Steric and Electronic Effects in Cyclic Alkoxyamines—Synthesis and Applications as Regulators for Controlled/Living Radical Polymerization

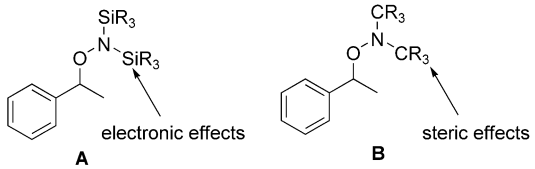
Christian Wetter, Johannes Gierlich, Christoph Alexander Knoop, Christoph Müller, Tobias Schulte, and Armido Studer*[a]

Abstract: The synthesis of new six- and seven-membered cyclic alkoxyamines bearing ethyl groups at the α-*N* position of the alkoxyamines is described. The key step in the synthesis of the sterically hindered six-membered cyclic alkoxyamines is a Wadsworth–Horner–Emmons olefination with bisphosphonate **1**. The seven-membered cyclic alkoxyamines were prepared from the corresponding six-membered keto alkoxyamines by ring-enlargement with trimethylsilyl(TMS)-diazomethane. The use of the new alkoxyamines as regulators/initiators for radical polymerization is discussed. Efficient controlled and living polymerization of styrene and *n*-butyl acrylate was obtained with the six-membered tetraethyl alkoxyamine **13**. Controlled polymerizations can be conducted even at 90 °C. In addition, alkoxyamine **13** can be used for the preparation of AB diblock and ABA triblock copolymers with narrow polydispersities. The influence of the replacement of methyl groups in the α-position of the N atom in cyclic alkoxyamines by larger ethyl groups on the styrene polymerization (reaction time, PDI, kinetics of the C–O bond homolysis) is discussed. In addition, thermal decomposition of the new alkoxyamines was studied. Furthermore, the synthesis of *N*,*N*-bissilylated alkoxyamines is described. The silylated alkoxyamines are not suitable as regulators/initiators for the controlled/living radical polymerization. The C–O bonds in silylated alkoxyamines are stronger than the C–O bonds in analogous *N*,*N*-dialkylated alkoxyamines. The experimental results are verified by calculations with Gaussian 98 (A.9).

Keywords: alkoxyamines · block copolymers · kinetics · nitroxides · radical polymerization

Introduction

During the last ten years, radical polymerization has gained renewed interest. Different methods have been introduced that allow controlled living radical polymerizations. Nowadays, polymers with narrow polydispersities (PDI < 1.2) can be prepared by nitroxide-mediated polymerizations (NMPs),[1] atom-transfer radical polymerizations (ATRPs),[2] or reversible addition–fragmentation chain transfer (RAFT) polymerizations.[3] The NMP and ATRP processes are controlled by the persistent radical effect (PRE).[4] For NMP, reversible formation of a dormant alkoxyamine from the corresponding nitroxide and the chain-growing polymer radical is the key to the success of the controlled/living polymerization. The equilibrium in the NMP lies well towards the side of the dormant alkoxyamine, thus ensuring a low concentration of free radicals during the polymerization. The equilibrium constant between the nitroxide-capped polymer and the free nitroxide and polymer radical, respectively, is of great importance. Various parameters, such as H bonding,[5] steric and electronic effects among others, influence the equilibrium.[6,7] Based on calculations, Moad and Rizzardo predicted small C–O bond dissociation energies for silylated alkoxyamines of type **A** (Scheme 1).[8] Moreover, they showed that increasing the steric bulk around the N atom in the alkoxyamines should decrease the C–O bond strength (→**B**). Very recently, Fischer discussed steric effects of ring substituents in cyclic alkoxyamines on the equilibrium constant based on experimental results.[9] In agreement



Scheme 1. Variation of the steric and electronic effects of the N substituents in alkoxyamines.

[a] Dipl. Chem. C. Wetter, Dipl. Chem. J. Gierlich, Dipl. Chem. C. A. Knoop, Dipl. Chem. C. Müller, Dipl. Chem. T. Schulte, Prof. Dr. A. Studer
Fachbereich Chemie der Universität Marburg
Hans-Meerwein-Strasse, 35032 Marburg (Germany)
Fax: (+49) 6421-282-5629

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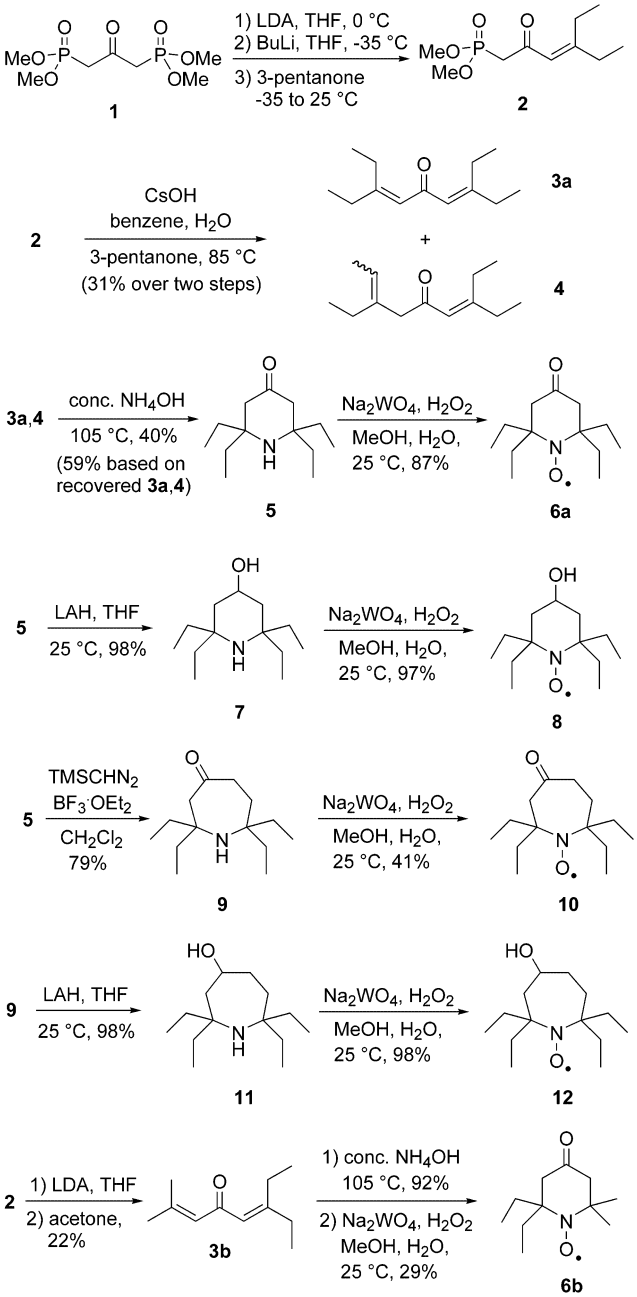
with the theoretical predictions, an increase in the size of the substituents leads to a decrease of the C–O bond dissociation energy.

Herein we present results on the synthesis of new sterically hindered styryl-TEMPO derivatives (TEMPO = 2,2,6,6-tetramethylpiperidinyl-1-oxyl). In addition, the synthesis of silylated alkoxyamines is described. The efficiency of the new alkoxyamines as regulators for the polymerization of styrene and *n*-butyl acrylate is discussed. In addition, the preparation of AA and AB diblock as well as of ABA triblock copolymers is presented. Furthermore, rate constants for the C–O bond homolysis of the new alkoxyamines derived from these nitroxides and decomposition studies of the new alkoxyamines are given. Finally, calculations on the C–O bond dissociation energy of silylated alkoxyamines is described.

Results and Discussion

Preparation of the alkoxyamines: Bisphosphonate **1** was prepared according to a literature procedure in two steps starting from commercially available methallyl dichloride.[10] Wadsworth–Horner–Emmons (WHE) olefination with 3-pentanone was attempted under different conditions. With LiBr/1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)/THF,[11] $KHCO_3$/*t*BuOH/H_2O, $Ba(OH)_2$/THF/H_2O, and LDA/THF the desired olefin **2** was not observed. With NaH in THF the product was obtained in moderate yields; however, upscaling was not possible. It turned out that dianion formation is essential for this particular WHE reaction. Thus, treatment of **1** with LDA and subsequent addition of BuLi afforded the corresponding dianion that was reacted with 3-pentanone to give phosphonate **2**, which was used for the second olefination without any purification (Scheme 2). Unfortunately, one-pot bis-olefination could not be accomplished. The second WHE reaction with 3-pentanone was difficult to achieve. Olefination with LiBr/DBU/THF,[11] LDA/THF, NaH/THF, $MgBr_2$/NEt_3/THF,[12] and $Ba(OH)_2$/THF/

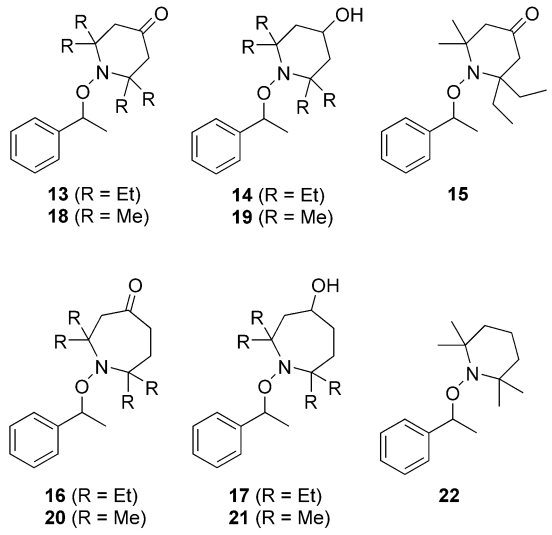
Abstract in German: *In dieser Arbeit wird die Herstellung von zyklischen 6- und 7-Ring-Alkoxyaminen beschrieben, die in α-Stellung zum Stickstoffatom Ethylgruppen tragen. Der Schlüsselschritt in der Synthese dieser sterisch gehinderten Alkoxyamine beinhaltet eine Wadsworth–Horner–Emmons-Olefinierung am Bisphosphonat **1**. Die 7-gliedrigen Homologen wurden ausgehend von den entsprechenden Piperidinonen hergestellt. Die Ringerweiterung wurde mit TMS-Diazomethan durchgeführt. Es wird über die Verwendung der neuen Alkoxyamine als Regulatoren/Initiatoren in der radikalischen Polymerisation berichtet. Effiziente kontrollierte und lebende Polymerisation von Styrol und n-Butylacrylat wurde mit dem Tetraethylpiperidinon-Alkoxyamin **13** erzielt. Kontrollierte Polymerisationen konnten sogar bei 90 °C durchgeführt werden. Außerdem kann das Alkoxyamin **13** für den Aufbau von AB-Diblock- und ABA-Triblock-Copolymeren mit niedrigen Polydispersitäten verwendet werden. Es wird diskutiert, welchen Einfluss der Austausch von Methyl- durch Ethylgruppen in α-Stellung zum Stickstoff in zyklischen Alkoxyaminen auf die Styrolpolymerisation ausübt (Reaktionsdauer, PDI, Kinetiken der C–O-Bindungshomolyse). Die thermische Zersetzung der neuen Alkoxyamine wurde untersucht. Des Weiteren wird die Herstellung von N,N-bissilylierten Alkoxyaminen beschrieben. Die silylierten Alkoxyamine sind als Initiatoren/Regulatoren für kontrollierte/lebende Polymerisationen nicht geeignet. Die C–O-Bindungen in silylierten Alkoxyaminen sind stärker als die C–O-Bindungen in entsprechenden dialkylierten Alkoxyaminen. Die experimentellen Ergebnisse wurden mit Hilfe von Berechnungen mit Gaussian 98 (A. 9) bestätigt.*



Scheme 2. Synthesis of the nitroxides **6a**,**b**, **8**, **10**, and **12**.

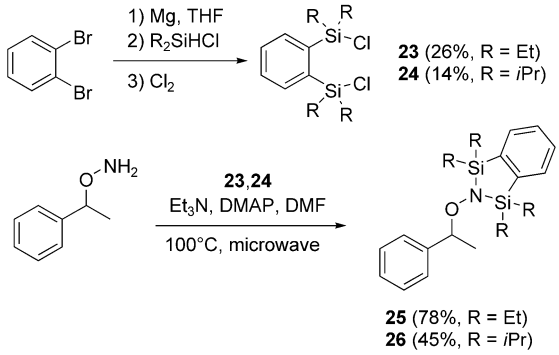
H_2O failed. Pleasingly, a smooth olefination was observed with CsOH in a benzene/H_2O mixture. The WHE products were isolated in 31% overall yield as a mixture of the desired ketone **3a** along with the isomerized β,γ-unsaturated ketones **4** (*cis*/*trans* mixture of isomers; ratio **3a**/**4** = 1:6). Prolonged heating under the reaction conditions did not alter the isomer ratio (thermodynamic product control). Separation of the isomers was not necessary because isomerization occurred under the conditions applied for the subsequent cyclization reaction (concentrated NH_4OH, 105°C). Heating of the **3a**,**4** mixture in concentrated NH_4OH at 105°C in a sealed tube for 20 h afforded piperidinone **5** (40%, 59% based on recovered **3a** and **4**), that was oxidized with Na_2WO_4/H_2O_2 in $MeOH/H_2O$[13] to give nitroxide **6a** in 87% isolated yield. Nitroxide **6b** was prepared in analogy from **2** via ketone **3b**.

Hydroxy derivative **8** was obtained via reduction of **5** (LAH, →**7**) and subsequent oxidation (95% overall). Ring-enlargement of **5** with $TMSCHN_2/BF_3{\cdot}OEt_2$ (→**9**)[7] and oxidation afforded keto nitroxide **10** in 33% overall yield. LAH reduction of **9** gave alcohol **11** that was directly oxidized to give nitroxide **12** (96%). The alkoxyamines **13**–**17** were prepared from 1-phenylethyl bromide and the corresponding nitroxides according to the Matyjaszewski protocol (Scheme 3).[14] For a proper discussion of the steric effects of the ring substituents of our new alkoxyamines on the polymerizations, results previously obtained with the smaller methyl-substituted alkoxyamines **18**–**22** are also considered in the present study.



Scheme 3. New sterically hindered alkoxyamines **13**–**17** and the corresponding known methyl derivatives **18**–**22**.

The silylated alkoxyamines were prepared from commercially available 1,2-dibromobenzene. Formation of the bis-Grignard reagent from 1,2-dibromobenzene and silylation with diethylchlorosilane or diisopropylchlorosilane afforded the corresponding dialkylarylsilanes (Scheme 4). The chlorosilanes were readily obtained from the silanes upon treatment with Cl_2 (→**23**,**24**).[15,16a] Silylation of 1-phenylethoxyamine[16b] with **23** and **24** to give **25** and **26** was best achieved under microwave irradiation in DMF with Et_3N and catalytic amounts of DMAP.



Scheme 4. Synthesis of the silylated alkoxyamines **25** and **26**.

Polymerization of styrene with alkoxyamines 13–17: The polymerizations were conducted in sealed tubes with 1% of the alkoxyamine initiator at 90–125°C and were stopped after 6–56 h. The conversion was determined gravimetrically. The polydispersity index (PDI) and the molecular weight of the polymers were analyzed by means of size-exclusion chromatography (SEC). The results are summarized in Table 1.

The fastest polymerization was observed for the six-membered keto alkoxyamine **13** for which a 79% conversion was obtained after 6 h. Furthermore, excellent control of the polymerization was achieved (PDI = 1.12, Table 1, entry 1). As expected, the ethyl groups accelerate the polymerization process: styrene polymerization with the corresponding smaller methyl-substitut-

Table 1. Polymerization of styrene using alkoxyamines **13**–**17**.

Entry	Alkoxyamine (mol%)	Temp [°C]	Time [h]	$M_{n,\mathrm{exp}}$ [g mol^{-1}]	$M_{n,\mathrm{theory}}$ [g mol^{-1}]	PDI	Conversion [%]	Ref.
1	**13** (1)	125	6	10900	8200	1.12	79	[a]
2	**14** (1)	125	6	11700	7100	1.36	68	[a]
3	**15** (1)	125	6	7400	6800	1.14	65	[a]
4	**16** (1)	125	6	7700	6900	1.13	66	[a]
5	**17** (1)	125	6	10600	5800	1.64	56	[a]
6	**18** (1)	125	6	3000	2900	1.23	28	[b]
7	**19** (1)	125	6	2200	2700	1.27	26	[b]
8	**20** (1)	125	6	9000	8700	1.10	84	[b]
9	**21** (1)	125	6	3300	3100	1.23	30	[b]
10	**13** (0.2)	125	6	43500	38500	1.32	74	[a]
11	**13** (1)	105	24	9400	7200	1.09	69	[a]
12	**13** (0.2)	105	24	37500	38000	1.16	73	[a]
13	**13** (0.1)	105	24	62400	73900	1.24	71	[a]
14	**13** (1)	90	56	10500	7600	1.08	73	[a]
15	**22** (1)	125	6	1800	2000	1.30	19	[a]

[a] This work. [b] Ref. [7]

ed six-membered keto alkoxyamine regulator **18** afforded only 28% conversion under the same conditions (Table 1, entry 6). The well-known styryl-TEMPO alkoxyamine **22** gave a conversion of only 19% with a PDI of 1.30 under the same conditions (Table 1, entry 15). The same trend was observed for the six-membered hydroxy-alkoxyamines **14** and **19** . With the larger ethyl-substituted initiator, **14**, polymerization was faster than with **19** (Table 1, entries 2, 7). However, the control of the polymerization was not satisfactory for the hydroxy-alkoxyamines **14** and **19** (PDI > 1.2). We have previously[7] shown that hydroxy-substituted cyclic alkoxyamines are not sufficiently stable under the reaction conditions. This is probably the reason for the modest control obtained with regulator **14**. Stability studies are discussed below. The methyl-ethyl-substituted initiator **15** provided a fast polymerization and a good control (Table 1, entry 3). A good result was obtained with the seven-membered alkoxyamine **16** (66% conversion, PDI = 1.13, Table 1, entry 4). Contrary to our expectations, a higher conversion was measured for the smaller methyl congener **20** (Table 1, entry 8). As for the six-membered alkoxyamines, polymerization was not controlled with the hydroxy derivative **17** (Table 1, entry 5). From these initial results we can conclude that, for six-membered alkoxyamines, the substitution of methyl groups with larger ethyl groups leads to an improvement of the initiator/regulator efficiency. However, for the seven-membered systems, the size of the substituents did not influence the polymerization process to a large extent. In fact, the tetramethyl-substituted seven-membered alkoxyamine **20** turned out to be a slightly better initiator/regulator than the ethyl congener **16** for the styrene polymerization. Furthermore, keto groups in the rings are tolerated, whereas 4-hydroxy-substituted cyclic alkoxyamines provide moderate results.

Further polymerization studies were conducted with the efficient alkoxyamine **13**. We first attempted to prepare high molecular-weight polystyrene using **13**. The reaction was performed with 0.2 mol% of **13** under otherwise identical conditions (Table 1, entry 10). Disappointingly, the polymerization was not well controlled (PDI = 1.32, M_n = 43500 g mol^{-1}). We repeated the polymerization at 105°C (Table 1, entry 11, 1 mol% **13**). To our delight, polymerization over a period of 24 h afforded polystyrene with a PDI of 1.09 (69% conversion). Therefore, lowering of the temperature is important for a successful polymerization. High molecular weight polystyrene (up to 62500 g mol^{-1}) with a narrow PDI can be prepared at 105°C (Table 1, entries 12, 13). Even at 90°C, controlled (but slow) polymerization of styrene can be performed with our new alkoxyamine **13** (Table 1, entry 14).

To prove the controlled/living character of the **13**-mediated styrene polymerization, we determined the conversion as a function of time and we analyzed the molecular weight as a function of monomer conversion (Figure 1). The linear increase of $\ln([M_o]/[M])$ versus time and molecular weight versus monomer consumption proves the controlled character of the polymerization.

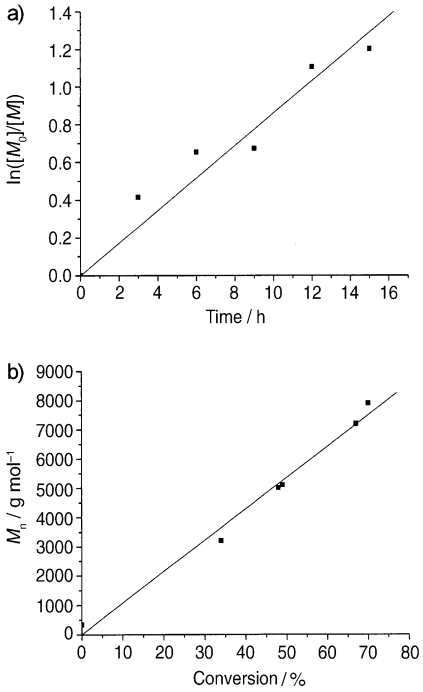


Figure 1. a) Monomer conversion versus time (styrene, 105°C, 1 mol% **13**). b) Molecular weight vs monomer conversion (styrene, 105°C, 1 mol% **13**, 15 h).

It is well-known that styryl-TEMPO **22** is not able to control the acrylate polymerization.[1c] To date, controlled nitroxide-mediated polymerization of acrylates is only possible with two types of nitroxides.[6g,17,18] To control the acrylate polymerization, however, sacrificial nitroxide has to be added to the reaction mixture in these systems. Therefore, we focused on the polymerization of *n*-butyl acrylate with alkoxyamine **13** and *without additional nitroxide*. The polymerizations were conducted at 105 or 125°C in neat *n*-butyl acrylate (Table 2). We were very pleased to observe that polymerization was efficient and controlled at 125°C (Table 2, entry 1). Even better results were obtained on lowering the reaction temperature to 105°C. Reaction for 32 h provided poly(*n*-butyl acrylate) with a PDI of 1.12 with M_n of 18600 g mol^{-1} (Table 2, entry 2). It is important to note that no nitroxide has to be added to the reaction mixture. To our knowledge, this is the first report of a successfully controlled polymerization of an acrylate mediated by a cyclic nitroxide.[19]

Table 2. Polymerization of *n*-butyl acrylate with **13** under different conditions.

Entry	Alkoxyamine (mol%)	Temp [°C]	Time [h]	$M_{n,\mathrm{exp}}$ [g mol^{-1}]	$M_{n,\mathrm{theory}}$ [g mol^{-1}]	PDI	Conversion [%]
1	**13** (1)	125	9	20500	11400	1.18	89
2	**13** (1)	105	32	18600	10600	1.12	83
3	**13** (0.2)	105	32	73000	53800	1.21	84
4	**13** (0.1)	105	32	91300	83300	1.34	65
5	**13** (1)	90	96	12300	9000	1.13	70

All the following experiments were therefore conducted at 105 °C. With 0.2 mol % **13**, high conversion (84 %) and good control (PDI = 1.21) was obtained after 32 h (Table 2, entry 3). High molecular-weight poly(*n*-butyl acrylate) was prepared with 0.1 mol % of the alkoxyamine (M_n = 91300 g mol^{-1}, Table 2, entry 4). However, the polydispersity slightly increased. *We also showed that the butyl acrylate polymerization can be conducted at 90 °C* (Table 2, entry 5, 96 h, PDI = 1.13, 70 % conversion).

We next studied the preparation of block copolymers with alkoxyamine **13**. To this end, alkoxyamine-terminated polystyrene and poly(*n*-butyl acrylate) were used as macroinitiators. Polymerizations were conducted under bulk conditions at 105 and 125 °C. The results are summarized in Table 3. Styrene polymerization at 125 °C with a polystyrene macroinitiator (PDI = 1.10, M_n = 9300 g mol^{-1}) afforded polystyrene with an increased PDI (PDI = 1.45, Table 3, entry 1). A slightly better result was obtained if a poly(*n*-butyl acrylate) was used as a macroinitiator (Table 3, entry 2). The poly(*n*-butyl acrylate)-*block*-polystyrene (P(*n*-BA)-*b*-PS) diblock copolymer was formed with a PDI of 1.28. We thought that decreasing the reaction temperature would further improve the results. Indeed, styrene polymerization with a PS-macroinitiator at 105 °C afforded polystyrene with a narrow PDI (PDI = 1.08, Table 3, entry 3). Furthermore, a polystyrene-*block*-poly(*n*-butyl acrylate) (PS-*b*-P(*n*-BA)) diblock copolymer with an M_n of 66400 g mol^{-1} and a narrow PDI (1.08) was prepared at 105 °C starting with a PS macroinitiator (Table 2, entry 4). GPC traces of the PS macroinitiator and the PS-*b*-P(*n*-BA) diblock copolymer are presented in Figure 2 (traces a and b). Nitroxide-mediated polystyrene-*block*-poly(*n*-butyl acrylate) diblock formation was not successful with the alkoxyamines known to date.[17] P(*n*-BA)-*b*-PS diblock copolymer formation worked very well with alkoxyamine **13** (Table 3, entry 5). Encouraged by these results, we then focused on the formation of ABA triblock copolymers. To this end, a P(*n*-BA)-*b*-PS macroinitiator (M_n = 39200 g mol^{-1}, PDI = 1.15) was used for the neat acrylate polymerization at 105 °C. We were very pleased to observe that ABA triblock copolymerization worked well. P(*n*-BA)-*b*-PS-*b*-(*n*-BA) with a M_n of 30900 g mol^{-1} and a narrow PDI of 1.14 was formed (Table 3, entry 6, Figure 2, trace d). In analogy, we prepared a PS-*b*-P(*n*-BA)-*b*-PS triblock copolymer with excellent control (PDI = 1.14, Table 3,entry 7). We can conclude that AB diblock and ABA triblock copolymers with narrow PDIs can be efficiently prepared with alkoxyamine **13**.

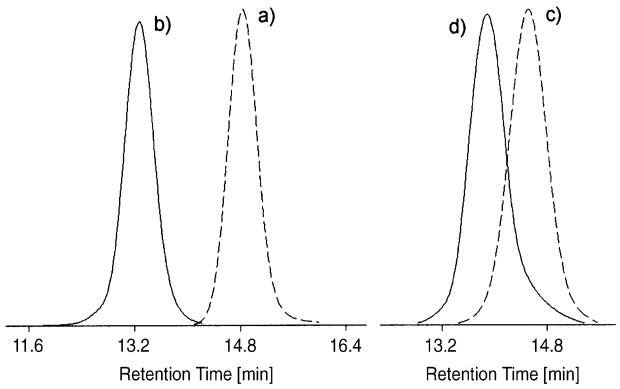


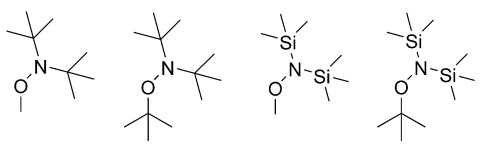
Figure 2. GPC traces of the PS-*b*-P(*n*-BA) diblock copolymer (trace b) and the P(*n*-BA)-*b*-PS-*b*-(*n*-BA) triblock copolymer (trace d) and the corresponding macroinitiators (trace a: PS macroinitiator; trace c: P(*n*-BA)-*b*-PS-macroinitiator).

Table 3. Preparation of di- and triblock copolymers using alkoxyamine **13**.

Entry	Macroinitiator (M_n, PDI, mol %)	Monomer	T [°C]	Time [h]	$M_{n,\mathrm{exp}}$ [g mol^{-1}]	$M_{n,\mathrm{theory}}$ [g mol^{-1}]	PDI	Conversion [%]
1	PS (9300, 1.10, 0.2 %)	styrene	125	6	33600	48900	1.45	58
2	P(*n*-BA) (18600, 1.12, 0.2 %)	styrene	125	6	42000	70700	1.28[a]	50
3	PS (5000, 1.12, 1 %)	styrene	105	12	19400	10300	1.08	51
4	PS (10500, 1.08, 0.2 %)	*n*-butyl acrylate	105	32	66400	74600	1.08[b]	57
5	P(*n*-BA) (17800, 1.13, 0.2 %)	styrene	105	12	39200	57400	1.15[a]	42
6	P(*n*-BA)-*b*-PS (16700, 1.12, 0.5 %)	*n*-butyl acrylate	105	32	30900	24700	1.14[b]	31
7	PS-*b*-P(*n*-BA) (6600, 1.15, 0.5 %)	styrene	105	16	25400	22200	1.14[a]	61

[a] Measured with polystyrene standard solution. [b] Measured with poly(methylmethacrylate) standard solution.

Polymerization studies with the silylated alkoxyamines: We then studied styrene polymerizations with the silylated alkoxyamines **25** and **26**. The polymerizations were conducted under the conditions described above. Disappointingly, neither **25** nor **26** were able to control the polymerization (PDI > 2.0). Polymerizations are governed by the autopolymerization of styrene.[20] The alkoxyamines are only spectators in these polymerizations! Contrary to the calculations reported in the literature,[8] C–O bonds in silylated alkoxyamines are obviously stronger than in the corresponding *N*,*N*-dialkylated alkoxyamines. Therefore, we decided to reinvestigate the C–O bond strengths in silylated alkoxyamines by computational methods. Alkoxyamines **27**–**30** were chosen as model compounds to elucidate the effect of *N*-silyl substitution in alkoxyamines.



27 **28** **29** **30**

Structures were optimized with Gaussian 98 (A.9)[21] at the B3LYP level of theory. Unless otherwise stated, the bond energies were BSSE (basis-superposition error)-cor-

rected (counterpoise method).[22] Calculated C–O bond energies and bond lengths of the alkoxyamines **27**–**30** are presented in Table 4.

Similar C–O bond lengths were calculated for the silylated and *N*,*N*-*tert*-butylated alkoxyamines (compare **27** with **29** and **28** with **30**). As expected for steric reasons, C–O bonds in alkoxyamines **28** and **30**, which are derived from *tert*-butyl radicals, are longer than the corresponding methyl-substituted alkoxyamines **27** and **29**. As a direct consequence of the steric repulsion and the additional stability of a tertiary radical compared to a primary radical, C–O bonds are stronger in the methyl-substituted alkoxyamines **27** and **29** compared to their *tert*-butyl derivatives **28** and **30** (59.9 kJ mol^{-1} for **27**/**28** and 51.7 kJ mol^{-1} for **29**/**30**). As predicted from our experimental results, C–O bonds for the silylated alkoxyamines are stronger than for the corresponding dialkylated alkoxyamines. Thus, replacement of both *tert*-butyl groups in **27** with two trimethylsilyl groups (→**29**) leads to an increase of the C–O bond energy by 32.7 kJ mol^{-1}. In analogy, for the sterically more hindered *tert*-butyl compounds, a 40.8 kJ mol^{-1} stronger C–O bond was calculated for the silyl-substituted alkoxyamine **30**. Hence, we can conclude that, in contrast to previous calculations, replacement of the N substituents in alkoxyamines by silyl groups leads to an increase in the C–O bond energy and, therefore, silylated alkoxyamines are not useful as regulators/initiators for the controlled free-radical polymerization.

Table 4. Calculated C–O bond energies and bond lengths.

Compound	N–O [Å]	Si–N [Å]	C–N [Å]	C–O [Å]	ΔE [C–O] [kJ mol^{-1}]
27	1.451	–	1.515	1.422	−138.25
28	1.449	–	1.527	1.480	−78.38
29	1.476	1.797	–	1.423	−170.91
30	1.470	1.806	–	1.473	−119.20

Kinetics of the C–O bond homolysis—EPR experiments: The kinetic experiments were conducted in *tert*-butylbenzene at 403 K. Oxygen was used to scavenge the styryl radical and the concentration of the released nitroxide was measured by EPR spectroscopy, as previously described.[5,6h,k,7,23] The experimental cleavage rate constants k_d were calculated by means of Equation (1) (conversions up to 30 %). The activation energies E_a were estimated from the rate constants, whereby $A = 2.4\times10^{14}$ s^{-1}.[5,6h,7]

$$\ln\left(\frac{[\text{nitroxide}]_\infty - [\text{nitroxide}]_t}{[\text{nitroxide}]_\infty}\right) = -k_d \cdot t \quad (1)$$

The fastest C–O bond homolysis was measured for the six-membered ethyl-substituted alkoxyamines **13** and **14** (Table 5; entries 1 and 2; **13**: 2.2×10^{-2} s^{-1}; **14**: 2.9×10^{-2} s^{-1}). For the corresponding methyl derivatives, homolytic cleavage rate constants k_d of 5.7×10^{-4} s^{-1} (**18** at 407 K) and 3.3×10^{-3} s^{-1} (**19** at 413 K) have been reported.[7] This clearly shows that increasing the size of the α-N substituents in cyclic alkoxyamines leads to an increase in the rate constant for the C–O bond homolysis, in agreement with recent reports from the Fischer laboratory for other cyclic alkoxyamines.[9] Interestingly, replacement of two of the four methyl groups in **18** by ethyl groups leads to a rate constant that lies in the middle between the those of tetramethyl derivative **18** and the tetraethyl derivative **13** (→**15**, k_d of 4.9×10^{-3} s^{-1}, Table 5, entry 3). To our surprise, the ring-enlarged seven-membered alkoxyamines **16** and **17** homolyze more slowly than the corresponding six-membered compounds **13** and **14** (compare Table 5, entries 1 and 2 with 4 and 5). This is in contrast to the methyl series where the seven-membered alkoxyamines **20** and **21** homolyze faster than the six-membered derivatives **18** and **19** (**20**: 2.0×10^{-3} s^{-1} at 407 K; **21**: 2.7×10^{-2} s^{-1} at 407 K).[7]

Thermal stability of the alkoxyamines: The thermal decomposition of a polymeric alkoxyamine leading to a terminally unsaturated polymer and the corresponding hydroxylamine is an important side reaction in NMP. This process can occur by transfer of a β-hydrogen atom from the transient polymer radical to the nitroxide or by a non-radical direct ionic elimination.[24b] We decided to study the thermal decomposition of the various alkoxyamines to styrene and the corresponding hydroxylamine. To this end, the alkoxyamine was dissolved in a NMR tube in perdeutero *p*-xylene (0.03–0.06 M). The degassed sample was heated to 398 K within the cavity of a ^{1}H NMR spectrometer (500 MHz) and the decomposition was followed by monitoring the decrease of the alkoxyamine signals as well as the increase of the styrene resonances. The signal of the benzylic H atom at ≈4.7 was used to estimate the alkoxyamine concentration. Similar experiments have previously been described.[7,24] Spectra were re-

Table 5. Rate constants for the C–O bond homolysis and decomposition rate constants of alkoxyamines **13**–**17** and EPR parameters of the corresponding nitroxides.

Entry	Alkoxyamine	k_d [s^{-1}][a]	E_a [kJ mol^{-1}][b]	k_{decomp} [s^{-1}][c]	Nitroxide	a_N [G][d]	g
1	**13**	2.2×10^{-2}	123.7	1.5×10^{-5}	**6a**	14.16	2.006
2	**14**	2.9×10^{-2}	122.8	1.2×10^{-4}	**8**	14.51	2.006
3	**15**	4.9×10^{-3}	128.7	1.1×10^{-5}	**6b**	14.51	2.006
4	**16**	5.9×10^{-3}	128.1	6.6×10^{-5}	**10**	13.58	2.006
5	**17**	1.2×10^{-2}	125.7	2.1×10^{-4}	**12**	14.09	2.006

[a] Measured at 403 K. [b] E_a was calculated with $A = 2.4\times10^{14}$ s^{-1}; see ref. [6h]. Statistical errors 2–3 kJ mol^{-1}. [c] Measured at 398 K. [d] EPR data were recorded in *t*BuPh saturated with O_2 and are given with an error of ±0.14 G.

corded every 5 minutes. The decomposition rate constants (k_{decomp}) for the various alkoxyamines were determined with Equation (2), according to Fukuda's work[24a] ([S] = styrene concentration; [A] = alkoxyamine concentration) and are summarized in Table 5.

$$\ln([S]/[A]+1) = k_{decomp} \cdot t \quad (2)$$

The hydroxy-substituted alkoxyamine **14** decomposes one order of magnitude faster than the corresponding keto alkoxyamine **13** (Table 3, entries 1,2). The broader polydispersity obtained in the **14**-mediated styrene polymerization can therefore be explained by the instability of the regulator. It is important to note that the ethyl-substituted six-membered alkoxyamines are less stable than the methyl congeners (k_{decomp} (**18**) = $5.9\times10^{-6}\,s^{-1}$; k_{decomp} (**19**) = $1.3\times10^{-5}\,s^{-1}$).[7,24a] Because of this instability, the best polymerization results with **13** were achieved at lower temperatures (105 °C). Alkoxyamine **14** is not stable enough for an efficient regulator/initiator. Similar trends were observed for the seven-membered alkoxyamines **16** and **17** (Table 5, entries 4 and 5).[25] The hydroxy derivative **17** was the least stable compound studied. Similar decomposition rate constants have been obtained for the corresponding methyl substituted alkoxyamines **20** and **21** (see ref. [7]) In agreement with the experimental results, the replacement of the α-*N*-methyl groups in seven-membered alkoxyamines by ethyl groups has only a small effect on the decomposition rate constant.

Conclusion

We presented the synthesis of new sterically hindered six- and seven-membered cyclic alkoxyamines. The alkoxyamines were tested as regulator/initiators in controlled/living radical polymerizations. We showed that replacement of methyl groups in the α position to the N atom in six-membered cyclic alkoxyamines by ethyl groups leads to highly efficient regulators. For the seven-membered cyclic alkoxyamines, however, the replacement of methyl by ethyl groups only has a small (detrimental) effect on the polymerization. We presented kinetic data that show that the replacement of methyl by ethyl groups in six-membered cyclic alkoxyamines leads to an increase of the rate constant of the C–O bond homolysis, which is an important parameter in NMP. Along with the desired increase of the homolysis rate constant, a decrease of the alkoxyamine stability was measured for the ethyl derivatives. However, we found that the six-membered alkoxyamine **13** is sufficiently stable and sufficiently active at 105 °C. Controlled polymerization of styrene and *n*-butyl acrylate was achieved by the use of this new sterically highly hindered alkoxyamine. Controlled polymerizations can even be performed at 90 °C. It is important to note that NMP of *n*-butyl acrylate is currently only possible if noncyclic alkoxyamines are used.[1c,19] Furthermore, addition of sacrificial nitroxide is not necessary for the polymerization of *n*-butyl acrylate with our new initiator/regulator **13**. This is important for the formation of polymer brushes from surfaces (grafting from) where the exact concentration of surface-bound alkoxyamine initiator is difficult to determine. Formation of AA and AB diblock and ABA triblock copolymers with excellent control was achieved with alkoxyamine **13**.

Furthermore, we showed that silylated alkoxyamines are not suitable as regulators/initiators for controlled living radical polymerization. In contrast to previous literature reports, the C–O bonds in silylated alkoxyamines are stronger than the C–O bonds in analogous *N*,*N*-dialkylated alkoxyamines.

Experimental Section

General: ^1H and ^{13}C NMR spectra were recorded on a Bruker ARX 500, ARX 400, ARX 300, ARX 200 or a AC 200 spectrometer. Chemical shifts are referenced to $SiMe_4$ as an internal standard. TLC was carried out on Merck silica gel 60 F_{254} plates, detection by UV or dipping into a solution of $KMnO_4$ (3.0 g), $NaHCO_3$ (10.0 g), and H_2O (800 mL) or a solution of $Ce(SO_4)_2{\cdot}H_2O$ (10 g), phosphomolybdic acid hydrate (25 g), concentrated H_2SO_4 (60 mL), and H_2O (940 mL), followed by heating. FC was carried out on Merck or Fluka silica gel 60 (40–63 μm) at ≈0.4 bar. IR spectra were recorded on a IR 750 (Nicolet Magna) or a IFS-200 (Bruker). MS were recorded on a VG Tribid, Varian CH7 (EI), IonSpec Ultima, Finnigan MAT TSQ 700 or a Finnigan MAT 95S (ESI) in *m*/*z* (% of basis peak). Size-exclusion chromatography (SEC) was carried out with THF as eluent at a flow rate of 1.0 mL min^{-1} at room temperature on a system consisting of a L6200A Intelligent Pump (Merck Hitachi), a set of two PLgel 5 μm MIXED-C columns (300×7.5 mm, Polymer Laboratories), and a RI-101 detector (Shodex). Data were acquired through a PL Datastream unit (Polymer Laboratories) and analyzed with Cirrus GPC software (Polymer Laboratories) based upon calibration curves based on polystyrene and poly(methyl methacrylate) standards (Polymer Laboratories Polystyrene Medium MW Calibration Kit S-M-10 to determine the molecular weight of polystyrene and Polymer Laboratories Polymethylmethacrylate Medium MW Calibration Kit M-M-10 to determine the molecular weight of *n*-butyl acrylate) with peak molecular weights ranging from 500–3 000 000 g mol^{-1}. EPR spectra were recorded on a ESP 300 E (Bruker) equipped with a Nicolet Cavity (Bruker) and a B-TC 80/15 (Bruker). The nitroxide concentrations were determined by double integration of the EPR spectra and calibration with a TEMPO solution in *tert*-butylbenzene. Microwave-assisted heating was performed in an MLS-Ethos 1600 Microwave System (MLS). Solvents were purified by standard methods. Compounds sensitive to air and moisture were handled under argon by means of Schlenk techniques.

(4-Ethyl-2-oxohex-3-enyl)-dimethylphosphonate (2): A solution of diisopropylamine (5.6 mL, 40.13 mmol) in THF (250 mL) was treated with butyllithium (BuLi) in hexanes (40.13 mmol) at 0 °C. After stirring for 30 min at 0 °C, ketodiphosphonate **1** (10.00 g, 36.48 mmol) dissolved in THF (50 mL) was added dropwise. The solution turned deep yellow. After stirring for another 40 min, the solution was chilled to −35 °C and BuLi in hexanes (80.26 mmol) was added dropwise. The reaction mixture turned dark red. After stirring for 1 h at −35 °C, 3-pentanone was added slowly. The solution was allowed to warm to room temperature and was stirred overnight. The reaction mixture was treated with brine, extracted with *t*-butyl methyl ether (MTBE), and the organic layer was dried ($MgSO_4$). Evaporation of the solvents in vacuo yielded the crude product **2** (8.47 g), which was used for the next step without further purification. An analytical sample was purified by FC (MTBE/acetone 4:1 to acetone/MeOH 10:1). IR (film): $\tilde{\nu}$ = 3468 br, 2970 m, 1684 s, 1613 s, 1463 m, 1396 w, 1258 s, 1032 s cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 6.11 (s, 1H, CH), 3.76 (d, J(H,P) = 11.2 Hz, 6H, CH_3), 3.08 (d, J(H,P) = 22.5 Hz, 2H, CH_2), 2.55 (q, J = 7.5 Hz, 2H, CH_2), 2.19 (dq, J_1 = 7.5 Hz, J_2 = 1.3 Hz, 2H, CH_2), 1.06 (t, J = 7.5 Hz, 3H, CH_3), 1.02 ppm (t, J = 7.5 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 190.2 (d, J(C,P) = 6.2 Hz, C), 169.4 (C), 121.0 (d, J(C,P) = 2.2 Hz, CH), 52.7 (d, J(C,P) = 6.2 Hz, 2CH_3), 42.5 (d, J(C,P) = 126.9 Hz, CH_2), 31.1 (CH_2), 25.9 (CH_2), 12.5 (CH_3), 11.8 ppm (CH_3); MS (EI): 234 (25 $[M]^+$), 151 (44), 124 (100), 111 (26), 95 (70), 55 (29); HRMS (EI) calcd for $C_{10}H_{19}O_5P$ ($[M]^+$): 234.1021; found: 234.1019.

3,7-Diethylnona-3,6-dien-5-one (3a) and 3,7-diethylnona-2,6-dien-5-one (4): To the phosphonate **2** (8.47 g, 36.15 mmol) dissolved in benzene (90 mL) was added $CsOH·H_2O$ (15.18 g, 90.37 mmol), 3-pentanone (38.3 mL, 0.362 mol) and water (2.3 mL). After heating to 60 °C for 14 h and then refluxing for 4 h, the reaction mixture was cooled to room temperature and treated with a 2 M HCl solution. The mixture was then extracted with diethyl ether, and the organic layer was dried ($MgSO_4$). Evaporation of the solvents in vacuo and purification of the crude product by FC (diethyl ether/pentane 1:100) afforded the unsaturated ketones **3a** and **4** (2.21 g, **3/4** 1:6.4, 31 % over two steps) as a yellow oil. The undesired isomer **4** could be transformed into the desired isomer **3a** under basic conditions. IR (film): $\tilde{\nu}$ = 3440 br, 2969 s, 2935 s, 2875 s, 1670 m, 1621 s, 1426 m, 1119 m cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 6.00 (s, 2H, CH), 2.60 (q, J = 7.5 Hz, 4H, CH_2), 2.17 (q, J = 7.3 Hz, 4H, CH_2), 1.07 ppm (t, J = 7.3 Hz, 12H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 191.4 (C), 164.8 (C), 164.7 (C), 124.0 (2CH), 30.9 (CH_2), 25.5 (CH_2), 13.0 (CH_3), 12.1 ppm (CH_3); MS (EI): 194 (10, $[M]^+$), 165 (69), 137 (33), 111 (100), 55 (77); HRMS (EI) calcd for $C_{13}H_{22}O$ ($[M]^+$): 194.1671; found: 194.1677.

6-Ethyl-2-methylocta-2,5-dien-4-one (3b): To a solution of diisopropylamine (2.7 mL, 19.13 mmol) in THF (95 mL) was added BuLi in hexanes (19.13 mmol) at 0 °C. After the mixture had been stirred for 15 min, a solution of phosphonate **2** (2.99 g, 12.76 mmol) in THF (45 mL) was added dropwise. The mixture was heated to reflux for 30 min, then acetone (7.26 mL, 127.6 mmol) was added. After refluxing overnight, the reaction mixture was cooled to room temperature and a saturated aqueous solution of NH_4Cl was added. Extraction (diethyl ether), drying ($MgSO_4$), evaporation of the solvents in vacuo, and purification by FC (diethyl ether/pentane 1:50) yielded **3b** (484 mg, 22 %). IR (film): $\tilde{\nu}$ = 3441 br, 2970 s, 2935 s, 2876 s, 1673 m, 1627 s, 1443 m, 1114 m cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 6.06 (s, 1H, CH), 5.95 (s, 1H, CH), 2.57 (q, J = 7.3 Hz, 2H, CH_2), 2.18–2.11 (m, 5H, CH_2, CH_3), 1.86 (s, 3H, CH_3), 1.05 (t, J = 7.3 Hz, 3H, CH_3), 1.04 ppm (t, J = 7.3 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 191.4 (C), 165.2 (C), 154.0 (C), 126.3 (CH), 123.6 (CH), 30.9 (CH_2), 27.6 (CH_3), 25.5 (CH_2), 20.4 (CH_3), 13.0 (CH_3), 12.1 ppm (CH_3); MS (EI): 166 (32, $[M]^+$), 151 (100), 123 (48), 109 (26), 83 (75), 55 (47); HRMS (EI) calcd for $C_{11}H_{18}O$ ($[M]^+$): 166.1358; found: 166.1357.

2,2,6,6-Tetraethylpiperidin-4-one (5): The ketones **3a** and **4** (2.21 g, 11.43 mmol) and a concentrated aqueous solution of NH_4OH (17.6 mL, 114.3 mmol) were heated to 105 °C in a sealed tube for 20 h. The reaction mixture was cooled to room temperature, treated with brine, and extracted with MTBE. The organic layer was dried ($MgSO_4$). Evaporation of the solvents in vacuo and purification of the crude product by FC (diethyl ether/pentane 1:5) afforded the piperdinone **5** (960 mg, 40 %) as an orange oil along with unreacted **3a** and **4** (700 mg, 32 %). IR (film): $\tilde{\nu}$ = 3354 br, 2945 s, 2832 s, 2524 w, 2045 w, 1451 m, 1032 s, 662 br cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 2.18 (s, 4H, CH_2), 1.47–1.28 (m, 8H, CH_2), 0.77 ppm (t, J = 5.1 Hz, 12H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 212.1 (C), 58.4 (2C), 49.7 (2CH_2), 33.0 (4CH_2), 7.9 ppm (4CH_3); MS (ESI): 234 (60 $[M+Na]^+$), 212 (13, $[M+H]^+$), 194 (25), 154 (100), 111 (28); HRMS (ESI) calcd for $C_{13}H_{25}NNaO$ ($[M+Na]^+$): 234.1834; found: 234.1840.

2,2,6,6-Tetraethylpiperidin-4-one-*N*-oxyl radical (6a): To a solution of the aminoketone **5** (300 mg, 1.42 mmol) in MeOH (3.0 mL) and water (1.0 mL) was added $Na_2WO_4·2H_2O$ (118 mg, 0.36 mmol) and a 35 % aqueous solution of H_2O_2 (0.85 mL, 8.52 mmol). The reaction mixture was stirred for 24 h at 25 °C, quenched with a saturated aqueous solution of K_2CO_3 and extracted with diethyl ether. The organic layer was dried ($MgSO_4$). Evaporation of the solvents in vacuo and purification by FC (diethyl ether/pentane 1:3) yielded **6a** (280 mg, 87 %) as an orange oil. EPR: α_N = 14.16 G.

2,2-Diethyl-6,6-dimethylpiperidin-4-one-*N*-oxyl radical (6b): 6-Ethyl-2-methylocta-2,5-dien-4-one **3b** (250 mg, 1.29 mmol) and a concentrated aqueous solution of NH_4OH (2.0 mL, 12.87 mmol) were heated to 105 °C in a sealed tube for 17 h. After cooling to room temperature, the reaction mixture was treated with brine and then extracted with MTBE. The organic layer was dried ($MgSO_4$). Evaporation of the solvents in vacuo and purification of the crude product by FC (diethyl ether/pentane 1:5) afforded 2,2-diethyl-5,5-dimethylpiperidin-4-one (261 mg, 92 %). IR (film): $\tilde{\nu}$ = 3333 br, 2966 s, 1709 s, 1620 w, 1462 m, 1381 m, 1295 m cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 2.22 (s, 2H, CH_2), 2.18 (s, 2H, CH_2), 1.57–1.24 (m, 4H, CH_2), 1.18 (s, 6H, CH_3), 0.77 ppm (t, J = 7.5 Hz, 6H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 211.4 (C), 59.7 (C), 54.5 (C), 54.4 (CH_2), 50.4 (CH_2), 32.1 (CH_3), 32.0 (CH_2), 7.6 ppm (CH_3); MS (ESI): 367 (14 $[2M+H]^+$), 184 (100, $[M+H]^+$); HRMS (ESI) calcd for $C_{11}H_{22}NO$ ($[M+H]^+$): 184.1701; found: 184.1708.

To a solution of 2,2-diethyl-5,5-dimethylpiperidin-4-one (271 mg, 1.48 mmol) in MeOH (3.0 mL) and water (1.0 mL) was added $Na_2WO_4·2H_2O$ (81 mg, 0.25 mmol) and a 35 % aqueous solution of H_2O_2 (0.90 mL, 8.87 mmol). The reaction mixture was stirred for 24 h at 25 °C, quenched with brine and extracted with MTBE. The organic layer was dried ($MgSO_4$). Evaporation of the solvents in vacuo yielded the **6b** (85 mg, 29 %) as an orange oil. EPR: α_N = 14.51 G.

2,2,6,6-Tetraethylpiperidin-4-ol (7): To a solution of aminoketone **5** (200 mg, 0.95 mmol) in THF (10 mL) was added lithium aluminum hydride (LAH) (36 mg, 0.95 mmol). The reaction mixture was stirred at 25 °C for 12 h, then heated to reflux for 4 h. After the mixture had been cooled to room temperature, water (45 μL), a 15 % aqueous solution of NaOH (45 μL), and water (90 μL) were added to the stirred mixture in 5 min intervals. The suspension was finally allowed to stir for 20 min while a white precipitate formed. Filtration, washing with MTBE, drying ($MgSO_4$), and evaporation of the solvents in vacuo yielded alcohol **7** (203 mg, 98 %) which was used without further purification. IR (film): $\tilde{\nu}$ = 3343 br, 2965 s, 2965 s, 2876 m, 1460 s, 1378 m, 1058 s, 1031 m cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 3.95 (tt, J_1 = 11.6 Hz, J_2 = 4.0 Hz, 2H, CH_2), 1.84 (dd, J_1 = 11.9 Hz, J_2 = 3.6 Hz, 2H, CH_2), 1.57–1.16 (m, 8H, CH_2), 0.93 (dd, J_1 = J_2 = 11.9 Hz, 2H, CH_2), 0.78 ppm (dt, J_1 = 7.3 Hz, J_2 = 3.0 Hz, 12H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 64.4 (CH), 55.8 (2C), 44.4 (2CH_2), 34.5 (2CH_2), 29.9 (2CH_2), 8.4 (2CH_3), 7.5 ppm (2CH_3); MS (ESI): 214 (100, $[M+H]^+$), 86 (4); HRMS (ESI) calcd for $C_{13}H_{28}NO$ ($[M+H]^+$): 214.2171; found: 214.2177.

2,2,6,6-Tetraethylpiperidin-4-ol-*N*-oxyl radical (8): To a solution of the aminoketone **7** (579 mg, 2.71 mmol) in MeOH (5.5 mL) and water (1.8 mL) was added $Na_2WO_4·2H_2O$ (149 mg, 0.45 mmol) and a 35 % aqueous solution of H_2O_2 (1.63 mL, 16.26 mmol). The reaction mixture was stirred for 24 h at 25 °C, quenched with brine, and extracted with MTBE. The organic layer was dried ($MgSO_4$). Evaporation of the solvents in vacuo yielded nitroxide **8** (625 mg, 97 %) as an orange oil. EPR: α_N = 14.51 G.

2,2,7,7-Tetraethylazepan-4-one (9): To a solution of aminoketone **5** (620 mg, 2.93 mmol) in CH_2Cl_2 (30 mL) over 3 Å molecular sieves (8.8 g) at −78 °C were added $BF_3·OEt_2$ (0.40 mL, 3.22 mmol) and subsequently a 2 M solution of Me_3SiCHN_2 in Et_2O (4.4 mL, 8.79 mmol). The reaction mixture was stirred at −78 °C for 3.5 h and then quenched with a saturated aqueous solution of $NaHCO_3$ at −78 °C. Filtration, extraction with diethyl ether, drying of the organic layers ($MgSO_4$), and evaporation of the solvents in vacuo yielded the crude homologue. This was dissolved in MeOH (50 mL), and pyridinium *p*-toluenesulfonate (92 mg, 0.37 mmol) was added. After the mixture had been stirred for 14 h at 25 °C, Et_3N (0.21 mL, 1.48 mmol) was added. Then the mixture was stirred for an additional 30 min, the solvent was evaporated in vacuo, and a saturated solution of NH_4Cl was added. Extraction (MTBE), drying ($MgSO_4$), evaporation of the solvents in vacuo, and purification by FC (diethyl ether/pentane 1:6) yielded the azepane **9** (521 mg, 79 %). IR (film): $\tilde{\nu}$ = 3453 w, 2962 s, 2930 s, 1706 s, 1456 m, 1359 m, 1271 w, 1176 w cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.56 (s, 2H, CH_2), 2.30 (t, J = 6.2 Hz, 2H, CH_2), 1.86 (t, J = 6.2 Hz, 2H, CH_2), 1.51–1.45 (m, 4H, CH_2), 1.39 (q, J = 7.5 Hz, 4H, CH_2), 0.85–0.77 ppm (m, 12H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.6 (C), 57.4 (C), 57.3 (C), 51.1 (CH_2), 38.9 (CH_2), 32.4 (2CH_2), 32.0 (CH_2), 31.0 (2CH_2), 8.0 (2CH_3), 7.9 ppm (2CH_3); MS (ESI): 226 (100, $[M+H]^+$); HRMS (ESI) calcd for $C_{14}H_{28}NO$ ($[M+H]^+$): 226.2171; found: 226.2165.

2,2,7,7-Tetraethylazepan-4-one-*N*-oxyl radical (10): To a solution of the azepanone **9** (457 mg, 2.03 mmol) in MeOH (4.8 mL) and water (1.4 mL) was added $Na_2WO_4·2H_2O$ (112 mg, 0.34 mmol) and a 35 % aqueous solution of H_2O_2 (1.22 mL, 12.2 mmol). The reaction mixture was stirred for 18 h at 25 °C, quenched with brine, and extracted with diethyl ether. The organic layer was dried ($MgSO_4$). Evaporation of the solvents in vacuo and purification by FC (diethyl ether/pentane 1:8) yielded **10** (200 mg, 41 %) as an orange oil. EPR: α_N = 13.58 G.

2,2,7,7-Tetraethylazepan-4-ol (11): To a solution of azepanone **9** (63 mg, 0.32 mmol) in THF (2 mL) was added LAH (36 mg, 0.32 mmol). The reaction mixture was stirred at 25 °C for 12 h, then heated to reflux for 4 h. After the mixture had been cooled to room temperature, water (15 μL), a 15% aqueous solution of NaOH (15 μL), and water (30 μL) were added with 5 min intervals with stirring. The suspension was finally allowed to stir for 20 min while a white precipitate formed. Filtration, washing with MTBE, drying ($MgSO_4$), and evaporation of the solvents in vacuo yielded the alcohol **11** (57 mg, 78%), which was used without further purification. IR (film): $\tilde{\nu}$ = 3347 br, 2966 s, 2936 s, 2878 m, 1461 s, 1377 m, 11180 m, 1032 m cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 3.95–3.89 (m, 1H, CH), 1.86–1.76 (m, 2H, CH_2), 1.70–1.57 (m, 3H, CH_2), 1.55–1.24 (m, 9H, CH_2), 0.83–0.72 ppm (m, 12H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 69.6 (CH), 57.3 (C), 56.5 (C), 45.7 (CH_2), 34.0 (CH_2), 33.5 (CH_2), 32.5 (CH_2), 32.4 (CH_2), 30.8 (CH_2), 30.0 (CH_2), 8.5 (CH_3), 8.2 (CH_3), 7.8 (CH_3), 7.2 ppm (CH_3); MS (ESI): 250 (12, $[M+Na]^+$), 228 (100, $[M+H]^+$); HRMS (ESI) calcd for $C_{14}H_{30}NO$ ($[M+H]^+$): 228.2327; found: 228.2334.

2,2,7,7-Tetraethylazepan-4-ol-*N*-oxyl radical (12): To a solution of the azepanol **11** (151 mg, 0.66 mmol) in MeOH (1.5 mL) and water (0.5 mL) was added $Na_2WO_4{\cdot}2H_2O$ (36 mg, 0.11 mmol) and a 35% aqueous solution of H_2O_2 (0.40 mL, 3.96 mmol). The reaction mixture was stirred for 24 h at 25 °C, quenched with brine, and extracted with MTBE. The organic layer was dried ($MgSO_4$). Evaporation of the solvents in vacuo yielded **12** (170 mg, 98%) as an orange oil. EPR: α_N = 14.09 G.

2,2,6,6-Tetraethyl-1-(1-phenylethoxy)piperidin-4-one (13): Nitroxide **6a** (510 mg, 2.23 mmol), Cu dust (142 mg, 2.23 mmol), $Cu(OTf)_2$ (40 mg, 0.11 mmol), (4,4′-di-*tert*-butyl)-2,2′-bipyridine (60 mg, 0.45 mmol), 1-phenylethylbromide (413 mg, 2.23 mmol), and benzene (7.0 mL) were heated for 18 h to 75 °C in a sealed tube under an argon atmosphere. Filtration over a thin pad of SiO_2, washing with MTBE, evaporation of the solvents in vacuo, and purification by FC (diethyl ether/pentane 1:20) yielded **13** (456 mg, 61%). IR (film): $\tilde{\nu}$ = 3029 w, 2971 s, 2881 m, 1718 s, 1464 m, 1251 m, 1060 s cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.32–7.24 (m, 5H, CH), 4.72 (q, J = 6.7 Hz, 1H, CH), 2.46–2.26 (br m, 4H, CH_2), 2.13–1.98 (br m, 1H, CH_2), 1.89–1.55 (br m, 7H, CH_2), 1.46 (d, J = 6.7 Hz, 3H, CH_3), 1.15–0.57 ppm (br m, 12H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 211.0 (C), 145.0 (C), 128.1 (2CH), 127.2 (CH), 126.5 (2CH), 83.1 (CH), 66.2 (C), 66.1 (C), 46.7 (CH_2), 31.3 (CH_2), 31.0 (CH_2), 29.3 (CH_2), 29.0 (CH_2), 23.5 (CH_3), 9.9 (CH_3), 9.5 (CH_3), 8.6 (CH_3), 8.3 ppm (CH_3); MS (ESI): 354 (31, $[M+Na]^+$), 260 (100); HRMS (ESI) calcd for $C_{21}H_{33}NNaO_2$ ($[M+Na]^+$): 354.2409; found: 354.2393.

2,2,6,6-Tetraethyl-1-(1-phenylethoxy)piperidin-4-ol (14): Nitroxide **8** (200 mg, 0.88 mmol), Cu dust (54 mg, 0.85 mmol), $Cu(OTf)_2$ (16 mg, 0.044 mmol), (4,4′-di-*tert*-butyl)-2,2′-bipyridine (24 mg, 0.176 mmol), 1-phenylethylbromide (154 mg, 0.83 mmol), and benzene (3.0 mL) were heated for 19 h to 75 °C in a sealed tube under an argon atmosphere. Filtration over a thin pad of SiO_2, washing with MTBE, evaporation of the solvents in vacuo, and purification by FC (diethyl ether/pentane 1:5) yielded **14** (83 mg, 30%). IR (film): $\tilde{\nu}$ = 3440 br, 2970 s, 2880 m, 1727 w, 1537 w, 1463 m, 1375 m cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.33–7.19 (m, 5H, CH), 4.68 (q, J = 6.7 Hz, 1H, CH), 3.88 (tt, J_1 = 11.4 Hz, J_2 = 4.0 Hz, 1H, CH), 2.20–2.10 (m, 1H, CH_2), 2.01–1.92 (m, 1H, CH_2), 1.81–1.60 (m, 5H, CH_2), 1.55–1.24 (m, 3H, CH_2), 1.41 (d, J = 6.7 Hz, 3H, CH_3), 1.07 (t, J = 7.3 Hz, 3H, CH_3), 0.97–0.75 (m, 2H, CH_2), 0.92 (t, J = 7.7 Hz, 3H, CH_3), 0.70 (t, J = 7.5 Hz, 3H, CH_3), 0.64 ppm (t, J = 7.1 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.5 (C), 127.9 (2CH), 126.6 (CH), 125.9 (2CH), 82.3 (CH), 65.5 (C), 65.1 (C), 62.7 (CH), 40.0 (CH_2), 39.6 (CH_2), 30.1 (CH_2), 29.1 (CH_2), 27.4 (CH_2), 27.0 (CH_2), 24.9 (CH_3), 10.2 (CH_3), 9.9 (CH_3), 8.2 (CH_3), 8.0 ppm (CH_3); MS (ESI): 334 (100, $[M+H]^+$), 318 (86); HRMS (ESI) calcd for $C_{21}H_{36}NO_2$ ($[M+H]^+$): 334.2746; found: 334.2740.

2,2-Diethyl-6,6-dimethyl-1-(1-phenylethoxy)piperidin-4-one (15): 2,2-Diethyl-6,6-dimethylpiperidin-4-one-*N*-oxyl radical (**6b**) (72 mg, 0.363 mmol), Cu dust (22 mg, 0.347 mmol), $Cu(OTf)_2$ (6 mg, 0.017 mmol), (4,4′-di-*tert*-butyl)-2,2′-bipyridine (18 mg, 0.066 mmol), 1-phenylethylbromide (61 mg, 0.320 mmol), and benzene (1.2 mL) were heated for 24 h to 75 °C in a sealed tube under an argon atmosphere. Filtration over a thin pad of SiO_2, washing with MTBE, evaporation of the solvents in vacuo, and purification by FC (diethyl ether/pentane 1:10) yielded **15** (79 mg, 72%). IR (film): $\tilde{\nu}$ = 3441 w, 2974 s, 2938 s, 2880 m, 1719 s, 1494 w, 1454 m, 1305 m cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.23 (m, 5H, CH), 4.77 (br, 1H, CH), 2.41–2.27 (m, 4H, CH_2), 2.32 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 1.49 (d, J = 5.4 Hz, 3H, CH_3), 1.31–1.21 (m, 10H), 0.88 ppm (t, J = 5.6 Hz, 6H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 209.8 (C), 144.2 (C), 128.1 (2CH), 127.4 (CH), 126.6 (2CH), 83.3 (CH), 65.8 (C), 60.4 (C), 53.1 (CH_2), 47.4 (CH_2), 33.4 (CH_3), 33.3 (CH_3), 30.9 (CH_2), 28.5 (CH_2), 23.5 (CH_3), 9.5 (CH_3), 8.4 ppm (CH_3); MS (ESI): 326 (100, $[M+Na]^+$), 304 (41, $[M+H]^+$), 242 (53); HRMS (ESI) calcd for $C_{19}H_{29}NNaO_2$ ($[M+Na]^+$): 326.2096; found: 326.2091.

2,2,7,7-Tetraethyl-1-(1-phenylethoxy)azepan-4-one (16): Nitroxide **10** (200 mg, 0.83 mmol), Cu dust (53 mg, 0.83 mmol), $Cu(OTf)_2$ (15 mg, 0.042 mmol), (4,4′-di-*tert*-butyl)-2,2′-bipyridine (23 mg, 0.168 mmol), 1-phenylethylbromide (154 mg, 0.83 mmol), and benzene (3.0 mL) were heated for 48 h to 75 °C in a sealed tube under an argon atmosphere. Filtration over a thin pad of SiO_2, washing with MTBE, evaporation of the solvents in vacuo, and purification by FC (diethyl ether/pentane 1:30) yielded **16** (64 mg, 22%) as a mixture of two diastereoisomers because of the chirality at the nitrogen atom (d.r. = 1.1:1). IR (film): $\tilde{\nu}$ = 3369 w, 2963 s, 2878 s, 1705 s, 1462 s, 1359 m, 1180 m cm^{-1}; MS (ESI): 346 (36, $[M+H]^+$), 305 (100); HRMS (ESI) calcd for $C_{22}H_{36}NO_2$ ($[M+H]^+$): 346.2746; found: 346.2739.

Major isomer: ^1H NMR (500 MHz, $CDCl_3$): δ = 7.29–7.25 (m, 4H, CH), 7.23–7.20 (m, 1H, CH), 4.54 (q, J = 6.9 Hz, 1H, CH), 2.79 (dd, J_1 = 12.4 Hz, J_2 = 7.1 Hz, 2H, CH_2), 2.29–0.80 (m, 10H, CH_2), 2.14 (s, 2H, CH_2), 1.39 (d, J = 6.9 Hz, 3H, CH_3), 1.26 (t, J = 7.1 Hz, 3H, CH_3), 0.92 (t, J = 7.6 Hz, 3H, CH_3), 0.84 (t, J = 7.6 Hz, 3H, CH_3), 0.71 ppm (t, J = 7.6 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 208.5 (C), 145.0 (C), 128.0 (2CH), 127.4 (CH), 126.9 (2CH), 82.2 (CH), 71.3 (C), 65.1 (C), 50.2 (CH_2), 32.3 (CH_2), 31.5 (CH_2), 31.1 (CH_2), 25.7 (CH_2), 24.4 (CH_2), 22.7 (CH_3), 10.2 (CH_3), 9.2 (CH_3), 8.6 (CH_3), 8.2 ppm (CH_3).

Minor isomer: ^1H NMR (500 MHz, $CDCl_3$): δ = 7.29–7.25 (m, 4H, CH), 7.23–7.20 (m, 1H, CH), 4.59 (q, J = 6.7 Hz, 1H, CH), 2.76 (dd, J_1 = 12.4 Hz, J_2 = 6.9 Hz, 2H, CH_2), 2.29–0.80 (m, 10H, CH_2), 2.07 (s, 2H, CH_2), 1.38 (d, J = 6.7 Hz, 3H, CH_3), 0.95 (t, J = 7.3 Hz, 3H, CH_3), 0.92 (t, J = 7.3 Hz, 3H, CH_3), 0.67 (t, J = 7.3 Hz, 3H, CH_3), 0.66 ppm (t, J = 7.3 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 208.5 (C), 144.9 (C), 128.0 (2CH), 127.2 (CH), 126.6 (2CH), 82.1 (CH), 71.0 (C), 65.9 (C), 50.0 (CH_2), 32.2 (CH_2), 31.8 (CH_2), 31.2 (CH_2), 25.4 (CH_2), 24.3 (CH_2), 23.4 (CH_3), 10.0 (CH_3), 9.4 (CH_3), 8.7 (CH_3), 7.3 ppm (CH_3).

2,2,7,7-Tetraethyl-1-(1-phenylethoxy)azepan-4-ol (17): Nitroxide **12** (81 mg, 0.33 mmol), Cu dust (20 mg, 0.32 mmol), $Cu(OTf)_2$ (5.4 mg, 0.015 mmol), (4,4′-di-*tert*-butyl)-2,2′-bipyridine (8.1 mg, 0.060 mmol), 1-phenylethylbromide (56 mg, 0.30 mmol), and benzene (1.0 mL) were heated for 14 h to 75 °C in a sealed tube under an argon atmosphere. Filtration over a thin pad of SiO_2, washing with MTBE, evaporation of the solvents in vacuo, and purification by FC (MTBE/pentane 1:2) yielded the alkoxyamine **17** (76 mg, 73%) as a mixture of diastereoisomers (d.r. = 1.7:1). IR (film): $\tilde{\nu}$ = 3447 br, 2972 s, 2879 s, 1691 w, 1465 s, 1373 m, 1056 s cm^{-1}; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.4 (C), 127.8 (2CH), 126.6 (CH), 125.8 (2CH), 82.3 (CH), 65.4 (C), 65.1 (C), 62.6 (CH), 40.0 (CH_2), 39.6 (CH_2), 30.1 (CH_2), 29.6 (CH_2), 29.1 (CH_2), 27.3 (CH_2), 27.0 (CH_2), 24.8 (CH_3), 10.1 (CH_3), 9.8 (CH_3), 8.2 (CH_3), 7.9 ppm (CH_3); MS (ESI): 370 (25, $[M+Na]^+$), 348 (19, $[M+H]^+$), 318 (100); HRMS (ESI) calcd for $C_{22}H_{37}NNaO_2$ ($[M+H]^+$): 370.2722; found: 370.2709.

Major isomer: ^1H NMR (500 MHz, $CDCl_3$): δ = 7.30–7.22 (m, 5H, CH), 4.69–4.66 (m, 1H, CH), 3.96–3.88 (m, 1H, CH), 2.34–0.53 ppm (m, 29H).

Minor isomer: ^1H NMR (500 MHz, $CDCl_3$): δ = 7.30–7.22 (m, 5H, CH), 4.76–4.71 (m, 1H, CH), 4.11–4.05 (m, 1H, CH), 2.34–0.53 ppm (m, 29H).

1,2-Bis(chlorodiethylsilanyl)benzene (23): 1,2-Dibromobenzene (6.58 g, 27.90 mmol) was added dropwise to magnesium turnings (1.40 g, 57.68 mmol) and diethyl chlorosilane (7.12 g, 58.01 mmol) in THF (35 mL). The mixture was heated to reflux for 4 h, and, after cooling to room temperature, hexane was added (30 mL). The organic layer was washed with 2 N HCl (30 mL) and water (30 mL) and was dried ($MgSO_4$). Evaporation of the solvents in vacuo and purification by distillation (≈ 90 °C, 1.1 mbar) yielded the bis(diethylsilanyl)benzene (2.04 g, 29%); ^1H NMR (300 MHz): δ = 7.83 (dd, J_1 = 5.4 Hz, J_2 = 3.3 Hz, 2H, CH), 7.60 (dd, J_1 = 5.6 Hz, J_2 = 3.1 Hz, 2H, CH), 4.37 (qn, J = 3.3 Hz, 2H, SiH), 0.97–0.91 (m, 12H, CH_3), 0.90–0.88 ppm (m, 8H, CH_2).

Bis(diethylsilanyl)benzene (2.03 g, 8.10 mmol) was saturated with chlorine at 0 °C. Purging with argon removed excess chlorine and yielded the product **23** (2.34 g, 90 %); ^{1}H NMR (300 MHz): δ = 7.86 (dd, J_1 = 5.6 Hz, J_2 = 3.4 Hz, 2H, CH), 7.44 (dd, J_1 = 5.6 Hz, J_2 = 3.2 Hz, 2H, CH), 1.25–1.15 (m, 8H, CH_2), 1.06–0.99 ppm (m, 12H, CH_3). The physical data are in agreement with the values reported in literature.[15,16]

1,2-Bis(chlorodiisopropylsilanyl)benzene (24): 1,2-Dibromobenzene (0.36 g, 0.15 mmol) was added dropwise to magnesium turnings (1.66 g, 68.20 mmol) in THF (35 mL) in order to start the reaction. Diisopropylchlorosilane (8.62 g, 57.19 mmol) was added. 1,2-Dibromobenzene (6.910 g, 29.29 mmol) in THF (50 mL) was added slowly to allow the reaction to reflux gently before heating to reflux for 42 h. After the mixture was cooled to room temperature, hexane was added (110 mL). Filtration of the salts, evaporation of the solvents in vacuo, and purification by FC (pentane/Et_3N = 100:1) yielded the bis(diisopropylsilanyl)benzene (1.34 g, 14 %); ^{1}H NMR (200 MHz): δ = 7.53–7.49 (m, 2H, CH), 7.37–7.30 (m, 2H, CH), 4.30 (t, J = 3.5 Hz, 2H, SiH), 1.40–1.13 (m, 4H, CH), 1.12–0.91 ppm (m, 24H, CH_3).

Bis(isopropylsilanyl)benzene (600 mg, 1.96 mmol) was saturated with chlorine at 0 °C. Purging with argon removed excess chlorine and yielded the product **24** (735 mg, >98 %); ^{1}H NMR (300 MHz): δ = 7.87 (dd, J_1 = 5.7 Hz, J_2 = 3.4 Hz, 2H, CH), 7.41 (dd, J_1 = 5.6 Hz, J_2 = 3.4 Hz, 2H, CH), 1.69 (sept., J = 7.3 Hz, 4H, CH), 1.14 (d, J = 7.1 Hz, 12H, CH_3), 0.90 ppm (d, J = 7.3 Hz, 12H, CH_3). The physical data are in agreement with the values reported in literature.[15,16]

1,1,3,3-Tetraethyl-2-(1-phenyl-ethoxy)-2,3-dihydro-1*H*-benzo[1,2,5]azadisilole (25): To a solution of 1,2-bis(chlorodiethylsilyl)benzene (0.11 g, 0.35 mmol) and a catalytic amount of 4-(*N*,*N*-dimethylamino)pyridine in dry DMF (2 mL) in a sealed tube was added a mixture of *O*-(1-phenylethyl)hydroxylamine (32 mg, 0.23 mmol) and NEt_3 (71 mg, 0.70 mmol). The reaction mixture was heated to 100 °C for 8 min in a sealed tube under microwave irradiation. The solvent was evaporated in vacuo, and the crude product was dissolved in pentane. Filtration, evaporation of the solvent in vacuo, and purification by FC (MTBE/pentane/NEt_3 = 20:80:1) yielded the product **25** (69 mg, 78 %). IR (film): $\tilde{\nu}$ = 3047 s, 2874 s, 1456 m, 1411 w, 1369 w, 1233 m, 1121 m, 1075 m, 1054 m, 1006 m, 929 s, 876 m, 760 s, 700 s cm^{-1}; ^{1}H NMR (300 MHz): δ = 7.41–7.29 (m, 9H, CH), 4.58 (q, J = 6.6 Hz, 1H, CH), 1.47 (d, J = 6.6 Hz, 3H, CH_3), 1.00–0.79 (m, 14H), 0.72 ppm (t, J = 7.5 Hz, 6H, CH_3); ^{13}C NMR (75 MHz): δ = 144.36 (2C), 132.02 (2CH), 131.61 (2CH), 128.72 (CH), 128.41 (CH), 128.20 (CH), 127.71 (CH), 126.78 (CH), 126.33 (C), 84.7 (CH), 23.04 (CH_3), 7.31 (2 CH_3), 7.21 (2 CH_3), 6.62 (2 CH_2), 6.20 ppm (2 CH_2); MS (EI): 383 (14, $[M]^+$), 279 (100), 207 (54), 179 (34), 105 (58); HRMS (EI): calcd for $C_{22}H_{33}NOSi_2$: 383.2101; found: 383.2089.

1,1,3,3-Tetraisopropyl-2-(1-phenyl-ethoxy)2,3-dihydro-1*H*-benzo[1,2,5]-azadisilole (26): To a solution of 1,2-bis(chlorodiethylsilyl)benzene (119 mg, 0.32 mmol) and a catalytic amount of 4-(*N*,*N*-dimethylamino)-pyridine in dry DMF (2 mL) in a sealed tube was added a mixture of *O*-(1-phenyl-ethyl)hydroxylamine (36 mg, 0.26 mmol) and NEt_3 (80 mg, 0.79 mmol). The reaction mixture was heated to 90 °C for 10 min in a sealed tube under microwave irradiation. The solvent was evaporated in vacuo, and the crude product was dissolved in pentane. Filtration, evaporation of the solvent in vacuo, and purification by FC (MTBE/pentane/NEt_3 = 20:80:1) yielded the product **26** (51 mg, 45 %). IR (film): $\tilde{\nu}$ = 3048 m, 2943 s, 2891 s, 1464 s, 1383 m, 1364 m, 1115 m, 1072 m, 994 m, 918 s, 883 s, 749 m, 698 s, 683 s, 622 m, 502 m, 460 m cm^{-1}; ^{1}H NMR (300 MHz): δ = 7.50–7.29 (m, 9H, CH), 4.61 (q, J = 6.5 Hz, 1H, CH), 1.50 (d, J = 6.6 Hz, 3H, CH_3), 1.44–1.28 (m, 2CHSi), 1.27–1.11 (m, 2H, CH), 1.10–1.02 ppm (m, 24H); ^{13}C NMR (75 MHz): δ = 144.3 (3C), 133.0 (2CH), 128.1 (2CH), 128.1 (2CH), 127.6 (CH), 126.9 (2CH), 84.2 (CH), 23.1 (CH_3), 18.6 (CH_3), 18.5 (CH_3), 18.3 (CH_3), 18.2 (CH_3), 13.8 (2CH), 13.6 ppm (2 CH); EI-MS: 439 (25, $[M]^+$), 367 (22), 365 (23), 335 (60), 333 (96), 331 (100), 277 (87), 269 (81); HRMS (EI) calcd for $C_{26}H_{41}NOSi_2$ ($[M]^+$): 439.2727; found: 439.2724.

Typical procedure for the polymerization of styrene: A Schlenk tube was charged with the alkoxyamine initiator **13** (30 mg, 90.0 μmol) and styrene (1.03 mL, 8.996 mmol) under argon. The styrene was previously degassed in three freeze–thaw cycles and sealed off under argon. The polymerization was carried out under argon at 105 °C for 24 h. The resulting mixture was cooled to room temperature, dissolved in CH_2Cl_2, and poured onto an aluminum dish. Residual monomer was removed in a vacuum drying cabinet at 60 °C for 12 h. Conversion was evaluated gravimetrically; molecular weight and polydispersity index (PDI) were determined by size-exclusion chromatography (SEC). Conversion = 69 %; M_n = 9400 g mol^{-1}; PDI = 1.09.

Typical procedure for the polymerization of *n*-butyl acrylate: A Schlenk tube was charged with the alkoxyamine initiator **13** (30 mg, 90.0 μmol) and *n*-butyl acrylate (1.28 mL, 8.996 mmol) under argon. The *n*-butyl acrylate was previously degassed in three freeze–thaw cycles and sealed off under argon. The polymerization was carried out under argon at 105 °C for 32 h. The resulting mixture was cooled to room temperature, dissolved in CH_2Cl_2, and poured onto an aluminum dish. Residual monomer was removed in a vacuum drying cabinet at 60 °C for 12 h. Conversion was evaluated gravimetrically; molecular weight and polydispersity index (PDI) were determined by size exclusion chromatography (SEC). Conversion = 83 %; M_n = 18600 g mol^{-1}; PDI = 1.12.

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