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Hydrosilylation of unsaturated fatty acid *N*-phenyl amides

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The synthesis and the characterization of new silylated fatty acid *N*-phenyl amides as novel precursors for structured materials are described. Hydrosilylation of vinylic groups in terminal *N*-phenyl unsaturated fatty amides was efficiently catalyzed by Karstedt's catalyst. Radical initiators have been found to be active for both terminal and internal double bonds of unsaturated fatty *N*-phenyl amides at the necessary condition to suppress initially the conjugation in the amide function, the anilide moiety acting as a radical inhibitor. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: fatty acid amides; hydrosilylation; radical initiation; radical autoinhibition

INTRODUCTION

Oils and fats are one of the most important renewable raw materials for the chemical industry and thus are of great significance for economic and ecological reasons.[1] Hitherto, the efforts of industrial oleochemistry have been mainly concentrated on the carboxy functionality of fatty derivatives but, more recently, a wide study of the selective functionalization of the alkyl chain has been developed. For example, various radical, electrophilic, nucleophilic and pericyclic additions to the C–C double bond of unsaturated fatty acids derivatives have led to a series of new fatty compounds.[2] Moreover, transition metal-catalyzed hydrosilylation of olefins, which has been the methodology of choice to attach organic group on a chain,[3,4] has also been explored in the case of fatty compounds.[5,6] In this context, we recently reported the syntheses of organohalosilyl fatty acid methyl esters (FAME) by hydrosilylation of unsaturated FAME (methylundecenoate and 9-methyloleate) for the preparation of ambiphilic polysiloxanes.[7] In contrast, to the best of our knowledge, the hydrosilylation of fatty acid amides has never been developed and remains a stimulating challenge as the fatty acid amides represent an important class of bioactive lipids in human and other mammals.[8] Besides their important properties of biocompatibility, they have also been shown to exhibit unique properties of self-organization.[9–11] The presence of alkyl chain and amide groups that are attractive functions for self-assembly respectively through hydrophobic interaction[12–15] and hydrogen bonding[16–18] makes silylated fatty anilides good candidates as precursors for designing polysiloxanes. This work describes the synthesis and the characterization of new silylated fatty acid *N*-phenyl amides. Transition metal catalyzed and radical initiated hydrosilylation have been investigated with the aim of optimizing these reactions.

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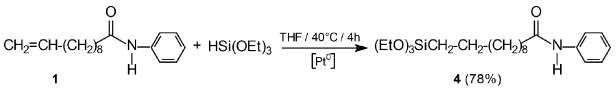
RESULTS AND DISCUSSION

Hydrosilylation of undecenoic acid anilide

The fatty acid derivatives exhibit an almost endless variety of structures which differ in their chain lengths, the position and the number of unsaturations. The monounsaturated ones usually represent a non-negligible fraction, which has focused much interest, due to their functional potential. Among this family of compounds, two of them are usually used as representative fatty acids: undecenoic and oleic acids. We thus prepared the amide version of these products and concentrated our efforts on the study of the *N*-phenyl-10-undecenamide **1**[19] and *N*-phenyl-*cis*-9,10-octadecenamide **2**.[20] **1** and **2** are readily prepared from the respective fatty acid methyl esters by treatment with aniline at 200 °C for 24 h.

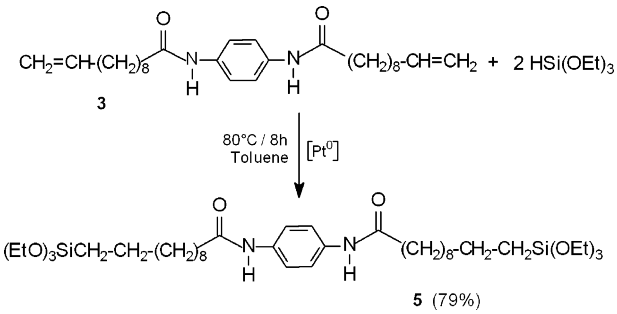
Using the same experimental conditions, a low yield (36%) of *N*,*N*′-diundecenoylbenzene-1,4-diamine **3**[9] was obtained. The amination of the corresponding acid chloride with *para*-diaminobenzene at the reflux of pyridine during 3 h was a more efficient route for preparing **3**.

Similarly to their ester counterparts, hydrosilylation of terminal unsaturation is straightforward using Karstedt's catalyst: the addition of triethoxysilane to a THF solution of **1** gives selectively the anti-Markovnikov adduct **4** in the presence of the [Pt^0] complex [equation (1)]. Gentle heating (40 °C) for 4 h was required to achieve a complete consumption of starting materials.



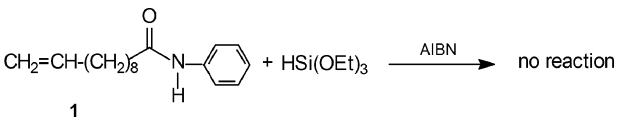
Equation (1)

Interestingly, the scope of this reaction can be extended to diamides which may exhibit valuable self-organization properties. Starting from the diamide **3**, the addition of two equivalents of $(EtO)_3SiH$ was easily performed using Karstedt's catalyst at 80 °C, leading to the quantitative formation of the corresponding adduct **5** [equation (2)].

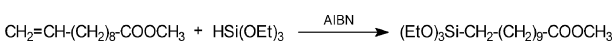


Equation (2)

Surprisingly, despite the high reactivity of the terminal double bond, radical hydrosilylation initiated by AIBN at 120 °C [equation (3)] was ineffective while a comparable procedure allowed the hydrosilylation of the methyl undecenoate [equation (4)] with a good yield (68%) (El Kadib A, Katir N, Castel A, Rivière P, unpublished work).



Equation (3)

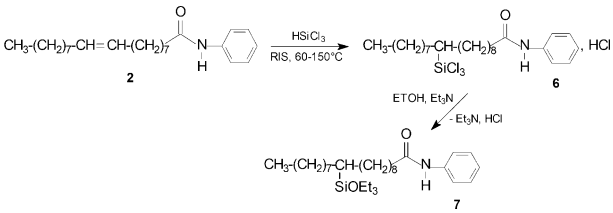


Equation (4)

This unexpected inactivation of fatty acid amides may be attributed to the presence of a delocalized amide group which could inhibit the radical-initiated reaction. A comparable effect has indeed been shown recently in functional ethylenic compounds (limonene, carveol, carvone)[21] and has been studied in detail.

Hydrosilylation of oleic acid anilide

Among the whole family of unsaturated fatty acids, terminal unsaturated ones represent a small minority, particularly when considering those existing in natural products. In addition, internal unsaturations are known to exhibit much lower reactivity compared with their terminal counterparts.[22] These results prompted us to study oleic acid anilide as a model. However, no reaction occurred between triethoxysilane and oleic acid anilide **2** using either Karstedt's catalyst or radical initiation (AIBN or radical initiation sequence, RIS).[21] Such a low reactivity of the internal double bond of fatty acid esters was previously reported in the case of hydrosilylation of ethyloleate:[22] no product was obtained with H_2PtCl_6 as catalyst, and the use of catalytic amount of $SnCl_4$ as Lewis acid catalyst yielded only traces of the hydrochlorination product. Unexpectedly, the use of the more reactive trichlorosilane,[7] and of drastic procedures (RIS)[21] followed by treatment by ethanol in the presence of triethylamine yielded cleanly, after elimination of $Et_3N.HCl$, the desired triethoxysilylated compound **7** [equation (5)].



Equation (5)

This radical hydrosilylation of amide **2** is surprising because the presence of a delocalized amide group should have inhibited such a radical process. Additionally, using Ph_3GeH, which is more reactive than Cl_3SiH in radical processes,[21,23] no reaction occurred in the same experimental conditions.

This totally unanticipated result encouraged us to analyze this reaction in detail. The study of the first step [trichlorosilane in the presence of radical initiators at high temperature, equation (5)] allowed the characterization and the identification of the new hydrochlorinated adduct **6**.

In the ^{13}C {^1H} NMR spectrum, the disappearance of the characteristic ethylenic carbon signals and the appearance of a new singlet at 31.92 ppm assigned to the Cl_3SiCH group indicates the formation of only one isomer. This result was further confirmed by ^{29}Si NMR since the spectrum exhibits a unique signal at 14.5 ppm characteristic

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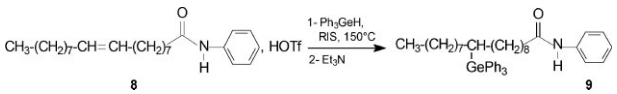
of Cl_3SiCH. The EI mass spectrometry study provides useful structural information: first, the fragmentations are in agreement with the C(10)-silylated adduct, which is generally observed with radical initiated hydrosilylation.[7] Moreover, the observation of molecular ion at m/z 527 confirmed both the hydrosilylation of the internal double bond, and the hydrochloration of the amide function. This is corroborated by the IR spectrum, which shows absorption of the carbonyl group at 1704 cm^{-1}, characteristic of a non-conjugated carbonyl whereas, in the case of amides, this vibration is observed at lower frequencies (around 1660 cm^{-1}).

Consequently, the involvement of **6** is thought to be the key point for rationalizing the different behavior of the chlorosilane and alkoxysilane or arylgermane in this reaction. Indeed, if a classical radical-based hydrosilylation is assumed, no reaction is expected either for these silanes or germanes. One can hypothesize that, in a first step, hydrochloration of the amide, resulting in the loss of conjugated character of the amide group (and of its inhibitor property) allows, in a second step, hydrosilylation with Cl_3SiH. In order to test this assumption, we prepared separately, using trifluoromethanesulfonic acid, the triflate salt of oleic acid anilide **8** and made it react with Ph_3GeH. This reaction yielded the expected germylated adduct **9** in a good yield [equation (6)].



8 9

Equation (6)

CONCLUSIONS

The anilides act as very efficient radical inhibitors for radical initiated hydrometalation of C–C double bonds. As a consequence, auto-inhibition of unsaturated fatty acid phenylamides **1, 2** and **3** prevented their hydrosilylation. In the case of vinylic fatty anilides (**1** and **3**), metal catalysis is recommended to obtain the hydrometalation of the C–C double bond. Concerning internal unsaturations, which are known to exhibit a lower reactivity, the recourse to RIS is the only alternative, at the necessary condition to initially suppress the conjugation in the anilide moiety. Thus, by means of these two strategies (transition metal catalysis and radical initiation sequence), we synthesized various hydrolyzable trialkoxysilyl-fatty acid amides. Their condensation by sol–gel chemistry opens up the way to direct synthesis of novel structured materials and is currently under investigation.

EXPERIMENTAL

All reactions were performed under nitrogen using standard Schlenk tube techniques, Carius tubes and dry solvents. NMR spectra were recorded on Bruker AC 200 (^{1}H, 200.13 MHz), Avance 300 (^{1}H, 300.13 MHz), AC 250 (^{13}C, 62.89 MHz), Avance 300 (^{13}C, 75.48 MHz) and Avance 300 MHz (^{29}Si, 59.62 MHz, DEPT, D1 = 120 s) spectrometers. Gas chromatography (GC) was undertaken on a Hewlett-Packard HP 6890 instrument, and mass spectra were recorded with a Hewlett-Packard HP 5989 instrument in the electron impact mode (EI, 70 eV) or with Applied Biosystems in the Electrospray mode (QTrap). Infrared spectra were recorded on a Perkin Elmer 1600 FT spectrometer. Melting points were measured on a Leitz microscope. Elemental analyses were done at the Centre de Microanalyses de l'Ecole Nationale Supérieure de Chimie de Toulouse. All organic reagents (methyl undec-10-enoate, *cis*-9-methyl oleate, undec-10-enyle chloride, and trifluoromethane sulfonic acid) were purchased from Aldrich and used without supplementary purification. The silanes ($HSiCl_3$ and $HSi(OEt)_3$) were purchased from Aldrich. Triphenylgermane was prepared according to the literature procedure.[24] Karstedt's catalyst [Pt^0] [platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex, 0.100 M in poly(dimethylsiloxane)] and initiators were used in a 1% concentration relative to organic reagents. The radical initiation sequence (RIS) was performed with a mixture of radical initiators: AIBN (half-life time $t_{1/2}$: 2 h, 80 °C); Ph-COO-O^{t}Bu ($t_{1/2}$: 1 h, 125 °C); ^{t}Bu$_2$O$_2$ ($t_{1/2}$: 6 h, 130 °C) in a programmed range of temperature from 25 to 150 °C.

Preparation of $(CH_3\text{-}CH_2\text{-}O)_3Si\text{-}CH_2\text{-}(CH_2)_8\text{-}CH_2\text{-}CONHPh$ (4)

A solution of *N*-phenyl-10-undecenamide **1** (1.30 g, 5.02 mmol) and triethoxysilane (1.10 g, 6.70 mmol) in THF (3 ml) was heated in the presence of Karstedt's catalyst (Pt^0) at 40 °C for 4 h. The reaction was almost quantitative (^{1}H NMR analysis). The mixture was distilled to give 1.65 g of **4**. Yield: 78%. b.p. 165 °C/0.08 mmHg. ^{1}H NMR (200 MHz, $CDCl_3$, 20 °C): 0.61 (m, 2H, Si-C*H*$_2$); 1.21 (t, $^3J_{H,H}$ = 7.0 Hz, 9H, OCH_2CH_3); 1.25 [m, 16H, (C*H*$_2$)$_8$]; 2.33 (t, $^3J_{H,H}$ = 7.4 Hz, 2H, C*H*$_2$CO); 3.80 (q, $^3J_{H,H}$ = 7.0 Hz, 6H, OC*H*$_2$CH$_3$); 7.05–7.90 (m, 5H, C$_6$*H*$_5$); 8.65 (s, 1H, N*H*) ppm. ^{13}C NMR (62.89 MHz, $CDCl_3$, 20 °C): 10.31 (*C*H$_2$Si); 18.25 (OCH$_2$*C*H$_3$); 22.72, 25.75, 29.19, 29.34, 29.41, 31.18, 34.54 (*C*H$_2$)$_8$; 38.13 (*C*H$_2$CO); 58.25 (O*C*H$_2$CH$_3$); 120.14, 123.71, 127.25 [*C*$_6$H$_5$(o, m, p)]; 138.53 [*C*$_6$H$_5$(i)]; 172.41 (*C*O) ppm. ^{29}Si NMR (59.62 MHz, $CDCl_3$, 20 °C): −44.5 ppm. IR ($CDCl_3$): ν = 1661 (C=O), 3324 (N–H) cm^{-1}. MS (EI): m/z = 423 [M^+]. Anal. found, C 65.40, H 9.94, N 3.30; calcd for $C_{23}H_{41}NO_4Si$, C 65.21, H, 9.75, N 3.31%.

Preparation of $[(CH_3\text{-}CH_2\text{-}O)_3Si\text{-}CH_2\text{-}(CH_2)_7\text{-}CH_2\text{-}CH_2\text{-}CONH]_2Ph$ (5)

A mixture of **3** (2.00 g, 4.54 mmol) and triethoxysilane (1.64 g, 10 mmol) was dissolved in toluene (3 ml) and heated in the presence of Karstedt's catalyst [Pt^0] at 80 °C for 8 h. The solvent was evaporated and the reaction was almost quantitative (^{1}H NMR analysis). The solution was treated with 2 ml of dichloromethane. After filtration, compound **5**

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was obtained as a white powder. Yield: 2.75 g (79%); m.p. 233 °C. ^{1}H NMR (200 MHz, DMSO, 20 °C): 0.51 (m, 4H, Si-CH_2); 1.08 (t, $^3J_{H,H} = 6.9$ Hz, 18H, OCH_2CH_3); 1.22 (m, 28H, $(CH_2)_7$); 1.53 (m, 4H, CH_2-CH_2-CO); 2.25 (t, $^3J_{H,H} = 7.2$ Hz, 4H, CH_2CO); 3.70 (q, $^3J_{H,H} = 6.9$ Hz, 12H, OCH_2CH_3); 7.45 (s, 4H, C_6H_4); 9.72 (s, 2H, N*H*) ppm. ^{13}C NMR (62.89 MHz, DMSO, 20 °C): 10.35 (CH_2Si); 18.31 (OCH_2CH_3); 22.82, 23.07, 25.63, 26.73, 28.96, 29.39, 31.10, 32.43, 33.65 $(CH_2)_8$; 39.44 (CH_2CO); 58.14 (OCH_2CH_3); 120.93 [C_6H_4 (o, m)]; 135.06 [C_6H_4 (i)]; 171.28 (*C*O) ppm. ^{29}Si NMR (59.62 MHz, DMSO, 20 °C): −45.1 ppm. IR (DMSO): $\nu = 1654$ (C=O), 3400 (N–H) cm^{-1}. MS (EI): $m/z = 768$ [M$^+$]. Anal. found, C 62.05, H 9.74, N 3.63; calcd for $C_{40}H_{76}N_2O_8Si_2$: C 62.46, H, 9.96, N 3.64%.

Preparation of CH_3-$(CH_2)_7$-$CHSiCl_3$-$(CH_2)_7$-CH_2-$CONH_2^+$ Ph,Cl^- (6)

A mixture of **2** (1.00 g, 2.80 mmol) and Cl_3SiH (1.12 g, 8.4 mmol) was heated from 60 °C until 150 °C under RIS conditions for 45 h. The reaction was almost quantitative (^{1}H NMR analysis). This solution was treated twice with THF (3 ml) and filtered. After filtration, the concentration of the filtrate led to a viscous residue identified to **6** (quantitative yield). ^{1}H NMR (200 MHz, $CDCl_3$, 20 °C): 0.82 (t, $^3J_{H,H} = 6.5$ Hz, 3H, CH_3); 1.20 [s.br, 29H, $(CH_2)_7$-$CH$$SiCl_3$-$(CH_2)_7$]; 2.28 (t, $^3J_{H,H} = 7.1$ Hz, 2H, CH_2CO); 7.04–7.50 (m, 5H, C_6H_5) ppm. ^{13}C NMR (62.89 MHz, $CDCl_3$, 20 °C): 14.17 (CH_3); 22.69, 25.62, 26.52, 28.87, 29.20, 29.36, 29.55, 29.66, 31.35, 34.19 $(CH_2)_7$; 31.92 (*C*HSi); 38.53 (CH_2CO); 120.78, 123.83, 127.55 [C_6H_5 (o, m, p)]; 138.47 [C_6H_5 (i)]; 170.20 (*C*O) ppm. ^{29}Si NMR (59.62 MHz, $CDCl_3$, 20 °C): 14.5 ppm. IR ($CDCl_3$): $\nu = 1704$ (C=O), 3126 (N–H) cm^{-1}. MS (EI): $m/z = 527$ [M$^+$], 491 [M-HCl], 378 [$CH(SiCl_3)(CH_2)_8CONHPh^+$]. MS (electrospray): 494.04 [CH_3-$(CH_2)_7$-$CH(SiCl_3)$-$(CH_2)_8$-$CONH_2^+$Ph], 35.45 [Cl^-].

Preparation of CH_3-$(CH_2)_7$-$CHSi(OEt)_3$-$(CH_2)_7$-CH_2-CONHPh (7)

To a solution of **6** [prepared from **2** (1.00 g, 2.80 mmol) and Cl_3SiH (1.12g, 8.4 mmol)] in toluene (12 ml) was added dropwise a large excess of Et_3N (12 ml) and EtOH (5 ml) at −40 °C. The reaction mixture was kept at −40 °C for 20 mn and stirred at 20 °C for 4 h. The solvents were removed *in vacuo* and the residue dissolved in pentane (6 ml). The salt (NEt_3, HCl) was eliminated by filtration, the solvent was removed under reduced pressure and distillation gives compound **7** as a colorless liquid. Yield: 0.61 (42%); b.p., 227 °C/0.06 mmHg. ^{1}H NMR (200 MHz, $CDCl_3$, 20 °C): 0.92 (t, $^3J_{H,H} = 6.5$ Hz, 3H, CH_3); 1.18 (t, $^3J_{H,H} = 6.9$ Hz, 9H, OCH_2CH_3), 1.33 [s.br., 29H $(CH_2)_7$-CHSi-$(CH_2)_7$]; 2.35 (t, $^3J_{H,H} = 7.3$ Hz, 2H, CH_2CO); 3.76 (q, $^3J_{H,H} = 6.9$ Hz, 6H, OCH_2CH_3); 7.05–7.52 (m, 5H, C_6H_5) ppm. ^{13}C NMR (62.89 MHz, $CDCl_3$, 20 °C): 14.33 (CH_3); 18.56 (OCH_2CH_3); 22.57 (*C*HSi); 22.34, 25.43, 25.57, 27.28, 29.48, 29.89, 30.17, 30.70, 31.84, 32.36, 34.24 $(CH_2)_7$; 38.55 (CH_2CO); 58.55 (OCH_2CH_3); 120.08, 124.42, 129.27 [C_6H_5 (o, m, p)]; 137.28 [C_6H_5 (i)]; 172.65 (*C*O) ppm. ^{29}Si NMR (59.62 MHz, $CDCl_3$, 20 °C): −44.8 ppm. IR ($CDCl_3$): $\nu = 1665$ (C=O), 3336 (N–H) cm^{-1}. MS (EI): $m/z = 521$ [M$^+$], 408 [$CH(Si(OEt)_3$-$(CH_2)_8$-$CONHPh^+$]. Anal. found, C 69.47, H 10.37, N 2.82; calcd for $C_{30}H_{55}NO_4Si$: C 69.05, H, 10.62, N 2.68%.

Preparation of $[CH_3$-$(CH_2)_6$-CH_2-CH=CH-CH_2-$(CH_2)_4$-CH_2-CH_2-$CONH_2Ph]^+$ $[CF_3$-SO_2-$O]^-$ (8)

To a solution of *N*-phenylocta-9-enamide **2** (1.00 g, 2.80 mmol) in $CHCl_3$ (4 ml) was added dropwise trifluoromethanesulfonic acid (0.42 g, 2.80 mmol). The mixture was stirred for 15 min, and evaporation *in vacuo* led to a viscous residue identified as **8** (quantitative yield). ^{1}H NMR (200 MHz, $CDCl_3$, 20 °C): 0.84 (t, $^3J_{H,H} = 6.5$ Hz, 3H, CH_3); 1.23 [m, 20H, $(CH_2)_4$ and $(CH_2)_6$]; 1.68 (m, 2H, CH_2CH_2CO); 2.06 (m, 4H, CH_2-CH=); 2.29 (t, $^3J_{H,H} = 7.1$ Hz, 2H, CH_2CO); 5.25–5.40 (m, 2H, CH=C*H*); 7.28–7.58 (m, 5H, C_6H_5) ppm. ^{13}C NMR (62.89 MHz, $CDCl_3$, 20 °C): 14.15 (CH_3); 22.71, 26.86, 27.21, 27.26, 29.11, 29.35, 29.68, 31.92, 32.64 $(CH_2)_7$; 34.36 (CH_2CO); 119.72 (q, $^2J_{C,F} = 318.2$ Hz, CF_3), 120.15, 122.45, 127.50 [C_6H_5 (o, m, p)]; 129.63, 130.05 (*C*H=*C*H); 134.83 [C_6H_5 (i)]; 177.60 (*C*O) ppm. IR ($CDCl_3$): $\nu = 1701$ (C=O), 3121 (N-H) cm^{-1}. MS (electrospray): 358.58 [CH_3-$(CH_2)_7$-CH=CH-$(CH_2)_7$-$CONH_2^+$Ph]; 149.05 [CF_3-SO_2-O^-]. Using similar experimental conditions, no reaction was observed with trifluoroacetic acid. The reaction of AgOTf led to the cleavage of C–N bond and the one with hydrofluoride acid yielded a mixture of unidentified products.

Preparation of CH_3-$(CH_2)_7$-$CH(GePh_3)$-$(CH_2)_7$-CH_2-CONHPh (9)

To a solution of *N*-phenylocta-9-enamide **2** (1.00 g, 2.80 mmol) in $CHCl_3$ (4 ml) was added dropwise trifluoromethanesulfonic acid (0.42 g, 2.80 mmol). After 15 min, the solution was evaporated and Ph_3GeH (0.94 g, 3.08 mmol) was then added. The mixture was heated in a Carius tube under RIS conditions from 60 to 150 °C for 24 h. The residue was dissolved in diethyl ether (3 ml) and Et_3N (0.28 g, 2.80 mmol) was then added. The salt ($HNEt_3$,OTf) was eliminated by filtration. The solvent was removed and the solution was triturated twice with pentane (3 ml). After filtration, the solvent was evaporated and distillation gave 0.96 g of **9**. Yield: 52%; b.p., 233 °C/0.05 mmHg. ^{1}H NMR (200 MHz, $CDCl_3$, 20 °C) : 0.85 (t, $^3J_{H,H} = 6.5$ Hz, 3H, CH_3); 1.20 [s.br., 29H $(CH_2)_7$-$CH(GePh_3)$-$(CH_2)_7$]; 2.36 (t, $^3J_{H,H} = 6.9$ Hz, 2H, CH_2CO); 6.68–7.58 (m, 20H, C_6H_5) ppm. ^{13}C NMR (62.89 MHz, $CDCl_3$, 20 °C) = 14.13 (CH_3); 22.67, 25.72, 29.16, 29.30, 29.51, 29.63, 31.36, 31.90, 32.59 $(CH_2)_7$; 30.02 (*C*HGe); 39.20 (CH_2CO); 120.12, 123.69, 127.04 [$NHCOC_6H_5$ (o, m, p)]; 128.15, 130.38, 134.05 [GeC_6H_5 (o, m, p)]; 138.69, 139.70 [C_6H_5 (i)]; 172.27 (*C*O) ppm. IR ($CDCl_3$): $\nu = 1674$ (C=O), 3324 (N–H) cm^{-1}. MS (EI): $m/z = 663$ [M$^+$], 550 [$CH(GePh_3)(CH_2)_8CONHPh^+$]. Anal. found, C 75.78, H 8.13, N 2.25; calcd for $C_{42}H_{55}GeNO$: C 76.15, H, 8.37, N 2.11%.

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