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Linear (CH_2)-Bridged Oligo(catechol) Compounds for Metal-directed Self-organization Processes

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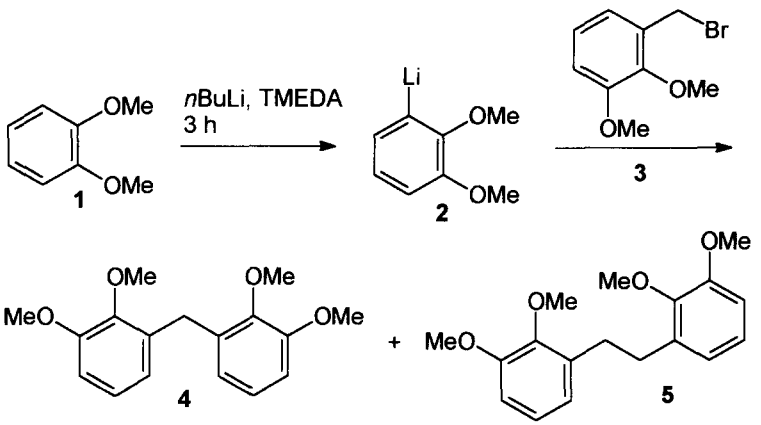
Abstract: Linear alkyl bridged bis- (**9**, **11**), tris- (**16**), and tetra(catechol) compounds (**21**) easily can be synthesized by addition of 2,3-dimethoxybenzaldehyde (**6**) to lithio(dimethoxybenzene) derivatives (**2**, **12**, **17**) followed by removal of the resulting alcohol functionality and cleavage of the methyl aryl ethers.

The discovery that cyclic polyethers as crown ethers or cryptands are able to bind alkali cations selectively opened up the way for the development of supramolecular chemistry.[1] In metallo-supramolecular chemistry mainly nitrogen donor ligands were established for the investigation of e. g. self-assembly processes.[2] Recently oligo(oxygen) donor compounds were used in this context.[3] For example, hard catecholate ligand systems form coordination compounds with early transition or main group metals and novel supramolecular compounds with new coordination geometries (trigonal prism at Fe(III), V(IV) or Ti(IV))[4], new structures (*meso*-helicate)[5], new electron transfer properties[6], and new receptor type properties (selective binding of alkali cations by self-assembled supermolecules)[5,7] are obtained.
Thus, we developed synthetic strategies for several $(CH_2)_2$- to $(CH_2)_6$-bridged bis(catechol) ligands and one bis$(CH_2)_2$-bridged tris(catechol) ligand using a variety of C-C coupling reactions (Wurtz, Stephens-Castro, Glaser).[7,8] However, for every single ligand system the synthetic method had to be modified and the upscale of the synthesis of ligands with more than two catechol units turned out to be a problem (the bis-$(CH_2)_2$-bridged tris(catechol) compound could be obtained on a 100-200 mg scale only). In this paper we describe a more general route towards linear CH_2-bridged bis-, tris-, and tetra(catechol) compounds that provides reasonable amounts of the desired ligand systems.

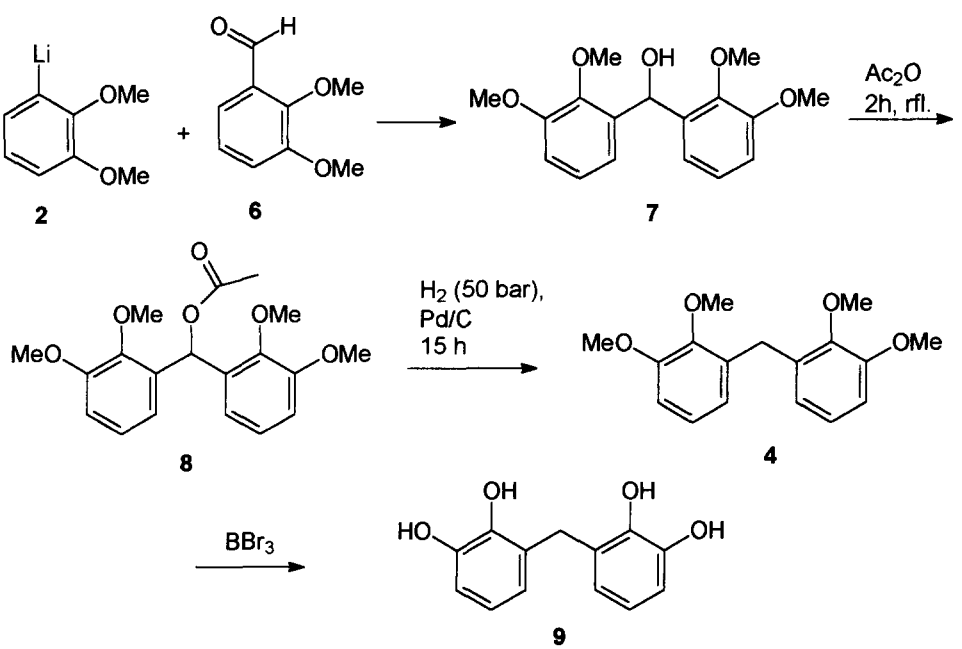
Our first attempt to synthesize bis(2,3-dihydroxyphenyl)methane (**9**) was a sequence starting with *ortho*-lithiation of 1,2-dimethoxybenzene (**1**) (*n*BuLi, TMEDA, ether, 3 h)[9] to generate 1,2-dimethoxy 3-lithiobenzene (**2**). Subsequently 2,3-dimethoxybenzyl bromide (**3**)[10] was added (Scheme 1) as an electrophile. Unfortunately only a mixture of the CH_2- (**4**) and the $(CH_2)_2$-bridged compound (**5**) could be obtained. Separation of the two

components failed. Probably **5** is formed by lithium bromine exchange reaction between **2** and **3** followed by a Wurtz-type coupling of the obtained benzyl lithium species with a second molecule of **3**.



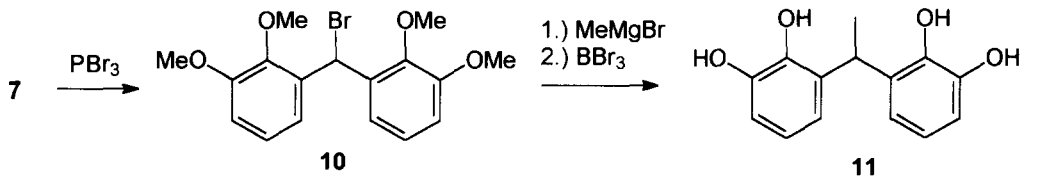
Scheme 1

Thus, we had to apply another strategy to avoid the metal bromine exchange (Scheme 2). By addition of the *in situ* generated nucleophile **2** (see above) to 2,3-dimethoxybenzaldehyde (**6**) as electrophile we obtained after column chromatography (silica gel, dichloromethane) bis(2,3-dimethoxyphenyl)methanol (**7**) in 88 % yield as a colorless oil.



Scheme 2

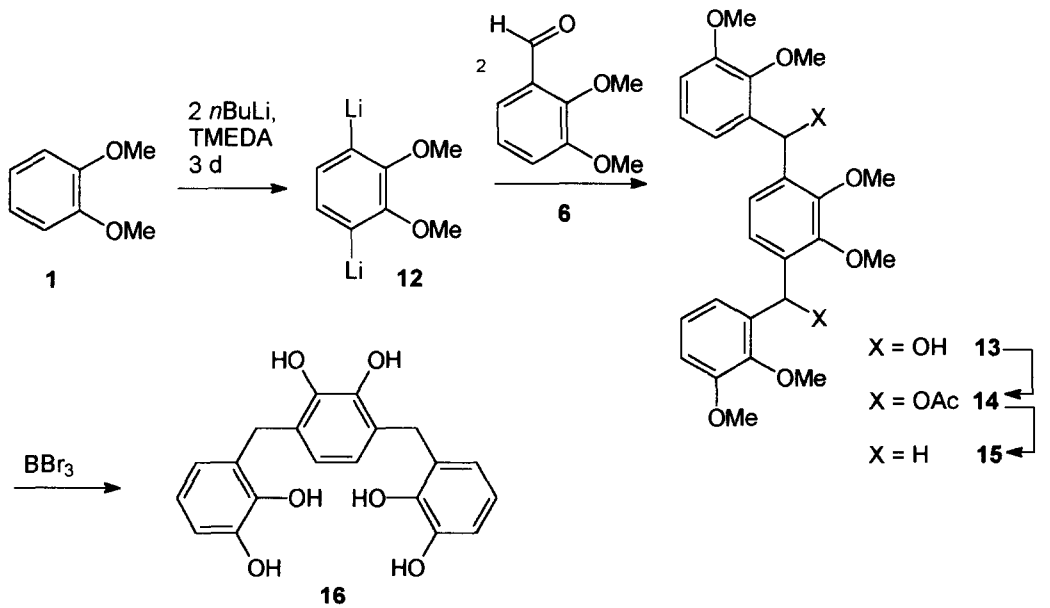
The hydroxy functionality of 7 was removed by reaction with acetic anhydride (rfl., 2.5 h, 100 %) and conversion of the resulting ester **8** under hydrogenolytic conditions (H_2 [45 bar], Pd/C, ethyl acetate / methanol, 15 h) yielded the corresponding alkane **4** (93 %). Final ether cleavage (BBr_3, dichloromethane, 18 h, 96 %) deliberated bis(2,3-dimethoxyphenyl)methane (**9**), a CH_2-bridged bis(catechol) ligand. In this synthesis only the alcohol **7** needed to be purified by a simple chromatography to separate the product from remaining starting material and TMEDA. The further reaction steps proceed quantitatively and always pure product was obtained after extractive work up. This enables the preparation of the ligand **9** at least on a gramme scale.



Scheme 3

In a further study we tested whether the alcohol **7** might be used to introduce alkylgroups at the methylene spacer which connects the two aromatic moieties. For this purpose **7** was transformed into the bromide **10** (PBr_3, ether, 14 h, 94 %). Addition of methyl magnesium bromide (ether, 0 °C, 4 h, 20 %) afforded the protected ligand system **11'** which was deprotected (BBr_3) to give ligand **11** in quantitative yield (Scheme 3).

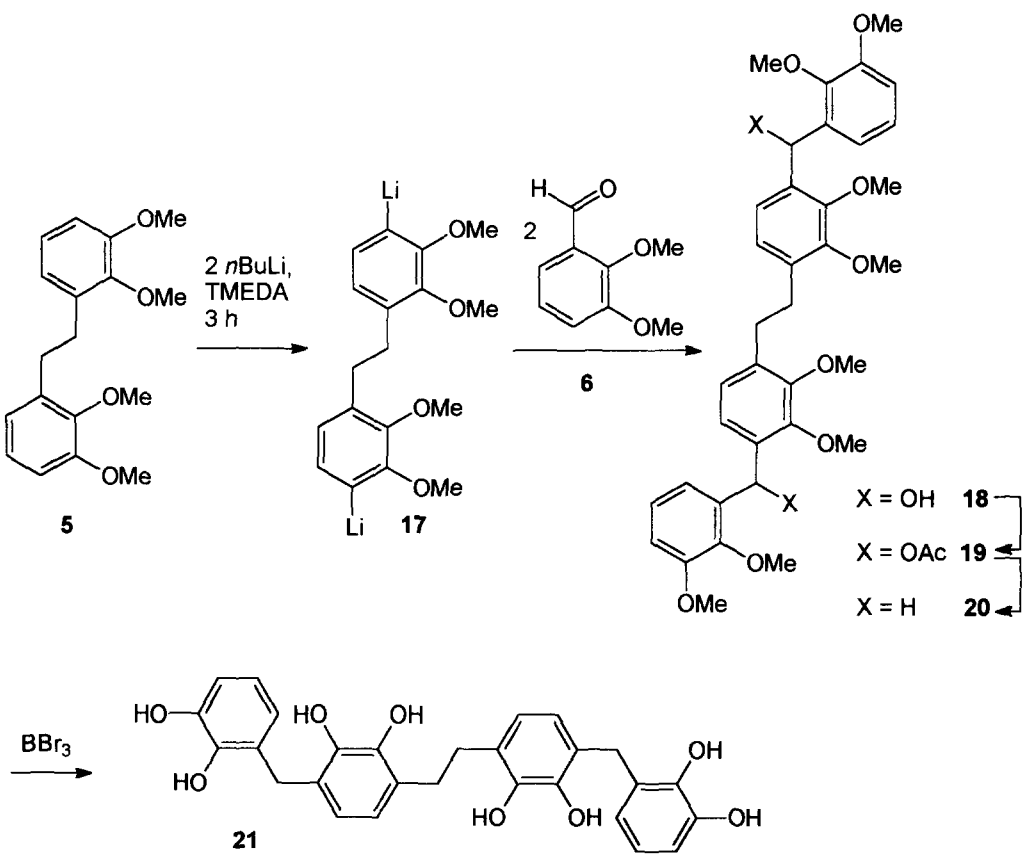
Compounds with more than two catechol units can be prepared using the same synthetic strategy as described for the preparation of **9**. Dilithio(dimethoxybenzene) (**12,17**) derivatives hereby have to be used instead of **2**.



Scheme 4

1,2-Dimethoxybenzene (**1**) easily can be lithiated twice (2 eq. *n*BuLi, 2 eq. TMEDA, ether, 3 d)[11] to generate the dianion **12**. The latter reacts with two equivalents of the 2,3-dimethoxybenzaldehyde (**6**) (ether, RT) to obtain **13** as a mixture of two diastereomers (1:1 by NMR) in 31 % yield. The alcohol functionalities of **13** are removed in a two step sequence as described above. Reaction of **13** with acetic anhydride gives **14** in 92 % and the following hydrogenolytic ester cleavage (H_2 [50 bar], Pd/C, ethyl acetate / methanol, 24 h) provides **15** in 96 % yield. Finally, the free bis-(CH_2)-bridged tris(catechol) ligand **16** is obtained by reaction with BBr_3 (dichloromethane) in 95 % yield (Scheme 4).

For the synthesis of a linear tetra(catechol) compound the ethylene bridged derivative **5** can be bislithiated (2 eq. *n*BuLi, 2 eq. TMEDA, ether, 3 h).[8] The obtained reagent **17** can react with two equivalents of **6** to form the bisalcohol **18** in 48 % yield as a mixture of diastereomers (1:1). Again the hydroxy groups are removed by esterification (acetic anhydride, rfl., 3 h, 100 % of **19**) and hydrogenation (H_2 [45 bar], Pd/C, ethyl acetate / methanol, 15 h, 91 %). The obtained derivative **20** finally is converted to the tetra(catechol) ligand **21** (BBr_3, dichloromethane, 72 %) (Scheme 5).



Scheme 5

Conclusions. We have developed a very convenient synthetic method for the preparation of bis, tris, and tetra(catechol) ligands. The synthesis is achieved by addition of 2,3-dimethoxybenzaldehyde (**6**) to *in situ* generated mono- or bislithiated 1,2-dimethoxybenzene derivatives (**2**,**12**,**17**) followed by removal of the resulting alcohol functionality in a two step sequence (esterification with acetic anhydride and hydrogenolytic removal of the ester group) and final methyl aryl ether cleavage. The described procedure makes some new oligo(catechol) ligands available for their use in metal-directed self-assembly processes. Investigations towards the coordination behavior of the linear ligand systems are currently in progress.

Experimental Section

Melting points were measured on a Büchi 535 (uncorrected). IR spectra were obtained on a Bruker IFS spectrometer (diffuse reflection (KBr) or as film on KBr plates). MS and HRMS spectra were detected on a Finnigan MAT 90 (EI, 70 eV). For ^{1}H-NMR and ^{13}C-NMR (BB/DEPT) spectra a Bruker AM 400 or a WM 250 was used; internal standard: chloroform or methanol; coupling constants in Hz.

Bis(2,3-dimethoxyphenyl)methanol (7)

To 1,2-dimethoxybenzene (**1**) (1.20 g, 8.70 mmol) and 1.2 ml TMEDA in 20 ml of ether under argon 5.6 ml of 1.6 M *n*BuLi in hexane (8.96 mmol) are added. The mixture is stirred for 3 h and a solution of 2,3-dimethoxybenzaldehyde (**6**) (1.40 g, 8.43 mmol) in 20 ml of ether is added. After 2 h the reaction is quenched by addition of 4 N HCl. Phases are separated and the aqueous phase is extracted with ether. The combined organic phases are taken to dryness and the remaining oil is purified by column chromatography (silica gel, dichloromethane) to obtain 2.26 g of **7** (88 %) as a colorless oil.

IR (neat): ν 3461, 2938, 2835, 1586, 1482, 1271, 1223, 1085, 1008, 753 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.14 (d, J = 5.1, 1 H, OH), 3.71 (s, 6 H), 3.84 (s, 6 H), 6.37 (d, J = 5.1, 1 H), 6.84 (dd, J = 7.9, 1.5, 2 H), 6.94 (dd, J = 7.9, 1.5, 2 H), 7.03 (t, J = 7.9, 2 H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 55.9 (CH_3), 60.6 (CH_3), 67.1 (CH), 111.9 (CH), 119.9(CH), 124.0 (CH), 137.4 (C), 146.5 (C), 152.7 (C). MS: m/z 304 (M^+, 9), 168 (100). HRMS calcd. for $C_{17}H_{20}O_5$ (M^+): 304.1311, found: 304.1300.

Bis(2,3-dimethoxyphenyl)methyl acetate (8)

Bis(2,3-dimethoxyphenyl)methanol (**7**) (430 mg, 1.41 mmol) is dissolved in 5 ml of acetic anhydride and the mixture is refluxed for 2.5 h. Solvent is removed in vacuo and the remaining oil is dissolved in dichloromethane. Washing with saturated aqueous $NaHCO_3$, drying ($MgSO_4$), and evaporation of dichloromethane affords **8** (487 mg, 100 %) as a yellow oil.

IR (neat): ν 2939, 2836, 1742, 1588, 1483, 1283, 1233, 1008, 754 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 2.11 (s, 3 H), 3.79 (s, 6 H), 3.83 (s, 6 H), 6.86 (d, J = 8.0, 4 H), 7.02 (t, J = 8.0, 2 H), 7.51 (s, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 21.2 (CH_3), 55.8 (CH_3), 60.4 (CH_3), 67.4 (CH), 112.2 (CH), 119.9 (CH), 123.7 (CH), 133.7 (C), 146.8 (C), 152.8 (C), 169.7 (CO). MS: m/z 346 (M^+, 21), 210 (92), 167 (100). HRMS calcd. for $C_{19}H_{22}O_6$ (M^+): 346.1416, found: 346.1404.

Bis(2,3-dimethoxyphenyl)methane (4)

Bis(2,3-dimethoxyphenyl)methyl acetate (**8**) (475 mg, 1.37 mmol) is dissolved in 20 ml of ethyl acetate / methanol (5:1) and Pd / C (100 mg) is added. The mixture is stirred under a hydrogen atmosphere (45 bar) for 15 h. After filtration and removal of solvent the residue is dissolved in dichloromethane. Washing with saturated aqueous $NaHCO_3$, drying ($MgSO_4$), and evaporation of dichloromethane deliberates 366 mg of **4** (93 %) as a white solid; m.p. 71-74 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.78 (s, 6 H), 3.87 (s, 6 H), 4.05 (s, 2 H), 6.71 (m, 2 H), 6.80 (m, 2 H), 7.00 (m, 2 H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 31.3 (CH_2), 55.7 (CH_3), 60.3 (CH_3), 110.3 (CH), 122.5 (CH), 123.7 (CH), 134.9 (C), 147.1 (C), 152.7 (C). MS: m/z 288 (M^+, 100). HRMS calcd. for $C_{17}H_{20}O_4$ (M^+): 288.1362, found: 288.1378.

Bis(2,3-dihydroxyphenyl)methane (9)

To bis(2,3-dimethoxyphenyl)methane (**4**) (200 mg, 0.69 mmol) in 20 ml of dichloromethane a 1 molar solution of BBr_3 in dichloromethane (3.5 ml) is added at 0 °C. The mixture is warmed up and stirred for 18 h. 5 ml of methanol are added. The mixture is taken to dryness and the residue is dissolved in ether. After washing with water, drying ($MgSO_4$), and evaporation of the ether 160 mg of **9** (96 %) are obtained as a white hygroscopic solid; m. p. 160-162 °C.

IR (KBr): ν 3472, 3320, 1594, 1484, 1475, 1357, 975 cm^{-1}. ^{1}H-NMR (400 MHz, methanol-d_4): δ 3.89 (s, 2 H), 6.59 (m, 6 H). ^{13}C-NMR (100 MHz, methanol-d_4): δ 31.6 (CH_2), 114.1 (CH), 120.7 (CH), 122.3 (CH), 129.3 (C), 143.6 (C), 146.1 (C). MS: m/z 232 (M^+, 52), 123 (100). HRMS calcd. for $C_{13}H_{12}O_4$ (M^+): 232.0736, found: 232.0722. Anal. calcd. for $C_{13}H_{12}O_4 \bullet 0.5\ H_2O$: C 64.72, H 5.43; found: C 64.52, H 5.22.

Bromo bis(2,3-dimethoxyphenyl)methane (10)

The alcohol **7** (760 mg, 2.50 mmol) and 1 ml of pyridine are dissolved in 40 ml of ether. At -30 °C a solution of PBr_3 (0.1 ml) in 10 ml of ether is added. The mixture is allowed to warm up and is stirred for additional 14 h. After addition of water the phases are separated. The organic phase is dried ($MgSO_4$) and ether is removed in vacuum to obtain **10** (860 mg, 94 %) as a yellow oil.

IR (neat): ν 2938, 2853, 1585, 1480, 1280, 1090, 1073, 1005, 750 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.80 (s, 6 H), 3.85 (s, 6 H), 6.85 (dd, J = 7.9, 1.4, 2 H), 7.04 (t, J = 7.9, 2 H), 7.12 (s, 1 H), 7.18 (dd, J = 7.9, 1.4, 2 H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 43.6 (CH), 56.0 (CH_3), 60.6 (CH_3), 112.3 (CH), 122.3 (CH), 124.0 (CH), 135.3 (C), 145.9 (C), 152.7 (C). MS: m/z 368/366 (M^+, 1), 287 (94), 151 (100). HRMS calcd. for $C_{17}H_{19}BrO_4$ (M^+): 366.0467, found: 366.0447.

1,1-Bis(2,3-dimethoxyphenyl)ethane (11')

The bromide **10** (818 mg, 2.23 mmol) is dissolved in 20 ml of ether and at 0 °C a solution of methyl magnesium bromide (1 ml, 3 molar in THF) is added. The mixture is allowed to warm up. After 4 h water is added and the phases are separated. The organic phase is dried ($MgSO_4$) and solvent is removed in vacuum. The residue is purified by column chromatography (silica gel, dichloromethane) to obtain 130 mg of **11'** (20 %) as a white solid.

IR (KBr): ν 2972, 2934, 1585, 1479, 1047, 1008, 788 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$): δ 1.49 (d, J = 7.2, 3 H), 3.66 (s, 6 H), 3.83 (s, 6 H), 4.89 (q, J = 7.2, 1 H), 6.75 (d, J = 7.9, 4 H), 6.97 (t, J = 7.9, 2 H). ^{13}C-NMR

(62.9 MHz, $CDCl_3$): δ 21.1 (CH_3), 31.9 (CH), 55.6 (CH_3), 60.0 (CH_3), 110.2 (CH), 119.8 (CH), 123.5 (CH), 140.4 (C), 146.5 (C), 152.6 (C). Anal. calcd. for $C_{18}H_{22}O_4$: C 71.50, H 7.33; found: C 71.37, H 7.39.

1,1-Bis(2,3-dihydroxyphenyl)ethane (11)

Ether cleavage is achieved as described for the synthesis of **9**. Starting with **11'** (115 mg, 0.38 mmol), 93 mg of **11** (99 %) are obtained as a white solid.

^{1}H-NMR (250 MHz, methanol-d_4): δ 1.54 (d, J = 7.2, 3 H), 4.79 (q, J = 7.2, 1 H), 6.58-6.72 (m, 6 H).). ^{13}C-NMR (62.9 MHz, methanol-d_4): δ 22.5 (CH_3), 34.1 (CH), 116.1 (CH), 122.1 (CH), 123.0 (CH), 136.7 (C), 145.6 (C), 148.3 (C).

3,6-Bis(2,3dimethoxyphenyl hydroxymethyl) 1,2-dimethoxybenzene (13)

A 1.6 molar solution of *n*BuLi in hexane (9.5 ml, 15.2 mmol) is added to a mixture of 1,2-dimethoxybenzene (**1**) (1.00 g, 7.25 mmol) and 2 ml of TMEDA in 40 ml of ether under argon. The immediately formed suspension is stirred for three days and the *in situ* generated 3,6-dilithio 1,2-dimethoxybenzene (**12**) is quenched by addition of 2,3-dimethoxybenzaldehyde (**6**) (2.40 g, 14.5 mmol) in 20 ml of ether. After 4 h 4 N HCl is added and the phases are separated. The organic phase is dried ($MgSO_4$) and solvent is removed in vacuum. After column chromatography (silica gel, gradient: dichloromethane - dichloromethane/methanol (2%)) **13** (1.04 g, 31 %) is obtained as a white solid.

IR (KBr): ν 3439, 2939, 2835, 1586, 1480, 1270, 1011, 755 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$, mixture of diastereomers: 1:1): δ 3.10 / 3.19 (2 d, J = 4.5 / 4.0, Σ 2 H, OH), 3.64 / 3.67 (2 s, Σ 6 H), 3.68 / 3.71 (2 s, Σ 6 H), 3.83 / 3.84 (2 s, Σ 6 H), 6.31 / 6.35 (2 d, J = 4.5 / 4.0, Σ 2 H), 6.82-6.92 (m, 4 H), 6.99-7.06 (m, 4 H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 55.6 (2 signals, CH_3), 59.8 / 60.0 (CH_3), 60.2 / 60.4 (CH_3), 66.4 / 66.8 (CH_3), 111.6 / 111.7 (CH), 119.3 / 119.6 (CH), 122.2, 122.5 (CH), 123.7 / 123.8 (CH), 136.7 / 136.8 (CH), 136.9 (C), 137.0 (C), 146.1 / 146.2 (C), 149.9 / 150.1 (C), 152.4 (C). MS: m/z 470 (M^+, 47), 165 (100). HRMS calcd. for $C_{26}H_{30}O_8$ (M^+): 470.1941, found: 470.1948. Anal. calcd. for $C_{26}H_{30}O_8$: C 66.37, H 6.43; found: C 65.59, H 6.55.

3,6-Bis(2,3dimethoxyphenyl acetoxymethyl) 1,2-dimethoxybenzene (14)

A solution of the bisalcohol **13** (932 mg, 1.98 mmol) in 50 ml of acetic anhydride is heated to reflux for 2.5 h. After cooling to room temperature the solvent is removed in vacuum and the residue is dissolved in dichloromethane. The organic phase is washed with saturated aqueous $NaHCO_3$. Finally it is dried ($MgSO_4$) and dichloromethane is removed in vacuum to obtain **14** (1.00 g, 92 %) as a yellow wax.

IR (neat): ν 2936, 2833, 1743, 1585, 1481, 1273, 1223, 1082, 1011, 754 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$, mixture of diastereomers: 1:1): δ 2.11 (s, 6 H), 3.71 / 3.77 (2 s, Σ 6 H), 3.78 / 3.81 (2 s, Σ 6 H), 3.84 / 3.85 (2 s, Σ 6 H), 6.82-6.89 (m, 4 H), 6.95 / 6.99 (2 s, Σ 2 H), 6.99-7.04 (m, 2 H), 7.48 (2 s, Σ 4 H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 21.1 (CH_3), 55.7 (CH_3), 59.8 / 59.9 (CH_3), 60.2 / 60.3 (CH_3), 67.0 / 67.1 (CH), 112.1 / 112.2 (CH), 119.6, 119.8 (CH), 122.3 / 122.6 (CH), 123.7 (CH), 133.4 / 133.5 (C), 133.7 (C), 146.5 / 146.6 (C), 150.5 / 150.6 (C), 152.6 (C), 169.6 (C). MS: m/z 438 (M^+, 1), 288 (100). HRMS calcd. for $C_{30}H_{34}O_{10}$ (M^+): 554.2152, found: 554.2167.

3,6-Bis(2,3-dimethoxybenzyl) 1,2-dimethoxybenzene (15)

A mixture of bisacetate **14** (940 mg, 1.70 mmol), Pd / C (100 mg), and 50 ml of ethyl acetate / methanol (5:1) is stirred under a hydrogen atmosphere (50 bar) for 24 h. After filtration the solvent is removed and the residue is dried in vacuum to obtain 715 mg of **15** (96 %) as a colorless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.77 (s, 6 H), 3.79 (s, 6 H), 3.86 (s, 6 H), 4.01 (s, 4 H), 6.69 (dd, J = 8.0, 1.3, 2 H), 6.74 (s, 2 H), 6.79 (dd, J = 8.0, 1.3, 2 H), 6.96 (t, J = 8.0, 2 H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 29.7 (CH_2), 55.9 (CH_3), 60.3 (CH_3), 60.5 (CH_3), 110.6 (CH), 122.7 (CH), 123.9 (CH), 125.4 (CH), 133.3 (C), 135.2 (C), 147.4 (C), 151.4 (C), 153.0 (C). MS: m/z 438 (M^+, 4), 288 (100). HRMS calcd. for $C_{26}H_{30}O_6$ (M^+): 438.2041, found: 438.2032.

3,6-Bis(2,3-dihydroxybenzyl) 1,2-dihydroxybenzene (16)

Ether cleavage is achieved as described for the synthesis of **9**. Starting with **15** (610 mg, 1.39 mmol), 490 mg of **16** (95 %) are obtained as a white hygroscopic solid; m.p. 213-214 °C.

IR (KBr): ν 3454, 3049, 2938, 1624, 1598, 1479, 1377, 1276, 756, 731 cm^{-1}. ^{1}H-NMR (400 MHz, methanol-d_4): δ 3.84 (s, 4 H), 6.54 (s, 2 H) 6.55-6.65 (m, 6 H). ^{13}C-NMR (100 MHz, methanol-d_4): δ 30.8 (CH_2), 114.1 (CH), 120.8 (CH), 122.2 (CH), 122.3 (CH), 127.2 (C), 129.3 (C), 143.4 (C), 143.6 (C), 146.0 (C). MS: m/z 354 (M^+, 41), 232 (65), 123 (100). HRMS calcd. for $C_{20}H_{18}O_6$ (M^+): 354.1103, found: 354.1115. Anal. calcd. for $C_{20}H_{18}O_6 \bullet H_2O$: C 64.51, H 5.41; found: C 64.93, H 5.41.

1,2-Bis(4-((2,3-dimethoxyphenyl)hydroxymethyl) 2,3-dimethoxyphenyl)ethane (18)

1,2-Bis(2,3-dimethoxyphenyl)ethane (**5**) (1.00 g, 3.31 mmol), 1 ml of TMEDA, and 4.4 ml of *n*BuLi / hexane (1.6 molar, 7.04 mmol) in 40 ml of ether are stirred under argon for 3 h. A solution of 2,3-dimethoxybenzaldehyde (**6**) (1.10 g, 6.63 mmol) is added to the *in situ* generated dilithio compound **17** and the mixture is stirred for additional 4 h. After addition of 4 N HCl the organic phase is dried ($MgSO_4$) and solvent is evaporated. Column chromatography (5 cm silica gel, gradient: dichloromethane/methanol (1%) - dichloromethane/methanol (3%)) provides 1.01 g of **18** (48 %) as a white solid; m.p. 59-61 °C.

IR (KBr): ν 3470, 2937, 2834, 1586, 1480, 1272, 1016, 757 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$, mixture of diastereomers: 1:1): δ 2.84 (s, 4 H), 3.70 (s, 6 H), 3.71 (s, 6 H), 3.81 (s, 6 H), 3.85 (s, 6 H), 6.32 (s, 2 H), 6.84-7.07 (m, 10 H), OH-resonances are not observed. ^{13}C-NMR (100 MHz, $CDCl_3$): δ 31.1 (CH_2), 55.6 (CH_3), 60.0 (CH_3), 60.2 (CH_3), 60.3 (CH_3), 66.9 (CH), 111.6 (CH), 119.4 (CH), 122.2 (CH), 123.7 (CH), 124.5 (CH), 135.2 (C), 135.4 (C), 137.1 (C), 146.2 (C), 150.2 (C), 150.9 (C), 152.4 (C). MS: m/z 634 (M^+, 11), 165 (100). HRMS calcd. for $C_{36}H_{42}O_{10}$ (M^+): 634.2778, found: 634.2762. Anal. calcd. for $C_{36}H_{42}O_{10}$: C 68.12, H 6.67; found: C 67.41, H 6.80.

1,2-Bis(4-((2,3-dimethoxyphenyl)acetoxymethyl) 2,3-dimethoxyphenyl)ethane (19)

Bisalcohol **18** (910 mg, 1.43 mmol) is refluxed in acetic anhydride (30 ml) for 3 h. Solvent is removed and the residue is dissolved in dichloromethane. Extraction with saturated aqueous $NaHCO_3$, drying ($MgSO_4$), and evaporation of solvent yields 1.025 g of **19** (100 %) as a beige solid, m.p. 65-69 °C.

IR (KBr): ν 2938, 2834, 1742, 1587, 1482, 1261, 1021, 769 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$, mixture of diastereomers: 1:1): δ 2.11 (s, 6 H), 2.83 (s, 4 H), 3.75 (s, 6 H), 3.78 (s, 6 H), 3.80 (s, 6 H), 3.84 (s, 6 H), 6.85-6.92 (m, 8 H), 6.99-7.05 (m, 2 H), 7.47 (s, 2 H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 21.3 (CH_3), 31.2 (CH_2),

55.8 (CH_3), 60.0 (CH_3), 60.3 (CH_3), 60.4 (CH_3), 67.3 (CH), 112.1 (CH), 119.7 (CH), 122.6 (CH), 123.8 (CH), 124.5 (CH), 131.9 (C), 133.9 (C), 136.1 (C), 146.6 (C), 150.7 (C), 151.2 (C), 152.7 (C), 169.8 (C). MS: m/z 718 (M^+, 42), 299 (100), 165 (96). HRMS calcd. for $C_{40}H_{46}O_{12}$ (M^+): 718.2989, found: 718.2966. Anal. calcd. for $C_{36}H_{42}O_{10}$: C 66.84, H 6.45; found: C 66.03, H 6.51.

1,2-Bis(4-(2,3-dimethoxybenzyl) 2,3-dimethoxyphenyl)ethane (20)

Bisacetate **19** (950 mg, 1.32 mmol) and 100 mg of Pd / C in 50 ml of ethyl acetate/methanol (3:1) are stirred under hydrogen (45 bar) for 15 h. Filtration and evaporation of solvent in vacuum provides 724 mg of **20** (91 %) as a yellow oil.

^{1}H-NMR (250 MHz, $CDCl_3$): δ 2.84 (s, 4 H), 3.76 (s, 12 H), 3.84 (s, 6 H), 3.86 (s, 6 H), 3.99 (s, 4 H), 6.64-6.83 (m, 8 H), 6.95 (t, J = 7.9, 2 H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 29.5 (CH_2), 31.3 (CH_2), 55.7 (CH_3), 60.0 (CH_3), 60.4 (CH_3, double intensity), 110.3 (CH), 122.4 (CH), 123.7 (CH), 124.6 (CH), 125.1 (CH), 133.0 (C), 134.2 (C), 135.1 (C), 147.1 (C), 151.1 (C), 151.2 (C), 152.8 (C). MS: m/z 602 (M^+, 74), 301 (100). HRMS calcd. for $C_{36}H_{42}O_8$ (M^+): 602.2880, found: 602.2890.

1,2-Bis(4-(2,3-dihydroxybenzyl) 2,3-dihydroxyphenyl)ethane (21)

Ether cleavage is achieved as described for the synthesis of **9**. Starting with **20** (880 mg, 1.46 mmol), 510 mg of **21** (72 %) are obtained as a gray, hygroscopic solid; m.p. 225-228 °C.

IR (KBr): ν 3372, 2938, 1624, 1596, 1475, 1373, 1284, 730 cm^{-1}. ^{1}H-NMR (250 MHz, methanol-d_4): δ 2.78 (s, 4 H), 3.86 (s, 4 H), 6.53-6.67 (m, 10 H). ^{13}C-NMR (100 MHz, methanol-d_4): δ 31.0 (CH_2), 31.7 (CH_2), 114.1 (CH), 120.9 (CH), 121.9 (CH, double intensity), 122.2 (CH), 127.1 (C), 128.4 (C), 129.4 (C), 143.2 (C), 143.4 (C), 144.2 (C), 146.0 (C). MS: m/z 490 (M^+, 3 %), 368 (73), 245 (100), 123 (61). HRMS calcd. for $C_{28}H_{26}O_8$ (M^+): 490.1628, found: 490.1618. Anal. calcd. for $C_{28}H_{26}O_8 \bullet 1.5\ H_2O$: C 64.98, H 5.65; found: C 65.01, H 5.79.

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