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Nematic tribenzosilatrane

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The linkage of benzylsilatrane groups to laterally functionalized mesogens allows the investigation of molecular systems which contain propeller shaped mesogens and exhibit nematic phase behaviour.

1. Introduction

Thermotropic liquid crystalline systems are typically built up from extended aromatic groups, which promote crystalline behaviour. The strength of the van der Waals interactions of the aromatic groups in the condensed phase is modulated by the attachment of flexible chains, facilitating the formation of liquid crystalline phases. In most cases alkyl chains are used to achieve the orientational (nematic) or orientational and positional ordering (smectic, columnar) in the desired temperature range. The conceptualization of these molecules as extended or truncated cylinders (convex objects) has been very successful in the description of their low ordered mesomorphic phases (N, SmA, SmC, Col) [1].

The small class of compounds in which mesomorphism is connected with molecular systems which are non-convex in their structure, e.g. triptycenes, silatrane or some metallomesogens, is very often associated with highly ordered LC phases. [2–4] Such systems are of considerable fundamental interest, as they potentially allow the formation of mesomorphic behaviour, due to anisotropic correlations of interdigitated non-convex molecules [5, 6]. Thus a potentially promising approach is to combine a non-convex molecular structure ('propeller') with mesogenic systems, as this allows the investigation of structure–properties relationships and the formulation of design rules for these different classes of molecular systems [7].

As a non-convex propeller-shaped system, a tribenzosilatrane unit **5** (see figure 1 and scheme 1) was selected, as this unit has three aromatic 'blades' where the three aromatic rings are connected via a nitrogen and a silicon–oxy function, resulting in a large internal dipole moment. Due to the direction of the free electron pair of the nitrogen towards the silicon, this leads to a silicon with a five-fold functionality [8, 9]. Initial miscibility

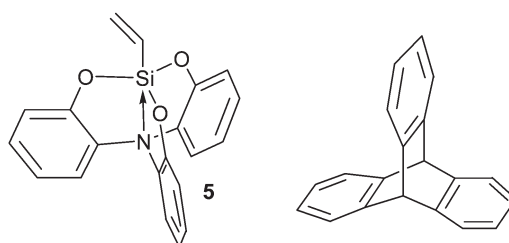
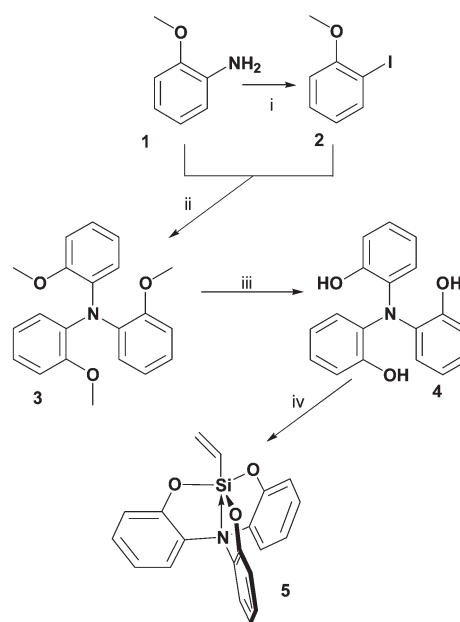


Figure 1. Tribenzosilatrane **5** seen on the left, and a triptycene core shown on the right.



Scheme 1. Synthesis of the tribenzosilatrane unit **5**. Reagents and conditions: (i) H_2SO_4 , NaNO_2 , KI ; (ii) K_2CO_3 , Cu powder, 18-crown-6 ether, (1, 2)-dichlorobenzene; (iii) BBr_3 , DCM ; (iv) trichlorovinylsilane, dry dibutyl ether.

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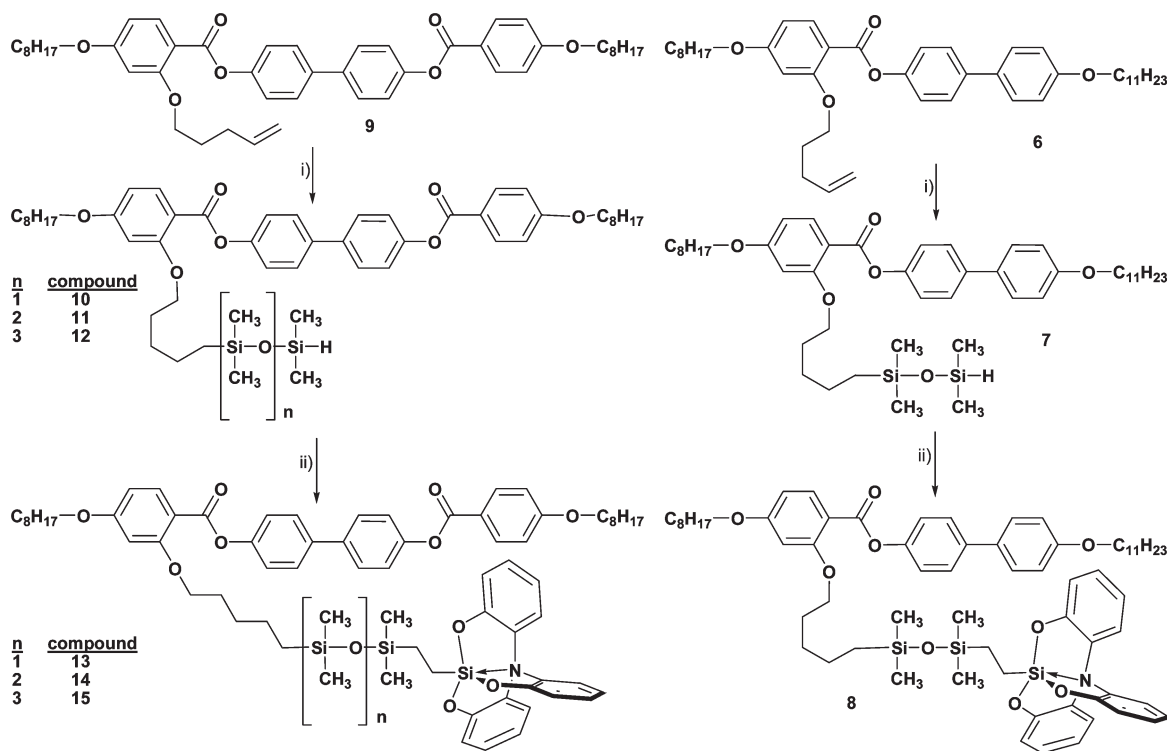
studies of the propeller **5** with rod-shaped liquid crystals resulted in either heterogeneous mixtures due to the high melting point of the tribenzosilatrane unit and the differences in shape, or almost complete lack of miscibility. It was thus decided to connect the silatrane unit covalently to the mesogens.

Having in view the target of a low ordered mesomorphic phase, the laterally attached systems **6** and **9** shown in scheme 2 were selected as starting materials, as they promote nematic or smectic phase behaviour [10]. Furthermore, their structure, due to the lateral attachment of the spacer groups, was expected to lead to good compatibility with the directionality of the interactions provided by the silatrane groups. As a connecting group between the silatrane unit and the rod shaped moieties siloxane spacers were selected, as such systems provide for high molecular flexibility, leading to suppression of the crystalline phase and low glass transition temperatures. This is particularly important for systems where the components have very different melting points. Additionally, the tendency of siloxane groups in calamitic liquid crystals to influence the phase structure due to nanosegregation and odd–even effects was to be explored. Thus it was expected that variation in length of the siloxane spacer groups should provide insight into the packing behaviour.

2. Synthesis

The synthetic approach towards the nematic silatranes is convergent, with the silatrane units and the rod-shaped groups being prepared separately and coupled in the last step. The synthesis of the tribenzosilatrane unit follows broadly the literature-reported methodology [8, 11]. Compound **5** was obtained in a four-step synthesis, as outlined in scheme 1. Firstly *o*-anisidine **1** was converted to *o*-iodoanisole **2** in moderate yield using a classical diazotization and iodation reaction sequence. The reaction of compounds **1** and **2** in the presence of copper powder and potassium carbonate resulted in the formation of the triarylamine **3** which was subsequently deprotected with boron tribromide at -78°C to yield the trihydroxyarylamine **4**. The reaction of compound **4** with trichlorovinylsilane in refluxing dibutyl ether gave the desired tribenzosilatrane **5**.

The synthesis of compounds **6**, **7** and **9** has been reported elsewhere [10]. The functionalization of the calamitic mesogen **6** with 1,1,3,3-tetramethyldisiloxane in toluene using Karstedt's catalyst yielded **7**, which carries a functional silane group. The reaction of **9** under similar conditions with 1,1,3,3-tetramethyldisiloxane yielded **10**; reaction of **9** with 1,1,3,3,5,5-hexamethyltrisiloxane and 1,1,3,3,5,5,7,7-octamethyltetrasiloxane resulted in compounds **11** and **12**, respectively.



Scheme 2. Synthesis of the laterally functionalized mesogens. Reagents and conditions: (i) Karstedt's catalyst, siloxane derivative, dry toluene; (ii) compound **5**, Karstedt's catalyst, dry toluene.

Conversion to the materials containing silatrane units and calamitic moieties was achieved in a second hydrosilylation reaction between **5** and the functional groups **7**, **10**, **11** and **12**, to furnish materials **8**, **13**, **14** and **15**, respectively.

3. Liquid crystal phase behaviour

The combined systems **13**, **14** and **15** were found to exhibit nematic phase behaviour. The combination of a tribenzosilatrane unit with laterally connected calamitic mesogens, linked to the silatrane unit at the apex via alkyl spacers and siloxane groups, was found to lead in all cases to lower transition temperatures than for the non-functionalized calamitic mesogens.

For mesogen **7**, which contains three aromatic rings, a clearing from the nematic to the isotropic phase just above ambient (N 38.5 I) was observed. The connection of **7** to the benzylsilatrane group **5**, resulting in compound **8**, led to a complete loss of mesomorphic behaviour. This indicates that the silatrane unit is disruptive with regards to mesomorphic behaviour for the selected calamitic mesogens.

For further investigations materials connected to mesogenic groups based on compound **9** were used. Material **9** is of overall similar size to **7**, however the aromatic grouping has been extended by one ring at the expense of the length of the aliphatic chains. Further functionalization with a tetramethyldisiloxane group in a hydrosilylation reaction leads to compound **10**, clearing from the nematic to the isotropic at 121.9°C; reaction with the benzosilatrane unit leads to **13** which clears from a nematic phase to the isotropic state at 57.4°C, and which exhibits a glass transition at 12.0°C. The enthalpy of the nematic to isotropic transition was found to be 0.40 J g⁻¹ and the texture exhibited under polarising optical microscopy (POM) was the common schlieren and marbled texture of a nematic phase,

shown in figure 2. This is, to the best of our knowledge, the first example of a silatrane unit incorporated into a low ordered LC phase.

The attachment of the tetramethyldisiloxane group to **9**, results in a lowering of both the isotropization and the crystalline or SmC transition temperatures, so that the nematic phase range remains broadly similar for **9** (74.2°C) and **10** (64.8°C). For **13** the stability of the nematic phase is drastically reduced, however the crystalline phase is lost, and thus the fluid nematic phase range is 45.4°C. The transition temperatures and corresponding enthalpies for the second heating cycle obtained by differential scanning calorimetry (DSC) are listed in table 1.

The results of the extension of the siloxane spacers using materials **11** (hexamethyltrisiloxane spacer attached to **9**) and **12** (octamethyltetrasiloxane spacer) are illustrative. Increasing the spacer length results in a reduction of the nematic phase by 12.1°C on going from **10** (121.9°C) to **12** (109.8°C). Interestingly, the material with the odd spacer **11** has a higher clearing point of 123.9°C and the lowest crystallization temperature of this series at 48.5°C.

Table 1. Transition temperatures and enthalpy changes as determined by DSC. Cr=crystalline, SmC=smectic C, N=nematic, I=isotropic liquid, g=glass.

Compound	Transition/°C	$\Delta H_{NI}/\text{J g}^{-1}$
7	Cr 17.0 N 38.5 I	0.70
8	g -8.2 I	
9	Cr 99.0 N 173.2 I	1.84
10	Cr 57.1 (SmC 47.5) N 121.9 I	0.60
11	Cr 48.5 (SmC 63.3) N 123.9 I	0.85
12	Cr 63.4 (SmC 67.5) N 109.8 I	0.45
13	g 12.0 N 57.4 I	0.40
14	g 4.7 N 53.3 I	0.17
15	g -4.3 N 50.9 I	0.16

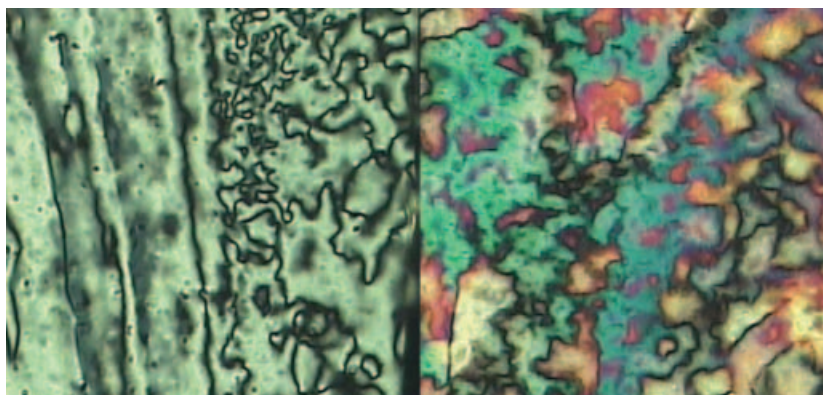


Figure 2. POM pictures of the nematic textures exhibited by compound **13**: (left) schlieren texture, (right) marbled texture.

The attachment of **11** or **12** to **5** leads to compounds **14** and **15**, respectively. Both show nematic phase behaviour. The clearing points are 53.3°C for **14** and 50.9°C for **15**; the glass transition temperatures are very low, 4.7°C for **14** and -4.3°C for **15**. There is no (or only a very weak) odd-even effect of the spacer group in this series of nematic silatranes. It is noteworthy that the mesomorphic range is reduced only by 7°C on going from **13** to **15**, although the very bulky siloxane spacer has doubled in size. Remarkable are the rather low values of the transition enthalpies, ranging from 0.4 J g⁻¹ for **13**, to 0.16 and 0.17 J g⁻¹ for **14** and **15**, respectively. This indicates that the transition from the liquid crystal to the isotropic state is not accompanied by large changes in the spatial arrangements of the molecules, which suggests the existence of a highly disordered mesophase. The glass transitions of compounds **13**, **14** and **15** range between 12 and -4.3°C, indicating that the lengthening of the siloxane spacer leads to a lowering of the glass transition, a plastification effect of the siloxane groups. It is interesting that the range of the fluid nematic phase is the largest in system **15** at 55.2°C.

A miscibility study was carried out by depositing compounds **10** and **14** close to each other on a microscope slide. On heating, the two samples started to flow, came into contact with each other and mixed slowly at the interface, resulting in a continuous composition gradient between **10** and **14**. Above the isotropization temperature of **10** no mesomorphic behaviour was observed. On cooling from the isotropic phase, liquid crystal behaviour reappeared at the edge of the compound **10** zone at the temperature for a pure material, and on further cooling the nematic texture extended further towards the mixed region. With decreasing temperature the mesomorphic behaviour advanced towards the region of pure compound **14**. When the temperature reached 53°C, pure compound **14** showed the nematic behaviour illustrated in figure 3. The experiment indicates that the tribenzosilatranecontaining mesogen **14** mixes with **10** with no miscibility gap, essentially confirming the nematic structure of the LC phase.

For the correlation between chemical structure and physical properties of the systems investigated, a comparison with the parent compound of the series, **16** (see figure 4), is useful [12]. This material melts from the nematic to the isotropic phase at 300°C (with slow decomposition); the attachment of a pentenyloxy chain in **9** reduces the transition temperature by 130°C. The attachment of siloxane groups leads to transition temperatures in the range 109.8–123.9°C, a reduction of 40–50°C. The addition of the silatranec unit results in

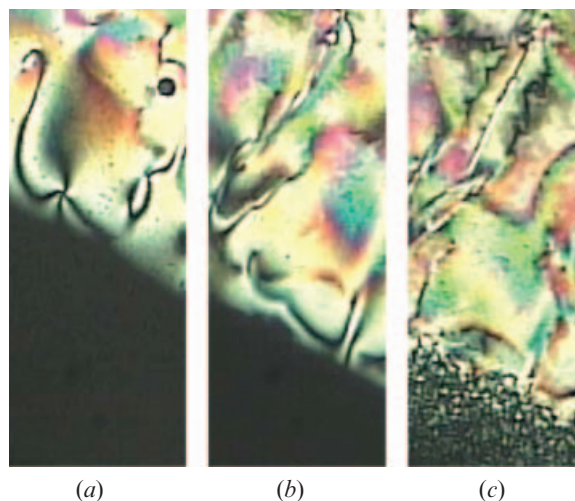


Figure 3. Optical polarizing microscope pictures of the interface texture created by mixing compounds **10** (top) and **14** (bottom): (a) at 70°C more than 50% of the mixture remains isotropic; (b) at 60°C around 33% of the mixture is still isotropic; (c) at 53°C the interface reaches the non mixed compound **14** seen at the bottom of the picture (onset of the formation of nematic droplets).

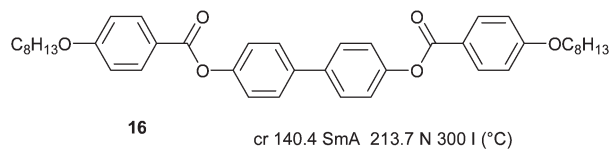


Figure 4. Calamitic reference system **16**.

a reduction of the isotropization temperatures by a further 50–60°C. The molecular mass of the silatranec unit ($M=345.42$) is considerably larger than both that of the siloxane (tetramethyldisiloxane, $M=134.22$) and the alkene (4-pentene-1-ol, $M=86.13$) functions, individually or taken together. In the absence of any interactions contributing to mesomorphic behaviour, the size of lateral groups and the reduction of the mesophase behaviour are often directly related. In other words a greater reduction in mesophase behaviour could have been anticipated for a system where the propeller-shaped group would not be incorporated into the mesophase assembly [1].

4. X-ray diffraction

In order to obtain further information on the packing of the propeller-shaped molecules in the nematic phase, X-ray powder diffraction (XRD) studies of a partially aligned sample were carried out for the final material **13** (at 45°C) (Attempts to obtain an aligned sample using our set-up were unsuccessful, partly due to high viscosity exhibited by the final compounds bearing the

tribenzosilatrane moiety.) The results are shown in figure 5 and the reflections are collected in table 2. The diffractogram is characterized by diffuse reflections. The low intensity small angle reflection A ($d=24.7 \text{ \AA}$) is associated with the length of the calamitic mesogen, consisting of four aromatic rings and two internal ester groups. The very weak reflection B ($d=6.3 \text{ \AA}$) is at a value found for siloxane groups in LC systems [13]. The diffractogram is dominated by the wide angle peak C ($d=4.4 \text{ \AA}$) at the value typical for fluidic mesogenic groups in the mesophase.

The broad shape of the small angle reflections, and their weakness compared with the intensities recorded for the wide angle data, indicate the presence of a low ordered phase. In other words, any nanophase segregated regions of the calamitic mesogen, the siloxane groups and the propeller shaped silatrane moiety are randomly distributed.

5. Conclusion

A series of laterally functionalized mesogens have been connected to a benzylsilatrane unit. Nematic mesophase behaviour was observed for the first time for silatrane-based systems. POM, DSC, miscibility studies and XRD investigations confirm the nematic phase structure. There is no evidence of nanophase separation, as often

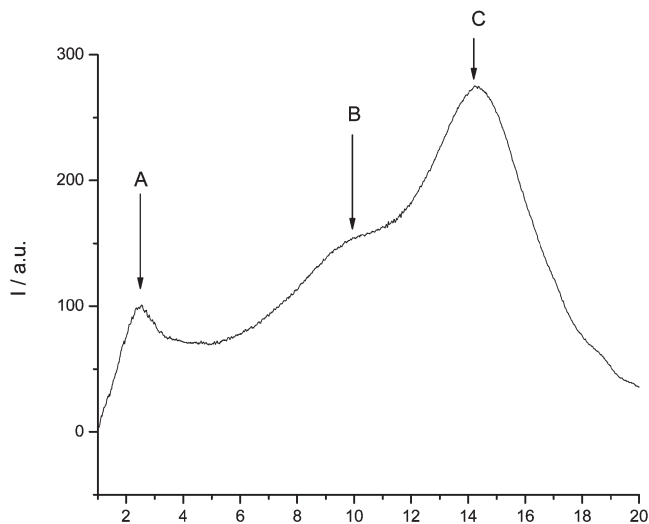


Figure 5. X-ray diffraction pattern of compound 13.

Table 2. X-ray data for 13.

Maximum	q/nm^{-1}	$d/\text{\AA}$
A	2.55	24.7
B	9.99	6.3
C	14.25	4.4

associated with silicon-containing mesogens forming mesomorphic phases. Conversely, this indicates that both the non-convex-shaped silatrane unit and the convex calamitic groups make up the nematic matrix.

6. Experimental

All materials and solvents were used as purchased unless mentioned otherwise. Column chromatography was performed on silica gel (Fluorochem, 35–70 μ , 60 \AA). The purity of the synthesis products was checked by thin layer chromatography (TLC) carried out on silica gel 60 F254 (Merck) plates, and subsequent detection was performed by UV fluorescence (254 nm). Melting points measured in capillary tubes on a Gallenkamp apparatus, are uncorrected. ^1H , ^{13}C and ^{29}Si NMR spectra were recorded on a JEOL Lambda 400 spectrometer (400, 100 and 55 MHz, respectively, for ^1H , ^{13}C and ^{29}Si) using tetramethylsilane as internal standard. Chemical shifts are given in ppm and coupling constants in Hz. Elemental analyses of products were carried out using a Fisons EA 1108 CHN analyser. The identification of previously reported compounds was made by ^1H NMR and melting points, in comparison with literature data.

Transition temperatures were measured using a Mettler FP52 heating stage and FP5 control unit in conjunction with an Olympus BH2 polarizing microscope, and were confirmed using differential scanning calorimetry (Perkin-Elmer DSC 7 with an indium standard). Pictures of the mesophases were taken using a JVC digital video camera connected to a PC. Software Studio Capture, supplied by Studio86Designs was used for image capturing. X-ray diffraction measurements were performed on a MAR345 diffractometer with a 2D image plate detector (Cu- K_{α} radiation, graphite monochromator, $\lambda=1.54 \text{ \AA}$). The samples were heated in the presence of a magnetic field using a home-built capillary furnace.

The synthesis of compound 8 is described in detail. Analogous methods were used for compounds 10–15, and are reported briefly in terms of reagents and reaction conditions.

6.1. Compound 2

In a 500 ml beaker were placed 75 ml of water and 30 ml of sulphuric acid (conc.); *o*-anisidine (24.6 g, 0.20 mmol) was added to the hot mixture. Finely crushed ice (150 g) was then added to the reaction with stirring, reducing the temperature to 0°C. At this point sodium nitrite (15 g, 0.22 mol) in 50 ml of water was added dropwise with stirring, keeping the temperature below 8°C. Solid urea (2.5 g, 0.041 mol) was then added to the solution to

destroy the excess of nitrite ions. A potassium iodide solution (40 g, 0.241 mol, in 75 ml H₂O) was poured into the reaction mixture, and after 30 min stirring at room temperature, the solution was heated to 60°C. The aqueous solution was decanted from the oily product which was washed with warm aqueous potassium carbonate 5% (200 ml), aqueous sodium bisulphite 5% (200 ml) and water (250 ml × 3). The brown oil was dried with magnesium sulphate and distilled under reduced pressure (60°C, 0.2 mm Hg). The product was obtained as a yellow liquid (115 g, 82%). TLC (SiO₂, DCM): $R_F=0.73$. ¹H NMR (CDCl₃) δ: 3.85(3H, s), 6.70(1H, t), 6.80(1H, d), 7.30(1H, t), 7.70 (1H, d). ¹³C NMR (CDCl₃) δ: 56.05, 85.77, 110.75, 122.26, 129.33, 139.17, 157.72. Anal. for C₇H₇IO(234.03): calcd, C 35.92, H 3.01; found, C 35.47, H 2.90%.

6.2. Compound 3

In a 500 ml three necked round bottom flask fitted with stirrer, reflux condenser and nitrogen purge, a mixture of *o*-anisidine **1** (7.38 g, 60 mmol), *o*-iodoanisole **2** (32.6 g, 140 mmol), powdered anhydrous potassium carbonate (41.8 g, 0.3 mol), copper powder (13.2 g, 0.2 mol), 18-crown-6 ether (2 g, 7.56 mmol) and 1,2-dichlorobenzene (250 ml) was heated under reflux for 60 h. After cooling, the insoluble inorganic solid was filtered off under suction and the organic solution collected. The solid was washed with DCM (4 × 500 ml). The organic extracts were combined and washed with dilute aqueous ammonia, then with water and dried with magnesium sulphate. The solvent DCM was removed using the rotatory evaporator. The remaining solution was distilled under reduced pressure to remove 1,2-dichlorobenzene (45°C, 0.5 mm Hg). The brown solid residue was recrystallized from hexane/ethanol (2/1) to give the product as a light brown powder (10.26 g, 51%), m.p. 142°C. TLC (SiO₂, ether) : $R_F=0.62$. ¹H NMR (CDCl₃) δ: 3.53(9H, s), 6.73(3H, m), 6.76(3H, m), 6.84(3H, m), 6.99(3H, m). ¹³C NMR (CDCl₃) δ: 55.67, 112.38, 120.56, 123.72, 124.43, 137.66, 153.05. Anal. for C₂₁H₂₁NO₃ (335.40): calcd, C 75.20, H 6.31, N 4.18; found, C 75.16, H 6.48, N 4.23%.

6.3. Compound 4

A solution of compound **3** (2.51 g, 7.5 mmol) in 30 ml of dichloromethane was cooled to -78°C in an acetone dry ice bath. Boron tribromide (7.52 g, 0.03 mol) in 40 ml of DCM at -78°C was added dropwise over a 10 min period. The reaction mixture was stirred for 30 min at -78°C, followed by 20 h at room temperature. It was then poured carefully into a beaker containing water (200 ml) and the mixture as stirred for 30 min at

room temperature. The organic phase was extracted with ether (3 × 100 ml) and the combined organic extracts were dried over magnesium sulphate. The solvent was evaporated under reduced pressure and the white residue recrystallized from hexane/ethanol (1/1) to give compound **4** as white crystals (1.53 g, 70%), m.p. 164°C. TLC [SiO₂, DCM/ether (2/1)]: $R_F=0.42$. ¹H NMR (CDCl₃) δ: 5.4(3H, s), 6.88(3H, m), 6.95(6H, m), 7.11(3H, m). ¹³C NMR (CDCl₃) δ: 117.25, 121.54, 125.38, 126.79, 133.19, 149.87. Anal. for C₁₈H₁₅NO₃ (293.32): calcd, C 73.70, H 5.15, N 4.77; found, C 73.49, H 5.31 N 4.63%.

6.4. Compound 5

A stirred mixture of compound **4** (1.30 g, 4.43 mmol) and trichlorovinylsilane (0.86 g, 5.32 mmol) in 50 ml of dry dibutyl ether was heated under reflux for 4 h under a nitrogen atmosphere. After cooling, a white solid precipitated and was removed. The solvent was removed *in vacuo* and the residue purified by column chromatography (DCM eluant) to give a light yellow solid (0.98 g, 64%), m.p. 270°C. TLC (SiO₂,DCM) : $R_F=0.70$. ¹H NMR (CDCl₃) δ: 6.12(2H, m), 6.23(1H, m), 6.86(3H, dt), 6.95(3H, dd), 7.06(3H,dt), 7.70(3H, dd). ¹³C NMR(CDCl₃) δ: 117.76, 122.40, 126.07, 129.03,132.87, 134.51, 136.43, 153.26. ²⁹Si NMR DEPT (CDCl₃) δ: -73.6. Anal. for C₂₀H₁₅NO₃Si (345.42): calcd, C 69.54, H 4.37, N 4.05; found, C 69.35, H 4.46, N 4.10%.

6.5. Compound 8

To a stirred solution of compounds **5** (0.12 g, 0.35 mmol) and **7** (0.20 g, 0.25 mmol) in 15 ml of dry toluene, was added Karstedt's catalyst (platinum(0)-1,3-divinyl-1,1,3,3-tetramethyl-disiloxane complex, 25 μl, 5% xylene). The mixture was aerated for a few minutes using a glass pipette, to activate the catalyst. After stirring for 20 h at room temperature the solvent was removed under reduced pressure and the liquid residue purified by column chromatography using a dichloromethane/hexane gradient mixture to obtain compound **8** as a colourless oil (0.150 g, 38%). TLC (SiO₂,DCM) : $R_F=0.75$. ¹H NMR (CDCl₃) δ: 0.00(6H, s), 0.04(6H, s), 0.47(2H, m), 0.79(10H, m), 1.18–1.47(30H, m), 1.76(6H, m), 3.87(6H, m), 6.40(2H, m), 6.80(8H, m), 7.02(3H, m), 7.15(2H, m), 7.39(4H, m), 7.62(3H, m), 7.94(1H, d). ¹³C NMR (CDCl₃) δ: -0.15, 0.42, 5.24, 10.35, 14.11, 14.13, 18.32, 22.64, 22.68, 23.09, 25.98, 26.04, 28.88, 29.12, 29.21, 29.28, 29.33, 29.40, 29.57, 29.61, 29.66, 31.79, 31.90, 68.04, 68.28, 68.92, 100.12, 105.23, 111.22, 114.71, 117.76, 121.83, 122.16, 126.54, 127.59, 128.07, 128.84, 132.95, 134.40, 136.57, 138.23, 150.11, 153.75,

158.61, 161.66, 164.21, 164.39. ^{29}Si NMR DEPT (CDCl_3) δ : -57.40, 7.75, 9.22. Anal. for $\text{C}_{67}\text{H}_{89}\text{NO}_9\text{Si}_3$ (1136.70): calcd, C 70.80, H 7.90, N 1.23; found, C 72.40, H 7.66, N 1.08%.

6.6. Compound 10

Compound **9** (0.60 g, 0.82 mmol) and 1,1,3,3-tetra-methyl-disiloxane (1.10 g, 8.16 mmol, 10 equiv); reaction time 4 h. Purification of the solid residue was performed by column chromatography using hexane/dichloromethane gradient mixture to yield **10** as a white solid (0.460 g, 64.8%). TLC (SiO_2 , DCM): R_F =0.35. ^1H NMR (CDCl_3) δ : 0.01(6H, s), 0.10–0.12(6H, d), 0.46(2H, m), 0.82(6H, t), 1.16–1.52(24H, m), 1.70–1.86(6H, m), 3.93(6H, m), 4.62(1H, m), 6.42(2H, m), 6.86(2H, d), 7.20(4H, m), 7.52(4H, m), 7.97(1H, d), 8.08(2H, d). ^{13}C NMR (CDCl_3) δ : 0.04, 0.87, 14.01, 17.89, 22.55, 22.83, 25.87, 28.02, 28.98, 29.02, 29.12, 29.23, 31.70, 68.15, 68.72, 100.02, 105.13, 111.00, 114.15, 121.33, 121.97, 122.20, 127.89, 127.94, 132.15, 134.33, 137.60, 138.02, 150.36, 150.60, 161.58, 163.43, 163.86, 164.34, 164.77. ^{29}Si NMR DEPT (CDCl_3) δ : -6.22, 10.35. Anal. for $\text{C}_{51}\text{H}_{72}\text{O}_8\text{Si}_2$ (869.29): calcd, C 70.47, H 8.35; found, C 70.57, H 8.15%.

6.7. Compound 11

Compound **9** (0.60 g, 0.82 mmol) and 1,1,3,3,5,5-hexamethyltrisiloxane (1.70 g, 8.16 mmol, 10 equiv); reaction time 4 h. Purification as for **10** yielded **11** as a white solid (0.520 g, 67.5%). TLC (SiO_2 , DCM): R_F =0.29. ^1H NMR (CDCl_3) δ : 0.00(12H, d), 0.10(6H, d), 0.44(2H, m), 0.80(6H, t), 1.16–1.50(24H, m), 1.68–1.84(6H, m), 3.91(6H, m), 4.60(1H, m), 6.40(2H, m), 6.84(2H, m), 7.18(4H, m), 7.50(4H, m), 7.95(1H, d), 8.06(2H, d). ^{13}C NMR (CDCl_3) δ : 0.05, 0.60, 0.87, 14.02, 17.90, 22.56, 22.84, 25.88, 28.03, 28.99, 29.03, 29.13, 29.24, 31.71, 68.16, 68.73, 100.03, 105.14, 111.01, 114.16, 121.34, 121.98, 122.21, 127.90, 127.95, 132.16, 134.34, 137.61, 138.03, 150.37, 150.61, 161.59, 163.44, 163.87, 164.35, 164.78. ^{29}Si NMR DEPT (CDCl_3) δ : -18.89, -6.51, 8.23. Anal. for $\text{C}_{53}\text{H}_{78}\text{O}_9\text{Si}_3$ (943.45): calcd, C 67.47, H 8.33; found, C 67.56, H 8.21%.

6.8. Compound 12

Compound **9** (0.60 g, 0.82 mmol) and 1,1,3,3,5,5,7,7-octamethyltetrasiloxane (2.31 g, 8.16 mmol, 10 equiv); reaction time 4 h. Purification as for **10** yielded **12** as a white solid (0.670 g, 80%). TLC (SiO_2 , DCM): R_F =0.22. ^1H NMR (CDCl_3) δ : 0.00(18H, m), 0.13(6H, d), 0.50(2H, m), 0.82(6H, t), 1.18–1.52(24H, m), 1.72–1.86(6H, m), 3.95(6H, m), 4.64(1H, m), 6.44(2H, m), 6.88(2H, d), 7.22(4H, m), 7.54(4H, m), 7.99(1H, d),

8.10(2H, d). ^{13}C NMR (CDCl_3) δ : 0.07, 0.59, 0.78, 1.05, 14.00, 17.88, 22.54, 22.82, 25.86, 28.01, 28.97, 29.01, 29.11, 29.22, 31.69, 68.14, 68.71, 100.00, 105.12, 111.00, 114.14, 121.32, 121.96, 122.19, 127.88, 127.93, 132.14, 134.32, 137.58, 138.01, 150.34, 150.59, 161.57, 163.42, 163.85, 164.33, 164.74. ^{29}Si NMR DEPT (CDCl_3) δ : -20.92, -20.82, -6.33, 8.10. Anal. for $\text{C}_{55}\text{H}_{84}\text{O}_{10}\text{Si}_4$ (1017.60): calcd, C 64.92, H 8.32; found, C 65.22, H 8.20%.

6.9. Compound 13

Compounds **5** (0.23 g, 0.67 mmol) and **9** (0.40 g, 0.46 mmol), reaction time 24 h. Purification as for **10** yielded **13** as a white solid (0.310 g, 55.5%). TLC (SiO_2 , DCM): R_F =0.49. ^1H NMR (CDCl_3) δ : 0.00(6H, s), 0.03(6H, s), 0.45(2H, m), 0.79(10H, m), 1.18–1.51(26H, m), 1.66(6H, m), 3.91(6H, m), 6.41(2H, m), 6.80(3H, m), 6.97(5H, m), 6.98(3H, m), 7.14(4H, d), 7.48(4H, m), 7.65(3H, m), 7.95(1H, d), 8.06(2H, d). ^{13}C NMR (CDCl_3) δ : -0.19, 0.36, 5.23, 10.33, 14.04, 18.25, 22.57, 23.02, 25.89, 28.89, 29.03, 29.19, 29.24, 29.59, 31.71, 68.18, 68.81, 100.07, 105.19, 111.07, 114.19, 117.63, 121.38, 121.77, 121.99, 122.24, 126.45, 127.94, 128.00, 128.75, 132.19, 134.35, 136.50, 137.63, 138.07, 150.37, 150.64, 153.63, 161.63, 163.46, 163.96, 164.38, 164.82. ^{29}Si NMR DEPT (CDCl_3) δ : -57.69, 7.91, 9.27. Anal. for $\text{C}_{71}\text{H}_{87}\text{NO}_{11}\text{Si}_3$ (1214.72): calcd, C 70.20, H 7.11, N 1.15; found, C 70.41, H 7.40, N 1.14%.

6.10. Compound 14

Compounds **5** (0.25 g, 0.72 mmol) and **11** (0.50 g, 0.53 mmol); reaction time 24 h. Purification as for **10** yielded **14** as a white solid (0.28 g, 41%). TLC (SiO_2 , DCM): R_F =0.57. ^1H NMR (CDCl_3) δ : -0.03(6H, s), 0.03(12H, d), 0.10(6H, s), 0.45(2H, m), 0.78(10H, m), 1.17–1.50(26H, m), 1.65(6H, m), 3.90(6H, m), 6.40(2H, m), 6.79(3H, m), 6.96(5H, m), 6.97(3H, m), 7.13(4H, d), 7.47(4H, m), 7.64(3H, m), 7.94(1H, d), 8.05(2H, d). ^{13}C NMR (CDCl_3) δ : 0.03, 0.49, 0.86, 5.57, 10.50, 14.48, 18.46, 22.89, 23.29, 26.27, 29.23, 29.45, 29.47, 29.56, 29.67, 29.99, 68.63, 69.22, 100.51, 105.55, 111.47, 114.59, 118.05, 121.79, 122.16, 122.39, 122.63, 126.87, 128.37, 128.43, 129.15, 132.61, 134.76, 136.92, 138.08, 138.53, 150.77, 151.03, 154.08, 162.01, 163.84, 164.37, 164.79, 165.27. ^{29}Si NMR DEPT (CDCl_3) δ : -57.74, -20.51, 7.83, 9.25. Anal. for $\text{C}_{73}\text{H}_{93}\text{NO}_{12}\text{Si}_4$ (1288.88): calcd, C 68.03, H 7.27, N 1.09; found, C 67.83, H 7.47, N 1.17%.

6.11. Compound 15

Compounds **5** (0.20 g, 0.58 mmol) and **12** (0.52 g, 0.51 mmol); reaction time 24 h. Purification as for **10**

yielded **15** as a white solid (0.31 g, 44%). TLC (SiO₂, DCM): $R_F=0.56$. ¹H NMR (CDCl₃) δ : 0.00(18H, m), 0.13(6H, s), 0.50(2H, m), 0.83(10H, m), 1.17–1.53(26H, m), 1.68(6H, m), 3.93(6H, m), 6.43(2H, m), 6.84(3H, m), 6.99(5H, m), 7.01(3H, m), 7.16(4H, d), 7.51(4H, m), 7.68(3H, m), 7.98(1H, d), 8.09(2H, d). ¹³C NMR (CDCl₃) δ : 0.00, 0.51, 0.87, 1.57, 5.54, 10.54, 14.41, 18.47, 22.95, 23.25, 26.28, 29.16, 29.38, 29.43, 29.51, 29.62, 29.94, 68.59, 69.20, 100.52, 105.54, 111.46, 114.59, 118.04, 121.78, 122.14, 122.38, 122.61, 126.86, 128.35, 128.42, 129.13, 132.59, 134.74, 136.90, 138.06, 138.51, 150.77, 151.01, 154.05, 162.00, 163.85, 164.35, 164.76, 165.25. ²⁹Si NMR DEPT (CDCl₃) δ : –57.70, –21.07, –21.01, 7.97, 9.36. Anal. for C₇₅H₉₉NO₁₃Si₅ (1363.08): calcd, C 66.08, H 7.32, N 1.03; found, C 66.38 H 7.57, N 1.05%.

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