Synthesis of Sterically Hindered 1,3-Connected Polyarylmethanes

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Sterically hindered 1,3-connected polyarylmethanes were prepared by repetitive additions of aryllithiums to carbonyl compounds. Synthetic routes with various degree of convergence were used. Variable temperature NMR spectroscopy, in conjunction with other techniques, was used to characterize the products.

Introduction

Preparation of organic molecules with two or more unpaired electrons is relevant to the emerging field of organic magnetism.[2-8] High spin polyradicals based upon 1,3-connected polyarylmethanes are especially promising; star-branched ($S = 5$) decaradical, dendritic polyradical with 31 sites for unpaired electrons, and stable (at ambient temperature) tri- and tetraradicals have been reported.[6-8] Typical procedure for generation of a polyradical consists of treatment of the polyarylmethane-based polyether with alkali metal and, then, oxidation of the resultant carbopolyanion with iodine at low temperature. Stability of polyradicals is increased by steric hindrance. Therefore, synthesis of sterically hindered polyarylmethanes is a prerequisite for preparation and study of polyradicals at temperatures readily accessible to solution chemistry.

Synthesis of star-branched 1,3-connected polyarylmethane-based tetra-, hepta-, and decaethers was reported.[9] Here, we describe the synthesis of sterically hindered tri-, tetra- and heptaethers (Figure 1). The steric hindrance is achieved via Me- and *i*-Pr-substitution (R = Me and R = *i*-Pr in Figure 1). Polyradicals derived from tri-, tetra-, and heptaethers **3**, **4**, and **5** were already reported.[8,10] Also, synthesis of large dendrimers, which used methodology developed in this work and triether **2** as starting material, was published;[7] their structure assignment rests on the small and intermediate size homologues, which are described in this work.

Results and Discussion

1. Synthesis of Polyethers. The synthesis is based upon a convergent route with carbon–carbon bond-forming consecutive sequences of three steps: (1) Br/Li exchange, (2) addition of the organolithium to carbonyl compound, (3) etherification of triarylmethyl alcohols; the steps 1 and 2 are carried out in one pot (Figure 1).

Monolithiation via Br/Li exchange using 4,6-dibromo-1,3-dialkylbenzene, which is followed by addition of the aryllithium to 4,4′-di-*tert*-butylbenzophenone, gives triarylmethyl alcohol **1-Me-OH** or **1-*i*-Pr-OH**. Treatment with sodium hydride in tetrahydrofuran (THF) and alkylation of the alkoxide with iodomethane gives the corresponding ethers **1-Me-OMe** or **1-*i*-Pr-OMe**.

The aryllithium, which is produced by the Br/Li exchange using **1-Me-OMe**, is added to the following carbonyl compounds: (a) methyl 5-bromo-2,4-dimethylbenzoate, which gives triarylmethyl alcohol **2-Me-OH** and, after etherification, triether **2-Me-OMe**; (b) methyl 4-*tert*-butylbenzoate, which gives triarylmethyl alcohol **3-Me-OH**; subsequent treatment with sodium hydride and alkylation of the alkoxide with iodomethane produces triether **3-Me-OMe**; (c) dimethyl carbonate, which gives triarylmethyl alcohol **4-Me-OH**; the etherification using MeOH in trifluoroacetic acid or NaH/MeI in THF gives tetraether **4-Me-OMe**.

The more sterically hindered aryllithium, which is generated from **1-*i*-Pr-OMe**, reacts similarly to the R = Me analogue, except for the failure of the triple addition to dimethyl carbonate. Synthesis of tetraether **4-*i*-Pr-OMe** is accomplished via partially divergent route; that is, the Br/Li exchange using **2-*i*-Pr-OMe** is followed by the addition of the aryllithium to 4,4′-di-*tert*-butylbenzophenone to give alcohol **4-*i*-Pr-OHs** and, after etherification with NaH/MeI in THF, tetraether **4-*i*-Pr-OMe**.

The aryllithium obtained from Br/Li exchange using **2-Me-OMe** is added to either methyl 4-*tert*-butylbenzoate or 4,4′-di-*tert*-butylbenzophenone to give alcohols **5-Me-OH** or **4-Me-OHs**, respectively. Treatment of **5-Me-OH** with sodium hydride in dimethylformamide (DMF) and alkylation of the alkoxide with iodomethane gives heptaether **5-Me-OMe**.

2. Hydrocarbons. Characterization of the sterically hindered polyethers is aided by preparation of the corresponding hydrocarbons. Treatment of polyethers in THF with lithium metal for several days gives carbopolyanions, which, after quenching with MeOH, affords hydrocarbons 3–5 (Figure 2); the deuterated analogues can be obtained using MeOD. The hydrocarbons are also obtained by reduction of polyethers (or alcohols) using sodium borohydride in CF_3COOH/MeOH.[11]

When the last method is applied to **1-Me-OH** and, then, followed by Br/Li exchange and addition of the aryllithium to dimethyl carbonate, alcohol **6-Me-OH** is

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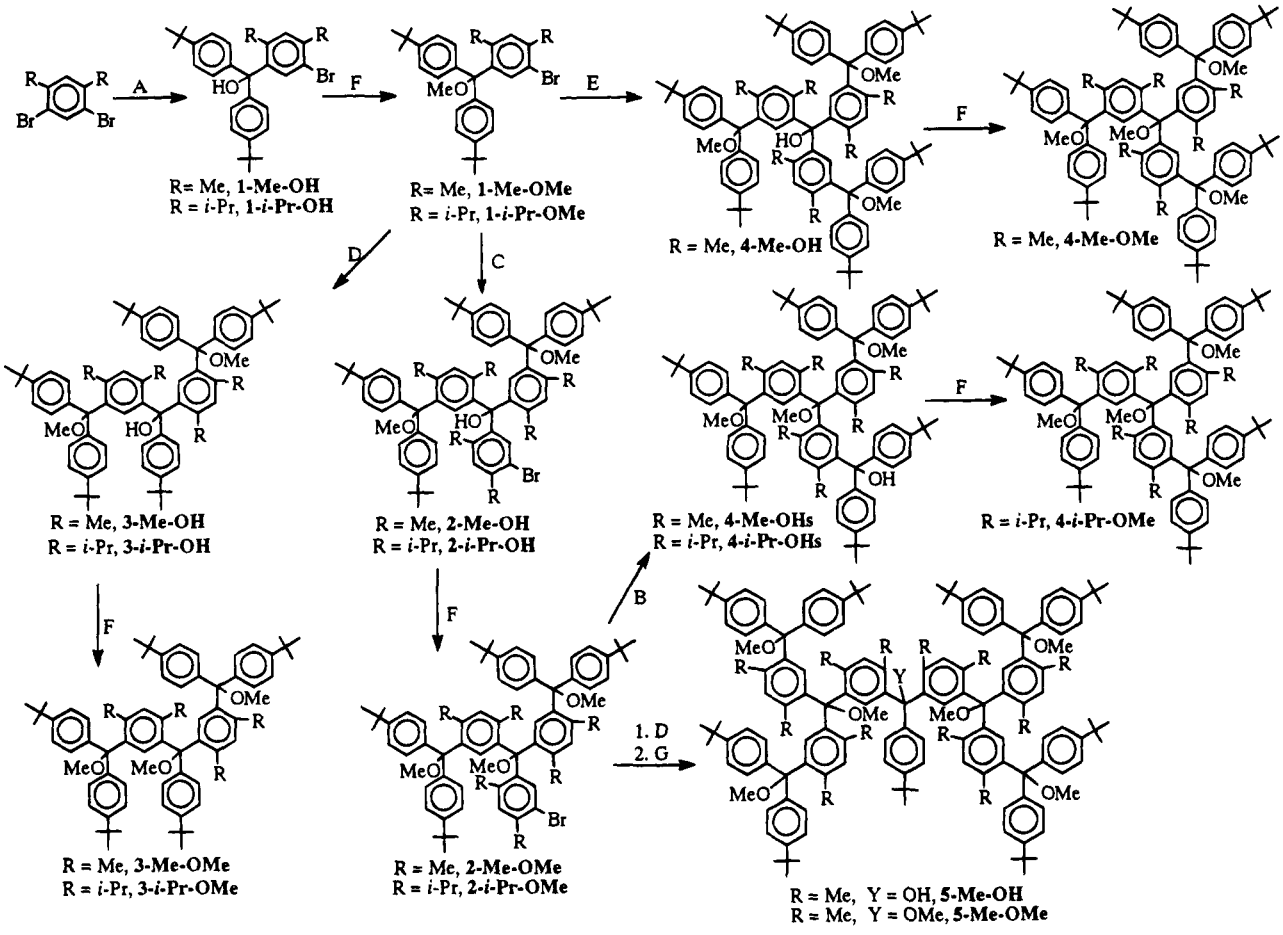
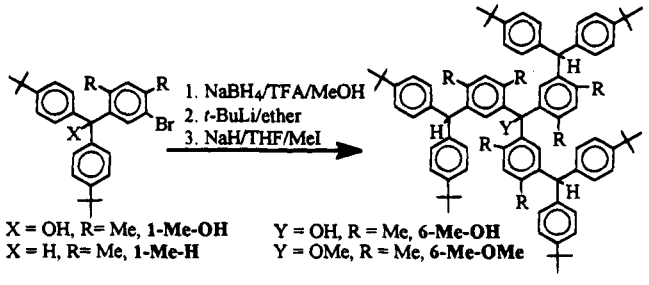


Figure 1. Synthesis of polyethers. The synthetic steps are as follows: A, (1) *n*-BuLi/ether, (2) 4,4′-di-*tert*-butylbenzophenone; B, (1) *t*-BuLi/ether, (2) 4,4′-di-*tert*-butylbenzophenone; C, (1) *t*-BuLi/ether, (2) methyl 5-bromo-2,4-dialkylbenzoate; D, (1) *t*-BuLi/ether, (2) methyl 4-*tert*-butylbenzoate; E, (1) *t*-BuLi/ether, (2) $(MeO)_2CO$; F, NaH/THF/MeI; G, NaH/DMF/MeI.

obtained; after etherification with MeOH/trifluoroacetic acid, ether **6-Me-OMe** is isolated.

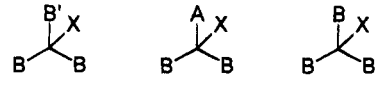


3. Characterization and Propeller Isomerism. Similarly to the previously reported large dendritic homologues and star-branched analogues, all polyether target compounds and selected alcohol intermediates give acceptable C/H elemental analyses. Expected positive ions are detected by fast atom bombardment MS (FABMS), i.e., $(M - OCH_3)^+$ for polyethers, $(M - OH)^+$ and $(M - OCH_3)^+$ for intermediate alcohols with COH and COMe functionalities, and $M^+/(M + 1)^+$ for hydrocarbons, including mass shift for deuterated isotopomers.

A single crystal X-ray structure for hydrocarbon **4-Me-H** is obtained.[14] The crystal is cubic (space group $Pa\bar{3}$). The molecule belongs to point group C_3 (Figure 3).

Unlike the large dendritic homologues, for which NMR spectra are severely broadened at all routinely accessible temperatures, and the star-branched analogoues, for which well-resolved NMR spectra at ambient temperature are available, the present molecules can be analyzed via variable temperature ^1H and ^{13}C NMR spectroscopy on polyethers and their derivatives with varying degree of steric congestion. The spectra are obtained in $CDCl_3$, C_6D_6, and tetrachloroethylene/C_6D_6 (TCE/C_6D_6).

Considering the most sterically hindered (central) triarylmethyl propeller as the only source of dynamic behavior on the NMR time scale, three types of the present molecules can be distinguished: (1) compounds **2**, (2) compounds **3** and **5**, (3) compounds **4** and **6**. A and B (and B′) correspond to aryls with local C_2- and C_1-symmetry, respectively; X may be H, D, OMe, or OH.



The correlated motion in these propellers via a fast (on the NMR time scale) two-ring flip mechanism is expected to give isomers with C_1-symmetry (compounds **2**), isomers with C_2-symmetry (compounds **3** and **5**), and isomers with C_1- and C_3-symmetry (compounds **4** and **6**).[12] In this time scale range, a well-resolved spectrum for one isomer is observed; the exception is **6-Me-OH**, for which both C_1- and C_3-symmetric isomers are found (Figure 4). At high temperatures and/or for the least sterically hindered propellers, the other mechanisms (in addition to the two-ring flip) may contribute to propeller motion and the NMR spectra are either simplified or broadened. At low

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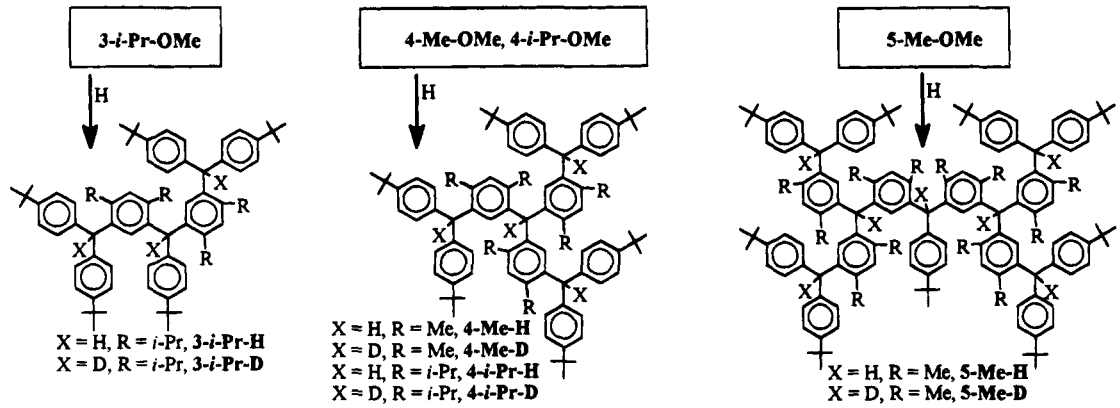

Figure 2. Conversion of the target polyethers to the corresponding hydrocarbons (and their deuterated isotopomers); step H is *one* of the following: (i) Li/THF, followed by either MeOH or MeOD ("carbanion method"), (ii) $NaBH_4/CF_3COOH/MeOH$ ("acidic method").

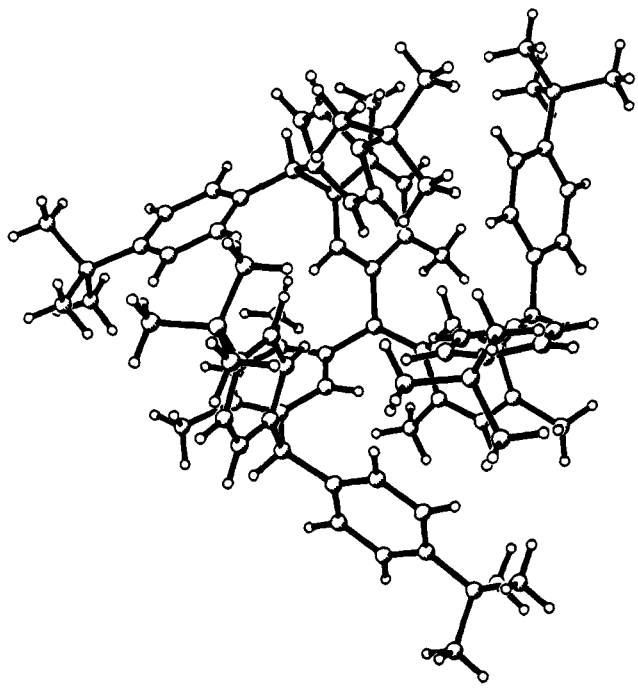

Figure 3. Structure of hydrocarbon **4-Me-H** from the X-ray crystallographic analysis: the view along the C_3 axis.

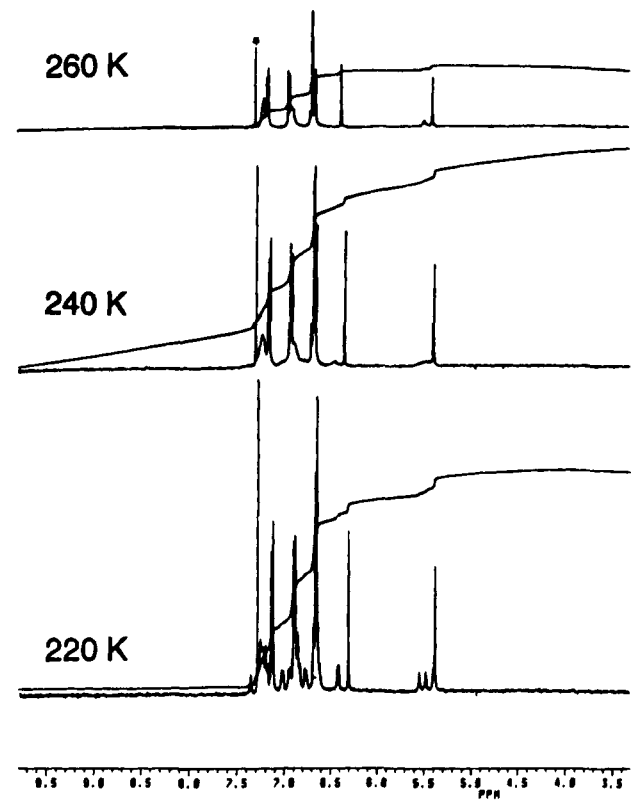

Figure 4. Partial ^1H NMR spectra for **6-Me-OH** in $CDCl_3$ at 220 K (bottom), 240 K (middle), and 260 K (top).

temperatures and/or for sterically hindered propellers, the two-ring flip may become slow on the NMR time scale, leading to appearance of more than one isomer; the spectra are complex and broadened.

NMR spectra for **2-Me-OMe**, which sharpen at higher temperature in the 300–340 K range, reflect two-fold-symmetric structure on the NMR time scale; furthermore, multiplet structure of the aromatic region of the ^1H NMR (TCE/C_6D_6) spectrum is consistent with diastereotopic 4-*tert*-butylphenyl groups (2:2). At lower temperatures, spectra become more complex, e.g., for the ^{13}C NMR spectrum in the 280–260 K range, three (1:1:1) resonances for OCH_3 groups and three (1:1:1) resonances for COH quarternary carbons are found. Moreover, one of the three resonances for OCH_3 broadens at 240 and, at 210 K, four resonances are observed. These observations suggest C_1-symmetric structure in the 280–260 K range and appearance of additional propeller isomer(s) at lower temperatures.

For **2-Me-OH**, well-resolved NMR spectra, corresponding to a C_1-symmetric structure, are observed at 300 K on the NMR time scale; e.g., the ^1H NMR (1D and COSY) spectrum (in C_6D_6) shows OCH_3 (1:1), *tert*-Bu groups (1:1:1:1), $ArCH_3$ (1:1:3:1), OH (1), and eight two-proton doublets in the aromatic region corresponding to four inequivalent 4-*tert*-butylphenyl groups. Analogous features are found in the ^1H NMR spectrum (in $CDCl_3$) and ^{13}C NMR spectra (in $CDCl_3$ and C_6D_6); in particular, six resonances for $ArCH_3$ are resolved. At higher temperatures (320 and 340 K), spectra are broadened. At lower temperatures (280–210 K range), more complex and broadened patterns emerge; e.g., resonance for the COH quarternary carbon broadens to the base line at ~260 K, which is consistent with intervention of additional propeller isomers.

Structures of **2-*i*-Pr-OMe** and **2-*i*-Pr-OH** at 300 K on the NMR time scale are C_1-symmetric, similarly to **2-Me-**

OH. Two-fold symmetry is not attained on the NMR time scale in the 300−390 K range.

The least sterically hindered target polyether, triether **3-Me-OMe**, and its alcohol predecessor **3-Me-OH**, have simple and well-resolved NMR spectra at 300 K; for **3-Me-OMe**, two-fold molecular symmetry with diastereotopic 4-*tert*-butylphenyl groups are found. Characteristic spectral features for **3-Me-OMe** are as follows: Ar-CH_3 (1:1), OCH_3 (2:1), *tert*-Bu (2:2:1) in the ^1H NMR (TCE/C_6D_6) spectrum, and ten resonances for the quarternary aromatic carbons in the ^{13}C NMR spectrum.

The more sterically hindered *i*-Pr-derivatives, **3-*i*-Pr-OH**, **3-*i*-Pr-OMe**, **3-*i*-Pr-H**, also possess two-fold symmetry at 300 K on the NMR time scale. Both 4-*tert*-butylphenyl groups and the methyls of the *i*-Pr-groups are diastereotopic in the 300−380 K range for **3-*i*-Pr-OH** and **3-*i*-Pr-OMe**, and at 300 K for **3-*i*-Pr-H**. The last hydrocarbon possesses well-resolved spectra at 300 K and is not studied at other temperatures. The characteristic spectral features for these three *i*-Pr derivatives: CH in Ar-*i*-Pr (2:2), Me in *i*-Pr (2:2:2:2), *tert*-Bu (2:2:1), trityl OCH_3 (2:1), trityl H (2:1), trityl OCH_3 and/or OH (2:1).

The least sterically hindered tetrakis(arylmethyl) derivative, **4-Me-H**, has three-fold-symmetric structure with diastereotopic 4-*tert*-butylphenyl groups (3:3) at 300 K. This is in agreement with C_3-symmetric structure found in the solid state (Figure 3). At higher temperatures (in the 380−390 K range), all 4-*tert*-butylphenyl groups become equivalent on the NMR time scale; e.g., a sharp 16-line ^{13}C NMR spectrum is obtained. Similar behavior is found for **4-Me-OMe** in the 300−380 K range; however, the ^1H NMR (CD_2Cl_2) spectrum at 220 K shows ten three-proton resonances in the 3.1−1.5 ppm range (OCH_3 and $ArCH_3$), which suggests a C_1-symmetric structure on the NMR time scale. At even lower temperatures (200 and 180 K), the spectrum becomes substantially broadened.

The corresponding *i*-Pr-derivatives, **4-*i*-Pr-H**, **4-*i*-Pr-OMe**, are analogous to their Me counterparts, except the similar time scale behavior is obtained at comparable or higher temperatures for those more sterically hindered compounds. Broadened NMR spectra at 300 K of **4-*i*-Pr-H** sharpen in the 380−390 K range and correspond to the three-fold-symmetric structure with all-equivalent 4-*tert*-butylphenyl groups; at low temperatures in the 280−210 K range, spectra become very complex. NMR spectra for **4-*i*-Pr-OMe** at 300 K are less broadened than those for **4-*i*-Pr-H** and are best assigned to C_1-symmetric structure with six different 4-*tert*-butylphenyl groups; in the 380−390 K range, the spectra approach the three-fold symmetric structure. At lower temperatures in the 280−260 K range, the spectra for the C_1-symmetric structure sharpen, e.g., six and four ^1H-resonances for *t*-Bu and OCH_3 groups, two sets of four ^{13}C-resonances for OCH_3 groups (quarternary and methyl carbons). At the lowest temperatures in the 240−210 K range, the spectra become broadened; in particular, resonances associated with OCH_3 groups are broadened.

In **6-Me-OH**, the ^1H NMR spectrum at 220 K reveals a mixture of C_3- and C_1-propellers; this is unlike the previously discussed propellers **4-Me-OMe** and **4-*i*-Pr-OMe**, where only the C_1-symmetric isomer was identified. At higher temperatures in the 240−260 K range, averaging of resonances on the NMR time scale in the C_1-symmetric propeller is observed (Figure 4); this is analogous to **4-Me-OMe**, **4-*i*-Pr-OMe**, and other propellers. At 300 K, a broadened ^1H NMR spectrum is obtained, corresponding to the intermediate rate of the exchange between the two isomers.

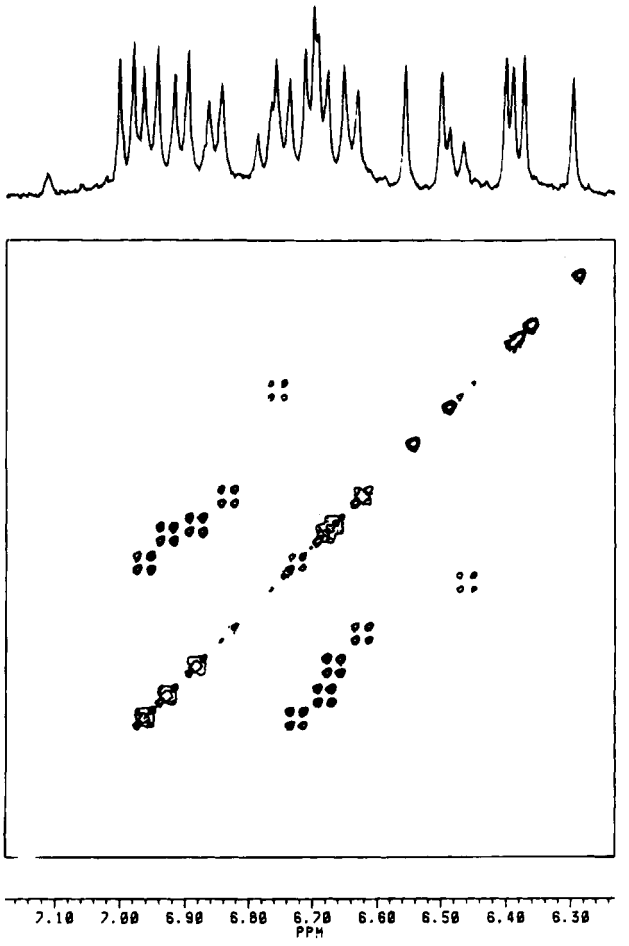

Figure 5. Partial $^1H-^1H$ COSY NMR spectrum for hydrocarbon **5-Me-H** in TCE/C_6D_6 at 380 K.

Heptakis(arylmethyl) propellers, **5-Me-OH**, **5-Me-OMe**, and **5-Me-H**, have broad, unresolved NMR spectra at 300 K. The spectra are highly temperature dependent and, only for **5-Me-H**, a well-resolved ^1H NMR ((TCE/C_6D_6) spectrum is obtained at 380 K. Prominent spectral features in the 1D ^1H NMR spectrum are the singlets for ArCH (2:2:2:1) and $ArCH_3$ (1:1:1:1:1:1); furthermore, the COSY spectrum for the aromatic region reveals six uncoupled singlets (1:1:1:1:1:1) and five coupled pairs of doublets (2:2:2:2:1) (Figure 5). A C_2-symmetric structure is compatible with these spectral assignments.

Conclusion

The present study establishes the structures of the sterically hindered polyarylmethyl tri-, tetra-, hepta-ethers, and their derivatives. Observation of the dynamical behavior for these molecules on the NMR time scale indicates that well-resolved NMR spectra are obtained in the regime of the fast two-ring flip for the most sterically hindered propeller in the molecule. For the heptakis(arylmethyl) propellers, which are the largest molecules in this study, the fast two-ring flip is attainable only for the least sterically hindered hydrocarbon **5-Me-H** and only at high temperature. Therefore, the present molecules are approaching the limit of the high resolution NMR spectroscopy, and the NMR spectroscopic characterization of the higher homologues may not be informative.[7]

Experimental Section

Materials. Tetrahydrofuran (THF) and diethyl ether (ether) were distilled from a blue/purple benzophenone/sodium in a nitrogen atmosphere immediately before use. Lithium metal (98+%, high in sodium) was obtained from Aldrich. All other important reagents were purchased from Aldrich.

4,6-Dibromo-1,3-xylene and 4,6-dibromo-1,3-diisopropylbenzene were prepared according to modified literature procedures.[13] Synthesis of 4,4'-di-*tert*-butylbenzophenone was previously reported.[9] Preparation of methyl 4-*tert*-butylbenzoate, which is also available from Aldrich, was similar to those for methyl 5-bromo-2,4-dialkylbenzoates, which are described below.

Typically, column chromatography employed TLC standard grade silica gel from Aldrich (pH ~6.8) and the elution was done under elevated pressure (<20 psig).

Procedures and Analyses. All reactions involving organometallics were carried out on 10^{-3} Torr vacuum line, which was already described.[9] Elemental analyses were completed by Dr. G. M. Dabkowski, Director-Microlytics, P.O. Box 199, So. Deerfield, MA 01373.

NMR. Bruker WM-400 (^{1}H, 400.1 MHz, and ^{13}C, 100.6 MHz) was employed for measurement of NMR spectra. COSY spectra were obtained in the magnitude mode with the quadrature detection in both dimensions; 256 increments of 1 K with 16 scans per increment were accumulated. Zero filling, multiplication by the sine-window function, Fourier transform, and symmetrization were applied. Where indicated explicitly, ^{1}H NMR spectra were obtained at 300 or 500 MHz using Omega instruments.

The chemical shifts in (δ) $CDCl_3$ and tetrachloroethylene/C_6D_6 (TCE/C_6D_6, ~9/1) were referenced to tetramethylsilane (0.0 ppm) and hexamethyldisiloxane (0.0 ppm), respectively, and coupling constants (J) are reported in hertz. TCE (99.9+%, spectrophotometric or HPLC grade) was obtained from Aldrich.

Methyl 5-Bromo-2,4-dimethylbenzoate. *n*-BuLi (46.0 mL of a 2.5 M solution in hexanes, 0.115 mol) was added to a solution of 4,6-dibromo-1,3-xylene (30.67 g) in ether (300 mL) at −10 °C. After 45 min, the mixture was poured over crushed dry ice (400 g) and allowed to attain ambient temperature. The extraction with 3% $NaOH_{aq}$ (300 mL) was followed by washing of the aqueous extract with ether and acidification with 10% $H_2SO_{4\,aq}$. The white precipitate of crude acid was filtered off and dried (24.10 g, 90%).

The crude acid was dissolved in methanol (250 mL). Thionyl chloride (23 mL) was added dropwise over 15 min. The rate of addition was such that the reaction mixture was boiling. Subsequently, the reaction flask was stopped with a rubber septum. After 24 h at ambient temperature, the reaction mixture was evaporated in vacuo to dryness, dissolved in ether (200 mL), and washed with 10% $NaOH_{aq}$ and water. The ether layer was dried over $MgSO_4$ and, then, concentrated in vacuo. Recrystallization from methanol gave white crystals (17.25 g, mp 54 °C, 61% in two steps). Anal. Calcd for $C_{10}H_{11}O_2Br$: C, 49.38; H, 4.50. Found: C, 49.19; H, 4.62. ^{1}H NMR ($CDCl_3$): 8.08 (s, 1 H), 7.11 (s, 1 H), 3.88 (s, 3 H), 2.52 (s, 3 H), 2.39 (s, 3 H).

Methyl 5-Bromo-2,4-diisopropylbenzoate. *t*-BuLi (63.0 mL 1.7 M solution in pentane, 0.107 mol) was added to a solution of 4,6-dibromo-1,3-di-isopropylbenzene (16.7 g, 52.3 mmol) in ether (160 mL) at −78 °C. After 50 min, the reaction mixture was poured over crushed dry ice (400 g) under N_2 and allowed to attain to ambient temperature. The ether was allowed to evaporate in the hood. The remaining solid was dissolved in water (200 mL). After washing with ether, the aqueous layer was acidified with 10% $H_2SO_{4\,aq}$. The white precipitate was filtered off and dried in the stream of air on the filtering funnel. ^{1}H NMR ($CDCl_3$): 8.13 (s, 1 H), 7.35 (s, 1 H), 3.94 (q, J = 7, 1 H), 3.39 (q, J = 7, 1 H), 1.27 (d, J = 7, 12 H).

The crude acid was dissolved in methanol (125 mL). Thionyl chloride (13 mL) was added dropwise over 15 min. The rate of addition was such that the reaction mixture was boiling. Subsequently, the reaction flask was stopped with a rubber septum. After 24 h at ambient temperature, the reaction mixture was evaporated in vacuo to dryness, dissolved in ether (200 mL), and washed with 10% $NaHCO_{3\,aq}$ and water. The ether layer was dried over $MgSO_4$ and, then, concentrated in vacuo to give a colorless oil (13.42 g). The product could be further purified by distillation under reduced pressure (90−100 °C, p = 0.24 Torr). Anal. Calcd for $C_{14}H_{19}O_2Br$: C, 56.18; H, 6.35. Found: C, 56.44; H, 6.51. ^{1}H NMR ($CDCl_3$): 7.94 (s, 1 H), 7.31 (s, 1 H), 3.87 (s, 3 H), 3.76 (q, J = 7, 1 H), 3.36 (q, J = 7, 1 H), 1.25 (d, J = 7, 6 H), 1.24 (d, J = 7, 6 H).

General Procedure, Step A. *n*-BuLi (1 equiv of 2.5 M solution in hexanes) was added to a solution of 4,6-dibromo-1,3-dialkylbenzene (1 equiv) in ether at −10 °C. After 35 min, solid 4,4'-di-*tert*-butylbenzophenone (1 equiv) was added. The reaction mixture was allowed to attain ambient temperature overnight.

(3-Bromo-4,6-dimethylphenyl)bis(4-*tert*-butylphenyl)methanol, 1-Me-OH. From 4,6-dibromo-1,3-xylene (31.5 g, 0.119 mol) in ether (300 mL), after quenching the reaction mixture with water, the usual aqueous workup and crystallization from hexane gave white crystals (45.5 g, 94.9 mmol, 80%). A small sample was further recrystalized from hexane, mp 157−157.5 °C. Anal. Calcd for $C_{29}H_{35}OBr$: C, 72.64; H, 7.36. Found: C, 72.52; H, 7.43. ^{1}H NMR ($CDCl_3$): 7.32 (d, J = 8, 4 H), 7.12 (d, J = 8, 4 H), 7.09 (s, 1 H), 7.01 (s, 1 H), 2.79 (s, 1 H), 2.34 (s, 3 H), 1.97 (s, 3 H), 1.31 (s, 18 H). ^{13}C NMR/DEPT ($CDCl_3$): 150.1 (q), 144.5 (q), 143.0 (q), 137.0 (q), 136.7 (q), 134.7, 132.8, 127.4, 124.9, 121.2 (q), 82.1 (q), 34.5 (q), 31.4, 22.2, 21.6.

(3-Bromo-4,6-diisopropylphenyl)bis(4-*tert*-butylphenyl)methanol, 1-*i*-Pr-OH. From 4,6-dibromo-1,3-diisopropylbenzene (50.5 g, 0.159 mol) in ether (500 mL), after quenching the reaction mixture with water, the reaction mixture was stirred for 5 h at ambient temperature. The precipitate was filtered off, washed with water and ether, and dried to give 49.6 g (92.6 mmol, 59%) of a solid (mp 202−203 °C). Aqueous workup of the combined organic layers and, after concentration in vacuo, treatment with boiling acetone gave an additional 13.3 g of the product. ^{1}H NMR ($CDCl_3$): 300 K, 7.32 (d, J = 8, 4 H), 7.22 (s, 1 H), 7.15 (d, J = 8, 4 H), 7.04 (s, 1 H), 3.31 (q, J = 7, 1 H), 3.11 (q, J = 7, 1 H), 2.82 (s, 1 H), 1.31 (s, 18 H), 1.24 (d, J = 7, 6 H), 0.83 (d, J = 7, 6 H). ^{13}C NMR/DEPT ($CDCl_3$): 300 K, 150.1 (q), 148.5 (q), 146.4 (q), 143.5 (q), 143.4 (q), 132.6, 127.5, 126.0, 124.7, 120.2 (q), 81.9 (q), 34.5 (q), 32.7, 31.3, 29.8, 23.8, 22.8.

General Procedure, Step B. *t*-BuLi (2 equiv of a 1.7 M solution in pentane) was added to a solution of bromo triether (1 equiv) in ether or THF at −78 °C. After 40−60 min, the −78 °C bath was replaced with a 0 °C bath and 4,4'-di-*tert*-butylbenzophenone (1 equiv) was added. The reaction mixture was allowed to attain ambient temperature overnight. After addition of water, the ether layer was separated, washed with water, dried over $MgSO_4$, filtered, and concentrated in vacuo.

4-Me-OHs. From 2.23 g (2.11 mmol) of **2-Me-OMe** in ether/THF (45 mL/15 mL) and 0.595 g (2.02 mmol) of 4,4'-di-*tert*-butylbenzophenone was obtained 1.95 g (1.54 mmol, 76%) of the product as white crystals, after repeated flash column chromatography (silica, hexane/ether, 10/1), and crystallization from methanol. Mp 191−195 °C. FABMS (3-NBA), cluster: *m/z* (peak height) at $(M - OH)^+$, 1252.0 (16), 1253.0 (14.5); $(M - CH_3O)^+$, 1238.0 (8), 1239.0 (6.5). ^{1}H NMR ($CDCl_3$): 300 K, 7.41 (br), 7.2−7.1 (m), 6.72 (br), 2.95 (br), 2.47 (s), 2.17 (s), 1.90 (br), 1.87 (s), 1.26 (s), 1.25 (s). ^{1}H NMR (TCE/C_6D_6): 300 K, 320 K, 340 K, 360 K, 380 K, *tert*-Bu protons: 1.11 (s). ^{13}C NMR (TCE/C_6D_6): 300 K, 148.8, 148.7, 142.8, 142.5, 137.9, 137.4, 137.0 (br), 132.9 (br), 127.8, 124.8, 124.7, 91.4, 88.4, 53.9, 52.9, 34.5, 31.8, 22.6, 22.0. Supplementary material: ^{1}H NMR (TCE/C_6D_6): 300−380 K, ^{13}C NMR (TCE/C_6D_6): 320−380 K, ^{13}C DEPT, 380 K.

(13) Auwers, K.; Traun, F. A. *Chem. Ber.* **1899**, *32*, 3309.

(14) The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

4-*i*-Pr-OHs. From 1.88 g (1.53 mmol) of **2-*i*-Pr-OMe** in ether (20 mL) and 0.434 g (1.47 mmol) of 4,4'-*tert*-dibutylbenzophenone was obtained 1.65 g (1.15 mmol, 78%) of the product as white powder was obtained, after column chromatography (silica, hexane/ether, 35/1). An analytically pure product was obtained on the similar scale reaction with some modifications; i.e., (1) 4,4'-*tert*-dibutylbenzophenone was added in ether at −78 °C and (2) the following workup was carried out. Column chromatography (silica deactivated with Et_3N, hexane/EtOAc, 2/1), treatment with $NaBH_4$/MeOH, column chromatography, and recrystallization from ether/MeOH gave a white powder: 0.841 g (43%, mp 184−190 °C dec). Anal. Calcd for $C_{103}H_{136}O_4$: C, 86.07; H, 9.47. Found: C, 85.72; H, 9.58. FABMS (ONPOE), cluster: *m/z* (peak height) at $(M - OH)^+$: 1420.0 (6.5), 1421.1 (7), 1422.0 (4), 1423.1 (2); $(M - CH_3O)^+$, 1406.1 (10), 1407.0 (10), 1408.1 (5.5), 1409.0 (2). ^1H NMR ($CDCl_3$, 300 MHz): 293 K, 7.94 (bs, 1 H), 7.60−6.95 (bm, 29 H), 4.50−2.00 (bs, >5 resonances, 16 H), 1.40−1.00 (two 2/1 *t*-Bu singlets at 1.30 and 1.25; broad underlying resonances), 0.90 (bs), 0.70 (bs), 0.45 (bs), 0.10 (bs), −1.00 (bs). Supplementary material: ^1H and ^{13}C NMR (TCE/C_6D_6): 300−390 K, poorly resolved spectra.

General Procedure, Step C. *t*-BuLi (4 equiv of a 1.7 M solution in pentane) was added to a solution of the bromo ether (2 equiv) in ether at −78 °C. After 40−60 min, while the reaction mixture was kept in either a −78 °C bath or higher temperature bath, methyl 5-bromo-2,4-dialkylbenzoate (1.00−0.95 equiv) was added. The reaction mixture was allowed to attain ambient temperature overnight. After addition of water, the ether layer was separated, washed with water, dried over $MgSO_4$, filtered, and concentrated in vacuo.

2-Me-OH. From 26.6 g (54.9 mmol) of **1-Me-OMe** in ether (260 mL) and 6.47 g (26.6 mmol) of methyl 5-bromo-2,4-dimethylbenzoate, which was added at −78 °C, was obtained 23.3 g (22.4 mmol, 84%) of the product as white crystals (mp ~165 °C dec), after crystallization from acetone. FABMS (3-NBA), cluster: *m/z* (peak height) at M^+ 1037.6 (1.5), 1038.6 (1), 1039.6 (1.5), 1040.6 (1); $(M - OH + H)^+$ 1021.6 (6), 1022.6 (4.5), 1023.6 (7), 1024.6 (4); $(M - CH_3O + H)$ 1007.6 (16), 1008.6 (11), 1009.6 (15.5), 1010.6 (9). ^1H NMR ($CDCl_3$): 300 K, 7.2−7.0 (m, 19 H), 6.95 (s, 1 H), 6.87 (s, 1 H), 6.84 (s, 1 H), 2.79 (s, 3 H), 2.77 (s, 4 H), 2.29 (s, 3 H), 2.15 (s, 3 H), 2.13 (s, 3 H), 1.98 (s, 3 H), 1.95 (s, 3 H), 1.79 (br, 3 H), 1.265 (s, 9 H), 1.261 (s, 9 H), 1.250 (s, 9 H), 1.247 (s, 9 H). ^{13}C NMR ($CDCl_3$): 300 K, 148.97, 148.87, 148.84, 148.77, 143.9, 141.2, 140.9, 140.5, 139.56, 139.51, 138.1, 138.0, 137.5, 137.23, 137.17, 136.3, 136.1, 135.9, 134.5, 132.6, 131.1, 130.9, 128.1, 127.65, 127.55, 127.47, 124.40, 124.38, 124.30, 121.4, 87.7, 87.6, 84.7, 52.2, 52.0, 34.3, 31.4, 22.24, 22.21, 21.94, 21.74, 21.65, 21.49. Supplementary material: ^1H NMR ($CDCl_3$): 320−210 K, ^1H NMR (C_6D_6): 300 K (COSY)−340 K, ^{13}C NMR ($CDCl_3$): 320−210 K, ^{13}C NMR (C_6D_6): 300 K (DEPT)−340 K.

2-*i*-Pr-OH. From 10.1 g (18.3 mmol) of **1-*i*-Pr-OMe** in ether (100 mL) and 2.0 mL (8.69 mmol) of methyl 5-bromo-2,4-diisopropylbenzoate, which was added at 5 °C, was obtained 5.59 g (4.74 mmol, 55%) of the product as white glass, after triple column chromatography (silica, hexane/ether, 35/1). Mp 175−179 °C. ^1H NMR ($CDCl_3$): 300 K, broadened spectrum, a broad peak at −0.4 ppm. ^{13}C NMR (TCE/C_6D_6): 300 K, broadened spectrum, e.g., 149.4 (br), 90.0−80.0 (broadened to the baseline), 52.1 (br), 25.5−22.5 (one broadened and two sharp peaks). Supplementary material: ^1H NMR (TCE/C_6D_6): 300−380 K, ^{13}C NMR (TCE/C_6D_6): 320−380 K.

General Procedure, Step D. *t*-BuLi (4 equiv of a 1.7 M solution in pentane) was added to a solution of bromo ether or bromo triether (2 equiv) in ether or THF at −78 °C. After 40−60 min, methyl 4-*tert*-butylbenzoate (1 equiv) was added. The reaction mixture was allowed to attain ambient temperature overnight. After addition of water, the ether layer was separated, washed with water, dried over $MgSO_4$, filtered, and concentrated in vacuo.

3-Me-OH. From 1.02 g (2.07 mmol) of **1-Me-OMe** in ether (25 mL) and 0.197 g (1.02 mmol) of methyl 4-*tert*-butylbenzoate was obtained 0.799 g (0.807 mmol, 78%) of the product as white crystals, after recrystallization from MeOH. A small sample was further purified by column chromatography (silica, hexane/CH_2Cl_2, 3/2) and crystallization (MeOH/acetone). Mp 162−163 °C. ^1H NMR ($CDCl_3$): 7.19−6.90 (m, 24 H), 2.834 (s, 1H), 2.772 (s, 6 H), 2.210 (s, 6 H), 2.012 (s, 6 H), 1.265, 1.250 (s, 45 H). ^{13}C NMR (TCE/C_6D_6): 300 K, 149.1, 148.9, 148.7, 144.6, 142.7, 141.2, 140.8, 138.6, 137.2, 136.3, 132.3, 128.8, 128.2, 127.7, 124.7, 124.4, 88.5, 84.5, 52.2, 34.51, 34.45, 31.8, 31.7, 22.1. Supplementary Material: ^1H NMR (TCE/C_6D_6): 300 K, ^{13}C NMR (TCE/C_6D_6): 320 K, ^{13}C DEPT, 310 K.

3-*i*-Pr-OH. From 5.01 g (9.13 mmol) of **1-*i*-Pr-OMe** in ether (50 mL) and 0.8 mL (~4 mmol) of methyl 4-*tert*-butylbenzoate, 4.33 g (3.92 mmol, 90%) of the product as white solid was obtained, after column chromatography (silica, hexane/ether, 15/1). The product with mp 153−167 °C possessed sufficient purity for the next step in synthesis. ^1H NMR ($CDCl_3$): 300 K, 7.6−7.1 (m, 24 H), 3.3 (br, 2 H), 2.9 (s, sh, 3 H), 2.64 (s, 6 H), 1.30 (s, 18 H), 1.28 (s, 9 H), 1.25 (s, 18 H), 1.00−0.80 (br, br, 12 H), 0.68−0.63 (d, d, $J = 7$, $J = 7$, 12 H). ^{13}C NMR (TCE/C_6D_6): 300−320 K, the spectra are similar to that at 340−340 K, ^{13}C NMR/DEPT, 149.6 (q), 149.2 (q), 149.1 (q), 147.9 (q), 147.4 (q), 145.7 (q), 141.6 (q), 141.1 (q), 141.0 (q), 137.6 (q), 129.7, 129.5, 129.3, 128.6, 127.1, 124.5, 87.6 (q), 84.6 (q), 52.5, 34.5 (q), 31.7, 31.5, 30.3, 29.6, 24.8, 24.7, 24.3, 24.0. Supplementary material: ^1H NMR (TCE/C_6D_6): 300−340 K.

5-Me-OH. From 3.00 g (2.85 mmol) of **2-Me-OMe** in ether/THF (60 mL/18 mL) and 0.272 g (1.41 mmol) of methyl 4-*tert*-butylbenzoate was obtained 2.15 g (1.02 mmol, 72%) of the product as white solid, after flash column chromatography (silica, hexane/ether, 10/1). Mp 222−226 °C dec. FABMS (3-NBA), cluster: *m/z* (peak height) at $(M - CH_3O + H)^+$ 2078.4 (7), 2079.4 (10), 2080.4 (8), 2081.4 (4). ^1H NMR ($CDCl_3$): 300 K, 7.5−6.4 (br m), 2.84 (br), 2.5−2.2 (br), 2.0−1.5 (br), 1.17 (br). Supplementary material: ^1H NMR (TCE/C_6D_6): 300−380 K, ^{13}C NMR (TCE/C_6D_6): 300−380 K.

General Procedure, Step E. *t*-BuLi (6 equiv of a 1.7 M solution in pentane) was added to a solution of aryl bromide (3 equiv) in ether or THF at −78 °C. After 40−60 min, dimethyl carbonate (1 equiv) was added. The reaction mixture was allowed to attain ambient temperature overnight. After addition of water, the ether layer was separated, washed with water, dried over $MgSO_4$, filtered, and concentrated in vacuo.

4-Me-OH. From 5.17 g (10.5 mmol) of **1-Me-OMe** in ether (50 mL) and 0.3 mL (d = 1.069, 3.6 mmol) of dimethyl carbonate was obtained 2.88 g (2.27 mmol, 62%) of the product as white solid, after flash column chromatography (silica, hexane/ether, 10/1). ^1H NMR ($CDCl_3$): 300 K, 7.6−6.5 (br m, 30 H), 3.0−1.8 (br m, 28 H), 1.25 (br s, 54 H). Supplementary material: ^1H NMR ($CDCl_3$): 260−220 K.

6-Me-OH. From 1.00 g (2.16 mmol) of **1-Me-H** in THF (25 mL) and 0.055 mL (d = 1.069, 0.65 mmol) of dimethyl carbonate was obtained 0.520 g (0.441 mmol, 67%) of the product as white solid, after crystallization from MeOH (two crops). A small sample was further recrystallized from MeOH/EtOAc (mp > 260 °C). Anal. Calcd for $C_{88}H_{106}O$: C, 89.59; H, 9.06. Found: C, 89.92; H, 9.16. FABMS (3-NBA), cluster: *m/z* (peak height) at $(M - OH + H)^+$ 1162.9. ^1H NMR ($CDCl_3$): 220 K, 7.35 (s, 1 H), 7.28−7.16 (m, 8−11 H), 7.13 (d, $J = 8$, 6−9 H), 7.01 (br d, 2 H), 6.93 (br d, 2 H), 6.95−6.80 (m, 9−13 H), 6.76 (br d, 2 H), 6.70−6.58 (m, 14−18 H; intense singlet at 6.65), 6.43−6.40 (br s, br s, 2 H), 6.30 (s, 3 H), 5.55 (s, 1 H), 5.47 (s, 1 H), 5.40 (s, 1 H), 5.38 (s, 3 H), 2.82 (s, 1 H), 2.50 (s, 1 H), 2.18 (br s, 12 H), 2.12 (br s, 6 H), 1.94 (s, 9 H), 1.86 (br s, 3 H), 1.77 (br s, 3 H), 1.35−1.20 (1:2:1:1:1, s, 54 H), 1.10 (s, 54 H), 0.98 (br s, 3 H); the integration ratio between the *t*-Bu-peaks at 1.35−1.20 vs 1.10 is 43/49; 240 K, all the above 1 H and 2 H peaks broaden, in particular, the 5.55, 5.47, and 5.40 resonances collapse into one broad peak at 5.44 ppm; also, 1.86, 1.77, and 0.98 resonances are not visible, instead one broad peak at 1.68 ppm appears; peaks in the 1.35−1.20 region collapse into a broad singlet (with shoulder) at 1.30 ppm and the 1.10 peak appears as two resonances at 1.13 and 1.12; the integration of the 1.30 and the 1.12/1/13 *t*-Bu-peaks is as 13/18; 260 K, the 5.44 resonance becomes less broad and appears at 5.47 ppm; the 1.68 peak merges with the baseline; *t*-Bu-peaks appear at 1.29, 1.28, 1.14, 1.12, the integration ratio between 1.29/1.28 and 1.14/1.12 is 21/34; 300 K, 7.15 (br),

6.90 (br), 6.68 (br), 6.61 (s), 6.40 (br), 5.43 (br), 5.38 (br), 2.7 (br, weak), 2.4 (br, weak), 2.13 (br), 1.91 (br), 1.57 (br), 1.27 (br), 1.14 (br), the integration ration between the *t*-Bu-peaks at 1.27 and 1.14 is about 1/2; similarly for the Me group peaks at 2.13, 1.91, 1.57, the ratio is 3/2/1. ^{1}H NMR (TCE/C_6D_6): 300 K, similar to the spectrum in $CDCl_3$ but less resolved. ^{13}C NMR (TCE/C_6D_6): 300 K, poorly resolved spectrum.

General Procedure, Step F. Sodium hydride (multifold molar excess of 60% dispersion in oil) was washed three times with hexane by decantation under N_2 and dried on vacuum line. Subsequently, a solution of an alcohol (1 equiv) in THF was added via transfer needle under N_2. After 1–12 h, iodomethane (multifold molar excess) was added at 0 °C and, then, the reaction mixture was allowed to attain ambient temperature overnight. After quenching the reaction mixture with water and addition of ether, the organic layer was separated, washed twice with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo.

[(3-Bromo-4,6-dimethylphenyl)bis(4-*tert*-butylphenyl)-methoxy]methane, 1-Me-OMe. From 44.5 g (92.8 mmol) of **1-Me-OH** in THF (450 mL) and 14.4 mL of iodomethane was obtained 40.2 g (81.5 mmol, 87%) of the product as white crystals, after recrystallization from acetone. A small sample was again recrystallized from acetone and then treated with hexane to remove traces of acetone; mp 140–141 °C. Anal. Calcd for $C_{30}H_{37}OBr$: C, 73.01; H, 7.56. Found: C, 73.16; H, 7.82. ^{1}NMR ($CDCl_3$): 300 K, 7.68 (s, 1 H), 7.27 (s, 4 H), 6.98 (s, 1 H), 3.07 (s, 3 H), 2.35 (s, 3 H), 1.87 (s, 3 H), 1.29 (s, 18 H). ^{13}C NMR/DEPT ($CDCl_3$): 300 K, 149.3 (q), 140.7 (q), 140.6 (q), 137.9 (q), 136.7 (q), 134.8, 133.7, 127.7, 124.6, 121.2 (q), 86.9 (q), 52.5, 34.4 (q), 31.3, 22.3, 21.3.

[(3-Bromo-4,6-diisopropylphenyl)bis(4-*tert*-butyl-phenyl)methoxy]methane, 1-*i*-Pr-OMe. From 53.8 g (0.100 mol) of **1-*i*-Pr-OH** in THF (550 mL), 8.6 g of NaH/oil, and 9.4 mL of iodomethane was obtained 50.8 g (92.4 mmol, 92%) of the product as white crystals, after recrystallization from acetone; mp 187.5–188 °C. Anal. Calcd for $C_{34}H_{45}OBr$: C, 74.30; H, 8.25. Found: C, 74.53; H, 8.51. ^{1}H NMR ($CDCl_3$): 300 K, 7.78 (s, 1 H), 7.30, 7.29 (AB, J = 8, 8 H), 7.18 (s, 1 H), 3.33 (q, J = 7, 1 H), 3.09 (s, 3 H), 3.00 (q, J = 7, 1 H), 1.28 (s, 18 H), 1.24 (d, J = 7, 6 H), 0.69 (d, J = 7, 6 H); 210 K, the peaks 7.78 and 3.00 become very broad. ^{13}C NMR/DEPT ($CDCl_3$): 300 K, 149.4 (q), 148.6 (q), 146.2 (q), 140.6 (q), 140.0 (q), 132.8, 128.1, 125.9, 124.5, 120.4 (q), 86.7 (q), 52.8, 34.4 (q), 32.6, 31.3, 29.2, 23.6, 22.8.

2-Me-OMe. From 22.50 g (21.6 mmol) of **2-Me-OH** in THF (220 mL), 2.1 g of NaH/oil, and 2.0 mL of iodomethane was obtained 21.87 g (20.7 mmol, 96%) of the product as white crystals, after recrystallization from acetone; mp 222–224 °C dec). Anal. Calcd for $C_{70}H_{85}O_3Br{\cdot}0.5\ H_2O$: C, 79.07; H, 8.15. Found: C, 79.29; H, 8.34. FABMS (3-NBA/NaI), cluster: *m/z* (peak height) at $(M - CH_3O)^+$ 1021.5 (13.5), 1022.5 (10), 1023.5 (12), 1024.5 (9.5); $(M - CH_3O + Na)^+$ 1075.5 (7.5), 1076.5 (6), 1077.5 (10), 1078.5 (7). ^{1}H NMR ($CDCl_3$): 300 K, 7.36 (s, 2 H), 7.30 (s, 1 H), 7.19 (br, 16 H), 7.0–6.8 (br, 2 H), 8.89 (s, 1 H), 3.00 (s, 6 H), 2.54 (s, 3 H), 2.29 (s, 3 H), 2.16 (s, 3 H), 1.97 (s, 3 H), 1.90 (br, 9 H), 1.26, 1.25 (s, 36 H). ^{13}C NMR ($CDCl_3$): 300 K, 148.9, 148.8, 141.8 (br, asymm), 139.1, 138–136 (v br), 137.8, 137.0, 136.2, 134.7, 134.4, 131.9 (br), 127.4, 124.4, 120.3, 90.4, 87.9, 53.6, 52.8, 34.3, 31.4, 22.22, 22.17, 21.7, 21.3. Supplementary material: ^{1}H NMR (TCE/C_6D_6): 300–340 K, ^{13}C NMR ($CDCl_3$): 320–210 K, ^{13}C NMR (TCE/C_6D_6): 300–340 K (DEPT).

2-*i*-Pr-OMe. From 2.49 g (2.06 mmol) of **2-*i*-Pr-OH** in THF (30 mL), 0.5 g of NaH/oil, and 0.3 mL of iodomethane was obtained 1.69 g (1.38 mmol, 67%) of the product as white crystals, after column chromatography (silica, hexane/ether, 50/1) and treatment with boiling MeOH (mp 222–224 °C dec). Anal. Calcd for $C_{82}H_{109}O_3Br$: C, 81.61; H, 9.00. Found: C, 81.47; H, 9.29. FABMS (3-NBA), cluster: *m/z* at $(M - CH_3O + H)^+$ 1190. ^{1}H NMR ($CDCl_3$): 300 K, 7.78 (s, 1 H), 7.59 (s, 1 H), 7.56 (s, 1 H), 7.4–7.1 (m, 19 H), 4.1 (br, 1 H), 3.3 (br, 1 H), 3.09 (s, sh, sh, 6 H), 2.66 (s, sh, 4 H), 2.31 (s, 3 H), 1.35–1.20 (4 singlets for *t*-Bu groups at 1.32, 1.28, 1.26, 1.20, which are overlapped with some resonances from *i*-Pr groups, 48 H), 1.16 (d, J = 7, 3 H), 1.15 (d, J = 7, 3 H), 0.87 (d, J = 7, 3 H), 0.84 (d, J = 7, 3 H), 0.60 (br, 3 H), 0.50 (d, J = 7, 3 H), 0.28 (d, J = 7, 3 H), 0.06 (br, 3 H). ^{13}C NMR (TCE/C_6D_6): 300 K, 149.74, 149.66, 149.2, 149.1, 149.0, 148.3, 147.0, 146.0, 143 (br), 141.7 (br), 139.8 (br), 137.3, 137.1, 135.4, 134.6, 130.1, 129.9, 129.7, 128.9, 128.5, 127.6, 127.3, 125.9, 124.6, 124.4, 119.9, 91.7, 91.6–82.0 (br), 54.7, 53.1, 51.6, 34.6 (br), 32.9, 31.7, 30.7 (br), 30.2, 29.7, 29.4, 29.3, 25.9 (br), 25.3, 24.9, 24.8, 24.5, 24.1, 24.0, 23.7, 23.6, 22.8. Supplementary material: ^{1}H NMR (TCE/C_6D_6): 300–390 K, ^{13}C NMR (TCE/C_6D_6): 320–390 K (DEPT).

3-Me-OMe. From crude **3-Me-OH** (5.55 g, obtained from 5.05 g, 10.5 mmol of **1-Me-OMe**) in THF (55 mL), 0.34 g of NaH/oil, and 0.8 mL of iodomethane was obtained 2.21 g (2.20 mmol, 42% for two steps) of the product as white crystals, after column chromatography (silica, hexane/ether, 10/1) and treatment with boiling methanol overnight. A small sample for elemental analysis was recrystallized from MeOH/acetone, mp 156–157 °C. Anal. Calcd for $C_{72}H_{90}O_3$: C, 86.18; H, 9.04. Found: C, 86.27; H, 8.96. FABMS (3-NBA), cluster: *m/z* (peak height) at $(M - CH_3O)^+$ 971.6 (10), 972.6 (7.5), 973.6 (3). FABMS (3-NBA/Na_2CO_3) at $(M - CH_3O)^+$ 971.6 (10), 972.6 (7), 973.6 (3); $(M - CH_3O + Na)^+$ 1025.6 (5), 1026.6 (4), 1027.6 (2). ^{1}H NMR ($CDCl_3$): 300 K, 7.519 (s, 2 H), 7.25–7.15 (m, 16 H), 7.15, 7.12 (AB, J = 8, 4 H), 6.828 (s, 2 H), 2.921 (s, 6 H), 2.780 (s, 3 H), 1.983 (s, 6 H), 1.937 (s, 6 H), 1.264, 1.258 (s, 45 H). ^{13}C NMR ($CDCl_3$): 300 K, 148.9, 148.9, 141.4, 140.9, 139.3, 137.6, 137.4, 136.9, 136.9, 136.7, 131.1, 128.8, 127.8, 124.4, 124.3, 123.9, 89.3, 87.8, 53.1, 52.5, 34.3, 31.3, 21.8, 21.4. Supplementary material: ^{1}H NMR (TCE/C_6D_6): 300 K, ^{13}C NMR ($CDCl_3$): 280–220 K, ^{13}C NMR/DEPT (TCE/C_6D_6).

3-*i*-Pr-OMe. From 3.51 g (3.18 mmol) of **3-*i*-Pr-OH** in THF (35 mL), 0.25 g of NaH/oil, and 0.3 mL of MeI was obtained 1.48 g (1.32 mmol, 41%) of the product as white solid, after column chromatography (silica, hexane/ether, 20/1) and treatment with boiling MeOH overnight (mp 222.5–224 °C dec). Anal. Calcd for $C_{80}H_{106}O_3$: C, 86.02; H, 9.58. Found: C, 86.20; H, 9.62. FABMS (3-NBA), cluster: *m/z* at $(M - CH_3O + H)^+$ 1084. ^{1}H NMR ($CDCl_3$): 300 K, 7.77 (s, 2 H), 7.35–7.20 (m, 22 H), 3.5–2.8 (br, br, 10 H), 2.72 (s, 3 H), 1.29 (s, 9 H), 1.282 (s, 18 H), 1.276 (s, 18 H), 0.85–0.60 (d, br, d, 12 H). ^{13}C NMR (TCE/C_6D_6): 300–320 K, similar to the spectrum at 340 K, except for increasing broadening at lower temperatures at 124.2 and, to a less extent, at 148.3 and 148.1; also, accidental isochrony at 24.2; 340 K, ^{13}C NMR/DEPT, 150.0 (q), 149.3 (q), 149.2 (q), 148.3 (q), 148.1 (q), 142.4 (q), 142.2 (q), 138.7 (q), 138.6 (q), 137.3 (q), 131.2, 130.6, 129.1, 129.0, 127.2, 124.5, 124.0, 89.7 (q), 88.3 (q), 53.8, 52.8, 34.6 (q), 34.5 (q), 31.7 (br), 29.7, 29.5, 24.6, 24.3, 24.22, 24.17; 360 K, similar to the above, except the *t*-Bu (CH_3) peak resolves into two peaks ar 31.74 and 31.69. Supplementary material: ^{1}H NMR (TCE/C_6D_6): 300–380 K.

4-Me-OMe. From 2.88 g (2.27 mmol) of **4-Me-OH** in THF (30 mL), 0.11 g of NaH/oil, and 0.21 mL of iodomethane was obtained 1.39 g (1.08 mmol, 47%) of the product as white crystals, after column chromatography (silica, hexane/ether, 15/1) and recrystallization from MeOH/acetone. The identical product was obtained using etherification under acidic conditions: CF_3COOH (1 drop) was added to a suspension of **4-Me-OH** (0.461 g, 0.363 mmol) in CH_2Cl_2/CH_3OH (5/30 mL); after 4 h, TLC of the red reaction indicated absence of the substrate. Usual aqueous workup with ether, which was followed by crystallization from MeOH, gave 0.361 g (0.281 mmol, 77%) of white crystals (mp 222–223 °C). Anal. Calcd for $C_{92}H_{114}O_4$: C, 86.07; H, 8.95. Found: C, 86.20; H, 9.01. FABMS (3-NBA/Na_2CO_3), cluster: *m/z* (peak height) at M^+ 1287.7 (1); $(M + Na)^+$ 1305.7 (1); $(M - CH_3O)^+$ 1251.7 (10). ^{1}H NMR ($CDCl_3$): 300 K, 7.40 (br, 3 H), 7.19, 7.18 (s, 24 H), 6.72 (s, 3 H), 2.95 (s, 9 H), 2.47 (s, 3 H), 1.90 (br, 9 H), 1.87 (s, 9 H), 1.25, 1.26 (s, 54 H). ^{13}C NMR (TCE/C_6D_6): 300 K, 148.8, 148.7, 142.8, 142.5, 137.9, 137.4, 137.0 (br), 132.9 (br), 128.0, 127.8, 124.8, 124.7, 91.3, 88.4, 53.9, 52.9, 34.5, 31.7, 22.6, 22.0. Supplementary material: ^{1}H NMR (CD_2Cl_2): 260–180 K, ^{1}H NMR (TCE/C_6D_6): 300 K, ^{13}C NMR (TCE/C_6D_6): 340 K (DEPT)–360 K.

6-Me-OMe. The etherification was carried out under acidic conditions only. CF_3COOH (2.3 mL) was added to crude **6-Me-OH** (obtained from 5.15 g of **1-Me-H** and 0.3 mL of dimethyl

carbonate) in CH_2Cl_2/CH_3OH (50/100 mL); after 1.5 h, the reaction mixture was alkalized with MeOH/MeONa and evaporated to dryness. Purification by column chromatography (silica) and treatment with boiling MeOH, gave 1.99 g (1.67 mmol, 46% from dimethyl carbonate) of a white solid (mp >260 °C). ^{1}H NMR ($CDCl_3$): 300 K, 7.26–6.60 (br m, 30 H), 5.46 (s, 3 H), 2.41 (s, 3 H), 2.08 (s, 9 H), 1.6 (br s, 9 H), 1.3–1.2 (two 1:1 singlets at 1.29 and 1.27, 54 H). ^{1}H NMR (TCE/C_6D_6): 300 K, similar to the spectrum in $CDCl_3$. ^{13}C NMR (TCE/C_6D_6): 300 K, 148.44, 148.36, 141.3, 137.9 (br), 134.9, 134.5, 132.0 (br), 129.8, 129.7, 125.2, 125.15, 125.09, 91.1, 53.1, 53.0, 34.6, 31.9, 22.3, 19.6.

4-*i*-Pr-OMe. From 1.64 g (1.14 mmol) of **4-*i*-Pr-OHs** in THF (20 mL), 0.23 g of NaH/oil, and 0.18 mL of iodomethane was obtained 1.31 g of the product as white crystals, after column chromatography (silica, hexane/ether, 50/1), and treatment with boiling methanol gave 1.31 g (0.902 mmol, 79%) of white solid (mp >260 °C). Anal. Calcd for $C_{104}H_{138}O_4$: C, 86.02; H, 9.58. Found: C, 86.29; H, 9.79. FABMS (3-NBA), cluster: *m/z* at $(M - CH_3O + H)^+$ 1420.0. ^{1}H NMR ($CDCl_3$): 300 K, 8.01 (s, 1 H), 7.83 (s, 1 H), 7.5–7.0 (m, 28 H), 4.07 (br, 1 H), 3.50 (br, 1 H), 3.10 (s, br sh, 4 H), 2.77 (s, br sh, 5 H), 2.53 (s, br, 4 H), 2.35 (s, 3 H), 1.31, 1.24 (br, 66 H), 1.09 (br, 3 H), 0.77 (br, 9 H), 0.59, 0.56 (br, 6 H), 0.08 (br, 3 H), −0.94 (br, 3 H); (500 MHz, resolution enchanced spectrum: *t*-Bu groups as 1:2:2:1 four singlets; Me resonances for *i*-Pr groups in the 1.1 to −1.1 region appear as broadened doublets, 1:2:1:1:1:1:1). ^{13}C NMR ($CDCl_3$): 300 K, 150.3, 150.0, 149.5, 149.0, 148.9, 148.7, 147.8, 147.7, 146.3, 144.3, 143.8, 142.6, 141.4, 139.6, 138.7, 138.6, 137.4, 136.4, 135.9, 135.5, 135.1, 130.9, 130.3, 129.4, 128.5, 128.1, 127.3, 127.0, 126.0, 124.8, 124.3, 124.2, 124.0, 92.6, 88.2, 87.4, 85.0, 55.3, 52.9, 52.6, 50.1, 34.5, 34.3, 31.3, 30.6, 29.9, 29.5, 29.2, 28.8, 28.7, 26.6, 25.3, 24.9, 24.7, 24.5, 23.6, 23.4, 23.0, 22.7. Supplementary material: ^{1}H NMR ($CDCl_3$): 280–210 K, ^{1}H NMR (TCE/C_6D_6): 300–380 K, ^{13}C NMR ($CDCl_3$): 280–210 K, ^{13}C NMR (TCE/C_6D_6): 300–390 K (DEPT).

General Procedure, Step G. 5-Me-OMe. Sodium hydride (0.5 g of 60% dispersion in oil) was washed three times with hexane by decantation under N_2 and dried on a vacuum line. Subsequently, a solution of **5-Me-OH** (1.04 g, 0.493 mmol) in DMF (10 mL) was added under N_2. After 30 min, MeI (0.5 mL) was added. After stirring overnight at ambient temeperature, the reaction mixture was quenched with methanol, and ether (100 mL) was added. The organic layer was washed twice with water and then with brine. After drying over $MgSO_4$, concentration in vacuo gave a solid residue (0.914 g). Column chromatography (silica, hexane/ether, 10/1) and treatment with boiling MeOH for several hours gave 0.675 g (0.318 mmol, 64%) of a white solid (mp ~230 °C dec). Anal. Calcd for $C_{152}H_{186}O_7$: C, 85.91; H, 8.82. Found: C, 85.92; H, 8.86. FABMS (3-NBA), cluster: *m/z* (peak height) at $(M - CH_3O + H)^+$ 2092.5 (7), 2093.5 (10), 2094.5 (8), 2095.5 (4.5). ^{1}H NMR ($CDCl_3$): 300 K, 7.42 (br), 7.18 (br), 6.77 (br), 3.1–1.1 (br m). Supplementary material: ^{1}H NMR (TCE/C_6D_6): 320–380 K; ^{13}C NMR (TCE/C_6D_6): 320–380 K.

General Procedure, Step H. Carbanion Method. The polyether (50 mg) was stirred with excess lithium metal in THF (1 mL) for several days. The red reaction mixture was quenched with either MeOH or MeOD and subjected to standard aqueous workup. The ether extract was dried over $MgSO_4$ and then concentrated in vacuo.

Acidic Method. Sodium borohydride pellets (multifold excess) were added over 1–5 days to a suspension of the polyether or alcohol (50–100 mg, unless indicated otherwise) in MeOH or CH_2Cl_2 (5 mL, unless indicated otherwise) and trifluoroacetic acid (5 mL, unless indicated otherwise) at 0 °C. The reaction mixture was quenched with water (≥5 mL), alkalized with 10% $NaOH_{aq}$, and extracted with ether. The ether layer was washed with water and dried over $MgSO_4$; subsequent concentration in vacuo gave crude product.

1-Me-H. Acidic Method. Using crude **1-Me-OH**, which was obtained according to step A from 4,6-dibromo-1,3-xylene (10.64 g), in methylene chloride (60 mL), recrystallization from methylene chloride/MeOH gave 16.23 g (91%) of white crystals (mp 188.5–190 °C). ^{1}H NMR (TCE/C_6D_6): 300 K, 7.06 (d, *J* = 8, 4 H), 6.90 (s, 1 H), 6.79 (d, *J* = 8, 4 H), 6.74 (s, 1 H), 5.33 (s, 1 H), 2.15 (s, 3 H), 1.92 (s, 3 H), 1.13 (s, 18 H). ^{13}C NMR/DEPT (TCE/C_6D_6): 300 K, 149.1 (q), 142.8 (q), 140.3 (q), 135.8 (q), 135.6 (q), 133.6, 132.9, 129.7, 127.8, 125.5, 122.8 (q), 52.8, 34.6 (q), 22.7, 19.7.

3-*i*-Pr-H. Carbanion Method. From 50.5 mg of **3-*i*-Pr-OMe** was obtained 37.2 mg of the product as white powder, after treatment with boiling methanol. Acidic Method. From 100.1 mg of **3-*i*-Pr-OMe** in MeOH (5 mL) and CF_3COOH (5 mL) was obtained 88.9 mg of the product as white powder; that is, following the addition of 10% $NaOH_{aq}$, the precipitate was filtered off, washed with water, and MeOH. Mp 239–240 °C. FABMS (3-NBA), cluster: *m/z* (peak height) at M^+ 1023.8 (6.5), 1024.8 (10), 1025.8 (7.5). M^+, calcd for $^{12}C_{77}{}^1H_{100}$ 1024.7825, found 1024.7802 (dev −2.1 ppm). ^{1}H NMR ($CDCl_3$): 300 K, 7.11 (s, 2 H), 7.08–7.02 (m, 10 H), 6.84 (d, *J* = 8, 4 H), 6.74 (d, *J* = 8, 4 H), 6.70 (d, *J* = 8, 2 H), 6.46 (s, 2 H), 5.73 (s, 1 H), 5.51 (s, 2 H), 3.13 (q, *J* = 7, 2 H), 3.30 (q, *J* = 7, 2 H), 1.26 (s, 9 H), 1.24–1.22 (1:1 s, 36 H), 1.13 (d, *J* = 7, 6 H), 0.97–0.92 (m, 18 H). ^{13}C NMR/DEPT ($CDCl_3$): 300 K, 148.2 (q), 148.1 (q), 148.0 (q), 144.5 (q), 144.4 (q), 141.4 (q), 141.3 (q), 140.8 (q), 138.1 (q), 137.1 (q), 132.0, 129.3, 129.2, 128.9, 124.7, 124.6, 124.5, 122.4, 51.4, 48.7, 34.3 (q), 31.4, 28.7, 28.4, 24.3, 24.1, 24.0, 23.5. Supplementary material: ^{13}C NMR/DEPT (C_6D_6): 300 K.

3-*i*-Pr-D. Carbanion Method. From 50.4 mg of **3-*i*-Pr-OMe** was obtained 29.0 mg of the product as white powder, after PTLC (silica, hexane/ether, 10/1) and treatment with boiling MeOH. Mp 237.5–238 °C. FABMS (3-NBA), cluster: *m/z* (peak height) at M^+ 1025.8 (5), 1026.8 (7), 1027.8 (10), 1028.8 (6.5). M^+ isotopic distribution, calcd for $C_{77}H_{97}D_3$: 1027.8 (10), 1028.8 (9), 1029.8 (4); calcd for $C_{77}H_{98}D_2$: 1026.8 (10), 1027.8 (9), 1028.8 (4). ^{1}H NMR ($CDCl_3$): 300 K, the spectrum is identical to that of the protio analogue, except the 5.73 and 5.51 peaks are negligible. ^{13}C NMR (TCE/C_6D_6): 300 K, the spectrum is similar to that of the protio analogue in C_6D_6, except the 52.2 and 49.5 peaks are not detected.

4-Me-H. Carbanion Method. From 50.2 mg of **4-Me-OMe** was obtained 17.9 mg of the product as white powder, after PTLC (silica, hexane/ether, 20/1). Acidic Method. From 51.1 mg of **4-Me-OMe**, 27.1 mg of white powder was obtained as above (mp >260 °C). FABMS (3-NBA), cluster: *m/z* (peak height) at M^+ 1161 (4), 1162 (10), 1163 (8), 1164 (3.5). ^{1}H NMR ($CDCl_3$): 300 K, 7.12 (br, 6 H), 6.98 (br, 6 H), 6.66–6.62 (s at 6.66, br at 6.62, 15 H), 6.42 (s, 3 H), 5.36 (s, 3 H), 5.33 (s, 1 H), 2.18 (s, 9 H), 1.80 (s, 9 H), 1.4 −1.0 (1:1 br s at 1.13 and 1.08, 54 H). ^{13}C NMR (TCE/C_6D_6): 300 K, 148.4, 147.6, 141.6, 140.7, 140.1, 139.3, 134.2, 133.2, 132.5, 130.2, 129.5 (br), 129.1 (br), 127.8 (br), 125.5 (br), 52.1, 48.5 (br), 34.6, 34.5, 31.9, 31.8, 20.4, 19.0. Supplementary material: ^{1}H NMR (TCE/C_6D_6): 300–390 K, ^{13}C NMR (TCE/C_6D_6): 320–380 K (DEPT).

4-Me-D. Carbanion Method. From 55.3 mg of **4-Me-OMe**, 12.1 mg of the product as white powder was obtained, after PTLC (silica, hexane/ether, 20/1). ^{1}H NMR ($CDCl_3$): 300 K, the spectrum is identical to that of the protio analogue, except that the resonances in the 5.5–5.0 region, which correspond to Ar_3CH, are negligible. ^{1}H and ^{13}C NMR (C_6D_6): 340 K, the spectra are similar to those of the protio analogue in TCE/C_6D_6, except that the resonances in the 5.5–5.0 region, which corresponds to Ar_3CH, are negligible.

4-*i*-Pr-H. Carbanion Method. From 52.4 mg of **4-*i*-Pr-OMe** was obtained 32.4 mg of the product as white powder, after PTLC (silica, hexane/ether, 35/1). Mp 259–260 °C. ^{1}H NMR ($CDCl_3$): 300 K, 7.02, 6.94, 8.85, 6.74 (br, 30 H), 5.8 (br, 1 H), 5.52 (br, 3 H), 3.15 (br, 3 H), 2.81 (br, 3 H), 1.14, 0.99 (br, 81 H), 0.56 (br, 9 H). ^{13}C NMR (TCE/C_6D_6): 300 K, 148.2 (br), 145.0, 144.5, 141.9 (br), 138.8, 137.8, 131.8, 129.4, 125.2, 125.0, 122.9, 52.0 (br), 34.4, 31.8, 29.3, 28.8, 25.0 (br), 24.2 (br), 23.3 (br). Supplementary material: ^{1}H NMR ($CDCl_3$): 280–210 K, ^{1}H NMR (TCE/C_6D_6): 300–390 K, ^{13}C NMR (TCE/C_6D_6): 320–380 K (DEPT).

4-*i*-Pr-D. Carbanion Method. From 51.3 mg of **4-*i*-Pr-OMe** was obtained 40.0 mg of the product as white powder, after PTLC (silica, hexane/ether, 35/1). Mp 258–259 °C. FABMS (3-NBA), cluster: *m/z* (peak height) at M^+ 1333.0 (3), 1334.0

(5), 1335.1 (10), 1336.0 (8), 1337.1 (4). ^{1}H NMR ($CDCl_3$): the spectrum is identical to that of non-deuterated compound, except the 5.8 and 5.5 ppm peaks are undetectable. ^{13}C NMR ($CDCl_3$): 148.0, 147.8, 144.5, 144.1, 141.7 (br), 141.4 (br), 138.3 (br), 137.1, 131.1 (br), 128.9, 124.8, 124.5, 122.5, 34.2, 31.4, 28.8, 28.3, 24.6 (br), 23.9 (br), 23.0 (br).

5-Me-H. Carbanion Method. From 49.3 mg of **5-Me-OMe** was obtained 36.0 mg of the product as white powder, after PTLC (silica, hexane/ether, 20/1). Acidic Method. From 50.0 mg of **5-Me-OMe** was obtained 35.1 mg of the product as white powder, after PTLC (silica, hexane/ether, 10/1). Mp 204–206 °C. FABMS (3-NBA), cluster: *m/z* at M^+ 1913. M^+, calcd for $^{12}C_{145}{}^1H_{172}$ 1913.3459, found 1913.3363 (dev −5.0 ppm). ^{1}H NMR ($CDCl_3$): 300 K, 7.15–6.20 (br m), 5.39 (s), 5.38 (s), 5.2–5.0 (br), 2.3–0.9 (br m). ^{1}H NMR (TCE/C_6D_6): 300 K, 7.0–6.2 (br m), 5.23 (br s), 5.20–4.90 (br), 2.3–0.8 (br m); 320 K, 7.0–6.2 (less broadened than above), 5.25 (s), 5.24 (s), 5.11 (br s), 5.03 (br s), 2.00 (br s), 1.64 (br s), 1.59 (br s), 1.50 (br s), 1.06 (br s), 0.99 (s); 340 K, 7.0–6.2 (br m, 48 H), 5.26 (s, 2 H), 5.24 (s, 2 H), 5.12 (br s, 2 H), 5.05 (br s, 1 H), 2.00 (s, 6 H), 1.98 (s, 6 H), 1.64 (br s, 6 H), 1.58 (br s, 6 H), 1.50 (br s, 12 H), 1.07 (br s, 72 H), 1.01 (s, 9 H); 360 K, further line narrowing; 380 K, COSY cross-peaks in the aromatic region: 6.97 (d, J = 8, 4 H) and 6.73 (d, J = 8, 4 H), 6.93 (d, J = 8, 4 H) and 6.69 (d, J = 8, 4 H), 6.89 (d, J = 8, 4 H) and 6.67 (d, J = 8, 4 H), 6.84 (d, J = 8, 4 H) and 6.63 (d, J = 8, 4 H), 6.76 (d, J = 8, 2 H) and 6.47 (d, J = 8, 2 H); no crosspeaks in the aroamtic region: 6.55 (s, 2 H), 6.49 (s, 2 H), 6.43 (s, 2 H), 6.40 (s, 2 H), 6.37 (s, 2 H), 6.30 (s, 2 H); peaks outside aromatic region: 5.27 (s, 2 H), 5.25 (s, 2 H), 5.14 (s, 2 H), 5.07 (s, 1 H), 2.00 (s, 6 H), 1.98 (s, 6 H), 1.64 (s, 6 H), 1.58 (s, 6 H), 1.53 (s, 6 H), 1.50 (s, 6 H), 1.083, 1.077, 1.074 (s, s, s, 72 H), 1.03 (s, 9 H). ^{13}C NMR ($CDCl_3$): 300 K, 280 K, 240 K, broad and poorly resolved spectra. ^{13}C NMR (TCE/C_6D_6): 300 K, 320 K, 340 K, 300 K, the spectra become sharper with increased number of the resolved lines; 380 K, ^{13}C NMR/^{13}C DEPT, 148.7 (q), 148.6 (q), 148.5 (q), 141.6 (q), 141.53 (q), 141.47 (q), 140.8 (q), 139.9 (q), 139.3 (q), 139.2 (q), 139.1 (q), 138.7 (q), 134.9 (q), 134.7 (q), 133.9, 133.7 (q), 133.0, 132.9, 131.54, 131.49, 129.6, 129.53, 129.47, 129.3, 125.2, 125.1, 125.0, 124.9, 53.1, 53.0, 50.6 (br), 34.5 (q), 31.8, 20.4, 19.7, 19.4, 19.22, 19.17. Supplementary material: ^{1}H NMR ($CDCl_3$): 280–210 K.

5-Me-D. Carbanion Method. From 50.8 mg of **5-Me-OMe** was obtained 34.4 mg of the product as white powder, after PTLC (silica, hexane/ether, 20/1). Mp 207–211 °C. FABMS (3-NBA), cluster: *m/z* (peak height) at M^+ 1919.4 (3.5), 1920.5 (8), 1921.5 (10), 1922.5 (7), 1923.5 (4). M^+ isotopic distribution, calcd for $C_{145}H_{165}D_7$: 1920.4 (6), 1921.4 (10), 1922.4 (8), 1923.4 (4.5); calcd for $C_{145}H_{166}D_6$: 1920.4 (10), 1921.4 (8), 1922.4 (4.5), 1923.4 (2). ^{1}H NMR (TCE/C_6D_6) and ^{13}C NMR (TCE/C_6D_6): 300 K, the spectra are identical to those for the protio analogue, except for the absence of the resonances from Ar_3-CD groups.

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Supplementary Material Available: Selected ^{1}H NMR spectra for polyethers, hydrocarbons **2–5**, alcohol **6-Me-OH** (Figures 1s–44s) and variable temperature ^{1}H, $\{^1H\}^{13}C$, ^{13}C DEPT NMR data summaries, which are not included in the Experimental Section, details of x-ray crystallography for **4-Me-H**, and synthesis and characterization of triether **3-H-OEt**, which is derived from **3-Me-OMe** by replacing ArMe and OMe with ArH and OEt, respectively (67 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.