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Supporting Information

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Palladium-catalyzed Synthesis of Substituted Seven-Membered Carbocyclic 1,4-Diketones by Asymmetric Ring-Expanding Allylation (AREA)

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1) GENERAL REMARKS

All Pd-catalyzed reactions were carried out under an atmosphere of argon in oven-dried glassware with magnetic stirring. Solvents for Pd-catalyzed were distilled from sodium-benzophenone and degassed prior to use. [$Pd_2(dba)_3$] was purchased from Aldrich, (*R*)-BINAP (**3**) and (*S*)-*i*Pr-phox (**5**) were purchased from Fluka. A sample of (*S*)-*t*Bu-phox (**6**) was donated to us by G. Helmchen which we gratefully acknowledge. Trost-ligand **4** was purchased from *Strem*. Phosphoramidit ligand **7** was prepared after a modified literature procedure.[1] All the reagents were used as obtained unless otherwise noted.

[1] Polet, D.; Alexakis, A. *Org. Lett.* **2005**, 7, 1621.

Flash chromatography was performed with *Merck* silica gel (0.03-0.06 μm grade). Analytical thin-layer chromatography was performed with 0.2 mm coated commercial silica gel plates (*Merck*, DC-Plastikfolien, Kieselgel 60 F_{254}). Proton nuclear magnetic resonance (^{1}H-NMR) data were acquired on a Bruker AV 400 (400 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, in parts per million (ppm) with the residual proton signal as an internal standard.[2] Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartett; p, pentet; m, multiplet; br, broad. Carbon-13 nuclear magnetic resonance (^{13}C-NMR) data were acquired on a Bruker AV 400 spectrometer at 100 MHz. Chemical shifts are reported in ppm relative to the center line of a triplet at 77.1 ppm for $CDCl_3$. Infrared spectra were acquired in the ATR (attenuated total reflectance) mode on a *Perkin-Elmer* Infrared-Spectrometer 881. Absorbance frequencies are reported in reciprocal centimeters (cm^{-1}). Chiral GC analyses were performed on a HP 5890 Series II GC system using a Lipodex E column (*Macherey-Nagel*, 25 m length, 0.25 mm). Optical rotations were measured on a *Perkin-Elmer* Polarimeter 341.

2) GENERAL PROCEDURE FOR THE SYNTHESIS OF MIXED ALLYL ENOL CARBONATES

A suspension of the corresponding 1,3-diketone (30 mmol) and K_2CO_3 (60 mmol, 2 equiv.) in 50 mL abs. acetone was cooled to 0 °C. Allyl chloroformate (33 mmol, 1.1 equiv.) was added dropwise over a period of 15 minutes. The suspension was slowly warmed to rt and stirred until TLC showed completion of the reaction (typically 3 h or over night). The slurry was then filtered over Celite and all volatiles were removed under reduced pressure. The residue was then purified by flash chromatography on silica (hexanes/TBME). The yield for this transformation was typically more than 90 %.

3) GENERAL PROCEDURE FOR THE SYNTHESIS OF BICYCLO[3.2.0]HEPTAN-2-ONES

Into a precooled (-55 °C) solution of the allyl carbonate in CH_2Cl_2 was condensated ethylene (or allene) (~ 10 equiv.). The solution was kept at this temperaurure and irradiated with a mercury vapour lamp until the TLC-control showed complete consumption of the starting material (ca. 8–12 h). After warming to room temperature the solvent was evaporated under reduced pressure. The residue was purified by flash chromatography on silica (hexanes/TBME). The yield for the cycloaddition was typically around 50-70 %.

[2] H. E. Gottlieb, V. Kotlyar, A. Nudelmann, *J. Org. Chem.* **1997**, 62, 7512.

4) GENERAL PROCEDURE FOR THE ASYMMETRIC RING-EXPANDING ALLYLATION (AREA)

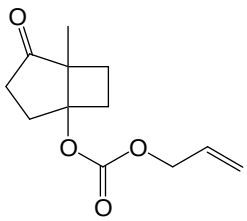
A 25 mL Schlenk flask was equipped with a magnetic stirrer and flame dried under vacuum. After cooling and flushing with argon, $[Pd_2(dba)_3]$ (6.7 mg, 0.025 equiv.) and (*S*)-*t*Bu-phox (7.3 mg, 0.065 equiv.) were added. The flask containing the solids was evacuated for 10 min and then refilled with argon. Dry and degassed 1,4-dioxane (6 mL) and THF (2 mL) were then added and the resulting deep red solution stirred at 25 °C for 30 min until the colour of the solution changed into orange. At this point, the solution was cooled to 10 °C by means of a kryostate and the corresponding allyl carbonate (293 μmol) was added via syringe in one portion. When the reaction was complete by TLC, the reaction mixture was allowed to warm to rt, evaporated under reduced pressure and the residue purified by column chromatography (SiO_2, cyclohexane/MTBE 7:1) to afford the desired product.

5) GENERAL PROCEDURE FOR THE CONVERSION OF EXOMETHYLENE CYCLOHEPTANEDIONES TO THE CORRESPONDING ENONES

To the reaction mixture of the AREA-product (**9b**) was added diazabicyclo[5.4.0]undec-5-ene (DBU) (20-30 mol%) and stirred at rt for 18h. The mixture was evaporated and the crude purified by flash chromatography (SiO_2, cyclohexane/MTBE 7:1); yield >80%.

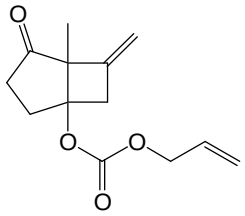
6) SPECTROSCOPIC DATA FOR THE AREA REACTION PRECURSORS

Carbonic acid allyl ester 5-methyl-4-oxo-bicyclo[3.2.0]hept-1-ylester (1)



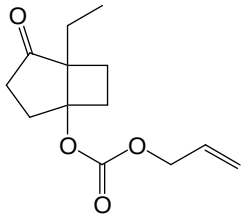
^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.17 (s, 3 H); 1.73 (dd, *J* = 0.9 Hz, *J* = 10.0 Hz, 1 H); 1.74 (d, *J* = 10.0 Hz, 1 H); 2.23-2.32 (m, 2 H); 2.39-2.52 (m, 2 H); 2.55-2.60 (m, 2 H); 4.51-4.54 (m, 2 H); 5.21 (qd, *J* = 1.5 Hz, *J* = 17.1 Hz, 1 H); 5.29 (qd, *J* = 1.5 Hz, *J* = 10.5 Hz, 1 H); 5.85 (tdd, *J* = 5.9 Hz, *J* = 10.5 Hz, *J* = 17.1 Hz, 1 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 13.9; 24.9; 31.8; 32.8; 37.1; 54.1 (C_q); 68.4; 83.4 (C_q); 119.2; 131.3; 153.3 (C_q); 218.3 (C_q).
IR (ATR): ν (cm^{-1}) = 3087 (w); 2974 (w); 2950 (w); 2870 (w); 1739 (s); 1649 (w); 1447 (m); 1410 (w); 1368 (m); 1298 (m); 1262 (m); 1243 (s); 1195 (m); 1183 (m); 1112 (w); 1082 (m); 1020 (m); 994 (m); 962 (m); 948 (m); 932 (m); 908 (m); 792 (m); 759 (w); 694 (w).
MS (EI, 70 eV): m/z (%) = 225 [M^++H] (4); 169 (7); 141 (9); 123 (26); 109 (11); 97 (14); 95 (30); 83 (24); 81 (39); 79 (31); 77 (32); 69 (100); 67 (30); 57 (48); 55 (58); 53 (18).
HRMS for $C_{12}H_{17}O_4$ (= [M^++H]): calc.: 225.1127; found: 225.1137
Elemental analysis: calc.: C : 64.27 %, H : 7.19 %; found: C : 64.45 %, H : 7.35 %

Carbonic acid allyl ester (5-methyl-6-methylen-4-oxo-bicyclo[3.2.0]hept-1-yl) ester (9a)



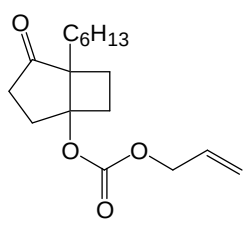
^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.29 (s, 3 H); 2.22-2.33 (m, 1 H); 2.51-2.66 (m, 3 H); 3.08 (td, *J* = 2.0 Hz, *J* = 16.5 Hz, 1 H); 3.26 (dtd, *J* = 1.8 Hz, *J* = 2.8 Hz, *J* = 16.5 Hz, 1 H); 4.62 (tdd, *J* = 1.5 Hz, *J* = 2.0 Hz, *J* = 5.8 Hz, 2 H); 4.98-5.00 (m, 1 H); 5.03-5.05 (m, 1 H); 5.29 (qd, *J* = 1.2 Hz, *J* = 10.6 Hz, 1 H); 5.37 (qd, *J* = 1.5 Hz, *J* = 17.2 Hz, 1 H); 5.93 (tdd, *J* = 5.8 Hz, *J* = 10.5 Hz, *J* = 17.2 Hz).
^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 13.7; 32.8; 37.4; 43.2; 63.1 (C_q); 68.5; 82.4; 109.9; 119.3; 131.3 (C_q); 142.7 (C_q); 153.4 (C_q); 213.8 (C_q).
IR (ATR): ν (cm^{-1}) = 3082 (w); 2975 (w); 2931 (w); 2870 (w); 1742 (s); 1672 (w); 1649 (w); 1450 (w); 1413 (w); 1384 (w); 1368 (m); 1297 (s); 1261(s); 1236 (s); 1181 (m); 1080 (w); 1030 (w); 1011 (m); 996 (m); 958 (w); 944 (w); 893 (w); 791 (m).
MS (EI, 70 eV): m/z (%) = 225 [M^+-CO_2] (3); 177 (7); 164 (6); 151 (10); 149 (12); 136 (14); 135 (39); 123 (32); 109 (55); 107 (29); 105 (21); 95 (100); 93 (43); 91 (70); 79 (37); 77 (38); 67 (50); 65 (18); 55 (26); 53 (25); 51 (12).
HRMS for $C_{12}H_{16}O_2$ (= [M^+-CO_2]): calc.: 192.1150; found: 192.1152.

Carbonic acid allyl ester 5-ethyl-4-oxo-bicyclo[3.2.0]hept-1-yl ester (10a)



^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 0.99 (t, *J* = 7.4 Hz, 3 H); 1.77 (q, *J* = 7.4 Hz, 2 H); 1.66-1.84 (m, 2 H); 2.20-2.45 (m, 4 H); 2.55-2.62 (m, 2 H); 4.61 (qd, *J* = 1.1 Hz, *J* = 5.9 Hz, 2 H); 5.28 (qd, *J* = 1.3 Hz, *J* = 10.5 Hz, 1 H); 5.36 (qd, *J* = 1.3 Hz, *J* = 17.2 Hz, 1 H); 5.98 (tdd, *J* = 5.9 Hz, *J* = 10.5 Hz, *J* = 17.2 Hz, 1 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 9.1; 22.6; 22.9; 31.5; 33.0; 37.7; 57.0 (C_q); 68.3; 119.1; 131.5; 153.3 (C_q); 173.3 (C_q); 218.8 (C_q).
IR (ATR): ν (cm^{-1}) = 3087 (w); 2969(m); 2943 (m); 2884 (w); 1737 (s); 1649 (w); 1585 (w); 1525 (w); 1461 (m); 1447 (m); 1412 (w); 1380 (m); 1366 (m); 1296 (s); 1263 (s); 1244 (s); 1229 (s); 1176 (s); 1100 (m); 1084 (m); 1019 (m); 995 (m); 957 (m); 932 (m); 792 (m).
MS (EI, 70 eV): m/z (%) = 238 [M^+] (<1); 154 (55); 139 (19); 137 (24); 125 (12); 111 (20); 109 (9); 99 (25); 95 (11); 93 (11); 83 (15); 79 (13); 69 (13); 67 (14); 57 (100); 55 (57); 53 (12).
HRMS for $C_{13}H_{18}O_4$: calc.: 238.1205; found: 238.1211
Elemental analysis: calc.: C : 65. 53 %, H : 7.61 %; found: C : 65.56 %, H : 7.77 %.

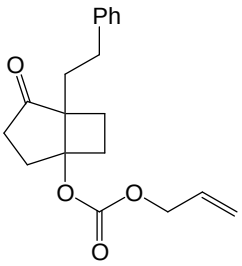
Carbonic acid allyl ester 5-hexyl-4-oxo-bicyclo[3.2.0]hept-1-yl ester (11a)



^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 0.87 (t, *J* = 6.8 Hz, 3 H); 1.23-1.33 (m, 8 H); 1.66-1.75 (m, 3 H); 1.98 (ddd, *J* = 4.6 Hz, *J* = 8.7 Hz, *J* = 12.9 Hz, 1 H); 2.19-2.28 (m, 1 H); 2.36 (ddd, *J* = 4.6 Hz, *J* = 8.7 Hz, *J* = 12.9 Hz, 1 H); 2.44-2.53 (m, 2 H); 2.55-2.61 (m, 2 H); 4.61 (qd, *J* = 1.3 Hz, *J* = 5.8 Hz, 2 H); 5.29 (qd, *J* = 1.4 Hz, *J* = 10.5 Hz, 1 H); 5.37 (qd, *J* = 1.4 Hz, *J* = 17.2 Hz, 1 H); 5.94 (tdd, *J* = 5.8 Hz, *J* = 10.5 Hz, *J* = 17.2 Hz, 1 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 14.0; 22.6; 23.4; 24.3; 29.8; 30.0; 31.3; 31.5; 32.9; 37.7; 56.7 (C_q); 68.3; 84.9 (C_q); 119.0; 131.5; 153.4 (C_q); 219.0 (C_q).

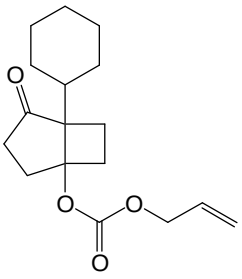
IR (ATR): ν (cm^{-1}) = 3086 (w); 2954 (m); 2932 (m); 2872 (m); 2858 (w); 1740 (s); 1649 (w); 1457 (m); 1447 (m); 1412 (w); 1366 (m); 1296 (m); 1261 (s); 1243 (s); 1196 (m); 1174 (m); 1112 (w); 1084 (m); 933 (m); 940 (m); 792 (m); 726 (w);
MS (EI, 70 eV): m/z (%) = 295 [M^++H] (2); 209 (5); 193 (11); 165 (9); 151 (10); 139 (15); 125 (18); 111 (37); 99 (40); 95 (49); 91 (36); 79 (46); 69 (66); 67 (39); 55 (100); 53 (32).
HRMS for $C_{17}H_{27}O_4$ (= [M^++H]): calc.: 295.1909; found: 295.1910

Carbonic acid allyl ester 4-oxo-5-phenethyl-bicyclo[3.2.0]hept-1-yl ester (12a)



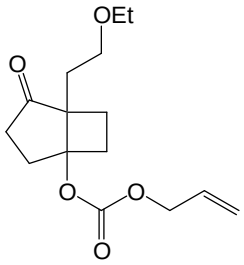
^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.73-1.82 (m, 1 H); 1.98-2.06 (m, 3 H); 2.23-2.32 (m, 1 H), 2.39-2.46 (m, 1 H); 2.52-2.67 (m, 5 H); 2.82-2.91 (m, 1 H); 4.62 (dt, *J* = 1.3 Hz, *J* = 5.7 Hz, 2 H); 5.29 (qd, *J* = 1.3 Hz; *J* = 10.4 Hz, 1 H); 5.37 (qd, *J* = 1.5 Hz, *J* = 17.1 Hz, 1 H); 5.95 (tdd, *J* = 5.8 Hz, *J* = 10.4 Hz, *J* = 17.2 Hz, 1 H); 7.12-7.31 (m, 5 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 23.4; 30.9; 31.3; 32.1; 32.9; 37.7; 56.4 (C_q); 68.3; 84.6 (C_q); 119.1; 125.8; 128.3; 128.4; 131.4; 142.4 (C_q); 153.3 (C_q); 218.4 (C_q).
IR (ATR): ν (cm^{-1}) = 3085 (w); 3062 (w); 3026 (m); 2983 (w); 2946 (m); 2868 (w); 1736 (s); 1649 (w); 1603 (m); 1584 (w); 1497 (s); 1453 (m); 1412 (m); 1383 (m); 1366 (m); 1296 (s); 1262 (s); 1242 (s); 1233 (s); 1196 (m); 1170 (m); 1139 (m); 1081 (m); 1017 (m); 993 (m); 937 (m); 791 (m); 753 (m); 701 (m).
MS (EI, 70 eV): m/z (%) = 314 [M^+]; 212 (16); 201 (15); 179 (14); 131 (11); 115 (11); 104 (23); 91 (100); 79 (8).
HRMS for $C_{19}H_{22}O_4$ (= [M^++H]): calc.: 314.1518; found: 314.1527

Carbonic acid allyl ester 5-cyclohexyl-4-oxo-bicyclo[3.2.0]hept-1-yl ester (13a)



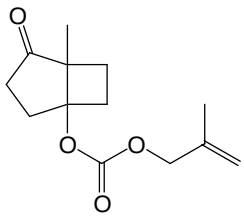
^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.03-1.21 (m, 2 H); 1.22-1.30 (m, 2 H); 1.49-1.83 (m, 9 H); 2.04-2.23 (m, 2 H); 2.29-2.39 (m, 2 H); 2.45-2.62 (m, 2 H); 4.60 (td, *J* = 1.4 Hz, *J* = 5.8 Hz, 2 H); 5.24-5.40 (m, 2 H); 5.95 (tdd, *J* = 5.9 Hz, *J* = 10.3 Hz, *J* = 16.6 Hz, 1 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 14.5; 18.0; 22.8; 26.2; 26.3; 26.6; 28.6; 29.0; 30.2; 31.3; 32.3; 37.3; 38.5; 39.8; 49.2; 59.1 (C_q); 60.4; 67.8; 68.3; 85.3 (C_q); 86.8 (C_q); 118.5; 119.0; 131.5; 131.9; 153.0 (C_q); 153.2 (C_q); 173.3 (C_q); 219.8 (C_q).
IR (ATR): ν (cm^{-1}) = 3086 (w); 2979 (m); 2927 (m); 2927 (m); 2852 (m); 2669 (w); 1741 (s); 1649 (w); 1449 (m); 1412 (m); 1366 (m); 1293 (m); 1278 (s); 1259 (s); 1247 (s); 1224 (s); 1181 (m); 1173 (m); 1126 (m); 1092 (m); 1084 (m); 1072 (m); 1027 (m); 993 (m); 946 (m); 891 (m); 873 (w); 791 (m).
MS (EI, 70 eV): m/z (%) = 293 [M^++H] (3); 191 (39); 179 (39); 129 (51); 111 (35); 109 (100); 101 (40); 81 (35); 67 (34).
HRMS for $C_{17}H_{24}O_4$ (= [M^++H]): calc.: 292.1675; found: 293.1767

Carbonic acid allyl ester 5-ethoxyethyl-4-oxo-bicyclo[3.2.0]hept-1-yl ester (14a)



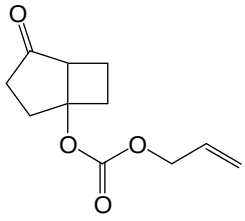
^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.11 (t, *J* = 7.0 Hz, 3 H); 1.71 (ddd, *J* = 7.7 Hz, *J* = 8.6 Hz, *J* = 16.4 Hz, 1 H); 1.96 (ddd, *J* = 5.2 Hz, *J* = 7.5 Hz, *J* = 14.0 Hz, 1 H); 2.03-2.12 (m, 2 H); 2.15-2.23 (m, 1 H); 2.32 (ddd, *J* = 5.4 Hz, *J* = 8.7 Hz, *J* = 13.1 Hz, 1 H); 2.42-2.63 (m, 4 H); 3.39 (ddd, *J* = 2.3 Hz, *J* = 6.9 Hz, *J* = 16.8 Hz, 1 H); 3.39 (t, *J* = 7.2 Hz, 1 H); 3.47-3.59 (m, 2 H); 4.57 (td, *J* = 1.4 Hz, *J* = 5.8 Hz, 2 H); 5.25 (qd, *J* = 1.4 Hz, *J* = 10.4 Hz, 1 H); 5.33 (qd, *J* = 1.4 Hz, *J* = 17.1 Hz, 1 H); 5.90 (tdd, *J* = 5.8 Hz, *J* = 10.4 Hz, *J* = 17.1 Hz, 1 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 15.1; 24.0; 30.3; 30.7; 32.6; 37.3; 54.7 (C_q); 66.0; 66.5; 68.3; 85.4 (C_q); 119.0; 131.4; 153.3 (C_q); 218.1 (Cq).
IR (ATR): ν (cm^{-1}) = 3087 (w); 2975 (m); 2946 (m); 2868 (m); 1738 (s); 1649 (w); 1490 (w); 1447 (m); 1412 (m); 1379 (m); 1367 (m); 1295 (m); 1260 (s); 1243 (s); 1189 (m); 1176 (m); 1109 (m); 1020 (m); 947 (m); 791 (m).
MS (EI, 70 eV): m/z (%) = 282 [M^+] (16); 181 (35); 151 (100); 135 (50); 109 (32); 81 (23); 59 (72).
HRMS for $C_{15}H_{22}O_5$ (= [M^++H]): calc.: 282.1543; found: 282.1547

Carbonic acid 2-methyl-allyl ester 5-methyl-4-oxo-bicyclo[3.2.0]hept-1-yl ester (15a)



^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.23 (s, 3 H); 1.76 (p, *J* = 0.5 Hz, 3 H); 1.79 (d, *J* = 10.3 Hz, 1 H); 1.80 (d, *J* = 10.3 Hz, 1 H); 2.29-2.38 (m, 2 H, H_F); 2.50 (td, *J* = 8.6 Hz, *J* = 14.7 Hz, 1 H); 2.56 (dq, *J* = 1.3 Hz, *J* = 11.9 Hz, 1 H); 2.62 (d, *J* = 8.0 Hz, 1 H); 2.64 (dd, *J* = 2.7 Hz, *J* = 8.0 Hz, 1 H); 4.51 (dd, *J* = 0.5 Hz, *J* = 4.6 Hz, 2 H); 4.95 (p, *J* = 0.7 Hz, 1 H); 5.00 (t, *J* = 1.0 Hz, 1 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 13.9; 19.3; 24.9; 31.8; 32.8; 37.1; 54.1 (C_q); 71.0; 83.3 (C_q); 113.6; 139.2 (C_q); 153.4 (C_q); 218.3 (C_q).
IR (ATR): ν (cm^{-1}) = 3085 (w); 2976 (w); 2947 (w); 2870 (w); 1739 (s); 1660 (w); 1587 (w); 1522 (w); 1146 (m); 1407 (w); 1372 (m); 1302 (s); 1265 (s); 1240 (s); 1195 (m); 1183 (m); 1085 (m); 1019 (m); 963 (w); 939 (m); 909 (m); 854 (w); 792 (m); 652 (w).
MS (EI, 70 eV): m/z (%) = 239 [M^++H] (<1); 125 (3); 123 (15); 109 (4); 96 (5); 95 (8); 81 (18); 69 (7); 67 (7); 55 (100); 53 (11).
HRMS for $C_{13}H_{19}O_4$ (= [M^++H]): calc.: 239.1283; found: 239.1288
Elemental analysis: calc: C : 65.53 %, H : 7.61 %; found: C: 65.17 %, H : 7.78 %.

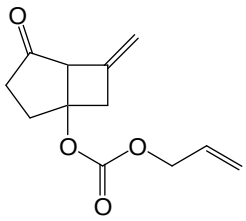
Carbonic acid allyl ester 4-oxo-bicylo[3.2.0]hept-1-yl ester (16a)



^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.66-1.76 (m, 1 H); 2.33-2.53 (m, 4 H); 2.56-2.74 (m, 3 H); 3.11 (dd, *J* = 7.4 Hz, *J* = 10.7 Hz, 1 H); 4.61 (dt, *J* = 1.1 Hz, *J* = 5.9 Hz, 2 H); 5.27-5.39 (m, 2 H); 5.93 (tdd, *J* = 5.7 Hz, *J* = 10.7 Hz, *J* = 17.2 Hz, 1 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 17.2 ; 32.8 ; 33.7 ; 38.3 ; 51.0 ; 68.4 ; 83.1 (C_q) ; 119.2 ; 131.3 ; 153.3 (C_q) ; 216.7 (C_q).
IR (ATR): ν (cm^{-1}) = 3460 (w); 3089 (w); 2984 (m); 2873 (m); 1739 (s); 1649 (m); 1584 (w); 1448 (m); 1411 (m); 1384 (m); 1368 (m); 1302 (s); 1264 (s); 1244 (m); 1204 (m); 1169 (m); 1090 (m); 1074 (m); 1062 (m); 993 (m); 946 (m); 895 (m); 791 (m); 685 (w).

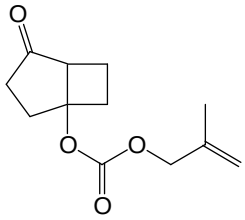
MS (EI, 70 eV): m/z (%) = 211 [M^++H] (10); 155 (14); 126 (18); 109 (100); 108 (43); 85 (32); 55 (31).
HRMS for $C_{11}H_{14}O_4$ (= [M^++H]): calc.: 210.0892; found: 211.0972

Carbonic acid allyl ester 6-methylene-4-oxo-bicyclo[3.2.0]hept-1-yl ester (17a)



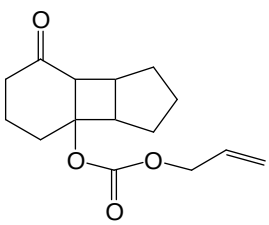
^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 2.28-2.74 (m, 4 H); 2.98-3.34 (m, 2 H); 3.68 (s, 1 H); 4.64 (d, *J* = 5.9 Hz, 2 H); 4.99 (s, 1 H); 5.21 (s, 1 H); 5.24-5.48 (m, 2 H); 5.93 (ddt, *J* = 5.9 Hz, *J* = 10.3 Hz, *J* = 17.2 Hz, 1H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 33.6; 38.7; 44.4; 68.5; 80.8 (C_q); 111.9; 119.2; 131.1; 135.6 (C_q); 153.3 (C_q); 153.3 (C_q); 211.7 (C_q).
IR (ATR): ν (cm^{-1}) = 3085 (w); 2983 (w); 2950 (w); 2831 (w); 1743 (s); 1676 (w); 1649 (w); 1582 (w); 1541 (m); 1423 (m); 1413 (m), 1384 (m); 1368 (m); 1298 (m); 1264 (s); 1246 (s); 1185 (m); 1163 (m); 1111 (m); 1087 (m); 1052 (m); 1014 (m); 992 (m); 964 (m); 944 (m); 897 (m); 876 (m); 836 (w); 791 (m).
MS (EI, 70 eV): m/z (%) = 223 [M^++H] (6); 166 (45); 137 (44); 121 (67); 95 (69); 91 (100); 77 (64).
HRMS for $C_{12}H_{14}O_4$ (= [M^++H]): calc.: 222.0892; found: 223.0972

Carbonic acid 2-methyl-allyl ester 4-oxo-bicyclo[3.2.0]hept-1-yl ester (18a)



^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.67 (m, 1 H); 1.79 (s, 3 H); 2.31-2.55 (m, 4 H); 2.56-2.76 (m, 3 H); 3.10-3.16 (m, 1 H); 4.54 (s, 2 H); 5.98 (s, 1 H); 5.03 (s, 1 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 17.2; 19.4; 32.8; 33.7; 38.3; 51.0; 71.1; 83.0 (C_q); 113.8; 139.1 (C_q); 153.4 (C_q); 216.8 (C_q).
IR (ATR): ν (cm^{-1}) = 3084 (w); 2979 (w); 2949 (m); 2873 (w); 1739 (s); 1660 (m); 1447 (m); 1409 (m); 1378 (m); 1369 (m); 1305 (s); 1266 (s); 1241 (m); 1204 (m); 1169 (m); 1092 (m); 1074 (m); 998 (m); 972 (m); 909 (m); 791 (m); 681 (w).
MS (EI, 70 eV): m/z (%) = 225 [M^++H] (6); 162 (12); 109 (25); 82 (16); 55 (100).
HRMS for $C_{12}H_{16}O_4$ (= [M^++H]): calc.: 224.1049; found: 225.1131

Carbonic acid allyl ester 7-oxo-decahydro-cyclopenta[3,4]cyclobuta[1,2]benzen-3b-yl ester (19a)

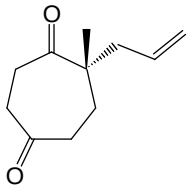


^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.55-1.57 (m, 1 H); 1.57-1.66 (m, 1 H); 1.70-1.90 (m, 4 H); 1.91-2.05 (m, 4 H); 2.09-2.25 (m, 1 H); 2.29-2.40 (m, 1 H); 2.44-2.53 (m, 2 H); 2.59-2.62 (m, 1 H); 2.79-2.85 (m, 1 H); 4.56-4.60 (m, 1 H); 5.27 (qd, *J* = 1.1 Hz, *J* = 10.4 Hz, 1 H); 5.35 (qd, *J* = 1.6 Hz, *J* = 17.2 Hz, 1 H); 5.92 (tdd, *J* = 5.2 Hz, *J* = 10.3 Hz, *J* = 17.0 Hz, 1 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 18.1; 25.1; 27.3; 32.4; 32,6; 37.9; 38.6; 47.5; 55.3; 68.1; 79.7 (C_q); 118.9; 131.4; 153.0 (C_q); 210.1 (C_q).
IR (ATR): ν (cm^{-1}) = 3086 (w); 2950 (m); 2875 (m); 1740 (s); 1704 (s); 1649 (m); 1462 (m); 1447 (m); 1412 (m); 1383 (m); 1367 (m); 1321 (m); 1293 (s); 1280 (s); 1255 (s); 1234 (s); 1192 (s); 1156 (m); 1126 (m); 1057 (m); 992 (m); 971 (m); 939 (m); 896 (m); 881 (m); 828 (w); 810 (w); 792 (m); 744 (w).

MS (EI, 70 eV): m/z (%) = 264 [M^+] (6); 197 (24); 163 (22); 153 (100); 125 (24); 113 (22); 91 (23); 83 (23); 67 (40); 55 (40).
HRMS for $C_{15}H_{20}O_4$ (= [M^++H]): calc.: 264.1362; found: 264.1369

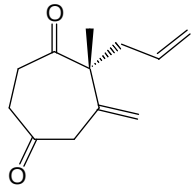
7) SPECTROSCOPIC DATA FOR THE AREA REACTION PRODUCTS

(*S*)-5-Allyl-5-methyl-cycloheptane-1,4-dione (2)



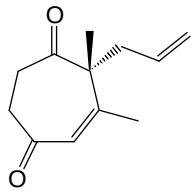
^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.16 (s, 3 H); 1.76 (ddd, *J* = 2.4 Hz, *J* = 9.3 Hz, *J* = 15.3 Hz, 1 H); 1.98 (ddd, *J* = 2.4 Hz, *J* = 10.1 Hz, *J* = 15.3 Hz, 1 H); 2.28 (dd, *J* = 7.5 Hz, *J* = 14.0 Hz, 1 H); 2.39 (dd, *J* = 7.5 Hz, *J* = 14.0 Hz, 1H); 2.46-2.63 (m, 5 H); 2.76-2.83 (m,1 H); 5.05-5.13 (m, 2 H); 5.71 (tdd, *J* = 7.5 Hz, *J* = 10.0 Hz, *J* = 16.9 Hz,1 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 21.6; 32.5; 34.1; 39.2; 39.5; 42.3; 51.3 (C_q); 118.9; 133.0; 209.7 (C_q); 214.1 (C_q).
IR (ATR): ν (cm^{-1}) = 3387 (w); 3076 (w); 2972 (m); 2934 (m); 2872 (w); 1702 (s); 1639 (w); 1463 (m); 1439 (m); 1379 (w); 1319 (m); 1260 (w); 1187 (w); 1161 (w); 1113 (w); 1072 (w); 1055 (w); 998 (m); 980 (w); 920 (m).
MS (EI, 70 eV): m/z (%) = 180 [M^+] (27); 152 (15); 137 (11); 123 (18); 111 (39); 109 (19); 98 (70); 95 (34); 82 (69); 81 (36); 79 (25); 70 (30); 67 (100); 56 (34); 55 (39); 53 (23).
HRMS for $C_{11}H_{16}O_2$: calc.: 180.1150; found: 180.1150
Optical Rotation: $[\alpha]_D^{20}$ = -50.3 ° ($CHCl_3$, c = 0.24)

(*S*)-5-Allyl-5-methyl-6-methylene-cycloheptane-1,4-dione (9b)



^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.25 (s, 3 H); 2.42 (dd, *J* = 6.9 Hz, *J* = 14.2 Hz, 1 H); 2.53 (dd, *J* = 8.1 Hz, *J* = 14.2 Hz, 1 H); 2.54-2.63 (m, 3 H); 2.70-2.77 (m, 1 H); 3.08 (d, *J* = 13.5 Hz, 1 H); 3.12 (d, *J* = 13.5 Hz, 1 H); 5.02-5.09 (m, 2 H); 5.19 (s, 1 H); 5.29 (s, 1 H); 5.55-5.66 (m, 1 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 20.6; 35.1; 39.2; 41.6; 50.4; 57.4 (Cq); 116.9; 118.5; 133.2; 142.2 (C_q); 204.8 (C_q); 213.2 (C_q).
IR (ATR): ν (cm^{-1}) = 3077 (w); 2976 (m); 2934 (w); 2871 (w); 2856 (w); 1710 (s); 1638 (m); 1455 (m); 1439 (m); 1373 (m); 1315 (m); 1265 (m); 1245 (m); 1184 (m); 1169 (m); 1137 (m); 1102 (m); 1069 (m); 996 (m); 975 (m); 916 (m); 820 (w); 796 (w); 752 (w).
MS (EI, 70 eV): m/z (%) = 270 [M^+] (7); 149 (35); 109 (42); 107 (52); 93 (80); 91 (52); 79 (100); 67 (47); 55 (47); 41 (76); 39 (51).
HRMS for $C_{16}H_{26}O_2$: calc.: 192.1152; found: 192.1150
Optical Rotation: $[\alpha]_D^{20}$ = -6.9 ° ($CHCl_3$, c = 0.31)

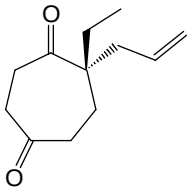
(*S*)-7-Allyl-6,7-dimethyl-cyclohept-5-ene-1,4-dione (9c)



^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.35 (s, 3 H); 2.02 (d, *J* = 1.2 Hz, 3 H); 2.26-2.33 (m,1 H); 2.59-2.65 (m, 2 H); 2.74-2.81 (m, 2 H); 2.95 (qd, *J* = 5.4 Hz, *J* = 11.3 Hz, *J* = 15.6 Hz, 1 H); 5.02-5.04 (m, 1 H); 5.04-5.08 (m, 1 H); 5.45-5.56 (m, 1 H); 6.04 (s, 1 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 22.6; 23.4; 35.0; 37.7; 41.3; 59.5 (C_q); 118.8; 130.0; 132.9; 153.2 (C_q); 200.9 (C_q); 211.1 (C_q).

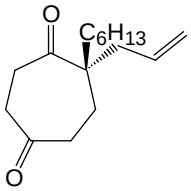
IR (ATR): ν (cm^{-1}) = 3484 (w); 3397 (w); 3077 (w); 2978 (m); 2929 (w); 2875 (m); 2857 (m); 1709 (s); 1661 (s); 1608 (m); 1443 (m); 1412 (m); 1383 (m); 1373 (m); 1322 (m); 1260 (m); 1197 (m); 1169 (m); 1090 (m); 1031 (m); 996 (m); 980 (m); 920 (m); 888 (m); 844 (m); 780 (w); 759 (w); 704 (w).
MS (EI, 70 eV): m/z (%) = [M^+] (7); 123 (100); 109 (58); 95 (37); 93 (53); 91 (37); 41 (53); 39 (40).
HRMS for $C_{12}H_{16}O_2$: calc.: 192.1152; found: 192.1155
Optical Rotation: $[\alpha]_D^{20}$ = -5.4 ° ($CHCl_3$, c = 0.32)

(*S*)-5-Allyl-5-ethyl-cycloheptane-1,4-dione (10b)



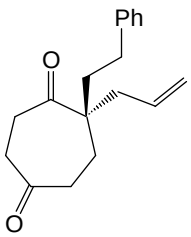
^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 0.82 (t, *J* = 7.8 Hz, 3 H); 1.51-1.61 (m, 1 H); 1.81-1.89 (m, 2 H); 2.25 (dd, *J* = 7.8 Hz; *J* = 14.8 Hz, 1 H); 2.39-2.63 (m, 7 H), 2.75-2.85 (m, 1 H); 5.04-5.11 (m, 2 H); 5.68 (tdd, *J* = 7.8 Hz, *J* = 10.5 Hz; *J* = 16.6 Hz, 1 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 8.2; 29.6; 29.9; 34.5; 37.7; 39.1; 53.9 (C_q); 118.6; 133.4 (Cq); 210.0 (C_q); 213.9 (C_q).
IR (ATR): ν (cm^{-1}) = 3528 (w); 3387 (w); 3076 (w); 2967 (m); 2938 (m); 2880 (m); 1702 (s); 1639 (m); 1463 (m); 1440 (m); 1384 (w); 1354 (w); 1318 (m); 1259 (m); 1185 (m); 1169 (m); 1111 (m); 1079 (m); 999 (m); 918 (m); 803 (w); 771 (w).
MS (EI, 70 eV): m/z (%) = 194 [M^+] (11); 166 (43); 165 (30); 154 (16); 137 (63); 125 (53); 124 (34); 111 (30); 109 (43); 99 (28); 98 (89); 95 (41); 93 (20); 83 (17); 81 (95); 79 (47); 77 (20); 70 (34); 67 (100); 65 (14); 57 (66); 55 (50); 53 (25); 51 (9).
HRMS for $C_{12}H_{18}O_2$: calc.: 194.1307; found: 194.1312
Optical Rotation: $[\alpha]_D^{20}$ = +43.8 ° ($CHCl_3$, c = 1.04)

(*S*)-5-Allyl-5-hexyl-cycloheptane-1,4-dione (11b)



^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 0.86 (t, *J* = 6.5 Hz, 3 H); 1.20-1.30 (m, 7 H); 1.46-1.54 (m, 1 H); 1.57-1.66 (m, 1 H); 1.78-1.91 (m, 2 H); 2.25 (dd, *J* = 7.7 Hz, *J* = 14.4 Hz, 1 H); 2.41-2.59 (m, 6 H); 2.78-2.87 (m, 2 H); 5.03-5.11 (m, 2 H); 5.69 (tdd, *J* = 7.4 Hz, *J* = 10.3 Hz, *J* = 17.4 Hz, 1 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 14.9; 23.9; 24.0; 29.5, 30.0; 31.5; 34.5; 34.9; 36.9; 39.0; 54.2 (C_q); 118.7; 135.5; 210,0 (C_q); 214.1 (C_q).
IR (ATR): ν (cm^{-1}) = 3075 (w); 2954 (m); 2929 (m); 2858 (m); 1703 (s); 1639 (w); 1466 (m); 1441 (m); 1378 (w); 1316 (m); 1258 (w); 1183 (w); 1159 (w); 1117 (w); 1101 (w); 997 (m); 917 (m); 726 (w).
MS (EI, 70 eV): m/z (%) = 250 [M^+] (7); 193 (36); 181 (42); 166 (100); 109 (28); 95 (31); 81 (36); 79 (31); 67 (60); 55 (40); 53 (19).
HRMS for $C_{16}H_{26}O_2$: calc.: 250.1993; found: 250.1933
Optical Rotation: $[\alpha]_D^{20}$ = +39.9 ° ($CHCl_3$, c = 0.28)

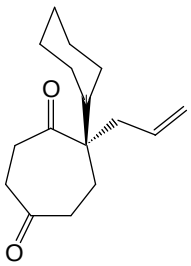
(*S*)-5-Allyl-5-phenethyl-cycloheptane-1,4-dione (12b)



^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.81-1.97 (m, 4 H); 2.34-2.46 (m, 2 H); 2.48-2.67 (m, 7 H); 2.83-2.92 (m, 1 H); 5.15-5.18 (m, 1 H); 5.19-5.21 (m, 1 H); 5.79 (tdd, *J* = 7.6 Hz, *J* = 11.4 Hz, *J* = 17.7 Hz, 1 H); 7.13-7.18 (m, 2 H); 7.19-7.23 (m, 1 H); 7.27-7.33 (m, 2 H).

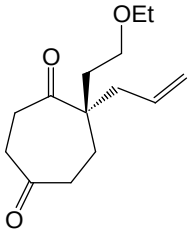
^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 30.5; 31.0; 34.5; 37.1; 37.5; 39.2; 39.3; 54.3 (C_q); 119.2; 126.2; 128.3; 128.6; 133.2; 141.5 (C_q); 209.9 (C_q); 213.7 (C_q).
IR (ATR): ν (cm^{-1}) = 3493 (w); 3387 (w); 3073 (m); 3063 (m); 3026 (m); 3002 (m); 2933 (m); 2863 (m); 1701 (s); 1638 (m); 1603 (m); 1584 (w); 1497 (m); 1454 (m); 1441 (m); 1416 (m); 1317 (m); 1260 (m); 1182 (m); 1156 (m); 1132 (m); 1096 (m); 1077 (m); 1050 (m); 1030 (m); 997 (m); 918 (m); 750 (m); 700 (m).
MS (EI, 70 eV): m/z (%) = 270 [M^+] (3); 167 (8); 166 (84); 129 (7); 109 (10); 91 (100); 79 (9); 68 (10); 65 (9).
HRMS for $C_{16}H_{26}O_2$: calc.: 270.1620; found: 270.1627
Optical Rotation: $[\alpha]_D^{20}$ = +33.2 ° ($CHCl_3$, c = 0.53)

(*S*)-5-Allyl-5-cyclohexyl-cycloheptane-1,4-dione (13b)



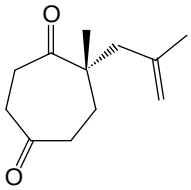
^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.04-1.29 (m, 4 H); 1.60-2.00 (m, 8 H); 2.15 (dd, *J* = 8.4 Hz, *J* = 14.0 Hz, 1 H); 2.28-2.60 (m, 7 H); 2.89 (ddd, *J* = 4.7 Hz, *J* = 12.2 Hz, *J* = 12.4 Hz, 1 H); 4.11 (q, *J* = 7.2 Hz, 2 H); 4.99-5.06 (m, 2 H); 5.82 (dddd, *J* = 6.3 Hz, *J* = 8.3 Hz, *J* = 10.5 Hz, *J* = 17.0 Hz, 1 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 11.1; 17.9; 19.8; 27.0; 28.7; 29.3; 30.6; 34.1; 37.9; 57.4 (C_q); 60.5; 117.8; 135.3; 174.7 (C_q); 210.7 (C_q); 213.7 (C_q).
IR (ATR): ν (cm^{-1}) = 3463 (m); 3075 (w); 2927 (s); 2853 (m); 1732 (m); 1702 (s); 1636 (m); 1562 (m); 1448 (m); 1372 (m); 1307 (m); 1284 (m); 1261 (m); 1179 (m); 1127 (m); 1109 (m); 1033 (m); 959 (m); 916 (m).
MS (EI, 70 eV): m/z (%) = 248 [M^+] (10); 191 (27); 166 (80); 144 (27); 109 (47); 98 (63); 91 (55); 81 (83); 79 (51); 69 (90); 57 (55); 55 (100).
HRMS for $C_{16}H_{26}O_2$: calc.: 248.1776; found: 248.1773
Optical Rotation: $[\alpha]_D^{20}$ = +11.2 ° ($CHCl_3$, c = 0.13)

(*S*)-5-Allyl-5-(2-ethoxyethyl)-cycloheptane-1,4-dione (14b)



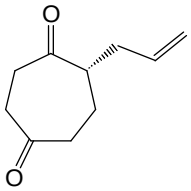
^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.10 (t, *J* = 7.0 Hz, 3 H); 1.77-1.91 (m, 3 H); 2.00 (ddd, *J* = 5.7 Hz, *J* = 8.2 Hz, *J* = 14.2 Hz, 1H); 2.31 (dd, *J* = 7.4 Hz, *J* = 13.6 Hz, 1 H); 2.40-2.67 (m, 6 H); 2.91-2.99 (m, 1 H); 3.28-3.39 (m, 3 H); 3.47 (td, *J* = 1.4 Hz, *J* = 9.8 Hz, 1 H); 5.04-5.13 (m, 2 H); 5.71 (tdd, *J* = 7.5 Hz, *J* = 10.3 Hz, *J* = 16.9 Hz, 1 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 14.9; 30.5; 34.7; 35.6; 37.8; 39.1; 52.7 (C_q); 66.0; 66.4; 119.1; 133.5; 210.5 (C_q); 213.4 (C_q).
IR (ATR): ν (cm^{-1}) = 3509 (w); 3388 (w); 3075 (w); 2974 (m); 2931 (m); 2867 (m); 2803 (m); 1701 (s); 1638 (m); 1488 (m); 1457 (m); 1441 (m); 1417 (m); 1377 (m); 1356 (m); 1317 (m); 1261 (m); 1183 (m); 1154 (m); 1111 (s); 1073 (m); 998 (m); 917 (m); 828 (w); 750 (w).
MS (EI, 70 eV): m/z (%) = 238 [M^+] (8); 166 (84); 135 (72); 109 (52); 98 (99); 95 (60); 81 (61); 79 (72); 68 (100); 59 (93); 55 (73).
HRMS for $C_{14}H_{22}O_3$: calc.: 238.1569; found: 238.1566
Optical Rotation: $[\alpha]_D^{20}$ = +35.1 ° ($CHCl_3$, c = 0.17)

(*S*)-5-Methyl-5-(2-methyl-allyl)-cycloheptane-1,4-dione (15b)



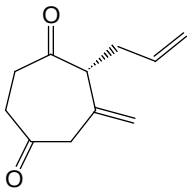
^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.17 (s, 3 H); 1.68 (t, *J* = 1.1 Hz, 3 H); 1.75 (ddd, *J* = 1.9 Hz, *J* = 9.6 Hz, *J* = 15.2 Hz, 1 H); 2.04 (ddd, *J* = 1.7 Hz, *J* = 10.6 Hz, *J* = 15.2 Hz); 2.28 (dd, *J* = 0.7 Hz, *J* = 13.8 Hz, 1 H); 2.41-2.65 (m, 5 H); 2.45 (d, *J* = 13.8 Hz, 1 H); 2.97 (ddd, *J* = 11.0 Hz, *J* = 11.1 Hz, *J* = 11.5 Hz, 1 H); 6.68 (m, 1 H); 4.88 (pent., *J* = 1.7 Hz, 1 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 21.8; 24.2; 33.7; 34.3; 39.5; 39.6; 46.6; 51.7 (C_q); 115.6; 141.1 (C_q); 209.6 (C_q); 214.8 (C_q).
IR (ATR): ν (cm^{-1}) = 3522 (w); 3388 (w); 3075 (w); 2968 (m); 2931 (m); 2871 (w); 2733 (w); 1704 (s); 1643 (w); 1497 (w); 1459 (m); 1440 (m); 1379 (m); 1350 (w); 1319 (m); 1260 (m); 1184 (m); 1163 (m); 1098 (m); 1060 (m); 1011 (w); 979 (m); 898 (m); 805 (w).
MS (EI, 70 eV): m/z (%) = 194 [M^+] (34); 166 (17); 123 (17); 111 (25); 109 (49); 98 (30); 96 (67); 95 (28); 81 (100); 79 (15); 67 (30); 56 (23); 55 (51); 53 (21).
HRMS for $C_{12}H_{18}O_2$: calc.: 194.1307; found: 194.1310
Optical Rotation: $[\alpha]_D^{20}$ = +20.0 ° ($CHCl_3$, c = 1.05)

(*S*)-5-Allyl-cycloheptane-1,4-dione (16b)



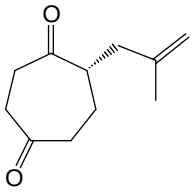
^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.54-1.65 (m, 1 H); 2.02-2.15 (m, 2 H); 2.49-2.77 (m, 8 H); 5.03-5.09 (m, 2 H); 5.73 (tdd, *J* = 6.2 Hz, *J* = 10.6 Hz, *J* = 16.6 Hz, 1 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 15.2; 26.1; 34.7; 37.8; 41.9; 51.6; 117.3; 135.6; 210.4 (C_q); 211.2 (C_q).
IR (ATR): ν (cm^{-1}) = 3523 (w); 3388 (w); 3077 (w); 2975 (m); 2930 (m); 2865 (w); 1703 (s); 1641 (m); 1439 (m); 1416 (m); 1373 (w); 1321 (m); 1271 (w); 1190 (m); 1150 (m); 1104 (w); 1074 (w); 997 (m); 919 (s); 771 (w).
MS (EI, 70 eV): m/z (%) = 166 [M^+] (28); 109 (43); 98 (100); 95 (40); 68 (77); 56 (38).
HRMS for $C_{10}H_{14}O_2$: calc.: 166.0994; found: 166.0992
Optical Rotation: $[\alpha]_D^{20}$ = -24.9 ° ($CHCl_3$, c = 0.31)

(*S*)-5-Allyl-6-methylen-cycloheptane-1,4-dione (17b)



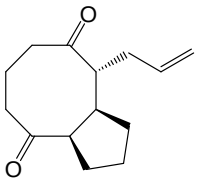
^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 2.50-2.72 (m, 6 H); 3.19 (s, 2 H); 3.25 (t, *J* = 9.0 Hz, 1 H); 4.90-5.21 (m; 4 H); 5.63 (ddt, *J* = 5.9 Hz, *J* = 10.4 Hz, *J* = 17.0 Hz, 1 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 32.9; 38.3; 51.3; 59.9; 117.0; 119.5; 134.9; 137.2 (C_q); 206.5 (C_q); 207.7 (C_q).
IR (ATR): ν (cm^{-1}) = 3480 (w); 3399 (w); 3078 (w); 2959 (w); 2924 (m); 2853 (w); 1707 (s); 1641 (m); 1438 (m); 1417 (m); 1377 (m); 1377 (w); 1316 (m); 1248 (m); 1134 (m); 1120 (m); 1095 (m); 997 (m); 916 (m).
MS (EI, 70 eV): m/z (%) = 178 [M^+] (12); 150 (37); 95 (52); 85 (40); 79 (100); 55 (48).
HRMS for $C_{10}H_{14}O_2$: calc.: 178.1005; found: 178.0993
Optical Rotation: $[\alpha]_D^{20}$ = -3.2 ° ($CHCl_3$, c = 0.11)

(*S*)-5-(2-Methylallyl)-cycloheptane-1,4-dione (18b)



^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.52-1.63 (m, 3 H); 1.71 (s, 3 H); 2.51 (dd, *J* = 5.9 Hz, *J* = 14.8 Hz, 1 H); 2.57-2.72 (m, 6 H); 2.82-2.90 (m, 1 H); 4.68 (s, 1 H); 4.81 (s, 1 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 22.4; 26.0; 37.6; 38.0; 38.4; 41.9; 49.8; 112.6; 142.5 (C_q); 210.5 (C_q); 211.5 (C_q).
IR (ATR): ν (cm^{-1}) = 3075 (w); 2963 (m); 2928 (m); 2857 (m); 1703 (s); 1647 (m); 1445 (m); 1412 (m); 1376 (m); 1318 (m); 1290 (m); 1266 (m); 1187 (m); 1168 (m); 1145 (m); 1118 (m);1073 (w); 1029 (w); 939 (m); 891 (m); 796 (w); 702 (w).
MS (EI, 70 eV): m/z (%) = 180 [M^+] (11); 109 (17); 98 (16); 95 (27); 82 (100); 67 (37); 55 (20); 53 (11).
HRMS for $C_{11}H_{16}O_2$: calc.: 180.1150; found: 180.1150
Optical Rotation: $[\alpha]_D^{20}$ = -12.0 ° ($CHCl_3$, c = 0.10)

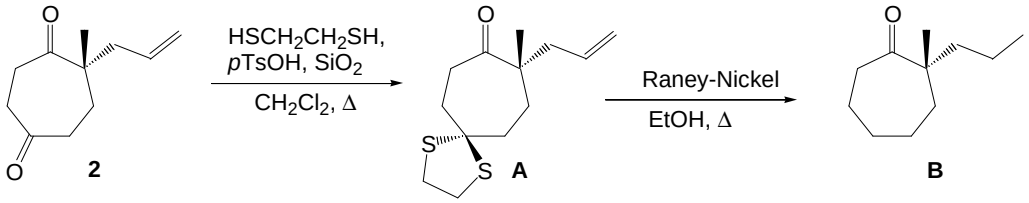
(*S*)-9-Allyl-octahydro-cyclopentacyclooctane-4,8-dione (19b)



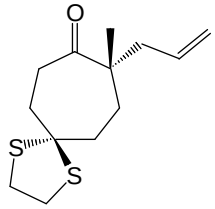
^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.36-1.48 (m, 1 H); 1.62-1.69 (m, 1 H); 1.83-1.91 (m, 3 H); 2.10-2.29(m, 5 H); 2.29-2.34 (m, 1 H); 2.35-2.43 (m, 1 H); 2.44-2.48 (m, 1 H); 2.50-2.60 (m, 3 H); 3.14 (td, *J* = 3.0 Hz, *J* = 7.7 Hz, 1 H); 4.93-5.01 (m, 2 H); 5.64 (tdd, *J* = 6.5 Hz, *J* = 10.4 Hz, *J* = 17.9 Hz, 1 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 23.2; 23.6; 28.4; 29.5; 36.8; 45.1; 45.6; 49.2; 51.4; 52.2; 117.1; 135.0; 216.8 (C_q); 217.5 (C_q).
IR (ATR): ν (cm^{-1}) = 3515 (w); 3376 (w); 3077 (w); 2954 (m); 2868 (m); 1737 (m); 1697 (s); 1641 (m); 1439 (m); 1415 (m); 1368 (m); 1357 (m); 1308 (m); 1281 (m); 1256 (m); 1238 (m); 1194 (m); 1160 (m); 1134 (m); 1101 (m); 1077 (m); 996 (m); 967 (m); 917 (m); 875 (m); 820 (m); 793 (w); 746 (w); 692 (w).
MS (EI, 70 eV): m/z (%) = 220 [M^+] (60); 125 (53); 123 (95); 96 (72); 95 (53); 83 (61); 79 (77); 67 (58); 55 (100); 53 (44).
HRMS for $C_{14}H_{20}O_2$: calc.: 220.1463; found: 220.1466
Optical Rotation: $[\alpha]_D^{20}$ = -4.0 ° ($CHCl_3$, c = 0.50)

8) DETERMINATION OF THE ABSOLUTE CONFIGURATION OF (*S*)-2

The absolute configuration of **2** was determined by comparison of the optical rotation of **B** with (*S*)-2-allyl-2-methyl-cycloheptane, whose optical rotation was reported in the literature.[3] Cycloheptanone **B** was synthesized by selective thioketalization of the less sterically hindered carbonyl group. The dithiolane **A** could be reduced by reaction with Raney-nickel to give **B**.



(*S*)-9-Allyl-9-methyl-1,4-dithia-spiro[4.6]undecan-8-one (A)



To a suspension of **2** (200 mg, 1.11 mmol), silica (1.8 g), and ethanedithiol (85 µl, 1.00 mmol) in DCM (10 mL) was added a catalytic amount of *p*-TsOH. The slurry was heated to reflux for 10 hours.[4] After cooling to room temperature, the suspension was filtered over celite and all volatiles were removed under reduced pressure. The residue was purified by flash chromatography on silica (hexanes/TBME 19:1). The product was obtained as a colourless liquid (222 mg, 866 µmol, 78 %).

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.06 (s, 3 H); 1.66-1.74 (m, 1 H); 1.97-2.13 (m, 3 H); 2.16-2.30 (m, 4 H); 2.52 (td, *J* = 2.5 Hz, *J* = 10.4 Hz; 1.H); 2.77 (td, *J* = 2.12 Hz, *J* = 11.6 Hz, 1 H); 3.28-3.35 (m, 4 H); 5.00-5.10 (m, 2 H); 5.69 (tdd, *J* = 7.7 Hz, *J* = 10.1 Hz, J = 17.1 Hz, 1 H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 22.4; 35.2; 38.5; 38.8; 39.5; 40.8; 42.4; 43.3; 51.0 (C_q); 71.3 (C_q); 118.6; 133.3; 216.1 (C_q).

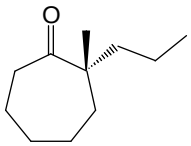
IR (ATR): ν (cm^{-1}) = 3074 (w); 2963 (m); 2926 (m); 2868 (w); 2842 (w); 1701 (s); 1638 (m); 1459 (m); 1431 (m); 1375 (m); 1339 (m); 1313 (m); 1277 (m); 1255 (w); 1236 (m); 1198 (w); 1176 (w); 1143 (w); 1089 (m); 1067 (m); 1041 (m); 996 (m); 917 (m); 855 (w); 830 (w); 808 (w); 787 (w); 738 (w); 685 (w).

MS (EI, 70 eV): m/z (%) = [M^+] 256 (49); 195 (24); 163 (16); 132 (24); 131 (97); 118 (100); 110 (17); 91 (17); 86 (17); 81 (20); 79 (17); 71 (23); 61 (22); 53 (22).

HRMS for $C_{13}H_{20}OS_2$: calc.: 256.0956; found: 256.0955

Optical Rotation: $[\alpha]_D^{20}$ = -45.2 ° ($CHCl_3$, c = 0.50)

(*S*)-2-methyl-2-propyl-cycloheptanone (B)



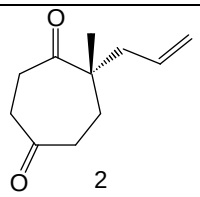
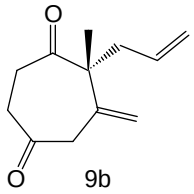
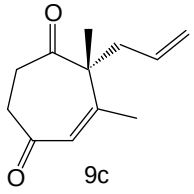
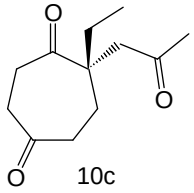
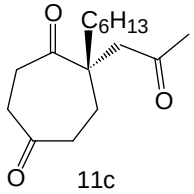
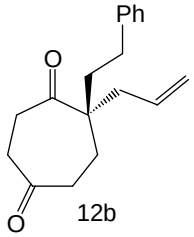
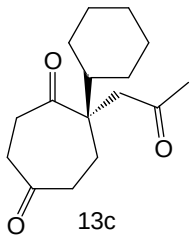
Ni/Al-alloy (5.0 g) was suspended in 50 mL of distilled water and treated with solid NaOH (~ 8 g) until the evolution of gas had stopped. The freshly prepared Ra-Ni was washed with distilled water (20×20 mL), 1 % acetic acid (3×20 mL) and ethanol (3×20 mL). The deactivated Ra-Ni was then suspended in 50 mL of ethanol, compound A (100 mg, 390 µmol) was added and the suspension was refluxed for 6 h. After cooling to rt, the suspension was flitered over

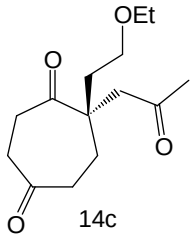
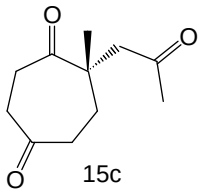
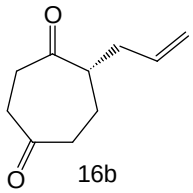
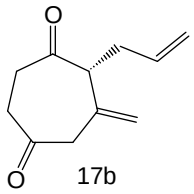
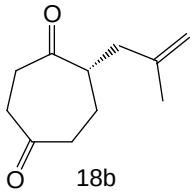
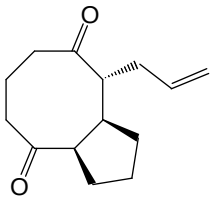
[3] D. C. Behenna, B. M. Stoltz, *J. Am. Chem. Soc.* **2004**, *126*, 15044.
[4] M. H. Ali, M. Goretti Gomez, *Synthesis* **2005**, 1326.

celite, concentrated and subjected to chromatography on silica (hexanes/TBME 19:1) to yield the product as a colourless liquid (32 mg, 192 µmol, 50 %).
^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 0.89 (t, *J* = 7.31 Hz, 3 H); 1.04 (s, 3 H); 1.12-1.32 (m, 3 H); 1.39-1.50 (m, 4 H); 1.64-1.69 (m, 2 H); 1.67-1.74 (m, 1 H); 1.74-1.87 (m, 2 H); 2.32-2.39 (m, 1 H); 2.65-2.73 (m, 1 H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 14.7; 17.3; 21.6; 24.5; 26.7; 30.7; 37.8; 40.3; 42.6; 51.0 (C_q); 218.1 (C_q).
IR (ATR): ν (cm^{-1}) = 2958 (s); 2930 (s); 2871 (m); 2856 (m); 1735 (m); 1701 (s); 1467 (m); 1457 (m); 1457 (m); 1444 (m); 1367 (m); 1347 (m); 1326 (m); 1311 (w); 1262 (m); 1247 (w); 1192 (w); 1173 (w); 1129 (m); 1121 (m); 1075 (m); 1056 (m); 1037 (w); 1011 (w); 956 (m); 939 (m); 920 (m); 908 (w); 886 (w); 861 (w); 840 (w); 801 (w); 740 (w).
MS (EI, 70 eV): m/z (%) = [M^+] 167 (23); 149 (62); 129 (17); 126 (100); 97 (51); 84 (17); 83 (20); 81 (22); 69 (51); 57 (50); 55 (80).
HRMS for $C_{11}H_{20}O_{1:}$ calc.: 167.1436; found: 167.1451
Optical Rotation: $[\alpha]_D^{20}$ = -37.5 ° ($CHCl_3$, c = 0.70)

8) AREA REACTION PRODUCTS RETENTION TIMES ON CHIRAL GC

Table 1. Retention times on chiral GC[a]

Entry	Product	Assay Conditions	retention time of the major prod. [min]	retention time of the minor prod. [min]	*ee* [%]
1	 2	130 °C isoth. 6.5 psi	26.060	25.246	90
2	 9b	150 °C isoth. 10 psi	6.531	6.260	90
3	 9c	150 °C 10 psi	7.853	7.509	90
4[b]	 10c	150 °C 10 psi	21.401	19.815	92
5[b]	 11c	165 °C 10 psi	28.908	26.804	91
6	 12b	180 °C 6 psi	18.371	17.334	86
7[b]	 13c	130 °C (5 ’) (1 °C/min)→ 180 °C (30 ‘) 8 psi	67.746	66.545	83

8[b]	 14c	163 °C isoth. 10 psi	9.065	10.238	68
9[b]	 15c	150 °C (15 ’) (10 °C/min)→ 163 °C 9 psi	18.117	17.207	53
10	 16b	135 °C isoth. 10 psi	11.409	12.762	73
11	 17b	140 °C isoth. 10 psi	9.711	9.416	62
12	 18b	140 °C isoth. 10 psi	10.168	11.312	41
13	 19b	175 °C isoth. 10 psi	4.051	3.850	48

[a] All the GC-experiments were conducted on a HP 5890 Series II with a Lipodex E (25 m×0.25 mm) column.

[b] The enantiomeric excess was determined after conversion of the olefin to the corresponding methyl ketone