evaporated to afford a 1:1 mixture of the amino acid hydrochloride and methylammonium chloride, which was adsorbed to acidic ion-exchange resin Dowex 50W × 8. The resin was washed with distilled $H_2O$ till the washings came out neutral, and then the free amino acid was recovered wtih 1.5 M aqueous $NH_3$. Evaporation afforded the crystalline amino acid, which was dried under high vacuum at 40 °C.

**α-Methyl-β-aminopropionic Acid [(±)-10].** Derivative 5 (576 mg, 2 mmol) was hydrolyzed according to the general procedure to afford 192 mg (69% yield) of pure, free amino acid 10: mp 170–171 °C (lit.[20] mp 173–174 °C); $^1H$ and $^{13}C$ NMR data are in Tables V and VI, respectively; HRMS, $m/z$ ($M^+$) 103.0607 (calcd for $C_4H_9NO_2$ 103.0633).

Anal. Calcd for $C_4H_9NO_2 \cdot H_2O$: C, 39.66; H, 9.15; N, 11.56. Found: C, 39.44; H, 9.12; N, 11.29.

**α-Benzyl-β-aminopropionic Acid [(±)-11].** Derivative 6 (728 mg, 2 mmol) was hydrolyzed according to the general procedure to afford 280 mg (66% yield) of the pure, free amino acid 11: mp 240–241 °C; $^1H$ and $^{13}C$ NMR data are in Tables V and VI, respectively; HRMS, $m/z$ ($M^+$) 179.0958 (calcd for $C_{10}H_{13}NO_2$ 179.0946).

**α-*n*-Butyl-β-aminopropionic Acid [(±)-12].** Derivative 7 (660 mg, 2 mmol) was hydrolyzed according to the general procedure to afford 232 mg (64% yield) of the pure, free amino acid 12: mp 230–231 °C; $^1H$ and $^{13}C$ NMR data are in Tables V and VI, respectively; HRMS, $m/z$ ($M^+$) 145.0772 (calcd for $C_7H_{15}NO_2$ 145.1103).

**α-*n*-Hexyl-β-aminopropionic Acid [(±)-13].** Derivative 8 (716 mg, 2 mmol) was hydrolyzed according to the general procedure to afford 258 mg (62% yield) of the pure, free amino acid 13: mp 215–216 °C; $^1H$ and $^{13}C$ NMR data are in Tables V and VI, respectively; HRMS, $m/z$ ($M^+$) 173.1573 (calcd for $C_9H_{19}NO_2$ 173.1416).

***cis*- and *trans*-3-Carboxy-5-methylpyrrolidines [(±)-14].** Derivative 9 (314 mg, 1 mmol) was hydrolyzed according to the general procedure to afford 158 mg (68% yield) of the pure, free diastereomeric amino acids, *cis*- and *trans*-14: mp 140–143 °C; $^1H$ and $^{13}C$ NMR data are in Tables V and VI, respectively; HRMS, $m/z$ ($M^+$) 128.0759 (calcd for $C_6H_{11}NO_2$ 128.0711).

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**Registry No.** 2, 131932-56-4; 3, 51739-61-8; 4, 131932-57-5; 5, 131932-58-6; *epi*-5, 131932-66-6; 6, 131932-59-7; 7, 131932-60-0; 8, 131932-61-1; 9, 131932-62-2; (±)-10, 10569-72-9; (±)-11, 114746-81-5; (±)-12, 104883-55-8; (±)-13, 131932-63-3; *cis*-(±)-14, 131932-64-4; *trans*-(±)-14, 131932-65-5; $H_2NCH_2CH_2COOH$, 107-95-9; $H_2NCH_2CH_2CO_2Me \cdot HCl$, 3196-73-4; $MeNH_2$, 74-89-5; $Me_3CCHO$, 630-19-3; $Bz_2O$, 93-97-0; MeI, 74-88-4; $PhCH_2Br$, 100-39-0; BuI, 542-69-8; $C_6H_{13}I$, 638-45-9; $ClCH_2CH{=}CH_2$, 107-05-1.

**Supplementary Material Available:** Crystal structures for 2 and 6 and $^1H$ and $^{13}C$ NMR spectra for 4 and 11–14 (13 pages). Ordering information is given on any current masthead page.

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# Synthesis of 1,3-Connected Polyarylmethanes

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1,3-Connected polyarylmethanes were synthesized using repetitive additions of aryllithiums to carbonyl compounds. The polyarylmethanes with molecular mass up to 2900 amu were purified by chromatography and characterized using FABMS, NMR, and elemental analyses. FABMS and 2D COSY NMR were found particularly useful in characterization of large polyarylmethanes.

## Introduction

Can ferromagnetism be achieved by preparing an organic solid using large high-spin molecules, which would mimic ferromagnetic domains? Recently, first molecular organometallic ferromagnets and ferrimagnets have been reported;[1-5] however, they are based on small molecules.

Synthesis of strictly organic high-spin ($S$) molecules mimicking ferromagnetic domains may greatly contribute to understanding of ferromagnetism.[6] Having electronically simple atoms such as carbons as sources of magnetic moments could simplify elucidation of mechanisms for ferromagnetism. Moreover, such organic magnets should possess unique material properties; that is, organics are much different from ceramics or typical metals. Organic molecules with $S > 2$ are rare. The highest spin organic molecule is the $S = 5$ pentacarbene, which consists of five meta-connected benzylidene fragments.[6a] Among polyradicals the highest spin achieved is $S = 2$.[7-9] The theo-

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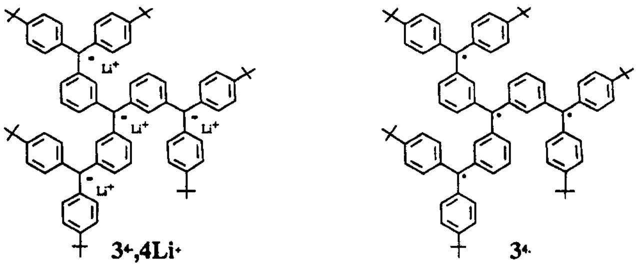
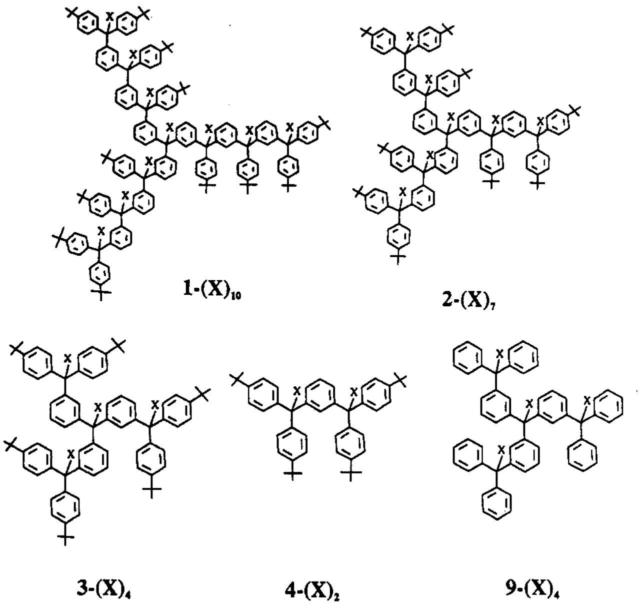


**3**$^{4-}$,4Li$^{+}$ **3**$^{4\bullet}$

Figure 1. Carbotetraanion **3**$^{4-}$,4Li$^{+}$ and tetraradical **3**$^{4\bullet}$.



**1-(X)$_{10}$** **2-(X)$_7$** **3-(X)$_4$** **4-(X)$_2$** **9-(X)$_4$**

Figure 2. Target molecules. 1,3-connected polyarylmethanes with X = OEt, H, and D for compounds 1–4 and X = OEt for compound **9**.

retical predictions for high-spin ground states, large intramolecular magnetic interactions, simplicity of the electronic structure, and consideration of stability have prompted us to investigate sterically hindered 1,3-connected polyarylmethyls.[10] We have reported preparation of quintet ($S = 2$) tetraradical **3**$^{4\bullet}$ and the related carbotetraanion **3**$^{4-}$,4Li$^{+}$ (Figure 1).[11]

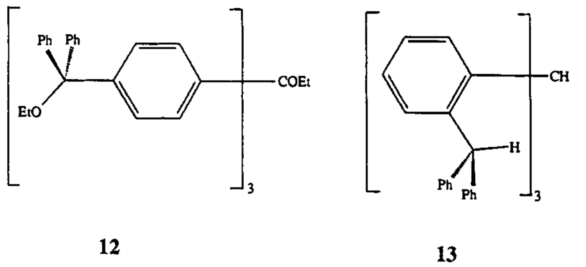
Now we report the synthesis of the precursors for the polyradicals with up to 10 unpaired electrons. The goal of our synthesis are polyether precursors 1–4 (Figure 2).

Such polyethers are particularly suitable for the following sequence for preparation of polyradicals.

$$\text{polyether precursor} \rightarrow \text{carbopolyanion} \rightarrow \text{polyradical} \tag{1}$$

For example, **3-(OEt)$_4$** is the polyether precursor to carbotetraanion **3**$^{4-}$,4Li$^{+}$ and tetraradical **3**$^{4\bullet}$ (Figures 1 and 2).

Our largest molecules possess diameters of 30 Å in their extended conformations and molecular masses of 2800+ amu. Polyradicals derived from compounds 1–4 should provide the answer to the question if a high-spin ground state is preferred as the molecular size approaches the spatial extent of a ferromagnetic domain, i.e., can "a 2D ferromagnetic domain" exist? The prerequisite to the generation of the polyradicals is the synthesis of the appropriate precursors as described in this report.



**12** **13**

Figure 3. Previously reported 1,4- and 1,2-connected polyarylmethanes **12** and **13**.

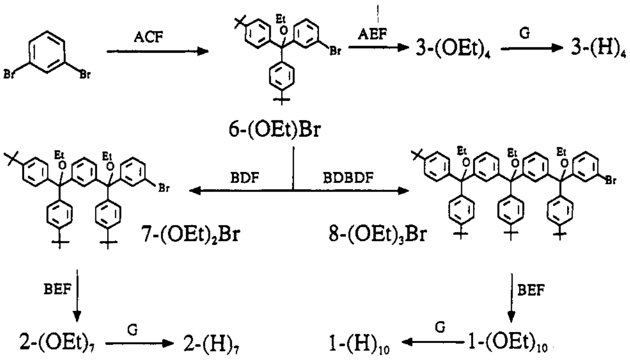


Figure 4. Synthesis of the target molecules: A = $n$-BuLi, ether; B = $t$-BuLi, ether; C = 4,4′-di-*tert*-butylbenzophenone; D = 3-bromo-4′-*tert*-butylbenzophenone; E = $(MeO)_2CO$; F = EtOCOCl, EtOH; G = (1) Li, THF, (2) MeOH.

## Results and Discussion

**Synthesis.** Two examples of 1,2- and 1,4-connected polyarylmethanes, **12** and **13**, which are analogues of **3-(OEt)$_4$** and **9-(OEt)$_4$**, have been reported (Figure 3).[12,13] Similar organolithium methods have been employed in their preparation.

The synthesis of polyethers **1-(OEt)$_{10}$** through **4-(OEt)$_2$** and **9-(OEt)$_4$** is outlined in the Figure 4. The symmetry-related fragments, **6-(OEt)Br**, **7-(OEt)$_2$Br**, **8-(OEt)$_3$Br**, **10-(OEt)Br**, are prepared and, then, combined with dimethyl carbonate or 4,4′-di-*tert*-butylbenzophenone. The carbon–carbon bonds are formed using a one-pot sequence: (1) Br/Li exchange, (2) addition of aryllithium to carbonyl compound, (3) conversion of the alkoxide to ethyl triarylmethyl ether.

Step 1. 1,3-**Dibromobenzene** is monolithiated via the Br/Li exchange with $n$-BuLi in ether.[15] Quenching of the lithium compound with appropriate benzophenone is followed by etherification with ethyl chloroformate in the same pot.[13,14] When 4,4′-di-*tert*-butylbenzophenone and benzophenone are used, **6-(OEt)Br** and **10-(OEt)Br** are isolated, respectively.

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**Table I. Aromatic Region of the $^1$H NMR Spectra in CDCl$_3$ for 1-(H)$_{10}$, 2-(H)$_7$, and 3-(H)$_4$ and C$_6$D$_6$ for the Other Compounds**[a]

| ring | **3-(OEt)$_4$** | **2-(OEt)$_7$** | **1-(OEt)$_{10}$** |
|---|---|---|---|
| $I_1$ | 7.90 7.53 7.37 7.11 | 7.93 7.37 7.32 7.06 | 7.92 7.35 7.29 7.05 |
| $I_2$ | | 7.98 7.50 7.35 7.07 | 7.97 7.51 7.40 7.10 |
| $I_3$ | | | 7.97 7.39 7.36 7.08 |
| $P_1/P_2$ | 7.50 7.21 | 7.54 7.54 7.24 7.23 | 7.55 7.55 7.23 7.23 |
| $P_3$ | | 7.44 7.21 | 7.47 7.22 |
| $P_4$ | | | 7.41 7.19 |
| ring | **6-(OEt)Br** | **7-(OEt)$_2$Br** | **8-(OEt)$_3$Br** |
| $I_1$ | 8.12 7.41 7.15 6.73 | 8.01 7.35 7.14 6.73 | 8.00 7.33 7.14 6.71 |
| $I_2$ | | 7.85 7.56 7.38 7.09 | 7.84 7.44 7.37 7.08 |
| $I_3$ | | | 7.95 7.53 7.40 7.12 |
| $P_1/P_2$ | 7.47 7.22 | 7.53 7.53 7.26 7.25 | 7.52 7.52 7.23 7.23 |
| $P_3$ | | 7.41 7.21 | 7.39 7.19 |
| $P_4$ | | | 7.46 7.25 |
| ring | **3-(H)$_4$** | **2-(H)$_7$** | **1-(H)$_{10}$** |
| $I_1$ | 6.89 6.81 6.91 7.09 | 6.89 6.76 6.84 7.04 | 6.87 6.73 6.79 6.99 |
| $I_2$ | | 6.98 6.83 6.91 7.08 | 6.91 6.78 6.82 7.02 |
| $I_3$ | | | 6.96 6.82 6.89 7.07 |
| $P_1/P_2$ | 7.21 6.94 | 7.23 7.23 6.97 6.97 | 7.22 7.22 6.96 6.96 |
| $P_3$ | | 7.19 6.90 | 7.18 6.89 |
| $P_4$ | | | 7.15 6.85 |

[a] The chemical shifts for the spin multiplets in the inner ("I", without the *t*-Bu groups) rings are in the following order: singlet, doublet, doublet, and triplet. The peripheral ("P", with the *t*-Bu groups) rings appear as doublets.[18]

Step 2. The Br/Li exchange using **6-(OEt)Br** and *t*-BuLi produces **6-(OEt)Li**; quenching of the organolithium compound with 3-bromo-4′-*tert*-butylbenzophenone and the etherification of the resultant lithium alkoxide gives **7-(OEt)$_2$Br**. When the Br/Li exchange, quenching, Br/Li exchange, quenching, and etherification is applied to **6-(OEt)Br** in the same pot then **8-(OEt)$_3$Br** is obtained.

Step 3. The compounds **6**, **7**, **8**, and **10** are subjected to the Br/Li exchange, quenching with dimethyl carbonate, and etherification; **3-(OEt)$_4$**, **2-(OEt)$_7$**, **1-(OEt)$_{10}$**, and **9-(OEt)$_4$** are isolated. Similarly, **4-(OEt)$_2$** is obtained from **6-(OEt)Br** by using 4,4′-di-*tert*-butylbenzophenone (instead of dimethyl carbonate) for the quenching. The analogous procedure is used for the simple monoether, tris(4-*tert*-butylphenyl)methoxyethane (**5-OEt**), but **6-(OEt)Br** is replaced with 4-*tert*-butylbromobenzene. The overall isolated yields are 10–40%. Also, in the preparation of **1-(OEt)$_{10}$** the side product, **11-(OEt)$_3$(OEt)(OEt)$_3$**, which can be thought as the product of the coupling of **8-(OEt)$_3$Li** (2 equiv) and *t*-BuLi (1 equiv) with dimethyl carbonate, is isolated.[18]

Reaction of the polyethers with lithium in tetrahydrofuran for 1–10 days yielded, after quenching with MeOH, compounds **1-(H)$_{10}$**, **2-(H)$_7$**, **3-(H)$_4$**, and **4-(H)$_2$**. The quenching with MeOD gave the deuterated analogues. The overall yields of the crude products are quantitative.

**Characterization.** The most useful methods for characterization of our molecules are fast atom bombardment (FAB) MS and 2D COSY NMR. The elemental analyses are less valuable because of similar elemental content and large number of atoms in our molecules, e.g., the obtained C/H analyses for **3-(OEt)$_4$**, **2-(OEt)$_7$**, and **1-(OEt)$_{10}$** are almost identical.

**FABMS.** For the large polyether molecules, **3-(OEt)$_4$**, **2-(OEt)$_7$**, and **1-(OEt)$_{10}$**, the highest mass molecular fragments are compatible with the loss of one EtOH molecule. Because of the insufficient instrumental mass range only the average mass peak can be observed for our largest molecule, **1-(OEt)$_{10}$**. For the small diether, **4-(OEt)$_2$**, the fragment corresponding to the loss of EtOH is accompanied by a weak signal from the molecular mass cluster. Similar behavior is observed for **8-(OEt)$_3$Br** and **7-(OEt)$_2$Br**.

When the labile OEt groups are replaced with the hydrogens or deuteria as in ***N*-(H)$_n$** and ***N*-(D)$_n$** ($N$ = 1–3; $n$ = 10, 7, and 4) the expected molecular mass clusters can be detected. For example, the molecular mass clusters for **1-(H)$_{10}$** and **1-(D)$_{10}$** are centered at 2373 and 2383 amu, respectively, and possess similar mass distribution. Therefore, the additional support for the structure of the polyethers is obtained.

**NMR.** All molecules are characterized by $^{13}$C and $^1$H NMR; DEPT pulse sequence is used for the assignment of quaternary carbons and CH$_2$ groups. The aromatic regions of the $^1$H NMR spectra show the major structural features of our molecules; all aromatic rings in **1-(OEt)$_{10}$**, **1-(H)$_{10}$**, and their lower homologues can be traced in each molecule using 2D COSY (Table I).[18] For **1-(OEt)$_{10}$**, which is 3-fold symmetric on the NMR time scale, three rings without the *tert*-butyl groups and four rings with the *tert*-butyl groups can be found. The former rings possess singlet/doublet/doublet/triplet spin systems and the latter rings exhibit doublet/doublet coupling. Similar analysis can be carried out for **2-(OEt)$_7$** (Table I, Figure 5, and Figure 6).

The partial $^1$H NMR spectra of the Et and *t*-Bu groups are amenable to simple analysis only for small molecules such as **3**, **4**, **9**, and their precursors, which do not possess chiral carbons.

The $^{13}$C NMR spectra of **3**, **4**, **9**, and their precursors are straightforward. In the larger molecules, not all $^{13}$C resonances can be resolved because of the spectral overlap. In **7-(OEt)$_2$Br**, which possess one chiral carbon, the $^{13}$C resonances for two *t*-Bu groups are overlapped at 34.36 and 31.36 ppm. For the higher homologue, **8-(OEt)$_3$Br**, the spectral overlap is more of a problem. The single diastereomer should possess 48 nonequivalent carbons; however, 62 $^{13}$C resonances can be resolved ($\Delta\nu_{1/2}$ = 0.5 Hz = 0.005 ppm). Therefore, **8-(OEt)$_3$Br** is a mixture of two diastereomers. Not surprisingly, the $^{13}$C NMR spectra for polyethers **1-(OEt)$_{10}$** and **2-(OEt)$_7$** (and the corresponding methanes) possess broad peaks that cannot account for all

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[18] Supplementary material: pages 1s–2s, experimental procedure for the preparation of 4,4′-di-*tert*-butylbenzophenone and 3-bromo-4′-*tert*-butylbenzophenone; pages 3s–9s (Figures 1s–7s), structures and partial COSY spectra for **1-(H)$_{10}$**, **2-(H)$_7$**, **3-(H)$_4$**, **3-(OEt)$_4$**, **7-(OEt)$_2$Br**, **8-(OEt)$_3$Br**, and **11-(OEt)$_3$(OEt)(OEt)$_3$**; pages 10s–43s (Figures 8s–41s) full $^1$H and $^{13}$C NMR spectra for selected compounds.

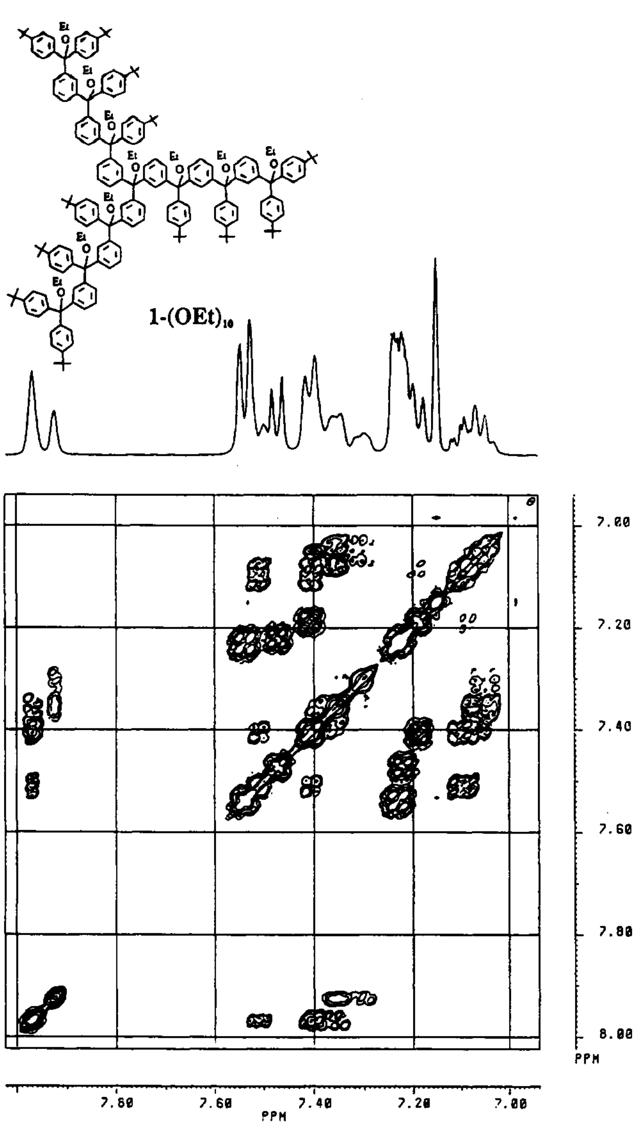

**Figure 5.** 1-(OEt)$_{10}$: partial COSY spectrum in $C_6D_6$.

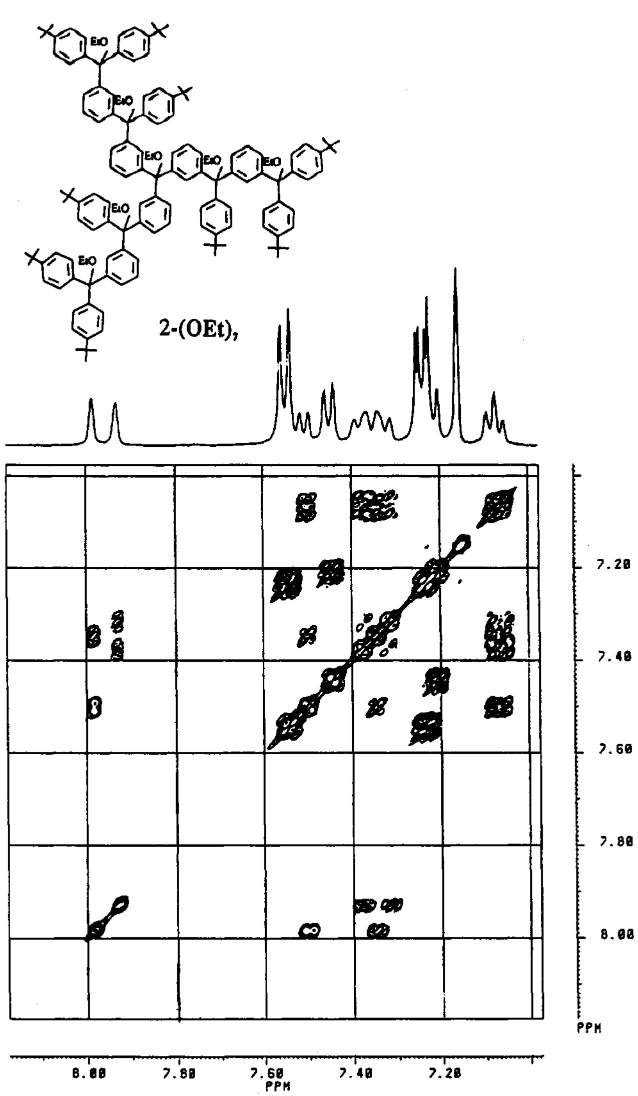

**Figure 6.** 2-(OEt)$_7$: partial COSY spectrum in $C_6D_6$.

carbons even in one isomer. Most probably these compounds are diastereomeric mixtures. In fact, for 2-(H)$_7$ 11 quaternary $^{13}C$ resonances can be resolved, which is more than the expected ten resonances for one isomer. The separation of each diastereomer is not practical because, later in the synthesis, all chiral centers are removed when the corresponding carbopolyanions are generated.

Another factor limiting the resolution of the $^{13}C$ NMR spectra is the presence of very similar but not identical molecular fragments in the large molecules 1 and 2. A typical example is the most downfield resonance in 3-(H)$_4$ at 148.7 ppm, which is separated from the nearest neighbor resonance by over 4 ppm; in 2-(H)$_7$, three most downfield resonances are also at 148.7 ppm and within 0.04 ppm! The consequence of such severe spectral overlap is that the number of the resolved $^{13}C$ resonances in 1-(H)$_{10}$ is even less than in 2-(H)$_7$.

## Conclusion

It appears that the synthetic strategy, which is employed in this work, may allow for the preparation of higher homologues of 1-(OEt)$_{10}$ by adding more 3-bromo-4′-*tert*-butylbenzophenone segments. This is important because the modeling of a 2D ferromagnetic domain may require the molecules which are substantially larger than 1. For purification, the solubility of compounds 1–4 in both nonpolar and polar solvents is very helpful. The homologues of 1–4 are expected to be similarly soluble. The characterization of such nonpolar molecules in the $10^4$ amu mass range using MS and NMR spectroscopy will be challenging.

## Experimental Section

**Materials.** Tetrahydrofuran (THF) and diethyl ether (ether) were distilled from a blue/purple $Ph_2CO/Na$ in an Ar or $N_2$ atmosphere immediately before use. Lithium metal (98+%, high in sodium) was purchased from Aldrich. All other important reagents were purchased from Aldrich except for *n*-BuLi (Alfa) and 1,3-dibromobenzene (Kodak). Addition of (4-*tert*-butylphenyl)lithium to 4-*tert*-butylbenzonitrile[16] gave 4,4′-di-*tert*-butylbenzophenone.[17,18] Similarly, addition of (3-bromophenyl)lithium to 4-*tert*-butylbenzonitrile gave 3-bromo-4′-*tert*-butylbenzophenone.[18]

**Procedures and Analyses.** All organometallic reactions were carried out on a $10^{-3}$ Torr vacuum line equipped with high vacuum three-way Teflon stopcocks (Kontes), Kalrez O-rings (Kontes), Fisher-Porter Solv-Seal joints (Lab-Crest), stainless steel flexible connections (Cajon), and thermocouple (Varian). For the submillimole-scale reactions the solvents were transferred over the vacuum line. For the millimole-scale reactions Hamilton gas-tight syringes were used.

Elemental analyses were carried out by Dr. G. M. Dabkowski, Director-Microlytics, P.O. Box 199, So. Deerfield, MA 01373.

**NMR.** Bruker WM-400 ($^1H$, 400.1 MHz, and $^{13}C$, 100.6 MHz) was employed for measurement of the NMR spectra at 303 K. 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 (complete phase cycle). Zero filling, multiplication by the sine-window function, Fourier transform, and symmetrization were applied.

**[(3-Bromophenyl)bis(4-*tert*-butylphenyl)methoxy]ethane, 6-(OEt)Br.** *n*-BuLi (13.7 mL of a 2.2 M solution in hexane) was added to a solution of 1,3-dibromobenzene (7.160 g) in ether (75 mL) at −25 °C. After 10 min at −25 °C, 4,4′-di-*tert*-butylbenzophenone (8.882 g, 30.17 mmol) in ether (75 mL) was added. The temperature in the cooling bath was allowed to raise to −15 °C over 1 h and, then, EtOCOCl (2.90 mL) was added. After 15 h at ambient temperature, a concentrated aqueous solution of potassium carbonate was added. After extraction with ether (250 mL) and drying over $MgSO_4$, concentration in vacuo afforded 16.12 g of an yellow glass. Boiling with ethanol (75 mL, 100%) and filtration at ambient temperature gave 10.56 g of a colorless solid (mp 158–159 °C). $^1$H NMR ($CDCl_3$): 7.688 (t, $J$ = 1.8, 1 H), 7.367 (m, 0.5 H), 7.348 (m, 0.5 H), 7.331 (m, 0.5 H), 7.311 (m, 0.5 H), 7.295 (s, 8 H), 7.127 (t, $J$ = 7.9, 1 H), 3.063 (q, $J$ = 7.0, 2 H), 1.305 (s, 18 H), 1.219 (t, $J$ = 7.0, 3 H). $^1$H NMR ($C_6D_6$): 8.12 (t, $J$ = 2, 1 H), 7.47 (d, $J$ = 8, 4 H), 7.41 (bd, $J$ = 8, 1 H), 7.22 (d, $J$ = 8, 4 H), 7.15 (bd, under the solvent peak), 6.73 (t, $J$ = 8, 1 H), 3.09 (q, $J$ = 7, 2 H), 1.18 (s, 18 H), 1.09 (t, $J$ = 7, 3 H). $^{13}$C NMR ($CDCl_3$): 149.8, 148.4, 140.5, 130.9, 129.6, 129.2, 128.5, 127.0, 124.7, 122.0, 85.8, 59.4, 34.4, 31.4, 15.3. $^{13}$C DEPT (135°) CH, $CH_3$: 130.9, 129.6, 129.2, 128.5, 127.0, 124.7, 31.4, 15.3; $CH_2$: 59.4.

A small sample was recrystallized from ethanol for elemental analysis. Anal. Calcd for $C_{29}H_{35}BrO$: C, 72.64; H, 7.36. Found: C, 72.68; H, 7.18.

**[Tris(4-*tert*-butylphenyl)methoxy]ethane, 5-OEt.** *n*-BuLi (2.27 mL of a 2.2 M solution in hexane, 5.0 mmol) was added to a solution of 4-*tert*-butylbromobenzene (0.87 mL, 5.0 mmol) in ether (20 mL) at −12 °C. After 45 min a solid 4,4′-di-*tert*-butylbenzophenone (900.0 mg) was added, and the reaction mixture was allowed to attain ambient temperature. After 3 h at ambient temperature EtOCOCl (0.48 mL, 5.0 mmol) was added. After 17 h at ambient temperature the reaction was quenched with a concentrated solution of $K_2CO_3$ in water and extracted with ether. The ether layer was washed with $NaOH_{aq}$ and water and, then, dried over $MgSO_4$. Concentration in vacuo gave a yellowish oily solid (1.397 g). Crystallization from ethanol afforded colorless crystals (620.2 mg). Anal. Calcd for $C_{33}H_{44}O$: C, 86.79; H, 9.71. Found: C, 87.00; H, 9.95. $^1$H NMR ($CDCl_3$): 7.330 (dt, $J$ = 2, $J$ = 9, 6 H), 7.281 (dt, $J$ = 2, $J$ = 9, 6 H), 3.077 (q, $J$ = 7.0, 2 H), 1.297 (s, 9 H), 1.210 (t, $J$ = 7.0, 3 H). $^{13}$C NMR ($CDCl_3$): 149.2, 141.8, 128.3, 124.4, 86.0, 59.2, 34.4, 31.4, 15.3. $^{13}$C DEPT (135°) CH, $CH_3$: 128.3, 124.4, 31.4, 15.3; $CH_2$: 59.2.

**[(3-Bromophenyl)bis(phenyl)methoxy]ethane, 10-(OEt)-Br.** *n*-BuLi (28.7 mL of a 2.2 M solution in hexane, 63.1 mmol) was added to a solution of 1,3-dibromobenzene (14.88 g, 63.06 mmol) in ether (75 mL) at −25 °C. After 10 min at −25 °C, solid benzophenone (11.53 g, 63.28 mmol) was added. The temperature in the cooling bath was allowed to raise to −17 °C over 90 min and, then, EtOCOCl (6.0 mL, 63 mmol) was added. After 18 h at ambient temperature, a concentrated aqueous solution of potassium carbonate was added. After extraction with ether (250 mL) and drying over $MgSO_4$, concentration in vacuo followed by treatment with boiling EtOH gave crude **10-(OEt)Br** as yellow oil (22.92 g). A 6.30-g portion of the crude product was purified by chromatography at elevated pressure (20 psi, 40 μm silica gel, hexane/$CH_2Cl_2$, 8/1) to give 3.72 g (58%) of a colorless oil. Anal. Calcd for $C_{21}H_{19}BrO$: C, 68.67; H, 5.21. Found: C, 68.80; H, 5.29. $^1$H NMR ($CDCl_3$): 7.674 (t, $J$ = 1.8, 1 H), 7.45–7.20 (m, 12 H), 7.124 (t, $J$ = 8, 1 H), 3.081 (q, $J$ = 7, 2 H), 1.230 (t, $J$ = 7.0, 3 H). $^{13}$C NMR ($CDCl_3$): 147.7, 143.5, 131.1, 129.8, 129.3, 128.7, 127.8, 127.13, 127.07, 122.0, 86.2, 59.5, 15.2. $^{13}$C DEPT (135°) CH, $CH_3$: 131.0, 129.8, 129.3, 128.7, 127.8, 127.14, 127.05, 15.2; $CH_2$: 59.5.

**4-(OEt)$_2$.** *n*-BuLi (0.92 mL of a 2.2 M solution in hexane, 2.0 mmol) was added to a suspenion of **6-(OEt)Br** (971.6 mg, 2.026 mmol) in ether (9 mL) at −30 °C. The temperature of the cooling bath was allowed to raise to −20 °C over a period of 2 h and, then, solid 4,4′-di-*tert*-butylbenzophenone (596.4 mg, 2.026 mmol) was added. The cooling bath was taken off, and after 21 h EtOCOCl (0.19 mL, 2.0 mmol) was added. After 24 h a concentrated aqueous solution of $K_2CO_3$ was added, followed by extraction of the reaction mixture with ether. The ether layer was dried over $MgSO_4$ and, then, concentrated in vacuo to give 1.612 g of a yellowish solid. Crystallization from ethanol afforded 985.4 mg of a yellow solid which was further purified by column chromatography (silica gel, 70–230 mesh; hexane/$CH_2Cl_2$, 6/1). Pure product was obtained as a colorless solid (193.5 mg); the purity is better than 95% according to NMR (no extraneous peaks are observed). Anal. Calcd for $C_{52}H_{66}O_2$: C, 86.38; H, 9.20. Found: C, 86.72; H, 9.23. FABMS (ONPOE), cluster: $m/z$ (peak height) at $(M + H)^+$ 722 (1), $(M - C_2H_5OH)^+$ 676 (2), 677 (20), 678 (10), 679 (3). $^1$H NMR ($CDCl_3$): 7.444 (bs, 1 H), 7.331 (dd, $J$ = 1.8, $J$ = 7.5, 2 H), 7.23 (m, 17 H), 2.946 (q, $J$ = 7.0, 4 H), 1.291 (s, 36 H), 1.112 (t, $J$ = 7.0, 6 H). $^{13}$C NMR ($CDCl_3$): 149.3, 144.0, 141.7, 129.7, 128.4, 127.2, 126.3, 124.3, 86.3, 59.3, 34.4, 31.4, 15.3. $^{13}$C DEPT (135°) CH, $CH_3$: 129.7, 128.4, 127.2, 126.3, 124.3, 31.4, 15.3; $CH_2$: 59.3.

**3-(OEt)$_4$.** *n*-BuLi (1.8 mL of a 2.2 M solution in hexane) was added to a suspension of **6-(OEt)Br** (1.920 g) in ether (17 mL) at −30 °C. The temperature of the cooling bath was allowed to increase to −20 °C over a period of 2 h 45 min and, then, $(MeO)_2CO$ (0.11 mL) was added. After 30 min the cooling bath was taken off and after an additional 1 h, EtOCOCl (0.45 mL) was added. After 17 h a concentrated aqueous solution of $K_2CO_3$ was added, followed by extraction of the reaction mixture with ether (75 mL). The ether layer was dried over $MgSO_4$ and, then, concentrated in vacuo to give 1.895 g of an yellow glass. Precipitation from ethanol afforded 1.061 g of an yellow solid that is about 80% pure according to NMR. Column chromatography (silica gel, 70–230 mesh; hexane/$CH_2Cl_2$, from 6/1 to 3/1) gave 204.5 mg of colorless solid. Anal. Calcd for $C_{90}H_{110}O_4$: C, 86.08; H, 8.83. Found: C, 86.29; H, 8.74. FABMS (3-NBA and 3-NBA/LiI), cluster: $m/z$ (peak height) at $(M + H - C_2H_5OH)^+$ 1210 (30), 1211 (30), 1212 (15). $^1$H NMR ($CDCl_3$): 7.37 (bt, 3 H), 7.27 (m, 3 H), 7.193 (s, 12 H), 7.186 (s, 12 H), 7.16 (bs, 3 H), 7.09 (m, 3 H), 2.96 (q, $J$ = 7.0, 6 H), 2.84 (q, $J$ = 7.0, 2 H), 1.26 (s, 54 H), 1.07 (t, $J$ = 7.0, 9 H), 0.86 (t, 3 H). $^1$H NMR ($C_6D_6$): 7.90 (t, $J$ = 2, 3 H), 7.53 (bd, $J$ = 8, 3 H), 7.50 (d, $J$ = 8, 12 H), 7.37 (bd, $J$ = 8, 3 H), 7.21 (d, $J$ = 8, 12 H), 7.11 (t, $J$ = 8, 3 H), 3.19–3.05 (m, 8 H), 1.20 (s, 54 H), 1.11 (t, $J$ = 7, 9 H), 1.01 (t, $J$ = 7, 3 H). $^{13}$C NMR ($CDCl_3$): 149.1, 144.0, 143.6, 141.7, 129.3, 128.2, 127.0, 126.9, 126.8, 124.3, 86.6, 86.2, 59.3, 59.1, 34.3, 31.4, 15.2, 15.1. $^{13}$C DEPT (135°) CH, $CH_3$: 129.3, 128.2, 127.0, 126.9, 126.8, 124.3, 31.4, 15.2, 15.1; $CH_2$: 59.3, 59.1.

**9-(OEt)$_4$.** *n*-BuLi (3.32 mL of a 2.2 M solution in hexane, 7.30 mmol) was added to a suspension of **10-(OEt)Br** (2.682 g, 7.303 mmol) in ether (30 mL) at −30 °C. The temperature of the cooling bath was allowed to increase to −20 °C over a period of 3 h and, then, $(MeO)_2CO$ (0.18 mL, 2.1 mmol) was added. After 1 h the cooling bath was taken off. After 1 h, EtOCOCl (0.69 mL, 7.2 mmol) was added. After 18 h a concentrated aqueous solution of $K_2CO_3$ was added. Ether (30 mL) was added, and a suspension of a solid in ether was repeatedly washed with water. Concentration in vacuo of the ether suspension gave a yellow solid (2.606 g). Washing with ether and filtration produced 792.6 mg of a colorless solid. Column chromatography (silica gel, 70–230 mesh; hexane/$CH_2Cl_2$, from 6/1 to 3/1) gave 204.5 mg of a colorless solid. The solid was dissolved in EtOH; EtOH was removed in vacuo and, then, the residue was pumped at $10^{-3}$ Torr for 24 h. No extraneous NMR peaks are observed. Anal. Calcd for $C_{66}H_{62}O_4$: C, 86.24; H, 6.80. Found: C, 86.41; H, 6.85. FABMS (3-NBA), cluster: $m/z$ (peak height) at $(M + H - C_2H_5OH)^+$ 873 (3), 874 (2). $^1$H NMR ($CDCl_3$): 7.419 (s, 3 H), 7.35–7.05 (m, 39 H), 2.957 (q, $J$ = 7, 6 H), 2.859 (q, $J$ = 7, 2 H), 1.099 (t, $J$ = 7, 9 H), 0.909 (t, $J$ = 7, 3 H). $^{13}$C NMR ($CDCl_3$): 144.8, 143.8, 143.4, 129.2, 128.5, 127.6, 127.2, 127.04, 126.96, 126.6, 86.6, 86.5, 59.4, 59.3, 15.2, 15.0. $^{13}$C DEPT (135°) CH, $CH_3$: 129.2, 128.5, 127.6, 127.2, 127.05, 126.96, 126.6, 15.2, 15.0; $CH_2$: 59.4, 59.3.

**7-(OEt)$_2$Br.** *n*-BuLi (11.4 mL of a 2.2 M solution in hexane, 25.1 mmol) was added to a suspension of **6-(OEt)Br** (12.05 g, 25.13 mmol) in ether (100 mL) at −35 °C. After stirring for 3 h 30 min at −25 °C solid 3-bromo-4′-*tert*-butylbenzophenone (7.972 g, 25.13 mmol) was added to the homogeneous reaction mixture at −35 °C. The temperature in the cooling bath was allowed to raise to 15 °C over 6-h period and, then, EtOCOCl (2.40 mL, 25.1 mmol) was added. After 12 h at ambient temperature, a concentrated aqueous solution of potassium carbonate was added. After extraction with ether and drying over $MgSO_4$, concentration in vacuo followed by treatment with boiling EtOH afforded 19.5 g of an yellow glass. Column chromatography (silica gel, 70–230 mesh;

hexane/$CH_2Cl_2$, from 7/1 to 7/5) gave 10.97 g (58%) of a colorless solid. Anal. Calcd for $C_{48}H_{57}BrO_2$: C, 77.29; H, 7.70. Found: C, 77.18; H, 7.77. FABMS (3-NBA), cluster: $m/z$ (peak height) at $(M + H)^+$ 743 (2.5), 744 (3), 745 (3), 746 (2); $(M + H - C_2H_5OH)^+$ 699 (12), 700 (6), 701 (12), 702 (12). $^1$H NMR ($CDCl_3$): 7.59 (s, 1 H), 7.4–7.2 (m, 18 H), 7.07 (t, $J$ = 8, 1 H), 3.1–2.9 (m, 4 H), 1.298 (s, 9 H), 1.295 (s, 9 H), 1.291 (s, 9 H), 1.2–1.1 (m, 6 H). $^1$H NMR ($C_6D_6$): 8.01 (bs, 1 H), 7.35 (bd, $J$ = 8, 1 H), 7.14 (bd, $J$ = 8, 1 H), 6.73 (t, $J$ = 8, 1 H), 7.85 (bs, 1 H), 7.56 (bd, $J$ = 8, 1 H), 7.38 (bd, $J$ = 8, 1 H), 7.09 (t, $J$ = 8, 1 H), 7.53 (d, $J$ = 8, 2 H), 7.53 (d, $J$ = 8, 2 H), 7.260 (d, $J$ = 8, 2 H), 7.250 (d, $J$ = 8, 2 H), 7.406 (d, $J$ = 8, 2 H), 7.206 (d, $J$ = 8, 2 H), 3.166 (q, $J$ = 7, 2 H), 3.03 (m, 2 H), 1.212 (s, 9 H), 1.206 (s, 9 H), 1.190 (s, 9 H), 1.137 (t, $J$ = 7, 3 H), 1.032 (t, $J$ = 7, 3 H). $^{13}$C NMR ($CDCl_3$): 149.82, 149.34, 149.31, 148.33, 144.49, 142.72, 141.57, 141.40, 140.20, 131.00, 129.74, 129.59, 129.10, 128.52, 128.32, 128.25, 127.40, 126.92, 126.75, 126.50, 124.60, 124.45, 124.42, 121.89, 86.24, 86.09, 59.42, 59.30, 34.40, 34.36 (broad), 31.36 (broad), 31.33, 15.26, 15.18. $^{13}$C DEPT (135°) CH and $CH_3$: 131.00, 129.74, 129.59, 129.10, 128.52, 128.32, 128.25, 127.40, 126.92, 126.75, 126.50, 124.60, 124.45, 124.42, 31.36 (broad), 31.33, 15.26, 15.18; $CH_2$: 59.42, 59.30.

**2-(OEt)$_7$.** $t$-BuLi (4.31 mL of a 1.7 M solution in pentane, 7.34 mmol) was added to a solution of **7-(OEt)$_2$Br** (2.736 g, 3.668 mmol) in ether (24 mL) at −78 °C. After stirring for 45 min at −78 °C $(MeO)_2CO$ (0.100 mL, 1.19 mmol) was added to the homogeneous reaction mixture at −78 °C. The temperature in the cooling bath was allowed to raise to 15 °C over 5-h period and, then, EtOCOCl (0.35 mL, 3.7 mmol) was added. After 12 h at ambient temperature, a concentrated aqueous solution of potassium carbonate was added. After extraction with ether and drying over $MgSO_4$, concentration in vacuo afforded 2.72 g of yellow glass. Treatment with boiling EtOH (30 mL), cooling to −20 °C, and filtration produced 1.85 g of crude product as light yellow glass. Column chromatography (silica gel, 70–230 mesh; hexane/$CH_2Cl_2$, from 2.5/1 to 10/7) gave 0.933 g (37%) of pure product as colorless solid. Recrystallization (EtOH) gave 0.736 g of the analytically pure product. Anal. Calcd for $C_{147}H_{176}O_7$: C, 85.92; H, 8.63. Found: C, 86.24; H, 8.63. FABMS (ONPOE), cluster: $m/z$ (peak height) $(M - C_2H_5OH)^+$: 2008 (2), 2009 (2.5), 2010 (2), 2011 (1). $^1$H NMR ($CDCl_3$): 7.468 (bs, 6 H), 7.3–7.0 (m, 54 H), 2.976 (q, $J$ = 7, 6 H), 2.844 (bq, 6 H), 2.779 (q, $J$ = 7, 2 H), 1.270 (s, 54 H), 1.252 (s, 27 H), 1.068 (t, $J$ = 7, 9 H), 0.893 (bt, 9 H), 0.806 (t, $J$ = 7, 3 H). $^1$H NMR ($C_6D_6$): 7.983 (s, 3 H), 7.927 (s, 3 H), 7.540 (d, $J$ = 8, 12 H), 7.500 (d, $J$ = 8, 3 H), 7.442 (d, $J$ = 8, 6 H), 7.4–7.3 (m, 9 H), 7.25–7.20 (m, 18 H), 7.065 (t, $J$ = 8, 6 H), 3.163 (q, $J$ = 7, 6 H), 3.1–3.0 (m, 7 H), 1.221 (s, 27 H), 1.208 (s, 27 H), 1.203 (s, 27 H), 1.111 (t, $J$ = 7, 9 H), 1.019 (t, $J$ = 7, 9 H), 0.961 (t, $J$ = 7, 3 H). $^{13}$C NMR ($CDCl_3$): 149.2, 149.1, 143.9, 143.8, 143.7, 141.7, 141.7, 129.1, 128.6, 128.3, 127.2, 127.0, 126.9, 126.7, 126.6, 124.3, 124.3, 86.7, 86.5, 86.3, 59.4, 59.3, 34.3, 34.3, 31.4, 15.2, 15.1, 15.0.

**8-(OEt)$_3$Br.** $t$-BuLi (9.50 mL of a 1.7 M solution in pentane, 16.2 mmol) was added to a solution of **6-(OEt)Br** (3.844 g, 8.017 mmol) in ether (42 mL) at −78 °C. After stirring for 1 h at −78 °C, solid 3-bromo-4′-*tert*-butylbenzophenone (2.548 g, 8.032 mmol) was added to the homogeneous reaction mixture at −78 °C. The temperature in the cooling bath was allowed to raise to ambient temperature over 5 h. Subsequently, the second portion of $t$-BuLi (9.40 mL of a 1.7 M solution in pentane, 16.0 mmol) was added at −78 °C and after 1 h at −78 °C the second portion of solid 3-bromo-4′-*tert*-butylbenzophenone (2.541 g, 8.010 mmol) followed. The reaction mixture was allowed to attain ambient temperature over a 12-h period and, then, EtOCOCl (1.53 mL, 16.0 mmol) was added at 0 °C. After 24 h at ambient temperature, a concentrated aqueous solution of potassium carbonate was added. After extraction with ether and drying over $MgSO_4$, concentration in vacuo afforded 8.68 g of yellow glass. Crystallization (EtOH, 45 mL) at −20 °C produced 6.14 g of crude product as light yellow glass. Column chromatography (silica gel, 70–230 mesh; hexane/$CH_2Cl_2$, from 3.5/1 to 3/1) gave 3.102 g (38%) of pure product as colorless solid. A small sample (0.717 g) was recrystallized (EtOH, 9 mL) to produce 0.291 g of the analytically pure product. Anal. Calcd for $C_{67}H_{79}BrO_3$: C, 79.50; H, 7.87. Found: C, 79.71; H, 8.01. FABMS (3-NBA/LiI), cluster: $m/z$ (peak height) at $(M + H - C_2H_5OH)^+$: 965 (4), 966 (3), 967 (4), 968 (3). $^1$H NMR ($CDCl_3$): 7.59–7.58 (m, 1 H), 7.44 (bs, 1 H), 7.39 (bs, 1 H), 7.32–7.15 (m, 24 H), 7.04 (t, $J$ = 8, 1 H), 3.01–2.92 (m, 6 H), 1.287, 1.284, 1.280 (s, 36 H), 1.12–1.07 (m, 6 H), 1.03–0.98 (m, 3 H). $^1$H NMR ($C_6D_6$): 8.00 (bs, 1 H), 7.95 (bs, 1 H), 7.84 (bs, 1 H), 7.52 (m, 5 H), 7.5–7.3 (m, 8 H), 7.28–7.16 (m, 8 H), 7.14–7.05 (m, 3 H), 6.71 (t, $J$ = 8, 1 H), 3.15 (q, $J$ = 7, 2 H), 3.11 (q, $J$ = 7, 2 H), 3.06–2.98 (m, 2 H), 1.226 (s, 9 H), 1.207, 1.205, 1.203 (s, 18 H), 1.191, 1.187 (s, 9 H), 1.120 (t, $J$ = 7, 3 H), 1.074, 1.071 (t, $J$ = 7, 3 H), 1.023, 1.017 (t, $J$ = 7, 3 H). $^{13}$C NMR ($CDCl_3$): 149.78, 149.76, 149.34, 149.24, 149.23, 148.34, 144.37, 144.29, 144.15, 144.13, 143.77, 143.58, 142.79, 141.68, 141.66, 141.37, 141.26, 140.25, 130.92, 129.58, 129.50, 129.50, 129.30, 129.23, 129.11, 128.50, 128.48, 128.36, 128.33, 128.31, 127.59, 127.29, 127.20, 127.19, 127.07, 126.92, 126.90, 126.78, 126.76, 126.68, 126.64, 124.59, 124.38, 124.35, 121.90, 86.50, 86.48, 86.28, 86.08, 59.46, 59.36, 59.29, 34.40, 34.39, 34.34, 31.37, 31.33, 31.21, 15.24, 15.19, 15.17, 15.14.

**1-(OEt)$_{10}$ and 11-(OEt)$_3$(OEt)(OEt)$_3$.** $t$-BuLi (5.80 mL of 1.7 M solution in pentane, 9.86 mmol) was added to a solution of **8-(OEt)$_3$Br** (4.921 g, 4.861 mmol) in ether (26 mL) at −78 °C. After stirring for 1 h at −78 °C $(MeO)_2CO$ (0.130 mL, 1.54 mmol) was added to the homogeneous reaction mixture at −50 °C. The temperature in the cooling bath was allowed to raise to 10 °C over a 17-h period and, then, EtOCOCl (0.47 mL, 4.9 mmol) was added at 0 °C. After 30 h at ambient temperature, a concentrated aqueous solution of potassium carbonate was added. After extraction with ether and drying over $MgSO_4$, concentration in vacuo afforded 5.00 g of a yellow glass. Treatment with boiling EtOH (80 mL), cooling to −20 °C, and filtration produced 3.53 g of crude product as light yellow glass. Column chromatography (silica gel, 70–230 mesh; hexane/$CH_2Cl_2$, from 1/3 to 9/10) gave two products: **1-(OEt)$_{10}$**, 0.841 g (18%, more polar fraction), as a yellow solid and **11-(OEt)$_3$(OEt)(OEt)$_3$**, 0.321 g (6%, less polar fraction), as colorless solid; the recrystallizations afforded analytically pure products: 0.614 g (EtOH, 40 mL) and 0.238 g (EtOH, 9 mL), respectively. **1-(OEt)$_{10}$**. Anal. Calcd for $C_{204}H_{242}O_{10}$: C, 85.85; H, 8.55. Found: C, 86.08; H, 8.62. FABMS (NBA) $(M + H - C_2H_5OH)^+$ $m/z$ at 2806.7 (average). $^1$H NMR ($CDCl_3$): 7.50–7.42 (m, 9 H), 7.30–6.95 (m, 75 H), 2.97 (q, $J$ = 7, 6 H), 2.89 (q, $J$ = 7, 6 H), 2.85–2.76 (m, 8 H), 1.267, 1.263 (s, 81 H), 1.230 (bs, 27 H), 1.08 (t, $J$ = 7, 9 H), 0.98–0.83 (m, 18 H), 0.80 (t, $J$ = 7, 3 H). $^1$H NMR ($C_6D_6$): 7.97 (bs, 6 H), 7.92 (bs, 3 H), 7.58–7.45 (m, 21 H), 7.45–7.26 (m, 21 H), 7.26–7.16 (m, 24 H), 7.13–7.01 (m, 9 H), 3.16 (q, $J$ = 7, 6 H), 3.13–3.00 (m, 14 H), 1.224 (bs, 54 H), 1.209 (s, 27 H), 1.204 (s, 27 H), 1.12 (t, $J$ = 7, 9 H), 1.09–0.93 (m, 21 H). $^{13}$C NMR ($CDCl_3$): 149.18, 149.08, 143.95, 143.85, 143.82, 143.76, 141.72, 141.69, 141.61, 141.55, 129.21, 128.71, 128.49, 128.37, 128.30, 127.11, 126.98, 126.81, 126.76, 126.61, 124.33, 124.28, 86.68, 86.52, 86.48, 86.28, 59.37, 59.32, 59.28, 34.32, 34.27, 31.36, 15.22, 15.10, 15.03.

**11-(OEt)$_3$(OEt)(OEt)$_3$.** Anal. Calcd for $C_{141}H_{172}O_7$: C, 85.58; H, 8.76. Found: C, 85.81; H, 8.83. FABMS (3-NBA), cluster: $m/z$ (peak height) at $(M + H - C_2H_5OH)^+$: 1932 (2), 1933 (3), 1934 (2), 1935 (1). $^1$H NMR ($CDCl_3$): 7.52 (bs, 4 H), 7.46 (s, 2 H), 7.28–7.10 (m, 50 H), 3.00–2.90 (m, 12 H), 2.80–2.70 (m, 2 H), 1.28, 1.26 (s, 72 H), 1.09 (t, $J$ = 7, 6 H), 1.00 (bs, 12 H), 0.80 (bs, 12 H). $^1$H NMR ($C_6D_6$): 8.00 (bs, 2 H), 7.97 (bs, 4 H), 7.56–7.35 (m, 28 H), 7.23 (bd, 16 H), 7.15–7.05 (m, 6 H), 3.20–3.08 (m, 12 H), 2.99 (bq, $J$ = 8, 2 H), 1.23, 1.21, 1.21 (s, 72 H), 1.15–1.05 (m, 27 H), 0.94 (bs, 3 H). $^{13}$C NMR ($CDCl_3$): 149.2, 144.0, 144.0, 143.9, 143.8, 143.8, 143.6, 141.7, 141.6, 141.6, 141.2, 141.2, 140.6, 140.7, 130.6, 130.6, 130.5, 130.5, 129.3, 129.0, 128.8, 128.5, 128.3, 127.0, 126.8, 126.8, 126.6, 125.8, 125.8, 124.3, 124.3, 88.9, 86.5, 86.3, 59.9, 59.3, 40.4, 34.3, 31.4, 28.1, 15.2, 15.1, 15.1. $^{13}$C DEPT (135°) CH, $CH_3$: 130.6, 130.6, 130.5, 130.5, 129.3, 129.0, 128.8, 128.5, 128.3, 127.0, 126.8, 126.8, 126.6, 125.8, 125.8, 124.3, 124.3, 31.4, 28.1, 15.2, 15.1, 15.1; $CH_2$: 59.9, 59.3.

***N*-(H)$_n$ and *N*-(D)$_n$ ($N$ = 1–4, $n$ = 10, 7, 4, 2). General Procedure.** Polyether ***N*-(OEt)$_n$** (40 mg) was stirred with excess lithium metal in THF (1.5 mL) for several days. One part of the red reaction mixture was filtered through a medium-porosity glass frit and quenched with MeOD. The other part was quenched with MeOH. The two reaction mixtures were subjected to separate standard aqueous workup. The ether extracts were dried over $MgSO_4$. The yields of both nondeuterated and deuterated products were quantitative. Column chromatography or preparative TLC (silica gel, $CH_2Cl_2$/hexane) were used to obtain TLC- and NMR-pure products (isolated yield: 50–80%).

**1-(H)$_{10}$.** FABMS (ONPOE), cluster *m/z* (peak height) at (M + H)$^+$: 2371 (3.5), 2372 (7), 2373 (9), 2374 (7.5), 2375 (4.5). $^1$H NMR (CDCl$_3$): 7.23–7.10 (m, 24 H), 7.10–6.70 (m, 60 H), 5.34 (s, 3 H), 5.31 (s, 3 H), 5.27 (s, 4 H), 1.261 (bs, 54 H), 1.253, 1.251 (s, 27 H), 1.233, 1.231 (s, 27 H). $^{13}$C NMR (CDCl$_3$): 148.71, 148.67, 148.64, 144.06, 143.96, 143.88, 143.85, 141.18, 141.13, 140.99, 130.83, 130.77, 128.94, 128.88, 127.99, 127.15, 124.99, 124.93, 56.52, 56.24, 55.95, 34.31, 31.40; $^{13}$C DEPT (135°) CH, CH$_3$: 130.83, 130.77, 128.94, 128.88, 127.99, 127.15, 124.99, 124.93, 56.52, 56.24, 55.95, 31.40.

**1-(D)$_{10}$.** FABMS (ONPOE), cluster *m/z* (peak height) at (M + H)$^+$: 2381 (7), 2382 (9), 2383 (11), 2384 (9), 2385 (6). $^1$H NMR (CDCl$_3$): 5.34, 5.31, 5.27 (s, <1 H).

**2-(H)$_7$.** FABMS (ONPOE), cluster *m/z* (peak height) at (M + H)$^+$: 1745 (14), 1746 (15), 1747 (11). $^1$H NMR (CDCl$_3$): 7.25–7.17 (m, 18 H), 7.11–7.00 (m, 6 H), 7.00–6.95 (m, 15 H), 6.94–6.87 (m, 12 H), 6.86–6.80 (m, 6 H), 6.76 (bd, $J$ = 8, 3 H), 5.36 (s, 3 H), 5.32 (s, 3 H), 5.30 (s, 1 H), 1.26 (bs, 54 H), 1.25 (bs, 27 H). $^{13}$C NMR (CDCl$_3$): 148.70, 148.69, 148.66, 144.07, 144.02, 143.89, 143.85, 141.17, 141.12, 141.01, 141.00, 130.82, 130.75, 128.94, 128.90, 128.01, 127.94, 127.19, 127.14, 127.10, 124.99, 124.98, 124.93, 56.52, 56.25, 55.93, 34.31, 31.40. $^{13}$C DEPT (135°) CH, CH$_3$: 130.82, 130.75, 128.94, 128.90, 128.01, 127.94, 127.19, 127.14, 127.10, 124.99, 124.98, 124.93, 56.52, 56.25, 55.93, 31.40.

**2-(D)$_7$.** FABMS (ONPOE), cluster *m/z* (peak height) at (M + H)$^+$: 1751 (50), 1752 (55), 1753 (45). $^1$H NMR (CDCl$_3$): 5.4–5.2 (s, <0.3 H). $^{13}$C NMR (CDCl$_3$): 56.2–55.3 (m, negligible intensity).

**3-(H)$_4$.** FABMS (3-NBA/GLY), cluster *m/z* (peak height) at M$^+$: 1077 (3), 1078 (10), 1079 (9), 1080 (5); (M – C$_4$H$_8$)$^+$: 1022 (4), 1023 (3); M$^+$, calc for C$_{82}$H$_{94}$ 1078.735550, found 1078.7367 and 1078.7339. $^1$H NMR (CDCl$_3$): 7.21 (d, $J$ = 7, 12 H), 7.09 (t, $J$ = 7, 3 H), 6.94 (d, $J$ = 7, 12 H), 6.91 (bd, $J$ = 8, 3 H), 6.89 (bs, 3 H), 6.81 (bd, $J$ = 7, 3 H), 5.33 (s, 4 H), 1.27 (s, 54 H). $^{13}$C NMR (CDCl$_3$): 148.7, 144.1, 143.9, 141.2, 130.8, 128.9, 127.9, 127.21, 127.16, 125.0, 56.5, 56.0, 34.3, 31.4. $^{13}$C DEPT (135°): CH, CH$_3$; 130.8, 128.9, 127.9, 127.22, 127.17, 125.0, 56.5, 56.0, 31.4.

**3-(D)$_4$.** FABMS (3-NBA/GLY), cluster *m/z* (peak height) at M$^+$: 1081 (10), 1082 (9), 1083 (8), 1084 (5); (M – C$_4$H$_8$)$^+$: 1026 (4), 1027 (3). $^1$H NMR (CDCl$_3$): 5.33 (s, <0.2 H). $^{13}$C NMR (CDCl$_3$): 56.5 (undetected), 56.0 (undetected).

**4-(H)$_2$.** $^1$H NMR (CDCl$_3$): 7.175 (d, $J$ = 8, 8 H), 7.094 (t, $J$ = 8, 1 H), 6.974 (s, 1 H), 6.920 (d, $J$ = 8, 8 H), 6.867 (d, $J$ = 8, 2 H), 5.31 (s, 2 H), 1.21 (s, 1 H). $^{13}$C NMR (CDCl$_3$): 148.8, 144.2, 141.2, 130.9, 129.0, 128.0, 127.2, 125.0, 56.0, 34.4, 31.4.

**4-(D)$_2$.** $^1$H NMR (CDCl$_3$): 5.38 (s, <0.1 H). $^{13}$C NMR (CDCl$_3$): 56.0 (s, negligible intensity), 55.5 (t, $J_{CD}$ = 17).

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**Supplementary Material Available:** Experimental procedure for the preparation of 4,4′-di-*tert*-butylbenzophenone and 3-bromo-4-*tert*-butylbenzophenone; structures and partial COSY spectra for **1-(H)$_{10}$**, **2-(H)$_7$**, **3-(H)$_4$**, **3-(OEt)$_4$**, **7-(OEt)$_2$Br**, **8-(OEt)$_3$Br**, and **11-(OEt$_3$)(OEt)(OEt$_3$)**; and $^1$H and $^{13}$C NMR spectra for selected compounds (43 pages). Ordering information is given on any current masthead page.

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# Alkylation of Allylic Derivatives. 17. Cross-Coupling Reactions of Diallylic Pivalates with Butyl- and Phenylcopper Reagents

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Cross coupling (*Z*)-1-phenyl-1,4-pentadien-3-yl pivalate (*cis*-**1**-OPiv) with LiCuBu$_2$, LiCu(CN)Bu, LiCuPh$_2$, and LiCu(CN)Ph gives only the fully conjugated γ-coupling product. With LiCuBu$_2$, substantial loss of double-bond configuration occurs to give primarily the all-trans coupling product. With other cuprates, no detectable loss of double-bond configuration was observed. Cross coupling (*Z*)-3-(2-phenylethenyl)-2-cyclohexen-1-yl pivalate (*cis*-**18**-OPiv) with LiCuBu$_2$, LiCuPh$_2$, and LiCu(CN)Ph gives only α coupling product; with LiCu(CN)Bu, a mixture of α, γ, and ϵ coupling product was obtained. Cross coupling with LiCuBu$_2$ results in loss of double-bond configuration in the α-alkylation product. With the other cuprates, no loss of double-bond configuration was detected in the α and γ coupling product. These results have profound mechanistic implications, which are discussed. The relationship between structure and reactivity was also investigated. A variety of diallylic pivalates (**1**–**5**-OPiv) were prepared and cross coupled with LiCuBu$_2$, LiCu(CN)Bu, LiCuPh$_2$, and LiCu(CN)Ph. Generally, coupling occurs at the least-substituted allylic system; mechanistic implications are discussed.

In earlier work[1] we investigated the relationship between structure and reactivity for alkylation of allylic carboxylates with LiCuMe$_2$ in ether. In this study a competitive reaction technique[1,2] was used to determine rate constant ratios for pairs of allylic carboxylates. The competitive method, in which pairs of allylic carboxylates compete for a limited amount of cuprate, is foolproof with regard to comparison of two substrates under identical conditions. This method circumvents the problems associated with obtaining absolute rate measurements; for these coupling reactions, reproducing reaction conditions is difficult because of the rapid rate of reaction (typically <10 min at 0 °C) and simultaneous decomposition of cuprate.

This paper reports an investigation into the relationship between structure and reactivity for the cross coupling diallylic pivalates (**1**–**5**-OPiv) with sp$^3$-copper reagents (LiCuBu$_2$ and LiCu(CN)Bu) and with sp$^2$-copper reagents (LiCuPh$_2$ and LiCu(CN)Ph) by an internal competitive

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