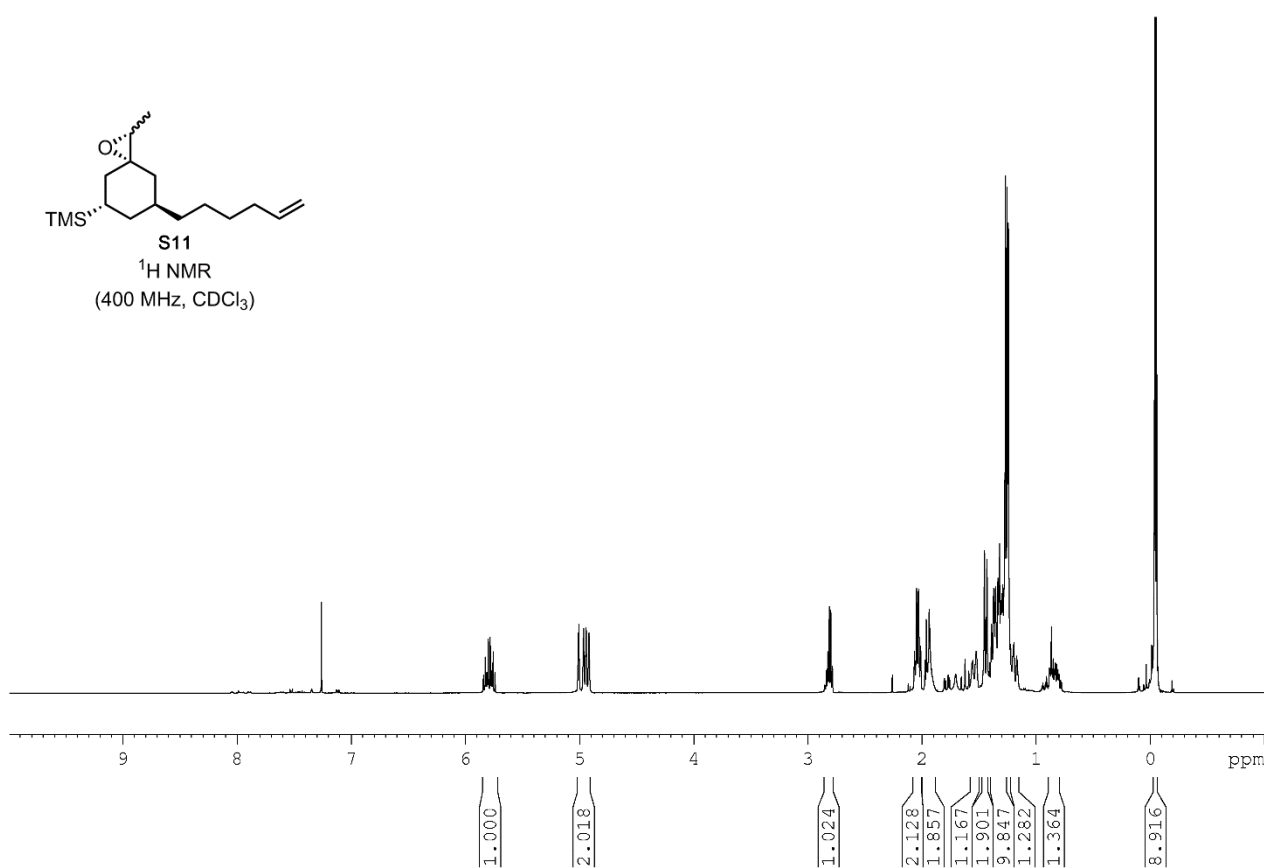


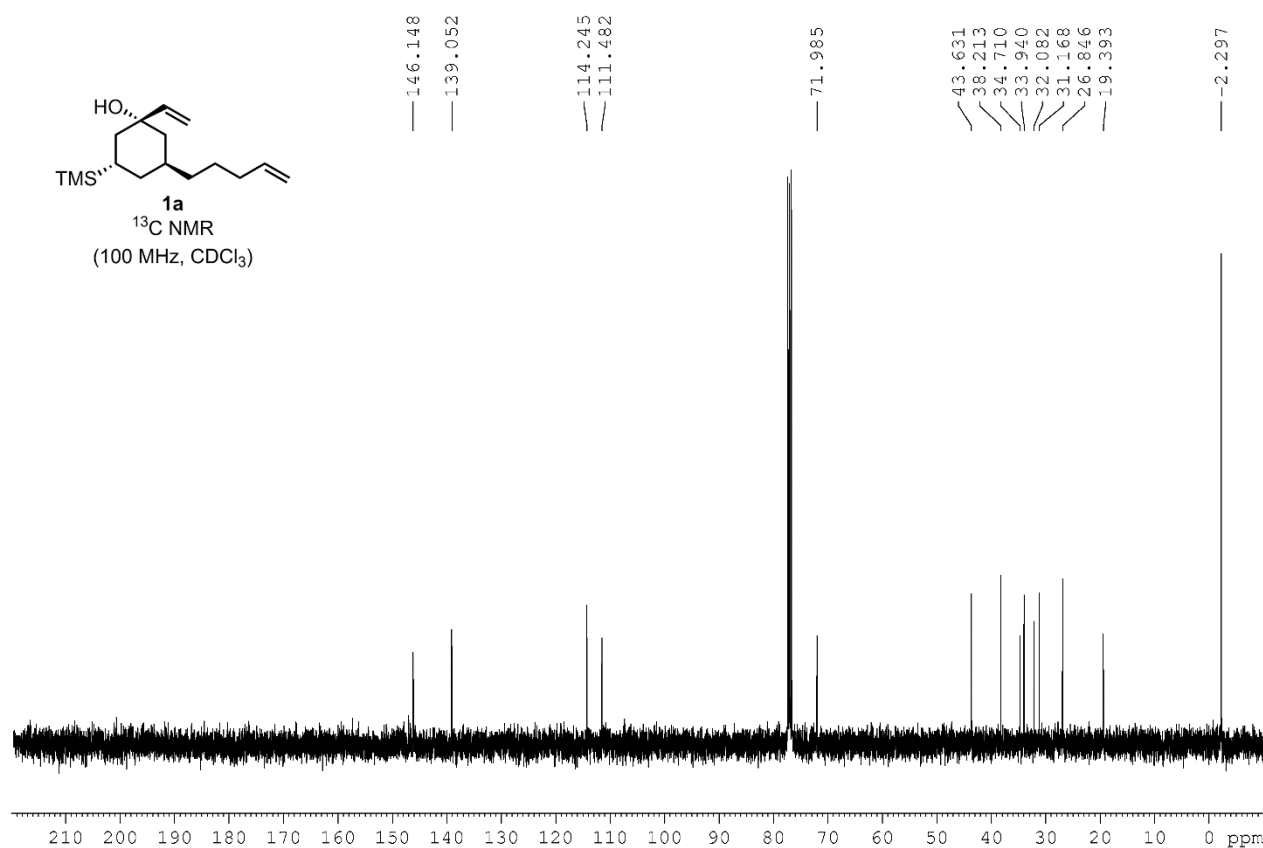
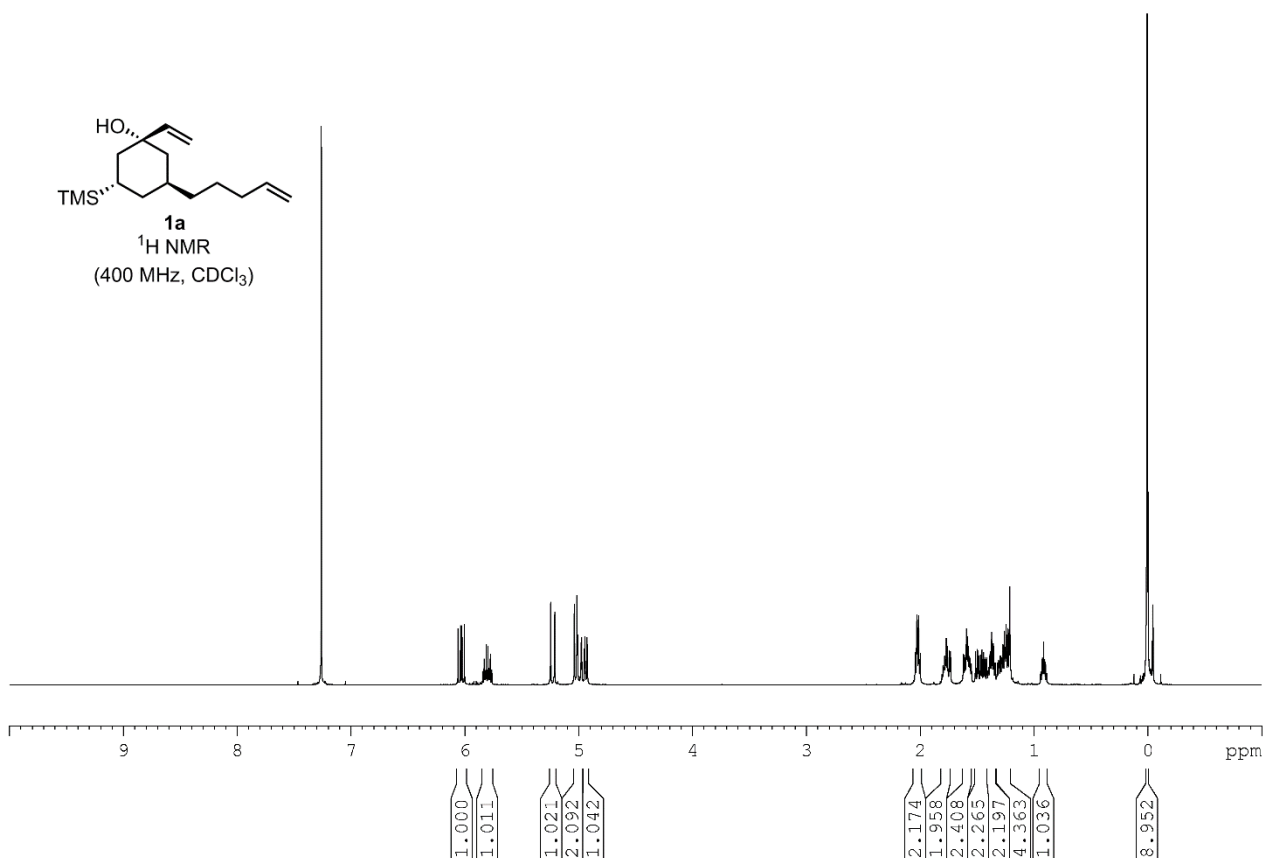
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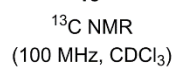
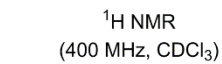


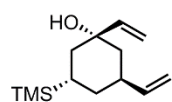


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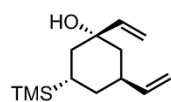
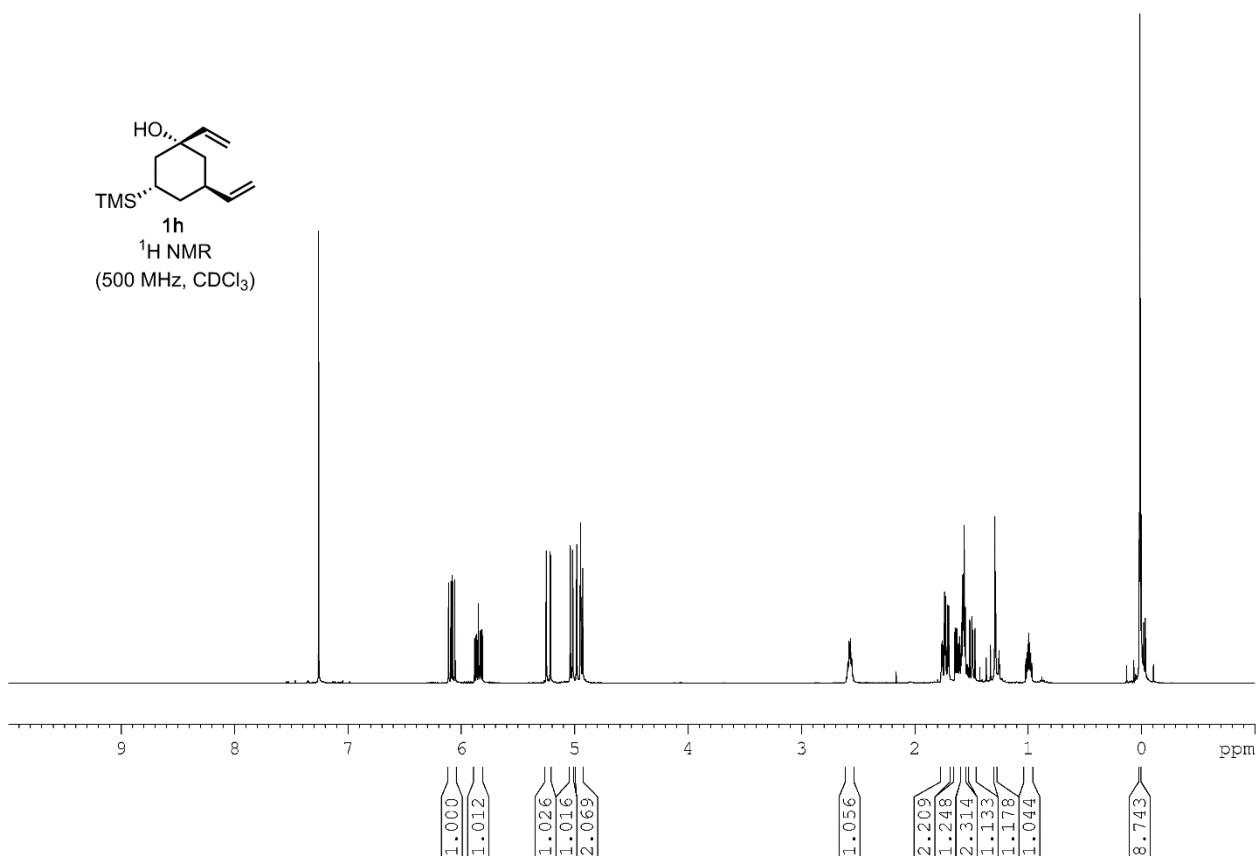




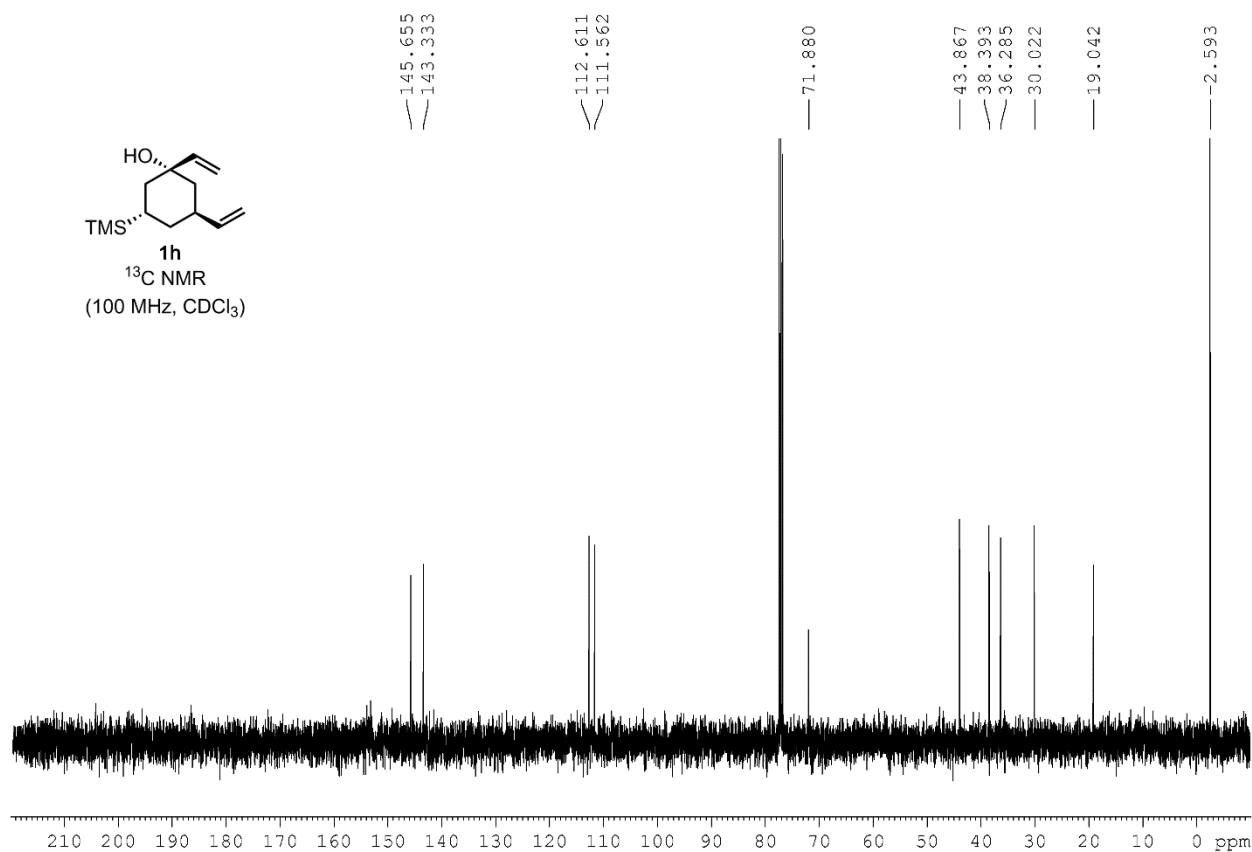


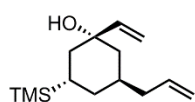


¹H NMR
(500 MHz, CDCl₃)

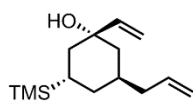
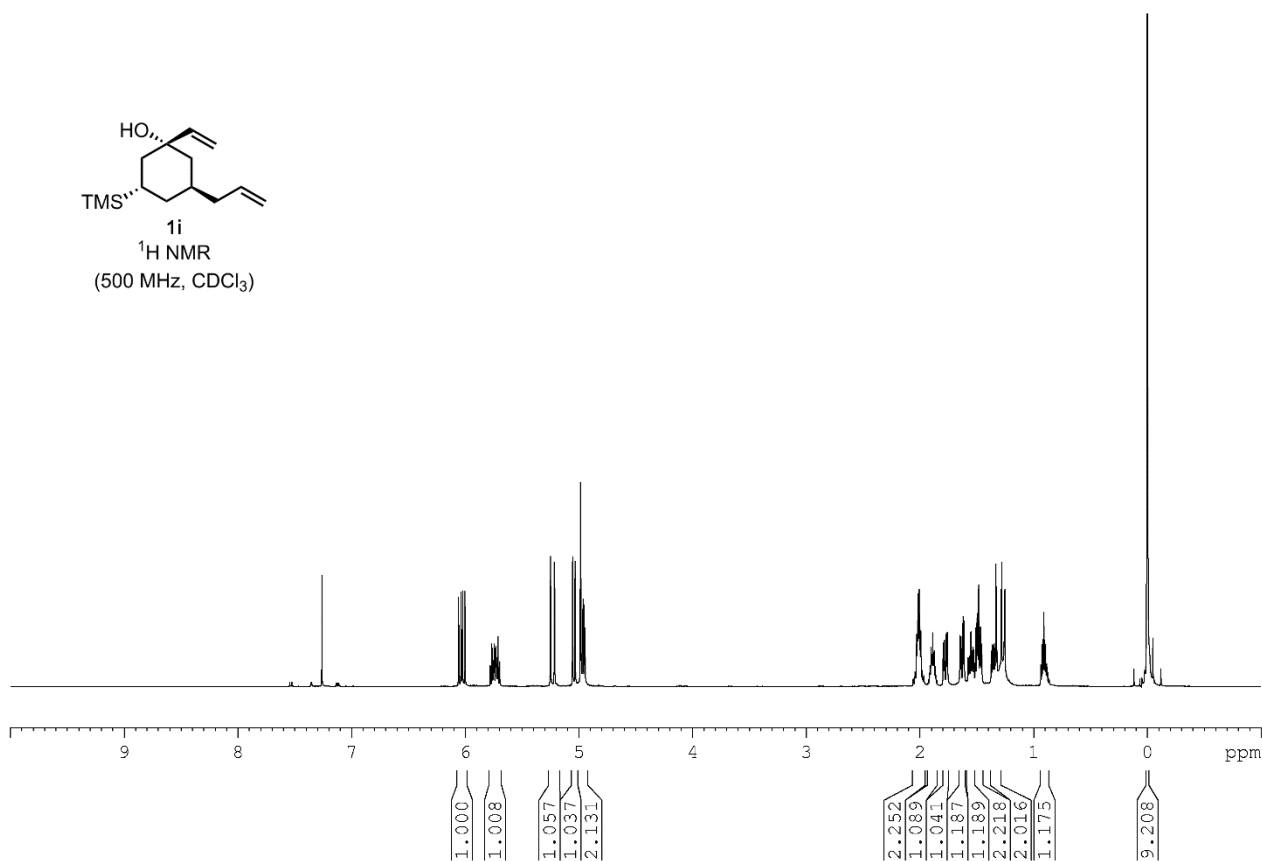


¹³C NMR
(100 MHz, CDCl₃)

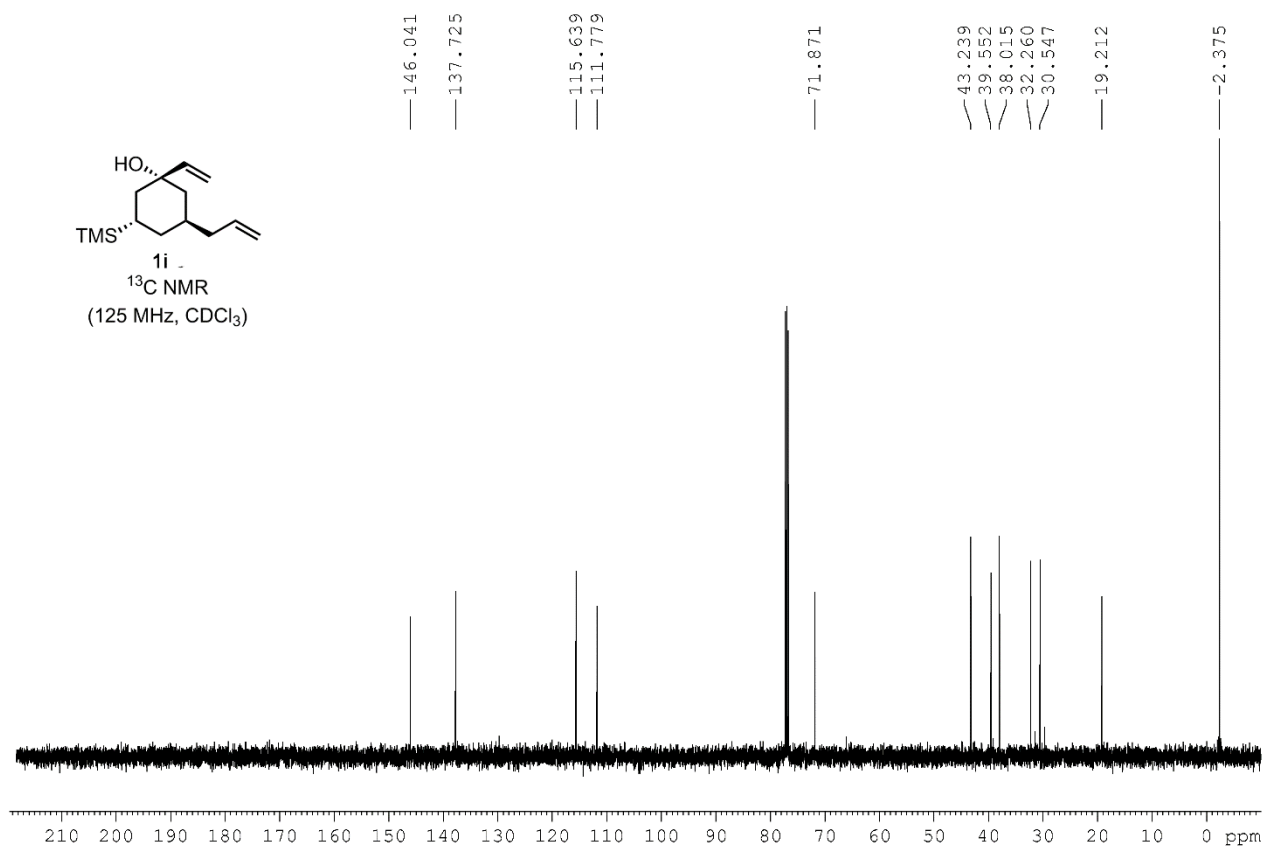


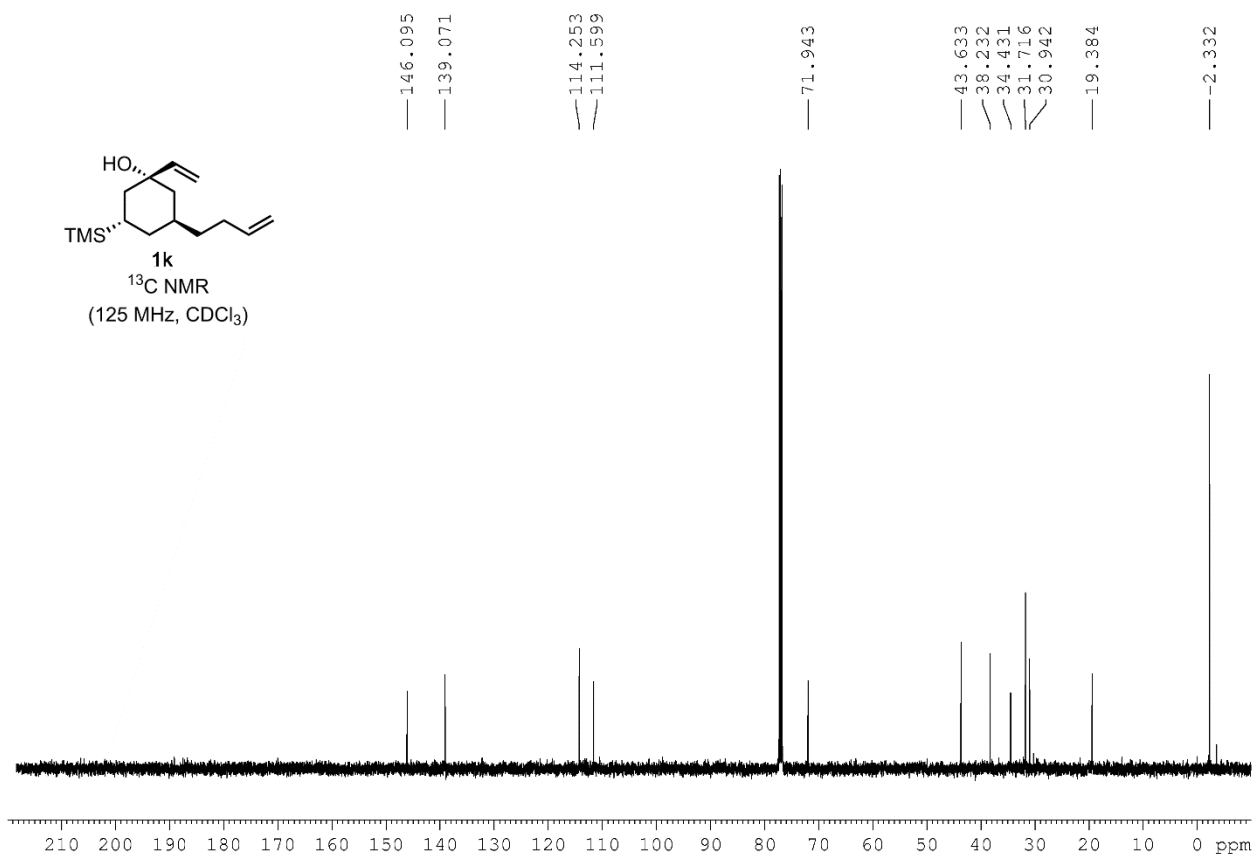
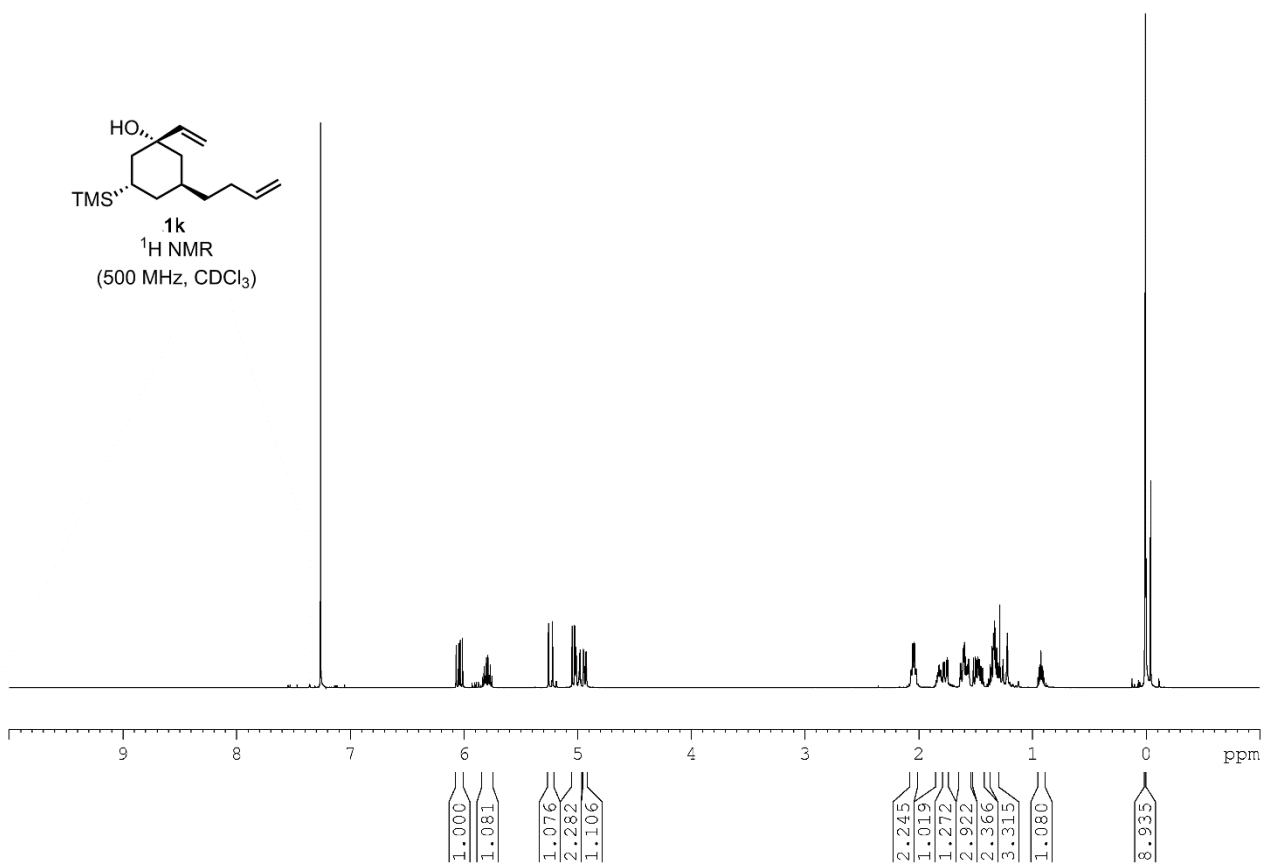


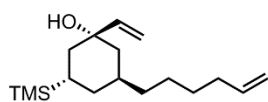
1i
¹H NMR
 (500 MHz, CDCl₃)



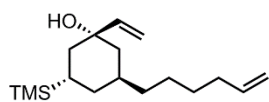
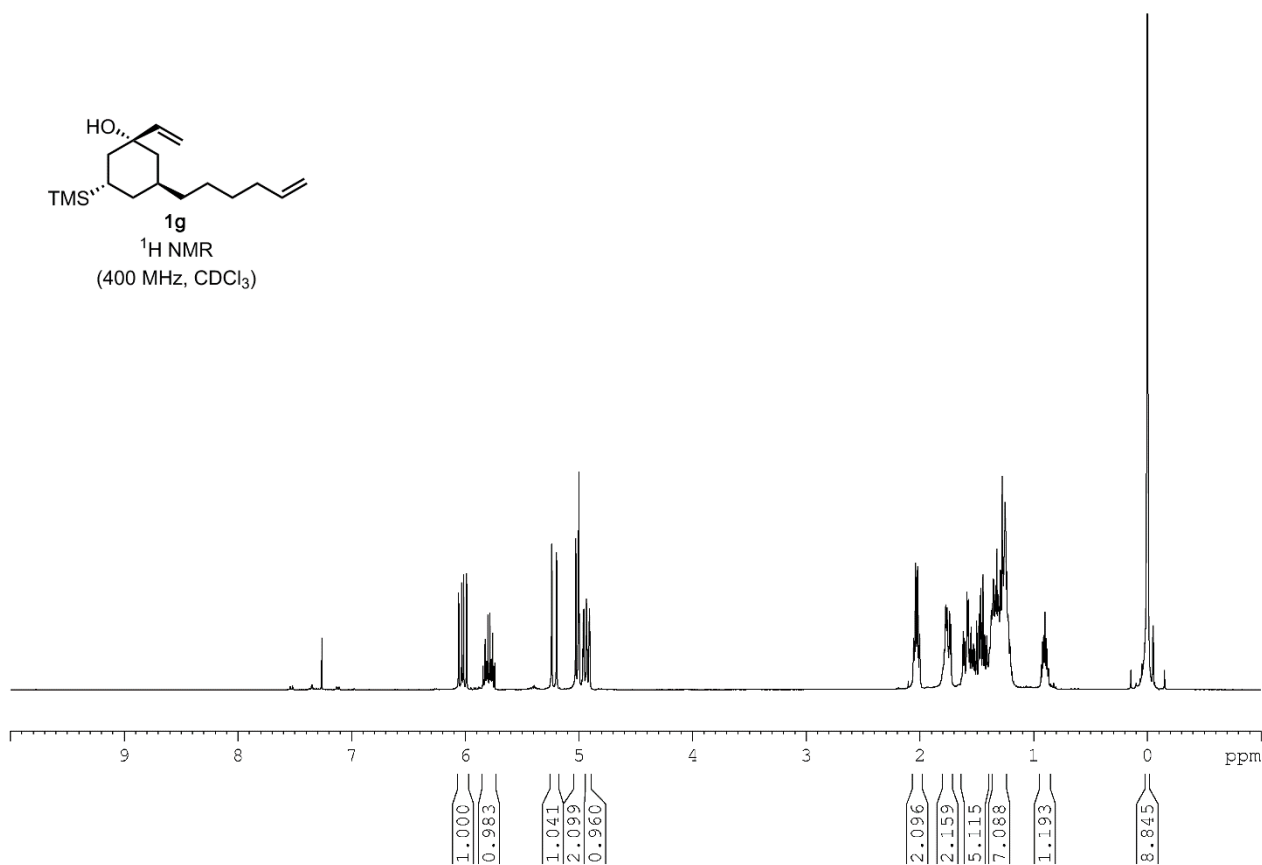
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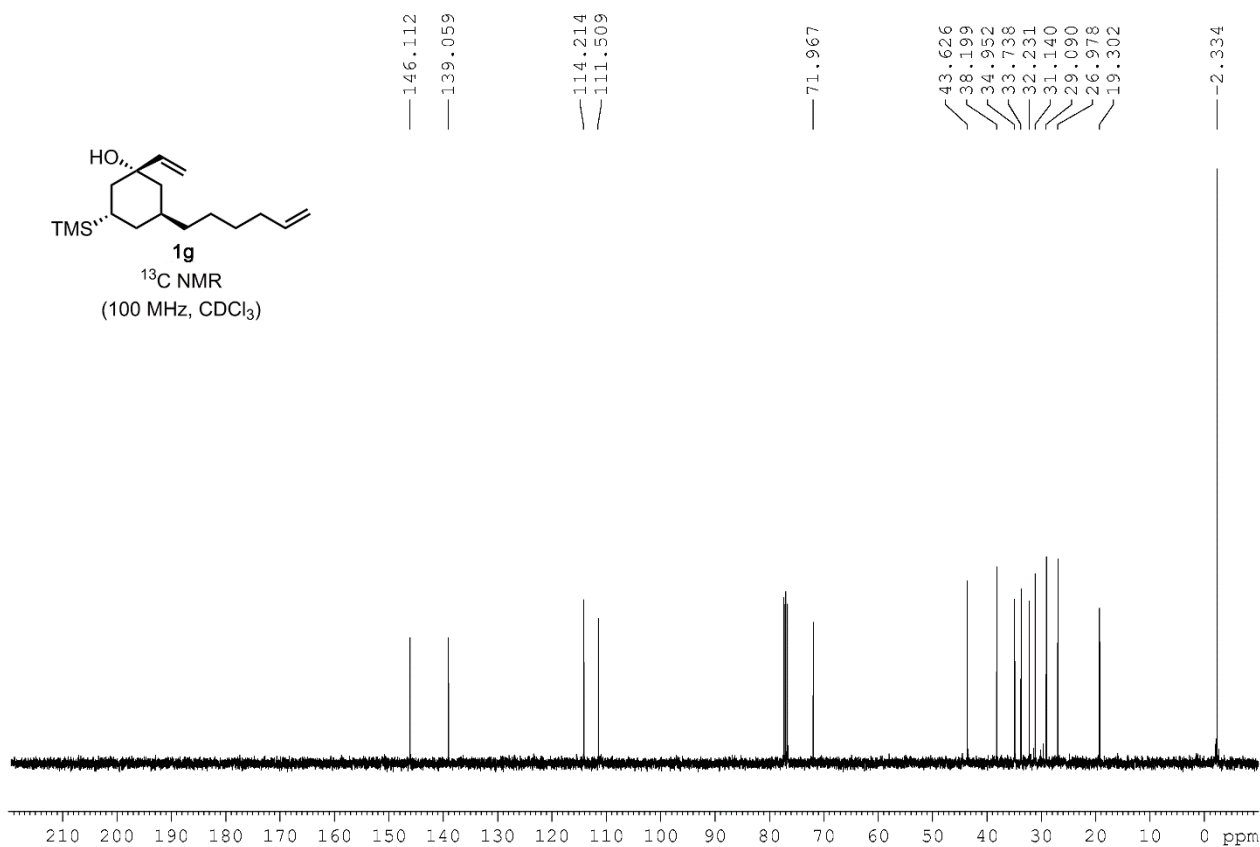


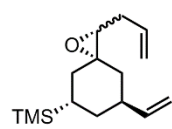


1g
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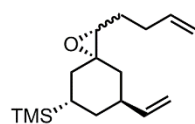
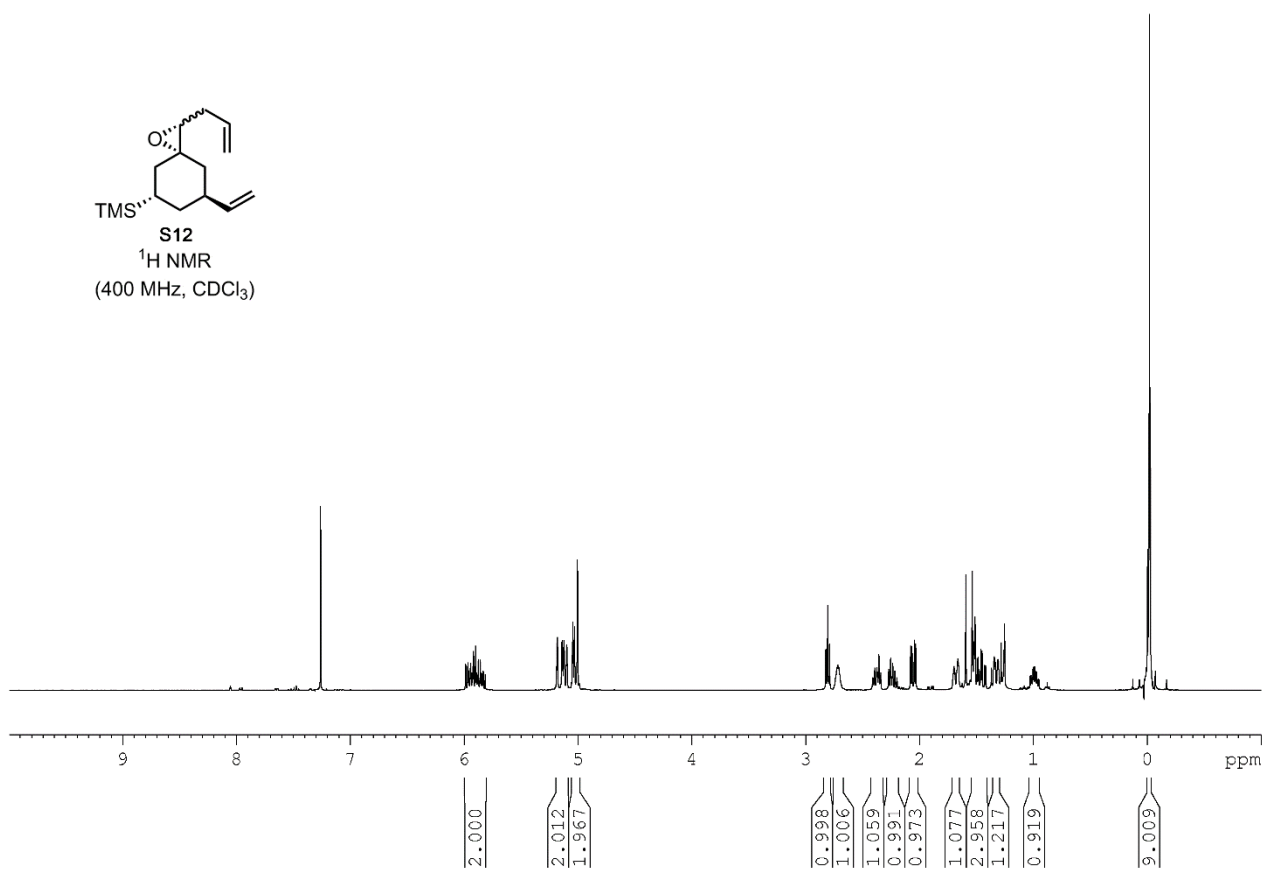


1g
 ^{13}C NMR
 (100 MHz, CDCl_3)

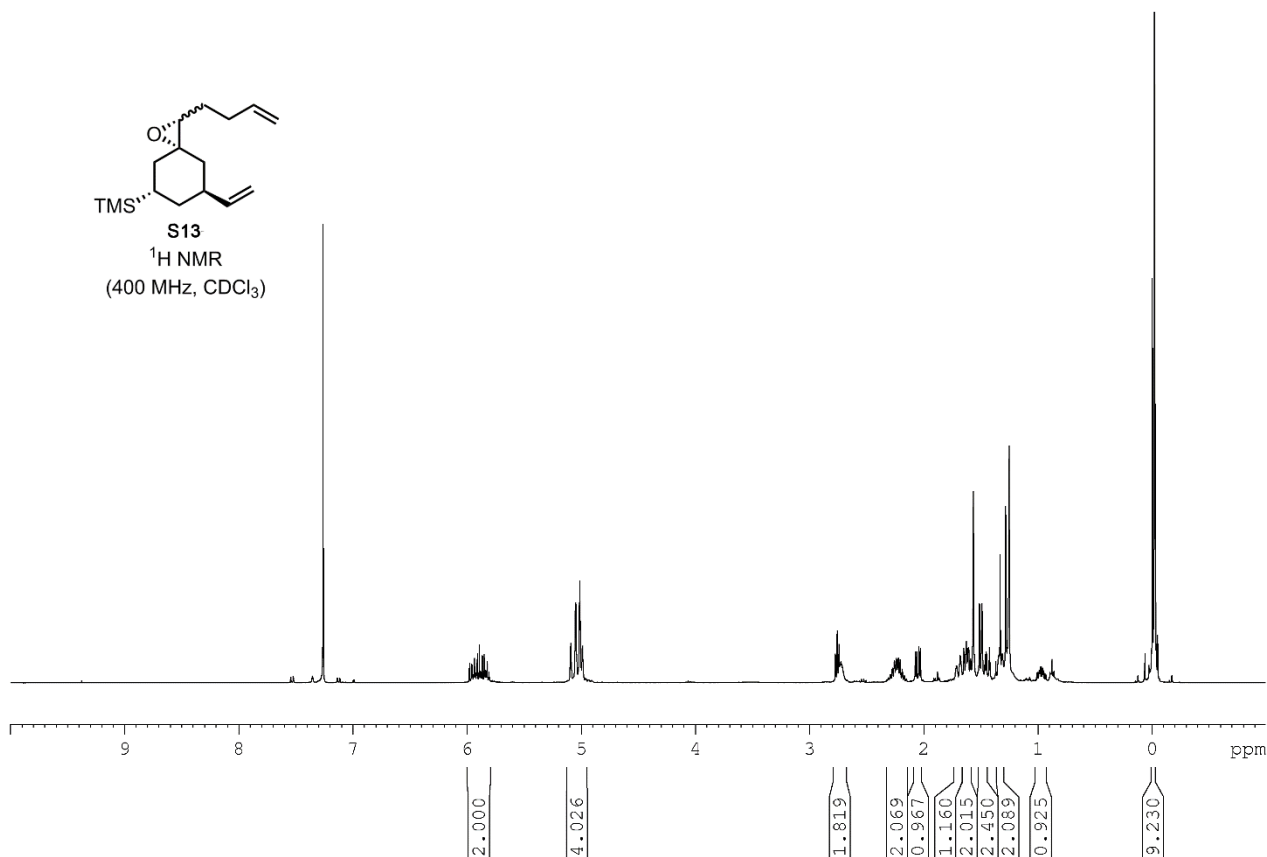


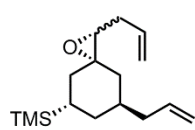


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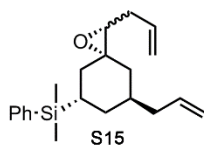
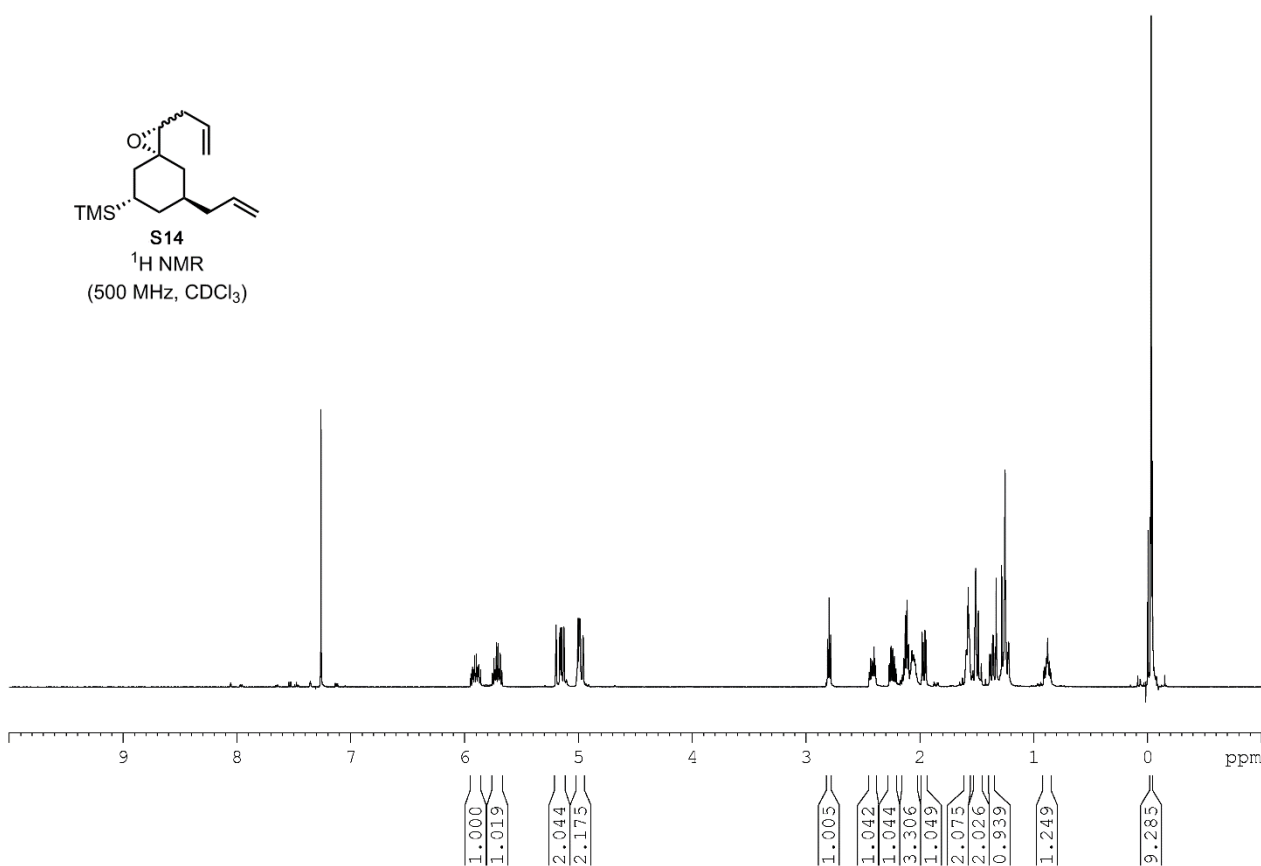


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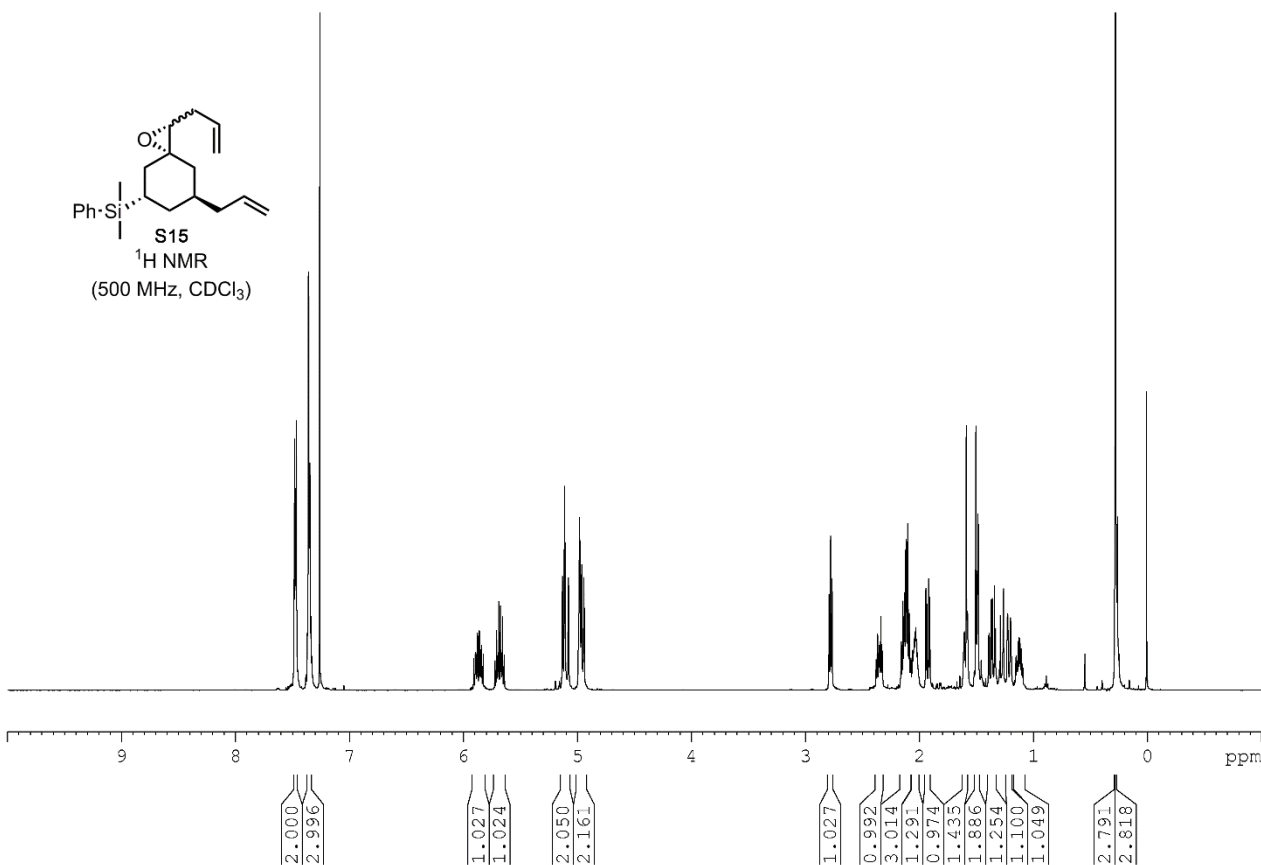


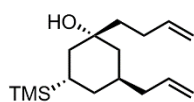


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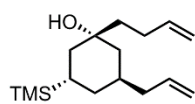
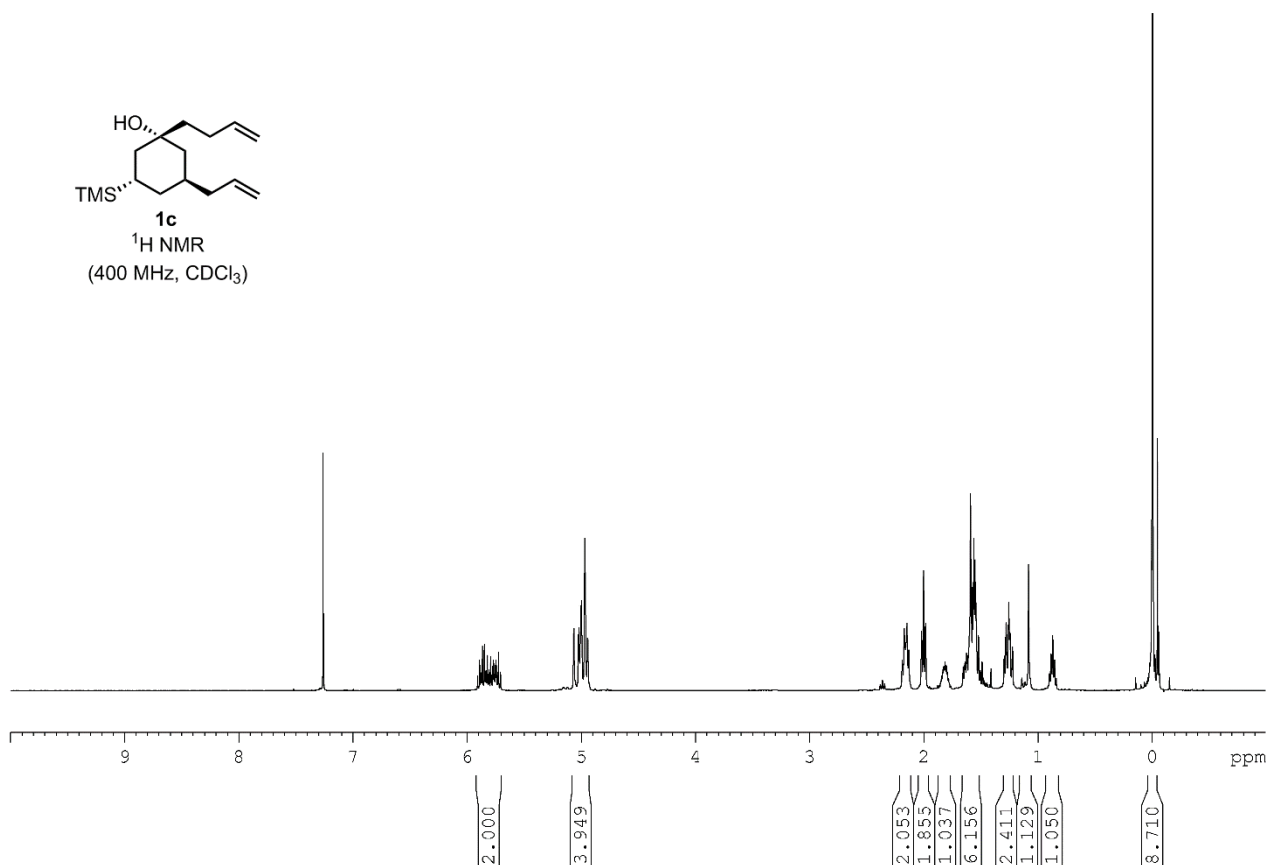


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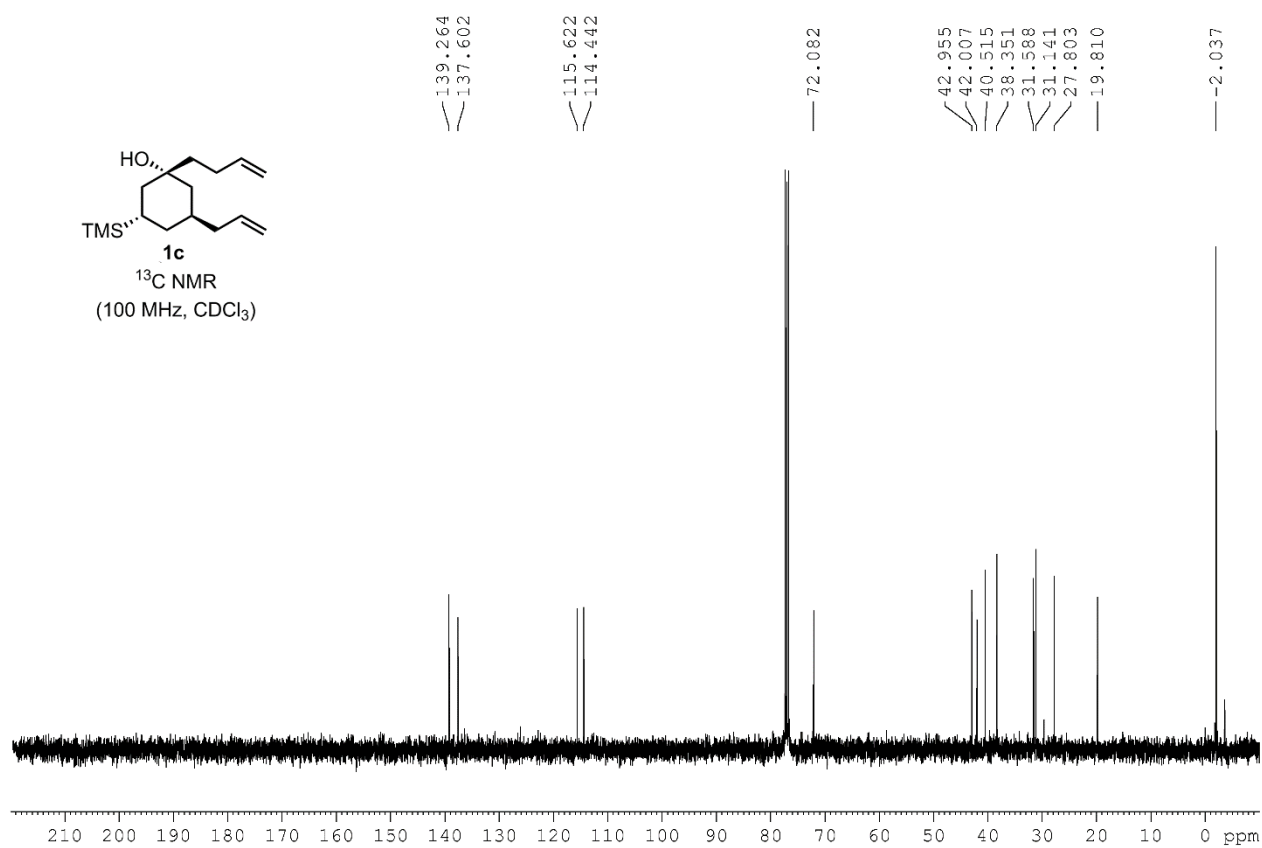


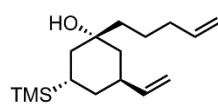


¹H NMR
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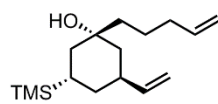
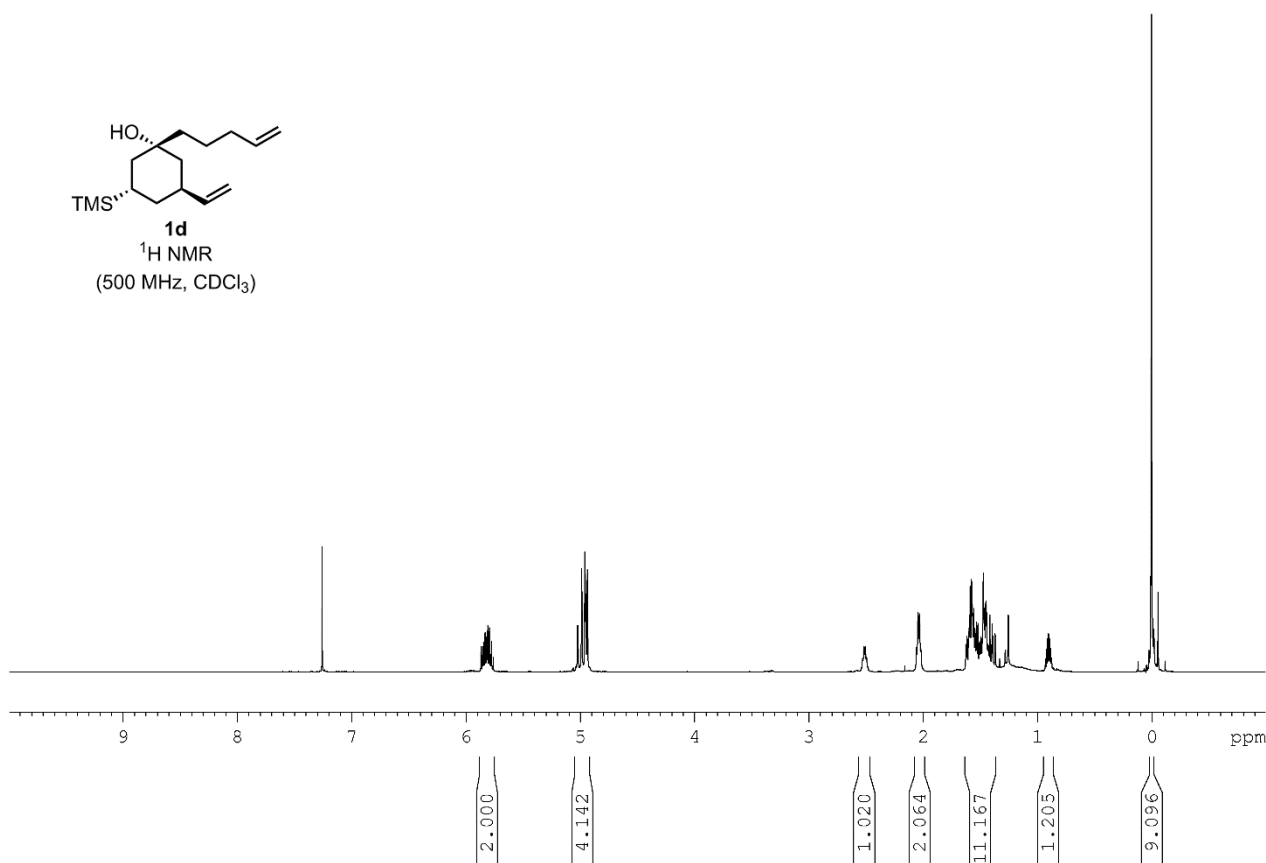


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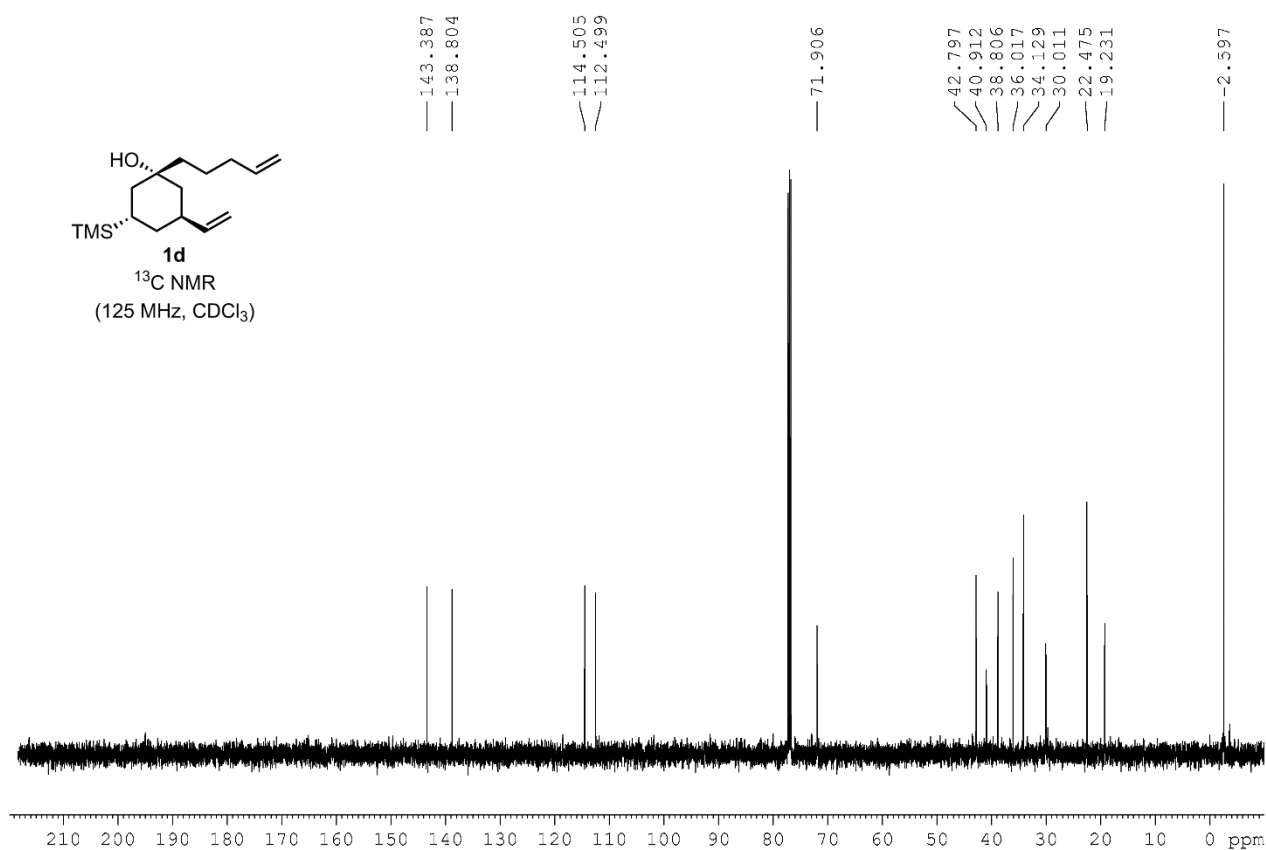


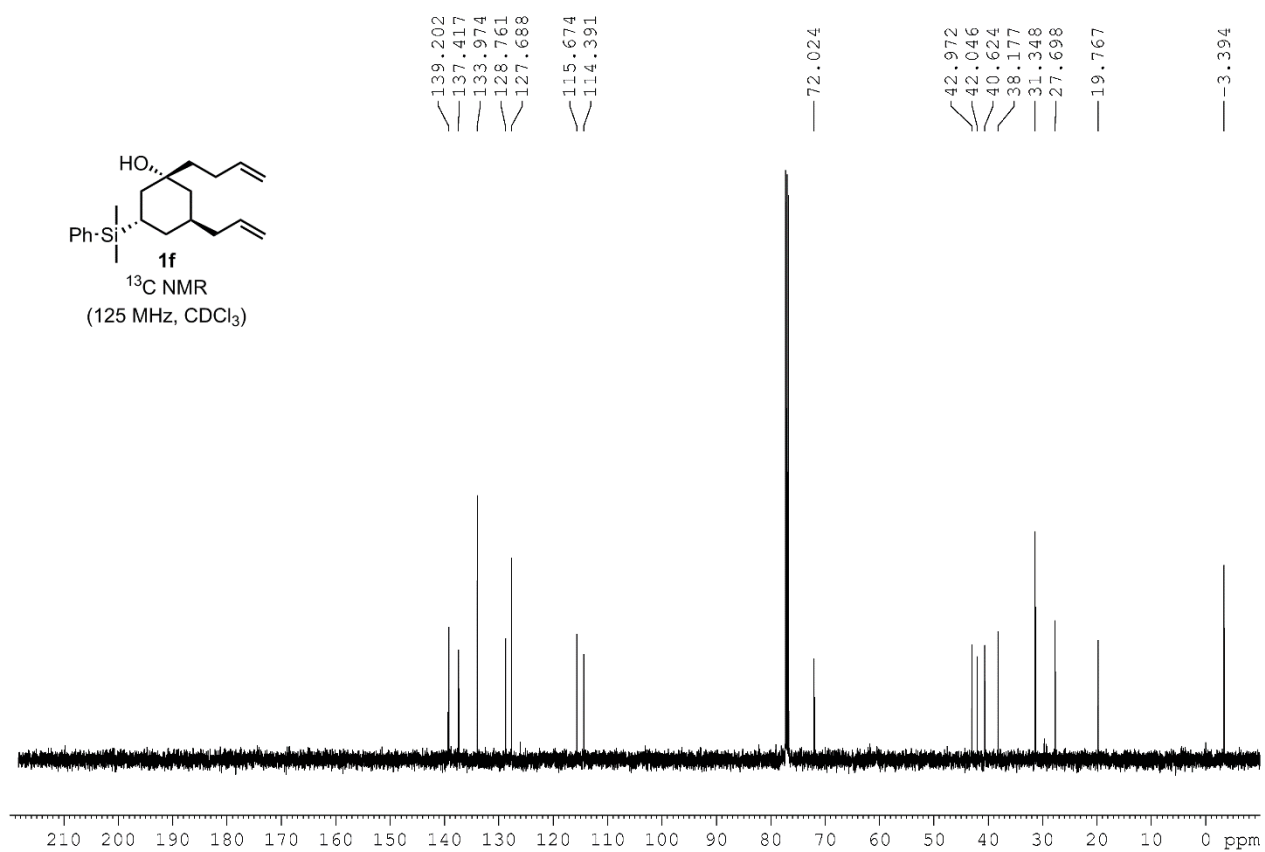
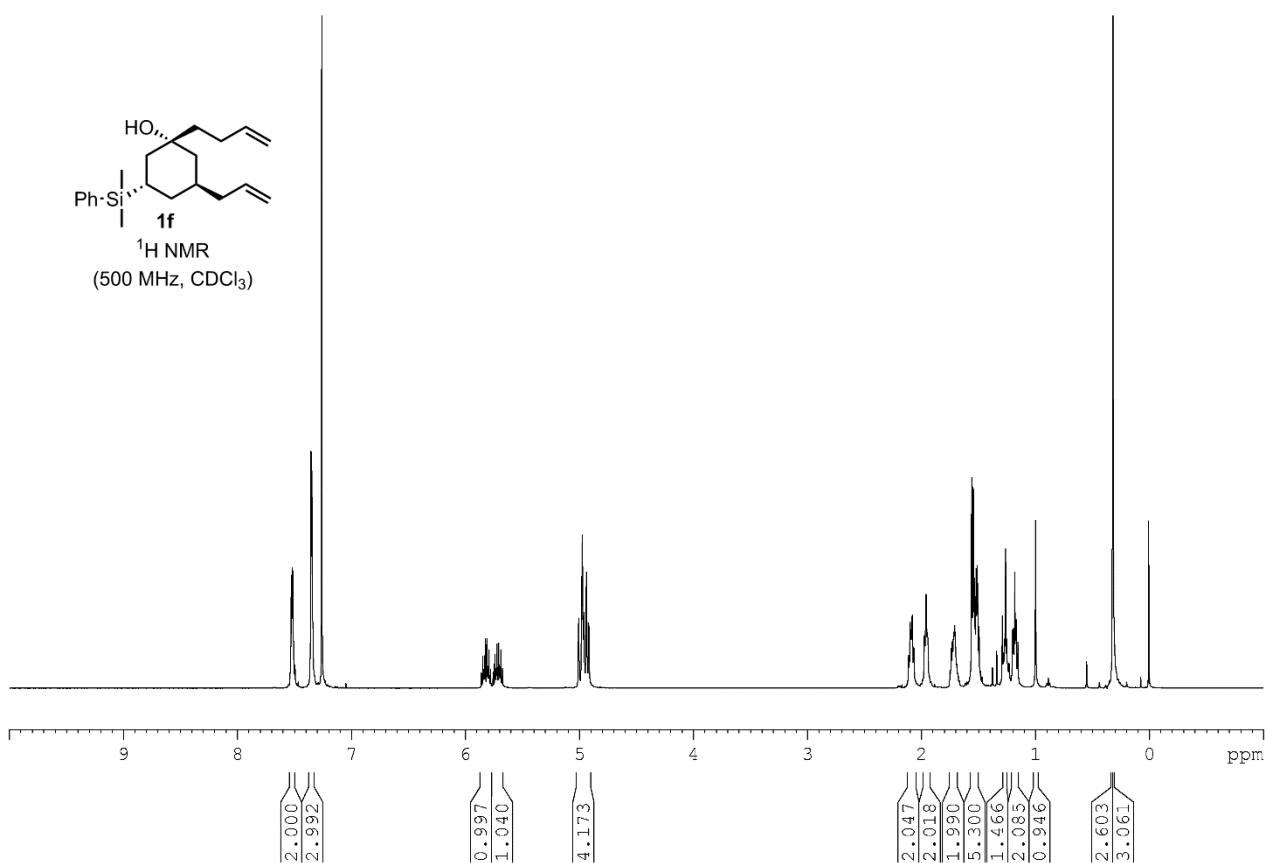


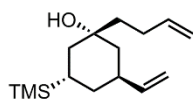
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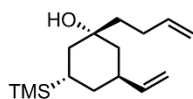
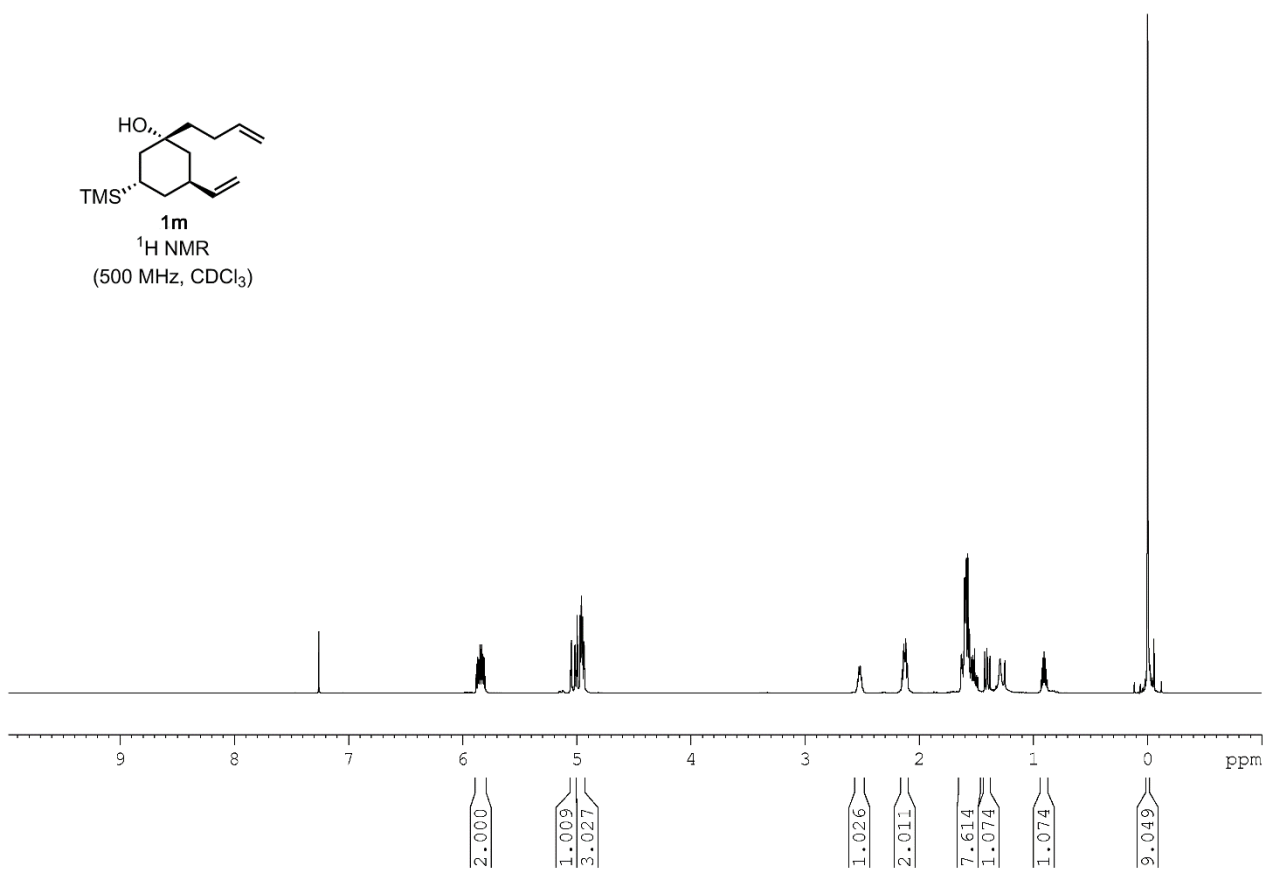
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(125 MHz, CDCl_3)



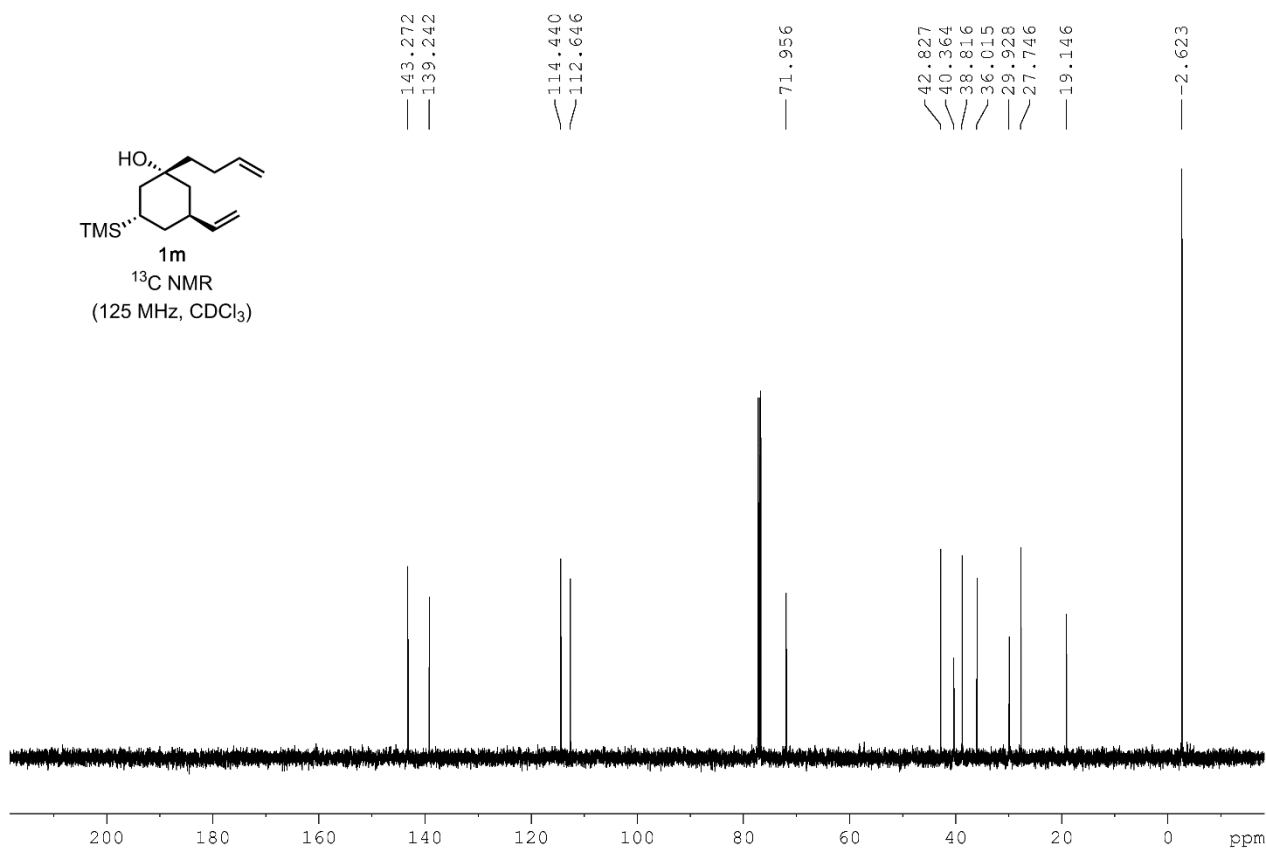


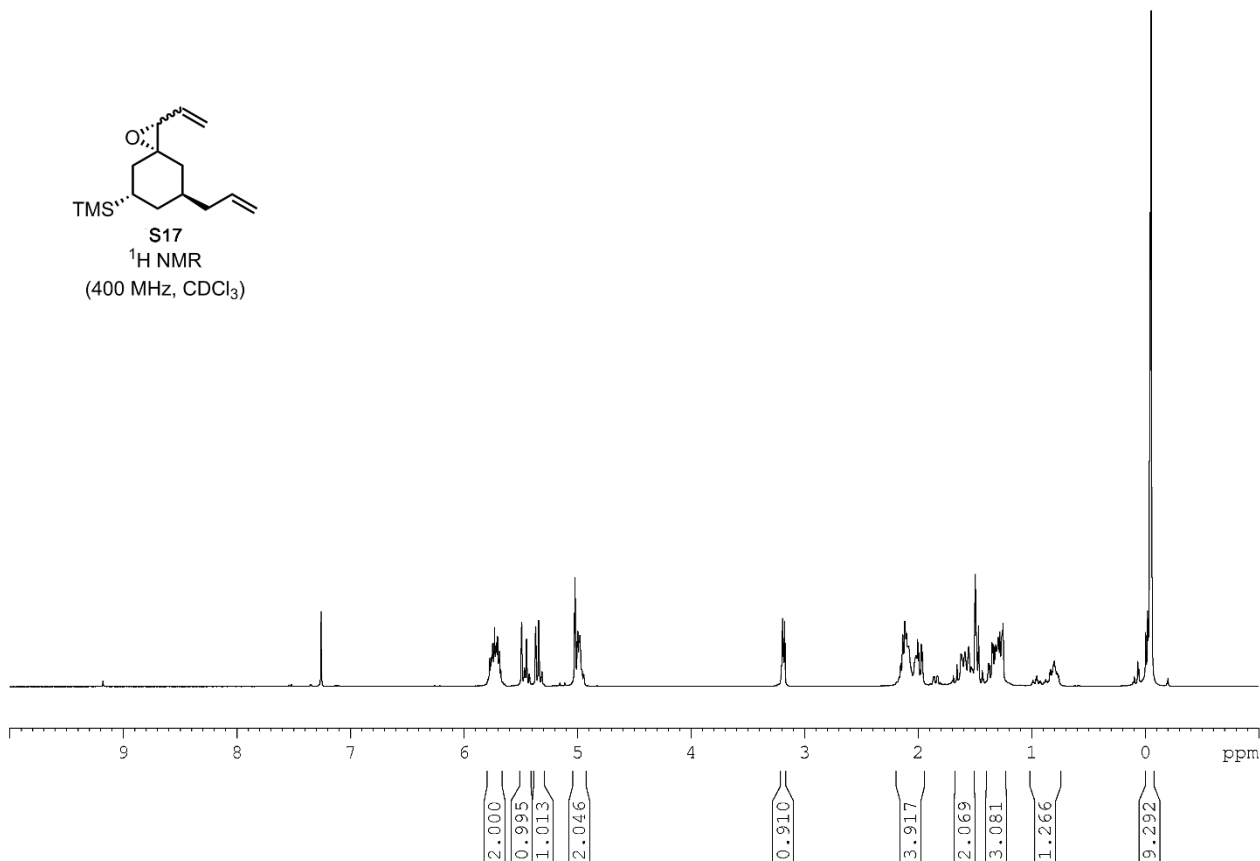
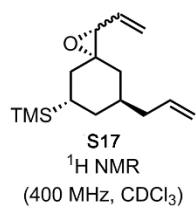
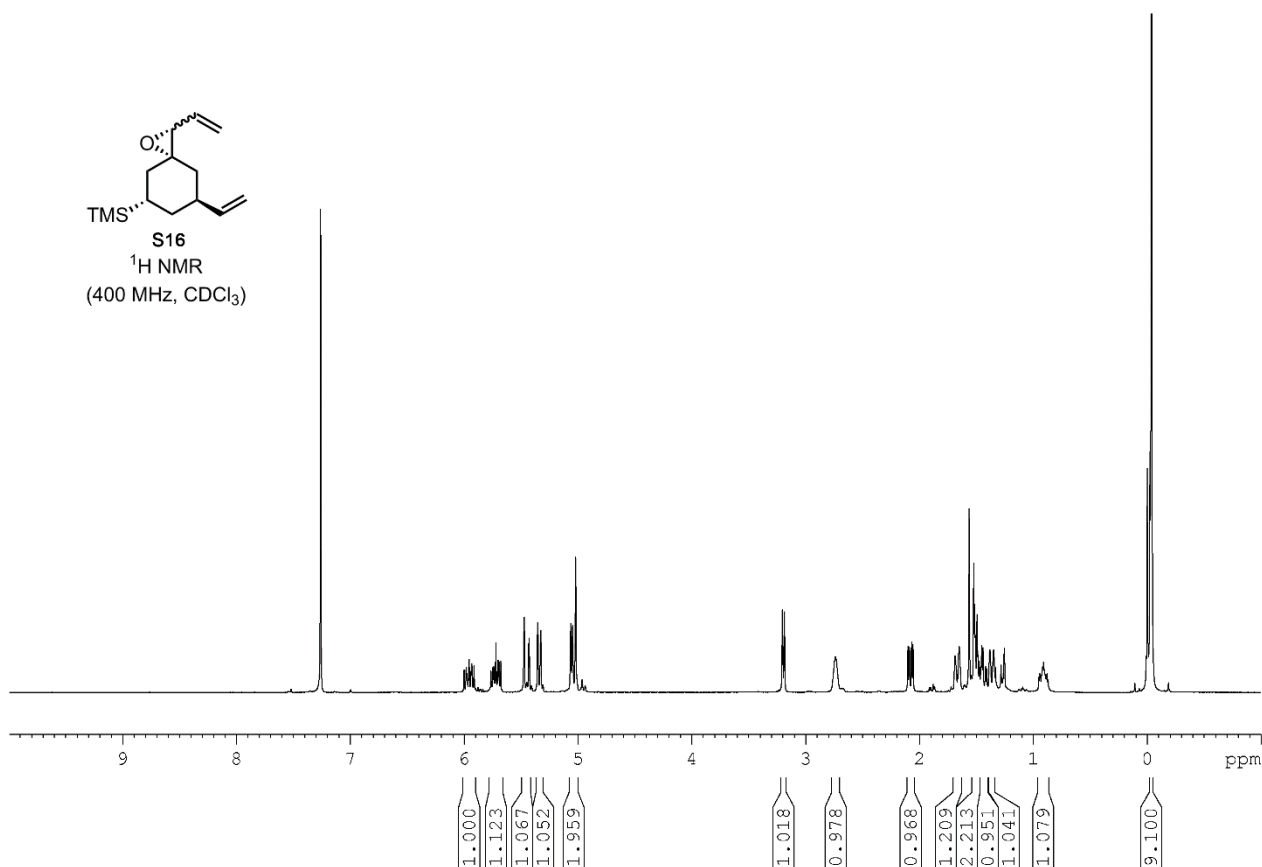
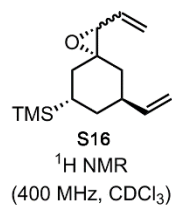


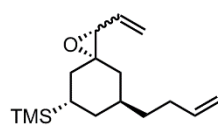
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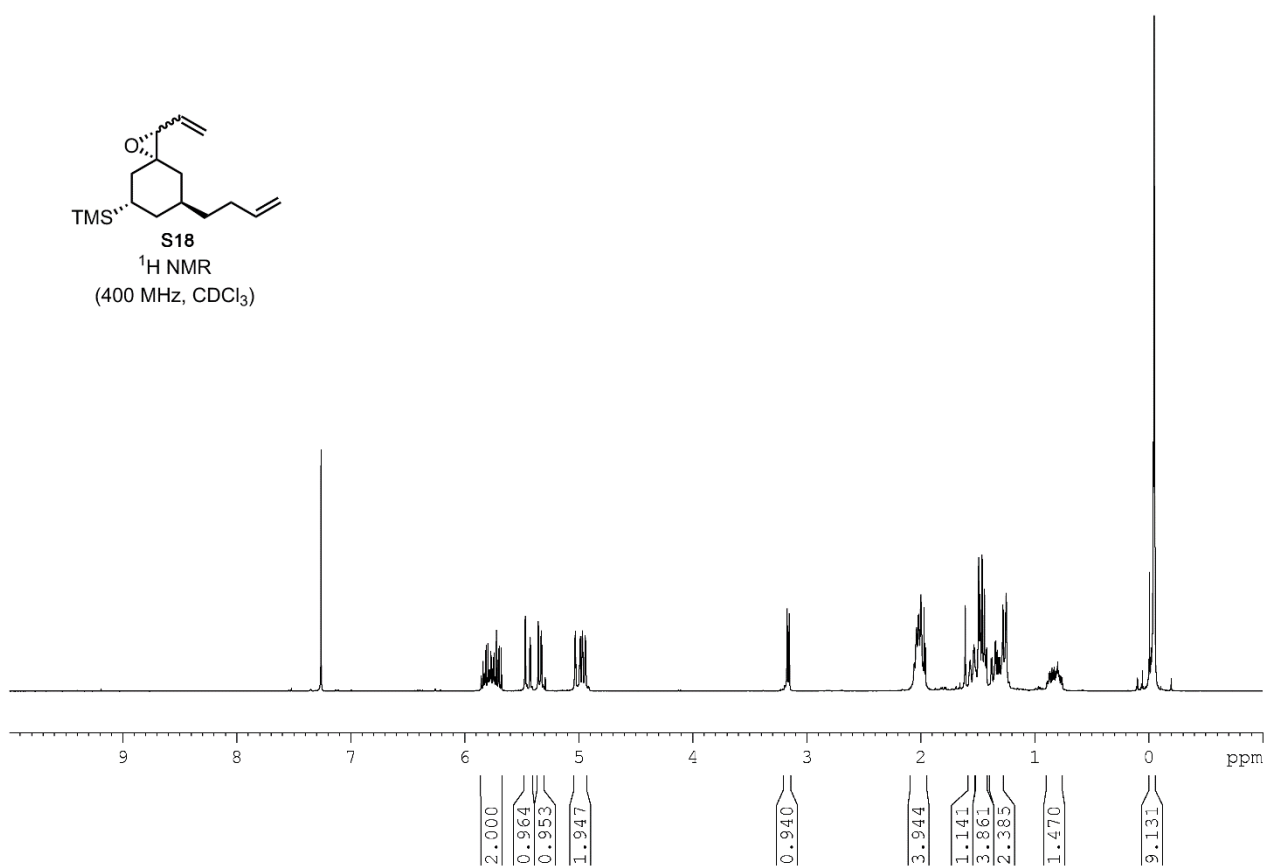
¹³C NMR
(125 MHz, CDCl₃)

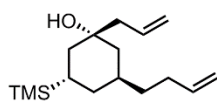




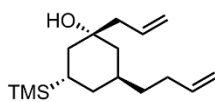
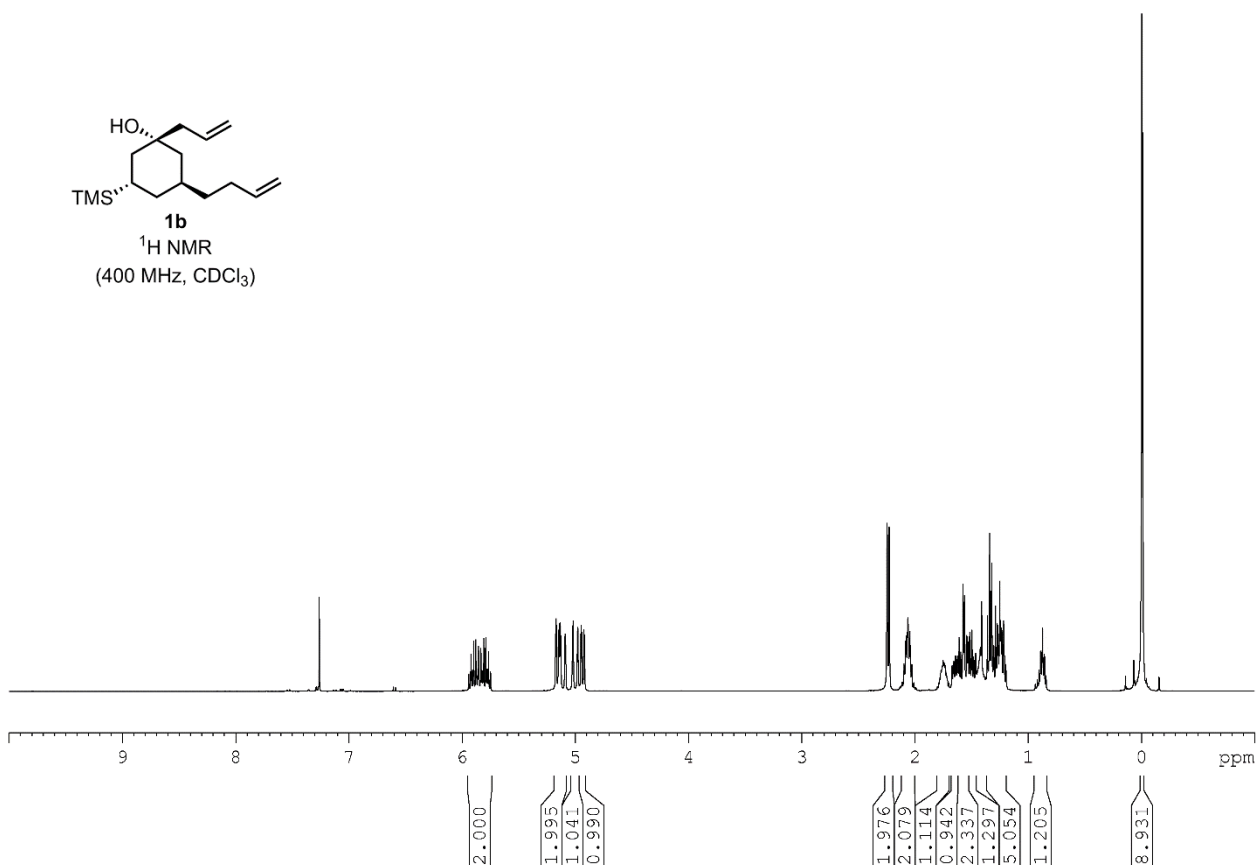


S18
 ^1H NMR
 (400 MHz, CDCl_3)

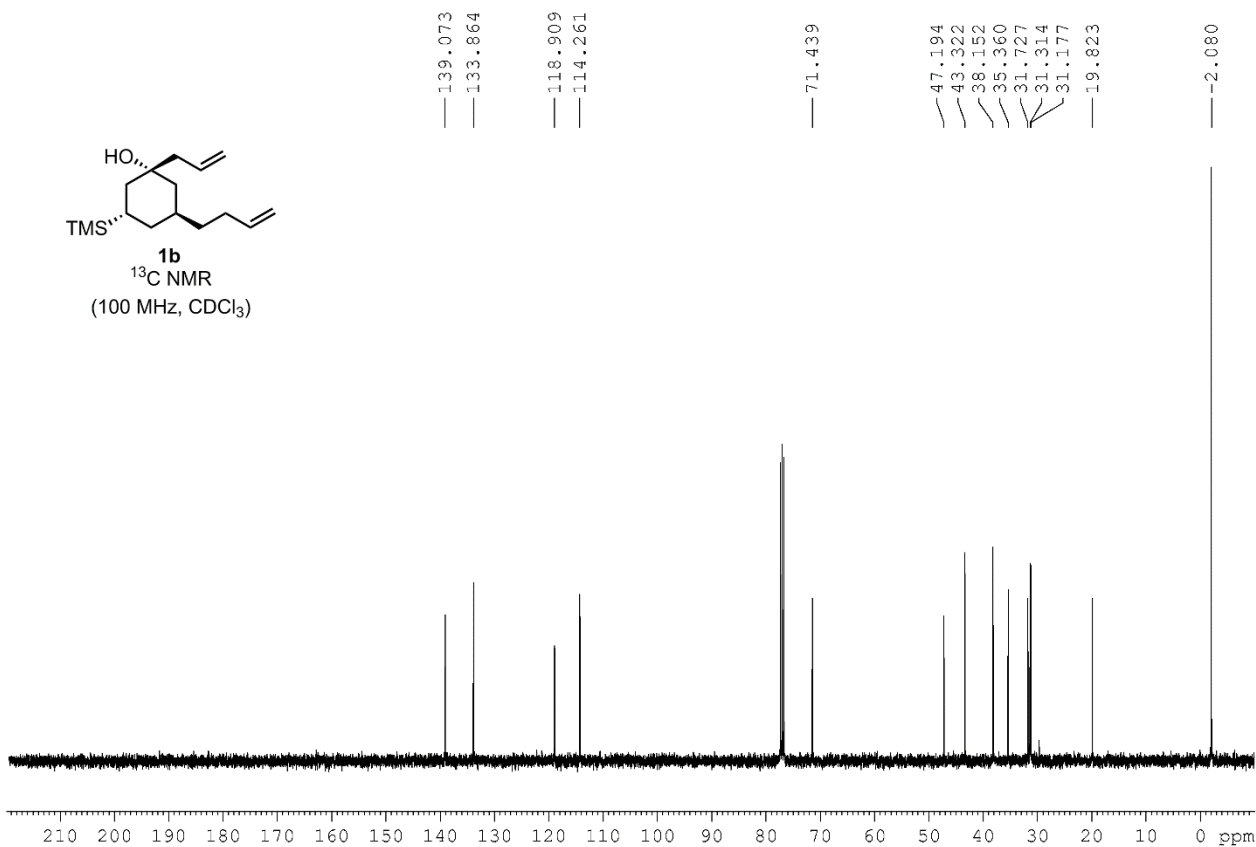


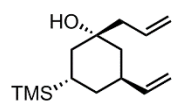


^1H NMR
(400 MHz, CDCl_3)

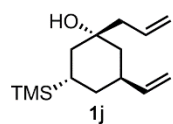
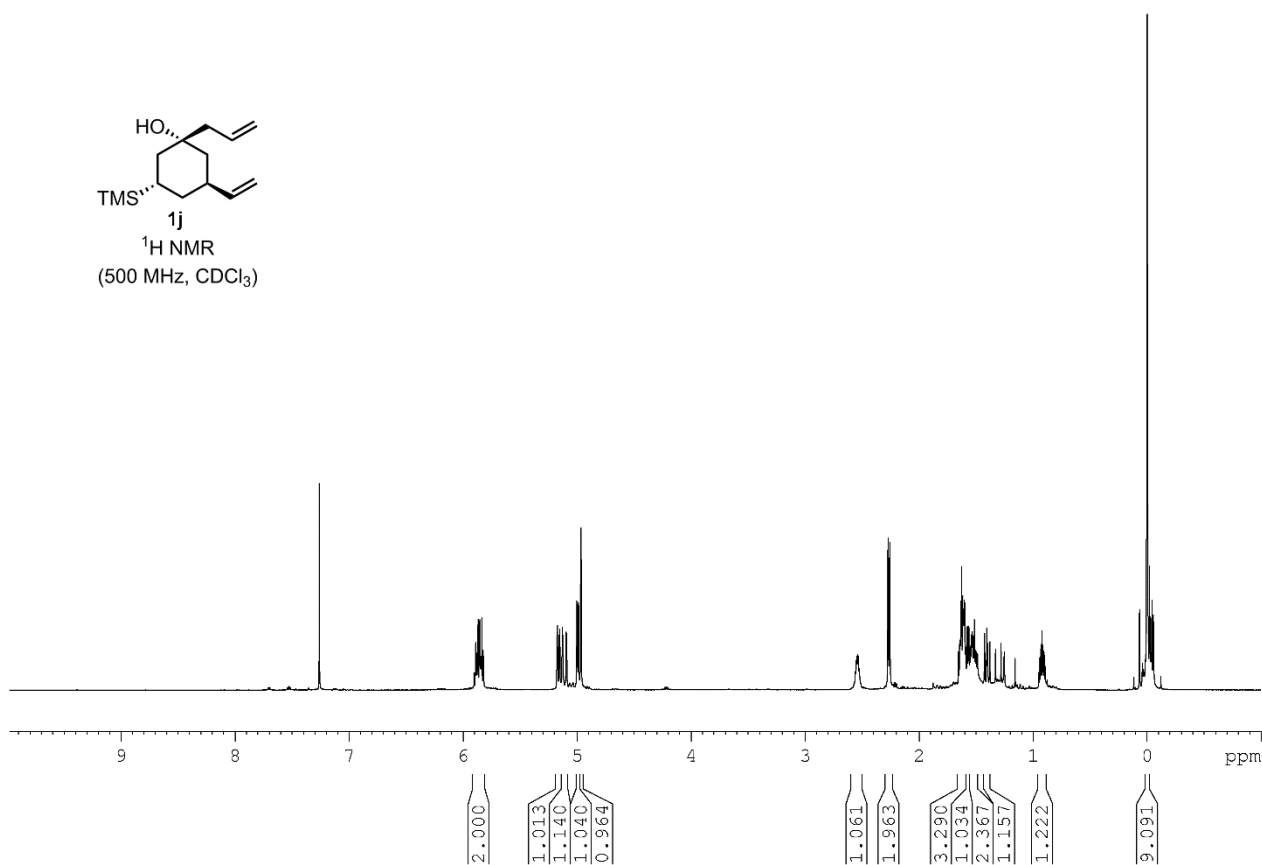


^{13}C NMR
(100 MHz, CDCl_3)

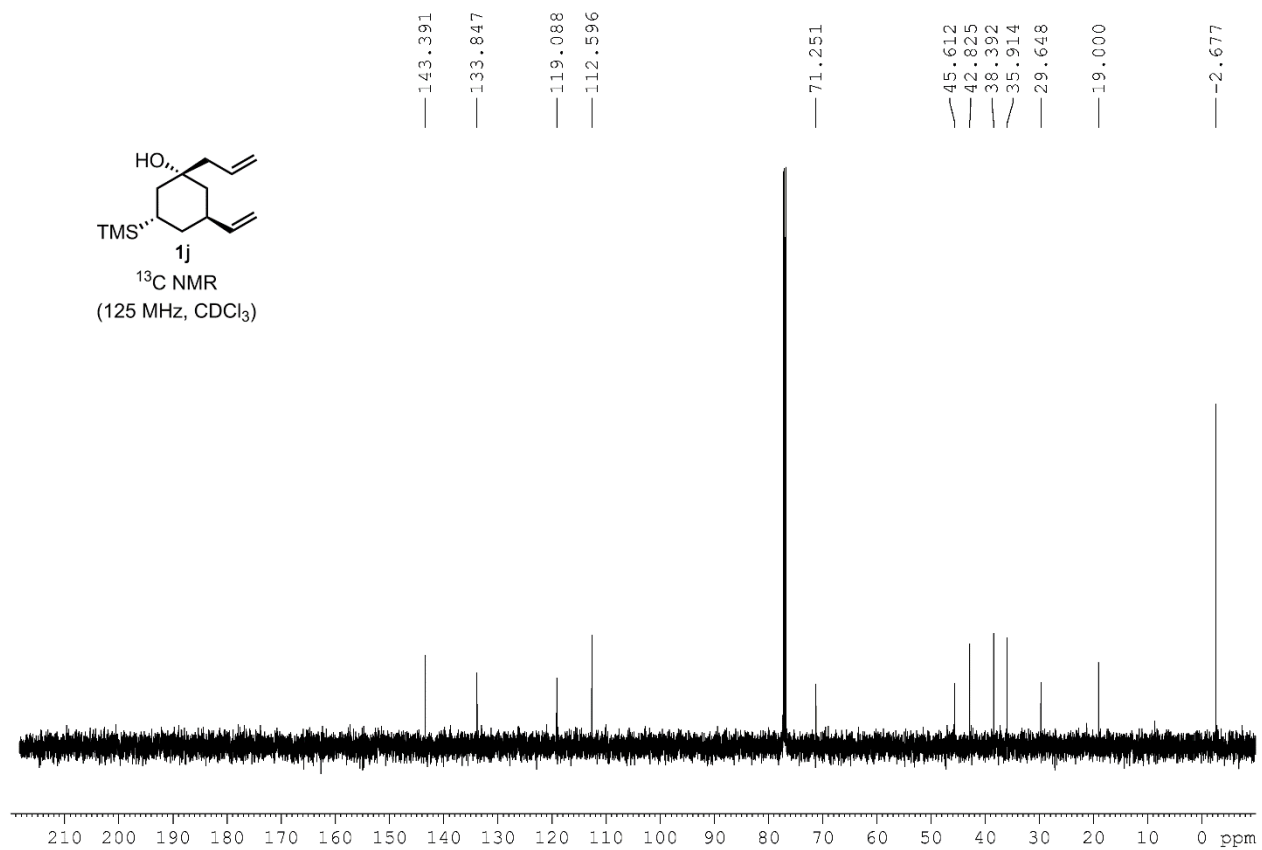


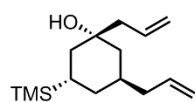


^1H NMR
(500 MHz, CDCl_3)

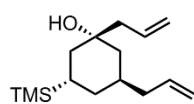
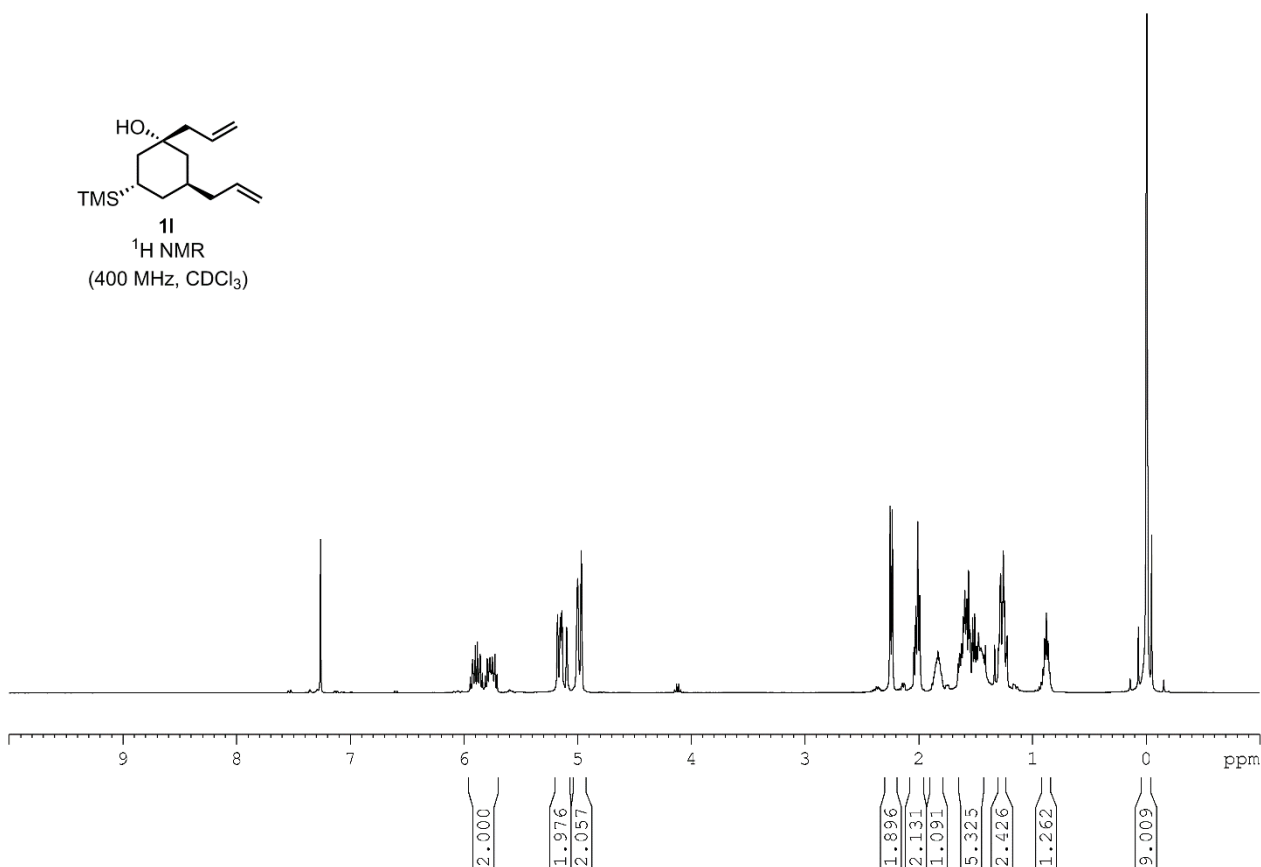


^{13}C NMR
(125 MHz, CDCl_3)

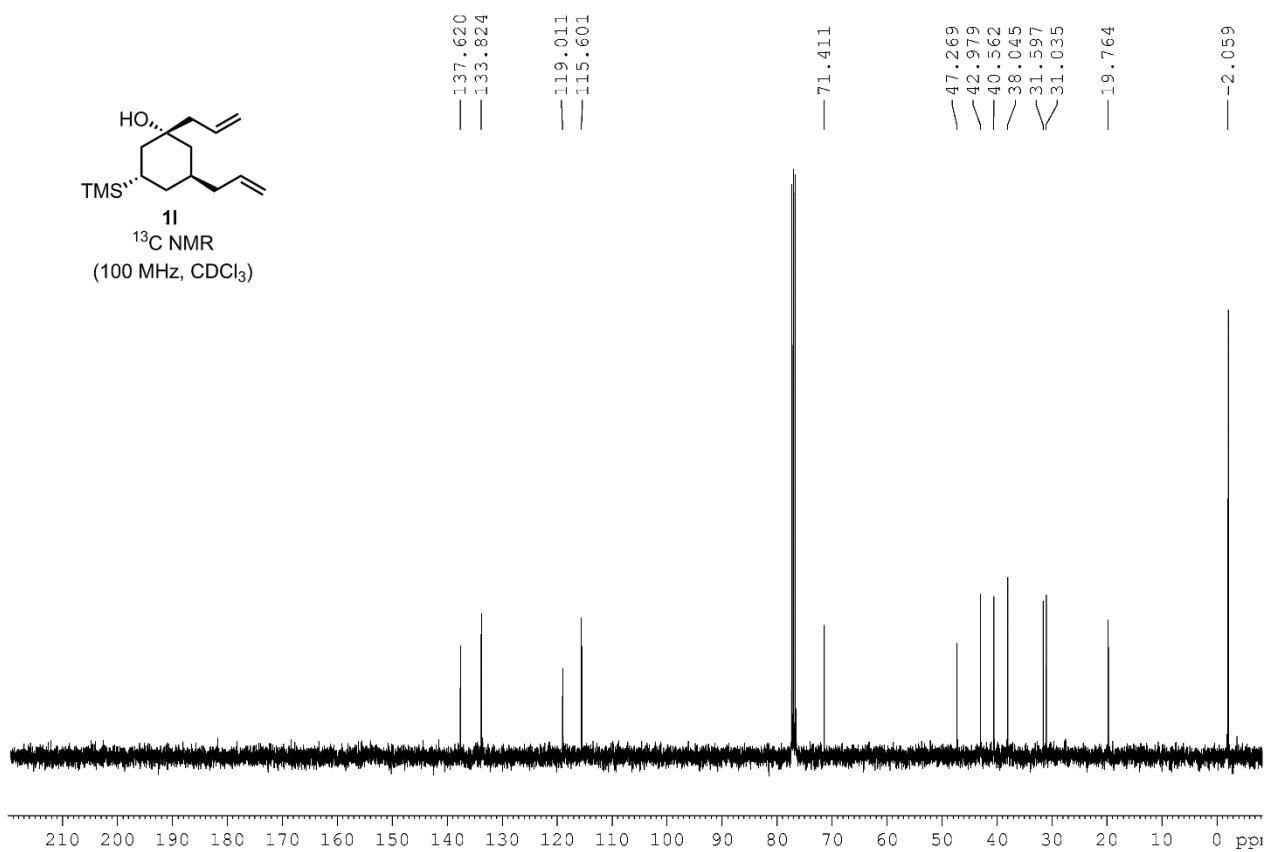


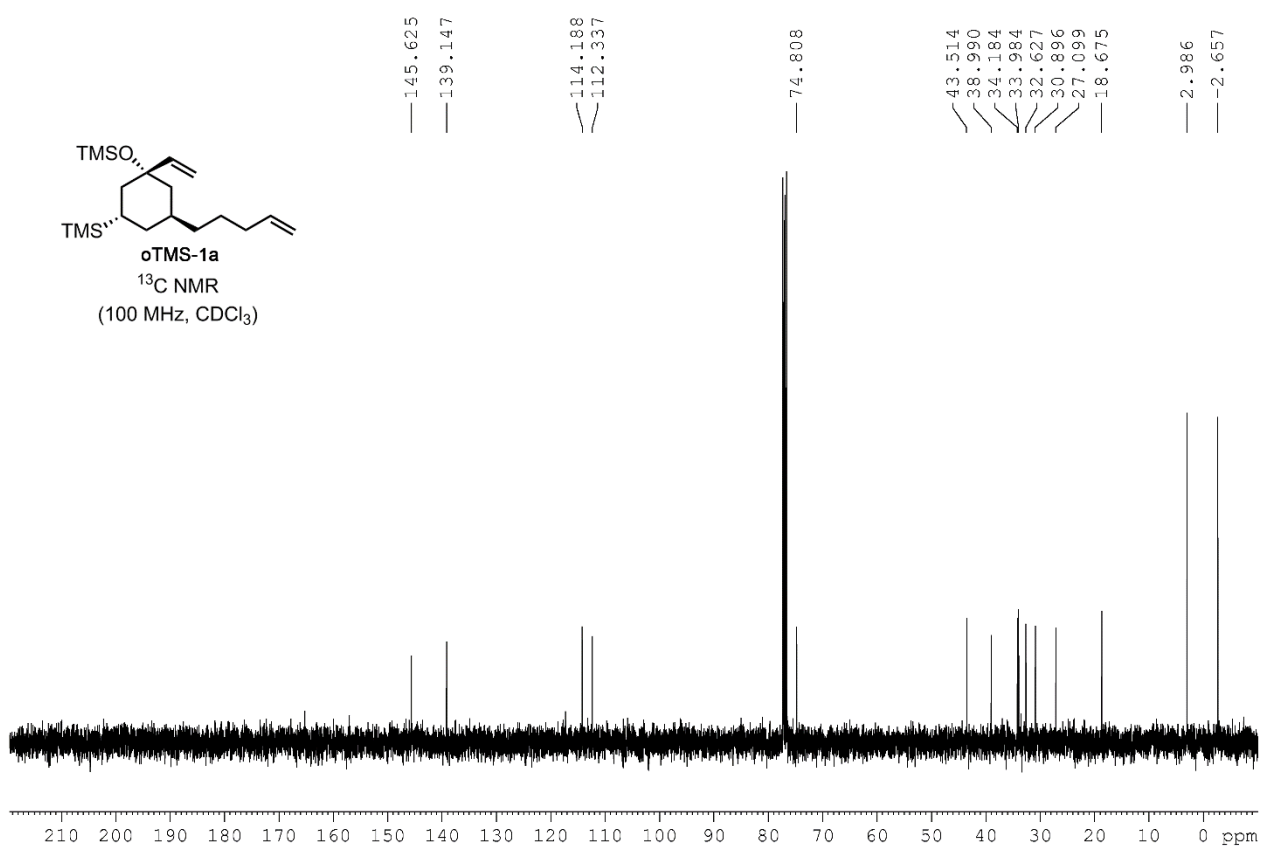
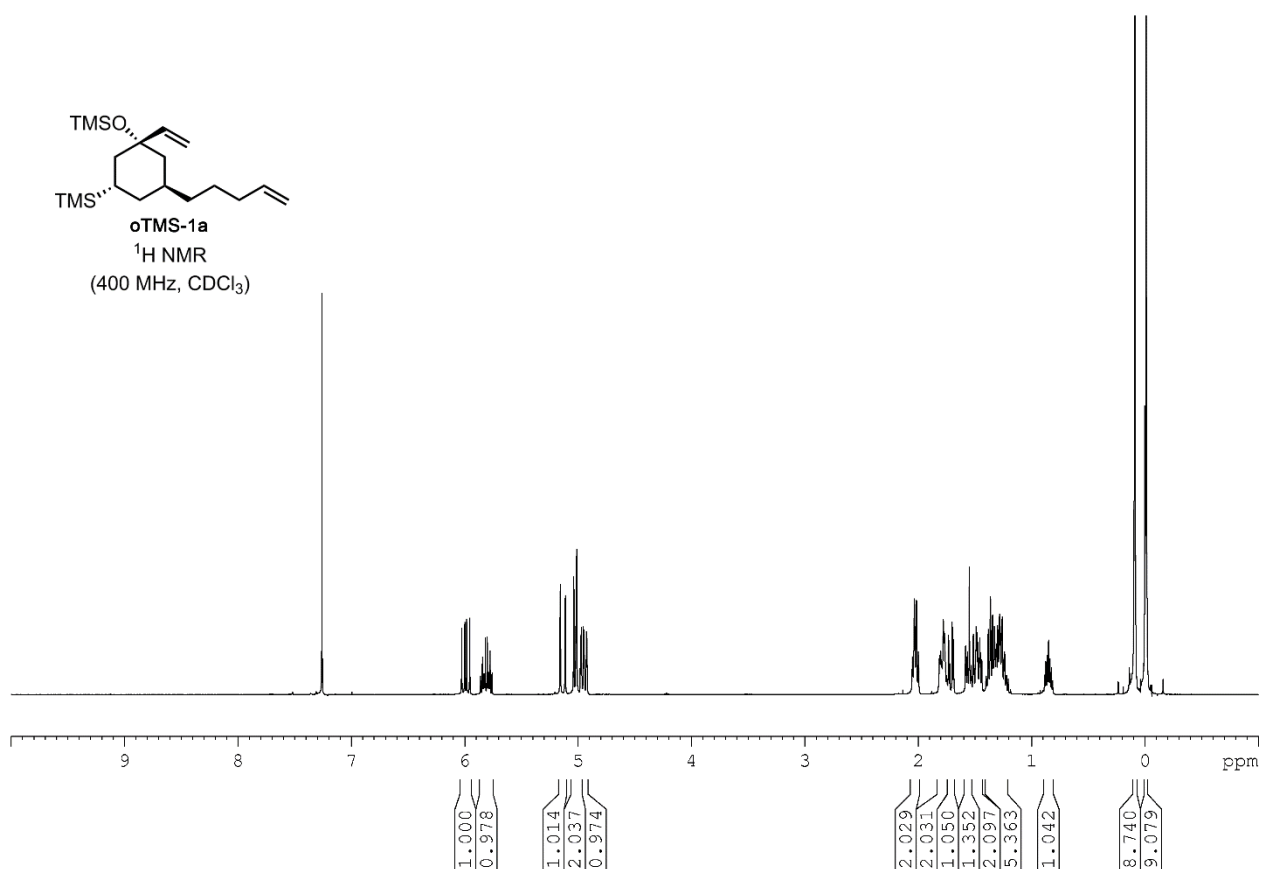


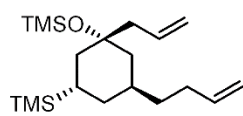
1l
 ^1H NMR
 (400 MHz, CDCl_3)



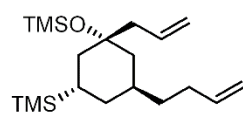
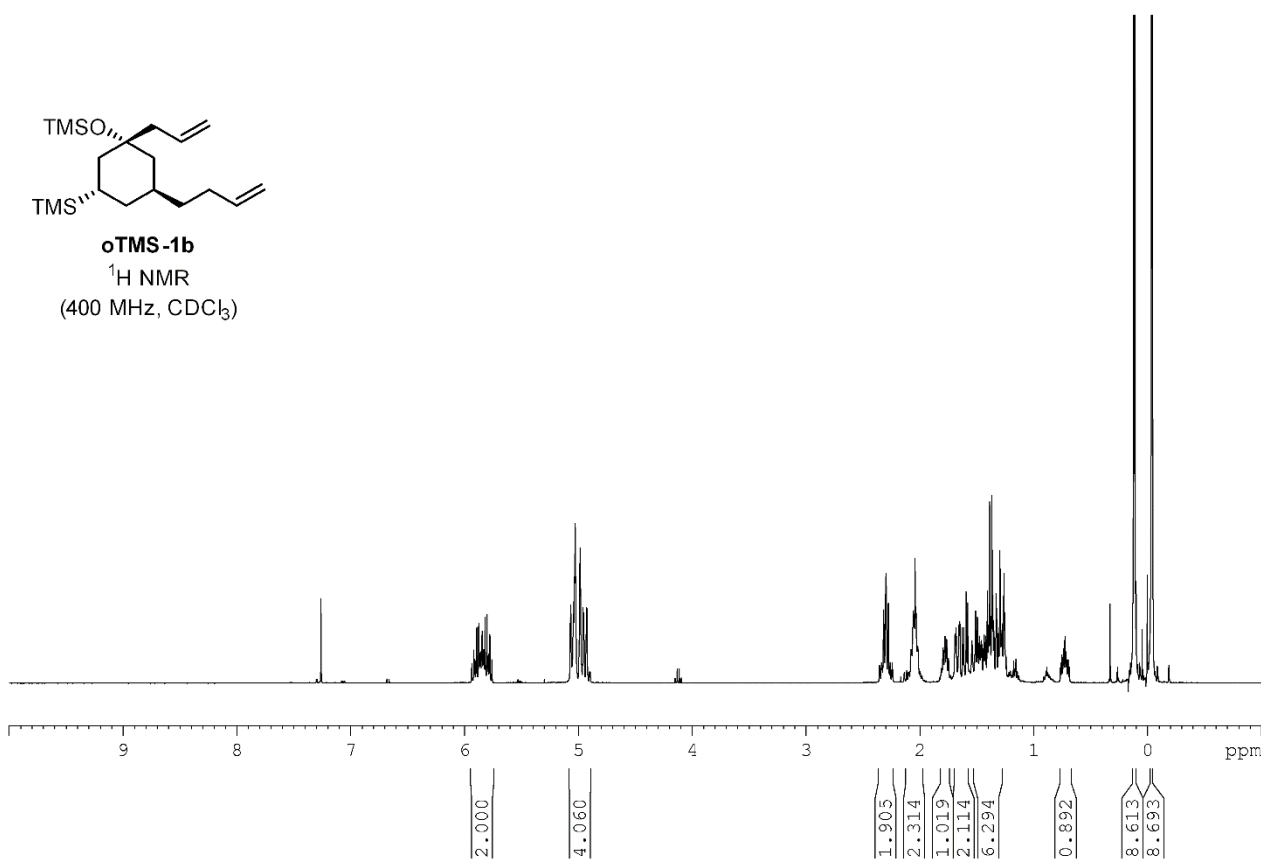
1l
 ^{13}C NMR
 (100 MHz, CDCl_3)



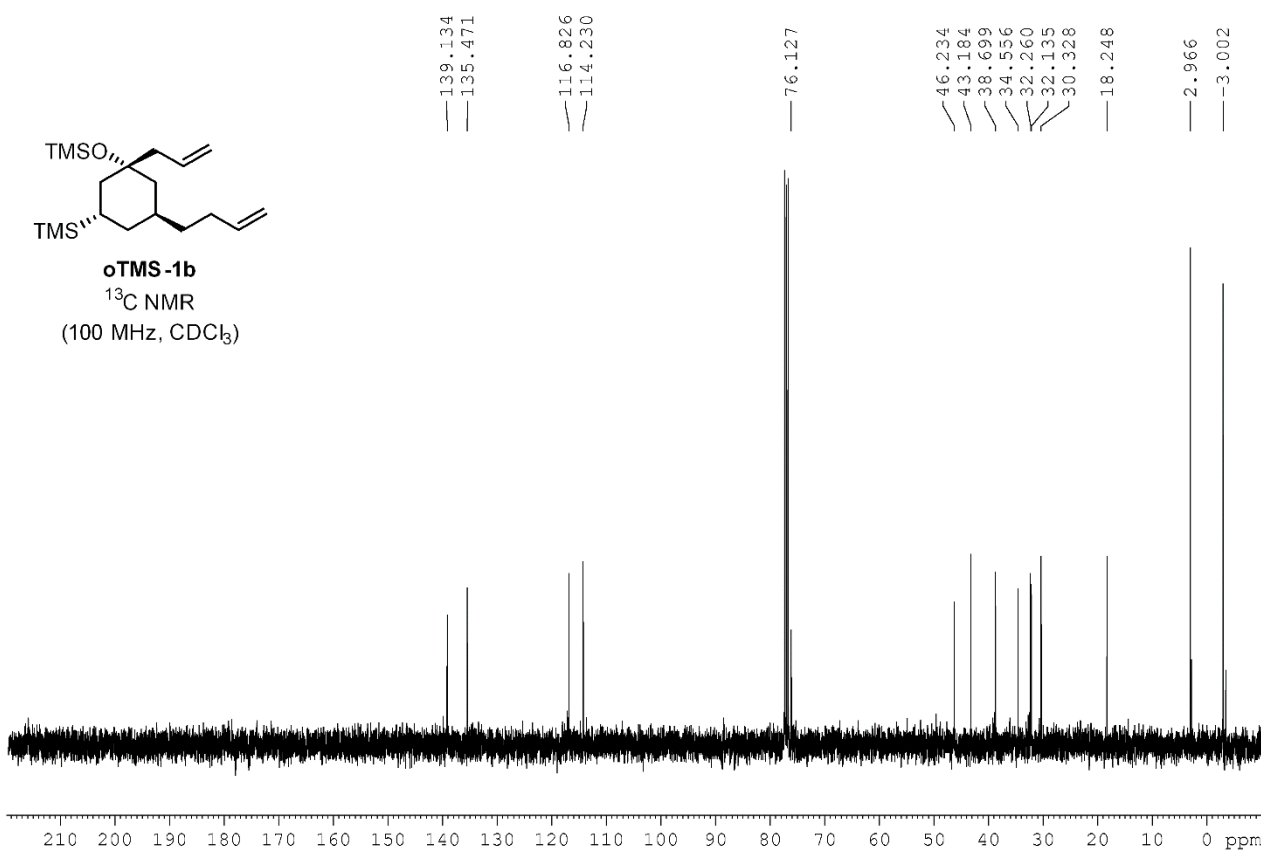


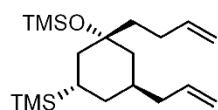


oTMS-1b
¹H NMR
 (400 MHz, CDCl₃)

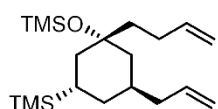
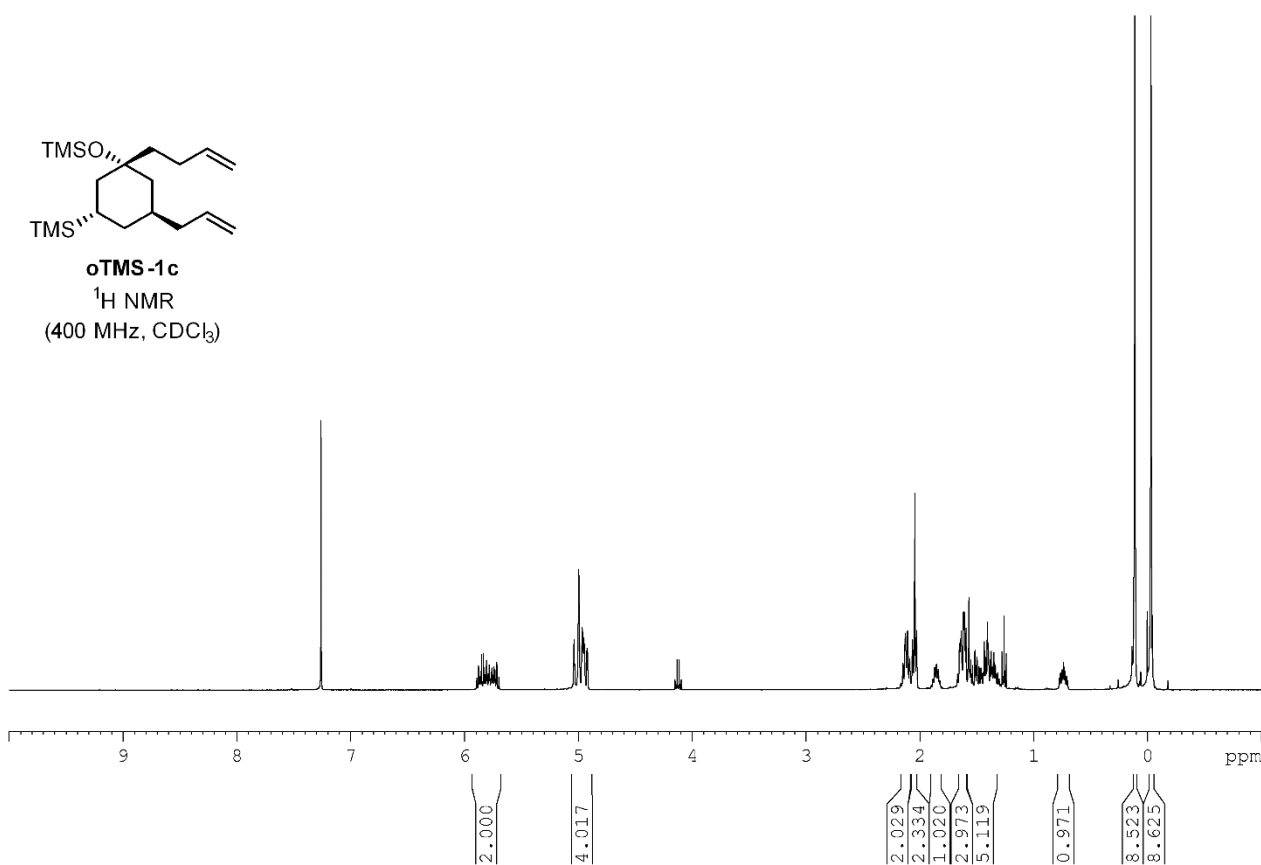


oTMS-1b
¹³C NMR
 (100 MHz, CDCl₃)

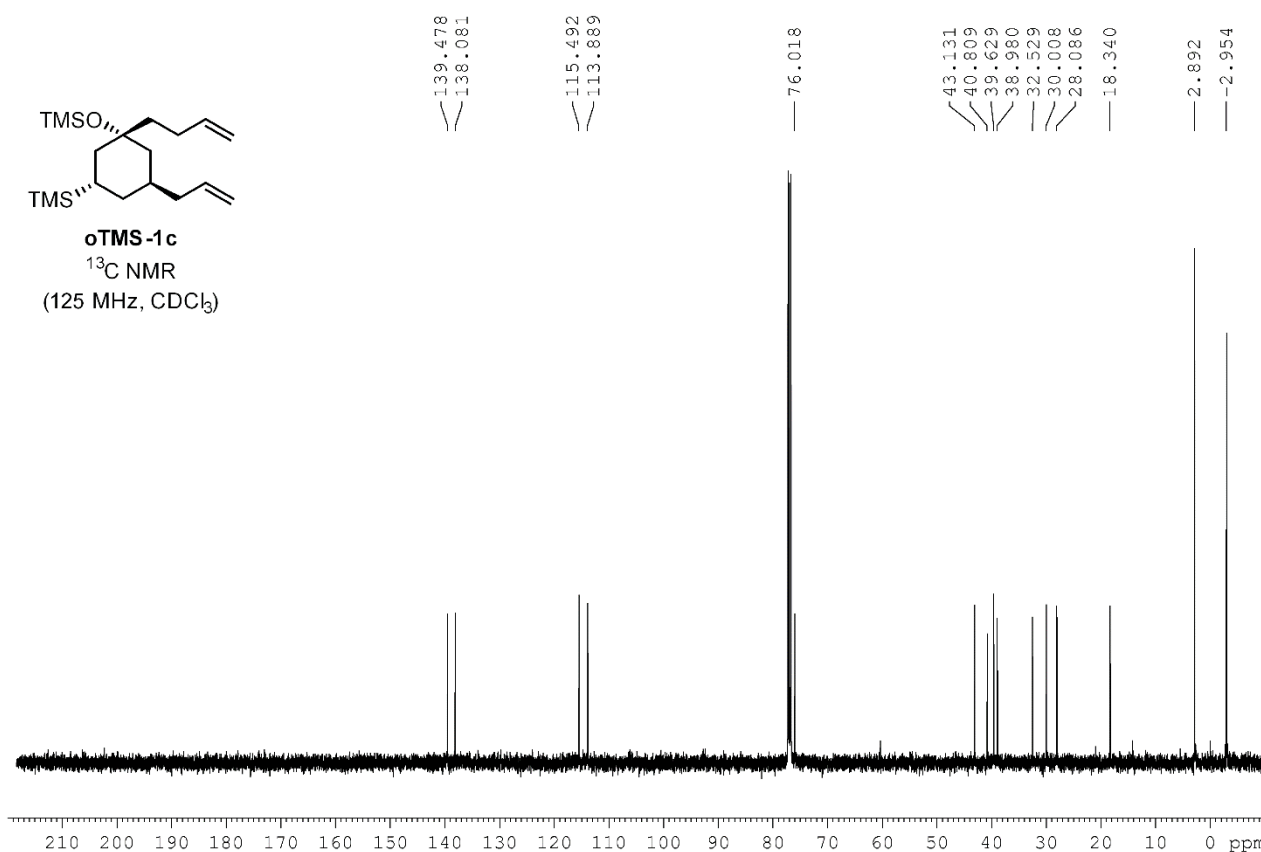


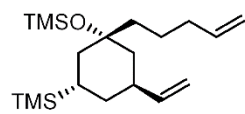


oTMS-1c
 ^1H NMR
 (400 MHz, CDCl_3)



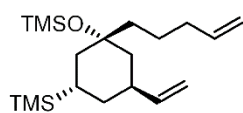
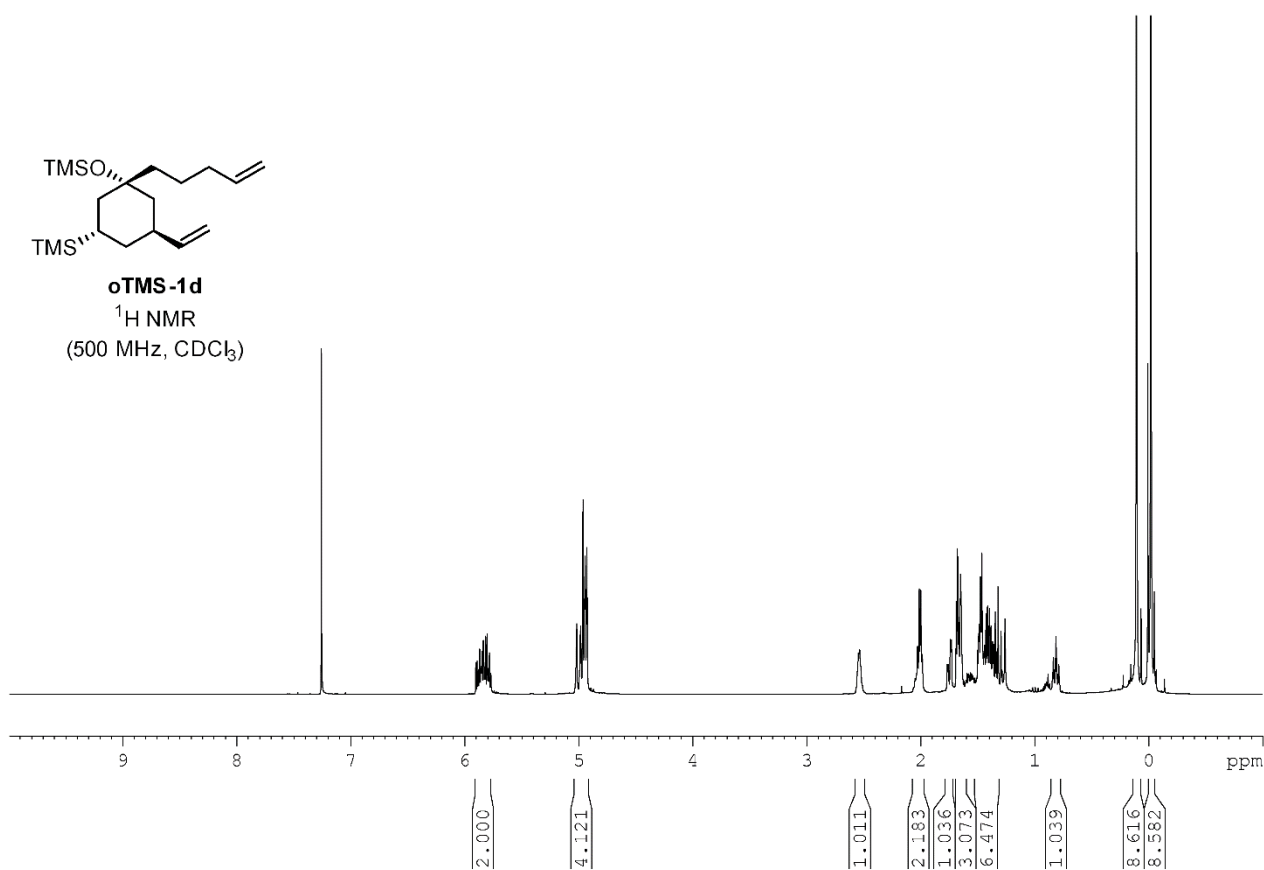
oTMS-1c
 ^{13}C NMR
 (125 MHz, CDCl_3)





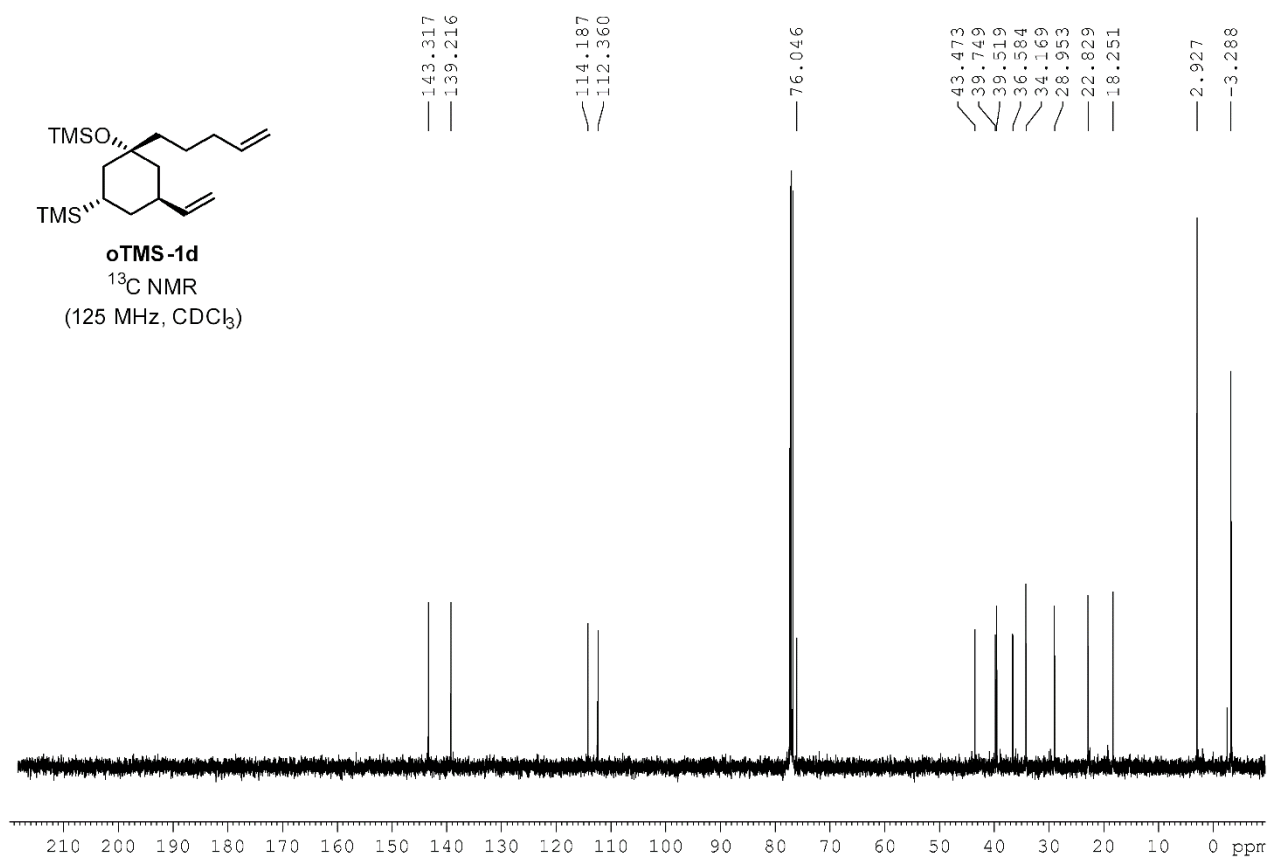
oTMS-1d

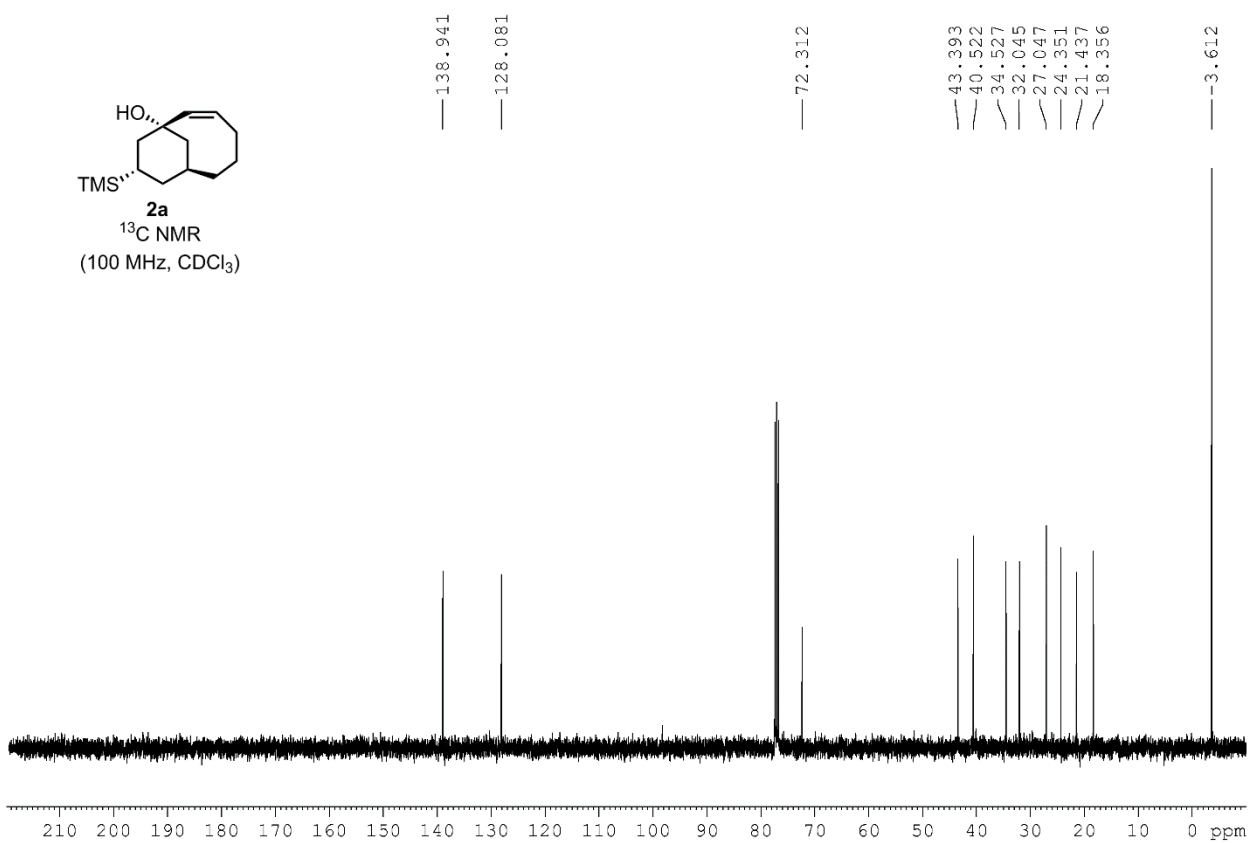
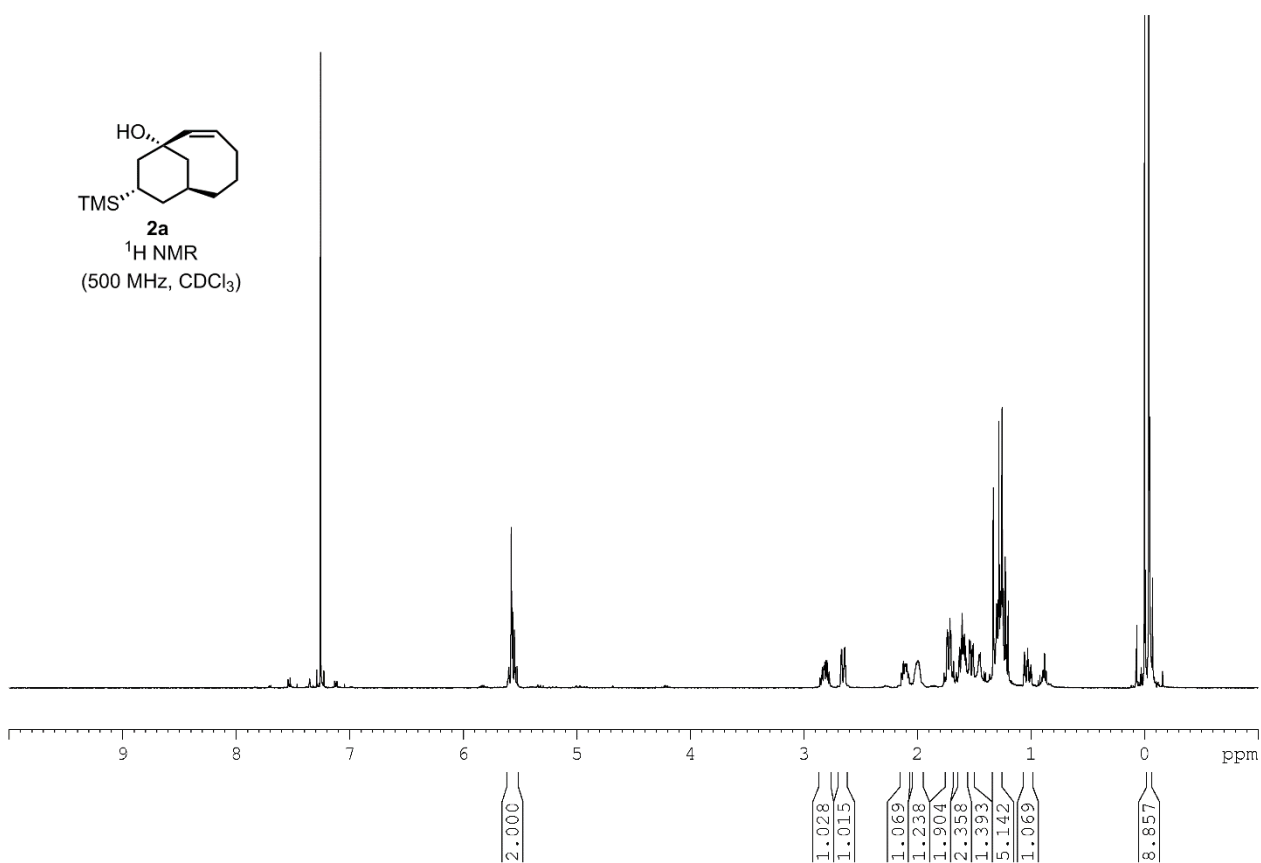
^1H NMR
(500 MHz, CDCl_3)

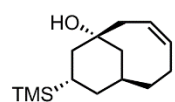


oTMS-1d

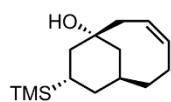
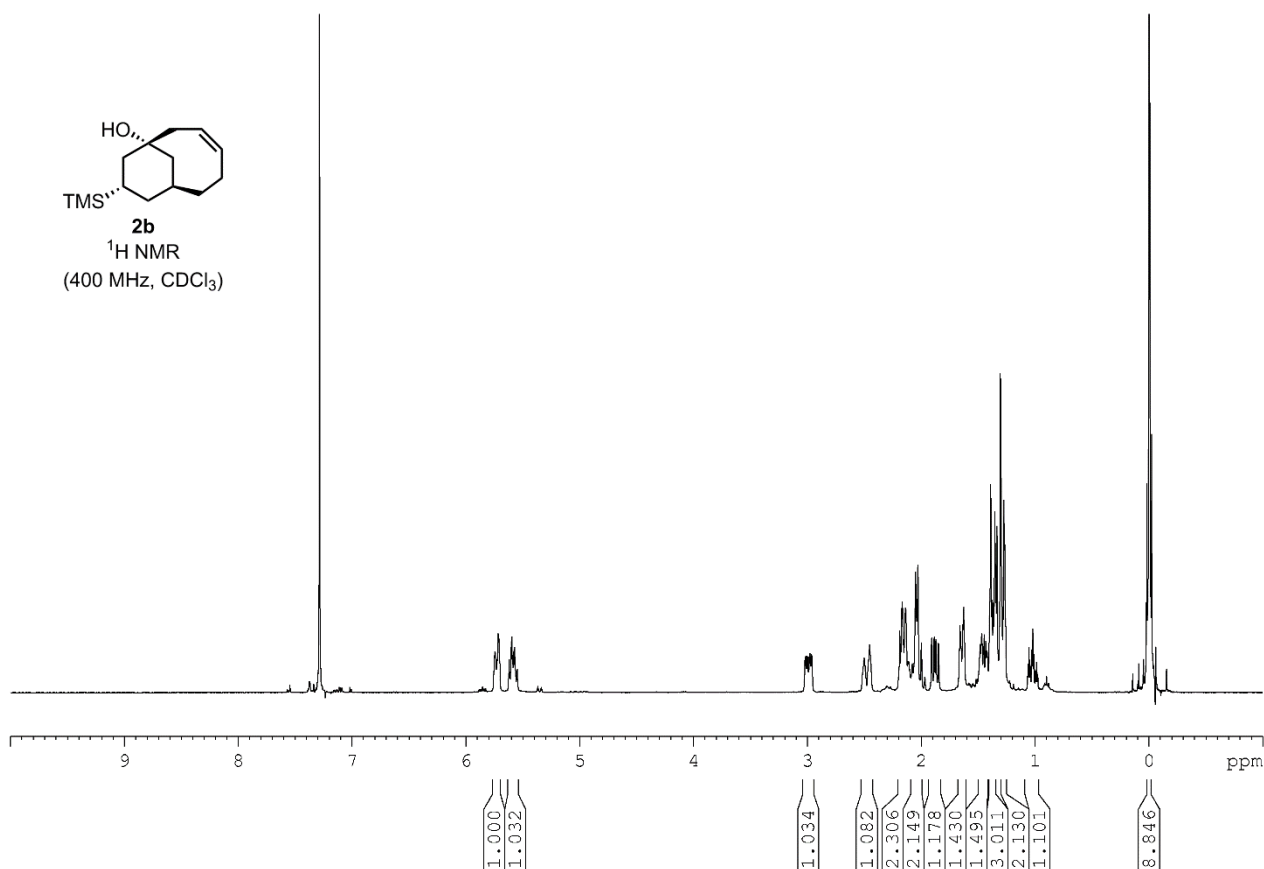
^{13}C NMR
(125 MHz, CDCl_3)



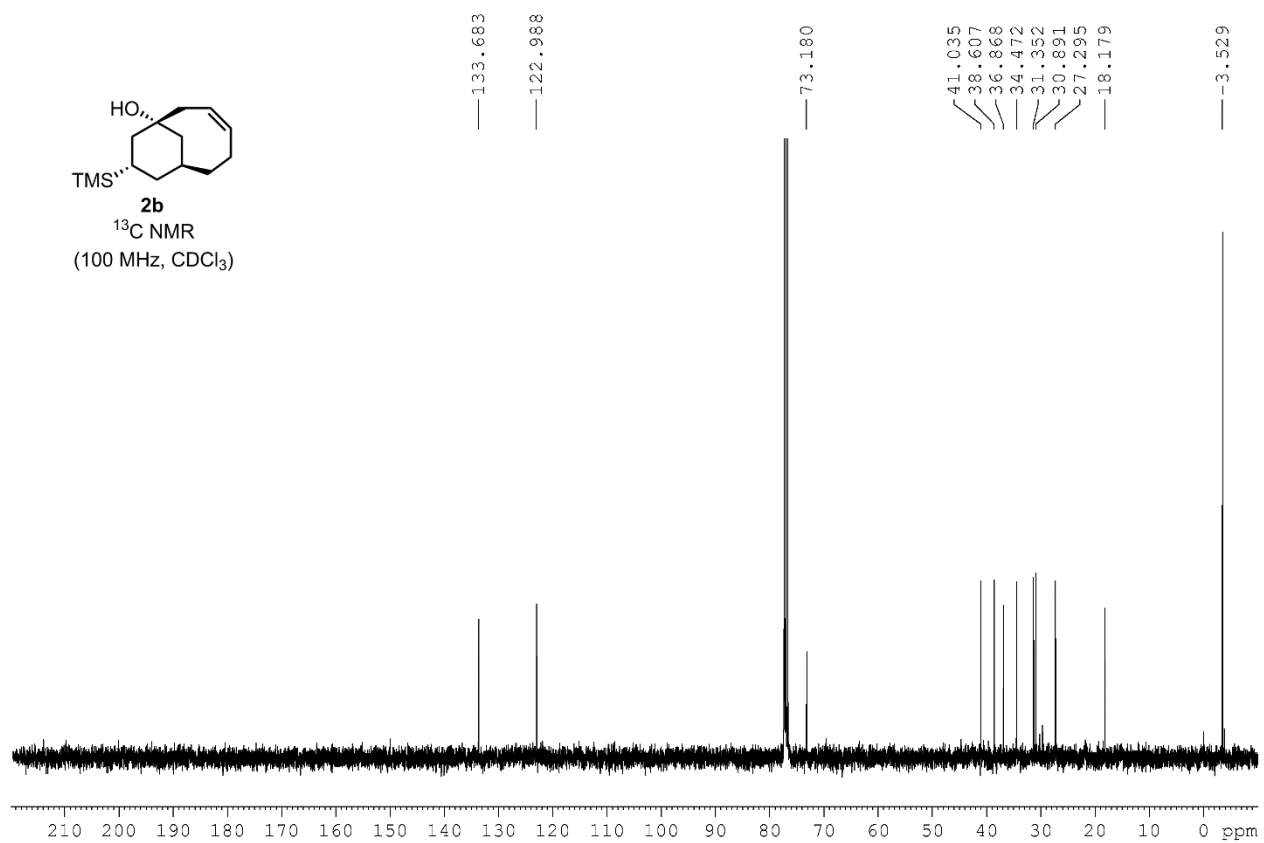


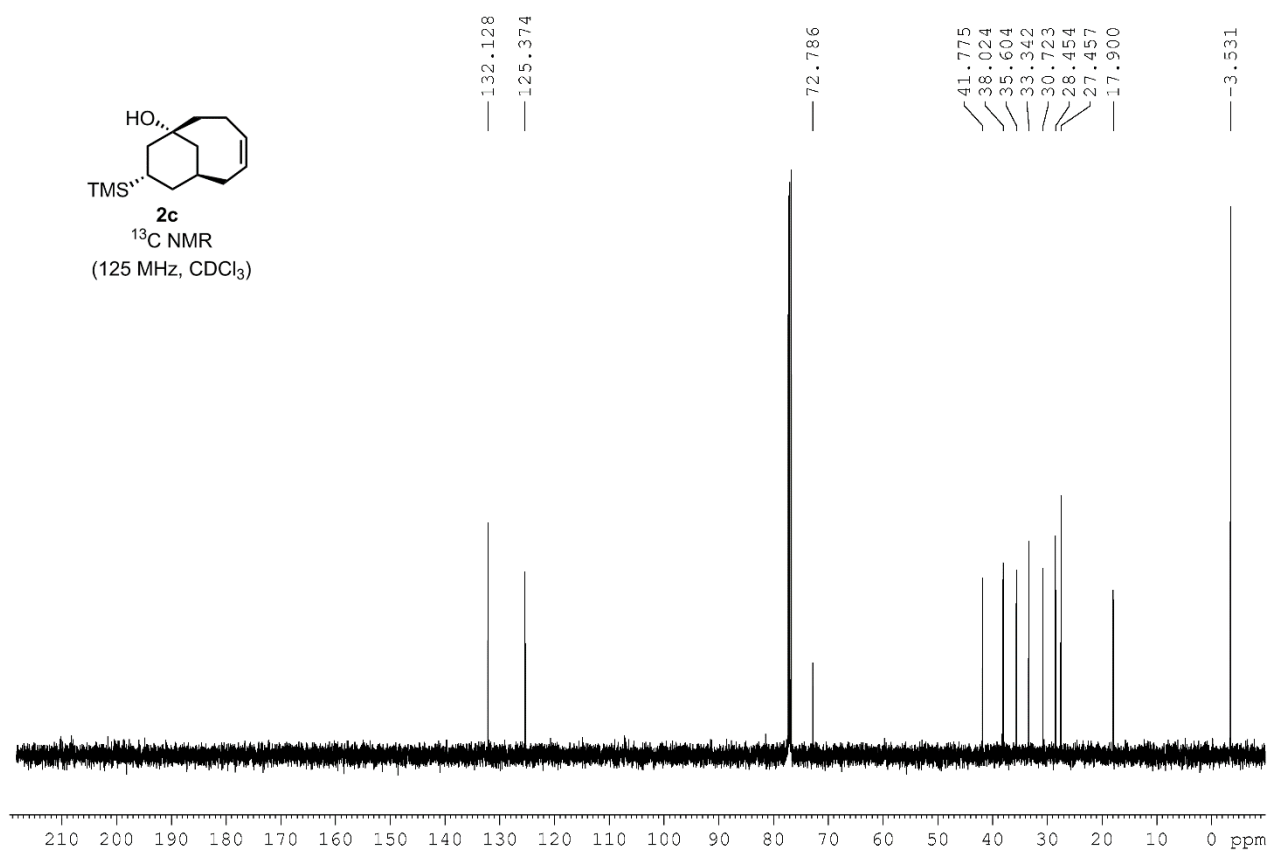
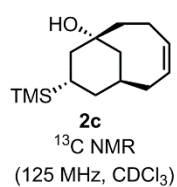
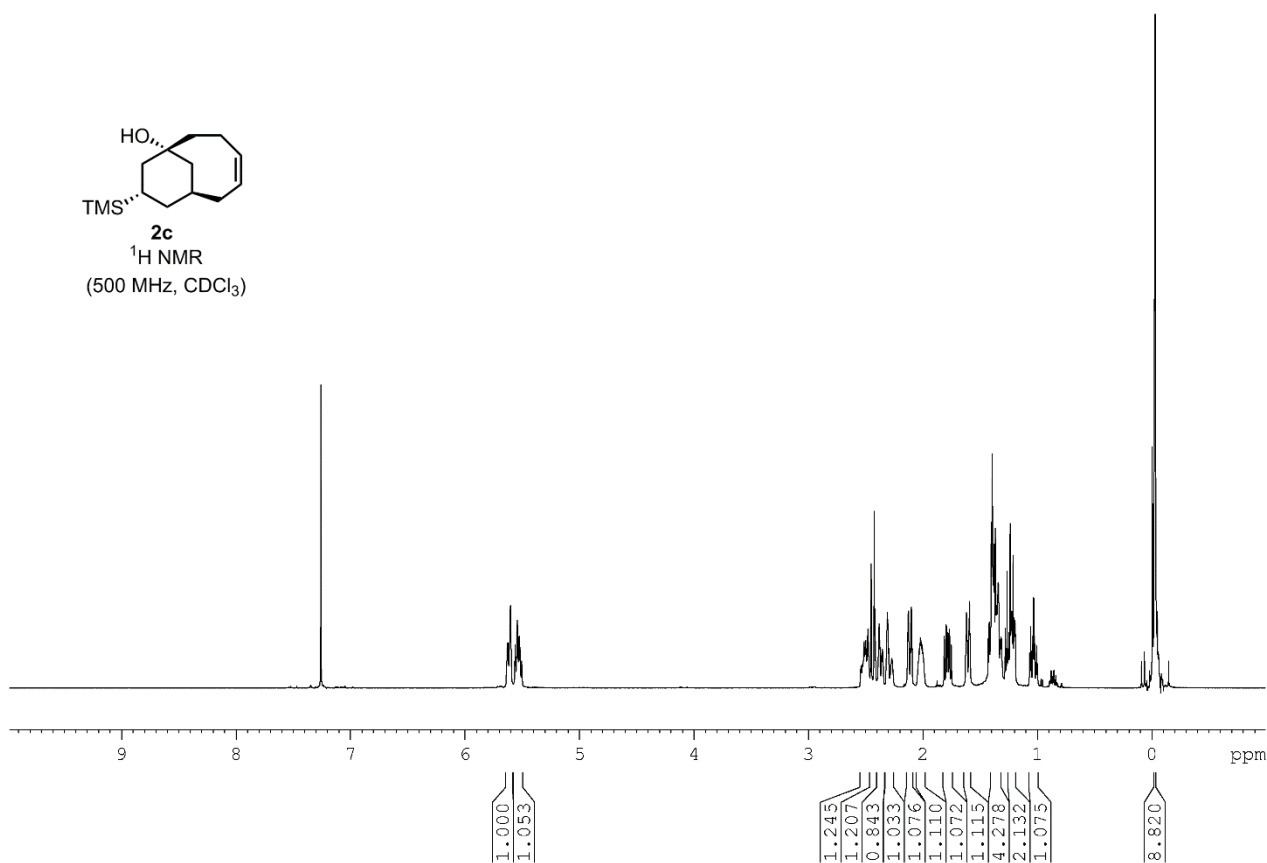
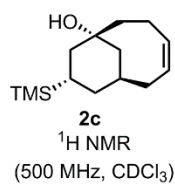


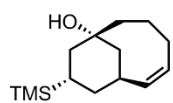
2b
 ^1H NMR
 (400 MHz, CDCl_3)



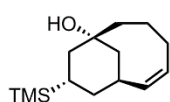
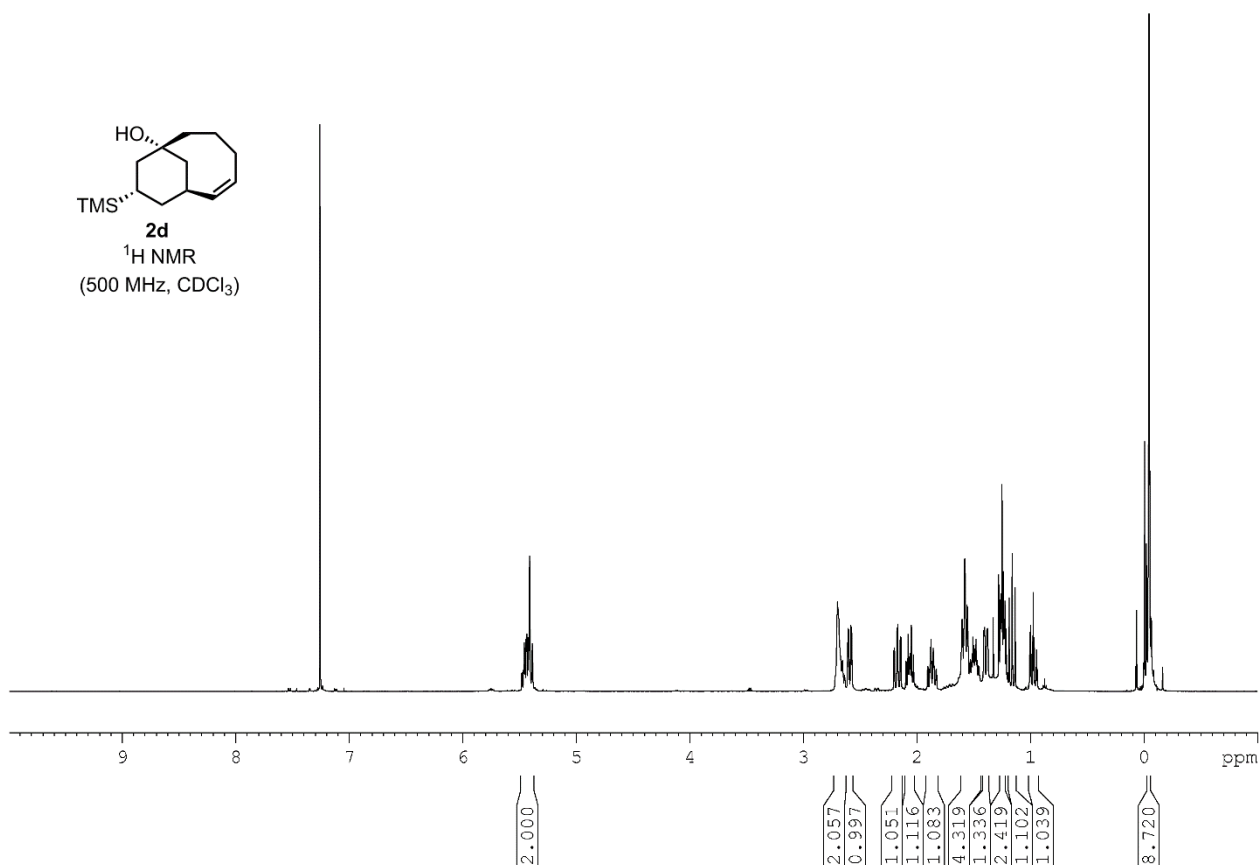
2b
 ^{13}C NMR
 (100 MHz, CDCl_3)



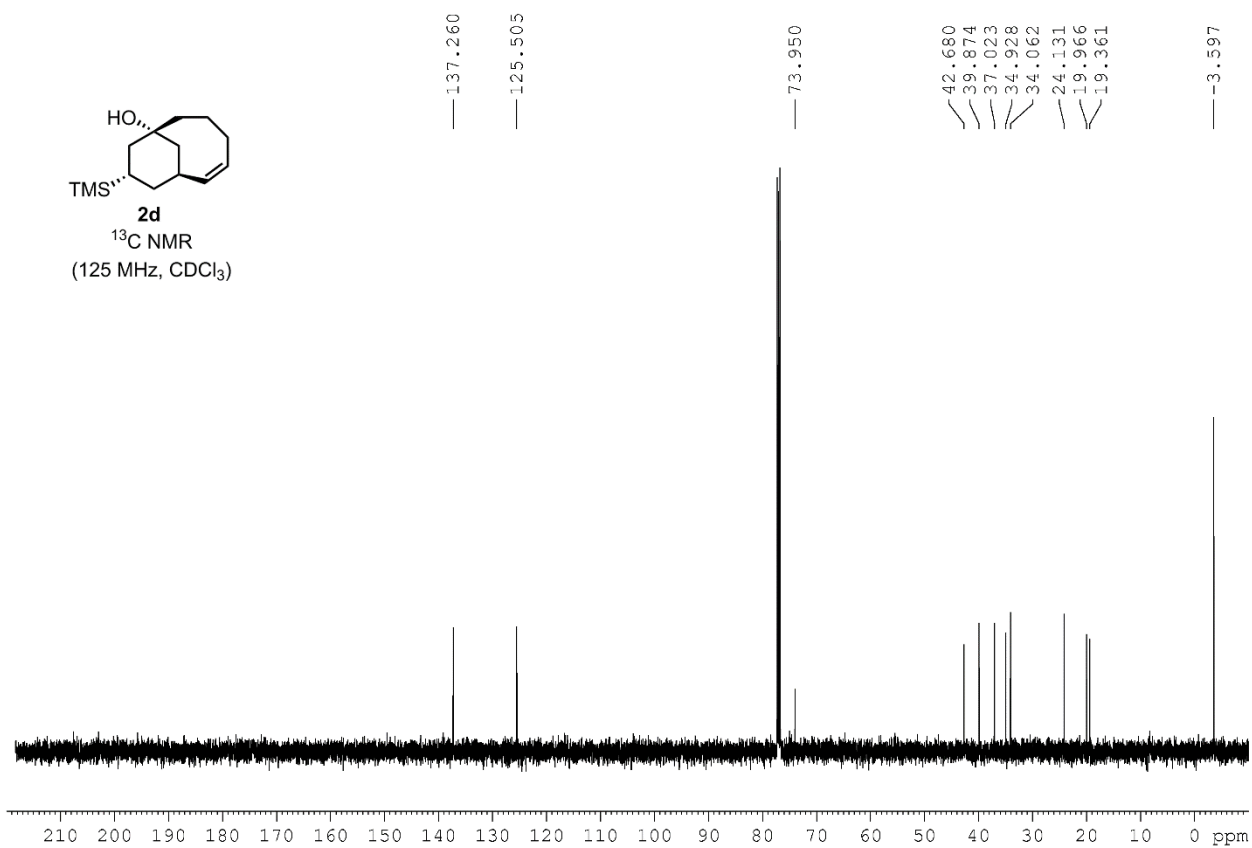


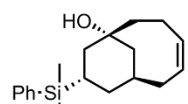


¹H NMR
(500 MHz, CDCl₃)

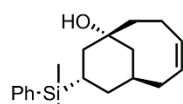
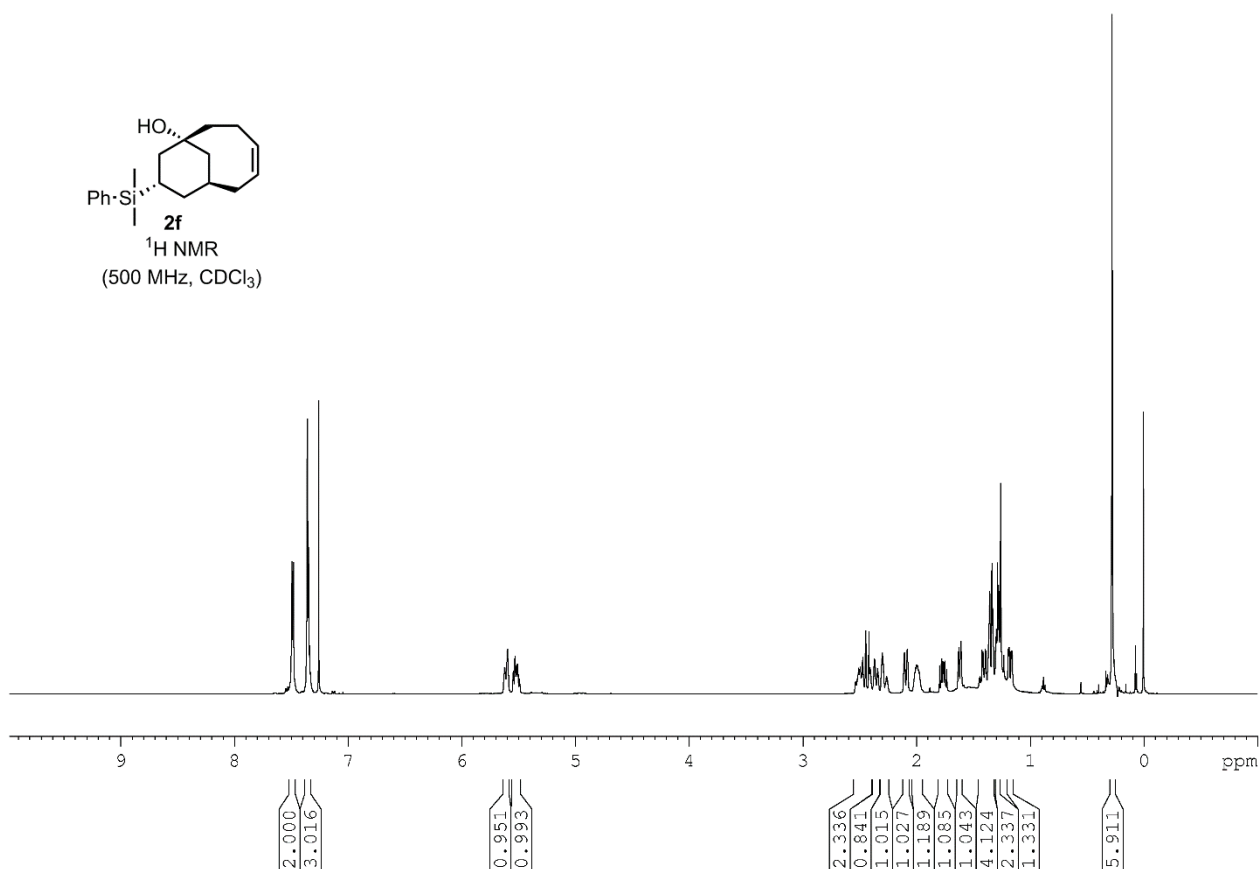


¹³C NMR
(125 MHz, CDCl₃)

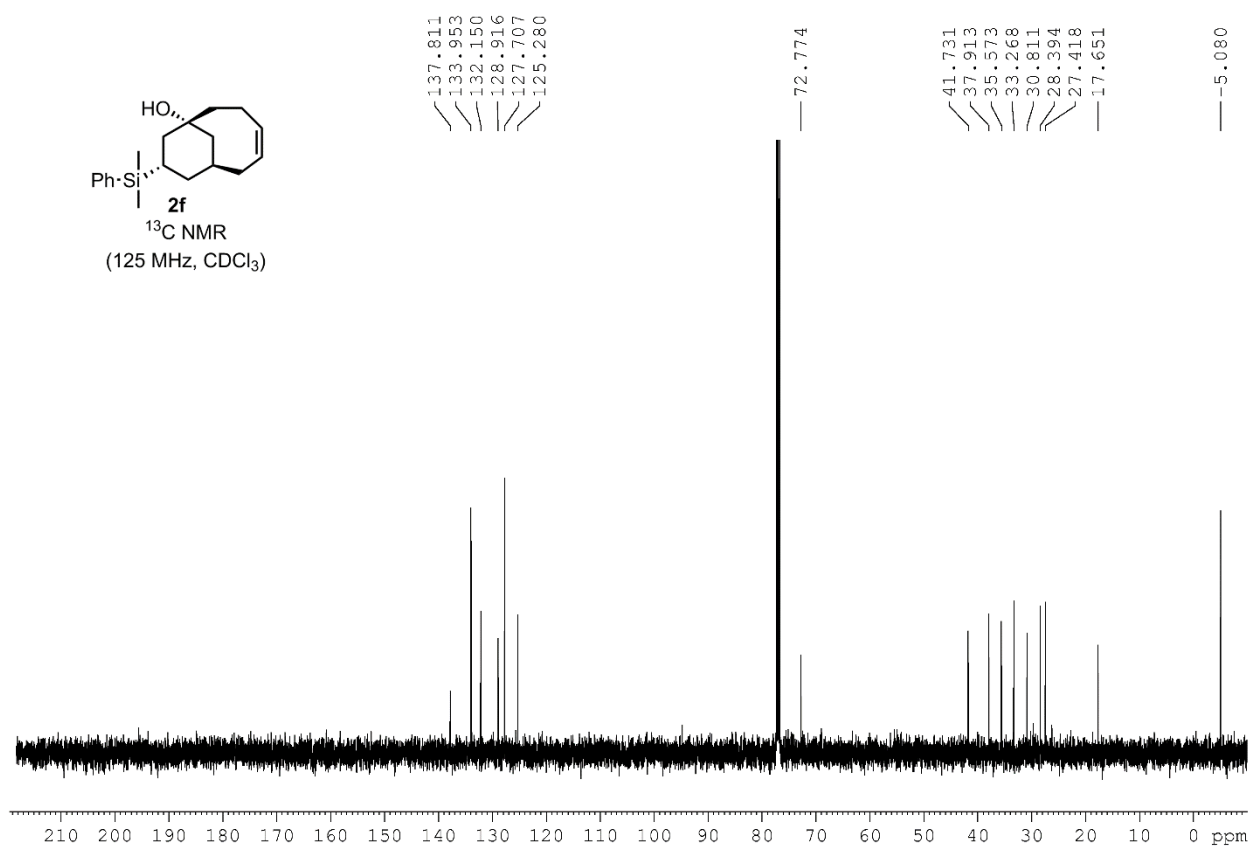


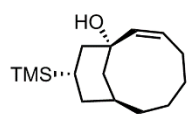


¹H NMR
 (500 MHz, CDCl₃)

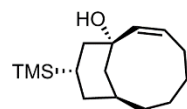
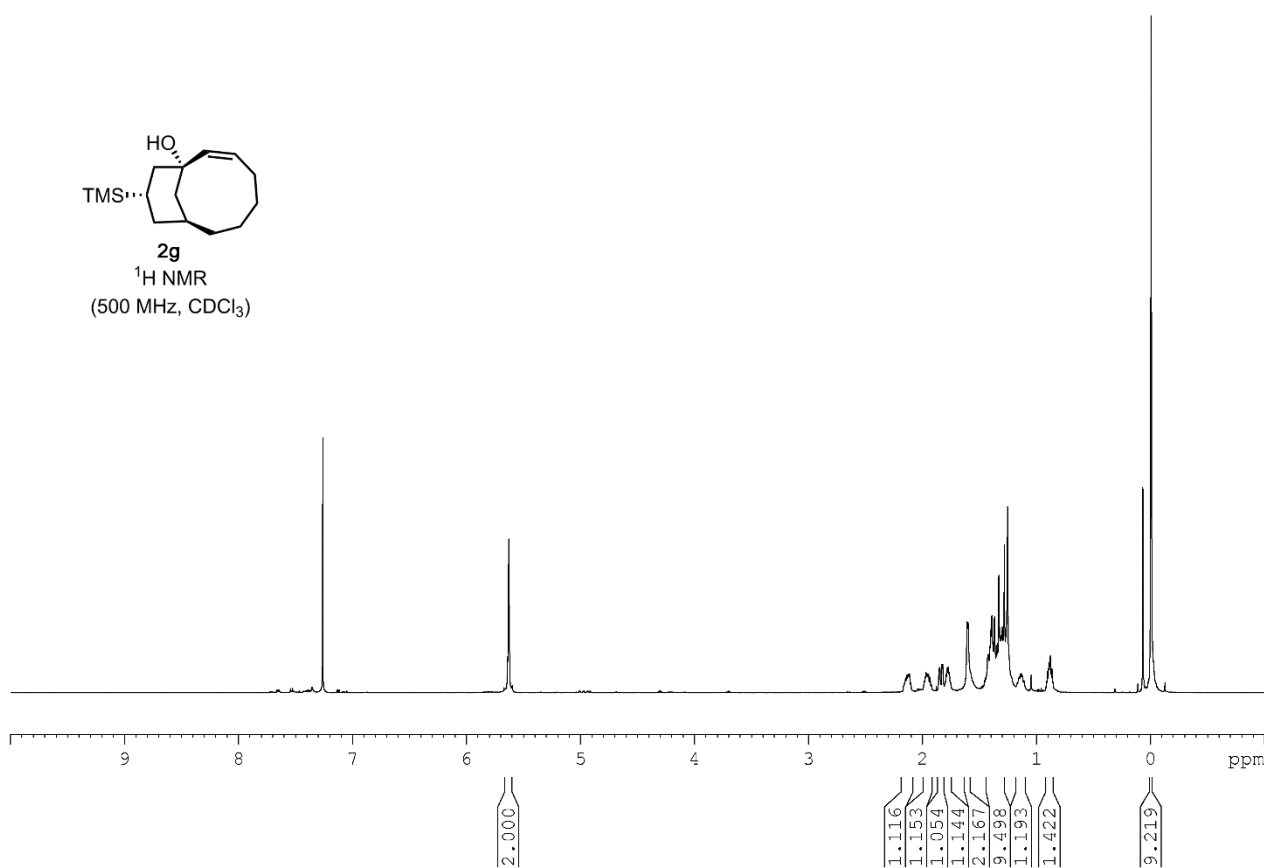


¹³C NMR
 (125 MHz, CDCl₃)

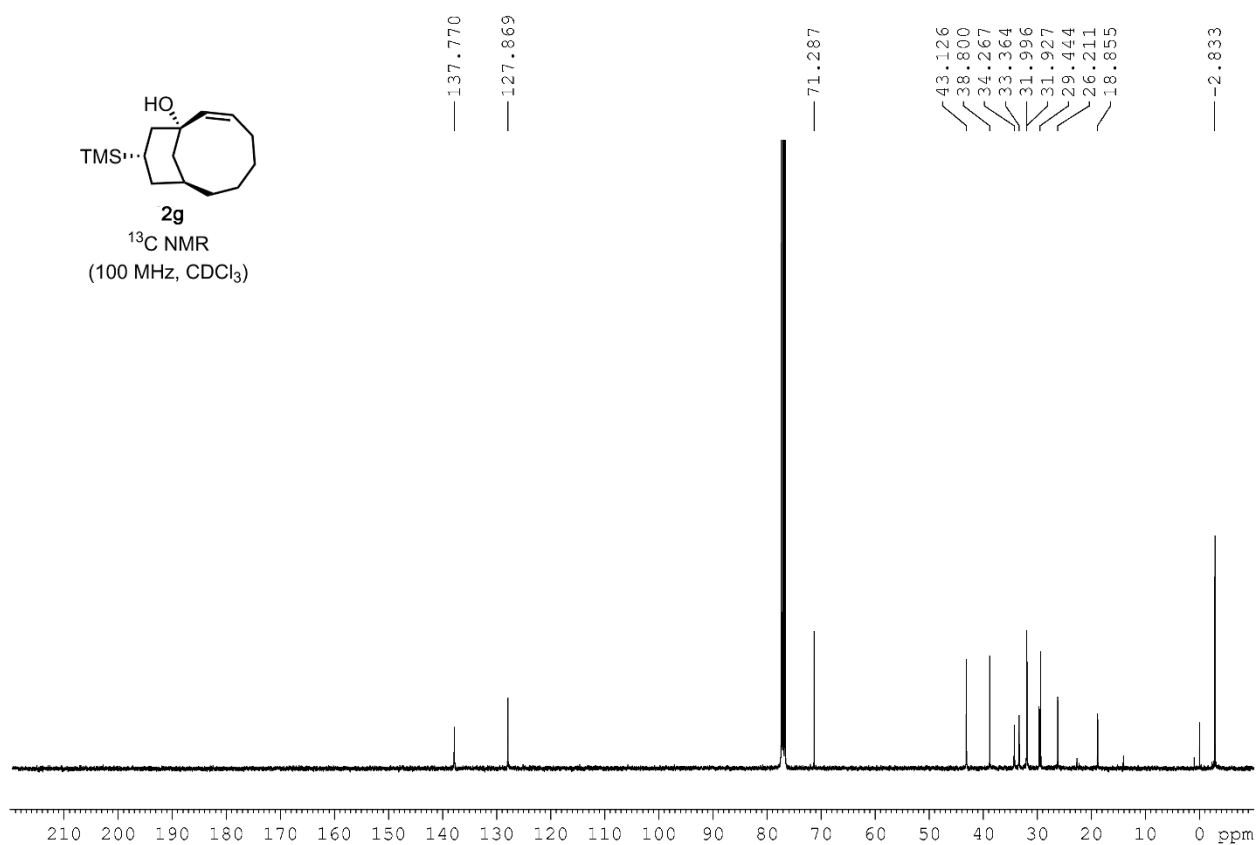


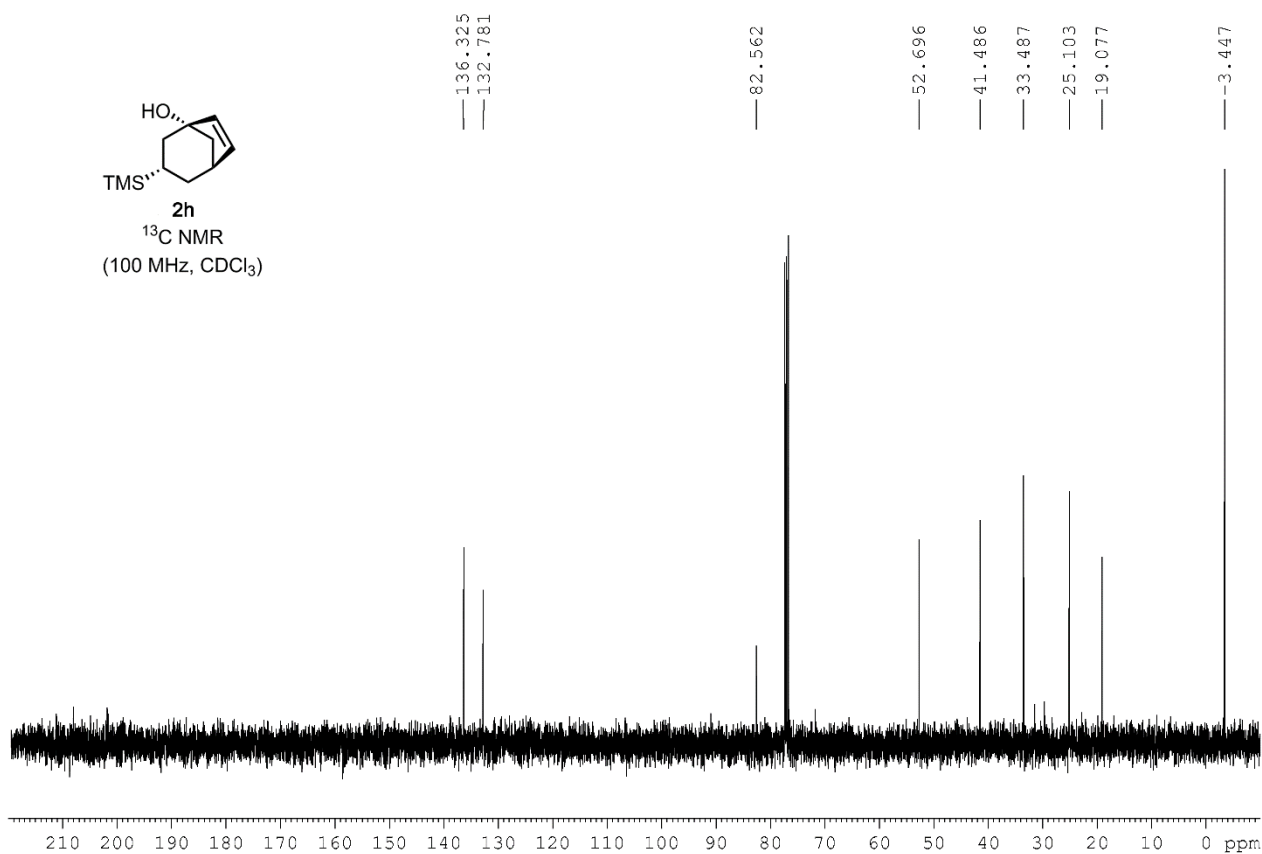
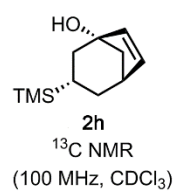
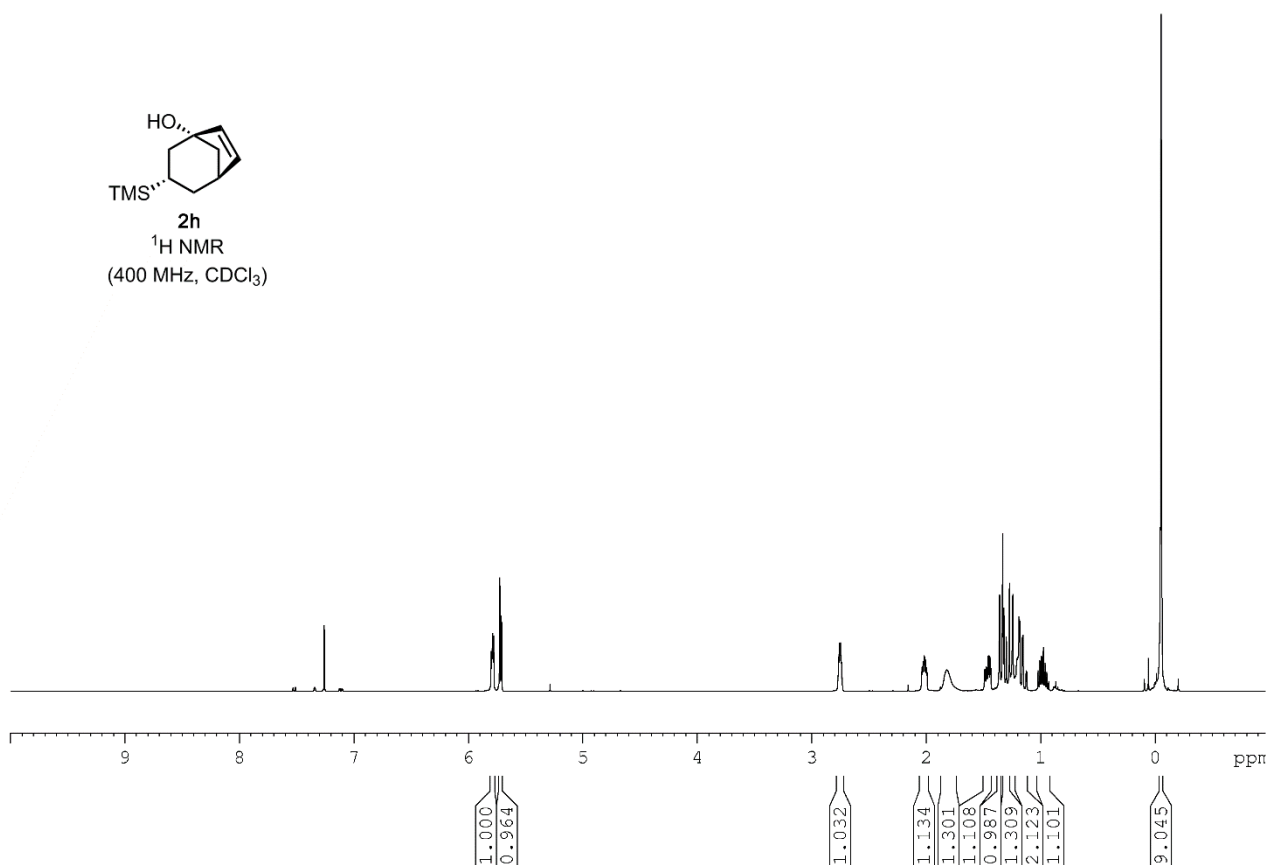
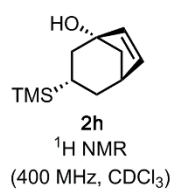


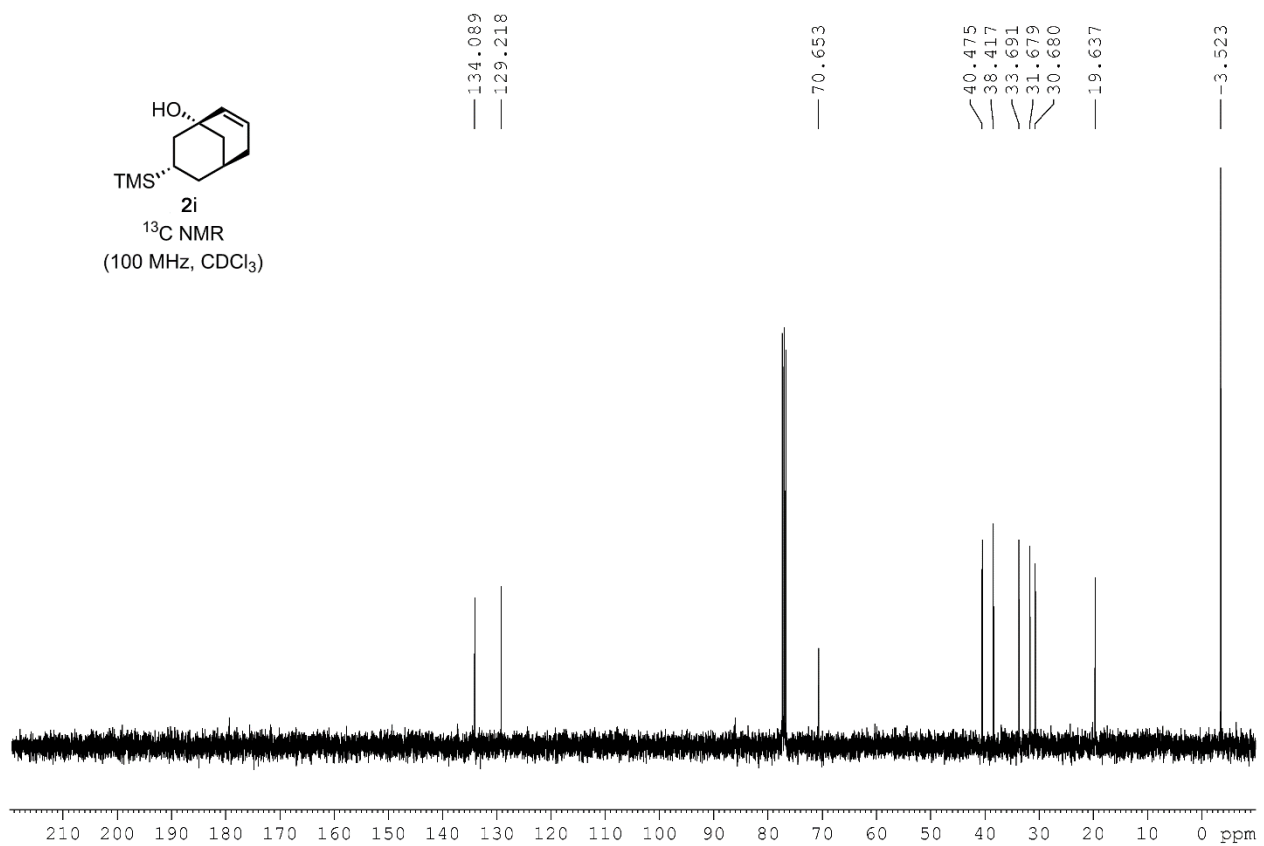
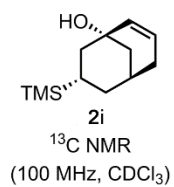
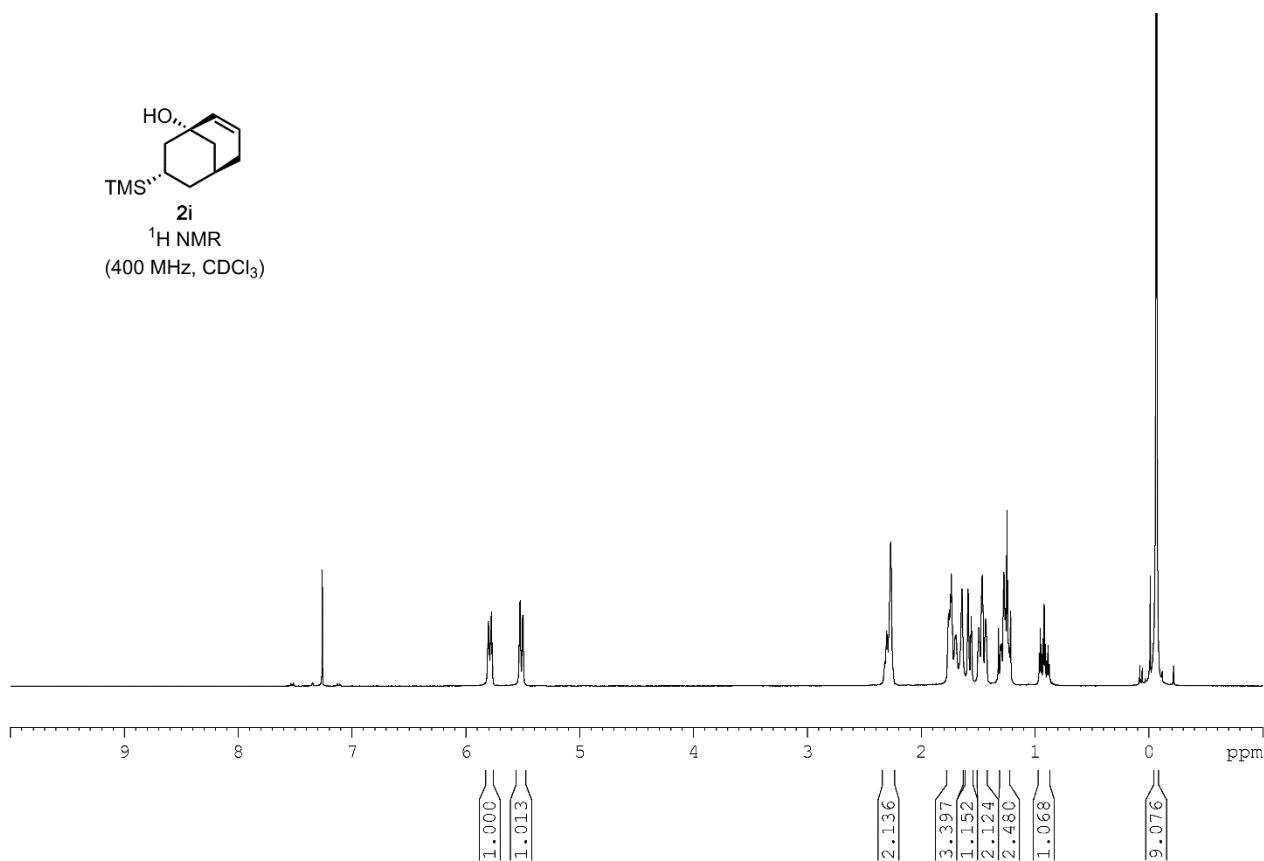
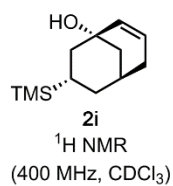
2g
 ^1H NMR
 (500 MHz, CDCl_3)

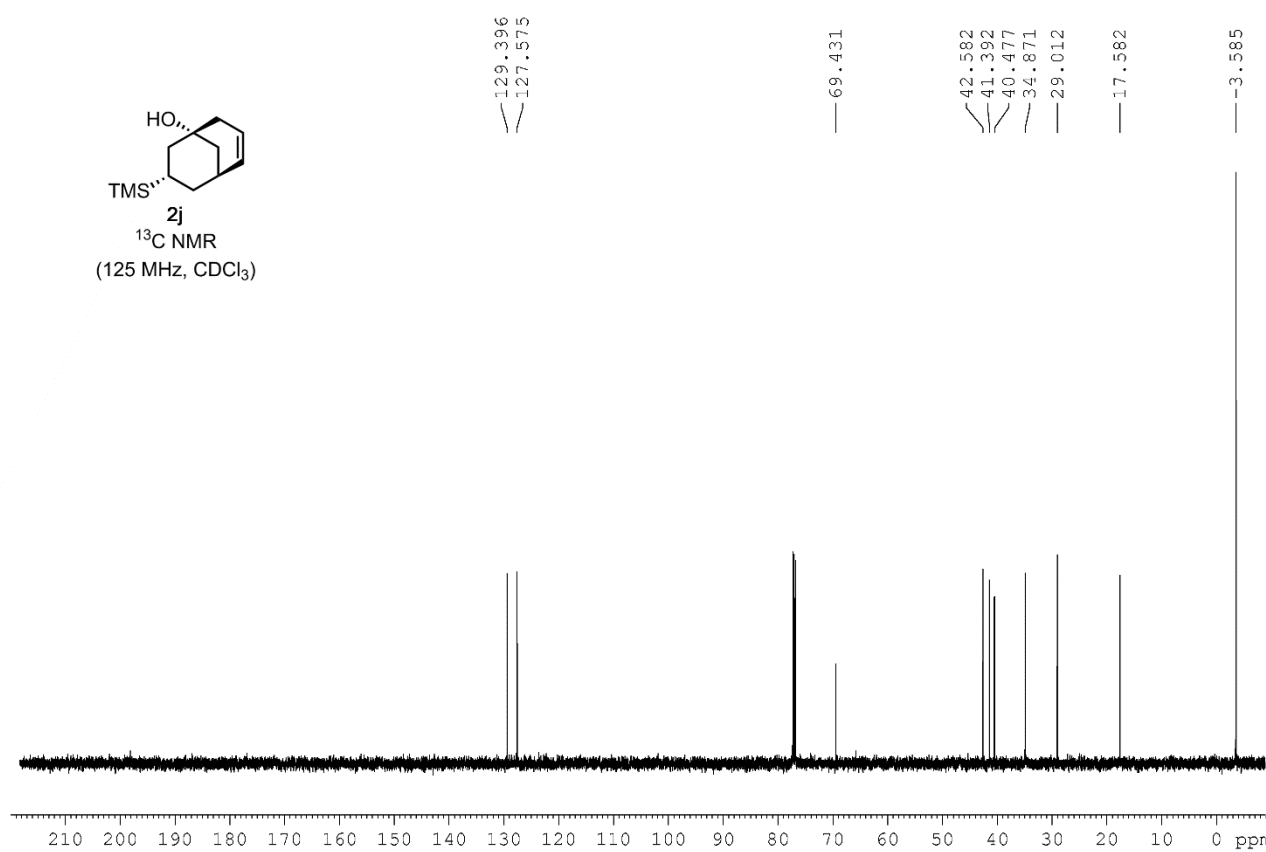
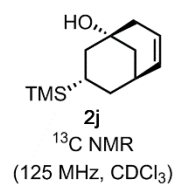
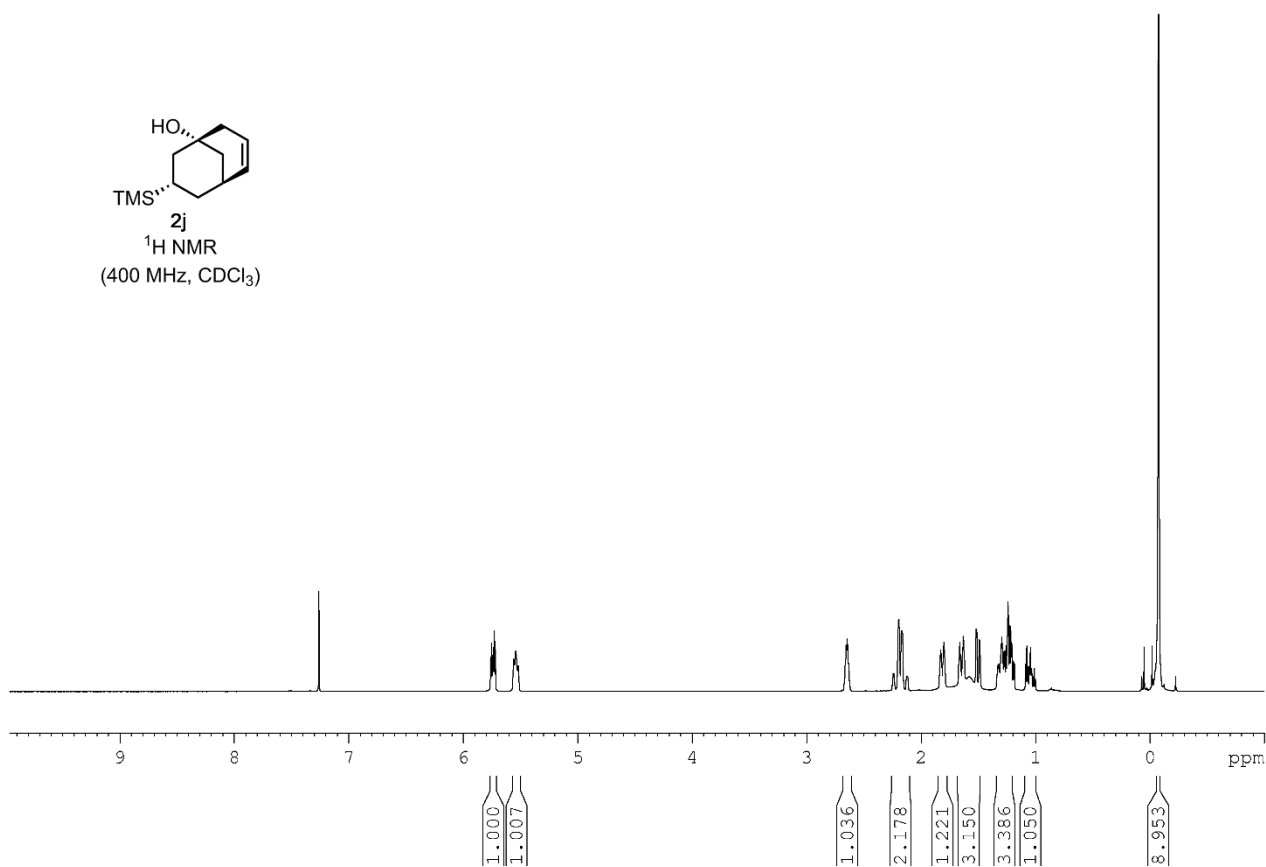
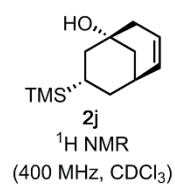


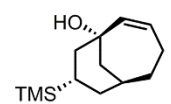
2g
 ^{13}C NMR
 (100 MHz, CDCl_3)



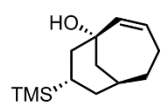
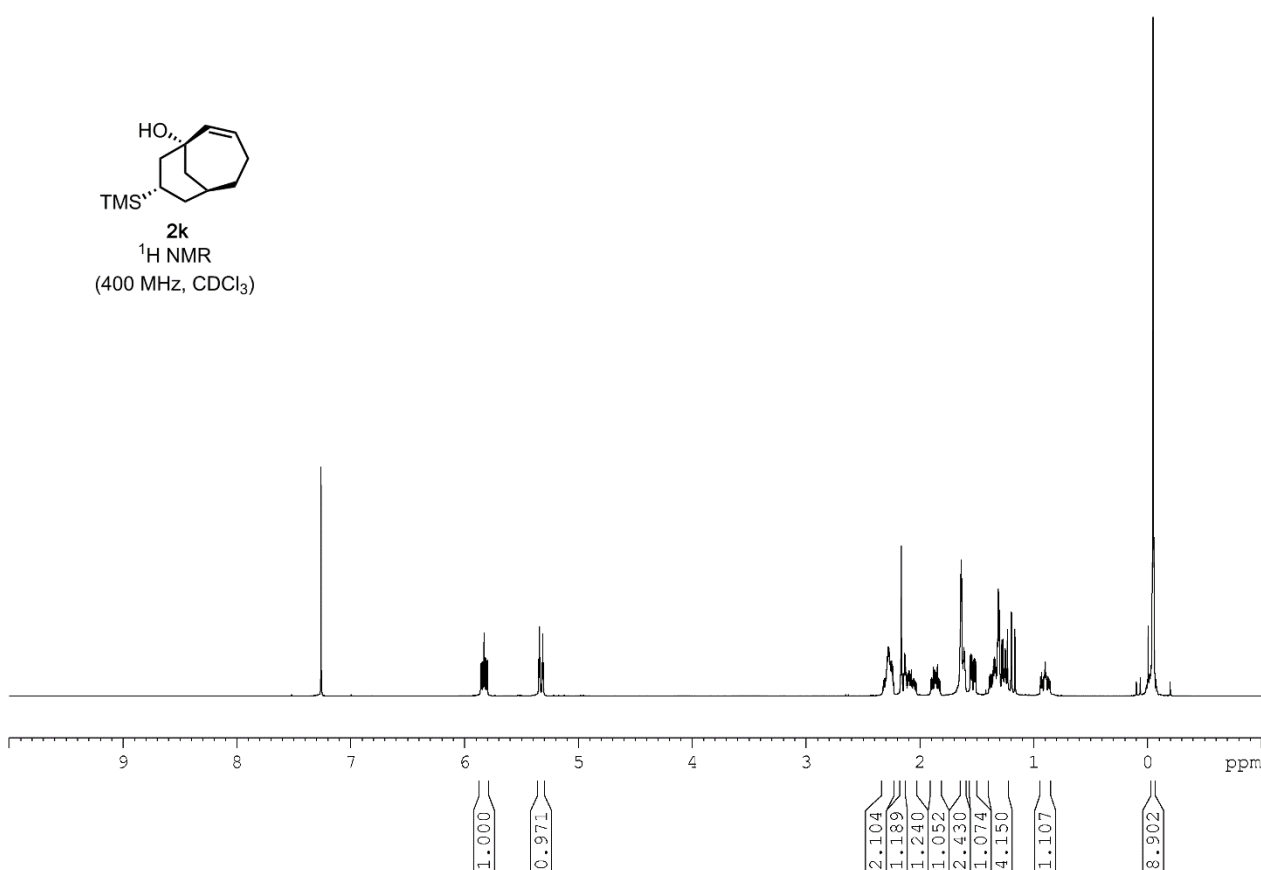




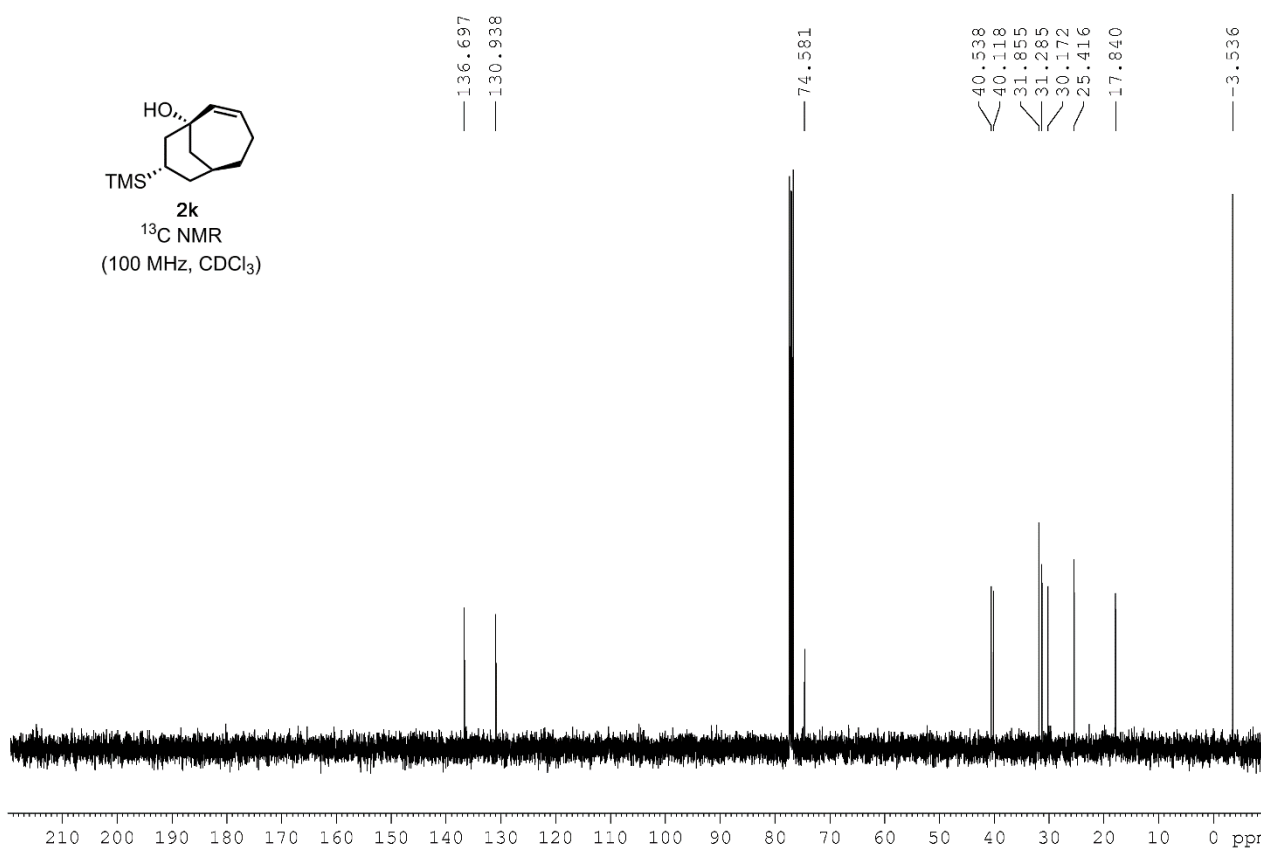


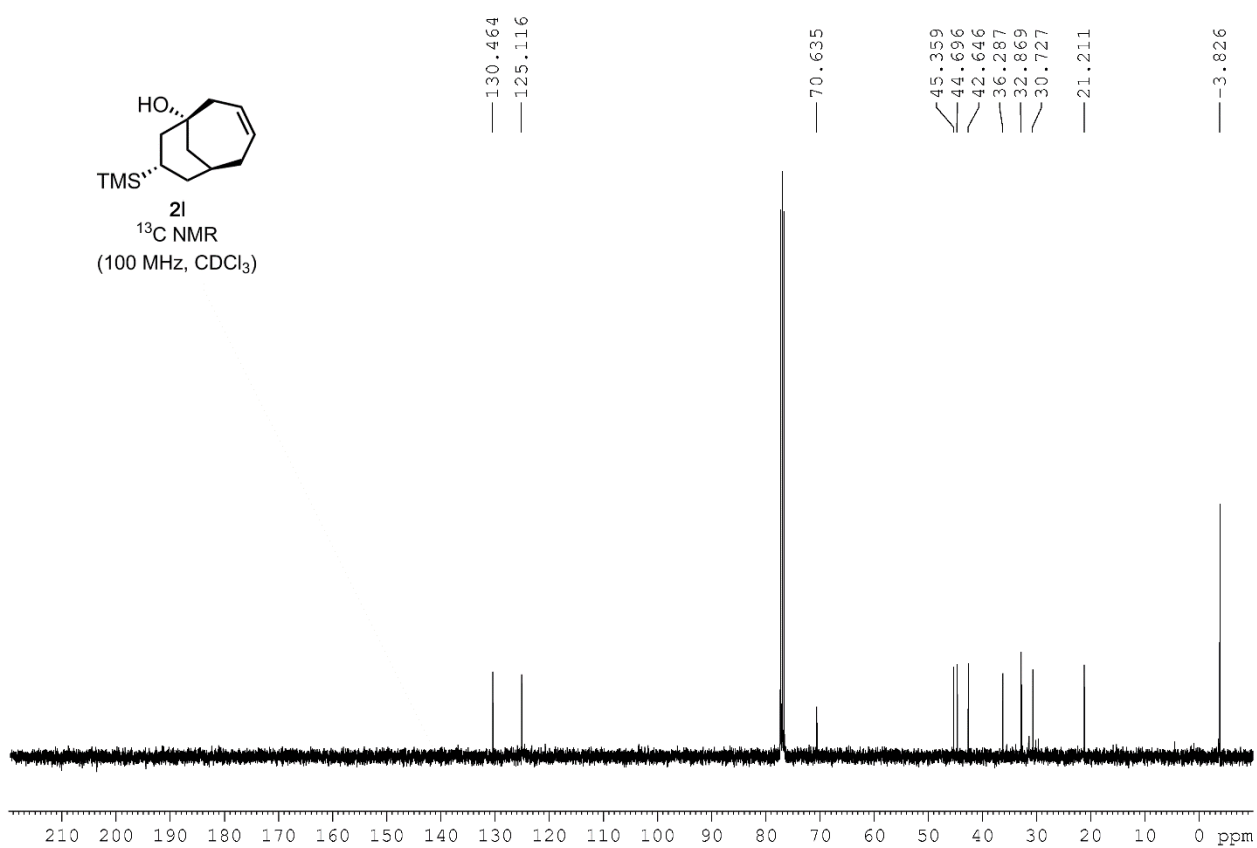
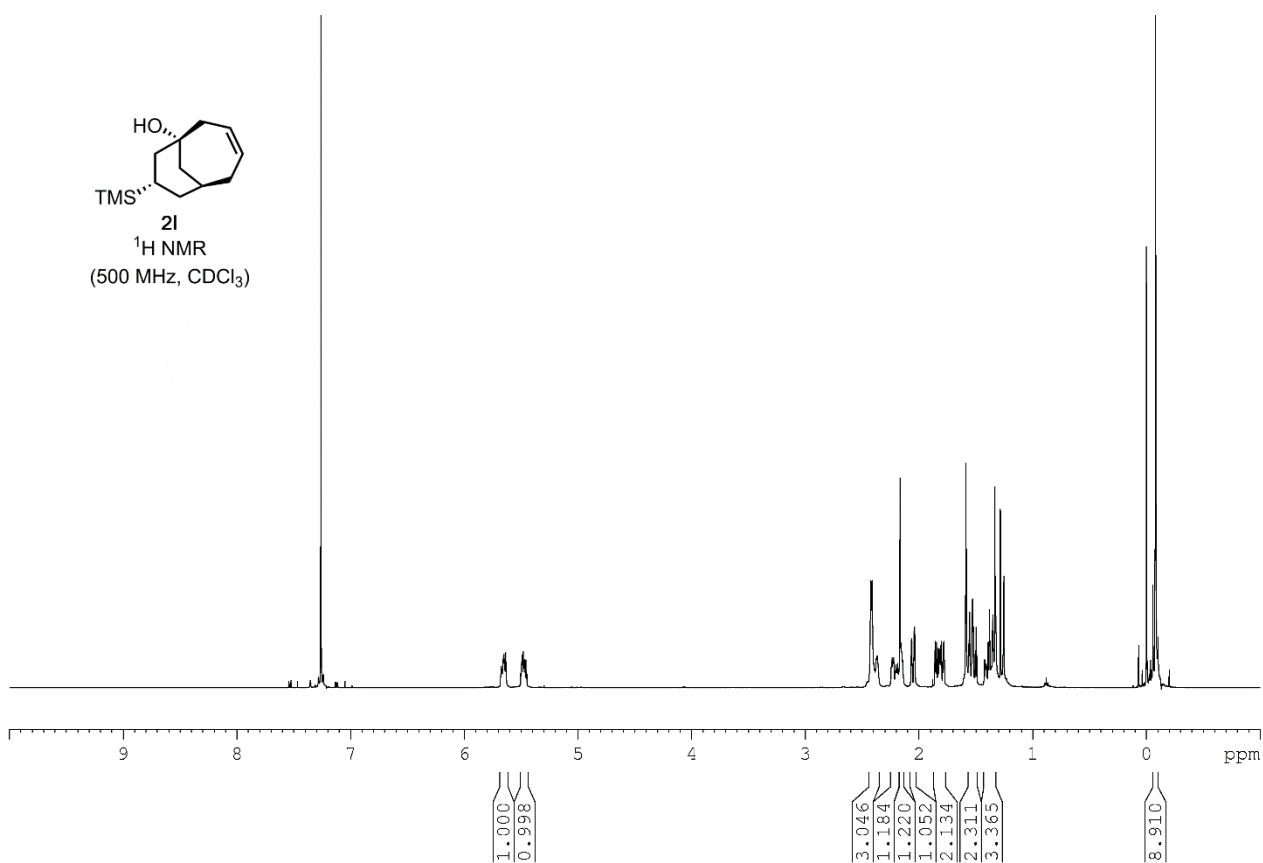


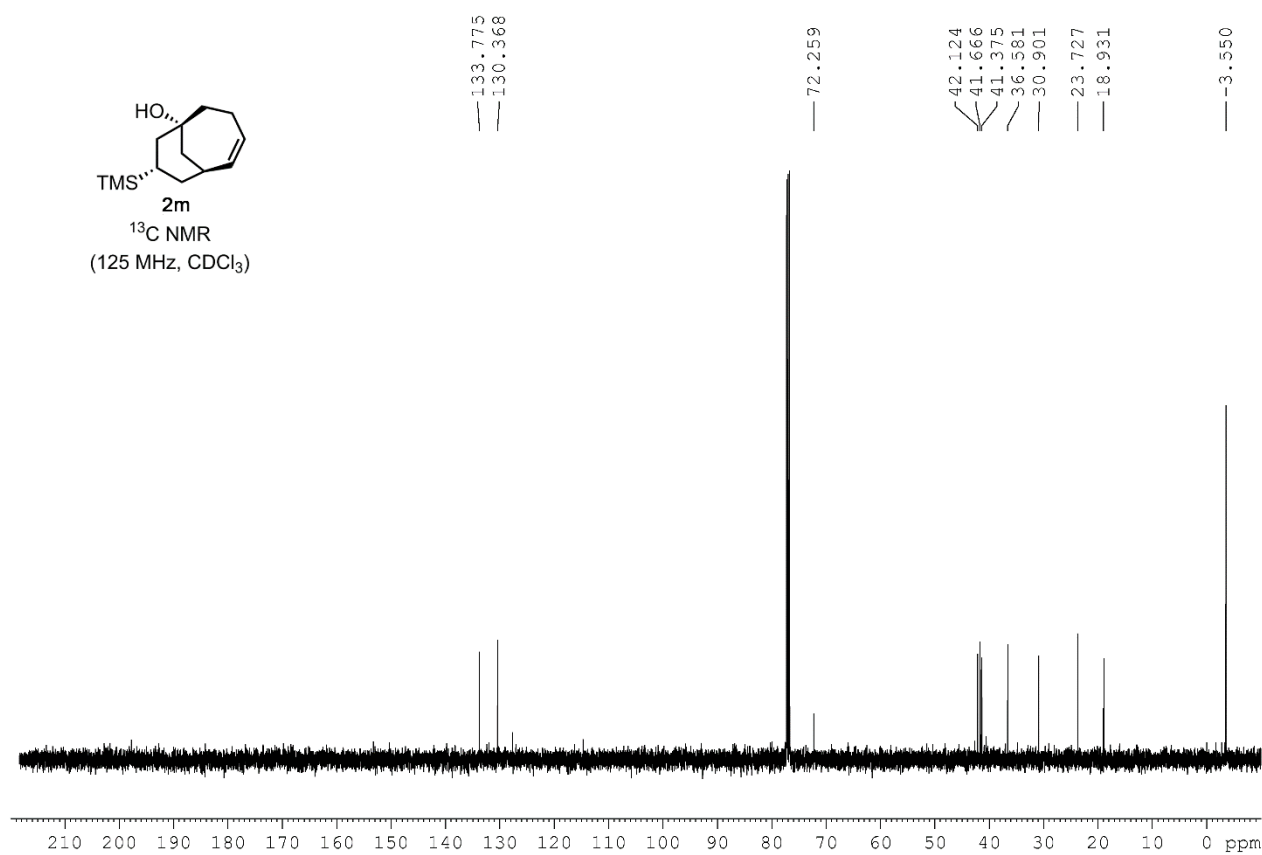
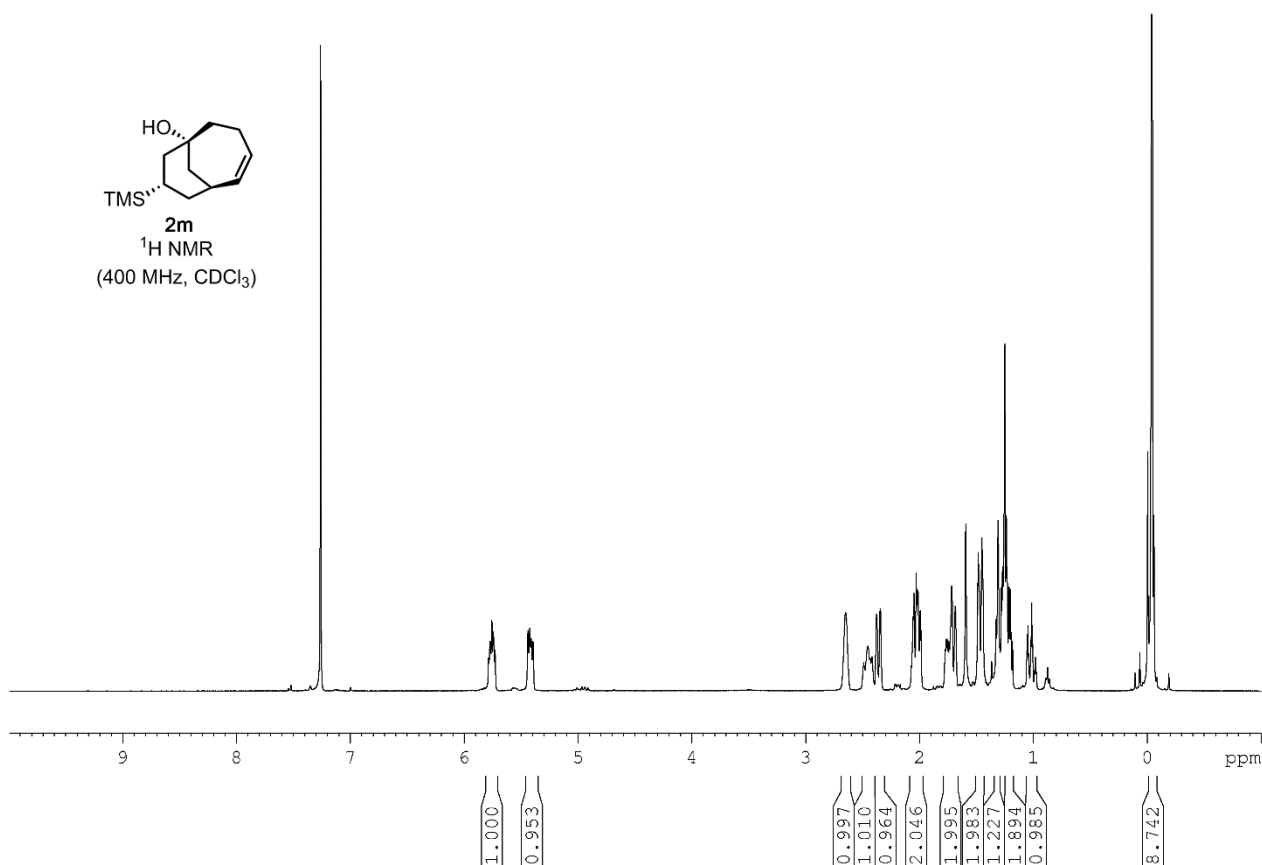
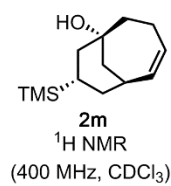
2k
¹H NMR
 (400 MHz, CDCl₃)

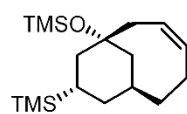


2k
¹³C NMR
 (100 MHz, CDCl₃)

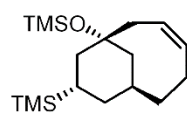
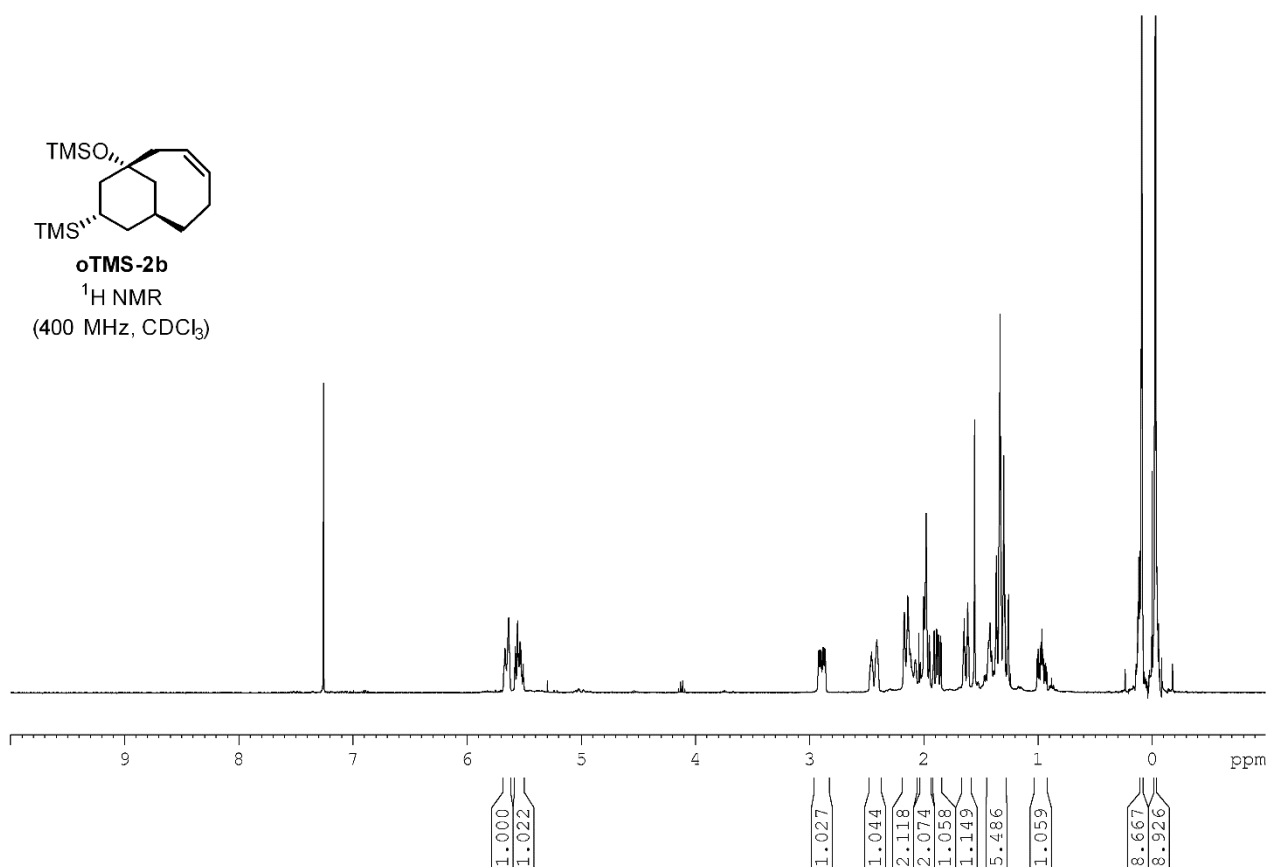




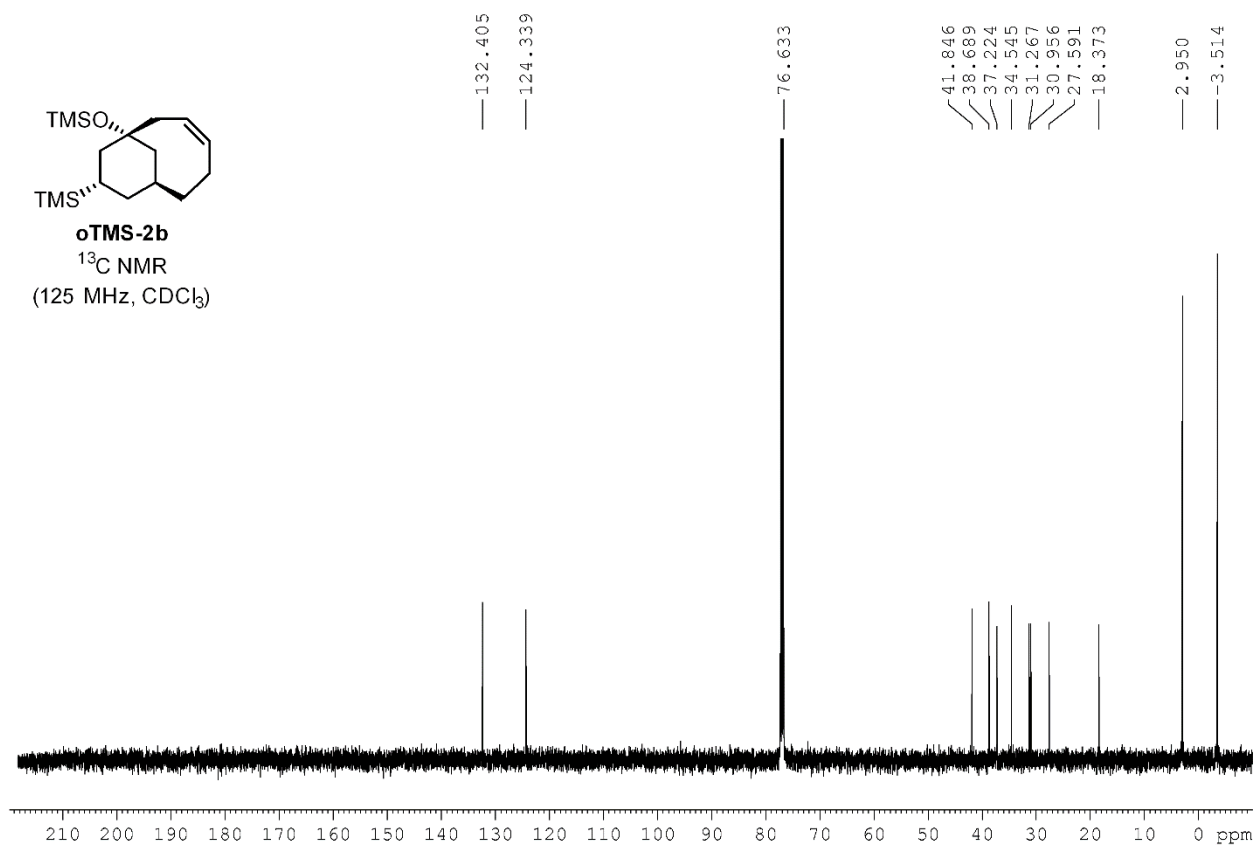


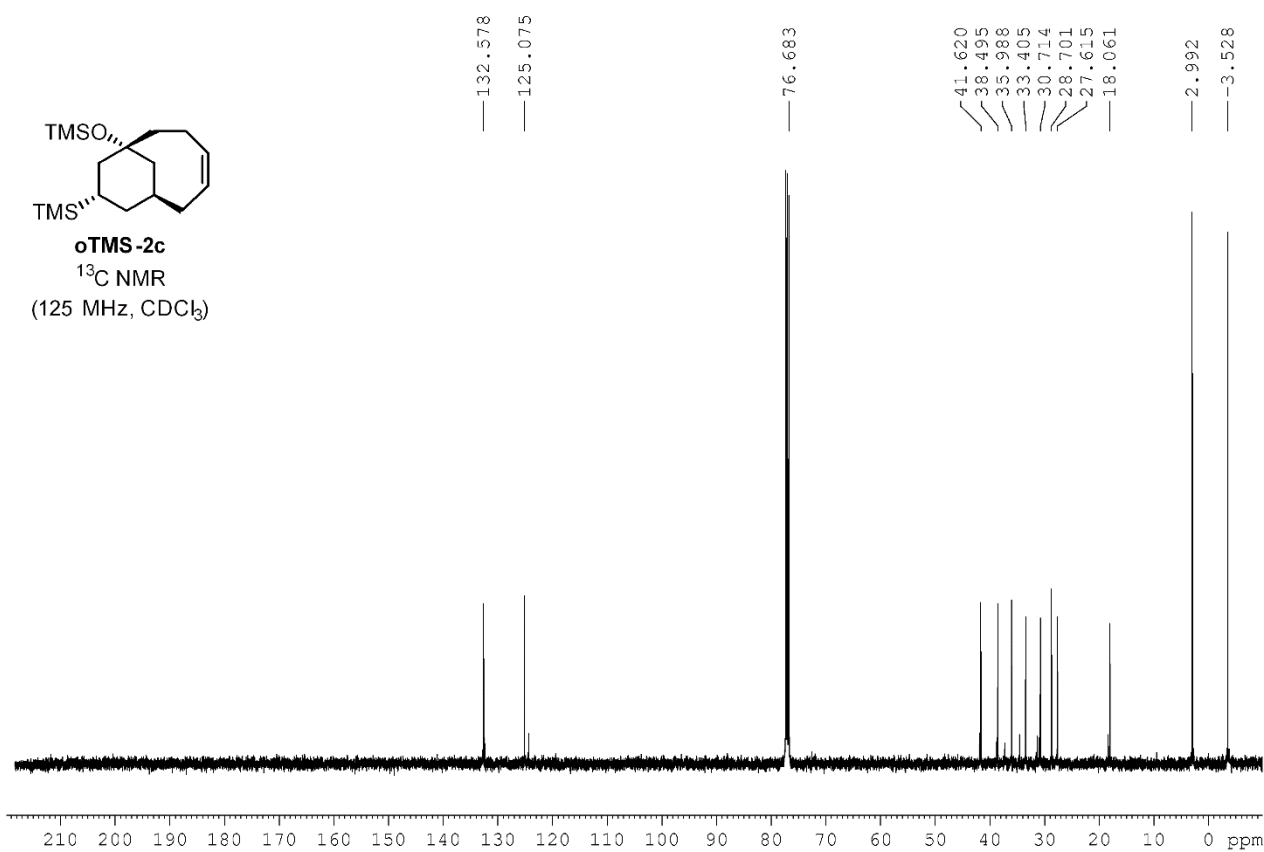
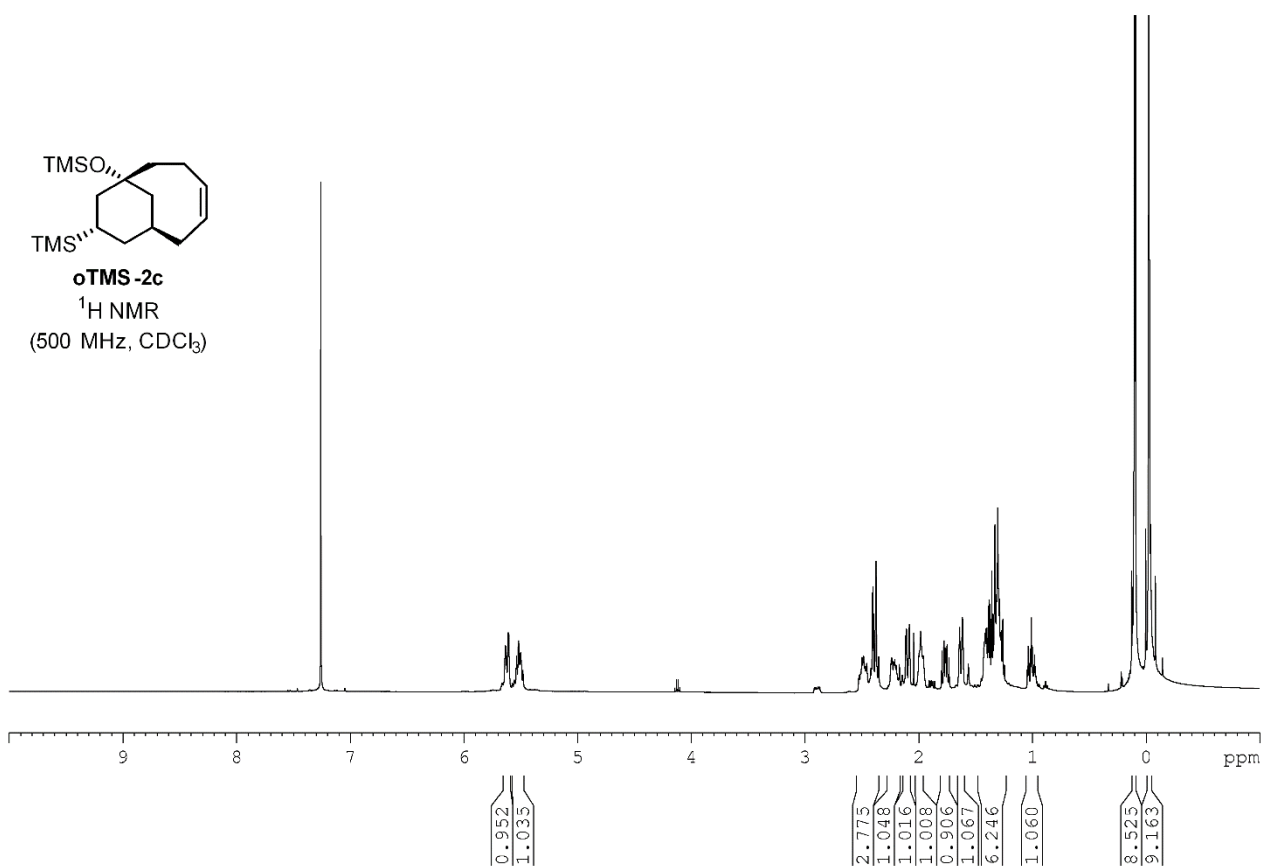


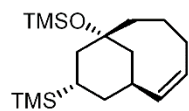
oTMS-2b
 ^1H NMR
 (400 MHz, CDCl_3)



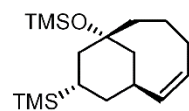
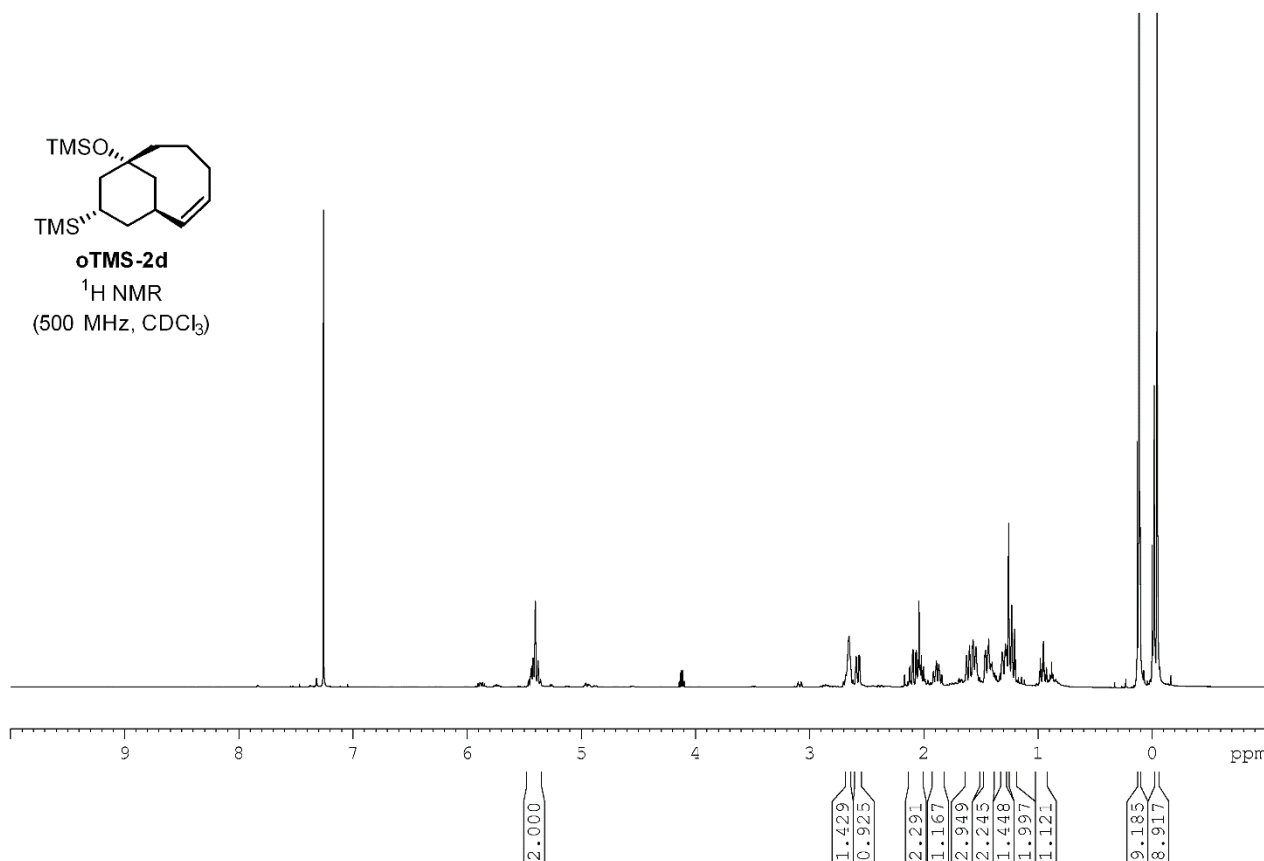
oTMS-2b
 ^{13}C NMR
 (125 MHz, CDCl_3)



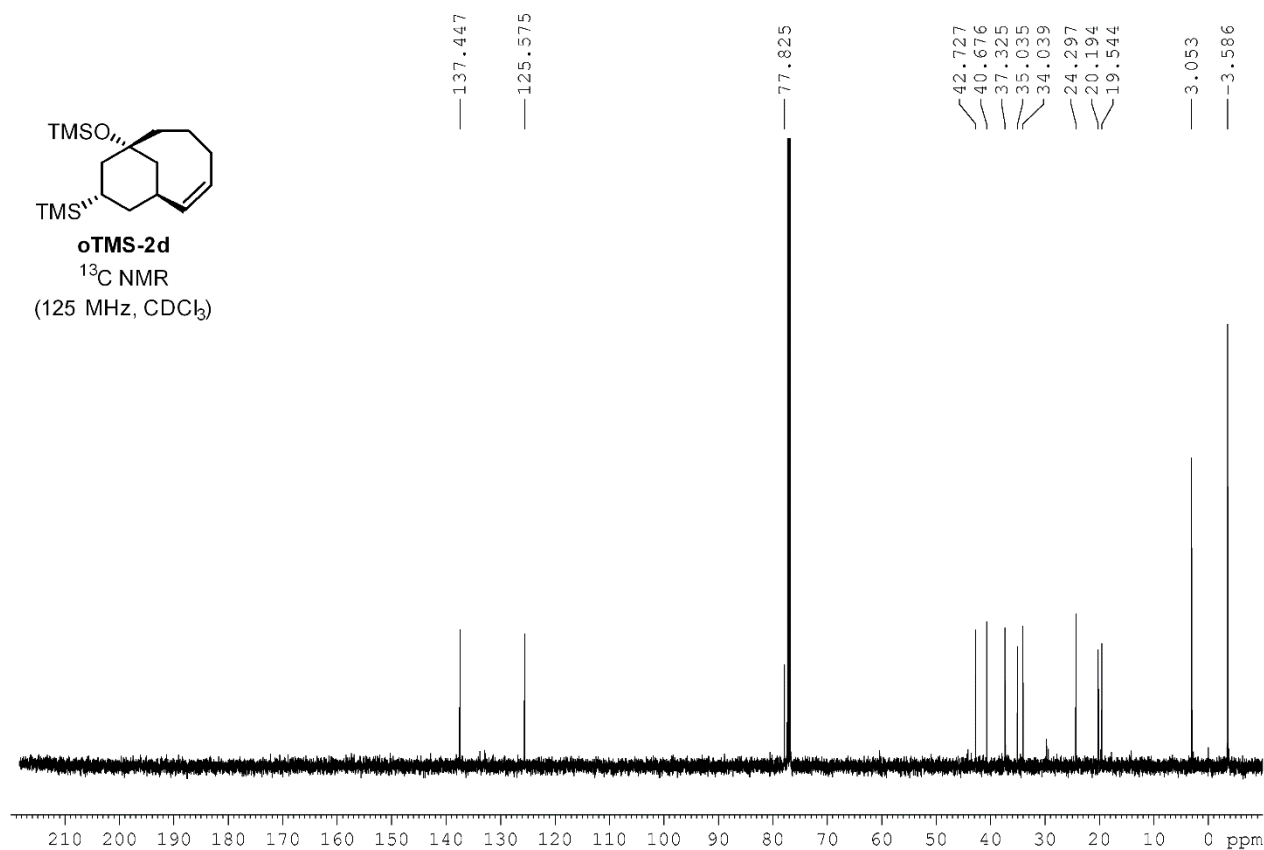


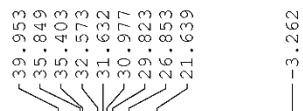
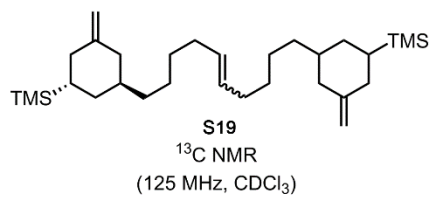
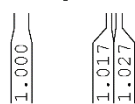
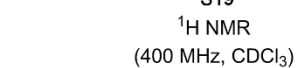


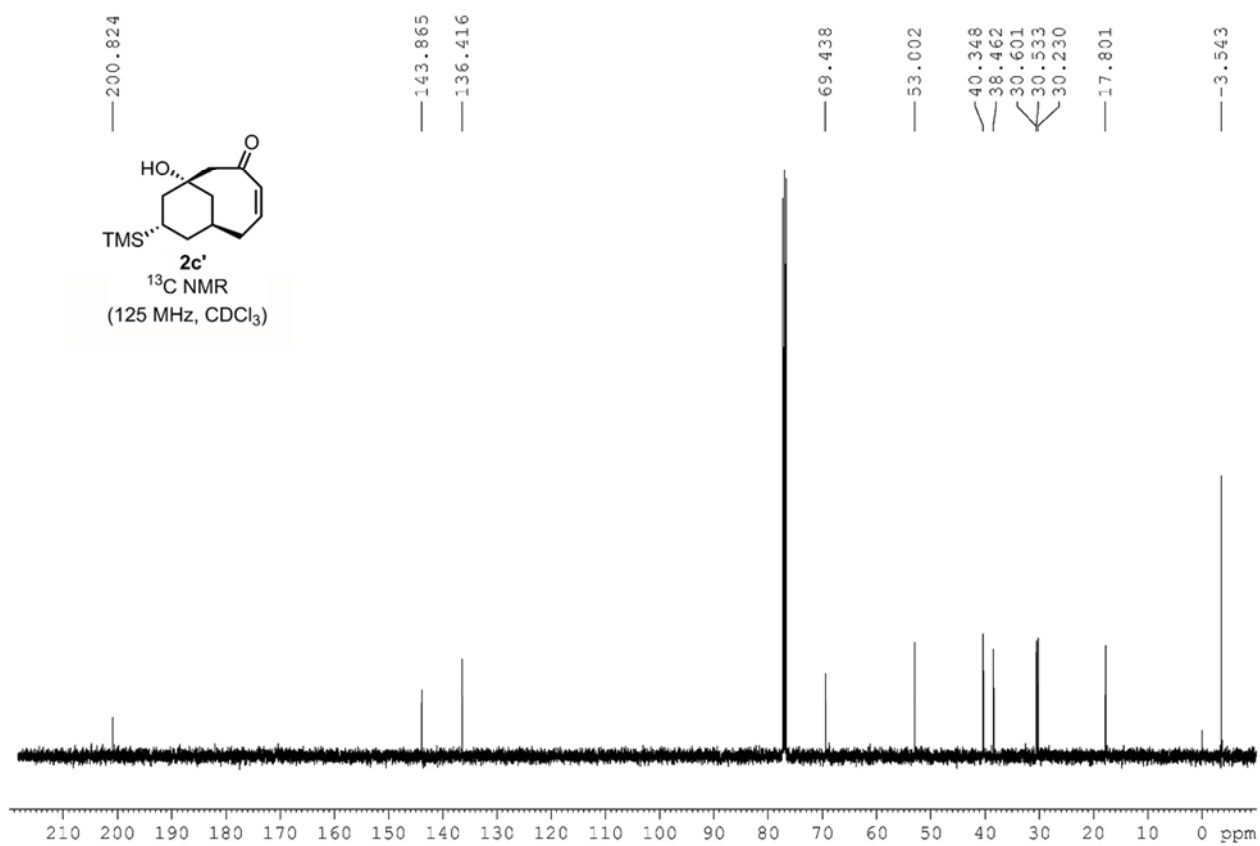
oTMS-2d
¹H NMR
 (500 MHz, CDCl₃)

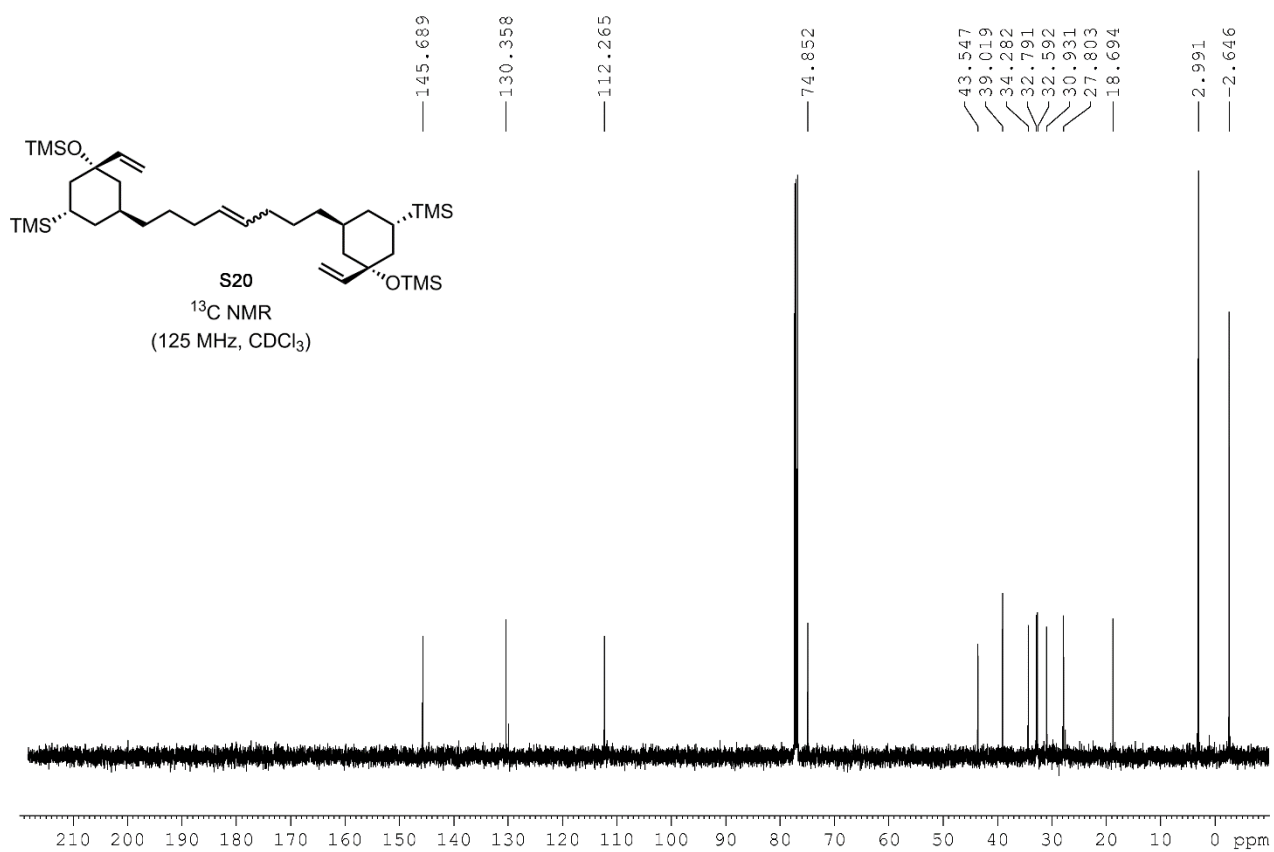
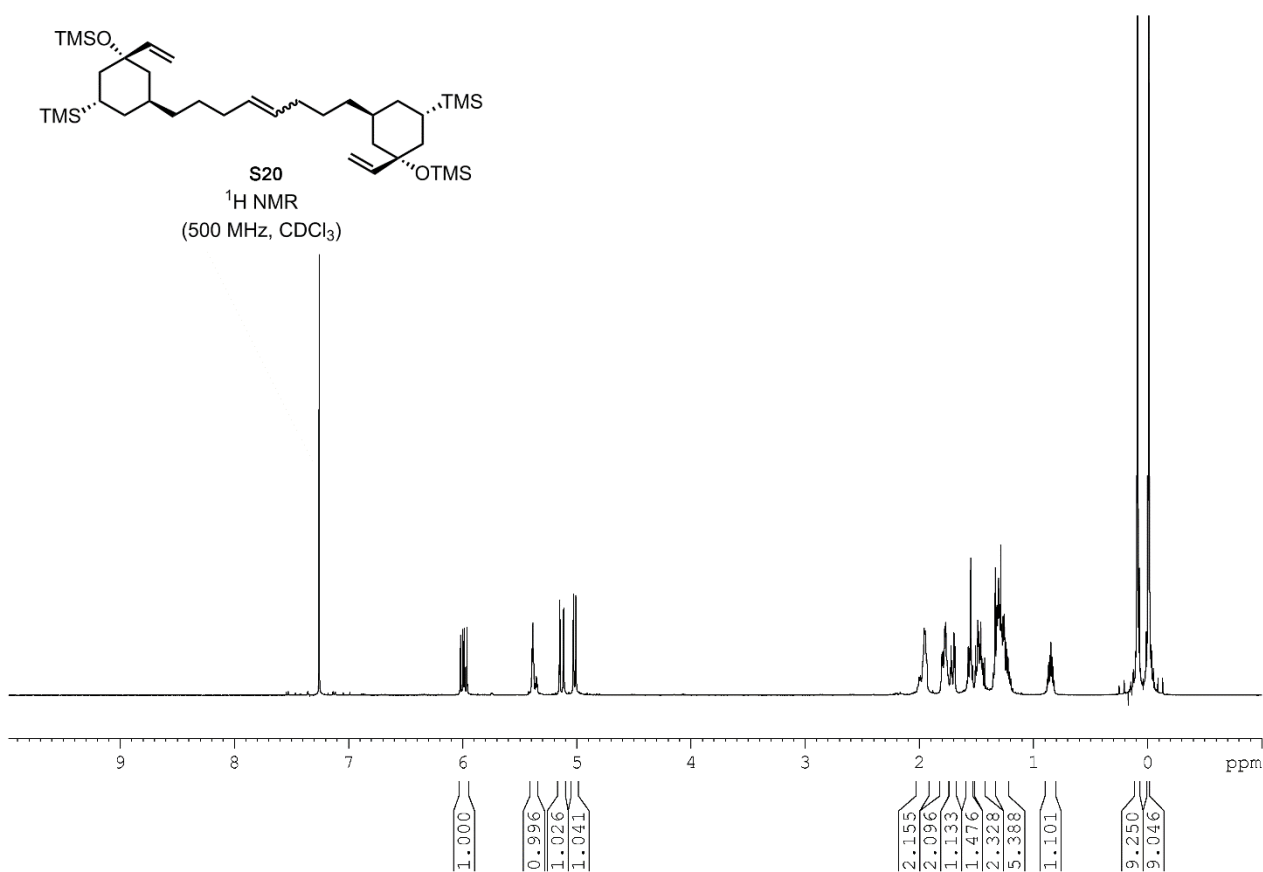


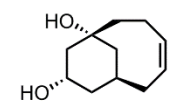
oTMS-2d
¹³C NMR
 (125 MHz, CDCl₃)



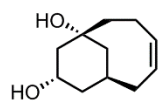
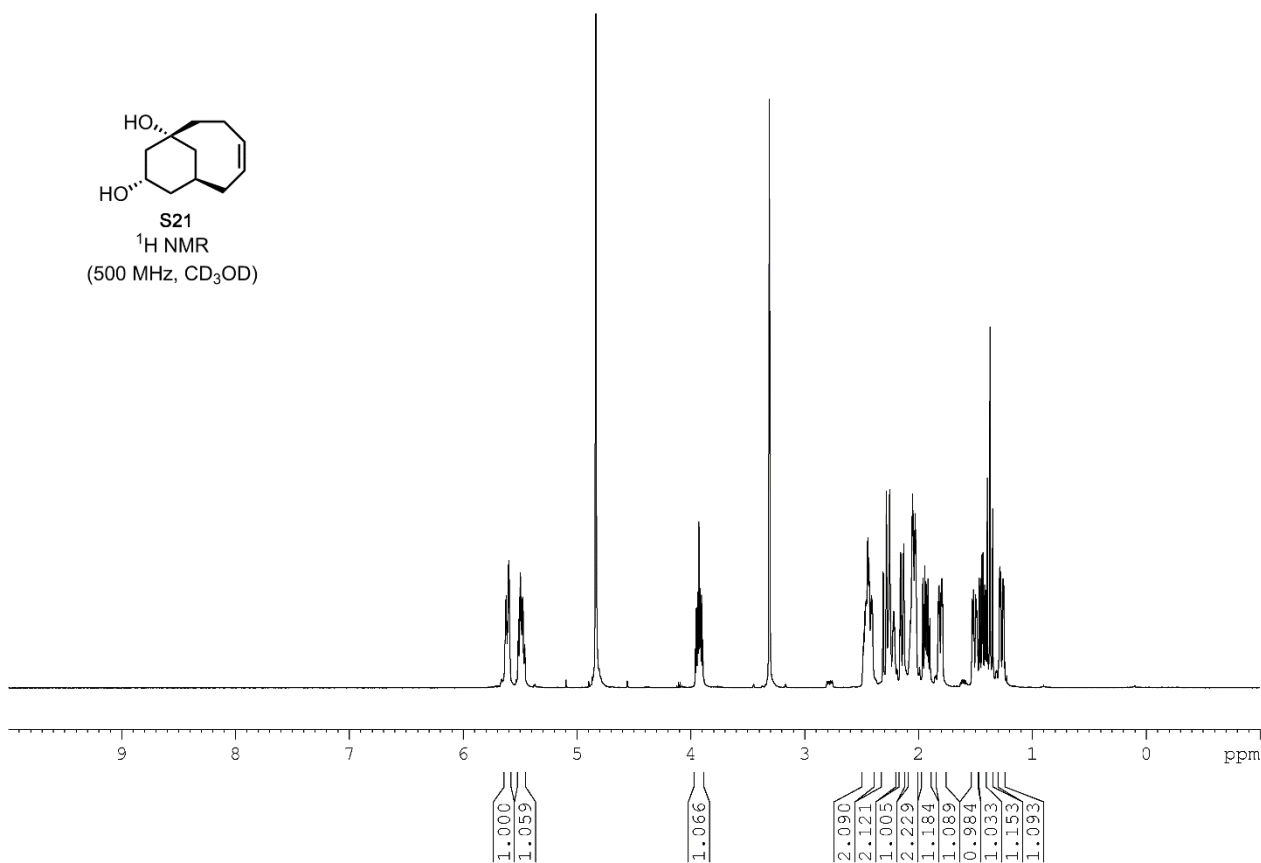




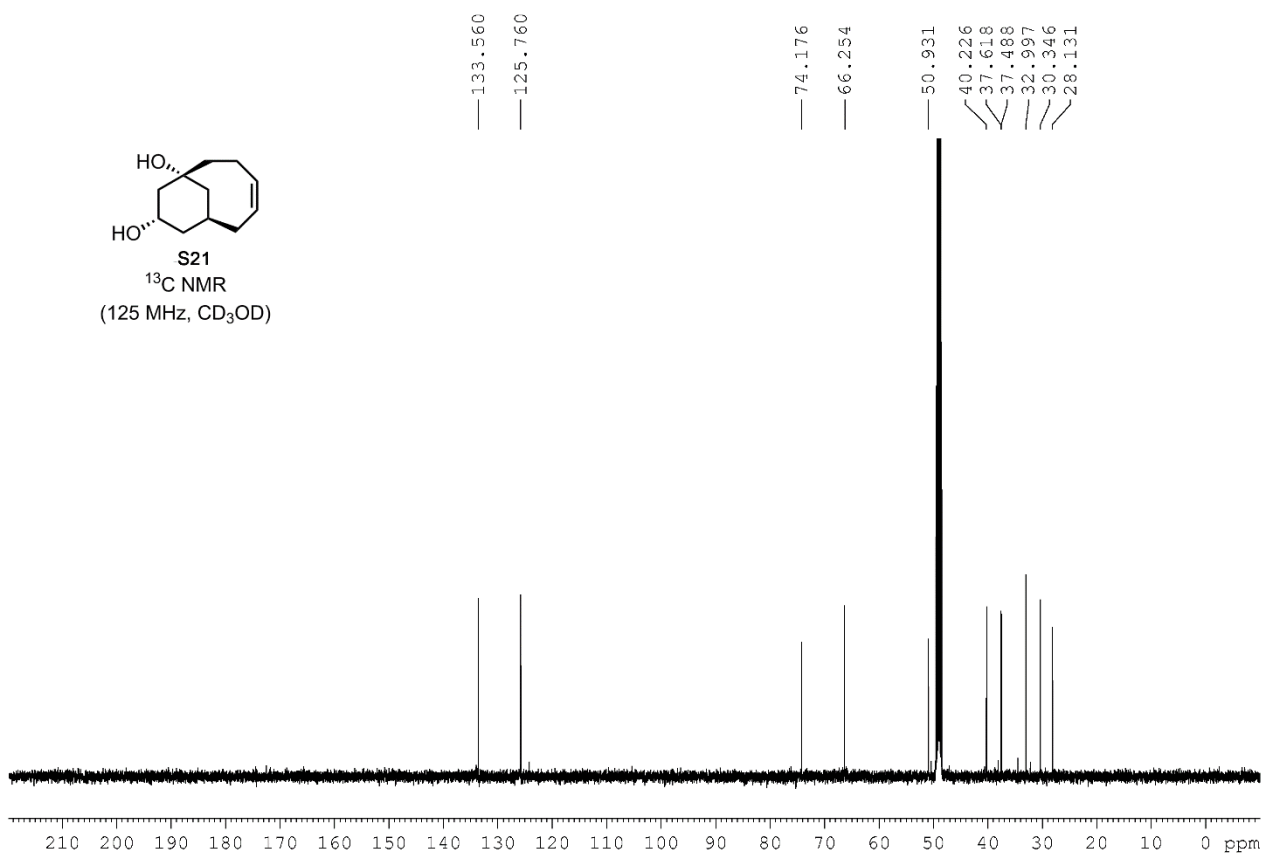


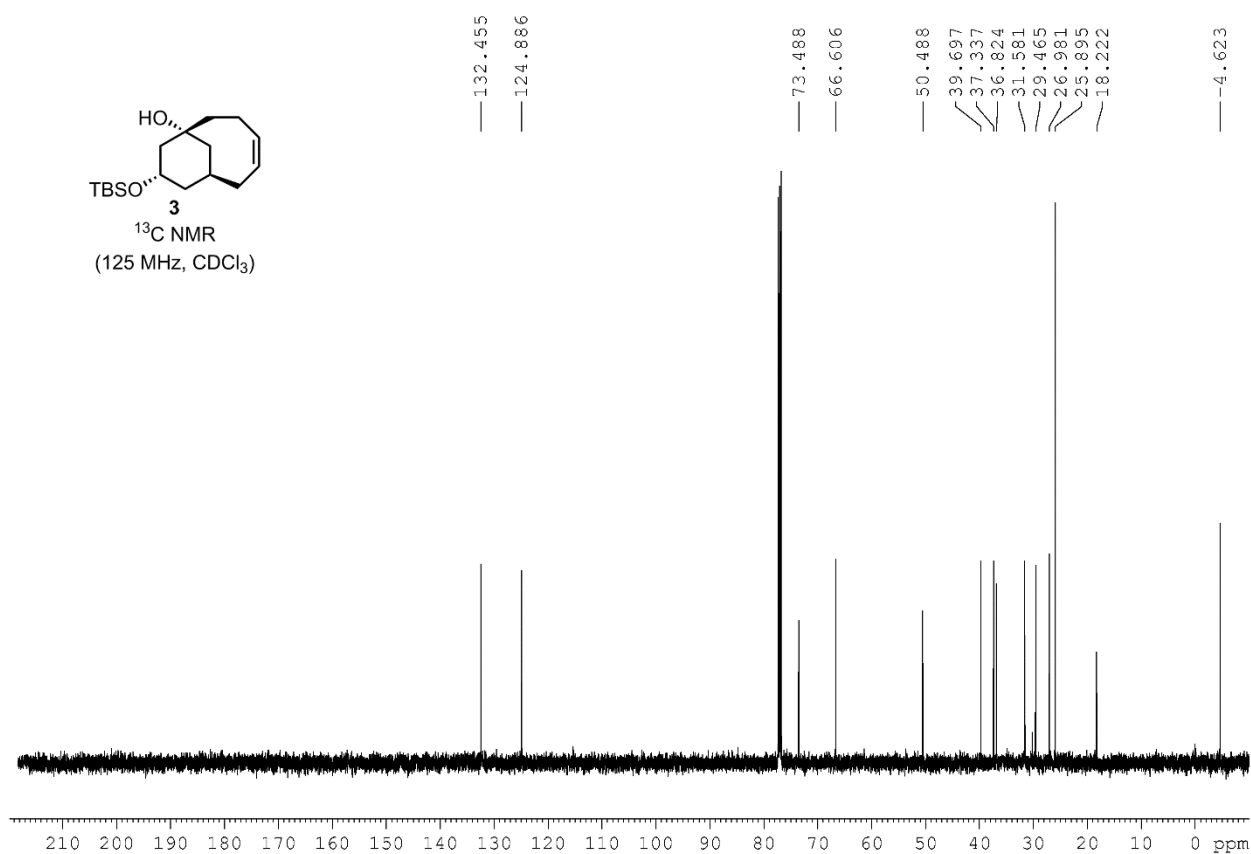
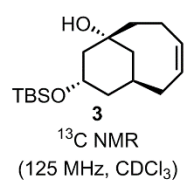
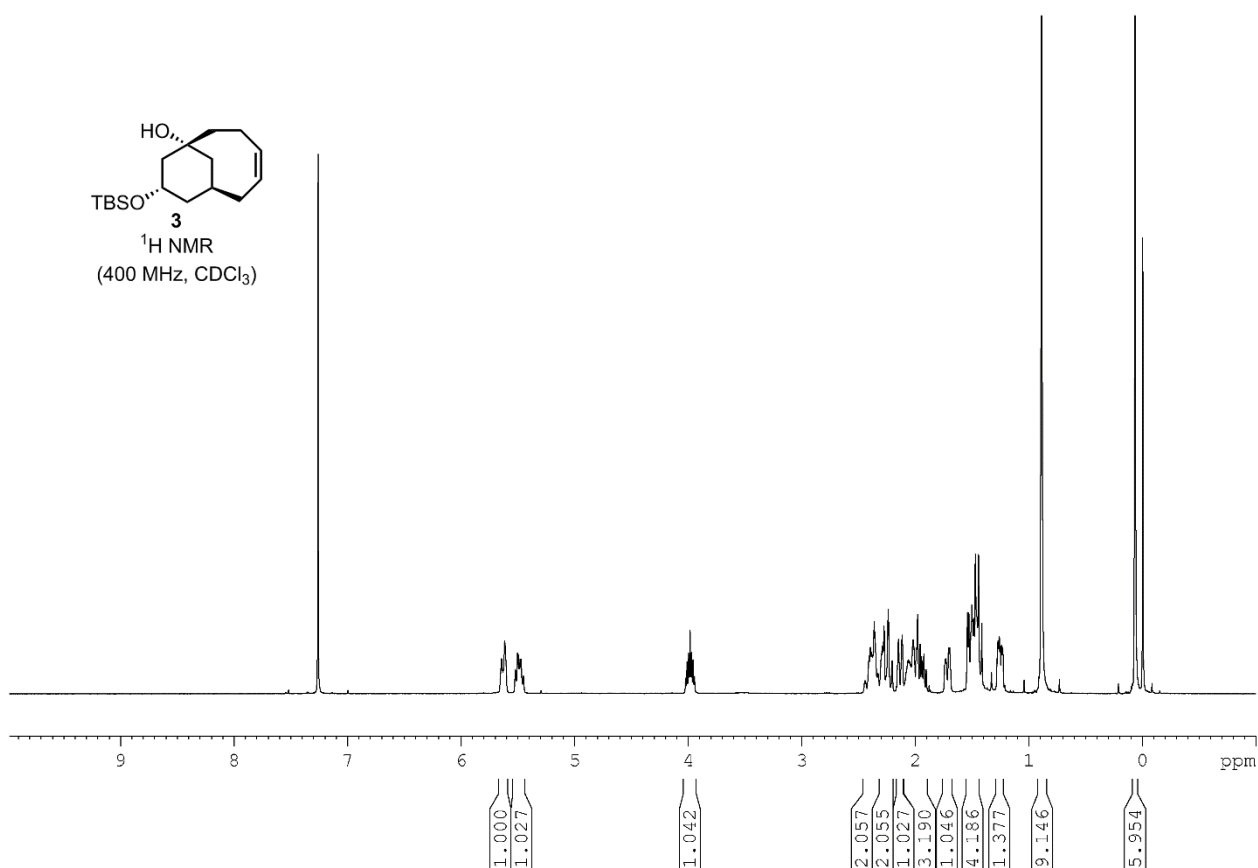
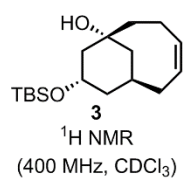


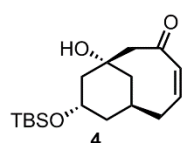
S21
¹H NMR
 (500 MHz, CD₃OD)



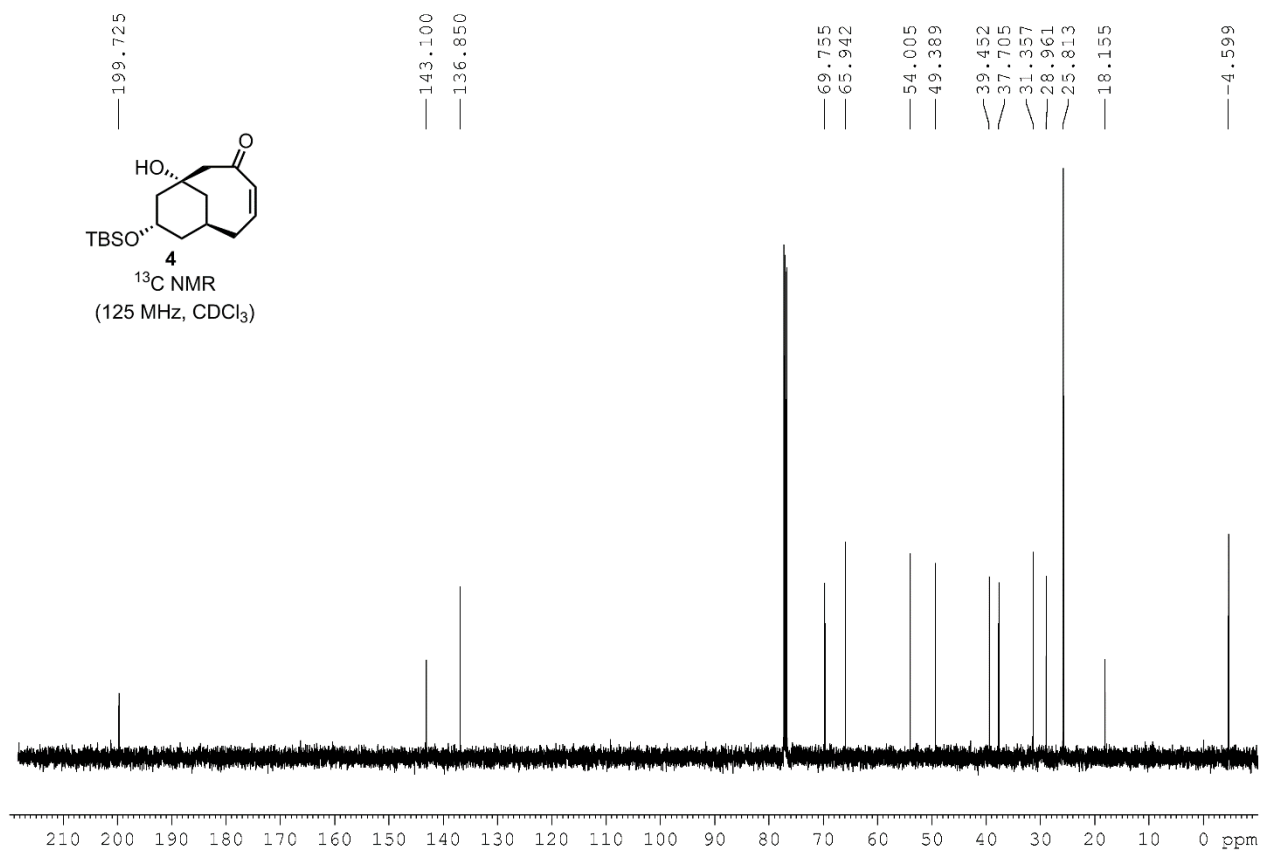
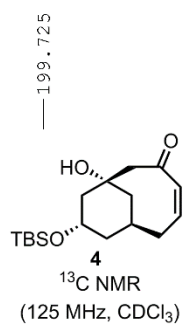
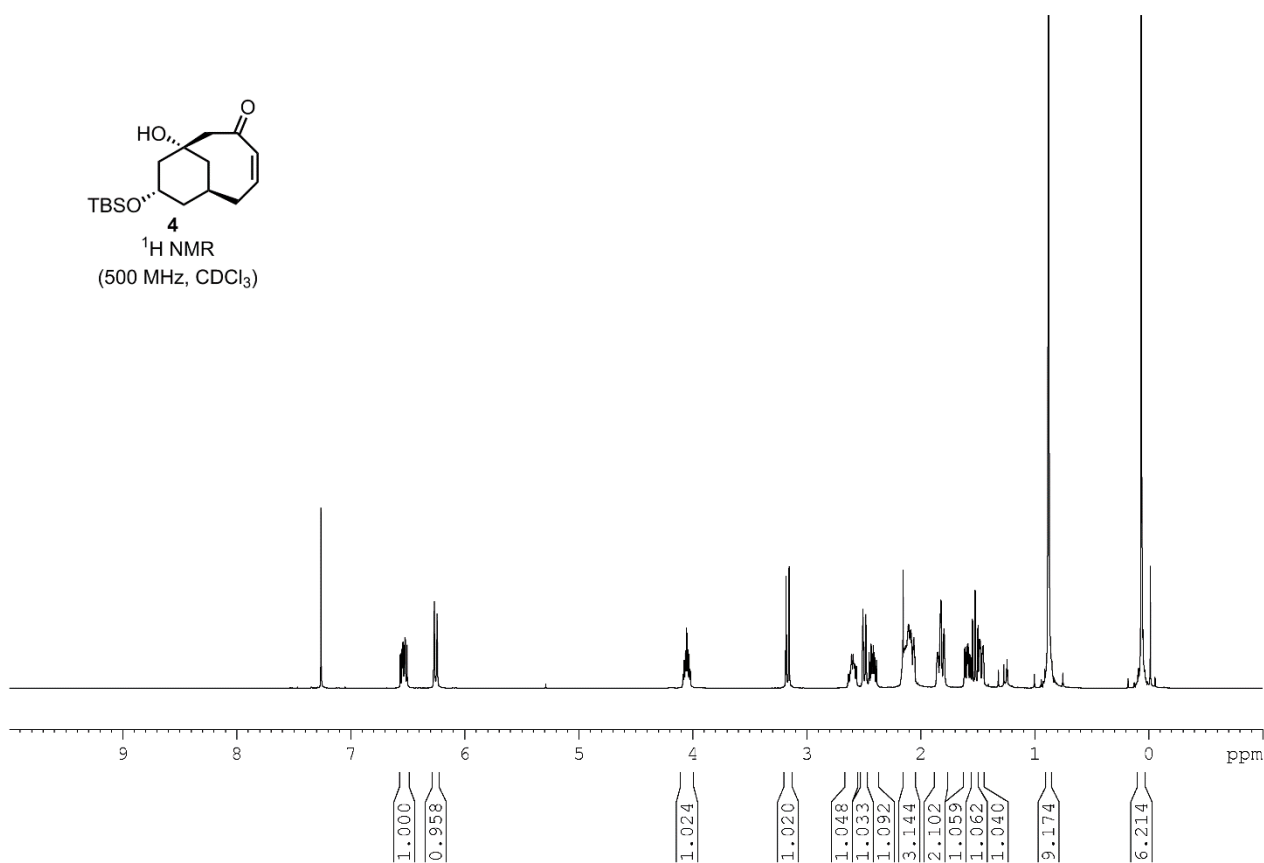
S21
¹³C NMR
 (125 MHz, CD₃OD)

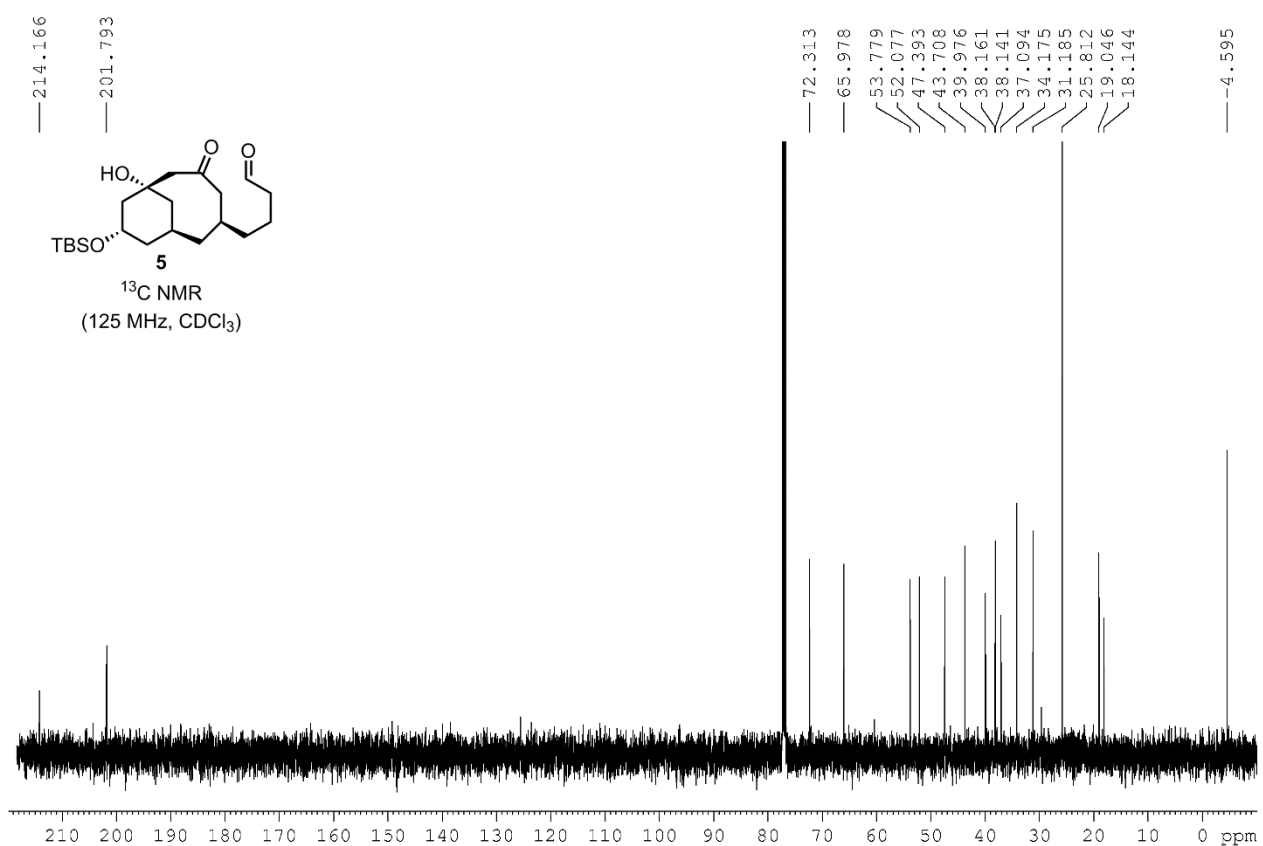
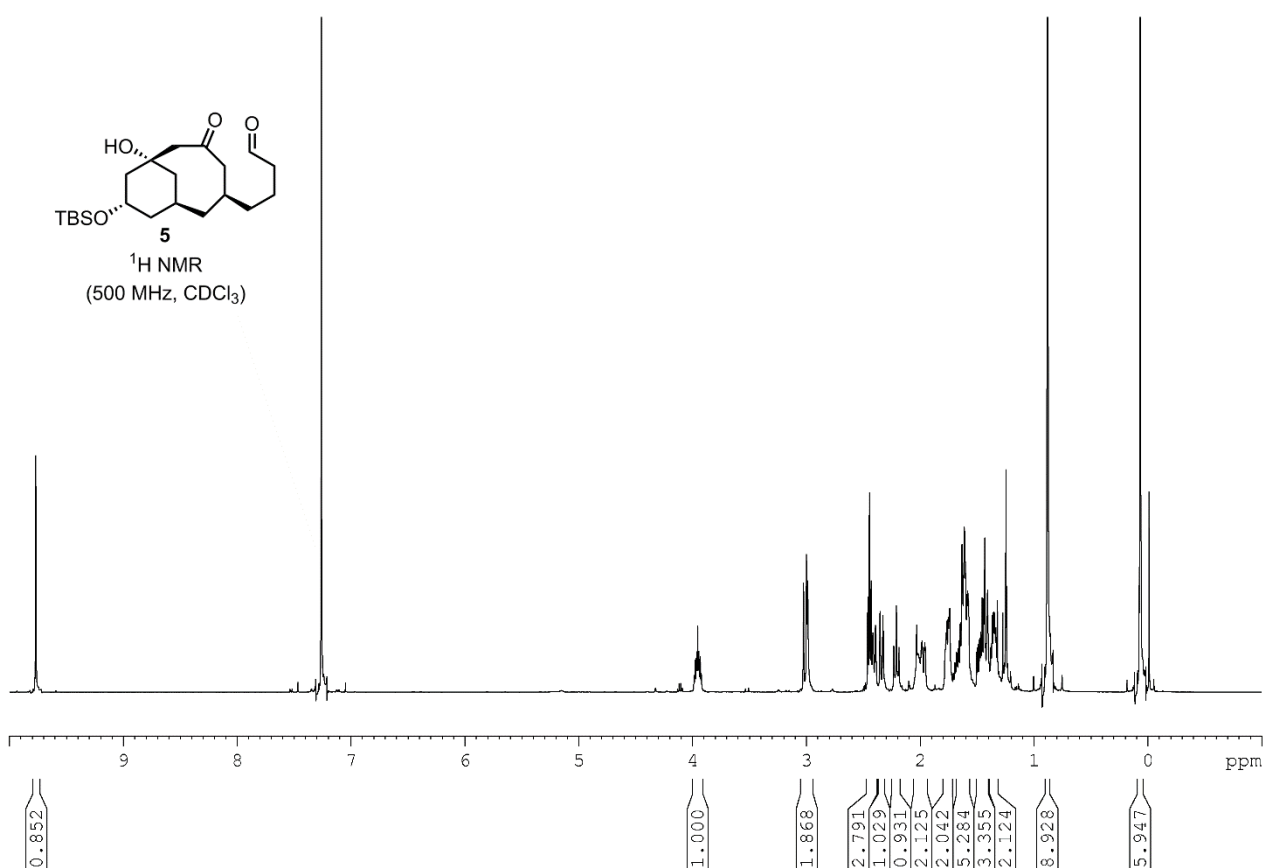


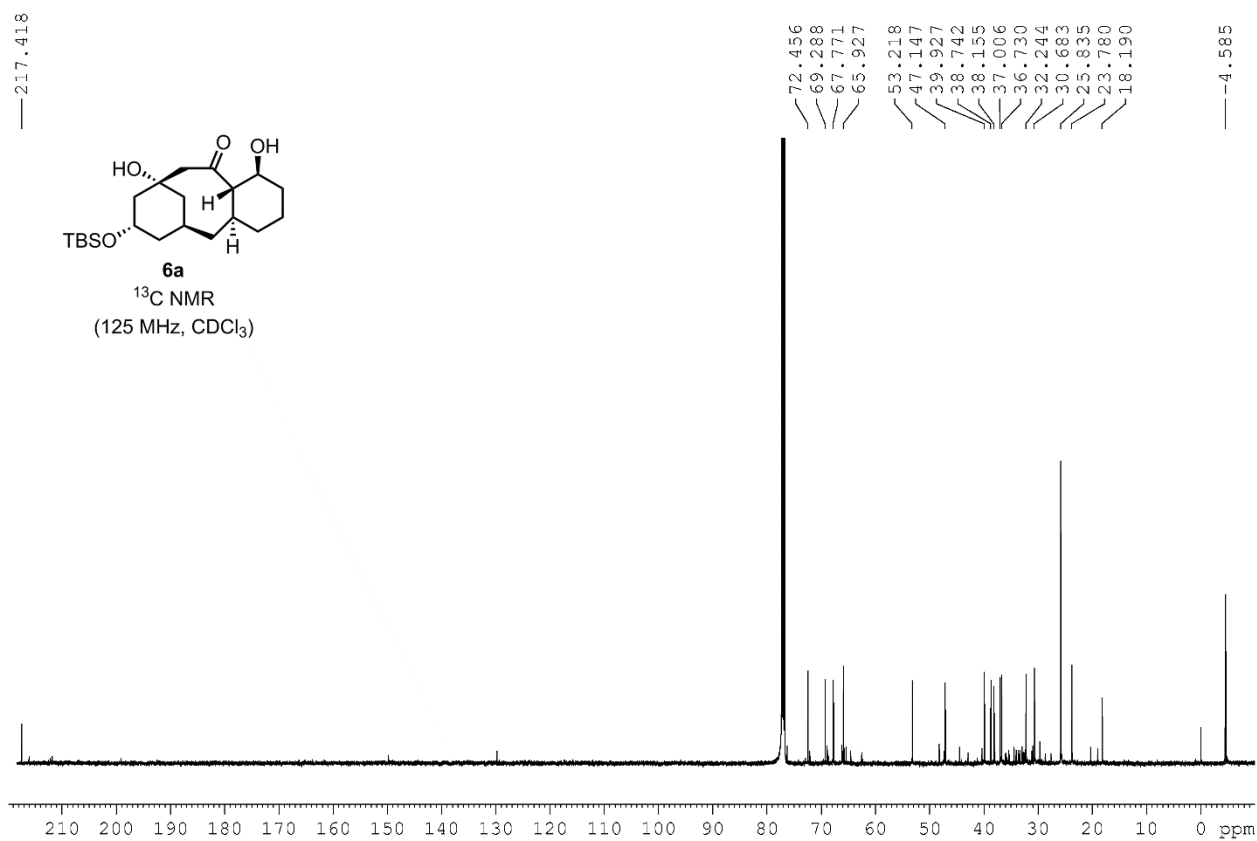
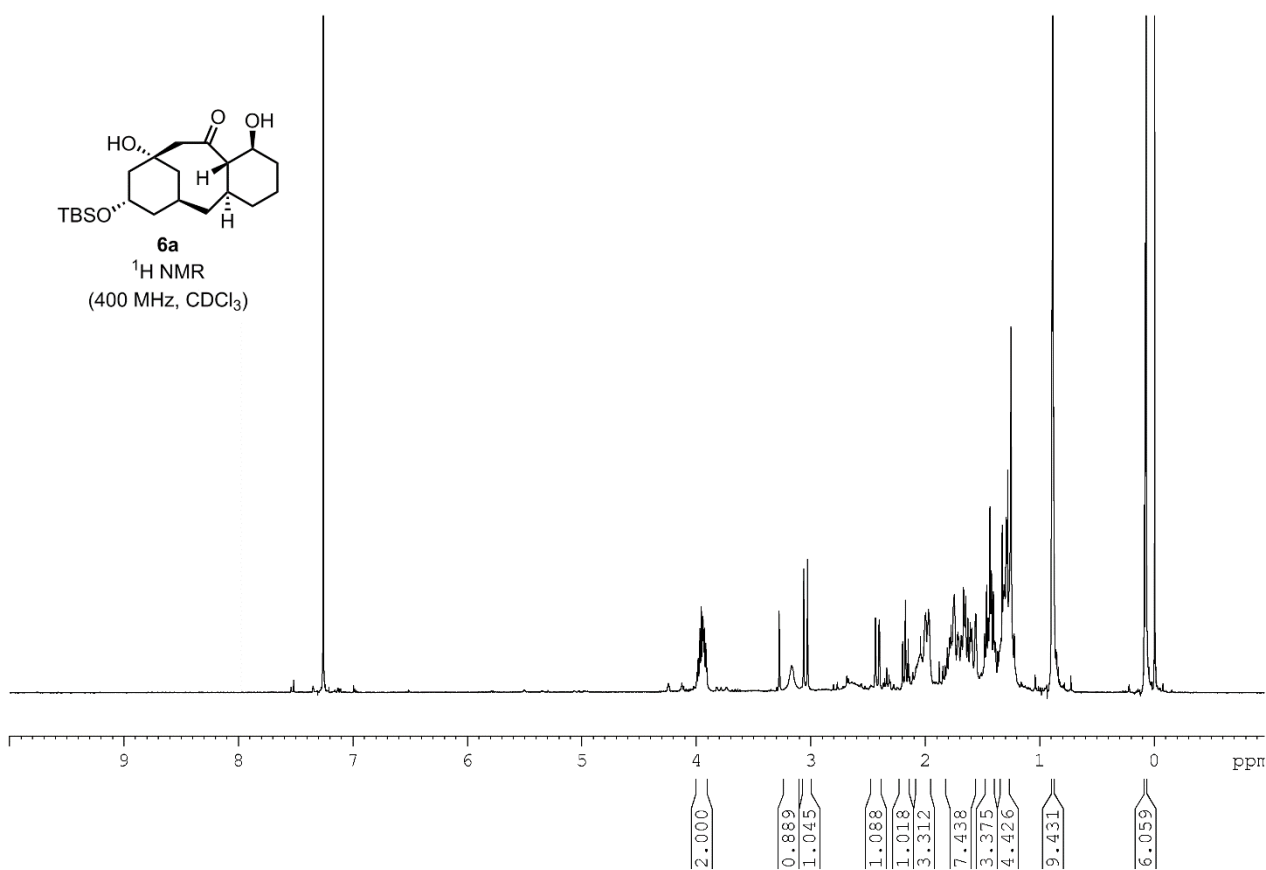


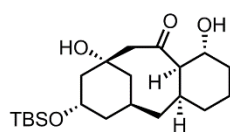


¹H NMR
(500 MHz, CDCl₃)

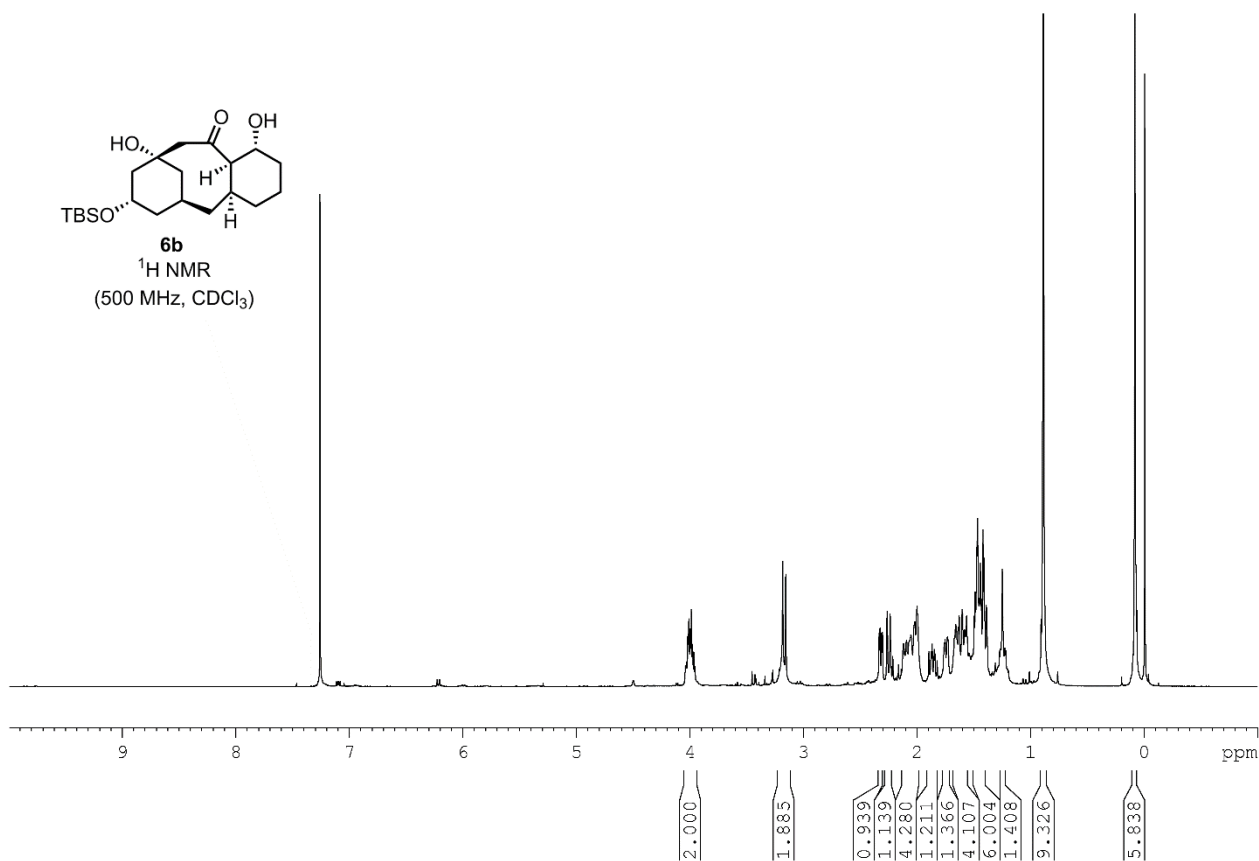




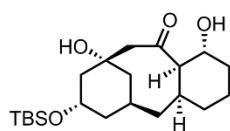




6b
 ^1H NMR
 (500 MHz, CDCl_3)



— 216.221



6b
 ^{13}C NMR
 (125 MHz, CDCl_3)

