Supporting Information

Domino Enyne Metathesis en Route to Skeletally Diverse, Privileged Scaffolds: Synthesis of Tricyclic Core of Pseudolaric Acid F

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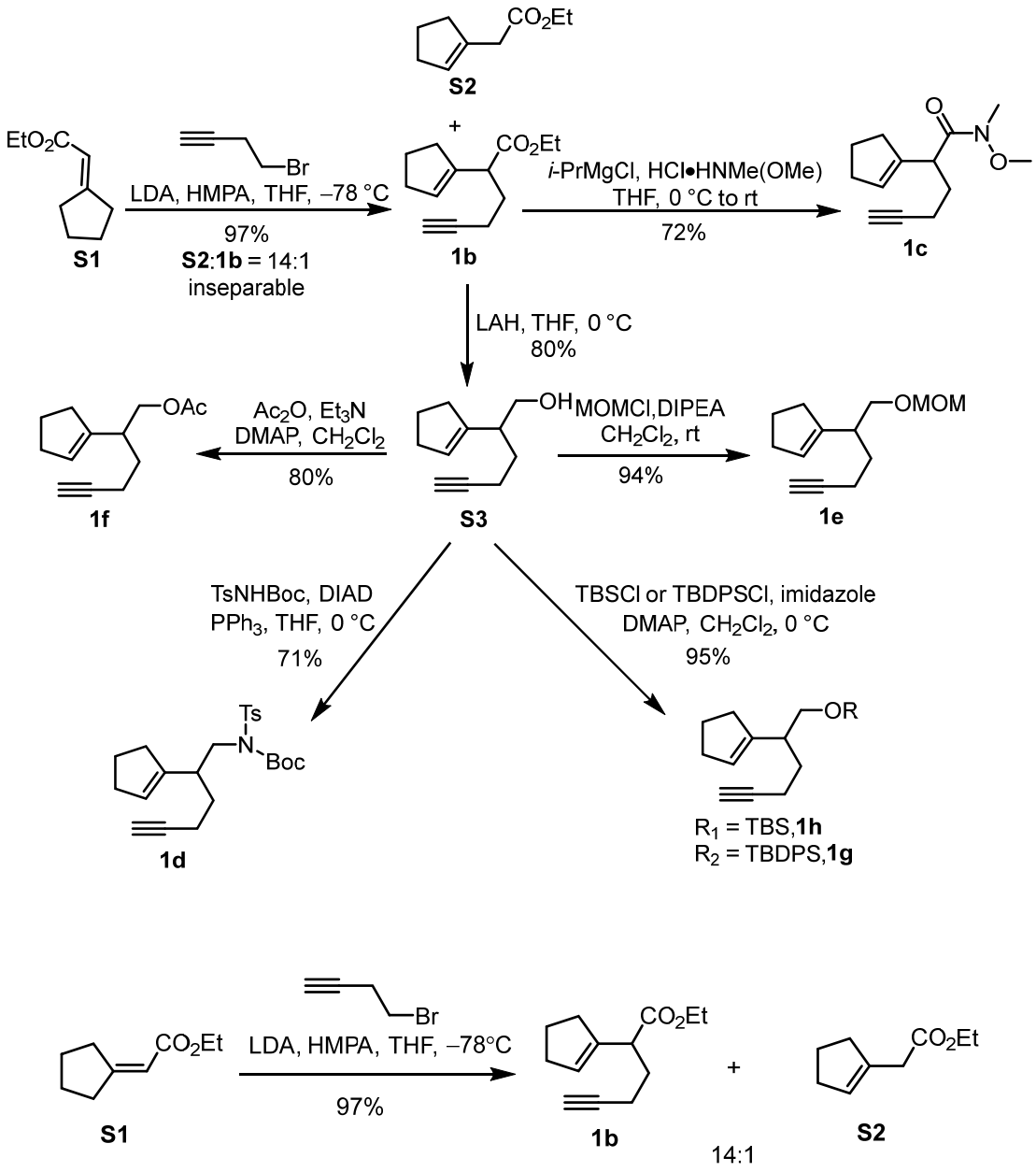
1. General Information

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 ºC. Tetrahydrofuran (THF) was distilled from sodium-benzophenone; Dichloromethane (CH_2Cl_2) was distilled from calcium hydride. Toluene was distilled from sodium under argon atmosphere. HMPA was distilled *in vacuo* from calcium hydride; Diisopropylamine (DIPA) was distilled from calcium hydride under argon atmosphere; 1,2-Dichloroethane (DCE) was distilled from calcium hydride under argon atmosphere. Super-dry N,N-Dimethylformamide (DMF) were purchased from Innochem Science & Technology Co., Ltd. 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) were recorded on a Micromass QTOF2 Quadrupole/Time-of-Flight Tandem mass spectrometer using electron spray ionization. NMR spectra were recorded on Bruker AV-400 and Bruker AV-500 instruments and were calibrated using residual undeuterated solvents ($CHCl_3$, δ_H = 7.26 ppm) and deuterated solvents ($CDCl_3$, δ_C = 77.0 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

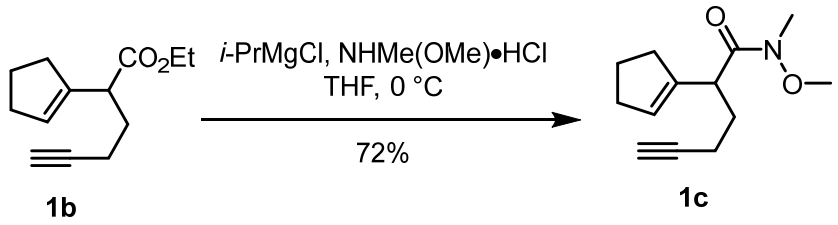
2.1) Procedures for the preparation of enyne-I



To a solution of DIPA (31.8 mL, 226.2 mmol) in THF (300 mL) at 0 °C was added *n*-BuLi (68 mL, 2.5 M in hexane). After being stirred for 30 min, the reaction was cooled to –78 °C, and then a solution of α,β-unsaturated ester **S1** (17.4 g, 113.1 mmol) in THF (50 mL) was added slowly and the stirring was continued for another 1 h. The distilled HMPA (118.1 mL, 678.6 mmol) was added slowly. The mixture was stirred for another 30 min and the bromide (21.0 mL, 170.0 mmol) in THF (50 mL) was added dropwise. The reaction was stirred for 2 days, and the saturated NH_4Cl solution (150 mL) was

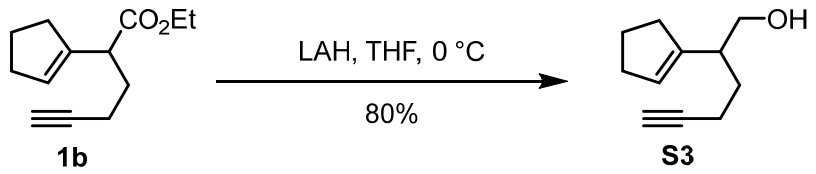
added and the resulting mixture was extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the residue by flash chromatography (PE/EtOAc = 100:1) afforded **1b** (22.63 g, 97%) as a colorless oil. The product contained 6.6 mol% of **S2**.

Ethyl 2-(cyclopent-1-en-1-yl)hex-5-ynoate (1b). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.60 – 5.56 (m, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.36 (t, *J* = 7.4 Hz, 1H), 2.35 – 2.24 (m, 4H), 2.20 – 2.14 (m, 2H), 2.07 – 1.98 (m, 1H), 1.96 (t, *J* = 2.6 Hz, 1H), 1.90 – 1.77 (m, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 140.3, 127.9, 83.4, 68.9, 60.5, 46.3, 32.8, 32.3, 28.9, 23.2, 16.4, 14.2. IR (KBr, cm^{-1}): 2956, 1732, 1157, 1043, 634. HRMS (ESI, m/z) calc for $C_{13}H_{18}O_2$ $[M+H]^+$: 207.1380, found: 207.1377.



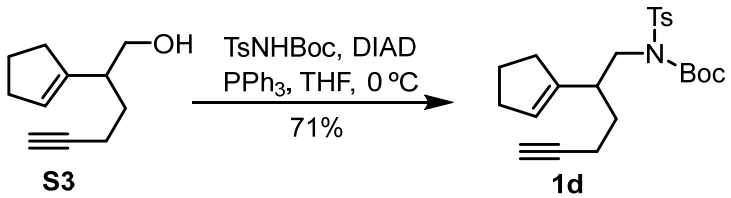
To a suspension of ester **1b** (1.0 g, 4.9 mmol) and NH(OMe)Me•HCl (0.71 g, 7.3 mmol) in THF (50 mL) at 0 °C was added *i*-PrMgCl (7.3 mL, 14.7 mmol, 2 M in THF) over 15 min. The reaction mixture was stirred at 0 °C for 0.5 h before being quenched with a saturated NH_4Cl solution (20 mL). The mixture was extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the residue by flash chromatography (PE/EtOAc = 10:1) afforded **1c** (0.77 g, 72%) as a colorless oil.

2-(Cyclopent-1-en-1-yl)-*N*-methoxy-*N*-methylhex-5-ynamide (1c). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.53 – 5.49 (m, 1H), 3.92 – 3.79 (brs, 1H), 3.66 (s, 3H), 3.16 (s, 3H), 2.32 – 2.24 (m, 4H), 2.22 – 2.10 (m, 2H), 2.04 – 1.95 (m, 1H), 1.93 (t, *J* = 2.63 Hz, 1H), 1.86 – 1.72 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.9, 141.3, 127.2, 83.9, 68.7, 61.3, 41.8, 33.1, 32.2, 29.1, 23.1, 16.4. IR (KBr, cm-1): 2937, 1660, 1383, 992, 629. HRMS (ESI, m/z) calc for $C_{13}H_{19}NO_2$ $[M+Na]^+$: 244.1308, found: 244.1310.



To a stirred suspension of $LiAlH_4$ (0.20 g, 5.3 mmol) in THF (10 mL) at 0 °C was added dropwise a solution of ester **1b** (1.0 g, 4.9 mmol) in THF (20 mL), and the mixture was stirred for 10 min. The reaction was quenched with saturated NH_4Cl solution (10 mL). The mixture was extracted with Et_2O. The organic phase was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. Purification of the residue by flash chromatography (PE/EtOAc = 10:1) afforded the desired alcohol **S3** (0.63 g, 80%) as a colorless oil.

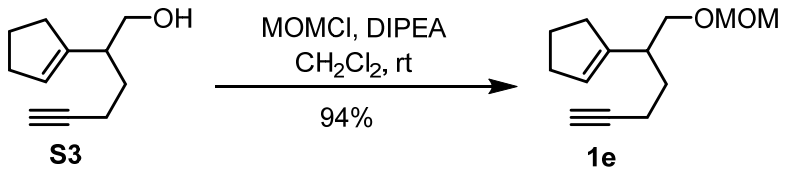
2-(Cyclopent-1-en-1-yl)hex-5-yn-1-ol (S3). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.56 (dq, *J* = 3.4, 1.9 Hz, 1H), 3.59 – 3.46 (m, 2H), 2.62 – 2.53 (m, 1H), 2.37 – 2.29 (m, 2H), 2.24 – 2.15 (m, 3H), 2.15 – 2.06 (m, 1H), 1.94 (t, *J* = 2.7 Hz, 1H), 1.90 – 1.83 (m, 2H), 1.70 – 1.55 (m, 2H), 1.45 (t, *J* = 4.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.2, 128.1, 84.2, 68.4, 63.9, 43.1, 32.2, 31.8, 28.4, 23.1, 16.3. IR (KBr, cm^{-1}): 3291, 2936, 1433, 1039, 639. HRMS (ESI, m/z) calc for $C_{11}H_{16}O$ $[M+H]^+$: 165.1274, found: 165.1273.



To a stirred solution of alcohol **S3** (0.10 g, 0.61 mmol) in THF at 0 °C was added TsNHBoc (0.22 g, 0.82 mmol), Diisopropyl azodicarboxylate (DIAD) (0.19 mL, 0.92 mmol) and PPh_3 (0.32 g, 1.22 mmol) successively. The mixture was stirred at 0 °C for 1 h before being quenched with H_2O and extracted with Et_2O. The combined organic phases were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the residue by flash chromatography (PE/EtOAc = 20:1) afforded **1d** (0.18 g, 71%) as a colorless oil.

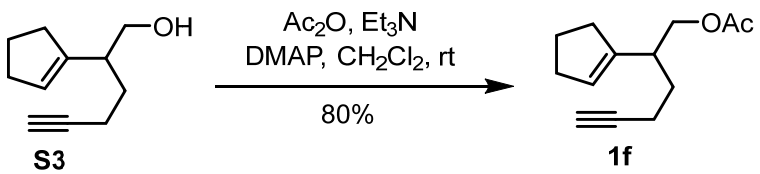
***tert*-Butyl (2-(cyclopent-1-en-1-yl)hex-5-yn-1-yl)(tosyl)carbamate (1d).** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 – 7.76 (d, *J* = 8.4 Hz, 2H), 7.30 – 7.27 (d, *J* = 8.4Hz, 2H),

5.54 – 5.51 (m, 1H), 3.92 – 3.86 (dd, *J* = 14.1, 8.0 Hz, 1H), 3.81 – 3.75 (dd, *J* = 14.1, 7.0 Hz, 1H), 3.00 – 2.90 (m, 1H), 2.43 (s, 3H), 2.35 – 2.25 (m, 3H), 2.25 – 2.15 (m, 2H), 2.11 – 2.03 (m, 1H), 1.96 – 1.93 (t, *J* = 2.6 Hz, 1H), 1.89 – 1.82 (m, 2H), 1.77 – 1.69 (m, 1H), 1.65 – 1.57 (m, 1H), 1.31 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.1, 144.0, 142.5, 137.6, 129.1, 128.8, 127.9, 84.2, 84.0, 68.4, 49.7, 40.9, 32.2, 31.0, 29.3, 27.8, 23.2, 21.6, 16.4. IR (KBr, cm^{-1}): 3286, 2933, 2847, 1728, 1355, 1088, 545. HRMS (ESI, m/z) calc for $C_{23}H_{31}NO_4S$ $[M+Na]^+$: 440.1866, found: 440.1870.



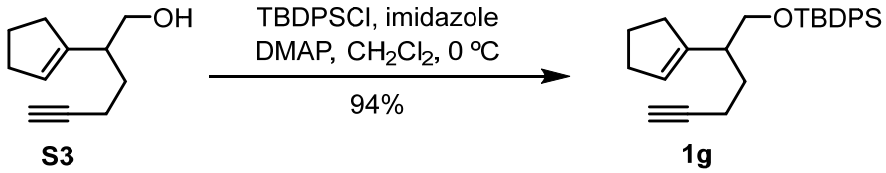
To a stirred solution of alcohol **S3** (0.54 g, 3.29 mmol) in CH_2Cl_2 (30 mL) at rt was added DIPEA (2.17 mL, 13.2mmol) and MOMCl (0.75 mL, 9.88 mmol). The reaction mixture was stirred at rt for 2 h before being quenched with saturated $NaHCO_3$ solution (10 mL) and extracted with CH_2Cl_2. The combined organic phases were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the residue by flash chromatography (PE/EtOAc = 50:1) afforded **1e** (0.64 g, 94%) as a colorless oil.

1-(1-(Methoxymethoxy)hex-5-yn-2-yl)cyclopent-1-ene (1e). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.49 – 5.45 (m, 1H), 4.59 (s, 2H), 3.51 (dd, *J* = 9.6, 6.6 Hz, 1H), 3.45 (dd, *J* = 9.6, 6.6 Hz, 1H), 3.33 (s, 3H), 2.68 – 2.59 (m, 1H), 2.32 – 2.26 (m, 2H), 2.23 – 2.09 (m, 4H), 1.92 (t, *J* = 2.7 Hz, 1H), 1.86 – 1.73 (m, 3H), 1.62 – 1.52 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 126.4, 96.4, 84.3, 69.9, 68.2, 55.1, 40.3, 32.1, 32.0, 28.9, 23.1, 16.2. IR (KBr, cm^{-1}): 3312, 2925, 2852, 1463, 1045, 630. HRMS (ESI, m/z) calc for $C_{13}H_{20}O_2$ $[M+Na]^+$: 231.1356, found: 231.1356.



To a stirred solution of alcohol **S3** (0.4 g, 2.4 mmol) in CH_2Cl_2 (20 mL) at rt was added Et_3N (0.68 mL, 4.9 mmol) and DMAP (0.03 g, 0.24 mmol) and acetic anhydride (0.35 mL, 3.7 mmol) in sequence. The reaction mixture was stirred at rt for 3 h before being quenched with saturated $NaHCO_3$ solution (10 mL), and extracted with CH_2Cl_2. The combined organic phases were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the residue by flash chromatography (PE/EtOAc = 100:1) afforded **1f** (0.40 g, 80%) as a colorless oil.

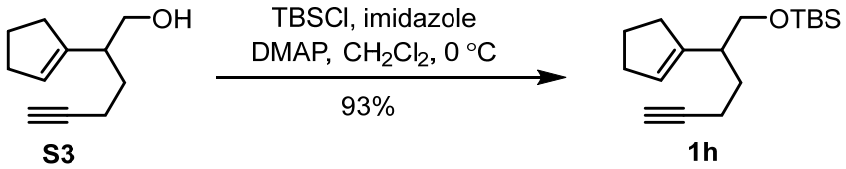
2-(Cyclopent-1-en-1-yl)hex-5-yn-1-yl acetate (1f). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.48 (s, 1H), 4.07 (dd, *J* = 10.8, 6.6 Hz, 1H), 3.99 (dd, *J* = 10.8, 6.9 Hz, 1H), 2.77 – 2.59 (m, 1H), 2.32 – 2.25 (m, 2H), 2.24 – 2.05 (m, 4H), 2.02 (s, 3H), 1.93 (t, *J* = 2.6 Hz, 1H), 1.87 – 1.78 (m, 2H), 1.76 – 1.54 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 142.5, 127.1, 84.0, 68.5, 66.2, 39.4, 32.2, 32.2, 28.9, 23.2, 20.9, 16.2. IR (KBr, cm^{-1}): 2950, 1741, 1365, 1240, 1037, 634. HRMS (ESI, m/z) calc for $C_{13}H_{18}O_2$ $[M+Na]^+$: 229.1199, found: 229.1196.



To a stirred solution of alcohol **S3** (0.63 g, 3.8 mmol) in CH_2Cl_2 (20 mL) was treated with TBDPSCl (1.31 mL, 5.0 mmol), imidazole (0.53 g, 7.7 mmol), and a catalytic amount of DMAP. The reaction mixture was stirred at rt for 0.5 h before being quenched with H_2O (20 mL). The resulting mixture was extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the residue by column chromatography (PE/EtOAc = 100:1) afforded **1g** (1.45 g, 94%) as a colorless oil.

***tert*-Butyl((2-(cyclopent-1-en-1-yl)hex-5-yn-1-yl)oxy)diphenylsilane (1g).** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 – 7.66 (m, 4H), 7.45 – 7.38 (m, 6H), 5.47 – 5.43 (m, 1H), 3.63 (qd, *J* = 9.9, 6.3 Hz, 2H), 2.61 – 2.54 (m, 1H), 2.33 – 2.28 (m, 2H), 2.24 – 2.07 (m, 4H), 1.95 (t, *J* = 2.6 Hz, 1H), 1.92 – 1.79 (m, 3H), 1.68 – 1.59 (m, 1H), 1.07 (s, 9H).

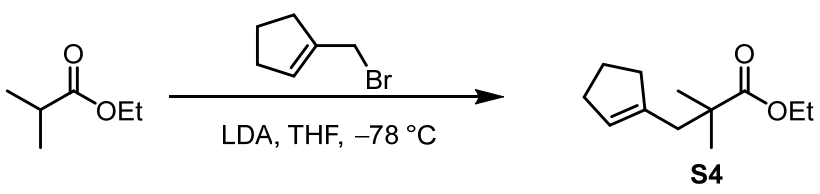
^{13}C NMR (125 MHz, $CDCl_3$) δ 143.8, 135.6, 135.6, 133.9, 133.9, 129.5, 129.5, 127.6, 126.2, 84.8, 68.1, 66.1, 42.8, 32.6, 32.2, 28.8, 26.8, 23.2, 19.3, 16.4. IR (KBr, cm^{-1}): 2930, 1427, 1111, 701, 504. HRMS (ESI, m/z) calc for $C_{27}H_{34}OSi$ $[M+Na]^+$: 425.2271, found: 425.2274.



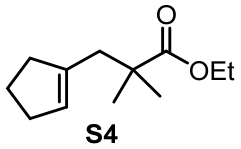
To a stirred solution of alcohol **S3** (1.97 g, 12.0 mmol) in CH_2Cl_2 (40 mL) was added TBSCl (2.72 g, 18.1 mmol), imidazole (1.64 g, 24.1 mmol), and a catalytic amount of DMAP in sequence. The reaction mixture was stirred at rt for 0.5 h before being quenched with H_2O (40 mL). The resulting mixture was extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the residue by column chromatography (PE/EtOAc = 100:1) afforded **1h** (3.12 g, 93%) as a colorless oil.

***tert*-Butyl((2-(cyclopent-1-en-1-yl)hex-5-yn-1-yl)oxy)dimethylsilane (1h).** ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.44 – 5.41 (m, 1H), 3.59 (dd, J = 9.9, 5.7 Hz, 1H), 3.50 (dd, J = 9.9, 7.1 Hz, 1H), 2.52 – 2.44 (m, 1H), 2.31 – 2.26 (m, 2H), 2.24 – 2.15 (m, 3H), 2.13 – 2.04 (m, 1H), 1.92 (t, J = 2.7 Hz, 1H), 1.86 – 1.77 (m, 3H), 1.60 – 1.53 (m, 1H), 0.88 (s, 9H), 0.03 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.0, 126.0, 84.8, 68.0, 65.6, 43.0, 32.7, 32.2, 28.9, 25.9, 23.3, 18.3, 16.4, -5.4. IR (KBr, cm^{-1}): 2929, 2856, 1254, 1110, 836, 628. HRMS (ESI, m/z) calc for $C_{17}H_{30}OSi$ $[M+H]^+$: 279.2139, found: 279.2136.

2.2) Procedures for the preparation of enynes-1r,1n,1s,1i,1k,1l,1m,1a

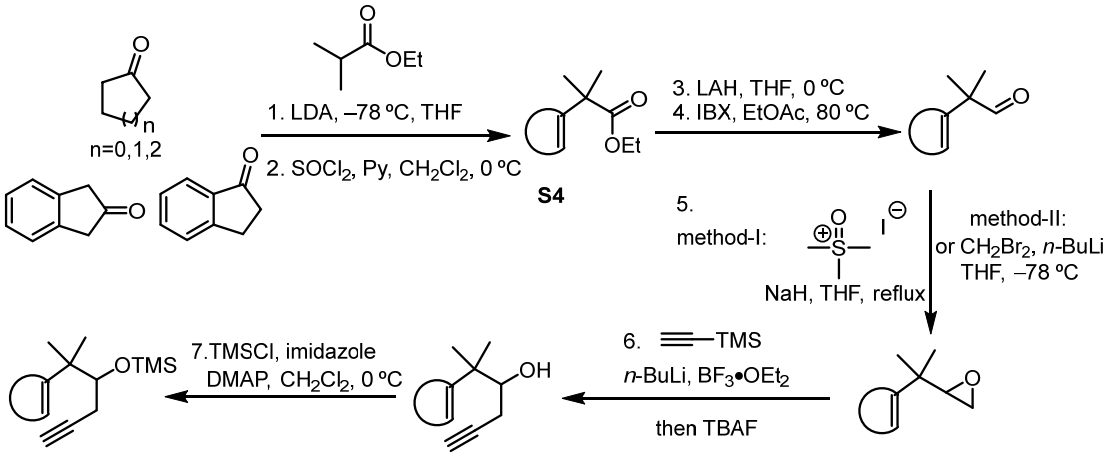


To a stirred solution of DIPA (0.58 mL, 4.11 mmol) in THF (40 mL) at 0 °C was added *n*-BuLi (1.64 mL, 2.5 M in hexane). After 30 min, the reaction was cooled to −78 °C, and then a solution of ethyl isobutyrate (0.48 g, 4.11 mmol) in THF was added slowly and the stirring was continued for another 1 h. The 1-(bromomethyl)cyclopent-1-ene (0.508 g, 3.16 mmol) in THF was added dropwise. The reaction was stirred for 2h at this temperature before being quenched with saturated NH_4Cl solution (20 mL) and extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the residue by column chromatography (PE/EtOAc = 100:1) afforded **S4** (0.50 g, 2.55 mmol).



S4

Ethyl 3-(cyclopent-1-en-1-yl)-2,2-dimethylpropanoate (S4). All spectral data were in agreement with reported values.[1]



Step 1. To a stirred solution of DIPA (1.3 equiv) in THF (0.2 M) at 0 °C was added *n*-BuLi (1.3 equiv, 2.5 M in hexane). After 30 min, the reaction was cooled to −78 °C, and then a solution of ethyl isobutyrate (1.3 equiv) in THF was added slowly and the stirring was continued for another 1 h. The ketone (1.0 equiv) in THF was added dropwise. The reaction was stirred for 2h before being quenched with saturated NH_4Cl solution and extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo* to afford the crude aldol products which was used

for next step without further purification.

Step 2. To a stirred solution of the alcohol (1.0 equiv) in CH_2Cl_2 (0.3 M) and pyridine (3.0 equiv) at 0 °C was added $SOCl_2$ (1.5 equiv). The mixture wa stirred for 1 h at this temperature, then poured into ice water and stirred for an additional 20 min at rt. The two-phase system was extracted with CH_2Cl_2. The combined extracts were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo* to afford the unsaturated ester.

Step 3. To a stirred suspension of $LiAlH_4$ (1.1 equiv) in THF at 0 °C was added a solution of above unsaturated ester (1.0 equiv) in THF (0.1 M) dropwise. The mixture was stirred for 10 min before being quenched with H_2O and extracted with Et_2O. The combined organic layers was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo* to afford the reduction product alcohol.

Step 4. To alcohol (1.0 equiv) in EtOAc (0.3 M) was added IBX (1.5 equiv.). The resulting suspension was immersed in an oil bath preheated to 80 °C and stirred vigorously open to the air atmosphere. After being stirred for 4 h, the reaction was cooled to rt and filtered. The filter cake was washed with EtOAc, and the combined filtrates were concentrated *in vacuo.* Purification of the residue by column chromatography (PE/EtOAc = 100:1) afforded aldehyde.

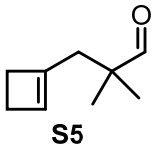
Step 5. Epoxide formation method I: To a stirred solution of trimethylsulfonium iodide (2.5 equiv) in THF (0.1 M) was added sodium hydride (60% in mineral oil, 3.0 equiv) and the reaction mixture was heated to reflux for 1h. A solution of aldehyde (1.0 equiv) in THF was added dropwise. After 4 h, the reaction was cooled to rt and was quenched with saturated NH_4Cl solution and extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the residue by column chromatography (PE/EtOAc = 100:1) afforded the epoxide.

Epoxide formation method II: To a stirred solution of aldehyde (1.0 equiv) and dibromomethane (1.3 equiv) in THF (0.1 M) at –78 °C was added dropwise *n*-BuLi (1.3 equiv, 2.5 M in hexane).[3] The resulting pale yellow mixture was stirred for overnight while allowing the bath temperature to rise to rt. The reaction was then quenched with saturated NH_4Cl solution and extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the residue by column chromatography (PE/EtOAc = 100:1) afforded the epoxide.

Step 6. To a solution of trimethylsilylacetylene (2.5 equiv) and THF (0.1 M) at –78°C was added *n*-BuLi (2.5 equiv, 2.5 M in hexane) dropwise. The resulting solution was stirred at the same temperature for 30 min before the addition of $BF_3{\bullet}OEt_2$ (1.0 equiv). After being stirring for an additional 10 min at –78 °C, a solution of epoxide (1.0 equiv) in THF was added dropwise via syringe. When TLC analysis indicated complete consumption of the epoxide, the reaction was quenched with saturated $NaHCO_3$ solution and extracted with Et_2O. The combined organic layers were washed with brine, dried with $MgSO_4$ and concentrated *in vacuo* to give the crude enyne alcohol.

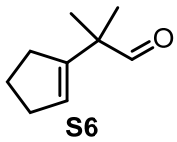
To a stirred solution of enyne (1.0 equiv) in THF (0.3 M) was added TBAF (1.5 equiv, 1.0 M in THF), and the resulting mixture was stirred at rt for 0.5 h. The reaction was quenched with H_2O and extracted with ether. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the residue by column chromatography (PE/EtOAc = 20:1) afforded the alkyne alcohol.

Step 7. To a solution of above alcohol (1.0 equiv) CH_2Cl_2 (0.1 M) at 0 °C was added imidazole (2.5 equiv), DMAP (0.1 equiv) and TMSCl (2.0 equiv) in sequence. After being stirred for 0.5 h, the reaction mixture was poured into H_2O and extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the residue by column chromatography (PE/EtOAc = 100:1) afforded the siloxane.



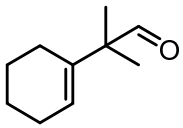
S5

3-(Cyclobut-1-en-1-yl)-2,2-dimethylpropanal (S5). It was used without further purification immediately because it was instable.



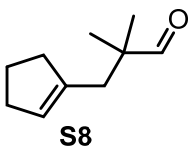
S6

2-(Cyclopent-1-en-1-yl)-2-methylpropanal (S6). 3.00 g (21.74 mmol) of **S6** was prepared from 3.62 g (43.04 mmol) of cyclopentanone (51% yield). All spectral data were in agreement with reported values.[2]



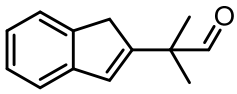
S7

2-(Cyclohex-1-en-1-yl)-2-methylpropanal (S7). 4.30 g (28.29 mmol) of **S7** was prepared from 3.0 g (30.55 mmol) of cyclohexanone (93% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.25 (s, 1H), 5.61 – 5.55 (m, 1H), 2.10 – 2.03 (m, 2H), 1.87 – 1.81 (m, 2H), 1.62 – 1.50 (m, 4H), 1.14 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.4, 137.0, 124.6, 51.6, 25.7, 25.2, 23.0, 22.1, 20.3. IR (KBr, cm^{-1}): 2930, 1727, 1137, 919, 555. HRMS (ESI, m/z) calc for $C_{10}H_{16}O$ $[M+H]^+$: 153.1274, found: 153.1274.



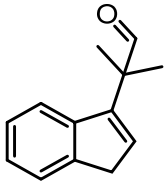
S8

3-(Cyclopent-1-en-1-yl)-2,2-dimethylpropanal (S8). 0.68 g (4.47 mmol) of **S8** was prepared from 1.33 g (6.79 mmol) from the corresponding ester (66% yield). All spectral data were in agreement with reported values.[1]



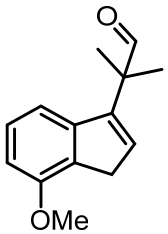
S9

2-(1*H*-Inden-2-yl)-2-methylpropanal (S9). 1.94 g (10.43 mmol) of **S9** was prepared from 2.28 g (17.27 mmol) of 1,3-dihydro-2*H*-inden-2-one (60% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.47 (s, 1H), 7.46 – 7.41 (m, 1H), 7.38 (d, *J* = 7.5 Hz, 1H), 7.31 – 7.26 (m, 1H), 7.22 – 7.17 (m, 1H), 6.78 – 6.75 (m, 1H), 3.37 – 3.35 (m, 2H), 1.45 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.3, 148.9, 144.3, 143.2, 128.9, 126.4, 124.6, 123.6, 120.7, 49.1, 38.5, 21.7. IR (KBr, cm^{-1}): 2971, 1722, 1462, 913, 753. HRMS (ESI, m/z) calc for $C_{13}H_{14}O$ $[M+Na]^+$: 209.0937, found: 209.0937.



S10

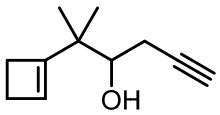
2-(1*H*-Inden-3-yl)-2-methylpropanal (S10). 4.09 g (22.0 mmol) of **S10** was prepared from 3.0 g (22.72 mmol) of 2,3-dihydro-1*H*-inden-1-one (97% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.58 (s, 1H), 7.49 (d, *J* = 7.2 Hz, 1H), 7.32 (d, *J* = 7.3 Hz, 1H), 7.29 – 7.19 (m, 2H), 6.48 (t, *J* = 1.9 Hz, 1H), 3.41 (d, *J* = 1.5 Hz, 2H), 1.51 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.1, 145.0, 144.9, 142.8, 130.6, 126.1, 124.8, 124.1, 121.0, 48.4, 37.7, 21.2. IR (KBr, cm^{-1}): 2972, 1731, 1459, 903, 766. HRMS (ESI, m/z) calc for $C_{13}H_{14}O$ $[M+Na]^+$: 209.0937, found: 209.0938.



S11

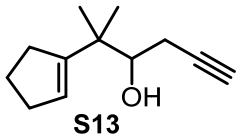
2-(7-Methoxy-1*H*-inden-3-yl)-2-methylpropanal (S11). 2.40 g (11.11 mmol) of **S11** was prepared from 3.12 g (19.23 mmol) of 4-methoxy-2,3-dihydro-1*H*-inden-1-one (58%

yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.57 (s, 1H), 7.26 (t, *J* = 7.9 Hz, 1H), 6.97 (d, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 8.2 Hz, 1H), 6.48 (t, *J* = 1.9 Hz, 1H), 3.90 (s, 3H), 3.37 (d, *J* = 1.8 Hz, 2H), 1.50 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.2, 155.4, 144.9, 144.6, 131.8, 130.7, 127.8, 114.1, 107.2, 55.1, 48.4, 35.0, 21.2. IR (KBr, cm^{-1}): 2971, 1727, 1478, 1259, 776. HRMS (ESI, m/z) calc for $C_{14}H_{16}O$ $[M+Na]^+$: 239.1043, found: 239.1041.



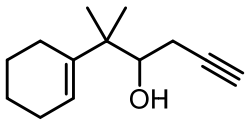
S12

2-(Cyclobut-1-en-1-yl)-2-methylhex-5-yn-3-ol (S12). 1.07 g (6.52 mmol) of **S12** was prepared from 2.8 g (40.0 mmol) of cyclobutanone (16% yield) via **step 5**, method I, and the 2-(cyclobut-1-en-1-yl)-2-methylpropanal intermediate was unstable. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.77 (t, *J* = 0.8 Hz, 1H), 3.65 – 3.60 (m, 1H), 2.50 – 2.40 (m, 3H), 2.31 – 2.22 (m, 3H), 2.07 (d, *J* = 3.6 Hz, 1H), 2.05 (t, *J* = 2.6 Hz, 1H), 1.03 (s, 3H), 1.01 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.9, 127.9, 82.3, 75.2, 70.2, 40.5, 29.0, 25.7, 22.6, 21.5, 20.9. IR (KBr, cm^{-1}): 3308, 2920, 1362, 1061, 857, 632. HRMS (ESI, m/z) calc for $C_{11}H_{16}O$ $[M+Na]^+$: 187.1093, found: 187.1092.



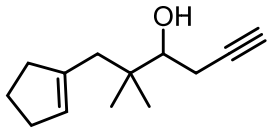
S13

2-(Cyclopent-1-en-1-yl)-2-methylhex-5-yn-3-ol (S13). 0.50g (2.81 mmol) of **S13** was prepared from 1.0 g (5.37 mmol) of the corresponding aldehyde (52% yield) via **step 5**, method I. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.50 – 5.45 (m, 1H), 3.69 (dt, *J* = 9.7, 3.0 Hz, 1H), 2.36 – 2.15 (m, 6H), 2.05 – 2.00 (m, 2H), 1.87 – 1.77 (m, 2H), 1.08 (s, 3H), 1.04 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 125.1, 82.6, 74.9, 69.9, 40.6, 32.1, 31.8, 23.6, 23.0, 22.3, 21.9. IR (KBr, cm^{-1}): 3308, 2964, 1362, 1064, 958, 632. HRMS (ESI, m/z) calc for $C_{12}H_{18}O$ $[M+Na]^+$: 201.1250, found: 201.1248.



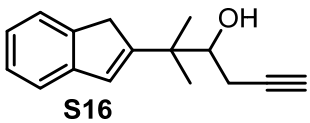
S14

2-(Cyclohex-1-en-1-yl)-2-methylhex-5-yn-3-ol (S14). 0.46 g (2.4 mmol) of **S14** was prepared from 1.0 g (6.58 mmol) the corresponding aldehyde (36% yield) via **step 5** method I. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.59 – 5.55 (m, 1H), 3.71 (dt, *J* = 9.8, 2.7 Hz, 1H), 2.36 – 2.30 (m, 1H), 2.23 – 2.16 (m, 1H), 2.07 – 1.99 (m, 5H), 1.96 – 1.88 (m, 1H), 1.66 – 1.48 (m, 4H), 1.03 (s, 3H), 0.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 122.5, 82.8, 74.5, 69.8, 43.1, 25.6, 24.7, 23.3, 22.3, 22.1, 21.5. IR (KBr, cm^{-1}): 3308, 2927, 1384, 1061, 921, 632. HRMS (ESI, m/z) calc for $C_{13}H_{20}O$ $[M+Na]^+$: 215.1406, found: 215.1406.



S15

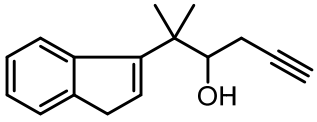
1-(Cyclopent-1-en-1-yl)-2,2-dimethylhex-5-yn-3-ol (S15). 0.41 g (2.14 mmol) of **S15** from 0.66 g (4.34 mmol) of the corresponding aldehyde (49% yield) via **step 5**, method I. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.44 – 5.40 (m, 1H), 3.55 – 3.50 (m, 1H), 2.46 – 2.41 (m, 1H), 2.31 – 2.24 (m, 5H), 2.21 (d, *J* = 13.1 Hz, 1H), 2.15 (d, *J* = 3.7 Hz, 1H), 2.06 – 2.00 (m, 2H), 1.88 – 1.80 (m, 2H), 0.91 (s, 3H), 0.88 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.6, 128.4, 82.5, 76.3, 70.3, 40.4, 38.1, 37.6, 32.4, 24.1, 23.8, 22.9, 22.3. IR (KBr, cm^{-1}): 3308, 2954, 1384, 1061, 844, 633. HRMS (ESI, m/z) calc for $C_{13}H_{20}O$ $[M+Na]^+$: 215.1406, found: 215.1405.



S16

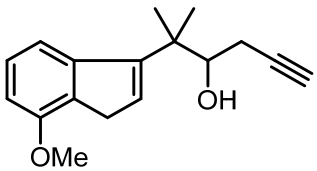
2-(1*H*-Inden-2-yl)-2-methylhex-5-yn-3-ol (S16). 0.60 g (2.65 mmol) of **S16** was prepared from 1.0 g (5.38 mmol) of the corresponding aldehyde (49% yield) via **step 5**, method I. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.3 Hz, 1H), 7.33 (d, *J* = 7.4 Hz, 1H), 7.29 – 7.22 (m, 1H), 7.15 (td, *J* = 7.4, 1.1 Hz, 1H), 6.64 (s, 1H), 3.83 (dd, *J* =

9.8, 2.8 Hz, 1H), 3.45 (q, *J* = 22.6 Hz, 2H), 2.39 (dt, *J* = 16.8, 2.7 Hz, 1H), 2.28 – 2.11 (m, 2H), 2.04 (t, *J* = 2.6 Hz, 1H), 1.29 (d, *J* = 5.5 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 144.6, 143.2, 127.1, 126.3, 124.2, 123.5, 120.4, 82.1, 76.5, 70.5, 41.1, 38.8, 24.6, 23.2, 22.8. IR (KBr, cm^{-1}): 3292, 2966, 1390, 1066, 753, 718, 635. HRMS (ESI, m/z) calc for $C_{16}H_{18}O$ $[M+Na]^+$: 249.1250, found: 249.1247.



S17

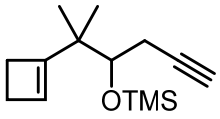
2-(1*H*-Inden-3-yl)-2-methylhex-5-yn-3-ol (S17). 0.62 g (2.74 mmol) of **S17** was prepared from 2.0 g (10.57 mmol) of the corresponding aldehyde (26% yield) via **step 5**, method II. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.7 Hz, 1H), 7.51 – 7.46 (m, 1H), 7.32 – 7.27 (m, 1H), 7.21 (td, *J* = 7.4, 0.9 Hz, 1H), 6.35 (t, *J* = 2.1 Hz, 1H), 4.46 – 4.32 (m, 1H), 3.34 (d, *J* = 1.5 Hz, 2H), 2.33 – 2.28 (m, 2H), 2.15 (d, *J* = 3.5 Hz, 1H), 2.02 (t, *J* = 2.6 Hz, 1H), 1.45 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 145.6, 143.1, 129.8, 125.8, 124.4, 124.1, 122.2, 82.3, 73.9, 70.3, 41.4, 37.4, 23.6, 22.7, 21.8. IR (KBr, cm^{-1}): 3292, 2971, 1391, 1065, 767, 722, 639. HRMS (ESI, m/z) calc for $C_{16}H_{18}O$ $[M+Na]^+$: 249.1250, found: 249.1248.



S18

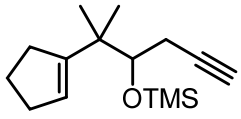
2-(7-Methoxy-1H-inden-3-yl)-2-methylhex-5-yn-3-ol (S18). 0.50 g (1.95 mmol) of **S18** was prepared from 1.36 g (6.27 mmol) the corresponding aldehyde (31% yield) via **step 5**, method II. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 2H), 6.77 (dd, *J* = 7.5, 1.2 Hz, 1H), 6.34 (t, *J* = 2.1 Hz, 1H), 4.40 – 4.33 (m, 1H), 3.89 (s, 3H), 3.31 – 3.26 (m, 2H), 2.33 – 2.24 (m, 2H), 2.12 (d, *J* = 3.4 Hz, 1H), 2.01 (t, *J* = 2.7 Hz, 1H), 1.43 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.4, 149.7, 144.9, 132.7, 129.9, 127.5, 115.5, 106.9, 82.4, 74.0, 70.3, 55.2, 41.3, 34.6, 23.8, 22.7, 21.8. IR (KBr, cm^{-1}):

3290, 2969, 1477, 1256, 1020, 775. HRMS (ESI, m/z) calc for $C_{17}H_{20}O_2$ $[M+Na]^+$: 279.1356, found: 279.1353.



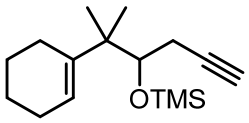
1m

((2-(Cyclobut-1-en-1-yl)-2-methylhex-5-yn-3-yl)oxy)trimethylsilane (1m). 1.15 g (4.87 mmol) of **1m** was prepared from 1.07 g (6.52 mmol) of alcohol **S14** (75% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.69 (t, *J* = 0.8 Hz, 1H), 3.66 (dd, *J* = 8.6, 2.8 Hz, 1H), 2.44 – 2.37 (m, 3H), 2.29 – 2.25 (m, 2H), 2.20 – 2.13 (m, 1H), 1.96 (t, *J* = 2.7 Hz, 1H), 0.98 (s, 3H), 0.94 (s, 3H), 0.16 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.5, 127.0, 84.0, 77.7, 69.4, 41.3, 29.1, 25.7, 23.8, 23.8, 19.8, 0.7. IR (KBr, cm^{-1}): 2958, 1250, 1105, 929, 841, 635. HRMS (ESI, m/z) calc for $C_{14}H_{24}OSi$ $[M+Na]^+$: 259.1489, found: 259.1486.



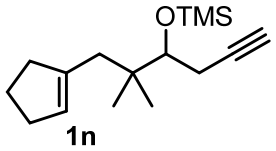
1a

((2-(Cyclopent-1-en-1-yl)-2-methylhex-5-yn-3-yl)oxy)trimethylsilane (1a). 0.47 g (1.89 mmol) of **1a** was prepared from 0.37 g (2.05 mmol) of alcohol **S15** (92% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.42 – 5.37 (m, 1H), 3.75 (dd, *J* = 8.8, 2.5 Hz, 1H), 2.35 – 2.16 (m, 5H), 2.15 – 2.04 (m, 1H), 1.94 (t, *J* = 2.6 Hz, 1H), 1.87 – 1.76 (m, 2H), 1.01 (d, *J* = 6.2 Hz, 6H), 0.16 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 124.2, 84.3, 77.8, 69.3, 41.4, 32.1, 32.0, 25.5, 23.6, 23.6, 21.0, 0.7. IR (KBr, cm^{-1}): 2956, 1249, 1102, 841, 929, 634. HRMS (ESI, m/z) calc for $C_{15}H_{26}OSi$ $[M+Na]^+$: 273.1645, found: 273.1642.



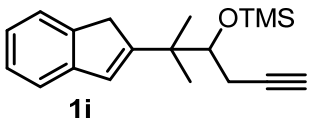
1r

((2-(Cyclohex-1-en-1-yl)-2-methylhex-5-yn-3-yl)oxy)trimethylsilane (1r). 0.56 g (2.12 mmol) of **1r** was prepared from 0.46 g (2.40 mmol) of alcohol **S16** (88% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.52 – 5.46 (m, 1H), 3.80 (dd, *J* = 8.9, 2.3 Hz, 1H), 2.30 (dt, *J* = 17.0, 2.5 Hz, 1H), 2.12 – 1.98 (m, 4H), 1.96 – 1.83 (m, 2H), 1.64 – 1.48 (m, 4H), 0.98 (s, 3H), 0.94 (s, 3H), 0.16 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 121.3, 84.5, 77.4, 77.0, 77.0, 69.2, 43.8, 25.6, 25.4, 25.0, 23.4, 23.4, 22.4, 20.0, 0.8. IR (KBr, cm^{-1}): 2929, 1249, 1103, 840, 633. HRMS (ESI, m/z) calc for $C_{16}H_{28}OSi$ $[M+Na]^+$: 287.1802, found: 287.1800.



1n

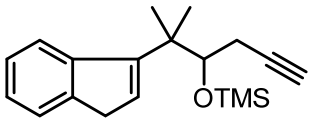
((1-(Cyclopent-1-en-1-yl)-2,2-dimethylhex-5-yn-3-yl)oxy)trimethylsilane (1n). 0.39 g (1.48 mmol) of **1n** was prepared from 0.38 g (1.98 mmol) of alcohol **S17** (75% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.38 – 5.34 (m, 1H), 3.56 (dd, *J* = 8.5, 2.9 Hz, 1H), 2.48 – 2.43 (m, 1H), 2.31 – 2.24 (m, 4H), 2.22 – 2.16 (m, 1H), 2.08 – 1.99 (m, 2H), 1.96 (t, *J* = 2.7 Hz, 1H), 1.87 – 1.80 (m, 2H), 0.85 (s, 3H), 0.83 (s, 3H), 0.16 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.7, 127.9, 84.0, 79.5, 69.5, 39.6, 38.9, 37.8, 32.4, 24.1, 23.7, 23.3, 22.9, 0.7. IR (KBr, cm^{-1}): 2956, 1249, 1096, 841, 635. HRMS (ESI, m/z) calc for $C_{16}H_{28}OSi$ $[M+Na]^+$: 287.1802, found: 287.1799.



1i

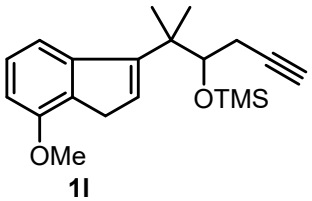
((2-(1*H*-Inden-2-yl)-2-methylhex-5-yn-3-yl)oxy)trimethylsilane (1i). 0.74 g (2.49 mmol) of **1i** was prepared from 0.60 g (2.66 mmol) of alcohol **S19** (94% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.4 Hz, 1H), 7.32 (d, *J* = 7.4 Hz, 1H), 7.27 – 7.23 (m, 1H), 7.17 – 7.12 (m, 1H), 6.63 – 6.58 (m, 1H), 3.88 (dt, *J* = 11.2, 5.6 Hz, 1H), 3.50 (d, *J* = 22.6 Hz, 1H), 3.36 (d, *J* = 22.6 Hz, 1H), 2.35 (dt, *J* = 17.1, 2.8 Hz, 1H), 2.13 (ddd, *J* = 17.1, 8.5, 2.7 Hz, 1H), 1.93 (t, *J* = 2.7 Hz, 1H), 1.24 (d, *J* = 3.9 Hz,

6H), 0.21 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.5, 144.8, 143.3, 126.7, 126.2, 123.9, 123.4, 120.3, 83.7, 79.1, 69.7, 42.1, 39.0, 26.5, 23.8, 22.9, 0.7. IR (KBr, cm^{-1}): 2961, 1249, 1102, 928, 841, 751, 717, 635. HRMS (ESI, m/z) calc for $C_{19}H_{26}OSi$ $[M+Na]^+$: 321.1645, found: 321.1643.



1k

((2-(1*H*-Inden-3-yl)-2-methylhex-5-yn-3-yl)oxy)trimethylsilane (1k). 0.81 g (2.72 mmol) of **1k** was prepared from 0.62 g (2.74 mmol) of alcohol **S20** (99% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.8 Hz, 1H), 7.47 (d, *J* = 7.2 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.20 (td, *J* = 7.4, 0.8 Hz, 1H), 6.28 (t, *J* = 2.1 Hz, 1H), 4.46 (dd, *J* = 8.7, 3.0 Hz, 1H), 3.30 (d, *J* = 2.0 Hz, 2H), 2.28 (dt, *J* = 16.9, 2.9 Hz, 1H), 2.21 (ddd, *J* = 16.9, 8.7, 2.7 Hz, 1H), 1.89 (t, *J* = 2.7 Hz, 1H), 1.37 (s, 3H), 1.31 (d, *J* = 3.7 Hz, 3H), 0.15 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.5, 145.6, 143.5, 129.2, 125.7, 124.2, 124.1, 122.2, 83.9, 76.1, 69.5, 42.2, 37.3, 24.6, 23.6, 21.7, 0.7. IR (KBr, cm^{-1}): 2956, 1249, 1104, 928, 841, 755, 722, 632. HRMS (ESI, m/z) calc for $C_{19}H_{26}OSi$ $[M+Na]^+$: 321.1645, found: 321.1638.

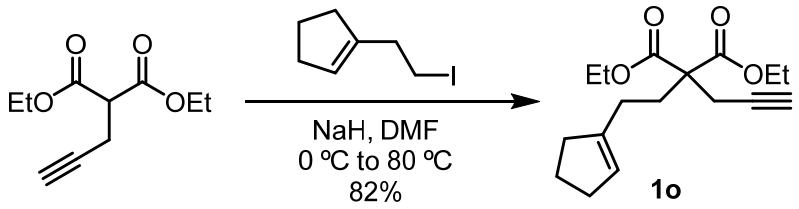


1l

((2-(7-Methoxy-1*H*-inden-3-yl)-2-methylhex-5-yn-3-yl)oxy)trimethylsilane (1l). 0.50 g (1.52 mmol) of **1l** was prepared from 0.46 g (1.74 mmol) of alcohol **S21** (87% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.22 (m, 2H), 6.76 (d, *J* = 7.5 Hz, 1H), 6.30 – 6.25 (m, 1H), 4.46 (dd, *J* = 8.5, 3.1 Hz, 1H), 3.90 (s, 3H), 3.26 (d, *J* = 1.8 Hz, 2H), 2.32 – 2.15 (m, 2H), 1.89 (t, *J* = 2.6 Hz, 1H), 1.36 (s, 3H), 1.30 (s, 3H), 0.15 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 150.4, 145.4, 132.7, 129.3, 127.3, 115.5, 106.7, 83.9, 76.2, 69.5, 55.2, 42.2, 34.6, 24.8, 23.6, 21.7, 0.7. IR (KBr, cm^{-1}): 2956,

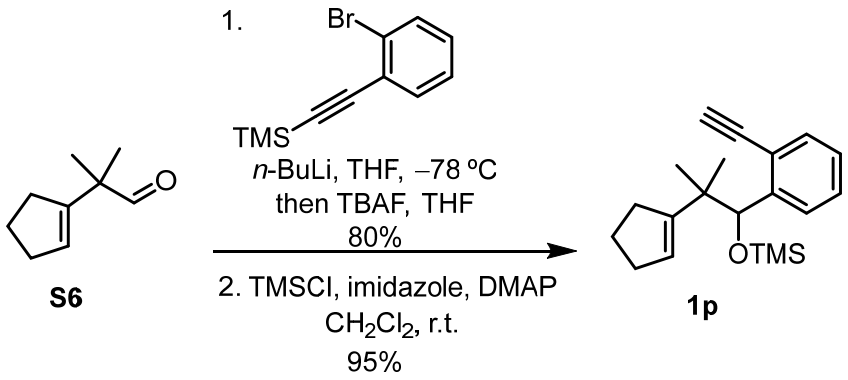
1477, 1257, 1102, 927, 842, 773, 722, 634. HRMS (ESI, m/z) calc for $C_{20}H_{28}O_2Si$ $[M+Na]^+$: 351.1751, found: 351.1747.

2.3) Procedures for the preparation of enynes-1o,1p,1j,1q



To a suspension of NaH (0.11 g, 2.64 mmol, 60% dispersion in mineral oil) in DMF (5 mL) at 0 °C was added dropwise a solution of diethyl 2-(prop-2-yn-1-yl)malonate (0.5 g, 2.52 mmol) in DMF (5 mL). The reaction mixture was stirred for 1 h. A solution of 1-(2-iodoethyl)cyclopent-1-ene (0.67 g, 3.03 mmol) in DMF (5 mL) was added dropwise , and then the reaction mixture was heated to 80 °C for 2 h. After being cooled to rt, the reaction was quenched with saturated NH_4Cl solution (5 mL) and extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the residue by flash chromatography (PE/EtOAc = 100:1) afforded **1o** (0.58 g, 82%) as a colorless oil.

Diethyl 2-(2-(cyclopent-1-en-1-yl)ethyl)-2-(prop-2-yn-1-yl)malonate (1o). ^1H NMR (400 MHz, $CDCl_3$) δ 5.39 – 5.35 (m, 1H), 4.22 – 4.15 (m, 4H), 2.82 (d, J = 2.7 Hz, 2H), 2.30 – 2.17 (m, 6H), 1.99 – 1.92 (m, 3H), 1.87 – 1.78 (m, 2H), 1.24 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 143.2, 123.9, 78.9, 71.2, 61.5, 56.6, 35.1, 32.4, 30.0, 25.5, 23.3, 22.6, 14.0. IR (KBr, cm^{-1}): 2936, 1733, 1195, 1022, 643. HRMS (ESI, m/z) calc for $C_{17}H_{24}O_4$ $[M+Na]^+$:315.1567, found: 315.1568.



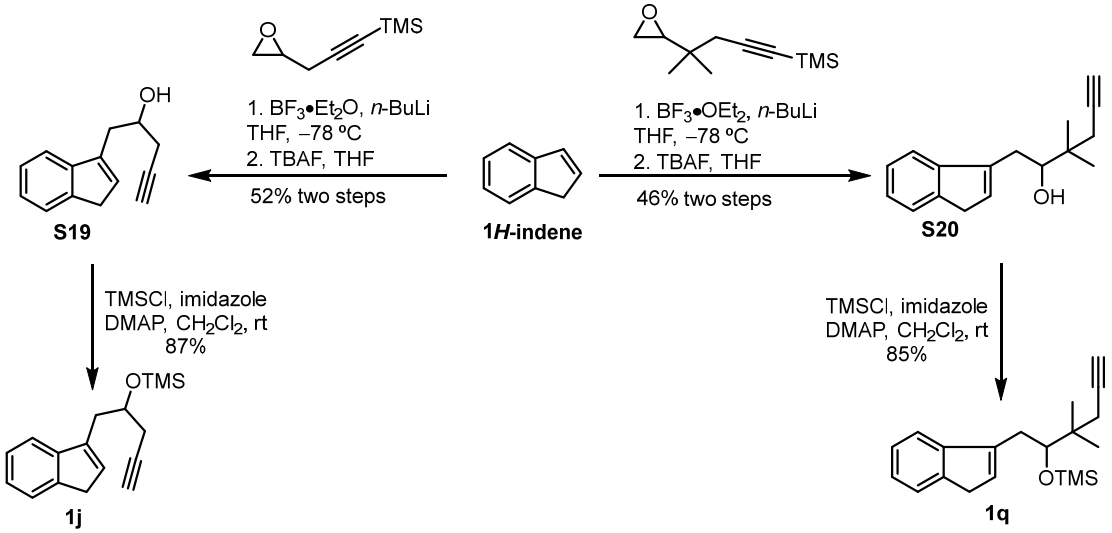
To a solution of 1-bromo-2-[(trimethylsilyl)ethynyl]benzene (1.10 g, 4.34 mmol) in THF (30 mL) was dropped *n*-BuLi (1.74 mL, 2.5 M in hexane) at –78 °C. The mixture was stirred for 1 h before the addition of aldehyde **S6** (0.5 g, 3.62 mmol) in THF (10 mL). The resulting mixture was stirred for another 2 h at this temperature before being quenched with saturated NH_4Cl solution and extracted with Et_2O. And the combined organic layers were washed with brine, dried with $MgSO_4$ and concentrated *in vacuo* to give the crude enyne.

To a stirred solution of the crude enyne in THF (15 mL) was added TBAF (5.4 mL, 1.0 M in THF), and the resulting mixture was stirred at rt for 0.5 h. The reaction was quenched with H_2O and extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the residue by flash chromatography (PE/EtOAc = 20:1) afforded alcohol (0.69 g, 80%) as a colorless oil.

To a stirred solution of the alcohol (0.25 g, 1.04 mmol) in CH_2Cl_2 (20 mL) at 0°C was added DMAP (13 mg, 0.036 mmol), imidazole (0.176 g, 2.59 mmol), and TMSCl (0.26 mL, 2.07 mmol) in sequence. After being stirred for 0.5 h, the reaction mixture was poured into H_2O and extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the residue by flash chromatography (PE/EtOAc = 100:1) afforded **1p** (0.31 g, 95%) as a colorless oil.

(2-(Cyclopent-1-en-1-yl)-1-(2-ethynylphenyl)-2-methylpropoxy)trimethylsilane (1p). ^1H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.39 (m, 2H), 7.30 – 7.26 (m, 1H), 7.17 (td,

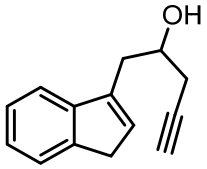
J = 7.5, 1.3 Hz, 1H), 5.28 – 5.25 (m, 1H), 5.16 (s, 1H), 3.27 (s, 1H), 2.42 – 2.33 (m, 2H), 2.32 – 2.20 (m, 2H), 1.90 – 1.75 (m, 2H), 1.07 (s, 3H), 1.02 (s, 3H), -0.08 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.0, 145.4, 132.0, 128.6, 127.8, 126.5, 124.9, 121.1, 82.8, 81.0, 77.3, 42.3, 33.1, 32.4, 24.3, 23.6, 22.5, -0.2. IR (KBr, cm^{-1}): 2955, 1382, 1251, 1067, 885, 760, 607. HRMS (ESI, m/z) calc for $C_{20}H_{28}OSi$ $[M+Na]^+$: 335.1802, found: 335.1796.



To a solution of 1*H*-indene (1.1 equiv) in THF (0.1 M) at −78 °C was added *n*-BuLi (1.2 equiv, 2.5 M in hexane) dropwise. The reaction mixture was stirred for 1 h before the addition of BF_3•OEt_2 (1.0 equiv). The mixture was stirred for 0.5 h before the addition of epoxide (1.0 equiv) in THF and then stirred for another 2 h. The reaction was quenched with saturated NH_4Cl solution and extracted with Et_2O. The combined organic layers were washed with brine, dried with $MgSO_4$ and concentrated *in vacuo* to give the crude enyne.

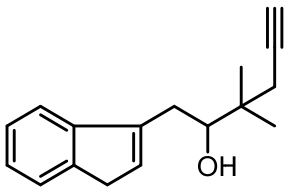
To a stirred solution of crude enyne in THF (0.3 M) was added TBAF (1.5 equiv, 1.0 M in THF), and the resulting mixture was stirred at rt for 0.5 h. H_2O was added, and the mixture was extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the residue by flash chromatography (PE/EtOAc = 20:1) afforded the alcohol **S19** or **S20**.

Alcohol **S19** or **S20** (1 equiv) was dissolved in CH_2Cl_2 (0.1 M), and then treated with imidazole (2.5 equiv), DMAP (0.1 equiv) and TMSCl (2.0 equiv) at 0°C. After being stirred for 0.5 h, the reaction mixture was poured into H_2O and extracted with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the residue by flash chromatography (PE/EtOAc = 100:1) afforded the **1j** or **1q** as a colorless oil.



S19

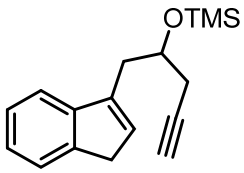
1-(1*H*-Inden-3-yl)pent-4-yn-2-ol (S19). 0.48 g (2.44 mmol) of **S19** was prepared from 0.72 g (4.69 mmol) of the corresponding epoxide (52% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.3 Hz, 1H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.23 (t, *J* = 7.4 Hz, 1H), 6.39 (s, 1H), 4.22 – 4.09 (m, 1H), 3.39 (s, 2H), 2.98 – 2.89 (m, 1H), 2.82 (dd, *J* = 14.4, 7.6 Hz, 1H), 2.58 – 2.41 (m, 2H), 2.16 – 2.09 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 144.4, 140.3, 131.0, 126.1, 124.8, 123.8, 119.1, 80.6, 71.0, 68.4, 38.0, 34.7, 26.8. IR (KBr, cm^{-1}): 3293, 2916, 1460, 1077, 770, 722, 644. HRMS (ESI, m/z) calc for $C_{14}H_{14}O$ $[M+Na]^+$: 221.0937, found: 221.0935.



S20

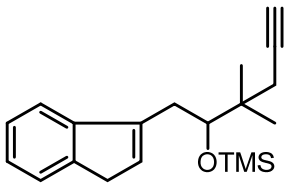
1-(1*H*-Inden-3-yl)-3,3-dimethylhex-5-yn-2-ol (S20). 0.28 g (1.17 mmol) of **S20** was prepared from 0.5 g (2.55 mmol) of the corresponding epoxide (46% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.3 Hz, 1H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.27 – 7.21 (m, 1H), 6.40 (s, 1H), 3.83 (dd, *J* = 8.7, 2.2 Hz, 1H), 3.39 (s, 2H), 2.94 – 2.84 (m, 1H), 2.61 – 2.52 (m, 1H), 2.44 – 2.24 (m, 2H), 2.03 (t, *J* = 2.7 Hz, 1H), 1.79 (d, *J* = 3.1 Hz, 1H), 1.15 (s, 3H), 1.12 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ

144.8, 144.5, 141.6, 130.8, 126.1, 124.8, 123.9, 119.1, 82.3, 74.5, 70.2, 37.9, 37.5, 30.4, 29.1, 23.5, 22.0. IR (KBr, cm^{-1}): 3300, 2963, 1427, 1056, 770, 722, 632. HRMS (ESI, m/z) calc for $C_{17}H_{20}O$ $[M+Na]^+$: 263.1406, found: 263.1403.



1j

((1-(1*H*-Inden-3-yl)pent-4-yn-2-yl)oxy)trimethylsilane (1j). 0.55 g (2.04 mmol) of **1j** was prepared from 0.46 g (2.34 mmol) of **S19** (87% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.3 Hz, 1H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.21 (t, *J* = 7.4 Hz, 1H), 6.33 (s, 1H), 4.18 – 4.10 (m, 1H), 3.35 (s, 2H), 3.01 – 2.94 (m, 1H), 2.76 (dd, *J* = 14.0, 7.2 Hz, 1H), 2.50 – 2.33 (m, 2H), 2.10 – 2.05 (m, 1H), 0.02 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4, 144.2, 140.9, 131.0, 125.9, 124.50 123.7, 119.3, 81.6, 70.3, 70.2, 37.8, 35.3, 27.6, 0.0. IR (KBr, cm^{-1}): 2954, 1251, 1098, 842, 758, 639. HRMS (ESI, m/z) calc for $C_{17}H_{222}Si$ $[M+Na]^+$: 293.1332, found: 293.1334.

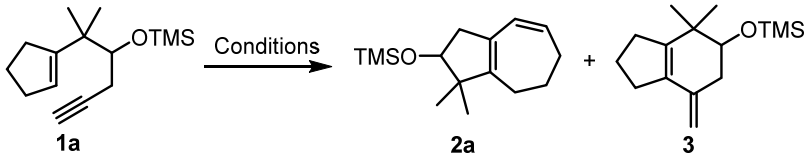


1q

((1-(1*H*-Inden-3-yl)-3,3-dimethylhex-5-yn-2-yl)oxy)trimethylsilane (1q). 0.29 g (0.93 mmol) of **1q** was prepared from 0.26 g (1.10 mmol) of **S20** (85% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.3 Hz, 1H), 7.40 (d, *J* = 7.5 Hz, 1H), 7.33 – 7.27 (m, 1H), 7.21 (td, *J* = 7.4, 1.0 Hz, 1H), 6.31 – 5.27 (m, 1H), 4.01 (dd, *J* = 9.9, 2.2 Hz, 1H), 3.34 (s, 2H), 2.85 – 2.78 (m, 1H), 2.59 (dd, *J* = 13.9, 9.9 Hz, 1H), 2.33 – 2.19 (m, 2H), 2.05 (t, *J* = 2.7 Hz, 1H), 1.11 (d, *J* = 6.0 Hz, 3H), 1.09 (s, 3H), -0.20 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4, 144.3, 142.1, 131.0, 125.9, 124.4, 123.8, 119.2, 82.7, 77.1, 70.3, 38.6, 37.6, 31.2, 29.2, 23.7, 22.6, 0.4. IR (KBr, cm^{-1}): 2960, 1249, 1092, 839, 771, 719, 634. HRMS (ESI, m/z) calc for $C_{20}H_{28}OSi$ $[M+Na]^+$: 335.1802, found: 335.1798.

3. Optimization of EYM Conditions

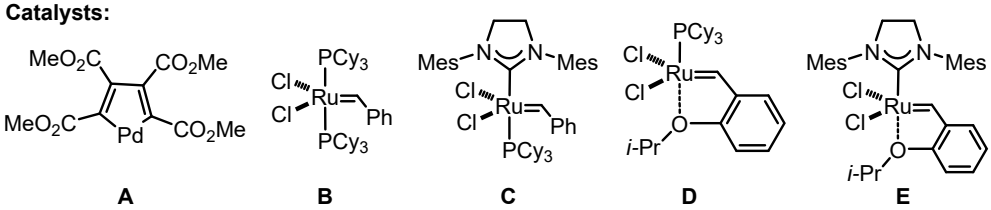
3.1) Table S1. Optimization of EYM Reaction Conditions[a].



1a **2a** **3**

Entry	Catalyst [mol %]	Solvent	T(°C)	t [h]	Yield [%][b] (**2a**:**3**)
1[e]	$PtCl_2$ (5)	Toluene	80	1	66 (1:2.4)[c]
2[d]	A (5)	DCE	reflux	1.5	86 (1:1.2)[c]
3	B (5)	CH_2Cl_2	reflux	4	30 (**2a**)[f]
4	C (5)	CH_2Cl_2	reflux	24	30 (**2a**)[g]
5	E (5)	CH_2Cl_2	reflux	1	81 (**2a**)
6	D (5)	CH_2Cl_2	reflux	1	93 (**2a**)
7	D (5)	Toluene	80	1	79 (**2a**)
8	**D (3)**	**CH_2Cl_2**	**reflux**	**1**	**90** (**2a** ,87[c])
9[e]	D (5)	CH_2Cl_2	reflux	12	88 (**2a**)

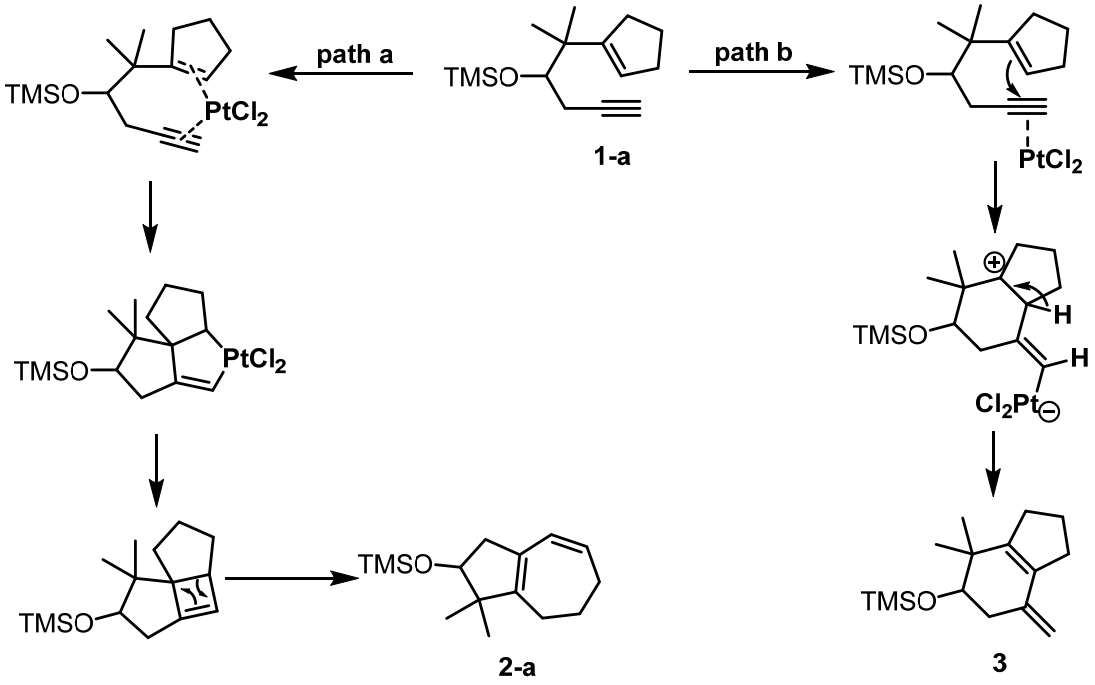
Catalysts:



A **B** **C** **D** **E**

[a]Reactions were performed with 0.5 mmol of **1a**, 3−5 mol% of catalyst under ethylene in specified solvent (0.03 M) unless otherwise stated. [b] NMR yield with anthracene as an internal standard. [c]Isolated yield, the ratio was determined by ^{1}H NMR. [d]5 mol% A, 5 mol% $P(OPh)_3$, DMAD (1.0 equiv), DCE, 80 °C, 1.5 h. [e]Reaction was run under argon atmosphere. [f]With a 40% yield of recycling starting material **1a**. [g]With a 10% yield of recycling starting material **1a**

3.2) Proposed mechanism of the formation of byproduct 3



Scheme S1. Proposed mechanism of the formation of byproduct **3**

3.3) Typical procedure for EYM reaction

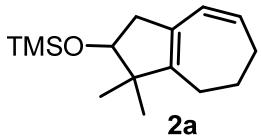
Method I: To a solution of enyne (1.0 equiv) in CH_2Cl_2 (0.03 M) was added G-II (3 mol%), and the solution was refluxed under an atmosphere of ethylene for 4 h. Then the solvent was removed *in vacuo*. Purification of the residue by flash chromatography afforded the corresponding diene.

Method II: To a solution of enyne (1.0 equiv) in CH_2Cl_2 (0.03 M) was added G-II (3 mol%), and the solution was refluxed under an atmosphere of ethylene for 4 h. After the solvent was removed, the residue was redissolved in THF (0.5 M), and then treated with TBAF (1.5 equiv, 1 M in THF). After 0.5 h, water was added, and the mixture was extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ concentrated *in vacuo*. Purification of the residue by flash chromatography afforded the corresponding diene.

Method III: To a solution of enyne (1.0 equiv) in CH_2Cl_2 (0.03 M) was added G-II (3 mol%), and the solution was refluxed under an atmosphere of ethylene for 4 h. Then the second portion of G-II (3 mol%) was added again, and then the reaction was run for another 12h. Then the solvent was removed in vacuo. Purification of the residue by flash chromatography afforded the corresponding diene.

Method IV: To a solution of enyne (1.0 equiv) in CH_2Cl_2 (0.005 M) was added G-II (5 mol%), and the solution was refluxed under an atmosphere of ethylene for 12 h. After the solvent was removed, the residue was redissolved in THF (0.5 M), and then treated with TBAF (1.5 equiv, 1 M in THF). After stirred for 0.5 h, the mixture was quenched with H_2O and extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the residue by flash chromatography afforded the corresponding diene.

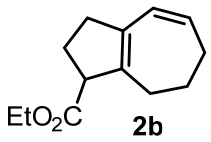
4. Characterization of Bicyclic Dienes 2a-2r



2a

((3,3-Dimethyl-1,2,3,4,5,6-hexahydroazulen-2-yl)oxy)trimethylsilane (2a).

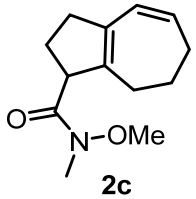
Following the typical procedure method I, diene **2a** (0.81 g, 3.23 mmol) was obtained from enyne **1a** (0.93 g, 3.69 mmol) as a colorless oil in 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.75 – 5.63 (m, 2H), 3.86 (t, *J* = 7.3 Hz, 1H), 2.44 – 2.20 (m, 6H), 1.90 – 1.70 (m, 2H), 0.96 (s, 3H), 0.88 (s, 3H), 0.12 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0, 132.0, 127.1, 125.3, 79.5, 50.3, 43.3, 31.4, 28.5, 24.7, 24.6, 18.9, 0.2. IR (KBr, cm^{-1}): 2956, 1250, 1090, 898, 840, 748. HRMS (ESI, m/z) calc for $C_{15}H_{26}OSi$ $[M+Na]^+$: 273.1645, found: 273.1644.



2b

Ethyl 1,2,3,6,7,8-hexahydroazulene-1-carboxylate (2b).

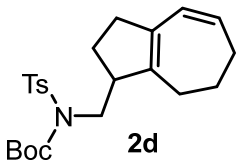
Following the typical procedure method I, diene **2b** (2.01 g, 9.95 mmol) was obtained from enyne **1b** (3.0 g, 14.85 mmol) as a colorless oil in 67% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.82 – 5.71 (m, 2H), 4.18 – 4.11 (m, 2H), 3.46 (t, *J* = 6.9 Hz, 1H), 2.65 – 2.56 (m, 1H), 2.45 – 2.28 (m, 5H), 2.10 – 2.04 (m, 2H), 1.90 – 1.72 (m, 2H), 1.28 – 1.22 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.1, 137.6, 135.4, 133.3, 124.3, 60.3, 56.7, 37.5, 31.1, 30.9, 26.9, 24.2, 14.3. IR (KBr, cm^{-1}): 2935, 1728, 1182, 1038, 840. HRMS (ESI, m/z) calc for $C_{13}H_{18}O_2$ $[M+Na]^+$: 229.1199, found: 229.1196.



2c

***N*-Methoxy-*N*-methyl-1,2,3,6,7,8-hexahydroazulene-1-carboxamide (2c).**

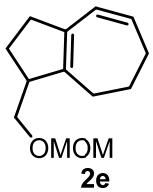
Following the typical procedure method I, diene **2c** (1.20 g, 5.43 mmol) was obtained from enyne **1c** (1.54 g, 6.97 mmol) as a colorless oil in 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.79 – 5.68 (m, 2H), 3.99 (s, 1H), 3.67 (s, 3H), 3.19 (s, 3H), 2.63 – 2.52 (m, 1H), 2.50 – 2.40 (m, 1H), 2.35 – 2.24 (m, 3H), 2.23 – 2.03 (m, 2H), 2.00 – 1.91 (m, 1H), 1.87 – 1.70 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.5, 138.5, 135.4, 132.8, 124.5, 61.3, 52.7, 37.7, 32.4, 31.0, 27.4, 24.3. IR (KBr, cm^{-1}): 2936, 1657, 1384, 1177, 992, 842, 733. HRMS (ESI, m/z) calc for $C_{13}H_{19}NO_2$ $[M+Na]^+$: 244.1308, found: 244.1304.



2d

***tert*-Butyl ((1,2,3,6,7,8-hexahydroazulen-1-yl)methyl)(tosyl)carbamate (2d).**

Following the typical procedure method I, diene **2d** (0.11 g, 0.26 mmol) was obtained from enyne **1d** (0.18 g, 0.43 mmol) as a colorless oil in 60% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 – 7.75 (d, *J* = 8.3 Hz, 2H), 7.31 – 7.27 (d, *J* = 8.3 Hz, 2H), 5.80 – 5.72 (m, 2H), 3.91 – 3.86 (dd, *J* = 14.0, 4.1 Hz, 1H), 3.82 – 3.76 (dd, *J* = 14.0, 10.1 Hz, 1H), 3.12 – 3.04 (m. 1H), 2.61 – 2.49 (m. 1H), 2.43 (s, 3H), 2.42 – 2.37 (m, 2H), 2.37 – 2.27 (m, 3H), 1.99 – 1.90 (m, 1H), 1.89 – 1.76 (m, 3H), 1.32 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.3, 144.0, 140.8, 137.7, 134.1, 132.6, 127.9, 124.8, 84.1, 51.9, 49.4, 36.2, 31.3, 30.9, 27.0, 24.4, 21.6. IR (KBr, cm^{-1}): 2978, 2933, 1727, 1354, 1154, 674, 545. HRMS (ESI, m/z) calc for $C_{23}H_{31}NO_4S$ $[M+Na]^+$: 440.1866, found: 440.1867.

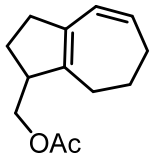


2e

3-((Methoxymethoxy)methyl)-1,2,3,4,5,6-hexahydroazulene (2e).

Following the typical procedure method I, diene **2e** (0.255 g, 1.23 mmol) was obtained from enyne **1e** (0.416 g, 2.0 mmol) as a colorless oil in 62% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.77 – 5.69 (m, 2H), 4.65 – 4.60 (m, 2H), 3.59 (dd, *J* = 9.4, 4.5 Hz, 1H), 3.43

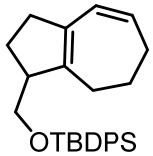
(dd, J = 9.4, 7.4 Hz, 1H), 3.36 (s, 3H), 2.84 (brs, 1H), 2.46 – 2.28 (m, 6H), 2.04 – 1.93 (m, 1H), 1.86 – 1.67 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 133.7, 132.2, 125.0, 96.6, 70.2, 55.1, 51.5, 36.6, 31.1, 30.8, 26.7, 24.4. IR (KBr, cm^{-1}): 3360, 2925, 1439, 1044, 811. HRMS (ESI, m/z) calc for $C_{13}H_{20}O_2$ $[M+Na]^+$: 231.1356, found: 231.1355.



2f

(1,2,3,6,7,8-Hexahydroazulen-1-yl)methyl acetate (2f).

Following the typical procedure method I, diene **2f** (0.14 g, 0.68 mmol) was obtained from enyne **1f** (0.21 g, 1.02 mmol) as a colorless oil in 66% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.78 – 5.68 (m, 2H), 4.12 (dd, J = 10.8, 4.7 Hz, 1H), 3.97 (dd, J = 10.8, 7.4 Hz, 1H), 2.86 (brs, 1H), 2.51 – 2.25 (m, 6H), 2.05 – 1.92 (m, 4H), 1.96 – 7.73 (m, 2H), 1.67 – 1.57 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 139.7, 134.2, 132.7, 124.6, 66.5, 50.4, 36.5, 31.1, 30.7, 26.6, 24.3, 20.9. IR (KBr, cm^{-1}): 2937, 1739, 1365, 1236, 1034, 802. HRMS (ESI, m/z) calc for $C_{13}H_{18}O_2$ $[M+Na]^+$: 229.1199, found: 229.1197.

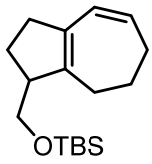


2g

***tert*-Butyl((1,2,3,6,7,8-hexahydroazulen-1-yl)methoxy)diphenylsilane (2g).**

Following the typical procedure method I, diene **2g** (1.454 g, 3.61 mmol) was obtained from enyne **1g** (0.90 g, 2.24 mmol) as a colorless oil in 62% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.70 (m, 4H), 7.45 – 7.40 (m, 6H), 5.81 – 5.72 (m, 2H), 3.76 (dd, J = 9.9, 4.7 Hz, 1H), 3.61 (dd, J = 9.9, 6.6 Hz, 1H), 2.82 (brs, 1H), 2.55 – 2.45 (m, 1H), 2.40 – 2.24 (m, 5H), 2.04 – 1.94 (m, 1H), 1.88 – 1.75 (m, 3H), 1.09 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.3, 135.6, 135.6, 135.5, 134.1, 134.0, 133.6, 132.0, 129.5, 127.5, 125.1, 66.2, 53.9, 36.8, 31.1, 31.0, 26.8, 26.4, 24.5, 19.3. IR (KBr, cm^{-1}): 2930, 1427, 1111, 822, 739, 702, 612, 504. HRMS (ESI, m/z) calc for $C_{27}H_{34}OSi$ $[M+Na]^+$:

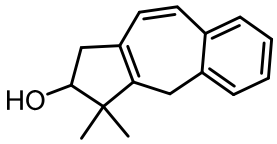
455.2271, found: 455.2277



2h

***tert*-Butyl((1,2,3,6,7,8-hexahydroazulen-1-yl)methoxy)dimethylsilane (2h).**

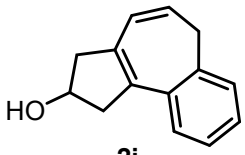
Following the typical procedure method I, diene **2h** (2.30 g, 8.26 mmol) was obtained from enyne **1h** (3.12 g, 11.2 mmol) as a colorless oil in 74% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.75 – 5.69 (m, 2H), 3.67 (dd, *J* = 9.8, 4.9 Hz, 1H), 3.47 (dd, *J* = 9.8, 7.2 Hz, 1H), 2.77 – 2.71 (m, 1H), 2.47 – 2.28 (m, 6H), 1.97 – 1.88 (m, 1H), 1.87 – 1.75 (m, 2H), 1.66 (ddd, *J* = 13.5, 9.4, 4.8 Hz, 1H), 0.89 (s, 9H), 0.04 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.5, 133.4, 132.0, 125.1, 65.6, 54.0, 36.6, 31.2, 31.1, 26.4, 25.9, 24.6, 18.3, -5.3, -5.3. IR (KBr, cm^{-1}): 2929, 1471, 1255, 1101, 836, 776. HRMS (ESI, m/z) calc for $C_{17}H_{30}OSi$ $[M+Na]^+$: 301.1958, found: 301.1958.



2i

3,3-Dimethyl-1,2,3,4-tetrahydrobenzo[*f*]azulen-2-ol (2i).

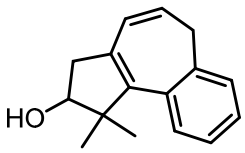
Following the typical procedure method II, diene **2i** (0.15 g, 0.67 mmol) was obtained from enyne **1i** (0.30 g, 1.0 mmol) as a white solid in 67% yield. M.P. 77 – 79 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.23 – 7.18 (m, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 11.4 Hz, 1H), 6.36 (d, *J* = 11.4 Hz, 1H), 3.96 (t, *J* = 7.4 Hz, 1H), 3.12 (d, *J* = 13.7 Hz, 1H), 2.99 (d, *J* = 13.7 Hz, 1H), 2.51 (dd, *J* = 14.6, 7.3 Hz, 1H), 2.36 (dd, *J* = 14.6, 7.5 Hz, 1H), 1.12 (s, 3H), 1.00 (s, 3H), 0.11 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 136.4, 136.1, 131.5, 128.6, 128.6, 128.2, 127.7, 127.4, 125.3, 80.4, 49.6, 40.3, 32.4, 25.2, 19.6, 0.1. IR (KBr, cm^{-1}): 3375, 2953, 1461, 1060, 788, 738. HRMS (ESI, m/z) calc for $C_{16}H_{18}O$ $[M+Na]^+$: 249.1250, found: 249.1245.



2j

1,2,3,6-Tetrahydrobenzo[*e*]azulen-2-ol (2j).

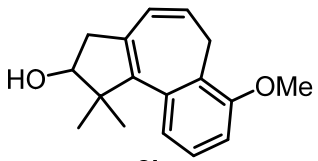
Following the typical procedure method II, diene **2j** (0.18 g, 0.91 mmol) was obtained from enyne **1j** (0.27 g, 1.0 mmol) as a colorless oil in 91% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 2H), 7.29 – 7.24 (m, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 6.09 (d, *J* = 9.7 Hz, 1H), 5.76 (dt, *J* = 9.6, 6.8 Hz, 1H), 4.67 – 4.59 (m, 1H), 3.42 – 3.30 (m, 1H), 3.12 – 2.97 (m, 4H), 2.74 (d, *J* = 17.4 Hz, 1H), 2.08 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.6, 136.4, 135.7, 134.9, 128.5, 127.7, 125.7, 125.7, 125.5, 125.1, 70.3, 46.7, 45.5, 34.9. IR (KBr, cm^{-1}): 3340, 2924, 1487, 1035, 822, 758, 729, 628. HRMS (ESI, m/z) calc for $C_{14}H_{14}O$ $[M+Na]^+$: 221.0937, found: 221.0935.



2k

1,1-Dimethyl-1,2,3,6-tetrahydrobenzo[*e*]azulen-2-ol (2k).

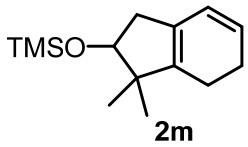
Following the typical procedure method II, diene **2k** (0.07 g, 0.31 mmol) was obtained from enyne **1k** (0.145 g, 0.49 mmol) as a colorless oil in 63% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 7.9, 0.8 Hz, 1H), 7.31 (td, *J* = 7.4, 1.3 Hz, 1H), 7.26 – 7.22 (m, 1H), 7.21 (dd, *J* = 7.5, 1.0 Hz, 1H), 6.02 (d, *J* = 9.6 Hz, 1H), 5.80 (dt, *J* = 9.5, 6.7 Hz, 1H), 3.98 (t, *J* = 6.1 Hz, 1H), 3.05 – 2.84 (m, 3H), 2.61 (dd, *J* = 15.7, 5.9 Hz, 1H), 1.83 (brs, 1H), 1.43 – 1.35 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.2, 138.5, 136.0, 134.0, 127.8, 127.7, 127.1, 125.8, 125.1, 125.1, 80.6, 41.5, 35.0, 29.6, 25.8, 20.0. IR (KBr, cm^{-1}): 3390, 2927, 1461, 1081, 768, 728, 662. HRMS (ESI, m/z) calc for $C_{16}H_{18}O$ $[M+Na]^+$: 249.1250, found: 249.1247.



2l

7-Methoxy-1,1-dimethyl-1,2,3,6-tetrahydrobenzo[*e*]azulen-2-ol (2l).

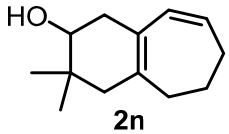
Following the typical procedure method II, diene **2l** (0.18 g, 0.70 mmol) was obtained from enyne **1l** (0.33 g, 1.0 mmol) as a white solid in 70% yield. M.P. 119 – 121 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, *J* = 7.7 Hz, 1H), 7.20 – 7.15 (m, 1H), 6.92 (d, *J* = 7.9 Hz, 1H), 6.05 (d, *J* = 9.4 Hz, 1H), 5.84 (dt, *J* = 9.4, 6.9 Hz, 1H), 4.00 – 3.95 (m, 1H), 3.86 (s, 3H), 2.86 (brs, 2H), 2.61 (dd, *J* = 15.6, 5.6 Hz, 1H), 1.83 (s, 1H), 1.46 – 1.31 (m, 7H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.2, 146.3, 136.4, 135.6, 127.5, 126.8, 126.3, 125.0, 117.6, 109.6, 80.7, 55.7, 41.6, 25.9, 25.2, 20.0. IR (KBr, cm^{-1}): 3410, 2931, 1471, 1265, 1107, 790, 726, 643. HRMS (ESI, m/z) calc for $C_{17}H_{20}O_2$ $[M+Na]^+$: 279.1356, found: 279.1356.



2m

((3,3-Dimethyl-2,3,4,5-tetrahydro-1*H*-inden-2-yl)oxy)trimethylsilane (2m).

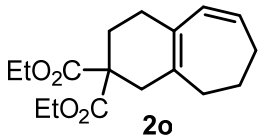
Following the typical procedure method I, diene **2m** (0.40 g, 1.69 mmol) was obtained from enyne **1m** (0.47 g, 2.00 mmol) as a colorless oil in 85% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.84 (dt, *J* = 9.5, 1.9 Hz, 1H), 5.68 – 5.63 (m, 1H), 3.95 (t, *J* = 7.0 Hz, 1H), 2.43 (ddt, *J* = 15.1, 7.1, 2.2 Hz, 1H), 2.25 – 2.18 (m, 3H), 2.09 – 2.02 (m, 2H), 0.98 (s, 3H), 0.89 (s, 3H), 0.12 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.1, 127.6, 124.7, 123.9, 80.6, 47.8, 39.8, 24.7, 23.4, 19.6, 19.0, 0.1. IR (KBr, cm^{-1}): 2956, 1462, 1250, 1093, 840, 750. HRMS (ESI, m/z) calc for $C_{14}H_{24}OSi$ $[M+Na]^+$: 259.1489, found: 259.1485.



2n

3,3-Dimethyl-2,3,4,5,6,7-hexahydro-1*H*-benzo[7]annulen-2-ol (2n).

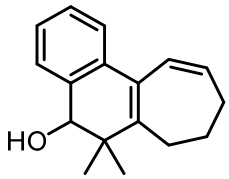
Following the typical procedure method II, diene **2n** (0.105 g, 0.55 mmol) was obtained from enyne **1n** (0.264 g, 1.00 mmol) as a colorless oil in 55% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.77 – 5.71 (m, 1H), 5.57 (d, *J* = 11.9 Hz, 1H), 3.50 (t, *J* = 5.8 Hz, 1H), 2.41 – 2.32 (m, 1H), 2.23 (dd, *J* = 11.9, 5.9 Hz, 2H), 2.14 – 1.94 (m, 5H), 1.86 – 1.79 (m, 2H), 1.42 (brs, 1H), 0.92 (s, 3H), 0.90 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.7, 131.3, 130.1, 123.5, 74.1, 45.1, 37.3, 35.4, 33.7, 31.2, 28.0, 26.2, 21.8. IR (KBr, cm^{-1}): 3404, 2924, 1448, 1043, 722. HRMS (ESI, m/z) calc for $C_{13}H_{20}O$ $[M+Na]^+$: 215.1406, found: 215.1405.



2o

Diethyl 1,3,4,7,8,9-hexahydro-2*H*-benzo[7]annulene-2,2-dicarboxylate (2o).

Following the typical procedure method I, diene **2o** (0.15 g, 0.54 mmol) was obtained from enyne **1o** (0.28 g, 1.00 mmol) as a colorless oil in 54% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.78 – 5.72 (m, 1H), 5.61 (d, *J* = 11.8 Hz, 1H), 4.19 – 4.14 (m, 4H), 2.55 (s, 2H), 2.24 – 2.15 (m, 4H), 2.11 – 2.05 (m, 4H), 1.85 – 1.78 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.5, 135.6, 131.5, 130.0, 124.6, 61.1, 53.5, 35.9, 35.0, 31.0, 29.6, 28.2, 27.7, 14.0. IR (KBr, cm^{-1}): 2934, 1731, 1446, 1250, 1095, 864. HRMS (ESI, m/z) calc for $C_{17}H_{24}O_4$ $[M+Na]^+$: 315.1572, found: 315.1571.

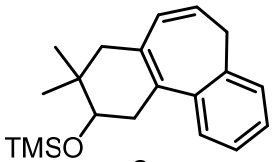


2p

6,6-Dimethyl-6,7,8,9-tetrahydro-5*H*-cyclohepta[*a*]naphthalen-5-ol (2p).

Following the typical procedure method II, diene **2p** (0.083g, 0.35 mmol) was obtained from enyne **1p** (0.25 g, 0.80 mmol) as a colorless oil in 43% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.35 (m, 1H), 7.30 – 7.26 (m, 2H), 7.23 – 7.19 (m, 1H), 6.47 (d, *J* =

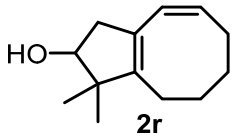
11.0 Hz, 1H), 6.29 – 6.23 (m, 1H), 4.28 (d, *J* = 8.0 Hz, 1H), 2.34 – 2.24 (m, 2H), 2.16 – 2.05 (m, 4H), 1.70 (d, *J* = 8.1 Hz, 1H), 1.19 (s, 3H), 1.08 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.1, 135.7, 134.1, 133.4, 128.2, 128.0, 127.6, 126.8, 126.6, 123.2, 77.8, 41.0, 36.1, 27.7, 27.6, 24.9, 21.0. IR (KBr, cm^{-1}): 3464, 2928, 1484, 1298, 1043, 739, 613. HRMS (ESI) *m/z* calc'd for $C_{17}H_{20}O$ $[M+Na]^+$: 263.1406, found:263.1411



2q

((3,3-Dimethyl-2,3,4,7-tetrahydro-1*H*-dibenzo[*a,c*][7]annulen-2-yl)oxy)trimethylsilane (2q).

Following the typical procedure method III, diene **2q** (0.195 g, 0.23 mmol) was obtained from enyne **1q** (0.231 g, 0.74 mmol) as a colorless oil in 84% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.31 – 7.24 (m, 2H), 7.17 (dd, *J* = 7.2, 1.7 Hz, 1H), 5.84 (dt, *J* = 9.7, 6.7 Hz, 1H), 5.76 (d, *J* = 9.8 Hz, 1H), 3.78 – 3.70 (m, 1H), 3.20 – 2.60 (m, 4H), 2.26 (s, 2H), 1.03 (s, 3H), 1.02 (s, 3H), 0.17 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.6, 138.5, 132.8, 132.2, 129.5, 127.5, 126.9, 126.4, 125.7, 125.5, 74.4, 37.1, 34.3, 34.1, 27.1, 0.4. IR (KBr, cm^{-1}): 2956, 1448, 1082, 839, 756, 718. HRMS (ESI, m/z) calc for $C_{20}H_{28}OSi$ $[M+Na]^+$: 335.1802, found: 335.1800.



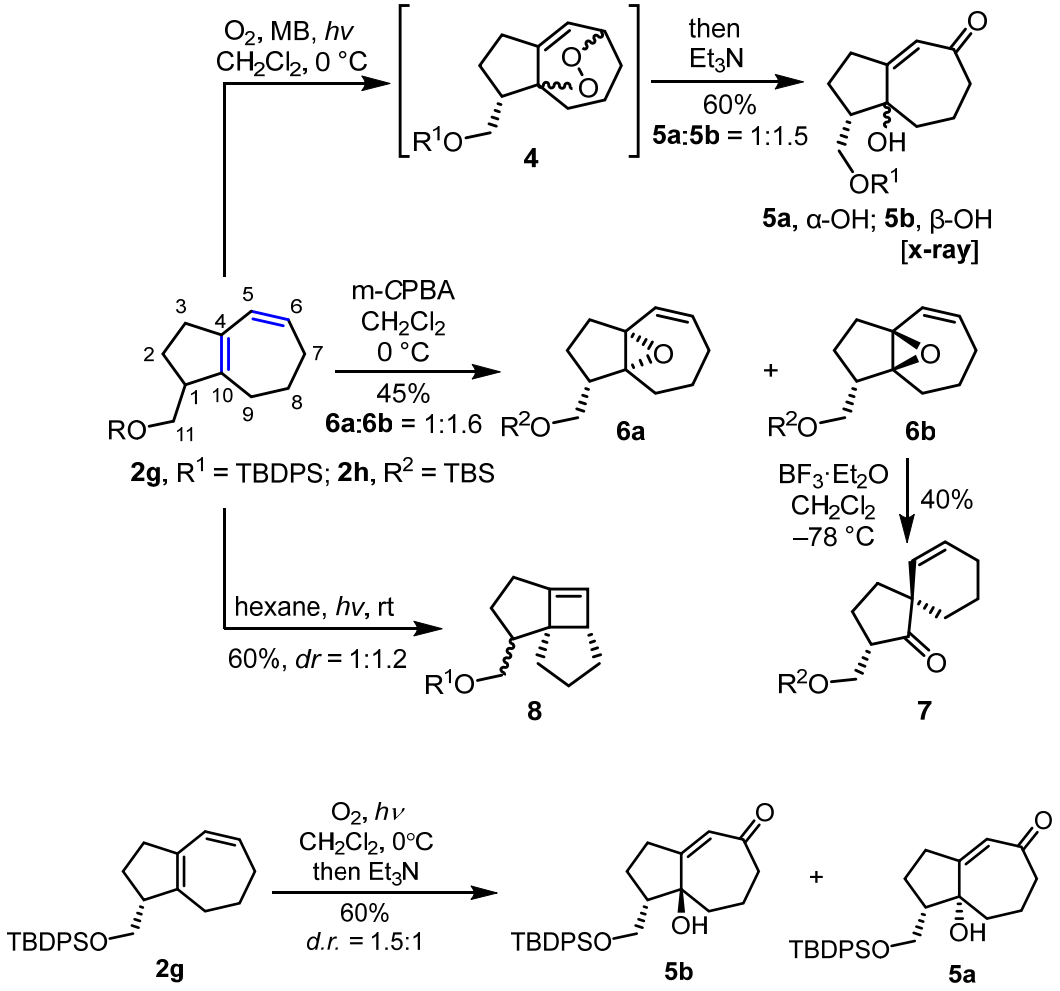
2r

(*Z*)-3,3-Dimethyl-2,3,4,5,6,7-hexahydro-1*H*-cyclopenta[8]annulen-2-ol (2r).

Following the typical procedure method IV, diene **2r** (0.133 g, 0.69 mmol) was obtained from enyne **1r** (0.528 g, 2.0 mmol) as a colorless oil in 34% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.76 (d, *J* = 11.2 Hz, 1H), 5.55 (dt, *J* = 11.2, 7.2 Hz, 1H), 3.87 (q, *J* = 6.2 Hz, 1H), 2.57 (dd, *J* = 15.5, 6.6 Hz, 1H), 2.23 – 2.15 (m, 3H), 2.10 (t, *J* = 5.7 Hz, 2H), 1.65 – 1.48 (m, 5H), 1.01 (s, 3H), 0.98 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.0, 130.0, 128.1, 126.5, 79.8, 50.3, 42.5, 27.8, 25.6, 25.0, 24.9, 23.2, 19.0. IR (KBr,

cm^{-1}): 3391, 2925, 1448, 1060, 745. HRMS (ESI, m/z) calc for $C_{13}H_{20}O$ [M+Na]$^+$: 215.1406, found:215.1405

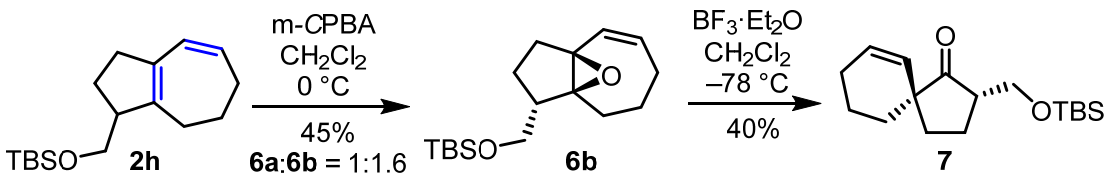
5. Syntheses of Skeletally Diverse, Privileged Scaffolds from 2g and 2h.



To a stirred solution of diene **2g** (0.72 g, 1.79 mmol) in CH_2Cl_2 (300 mL) at 0 °C was treated methylene blue (0.050 g), and the mixture was irradiated with a 300 W tungsten lamp while bubbled with O_2 until no starting material left. Then Et_3N (1.24 mL, 9.0 mmol) was added[4] and the mixture was stirred at rt overnight. The solvent was removed *in vacuo*. Purification of the residue by flash chromatography (PE/EtOAc = 20:1~4:1) afforded the **5b** (0.28 g, 0.65 mmol, 36%) as a white solid and **5a** (0.19 g, 0.44 mmol, 24%) as a colorless oil.

***rac*-(1*S*,8a*S*)-1-(((tert-Butyldiphenylsilyl)oxy)methyl)-8a-hydroxy-2,3,6,7,8,8a-hexahydroazulen-5(1*H*)-one (5b).** M.P. 103 – 105 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 – 7.64 (m, 4H), 7.46 – 7.38 (m, 6H), 5.92 (s, 1H), 3.77 (dd, *J* = 10.4, 7.8 Hz, 1H), 3.70 (dd, *J* = 10.4, 5.9 Hz, 1H), 3.05 (ddd, *J* = 16.9, 10.7, 2.5 Hz, 1H), 2.74 – 2.65 (m, 1H), 2.53 (dddd, *J* = 18.1, 7.6, 3.8, 1.4 Hz, 1H), 2.46 – 2.38 (m, 1H), 2.35 – 2.25 (m, 1H), 2.08 – 2.00 (m, 2H), 1.95 – 1.87 (m, 1H), 1.83 – 1.70 (m, 2H), 1.44 – 1.34 (m, 1H), 1.06 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.3, 163.0, 135.5, 135.5, 133.0, 133.0, 129.8, 127.8, 127.8, 125.5, 81.8, 63.4, 55.3, 41.7, 32.3, 31.7, 26.8, 24.8, 19.1. IR (KBr, cm-1): 3406, 2930, 1656, 1427, 1111, 832, 702, 504. HRMS (ESI, m/z) calc for $C_{27}H_{34}O_3Si$ $[M+Na]^+$: 457.2169, found: 457.2168.

***rac*-(1*S*,8a*R*)-1-(((tert-Butyldiphenylsilyl)oxy)methyl)-8a-hydroxy-2,3,6,7,8,8a-hexahydroazulen-5(1*H*)-one (5a).** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 – 7.66 (m, 4H), 7.47 – 7.40 (m, 6H), 5.91 (s, 1H), 4.04 (dd, *J* = 11.0, 3.4 Hz, 1H), 3.98 (brs, 1H), 3.87 (dd, *J* = 11.0, 4.0 Hz, 1H), 3.01 (ddd, *J* = 15.1, 8.4, 4.1 Hz, 1H), 2.78 (ddt, *J* = 18.3, 9.0, 2.0 Hz, 1H), 2.51 – 2.41 (m, 2H), 2.33 (ddd, *J* = 14.2, 5.9, 4.4 Hz, 1H), 2.27 – 2.13 (m, 2H), 1.85 – 1.71 (m, 3H), 1.67 (ddd, *J* = 14.3, 9.9, 4.5 Hz, 1H), 1.08 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.1, 164.4, 135.5, 135.5, 132.4, 132.2, 123.0, 129.9, 127.8, 125.9, 81.1, 62.9, 51.5, 43.6, 36.9, 31.9, 26.7, 24.5, 19.0, 18.9. IR (KBr, cm-1): 3439, 2929, 1655, 1471, 1255, 1093, 837, 776. HRMS (ESI, m/z) calc for $C_{27}H_{34}O_3Si$ $[M+Na]^+$: 457.2169, found: 457.2164.



To a stirred solution of diene **2h** (1.0 g, 3.59 mmol) in CH_2Cl_2 (20 mL) at 0 °C was added $NaHCO_3$ (0.60 g, 7.2 mmol) and *m*-CPBA (0.84 g, 3.66 mmol, contains ca. 25% water). After being stirred for 10 min, the mixture was filtered through a pad of basic aluminium oxide and washed with PE/EtOAc = 20:1. The filtrate was concentrated *in*

vacuo. Purification of the residue by column chromatography (aluminium oxide, basic. PE/EtOAc = 100:1) afforded the α-epoxide **6a** (0.19 g, 0.65 mmol, 18%) as a colorless oil and β-epoxide **6b** (0.29 g, 0.99 mmol, 27%) as a colorless oil.

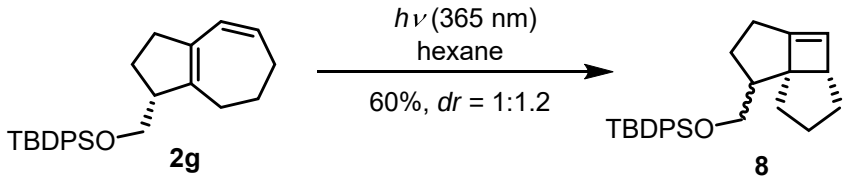
***tert*-butyldimethyl(((3S,3aR,8aR)-2,3,5,6-tetrahydro-1H,4H-3a,8a-epoxyazulen-3-yl)methoxy)silane (6a).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.89 – 5.81 (ddd, *J* = 11.6, 7.2, 2.8 Hz, 1H), 5.74 – 5.68 (dd, *J* = 11.6, 2.8 Hz, 1H), 3.86 – 3.80 (dd, *J* = 10.0, 7.2 Hz, 1H), 3.59 – 3.53 (dd, *J* =10.0, 6.8 Hz, 1H), 2.47 – 2.38 (m, 1H), 2.35 – 2.25 (m, 1H), 2.22 – 2.16 (m, 1H), 2.07 – 1.89 (m, 4H), 1.75 – 1.62 (m, 3H), 1.09 – 0.98 (m, 1H), 0.92 (s, 9H), 0.08 (s, 3H). ^{13}C NMR (150 MHz, CDCl3) δ 136.5, 125.7, 75.2, 69.8, 63.7, 46.8, 31.8, 31.1, 30.4, 25.9, 23.2, 22.6, -5.4. IR (KBr, cm^{-1}): 2925, 2354, 1542, 810. HRMS (ESI, m/z) calc for $C_{17}H_{30}O_2Si$ $[M+Na]^+$: 317.1907, found: 317.1913.

***tert*-butyldimethyl(((3S,3aS,8aS)-2,3,5,6-tetrahydro-1H,4H-3a,8a-epoxyazulen-3-yl)methoxy)silane (6b).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88 – 5.80 (ddd, *J* = 11.6, 7.1, 2.6 Hz, 1H), 5.76 – 5.71 (dd, *J* = 11.6, 2.8 Hz, 1H), 3.74 – 3.68 (dd, *J* = 10.1, 4.6 Hz, 1H), 3.67 – 3.62 (dd, *J* = 10.1, 3.8 Hz, 1H), 2.35 – 2.25 (m, 1H), 2.23 – 2.16 (m, 2H), 2.10 – 1.89 (m, 4H), 1.73 – 1.65 (m, 2H), 1.62 – 1.56 (m, 1H), 1.47 – 1.40 (m, 1H), 0.89 (s, 9H), 0.06 (s, 6H). ^{13}C NMR (100 MHz, CDCl3) δ 136.8, 125.4, 75.8, 70.0, 64.2, 47.3, 32.9, 31.4, 29.2, 25.9, 23.8, 22.0, 18.1, -5.6. IR (KBr, cm^{-1}): 2917, 1577, 1031, 419. HRMS (ESI, m/z) calc for $C_{17}H_{30}O_2Si$ $[M+Na]^+$: 317.1907, found: 317.1902.

To a stirred solution of β-epoxide **6b** (0.294 g, 1.0 mmol) in CH_2Cl_2 (10 mL) at –78 °C was added BF_3•OEt_2 (0.16 mL, 48% boron fluoride in Et_2O) dropwise. After being stirred for 0.5 h, the mixture was quenched with aqueous NaOH solution (5 mL, 1 M) and then extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the residue by column chromatography (PE/EtOAc = 50:1) afforded the spiro compound **7** (0.12 g, 40%) as a colorless oil.

***rac*-(2*S*,5*S*)-2-(((tert-Butyldimethylsilyl)oxy)methyl)spiro[4.5]dec-6-en-1-one (7).** ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.92 (dt, *J* = 10.0, 3.8 Hz, 1H), 5.29 (dt, *J* = 10.0, 2.1 Hz, 1H), 3.93 (dd, *J* = 9.9, 4.0 Hz, 1H), 3.68 (dd, *J* = 9.9, 3.3 Hz, 1H), 2.31 – 2.25 (m,

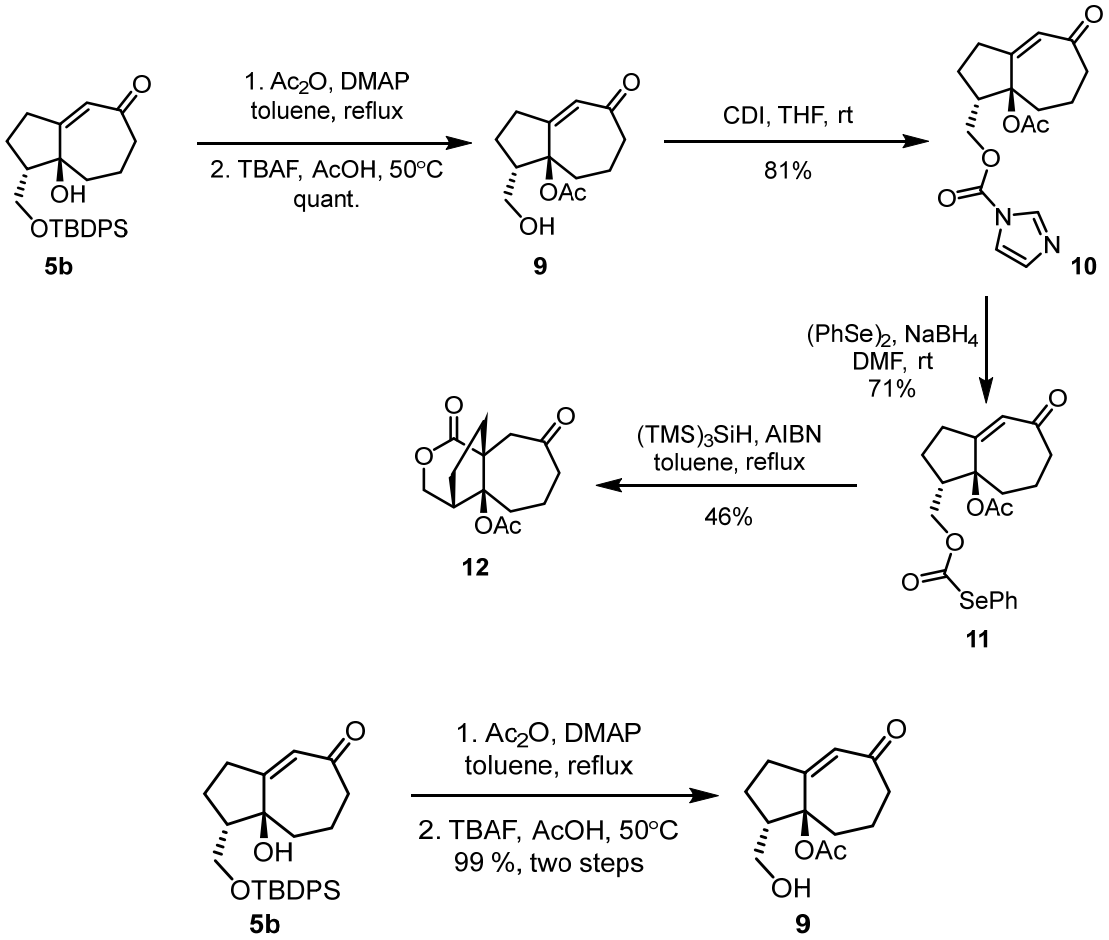
1H), 2.08 – 1.98 (m, 4H), 1.89 (ddd, *J* = 12.8, 5.3, 3.2 Hz, 1H), 1.82 – 1.69 (m, 4H), 1.55 – 1.47 (m, 1H), 1.42 – 1.36 (m, 1H), 0.86 (s, 9H), 0.03 (s, 3H), 0.01 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 220.8, 130.1, 128.9, 61.3, 51.1, 51.0, 35.9, 28.6, 25.8, 24.7, 21.8, 18.4, 18.2, -5.5, -5.6. IR (KBr, cm^{-1}): 2927, 1737, 1463, 1255, 1092, 836, 775. HRMS (ESI, m/z) calc for $C_{17}H_{30}O_2Si$ $[M+Na]^+$: 317.1907, found: 317.1903.



A stirred solution of diene **2g** (0.20 g, 0.50 mmol) in *n*-hexane equipped in quartz reaction tube was degassed with argon for 5 min and then irradiated with 365 nm UV lamp (8 W × 4) for 12 h. TLC showed no starting materials left, the solvent was removed *in vacuo*. Purification of the residue by flash chromatography (PE/EtOAc = 100:1) afforded two inseparable diastereoisomers **8** (0.12 g, 60%) as a colorless oil.

***rac-tert*-Butyl(((4a*S*,7a*S*)-2,3,4a,5,6,7-hexahydro-1*H*-cyclobuta[1,2:1,4]di[5]annulen-1-yl)methoxy)diphenylsilane (8).** ^{1}H NMR (500 MHz, CDCl3) δ 7.75 – 7.60 (m, 4H), 7.50 – 7.30 (m, 6H), 5.54 – 5.48 (m, 1H), 3.74 – 3.64 (m, 1H), 3.64 – 3.40 (m, 1H), 2.84 – 2.54 (m, 1H), 2.20 – 2.12 (m, 1H), 2.12 – 1.9 (m, 3H), 1.75 – 1.54 (m, 5H), 1.28 – 1.14 (m, 2H), 1.06 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.8, 156.3, 135.6, 134.2, 134.1, 129.5, 127.6, 124.3, 123.6, 65.0, 64.7, 60.8, 60.5, 47.0, 45.4, 44.0, 42.5, 32.5, 32.0, 31.6, 26.9, 26.8, 26.6, 26.5, 24.6, 24.0, 23.8, 23.4, 23.1, 19.2. HRMS (ESI, m/z) calc for $C_{27}H_{34}OSi$ $[M+Na]^+$: 425.2271, found: 425.2276.

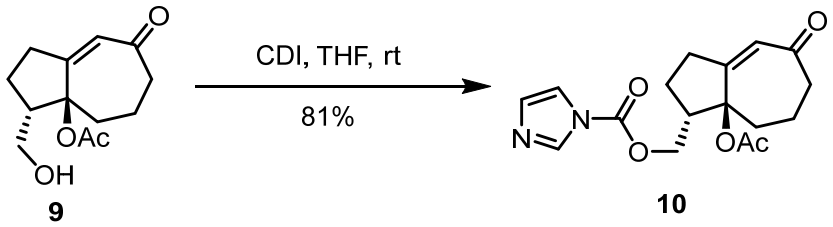
6. Construction of the Core Skeleton of Pseudolaric Acid F.



To a stirred solution of **5b** (0.435 g, 1.0 mmol) in toluene (15 mL) was added DMAP (0.122 g, 1.0 mmol), Et_3N (0.56 mL, 4.0 mmol) and Ac_2O (0.28 mL, 3.0 mmol) successively, and the mixture was heated to reflux for 5 h. After being cooled to rt, the mixture was quenched with H_2O (20 mL) and extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo* to give the crude acetylation product.

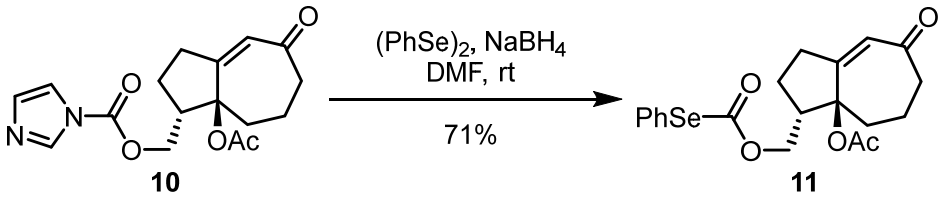
The above crude acetylation product was dissolved with THF (10 mL), AcOH (0.17 mL, 3.0 mmol) and TBAF (1.5 mL, 1 M in THF) was added successively. The mixture was heated at 50 °C for 2 h. After being cooled to rt, the mixture was quenched with H_2O (10 mL) and extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the residue by column chromatography (PE/EtOAc = 4:1~1:1) afforded the alcohol **9** (0.238 g, 99%) as a colorless oil.

***rac*-(3*S*,3a*S*)-3-(Hydroxymethyl)-7-oxo-2,3,4,5,6,7-hexahydroazulen-3a(1*H*)-yl acetate (9).** ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.97 – 5.91 (m, 1H), 3.81 (dd, *J* = 11.0, 6.8 Hz, 1H), 3.62 (dd, *J* = 11.0, 6.7 Hz, 1H), 3.05 – 2.98 (m, 1H), 2.96 – 2.87 (m, 1H), 2.84 – 2.76 (m, 1H), 2.53 – 2.43 (m, 3H), 2.05 – 1.99 (m, 1H), 1.97 (s, 3H), 1.92 – 1.86 (m, 1H), 1.85 – 1.73 (m, 3H), 1.43 – 1.34 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.1, 169.7, 161.0, 125.9, 89.0, 61.8, 50.2, 40.6, 32.4, 28.5, 25.9, 21.8, 18.6. IR (KBr, cm^{-1}): 3439, 2950, 1734, 1661, 1236, 1049, 960. HRMS (ESI, m/z) calc for $C_{13}H_{18}O_4$ $[M+Na]^+$: 261.1097, found: 261.1099.



To a stirred solution of alcohol **9** (0.219 g, 0.92 mmol) in THF (10 mL) at rt was added CDI (0.448 g, 2.76 mmol), and the mixture was stirred for 12 h. When TLC showed no starting material left, the solvent was removed *in vacuo*. Purification of the residue by flash chromatography (PE/EtOAc = 2:1~1:1) afforded the product **10** (0.246 g, 0.74 mmol, 81%) as a yellow oil.

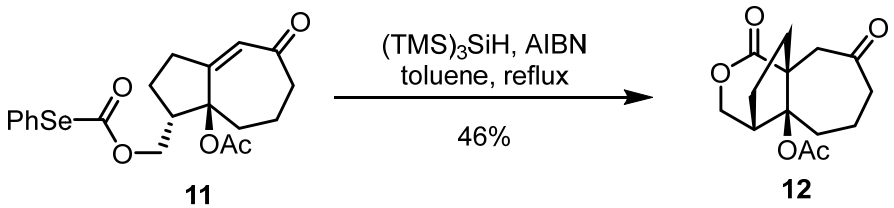
***rac*-((1*S*,8a*S*)-8a-Acetoxy-5-oxo-1,2,3,5,6,7,8,8a-octahydroazulen-1-yl)methyl 1*H*-imidazole-1-carboxylate (10).** ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.38 (t, *J* = 1.4 Hz, 1H), 7.07 (dd, *J* = 1.5, 0.7 Hz, 1H), 5.94 (s, 1H), 4.54 (dd, *J* = 11.1, 7.2 Hz, 1H), 4.46 (dd, *J* = 11.1, 7.2 Hz, 1H), 3.43 – 3.35 (m, 1H), 3.06 – 2.96 (m, 1H), 2.83 – 2.75 (m, 1H), 2.55 (dd, *J* = 17.2, 7.3 Hz, 1H), 2.50 – 2.43 (m, 1H), 2.40 – 2.31 (m, 1H), 2.12 – 2.05 (m, 1H), 1.98 – 1.94 (m, 1H), 1.92 (s, 3H), 1.85 – 1.77 (m, 2H), 1.43 (ddd, *J* = 24.1, 11.8, 7.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.0, 169.2, 158.8, 148.3, 136.9, 130.8, 125.6, 116.9, 88.1, 67.0, 46.0, 39.9, 32.0, 28.6, 26.0, 21.5, 18.7. IR (KBr, cm-1): 2921, 1762, 1736, 1665, 1377, 1239, 1004, 769. HRMS (ESI, m/z) calc for $C_{17}H_{20}N_2O_5$ $[M+Na]^+$: 355.1264, found: 355.1265.



10 11

To a stirred solution of $(PhSe)_2$ (188 mg, 0.60 mmol) in DMF (5 mL) at rt was added with $NaBH_4$ (23 mg, 0.62 mmol).[5] The mixture was stirred for 10 min and then transferred to a stirred solution of starting material **10** (100 mg, 0.301 mmol) in DMF (5 mL). The reaction mixture was stirred for 0.5 h and TLC showed no starting material left. The mixture was diluted with Et_2O (10 mL) and then quenched with saturated $NaHCO_3$ solution (10 mL) and extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the residue by column chromatography (PE/EtOAc = 8:1~4:1) afforded the product **11** (90 mg, 0.213 mmol, 71%) as a colorless oil..

***rac*-(3*S*,3a*S*)-7-Oxo-3-((((phenylselanyl)carbonyl)oxy)methyl)-2,3,4,5,6,7-hexahydroazulen-3a(1*H*)-yl acetate (11).** ^1H NMR (500 MHz, $CDCl_3$) δ 7.66 – 7.62 (m, 2H), 7.44 – 7.37 (m, 3H), 5.95 (s, 1H), 4.42 (dd, *J* = 11.1, 6.8 Hz, 1H), 4.35 (dd, *J* = 11.1, 6.7 Hz, 1H), 3.31 – 3.23 (m, 1H), 3.03 – 2.93 (m, 1H), 2.83 (ddd, *J* = 17.0, 12.4, 3.2 Hz, 1H), 2.55 – 2.46 (m, 2H), 2.35 – 2.29 (m, 1H), 2.04 – 1.99 (m, 4H), 1.97 – 1.91 (m, 1H), 1.84 – 1.67 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.2, 169.2, 166.7, 159.6, 135.7, 129.3, 129.2, 125.7, 125.6, 88.1, 66.5, 46.2, 40.1, 32.1, 28.6, 25.8, 21.7, 18.7. IR (KBr, cm^{-1}): 2926, 1734, 1666, 1367, 1236, 1119, 1020, 741, 690. HRMS (ESI, m/z) calc for $C_{20}H_{22}O_5Se$ $[M+Na]^+$: 445.0525, found: 445.0519.



11 12

To a stirred solution of compound **11** (90 mg, 0.213 mmol) in toluene (10 mL) at rt was added with AIBN (18 mg, 0.107 mmol) and $(TMS)_3SiH$ (0.154 mL, 0.426 mmol) successively. The resulting mixture was heated to reflux for 12 h. After being cooled to rt, the mixture was concentrated *in vacuo*. Purification of the residue by flash

chromatography (PE/EtOAc = 8:1~4:1) afforded the tricyclic compound **10** (26 mg, 0.098 mmol, 46%) as a white solid.

***rac*-(4*S*,4a*S*,9a*R*)-1,8-Dioxohexahydro-1*H*-4,9a-ethanocyclohepta[c]pyran-4a(5*H*)-yl acetate (12).** M.P. 108 – 110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.52 – 4.45 (m, 1H), 4.22 (d, *J* = 11.4 Hz, 1H), 3.42 (dd, *J* = 6.2, 2.9 Hz, 1H), 3.19 – 3.12 (m, 1H), 3.05 (d, *J* = 17.4 Hz, 1H), 2.77 (d, *J* = 17.4 Hz, 1H), 2.60 (dd, *J* = 16.5, 6.4 Hz, 1H), 2.38 – 2.28 (m, 1H), 2.23 – 2.05 (m, 5H), 2.00 – 1.91 (m, 1H), 1.85 – 1.76 (m, 2H), 1.72 – 1.63 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.2, 173.8, 169.5, 88.6, 73.0, 55.1, 44.3, 43.1, 42.5, 37.0, 30.8, 26.5, 21.7, 18.2. IR (KBr, cm^{-1}): 2921, 1736, 1697, 1229, 1180, 1028, 945. HRMS (ESI) *m/z* calc'd for $C_{14}H_{18}O_5$ $[M+Na]^+$: 289.1046, found: 289.1039.

7. X-ray Crystal Structures

Fig. S1 X-ray crystallographic structure of 2i (CCDC 1907870).

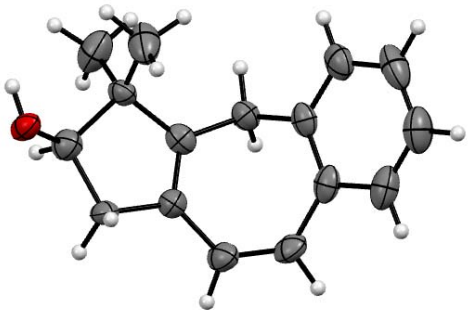


Table 2. Crystal data and structure refinement for 2i.

Identification code	a
Empirical formula	$C_{16}H_{18}O$
Formula weight	226.30
Temperature/K	273.15
Crystal system	trigonal
Space group	R3
a/Å	20.961(8)
b/Å	20.961(8)
c/Å	7.086(3)
α/°	90.00
β/°	90.00
γ/°	120.00
Volume/Å^3	2696.0(18)
Z	9
ρ_{calc}g/cm^3	1.254
μ/mm^{-1}	0.076
F(000)	1098.0
Crystal size/mm^3	0.12 × 0.11 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.88 to 58.2
Index ranges	$-28 \le h \le 15$, $-21 \le k \le 27$, $-9 \le l \le 9$
Reflections collected	5824
Independent reflections	2880 [R_{int} = 0.0519, R_{sigma} = 0.0935]
Data/restraints/parameters	2880/1/157
Goodness-of-fit on F^2	0.936
Final R indexes [I>=2σ (I)]	R_1 = 0.0714, wR_2 = 0.1619
Final R indexes [all data]	R_1 = 0.1082, wR_2 = 0.1846
Largest diff. peak/hole / e Å^{-3}	0.43/-0.18
Flack parameter	-1(3)

Fig. S2 X-ray crystallographic structure of 5b (CCDC 1907871).

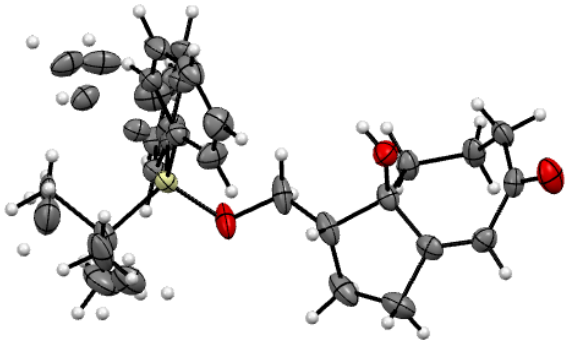


Table 3. Crystal data and structure refinement for 5b.

Identification code	mon
Empirical formula	C27H34O3Si
Formula weight	434.63
Temperature/K	293(2)
Crystal system	monoclinic
Space group	C2/c
a/Å	42.742(3)
b/Å	10.4771(9)
c/Å	10.9037(9)
α/°	90
β/°	93.609(6)
γ/°	90
Volume/Å3	4873.1(7)
Z	8
ρcalcg/cm3	1.185
μ/mm-1	0.121
F(000)	1872.0
Crystal size/mm3	0.3 × 0.3 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6 to 51.992
Index ranges	-52 ≤ h ≤ 45, -12 ≤ k ≤ 10, -13 ≤ l ≤ 11
Reflections collected	10004
Independent reflections	4772 [Rint = 0.0366, Rsigma = 0.0567]
Data/restraints/parameters	4772/0/333
Goodness-of-fit on F2	1.105
Final R indexes [I>=2σ (I)]	R1 = 0.0697, wR2 = 0.1464
Final R indexes [all data]	R1 = 0.0939, wR2 = 0.1574
Largest diff. peak/hole / e Å-3	0.44/-0.40

Fig. S3 X-ray crystallographic structure of 12 (CCDC 1907872).

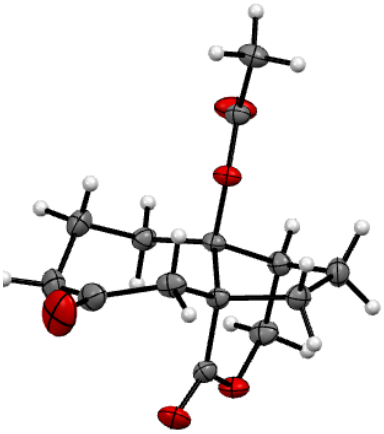


Table 4. Crystal data and structure refinement for 12.

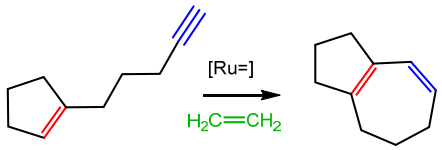
Identification code	lmg
Empirical formula	$C_{14}H_{18}O_5$
Formula weight	266.28
Temperature/K	185.1(6)
Crystal system	triclinic
Space group	P-1
a/Å	7.3423(10)
b/Å	8.4321(9)
c/Å	10.4623(11)
α/°	85.681(8)
β/°	85.985(10)
γ/°	78.332(10)
Volume/Å^3	631.54(13)
Z	2
ρ_{calc}g/cm^3	1.400
μ/mm^{-1}	0.106
F(000)	284.0
Crystal size/mm^3	0.7 × 0.4 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.108 to 54.99
Index ranges	$-4 \leq h \leq 9$, $-10 \leq k \leq 10$, $-13 \leq l \leq 13$
Reflections collected	4909
Independent reflections	2890 [R_{int} = 0.0272, R_{sigma} = 0.0428]
Data/restraints/parameters	2890/0/173
Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0443, wR_2 = 0.1051
Final R indexes [all data]	R_1 = 0.0525, wR_2 = 0.1100
Largest diff. peak/hole / e Å^{-3}	0.30/-0.22

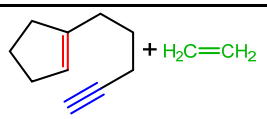
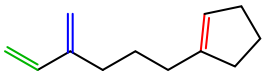
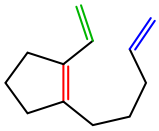
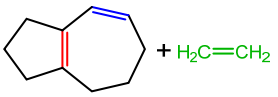
8. Theoretical Calculations

8.1 Computational methods

All of the structures were optimized at the B3LYP/6-311++G(d,p) level of DFT.[6] The frequency calculations were performed to confirm the characteristics of the calculated structures as minima. The Gibbs Free Energies (GFEs) are all calculated in gas phase without any solvent. All the optimizations were performed with the Gaussian 09 software package.[7]

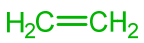
8.2 DFT calculated results



Compound	Gibbs Free Energy
 F	0.0
 G	-20.0
 H	-22.8
 I	-29.8 Most Stable

8.3 Cartesian coordinates

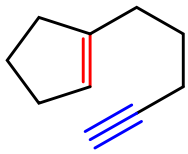
$H_2C=CH_2$



E = -78.61553852 (G = -78.586288)

C	0.000000	0.664397	0.000000
H	0.922912	1.235124	0.000000
H	-0.922864	1.235183	0.000000
C	0.000000	-0.664397	0.000000
H	-0.922912	-1.235124	0.000000
H	0.922864	-1.235183	0.000000

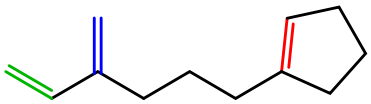
F



E = -389.5201430 (G = -389.346557)

C	-3.077439	-0.052312	0.359555
C	-1.878717	-1.019804	0.203072
C	-0.824983	-0.175474	-0.494274
C	-1.158736	1.118867	-0.463581
C	-2.469883	1.369653	0.242028
H	-3.627111	-0.204158	1.290904
H	-2.136616	-1.920372	-0.365405
H	-1.511467	-1.367284	1.178493
H	-0.545094	1.917310	-0.867610
H	-3.123380	2.058788	-0.302333
H	-2.299005	1.822314	1.228453
H	-3.780738	-0.212737	-0.462331
C	0.418505	-0.772317	-1.090411
H	0.970755	-0.001211	-1.635742
H	0.131129	-1.534757	-1.825970
C	1.357536	-1.438837	-0.064647
H	2.166632	-1.945046	-0.599439
H	0.814748	-2.211840	0.489244
C	1.970743	-0.458599	0.958247
H	1.169771	0.069726	1.487474
H	2.522417	-1.026569	1.715406
C	2.871963	0.524798	0.361984
C	3.619065	1.324395	-0.138277
H	4.279634	2.033626	-0.573328

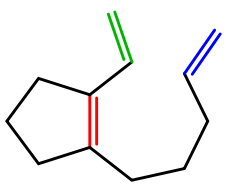
G



E = -468.1907883 (G = -467.964650)

C	-3.669404	0.789927	0.744205
C	-2.297974	0.224326	1.187659
C	-1.877706	-0.654325	0.021447
C	-2.642652	-0.417923	-1.049281
C	-3.692198	0.638567	-0.798983
H	-3.830158	1.818971	1.072639
H	-2.357010	-0.331161	2.130202
H	-1.562886	1.024548	1.348384
H	-4.680895	0.357762	-1.175935
H	-3.425609	1.577327	-1.303868
H	-4.468507	0.182263	1.177851
C	-0.728130	-1.616738	0.120191
H	-0.643061	-2.178966	-0.816430
H	-0.948884	-2.351196	0.906203
C	0.630140	-0.963176	0.450386
H	1.369964	-1.755194	0.605983
H	0.561324	-0.421453	1.400170
C	1.129548	-0.000993	-0.641652
H	1.193215	-0.550706	-1.591114
H	0.397507	0.796066	-0.794453
C	2.483100	0.604934	-0.335445
C	2.633839	1.915562	-0.102997
H	1.782796	2.588117	-0.099299
H	3.609597	2.355043	0.070086
H	-2.512273	-0.899884	-2.012995
C	3.629517	-0.328188	-0.334725
H	3.576650	-1.134033	-1.066286
C	4.682479	-0.282329	0.485403
H	5.491840	-0.998680	0.402304
H	4.763042	0.463311	1.269302

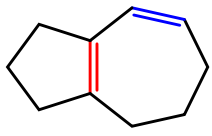
H



E = -468.1953317 (G = -467.969134)

C	-2.773207	-1.353817	0.585531
C	-1.389395	-1.860014	0.123016
C	-0.737309	-0.633252	-0.482633
C	-1.410686	0.491948	-0.149629
C	-2.607548	0.175076	0.730118
H	-3.116096	-1.833596	1.504662
H	-1.456792	-2.690265	-0.589429
H	-0.793840	-2.232445	0.968285
H	-3.506579	0.719764	0.426675
H	-2.401542	0.466630	1.768591
H	-3.514861	-1.567034	-0.189269
C	0.507883	-0.763148	-1.313648
H	0.821197	0.210298	-1.697762
H	0.270268	-1.373670	-2.195566
C	1.691520	-1.441792	-0.587698
H	2.513691	-1.558956	-1.301406
H	1.395690	-2.453147	-0.289049
C	2.214637	-0.699623	0.660180
H	1.383670	-0.562402	1.363678
H	2.952520	-1.334257	1.161712
C	2.835088	0.638909	0.369539
H	2.168895	1.410867	-0.010136
C	4.120654	0.938144	0.547759
H	4.826475	0.208362	0.934609
H	4.513407	1.922866	0.319727
C	-1.059854	1.852694	-0.524538
H	-0.200512	1.971181	-1.179012
C	-1.708056	2.959922	-0.134001
H	-2.573353	2.923639	0.518172
H	-1.384607	3.941878	-0.458452
H	0.321961	2.656974	-0.264841
H	2.581658	2.256130	0.072785
H	3.646345	0.160617	0.082535
H	0.738356	-1.989696	1.114455
H	1.910975	-0.857111	-1.481976
H	2.703142	-1.959060	-0.369104
H	2.574330	-0.152434	1.423363
H	0.363846	-2.517250	-0.501099
C	-1.927712	-1.210416	-0.002634
H	-2.133893	-1.677900	-0.977087
H	-2.083833	-1.993729	0.748362
C	-1.926475	1.222106	-0.187355
H	-2.130737	1.531627	-1.221755
H	-2.085524	2.106343	0.438302
C	-2.811549	0.031531	0.236550
H	-3.761216	-0.009472	-0.301536
H	-3.044047	0.112593	1.302332

I



E = -389.5743570 (G = -389.394064)

C	-0.506699	0.681770	-0.075966
C	0.612057	1.621514	-0.098795
C	1.921174	1.392958	0.096120
C	-0.513955	-0.665010	0.017883
C	2.587410	0.066654	0.345849
C	0.637401	-1.626896	0.081063
C	1.994788	-1.125482	-0.423504

9. References

(1) J. Tormo, A. Moyano, M. A. Pericàs and A. Riera, *J. Org. Chem.*, 1997, **62**, 4851.

(2) R. A. Bunce and C. L. Schilling III, *J. Org. Chem.*, 1995, **60**, 2748.

(3) T. J. Michnick and D. S. Matteson, *Synlett*, 1991, **8**, 631.

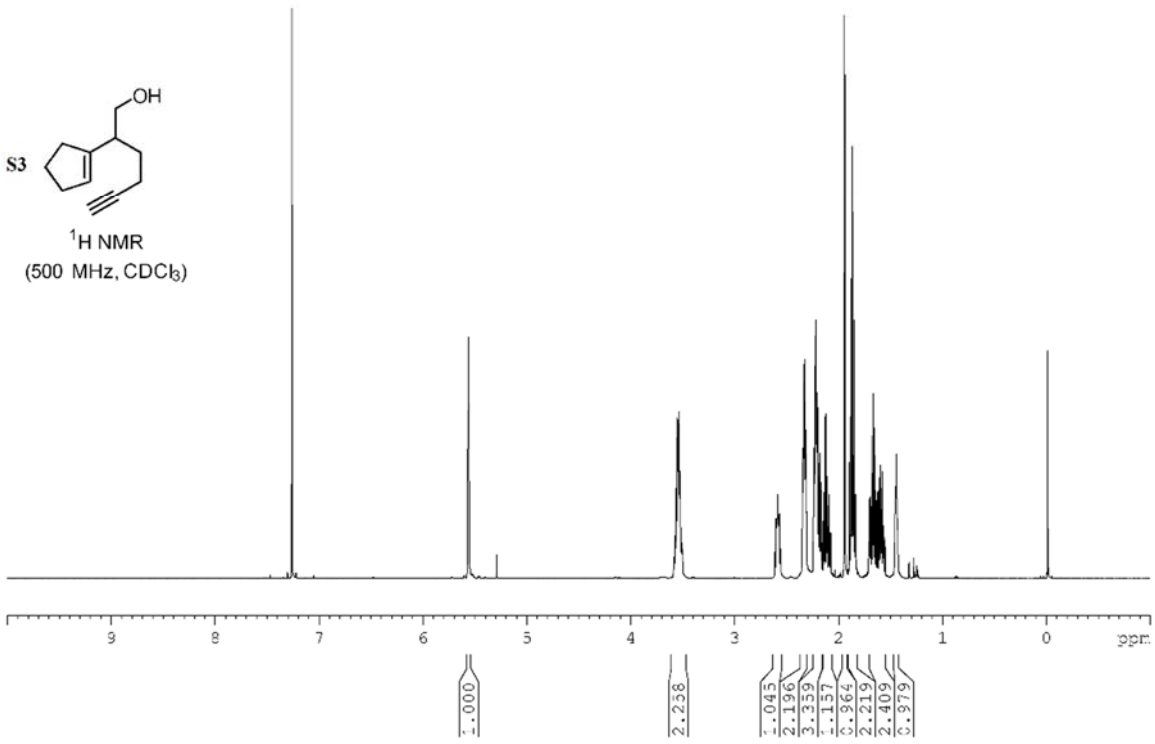
(4) (a) H. S. Bansal and A. J. Pearson, *Tetrahedron Lett.* 1986, **27**, 283; (b) M. A. Avery, *J. Med. Chem.* 2010, **53**, 7864.

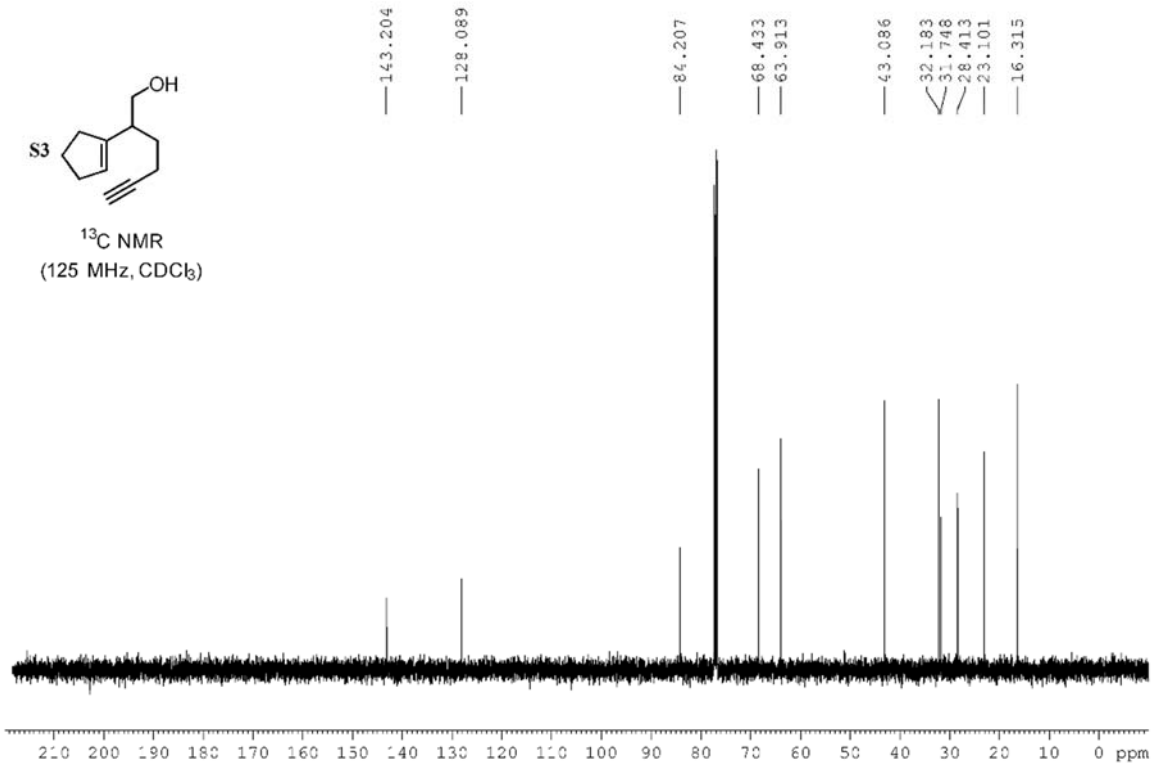
(5) A. Meyer, J. Waser and B. M. Trost, *J. Am. Chem. Soc.* 2008, **130**, 16424.

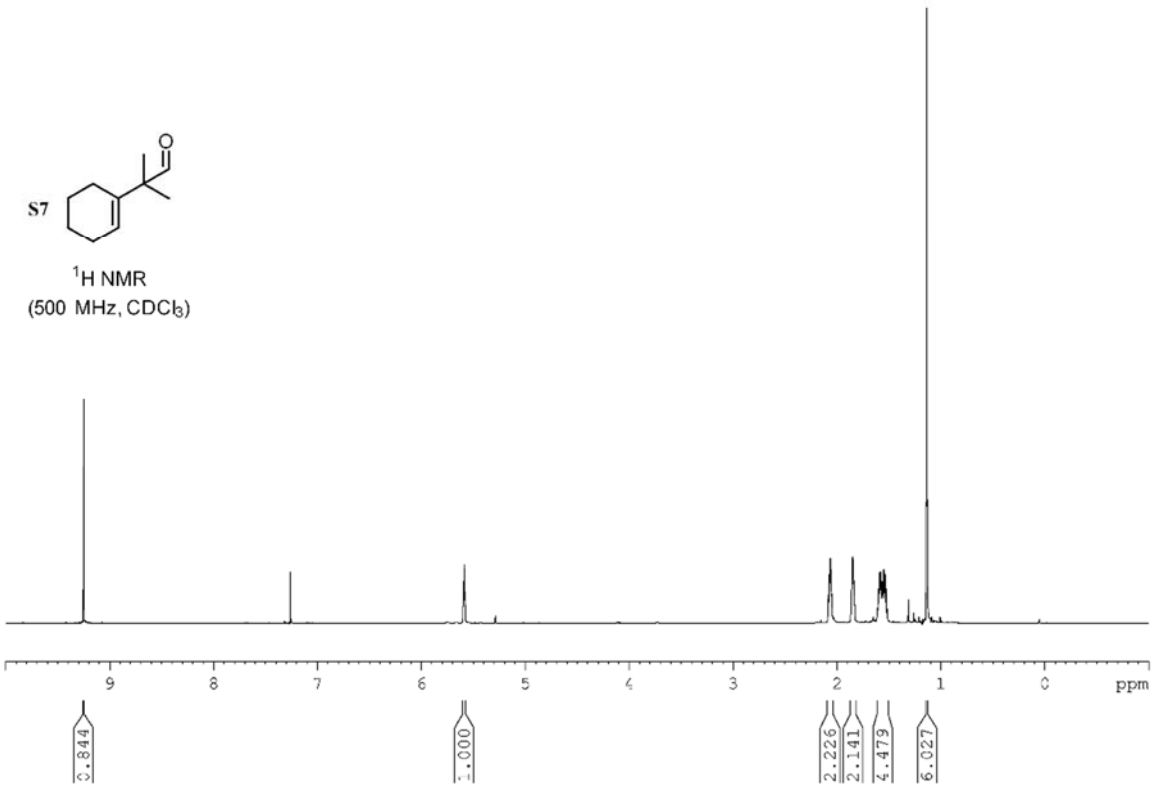
(6) (a) A . D. Becke, *J. Chem. Phys.* 1993, **98**, 5648; (b) B. Miehlich, A. Savin, H. Stoll and H. Preuss, *Chem. Phys. Lett.* 1989, **157**, 200; (c) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B.* 1988, **37**, 785.

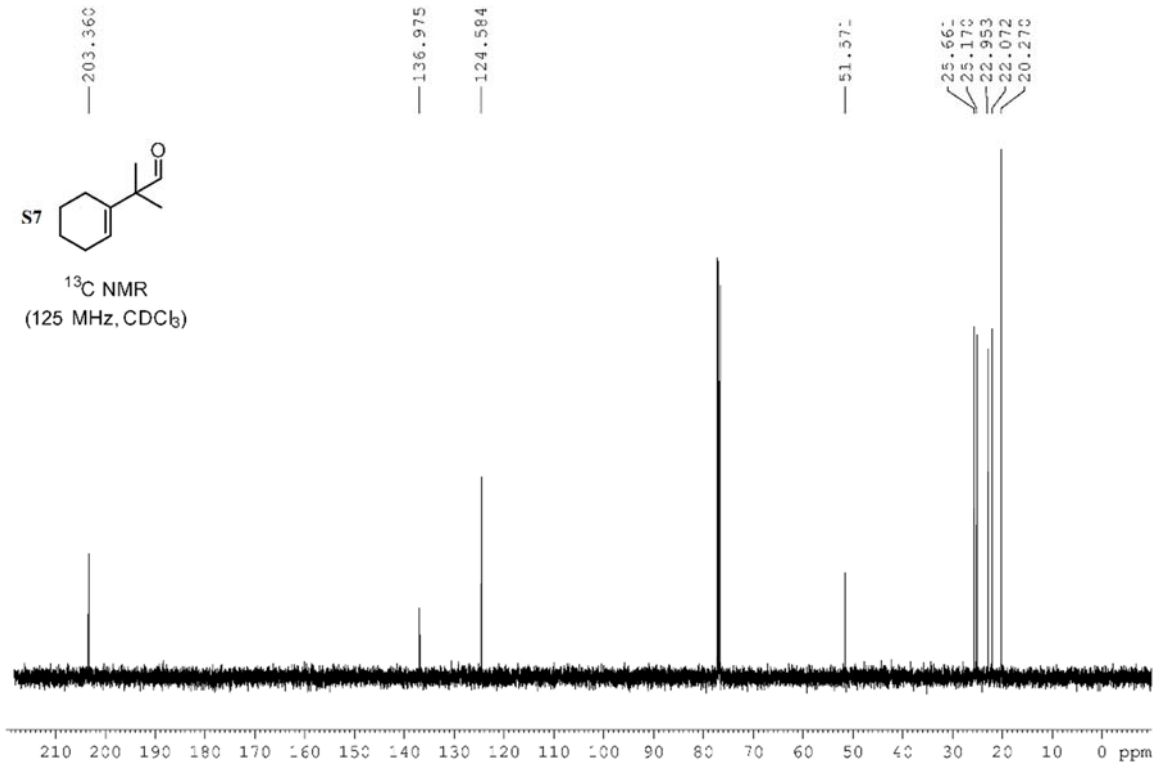
(7) M. J. Frisch, et al. *Gaussian 09*, revision B.01; Gaussian, Inc.: Wallingford, CT, **2009**.

10. NMR Spectra Data

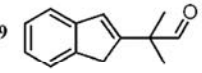





S7
O
^{1}H NMR
(500 MHz, CDCl$_3$)
9
8
7
6
5
4
3
2
1
0
ppm
3.844
1.000
2.226
2.141
4.479
6.027

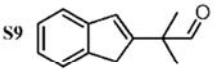

203.360
136.975
124.584
51.37
25.66
25.17
22.95
22.07
20.27
S7
O
^{13}C NMR
(125 MHz, CDCl$_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

S9

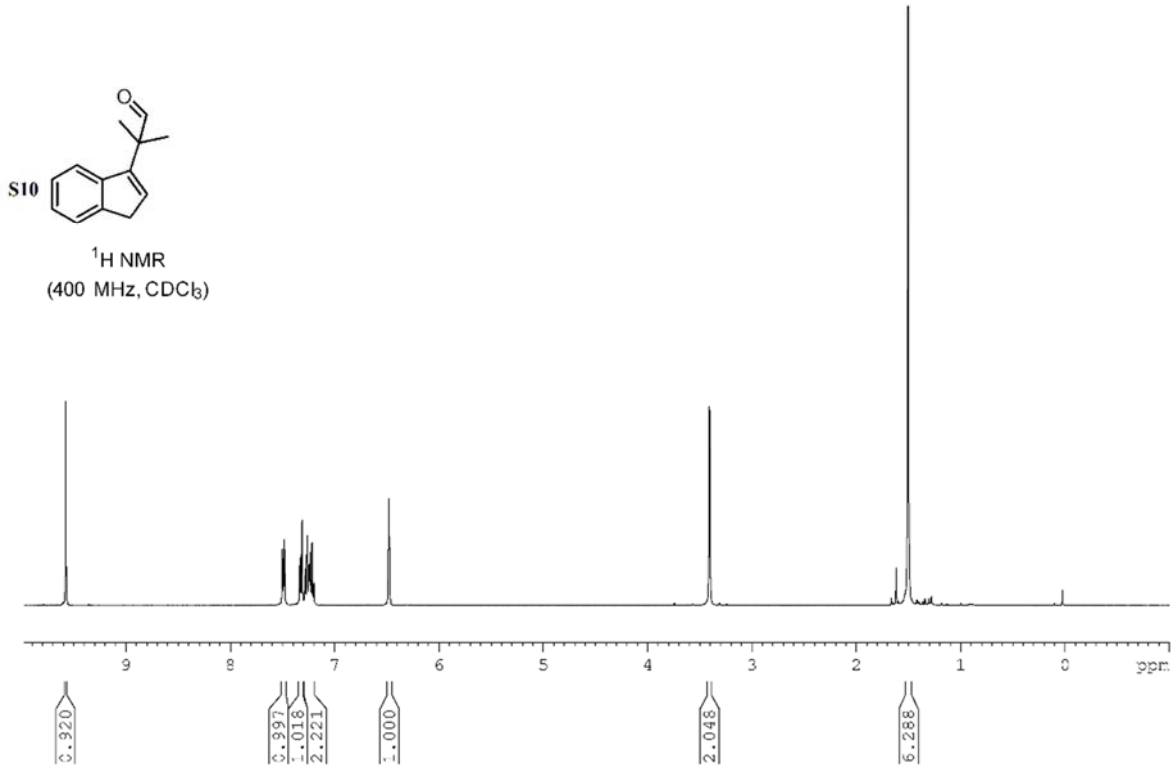


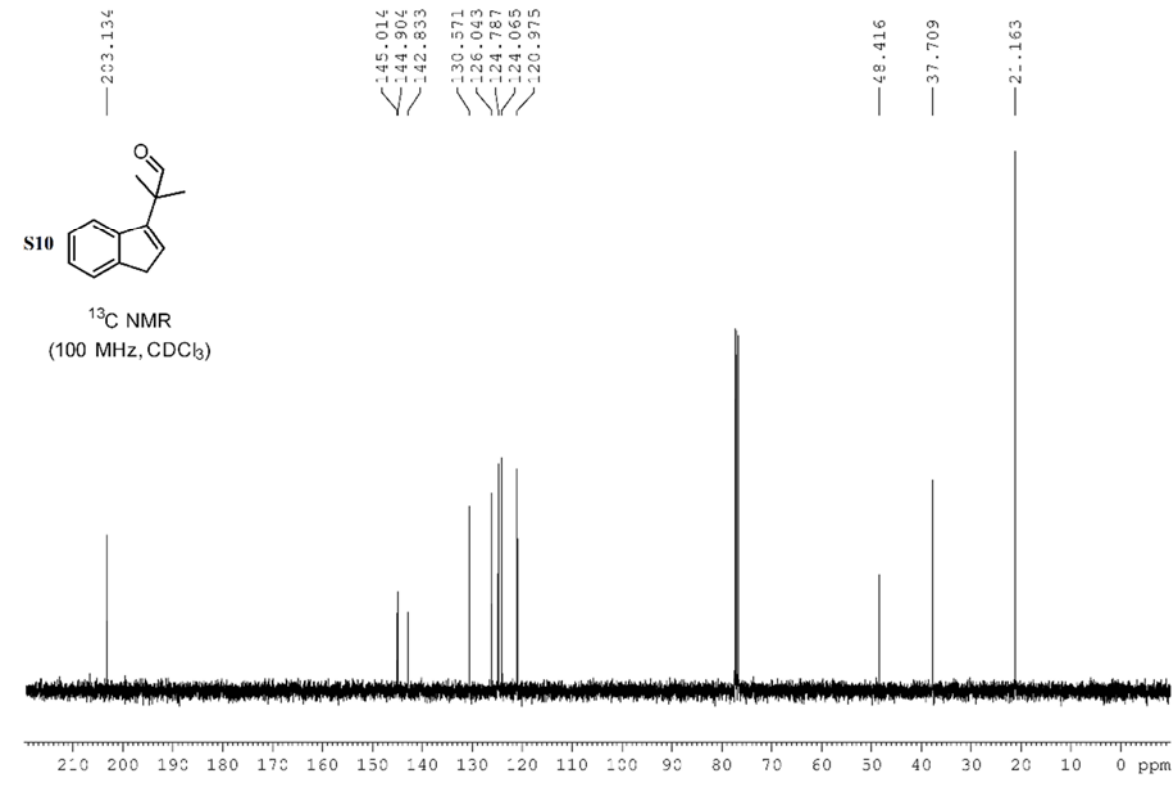
^{1}H NMR
(400 MHz, $CDCl_3$)

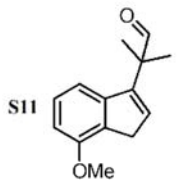
S9



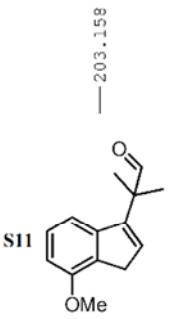
^{13}C NMR
(100 MHz, $CDCl_3$)


S10
^{1}H NMR
(400 MHz, CDCl$_3$)
9
8
7
6
5
4
3
2
1
0
ppm
0.920
3.997
1.018
2.221
1.000
2.048
6.288

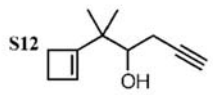

203.134
145.014
144.904
142.833
130.571
126.043
124.787
124.065
120.975
48.416
37.709
21.163
S10
^{13}C NMR
(100 MHz, CDCl$_3$)
220 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



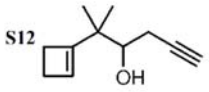
^{1}H NMR
(400 MHz, $CDCl_3$)



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

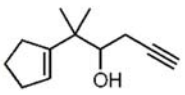


^{1}H NMR
(500 MHz, $CDCl_3$)



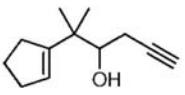
^{13}C NMR
(125 MHz, $CDCl_3$)

S13



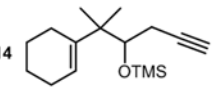
^{1}H NMR
(400 MHz, $CDCl_3$)

S13

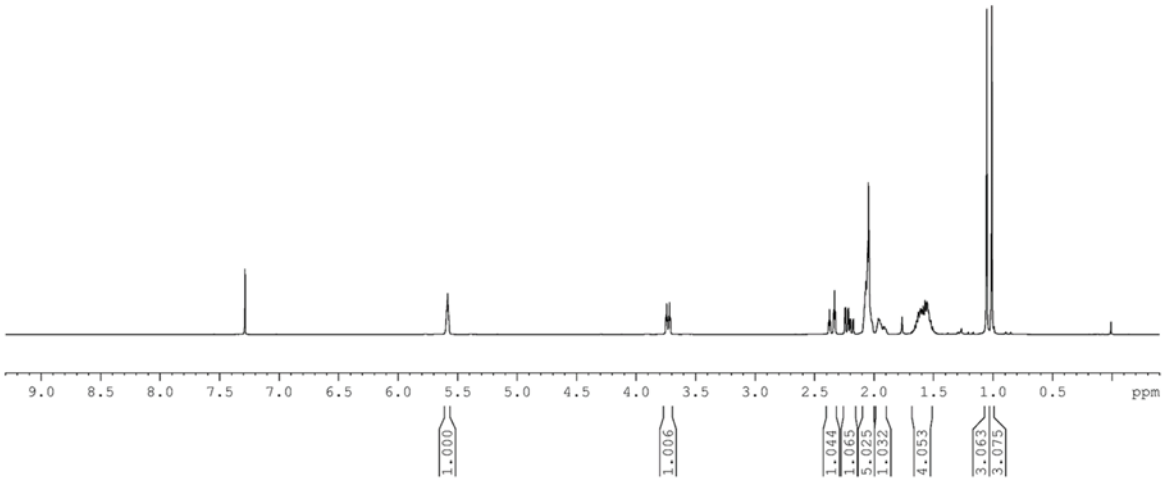


^{13}C NMR
(100 MHz, $CDCl_3$)

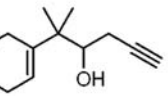
S14



^{1}H NMR
(400 MHz, $CDCl_3$)

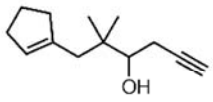


S14



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

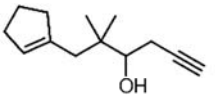
S15



^{1}H NMR

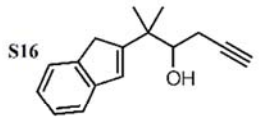
(500 MHz, $CDCl_3$)

S15

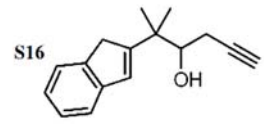


^{13}C NMR

(125 MHz, $CDCl_3$)

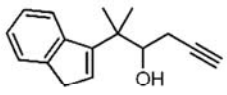


^{1}H NMR
(400 MHz, $CDCl_3$)



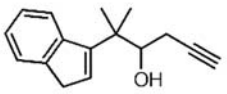
^{13}C NMR
(100 MHz, $CDCl_3$)

S17

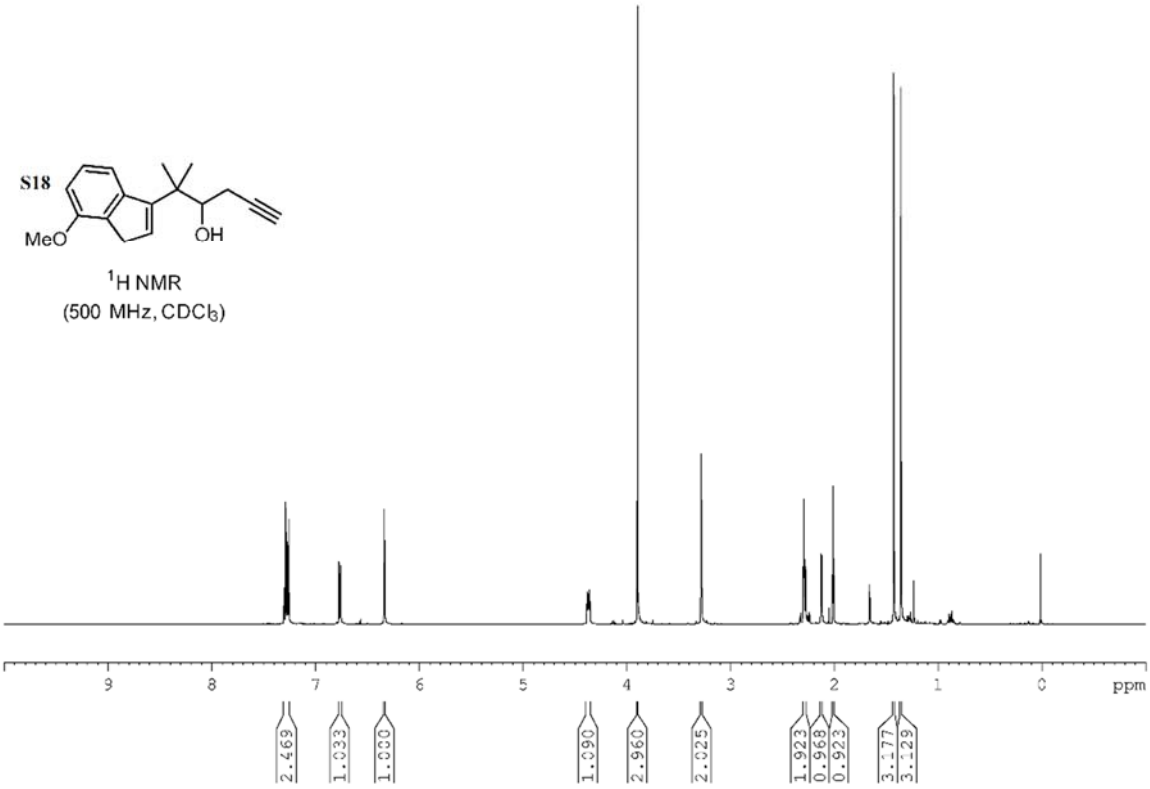


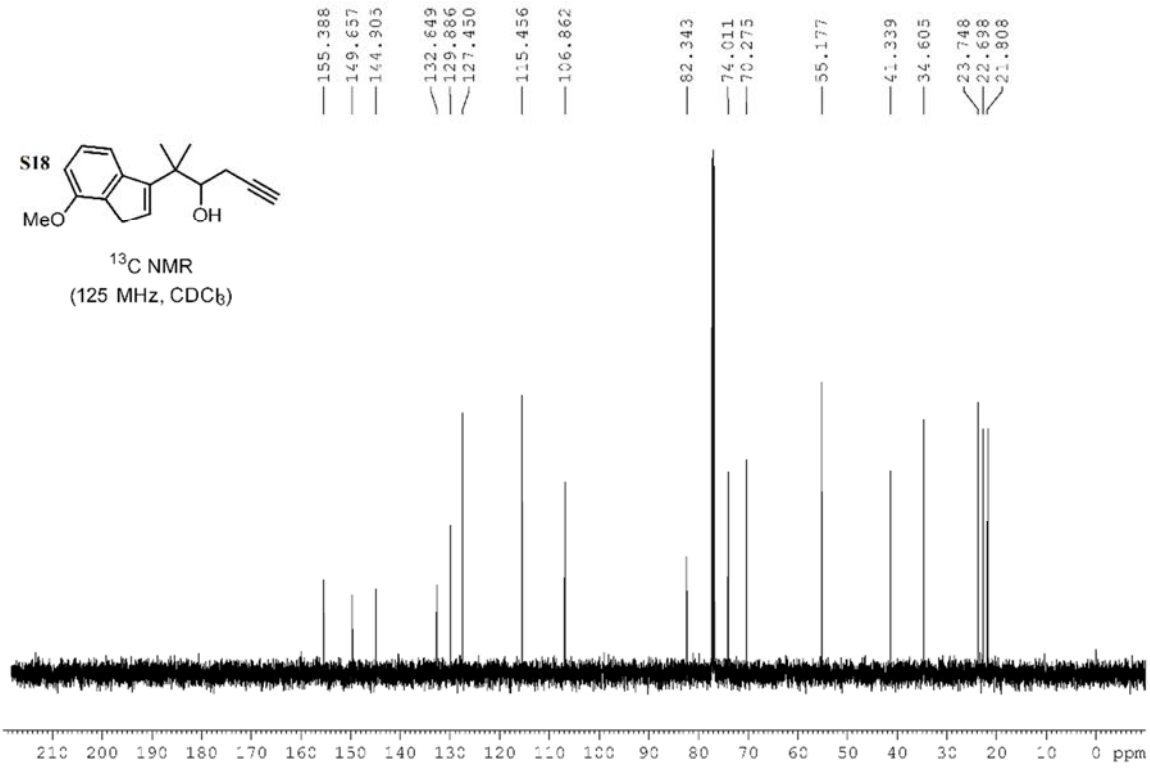
^{1}H NMR
(400 MHz, $CDCl_3$)

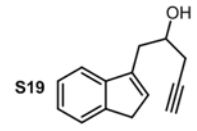
S17



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

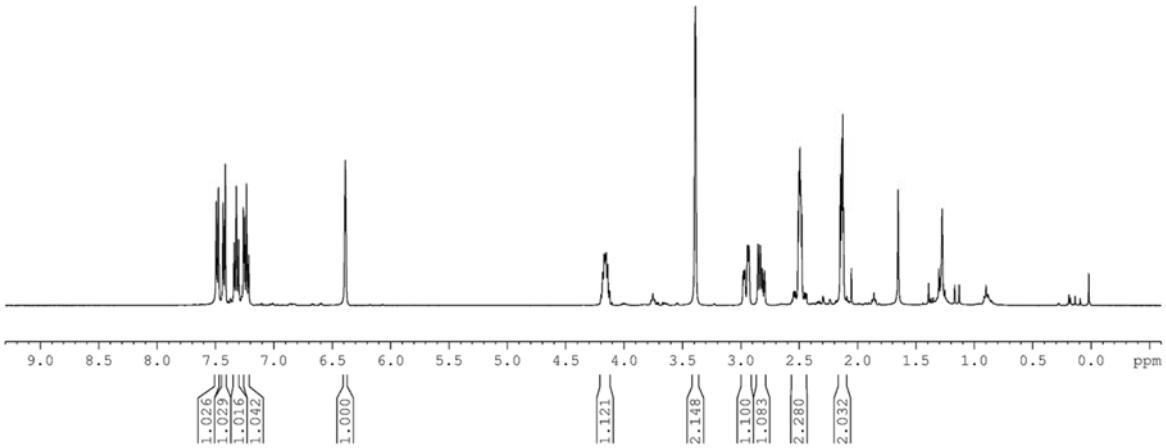

S18
MeO
OH
^{1}H NMR
(500 MHz, CDCl$_3$)
9
8
7
6
5
4
3
2
1
0
ppm
2.469
1.033
1.000
1.090
2.960
2.025
1.923
0.968
0.923
3.177
3.129

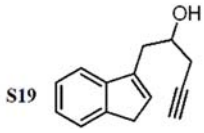

155.388
149.657
144.905
132.649
129.886
127.450
115.456
106.862
82.343
74.011
70.275
55.177
41.339
34.605
23.748
22.698
21.808
S18
MeO
OH
^{13}C NMR
(125 MHz, CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



S19

^{1}H NMR
(400 MHz, $CDCl_3$)

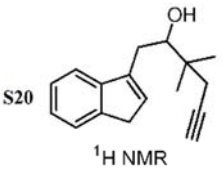




S19

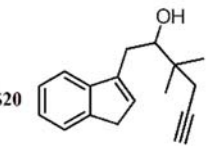
^{13}C NMR
(100 MHz, $CDCl_3$)

S20

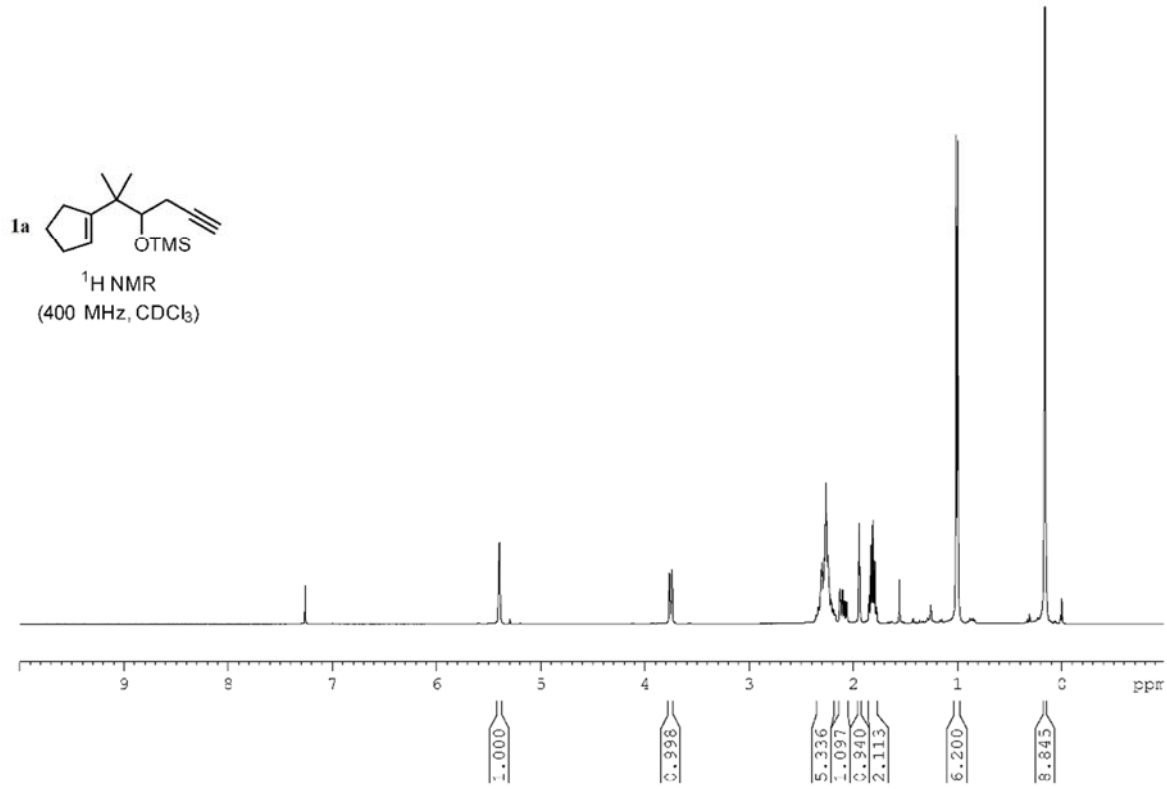


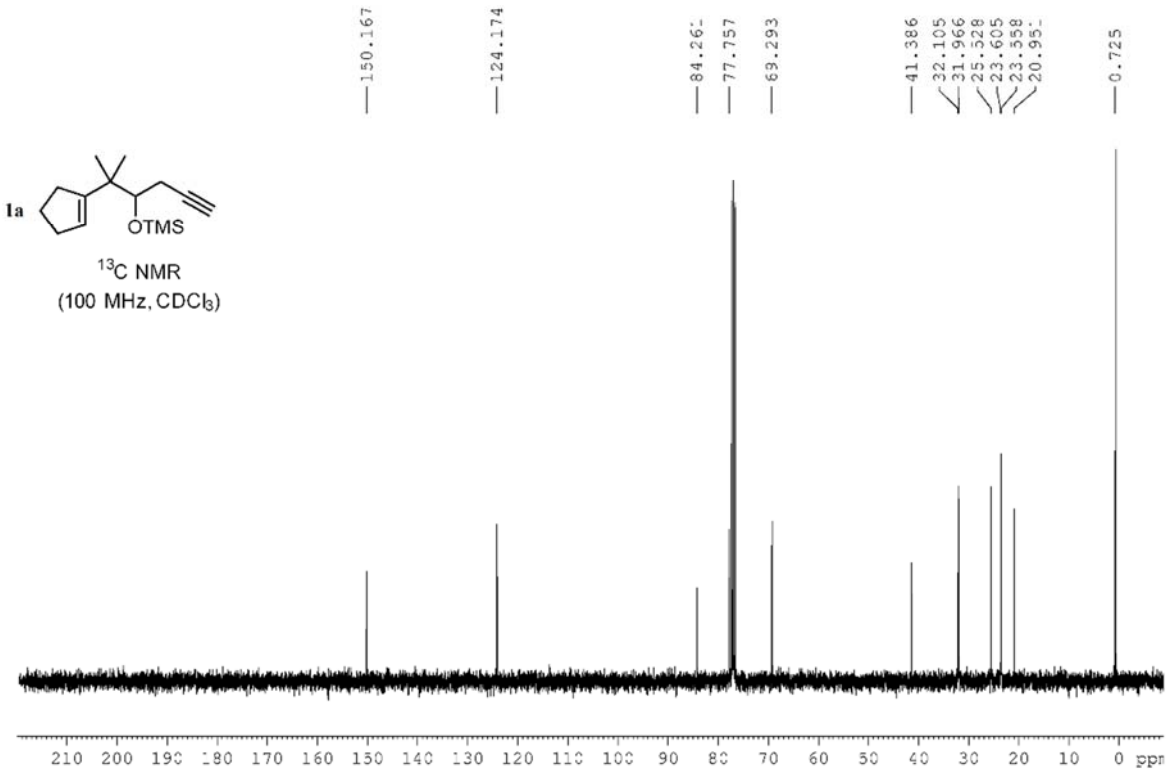
^{1}H NMR
(400 MHz, $CDCl_3$)

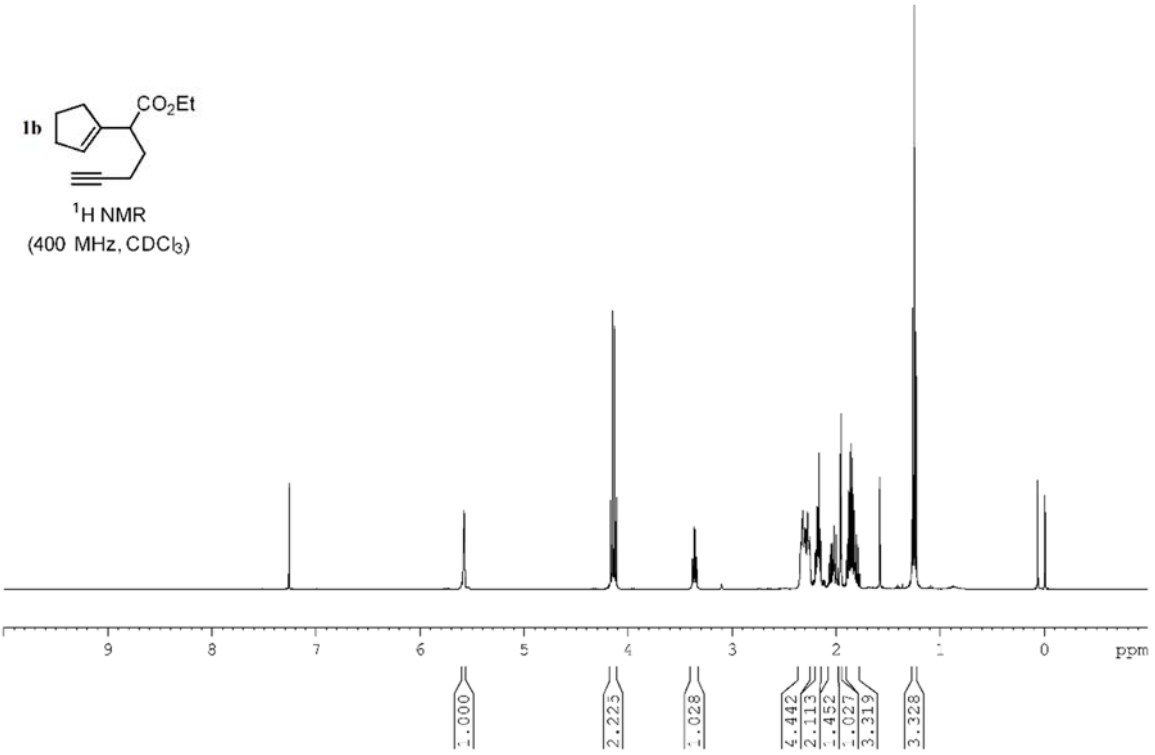
S20

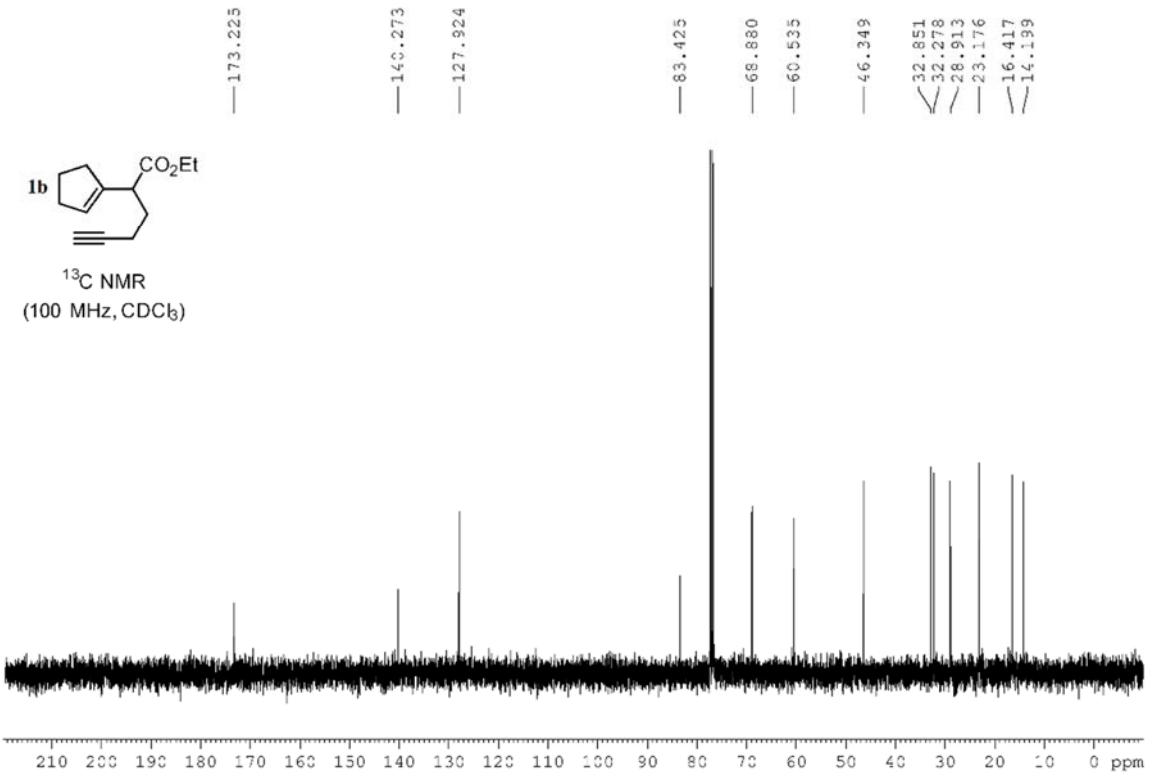


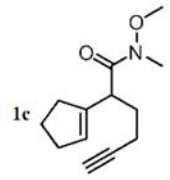
^{13}C NMR
(100 MHz, $CDCl_3$)


1a
OTMS
1H NMR
(400 MHz, CDCl3)
9
8
7
6
5
4
3
2
1
0
ppm
2.000
0.998
5.336
2.097
2.340
2.113
6.200
8.845


150.167
124.174
84.26
77.757
69.293
41.386
32.105
31.966
25.328
23.605
23.358
20.95
0.725
1a
OTMS
13C NMR
(100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

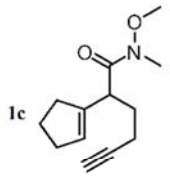

1b
CO2Et
1H NMR
(400 MHz, CDCl3)
9
8
7
6
5
4
3
2
1
0
ppm
1.000
2.225
1.028
4.442
2.113
2.452
1.027
3.319
3.328


173.225
140.273
127.924
83.425
68.880
60.535
46.349
32.851
32.278
28.913
23.176
16.417
14.199
1b
CO2Et
13C NMR
(100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm



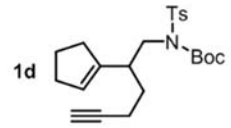
1c

^{1}H NMR
(500 MHz, $CDCl_3$)



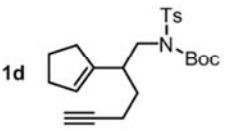
1c

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



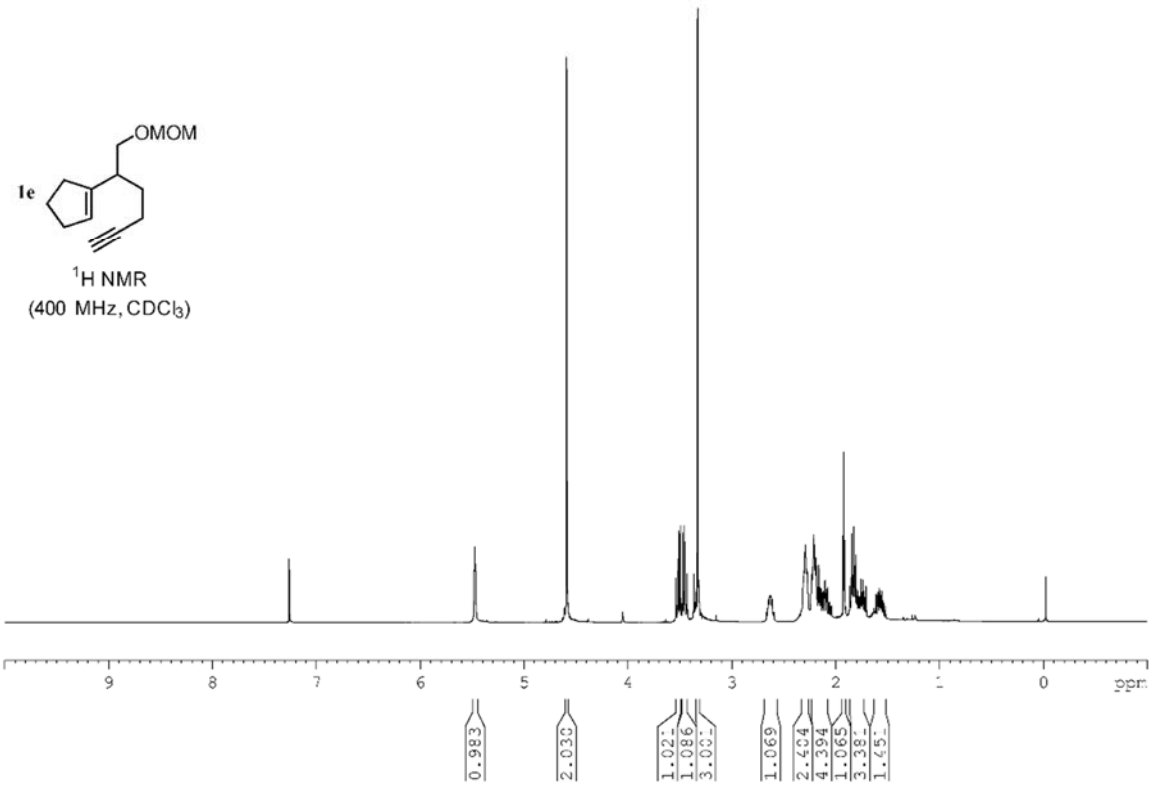
1d

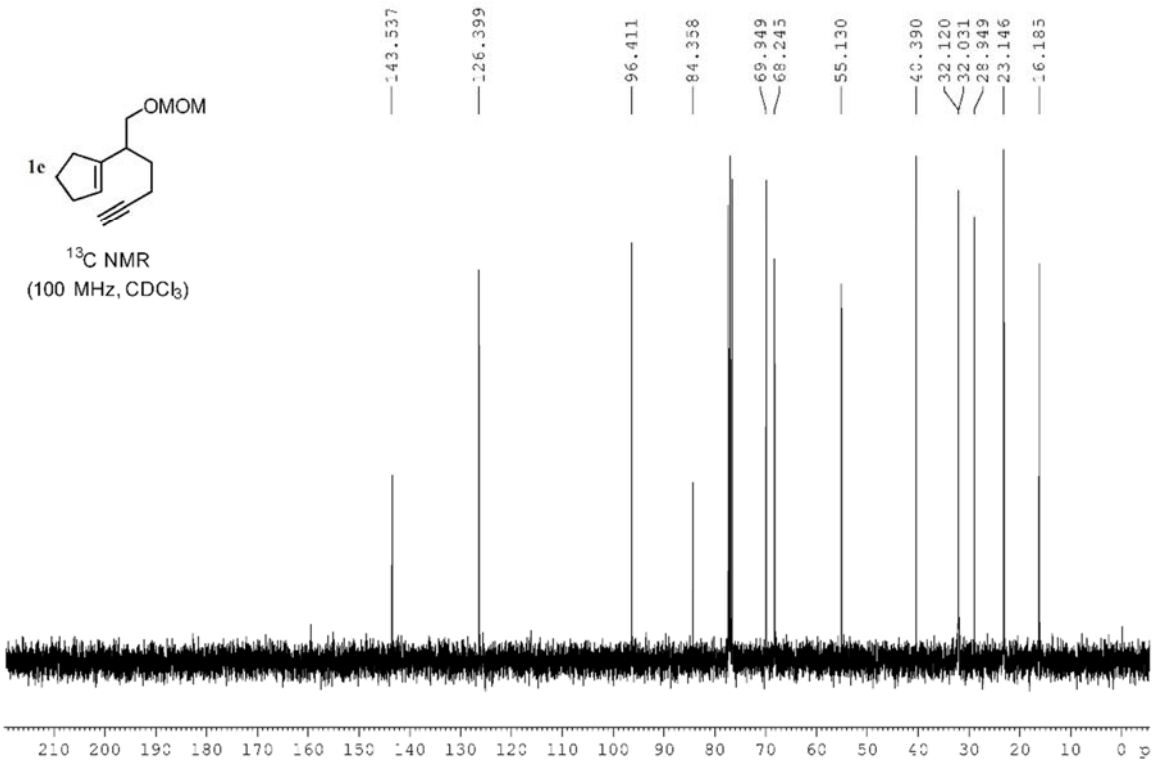
^{1}H NMR
(500 MHz, $CDCl_3$)

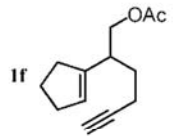


1d

^{1}H NMR
(500 MHz, $CDCl_3$)

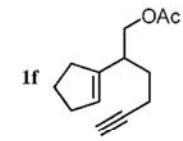

OMOM
1e
^{1}H NMR
(400 MHz, CDCl$_3$)
9
8
7
6
5
4
3
2
0
ppm
0.983
2.030
1.069
2.404
4.394
1.065


OMOM
1e
^{13}C NMR
(100 MHz, CDCl$_3$)
143.537
126.399
96.411
84.356
69.949
68.245
55.130
40.390
32.120
32.031
28.949
23.146
16.185
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



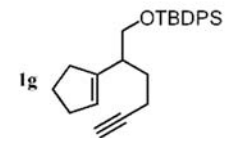
1f

^{1}H NMR
(400 MHz, $CDCl_3$)

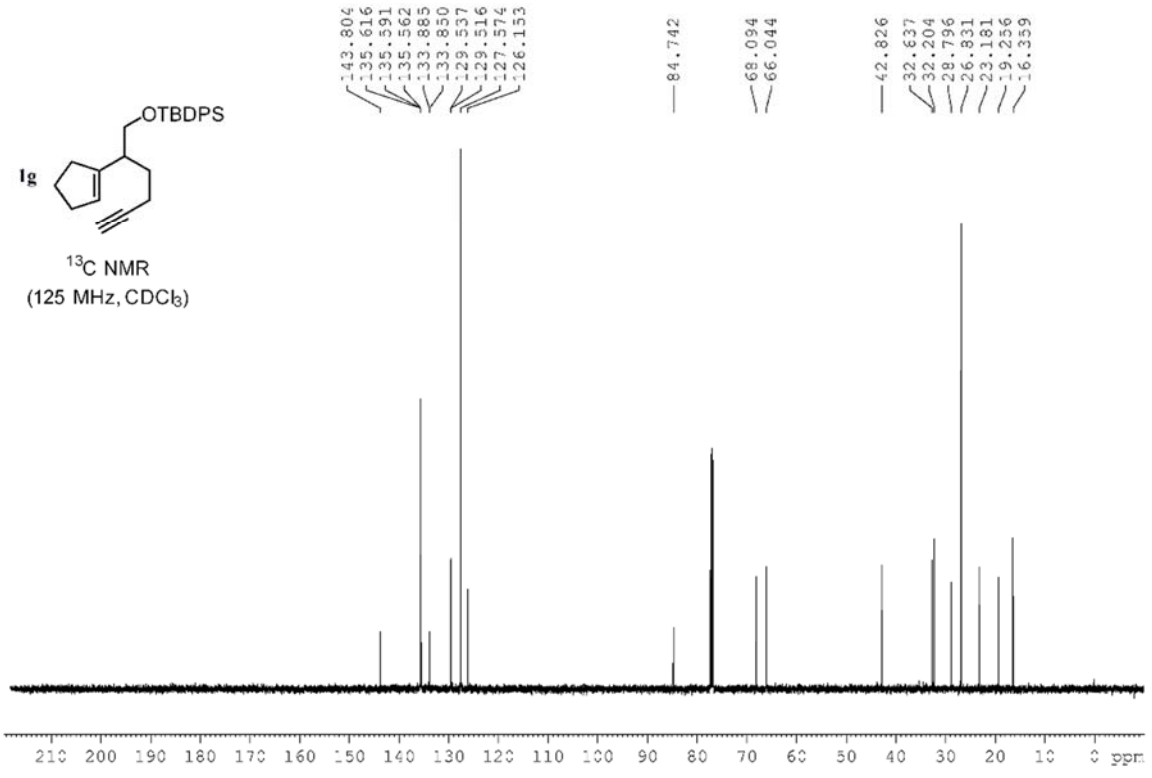


1f

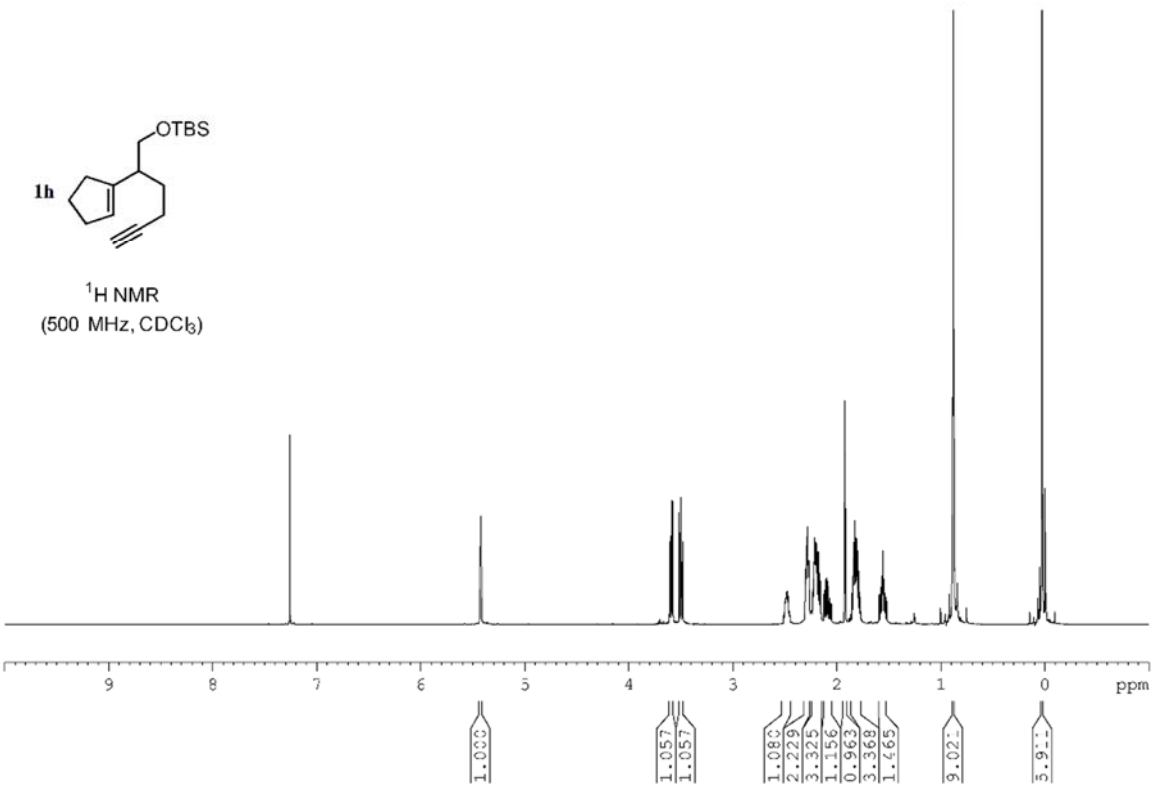
^{13}C NMR
(100 MHz, $CDCl_3$)

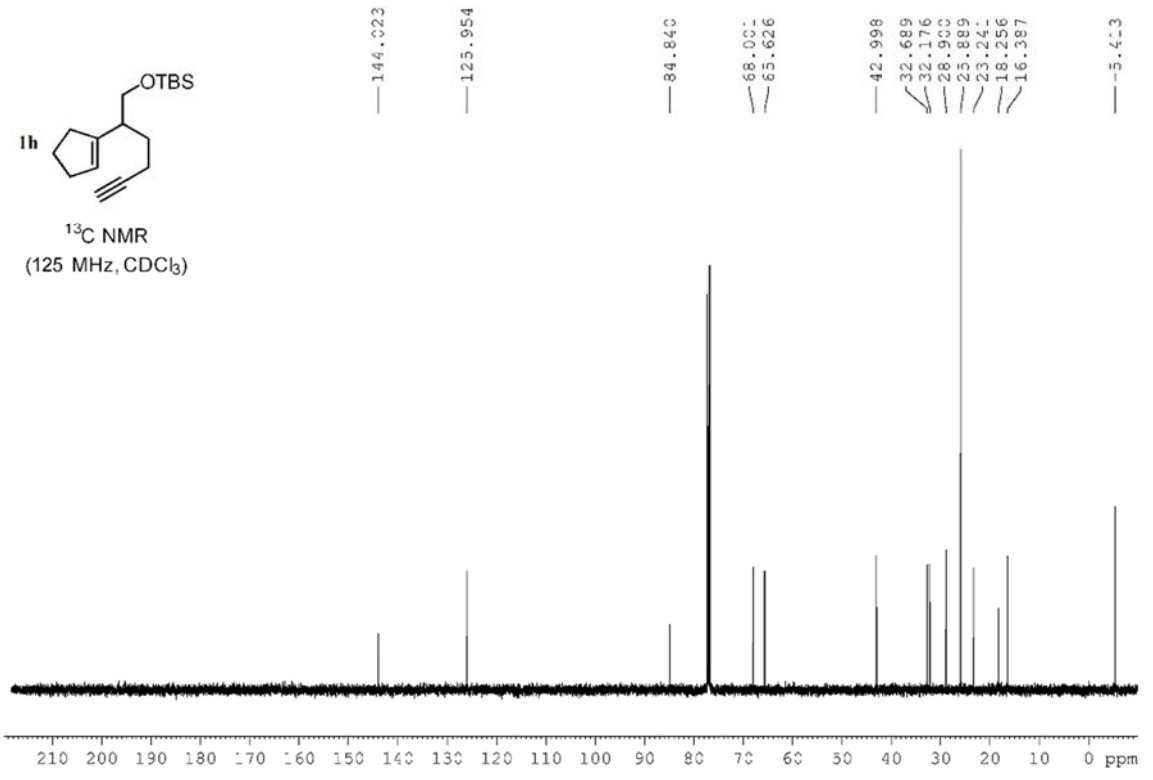


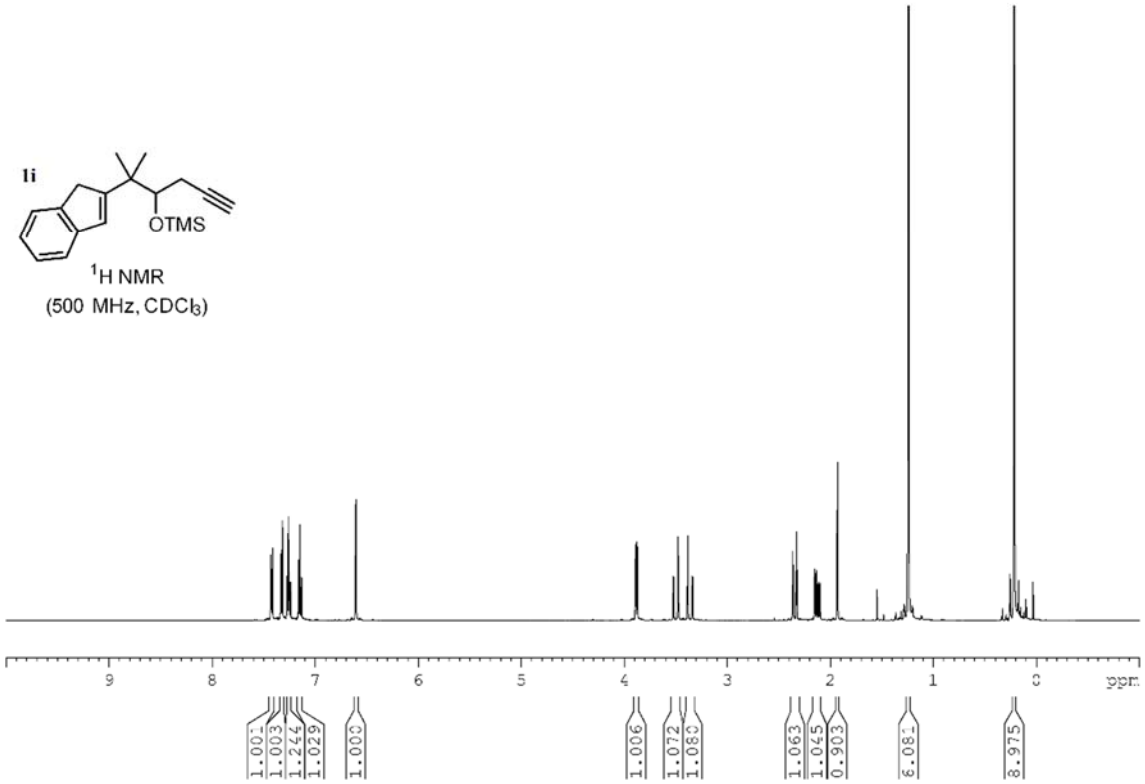
^{1}H NMR
(500 MHz, $CDCl_3$)

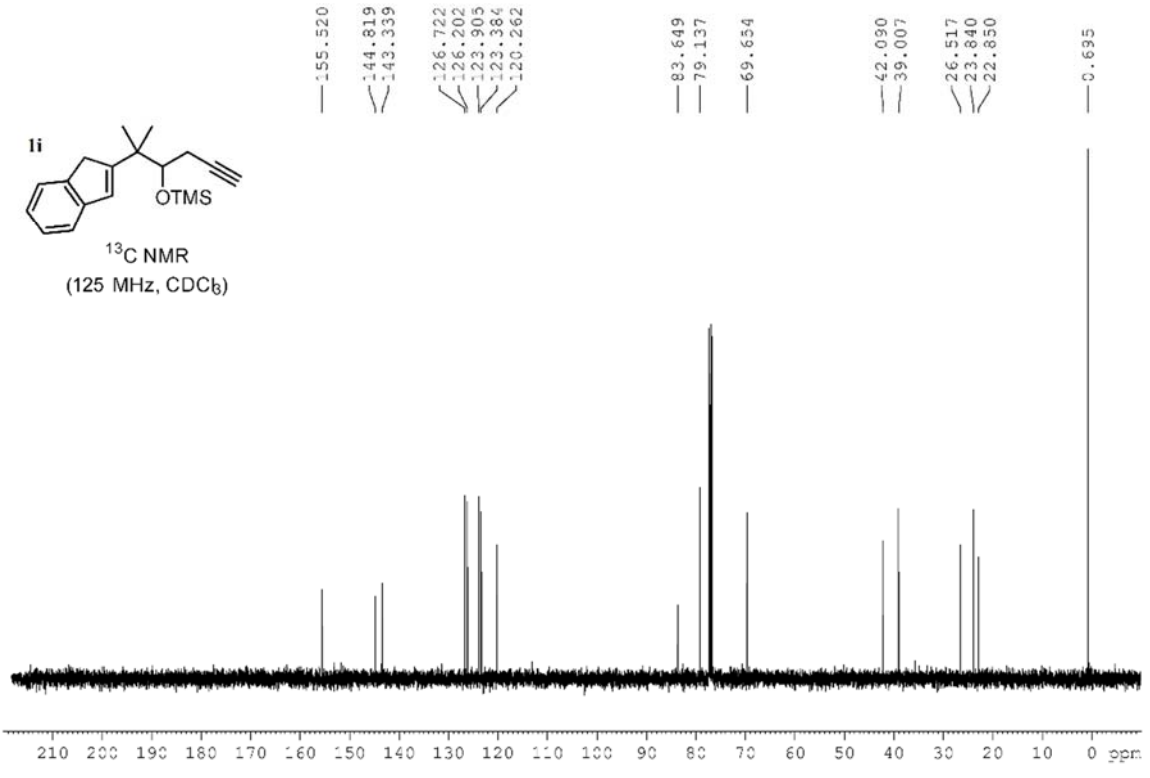


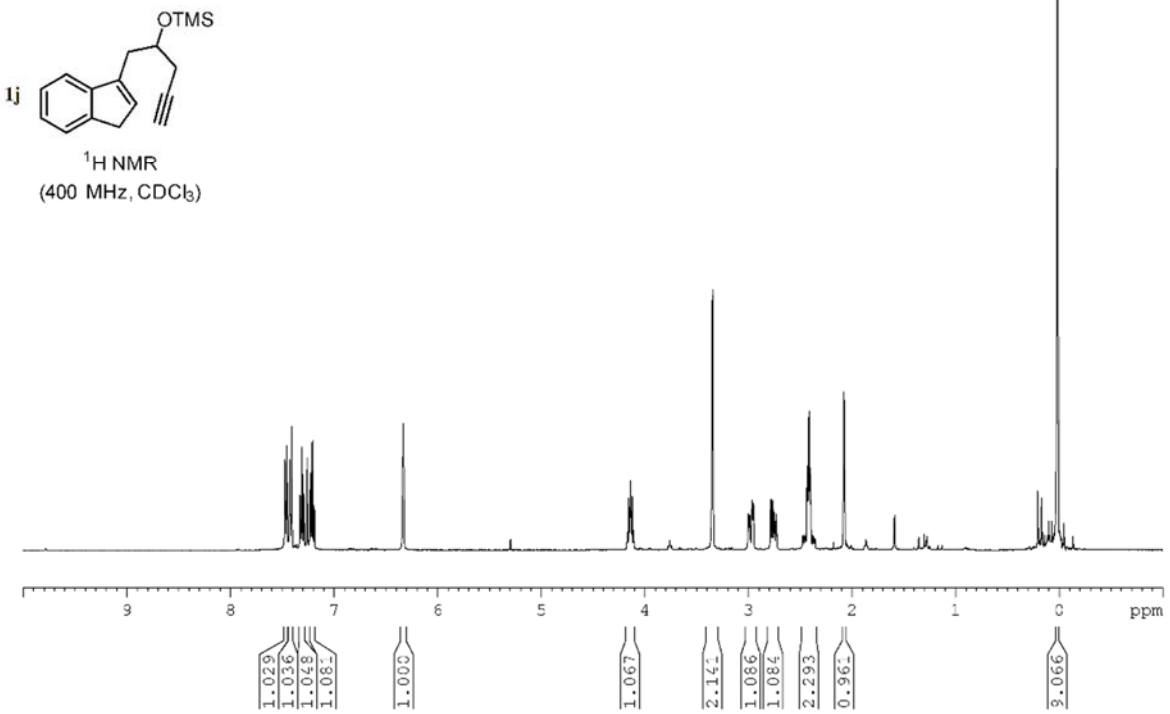
^{13}C NMR
(125 MHz, $CDCl_3$)

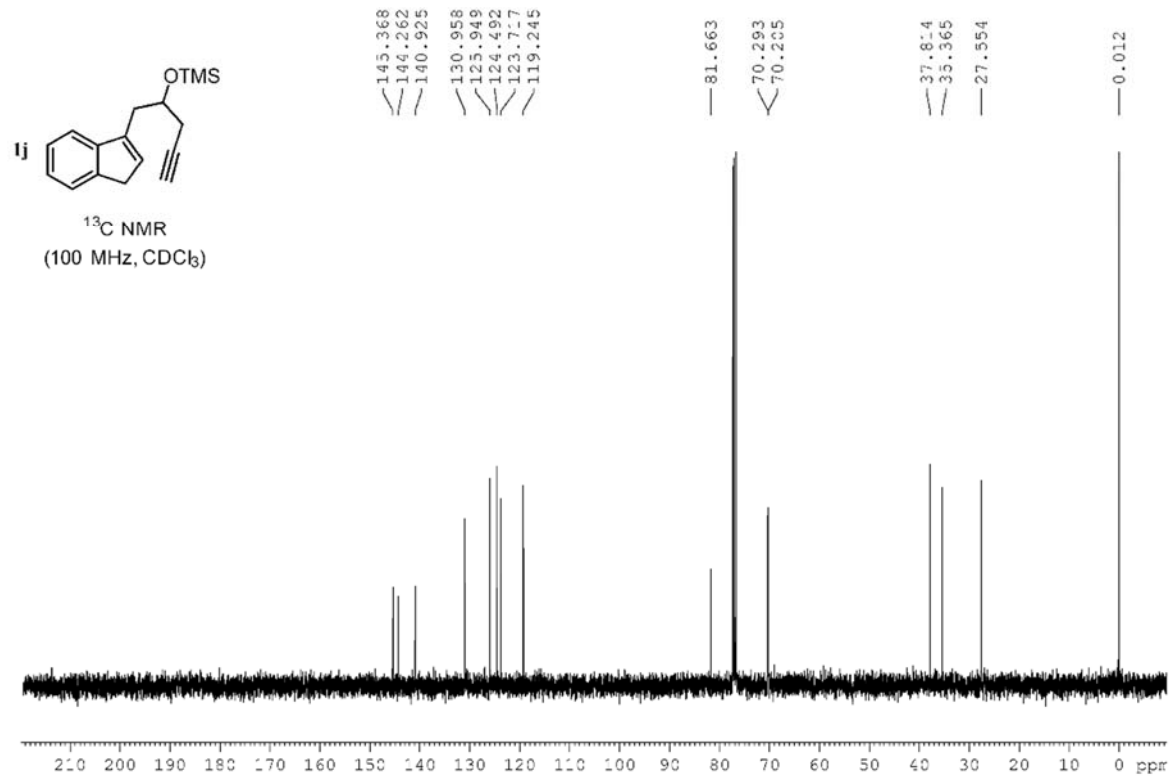

OTBS
1h
^{1}H NMR
(500 MHz, CDCl$_3$)
9
8
7
6
5
4
3
2
1
0
ppm
1.000
1.057
1.057
1.080
2.229
3.325
1.156
0.963
3.368
1.465
9.021
3.911


OTBS
1h
^{13}C NMR
(125 MHz, CDCl$_3$)
144.023
125.954
84.840
68.001
65.626
42.998
32.689
32.176
28.900
25.889
23.241
18.256
16.387
-5.413
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

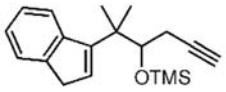

1i
OTMS
^{1}H NMR
(500 MHz, CDCl$_3$)
1.001
1.003
1.244
1.029
1.000
1.006
1.072
1.080
1.063
1.045
0.903
6.082
8.975
ppm


1i
OTMS
^{13}C NMR
(125 MHz, CDCl$_3$)
155.520
144.819
143.339
126.722
126.202
123.905
123.384
120.262
83.649
79.137
69.654
42.090
39.007
26.517
23.840
22.850
0.695
ppm


OTMS
1j
^{1}H NMR
(400 MHz, CDCl$_3$)
9
8
7
6
5
4
3
2
1
0
ppm
1.029
1.036
1.049
1.081
1.000
1.067
2.142
1.086
1.084
2.293
0.962
3.066

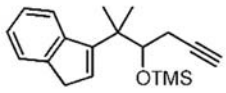

OTMS
1j
^{13}C NMR
(100 MHz, CDCl$_3$)
143.368
144.262
140.925
130.958
125.949
124.492
123.717
119.245
81.663
70.293
70.205
37.814
35.365
27.554
0.012
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

1k

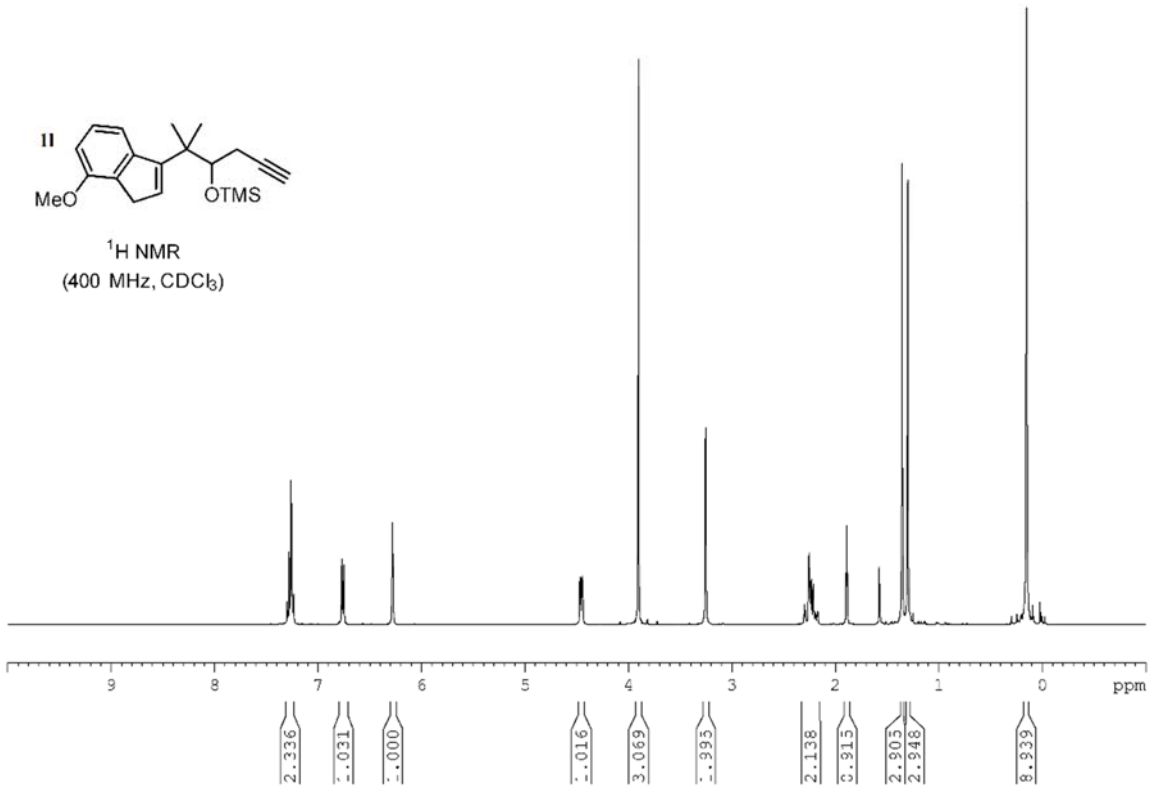


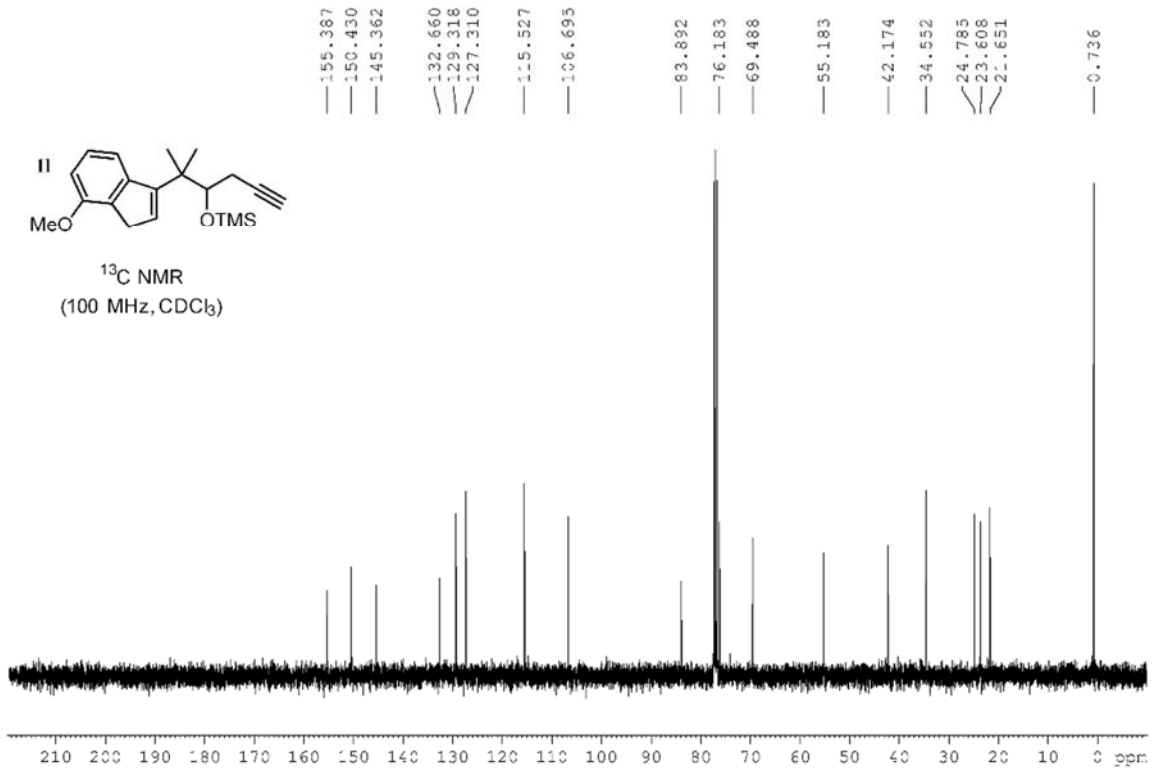
^{1}H NMR
(500 MHz, $CDCl_3$)

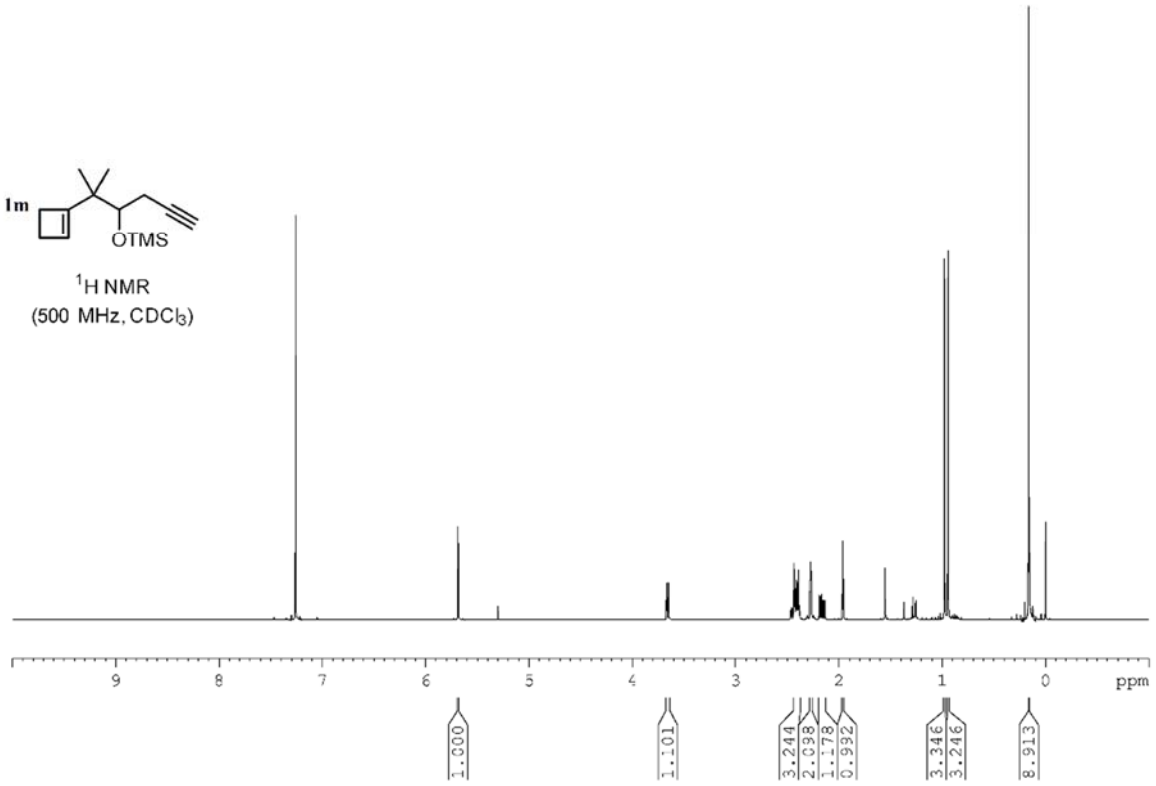
1k

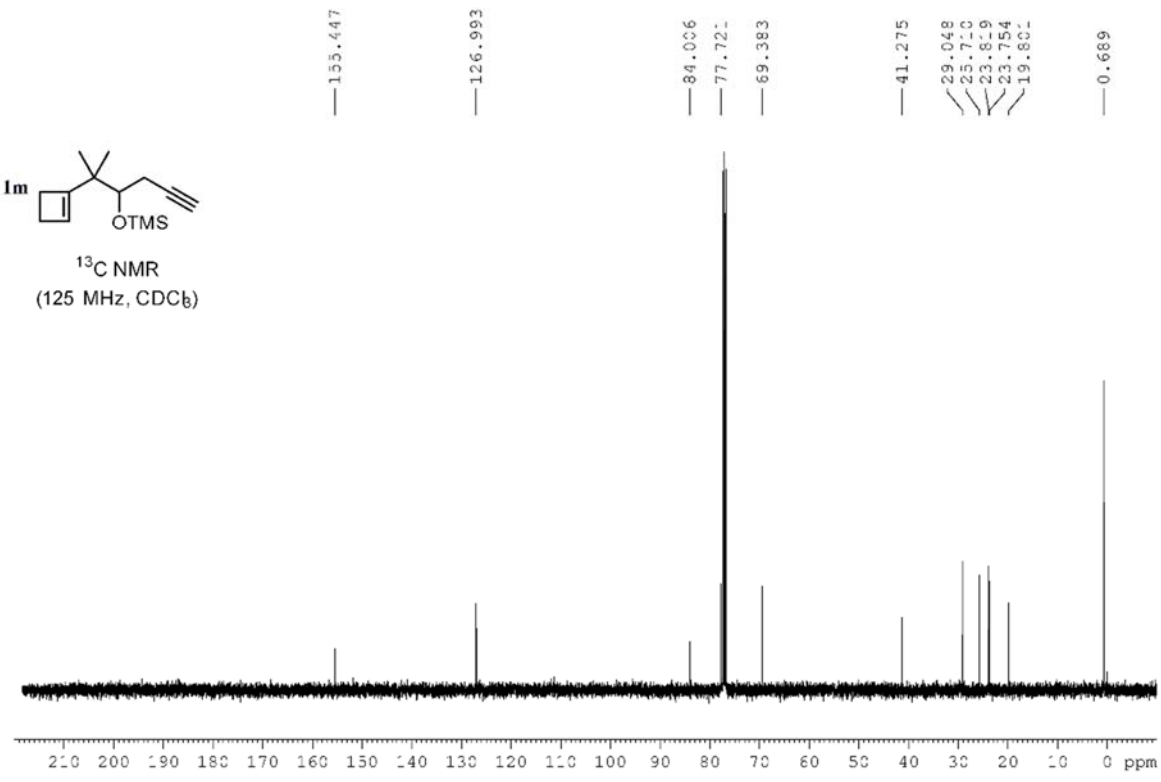


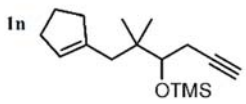
^{13}C NMR
(125 MHz, $CDCl_3$)


II
MeO
OTMS
^{1}H NMR
(400 MHz, CDCl$_3$)
9
8
7
6
5
4
3
2
1
0
ppm
2.336
2.031
1.000
2.016
3.069
1.993
2.138
3.915
2.903
2.948
8.939

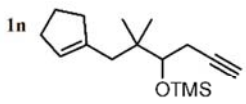

155.387
150.430
145.362
132.660
129.318
127.310
115.527
106.695
83.892
76.183
69.488
55.183
42.174
34.552
24.785
23.608
21.651
0.736
II
MeO
OTMS
^{13}C NMR
(100 MHz, CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


1m
OTMS
^{1}H NMR
(500 MHz, CDCl$_3$)
9
8
7
6
5
4
3
2
1
0
ppm
1.000
1.101
3.244
2.038
1.178
0.932
3.346
3.246
8.913

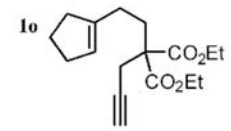

155.447
126.993
84.006
77.721
69.383
41.275
29.048
25.710
23.819
23.754
19.801
0.689
1m
OTMS
^{13}C NMR
(125 MHz, CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



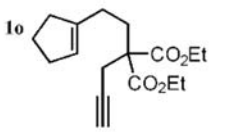
^{1}H NMR
(500 MHz, $CDCl_3$)



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

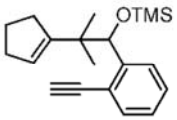


^{1}H NMR
(400 MHz, $CDCl_3$)



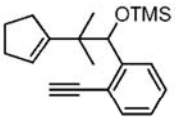
^{13}C NMR
(100 MHz, $CDCl_3$)

1p

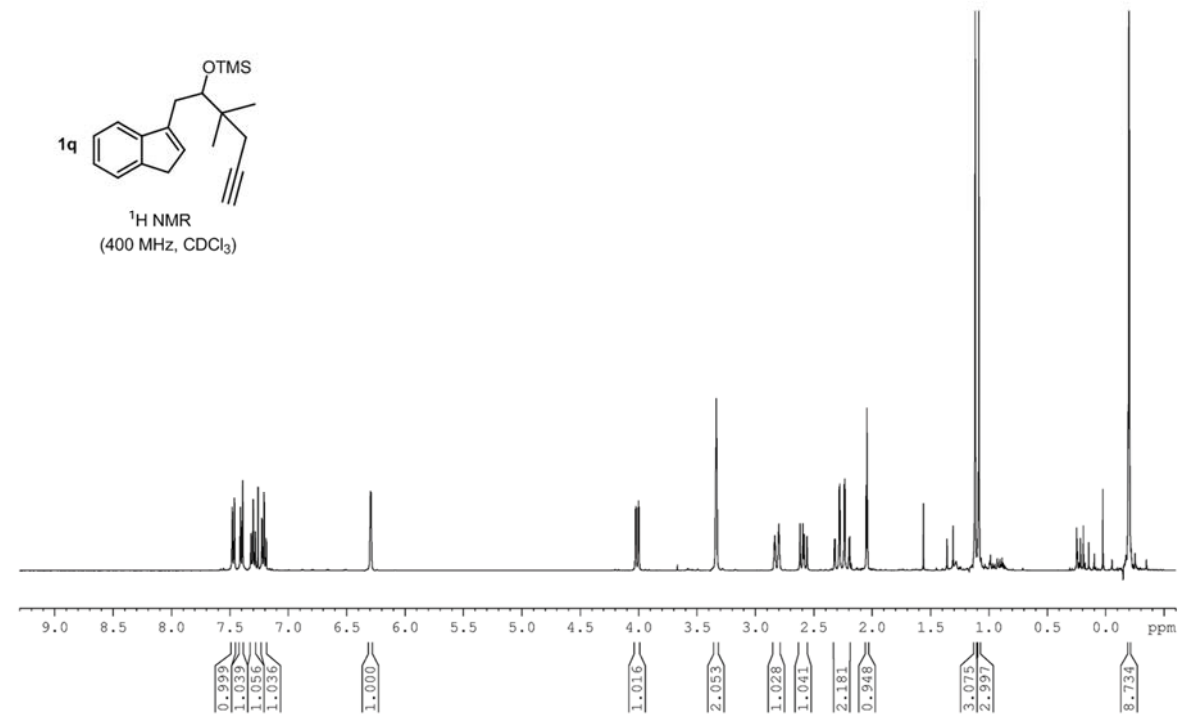


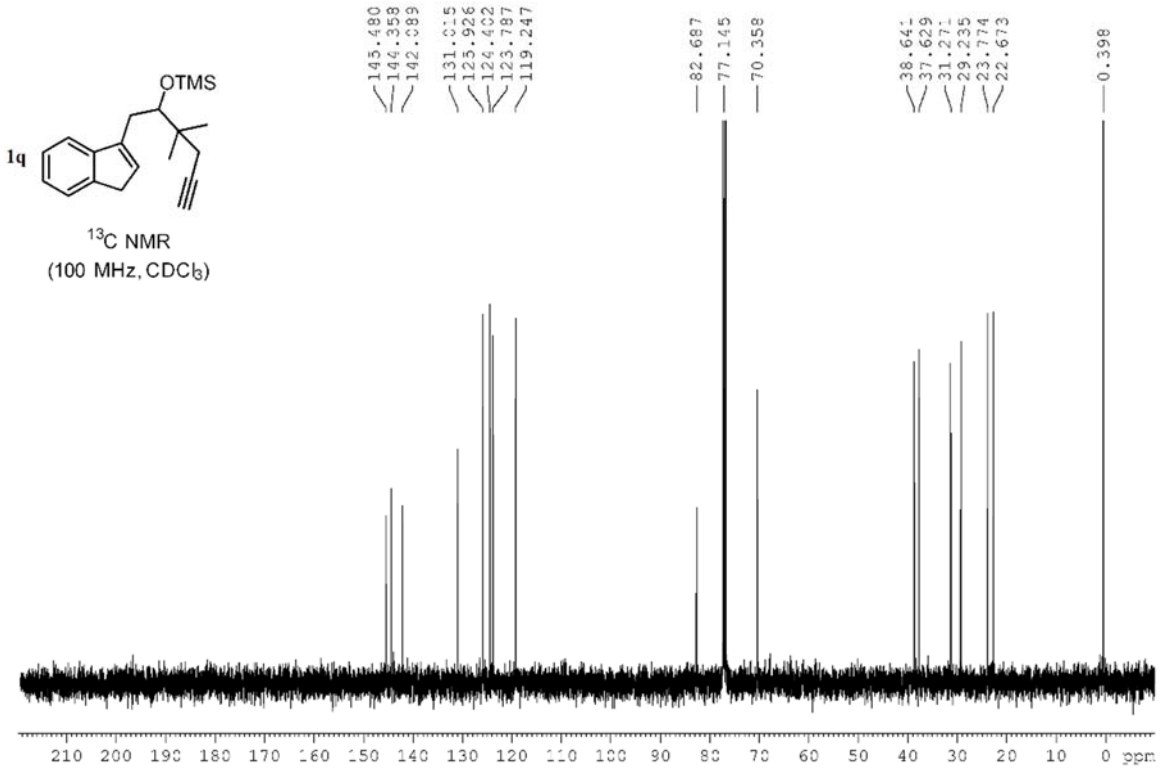
^{1}H NMR
(500 MHz, $CDCl_3$)

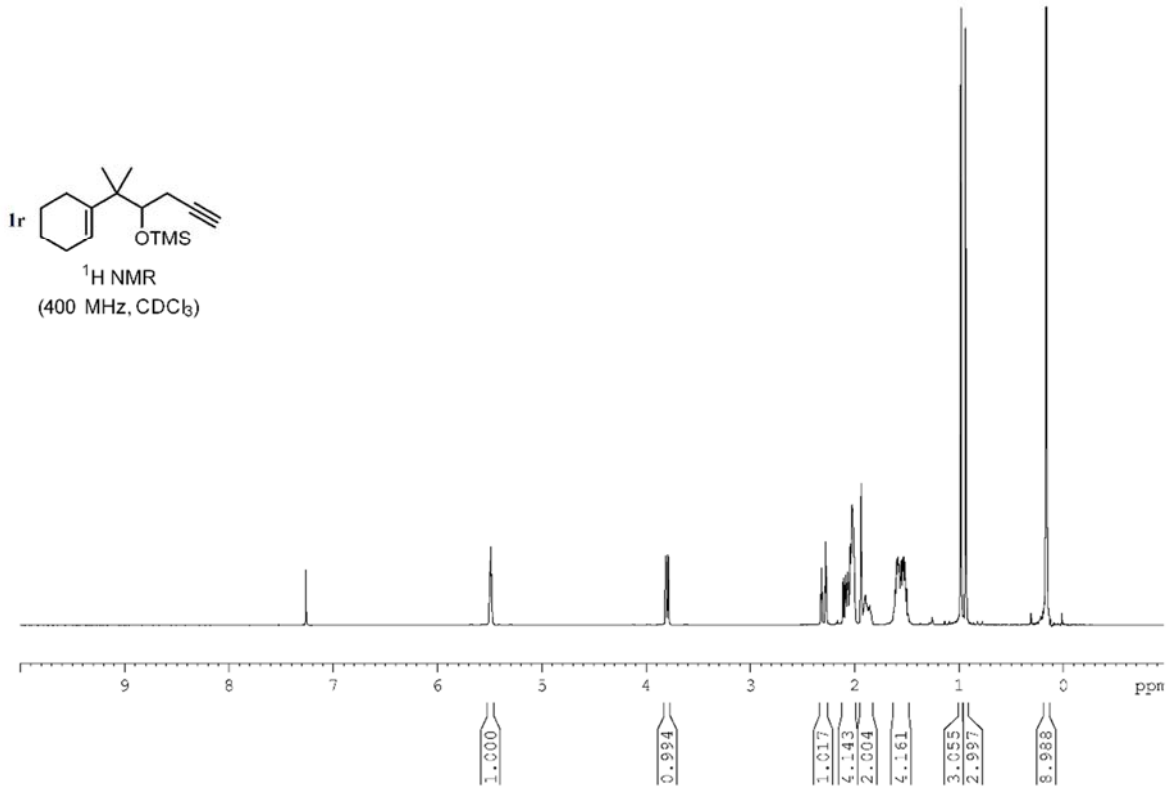
1p

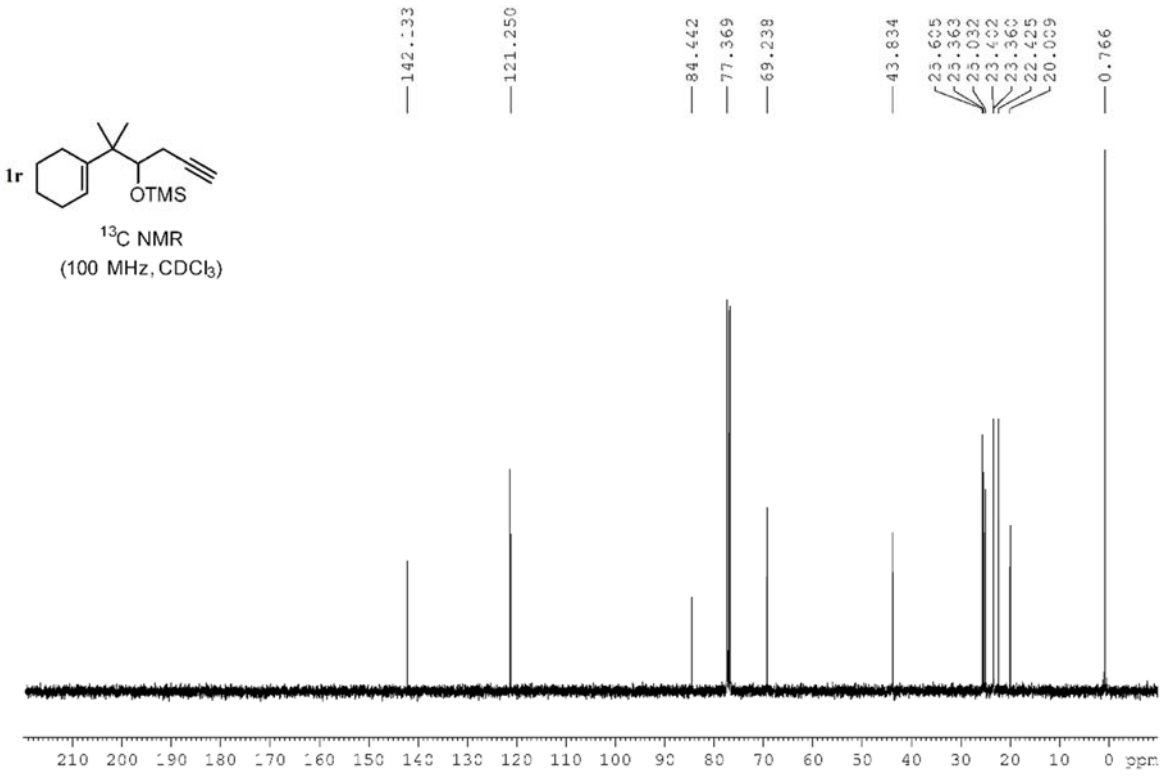


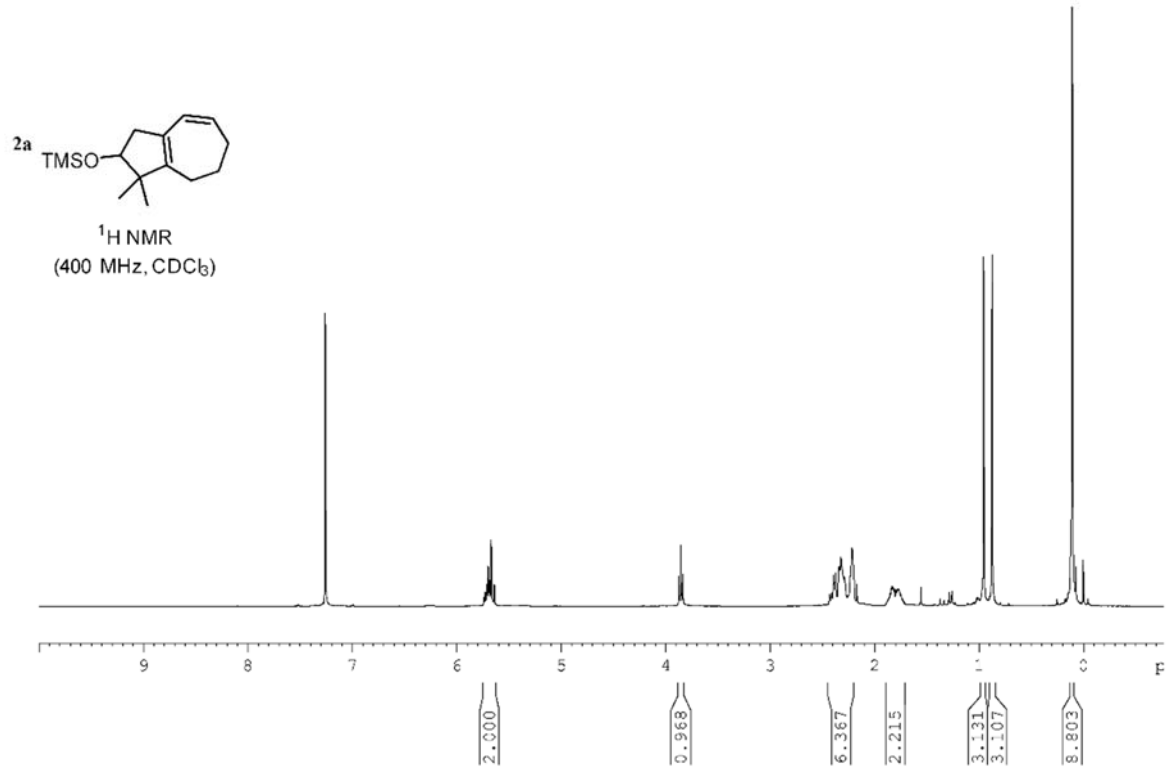
^{13}C NMR
(125 MHz, $CDCl_3$)

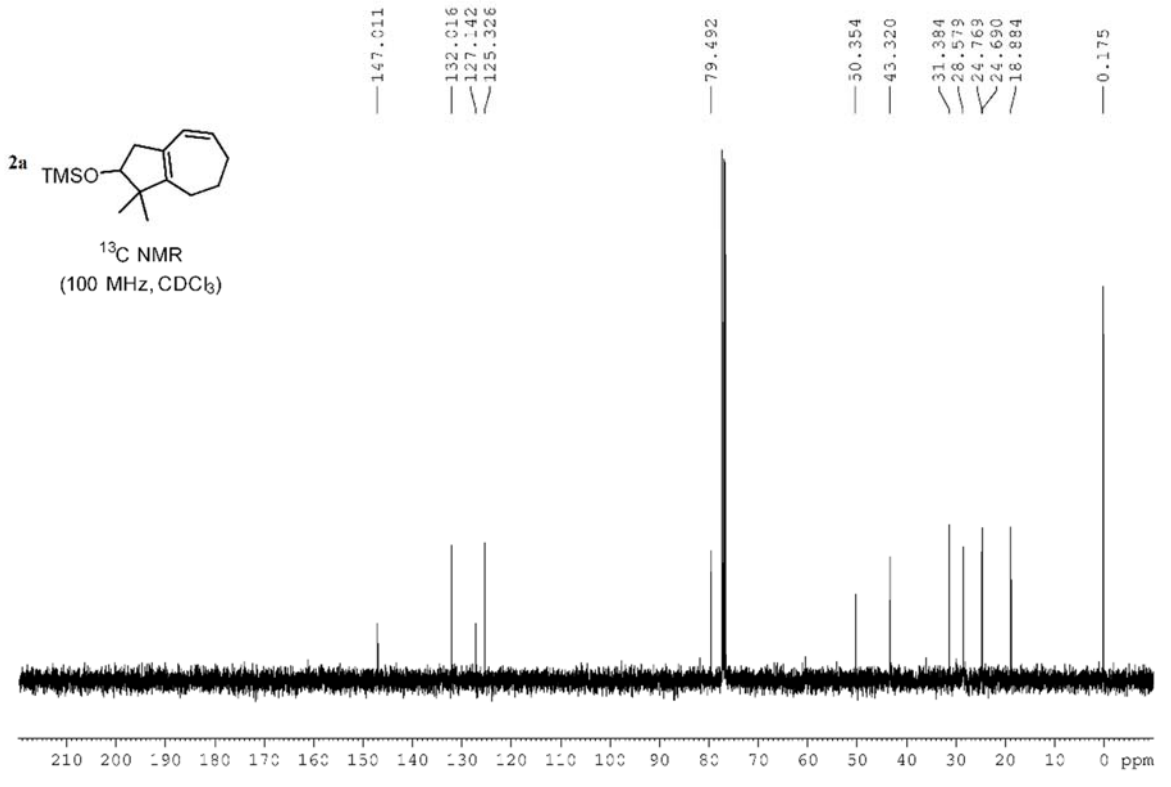

OTMS
1q
^{1}H NMR
(400 MHz, CDCl$_3$)
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.999
1.039
1.056
1.036
1.000
1.016
2.053
1.028
1.041
2.181
0.948
3.075
2.997
8.734

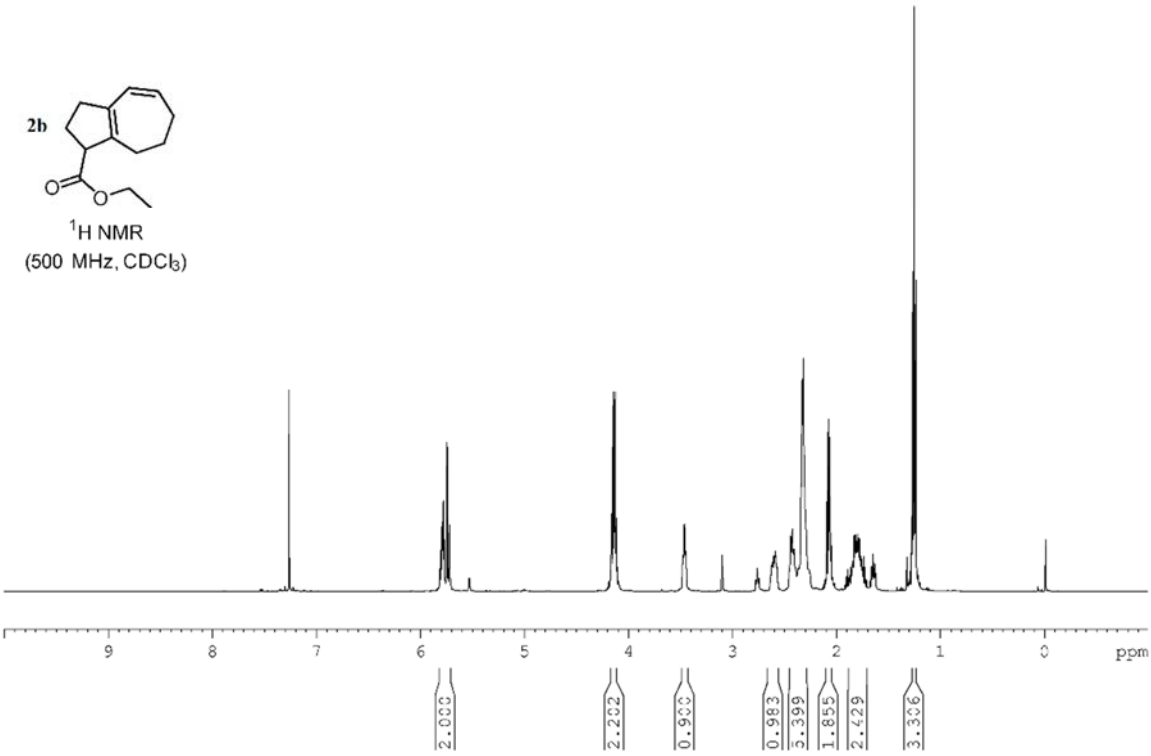

OTMS
1q
^{13}C NMR
(100 MHz, CDCl$_3$)
145.480
144.358
142.089
131.825
125.926
124.402
123.787
119.247
82.687
77.145
70.358
38.641
37.629
31.271
29.235
23.774
22.673
0.398
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

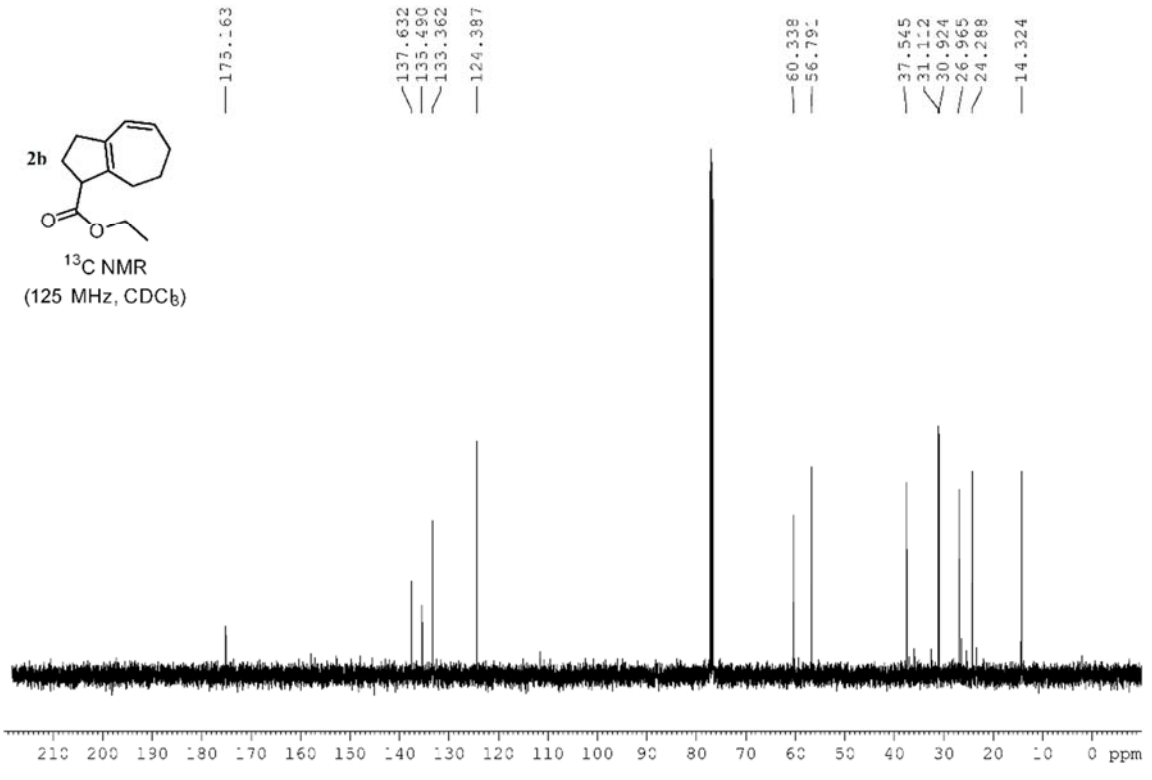

1r
OTMS
^{1}H NMR
(400 MHz, CDCl$_3$)
9
8
7
6
5
4
3
2
1
0
ppm
1.000
0.994
1.017
4.143
2.004
4.161
3.055
2.997
8.988

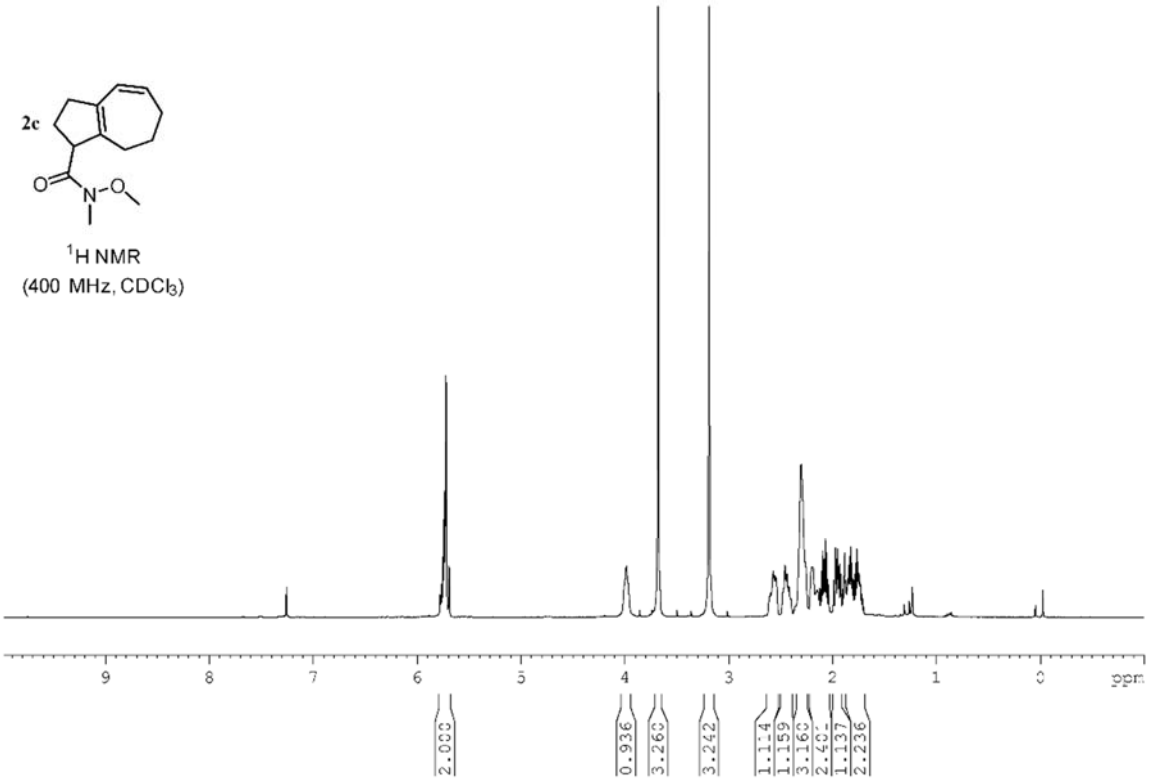

142.133
121.250
84.442
77.369
69.238
43.834
25.605
25.363
25.032
23.432
23.360
22.425
20.009
0.766
1r
OTMS
^{13}C NMR
(100 MHz, CDCl$_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

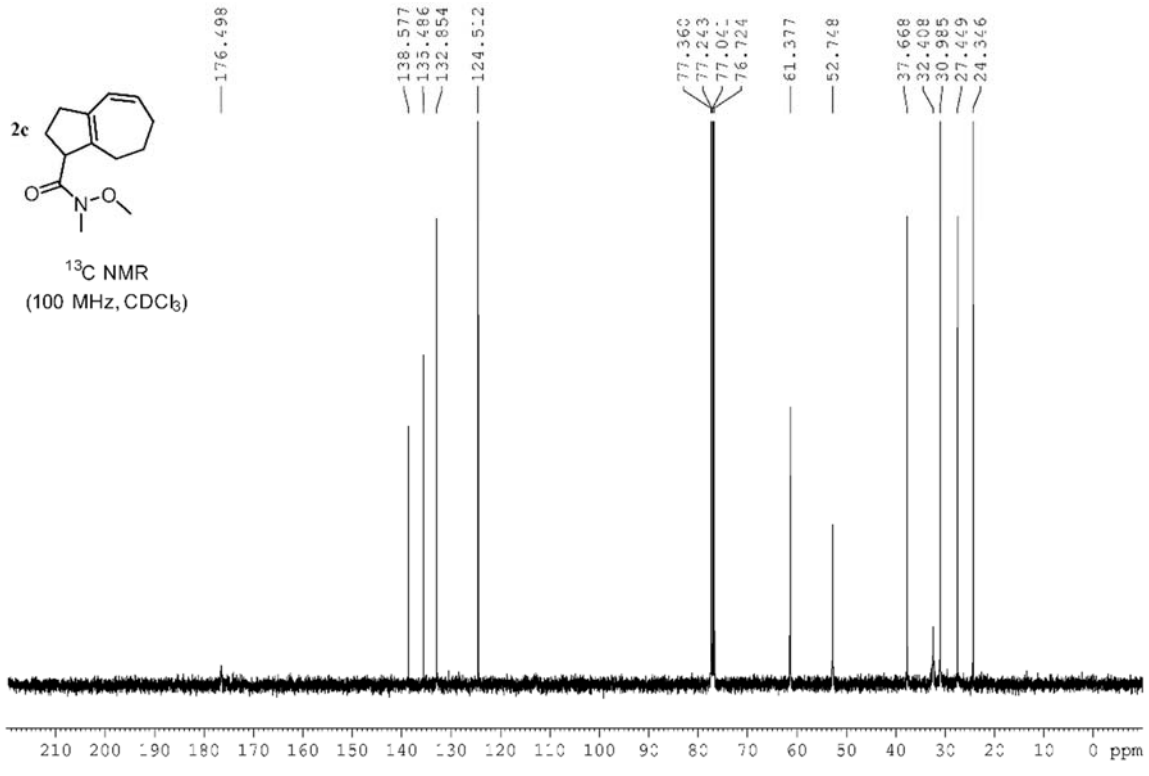

2a
TMSO
^{1}H NMR
(400 MHz, $CDCl_3$)
2.000
0.968
6.367
2.215
3.131
3.107
8.803

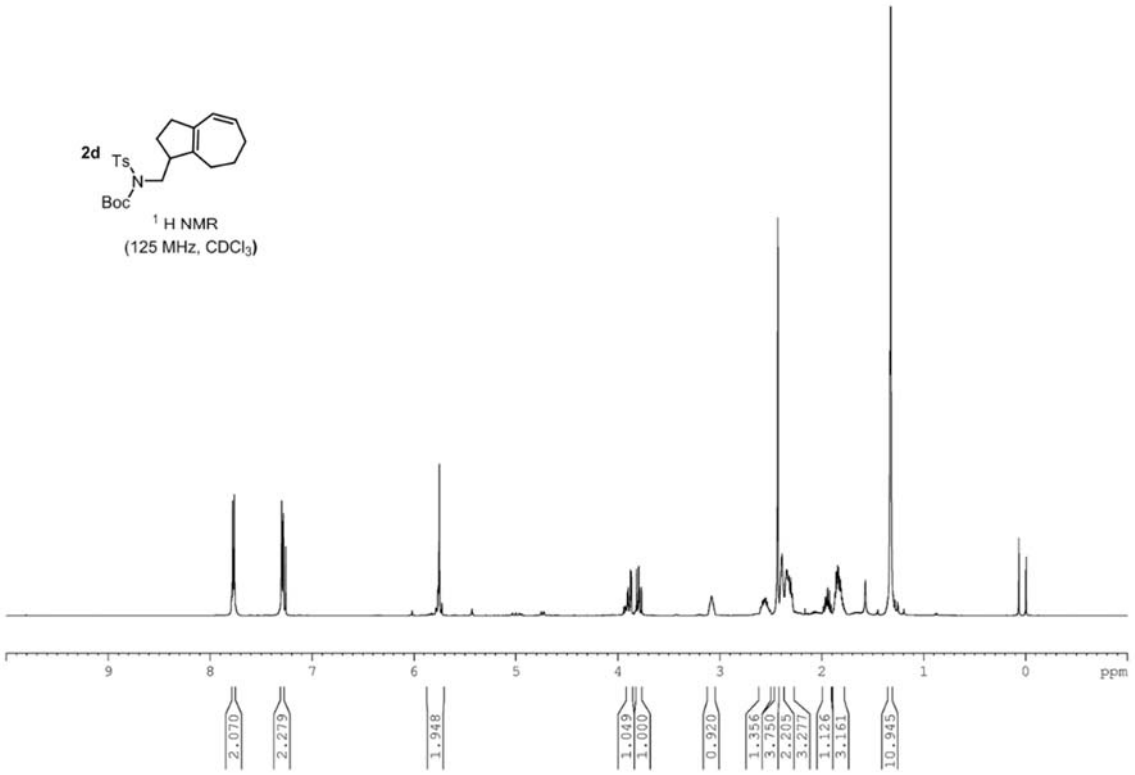

2a
TMSO
^{13}C NMR
(100 MHz, $CDCl_3$)
147.011
132.016
127.142
125.326
79.492
50.354
43.320
31.384
28.579
24.769
24.690
18.884
0.175
0 ppm

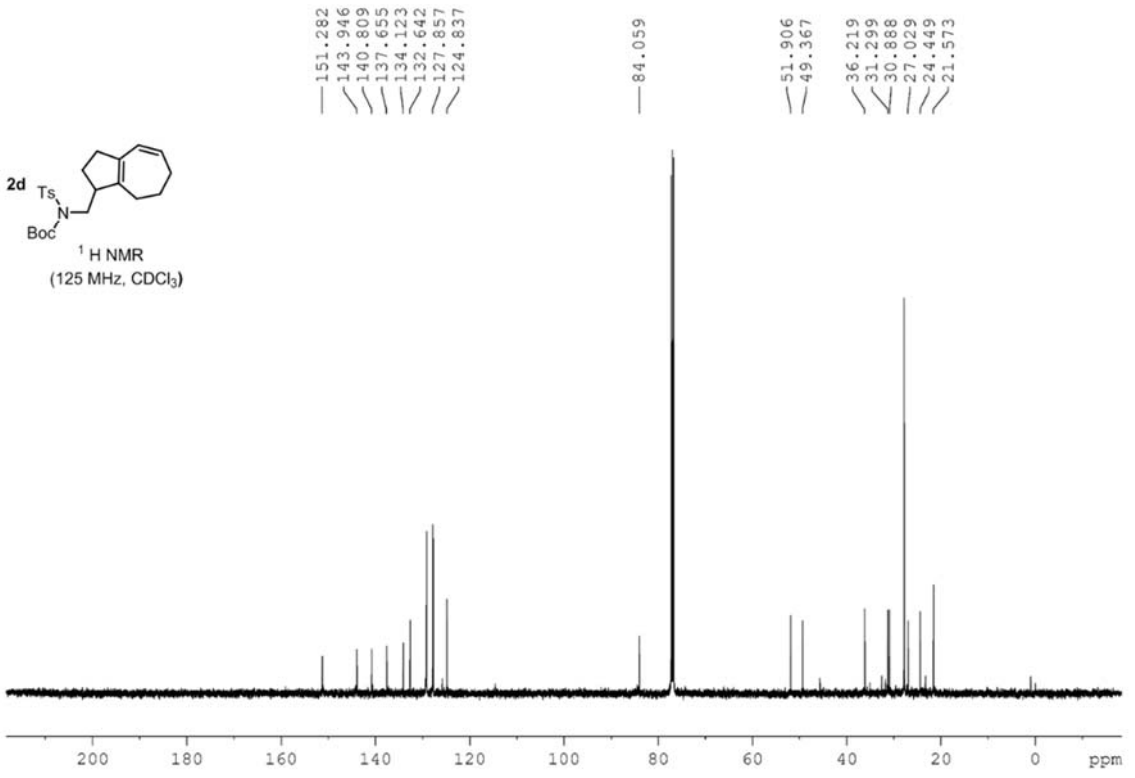

2b
^{1}H NMR
(500 MHz, $CDCl_3$)
9
8
7
6
5
4
3
2
1
0
ppm
2.000
2.202
0.900
0.983
3.399
1.855
2.429
3.306

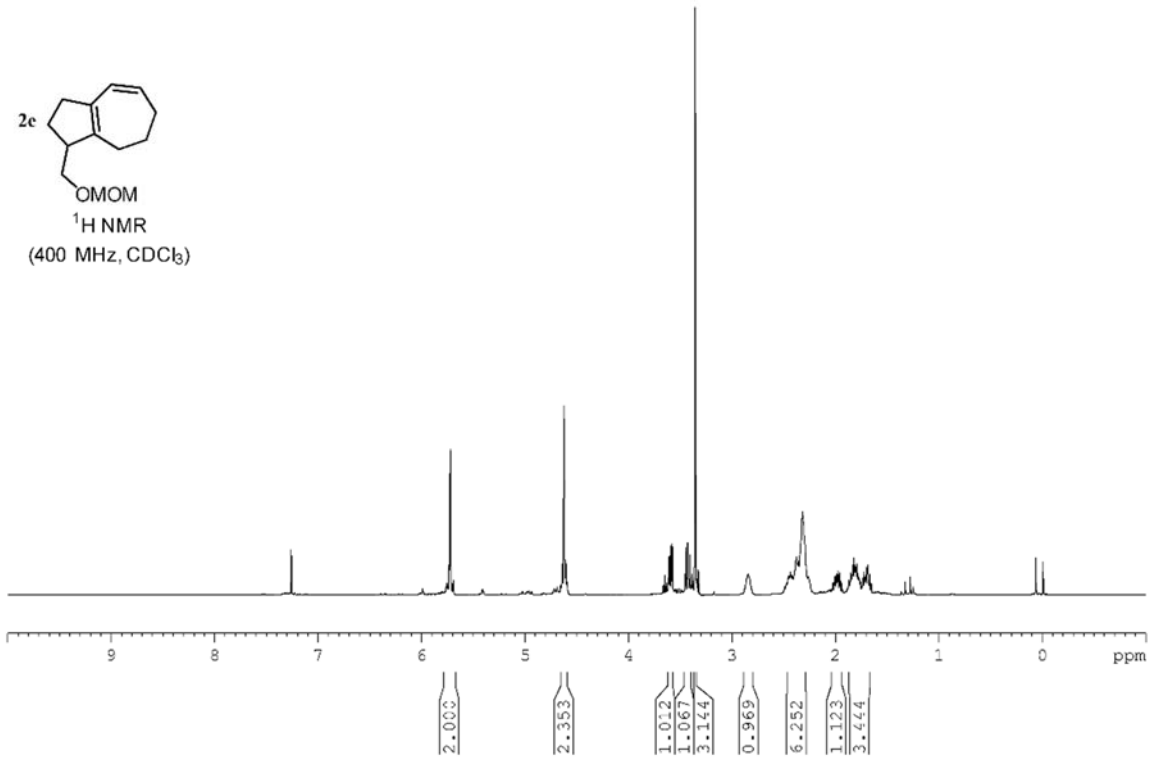

175.163
137.632
133.490
133.362
124.387
60.338
56.791
37.545
31.112
30.924
26.965
24.288
14.324
2b
^{13}C NMR
(125 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

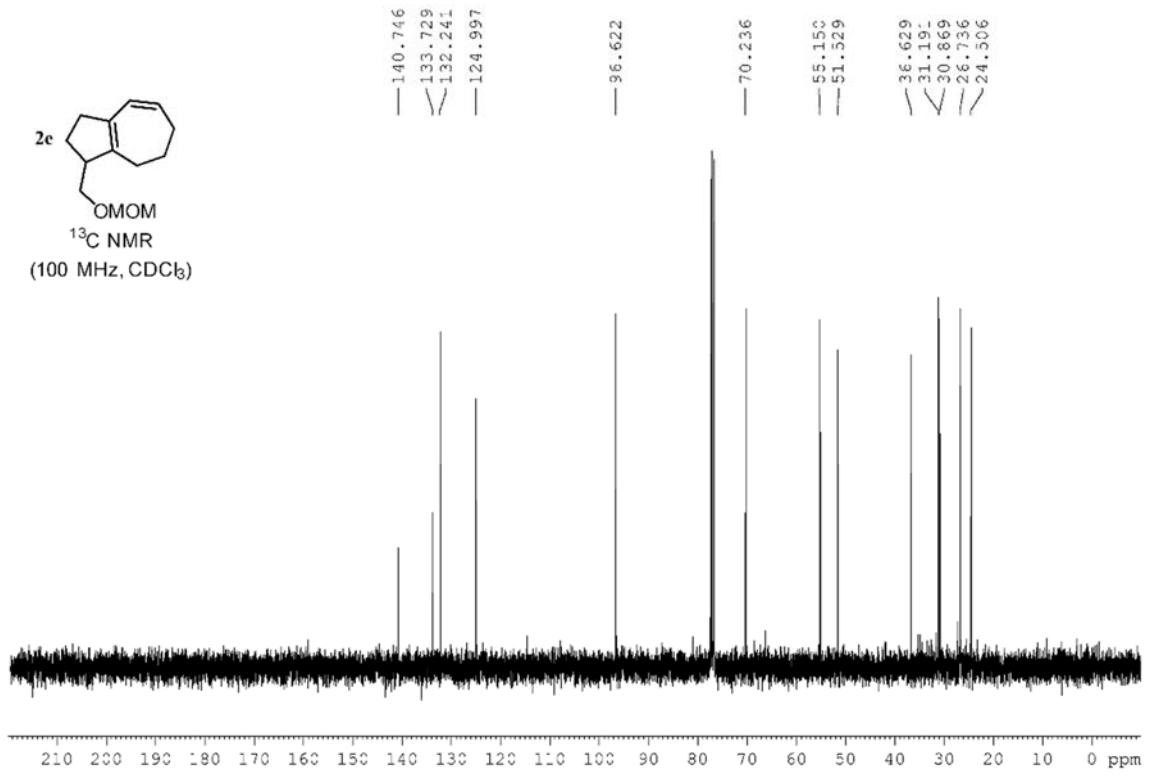

2c
^{1}H NMR
(400 MHz, CDCl$_3$)
9
8
7
6
5
4
3
2
1
0
ppm
2.000
0.936
3.260
3.242
1.114
1.159
3.160
2.400
1.137
2.236

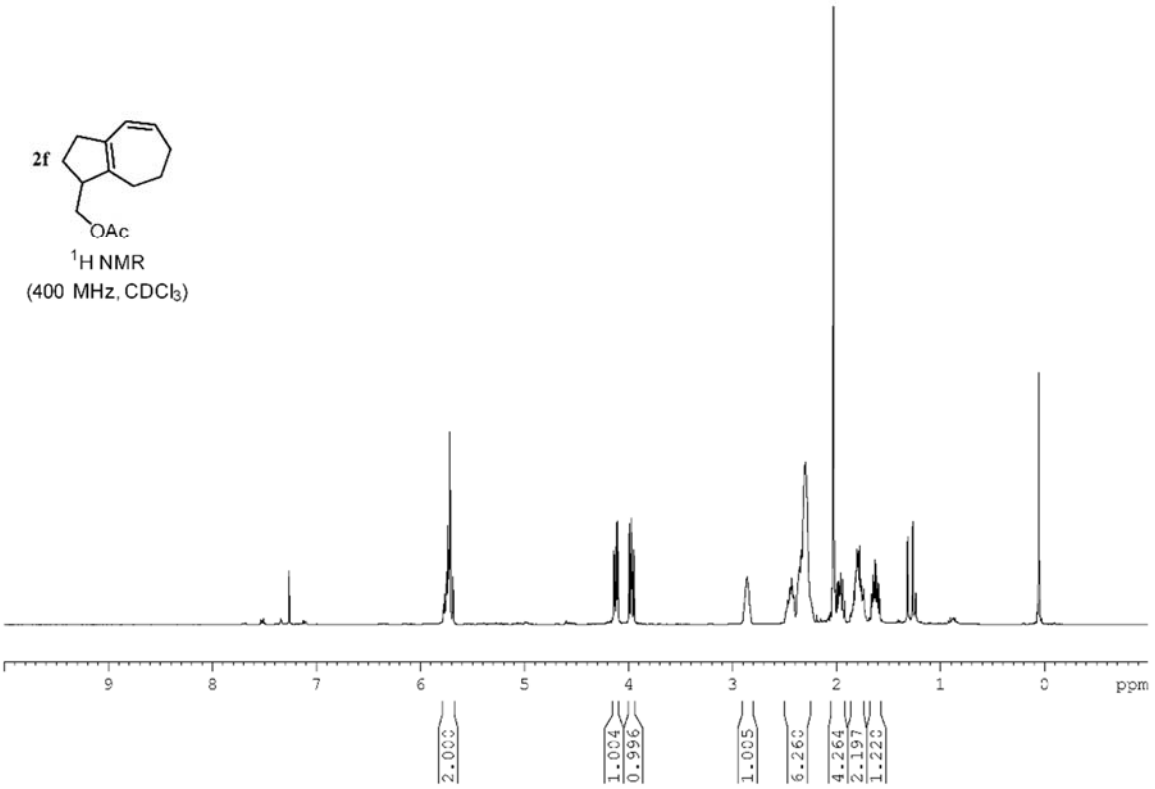

2c
^{13}C NMR
(100 MHz, CDCl$_3$)
176.498
138.577
135.486
132.854
124.512
77.360
77.243
77.041
76.724
61.377
52.748
37.668
32.408
30.985
27.449
24.346
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

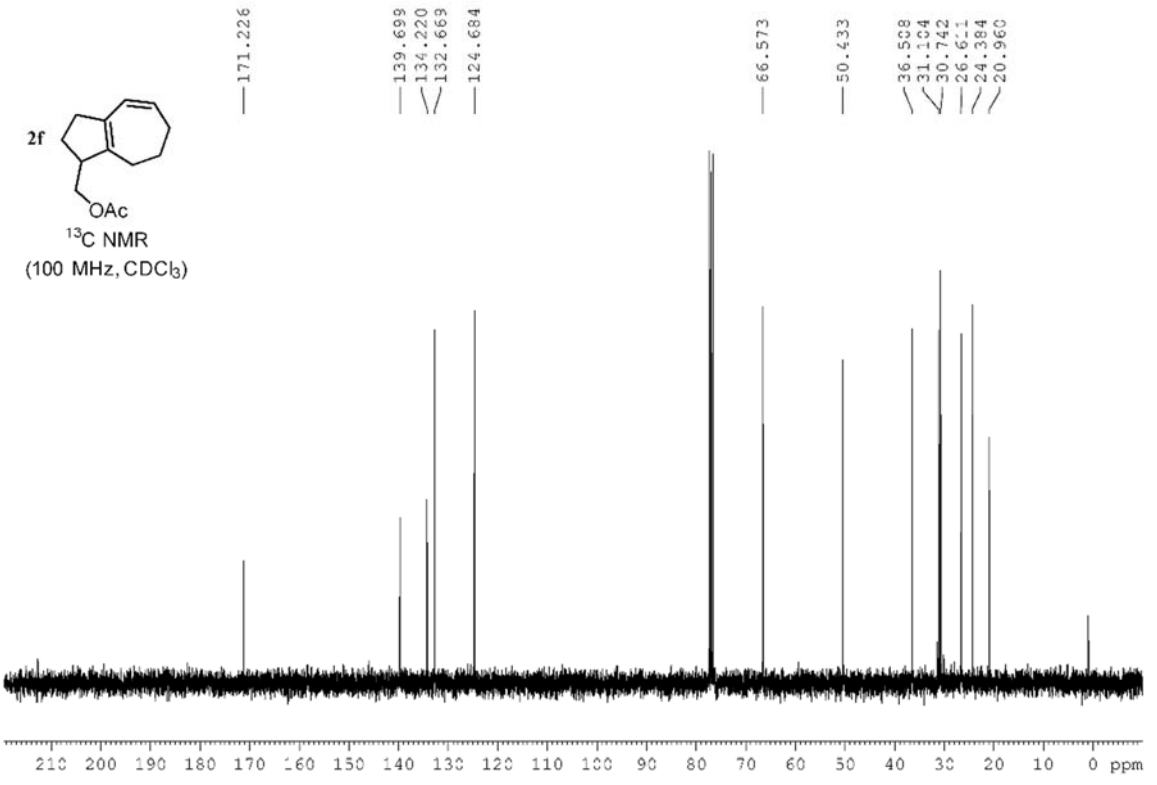

2d
Ts
N
Boc
1 H NMR
(125 MHz, CDCl3)
9
8
7
6
5
4
3
2
1
0
ppm
2.070
2.279
1.948
1.049
1.000
0.920
1.356
3.750
2.205
3.277
1.126
3.161
10.945

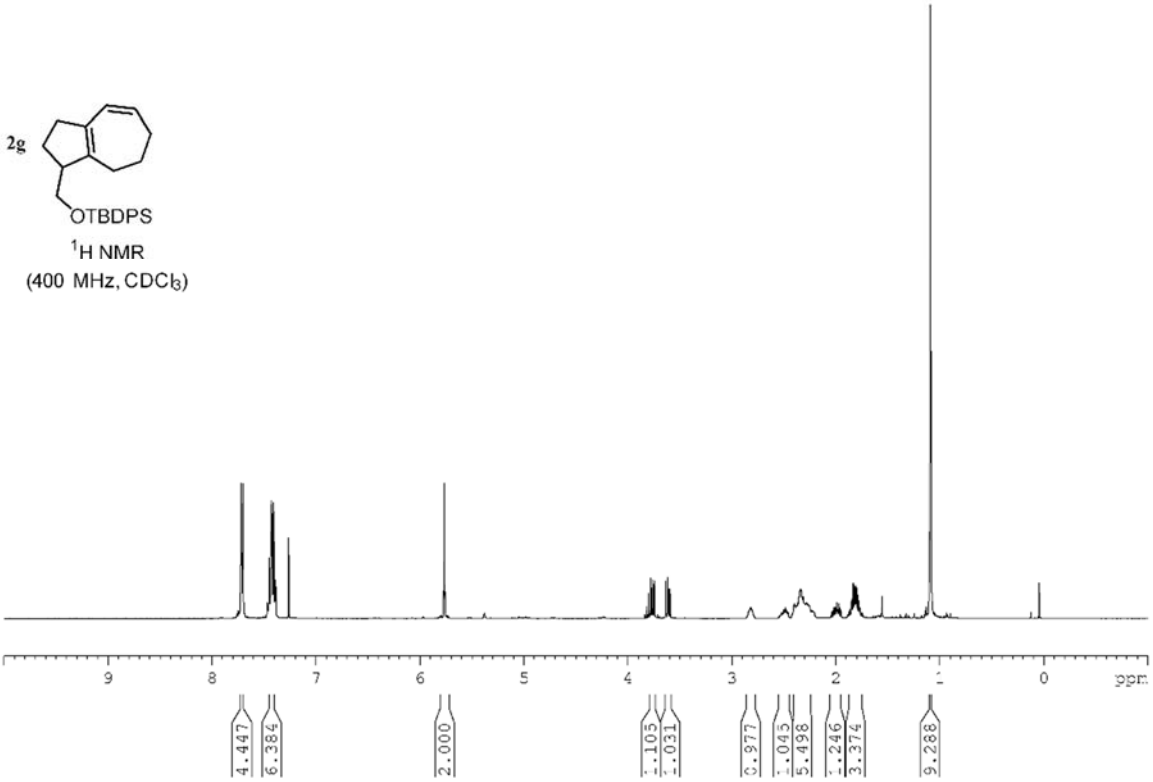

151.282
143.946
140.809
137.655
134.123
132.642
127.857
124.837
84.059
51.906
49.367
36.219
31.299
30.888
27.029
24.449
21.573
2d
Ts
N
Boc
1 H NMR
(125 MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
0
ppm

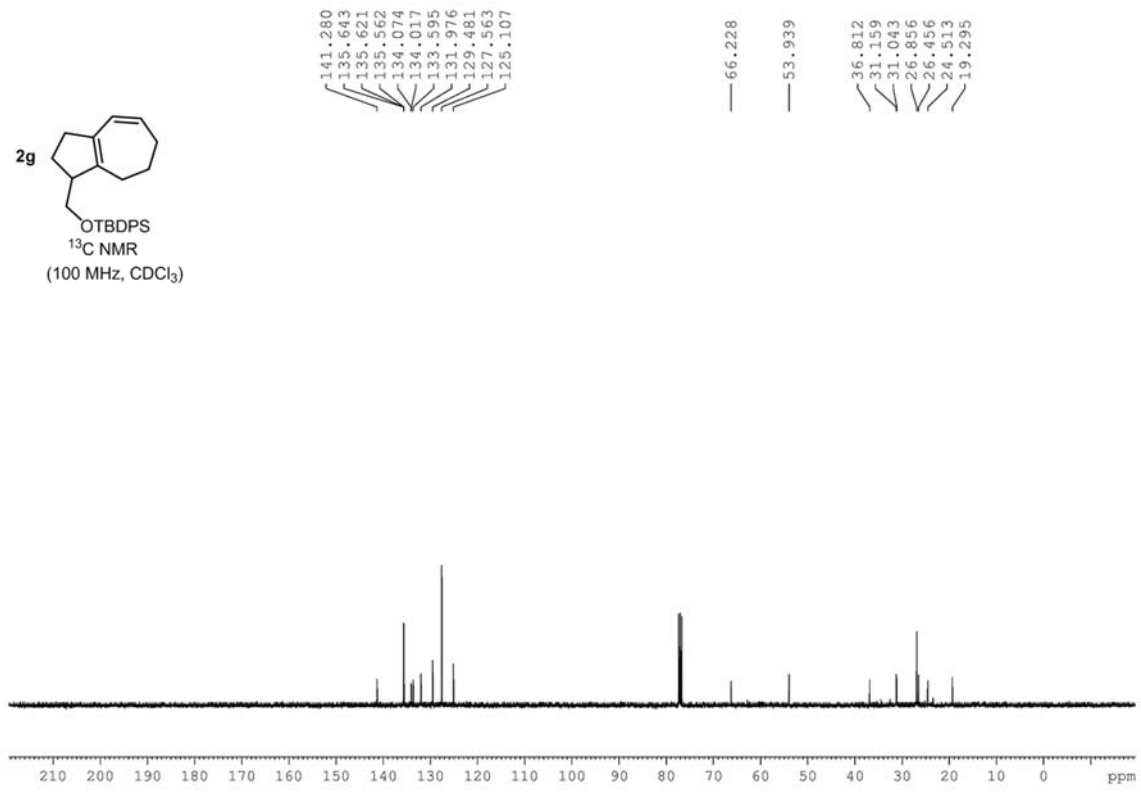

2e
OMOM
^{1}H NMR
(400 MHz, CDCl$_3$)
9
8
7
6
5
4
3
2
1
0
ppm
2.000
2.353
1.012
1.067
3.144
0.969
6.252
1.123
3.444

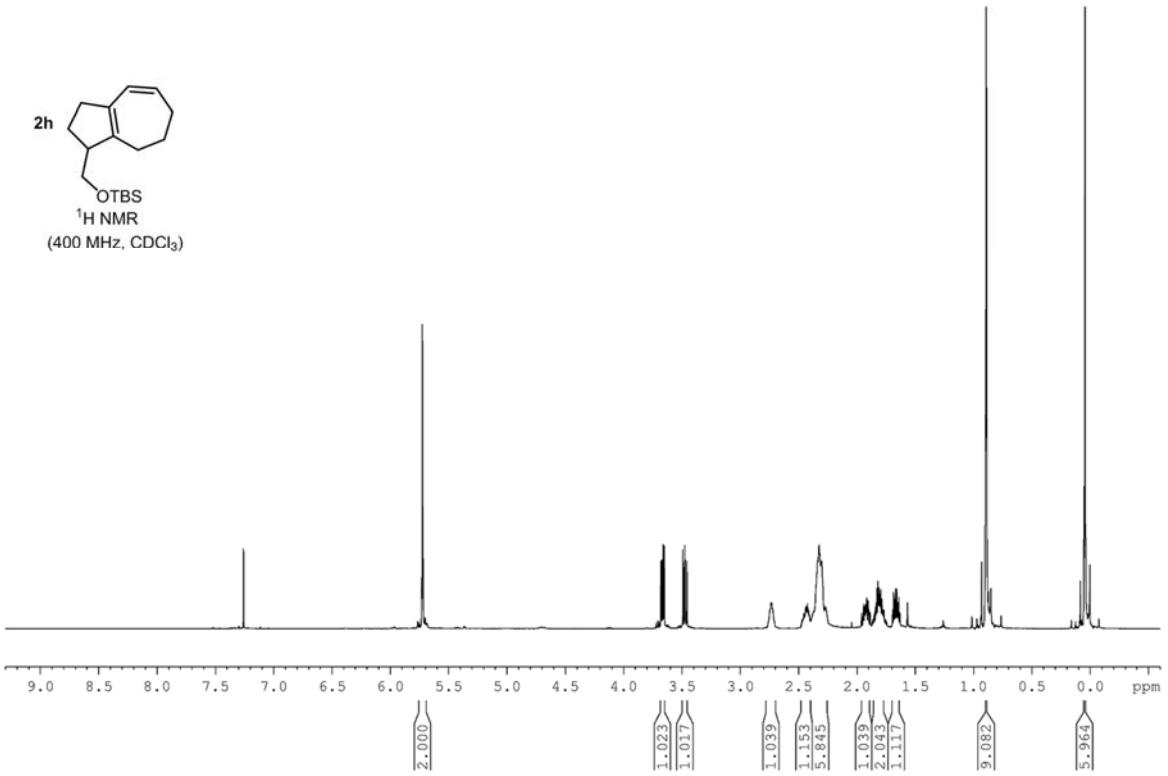

2e
OMOM
^{13}C NMR
(100 MHz, CDCl$_3$)
140.746
133.729
132.241
124.997
96.622
70.236
55.150
51.529
36.629
31.191
30.869
26.736
24.506
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

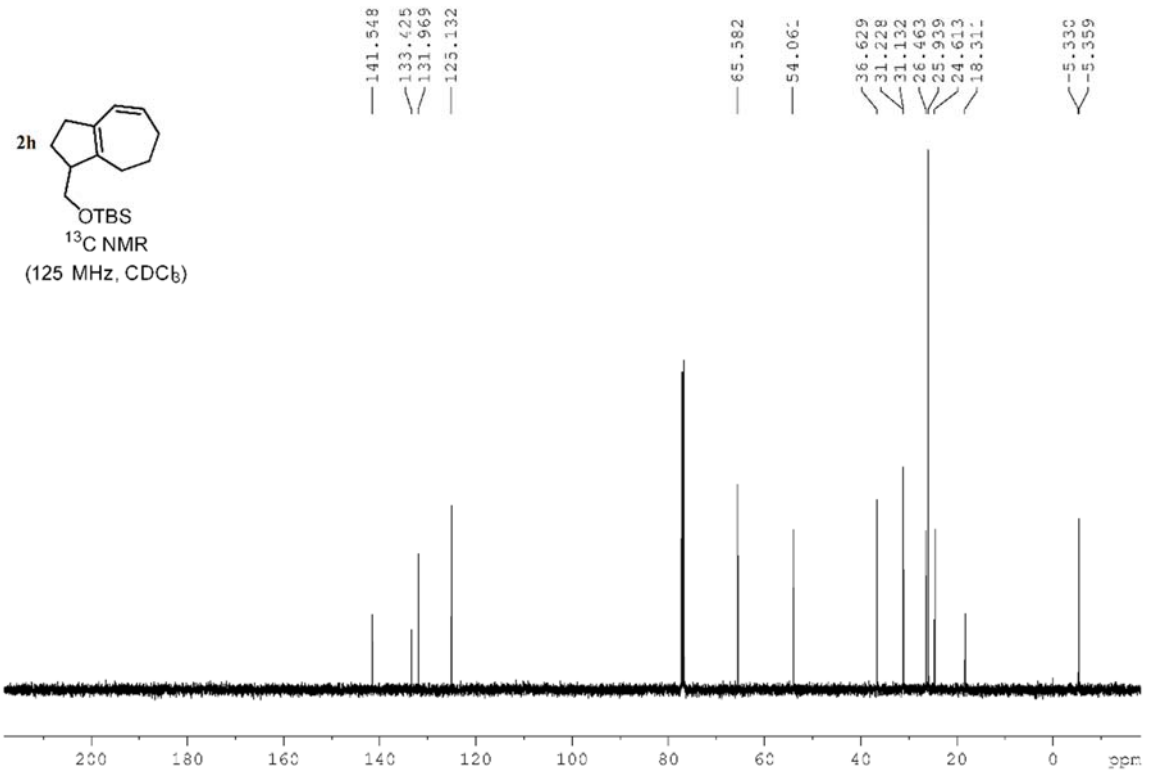

2f
OAc
^{1}H NMR
(400 MHz, $CDCl_3$)
9
8
7
6
5
4
3
2
1
0
ppm
2.000
1.004
0.996
1.005
6.260
4.264
2.197
1.220

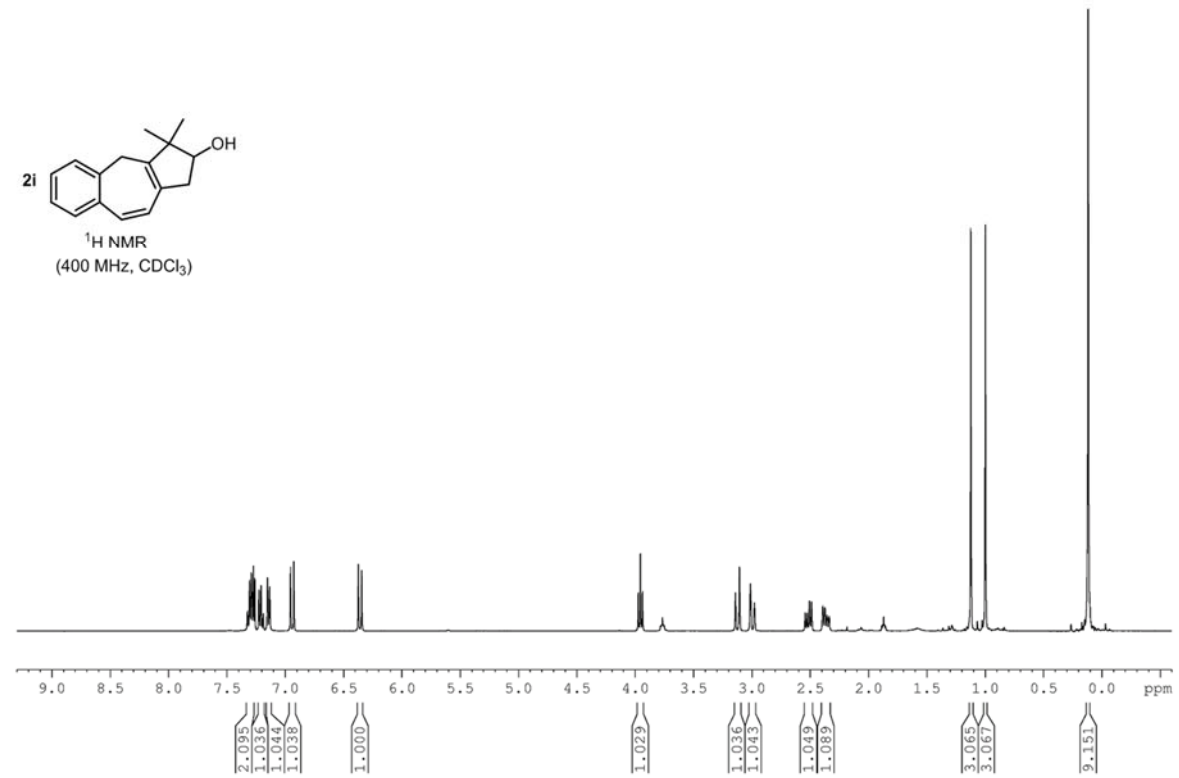

171.226
139.699
134.220
132.669
124.684
66.573
50.433
36.508
31.134
30.742
26.611
24.384
20.960
2f
OAc
^{13}C NMR
(100 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

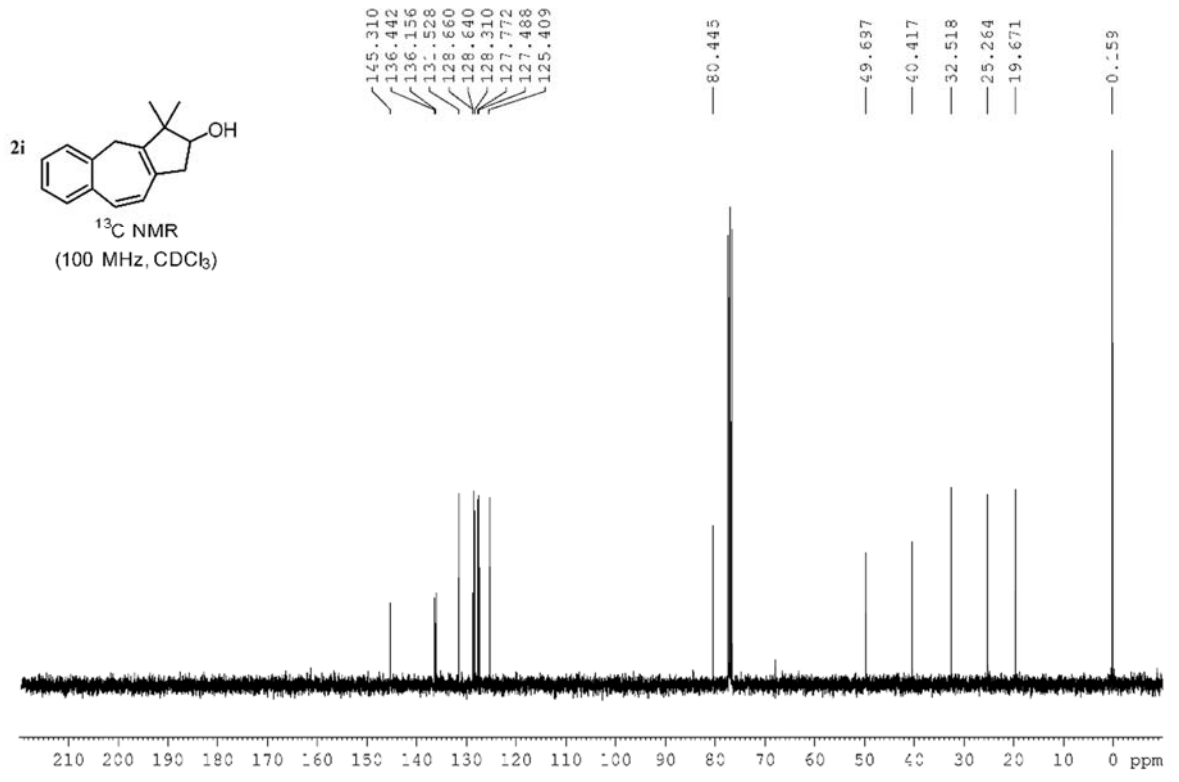

2g
OTBDPS
^{1}H NMR
(400 MHz, CDCl$_3$)
9
8
7
6
5
4
3
2
0
ppm
4.447
6.384
2.000
3.374
9.288

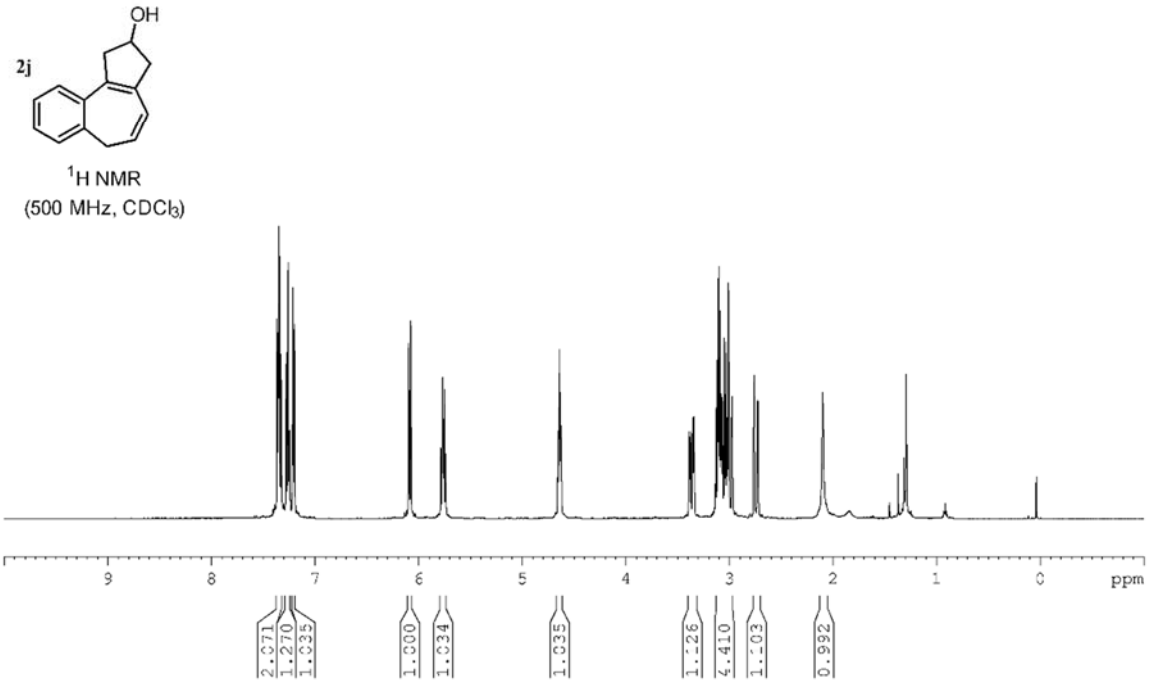

141.280
135.643
135.621
135.562
134.074
134.017
133.595
131.976
129.481
127.563
125.107
66.228
53.939
36.812
31.159
31.043
26.856
26.456
24.513
19.295
2g
OTBDPS
^{13}C NMR
(100 MHz, CDCl$_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

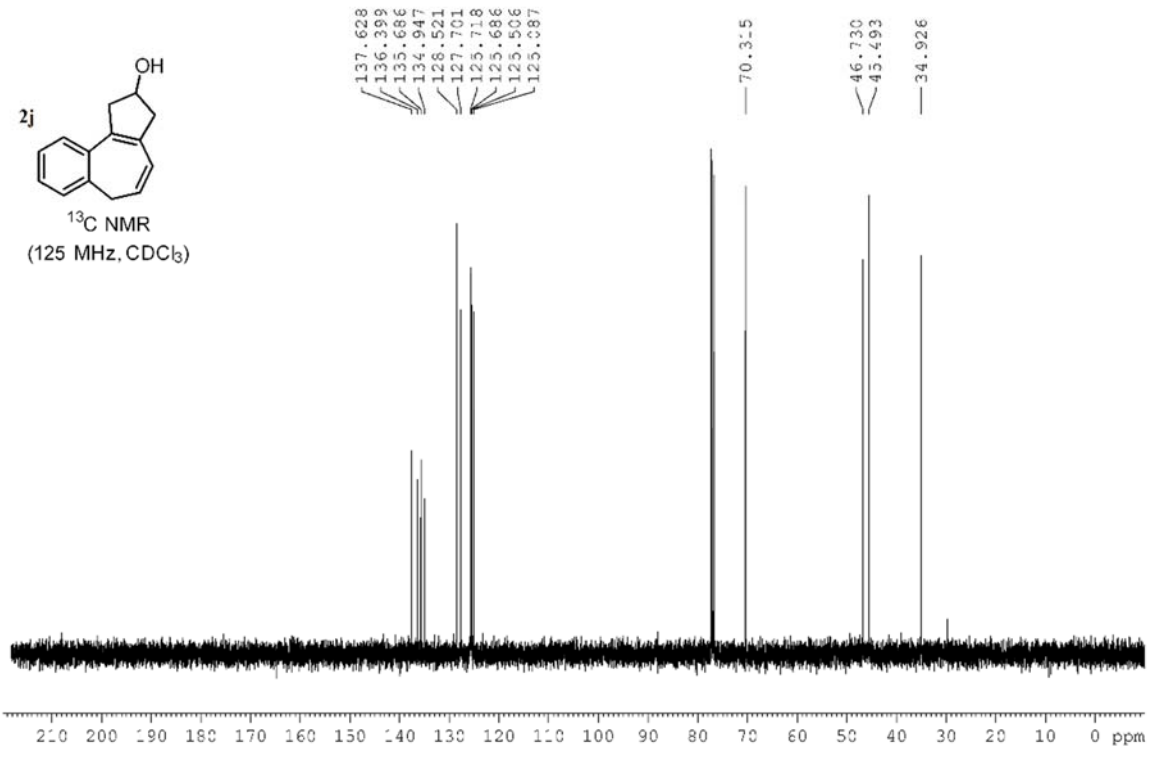

2h
OTBS
^{1}H NMR
(400 MHz, $CDCl_3$)
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.000
1.023
1.017
1.039
1.153
5.845
1.039
2.043
1.117
9.082
5.964

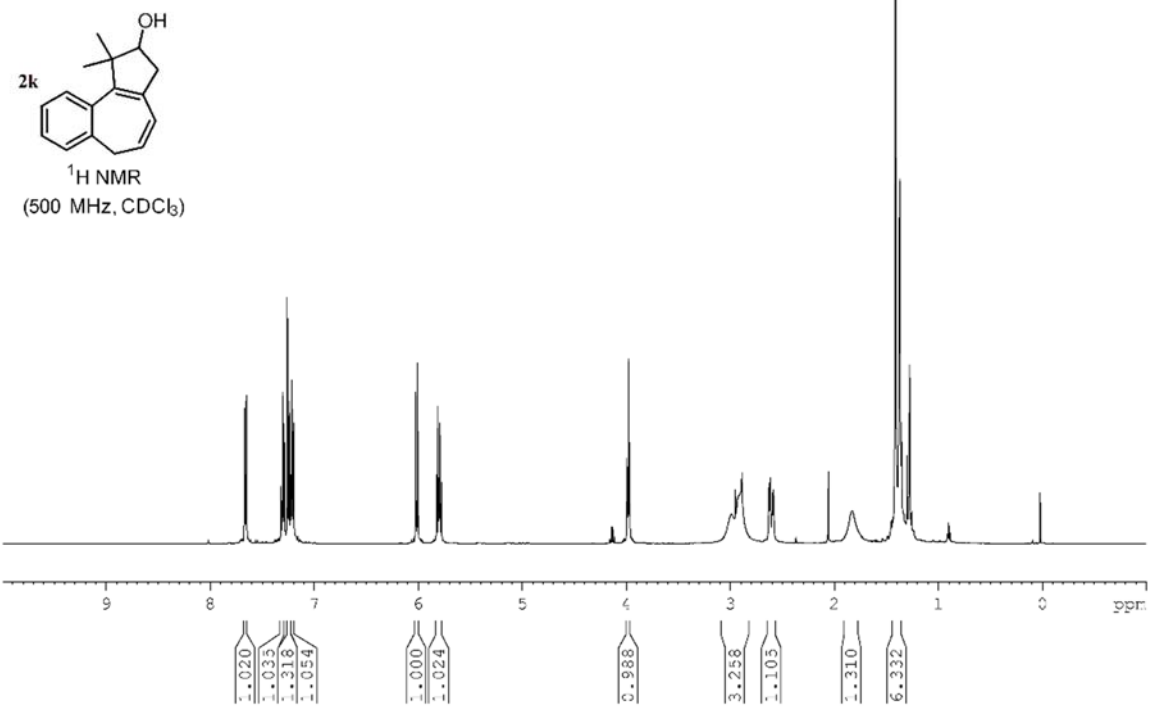

2h
OTBS
^{13}C NMR
(125 MHz, $CDCl_3$)
141.548
133.425
131.969
125.132
65.582
54.06
36.629
31.228
31.132
26.463
25.939
24.613
18.31
-5.330
-5.359
200 180 160 140 120 100 80 60 40 20 0 ppm

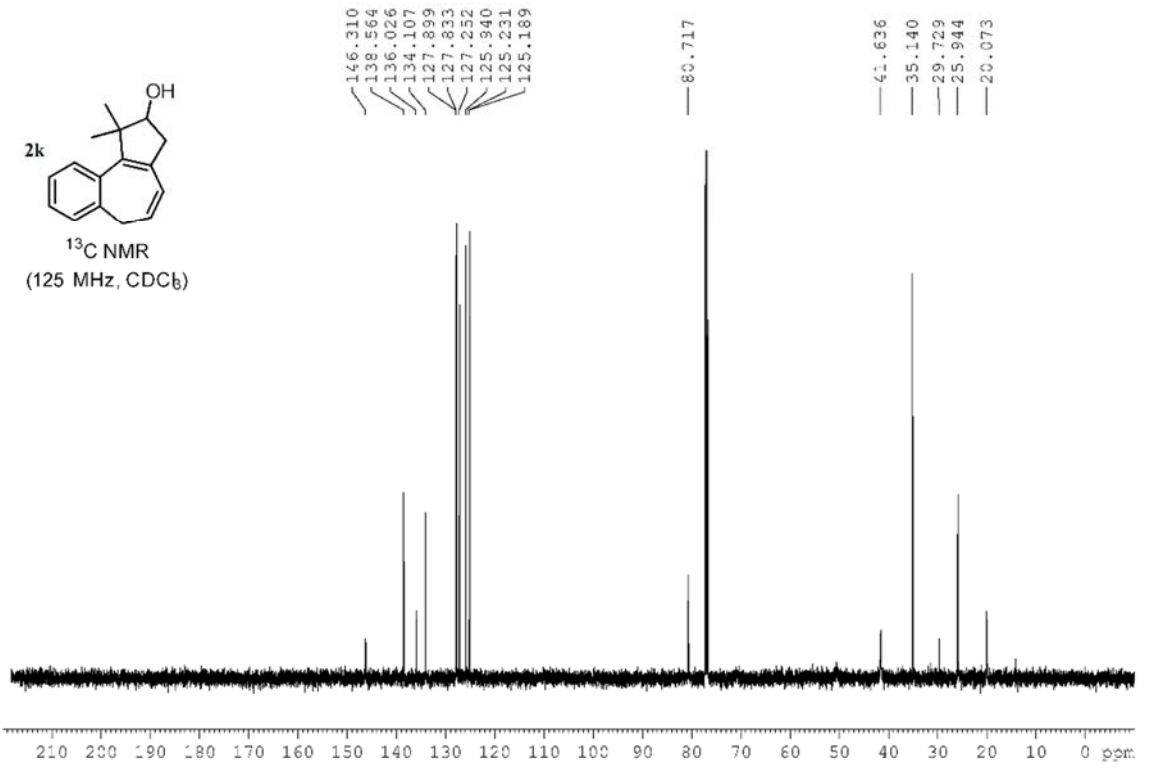

2i
OH
^{1}H NMR
(400 MHz, $CDCl_3$)
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.095
1.036
1.044
1.038
1.000
1.029
1.036
1.043
1.049
1.089
3.065
3.067
9.151

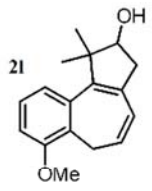

2i
OH
^{13}C NMR
(100 MHz, $CDCl_3$)
145.310
136.442
136.156
13..528
128.660
128.640
128.310
127.772
127.488
125.409
80.445
49.697
40.417
32.518
25.264
19.671
0.159
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


OH
2j
^{1}H NMR
(500 MHz, CDCl$_3$)
9
8
7
6
5
4
3
2
1
0
ppm
2.071
1.270
1.035
1.000
1.034
1.035
1.126
4.410
1.103
0.992

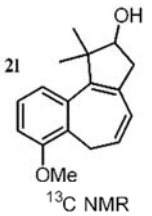

OH
2j
^{13}C NMR
(125 MHz, CDCl$_3$)
137.628
136.399
135.686
134.947
128.521
127.701
125.718
125.686
125.506
125.087
70.345
46.730
45.493
34.926
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


OH
2k
1H NMR
(500 MHz, CDCl3)
9
8
7
6
5
4
3
2
1
0
ppm
1.020
1.033
1.318
1.054
1.000
1.024
3.988
3.258
1.105
2.310
6.332

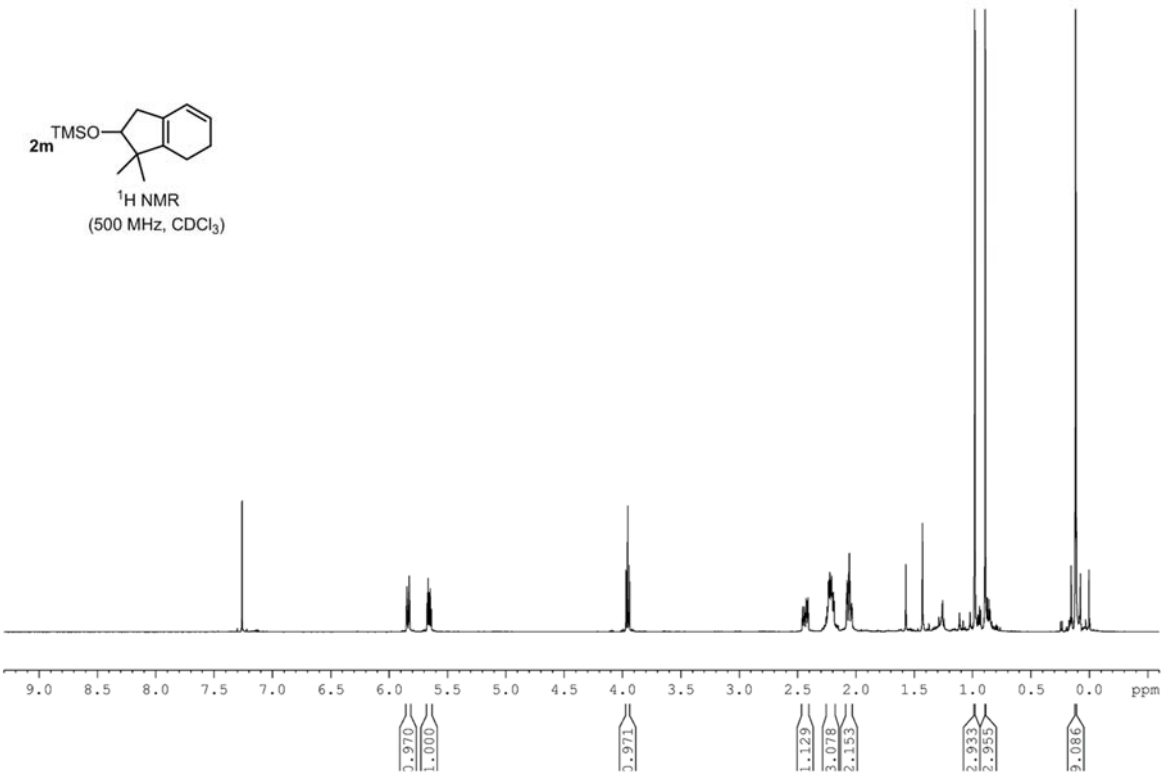

OH
2k
13C NMR
(125 MHz, CDCl3)
146.310
138.564
136.026
134.107
127.899
127.833
127.252
125.940
125.231
125.189
80.717
41.636
35.140
29.729
25.944
20.073
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

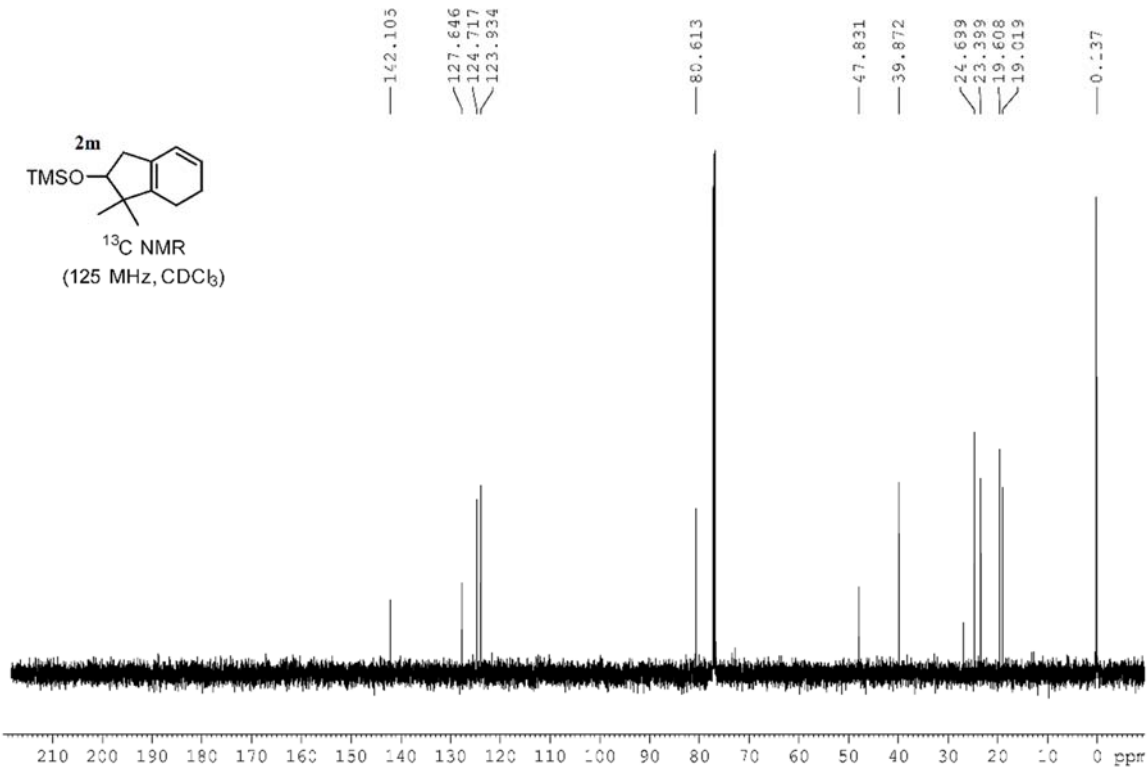


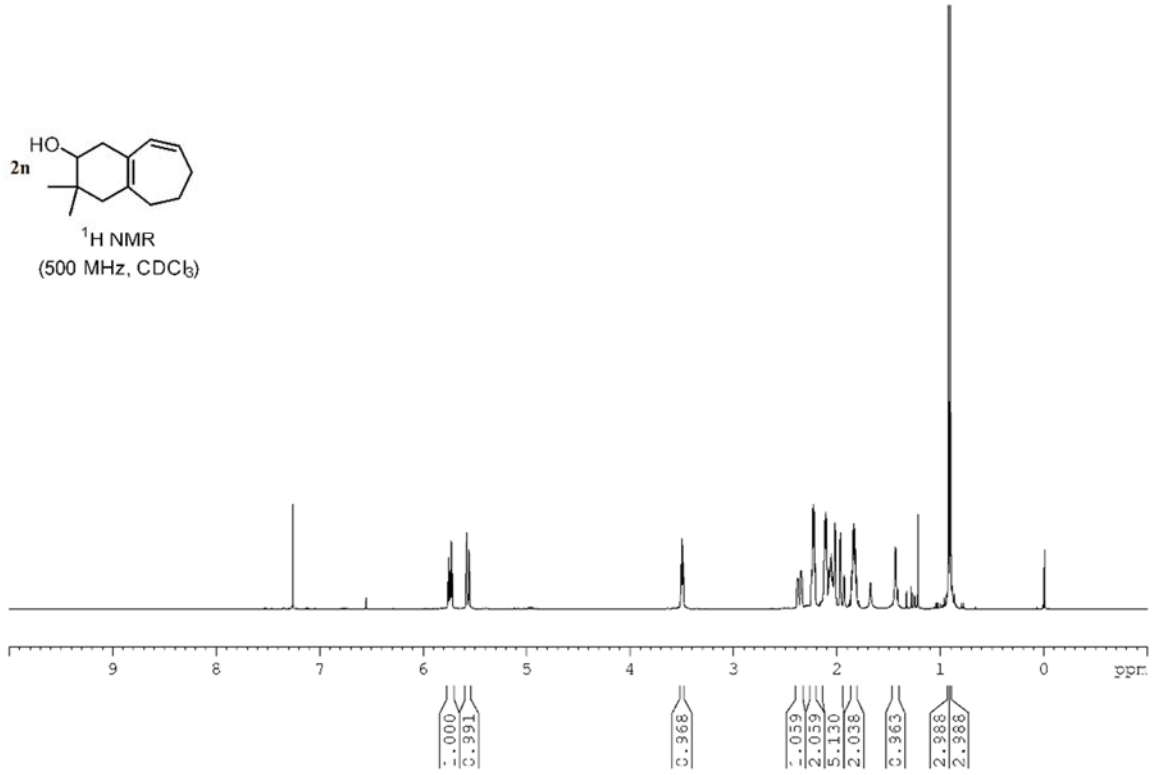
^{1}H NMR
(500 MHz, $CDCl_3$)

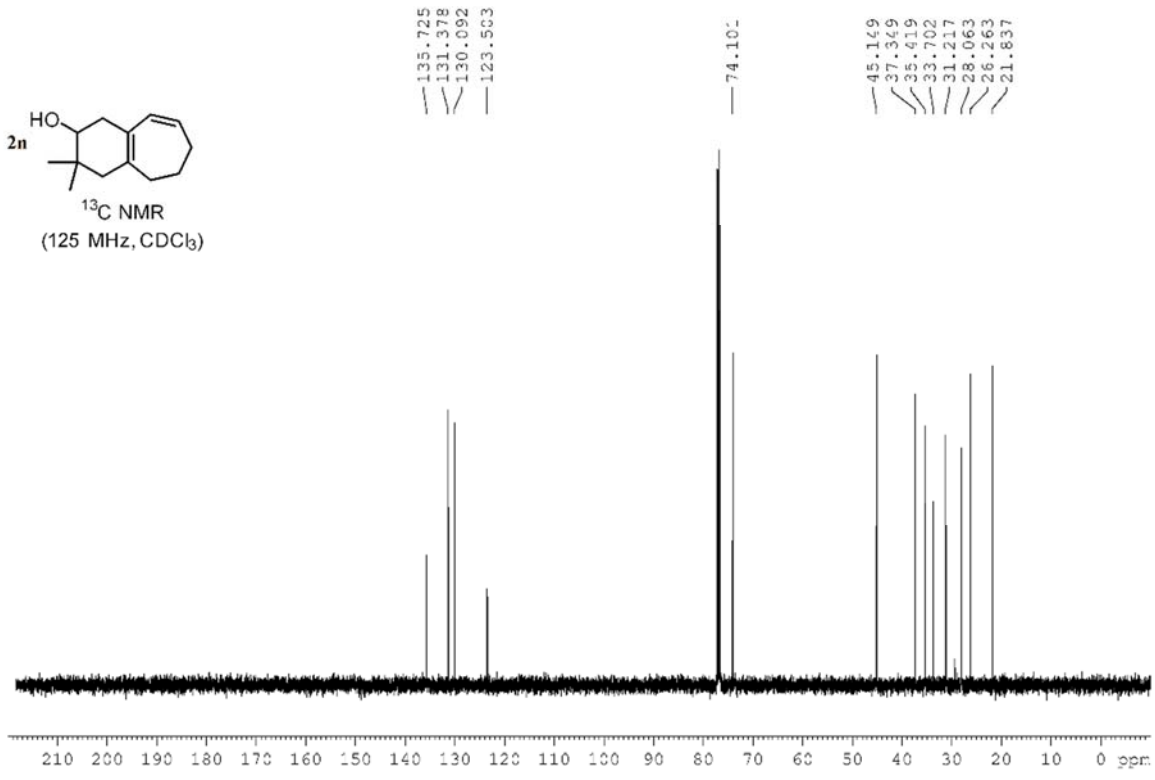


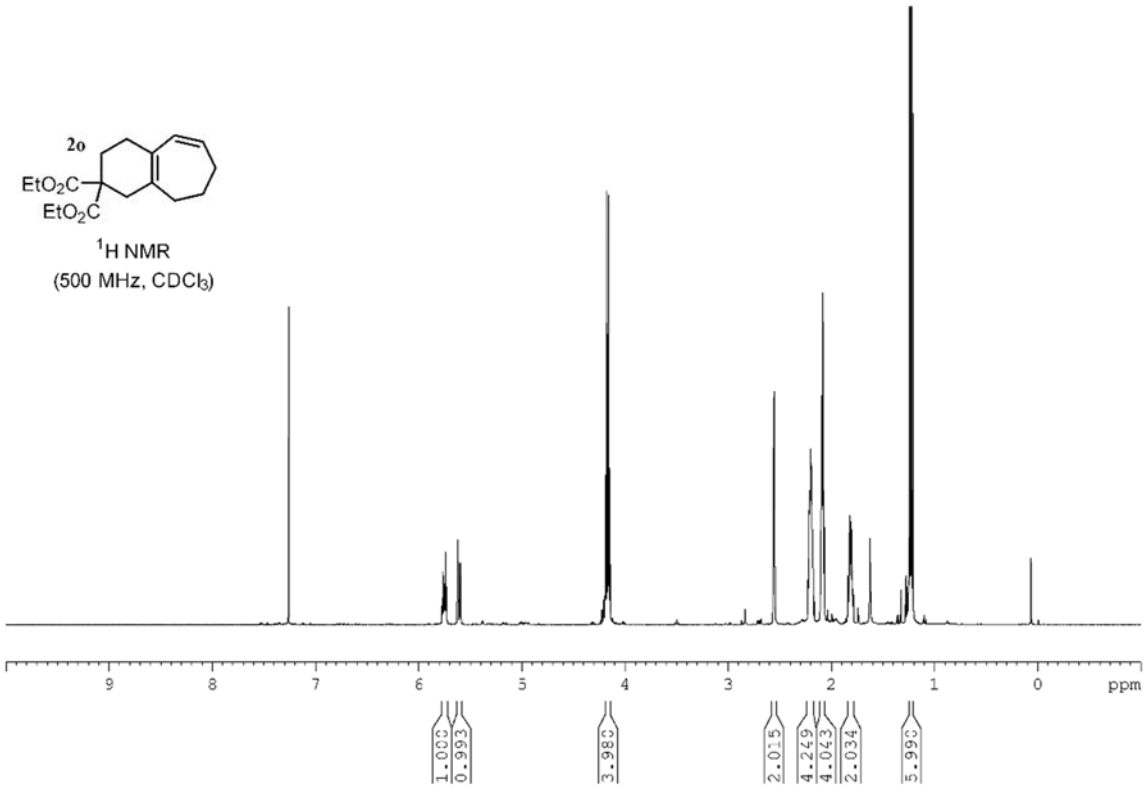
^{13}C NMR
(125 MHz, $CDCl_3$)

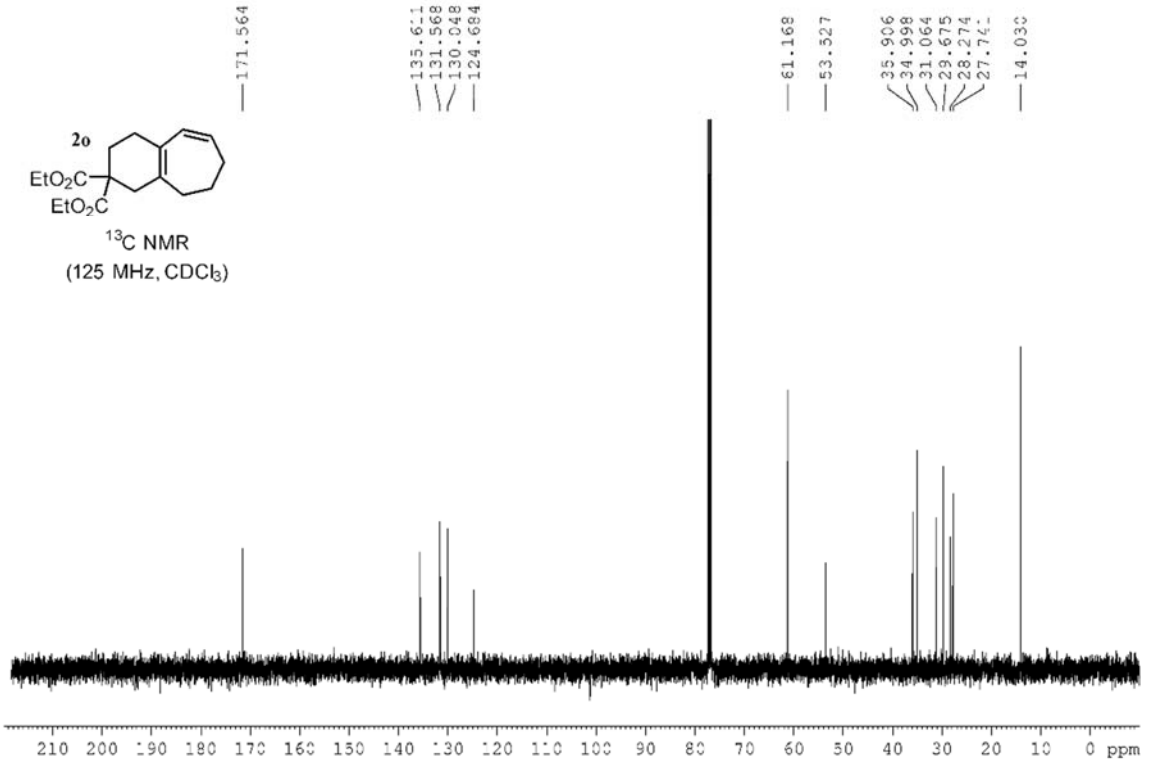

2m
TMSO
^{1}H NMR
(500 MHz, CDCl$_3$)
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.970
1.000
0.971
1.129
3.078
2.153
2.933
2.955
9.086

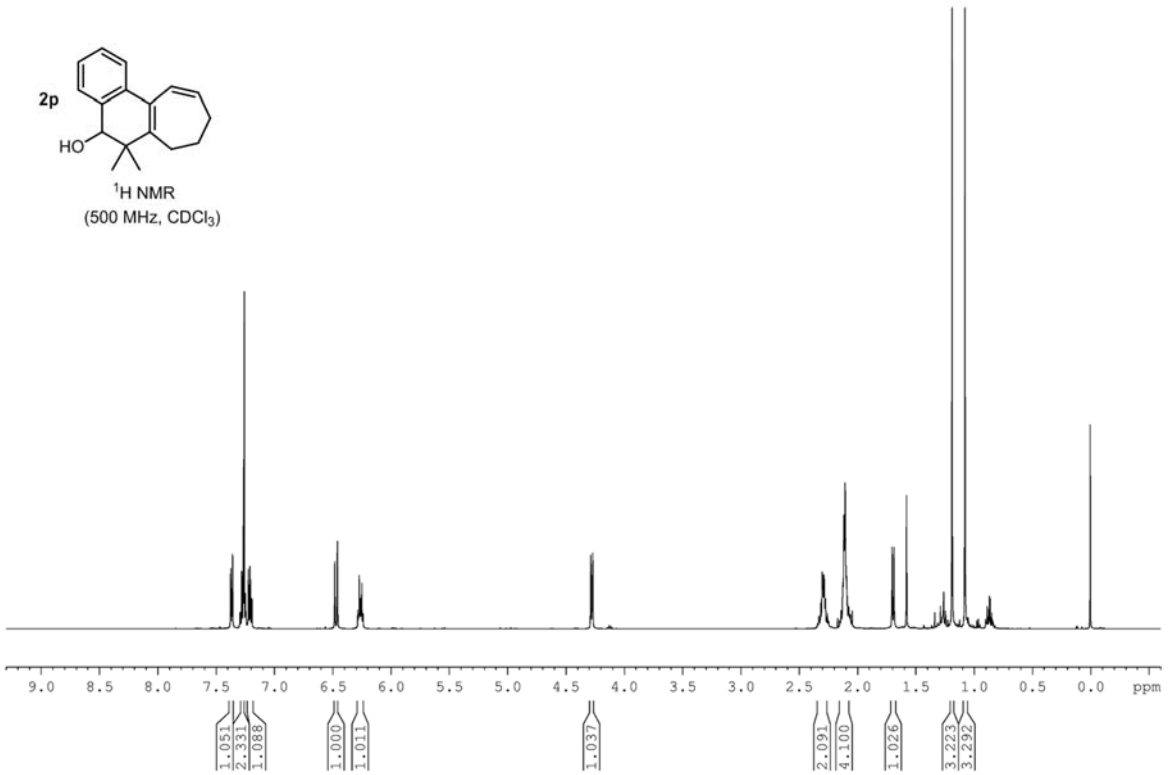

142.105
127.646
124.717
123.934
80.613
47.831
39.872
24.699
23.399
19.608
19.019
0.137
2m
TMSO
^{13}C NMR
(125 MHz, CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

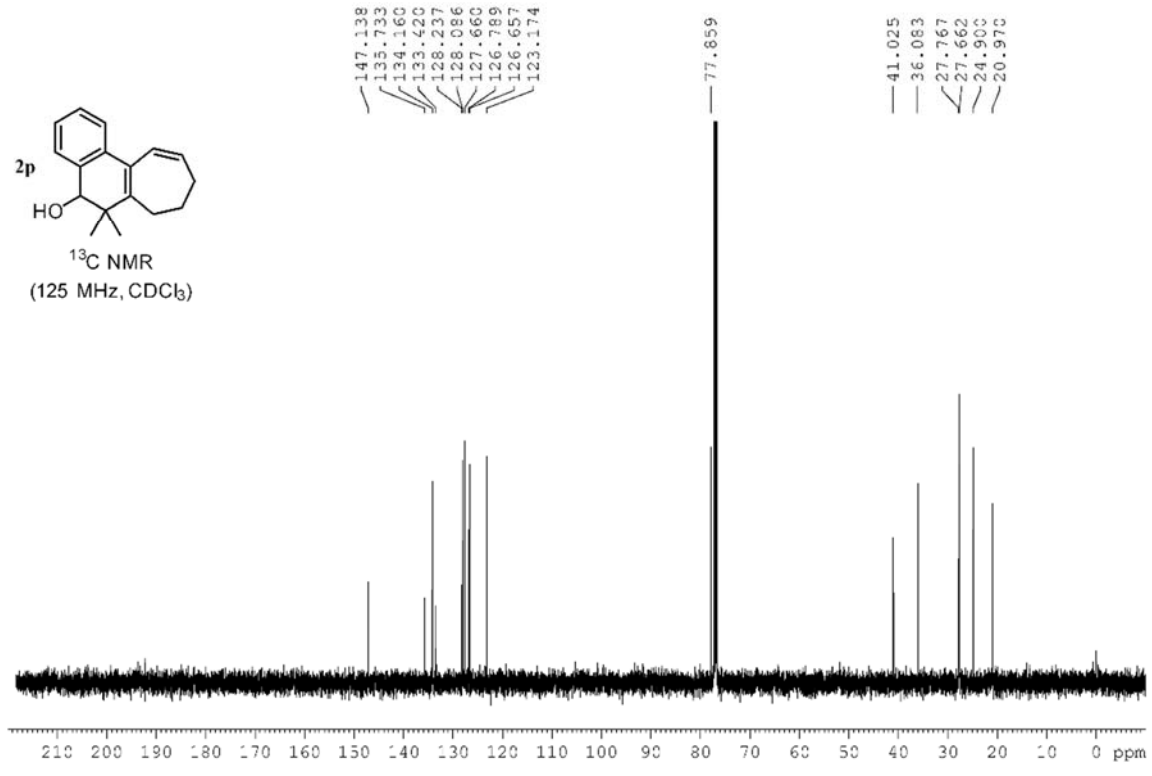

HO
2n
1H NMR
(500 MHz, CDCl3)
9
8
7
6
5
4
3
2
1
0
ppm
1.000
0.391
0.968
2.059
2.059
5.130
2.038
0.963
2.988
2.388

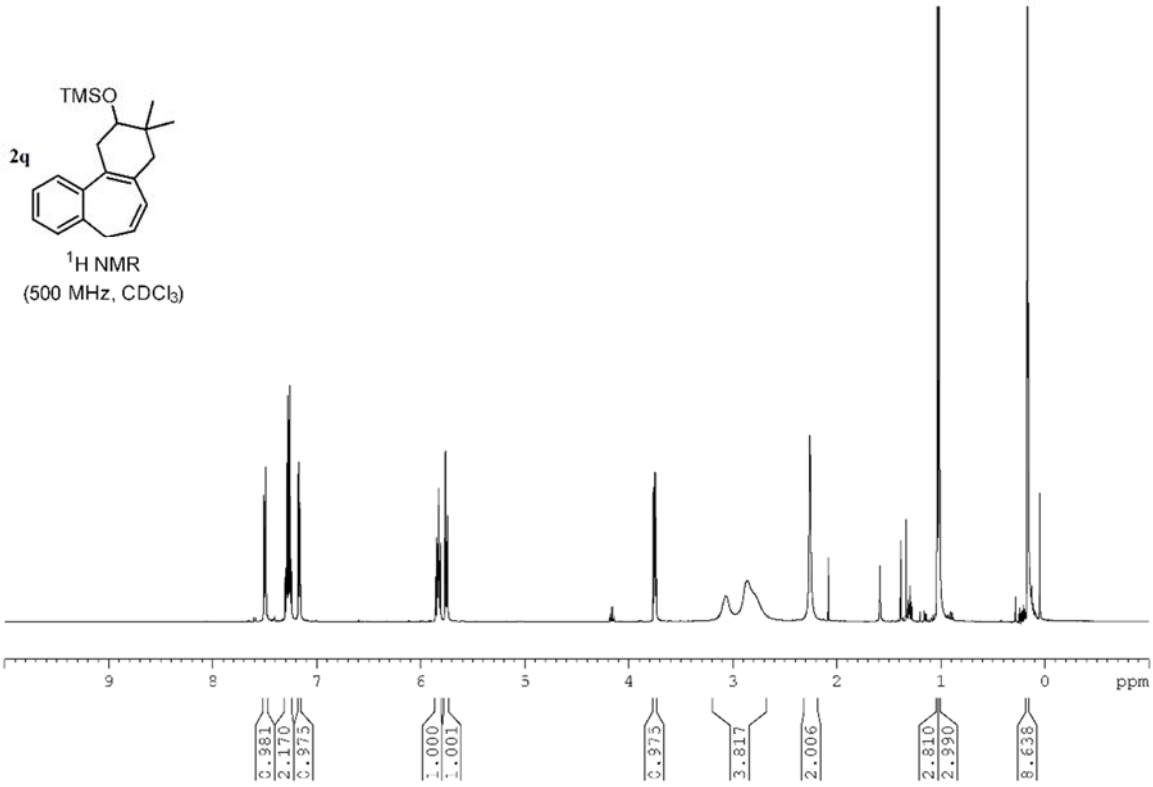

HO
2n
13C NMR
(125 MHz, CDCl3)
135.725
131.378
130.092
123.503
74.10
45.149
37.349
35.419
33.702
31.217
28.063
26.263
21.837
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

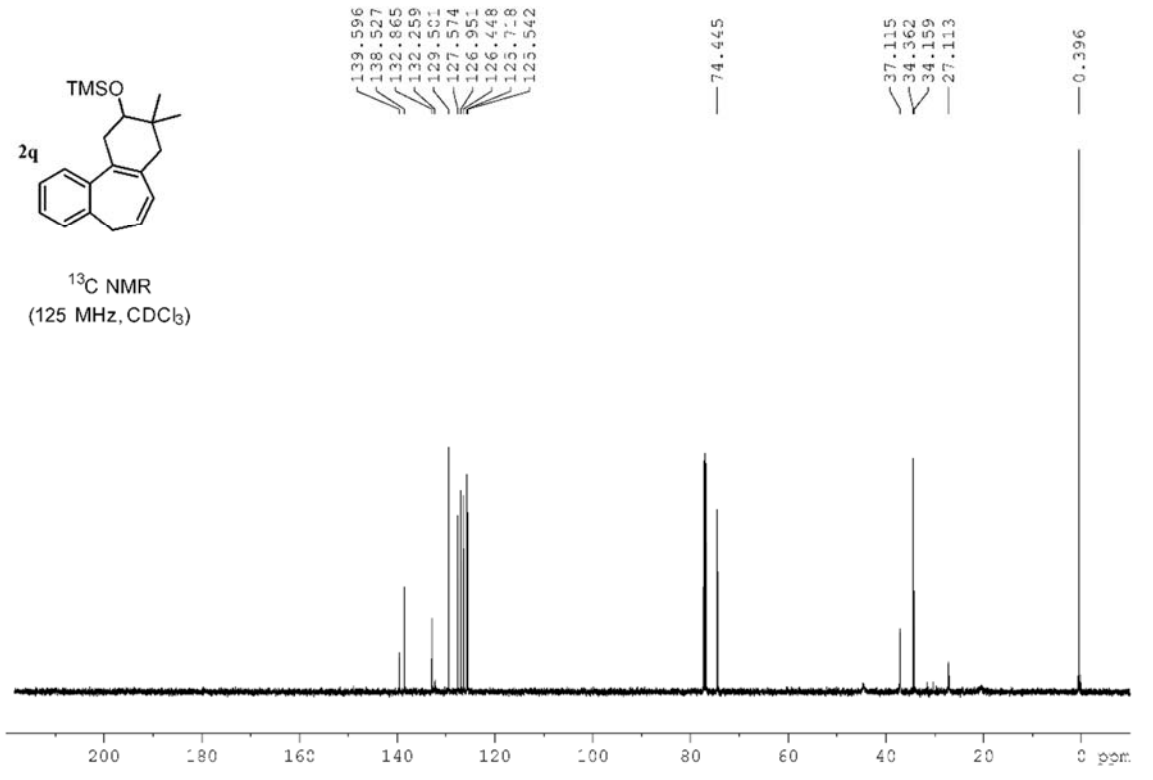

2o
EtO2C
EtO2C
1H NMR
(500 MHz, CDCl3)
9
8
7
6
5
4
3
2
1
0
ppm
1.000
0.993
3.980
2.015
4.249
4.043
2.034
5.990

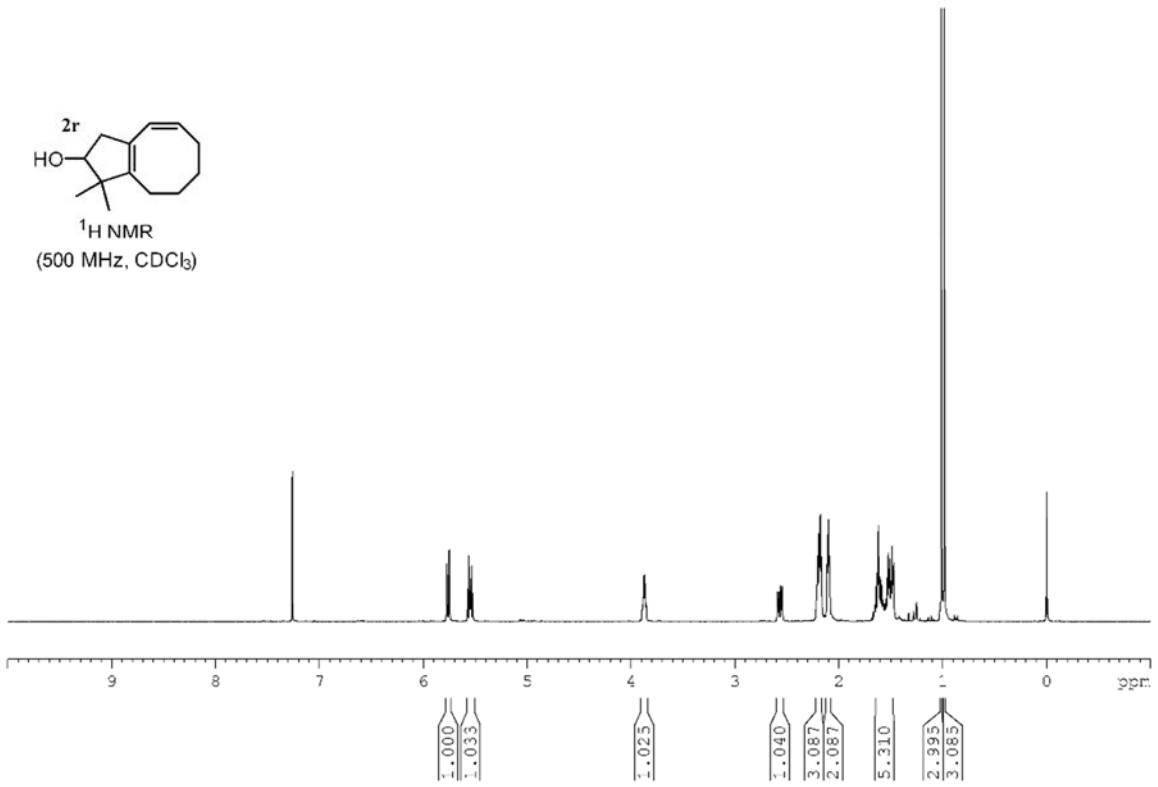

171.564
135.611
131.568
130.048
124.684
61.168
53.527
35.906
34.998
31.064
29.675
28.274
14.030
2o
EtO2C
EtO2C
13C NMR
(125 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

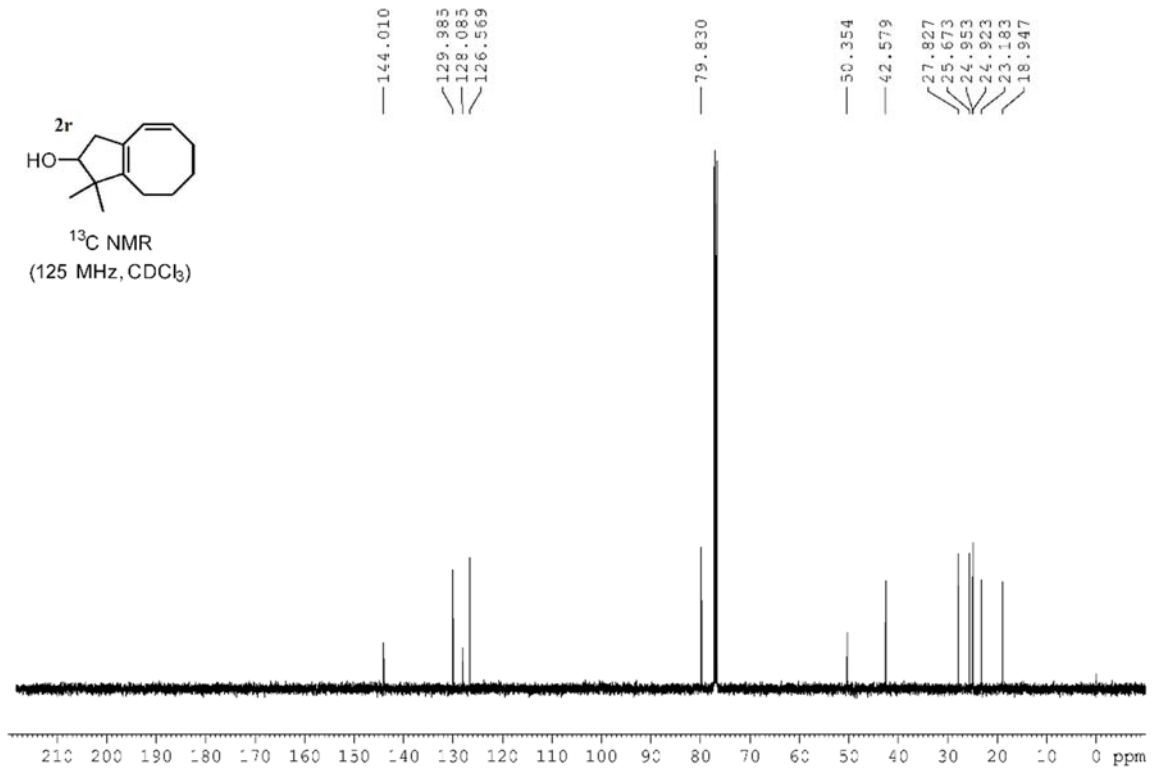

2p
HO
^{1}H NMR
(500 MHz, $CDCl_3$)
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.051
2.331
1.088
1.000
1.011
1.037
2.091
4.100
1.026
3.223
3.292

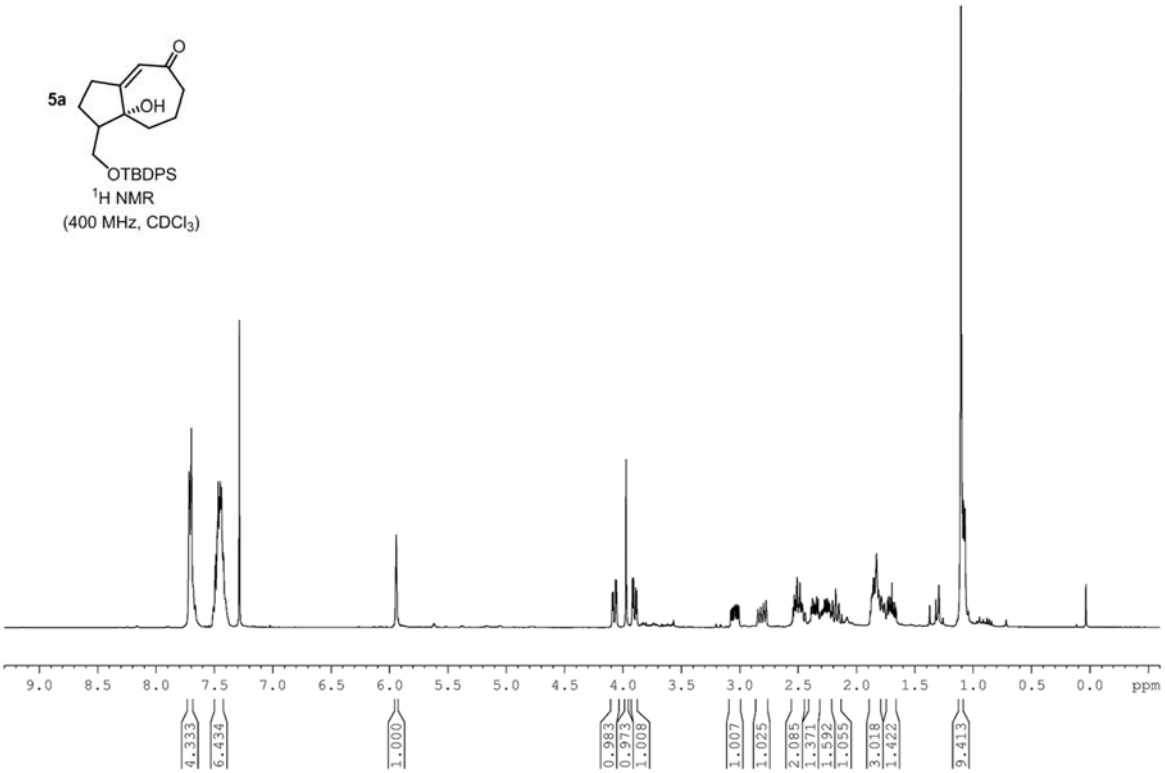

2p
HO
^{13}C NMR
(125 MHz, $CDCl_3$)
147.138
135.733
134.160
133.420
128.237
128.086
127.660
126.789
126.657
123.174
77.859
41.025
36.083
27.767
27.662
24.900
20.970
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

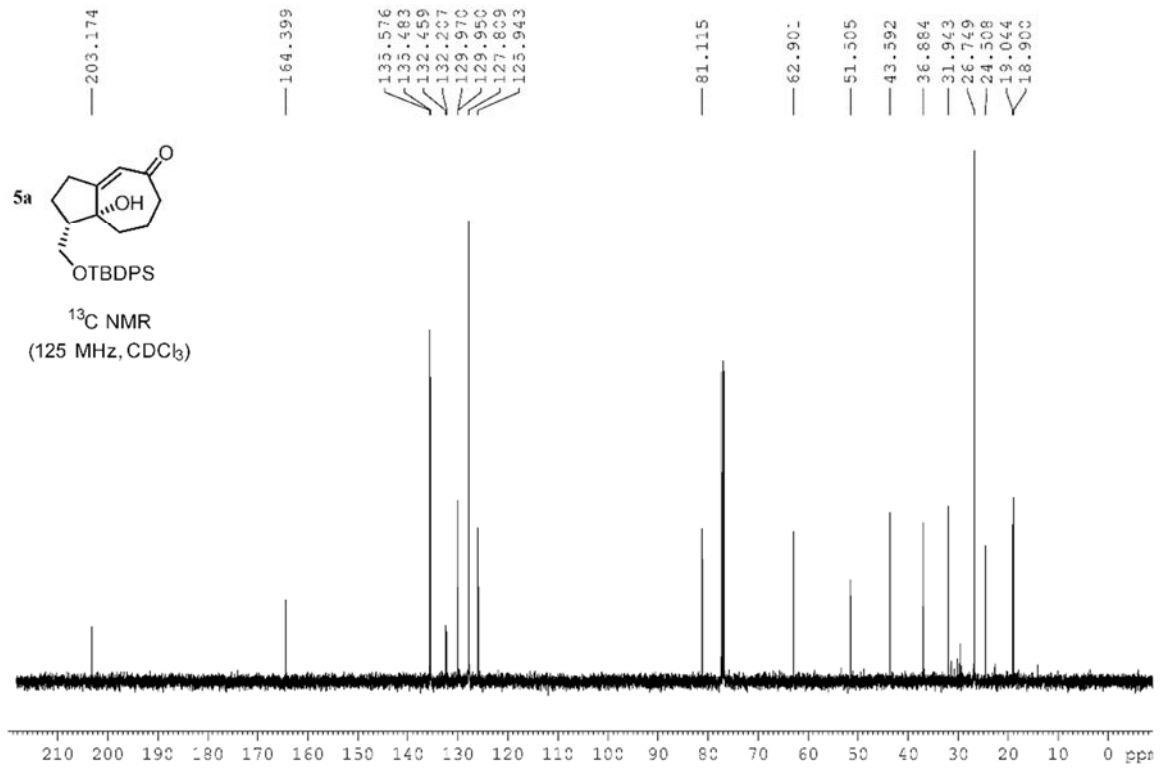

TMSO
2q
^{1}H NMR
(500 MHz, CDCl$_3$)
9
8
7
6
5
4
3
2
1
0
ppm
0.981
2.170
0.975
1.000
1.001
0.975
3.817
2.006
2.810
2.990
8.638

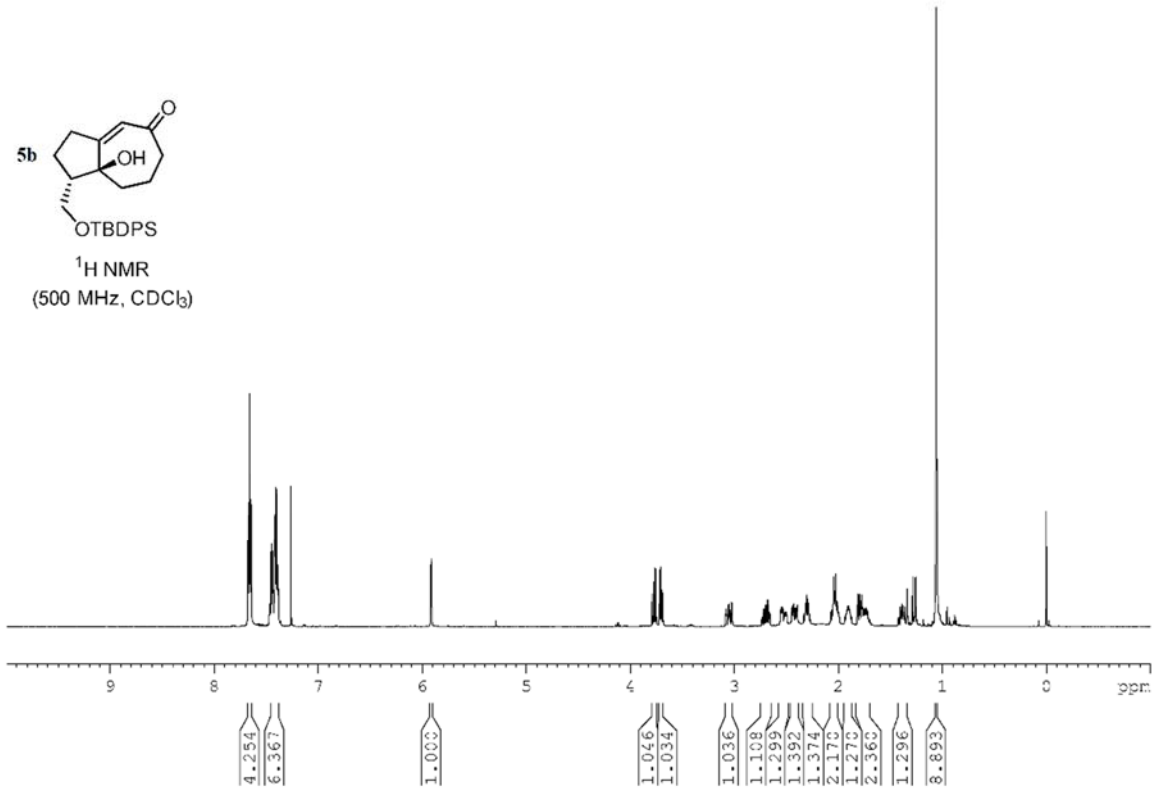

TMSO
2q
^{13}C NMR
(125 MHz, CDCl$_3$)
139.596
138.527
132.865
132.259
129.581
127.574
126.951
126.448
123.718
123.542
74.445
37.115
34.362
34.159
27.113
0.396
200
180
160
140
120
100
80
60
40
20
0 ppm

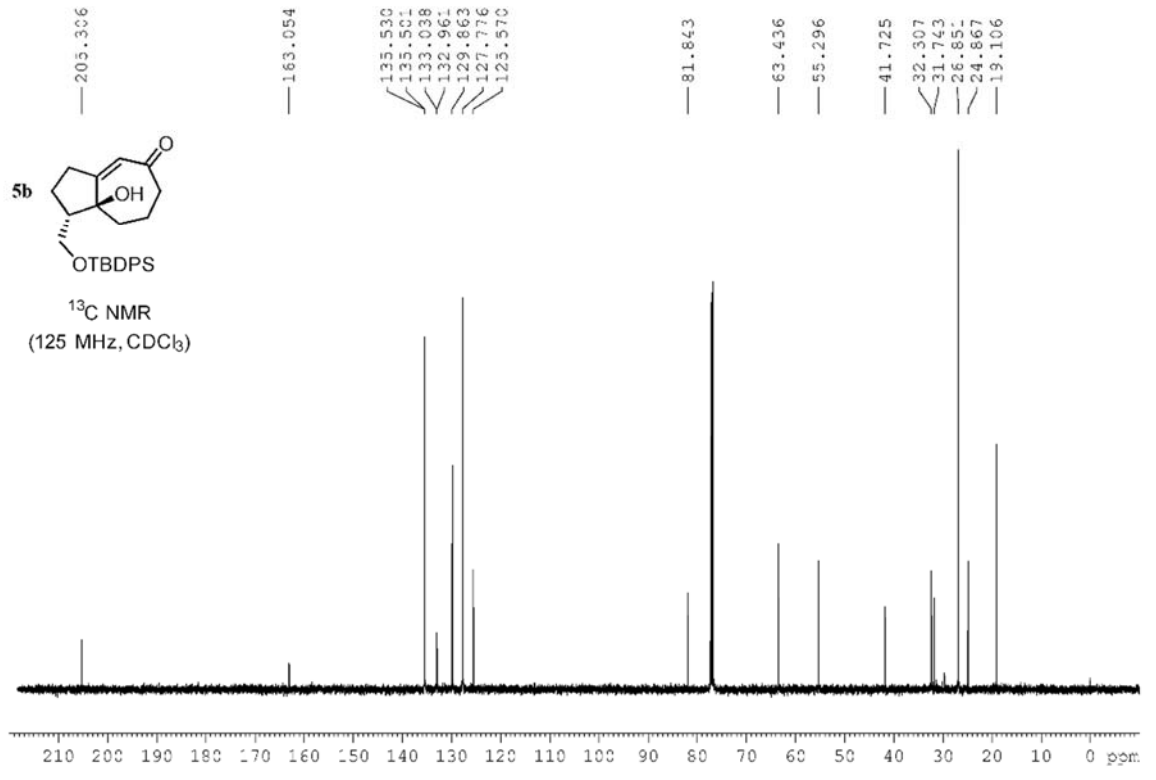

2r
HO
1H NMR
(500 MHz, CDCl3)
9
8
7
6
5
4
3
2
1
0
ppm
1.000
1.033
1.025
1.040
3.087
2.087
5.310
2.995
3.085

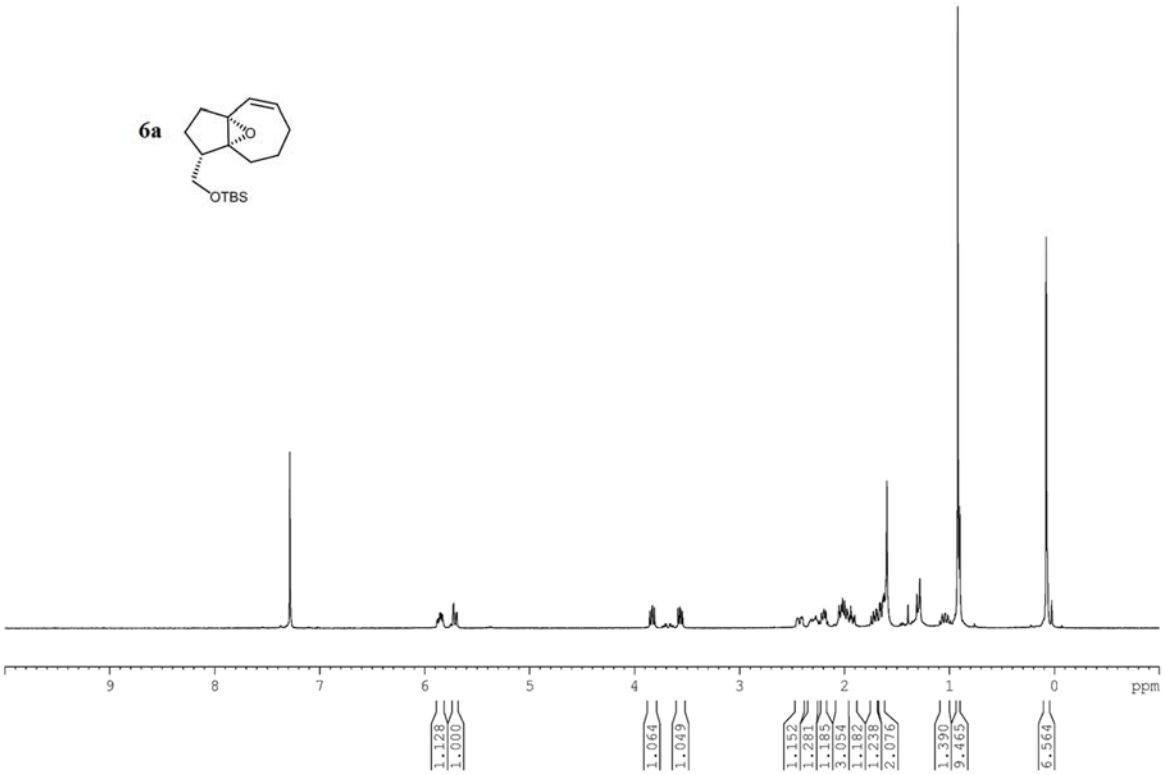

144.010
129.385
128.085
126.569
79.830
50.354
42.579
27.827
25.673
24.953
24.923
23.183
18.947
2r
HO
13C NMR
(125 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

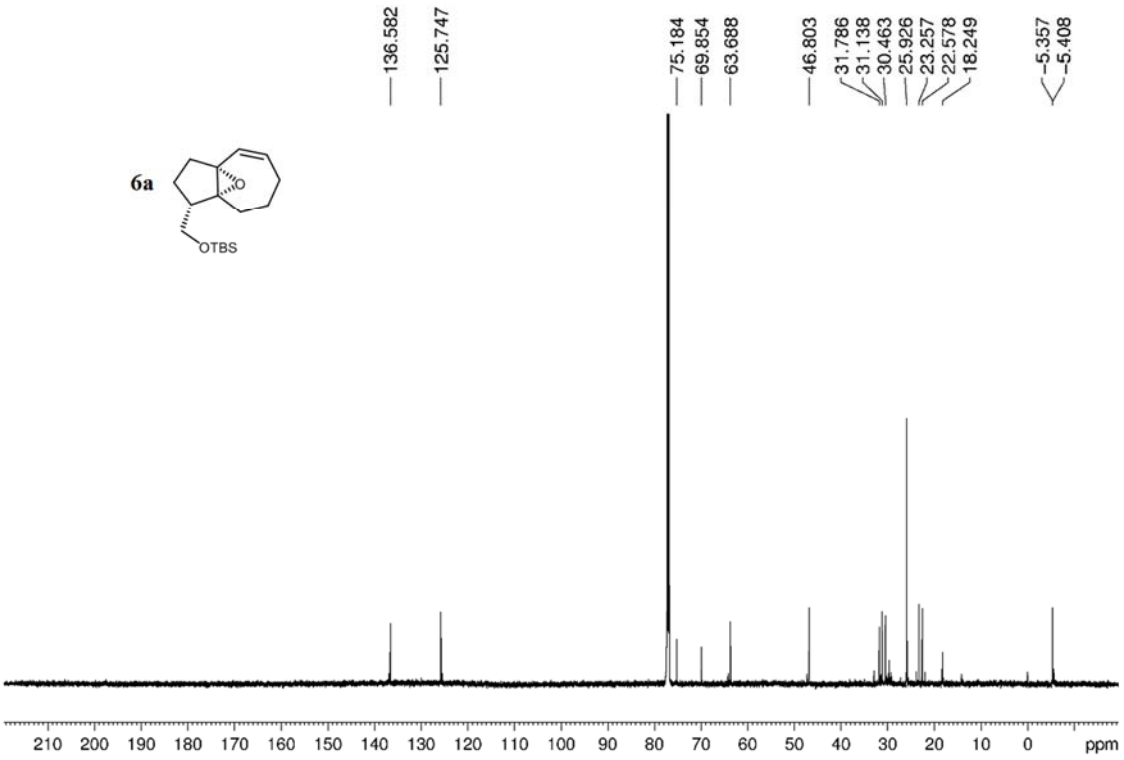

5a
OH
OTBDPS
^{1}H NMR
(400 MHz, $CDCl_3$)
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
4.333
6.434
1.000
0.983
0.973
1.008
1.007
1.025
2.085
1.371
1.592
1.055
3.018
1.422
9.413

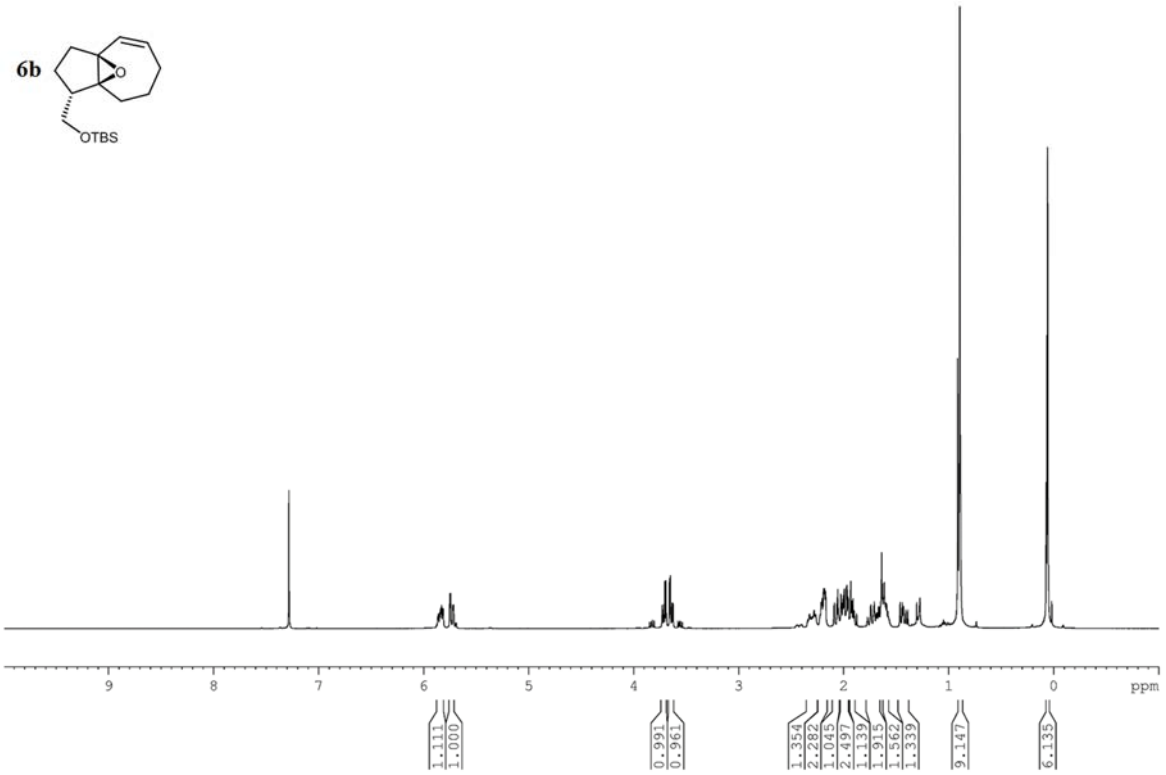

203.174
164.399
135.576
135.483
132.459
132.207
129.970
129.950
127.809
125.943
81.115
62.901
51.505
43.592
36.884
31.943
26.749
24.508
19.044
18.900
5a
OH
OTBDPS
^{13}C NMR
(125 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

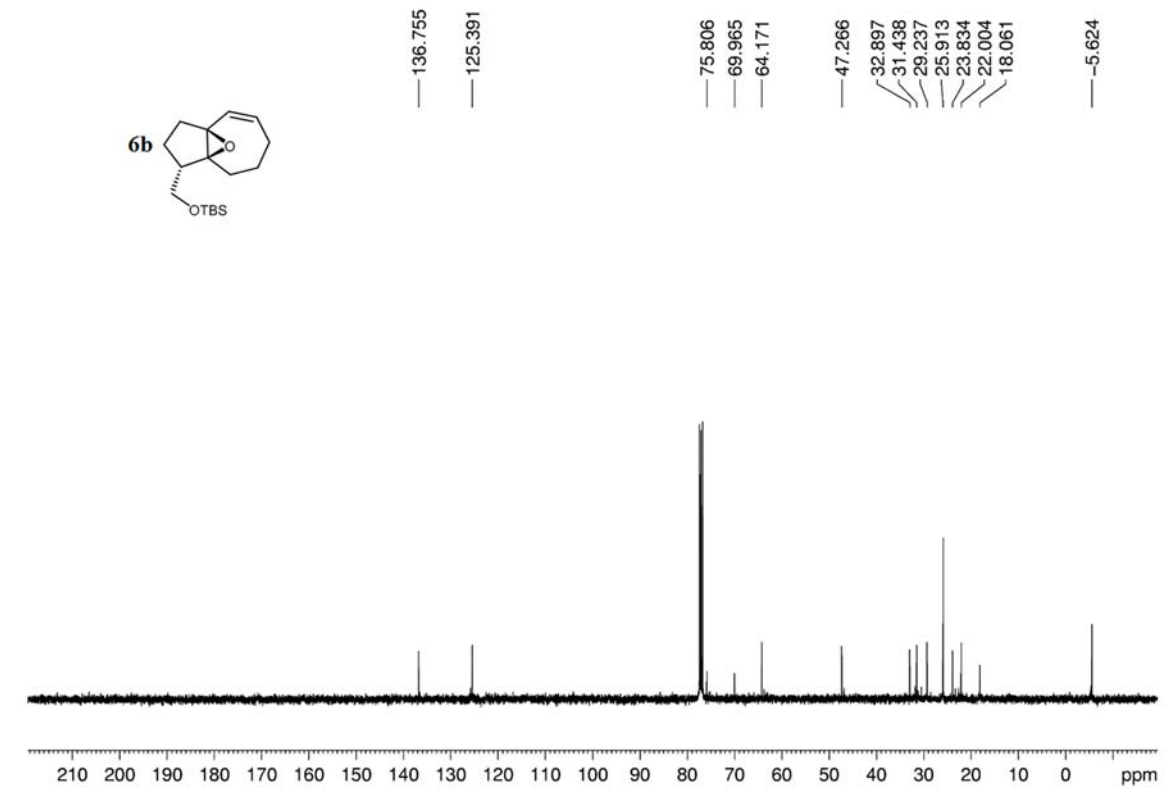

5b
OH
O
OTBDPS
^{1}H NMR
(500 MHz, CDCl$_3$)
9
8
7
6
5
4
3
2
1
0
ppm
4.254
6.367
1.000
1.046
1.034
1.036
1.108
1.299
1.392
1.374
2.178
1.278
2.360
1.296
8.893

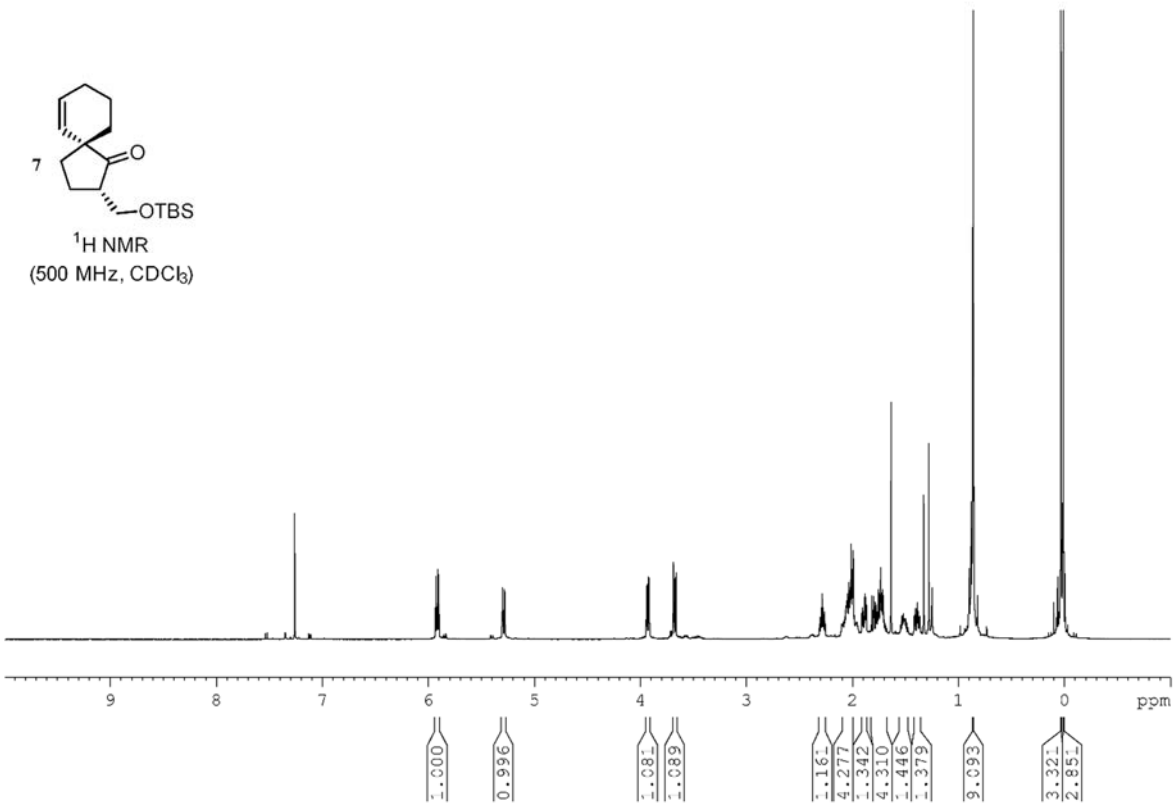

205.306
163.054
135.530
135.501
133.038
132.961
129.863
127.776
125.570
81.843
63.436
55.296
41.725
32.307
31.743
26.851
24.867
19.106
5b
OH
O
OTBDPS
^{13}C NMR
(125 MHz, CDCl$_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

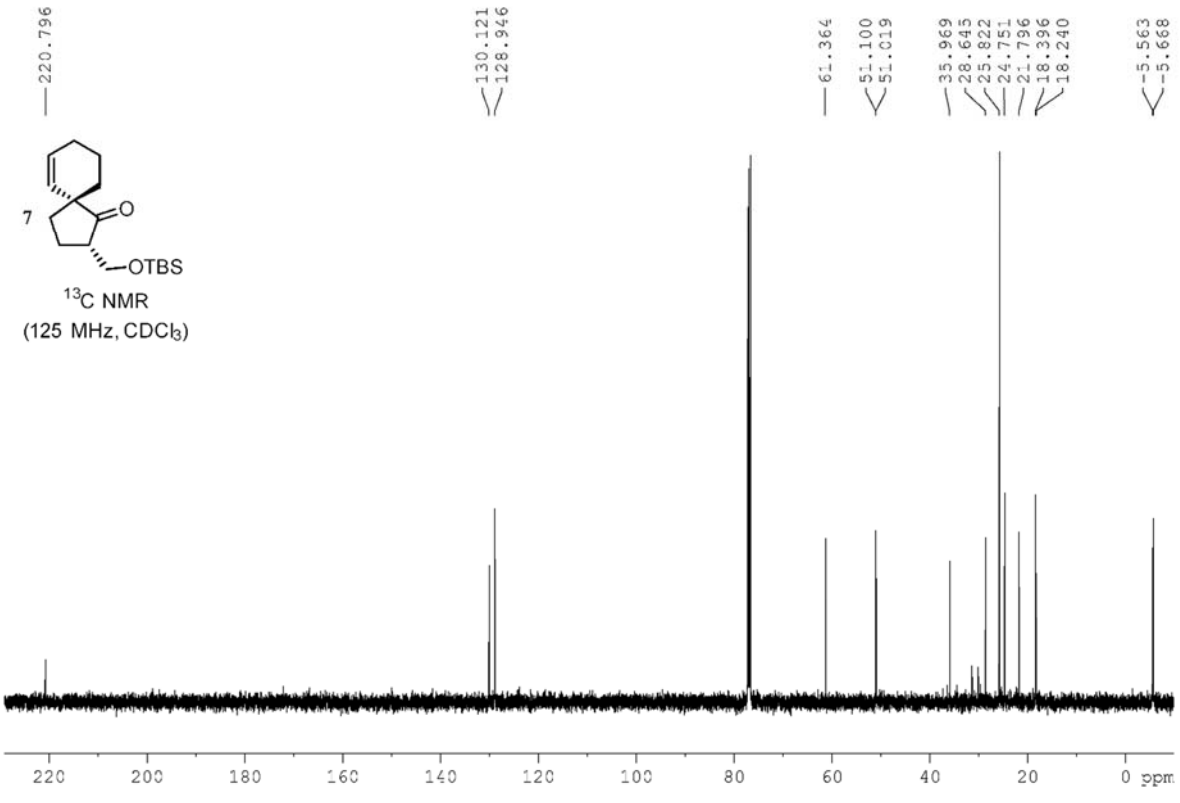

6a
OTBS
9
8
7
6
5
4
3
2
1
0
ppm
1.128
1.000
1.064
1.049
1.152
1.281
1.185
3.054
1.182
1.238
2.076
1.390
9.465
6.564

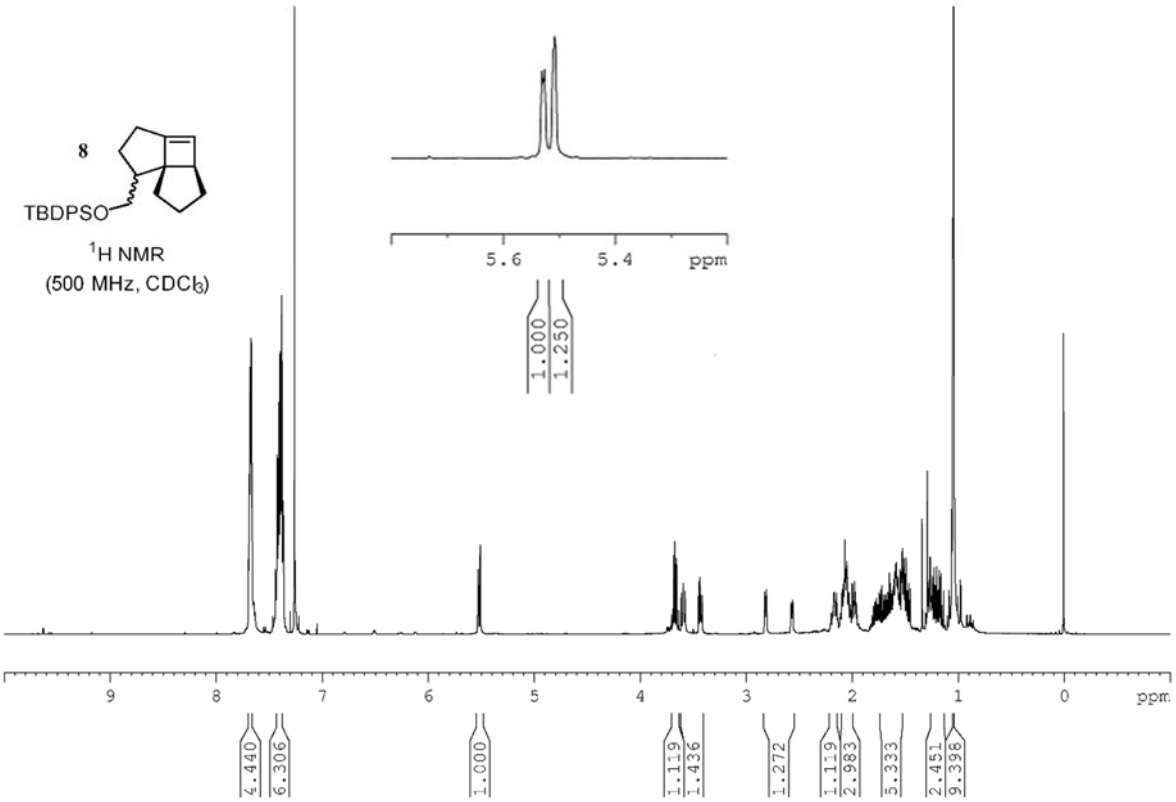

136.582
125.747
75.184
69.854
63.688
46.803
31.786
31.138
30.463
25.926
23.257
22.578
18.249
-5.357
-5.408
6a
OTBS
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

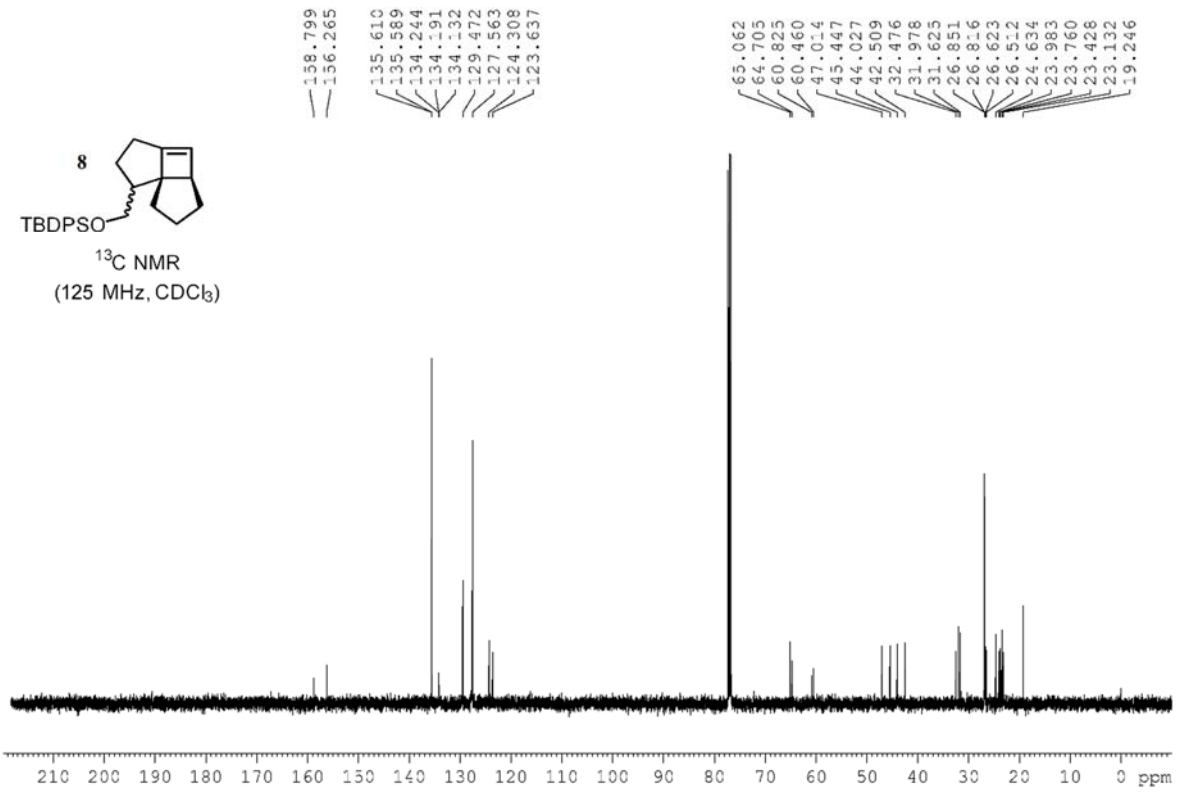

6b
OTBS
9
8
7
6
5
4
3
2
1
0
ppm
1.111
1.000
0.991
0.961
1.354
2.282
1.045
2.497
1.139
1.915
1.562
1.339
9.147
6.135

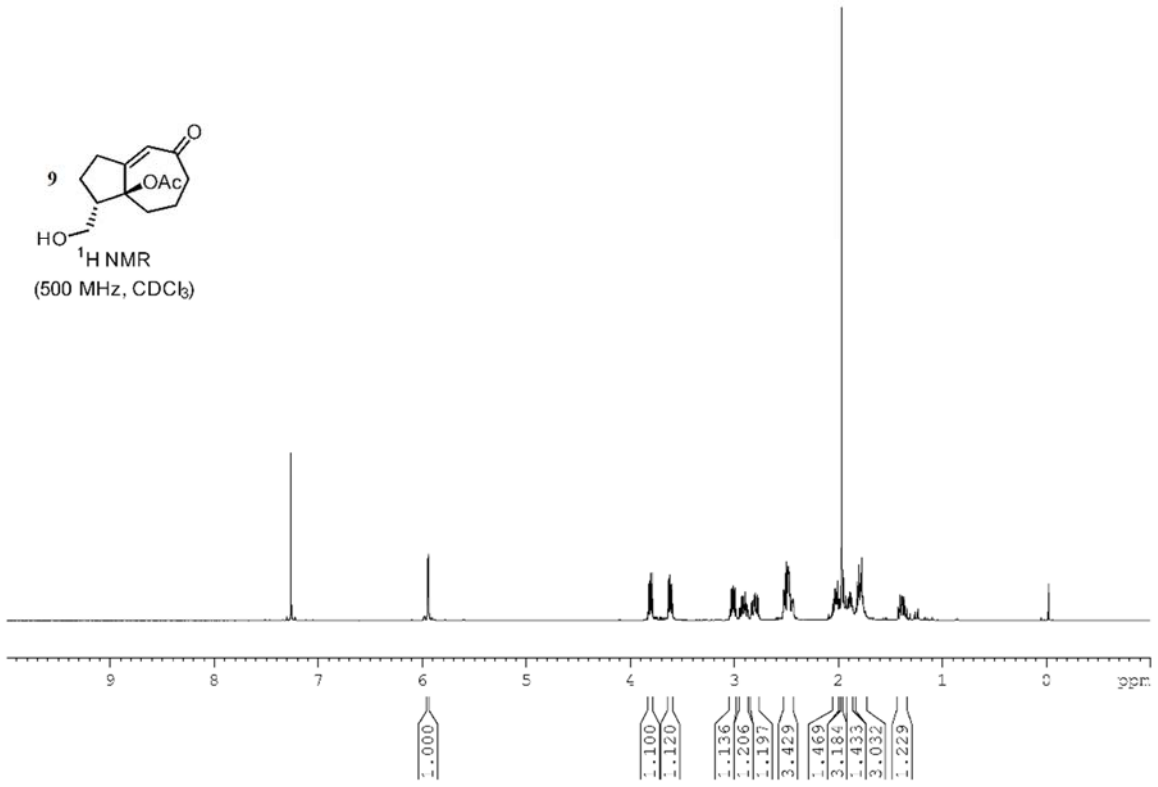

136.755
125.391
75.806
69.965
64.171
47.266
32.897
31.438
29.237
25.913
23.834
22.004
18.061
-5.624
6b
OTBS
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

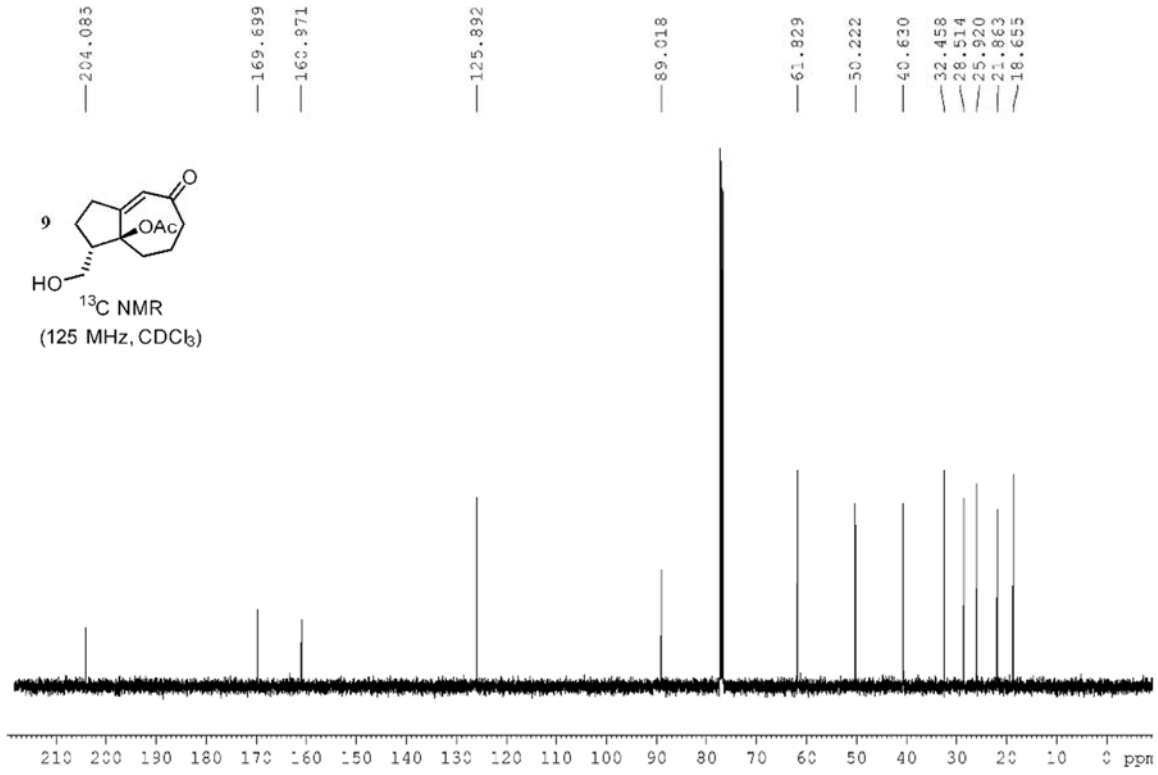

7
O
OTBS
1H NMR
(500 MHz, CDCl3)
9
8
7
6
5
4
3
2
1
0
ppm
1.000
0.996
1.081
1.089
1.161
4.277
1.342
4.310
1.446
1.379
9.093
3.321
2.851

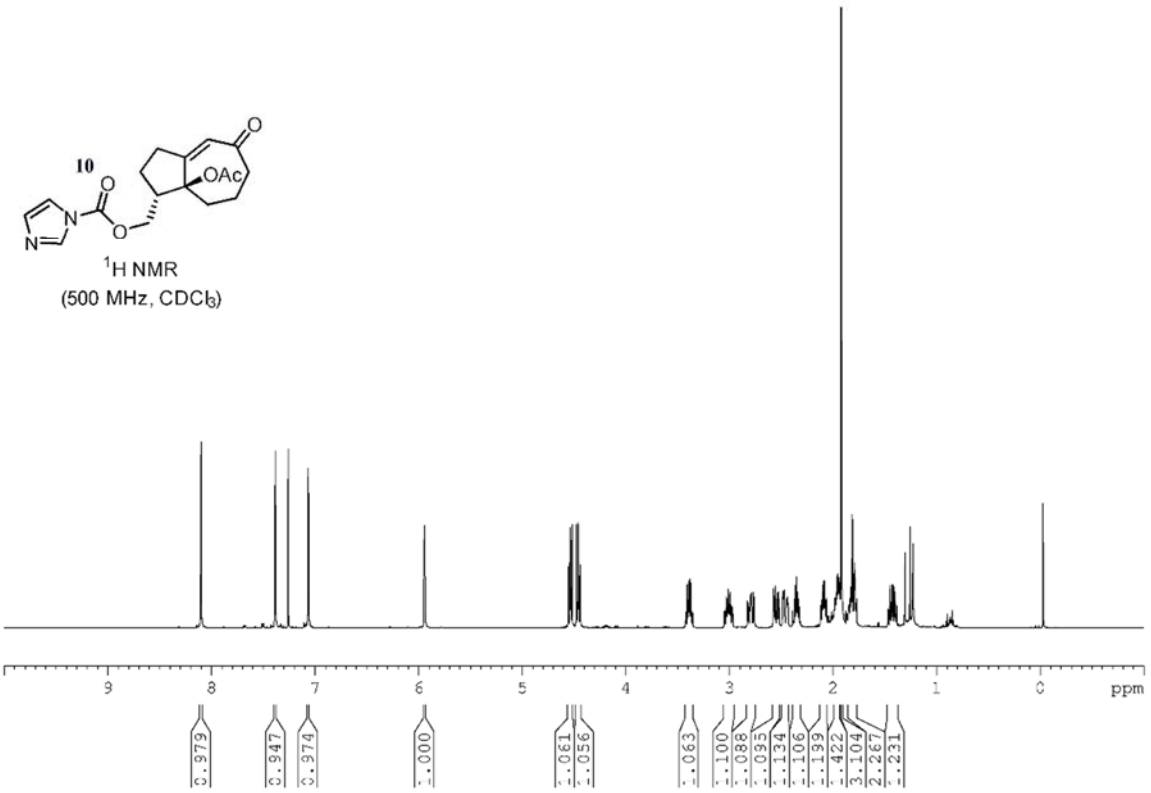

220.796
130.121
128.946
61.364
51.100
51.019
35.969
28.645
25.822
24.751
21.796
18.396
18.240
-5.563
-5.668
7
O
OTBS
13C NMR
(125 MHz, CDCl3)
220
200
180
160
140
120
100
80
60
40
20
0 ppm

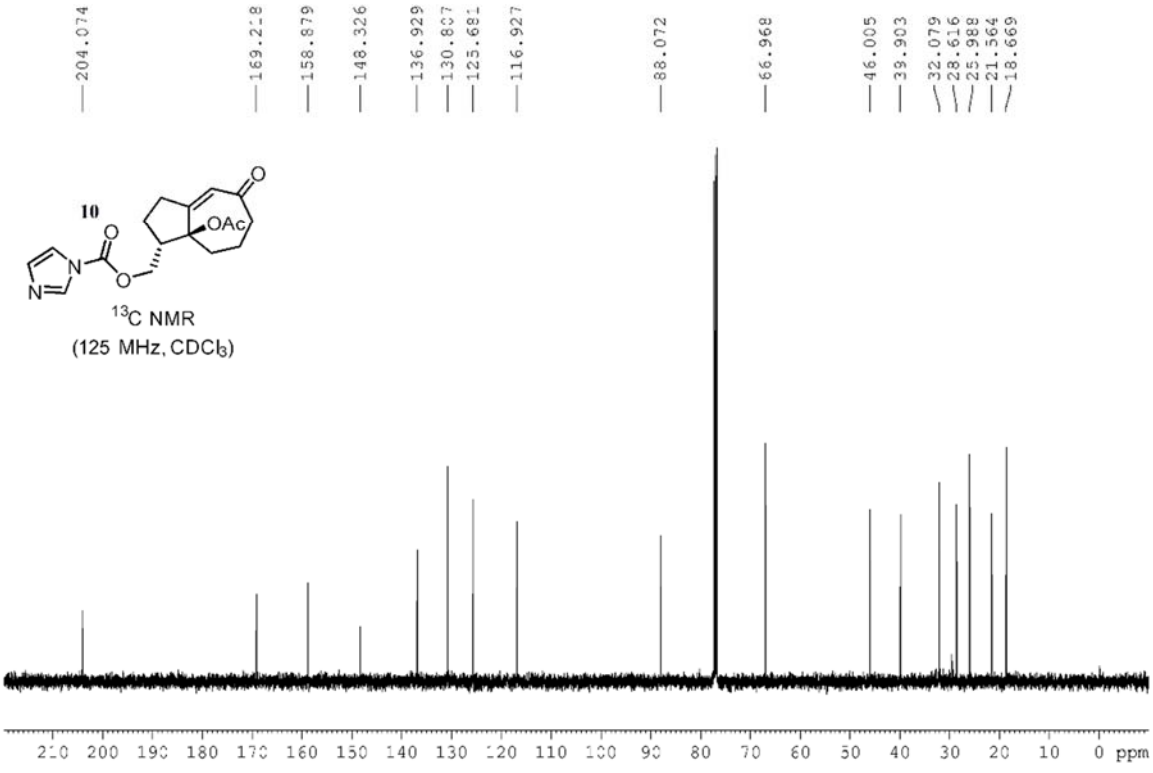

8
TBDPSO
^{1}H NMR
(500 MHz, CDCl$_3$)
5.6
5.4
ppm
1.000
1.250
9
8
7
6
5
4
3
2
1
0
ppm
4.440
6.306
1.000
1.119
1.436
1.272
1.119
2.983
5.333
2.451
9.398

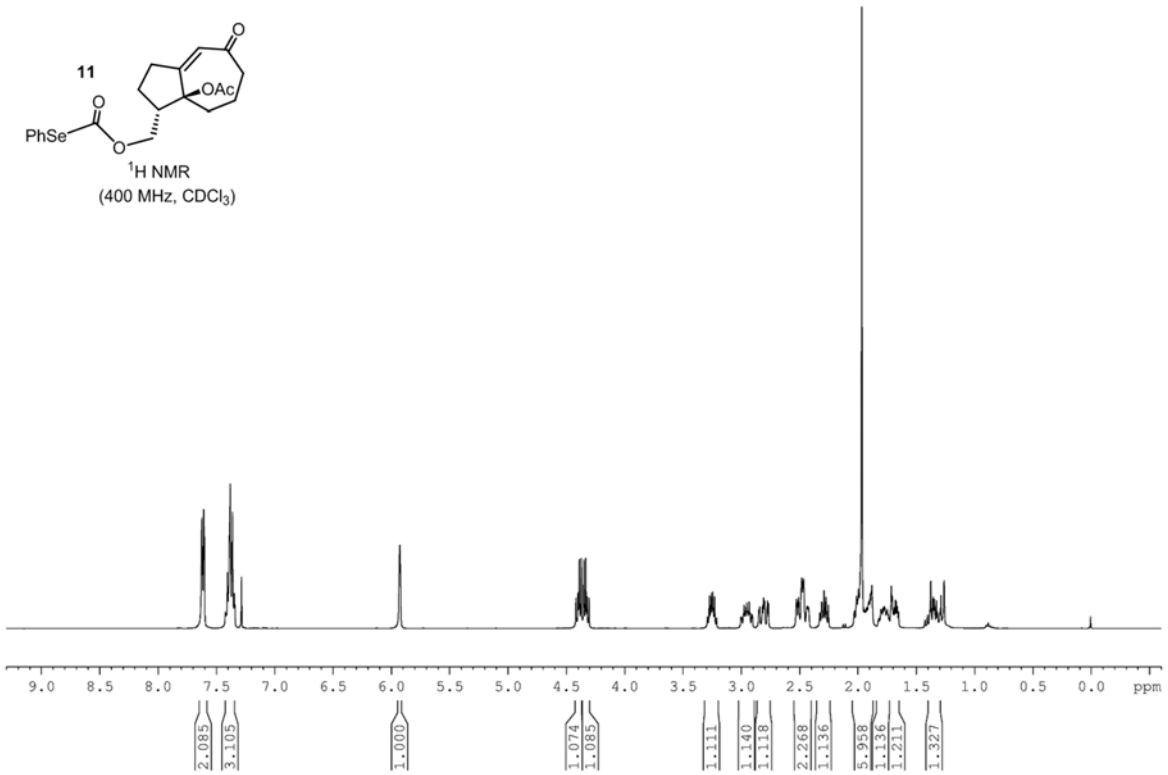

158.799
156.265
135.610
135.589
134.244
134.191
134.132
129.472
127.563
124.308
123.637
65.062
64.705
60.825
60.460
47.014
45.447
44.027
42.509
32.476
31.978
31.625
26.851
26.816
26.623
26.512
24.634
23.983
23.760
23.428
23.132
19.246
8
TBDPSO
^{13}C NMR
(125 MHz, CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

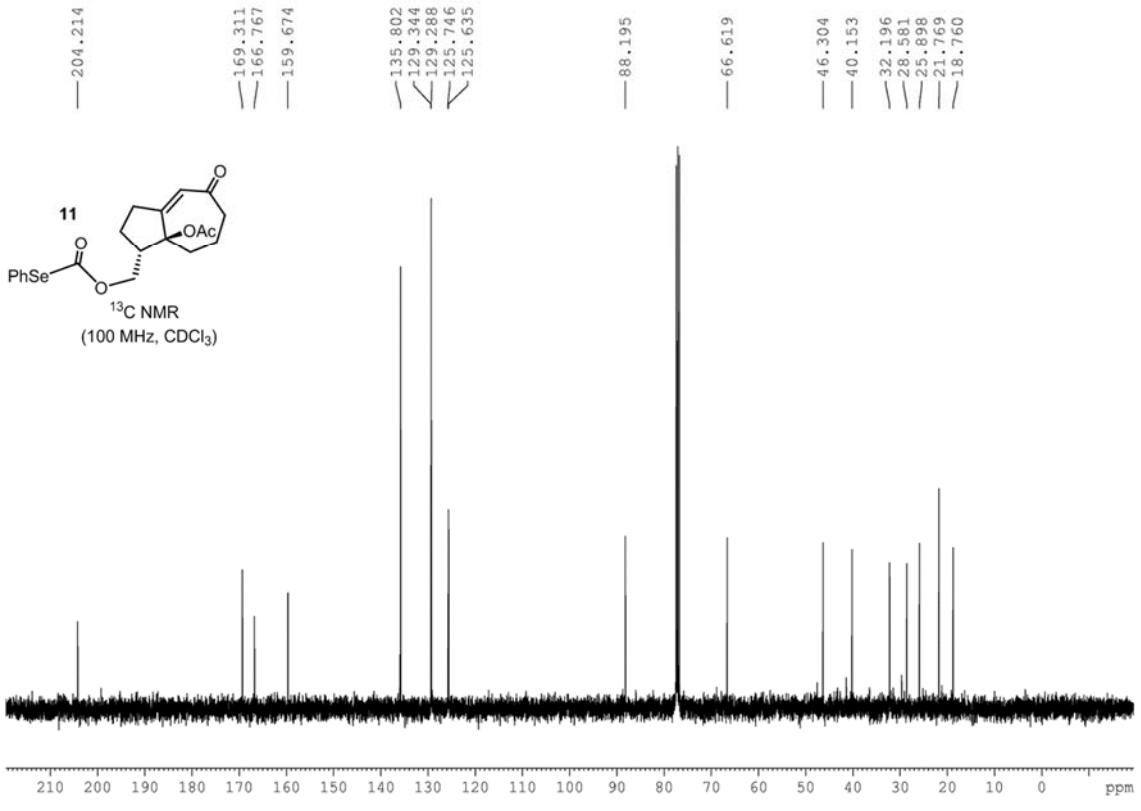

9
OAc
O
HO
^{1}H NMR
(500 MHz, CDCl$_3$)
9
8
7
6
5
4
3
2
1
0
ppm
1.000
1.100
1.120
1.136
1.206
1.197
3.429
1.469
3.184
1.433
3.032
1.229

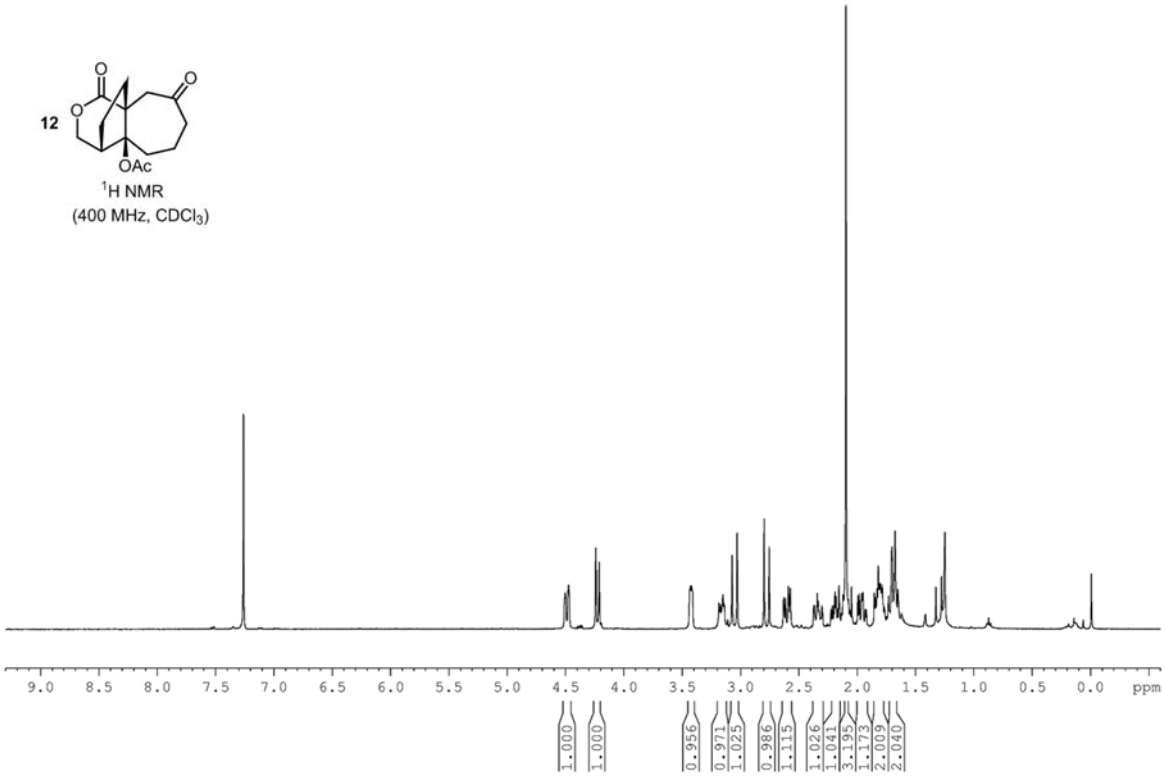

204.085
169.699
160.971
125.892
89.018
61.929
50.222
40.630
32.458
28.514
25.920
21.863
18.655
9
OAc
O
HO
^{13}C NMR
(125 MHz, CDCl$_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

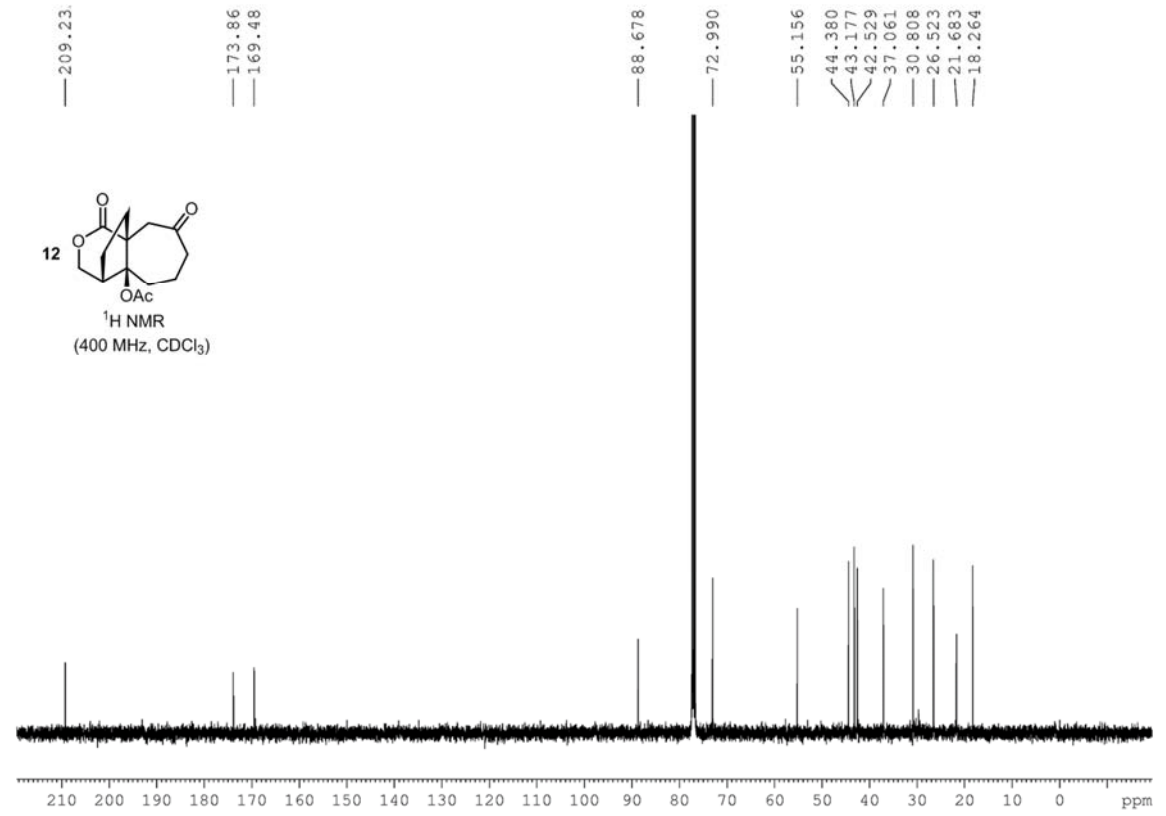

10
OAc
^{1}H NMR
(500 MHz, CDCl$_3$)
9
8
7
6
5
4
3
2
1
0
ppm
0.979
0.947
0.974
1.000
1.061
1.056
1.063
1.100
1.088
1.095
1.134
1.106
1.199
1.422
3.104
2.267
1.231


204.074
169.218
158.879
148.326
136.929
130.807
125.681
116.927
88.072
66.968
46.005
39.903
32.079
28.616
25.988
21.564
18.669
10
OAc
^{13}C NMR
(125 MHz, CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


11
OAc
PhSe
O
O
O
^{1}H NMR
(400 MHz, CDCl$_3$)
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.085
3.105
1.000
1.074
1.085
1.111
1.140
1.118
2.268
1.136
5.958
1.136
1.211
1.327


204.214
169.311
166.767
159.674
135.802
129.344
129.288
125.746
125.635
88.195
66.619
46.304
40.153
32.196
28.581
25.898
21.769
18.760
11
OAc
PhSe
O
O
O
^{13}C NMR
(100 MHz, CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


12
OAc
^{1}H NMR
(400 MHz, $CDCl_3$)
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.000
1.000
0.956
0.971
1.025
0.986
1.115
1.026
1.041
3.195
1.173
2.009
2.040


209.23
173.86
169.48
88.678
72.990
55.156
44.380
43.177
42.529
37.061
30.808
26.523
21.683
18.264
12
OAc
^{1}H NMR
(400 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm