Radical Cyclization Cascades of Unsaturated Meldrum's Acid Derivatives

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General experimental

All experiments were performed under an atmosphere of nitrogen, using anhydrous solvents unless stated otherwise. Tetrahydrofuran was distilled from sodium/benzophenone and stored under nitrogen or taken from a solvent purification system (SPS), and was deoxygenated by bubbling with nitrogen for thirty minutes when used in conjunction with samarium diiodide. Dichloromethane, triethylamine and diisopropylamine were distilled from calcium hydride and stored under nitrogen. Water when used in conjunction with samarium diiodide was distilled before being deoxygenated by bubbling with nitrogen for four hours. All other dry solvents were used as purchased from Sigma-Aldrich. Potassium carbonate was dried in the oven overnight prior to use.

^{1}H NMR and ^{13}C NMR were recorded on 300, 400 and 500 MHz spectrometers, with chemical shift values being reported in ppm relative to residual chloroform (δ_H = 7.27 or δ_C = 77.2) as internal standards. All coupling constants (*J*) are reported in Hertz (Hz).

Mass spectra were obtained using positive or negative electrospray (ES±) or electron ionization (EI±) methodology. Infra-red spectra were recorded as evaporated films or neat using FT/IR spectrometers. Melting points were measured on material obtained after column chromatography.

Column chromatography was carried out using 40-60 μ, 60Å silica gel. Routine TLC analysis was carried out on aluminum sheets coated with silica gel 60 F254, 0.2 mm thickness. Plates were viewed using a 254 nm ultraviolet lamp and dipped in *para*-anisaldehyde.

Preparation of samarium diiodide

Samarium iodide was prepared by a modification of the procedure of Imamoto and Ono.[1] Samarium powder (1.16 g, 7.98 mmol, 1.4 eq) was added to an oven dried round bottom flask, the flask sealed and backfilled with argon for 3 times. THF (55 mL) and iodine (1.40 g, 5.52 mmol, 1.0 eq) were added and the flask covered with aluminum foil and heated to 65 °C for 18 hours. The approximate 0.1 M solution was allowed to cool to room temperature and then used directly.

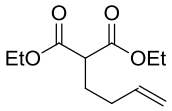
[1] Imamoto, T.; Ono, M. *Chem. Lett.* **1987**, *16*, 51.

Experimental

Literature procedures

Phenyl substituted alkynes were synthesized from the corresponding terminal alkynes according to the procedure described by Müller.[2] Reduction of the alkyne when necessary was performed with $LiAlH_4$ using standard condition. Conversions to bromides were carried out using standard Appel conditions. Homo-allyl bromides were synthesized according to Wong's procedure.[3]

General procedure A – Alkylations of diethyl malonate

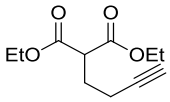


Diethyl 2-(but-3-en-1-yl)malonate[4]

To a stirred solution of sodium hydride (60% in oil, 2.86 g, 71.4 mmol, 1.0 eq) in THF (100 mL) at 0 °C was added diethyl malonate (11.0 mL, 72.4 mmol, 1.0 eq) and the solution stirred at room temperature for 30 min. Sodium iodide (5.27 g, 35.1 mmol, 0.5 eq) and 4-bromo-1-butene (8.0 mL, 78.8 mmol, 1.1eq) were added and the solution stirred at 65 °C overnight. The reaction was quenched with H_2O (50 mL) and the aqueous phase extracted with ethyl acetate (3 × 50 mL). The combined organic phases were dried (Na_2SO_4 or $MgSO_4$) and concentrated *in vacuo*. Purification by column chromatography on silica gel, eluting with a gradient 0-5% ethyl acetate in petroleum ether (40-60 °C) gave diethyl 2-(but-3-en-1-yl)malonate (11.5 mg, 53.8 mmol, 75%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.26 (6 H, t, *J* = 7.1 Hz, 2 × CH_3), 1.94 - 2.05 (2 H, m, CHC*H*$_2$), 2.05 - 2.14 (2 H, m, C*H*$_2$CH=CH$_2$), 3.34 (1 H, t, *J* = 7.3 Hz, C*H*CH$_2$), 4.19 (4 H, q, *J* = 7.1 Hz, 2 × OCH_2), 4.97 - 5.08 (2 H, m, CH=C*H*$_2$), 5.69 - 5.84 (1 H, m, C*H*=CH$_2$);
^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 14.0 (2 × CH_3), 27.8 (CH*C*H$_2$), 31.2 (*C*H$_2$C=CH), 51.1 (*C*HCH$_2$), 61.3 (2 × OCH_2), 115.9 (CH=*C*H$_2$), 136.8 (*C*H=CH$_2$), 169.4 (2 × C=O);
Data in accordance with the literature.[4]

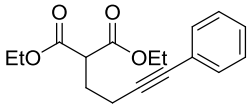
[2] Berkessel, A.; Sebastian-Ibarz, M. L.; Müller, T. N. *Angew. Chem. Int. Ed.* **2006**, *45*, 6567.
[3] Wong, K.-T.; Hung, Y.-Y. *Tetrahedron Lett.* **2003**, *44*, 8033.
[4] Yip, K.-T.; Zhu, N.-Y.; Yang, D. *Org. Lett.* **2009**, *11*, 1911.



Diethyl 2-(but-3-yn-1-yl)malonate[5]

As for general procedure A, reaction of sodium hydride (60% in oil, 0.50 g, 12.5 mmol, 1.0 eq) and diethyl malonate (1.90 mL, 12.5 mmol, 1.0 eq) in THF (10 mL) with sodium iodide (0.94 mg, 6.27 mmol, 0.5 eq) and 4-bromobut-1-yne (1.29 mL, 13.8 mmol, 1.1 eq), after column chromatography on silica gel, eluting with 5% ethyl acetate in petroleum ether (40-60 °C) gave diethyl 2-(but-3-yn-1-yl)malonate (1.73 g, 8.15 mmol, 65%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.28 (6 H, t, *J* = 7.1 Hz, 2 × CH_3), 2.01 (1 H, t, *J* = 2.6 Hz, C*H*CH_2), 2.13 (2 H, q, *J* = 7.4 Hz, CHC*H*$_2$), 2.28 - 2.34 (2 H, m, C*H*$_2$C≡CH), 3.58 (1 H, t, *J* = 7.4 Hz, CH_2C≡C*H*), 4.22 (4 H, qd, *J* = 7.1, 1.9 Hz, 2 × OCH_2);
^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 14.0 (2 × CH_3), 16.4 (*C*H_2C≡CH), 27.3 (CH*C*H_2), 50.5 (*C*HCH_2), 61.5 (2 × OCH_2), 69.6 (CH_2C≡*C*H), 82.4 (CH_2*C*≡CH), 169.0 (2 × C=O);
Data in accordance with the literature.[5]

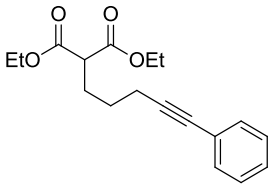


Diethyl 2-(4-phenylbut-3-yn-1-yl)malonate[5]

As for general procedure A, reaction of sodium hydride (60% in oil, 0.30 g, 7.39 mmol, 1.0 eq) and diethyl malonate (1.12 mL, 7.39 mmol, 1.0 eq) in THF (20 mL) with sodium iodide (0.55 mg, 3.68 mmol, 0.5 eq) and (4-bromobut-1-yn-1-yl)benzene (1.70 g, 8.13 mmol, 1.1 eq), after column chromatography on silica gel, eluting with 5% ethyl acetate in petroleum ether (40-60 °C) gave diethyl 2-(4-phenylbut-3-yn-1-yl)malonate (1.10 g, 3.47 mmol, 52%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.20 (6 H, t, *J* = 7.1 Hz, 2 × CH_3), 2.13 (2 H, q, *J* = 7.2 Hz, CHC*H*$_2$), 2.45 (2 H, t, *J* = 6.9 Hz, C*H*$_2$C≡C), 3.55 (1 H, t, *J* = 7.2 Hz, C*H*CH_2), 4.14 (4 H, q, *J* = 7.2 Hz, 2 × OCH_2), 7.18 - 7.23 (3 H, m, 3 × ArH), 7.30 - 7.35 (2 H, m, 2 × ArH);
^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 14.0 (2 × CH_3), 17.4 (*C*H_2C≡C), 27.6 (CH*C*H_2), 50.8 (CH), 61.5 (2 × OCH_2), 81.8 (C≡*C*Ar), 87.9 (*C*≡CAr), 123.5 (ArC^q), 127.8 (ArCH), 128.2 (2 × ArCH), 131.6 (2 × ArCH), 169.1 (2 × C=O);
Data in accordance with the literature.[5]

[5] Day, J. E. H.; Sharp, S. Y.; Rowlands, M. G.; Aherne, W.; Workman, P.; Moody, C. J. *Chem. Eur. J.* **2010**, *16*, 2758.

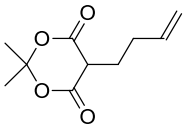


Diethyl 2-(5-phenylpent-4-yn-1-yl)malonate

As for general procedure A, reaction of sodium hydride (60% in oil, 0.31 g, 7.83 mmol, 1.0 eq) and diethyl malonate (1.20 mL, 7.90 mmol, 1.0 eq) in THF (11 mL) with sodium iodide (0.58 mg, 3.88 mmol, 0.5 eq) and (5-bromopent-1-yn-1-yl)benzene (2.41 g, 8.53 mmol, 1.1 eq), after column chromatography on silica gel, eluting with 5% ethyl acetate in petroleum ether (40-60 °C) gave diethyl 2-(5-phenylpent-4-yn-1-yl)malonate (2.11 g, 7.00 mmol, 89%) as a colorless oil.

ν_{max} (neat)/cm^{-1} 2981, 2937, 2905, 2871, 1728 (C=O), 1599, 1490, 1443, 1369, 1333, 1290, 1239, 1213, 1176, 1095, 1025, 862, 756, 692;
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.27 (6 H, t, *J* = 7.2 Hz, 2 × CH_3), 1.61 - 1.71 (2 H, m, $CHCH_2CH_2$), 2.04 - 2.12 (2 H, m, $CHCH_2$), 2.46 (2 H, t, *J* = 7.1 Hz, $CH_2C{\equiv}C$), 3.40 (1 H, t, *J* = 7.6 Hz, CH), 4.21 (4 H, qd, *J* = 7.2, 1.6 Hz, 2 × OCH_2), 7.24 - 7.30 (3 H, m, 3 × ArH), 7.36 - 7.42 (2 H, m, 2 × ArH);
^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 14.0 (2 × CH_3), 19.0 ($CH_2C{\equiv}C$), 26.3 ($CHCH_2$), 27.9 ($CHCH_2CH_2$), 51.5 (CH), 61.3 (2 × OCH_2), 81.1 ($C{\equiv}CAr$), 89.0 ($C{\equiv}CAr$), 123.7 (ArC^q), 127.5 (ArCH), 128.1 (2 × ArCH), 131.5 (2 × ArCH), 169.3 (2 × C=O);
m/z (ES+) 325 ((M + Na), 100%), 326 (19), 383 (15). (Found: (M + Na) 325.1406. $C_{18}H_{22}O_4Na$ requires *M*, 325.1411).

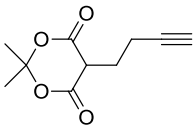
General procedure B – Hydrolysis and ketalizations



5-(But-3-enyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (4)

To a stirred solution of diethyl 2-(but-3-en-1-yl)malonate (11.5 g, 53.8 mmol, 1.0 eq) in MeOH (230 mL) and H_2O (76 mL), NaOH (10.9 g, 272 mmol, 5.1 eq) was added and the solution stirred at 85 °C overnight. The reaction was quenched with HCl (36%, 24 mL), the volume reduced to ~50 mL *in vacuo*, and the aqueous phase extracted with ethyl acetate (3 × 50 mL). The combined organic phases were dried (Na_2SO_4 or $MgSO_4$) and concentrated *in vacuo*. To the residue was added isopropenyl acetate (6.75 mL, 61.3 mmol, 1.1 eq) and the suspension stirred during 10 min. H_2SO_4 (30 drops) was subsequently added over 30 min and the reaction stirred at room temperature during 3 hours. Purification by column chromatography on silica gel, eluting with 30% ethyl acetate in petroleum ether (40-60 °C) gave 5-(but-3-enyl)-2,2-dimethyl-1,3-dioxane-4,6-dione **4** (7.54 g, 38.0 mmol, 71%) as a white solid.

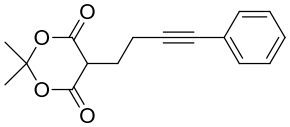
mp 64-66 °C;
ν_{max} (neat)/cm^{-1} 3081, 2997, 2977, 2947, 2882, 1787, 1743 (C=O), 1640, 1454, 1377, 1335, 1279, 1248, 1204, 1119, 1056, 995, 970, 935, 901, 870, 854, 698, 645;
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.76 (3 H, s, CH_3), 1.79 (3 H, s, CH_3), 2.19 - 2.27 (2 H, m, CHCH_2), 2.27 - 2.35 (2 H, m, CH_2CH=CH_2), 3.54 (1 H, t, *J* = 5.0 Hz, CH), 5.04 - 5.13 (2 H, m, CH=CH_2), 5.79 (1 H, ddt, *J* = 17.1, 10.3, 6.6 Hz, C*H*=CH_2);
^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 25.2 (CH*C*H_2), 26.7 (CH_3), 28.4 (CH_3), 30.6 (*C*H_2CH=CH_2), 44.9 (CH), 104.9 (OCO), 116.7 (CH=*C*H_2), 136.7 (*C*H=CH_2), 165.5 (2 × C=O);
m/z (ES−) 197 ((M − H), 100%). (Found: (M − H) 197.0811. $C_{10}H_{13}O_4$ requires *M*, 197.0819).



5-(But-3-yn-1-yl)-2,2-dimethyl-1,3-dioxane-4,6-dione

As for general procedure B, reaction of diethyl 2-(but-3-yn-1-yl)malonate (1.10 g, 5.18 mmol, 1.0 eq) in MeOH (25 mL) and H_2O (6 mL) with NaOH (1.04 g, 25.9 mmol, 5 eq), and treatment of the residue with isopropenyl acetate (0.86 mL, 7.77 mmol, 1.5 eq) and H_2SO_4 (3 drops), after column chromatography on silica gel, eluting with 30% ethyl acetate in petroleum ether (40-60 °C) gave 5-(but-3-yn-1-yl)-2,2-dimethyl-1,3-dioxane-4,6-dione (454 mg, 2.31 mmol, 45%).

ν_{max} (neat)/cm^{-1} 3304, 2999, 2950, 2885, 1785, 1738 (C=O), 1450, 1375, 1335, 1288;
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.78 (3 H, s, CH_3), 1.85 (3 H, s, CH_3), 2.05 (1 H, t, *J* = 2.6 Hz, C≡CH), 2.31 (2 H, q, *J* = 6.7 Hz, CCH_2), 2.60 (2 H, td, *J* = 6.9, 2.5 Hz, CHCH_2), 3.82 (1 H, t, *J* = 5.8 Hz, C*H*CH_2);
^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 16.2 (CH*C*H_2), 24.5 (*C*H_2C≡C), 26.4 (CH_3), 28.5 (CH_3), 44.4 (*C*HCH_2), 70.7 (*C*≡CH), 82.2 (C≡*C*H), 105.1 (OCO), 165.2 (2 × C=O);
m/z (ES−) 195 ((M − H), 100%). (Found: (M − H) 195.0664. $C_{10}H_{11}O_4$ requires *M*, 195.0662).

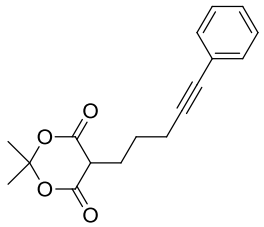


2,2-Dimethyl-5-(4-phenylbut-3-yn-1-yl)-1,3-dioxane-4,6-dione

As for general procedure B, reaction of diethyl 2-(4-phenylbut-3-yn-1-yl)malonate (0.72 g, 1.97 mmol, 1.0 eq) in MeOH (8.5 mL) and H_2O (2.8 mL) with NaOH (0.40 g, 10.1 mmol, 6.1 eq), and treatment of the residue with isopropenyl acetate (0.25 mL, 2.27 mmol, 1.1 eq) and H_2SO_4 (2 drops), after column chromatography on silica gel, eluting with 30% ethyl acetate in petroleum ether (40-60 °C) gave 2,2-dimethyl-5-(4-phenylbut-3-yn-1-yl)-1,3-dioxane-4,6-dione (319 mg, 1.17 mmol, 60%) as a white solid.

mp 85-87 °C;
ν_{max} (neat)/cm^{-1} 3046, 3000, 2972, 2944, 2884, 1772, 1728 (C=O), 1597, 1490, 1441, 1395, 1378, 1364, 1324, 1276, 1203, 1184, 1079, 1052, 1013, 974, 914, 902, 854, 836, 757, 733, 714, 691, 628;

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.74 (3 H, s, CH_3), 1.83 (3 H, s, CH_3), 2.42 (2 H, td, *J* = 6.9, 5.5 Hz, $CHCH_2$), 2.81 (2 H, t, *J* = 6.9 Hz, $CH_2C{\equiv}C$), 3.85 (1 H, t, *J* = 5.5 Hz, $CHCH_2$), 7.28 - 7.32 (3 H, m, 3 × ArH), 7.36 - 7.42 (2 H, m, 2 × ArH);
^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 17.0 ($CH_2C{\equiv}C$), 24.8 ($CHCH_2$), 26.5 (CH_3), 28.4 (CH_3), 44.5 ($CHCH_2$), 77.2 ($C{\equiv}CAr$), 87.4 ($C{\equiv}CAr$), 105.1 (OCO), 123.1 (ArC^q), 128.0 (ArCH), 128.3 (2 × ArCH), 131.6 (2 × ArCH), 165.3 (2 × C=O);
m/z (ES−) 271 ((M − H), 100%). (Found: (M − H) 271.0969. $C_{16}H_{15}O_4$ requires *M*, 271.0975).

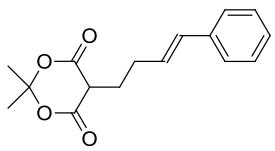


2,2-Dimethyl-5-(5-phenylpent-4-yn-1-yl)-1,3-dioxane-4,6-dione

As for general procedure B, reaction of diethyl 2-(5-phenylpent-4-yn-1-yl)malonate (2.00 g, 6.61 mmol, 1.0 eq) in MeOH (30 mL) and H_2O (10 mL) with NaOH (1.35 g, 33.8 mmol, 5.1 eq), and treatment of the residue with isopropenyl acetate (0.8 mL, 7.27 mmol, 1.1 eq) and H_2SO_4 (4 drops), after column chromatography on silica gel, eluting with 30% ethyl acetate in petroleum ether (40-60 °C) gave 2,2-dimethyl-5-(5-phenylpent-4-yn-1-yl)-1,3-dioxane-4,6-dione (998 mg, 3.49 mmol, 53%) as a yellow oil.

ν_{max} (neat)/cm^{-1} 3056, 3001, 2944, 2873, 1783, 1742 (C=O), 1490, 1442, 1382, 1290, 1203, 1101, 1057, 981, 921, 887, 846, 757, 692;
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.75 (3 H, s, CH_3), 1.76 (3 H, s, CH_3), 1.81 - 1.86 (2 H, m, $CH_2CH_2CH_2$), 2.26 - 2.32 (2 H, m, $CHCH_2$), 2.50 (2 H, t, *J* = 6.9 Hz, $CH_2C{\equiv}C$), 3.69 (1 H, t, *J* = 5.2 Hz, CH), 7.25 - 7.29 (2 H, m, 2 × ArH), 7.37 - 7.42 (3 H, m, 3 × ArH);
^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 19.3 ($CH_2C{\equiv}C$), 25.5 ($CH_2CH_2CH_2$), 25.7 ($CHCH_2$), 26.6 (CH_3), 28.4 (CH_3), 45.8 (CH), 81.4 ($C{\equiv}CAr$), 89.0 ($C{\equiv}CAr$), 104.9 (OCO), 123.6 (ArC^q), 127.6 (ArCH), 128.2 (2 × ArCH), 131.5 (2 × ArCH), 165.4 (2 × C=O);
The mass spectrum was not informative.

Cross-metathesis



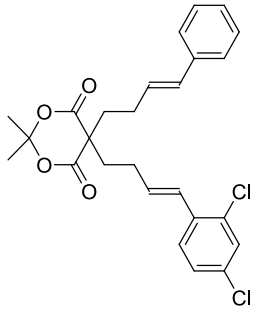
(*E*)-2,2-Dimethyl-5-(4-phenylbut-3-enyl)-1,3-dioxane-4,6-dione (5)

To a stirred solution of 5-(but-3-enyl)-2,2-dimethyl-1,3-dioxane-4,6-dione **4** (4.02 g, 20.3 mmol, 1.0 eq) and *trans*-stilbene (11.1 g, 61.3 mmol, 3.0 eq) in CH_2Cl_2 (50 mL), Hoveyda–Grubbs II (295 mg,

0.47 mmol, 2.3 mol%) was added and the solution stirred at room temperature overnight under a light stream of nitrogen. The solvent was then removed *in vacuo*. Purification by column chromatography on silica gel, eluting with a gradient 20-80% dichloromethane in petroleum ether (40-60 °C) gave (*E*)-2,2-dimethyl-5-(4-phenylbut-3-enyl)-1,3-dioxane-4,6-dione **5** (3.54 mg, 12.9 mmol, 64%) as a white solid.

mp 86-88 °C;
ν_{max} (neat)/cm^{-1} 3081, 3059, 3025, 2997, 2940, 2889, 1782, 1735 (C=O), 1495, 1446, 1382, 1329, 1277, 1254, 1200, 1174, 1096, 1070, 1014, 963, 870, 848, 753, 695, 630;
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.70 (3 H, s, CH_3), 1.76 (3 H, s, CH_3), 2.34 (2 H, dt, *J* = 7.8, 5.7 Hz, CHC*H*$_2$), 2.48 (2 H, q, *J* = 7.4 Hz, C*H*$_2$CH=CH), 3.56 (1 H, t, *J* = 5.0 Hz, CH), 6.17 (1 H, dt, *J* = 15.7, 7.2 Hz, C*H*=CHAr), 6.45 (1 H, d, *J* = 15.7 Hz, CH=C*H*Ar), 7.19 - 7.25 (1 H, m, ArH), 7.28 - 7.38 (4 H, m, 4 × ArH);
^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 25.9 (CH*C*H$_2$), 26.8 (CH_3), 28.3 (CH_3), 29.8 (*C*H$_2$CH=CH), 44.8 (CH), 104.9 (OCO), 126.1 (2 × ArCH), 127.3 (ArCH), 128.3 (*C*H=CHAr), 128.4 (2 × ArCH), 132.1 (CH=*C*HAr), 137.1 (ArC^q), 165.6 (2 × C=O);
m/z (ES−) 273 ((M − H), 100%). (Found: (M − H) 273.1139. $C_{16}H_{17}O_4$ requires *M*, 273.1132).

General procedure C – Alkylations of Meldrum's acid

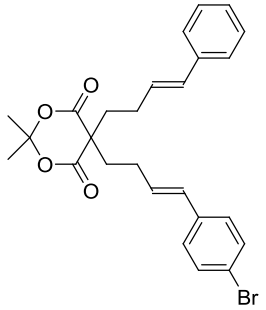


5-((*E*)-4-(2,4-Dichlorophenyl)but-3-enyl)-2,2-dimethyl-5-((*E*)-4-phenylbut-3-enyl)-1,3-dioxane-4,6-dione (1e)

To a stirred solution of (*E*)-2,2-dimethyl-5-(4-phenylbut-3-enyl)-1,3-dioxane-4,6-dione **5** (499 mg, 1.82 mmol, 1.0 eq) in DMF (5.0 mL), K_2CO_3 (505 mg, 3.66 mmol, 2.0 eq) was added and the solution stirred during 30 min. (*E*)-1-(4-Bromobut-1-enyl)-2,4-dichlorobenzene (622 mg, 2.22 mmol, 1.2 eq) was subsequently added and the reaction stirred at room temperature for 4 days. The reaction was quenched with H_2O (5 mL), and the aqueous phase extracted with ethyl acetate (3 × 10 mL). The combined organic phases were dried (Na_2SO_4 or $MgSO_4$) and concentrated *in vacuo*. Purification by column chromatography on silica gel, eluting with 5% ethyl acetate in petroleum ether (40-60 °C) gave 5-((*E*)-4-(2,4-dichlorophenyl)but-3-enyl)-2,2-dimethyl-5-((*E*)-4-phenylbut-3-enyl)-1,3-dioxane-4,6-dione **1e** (447 mg, 0.94 mmol, 52%) as a light yellow oil.

ν_{max} (neat)/cm^{-1} 3083, 3061, 3026, 3000, 2932, 2852, 1773, 1736 (C=O), 1584, 1470, 1447, 1391, 1379, 1282, 1258, 1238, 1201, 1100, 1049, 965, 887, 851, 744, 693;
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.76 (6 H, s, 2 × CH_3), 2.19 - 2.37 (8 H, m, 2 × C*H*$_2$CH$_2$CH=CH, 2 × CH$_2$C*H*$_2$CH=CH), 6.04 - 6.16 (2 H, m, 2 × C*H*=CHAr), 6.43 (1 H, d, *J* = 15.6 Hz, CH=C*H*Ar),

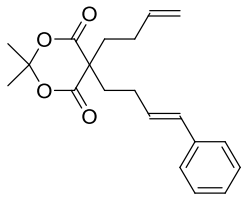
6.73 (1 H, d, J = 15.6 Hz, CH=C*H*Ar), 7.19 (1 H, dd, J = 8.3, 1.8 Hz, ArH), 7.21 - 7.25 (1 H, m, ArH), 7.28 - 7.34 (4 H, m, 4 × ArH), 7.35 (1 H, d, J = 2.3 Hz, ArH), 7.39 (1 H, d, J = 8.6 Hz, ArH);
^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 29.0 (*C*$H_2$$CH_2$CH=CH), 29.1 (*C*$H_2$$CH_2$CH=CH), 29.7 ($CH_3$), 29.7 ($CH_3$), 38.2 ($CH_2$*C*$H_2$CH=CH), 38.7 ($CH_2$*C*$H_2$CH=CH), 53.7 ($C^q$), 105.7 (OCO), 126.0 (2 × ArCH), 126.8 (*C*H=CHAr), 127.2 (ArCH), 127.3 (ArCH), 127.4 (*C*H=CHAr), 127.4 (ArCH), 128.5 (2 × ArCH), 129.3 (ArCH), 131.2 (CH=*C*HAr), 131.7 (CH=*C*HAr), 133.1 (ArC^q), 133.2 (ArC^q), 133.7 (ArC^q), 137.0 (ArC^q), 168.9 (2 × C=O);
The mass spectrum was not informative.



5-((*E*)-4-(4-Bromophenyl)but-3-enyl)-2,2-dimethyl-5-((*E*)-4-phenylbut-3-enyl)-1,3-dioxane-4,6-dione (1f)

As for general procedure C, reaction of (*E*)-2,2-dimethyl-5-(4-phenylbut-3-enyl)-1,3-dioxane-4,6-dione **5** (500 mg, 1.82 mmol, 1.0 eq) in DMF (4.6 mL) with K_2CO_3 (509 mg, 3.68 mmol, 2.0 eq) and (*E*)-1-bromo-4-(4-bromobut-1-enyl)benzene (647 mg, 2.23 mmol, 1.2 eq), after column chromatography on silica gel eluting with 5% ethyl acetate in petroleum ether (40-60 °C) gave 5-((*E*)-4-(4-bromophenyl)but-3-enyl)-2,2-dimethyl-5-((*E*)-4-phenylbut-3-enyl)-1,3-dioxane-4,6-dione **1f** (301 mg, 0.62 mmol, 34%) as a white solid.

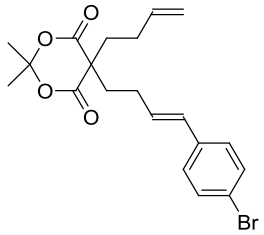
mp 105-107 °C;
ν_{max} (neat)/cm^{-1} 3048, 3018, 2998, 2940, 2893, 2836, 1771, 1739 (C=O), 1489, 1447, 1392, 1328, 1267, 1255, 1233, 1199, 1117, 1103, 1074, 1046, 962, 887, 843, 793, 766, 727, 693;
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.75 (3 H, s, CH_3), 1.76 (3 H, s, CH_3), 2.17 - 2.32 (8 H, m, 2 × C*H*$_2$$CH_2$CH=CH, 2 × C*H*$_2$CH=CH), 6.05 - 6.15 (2 H, m, 2 × C*H*=CHAr), 6.36 (1 H, d, J = 15.6 Hz, CH=C*H*Ar), 6.42 (1 H, d, J = 15.6 Hz, CH=C*H*Ar), 7.16 - 7.21 (2 H, m, 2 × ArH), 7.21 - 7.25 (1 H, m, ArH), 7.27 - 7.34 (4 H, m, 4 × ArH), 7.40 - 7.44 (2 H, m, 2 × ArH);
^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 29.0 (2 × *C*$H_2$$CH_2$CH=CH), 29.7 ($CH_3$), 29.8 ($CH_3$), 38.4 (*C*$H_2$CH=CH), 38.6 (*C*$H_2$CH=CH), 53.7 ($C^q$), 105.7 (OCO), 121.0 ($ArC^q$), 126.0 (2 × ArCH), 127.3 (ArCH), 127.5 (*C*H=CHAr), 127.6 (2 × ArCH), 128.5 (*C*H=CHAr), 128.5 (2 × ArCH), 130.5 (CH=*C*HAr), 131.6 (2 × ArCH), 131.7 (CH=*C*HAr), 135.9 (ArC^q), 137.0 (ArC^q), 168.9 (2 × C=O);
The mass spectrum was not informative.



(*E*)-5-(But-3-enyl)-2,2-dimethyl-5-(4-phenylbut-3-enyl)-1,3-dioxane-4,6-dione (1a)

As for general procedure C, reaction of (*E*)-2,2-dimethyl-5-(4-phenylbut-3-enyl)-1,3-dioxane-4,6-dione **5** (503 mg, 1.83 mmol, 1.0 eq) in DMF (4.6 mL) with K_2CO_3 (508 mg, 3.68 mmol, 2.0 eq) and 4-bromo-1-butene (0.3 mL, 2.96 mmol, 1.6 eq), after column chromatography on silica gel eluting with 5% ethyl acetate in petroleum ether (40-60 °C) gave (*E*)-5-(but-3-enyl)-2,2-dimethyl-5-(4-phenylbut-3-enyl)-1,3-dioxane-4,6-dione **1a** (395 mg, 1.20 mmol, 66%) as a colorless oil.

ν_{max} (neat)/cm^{-1} 3077, 3065, 2998, 2937, 2873, 1772, 1732 (C=O), 1641, 1495, 1450, 1392, 1380, 1259, 1241, 1201, 1072, 1062, 1026, 991, 965, 913, 884, 753, 699, 638, 616;
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.75 (3 H, s, CH_3), 1.76 (3 H, s, CH_3), 2.06 - 2.16 (4 H, m, C*H*$_2$CH$_2$CH=CH$_2$, CH$_2$C*H*$_2$CH=CH$_2$), 2.17 - 2.29 (4 H, m, C*H*$_2$CH$_2$CH=CH, CH$_2$C*H*$_2$CH=CH), 4.99 - 5.11 (2 H, m, CH=C*H*$_2$), 5.68 - 5.80 (1 H, m, C*H*=CH$_2$), 6.10 (1 H, dt, *J* = 15.9, 6.4 Hz, C*H*=CHAr), 6.41 (1 H, d, *J* = 15.9 Hz, CH=C*H*Ar), 7.19 - 7.26 (1 H, m, ArH), 7.27 - 7.35 (4 H, m, 4 × ArH);
^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 29.1 (*C*H$_2$CH$_2$CH=CH), 29.6 (*C*H$_2$CH$_2$CH=CH$_2$), 29.8 (2 × CH_3), 38.3 (CH$_2$*C*H$_2$CH=CH$_2$), 38.6 (CH$_2$*C*H$_2$CH=CH), 53.8 (C^q), 105.7 (OCO), 116.3 (CH=*C*H$_2$), 126.0 (2 × ArCH), 127.3 (ArCH), 127.6 (*C*H=CHAr), 128.5 (2 × ArCH), 131.6 (CH=*C*HAr), 135.9 (*C*H=CH$_2$), 137.0 (ArC^q), 169.0 (2 × C=O);
m/z (ES+) 249 (88%), 309 (25), 351 ((M + Na), 100), 352 (21), 367 (53), 381 (76), 383 (32). (Found: (M + NH_4) 346.2011. $C_{20}H_{28}O_4N$ requires *M*, 346.2013).

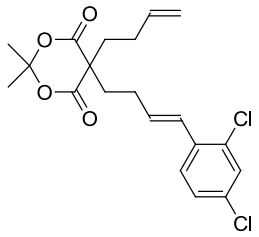


(*E*)-5-(4-(4-Bromophenyl)but-3-en-1-yl)-5-(but-3-en-1-yl)-2,2-dimethyl-1,3-dioxane-4,6-dione (1b)

As for general procedure C, reaction of 5-(but-3-enyl)-2,2-dimethyl-1,3-dioxane-4,6-dione **4** (503 mg, 2.54 mmol, 1 eq) in DMF (6.5 mL) with K_2CO_3 (701 mg, 5.07 mmol, 2.0 eq) and (*E*)-1-bromo-4-(4-bromobut-1-enyl)benzene (948.0 mg, 3.27 mmol, 1.3 eq), after column chromatography on silica gel eluting with 5% ethyl acetate in petroleum ether (40-60 °C) gave (*E*)-5-(4-(4-bromophenyl)but-3-en-1-yl)-5-(but-3-en-1-yl)-2,2-dimethyl-1,3-dioxane-4,6-dione **1b** (326 mg, 0.80 mmol, 32%) as a colorless oil.

ν_{max} (neat)/cm^{-1} 3076, 2999, 2934, 2848, 1773, 1736 (C=O), 1641, 1587, 1487, 1448, 1391, 1378, 1284, 1257, 1239, 1201, 1071, 1007, 965, 916, 881, 849, 833, 801, 714, 638;
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.74 (3 H, s, CH_3), 1.76 (3 H, s, CH_3), 2.09 - 2.14 (4 H, m, C*H*$_2$CH$_2$CH=CH$_2$, C*H*$_2$CH=CH$_2$), 2.19 - 2.28 (4 H, m, C*H*$_2$CH$_2$CH=CH, C*H*$_2$CH=CH), 5.00 - 5.10 (2

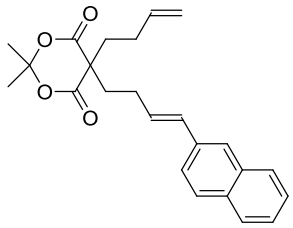
H, m, CH=CH_2), 5.67 - 5.79 (1 H, m, CH=CH_2), 6.09 (1 H, dt, J = 15.9, 6.3 Hz, CH=CHAr), 6.35 (1 H, d, J = 15.9 Hz, CH=CHAr), 7.16 - 7.20 (2 H, m, 2 × ArH), 7.39 - 7.44 (2 H, m, 2 × ArH);
^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 29.0 ($C$$H_2$$CH_2$CH=CH), 29.6 ($C$$H_2$$CH_2$CH=$CH_2$), 29.7 ($CH_3$), 29.8 ($CH_3$), 38.3 ($C$$H_2$CH=CH), 38.3 ($C$$H_2$CH=$CH_2$), 53.7 ($C^q$), 105.7 (OCO), 116.4 (CH=$C$$H_2$), 121.0 ($ArC^q$), 127.6 (2 × ArCH), 128.5 (CH=CHAr), 130.5 (CH=CHAr), 131.6 (2 × ArCH), 135.9 (CH=CH_2), 136.0 (ArC^q), 169.0 (2 × C=O);
The mass spectrum was not informative.



(*E*)-5-(But-3-en-1-yl)-5-(4-(2,4-dichlorophenyl)but-3-en-1-yl)-2,2-dimethyl-1,3-dioxane-4,6-dione (1c)

As for general procedure C, reaction of 5-(but-3-enyl)-2,2-dimethyl-1,3-dioxane-4,6-dione **4** (499 mg, 2.52 mmol, 1.0 eq) in DMF (6.5 mL) with K_2CO_3 (700 mg, 5.07 mmol, 2.0 eq) and (*E*)-1-(4-bromobut-1-enyl)-2,4-dichlorobenzene (847 mg, 3.03 mmol, 1.2 eq), after column chromatography on silica gel eluting with 5% ethyl acetate in petroleum ether (40-60 °C) gave (*E*)-5-(but-3-en-1-yl)-5-(4-(2,4-dichlorophenyl)but-3-en-1-yl)-2,2-dimethyl-1,3-dioxane-4,6-dione **1c** (621 mg, 1.56 mmol, 62%) as a colorless oil.

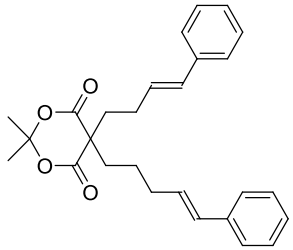
ν_{max} (neat)/cm^{-1} 3078, 2999, 2934, 2852, 1774, 1736 (C=O), 1642, 1584, 1552, 1470, 1448, 1391, 1379, 1284, 1257, 1238, 1200, 1100, 1048, 965, 916, 881, 866, 850, 807, 756, 637;
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.75 (3 H, s, CH_3), 1.77 (3 H, s, CH_3), 2.07 - 2.16 (4 H, m, C$H_2$$CH_2$CH=$CH_2$, C$H_2$CH=$CH_2$), 2.19 - 2.25 (2 H, m, CH_2CH=CHAr), 2.26 - 2.34 (2 H, m, C$H_2$$CH_2$CH=CHAr), 5.00 - 5.11 (2 H, m, CH=CH_2), 5.68 - 5.79 (1 H, m, CH=CH_2), 6.07 (1 H, dt, J = 15.7, 6.7 Hz, CH=CHAr), 6.71 (1 H, d, J = 15.7 Hz, CH=CHAr), 7.19 (1 H, ddd, J = 8.6, 2.3, 0.5 Hz, ArH), 7.35 (1 H, d, J = 2.3 Hz, ArH), 7.39 (1 H, d, J = 8.6 Hz, ArH);
^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 29.2 ($C$$H_2$CH=CH), 29.6 ($C$$H_2$CH=$CH_2$), 29.7 ($CH_3$), 29.8 ($CH_3$), 38.1 ($C$$H_2$$CH_2$CH=CH), 38.4 ($C$$H_2$$CH_2$CH=$CH_2$), 53.7 ($C^q$), 105.8 (OCO), 116.4 (CH=$C$$H_2$), 126.8 (CH=$C$HAr), 127.2 (ArCH), 127.4 (ArCH), 129.3 (ArCH), 131.2 (CH=CHAr), 133.1 (ArC^q), 133.3 (ArC^q), 133.7 (ArC^q), 135.9 (CH=CH_2), 168.9 (2 × C=O);
The mass spectrum was not informative.



(*E*)-5-(But-3-en-1-yl)-2,2-dimethyl-5-(4-(naphthalen-2-yl)but-3-en-1-yl)-1,3-dioxane-4,6-dione (1d)

As for general procedure C, reaction of 5-(but-3-enyl)-2,2-dimethyl-1,3-dioxane-4,6-dione **4** (300 mg, 1.51 mmol, 1.0 eq) in DMF (3.9 mL) with K_2CO_3 (425 mg, 3.07 mmol, 2.0 eq) and (*E*)-2-(4-bromobut-1-enyl)naphthalene (475 mg, 1.82 mmol, 1.2 eq), after column chromatography on silica gel eluting with 5% ethyl acetate in petroleum ether (40-60 °C) gave (*E*)-5-(but-3-en-1-yl)-2,2-dimethyl-5-(4-(naphthalen-2-yl)but-3-en-1-yl)-1,3-dioxane-4,6-dione **1d** (292 mg, 0.77 mmol, 51%) as a white solid.

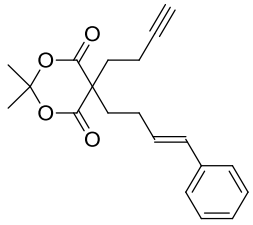
mp 99-101 °C;
ν_{max} (neat)/cm^{-1} 3073, 3059, 2995, 2978, 2941, 2836, 1773, 1732 (C=O), 1640, 1507, 1452, 1380, 1312, 1289, 1256, 1237, 1202, 1149, 1114, 1072, 1028, 962, 911, 872, 862, 807, 749, 711, 640, 619;
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.76 (3 H, s, CH_3), 1.77 (3 H, s, CH_3), 2.07 - 2.19 (4 H, m, C$H_2$$CH_2$CH=$CH_2$, C$H_2$CH=$CH_2$), 2.21 - 2.28 (2 H, m, C$H_2$$CH_2$CH=CH), 2.28 - 2.36 (2 H, m, CH_2CH=CH), 5.00 - 5.11 (2 H, m, CH=CH_2), 5.69 - 5.81 (1 H, m, C*H*=CH_2), 6.23 (1 H, dt, *J* = 15.8, 6.5 Hz, C*H*=CHAr), 6.58 (1 H, d, *J* = 15.8 Hz, CH=C*H*Ar), 7.40 - 7.49 (2 H, m, 2 × ArH), 7.54 (1 H, dd, *J* = 8.6, 1.5 Hz, ArH), 7.66 (1 H, s, ArH), 7.75 - 7.82 (3 H, m, 3 × ArH);
^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 29.2 (*C*H_2CH=CH), 29.7 (*C*H_2CH=CH_2), 29.8 (CH_3), 29.8 (CH_3), 38.4 (*C*$H_2$$CH_2$CH=$CH_2$), 38.6 (*C*$H_2$$CH_2$CH=CH), 53.8 ($C^q$), 105.7 (OCO), 116.3 (CH=*C*H_2), 123.4 (ArCH), 125.7 (ArCH), 125.8 (ArCH), 126.2 (ArCH), 127.6 (*C*H=CHAr), 127.9 (ArCH), 128.0 (ArCH), 128.2 (ArCH), 131.8 (CH=*C*HAr), 132.8 (ArC^q), 133.6 (ArC^q), 134.5 (ArC^q), 136.0 (*C*H=CH_2), 169.0 (2 × C=O);
The mass spectrum was not informative.



2,2-Dimethyl-5-((*E*)-4-phenylbut-3-enyl)-5-((*E*)-5-phenylpent-4-enyl)-1,3-dioxane-4,6-dione (1g)

As for general procedure C, reaction of (*E*)-2,2-dimethyl-5-(4-phenylbut-3-enyl)-1,3-dioxane-4,6-dione **5** (314 mg, 1.14 mmol, 1.0 eq) in DMF (2.9 mL) with K_2CO_3 (320 mg, 2.32 mmol, 2.0 eq) and (*E*)-(5-bromopent-1-enyl)benzene (309.2 mg, 1.37 mmol, 1.2 eq), after column chromatography on silica gel eluting with 5% ethyl acetate in petroleum ether (40-60 °C) gave 2,2-dimethyl-5-((*E*)-4-phenylbut-3-enyl)-5-((*E*)-5-phenylpent-4-enyl)-1,3-dioxane-4,6-dione **1g** (228 mg, 0.54 mmol, 48%) as a white solid.

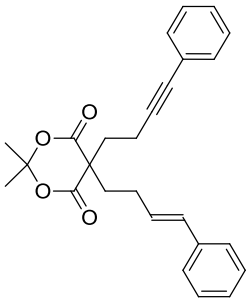
mp 111-113 °C;
ν_{max} (neat)/cm^{-1} 3057, 3025, 2921, 2854, 1771, 1727 (C=O), 1598, 1492, 1447, 1380, 1274, 1233, 1204, 1114, 1060, 1024, 964, 904, 850, 743, 716, 691;
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.47 - 1.57 (2 H, m, $CH_2CH_2CH_2$), 1.75 (3 H, s, CH_3), 1.76 (3 H, s, CH_3), 2.07 - 2.14 (2 H, m, $CCH_2CH_2CH_2$), 2.18 - 2.29 (6 H, m, CCH_2CH_2CH=CH, CCH_2CH_2CH=CH, $CCH_2CH_2CH_2$), 6.05 - 6.18 (2 H, m, 2 × C*H*=CHAr), 6.39 (1 H, d, *J* = 15.9 Hz, CH=C*H*Ar), 6.41 (1 H, d, *J* = 15.6 Hz, CH=C*H*Ar), 7.18 - 7.24 (2 H, m, 2 × ArH), 7.27 - 7.36 (8 H, m, 8 × ArH);
^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 25.3 ($CH_2CH_2CH_2$), 29.1 (CH_2CH=CH), 29.7 (CH_3), 29.8 (CH_3), 32.7 (CH_2CH=CH), 38.6 (CCH_2), 38.8 (CCH_2), 54.2 (C^q), 105.7 (OCO), 126.0 (2 × ArCH), 126.0 (2 × ArCH), 127.1 (ArCH), 127.3 (ArCH), 127.6 (*C*H=CHAr), 128.5 (2 × ArCH), 128.5 (2 × ArCH), 128.9 (*C*H=CHAr), 131.0 (CH=*C*HAr), 131.6 (CH=*C*HAr), 137.1 (ArC^q), 137.3 (ArC^q), 169.2 (2 × C=O);
m/z (ES+) 151 (18%), 183 (20), 273 (18), 339 (18), 441 ((M + Na), 100), 442 (28). (Found: (M + Na) 441.2027. $C_{27}H_{30}O_4Na$ requires *M*, 441.2036).
The mass spectrum was not informative.



(*E*)-5-(But-3-yn-1-yl)-2,2-dimethyl-5-(4-phenylbut-3-en-1-yl)-1,3-dioxane-4,6-dione (1i)

As for general procedure C, reaction of 5-(but-3-yn-1-yl)-2,2-dimethyl-1,3-dioxane-4,6-dione (445 mg, 2.27 mmol, 1.0 eq) in DMF (6.0 mL) with K_2CO_3 (627 mg, 4.54 mmol, 2.0 eq) and (*E*)-(4-bromobut-1-en-1-yl)benzene (575 mg, 2.72 mmol, 1.2 eq), after column chromatography on silica gel eluting with 5% ethyl acetate in petroleum ether (40-60 °C) gave (*E*)-5-(but-3-yn-1-yl)-2,2-dimethyl-5-(4-phenylbut-3-en-1-yl)-1,3-dioxane-4,6-dione **1i** (241 mg, 0.74 mmol, 33%).

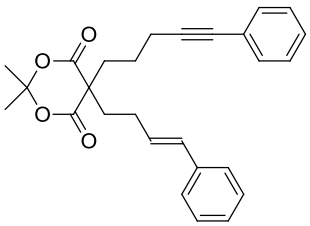
mp 62-64 ºC;
ν_{max} (neat)/cm^{-1} 3289, 3026, 3000, 2941, 1773 (C=O), 1736 (C=O), 1447, 1393, 1380, 1291;
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.75 (3 H, s, CH_3), 1.79 (3 H, s, CH_3),2.04 (1 H, s, C≡C*H*), 2.15 - 2.29 (4 H, m, CH_2CH_2CH=CH, CH_2CH=CH), 2.31 - 2.33 (4 H, m, CH_2CH_2C≡C, CH_2C≡C), 6.09 (1 H, dt, *J* = 15.9, 6.4 Hz, C*H*=CHAr), 6.42 (1 H, d, *J* = 15.9 Hz, CH=C*H*Ar), 7.18 - 7.26 (1 H, m, ArCH), 7.28 - 7.35 (4 H, m, ArCH);
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 15.0 (CH_2C≡C), 28.9 (CH_2CH=CH), 29.6 (CH_3), 29.8 (CH_3), 36.7 (CH_2CH_2C≡C), 38.9 (CH_2CH_2CH=CH), 53.1 (C^q), 70.6 (C≡*C*H), 81.6 (CH_2C≡C), 106.0 (OCO), 126.1 (2 × ArCH), 127.4 (*C*H=CHAr, ArCH), 128.6 (2 × ArCH), 131.8 (CH=*C*HAr), 137.0 (ArC^q), 168.5 (2 × C=O);
The mass spectrum was not informative.



(*E*)-2,2-Dimethyl-5-(4-phenylbut-3-en-1-yl)-5-(4-phenylbut-3-yn-1-yl)-1,3-dioxane-4,6-dione (1j)

As for general procedure C, reaction of 2,2-dimethyl-5-(4-phenylbut-3-yn-1-yl)-1,3-dioxane-4,6-dione (390 mg, 1.43 mmol, 1.0 eq) in DMF (4.0 mL) with K_2CO_3 (396 mg, 2.86 mmol, 2.0 eq) and (*E*)-(4-bromobut-1-en-1-yl)benzene (465 mg, 2.20 mmol, 1.2 eq), after column chromatography on silica gel eluting with 5% ethyl acetate in petroleum ether (40-60 °C) gave (*E*)-2,2-dimethyl-5-(4-phenylbut-3-en-1-yl)-5-(4-phenylbut-3-yn-1-yl)-1,3-dioxane-4,6-dione **1j** (221 mg, 0.53 mmol, 30%).

ν_{max} (neat)/cm^{-1} 2940, 2846, 1772 (C=O), 1736 (C=O), 1491, 1443, 1392, 1240, 1201, 966;
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.65 (3 H, s, CH_3), 1.66 (3 H, s, CH_3), 2.09 - 2.22 (4 H, m, C*H*$_2$CH$_2$CH=CH, C*H*$_2$CH=CH), 2.27 - 2.37 (2 H, m, C*H*$_2$CH$_2$C≡C), 2.42 - 2.50 (2 H, m, CH$_2$C*H*$_2$C≡C), 6.00 (1 H, dt, *J* = 15.9, 6.4 Hz, C*H*=CHAr), 6.33 (1 H, d, *J* = 15.9 Hz, CH=C*H*Ar), 7.09 - 7.25 (8 H, m, 8 × ArCH), 7.28 - 7.35 (2 H, m, 2 × ArCH);
^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 16.0 (*C*H$_2$C≡C), 28.9 (*C*H$_2$CH=CH), 29.6 (CH_3), 29.7 (CH_3), 36.9 (*C*H$_2$CH$_2$C≡C), 39.4 (*C*H$_2$CH$_2$C=C), 53.2 (C^q), 82.9 (CH$_2$*C*≡*C*), 87.2 (CH$_2$*C*≡C), 106.0 (OCO), 123.2 (ArC^q), 126.1 (2 × ArCH), 127.4 (ArCH), 127.5 (ArCH), 128.0 (ArCH), 128.3 (ArCH), 128.6 (2 × ArCH), 131.5 (ArCH), 131.8 (ArCH), 137.0 (ArC^q), 168.5 (2 × C=O);
Mass spectroscopy was not informative.

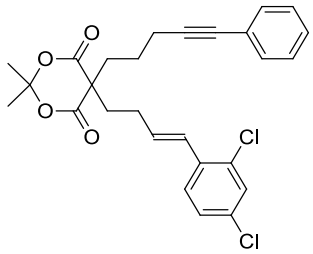


(*E*)-2,2-Dimethyl-5-(4-phenylbut-3-en-1-yl)-5-(5-phenylpent-4-yn-1-yl)-1,3-dioxane-4,6-dione (1h)

As for general procedure F, reaction of (*E*)-2,2-dimethyl-5-(4-phenylbut-3-en-1-yl)-1,3-dioxane-4,6-dione **5** (500 mg, 1.82 mmol, 1.0 eq) in DMF (4.6 mL) with K_2CO_3 (503 mg, 3.65 mmol, 2.0 eq) and (5-bromopent-1-yn-1-yl)benzene (524 mg, 2.19 mmol, 1.2 eq), after column chromatography on silica gel eluting with 5% ethyl acetate in petroleum ether (40-60 °C) gave (*E*)-2,2-dimethyl-5-(4-phenylbut-3-en-1-yl)-5-(5-phenylpent-4-yn-1-yl)-1,3-dioxane-4,6-dione **1h** (314 mg, 0.75 mmol, 41%).

mp 83-85 ºC;
ν_{max} (neat)/cm^{-1} 2933, 2860, 1773 (C=O), 1738 (C=O), 1391, 1379, 1260, 1201, 1062, 967;

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.62 - 1.73 (2 H, m, CH_2CH$_2$C≡C), 1.75 (3 H, s, CH_3), 1.78 (3 H, s, CH_3), 2.17 - 2.29 (6 H, m, 2 × CCH_2, CH_2CH=CH), 2.46 (2 H, t, *J* = 6.9 Hz, CH_2C≡C), 6.03 - 6.21 (1 H, m, C*H*=CHAr), 6.43 (1 H, d, *J* = 15.8 Hz, CH=C*H*Ar), 7.16 - 7.46 (10 H, m, 10 × ArCH);
^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 19.4 (*C*H_2C≡C), 24.7 (*C*H_2CH$_2$C≡C), 29.1 (*C*H_2CH=CH), 29.7 (CH_3), 29.8 (CH_3), 38.3 (*C*H_2CH$_2$CH$_2$C≡C, *C*H_2CH$_2$CH=CH), 54.0 (C^q), 81.7 (C≡*C*Ar), 88.2 (*C*≡CAr), 105.7 (OCO), 123.6 (ArC^q), 126.1 (2 × ArCH), 127.3 (ArCH), 127.7 (ArCH), 127.8 (CH=*C*HAr), 128.2 (2 × ArCH), 128.6 (2 × ArCH), 131.6 (2 × ArCH), 131.7 (*C*H=CHAr), 137.1 (ArC^q), 169.0 (2 × C=O);
Mass spectroscopy was not informative.

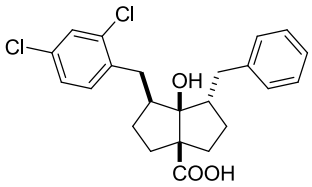


(*E*)-5-(4-(2,4-Dichlorophenyl)but-3-en-1-yl)-2,2-dimethyl-5-(5-phenylpent-4-yn-1-yl)-1,3-dioxane-4,6-dione (1k)

As for general procedure F, reaction of 2,2-dimethyl-5-(5-phenylpent-4-yn-1-yl)-1,3-dioxane-4,6-dione (499 mg, 1.74 mmol, 1.0 eq) in DMF (6.0 mL) with K_2CO_3 (483 mg, 3.49 mmol, 2.0 eq) and (*E*)-1-(4-bromobut-1-enyl)-2,4-dichlorobenzene (592 mg, 2.11 mmol, 1.2 eq), after column chromatography on silica gel eluting with 5% ethyl acetate in petroleum ether (40-60 °C) gave (*E*)-5-(4-(2,4-dichlorophenyl)but-3-en-1-yl)-2,2-dimethyl-5-(5-phenylpent-4-yn-1-yl)-1,3-dioxane-4,6-dione **1k** (367 mg, 0.76 mmol, 43%) as a colorless oil.

ν_{max} (neat)/cm^{-1} 2996, 2935, 2862, 1771, 1736 (C=O), 1467, 1391, 1379, 1279, 1262, 1198, 1101, 1051, 969, 905, 864, 850, 756, 730, 692, 648;
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.64 - 1.72 (2 H, m, CH_2CH$_2$C≡C), 1.74 (3 H, s, CH_3), 1.77 (3 H, s, CH_3), 2.19 - 2.34 (6 H, m, 2 × CCH_2, CH_2CH=CH), 2.45 (2 H, t, *J* = 6.8 Hz, CH_2C≡C), 6.07 (1 H, dt, *J* = 15.6, 6.5 Hz, C*H*=CHAr), 6.71 (1 H, d, *J* = 15.6 Hz, CH=C*H*Ar), 7.16 - 7.20 (1 H, m, ArH), 7.27 - 7.31 (3 H, m, 3 × ArH), 7.35 (1 H, d, *J* = 2.3 Hz, ArH), 7.36 - 7.41 (3 H, m, 3 × ArH);
^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 19.3 (*C*H_2C≡C), 24.6 (*C*H_2CH$_2$C≡C), 29.2 (*C*H_2CH=CH), 29.7 (CH_3), 29.7 (CH_3), 37.9 (*C*H_2CH$_2$CH=CH), 38.3 (*C*H_2CH$_2$CH$_2$C≡C), 53.8 (C^q), 81.7 (C≡*C*Ar), 88.1 (*C*≡CAr), 105.7 (OCO), 123.5 (ArC^q), 126.8 (CH=*C*HAr), 127.2 (ArCH), 127.4 (ArCH), 127.7 (ArCH), 128.2 (2 × ArCH), 129.3 (ArCH), 131.3 (*C*H=CHAr), 131.5 (2 × ArCH), 133.1 (ArC^q), 133.2 (ArC^q), 133.7 (ArC^q), 168.9 (2 × C=O);
The mass spectrum was not informative.

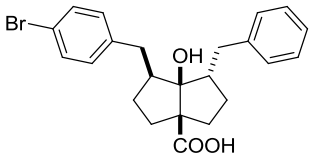
General procedure D – SmI_2–H_2O mediated cyclization cascades



***rac*-(1S,3aS,6S,6aR)-1-Benzyl-6-(2,4-dichlorobenzyl)-6a-hydroxyoctahydropentalene-3a-carboxylic acid (2e)**

To a stirred solution of 5-((*E*)-4-(2,4-dichlorophenyl)but-3-enyl)-2,2-dimethyl-5-((*E*)-4-phenylbut-3-enyl)-1,3-dioxane-4,6-dione **1e** (99 mg, 0.21 mmol, 1.0 eq) in THF (4.6 mL) and H_2O (4.6 mL, 1200 eq) at room temperature was added SmI_2 (0.1 M in THF, 17.0 mL, 1.70 mmol, 8.1 eq) dropwise using a syringe pump over 2 hours. After decolorization of the reaction mixture, the reaction was opened to air and H_2O (10 mL) and tartaric acid (25 mg) were added. The aqueous phase was extracted with ethyl acetate (3 × 20 mL) and the combined organic phases dried (Na_2SO_4 or $MgSO_4$) and concentrated *in vacuo*. Purification by column chromatography on silica gel, eluting with a gradient 10-20% ethyl acetate in hexane with 1% acetic acid gave 1-benzyl-6-(2,4-dichlorobenzyl)-6a-hydroxyoctahydropentalene-3a-carboxylic acid **2e** (46 mg, 0.11 mmol, 52%) as a white solid.

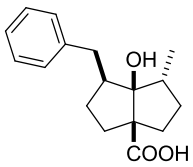
mp 164-166 °C;
ν_{max} (neat)/cm^{-1} 3381 (br.OH), 2933, 2865, 1774 (C=O), 1735, 1703, 1598, 1586, 1558, 1494, 1471, 1449, 1381, 1261, 1232, 1201, 1103, 1074, 1046, 1030, 962, 899, 864, 849, 806, 750, 696;
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.22 (1 H, td, *J* = 12.8, 6.2 Hz, 1 H from $CHCH_2CH_2$), 1.35 (1 H, qd, *J* = 12.6, 6.6 Hz, 1 H from $CHCH_2CH_2$), 1.47 - 1.59 (2 H, m, 1 H from $CHCH_2CH_2$, 1 H from $CHCH_2CH_2$), 1.59 - 1.73 (2 H, m, 2 H from $CHCH_2CH_2$), 2.06 - 2.27 (3 H, m, 2 × CH, 1 H from $CHCH_2CH_2$), 2.49 (1 H, dd, *J* = 12.9, 5.8 Hz, 1 H from $CHCH_2CH_2$), 2.68 - 2.84 (2 H, m, 2 H from $CHCH_2Ar$), 3.17 (1 H, dd, *J* = 13.6, 3.5 Hz, 1 H from $CHCH_2Ar$), 3.27 (1 H, dd, *J* = 12.7, 2.9 Hz, 1 H from $CHCH_2Ar$), 7.19 (2 H, s, 2 × ArH), 7.20 - 7.26 (3 H, m, 3 × ArH), 7.28 - 7.34 (2 H, m, 2 × ArH), 7.39 (1 H, s, ArH);
^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 27.6 ($CHCH_2CH_2$), 31.5 ($CHCH_2CH_2$), 33.5 ($CHCH_2Ar$), 35.0 ($CHCH_2CH_2$), 35.4 ($CHCH_2Ar$), 35.7 ($CHCH_2CH_2$), 45.3 (CH), 55.4 (CH), 64.3 (C^q), 92.8 (C^q), 126.0 (ArCH), 126.9 (ArCH), 128.4 (2 × ArCH), 128.8 (2 × ArCH), 129.3 (ArCH), 132.3 (ArCH, ArC^q), 134.6 (ArC^q), 138.0 (ArC^q), 141.3 (ArC^q), 181.8 (C=O);
m/z (ES+) 436 (21%), 441 ((M + Na), 100), 443 (93). (Found: (M + Na) 441.0981. $C_{23}H_{24}O_3Cl_2Na$ requires *M*, 441.0995).



***rac*-(1S,3aS,6S,6aR)-1-Benzyl-6-(4-bromobenzyl)-6a-hydroxyoctahydropentalene-3a-carboxylic acid (2f)**

As for general procedure D, reaction of 5-((*E*)-4-(4-bromophenyl)but-3-enyl)-2,2-dimethyl-5-((*E*)-4-phenylbut-3-enyl)-1,3-dioxane-4,6-dione **1f** (30 mg, 62.1 μmol, 1 eq) in THF (2.00 mL) and H_2O (1.34 mL, 1200 eq) with SmI_2 (0.1 M in THF, 5.0 mL, 0.50 mmol, 8.1 eq), after column chromatography on silica gel, eluting with a gradient 10-20% ethyl acetate in hexane with 1% acetic acid gave 1-benzyl-6-(4-bromobenzyl)-6a-hydroxyoctahydropentalene-3a-carboxylic acid **2f** (17 mg, 39.1 μmol, 63%) as a white solid.

mp 77-79 °C;
ν_{max} (neat)/cm^{-1} 3430 (br. OH), 3026, 2952, 2931, 2854, 1695 (C=O), 1610, 1511, 1453, 1246, 1177, 1098, 1034, 836, 807, 752, 699, 667;
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.12 - 1.23 (1 H, m, 1 H from CH_2CH$_2$CH), 1.49 (1 H, dd, *J* = 12.6, 6.1 Hz, 1 H from CH_2CH$_2$CH), 1.54 - 1.78 (4 H, m, 2 × CH_2CH), 1.95 - 2.05 (1 H, m, CH), 2.07 - 2.20 (2 H, m, CH, 1 H from CH_2CH$_2$CH), 2.41 - 2.61 (3 H, m, 2 × 1 H from CH_2Ar, 1 H from CH_2CH$_2$CH), 2.99 - 3.11 (1 H, m, 1 H from CH_2Ar), 3.22 - 3.33 (1 H, m, 1 H from CH_2Ar), 7.05 - 7.11 (2 H, m, 2 × ArH), 7.18 - 7.24 (3 H, m, 3 × ArH), 7.26 - 7.32 (2 H, m, 2 × ArH), 7.37 - 7.43 (2 H, m, 2 × ArH);
^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 27.6 (*C*H_2CH), 31.9 (*C*H_2CH), 34.8 (*C*H_2CH$_2$CH), 35.8 (CH_2Ar), 36.0 (CH_2Ar), 36.0 (*C*H_2CH$_2$CH), 48.0 (CH), 55.1 (CH), 64.4 (C^q), 92.6 (C^q), 126.9 (ArCH), 128.4 (2 × ArCH), 128.8 (ArCH), 128.8 (ArCH), 130.6 (ArCH), 130.5 (ArCH), 131.4 (2 × ArCH), 140.3 (ArC^q), 141.0 (ArC^q), 141.9 (ArC^q), 181.5 (C=O);
m/z (ES−) 427 ((M − H), 100%), 429 (58). (Found: (M − H) 427.0907. $C_{23}H_{24}O_3Br$ requires *M*, 427.0914).

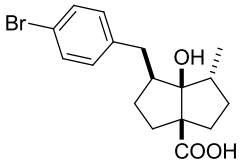


***rac*-(1S,3aS,6R,6aR)-1-Benzyl-6a-hydroxy-6-methyloctahydropentalene-3a-carboxylic acid (2a)**

As for general procedure D, reaction of (*E*)-5-(but-3-enyl)-2,2-dimethyl-5-(4-phenylbut-3-enyl)-1,3-dioxane-4,6-dione **1a** (30 mg, 91.4 μmol, 1.0 eq) in THF (2.0 mL) and H_2O (2.0 mL, 1200 eq) with SmI_2 (0.1 M in THF, 7.5 mL, 0.75 mmol, 8.3 eq), after column chromatography on silica gel, eluting with a gradient 10-20% ethyl acetate in hexane with 1% acetic acid gave 1-benzyl-6a-hydroxy-6-methyloctahydropentalene-3a-carboxylic acid **2a** (13 mg, 45.7 μmol, 50%) as an amorphous solid.

ν_{max} (neat)/cm^{-1} 3432 (br. OH), 3061, 3025, 2954, 2924, 2855, 1693 (C=O), 1496, 1453, 1377, 1282, 1220, 1200, 1059, 970, 907, 868, 807, 754, 698, 667;

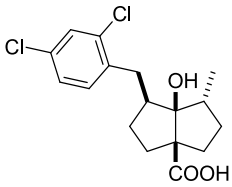
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.09 - 1.19 (1 H, m, 1 H from $CHCH_2CH_2$), 1.24 (3 H, d, *J* = 6.8 Hz, CH_3), 1.29 - 1.39 (1 H, m, 1 H from $CHCH_2CH_2$), 1.53 (1 H, dd, *J* = 12.9, 6.6 Hz, 1 H from $CHCH_2CH_2$), 1.62 (1 H, dd, *J* = 12.2, 6.2 Hz, 1 H from $CHCH_2CH_2$), 1.66 - 1.73 (1 H, m, 1 H from $CHCH_2CH_2$), 1.73 - 1.80 (1 H, m, 1 H from $CHCH_2CH_2$), 1.92 (1 H, qd, *J* = 6.1, 2.8 Hz, CH), 2.01 (1 H, dt, *J* = 13.0, 6.4 Hz, CH), 2.29 (1 H, td, *J* = 12.7, 6.7 Hz, 1 H from $CHCH_2CH_2$), 2.45 (1 H, ddd, *J* = 13.4, 6.3, 1.3 Hz, 1 H from $CHCH_2CH_2$), 2.52 (1 H, dd, *J* = 13.6, 11.3 Hz, 1 H from $CHCH_2Ar$), 3.03 (1 H, dd, *J* = 13.6, 2.5 Hz, 1 H from $CHCH_2Ar$), 7.17 - 7.23 (3 H, m, 3 × ArH), 7.28 - 7.32 (2 H, m, 2 × ArH);
^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 13.5 (CH_3), 30.6 ($CHCH_2CH_2$), 31.8 ($CHCH_2CH_2$), 34.9 ($CHCH_2CH_2$), 36.0 ($CHCH_2CH_2$), 36.4 ($CHCH_2Ar$), 47.3 (CH), 47.7 (CH), 64.3 (C^q), 93.0 (C^q), 125.8 (ArH), 128.3 (2 × ArH), 128.8 (2 × ArH), 142.2 (ArC^q), 181.6 (C=O);
m/z (ES−) 273 ((M − H), 100%), 274 (19). (Found: (M − H) 273.1493. $C_{17}H_{21}O_3$ requires *M*, 273.1496).



***rac*-(1S,3aS,6R,6aR)-1-(4-Bromobenzyl)-6a-hydroxy-6-methyloctahydropentalene-3a-carboxylic acid (2b)**

As for general procedure D, reaction of (*E*)-5-(4-(4-bromophenyl)but-3-en-1-yl)-5-(but-3-en-1-yl)-2,2-dimethyl-1,3-dioxane-4,6-dione **1b** (31 mg, 77.1 μmol, X eq) in THF (1.6 mL) and H_2O (1.6 mL, 1200 eq) with SmI_2 (0.1 M in THF, 6.0 mL, 0.60 mmol, 7.8 eq), after column chromatography on silica gel, eluting with a gradient 10-20% ethyl acetate in hexane with 1% acetic acid gave 1-(4-bromobenzyl)-6a-hydroxy-6-methyloctahydropentalene-3a-carboxylic acid **2b** (13 mg, 35.4 μmol, 46%) as a colorless oil.

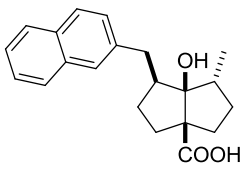
ν_{max} (neat)/cm^{-1} 3416 (br. OH), 2953, 2873, 1694 (C=O), 1486, 1458, 1402, 1283, 1220, 1159, 1131, 1100, 1072, 1011, 970, 906, 842, 795, 733, 671;
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.12 (1 H, dd, *J* = 13.0, 6.7 Hz, 1 H from $CH_2CH_2CHCH_2$), 1.21 (3 H, d, *J* = 6.8 Hz, CH_3), 1.31 (1 H, dd, *J* = 12.6, 6.7 Hz, CH_2CHCH_3), 1.52 - 1.55 (1 H, m, *J* = 12.6, 6.3 Hz, 1 H from $CH_2CH_2CHCH_3$), 1.56 - 1.69 (2 H, m, CH_2CHCH_2Ar), 1.75 (1 H, dt, *J* = 12.6, 6.3 Hz, 1 H from CH_2CHCH_3), 1.80 - 1.90 (1 H, m, $CHCH_2Ar$), 1.93 - 2.05 (1 H, m, $CHCH_3$), 2.28 (1 H, td, *J* = 12.6, 6.7 Hz, 1 H from $CH_2CH_2CHCH_3$), 2.40 - 2.52 (2 H, m, 1 H from $CH_2CH_2CHCH_2$, 1 H from CH_2Ar), 2.96 (1 H, dd, *J* = 13.9, 2.5 Hz, 1 H from CH_2Ar), 7.06 (2 H, d, *J* = 8.3 Hz, 2 × ArH), 7.40 (2 H, d, *J* = 8.3 Hz, 2 × ArH);
^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 13.5 (CH_3), 30.6 (CH_2CHCH_3), 31.7 (CH_2CHCH_2Ar), 34.9 ($CH_2CH_2CHCH_3$), 35.8 (CH_2Ar), 36.0 ($CH_2CH_2CHCH_2$), 47.2 (CH), 47.5 (CH), 64.3 (C^q), 92.9 (C^q), 119.5 (ArC^q), 130.6 (2 × ArCH), 131.3 (2 × ArCH), 141.2 (ArC^q), 181.5 (C=O);
m/z (ES−) 351 ((M − H), 100%), 353 (94). (Found: (M − H) 351.0595. $C_{17}H_{20}O_3Br$ requires *M*, 351.0601).



***rac*-(1S,3aS,6R,6aR)-1-(2,4-Dichlorobenzyl)-6a-hydroxy-6-methyloctahydropentalene-3a-carboxylic acid (2c)**

As for general procedure D, reaction of (*E*)-5-(but-3-en-1-yl)-5-(4-(2,4-dichlorophenyl)but-3-en-1-yl)-2,2-dimethyl-1,3-dioxane-4,6-dione **1c** (30 mg, 75.8 μmol, 1.0 eq) in THF (1.70 mL) and H_2O (1.65 mL, 1200 eq) with SmI_2 (0.1 M in THF, 6.0 mL, 0.60 mmol, 7.9 eq), after column chromatography on silica gel, eluting with a gradient 10-20% ethyl acetate in hexane with 1% acetic acid gave 1-(2,4-dichlorobenzyl)-6a-hydroxy-6-methyloctahydropentalene-3a-carboxylic acid **2c** (11 mg, 32.6 μmol, 43%) as a colorless oil.

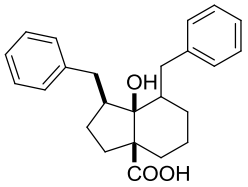
ν_{max} (neat)/cm^{-1} 3428 (br. OH), 2953, 2873, 1691 (C=O), 1586, 1560, 1471, 1382, 1272, 1216, 1159, 1102, 1048, 997, 969, 940, 904, 865, 849, 820, 755, 708, 668, 645;
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.16 (1 H, td, *J* = 12.9, 6.1 Hz, 1 H from CH_2CH$_2$CHCH$_2$), 1.23 (3 H, d, *J* = 7.1 Hz, CH_3), 1.35 (1 H, qd, *J* = 12.7, 6.8 Hz, 1 H from CH_2CHCH$_3$), 1.46 (1 H, dt, *J* = 11.8, 5.8 Hz, 1 H from CH_2CHCH$_2$Ar), 1.54 (1 H, dd, *J* = 12.7, 6.2 Hz, 1 H from CH_2CH$_2$CHCH$_3$), 1.63 (1 H, qd, *J* = 12.4, 6.3 Hz, 1 H from CH_2CHCH$_2$Ar), 1.76 (1 H, dt, *J* = 12.7, 6.2 Hz, 1 H from CH_2CHCH$_3$), 1.94 - 2.11 (2 H, m, 2 × CH), 2.29 (1 H, td, *J* = 12.7, 6.8 Hz, 1 H from CH_2CH$_2$CHCH$_3$), 2.42 - 2.50 (1 H, m, 1 H from CH_2CH$_2$CHCH$_2$), 2.74 (1 H, t, *J* = 13.7, 11.5 Hz, 1 H from CH$_2$Ar), 3.05 (1 H, dd, *J* = 13.7, 3.7 Hz, 1 H from CH$_2$Ar), 7.15 - 7.18 (2 H, m, 2 × ArH), 7.35 - 7.38 (1 H, m, ArH);
^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 13.3 (CH_3), 30.6 (*C*H$_2$CHCH$_3$), 31.5 (*C*H$_2$CHCH$_2$Ar), 33.2 (CH$_2$Ar), 35.1 (*C*H$_2$CH$_2$CHCH$_3$), 35.7 (*C*H$_2$CH$_2$CHCH$_2$), 45.0 (*C*HCH$_2$Ar), 47.4 (*C*HCH$_3$), 64.3 (C^q), 93.2 (C^q), 126.8 (ArCH), 129.2 (ArCH), 132.1 (ArC^q), 132.2 (ArCH), 134.6 (ArC^q), 138.2 (ArC^q), 182.0 (C=O);
m/z (ES−) 341 ((M − H), 100%), 343 (76). (Found: (M − H) 341.0701. $C_{17}H_{19}O_3Cl_2$ requires *M*, 341.0716).



***rac*-(1R,3aS,6S,6aR)-6a-Hydroxy-1-methyl-6-(naphthalen-2-ylmethyl)octahydropentalene-3a-carboxylic acid (2d)**

As for general procedure D, reaction of (*E*)-5-(but-3-en-1-yl)-2,2-dimethyl-5-(4-(naphthalen-2-yl)but-3-en-1-yl)-1,3-dioxane-4,6-dione **1d** (30 mg, 78.0 μmol, 1.0 eq) in THF (1.7 mL) and H_2O (1.7 mL, 1200 eq) with SmI_2 (0.1 M in THF, 6.5 mL, 0.65 mmol, 8.3 eq), after column chromatography on silica gel, eluting with a gradient 10-20% ethyl acetate in hexane with 1% acetic acid gave 6a-hydroxy-1-methyl-6-(naphthalen-2-ylmethyl)octahydropentalene-3a-carboxylic acid **2d** (11 mg, 34.2 μmol, 44%) as a colorless oil.

ν_{max} (neat)/cm^{-1} 3409 (br. OH), 3050, 2953, 2873, 1691 (C=O), 1599, 1507, 1457, 1378, 1282, 1222, 1205, 1159, 1125, 1099, 1057, 995, 970, 906, 855, 819, 729, 661, 648;
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.09 - 1.20 (1 H, m, 1 H from CH_2CH$_2$CHCH$_2$), 1.30 (3 H, d, *J* = 6.6 Hz, CH$_3$), 1.36 (1 H, dd, *J* = 12.6, 6.8 Hz, 1 H from CH_2CHCH$_3$), 1.55 (1 H, dd, *J* = 12.6, 6.3 Hz, 1 H from CH_2CH$_2$CHCH$_3$), 1.65 - 1.73 (2 H, m, CH_2CHCH$_2$Ar), 1.78 (1 H, dt, *J* = 12.6, 6.3 Hz, 1 H from CH_2CHCH$_3$), 1.98 - 2.09 (2 H, m, 2 × CH), 2.31 (1 H, td, *J* = 12.6, 6.8 Hz, 1 H from CH_2CH$_2$CHCH$_3$), 2.42 - 2.51 (1 H, m, 1 H from CH_2CH$_2$CHCH$_2$), 2.70 (1 H, dd, *J* = 13.7, 11.5 Hz, 1 H from CH$_2$Ar), 3.20 (1 H, dd, *J* = 13.7, 2.1 Hz, 1 H from CH$_2$Ar), 7.36 (1 H, d, *J* = 8.3 Hz, ArH), 7.40 - 7.49 (2 H, m, 2 × ArH), 7.63 (1 H, s, ArH), 7.75 - 7.84 (3 H, m, 3 × ArH);
^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 13.6 (CH$_3$), 30.6 (*C*H$_2$CHCH$_3$), 31.9 (*C*H$_2$CHCH$_2$Ar), 34.9 (*C*H$_2$CH$_2$CHCH$_3$), 36.0 (*C*H$_2$CH$_2$CHCH$_2$), 36.5 (CH$_2$Ar), 47.3 (CH), 47.7 (CH), 64.4 (C^q), 93.1 (C^q), 125.1 (ArH), 125.9 (ArH), 126.8 (ArH), 127.4 (ArH), 127.6 (ArH), 127.7 (ArH), 127.8 (ArH), 131.9 (ArC^q), 133.6 (ArC^q), 139.8 (ArC^q), 181.8 (C=O);
m/z (ES+) 307 (21%), 325 (45), 342 (100), 347 ((M + Na), 76), 348 (23). (Found: (M + Na) 347.1614. $C_{21}H_{24}O_3Na$ requires *M*, 347.1618).

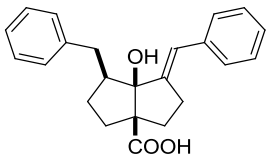


***rac*-(1S,3aS,7aR)-1,7-Dibenzyl-7a-hydroxyoctahydro-1H-indene-3a-carboxylic acid (2g)**

As for general procedure D, reaction of 2,2-dimethyl-5-((*E*)-4-phenylbut-3-enyl)-5-((*E*)-5-phenylpent-4-enyl)-1,3-dioxane-4,6-dione **1g** (30 mg, 71.0 μmol, 1.0 eq) in THF (2.00 mL) and H_2O (1.55 mL, 1200 eq) with SmI_2 (0.1 M in THF, 5.8 mL, 0.58 mmol, 8.1 eq), after column chromatography on silica gel, eluting with a gradient 10-20% ethyl acetate in hexane with 1% acetic acid gave 1,7-dibenzyl-7a-hydroxyoctahydro-1H-indene-3a-carboxylic acid **2g** (17 mg, 47.7 μmol, 67%) as a white solid and as a 1.3:1 mixture of diastereoisomers.

mp 68-70 °C;
ν_{max} (neat)/cm^{-1} 3433 (br. OH), 3061, 3025, 2939, 2869, 1688 (C=O), 1602, 1495, 1452, 1386, 1260, 1216, 1156, 1095, 1030, 751, 698;
For a 1.3:1 mixture of diastereoisomers:
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.13 - 1.32 (1 H, m, 1 H from CH$_2$), 1.37 - 1.58 (6 H, m, 6 H from CH$_2$), 1.59 - 1.77 (7 H, m, 7 H from CH$_2$), 1.77 - 1.89 (2 H, m, 2 H from CH$_2$), 2.04 - 2.27 (5 H, m, CH (major), CH (minor), 3 H from CH$_2$), 2.29 - 2.46 (3 H, m, 1 H from CH$_2$Ar (major), 1 H from CH$_2$Ar (minor), 1 H from CH$_2$), 2.58 (1 H, dd, *J* = 13.0, 10.7 Hz, 1 H from CH$_2$Ar (minor)), 2.63 - 2.73 (3 H, m, CH (major), CH (minor), 1 H from CH$_2$Ar (major)), 2.95 (1 H, dd, *J* = 13.0, 3.5 Hz, 1 H from CH$_2$Ar (minor)), 3.12 (1 H, dd, *J* = 13.4, 2.8 Hz, 1 H from CH$_2$Ar (minor)), 3.17 - 3.27 (1 H, m, 1 H from CH$_2$Ar (major)), 3.58 (1 H, d, *J* = 11.3 Hz, 1 H from CH$_2$Ar (major)), 7.13 - 7.24 (8 H, m, 8 × ArH), 7.25 - 7.34 (12 H, m, 12 × ArH);
^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 18.3 (CH$_2$), 23.0 (CH$_2$), 24.9 (CH$_2$), 27.5 (CH$_2$), 28.1 (2 × CH$_2$), 28.4 (CH$_2$), 31.9 (CH$_2$), 33.1 (CH$_2$), 33.6 (CH$_2$), 33.7 (CH$_2$Ar (minor)), 36.3 (CH$_2$Ar (minor)), 37.4 (CH$_2$Ar (major)), 37.7 (CH$_2$Ar (major)), 41.9 (CH (major)), 42.7 (CH (major)), 46.9 (CH (minor)), 48.0 (CH (minor)), 54.4 (C^q), 58.7 (C^q), 83.8 (C^q), 84.9 (C^q), 125.8 (2 × ArCH), 125.9 (2 × ArCH),

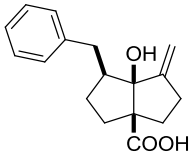
125.9 (2 × ArCH), 128.2 (2 × ArCH), 128.3 (2 × ArCH), 128.4 (2 × ArCH), 128.8 (2 × ArCH), 128.9 (2 × ArCH), 129.1 (2 × ArCH), 129.2 (2 × ArCH), 141.3 (ArC^q), 141.6 (ArC^q), 141.8 (ArC^q), 141.9 (ArC^q), 182.0 (C=O), 182.2 (C=O);
m/z (ES−) 363 ((M − H), 100%), 364 (25). (Found: (M − H) 363.1956. $C_{24}H_{27}O_3$ requires *M*, 363.1965).



***rac*-(1S,3aR,6aS,*E*)-1-Benzyl-6-benzylidene-6a-hydroxyoctahydropentalene-3a-carboxylic acid (2j)**

As for general procedure D, reaction of (*E*)-2,2-dimethyl-5-(4-phenylbut-3-en-1-yl)-5-(4-phenylbut-3-yn-1-yl)-1,3-dioxane-4,6-dione **1j** (30 mg, 75.0 μmol, 1 eq) in THF (2.00 mL) and H_2O (1.6 mL, 1200 eq) with SmI_2 (0.1 M in THF, 5.9 mL, 0.59 mmol, 8.0 eq), after column chromatography on silica gel, eluting with a 30% ethyl acetate in hexane with 1% acetic acid gave (*E*)-1-benzyl-6-benzylidene-6a-hydroxyoctahydropentalene-3a-carboxylic acid **2j** (12.0 mg, 34.0 μmol, 46%) as a colorless oil and as a 2:1 mixture of double-bond isomers.

ν_{max} (neat)/cm^{-1} 3484 (br. OH), 3275, 3060, 2942, 2867, 1740 (C=O), 1692 (C=O), 1600, 1491, 1451;
For the major double-bond isomer:
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.66 - 1.77 (1 H, m, 1 H from C*H*$_2$CH$_2$CH), 1.78 - 1.88 (3 H, m, CH$_2$C*H*$_2$CH, 1 H from C*H*$_2$CH$_2$C=C), 2.07 - 2.17 (1 H, m, CH), 2.33 - 2.50 (2 H, m, 1 H from C*H*$_2$CH$_2$CH, 1 H from C*H*$_2$CH$_2$C=C), 2.54 - 2.64 (1 H, m, 1 H from CH$_2$Ar), 2.72 - 2.84 (1 H, m, 1 H from C*H*$_2$C=C), 2.86 - 2.97 (1 H, m, 1 H from C*H*$_2$C=C), 2.97 - 3.05 (1 H, m, 1 H from CH$_2$Ar), 6.57 (1 H, s, C=CH), 7.11 - 7.20 (3 H, m, 3 × ArCH), 7.21 - 7.32 (3 H, m, 3 × ArCH), 7.32 - 7.40 (4 H, m, 4 × ArCH);
^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 27.9 (*C*H$_2$C=CH), 30.6 (CH$_2$*C*H$_2$CH), 32.8 (*C*H$_2$CH$_2$CH), 33.8 (CH$_2$Ar), 34.7 (*C*H$_2$CH$_2$C=CH), 51.3 (CH$_2$CH$_2$*C*H), 62.4 (C^q), 92.4 (C^q), 121.9 (C=*C*H), 125.7 (ArCH), 126.6 (ArCH), 128.3 (2 × ArCH), 128.4 (2 × ArCH), 128.7 (2 × ArCH), 128.9 (2 × ArCH), 137.5 (ArC^q), 141.7 (ArC^q), 146.9 (*C*=CH), 181.1 (C=O);
m/z (ES+) 151 (44%), 371 ((M + Na), 100), 372 (34). (Found: (M + Na) 371.1612. $C_{23}H_{24}O_3Na$ requires *M*, 371.1618).

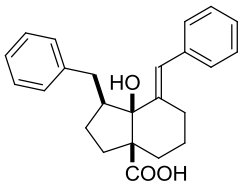


***rac*-(1S,3aR,6aS)-1-Benzyl-6a-hydroxy-6-methyleneoctahydropentalene-3a-carboxylic acid (2i)**

As for general procedure D, reaction of (*E*)-5-(But-3-yn-1-yl)-2,2-dimethyl-5-(4-phenylbut-3-en-1-yl)-1,3-dioxane-4,6-dione **1i** (30 mg, 92.0 μmol, 1 eq) in THF (2.00 mL) and H_2O (1.99 mL, 1200 eq) with SmI_2 (0.1 M in THF, 7.4 mL, 0.74 mmol, 8.0 eq), after column chromatography on silica gel,

eluting with a 30% ethyl acetate in hexane with 1% acetic acid gave 1-benzyl-6a-hydroxy-6-methyleneoctahydropentalene-3a-carboxylic acid **2i** (16 mg, 59.0 μmol, 64%) as a colorless oil.

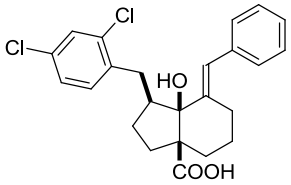
ν_{max} (neat)/cm^{-1} 3083, 3061, 3024, 2951, 1693 (C=O), 1603, 1495, 1453, 1374, 1281;
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.56 (1 H, dt, *J* = 13.4, 8.7 Hz, 1 H from C*H*$_2$CH$_2$CH), 1.65 - 1.73 (1 H, m, 1 H from C*H*$_2$CH$_2$C=CH$_2$), 1.73 - 1.81 (2 H, m, C*H*$_2$CH), 1.92 - 2.02 (1 H, m, CH$_2$C*H*), 2.32 (1 H, ddd, *J* = 13.4, 8.7, 7.2 Hz, 1 H from C*H*$_2$CH$_2$C=CH$_2$), 2.45 - 2.51 (1 H, m, 1 H from C*H*$_2$CH$_2$CH), 2.52 - 2.60 (3 H, m, 1 H from CH$_2$Ar and C*H*$_2$C=CH$_2$), 2.94 (1 H, dd, *J* = 13.6, 3.3 Hz, 1 H from CH$_2$Ar), 5.00 - 5.02 (1 H, m, 1 H from C=CH$_2$), 5.13 - 5.15 (1 H, m, 1 H from C=CH$_2$), 7.14 - 7.21 (3 H, m, 3 × ArCH), 7.24 - 7.30 (2 H, m, 2 × ArCH);
^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 29.3 (*C*H$_2$C=CH$_2$), 30.9 (*C*H$_2$CH$_2$CH), 33.7 (CH$_2$*C*H$_2$CH), 33.9 (CH$_2$Ar), 34.3 (*C*H$_2$CH$_2$C=CH$_2$), 51.5 (CH$_2$CH$_2$*C*H), 63.4 (C^q), 91.1 (C^q), 106.1 (C=*C*H$_2$), 125.7 (ArCH), 128.2 (2 × ArCH), 128.9 (2 × ArCH), 141.8 (ArC^q), 154.9 (*C*=CH$_2$), 181.4 (C=O);
m/z (ES−) 271 ((M − H), 100%). (Found: (M − H) 271.1339. $C_{17}H_{19}O_3$ requires *M*, 271.1339).



***rac*-(1S,3aS,7aS,*E*)-1-Benzyl-7-benzylidene-7a-hydroxyoctahydro-1H-indene-3a-carboxylic acid (2h)**

As for general procedure D, reaction of (*E*)-2,2-dimethyl-5-(4-phenylbut-3-en-1-yl)-5-(5-phenylpent-4-yn-1-yl)-1,3-dioxane-4,6-dione **1h** (30 mg, 72.0 μmol, 1 eq) in THF (2.0 mL) and H_2O (1. 6 mL, 1200 eq) with SmI_2 (0.1 M in THF, 5.77 mL, 0.58 mmol, 8.0 eq), after column chromatography on silica gel, eluting with 30% ethyl acetate in hexane and 1% acetic acid gave (*E*)-1-benzyl-7-benzylidene-7a-hydroxyoctahydro-1H-indene-3a-carboxylic acid **2h** (14 mg, 39.0 μmol, 54%) as a colorless oil and as a 10:1 mixture of double-bond isomers.

ν_{max} (neat)/cm^{-1} 3438 (br. OH), 3273, 3024, 2937, 2871, 1690 (C=O), 1493, 1452, 1278, 1075;
For the major double-bond isomer:
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.30 - 1.46 (1 H, m, 1 H from C*H*$_2$CH$_2$C=C), 1.57 - 1.87 (4 H, m, 1 H from CH$_2$C*H*$_2$CH, 1 H from C*H*$_2$CH$_2$CH, 1 H from C*H*$_2$CH$_2$CH$_2$C=C, 1 H from C*H*$_2$CH$_2$C=C), 1.93 (1 H, td, 1 H from C*H*$_2$C=C), 2.06 (1 H, t, *J* = 13.0 Hz, 1 H from CH$_2$C*H*$_2$CH), 2.21 (1 H, d, *J* = 13.9 Hz, 1 H from C*H*$_2$CH$_2$CH$_2$C=C), 2.39 (1 H, td, *J* = 12.3, 5.4 Hz, 1 H from C*H*$_2$CH$_2$CH), 2.51 - 2.66 (2 H, m, CH, 1 H from CH$_2$Ar), 2.85 (1 H, dd, *J* = 12.9, 2.3 Hz, 1 H from CH$_2$Ar), 2.97 (1 H, d, *J* = 14.9 Hz, 1 H from C*H*$_2$C=C), 6.91 (1 H, s, C=CH), 7.13 - 7.37 (10 H, m, ArCH);
^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 24.1 (*C*H$_2$CH$_2$C=C), 26.7 (*C*H$_2$C=C), 27.3 (CH$_2$*C*H$_2$CH), 34.2 (*C*H$_2$CH$_2$CH$_2$C=C, *C*H$_2$CH$_2$CH), 34.5 (*C*H$_2$Ar), 46.7 (CH), 59.5 (C^q), 84.1 (C^q), 124.6 (C=*C*H), 125.6 (ArCH), 126.2 (ArCH), 128.0 (2 × ArCH), 128.3 (2 × ArCH), 128.8 (2 × ArCH), 129.2 (2 × ArCH), 138.1 (ArC^q), 141.2 (ArC^q), 142.0 (*C*=CH), 182.1 (C=O);
m/z (ES+) 279 (33%), 385 ((M + Na), 91), 449 (57), 465 (45), 481 (100), 483 (53). Found: (M + Na) 385.1775. $C_{24}H_{26}O_3Na$ requires 385.1775.

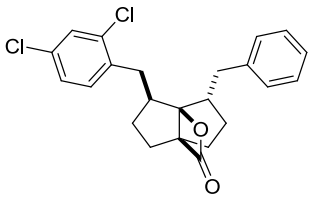


***rac*-(1S,3aS,7aS,*E*)-7-Benzylidene-1-(2,4-dichlorobenzyl)-7a-hydroxyoctahydro-1H-indene-3a-carboxylic acid (2k)**

As for general procedure D, reaction of (*E*)-5-(4-(2,4-dichlorophenyl)but-3-en-1-yl)-2,2-dimethyl-5-(5-phenylpent-4-yn-1-yl)-1,3-dioxane-4,6-dione **1k** (31 mg, 63.9 μmol, 1 eq) in THF (1.4 mL) and H_2O (1.4 mL, 1200 eq) with SmI_2 (0.1 M in THF, 5.00 mL, 0.50 mmol, 8.0 eq), after column chromatography on silica gel, eluting with 30% ethyl acetate in hexane and 1% acetic acid gave (*E*)-7-benzylidene-1-(2,4-dichlorobenzyl)-7a-hydroxyoctahydro-1H-indene-3a-carboxylic acid **2k** (18 mg, 42.0 μmol, 66%) as a white solid and as a 10:1 mixture of double-bond isomers.

mp 175-177 °C;
ν_{max} (neat)/cm^{-1} 3477 (br. OH), 3077, 3057, 3020, 2942, 2867, 1683 (C=O), 1583, 1471, 1445, 1384, 1342, 1291, 1259, 1231, 1165, 1103, 1049, 906, 866, 846, 816, 730, 699, 648;
For the major double-bond isomer:
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.25 - 1.41 (1 H, m, 1 H from CH_2CH$_2$C=CH), 1.61 - 1.71 (1 H, m, 1 H from CH_2CH$_2$C=CH), 1.72 - 1.80 (2 H, m, 1 H from CH_2CH$_2$CH, 1 H from CH_2CH$_2$CH$_2$C=CH), 1.80 - 1.88 (2 H, m, CH$_2$CH_2CH), 2.06 - 2.16 (1 H, m, 1 H from CH_2C=CH), 2.17 - 2.24 (1 H, m, 1 H from CH_2CH$_2$CH$_2$C=CH), 2.34 - 2.44 (1 H, m, 1 H from CH_2CH$_2$CH), 2.56 (1 H, dd, *J* = 13.3, 10.1 Hz, 1 H from CH_2Ar), 2.65 - 2.76 (1 H, m, CH), 2.89 - 2.97 (1 H, m, 1 H from CH_2C=CH), 3.05 (1 H, dd, *J* = 13.3, 3.4 Hz, 1 H from CH_2Ar), 6.89 (1 H, s, C=CH), 7.10 - 7.17 (2 H, m, 2 × ArH), 7.17 - 7.25 (3 H, m, 3 × ArH), 7.31 - 7.37 (3 H, m, 3 × ArH);
^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 24.0 (*C*H$_2$CH$_2$C=CH), 26.8 (*C*H$_2$C=CH), 27.0 (CH$_2$*C*H$_2$CH), 32.2 (CH$_2$Ar), 34.1 (*C*H$_2$CH$_2$CH), 34.4 (*C*H$_2$CH$_2$CH$_2$C=CH), 44.0 (CH), 59.5 (C^q), 84.0 (C^q), 124.5 (C=*C*H), 126.2 (ArCH), 126.8 (ArCH), 128.0 (2 × ArCH), 129.1 (2 × ArCH), 129.2 (ArCH), 132.1 (ArCH), 132.2 (*C*=CH), 134.5 (ArC^q), 137.9 (ArC^q), 138.0 (ArC^q), 141.1 (ArC^q), 182.3 (C=O);

Lactonization



***rac*-(3S,3aR,4S,6aS)-3-Benzyl-4-(2,4-dichlorobenzyl)hexahydro-3a,6a-(epoxymethano)pentalen-7-one (6)**

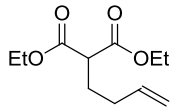
To a stirred solution of 1-benzyl-6-(2,4-dichlorobenzyl)-6a-hydroxyoctahydropentalene-3a-carboxylic acid **2e** (23 mg, 54.9 μmol, 1.0 eq) and benzoyl chloride (7.0 μL, 60.3 μmol, 1.1 eq) in THF (1.0 mL), triethylamine (16.0 μL, 114.8 μmol, 2.1 eq) was added dropwise. 4-dimethylaminopyridine (3 mg, 23.0 μmol, 0.4 eq) was then added and the reaction stirred at room temperature during 20 hours. The

reaction was quenched with HCl (1N, 1 mL), H_2O added (4 mL), and the aqueous phase extracted with ethyl acetate (3 × 10 mL). The combined organic phases were dried (Na_2SO_4 or $MgSO_4$) and concentrated *in vacuo*. Purification by column chromatography on silica gel, eluting with 5% ethyl acetate in hexane gave 3-benzyl-4-(2,4-dichlorobenzyl)hexahydro-3a,6a-(epoxymethano)pentalen-7-one **6** (19 mg, 47.3 μmol, 86%) as a white solid.

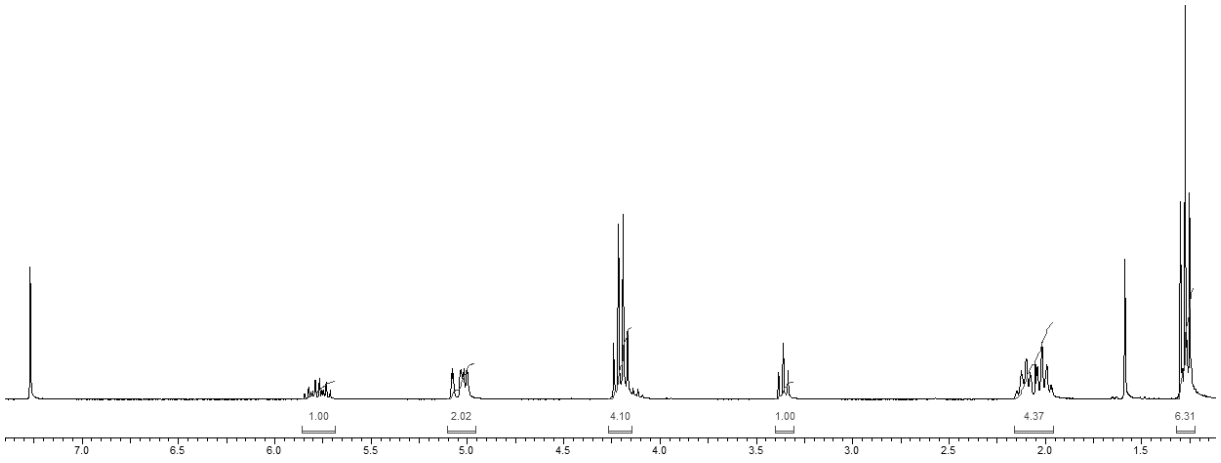
mp 129-131 °C;
ν_{max} (neat)/cm^{-1} 3084, 3059, 3023, 2954, 2863, 1817 (C=O), 1587, 1559, 1472, 1453, 1382, 1263, 1178, 1119, 1050, 1030, 846, 819, 738, 699;
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.43 - 1.50 (1 H, m, 1 H from C*H*$_2$CH$_2$CH), 1.50 - 1.56 (1 H, m, 1 H from C*H*$_2$CH$_2$CH), 1.75 - 1.83 (1 H, m, 1 H from CH$_2$C*H*$_2$CH), 1.87 - 1.96 (1 H, m, 1 H from C*H*$_2$Ar), 1.99 - 2.09 (3 H, m, CH, 1 H from CH$_2$C*H*$_2$CH, 1 H from C*H*$_2$CH$_2$CH), 2.09 - 2.15 (2 H, m, , 1 H from C*H*$_2$Ar, 1 H from CH$_2$C*H*$_2$CH), 2.15 - 2.22 (1 H, m, 1 H from C*H*$_2$CH$_2$CH), 2.33 (1 H, dt, *J* = 12.9, 6.4 Hz, 1 H from CH$_2$C*H*$_2$CH), 2.54 - 2.64 (1 H, m, CH), 2.89 (1 H, dd, *J* = 13.2, 9.8 Hz, , 1 H from C*H*$_2$Ar), 3.06 (1 H, dd, *J* = 13.2, 5.5 Hz, 1 H from C*H*$_2$Ar), 6.69 - 6.74 (2 H, m, 2 × ArH), 7.15 - 7.21 (1 H, m, ArH), 7.22 - 7.26 (2 H, m, 2 × ArH), 7.28 - 7.32 (2 H, m, 2 × ArH), 7.41 (1 H, d, *J* = 1.5 Hz, ArH);
^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 27.2 (*C*H$_2$CH$_2$CH), 29.3 (*C*H$_2$CH$_2$CH), 32.2 (*C*H$_2$CH), 32.8 (CH$_2$Ar), 35.2 (CH$_2$Ar), 36.4 (*C*H$_2$CH), 38.9 (CH), 42.9 (CH), 75.8 (C^q), 100.2 (C^q), 126.3 (ArCH), 127.2 (ArCH), 128.5 (2 × ArCH), 128.8 (2 × ArCH), 129.4 (ArCH), 132.7 (ArCH), 133.3 (ArC^q), 134.8 (ArC^q), 136.4 (ArC^q), 139.3 (ArC^q), 174.1 (C=O);
m/z (ES+) 435 ((M + Na), 100%), 437 (94), 439 (30). (Found: (M + NH_4) 418.1324. $C_{23}H_{26}NO_2Cl_2$ requires *M*, 418.1336).

NMR spectra

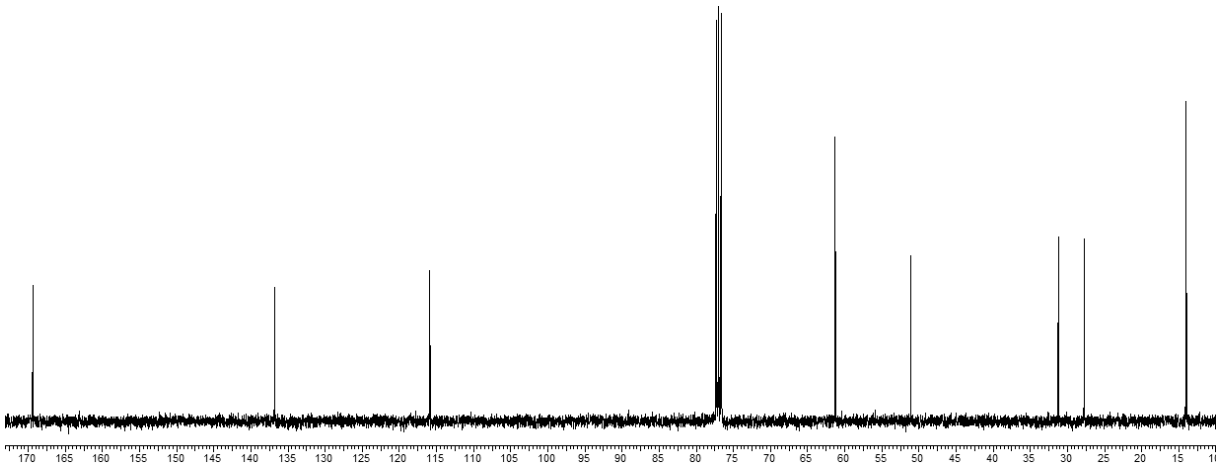
Diethyl 2-(but-3-en-1-yl)malonate from page S4



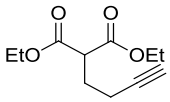
^{1}H NMR (400 MHz, $CDCl_3$):



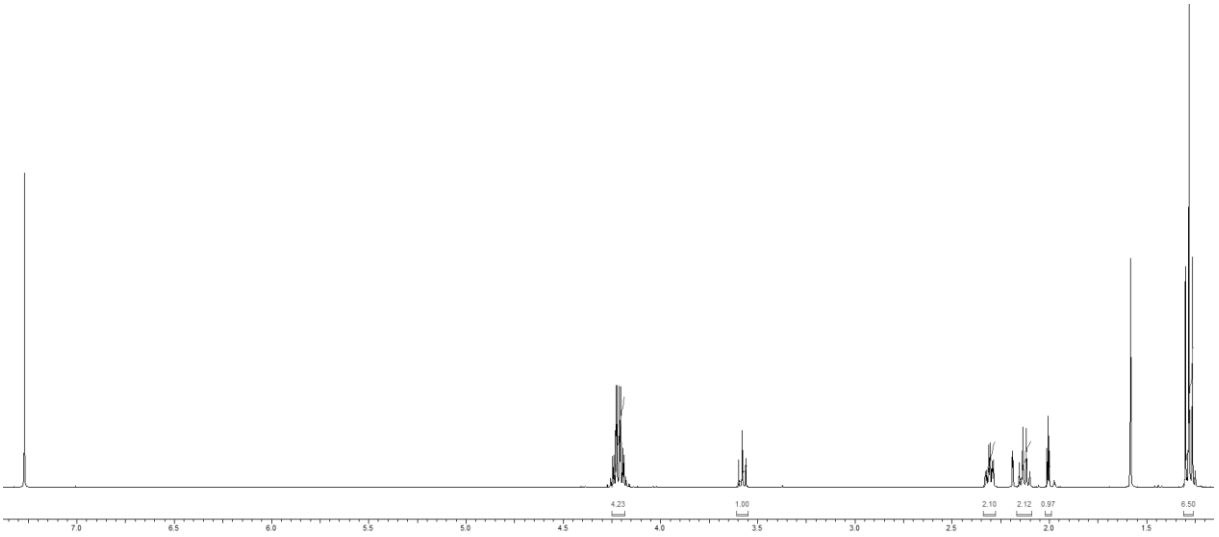
^{13}C NMR (100 MHz, $CDCl_3$):



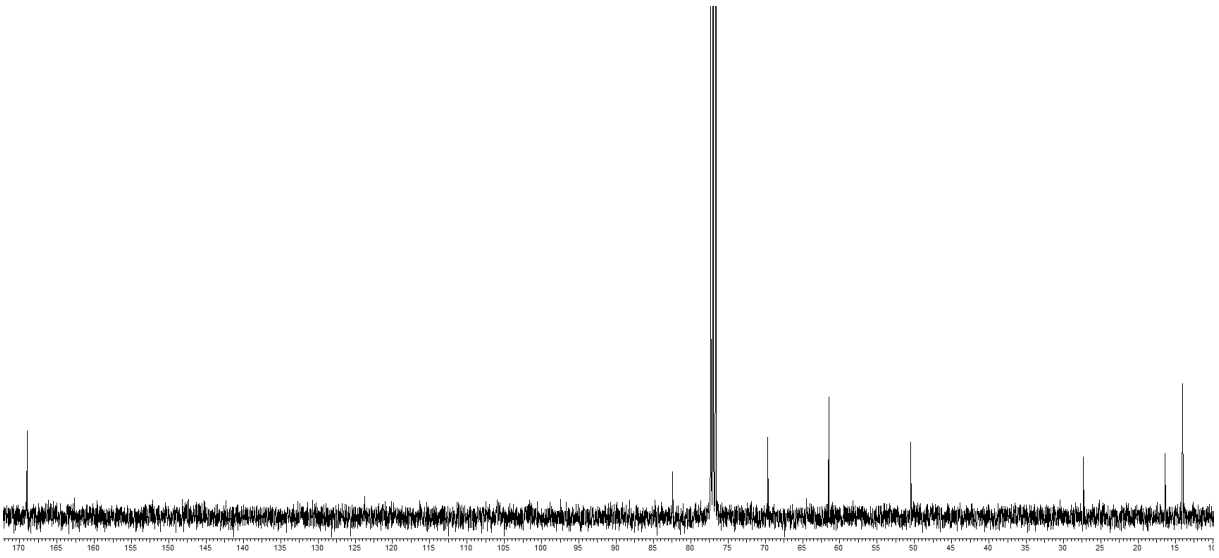
Diethyl 2-(but-3-yn-1-yl)malonate from page S5



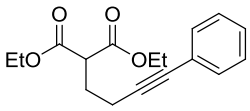
^{1}H NMR (400 MHz, $CDCl_3$):



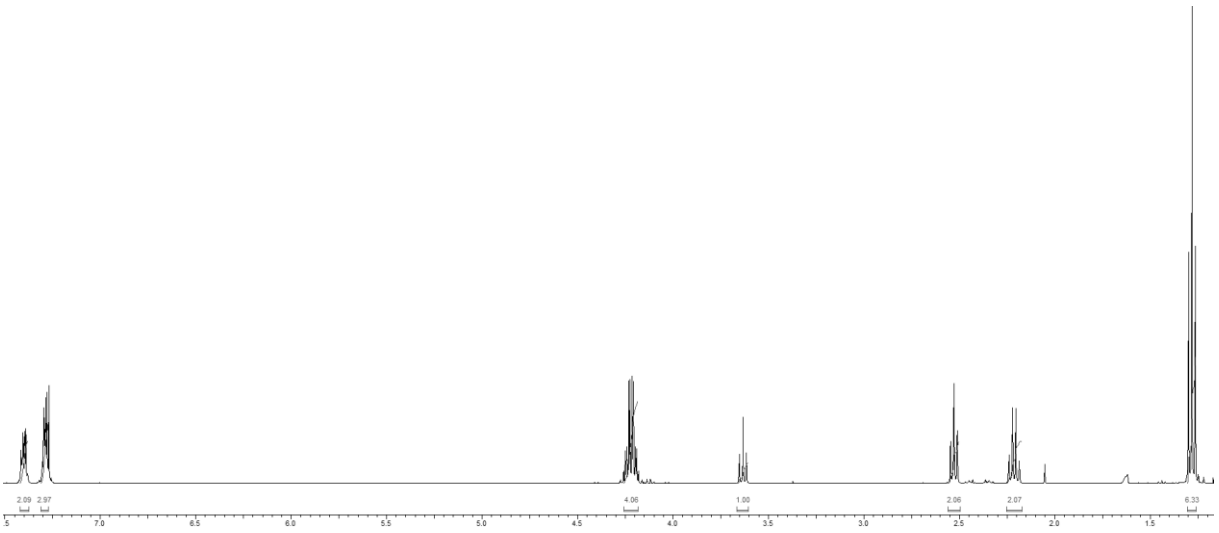
^{13}C NMR (100 MHz, $CDCl_3$):



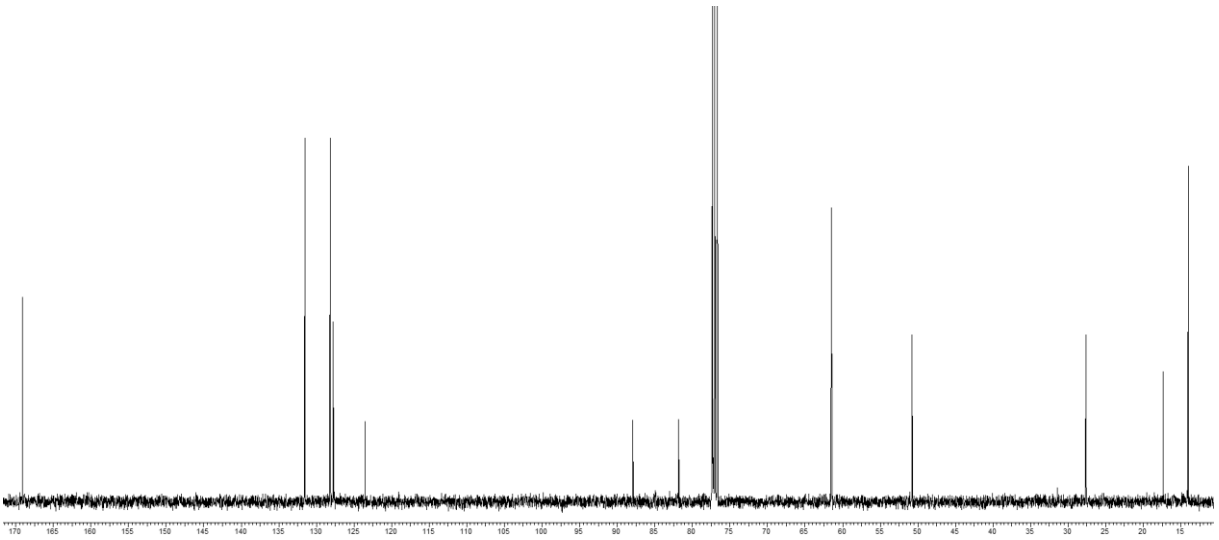
Diethyl 2-(4-phenylbut-3-yn-1-yl)malonate from page S5



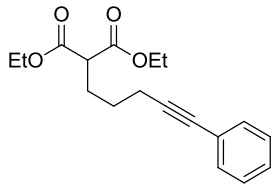
^{1}H NMR (400 MHz, $CDCl_3$):



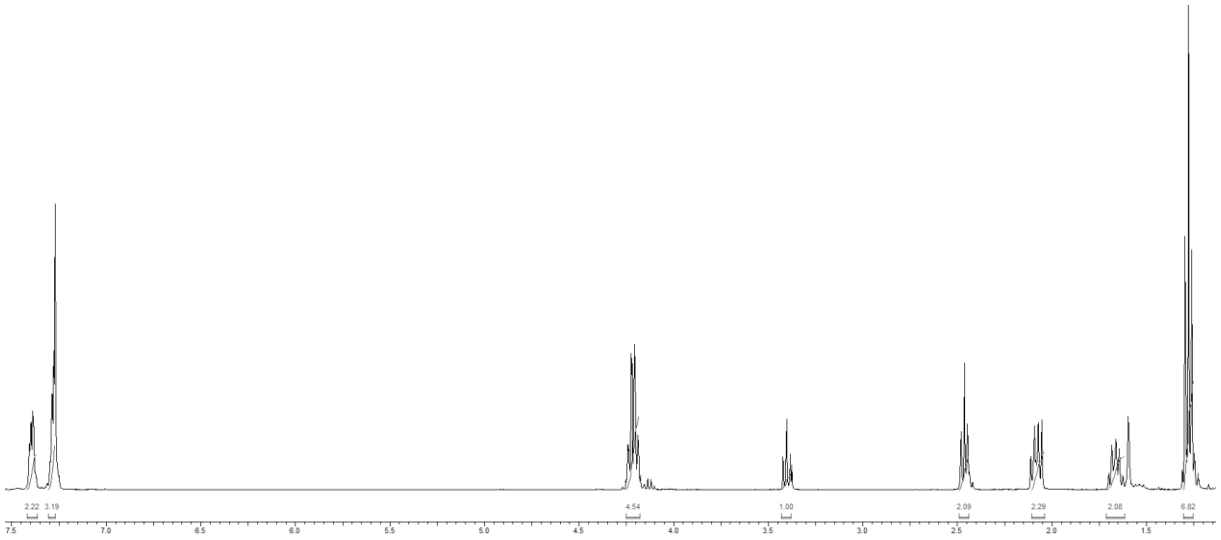
^{13}C NMR (100 MHz, $CDCl_3$):



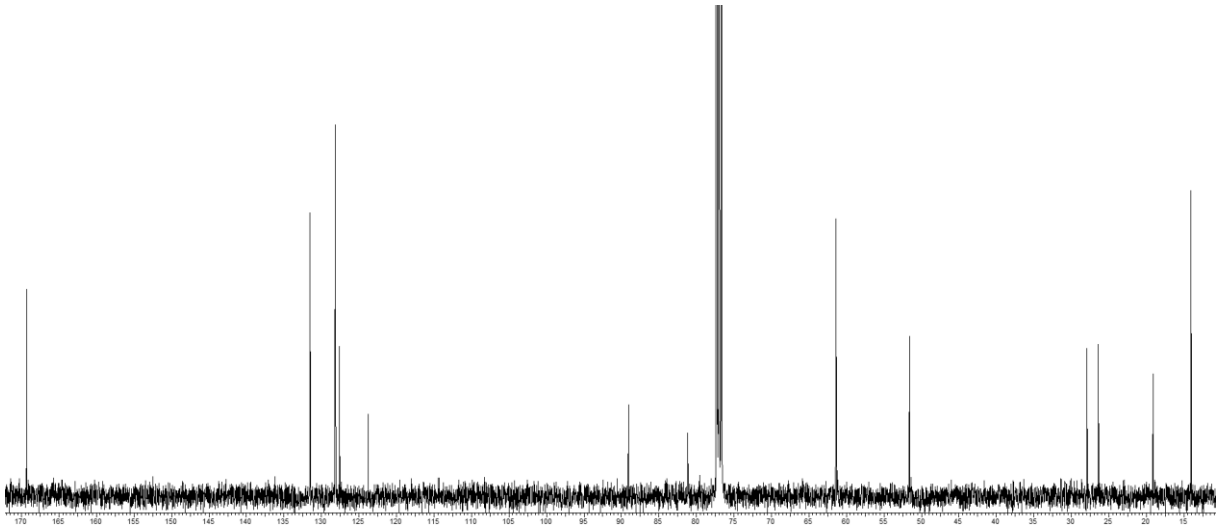
Diethyl 2-(5-phenylpent-4-yn-1-yl)malonate from page S6



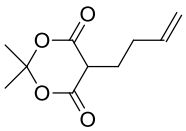
^{1}H NMR (400 MHz, $CDCl_3$):



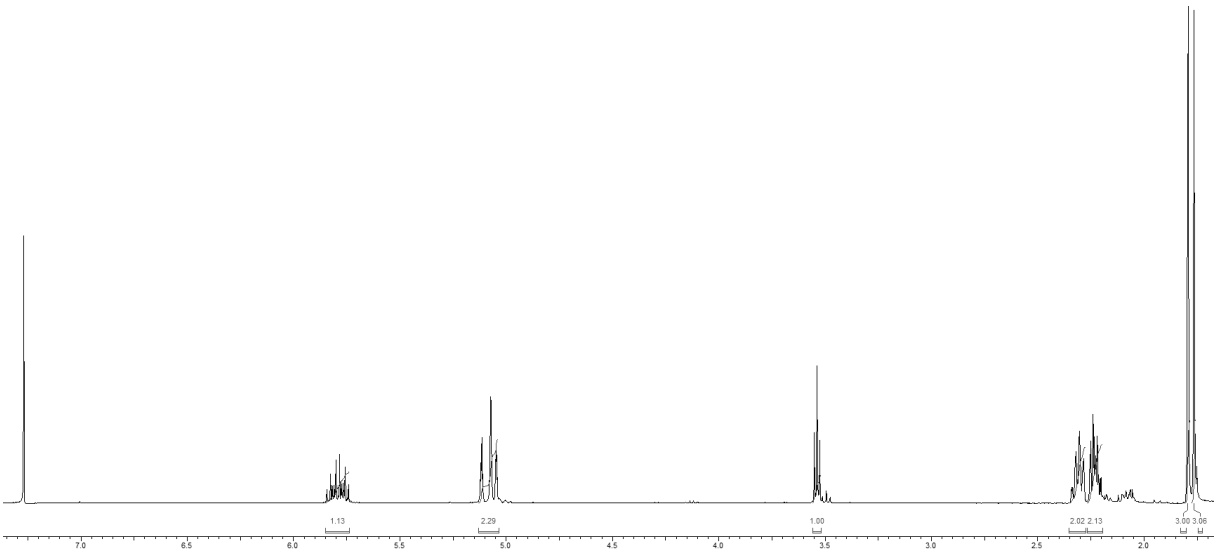
^{13}C NMR (100 MHz, $CDCl_3$):



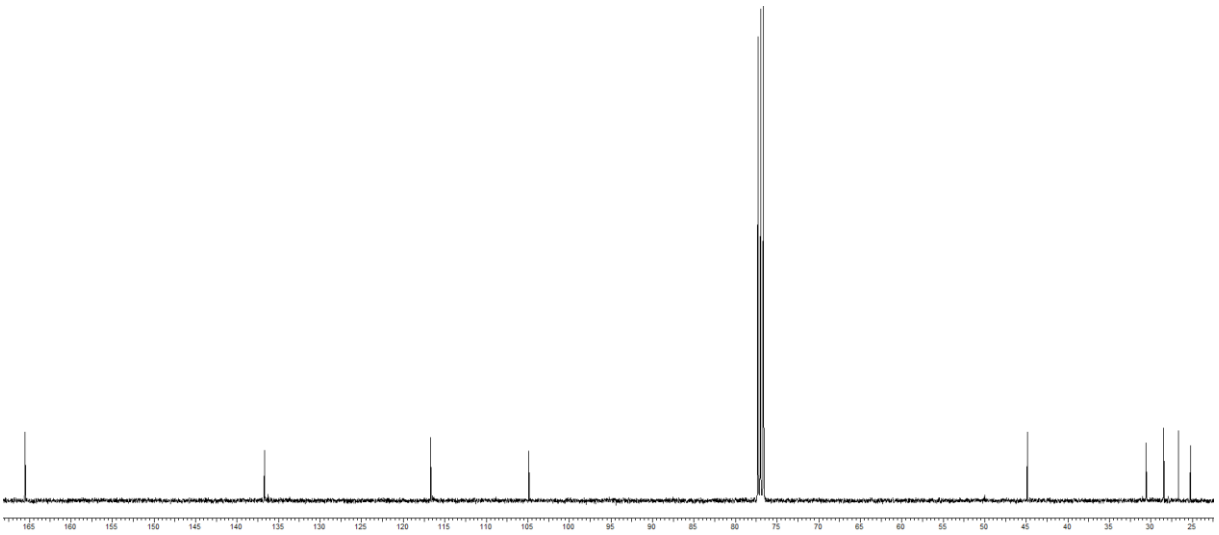
5-(But-3-enyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (4) from page S6



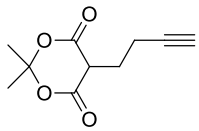
^{1}H NMR (400 MHz, $CDCl_3$):



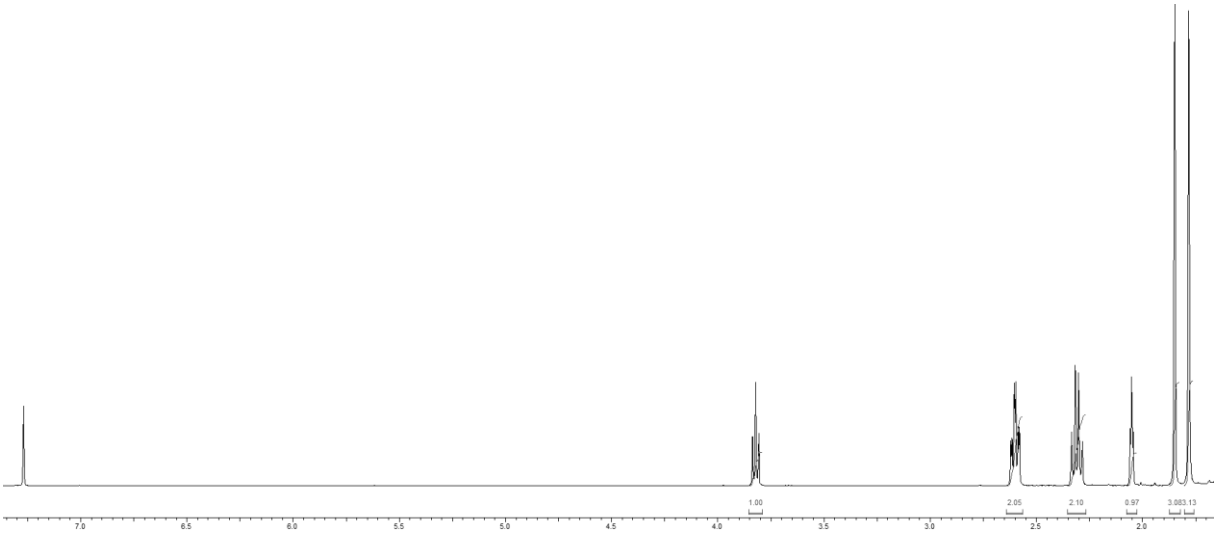
^{13}C NMR (100 MHz, $CDCl_3$):



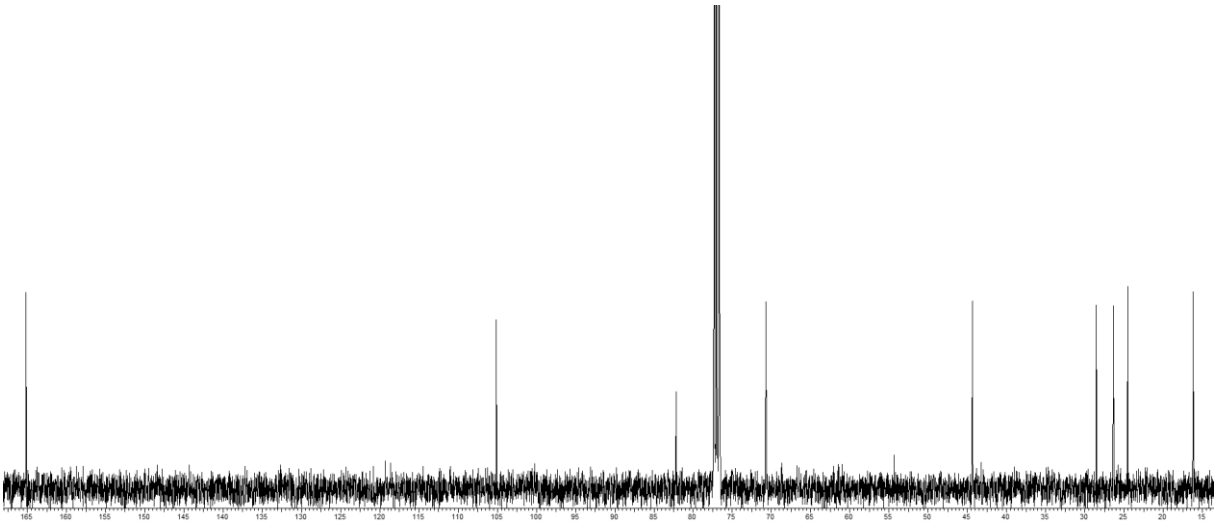
5-(But-3-yn-1-yl)-2,2-dimethyl-1,3-dioxane-4,6-dione from page S7



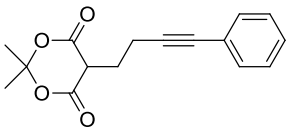
^{1}H NMR (400 MHz, $CDCl_3$):



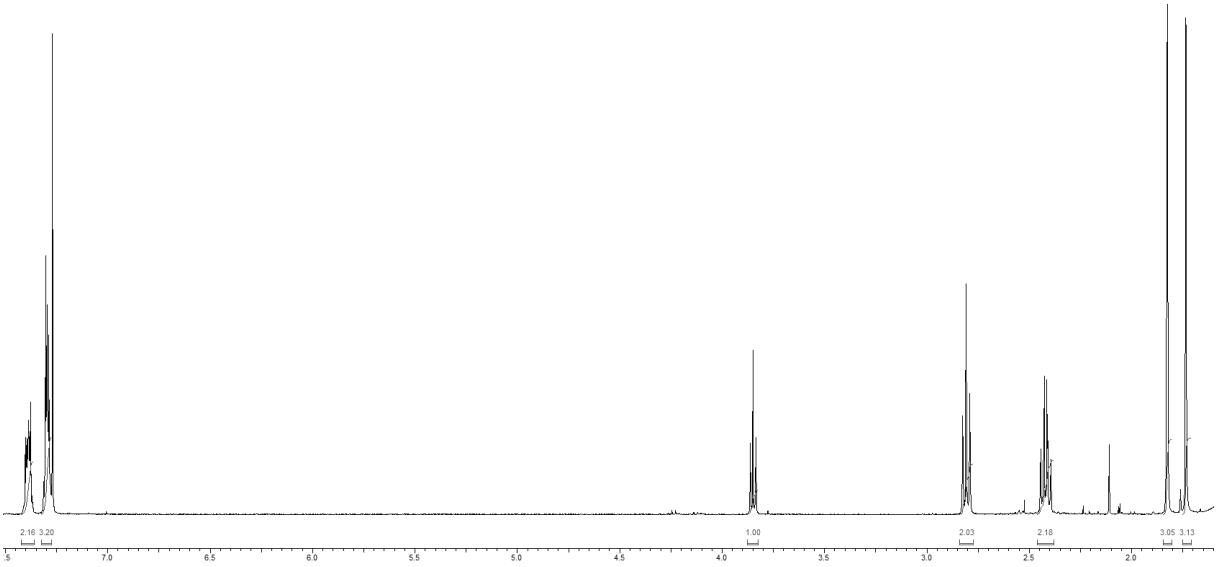
^{13}C NMR (100 MHz, $CDCl_3$):



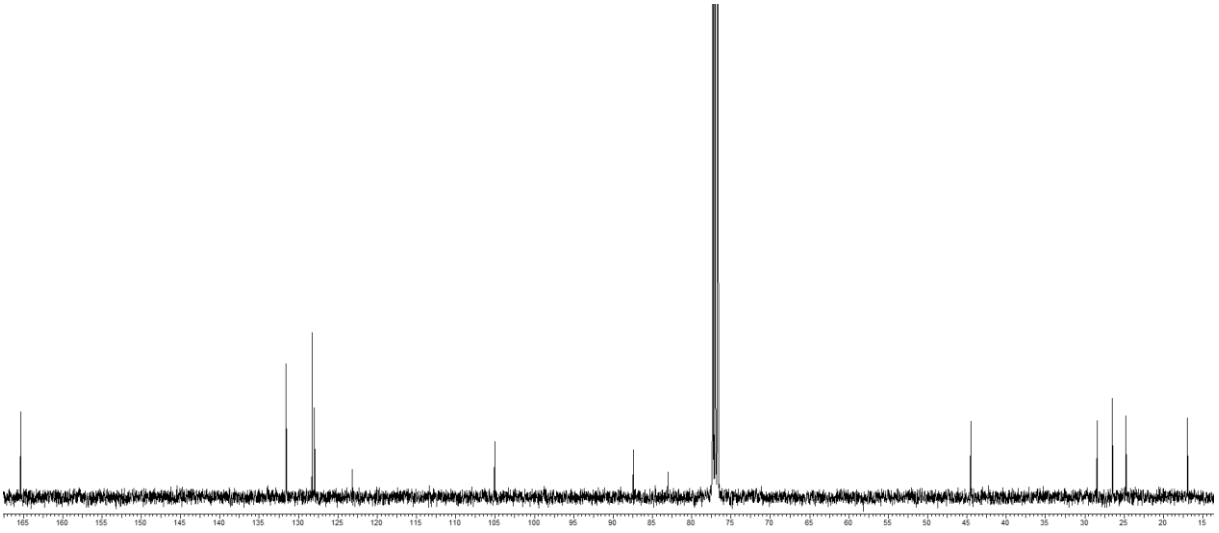
2,2-Dimethyl-5-(4-phenylbut-3-yn-1-yl)-1,3-dioxane-4,6-dione from page S7



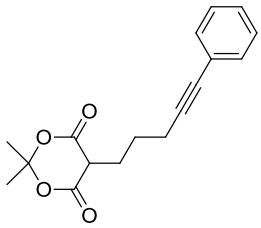
^{1}H NMR (400 MHz, $CDCl_3$):



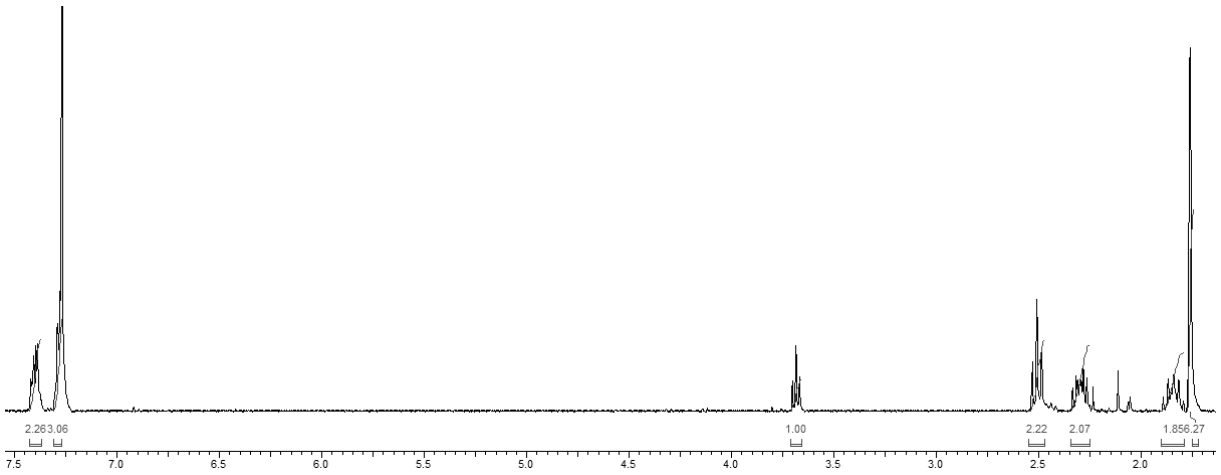
^{13}C NMR (100 MHz, $CDCl_3$):



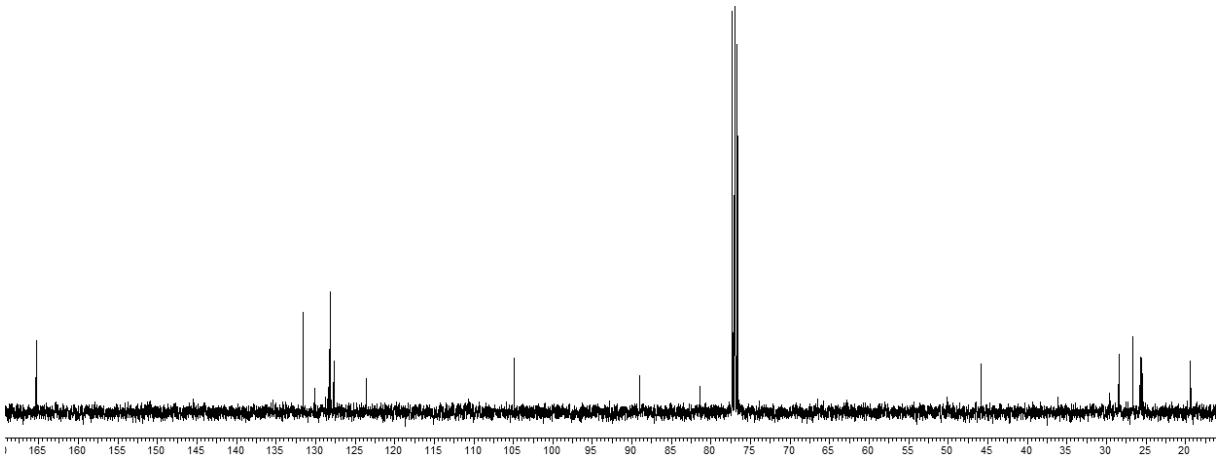
2,2-Dimethyl-5-(5-phenylpent-4-yn-1-yl)-1,3-dioxane-4,6-dione from page S8



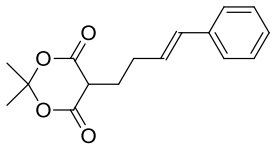
^{1}H NMR (300 MHz, $CDCl_3$):



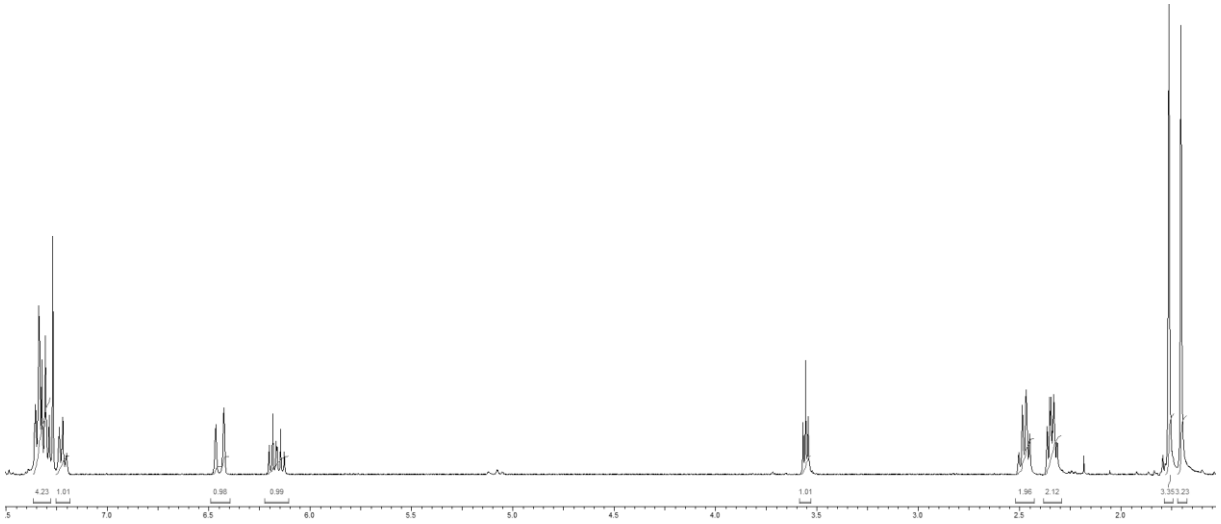
^{13}C NMR (100 MHz, $CDCl_3$):



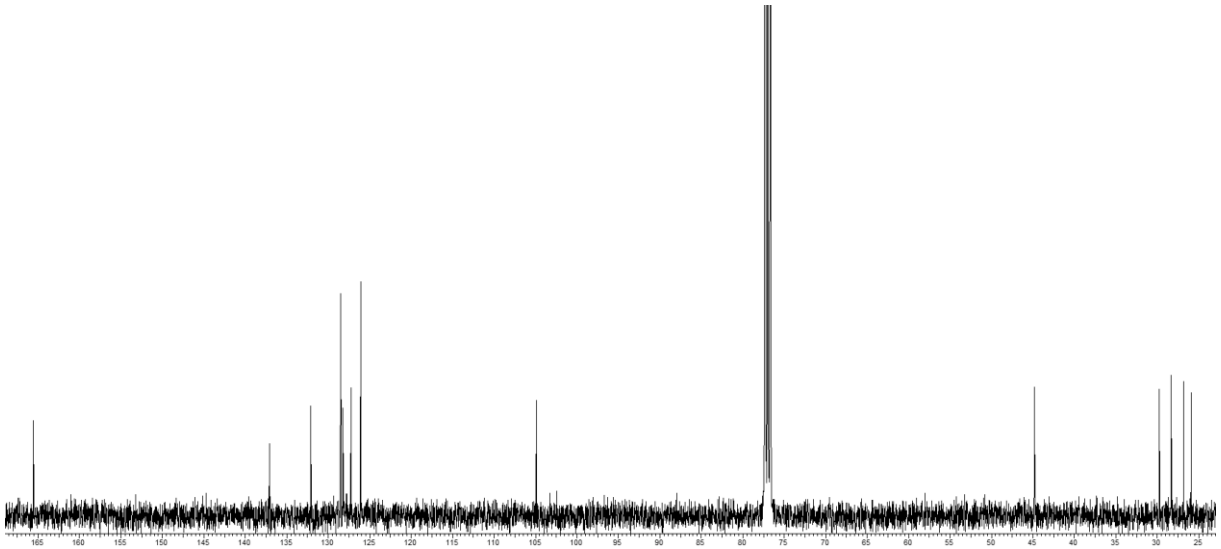
(*E*)-2,2-Dimethyl-5-(4-phenylbut-3-enyl)-1,3-dioxane-4,6-dione (5) from page S8



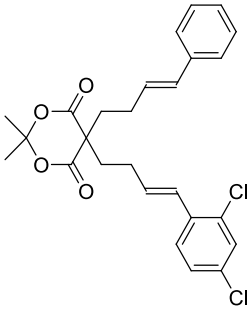
^{1}H NMR (400 MHz, $CDCl_3$):



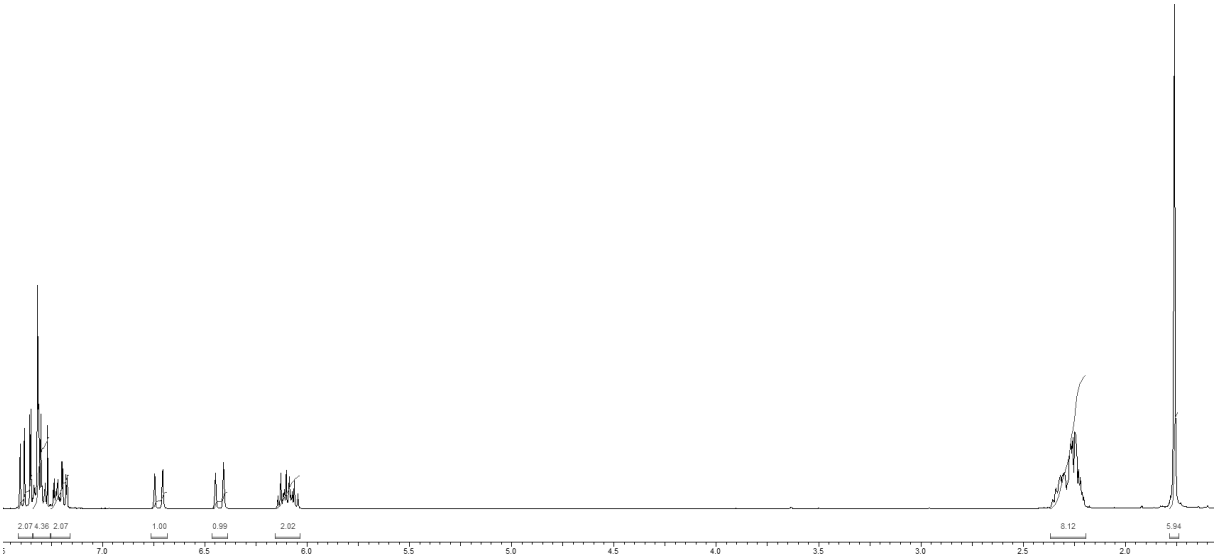
^{13}C NMR (100 MHz, $CDCl_3$):



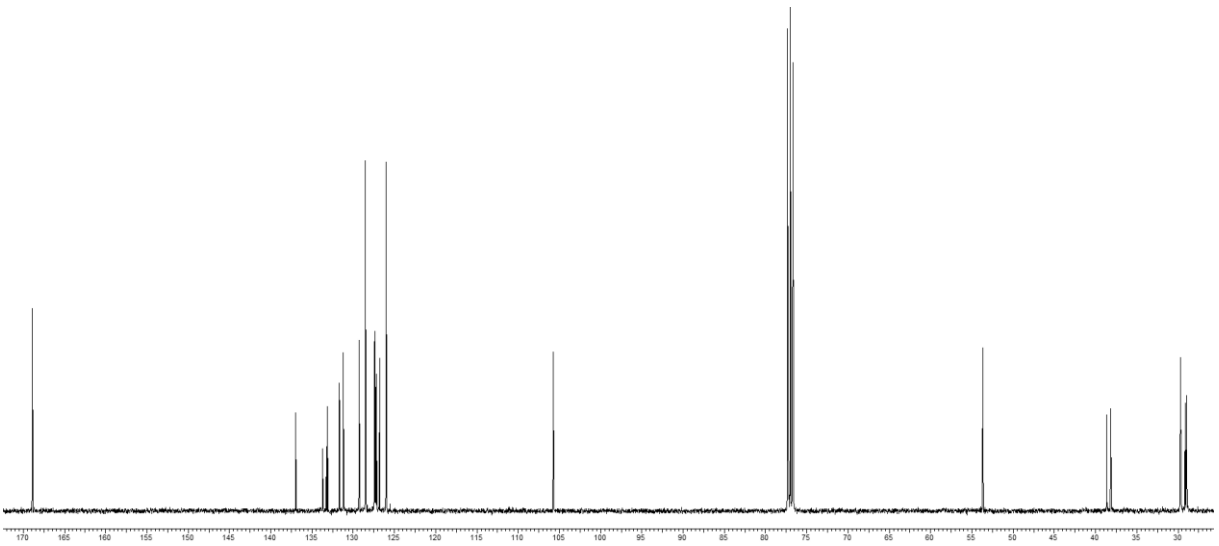
5-((*E*)-4-(2,4-Dichlorophenyl)but-3-enyl)-2,2-dimethyl-5-((*E*)-4-phenylbut-3-enyl)-1,3-dioxane-4,6-dione (1e) from page S9



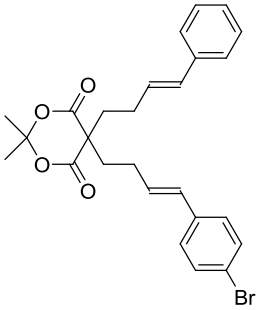
^{1}H NMR (400 MHz, $CDCl_3$):



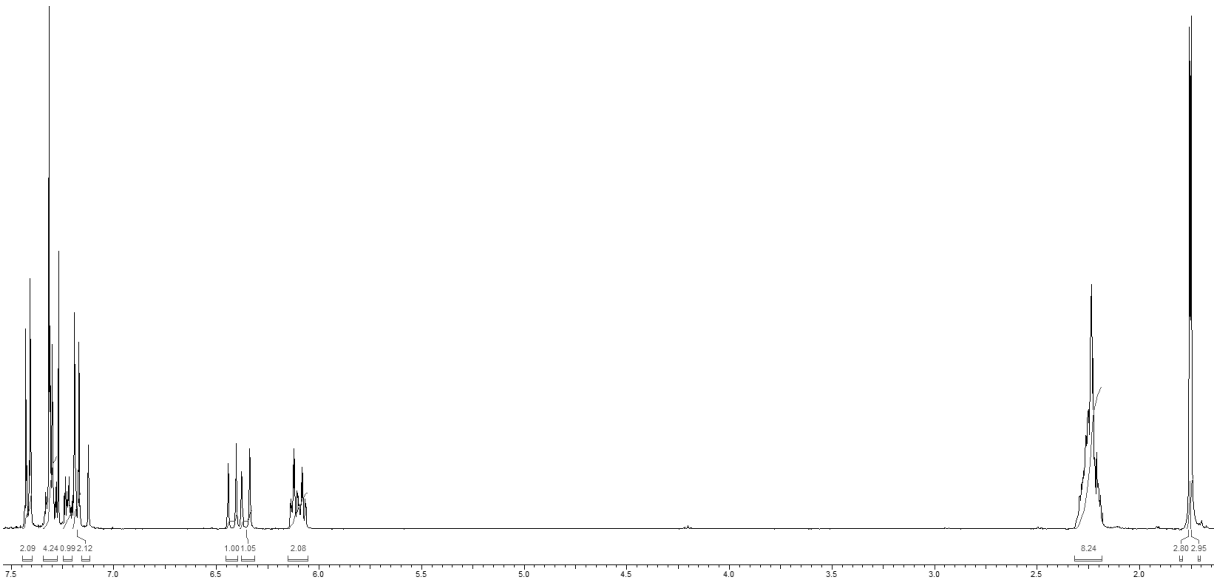
^{13}C NMR (100 MHz, $CDCl_3$):



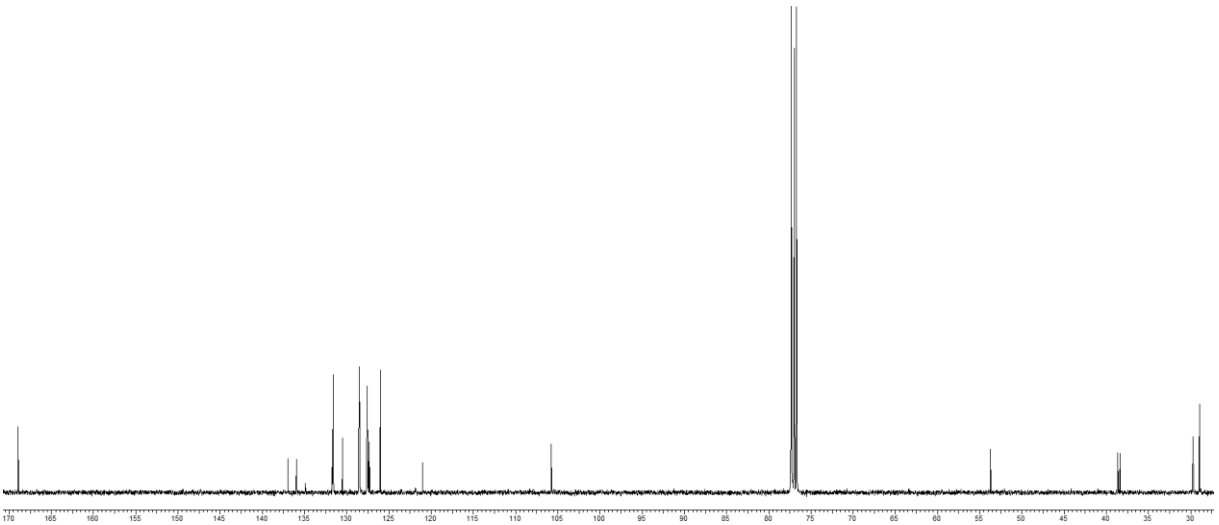
5-((*E*)-4-(4-Bromophenyl)but-3-enyl)-2,2-dimethyl-5-((*E*)-4-phenylbut-3-enyl)-1,3-dioxane-4,6-dione (1f) from page S10



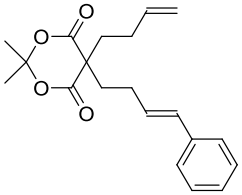
^{1}H NMR (400 MHz, $CDCl_3$):



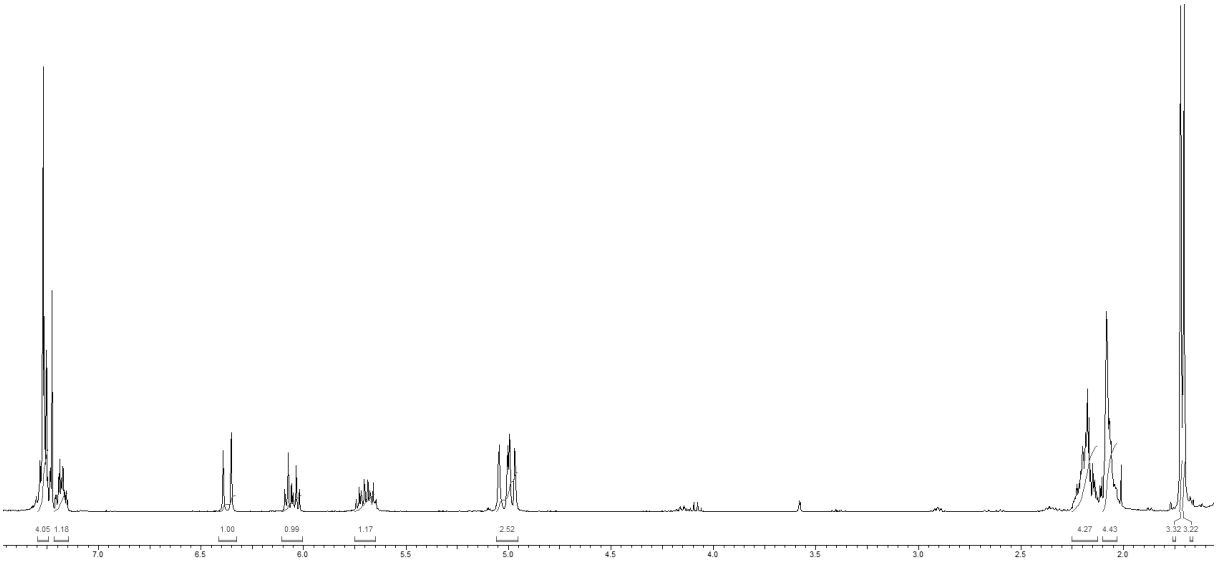
^{13}C NMR (100 MHz, $CDCl_3$):



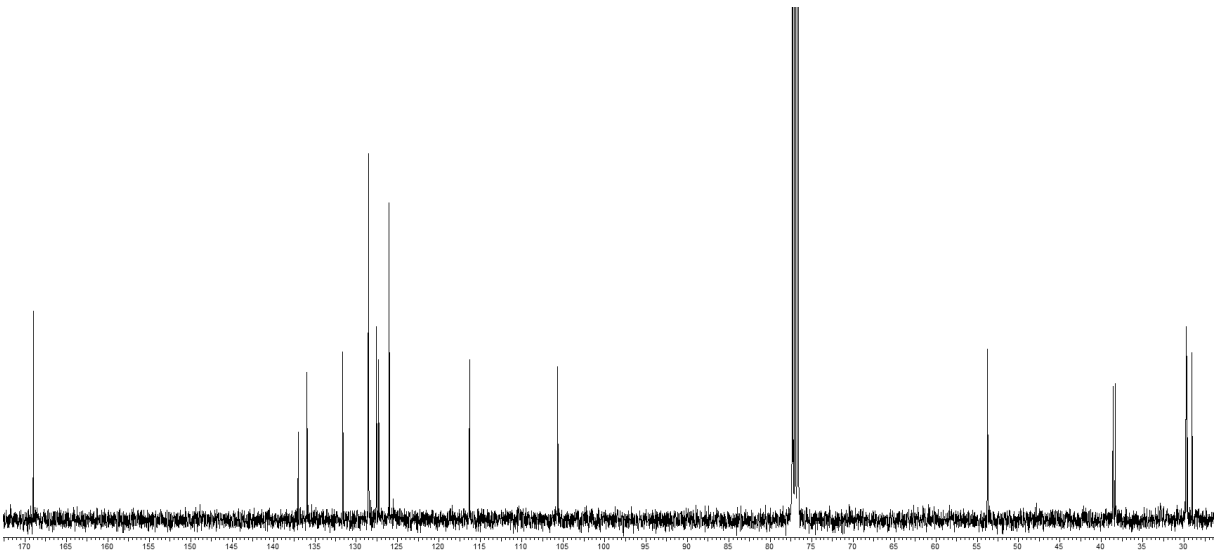
(*E*)-5-(But-3-enyl)-2,2-dimethyl-5-(4-phenylbut-3-enyl)-1,3-dioxane-4,6-dione (1a) from page S11



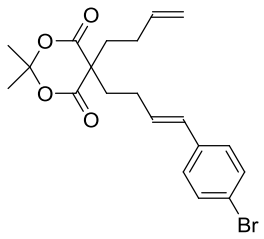
^{1}H NMR (400 MHz, $CDCl_3$):



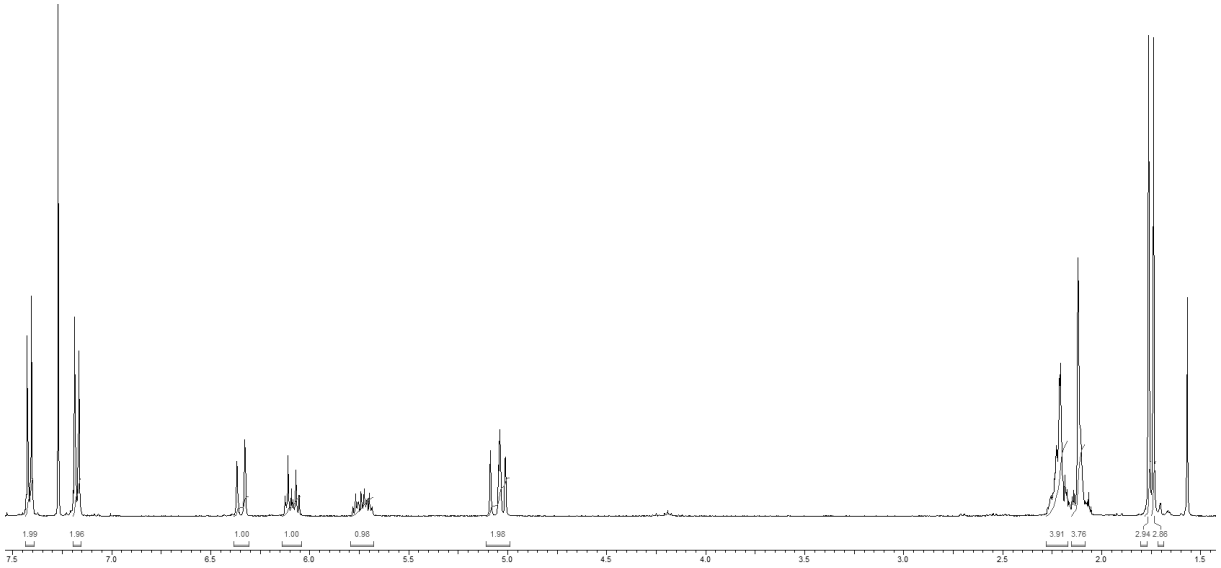
^{13}C NMR (100 MHz, $CDCl_3$):



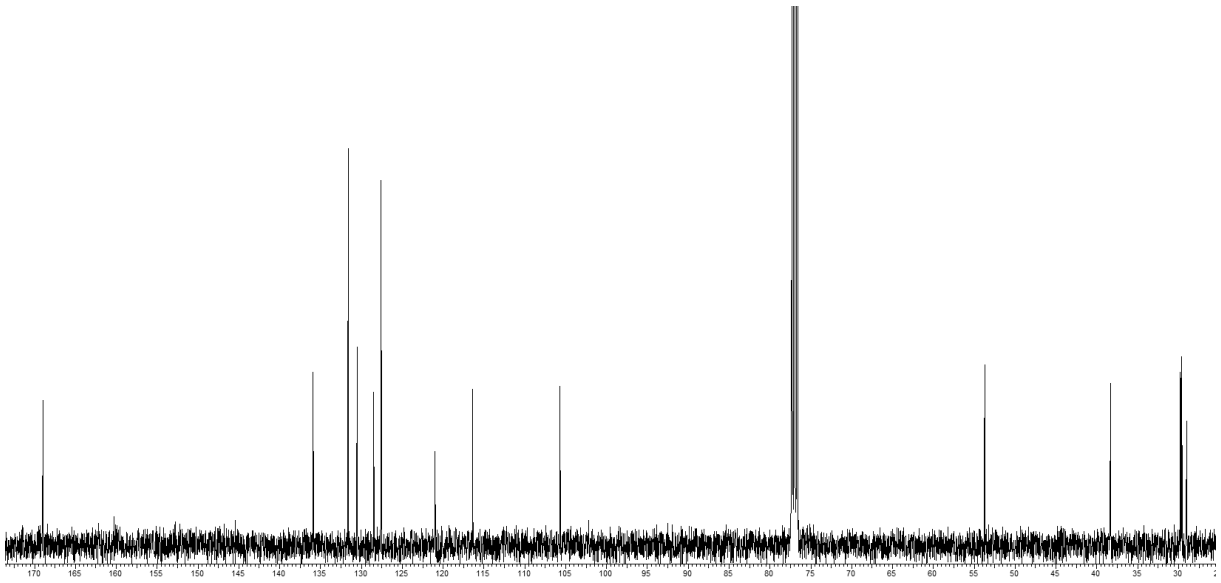
(*E*)-5-(4-(4-Bromophenyl)but-3-en-1-yl)-5-(but-3-en-1-yl)-2,2-dimethyl-1,3-dioxane-4,6-dione (1b) from page S11



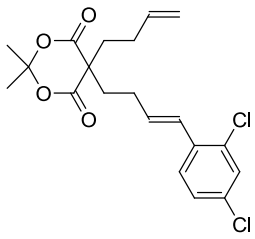
^{1}H NMR (400 MHz, $CDCl_3$):



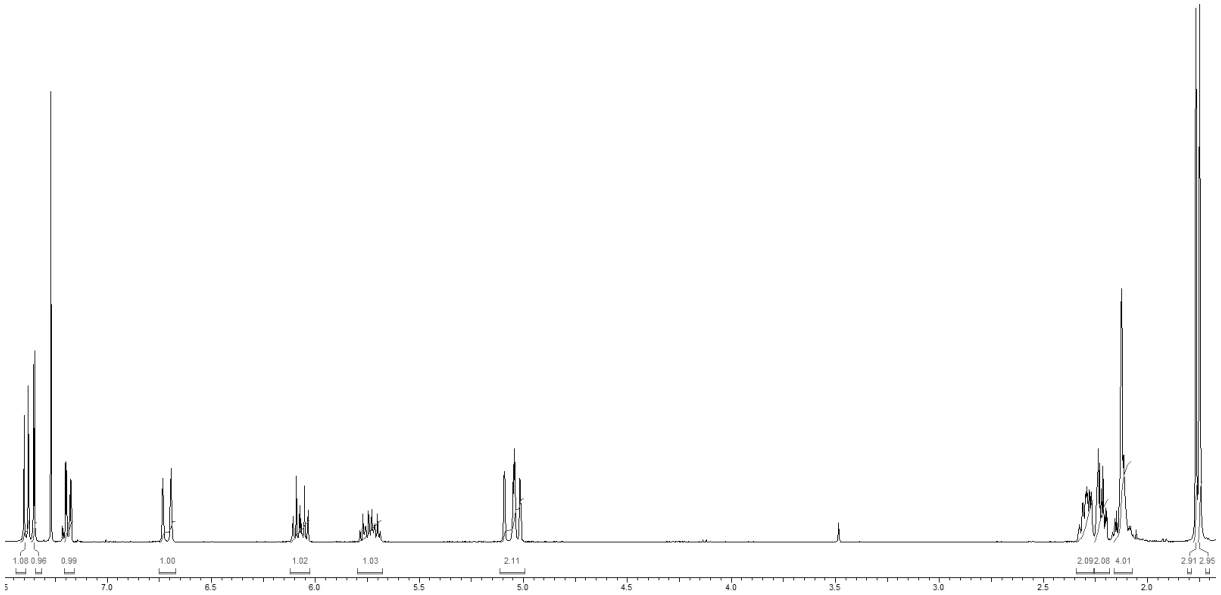
^{13}C NMR (100 MHz, $CDCl_3$):



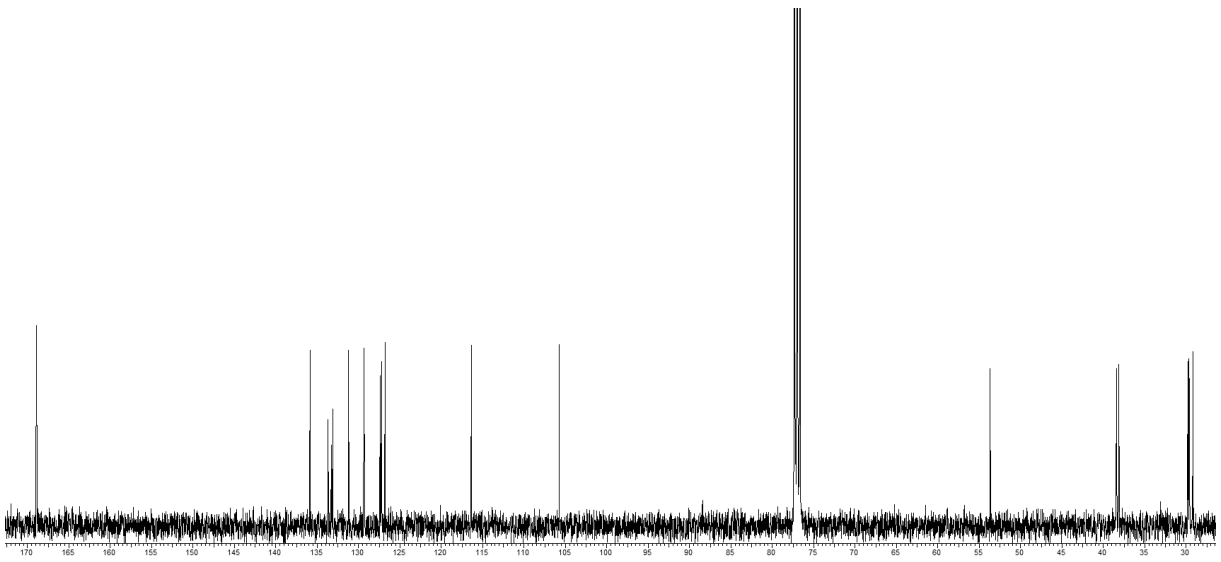
(*E*)-5-(But-3-en-1-yl)-5-(4-(2,4-dichlorophenyl)but-3-en-1-yl)-2,2-dimethyl-1,3-dioxane-4,6-dione (1c) from page S12



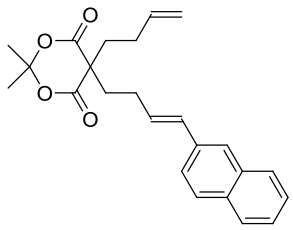
^{1}H NMR (400 MHz, $CDCl_3$):



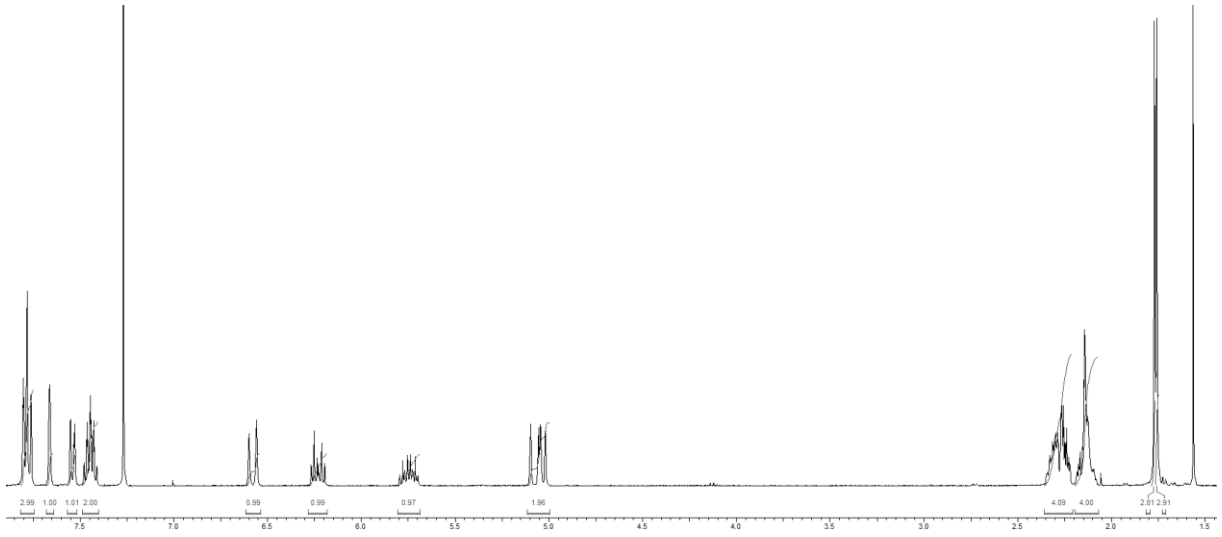
^{13}C NMR (100 MHz, $CDCl_3$):



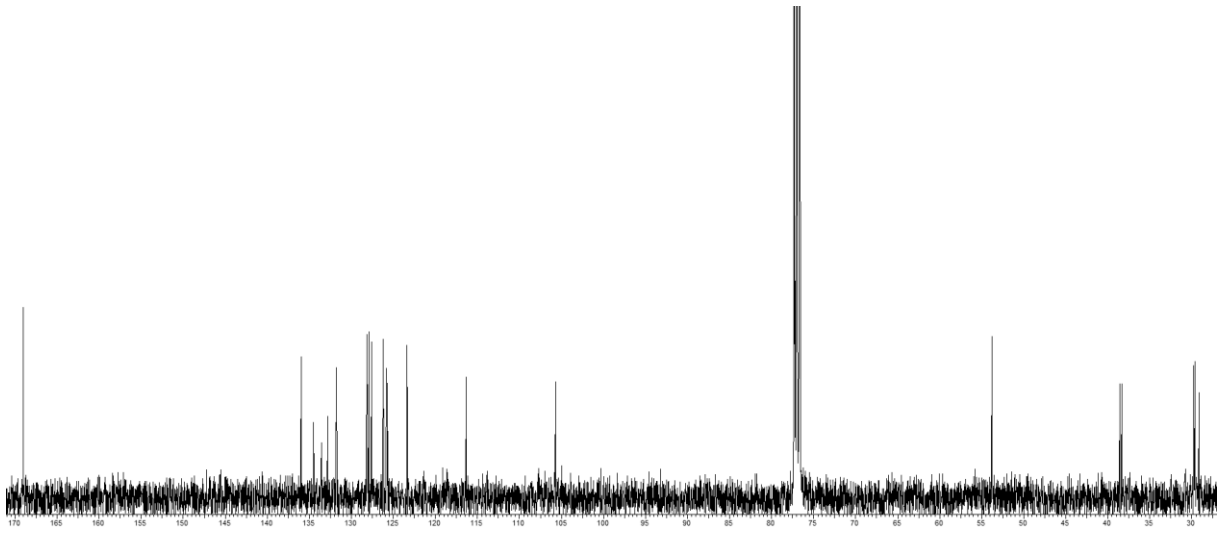
(*E*)-5-(But-3-en-1-yl)-2,2-dimethyl-5-(4-(naphthalen-2-yl)but-3-en-1-yl)-1,3-dioxane-4,6-dione (1d) from page S13



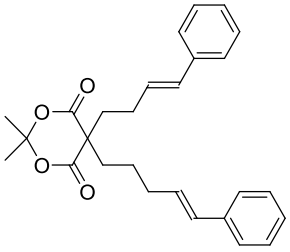
^{1}H NMR (400 MHz, $CDCl_3$):



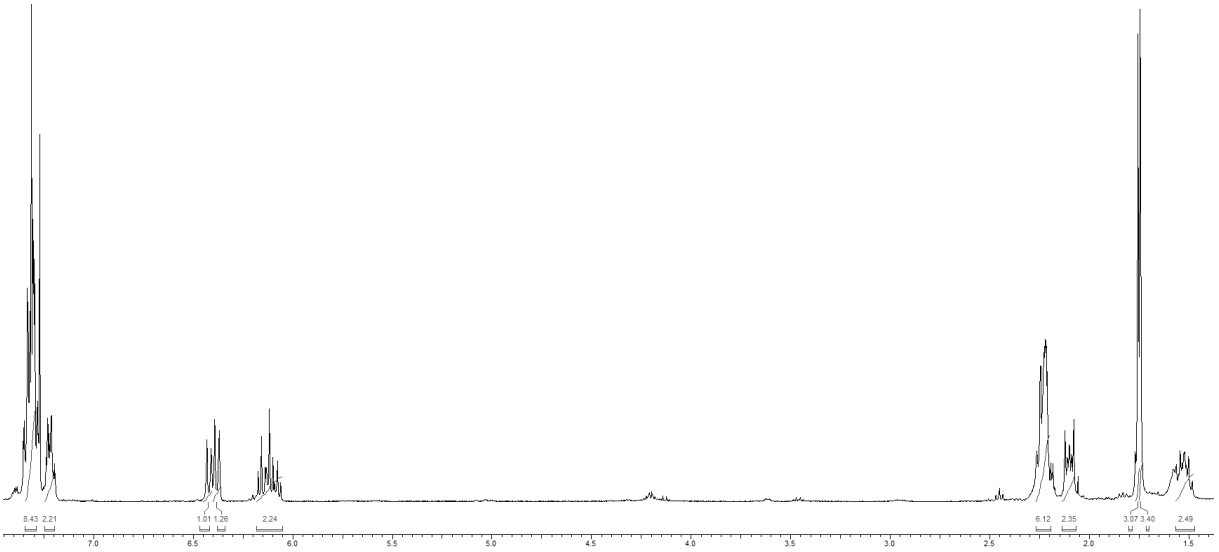
^{13}C NMR (100 MHz, $CDCl_3$):



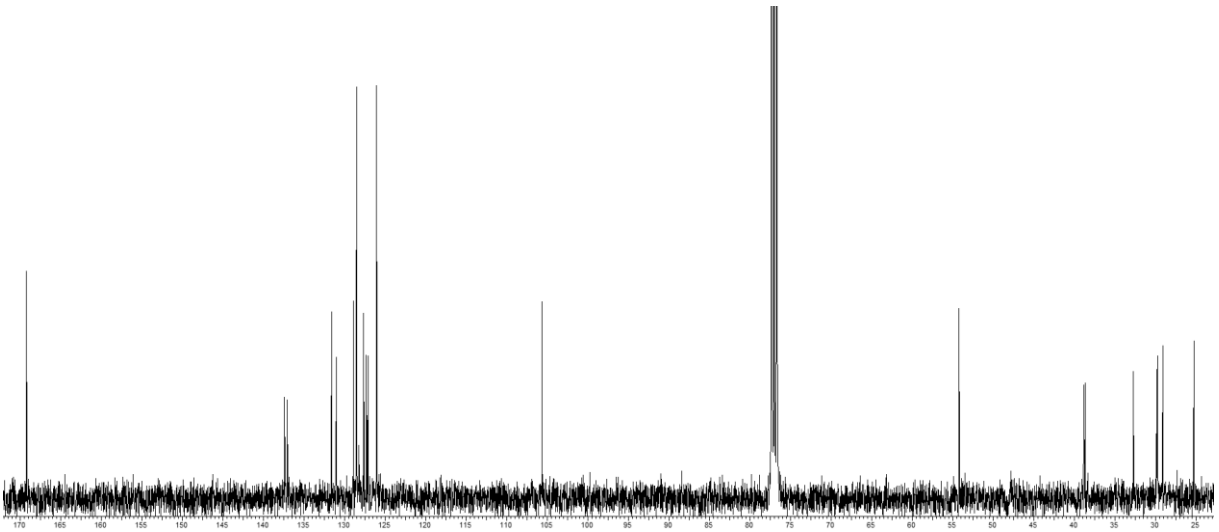
2,2-Dimethyl-5-((*E*)-4-phenylbut-3-enyl)-5-((*E*)-5-phenylpent-4-enyl)-1,3-dioxane-4,6-dione (1g) from page S13



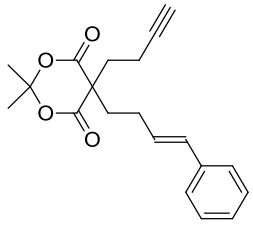
^{1}H NMR (400 MHz, $CDCl_3$):



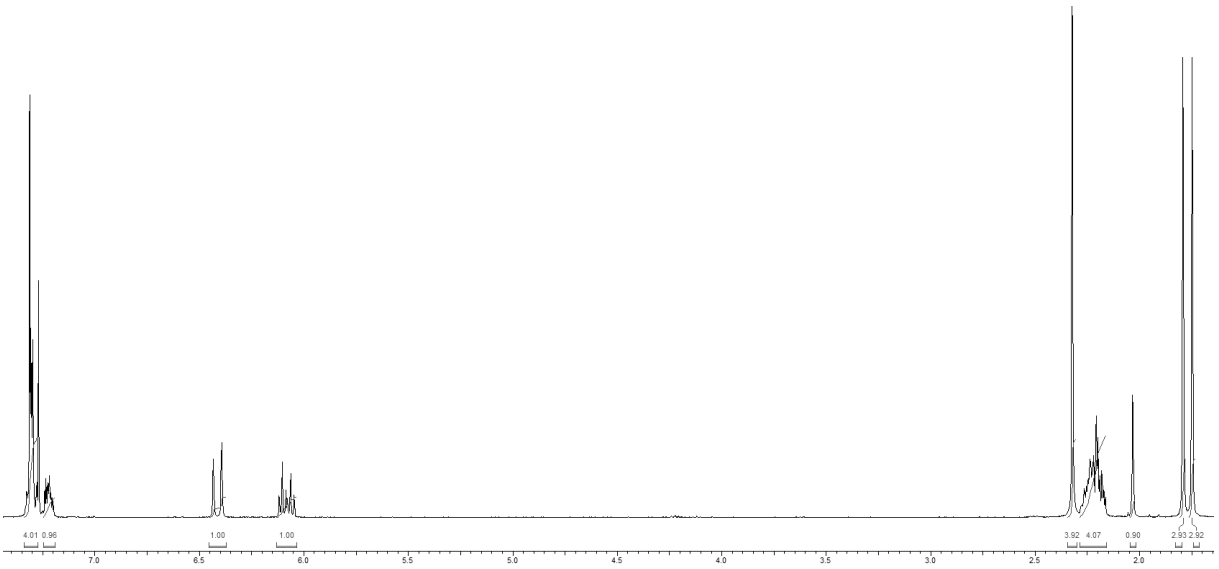
^{13}C NMR (100 MHz, $CDCl_3$):



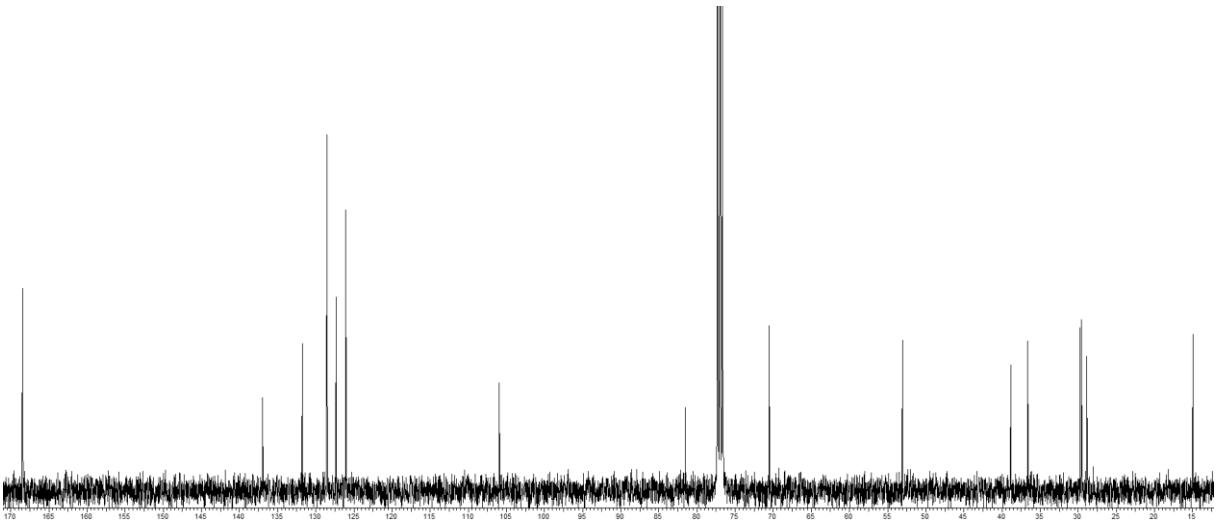
(*E*)-5-(But-3-yn-1-yl)-2,2-dimethyl-5-(4-phenylbut-3-en-1-yl)-1,3-dioxane-4,6-dione (1i) from page S14



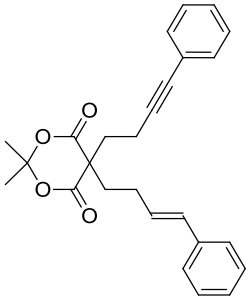
^{1}H NMR (400 MHz, $CDCl_3$):



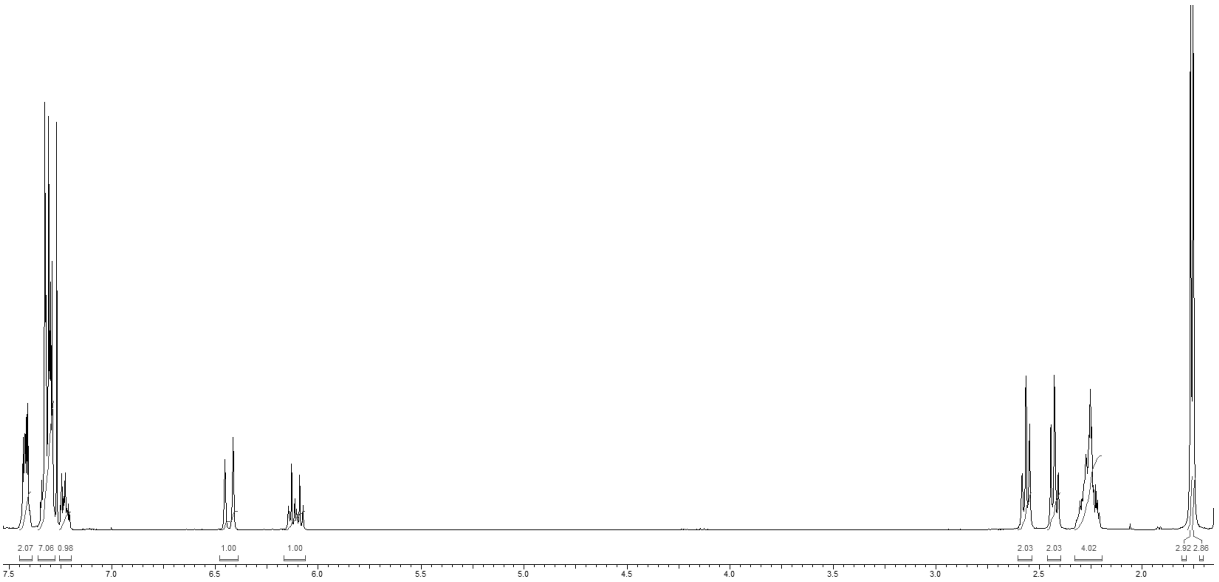
^{13}C NMR (100 MHz, $CDCl_3$):



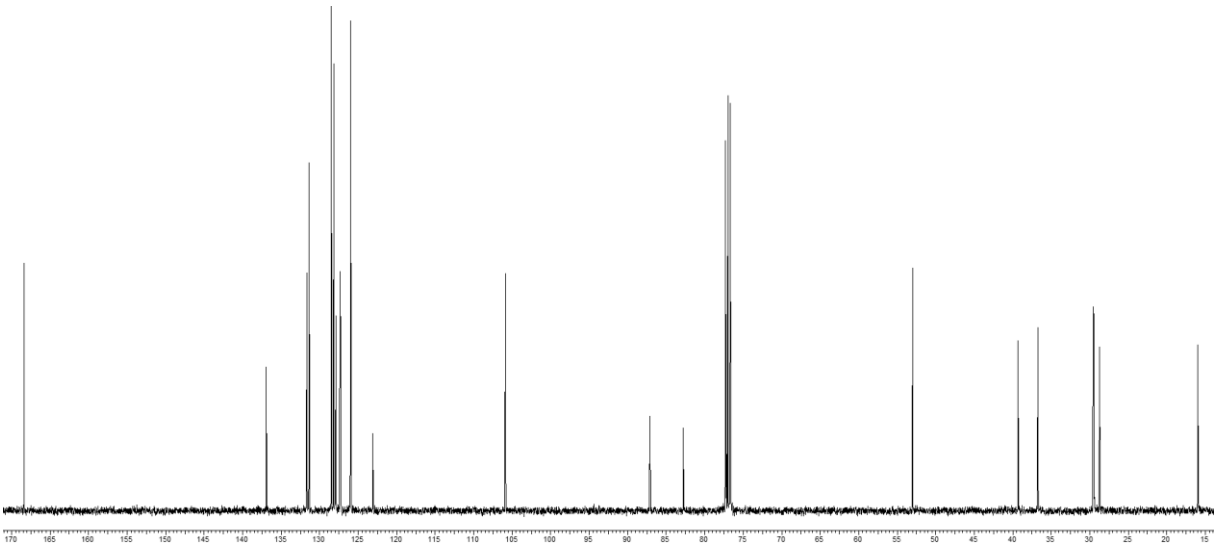
(*E*)-2,2-Dimethyl-5-(4-phenylbut-3-en-1-yl)-5-(4-phenylbut-3-yn-1-yl)-1,3-dioxane-4,6-dione (1j) from page S15



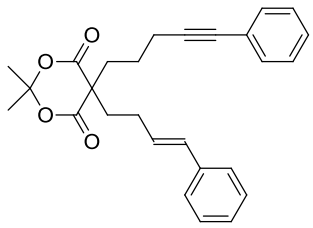
^{1}H NMR (400 MHz, $CDCl_3$):



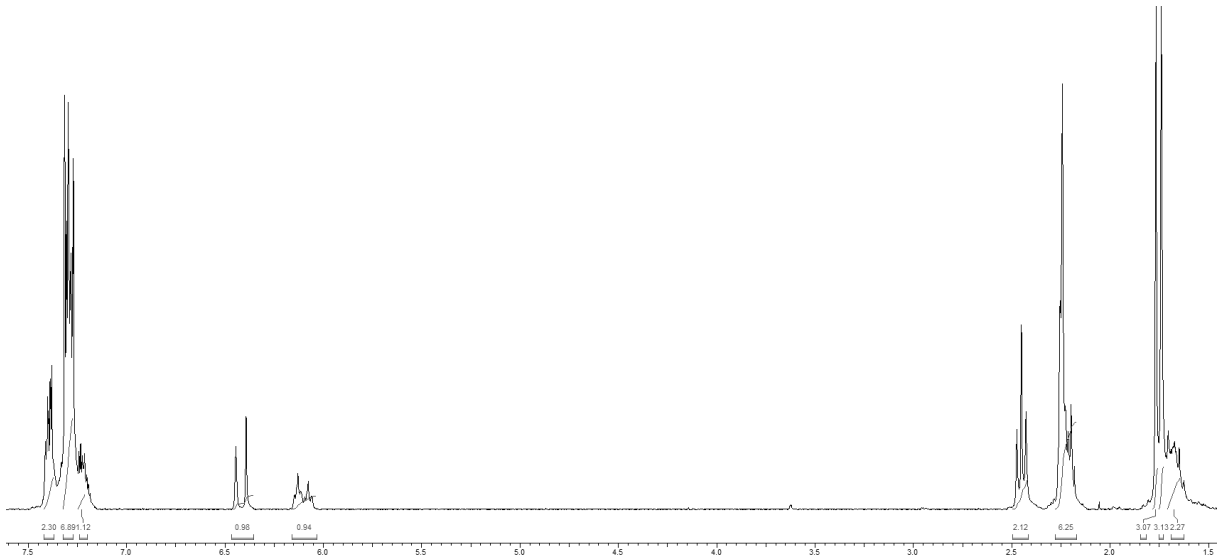
^{13}C NMR (100 MHz, $CDCl_3$):



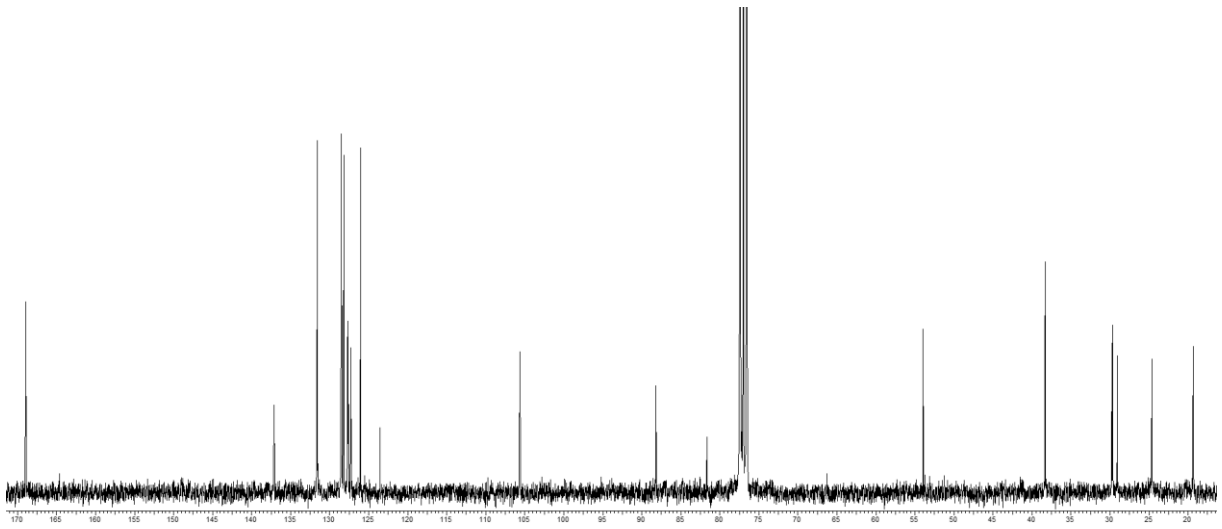
(*E*)-2,2-Dimethyl-5-(4-phenylbut-3-en-1-yl)-5-(5-phenylpent-4-yn-1-yl)-1,3-dioxane-4,6-dione (1h) from page S15



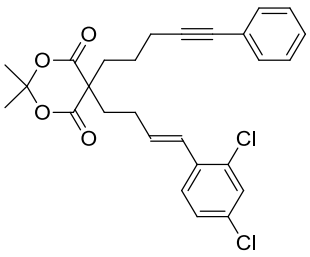
^{1}H NMR (300 MHz, $CDCl_3$):



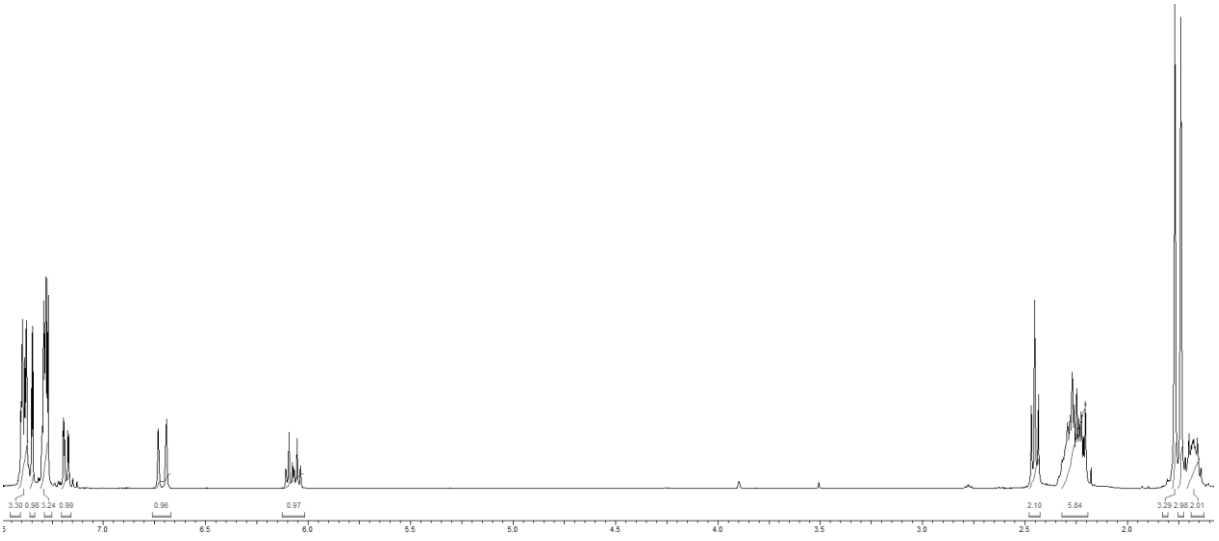
^{13}C NMR (75 MHz, $CDCl_3$):



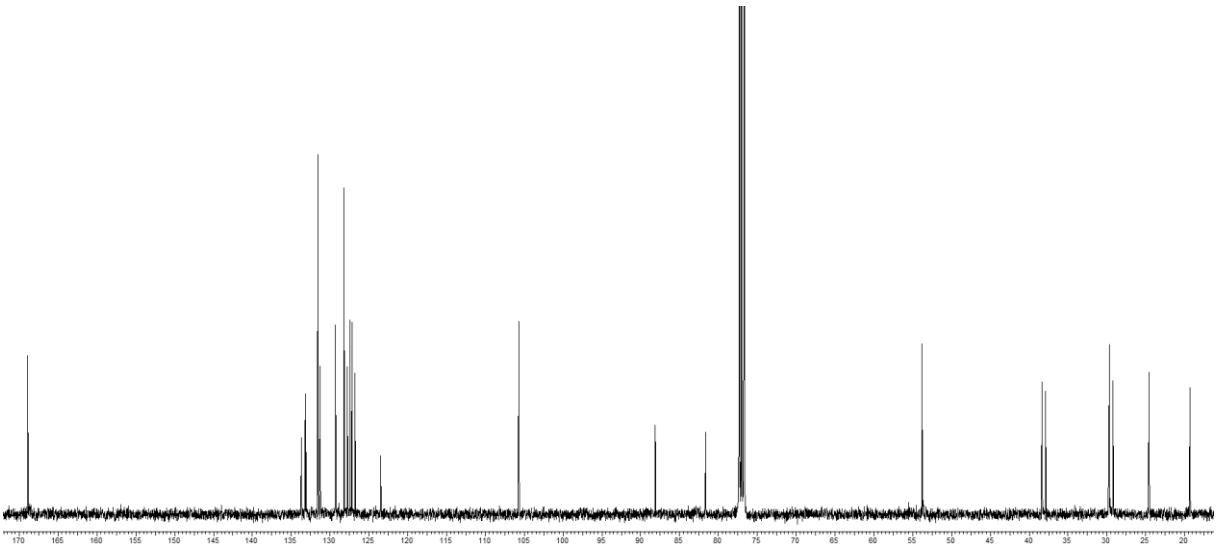
(*E*)-5-(4-(2,4-Dichlorophenyl)but-3-en-1-yl)-2,2-dimethyl-5-(5-phenylpent-4-yn-1-yl)-1,3-dioxane-4,6-dione (1k) from page S16



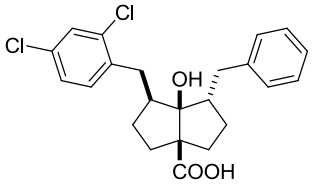
^{1}H NMR (400 MHz, $CDCl_3$):



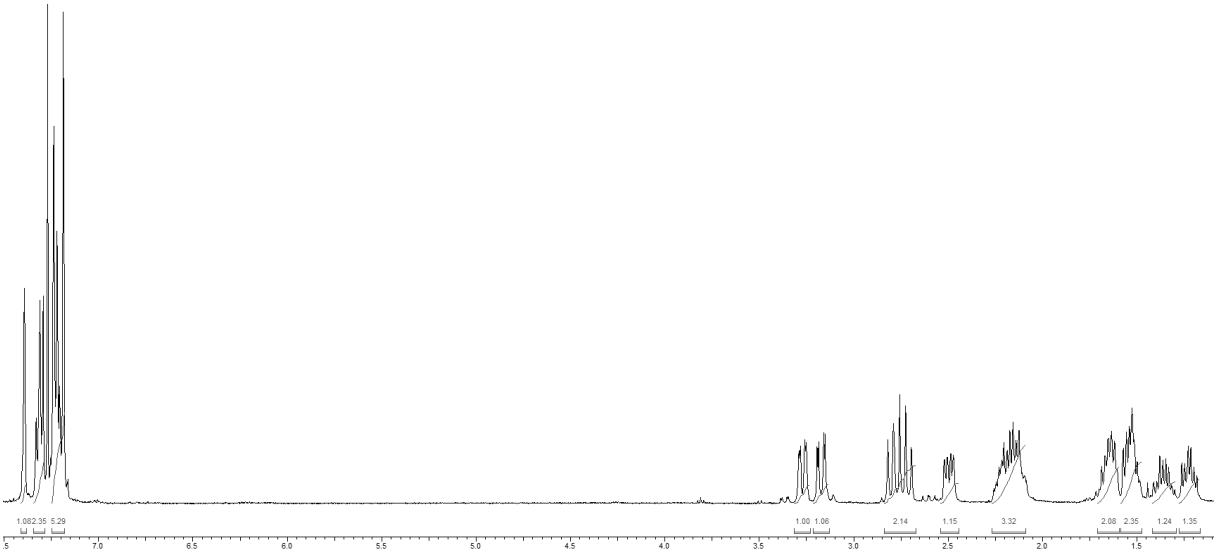
^{13}C NMR (100 MHz, $CDCl_3$):



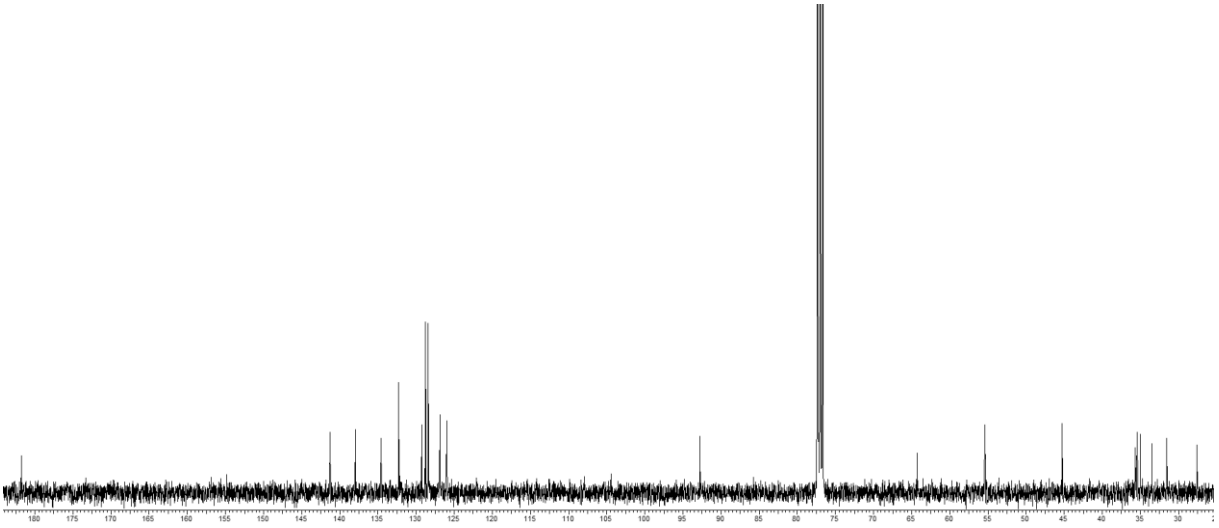
***rac*-(1S,3aS,6S,6aR)-1-Benzyl-6-(2,4-dichlorobenzyl)-6a-hydroxyoctahydropentalene-3a-carboxylic acid (2e) from page S17**



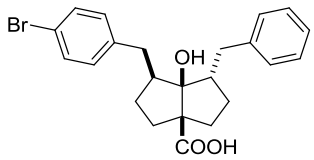
^{1}H NMR (400 MHz, $CDCl_3$):



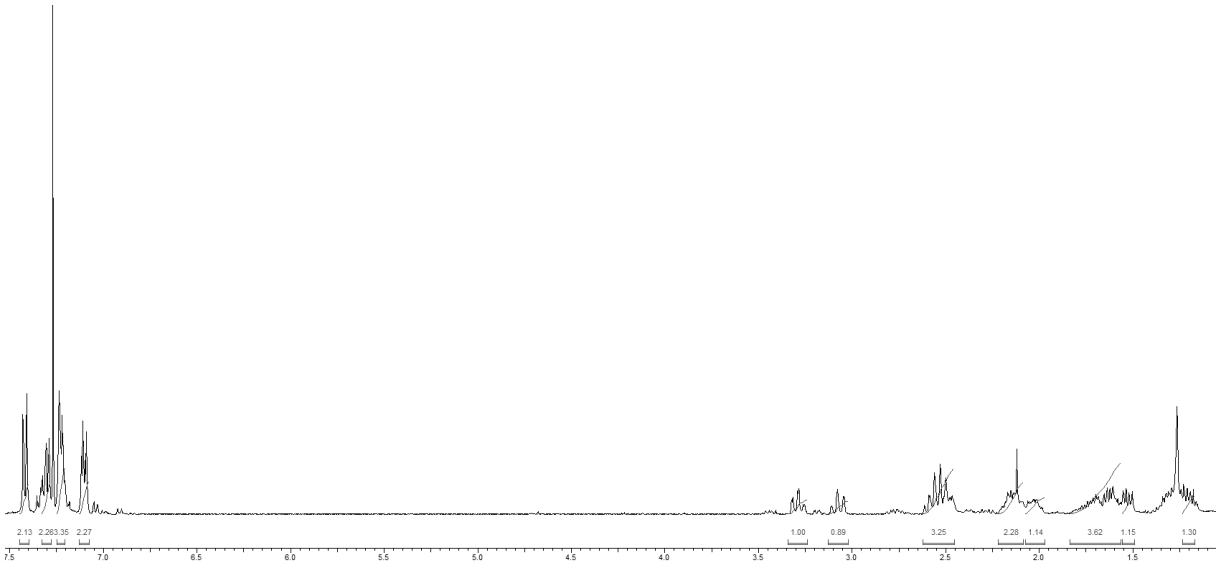
^{13}C NMR (100 MHz, $CDCl_3$):



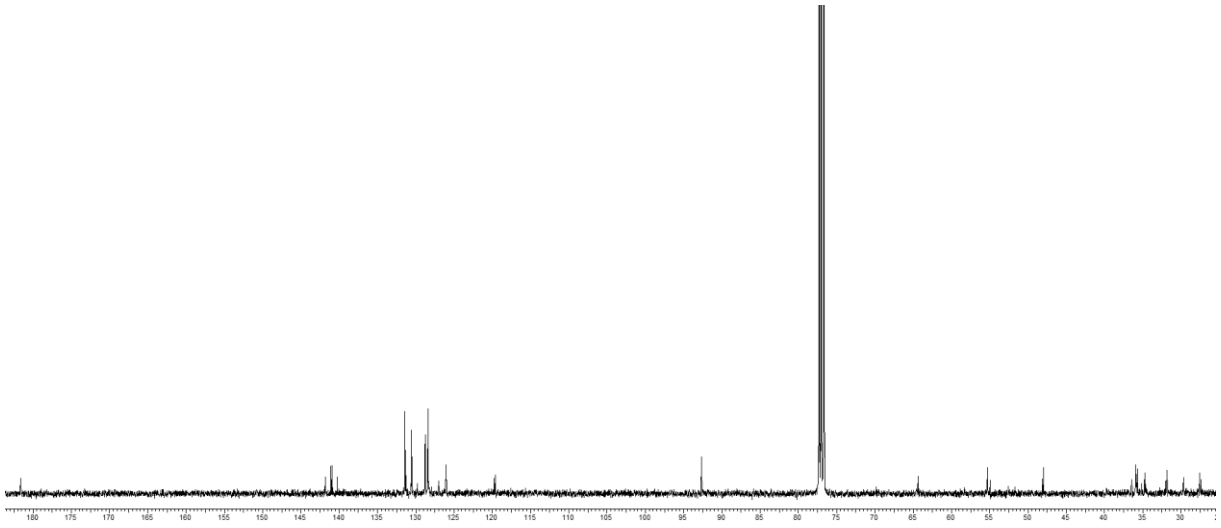
***rac*-(1S,3aS,6S,6aR)-1-Benzyl-6-(4-bromobenzyl)-6a-hydroxyoctahydropentalene-3a-carboxylic acid (2f) from page S18**



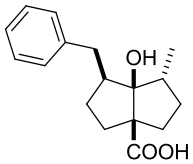
^{1}H NMR (400 MHz, $CDCl_3$):



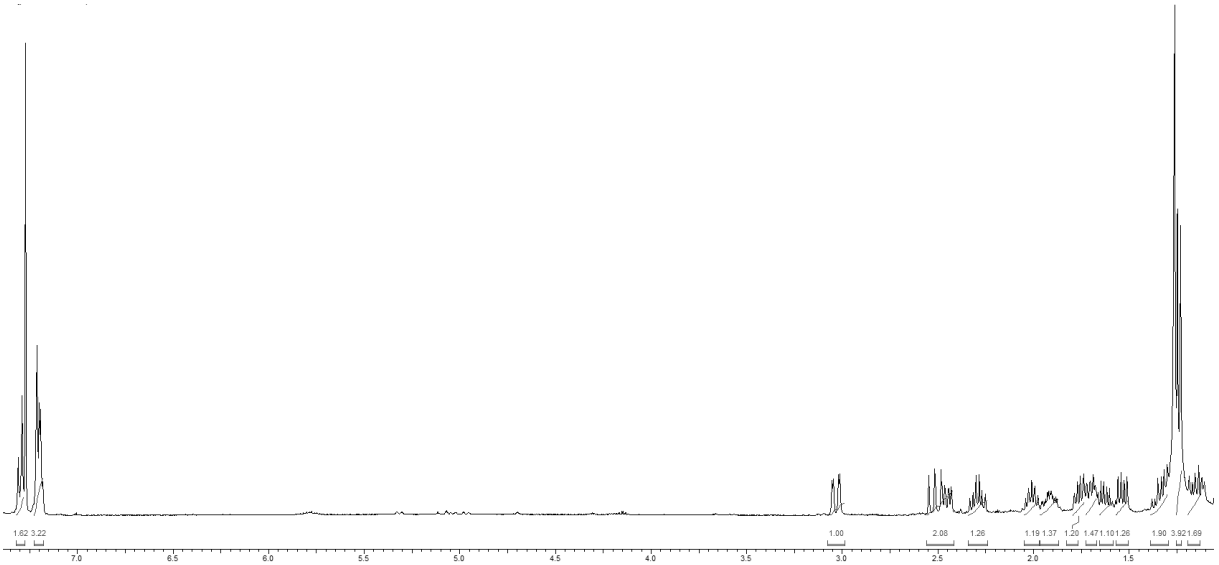
^{13}C NMR (100 MHz, $CDCl_3$):



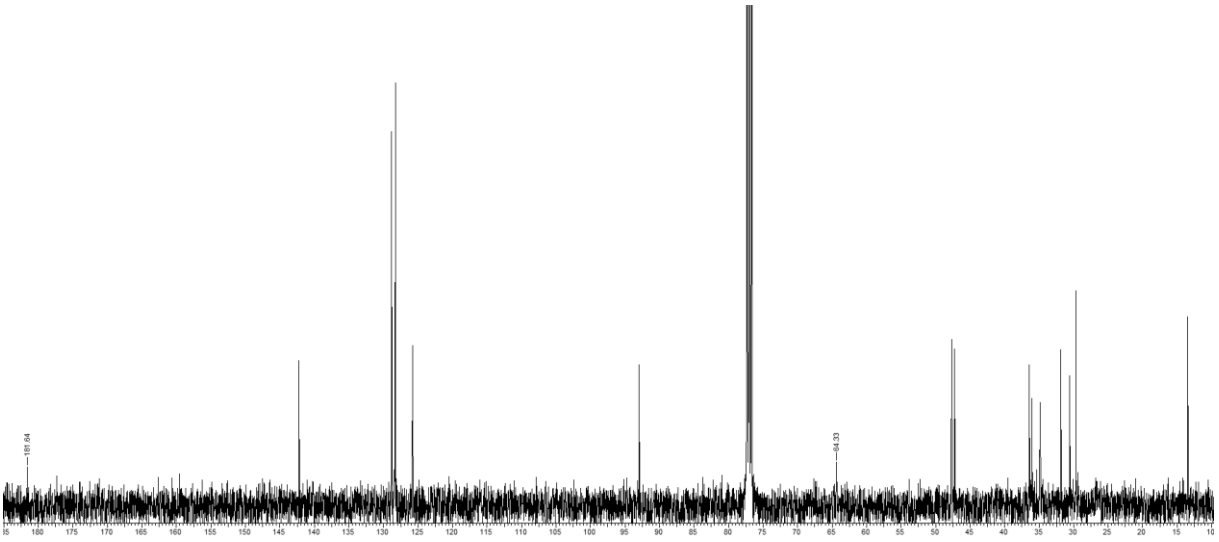
***rac*-(1S,3aS,6R,6aR)-1-Benzyl-6a-hydroxy-6-methyloctahydropentalene-3a-carboxylic acid (2a) from page S18**



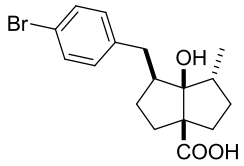
^{1}H NMR (400 MHz, $CDCl_3$):



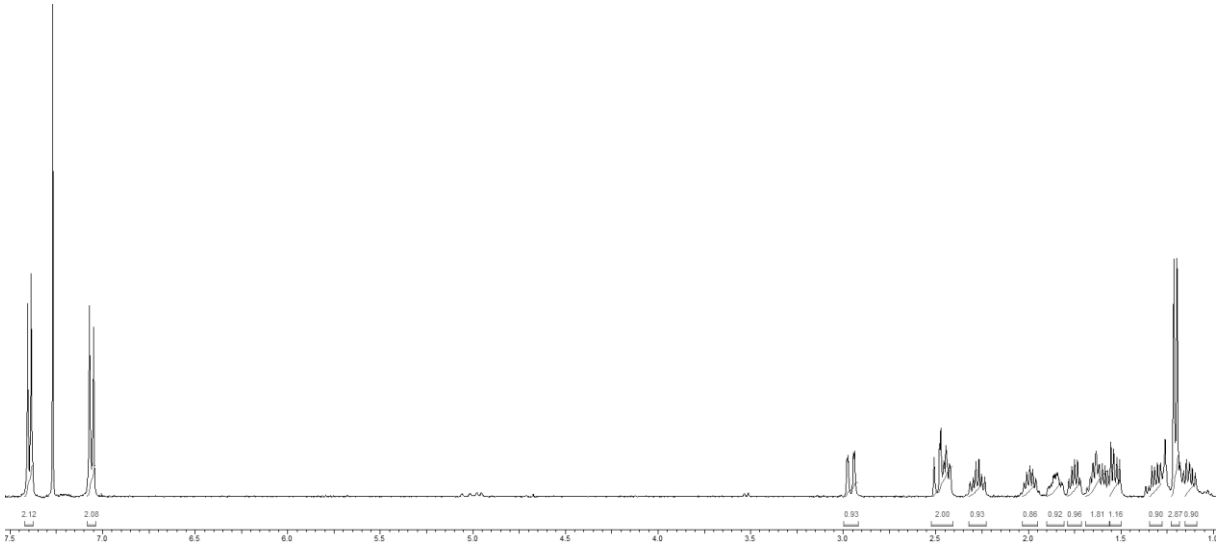
^{13}C NMR (100 MHz, $CDCl_3$):



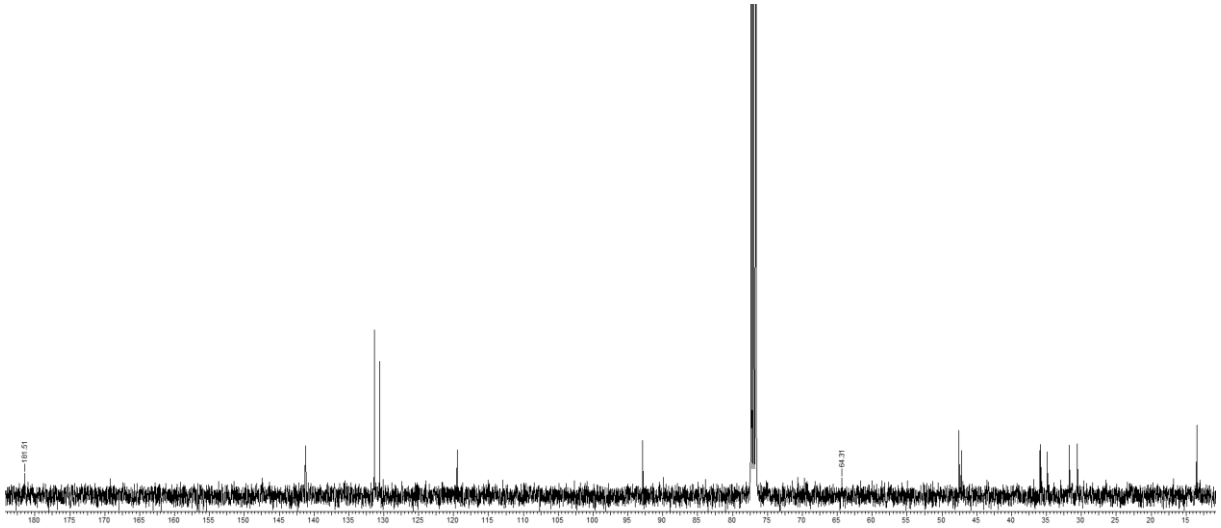
***rac*-(1S,3aS,6R,6aR)-1-(4-Bromobenzyl)-6a-hydroxy-6-methyloctahydropentalene-3a-carboxylic acid (2b) from page S19**



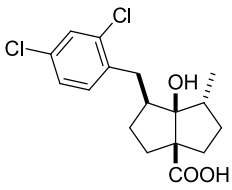
^{1}H NMR (400 MHz, $CDCl_3$):



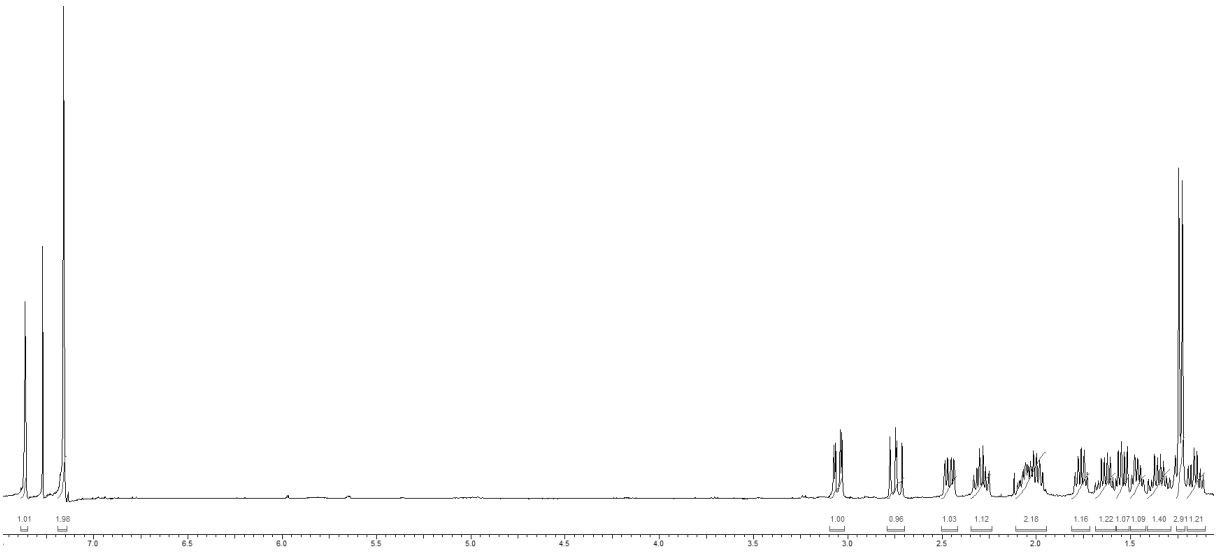
^{13}C NMR (100 MHz, $CDCl_3$):



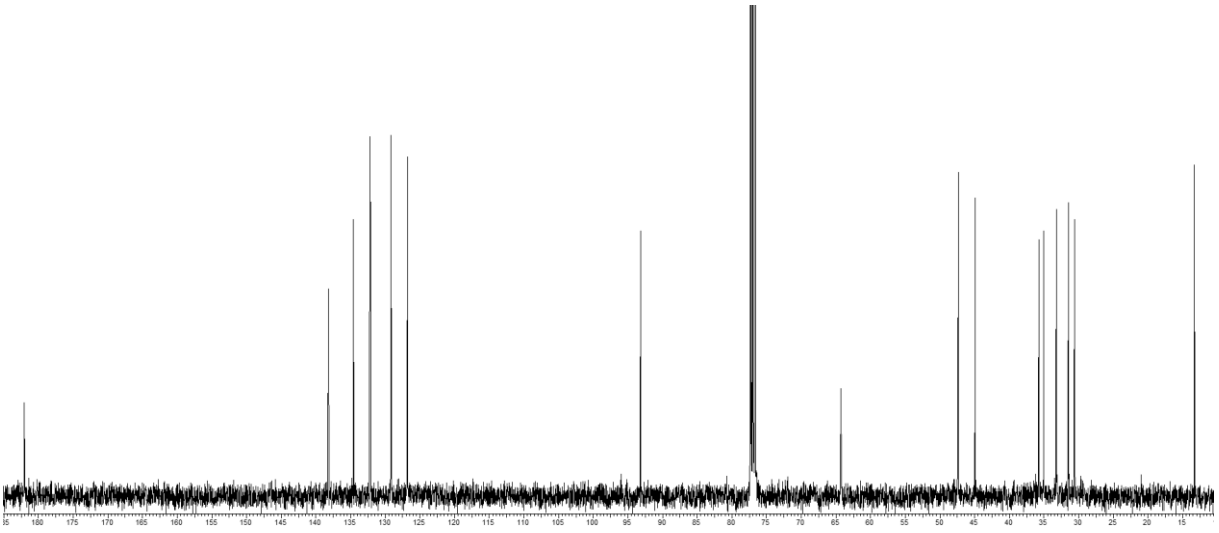
***rac*-(1S,3aS,6R,6aR)-1-(2,4-Dichlorobenzyl)-6a-hydroxy-6-methyloctahydropentalene-3a-carboxylic acid (2c) from page S20**



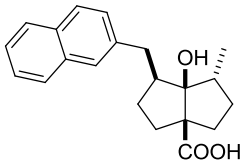
^{1}H NMR (400 MHz, $CDCl_3$):



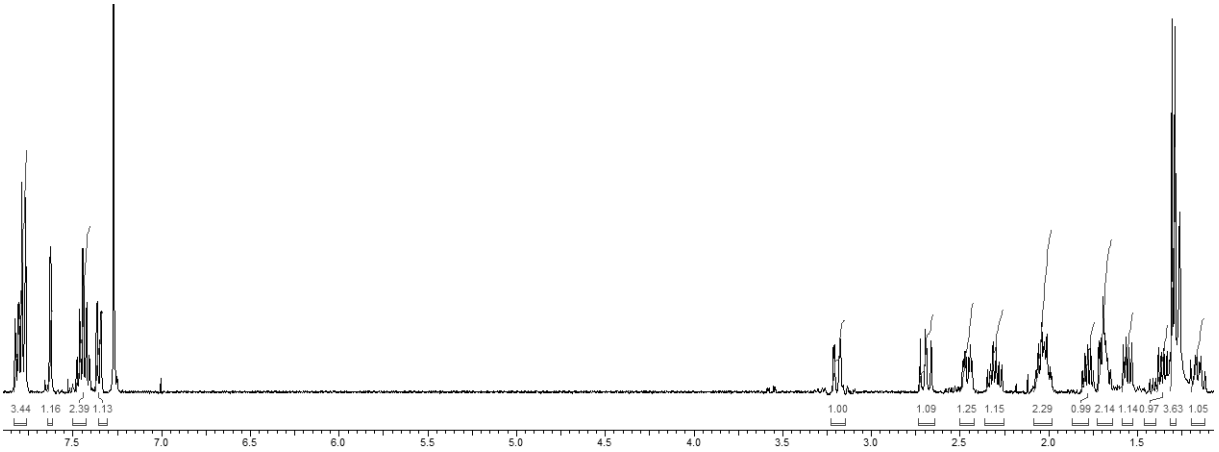
^{13}C NMR (100 MHz, $CDCl_3$):



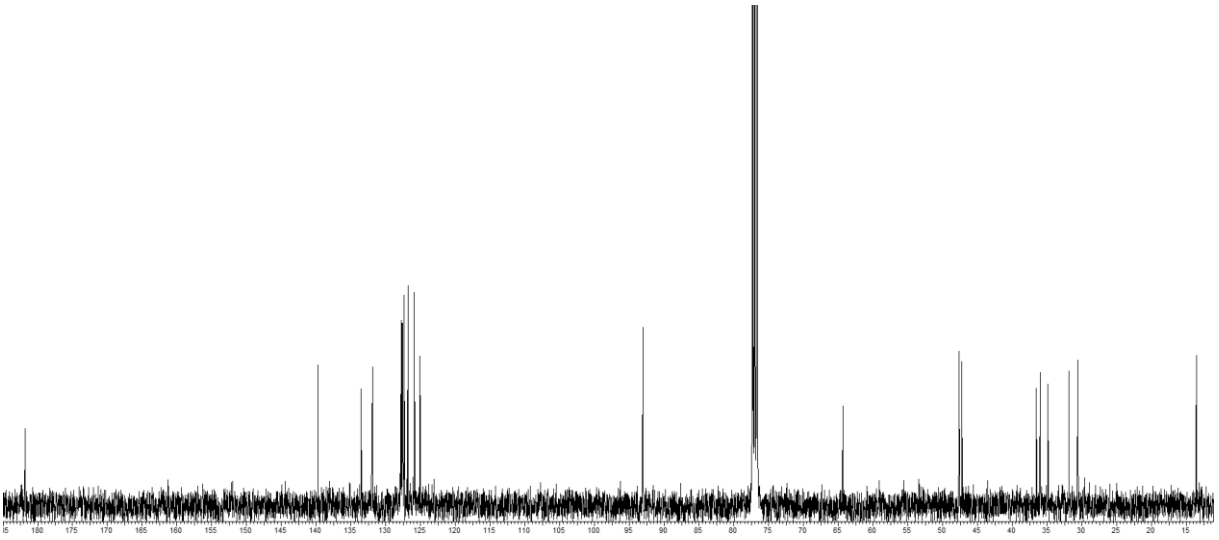
***rac*-(1R,3aS,6S,6aR)-6a-Hydroxy-1-methyl-6-(naphthalen-2-ylmethyl)octahydropentalene-3a-carboxylic acid (2d) from page S20**



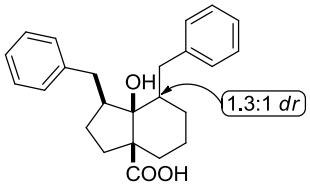
^{1}H NMR (400 MHz, $CDCl_3$):



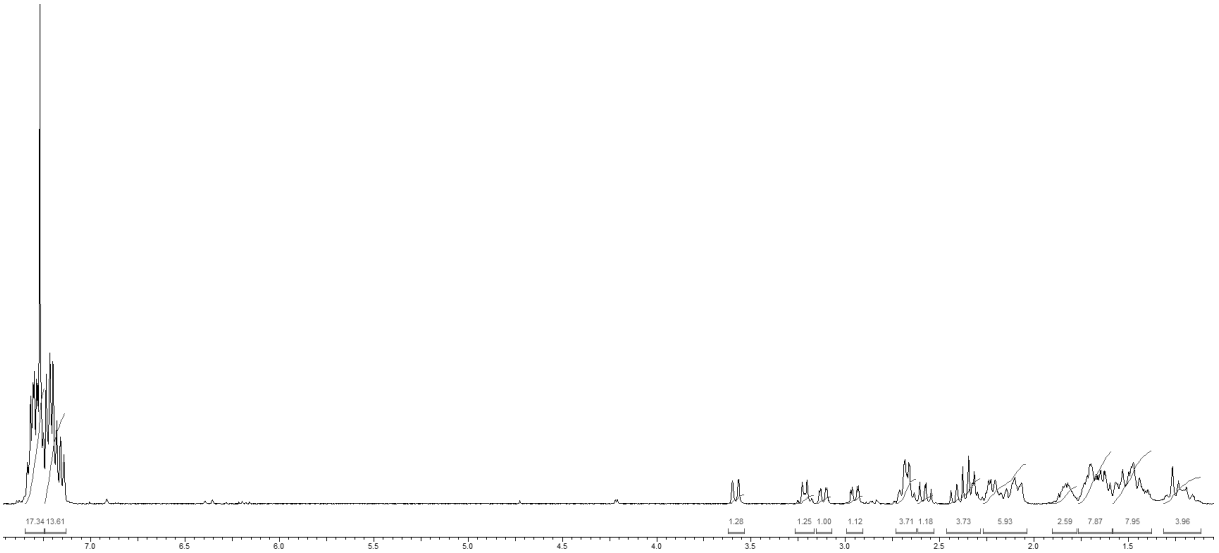
^{13}C NMR (100 MHz, $CDCl_3$):



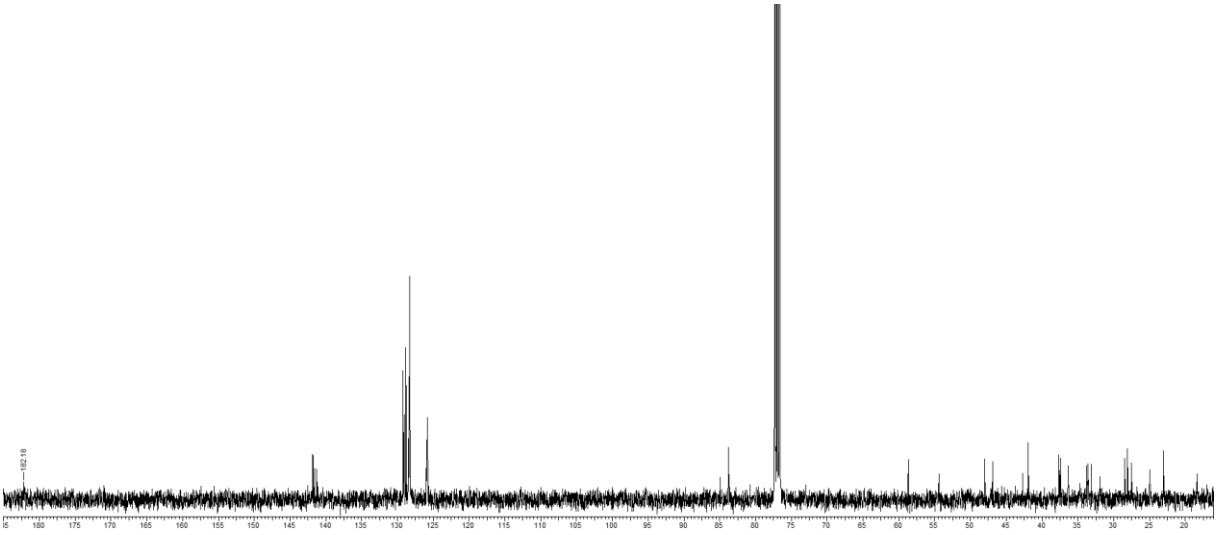
***rac*-(1S,3aS,7aR)-1,7-Dibenzyl-7a-hydroxyoctahydro-1H-indene-3a-carboxylic acid (2g) from page S21**



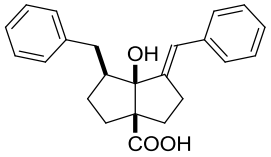
^{1}H NMR (400 MHz, $CDCl_3$):



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

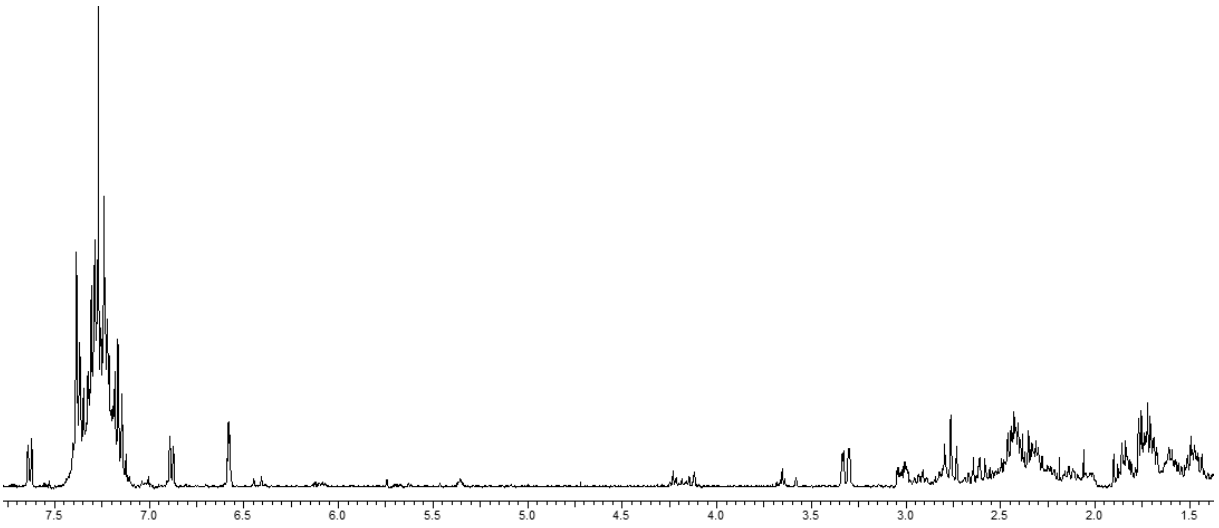


***rac*-(1S,3aR,6aS,*E*)-1-Benzyl-6-benzylidene-6a-hydroxyoctahydropentalene-3a-carboxylic acid (2j) from page S22**



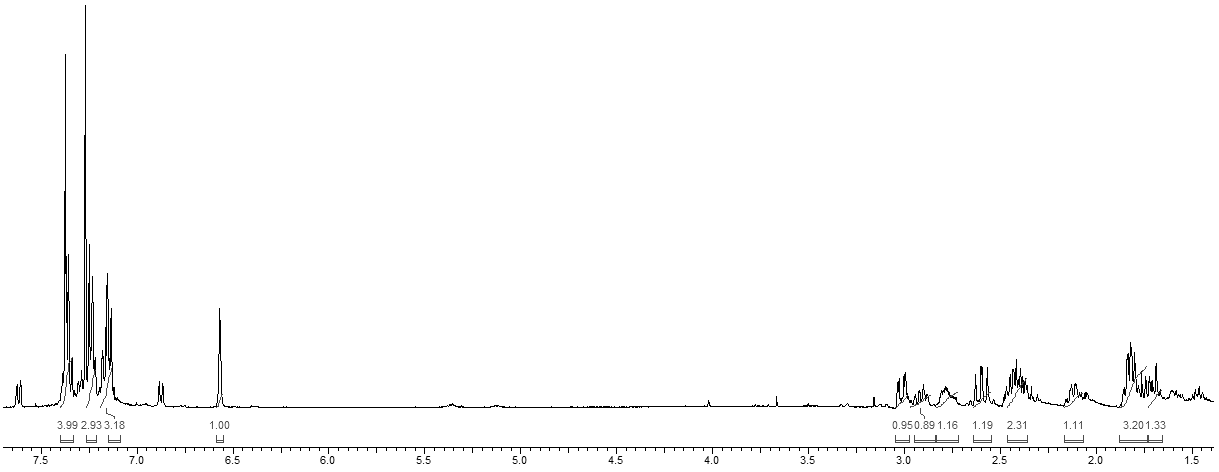
1H NMR of the 2:1 mixture of alkene isomers:

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

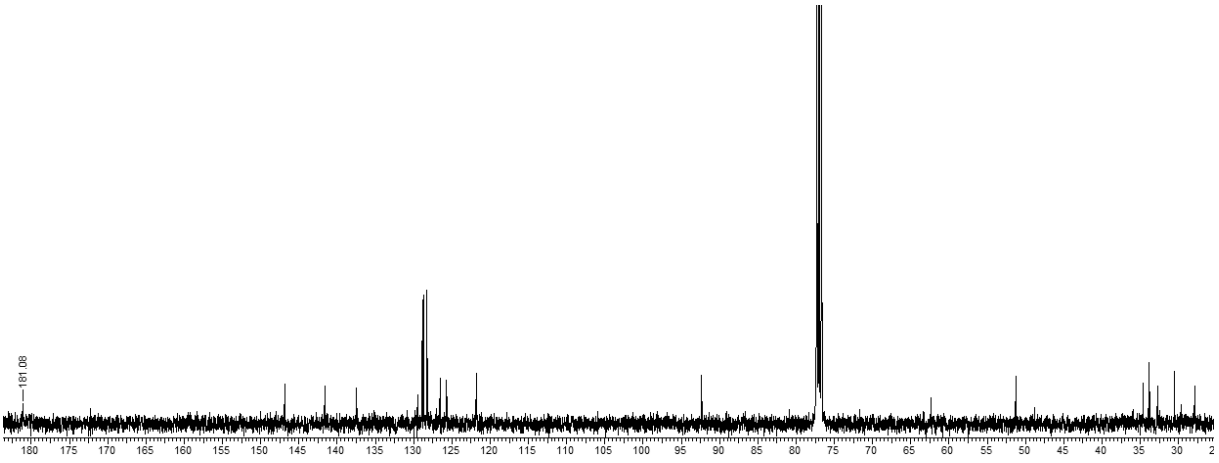


1H NMR of a mixture enriched in the major alkene isomer:

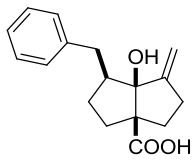
^{1}H NMR (400 MHz, $CDCl_3$):



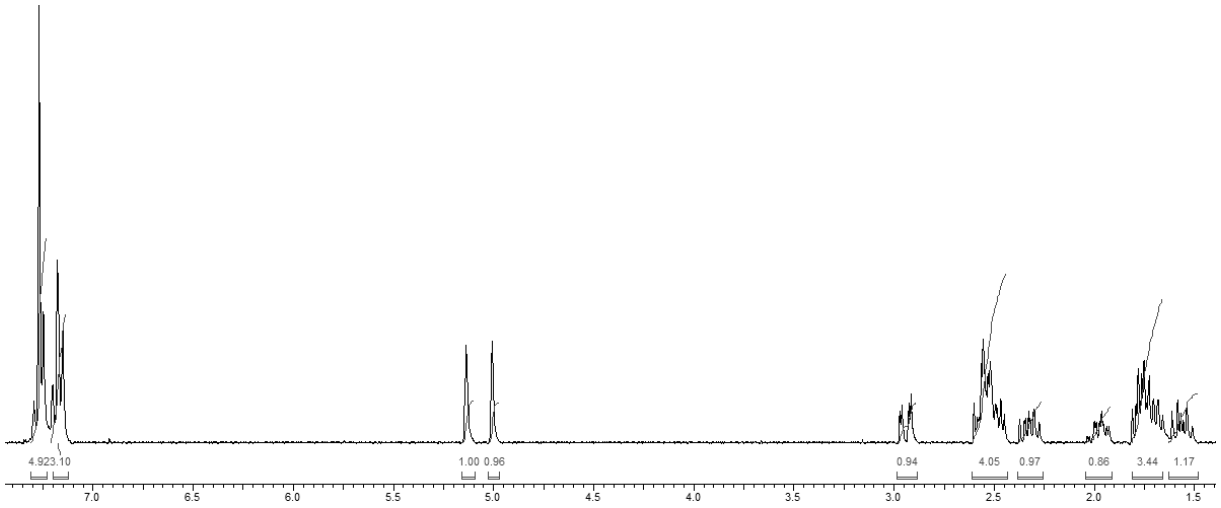
^{13}C NMR (100 MHz, $CDCl_3$):



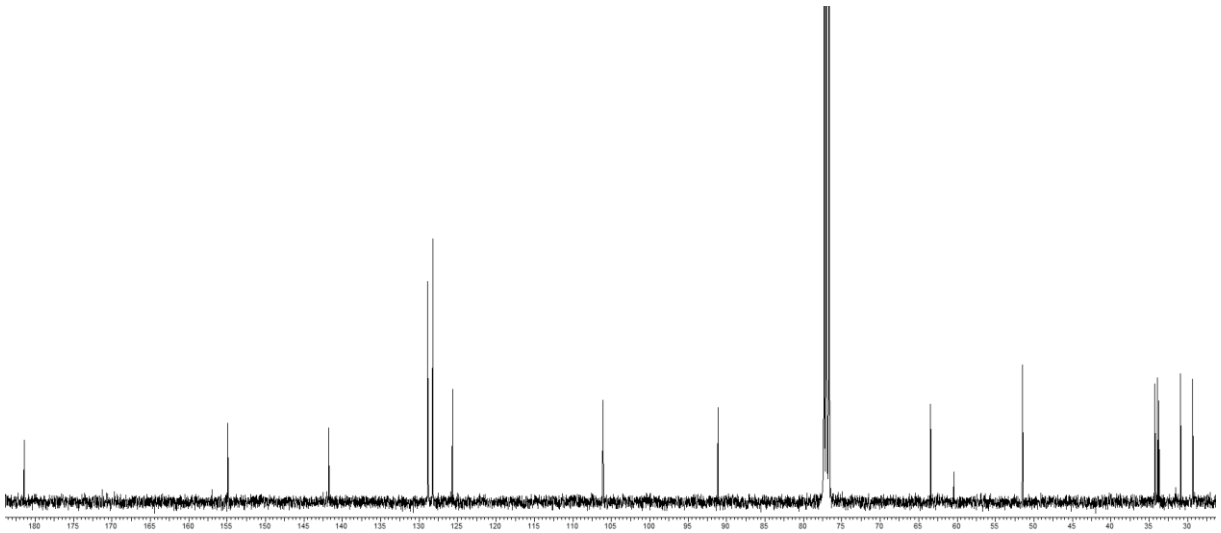
***rac*-(1S,3aR,6aS)-1-Benzyl-6a-hydroxy-6-methyleneoctahydropentalene-3a-carboxylic acid (2i) from page S22**



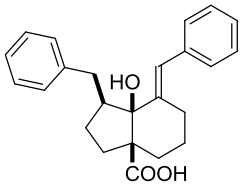
^{1}H NMR (300 MHz, $CDCl_3$):



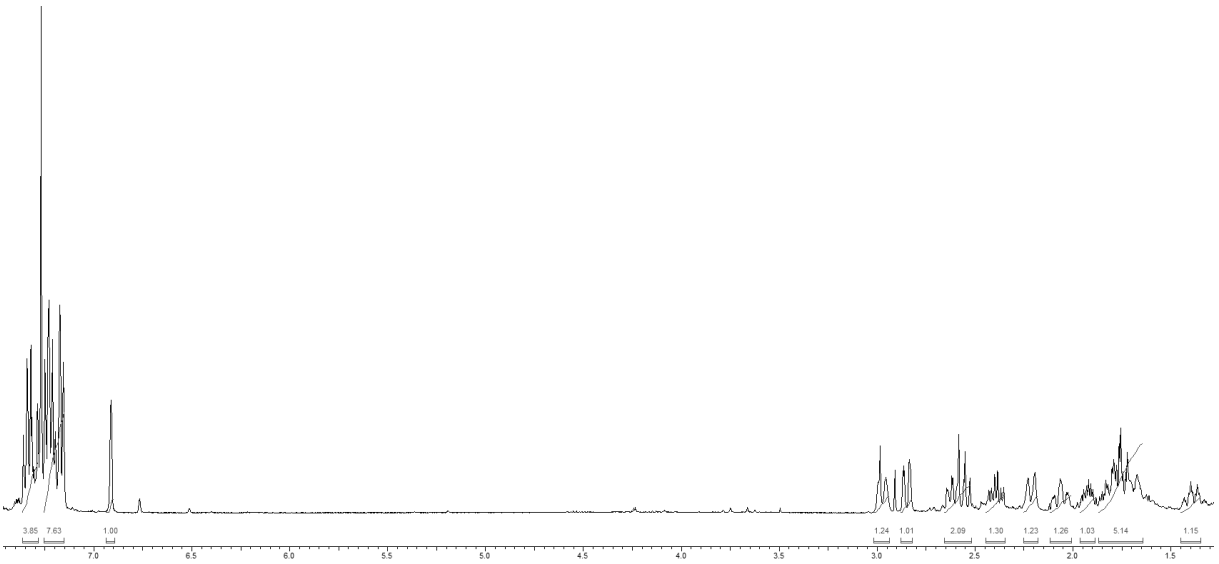
^{13}C NMR (100 MHz, $CDCl_3$):



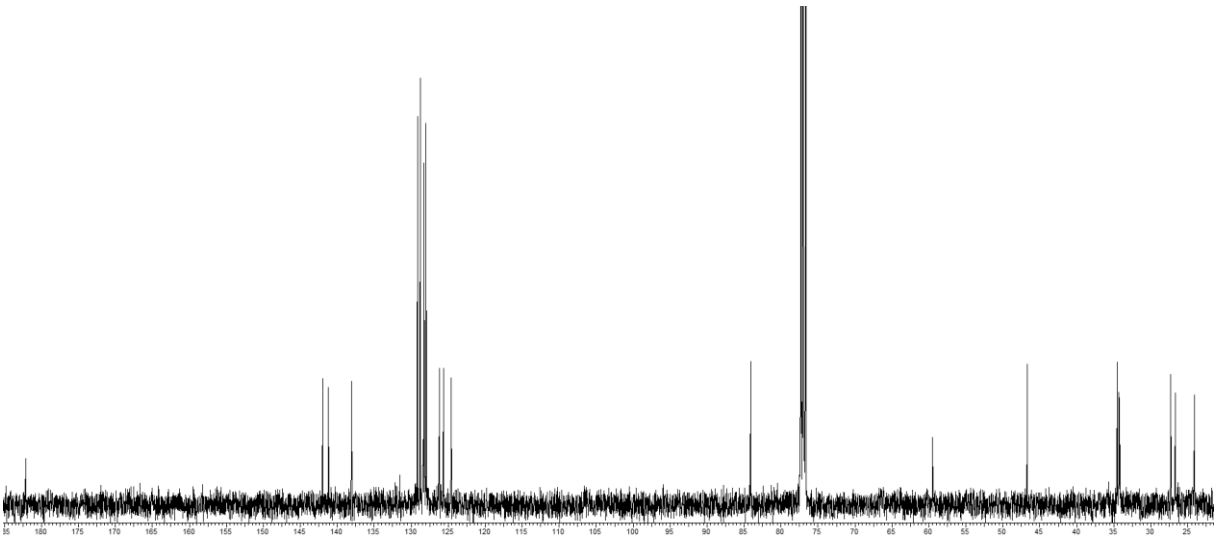
***rac*-(1S,3aS,7aS,*E*)-1-Benzyl-7-benzylidene-7a-hydroxyoctahydro-1H-indene-3a-carboxylic acid (2h) from page S23**



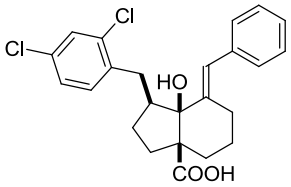
^{1}H NMR (400 MHz, $CDCl_3$):



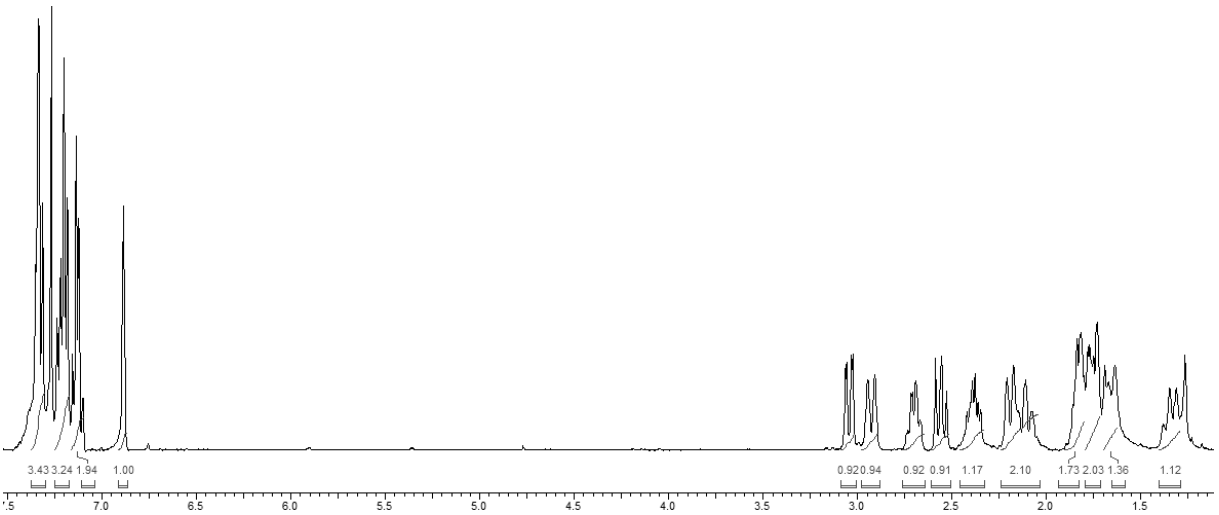
^{13}C NMR (100 MHz, $CDCl_3$):



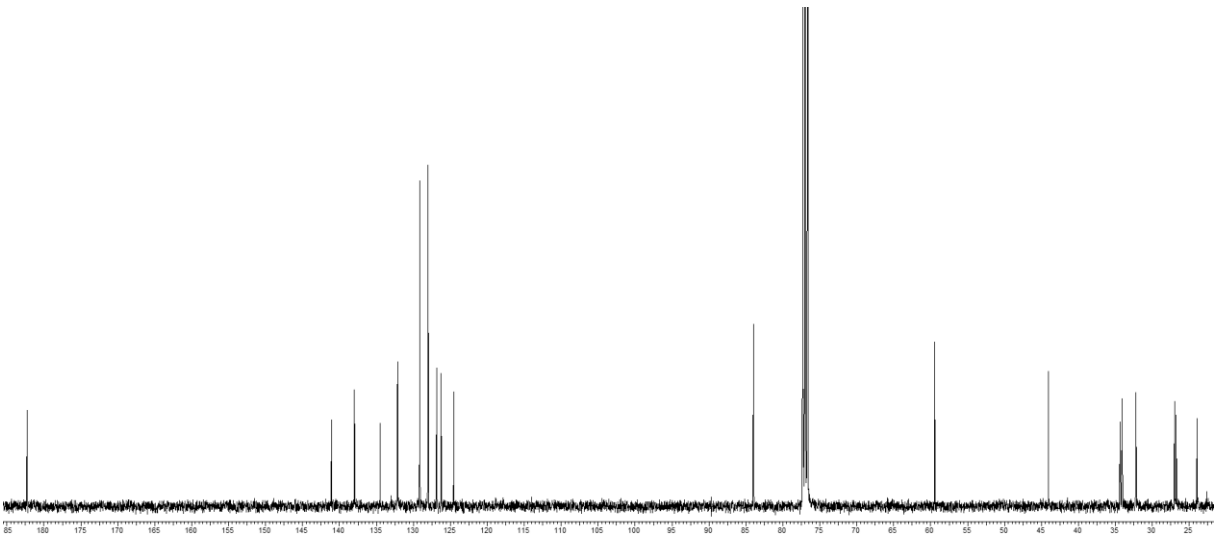
***rac*-(1S,3aS,7aS,*E*)-7-Benzylidene-1-(2,4-dichlorobenzyl)-7a-hydroxyoctahydro-1H-indene-3a-carboxylic acid (2k) from page S24**



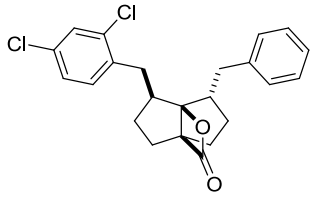
^{1}H NMR (400 MHz, $CDCl_3$):



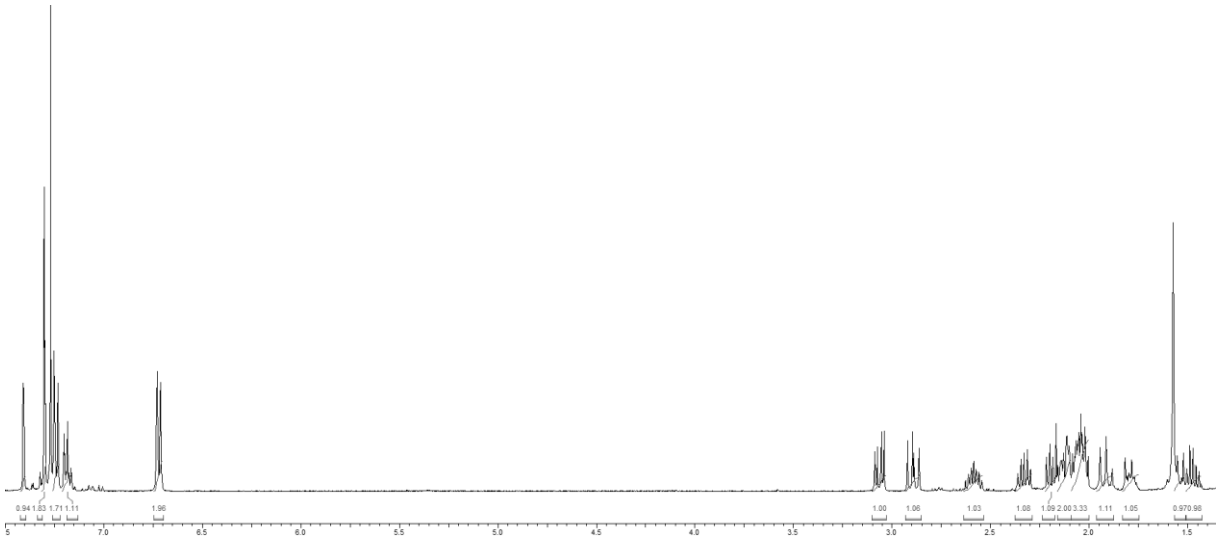
^{13}C NMR (100 MHz, $CDCl_3$):



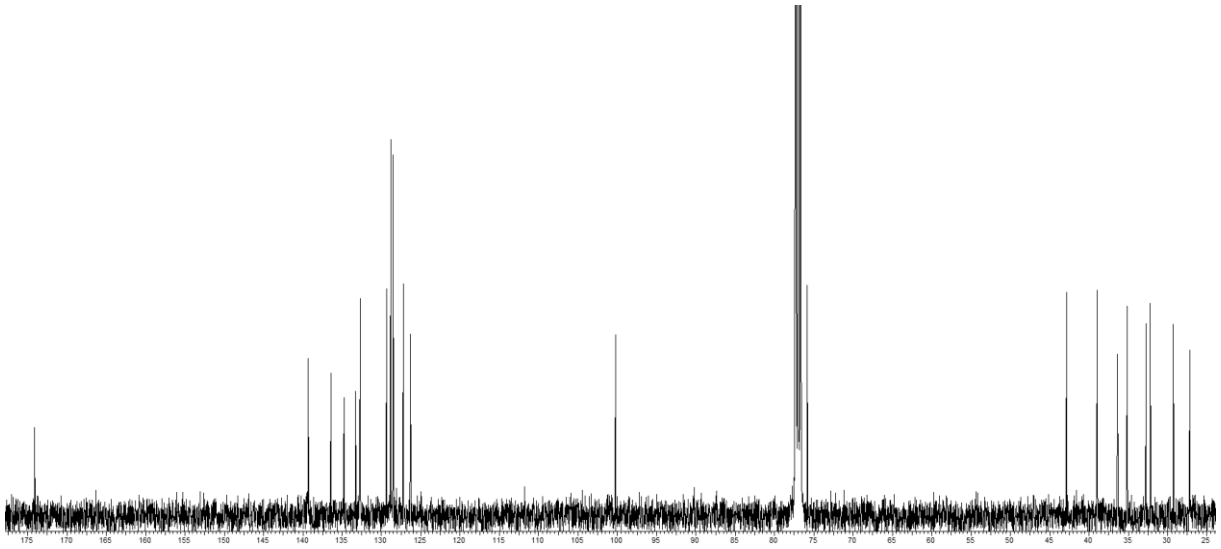
***rac*-(3S,3aR,4S,6aS)-3-Benzyl-4-(2,4-dichlorobenzyl)hexahydro-3a,6a-(epoxymethano)pentalen-7-one (6) from page S24**



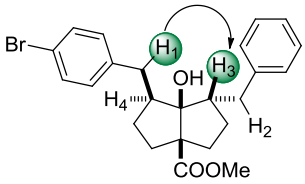
^{1}H NMR (400 MHz, $CDCl_3$):

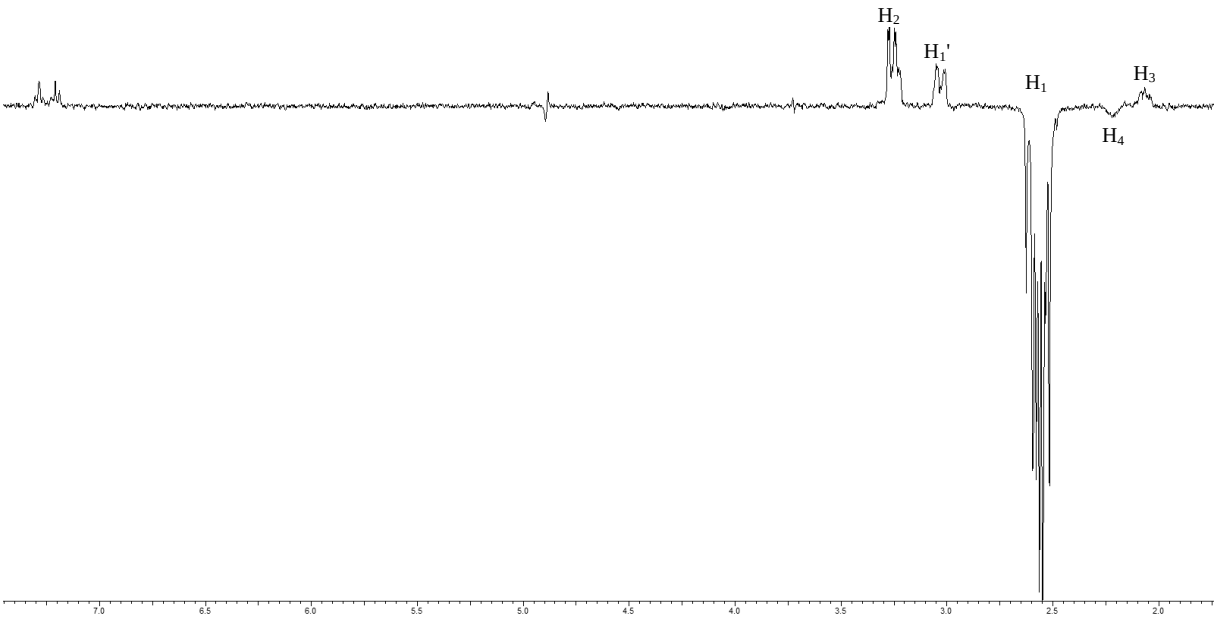


^{13}C NMR (100 MHz, $CDCl_3$):

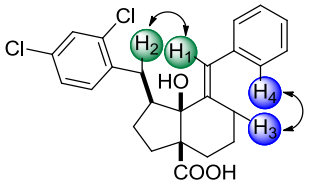


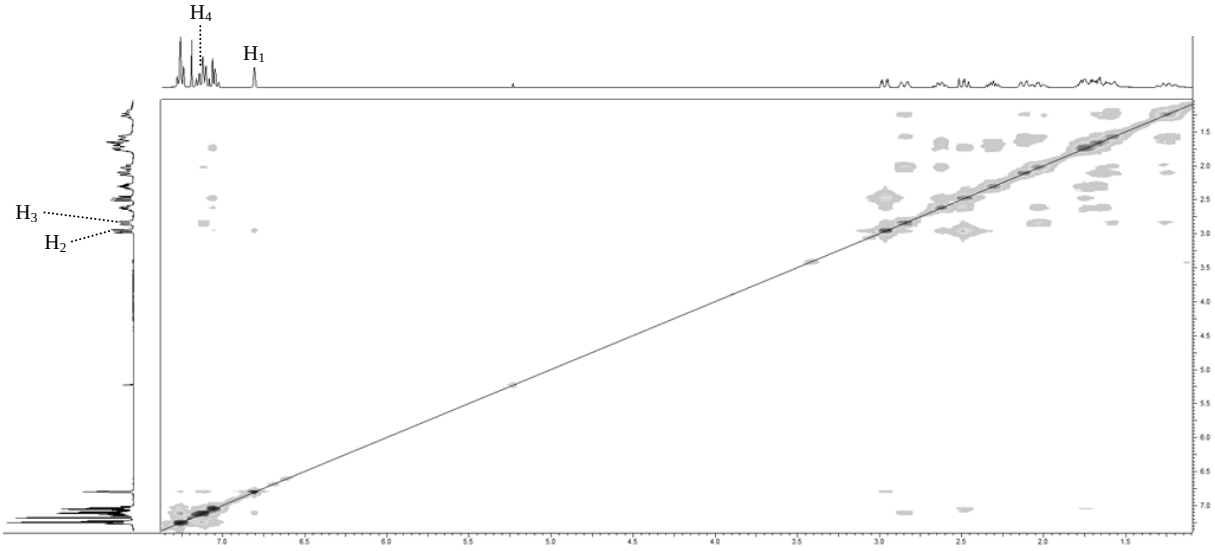
nOe data





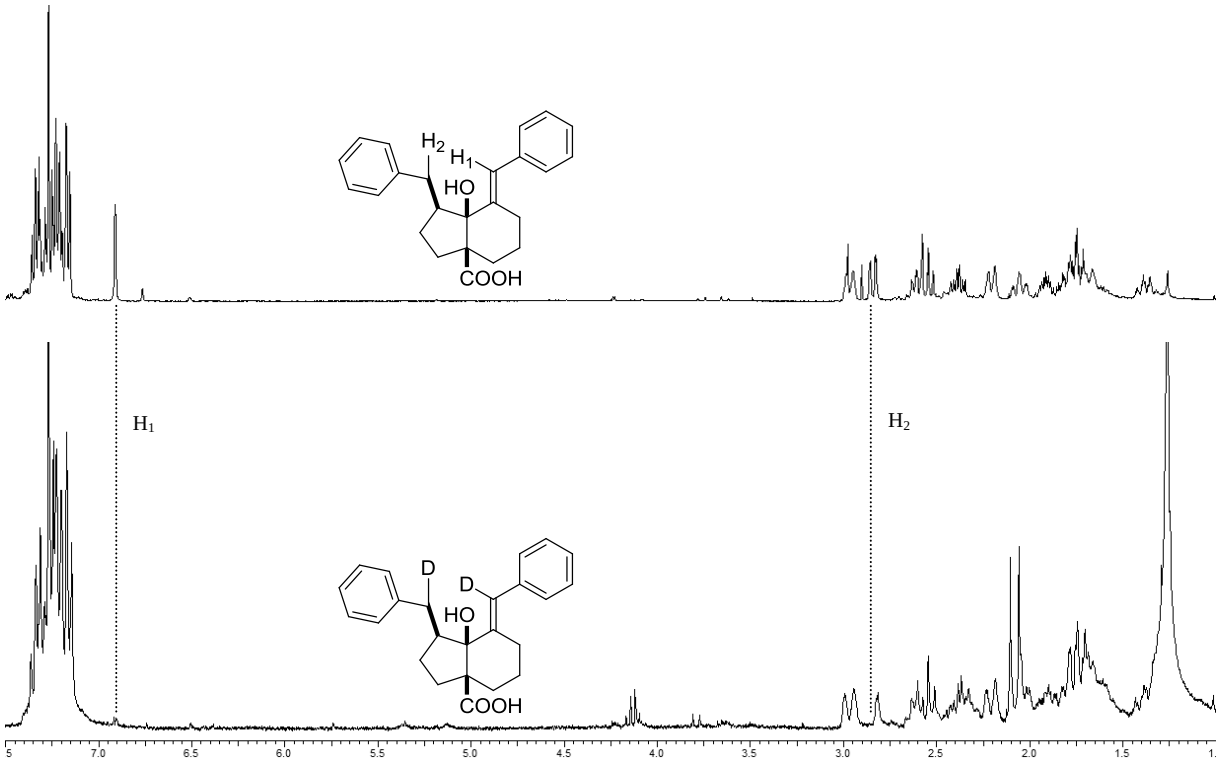
NOESY data



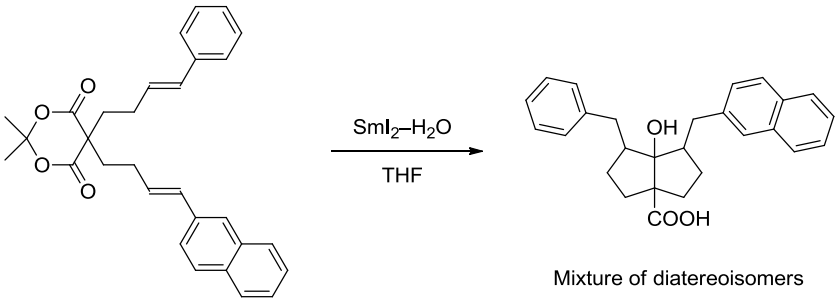


D_2O experiment

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

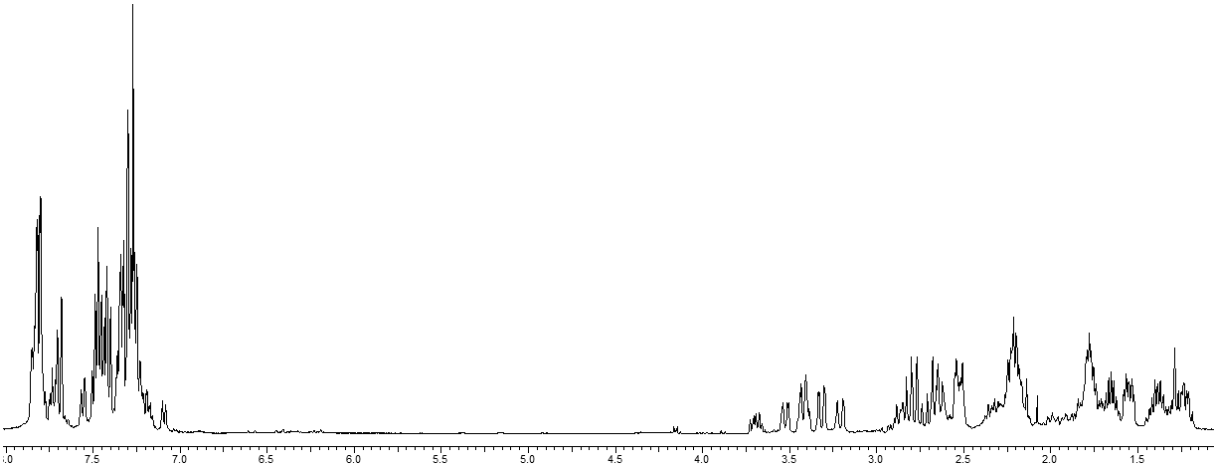


Cascade cyclization of a substrate bearing similarly activated alkenes



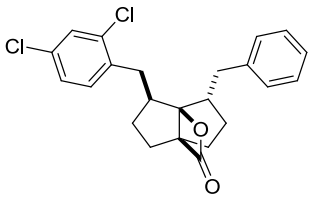
Mixture of diatereoisomers

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

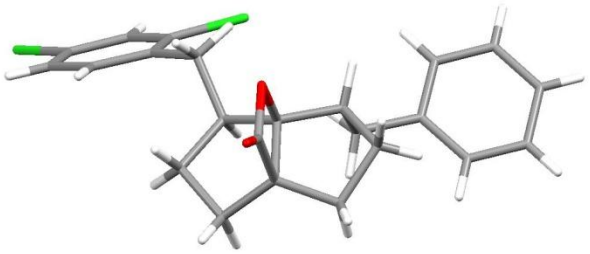


X-ray crystal structures

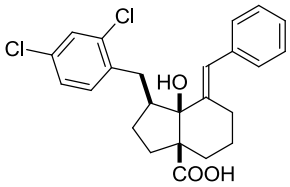
rac-(3S,3aR,4S,6aS)-3-Benzyl-4-(2,4-dichlorobenzyl)hexahydro-3a,6a-(epoxymethano)pentalen-7-one (6)



CCDC 849642



***rac*-(1S,3aS,7aS,*E*)-7-Benzylidene-1-(2,4-dichlorobenzyl)-7a-hydroxyoctahydro-1H-indene-3a-carboxylic acid (2k)**



CCDC 851256