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Supplementary Information

The Enantioselective Total Synthesis of (+)-Clusianone

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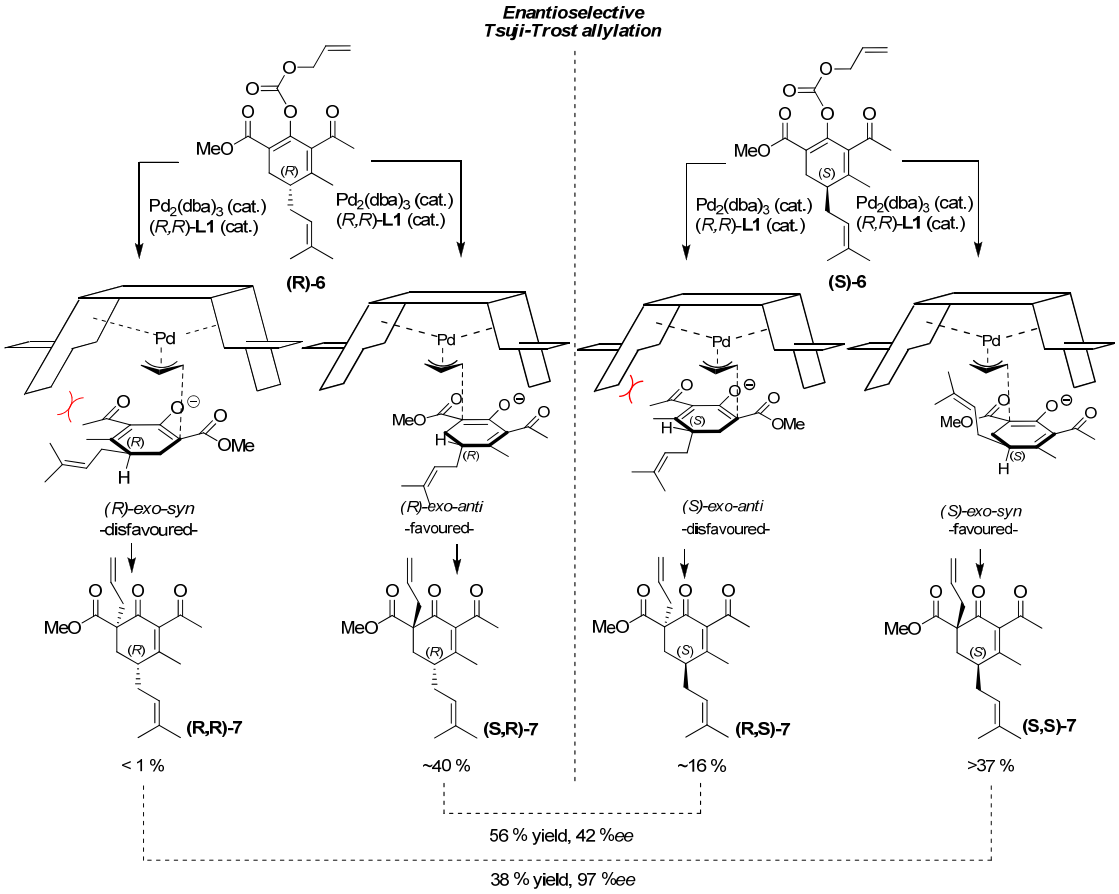
Part I

Stereoselective course of the asymmetric Tsuji-Trost allylation



Scheme 1. Rationale for the stereoselective course of the asymmetric Tsuji-Trost allylation

The enantiodifferentiation of the asymmetric Tsuji-Trost allylation might be rationalized using the commonly accepted mnemonic device developed by Trost. Assuming, that an *endo*-orientation of the bulky nucleophile can be discarded, four different diastereomeric transition state (TS) models have to be considered. The (R)-*exo-syn* TS displays the strongest interaction between one phenyl flap of the phosphine ligand and the exocyclic acyl-group in the nucleophile. In addition, the methyl- and isoprenylgroups also interact with the ligand. The TS is strongly disfavoured. However, the steric repulsions are not found in the diastereomeric (R)-*exo-anti* TS. All the groups mentioned above are pointing into the open side of the ligand, resulting in a high degree of diastereoselectivity for the (R)-series in favour of the formation of the 2,4-*trans*-allylated cyclohexenone **(S,R)-7**. Inversion of the configuration at C4 leads to more complex TS´s. The (S)-*exo-anti* TS shows a weak

interaction between the exocyclic acyl group and one aryl flap of the phosphine ligand. The diastereomeric (S)-*exo*-*syn* TS is lacking this interaction but shows a small steric repulsion between ligand and iso-prenyl group. The diastereoselectivity within this series is only about 2.1 : 1 in favour of the *cis*-allylated cyclohexenone **(S,S)-7**. In summary, the *trans*-diastereomer is formed as a mixture of 40 % **(S,R)-7** and 16 % of the enantiomeric **(R,S)-7**. The cis-product however shows high levels of enantioenrichment due to the very unfavourable formation of *cis*-enantiomer **(R,R)-7**.

Part II

Experimental procedures

General Remarks

All reactions and manipulations which are sensitive to air or moisture were performed under dry nitrogen by using standard Schlenk techniques. All solvents were purified prior to use. All chemicals were purchased from Acros Organics, Sigma Aldrich or Alfa Aesar. Reactions were monitored with thin layer chromatography on 0.20 mm Macherey – Nagel Alugram Xtra Sil silica gel plates. Purification via semi-preparative HPLC was carried out with a Knauer System, pump K-501 and RI-detector K-2400, and a Nucleodur 100-5 Si (250 mm x 20 mm) column. NMR spectra were recorded on a spectrometer at 300 MHz (^{1}H-NMR), 75 MHz (^{13}C-NMR) from Burker Avance 300 or on a spectrometer at 500 MHz (^{1}H-NMR), 125.6 MHz (^{13}C-NMR) from Bruker Avance 500.^{1}H-chemical shifts are expressed in ppm with residual chloroform (δ = 7.26 ppm) as reference. Chemical shifts (δ) are reported with multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet) and coupling constants (*J*) in Hz. ^{13}C-chemical shifts are reported as chemical shifts (δ) with residual chloroform (δ = 77.16 ppm) as internal reference. IR spectra were measured on a FT-IR spectrometer, Vektor 22 from Bruker, in an ATR mode. Mass spectra were measured using electrospray ionization on a Bruker Micro-TOF-Q.

General procedures GP-I – GP-IV:

General procedure I (GP-I): [1]

Substrate (335 mg, 1 mmol, 1 eq.) was dissolved in dimethyl formamide (5 mL) and cooled to 0 °C. Sodium hydride (60% in mineral oil, 48 mg, 1.2 mmol, 1.2 eq.) was added portionwise and after one hour allyl chloroformate (160 µL, 1.5 mmol, 1.5 eq.) was added. The reaction mixture was stirred over night at room temperature. The solution was quenched with sat. NH_4Cl-solution (5 mL) and extracted with ethyl acetate (3 x 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified via column chromatography.

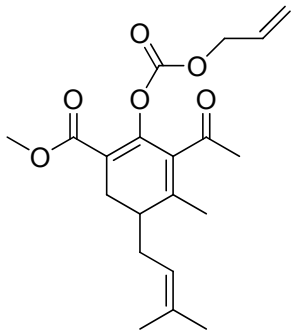
General procedure II (GP-II):[2]

LiCl (428 mg, 10.1 mmol, 2.05 eq.) was heated at 80 °C for 3 h under vacuo (1 mbar). THF (40 mL) and CuI (1.90 g, 10 mmol, 2 eq.) were added at room temperature. After stirring for 5 minutes at this temperature the suspension was cooled to -78 °C and the methylmagnesium bromide (3 M in THF, 10 mmol, 2 eq.), TMSCl (1.28 mL, 10 mmol, 2 eq.) and a solution of corresponding educt (5 mmol, 1 eq.) in THF (30 mL) were successively added. The resulting mixture was stirred at -78 °C for 5 h. The reaction was hydrolysed with NH_4Cl/2N HCl (1:1, 100 mL) and extracted with ethyl acetate (3 x 100 mL). The combined organic layers were washed with NH_4Cl/NH_3 (1:1, until the organic layer was colourless), brine, dried over Na_2SO_4 filtered and concentrated in vacuo. The crude product was purified via flash chromatography.

General procedure III (GP-III): [1]

Tris(dibenzylideneacetone)dipalladium(0) (23 mg, 25 µmol, 0.05 eq.) and Tri(*p*-tolyl)phosphine (38 mg, 0.125 mmol, 0.25 eq.) were dissolved in 1,4-dioxane (5 mL) and stirred for 15 min. at 60 °C. Substrate was added dissolved in 1,4-dioxane (1 mL). The resulting mixture was stirred at 60 °C for 1 h and then filtered through silica (petroleum ether/ethyl acetate, 5:1) The crude product was purified via HPLC. The product was isolated as a mixture of diastereomers.

Preparation of compound 6:



6

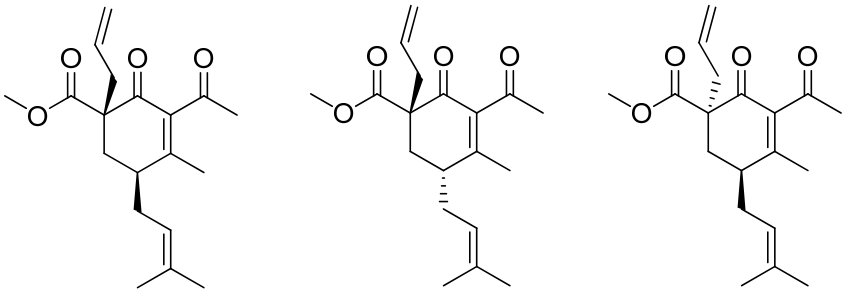
The corresponding diester[2] (10 mmol, 1 eq.) was dissolved in THF (30 mL) cooled to 0 °C and NaH (60% in mineral oil, 440 mg, 11 mmol, 1.1 eq.) was added portionwise. After stirring for 1 h at this temperature methyllithium (1.6 M in THF, 14.4 mL, 23 mmol, 2.3 eq.) was added dropwise and the mixture was stirred for 3 h at 0 °C. The solution was hydrolysed with sat. NH_4Cl-solution (3 mL) and extracted with ethyl acetate (3 x 25 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was used without further purification.

According to **GP-I** crude product (400 mg, 1.44 mmol) was treated with sodium hydride (60% in mineral oil, 68.6 mg, 1.72 mmol) and allyl chloroformate (287 µL, 2.16 mmol) to yield **6** after HPLC (silica gel, petroleum ether/ethyl acetate; 6:1) as a yellow oil (470 mg , 1.29 mmol, 78%).

R_f = 0.58 (petroleum ether/ ethyl acetate 6:1);**^{1}H-NMR** ($CDCl_3$, 500 MHz) δ 5.99 - 5.91 (m, 1H), 5.47 - 5.29 (m, 2H), 5.10 – 5.00 (m, 1H), 4.71 - 4.68 (m, 2H), 3.73 (s, 3H), 2.72 - 2.67 (m, 2H), 2.60 - 2.55 (m, 1H), 2.30 (s, 3H), 2.23 – 2.18 (m, 1H), 2.14 – 2.05 (m, 2H), 1.94 (s, 3H), 1.71 (s, 3H), 1.54 (s, 3H) ppm;

^{13}C-NMR ($CDCl_3$, 125 MHz) δ 201.5, 165.6, 151.6, 150.8, 148.7, 134.9, 132.3, 131.0, 121.1, 119.4, 111.1, 69.4, 51.8, 40.1, 31.6, 28.0, 26.2, 25.8, 19.7, 17.5 ppm; **IR** (film) v 2912 (w), 1766 (s), 1698 (s), 1433 (m), 1233 (s), 1181 (s) cm^{-1}; **GC/MS** (EI, 70 eV): m/z 385 (100); **HRMS** [$C_{20}H_{26}O_6$]:calculated 385.1622, found: 385.1633.

Preparation of compounds (S,R)-7, (R,S)-7 and (S,S)-7: [3]



(S,S)-7 **(S,R)-7** **(R,S)-7**

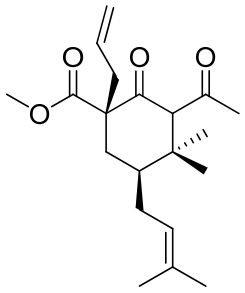
Substrate **6** (45.3 mg, 0.125 mmol, 1 eq.) was placed in a test tube under nitrogen and was dissolved in solvent (3.75 mL). The solution was cooled to 0°C and a premixed orange solution of $Pd_2(dba)_3$ (1.03 mg, 0,001 mmol) and the corresponding Ligand (0,003 mmol) was added to the reaction mixture. The resulting solution was stirred for 18 h and then filtered through silica. The obtained yellow oil was purified via HPLC (silica gel, petroleum ether/ethyl acetate; 6:1) to yield products **7** (37.8 mg, 0.11 mmol, 95%) as a yellow oil and a mixture of diastereomers (cis:trans 1:1.9). Enantiomeric excess was determined by chiral HPLC (AD-H, heptane/*iso*propanol 90:10).

R_f = 0.27 – 0.31 (petroleum ether/ ethyl acetate 10:1);

Diastereomere *cis*: **^{1}H-NMR** ($CDCl_3$, 500 MHz) δ 5.78 - 5.71 (m, 1H), 5.10 - 5.05 (m, 2H), 5.00 – 4.95 (m, 1H), 3.71 (s, 3H), 2.66 - 2.59 (m, 2H), 2.51 - 2.45 (m, 1H), 2.43 – 2.32 (m, 2H), 2.28 (s, 3H), 2.21 – 2.14 (m, 1H), 1.88 (s, 3H), 1.71 (s, 3H), 1.60 (s, 3H), 1.57 – 1.52 (m, 2H) ppm; **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 203.5, 193.4, 171.3, 160.6, 140.3, 135.0, 132.8, 119.4, 118.9, 56.4, 52.4, 38.8, 38.5, 34.9, 31.0, 30.5, 25.8, 19.2, 18.0 ppm; **IR** (film) v 2915 (w), 1734 (s), 1703 (s), 1674 (s), 1434 (m), 1353 (m), 1206 (s), 1157 (s) cm^{-1}; **GC/MS** (EI, 70 eV): m/z 397 (12), 357 (21), 341 (100), 301 (3); **HRMS** [$C_{19}H_{26}O_4$]:calculated 341.1723, found: 341.1715. $[\alpha]_D^{20}$: +25.2 (c = 3.53, $CHCl_3$)

Diastereomere *trans*: **^{1}H-NMR** ($CDCl_3$, 500 MHz) δ 5.83 - 5.76 (m, 1H), 5.15 - 5.10 (m, 2H), 5.08 – 5.04 (m, 1H), 3.75 (s, 3H), 2.70 - 2.65 (m, 1H), 2.50 - 2.38 (m, 3H), 2.30 (s, 3H), 2.29 – 2.26 (m, 1H), 2.15 – 2.05 (m, 2H), 1.94 (s, 3H), 1.72 (s, 3H), 1.62 (s, 3H) ppm; **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 203.9, 194.4, 172.3, 160.5, 138.8, 134.8, 133.3, 120.3, 119.1, 56.1, 52.4, 37.9, 37.4, 32.8, 31.3, 30.4, 25.8, 19.4, 18.0 ppm; **IR** (film) v 2918 (w), 1737 (s), 1703 (s), 1660 (s), 1435 (m), 1279 (s) cm^{-1}; **GC/ MS** (EI, 70 eV): m/z 341 (100), 319 (2); **HRMS** [$C_{19}H_{26}O_4$]:calculated 341.1723, found: 341.1725. $[\alpha]_D^{20}$: +5.9 (c = 3.53, $CHCl_3$)

Preparation of compound 8:

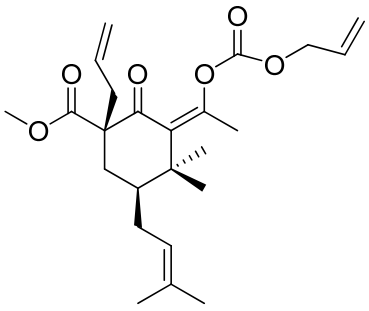


8

According to **GP-II 7** (34 mg, 0.1 mmol) was treated with lithium chloride (18 mg, 0.2 mmol), copper iodide (82 mg, 0.2 mmol), methylmagnesium bromide (3 M in Et_2O, 0.14 mL, 0.2 mmol) and TMSCl (55 µL, 0.2 mmol) to yield product **8** after flash chromatography (silica gel, petroleum ether/ethyl acetate; 6:1) as yellow oil (31 mg, 0.09 mmol, 91%).

R_f = 0.35 (petroleum ether/ethyl acetate 10:1); **^{1}H-NMR** ($CDCl_3$, 300 MHz): δ 5.80 - 5.72 (m, 1H), 5.15 – 5.11 (m, 1H), 5.08 – 5.01 (m, 2H), 3.78 (s, 3H) 3.58 (s, 1H), 2.59 – 2.54 (m, 1H), 2.51 – 2.46 (m, 1H), 2.33 - 2.27 (m, 1H), 2.22 - 2.16 (m, 1H), 2.11 (s, 3H), 1.74 (s, 3H), 1.69 - 1.61 (m, 1H), 1.59 (s, 3H), 1.58 – 1.52 (m, 1H), 1.32 – 1.26 (m, 1H), 1.08 (s, 3H), 0.97 (s, 3H) ppm; **^{13}C-NMR** ($CDCl_3$, 125 MHz): δ 204.2, 203.8, 171.9, 133.1, 132.8, 122.5, 118.6, 71.7, 61.3, 52.5, 45.7, 43.4, 39.2, 37.1, 32.1, 27.2, 26.2, 25.8, 17.9, 15.4 ppm; **IR** (film): v = 2916 (w), 1724 (s), 1709 (s), 1436 (m), 1355 (m), 1285 (s) cm^{-1}; **MS** (ESI): m/z (%) = 357 (100), 335 (31); **HRMS:** [$C_{20}H_{30}O_4$ + Na] calculated: 357.2036, found: 357.2039.

Preparation of compound 9:



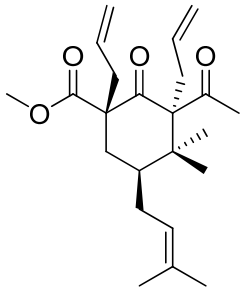
9

According to **GP-I** substrate (577 mg, 2.07 mmol) was treated with sodium hydride (60% in mineral oil, 99.5 mg, 2.48 mmol) and allyl chloroformate (331 µL, 3.1 mmol)

to yield **9** after purification by HPLC (silica gel, petroleum ether/ethyl acetate; 10:1) as a yellow oil (788 mg, 1.88 mmol, 91%) .

R_f = 0.57 (petroleum ether/ethyl acetate 10:1); **^{1}H-NMR** ($CDCl_3$, 300 MHz): δ 5.95 - 5.87 (m, 1H), 5.77 – 5.67 (m, 1H), 5.38 – 5.26 (m, 2H), 5.11 – 5.06 (m, 3H), 4.62 – 4.58 (m, 2H), 3.70 (s, 3H), 2.54 – 2.51 (m, 2H), 2.28 (s, 3H), 2.16 - 2.10 (m, 1H), 2.02 – 1.98 (m, 1H), 1.71 (s, 3H), 1.70 – 1.61 (m, 2H), 1.59 (s, 3H), 1.47 – 1.42 (m, 1H), 1.09 (s, 3H), 1.08 (s, 3H) ppm; **^{13}C-NMR** ($CDCl_3$, 125 MHz): δ 203.9, 173.4, 152.4, 143.3, 141.8, 133.3, 133.0, 131.0, 122.8, 119.5, 118.8, 69.2, 52.4, 49.9, 41.6, 39.9, 38.1, 33.2, 27.5, 25.8, 25.0, 20.9, 17.9 ppm; **IR** (film): v = 2969 (w), 1763 (m), 1733 (m), 1698 (m), 1444 (m), 1364 (m), 1225 (s), 1134 (m) cm^{-1}; **MS** (ESI): m/z (%) = 441 (100); **HRMS:** [$C_{24}H_{34}O_6$ + Na] calculated: 441.2248, found: 441.2248.

Preparation of compound 10:

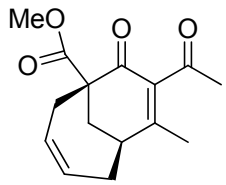


10

According to **GP-III** **9** (56.0 mg, 0.13 mmol) were treated with tris(dibenzylideneacetone)dipalladium(0) (6.0 mg, 6.6 µmol) and tri(*p*-tolyl)phosphine (10.0 mg, 33.0 µmol) to yield product **10** (46.3 mg, 0.12 mmol, 95%) after purification by HPLC (silica gel, petroleum ether/ethyl acetate; 20:1).

R_f = 0.62 (petroleum ether/ethyl acetate 10:1); **^{1}H-NMR** ($CDCl_3$, 300 MHz): δ 5.72 - 5.60 (m, 1H), 5.27 – 5.21 (m, 2H), 5.16 – 5.10 (m, 2H), 4.94 – 4.87 (m, 2H), 3.65 (s, 3H), 3.03 – 2.99 (m, 1H), 2.77 – 2.73 (m, 1H), 2.64 - 2.60 (m, 1H), 2.46 – 2.41 (m, 1H), 2.23 – 2.10 (m, 6H), 1.76 (s, 3H), 1.75 – 1.71 (m, 1H), 1.63 (s, 3H), 1.48 – 1.42 (m, 1H), 0.94 (s, 3H), 0.89 (s, 3H) ppm; **^{13}C-NMR** ($CDCl_3$, 125 MHz): δ 206.6, 205.9, 170.2, 133.3, 133.0, 132.5, 122.8, 119.8, 117.3, 74.9, 59.3, 52.3, 41.8, 41.2, 39.0, 34.6, 33.4, 32.8, 27.9, 25.8, 22.1, 22.0, 18.0 ppm; **IR** (film): v = 3078 (w), 2975 (w), 1733 (m), 1697 (s), 1393 (m), 1276 (m), 1213 (m) cm^{-1}; **MS** (ESI): m/z (%) = 397 (100); **HRMS:** [$C_{23}H_{34}O_4$ + Na] calculated: 397.2349, found: 397.2363.

Preparation of compound 13:

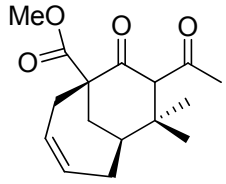


13

To a solution of **(S,S)-7** (399 mg, 1.25 mmol, 1 eq.) in DCM (10 mL) was added Grubbs II (10.6 mg, 1.25 µmol, 1 mol-%.). The reaction mixture was stirred at 45 °C over night. After cooling to room temperature and filtration over silica, crude product was purified by HPLC (silica gel, petroleum ether/ethyl acetate; 5:1) to yield **13** (235 mg, 0.9 mmol, 73%) as a colourless oil.

R_f = 0.16 (petroleum ether/ ethyl acetate 6:1);**^{1}H-NMR** ($CDCl_3$, 500 MHz) δ 5.76 - 5.70 (m, 1H), 5.66 - 5.60 (m, 1H), 3.71 (s, 3H), 3.02 - 2.94 (m, 2H), 2.71 - 2.67 (m, 1H), 2.58 – 2.52 (m, 3H), 2.30 (s, 3H), 2.11 – 2.05 (m, 1H), 1.93 (s, 3H) ppm; **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 203.5, 194.6, 173.3, 160.5, 141.4, 128.7, 127.7, 53.2, 52.6, 39.5, 36.3, 36.2, 32.4, 31.5, 20.3 ppm; **IR** (film) v 2952 (w), 1736 (s), 1703 (s), 1655 (s), 1351 (m), 1246 (m), 1104 (s), 1062 (s) cm^{-1}; **GC/MS** (EI, 70 eV): m/z 285 (100); **HRMS** [$C_{15}H_{18}O_4$]:calculated 285.1097, found: 285.1089. $[\alpha]_D^{20}$: +14.7 (c = 3.53, $CHCl_3$)

Preparation of precursor to 11:

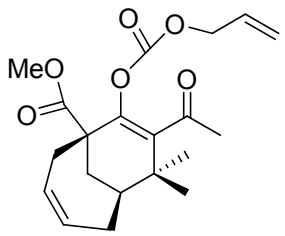


According to **GP-II 13** (235 mg, 0.9 mmol) was treated with lithium chloride (75.5 mg, 1.8 mmol), copper iodide (341 mg, 1.8 mmol), methylmagnesium bromide (3 M in Et_2O, 0.6 mL, 1.8 mmol) and TMSCl (228 µL, 1.8 mmol) to yield product after flash chromatography (silica gel, petroleum ether/ethyl acetate; 6:1) as yellow oil (205 mg, 0.74 mmol, 82%).

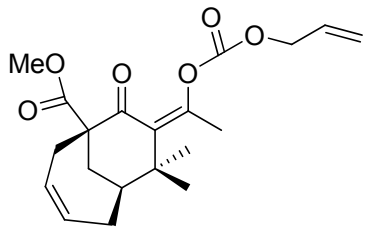
R_f = 0.50 – 0.46 (petroleum ether/ ethyl acetate 6:1); **^{1}H-NMR** ($CDCl_3$, 500 MHz) δ 5.94 - 5.86 (m, 1H), 5.67 - 5.61 (m, 1H), 4.02 (s, 1H), 3.76 (s, 3H), 3.18 - 3.12 (m,

1H), 2.78 - 2.66 (m, 3H), 2.36 – 2.30 (m, 1H), 2.13 (s, 3H), 2.04 - 1.94 (m, 1H), 1.77 - 1.73 (m, 1H), 1.32 (s, 3H), 1.11 (s, 3H) ppm; **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ 207.7, 205.5, 173.2, 130.8, 126.5, 70.3, 58.5, 52.7, 41.2, 41.1, 38.2, 37.0, 32.9, 31.9, 27.0, 26.2 ppm; **IR** (film) v 2953 (w), 2879 (w), 1734 (s), 1695 (s), 1432 (m), 1217 (s) cm^{-1}; **GC/MS** (EI, 70 eV): m/z 301 (100), 279 (3); **HRMS** [$C_{16}H_{22}O_4$+Na]: calculated: 301.1410, found: 301.1410.

Preparation of compounds 11a and 11b:



11a



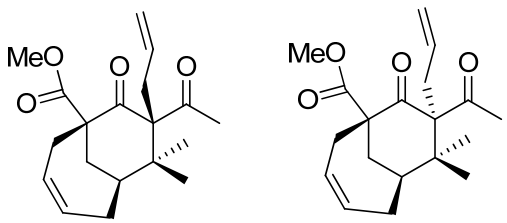
11b

Substrate (147 mg, 0.53 mmol, 1 eq.) was dissolved in dimethyl formamide (3 mL) and cooled to 0 °C. Sodium hydride (60% in mineral oil, 25 mg, 0.63 mmol, 1.2 eq.) was added portionwise and after one hour allyl chloroformate (85.0 µL, 0.80 mmol, 1.5 eq.) was added. The reaction mixture was stirred over night at room temperature. The solution was quenched with sat. NH_4Cl-solution (5 mL) and extracted with ethyl acetate (3 x 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified via HPLC (silica gel, petroleum ether/ethyl acetate; 5:1) to yield product **11a** and **11b** (214 mg, 0.5 mmol, 97%) as a yellow oil and a mixture of regioisomers (a:b 1:1).

Regioisomere a: R_f = 0.47 (petroleum ether/ethyl acetate 4:1); **^{1}H-NMR** ($CDCl_3$, 500 MHz): δ 6.00 - 5.91 (m, 1H), 5.73 – 5.68 (m, 1H), 5.58 – 5.53 (m, 1H), 5.43 – 5.30 (m, 2H), 4.70 – 4.68 (m, 2H), 3.72 (s, 3H), 3.05 – 3.00 (m, 1H), 2.86 – 2.82 (m, 1H), 2.59 - 2.53 (m, 1H), 2.27 - 2.08 (m, 3H), 2.07 (s, 3H), 1.73 – 1.69 (m, 1H), 1.35 (s, 3H), 1.27 (s, 3H) ppm; **^{13}C-NMR** ($CDCl_3$, 125 MHz): δ 202.8, 173.6, 155.0, 151.8, 133.1, 131.0, 128.5, 126.7, 119.5, 69.0, 56.4, 52.6, 42.5, 42.2, 35.9, 34.3, 29.3, 29.2, 26.4, 20.1 ppm; **IR** (Film): v = 2953 (w), 1757 (m), 1738 (m), 1688 (m), 1552 (m), 1208 (s), 1164 (s), 1097 (m) cm^{-1}; **GC/MS** (EI, 70 eV): m/z 385 (100); **HRMS:** [$C_{20}H_{26}O_6$ + Na] calculated: 385.1622, found: 385.1620.

Regioisomere b: R_f = 0.41 (petroleum ether/ethyl acetate 4:1); **^{1}H-NMR** ($CDCl_3$, 500 MHz): δ 6.00 - 5.91 (m, 1H), 5.73 – 5.68 (m, 1H), 5.58 – 5.53 (m, 1H), 5.43 – 5.30 (m, 2H), 4.70 – 4.68 (m, 2H), 3.72 (s, 3H), 3.05 – 3.00 (m, 1H), 2.86 – 2.82 (m, 1H), 2.59 - 2.53 (m, 1H), 2.27 - 2.08 (m, 3H), 2.07 (s, 3H), 1.73 – 1.69 (m, 1H), 1.35 (s, 3H), 1.27 (s, 3H) ppm; **^{13}C-NMR** ($CDCl_3$, 125 MHz): δ 202.8, 173.6, 155.0, 151.8, 133.1, 131.0, 128.5, 126.7, 119.5, 69.0, 56.4, 52.6, 42.5, 42.2, 35.9, 34.3, 29.3, 29.2, 26.4, 20.1 ppm; **IR** (Film): v = 2953 (w), 1757 (m), 1738 (m), 1688 (m), 1552 (m), 1208 (s), 1164 (s), 1097 (m) cm^{-1}; **GC/MS** (EI, 70 eV): m/z 385 (100), 283 (58); **HRMS:** [$C_{20}H_{26}O_6$ + Na] calculated: 385.1622, found: 385.1619.

Preparation of compound 12:



12(cis) **12(trans)**

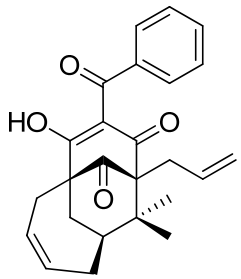
According to **GP-III** **11** (216 mg, 0.58 mmol) were treated with tris(dibenzylideneacetone)dipalladium(0) (26.3 mg, 29.0 µmol) and tri(*p*-tolyl)phosphine (49.4 mg, 145 µmol) to yield product **12** (170 mg, 0.53 mmol, 92%) after purification by HPLC (silica gel, petroleum ether/ethyl acetate; 5:1) as a colourless oil and a mixture of diastereomers (a:b 85:15).

Diastereomere 12(cis): R_f = 0.67 (petroleum ether/ethyl acetate 5:1); **^{1}H-NMR** ($CDCl_3$, 500 MHz): δ 5.65 - 5.59 (m, 1H), 5.49 – 5.44 (m, 1H), 5.37 – 5.28 (m, 1H), 4.86 – 4.75 (m, 2H), 3.77 (s, 3H), 2.96 – 2.90 (m, 2H), 2.79 – 2.69 (m, 3H), 2.63 - 2.59 (m, 1H), 2.46 - 2.38 (m, 1H), 2.15 (s, 3H), 2.10 – 2.04 (m, 1H), 1.92 – 1.88 (m, 1H), 1.25 (s, 3H), 1.12 (s, 3H) ppm; **^{13}C-NMR** ($CDCl_3$, 125 MHz): δ 211.1, 206.7, 174.0, 134.8, 129.7, 124.4, 116.1, 71.0, 58.4, 52.6, 41.5, 40.4, 39.9, 36.6, 34.0, 32.1, 31.9, 30.3, 22.9 ppm; **IR** (Film): **v** = 2951 (w), 1740 (s), 1701 (m), 1684 (s), 1432 (m), 1394 (m), 1247 (s) cm^{-1}; **MS** (ESI): m/z (%) = 441 (12), 341 (100); **HRMS:** [$C_{19}H_{26}O_4$ + Na] calculated: 341.1723, found: 341.1703. $[\alpha]_D^{20}$: +116.1 (c = 3.53, $CHCl_3$)

Diastereomere 12(trans): R_f = 0.58 (petroleum ether/ethyl acetate 5:1); **^{1}H-NMR** ($CDCl_3$, 500 MHz): δ 5.58 - 5.45 (m, 2H), 5.01 – 4.92 (m, 1H), 3.72 (s, 3H), 3.07 – 3.02 (m, 1H), 2.95 – 2.89 (m, 1H), 2.78 - 2.68 (m, 3H), 2.64 - 2.59 (m, 1H), 2.27 –

2.19 (m, 1H), 2.03 (s, 3H), 2.02 – 1.97 (m, 1H), 1.85 – 1.82 (m, 1H), 1.36 (s, 3H), 1.17 (s, 3H) ppm; **^{13}C-NMR** ($CDCl_3$, 125 MHz): δ 211.0, 204.5, 173.0, 135.0, 131.2, 124.9, 117.0, 72.8, 58.2, 52.6, 41.6, 41.3, 39.2, 37.9, 34.7, 31.6, 30.0, 29.7, 26.1 ppm; **IR** (Film): **v** = 2951 (w), 1740 (s), 1700 (m), 1682 (s), 1432 (m), 1394 (m), 1215 (s) cm^{-1}; **MS** (ESI): m/z (%) = 441 (10), 341 (100); **HRMS:** [$C_{19}H_{26}O_4$ + Na] calculated: 341.1723, found: 341.1703. $[\alpha]_D^{20}$: -53.5 (c = 3.53, $CHCl_3$)

Preparation of compound 14:



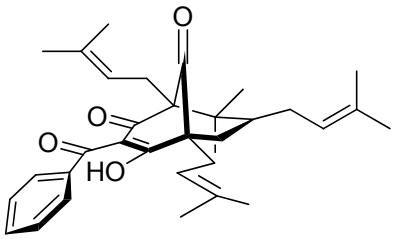
14

Substrate **12** (69.1 mg, 0.24 mmol, 1 eq.) was dissolved in THF (7 mL) and cooled to 0 °C. potassium *tert*-butanolate (53 mg, 0.48 mmol, 2 eq.) was added. The reaction mixture was stirred for 30 min at 0 °C. Benzoyl cyanide (104 mg, 0.79 mmol, 3.3 eq.) was added portionwise and the mixture was stirred at 40 °C for 24h. The solution was quenched with sat. NH_4Cl-solution (10 mL) and extracted with ethyl acetate (3 x 20 mL). The combined organic layers were washed with $NaHCO_3$ (10 mL), brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified via column chromatography (silica gel, petroleum ether/ethyl acetate; 2:1) to yield **14** as a white solid (85.8 mg, 0.21 mmol, 91%).

R_f = 0.48 (petroleum ether/ethyl acetate 2:1); **^{1}H-NMR** ($CDCl_3$, 500 MHz, 5.5:1 mixture of enol tautomers as determined by H^1 NMR analysis): δ 18.1 (s, 1H), 17.70 (s, 0.2H), 8.17 – 8.15 (m, 1H),7.80 – 7.77 (m, 0.6H), 7.63 – 7.59 (m, 1H), 7.55 – 7.49 (m, 1.8H), 7.45 – 7.37 (m, 4.7H), 5.72 – 5.51 (m, 3.6 H), 5.16 – 4.96 (m, 2.4 H), 2.92 – 2.82 (m, 2.3H), 2.77 – 2.73 (m, 1.3 H), 2.66 – 2.56 (m, 2H), 2.53 – 2.41 (m 1.2H), 2.09 – 1.94 (m, 4H), 1.40 (s, 3H), 1.18 (s, 0.7H), 1.10 (s, 3H), 0.98 (s, 0.7H) ppm; **^{13}C-NMR** ($CDCl_3$, 125 MHz, 5.5:1 mixture of enol tautomers as determined by H^1 NMR analysis):): δ 207.7, 200.2, 195.8, 190.1, 167.9, 136.8, 136.3, 133.9, 133.3, 133.0, 132.1, 131.7, 130.5, 129.5, 128.3, 128.2, 127.7, 127.5, 127.4, 127.0, 126.0, 125.4, 119.5. 119.3, 111.4, 65.0, 62.8, 47.8, 47.6, 44.7, 43.8, 39.8, 37.8, 34.7, 33.8,

29.0, 28.2, 26.5, 26.0, 25.9, 23.9, 23.7 ppm;.**IR** (Film): v = 3017 (w), 2984 (w), 1730 (m), 1680 (s), 1528 (m), 1394 (m) cm^{-1}; **MS** (ESI): m/z (%) = 435 (25), 413 (100), 391 (8), 301 (3); **HRMS:** [$C_{25}H_{26}O_4$ + Na] calculated: 413.1723, found: 413.1724. $[\alpha]_D^{20}$: -77.9 (c = 3.53, $CHCl_3$)

Preparation of (+)-Clusianone:



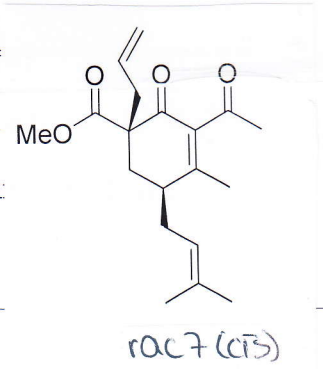
1

Substrate **14** (9 mg, 0.02 mmol, 1 eq.), amylene (0.2 mL, 2.3 mmol, 100 eq.) and Grubb`s II (0.002 mmol, 10 mol%) were dissolved in DCM (0.2 mL) and heated to reflux for 2h. The solvent was removed in vacuo and the crude product filtered over silica (petroleum ether/ethyl acetate; 5:1). The crude product was purified via HPLC (silica gel, petroleum ether/ethyl acetate; 5:1) to yield (+)-clusianone **7** (6.5 mg, 0,013 mmol, 65%). Spectroscopic data were identical to those described in the literature.[4]
R_f = 0.54 (petroleum ether/ethyl acetate 5:1); **^{1}H-NMR** ($CDCl_3$, 500 MHz, 5.5:1 mixture of enol tautomers as determined by H^1 NMR analysis): δ 17.56 (s, 0.9H), 17.50 (s, 0.6H), 7.57 – 7.49 (m, 5H), 7.39 – 7.34 (m, 3.3H), 5.20 – 5.11 (m, 1.6H), 5.05 – 5.01 (m, 0.6H), 4.98 – 4.94 (m, 0.7H), 4.92 – 4.88 (m, 1H), 4.84 – 4.79 (m, 1H), 2.75 – 2.71 (m, 2.5H), 2.66 – 2.61 (m, 1.1H), 2.57 – 2.52 (m, 1H), 2.49 – 2.38 (m, 1.7H), 2.16 – 2.05 (m, 2.4H), 2.03 – 1.98 (m, 1H), 1.78 (s, 2H), 1.76 (s, 2H), 1.72 – 1.68 (m, 8H), 1.66 (s, 2H), 1.64 (s, 3H), 1.62 (s, 3H), 1.61 (s, 2H), 1.59 – 1.56 (m, 1H), 1.54 (s, 3H), 1.53 (s, 3H), 1.51 (s, 3H), 1.41 – 1.35 (m, 1H), 1.23 (s, 3H), 1.05 (s, 2H), 0.83 (s, 3H), 0.73 (s, 2H) ppm; **^{13}C-NMR** ($CDCl_3$, 125 MHz, 5.5:1 mixture of enol tautomers as determined by H^1 NMR analysis): δ 207.5, 207.3, 197.8, 197.5, 195.4, 194.7, 193.9, 192.6, 137.2, 134.6, 134.5, 133.3, 132.5, 132.5, 128.9, 128.9, 127.8, 127.7, 122.3, 122.2, 120.3, 119.9, 119.1. 119.0, 116.8, 116.1, 71.0, 67.2, 64.6, 59.6, 48.5, 47.6, 42.9, 42.3, 41.5, 30.6, 29.8, 29.7, 28.5, 28.1, 26.1, 26.1, 26.0, 25.8, 25.7, 25.5, 24.9, 23.7, 22.6, 18.2, 18.1, 18.1, 18.0, 17.9, 16.4, 16.2 ppm;.**IR** (Film): v = 2974 (w), 2913 (w), 1727 (m), 1665 (m), 1543 (m), 1375 (m), 908 (m), 729 (s), 691

(m) cm^{-1}; **MS** (ESI): m/z (%) = 547 (32), 525 (100), 511 (51); **HRMS:** [$C_{33}H_{42}O_4$ + Na] calculated: 525.2975, found: 525.2968. $[\alpha]_D^{20}$: +30.6 (c = 3.53, $CHCl_3$)

Data File C:\HPCHEM\2\DATA\IA\FH6-0510.D Sample Name: FH6-051

Chiracel AD-H, 0.5ml/min, 90:10, 1µl



rac 7 (cis)

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Injection Date : 04.04.14 15:42:13
Sample Name : FH6-051
Acq. Operator : Fiene

Vi

Inj Volu

Method : C:\HPCHEM\2\METHODS\BP98_2.M
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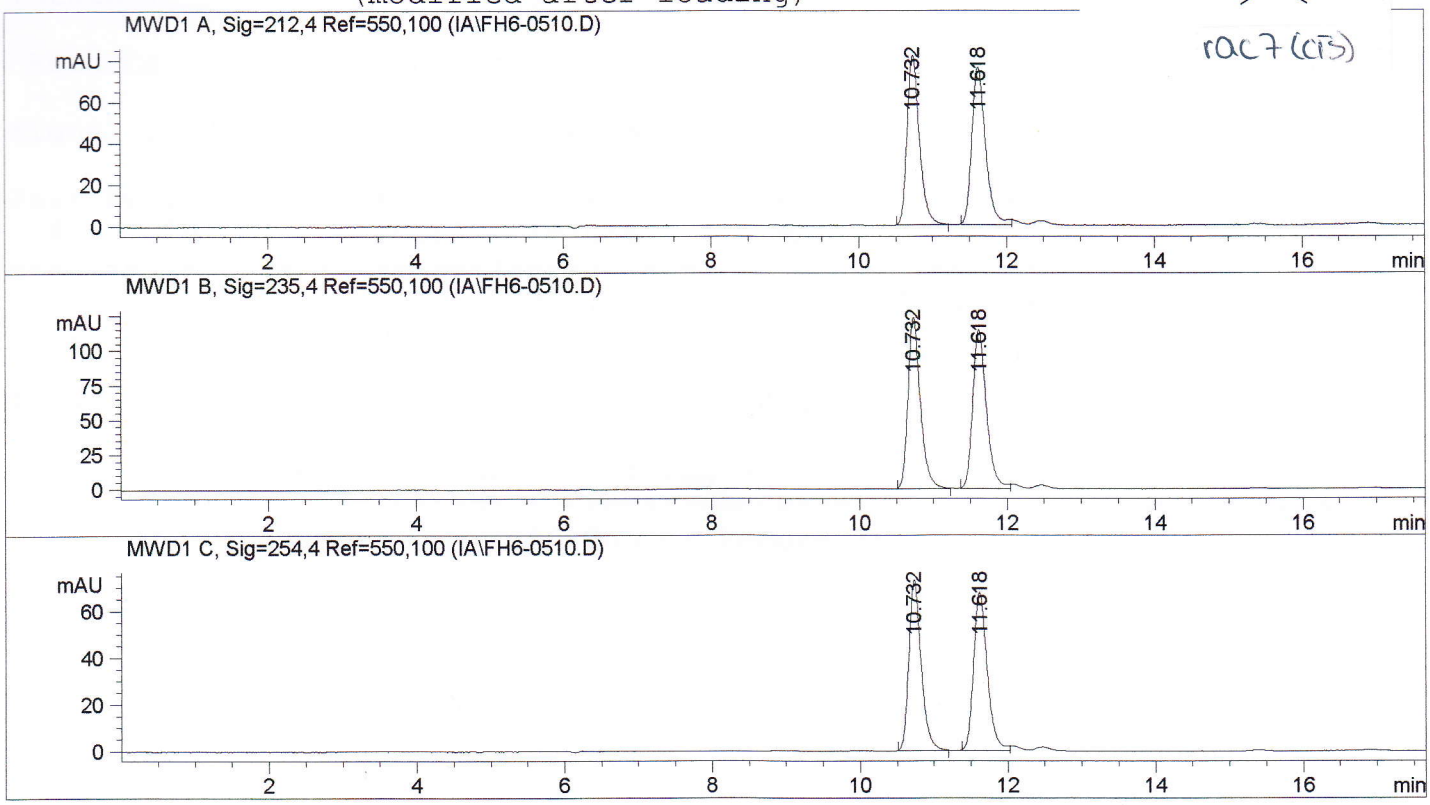

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Area Percent Report

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rac cis!!

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Sample Amount : 1.00000 [ng/ul] (not used in calc.)

Signal 1: MWD1 A, Sig=212,4 Ref=550,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.732	BB	0.1817	967.29578	81.96939	49.2792
2	11.618	BB	0.1997	995.59174	76.54868	50.7208

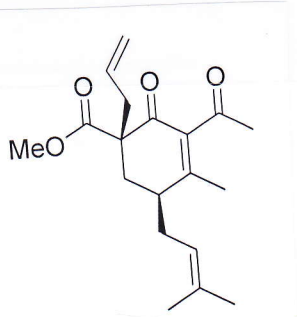
Totals : 1962.88751 158.51807

Results obtained with enhanced integrator!

ata File C:\HPCHEM\2\DATA\CS\FH6-0991.D

Sample Name: FH6-099cis

Chiracel AD-H, 0.5ml/min, 90:10, 1µl



cis-7

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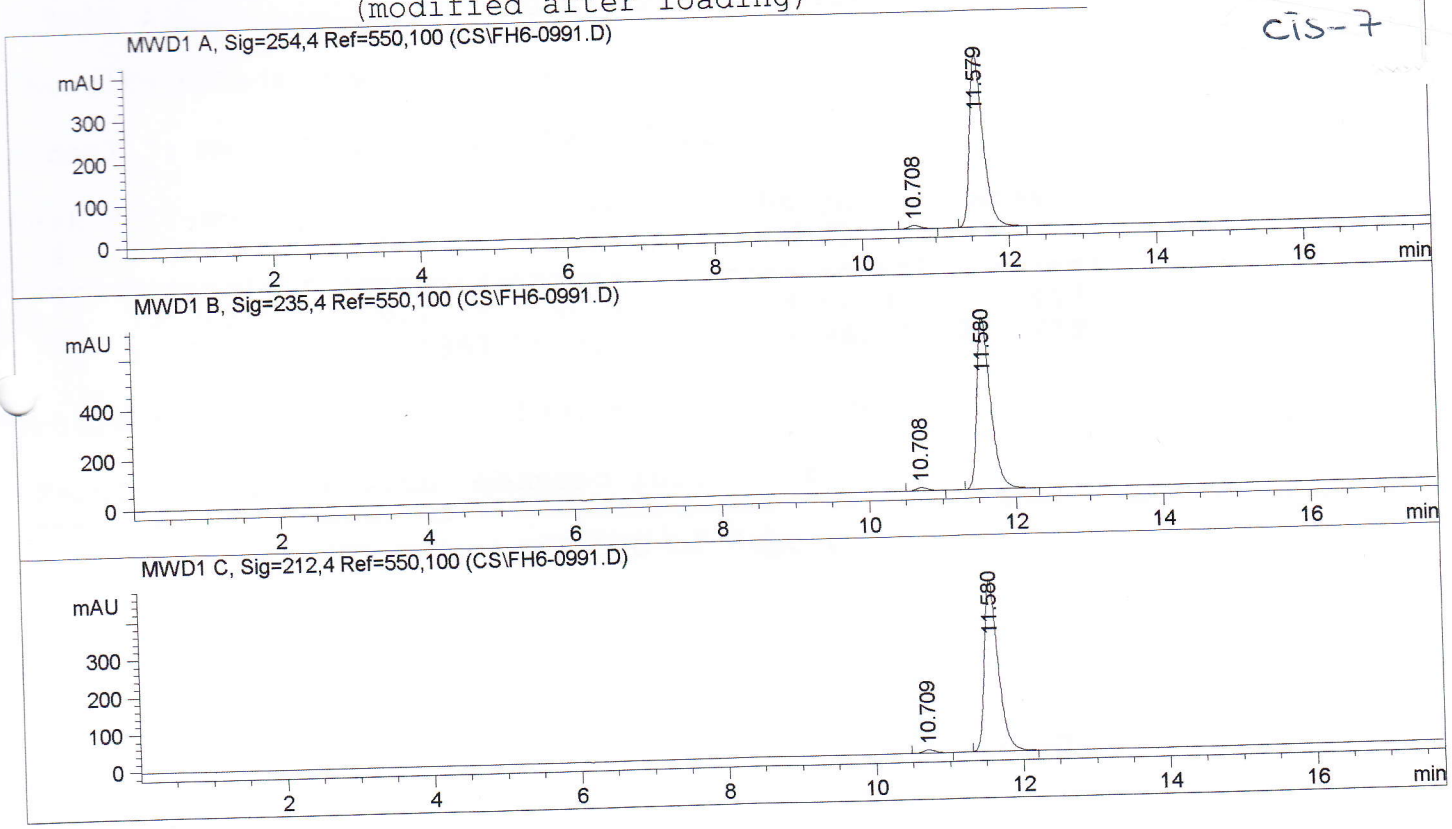
Injection Date : 16.05.14 17:15:10
Sample Name : FH6-099cis
Acq. Operator : Fiene

Vi

Inj Volu

Method : C:\HPCHEM\2\METHODS\BP98_2.M
Last changed : 16.05.14 17:13:09 by Fiene
(modified after loading)



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Area Percent Report

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96,52%

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Sample Amount : 1.00000 [ng/ul] (not used in calc.)

Signal 1: MWD1 A, Sig=254,4 Ref=550,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.708	PB	0.1765	92.72221	7.92688	1.7400
2	11.579	BB	0.1965	5236.20947	405.85696	98.2600
Totals :				5328.93168	413.78384	

Results obtained with enhanced integrator!

Data File C:\HPCHEM\2\DATA\FH\FH6-0730.D Sample Name: FH6-073trans

Chiracel AD-H, 0.5ml/min, 90:10, 1µl

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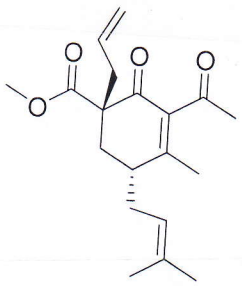
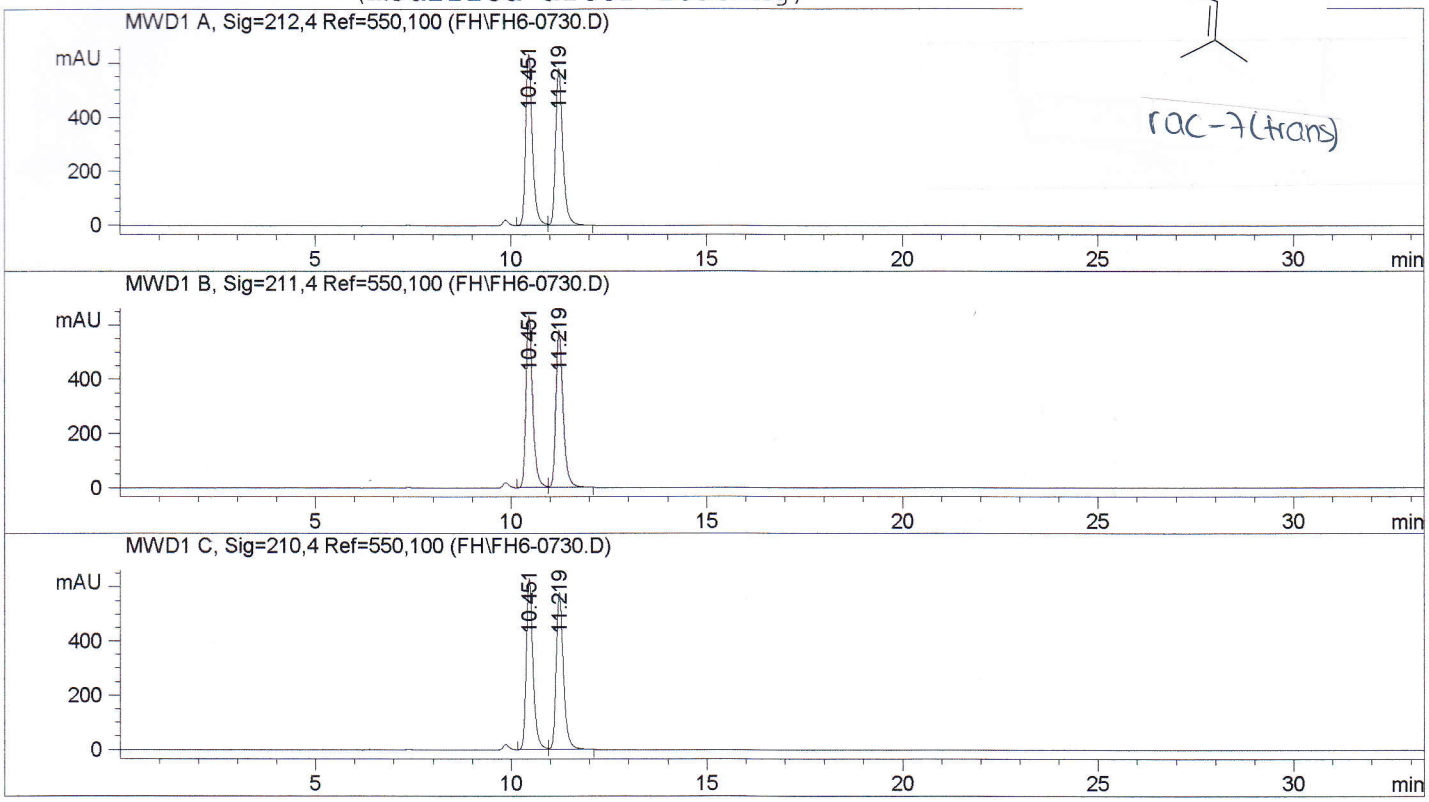
Injection Date : 28.04.14 14:00:50
Sample Name : FH6-073trans
Acq. Operator : Fiene

Inj Vc



rac-7(trans)

Method : C:\HPCHEM\2\METHODS\BP98_2.M
Last changed : 28.04.14 12:54:51 by Fiene
(modified after loading)



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Area Percent Report

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rac

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Sample Amount : 1.00000 [ng/ul] (not used in calc.)

Signal 1: MWD1 A, Sig=212,4 Ref=550,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.451	VV	0.1815	7574.48096	633.62378	50.3046
2	11.219	VB	0.1941	7482.74707	581.43042	49.6954
Totals :				1.50572e4	1215.05420	

Results obtained with enhanced integrator!

ata File C:\HPCHEM\2\DATA\CS\FH6-0990.D Sample Name: FH6-099trans

Chiracel AD-H, 0.5ml/min, 90:10, 1µl

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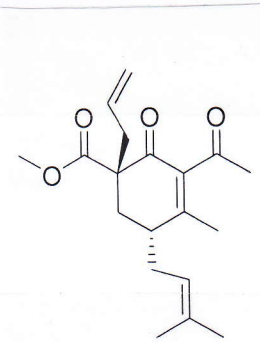
Injection Date : 16.05.14 17:01:
Sample Name : FH6-099trans
Acq. Operator : Fiene

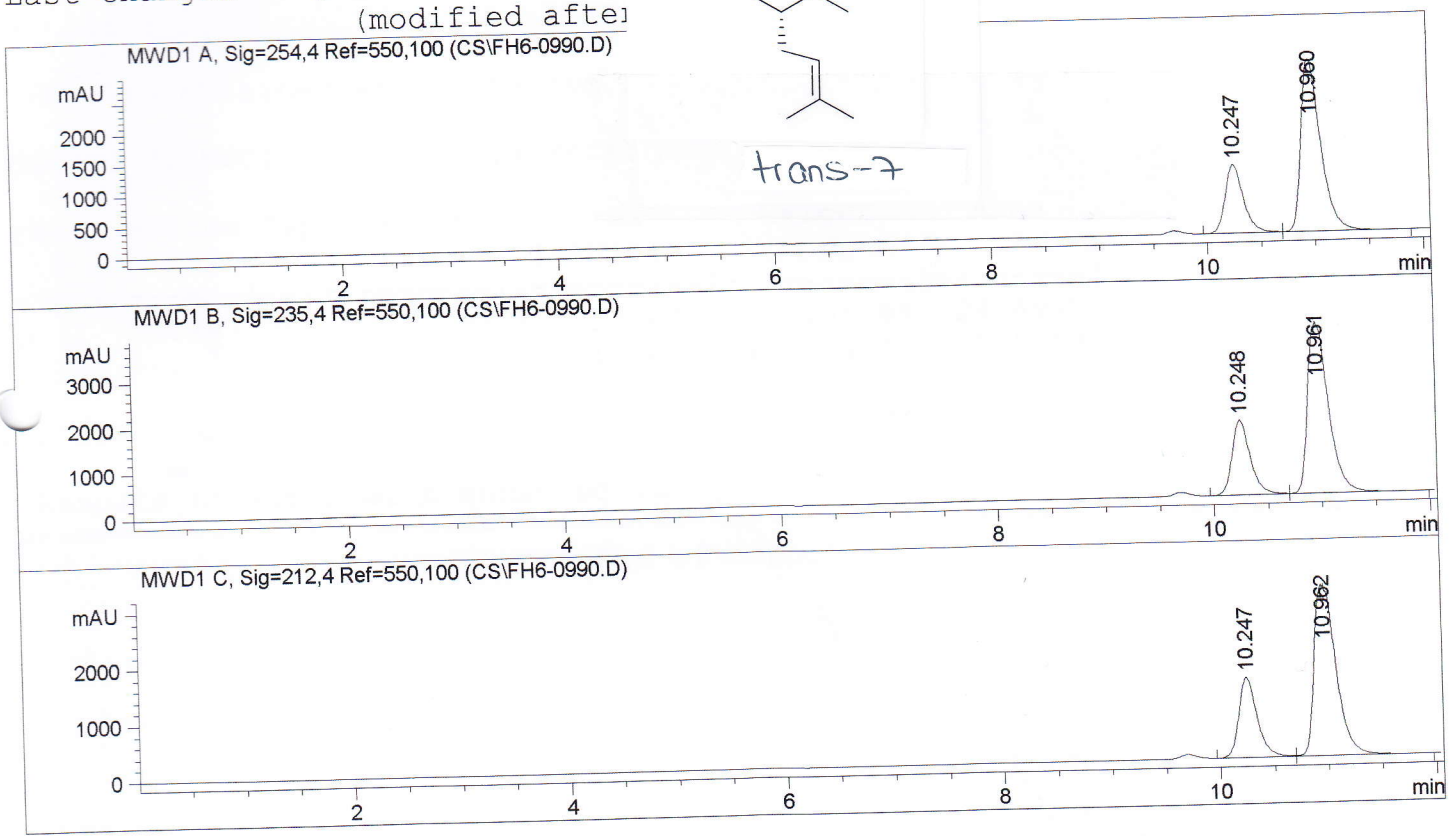
Method : C:\HPCHEM\2\ME
Last changed : 16.05.14 17:13:
(modified after

Vial : 10

Volume : 5 µl



trans-7



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Area Percent Report

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461.

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Sample Amount : 1.00000 [ng/ul] (not used in calc.)

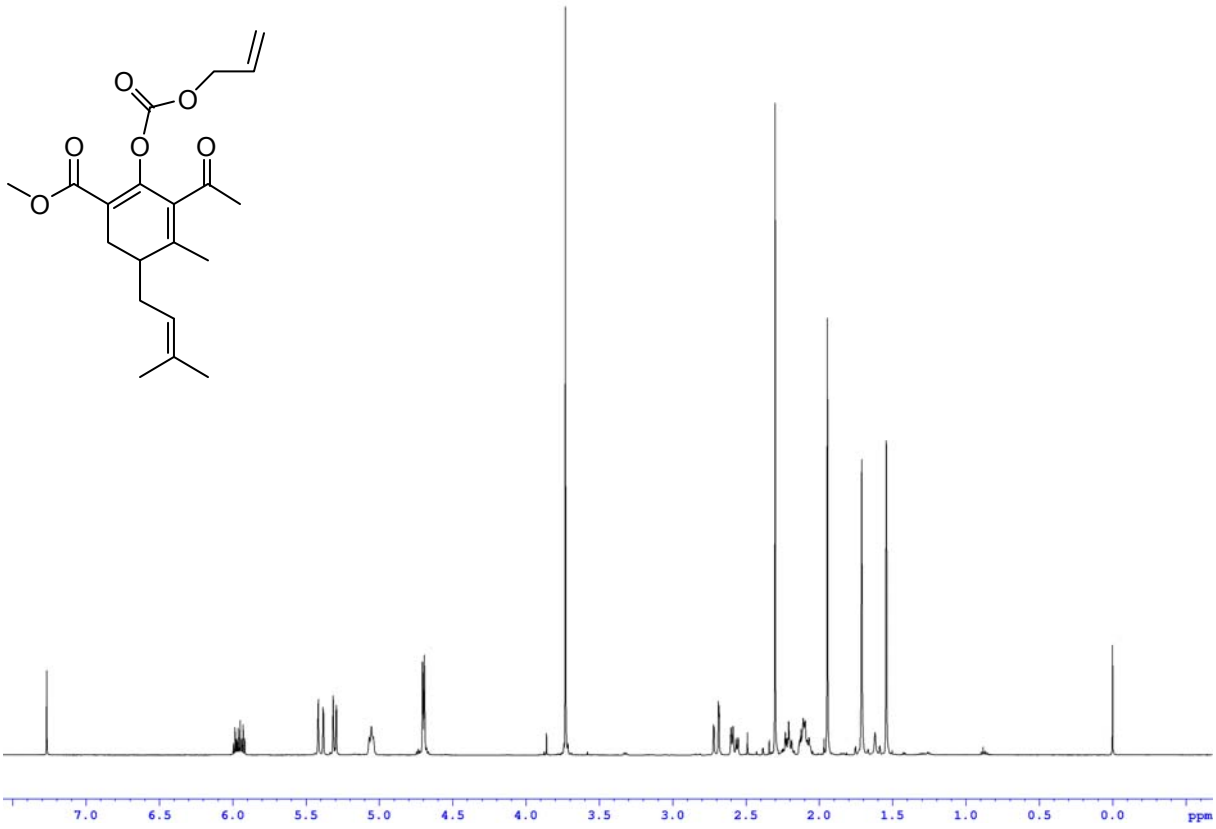
Signal 1: MWD1 A, Sig=254,4 Ref=550,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.247	VV	0.1790	1.30550e4	1111.77527	27.1166
2	10.960	VB	0.1935	3.50889e4	2775.43188	72.8834
Totals :				4.81439e4	3887.20715	

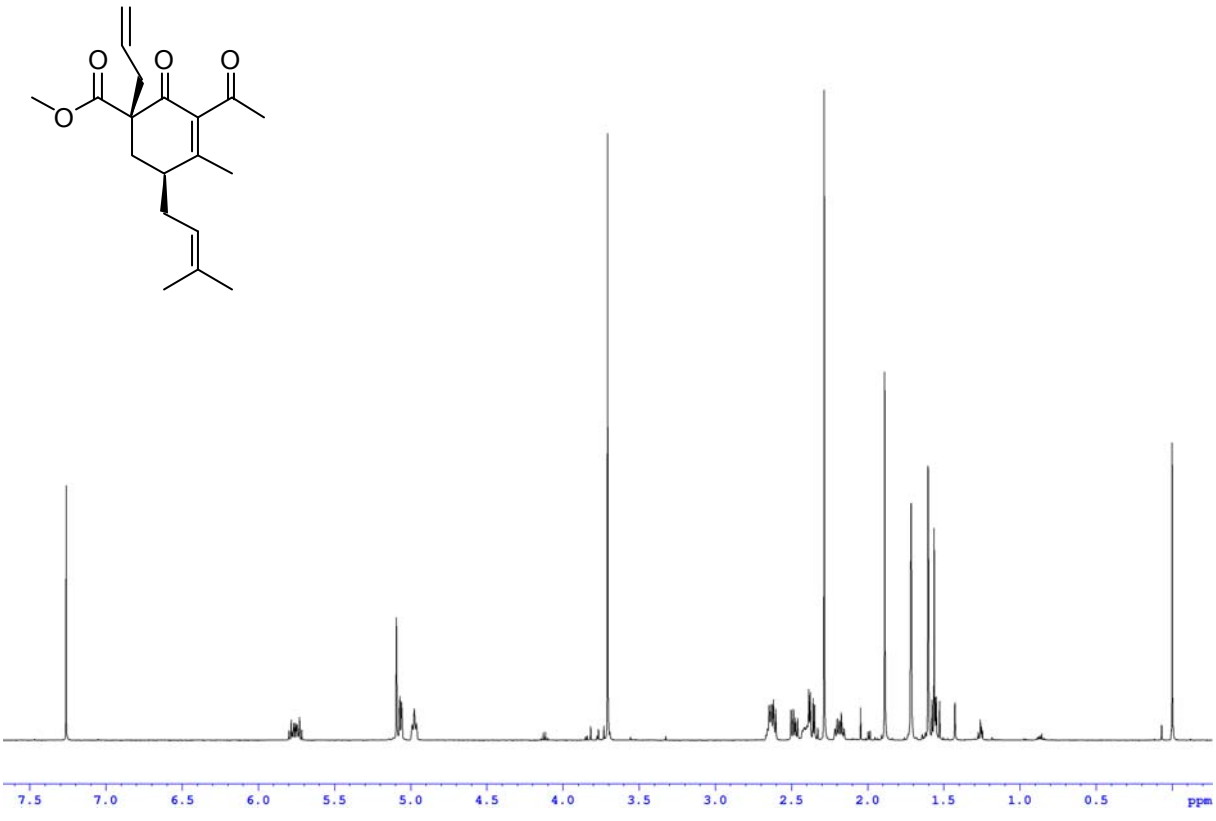
Results obtained with enhanced integrator!

Part III – NMR Spectra

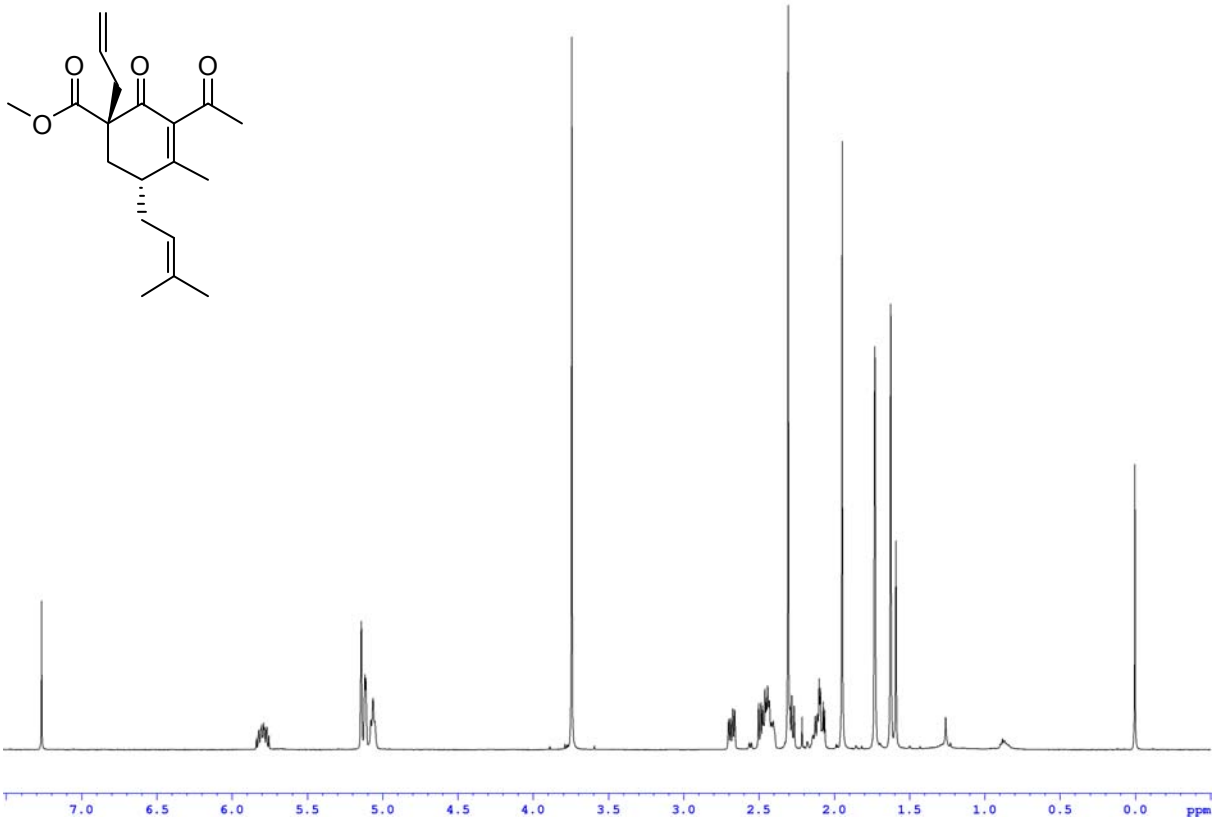
Supplementary Figure 1. ^{1}H NMR spectrum of synthetic **6** $CDCl_3$ (500 MHz):



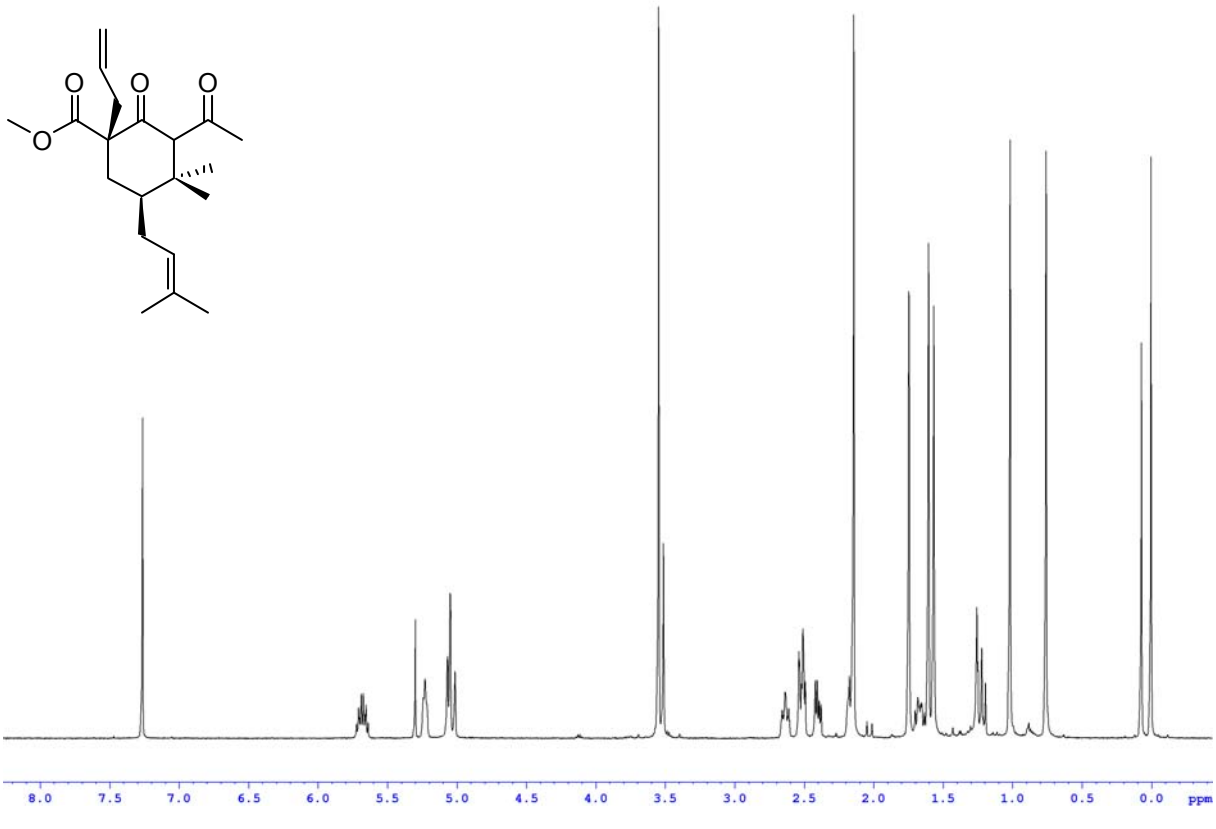
Supplementary Figure 2. ^{1}H NMR spectrum of synthetic **cis-7** $CDCl_3$ (500 MHz):



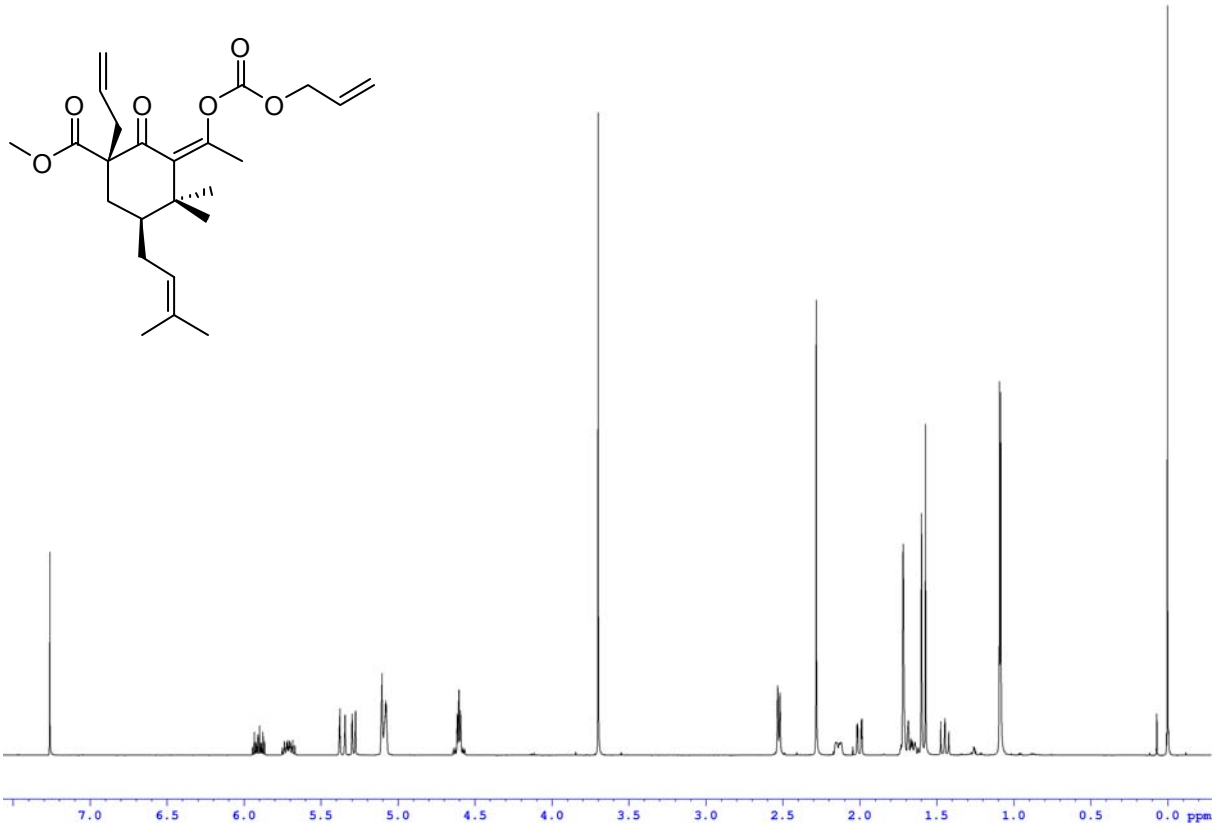
Supplementary Figure 3. ^{1}H NMR spectrum of synthetic **trans-7** $CDCl_3$ (500 MHz):



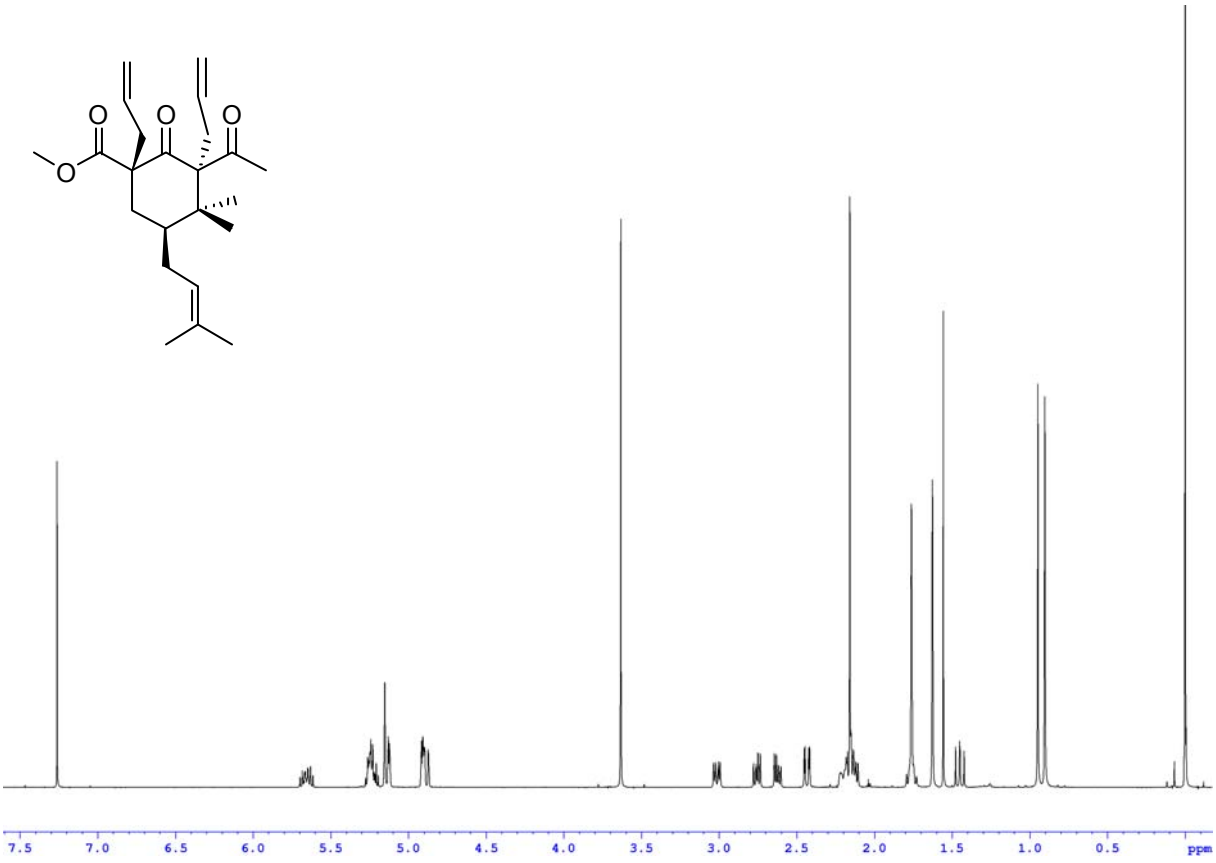
Supplementary Figure 4. ^{1}H NMR spectrum of synthetic precursor to **8** $CDCl_3$ (500 MHz):



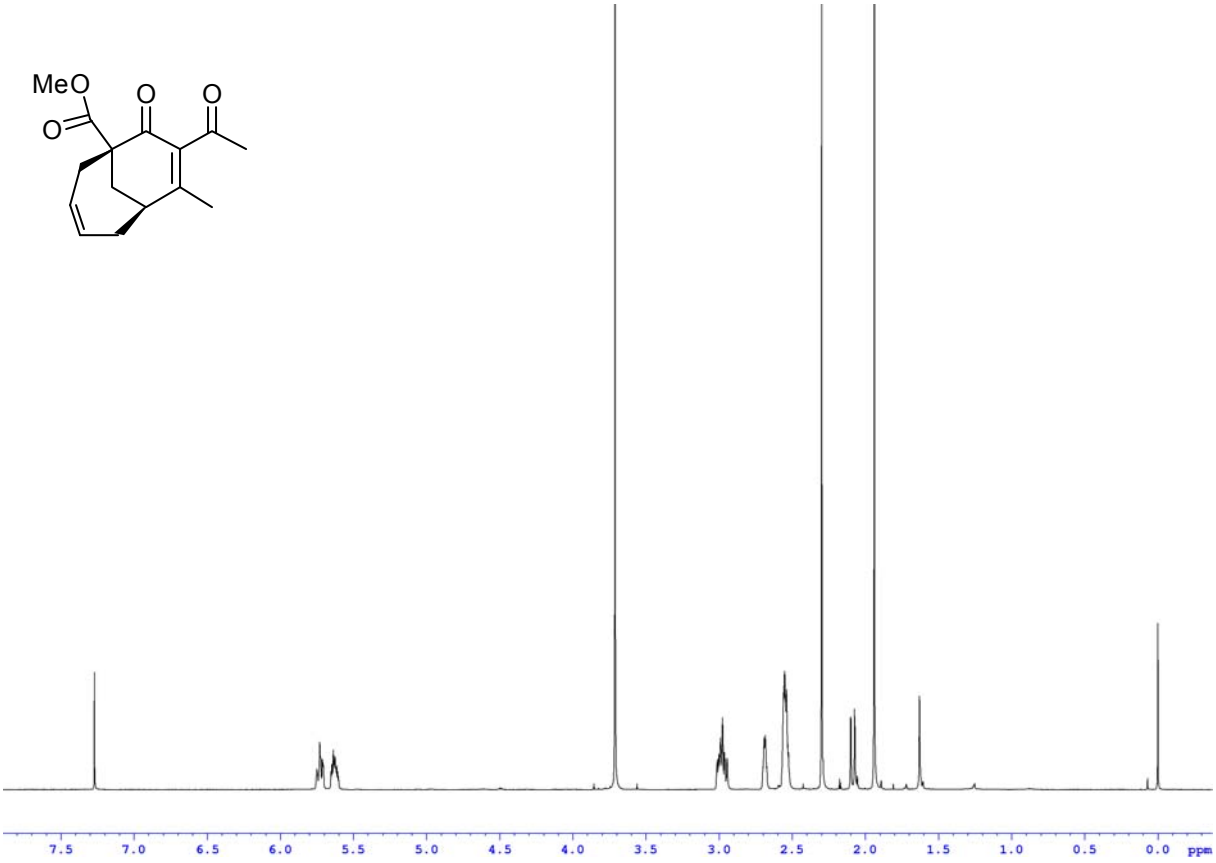
Supplementary Figure 5. ^{1}H NMR spectrum of synthetic **9** $CDCl_3$ (500 MHz):



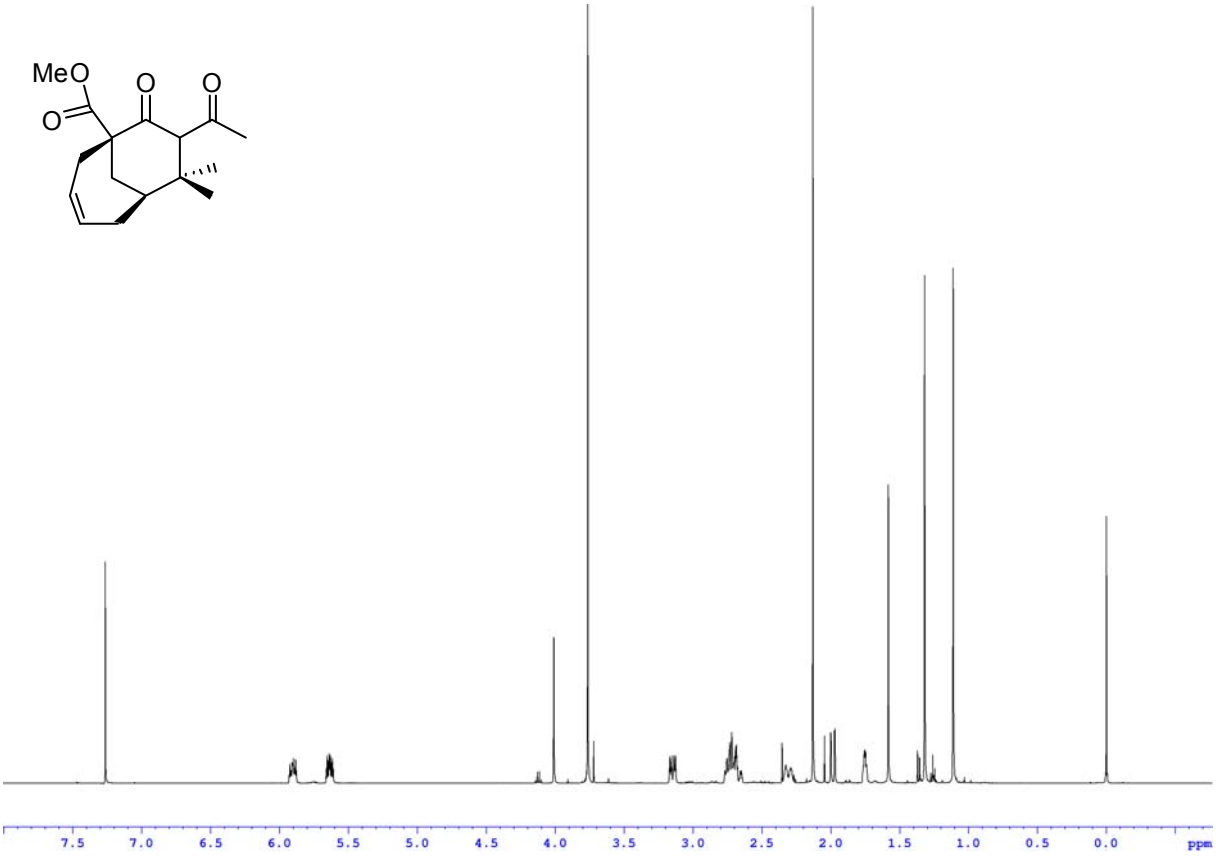
Supplementary Figure 6. ^{1}H NMR spectrum of synthetic **10** $CDCl_3$ (500 MHz):



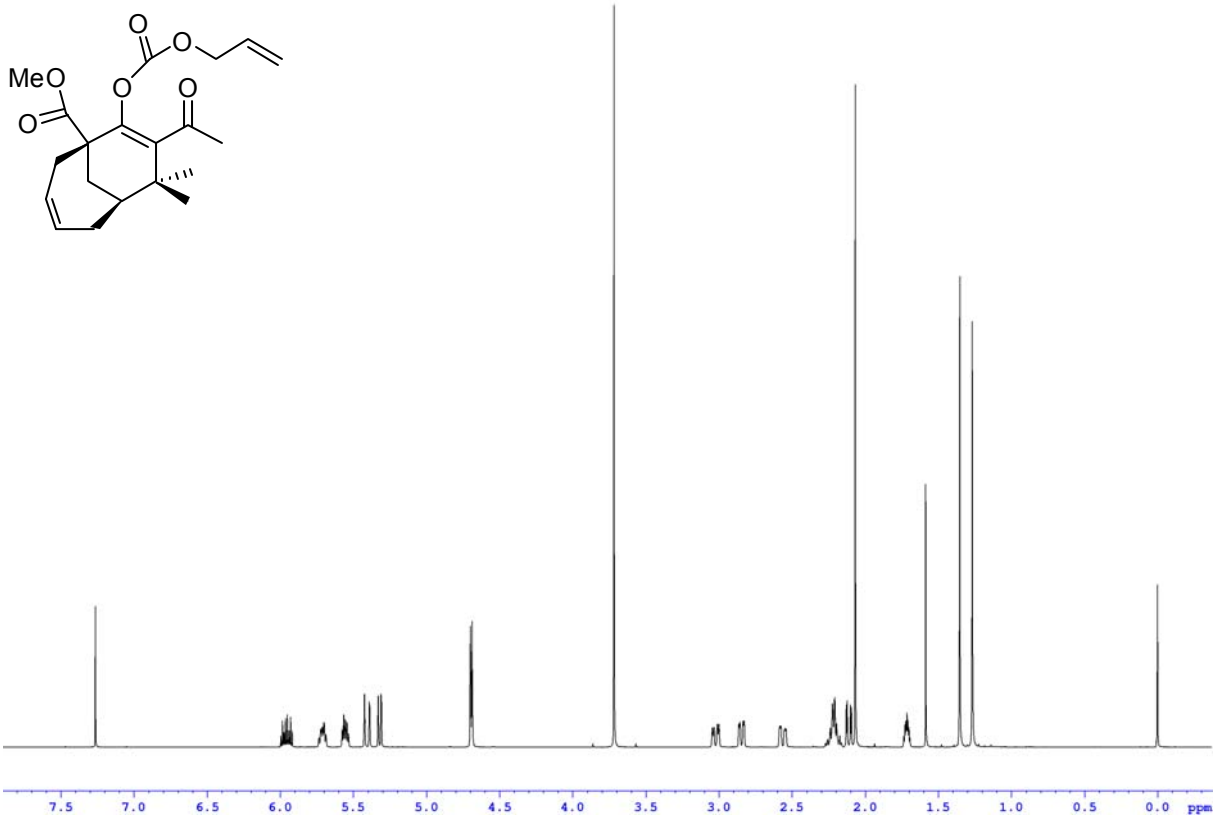
Supplementary Figure 7. ^{1}H NMR spectrum of synthetic **13** $CDCl_3$ (500 MHz):



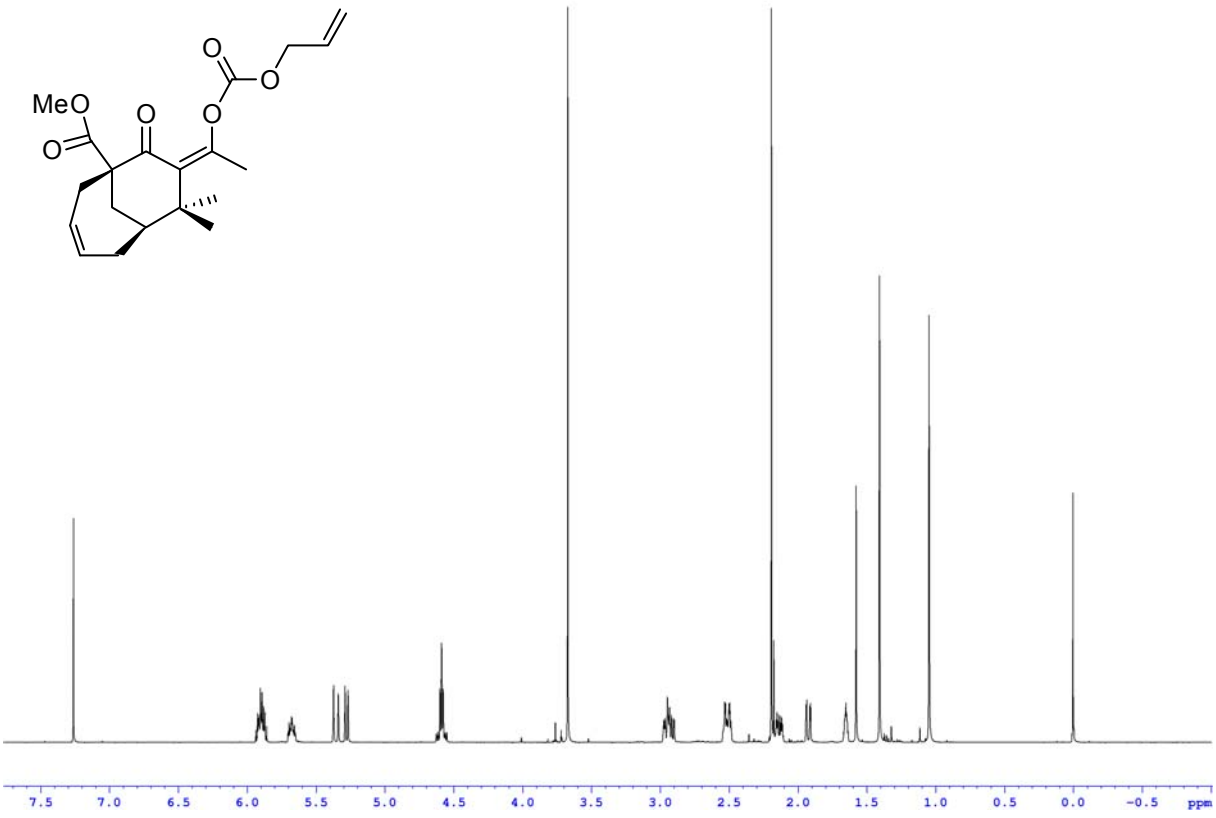
Supplementary Figure 8. ^{1}H NMR spectrum of synthetic **precursor to 11** $CDCl_3$ (500 MHz):



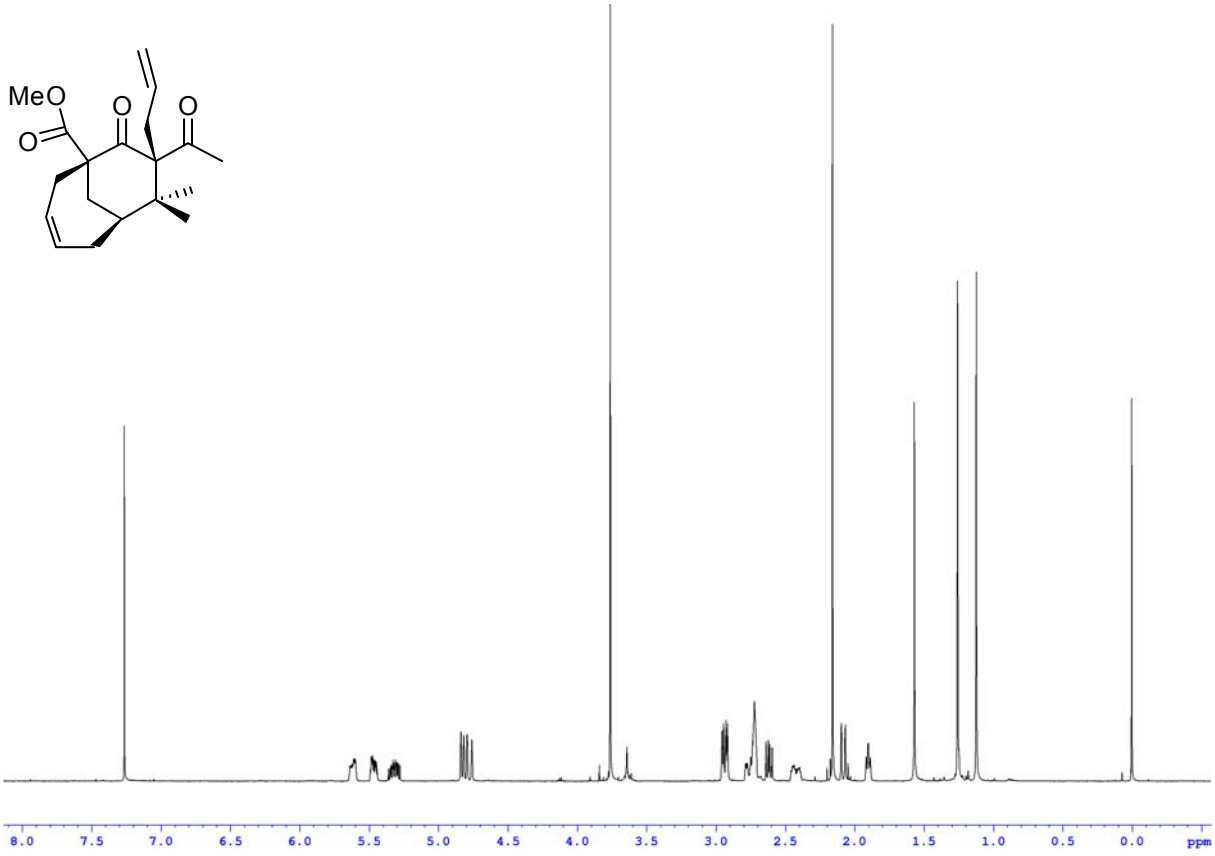
Supplementary Figure 9. ^{1}H NMR spectrum of synthetic **11a** $CDCl_3$ (500 MHz):



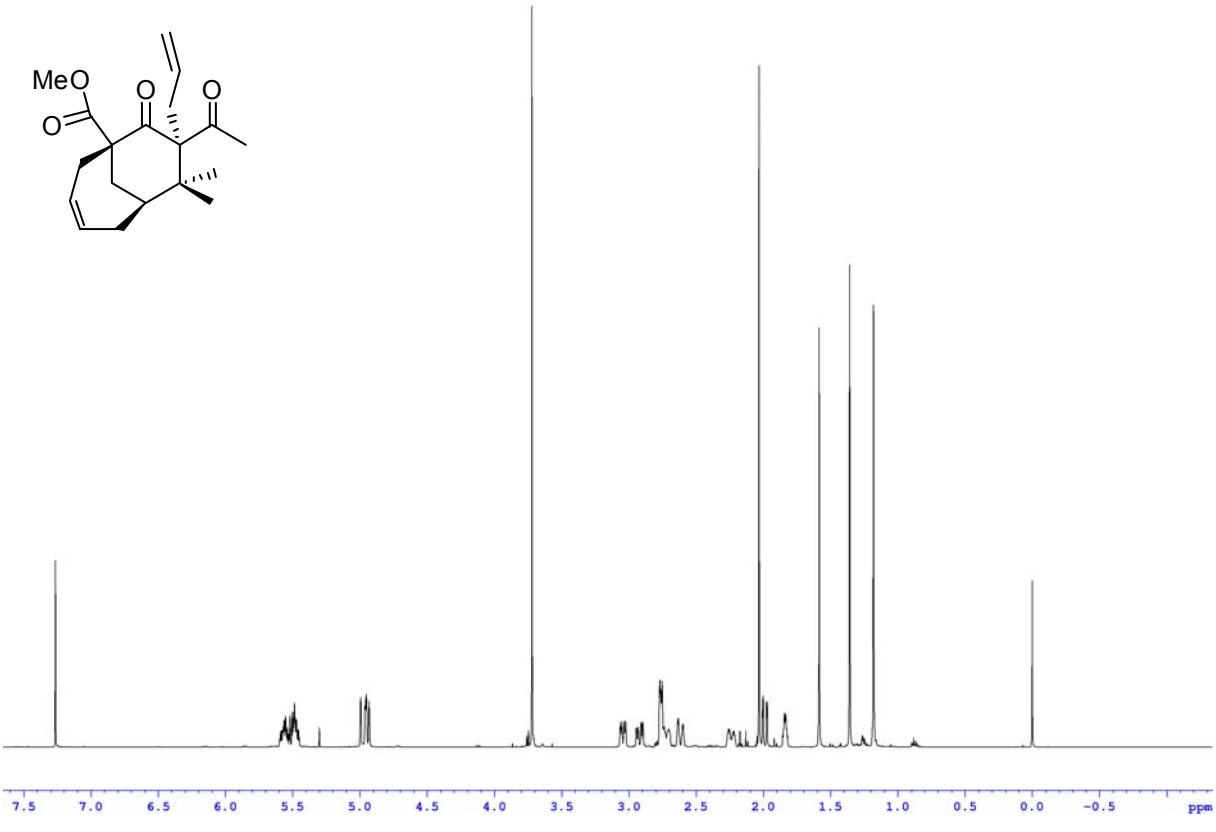
Supplementary Figure 10. ^{1}H NMR spectrum of synthetic **11b** $CDCl_3$ (500 MHz):



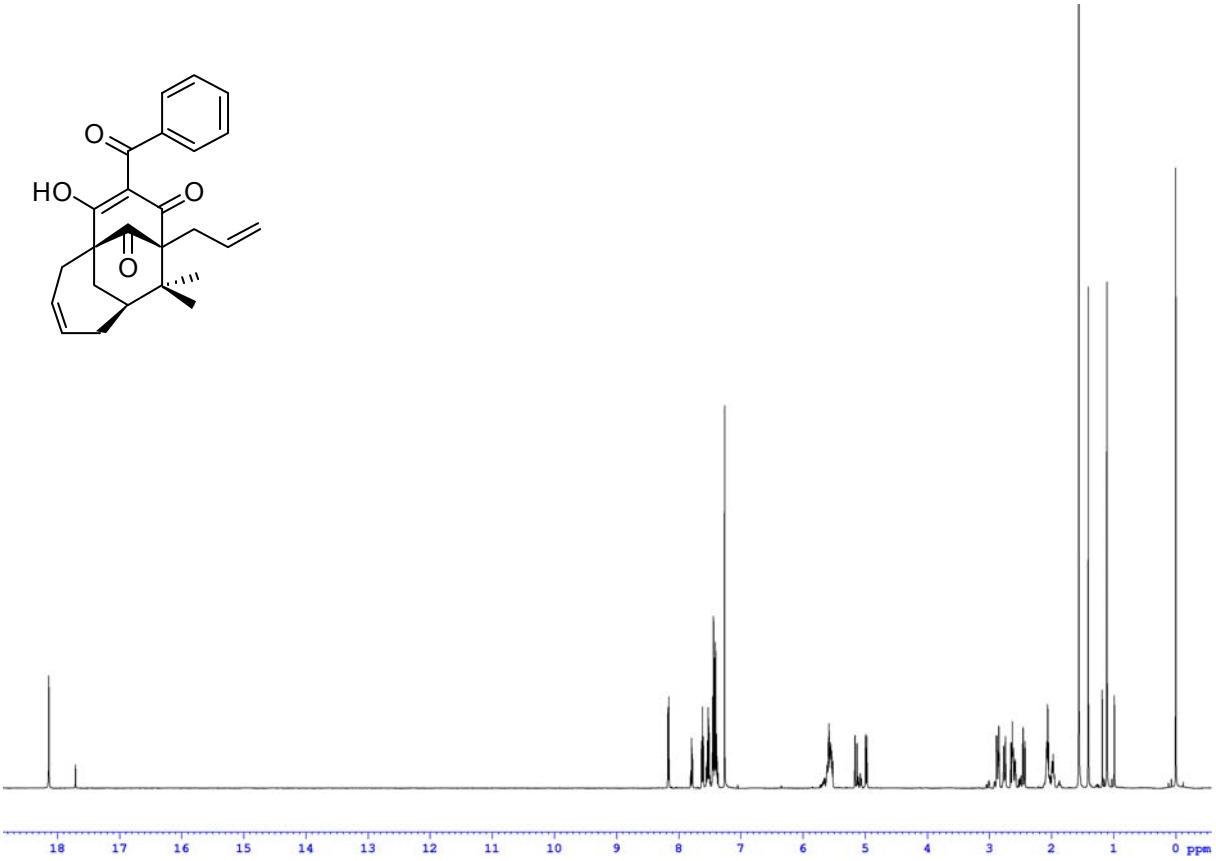
Supplementary Figure 11. ^{1}H NMR spectrum of synthetic **12(cis)** $CDCl_3$ (500 MHz):



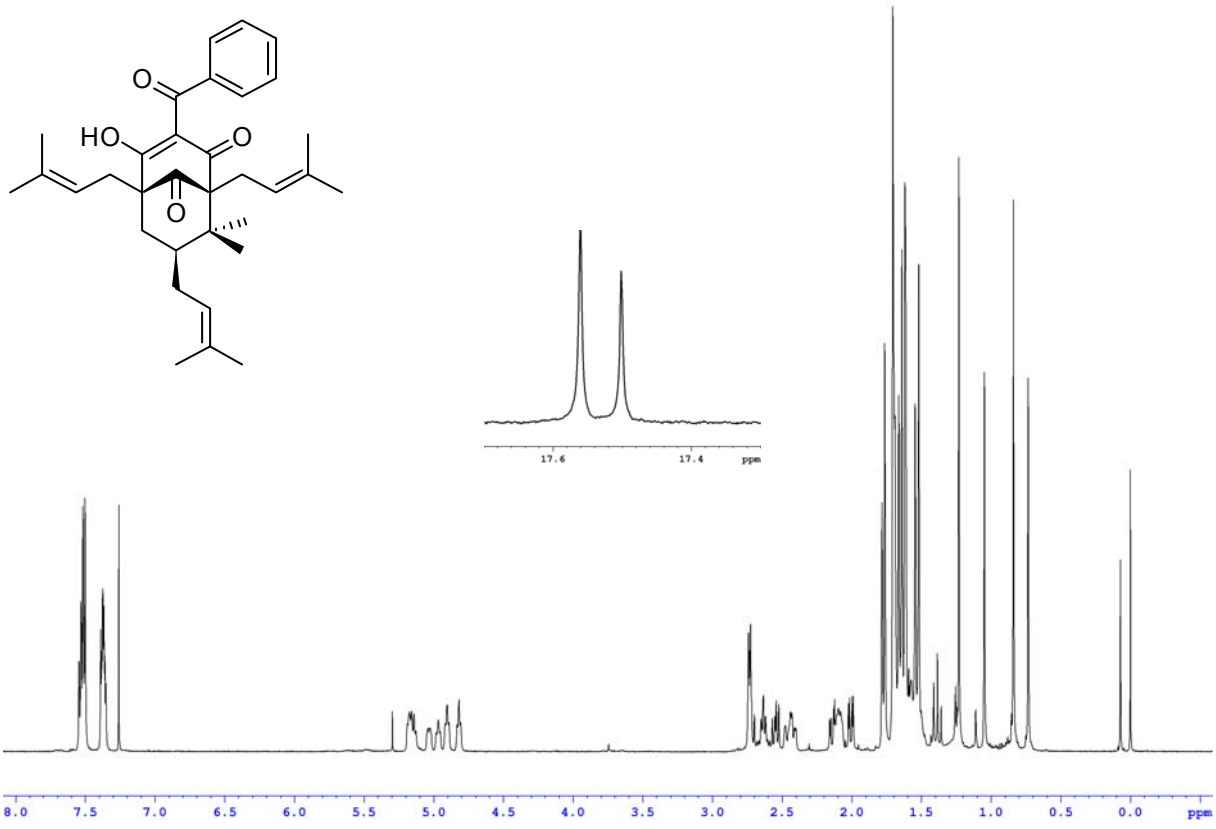
Supplementary Figure 12. ^{1}H NMR spectrum of synthetic **12(trans)** $CDCl_3$ (500 MHz):



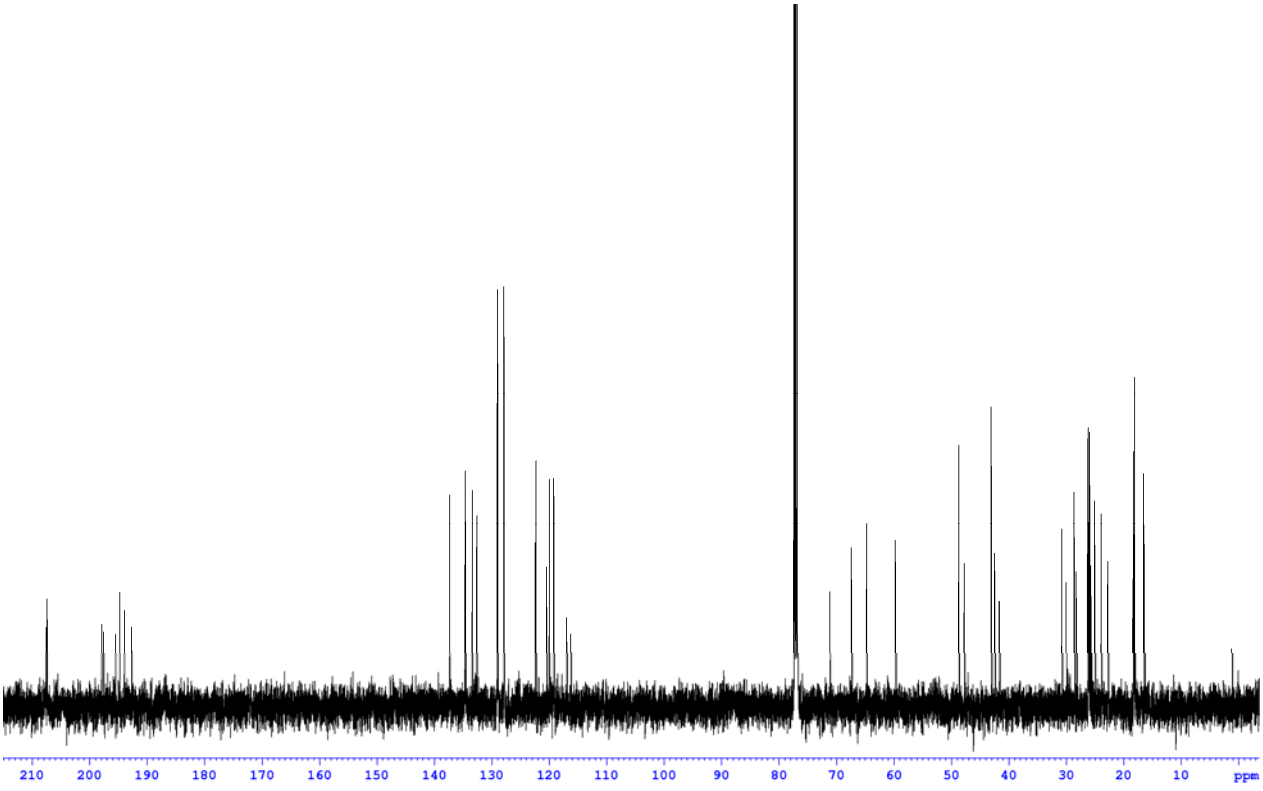
Supplementary Figure 13. ^{1}H NMR spectrum of synthetic **14** $CDCl_3$ (500 MHz):



Supplementary Figure 14. ^{1}H NMR spectrum of synthetic (+)-clusianone **1** $CDCl_3$ (500 MHz):



Supplementary Figure 15. ^{13}C NMR spectrum of synthetic (+)-clusianone **1** $CDCl_3$ (125 MHz):



Part III

Additional Information

Supplementary Figure 16 X-ray of compound **13**

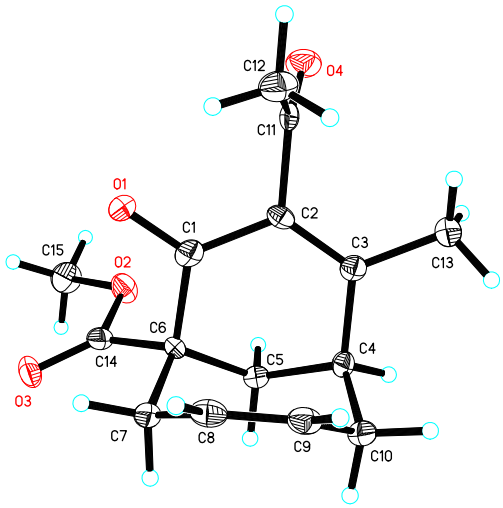


Table 1. Crystal data and structure refinement for **13**

Identification code	s2091lm
Empirical formula	C15 H18 O4
Formula weight	262.29
Temperature	100(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21/c
Unit cell dimensions	a = 8.5618(7) A alpha = 90 deg. b = 8.4049(9) A beta = 93.163(5) c = 18.442(2) A gamma = 90 deg.
Volume	1325.1(2) A^3
Z, Calculated density	4, 1.315 Mg/m^3

Absorption coefficient	0.095 mm^-1
F(000)	560
Crystal size	0.14 x 0.13 x 0.09 mm
Theta range for data collection	2.21 to 26.48 deg.
Limiting indices	-8<=h<=10, -9<=k<=10, -19<=l<=23
Reflections collected / unique	9858 / 2731 [R(int) = 0.0907]
Completeness to theta = 26.48	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7438 and 0.6938
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2731 / 0 / 176
Goodness-of-fit on F^2	1.024
Final R indices [I>2sigma(I)]	R1 = 0.0538, wR2 = 0.0736
R indices (all data)	R1 = 0.1314, wR2 = 0.0840
Extinction coefficient	0.0060(8)
Largest diff. peak and hole	0.261 and -0.269 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for s2091lm.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	546(2)	8607(2)	3504(1)	19(1)
C(1)	1237(2)	7425(3)	3754(1)	16(1)
O(2)	2291(2)	8958(2)	5052(1)	22(1)
C(2)	450(2)	5897(3)	3801(1)	14(1)
O(3)	3802(2)	10282(2)	4295(1)	24(1)
C(3)	1223(2)	4545(3)	3973(1)	15(1)
O(4)	-2225(2)	5829(2)	4071(1)	25(1)
C(4)	2961(2)	4547(3)	4150(1)	15(1)
C(5)	3480(2)	6135(3)	4478(1)	17(1)
C(6)	2970(2)	7570(3)	4008(1)	14(1)
C(7)	3941(2)	7738(3)	3332(1)	17(1)
C(8)	3549(2)	6561(3)	2735(1)	20(1)
C(9)	3514(2)	4994(3)	2802(1)	20(1)
C(10)	3874(2)	4055(3)	3483(1)	20(1)
C(11)	-1283(2)	5905(3)	3602(1)	16(1)
C(12)	-1762(2)	6016(3)	2817(1)	24(1)
C(13)	424(2)	2956(3)	3991(1)	23(1)
C(14)	3105(2)	9105(3)	4454(1)	17(1)
C(15)	2339(3)	10313(3)	5540(1)	27(1)

Table 3. Bond lengths [A] and angles [deg] for s2091lm.

O(1)-C(1)	1.233(2)
C(1)-C(2)	1.455(3)
C(1)-C(6)	1.536(3)
O(2)-C(14)	1.343(2)
O(2)-C(15)	1.451(2)
C(2)-C(3)	1.344(3)
C(2)-C(11)	1.508(3)
O(3)-C(14)	1.199(3)
C(3)-C(13)	1.501(3)
C(3)-C(4)	1.506(3)
O(4)-C(11)	1.216(2)
C(4)-C(5)	1.521(3)
C(4)-C(10)	1.549(3)
C(4)-H(4)	1.0000
C(5)-C(6)	1.535(3)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(6)-C(14)	1.530(3)
C(6)-C(7)	1.543(3)
C(7)-C(8)	1.505(3)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-C(9)	1.323(3)
C(8)-H(8)	0.9500
C(9)-C(10)	1.502(3)
C(9)-H(9)	0.9500
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(11)-C(12)	1.486(3)
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800

C(12)-H(12C)	0.9800
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800

O(1)-C(1)-C(2)	121.2(2)
O(1)-C(1)-C(6)	119.1(2)
C(2)-C(1)-C(6)	119.64(19)
C(14)-O(2)-C(15)	116.05(19)
C(3)-C(2)-C(1)	122.46(19)
C(3)-C(2)-C(11)	121.7(2)
C(1)-C(2)-C(11)	115.72(19)
C(2)-C(3)-C(13)	122.58(19)
C(2)-C(3)-C(4)	121.19(19)
C(13)-C(3)-C(4)	116.23(19)
C(3)-C(4)-C(5)	110.54(17)
C(3)-C(4)-C(10)	111.29(17)
C(5)-C(4)-C(10)	113.63(18)
C(3)-C(4)-H(4)	107.0
C(5)-C(4)-H(4)	107.0
C(10)-C(4)-H(4)	107.0
C(4)-C(5)-C(6)	113.40(17)
C(4)-C(5)-H(5A)	108.9
C(6)-C(5)-H(5A)	108.9
C(4)-C(5)-H(5B)	108.9
C(6)-C(5)-H(5B)	108.9
H(5A)-C(5)-H(5B)	107.7
C(14)-C(6)-C(5)	110.43(18)
C(14)-C(6)-C(1)	105.90(17)
C(5)-C(6)-C(1)	110.49(18)
C(14)-C(6)-C(7)	109.19(18)

C(5)-C(6)-C(7)	112.25(18)
C(1)-C(6)-C(7)	108.37(17)
C(8)-C(7)-C(6)	115.05(18)
C(8)-C(7)-H(7A)	108.5
C(6)-C(7)-H(7A)	108.5
C(8)-C(7)-H(7B)	108.5
C(6)-C(7)-H(7B)	108.5
H(7A)-C(7)-H(7B)	107.5
C(9)-C(8)-C(7)	126.2(2)
C(9)-C(8)-H(8)	116.9
C(7)-C(8)-H(8)	116.9
C(8)-C(9)-C(10)	126.6(2)
C(8)-C(9)-H(9)	116.7
C(10)-C(9)-H(9)	116.7
C(9)-C(10)-C(4)	115.80(18)
C(9)-C(10)-H(10A)	108.3
C(4)-C(10)-H(10A)	108.3
C(9)-C(10)-H(10B)	108.3
C(4)-C(10)-H(10B)	108.3
H(10A)-C(10)-H(10B)	107.4
O(4)-C(11)-C(12)	122.51(19)
O(4)-C(11)-C(2)	120.55(19)
C(12)-C(11)-C(2)	116.93(18)
C(11)-C(12)-H(12A)	109.5
C(11)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(11)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(3)-C(13)-H(13A)	109.5
C(3)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(3)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5

H(13B)-C(13)-H(13C)	109.5
O(3)-C(14)-O(2)	124.3(2)
O(3)-C(14)-C(6)	126.0(2)
O(2)-C(14)-C(6)	109.6(2)
O(2)-C(15)-H(15A)	109.5
O(2)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
O(2)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for s2091lm.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(1)	16(1)	16(1)	25(1)	2(1)	3(1)	3(1)
C(1)	19(1)	18(2)	11(1)	-2(1)	6(1)	3(1)
O(2)	25(1)	18(1)	24(1)	-7(1)	9(1)	-5(1)
C(2)	13(1)	18(1)	10(1)	-1(1)	4(1)	-3(1)
O(3)	26(1)	14(1)	34(1)	0(1)	8(1)	-5(1)
C(3)	16(1)	16(2)	14(1)	0(1)	4(1)	1(1)
O(4)	19(1)	30(1)	28(1)	2(1)	8(1)	2(1)

C(4)	16(1)	12(1)	18(1)	4(1)	0(1)	1(1)
C(5)	13(1)	16(1)	20(1)	0(1)	1(1)	1(1)
C(6)	11(1)	12(1)	20(1)	1(1)	3(1)	-2(1)
C(7)	15(1)	17(2)	21(1)	2(1)	4(1)	1(1)
C(8)	16(1)	29(2)	17(1)	1(1)	4(1)	0(1)
C(9)	15(1)	25(2)	20(1)	-5(1)	4(1)	-1(1)
C(10)	14(1)	18(1)	26(1)	-2(1)	1(1)	1(1)
C(11)	18(1)	8(1)	23(1)	-3(1)	2(1)	0(1)
C(12)	19(1)	30(2)	24(1)	-4(1)	-2(1)	3(1)
C(13)	20(1)	17(2)	32(2)	-2(1)	4(1)	-1(1)
C(14)	12(1)	19(2)	21(1)	3(1)	0(1)	0(1)
C(15)	30(2)	23(2)	29(2)	-12(1)	7(1)	0(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for s2091lm.

	x	y	z	U(eq)
H(4)	3175	3719	4532	18
H(5A)	4635	6139	4550	20
H(5B)	3042	6246	4961	20
H(7A)	3791	8825	3134	21
H(7B)	5062	7621	3486	21
H(8)	3303	6983	2265	25
H(9)	3233	4402	2375	24
H(10A)	5007	4151	3615	23

H(10B)	3655	2919	3378	23
H(12A)	-2907	6029	2755	37
H(12B)	-1356	5095	2561	37
H(12C)	-1341	6996	2616	37
H(13A)	132	2730	4487	34
H(13B)	1136	2128	3834	34
H(13C)	-518	2974	3664	34
H(15A)	3391	10412	5774	41
H(15B)	1579	10158	5912	41
H(15C)	2080	11283	5265	41

Table 6. Torsion angles [deg] for s2091lm.

O(1)-C(1)-C(2)-C(3)	170.3(2)
C(6)-C(1)-C(2)-C(3)	-8.7(3)
O(1)-C(1)-C(2)-C(11)	-6.3(3)
C(6)-C(1)-C(2)-C(11)	174.75(17)
C(1)-C(2)-C(3)-C(13)	-177.4(2)
C(11)-C(2)-C(3)-C(13)	-1.0(3)
C(1)-C(2)-C(3)-C(4)	1.9(3)
C(11)-C(2)-C(3)-C(4)	178.23(18)
C(2)-C(3)-C(4)-C(5)	29.0(3)
C(13)-C(3)-C(4)-C(5)	-151.67(18)
C(2)-C(3)-C(4)-C(10)	-98.2(2)
C(13)-C(3)-C(4)-C(10)	81.1(2)
C(3)-C(4)-C(5)-C(6)	-53.8(2)
C(10)-C(4)-C(5)-C(6)	72.2(2)
C(4)-C(5)-C(6)-C(14)	163.84(17)
C(4)-C(5)-C(6)-C(1)	47.0(2)
C(4)-C(5)-C(6)-C(7)	-74.1(2)
O(1)-C(1)-C(6)-C(14)	45.3(2)

C(2)-C(1)-C(6)-C(14)	-135.7(2)
O(1)-C(1)-C(6)-C(5)	164.91(19)
C(2)-C(1)-C(6)-C(5)	-16.1(3)
O(1)-C(1)-C(6)-C(7)	-71.7(2)
C(2)-C(1)-C(6)-C(7)	107.3(2)
C(14)-C(6)-C(7)-C(8)	-162.31(18)
C(5)-C(6)-C(7)-C(8)	74.9(2)
C(1)-C(6)-C(7)-C(8)	-47.4(3)
C(6)-C(7)-C(8)-C(9)	-53.7(3)
C(7)-C(8)-C(9)-C(10)	-0.7(4)
C(8)-C(9)-C(10)-C(4)	52.9(3)
C(3)-C(4)-C(10)-C(9)	53.9(3)
C(5)-C(4)-C(10)-C(9)	-71.6(2)
C(3)-C(2)-C(11)-O(4)	78.8(3)
C(1)-C(2)-C(11)-O(4)	-104.6(2)
C(3)-C(2)-C(11)-C(12)	-101.4(2)
C(1)-C(2)-C(11)-C(12)	75.1(2)
C(15)-O(2)-C(14)-O(3)	-2.7(3)
C(15)-O(2)-C(14)-C(6)	178.57(17)
C(5)-C(6)-C(14)-O(3)	126.5(2)
C(1)-C(6)-C(14)-O(3)	-113.9(2)
C(7)-C(6)-C(14)-O(3)	2.6(3)
C(5)-C(6)-C(14)-O(2)	-54.8(2)
C(1)-C(6)-C(14)-O(2)	64.9(2)
C(7)-C(6)-C(14)-O(2)	-178.65(17)

Symmetry transformations used to generate equivalent atoms:

Part V Supplementary References

[1] F. Horeischi, N. Biber, B. Plietker, *J. Am. Chem. Soc.,* 2014, **136***,* 4026.

[2] N. Biber, K. Möws, B. Plietker, *Nature Chem.* 2011, **3**, 938.

[3] B. M. Trost, B. Schäffner, M. Osipov, D. A. A. Wilton, *Angew. Chem. Int. Ed*., 2011, **50**, 3548.

[4] J. H. Boyce, J. A. Porco Jr., *Angew. Chem. Int. Ed*., 2014, **53**, 7832.