



Preparation of Bifluorenes via the Synthesis and Thermal Decomposition of Fluorenyltitanium(IV) Trichlorides. Molecular and Crystal Structure of 9,9'-bis(trimethylsilyl)-bi-9,9'-fluorene

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Abstract: The reaction of 9-substituted trimethyltinfluorenes with TiCl_4 in hexanes at -40°C leads to unstable fluorenyltitanium(IV) trichlorides which thermal radical decomposition gives quantitatively TiCl_3 and corresponding bifluorenes: $(\text{C}_{13}\text{H}_9)_2$ (**3a**), $(9\text{-EtC}_{13}\text{H}_8)_2$ (**3b**) and $(9\text{-SiMe}_3\text{C}_{13}\text{H}_8)_2$ (**3c**). Crystals of **3c** are monoclinic (space group $P 2_1/n$), $a = 15.059 \text{ \AA}$, $b = 10.254 \text{ \AA}$, $c = 18.172 \text{ \AA}$, $\beta = 109.20 \text{ deg}$. **3c** dissociates at 100°C to give two radicals which initiate effectively radical polymerizations of methyl methacrylate and styrene. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Coupling reactions; Fluorenes; Titanium compounds; Polymerisation

INTRODUCTION

Synthetic routes for bifluorenes are usually based on the oxidation of the fluorenyl anion by organic electron acceptors to the fluorenyl radical¹, Clemmenson reduction of 9-fluorenone² or on the reduction of 9-bromofluorene by TiCl_2 ³. In all the cases, the bifluorenes are not unique reaction products and their separation requires supplementary purification steps.

On the other hand, the syntheses of metallocenes, especially of titaniumfluorocene(IV) halides^{4,5} are known to be accompanied by back-side reactions associated with the oxidative coupling of macroligands leading to dimer or polymer products. The $\text{Ti}(+4)$ cation is prone to reduction to Ti(III) or Ti(II) thereby promotes the oxidation of macroligand anions to radicals followed by radical coupling products. Moreover, it is impossible to prepare fluorenyltitanium^{5,6} and some indenyltitanium⁷ complexes starting from lithium (sodium, potassium) fluorenyl or indenylide.

Usually, the researchers consider bifluorenes as useless by-products. Nevertheless, some of them may be of intrinsic value. We report here the preparation of a number of bifluorenes via the syntheses and decay

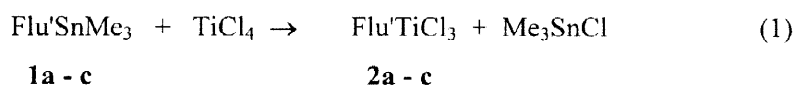
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reactions of Flu'TiCl₃, including the X ray characterization of 9,9'-bis(trimethylsilyl)-bi-9,9'-fluorene.

RESULTS AND DISCUSSIONS

Preparation of fluorenyltitanium trichlorides

We explored the reaction between TiCl₄ and Flu'SnMe₃ (Flu' = C₁₃H₉ (**1a**), 9-EtC₁₃H₈ (**1b**), 9-SiMe₃C₁₃H₈ (**1c**)) (Eq. 1). All of the trimethyltinfluorenes are soluble and stable to air and moisture. Reactions (1) were performed in hexanes at -40 °C (the lowest temperature at which the reaction occurs at a reasonable rate) affording a green-yellowish precipitate of **2a** or red solutions of **2b** and **2c**.



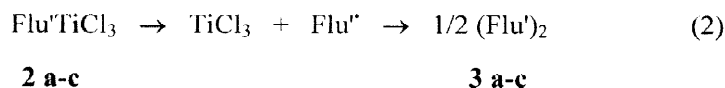
In no case was the darkening of the reaction mixture observed. Trimethyltinchloride was separated by washing solid **2a** with cooled hexane (-30 °C) or filtering the solutions of **2b** and **2c** previously cooled down to -78 °C. **2b** and **2c** are extremely soluble substances that could not be crystallized even at very low temperature. The red color of **2b** and **2c** in hexane is similar to the color of known η^5 -monocyclopentadienyl- and η^5 -monoindenyltitanium trichlorides.⁸ Thus, we tentatively supposed that the formation of Flu'TiCl₃ had taken place in reaction (3). The thermal decomposition of η^5 -fluorenyl complexes of transition metals is known to proceed through η^3 - and η^1 -bonded products.^{7,9} Thus, green-yellowish color and poor solubility of the complex **2a** may be related to the change of binding between fluorenyl and titanium atom.

Formation of bifluorenes.

The isolation of fluorenyltitanium trichlorides as pure substances, and accordingly their study, seem to be impossible due to their thermal instability. Although **2a** is rather stable as a dry solid, its treatment with ether, benzene, toluene, tetrahydrofuran, pyridine, chloroform or methylene chloride results in its rapid decomposition accompanied by the precipitation of violet TiCl₃ (violet or red solutions in tetrahydrofuran and pyridine). White crystalline (C₁₃H₉)₂ (**3a**) was obtained in 60% yield (based on the initial amount of fluorene) after the separation of TiCl₃ and the removal of solvent.

Warming solutions of **2b** and **2c** to -20 °C leads to darkening in color. At 0 °C their decomposition was complete in 2 hours. During the decomposition process, the color of the solutions became green, then violet, and finally forming a precipitate of violet TiCl₃ and white bifluorene. After the solvent was removed, the dried mixtures were washed with methanol to remove 9-H-fluorenes and titanium compounds, and the residues were dried at 70 °C. The bifluorenes (9-EtC₁₃H₈)₂ (**3b**) and (9-SiMe₃C₁₃H₈)₂ (**3c**) were obtained in 70% yield (based on the initial amount of 9-alkylfluorene) as white crystalline substances practically insoluble in hexane, benzene, toluene, methanol and ethanol, and poorly soluble in chloroform, CH₂Cl₂ and THF. The single crystals of **3c** were obtained by the crystallization from THF.

The formation of bifluorenes **3a-3c** is obviously associated with an intra- or intermolecular redox process with formation of TiCl_3 and a radical derived from the fluorenyl anion. The dimerization of two radicals affords the products **3a-3c** (Eq. 2).



The preparation of the bifluorenes described here can be considered as a relatively convenient method for the synthesis of these substances as they are the unique methanol insoluble products which are formed in this system. In no case were other radical coupling products observed by GC/MS. For preparative purposes, the cold filtration of SnMe_3Cl is not necessary as this compound does not affect the thermal decomposition of $\text{Flu}^{\cdot}\text{TiCl}_3$ and can be readily removed with methanol. The reaction (3) in diethyl ether at $-40\text{ }^{\circ}\text{C}$ followed by warming the solution may be also applied, but in this case the yield of pure bifluorenes does not exceed 30%. The same yields of oxidative coupling products were reported in ^{5,7}.



Structure determination of **3c**.

The asymmetric unit of **3c** contains two independent molecules occupying centrosymmetrical positions (Fig. 1, Table 1). Both molecules have practically identical conformations and geometrical features equal to within 0.02 Å. Due to special position in each molecule the fluorene moieties are parallel with the distances between their mean planes of 1.66 Å. Each fluorene moiety adopts a "butterfly" conformation. The angle between benzene rings planes is 166.6° (169.3°), whereas in fluorene itself this angle is 179.1° .¹⁰ In 5-membered rings the "flap" atoms C(13) and C(13A) deviate from four-atoms planes by 0.106 (0.104) Å. The molecule is strongly sterically strained, which results in an unusually long bridge C(13)-C(13A) distance 1.621 Å. In unsubstituted 9,9'-bifluorenyl⁹ this distance is 1.542 Å. The elongation of the bridge distance in analogous molecules was found in 9-*tert*-butyl-9-(9-fluorenyl)fluorene to be 1.585 Å¹², in 2,2'-dinitro-(9,9'-bifluorenyl)-9,9'-dicarboxylic acid anhydride to be 1.581 Å¹³ and in 9,9':9,9''-terfluorene to be 1.580 Å.¹⁴ The steric hindrance also affects the silicon environment. The Si-C distances are substantially unequal, the Si-C(Me) are 1.864 and 1.867 Å (mean values) and the Si-C(13)(C(13A)) are longer (1.933 and 1.941 Å). These distances may be also compared with the C-Si(Me)₃ bonds in strained molecules: 1.914 and 1.933 Å in *cis*- and *trans*-9,10-bis(trimethylsilyl)-9,10-dihydroanthracene¹⁵, 1.946 Å in 9-fluorenyl-tris(trimethylsilyl)silane¹⁶, 1.971 Å in bromo-9-(9-trimesylfluorenyl)-bis(trimethylsilyl)silane.¹⁷

Polymerizations of methyl methacrylate and styrene with **3c**.

The elongation of the bond C13-C13(A) length in **3c** implies its ready radical break. A solution of **3c** in

1,2,4-Cl₃C₆D₃ - DMSO-*d*₆ becomes yellow when heated to 90 °C. The ¹H-NMR spectrum of **3c** cannot be observed above 120°C, presumably owing to the formation of SiMe₃Flu radicals in significant amount. The behaviour of **3c** indicates that it might be employed as an initiator for radical polymerization. We tested **3c** in bulk polymerizations of methyl methacrylate and styrene at 100 °C. Atactic PMMA (30 min, 26.5% conversion, M_n=62100, M_w/M_n=1.47) and an atactic polystyrene (30 min, 52.1% conversion, M_n=73300, M_w/M_n=1.71) were obtained.

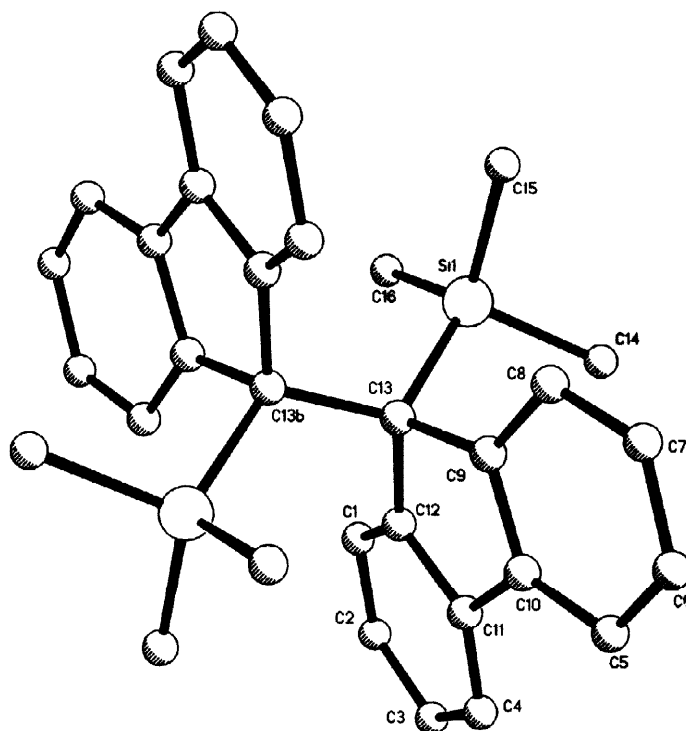


Fig.1. Molecular structure of 9,9'-bis(trimethylsilyl)-bi-9,9'-fluorene (**3c**).

EXPERIMENTAL

General considerations.

All operations were performed under argon by using standard Schlenk techniques. Fluorene, TiCl₄ and butyllithium (hexane solution) were all used as purchased (Aldrich). Diethyl ether was distilled over LiAlH₄ before use. Hexane was washed with H₂SO₄, five times with water, were then dried over CaCl₂ and further refluxed over LiAlH₄ for 3 hours and were distilled before use. Methyl methacrylate was washed twice with a 5% aqueous solution of KOH, five times with water, then was dried over Na₂SO₄, CaH₂ for 4 days and activated molecular sieves 3A for a week and finally was distilled before use. Styrene was washed twice with a

5% aqueous solution of KOH, five times with water, then was dried over Na_2SO_4 , CaH_2 for 4 days and activated molecular sieves 3A for a week, and finally distilled before use. 9-ethylfluorene was prepared as described.¹⁸

Lithium fluorenides were obtained by adding BuLi (1.6 M solution in hexane, 20% excess) to a fluorene solution in benzene ($\text{C}_{13}\text{H}_{10}$) or in pentane (9-Et C_{13}H_9 and 9-SiMe $_3\text{C}_{13}\text{H}_9$) at ambient temperature. The mixture was stirred for 12 hours, and the precipitated lithium fluorenide was filtered, washed twice with hexane or pentane, correspondingly, and dried in vacuum for 2 hours. Yield is 80-85%.

NMR spectra were recorded on a Varian Gemini-200 spectrometer (200 MHz). Gel permeation chromatographic analyses were run on a Hewlett Packard 1050 using 10⁵A, 10⁴A and 10A Styragel columns in THF. The molecular weights of polymers were determined using polystyrene standards. Elemental analysis were performed on a Perkin Elmer Series II CHNS/O Analyzer 2400. Analysis for titanium, silicon and tin were done using Atomic Absorption Spectrometer Varian SpectrAA-250plus.

X-ray structure determination

$\text{C}_{32}\text{H}_{34}\text{Si}_2$ (**3c**), white prism of dimensions 0.34 x 0.18 x 0.12 mm; monoclinic; space group $P2_1/n$; $a=15.059(3)$ Å, $b=10.254(2)$ Å, $c=18.172(4)$ Å; $\beta=109.20(2)^\circ$; $V=2649.9(9)$ Å³; $Z=4$; $d_{\text{calc}}=1.190$ g/cm³; CAD-4 diffractometer (MoK α ; $\lambda=0.71073$ Å); collection method $\theta/2\theta$; β -filter; standards number, 3; standards decay, 3%; absorption coefficient, 0.15 mm⁻¹; $F(000)=1016$; θ range for data collection, 1.53 to 22.45°; independent reflections, 1726; goodness-of-fit on F^2 , 1.023; final R indices [$I>2\sigma(I)$], $R1=0.0249$, $wR2=0.0637$; structure elucidation by direct method with SHELXTL; refinement by full-matrix anisotropic least-squares on F^2 with SHELXL-93.

Anisotropic temperature factors, hydrogen atom parameters, additional details on the crystal structure studies, and the complete set of bond distances and angles can be received from the authors on request.

9-SnMe₃Flu' (1a-1c)

Trimethyltinfluorenes were obtained as follows. A solution of Me $_3\text{SnCl}$ in hexane (1-2% excess) was slowly added with vigorous stirring to a solution of Flu'Li in diethyl ether at -40°C. The mixture was heated to ambient temperature with stirring for 30 min until it became colorless. LiCl was filtered, the solvents were removed in vacuum. The residue was dried in vacuum at 50°C for 10 hours and then crystallized from hexane at -40°C.

9-SnMe₃Flu (1a): white crystals, yield 94%. Found, %: C, 58.87; H, 5.35; Sn, 36.0; calculated for $\text{C}_{16}\text{H}_{18}\text{Sn}$, %: C, 58.43; H, 5.08; Sn, 36.1. ¹H NMR (CDCl_3 , 22°C, δ ppm): 7.94 d. (2H), 7.48 m. (2H), 7.33 m. (4H), 4.33 s. with two satellites (1H, $J_{\text{Sn-H}}=40.3$ Hz), -0.05 s. with two satellites (9H, $J_{\text{Sn-H}}=26.2$ Hz). ¹³C NMR (CDCl_3 , 22°C, δ ppm): 146.95; 138.60; 126.06; 124.25; 122.54; 120.11; 39.62; -9.68.

9-Et-9-SnMe₃Flu (1b): yellowish dense honey, yield 91%. Found, %: C, 60.99; H, 6.34; Sn, 32.8; calculated for $\text{C}_{18}\text{H}_{22}\text{Sn}$, %: C, 60.55; H, 6.21; Sn, 33.2. ¹H NMR (CDCl_3 , 22°C, δ ppm): 7.78 d. (2H), 7.63 m. (2H), 7.35 m. (4H), 2.26 q. (2H), 0.81 t. (3H), -0.08 s. with two satellites (9H, $J_{\text{Sn-H}}=26.0$ Hz). ¹³C NMR

Table 1. Bond Lengths (Å) and Angles (deg) for 3c.

bond lengths		angles	
Si(1)-C(13)	1.941(3)	C(9)-C(8)-C(7)	119.3(4)
C(1)-C(12)	1.382(4)	C(8)-C(9)-C(10)	118.4(3)
C(1)-C(2)	1.388(5)	C(8)-C(9)-C(13)	130.6(3)
C(2)-C(3)	1.376(5)	C(10)-C(9)-C(13)	110.9(3)
C(3)-C(4)	1.376(5)	C(5)-C(10)-C(9)	121.6(3)
C(4)-C(11)	1.388(4)	C(5)-C(10)-C(11)	129.1(3)
C(5)-C(6)	1.365(5)	C(9)-C(10)-C(11)	109.3(3)
C(5)-C(10)	1.390(4)	C(4)-C(11)-C(12)	121.6(3)
C(6)-C(7)	1.375(5)	C(4)-C(11)-C(10)	129.3(3)
C(7)-C(8)	1.389(5)	C(12)-C(11)-C(10)	108.8(3)
C(8)-C(9)	1.387(4)	C(1)-C(12)-C(11)	118.4(3)
C(9)-C(10)	1.393(4)	C(1)-C(12)-C(13)	130.8(3)
C(9)-C(13)	1.537(4)	C(11)-C(12)-C(13)	110.6(3)
C(10)-C(11)	1.450(4)	C(9)-C(13)-C(12)	100.1(2)
C(11)-C(12)	1.401(4)	C(9)-C(13)-C(13b)	113.0(3)
C(12)-C(13)	1.543(4)	(12)-C(13)-C(13b)	112.7(3)
C(13)-C(13b)	1.620(6)	C(9)-C(13)-Si(1)	107.3(2)
Si(1A)-C(13A)	1.933(3)	C(12)-C(13)-Si(1)	106.1(2)
C(1A)-C(12A)	1.381(4)	C(13A)-C(13)-Si(1)	116.2(2)
C(1A)-C(2A)	1.383(5)	C(12A)-C(1A)-C(2A)	119.6(4)
C(2A)-C(3A)	1.373(5)	C(3A)-C(2A)-C(1A)	121.3(4)
C(3A)-C(4A)	1.374(5)	C(2A)-C(3A)-C(4A)	119.5(4)
C(4A)-C(11A)	1.378(4)	C(3A)-C(4A)-C(11A)	119.8(4)
C(5A)-C(6A)	1.376(6)	C(6A)-C(5A)-C(10A)	119.5(4)
C(5A)-C(10A)	1.381(5)	C(7A)-C(6A)-C(5A)	119.3(4)
C(6A)-C(7A)	1.366(6)	C(6A)-C(7A)-C(8A)	122.3(4)
C(7A)-C(8A)	1.376(5)	C(7A)-C(8A)-C(9A)	119.4(4)
C(8A)-C(9A)	1.389(5)	C(8A)-C(9A)-C(10A)	118.1(3)
C(9A)-C(10A)	1.402(4)	C(8A)-C(9A)-C(13A)	131.0(3)
C(9A)-C(13A)	1.539(4)	C(10A)-C(9A)-C(13A)	110.7(3)
C(10A)-C(11A)	1.454(4)	C(5A)-C(10A)-C(9A)	121.3(3)
C(11A)-C(12A)	1.395(4)	C(5A)-C(10A)-C(11A)	129.5(3)
C(12A)-C(13A)	1.545(4)	C(9A)-C(10A)-C(11A)	109.0(3)
		C(4A)-C(11A)-C(12A)	120.9(3)
		C(4A)-C(11A)-C(10A)	129.9(3)
		C(12A)-C(11A)-C(10A)	108.9(3)
		C(1A)-C(12A)-C(11A)	118.8(3)
		C(1A)-C(12A)-C(13A)	130.0(3)
		C(11A)-C(12A)-C(13A)	110.9(3)
		C(9A)-C(13A)-C(12A)	100.0(2)
		C(9A)-C(13A)-Si(1A)	106.7(2)
		C(12A)-C(13A)-Si(1A)	106.5(2)
angles			
C(12)-C(1)-C(2)	119.8(3)		
C(3)-C(2)-C(1)	120.9(4)		
C(2)-C(3)-C(4)	120.5(4)		
C(3)-C(4)-C(11)	118.7(4)		
C(6)-C(5)-C(10)	119.1(3)		
C(5)-C(6)-C(7)	120.1(4)		
C(6)-C(7)-C(8)	121.3(4)		

(CDCl₃, 22°C, δ ppm): 147.59; 139.20; 126.45; 124.21; 122.94; 120.10; 43.13; 21.01; 14.56; -9.85.

9-SiMe₃-9-SnMe₃Flu (1c): white amorphous solid, yield 91.5%. Found, %: C, 57.11; H, 6.66; Si, 6.8; Sn, 30.0; calculated for C₁₉H₂₆SiSn, %: C, 56.88; H, 6.52; Si, 7.0; Sn, 29.6. ¹H NMR (CDCl₃, 22°C, δ ppm): 7.67 d. (2H), 7.36 m. (2H), 7.33 m. (4H), -0.23 s. (9H), -0.32 s. with two satellites (9H, *J*_{Sn-H}=32.2 Hz). ¹³C NMR (CDCl₃, 22°C, δ ppm): 149.28, 139.69, 126.42, 124.39, 123.59, 120.71, 37.28, -0.20, -8.16.

FluTiCl₃ (2a).

A solution of **1a** (9.47 g, 28.8 mmol) in hexane (100 ml) was slowly added with vigorous stirring to a solution of TiCl₄ (5.47 g, 28.8 mmol) in hexane (100 ml) at -40°C. The formation of a green-yellowish precipitate was observed immediately. The mixture was stirred at this temperature for 30 min and was then filtered through a glass filter at -30°C. The solid was twice washed at this temperature with previously cooled hexane and the residue was dried in vacuum at -20°C for 10 hours and then at 0°C for 5 hours, affording 5.71 g (62%) of **2a**. Found, %: C, 49.01; H, 2.67; Ti, 14.9; Cl, 33.0, Sn, < 0.1; calculated for C₁₃H₉TiCl₃, %: C, 48.87; H, 2.83; Ti, 15.0; Cl, 33.3.

(C₁₃H₉)₂ (3a). A typical example is given below.

CH₂Cl₂ (100 ml) was added to **2a** (5.11 g, 16 mmol) at -20°C. The suspension was stirred at this temperature for 2 hours. No change of the solid or of the solvent color were observed. Heating the mixture to 0°C resulted in the darkening of the solid. Stirring the mixture at this temperature for 2 hours afforded a violet precipitate and a colorless solution. The mixture was filtered, the solvent was evacuated in vacuum. A grey solid residue was washed with methanol affording 2.55 g (96.5%) of white crystalline **3a**. Found, %: C, 94.61; H, 5.37; Ti, <0.01; Sn, < 0.001; calculated for C₂₆H₁₈, %: C, 94.51; H, 5.49.

(9-EtC₁₃H₈)₂ (3b).

A solution of **1b** (18.6 mmol) in hexane (100 ml) was slowly added with vigorous stirring to a solution of TiCl₄ (3.55g, 18.7 mmol) in hexanes (50 ml) at -40°C. The mixture was stirred at this temperature for 2 hours, was then cooled to -78°C, and held at this temperature for 4 hours. A dark-red supernatant solution was removed from solids through a filter-transfer needle thermostated at -78°C. The solution was heated to 0°C. Stirring the solution at this temperature for 2 hours afforded a precipitate of violet and white solids in colorless solvent. The mixture was filtered, the solids were abundantly washed with methanol until all of the dark particles were removed. The residual white solid was dried in vacuum at 70°C affording 3.27g (91%) of **3b**; mp 214°C. Found, %: C, 93.01; H, 6.95; Ti, <0.01; Sn, < 0.001; calculated for C₃₀H₂₆, %: C, 93.22; H, 6.78. ¹H NMR (CDCl₃, 22°C, δ ppm): 7.34 d. (4H), 7.13 t. (4H), 6.97 t. (4H), 6.70 d. (4H), 2.72 q. (4H), 0.15 t. (4H). ¹³C NMR (CDCl₃, 22°C, δ ppm): 147.17, 142.05, 126.76, 125.48, 124.30, 118.76, 61.74, 25.45, 8.76. *M/Z*⁺ 386.5.

(9-SiMe₃C₁₃H₈)₂ (3c).

9,9'-bis(trimethylsilyl)-bi-9,9'-fluorene was obtained from **1c** and TiCl₄ as described for **3b**. Yield 92.5%;

decomposition temp. is 198°C. Found, %: C, 81.17; H, 7.53; Si, 11.55; Ti, <0.01; Sn, < 0.001; calculated for C₃₂H₃₄Si₂, %: C, 80.95; H, 7.22; Si, 11.83. ¹H NMR (CDCl₃, 22°C, δ ppm): 7.54 d. (4H), 7.26 d. (4H), 7.05 t. (4H), 6.88 t. (4H), -0.61 s. (18H). ¹³C NMR (CDCl₃, 22°C, δ ppm): 147.85; 141.36; 127.61; 127.39 (C13); 126.16; 125.14; 119.50; -0.06. M/Z⁺ 238.4.

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