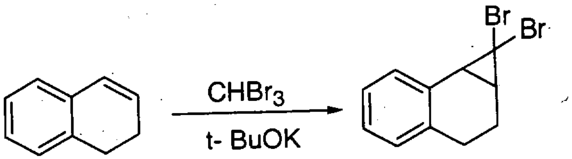
ol0100881

Supporting information.

All reagents were obtained from commercial suppliers and used without further purification unless otherwise indicated. Tetrahydrofuran (THF) and ether were distilled from benzophenone ketyl sodium under nitrogen. Methylene chloride was distilled from CaH_2 under nitrogen. Benzene was distilled from Na under nitrogen. Routine NMR spectra were recorded on 300 MHz, 400 MHz and 500 MHz Bruker and Varian instruments. Proton signal assignments in ^{1}H-NMR spectra, when not obvious from the chemical shift and multiplicity data, were performed using standard COSY experiment. Carbon signal multiplicities in ^{13}C spectra were determined from the standard DEPT experiment. Mass spectra were obtained from the University of Zürich or Michigan State University Mass Spectrometry Facilities. High resolution mass spectra were obtained from the Michigan State University Mass Spectrometry Facility. Elemental analyses were done by the University of Zürich Element Analysis Facility or by Galbraith Laboratories in Knoxville, TN.

7,7-Dibromo-2,3-benzobicyclo[4.1.0]heptene (8a).

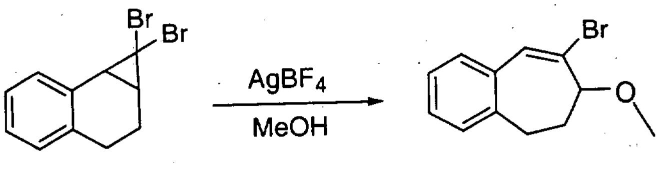


To the stirred solution of 1,2-dihydronaphthalene (2.6 g, 0.02 mol) in 60 mL of pentane at 0 °C t-BuOK (3.92 g , 0.035 mol) was added under nitrogen. Then to the stirred suspension bromoform (10.12 g, 0.04 mol) was added dropwise at 0 °C over a period of 0.5 hours. The suspension was stirred at this temperature 1 hour and then warmed slowly to room temperature and stirred 4 hours. After that the reaction was quenched by the excess of water, organic layer was separated, water layer was extracted 2 times with ether. Organic layers were united and dried over $MgSO_4$. Solvent was evaporated. The residue was purified by flash chromatography on the silica gel (hexane) to give **8a**[17] (4.9 g, 82 %). Colorless oil.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.88-1.92 (m,1H), 2.31-2.35 (m, 2H), 2.66-2.79 (m, 3H), 7.07 (d,1H, J = 8.2 Hz), 7.19-7.22 (m, 2H), 7,37 (d, 1H, J = 7 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 16.2, 20.3, 23.0, 24.2, 30.0, 100.1, 100.8, 101.7, 103.3, 104.4, 108.4.

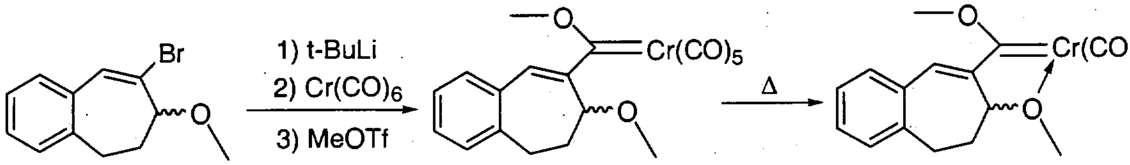
1-Bromo-7-methoxy-3,4-benzo-1,3-cycloheptadiene (1a).



To the stirred solution of $AgBF_4$ (4.88 g, 0.025 mol) in 50 mL of methanol the solution of **8a** (5.9 g, 0.019 mol) in 50 mL of methanol was added dropwise. The mixture was refluxed for 24 hours. After that it was cooled to room temperature, then the excess of NaCl solution in water was added to remove the rest of silver. The 10 % $NaHCO_3$ solution was then added until the mixture is no more acidic. The precipitation was filtered away and carefully washed with ether. Then the solvent was removed from the filtrate *in vacuo*, the residue was extracted with ether 3 times, organic layers were united and dried over $MgSO_4$, the solvent was evaporated. The residue was purified by flash chromatography on the silica gel (hexane followed by 5 % ether in hexane) to give **1a** (4.45 g, 91 %). Bright yellow oil, b.p. = 125 °C$^{0.2}$.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.74-1.81 (m, 1H, C6-Ha), 2.31-2.38 (m, 1H, C6-Hb), 2.69 (dd, 1H, J = 15.2, 8 Hz, C5-Ha), 2.93 (dd, 1H, J = 15.1, 8 Hz, C5-Hb), 3.47 (s, 3H, OCH_3), 4.00 (m, 1H, C7-H), 7.07 (s, 1H, C2-H), 7.12-7.20 (m, 4H, Ar). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 28.8 (CH_2), 29.6 (CH_2), 57.0 (CH_3), 83.0 (CH), 125.9 (CH), 127.7 (C), 127.9 (CH), 128.8 (CH), 131.6 (CH), 133.3 (C), 135.1 (CH), 141.9 (C). Mass-spectrum (EI) *m/z* (% rel. intensity) 254 M^+ (16, ^{81}Br), 252 M^+ (18, ^{79}Br), 222 M^+ - MeOH (31, ^{81}Br), 220 M^+ - MeOH (34, ^{79}Br), 173 M^+ - Br (94), 141 M^+ - Br - MeOH (100), 128 (31), 115 (42). IR (neat, cm^{-1}) 2930(s), 2822 (m), 1624 (w), 1448 (m). Anal. calcd for $C_{12}H_{13}BrO$: C, 56.92; H, 5.14. Found: C, 56.89; H, 5.27.

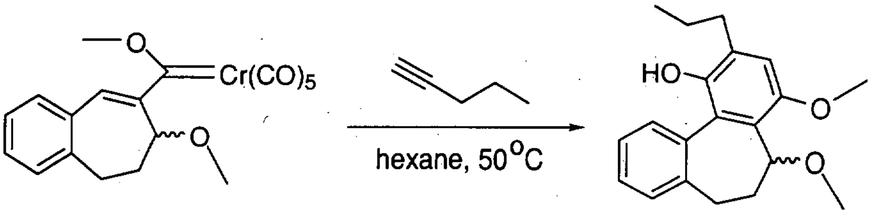
(7-Methoxy-3,4-benzo-1,3-cycloheptadienyl)methoxymethylene chromium pentacarbonyl complex (2a).



To the stirred solution of **1a** (0.5 g, 2 mmol) in 20 mL of ether at –78 °C 1.5 M t-BuLi (2.67 mL, 4 mmol) was added dropwise. The solution was stirred 15 min at –78 °C and then transferred via cannula to the stirred at 0 °C suspension of $Cr(CO)_6$ (0.44 g, 2 mmol) in 20 mL of ether. The mixture was stirred 0.5 hours at 0 °C and then 1.5 hours at room temperature. Carbonyl was gradually dissolved, yellow precipitation appeared. After that ether was removed *in vacuo*, the residue was dissolved in 50 mL of CH_2Cl_2 which was pre-deoxygenated with Ar. MeOTf (1.52 g, 10 mmol) was added to the solution and the mixture was stirred 1.5 hours. Then it was quenched with 10 % $NaHCO_3$ solution, organic layer was separated, aqueous layer was extracted twice with ether. Organic layers were united, solvent was removed *in vacuo*. The red residue was dissolved in hexane and purified by flash chromatography on silica gel (5 % ether in hexane) to give the carbene complex **2a** as red oil (0.54 g, 66 %). Attempts to characterize the product by NMR failed due to the fast formation of paramagnetic compounds in NMR tube. But upon warming at 60 °C under vacuum the complex was completely transformed to its tetracarbonyl MeO-chelated derivative, which is crystalline and more appropriate for characterization. For tetracarbonyl chelate complex (dark-red):

^{1}H-NMR (400 MHz, C_6D_6) δ 1.80-1.84 (m, 1H), 1.93-1.96 (m, 1H), 1.96-2.06 (m, 1H), 2.27-2.35 (m, 1H), 2.61 (s, 3H), 3.43-3.50 (m, 1H), 4.49 (s, 3H), 6.82 (s, 2H), 6.95 (s, 3H). ^{13}C-NMR (400 MHz, CD_2Cl_2) δ 30.0, 37.5, 66.4, 68.1, 85.7, 118.2, 127.0, 129.3, 129.8, 132.2, 136.4, 141.2, 145.6, 217.1, 217.2, 231.2, 232.9, 338.0. IR (CH_2Cl_2, cm^{-1}) 2014 (s, CO), 1915 (vs, CO), 1842 (s, CO). Mass-spectrum (EI) *m/z* (% rel. intensity) 380 M^+ (17), 352 M^+ - CO (30), 324 M^+ - 2CO (18), 296 M^+ - 3CO (27), 268 M^+ - 4CO (21), 182 (53), 180 (62), 141 (66), 115 (31), 52 Cr^+ (100). HRMS (EI) calcd for $C_{18}H_{16}CrO_6$ 380.0352, found 380.0349.

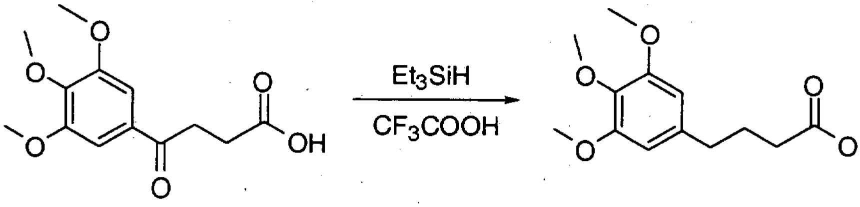
4,5-Dimethoxy-2-propyl-6,7-dihydro-5*H*-dibenzo[a,c]cyclohepten-1-ol (3a).



A solution of **2a** (0.6 g, 1.47 mmol) and 1-pentyne (0.51 g, 4.41 mmol) in 10 mL of hexane was deoxygenated by the freeze-pump-thaw method (-196 °C / 25 °C, 4 cycles). The flask was filled with Ar and the solution was heated for 24 hours at 50 °C. The red solution gradually changed to a brown mixture. Then 10 mL of THF was added and the reaction mixture was stirred in the open flask 12 hours. The solvent was removed *in vacuo* and the crude product was purified by flash chromatography on silica gel (10 % ether in hexane) to give the light-yellow oil. The oil solidified to give yellowish solid, which was identified as phenol product **3a** (0.3 g, 65 %). M.p. 88.8 - 89.4 °C (ether/hexane).

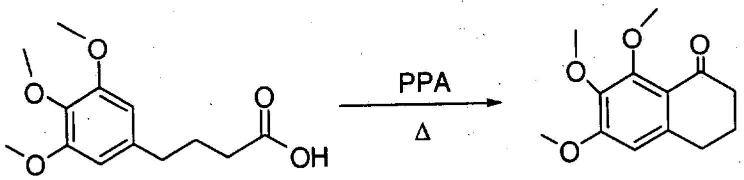
^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.01 (t, 3H, J = 7.3 Hz, $C\underline{H}_3CH_2CH_2$), 1.70 (m, 2H, $CH_3C\underline{H}_2CH_2$), 2.29-2.31 (m, 2H, C6-H_2), 2.45-2.50 (m, 1H, C7-Ha), 2.54-2.61 (m, 1H, C7-Hb), 2.63-2.68 (m, 2H, $CH_3CH_2C\underline{H}_2$), 2.74 (s, 3H, C5-OCH_3), 3.80 (s, 3H, C4-OCH_3), 5.06 (dd, 1H, J = 5.0, 1.9 Hz, C5-H), 5.35 (s, 1H, OH), 6.74 (s, 1H, C3-H), 7.27-7.29 (m, 3H, Ar), 7.35-7.37 (m, 1H, Ar). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.1, 22.9, 30.1, 32.9, 39.4, 55.0, 56.8, 73.0, 113.1, 124.3, 125.2, 126.5, 126.6, 127.9, 129.0, 129.3, 135.6, 142.0, 144.2, 150.7. IR (CH_2Cl_2, cm^{-1}) 3544 (s, OH). Mass-spectrum (EI) *m/z* (% rel. intensity) 312 M^+ (100), 281 M^+ - MeO (39), 280 M^+ - MeOH (25), 237 (35), 165 (33), 114 (20). HRMS (EI) calcd for $C_{20}H_{24}O_3$ 312.1725, found 312.1730. Anal. calcd for $C_{20}H_{24}O_3$: C, 76.92; H, 7.69. Found: C, 77.07; H, 7.67.

4-(3,4,5-Trimethoxyphenyl)butanoic acid.



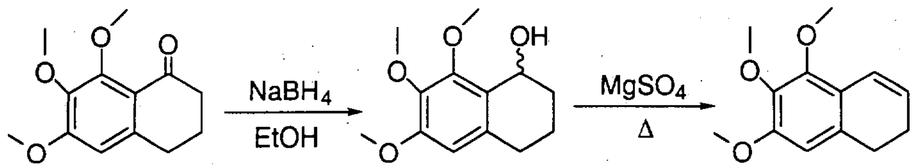
4-(3,4,5-Trimethoxyphenyl)butanoic acid was prepared by the procedure which was used earlier in the preparation of 4-(3,4-dimethoxyphenyl)butanoic acid[20a].
To the solution of 3-(3,4,5-trimethoxybenzoyl)propionic acid[19] (130 g, 0.48 mol) in 325 mL of trifluoroacetic acid Et_3SiH (165 g, 1.39 mol) was added dropwise. The solution was stirred vigorously at room temperature for 12 hours, then the solvent was removed *in vacuo*, the resulting oil was dissolved in ether and washed with water twice. The product was then extracted with 300 mL of 10 % NaOH solution, aqueous layer was separated, acidified with 10 % HCl solution and extracted with ether. Ether layer was dried over $MgSO_4$, the solvent was removed to give slightly brown solid, identified as 4-(3,4,5-trimethoxyphenyl)butanoic acid (103 g, 80 %). Colorless crystals (ether/hexane). M.p. 82.5 - 83.5 °C (reported[19] 83 – 84 °C).
^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.97 (m, 2H), 2.40 (t, 2H, J = 7.5 Hz), 2.62 (t, 2H, J = 7.5 Hz), 3.82 (s, 3H), 3.85 (s, 6H), 6.40 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 26.2, 33.2, 35.4, 56.0, 60.8, 105.2, 136.1, 137.0, 153.1, 179.6.

6,7,8-Trimethoxy-3,4-dihydro-2*H*-naphtalen-1-one (9).



9 was prepared using the standard polyphosphoric acid cyclization procedure[20b].
4-(3,4,5-Trimethoxyphenyl)butanoic acid (6.5 g, 26 mmol) was thoroughly mixed with polyhosphoric acid (65 g). The viscous mixture was warmed up in a beaker and stirred with thermometer at 60 – 70 °C for 15 minutes. The mixture became less viscous and yellow, then turned brown. After that it was stirred for additional 15 minutes at 70 – 80 °C. Then it was poured into 100 mL of ice water and dissolved with stirring. The reaction beaker was washed with additional portion of ice water. The crude product was isolated by suction, filtrate was extracted with dichloromethane. Organic layer was isolated and the crude product was dissolved in it. The resulting solution was washed with 100 mL of 1 % NaOH solution. Organic layer was separated, aqueous layer was extracted once with dichloromethane and once with ether. Organic layers were united and dried over $MgSO_4$, solvent was removed *in vacuo* to give **9** as bright yellow crystals (5.32 g, 88 %) which was pure by NMR. The product can be recrystallized from ether/hexane to give colorless crystals. M.p. 124.5 – 125 °C (reported[19] 125 °C).
^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.05 (m, 2H), 2.58 (t, 2H, J = 6.5 Hz), 2.88 (t, 2H, J = 6.5 Hz), 3.85 (s, 3H), 3.89 (s, 3H), 3.91 (s, 3H), 6.54 (s, 1H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 23.0, 31.0, 40.4, 55.9, 61.1, 61.4, 106.7, 120.6, 141.4, 142.5, 155.1, 156.9, 196.1.

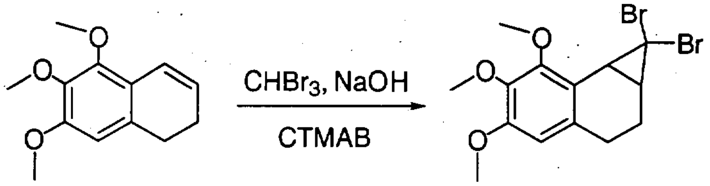
5,6,7-Trimethoxy-1,2-dihydronaphthalene (10).



To the stirred suspension of **9** (9.25 g, 39 mmol) in 100 mL of 95 % ethanol $NaBH_4$ (0.76 g, 20 mmol) was added in small portions. After the addition is complete the mixture was stirred 30 minutes at room temperature and refluxed for 40 minutes. The progress of the reaction was monitored by TLC (40 % EtOAc in hexane). Then the solution was cooled to room temperature and water (100 mL) was added. Ethanol was removed *in vacuo*, the product was extracted with dichloromethane. Organic layer was dried over $MgSO_4$, the solvent was removed *in vacuo*. The residue was dissolved in 125 mL of dry benzene and refluxed for 1.5 hours with 20 g of anhydrous $MgSO_4$. Then the mixture was cooled to room temperature, filtered. The precipitate was washed several times with ether. Filtrate was evaporated and the residue was eluted through the short column with silica gel (15 % ether in hexane). Solvent was removed *in vacuo* to give pure **10** as a colorless oil (7.66 g, 89 %). The oil was solidified slowly at room temperature to give colorless crystals. M.p. 28.5 – 29 °C, B.p. 105 $°C^{0.01}$.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.23-2.28 (m, 2H, C2-H_2), 2.69 (t, 2H, J = 8.3 Hz, C1-H_2), 3.84 (s, 3H, OCH_3), 3.85 (s, 6H, $2OCH_3$), 5.91-5.95 (m, 1H, C3-H), 6.47 (s, 1H, C8-H), 6.69 (d, 1H, J = 9.8 Hz, C4-H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 22.8 (CH_2), 27.7 (CH_2), 55.8 (CH_3), 60.8 (CH_3), 61.1 (CH_3), 107.2 (CH), 120.6 (C), 121.3 (CH), 125.9 (CH), 131.4 (C), 140.2 (C), 149.2 (C), 151.8 (C). IR (neat, cm^{-1}) 2936 (s), 2928 (m), 1580 (m). Mass-spectrum (EI) *m/z* (% rel. intensity) 220 M^+ (100), 205 M^+ - Me (34), 189 M^+ - MeO (17), 177 (16), 145 (16), 115 (17), 91 (29). HRMS (EI) calcd for $C_{13}H_{16}O_3$ 220.1099, found 220.1100. Anal. calcd for $C_{13}H_{16}O_3$: C, 70.91; H, 7.27. Found: C, 71.13; H, 7.16.

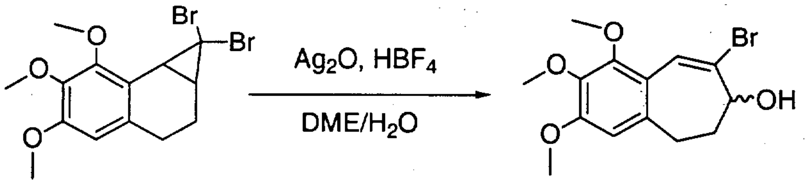
1,1-Dibromo-5,6,7-trimethoxy-1a,2,3,7b-tetrahydro-1*H*-cyclopropa[a]naphthalene (8b).



To the stirred solution of **10** (45.7 g, 0.21 mol), bromoform (212.52 g, 0.84 mol, 75.4 mL) and cetyltrimethylammonium chloride (CTMAC) (2.69 g, 8.4 mmol) in 150 mL of hexane 50 % solution of NaOH in water (33.6 g, 0.42 mol) was added dropwise. The mixture was stirred at room temperature for 2 hours, then another portion of 50 % NaOH (33.6 g, 0.42 mol) was added dropwise. The mixture was then refluxed for 2 hours. The last portion of 50 % NaOH (33.6 g, 0.42 mol) was then added and the mixture was refluxed for 5 hours until only excess of bromoform and dibromocyclopropane product are seen by GC. The mixture was quenched with the excess of 10 % HCl, hexane was removed *in vacuo*. Water was added to the residue and the dark brown organic layer was separated and dried *in vacuo*. Aqueous layer was carefully (emulsion formation) extracted with 50 mL of CH_2Cl_2, and then extracted with two 50 mL portions of ether. Organic layers were united, dried over $MgSO_4$ and added to the previously separated dark brown organic layer. The solvent was removed *in vacuo*, bromoform was distilled from the residue under the reduced pressure, the resulting mixture was boiled 0.5 hours with 200 mL of ether, then cooled to room temperature, the crude product was collected by suction and then recrystallized from ethanol, giving 28.36 g of the cyclopropane. Etheral solution from the previous step and ethanolic solution from the recrystallization were combined, the solvent was removed. The residue was filtered through the 30 cm high and 4.5 cm wide column with silica gel. Bromoform was first eluted with hexane, then the product was eluted with 5 % EtOAc in hexane. After the solvent removal the product was dissolved in minimal amount of CH_2Cl_2, hexane was added to the solution. During the slow removal of CH_2Cl_2 *in vacuo* the precipitate was formed, which was collected by suction and washed twice with pentane, giving 17 g of the cyclopropane. Filtrate was collected and checked by GC. It was found to contain approximately 1.75:1 mixture of the cyclopropane product and the starting material as well as the number of sideproducts and can be further purified or used crude in the next step. The combined yield of **8b** 45.36 g (55 %). Colorless crystals (ether/hexane). M.p. 89.5 – 90 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.78-1.87 (m, 1H, C2-Ha), 2.28 (ddd, 1H, J = 10.4, 8.8, 4.8 Hz, C1a-H), 2.36-2.45 (m, 1H, C2-Hb), 2.54 (ddd, 1H, J = 15.6, 6.0, 4.2 Hz, C3-Ha), 2.63–2.71 (m, 1H, C3-Hb), 2.81 (d, 1H, J = 10.4 Hz, C7b-H), 3.83(s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 4.05 (s, 3H, OCH_3), 6.39 (s, 1H, C4-H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 22.0 (CH_2), 27.0 (CH_2), 28.0 (CH), 28.8 (CH), 40.4 (C), 55.9 (CH_3), 60.9 (CH_3), 61.1 (CH_3), 107.0 (CH), 118.7 (C), 132.8 (C), 140.3 (C), 152.7 (C), 153.2 (C). IR (CH_2Cl_2, cm^{-1}) 2943 (m), 1603 (m). Mass-spectrum (EI) *m/z* (% rel. intensity) 394 M^+ (4, ^{81}Br), 392 M^+ (8, ^{81}Br, ^{79}Br), 390 M^+ (5, ^{79}Br), 361 (15), 313 M^+-Br (97, ^{81}Br), 311 M^+-Br (100, ^{79}Br), 232 M^+-2Br (51), 217 (54), 201 (47), 131 (29), 115 (42), 77 (32). Anal. calcd for $C_{14}H_{16}Br_2O_3$: C, 42.86; H, 4.08. Found: C, 42.91; H, 4.17.

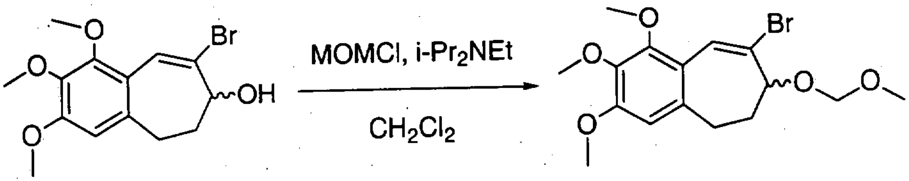
8-Bromo-1,2,3-trimethoxy-6,7-dihydro-5*H*-benzocyclohepten-7-ol (1c).



The solution of $AgBF_4$ was prepared *in situ* by the addition of solid Ag_2O (1.4 g, 6.0 mmol) to the 50 % solution of HBF_4 (2.46 g, 14 mmol). The solution was then diluted with 20 mL of water and added to the solution of **8b** (4 g, 10.2 mmol) in 80 mL of 1,2-dimethoxyethane. The resulting solution was stirred for 36 hours at 80 °C. After that the mixture was cooled to room temperature and quenched with the excess of the 10 % aqueous $NaHCO_3$ solution until the mixture is no longer acidic. The precipitation was then filtered away and carefully washed with ether. The solvent was removed from the filtrate *in vacuo*, 100 mL of water was added to the residue and the crude product was extracted with ether. Ether layer was dried over $MgSO_4$, concentrated *in vacuo*. The crude product was purified by flash chromatography (silica gel, 10 % EtOAc in hexane,

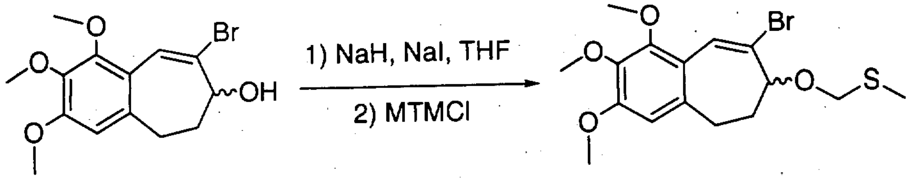
followed by 33 %), giving the starting material **8b** (0.551 g, 14 %) and the target **1c** (2.768 g, 82.5% (96%[a])). Colorless crystals. M.p. 112.5 – 113 °C.
^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.85-1.95 (m, 1H, C6-Ha), 2.21-2.32 (m, 1H, C6-Hb), 2.60 (br.s, 1H, OH), 2.67 (dd, 1H, J = 15, 8.25 Hz, C5-Ha), 2.88 (dd, 1H, J = 15, 10.5 Hz, C5-Hb), 3.84 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 3.88 (s, 3H, OCH_3), 4.49 (t, 1H, J = 4.35 Hz, C7-H), 6.48 (s, 1H, C4-H), 7.34 (s, 1H, C9-H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 29.5 (CH_2), 33.1 (CH_2), 55.9 (CH_3), 60.9 (CH_3), 61.5 (CH_3), 74.5 (CH), 107.8 (CH), 119.7 (C), 127.1 (CH), 129.6 (C), 139.1 (C), 140.0 (C), 152.2 (C), 153.0 (C). IR (CH_2Cl_2, cm^{-1}) 3591 (s), 2941 (s), 1595 (m), 1435 (s), 1273 (s). Mass-spectrum (EI) *m/z* (% rel. intensity) 330 M^+ (70, ^{81}Br), 328 M^+ (74, ^{79}Br), 249 M^+-Br (100), 231 M^+-Br-H_2O (28), 191 (23), 173 (14), 91 (14). HRMS (EI) calcd for $C_{14}H_{17}BrO_4$ 328.0310, found 328.0317. Anal. calcd for $C_{14}H_{17}BrO_4$: C, 51.06; H, 5.17. Found C, 51.09; H, 5.47.

8-Bromo-7-methoxymethylene-1,2,3-trimethoxy-6,7-dihydro-5*H*-benzocycloheptene (1d).



To the stirred under N_2 solution of **1c** (0.41 g, 1.25 mmol) in 10 mL of dry CH_2Cl_2 i-Pr_2NEt (0.884 g, 6.85 mmol) was added at 0 °C, followed by the dropwise addition of MOMCl (0.502 g, 6.23 mmol). The mixture was stirred at 0 °C 10 minutes, then refluxed for 38 hours. After that the CH_2Cl_2 solution was extracted with water, aqueous layer was extracted once with ether. Organic layers were united and dried over $MgSO_4$. The solvent was removed *in vacuo* and the residue was filtered through the short chromatography column (silica gel, 10 % EtOAc in hexane), giving after the solvent removal **1d** (0.452 g, 97 %). Colorless crystals. M.p. 68 - 68.5 °C.
^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.87-1.93 (m, 1H, C6-Ha), 2.27-2.33 (m, 1H, C6-Hb), 2.64 (dd, 1H, J = 15.3, 8.5 Hz, C5-Ha), 2.92 (dd, 1H, J = 15.3, 10.5 Hz, C5-Hb), 3.49 (s, 3H, $OCH_2OC\underline{H}_3$), 3.84 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 4.38 (t, 1H, J = 4.5 Hz, C7-H), 4.82 (AB, 2H, $OC\underline{H}_2OCH_3$), 6.47 (s, 1H, C4-H), 7.40 (s, 1H, C9-H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 29.7 (CH_2), 32.7 (CH_2), 56.1 (CH_3), 56.3 (CH_3), 61.1 (CH_3), 61.7 (CH_3), 80.2 (CH), 96.4 (CH_2), 108.1 (CH), 120.3 (C), 126.5 (C), 128.7 (CH), 139.1 (C), 140.3 (C), 152.5 (C), 153.2 (C). IR (CH_2Cl_2, cm^{-1}) 2988 (s), 1595 (m), 1452 (s), 1261 (s). Mass-spectrum (EI) *m/z* (% rel. intensity) 374 M^+ (47, ^{81}Br), 372 M^+ (43, ^{79}Br), 312 M^+-CH_3OCH_2OH (33, ^{81}Br), 310 M^+-CH_3OCH_2OH (35, ^{79}Br), 231 M^+-CH_3OCH_2OH-Br (100), 201 (23), 115 (15). Anal. calcd for $C_{16}H_{21}BrO_5$: C, 51.47; H, 5.63. Found C, 51.45; H, 5.60.

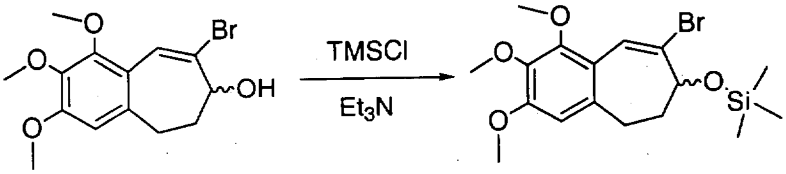
8-Bromo-7-methylthiomethylene-1,2,3-trimethoxy-6,7-dihydro-5*H*-benzocycloheptene (1e).



NaH (50 % suspension in mineral oil) (0.208 g, 4.33 mmol) was washed with pentane, dried with N_2 and suspended in 3 mL of absolute THF. NaI (0.325 g, 2.16 mmol) was then added in solid, the stirred suspension was cooled to 0 °C and the solution of **1c** (0.712 g, 2.16 mmol) in 2.5 mL of THF was added dropwise under N_2. The mixture was stirred for 15 minutes, then MTMCl (0.362 g, 3.75 mmol) was slowly added to it. The mixture was warmed to room temperature, first stirred for 17 hours and then refluxed for 4 hours. After that it was cooled to room temperature and quenched by the addition of the excess of saturated $NaHCO_3$ solution. The product was extracted 2 times with ether, ether layers were united and dried over $CaCl_2$, solvent was removed. The crude product was purified by flash chromatography (silica gel, 10 % EtOAc in hexane), giving after the solvent removal *in vacuo* the target **1e** (0.507 g, 60 %). Yellowish crystals. M.p. 83.5 – 84 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.82-1.94 (m, 1H, C6-Ha), 2.25-2.35 (m, 1H, C6-Hb), 2.26 (s, 3H, $OCH_2SC\underline{H}_3$), 2.63 (dd, 1H, J = 15.0, 7.7 Hz, C5-Ha), 2.88 (dd, 1H, J = 15.0, 10.4 Hz, C5-Hb), 3.83 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 4.50 (t, 1H, J = 4.6 Hz, C7-H), 4.79 (AB, 2H, $OC\underline{H}_2SCH_3$), 6.47 (s, 1H, C4-H), 7.40 (s, 1H, C9-H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 14.2 (CH_3), 29.4 (CH_2), 31.4 (CH_2), 55.8 (CH_3), 60.7 (CH_3), 61.3 (CH_3), 73.6 (CH_2), 78.6 (CH), 107.6 (CH), 120.0 (C), 125.9 (C), 128.5 (CH), 138.5 (C), 140.0 (C), 152.1 (C), 152.9 (C). IR (CH_2Cl_2, cm^{-1}) 3055 (s), 1595 (m), 1452 (s), 1267 (s). Mass-spectrum (EI) *m/z* (% rel. intensity) 311 (5), 309 M^+- Br (24), 279 (100), 232 (25), 231 (29), 217 (20), 201 (19), 61 $CH_3SCH_2^+$ (18). Anal. calcd for $C_{16}H_{21}O_4BrS$: C, 49.36; H, 5.40; S, 8.23. Found C, 49.31; H, 5.17; S, 8.34.

8-Bromo-7-trimethylsiloxy-1,2,3-trimethoxy-6,7-dihydro-5*H*-benzocycloheptene (1f).

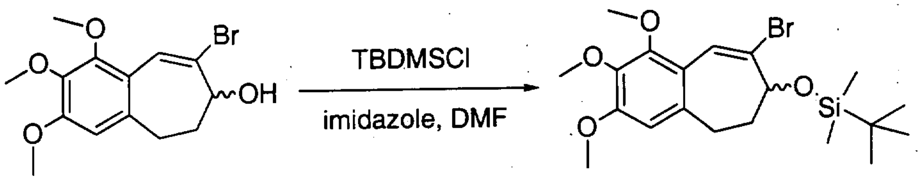


To the stirred under N_2 solution of **1c** (0.8 g, 2.43 mmol) and Et_3N (1.47 g, 14.6 mmol) in 10 mL of dry ether TMSCl was added dropwise at room temperature. The mixture was stirred 16 hours, then diluted with water, extracted with ether twice. Organic layers were united and dried over $CaCl_2$. The solvent was removed and the crude product was purified by flash chromatography (silica gel, 5 % EtOAc in hexane, 3-4 drops of Et_3N per every 100 mL of the solvent) to give **1f** as a yellowish oil (0.681 g, 70 %).

^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.22 (s, 9H, $Si(CH_3)_3$), 1.82-1.94 (m, 1H, C6-Ha), 2.05-2.17 (m, 1H, C6-Hb), 2.60 (dd, 1H, J = 15.3, 8.2 Hz, C5-Ha), 2.96 (dd, 1H, J = 15.3, 10.6

Hz, C5-Hb), 3.83 (s, 3H, OCH$_3$), 3.85 (s, 6H, 2OCH$_3$), 4.50 (dd, 1H, J = 5.3, 4.0 Hz, C7-H), 6.46 (s, 1H, C4-H), 7.33 (s, 1H, C9-H). ^{13}C-NMR (75 MHz, CDCl$_3$) δ 0.5 (CH$_3$), 29.2 (CH$_2$), 34.3 (CH$_2$), 55.8 (CH$_3$), 60.8 (CH$_3$), 61.4 (CH$_3$), 75.1 (CH), 107.9 (CH), 120.2 (C), 126.9 (CH), 129.3 (C), 138.9 (C), 140.1 (C), 152.2 (C), 152.8 (C). IR (CH$_2$Cl$_2$, cm^{-1}) 2855 (s), 1740 (m), 1462 (m), 1242 (s). Mass-spectrum (EI) *m/z* (% rel. intensity) 402 M$^+$ (29, ^{81}Br), 400 M$^+$ (33, ^{79}Br), 321 (71), 312 M$^+$-(CH$_3$)$_3$SiOH (21, ^{81}Br), 310 M$^+$-(CH$_3$)$_3$SiOH (23, ^{79}Br), 231 (100), 139 (10), 73 (21). HRMS (EI) calcd for C$_{17}$H$_{25}$O$_4$BrSi 400.0706, found 400.0709.

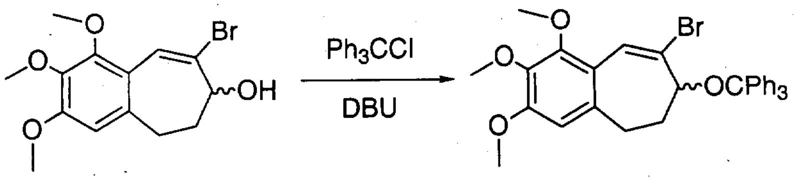
8-Bromo-7-t-butyldimethylsiloxy-1,2,3-trimethoxy-6,7-dihydro-5*H*-benzocycloheptene (1g).



To the solution of **1c** (1.2 g, 3.65 mmol) and imidazole (1.02 g, 15 mmol) in 2 mL of DMF TBDMSCl (1.1 g, 7.3 mmol) was added in solid. The mixture was stirred 16 hours at room temperature under N$_2$. Then it was diluted with ether and extracted with water 4 times. Organic layer was dried over CaCl$_2$. The solvent was removed and the residue was filtered through the short chromatography column (silica gel, 5 % EtOAc in hexane). After the solvent was removed *in vacuo* **1g** was obtained as a yellowish oil (1.601 g, 99 %).

^{1}H-NMR (300 MHz, CDCl$_3$) δ 0.14 (s, 3H, CH$_3$), 0.22 (s, 3H, CH$_3$), 0.94 (s, 9H, C(CH$_3$)$_3$), 1.8-1.91 (m, 1H, C6-Ha), 2.08-2.20 (m, 1H, C6-Hb), 2.59 (dd, 1H, J = 15.1, 7.9 Hz, C5-Ha), 3.00 (dd, 1H, J = 15.1, 10.7 Hz, C5-Hb), 3.83 (s, 3H, OCH$_3$), 3.85 (s, 3H, OCH$_3$), 3.86 (s, 3H, OCH$_3$), 4.48 (dd, 1H, J = 4.9, 3.7 Hz, C7-H), 6.47 (s, 1H, C4-H), 7.32 (s, 1H, C9-H). ^{13}C-NMR (75 MHz, CDCl$_3$) δ -4.6 (CH$_3$), -4.3 (CH$_3$), 18.2 (C), 25.9 (CH$_3$), 29.1 (CH$_2$), 35.2 (CH$_2$), 55.9 (CH$_3$), 60.8 (CH$_3$), 61.4 (CH$_3$), 75.1 (CH), 107.9 (CH), 120.3 (C), 126.7 (CH), 129.6 (C), 139.1 (C), 140.1 (C), 152.2 (C), 152.8 (C). IR (CH$_2$Cl$_2$, cm^{-1}) 2957 (s), 1595 (m), 1406 (s), 1267 (s). Mass-spectrum (EI) *m/z* (% rel. intensity) 444 M$^+$ (5, ^{81}Br), 442 M$^+$ (4, ^{79}Br), 387 M$^+$-(CH$_3$)$_3$C (100, ^{81}Br), 385 M$^+$-(CH$_3$)$_3$C (86, ^{79}Br), 357 M$^+$-(CH$_3$)$_3$C-2CH$_3$ (5, ^{81}Br), 355 M$^+$-(CH$_3$)$_3$C-2CH$_3$ (6, ^{79}Br), 313 M$^+$-OSiMe$_2$t-Bu (9, ^{81}Br), 311 M$^+$-OSiMe$_2$t-Bu (10, ^{79}Br), 231 (28), 139 (31), 73 (41). HRMS (FAB$^+$) calcd for C$_{20}$H$_{31}$O$_4$BrSi 442.1175, found 442.1165.

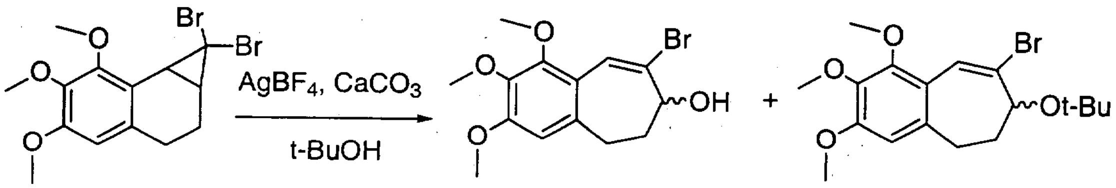
8-Bromo-1,2,3-trimethoxy-7-triphenylmethoxy-6,7-dihydro-5*H*-benzocycloheptene (1h).



To the stirred under N_2 solution of **1c** (0.5 g, 1.52 mmol) and Ph_3CCl (1.25 g, 4.5 mmol) in 5 mL of dry CH_2Cl_2 DBU (0.798 g, 5.25 mmol) was added dropwise. The solution immediately darkened. The stirring was continued at room temperature for 8 days, then the mixture was added to 25 mL of water, extracted with two 25 mL portions of CH_2Cl_2. Organic layers were united, dried over $CaCl_2$, the solvent was removed *in vacuo*. The residue was subjected to flash chromatography (silica gel, 10 % EtOAc in hexane, followed by 33 % EtOAc in hexane). The starting **1c** (0.277 g, 55 %) and the expected **1h** (0.312 g, 36 % (81 %[a])) were isolated after the solvent removal. Colorless crystals. M.p. 68.5 - 69.5 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.32-1.46 (m, 1H, C6-Ha), 1.87-2.00 (m, 1H, C6-Hb), 2.33 (ddd, 1H, J = 14.2, 5.7, 4.6 Hz, C5-Ha), 2.74 (ddd, 1H, J = 14.2, 10.4, 4.7 Hz, C5-Hb), 3.73 (s, 3H, OCH_3), 3.81 (s, 6H, $2OCH_3$), 4.09 (dd, 1H, J = 7.2, 5.0 Hz, C7-H), 6.38 (s, 1H, C4-H), 7.12 (s, 1H, C9-H), 7.16-7.29 (m, 9H, Ar), 7.48 (dd, 6H, J = 8.2, 1.9 Hz, Ar). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 30.3 (CH_2), 37.0 (CH_2), 55.9 (CH_3), 60.9 (CH_3), 61.2 (CH_3), 74.8 (CH), 88.1 (C), 107.8 (CH), 122.1 (C), 126.9 (CH), 127.5 (CH), 128.6 (CH), 129.2 (CH), 137.7 (C), 140.1 (C), 144.6 (C), 146.2 (C), 151.2 (C), 152.7 (C). IR (CH_2Cl_2, cm^{-1}) 3055 (s), 1267 (s). Mass-spectrum (EI) *m/z* (% rel. intensity) 572 M^+ (2, ^{81}Br), 570 M^+ (2, ^{79}Br), 329 M^+-Ph_3C (3, ^{81}Br), 327 M^+-Ph_3C (3, ^{79}Br), 299 (6), 243 Ph_3C^+ (100), 165 (81), 105 (30), 77 (10). Anal. calcd for $C_{33}H_{31}O_4Br$: C, 69.35; H, 5.43. Found C, 69.11; H, 5.54.

8-Bromo-7-t-butoxy-1,2,3-trimethoxy-6,7-dihydro-5*H*-benzocycloheptene (1b).



To the solution of **8b** (1 g, 2.55 mmol) and $AgBF_4$ (0.53 g, 2.7 mmol) in 25 mL t-BuOH $CaCO_3$ (2.5 g, 25 mmol) was added and the mixture was stirred for 36 hours at 80 °C. After that the mixture was cooled to room temperature and quenched with the excess of the 10 % aqueous $NaHCO_3$ solution until the mixture is no longer acidic. The precipitate was then filtered away and carefully washed with ether. The solvent was removed from the filtrate *in vacuo*, 50 ml of water was added to the residue and the crude product was extracted with ether. Ether layer was dried over $MgSO_4$, concentrated *in vacuo*. The product was purified by flash chromatography (silica gel, 10 % EtOAc in hexane), giving after the solvent removal **1c** (0.206 g, 25 %) and the target **1b**[1] (0.601 g, 61 % (66 %[a])). Colorless crystals. M.p. 66.8-67.3 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.27 (s, 9H, $C(CH_3)_3$), 1.93-2.00 (m, 1H, C6-Ha), 2.17-2.25 (m, 1H, C6-Hb), 2.55 (ddd, 1H, J = 14.7, 6.0, 3.0 Hz, C5-Ha), 2.91 (ddd, 1H, J = 14.4, 11.1, 3.0 Hz, C5-Hb), 3.85 (s, 6H, $2OCH_3$), 3.87 (s, 3H, OCH_3), 4.28 (dd, 1H, J = 7.2, 4.5 Hz, C7-H), 6.48 (s, 1H, C4-H), 7.27 (s, 1H, C9-H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ

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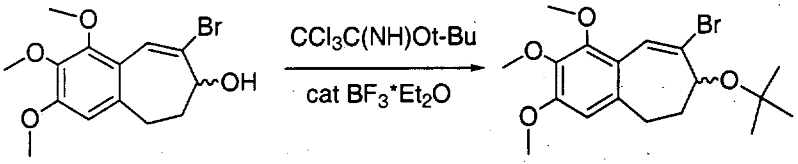
[1] Small amounts (3-5%) of the elimination product are sometimes formed and co-elute with **1b.**

28.8 (CH_3), 29.6 (CH_2), 36.9 (CH_2), 55.9 (CH_3), 60.9 (CH_3), 61.3 (CH_3), 73.0 (CH), 75.0 (C), 108.0 (CH), 121.2 (C), 126.9 (CH), 129.6 (C), 138.3 (C), 140.1 (C), 151.7 (C), 152.7 (C). IR (CH_2Cl_2, cm^{-1}) 2980 (s), 1595 (m), 1464 (s), 1271 (s). Mass-spectrum (EI) *m/z* (% rel. intensity) 386 M$^+$ (28, ^{81}Br), 384 M$^+$ (27, ^{79}Br), 312 M$^+$-t-BuOH (49, ^{81}Br), 310 M$^+$-t-BuOH (47, ^{79}Br), 249 (60), 231 M$^+$-Br-t-BuOH (100), 217 (17), 181 (24), 57 (31). Anal. calcd for $C_{18}H_{25}BrO_4$: C, 56.10; H, 6.49. Found: C, 55.96; H, 6.75.

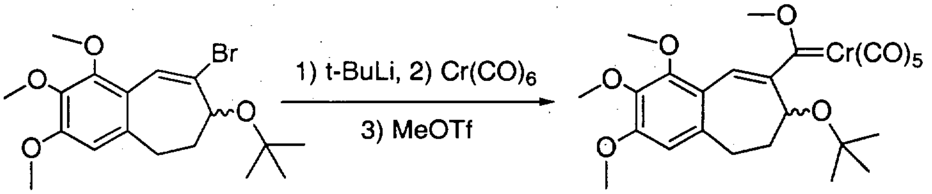
8-Bromo-7-t-butoxy-1,2,3-trimethoxy-6,7-dihydro-5*H*-benzocycloheptene (1b).



To the solution of **1c** (2.06 g, 6.26 mmol) in 6 mL of dry CH_2Cl_2 12 mL of distilled over NaH cyclohexane was added. Prepared as described[21] $CCl_3C(NH)Ot$-Bu (6.84 g, 31 mmol) was dissolved in this solution. 150 µL of BF_3*Et_2O was then added dropwise to the stirred solution under N_2. The mixture was stirred for 17 hours, then solid $NaHCO_3$ was added to it, the solvent was removed *in vacuo* and the product was filtered through the short plug of the silica gel (5 % ether in hexane), giving after the solvent removal 8-bromo-7-t-butoxy-1,2,3-trimethoxy-6,7-dihydro-5*H*-benzocycloheptene (0.771 g, 32 % (80 %[a])). The compound was identical with that prepared by the electrophilic ring opening reaction of **8 b** in t-butanol. The unreacted alcohol together with trichloroacetamide was washed from the silica gel with Et_2O, solvent was removed, the residue was dissolved in 60 mL of ethanol, NaOH (4 g, 0.1 mol) was added in solid. The mixture was refluxed 0.5 hours, then ethanol was removed, the residue was diluted with water, extracted with ether twice. Organic layers were united, dried over $MgSO_4$, volatiles were removed *in vacuo*, giving the recovered starting alcohol (1.228g, 60 %).

a) The yield of product based on the recovered starting material.

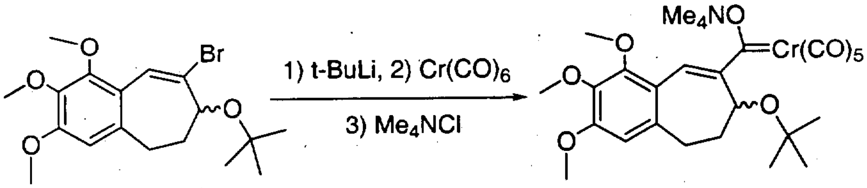
(7-t-Butoxy-1,2,3-trimethoxy-6,7-dihydro-5*H*-benzocyclohepten-8-yl)alkoxymethylene chromium pentacarbonyl complex (2b).



To the stirred at –78 °C solution of **1b** (0.738 g, 1.92 mmol) in 26 mL of absolute ether 1.6 M t-BuLi solution (2.4 mL, 3.83 mmol) was added dropwise under argon. The mixture was stirred at –78 °C for 15 minutes and then slowly (~5 minutes) transferred via cannula into the strred at 0 °C suspension of $Cr(CO)_6$ (0.422 g, 1.92 mmol) in 39 mL of absolute ether. The mixture was stirred 0.5 hours at 0 °C and 1.5 hours at room

temperature. Then ether was removed *in vacuo*, the residue dissolved in 50 mL of dry CH_2Cl_2[a] and methyl triflate (0.874 g, 5.75 mmol) was added to the solution, which was then stirred for 1 hour at room temperature. After that the red mixture was quenched with 25 mL of the 10 % aqueous $NaHCO_3$ solution, organic layer separated, aqueous layer extracted once with ether. Organic layers were united and dried over K_2CO_3. The solvent was removed *in vacuo* and the residue was subjected to the flash chromatography (15 % EtOAc in hexane). Orange-red pentacarbonyl complex **2b** was collected (0.559 g, 54 %), the small amount of dark-red tetracarbonyl chelate complex decomposed on the column. At room temperature either neat or in the solution the tetracarbonyl and pentacarbonyl complexes exist in equilibrium, therefore the approximate yield was determined from the mixture, which usually contains 5-15 % of tetracarbonyl complex. The mixture of pentacarbonyl and tetracarbonyl complexes is taken to the next step without further separation. Full characterization of the carbene complex is possible for the corresponding tetramethylammonium salt. For pentacarbonyl complex:
^{1}H-NMR (300 MHz, C_6D_6) δ 1.00 (s, 9H), 1.91-2.07 (m, 1H), 2.12-2.28 (m, 1H), 2.28-2.42 (m, 1H), 2.78-2.95 (m, 1H), 3.33 (s, 3H), 3.69 (s, 3H), 3.83 (s, 3H), 4.03 (s, 3H), 4.68 (br.s, 1H), 6.27 (s, 1H), 7.24 (br.s, 1H). IR (CH_2Cl_2, cm^{-1}) 2060 (m, CO), 1943 (vs, CO).

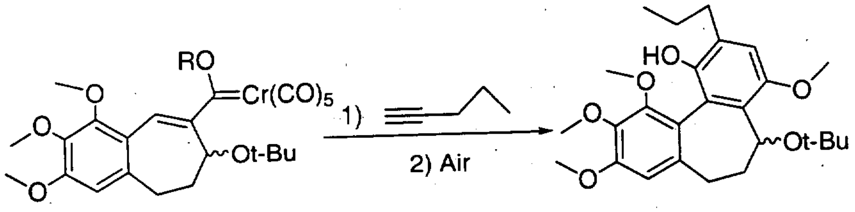
(7-t-Butoxy-1,2,3-trimethoxy-6,7-dihydro-5*H*-benzocyclohepten-8-yl)oxymethylene chromium pentacarbonyl complex, tetramethylammonium salt.



To the stirred at –78 °C solution of the corresponding bromide (0.137 g, 0.36 mmol) in 5 mL of absolute ether 1.7M t-BuLi solution (0.42 mL, 0.71 mmol) was added dropwise under argon. The mixture was stirred at –78 °C for 15 minutes and then slowly transferred via cannula into the stirred at 0 °C suspension of $Cr(CO)_6$ (0.078 g, 0.36 mmol) in 10 mL of absolute ether. The mixture was stirred 0.5 hours at 0 °C and 1.5 hours at room temperature. Then ether was removed *in vacuo*, the residue dissolved in water, filtered through the celite layer and extracted twice with hexane. Aqueous layer was separated and treated with the solution of Me_4NCl (0.153 g, 1.4 mmol) in 5 mL of water. The product was then carefully (emulsion) extracted with CH_2Cl_2 at least 5 times, until the aqueous layer is nearly colorless. CH_2Cl_2 layer was dried over K_2CO_3, solvent removed *in vacuo*. The residue amorphous yellow solid or sticky oil was pure tetramethylammonium salt of the corresponding chromium pentacarbonyl carbene complex (90 mg, 42 %).
^{1}H-NMR (300 MHz, Acetone-D6) δ 1.03 (s, 9H, $(CH_3)_3C$), 1.74-1.84 (m, 1H, C6-Ha), 2.11-2.22 (m, 1H, C6-Hb), 2.50 (ddd, 1H, J = 14.4, 9.3, 4.5 Hz, C5-Ha), 2.73 (ddd, 1H, J = 14.1, 7.5, 4.2 Hz, C5-Hb), 3.45 (br.s, 12H, $N(CH_3)_4$), 3.73 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 4.59 (t, 1H, J = 4.2 Hz, C7-H), 6.58 (s, 1H, C4-H), 7.35 (s,

1H, C9-H). ^{13}C-NMR (75 MHz, Acetone-D6) δ 29.1 (CH_3), 31.2 (CH_2), 40.0 (CH_2), 56.1 (CH_3), 56.2 (CH_3), 60.8 (CH_3), 61.5 (CH_3), 66.9 (CH), 73.5 (C), 107.3 (C), 109.1 (CH), 125.2 (C), 129.4 (CH), 139.2 (C), 141.2 (C), 152.7 (C), 160.3 (C), 224.6 (C), 229.1 (C), 288.3 (C). IR (CH_2Cl_2, cm^{-1}) 2031 (m, CO), 1906 (vs, CO). Mass-spectrum (FAB^-) *m/z* (% rel. intensity) 525 M^- (100), 497 M^--CO (23), 469 M^--2CO (15), 441 M^--3CO (27), 413 M^--4CO (15), 209 (35), 192 (33), 168 (25). HRMS (FAB^-) calcd for $C_{24}H_{25}O_{10}Cr$ 525.0853, found 525.0862.

7-t-Butoxy-11-hydroxy-1,2,3,8-tetramethoxy-10-propyl-5,6-dihydro-5H-dibenzo[a,c]cycloheptene (3b), isomers I and II.



To the solution of **2b** (0.72 g, 1.33 mmol) in 4 mL of dry benzene 1-pentyne (0.272 g, 4 mmol) was added and the resulting solution was deoxygenated by the freeze-pump-thaw method (-196 °C / 25 °C, 3 cycles). The flask was filled with Ar and the solution was heated for 24 hours at 55 – 58 °C. The red solution gradually changed to a dark mixture. After that the reaction mixture was opened to air and stirred in the open flask for 12 hours. The solvent was removed *in vacuo* and the crude product was diluted with 50 % EtOAc in hexane and filtered through the layer of silica gel. The crude product was purified by flash chromatography on silica gel (10 % EtOAc in hexane followed by 15 %) to give the diastereomeric phenols **3b**,I (0.19 g, 32 %) and **3b**,II (0.092 g, 16 %) as yellowish oils. Combined yield 48 %.

Diastereomer I (major).

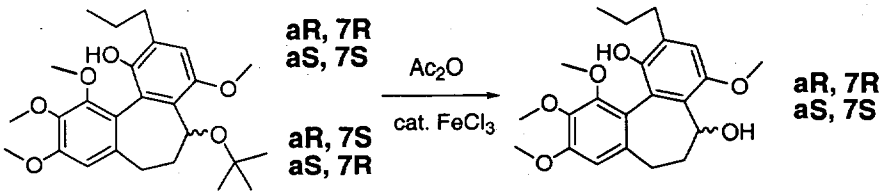
^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.87 (s, 9H, $C(CH_3)_3$), δ (t, 3H, J = 7.3 Hz, $CH_2CH_2C\underline{H}_3$), 1.62-1.74 (m, 2H, $CH_2C\underline{H}_2CH_3$), 2.10 (dt, 1H, J = 13.4, 6.0 Hz, C5-Ha), 2.26-2.43 (m, 3H, C5-Hb, C6-H_2), 2.65-2.76 (m, 2H, $C\underline{H}_2CH_2CH_3$), 3.71 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 3.88 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 5.26 (d, 1H, J = 5.6 Hz, C7-H), 6.62 (s, 1H, C4-H), 6.69 (s, 1H, OH), 6.72 (s, 1H, C9-H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 14.0 (CH_3), 23.4 (CH_2), 27.9 (CH_3), 31.1 (CH_2), 33.3 (CH_2), 42.5 (CH_2), 56.0 (CH_3), 56.3 (CH_3), 61.3 (CH_3), 61.5 (CH_3), 63.7 (CH), 73.2 (C), 108.8 (CH), 112.2 (CH), 124.2 (C), 125.4 (C), 129.6 (C), 130.9 (C), 138.2 (C), 140.1 (C), 145.4 (C), 148.4 (C), 148.9 (C), 152.0 (C). IR (mix. of diastereomers) (CH_2Cl_2, cm^{-1}) 3366 (s, OH), 1456 (m). Mass-spectrum (EI) *m/z* (% rel. intensity) 444 M^+ (89), 388 M^+-$(CH_3)_2CCH_2$ (53), 359 (20), 220 (17), 181 (100). HRMS (EI) calcd for $C_{26}H_{36}O_6$ 444.2512, found 444.2511.

Diastereomer II (minor).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.98 (t, 3H, J = 7.3 Hz, $CH_2CH_2C\underline{H}_3$), 1.01 (s, 9H, $C(CH_3)_3$), 1.62-1.73 (m, 2H, $CH_2C\underline{H}_2CH_3$), 2.00-2.10 (m, 1H, C6-Ha), 2.15-2.23 (m, 2H, C5-Ha, C6-Hb), 2.40 (dd, 1H, J = 12.3, 6.5 Hz, C5-Hb), 2.61-2.75 (m, 2H, $C\underline{H}_2CH_2CH_3$), 3.72 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 3.91 (s, 6H, 2OCH_3), 4.21 (dd, 1H, J = 11.4, 6.4 Hz, C7-H), 6.59 (s, 1H, OH), 6.65 (s, 1H, C4-H), 6.80 (s, 1H, C9-H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 14.0 (CH_3), 23.3 (CH_2), 27.8 (CH_3), 31.1 (CH_2), 33.0 (CH_2), 39.6 (CH_2), 55.9

(CH_3), 56.7 (CH_3), 61.2 (CH_3), 61.9 (CH_3), 71.3 (CH), 73.8 (C), 108.9 (CH), 115.5 (CH), 121.5 (C), 122.6 (C), 128.3 (C), 130.3 (C), 137.4 (C), 140.4 (C), 144.5 (C), 149.1 (C), 151.5 (C), 152.8 (C). IR (mix. of diastereomers) (CH_2Cl_2, cm^{-1}) 3366 (s, OH), 1456 (m). Mass-spectrum (EI) *m/z* (% rel. intensity) 444 M^+ (100), 388 M^+-$(CH_3)_2CCH_2$ (72), 359 (25), 220 (29), 181 (96). HRMS (EI) calcd for $C_{26}H_{36}O_6$ 444.2512, found 444.2506.

Preparation of (aR,7S, aS,7R)-7,11-dihydroxy-1,2,3,8-tetramethoxy-10-propyl-5,6-dihydro-5H-dibenzo[a,c]cycloheptene (3c).



To the stirred at 0 °C under Ar solution of **3b**, diastereomer I or II (0.09 g, 0.203 mmol) and Ac_2O (0.185 g, 1.81 mmol) 3 - 5 mg of anhydrous $FeCl_3$ was added quickly, in solid. The reaction was controlled by TLC for the disappearance of the starting material, which usually takes 15 minutes. Then the reaction was quenched with 2 mL of the saturated Na_2HPO_4 solution, stirred 1 hour, then extracted with ether twice, ether layers were united, dried over $MgSO_4$, solvent was removed *in vacuo*. The residue was dried thoroughly under high vacuum, then dissolved in1.5 mL of THF, 1M solution of $LiAlH_4$ in THF (0.203 ml, 0.203 mmol) was then added dropwise under Ar. After 1 hour of stirring the mixture was added dropwise to 50 mL of water, aqueous layer was acidified by 10 % HCl until the precipitate is dissolved. Then the product was extracted with two 25 mL portions of ether, organic layers were united, dried over $MgSO_4$, solvent was removed in vacuo. The residue was purified using column chromatography on the silica gel (30 % EtOAc in hexane) to give **3c** (0.057 g, 72 % from I, 0.059 g, 75 % from II). Yellowish oil.

^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.99 (t, 3H, J = 7.2 Hz, $CH_2CH_2C\underline{H}_3$), 1.63-1.74 (m, 2H, $CH_2C\underline{H}_2CH_3$), 2.28 (dt, 1H, J = 13.9, 6.0 Hz, C5-Ha), 2.38-2.53 (m, 3H, C5-Hb, C6-H_2), 2.66-2.77 (m, 2H, $C\underline{H}_2CH_2CH_3$), 3.69 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 3.91 (s, 6H, $2OCH_3$), 5.50 (d, 1H, J = 5.6 Hz, C7-H), 6.56 (s, 1H, OH), 6.73 (s, 1H, C4-H), 6.76 (s, 1H, C9-H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 13.9 (CH_3), 23.4 (CH_2), 30.9 (CH_2), 33.2 (CH_2), 42.2 (CH_2), 56.0 (CH_3), 56.4 (CH_3), 61.4 (CH_3), 61.9 (CH_3), 65.3 (CH), 109.2 (CH), 112.9 (CH), 122.1 (C), 123.8 (C), 128.0 (C), 132.0 (C), 137.6 (C), 140.9 (C), 145.4 (C), 149.3 (C), 149.7 (C), 153.1 (C). IR (CH_2Cl_2, cm^{-1}) 3584 (s, OH), 3389 (s, OH), 1458 (m). Mass-spectrum (EI) *m/z* (% rel. intensity) 388 M^+ (100), 370 (9), 339 (12), 220 (8), 181 (84). HRMS (EI) calcd for $C_{22}H_{28}O_6$ 388.1886, found 388.1885.