Supporting Information for:

Cycloisomerization of Allene-Enol Ethers under $Bi(OTf)_3$ Catalysis

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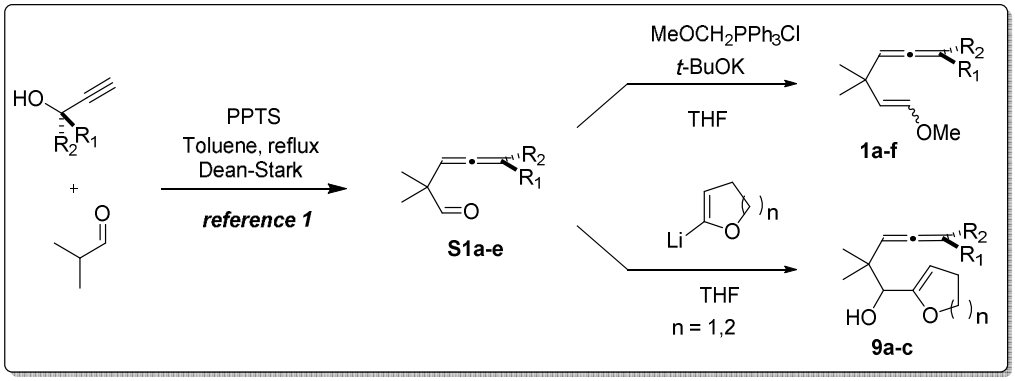
I General Experimental

Unless otherwise stated, reactions were conducted in flame-dried glassware under an atmosphere of nitrogen using anhydrous solvents. All solvents were used freshly distilled. THF and Et_2O were distilled over sodium-benzophenone/ketyl. CH_2Cl_2 and DMF were distilled over calcium hydride; CH_3NO_2 was dried over $CaCl_2$ and Et_3N was distilled from KOH. *n*-Butyllithium was purchased as a 2.5 M solution in hexanes. Other reagents and catalyst were commercially available and used reagent-grade without further purification, unless otherwise stated. NMR spectra (^1H, ^{13}C, DEPT, COESY, and NOESY) were recorded at room temperature (rt, approximately 25 °C), on a BRUKER AC 200 spectrometer or on a BRUKER AVANCE 500 spectrometer. HMQC, HMBC, HSQC correlations were used to identify the structure of some of the compounds synthesized. The chemical shift (δ) data for each signal is given in parts per million (ppm). The residual $CHCl_3$ was applied as an internal standard (δ = 7.26 ppm) for ^1H spectra while the $CDCl_3$ signal served as internal standard (δ = 77.0) for ^{13}C spectra. The coupling constants (*J*) are quoted in Hertz (Hz) and are recorded to the nearest 0.1 Hz. The multiplicity of each signal is indicated by: (s): singlet, (d): doublet, (t): triplet, (q): quartet, (sept): septet, (m): multiplet. High resolution mass spectrometry (HRMS) was performed at ERINI platform (Grasse, FRANCE) using a Waters APGC coupled with a Waters Xevo G2 QTOF spectrometer. Infrared spectra (IR) were recorded on a JASCO FT/IR-4600 (ATR diamond) spectrometer. Absorption maxima are reported in wavenumbers (cm^{-1}). All reactions were monitored by analytical Thin Layer Chromatography (TLC) carried out on 0.2 mm precoated plates Kieselgel MERCK 60F 254, thickness: 0.25 mm). Column chromatography was carried out over silica gel (spherical, neutral, 40-60 µm, Geduran Si 60, Merck KGaA). Petroleum ether used in column chromatography had a boiling range of 40-60 °C. Analytical GC/MS analyses were performed on a Shimadzu QP2010S-MS chromatograph (EI 70 eV).

II Experimental procedures

II.1 Synthesis of starting materials

The starting allenic enol ethers were mainly synthesized from the corresponding aldehydes obtained through a known Claisen-Cope rearrangement of propargyl vinyl ethers.[1] A Wittig-type olefination with (methoxymethylene)triphenylphosphane or addition of a lithiated cyclic enol ether gave rise to the cyclisation precursors (Scheme 1).



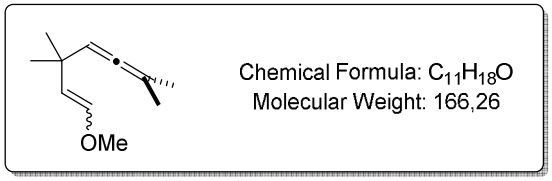
Scheme1

II.1.a Synthesis of allenic substrates 1a-f, 3 and 5

General procedure 1: Synthesis of allenic enol-ether (Wittig reaction)

A solution of potassium *tert*-butoxide, (1.35 eq.) in THF (2.1 M) was added dropwise to a stirred and ice-cooled suspension of methoxymethylenetriphenyl phosphonium chloride (1.50 eq., previously dried for 2 h under vacuum) in THF (0.5 M). After 30 min of stirring, a solution of the allenic aldehyde (1.0 eq.) in THF (1.2 M) was added dropwise to the red reaction mixture. After 2 h stirring at room temperature, the reaction was quenched with water. The organic layer was separated and the aqueous phase was extracted with Et_2O. The combined organic layers were washed with water and brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude residue was then stirred in petroleum ether (100 mL) for 30 min. The precipitate was filtered off, and the filtrate was concentrated. Purification by column chromatography over silica gel (PE/Et_2O 99:1) afforded the expected allenic enol-ether.

1-methoxy-3,3,6-trimethylhepta-1,4,5-triene 1a

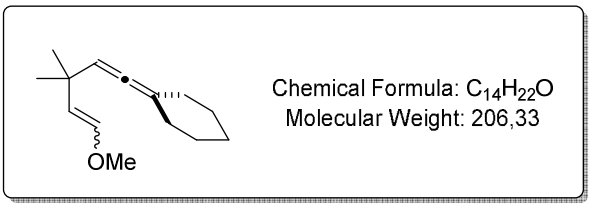


Allenic enol-ether **1a** (3.60 g, 60%, *trans/cis* 1.0:0.55), was obtained as a colourless oil following **general procedure 1** from the corresponding allenic aldehyde (5.00 g, 36.1 mmol).

[1] R. S. Bly, S. U. Koock, *J. Am. Chem. Soc.* **1969**, *91*, 3292–3298.

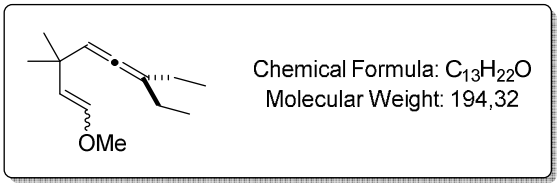
Cis isomer: **^{1}H NMR** (200 MHz, $CDCl_3$) δ 5.71 (d, *J* = 6.8 Hz, 1H), 5.16 (sept, *J* = 2.9 Hz, 1H), 4.29 (d, *J* = 6.9 Hz, 1H), 3.55 (s, 3H), 1.69 (d, *J* = 2.8 Hz, 6H), 1.18 (s, 6H). **^{13}C NMR** (50 MHz, $CDCl_3$) δ 198.7, 145.3, 115.0, 100.0, 96.9, 59.7, 35.4, 29.0, 20.8.
Trans isomer: **^{1}H NMR** (200 MHz, $CDCl_3$) δ 6.29 (d, *J* = 12.8 Hz, 1H), 4.92 (sept, *J* = 2.8 Hz, 1H), 4.81 (d, *J* = 12.9 Hz, 1H), 3.49 (s, 3H), 1.69 (d, *J* = 2.9 Hz, 6H), 1.09 (s, 6H). **^{13}C NMR** (50 MHz, $CDCl_3$) δ 199.3, 145.4, 113.8, 99.5, 97.1, 55.9, 35.0, 29.1, 20.8. **IR** (neat): 2961, 2932, 2868, 1393, 1457, 1361, 1106 cm^{-1}. **MS** (EI, 70 eV): $[M]^{\bullet+}$ 166 (0.17), 123 (100), 95 (98), 81 (19), 79 (19), 77 (16), 69 (27), 67 (45), 55 (35), 43 (65). **HRMS** (APGC) *m/z* calcd. for $C_{11}H_{18}O$ $[M]^{\bullet+}$: 166.1358, found: 166.1354.

1-methoxy-5-cyclohexylidene-3,3-dimethylbut-1,4-diene 1b



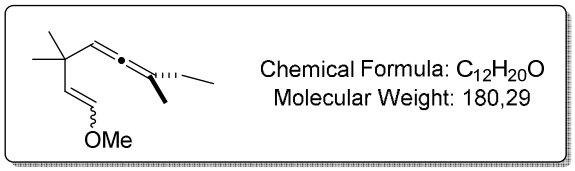
Allenic enol ether **1b** (2.32 g, 67%, trans/cis 1.0:0.84) was obtained as a colourless oil following **general procedure 1** from the corresponding allenic aldehyde (3.00 g, 16.8 mmol). **^{1}H NMR** (200 MHz, $CDCl_3$) δ 6.30 (d, *J* = 12.9 Hz, 1H *trans*), 5.72 (d, *J* = 6.9 Hz, 1H *cis*), 5.19 (s, 1H *cis*), 4.94 (s, 1H *trans*), 4.82 (d, *J* = 12.9 Hz, 1H *trans*), 4.29 (d, *J* = 6.9 Hz, 1H *cis*), 3.55 (s, 3H *cis*), 3.50 (s, 3H *trans*), 2.20-2.00 (m, 4H *cis* + 4H *trans*), 1.71-1.45 (m, 6H *cis* + 6H *trans*), 1.19 (s, 6H *cis* or *trans)*, 1.10 (s, 6H *cis* or *trans*). **^{13}C** NMR (50 MHz, $CDCl_3$) δ 195.9, 195.3, 145.4, 145.3, 115.1, 113.7, 104.7, 99.9, 99.4, 59.7, 55.9, 35.3, 34.8, 32.0, 32.0, 29.2, 29.0, 27.7, 27.6, 26.3, 26.2. **IR** (neat): 2924, 2853, 1966, 1649, 1458, 1205, 1103, 895 cm^{-1}. **MS** (EI, 70 eV): $[M]^{\bullet+}$ 206 (0.21), 195 (93), 177 (40), 107 (45), 124 (48), 93 (36), 91 (51), 67 (38), 55 (47), 43 (100). **HRMS** (APGC) *m/z* calcd. for $C_{14}H_{23}O$ $[MH]^{\bullet+}$: 207.1749, found: 207.1754.

6-ethyl-1-methoxy-3,3-dimethylocta-1,4,5-triene 1c



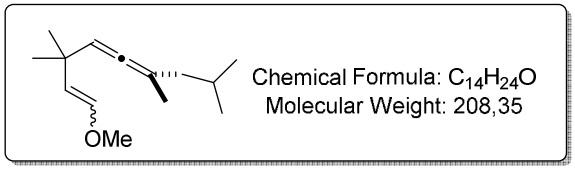
Allenic enol ether **1c** (449 mg, 64%, trans/cis 0.83:1.0) was obtained as a colourless oil following **general procedure 1** from the corresponding allenic aldehyde (600 mg, 3.61 mmol). **^{1}H NMR** (200 MHz, $CDCl_3$) δ 6.31 (d, *J* = 12.8 Hz, 1H *trans*), 5.71 (d, *J* = 6.9 Hz, 1H *cis*), 5.37 (m, 1H *trans*), 5.15 (m, 1H *cis*), 4.83 (d, *J* = 12.9 Hz, 1H *trans*), 4.29 (d, *J* = 6.9 Hz, 1H *cis*), 3.54 (s, 3H *trans*), 3.49 (s, 3H *cis*), 1.96 (qd, *J* = 7.3, 3.2 Hz, 4H *trans* + 4H *cis*), 1.19 (s, 6H *trans*), 1.09 (s, 6H *cis*), 0.99 (t, *J* = 7.3 Hz, 6H *trans* + 6H *cis*). **^{13}C NMR** (50 MHz, $CDCl_3$) δ (*cis/trans*) 197.4/196.8, 145.4/145.1, 115.2/113.9, 110.2/110.0, 104.3/103.7, 59.6, 55.9, 35.4, 34.9, 29.2, 29.0, 25.9, 25.8, 12.4, 12.4. **IR** (neat): 3029, 3000, 2964, 2933, 1459, 1211, 1106, 939 cm^{-1}. **MS** (EI, 70 eV): $[M]^{\bullet+}$ 194 (0.67), 123 (14), 119 (2), 100 (6), 99 (100), 91 (6), 69 (6), 67 (13), 65 (5), 55 (7). **HRMS** (APGC) *m/z* calcd. for $C_{13}H_{23}O$ $[MH]^{\bullet+}$: 195.1749, found: 195.1756.

1-methoxy-3,3,6-trimethylocta-1,4,5-triene 1d



Allenic enol ether **1d** (2.45 g, 70%, trans/cis 1.0:0.74), was obtained as a colourless oil following **general procedure 1** from the corresponding allenic aldehyde (3.00 g, 19.7 mmol). **H^1 NMR** (200 MHz, $CDCl_3$) δ 6.30 (d, *J* = 12.8 Hz, 1H *trans*), 5.71 (d, *J* = 6.8 Hz,1H *cis*), 5.31-5.22 (m, 1H *cis*), 5.08-4.99 (m, 1H *trans*), 4.82 (d, *J* = 12.8 Hz, 1H *trans*), 4.29 (d, *J* = 6.8 Hz, 1H *cis*), 3.55 (s, 3H *cis*), 3.49 (s, 3H *trans*), 1.94 (qd, *J* = 7.4, 3.2 Hz, 2H *cis* + 2H *trans*),1.69 (d, *J* = 2.8 Hz, 3H *cis* + 3H *trans*), 1.19 (s, 3H *cis*), 1.18 (s, 3H *cis*),1.09 (s, 6H *trans*), 0.99 (t, *J* = 7.4 Hz, 3H *cis* + 3H *trans*). **^{13}C NMR** (50 MHz, $CDCl_3$) δ (*cis/trans*) 198.3/197.7, 145.4/145.3, 115.1/113.9, 103.4/103.2, 102.1/101.5, 59.6/55.9, 35.4/35.0, 29.2/29.1, 29.0, 27.2/27.1, 19.4, 12.3. **MS** (EI, 70 eV): $[M]^{\bullet+}$ 180 (1), 123 (17), 100 (7), 99 (100), 91 (8), 69 (7), 67 (15), 65 (6), 53 (7), 45 (12). **HRMS** (APGC) *m/z* calcd. for $C_{12}H_{21}O$ $[MH]^{\bullet+}$: 181.1592, found: 181.1595.

1-methoxy-3,3,6,8-tetramethylnona-1,4,5-triene 1e

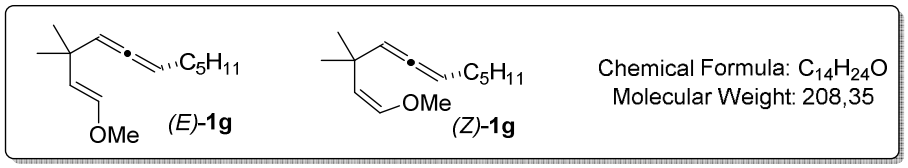


Allenic enol ether **1e** (2.48 g, 72%, trans/cis 1.0:0.52), was obtained as a colourless oil following **general procedure 1** from the corresponding allenic aldehyde (3.00 g, 16.6 mmol).

***Cis*-isomer**: **H^1 NMR** (200 MHz, $CDCl_3$) δ 5.71 (d, *J* = 6.8 Hz, 1H), 5.25-5.16 (m, 1H), 4.30 (d, *J* = 6.8 Hz, 1H), 3.55 (s, 3H), 1.89-1.72 (m, 3H), 1.65 (d, *J* = 2.9 Hz, 3H), 1.19 (s, 6H, H12,), 0.90 (d, *J* = 6.2 Hz, 6H). **^{13}C NMR** (50 MHz, $CDCl_3$) δ 189.5, 145.3, 115.2, 100.7, 100.2, 59.6, 44.0, 35.5, 29.1, 29.0, 26.4, 22.8, 22.6, 19.4.

***Trans*-isomer:** **H^1 NMR** (200 MHz, $CDCl_3$) δ 6.29 (d, *J* = 12.9 Hz, 1H), 4.98-4.94 (m, 1H), 4.82 (d, *J* = 12.8 Hz, 1H), 3.49 (s, 3H), 1.90-1.70 (m, 3H), 1.65 (d, *J* = 2.9 Hz, 3H), 1.10 (s, 6H), 0.91-0.84 (m, 6H). **^{13}C NMR** (50 MHz, $CDCl_3$) δ 199.4, 145.4, 113.9, 100.4, 100.0, 55.9, 44.0, 35.0, 29.2, 26.4, 22.7, 22.6, 19.4. **MS** (EI, 70 eV): $[M]^{\bullet+}$ 99 (100), 41 (29), 45 (16), 67 (12), 73 (10), 43 (9), 100 (7), 59 (6), 91 (6), 69 (6), 208 (1). **IR** (neat): 2955, 2929, 2868, 1658, 1461, 1389, 1282, 1102, 725 cm^{-1}. **HRMS** (APGC) *m/z* calcd. for $C_{14}H_{25}O$ $[MH]^{\bullet+}$: 209.1905, found: 209.1902.

1-methoxy-3,3,6-trimethylocta-1,4,5-triene 1f

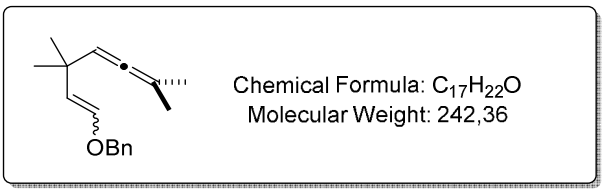


Allenic enol ethers (*E*)-**1f** and (*Z*)-**1f** (2.43 g, 70%, trans/cis 1.0:0.51) were obtained as colourless oils following **general procedure 1** from the corresponding allenic aldehyde (3.00 g, 16.6 mmol).

***(Z)*-1f: ^{1}H NMR** (200 MHz, $CDCl_3$) δ 5.72 (d, *J* = 6.8 Hz, 1H), 5.34-5.17 (m,1H), 5.17 (m, 1H), 4.29 (d, *J* = 6.8 Hz, 1H), 3.55 (s, 3H), 2.07-1.89 (m, 2H), 1.45-1.24 (m, 6H), 1.21 (s, 3H), 1.20 (s, 3H), 0.88 (t, *J* = 6.6 Hz, 3H). **^{13}C NMR** (50 MHz, $CDCl_3$) δ 200.9, 145.4, 114.7, 102.0, 93.2, 59.7, 35.0, 31.4, 29.2, 29.0 (2C), 28.9, 22.5, 14.1.

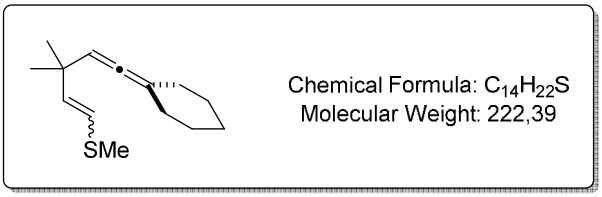
***(E)*-1f: ^{1}H NMR** (200 MHz, $CDCl_3$) δ 6.30 (d, *J* = 12.9 Hz, 1H), 5.25-5.17 (m, 1H), 5.17-5.03 (m, 1H), 4.82 (d, *J* = 12.9 Hz, 1H), 3.49 (s, 3H), 2.04-1.93 (m, 2H), 1.45-1.23 (m, 6H), 1.11 (s, 6H), 0.89 (t, *J* = 6.6 Hz, 3H). **^{13}C NMR** (50 MHz, $CDCl_3$) δ 201.4, 145.5, 113.5, 101.6, 93.3, 55.9, 34.5, 31.4, 29.1, 29.1, 29.00, 28.9, 22.5, 14.0. **IR** (neat): 2959, 2927, 2858, 1960, 1724, 1724, 1649, 1465, 1218, 1117, 939, 877 cm^{-1}. **MS** (EI, 70 eV): $[M]^{\bullet+}$ 208 (0.04), 123 (18), 100 (7), 99 (100), 91 (8), 69 (6), 67 (13), 55 (7), 45 (16), 43.10 (9). **HRMS** (APGC) *m/z* calcd. for $C_{14}H_{24}O$ $[M]^{\bullet+}$: 208.1827, found: 208.1831.

Allenic enol ether 3



Allenic enol ether **3** was obtained following a slightly modified literature procedure.[2] To a suspension of (benzyloxymethyl)triphenyl phosphonium chloride[3] (4.00 g, 9.56 mmol) in anhydrous THF (32 mL) and at -78 °C, was added KHMDS (0.7 M in toluene, 13.6 mL, 9.56 mmol) dropwise. The reaction mixture was then warmed up to -40 °C and stirred for 30 min. The deep red reaction mixture was cooled again to -78 °C and a solution of the corresponding allenic aldehyde (1.13 g, 8.2 mmol) in THF (8 ml) was added dropwise. After stirring at room temperature overnight, a saturated aqueous solution of NH_4Cl was added. The organic layer was separated and the aqueous phase was extracted with EtOAc. The combined organic layers were washed with water and brine, dried over $MgSO_4$ and concentrated. The crude residue was purified by column chromatography over silica gel (PE/Et_2O 99:1) to give the expected allenic enol ether **3** (500 mg, 25%, *cis*/*trans* 1.0:0.60) as a colourless oil. **^{1}H NMR** (200 MHz, $CDCl_3$) δ 7.31 (m, $5H_{cis}$ + $5H_{trans}$), 6.36 (d, *J* = 12.8 Hz, $1H_{trans}$), 5.88 (d, *J* = 6.9 Hz, $1H_{cis}$), 5.29-5.18 (m, $1H_{trans}$), 4.99 (d, *J* = 12.9 Hz, $1H_{trans}$), 4.97-4.87 (m, $1H_{cis}$), 4.79 (s, $2H_{cis}$), 4.70 (s, $2H_{trans}$), 4.36 (d, *J* = 6.9 Hz, $1H_{cis}$), 1.69 (d, *J* = 2.8 Hz, 24H, $12H_{cis}$ + $12H_{trans}$), 1.23 (s, $6H_{cis}$), 1.11 (s, $6H_{trans}$).**^{13}C NMR** (50 MHz, CDC_{l3}) δ 199.3, 198.6, 144.4, 143.6, 137.8, 137.3, 128.4, 128.4, 127.8, 127.7, 127.6, 127.1, 115.5, 115.4, 100.1, 99.3, 97.1, 97.0, 77.6, 77.0, 76.4, 73.9, 71.1, 35.4, 35.1, 29.0, 29.0, 20.8, 20.8. **IR** (neat): 3031, 2930, 2866, 2961, 1656, 1496, 1455, 1110, 733, 606 cm^{-1}. **MS** (EI, 70 eV): $[M]^{\bullet+}$ 242 (0.07), 151 (14), 123 (3), 92 (9), 91 (100), 83 (4), 81 (3), 67 (3), 65 (8), 43 (3). **HRMS** (APGC) *m/z* calcd. for $C_{17}H_{23}O$ $[MH]^{\bullet+}$: 243.1749, found: 243.1755.

Allenic enol ether 5

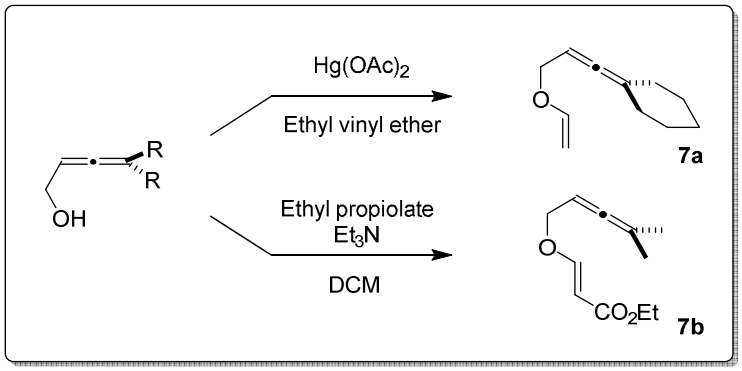


n-BuLi (2.5 M in hexane, 2.70 eq., 3.02 mL) was added dropwise to a suspension of (methylthiomethyl) triphenylphosphonium chloride (7.84 mmol, 2.80 eq., 2.81 mg) in THF at 0 °C and under nitrogen atmosphere. The solution was stirred at 0 °C for 30 minutes.[4] The aldehyde was then

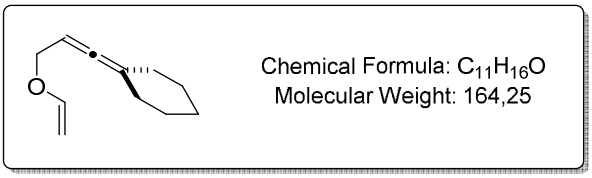
[2] K. D. Schleicher, Y. Sasaki, A. Tam, D. Kato, K. K. Duncan, D. L. Boger, *J. Med. Chem.* **2013**, *56*, 483-495.
[3] D. H. R. Barton, S. D. Géro, J. Cléophax, A. S. Machado, B. Quiclet-Sire, *J. Chem. Soc., chem. Commun.***1988**, 1184-1186.
[4] H. C. Xu, K. D. Moeller, *J. Am. Chem. Soc.* 2012, *132*, 2839-2844.

added dropwise over 10 minutes. After addition, the solution was warmed to room temperature and stirred overnight. When the reaction was complete, the reaction mixture was cooled to 0 °C, quenched with brine and diluted with Et_2O. The aqueous layer was extracted twice with Et_2O. The combined organic layers were dried over $MgSO_4$ and concentrated. Purification of the crude material by column chromatography over silica gel (PE) afforded **5** (530 mg, 85%, trans/cis 0.52:1.0) as a colourless oil. **^{1}H NMR** (200 MHz, $CDCl_3$) 5.97 (d, *J* = 15.2 Hz, 1H *trans*), 5.76 (d, *J* = 10.6 Hz, 1H *cis*), 5.46 (d, *J* = 10.6 Hz, 1H *cis*), 5.45 (d, *J* = 15.2 Hz, 1H *trans*), 5.19-5.10 (m, 1H *cis*), 4.98-4.89 (m, 1H *trans*), 2.24 (s, 3H *cis* + 3H *trans*), 2.22-2.02 (m, 4H *cis* + 4H *trans*), 1.69-1.46 (m, 6H *cis* + 6H *trans*), 1.20 (s, 6H *cis*), 1.11 (s, 6H *trans*). **^{13}C NMR** (50 MHz, $CDCl_3$) 196.3, 196.1 (*cis*, *trans*), 136.2, 135.4 (*cis*, *trans*), 126.2, 120.6 (*cis*, *trans*), 105.1, 104.9 (*cis*, *trans*), 98.4, 98.2 (*cis*, *trans*), 38.2, 37.3 (*cis*, *trans*), 31.9, 31.5 (*cis*, *trans*), 28.2 (*cis*, *trans*), 27.7, 27.6 (*cis*, *trans*), 26.3, 26.2 (*cis*, *trans*), 18.6 (*cis*), 15.0 (*trans*). **MS** (EI, 70 eV) $[M]^{\bullet+}$ 115 (100), 67 (41), 41 (35), 207 (26), 91 (18), 69 (15), 61 (14), 65 (14), 77 (12), 165 (11), 182 (0). **HRMS** (APGC) *m/z* calcd. for $C_{14}H_{22}O$ $[M]^{\bullet+}$: 222.1442, found: 222.1445.

II.1.b Synthesis of allenic substrates 7a and 7b



Allenic enol ether 7a



Allenic enol ether **7a** was obtained following a slightly modified literature procedure[5]. 3-cyclohexylideneprop-2-en-1-ol[6] (260 mg, 1.88 mmol), mercury (II) acetate (402 mg, 1.26 mmol) and ethyl vinyl ether (4.70 ml) were stirred at room temperature for 1 h. The mixture was then poured into a 5% potassium hydroxide solution (5 mL) and extracted twice with pentane. After drying over $MgSO_4$, the combined organic layers were concentrated under reduced pressure. The residue obtained was purified by column chromatography over basic alumina eluting with pentane to afford allenic enol ether **7a** (182 mg, 59%) as a colourless oil. **^{1}H NMR** (200 MHz, $CDCl_3$) δ 6.45 (dd, *J* = 14.3, 6.8 Hz, 1H), 5.12 (m, 1H), 4.24 (dd, *J* = 14.3, 1.9 Hz, 1H), 4.21 (d, *J* = 6.7 Hz, 3H), 4.03 (dd, *J* = 6.8, 1.9 Hz, 1H), 2.13 (m, 4H), 1.67-1.47 (m, 6H). **^{13}C NMR** (50 MHz, $CDCl_3$) δ 199.9, 151.2, 103.9, 87.2, 85.2, 67.6, 31.2, 27.2, 26.0. **IR** (**neat**): 2929, 2855, 1634, 1612, 1446, 1316, 1195. **MS** (EI, 70 eV): $[M^{+\cdot}]$ 164 (0.57), 79 (100), 67 (63), 93 (49), 77 (43), 91 (43), 41 (38), 55 (34), 65 (19), 53 (17).

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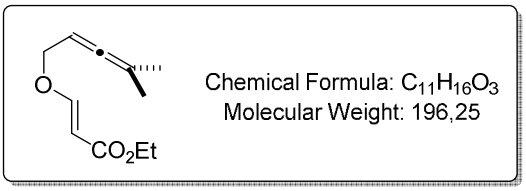
[5] K. Nonoshita, H. Banno, K. Maruoka, H. Yamamoto, *J. Am. Chem. Soc.* **1990**, *112*, 316-322.
[6] I. Diaf, G. Lemière, E. Duñach, *Angew. Chem. Int. Ed.* **2014,** *53*, 4177-4180.

Allenic enol ether 7b



To a solution of ethyl propiolate (258 µL, 2.50 mmol) and 4-methylpenta-2,3-dien-1-ol[7] (200 mg, 2.04 mmol) in CH_2Cl_2 (250 mL) at 0 °C was added Et_3N (286 µL, 2.04 mmol) dropwise over 15 min. The reaction mixture was stirred at room temperature for 14 h and quenched with 10% HCl.The aqueous layer was extracted with CH_2Cl_2 and the combined organic layers were washed with 10% HCl and brine, and dried over $MgSO_4$. The solution was filtered, concentrated and the residue was purified by column chromatography over silica gel (PE/EtOAc, 5:1) to give **7b** (370 mg, 92%) as a colourless oil.

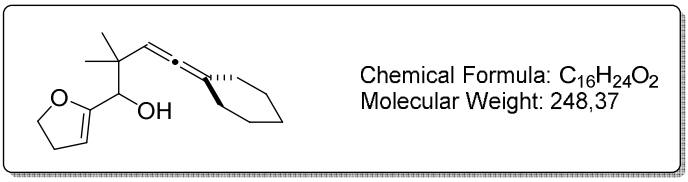
^{1}H NMR (200 MHz, $CDCl_3$) δ 7.58 (d, *J* = 12.6 Hz, 1H), 5.23 (d, *J* = 12.6 Hz, 1H), 5.16-5.01 (m, 1H), 4.34 (d, *J* = 6.8 Hz, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 1.71 (d, *J* = 2.8 Hz, 6H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (50 MHz, $CDCl_3$) δ 203.8, 167.8, 161.8, 97.7, 97.3, 84.4, 69.9, 59.7, 20.1, 14.3. **IR** (neat): 2982, 2940, 1713, 1644, 1626, 1448, 1368, 1236, 1133 cm^{-1}. **MS** (EI, 70 eV): $[M]^{\bullet+}$ 196 (0.19), 167 (21), 123 (14), 81 (86), 80 (13), 79 (100), 77 (14), 65 (14), 55 (15), 53 (56). **HRMS** (APGC) *m/z* calcd. for $C_{11}H_{16}O_3$ $[M]^{\bullet+}$: 196.1099, found: 196.1101.

II.1.c Synthesis of allenic substrates 9a-e

General procedure 2: Synthesis of allenic enol-ether (organolithium addition)

Allenic enol ethers **9** were obtained following a slightly modified literature procedure.[8] To a solution of enol ether (1.2 eq.) in dried THF (2.0 M) was added *tert*-BuLi (1.0 eq.) dropwise at -78ºC. The mixture was warmed up to -5 ºC and then stirred at that temperature for 5 h. The solution was then cooled again at -78ºC and the aldehyde (1.0 eq.) was added slowly. The mixture was warmed up to -5 °C over 5 h and then quenched with a saturated NH_4Cl solution. The mixture was extracted three times with Et_2O and the combined organic layers were dried over $MgSO_4$ and concentrated. The residue obtained was purified by column chromatography over silica gel (PE/EtOAc 95:5 containing 5% Et_3N).

Allenic enol ether 9a

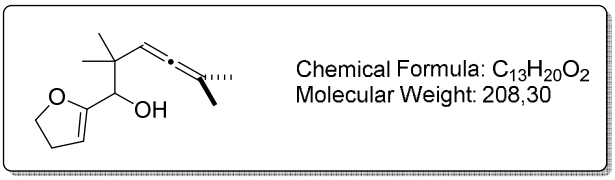


Allenic substrate **9a** (850 mg, 61%) was obtained as a yellow oil following **general procedure 2** from the corresponding allenic aldehyde (1.00 g, 5.6 mmol). **^{1}H NMR** (200 MHz, $CDCl_3$) δ 5.04-4.97 (m, 1H), 4.86-4.80 (m, 1H), 4.40-4.24 (m, 2H), 3.92 (d, *J* = 6.1 Hz, 1H), 2.70-2.55 (m, 2H), 2.16-2.02 (m, 5H), 1.66-1.43 (m, 6H), 1.05 (s, 3H), 1.02 (s, 3H). **^{13}C NMR** (50 MHz, $CDCl_3$) δ 197.7, 157.5, 104.6, 97.4, 95.8, 75.2, 69.9, 39.8, 31.9, 31.8, 29.7 (2C), 27.5, 26.1, 25.1, 23.8. **MS** (EI, 70 eV): $[M]^{\bullet+}$ 248 (4), 219 (15), 149 (35), 135 (17), 121 (20), 107 (66), 105 (28), 93 (75), 91 (52), 81 (100), 79 (61),

[7] G. Lemiere, B. Cacciuttolo, E. Belhassen, E. Dunach, *Org. Lett.* **2012**, *14*, 2750-2753.
[8] C. Nevado, C. Ferrer, A. M. Echavarren, *Org. Lett.* **2004**, *6*, 3191-3194.

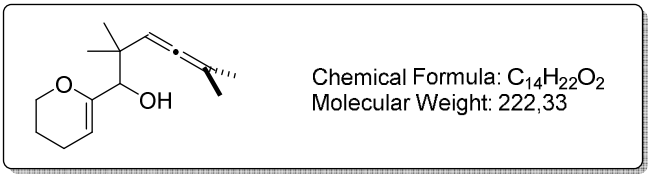
67 (48), 55 (45), 41 (80). **HRMS** (APGC) *m/z* calcd. for $C_{16}H_{25}O_2$ $[MH]^{\bullet+}$: 249.1855, found: 249.1567.

Allenic enol ether 9b



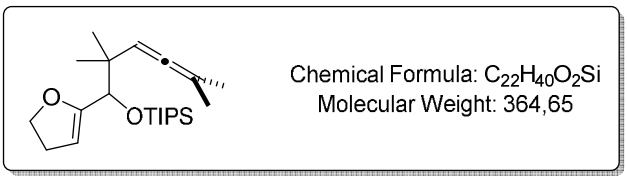
Allenic substrate **9b** (5.38 g, 89%) was obtained as a yellow oil following **general procedure 2** from the corresponding allenic aldehyde (4.00 g, 28.9 mmol). **^{1}H NMR** (200 MHz, $CDCl_3$) δ 5.04-4.93 (m, 1H), 4.84 (t, *J* = 2.4 Hz, 1H), 4.32 (td, *J* = 9.4, 1.7 Hz, 2H), 3.91 (d, *J* = 6.5 Hz, 1H), 2.63 (td, *J* = 9.4, 2.4 Hz, 2H), 2.08 (d, *J* = 6.5 Hz, 1H(OH)), 1.69 (d, *J* = 2.9 Hz, 6H), 1.03 (s, 3H), 1.01 (s, 3H). **^{13}C NMR** (50 MHz, $CDCl_3$) δ 201.1, 157.5, 97.3, 97.0, 96.0, 75.2, 69.9, 39.9, 29.7, 24.9, 23.7, 20.8, 20.7. **IR** (neat): 3401, 2965, 2914, 2855, 1445, 1375, 1174, 1107, 1041, 987, 889, 834, 797 cm^{-1}. **MS** (EI, 70 eV): $[M]^{\bullet+}$ 208 (0.53), 179 (10), 137 (9), 135 (14), 109 (32), 95 (22), 91 (13), 81 (32), 67 (100), 55 (31). **HRMS** (APGC) *m/z* calcd. for $C_{13}H_{21}O_2$ $[MH]^{\bullet+}$: 209.1542, found: 209.1548.

Allenic enol ether 9c



Allenic substrate **9c** (1.21 g, 75%) was obtained as a pale yellow oil following **general procedure 2** from the corresponding allenic aldehyde (1.00 g, 7.23 mmol). **^{1}H NMR** (200 MHz, $CDCl_3$) δ 5.07-4.93 (m, 1H), 4.68 (t, *J* = 3.7 Hz, 1H), 4.12-3.82 (m, 2H), 3.60 (d, *J* = 7.2 Hz, 1H), 2.17 (d, *J* = 7.3 Hz, 1H(OH)), 2.10-1.97 (m, 2H), 1.89-1.73 (m, 2H), 1.70 (dd, *J* = 2.8, 1.0 Hz, 6H), 1.02 (s, 3H), 1.00 (s, 3H). **^{13}C NMR** (50 MHz, $CDCl_3$) δ 200.8, 152.9, 98.8, 96.6, 96.4, 79.6, 65.8, 40.0, 25.1, 24.2, 22.4, 20.8, 20.7, 19.9. **IR** (neat): 3401, 2966, 2923, 2857, 1447, 1375, 1175, 1108, 1041, 987, 889 cm^{-1}. **HRMS** (APGC) *m/z* calcd. for $C_{14}H_{22}O_2$ $[M]^{\bullet+}$: 222.1620, found: 222.1613;

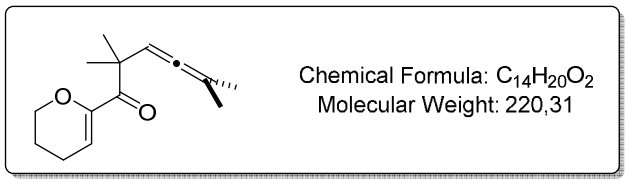
TIPS-protected alcohol substrate 9d



To a solution of the alcohol **9b** (700 mg, 3.37 mmol) in CH_2Cl_2 (7 mL) at 0 °C, was added 2,6-lutidine (721 mg, 6,73 mmol) and triisopropylsilyl trifluoromethanesulfonate (1.23 g, 4.04 mmol). The mixture was allowed to warm to room temperature over 12 h and the reaction was quenched with a saturated solution of NH_4Cl. The organic layer was separated and the aqueous phase was extracted three times with CH_2Cl_2. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. Purification of the crude material by column chromatography over silica gel (PE/EtOAc 98:2) afforded **9d** (677 mg, 55%) as a pale yellow oil. **^{1}H NMR** (200 MHz, $CDCl_3$) δ 5.19-5.07 (m, 1H), 4.78 (t, *J* = 2.4 Hz, 1H), 4.40-4.14 (m, 2H), 4.05 (s, 1H), 2.58 (td, *J* = 9.5, 2.4 Hz, 2H), 1.67 (d, *J* = 2.7 Hz, 6H), 1.11-1.03 (m, 21H), 1.01 (s, 6H). **^{13}C**

NMR (50 MHz, $CDCl_3$) δ 200.1, 159.2, 97.4, 97.3, 96.3, 76.7, 69.3, 40.4, 29.7, 24.5, 24.1, 20.7, 18.2, 18.1, 12.7. **IR** (neat): 2963, 2943, 2866, 1659, 1464, 1382, 1243, 1175, 1102, 1067, 1014, 1002, 936, 883, 823, 679 cm^{-1}. **MS** (EI, 70 eV): $[M]^{\bullet+}$ 364 (25), 293 (50), 255 (68), 213 (74), 157 (61), 147 (31), 134 (47), 115 (90), 87 (47), 75 (71). **HRMS** (APGC) *m/z* calcd. for $C_{22}H_{41}O_2Si$ $[MH]^{\bullet+}$: 365.2876, found: 365.2884.

Keto allene-enol ether 11



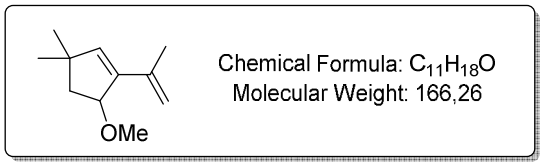
To a stirred solution of IBX (189 mg, 0.68 mmol) in DMSO (0.5 mL) was added a solution of alcohol **7c** (100 mg, 0.450 mmol) in THF (0.5 mL). The mixture was stirred at room temperature for 1 h. The reaction mixture was then quenched with water and the precipitate was filtered and washed with Et_2O. The aqueous layer was extracted with Et_2O and the combined organic layers were washed with a saturated solution of Na_2CO_3 and brine. The crude product was purified by column chromatography over silica gel (PE/EtOAc 95:5) to afford the desired ketone **11** (61.0 mg, 61%) as a yellowish oil. **^{1}H NMR** (200 MHz, $CDCl_3$) δ 5.91 (t, *J* = 4.2 Hz, 1H), 5.35-5.24 (m, 1H), 4.11-3.96 (m, 2H), 2.24-2.10 (m, 2H), 1.93-1.76 (m, 2H), 1.67 (d, *J* = 2.9 Hz, 6H), 1.25 (s, 6H). **^{13}C NMR** (50 MHz, $CDCl_3$) δ 200.8, 199.4, 151.7, 109.8, 98.0, 95.4, 65.6, 46.8, 25.1, 21.7, 20.6, 20.4. **HRMS** (APGC) *m/z* calcd. for $C_{14}H_{21}O_2$ $[MH]^{\bullet+}$: 221.1542, found: 209.1541.

II.2 Cycloisomerization products

General procedure 3: Allene-enol ether cycloisomerization

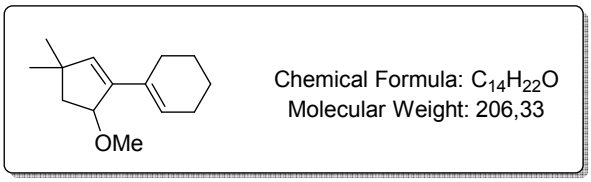
To a solution of the allenic substrate (1.0 eq.) in CH_2Cl_2 (0.2 M) under inert atmosphere was added $Bi(OTf)_3$ (0.1 mol%). After complete consumption of the starting allene, the reaction mixture was quenched with a saturated solution of $NaHCO_3$ and diluted in Et_2O. The aqueous phase was extracted twice with Et_2O and the combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated. Purification by column chromatography over silica gel (PE/Et_2O 99:1) gave the expected cyclic product.

Methoxycyclopentene 2a



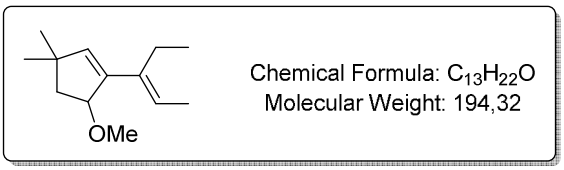
Diene **2a** (75.0 mg, 75%) was obtained as yellowish oil following **general procedure 3** from allenic enol ether **1a** (100 mg, 0.600 mmol). **^{1}H NMR** (200 MHz, $CDCl_3$) δ 5.73 (s, 1H), 5.12 (s, 1H), 4.99 (s, 1H), 4.58 (dd, *J* = 6.2, 3.3 Hz, 1H), 3.31 (s, 3H), 1.90 (s, 3H), 1.89 (d, *J* = 3.3 Hz, 1H), 1.84 (d, *J* = 3.3 Hz, 1H), 1.17 (s, 3H), 1.08 (s, 3H). **^{13}C NMR** (50 MHz, $CDCl_3$) δ 142.1, 141.1, 138.1, 113.3, 85.2, 55.8, 44.2, 43.6, 29.6, 29.4, 21.0. **IR** (neat): 2952, 2924, 2864, 2815, 1634, 1600, 1460, 1080, 866 cm^{-1}. **MS** (EI, 70 eV): $[M]^{\bullet+}$ 166 (5), 151 (39), 136 (72), 121 (68), 119 (100), 105 (33), 93 (36), 91 (71), 77 (39), 45 (43). **HRMS** (APGC) *m/z* calcd. for $C_{11}H_{18}O$ $[M]^{\bullet+}$: 166.1358, found: 166.1353.

Methoxycyclopentene 2b



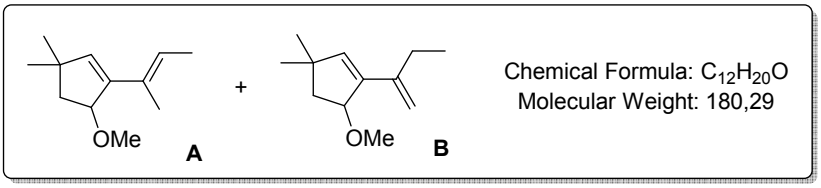
Diene **2b** (820 mg, 82%) was obtained as a yellowish oil following **general procedure 3** from allenic enol ether **1b** (1.00 g, 4.85 mmol,). **^{1}H NMR** (200 MHz, $CDCl_3$) δ 5.91 (s, 1H), 5.61 (s, 1H), 4.54 (t, *J* = 4.5 Hz, 1H), 3.32 (s, 3H), 2.22-2.10 (m, 4H), 1.82 (d, *J* = 4.6 Hz, 2H), 1.73-1.60 (m, 4H), 1.15 (s, 3H), 1.06 (s, 3H). **^{13}C NMR** (50 MHz, $CDCl_3$) δ 141.2, 138.5, 131.6, 125.4, 85.2, 55.9, 44.1, 43.4, 29.8, 29.6, 26.1, 25.8, 22.7, 22.3. **IR** (neat): 3035, 2924, 2861, 2833, 1448, 1350, 1132, 1082 cm^{-1}. **MS** (EI, 70 eV): $[M]^{\bullet+}$ 159 (100), 174 (82), 91 (64), 131 (57), 41 (50), 105 (50), 145 (42), 79 (39), 117 (36), 77 (36), 206 (16). **HRMS** (APGC) *m/z* calcd. for $C_{13}H_{19}$ $[M\text{-}CH_3O]^{\bullet+}$: 174.1409, found: 174.1407.

Methoxycyclopentene 2c



Diene **2c** (64.0 mg, 64%) was obtained as colourless oil following **general procedure 3** from allenic enol ether **1c** (100 mg, 0.515 mmol). Configuration of the double bond was assigned by NOESY NMR experiment. **^{1}H NMR** (200 MHz, $CDCl_3$) δ 5.67 (q, *J* = 6.9 Hz, 1H), 5.64 (s, 1H), 4.54 (dd, *J* = 6.4, 2.8 Hz, 1H), 3.29 (s, 3H), 2.27 (q, *J* = 7.5 Hz, 2H), 1.84-1.81 (m, 2H), 1.72 (d, *J* = 7.0 Hz, 3H), 1.16 (s, 3H), 1.01 (s, 3H), 1.01 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (50 MHz, $CDCl_3$) δ 140.5, 139.1, 136.9, 122.0, 85.3, 55.6, 44.0, 43.2, 29.7, 29.6, 21.5, 13.5, 13.5. **IR** (neat): 2954, 2933, 2865, 2816, 1466, 1360, 1306, 1135, 1084 cm^{-1}. **MS** (EI, 70 eV): $[M]^{\bullet+}$ 194 (10), 162 (31), 147 (100), 133 (48), 119 (33), 105 (42), 91 (35), 77 (18), 59 (20), 55 (18). **HRMS** (APGC) *m/z* calcd. for $C_{12}H_{19}O$ $[M\text{-}CH_3O]^{\bullet+}$: 163.1487, found: 163.1488.

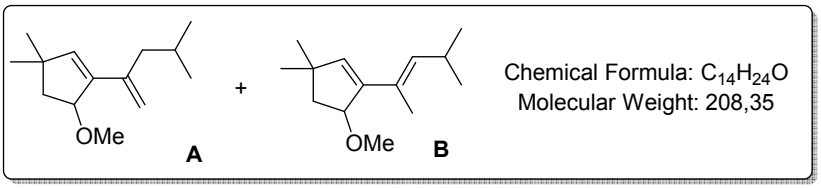
Methoxycyclopentene 2d



Dienes **2d A** and **B** (71.0 mg, 71%, **A/B** 5:1) were obtained as a yellowish oil, following **general procedure 3** from allenic enol ether **1d** (100 mg, 0.555 mmol).

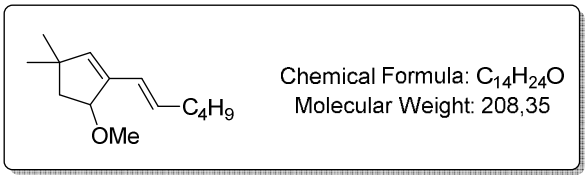
Isomer A (maj.): **^{1}H NMR** (200 MHz, $CDCl_3$) δ 5.72 (q, *J* = 6.4 Hz, 1H), 5.63 (s, 1H), 4.55 (t, *J* = 4.6 Hz, 1H), 3.31 (s, 3H), 1.82-1.84 (d, *J* = 4.6 Hz, 2H), 1.79 (s, 3H), 1.73 (d, *J* = 6.4 Hz, 3H), 1.16 (s, 3H), 1.07 (s, 3H). **^{13}C NMR** (50 MHz, $CDCl_3$) δ 142.1, 139.4, 130.4, 122.7, 85.1, 55.8, 44.1, 43.3, 29.8, 29.6, 13.9, 13.9. **IR** (neat): 3037, 2951, 2923, 2863, 2815, 1359, 1083, 864, 814 cm^{-1}. **MS** (EI, 70 eV): $[M]^{\bullet+}$ 180 (10), 148 (27), 133 (100), 105 (39), 93 (18), 91 (45), 79 (21), 77 (22), 59 (31), 45 (20). **HRMS** (APGC) *m/z* calcd. for $C_{12}H_{20}O$ $[M]^{\bullet+}$: 180.1514, found: 180.1514.

Methoxycyclopentene 2e



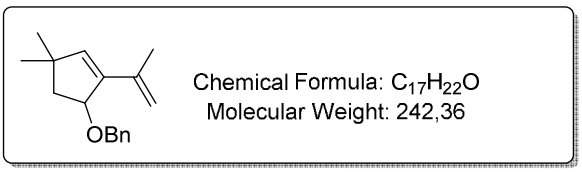
Dienes **2e A** and **B** (77.0 mg, 77%, **A/B** 0.5:1) were obtained as a yellowish oil, following **general procedure 3** from allenic enol ether **1e** (100 mg, 0.48 mmol). **^{1}H NMR** (200 MHz, $CDCl_3$) δ 5.70 (s, 1HA), 5.63 (s, 1HB), 5.45 (d, *J* = 9.3 Hz, 1HB), 5.18 (d, *J* = 2.1 Hz, 1HA), 4.93 (s, 1HA), 4.61-4.51 (m, 1H A+B), 3.30 (s, 3HB), 3.30 (s, 3HA), 2.73-2.53 (m, 2HB), 2.14-2.05 (m, 1HB), 1.81 (m, 4HA + 3HB), 1.16 (s, 3H), 1.07 (s, 3H), 1.02-1.96 (m, 6HA + 3HB), 0.89 (d, *J* = 6.6 Hz, 3HB). **^{13}C NMR** (50 MHz, $CDCl_3$) δ 142.3, 141.6, 139.8, 136.3, 127.2, 113.4, 85.6, 85.0, 55.7, 55.6, 44.2, 44.1, 44.1, 43.5, 43.3, 29.8, 29.6, 29.6, 29.5, 27.4, 26.9, 23.1, 22.9, 22.8, 14.3. **IR** (neat): 3035, 2953, 2926, 2866, 2816, 1724, 1464, 1360, 1135, 1085, 852 cm^{-1}. **MS** (EI, 70 eV): $[M]^{\bullet+}$ (Isomer A) 105 (100), 41 (94), 119 (83), 91 (82), 135 (73), 107 (63), 43 (53), 178 (53), 151 (52), 133 (49), 208 (2) ; (Isomer B) 161 (100), 119 (54), 73 (50), 105 (46), 41 (42), 55 (33), 91 (31), 133 (26), 107 (22), 120 (21), 208 (9) . **HRMS** (APGC) *m/z* calcd. for $C_{14}H_{25}O$ $[MH]^{\bullet+}$: 209.1905, found: 209.1903.

Methoxycyclopentene 2f



Diene **2f** (71.0 mg, 71%) was obtained as a yellowish oil following **general procedure 3** from allenic enol ether (*E*)-**1f** (100 mg, 0.480 mmol). **^{1}H NMR** (200 MHz, $CDCl_3$) δ 6.09 (d, *J* = 16.0 Hz, 1H), 5.85 (dt, *J* = 16.0, 6.7 Hz, 1H), 5.56 (s, 1H), 4.56 (dd, *J* = 6.9, 3.3 Hz, 1H), 3.31 (s, 3H), 2.10 (dd, J = 13.4, 6.3 Hz, 2H), 1.91 (dd, *J* = 13.6, 6.9 Hz, 1H), 1.76 (dd, *J* = 13.6, 3.3 Hz, 1H), 1.41-1.22 (m, 4H), 1.14 (s, 3H), 1.05 (s, 3H), 0.89 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (50 MHz, $CDCl_3$) δ 142.0, 139.1, 132.5, 124.7, 84.9, 55.5, 44.5, 43.2, 32.8, 31.4, 22.3, 29.6, 29.4, 14.0. **IR** (neat): 3024, 2954, 2924, 2862, 2815, 1725, 1464, 1378, 1133, 1085, 969 cm^{-1}. **MS** (EI, 70 eV): $[M]^{\bullet+}$ 208 (36), 193 (67), 161 (50), 133 (77), 119 (73), 105 (100), 93 (48), 91 (92), 55 (56), 41 (99), 45 (53). **HRMS** (APGC) *m/z* calcd. for $C_{14}H_{24}O$ $[M]^{\bullet+}$: 208.1827, found: 208.1830.

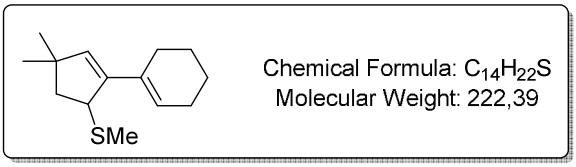
Benzyloxycyclopentene 4



Diene **4** (57.0 mg, 81%), was obtained as colourless oil following **general procedure 3** from **3** (70.0 mg, 0.413 mmol). **^{1}H NMR** (200 MHz, $CDCl_3$) δ 7.39-7.22 (m, 5H), 5.75 (s, 1H), 5.10 (s, 1H), 4.96 (s, 1H), 4.85-4.74 (m, 1H), 4.57 (d, *J* = 11.4 Hz, 1H), 4.43 (d, *J* = 11.4 Hz, 1H), 1.94-1.91 (m, 2H), 1.91 (s, 3H), 1.20 (s, 3H), 1.08 (s, 3H). **^{13}C NMR** (50 MHz, $CDCl_3$) δ 142.3, 141.1, 138.6, 138.1, 128.2, 128.2, 127.5, 113.5, 83.4, 70.5, 44.8, 43.6, 29.6, 29.4, 21.1. **IR** (neat): 3031, 2864, 2952, 1496, 1454, 1136, 1066, 1028, 969, 733, 697 cm^{-1}. **MS** (EI, 70 eV): $[M]^{\bullet+}$ 242 (0.01), 136 (54), 121 (100),

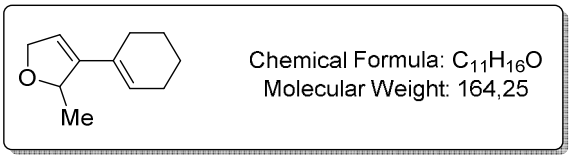
107 (13), 105 (14), 93 (12), 91 (87), 79 (12), 77 (13), 65 (13). **HRMS** (APGC) *m/z* calcd. for $C_{17}H_{21}O$ $[M–H]^+$: 241.1592, found: 241.1595.

Sulfane derivative 6



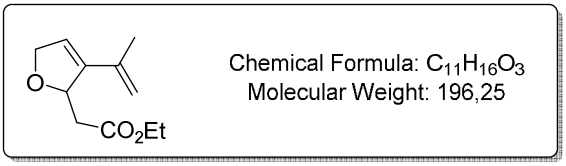
Diene **6** (85.0 mg, 85%) was obtained as a yellowish oil, following **general procedure 3** from **5** (0.450 mmol, 100 mg) and $Bi(OTf)_3$ (5 mol%), in CH_3NO_2 (2.25 mL). **^{1}H NMR** (200 MHz, $CDCl_3$) δ 6.05 (bs, 1H), 5.54 (s, 1H), 3.95 (dd, *J* = 7.8, 2.4 Hz, 1H), 2.23-2.10 (m, 6H), 2.09 (m, 3H), 1.73-1.54 (m, 4H), 1.21 (s, 3H), 1.08 (s, 3H). **^{13}C NMR** (50 MHz, $CDCl_3$) δ 140.9, 137.2, 131.3, 126.2, 50.6, 46.9, 44.0, 30.1, 28.8, 26.3, 25.7, 22.7, 22.3, 14.7. **IR** (neat): 3037, 2921, 2859, 2833, 1714, 1446, 830, 798, 714 cm^{-1}. **MS** (EI, 70 eV): $[M]^{\bullet+}$ 222 (38), 174 (74), 159 (82), 131 (56), 119 (46), 105 (77), 91 (100), 81 (57), 79 (48), 77 (47). **HRMS** (APGC) *m/z* calcd. for $C_{14}H_{22}S$ $[M]^{\bullet+}$: 222.1442, found: 222.1444.

Dihydrofuran 8a



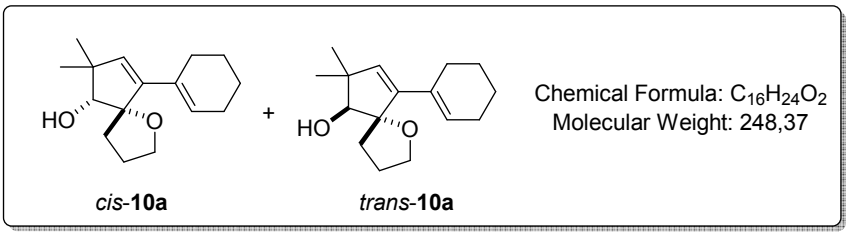
Dihydrofuran **8a** (42.0 mg, 70%) was obtained as a colourless oil, following **general procedure 3** from enol ether **7a** (60.0 mg, 0.450 mmol)**. ^{1}H NMR** (200 MHz, $CDCl_3$) δ 5.63 (s, 2H), 5.21-5.02 (m, 1H), 4.79-4.66 (m, 1H), 4.62 (d, *J* = 1.1 Hz, 1H), 2.28-1.95 (m, 4H), 1.79-1.44 (m, 4H), 1.32 (d, *J* = 6.2 Hz, 3H). **^{13}C NMR** (50 MHz, $CDCl_3$) δ 145.1, 130.2, 126.3, 118.1, 81.1, 74.0, 26.4, 25.6, 22.5, 22.1, 21.4. **IR** (neat): 2931, 2858, 1447, 1371, 1172, 1076, 836 cm^{-1}. **MS** (EI, 70 eV): $[M]^{\bullet+}$ 164 (0.94), 135 (100), 107 (32), 106 (50), 91 (97), 79 (67), 78 (36), 77 (39), 43 (37), 41 (29). **HRMS** (APGC) *m/z* calcd. for $C_{11}H_{14}O$ (M□H_2)$^+$: 162.1045, found: 162.1039.

Dihydrofuran 8b



Dihydrofuran **8b** (93.0 mg, 62%) was obtained as a colourless oil, following **general procedure 3** from enol ether **7b** (150 mg, 0.765 mmol) and $Bi(OTf)_3$ (5.00 mg, 1 mol%)**. ^{1}H NMR** (200 MHz, $CDCl_3$) δ 5.84 (s, *J* = 1.5 Hz, 1H), 5.51-5.35 (m, 1H), 5.03 (s, 1H), 4.83 (s, 1H), 4.74 (t, *J* = 7.4 Hz, 1H), 4.63 (d, *J* = 14.2 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.80 (dd, *J* = 15.5, 2.5 Hz, 1H), 2.42 (dd, *J* = 15.5, 9.1 Hz, 1H), 1.92 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 4H). **^{13}C NMR** (50 MHz, $CDCl_3$) δ 171.4, 142.2, 136.02, 123.5, 114.3, 81.8, 74.6, 60.5, 40.28, 21.2, 14.2. **HRMS** (APGC) *m/z* calcd. for $C_{11}H_{16}O_3$ $[M]^{\bullet+}$: 196.1099, found: 196.1100.

Oxaspirocycle 10a

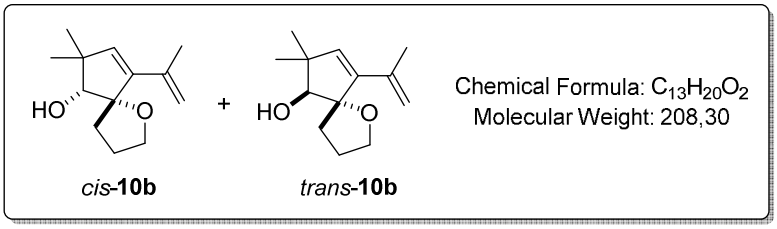


Oxaspirocycles *cis*-**10a** and *trans*-**10a** (90%, *cis*/*trans* 66:34) were obtained as yellowish oils, following **general procedure 3** from allenic substrate **9a** (100 mg, 0.403 mmol). The diastereosiomers were separated by column chromatography over silica gel.

***cis-10a*:** **^{1}H NMR** (200 MHz, $CDCl_3$) δ 5.87 (t, *J* = 3.9 Hz, 1H), 5.55 (s, 1H), 3.99 (dd, *J* = 7.3, 6.4 Hz, 2H), 3.39 (d, *J* = 5.7 Hz, 1H), 2.90 (d, *J* = 5.7 Hz, 1H), 2.45-2.28 (m, 1H), 2.24-1.95 (m, 6H), 1.95-1.79 (m, 1H), 1.74-1.49 (m, 4H), 1.05 (s, 3H), 1.03 (s, 3H). **^{13}C NMR** (50 MHz, $CDCl_3$) δ 141.0, 138.0, 131.1, 125.0, 93.8, 85.1, 68.9, 44.6, 35.3, 27.7, 27.3, 26.3, 25.6, 23.2, 22.8, 22.1. **IR** (neat): 3447, 2931, 2865, 1721, 1661, 1605, 1446, 1359, 1260, 1191, 1082, 1051, 1029, 971 cm^{-1}.

***trans-10a*:** **^{1}H NMR** (200 MHz, $CDCl_3$) δ 6.09-5.97 (m, 1H), 5.49 (s, 1H), 4.03-3.84 (m, 3H), 2.26-1.93 (m, 7H), 1.74-1.51 (m, 6H), 1.09 (s, 3H), 0.94 (s, 3H). **^{13}C NMR** (50 MHz, $CDCl_3$) δ 142.44, 134.32, 130.57, 125.39, 95.45, 88.38, 67.85, 42.15, 29.91, 27.80, 26.99, 26.64, 25.79, 22.81, 22.10, 22.05. **IR** (neat): 3424, 2952, 2932, 2868, 1712, 1659, 1605, 1360, 1261, 1195, 1145, 1087, 1049, 976 cm^{-1}. **HRMS** (APGC) *m/z* calcd. for $C_{16}H_{24}O_2$ $[M]^{\bullet+}$: 248.1776, found: 248.1777.

Oxaspirocycle 10b

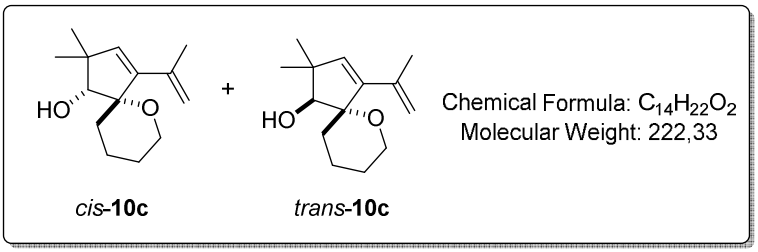


Oxaspirocycles *cis*-**10b** and *trans*-**10b** (73.0 mg, 73%, *cis*/*trans* 30:70) were obtained as a yellow oil and a colourless crystalline solid, respectively, following **general procedure 3** from allenic substrate **9b** (100 mg, 0.481 mmol). The diastereosiomers were separated by column chromatography over silica gel.

cis-**10b**: **^{1}H NMR** (200 MHz, $CDCl_3$) δ 5.67 (s, 1H), 5.08 (d, *J* = 1.6 Hz, 1H), 4.99 (d, *J* = 1.6 Hz, 1H), 4.07-3.94 (m, 2H), 3.42 (s, 1H), 2.93 (s, 1H), 2.47-2.28 (m, 1H), 2.18-1.98 (m, 2H), 1.97-1.81 (m, 4H), 1.08 (s, 3H), 1.06 (s, 3H). **^{13}C NMR** (50 MHz, $CDCl_3$) δ 141.0, 140.6, 137.6, 113.2, 93.6, 85.0, 69.0, 44.9, 35.2, 27.6, 26.3, 23.0, 22.6. **IR** (neat): 3443, 2963, 2929, 2873, 1718, 1672, 1467, 1371, 1274, 1188, 1149, 1087, 1053, 980 cm^{-1}.

trans-**10b**: **^{1}H NMR** (200 MHz, $CDCl_3$) δ 5.61 (s, 1H), 5.23 (d, *J* = 2.1 Hz, 1H), 4.98 (s, 1H), 4.02-3.88 (m, 3H), 2.33-2.17 (m, 1H), 2.16-1.89 (m, 3H), 1.86 (s, 3H), 1.83-1.74 (m, 1H), 1.10 (s, 3H), 0.96 (s, 3H). **^{13}C NMR** (50 MHz, $CDCl_3$) δ 142.1, 137.7, 137.0, 113.6, 95.2, 88.3, 68.0, 42.4, 29.80, 27.6, 27.0, 22.3, 21.9. **IR** (neat): 3430, 2961, 2936, 2877, 2361, 1722, 1672, 1464, 1368, 1270, 1154, 1089, 1051, 977 cm^{-1}. **HRMS** (APGC) *m/z* calcd. for $C_{13}H_{20}O_2$ $[M]^{\bullet+}$: 208.1463, found: 208.1465.

Oxaspirocycle 10c

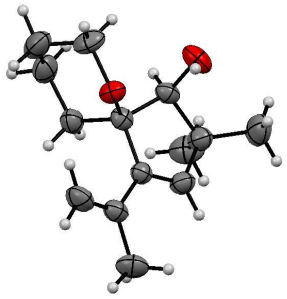


Oxaspirocycles *cis*-**10c** and *trans*-**10c** (71.0 mg, 71%, cis/trans 77:23) were obtained as yellow oils, following the **general procedure 3** from allenic substrate **9c** (100 mg, 0.450 mmol). The diastereosiomers were separated by column chromatography over silica gel.

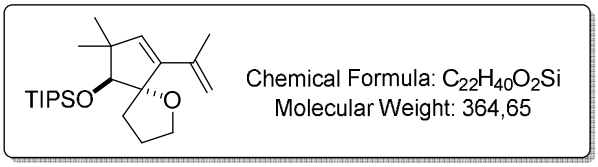
cis-**10c**: **^{1}H NMR** (200 MHz, $CDCl_3$) δ 5.66 (d, *J* = 2.3 Hz, 1H), 5.50 (s, 1H), 5.04 (s, 1H), 4.02-3.88 (m, 1H), 3.82 (d, *J* = 6.5 Hz, 1H), 3.78-3.65 (m, 1H), 2.93 (d, *J* = 6.5 Hz, 1H), 2.43-2.20 (m, 1H), 1.87 (s, 3H), 1.85-1.40 (m, 5H), 1.13 (s, 3H), 1.09 (s, 3H). **^{13}C NMR** (50 MHz, $CDCl_3$) δ 141.8, 138.3, 136.8, 114.4, 87.2, 79.6, 65.2, 45.9, 32.6, 27.9, 24.9, 23.9, 22.8, 20.7. **IR** (neat): 3464, 2976, 2947, 2932, 2881, 1622, 1596, 1454, 1441, 1357, 1263, 1078, 1041, 910, 872 cm^{-1}.

trans-**10c**: **^{1}H NMR** (200 MHz, $CDCl_3$) δ 5.71 (d, *J* = 2.2 Hz, 1H), 5.58 (s, 1H), 5.08-5.01 (m, 1H), 4.19 (d, *J* = 5.8 Hz, 1H), 3.96-3.80 (m, 2H), 2.34-2.00 (m, 2H), 1.85 (s, 3H), 1.74-1.53 (m, 5H), 1.14 (s, 3H), 1.01 (s, 3H). **^{13}C NMR** (50 MHz, $CDCl_3$) δ 142.6, 137.4, 136.5, 115.1, 89.4, 87.4, 63.6, 44.3, 28.4, 28.2, 25.2, 22.5, 22.2, 20.5. **IR** (neat): 3380, 2953, 2931, 2894, 2872, 1630, 1595, 1456, 1435, 1377, 1290, 1278, 1204, 1094, 1064, 1033, 894, 866 cm^{-1}. **HRMS** (APGC) *m/z* calcd. for $C_{14}H_{22}O_2$ $[M]^{\bullet+}$: 222.1620, found: 222.1625.

X-ray crystal structure of *cis*-10c (CCDC number 1020673)



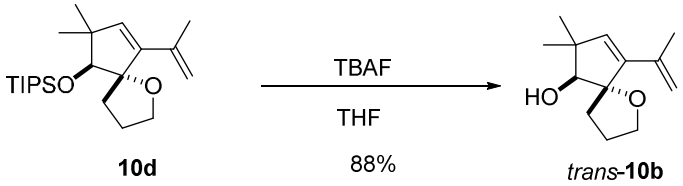
Oxaspirocycle 10d



Oxaspirocycle **10d** (165 mg, 83%) was obtained as a yellowish oil, following **general procedure 3** from **9d** (0.548 mmol, 200 mg)**. ^{1}H NMR** (200 MHz, $CDCl_3$) δ 5.54 (s, 1H), 5.17 (d, *J* = 1.8 Hz, 1H), 4.96 (s, 1H), 4.22 (s, 1H), 3.92 (t, *J* = 6.9 Hz, 2H), 2.61-2.35 (m, 1H), 2.12-1.91 (m, 2H), 1.86 (s, 3H), 1.82-1.64 (m, 1H), 1.20-1.07 (m, 21H), 1.11 (s, 3H), 0.94 (s, 3H). **^{13}C NMR** (50 MHz, $CDCl_3$) δ 143.2, 137.7, 137.4, 113.3, 96.5, 88.3, 68.3, 42.8, 30.3, 27.8, 27.2, 22.6, 22.4, 18.4, 18.2, 13.7. **IR** (neat): 2959, 2945, 2867, 2358, 2337, 1463, 1383, 1360, 1150, 1116, 1061, 1013, 884, 678 cm^{-1}. **MS** (EI, 70 eV): $[M]^{\bullet+}$ 364 (8), 348 (8), 321 (74), 191 (43), 173 (29), 159 (40), 147 (35), 131 (100), 119

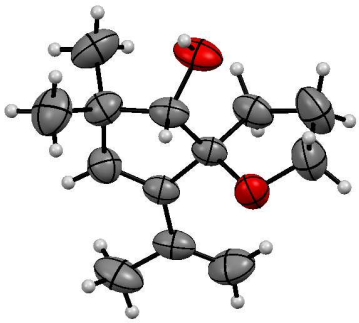
(31), 103 (56), 91 (28), 75 (66), 59 (59), 43 (29). **HRMS** (APGC) *m/z* calcd. for $C_{22}H_{41}O_2Si$ $[MH]^{\bullet+}$: 365.2876, found: 365.2888.

Determination of the stereochemistry: TBAF deprotection

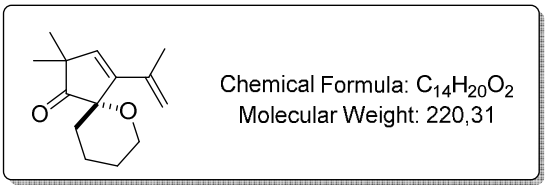


10d *trans*-**10b**

X-ray crystal structure of *trans*-10b (CCDC number 1020672)

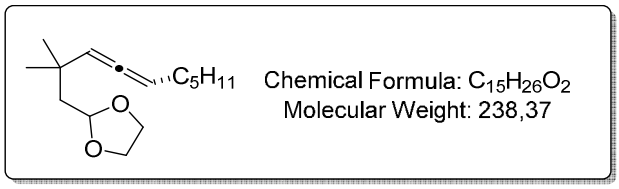


Oxaspirocycle 12



Oxaspirocycle **12** (45.0 mg, 74%) was obtained as a colourless oil, following **general procedure 3** from **11** (61.0 mg, 0.277 mmol) and $Bi(OTf)_3$ (1 mol%)**.** **^{1}H NMR** (200 MHz, $CDCl_3$) δ 6.00 (s, 1H), 5.66 (d, *J* = 1.8 Hz, 1H), 5.14 (s, 1H), 4.52-4.32 (m, 1H), 3.89-3.71 (m, 1H), 2.43-2.21 (m, 1H), 2.20-1.97 (m, 1H), 1.91 (s, 3H), 1.75-1.56 (m, 3H), 1.53-1.37 (m, 1H), 1.16 (s, 3H), 1.14 (s, 3H). **^{13}C NMR** (50 MHz, $CDCl_3$) δ 220.3, 143.2, 136.5, 136.1, 115.9, 80.3, 63.7, 47.4, 29.5, 25.3, 25.2, 24.8, 21.6, 18.2. **IR** (neat): 2954, 2867, 1743, 1466, 1378, 1283, 1211, 1082, 1040, 994, 905, 863 cm^{-1}. **HRMS** (APGC) *m/z* calcd. for $C_{14}H_{21}O_2$ $[MH]^+$: 221.1542, found: 221.1545.

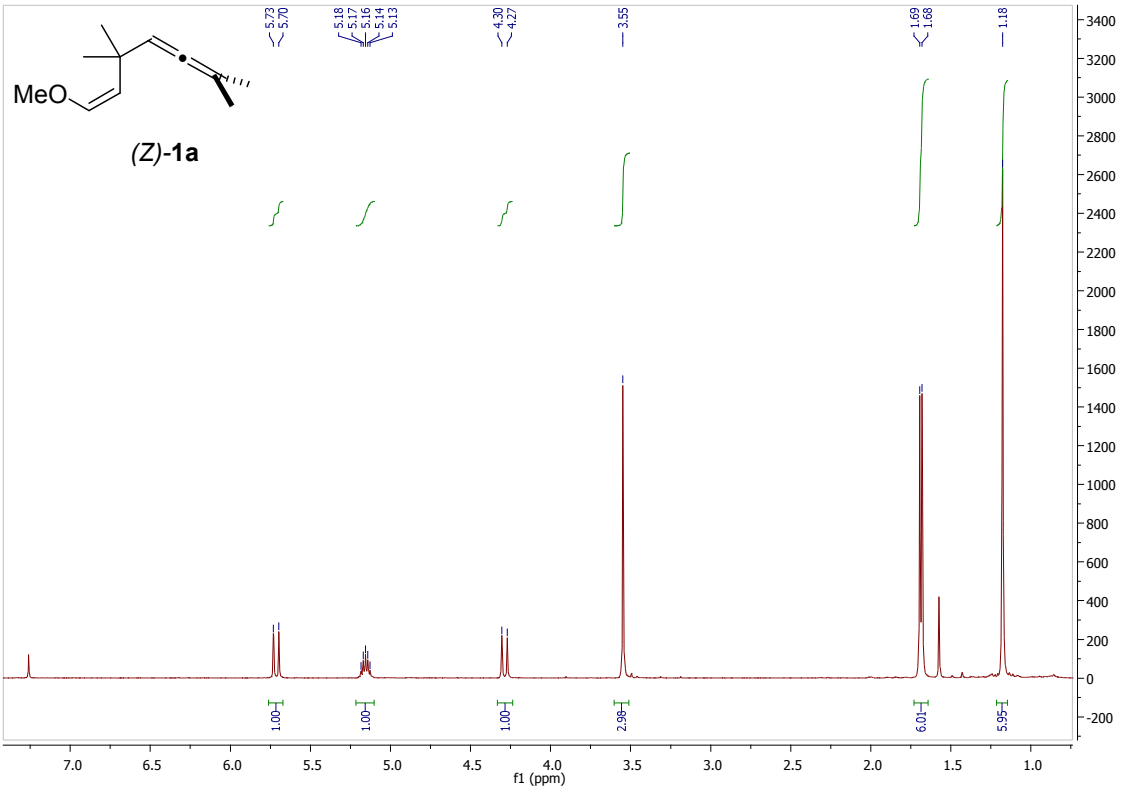
Acetal 13

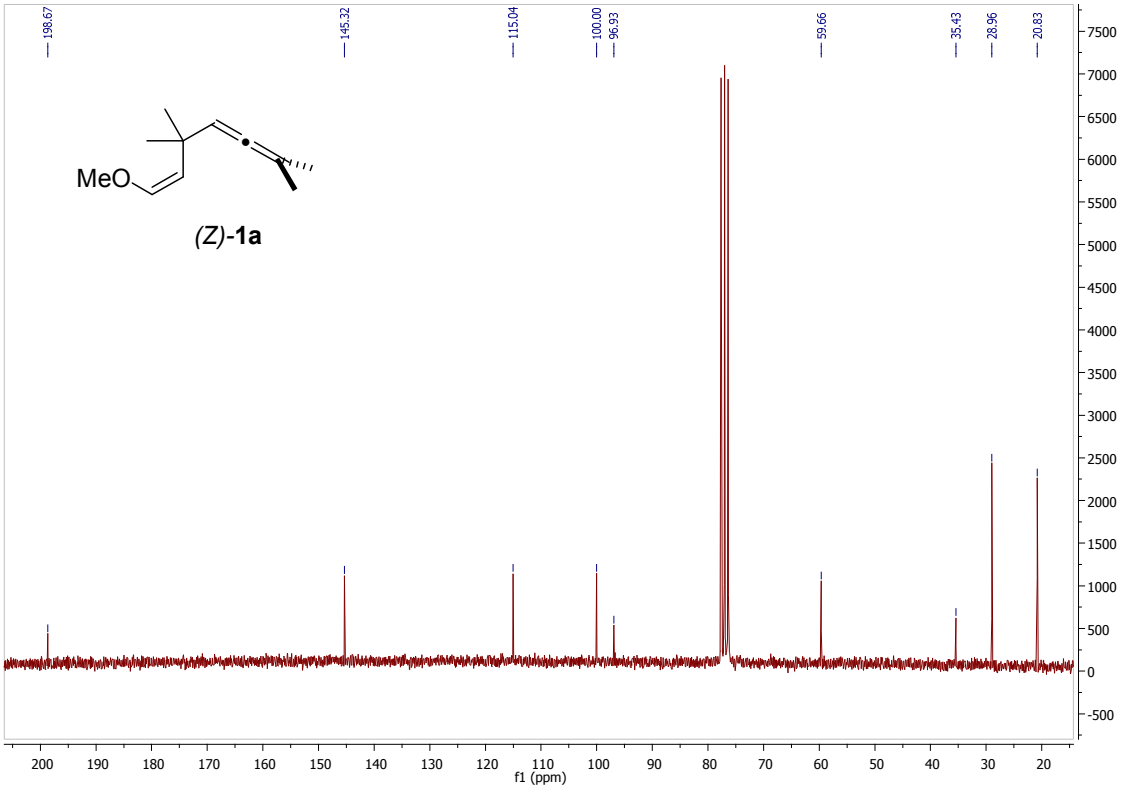


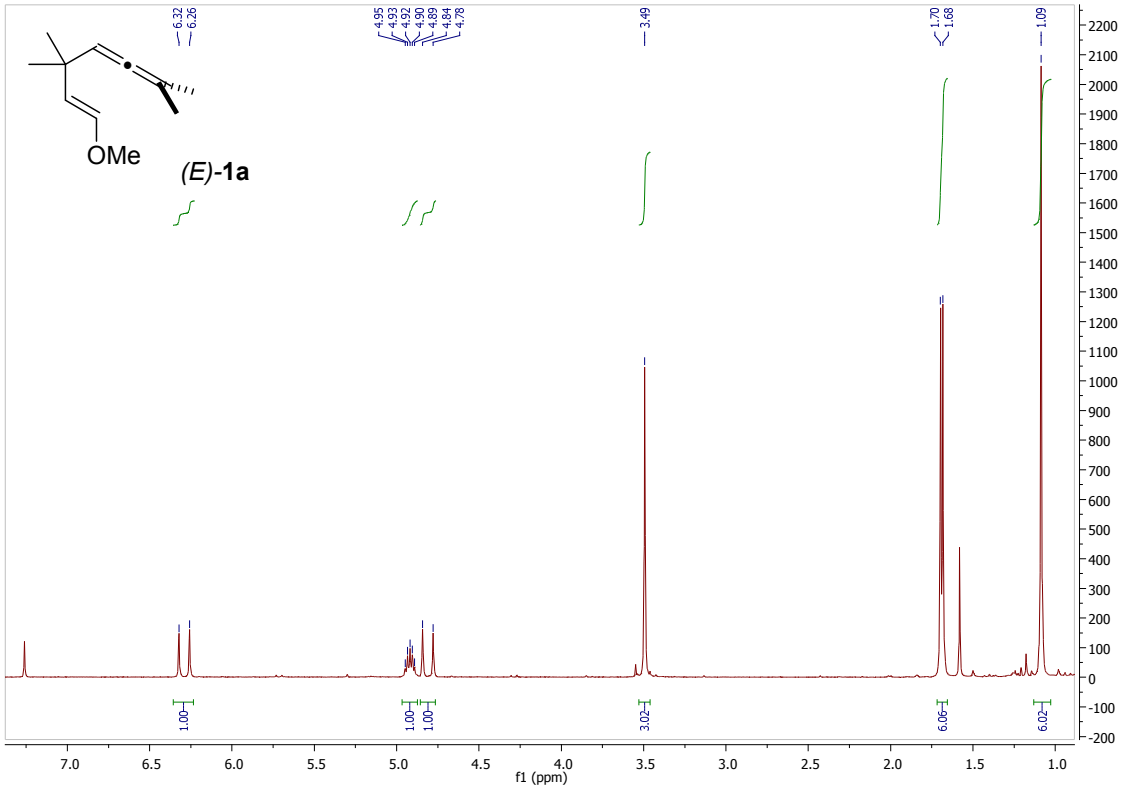
To a solution of the allenic substrate (*E*)-**1f** (100 mg, 0.48 mmol) and ethylene glycol (49 mg, 0.79 mmol) in CH_2Cl_2 (5.3 mL) under inert atmosphere was added $Bi(OTf)_3$ (3.46 mg , 1 mol%). The temperature was increased to 45 °C and the reaction was stirred for 3 hours. After complete consumption of the starting allene, the reaction mixture was quenched with a saturated solution of

$NaHCO_3$ and diluted in Et_2O. The aqueous phase was extracted twice with Et_2O and the combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated. Purification by column chromatography over silica gel (PE/Et_2O 99:1) gave the acetal **13** (107 mg, 85%) as a colorless oil. **^{1}H NMR** (200 MHz, $CDCl_3$) δ 5.24-5.03 (m, 2H), 4.88 (t, *J* = 4.7 Hz, 1H), 4.01-3.75 (m, 4H), 2.07-1.88 (m, 2H), 1.71 (d, *J* = 4.7 Hz, 2H), 1.48-1.22 (m, 6H), 1.07 (s, 6H), 0.88 (t, *J* = 6.6 Hz, 3H). **^{13}C NMR** (50 MHz, $CDCl_3$) δ. 201.73, 103.32 , 101.48 , 93.40 , 64.67 , 46.42 , 33.18 , 31.56 , 29.20 , 29.00 , 28.62, 22.65 , 14.20. **IR** (neat): 2957, 2925, 2872, 1466, 1407, 1387, 1363, 1127, 1050, 942, 875. **HRMS** (APGC) *m/z* calcd. for $C_{15}H_{27}O_2$ $[MH]^{\bullet+}$: 239.2011, found: 239.2013.

III NMR spectra






6.32
6.26
4.95
4.93
4.92
4.90
4.89
4.84
4.78
3.49
1.70
1.68
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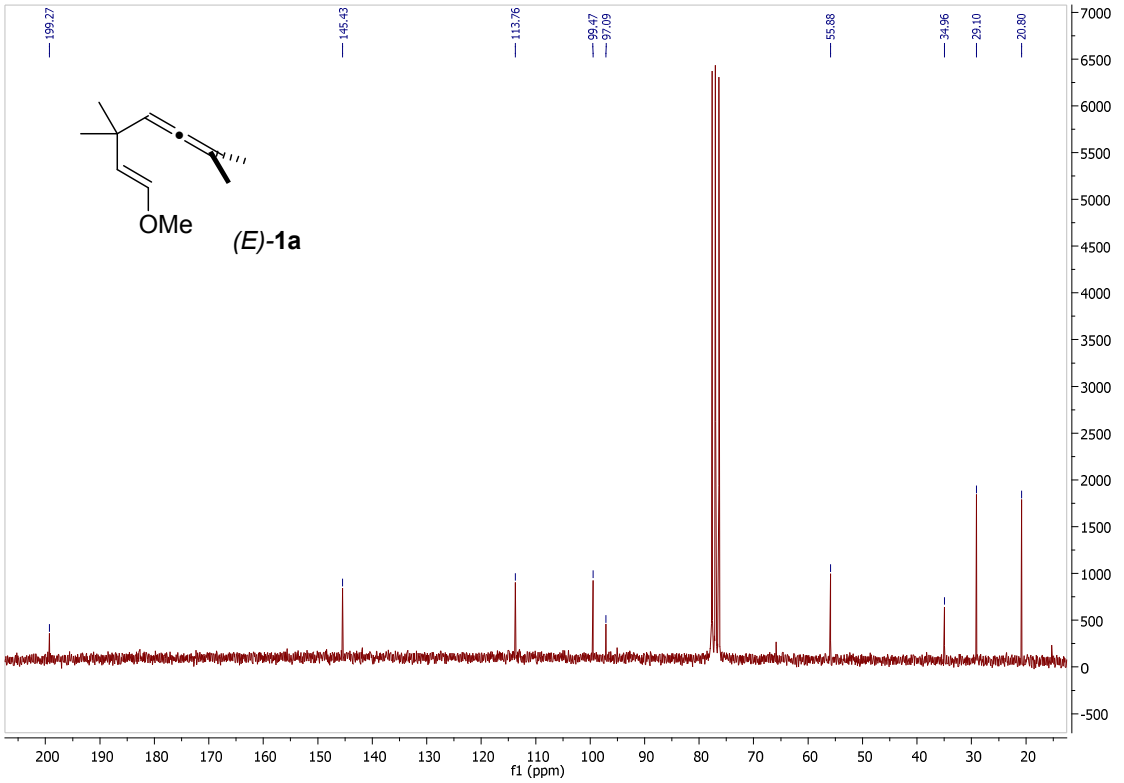
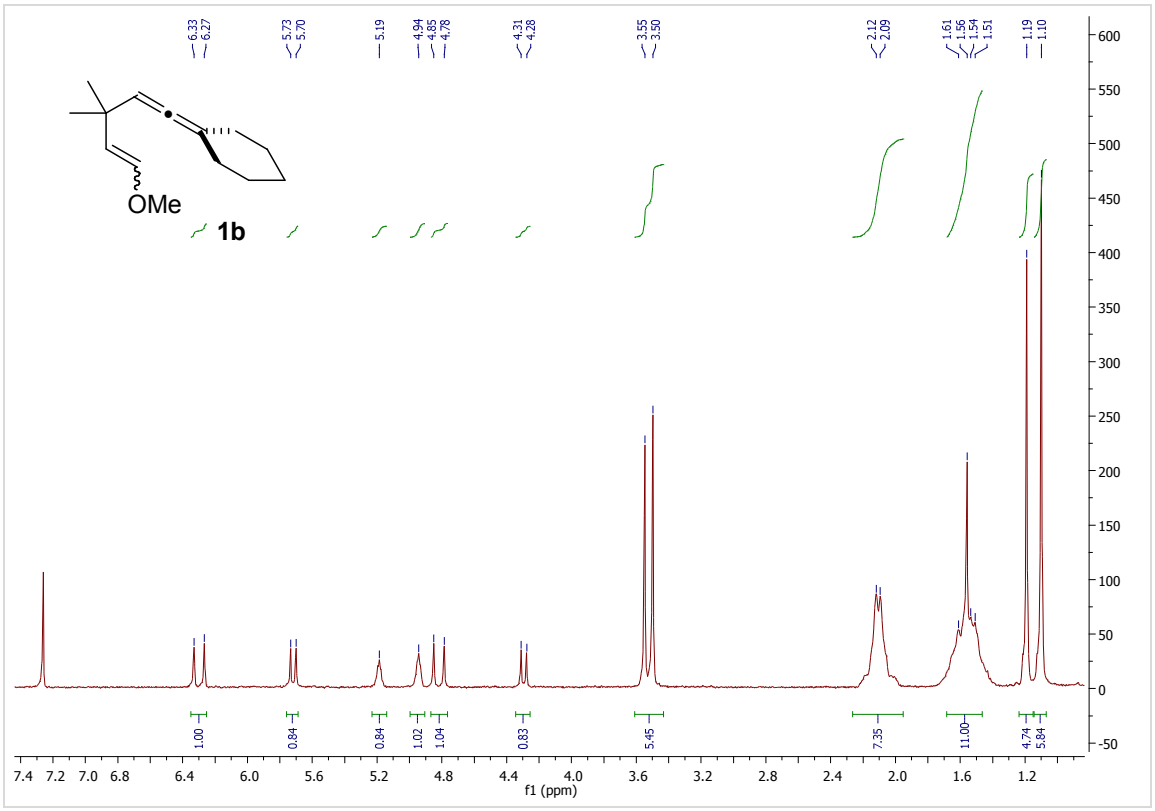
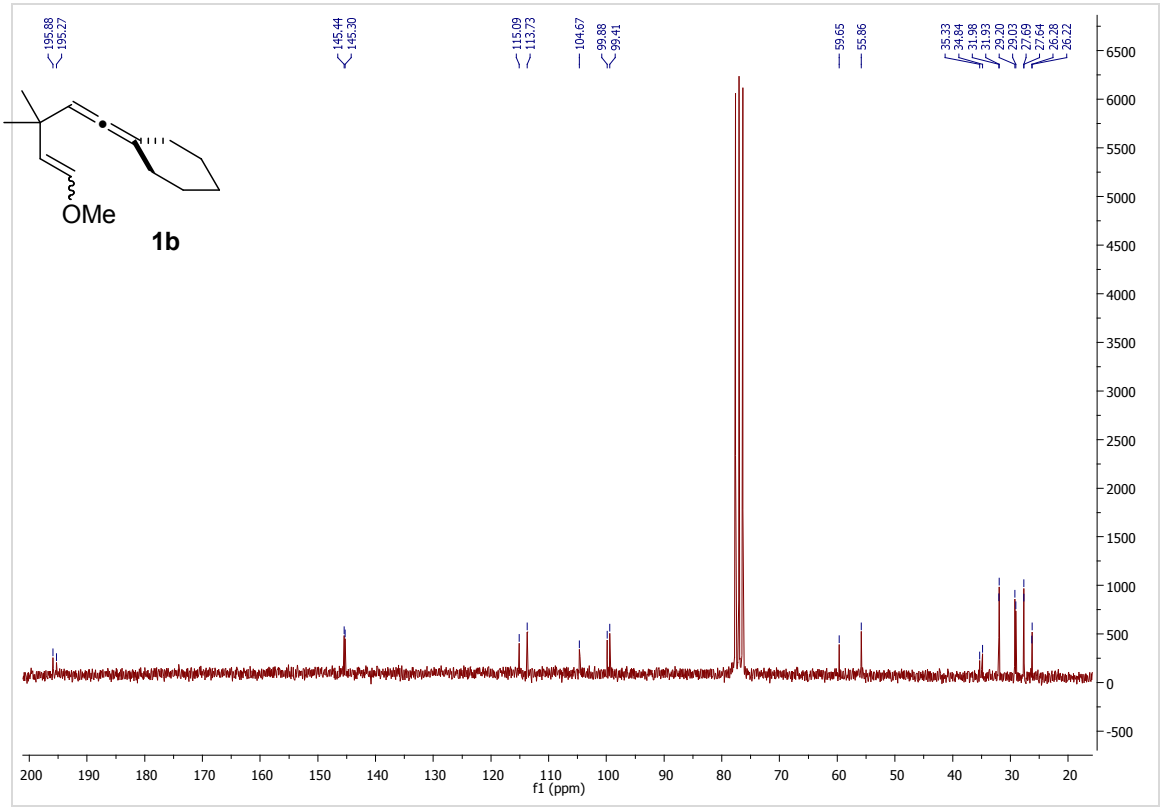
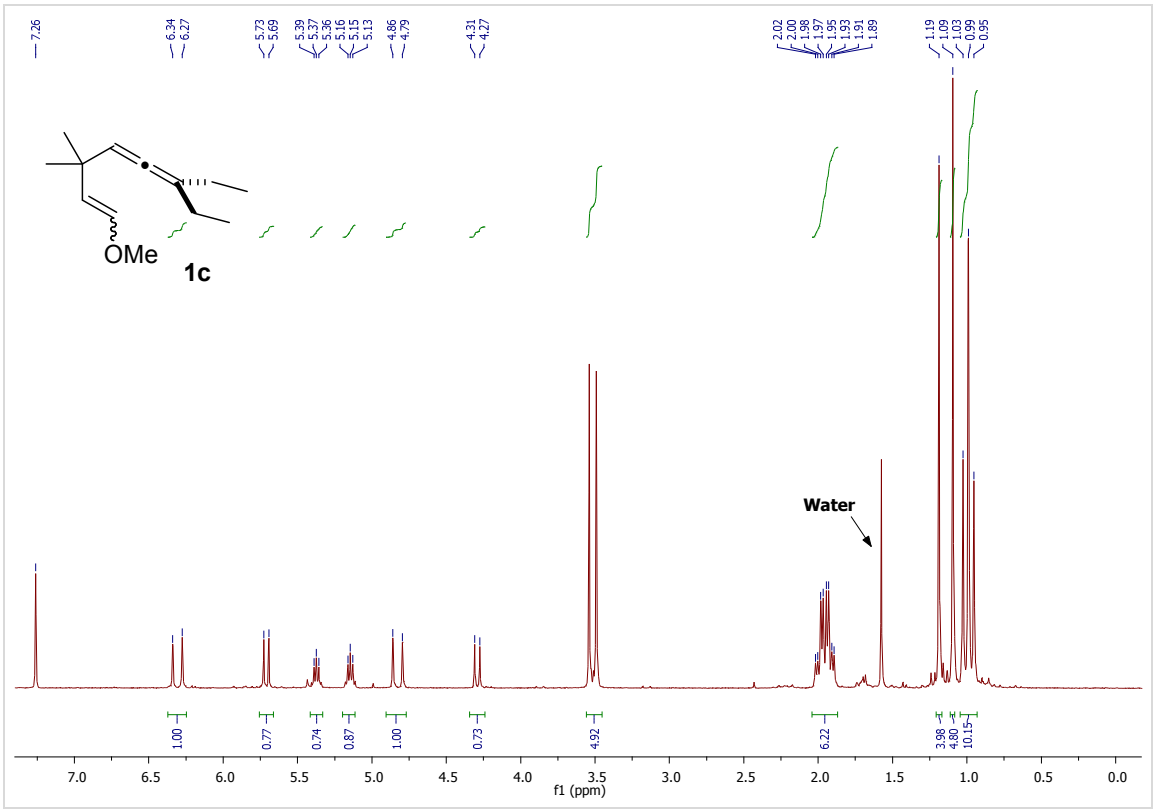
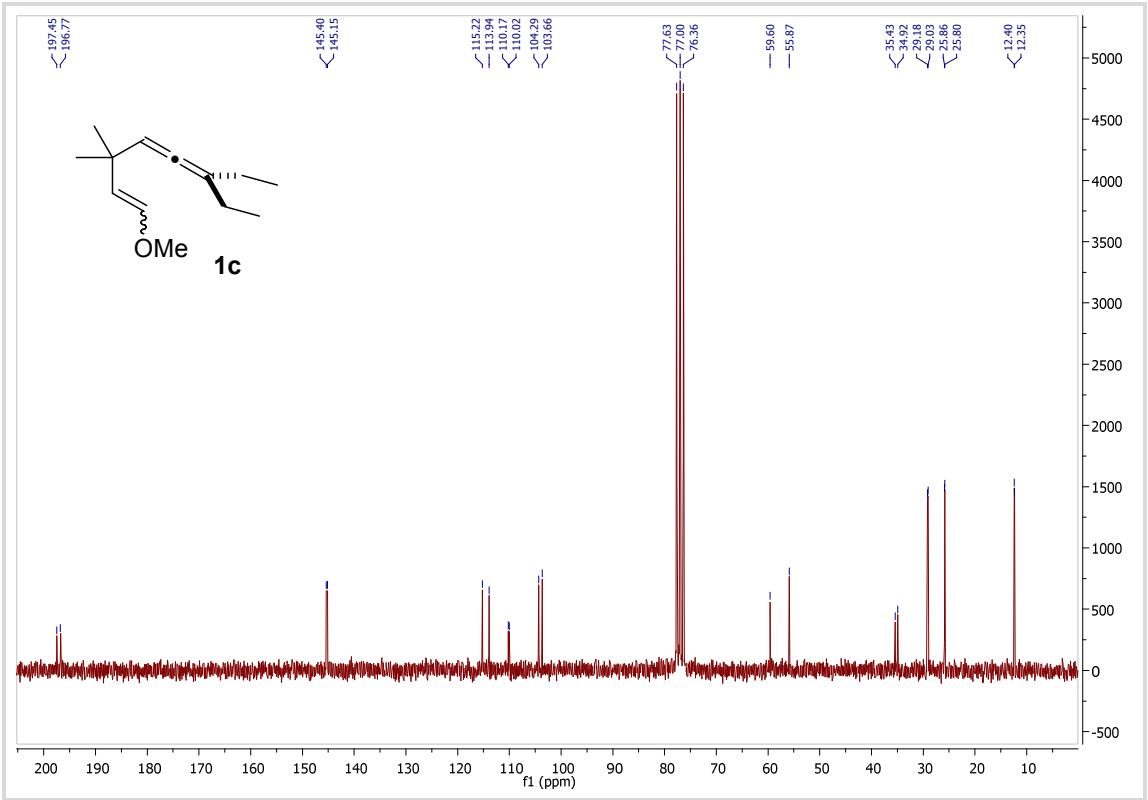
1.00
1.00
3.02
6.06
6.02
f1 (ppm)

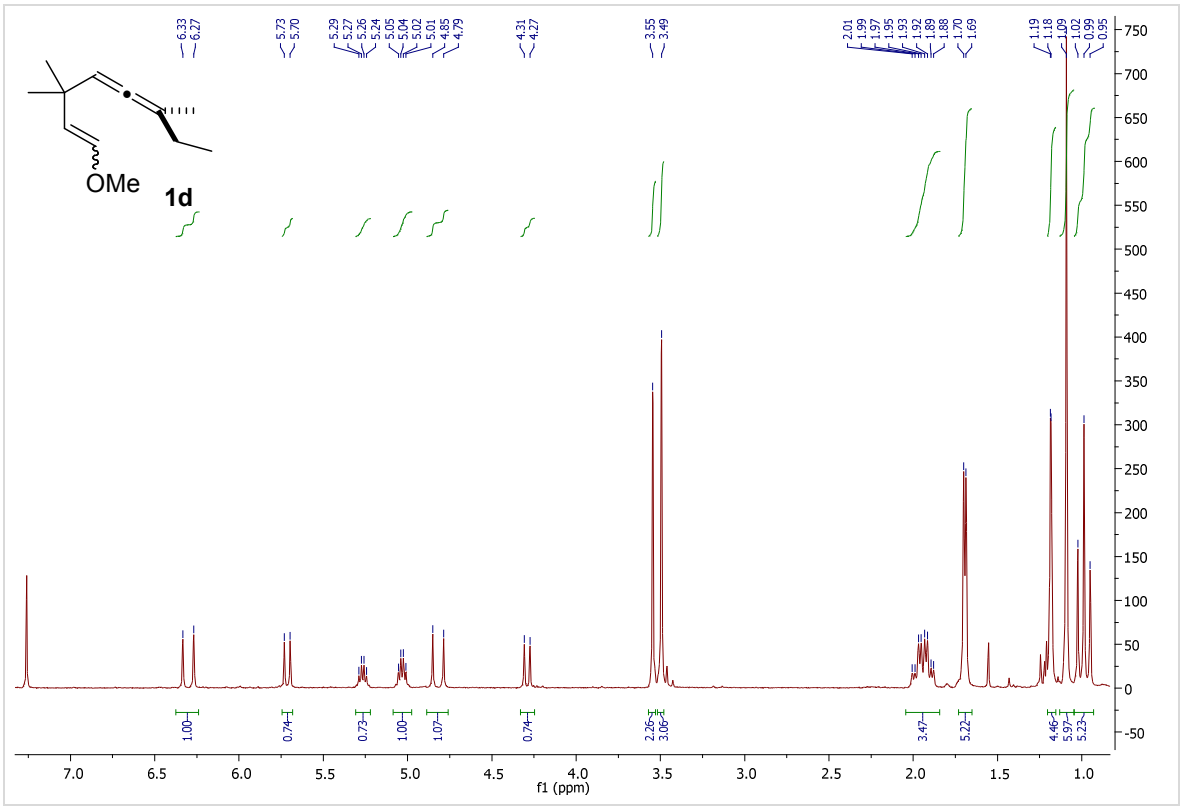

199.27
145.43
113.76
99.47
97.09
55.88
34.96
29.10
20.80
OMe
(E)-1a
f1 (ppm)

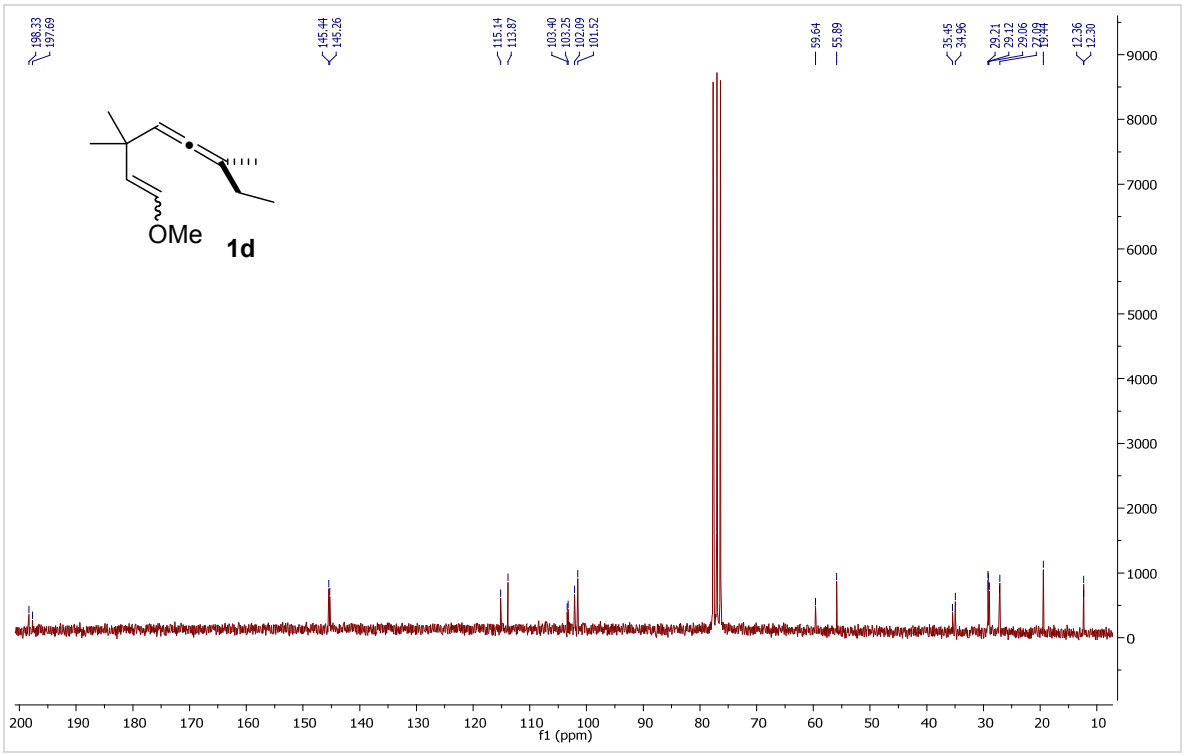

6.33
6.27
5.73
5.70
5.19
4.94
4.85
4.78
4.31
4.28
3.55
3.50
2.12
2.09
1.61
1.56
1.54
1.51
1.19
1.10
OMe
1b
1.00
0.84
0.84
1.02
1.04
0.83
5.45
7.35
11.00
4.74
5.84
f1 (ppm)

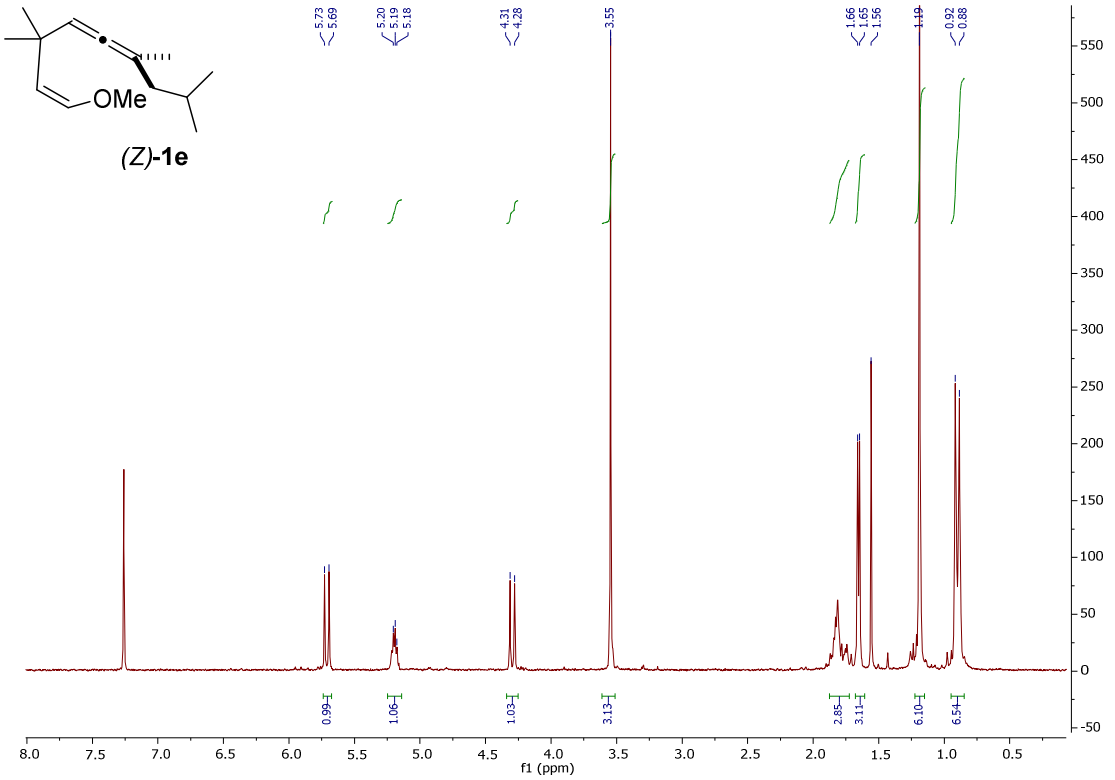

195.88
195.27
145.44
145.30
115.09
113.73
104.67
99.88
99.41
59.65
55.86
35.33
34.84
31.98
31.93
29.20
29.03
27.69
27.64
26.28
26.22
OMe
1b
f1 (ppm)

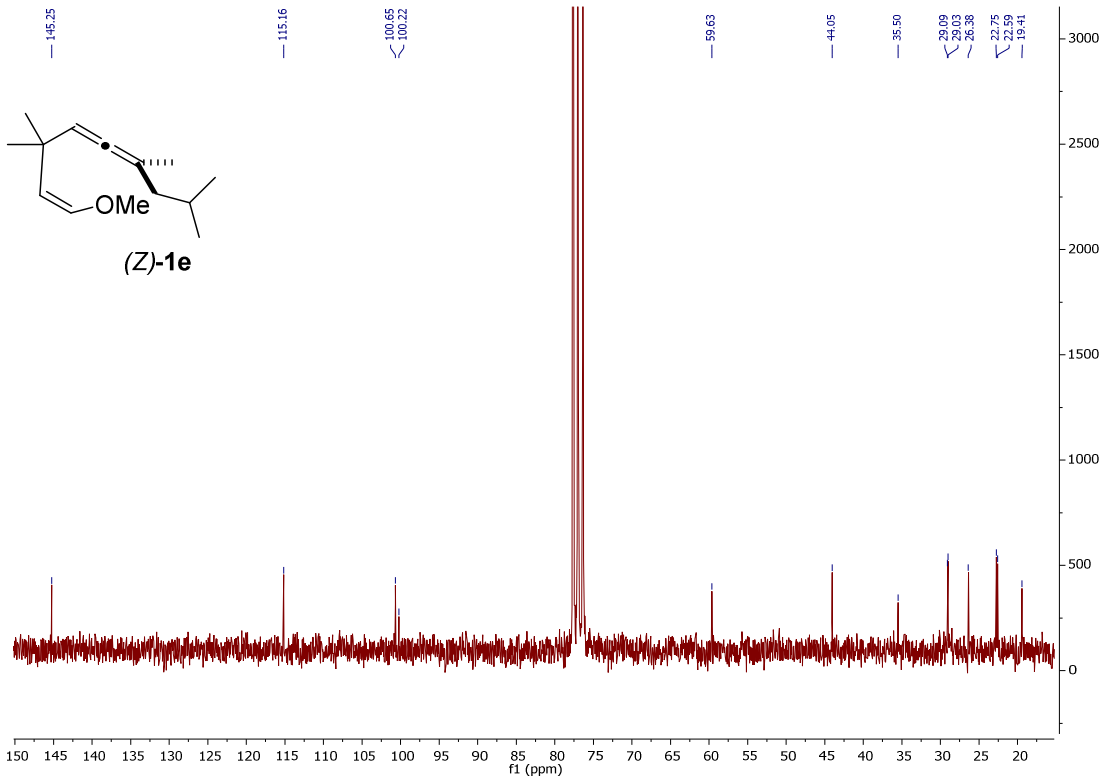

7.26
6.34
6.27
5.73
5.69
5.39
5.37
5.36
5.16
5.15
5.13
4.86
4.79
4.31
4.27
2.02
2.00
1.98
1.97
1.95
1.93
1.91
1.89
1.19
1.09
1.03
0.99
0.95
OMe
1c
Water
1.00
0.77
0.74
0.87
1.00
0.73
4.92
6.22
3.98
4.80
10.15
f1 (ppm)

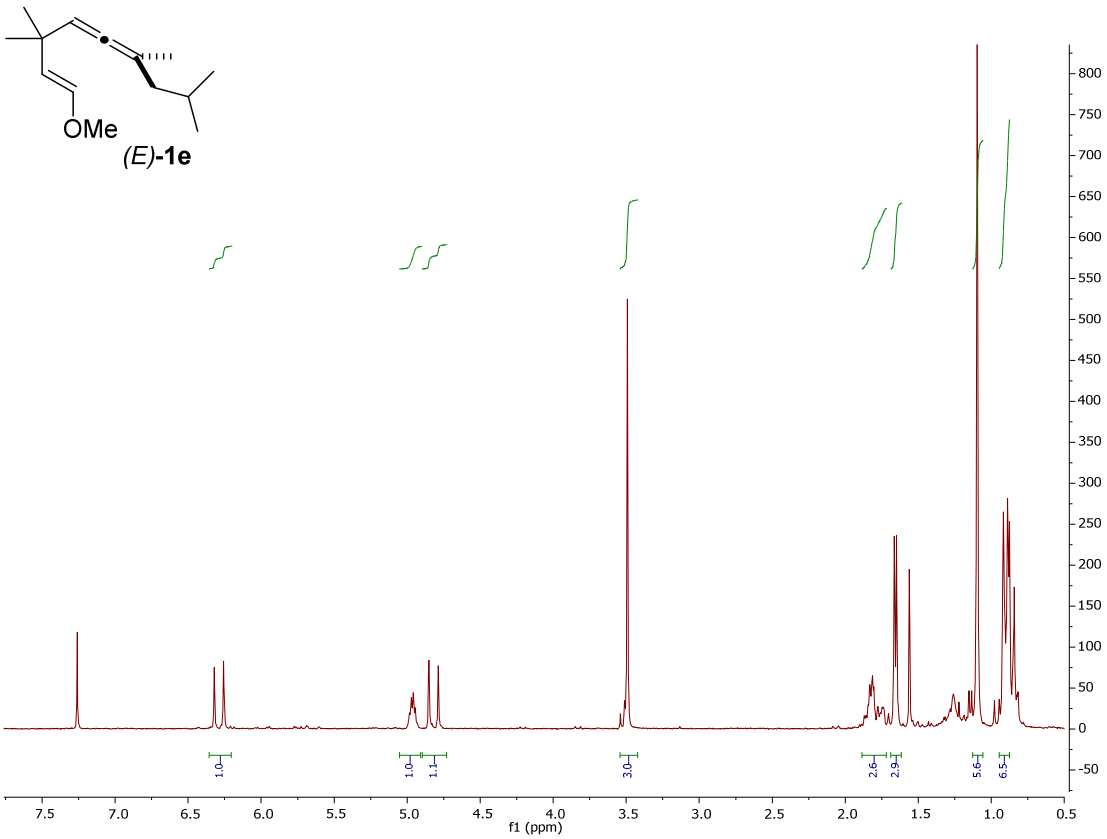

197.45
196.77
145.40
145.15
115.22
113.94
110.17
110.02
104.29
103.66
77.63
77.00
76.36
59.60
55.87
35.43
34.92
29.18
29.03
25.86
25.80
12.40
12.35
OMe
1c
f1 (ppm)

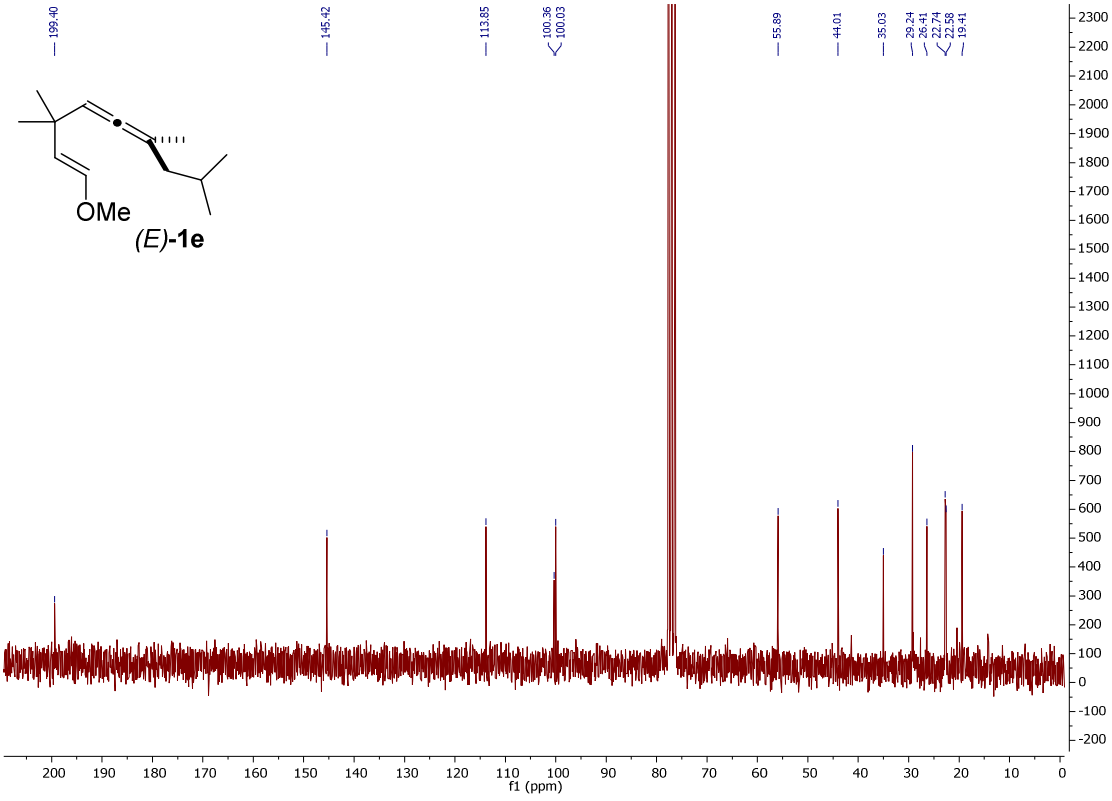

OMe
1d
f1 (ppm)

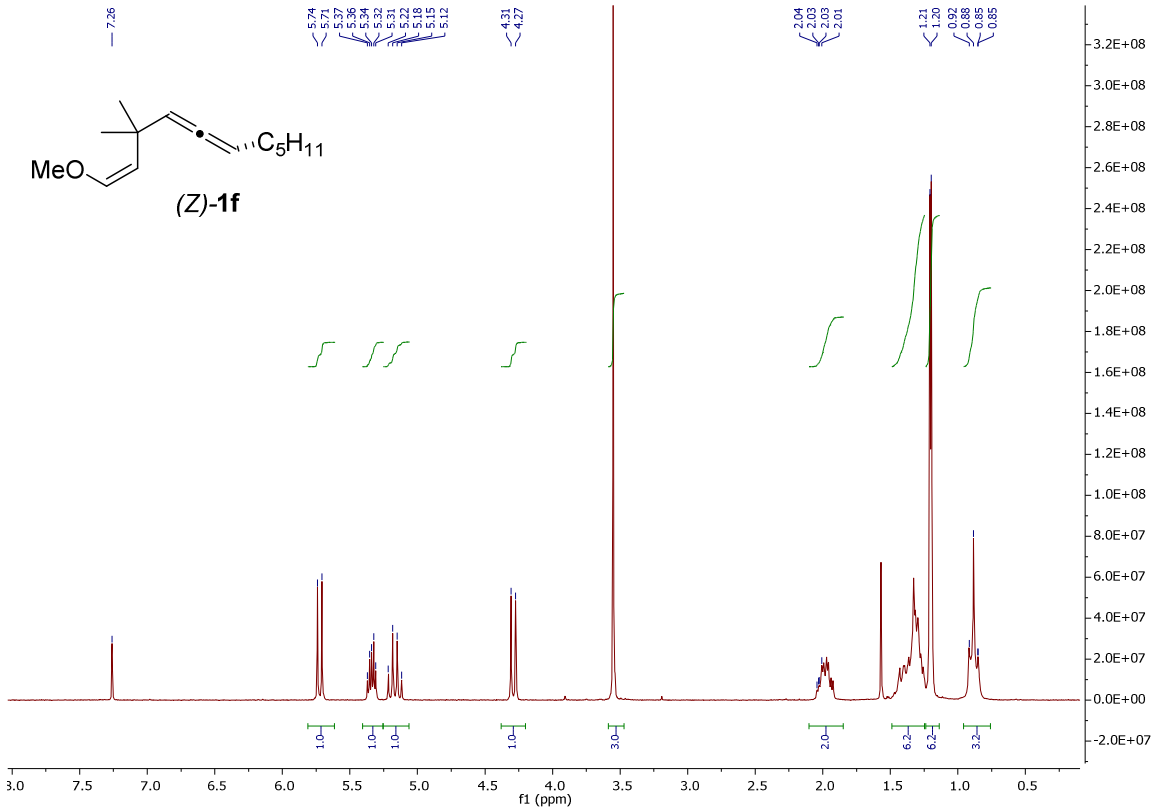

OMe
1d
f1 (ppm)

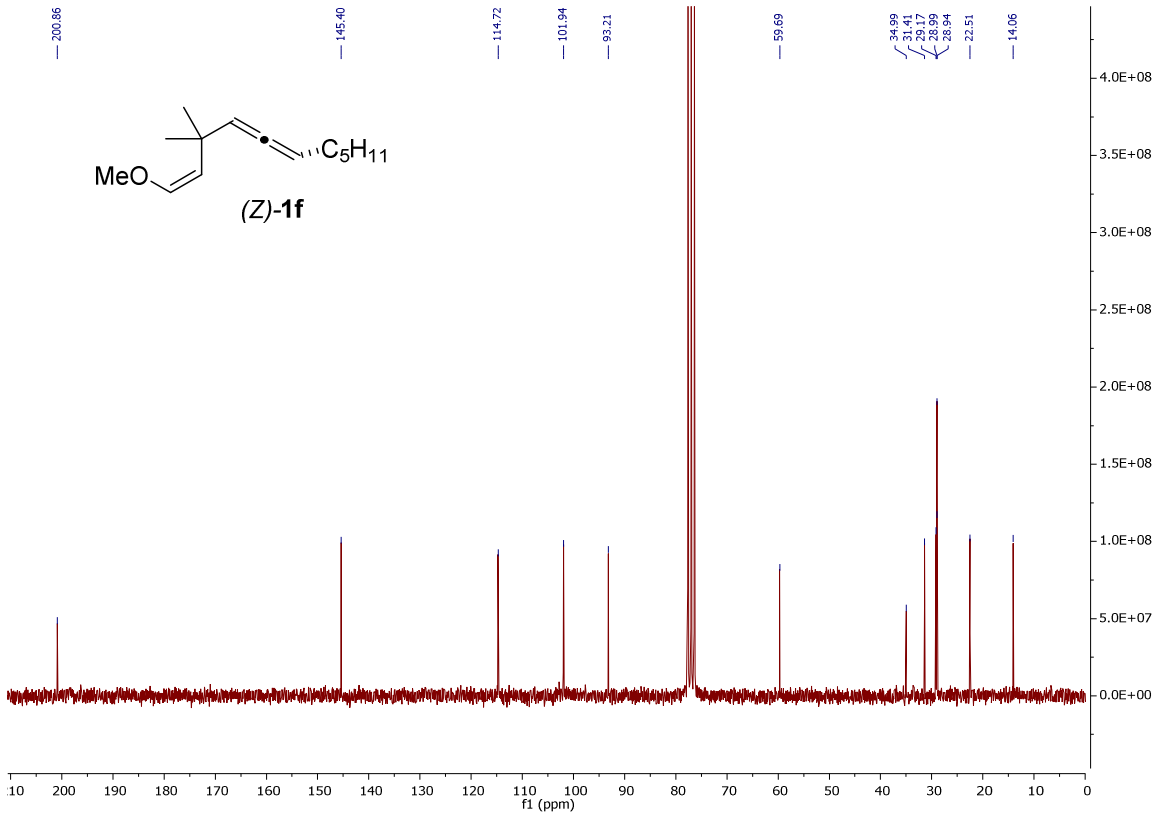

OMe
(Z)-1e
5.73
5.69
5.20
5.19
5.18
4.31
4.28
3.55
1.66
1.65
1.56
1.19
0.92
0.88
0.99
1.06
1.03
3.13
2.85
3.11
6.10
6.54
f1 (ppm)

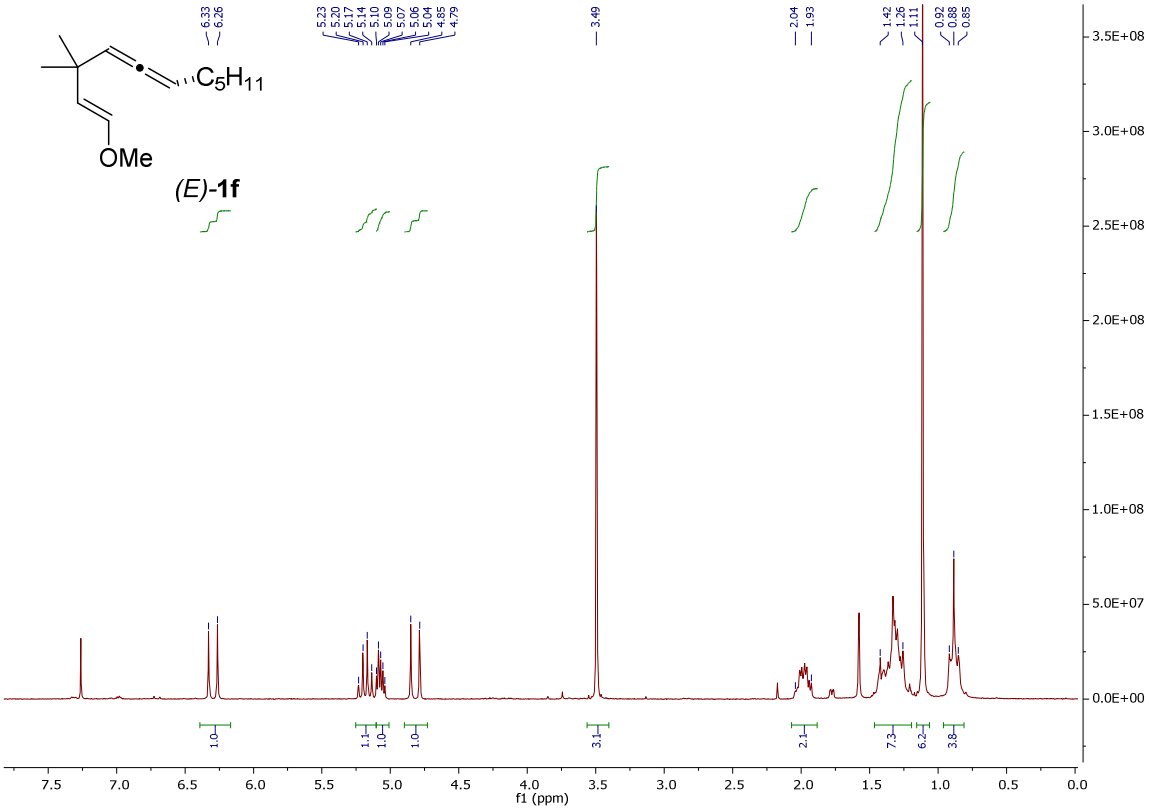

OMe
(Z)-1e
145.25
115.16
100.65
100.22
59.63
44.05
35.50
29.09
29.03
26.38
22.75
22.59
19.41
f1 (ppm)

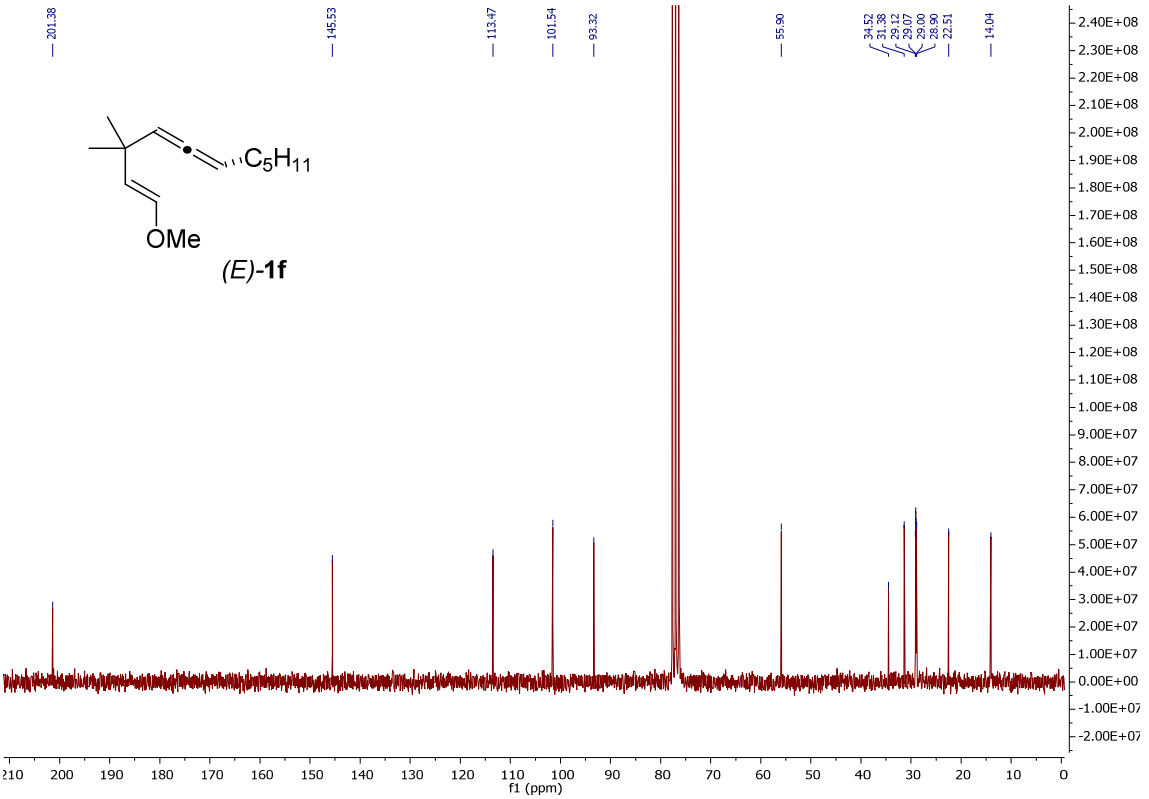

OMe
(E)-1e
f1 (ppm)

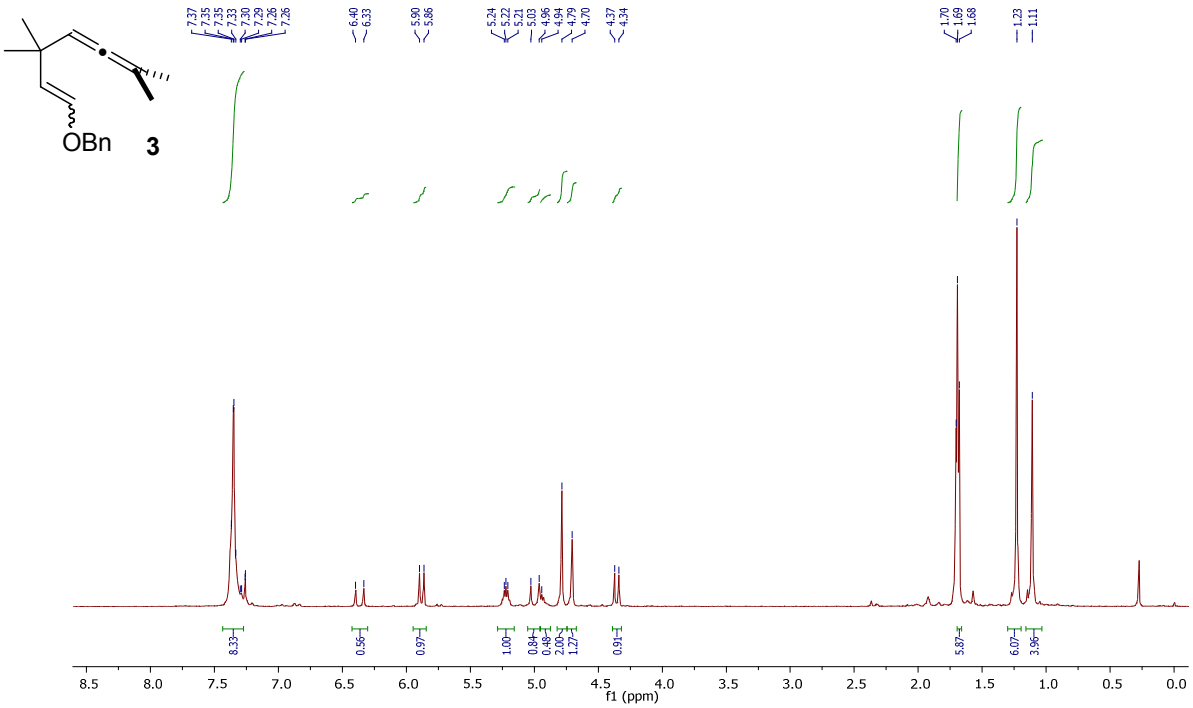

199.40
145.42
113.85
100.36
100.03
55.89
44.01
35.03
29.24
26.41
22.74
22.58
19.41
OMe
(E)-1e
f1 (ppm)

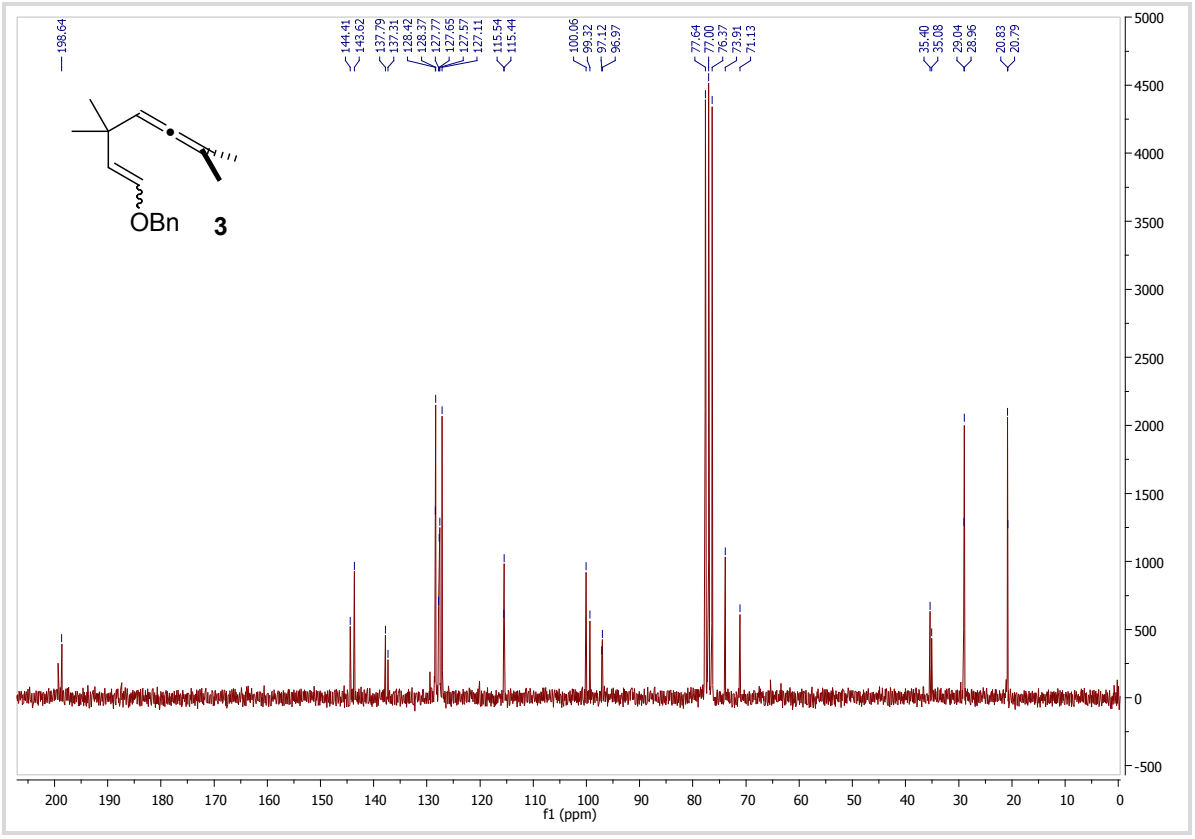

7.26
5.74
5.71
5.37
5.36
5.34
5.32
5.31
5.22
5.18
5.15
5.12
4.31
4.27
2.04
2.03
2.03
2.01
1.21
1.20
0.92
0.88
0.85
0.85
MeO
C_5H_{11}
(Z)-1f
f1 (ppm)

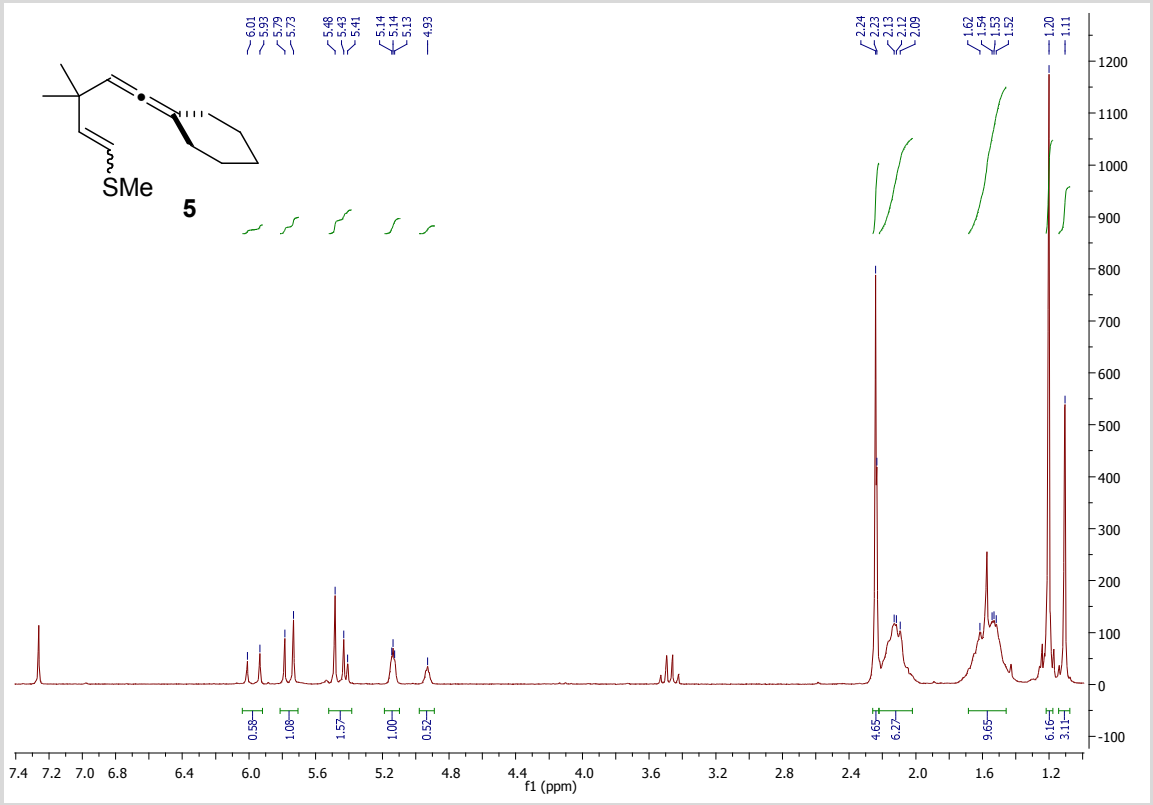

200.86
145.40
114.72
101.94
93.21
59.69
34.99
31.41
29.17
28.99
28.94
22.51
14.06
MeO
C_5H_{11}
(Z)-1f
f1 (ppm)

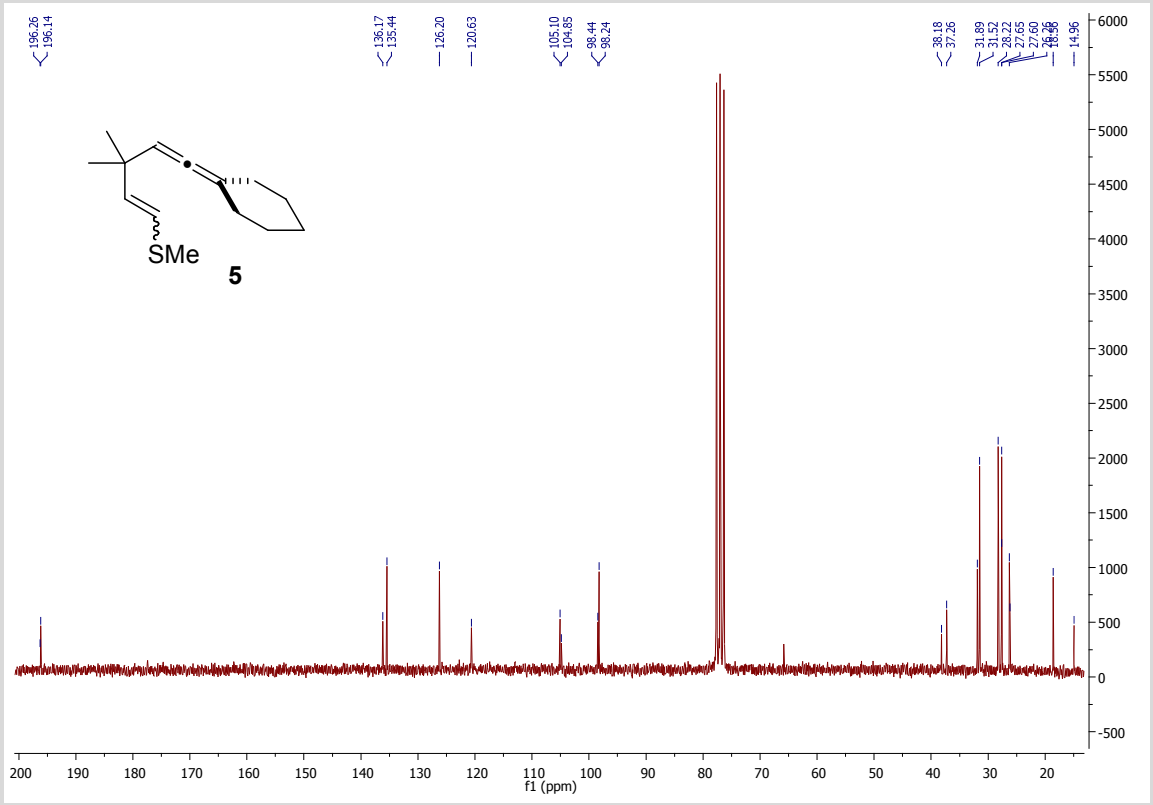

6.33
6.26
5.23
5.20
5.17
5.14
5.10
5.09
5.07
5.06
5.04
4.85
4.79
3.49
2.04
1.93
1.42
1.26
1.11
0.92
0.88
0.85
C5H11
OMe
(E)-1f
1.0
1.1
1.0
1.0
3.1
2.1
7.3
6.2
3.8
f1 (ppm)

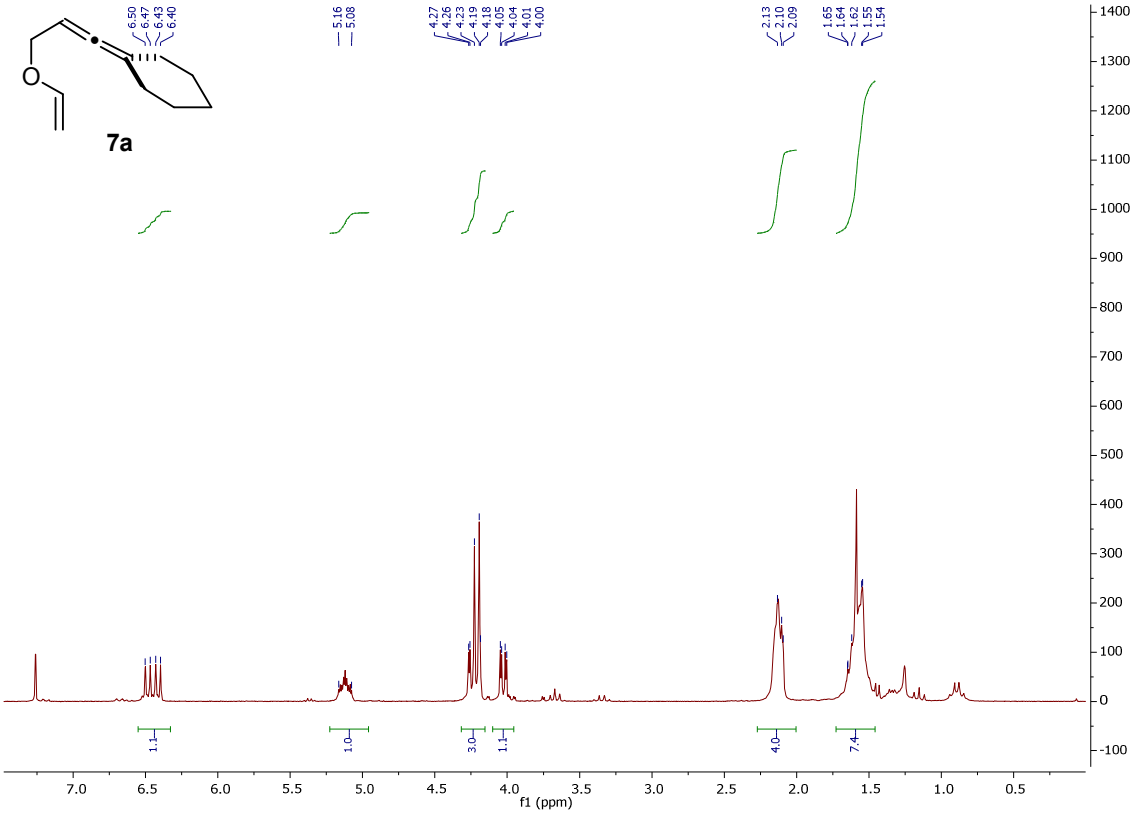

201.38
145.53
113.47
101.54
93.32
55.90
34.52
31.38
29.12
29.07
29.00
28.90
22.51
14.04
C5H11
OMe
(E)-1f
f1 (ppm)

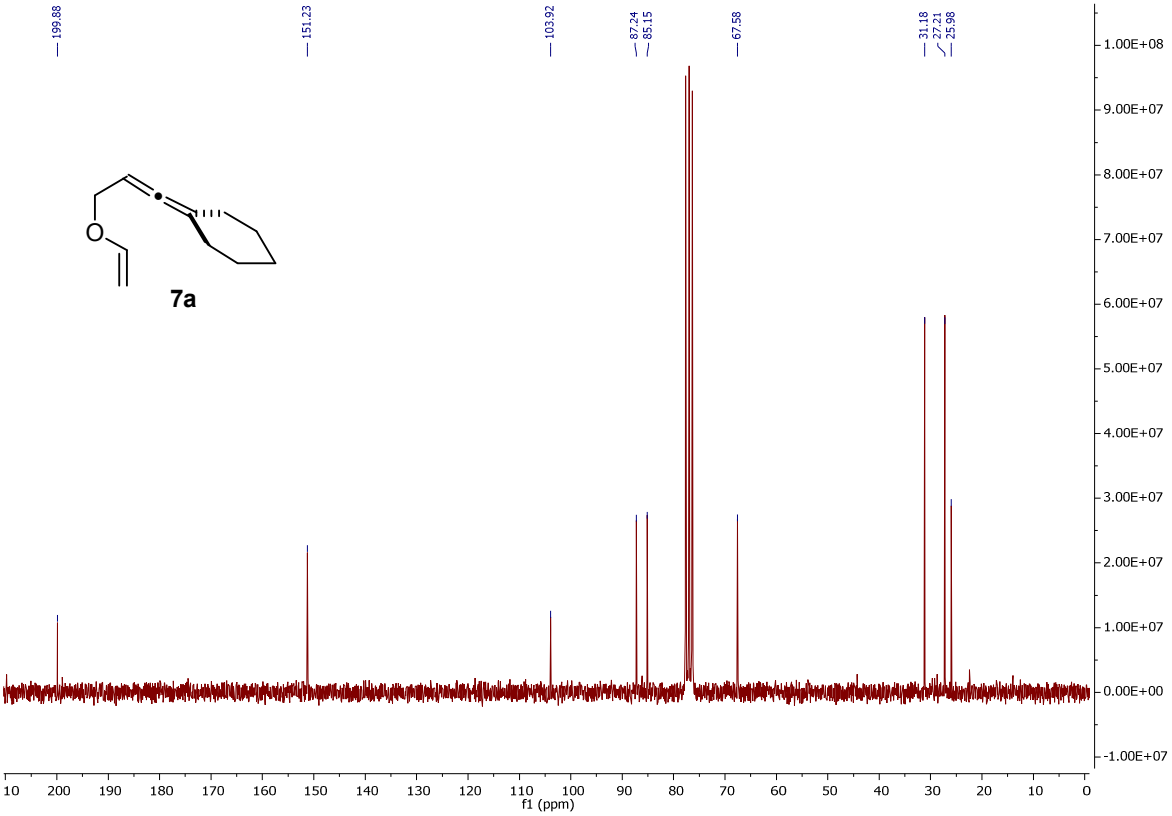

OBn
3
f1 (ppm)

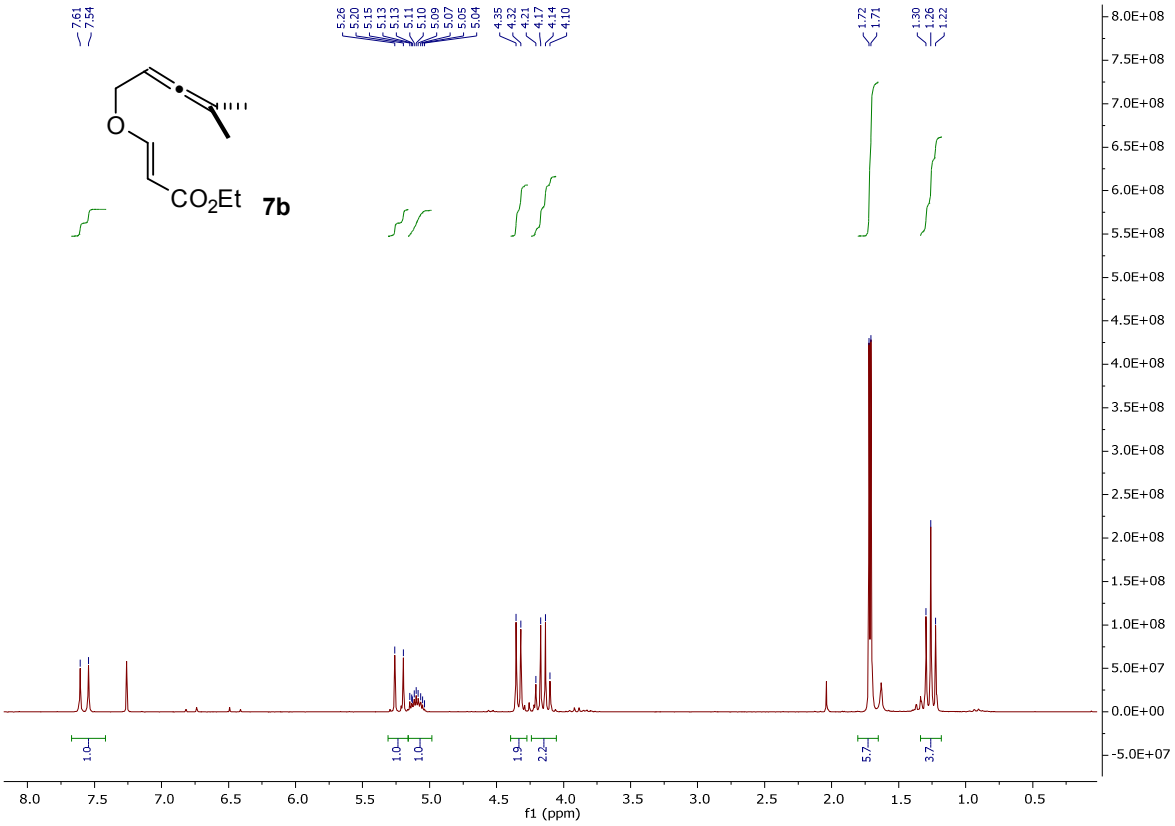

OBn
3
f1 (ppm)

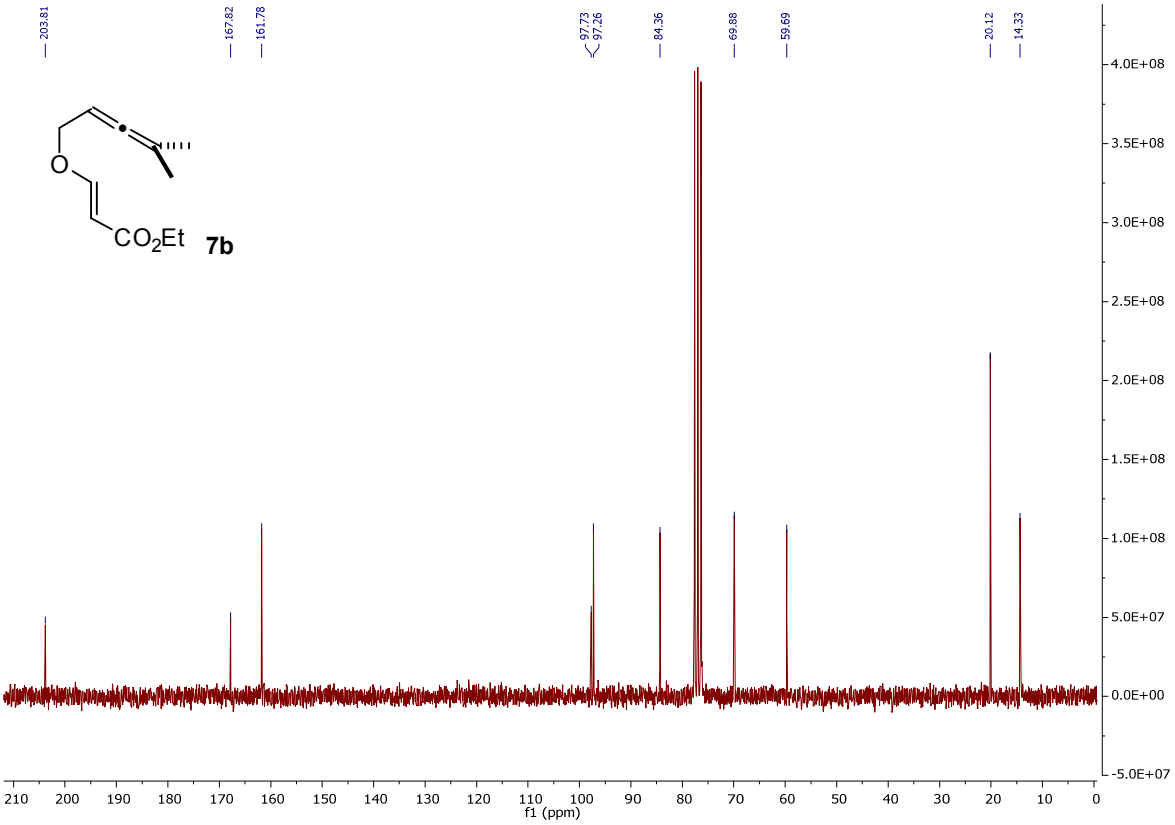

SMe
5
f1 (ppm)

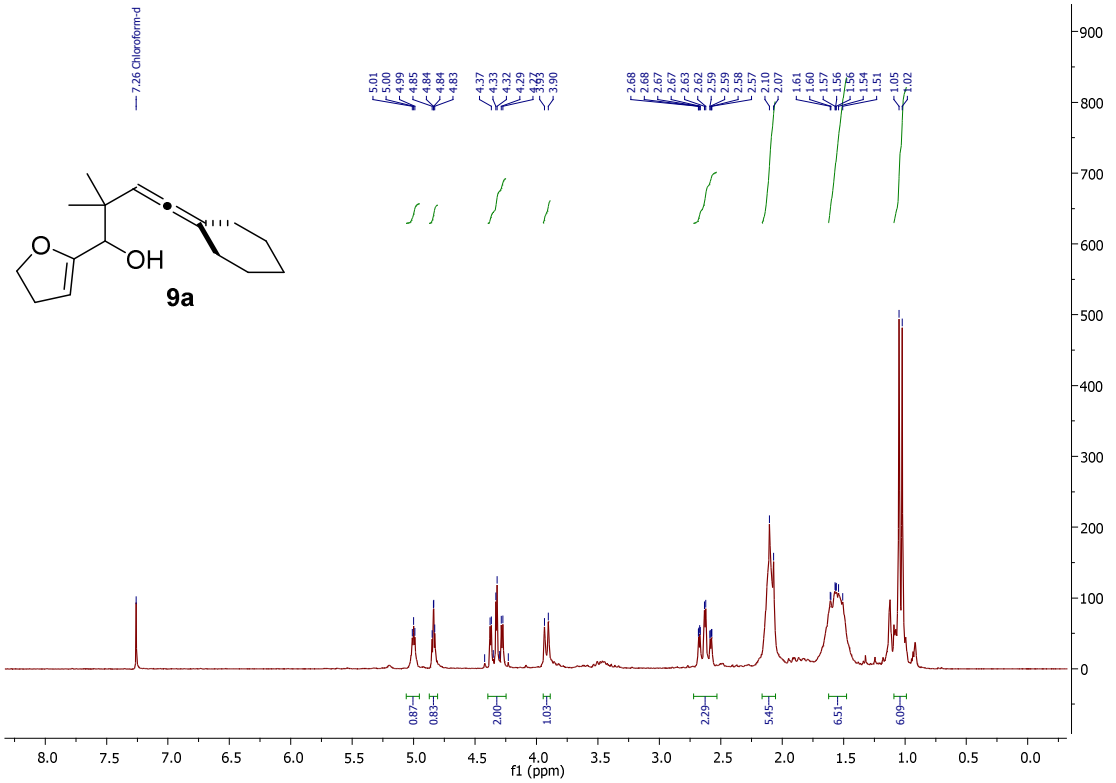

SMe
5
f1 (ppm)

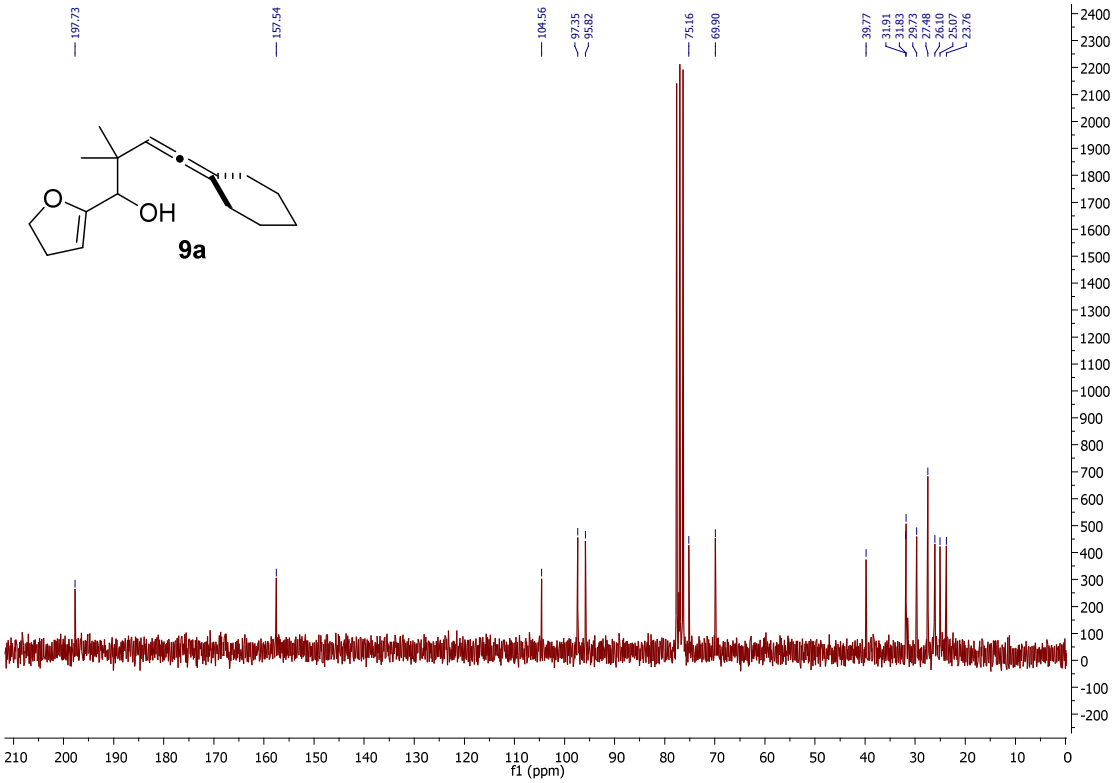

6.50
6.47
6.43
6.40
5.16
5.08
4.27
4.26
4.23
4.19
4.18
4.05
4.04
4.01
4.00
2.13
2.10
2.09
1.65
1.64
1.62
1.55
1.54
7a
1.1
1.0
3.0
1.1
4.0
7.4
f1 (ppm)

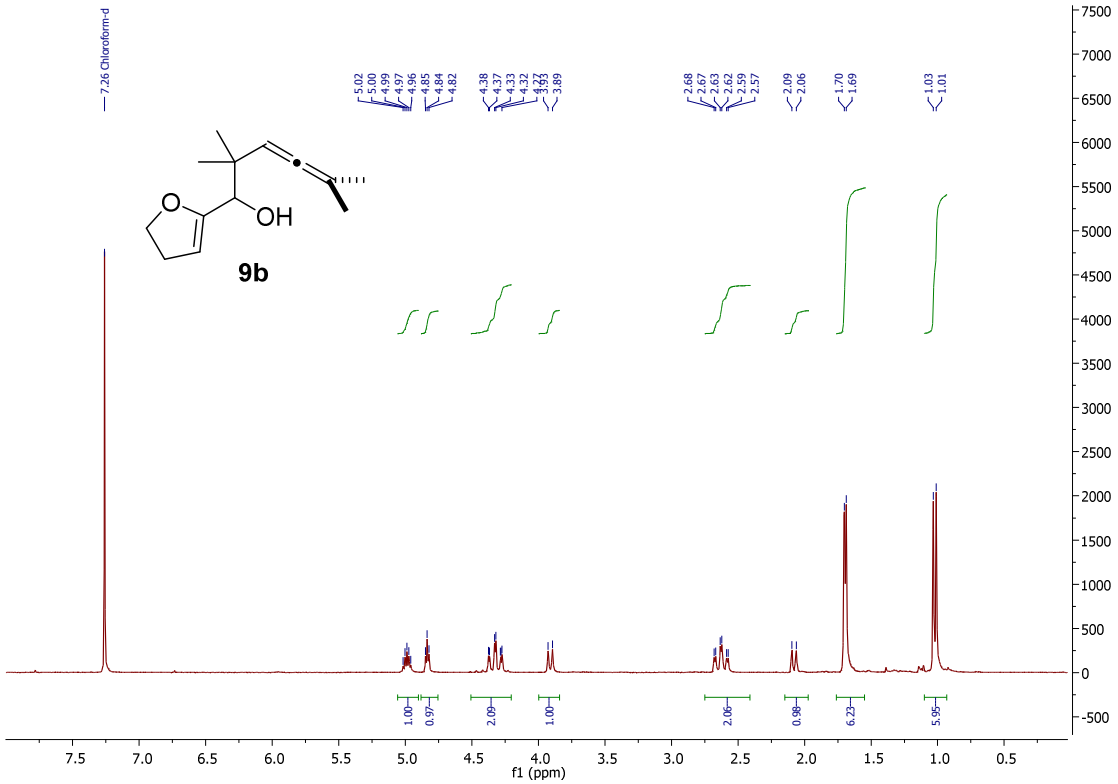

199.88
151.23
103.92
87.24
85.15
67.58
31.18
27.21
25.98
7a
f1 (ppm)

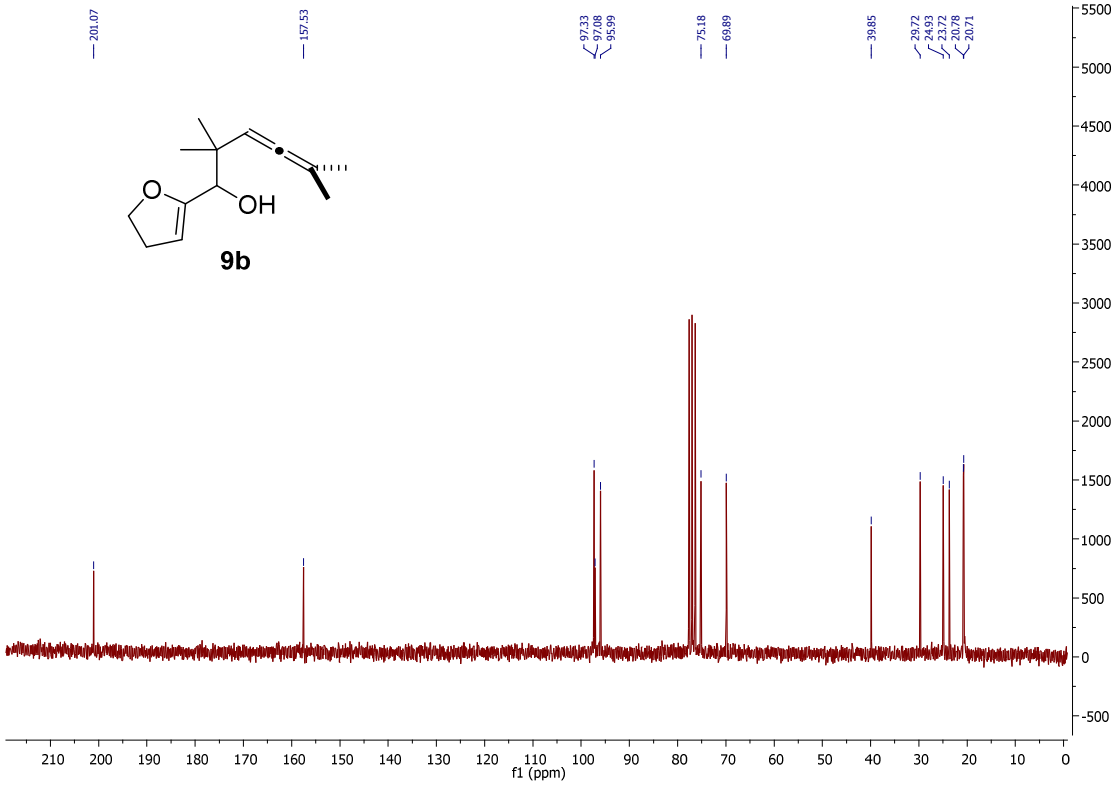

7.61
7.54
5.26
5.20
5.15
5.13
5.13
5.11
5.10
5.09
5.07
5.05
5.04
4.35
4.32
4.21
4.17
4.14
4.10
1.72
1.71
1.30
1.26
1.22
O
CO2Et
7b
1.0
1.0
1.0
1.9
2.2
5.7
3.7
f1 (ppm)

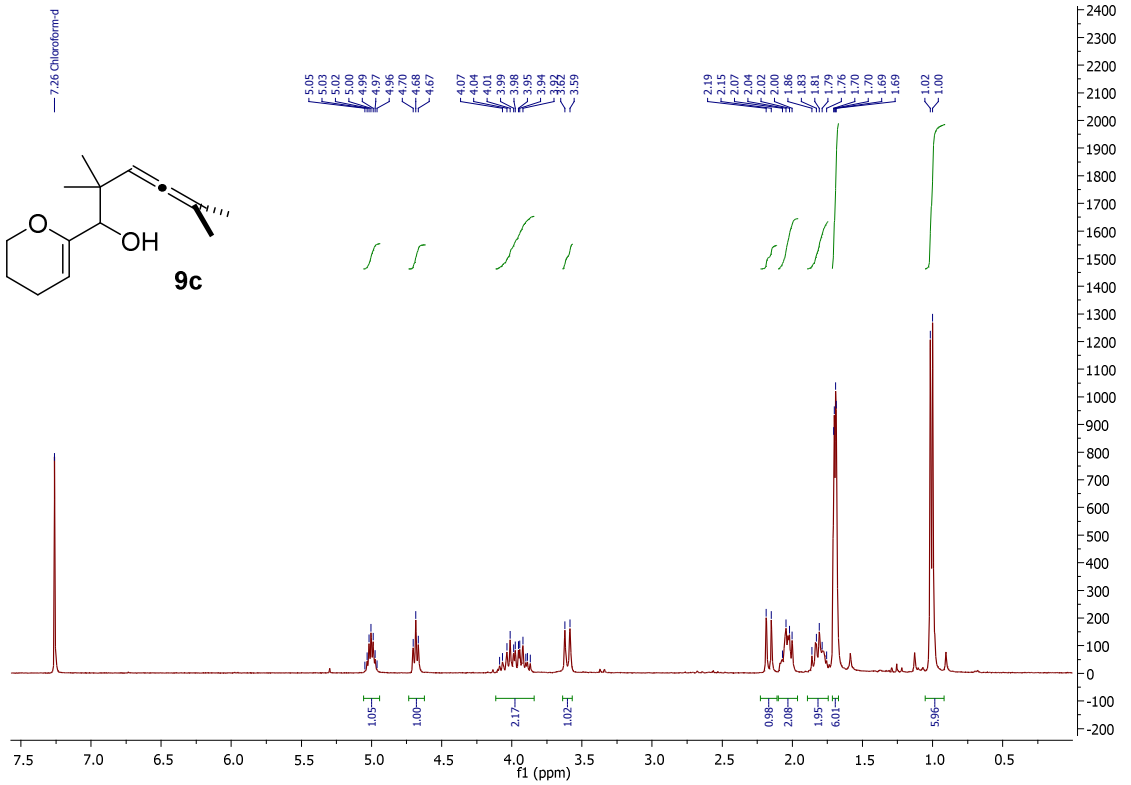

203.81
167.82
161.78
97.73
97.26
84.36
69.88
59.69
20.12
14.33
O
CO2Et
7b
f1 (ppm)

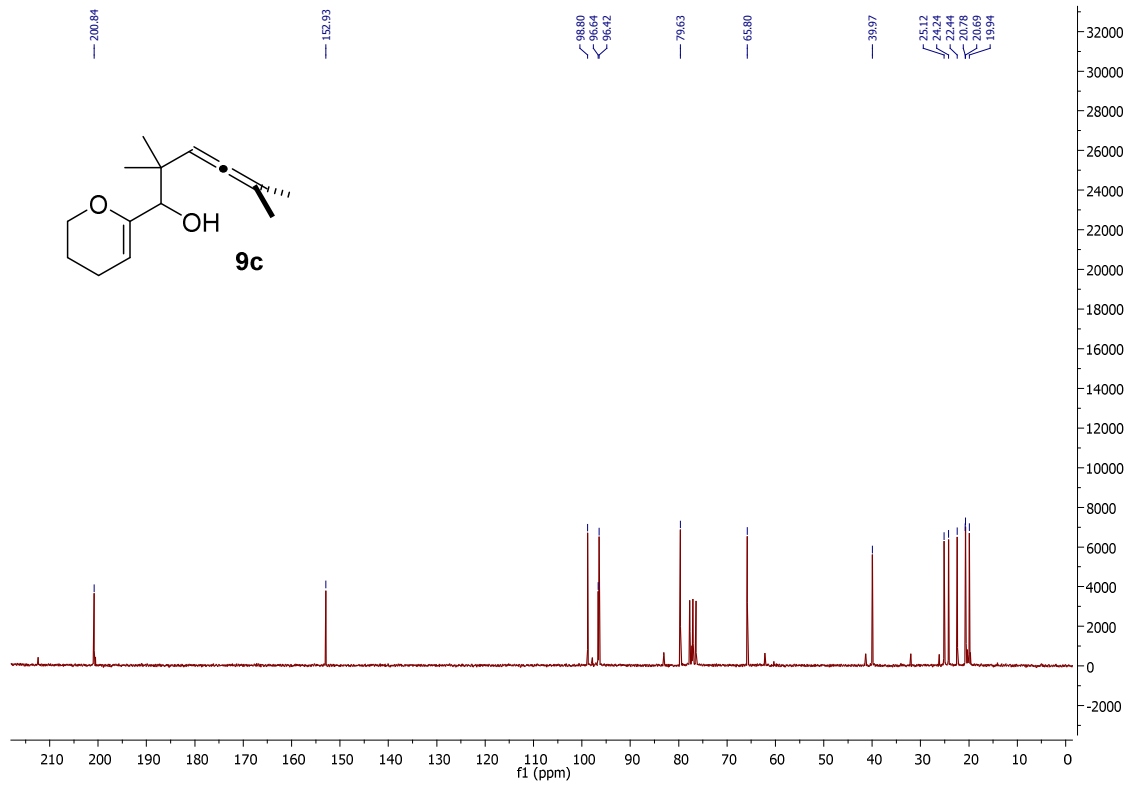

7.26 Chloroform-d
5.01
5.00
4.99
4.85
4.84
4.84
4.84
4.83
4.37
4.33
4.32
4.29
3.93
3.90
2.68
2.68
2.67
2.67
2.63
2.62
2.59
2.59
2.58
2.57
2.10
2.07
1.61
1.60
1.57
1.56
1.56
1.54
1.51
1.05
1.02
O
OH
9a
0.87
0.83
2.00
1.03
2.29
5.45
6.51
6.09
f1 (ppm)

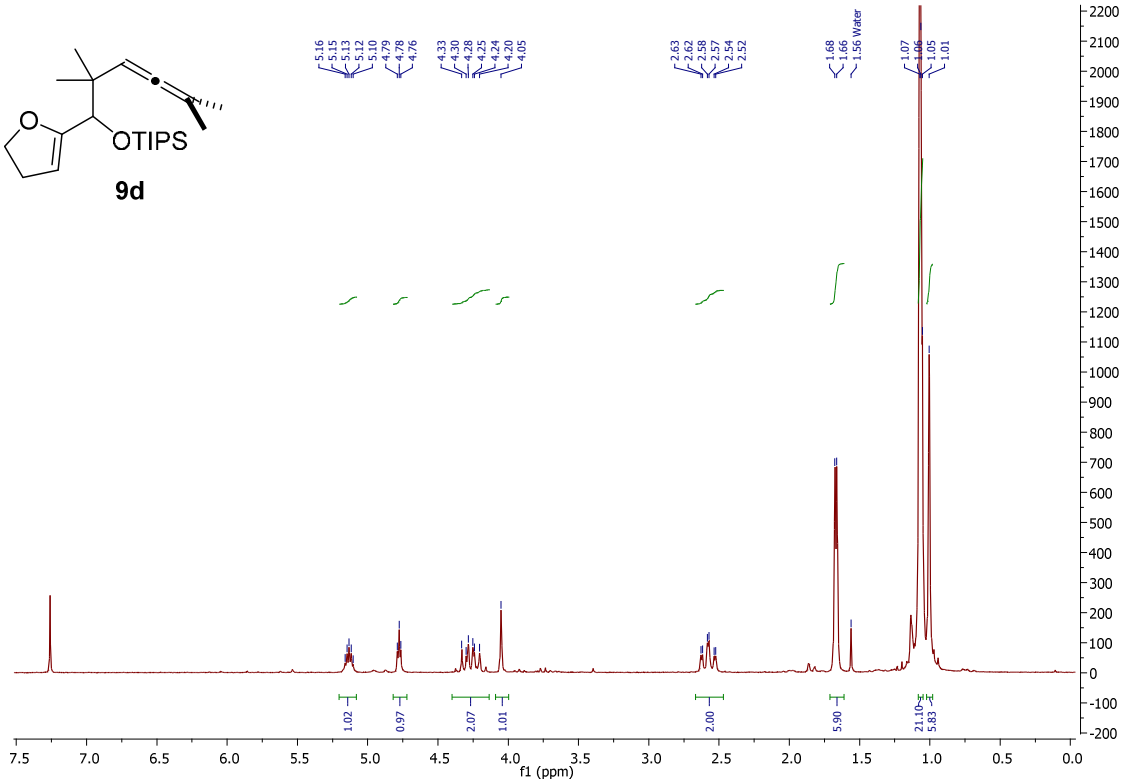

197.73
157.54
104.56
97.35
95.82
75.16
69.90
39.77
31.91
31.83
29.73
27.48
26.10
25.07
23.76
O
OH
9a
f1 (ppm)

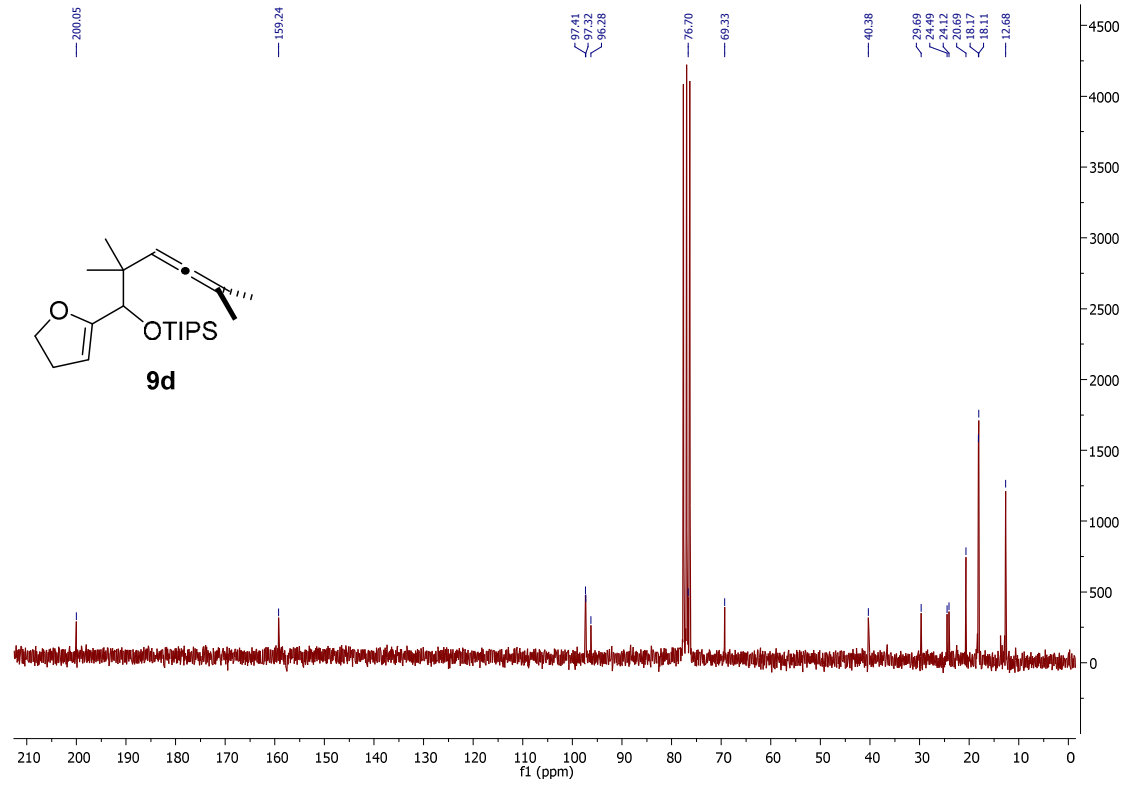

7.26 Chloroform-d
5.02
5.00
4.99
4.97
4.96
4.85
4.84
4.82
4.38
4.37
4.33
4.32
3.89
2.68
2.67
2.63
2.62
2.59
2.57
2.09
2.06
1.70
1.69
1.03
1.01
OH
9b
1.00
0.97
2.09
1.00
2.06
0.98
6.23
5.95
f1 (ppm)

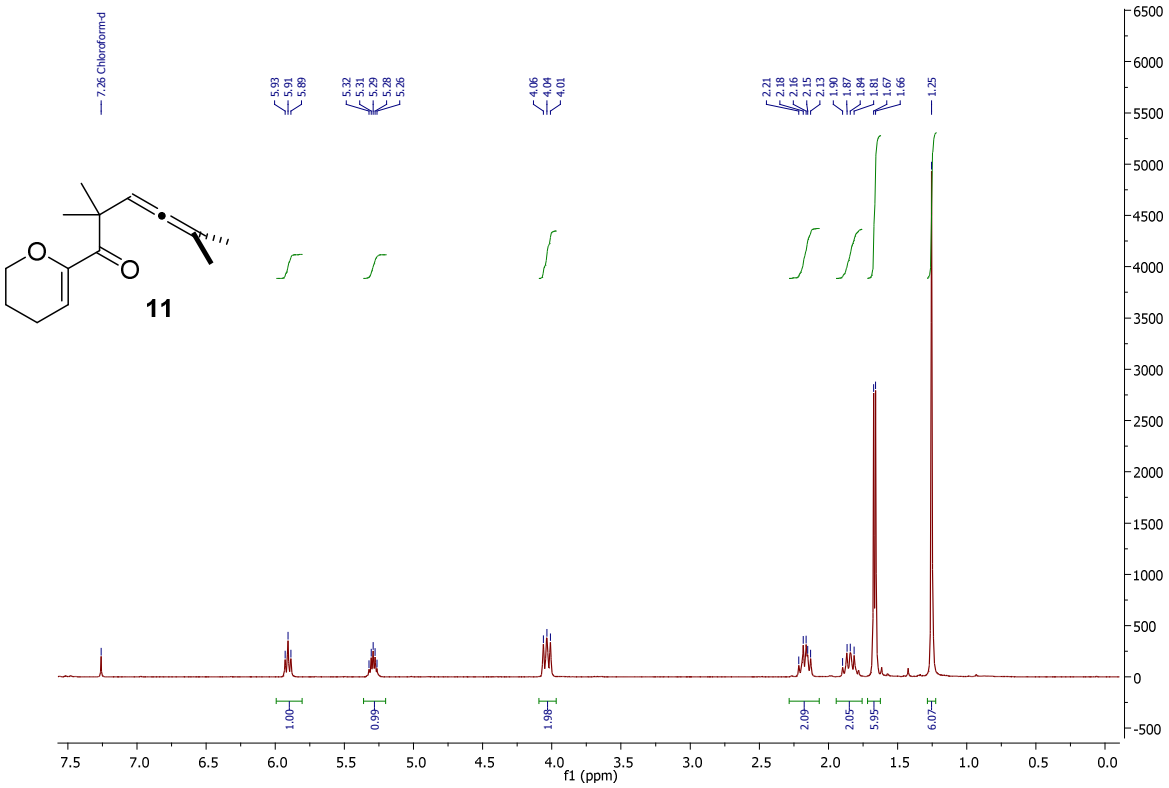

201.07
157.53
97.33
97.08
95.99
75.18
69.89
39.85
29.72
24.93
23.72
20.78
20.71
OH
9b
f1 (ppm)

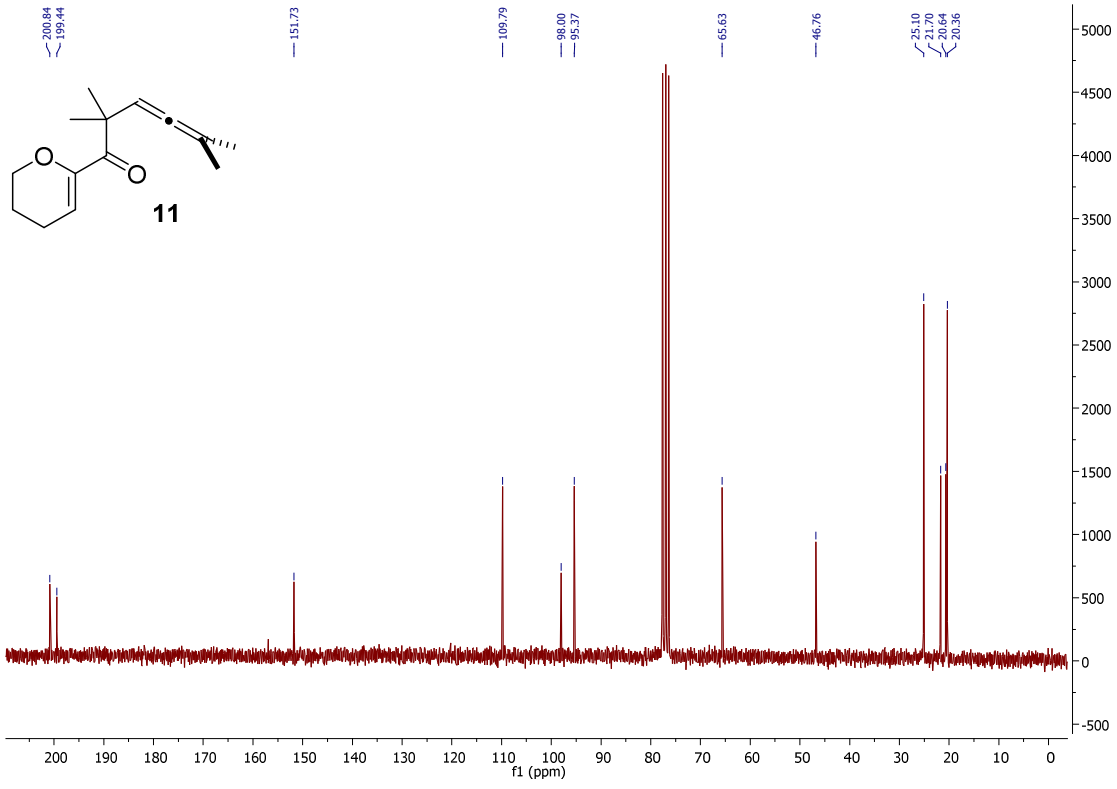

7.26 Chloroform-d
5.05
5.03
5.02
5.00
4.99
4.97
4.96
4.70
4.68
4.67
4.07
4.04
4.01
3.99
3.98
3.95
3.94
3.82
3.59
2.19
2.15
2.07
2.04
2.02
2.00
1.86
1.83
1.81
1.79
1.76
1.70
1.70
1.69
1.69
1.02
1.00
O
OH
9c
1.05
1.00
2.17
1.02
0.98
2.08
1.95
6.01
5.96
f1 (ppm)

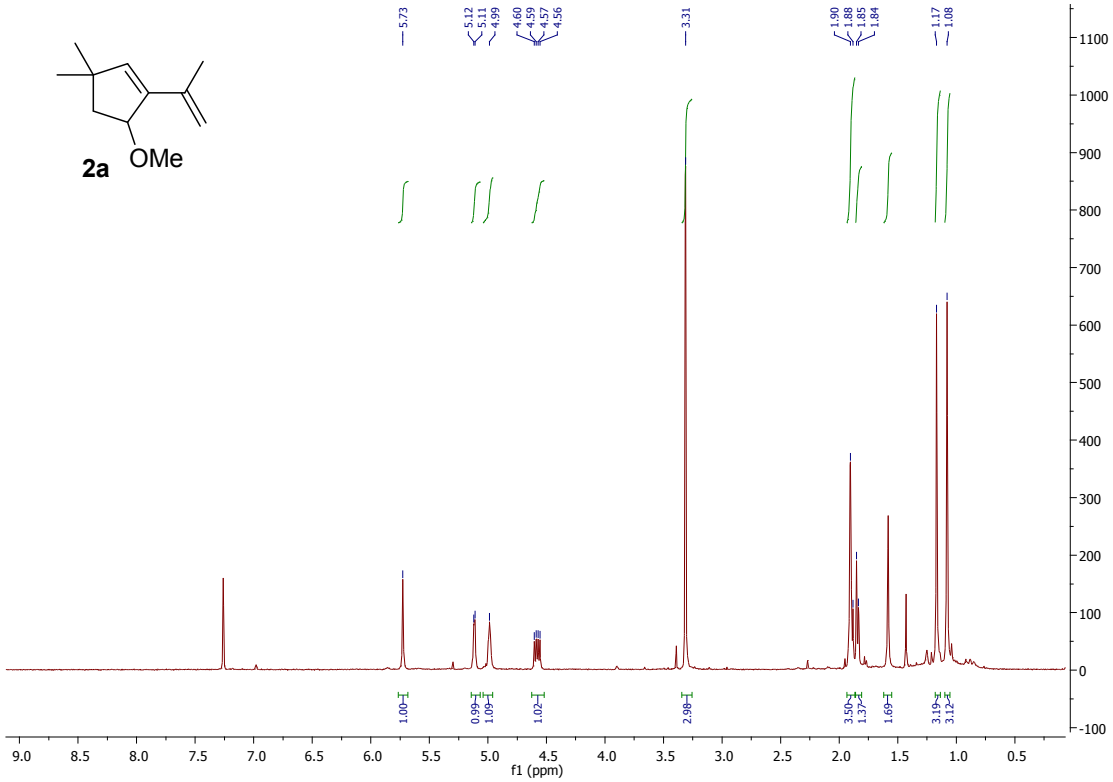

200.84
152.93
98.80
96.64
96.42
79.63
65.80
39.97
25.12
24.24
22.44
20.78
20.69
19.94
O
OH
9c
f1 (ppm)

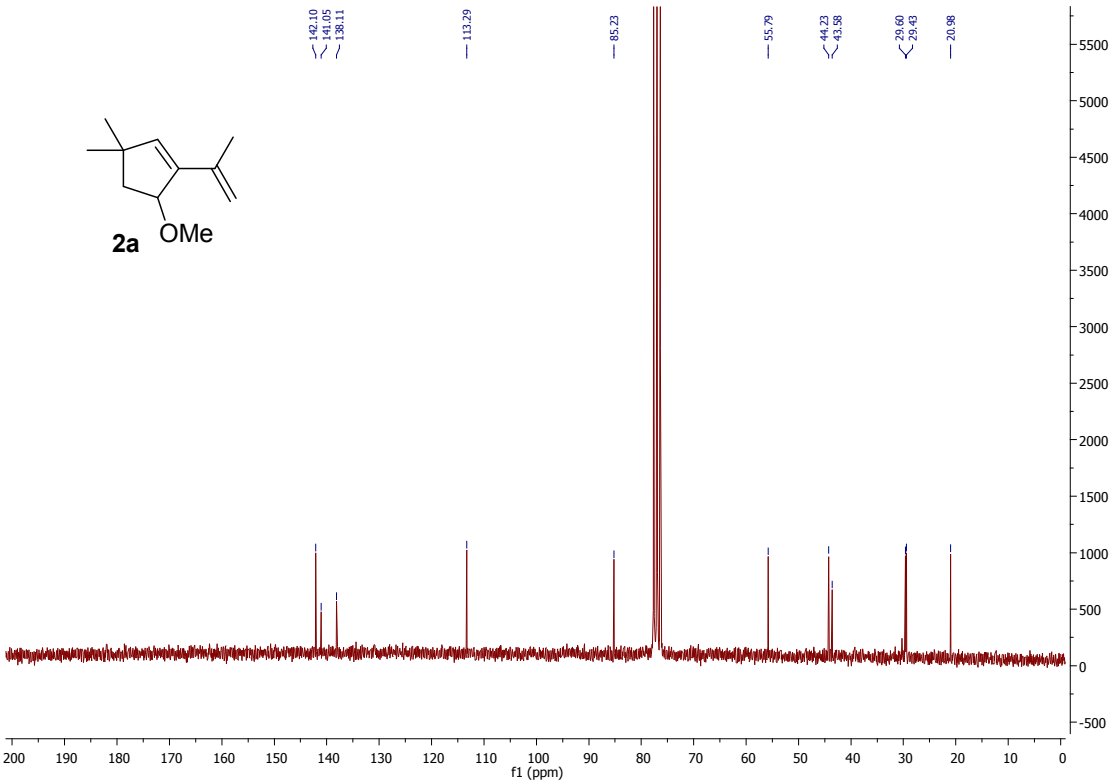

OTIPS
9d
5.16
5.15
5.13
5.12
5.10
4.79
4.78
4.76
4.33
4.30
4.28
4.25
4.24
4.20
4.05
2.63
2.62
2.58
2.57
2.54
2.52
1.68
1.66
1.56 Water
1.07
1.06
1.05
1.01
1.02
0.97
2.07
1.01
2.00
5.90
21.10
5.83
f1 (ppm)

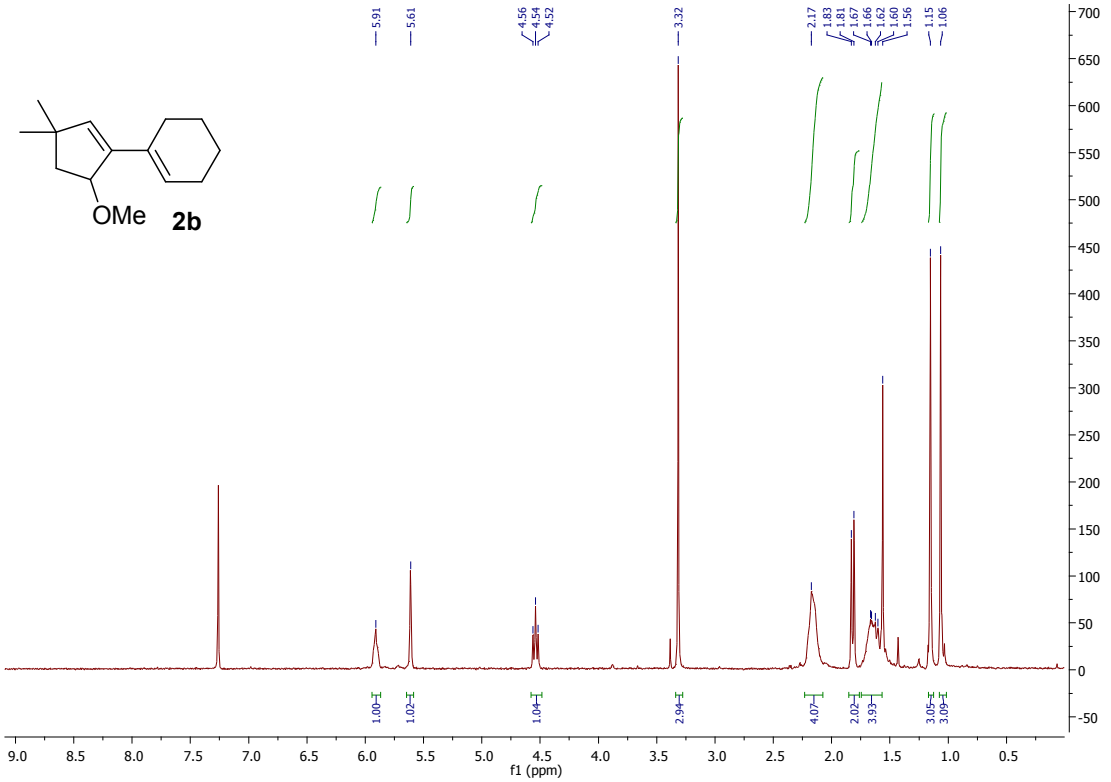

OTIPS
9d
200.05
159.24
97.41
97.32
96.28
76.70
69.33
40.38
29.69
24.49
24.12
20.69
18.17
18.11
12.68
f1 (ppm)

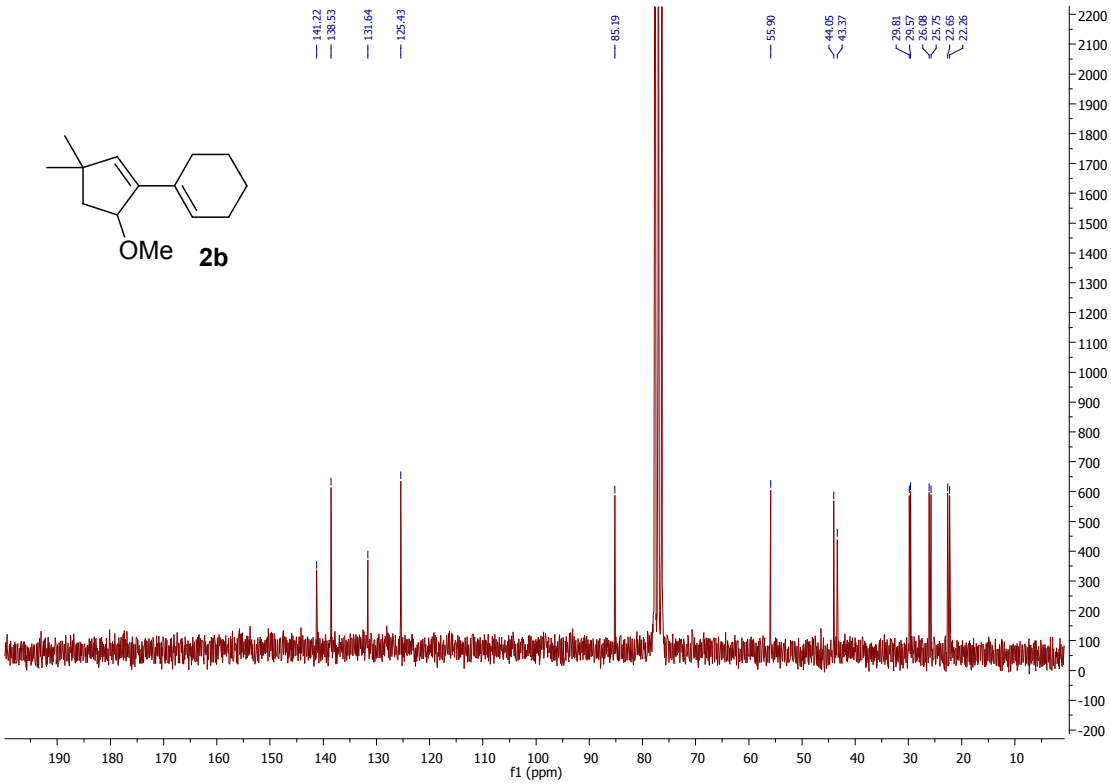

7.26 Chloroform-d
5.93
5.91
5.89
5.32
5.31
5.29
5.28
5.26
4.06
4.04
4.01
2.21
2.18
2.16
2.15
2.13
1.90
1.87
1.84
1.81
1.67
1.66
1.25
11
1.00
0.99
1.98
2.09
2.05
5.95
6.07
f1 (ppm)

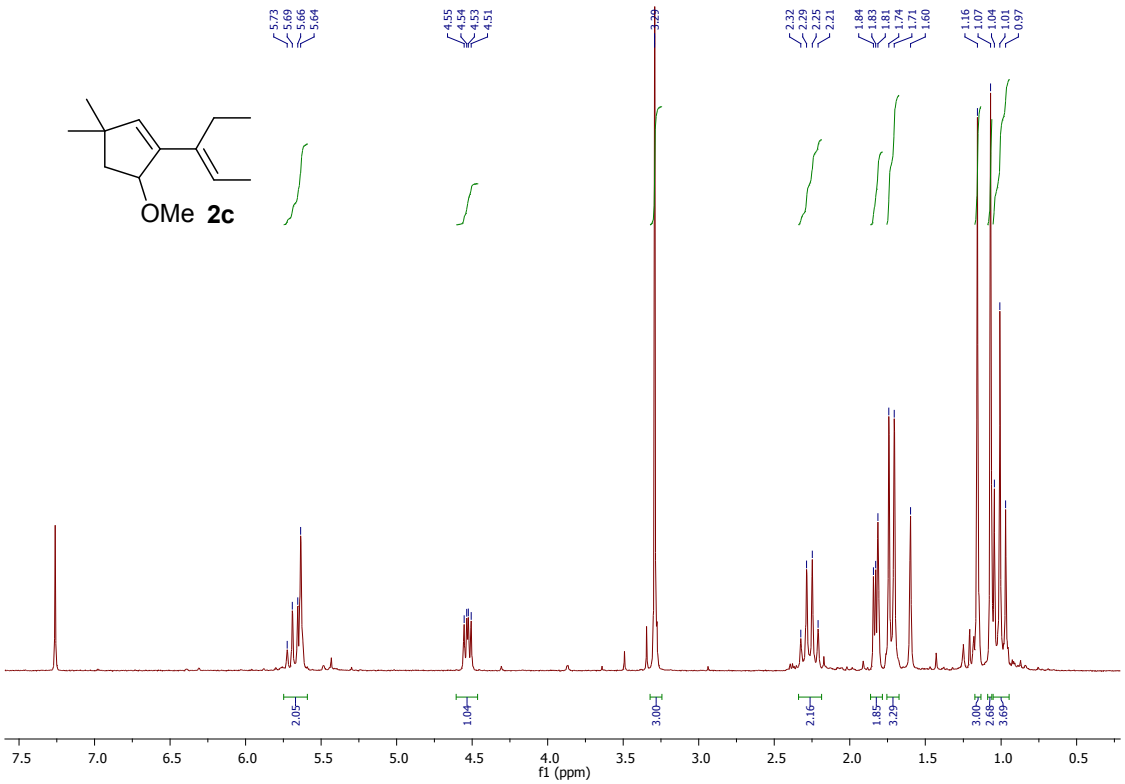

200.84
199.44
151.73
109.79
98.00
95.37
65.63
46.76
25.10
21.70
20.64
20.36
11
f1 (ppm)

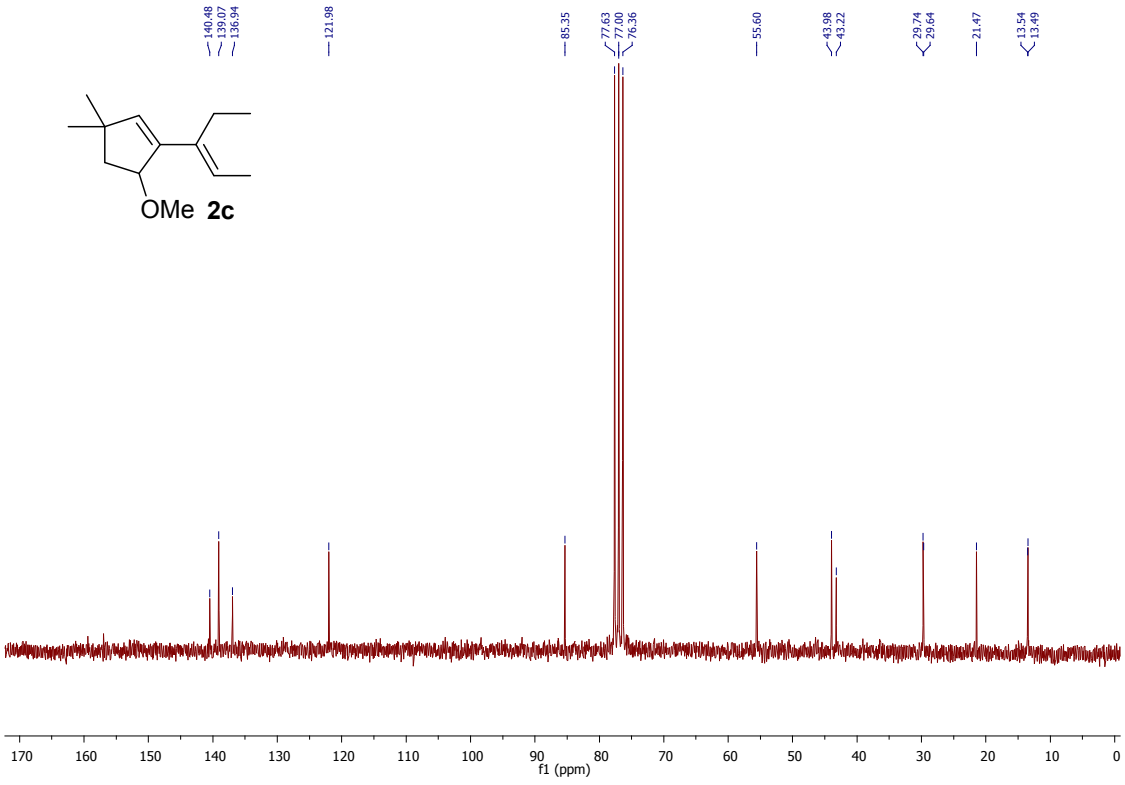

2a
OMe
5.73
5.12
5.11
4.99
4.60
4.59
4.57
4.56
3.31
1.90
1.88
1.85
1.84
1.17
1.08
1.00
0.99
1.09
1.02
2.98
3.50
1.37
1.69
3.19
3.12
f1 (ppm)

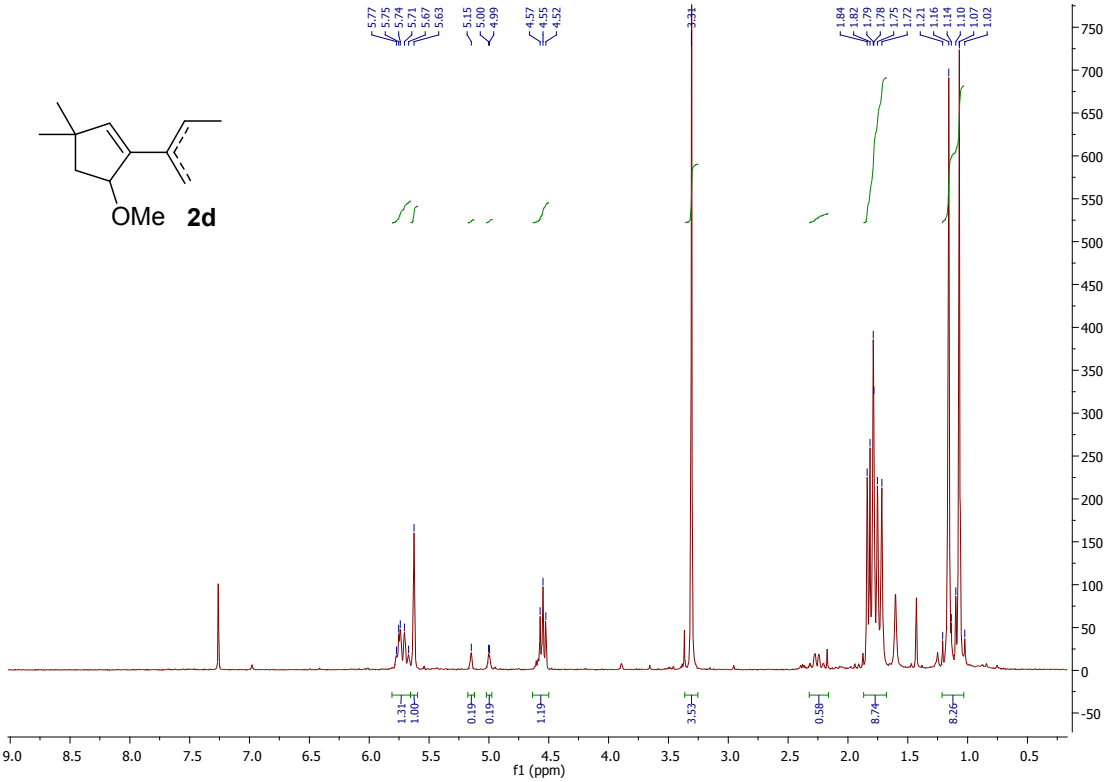

2a
OMe
142.10
141.05
138.11
113.29
85.23
55.79
44.23
43.58
29.60
29.43
20.98
f1 (ppm)

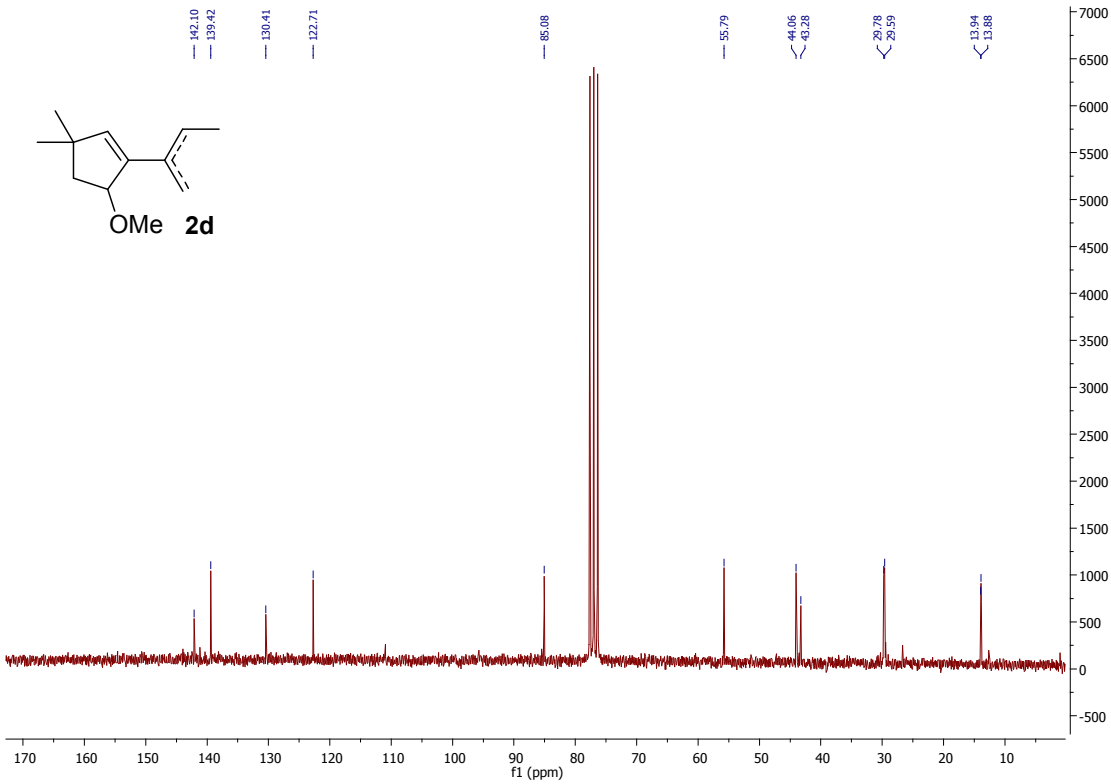

OMe
2b
5.91
5.61
4.56
4.54
4.52
3.32
2.17
1.83
1.81
1.67
1.66
1.62
1.60
1.56
1.15
1.06
1.00
1.02
1.04
2.94
4.07
2.02
3.93
3.05
3.09
f1 (ppm)

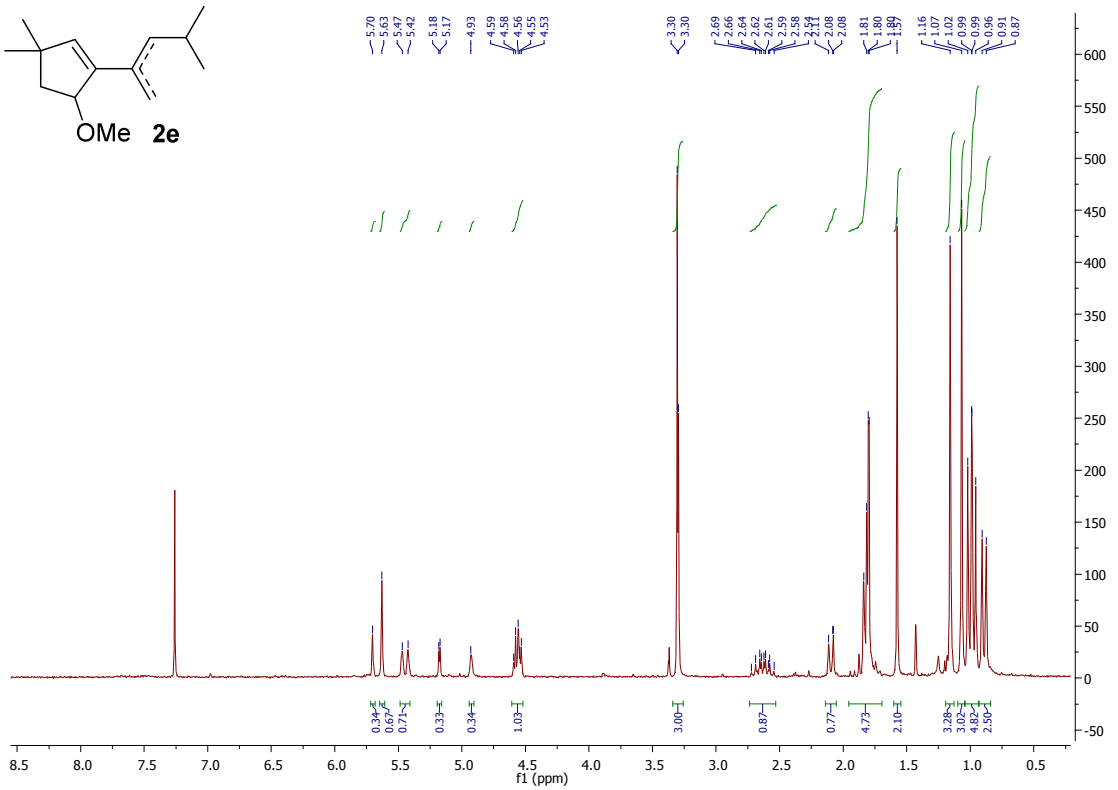

OMe
2b
141.22
138.53
131.64
125.43
85.19
55.90
44.05
43.37
29.81
29.57
26.08
25.75
22.65
22.26
f1 (ppm)

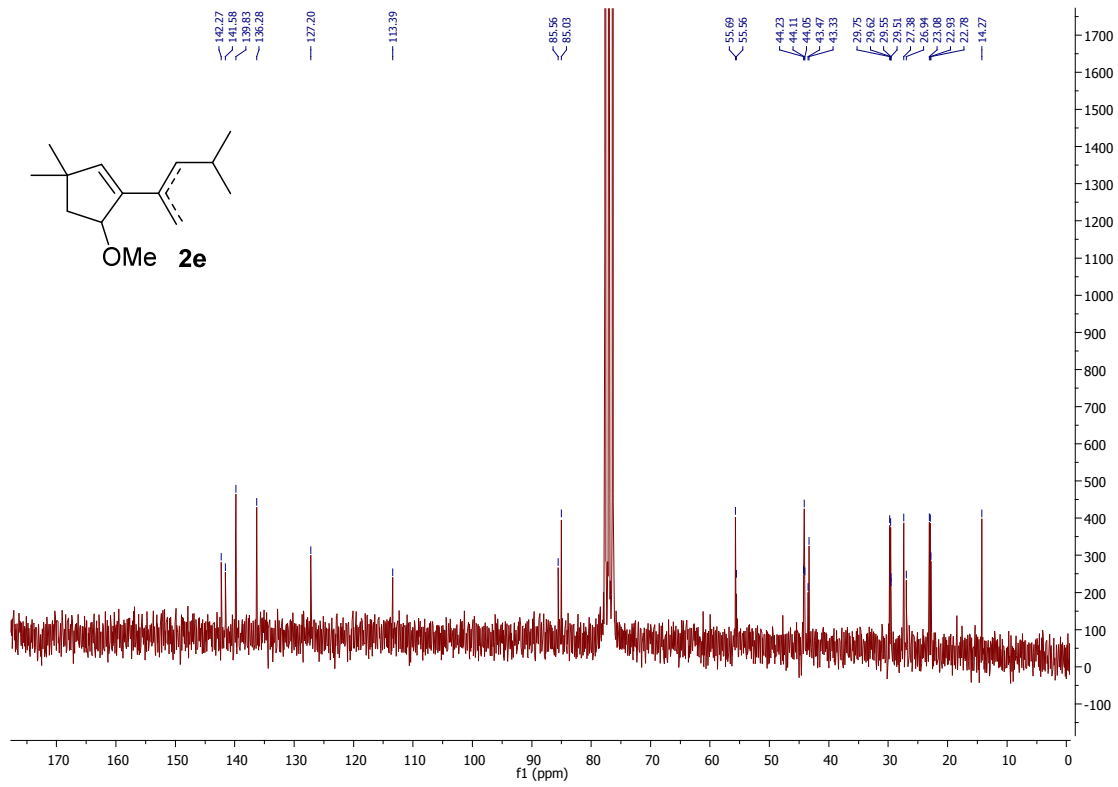

OMe 2c
5.73
5.69
5.66
5.64
4.55
4.54
4.53
4.51
3.29
2.32
2.29
2.25
2.21
1.84
1.83
1.81
1.74
1.71
1.60
1.16
1.07
1.04
1.01
0.97
2.05
1.04
3.00
2.16
1.85
3.29
3.00
2.68
3.69
f1 (ppm)

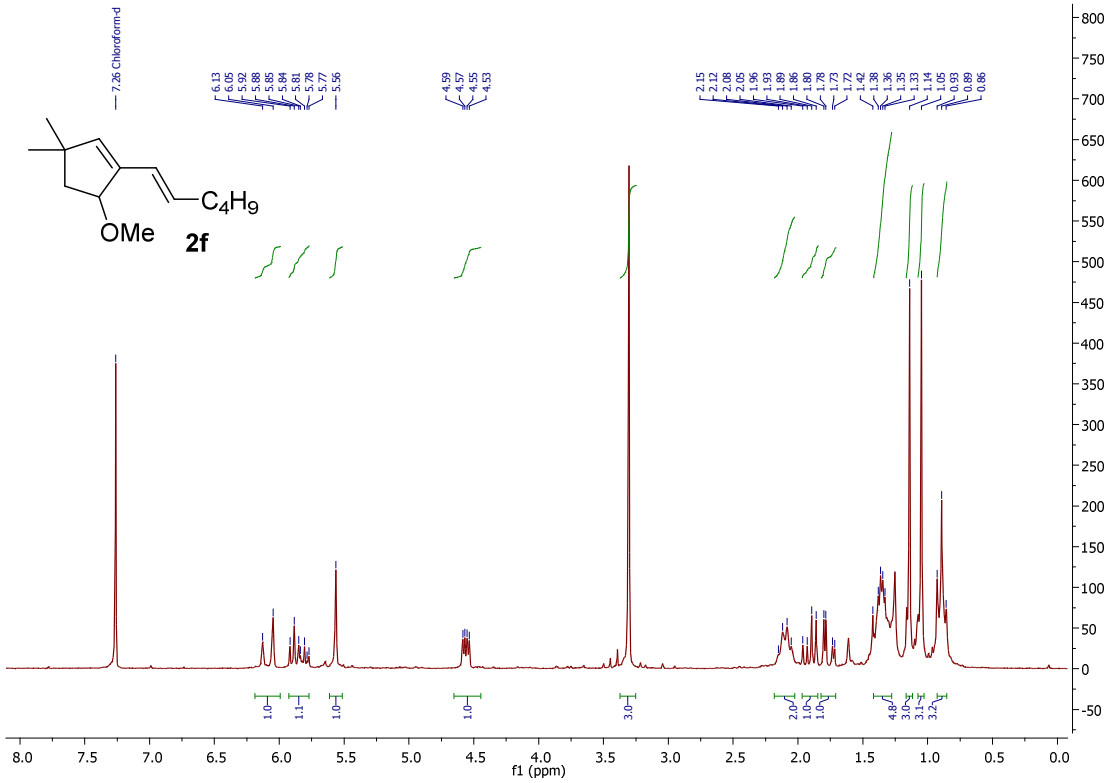

OMe 2c
140.48
139.07
136.94
121.98
85.35
77.63
77.00
76.36
55.60
43.98
43.22
29.74
29.64
21.47
13.54
13.49
f1 (ppm)

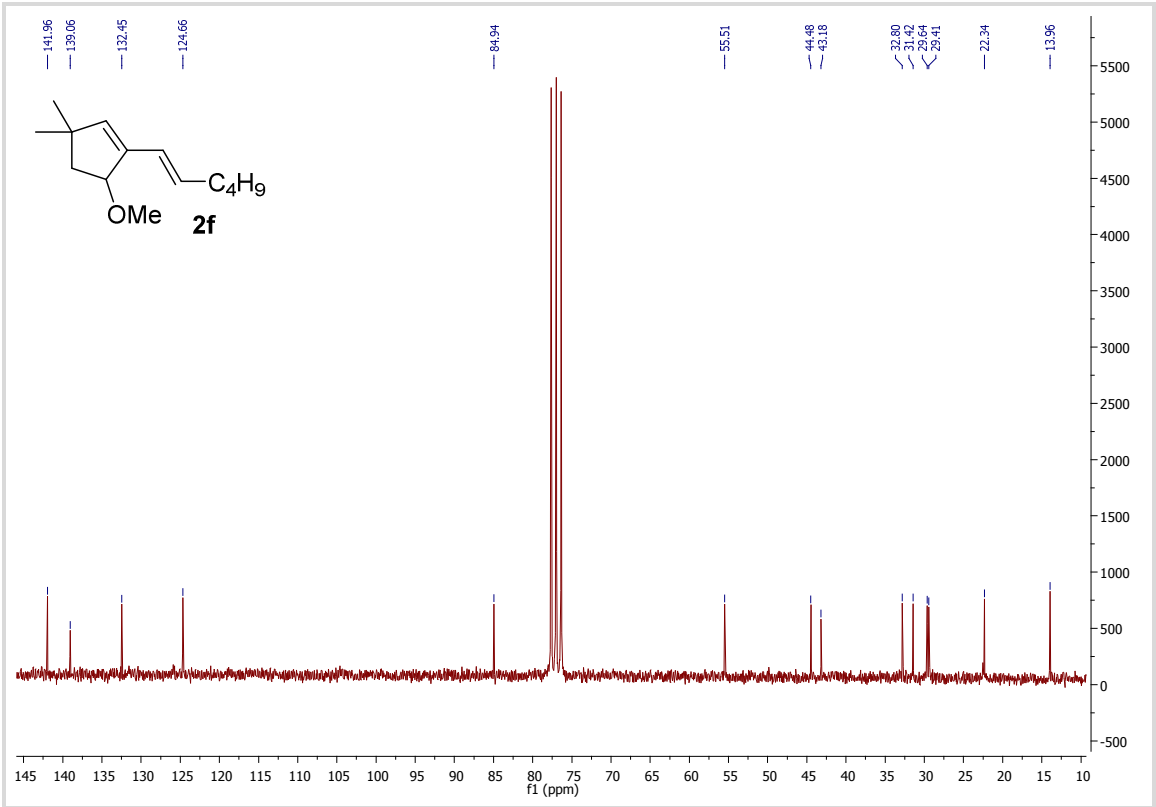

OMe 2d
5.77
5.75
5.74
5.71
5.67
5.63
5.15
5.00
4.99
4.57
4.55
4.52
3.31
1.84
1.82
1.79
1.78
1.75
1.72
1.21
1.16
1.14
1.10
1.07
1.02
1.31
1.00
0.19
0.19
1.19
3.53
0.59
8.74
8.26
f1 (ppm)

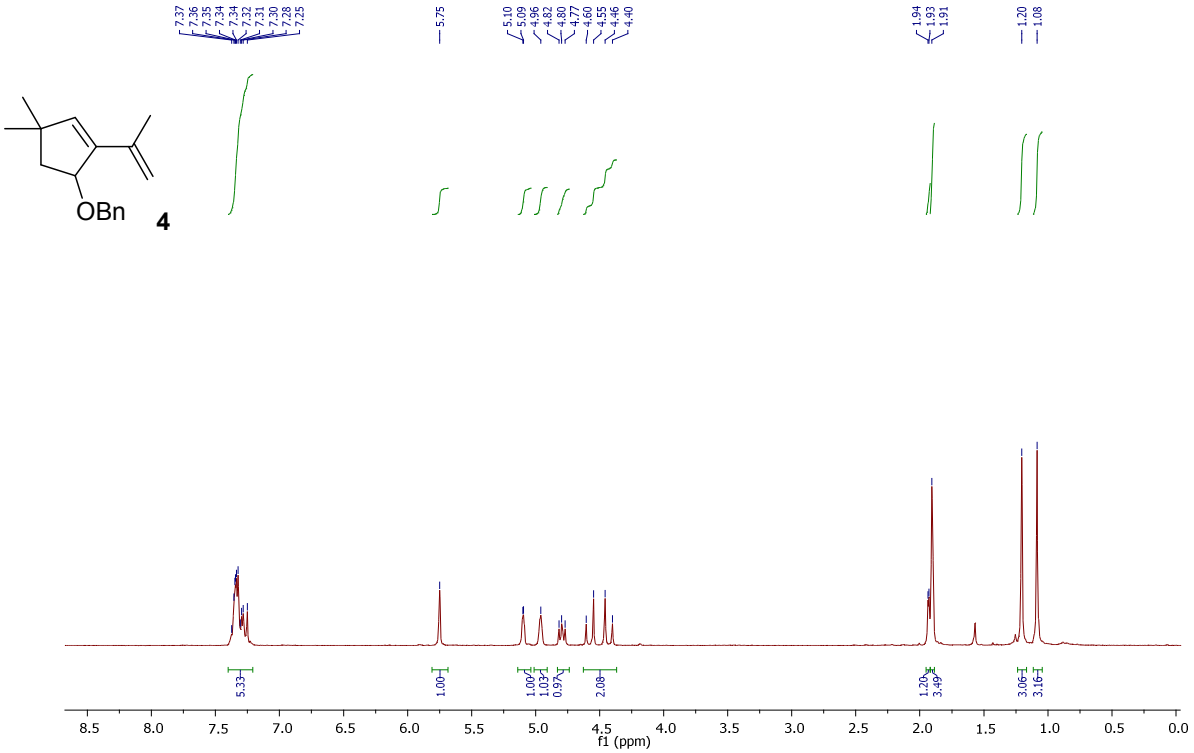

OMe 2d
142.10
139.42
130.41
122.71
85.08
55.79
44.06
43.28
29.78
29.59
13.94
13.88
f1 (ppm)

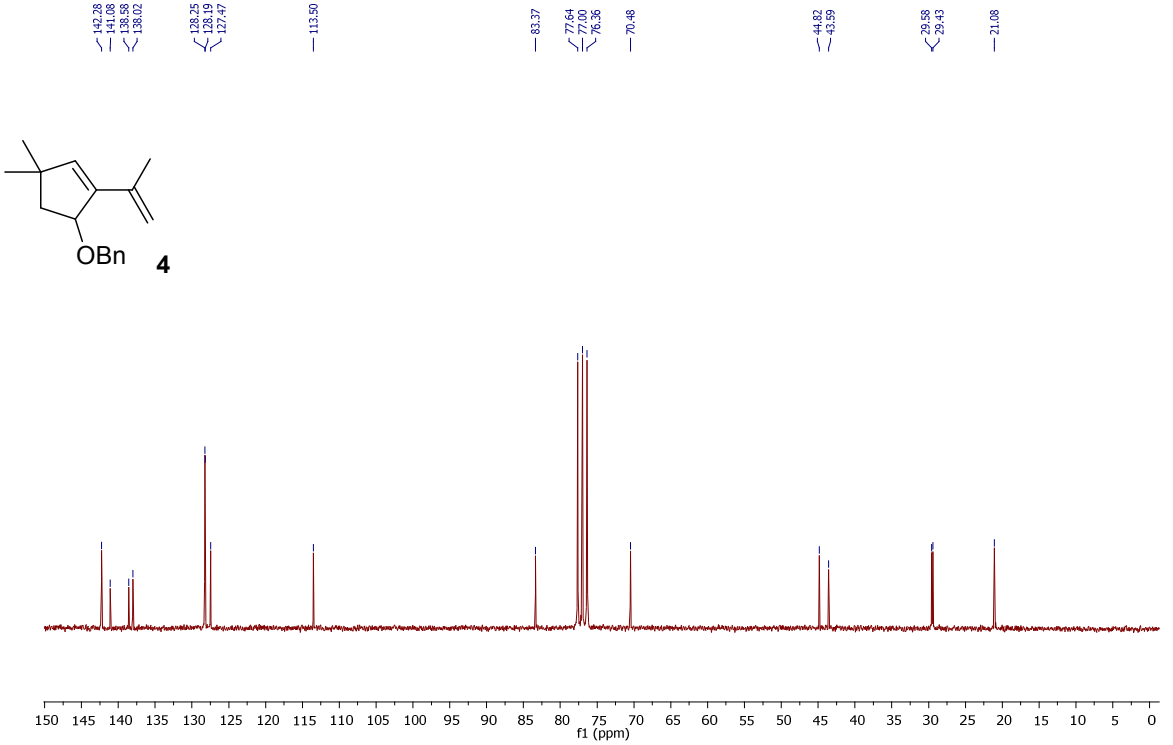

OMe 2e
f1 (ppm)

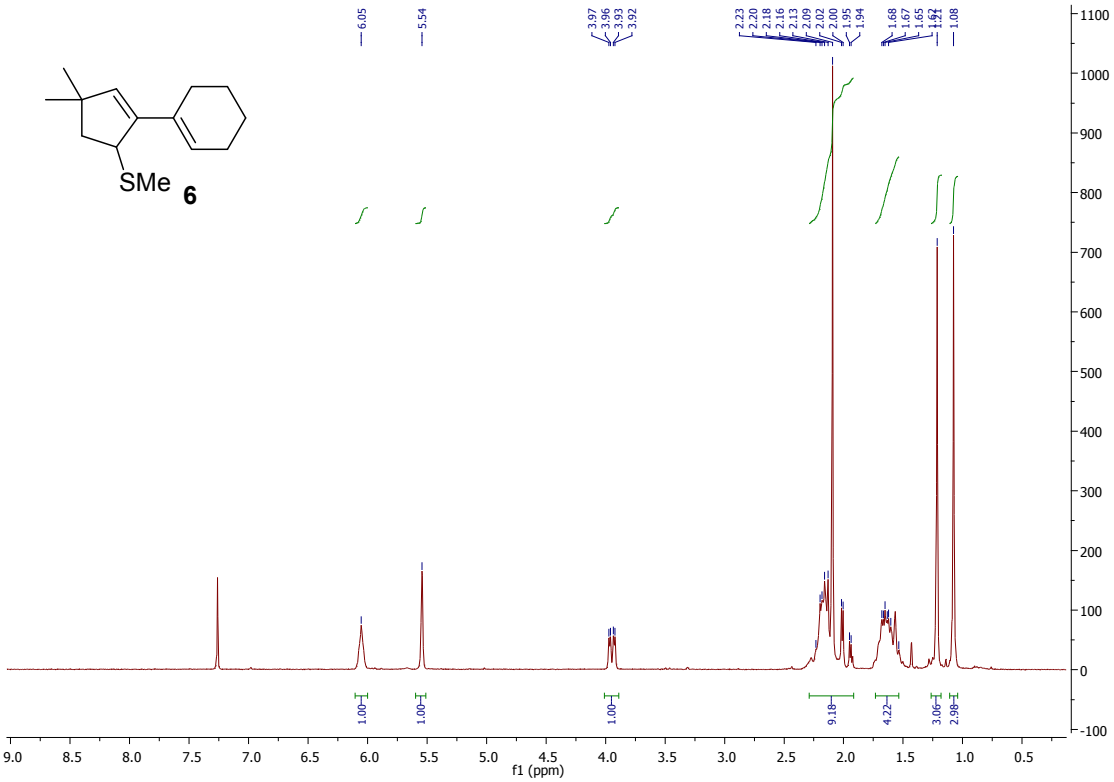

OMe 2e
f1 (ppm)

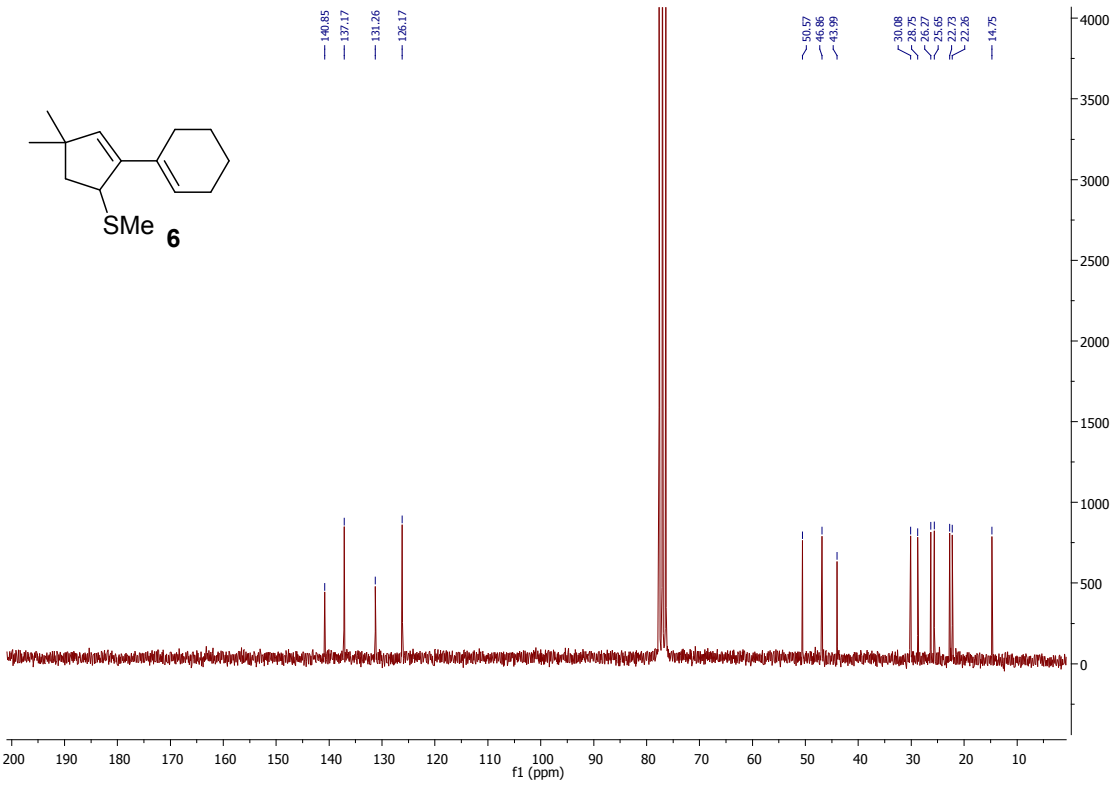

7.26 Chloroform-d
6.13
6.05
5.92
5.88
5.85
5.84
5.81
5.78
5.77
5.56
4.59
4.57
4.55
4.53
2.15
2.12
2.08
2.05
1.96
1.93
1.89
1.86
1.80
1.78
1.73
1.72
1.42
1.38
1.36
1.35
1.33
1.14
1.05
0.93
0.89
0.86
C4H9
OMe
2f
f1 (ppm)

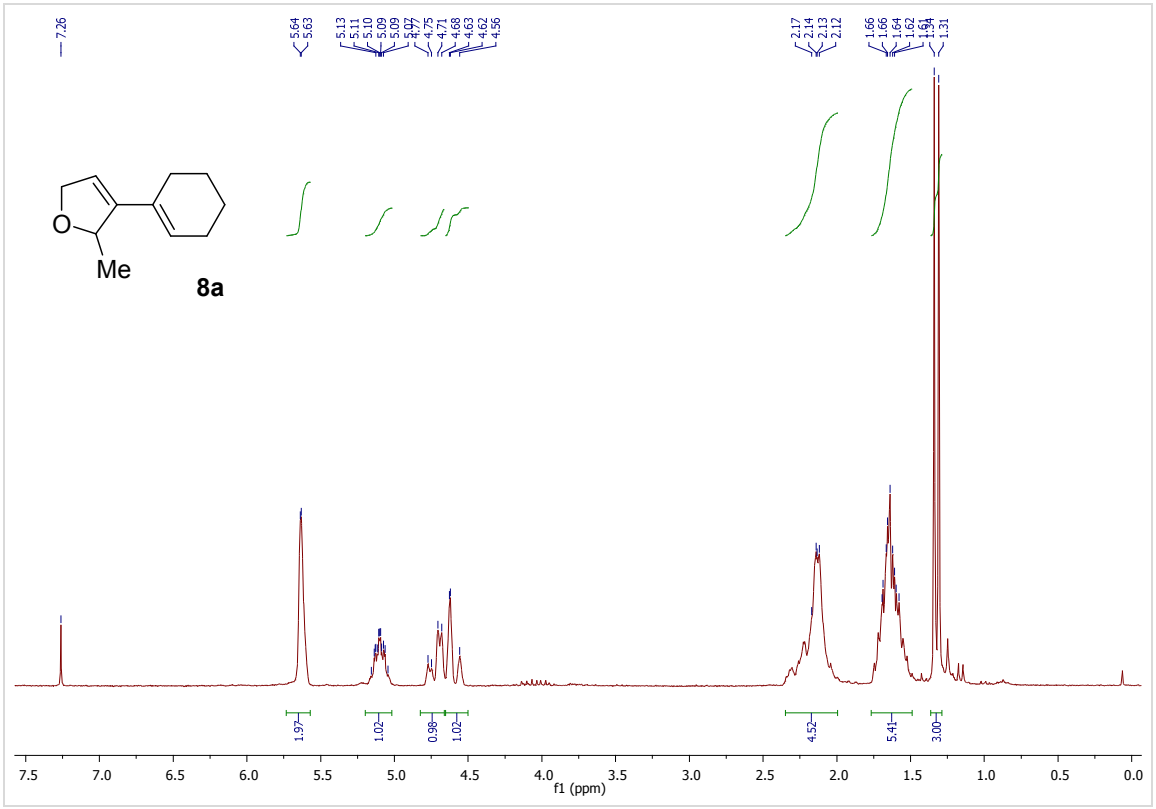

141.96
139.06
132.45
124.66
84.94
55.51
44.48
43.18
32.80
31.42
29.64
29.41
22.34
13.96
C4H9
OMe
2f
f1 (ppm)

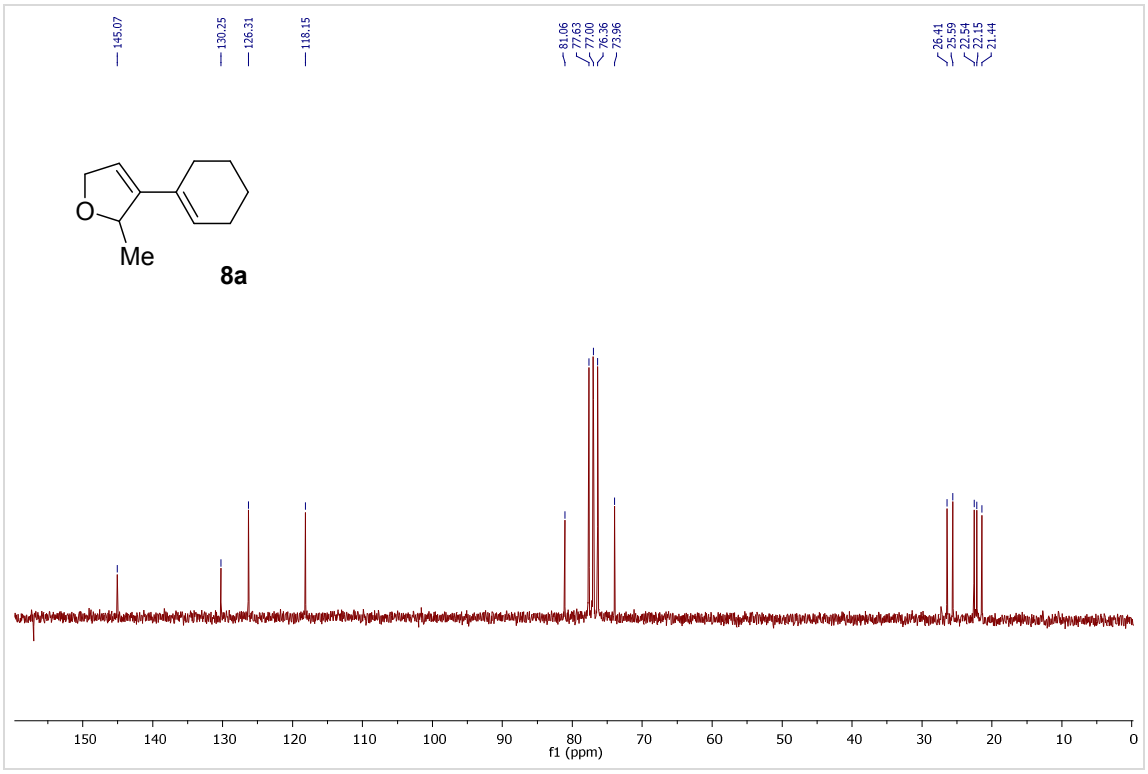

7.37
7.36
7.35
7.34
7.34
7.32
7.31
7.30
7.28
7.25
5.75
5.10
5.09
4.96
4.82
4.80
4.77
4.60
4.55
4.46
4.40
1.94
1.93
1.91
1.20
1.08
OBn
4
5.33
1.00
1.00
1.03
0.97
2.08
1.20
3.49
3.06
3.16
f1 (ppm)

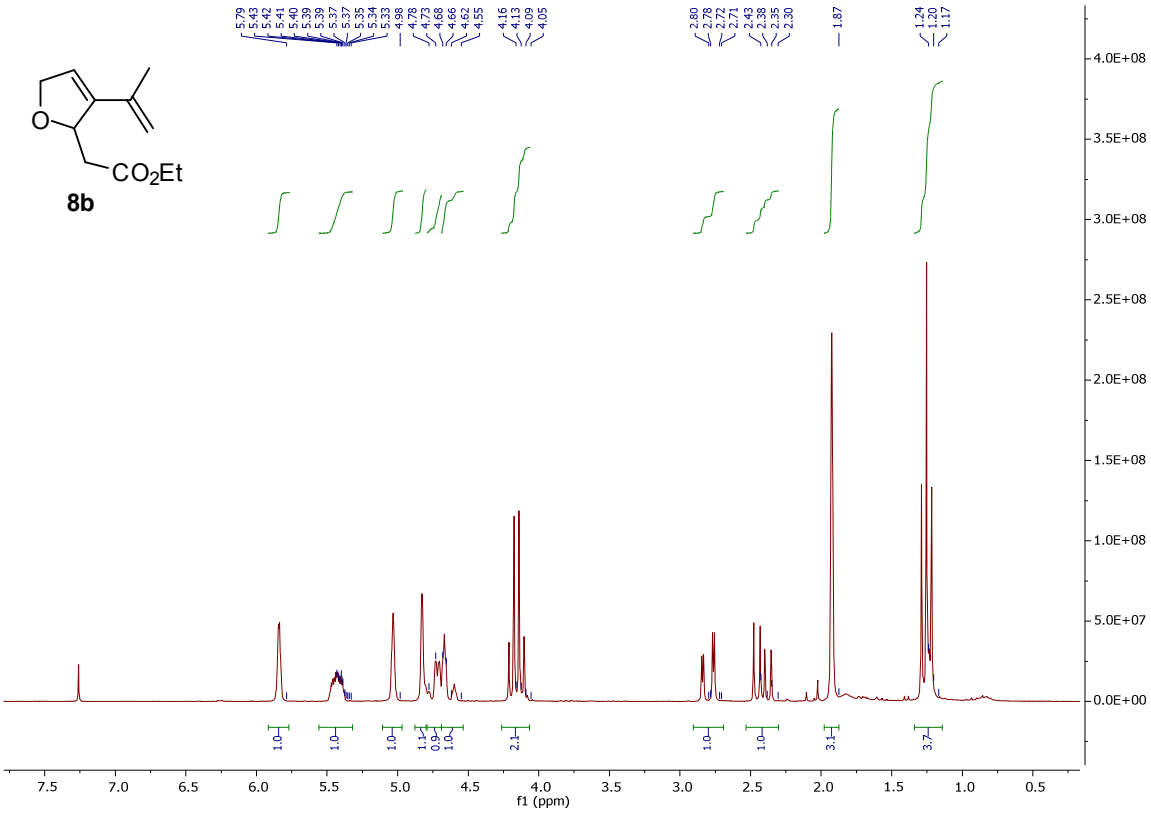

142.28
141.08
138.58
138.02
128.25
128.19
127.47
113.50
83.37
77.64
77.00
76.36
70.48
44.82
43.59
29.58
29.43
21.08
OBn
4
f1 (ppm)

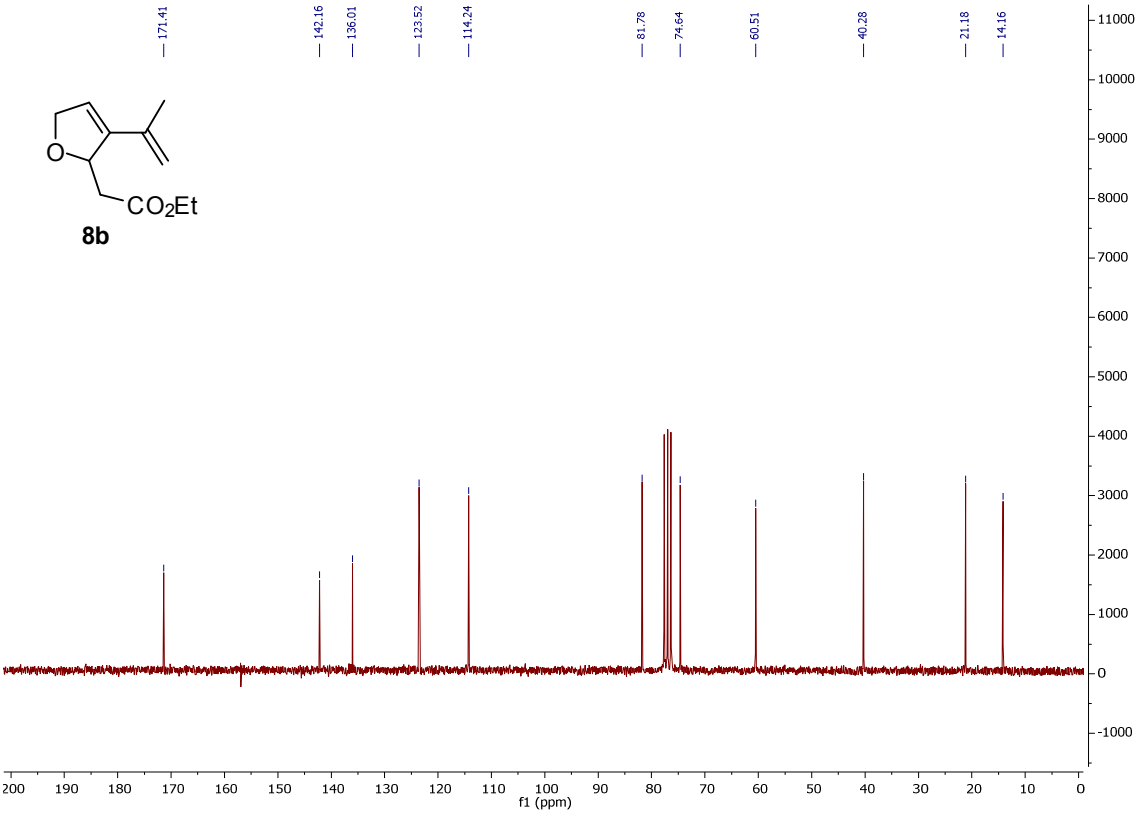

SMe
6
6.05
5.54
3.97
3.96
3.93
3.92
2.23
2.20
2.18
2.16
2.13
2.09
2.02
2.00
1.95
1.94
1.68
1.67
1.65
1.08
1.00
1.00
1.00
9.18
4.22
3.06
2.98
f1 (ppm)

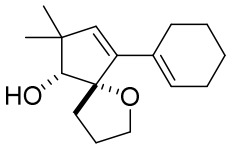

SMe
6
140.85
137.17
131.26
126.17
50.57
46.86
43.99
30.08
28.75
26.27
25.65
22.73
22.26
14.75
f1 (ppm)


7.26
5.64
5.63
5.13
5.11
5.10
5.09
5.09
5.07
4.77
4.75
4.71
4.68
4.63
4.62
4.56
2.17
2.14
2.13
2.12
1.66
1.66
1.64
1.62
1.54
1.31
O
Me
8a
1.97
1.02
0.98
1.02
4.52
5.41
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

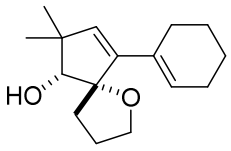

145.07
130.25
126.31
118.15
81.06
77.63
77.00
76.36
73.96
26.41
25.59
22.54
22.15
21.44
O
Me
8a
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8b
f1 (ppm)

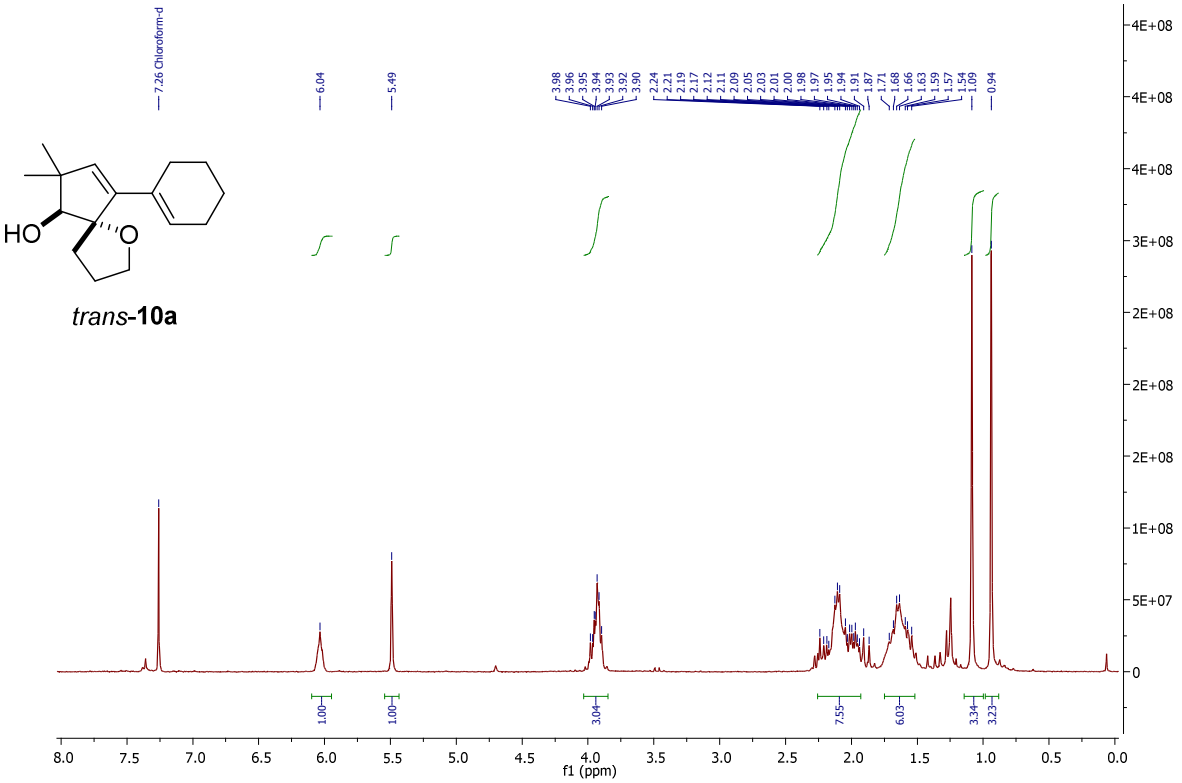

8b
f1 (ppm)

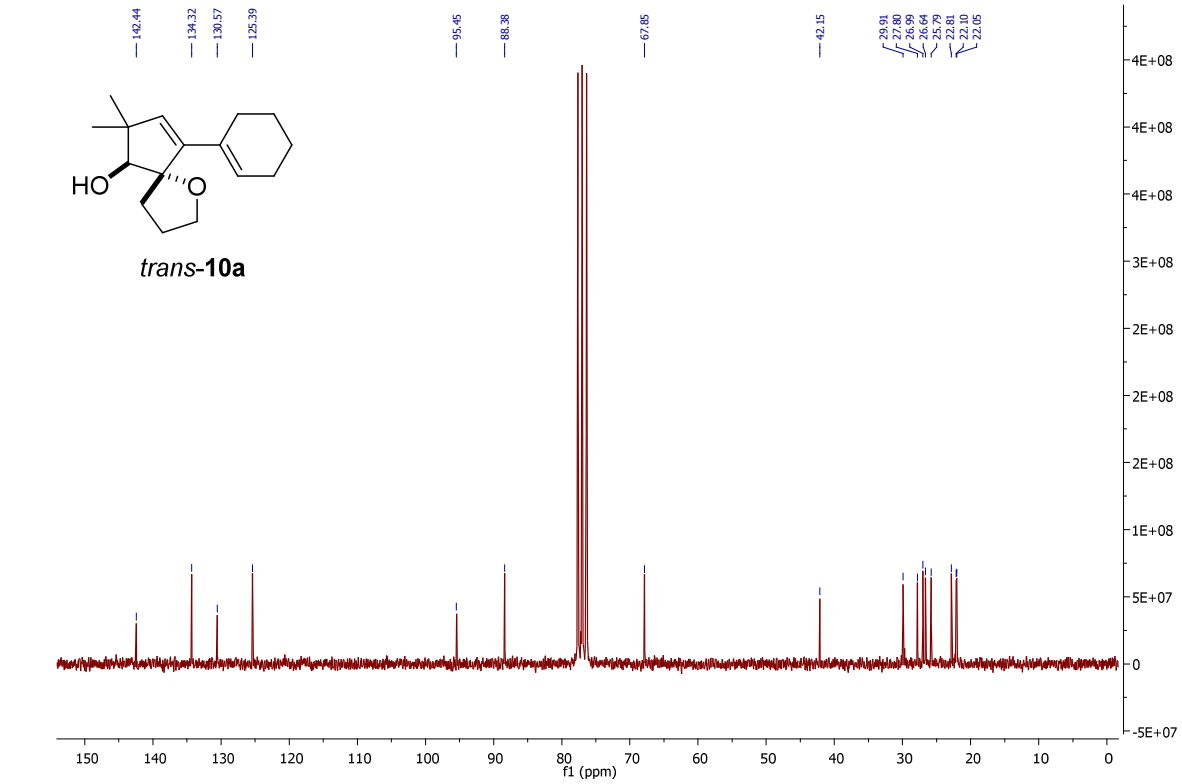


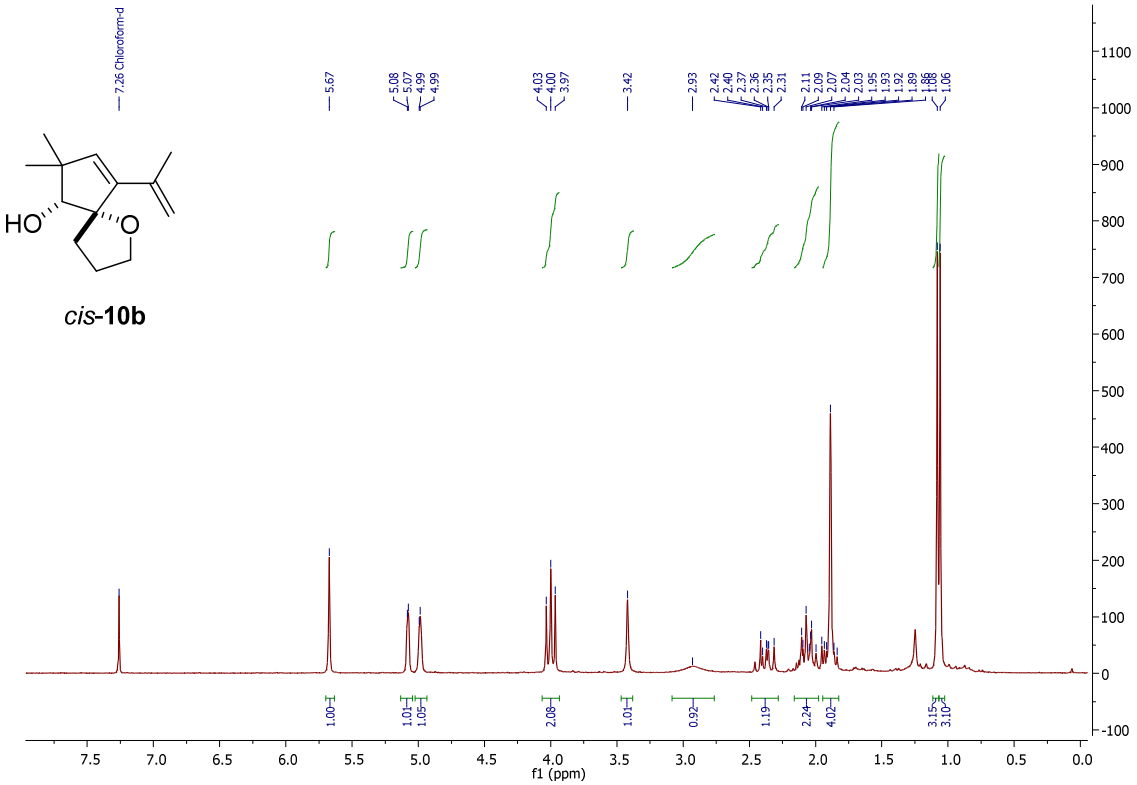
cis-**10a**

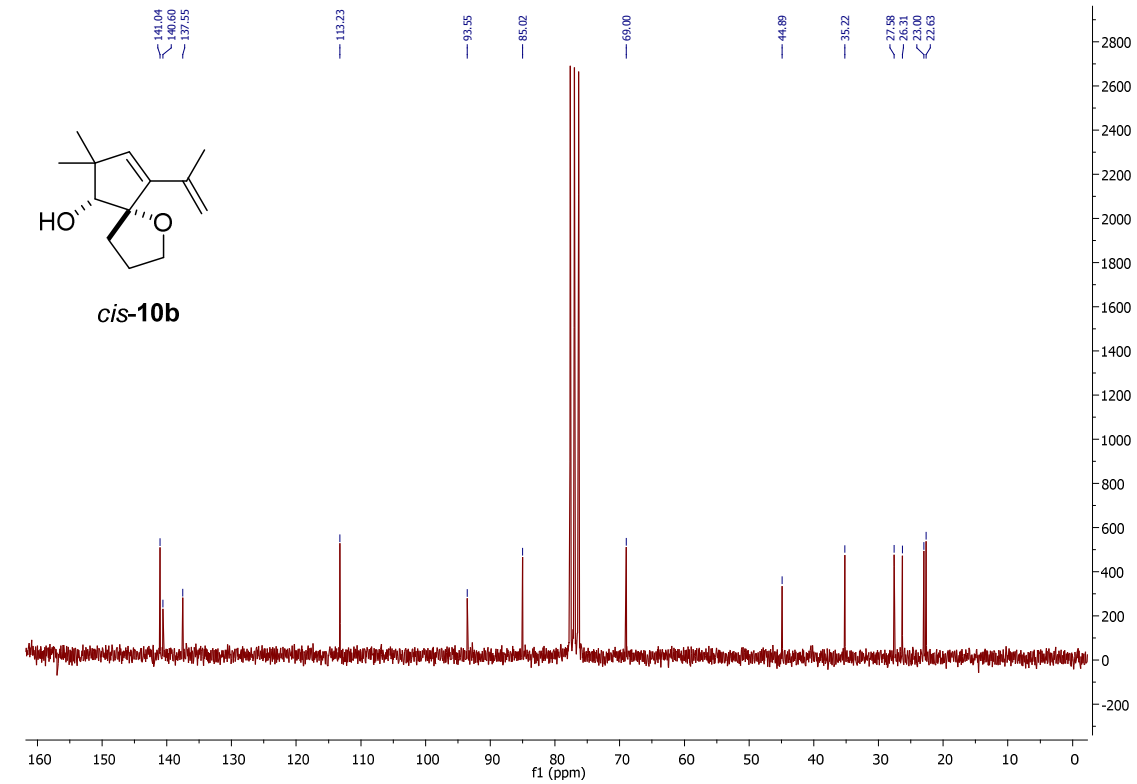


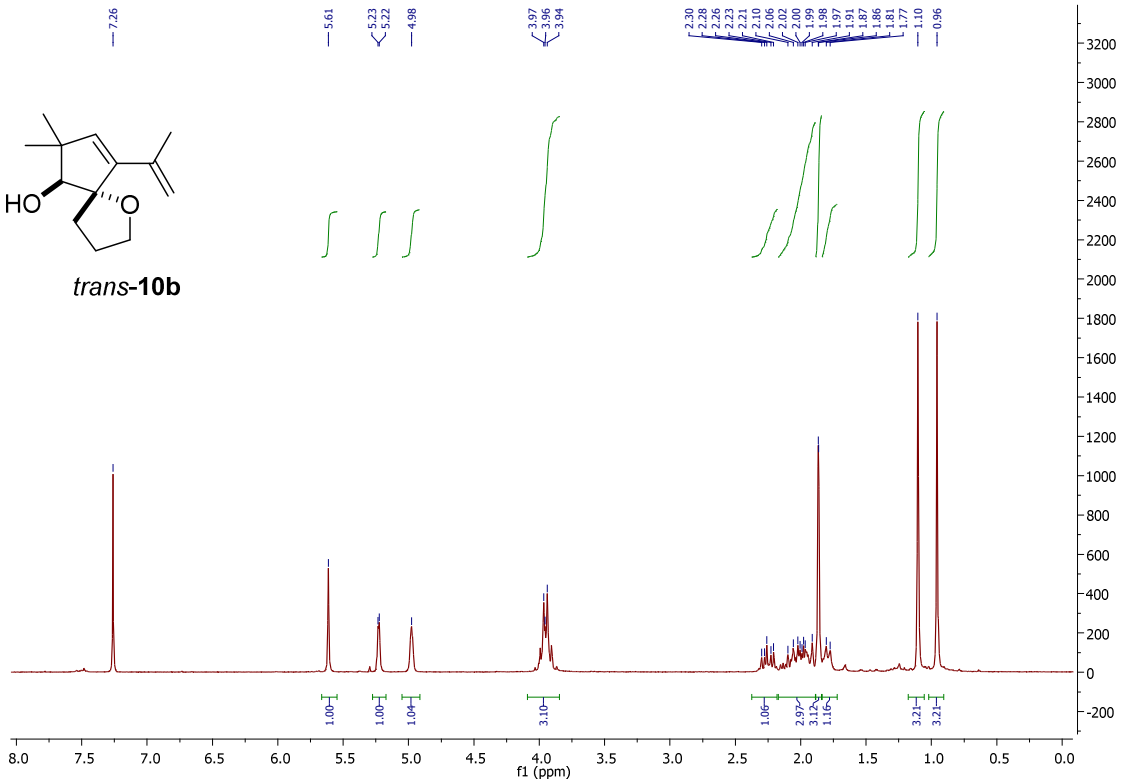
cis-**10a**


7.26 Chloroform-d
6.04
5.49
3.98
3.96
3.95
3.94
3.93
3.92
3.90
2.24
2.21
2.19
2.17
2.12
2.11
2.09
2.05
2.03
2.01
2.00
1.98
1.97
1.95
1.94
1.91
1.87
1.71
1.68
1.66
1.63
1.59
1.57
1.54
1.09
0.94
HO
O
trans-10a
1.00
1.00
3.04
7.55
6.03
3.34
3.23
f1 (ppm)

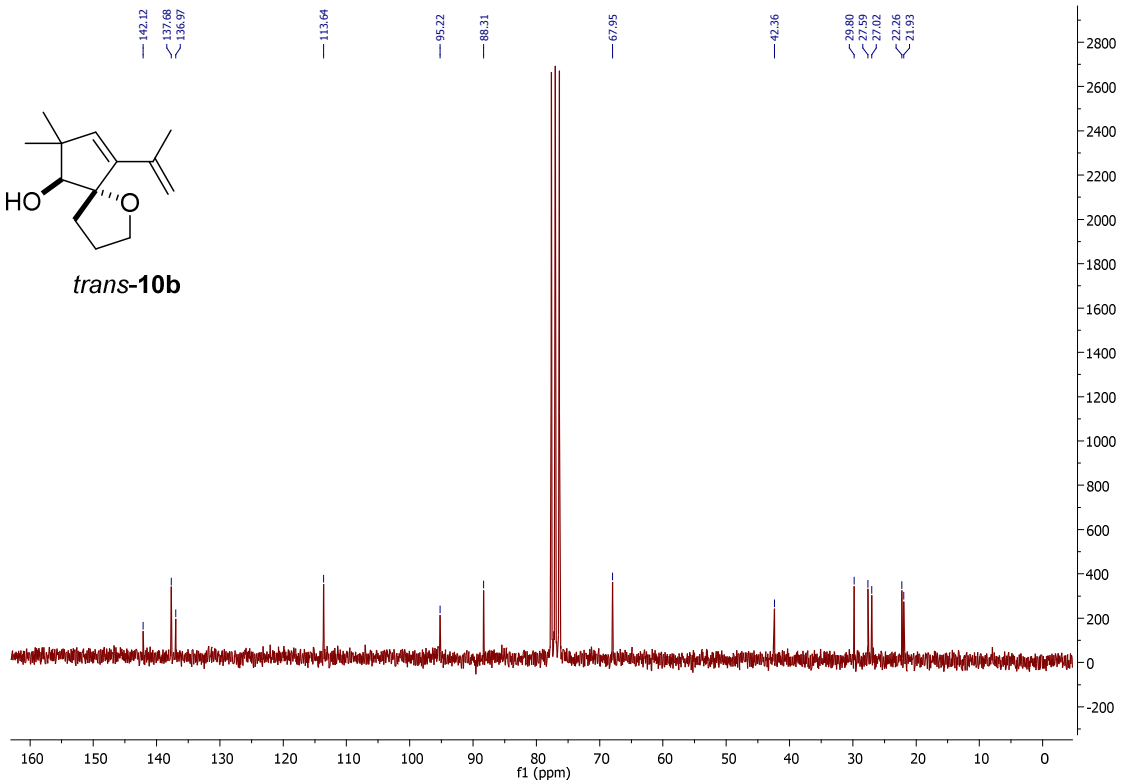

142.44
134.32
130.57
125.39
95.45
88.38
67.85
42.15
29.91
27.80
26.99
26.64
25.79
22.81
22.10
22.05
HO
O
trans-10a
f1 (ppm)


7.26 Chloroform-d
5.67
5.08
5.07
4.99
4.99
4.03
4.00
3.97
3.42
2.93
2.42
2.40
2.37
2.36
2.35
2.31
2.11
2.09
2.07
2.04
2.03
1.95
1.93
1.92
1.89
1.86
1.08
1.06
HO
O
cis-10b
1.00
1.01
1.05
2.08
1.01
0.92
1.19
2.24
4.02
3.15
3.10
f1 (ppm)

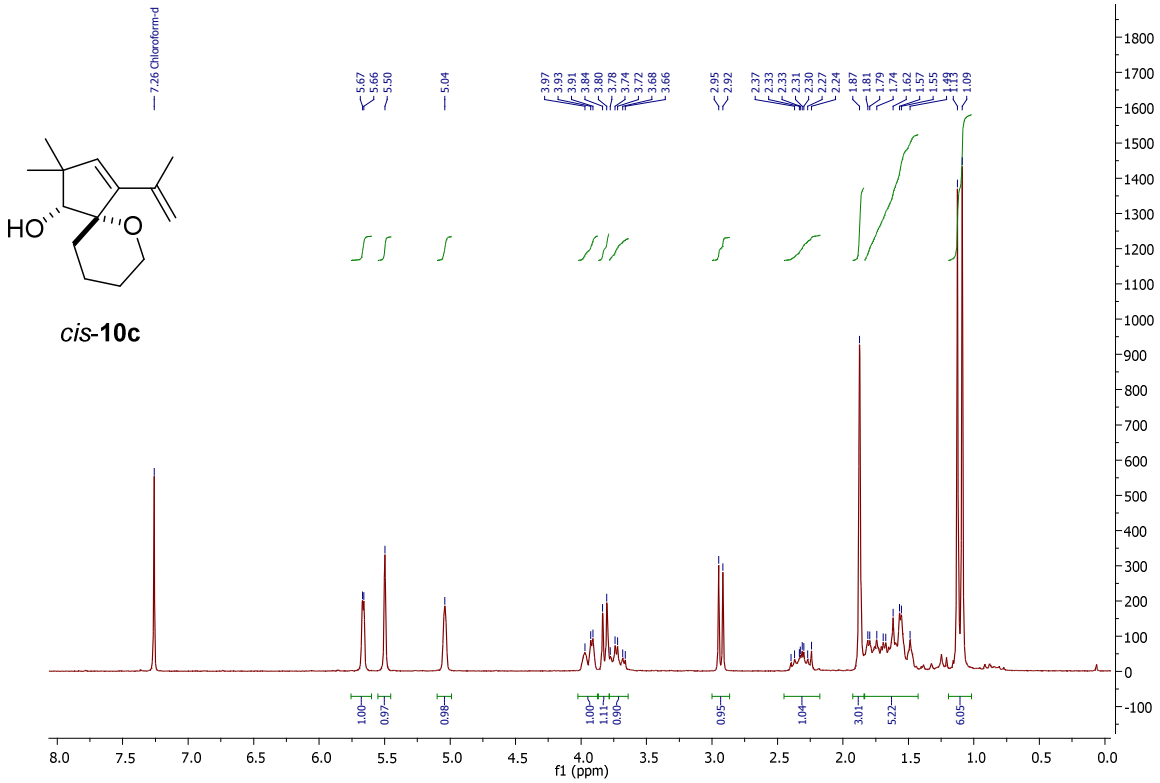

141.04
140.60
137.55
113.23
93.55
85.02
69.00
44.89
35.22
27.58
26.31
23.00
22.63
HO
O
cis-10b
f1 (ppm)



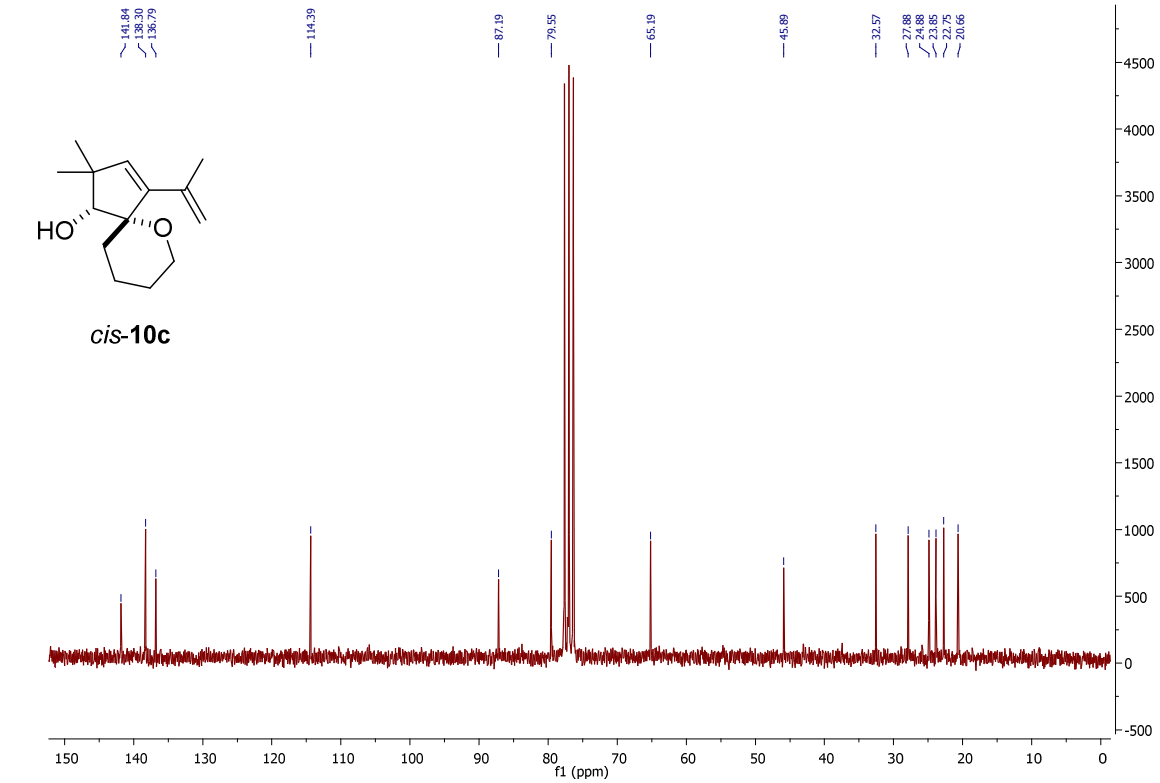
trans-**10b**



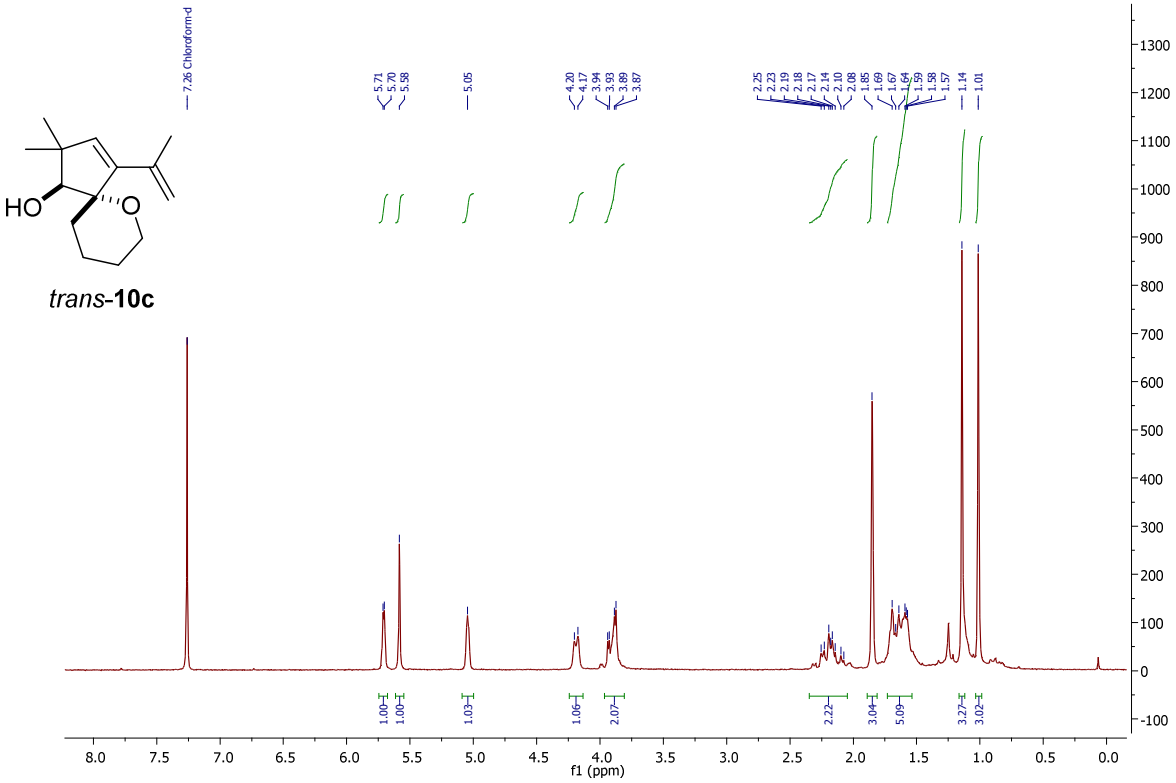
trans-**10b**



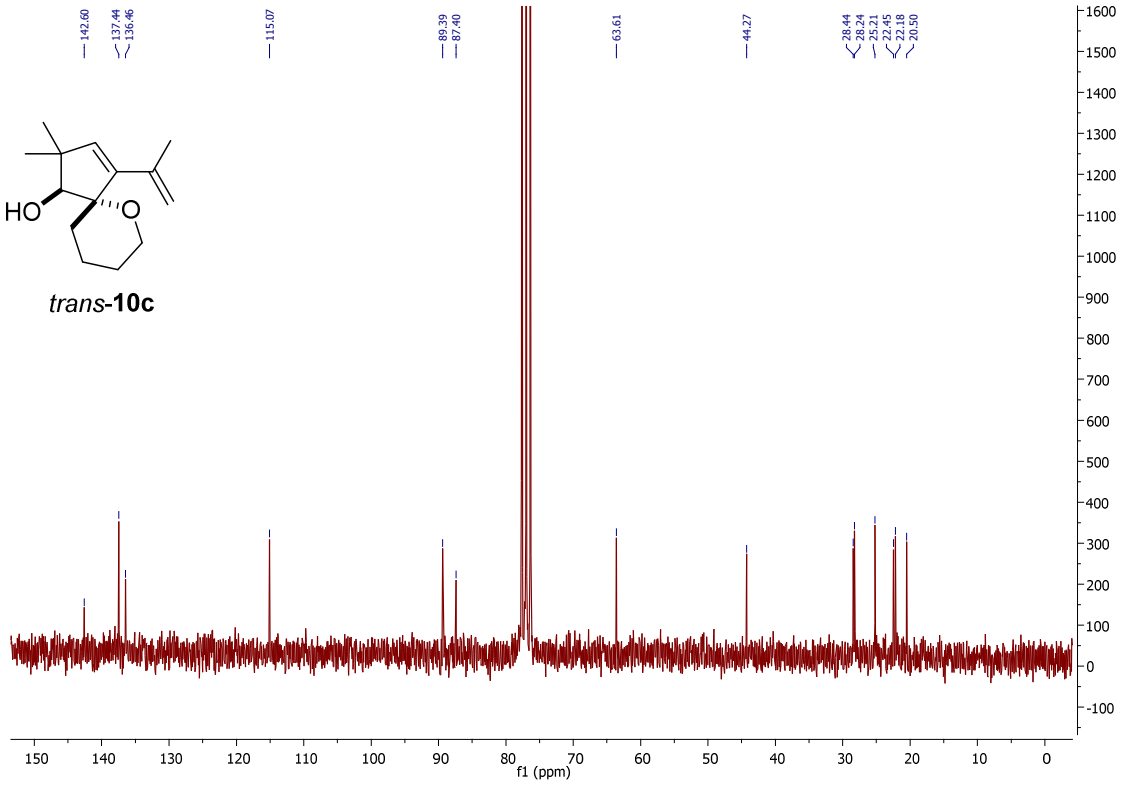
cis-**10c**



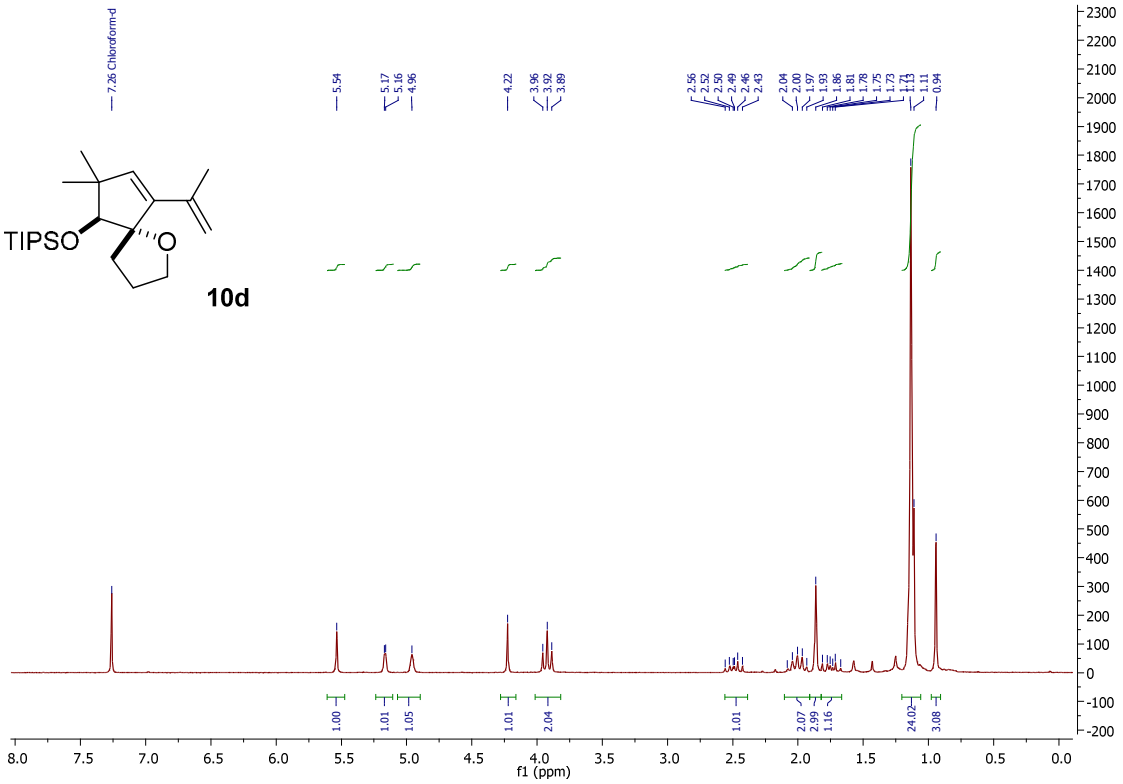
cis-**10c**

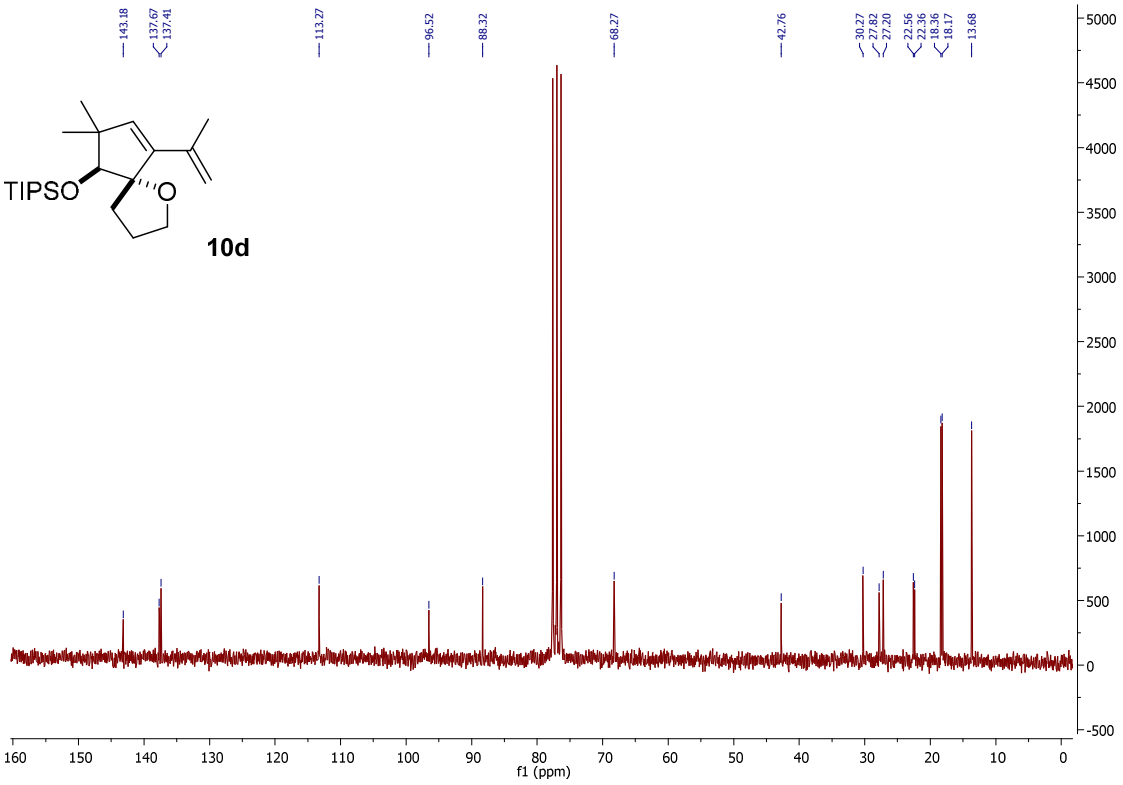


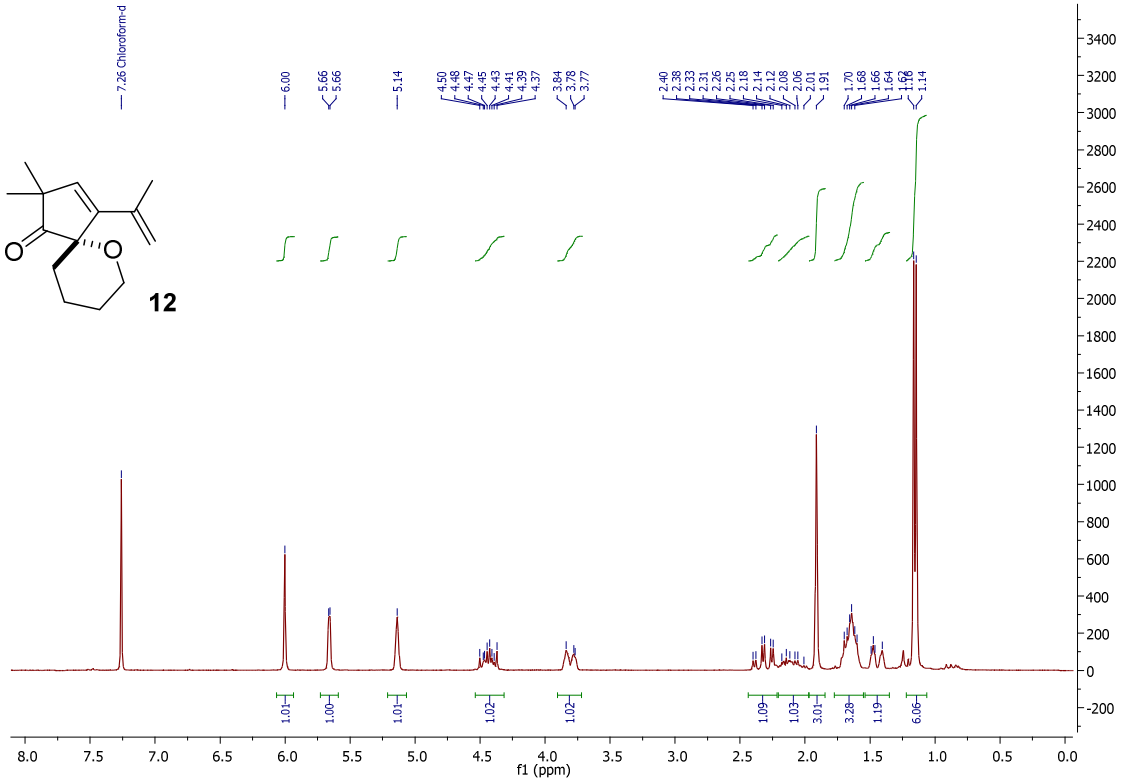
trans-**10c**

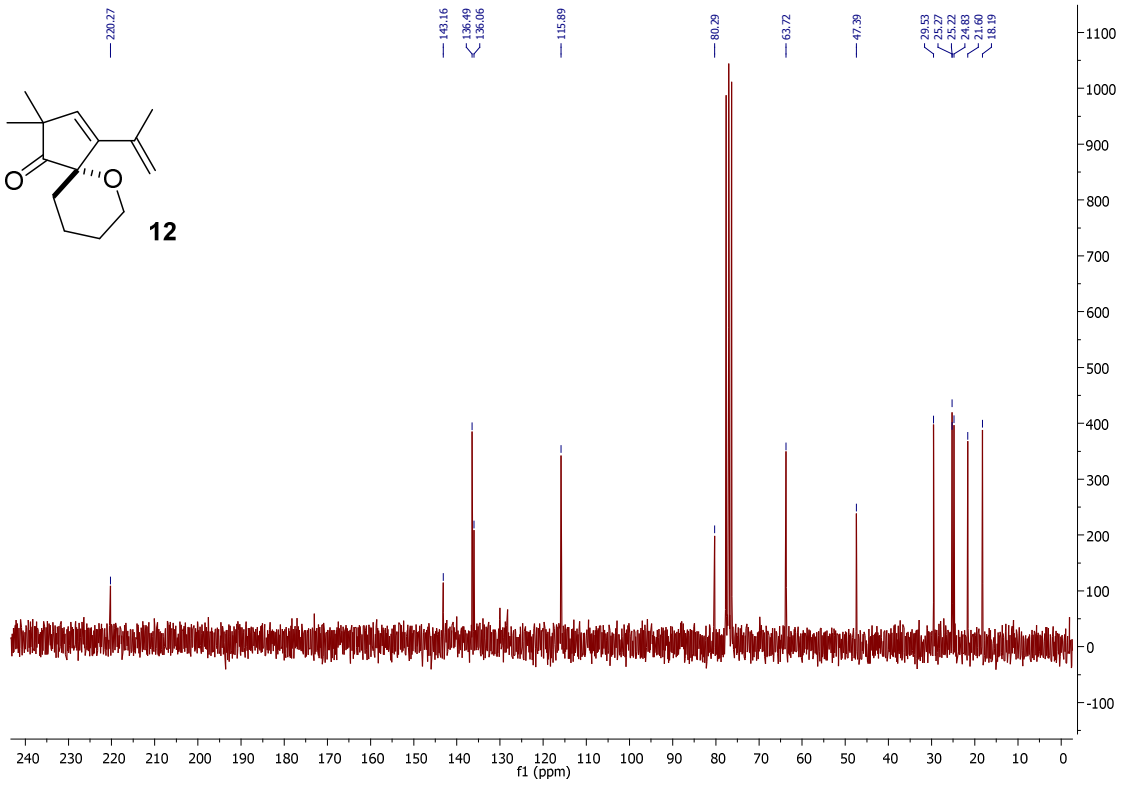


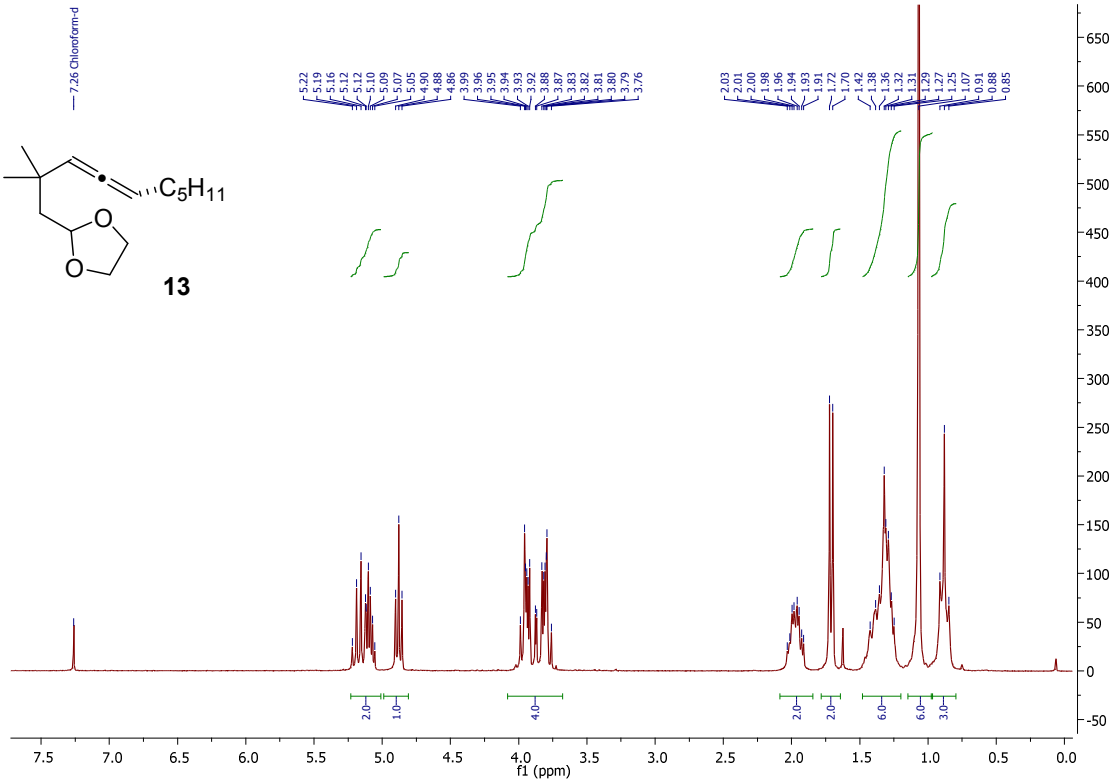
trans-**10c**

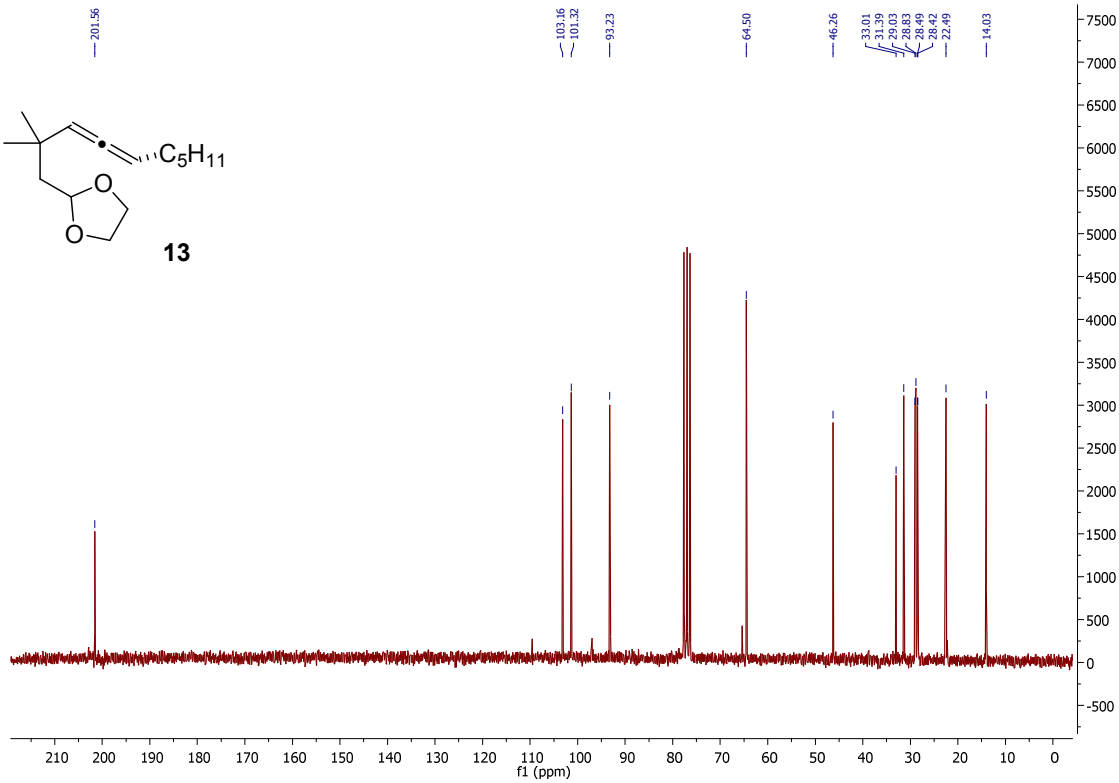

7.26 Chloroform-d
5.54
5.17
5.16
4.96
4.22
3.96
3.92
3.89
2.56
2.52
2.50
2.49
2.46
2.43
2.04
2.00
1.97
1.93
1.86
1.81
1.78
1.75
1.73
1.13
1.11
0.94
TIPSO
O
10d
1.00
1.01
1.05
1.01
2.04
1.01
2.07
2.99
1.16
24.02
3.08
f1 (ppm)


143.18
137.67
137.41
113.27
96.52
88.32
68.27
42.76
30.27
27.82
27.20
22.56
22.36
18.36
18.17
13.68
TIPSO
O
10d
f1 (ppm)


7.26 Chloroform-d
6.00
5.66
5.66
5.14
4.50
4.48
4.47
4.45
4.43
4.41
4.39
4.37
3.84
3.78
3.77
2.40
2.38
2.33
2.31
2.26
2.25
2.18
2.14
2.12
2.08
2.06
2.01
1.91
1.70
1.68
1.66
1.64
1.16
1.14
12
1.01
1.00
1.01
1.02
1.02
1.09
1.03
3.01
3.28
1.19
6.06
f1 (ppm)


220.27
143.16
136.49
136.06
115.89
80.29
63.72
47.39
29.53
25.27
25.22
24.83
21.60
18.19
12
f1 (ppm)


7.26 Chloroform-d
5.22
5.19
5.16
5.12
5.12
5.10
5.09
5.07
5.05
4.90
4.88
4.86
3.99
3.96
3.95
3.94
3.93
3.92
3.88
3.87
3.83
3.82
3.81
3.80
3.79
3.76
2.03
2.01
2.00
1.98
1.96
1.94
1.93
1.91
1.72
1.70
1.42
1.38
1.36
1.32
1.31
1.29
1.27
1.25
1.07
0.91
0.88
0.85
2.0
1.0
4.0
2.0
2.0
6.0
6.0
3.0
f1 (ppm)


201.56
103.16
101.32
93.23
64.50
46.26
33.01
31.39
29.03
28.83
28.49
28.42
22.49
14.03
f1 (ppm)