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Supporting Information

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Lithium benzocyclobuteneoxyde as a vinylogous enolate: Solvent-controlled synthesis of highly functionalized seven-membered benzocarbocycles

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Experimental Part

General Considerations: All reactions involving air sensitive compounds were carried out under a N_2 atmosphere (99.99%). All glassware was oven-dried (120 °C), evacuated and purged with nitrogen. All common reagents and solvents were obtained from commercial suppliers and used without any further purification unless otherwise indicated. Fischer carbene complexes **3** and **4a-g** were prepared following described procedures.[1a-f] Benzocyclobutenol was also synthesized following a previously described procedure.[2] Solvents were dried by standard methods. Hexane and ethyl acetate were distilled before use. TLC was performed on aluminum-backed plates coated with silica gel 60 with F_{254} indicator; the chromatograms were visualized under ultraviolet light and/or by staining with a Ce/Mo reagent, or anisaldehyde or phosphomolibdic acid solutions and subsequent heating. R_f values are reported on silica gel. Flash column

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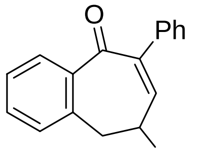
[1] a) K. H. Dötz, W. J. Kuhn *J. Organomet. Chem.* **1985**, *286*, C23-C26. b) K. S. Chan, W. D. Wulff *J. Am. Chem. Soc.* **1986**, *108*, 5229-5236. c) J. Barluenga, F. Aznar, S. Barluenga, M. Fernández, A. Martín, S. García-Granda, A. Piñera-Nicolás *Chem. Eur. J.* **1998**, *4*, 2280-2298. d) M. A. Palomero *Ph. D. Thesis*, Universidad de Oviedo **2002**, page 241. e) K. L. Faron, W. D. Wulff *J. Am. Chem. Soc.* **1988**, *110*, 8727-8729. f) Y. Jung, Y. J. Yong, K. S. Rhee, G. C. Shin, C. Sung *Chem. Lett.* **1994**, *5*, 859-862.

[2] W. A. Bubb, S. Sternhell *Aust. J. Chem.* **1976**, *29*, 1685-1697.

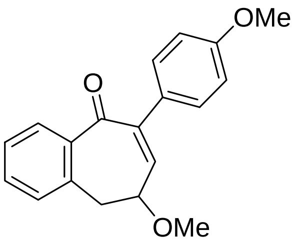
chromatography was carried out on silica gel 60, 230-240 mesh. Routine NMR measurements were recorded on Bruker AC-200, AC-300 or DPX-300 spectrometers. ^{1}H NMR: splitting pattern abbreviations are: s, singlet; bs, broad singlet; d, doublet; t, triplet; at, apparent triplet; dd, double doublet; dt, double triplet; adt, apparent double triplet; q, quartet; m, multiplet. ^{13}C NMR: multiplicities were determined by DEPT, abbreviations are: q, CH_3; t, CH_2; d, CH; s, quaternary carbons. COSY, HMQC, HMBC, and NOESY experiments were carried out on a Bruker AMX-400 spectrometer. Standard pulse sequences were employed for the DEPT experiments. FT-IR were performed with a Mattson 3000 FT-IR spectrometer using sodium chloride plates; samples were measured as films from deuterocloroform or dichloromethane. Mass spectra were determined by Universidad de Oviedo and Universidad de Vigo (CACTI) with a Finnigan Mat95 and a VG AutoSpec M Mass Spectrometers respectively for high resolution mass spectra (HRMS); low resolution mass spectra were obtained with a Hewlett-Packard 5880 A Spectrometer. In both cases, either electron impact (70 eV) or FAB techniques were employed. Melting points were determined on a Büchi-Tottoli apparatus and are uncorrected. Elemental analyses were carried out with a Perkin-Elmer 240 B microanalyzer.

Synthesis of benzocycloheptenones 7. General procedure. Butyl lithium (1.6 equiv.) was added to a solution of benzocyclobutenol (1.5 equiv.) in dry THF (15 mL) at –78 °C. After 30 min the temperature was raised to –25 °C, and after 10-15 min more (red solution observed), the corresponding carbene complex **4** (1 equiv., 0.5 mmol) was added in portions. The mixture was stirred until complete disappearance of the carbene complex was observed by TLC. Solvent was removed under reduced pressure, and the residue purified by flash chromatography; the corresponding benzocycloheptenone **7** was isolated in the yield reported in Table 1.



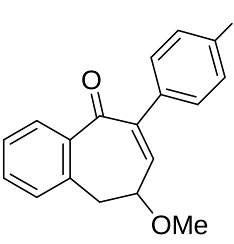
7a

8,9-dihydro-8-methoxy-6-phenyl-5*H*-benzocyclohepten-5-one 7a. Yellow oil; yield = 49 %; R_f = 0.24 (hexane/AcOEt 5/1); FT-IR (film): ν = 1772, 1675, 1597 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.81 (d, $^3J(H,H)$ = 7.7 Hz, 1 H), 7.53-7.34 (m, 7 H), 7.30 (d, $^3J(H,H)$ = 7.7 Hz, 1 H), 6.82 (m, 1 H), 4.27 (m, 1 H), 3.49 (s, 3 H), 3.44 (m, 1 H), 3.22 (ad, $^2J(H,H)$ = 14.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C): δ = 195.1 (s), 142.7 (d), 142.4 (s), 140.1 (s), 139.0 (s), 135.0 (s), 132.0 (d), 129.8 (d), 129.4 (d), 128.4 (d, 2 CH), 127.9 (d, 2 CH), 127.7 (d), 127. 0 (d), 77.2 (d), 56.5 (q), 39.2 (t); MS (FAB): *m/z* (%): 265 (100) $[M+1]^+$, 233 (35), 205 (36); HRMS (FAB) for $C_{18}H_{17}O_2$ $[M+1]^+$: calcd 265.1229; found 265.1224; elemental analysis calcd (%) for $C_{18}H_{16}O_2$ (264.32): C 81.79, H 6.10; found C 81.75, H 6.08.



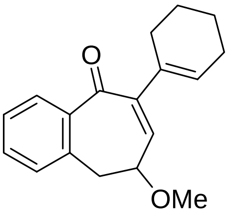
7b

8,9-dihydro-8-methoxy-6-(4-methoxyphenyl)-5*H*-benzocyclohepten-5-one 7b. Brownish oil; yield = 71 %; R_f = 0.20 (hexane/AcOEt 5/1); FT-IR (film): ν = 1684, 1605 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.82 (d, $^3J(H,H)$ = 7.6 Hz, 1 H), 7.46 (m, 1 H), 7.40-7.25 (m, 4 H), 6.92 (d, $^3J(H,H)$ = 8.8 Hz, 2 H), 6.78 (d, $^3J(H,H)$ = 2.4 Hz, 1 H), 4.27 (m, 1 H), 3.83 (s, 3 H), 3.50 (s, 3 H), 3.43 (m, 1 H), 3.23 (ad, $^2J(H,H)$= 14.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C): δ = 195.5 (s), 159.1 (s), 141.8 (s), 141.0 (d), 140.1 (s), 134.9 (s), 131.8 (d), 131.3 (s), 129.7 (d), 129.4 (d, 2 CH), 129.1 (d), 126.9 (d), 113.3 (d, 2 CH), 77.0 (d), 56.3 (q), 55.0 (q), 39.0 (t); MS (FAB): *m/z* (%): 295 (100) $[M+1]^+$, 294 (89), 263 (72), 235 (37), 223 (80); HRMS (FAB) for $C_{19}H_{19}O_3$ $[M+1]^+$: calcd 295.1334; found 295.1348; elemental analysis calcd (%) for $C_{19}H_{18}O_3$ (294.34): C 72.36, H 5.06; found C 72.17, H 5.01.



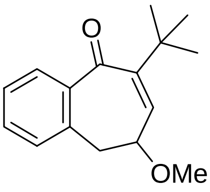
7c

6-(4-chlorophenyl)-8,9-dihydro-8-methoxy-5*H*-benzocyclohepten-5-one 7c. Purple oil; yield = 67 %; R_f = 0.26 (hexane/AcOEt 5/1); FT-IR (film): ν = 1773, 1653, 1595 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.82 (dd, ^3J(H,H) = 7.6 Hz and ^4J(H,H) = 1.4 Hz, 1 H), 7.53-7.27 (m, 7 H), 6.82 (dd, ^3J (H,H) = 3.2 Hz and ^4J(H,H)= 1.4 Hz, 1 H), 4.27 (m, 1 H), 3.51 (s, 3 H), 3.44 (m, 1 H), 3.23 (ad, ^2J(H,H) = 14.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C): δ = 194.5 (s), 143.7 (d), 141.3 (s), 139.9 (s), 137.6 (s), 135.0 (s), 133.7 (s), 132.3 (d), 129.9 (d, 3 CH), 129.7 (d), 128.2 (d, 2 CH), 127.2 (d), 77.3 (d), 56.6 (q), 39.3 (t); MS (FAB): *m/z* (%): 299 (60) $[M+1]^+$, 239 (80), 203 (68), 202 (100), 189 (68); HRMS (FAB) for $C_{18}H_{16}O_2Cl$ $[M+1]^+$: calcd 299.0839; found 299.0833.



7d

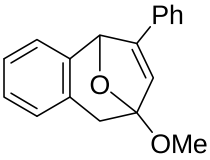
6-(cyclohex-1-enyl)-8,9-dihydro-8-methoxy-5*H*-benzocyclohepten-5-one 7d. Yellow oil; yield = 52 %; R_f = 0.41 (hexane/AcOEt 5/1); FT-IR (film): ν = 1724, 1680 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.67 (d, ^3J(H,H) = 7.6 Hz, 1 H), 7.44-7.19 (m, 3 H), 6.30 (d, ^3J(H,H) = 4.3 Hz, 1 H), 5.79 (bs, 1 H), 4.21 (m, 1 H), 3.39 (s, 3 H), 3.36-3.15 (m, 2 H), 2.20-2.05 (m, 4 H), 1.72-1.52 (m, 4 H); ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C): δ = 198.0 (s), 145.1 (s), 139.7 (s), 135.9 (s), 134.6 (s), 132.6 (d), 131.7 (d), 130.3 (d), 128.7 (d), 127.7 (d), 126.7 (d), 76.3 (d), 56.4 (q), 38.8 (t), 26.4 (t), 25.6 (t), 22.5 (t), 21.8 (t); MS (FAB): *m/z* (%): 269 (79) $[M+1]^+$, 237 (100), 223 (91), 191 (72), 165 (88); HRMS (FAB) for $C_{18}H_{21}O_2$ $[M+1]^+$: calcd 269.1542; found 269.1532; elemental analysis calcd (%) for $C_{18}H_{20}O_2$ (268.35): C 72.36, H 5.06; found C 72.33, H 5.05.



7e

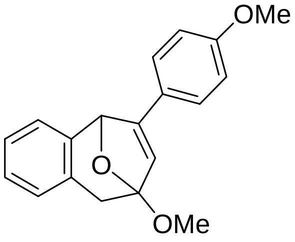
6-(*tert*-butyl)-8,9-dihydro-8-methoxy-5*H*-benzocyclohepten-5-one 7e. Compound not isolated. Data retrieved from an enriched mixture after column chromatography. Brown oil; estimated yield = 50 %; R_f = 0.43 (hexane/AcOEt 5/1); ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, TMS): δ = 7.62 (d, ^3J(H,H) = 7.6 Hz, 1 H), 7.45-7.16 (m, 3 H), 6.18 (d, ^3J(H,H) = 4.8 Hz, 1 H), 4.29 (m, 1 H), 3.39 (s, 3 H), 3.23 (m, 2 H), 1.20 (s, 9 H).

Synthesis of benzocycloheptene ketals 8. General procedure. Butyl lithium (1.6 equiv.) was added to a solution of benzocyclobutenol (1.5 equiv.) in dry diethyl ether (15 mL) at –78 °C. After 30 min the temperature was raised to –25 °C, and after 10-15 min, carbene complex **4** (1 equiv., 0.5 mmol) was added in portions. The mixture was stirred until complete disappearance of the carbene complex was observed by TLC. Solvent was removed under reduced pressure, and the residue purified by flash chromatography; the corresponding benzocycloheptene ketal **8** was isolated in the yield reported in Table 2.



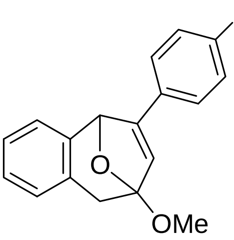
8a

9-methoxy-12-oxa-11-phenyl-tricyclo[7.2.1.0^{2,7}]dodeca-2(7),3,5,10-tetraene 8a. Yellow solid; yield = 50 %; R_f = 0.27 (hexane/AcOEt 5/1); FT-IR (film): ν = 1160, 1009 cm^{-1}; m.p. = 110-112 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.58-7.10 (m, 9 H), 6.24 (s, 1 H), 5.88 (s, 1 H), 3.59 (s, 3 H), 3.29 (d, ^2J(H,H) = 16.8 Hz, 1 H), 2.93 (d, ^2J(H,H) = 16.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C): δ = 151.8 (s), 137.8 (s), 134.1 (s), 131.2 (s), 130.0 (d), 128.7 (d), 128.6 (d, 2 CH), 127.1 (d), 126.2 (d, 2 CH), 125.3 (d), 123.8 (d), 121.3 (d), 110.9 (s), 80.4 (d), 51.2 (q), 35.4 (t); MS (FAB): *m/z* (%): 265 (39) [*M+1*]$^+$, 257 (74), 205 (100), 202 (80), 165 (99); HRMS (FAB) for $C_{18}H_{17}O_2$ [*M+1*]$^+$: calcd 265.1229; found 265.1231; elemental analysis calcd (%) for $C_{18}H_{16}O_2$ (264.32): C 81.79, H 6.10; found C 81.74, H 6.09.



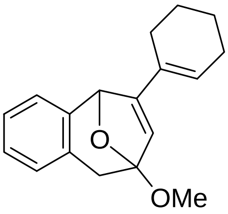
8b

9-methoxy-11-(4-methoxyphenyl)-12-oxa-tricyclo[7.2.1.0^{2,7}]dodeca-2(7),3,5,10-tetraene 8b. Brown oil; yield = 56 %; R_f = 0.24 (hexane/AcOEt 5/1); FT-IR (film): ν = 1161, 1029 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.48 (d, ^3J(H,H) = 9.0 Hz, 2 H), 7.27-7.14 (m, 4 H), 6.91 (d, ^3J(H,H) = 9.0 Hz, 2 H), 6.10 (s, 1 H), 5.87 (s, 1 H), 3.81 (s, 3 H), 3.60 (s, 3 H), 3.30 (d, ^2J(H,H) = 16.7 Hz, 1 H), 2.95 (d, ^2J(H,H) = 16.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C): δ = 159.8 (s), 151.2 (s), 138.0 (s), 134.1 (s), 130.0 (d), 127.5 (d, 2 CH), 127.0 (d), 125.1 (d), 123.8 (s), 123.6 (d), 118.8 (d), 113.9 (d, 2 CH), 110.9 (s), 80.3 (d), 55.1 (q), 51.0 (q), 35.5 (t); MS (EI): *m/z* (%): 294 (30) [*M*]$^+$, 262 (61), 235 (100), 220 (50), 203 (34); HRMS (EI) for $C_{19}H_{18}O_3$ [*M*]$^+$: calcd 294.1256; found 294.1254; elemental analysis calcd (%) for $C_{19}H_{18}O_3$ (294.34): C 77.53, H 6.16; found C 77.37, H 6.12.



8c

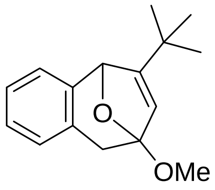
11-(4-chlorophenyl)-9-methoxy-12-oxa-tricyclo[7.2.1.0^{2,7}]dodeca-2(7),3,5,10-tetraene 8c. Red oil; yield = 86 %; R$_f$ = 0.28 (hexane/AcOEt 5/1); ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, TMS): δ = 7.43 (d, ^3J(H,H) = 8.6 Hz, 2 H), 7.31 (d, ^3J(H,H) = 8.6 Hz, 2 H), 7.21-7.07 (m, 4 H), 6.21 (s, 1 H), 5.82 (s, 1 H), 3.57 (s, 3 H), 3.27 (d, ^2J(H,H) = 17.0 Hz, 1 H), 2.91 (d, ^2J(H,H) = 17.0 Hz, 1 H); ^{13}C NMR (CDCl$_3$, 75 MHz, 25 °C): δ = 150.6 (s), 137.5 (s), 134.5 (s), 134.0 (s), 130.1 (d), 129.6 (s), 128.8 (d, 2 CH), 127.4 (d, 2 CH), 127.3 (d), 125.3 (d), 123.6 (d), 122.0 (d), 110.9 (s), 80.2 (d), 51.2 (q), 35.2 (t); MS (EI): *m/z* (%): 298 (32) [*M*]$^+$, 239 (99), 204 (100), 101 (78); HRMS (EI) for $C_{18}H_{15}O_2Cl$ [*M*]$^+$: calcd 298.0755; found 298.0757.



8d

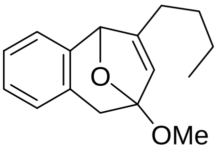
11-(cyclohex-1-enyl)-9-methoxy-12-oxa-tricyclo[7.2.1.0^{2,7}]dodeca-2(7),3,5,10-tetraene 8d. Yellow oil; yield = 55 %; R$_f$ = 0.49 (hexane/AcOEt 5/1); ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, TMS): δ = 7.33-7.09 (m, 4 H), 6.08 (bs, 1 H), 5.65 (s, 1 H), 5.63 (s, 1 H) 3.52 (s, 3 H), 3.22 (d, ^2J(H,H) = 16.7 Hz, 1 H), 2.85 (d, ^2J(H,H) = 16.7 Hz, 1 H), 2.24-2.08 (m, 4 H), 1.65-1.54 (m, 4 H) ; ^{13}C NMR (CDCl$_3$, 75 MHz, 25 °C): δ = 153.6 (s), 138.6 (s), 134.2 (s), 129.9 (d), 129.5 (s), 128.3 (d), 126.8 (d), 125.0 (d), 123.7 (d), 119.1 (d), 110.5 (s), 79.6 (d), 50.9 (q), 35.6 (t), 25.7 (t, 2 CH), 22.1 (t), 21.8 (t); MS (FAB): *m/z* (%): 269 (22) [*M+1*]$^+$, 223 (100), 166 (18); HRMS (FAB) for $C_{18}H_{21}O_2$ [*M+1*]$^+$: calcd

269.1542; found 269.1545; elemental analysis calcd (%) for $C_{18}H_{20}O_2$ (268.35): C 80.56, H 7.51; found C 80.39, H 7.48.



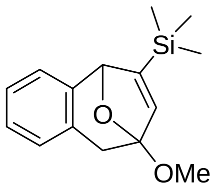
8e

11-*tert*-butyl-9-methoxy-12-oxa-tricyclo[7.2.1.0^{2,7}]dodeca-2(7),3,5,10-tetraene 8e. Yellow oil; yield = 50 %; R_f = 0.42 (hexane/AcOEt 5/1); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.15-7.06 (m, 4 H), 5.54 (s, 1 H), 5.45 (s, 1 H), 3.48 (s, 3 H), 3.13 (d, ^2J(H,H) = 16.6 Hz, 1 H), 2.83 (d, ^2J(H,H) = 16.6 Hz, 1 H), 1.06 (s, 9 H); ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C): δ = 163.8 (s), 139.0 (s), 134.4 (s), 129.8 (d), 126.7 (d), 124.7 (d), 124.6 (d), 119.9 (d), 110.0 (s), 80.5 (d), 50.5 (q), 35.0 (t), 32.4 (s), 29.4 (q, 3 CH_3); MS (FAB): *m/z* (%): 245 (21) [*M+1*]$^+$, 227 (74), 221 (81), 207 (100), 193 (40), 191 (44); HRMS (FAB) for $C_{16}H_{21}O_2$ [*M+1*]$^+$: calcd 245.1542; found 245.1540.



8f

11-*n*-butyl-9-methoxy-12-oxa-tricyclo[7.2.1.0^{2,7}]dodeca-2(7),3,5,10-tetraene 8f. Orange oil; yield = 25 %; R_f = 0.44 (hexane/AcOEt 5/1); FT-IR (neat): ν = 1160, 1021 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.23-7.03 (m, 4 H), 5.44 (s, 1 H), 5.15 (s, 1 H), 3.50 (s, 3 H), 3.16 (d, ^2J(H,H) = 16.7 Hz, 1 H), 2.76 (d, ^2J(H,H) = 16.7 Hz, 1 H), 2.14-2.01 (m, 2 H), 1.52-1.22 (m, 4 H), 0.87 (t, ^3J(H,H) = 7.1 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C): δ = 155.0 (s), 138.3 (s), 134.4 (s), 130.0 (d), 127.0 (d), 125.2 (d), 123.2 (d), 120.1 (d), 110.7 (s), 82.4 (d), 50.8 (q), 35.3 (t), 28.8 (t), 26.8 (t), 22.2 (t), 13.7 (q); MS (EI): *m/z* (%): 244 (<5) [*M*]$^+$, 222 (86), 179 (47), 178 (100), 134 (65), 119 (52); HRMS (EI) for $C_{16}H_{20}O_2$ [*M*]$^+$: calcd 244.1463; found 244.1458.



8g

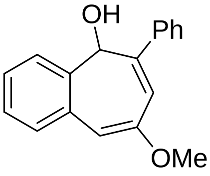
9-methoxy-12-oxa-11-trimethylsilyl-tricyclo[7.2.1.0^{2,7}]dodeca-2(7),3,5,10-tetraene 8g. Brown oil; yield = 38 %; R_f = 0.42 (hexane/AcOEt 5/1); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.17-7.06 (m, 4 H), 6.05 (s, 1 H), 5.54 (s, 1 H), 3.51 (s, 3 H), 3.17 (d, ^2J(H,H) = 16.7 Hz, 1 H), 2.78 (d, ^2J(H,H) = 16.7 Hz, 1 H), 0.06 (s, 9 H); ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C): δ = 155.0 (s), 138.5 (s), 136.3 (d), 133.8 (s), 129.8 (d), 126.8 (d), 125.0 (d), 123.4 (d), 110.8 (s), 83.6 (d), 51.0 (q), 34.7 (t), -1.58 (q, 3 CH_3).

Optimized procedure for the synthesis of benzocycloheptene ketal 8a. Butyl lithium (1.72 mL, 1.6M, 5.5 equiv.) was added to a solution of benzocyclobutenol (0.300 g, 5 equiv.) in dry diethyl ether (15 mL) at –78 °C. After 30 min the temperature was raised to –25 °C, and after 10-15 min, the carbene complex (0.234 g, 1 equiv., 0.5 mmol) was added in portions. The mixture was stirred until complete disappearance of the carbene complex was observed by TLC. Solvent was removed under reduced pressure, and the residue purified by flash chromatography to give 0.093 g of **8a** (70% yield).

Base-promoted ring opening of benzocycloheptene ketals 8. Synthesis of benzocycloheptadienols 9.

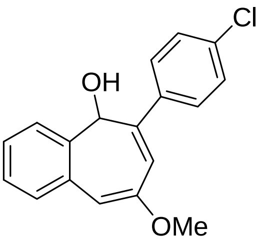
Method A: Butyl lithium (3 equiv.) was slowly added to a solution of the correponding compound **8** (1 equiv., 0.5 mmol) in a 10 mL mixture of diethyl ether-pentane 1:1 at 0°C. After 10 min the mixture was quenched with water (10 mL) and extracted with diethyl ether. Solvent was removed under reduced pressure to give benzocycloheptadienols **9** in the yields reported in Scheme 3. Compounds **9** decomposed when purification by flash column chromatography on silica gel was attempted. However, after the diethyl ether extraction, they were obtained with purity enough to allow for their complete characterization.

Method B: *t*-Butyl lithium (3 equiv.) was slowly added to a solution of the correponding compound **8** (1 eq., 0.5 mmol) in a 10 mL mixture of diethyl ether-pentane 1:1 at –78 °C. After 10 min the mixture was quenched with water (10 mL) and extracted with diethyl ether. Solvent was removed under reduced pressure to give to give benzocycloheptadienols **9** in the yields reported in Scheme 3.



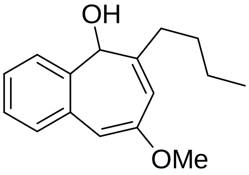
9a

8-methoxy-6-phenyl-5*H*-benzocyclohepten-5-ol 9a. Yellow oil; yield = quantitative (method A), quantitative (method B); R_f = 0.55 (hexane/AcOEt 1/1); FT-IR (film): ν = 3415, 1633 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.59-7.30 (m, 9 H), 6.50 (d, $^4J(H,H)$ = 1.6 Hz, 1 H), 6.30 (d, $^4J(H,H)$ = 1.6 Hz, 1 H), 5.44 (bs, 1 H), 3.85 (s, 3 H), the signal of the H of the hydroxyl group was not observed; ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C): δ = 155.9 (s), 144.0 (s), 139.4 (s), 135.6 (s), 132.2 (s), 128.6 (d), 128.3 (d, 2 CH), 127.8 (d), 127.6 (d, 2 CH), 127.0 (d), 126.9 (d), 126.2 (d), 120. 3 (d), 105.0 (d), 73.8 (d), 54.8 (q); MS (EI): m/z (%): 264 (<5) $[M]^+$, 247 (100); HRMS (EI) for $C_{18}H_{16}O_2$ $[M]^+$: calcd 264.11150; found 264.1139.



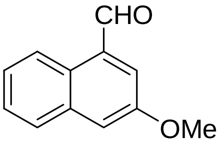
9b

6-(4-chlorophenyl)-8-methoxy-5*H*-benzocyclohepten-5-ol 9b. Yellow oil; yield = 80 %; R_f = 0.17 (hexane/AcOEt 5/1); FT-IR (film): ν = 3385, 1640 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.47-7.28 (m, 8 H), 6.48 (s, 1 H), 6.24 (s, 1 H), 5.35 (s, 1 H), 3.84 (s, 3 H), the signal of the H of the hydroxyl group was not observed; ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C): δ = 155.8 (s), 142.8 (s), 137.8 (s), 137.5 (s), 133.8 (s), 132.2 (s), 129.1 (d, 2 CH), 128.7 (d), 128.5 (d, 2 CH), 128.4 (d), 127.2 (d), 127.0 (d), 120.6 (d), 105.2 (d), 73.6 (d), 54.9 (q); MS (EI): *m/z* (%): 298 (<5) [*M*]$^+$, 281 (100); HRMS (EI) for $C_{18}H_{15}O_2Cl$ [*M*]$^+$: calcd 298.0761; found 298.0748.



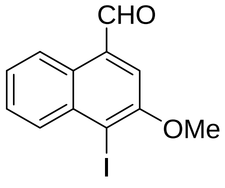
9c

6-*n*-butyl-8-methoxy-5*H*-benzocyclohepten-5-ol 9c. Yellow oil; yield = 82 %; R_f = 0.51 (hexane/AcOEt 5/1); FT-IR (film): ν = 1642 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.45 (bs, 1 H), 7.39-7.25 (m, 3 H), 6.34 (s, 1 H), 5.80 (s, 1 H), 4.77 (bs, 1 H), 3.79 (s, 3 H), 2.44-2.34 (m, 3 H), 1.52-1.50 (m, 2 H), 1.32-1.29 (m, 2 H), 0.90 (t, ^3J(H,H) = 7.1 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C): δ = 156.6 (s), 147.0 (s), 136.4 (s), 132.1 (s), 127.8 (d), 126.6 (d), 126.2 (d), 123.6 (d), 116.3 (d), 103.7 (d), 73.2 (d), 54.6 (q), 33.3 (t), 30.5 (t), 22.3 (t), 13.8 (q); MS (EI): *m/z* (%): 244 (<5) [*M*]$^+$, 226 (100); HRMS (EI) for $C_{16}H_{20}O_2$ [*M*]$^+$: calcd 244.1463; found 244.1462.



10

Synthesis of 3-methoxynaphthalene-1-carbaldehyde 10. IPy_2BF_4 (0.335 g, 2 equiv., 0.90 mmol) was added to a solution of **8g** (0.118 g, 1 equiv., 0.45 mmol) in 1,2-dichloroethane (10 mL) at room temperature. The mixture was stirred until complete disappearance of **8g** was observed by TLC. Sodium thiosulfate solution was added, and the mixture extracted with diethyl ether, dried over Na_2SO_4, and concentrated in vacuo to give a crude oil. Flash column chromatography on silica gel, using mixtures of hexane/AcOEt with gradual increase of polarity as eluent, afforded naphthalene **10.** Yellow oil; yield = 61 %; R_f = 0.28 (hexane/AcOEt 5/1); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 10.38 (s, 1 H), 9.10 (m, 1 H), 7,82 (m, 1 H), 7.67 (d, ^4J(H,H) = 2.6 Hz, 1 H,), 7.55 (m, 2 H), 7.41 (d, 1 H, ^4J(H,H) = 2.4 Hz), 3.99 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C): δ = 192.9 (d), 156.5 (s), 135.4 (s), 132.8 (s), 128.4 (d), 127.4 (d), 127.2 (d), 126.5 (d), 126.1 (s), 124.7 (d), 113.l (d), 55.6 (q); MS (EI): *m/z* (%): 186 (100) $[M]^+$, 158 (10), 128 (18), 115 (64); elemental analysis calcd (%) for $C_{12}H_{10}O_2$ (186.21): C 77.40, H 5.41; found C 77.63, H 5.52.



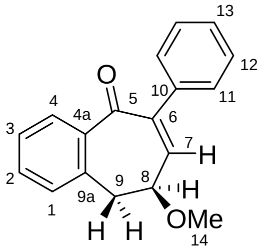
11

Synthesis of 4-iodo-3-methoxynaphthalene-1-carbaldehyde 11. IPy_2BF_4 (0.037 g, 1.1 equiv.) and HBF_4 (0.025 mL, 2 equiv.) were subsequently added to a solution of **10** (0.017 g, 1 equiv., 0.09 mmol) in dichloromethane (3 mL) at room temperature. The mixture was stirred until complete disappearance of **10** was observed by TLC. Sodium thiosulfate solution was added, and the mixture extracted with diethyl ether, dried over Na_2SO_4, and concentrated in vacuo to give a crude oil. Flash column chromatography on silica gel afforded naphthalene **11.** Yellow solid; yield = 72 %; R_f = 0.31 (hexane/AcOEt 5/1); FT-IR (film): ν = 1692 cm^{-1}; m.p. = 110-112 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 10.5 (s, 1 H), 9.00 (dd, ^3J(H,H) = 8.3 Hz and ^4J(H,H) = 1.5 Hz, 1 H), 8.29 (dd, ^3J(H,H) = 8.9 Hz and ^4J(H,H) = 1.5 Hz, 1 H), 7.67 (s, 1 H), 7.65 (m, 2 H), 4.12 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C): δ = 191.5

(d), 156.1 (s), 136.2 (s), 132.5 (s), 132.0 (d), 128.9 (d), 127.1 (d + s), 124.0 (d), 119.2 (d), 98.1 (s), 57.3 (q); MS (EI): *m/z* (%): 312 (100) $[M]^+$, 298 (24); HRMS (EI) for $C_{12}H_9O_2I$ $[M]^+$: calcd 311.9647; found 311.9642; elemental analysis calcd (%) for $C_{12}H_9IO_2$ (312.10): C 46.18, H 2.91; found C 45.95, H 3.01.

Tables with the 2D-NMR Experiments (HSQC, COSY, HMBC and NOESY) for selected compounds

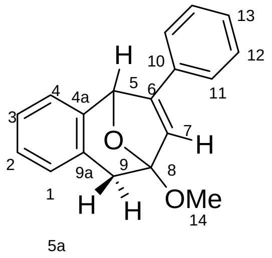
Compound 7a



7a

Site	^{13}C-NMR (ppm)	DEPT	^{1}H-NMR	COSY	HMBC	NOESY
1	129.8	CH	7.29 (1H, dt, J = 7.5 Hz)	7.37 - 7.31	39.2, 140.1	3.23
2	127.0 / 127.6	C	7.37 - 7.31 (6H)		140.1	
3	127.0 / 127.6	C	7.37 - 7.31 (6H)		140.1	
4	129.4	CH	7.81 (1H, dd, J = 7.7, 1.0 Hz)	7.37 - 7.31	135.0	7.37 - 7.31
4a	140.1	C				
5	195.0	C				
6	139.0 / 142.3	C				
7	142.7	CH	6.81 (1H, dd, J = 3.2, 1.3)	3.23, 4.27	39.2, 139.0, 142.3, 195.0	3.49, 4.27, 7.37-7.31
8	77.2	CH	4.27 (1H, ddd, J = 10.8, 3.2, 2.8)	3.23, 3.45, 6.81	39.2, 135.0, 142.7	3.21, 3.49, 6.82
9	39.2	CH$_2$	3.45 (1H, dd, J = 14.5, 10.8 Hz)	3.23, 4.27	77.2	3.23
			3.23 (1H, d, J = 14.5 Hz)	3.45, 4.27, 6.81	77.2	3.45, 4.27
9a	135.0	C				
10	139.0 / 142.3	C				
11	127.9 / 128.4	CH	7.37 - 7.31 (6H)			6.81
12	127.9 / 128.4	CH	7.37 - 7.31 (6H)			
13	132.0	CH	7.46 (1H, dt, J = 7.4, 1.3 Hz)	7.37 - 7.31		
14	56.4	CH$_3$	3.49 (3H, s)		77.2	4.27, 6.82

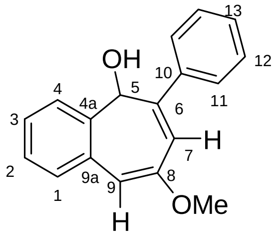
Compound 8a



8a

Site	^{13}C-NMR (ppm)	DEPT	^{1}H-NMR	COSY	HMBC	NOESY
1	130.1	CH	7.11 (3H, m)		35.4, 137.9	2.92, 3.26
2	127.2	CH	7.11 (3H, m)		123.8, 134.2	
3	125.3	CH	7.11 (3H, m)		137.9	
4	123.8	CH	7.25 (1H, m)	7.11 (3H, m)	80.4, 127.2, 134.2	5.86, 7.11, 7.51
4a	137.9	C				
5	80.4	CH	5.86 (1H, s)		110.9, 123.8, 134.2, 151.8	7.25, 7.51
6	151.8	C				
7	121.4	CH	6.22 (1H, s)		80.4, 110.9, 131.3, 137.9, 151.8	2.92, 3.26, 7.51
8	110.9	C				
9	35.4	CH_2	2.92 (1H, d, J = 6.7 Hz)	3.26	110.9, 121.4, 130.1, 134.2	3.26, 6.22, 7.11
			3.26 (1H, d, J = 6.7 Hz)	2.92	110.9, 121.4, 134.2	2.92, 3.60, 7.11
9a	134.2	C				
10	131.3	C				
11	126.3	CH	7.51 (2H, d, J = 7.4 Hz)	7.35	128.7, 128.8	5.86, 6.22, 7.35
12	128.7	CH	7.35 (2H, pseudot, J = 7.1, 7.7 Hz)	7.51	128.8	7.51
13	128.8	CH	7.30 (1H, d, J = 7.2 Hz)		126.3	
14	51.2	CH_3	3.60 (3H, s)		110.4	6.22

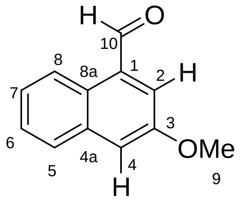
Compound 9a



9a

Site	^{13}C-NMR (ppm)	DEPT	^{1}H-NMR	COSY	HMBC	NOESY
1	128.8	CH	7.51 (2H, m)	6.51, 7.40		6.51
2	127.1 / 127.2	CH	7.40 (5H, m)			
3	127.1 / 127.2	CH	7.40 (5H, m)			
4	128.0	CH	7.51 (2H, m)	7.40	132.4, 135.8, 144.3	5.45
4a	135.8	C				
5	74.0	CH	5.45 (1H, bs)		120.5, 132.4, 135.8, 139.6, 144.3	7.51, 7.56
6	132.4	C				
7	120.5	CH	6.33 (1H, d, J = 1.4 Hz)	6.51	74.0, 105.2, 139.6, 144.3, 156.1	3.86, 7.56
8	156.1	C				
9	105.2	CH	6.51 (1H, d, J = 1.4 Hz)	6.33, 7.56	120.5, 128.8, 138.7, 144.3, 156.1	3.86, 7.51
9a	144.3	C				
10	139.6	C				
11	127.8	CH	7.56 (2H, m)	7.40		5.45, 6.33
12	128.5	CH	7.40 (5H, m)	7.56		
13	128.5	CH	7.40 (5H, m)			
14	55.0	CH_3	3.86 (3H, s)		105.2, 156.1	6.33, 6.51
OH-5			3.69 (1H, bs)			

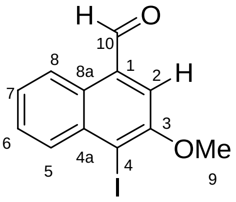
Compound 10



10

Site	^{13}C-NMR (ppm)	DEPT	^{1}H-NMR	COSY	HMBC	NOESY
1	132.8	C				
2	128.4	CH	7.67 (1H, d, J = 2.6 Hz)	7.41	113.1, 126.1, 156.5, 192.9	
3	156.5	C				
4	113.1	CH	7.41 (1H, d, J = 2.6 Hz)		126.1, 128.4, 156.5	3.99, 7.82
4a	135.4	C				
5	127.2	CH	7.82 (1H, m)	7.55	113.1, 126.1	7.41
6	126.5 / 127.4	CH	7.55 (2H, m)	7.82, 9.10	124.7, 127.2, 135.4	
7	126.5 / 127.4	CH	7.55 (2H, m)	7.82, 9.10	124.7, 127.2, 135.4	
8	124.7	CH	9.10 (1H, m)	7.55	126.5, 127.4, 135.4	
8a	126.1	C				
9	55.6	CH_3	3.99 (3H, s)		156.5	
10	192.9	CH	10.38 (1H, s)		126.1, 128.4, 132.8	7.67, 9.10

Compound 11



11

Site	^{13}C-NMR (ppm)	DEPT	^{1}H-NMR	COSY	HMBC	NOESY
1	132.5	C				
2	119.2	CH	7.66 (1H, s)		98.1, 127.0, 136.2, 156.1, 191.5	10.54
3	156.1	C				
4	98.1	C				
4a	136.2	C				
5	132.0	CH	8.28 (1H, dd, J = 8.0, 1.7 Hz)	7.61	127.0	
6	128.9	CH	7.61 (2H, m)		124.0, 127.0, 127.1, 136.2	
7	127.1	CH	7.61 (2H, m)		127.0, 132.0	
8	124.0	CH	9.00 (1H, dd, J = 8.3, 1.4 Hz)	7.61	128.9, 136.2	10.54
8a	127.0	C				
9	57.3	CH_3	4.12 (3H, s)		156.1	
10	191.5	CH	10.54 (1H, s)		119.2, 127.0, 132.5	7.66, 9.00