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Synthesis and Evaluation of Molecular Rotors with Large and Bulky *tert*-Butyldiphenylsilyloxy-Substituted Trityl Stators

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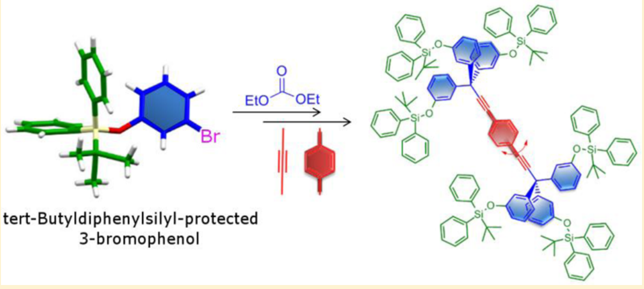
Supporting Information

ABSTRACT: The search for voluminous stators that may accommodate large rotator units and speed rotational dynamics in the solid state led us to investigate a simple and efficient method for the synthesis of molecular rotors with *tert*-butyldiphenylsilyl-protected (TBDPS) triphenylmethyl stators. Additionally, solid state characterization of these systems with two-, four-, and six-TBDPS groups provided us with a description of their crystallinity and thermal stability. Among them, molecular rotor **7c** with the largest and most symmetric stator resulting from six peripheral silyl groups showed the best tendency to crystallize, and the study of its isotopologue **7c**-d_4 by solid state ^{2}H NMR revealed a 2-fold motion of the 1,4-diethynylphenylene-d_4 rotator in the kHz regime.



INTRODUCTION

The study and control of rotational motion at the molecular scale is attractive for the development of functional materials with functions that can be traced to mechanical processes at the macroscopic level.[1,2] In recent years, our group has focused on the design, synthesis, and dynamic characterization of *amphidynamic crystals*,[3] built with components that form an ordered rigid framework linked to structural elements that are able to experience fast internal motion. Although the conjunction of phase order and rapid dynamics are intuitively regarded as mutually exclusive in condensed-phase matter, we and others have shown that internal motion in crystalline solids may be successfully engineered by taking advantage of several suitable platforms and fine-tuned structures.[3a,4] In our group, we have explored a series of molecular rotors intended to emulate the structure and function of macroscopic gyroscopes.

The blueprints for molecular rotors that can form amphidynamic molecular crystals require three essential elements: (1) a mobile part, or *rotator*, that performs the rotary motion, (2) an ideally barrierless *axle*, that connects the rotator to the stator, and (3) a bulky static group acting as the shielding framework to take the role of a *stator* (Figure 1). The characterization of their internal molecular dynamics using several solid state NMR techniques has shown that their rotational frequencies can reach the GHz regime. It has been shown, experimentally[3,5] and computationally,[6] that the frequency and geometry of motion of the rotator frequently depend on the close contacts with neighboring rotors or intermolecular interactions with solvent molecules within the crystal lattice. Current efforts to control the frequency of the internal motion are based on the use of rotators with higher axial symmetry to reduce rotational barriers[7] and on changes in

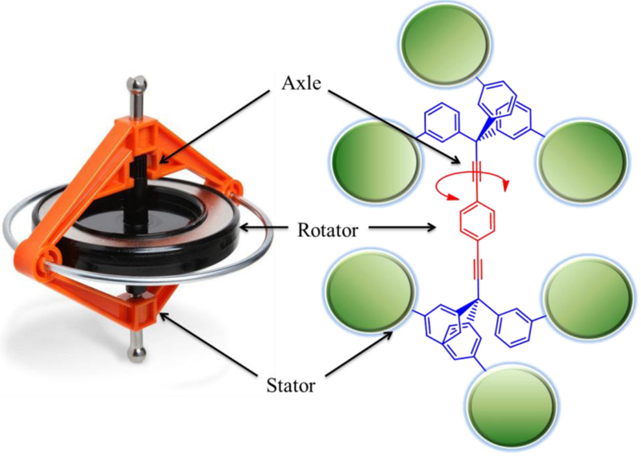


Figure 1. Diagram showing the analogy between macroscopic and molecular gyroscopes.

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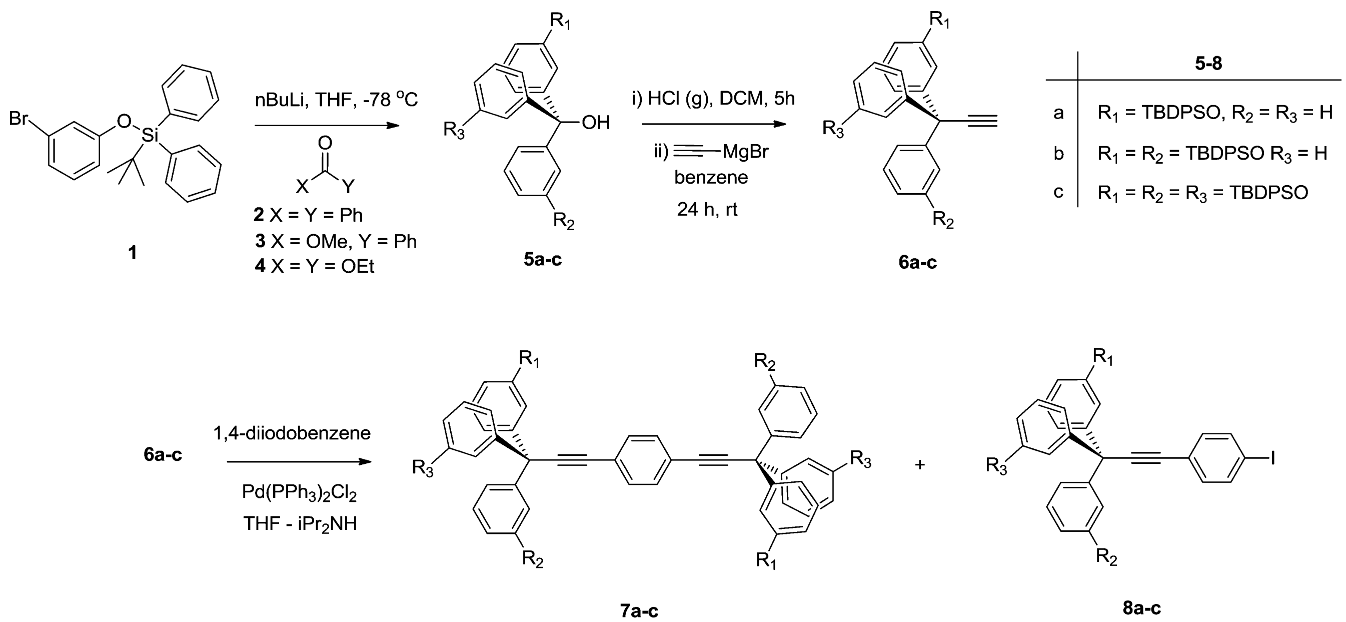
Scheme 1



the architecture of the static components to isolate the rotary parts. The latter approach comprises the study of several stator structures, including substituted triptycenes,[7] substituted trityl groups,[8,9] steroids,[10] and the use of porous solids, such as metal−organic frameworks (MOFs).[11]

Considering that the relatively large dimensions of biomolecular rotors such as the bacterial flagellum (cross-section ca. 20−40 nm)[12] and ATP synthase (cross-section ca. 8 nm)[13] may be essential for their complex function, we believe that one of the most interesting structural variables in the field of artificial molecular rotors will be an increase in the size of the molecular components.[1,4,14] With that in mind, we begun a search for simple strategies that produce much larger molecular stators that may be able to shield and support the motion of significantly larger molecular rotators. In this paper we report the synthesis of molecular rotors with *tert*-butyldiphenylsilyl-protected triphenylmethyl stators. The desired structures place the *tert*-butyldiphenylsilyl functionalities (TBDPS) on the *meta*-position of the phenyl rings in the trityl groups to increase the molecular volume and steric shielding around the rotator. We selected the bulky silyloxy groups due to their potentially simple installation using a modular and convergent synthetic approach. The selection of TBDPS, in particular, was based on its large size and higher stability under acidic or basic conditions as compared to that of other silyl-protecting groups.[15] We report here the synthesis of symmetric molecular rotors **7a−c** with one, two, or three protecting groups in each half of the stator and a small phenylene rotator, by following a simple four step methodology. After establishing the solid state properties and crystallinity of all the samples, the hexasilyl-substituted derivative **7c**, with a molecular weight of 2137.2 amu, gave the most promising crystals, which were selected to explore the internal dynamics of the rotator in the solid state by taking advantage of quadrupolar echo ^{2}H NMR. The ^{2}H NMR line shape of phenylene-labeled **7c**-d_4 obtained at 298 K suggested that the 1,4-diethynylphenylene rotator undergoes a 2-fold flip motion with a frequency in the kilohertz regime.

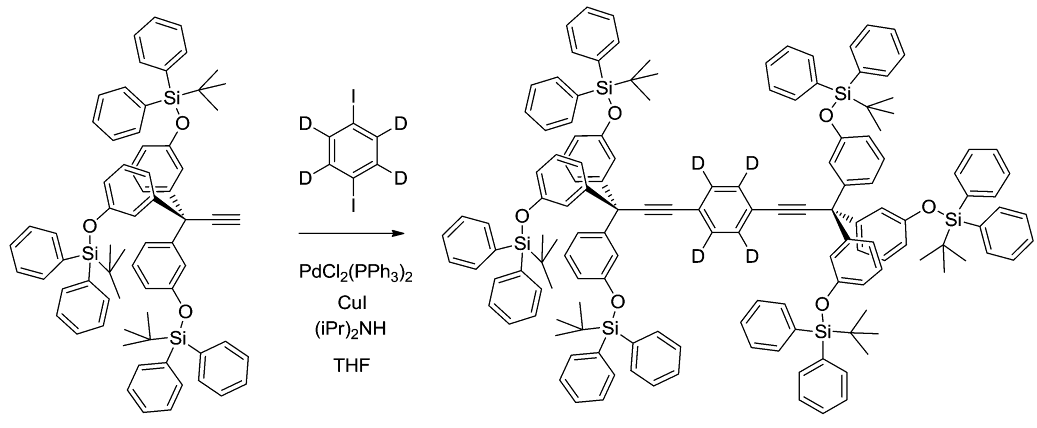
■ RESULTS AND DISCUSSION

Synthesis and Characterization. Substituted trityl alcohols **5a−c** with the *tert*-butyldiphenylsilyl protecting groups in *meta*-position were obtained by lithiation with *n*-butyllithium of previously reported (3-bromophenoxy)-*tert*-butyldiphenylsilane **1**[16] and subsequent reaction with the appropriate carbonyl compound **2−4** as outlined in Scheme 1. The reaction with benzophenone **2** gave alcohol **5a** in 88% yield. Similarly, trityl alcohols **5b** and **5c** were isolated pure in 82 and 80% starting from methyl benzoate **3** and diethyl carbonate **4**, respectively.

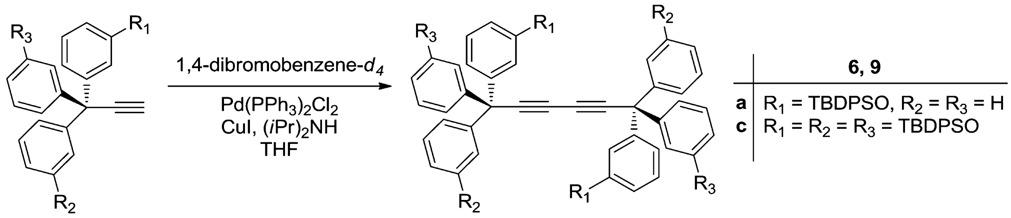
For compounds **5a−c**, the IR spectra showed O−H hydroxyl stretching broad bands between 3567 and 3446 cm^{-1}. They also presented characteristic signals in ^{1}H NMR that correspond to the proton in the −OH group at δ = 2.60−2.18 and those from the *tert*-butyl group at δ = 1.07. Solution ^{13}C NMR experiments for compounds **5a−c** revealed signals at δ = 155.3 that confirm the phenoxy-substituted carbon atom and two signals in the aliphatic region ca. 26.8 and 19.6 ppm corresponding to the *tert*-butyl substituent from the quaternary and methyl carbons, respectively. Additionally, ^{29}Si NMR spectra of these compounds showed a singlet between δ = −5.13 and −5.29 that corroborates the presence of the silane groups.

Alcohols **5a−c** were subsequently converted into their alkynyl derivatives by a two-step sequence that involves the exchange of the −OH group to −Cl using HCl in a solution of the compounds **5a−c** in CH_2Cl_2. The resultant solid was dissolved and reacted with ethynylmagnesium bromide, to give the desired alkyne compounds **6a−c** with moderate yields between 59 and 77%. The infrared analysis of compounds **6a−c** showed a band in the region 3304−3296 cm^{-1} attributable to the stretching of the C−H bond in free alkynes. In addition to the signals from the aromatic stator, the ^{1}H NMR spectra presented a singlet in the interval δ = 2.55−2.20 ppm from the proton in the alkyne group. The same functional group is responsible for the signals at ca. 89 and 73 ppm in ^{13}C NMR in all derivatives. Additional structural information may be gathered from the crystal structure of compound **6a**, which

Scheme 2



Scheme 3



crystallizes from hexanes/ethyl acetate in a $P2_1/c$ space group (see Table S1, Supporting Information).

The alkynes **6a−c** were further reacted with 1,4-diiodobenzene to afford the desired molecular rotors **7a−c** using the Sonogashira cross coupling method with Pd(0) under N_2 atmosphere; each reaction gave moderate yields of ca. 75%. In addition to the desired rotors, monocoupled compounds **8a−c** were also obtained as minor products. High resolution mass spectrometry confirmed the synthesis of desired molecular rotors **7a−c**, with observed peaks at m/z 1119.4974, 1627.7207, and 2135.9479 that match with the expected molecular ions for molecules with two, four, and six silyl-protecting groups, respectively. Compound **7c** has the largest formula weight of all the compounds studies in our group to date, with a bis(tri-(*meta*-terphenyl)methyl) derivative that has a FW = 1523.94 as a relatively distant second. The synthesis of molecular rotors **7a−c** from alkynes **6a−c** was also corroborated by ^{13}C NMR spectroscopy, where two additional signals coming from the central phenylene ring appeared at ca. 131 (CH carbons) and 123 ppm (*ipso* carbons). Furthermore, ^{29}Si NMR confirms the presence of the silyl protecting groups, with chemical shifts at −4.81, −5.01, and −5.16 ppm. On the other hand, monocoupling products **8a−c** were readily identified by the characteristic ^{13}C NMR signal approximately at 93 ppm that corresponds to the aryl-iodide substitution.

In order to study the internal dynamics of **7c** by means of ^{2}H solid state NMR, we pursued the synthesis of the deuterated analogue **7c**-d_4 (Scheme 2). This molecular rotor was obtained from the reaction of compound **6c** with 1,4-diiodobenzene-d_4, prepared as described in the literature.[17]

It is important to note that initial reactions using the same Sonogashira coupling conditions but longer reaction times between alkynes **6a** and **6c** with commercially available 1,4-dibromobenzene-d_4 (Scheme 3) afforded dialkynyl compounds **9a** and **9c** as main products (50 and 90% yield, respectively), with the homocoupling product **9c** easily crystallizing after column with its structure solved in the space group $P\bar{1}$ (see Table S1, Supporting Information).

Detailed inspection of the crystalline packing of homocoupling product **9c** showed that the silyl-protecting groups fold toward the dialkynyl axis. The puckered array may be favored by intramolecular interactions of the C−H···π type between phenyl rings in the TBDPS moieties lying in the opposite trityl fragment. This conformation of the silyl groups allowed the presence of six-phenyl embrace interactions (6PE) between adjacent molecules as shown in Figure 2. The observation that

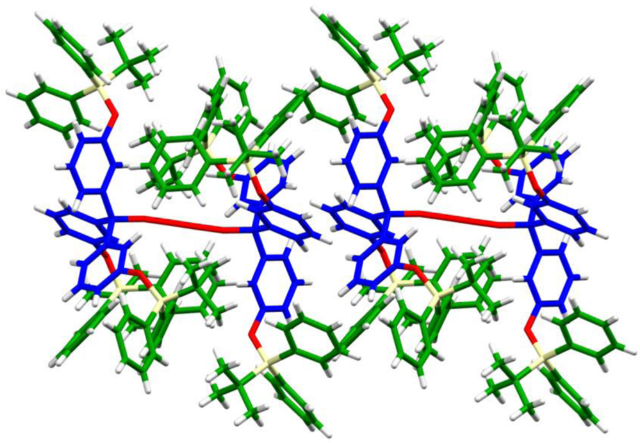


Figure 2. Diagram of the homocoupling compound **9c** showing the collinear intermolecular interaction between trityl groups in blue, forming a six-phenyl embrace. The *tert*-butyldiphenyl fragments in green accommodate around the butadiyne molecular axis, shown here in red.

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the adopted conformation of a given substituent could permit or interfere with the 6PE was previously examined by Dance et al. in a detailed manner.[18] It is interesting to note that the CH···π interactions found in compound **9c** (and also in derivative **6c**) fall into the commonly observed type III classification introduced by Malone et al.,[19] significantly deviated from an ideal T geometry. The occurrence of this geometry is attributed to the shallow potential, which allows many binding arrangements of similar energy.

Solid State Characterization. *Calorimetric and X-ray Diffraction Experiments.* Recrystallized samples of compounds **7a–c** were studied by differential scanning calorimetry and thermogravimetric analysis to ascertain their thermal stability upon heating in the range 25–300 °C. Compounds **7a** and **7c** solidified after their respective purification steps, but compound **7b** formed an oil that could be solidified only at low temperatures. A common feature observed in all DSC experiments is a broad, endothermic transition starting about 40 °C that was correlated to the loss of dichloromethane according to TGA experiments. After desolvation, compound **7a** melts at 178–182 °C, in agreement with the visual observation of the melting point. A third endothermic transition occurs between 190 and 195 °C, which was attributed to decomposition of the sample. Solid samples of **7b** showed no additional transitions after the solvent loss as the compound gradually became an oil. Compound **7c** and its deuterated analogue were crystallized from dichloromethane. From the DSC trace, after the initial endothermic transition ascribed to loss of solvent, a peak corresponding to the melting process was observed beginning at 97 °C and ending at 114 °C.

Although no high quality single crystals from molecular rotors **7a–c** have been obtained, crystallization attempts with dichloromethane yielded weakly diffracting crystals of compound **7c**. The structure was solved in the space group $P2_1/c$ and confirmed the connectivity of the desired molecular rotor (Figure 3a). The structure contained considerable degree of disorder, particularly severe in the *tert*-butyldiphenylsilyl groups, and could not be further refined to acceptable publication standards. Nevertheless, the coordinates of the proposed model were employed to calculate the X-ray powder pattern and determine the identity of the bulk solids prior to solid state spectroscopic studies.

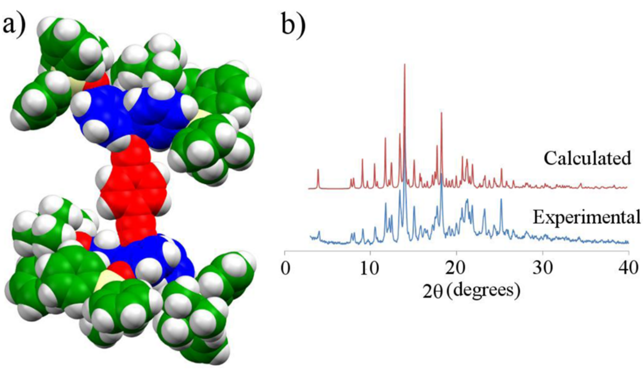

Figure 3. (a) Space filling model showing only one molecule of the highly disordered compound **7c** with the central 1,4-diethynylphenylene fragment in red, the trityl groups in blue, and the protecting groups in green. (b) Comparison between the calculated (top, red) and experimental powder X-ray patterns of solid samples of **7c**-d_4 from dichloromethane (bottom, blue).

As mentioned above, powder X-ray diffraction analysis was employed to explore the crystallinity of samples **7a**, **7b**, and **7c**-d_4, and it was also used to select the samples that were later studied by solid state NMR. The powder pattern from compound **7a** showed broad Bragg diffraction peaks in the 4–50 degrees (2θ) range indicating low crystallinity of the sample. The X-ray diffractogram of **7b** was consistent with an amorphous solid, with a broad featureless pattern. Conversely, freshly recrystallized samples of **7c**–d_4 from a saturated dichloromethane solution presented a powder pattern with sharp peaks between the 4–50 degrees (2θ) range that agrees very well with the calculated[20,21] diffractogram obtained from the structural model proposed above (Figure 3b), giving us confidence that our model is qualitatively correct.

Solid State NMR Experiments. The analysis and ^{13}C NMR characterization in solution of silyl-protected molecular rotors **7a–c** revealed a highly congested aromatic region in the spectra that would prevent a detailed line shape analysis using variable temperature solid state NMR. ^{13}C NMR CPMAS experiments at room temperature of the molecular rotor **7a** confirmed this assumption. To circumvent this, crystalline samples of molecular rotor **7c**-d_4 synthesized as described above were studied using ^{2}H NMR spin echo line shape analysis.

Deuterium solid state NMR is a technique widely used to describe rotational dynamics in molecular crystals because the quadrupolar moment of the deuterium nucleus gives rise to quadrupole coupling constants in the 140–220 kHz range, which results in linewidths that are very highly sensitive to nuclear motion over a wide dynamic range.[22] The pattern of a single crystal with only one type of C–^{2}H bond with a symmetric quadrupolar tensor would give a doublet with a quadrupolar splitting Δν that depends on the orientation angle β that the bond makes with respect to the external field:

$$\Delta\nu = 3/4(e^2 q_{zz} Q/h)(3\cos^2\beta - 1)$$
$$= 3/4(\mathrm{QCC})(3\cos^2\beta - 1)$$

The variable Q represents the electric quadrupole moment of the deuterium, e and h are the electric charge and Planck constant, and q_{zz} is the magnitude of the principal component of electric field gradient tensor, which lies along the C–^{2}H bond. The technique is based on the analysis of the changes in the shape of the powder spectrum at different temperatures. The line shape of the powder pattern is sensitive to the frequency and geometry of molecular motions with correlation times of the order of 10^4 to 10^7 Hz. Variations in line shape can be described with angular displacements of the C–^{2}H bonds between specific sites in purposely enriched samples.

Spin echo experiments at room temperature of compound **7c**-d_4 showed a poor signal-to-noise ratio even at higher number of transients (ca. 80 000). The central phenylene in the molecule with 98 atom % D, represents only 0.37% of the total mass of the sample. In spite of this dilution, the experimental signal was used to establish a qualitative reference of the molecular dynamics using a conic model based on a 180° jump motion. Knowing that deuterium line shape from samples with slow exchanging components (frequencies <10 kHz) display a Pake pattern with peaks splitting by ca. 130–132 kHz (Figure 4b, bottom), it was observed that the central phenylene in **7c**-d_4 is not completely static. As shown in Figure 4b (middle), the line shape at ambient temperature could be approximately simulated[23] using a 2-fold flip model with a rotational frequency that is higher than 10 kHz but lower than the ca. 10.0 MHz

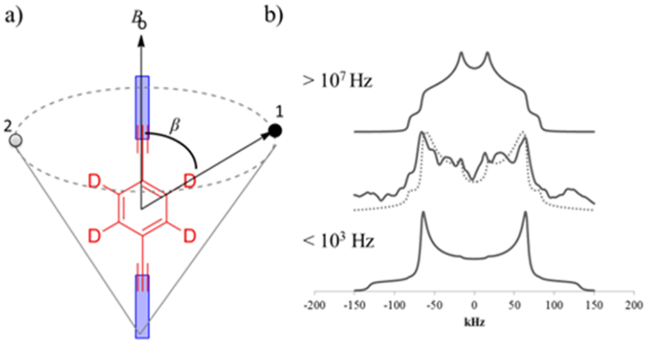

Figure 4. (a) Cone model employed to describe the motion of the phenylene ring between two sites related by 180°. (b) Calculated deuterium lineshapes from a rotator undergoing 2-fold flips in the fast exchange (top) and static regime (bottom). In the middle, experimental line shape of **7c**-d_4 situated in the intermediate regime (the dotted line, included as visual reference, represents a 150 kHz frequency motion).

limit of the fast exchange regime, which is shown in the top frame of Figure 4b. This type of low frequency motion observed in **7c**-d_4 has been also reported in molecular rotors containing smaller stators and high activation barriers that result from several intermolecular contacts,[3a] which could be the case in the present system.

CONCLUSIONS

We have synthesized molecular rotors **7a**–**c** with one, two, and three *tert*-butyldiphenylsilyl groups in each of the two trityl groups of the stator using an effective four step methodology, which also proved the high stability of the bulky silyl groups. Samples with the small diethynyl phenylene rotator were characterized by the inclusion of solvent molecules, which were able to escape under normal temperature and pressure, making the crystals difficult to maintain and characterize. It was shown that the sample with three silyl substituents on each end of the molecule, **7c**, gives the most promising crystals, highlighting the importance of symmetry in the crystallization of these relatively large compounds. After showing that a relatively low quality crystal structure of **7c** resulted in a calculated powder X-ray diffraction pattern that is nearly identical to the one obtained from experiment, we decided to explore the rotational dynamics of the central phenylene of **7c** using solid state NMR. Knowing that the large number of aromatic rings would limit the information available from solid state ^{13}C NMR, we investigated the rotational dynamics of **7c** using solid state ^{2}H NMR with the deuterated analogue **7c**-d_4. Although a complete description of the internal motion by solid state ^{2}H NMR was not practical because of the high dilution of the deuterons (0.37%) and the low stability of the solvent-containing crystals, the experimental line shape showed that the rotation of the central phenylene occurs in the intermediate regime, with the 1,4-diethynylphenylene-d_4 rotator undergoing 180° jumps at ca. 150 kHz. We conclude from these studies that more symmetric silyl derivatives in the most symmetric conformations may provide suitable stators for a new generation of molecular rotors that have larger rotating units.

EXPERIMENTAL SECTION

(3-Bromo-phenoxy)-*tert*-butyl-diphenyl-silane (1). The compound **1** was obtained following the described procedure[24] to afford a transparent liquid (14.0 g, 98%): IR (KBr) ν 3417, 3136, 1642, 1472, 1401, 1328, 1112, 935, 777, 701, 614, 515; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79–7.76 (4H, m), 7.53–7.41 (6H, m), 7.09 (1H, t, *J* = 2.0 Hz), 7.06 (1H, ddd, *J* = 8.0, 2.0, 1.0 Hz), 6.94 (1H, t, *J* = 8.0 Hz), 6.59 (1H, ddd, *J* = 8.0, 2.0, 1.0 Hz), 1.17 (9H, s); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 156.6, 135.7, 132.5, 130.4, 130.3, 128.1, 124.5, 123.4, 122.6, 118.6, 26.7, 19.7; ^{29}Si NMR (59.6 MHz, $CDCl_3$) δ −4.55; MS (DIP) 412 ([M + 1]$^+$, 29), 411 (M$^+$, 0.6), 356 (24), 355 (100), 354 (24), 353 (93), 277 (10) 274 (11), 273 (12). Anal. Calcd for $C_{22}H_{23}BrOSi$: C, 64.23; H, 5.63. Found: C, 64.17; H, 5.87.

[3-(*tert*-Butyl-diphenyl-silanyloxy)-phenyl]-diphenyl-methanol (5a). A solution of **1** (3.00 g, 7.3 mmol) in freshly distilled THF (50 mL) was cooled down to −78 °C in a dry ice bath. Subsequently, *n*-butyllithium (3.2 mL, 2.5 M in hexanes, 8.0 mmol) was added dropwise, and the reaction mixture was stirred for 30 min at −78 °C. Then, benzophenone **2** (1.33 g, 7.3 mmol) dissolved in dry THF (50 mL) was added. After stirring for 2 h at −78 °C, the reaction was quenched with saturated solution of NH_4Cl. The aqueous phase was extracted with CH_2Cl_2, and the organic phase was dried over anhydrous Na_2SO_4. Purification on silica gel column chromatography, eluting with hexane/ethyl ether (200:3) yielded compound **5a** (3.50 g, 93%) as a white crystalline solid: mp 88–89 °C; IR (KBr) ν 3567, 3447, 3058, 2930, 2858, 1596, 1481, 1428, 1391, 1286, 1255, 701, 614, 498; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.62 (4H, d, *J* = 7.1 Hz), 7.41–7.38 (2H, m), 7.34–7.29 (4H, t, *J* = 7.1 Hz), 7.21–7.19 (6H, m), 7.07–7.05 (5H, m), 6.84 (1H, d, *J* = 7.5 Hz), 6.77 (1H, d, *J* = 8.0 Hz), 6.58 (1H, d, *J* = 1.6 Hz), 2.60 (1H, s), 1.07 (9H, s, $C(CH_3)_3$); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 155.3, 148.3, 146.7, 135.7, 132.9, 130.0, 129.0, 127.9, 127.9, 127.8, 127.2, 120.7, 120.1, 118.8, 81.9, 26.8, 19.6; ^{29}Si NMR (59.6 MHz, $CDCl_3$) δ −5.13; HRMS (APCI-TOF) Calcd for $C_{35}H_{35}O_2Si-H_2O$, 497.2295, found 497.2290, error 1.04 ppm; MS (DIP) 515 ([M + 1]$^+$, 4), 514 (M$^+$, 8), 458 (38), 457 (100), 361 (24), 301 (10), 259 (19). Anal. Calcd for $C_{35}H_{34}O_2Si$: C, 81.67; H, 6.66. Found: C, 81.71; H, 6.61.

***tert*-Butyl-[3-(1,1-diphenyl-prop-2-ynyl)-phenoxy]-diphenyl-silane (6a).** Hydrochloric acid gas (generated in situ by dropwise addition of H_2SO_4 to NaCl) was slowly bubbled through a solution of alcohol **5a** (0.77 g, 1.5 mmol) in CH_2Cl_2 (50 mL) at room temperature. After 5 h stirring, the solvent was completely removed at reduced pressure, and the solid was redissolved in benzene (25 mL); ethynylmagnesium bromide (6.0 mL, 0.5 M in THF, 3.0 mmol) was then added, and the reaction was stirred at room temperature over 48 h. After this time, the reaction was quenched by addition of saturated NH_4Cl, the organic phase was extracted twice with CH_2Cl_2, and the combined organic portions were dried over anhydrous Na_2SO_4. Column chromatography purification on silica gel, with hexane/ethyl ether (200:1) yielded compound **6a** (0.60 g, 77%) as a white crystalline solid: mp 143–145 °C; IR (KBr) ν 3303, 3071, 2932, 2859, 1596, 1488, 1428, 1262, 1113, 884, 742, 698; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.59–7.56 (4H, d, *J* = 7.4 Hz), 7.42–7.24 (6H, m), 7.17–7.11 (6H, m), 7.09–6.98 (5H, m), 6.88 (1H, d, *J* = 7.8 Hz), 6.76 (1H, d, *J* = 8.1 Hz), 6.55 (1H, s), 2.55 (1H, s), 1.04 (9H, s); ^{13}C NMR (67.9 MHz) δ 155.3, 145.9, 144.6, 135.7, 132.8, 129.8, 129.0, 128.0, 127.8, 126.8, 122.0, 121.1, 118.5, 89.6, 73.4, 55.3, 26.7, 19.5; ^{29}Si NMR (53.6 MHz, $CDCl_3$) δ −4.95; HRMS (APCI-TOF) Calcd for $C_{37}H_{35}OSi$, 523.2442, found 523.2451, error 2.34 ppm; MS (DIP) 523 ([M + 1]$^+$, 3), 522 (M$^+$, 8), 466 (20), 465 (47), 388 (33), 387 (100), 309 (23), 265 (15). Anal. Calcd for $C_{37}H_{34}OSi$: C, 85.01; H, 6.56. Found: C, 85.06; H, 6.29.

1,4-Bis-{[(3-(*tert*-butyl-diphenyl-silanyloxy)-diphenyl)-phenylmethyl]-ethynyl}-phenylene (7a). A mixture of 1,4-diiodobenzene (0.095 g, 0.3 mmol), alkyne **6a** (0.30 g, 0.6 mmol) $Pd(PPh_3)_2Cl_2$ (0.021 g, 0.03 mmol), CuI (0.011 g, 0.06 mmol) and diisopropyl amine (0.5 mL) in THF (25 mL) previously degassed was refluxed for 2.5 h. After this time, the reaction was cooled down to room temperature and quenched with saturated NH_4Cl. The organic phase was twice extracted with CH_2Cl_2, and the combined organic portions were dried over anhydrous Na_2SO_4. The solvent was removed at reduced pressure followed by purification by column chromatography on neutral alumina, eluting with hexane/ethyl ether (199:1) to afford 0.24 g (74%) of rotor **7a** as a white crystalline solid: mp 183–184 °C;

IR (KBr) ν 3069. 2958, 2932, 2859, 1957, 1725, 1595, 1486, 1428, 1262, 1112, 975, 699, 500; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (4H, d, J = 7.1 Hz), 7.38 (2H, t, J = 7.8 Hz), 7.22−7.16 (6H, m), 7.12−7.06 (5H, m), 6.92 (1H, dt, J = 7.9, 0.9 Hz), 6.79 (1H, dd, J = 8.1, 2.4 Hz), 6.60, (1H, t, J = 1.8 Hz), 1.06 (9H, s); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 155.3, 146.3, 145.0, 135.6, 132.7, 131.4, 129.8, 129.0, 128.9, 127.9, 127.7, 126.7, 123.2, 122.1, 121.1, 118.5, 97.1, 84.8, 55.9, 26.6, 19.4; ^{29}Si NMR (79.5 MHz, $CDCl_3$) δ −4.81; MS (FAB) 1120 (3) [(M + H)$^+$], 1042 (5), 787 (9), 497 (70), 197 (78), 135 (100), 105 (47); HRMS (APCI-TOF) Calcd for $C_{80}H_{71}O_2Si_2$, 1119.4987, found 1119.4974, error 1.17. Anal. Calcd for $C_{80}H_{70}O_2Si_2$: C, 85.82; H, 6.30. Found: C, 85.65; H, 6.75.

([3-(*tert*-Butyl-diphenyl-silanyloxy)-diphenyl]-phenylmethyl)-4-iodophenylethyne (8a). Colorless oil (0.05 g, 24%): IR (KBr) ν 3067, 2933, 2859, 1595, 1484, 1428, 1264, 756, 700, 614, 500; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.66−7.51 (8H, m), 7.41−7.31 (2H, m), 7.30−7.22 (4H, m), 7.15 (6H, t, J = 3.2 Hz), 7.10−7.01 (5H, m), 6.89−6.84 (1H, m), 6.76 (1H, dd, J = 8.0, 2.3 Hz), 6.57 (1H, t, J = 2.3 Hz), 1.03 (9H, s); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 155.4, 146.2, 144.9, 137.4, 135.6, 133.3, 132.8, 129.9, 129.0, 129.0, 128.0, 127.0, 126.8, 123.2, 122.1, 121.1, 118.6, 97.0, 93.8, 84.1, 55.9, 26.7, 19.5; ^{29}Si NMR (53.6 MHz, $CDCl_3$) δ −4.89; MS (DIP) 725 ([M + 1]$^+$, 6), 724 (M$^+$, 13), 668 (50), 667 (100), 589 (26), 513 (11), 463 (29), 385 (46), 361 (36), 259 (14), 239 (17), 167 (14), 135 (15); HRMS (APCI-TOF) Calcd for $C_{43}H_{38}IOSi$ H, 725.1731, found 725.1735, error 0.52. Anal. Calcd for $C_{43}H_{37}IOSi$: C, 71.26; H, 5.15. Found: C, 71.05; H, 5.12.

1,6-Bis(3-((*tert*-butyldiphenylsilyl)oxy)phenyl)-1,1,6,6-tetraphenylhexa-2,4-diyne (9a). A solution of 1,4-dibromobenzene-d_4 (0.046 g, 0.2 mmol) and alkyne **5** (0.20 g, 0.4 mmol) in THF (25 mL) containing $Pd(PPh_3)_2Cl_2$ (0.014 g, 0.02 mmol), CuI (0.007 g, 0.04 mmol) and diisopropyl amine (0.5 mL) previously degassed was refluxed for 2.5 h. At this time, the reaction was cooled to room temperature and quenched with saturated NH_4Cl. The aqueous phase was twice extracted with CH_2Cl_2, and the combined organic portions were dried over anhydrous Na_2SO_4. The solvent was removed at reduced pressure, followed by purification by column chromatography on neutral alumina, eluting with hexane/ethyl ether (99:1) to afford 0.20 g (50%) of the dialkyne compound as the main product, a white crystalline solid: mp 223−224 °C; IR (KBr) ν 3055, 2934, 2859, 1595, 1487, 1427, 1265, 1111, 971, 881, 742, 698, 503; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.55−7.51 (8H, dt, J = 6.0, 1.5 Hz), 7.36−7.20 (12H, m), 7.17−7.09 (12H, m), 7.05 (2H, t, J= 8.0 Hz), 6.98−6.93 (8H, m), 6.88−6.82 (2H, m), 6.73 (2H, ddd, J = 8.0, 2.5, 1.0 Hz), 1.00 (18H, s); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 155.3, 145.5, 144.2, 135.6, 132.7, 129.8, 129.0, 128.0, 127.7, 126.8, 122.1, 121.0, 118.6, 83.8, 69.8, 56.0, 26.6, 19.4; ^{29}Si NMR (53.7 MHz, $CDCl_3$) δ −4.77 (2 Si); HRMS (APCI-TOF) Calcd for $C_{74}H_{67}O_2Si_2$, 1043.4674, found 1043.4677, error 0.27 ppm.

Bis-[3-(*tert*-butyl-diphenyl-silanyloxy)-phenyl]-phenylmethanol (5b). A solution of **1** (1.00 g, 2.4 mmol) in THF (50 mL) was cooled down to −78 °C in a dry ice bath. Subsequently, *n*-butyllithium (1.1 mL, 2.5 M in THF, 2.7 mmol) was added to the mixture and stirred for 0.5 h at −78 °C. Then, methyl benzoate **3** (0.17 g, 1.2 mmol) was added. After stirring for 2 h at −78 °C, the reaction was quenched with saturated solution of NH_4Cl. The organic phase was extracted with CH_2Cl_2 and dried over anhydrous Na_2SO_4. Column chromatography on silica gel, using hexanes yielded **5b** (0.77 g, 83%) as a yellow oil: IR (KBr) ν 3472, 3071, 2933, 2859, 1596, 1483, 1429, 1277, 1112, 1003, 871, 701, 613, 501; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (8H, dt, J = 8.0, 1.2 Hz), 7.47−7.39 (4H, m), 7.38−7.31 (8H, m), 7.21−7.11 (3H, m), 7.00−6.94 (4H, m), 6.73−6.65 (4H, m), 6.63−6.58 (2H, dq, J = 17.7, 0.9 Hz), 2.44 (1H, s), 1.12 (18H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 148.1, 146.4, 135.7, 135.7, 133.0, 129.9, 128.7, 127.8, 127.7, 127.7, 127.0, 120.9, 119.7, 118.6, 81.5, 26.8, 19.6; ^{29}Si NMR (59.6 MHz, $CDCl_3$) δ −5.29; HRMS (APCI-TOF) Calcd for $C_{51}H_{53}O_3Si_2$−H_2O, 751.3422, found 751.3431, error 1.17 ppm; MS (DIP) 769 ([M + 1]$^+$, 3), 768 ([M$^+$], 5), 712 (61), 711 (100), 693 (19), 514 (29), 513 (66), 495 (5), 435 (10), 361 (7), 199 (8), 135 (12). Anal. Calcd for $C_{51}H_{52}O_3Si_2$: C, 79.64; H, 6.81. Found: C, 79.67; H, 6.88.

3,3-Bis-[3-(*tert*-butyl-diphenyl-silanyloxy)-phenyl]-3-phenyl-propyne (6b). Hydrochloric acid gas (generated in situ by dropwise addition of H_2SO_4 to NaCl) was bubbled slowly through a solution of alcohol **5b** (1.00 g, 1.3 mmol) in CH_2Cl_2 (50 mL) at room temperature. After 5 h of bubbling, the solvent was completely removed at reduced pressure, and the solid was redissolved in benzene (25 mL). Then, ethynylmagnesium bromide (5.21 mL, 0.5 M, 2.6 mmol) was added, and the reaction was stirred 48 h at room temperature. After this time, the reaction was quenched with saturated solution of NH_4Cl, and the organic phase extracted twice with CH_2Cl_2. The combined organic portions were dried over anhydrous Na_2SO_4. Removal of the solvent followed by purification by column chromatography on silica gel, using hexanes/ethyl ether (200:1) yielded compound **6b** (0.60 g, 59%) as a colorless oil: IR (KBr) ν 3304, 3071, 2934, 2860, 1594, 1482, 1429, 1258, 1112, 1002, 889, 870, 761, 701, 615, 500; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67−7.56 (8H, dt, J = 8.0, 1.6 Hz), 7.43−7.26 (12H, m), 7.15−7.04 (3H, m), 6.96−6.87 (4H, m), 6.70−6.63 (4H, m), 6.59−6.50 (2H, d, J = 8.0 Hz), 2.41 (1H, s), 1.07 (18H, s); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 155.4, 145.9, 144.5, 135.8, 133.1, 129.9, 128.9, 128.7, 127.9, 126.7, 122.1, 121.2, 118.5, 89.4, 73.3, 55.2, 26.9, 19.6; ^{29}Si NMR (53.6 MHz, $CDCl_3$) δ −5.07; HRMS (APCI-TOF) Calcd for $C_{53}H_{54}O_2Si_2$, 777.3578, found 777.3579, error 0.045 ppm MS (DIP) 777 ([M + 1]$^+$, 15), 776 ([M$^+$], 22), 641 (24), 585 (18), 466 (42), 465 (100), 403 (27), 387 (18), 367 (21), 331 (18), 259 (44).

1,4-Bis-(3,3-bis-[3-(*tert*-butyl-diphenyl-silanyloxy)-phenyl]-3-phenyl-propynyl)-phenylene (7b). A solution of 1,4-diiodobenzene (0.053 g, 0.2 mmol), alkyne **6b** (0.25 g, 0.3 mmol), $Pd(PPh_3)_2Cl_2$ (0.011 g, 0.02 mmol), CuI (0.006 g, 0.03 mmol) and diisopropyl amine (0.5 mL) in THF (25 mL) previously degassed was refluxed for 2.5 h. After this time, the reaction was cooled down to room temperature and quenched with saturated NH_4Cl. The organic phase was twice extracted with CH_2Cl_2, and the combined organic portions were dried over anhydrous Na_2SO_4. The solvent was removed followed by column chromatography purification on neutral alumina using hexanes/ethyl ether (200:1) yielded 0.19 g (73%) of the rotor **7b**, as colorless oil that slowly solidifies at low temperature: IR (KBr) ν 3069, 2931, 2857, 2346, 1594, 1483, 1427, 1258, 1111, 1001, 868, 699, 500; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.66−7.57 (8H, dd, J = 6.6, 1.2 Hz), 7.41−7.22 (12H, m), 7.17−7.05 (5H, m), 7.00−6.94 (4H, m), 6.74 (2H, t, J = 2.0 Hz), 6.69 (2H, dd, J = 7.9, 1.6 Hz), 6.60 (2H, d, J = 7.6 Hz), 1.08 (18H, s); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 155.4, 146.3, 144.9, 135.7, 133.0, 131.4, 129.9, 129.0, 128.7, 127.8, 126.7, 123.2, 122.1, 121.1, 118.4, 96.9, 84.9, 55.8, 26.8, 19.6; ^{29}Si NMR (53.6 MHz, $CDCl_3$) δ −5.01; MS (FAB) 1627 (2) [(M$^+$ + H)$^+$], 1626 (1) [(M +)], 1550 (1), 1315 (1), 1295 (3), 751 (6), 259 (10), 197 (70), 135 (100), 121 (10), 105 (12); HRMS (APCI-TOF) Calcd for $C_{112}H_{107}O_4Si_4$, 1627.7241, found 1627.7207, error 1.77 ppm. Anal. Calcd for $C_{112}H_{106}O_4Si_4$: C, 82.61; H, 6.56. Found: C, 82.42; H, 6.39.

(Bis-[3-(*tert*-butyl-diphenyl-silanyloxy)-phenyl]-phenylmethyl)-4-iodophenylethyne (8b). Colorless oil (0.05 g, 24%): IR (KBr) ν 3067, 2933, 2859, 1595, 1484, 1428, 1264, 756, 700, 614, 500; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.66−7.51 (8H, m), 7.41−7.31 (2H, m), 7.30−7.22 (4H, m), 7.15 (6H, t, J = 3.2 Hz), 7.10−7.01 (5H, m), 6.89−6.84 (1H, m), 6.76 (1H, dd, J = 8.0, 2.3 Hz), 6.57 (1H, t, J = 2.3 Hz), 1.03 (9H, s); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 155.4, 146.2, 144.9, 137.4, 135.6, 133.3, 132.8, 129.9, 129.0, 129.0, 128.0, 127.0, 126.8, 123.2, 122.1, 121.1, 118.6, 97.0, 93.8, 84.1, 55.9, 26.7, 19.5; ^{29}Si NMR (53.6 MHz, $CDCl_3$) δ −4.89; HRMS (APCI-TOF) Calcd for $C_{43}H_{38}IOSi$, 725.1731, found 725.1735, error 0.52 ppm; MS (DIP) 725 ([M + 1]+, 6), 724 (M + , 13), 668 (50), 667 (100), 589 (26), 513 (11), 463 (29), 385 (46), 361 (36), 259 (14), 239 (17), 167 (14), 135 (15). Anal. Calcd for $C_{59}H_{55}IO_2Si_2$: C, 72.37; H, 5.66. Found: C, 72.26; H, 5.50.

Tris-[3-(*tert*-butyl-diphenyl-silanyloxy)-phenyl]-methanol (5c). A solution of **1** (3.00 g, 7.3 mmol) in THF (50 mL) was cooled down to −78 °C in a dry ice bath. Subsequently, *n*-butyllithium (3.2 mL, 2.5 M in THF, 8.0 mmol) was added, and the mixture was stirred for 30 min at −78 °C. Then, diethyl carbonate **4** (0.29 g, 2.4 mmol) in THF (20 mL) was added. After stirring for 2 h at −78 °C, the reaction was quenched with a saturated solution of NH_4Cl. The organic phase was extracted twice with CH_2Cl_2, and the organic phases were dried over anhydrous Na_2SO_4. Column chromatography on silica gel, eluting with hexanes/ethyl ether (199:1) yielded compound **5c** (2.00 g, 80%) as a white crystalline solid: mp 100−101 °C; IR (KBr) ν 3446, 3052, 2932, 2858, 1583, 1480, 1429, 1283, 1245, 1111, 1001, 954, 864, 788, 701, 616, 503; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.67−7.58 (12H, m), 7.44−7.23 (20H, m), 6.82 (3H, t, J = 8.0 Hz), 6.66 (3H, t, J = 2.2 Hz), 6.57 (3H, ddd, J = 8.0, 2.4, 0.9 Hz), 6.38 (3H, dq, J = 7.8 Hz, 1.7 Hz), 2.18 (1H, br, −OH), 1.08 (27H, s); ^{13}C NMR: (67.9 MHz, $CDCl_3$) δ 155.2, 148.0, 135.8, 133.2, 130.0, 128.5, 127.9, 121.0, 119.6, 118.6, 81.4, 26.9, 19.7; ^{29}Si NMR (53.6 MHz, $CDCl_3$) δ −5.20; HRMS (APCI-TOF) Calcd for $C_{67}H_{71}O_4Si_3$−H_2O, 1005.4549, Found 1005.4545; MS (FAB) 1007 (14) [(M−CH_3)$^+$], 965 (9), 767 (7), 691 (4), 359 (10), 197 (60), 135 (100), 121 (18); 0.40 ppm Anal. Calcd for $C_{67}H_{70}O_4Si_3$: C, 78.62; H, 6.89. Found: C, 78.66; H, 6.84.

Tris-[3-(*tert*-butyl-diphenyl-silanyloxy)-phenyl]-methane-ethyne (6c). Hydrochloric acid gas (generated in situ by dropwise addition of H_2SO_4 to NaCl) was slowly bubbled through a solution of alcohol **5c** (1.0 g, 1.0 mmol) in CH_2Cl_2 (50 mL) at room temperature. After 5 h of reaction, the solvent was completely removed at reduced pressure, and the solid was redissolved in benzene (25 mL); then, ethynylmagnesium bromide (3.91 mL, 0.5 M, 2.0 mmol) was added, and the reaction was stirred at room temperature over the weekend. After this time, the reaction was quenched with saturated solution of NH_4Cl, and the organic phase was extracted twice with CH_2Cl_2. The combined organic portions were dried over anhydrous Na_2SO_4. Removal of the solvent followed by column chromatography purification on silica gel, using hexanes/ethyl ether (199.5:0.5) yielded compound **6c** (0.66 g, 66%) as a colorless oil: IR (KBr) ν 3296, 3052, 2932, 2857, 1596, 1476, 1429, 1282, 1244, 1112, 947, 863, 787, 700, 619, 503; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.60 (12H, d, J = 6.6 Hz), 7.38−7.22 (18H, m), 6.78 (3H, dt, J = 8.0, 1.5 Hz), 6.69 (3H, d, J = 1.8 Hz), 6.54 (3H, dd, J = 8.0, 0.7 Hz), 6.31 (3H, d, J = 8.0 Hz), 2.20 (1H, s), 1.04 (27H, s); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 155.3, 145.8, 135.8, 133.2, 129.9, 128.5, 127.8, 122.0, 121.0, 118.3, 89.0, 73.3, 55.0, 26.9, 19.7; ^{29}Si NMR (79.4 MHz, $CDCl_3$) δ −5.23; MS (FAB) 1031 (2) [(M + H)$^+$], 895 (2), 699 (10), 641 (5), 621 (4), 259 (20), 197 (90), 135 (100). Anal. Calcd for $C_{69}H_{70}O_3Si_3$: C, 80.34; H, 6.84. Found: C, 80.38; H, 6.80.

1,4-Bis-((tris-[3-(*tert*-butyl-diphenyl-silanyloxy)-phenyl]-methanyl)-ethynyl)-phenylene (7c). A solution of 1,4-diiodobenzene (0.3 g, 0.1 mmol) and alkyne **6c** (0.20 g, 0.2 mmol) in THF (25 mL) containing $Pd(PPh_3)_2Cl_2$ (0.007 g, 0.01 mmol), CuI (0.004 g, 0.02 mmol) and diisopropyl amine (0.5 mL) previously degassed was refluxed for 2.5 h. After this time, the reaction was cooled down to room temperature and quenched with saturated solution of NH_4Cl. The organic phase was extracted twice with CH_2Cl_2, and the combined organic portions were dried over anhydrous Na_2SO_4. The solvent was removed at reduced pressure followed by column chromatography purification on neutral alumina, using hexanes/ethyl ether (199:1) to afford compound **7c** (0.16 g, 75%) as a white crystalline solid: mp 125−127 °C; IR (KBr) ν 3070, 2933, 2858, 2221, 1593, 1481, 1428, 1256, 1111, 1004, 901, 865, 700, 612, 501; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (24H, dd, J = 8.0, 1.4 Hz), 7.40−7.24 (36H, m), 7.04 (4H, s), 6.90−6.82 (12H, m), 6.68−6.63 (6H, m), 6.39 (6H, d, J = 8.4 Hz), 1.09 (54H, s); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 155.2, 146.1, 135.6, 133.1, 131.3, 129.9, 128.5, 127.8, 123.0, 122.0, 121.0, 118.3, 96.5, 84.9, 55.6, 26.8, 19.6; ^{29}Si NMR (79.4 MHz, $CDCl_3$) δ −5.16; HRMS (APCI-TOF) Calcd for $C_{144}H_{143}O_6Si_6$, 2135.9494, found 2135.9479, error 0.74 ppm; MS (FAB) 2136 (4) [(M + H)$^+$], 1924 (2), 1806 (4), 1590 (3), 1323 (2), 1207 (3), 1037 (3), 899 (3), 622 (25), 391 (21), 219 (100). Anal. Calcd for $C_{144}H_{142}O_6Si_6$: C, 80.93, H, 6.70. Found C, 80.44, H, 6.58.

Tris-[3-(*tert*-butyl-diphenyl-silanyloxy)-phenyl]-methyl)-4-iodophenylethyne (8c). Colorless oil (0.025 g, 20%): IR (KBr) ν 3438, 3070, 2930, 2857, 1594, 1482, 1427, 1252, 1111, 1005, 863, 785, 737, 698, 610, 500; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.70−7.50 (12H, m), 7.38−7.20 (22H, m), 6.84−6.68 (6H, m) 6.63−6.53 (3H, m), 6.31 (3H, t, J = 7.8 Hz), 1.05 (27H, s); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 155.2, 145.9, 137.2, 135.6, 133.3, 133.0, 129.9, 128.5, 127.7, 123.2, 121.9, 120.9, 118.3, 96.5, 93.4, 84.0, 55.5, 26.8, 19.6; ^{29}Si NMR (53.7 MHz, $CDCl_3$) δ −5.3; HRMS (APCI-TOF) Calcd for $C_{75}H_{74}IO_3Si_3$, 1233.3985, found 1233.3985, error 0.009 ppm. Anal. Calcd for $C_{75}H_{73}IO_3Si_3$: C, 73.03; H, 5.96. Found: C, 72.93; H, 5.85.

1,4-Bis-((tris-[3-(*tert*-butyl-diphenyl-silanyloxy)-phenyl]-methanyl)-ethynyl)-phenylene-d_4 (7c-d_4). A solution of 1,4-diiodobenzene-d_4 (0.053 g, 0.2 mmol) and alkyne **6c** (0.328 g, 0.3 mmol) in THF (50 mL) containing $Pd(PPh_3)_3Cl_2$ (0.011 g, 0.02 mmol), CuI (0.006 g, 0.03 mmol) and diisopropyl amine (1 mL) previously degassed was refluxed (6 h). After this time, the reaction was cooled down to room temperature and quenched with saturated solution of NH_4Cl. The organic phase was extracted with CH_2Cl_2, and the combined organic portions were dried over anhydrous Na_2SO_4. The solvent was removed at reduced pressure followed by chromatography purifications on neutral alumina, using hexanes/ethyl ether (199:1) to afford 0.17 g, (50%) of compound **7c**-d_4 as a white crystalline solid: mp 118−119 °C; FTIR (ATR) ν 3072, 2955, 2931, 2857, 1959, 1594, 1582, 1481, 1428, 1277, 1254, 1113, 1005, 998, 959, 898, 861, 695, 610, 499, 491; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.64−7.56 (24H, m), 7.34−7.24 (36H, m), 6.84 (6H, t, J = 8.1 Hz), 6.80 (6H, m), 6.60 (6H, dd, J = 7.8, 2.7 Hz), 6.40 (6H, d, J = 7.8 Hz), 1.07 (54H, s); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 155.2, 146.1, 135.6, 133.0, 129.9, 128.5, 127.8, 122.8, 122.0, 121.0, 118.2, 96.5, 84.8, 55.6, 26.8, 19.6; ^{29}Si NMR (53.7 MHz, $CDCl_3$) δ −5.16; HRMS (APCI-TOF) Calcd for $C_{144}H_{147}O_6Si_6$, 2139.9807, found 2139.9838, error 1.40 ppm. Anal. Calcd for $C_{144}H_{138}D_4O_6Si_6$: C, 80.77, H, 6.87 Found for C, 80.71, H, 6.70.

1,1,1,6,6,6-Hexakis(3-((*tert*-butyldiphenylsilyl)oxy)phenyl)-hexa-2,4-diyne (9c). A solution of 1,4-dibromobenzene-d_4 (0.015 g, 0.1 mmol) and alkyne **6c** (0.13 g, 0.1 mmol) in THF (50 mL) containing $Pd(PPh_3)_3Cl_2$ (0.004 g, 0.01 mmol), CuI (0.002 g, 0.01 mmol) and diisopropyl amine (1 mL) previously degassed was refluxed (6 h). After this time, the reaction was cooled down to room temperature and quenched with saturated solution of NH_4Cl. The organic phase was extracted with CH_2Cl_2, and the combined organic portions were dried over anhydrous Na_2SO_4. The solvent was removed at reduced pressure followed by chromatography purifications on neutral alumina, using hexanes/ethyl ether (199:1) to afford 0.08 g, (65%) of compound **9c** as a white crystalline solid: mp 171−172 °C; IR (KBr) ν 3053, 2931, 2856, 1596, 1474, 1428, 1281, 1110, 946, 862, 786, 697, 618; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.55 (12H, d, J = 6.6 Hz), 7.28−7.16 (18H, m), 6.76 (3H, t, J = 8.0 Hz), 6.55 (3H, t, J = 1.8 Hz), 6.50 (3H, dd, J = 8.0, 0.7 Hz), 6.41 (3H, d, J = 8.0 Hz), 1.00 (27H, s); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 155.1, 145.4, 135.6, 133.0, 129.9, 128.6, 127.8, 122.2, 121.0, 118.4, 83.4, 67.9, 55.87, 26.8, 19.6; ^{29}Si NMR (79.4 MHz, $CDCl_3$) δ −5.02; MS (FAB) 2062 (1) [M + H$^+$], 1984 (1), 1743 (1), 1029 (1), 675 (1), 259 (10), 197 (60), 135 (100).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H, ^{13}C NMR spectral data, CIF files for compounds **6a**, **9a**, **9c** and X-ray diffraction analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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