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# Unsymmetrical tetrahedrally substituted tribenzosilatranes

Corinne Soulié*

*Laboratoire de Chimie Inorganique et Matériaux Moléculaires, CNRS ESA 7071, Ecole Supérieure de Physique et Chimie Industrielles, 10 rue Vauquelin, 75231 Paris Cedex 05, France*

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**Abstract**—A tetraalkyltribenzosilatrane with four paraffinic chains of different length has been synthesized in 11 steps with an overall yield of 16%. In the resulting molecule, four different substituents are distributed at the apices of the pyramidal tribenzosilatrane rigid core. Formally, this molecular architecture is a chiral macrocentre. The experimental methods for investigating the chirality of such objects are discussed. © 2001 Elsevier Science Ltd. All rights reserved.

## 1. Introduction

Functional trichlorosilanes substituted with a number of different side groups are now available. These compounds are generally used as interface coupling agents in the surface chemistry of silica, glass and related oxides.[1] Their availability in a wide variety of forms and their price stimulates their further development not only as coatings but also in bulk molecular materials. In the presence of water, trichlorosilanes polymerize quickly in a hardly controllable way, giving rise to graft silica but with a trifunctional alcohol of suitable shape, such as triethanolamine or *tris*-(2-phenol)amine, bimolecular reactions are favored, giving rise to well-defined cyclic compounds.[2,3]

Thus, in a previous paper, we showed that the reaction of *tris*-(2-alkyl-5-phenol)amine with an alkyl trichlorosilane produces with a high yield a tetrahedrally substituted tribenzosilatrane (Fig. 1).[4] This process may be applied to graft a number of different $R_4$ substituents onto the silicon bridgehead by varying the starting trichlorosilane. However, in order to gather as many functions as possible in the same molecule, one must be able to attach four different side groups ($R_1 \neq R_2 \neq R_3$) onto the tribenzosilatrane skeleton. Here, we report the synthesis of a tetraalkyl tribenzosilatrane substituted with four alkyl chains of different lengths.

## 2. Results

The whole synthesis of symmetrical tribenzosilatranes starting from *p*-alkylanilines has already been described and these compounds are obtained in eight steps with an overall yield of 10%.[4] In this case, the starting triphenolamine is symmetrical ($R_1=R_2=R_3$ in Fig. 1) and may be obtained by direct arylation at nitrogen (Ullmann condensation, Scheme 1).

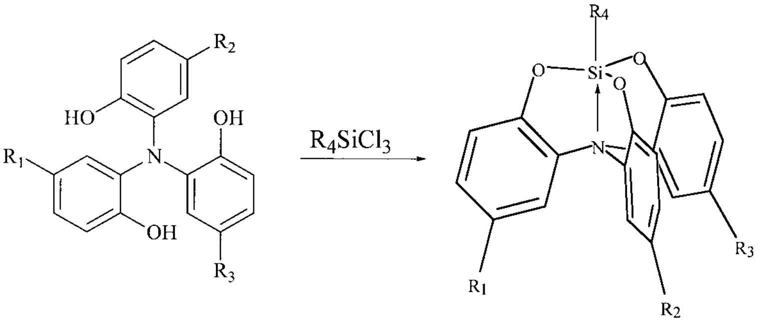

**Figure 1.** The 1:1 condensation of alkyltrichlorosilane onto a tris-(2-alkyl-5-phenol)amine leads to a symmetrical ($R_1=R_2=R_3$) or unsymmetrical ($R_1 \neq R_2 \neq R_3$) tetrahedrally substituted tribenzosiltrane.

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*Keywords*: chirality; cyclizations; silicon; synthetic methods; tribenzosilatranes.

* Tel.: +1-40-79-46-56; fax: +1-40-79-44-25; e-mail: Corinne.Soulie@espci.fr

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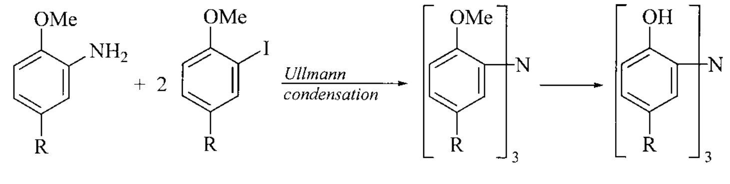


**Scheme 1.**

This method is often the simplest preparative route of secondary and tertiary aromatic amines, but special precautions have to be taken to avoid the over-arylation when secondary anilines are desired. In our attempts, 4-alkyl-2-anisidine has been reacted with various amounts of 4-alkyl-2-iodo-anisole; in all cases, the triarylated nitrogen was obtained, together with unreacted starting material, even when operating with a very large excess of primary anisidine (Scheme 2).

*ortho* Substituents are known to have a great influence on the rate and yield of the Ullmann condensation.[5] In our case, the methoxy group is rather small[6] and allows a fast substitution. Few synthetic routes to diarylamines can be found in literature: condensation of two nitro derivatives in the presence of hydrofluoric acid,[7] Chapman rearrangement in five steps from aniline,[8] hydrolysis of *N*,*N*-disulfonamides.[9] The most straight pathway is achieved in three steps from anisidine as shown in Scheme 3.

In the Goldberg reaction, a bromoaromatic derivative is reacted with an acetanilide in the presence of copper(I) iodide and potassium carbonate.[10–12] We found that 5-alkyl-2-methoxy acetanilide prepared by standard procedures[13,14] reacts readily with 2-iodo-4-alkyl anisole in presence of copper(0) and caesium carbonate (Scheme 3).

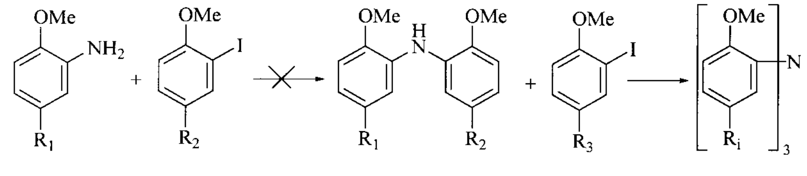
The diarylamine is then obtained by hydrolysis of the secondary acetanilide. The influence of *ortho* substituents on the rate of amide hydrolysis has been studied. Freeman showed that in the case of small substituents, such as *ortho* methyl groups, the basic hydrolysis takes place (with modest yields), whereas acidic hydrolysis is completely inefficient.[15] When operating with *ortho* methoxy substituents, we experienced that even in very rude conditions the hydrolysis with KOH failed. In our opinion this behavior may be related not only to the steric hindrance of *ortho* alkoxy substituents but also to the hydrophobicity of the long chains in compound **5**. As a matter of fact, when working with potassium *tert*-butanolate in place of KOH,[16] the secondary anisidine was obtained quantitatively. The latter was then arylated in the standard way and demethylated with $AlCl_3$ leading to the desired unsymmetrical *tris*(alkylphenol)amine (Scheme 1).

The cyclization with alkyltrichlrosilane was then achieved in dibutyl ether as already described (Fig. 1). The whole synthetic route is shown in Fig. 2. Starting from commercially available *para*-alkylphenols, 11 steps are necessary with an overall yield of 16%.[17,18]

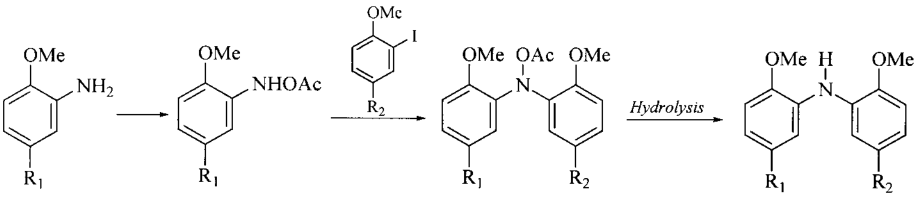
Compound **9abcd** with butyl, dodecyl, hexadecyl and octyl side chains was obtained as a viscous liquid. Attempts to crystallize it from solvents or by slow cooling down to −40°C under the polarizing microscope did not reveal any formation of crystalline seeds, in contrast to symmetric long-chains tribenzosilatranes, which were shown to be crystalline.[19] This feature may be related to the high entropic step associated with the ordering of polydisperse chains. It is noteworthy that due to the presence of four different side chains, the molecule is chiral. The mixture of two enantiomers in compound **9abcd** also contributes to increase the ordering entropy penalty.

## 3. Discussion

Resolution of racemic alkyl compounds seems rather difficult. Classical methods (preparation of diastereoisomers and separation,[20] gas[21] or liquid[22,23] chromatography, mechanical separation,[24] differential reactivity[25]) cannot be applied since they require generally a functional group such as



**Scheme 2.**



**Scheme 3.**

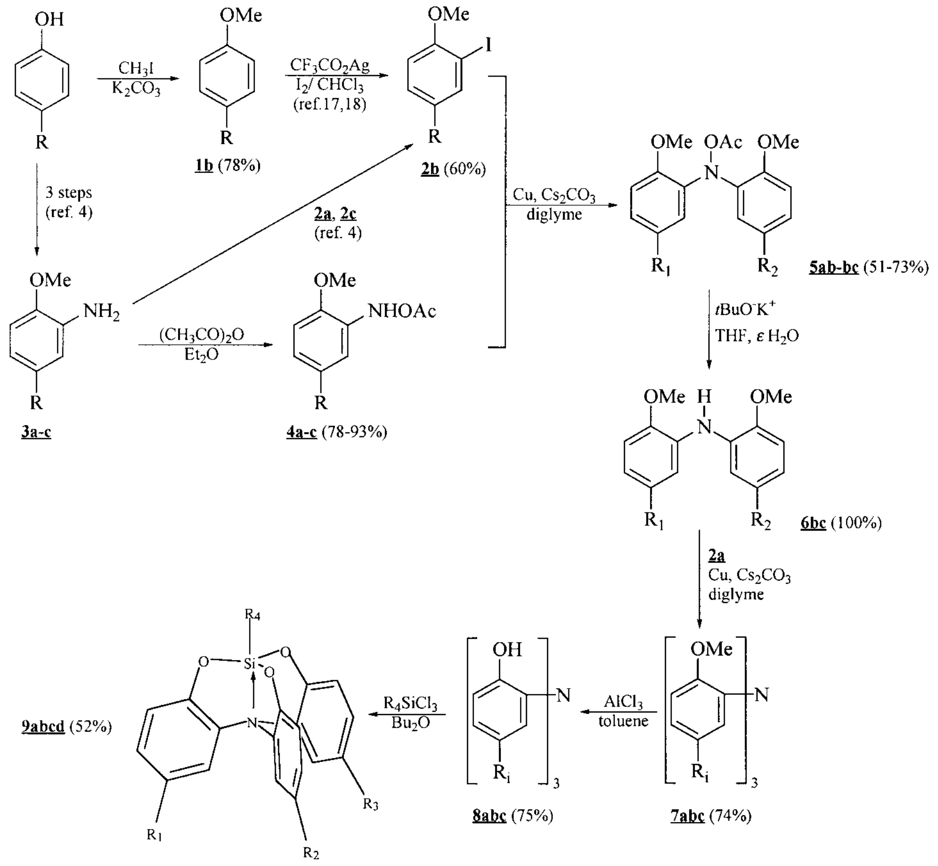


**Figure 2.** Chemical pathway to unsymmetrical tetraalkyltribenzosilatranes.

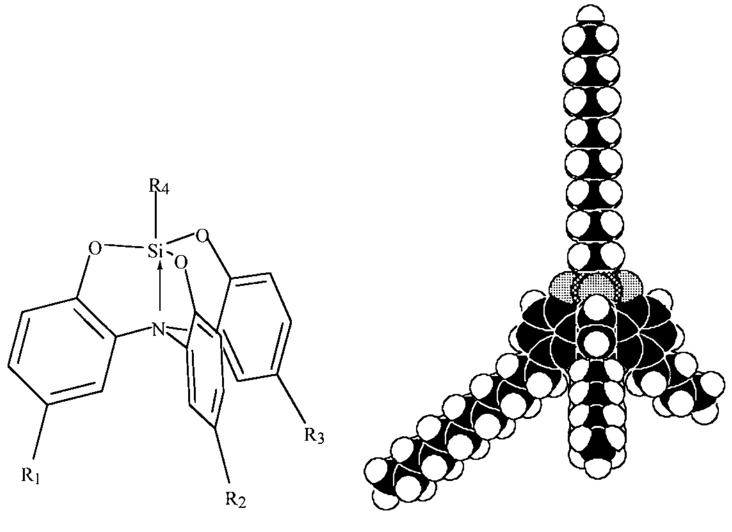


**Figure 3.** Schematic view and CPK model of an unsymmetrical tetrahedrally substituted tribenzosilatrane.

carboxylic acid, amine. For molecules with no functional groups, inclusion compounds are generally formed with urea,[26] chiral crown-ethers[27] or cyclodextrine derivatives.[†,28]

To our knowledge, the only other example of molecule whose chirality is attached to the length of alkyl chains is the family of tetraalkylmethanes. In this series, two synthetic routes can be followed. The first one is based upon the resolution of carboxylic derivatives before decarboxylation[29] and the second one is based upon stereoselective reactions.[30]

Another problem that takes place in the study of alkyl chains chiral compounds is the knowledge of their optical purity. An enantiomeric excess of 95±5% of

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[†] Cyclodextrine grafted stationary phases are known to be efficient for the resolution of saturated compounds with no functional groups. Our attemps using Chirose-bond® C1 columns were unsuccessful even on the analytical scale.

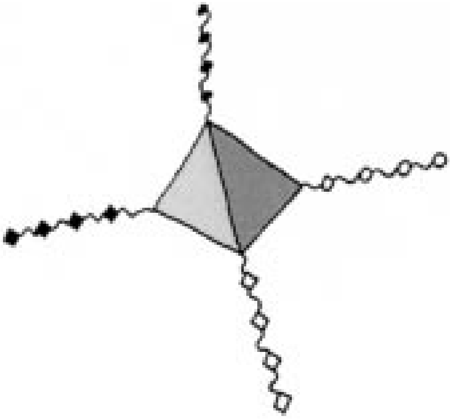

**Figure 4.** Schematic view of a starlike polyphilic compound: side chains of different nature may be used to control the self-assembling ability.

(−)-butylethylmethylpropylmethane gave rotatory power values from −0.608 to −0.198° for wavelengths varying from 365 to 578 nm.[31] This compound is, presently and as far as we know, the only optically active tetraalkylmethane. Same studies done on the optically pure butylethylhexylpropylmethane between 280 and 580 nm showed that the rotatory power was indeed too low to be measured.[29]

The CPK model of the *S* enantiomer of the unsymmetrical tetraalkyltribenzosilatrane is shown in Fig. 3. It can be seen that the four different chains are indeed tetrahedrally disposed on the tribenzosilatrane rigid core. So, instead of a chiral center encountered for the tetraalkylmethanes, we obtained a chiral *macrocentre* here. Indeed, it must be stressed that the unsymmetrical location of chemical groups around any given atom is not evident, unless in its very remote environment. If considering for instance the surrounding of nitrogen in compound **9abcd**, the distribution of close neighbors has the $C_{3v}$ symmetry up to a distance of eight chemical bonds. As a result, the chiral disturbance of molecular orbitals, which is responsible for the optical activity, is expected to be very small. Thus, according to the models developed for tetraalkylmethanes,[29,32] we estimate the molecular rotation of compound **9abcd** at the level of $10^{-5}$ degrees in the visible range.

Whereas numerous examples of optically active trialkylmethanes $R_1R_2R_3CH$ are known,[33] very few studies have been done on chiral tetraalkylmethanes. In 1965, Wynberg found no optical activity for butylethylhexylpropylmethane.[29] As theoretical models suggest the rotatory power to be very small, it might be thought that standard polarimeters are not convenient for such molecules, since the amount of rotation is known to depend upon the experimental measurements conditions. These conditions could then be modified to allow detection: for example, a polarimeter should measure rotations of less than 0.001° or should measure rotations at wavelengths around UV absorption maxima. For tetraalkylmethanes, the absorption maxima is expected at 176 nm in hexane ($\sigma \rightarrow \sigma^*$ transitions).[34] Classical polarimeters use wavelengths range of 600–260 nm, which is far to allow the measurement of the largest rotation value.

## 4. Conclusions

Thus, the unsymmetrical tetraalkyltribenzosilatrane **9abcd** was synthesized in 11 steps with an overall yield of 16% starting from *p*-alkylphenols. In conclusion, unsymmetrical tetrasubstituted tribenzosilatranes are then the first chiral macrocentres since, as their four substituents have a tetrahedral distribution, they can be considered as extended tetrahedrons ($C_1$ point group). They should be so able to display measurable optical activity, even a small one, with four different paraffinic tails. Of course, in compound **9abcd** synthesized so far, the four substituents differ only by their length and the only spectacular effect of this chemical constitution is merely a strong depression of the melting point. Less trivial behaviors may be expected whenever new functionality will be brought by four substituents of truly different nature. This should allow to modulate the self-assembling ability, dipole moment or polarizabilities, fluorescence or biological activity. Alternatively, reactive groups may be attached at the apices of the tribenzosilatrane extended tetrahedron and thus permit post-functionalization or grafting onto a polymeric backbone. As an example, four chains of comparable size but of different chemical nature like alkyl, perfluoroalkyl, might be used to construct a starlike polyphilic compound (Fig. 4) with unconventional structure.[35–37] It is clear that the presence of side groups other than alkyl will certainly affect the yields of the reactions, however, we hope that the method hereby presented will help the chemists in this endeavors to synthesize new silylated molecular materials with tunable physicochemical properties.

## 5. Experimental

### 5.1. General

Silica gel was used for column chromatographies (Merck 7734, 0,063–0,200 μm), NMR spectra were recorded in $CDCl_3$ using a Brucker 300 spectrometer, and IR-spectra using a Perkin–Elmer 1600 spectrophotometer.

Syntheses of compounds **2a**, **2c**, **5a–c** and starting *p*-alkylphenols have already been described in Ref. 4a. **a**=$C_4H_9$; **b**=$C_8H_{17}$; **c**=$C_{12}H_{25}$; **d**=$C_{16}H_{33}$.

**5.1.1. *p*-Octylanisole (1b).** 5.6 mL (24.25 mmol) of methyliodide was added to a mixture of *p*-octylphenol (5 g, 24.25 mmol) and potassium carbonate (20 g) in 20 mL of freshly distilled DMF. The reaction mixture was heated at 40°C over the night. After an excess of pure water has been added, the product was extracted with dichloromethane, washed with water and purified on a silica gel column (eluent: dichloromethane). Recrystallization from pentane gave the desired product in 70% yield as a white powder. $^1H$ NMR downfield from TMS ($CDCl_3$): $\delta$: 7.15–6.85 (4H, AB, Ar), 3.85 (3H, s, $OCH_3$), 2.55 (2H, t, Ar–$CH_2$), 1.65–0.9 (15H, m, $C_7H_{15}$). $^{13}C$ NMR ($CDCl_3$): $\delta$: 147.3 ($ArC_1$), 132.8 ($ArC_4$), 128.9 ($ArC_{3,5}$), 114.5 ($ArC_{2,6}$), 35.5 (Ar–$CH_2$), 33.3–14.9 ($C_{11}H_{23}$). IR (KBr): 1282m ($\nu_{C-H,\ OMe}$), 1255m ($\nu_{C-O}$).

**5.1.2. 2-Iodo-4-octylanisole (2b).** In a three-necked flask, fitted with a reflux condenser and a nitrogen purge line, were placed **1b** (4.6 g, 16.6 mmol) and silver trifluoroacetate (3.66 g, 16.6 mmol). A solution of diiodide in chloroform (4.3 g of $I_2$, 16.6 mmol in 50 mL of chloroform) was then added dropwise. The deep purple diiodide solution turned light-yellow rapidly when reacting. After 2 h, silver iodide was filtered out and the solution washed with water. The product was purified on a silica gel column (eluent: dichloromethane) and on a second one (eluent: dichloromethane/cyclohexane) yielding **2b** in 60% yield as a yellow liquid. $^1$H NMR downfield from TMS ($CDCl_3$): $\delta$: 7.5 (1H, d, $J$=5 Hz, Ar), 7.0 (1H, dd, $J$=5, 9 Hz, Ar), 6.7 (1H, d, $J$=9 Hz, Ar), 3.8 (3H, s, $OCH_3$), 2.4 (2H, t, Ar–$CH_2$), 1.6–0.8 (15H, m, $C_7H_{15}$). $^{13}$C NMR ($CDCl_3$): $\delta$: 156.0 (ArC$_1$), 139.1 (ArC$_5$), 137.1 (ArC$_6$), 129.2 (ArC$_4$), 110.6 (ArC$_3$), 85.7 (ArC$_2$), 56.3 ($OCH_3$), 34.4 (Ar–$CH_2$), 31.8–14.0 ($C_7H_{15}$). IR (KBr): 1280m ($\nu_{\text{C–H, OMe}}$), 1254s ($\nu_{\text{C–O}}$), 553w ($\nu_{\text{C–I}}$). TLC ($SiO_2$, $CH_2Cl_2/C_6H_{12}$, v/v: 1/1): $R_f$=0.76.

**5.1.3. 2-Methoxy-5-alkylacetanilides (4a–c).** To a solution of 2-methoxy-4-dodecylaniline **3c** (3.63 g, 12.5 mmol) in 50 mL of diethylether and 100 mL of distilled water were added 4 portions (2.5 mL each, 2.3 equiv.) of acetic anhydride over a total period of 1 h. The reaction was followed by $SiO_2$ TLC. The product was extracted with dichloromethane, washed with water, purified on a silica gel column (eluent: dichloromethane) and recrystallized from pentane. **4a**: 78% yield, beige plate-like crystals; **4b**: 86% yield, light-pink crystals; **4c**: 95% yield, white powder. $^1$H NMR downfield from TMS ($CDCl_3$): $\delta$: 8.2 (1H, s, Ar), 7.7 (1H, s, NH), 6.7 (2H, m, Ar), 3.8 (3H, s, $OCH_3$), 2.5 (2H, t, Ar–$CH_2$), 2.2 (3H, s, $NCOCH_3$), 1.3–0.9 (23H, m, $C_{11}H_{23}$). $^{13}$C NMR ($CDCl_3$): $\delta$: 168.0 (CO), 145.5 (ArC$_2$), 135.7 (ArC$_5$), 127.3 (ArC$_1$), 123.0 (ArC$_6$), 119.6 (ArC$_4$), 109.4 (ArC$_3$), 55.5 ($OCH_3$), 35.4–14.0 ($C_{12}H_{25}$), 22.5 ($COCH_3$). IR (KBr): 3276s ($\nu_{\text{N–H}}$), 1668s ($\nu_{\text{C=O, amide II}}$). TLC ($SiO_2$, dichloromethane): $R_f$=0.55.

**5.1.4. 5-Alkyl-5′-alkyl-2,2′-dimethoxydiacetanilides (5ab–bc).** In a three-necked flask, fitted with a condenser and a nitrogen purge line, were placed 2-methoxy-5-dodecylacetanilide **4c** (1.2 g, 3.6 mmol), 2-iodo-4-octylanisole **2b** (1.5 g, 4.32 mmol), spongy copper powder (0.482 g, 7.41 mmol), caesium carbonate (2.814 g, 8.64 mmol), 18-crown-6 (0.105 g, 0.432 mmol) and 10 mL of diglyme. The reaction mixture was refluxed for at least 24 h, then filtered on a Buchner funnel and washed with hot diglyme. The diglyme was removed by distillation under vacuum (bp=60.5°C/15 mmHg). The residue was purified on a silica gel column (eluent: dichloromethane). **5ab**: 56% yield, brown liquid; **5bc**: 73% yield, brown liquid. $^1$H NMR downfield from TMS ($CDCl_3$): $\delta$: 7.2–7.0 (4H, m, Ar), 6.9 (2H, m, Ar), 3.9 (6H, 2s, $OCH_3$), 2.4 (4H, 2t, Ar–$CH_2$), 2.0 (3H, s, $NCOCH_3$), 1.45–0.8 (38H, m, $C_7H_{15}+C_{11}H_{23}$). $^{13}$C NMR ($CDCl_3$): $\delta$: 172.4 (CO), 153.9–153.7 (ArC$_2$C$_{2'}$), 136.5–136.2 (ArC$_5$C$_{5'}$), 133.1–132.3 (ArC$_4$C$_{4'}$), 130.4–130.0 (ArC$_6$C$_{6'}$), 129.5–129.0 (ArC$_1$C$_{1'}$), 112.9–112.5 (ArC$_3$C$_{3'}$), 56.7–56.3 ($OCH_3$), 35.8–35.6 (Ar–$CH_2$), 32.8–14.9 ($C_{11}+C_7$), 22.8 ($COCH_3$). It is noteworthy that all peaks are double (except for the $COCH_3$ fragment) thus showing the embedded rotation of amides. IR (KBr): 1684s ($\nu_{\text{C=O, amide III}}$). TLC ($SiO_2$, dichloromethane): $R_f$=0.15.

**5.1.5. 5-Dodecyl-5′-octyl-2,2′-dimethoxydianiline (6bc).** In a three-necked flask, fitted with a condenser and a nitrogen purge line, 5-dodecyl-5′-octyl-2,2′-dimethoxydiacetanilide **5bc** (0.938 g, 1.7 mmol), freshly sublimated potassium *tert*-butylate (1.257 g, 11.22 mmol) and 15 mL of dry THF were introduced. The apparatus was purged and 66 μL of distilled water (3.4 mmol) were added. The mixture was refluxed 3 h and then cooled on an ice bath. The cold mixture was added with ice, extracted with diethylether and washed with water. The product was purified on a silica gel column yielding the desired aniline **6bc** quantitatively (eluent: dichloromethane). It is noteworthy that the reaction can be run with standard THF. In this case, catalytic amount of water is not required. $^1$H NMR downfield from TMS ($CDCl_3$): $\delta$: 7.15 (2H, d, $J$=1.5 Hz, Ar), 6.8 (2H, d, $J$=7.5 Hz, Ar), 6.6 (2H, dd, $J$=1.5, 7.5 Hz, Ar), 3.75 (6H, s, $OCH_3$), 2.45 (4H, t, Ar–$CH_2$), 1.6–0.8 (38H, m, $C_7H_{15}+C_{11}H_{23}$), 1.35 (1H, s, NH). $^{13}$C NMR ($CDCl_3$): $\delta$: 147.0 (ArC$_2$C$_{2'}$), 135.1 (ArC$_5$C$_{5'}$), 132.1 (ArC$_1$C$_{1'}$), 119.5 (ArC$_4$C$_{4'}$), 115.7 (ArC$_6$C$_{6'}$), 110.3 (ArC$_3$C$_{3'}$), 55.6 ($OCH_3$), 35.4 (Ar–$CH_2$), 31.8–14.2 ($C_{11}+C_7$). IR (KBr): 3424m ($\nu_{\text{N–H}}$), no band in the 1700–1650 region. TLC ($SiO_2$, dichloromethane): $R_f$=0.90.

**5.1.6. (5-Butyl-5′-dodecyl-5″-octyl-2,2′,2″-trimethoxytriphenyl)amine (7abc).** In a three-necked flask, fitted with a condenser and a nitrogen purge line, were placed 5-dodecyl-5′-octyl-2,2′-dimethoxydianiline **6bc** (0.169 g, 0.332 mmol), 2-iodo-4-butylanisole **2a** (0.137 g, 0.397 mmol), spongy copper powder (0.044 g, 0.681 mmol), caesium carbonate (0.258 g, 0.791 mmol), 18-crown-6 (0.010 g, 0.039 mmol) and 5 mL of diglyme. The reaction mixture was refluxed for 70 h, then filtered on a Buchner funnel and washed with hot diglyme. The diglyme was removed by distillation under vacuum and the residue purified on a silica preparative TLC plate (eluent: dichloromethane). The desired product was obtained as light-brown viscous liquid in 74% yield. $^1$H NMR downfield from TMS ($CDCl_3$): $\delta$: 6.75 (3H, dd, $J$=1.5, 7.5 Hz, Ar), 6.65 (3H, d, $J$=7.5 Hz, Ar), 6.5 (3H, d, $J$=1.5 Hz, Ar), 3.45 (9H, s, $OCH_3$), 2.35 (6H, t, Ar–$CH_2$), 1.4–0.8 (45H, m, $C_3H_7+C_7H_{15}+C_{11}H_{23}$). $^{13}$C NMR ($CDCl_3$): $\delta$: 151.0 (ArC$_2$C$_{2'}$C$_{2''}$), 137.3 (ArC$_5$C$_{5'}$C$_{5''}$), 134.9 (ArC$_1$C$_{1'}$C$_{1''}$), 124.4 (ArC$_6$C$_{6'}$C$_{6''}$), 122.9 (ArC$_4$C$_{4'}$C$_{4''}$), 112.2 (ArC$_3$C$_{3'}$C$_{3''}$), 55.6 ($OCH_3$), 34.9 (Ar–$CH_2$), 31.8–13.8 ($C_{11}+C_7+C_3$). IR (KBr): no band in the 3500–3300 region. TLC ($SiO_2$, dichloromethane): $R_f$=0.65.

**5.1.7. (5-Butyl-5′-dodecyl-5″-octyl-2,2′,2″-triphenol)amine (8abc).** In a three-necked flask, fitted with a condenser and a nitrogen purge line, were placed (5-butyl-5′-dodecyl-5″-octyl-2,2′,2″-trimethoxytriphenyl)amine **7abc** (0.165 g, 0.246 mmol), anhydrous aluminum chloride (0.100 g, 0.741 mmol) and 10 mL of dry toluene. The solution was refluxed for at least 4 h and then hydrolyzed with 10 mL of aqueous hydrochloric acid (10%, v/v). The organic part was washed with water and separated on a silica preparative TLC plate (eluent: dichloromethane). The desired product was obtained in 75% yield as a light-brown viscous liquid. $^1$H NMR downfield from TMS ($CDCl_3$): $\delta$: 6.8 (3H, dd, $J$=1.5, 7.5 Hz, Ar), 6.7 (3H, d, $J$=7.5 Hz, Ar), 6.6 (3H, d, $J$=1.5 Hz, Ar), 5.45 (3H, large peak, OH), 2.4 (6H, t, Ar–$CH_2$), 1.5–0.8 (45H, m,

$C_3H_7+C_7H_{15}+C_{11}H_{23}$). $^{13}C$ NMR ($CDCl_3$): $\delta$: 151.0 ($ArC_2C_{2'}C_{2''}$), 137.3 ($ArC_5C_{5'}C_{5''}$), 134.9 ($ArC_1C_{1'}C_{1''}$), 124.4 ($ArC_6C_{6'}C_{6''}$), 122.9 ($ArC_4C_{4'}C_{4''}$), 112.2 ($ArC_3C_{3'}C_{3''}$), 55.6 ($OCH_3$), 34.9 (Ar–$CH_2$), 31.8–13. ($C_{11}+C_7+C_3$). IR (KBr): 3422m ($\nu_{O-H}$). TLC ($SiO_2$, dichloromethane): $R_f$=0.1.

**5.1.8. 1-Hexadecyl-((13-butyl-17-dodecyl-21-octyl)-3,4,6,7,10,11-tribenzo)silatrane (9abcd).** In a three-necked flask, fitted with a condenser and a nitrogen purge line, were placed (5-butyl-5′-dodecyl-5″-octyl-2,2′,2″-triphenol)-amine **8abc** (0.116 g, 0.184 mmol), 5 mL of dry dibutylether and trichlorohexadecylsilane (0.066 g, 0.184 mmol). The solution was stirred under reflux for 18 h. The dibutylether was removed by distillation under vacuum and the residue was separated on a silica preparative TLC plate with a pentane/ethylacetate (v/v: 95/5) as the eluent. The silatrane was obtained in 52% yield as a light-yellow viscous liquid. $^1H$ NMR downfield from TMS ($CDCl_3$): $\delta$: 7.45 (3H, d, $J$=1.5 Hz, Ar), 6.8 (6H, m, Ar), 2.5 (6H, t, Ar–$CH_2$), 1.6–1.2 (64H, m, $C_2H_4+C_6H_{12}+C_{10}H_{20}+C_{14}H_{28}$), 0.8 (14H, m, 4×$CH_3$+$SiCH_2$). $^{13}C$ NMR ($CDCl_3$): $\delta$: 151.5 ($ArC_2C_{2'}C_{2''}$), 136.4 ($ArC_5C_{5'}C_{5''}$), 136.2 ($ArC_1C_{1'}C_{1''}$), 128.4 ($ArC_6C_{6'}C_{6''}$), 126.2 ($ArC_4C_{4'}C_{4''}$), 117.2 ($ArC_3C_{3'}C_{3''}$), 35.3–33.8 (Ar–$CH_2$), 33.2–22.1 ($(CH_2)_n$), 14.0–13.8 ($CH_3$), 13.5 (Si–$CH_2$). IR (KBr): 1295m ($\nu_{C-O}$), 916m ($\nu_{Si-O-Ar}$), 826m ($\nu_{Si-C}$), 595m ($\nu_{Si\rightarrow N}$). TLC ($SiO_2$, pentane+5% AcOEt): $R_f$=0.4.

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