An Effective and Selective Route to 1,5-Dihydropolyalkylated *s*-Indacenes: Characterization of Their Mono- and Dianions by Silylation. Structure of *trans*-1,5-Bis(trimethylsilyl)-2,6-diethyl-4,8-dimethyl-*s*-indacene

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2,5-Dimethyl-1,4-bis(carboxyalkyl)benzenes were prepared in almost quantitative yield by alkylation of malonic esters from 2,5-dimethyl-1,4-dibromomethylbenzene obtained by bromomethylation of 1,4-dimethylbenzene. The methyl groups on the central benzene ring induce intramolecular, regiospecific cycloeliminations leading selectively to the diketones, the precursors of the corresponding 1,5-dihydro-*s*-indacenes, which also were obtained in very high yield. These new ligand precursors were easily converted to the mono- or dianions, which were characterized by means of the mono- or disilylated compounds. Disilylation occurs in cis and trans position. The structure of the *trans*-1,5-bis(trimethylsilyl)-2,6-diethyl-4,8-dimethyl-*s*-indacene was obtained by X-ray diffraction. Hexaalkyl-1,5-dihydro-*s*-indacenes underwent regioselective monosilylation and regiospecific and stereoselective disilylation. Disilylation of the less hindered tetraalkyl-1,5-dihydro-*s*-indacenes was regioselective and stereoselective.

Introduction

There is currently a great interest in polynuclear transition metal compounds derived from *s*-indacene. The strong electronic interactions between the metal centers in these complexes make them potential model systems for organometallic polymers which might result in a range of interesting electronic, magnetic, and optical properties,[1−7] as well as useful in homogeneous catalysis due to the presence of cooperative chemical effects.[8]

However, the development of the chemistry of this fused polycyclic bridging ligand has been rather slow, apart from the nonsubstituted dihydro-*s*-indacene[9] and the stable 1,3,5,7-tetra-*tert*-butyl-*s*-indacene.[10] The synthesis of alkyl-substituted dihydro-*s*-indacenes has been limited to 1,7-dihydro-2,6-dimethyl-*s*-indacene obtained as a minor product in the preparation of 1,6-dihydro-2,7-dimethyl-*as*-indacene[11] and more recently to 1,2,3,4,5,6,7,8-octamethyl-1,5-dihydro-*s*-indacene, which so far, could not be doubly deprotonated.[12]

Here we report a general route to 2,4,6,8-tetra- and 1,2,4,5,6,8-hexaalkyl-1,5-dihydro-*s*-indacenes in a five-step synthesis, which gives very high yields, and the subsequent characterization of their mono- and dianions by silylation.

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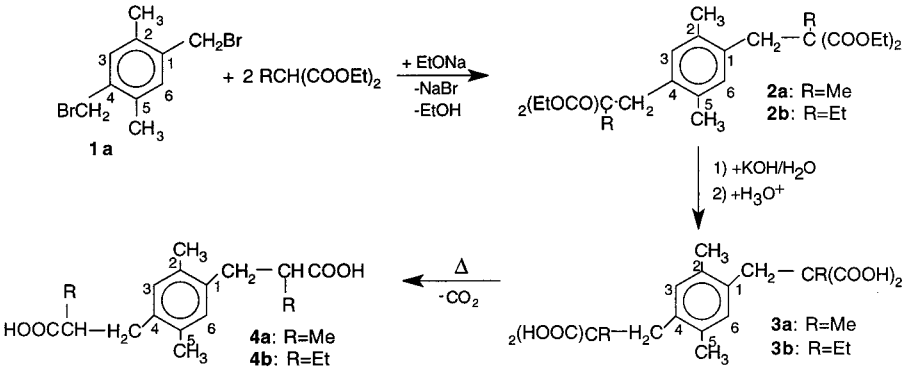
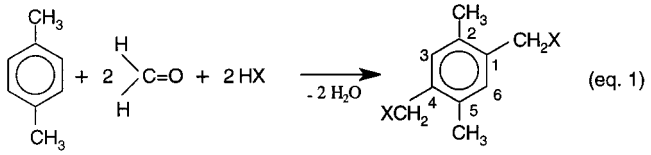
Scheme 1



Results and Discussion

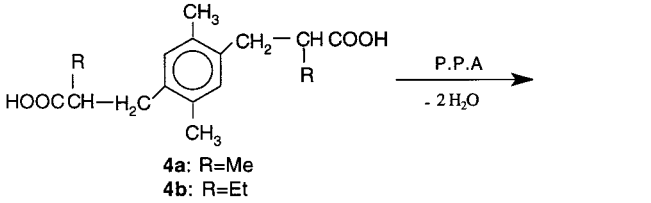
Bromomethylation of 1,4-dimethylbenzene gave an unexpected, almost quantitative yield of the dibromo compound, compared to the low yield of the chloromethylation usually performed[13] (eq 1).



1a: X=Br (90%)
1b: X=Cl (7-23%)[13a]

Alkylation of malonic esters with **1a** gave the corresponding diacids **4** (Scheme 1) in almost quantitative yield.

Upon treatment with polyphosphoric acid, the diacids **4**, underwent regioselective symmetrical cyclization to give the corresponding symmetrical diketones **5** (eq 2).



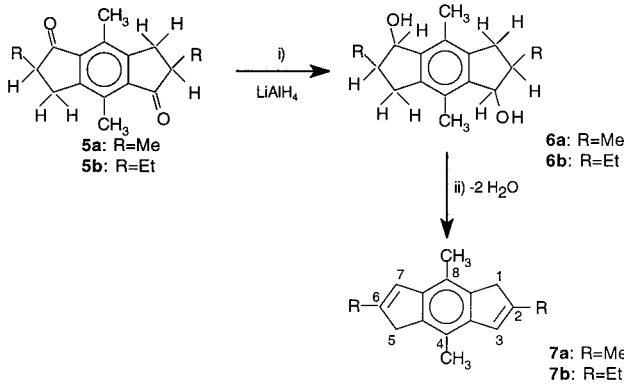
4a: R=Me
4b: R=Et

5a: R=Me
5b: R=Et

The high specificity of these reactions is due to the presence of the methyl groups on the starting material **1**, which prevent any other cyclization, contrary to previous results.[11] The 3,7-diols **6** are then easily formed by hydrogenation (Scheme 2, i). Subsequent acidic intramolecular dehydration of the alcohol functions led to 2,4,6,8-substituted 1,5-dihydro-*s*-indacenes **7** (Scheme 2, ii).

The overall yield of this five-step synthesis from 1,4-dimethylbenzene is above 40%, which is surprisingly high compared to the other published 1,5-dihydro-*s*-indacene syntheses.[9−12] The originality of our method lies in the choice of the starting material, which induces at the end a compulsory regiospecific cyclization. Furthermore, the diketones, according to ref 12, readily react with Grignard reagents to yield hexasubstituted 1,5-dihydro-*s*-indacenes **8** (eq 3).

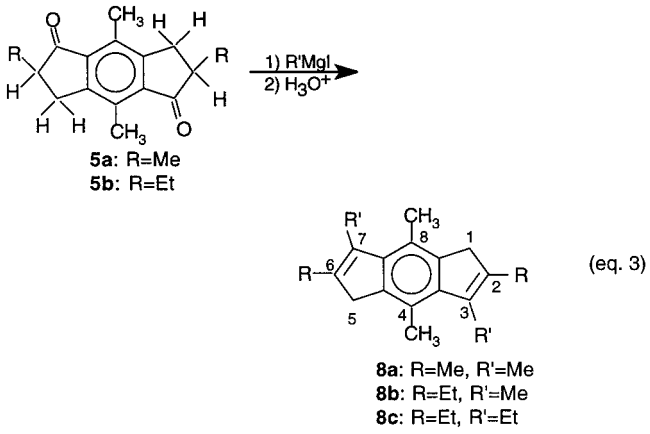
Scheme 2



5a: R=Me
5b: R=Et

6a: R=Me
6b: R=Et

7a: R=Me
7b: R=Et



5a: R=Me
5b: R=Et

8a: R=Me, R'=Me
8b: R=Et, R'=Me
8c: R=Et, R'=Et

Polyalkylated 1,5-dihydro-*s*-indacenes are soluble in most organic solvents. However, substitution by ethyl groups increased the solubility greatly, making these new ligands suitable as starting materials for organometallic polymers. To use these new, highly π-delocalized ligands as spacers in organometallic polymers, it is very important to find the best conditions to make the monoanions and then the corresponding dianions.

The preparation of the lithium derivatives was achieved by deprotonation with *n*-butyllithium in THF

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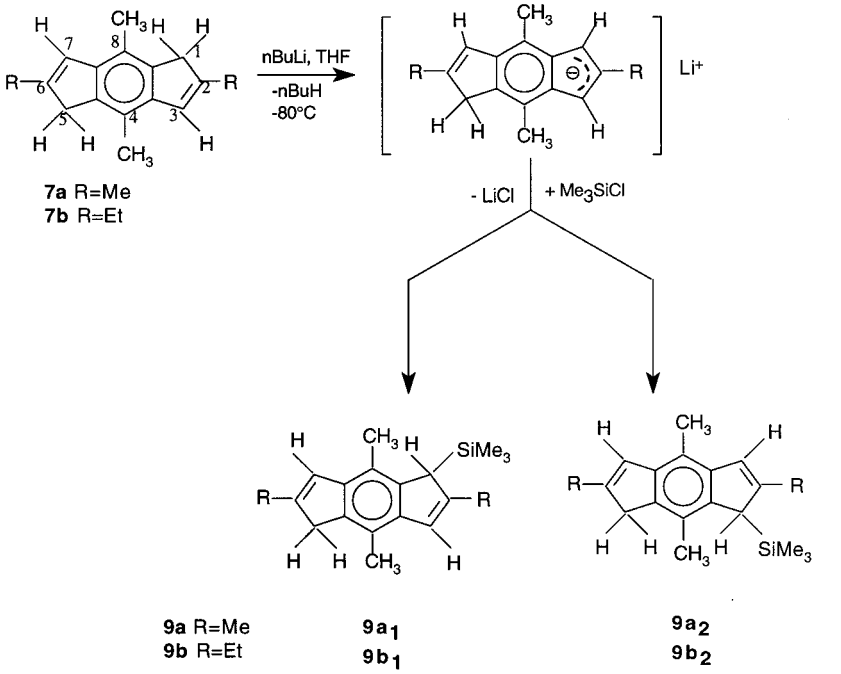
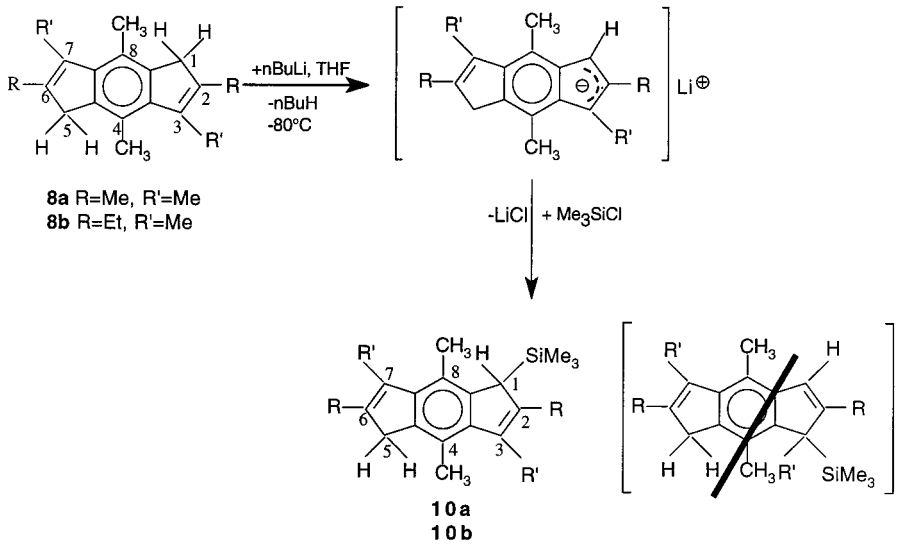
Scheme 3



Scheme 4



solution (see Experimental Section). In the case of the monolithium salt of **7**, silylation by trimethylchlorosilane gave the two expected isomers, the formation of which was easily observed in the ^{1}H NMR spectrum by the Me_3Si signals (Scheme 3). The two isomers [monosilylated in position 1 (**9a$_1$**, **b$_1$**) or 3 (**9a$_2$**, **b$_2$**)] were obtained in the same proportions, which can be explained by the delocalized structure of their anions. The well-known fluxional behavior of the cyclopentadienyl rings[14] could also explain the formation of these isomers. However, in this case, the presence of bulky substituents on the five-membered cycles disfavors the process.[14]

When the double bonds on the five-membered rings are more sterically hindered (**8a**,**b**), only one form is obtained (**10a**,**b**) (Scheme 4), as evident in ^{1}H NMR spectra by the absence of any ethylenic proton. Obviously Me_3SiCl reacts only on the less sterically hindered carbon of the transient carbanion (Scheme 4). Therefore, substitution by alkyl radicals on the sp^2 carbons of the five-membered rings in the starting 1,5-dihydro-*s*-indacene leads to selective silylation in position 1, without transposition of the double bond. Hexaalkyl-1,5-dihydro-*s*-indacene-derived anions give regiospecific monosilylation.

Starting from **8**, the dianion was easily obtained using 2 equiv of n-BuLi, in THF at −60 °C (Scheme 5). However, the presence of two asymmetric carbons led to diastereoisomers of **11** as evident by GC, GC/MS, and two series of signals in ^{1}H NMR spectra in relative proportions of ∼70/30. Treatment by hexane allowed the crystallization of one of the stereoisomers of **11b**, while the other was obtained nearly pure (GC and ^{1}H NMR) as a sticky viscous liquid. Dimetalation of hexaalkyl-1,5-dihydro-*s*-indacenes led to regiospecific and stereoselective σ-disilylation.

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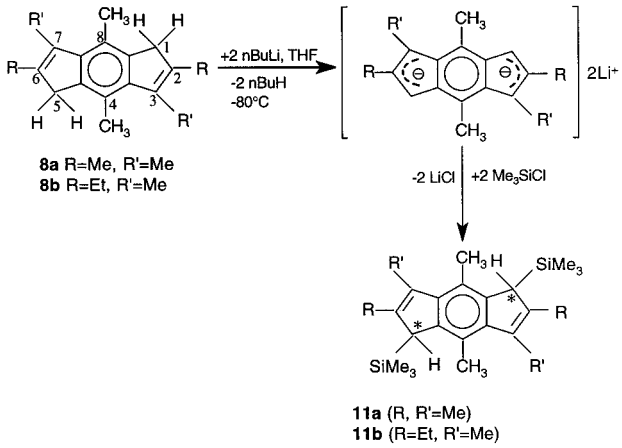
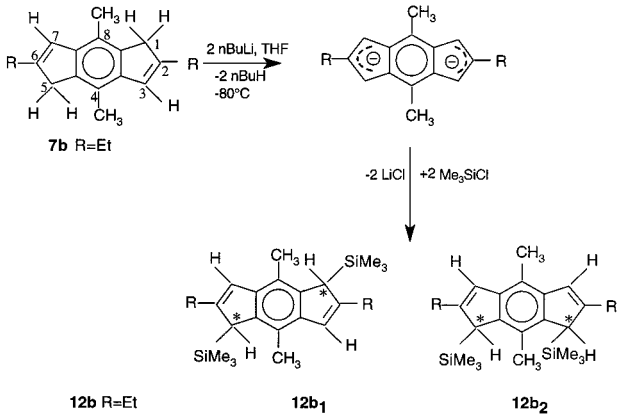
Scheme 5



When starting from the less stericaly hindered tetraalkyl-1,5-dihydro-*s*-indacenes **7** (**7b**), according to the results of the monosilylation (Scheme 3), one would expect two couples of diastereoisomers (**12b$_1$**, **12b$_2$**) from the delocalized structure of the dianion (Scheme 6).

Scheme 6



However, when we analyzed the reaction mixture kept a few weeks in pentane, we found two major isomers in relative proportions of 70/30%. Recrystallization of that mixture afforded crystals suitable for X-ray analysis, which revealed an almost planar tricyclic system (Figure 1, Table 1). The C(6) and C(8) atoms were 0.18 and 0.21 Å out of the best plane formed by C(1), C(2), C(3), C(4), and C(5). The slight deviation of the C(8) atom in the ethyl group can be explained by the steric hindrance due to the Me_3Si group. The bond distance C(4)−C(5) = 11.35 Å was very close to that of the standard double bond, indicating that it was a localized double bond. The two Me_3Si moieties were localized on opposite faces of the tricyclic system. The ^{1}H NMR data of these crystals confirmed that the major isomer isolated (70%) was the 1,5-bis(trimethylsilyl)tetraalkyl-*s*-indacene **12b$_1$**, with the trimethylsilyl groups in trans position. In the absence of an X-ray structure for the other isomer (30%), it is impossible to know if it is the corresponding cis-diastereoisomer or the other structure, **12b$_2$**. A variable-temperature experiment in ^{1}H NMR ($CDCl_3$, −55 °C to +55 °C) of the crude reaction mixture did not give any variation in the proportions between the different isomers. However, since **12b$_1$** (trans isomer) was clearly identified and characterized as the main product of the reaction, the disilylation of 1,5-dihydro-*s*-indacene is both regioselective and stereoselective.

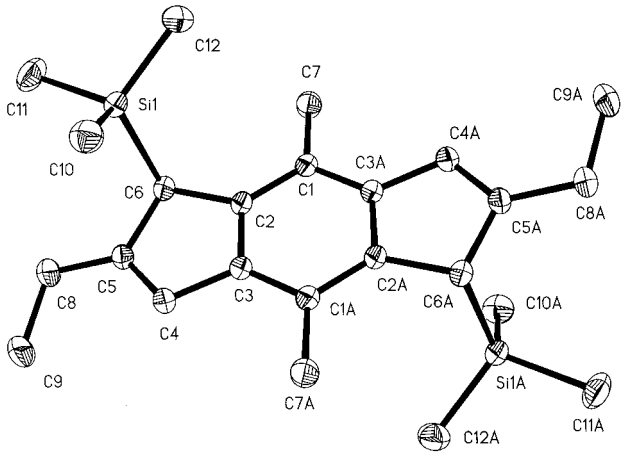


Figure 1. Molecular structure of **12b$_1$** in the crystal at the 50% probability level for the thermal ellipsoids.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 12b$_1$

C3−C4	1.460(2)	C4−C5−C6	109.62(11)
C4−C5	1.354(2)	C5−C6−C2	102.79(10)
C5−C6	1.515(2)	C5−C4−C3	110.31(11)
C6−C2	1.513(2)	C2−C6−Si1	109.71(8)
C2−C3	1.420(2)	C5−C6−Si1	106.50(8)
C3−C1A	1.404(2)	C4−C5−C8	126.89(12)
C1−C2	1.399(2)	C6−C5−C8	123.47(12)
C6−Si1	1.939(1)	C2−C3−C4	107.82(11)
C5−C8	1.506(2)		

In conclusion, the original synthesis of new 1,5-dihydro-*s*-indacene ligands in very high yield presented here open an easy access to new metallocene complexes we are studying. We observed that hexaalkyl-1,5-dihydro-*s*-indacenes led easily to mono- or dianions, the latter undergoing regiospecific and stereoselective disilylation. In the case of tetraalkylindacenes, disilylation was only regioselective and stereoselective.

Experimental Section

General Comments. All reactions were carried out under nitrogen or argon and in dry solvents. NMR spectra were recorded on Bruker AC80 at 80 MHz and AC 200 or 250 spectrometers (^{1}H) (^{13}C at 50.3 MHz, *J* mod sequence ^{1}H 200.1 MHz) (δ ppm/TMS); IR spectra on a Perkin-Elmer 1600 FT IR spectrometer or Bruker Vector 22; and mass spectra on a HP 5989 in the electron impact mode (70 eV) or on a Rybermag R10-10 spectrometer operating in the electron impact mode (EI) or by chemical desorption (DCI/CH_4). Elemental analyses were performed by the "Service Central de Microanalyse" of "Ecole Nationale Supérieure de Chimie de Toulouse", or using a Fisons EA 1108 microanalyzer in Santiago, for recrystallized compounds. Melting points were measured on a Leitz microscope.

Preparation of 1a. To a solution of 48% HBr (95 mL, 0.57 mol) in a round-bottomed flask (500 mL) were added paraformaldehyde (7.65 g, 0.25 mol) and *p*-xylene (15.20 mL, 0.12 mol). After 28 h of stirring at reflux, the mixture separated into two liquid phases, and a white precipitate, which was filtered, yielded 34 g of crude **1a** (97%). Recrystallization from CCl_4 gave 32 g of white needles of pure **1a**. Mp: 126−127 °C. Yield: 92%. ^{1}H NMR ($CDCl_3$, ppm): δ 2.35 (s, 6H, CH_3); 4.45 (s, 4H, CH_2); 7.16 (s, 2H, CH). ^{13}C NMR($CDCl_3$, ppm): δ 18.2 (CH_3); 31.7 (CH_2); 132.4 (CH); 135.2 (C_2, C_5); 136.4 (C_1, C_4).

MS (EI, *m*/*z*, %): $M^{\bullet+}$ 290 (9%); $M^{\bullet+}$ − Br 211 (55%); $M^{\bullet+}$ − 2Br 132 (100%). Anal. Calcd for **1a** $C_{10}H_{12}Br_2$: C, 41.38; H, 4.14. Found: C, 41.50; H, 4.08.

Preparation of 2. Synthesis of 2a. To 250 mL of ethanol in a 500 mL round-bottomed flask was added Na pieces (7.82 g, 0.34 mol) with stirring at room temperature. When all Na was consumed, diethyl methylmalonate (59 mL, 0.34 mol) was added slowly. After 30 min stirring at room temperature, **1a** (52 g, 0.17 mol) was added and the solution heated at reflux for 2.5 h. The excess of ethanol was distilled. To the residue were added at 0 °C water and diethyl ether. After stirring and decantation, the two phases were separated. The solvent of the organic phase was removed on a rotary evaporator, affording a white powder which was recrystallized from ethanol, yielding 51 g of pure **2a**. Mp: 50−51 °C. Yield: 63%. ^{1}H NMR ($CDCl_3$, ppm): δ 1.25 (t, 12H, C*H*$_3$-CH$_2$O, $^3J_{CH_2CH_3}$ = 6.06 Hz); 1.29 (s, 6H, R = CH_3); 2.20 [s, 6H, CH_3 (2,5)]; 3.35 (s, 4H, C*H*$_2$-Ph); 4.20 (q, 8H, O-C*H*$_2$-CH$_3$, $^3J_{CH_2CH_3}$ = 6.06 Hz); 6.80 (s, 2H, CH_{ar}). ^{13}C NMR ($CDCl_3$, ppm): δ 14.0 (*C*H$_3$-CH$_2$O); 19.5 [CH_3 (2,5)]; 19.6 (R = CH_3); 36.3 (*C*H$_2$-Ph); 55.1 (C_{IV}-R); 61.3 (O-*C*H$_2$-CH$_3$); 132.2 (CH_{ar}); 133.2, 134.4 ($C_{IV\ ar}$); 172.3 (C=O). IR (KBr): $\nu_{(CO)}$: 1735 cm^{-1}. MS (EI, *m*/*z*, %): $M^{\bullet+}$ 478 (17%); $M^{\bullet+}$ − (OCH_2CH_3) = 433 (12%); $M^{\bullet+}$ − 2(OCH_2CH_3) − CH_2-CH_3 359 (18%); $M^{\bullet+}$ − $CH_3C(COOEt)_2$ 305 (100%). Anal. Calcd for **2a** $C_{26}H_{38}O_4$: C, 70.3; H, 7.95. Found: C, 70.1; H, 8.05.

Synthesis of 2b. In the same way, **2b** was prepared with diethyl ethylmalonate (64 mL, 0.34 mol); Na (7.82 g, 0.34 mol); 300 mL ethanol; **1a** (52 g, 0.17 mol). **2b**: mp: 51−52 °C. Yield: 65%. ^{1}H NMR ($CDCl_3$, ppm): δ 0.88 (t, 6H, R = CH_2CH_3, $^3J_{CH_3-CH_2}$ = 6.65 Hz); 1.20 (t, 12H, C*H*$_3$-CH$_2$O,$^3J_{OEt}$ = 6.06 Hz); 1.18 (q, 4H, R = C*H*$_2$CH$_3$,$^3J_{CH_3-CH_2}$ = 6.65 Hz); 2.17 [s, 6H, CH_3 (2,5)]; 3.18 (s, 4H, C*H*$_2$-Ph); 4.15 (m, 8H, O-C*H*$_2$-CH$_3$); 6.79 (s, 2H, CH_{ar}). ^{13}C NMR ($CDCl_3$, ppm): δ 9.0 (R = CH_2CH_3); 14.0 (*C*H$_3$-CH$_2$O); 19.5 ([CH_3 (2,5)]; 25.6 (R = *C*H$_2$CH$_3$); 33.8 (*C*H$_2$-Ph); 59.2 (C_{IV}-R); 61.0 (O-*C*H$_2$-CH$_3$); 132.2 (CH_{ar}); 133.2, 134.2 ($C_{IV\ ar}$); 171.6 (C=O). IR (KBr): $\nu_{(CO)}$ 1731 cm^{-1}. MS (EI, *m*/*z*, %): $M^{\bullet+}$ 506 (21%); $M^{\bullet+}$ − (OCH_2CH_3) 461 (9%); $M^{\bullet+}$ − EtC($COOEt)_2$ 319 (100%). Anal. Calcd for **2b** $C_{28}H_{42}O_4$: C, 66.42; H, 8.35. Found: C, 66.61; H, 8.66.

Preparation of 3. Synthesis of 3a. To a solution of KOH (50 g, 0.90 mol) in 50 mL of H_2O, placed in a round-bottomed flask with a nitrogen inlet, was added **2a** (44 g, 0.09 mol). The mixture was warmed until the ester was completely dissolved. This new solution was poured into a mixture of water and ice. Then HCl (37%) was added until a pH of 3−4 was reached. The compound, insoluble in water, was filtered, washed with water, and dried, giving 29 g of **3a**. Mp: 176−177 °C. Yield: 87%. ^{1}H NMR (DMSO, ppm): δ 1.20 (s, 6H, R = CH_3); 2.23 [s, 6H, CH_3 (2,5)]; 3.15 (s, 4H, C*H*$_2$-Ph); 6.95 (s, 2H, CH_{ar}); 12.94 (s, 4H, COOH). ^{13}C NMR (DMSO, ppm): δ 18.9 (R = CH_3); 19.2 [CH_3 (2,5)]; 35.7 (*C*H$_2$-Ph); 53.8 (C_{IV}-R); 131.8 (CH_{ar}); 133.2, 133.7 ($C_{IV\ ar}$); 173.4 (*C*OOH). IR (KBr): $\nu_{(CO)}$ 1711 cm^{-1}; $\nu_{(OH)}$ 3410 cm^{-1} (large). MS (EI, *m*/*z*, %): thermal decomposition of **3a** into **4a**. Anal. Calcd for **3a** $C_{18}H_{22}O_8$: C, 59.02; H, 6.01. Found: C, 58.71; H, 6.05.

Synthesis of 3b. 3b was prepared under the same conditions using KOH (65 g, 1.16 mol) in 50 mL of H_2O; **2b** (48 g, 0.09 mol). Mp: 197−198 °C. Yield: 88%.^{1}H NMR (DMSO, ppm): δ 0.92 (t, 6H, R = CH_2CH_3,$^3J_{CH_3-CH_2}$ = 6.66 Hz);1.74 (q, 4H, R = C*H*$_2$CH$_3$,$^3J_{CH_3-CH_2}$ = 6.66 Hz); 2.23 [s, 6H, CH_3 (2,5)]; 3.11 (s, 4H, C*H*$_2$-Ph); 6.93 (s, 2H, CH_{ar}); 12.89 (s, 4H, COOH). ^{13}C NMR (DMSO, ppm): δ 8.8 (R = CH_2CH_3); 19.2 [CH_3 (2,5)]; 24.3 (R = *C*H$_2$CH$_3$); 32.8 (*C*H$_2$-Ph); 57.9 (C_{IV}-R); 131.6 (CH_{ar}); 133.0, 133.6 ($C_{IV\ ar}$); 172.9 (COOH). IR(KBr): $\nu_{(CO)}$ 1712 cm^{-1}; $\nu_{(OH)}$ 3314 cm^{-1} (large). MS (EI, *m*/*z*, %): thermal decomposition of **3b** into **4b**. Anal. Calcd for **3b** $C_{20}H_{26}O_8$: C, 60.91; H, 6.60. Found: C, 60.57; H, 6.43.

Preparation of 4. Synthesis of 4a. 3a (10 g, 27.32 mmol) was placed in a round-bottomed flask (500 mL) fitted with a nitrogen inlet and was melted and heated until CO_2 evolution ended. The cooled residue was 7.4 g of a white powder identified as **4a**. Mp: 180−181 °C. Yield: 98%. ^{1}H NMR (DMSO, ppm): δ 1.12 (d, 6H, R = CH_3,$^3J_{CH_3-CH}$ = 6.50 Hz); 2.27 [s, 6H, CH_3 (2,5)]; 2.60−2.70 (m, 4H, C*H*$_2$-Ph); 2.89−2.98 (m, 2H, R-C-H); 7.30 (s, 2H, CH_{ar}); 12.20 (s, 2H, COOH). ^{13}C NMR (DMSO, ppm): δ 16.7 (R = CH_3); 18.5 [CH_3 (2,5)]; 35.8 (*C*H$_2$-Ph); 39.3 (R-*C*-H); 131.1 (CH_{ar}); 132.7, 135.3 ($C_{IV\ ar}$); 176.9 (COOH). IR (KBr): $\nu_{(CO)}$ 1696 cm^{-1}; $\nu_{(OH)}$ 2977 cm^{-1} (large). MS (EI, *m*/*z*, %): $M^{\bullet+}$ 278 (20%); $M^{\bullet+}$ − H_2O 260 (11%); $M^{\bullet+}$ − CH(CH_3)COOH 205 (100%). Anal. Calcd for **4a** $C_{16}H_{22}O_4$: C, 69.09; H, 7.91. Found: C, 68.54; H, 8.03.

Synthesis of 4b. 4b (7.5 g) was obtained using the same procedure for **3b** (10 g, 25.38 mmol). Mp: 194−195 °C. Yield: 96%. ^{1}H NMR (DMSO, ppm): δ 0.95 (t, 6H, R = CH_2CH_3); 1.60 (m, 4H, R = C*H*$_2$CH$_3$); 2.26 [s, 6H, CH_3 (2,5)]; 2.45−2.88 (m, 6H, C*H*$_2$-Ph and R-C*H*); 6.94 (s, 2H, CH_{ar}); 12.19 (s, 2H, COOH), $^3J_{CH_3-CH_2}$ = 7.17 Hz. ^{13}C NMR (DMSO, ppm): δ 11.6 (R = CH_2CH_3); 18.6 [CH_3 (2,5)]; 25.0 (R = *C*H$_2$CH$_3$); 34.5 (*C*H$_2$-Ph); 47.3 (R-*C*H); 131.1 (CH_{ar}); 133.7, 135.4 ($C_{IV\ ar}$); 176.3 (COOH). IR (KBr): $\nu_{(CO)}$ 1702 cm^{-1}; $\nu_{(OH)}$ 3002 cm^{-1} (large). MS (EI, *m*/*z*, %): $M^{\bullet+}$ 306 (17%); $M^{\bullet+}$ − H_2O 288 (5%); $M^{\bullet+}$ − HCOOH 260 (7%). Anal. Calcd for **4b** $C_{18}H_{26}O_4$: C, 70.59; H, 8.49. Found: C, 70.78; H, 8.78.

Preparation of 5. Synthesis of 5a. Polyphosphoric acid (253 g) in large excess and **4a** (10 g, 35.97 mmol) were placed in a round-bottomed flask (1 L) fitted with a mechanical stirrer and a nitrogen inlet. The mixture was stirred vigorously under nitrogen at 80 °C for 2 h. The mixture was poured into a solution of 500 g of ice in 2 L of H_2O. The resulting yellow precipitate was filtered, washed with water, and dried, affording 7.90 g of **5a**. Mp: 163−164 °C. Yield: 91%. ^{1}H NMR ($CDCl_3$, ppm): δ 1.32 (d, 6H, R = CH_3,$^3J_{CH_3-CH}$ = 7.00 Hz); 2.60 (s, 6H, CH_3 on the aromatic ring); 2.56 (dd, 2H, CH_2 (3,7), $^2J_{gem}$ = 16.5 Hz,$^3J_{cis}$ = 4.5 Hz); 3.29 (dd, 2H, CH_2 (3,7), $^2J_{gem}$ = 16.5 Hz, $^3J_{trans}$ = 8.0 Hz); 2.73 (ddq, 2H, R−C*H* (2,6), $^3J_{CH_3-CH}$ = 7.00 Hz, $^3J_{trans}$ = 8.0 Hz, $^3J_{cis}$ = 4.5 Hz). Irradiation of CH_3 in 2,6 led to 2.73 (dd, 2H, R-C*H* (2,6), $^3J_{trans}$ = 8.0 Hz, $^3J_{cis}$ = 4.5 Hz) without modification of the signals at 2.56 and 3.29 ppm. ^{13}C NMR ($CDCl_3$, ppm): δ 12.9 (CH_3 on the aromatic ring); 16.5 (R = CH_3); 32.7 (*C*H$_2$-Ph); 43.0 (R-*C*H); 132.9, 136.9, 152.3 ($C_{IV\ ar}$); 211.2 (CO). IR (KBr): $\nu_{(CO)}$ 1697 cm^{-1}. MS (EI, *m*/*z*, %): $(M + 2H)^+$ 242 (100%); $((M + 2H) - CH_3)^+$ 227 (98%). Calcd for **5a** $C_{16}H_{16}O_2$: C, 79.34; H, 7.44. Found: C, 79.02; H, 7.44.

Synthesis of 5b. In the same way, **5b** (8.2 g) was prepared from **4b** (10 g, 32.68 mmol) and polyphosphoric acid (280 g, large excess). Mp: 150−151 °C. Yield: 93%. ^{1}H NMR ($CDCl_3$, ppm): δ 1.03 (t, 6H, R = CH_2CH_3, $^3J_{CH_3-CH_2}$ = 7 Hz); 1.51 (m, 50% of 4H R = C*H*$_2$CH$_3$), 1.96 (m, 50% of 4H, R = C*H*$_2$CH$_3$); 2.61 (s, 6H, CH_3-ar); 3.19 (d.d, 2H, 50% of 4H in 3,7; J^2_{gem} = 17.5 Hz, J^3_{trans} = 8.5 Hz); 2.60 (m, 50% of 4H in 3,7); 2.66 [m, 2H, (2,6)]. Irradiation of C*H*$_3$CH$_2$− led to a simplification of the CH_2 signal: 1.51 (d.d, J^2_{gem} = 14 Hz, J^3_{trans} = 13 Hz); 1.96 (d.d, J^2_{gem} = 14 Hz, J^3_{cis} = 4 Hz). ^{13}C NMR ($CDCl_3$, ppm): δ 11.6 (R = CH_2CH_3); 13.0 (CH_3 on the aromatic ring); 24.7 (R = *C*H$_2$CH$_3$); 30.1 (*C*H$_2$-Ph); 43.8 (R-*C*H); 132.8, 137.4, 152.6 (C_{IVar}); 210.6 (CO). IR (KBr): $\nu_{(CO)}$ 1697 cm^{-1}. MS (EI, *m*/*z*, %): $M^{\bullet+}$ 270 (88%); $M^{\bullet+}$ − C_2H_4 242 (98%); $M^{\bullet+}$ − 2 C_2H_4 214 (100%). Anal. Calcd for **5b** $C_{18}H_{20}O_2$: C, 80.00; H, 8.15. Found: C, 79.80; H, 8.01.

Preparation of 7 and Characterization of 6. Synthesis of 7a. To $LiAlH_4$ (0.72 g, 18.90 mmol) in 25 mL of diethyl ether placed in a round-bottomed flask (250 mL) was added slowly with stirring at room temperature **5a** (2 g, 8.30 mmol) in 25 mL of diethyl ether. After 3 h of stirring at reflux, the mixture was cooled to 0 °C and a solution of HCl (18%) was added. The white precipitate formed was filtered, dried under vacuo, and characterized by IR spectroscopy as the alcohol **6a** (1.96 g) ($\nu_{(OH)}$: 3540 cm^{-1}). This was added to 0.20 g of *p*-toluenesulfonic acid dissolved in 120 mL of C_6H_6 and placed in a round-bottomed flask (250 mL) fitted with a nitrogen inlet. After 2 h of stirring at 62 °C, the solution was cooled to 0 °C

and filtered to remove unreacted **6a**. The liquid phase was washed with water. The organic phase was dried over $MgSO_4$ for 18 h. After evaporation of the solvent in vacuo, crude **7a**, obtained as a white powder, was recrystallized from hexane and sublimed: 1.28 g. Mp: 181−182 °C.Yield: 76%. ^{1}H NMR ($CDCl_3$, ppm): δ 2.17 (d, 6H, R = CH_3); 2.34 [s, 6H, CH_3 (4,8)]; 3.21 [s, 4H, CH_2 (1,5)]; 6.60 [q, 2H, CH (3,7)], $^4J_{CH_3-CH} = 1.45$ Hz; (DMSO, ppm) δ 2.13 (s, 6H, C*H*$_3$C═C); 2.25 (s, 6H, C*H*$_3$-ar); 3.16 (s, 4H, CH_2); 6.61 (s, 2H, CH═). ^{13}C NMR($CDCl_3$, ppm): δ 15.1(CH_3 on C_4 and C_8); 17.1 (R = CH_3); 41.8 (C_1, C_5); 121.7 (C_2, C_6); 125.7 (C_3, C_7); 140.7, 143.7 ($C_{IV\ ar}$). IR (KBr): $\nu_{(C=C)}$ 1604 cm^{-1}. MS (EI, *m*/*z*, %): $M^{\bullet+}$ 210 (100%); $M^{\bullet+} - CH_3$ 195 (64%); $M^{\bullet+} - 2CH_3$ 180 (20%); %); $M^{\bullet+} - 3CH_3$ 165 (20%). Anal. Calcd for **7a** $C_{16}H_{18}$: C, 91.43; H, 8.57. Found: C, 91.03; H, 8.97.

6a formed here in the presence of HCl is often not pure because of partial dehydration. However, ^{1}H NMR shows two major isomers in relative proportions of 70/30%. ^{1}H NMR (DMSO, ppm): δ 1.03 (d, C*H*$_3$-CH, $^3J_{HH} = 7$ Hz, 70%); 1.10 (d, C*H*$_3$-CH, $^3J_{HH} = 7$ Hz, 30%); 4.57 (d, C*H*OH, $^3J_{CH-CHCH_3} = 3.6$ Hz, 70%); 4.77 (d, C*H*OH,$^3J_{CH-CHCH_3} = 5.5$ Hz, 30%); 3.03 (m, part of CH_2 (3,7), 30%); 4.14 (s, large, OH); 2.20 (s, 6H, CH_3 CH_3 on the aromatic ring); 2.00−2.80 (m, CH_2 (3,7) and CH_3-C*H* (2,6)).

Synthesis of 7b. 7b was obtained by the same procedure from **5b** (2 g, 7.40 mmol) in 25 mL of diethyl ether, $LiAlH_4$ (0.72 g, 18.90 mmol) in 25 mL of diethyl ether, and 0.20 g of *p*-toluenesulfonic acid in 120 mL of C_6H_6. **7b**: 1.43 g. Mp: 173−174 °C. Yield: 81%. ^{1}H NMR ($CDCl_3$, ppm): δ 1.24 (t, 6H, R = CH_2CH_3, $^3J_{CH_3-CH_2} = 6.7$ Hz); 2.36 [s, 6H, CH_3 (4,8)]; 2.64 (q d, 4H, R = CH_2CH_3, $^3J_{CH_3-CH_2} = 6.7$ Hz, $^4J_{CH_2-CH} = 3.0$ Hz); 3.24 (s, 4H, CH_2-Ph); 6.62 (t, 2H, CH (3, 7), $^4J_{CH_2-CH} = 3.0$ Hz). ^{13}C NMR ($CDCl_3$, ppm): δ 13.6 (R = CH_2CH_3); 14.0 (CH_3 on C_4 and C_8); 24.7 (R = CH_2CH_3); 40.0 (C_1, C_5); 123.7 (C_3, C_7); 121.9 (C_2, C_6); 140.5,140.6, 150.2 ($C_{IV\ ar}$). IR (KBr): $\nu_{(C=C)}$ 1597 cm^{-1}. MS (EI, *m*/*z*, %): $M^{\bullet+}$ 238 (100%); $M^{\bullet+} - CH_3$ 223 (69%); $M^{\bullet+} - 2CH_3$ 208 (20%). Anal. Calcd for **7b** $C_{18}H_{22}$: C, 90.75; H, 9.25. Found: C, 90.06; H, 9.95.

Preparation of 8. Synthesis of 8a. To **5a** (4 g, 16.66 mmol) in 50 mL of diethyl ether in a round-bottomed flask (500 mL) fitted with a nitrogen inlet and a reflux condenser was added 3 M CH_3MgI (11.20 mL; 33.33 mmol) and 50 mL of diethyl ether. After 5 h of stirring at reflux, the mixture was cooled to room temperature. Then, a solution of 37% HCl (50 mL) in 200 mL of water was added. The white precipitate formed was filtered and identified as **8a**. The liquid phases were treated again with HCl (50 mL, 37% in 200 mL of water), and the organic phase was separated. After extraction with diethyl ether, the ether layer was dried over $MgSO_4$ for one night prior to solvent removal on a rotary evaporator. An additional 1.3 g of **8a** was obtained and the total amount (3.3 g) recrystallized from toluene. **8a**: Mp: 140−141 °C. Yield: 83%. ^{1}H NMR ($CDCl_3$, ppm): δ 2.06 (s, 6H, R = CH_3); 2.24 [s, 6H, C*H*$_3$-C (3,7)]; 2.52 [s, 6H, CH_3 (4,8)]; 3.15 [s, 4H, CH_2-Ph (1,5)]. ^{13}C NMR ($CDCl_3$, ppm): δ 14.0 (R = CH_3, *C*H$_3$-C (3,7)]; 15.3 (CH_3 on C_4 and C_8); 41.7 (C_1, C_5); 122.5 (C_2, C_6); 134.1 (C_3, C_7); 136.7, 140.5, 141.4 ($C_{IV\ ar}$). IR (KBr): $\nu_{(C=C)}$ 1604 cm^{-1}. MS (EI, *m*/*z*, %): $M^{\bullet+}$ 238 (100%); $M^{\bullet+} - CH_3$ 223 (99%); $M^{\bullet+} - 2CH_3$ 208 (28%); $M^{\bullet+} - 3CH_3$ 193 (25%); $M^{\bullet+} - 4CH_3$ 178 (18%). Anal. Calcd for **8a** $C_{18}H_{22}$: C, 90.76; H, 9.24. Found: C, 91.02; H, 9.82.

Synthesis of 8b. 8b was obtained in the same way from **5b** (4 g, 14.81 mmol) and 3 M CH_3MgI (10 mL; 29.63 mmol). Mp: 163−164 °C. **8b** (3.5 g): Yield: 89%. ^{1}H NMR ($CDCl_3$, ppm): δ 1.14 (t, 6H, R = CH_2CH_3, $^3J_{CH_3-CH_2} = 6.06$ Hz); 2.25 [s, 6H, C*H*$_3$−C═ (3,7)]; 2.47 (q, 4H, R = CH_2CH_3, $^3J_{CH_3-CH_2} = 6.06$ Hz); 2.53 [s, 6H, CH_3 (4,8)]; 3.15 [s, 4H, CH_2-Ph (1,5)]. ^{13}C NMR ($CDCl_3$, ppm): δ 14.2, 14.3 (R = CH_2CH_3 and *C*H$_3$−C═); 15.4 (CH_3 on C_4 and C_8); 21.6 (R = CH_2CH_3); 39.0 (C_1, C_5); 122.8 (C_2, C_6); 133.3 (C_3, C_7); 140.0, 141.5, 143.0 ($C_{IV\ ar}$). IR (KBr): $\nu_{(C=C)}$ 1618 cm^{-1}. MS (EI, *m*/*z*, %): $M^{\bullet+}$ 266 (100%); $M^{\bullet+} - CH_3$ 251 (74%); $M^{\bullet+} - 2CH_3$ 236 (38%); $M^{\bullet+} - 3CH_3$ 221 (17%); $M^{\bullet+} - 4CH_3$ 206 (14%). Anal. Calcd for **8b** $C_{20}H_{26}$: C, 90.22; H, 9.77. Found: C, 89.89; H, 10.09.

Synthesis of 8c. Following the same experimental procedure with **5b** (4 g, 14.81 mmol) and EtMgBr in ether (0.32 mmol), **8c** (2.6 g) was obtained. Mp: 146−148 °C. Yield: 60%. ^{1}H NMR ($CDCl_3$, ppm): δ 1.21 (t, 12H, CH_3); 2.42 [q, 4H, CH_2 (2,6)]; 2.52 [s, 6H, CH_3 (4,8)]; 2.70 [q, 4H, CH_2 (3,7)]; 3.20[s, 4H, CH_2-Ph (1,5)], $J^3_{Et} = 8.1$ Hz. ^{13}CNMR ($CDCl_3$, ppm): 14.8, 15.0 (CH_3CH_2); 15.3 (*C*H$_3$ on C_4 and C_8); 20.1, 21.5 (CH_2CH_3); 38.9 (C_1, C_5); 122.6(C_2, C_6); 139.6(C_3, C_7); 139.8, 142.1, 143.1 ($C_{IV\ ar}$). IR (KBr): $\nu_{(C=C)}$ 1606 cm^{-1}. MS (EI, *m*/*z*, %): $M^{\bullet+}$ 294 (41%); $M^{\bullet+} - Et$ 265 (22%); $M^{\bullet+} - 2Et$ 236 (12%); $M^{\bullet+} - 3Et$ 207 (14%); $M^{\bullet+} - 4Et$ 178 (10%). Anal. Calcd for **8c** C, 89.79; H, 10.20. Found: C, 89.70; H, 10.30.

Preparation of 9. Synthesis of 9a. To **7a** (0.20 g, 0.95 mmol) in 5 mL of THF under nitrogen was added at −60 °C and with stirring a solution of 1.6 M BuLi in hexane (0.59 mL, 0.95 mmol). After 30 min of reaction at room temperature, Me_3SiCl (0.12 mL, 0.95 mmol) was added dropwise with stirring. After 2 h at room temperature, THF was evaporated under vacuum and replaced by 10 mL of pentane to precipitate LiCl, which was filtered. Evaporation of pentane in vacuo gave 0.19 g (yield: 73%) of a white solid identified as **9a**, under its two forms, **9a$_1$** (∼50%) and **9a$_2$** (∼50%). ^{1}H NMR ($CDCl_3$, ppm): δ −0.03, −0.02 (s, 9H, $(CH_3)_3Si$); 2.20, 2.18 (d, 6H, C*H*$_3$ (2,6), $J^4_{CH-CH_3} = 1$ Hz); 2.28, 2.36 and 2.44 (s, 6H, C*H*$_3$(4,8)); 3.22 (s large, 2H, C*H*$_2$(5)); 3.48 (s large, 1H, C*H*-Si (1)); 6.60 (s, 2H, ethylenic C*H*(3,7)). MS (EI, *m*/*z*, %): $M^{\bullet+}$ 282 (39%); $M^{\bullet+} - CH_3$ 267 (4%); $M^{\bullet+} - 2CH_3$ 252 (1%); $M^{\bullet+} - Si(CH_3)_3 - H$ 208 (40%). Anal. Calcd for **9a** $C_{19}H_{26}Si$: C, 80.78; H, 9.28. Found: C, 80.49; H, 8.98.

The other silylated products **9b**, **10a**, **10b**, **11a**, **11b**, and **12b** were prepared by the same method.

Preparation of 9b. From **7b** (0.20 g, 0.84 mmol), BuLi (0.52 mL, 0.84 mmol), and Me_3SiCl (0.10 mL, 0.84 mmol), **9b** (0.22 g, yield 85%) was obtained as a white solid as a mixture of its two isomeric forms, **9b$_1$** (≈50%) and **9b$_2$** (≈50%). **9b** ^{1}H NMR ($CDCl_3$, ppm): δ −0.04,−0.03 (s, 9H, $(CH_3)_3Si$); 1.25, 1.24 (t, 6H, CH_3CH_2, $^3J_{Et} = 7.4$ Hz); 2.48, 2.39, 2.38, 2.30 (s, 6H, C*H*$_3$ on 4 and 8); 2.54 (m, 4H, CH_3CH_2); 3.25 (s large, 2H, C*H*$_2$(5)); 3.59 (s large, 1H, C*H*-Si); 6.64 (m, 2H, ethylenic C*H* (3,7)). MS (EI, *m*/*z*, %): $M^{\bullet+}$ 310 (19%); $M^{\bullet+} - CH_3$ 295 (7%); $M^{\bullet+} - Et$ 281 (11%). Anal. Calcd for **9b** $C_{21}H_{30}Si$: C, 81.21; H, 9.73. Found: C, 80.97; H, 9.58.

Preparation of 10a. From **8a** (0.20 g, 0.84 mmol), BuLi (0.52 mL, 0.84 mmol), and Me_3SiCl (0.10 mL, 0.84 mmol) was obtained **10a** (0.20 g). Mp: 152−155 °C. Yield: 77%. ^{1}H NMR ($CDCl_3$, ppm): δ −0.08 (s, 9H, $(CH_3)_3Si$); 2.07, 2.05 (s, 6H, C*H*$_3$ (2,6)); 2.25 (s large, 6H, C*H*$_3$ (3,7)); 2.53, 2.51 (s, 6H, C*H*$_3$ (4,8)); 3.14 (s, 2H, C*H*$_2$(5); 3.41 (s, 1H, C*H*-Si(1)). ^{13}C NMR ($CDCl_3$, ppm): −0.9 (($CH_3)_3Si$); 14.1, 14.41, 14.5, 15.3, 17.9 (*C*H$_3$); 41.7 (C_5); 48.1 (C_1); 122.5 (C_2, C_6); 134.1 (C_3, C_7); 136.5, 136.8, 139.4, 139.6, 140.0, 141.4 ($C_{IV\ ar}$). MS (EI, *m*/*z*, %): $M^{\bullet+}$ 310 (24%); $M^{\bullet+} - CH_3$ 295 (1%); $M^{\bullet+} - Si(CH_3)_3-H$ 236 (23%). Anal. Calcd for **10a** $C_{21}H_{30}Si$: C, 81.21; H, 9.73. Found: C, 80.87; H, 9.63.

Preparation of 10b. From **8b** (0.20 g, 0.75 mmol), BuLi (0.47 mL, 0.75 mmol), and Me_3SiCl (0.09 mL, 0.75 mmol) was obtained 0.23 g of a sticky viscous liquid, practically pure in GC, which could not be recrystallized, and was identified as **10b**. Yield: 92%. ^{1}H NMR ($CDCl_3$, ppm): δ −0.08 (s, 9H, $(CH_3)_3Si$); 1.04−1.17 (m, 6H, CH_3CH_2); 2.26, 2.27 (s, 6H, C*H*$_3$ (3,7)); 2.46 (q, 2H, CH_3CH_2(6)); 2.69 (q, 2H, CH_3CH_2(2)); 2.55, 2.53 (s, 6H, C*H*$_3$(4,8)); 3.17 (s, 2H, C*H*$_2$(5)); 3.57 (s, 1H, C*H*-Si(1)); $J^3_{Et} = 6.5$ Hz. ^{13}C NMR ($CDCl_3$, ppm): −0.7 (($CH_3)_3Si$); 14.1, 14.3, 14.4, 15.9, 18.1 (*C*H$_3$); 21.7, 21.8 (CH_2CH_3); 38.9 (C_5); 45.0 (C_1); 121.5, 122.7 (C_2, C_6); 130.8, 133.8 (C_3, C_7); 139.8, 140.1, 140.2, 142.6, 144.5, 146.2 ($C_{IV\ ar}$). MS (EI, *m*/*z*, %): $M^{\bullet+}$ 338 (73%); $M^{\bullet+} - CH_3$ 323 (7%); $M^{\bullet+} - 2CH_3$ 308 (1%); $M^{\bullet+} - Si(CH_3)_3 - H$ 264 (61%). Anal. Calcd for $C_{23}H_{34}Si$: C, 81.58; H, 10.12. Found: C, 81.36; H, 10.18.

Preparation of 11a. From **8a** (0.20 g, 0.84 mmol), BuLi (1.10 mL, 1.78 mmol), and Me_3SiCl (0.21 mL, 1.78 mmol) was obtained 0.22 g of a viscous oil, a mixture of diastereoisomers (GC/MS) of **11a.** Yield: 69%. ^{1}H NMR ($CDCl_3$, ppm): δ −0.14 (s, 18H, (CH_3)$_3$Si, 68%); −0.07 (s, 18H, (CH_3)$_3$Si, 32%); 2.07 (s large, 6H, CH_3 (2,6)); 2.26 (s large, 6H, CH_3 (3,7)); 2.53 (s large, 6H, CH_3(4,8)); 3.44 (s, 2H, C*H*-Si (1,5), 68%); 3.41 (s, 2H, C*H*-Si (1,5), 32%). ^{13}CNMR ($CDCl_3$, ppm): −0.8, −1.25 ((*C*H$_3$)$_3$Si); 14.2, 15.4, 15.5, 18.0, 18.4 (*C*H$_3$); 47.8, 47.9 (C$_1$,C$_5$); 120.6 (C$_2$, C$_6$); 131.8 (C$_3$, C$_7$); 138.6, 139.1, 142.6 (C$_{IV\ ar}$). MS (EI, *m*/*z*, %): M$^{\bullet+}$ 382 (8%); M$^{\bullet+}$ − Si(CH$_3$)$_3$ 309 (3%); M$^{\bullet+}$ − Si(CH$_3$)$_3$ − CH$_3$ 294 (2%). Anal. Calcd for $C_{24}H_{38}Si_2$: C, 75.31; H, 10.01. Found: C, 75.07; H, 9.99.

Preparation of 11b. 8b (0.23 g, 0.86 mmol), BuLi (1.29 mL, 2.06 mmol), and Me_3SiCl (0.33 mL, 2.58 mmol) led to 0.28 g of a yellow sticky compound identified as a mixture of two diastereoisomers of **11b** (GC, GC/MS). Yield: 79%. Treatment by hexane allowed the precipitation of 0.08 g of crystals of one diastereoisomer of **11b**. Yield: 30%. Mp: 171 °C. ^{1}H NMR ($CDCl_3$, ppm): δ −0.05 (s, 18H, (CH_3)$_3$Si); 1.16 (t, 6H, $^3J_{CH_3-CH_2}$ = 7.5 Hz, CH_3CH$_2$); 2.28 (m, 2H, CH$_3$CH_2); 2.72 (m, 2H, CH$_3$CH_2); 2.29 (s, 6H, CH_3 (3,7)); 2.57 (s, 6H, CH_3 (4,8)); 3.58 (s, 2H, C*H*-Si (1,5)). ^{13}C NMR ($CDCl_3$, ppm): −0.53 (*C*H$_3$Si); 14.50 (*C*H$_3$ Et); 18.63 (*C*H$_3$Ph); 21.85 (*C*H$_2$Et); 44.57 (*C*HSi); 121.24 (C2, C6); 131.49 (C3, C7); 140.11, 142.64, 145.22 (C$_{IV}$ ar). MS (EI, *m*/*z*, %): M$^{\bullet+}$ 410 (66%); M$^{\bullet+}$ − CH$_3$ 395 (3%); M$^{\bullet+}$ − Si(CH$_3$)$_3$ 337 (47%); M$^{\bullet+}$ − Si(CH$_3$)$_3$ − CH$_3$ 322 (5%); M$^{\bullet+}$ − Si(CH$_3$)$_3$ − 2CH$_3$ 307 (7%). Anal. Calcd for $C_{26}H_{42}Si_2$: C, 76.02; H, 10.31. Found: C, 75.87; H, 10.02. Concentration of the filtrates led to a viscous sticky liquid (0.18 g) identified by GC analysis and GC/MS as the other diastereoisomer nearly pure (87%). ^{1}H NMR ($CDCl_3$, ppm): δ −0.12 (s, 18H, (CH_3)$_3$Si); 1.10 (t, 6H, $^3J_{CH_3-CH_2}$ = 7.5 Hz, CH_3CH$_2$); 2.30 (s, 6H, CH_3 (3,7)); 2.32 (m, 2H, CH$_3$CH_2); 2.72 (m, 2H, CH$_3$CH_2); 2.58 (s, 6H, CH_3 (4,8)); 3.61 (s, 2H, C*H*-Si (1,5)). ^{13}C NMR ($CDCl_3$, ppm): −1.01 (*C*H$_3$Si); 14.18 (*C*H$_3$ Et); 18.15 (*C*H$_3$Ph); 21.97 (*C*H$_2$Et); 44.75 (*C*HSi); 120.89 (C2, C6); 130.80 (C3, C7); 139.28, 142.85, 145.55 (C$_{IV}$ ar). MS (GC/MS, *m*/*z*, %): M$^{\bullet+}$ 410 (95%); M$^{\bullet+}$ − CH$_3$ 395 (7%); M$^{\bullet+}$ − Si(CH$_3$)$_3$ 337 (23%).

Preparation of 12b. 7b (0.20 g, 0.84 mmol), BuLi (1.04 mL, 1.68 mmol), and Me_3SiCl (0.20 mL, 1.68 mmol) led to 0.27 g of crude **12b**. Yield: 95%. A variable-temperature measurement of the ^{1}H NMR spectrum ($CDCl_3$, −55 °C to +55 °C) of crude **12b** did not give any variation of the proportions between the different isomers. ^{1}H NMR ($CDCl_3$, ppm): δ −0.08 (s, 18H, (CH_3)$_3$Si (1,5), **12b$_1$** 70%); −0.09 (s, 18H, (CH_3)$_3$Si (1,5), 30%); 1.25 (t, 6H, CH_3CH$_2$, $^3J_{Et}$ = 7.5 Hz); 2.37 (s, 6H, CH_3 (4,8)); 2.55 (m, 4H, CH$_3$CH_2); 3.54 (s, 2H, C*H*-Si, **12b$_1$** 70%); 3.57 (s, 2H, C*H*-Si, 30%); 6.60 (s, 2H, ethylenic C*H* (3,7), **12b$_1$** 70%); 6.63 (s, 2H, ethylenic C*H* (3,7), 30%). ^{13}CNMR ($CDCl_3$, ppm): −0.6 ((*C*H$_3$)$_3$Si, **12b$_1$** 70%); −0.3 ((*C*H$_3$)$_3$Si, 30%); 13.4, 17.6 (*C*H$_3$, 100%); 25.1(*C*H$_2$CH$_3$, **12b$_1$** 70%); 29.7(*C*H$_2$CH$_3$, 30%); 47.0 (C$_1$,C$_5$, **12b$_1$** 70%); 47.3 (C$_1$,C$_5$, 30%); 120.3 (C$_2$, C$_6$, 100%); 121.9 (C$_3$, C$_7$, **12b$_1$** 70%); 121.4 (C$_3$, C$_7$, 30%); 140.4, 141.4, 152.1 (C$_{IV\ ar}$, 100%). MS (EI, *m*/*z*, %): M$^{\bullet+}$ 382 (13%); M$^{\bullet+}$ − CH$_3$ 367 (1%); M$^{\bullet+}$ − 2Et 324 (1%); M$^{\bullet+}$ − Si(CH$_3$)$_3$ 309 (2%); M$^{\bullet+}$ − Si(CH$_3$)$_3$ − CH$_3$ 294 (3%). Recrystallization of **12b** from pentane gave **12b$_1$**. Mp: 134−135 °C. Yield: 85%. Anal. Calcd for **12b** $C_{24}H_{38}Si_2$: C, 75.31; H, 10.00. Found: C, 74.91; H, 9.60.

Crystal data for 12b$_1$: $C_{12}H_{19}Si$, M = 191.36, triclinic, $P\bar{1}$, a = 7.1030(3) Å, b = 8.9690(4) Å, c = 9.5849(5) Å, α = 80.147(1)°, β = 75.480(1)°, γ = 77.442(1)°, V = 572.57(5) Å^3, Z = 2, ρ_c 1.110 Mg m^{-3}, $F(000)$ = 210, λ = 0.71073 Å, T = 193(2) K, μ(Mo Kα) = 0.161 mm^{-1}, crystal size 0.2 × 0.4 × 0.5 mm, 3.01° ≤ θ ≤ 33.67°, 6438 reflections (4082 independent, R_{int} = 0.0156) were collected at low temperatures using an oil-coated shock-cooled crystal on a Bruker-AXS CCD 1000 diffractometer. The structure was solved by direct methods (SHELXS-97),[15] and 131 parameters were refined using the least-squares method on F^2.[16] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the molecules were geometrically idealized and refined using a riding model. Largest electron density residue: 0.412 e Å^{-3}, R_1 (for $F > 2\sigma(F)$) = 0.0469 and wR_2 = 0.1318 (all data) with $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR_2 = (\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2)^{0.5}$.

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Supporting Information Available: Tables giving crystal data and structure refinement details, positional and thermal parameters, and bond distances and angles for **12b$_1$**. This material is available free of charge via the Internet at http://pubs.acs.org.

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