Access to Unsymmetric Binaphthols through Oxidative Coupling of Silicon Bisnaphtholates

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The oxidative coupling of various symmetric (**5 - 7**) as well as unsymmetric silicon bisnaphtholates (**11**, **12**), initiated by different oxidants (iron(III), cerium(IV), copper(II) or hypervalent iodine), furnishes the corresponding symmetric and unsymmetric binaphthols **13 - 17**. The coupling reaction of the substrates follows strictly an intramolecular pathway.

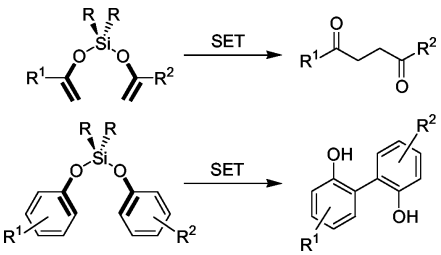
Key words: Oxidative Coupling, Electron Transfer, Binaphthols, Silicon Naphtholates

Introduction

Biaryl subunits are prevalent structural motifs in many classes of substances, such as pharmacologically active natural products [1] or as ligands in enantioselective catalysis [2]. The formation of the biaryl axis is the key step in most synthetic approaches. Aside of metal catalyzed reactions as the Suzuki [3] or Stille [4,5] coupling, the oxidative formation of the biaryl C-C bond has become an established procedure with electron-rich phenol derivatives [6]. In this context, symmetric coupling products may readily be prepared, recently even in enantioselective protocols [7], whereas there is still an extremely limited amount of concepts for the preparation of unsymmetric biaryl compounds [8]. While Ding *et al.* describe the oxidative cross-coupling of 2-naphthol and 2-naphthylamine as a hydrogen bonded complex in the solid state [8a], Kita *et al.* favor oxidative biaryl coupling using stable O,S,Si-tethers between the electron-rich arenes [8b].

Using a synthetic approach to unsymmetric silyl bisenolates as developed by Rathke [9] we have recently elaborated an oxidative, diastereoselective cross-coupling furnishing 1,4-dicarbonyl compounds with SET (single electron transfer) reagents (Scheme 1) [10]. We expected that starting from unsymmetric silyl bisphenolates SET procedure should analogously provide a route to the *ortho*-selective cross-coupling of phenols.

In the following we describe the preparation of several silyl bisphenolates, cyclic voltammetry investigations on their anodic behavior and preparative SET oxidations.



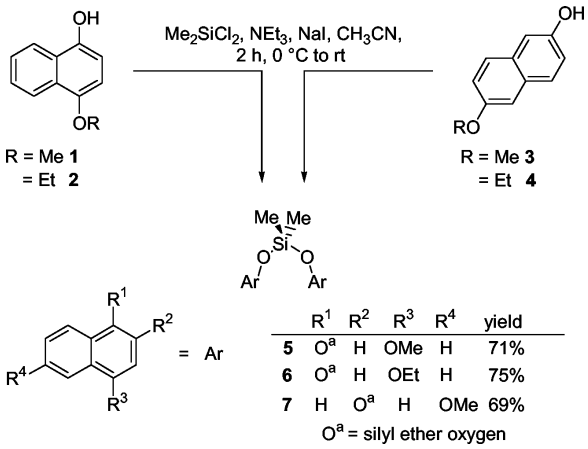
Scheme 1. Concept of the intramolecular oxidative coupling of enol and phenol derivatives.

Results and Discussion

Synthesis of the silicon bisnaphtholates

The 4-alkoxy-1-naphthols **1,2** [11], and 6-alkoxy-2-naphthols **3,4**, as starting materials for the generation of the silicon bisnaphtholates, were synthesized by procedures published in the literature [12].

The preparation of the symmetric silicon bisnaphtholates **5 - 7** was effected according to a procedure for silicon bisenolates starting from dichlorodimethylsilane that was treated with two equivalents of the appropriate naphthol in presence of triethylamine as base and sodium iodide as stoichiometric catalyst (Scheme 2). An iodo silane is formed *in situ* that possesses a higher electrophilicity than the corresponding chloro silane [13]. After purification of the crude product by recrystallization from *n*-hexane the desired products **5 - 7** were obtained in 69 – 75% yield.



Scheme 2. Preparation of symmetrical silicon bisnaphtholates.

For the preparation of the unsymmetric silicon bisnaphtholates **11** and **12** a procedure for unsymmetric silicon bisenolates was adapted [9]. Starting with aminochlorosilane **8** [14] the first naphthol component was connected to the silicon tether to furnish **9** and **10** that were isolated by extration of the reaction mixture with *n*-hexane and used in the following step without purification. By reaction of **9** or **10** with acetyl chloride the diethylamino group was substituted by a chloro substituent. The intermediate chlorosilane was then converted to target **11** or **12** by the addition of a second naphthol (Scheme 3). As recrystallization failed to afford clean **11** and **12**, isolation was achieved by preparative HPLC at a reversed-phase column, yielding pure **11** and **12** in 31% and 37% yield, respectively.

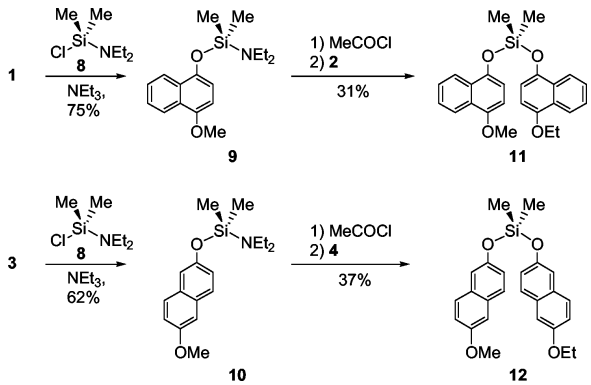
Cyclic voltammetry

The oxidation potentials of silicon bisnaphtholates **5**-**7**, **11** and **12** were measured by cyclic voltammetric experiments in acetonitrile at scan rates between 20 and 500 mV s^{-1}. All substrates showed irreversible oxidation waves that feature a characteristic scarped, very steep form. For the 4-alkoxy-1-naphthol derived compounds **5**, **6** and **11** the potential is E_{pa} = +0.66 V *vs.* $Fc/Fc^{\bullet+}$, whereas the potentials for **7** and **12** are slightly higher (E_{pa} = +0.79 V *vs.* $Fc/Fc^{\bullet+}$ and +0.78 V *vs.* $Fc/Fc^{\bullet+}$, respectively) (Table 1). After the addition of 2,6-di-*tert*-butylpyridine as a non-nucleophilic base the scarped waveform is attenuated and finally an ordinary irreversible wave is registered when more than two equivalents of base are added. This observation suggests that the electrochemical oxidation of the silicon bisnaphtholates leads to the immediate release of protons that already on the time scale of the cyclic voltammetry experiments hydrolyse the silicon bisnaphtholates to the corresponding naphtholes. As the latter are more readily oxidized than the silicon bisnaphtholates a very steep increase of the oxidation current is registered.

Table 1. Oxidation potentials of the investigated silicon bisnaphtholates[a].

Compound	5	6	7	11	12
E_{pa} [V *vs.* $Fc/Fc^{\bullet+}$]	+0.66	+0.66	+0.79	+0.66	+0.78

[a] Solvent: CH_3CN; v = 100 mV s^{-1}.

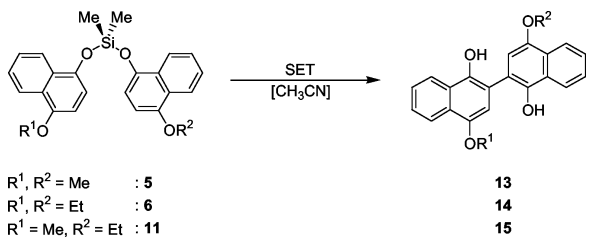


Scheme 3. Preparation of unsymmetrical silicon bisnaphtholates.

Preparative Oxidation

The preparative oxidation experiments of **5**, **6** and **11** were carried out with different one-electron oxidants (iron(III), cerium(IV), copper(II) salts) or with a hypervalent iodine(III) reagent (Table 2). For all attempts 2,6-di-*tert*-butylpyridine was added to intercept protons that are formed during the course of the oxidative coupling reaction.

Due to the low oxidation potential of the 4-alkoxy-1-naphthol derived silicon bisnaphtholates the oxidation reaction is exergonic with the used oxidants. This



Scheme 4. Oxidative coupling of silicon bisnaphtholates **5**, **6** and **11**.

Table 2. Preparative oxidation of **5**, **6** and **11**.

Silicon bisnaph-tholate	Oxidant	DTBP[a] [mol%]	Temp. [°C]	Reaction time	Product	Reisolated starting material
5	**FePhen**[b]	200	25	1 min	17% (**13**)	25%
5	**FePhen**	200	25	15 min	21% (**13**)	26%
5	**FePhen**	200	25	30 min	23% (**13**)	27%
5	**FePhen**	200	25	60 min	21% (**13**)	22%
5	**FePhen**	200	25	12 h	27% (**13**)	27%
5	**CAN**[c]	300	25	1 min	56% (**13**)	30%
5	$Cu(OTf)_2$	300	25	1 min	48% (**13**)	30%
5	**PIFA**[d]	200	−40	1.5 h	41% (**13**)	8%
5[e]	**PIFA**	200	−40	1.5 h	40% (**13**) 48% (**13**)	14%
5 + 6[f]	**CAN**	300	25	1 min	51% (**14**)	n. d.
11	**CAN**	300	25	1 min	42% (**15**)	n. d.

[a] 2,6-di-*tert*-butylpyridine; [b] **FePhen**: tris-(1,10-phenanthroline)-iron(III) hexafluoroantimonate; [c] **CAN**: tetrammoniumcerium(IV) nitrate; [d] **PIFA**: phenyliodine(III) bis(trifluoroacetate); [e] solvent: CF_3CH_2OH; [f] crossing experiment.

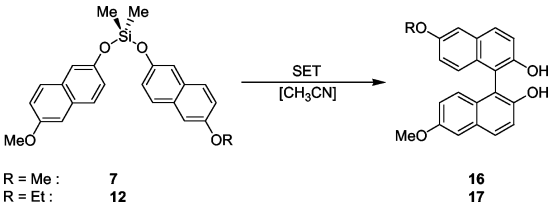
is seen by the time dependence of the yields in the oxidation of **5** with **FePhen** ($E_{1/2}$ = 0.69 V *vs.* $Fc/Fc^{\bullet+}$): yields are not much influenced by varying reaction times (1 min, 17%; 12 h, 27%). With $Cu(OTf)_2$ ($E_{1/2}$ = 0.67 V *vs.* $Fc/Fc^{\bullet+}$) a better yield (48%) was obtained after 1 min. The oxidation of **5** with the hypervalent iodine(III) reagent **PIFA** was carried out at low temperature (−40 °C) and furnished a yield of about 40%, independent of the used solvent (acetonitrile *vs.* 2,2,2-trifluoroethanol). The best results were obtained with **CAN** ($E_{1/2}$ = 0.78 V *vs.* $Fc/Fc^{\bullet+}$) as oxidant. Starting from **5**, **6** and **11** the binaphthols **13**, **14** and **15** were isolated in 42 – 56% yield. In case of **11** the symmetric binaphthols **13** and **14** were observed in minor amounts (ca. 5%) beside the main coupling product **15**. To verify if the side products are formed by intermolecular coupling processes of two silicon bisnaphtholates or if liberated protons cause a cleavage of the reactant and therefore the oxidative coupling takes place on stage of the free naphthols, another control experiment was performed. Oxidation of a 1:1 mixture of **5** and **6** only provided binaphthols **13** and **14**, indicating a strictly intramolecular coupling pathway.

When the symmetric 6-methoxy-2-naphthol derived silicon bisnaphtholate **7** was oxidized with **FePhen** for 12 h, coupling product **16** could be obtained in 43% yield. The long reaction time was chosen due to the higher oxidation potential of **7** (E_{pa} = 0.79 *vs.* $Fc/Fc^{\bullet+}$) and thereof the slightly endergonic electron transfer process. Under similar conditions, when **CAN** ($E_{1/2}$ = 0.78 V *vs.* $Fc/Fc^{\bullet+}$) and **TNPA** ($E_{1/2}$ = 1.25 V *vs.* $Fc/Fc^{\bullet+}$) were used as stronger oxidants **16** was furnished only in minor yields, presumably due to follow-up oxidation. Even with **PIFA** no product formation was observed. With $CuCl_2 \cdot 2\,H_2O$ as oxidant, methanol as solvent and addition of benzylamine to the reaction mixture, a remarkably higher yield (56%) of **16** was obtained. Also for **12**, the latter conditions furnished the best results (47% yield). It is noteworthy that in the oxidation experiment with **12** only the unsymmetric binaphthol **17** is isolated whereas potential symmetric coupling products were not observed.

Table 3. Preparative oxidation of **7**, **12**.

Silicon bisnaph-tholate	Oxidant	DTBP[a] [mol%]	Temp. [°C]	Reaction time	Yield[b]
7	**FePhen**	200	25	12 h	43% (**16**)
7	**CAN**	200	25	12 h	<5% (**16**)
7	**TNPA**[c]	200	25	12 h	10% (**16**)
7	**PIFA**	–	−40	2 h	–
7[d]	$CuCl_2 \cdot 2\,H_2O$	–	25	24 h	56% (**16**)
12[d]	$CuCl_2 \cdot 2\,H_2O$	–	25	24 h	47% (**17**)

[a] 2,6-di-*tert*-butylpyridine; [b] referred to isolated product; [c] **TNPA**: tris(4-nitrophenyl)aminium hexachloroantimonate; [d] 400 mol% of benzylamine, solvent methanol.



Scheme 5. Oxidative coupling of silicon bisnaphtholates **7** and **12**.

Conclusion

In summary, we have synthesized symmetric as well as unsymmetric silicon bisnaphtholates starting from 4-alkoxy-1-naphthols and 6-alkoxy-2-naphthols and investigated their oxidation by cyclic voltammetry. Oxidative coupling reactions of these substrates, initiated by various chemical oxidants, provided symmetric as well as unsymmetric binaphthol derivatives in an intramolecular reaction.

Experimental Section

General: ^1H and ^{13}C NMR spectra were recorded on Bruker AC-200 or AM-250 instruments and were calibrated with tetramethylsilane as an internal reference (TMS, δ = 0.0 ppm). IR spectra were recorded on a Perkin-Elmer 1605

series FT-IR spectrometer. Melting points were determined by using a Büchi Smp-20 apparatus. Elemental analyses were measured on a Carlo Erba Elemental Analyzer 1106. For mass spectra a MAT 90, Finnigan and a MAT 8200, Finnigan were used. Preparative HPLC was performed on a Kontron system (422 pump and detector 433). A Lichrosorb RP-18 column was used. For the cyclic voltammetry measurements in the range of 20-500 mVs^{-1} a potentiostat 362 from Princeton Applied Research and an XY-recorder PM 8271 (Philips) were used. Acetonitrile for cyclic voltammetry and oxidation experiments was purchased from Riedel-de-Haen (Chromasolv) and distilled from CaH_2. Tetra-*n*- butylammonium hexafluorophosphate was purchased from Fluka. **TNPA** [15a] and **FePhen** [15b] were prepared as described earlier.

General procedure: Dichlorodimethylsilane (185 mg, 1.44 mmol) and dry sodium iodide (430 mg, 2.88 mmol) were dissolved in dry acetonitrile (10 ml) and cooled to 0 °C. Dry triethylamine (303 mg, 3.00 mmol) and a solution of the naphthol (2.87 mmol) in dry THF (5 ml) were added subsequently. The ice bath was removed and the mixture was stirred for 2 h before hydrolysis with saturated aqueous $NaHCO_3$. After extraction with dichloromethane, the organic layer was washed with saturated aqueous NaCl and water and dried over Na_2SO_4. The solvent was evaporated and *n*-hexane was added to the residue. The remaining precipitate was removed by filtration and the filtrate was stored at −40 °C. The precipitating product was collected and dried under vacuum.

Bis-(4-methoxynaphth-1-yloxy)dimethylsilane **(5):** yield: 75% of as colorless solid. M. p. 123 °C. – IR (KBr): ν = 2960 (m), 2835 (m), 1593 (s), 1461 (s), 1387 (s), 1266 (s), 1094 (s), 982 (s), 888 (s), 812 (s), 768 (s) cm^{-1}. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.46 (s, 6 H, $(CH_3)_2Si$), 3.95 (s, 6 H, OCH_3), 6.63 (d, ^3J = 8.3 Hz, 2 H, 3-H, 3'-H), 6.97 (d, ^3J = 8.3 Hz, 2 H, 2-H, 2'-H), 7.50 (m, 4 H, 6-H, 6'-H, 7-H, 7'-H), 8.12 (m, 2 H, 8-H, 8'-H), 8.23 (m, 2 H, 5-H, 5'-H). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = −1.4 ($(CH_3)_2Si$), 56.7 (OCH_3), 104.4 (C-3, C-3'), 113.4, 122.9, 123.2, 126.6, 127.0, 127.0, 127.5, 144.8, 151.5. – $C_{24}H_{24}O_4Si$ (404.5): calcd. C 71.26, H 5.98; found C 71.19, H 6.12.

Bis-(4-ethoxynaphth-1-yloxy)dimethylsilane **(6):** yield 37% as colorless solid. M. p. 103 °C. – IR (KBr): ν = 2977 (m), 2878 (w), 1595 (s), 1458 (s), 1380 (s), 1232 (s), 1085 (s), 914 (s), 880 (s), 820 (s), 767 (s) cm^{-1}. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.46 (s, 6 H, $(CH_3)_2Si$), 1.52 (t, ^3J = 7.0 Hz, 6 H, CH_3CH_2O), 4.14 (q, ^3J = 7.0 Hz, 4 H, CH_3CH_2O), 6.62 (d, ^3J = 8.3 Hz, 2 H, 2-H, 2'-H), 6.96 (d, ^3J = 8.3 Hz, 2 H, 3-H, 3'-H), 7.50 (m, 4 H, 6-H, 6'-H, 7-H, 7'-H), 8.12 (m, 2 H, 8-H, 8'-H), 8.23 (m, 2 H, 5-H, 5'-H). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = −2.4 ($(CH_3)_2Si$), 14.9 (CH_3CH_2O), 63.9 (CH_3CH_2O), 104.5, 112.6, 122.0, 122.1, 125.5, 125.9, 126.7, 128.1, 143.7, 149.8. – $C_{26}H_{28}O_4Si$ (432.6): calcd. C 72.19, H 6.52; found C 71.78, H 6.66.

Bis-(6-methoxynaphth-2-yloxy)dimethylsilane **(7):** yield: 69% as a colorless solid. M. p. 116 °C. – IR (KBr): ν = 2962 (w), 1605 (s), 1505 (m), 1388 (m), 1237 (s), 1153 (m), 1119 (m), 980 (m), 855 (m), 810 (m) cm^{-1}. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.46 (s, 6 H, $(CH_3)_2Si$), 3.91 (s, 6 H, OCH_3), 7.11 (d, ^4J = 2.4 Hz, 2 H, 5-H, 5'-H), 7.13 (dd, ^3J = 10.0 Hz, ^4J = 2.4 Hz, 2 H, 7-H, 7'-H), 7.21 (dd, ^3J = 9.0 Hz, ^4J = 2.4 Hz, 2 H, 3-H, 3'-H), 7.34 (d, ^4J = 2.4 Hz, 2 H, 1-H, 1'-H), 7.60 (d, ^3J = 10.0 Hz, 2 H, 8-H, 8'-H), 7.66 (d, ^3J = 9.0 Hz, 2 H, 4-H, 4'-H). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = −2.2 ($(CH_3)_2Si$), 55.3 (OCH_3), 105.8, 115.1, 119.1, 121.8, 128.2, 128.3, 129.8, 130.4, 150.3, 156.4. – $C_{24}H_{24}O_4Si$ (404.5): calcd. C 71.26, H 5.98; found C 70.80, H 6.09.

N,N-Diethylamino-(4-methoxynaphth-1-yloxy)dimethylsilane **(9):** Chloro-*N,N*-diethylaminodimethylsilane (381 mg, 2.30 mmol) was dissolved in dry acetonitrile (10 ml) and dry triethylamine (233 mg, 2.30 mmol) was added at 0 °C. A solution of 4-methoxy-1-naphthol (400 mg, 2.30 mmol) in dry acetonitrile (5 ml) was added dropwise. After removing the ice bath, the reaction mixture was stirred for 2 h and then extracted with dry *n*-hexane (4 × 10 ml) under inert gas atmosphere. After evaporation of the *n*-hexane, 525 mg (75%) of a light yellow oil remained that was used without further purification. ^{1}H NMR: (200 MHz, $CDCl_3$): δ = 0.30 (s, 6 H, $(CH_3)_2Si$), 0.95, (t, ^3J = 7.0 Hz, 6 H, $(CH_3CH_2)_2N$), 2.80 (q, ^3J = 7.0 Hz, 4 H, $(CH_3CH_2)_2N$), 3.97 (s, 3 H, CH_3O), 6.66 (d, ^3J = 8.4 Hz, 1 H, 2-H), 6.87 (d, ^3J = 8.4 Hz, 1 H, 3-H), 7.50 (m, 2 H, 6-H, 7-H), 8.12 (m, 1 H, 8-H), 8.23 (m, 1 H, 5-H).

(4-Ethoxynaphth-1-yloxy)-(4-methoxynaphth-1-yloxy)dimethylsilane **(11):** At 0 °C acetylchloride (129 mg, 1.64 mmol) was added dropwise to a solution of *N,N*-diethylamino-(4-methoxynaphth-1-yloxy)dimethylsilane (500 mg, 1.64 mmol) in dry acetonitrile (15 ml). After stirring the solution for 30 min at 0 °C dry triethylamine (166 mg, 1.64 mmol) was added, followed by the addition of a solution of 4-ethoxy-1-naphthol (309 mg, 1.64 mmol) in dry acetonitrile (5 ml). After removal of the ice bath the mixture was stirred for 2 h and afterwards hydrolyzed with saturated aqueous $NaHCO_3$. The aqueous layer was extracted with *n*-hexane and the combined organic layers were washed with saturated aqueous NaCl and water. After drying over Na_2SO_4 and removal of the solvents, 660 mg of a brown oil remained. *n*-Hexane was added to the crude product and the solution was stored at 0 °C. The formed precipitate was collected and further purified by preparative HPLC (RP-18, acetonitrile) yielding 41% of a colorless oil. ^{1}H NMR: (200 MHz, $CDCl_3$): δ = 0.46 (s, 6 H, $(CH_3)_2Si$), 1.52 (t, ^3J = 6.9 Hz, 3 H, CH_3CH_2O), 3.95 (s, 3 H, CH_3O), 4.14 (q, ^3J = 6.9 Hz, 2 H, CH_3CH_2O), 6.61 (d, ^3J = 8.3 Hz,

^3J = 8.3 Hz, 2 H, 2-H or 2'-H), 6.62 (d, ^3J = 8.3 Hz, ^3J = 8.3 Hz, 2 H, 2-H or 2'-H), 6.96 (d, ^3J = 8.3 Hz, 1 H, 3-H or 3'-H), 6.98 (d, ^3J = 8.3 Hz, 1 H, 3-H or 3'-H), 7.50 (m, 4 H, 6-H, 6'-H, 7-H, 7'-H), 8.13 (m, 2 H, 8-H, 8'-H), 8.28 (m, 2 H, 5-H, 5'-H). – ^{13}C NMR: (50 MHz, $CDCl_3$): δ = −2.4 ($(CH_3)_2Si$), 14.9 (CH_3CH_2O), 55.6 (CH_3O), 63.9 (CH_3CH_2O), 103.4, 104.4, 112.4, 112.5, 121.9, 122.0, 122.1, 122.2, 125.5, 125.6, 125.9, 126.0, 126.5, 126.7, 128.0, 128.0, 143.6, 143.7, 149.8, 150.4. – MS (EI, 70 eV): *m/z* (%): 418.2 (69) [M^+], 389.1 (6), 231.2 (100), 201.1 (27), 187.1 (15), 185.1 (44), 173.1 (38), 159.1 (13), 145.1 (13), 128.2 (13), 115.2 (15), 102.2 (12), 75.0 (10), 29.1 (42). – HRMS: $C_{25}H_{26}O_4Si$: calcd. 418.1600, found 418.1609.

(6-Ethoxynaphth-2-yloxy)-(6-methoxynaphth-2-yloxy)dimethylsilane **(12):** The synthesis of **12** was performed according to that of **11** yielding 49% of a colorless oil. ^{1}H NMR: (200 MHz, $CDCl_3$): δ = 0.44 (s, 6 H, CH_3Si), 1.47 (t, ^3J = 7.1 Hz, 3 H, CH_3CH_2O), 3.90 (s, 3 H, CH_3O), 4.12 (q, ^3J = 7.1 Hz, 2 H, CH_3CH_2O), 7.00 – 7.20 (m, 8 H, H-Ph), 7.30 (m, 2 H, Ph-H), 7.60 (m, 4 H, H-Ph). – ^{13}C NMR: (50 MHz, $CDCl_3$): δ = −2.2 ($(CH_3)_2Si$), 14.8 (CH_3CH_2O), 55.3 (CH_3O), 63.4 (CH_3CH_2O), 105.7, 106.6, 115.1, 115.2, 119.0, 119.2, 121.7, 121.8, 128.1, 128.2, 128.3, 129.7, 129.7, 130.4, 130.5, 150.1, 150.2, 155.8, 156.5. – MS (EI, 70 eV): *m/z* (%): 418.2 (100) [M^+], 231.2 (29), 201.1 (15), 188.1 (12), 185.1 (14), 173.1 (25), 157. (11), 131.2 (25), 115.2 (21), 102.2 (32), 77.2 (12), 57.1 (25), 43.1 (47), 29.1 (76). – HRMS: $C_{25}H_{26}O_4Si$: calcd. 418.1600, found 418.1601.

Oxidation of **5-7, 11** *and* **12:** The oxidation experiments were carried out as described earlier by our group [10] and others (PIFA, [6f,16] $CuCl_2 \bullet H_2O$ [17] and purified by HPLC (Lichrosorb RP-18, acetonitrile/water 80 : 20). Products **13** [18], **14** [19] and **16** [20] were characterized by comparison to ^{1}H NMR data in the literature.

4,4'-Dimethoxy-[2,2']-binaphthalinyl-1,1'-diol **(13):** ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.94 (s, 6 H, CH_3O), 5.10 (s, 2 H, OH), 6.98 (s, 2 H, H-3, H-3'), 7.56 (m, 2 H, H-6, H-6', H-7, H-7'), 8.04 (d, ^3J = 8.7 Hz, 2 H, H-8, H-8'), 8.28 (d, ^3J = 8.8 Hz, 2 H, H-5, H-5') [18].

4,4'-Diethoxy-[2,2']-binaphthalinyl-1,1'-diol **(14):** ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.55 (t, ^3J = 7.0 Hz, 6 H, CH_3CH_2O), 4.18 (q, ^3J = 7.0 Hz, 4 H, CH_3CH_2O), 4.96 (s, 2 H, OH), 6.99 (s, 2 H, 3-H, 3'-H), 7.57 (m, 4 H, 6-H, 6'-H, 7-H, 7'-H), 8.03 (d, ^3J = 8.7 Hz, 2 H, 8-H, 8'-H), 8.32 (d, ^3J = 8.5 Hz, 2 H, 5-H, 5'-H) [19].

4-Methoxy-4'-ethoxy-[2,2']-binaphthalinyl-1,1'-diol **(15):** ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.54 (t, ^3J = 7.0 Hz, 6 H, CH_3CH_2O), 3.94 (s, 6 H, CH_3O), 4.17 (q, ^3J = 7.0 Hz, 4 H, CH_3CH_2O), 5.2 (br. s, 2 H, OH), 6.99 (2 s, 2 H, 3-H, 3'-H), 7.57 (m, 4 H, 6-H, 6'-H, 7-H, 7'-H), 8.03 (m, 2 H, 8-H, 8'-H), 8.32 (m, 2 H, 5-H, 5'-H). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 14.8 (CH_3CH_2O), 56.6 (CH_3O), 64.1 (CH_3CH_2O), 104.4, 106.1, 115.4, 115.5, 122.0, 122.2, 122.9, 123.1, 125.5, 125.6, 125.9, 126.0, 126.2, 126.5 126.7, 142.4, 142.5, 149.4, 149.1. – MS (EI, 70 eV): *m/z* (%): 360.2 [M^+] (33), 345.2 (12), 316.2 (7), 215.5 (5), 186.1 (9), 149.2 (5), 121.0 (11), 83.0 (24), 69.2 (9), 43.1 (100), 29.1 (14).

6,6'-Dimethoxy-[1,1']-binaphthalinyl-2,2'-diol **(16):** ^{1}H NMR (200 MHz, $CDCl_3$): 3.89 (s, 6 H, CH_3O), 4.97 (br. s, 2 H, OH), 6.96 (dd, ^3J = 9.3 Hz, ^3J = 2.5 Hz, 2 H, 7-H, 7'-H), 7.04 (d, ^3J = 9.3 Hz, 2 H, 8-H, 8'-H), 7.19 (d, ^3J =2.5 Hz, 2 H, 5-H, 5'-H), 7.32 (d, ^3J = 9.0 Hz, 2 H, 3-H, 3'-H), 7.84 (d, ^3J = 9.0 Hz, 2 H, 4-H, 4'-H). – ^{13}C NMR (50 MHz, $CDCl_3$): 55.3 (CH_3O), 106.8, 111.4, 118.1, 119.7, 125.8, 128.6, 129.9, 130.3, 150.9, 156.3 [20].

6'-Ethoxy-6-methoxy-[1,1']-binaphthalinyl-2,2'-diol **(17):** ^{1}H NMR (200 MHz, $CDCl_3$): 1.46 (t, ^3J = 6.8 Hz, 3 H, CH_3CH_2O), 3.90 (s, 3 H, CH_3O), 4.12 (q, ^3J = 6.8 Hz, 2 H, CH_3CH_2O), 4.92 (br. s, 2 H, OH), 6.96 (dd, ^3J = 9.3 Hz, ^3J = 2.5 Hz, 2 H, 7-H, 7'-H), 7.04 (2 d, ^3J = 9.3 Hz, 2 H, 8-H, 8'-H), 7.19 (2 d, ^3J = 2.5 Hz, 2 H, 5-H, 5'-H), 7.32 (2 d, ^3J = 9.0 Hz, 2 H, 3-H, 3'-H), 7.82 (2 d, ^3J = 9.0 Hz, 2 H, 4-H, 4'-H). – ^{13}C NMR (50 MHz, $CDCl_3$): 14.8 (CH_3CH_2O), 55.4 (CH_3O), 63.5 (CH_3CH_2O), 106.8, 107.6, 111.2 , 111.3, 118.0, 118.1, 119.7, 120.1, 125.7, 125.8, 128.3, 129.9, 130.3, 130.4, 150.9, 150.9, 156.4. – MS (EI, 70 eV): *m/z* (%): 360.2 [M^+] (43), 345.2 (8), 331.2 (7), 317.2 (2), 285.2 (7), 242.2 (7), 213.2 (13), 187.1 (5), 173.1 (4), 157.2 (5), 106.8 (7), 69.2 (9), 55.1 (15), 43.1 (29), 29.1 (100).

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