

Synthesis of Seven-Membered Carbocyclic Rings *via* Microwave-Assisted Tandem Oxyanionic 5-Exo Dig Cyclization–Claisen Rearrangement Process

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Supporting Information

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General Experimental.

^1H and ^{13}C NMR spectra were recorded in CDCl_3 . Chemical shifts are reported in units of parts per million (ppm), relative to tetramethylsilane at $\delta = 0.00$ ppm. Coupling constants (J) are reported in hertz (Hz). Infrared spectra are reported in cm^{-1} .

All microwave experiments were conducted in a CEM Focused MicrowaveTM Synthesis System, Model Discover microwave oven, equipped with an infrared temperature control system. All microwave reactions were performed in sealed 10 mL microwave vials.

Tetrahydrofuran (THF) was freshly distilled under N_2 from dark blue solutions of sodium benzophenone ketyl. Phenetole (PhOEt), CH_2Cl_2 (DCM), TMSCl , and Et_3N were freshly distilled from calcium hydride. The concentrations of solutions of organolithium reagents were determined by titrations with *sec*-butyl alcohol using 1,10-phenantroline as the indicator following the method of Watson and Eastham.¹ All glassware was flame-dried under an inert atmosphere and all reactions were performed under an atmosphere of dry argon or nitrogen.

Experimental Procedures

5-(2,5-Dimethoxyphenyl)pent-4-ynal (**1**)

To a solution of oxalyl chloride (0.1 mL, 1.2 mmol) in 10 mL CH_2Cl_2 was added DMSO (0.17 mL, 2.4 mmol) at -78°C and the resulting mixture was stirred for 20 min. To this was then added 5-(2,5-dimethoxyphenyl)pent-4-yn-1-ol (106 mg, 0.48 mmol) in 3 mL CH_2Cl_2 at -78°C . After 50 min of further stirring at this temperature, NEt_3 (486 mg, 4.8 mmol) was added and the reaction mixture was allowed to warm to room temperature. The mixture was then poured into saturated NaHCO_3 solution, the layers were separated and the aqueous layer was extracted with EtOAc. The combined organic extracts were washed with brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography (20% EtOAc in hexane) to give aldehyde **1** as yellow solid (99 mg, 95%). mp: 63°C ; IR (neat) 2924, 1716, 1496, 1039, 821; ^1H NMR (CDCl_3 , 500 MHz) δ 9.84 (s, 1 H), 6.90 (d, $J = 3.0$ Hz, 1 H), 6.81-6.75 (m, 2 H), 3.81 (s, 3 H), 3.74 (s, 3 H), 2.78-2.77 (m, 4 H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 200.6, 154.3, 153.1, 118.3, 115.1, 112.9, 111.8, 91.8, 77.6, 56.3, 55.7, 42.6, 13.0; HRMS (EI) calcd for $\text{C}_{13}\text{H}_{14}\text{O}_3$ (M^+) m/z 218.0943, found 218.0940.

¹ S. C. Watson, J. F. Eastham, *J. Organomet. Chem.* **1967**, 9, 165-168.

1-Cyclopentenyl-5-(2,5-dimethoxyphenyl)pent-4-yn-1-ol (2). To a -78°C solution of 1-iodocyclopentene (776 mg, 4.00 mmol) in 15 mL Et_2O was added $^t\text{BuLi}$ (1.7 M in pentane, 4.7 mL, 8.0 mmol) dropwise. The resulting solution was stirred at -78°C for 15 min, then warmed to 0°C and stirred for another 15 min at this temperature to destroy any excess $^t\text{BuLi}$. The solution was then cooled to -78°C , followed by the dropwise addition of aldehyde **1** (436 mg, 2.00 mmol) dissolved in Et_2O (15 mL). The reaction mixture was stirred thereafter for 20 min and then quenched by the addition of aqueous NH_4Cl . The layers were separated and the aqueous layer was extracted with Et_2O . The combined organic extracts were washed with brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography (20% EtOAc in hexane) to give alcohol **2** as a pale yellow oil (509 mg, 89%). IR (neat) 3446, 2927, 1605, 1495, 1049, 824 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 6.89 (d, $J = 3.0$ Hz, 1 H), 6.76-6.72 (m, 2 H), 5.63 (d, $J = 1.5$ Hz, 1 H), 4.45 (dd, $J = 6.0, 4.5$ Hz, 1 H), 3.79 (s, 3 H), 3.71 (s, 3 H), 2.58-2.46 (m, 2 H), 2.44 (br s, 1 H), 2.32-2.27 (m, 4 H), 1.92-1.80 (m, 4 H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 154.2, 153.0, 146.3, 125.4, 118.0, 114.6, 113.2, 111.6, 93.9, 77.1, 70.2, 56.1, 55.5, 34.1, 32.1, 31.2, 23.2, 16.0; HRMS (EI) calcd for $\text{C}_{18}\text{H}_{22}\text{O}_3$ (M^+) m/z 286.1569, found 286.1569.

(3aS*,4R*)-4-(2,5-Dimethoxyphenyl)-2,3,3a,4,6,7-hexahydroazulen-5(1H)-one (3)

General procedure for the microwave-assisted cyclization/Claisen rearrangement:

Alcohol **2** (100 mg, 0.35 mmol) was transferred to a 10 mL flame dried microwave vial along with anhydrous phenetole (1.5 mL). A ca. 10 mol% MeLi in Et_2O was added and the solution was heated at 210°C for 45 min in the microwave oven. The phenetole solvent was then removed *in vacuo* and the residue was directly purified by column chromatography (5% to 10% EtOAc in hexane) to give ketone **3** as a pale yellow oil (76mg, 76%).

IR (neat) 2936, 1705, 1496, 1225, 823 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 6.77- 6.69 (m, 3 H), 5.56 (s, 1 H), 3.76 (s, 3 H), 3.72 (s, 3 H), 3.54-3.50 (m, 1 H), 3.48 (br s, 1 H), 2.49-2.45 (m, 3 H), 2.41-2.39 (m, 3 H), 1.65-1.59 (m, 1 H), 1.50-1.45 (m, 1 H), 1.42-1.36 (m, 1 H), 1.23-1.18 (m, 1 H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 213.8, 153.4, 150.9, 146.1, 130.9, 118.9, 117.7, 112.0, 111.9, 61.3, 55.9, 55.6, 41.4, 40.7, 35.7, 34.0, 27.2, 24.6; HRMS (EI) calcd for $\text{C}_{18}\text{H}_{22}\text{O}_3$ (M^+) m/z 286.1569, found 286.1569.

7-(2,5-Dimethoxyphenyl)-2-methylhept-1-en-6-yn-3-ol (4). Following the procedure described for the synthesis of **2**, alcohol **4** was prepared as a pale yellow oil in 90% yield. IR (neat) 3430, 2936, 1652, 1498, 1047 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 6.90 (d, $J = 3.0$ Hz, 1 H), 6.78-6.74 (m, 2 H), 5.01 (s, 1 H), 4.86 (t, $J = 1.5$ Hz, 1 H), 4.29 (dt, $J = 7.5, 4.0$ Hz, 1 H), 3.80 (s, 3 H), 3.72 (s, 3 H), 2.58-2.49 (m, 2 H), 2.39 (d, $J = 2.5$ Hz, 1 H), 1.87-1.80 (m, 2 H), 1.74 (s, 3 H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 154.3, 153.0, 146.8, 118.1, 114.6, 113.2, 111.6, 110.9, 93.8, 77.2, 74.7, 56.2, 55.6, 33.7, 17.8, 16.2; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{20}\text{O}_3$ (M^+) m/z 260.1413, found 260.1416.

1-Cyclohexenylpent-4-yn-1-ol (6). To a -78°C solution of 1-iodocyclohexane (831 mg, 3.99 mmol) in 15 mL Et_2O was added $^t\text{BuLi}$ (1.7 M in pentane, 4.7 mL, 8.0 mmol) dropwise. The resulting solution was stirred at -78°C for 15 min, then warmed to 0°C and stirred for another 15 min at this temperature to destroy any excess $^t\text{BuLi}$. The solution was then cooled to -78°C , followed by the dropwise addition of 5-(trimethylsilyl)pent-4-ynal (308 mg, 2.00 mmol) dissolved in Et_2O (15 mL). The reaction mixture was stirred thereafter for 20 min and then quenched by the addition of aqueous NH_4Cl . The layers were separated and the aqueous layer was extracted with Et_2O . The combined organic extracts were washed with brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The residue was immediately dissolved in 10 mL THF, and TBAF (1.0 M in THF, 3.0 mL, 3.0 mmol) was added. The resulting mixture was stirred for 10 min at room temperature, followed by addition of water (3 mL) to quench the reaction. The layers were separated and the aqueous layer was extracted with ether (2 x 20 mL). The combined organic extracts were washed with brine, dried over MgSO_4 , filtered and concentrated under reduced pressure. The product was purified by column chromatography (15% EtOAc in hexane) to give alcohol **6** as a colorless oil (295 mg, two steps, 90%). IR (neat) 3308, 2927, 1558, 1051, 824 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 5.69 (s, 1 H), 4.10 (t, $J = 7.0$ Hz, 1 H), 2.26-2.21 (m, 2 H), 2.07-2.00 (m, 3 H), 1.96 (t, $J = 2.5$ Hz, 1 H), 1.92-1.86 (m, 1 H), 1.77 (dd, $J = 13.0, 6.5$ Hz, 2 H), 1.64-1.51 (m, 5 H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 139.2, 123.4, 84.2, 75.2, 68.5, 33.5, 24.9, 23.5, 22.6, 22.5, 15.0; HRMS (EI) calcd for $\text{C}_{11}\text{H}_{16}\text{O}$ (M^+) m/z 164.1201, found 164.1202.

7-(2,5-Dimethoxyphenyl)hept-1-en-6-yn-3-ol (8). To a solution of aldehyde **1** (150 mg, 0.69 mmol) in 8 ml of THF was added vinylmagnesium chloride (1.6 M in THF, 0.86 mL, 1.38 mmol) at -78°C and the resulting mixture was stirred for 15 min. A solution of aqueous NH_4Cl solution was then added to quench the reaction. The layers were separated and the aqueous layer was extracted with Et_2O . The combined organic extracts were washed with brine, dried over MgSO_4 , filtered and concentrated under reduced pressure. The crude product was purified by column chromatography (20% EtOAc in hexane) to give alcohol **8** as a pale yellow oil (160 mg, 94%). IR (neat) 3421, 2927, 1497, 1047, 824 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 6.91 (d, $J = 3.0$ Hz, 1 H), 6.80-6.75 (m, 2 H), 5.94- 5.87 (m, 1 H), 5.32 (d, $J = 17.0$ Hz, 1 H), 5.15 (d, $J = 9.5$ Hz, 1 H), 4.39-4.35 (m, 1 H), 3.81 (s, 3H), 3.74 (m, 3 H), 2.65-2.52 (m, 2 H), 2.28 (br s, 1 H), 1.90-1.80 (m, 2 H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 154.4, 153.1, 140.4, 118.1, 114.8, 114.7, 113.2, 111.7, 93.7, 77.4, 72.1, 56.2, 55.7, 35.4, 16.0; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{18}\text{O}_3$ (M^+) m/z 246.1256, found 246.1257.

6-methylhept-6-en-4-ynal. To a solution of 6-methylhept-6-en-4-yn-1-ol (430 mg, 3.46 mmol) in DCM (35 mL) was added Dess-Martin periodinane (2.20 g, 5.19 mmol) and the resulting mixture was stirred at room temperature for 12 h. Aqueous solutions of sat. Na_2CO_3 (10 mL) and sat. $\text{Na}_2\text{S}_2\text{O}_2$ (10 mL) were then added and the heterogeneous mixture was stirred rapidly thereafter for 30 min. The layers were separated and the aqueous layer was extracted with DCM (3x15 mL). The combined organic extracts were washed with brine, dried over MgSO_4 , filtered and concentrated under reduced pressure. The crude product was purified by column chromatography (10% EtOAc in hexane) to give the desired aldehyde as a clear oil (285 mg, 67%). IR (neat) 3067, 2923, 2865, 2740, 2316, 1772, 1733 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 9.79 (s, 1H), 5.18 (s, 1H), 5.13-5.14 (m, 1H), 2.64-2.69 (m, 2H), 2.58-2.62 (m, 1H), 1.82 (br s, 3H); 201.0, 127.1, 121.2, 86.5, 42.4, 23.8, 12.5 ppm; ^{13}C NMR (CDCl_3 , 125 MHz) δ 200.5, 126.8, 121.1, 86.4, 82.8, 42.4, 23.5, 12.4 ppm; HRMS (EI) calcd for $\text{C}_8\text{H}_{10}\text{O}$ (M^+) m/z 122.0732, found 122.0730.

1-Cyclohexenyl-6-methylhept-6-en-4-yn-1-ol (10). A solution of $t\text{BuLi}$ (6.20 mL, 1.7M in pentane, 10.6 mmol) was added dropwise to 1-bromocyclohexene (854 mg, 5.30 mmol) in diethyl ether at -78°C . After 5 min, the cooling bath was removed and the reaction mixture was

allowed to warm to room temperature. After 30 min of stirring at this temperature the reaction mixture was re-cooled to $-78\text{ }^{\circ}\text{C}$ whereupon a solution of 6-methylhept-6-en-4-ynal (210 mg, 1.72 mmol) in diethyl ether (10 mL) was added dropwise. After 30 min, the reaction was quenched by the addition of H_2O (3 mL) and the mixture was allowed to warm to $0\text{ }^{\circ}\text{C}$. Following the addition of more H_2O (15 mL), the layers were separated and the organic layer was extracted with diethyl ether (3x10 mL). The combined organic layers were dried over MgSO_4 , filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (70% ethyl acetate/hexanes) to give 245 mg (70%) of the desired alcohol as a clear oil. IR (neat) 3350, 3094, 2925, 2857, 2836, 2225, 1652, 1448, 1049 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 5.65-5.70 (m, 1H), 5.19 (br s, 1H), 5.12-5.14 (m, 1H), 4.08 (t, $J = 5.87$ Hz, 1H), 2.34 (dt, $J = 7.23, 4.43$ Hz, 2H), 1.88-2.05 (m, 5H), 1.85 (br s, 3H), 1.75 (app. q, $J = 6.83$, 2H), 1.52-1.656 (m, 4H) ppm; ^{13}C NMR (CDCl_3 , 125 MHz) δ 139.3, 127.2, 123.4, 120.5, 88.8, 82.2, 75.5, 33.8, 24.9, 23.8, 23.6, 22.6, 22.6, 15.9 ppm; HRMS (EI) calcd for $\text{C}_{14}\text{H}_{20}\text{O}$ (M^+) m/z 204.1514, found 204.1515.

5-(Propan-2-ylidene)-3,4,4a,5,7,8-hexahydro-1H-benzo[7]annulen-6(2H)-one (11). Ketone **11** was prepared as a colorless oil in 45% yield according to the general procedure described for the synthesis of **3**. IR (neat) 3012, 2925, 2859, 1700, 1652, 1558, 1456, 1050 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 5.49 (dt, $J = 9.3, 1.70$ Hz, 1H), 3.17 (dd, $J = 12.45, 3.66$ Hz, 1H), 2.44-2.54 (m, 2H), 2.14-2.20 (m, 1H), 1.90-2.02 (m, 2H), 1.72-1.78 (m, 2H), 1.73 (s, 3H), 1.64 (s, 3H), 1.57-1.1.63 (m, 2H), 1.34-1.44 (m, 1H), 1.16-1.27 (m, 2H) ppm; ^{13}C NMR (CDCl_3 , 125 MHz) δ 213.0, 124.9, 139.9, 128.3, 121.1, 44.7, 43.6, 37.9, 34.8, 28.4, 26.6, 21.7, 21.5, 19.1 ppm; HRMS (EI) calcd for $\text{C}_{14}\text{H}_{20}\text{O}$ (M^+) m/z 204.1514, found 204.1515.

1-Cyclopent-4-yn-1-ol (12). Alcohol **12** was prepared as a colorless oil in 88% yield according to the procedure described for the synthesis of **6**. IR (neat) 3307, 2928, 1495, 1050, 824 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 5.62 (s, 1 H), 4.39 (t, $J = 6.5$ Hz, 1 H), 2.34-2.26 (m, 6 H), 1.96 (t, $J = 2.5$ Hz, 1 H), 1.91-1.73 (m, 5 H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 146.3, 125.8, 84.1, 67.0, 68.6, 34.0, 32.1, 31.1, 23.3, 14.8; HRMS (EI) calcd for $\text{C}_{10}\text{H}_{14}\text{O}$ (M^+) m/z 150.1045, found 150.1049.

1-Cyclopentenyl-5-phenylpent-4-yn-1-ol (14). Alcohol **14** was prepared as a colorless oil in 87% yield according to the procedure described for the synthesis of **6**. IR (neat) 3352, 2927, 1490, 1069, 824 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 7.43-7.40 (m, 2 H), 7.32-7.28 (m, 3 H), 5.69 (s, 1 H), 4.48 (t, $J = 6.0$ Hz, 1 H), 2.53- 2.48 (m, 2 H), 2.39-2.33 (m, 4 H), 1.94-1.85 (m, 5 H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 146.3, 131.5(2C), 128.1(2C), 127.5, 125.8, 123.7, 89.6, 80.9, 70.2, 34.3, 32.2, 31.2, 23.3, 15.8; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{18}\text{O}$ (M^+) m/z 226.1358, found 226.1358.

1-Cyclohexenyl-5-(2,5-dimethoxyphenyl)pent-4-yn-1-ol (16). Alcohol **16** was prepared as a pale yellow oil in 87% yield according to the procedure described for the synthesis of **2**. IR (neat) 3446, 2926, 1496, 1049, 824 cm^{-1} ; δ 6.91 (d, $J = 2.0$ Hz, 1 H), 6.80-6.75 (m, 2 H), 5.73 (s, 1 H), 4.19 (t, $J = 6.5$ Hz, 1 H), 3.82 (s, 3 H), 3.74 (s, 3 H), 2.54-2.48 (m, 2 H), 2.09-2.02 (m, 4 H), 1.96-1.90 (m, 1 H), 1.88 (ddd, $J = 7.0, 1.5, 1.5$ Hz, 2 H), 1.66-1.54 (m, 4 H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 154.4, 153.1, 139.3, 123.1, 118.2, 114.8, 113.4, 111.7, 94.1, 77.2, 75.6, 56.3, 55.7, 33.8, 24.9, 23.7, 22.6, 22.6, 16.5; HRMS (EI) calcd for $\text{C}_{19}\text{H}_{24}\text{O}_3$ (M^+) m/z 300.1726, found 300.1722.

(E)-10-(tert-Butyldimethylsilyloxy)-1-(2,5-dimethoxyphenyl)dec-6-en-1-yn-5-ol (18).

Alcohol **18** was prepared as a pale yellow oil in 85% yield according to the procedure described for the synthesis of **2**. IR (neat) 3446, 2930, 1499, 1101, 835 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 6.90 (d, $J = 3.0$ Hz, 1 H), 6.79-6.74 (m, 2 H), 5.73-5.67(m, 1 H), 5.53-5.48 (m, 1 H), 4.30 (dd, $J = 12.5, 6.0$ Hz, 1 H), 3.80 (s, 3 H), 3.72 (s, 3 H), 3.60 (t, $J = 6.5$ Hz, 2 H), 2.61-2.48 (m, 2 H), 2.23 (s, 1 H), 2.10 (dd, $J = 14.5, 7.0$ Hz, 2 H), 1.85-1.76 (m, 2 H), 1.61-1.56 (m, 2 H), 0.88 (s, 9 H), 0.03 (s, 6 H); ^{13}C NMR (CDCl_3 , 125MHz) δ 154.3, 153.1, 132.4, 131.6, 118.1, 114.7, 113.3, 111.7, 93.8, 77.2, 71.9, 62.4, 56.2, 55.6, 35.8, 32.2, 28.4, 25.9, 18.2, 16.1, -5.4; HRMS (EI) calcd for $\text{C}_{24}\text{H}_{38}\text{O}_4\text{Si}$ (M^+) m/z 418.2539, found 418.2537.

Ethyl 6-hydroxyoct-7-en-2-ynoate (20). To a -78°C solution of ethyl 6-oxohex-2-ynoate (150 mg, 0.97 mmol) in 6 mL THF was added vinylmagnesium chloride (1.6 M in THF, 0.91mL, 1.45 mmol) and the resulting mixture was stirred at this temperature for an additional 15 min. The reaction was then quenched by the addition of aqueous NH_4Cl solution. Upon warming, the

layers were separated and the aqueous layer was extracted with Et₂O (2x20 mL). The combined organic extracts were washed with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography (20% EtOAc in hexane) to give alcohol **20** as a pale yellow oil (150 mg, 85%). IR (neat) 3422, 2929, 1707, 1686, 1260, 1075, 824 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 5.83 (ddd, *J* = 16.5, 5.5, 5.5 Hz, 1 H), 5.24 (d, *J* = 16.5 Hz, 1 H), 5.11 (d, *J* = 10.5 Hz, 1 H), 4.18-4.14 (m, 3 H), 2.45-2.35 (m, 3 H), 1.76-1.71 (m, 2 H), 1.27 (t, *J* = 7.5 Hz, 3 H); ¹³C NMR (CDCl₃, 125 MHz) δ 153.7, 139.9, 115.3, 88.7, 73.2, 71.2, 61.7, 34.2, 14.7, 13.9; HRMS (EI) calcd for C₁₀H₁₄O₃ (M⁺) *m/z* 182.0943, found 182.0943.

2-(2,5-Dimethoxyphenyl)-4-methylcyclohept-4-enone (5). Ketone **5** was prepared as a pale yellow oil in 73% yield according to the general procedure described for the synthesis of **3**. IR (neat) 2927, 1706, 1496, 1050, 824 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 6.79-6.73 (m, 3 H), 5.60 (br s, 1 H), 4.32 (dd, *J* = 7.0, 3.5 Hz, 1 H), 3.77 (s, 3 H), 3.73 (s, 3 H), 3.01-2.95 (m, 1 H), 2.90 (t, *J* = 15.5 Hz, 1 H), 2.65-2.57 (m, 2 H), 2.30-2.25 (m, 2 H), 1.77 (s, 3 H); ¹³C NMR (CDCl₃, 125 MHz) δ 212.7, 153.6, 150.7, 136.2, 130.9, 123.2, 115.6, 111.7, 111.4, 55.9, 55.6, 50.5, 42.3, 35.7, 26.6, 24.1; HRMS (EI) calcd for C₁₆H₂₀O₃ (M⁺) *m/z* 260.1413, found 260.1415.

3,4,4a,5,7,8-Hexahydro-1H-benzo[7]annulen-6(2H)-one (7). Ketone **7** was prepared as a colorless oil in 77% yield according to the general procedure described for the synthesis of **3**. IR (neat) 2926, 1706, 1495, 1050, 825 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 5.56 (t, *J* = 6.0 Hz, 1 H), 2.84 (dd, *J* = 11.5, 4.5 Hz, 1 H), 2.73 (dd, *J* = 11.5, 4.5 Hz, 1 H), 2.53-2.44 (m, 3 H), 2.30-2.23 (m, 2 H), 2.18-2.14 (m, 1 H), 1.95-1.90 (m, 1 H), 1.79-1.73 (m, 3 H), 1.42-1.36 (m, 1 H), 1.28-1.20 (m, 2 H); ¹³C NMR (CDCl₃, 125 MHz) δ 213.3, 143.7, 120.3, 47.1, 44.0, 40.8, 38.2, 36.1, 28.4, 26.5, 21.7; HRMS (EI) calcd for C₁₁H₁₆O (M⁺) *m/z* 164.1201, found 164.1203.

2-(2,5-Dimethoxyphenyl)cyclohept-4-enone (9). Ketone **9** was prepared as a colorless oil in 73% yield according to the general procedure described for the synthesis of **3**. IR (neat) 2934, 1706, 1497, 1226, 1049, 823 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 6.79-6.73 (m, 3 H), 5.85-5.77 (m, 2 H), 4.18 (dd, *J* = 11.5, 3.5 Hz, 1 H), 3.76 (s, 3 H), 3.72 (s, 3 H), 3.15 (ddd, *J* = 11.5, 4.0, 4.0 Hz, 1 H), 2.93-2.86 (m, 1 H), 2.66-2.54 (m, 2 H), 2.39-2.34 (m, 2 H); ¹³C NMR (CDCl₃, 125

MHz) δ 213.0, 153.6, 150.7, 131.1, 129.3, 128.5, 115.8, 111.9, 111.6, 55.9, 55.6, 52.6, 41.7, 30.3, 25.1; HRMS (EI) calcd for C₁₅H₁₈O₃ (M⁺) m/z 246.1256, found 246.1256.

2,3,3a,4,6,7-Hexahydroazulen-5(1H)-one (13). Ketone **13** was prepared as a colorless oil in 72% yield according to the general procedure described for the synthesis of **3**. IR (neat) 2937, 1706, 1495, 1650, 1049, 824 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 5.62 (dt, J = 6.0, 2.5 Hz, 1 H), 2.89-2.84 (m, 1 H), 2.77-2.74 (m, 1 H), 2.60 (dd, J = 15.5, 3.0 Hz, 1 H), 2.45 (dd, J = 15, 2.0 Hz, 1 H), 2.38-2.32 (m, 4 H), 2.28-2.22 (m, 1 H), 2.03-1.97 (m, 1 H), 1.73-1.66 (m, 1 H), 1.57-1.49 (m, 1 H), 1.36-1.28 (m, 1 H); ¹³C NMR (CDCl₃, 125 MHz) δ 213.1, 148.0, 119.2, 49.4, 42.3, 37.9, 35.1, 34.7, 25.5, 24.9; HRMS (EI) calcd for C₁₀H₁₄O (M⁺) m/z 150.1045, found 150.1046.

(3aS*,4R*)-4-Phenyl-2,3,3a,4,6,7-hexahydroazulen-5(1H)-one (15). Ketone **15** was prepared as a yellow oil in 77% yield according to the general procedure described for the synthesis of **3**. IR (neat) 2928, 1700, 1495, 1049, 824cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 7.26-7.23 (m, 2 H), 7.21-7.18 (m, 3 H), 5.51 (s, 1 H), 3.45 (d, J = 11.5 Hz, 1 H), 3.31- 3.26 (m, 1 H), 3.23 (ddd, J = 11.0, 5.5, 5.5 Hz, 1 H), 2.46-2.38 (m, 2 H), 2.36-2.32 (m, 3 H), 1.67- 1.60 (m, 1 H), 1.58-1.52 (m, 1 H), 1.45-1.47 (m, 1 H), 1.22-1.15 (m, 1 H); ¹³C NMR (CDCl₃, 125MHz) δ 211.8, 146.1, 138.6, 128.6 (2C), 128.3 (2C), 127.1, 119.0, 65.6, 42.2, 39.7, 35.9, 33.4, 28.0, 24.7; HRMS (EI) calcd for C₁₆H₁₈O (M⁺) m/z 226.1358, found 226.1357.

(4aS*,5R*)-5-(2,5-dimethoxyphenyl)-3,4,4a,5,7,8-hexahydro-1H-benzo[7]annulen-6(2H)-one (17). Ketone **17** was prepared as a yellow oil in 82% yield according to the general procedure described for the synthesis of **3**. IR (neat) 2928, 1700, 1495, 1049, 824 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 7.02 (d, J = 3.0 Hz, 1 H), 6.78-6.73 (m, 2 H), 5.61 (dd, J = 9.0, 4.5 Hz, 1 H), 4.93 (d, J = 11.5 Hz, 1 H), 3.79 (s, 3 H), 3.73 (s, 3 H), 2.95-2.87 (m, 1 H), 2.73-2.60 (m, 2 H), 2.49 (t, J = 11.5 Hz, 1 H), 2.21-2.18 (m, 1 H), 2.14-2.08 (m, 1 H), 1.99-1.94 (m, 1 H), 1.81-1.76 (m, 2 H), 1.72 (d, J = 13.0 Hz, 1 H), 1.39-1.27 (m, 2 H), 1.21-1.12 (m, 1 H); ¹³C NMR (CDCl₃, 125 MHz) δ 211.1, 153.6, 151.6, 144.4, 127.9, 119.6, 115.6, 111.4, 110.9, 56.1, 55.7, 49.7, 46.3, 45.6, 39.3, 33.8, 29.3, 26.7, 20.9; HRMS (EI) calcd for C₁₉H₂₄O₃ (M⁺) m/z 300.1726, found 300.1728.

(2*R,3*R**)-3-(3-(*tert*-Butyldimethylsilyloxy)propyl)-2-(2,5-dimethoxyphenyl)cyclohept-4-enone (19).** Ketone **19** was prepared as a yellow oil in 81% yield according to the general procedure described for the synthesis of **3**. IR (neat) 2928, 1700, 1496, 1050, 825 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 6.82 (d, *J* = 3.0 Hz, 1 H), 6.78-6.72 (m, 2 H), 5.75-5.71(m, 1 H), 5.65-5.62 (m, 1 H), 4.09 (d, *J* = 11.0 Hz, 1 H), 3.76 (s, 3 H), 3.73 (s, 3 H), 3.49 (dt, *J* = 6.0, 1.5 Hz, 2 H), 3.27-3.21 (m, 1 H), 3.13-3.08 (m, 1 H), 2.59-2.49 (m, 2 H), 2.43-2.37 (m, 1 H), 1.64-1.55 (m, 1 H), 1.48-1.39 (m, 1 H), 1.34-1.28 (m, 1 H), 1.22-1.13 (m, 1 H), 0.83 (s, 9 H), -0.03 (s, 3 H), -0.04 (s, 3 H); ¹³C NMR (CDCl₃, 125 MHz) δ 212.3, 153.5, 151.3, 134.2, 129.0, 128.6, 116.6, 111.9, 111.7, 63.1, 57.4, 55.9, 55.6, 41.5, 38.5, 29.9, 29.7, 25.9, 25.3, 18.2, -5.4; HRMS (EI) calcd for C₂₄H₃₈O₄Si (M⁺) *m/z* 418.2539, found 418.2536.

1-Cyclohexenyl-2,2-dimethylhex-4-yn-1-ol (22). Alcohol **22** was prepared as a pale yellow oil from 2,2-dimethylhex-4-ynal² in 65% yield according to the procedure described for the synthesis of **2**. IR (neat) 3448, 2929, 1653, 1136, 1050 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 5.64 (s, 1 H), 3.86 (s, 1 H), 2.20 (ddd, *J* = 16.5, 5.5, 2.5 Hz, 1 H), 2.14-2.10 (m, 1 H), 2.06-2.02 (m, 3 H), 1.98-1.95 (m, 1 H), 1.81 (d, *J* = 4.0 Hz, 1H), 1.80 (t, *J* = 3.0 Hz, 3H), 1.65-1.60 (m, 2 H), 1.54-1.50 (m, 2 H), 0.96 (s, 3 H), 0.93 (s, 3 H); ¹³C NMR (CDCl₃, 125 MHz) δ 138.7, 125.3, 82.1, 77.6, 77.2, 38.5, 30.1, 26.9, 25.1, 24.2, 23.1, 22.9, 22.6, 3.5; HRMS (EI) calcd for C₁₄H₂₂O (M⁺) *m/z* 206.1671, found 206.1672.

5,8,8-trimethyl-3,4,4a,5,7,8-hexahydro-1*H*-benzo[7]annulen-6(2*H*)-one (23). Ketone **23** was prepared as a colorless oil in 60% yield according to the general procedure described for the synthesis of **3**. IR (neat) 2930, 1700, 1652, 1456, 1049, 825 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 5.64 (s, 1 H), 5.13 (s, 0.5 H), 3.16-3.11 (m, 1 H), 2.83 (d, *J* = 12.5 Hz, 0.5 H), 2.62-2.59 (m, 0.5 H), 2.54 (dd, *J* = 33.0, 16.5 Hz, 1 H), 2.41 (dd, *J* = 5.0, 2.5 Hz, 0.5 H), 2.29-2.22 (m, 1.5 H), 2.20-2.10 (m, 2.5 H), 2.04-1.98 (m, 1 H), 1.96-1.90 (m, 0.5 H), 1.86- 1.75 (m, 4.5 H), 1.68-1.62 (m, 1.5 H), 1.40-1.34 (m, 3 H), 1.20 (s, 3 H), 1.17 (s, 1.5 H), 1.11 (d, *J* = 6.5 Hz, 1.5 H), 1.10 (s, 1.5 H), 1.07 (d, *J* = 6.5 Hz, 3 H), 1.04 (s, 3 H); ¹³C NMR (CDCl₃, 125 MHz) δ 213.6, 212.8, 142.1, 139.5, 131.7, 130.6, 56.5, 53.4, 51.3, 48.3, 46.3, 43.9, 39.6, 36.5, 34.5, 34.2, 33.7, 32.3,

² Cresson, P.; Corbier, J. C. R. *Hebd. Seances Acad. Sci. Ser. C* **1969**, 268, 1614.

32.3, 29.7, 29.3, 29.2, 28.8, 26.4, 25.6, 23.6, 15.6, 13.4; HRMS (EI) calcd for C₁₄H₂₂O (M⁺) *m/z* 206.1671, found 206.1671.