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Photochemical functionalizations of C_{60} with phenylpolysilanes

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Abstract

Photolyses of *tert*-butyl substituted disilanes **1a**–**1c**, and **1i** with C_{60} result in the formation of 1,16-adduct **2** through silyl radical addition to fullerene. The unusual products, **3**, **5**, **6** and **7** where the silyl and phenyl groups attached on 1,2-positions of fullerene are also obtained from the reaction of **1d**–**g** and **4**. The structures of all these compounds were determined by one- and two-dimensional NMR techniques. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Fullerene; Disilane; Oligosilane

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1. Introduction

Buckminsterfullerene and its related fullerenes have generated a rapidly growing and active research area [1–5]. As part of our current studies on the reactivity of polysilanes with C_{60} [6], we recently reported the isolation of 1,16- (and 1,29-) adduct by the reactions of bulky substituted silyllithium with C_{60} [6]f. It has been well established that virtually all disilanes which contain a particularly weak Si–Si bond, like $Ph_3SiSiMe_3$ and or bulky substituents, are cleaved by 254 nm ultraviolet radiation to give silyl radicals [7]. In this paper, we describe full details of the formation of 1,16-adducts (**2**) via silyl radical addition process and 1,2-adducts (**3**, **5**–**7**) via 1,4-silyl migration in the photolyses of substituted phenylpolysilanes [8].

2. Results and discussions

2.1. Photochemical reactions of tert-butyl- and trimethylsilyl-substituted disilanes 1a–1f with C_{60}

Irradiation of a solution of 1,1,2,2-tetrakis(4-methylphenyl)-1,2-di-*tert*-butyldisilane **1a** and C_{60} in benzene with a low-pressure mercury lamp (254 nm) for 0.5 h under an argon atmosphere, followed by purification by means of gel-permeation chromatography (Jaigel 1H and 2H columns, Japan Analytical; eluent toluene), afforded the red-brown adduct **2a** (Scheme 1, Table 1). Under similar conditions, 1,1,2,2-tetraphenyl-1,2-di-*tert*-butyldisilane (**1b**) and 1,2-diphenyl-1,1,2,2-tetra-*tert*-butyldisilane (**1c**) were reacted with C_{60} to give bis-adducts **2b** and **2c**. However, we found that photolysis of 2,3-bis(trimethylsilyl)-2,3-diphenyl-1,1,1,4,4,4-hexamethyltetrasilane (**1d**) in the presence of C_{60} affords 1,2-adduct **3d** together with **2d** (Scheme 1, Table 1). The photolysis of trimethylsilyl-substituted disilane **1e** with C_{60} to give **2e**, **3e** and **2h** in 16, 11 and 5% yields (based on recovered C_{60}) respectively. Additionally, trimethylsilyl-substituted disilane **1f** gave **3f** in the reaction with C_{60} in moderate yield.

2.2. Photochemical reactions of tris(trialkylsilyl)phenylsilanes 4j–4l with C_{60}

To clarify the mechanism of the formation of **3**, we photolyzed tris(trimethylsilyl)phenylsilane (**4j**) with C_{60} and but to give rearranged adducts **5j**, **6j** and **7j** (product ratio; **5j**: **6j**: **7j** = 1: 10: 9, Scheme 2, Table 2). Tris(triethylsilyl)phenylsilane **4k** and tris(trimethylsilyl)-4-methylphenylsilane **4l** react with C_{60} to give **5**, **6** and **7**. No silylene adduct was found under the reaction conditions. Note that the trimethylsilylphenylsilylene can be produced by the photolysis of tris(trimethylsilyl)

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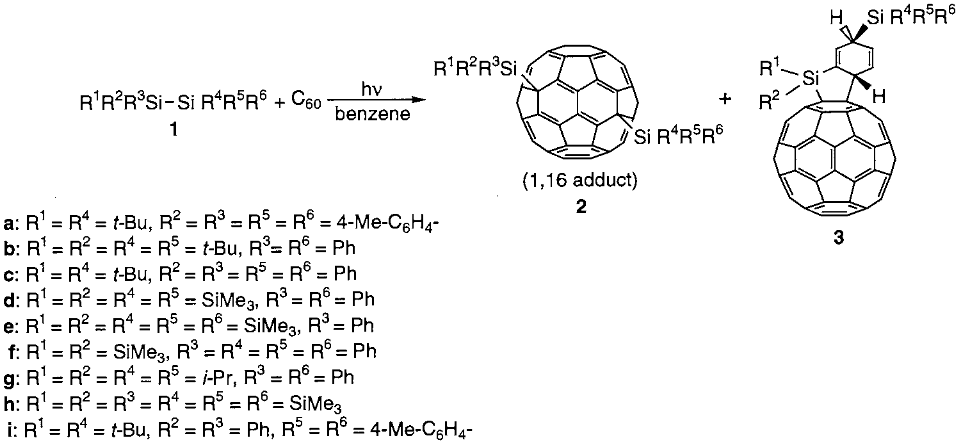


a: $R^1 = R^4 = t\text{-Bu}, R^2 = R^3 = R^5 = R^6 = 4\text{-Me-}C_6H_4\text{-}$
b: $R^1 = R^2 = R^4 = R^5 = t\text{-Bu}, R^3 = R^6 = Ph$
c: $R^1 = R^4 = t\text{-Bu}, R^2 = R^3 = R^5 = R^6 = Ph$
d: $R^1 = R^2 = R^4 = R^5 = SiMe_3, R^3 = R^6 = Ph$
e: $R^1 = R^2 = R^4 = R^5 = R^6 = SiMe_3, R^3 = Ph$
f: $R^1 = R^2 = SiMe_3, R^3 = R^4 = R^5 = R^6 = Ph$
g: $R^1 = R^2 = R^4 = R^5 = i\text{-Pr}, R^3 = R^6 = Ph$
h: $R^1 = R^2 = R^3 = R^4 = R^5 = R^6 = SiMe_3$
i: $R^1 = R^4 = t\text{-Bu}, R^2 = R^3 = Ph, R^5 = R^6 = 4\text{-Me-}C_6H_4\text{-}$

Scheme 1.

phenylsilane (**4j**) [9]; furthermore, the silylene adduct is observed in the photolysis of bis(trimethylsilyl)diarylsilane with C_{60} [6]a.

2.3. Spectroscopic characterization

The FAB mass spectra of **2a** exhibit one peak at *m*/*z* 1255–1258 ($C_{60}[SitBu(4\text{-Me-}C_6H_4)_2]_2$ $M^+ + 1$, molecular cluster ion). The ^{1}H-NMR spectrum of **2a** displays one *tert*-butyl signal and two methyl signals and two pairs of AB quartets. The ^{13}C-NMR spectrum of **2a** displays 29 signals for C_{60} carbon, supporting C_2 symmetry for the molecule. One signal has a relative intensity of 4, and 28 signals have a relative intensity of 2; thus, the number of carbon atoms sums up to 60. Of the 29, one fullerene carbon atom resonate at 58.87 ppm. The signals of all other carbons appear in the region between 130–160 ppm. The structures of **2b**–**2d** were determined in a similar manner. The FAB mass spectra of mixtures of **5j**, **6j** and **7j** exhibit one peak at *m*/*z* 1046–1048 ($C_{60}[(TMS)_3SiPh]$, $M^+ + 1$, molecular cluster ion). The ^{1}H-NMR spectrum of **5j** shows two aliphatic (δ 3.23 H^{5e}, 4.74 H^{5d}) and three olefinic protons (δ 5.91 H^{5f}, 5.98 H^{5g}, 6.84 H^{5h}, Chart 1). Additionally, ^{1}H–^{1}H coupling constant (6.0 Hz) of H^{5e} and H^{5d} was observed. After considering with theoretical calculations (vide infra), we decided the stereochemistry of compound **5j**. The ^{13}C-NMR spectrum of **5j** also shows two aliphatic (δ 29.66 C^{5e}, 51.59 C^{5d}) and three olefinic carbons (δ 120.48 C^{5g}, 130.34 C^{5f}, 135.22 C^{5h}).

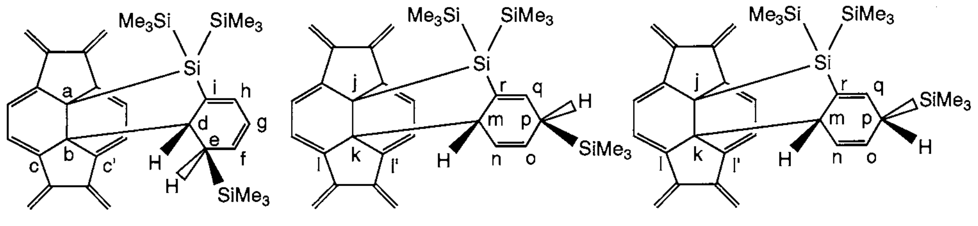
Table 1
Photochemical reactions of phenylsilanes with C_{60}

Phenylsilanes	Time (h)	Product and yield (%)[a]	
		2	**3**
1a	0.5	54	
1b	0.5	62	
1c	0.5	56	
1d	3	43	24
1f	3		35
1g	3		52

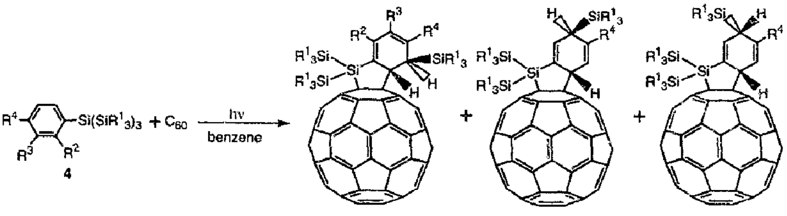
[a] Isolated yields.

The 2D ^{1}H–^{1}H COSY spectrum of **5j** shows characteristic correlation of olefinic protons H^{5h}, H^{5g} and H^{5f} (Fig. 1). The connectivities between these structural elements were determined by ^{13}C–^{1}H COLOC (correlation spectroscopy via long-range coupling) experiments (Figs. 2 and 3). It was shown that aliphatic proton H^{5d} (4.74 ppm) correlates with C_{60} carbons (δ 77.26 C^{5b}, 154.07 C^{5c} and 156.21 $C^{5c'}$). Additionally, aliphatic proton H^{5e} (3.23 ppm) correlates with C_{60} carbon C^{5b} at 77.26 ppm. The ^{1}H-NMR spectrum of **6j** also shows two aliphatic (δ 2.79 H^{6p}, 5.09 H^{6m}) and three olefinic protons (δ 6.02 H^{6n}, 6.61 H^{6o}, 6.68 H^{6q} (above)). Additionally, small ^{1}H–^{1}H coupling constant (6.9 Hz) of H^{6m} and H^{6p} was observed. The ^{13}C-NMR spectrum of **6j** also shows two aliphatic (δ 36.22 C^{6p}, 52.38 C^{6m}) and three olefinic carbons (δ 122.27

Chart 1



5j **6j** **7j**



j: $R^1 = Me, R^2 = R^3 = R^4 = H$
k: $R^1 = Et, R^2 = R^3 = R^4 = H$
l: $R^1 = Me, R^2 = R^3 = H, R^4 = Me$
m: $R^1 = R^2 = R^3 = Me, R^4 = H$

Scheme 2.

C^{6o}, 126.53 C^{6n}, 136.96 C^{6q} (above)). The 2D $^1H-^1H$ COSY spectrum of **6j** shows characteristic correlation of olefinic protons H^{6n} and H^{6o}, and shows isolated H^{6q} (Fig. 1). The connectivities between these structural elements were determined by $^{13}C-^1H$ COLOC experiments (Figs. 2 and 3). It was shown that aliphatic proton H^{6m} (5.09 ppm) correlates with C^{6o} (122.27 ppm), C^{6n} (126.53 ppm), C^{6r} (130.58 ppm) and C^{6q} (136.96 ppm). Additionally, aliphatic proton H^{6p} (2.79 ppm) correlates with C^{6o}, C^{6n}, C^{6r} and C^{6q}. These findings show the presence of 1,4-cyclohexadiene fragment in **6j**. The spectroscopic data of **7j** shows similar character with **6j** but only difference in coupling constants of H^{7m} and H^{7p} (10.4 Hz). The structure of **7j** should be a isomeric structure of **6j**. After considering with theoretical calculations (vide infra), we decided the stereochemistry of compounds **6j** and **7j**.

2.4. *Semiempirical calculations for adducts 5–7*

To predict the addition pattern of the fullerene moiety of adducts **5j**–**7j**, we examined AM1 calculations of stability of **5j**–**7j**. The 1,4-addition is energetically unfavorable than 1,2-addition mode: **5j**-*trans*-1,2-form, 1067 [heat of formation (kcal mol^{-1})]; **5j**-*trans*-1,4-form, 1106; **6j**-*trans*-1,2-form, 1071; **6j**-*trans*-1,4-form, 1100; **7j**-*trans*-1,2-form, 1070; **7j**-*trans*-1,4-form, 1102], all *cis*-isomers were energetically unfavorable than *trans*-isomers. In this calculations, **5j**-*trans*-1,2-form is 3–4 kcal mol^{-1} unstable than **6j**-*trans*-1,2-form and **7j**-*trans*-1,2-form. And also, stability of **6j**-*trans*-1,2-form and **7j**-*trans*-1,2-form are almost same. This is good agreement with product ratio of **5j**, **6j** and **7j**. In the photochemical reaction of **1e**–**1h** with C_{60}, one stereoisomer of product **3** was obtained. According to AM1 calculations of **3f**, the 1,2-*cis*-addition is energetically unfavorable than 1,2-*trans*-addition mode: **3f**-*trans*-form, 1032 [heat of formation (kcal mol^{-1})]; **3f**-*cis*-form, 1060. This agrees with selective formation of **3f**. Additionally, UV-vis spectrum of **3**, **5**–**7** shows characteristic bands at 417–423 and 444–448 nm which assigned as characteristic bands of 1,2-adducts [5].

In an attempt to provide a mechanism for the addition of disilane to fullerene, the unsymmetrical disilane, 1,1-diphenyl-2,2-bis(4-methylphenyl)-1,2-di-*tert*-butyldisilane (**1i**) is photolyzed in the presence of fullerene to give bis-adducts **2a**, **2c**, and **2d** in 10, 21, and 17% yields, respectively. Furthermore the reaction of 1:1 mixture of disilanes **1a** and **1c** with C_{60}, gave **2a**, **2c**, and **2d** in 10, 22, and 35% yields, respectively. These findings indicate that a silyl radical might be involved in the formation of bis-adduct **2** (Scheme 3).

In photochemical reaction of 1,1,2,2-tetra-isopropyl-1,2-diphenyldisilane (**1g**) with C_{60}, similar rearranged adduct **3g** was obtained (Scheme 1, Table 1). These results show that *tert*-butyl groups on silicon atom could inhibit the rearrangement of silyl groups to the phenyl rings.

Recently Leigh and Sluggett reported photolysis of 1,2-*tert*-butyl-1,1,2,2-tetraphenyldisilane **1c** [7]e produces *tert*-butyldiphenylsilyl radicals exclusively which was trapped by radical scavenger quantitatively.

One might have hoped that the photolysis of phenylpolysilane, proceeding through phenylsilyl radical, would lead to silylated-C_{60} radical intermediate shown in the first equation of Scheme 4. There is now a rapid equilibrium set up between this radical and the cyclohexadienyl radical obtained from attack of the C_{60}-centered radical site on the phenyl ring. The product mixture ultimately obtained now depends on which of these two radicals reacts fastest with the other silicon radical produced initially. Bulky phenylalkylsilylradicals react

Table 2
Photochemical reactions of **4** with C_{60}

4	Yield (%)[a]	Product ratio		
		5	**6**	**7**
i	69	1	10.0	9.2
j	79	1	1.7	2.3
k	76	1	3.5	2.5
l	79	1	0	0

[a] Isolated yields.

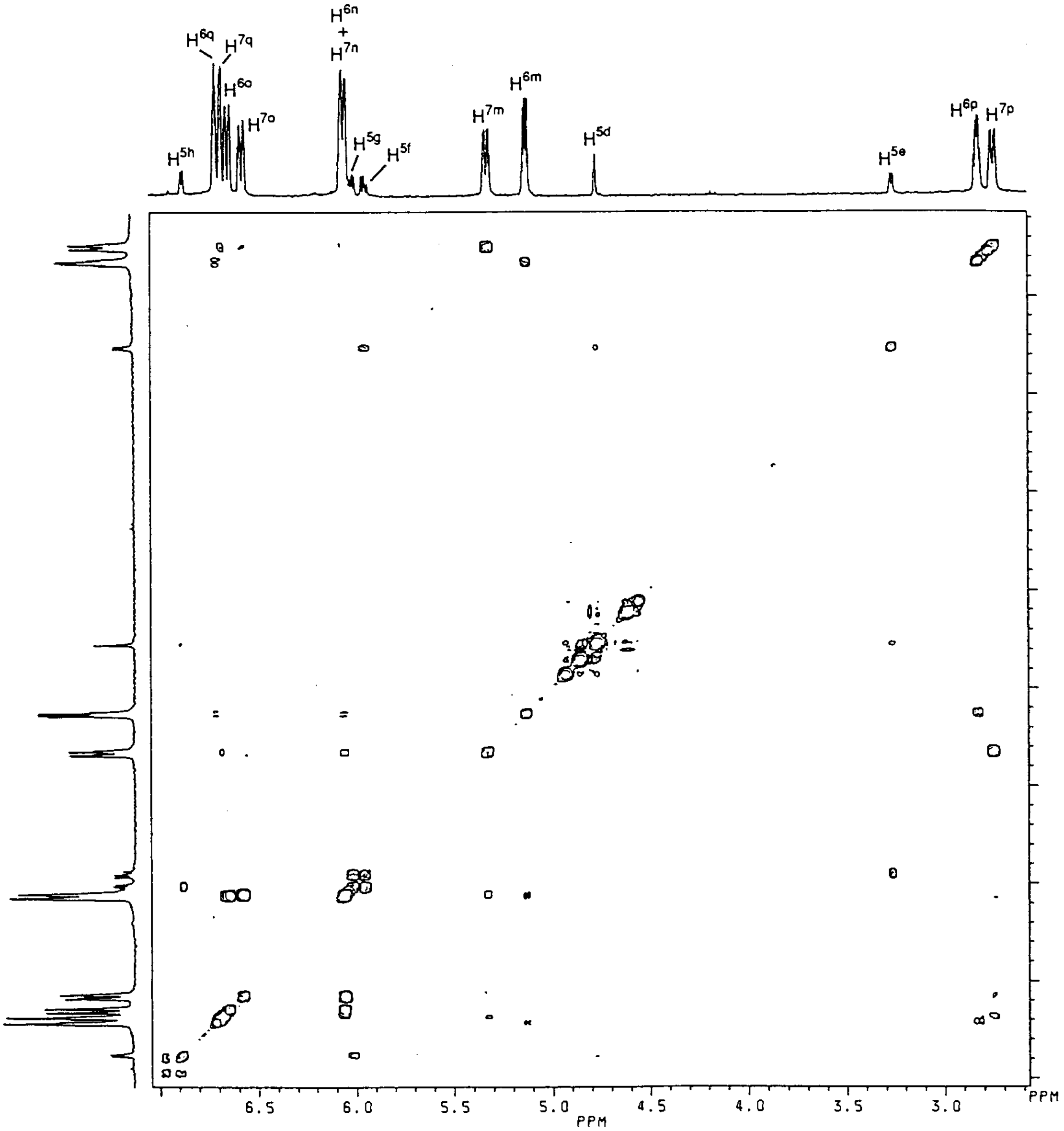


Fig. 1. $^1H-^1H$ COSY spectrum of **5j**, **6j** and **7j**.

preferentially at the 16 position of the C_{60} polycycle in the first-formed radical; trimethylsilyl and silylsilyl radicals react preferentially at the cyclohexadienyl ring of the second-formed radical: A related mechanism would be one in which we remove the reversibility of the first step in the above mechanism, Product selection is now driven by the differences in the relative rate of attack of the other silyl radical at the various position of this radical; bulky phenylalkylsilyl radicals react at the 16 position of the C_{60} polycycle, while trimethylsilyl and silylsilyl radicals react at the cyclohexadienyl ring [10]. To clarify the mechanistic pathway of the formation of **5**, **6**, **7**, we examined the photochemical reaction of **4m** with C_{60}, which gives a single product **5m** in high yield. This information supports the presence of radical intermediate **9** in Scheme 4.

3. Experimental details

3.1. General data

^1H-, ^{13}C- and ^{29}Si-NMR spectra were recorded on Bruker AM500 (500 and 125 MHz), AC400 (400, 100 and 80 MHz) and AC300 (300, 76 and 60 MHz) instruments, Mass spectra were obtained on Shimadzu QP-5000 and JEOL JMS SX102A mass spectrometers. Gel permeation chromatography (GPC) was performed on a LC 908 instrument (Japan Analytical) with a series of Jaigel 1H and 2H columns and toluene as eluent. The AM1 calculations were conducted using standard methods as implemented in the MOPAC 6.0 semiempirical molecular orbital package on a Silicon Graphics INDIGO2 machine. All solvents, and reagents were purified according to standard procedures.

3.2. Materials

1,2-Di-*tert*-butyl-1,1,2,2-tetraphenyldisilane (**1c**) [11] was prepared by the published procedure.

3.3. Preparation of bis(4-methylphenyl)-tert-butylsilane

3.3.1. General procedure A

A solution of *tert*-butyllithium (52 ml, 81.3 mmol) in hexane was added to a cooled (− 30°C) solution of 20.0 g of bis(4-methylphenyl)chlorosilane (81.3 mmol) in 40 ml of hexane. The mixture was warmed to room temperature for 6 h. All solids were removed by filtration, the solvent was evaporated, and the residue was fractionally distilled under reduced pressure to give 18.7 g (86%) of bis(4-methylphenyl)-*tert*-butylsilane as a colorless liquid, b.p. 119–121°C/3 Torr. ^{1}H-NMR (300 MHz, CDCl$_3$) δ 1.64 (s, 9H), 2.81 (s, 6H), 5.26 (s, 1H), 7.67 (d, 4H, $J = 7.7$ Hz), 8.13 (d, 4H, $J = 7.7$ Hz); ^{13}C-NMR (75.5 MHz, CDCl$_3$) δ 17.8 (s), 21.4 (q), 27.6 (q), 128.7 (d), 130.4 (s), 135.7 (d), 139.0 (s); MS *m*/*z* 268 (M$^+$); HRMS Calcd for C$_{18}$H$_{24}$Si: 268.1647. Found: 268.1652.

Di-*tert*-butylphenylsilane was prepared from 20.0 g of dichlorophenylsilane (114 mmol) according to method A, giving 18.9 g (76%) of colorless liquid, b.p. 70–72°C/3 Torr. ^{1}H-NMR (300 MHz, CDCl$_3$) δ 1.03 (s, 18H), 3.84 (s, 1H), 7.2–7.4 (m, 3H), 7.5–7.6 (m, 2H); ^{13}C-NMR (76 MHz, CDCl$_3$) δ 19.0 (s), 28.9 (q), 127.5 (d), 128.9 (d), 135.5 (s), 135.8 (d); MS *m*/*z* 220 (M$^+$).

3.4. Preparation of bis(4-methylphenyl)-tert-butylchlorosilane

3.4.1. General procedure B

A solution of 20.0 g of bis(4-methylphenyl)-*tert*-

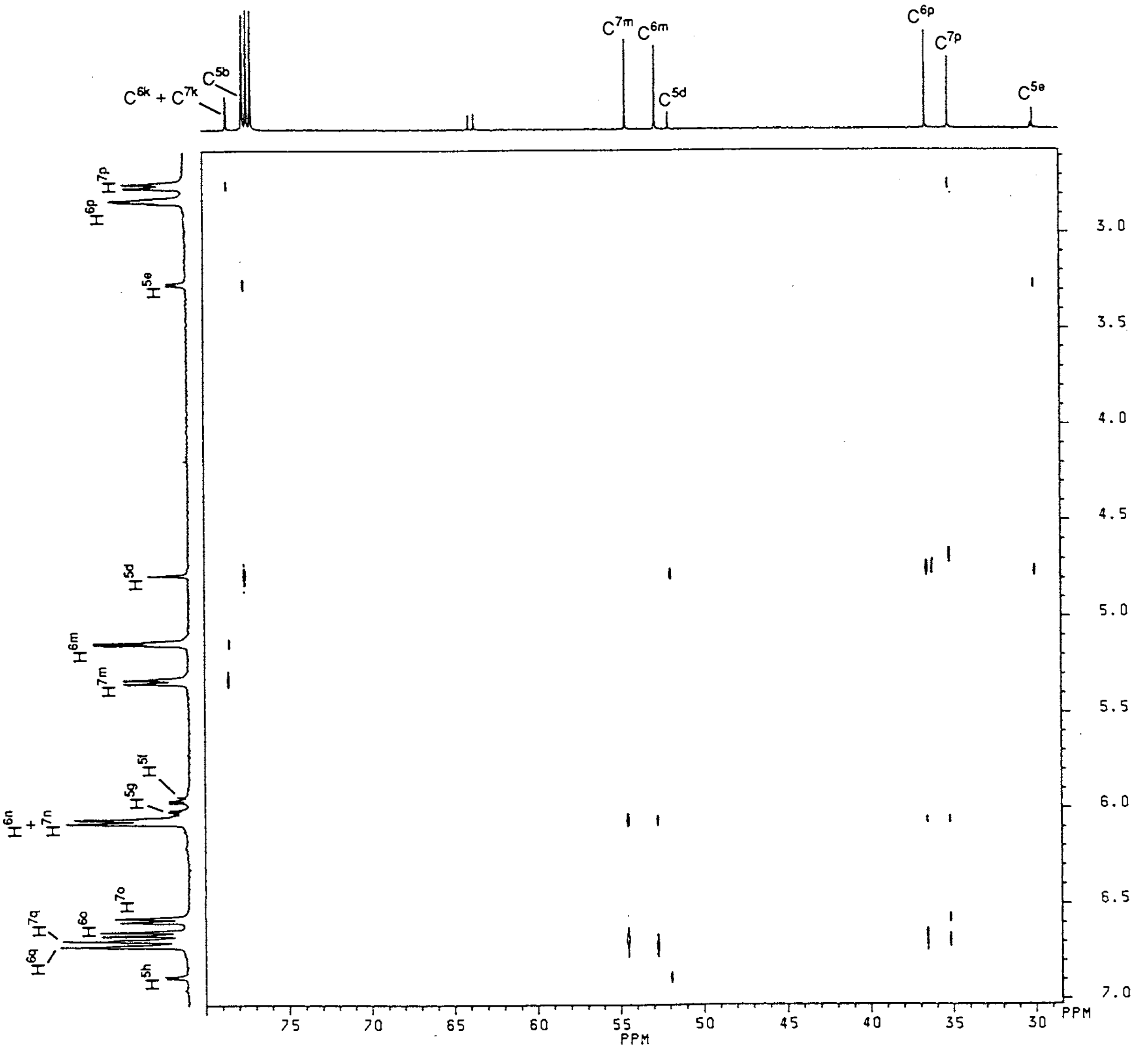


Fig. 2. ^{1}H–^{13}H COLOC spectrum of **5j**, **6j** and **7j**.

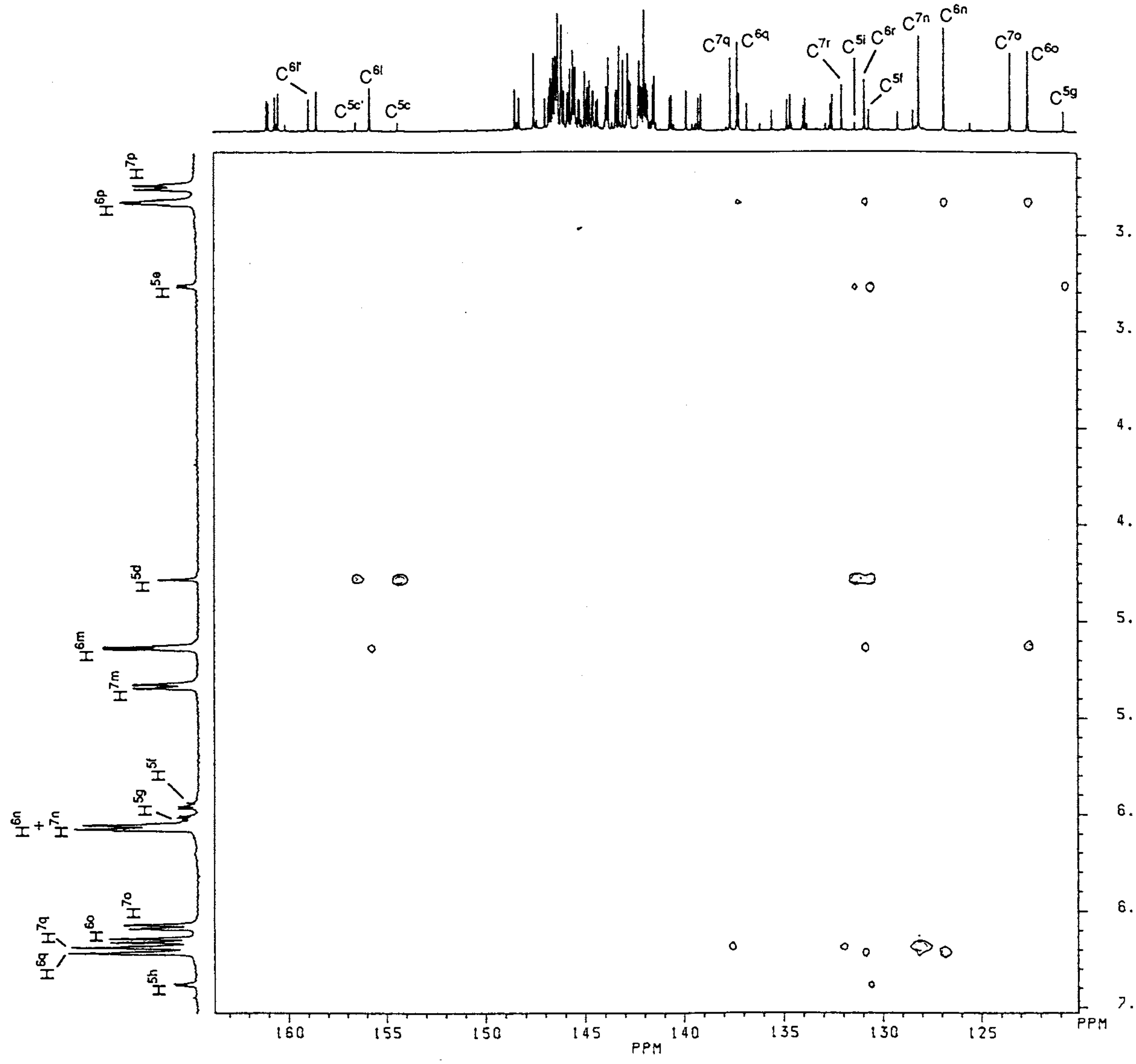


Fig. 3. ^{1}H–^{13}H COLOC spectrum of **5j**, **6j** and **7j**.

butylsilane (74.6 mmol) and catalytic amount of benzoylperoxide in 100 ml of CCl_4 was refluxed for 24 h. After evaporation of the solvent, the residue was fractionally distilled under reduced pressure to give 19.9 g (88%) of bis(4-methylphenyl)chloro-*tert*-butylsilane as a colorless liquid, b.p. 143–145°C/3 Torr. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.24 (s, 9H), 2.45 (s, 6H), 7.30 (d, 4H, $J = 7.7$ Hz), 7.75 (d, 4H, $J = 7.7$ Hz); ^{13}C-NMR 126 MHz, $CDCl_3$) *d* 20.7 (s), 21.5 (q), 26.5 (q), 128.7 (d), 129.1 (s), 135.2 (d), 140.2 (s); MS *m*/*z* 268 (M^+); HRMS Calcd for $C_{15}H_{25}ClSi$: 268.1414. Found: 268.1402.

Di-*tert*-butylchlorophenylsilane was prepared from 18.9 g of di-*tert*-butylphenylsilane (85.9 mmol) according to method B, giving 18.3 g (84%) of colorless liquid, b.p. 85–86°C/3 Torr. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.21 (s, 18H), 7.3–7.5 (m, 3H), 7.7–7.9 (m, 2H); ^{13}C-NMR (76 MHz, $CDCl_3$) δ 22.1 (s), 28.1 (q), 127.6 (d), 129.6 (d), 132.8 (s), 134.9 (d); MS *m*/*z* 254 (M^+); HRMS Calcd for $C_{14}H_{23}ClSi$: 254.1258. Found: 254.1262.

3.5. Preparation of bis(trimethylsilyl)chlorophenylsilane

A mixture of bis(trimethylsilyl)diphenylsilane [12] (46.0 g, 140 mmol), sublimed aluminum trichloride (0.100 g, 0.750 mmol), and 200 ml of benzene is placed in a three-necked flask. Dry hydrogen chloride gas is passed into the vigorously stirred mixture for 14 h. All solids are removed by filtration through Celite, the solvent is distilled off at reduced pressure, and the crude product is purified by distillation to give 26.6 g (66%) of bis(trimethylsilyl)chlorophenylsilane as a colorless liquid, b.p. 80–82°C/2 Torr. ^{1}H-NMR (500

MHz, $CDCl_3$) δ 0.24 (s, 18H), 7.3–7.4 (m, 3H), 7.5–7.6 (m, 2H); ^{13}C-NMR (126 MHz, $CDCl_3$) δ −1.95 (s), 128.1 (d), 129.0 (d), 133.2 (d), 135.2 (s); MS *m*/*z* 286 (M^+); HRMS Calcd for $C_{12}H_{23}Si_3Cl$: 286.0796. Found: 286.0799.

3.6. Preparation of 1,2-di-*tert*-butyl-1,1,2,2-tetrakis(4-methylphenyl)-disilane (**1a**)

A mixtures of lithium wire (916 mg, 132 mmol) and bis(4-methylphenyl)-*tert*-butylchlorosilane (10 g, 33.1 mmol) in 100 ml of THF was stirred for 12 h under an argon atmosphere. All solids are removed by filtration through Celite, the solvent is distilled off at ordinary pressure, and crystalline product was obtained from hexane. yield: 6.10 g (69%); m.p. 247–248°C; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.86 (s, 18H), 2.38 (s, 6H), 7.15 (d, 4H, $J = 7.7$ Hz), 7.61 (d, 4H, $J = 7.7$ Hz); ^{13}C-NMR (126 MHz, $CDCl_3$) δ 20.4 (s), 21.5 (q), 29.3 (q), 128.1 (d), 133.2 (s), 137.5 (d), 138.3 (s); MS *m*/*z* 534 (M^+); HRMS Calcd for $C_{36}H_{46}Si_2$: 534.3138. Found: 534.3128.

3.7. Preparation of 1,2-diphenyl-1,1,2,2-tetra-*tert*-butyl disilane (**1b**)

Chloro-di-*tert*-butylphenylsilane (1.00 g, 3.94 mmol) was stirred with excess lithium (136 mg, 19.7 mmol) in THF (20 ml) at room temperature for 4 h. After remove the excess lithium, a suspension of nitrosonium tetrafluoroborate (5.52 g, 47.3 mmol) in 10 ml of hexane was added to the desired silyllithium reagent at − 78°C. After stirring for 1 h, the mixture is warmed to room temperature. The solvent is removed under reduced pressure. The pure product is obtained after recrystallization from hexane as a colorless crystals. yield: 154 mg (1.0%); m.p. 215°C (dec.); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.15 (s, 36H), 7.3–7.4 (m, 6H), 7.69 (d, 4H, $J = 8.1$ Hz); ^{13}C-NMR (126 MHz, $CDCl_3$) δ 23.1 (s), 32.8 (q), 126.5 (d), 127.9 (d), 137.6 (d), 139.3 (s); MS *m*/*z* 478 (M^+); HRMS Calcd for $C_{32}H_{38}Si_2$: 478.2512. Found: 478.2503.

3.8. Preparation of 2,3-bis(trimethylsilyl)-2,3-diphenyl-1,1,1,4,4,4-hexamethyltetrasilane (**1d**) [13]

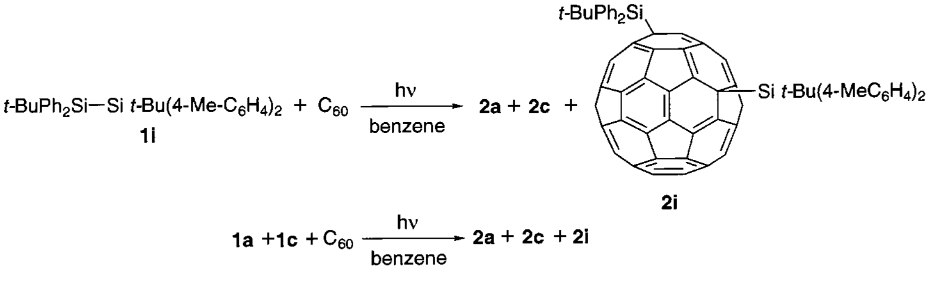
A solution of 4.92 g of bis(trimethylsilyl)chlorophenylsilane (17.2 mmol) in 40 ml of toluene was added to 793 mg of sodium (34.5 mmol), and the mixture was heated to reflux for 8 h. The precipitate was removed by filtration, and the solvent was evaporated. The pure product is obtained after recrystallization from hexane as a colorless crystals. yield: 3.44 g (80%); m.p. 235–236°C.

3.9. Preparation of 2-phenyl-1,1,1,4,4,4-hexamethyl-2,3,3-tris(trimethylsilyl)tetrasilane (**1e**)

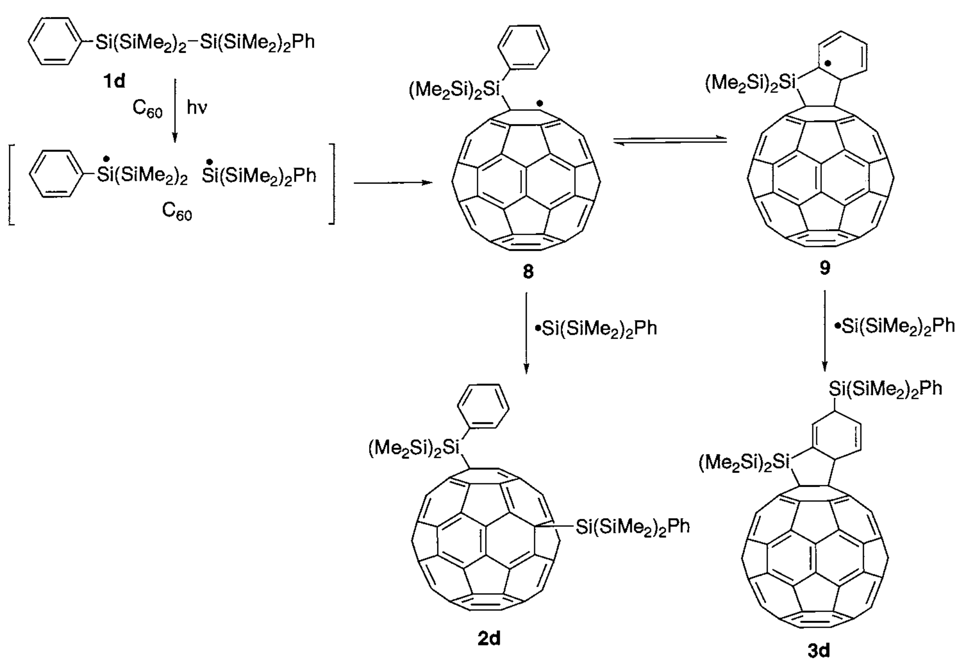
To a solution of 895 mg of bis(trimethylsilyl)chlorophenylsilane (3.13 mmol) in 20 ml of THF was added tris(trimethylsilyl)silyllithium prepared from 1.00 g of tetrakis(trimethylsilyl)silane (3.13 mmol) and 2.9 ml of ether solution of MeLi (3.13 mmol) at room temperature. After stirring for 3 h, the solvent is removed under reduced pressure. The pure product is obtained after recrystallization from hexane as a colorless crystals. yield: 945 mg (61%); m.p. 230–231°C; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.19 (s, 27H), 0.33 (s, 18H), 7.2–7.3 (m, 3H), 7.5–7.6 (m, 2H); ^{13}C-NMR (126 MHz, $CDCl_3$) δ 2.8 (q), 3.7 (q), 127.5 (d), 127.6 (d), 136.9 (s), 137.5 (d); MS *m*/*z* 498 (M^+); HRMS Calcd for $C_{21}H_{50}Si_7$: 498.2298. Found: 498.2302.

3.10. Preparation of 1,1,1-trimethyl-2,2,3,3,3-pentaphenyltrisilane (**1f**)

Chlorotriphenylsilane (1.00 g, 3.40 mmol) was stirred with excess lithium (118 mg, 17.0 mmol) in THF (10 ml) at room temperature for 12 h. After remove the excess lithium, desired silyllithium reagent was added to the solution of bis(trimethylsilyl)phenylchlorosilane (972 mg, 3.40 mmol) in 20 ml of THF at room temperature. After stirring for 3 h, the solvent is removed under reduced pressure. The pure product is obtained



Scheme 3.



Scheme 4.

after recrystallization from hexane as a colorless crystals. yield: 270 mg (16%); m.p. 239–240°C; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.10 (s, 18H), 7.16 (t, 2H, $J=7.5$ Hz), 7.2–7.4 (m, 12H), 7.50 (d, 6H, $J=7.6$ Hz); ^{13}C-NMR (126 MHz, $CDCl_3$) d 1.5 (q), 127.5 (d), 127.6 (d), 127.7 (d), 129.1 (d), 134.7 (s), 136.2 (s), 136.5 (d), 137.5 (s); MS *m/z* 506 (M^+); HRMS Calcd for $C_{27}H_{42}Si_5$: 506.2133. Found: 506.2112.

3.11. Preparation of 1,1-bis(4-methylphenyl)-2,2-diphenyl-1,2-di-tert-butyldisilane (**1i**)

tert-Butylchlorodiphenylsilane (5.00 g, 18.2 mmol) was stirred with excess lithium wire (630 mg, 90.8 mmol) in THF (100 ml) at room temperature for 3 h. After remove the excess lithium, bis(4-methylphenyl)-*tert*-butylchlorosilane (5.50 g, 18.2 mmol) was added to desired silyllithium reagent at room temperature. After stirring for 2 h, the solvent is removed under reduced pressure. The pure product is obtained after recrystallization from hexane as a colorless crystals. yield: 8.16 g (89%); m.p. 139–140°C; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.86 (s, 9H), 0.89 (s, 9H), 2.39 (s, 6H), 7.15 (d, 4H, $J=7.6$ Hz), 7.3–7.4 (m, 6H), 7.61 (d, 4H, $J=7.9$ Hz), 7.73 (d, 4H, $J=7.6$ Hz); ^{13}C-NMR (126 MHz, $CDCl_3$) δ 20.4 (s), 21.5 (q), 127.2 (d), 128.1 (d), 128.6 (d), 132.9 (s), 136.9 (s), 137.52 (d), 137.54 (d), 138.4 (s); MS *m/z* 506 (M^+); HRMS Calcd for $C_{34}H_{42}Si_2$: 506.2825. Found: 506.2813.

3.12. Preparation of (2,3-dimethylphenyl)trichlorosilane

To a solution of tetrachlorosilane (63.6 g, 379 mmol) in ether 1000 ml was added ether solution (200 ml) of (2,3-dimethylphenyl)magnesiumbromide prepared from 70.1 g of 2,3-dimethylbromobenzene (379 mmol) and 9.20 g of magnesium (379 mmol) at room temperature for 3 h. After stirring for 12 h, the precipitate was removed by filtration, and the solvent was removed under reduced pressure. The residue was fractionally distilled under reduced pressure to give 40.2 g (45%) of (2,3-dimethylphenyl)trichlorosilane as a colorless liquid; b.p. 110–112°C/10 Torr; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.37 (s, 3H), 2.62 (s, 3H), 7.28 (t, 1H, $J=7.6$ Hz), 7.43 (d, 1H, $J=7.4$ Hz), 7.80 (d, 1H, $J=7.5$ Hz); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 20.1 (q), 20.3 (q), 125.6 (d), 129.6 (s), 129.7 (s), 132.7 (d), 134.7 (d), 138.1 (s); MS *m/z* 238 (M^+); HRMS Calcd for $C_8H_9SiCl_3$: 237.9539. Found: 237.9542.

3.13. Preparation of tris(triethylsilyl)phenylsilane (**5j**)

3.13.1. General procedure C

A solution of 5.00 g of phenyltrichlorosilane (23.8 mmol) and 21.4 g of chlorotriethylsilane (143 mmol) in 40 ml of THF was dropewised to the suspension of 992 mg of lithium (143 mmol) in THF (20 ml) for 3 h. After stirring for 12 h, all solids were removed by filtration, the solvent is removed under reduced pressure. The residue was purified by silica gel chlomatography (hexane). yield: 1.23 g (11%); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.8–1.2 (m, 45H), 7.2–7.4 (m, 3H), 7.5–7.6 (m, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 6.2 (t), 8.8 (q), 127.0 (d), 127.2 (d), 136.8 (s), 137.2 (d); MS *m*/*z* 450 (M^+); HRMS Calcd for $C_{24}H_{50}Si_4$: 450.2990. Found: 450.3003.

4-Methylphenyl-tris(trimethylsilyl)silane (**5k**) was prepared from 5.00 g of 4-methylphenyltrichlorosilane (22.3 mmol) according to method C, giving 2.12 g (28%) of colorless liquid. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.28 (s, 27H), 2.37 (s, 3H), 7.14 (d, 2H, $J = 7.5$ Hz), 7.40 (d, 2H, $J = 7.5$ Hz); ^{13}C-NMR (76 MHz, $CDCl_3$) δ 1.1 (q), 21.3 (q), 128.6 (d), 131.1 (s), 136.5 (d), 136.9 (s); MS *m*/*z* 338 (M^+); HRMS Calcd for $C_{16}H_{34}Si_4$: 338.1738. Found: 338.1735.

2,3-Dimethylphenyl-tris(trimethylsilyl)silane (**5l**) was prepared from 34.0 g of 2,3-dimethylphenyltrichlorosilane (143 mmol) according to method C, giving 19.7 g (39%) of colorless liquid. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.29 (s, 27H), 2.26 (s, 3H), 2.37 (s, 3H), 7.01 (t, 1H, $J = 7.4$ Hz), 7.10 (d, 1H, $J = 7.2$ Hz), 7.43 (d, 1H, $J = 7.4$ Hz); ^{13}C-NMR (76 MHz, $CDCl_3$) δ 2.1 (q), 20.9 (q), 23.7 (q), 124.8 (d), 129.7 (d), 134.9 (s), 136.0 (d), 136.2 (s), 142.7 (s); MS *m*/*z* 352 (M^+); HRMS Calcd for $C_{17}H_{36}Si_4$: 352.1894. Found: 352.1890.

3.14. Photochemical reactions of tert-butyl-, trimethylsilyl-substituted disilanes (1a–1c, 1i) and tris(trimethylsilyl)phenylsilane derivatives (5i–5j) with C_{60}

3.14.1. General procedure D

Irradiation of a solution of 59.3 mg of 1,1,2,2-tetrakis(4-methylphenyl)-1,2-di-tert-butyldisilane **1a** (111 mmol) and 80.0 mg of C_{60} (111 mmol) in 40 ml of benzene with a low-pressure mercury lamp (254 nm) for 0.5–3 h under an argon atmosphere, followed by purification by means of gel-permeation chromatography (Jaigel 1H and 2H columns, Japan Analytical; eluent toluene), afforded 52.8 mg of the red-brown adducts **2a** in 54% yield (based on recovered C_{60}).

2a: red brown solid, ^{1}H-NMR (500 MHz, 1:1 $CDCl_3$–CS_2) δ 1.43 (s, 9H), 2.35 (s, 3H), 2.36 (s, 3H), 7.12 (d, 2H, $J = 7.7$ Hz), 7.17 (d, 2H, $J = 7.7$ Hz), 7.83 (d, 2H, $J = 7.7$ Hz), 7.89 (d, 2H, $J = 7.7$ Hz); ^{13}C-NMR (126 MHz, 1:1 $CDCl_3$–CS_2) δ 21.61 (q), 21.63 (q), 22.32 (s), 29.12 (q), 64.99 (s, 2C), 127.61 (s), 127.67 (s), 128.26 (d), 128.35 (d), 136.52 (s, 2C), 136.74 (s, 2C), 137.40 (d), 137.51 (d), 138.68 (s, 2C), 139.59 (s, 2C), 139.72 (s), 139.76 (s), 140.55 (s, 2C), 141.30 (s, 2C), 141.47 (s, 2C), 142.07 (s, 2C), 142.14 (s, 2C), 142.34 (s, 2C), 143.36 (s, 2C), 143.80 (s, 2C), 144.29 (s, 2C), 145.44 (s, 2C), 145.86 (s, 2C), 145.88 (s, 4C), 146.01 (s, 2C), 146.06 (s, 2C), 146.40 (s, 2C), 146.81 (s, 2C), 146.93 (s, 2C), 147.00 (s, 2C), 147.74 (s, 2C), 148.55 (s, 2C), 150.22 (s, 2C), 152.90 (s, 2C), 162.39 (s, 2C), 164.07 (s, 2C); ^{29}Si-NMR (80 MHz, 1:1 $CDCl_3$–CS_2) δ −3.71; FAB-Mass *m*/*z* 1255–1258 ($M^+ + 1$ cluster).

2b: red brown solid, ^{1}H-NMR (500 MHz, 1:1 $CDCl_3$–CS_2) δ 1.45 (s, 9H), 7.3–7.5 (m, 6H), 7.93 (d, 2H, $J = 6.8$ Hz), 8.01 (d, 2H, $J = 6.8$ Hz); ^{13}C-NMR (126 MHz, 1:1 $CDCl_3$–CS_2) δ 22.32 (s), 29.16 (q), 64.58 (s, 2C), 127.44 (d), 127.57 (d), 129.99 (d), 130.06 (d), 131.13 (s), 136.61 (s, 2C), 136.70 (s, 2C), 137.35 (d), 137.49 (d), 138.70 (s, 2C), 139.49 (s, 2C), 140.61 (s, 2C), 141.31 (s, 2C), 141.50 (s, 2C), 142.07 (s, 2C), 142.12 (s, 2C), 142.37 (s, 2C), 143.39 (s, 2C), 143.81 (s, 2C), 144.39 (s, 2C), 145.45 (s, 2C), 145.78 (s, 2C), 145.86 (s, 2C), 145.89 (s, 2C), 146.04 (s, 2C), 146.08 (s, 2C), 146.35 (s, 2C), 146.76 (s, 2C), 146.88 (s, 2C), 146.97 (s, 2C), 147.676 (s, 2C), 148.57 (s, 2C), 150.09 (s, 2C), 152.80 (s, 2C), 161.93 (s, 2C), 163.77 (s, 2C); ^{29}Si-NMR (80 MHz, 1:1 $CDCl_3$–CS_2) δ −3.99; FAB-Mass *m*/*z* 1199–1202 ($M^+ + 1$ cluster).

2c: red brown solid, ^{1}H-NMR (500 MHz, 1:1 $CDCl_3$–CS_2) δ 1.45 (s, 9H), 7.3–7.5 (m, 6H), 7.93 (d, 2H, $J = 6.8$ Hz), 8.01 (d, 2H, $J = 6.8$ Hz); ^{13}C-NMR (126 MHz, 1:1 $CDCl_3$–CS_2) δ 22.32 (s), 29.16 (q), 64.58 (s, 2C), 127.44 (d), 127.57 (d), 129.99 (d), 130.06 (d), 131.13 (s), 136.61 (s, 2C), 136.70 (s, 2C), 137.35 (d), 137.49 (d), 138.70 (s, 2C), 139.49 (s, 2C), 140.61 (s, 2C), 141.31 (s, 2C), 141.50 (s, 2C), 142.07 (s, 2C), 142.12 (s, 2C), 142.37 (s, 2C), 143.39 (s, 2C), 143.81 (s, 2C), 144.39 (s, 2C), 145.45 (s, 2C), 145.78 (s, 2C), 145.86 (s, 2C), 145.89 (s, 2C), 146.04 (s, 2C), 146.08 (s, 2C), 146.35 (s, 2C), 146.76 (s, 2C), 146.88 (s, 2C), 146.97 (s, 2C), 147.676 (s, 2C), 148.57 (s, 2C), 150.09 (s, 2C), 152.80 (s, 2C), 161.93 (s, 2C), 163.77 (s, 2C); ^{29}Si-NMR (80 MHz, 1:1 $CDCl_3$–CS_2) δ −3.99; FAB-Mass 1199–1202 ($M^+ + 1$ cluster).

2d: red brown solid, ^{1}H-NMR (500 MHz, 1:1 $CDCl_3$–CS_2) δ 0.41 (s, 18H), 0.42 (s, 18H), 7.2–7.4 (m, 3H), 7.74 (d, 4H, $J = 7.8$ Hz); ^{13}C-NMR (126 MHz, 1:1 $CDCl_3$–CS_2) δ 1.70 (q), 1.73 (q), 64.43 (s,2C), 127.98 (d), 129.48 (d), 132.88 (s), 135.74 (s,2C), 136.19 (s,2C), 137.25 (d), 139.27 (s, 2C), 139.96 (s, 2C), 140.62 (s, 2C), 141.03 (s, 2C), 141.66 (s,2C), 142.31 (s,2C), 142.49 (s, 2C), 143.06 (s, 2C), 143.50 (s,2C), 143.71 (s, 2C), 144.39 (s, 2C), 145.44 (s,2C), 145.70 (s,2C), 145.90 (s, 2C), 145.94 (s,2C), 146.10 (s,2C), 146.16 (s, 2C), 146.25 (s, 2C), 146.30 (s, 2C), 147.26 (s, 2C), 147.29 (s, 2C), 147.82 (s, 2C), 148.68 (s, 2C), 150.69 (s, 2C), 152.33 (s, 2C), 163.64 (s, 2C), 164.38 (s, 2C); ^{29}Si-NMR (60 MHz, 1:1 $CDCl_3$–CS_2) $\delta = -12.90, -13.01, -24.36$; FAB-Mass 1223–1226 ($M^+ + 1$ cluster).

2e: red brown solid; ^{1}H-NMR (500 MHz, 1:1 $CDCl_3$–CS_2) δ 0.35 (s, 27H), 0.43 (s, 9H), 0.46 (s, 9H), 7.2–7.4 (m, 3H), 7.76 (d, 2H, $J = 7.7$ Hz); ^{13}C-NMR (126 MHz, 1:1 $CDCl_3$–CS_2) δ 1.70 (q), 1.76 (q), 2.65 (q), 60.80 (s, 1C), 64.49 (s,1C), 128.02 (d), 129.51 (d), 132.91 (s), 135.02 (s, 1C), 135.65 (s, 1C), 135.79 (s, 1C), 136.30 (s, 1C), 137.28 (d), 139.30 (s, 1C), 139.35 (s, 1C), 139.95 (s, 2C), 140.67 (s, 1C), 140.70 (s, 2C), 140.97 (s, 1C), 141.66 (s, 1C), 141.78 (s, 1C), 142.38 (s, 1C), 142.41 (s, 2C), 142.54 (s, 1C), 142.67 (s, 1C), 143.06 (s, 1C), 143.24 (s, 1C), 143.53 (s, 1C), 143.60 (s, 1C), 143.75 (s, 2C), 144.36 (s, 2C), 145.09 (s, 1C), 145.55 (s, 1C), 145.66 (s, 1C), 145.72 (s, 1C), 145.92 (s, 1C), 145.96 (s, 2C), 146.08 (s, 1C), 146.14 (s, 1C), 146.15 (s, 2C), 146.21 (s, 2C), 146.39 (s, 2C), 147.08 (s, 1C), 147.24 (s, 1C), 147.30 (s, 1C), 147.37 (s, 1C), 147.83 (s, 1C), 147.86 (s, 1C), 148.68 (s, 1C), 148.73 (s, 1C), 150.51 (s, 1C), 151.63 (s, 1C), 151.69 (s, 1C), 152.30 (s, 1C), 163.49 (s, 1C), 164.57 (s, 1C), 146.80 (s, 1C), 165.55 (s, 1C); FAB-Mass 1218–1220 ($M^+ + 1$ cluster).

2h: red brown solid, ^{1}H-NMR (500 MHz, 1:2 $CDCl_3$–CS_2) δ 0.38 (s, 54H); ^{13}C-NMR (125 MHz, 1:1 $CDCl_3$–CS_2) δ 2.63 (q), 60.88 (s, 2C), 135.02 (s, 2C), 135.76 (s, 2C), 139.36 (s, 2C), 140.06 (s, 2C), 140.62 (s, 2C), 140.82 (s, 2C), 141.83 (s, 2C), 142.49 (s, 2C), 142.71 (s, 2C), 143.30 (s, 2C), 143.66 (s, 2C), 143.81 (s, 2C), 144.37 (s, 2C), 145.20 (s, 2C), 145.66 (s, 2C), 146.00 (s, 2C), 146.14 (s, 2C), 146.22 (s, 2C), 146.25 (s, 2C), 146.38 (s, 4C), 147.09 (s, 2C), 147.43 (s, 2C), 147.90 (s, 2C), 148.75 (s, 2C), 151.55 (s, 2C), 151.67 (s, 2C), 164.76 (s, 2C), 165.71 (s, 2C); ^{29}Si-NMR (60 MHz, 1:1, $CDCl_3$–CS_2) δ -52.72, -9.95; FAB-Mass 1215–1218 ($M^+ + 1$ cluster); UV-vis (toluene) λ_{max} (nm): 547, 566.

2i: red brown solid, ^{1}H-NMR (500 MHz, 1:1 $CDCl_3$–CS_2) $\delta = 1.42$ (s, 9H), 1.45 (s, 9H), 2.34 (s, 9H), 2.36 (s, 9H), 7.12 (d, 2H, $J = 7.6$ Hz), 7.16 (d, 2H, $J = 7.6$ Hz), 7.3–7.5 (m, 6H), 7.82 (d, 2H, $J = 7.8$ Hz), 7.88 (d, 2H, $J = 7.8$ Hz), 7.94 (d, 2H, $J = 7.6$ Hz), 8.01 (d, 2H, $J = 7.6$ Hz); ^{13}C-NMR (126 MHz, 1:1 $CDCl_3$–CS_2) $\delta = 21.60$ (q), 21.62 (q), 22.26 (s), 22.37 (s), 29.11 (q), 29.18 (q), 64.52 (s, 1C), 65.06 (s, 1C), 127.42 (d), 127.53 (d), 127.57 (s, two carbons), 128.26 (d), 128.37 (d), 129.96 (d), 130.03 (d), 131.21 (s), 131.17 (s), 136.56 (s, 1C), 136.57 (s, 2C), 136.68 (s, 1C), 137.34 (d), 137.40 (d), 137.48 (d), 137.54 (d), 138.65 (s, 1C), 138.73 (s, 1C), 139.41 (s, 1C), 139.67 (s, 1C), 139.74 (s, 1C), 139.80 (s, 1C), 140.57 (s, 1C), 140.58 (s, 1C), 141.29 (s, 1C), 141.33 (s, 1C), 141.48 (s, 1C), 141.50 (s, 1C), 142.07 (s, 2C), 142.19 (s, 1C), 142.33 (s, 1C), 142.39 (s, 1C), 143.38 (s, 2C), 143.79 (s, 1C), 143.82 (s, 1C), 144.32 (s, 1C), 144.36 (s, 1C), 145.44 (s, 1C), 145.46 (s, 1C), 145.80 (s, 1C), 145.84 (s, 1C), 145.86 (s, 2C), 145.90 (s, 2C), 146.02 (s, 2C), 146.06 (s, 1C), 146.09 (s, 1C), 146.36 (s, 1C), 146.39 (s, 1C), 146.75 (s, 1C), 146.83 (s, 1C), 146.91 (s, 1C), 146.92 (s, 1C), 146.96 (s, 1C), 147.02 (s, 1C), 147.73 (s, 1C), 147.77 (s, 1C), 148.55 (s, 1C), 148.57 (s, 1C), 149.77 (s, 1C), 150.56 (s, 1C), 152.85 (s, 1C), 162.06 (s, 1C), 162.27 (s, 1C), 163.79 (s, 1C), 164.06 (s, 1C); ^{29}Si-NMR (80 MHz, 1:1 $CDCl_3$–CS_2) $\delta = -3.67$, -4.07; FAB-Mass 1227–1230 ($M^+ + 1$ cluster).

3d: brown solid, ^{1}H-NMR (500 MHz, 1:3 $CDCl_3$–CS_2) $\delta = 0.27$ (s, 9H), 0.30 (s, 9H), 0.36 (s, 9H), 0.40 (s, 9H), 3.45 (m, 1H), 5.11 (m, 1H), 6.11 (m, 1H), 6.56 (m, 1H), 6.74 (m, 1H), 7.2–7.4 (m, 3H), 7.5–7.6 (m, 2H); ^{13}C-NMR (126 MHz, 1:3 $CDCl_3$–CS_2) $\delta = 0.20$ (q), 0.38 (q), 0.48 (q), 0.56 (q), 31.80 (d), 52.25 (d), 62.96 (s,1C), 77.97 (s,1C), 122.69 (d), 127.99 (d), 128.38 (d), 128.58 (d), 130.92 (s), 132.09 (s,1C), 133.45 (s,1C), 134.32 (s, 1C), 134.52 (s), 135.07 (d), 136.17 (s, 1C), 138.74 (s, 1C), 138.76 (d), 139.44 (s,1C), 140.15 (s, 1C), 140.99 (s,1C), 141.09 (s,1C), 141.37 (s, 1C), 141.45 (s, 1C), 141.50 (s, 1C), 141.53 (s, 1C), 141.55 (s, 1C), 141.64 (s, 1C), 141.66 (s, 1C), 141.74 (s, 1C), 141.78 (s, 1C), 142.22 (s, 1C), 142.30 (s, 1C), 142.59 (s, 1C), 142.81 (s, 2C), 142.90 (s, 1C), 143.35 (s, 1C), 143.41 (s, 1C), 143.45 (s, 1C), 143.90 (s, 1C), 144.11 (s, 1C), 144.24 (s, 1C), 144.41 (s, 1C), 144.47 (s, 1C), 144.80 (s, 1C), 144.99 (s, 1C), 145.02 (s,1C), 145.11 (s, 2C), 145.25 (s, 1C), 145.39 (s, 1C), 145.60 (s, 1C), 145.68 (s, 2C), 145.80 (s, 1C), 145.88 (s, 1C), 145.89 (s, 1C), 145.96 (s, 1C), 146.01 (s, 2C), 146.09 (s, 2C), 146.24 (s, 1C), 146.39 (s, 1C), 147.08 (s, 1C), 147.93 (s, 1C), 155.49 (s, 1C), 158.00 (s, 1C), 159.95 (s, 1C), 160.43 (s, 1C); FAB-Mass 1223–1226 ($M^+ + 1$ cluster); UV-vis (toluene) λ_{max} (nm): 421, 447.

3e: red brown solid; ^{1}H-NMR (500 MHz, 1:1 $CDCl_3$–CS_2) δ 0.31 (s, 9H), 0.32 (s, 27H), 0.46 (s, 9H), 3.27 (m, 1H), 5.15 (m, 1H), 6.08 (m, 1H), 6.50 (m, 1H), 6.80 (m, 1H); ^{13}C-NMR (126 MHz, 1:1 $CDCl_3$–CS_2) δ 0.57 (q), 0.99 (q), 1.68 (q), 28.95 (d), 52.4 (d), 63.46 (s, 1C), 78.53 (s, 1C), 122.00 (d), 130.0 (s, *ipso*), 130.32 (d), 132.40 (s, 1C), 133.66 (s, 1C), 134.60 (s, 1C), 136.27 (s, 1C),138.87 (s, 1C), 139.56 (s, 1C), 140.28 (s, 1C), 140.96 (d), 141.13 (s, 1C), 141.26 (s, 1C), 141.53 (s, 1C), 141.64 (s,1C), 141.68 (s, 2C), 141.73 (s, 1C), 141.82 (s, 1C), 141.88 (s, 1C), 141.93 (s, 1C), 141.95 (s, 1C), 142.38 (s, 1C), 142.46 (s, 1C), 142.53 (s, 1C), 142.79 (s, 1C), 142.98 (s, 1C), 143.10 (s, 1C), 143.50 (s, 1C), 143.56 (s, 1C), 143.64 (s, 1C), 144.07 (s, 1C), 144.30 (s, 1C), 144.42 (s, 1C), 144.59 (s, 1C), 144.77 (s, 1C), 144.95 (s, 1C), 145.16 (s, 1C), 145.21 (s, 1C), 145.26 (s, 1C), 145.29 (s, 1C), 145.42 (s, 1C), 145.50 (s, 1C), 145.85 (s, 2C), 145.91 (s, 1C), 146.00 (s, 1C), 146.07 (s, 2C), 146.13 (s, 1C), 146.18 (s, 1C), 146.20 (s, 1C), 146.26 (s, 1C), 146.28 (s, 1C), 146.43 (s, 1C), 146.73 (s, 1C), 147.27 (s, 1C), 148.19 (s, 1C), 155.88 (s, 1C), 158.23 (s, 1C), 160.27 (s, 1C), 160.74 (s, 1C); ^{29}Si-NMR (80.0 MHz, 1:1 $CDCl_3$–CS_2) δ -76.87, -19.82, -13.08, -12.93, -12.39; FAB-Mass 1218–1220 ($M^+ + 1$ cluster).

3f: brown solid, ^{1}H-NMR (500 MHz, 1:1 $CDCl_3$–CS_2) δ 0.09 (s, 9H), 0.42 (s, 9H), 3.62 (s, 1H), 5.25 (s, 1H), 6.21 (m,1H), 6.69 (m, 1H), 6.74 (m, 1H), 7.3–7.4 (m, 3H), 7.62 (d, 2H, $J = 6.2$ Hz); ^{13}C-NMR (126 MHz, 1:1 $CDCl_3$–CS_2) δ 0.10 (q), 0.31 (q), 31.90 (d), 53.38 (d), 63.47 (s, 1C), 78.07 (s, 1C), 127.95 (d), 129.83 (d), 132.41 (s, 1C), 132.84 (s), 133.32 (s, 1C), 133.65 (s), 134.19 (s, 1C),136.01 (d), 136.59 (s, 1C), 138.90 (s, 1C), 139.50 (s, 1C), 140.40 (s, 1C), 141.09 (s, 1C), 141.21 (s, 1C), 141.51 (s,1C), 141.53 (s, 1C), 141.64 (s. 1C), 141.73 (s, 2C). 141.88 (s, 2C), 141.93 (s, 1C), 142.34 (s, 1C), 142.38 (s, 1C), 142.45 (s, 2C), 142.55 (s, 1C), 142.92 (s, 2C), 143.00 (s, 1C), 143.46 (s, 1C), 143.60 (s, 1C), 144.01 (s, 1C), 144.22 (s, 1C), 144.36 (s, 1C), 144.51 (s, 1C), 144.58 (s, 1C), 144.95 (s. 1C), 145.13 (s, 1C), 145.14 (s, 1C), 145.22 (s, 2C), 145.30 (s, 1C), 145.41 (s, 1C), 145.62 (s, 1C), 145.77 (s, 1C), 145.80 (s, 1C), 145.95 (s, 2C), 146.00 (s, 1C), 146.03 (s, 1C), 146.07 (s, 1C), 146.11 (s, 2C), 146.17 (s, 1C), 146.33 (s, 1C), 146.37 (s, 1C), 147.20 (s, 1C), 147.94 (s, 1C), 155.08 (s, 1C), 158.47 (s, 1C), 160.33 (s, 1C), 160.62 (s, 1C); FAB-Mass 1230–1232 ($M^+ + 1$ cluster); UV-vis (toluene) λ_{max} (nm): 422, 445.

3g: brown solid, ^{1}H-NMR (500 MHz, 1:1 $CDCl_3$–CS_2) δ 1.22 (d, 3H, *J* = 7.2 Hz), 1.23 (d, 3H, *J* = 7.1 Hz), 1.24 (d, 3H, *J* = 7.4 Hz), 1.27 (d, 3H, *J* = 7.4 Hz), 1.31 (d, 3H, *J* = 7.4 Hz), 1.33 (d, 3H, *J* = 7.5 Hz), 1.35 (d, 3H, *J* = 7.7 Hz), 1.44 (d, 3H, *J* = 7.5 Hz), 1.5–1.6 (m, 4H), 1.7–1.9 (m, 4H), 3.40 (m, 1H), 4.93 (m, 1H), 6.12 (m, 1H), 6.57 (m, 1H), 6.91 (m, 1H). 6.3–6.4 (m, 3H), 6.6–6.7 (m. 2H); ^{13}C-NMR (126 MHz, 1:1 $CDCl_3$–CS_2) δ 11.24 (d), 11.54 (d), 12.79 (d), 14.53 (d), 18.49 (q), 18.52 (q), 18.56 (q, two carbons), 18.62 (q), 18.84 (q), 19.06 (q), 19.34 (q), 30.38 (d), 49.81 (d),64.27 (s, 1C), 78.05 (s, 1C), 122.48 (d), 127.05 (d), 127.85 (d), 129.23 (d), 129.23 (s), 132.82 (s), 133.44 (s, 1C), 134.13 (s, 1C), 134.28 (s, 1C), 134 96 (d), 135.95 (s, 1C), 138.86 (s, 1C), 139.54 (s, 1C), 139.71 (d), 140.06 (s. 1C), 140.09 (s, 1C), 141.19 (s, 1C), 141.37 (s, 1C), 141.44 (s, 1C), 141.51 (s, 1C), 141.60 (s, 1C), 141.69 (s, 1C), 141.73 (s, 1C), 141.84 (s, 1C), 141.89 (s, 2C), 142.34 (s, 1C), 142.42 (s, 1C), 142.47 (s, 1C), 142.48 (s, 1C), 142.51 (s, 1C), 142.92 (s, 1C), 142.95 (s, 1C), 143.43 (s, 1C), 143.50 (s, 1C), 143.82 (s, 1C), 144.04 (s, 1C), 144.23 (s, 1C), 144.35 (s, 1C), 144.50 (s, 1C), 144.83 (s, 1C), 145.11 (s, 1C), 145.16 (s. 2C), 145.21 (s, 1C), 145.37 (s. 2C), 145.44 (s. 1C), 145.80 (s, 1C), 145.88 (s, 1C), 145.93 (s, 1C), 145.99 (s, 2C), 146.10 (s, 3C), 146.21 (s, 1C), 146.27 (s, 1C), 146.30 (s, 1C), 146.49 (s, 1C), 147.17 (s, 1C), 148.14 (s, 1C), 155.58 (s. 1C), 157.93 (s, 1C), 159.23 (s, 1C), 159.39 (s, 1C); FAB-Mass 1102–1104 ($M^+ + 1$ cluster); UV-vis (toluene) λ_{max} (nm): 419, 444.

5j: brown solid, ^{1}H-NMR (500 MHz, 1:1 $CDCl_3$–CS_2) δ 0.234 (s, 9H), 0.306 (s, 9H), 0.52 (s, 9H), 3.23 (d, 1H, *J* = 6.0 Hz H^{5e}), 4.74 (t, 1H, *J* = 1.7 Hz, H^{5d}), 5.91 (m, 1H, H^{5f}), 5.98 (m, 1H. H^{5g}), 6.84 (m, 1H. H^{5h}); ^{13}C-NMR (126 MHz, 1:1 $CDCl_3$–CS_2) δ −3.42 (q), 0.50 (q), 1.03 (q), 29.66 (d, C^{5e}), 51.59 (s, C^{5d}), 63.24 (s, C^{5a}), 77.26 (s, C^{5b}). 120.48 (d, C^{5g}), 130.34 (d, C^{5f}), 131.05 (s, C^{5i}), 135 22 (d, C^{5h}), 154.07 (s. C^{5c}), 156.21 (s, C$^{5c'}$); FAB-Mass 1044–1046 ($M^+ + 1$ cluster, as mixtures of **5j, 6j, 7j**); UV-vis (toluene) λ_{max} (nm): 417, 446 (as mixtures of **5j, 6j, 7j**).

5k: brown solid, ^{1}H-NMR (500 MHz, 1:1 $CDCl_3$–CS_2) δ 0.6–1.2 (m, 45H), 3.45 (d, 1H, *J* = 5.9 Hz H^{5e}), 4.68 (s, 1H, H^{5d}), 5.9–6.0 (m, 2H. H^{5f}, H^{5g}), 6.92 (d, 1H. *J* = 5.4 Hz, H^{5h}); ^{13}C-NMR (126 MHz, 1:1 $CDCl_3$–CS_2) δ 2.50 (t), 5.47 (t), 5.75 (t), 7.78 (q), 8.81 (q), 9.11 (q), 27.04 (d, C^{5e}), 51.46 (d, C^{5d}), 63.95 (s, C^{5a}), 77.22 (s, C^{5b}), 120.92 (d. C^{5g}), 130.47 (d, C^{5f}), 132.38 (s, C^{5i}), 136 52 (d, C^{5h}), 154.45 (s, C^{5c}), 156.43 (s, C$^{5c'}$); FAB-Mass 1170–1172 ($M^+ + 1$ cluster, as mixtures of **5k**, **6k**, **7k**); UV-vis (toluene) λ_{max} (nm): 419, 448 (as mixtures of **5k**, **6k**, **7k**).

5l: brown solid, ^{1}H-NMR (500 MHz, 1:1 $CDCl_3$-CS_2) δ 0.26 (s, 9H), 0.30 (s, 9H), 0.53 (s. 9H), 1.72 (s, 3H, C^{5f}–C*H*$_3$), 3.02 (s, 1H, H^{5e}), 4.67 (s, 1H, H^{5d}), 5.85 (d, 1H, *J* = 5.5 Hz, H^{5g}), 6.89 (d, 1H, *J* = 5.5 Hz, H^{5h}); ^{13}C-NMR (126 Mhz, 1:1 $CDCl_3$–CS_2) δ −1.78 (q), 0.55 (q), 1.08 (q). 24.73 (q, C^{5f}–C*H*$_3$), 34.66 (d. C^{5e}), 53.73 (s, C^{5d}), 64.38 (s, C^{5a}), 76.30 (s, C^{5b}), 119.02 (d, C^{5g}), 128.16 (s, C^{5f}), 137.56 (d. C^{5h}), 139 30 (s, C^{5i}), 154.65 (s, C^{5c}), 156.28 (s, C$^{5c'}$); FAB-Mass 1058–1060 ($M^+ + 1$ cluster, as mixtures of **5l**, **6l**, **7l**); UV-vis (toluene) λ_{max} (nm): 423, 448 (as mixtures of **5l**. **6l**, **7l**).

5m: red brown solid, ^{1}H-NMR (500 MHz, 1:1 $CDCl_3$–CS_2) δ 0.19 (s, 9H), 0.31 (s, 9H), 0.54 (s, 9H), 1.91 (s, 3H, H^{5k}), 2.29 (s. 3H, H^{5j}), 3.14 (d. 1H, *J* = 5.9 Hz, H^{5e}), 4.70 (s. 1H, H^{5d}), 5.62 (d,1H, *J* = 5.9 Hz, H^{5f}); ^{13}C-NMR (126 MHz, 1:1 $CDCl_3$–CS_2) δ −2.95 (q), 1.36 (q), 1.41 (q), 20.47 (q, C^{5k}), 24.36 (q, C^{5j}), 29.25 (d, C^{7j}), 53.07 (d. C^{5d}), 64.91 (s. C^{5a}), 76.54 (s, C^{5b}), 125.99 (s, C^{5h}), 126 50 (d, C^{5f}), 129.61 (s, C^{5g}), 132.82 (s, 1C), 133.73 (s. 1C), 134.41 (s, 1C), 135. 21 (s, 1C), 139.13 (s, 1C), 139.16 (s, 1C), 139.50 (s, 1C), 140.91 (s. 1C), 141.03 (s, 1C), 141.31 (s, 1C), 141.38 (s, 1C), 141.54 (s, 1C), 141.63 (s, 1C), 141.78 (s. 1C), 141.84 (s, 2C), 141.88 (s. 1C), 141.91 (s, 1C), 142.42 (s, 2C), 142. 48 (s. 1C), 142.59 (s, 1C), 142.96 (s, 2C), 143.34 (s, 1C), 143.48 (s, 1C), 143. 62 (s, 1C). 143.78 (s, 1C), 144.03 (s, 1C), 144.25 (s, 1C), 144.33 (s, 1C), 144. 48 (s. 1C), 145.06 (s, C5f + 1C), 145.14 (s, 1C), 145.17 (s, 1C), 145.26 (s. 1C), 145.28 (s. 1C), 145. 39 (s, 1C), 145.71 (s, 1C), 145.77 (s, 1C), 145. 93 (s, 1C), 146.00 (s, 1C), 146.05 (s, 1C). 146. 08 (s, 1C). 146.10 (s, 1C), 146.12 (s, 2C), 146. 19 (s, 1C), 146.21 (s. 1C), 146.38 (s, 1C). 146. 43 (s, 1C), 147.07 (s, 1C), 147.34 (s, 1C). 148.00 (s, 1C), 154.77 (s, C5c), 156.12 (s, C), 160. 04 (s. 1C), 160.35 (s, 1C); FAB-Mass 1072–1074 ($M^+ + 1$ cluster).

6j: ^{1}H-NMR (500 MHz, 1:1 $CDCl_3$–CS_2) δ 0.225 (s, 9H), 0.322 (s. 9H), 0.46 (s, 9H), 2.79 (m, 1H, H^{6p}), 5.09 (m, 1H, H^{6m}), 6.02 (m, 1H, H^{6n}), 6.61 (m, 1H, H^{6o}), 6.68 (m, 1H, H^{6q}); ^{13}C-NMR (126 MHz, 1:1 $CDCl_3$–CS_2) δ −3.21 (q), 0.42 (q), 0.45 (q), 36.22 (d, C^{6p}), 52.38 (d, C^{6m}). (63.30, s, C^{6j}), 78.20 (s, C^{6k}), 122.27 (d, C^{6o}), 126 53 (d, C^{6n}), 130.58 (s, C^{6r}), 136.96 (d, C^{6q}). 155.48 (s, C^{6l}), 158.62 (s. C$^{6l'}$).

6k: ^{1}H-NMR (500 MHz, 1:1 $CDCl_3$–CS_2) δ 0.6–1.2 (m, 45H), 2.96 (m, 1H, H^{6p}), 7.17 (m, 1H. H^{6m}), 6.02

(m, 1H, H^{6n}), 6.58 (m, 1H, H^{6o}), 6.74 (m, 1H, H^{6q}); ^{13}C-NMR (126 MHz, 1:1 $CDCl_3$–CS_2) δ 2.80 (t), 5.49 (t), 5.56 (t), 7.73 (q), 8.88 (q), 9.09 (q) 32.78 (d, C^{6p}), 52.30 (d, C^{6m}), (64.03, s, C^{6j}), 78.31 (s, C^{6k}), 122.61 (d, C^{6o}), 126 73 (d, C^{6n}), 131.72 (s, C^{6r}), 138.21 (d, C^{6q}), 156.03 (s, C^{6l}), 158.69 (s, $C^{6l'}$).

6l: ^{1}H-NMR (500 MHz, 1:1 $CDCl_3$–CS_2) δ 0.26 (s, 9H), 0.32 (s, 9H), 0.46 (s, 9H), 1.87 (s, 3H, $C^{6o}-CH_3$), 2.73 (t, 1H, $J = 5.4$ Hz, H^{6p}), 5.07 (br s, 1H, H^{6m}), 6.36 (br s, 1H, H^{6n}), 6.68 (br s, 1H, H^{6q}); ^{13}C-NMR (126 MHz, 1:1 $CDCl_3$–CS_2) δ -1.61 (q), 0.46 (q), 0.51 (q), 24.20 (q, $C^{6o}-CH_3$), 40.74 (d, C^{6p}), 54.02 (d, C^{6m}), 63.89 (s, C^{6j}), 78.47 (s, C^{6k}), 118.25 (d, C^{6n}), 130.17 (s, C^{6o}), 134.04 (s, C^{6r}), 137.81 (s, C^{6q}), 155.66 (s, C^{6l}), 159.11 (s, $C^{6l'}$).

7j: ^{1}H-NMR (500 MHz, 1:1 $CDCl_3$–CS_2) δ 0.16 (s, 9H), 0.319 (s, 9H), 0.48 (s, 9H), 2.71 (m, 1H, H^{7p}), 5.29 (m, 1H, H^{7m}), 6.02 (m, 1H, H^{7n}), 6.54 (m, 1H, H^{7o}), 6.65 (m,1H, H^{7q}); ^{13}C-NMR (126 MHz, 1:1 $CDCl_3$–CS_2) δ -2.75 (q), 0.45 (q), 0.53 (q), 34.82 (d, C^{7p}), 54.18 (d, C^{7m}), 63.61 (s, C^{7j}), 78.27 (s, C^{7k}), 123.17 (d, C^{7o}), 127.82 (d, C^{7n}), 131.72 (s, C^{7r}), 137 31 (d, C^{7q}), 155.51 (s, C^{7l}), 158.22 (s, $C^{7l'}$).

7k: ^{1}H-NMR (500 MHz, 1:1 $CDCl_3$–CS_2) δ 0.6–1.2 (m, 45H), 2.87 (m, 1H, H^{7p}), 5.34 (m, 1H, H^{7m}), 6.04 (m, 1H, H^{7n}), 6.53 (m, 1H, H^{7o}), 6.70 (br s, 1H, H^{7q}); ^{13}C-NMR (126 MHz, 1:1 $CDCl_3$–CS_2) δ 2.68 (t), 5.47 (t, two carbons), 7.66 (q), 8.60 (q), 9.11 (q), 31.64 (d, C^{7p}), 54.10 (d, C^{7m}), 64.57 (s, C^{7j}), 78.40 (s, C^{7k}), 122.71 (d, C^{7o}), 128.20 (d, C^{7n}), 133.21 (s, C^{7r}), 137 77 (d, C^{7q}), 155.76 (s, C^{7l}), 158.16 (s, $C^{7l'}$).

7l: ^{1}H-NMR (500 MHz, 1:1 $CDCl_3$–CS_2) δ 0.18 (s, 9H), 0.32 (s, 9H), 0,48 (s, 9H), 2,69 (d, 1H, $J = 9.0$ Hz, H^{7p}), 5.31 (s, 1H, $J = 7.6$ Hz, H^{7m}), 6.22 (br s, 1H, H^{7n}), 6.68 (br s, 1H, H^{7q}); ^{13}C-NMR (126 MHz, 1:1 $CDCl_3$–CS_2) δ -0.99 (q), 0.70 (q), 0.76 (q), 25.02 (q, $C^{6o}-CH_3$), 38.80 (d, C^{7p}), 56.51 (d, C^{7m}), 64.25 (s, C^{7j}), 78.14 (s, C^{7k}), 118.74 (d, C^{7n}), 130.47 (s, C^{7o}), 136.26 (s, C^{7r}), 138 40 (d, C^{7q}), 155.81 (s, C^{7l}), 158.36 (s, $C^{7l'}$).

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