Sterically Hindered Free Radicals, 21 [1]

1,2- and 1,4-Additions of Diphenylmethyl Radicals to Substituted Acrylonitriles

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Received November 27, 1992

Key Words: Radical additions / Acrylonitriles / Diphenylmethyl radicals / Steric effects

Additions of the substituted diphenylmethyl radicals Ar^1-$Ar^2\dot{C}R$ **2** (R = CMe_3, $SiMe_3$, $GeMe_3$, $SnMe_3$, $OSiMe_3$, CF_3, CO_2Me, CN) to various acrylonitriles $CH_2=C(X)CN$ **3** (X = SMe, S*i*Pr, S*t*Bu, OAc, $OSiMe_3$, $OSiEt_3$, OMe, OEt) lead to 1,2-**5** or 1,4-adducts **6** (ketenimines), depending mainly on the steric hindrance by the substituents R and X. Bulky substituents like *t*Bu in **2** and *t*BuS in the acrylonitrile favour the formation of the extended and nearly strainless ketenimine system **6** (1,4-adduct); smaller substituents like $OSiMe_3$ (radical **2**) and SMe, OAc, $OSiMe_3$, $OSiEt_3$, OMe, OEt (acrylonitrile) allow isolation of the sterically crowded 1,2-adducts. Substituents of intermediate bulkiness like CF_3 (radical **2**) and S*i*Pr (acrylonitrile) give a mixture of 1,2-adducts (**6cb**, **hb**) and dimers **7** of the adduct radicals **4** (**7cb**, **hb**). The voluminous *t*Bu group directly bound to the olefin (**3j**, **k**) prevents addition. The latter is generally reversible, and the various adducts **5**, **6**, or **7** dissociate to the adduct radicals **4** and/or fragment to the initial radicals **2** at temperatures which reflect the steric strains of the corresponding substituents R, X. The complete inertness, even toward the electron-rich olefin **3i**, of the electrophilic α-carbonyl-substituted radicals **2q–s** (R = CHO, COMe, COPh) in the above additions is discussed. Additions of the radicals **2a–c**, **f**, **i**, **n**, **o** to the conjugated olefin **3n** are described and are in accordance with the conclusion that steric effects predominate in adduct formation, whereas electronic effects are of distinct but minor importance.

Over the past decade, free-radical carbon-carbon couplings have become a powerful method for impressive chemo-, regio-, and stereoselective synthesis[4–8]. In this context the additions of carbon-centered radicals to unsaturated systems represent one of the most useful applications of free-radical chemistry and are of great importance for polymer synthesis.

Experimental results[9–11] and theoretical calculations[12,13] indicate that the addition of small alkyl radicals to alkenes is usually exothermic and irreveresible, with early, unsymmetrical, reactant-like transition states, dominated by SOMO-LUMO (nucleophilic radicals) or SOMO-HOMO (electrophilic radicals) interactions[10]. However, "the complex interplay of polar, steric and bond-strengh terms"[14] seems to govern product formation[7–10].

Additions of bulky, resonance-stabilized radicals to alkenes are rare in the literature. The trityl radical appears to add only to conjugated systems, like isoprene, whereas it remains inert toward isolated double bonds[15,16]. We have recently reported our first results on the addition of sterically hindered diphenylmethyl radicals **2a–e** to the captodative (c,d)-substituted olefin **3c**. A novel, in the light of the c,d-concept an unexpected[17] 1,4-addition takes place providing the ketenimine adduct **6a**[18] (Scheme 1). These radicals retain their nucleophilic character as may be judged from their SOMO energy (IP for $Me^{\bullet}$: 9.84 eV[19a], $Ph\dot{C}H_2$: 7.20[19b], $^{n}h_2\dot{C}H$: 6.80[19c], and $Ph_3C^{\bullet}$: 7.26[19d]), and the bonds formed when attacking alkenes must not be stronger than ca. 64 kcal/mol[20]. Consequently, the addition should be a slightly exothermic or, more likely, a thermoneutral process with a transition state located late on the reaction coordinate, thus leading to an increased importance of steric interactions.

Extending our previous work[18], we present here the results of more than 60 additions of the substituted diphenylmethyl radicals **2** to various olefins and show that steric effects indeed are predominant in determining the product formation.

Results and Discussion

Table 1 contains the results of the additions of the radicals **2** to olefins **3**. Generally, **2** initially attacks the methylenic group of **3** leading to the adduct radical **4** (Scheme 1). In the second step, the adduct radical has three options; to dimerize to **7** or to be trapped by another radical **2** producing either the 1,2-adduct **5** or the ketenimine-type 1,4-adduct **6**. Moreover, **4** reverts to the initial radical **2** and to **3**. As radical source we employed the dimers **1**[21–25] which dissociate reversibly yielding **2**.

The most sterically hindered[21a] radicals **2a**, **b** (R = *t*Bu) give on the addition of the substituted olefins **3a–c** exclusively the nearly strainless (as indicated by spheric models) 1,4-adducts **6aa**, **ab**, **ac**, **bc**, regardless of the degree of bulkiness of the alkylthio substituent. After replacement of the alkylthio group by OAc, as in **3d**, only the 1,2-adduct **5bd** was formed. Radicals **2a** and **b** should have the same steric requirements.

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The radical **2c**, which is little less hindered[21a], reacts with the above olefins to yield all possible adducts. Whereas the small methylthio substituent in **3a** allows the formation of the sterically hindered 1,2-adduct **5ca**, the bulky *t*BuS group in **3c** leads exclusively to the ketenimine **6cc**, the 1,4-adduct. In the intermediate case of the *i*PrS substituent in **3b** we obtain both the adduct dimer **7cb** (isolated as a crystalline, air-insensitive compound) and the 1,4-adduct **6cb** (identified by the ketenimine infrared band at 2000 cm^{-1}). Again, the addition to the OAc- or $OSiMe_3$-substituted olefins **3d, e** yields, like in the addition of **2b**, only the 1,2-adducts **5cd, ce**.

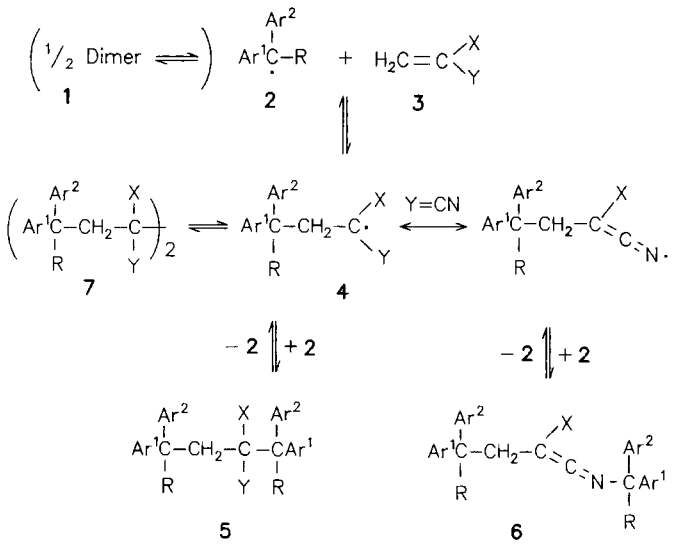
Obviously, the bulkiness of both the radical and the olefin substituents are the dominant parameters in determining the type of the adduct formed; small substituents allow the formation of the 1,2-adducts, bulkier lead to the almost strainless 1,4-adducts. The steric repulsions seem to increase in the order 1,4-adduct (**6**) < adduct dimer (**7**) < 1,2-adduct (**5**), in line with observations made by means of spheric models. All additions so far investigated are reversible (Scheme 1). By heating the various adducts in the cavity of the ESR spectrometer we obtain the spectra of the corresponding initial (**2**) and/or adduct radicals (**4**). The fragmen-

Table 1. Products of the additions according to Scheme 1

	Radical 2			Olefin 3			Product[a]			Fragment. Temp. (°C)	
	Ar^1	Ar^2	R		X	Y	5	6	7	4[a]	2
a	Ph	Ph	*t*Bu	**a**	SMe	CN		**aa**			70
				b	S*i*Pr	CN		**ab**		40	65
				c	S*t*Bu	CN		**ac**[18]		22	
b	2 × (4-Biph)		*t*Bu	**c**	S*t*Bu	CN		**bc**		20	60
				d	OAc	CN	**bd**			60	
c	Ph	Ph	$SiMe_3$	**a**	SMe	CN	**ca**			90	
				b	S*i*Pr	CN		**cb**[b]	**cb**	60[c]	115[c]
				c	S*t*Bu	CN		**cc**[18]		25	
				d	OAc	CN	**cd**				100
				e	$OSiMe_3$	CN	**ce**[18]				100
d	Ph	Ph	$GeMe_3$	**c**	S*t*Bu	CN		**dc**[18]		[d]	[d]
e	Ph	Ph	$SnMe_3$	**c**	S*t*Bu	CN		**ec**[18]		[d]	[d]
f	Ph	Ph	$OSiMe_3$	**a**	SMe	CN	**fa**[b]			[d]	[d]
				b	S*i*Pr	CN			**fb**[b]	70	
				d	OAc	CN	**fd**				150
				e	$OSiMe_3$	CN	**fe**[18]			[d]	[d]
				f	$OSiEt_3$	CN	**ff**			[d]	[d]
				g	OMe	CN	**fg**				110
				h	OEt	CN	**fh**				90
				j	*t*Bu	H	no reaction				
				k	*t*Bu	Me	no reaction				
g	Ph	4-Biph	$OSiEt_3$	**e**	$OSiMe_3$	CN	**ge**[b]			[d]	[d]
h	2 × (4-*t*BuC$_6$H$_4$)		CF_3	**a**	SMe	CN			**ha**		140
				b	S*i*Pr	CN		**hb**	**hb**	100[e]	70[e]
				c	S*t*Bu	CN		**hc**		[d]	[d]
i	Ph	Ph	Ph	no reaction with **3c–e**							
				m	Ph	Ph	no reaction				
n	[f]		4-MeC$_6$H$_4$	**d**	OAc	CN	**nd**				55
				h	OEt	CN	**nh**			[d]	[d]
o	[f]		4-MeOC$_6$H$_4$	**c**	S*t*Bu	CN	no reaction				
				d	OAc	CN	**od**			[d]	[d]
				e	$OSiMe_3$	CN	**oe**				55
j	Ph	Ph	CO_2Me	**c**	S*t*Bu	CN		**jc**[b]			
				e	$OSiMe_3$	CN	**je**			[d]	[d]
k	Ph	Ph	CN	**e**	$OSiMe_3$	CN	**ke**[a]			[d]	[d]
l	2 × (2-MeC$_6$H$_4$)		CN	**c**	S*t*Bu	CN	no reaction[24]				
m	2 × (4-*t*BuC$_6$H$_4$)		CN	no reaction with **3c, k**							
q	Ph	Ph	CHO	**i**	OEt	OEt	no reaction[24]				
				no reaction with **3c–e, i, k, l**[24]							
r	Ph	Ph	COMe	no reaction with **3c, e, k**[24]							
s	Ph	Ph	COPh	**l**	Ph	H	no reaction[24]				
p	[g]		2,4,6-Me$_3$C$_6$H$_2$	no reaction with **3c, d, h, k**[25]							

[a] The first letter denotes the radical **2** involved, the second one the type of the olefin **3**. The notion "no reaction" means recovering of the uncharged starting material. – [b] Not isolated (but spectroscopically identified). – [c] **7cb** fragments at 60 °C into adducts radicals **4** and at 115 °C to **2c**. – [d] Not measured. – [e] **6hb** fragments at 70 °C, **7hb** at 100 °C. – [f] Ar^1Ar^2C = 9-Fluorenyl, see formula **2n**, **2o**. – [g] Ar^1Ar^2C = 1,3-Dioxo-2-indanyl, see formula **2p**.

Scheme 1



tation temperature (Table 1) usually decreases as the radical[21a] and olefin substituents exhibit greater steric hindrance: tBu > $SiMe_3$ > $OSiMe_3$, and StBu > SiPr > SMe, consistent with the E_S values for the corresponding alkyl groups[26].

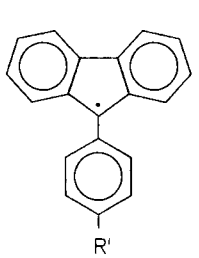
The ESR spectra of the adduct radicals **4** show temperature-dependent line-broadening effects owing to the restricted rotation of the methylene group[18]. **4cc** (R = $SiMe_3$) exhibits at 25°C a broad-line spectrum which changes at 90°C to a triplet of triplets [$\alpha^H_{CH_2}$ = 1.005 (2H), α^H_{CN} = 0.275 mT], representing, on the ESR time scale, the fast interconversion limit of the two methylene protons having the same time-average hyperfine splitting[27,28]. A slow interconversion limit could not be obtained because the signal disappears already at 5°C. On the other hand, the more hindered adduct radicals **4ac, bc** (R = tBu) fragment already at 60 to 65°C to the intial radicals **2a**, **2b**, thus preventing the detection of the fast interconversion limiting state as in the case of the radical **4cc**. At 22°C the broad central lines of the spectrum disappear completely indicating a state being closer to the slow interconversion limit than in the case of **4cc**. The difference reflects the larger steric repulsion of the tBu group in comparison with Me_3Si in the radicals **4ac, bc**, and **cc**, respectively.

The addition of ketyl radicals **2f, g** (R = $OSiMe_3$, $OSiEt_3$), the less hindered in this series, to the above olefins affords almost exclusively 1,2-adducts. In one case (olefin **3b**) the adduct dimer **7fb** is isolated. A comparison with **2c** (R = $SiMe_3$) shows that the presence of an oxygen atom between the radical center and the substituent $SiMe_3$ leads to a considerably more flexible system, allowing the formation of the 1,2-adducts **5fa**, **5d–h**, **5ge** regardless of the bulkiness of the olefin substituent. In contrast, no addition takes place in the case of the bulky olefins **3j, k**.

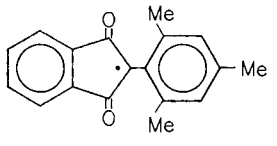
The marked influence of steric effects upon the type of adduct formed is further demonstrated by considering the addition of the α-trifluoromethyl-substituted radical **2h** to the alkenes **3a–c**. While the small methylthio group leads to the dimer **7ha**, the voluminous StBu gives rise to the formation of the 1,4-adduct **6hc**. In the intermediate case of the SiPr group, both the 1,4- adduct **6hb** (reaction time 3.5 h at 65°C) and the adduct dimer **7hb** (18 h at 65°C) are obtained. Obviously, the formation of **6hb** (ketenimine) is kinetically controlled, whereas prolonged heating leads to the thermodynamically more stable **7hb**[28a]. **6hb** dissociates at 70°C, and **7hb** at 100°C to the intial **2h** and the adduct radical **4hb**, respectively, the whole process evidently being reversible. This differs from the addition of **2c** to olefin **3b** where both adducts are formed (see above).

On the other hand, there are no indications of a possible 1,3-nitrogen-to-carbon rearrangement of the diphenylmethyl moiety of the ketenimines **6** leading to the 1,2-adducts **5**. The formation of the latter by such a rearrangement (without anticipating a mechanism) is not observed, but cannot be excluded, particularly since similar 1,3-N–C shifts are known[29]. In our case, the kentenimine adduct **6** fragments on heating to the starting radical **2** and the adduct radical **4**. The latter preferentially undergoes elimination of a second radical **2** to yield a stable compound, the olefin **3**.

A further example indicating the importance of steric factors is given by the fact that while the triphenylmethyl radical **2i** fails to react with the alkenes **3c–e, m**, the more planar fluorenyl radicals **2n, o** easily react with these alkenes to afford even 1,2-adducts. However, this explanation is not satisfactory if we consider that the addition of the more sterically hindered radical **2a** (R = tBu), in contrast to **2i**, yields 1,4-adducts (see above). On the other hand, it is well-known[9,10] that radicals bearing strongly resonance-stabilizing substituents, like phenyl, decelerate enormously their addition process, probably by increasing the activation energy and weakening the incoming carbon-carbon bond. This is clearly demonstrated by comparing the rates of addition of the *tert*-butyl and the benzyl radical to various olefins[30]. So, although all of the considered radicals retain their nucleophilic character, replacement of a *tert*-butyl by a phenyl group (**2a** to **2i**) causes the carbon-carbon bond formed by the addition to become weaker and thus the overall reaction slightly endothermic[20]. Consequently, a later transition state is expected which leads to a higher influence of the steric effects. Moreover, it should be stressed that mesomeric substituents, like phenyl or carbonyl, have considerably large rotational barriers[20c,37] making the radical center resistant to any deformation necessary for the approach to the transition state. Fischer et al.[30] make the resistance of



2n (R'=Me)
2o (R'=OMe)



2p

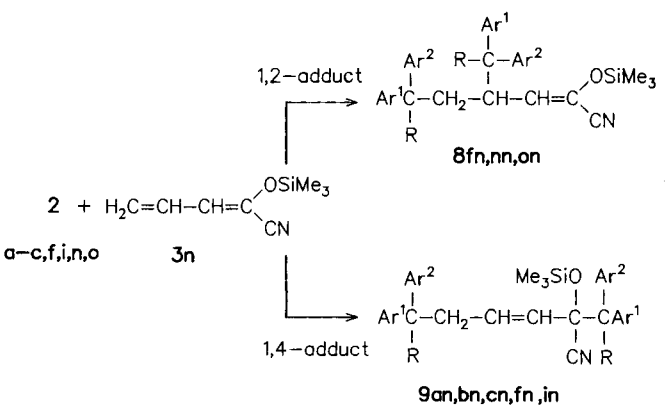
the benzyl radical toward pyramidalization responsible for its low reactivity in additions to double bonds.

Even harder to explain is the complete failure of the electrophilic[7,33–36] radicals **2p–s** (R = CHO, COMe, COPh) to add to various olefins **3c–e,h,i,k,l** (Table 1), although the related radicals **2j,k** (R = CO_2Me, CN) probably ambiphilic in character[7,31,32], behave "normally". Comparing for example the α-methoxycarbonyl radical **2j** with the α-acetyl radical **2r**, we note the increased electrophilic character of the latter and the similarity in steric requirements. Moreover, as we will describe later, **2r**, in contrast to $Ph_3C^{\bullet}$, remains unreactive even toward conjugated dienes. Even more surprising is the failure of any addition to the electron-rich olefin **3i** (X = Y = OEt). However, we should note that a recent theoretical study[38] suggests that 1,1-dialkoxyolefins suffer from a large ground-state stabilization which is responsible for their low reactivity.

The question to what extent nucleophilic and electrophilic radicals differ, during an addition to an alkene, in their corresponding transition states is still open. First experimental and theoretical results provide evidence that the transition state in both cases possesses similar geometries. However, the transition state is formed later on the reaction coordinate during the addition of an electrophilic radical with consequently larger contribution by steric effects[13]. Are the above conclusions and the fact that **2p–s** constitute carbon-centered radicals bearing strongly resonance-stabilizing substituents (phenyl, carbonyl) sufficient to account for the inertness of these radicals? Although the final answer is open, the captodative concept of "radicophilic olefins"[17a], which initiated many useful work in the past decade seems unable[17c] to throw more light on these complicated relationships.

Finally, we present some additions of the radicals **2a–c,f,i,n,o** to the conjugated olefin **3n** (Scheme 2). 1,2- or 1,4-addition to the diene system takes place, depending on the steric demands of the radical substituents. This is consistent with the conclusions and observations made above. The addition of radicals **2a–c,i** produce 1,4-adducts, those of **2n,o** 1,2-adducts. The addition of ketyl radical **2f** yields both the 1,2- and 1,4-adducts in a 4:1 molar ratio. In no case does the cyano group take part in these reactions of **3n**.

Scheme 2



We are grateful to the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie* for the support of this work. A. P. thanks the *Alexander von Humboldt Foundation* for a fellowship.

Experimental

Starting materials **1a**[21a], **1b,h,m**[22], **1c–e**[21b], **1f**[21c], **1g**[23], **1i**[21d], **1j,k,q–s**[21e], **1l**[24], **1m**[20], **1n**[21g], **1o**[21f], **1p**[25], **3a,c**[39d], **3d**[39b,c], **3e**[39d], **3h**[39e], **3i**[39f], **3k**[39g], **3n**[39d] were prepared according to literature procedures.

All reactions with air-sensitive compounds were performed under dry Ar. Instrumental equipment and methods have been published in refs.[18,21a].

N-[5,5-Dimethyl-2-(methylthio)-4,4-diphenyl-1-hexenylidene]-2,2-dimethyl-1,1-diphenyl-1-propanamine (**6aa**): A solution of 0.6 g (1.36 mmol) of **1a** and 0.15 g (1.5 mmol) of **3a** in 2 ml of benzene was heated at 40°C for 4 h. The progress of the reaction was monitored by ^{1}H-NMR or/and IR spectroscopy. The solvent was evaporated, and to the residue was added 3 ml methanol. A white solid precipitated and was recrystallized from methanol, 0.64 g (87%); m.p. 117°C (dec). – IR (KBr): $\tilde{\nu}$ = 2010 cm^{-1} (C=C=N). – ^{1}H NMR ($CDCl_3$): δ = 1.06 [s, 9H, $C(CH_3)_3$], 1.17 [s, 9H, $C(CH_3)_3$], 2.68 (s, 2H, CH_2), 7.05–7.44 (m, 20 aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 19.81, 29.47 [$C(CH_3)_3$], 28.19 (SCH_3), 36.47, 39.06 [$C(CH_3)$], 37.86 (CH_2), 58.81 ($PhC-CH_2$), 60.95 (C=C=N), 80.03 (Ph_2C-N), 125.44–131.57 ($C_{ar}H$), 144.71, 144.90 (C_{ar}), 182.79 (C=C=N).

$C_{38}H_{45}NS$ (547.8) Calcd. C 83.31 H 8.28 N 2.56
Found C 83.70 H 8.30 N 2.45

2-[(1-Methylethyl)thio]-2-propenenitrile (**3b**): The unknown olefin was synthesized according to a literature procedure[39a] in 76% yield; b.p. 63–65°C/12 Torr. – IR (film): $\tilde{\nu}$ = 2220 cm^{-1} (C≡N). – ^{1}H NMR (CCl_4): δ = 1.45 (d, 6H, CH_3), 3.47 [sept, 1H, $CH(CH_3)_3$], 6.03 (d, 2 olefinic H).

N-{5,5-Dimethyl-2-[(1-methylethyl)thio]-4,4-diphenyl-1-hexenylidene}-2,2-dimethyl-1,1-diphenyl-1-propanamine (**6ab**): According to the preparation of **6aa**, from 0.50 g (1.1 mmol) of **1a** and 0.14 g (1.2 mmol) of **3b** in 2 ml of benzene (16 h at 45°C) 0.52 g (87%) of crude **6ab** was obtained. – IR (film): $\tilde{\nu}$ = 2020 cm^{-1} (C=C=N). – ^{1}H NMR (CCl_4): δ = 0.97 [s, 9H, $C(CH_3)_3$], 1.05 [s, 9H, $C(CH_3)_3$], 1.37 [d, 3H, $CH(CH_3)_2$], 3.21 (s, 2H, CH_2), 3.64 [sept, 1H, $CH(CH_3)_2$], 6.83–7.55 (m, 20 aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 22.75, 28.15 [$C(CH_3)_3$], 29.49 [$SCH(CH_3)_2$], 37.92, 39.13 [$C(CH_3)_3$], 38.41 (SCH), 39.18 (CH_2), 58.61 (C=C=N), 58.96 ($PhC-CH_2$), 79.58 (Ph_2C-N), 125.41–130.31 ($C_{ar}H$), 144.40, 144.75 (C_{ar}), 181.38 (C=C=N).

1,1-Di(biphenyl-4-yl)-N-{4,4-di(biphenyl-4-yl)-2-[(1,1-dimethylethyl)thio]-5,5-dimethyl-1-hexenylidene}-2,2-dimethylpropanamine (**6bc**): According to the preparation of **6aa**, from 0.60 g (1.6 mmol) of **1b** and 0.11 ml (0.8 mmol) of **3c** in 2 ml of benzene (1.5 h at 60°C) 0.40 g (56%) of **6bc** was obtained; m.p. 119°C (dec.) (methanol). – IR (KBr): $\tilde{\nu}$ = 2000 cm^{-1} (C=C=N). – ^{1}H NMR (C_6D_6): δ = 0.90 [s, 9H, $C(CH_3)_3$], 1.00 [s, 9H, $C(CH_3)_3$], 1.13 [s, 9H, $SC(CH_3)_3$], 3.06 (s, 2H, CH_2), 6.83–7.85 (m, 36 aromatic H). – ^{13}C NMR (C_6D_6): δ = 30.63, 30.95 [$C(CH_3)_3$], 31.62 [$SC(CH_3)_3$], 37.94, 40.15 [$C(CH_3)_3$], 46.72 [$SC(CH_3)_3$], 31.24 (CH_2), 56.64 (C=C=N), 58.10 (Ar_2C-CH_2), 78.77 (Ar_2C-N), 125.95–131.72 ($C_{ar}H$), 137.25–143.21 (C_{ar}), 179.05 (C=C=N).

$C_{65}H_{65}NS$ (892.3) Calcd. C 87.49 H 7.34 N 1.57
Found C 87.20 H 7.60 N 1.35

2-Acetoxy-4,4-di(biphenyl-4-yl)-2-[1,1-di(biphenyl-4-yl)-2,2-dimethylpropyl]hexanenitrile (**5bd**): According to the preparation of

6aa, from 0.23 g (0.61 mmol) of **1b** and 0.09 g (0.7 mmol) of **3d** in 2 ml of benzene (3 h at 45°C), 0.17 g (32%) of **5bd** is obtained, m.p. 112°C (dec.) (*n*-hexane). – IR (KBr): $\tilde{\nu}$ = 1745 cm^{-1} (C=O). – ^1H NMR (CCl_4): δ = 1.03, 1.10 [s, 9H, $C(CH_3)_3$], 2.13 (s, 3H, $COCH_3$), 3.62 (s, 2H, CH_2), 7.06–7.83 (m, 36 aromatic H).

$C_{63}H_{54}NO_2$ (857.1) Calcd. C 88.28 H 6.35 N 1.63
Found C 87.40 H 5.75 N 1.05

2-[Diphenyl(trimethylsilyl)methyl]-2-(methylthio)-4,4-diphenyl-4-(trimethylsilyl)butanenitrile (**5ca**): As described for the preparation of **6aa**, from 0.47 g (1.0 mmol) of **1c** and 0.10 g (1.1 mmol) of **3a** in 2 ml of benzene (2 h at 60°C) 0.48 g (85%) of **5ca** was obtained; m.p. 157–158°C (dec.) (methanol). – IR (KBr): $\tilde{\nu}$ = 2215 cm^{-1} (C≡N). – ^1H NMR ($CDCl_3$): δ = –0.25, 0.00 [s, 9H, $Si(CH_3)_3$], 1.38 (s, 3H, SCH_3), 3.28, 3.70 (AB, $^2J_{AB}$ = 14.9 Hz, 2H, CH_2), 6.15–8.18 (m, 20 aromatic H). – ^{13}C NMR ($CDCl_3$): δ = –1.09, 2.96 [$Si(CH_3)_3$], 18.06 (SCH_3), 41.66 (CH_2), 44.68 (*C*SMe), 52.70, 62.66 (Ph_2C), 116.18 (CN), 122.15–134.28 ($C_{ar}H$), 140.25–143.18 (C_{ar}).

$C_{36}H_{43}NSSi_2$ (577.9) Calcd. C 74.82 H 7.50 N 2.42
Found C 74.35 H 7.25 N 2.25

2,3-Bis[2,2-diphenyl-2-(trimethylsilyl)ethyl]-2,3-[(1-methylethyl)thio]butanedinitrile (**7cb**): As described for the preparation of **6aa**, from 0.28 g (1.75 mmol) of **1c** and 0.42 g (3.0 mmol) of **3b** in 3 ml of benzene (18 h at 45°C) 0.84 g (66%) of **7cb** was obtained; m.p. 147–148°C (dec.) (*n*-hexane). – IR (KBr): $\tilde{\nu}$ = 2230 cm^{-1} (C≡N). – ^1H NMR (CCl_4): δ = 0.00 [s, 18H, $Si(CH_3)_3$], 0.93 [d, 6H, $SCH(CH_3)_2$], 1.25 [d, 6H, $SCH(CH_3)_2$], 2.30, 3.46 (AB, $^2J_{AB}$ = 15.0 Hz, 2H, CH_2), 3.50 [sept, 2H, $SCH(CH_3)_2$], 7.20–7.90 (m, 20 aromatic H). – ^{13}C NMR ($CDCl_3$): δ = –0.74 [$Si(CH_3)_3$], 23.94, 24.65 [$SCH(CH_3)_2$], 37.51 (CH_2), 39.84 [$SCH(CH_3)_2$], 44.33 (Ph_2C), 116.52 (CN), 125.45–131.39 ($C_{ar}H$), 140.90, 142.97 (C_{ar}). – MS (80 eV), *m/z* (%): 732 (1) [M^+], 366 (18) [$M^+/2$], 239 (35) [$Ph_2CSi(CH_3)_3^+$], 165 (25) [Ph_2C^+].

$C_{44}H_{56}N_2S_2Si_2$ (733.2) Calcd. C 72.07 H 7.70 N 3.82
Found C 71.75 H 7.95 N 3.70

2-Acetoxy-2-[diphenyl(trimethylsilyl)methyl]-4,4-diphenyl-4-(trimethylsilyl)butanenitrile (**5cd**): According to the preparation of **6aa**, from 1.0 g (2.14 mmol) of **1c** and 0.25 g (2.15 mmol) of **3d** (4 h at 70°C) 0.92 g (73%) of **5cd** was obtained; m.p. 155°C (dec.) (*n*-hexane). – IR (KBr): $\tilde{\nu}$ = 1755 cm^{-1} (C=O). – ^1H NMR (CCl_4): δ = –0.12 [s, 9H, $Si(CH_3)_3$], 0.05 [s, 9H, $Si(CH_3)_3$], 1.64 (s, 3H, $COCH_3$), 2.37, 2.75 (AB, $^2J_{AB}$ = 14.8 Hz, 2H, CH_2), 6.75–7.48 (m, 20 aromatic H).

$C_{37}H_{43}NO_2Si_2$ (589.9) Calcd. C 75.33 H 7.35 N 2.37
Found C 75.00 H 7.05 N 2.20

2-{Diphenyl[(trimethylsilyl)oxy]methyl}-2-methoxy-4,4-diphenyl-4-[(trimethylsilyl)oxy]butanenitrile (**5fg**): As described for the preparation of **6aa**, from 0.51 g (1.0 mmol) of **1f** and 0.091 g (1.1 mmol) of **3g** in 2 ml of benzene (48 h at reflux) 0.40 g (67%) of **5fg** was obtained; m.p. 92°C (*n*-hexane). – IR (KBr): $\tilde{\nu}$ = 2255 cm^{-1} (C≡N). – ^1H NMR ($CDCl_3$): δ = –0.21 [s, 9H, $Si(CH_3)_3$], –0.09 [s, 9H, $Si(CH_3)_3$], 2.57, 3.23 (AB, $^2J_{AB}$ = 14.5 Hz, 2H, CH_2), 2.87 (s, 3H, OMe), 7.09–7.63 (m, 20 aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 1.81 [$Si(CH_3)_3$], 48.33 (CH_2), 56.54 (OCH_3), 79.69, 82.45 (Ph_2C, *C*–OMe), 117.27 (CN), 126.27–130.03 ($C_{ar}H$), 142.40, 146.35 (C_{ar}).

$C_{36}H_{43}NO_3Si_2$ (593.9) Calcd. C 72.80 H 7.30 N 2.36
Found C 72.75 H 7.25 N 2.40

2-{Diphenyl[(trimethylsilyl)oxy]methyl}-2-ethoxy-4,4-diphenyl-4-[(trimethylsilyl)oxy]butanenitrile (**5fh**): According to the synthesis of **6aa**, from 1.0 g (2.0 mmol) of **1f** and 0.19 g (2.0 mmol) of **3h** (12 h at reflux) 1.0 g (83%) of **5fh** was obtained; m.p. 149–150°C (dec.) (*n*-hexane). – ^1H NMR (CCl_4): δ = –0.23 [s, 9H, $Si(CH_3)_3$], –0.17 [s, 9H, $Si(CH_3)_3$], 0.37 (t, 3H, OCH_2CH_3), 2.53, 3.20 (AB, $^2J_{AB}$ = 14.7 Hz, 2H, CH_2), 3.07 (q, 2H, OCH_2CH_3), 6.87–7.73 (m, 20 aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 1.07 [$Si(CH_3)_3$], 14.77 (OCH_2CH_3), 48.00 (Ph_2CCH_2), 65.03 (OCH_2CH_3), 79.69 (Ph_2C), 81.63 (CH_2CCN), 117.86 (CN), 126.18–130.02 ($C_{ar}H$), 142.30, 146.47 (C_{ar}). – MS (80 eV), *m/z* (%): 255 (100) [$Ph_2COSi(CH_3)_3^+$], 182 (8) [Ph_2CO^+], 165 (15) [Ph_2C^+].

$C_{37}H_{45}NO_3Si_2$ (607.9) Calcd. C 73.10 H 7.46 N 2.30
Found C 72.50 H 7.40 N 2.35

2-Acetoxy-2-{diphenyl[(trimethylsilyl)oxy]methyl}-4,4-diphenyl-4-[(trimethylsilyl)oxy]butanenitrile (**5fd**): According to the preparation of **6aa**, from 1.0 g (2.0 mmol) of **1f** and 0.24 g (2.1 mmol) of **3d** in 3 ml of benzene (overnight at reflux) 1.0 g (85%) of **5fd** was isolated; m.p. 143°C (dec.) (*n*-hexane). – ^1H NMR (CCl_4): δ = –0.10 [s, 9H, $Si(CH_3)_3$], –0.05 [s, 9H, $Si(CH_3)_3$], 1.10 (s, 3H, $COCH_3$), 2.55, 3.20 (AB, $^2J_{AB}$ = 15 Hz, 2H, CH_2), 6.83–7.60 (m, 20 aromatic H).

$C_{37}H_{43}NO_4Si_2$ (621.9) Calcd. C 71.45 H 6.97 N 2.25
Found C 71.80 H 7.15 N 2.45

2-[(Triethylsilyl)oxy]-2-propenenitrile (**3f**) was prepared according to a literature procedure[39d] in 60% yield; b.p. 155–158°C. – ^1H NMR (CCl_4): δ = 0.30–1.40 [m, 15H, $Si(CH_2CH_3)_3$], 4.98 (dd, 2H, olefinic H).

2-{Diphenyl[(trimethylsilyl)oxy]methyl}-4,4-diphenyl-2-[(triethylsilyloxy]-4-[(trimethylsilyl)oxy]butanenitrile (**5ff**): According to the preparation of **6aa**, from 5.1 g (10.0 mmol) of **1f** and 2.1 g (11.5 mmol) of **3f** in 5 ml of benzene (18 h at reflux) 5.7 g (82%) of **5ff** was obtained; m.p. 125–128°C (dec.) (*n*-pentane). – ^1H NMR (CCl_4): δ = –0.10 [s, 9H, $OSi(CH_3)_3$], 0.02 [s, 9H, $OSi(CH_3)_3$], 0.03–0.94 [m, 15H, $OSi(CH_2CH_3)_3$], 2.40, 3.30 [AB, $^2J_{AB}$ = 14.5 Hz, 2H, CH_2), 6.60–8.15 (m, 20 aromatic H).

$C_{41}H_{55}NO_3Si_3$ (694.1) Calcd. C 70.94 H 7.99 N 2.02
Found C 71.30 H 8.20 N 1.90

2,3-Bis{2,2-bis[4-(1,1-dimethylethyl)phenyl]-3,3,3-trifluoropropyl}-2,3-bis(methylthio)butanedinitrile (**7ha**): According to the preparation of **6aa**, from 0.30 g (0.43 mmol) of **1h** and 0.06 ml (0.5 mmol) of **3a** in 3 ml of benzene (2 d at 60°C) 0.24 g (70%) of **7ha** was obtained; m.p. 193°C (under Ar) (*n*-hexane). – ^1H NMR ($CDCl_3$): δ = 1.25 (s, 6H, SCH_3), 1.31 [s, 36H, $C(CH_3)_3$], 2.51, 3.58 (AB, $^2J_{AB}$ = 14.87 Hz, 4H, CH_2), 7.26–7.47 (m, 16 aromatic H).

N-{4,4-Bis[4-(1,1-dimethylethyl)phenyl]-2-[(1-methylethyl)-thio]-5,5,5-trifluoropentanylidene}-1,1-bis[4-(1,1-dimethylethyl)-phenyl]-2,2,2-trifluoroethanamine (**6hb**) *and 2,3-Bis{2,2-bis[4-(1,1-dimethylethyl)phenyl]-3,3,3-trifluoropropyl}-2,3-[(1-methylethyl)-thio]butanedinitrile* (**7hb**): According to the preparation of **6aa**, from 0.30 g (0.43 mmol) of **1h** and 0.07 ml (0.5 mmol) of **3b** in 3 ml of benzene (3.5 h at 65°C) **6hb** (containing impurities of **7hb**) was obtained (*n*-hexane). – IR (KBr): $\tilde{\nu}$ = 2013 cm^{-1} (C=C=N). – ^1H NMR ($CDCl_3$): δ = 1.32, 1.35 [s, 36H, $C(CH_3)_3$], 1.46 [d, 6H, $SCH(CH_3)_2$], 2.46–2.50 (m, 1H, H_{aliph}), 2.88–2.92 (m, 1H, H_{aliph}), 3.41 (sept, 1H, SCH), 7.13–7.42 (m, 16 aromatic H). – ^{13}C NMR($CDCl_3$): δ = 22.80 [$SCH(CH_3)$], 31.29 [$C(CH_3)_3$], 33.10 (CH_2), 34.42, 34.52 [$C(CH_3)_3$], 38.85 (SCH), 57.25 (m, CCF_3), 59.98 (C=C=N), 124.50–151.33 ($C_{ar}H$, CF_3, C_{ar}), 188.33 (C=C=N). On prolonged heating (18 h) we obtained **7hb** (containing impurities of **6hb**). – IR (KBr): no C=C=N. – ^1H NMR ($CDCl_3$): δ = 1.0–1.2 [m, 48H, $CH(CH_3)_3$, $SCH(CH_3)_2$], 2.71 (d, 2H, CH_2, ^2J = 14.75 Hz), 3.00 (broad signal, 2H, SCH), 7.22–7.43 (m, 16 aromatic

H). – ^{13}C NMR ($CDCl_3$): δ = 23.72, 24.37 [SCH(CH_3)$_2$], 31.27 [C(CH_3)$_3$], 34.48 [C(CH_3)$_3$], 38.72 (CH_2), 41.16 (SCH), 54.58 (C–CN), 56.51 (C–CF_3), 114.47, 114.72 (CN), 124.53–151.04 (C_{ar}H, C_{ar}, CF_3).

N-{4,4-Bis[4-(1,1-dimethylethyl)phenyl]-2-[(1,1-dimethylethyl)-thio]-5,5,5-trifluoro-1-pentanylidene}-1,1-bis[4-(1,1-dimethylethyl)-phenyl]-2,2,2-trifluoroethanamine (**6hc**): As described for the preparation of **6aa**, from 0.16 g (0.23 mmol) of **1h** and 0.035 ml (0.25 mmol) of **3c** in 2 ml of benzene (8 h at 65°C) 0.16 g (83%) of **6hc** was obtained; m.p. 174°C (dec.) (methanol). – IR (KBr): ν̃ = 2020 cm^{-1} (C=C=N). – ^{1}H NMR (CCl_4): δ = 1.05 [s, 9H, SC(CH_3)$_3$], 1.37 [s, 18H, C(CH_3)$_3$], 1.40 [s, 18H, C(CH_3)$_3$], 3.20 (s, 2H, CH_2), 6.90–7.50 (m, 16 aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 30.83 [C(CH_3)$_3$], 31.26 [SC(CH_3)$_3$], 34.33, 34.50 [C(CH_3)$_3$], 38.64 (CH_2), 47.16 [SC(CH_3)$_3$], 54.80 [Ar_2C], 58.16 (C=C=N), 74.95 (Ar_2C–N), 124.71–132.47 (C_{ar}H, CF_3), 134.28–151.21 (C_{ar}), 185 (C=C=N).

$C_{51}H_{63}F_6NS$ 6836.1) Calcd. C 73.20 H 7.59 N 1.68
Found C 73.50 H 7.65 N 1.70

2-Acetoxy-2,3-bis[9-(4-methylphenyl)-9H-fluoren-9-yl]propanenitrile (**5nd**): According to the preparation of **6aa**, from 0.50 g (1.0 mmol) of **1n** and 0.14 g (1.25 mmol) of **3d** in 10 ml of benzene (18 h at reflux) 0.45 g (73%) of **5nd** was obtained; m.p. 169–170°C (dec.) (*n*-pentane). – IR (KBr): ν̃ = 1765 cm^{-1} (C=O). – ^{1}H NMR ($CDCl_3$): δ = 1.25 (s, 3H, OCOCH_3), 2.07 (s, 3H, CH_3), 2.13 (s, 3H, CH_3), 2.85 (s, 2H, CH_2), 6.27–8.13 (m, 24 aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 20.32 (OCOCH_3), 20.56, 20.68 (ArCH_3), 41.37 (CH_2), 55.59, 66.82 [Fl(ArCH_3)C], 74.59 (CH_2CCN), 117.83 (CN), 119.84–128.93 (C_{ar}H), 134.66–149.91 (C_{ar}), 165.68 (C=O).

2-Ethoxy-2,3-bis[9-(4-methylphenyl)-9H-fluoren-9-yl]propanenitrile (**5nh**): As described for the preparation of **6aa**, from 0.5 g (1.0 mmol) of **1n** and 0.12 g (1.25 mmol) of **3h** in 10 ml of benzene (36 h at reflux) 0.46 g (76%) of **5nh** was obtained; m.p. 187–188°C (dec.) (*n*-pentane). – ^{1}H NMR ($CDCl_3$): δ = 0.53 (t, 3H, OCH_2CH_3), 2.10, 2.20 (s, 3H, $C_6H_4CH_3$), 2.13 (q, 2H, OCH_2CH_3), 2.73 (s, 1H, CH_2), 2.80 (s, 1H, CH_2), 6.40–8.20 (m, 24 aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 14.26 (OCH_2CH_3), 20.67, 20.77 ($C_6H_4CH_3$), 42.25 (CH_2), 55.93, 66.65 [Fl($C_6H_4CH_3$)], 65.90 (OCH_2CH_3), 116.52 (CN), 125.41–129.52 (C_{ar}H), 135.87–150.19 (C_{ar}).

2-Acetoxy-2,3-bis[9-(4-methoxyphenyl)-9H-fluoren-9-yl)]propanenitrile (**5od**): As described for the preparation of **6aa**, from 0.53 g (1.0 mmol) of **1o** and 0.11 g (1.0 mmol) of **3d** in 6 ml of benzene (17 h reflux) 0.57 g (88%) of **5od** was obtained; m.p. 242°C (dec.) (benzene/*n*-hexane). – IR (KBr): ν̃ = 1830 cm^{-1} (C=O), 2210 (C≡N). – ^{1}H NMR ($CDCl_3$): δ = 1.33 (s, 3H, OCOCH_3), 2.90 (s, 2H, CH_2), 3.66 (s, 3H, OCH_3), 3.69 (s, 3H, OCH_3), 6.57–8.10 (m, 24 aromatic H). – MS (80 eV), *m/z* (%): 653 (0.5) [M^+], 322 (1) [M^+ – **2o** – OAc], 271 (100) [**2o**$^+$].

$C_{45}H_{35}NO_4$ (653.7) Calcd. C 82.68 H 5.40 N 2.14
Found C 83.15 H 5.62 N 2.22

2,3-Bis[9-(4-methoxyphenyl)-9H-fluoren-9-yl]-2-[(trimethylsilyl)oxy]propanenitrile (**5oe**): As described for the preparation of **6aa**, from 1.0 g (1.85 mmol) of **1o** and 0.26 g (1.85 mmol) of **3e** in 5 ml of benzene (24 h at reflux) 0.92 g (73%) of **5oe** was obtained; m.p. 186°C (dec.) (*n*-pentane). – ^{1}H NMR ($CDCl_3$): δ = –0.56 [s, 9H, Si(CH_3)$_3$], 2.50, 2.87 (AB, $^2J_{AB}$ = 15 Hz, 2H, CH_2), 3.43 (s, 3H, OCH_3), 3.55 (s, 3H, OCH_3), 6.33–8.27 (m, 24 aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 0.53 [Si(CH_3)$_3$], 43.62 (CH_2), 54.87, 55.06 (OCH_3), 55.53, 67.27 [Fl(C_6H_4OMe)C], 75.80 (CH_2C–CN), 120.38 (CN), 125.55–130.96 (C_{ar}H), 138.73–158.84 (C_{ar}).

$C_{46}H_{41}NO_3Si$ (683.9) Calcd. C 80.78 H 6.04 N 2.05
Found C 80.45 H 6.05 N 1.95

Dimethyl 3-Cyano-2,2,5,5-tetraphenyl-3-[(trimethylsilyl)oxy]hexanedioate (**5je**): According to the preparation of **6aa**, from 1.05 g (2.3 mmol) of **1j** and 0.5 ml (2.5 mmol) of **3e** in 0.5 ml of benzene (2 h at 60°C) 1.2 g (80%) of **5je** was obtained; m.p. 137–140°C (dec.) (*n*-pentane). – IR (KBr): ν̃ = 1715 cm^{-1} (C=O). – ^{1}H NMR (C_6D_6): δ = 0.31 [s, 9H, Si(CH_3)$_3$], 2.12, 4.15 (AB, $^2J_{AB}$ = 15 Hz, 2H, CH_2), 6.70–8.30 (m, 20 aromatic H). – ^{13}C NMR (C_6D_6): δ = 2.52 [Si(CH_3)], 48.96 (CH_2), 51.93, 52.24 (CO_2CH_3), 71.49, 77.01 (Ph_2C-), 118.77 (CN), 127.07–131.79 (C_{ar}H), 138.04 to 145.79 (C_{ar}), 172.91, 173.18 (C=O). – MS (80 eV), *m/z* (%): = 591 (1) [M^+], 576 (5) [M^+ – CH_3], 532 (2) [M^+ – CO_2CH_3], 225 (100) [$Ph_2(CH_3OCO)C^+$].

2-(2,2-Dimethyl-1,1-diphenylpropyl)-6,6-diphenyl-7,7-dimethyl-2-[(trimethylsilyl)oxy]-3-octenenitrile (**9an**): As described for the preparation of **6aa**, from 0.93 g (2.1 mmol) of **1a** and 0.35 g (2.1 mmol) of **3n** (8 h at 50°C) 0.86 g (66%) of **9an** was obtained; m.p. 136°C (dec.) (ethanol/*n*-hexane). – ^{1}H NMR (CCl_4): δ = –0.03 [s, 9H, Si(CH_3)$_3$], 1.06 [s, 9H, C(CH_3)$_3$], 1.30 [s, 9H, C(CH_3)$_3$], 2.60–3.03 (broad signal, 2H, CH_2), 5.44–5.80 (m, 2 olefinic H), 6.93–7.70 (m, 20 aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 1.51 [Si(CH_3)$_3$], 29.33, 32.53 [C(CH_3)$_3$], 37.74, 40.19 [C(CH_3)$_3$], 39.67 (CH_2), 56.91, 67.05 (Ph_2C), 84.69 (C–CN), 120.50 (CN), 125.56–137.69 (C_{olef}H, C_{ar}H), 140.66, 141.93, 144.91, 146.10 (C_{ar}).

$C_{42}H_{51}NOSi$ (613.9) Calcd. C 82.17 H 8.37 N 2.28
Found C 82.00 H 8.40 N 2.20

2-[Diphenyl(trimethylsilyl)methyl]-6,6-diphenyl-6-(trimethylsilyl)-2-[(trimethylsilyl)oxy]-3-hexenenitrile (**9cn**): According to the synthesis of **6aa**, from 1.57 g (0.94 mmol) of **1c** and 0.47 g (1.0 mmol) of **3n** in 2 ml of benzene (18 h at 45–50°C) 0.47 g (78%) of **9cn** was obtained; m.p. 158°C (dec.) (*n*-hexane). – ^{13}C NMR ($CDCl_3$): δ = –1.11 [OSi(CH_3)$_3$], 1.50, 1.78 [Si(CH_3)$_3$], 38.19 (CH_2), 43.71, 58.19 (Ph_2C), 82.17 (C–CN), 119.20 (CN), 125.02–131.86 (C_{olef}H, C_{ar}H), 144.37, 146.04 (C_{ar}).

$C_{40}H_{51}NOSi_3$ (646.1) Calcd. C 74.35 H 7.96 N 2.17
Found C 74.25 H 7.85 N 2.00

4-{Diphenyl[(trimethylsilyl)oxy]methyl}-6,6-diphenyl-2,6-bis[(trimethylsilyl)oxy]-2-hexenenitrile (**8fn**) *and 2-{Diphenyl[(trimethylsilyl)oxy]methyl}-6,6-diphenyl-2,6-bis[(trimethylsilyl)oxy]-3-hexenenitrile* (**9fn**): According to the preparation of **6aa**, from 2.6 g (5.1 mmol) of **1f** and 1.0 g (5.3 mmol) of **3n** in 4 ml of benzene (16 h at reflux) a viscous oil was obtained. By addition of 3 ml of methanol, **8fn** precipitated as a white crystalline compound; yield: 1.8 g (53%), m.p. 125°C (dec.) (methanol). – IR (KBr): ν̃ = 2200 cm^{-1} (CN). – ^{1}H NMR (CCl_4): δ = –0.24 [s, 9H, Si(CH_3)$_3$], –0.23 [s, 9H, Si(CH_3)$_3$], 0.33 [s, 9H, Si(CH_3)$_3$], 2.97, 3.87 (AB, $^2J_{AB}$ = 14.5 Hz, 2H, CH_2), 3.43 (CH–CH=C), 4.74 (d, 1 olefinic H), 7.03–7.44 (m, 20 aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 0.64, 1.97, 2.03 [Si(CH_3)$_3$], 40.78 (CH_2CHCH=), 42.73 (CH_2CH), 80.58, 85.06 (Ph_2C), 117.10 (CN), 121.81 (CH=C–O), 126.66–128.80 (C_{olef}–H, C_{ar}H), 143.94, 147.01 (C_{ar}).

$C_{40}H_{51}NO_3Si_3$ (678.1) Calcd. C 70.85 H 7.58 N 2.07
Found C 70.40 H 7.25 N 1.85

From the mother liquor which was concentrated to ca. 50%, 0.4 g (12%) of **9fn** was crystallized after keeping the mixture in the refrigerator for 1 d; m.p. 124°C (dec.) (methanol.) – ^{1}H NMR (CCl_4): δ = –0.13, –0.12, –0.04 [s, 9H, OSi(CH_3)$_3$], 3.00 (m, 2H, CH_2), 5.15 (m, 1 olefinic H), 5.80 (m, 1 olefinic H), 7.14–7.48 (m, 20 aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 1.25, 1.75, 1.89 [Si(CH_3)$_3$], 43.97 (CH_2), 79.95, 85.71 (Ph_2C, C–CN), 120.13 (CN), 126.57–130.94 (C_{olef}H, C_{ar}H), 143.07, 143.19, 146.92, 147.11 (C_{ar}).

$C_{40}H_{51}NO_3Si_3$ (678.1) Calcd. C 70.85 H 7.58 N 2.07
Found C 71.05 H 7.65 N 2.00

6,6,6-Triphenyl-2-[(trimethylsilyl)oxy]-2-(triphenylmethyl)-3-hexenenitrile (**9in**): As described for the preparation of **6aa**, from 1.52 g (3.14 mmol) of **1i** and 0.33 g (1.96 mmol) of **3n** in 10 ml of benzene (18 h at reflux) 0.85 g (83%) of **9in** was obtained; m.p. 177–178°C (dec.) (*n*-pentane). – IR (KBr): $\tilde{\nu}$ = 2217 cm^{-1} (CN). – ^1H NMR ($CDCl_3$): δ = 0.38 [s, 9H, $Si(CH_3)_3$], 2.3 (m, 2H, CH_2), 4.8 (m, 2H, CH=CH), 7.25–7.35 (m, 30 aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 0.50 [$OSi(CH_3)_3$], 42.90 (CH_2), 56.08, 63.35 (CPh_3), 122.49 (CN), 126.05–129.49 ($C_{ar}H$, $C_{olef}H$), 136.10–148.90 (C_{ar}).

4,5-Bis[9-(4-methylphenyl)-9H-fluoren-9-yl]-2-[(trimethylsilyl)-oxy]-2-pentenenitrile (**8nn**): According to the preparation of **6aa**, from 0.80 g (1.57 mmol) of **1n** and 0.33 g (1.96 mmol) of **3n** in 10 ml of benzene (21 h at reflux) 0.73 g (70%) of **8nn** was obtained; m.p. 204–206°C (dec.) (*n*-pentane). – IR (KBr): $\tilde{\nu}$ = 2210 cm^{-1} (CN). – ^1H NMR ($CDCl_3$): δ = 0.03 [s, 9H, $Si(CH_3)_3$], 2.15 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 2.73 (m, 2H, CH_2), 3.47 (m, 1H, CH), 4.13 (m, 1 olefinic H), 6.77–7.87 (m, 24 aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 0.18 [$Si(CH_3)_3$], 20.72, 20.80 ($C_6H_4CH_3$), 38.28 (CH_2), 39.00 (CH_2CHCH), 57.47, 63.25 ($CH_3C_6H_4$–*C*), 115.86 (CHCH=*C*), 119.62 (CHCH=C), 121.58 (CN), 124.85–128.88 ($C_{ar}H$), 135.80–150.95 (C_{ar}).

4,5-Bis[9-(4-methoxyphenyl)-9H-fluoren-9-yl]-2-[(trimethylsilyl)oxy]-2-pentenenitrile (**8on**): According to the preparation of **6aa**, from 0.35 g (0.66 mmol) of **2o** and 0.13 g (0.66 mmol) of **3n** in 3 ml of benzene (20 h ar reflux) 0.31 g (66%) of **8on** was obtained; m.p. 168°C (dec.) (*n*-hexane). – IR (KBr): $\tilde{\nu}$ = 2210 cm^{-1} (CN). – ^1H NMR ($CDCl_3$): δ = 0.10 [s, 9H, $Si(CH_3)_3$], 2.77 (m, 2H, CH_2), 3.70 (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3), 4.25 (m, 2 olefinic H), 6.50 to 8.00 (m, 24 aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 0.23 [$OSi(CH_3)_3$], 38.38 (CH_2CHCH=), 39.14 (CH_2), 55.04, 55.30 (OCH_3), 57.16, 62.93 [($MeOC_6H_4C$], 113.54 (CHCH=C), 115.89 (CH-CH=*C*), 120.22 (CN), 124.87–128.05 ($C_{ar}H$), 134.08–158.26 (C_{ar}).

$C_{48}H_{43}NO_3Si$ (709.9) Calcd. C 81.21 H 6.11 N 1.97
Found C 81.35 H 6.20 N 2.00

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